# 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 methods ${ }^{1}$ 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( $1 \mathrm{H}, 1 \mathrm{H}, 2 \mathrm{H}, 2 \mathrm{H}$-perfluorooctyl)silane.


Figure S-1. Fabricationof full glass microchips with chrome structuring, wet etching and high temperature bonding.
2. Tagging-effect demonstrated for $[4 \mathrm{a}+\mathrm{H}]^{+}$


Figure S-2. Simulated harmonic IR spectra of $\left[4 a^{+}+\mathrm{H}\right]^{+}$. Both, the E - and $Z$-isomer is shown, with a $\mathrm{D}_{2}$-tagging molecule binding to various positions of the protonated $o-\mathrm{QM}$. The corresponding minimum-energy structures and their ZPEcorrected 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.


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

Table S-1. Experimental band positions, computed harmonic vibrational frequencies (in $\mathrm{cm}^{-1}$ ) and band assignments of $\left[4 a^{+}+\mathrm{H}\right]^{+}$.

| Band | B3LYP <br> (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 |
| $a_{1}^{\mathrm{Z}}$ | 1371 | 1382 | C-H bend, O-H bend |
| $a_{2}^{\mathrm{E}}$ | 1342 | $1362 / 1330$ | C-H bend |
| $a_{3}^{\mathrm{E}}$ | 1308 | 1310 | C-H bend |
| $a_{4}^{\mathrm{E}}$ | 1290 | 1243 | C-H bend |
| $a_{5}^{\mathrm{E}}$ | 1226 |  | C-H bend |
| $a_{6}^{\mathrm{E}}$ |  |  |  |


| $\mathrm{a}_{7}^{\mathrm{E}}$ | 1175 | 1188 | C-H bend, O-H bend |
| :--- | :--- | :--- | :--- |
| $\mathrm{a}_{8}^{\mathrm{E}}$ | 1146 | 1153 | C-H bend, O-H bend |

Table S-2. Experimental band positions, computed harmonic vibrational frequencies (in $\mathrm{cm}^{-1}$ ) and band assignments of $[4 b+H]^{+}$.

| Band | $\begin{gathered} \text { B3LYP } \\ \text { (scaled 0.975) } \end{gathered}$ | Experiment | Assignment |
| :---: | :---: | :---: | :---: |
| $\mathrm{b}_{1}^{\mathrm{z}}$ | 1384 | - | C-H bend |
| $\mathrm{b}_{2}^{\mathrm{z}}$ | 1355 | - | $\mathrm{C}=\mathrm{C}$ stretch (ring), O-H bend |
| $b_{3}^{z}$ | 1331 | - | C-H bend, C-H bend (OMe) |
| $\mathrm{b}_{4}^{\mathrm{Z}}$ | 1294 | - | C-H bend, C-O stretch |
| $\mathrm{b}_{5}^{\mathrm{z}}$ | 1208 | - | C-H bend |
| $\mathrm{b}_{6}^{\mathrm{Z}}$ | 1185 | - | C-H bend |
| $\mathrm{b}_{7}^{\mathrm{z}}$ | 1168 | - | C-H bend |
| $\mathrm{b}_{1}^{\mathrm{E}}$ | 1356 | 1363 | C-H bend, $\mathrm{C}=\mathrm{C}$ stretch (ring), O-H bend |
| $\mathrm{b}_{2}^{\mathrm{E}}$ | 1326 | 1330 | C-H bend, C-H bend (OMe) |
| $b_{3}^{\mathrm{E}}$ | 1281 | 1275 | C-H bend, C-O stretch |
| $\mathrm{b}_{4}^{\mathrm{E}}$ | 1252 | 1256 | C-H bend, $\mathrm{C}=\mathrm{C}$ stretch, $\mathrm{O}-\mathrm{H}$ bend |
| $\mathrm{b}_{5}^{\mathrm{E}}$ | 1178 | 1176 | C-H bend, O-H bend |
| $\mathrm{b}_{6}^{\mathrm{E}}$ | 1163 | 1162 | C-H bend, O-H bend |

