Supplementary material
Wavelength-dependent intersystem crossing dynamics of phenolic carbonyls in wildfire emissions

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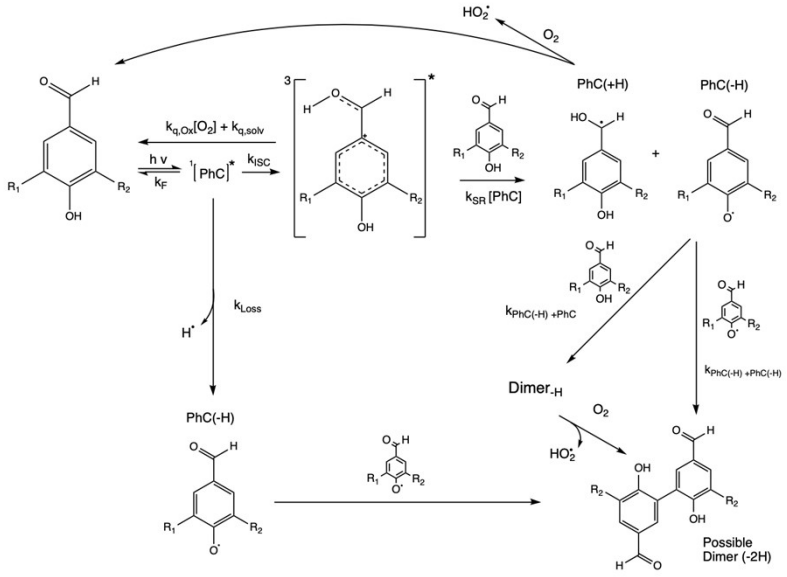
S1. Photochemical loss of Phenolic carbonyls scheme



Scheme S1. Photochemical loss of phenolic carbonyls.

Scheme shows a probable mechanism for loss of PhC (phenolic carbonyls) leading to formation of a dimer. Ground state PhC is excited to a singlet state, with efficient ISC to the triplet excited state. At pH = 2 the excited triplet state will be fully protonated. Bimolecular reaction between protonated triplet and ground state PhC forms 2 radicals, a phenoxy and a ketyl, that differ in the number of hydrogens relative to PhC, +1 and -1.(Anastasio 1997) At this point multiple pathways can lead to dimer formation. The two radicals formed can recombine within a solvent cage, followed by abstraction of 2 hydrogens. PhC_{-1} may also add to ground state vanillin, due to its relatively high concentration, followed by a single hydrogen abstraction. Combination of two PhC_{-1} directly yields the dimer, likely a major route to dimer formation.(Drozd et al. 2024) In the presence of dissolved oxygen, hydrogen abstraction from PH_{+1} will regenerate vanillin, reducing the observed quantum yield. Direct photolytic loss of a hydrogen, from either

the singlet or triplet state (shown only for singlet state), has been suggested by Vione et al.(Vione 2019)

References
*) C. Anastasio, B. C. Faust and C. Janakiram Rao, *Environmental Science & Technology*, 1997, **31**, 218–232.
*) D. Vione, A. Albinet, F. Barsotti, M. Mekic, B. Jiang, C. Minero, M. Brigante and S. Gligorovski, *Atmos Environ*, 2019, **206**, 197–207.
*) G. T. Drozd, T. Weltzin, S. Skiffington, D. Lee, R. Valiev, T. Kurtén, L. R. Madison, Y. He and L. Gargano, *Environ. Sci.: Atmos.*, 2024, **4**, 509–518

S2. LED Illumination

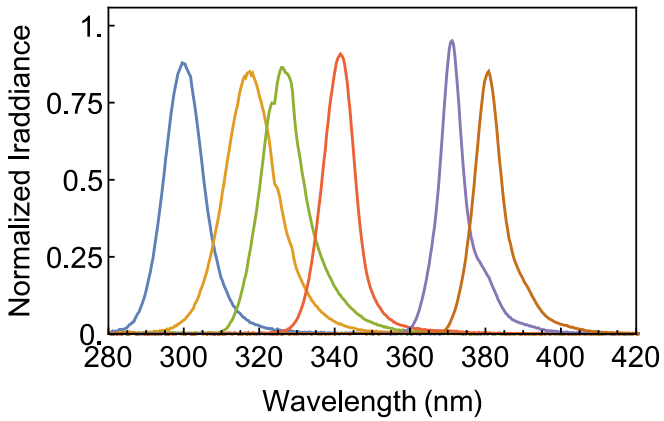


Figure S1. Spectral profiles of LED (light emitted diode) used for quantum yield determinations.

Typical total, volume-averaged photon fluxes were $2.0 * 10^{15} - 3 * 10^{17} \frac{photons}{cm^3\ sec}$. Greater fluxes were used for longer wavelengths where the molar absorptivity and the fraction of absorbed photons was low.

S3. Screening Effects

Due to absorption by the sample, the photon flux decreases as light penetrates the solution in the reaction vial; thus the reaction necessarily proceeds at a slower rate at the top of the vial. The light absorption weighted internal screening factor, S, is calculated to account for this effect. S is the ratio of the actual rate of absorption compared to the rate of absorption under optically thin

conditions. All calculated quantum yields are divided by S, to account for artificially slower volume-averaged reaction rates in solutions that are optically thicker (e.g. larger volume or higher concentration). In equation S1, ε_λ is molar absorptivity at a given wavelength, l is the pathlength, PhC is the concentration of phenolic carbonyl, and I_λ is the photon flux at a given wavelength.

$$S = \frac{\hat{a}\left(1 - 10^{-\hat{I}\mu_{\hat{I}\text{»}} * l * [PhC]}\right) * I_{\hat{I}\text{»}}}{\hat{a}2.303 * \hat{I}\mu_{\hat{I}\text{»}} * l * [PhC] * I_{\hat{I}\text{»}}} \quad \text{(S1)}$$

S4. Excited electronic energies (in eV) of equilibrium geometries relative to the equilibrium geometry of the ground electronic state.

State/Molecule	S(ππ*)	T(nπ*)
Van	4.12	3.41
Iso-Van	4.02	3.29
4HBA	4.50	3.33
Syr	4.03	3.39
ConfAld(Trans-I)	3.50	3.30
ConfAld(Trans-II)	3.35	3.15
ConfAld(Trans-III)	3.39	3.15
ConfAld(Trans-IV)	3.46	3.39
ConfAld(Cis-I)	4.48	4.46
ConfAld(Trans-II)	3.37	3.21

S5. Molecular structures

Molecular structures in S_0 state

Van

C	-1.226142000	1.303471000	-0.016496000
C	0.104946000	1.699696000	-0.042287000
C	-1.562094000	-0.065160000	0.004317000
H	0.330635000	2.759833000	-0.058638000
C	1.110460000	0.744996000	-0.046908000
C	-0.563753000	-1.016604000	-0.000603000
H	2.152314000	1.046377000	-0.069002000
H	-0.803338000	-2.073765000	0.015137000
C	0.782550000	-0.612219000	-0.026152000
O	-2.207561000	2.225757000	-0.011773000
H	-3.056213000	1.754032000	0.005800000
O	-2.903382000	-0.292324000	0.027991000
C	-3.355280000	-1.638629000	0.047238000
H	-3.023815000	-2.175584000	-0.846760000
H	-2.997370000	-2.159005000	0.940826000
H	-4.442715000	-1.594239000	0.063014000
C	1.811272000	-1.648938000	-0.030413000
O	3.020434000	-1.464140000	-0.047163000
H	1.427327000	-2.685951000	-0.017030000
O	4.496296000	0.942359000	-0.002782000
H	4.519961000	1.151570000	0.938692000