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

| Band | B3LYP <br> $($ scaled 0.975) | Experiment | Assignment |
| :---: | :---: | :---: | :---: |
| $c_{1}^{Z}$ | 1380 |  | C-H bend |
| $c_{2}^{Z}$ | 1329 | $\cdots$ | C-H bend, O-H bend |
| $c_{3}^{Z}$ | 1297 |  | C-H bend |
| $c_{4}^{Z}$ | 1257 |  | C-H bend, C-C stretch |
| $c_{5}^{Z}$ | 1217 |  | C-H bend |
| $c_{6}^{Z}$ | 1180 | 1359 | C-H bend, O-H bend |
| $c_{1}^{\mathrm{E}}$ | 1354 | 1324 | C=C stretch, O-H bend |
| $c_{2}^{\mathrm{E}}$ | 1323 | S5 | C-H bend, C-O stretch, |
|  |  |  |  |


| $\mathrm{C}_{3}^{\mathrm{E}}$ | 1284 | 1278 | C-H bend, C-O stretch |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}_{4}^{\mathrm{E}}$ | 1236 | 1240 | C-H bend |
| $\mathrm{C}_{5}^{\mathrm{E}}$ | 1212 | 1213 | C-H bend |
| $\mathrm{C}_{6}^{\mathrm{E}}$ | 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.
5. IRPD spectrum of $[4 \mathrm{~d}+\mathrm{H}]^{+}$


Figure S-5. (a) Simulated IR spectrum of $[4 \mathrm{~d}+\mathrm{H}]^{+}\left({ }^{13} \mathrm{C}\right.$-labeled) and $\left[4 \mathrm{a}^{+}+\mathrm{H}\right]^{+}(\mathrm{b})$, obtained from harmonic B3LYP/Def2TZVP 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 expermimentally obtained IRPD spectra of $\mathrm{D}_{2}$-tagged $[4 \mathrm{~d}+\mathrm{H}]^{+}(\mathrm{c})$ and $\left[4 a^{+}+\mathrm{H}\right]^{+}(\mathrm{d})$ are shown below. The IRPD spectra were measured at 13 K .

## 6. Activators

Table S-4. These different activators were used for the generation of the corresponding $o-\mathrm{QMs}$.

| Precursor | Activator |
| :---: | :---: |
| 1a | $\begin{gathered} \mathrm{HCO}_{2} \mathrm{H} \\ \mathrm{HCO}_{2} \mathrm{Na}, \mathrm{HCO}_{2} \mathrm{Cs} \\ \text { BINOL phosphric acid } \\ \text { KI } \end{gathered}$ |
| 1b | $\mathrm{HCO}_{2} \mathrm{H}$ BINOL phosphoric acid KI |
| 1 c | $\mathrm{HCO}_{2} \mathrm{H}$ |
| 1d | $\mathrm{HCO}_{2} \mathrm{H}$ |

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


Figure S-6. $\mathrm{D}_{2}$-tagged IRPD spectra of $\left[4 \mathbf{a}^{+}+\mathrm{H}\right]^{+}$, measured at 13 K . The particular o-QM $\left[4 \mathrm{a}^{+}+\mathrm{H}\right]^{+}$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.
8. IRPD spectra of $[4 b+H]^{+}$generated with different activators


KI


Figure S-7. $\mathrm{D}_{2}$-tagged IRPD spectra of $[4 \mathbf{b}+\mathrm{H}]^{+}$, measured at 13 K . The particular o-QM $[4 \mathbf{b}+\mathrm{H}]^{+}$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):

${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}$ 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 ( $7.26 \mathrm{ppm},{ }^{1} \mathrm{H}, 77.16 \mathrm{ppm},{ }^{13} \mathrm{C}$ ). 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 $(\mathrm{KOH})$, ethyl acetate $(\mathrm{KOH})$. Flash column chromatography was performed by using Merck silica gel 60 $230-400$ mesh ( $0.040-0.063 \mathrm{~mm}$ ). Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel precoated TLC-sheets AlugramXtra SIL G/UV254. Spots were visualized by UV ( $\lambda=254 \mathrm{~nm}$ ) and treated with a solution of vaniline in methanol (technical grade). $\mathrm{Et}_{3} \mathrm{~N}$ was destilled freshly prior to use over $\mathrm{CaH}_{2}$. The ${ }^{13} \mathrm{C}$-labeled paraformaldehyde 6 was purchased from Sigma Aldrich (isotope purity: 99 atom $\%{ }^{13} \mathrm{C}$ ), 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 $-{ }^{13} \mathrm{C}$-labeled benzhydryl alcohol 1 a was prepared according to the procedure of ${ }^{13} \mathrm{C}$-labeled benzhydryl alcohol 1 d , PMP-substituted benzhydryl alcohol 1 b 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 2 a and 2 b was reported earlier by Schneider (unpublished experiments). ${ }^{10}$