H	4.035164000	0.083844000	-0.034400000

IsoVan

C	1.464914000	-0.519390000	-0.257102000
C	0.287888000	-1.261377000	-0.280320000
C	1.410592000	0.879022000	-0.120444000
H	0.371368000	-2.336094000	-0.397540000
C	-0.947120000	-0.644898000	-0.158700000
C	0.176819000	1.496115000	0.014224000
H	-1.862892000	-1.225640000	-0.177058000
H	0.125865000	2.576557000	0.122383000
C	-1.000933000	0.741835000	-0.003419000
O	2.651759000	-1.165939000	-0.433299000
O	2.587234000	1.556234000	-0.146252000
C	-2.276650000	1.451106000	0.139117000
O	-3.382918000	0.934496000	0.143127000
H	-2.192711000	2.547716000	0.250702000
O	-4.137550000	-1.793412000	-0.015604000
H	-4.046962000	-2.083124000	0.900162000
H	-3.937980000	-0.840770000	0.025848000
C	3.551516000	-1.135753000	0.678380000
H	3.091789000	-1.603921000	1.554490000
H	4.425218000	-1.713286000	0.377417000

H	3.850331000	-0.114201000	0.919415000
H	2.425610000	2.501770000	-0.030014000

Syr

C	-1.208390000	1.064362000	-0.001674000
C	-1.834527000	-0.187353000	0.005208000
C	0.191858000	1.156041000	-0.016508000
C	-1.049396000	-1.333896000	-0.001970000
C	0.978340000	0.019776000	-0.023378000
H	-1.506448000	-2.315777000	0.003299000
H	2.059968000	0.077374000	-0.038473000
C	0.344935000	-1.228575000	-0.016413000
O	-1.961210000	2.183124000	0.005792000
H	-1.350398000	2.937960000	0.001552000
O	0.640146000	2.441203000	-0.023136000
C	2.044812000	2.655681000	-0.013828000
H	2.500086000	2.228865000	0.884860000
H	2.515439000	2.216755000	-0.898310000
H	2.186835000	3.734886000	-0.019853000
C	1.124636000	-2.464160000	-0.024215000
O	2.345250000	-2.543740000	-0.037011000
H	0.524786000	-3.392713000	-0.017762000
O	4.278562000	-0.479365000	-0.023490000

H	4.385217000	-0.298700000	0.918268000
H	3.667652000	-1.239142000	-0.043877000
O	-3.190327000	-0.160155000	0.019284000
C	-3.872391000	-1.403859000	0.025562000
H	-3.642199000	-1.990096000	-0.870147000
H	-3.624700000	-1.990783000	0.916147000
H	-4.934880000	-1.165267000	0.036066000

4HBA

C	2.161340000	-0.405683000	-0.000300000
C	2.067288000	0.988071000	0.036299000
C	1.005285000	-1.194654000	-0.039731000
C	0.820177000	1.581989000	0.032730000
C	-0.237352000	-0.591675000	-0.042733000
H	0.740373000	2.664858000	0.060825000
H	-1.137577000	-1.197397000	-0.075380000
C	-0.344303000	0.805316000	-0.006705000
O	3.399496000	-0.940562000	0.003758000
H	3.346816000	-1.905464000	-0.024213000
C	-1.639168000	1.478304000	-0.009615000
O	-2.734635000	0.934163000	-0.038932000
H	-1.588708000	2.582592000	0.017453000
O	-3.393423000	-1.810441000	-0.044140000

H	-3.376742000	-2.029268000	0.895293000
H	-3.224888000	-0.850159000	-0.058199000
H	1.092726000	-2.276787000	-0.067408000
H	2.976896000	1.576340000	0.066470000

ConfAld

Trans-I

C	-2.858329000	-0.564300000	0.013589000
C	-2.412306000	-1.874350000	0.028263000
C	-1.927407000	0.496443000	-0.007233000
H	-3.140758000	-2.676741000	0.044111000
C	-1.046780000	-2.135476000	0.022180000
C	-0.574602000	0.235521000	-0.013148000
H	-0.699963000	-3.163561000	0.033514000
H	0.133975000	1.053139000	-0.029159000
C	-0.114064000	-1.097002000	0.001553000
O	-4.179297000	-0.288012000	0.018826000
H	-4.276379000	0.677788000	0.005837000
O	-2.513773000	1.724157000	-0.019904000
C	-1.676218000	2.870743000	-0.043264000
H	-1.038839000	2.908656000	0.845481000
H	-1.051853000	2.881781000	-0.941923000
H	-2.341119000	3.732521000	-0.051312000

C	3.696138000	-1.119067000	-0.026993000
O	4.718732000	-0.440384000	-0.042117000
H	3.777193000	-2.222025000	-0.015587000
O	3.995582000	2.277134000	-0.011608000
H	3.898407000	2.450649000	0.932149000
H	4.359393000	1.371019000	-0.041325000
C	1.301206000	-1.428070000	-0.004365000
H	1.519747000	-2.495491000	0.007967000
C	2.350828000	-0.584161000	-0.022808000
H	2.259449000	0.497415000	-0.037970000

Trans-II

C	-2.584165000	-0.931959000	0.020150000
C	-1.774622000	-2.058891000	0.037693000
C	-2.003753000	0.349097000	-0.011486000
H	-2.242941000	-3.036234000	0.062251000
C	-0.394162000	-1.921747000	0.024004000
C	-0.629969000	0.483929000	-0.024798000
H	0.222147000	-2.813120000	0.038430000
H	-0.173370000	1.466220000	-0.049309000
C	0.198084000	-0.655421000	-0.007279000
O	-3.928597000	-1.056633000	0.033458000
H	-4.305480000	-0.162267000	0.017219000

O	-2.916736000	1.359183000	-0.025780000
C	-2.437856000	2.695540000	-0.056369000
H	-1.832537000	2.915678000	0.828355000
H	-1.846390000	2.879929000	-0.958454000
H	-3.319117000	3.334517000	-0.062350000
C	4.017001000	-1.022382000	-0.033778000
O	4.477005000	0.115606000	-0.050054000
H	4.718700000	-1.875191000	-0.032225000
O	3.117879000	2.581537000	0.017161000
H	2.986058000	2.719796000	0.962882000
H	3.648777000	1.763440000	-0.022809000
C	1.637163000	-0.446044000	-0.022298000
H	1.952161000	0.595833000	-0.040923000
C	2.607026000	-1.382348000	-0.016125000
H	2.387096000	-2.444789000	0.000366000

Trans-III

C	2.420818000	-1.157213000	-0.016293000
C	1.380986000	-2.070304000	-0.042761000
C	2.142851000	0.226577000	0.005774000
H	1.612485000	-3.129042000	-0.059212000
C	0.067569000	-1.614897000	-0.047558000
C	0.840528000	0.675906000	0.000443000

H	-0.747916000	-2.330421000	-0.068243000
H	0.636261000	1.738416000	0.017592000
C	-0.223667000	-0.249073000	-0.026663000
O	3.703524000	-1.576651000	-0.011008000
H	4.269889000	-0.788394000	0.008505000
O	3.263957000	0.997636000	0.031532000
C	3.109860000	2.408920000	0.056388000
H	2.584373000	2.761478000	-0.836377000
H	2.565923000	2.728023000	0.950740000
H	4.115804000	2.824366000	0.074530000
C	-3.544102000	1.672922000	-0.030439000
O	-4.437616000	0.831184000	-0.041789000
H	-3.825469000	2.741011000	-0.026339000
O	-4.235968000	-1.974175000	0.019400000
H	-4.162002000	-2.157371000	0.963744000
H	-4.373471000	-1.008484000	-0.016588000
C	-1.618749000	0.157269000	-0.033243000
H	-2.335081000	-0.662245000	-0.049990000
C	-2.112856000	1.411849000	-0.021705000
H	-1.471398000	2.286971000	-0.007103000