## 10. Synthesis of 2-Hydroxy-4,6-dimethylbenz ${ }^{13} \mathrm{C}$-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 $\mathrm{MgCl}_{2}$ and 490 mg ( 15.8 mmol , 4.00 equiv) ${ }^{13}$ C-paraformaldehyde (6). 10 mL THF and 1.29 mL ( $939 \mathrm{mg}, 9.28 \mathrm{mmol}, 2.35$ equiv) freshly distilled $\mathrm{Et}_{3} \mathrm{~N}$ were added, the apparatus flushed for 10 min with $\mathrm{N}_{2}$ 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 1 N HCl were added, the biphasic system stirred for 5 min and the phases separated. The aqueos phase was extracted with ethyl acetate ( $3 \times 25 \mathrm{~mL}$ ), the combined organic phases dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$ 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.
$\mathrm{R}_{f}$ (hexan/EE 2/1): 0.69. IR (KBr): 3442 (m), 2979 (w), 2969 (w), 2927 (w), 2872 (m), 1632 ( s$), 1614$ ( s$), 1580$ ( s$), 1570$
 724 (s), 502 (s). HRMS (ESI): calculated for ${ }^{13} \mathrm{CC}_{8} \mathrm{H}_{10} \mathrm{NaO}_{2}{ }^{+}[\mathrm{M}+\mathrm{Na}]^{+}: 174.0607$, found 174.0607. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ ( 400 MHz ; $\left.\mathrm{CDCl}_{3}\right): 11.94\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{C}}=0.9 \mathrm{~Hz}, 1 \mathrm{H}\right), 10.23\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{H}, \mathrm{C}}=175.3 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.62(\mathrm{bs}, 1 \mathrm{H}), 6.53(\mathrm{bs}, 1 \mathrm{H}), 2.55(\mathrm{~s}, 3 \mathrm{H}), 2.30(\mathrm{~s}$,
$3 \mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(101 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right)$ : $194.7,163.6,149.4,142.0\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=4.1 \mathrm{~Hz}\right), 123.3\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.8 \mathrm{~Hz}\right), 116.7\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}\right.$ $=56.0 \mathrm{~Hz}), 116.3\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}, \mathrm{C}}=2.3 \mathrm{~Hz}\right), 22.3,18.2\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=4.1 \mathrm{~Hz}\right)$.
11. Synthesis of 2-(hydroxy(phenyl) - ${ }^{13} \mathbf{C}$-methyl)-3,5-dimethylphenol (1d):