Trans-IV

C	-2.393368000	1.243260000	-0.013623000

C	-1.191245000	1.935591000	-0.031606000
C	-2.393004000	-0.163450000	0.005407000
H	-1.213928000	3.019254000	-0.045999000
C	0.009428000	1.240489000	-0.031098000
C	-1.197265000	-0.853811000	0.005712000
H	0.939349000	1.796730000	-0.045493000
H	-1.189610000	-1.937144000	0.020133000
C	0.026221000	-0.157272000	-0.012599000
O	-3.566679000	1.911476000	-0.014226000
H	-4.279158000	1.252386000	-0.000569000
O	-3.641490000	-0.705975000	0.022114000
C	-3.760014000	-2.120704000	0.041094000
H	-3.307044000	-2.564495000	-0.850783000
H	-3.292564000	-2.541778000	0.936519000
H	-4.826937000	-2.336339000	0.052454000
C	3.626203000	-1.406037000	-0.023024000
O	4.812587000	-1.091748000	-0.033668000
H	3.348477000	-2.476530000	-0.010098000
O	5.000782000	1.715015000	-0.014524000
H	4.957169000	1.915330000	0.927904000
H	5.054180000	0.739931000	-0.038820000
C	1.259140000	-0.929647000	-0.011630000
H	1.125444000	-2.011129000	0.002588000

C	2.523920000	-0.467256000	-0.025794000
H	2.782926000	0.586667000	-0.042442000

CIS-I

C	2.783986000	0.001390000	0.012255000
C	2.795342000	-1.384531000	0.020372000
C	1.555443000	0.690649000	-0.002250000
H	3.747203000	-1.902767000	0.031442000
C	1.593936000	-2.077713000	0.014136000
C	0.360964000	0.003558000	-0.008177000
H	1.610105000	-3.162559000	0.020333000
H	-0.584799000	0.525653000	-0.018945000
C	0.361751000	-1.407645000	-0.000006000
O	3.939225000	0.697086000	0.018123000
H	3.711532000	1.640955000	0.010693000
O	1.700281000	2.045747000	-0.009096000
C	0.525202000	2.842312000	-0.023943000
H	-0.070649000	2.645576000	-0.920421000
H	-0.085671000	2.656725000	0.864783000
H	0.859526000	3.878338000	-0.027578000
C	-2.961847000	-0.816656000	-0.028410000
O	-2.575851000	0.351776000	-0.029558000
H	-4.050522000	-0.997540000	-0.037007000
O	-5.116117000	1.489191000	-0.044331000

H	-5.337345000	1.505294000	0.893992000
H	-4.159918000	1.296169000	-0.051163000
C	-0.825889000	-2.244325000	-0.005435000
H	-0.568459000	-3.302076000	0.001467000
C	-2.166993000	-2.028819000	-0.016994000
H	-2.782672000	-2.923484000	-0.017975000

Cis-II

C	-1.907562000	1.284396000	-0.345426000
C	-0.661392000	1.566989000	-0.876882000
C	-2.202675000	-0.021556000	0.092472000
H	-0.462118000	2.568772000	-1.239797000
C	0.304053000	0.568187000	-0.955881000
C	-1.249520000	-1.015351000	0.001035000
H	1.255740000	0.792810000	-1.422113000
H	-1.474039000	-2.022511000	0.331061000
C	0.034177000	-0.724255000	-0.501331000
O	-2.853840000	2.245923000	-0.263367000
H	-3.648677000	1.842064000	0.119991000
O	-3.468363000	-0.157589000	0.573277000
C	-3.882942000	-1.437726000	1.026876000
H	-3.841140000	-2.173158000	0.217663000
H	-3.263110000	-1.777284000	1.862348000
H	-4.912477000	-1.322895000	1.361212000

C	3.101038000	-0.593195000	0.018440000
O	4.327867000	-0.566946000	0.051494000
H	2.532951000	0.278411000	0.378842000
O	4.478572000	1.980102000	1.141406000
H	4.401620000	1.805014000	2.086462000
H	4.640964000	1.097500000	0.756838000
C	1.010635000	-1.812142000	-0.563552000
H	0.583228000	-2.796263000	-0.747501000
C	2.350045000	-1.756475000	-0.422266000
H	2.938031000	-2.657604000	-0.568395000

Molecular structures in the first excited ππ* singlet state.

Van S_2

C	-2.048048000	-0.472772000	0.038239000
C	-1.723625000	-1.835510000	0.057907000
C	-0.975574000	0.486287000	-0.024970000
H	-2.524322000	-2.564486000	0.100989000
C	-0.409014000	-2.220257000	0.022591000
C	0.374263000	0.100009000	-0.061985000
H	-0.162227000	-3.277705000	0.037870000
H	1.162037000	0.841744000	-0.102271000
C	0.691030000	-1.264059000	-0.033819000

O	-3.325483000	-0.067379000	0.074261000
H	-3.352569000	0.903783000	0.054090000
O	-1.404406000	1.739129000	-0.040867000
C	-0.470628000	2.826790000	-0.115562000
H	0.213871000	2.791023000	0.732824000
H	0.087897000	2.769954000	-1.050841000
H	-1.073312000	3.730274000	-0.084329000
C	2.053271000	-1.717345000	-0.059355000
O	3.069124000	-0.965828000	-0.102385000
H	2.195157000	-2.810234000	-0.041840000
O	3.187271000	1.739151000	0.110527000
H	3.113104000	1.879172000	1.062065000
H	3.178271000	0.757030000	0.020878000

IsoVan S_2

C	1.455697000	-0.613969000	-0.025081000
C	0.235376000	-1.318262000	-0.067447000
C	1.381178000	0.828560000	0.016245000
H	0.289117000	-2.400681000	-0.101383000
C	-0.968345000	-0.674192000	-0.065593000
C	0.144606000	1.494720000	0.020681000
H	-1.892437000	-1.241721000	-0.098207000
H	0.144365000	2.580194000	0.055645000

C	-1.056328000	0.783317000	-0.019808000
O	2.566107000	-1.358651000	-0.038711000
O	2.524097000	1.503916000	0.048174000
C	-2.323597000	1.451860000	-0.017470000
O	-3.449032000	0.876656000	-0.053033000
H	-2.282659000	2.552498000	0.016533000
O	-4.124244000	-1.750223000	0.007345000
H	-4.072298000	-1.955081000	0.948352000
H	-3.895547000	-0.792552000	-0.030781000
C	3.888058000	-0.825640000	0.036553000
H	4.027447000	-0.253743000	0.956439000
H	4.542804000	-1.694991000	0.030838000
H	4.101861000	-0.186499000	-0.822558000
H	2.362048000	2.460623000	0.066446000

4HBA S_2

C	2.154157000	-0.431902000	-0.002575000
C	2.077688000	1.001393000	0.062315000
C	0.974508000	-1.214232000	-0.066336000
C	0.863555000	1.613918000	0.059439000
C	-0.249325000	-0.608018000	-0.070282000
H	0.794870000	2.695382000	0.108010000
H	-1.162072000	-1.190102000	-0.117654000
C	-0.351038000	0.844021000	-0.009352000

O	3.378433000	-0.954623000	0.002773000
H	3.348204000	-1.923950000	-0.043315000
C	-1.635520000	1.496131000	-0.019149000
O	-2.738338000	0.877909000	-0.082768000
H	-1.626436000	2.595781000	0.029609000
O	-3.382109000	-1.779481000	0.004178000
H	-3.313649000	-1.978057000	0.945559000
H	-3.174133000	-0.820047000	-0.041581000
H	1.059515000	-2.296241000	-0.110863000
H	3.005660000	1.558928000	0.112411000