In a 25 mL two necked round bottom flask with reflux condenser were added $167 \mathrm{mg}(6.88 \mathrm{mmol}, 2.60$ equiv $) \mathrm{Mg}$ turnings and the apparatus dried with a heat gun. 4 mL THF were added and additional $692 \mu(1.04 \mathrm{~g}, 6.62 \mathrm{mmol}$, 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 $0^{\circ} \mathrm{C}$ and $400 \mathrm{mg}(2.65 \mathrm{mmol}$, 1.00 equiv) 7 (dissolved in 5 mL THF) added at $0^{\circ} \mathrm{C}$. After 2 h stirring at rt the complete conversion of 7 was observed via TLC and subsequently $\left.15 \mathrm{~mL} \mathrm{NH} 4_{4} \mathrm{Cl}_{(\text {(qq) }}\right)$ were added. The two phases were stirred for 10 min at rt , the phases separated and the aqueous phase extracted with ethyl acetate ( $3 \times 25 \mathrm{~mL}$ ). The combined organic phases were washed with water and dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$. The solvent was removed under reduced pressure and the crude product purified via column chromatography ( $10 \% \mathrm{EE}$ in hexan). $588 \mathrm{mg}(97 \%$ ) of an amorphous colorless solid was obtained.
$\mathrm{R}_{f}$ (Hexan/EE 2/1): 0.61. IR (KBr): 3386 ( s$), 3246(\mathrm{~s}), 3028(\mathrm{w}), 2921(\mathrm{w}), 1627(\mathrm{~s}), 1577(\mathrm{~m}), 1494(\mathrm{~m}), 1460(\mathrm{~m}), 1447$ (m), $1400(\mathrm{w}), 1298(\mathrm{~s}), 1217(\mathrm{~m}), 1183(\mathrm{w}), 1132(\mathrm{~m}), 991(\mathrm{~s}), 852(\mathrm{~m}), 830(\mathrm{~s}), 723(\mathrm{~s}), 695(\mathrm{~m}), 639(\mathrm{~m}), 527(\mathrm{~m})$. HRMS (ESI): calculated for ${ }^{13} \mathrm{CC}_{14} \mathrm{H}_{16} \mathrm{NaO}_{2}{ }^{+}[\mathrm{M}+\mathrm{Na}]^{+}: 252.1076$, found $252.1081 .{ }^{1} \mathrm{H}-\mathrm{NMR}\left(400 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right): 8.47$ (s, 1H), $7.47-7.27(\mathrm{~m}, 5 \mathrm{H}), 6.62(\mathrm{bs}, 1 \mathrm{H}), 6.53(\mathrm{bs}, 1 \mathrm{H}), 6.15\left(\mathrm{dd},{ }^{1} \mathrm{~J}_{\mathrm{H}, \mathrm{C}}=144.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=2.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.01\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{C}}=\right.$ $\left.2.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=2.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 2.27(\mathrm{~s}, 3 \mathrm{H}), 2.14(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(101 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right): 156.3,141.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=47.5 \mathrm{~Hz}\right)$, 139.1, $135.8\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.8 \mathrm{~Hz}\right), 128.9\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.8 \mathrm{~Hz}\right), 128.4,127.2\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.1 \mathrm{~Hz}\right), 123.2\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.4 \mathrm{~Hz}\right), 121.3$ $\left(\mathrm{d},{ }^{1} J_{\mathrm{C}, \mathrm{C}}=49.3 \mathrm{~Hz}\right), 116.4\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=2.0 \mathrm{~Hz}\right), 74.8,21.1,19.7\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}, \mathrm{C}}=3.5 \mathrm{~Hz}\right)$.
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 $167 \mathrm{mg}(6.88 \mathrm{mmol}, 2.60$ equiv $) \mathrm{Mg}$ turnings and the apparatus dried with a heat gun. 4 mL THF were added and additional $692 \mu(1.04 \mathrm{~g}, 6.62 \mathrm{mmol}$, 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 $0^{\circ} \mathrm{C}$ and $398 \mathrm{mg}(2.65 \mathrm{mmol}$, 1.00 equiv) 2-hydroxy-4,6-dimethylbenzaldehyde (dissolved in 5 mL THF) added at $0^{\circ} \mathrm{C}$. After 2 h stirring at rt the complete conversion of the benzaldehyde was observed via TLC and subsequently $15 \mathrm{~mL} \mathrm{NH}_{4} \mathrm{Cl}_{(\text {aq, })}$ were added. The two phases were stirred for 10 min at rt , the phases separated and the aqueous phase extracted with ethyl acetate ( 3 x 25 mL ). The combined organic phases were washed with water and dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$. The solvent was removed under reduced
pressure and the crude product purified via column chromatography ( $10 \% \mathrm{EE}$ in hexan). 573 mg ( $95 \%$ ) of an amorphous colorless solid was obtained.
$\mathrm{R}_{f}$ (Hexan/EE 2/1): 0.61. IR (KBr): 3387 ( s$), 3248(\mathrm{~s}), 3029(\mathrm{w}), 2920(\mathrm{w}), 1626(\mathrm{~s}), 1578(\mathrm{~m}), 1494(\mathrm{~m}), 1460(\mathrm{~m}), 1447$
 HRMS (ESI): calculated for $\mathrm{C}_{15} \mathrm{H}_{16} \mathrm{NaO}_{2}{ }^{+}[\mathrm{M}+\mathrm{Na}]^{+}: 251.1043$, found $251.1040 .{ }^{1} \mathrm{H}-\mathrm{NMR}\left(400 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right)$ : 8.41 (s, $1 \mathrm{H}), 7.41-7.25(\mathrm{~m}, 5 \mathrm{H}), 6.63(\mathrm{bs}, 1 \mathrm{H}), 6.53(\mathrm{bs}, 1 \mathrm{H}), 6.17\left(\mathrm{~d},{ }^{3} \mathrm{~J}=2.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 2.84\left(\mathrm{~d},{ }^{3} \mathrm{~J}=3.0 \mathrm{~Hz}, 1 \mathrm{H}\right), 2.27(\mathrm{~s}, 3 \mathrm{H})$, $2.14(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(101 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right): 156.3,141.2,139.1,135.8,128.9,128.4,127.2,123.2,121.3,116.3,74.8$, 21.1, 19.7.

## 13. Synthesis of 4-(tertbutyl)-2-(hydroxy(4-methoxyphenyl)methyl)phenol (1c):



1c 97\%
In a 250 mL two necked round bottom flask with reflux condenser were added 1.42 g ( $58.5 \mathrm{mmol}, 2.60$ equiv) Mg turnings and the apparatus dried with a heat gun. 30 mL THF were added and additional $7.04 \mathrm{~mL}(10.5 \mathrm{~g}, 56.3 \mathrm{mmol}$, 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 $0^{\circ} \mathrm{C}$ and $4.01 \mathrm{~g}(22.5 \mathrm{mmol}$, 1.00 equiv) 5-(tert-butyl)-2-hydroxybenzaldehyde (dissolved in 10 mL THF) added at $0^{\circ} \mathrm{C}$. After 2 h stirring at rt the complete conversion of the benzaldehyde was observed via TLC and subsequently $150 \mathrm{~mL} \mathrm{NH}_{4} \mathrm{Cl}_{(\mathrm{aq})}$, were added. The two phases were stirred for 10 min at rt , the phases separated and the aqueous phase extracted with ethyl acetate ( 3 x 100 mL ). The combined organic phases were washed with water and dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$. The solvent was removed under reduced pressure and the crude product purified via column chromatography ( $10 \% \mathrm{EE}$ in hexan). 6.26 g ( $97 \%$ ) of an amorphous colorless solid was obtained.
 ( 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 $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NaO}_{3}{ }^{+}[\mathrm{M}+\mathrm{Na}]^{+}: 309.1461$, found 309.1463 . ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(400 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right): 7.70(\mathrm{~s}, 1 \mathrm{H}), 7.35-$ $7.26(\mathrm{~m}, 2 \mathrm{H}), 7.22(\mathrm{dd}, J=8.5,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.93-6.85(\mathrm{~m}, 3 \mathrm{H}), 6.84(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.95(\mathrm{bs}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H})$, $2.82(\mathrm{~d}, \mathrm{~J}=2.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.23(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(101 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right): 159.6,153.2,142.7,134.3,128.4,126.2,126.0$, 125.2, 116.9, 114.2, 77.4, 55.4, 34.2, 31.6.
14. NMR spectras of new compounds:


Figure S-8: ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ of benzaldehyde 7 .


Figure S-9: ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ of benzaldehyde 1 d .



Figure S-10: ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ of benzaldehyde 1 a .



| 90 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 | 10 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Figure $\mathrm{S}-11:{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ of benzaldehyde 1 c .
Overlay of ${ }^{13} \mathrm{C}$ labeled (1d) and non- ${ }^{13} \mathrm{C}$-labeled benzhydryl alcohol (1a):


Figure S-12: Overlay of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ of benzhydryl alcohol 1 d and 1a.
15. Coordinates of DFT geometries

Table S-6. $\mathrm{Z}-[4 \mathrm{~b}+\mathrm{H}]^{+}$
Total energy: - 691.831202 Hartree, zero-point energy: 0.236206 Hartree

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

Table S-7. $\mathrm{E}-[4 \mathrm{~b}+\mathrm{H}]^{+}$
Total energy: -691.835454 Hartree, zero-point energy: 0.236430 Hartree

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


| 5 | C | 3.283325 | -1.905581 | 0.376654 |
| :---: | :---: | :---: | :---: | :---: |
| 6 | C | 4.450137 | -1.176108 | 0.106691 |
| 7 | H | 5.310008 | 0.73789 | -0.3377 |
| 8 | H | 1.181722 | -1.813431 | 0.650692 |
| 9 | H | 3.346808 | -2.958151 | 0.612384 |
| 10 | H | 5.408426 | -1.678558 | 0.107863 |
| 11 | C | 0.755692 | 0.847604 | 0.129731 |
| 12 | O | 3.068586 | 2.157154 | -0.383855 |
| 13 | H | 3.937124 | 2.562413 | -0.505956 |
| 14 | H | 0.874476 | 1.91724 | 0.264325 |
| 15 | C | -0.568049 | 0.411977 | 0.014788 |
| 16 | C | -1.594754 | 1.330697 | 0.370145 |
| 17 | C | -0.96918 | -0.868725 | -0.469236 |
| 18 | C | -2.920087 | 0.988165 | 0.33344 |
| 19 | H | -1.311394 | 2.320299 | 0.705016 |
| 20 | C | -2.285822 | -1.211791 | -0.532832 |
| 21 | H | -0.228382 | -1.555945 | -0.847723 |
| 22 | C | -3.283643 | -0.299122 | -0.112004 |
| 23 | H | -3.671721 | 1.702097 | 0.632264 |
| 24 | H | -2.604719 | -2.168514 | -0.922119 |
| 25 | O | -4.524932 | -0.734679 | -0.199642 |
| 26 | C | -5.626561 | 0.112062 | 0.174531 |
| 27 | H | -6.515454 | -0.48821 | 0.013223 |
| 28 | H | -5.550108 | 0.391559 | 1.225408 |
| 29 | H | -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 | C | -2.381929 | -1.401914 | -0.2229 |
| 2 | C | -1.057687 | -1.00086 | -0.26867 |
| 3 | C | -0.694783 | 0.376272 | -0.074535 |
| 4 | C | -1.773823 | 1.323345 | 0.124026 |
| 5 | C | -3.065827 | 0.873256 | 0.188557 |
| 6 | H | -3.396039 | -0.486255 | 0.020146 |
| 7 | H | -2.624484 | -2.445203 | -0.387366 |
| 8 | C | -3.864184 | 1.580122 | 0.371605 |
| 9 |  | 0.605424 | 0.880395 | -0.160319 |


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

Table S-9. $\mathrm{E}-\left[4 \mathbf{a}^{+}+\mathrm{H}\right]^{+}$
Total energy: -655.918782 Hartree, zero-point energy: 0.258457 Hartree

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


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

Table S-10. Z-[4c $\left.{ }^{+}+\mathrm{H}\right]^{+}$
Total energy: -849.170099 Hartree, zero-point energy: 0.348291 Hartree

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


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

Table S-11. $\mathrm{E}-\left[4 \mathrm{c}^{+} \mathrm{H}\right]^{+}$
Total energy: -849.175804 Hartree, zero-point energy: 0.348392 Hartree

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


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

Table S-12. TS- $[4 \mathrm{a}+\mathrm{H}]^{+}$

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

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

Table S-13. TS-[4b+H] ${ }^{+}$
Total energy: -691.815405 Hartree, zero-point energy: 0.234811 Hartree

| Tag | Symbol | X | Y | Z |
| :--- | :--- | :--- | :--- | :--- |
| 1 | C | 3.840882 | 0.452481 | -0.953013 |
| 2 | C | 2.628583 | 0.851808 | -0.403181 |
| 3 | C | 2.006973 | 0.059424 | 0.567474 |


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

Table S-14. TS- $\left[4 \mathrm{c}^{+}+\mathrm{H}\right]^{+}$
Total energy: - 849.153099 Hartree, zero-point energy: 0.346665Hartree

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


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

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