Syr S_1

C	-1.203237000	1.087407000	0.013770000
C	-1.827768000	-0.207215000	0.017490000
C	0.202778000	1.161833000	-0.032986000
C	-1.059295000	-1.383031000	-0.022302000
C	0.965302000	0.025292000	-0.073147000
H	-1.541449000	-2.351363000	-0.017001000
H	2.047275000	0.072755000	-0.102561000
C	0.335168000	-1.295681000	-0.063687000
O	-1.965095000	2.186400000	0.053245000
H	-1.365908000	2.953971000	0.038915000
O	0.655895000	2.442061000	-0.031001000

C	2.059901000	2.648796000	-0.131276000
H	2.585536000	2.178767000	0.704540000
H	2.444846000	2.242946000	-1.071333000
H	2.209791000	3.726396000	-0.104358000
C	1.147120000	-2.475715000	-0.098926000
O	2.412795000	-2.482069000	-0.137073000
H	0.601594000	-3.432389000	-0.097150000
O	4.203334000	-0.474219000	0.202392000
H	4.169690000	-0.319120000	1.153767000
H	3.575003000	-1.222522000	0.069495000
O	-3.147019000	-0.164275000	0.060565000
C	-3.903375000	-1.380599000	0.064701000
H	-3.706636000	-1.948268000	-0.846489000
H	-3.652879000	-1.975846000	0.944554000
H	-4.945709000	-1.075022000	0.100771000

ConAld S_1

Trans-I

C	-2.861328000	-0.515788000	0.021622000
C	-2.463613000	-1.865931000	0.039718000
C	-1.875305000	0.519021000	-0.013270000
H	-3.229226000	-2.632402000	0.064185000
C	-1.135025000	-2.172833000	0.026399000
C	-0.534898000	0.218604000	-0.026361000

H	-0.817820000	-3.209917000	0.040448000
H	0.199202000	1.010617000	-0.053332000
C	-0.110562000	-1.146030000	-0.005020000
O	-4.152366000	-0.200098000	0.035674000
H	-4.234852000	0.770876000	0.019807000
O	-2.426123000	1.745980000	-0.029647000
C	-1.569994000	2.886137000	-0.062031000
H	-0.931328000	2.910028000	0.824641000
H	-0.954369000	2.876590000	-0.965079000
H	-2.226614000	3.753080000	-0.069730000
C	3.687244000	-1.109925000	-0.037651000
O	4.704646000	-0.371436000	-0.048577000
H	3.829779000	-2.207017000	-0.033161000
O	3.912489000	2.251252000	0.024881000
H	3.774111000	2.390442000	0.968991000
H	4.267676000	1.333647000	-0.020676000
C	1.245431000	-1.530908000	-0.012128000
H	1.451390000	-2.598220000	0.000192000
C	2.343692000	-0.653616000	-0.030381000
H	2.209025000	0.424298000	-0.040319000

Trans-II

C	-2.584590000	-0.956650000	0.021820000
C	-1.728211000	-2.064172000	0.038960000

C	-2.037578000	0.369638000	-0.011075000
H	-2.165251000	-3.055696000	0.063880000
C	-0.371626000	-1.877183000	0.023781000
C	-0.681170000	0.564613000	-0.026805000
H	0.279612000	-2.741303000	0.036944000
H	-0.264811000	1.563484000	-0.052047000
C	0.210140000	-0.549679000	-0.010470000
O	-3.903446000	-1.121987000	0.035714000
H	-4.326519000	-0.244403000	0.019228000
O	-2.992715000	1.314412000	-0.023005000
C	-2.602051000	2.686085000	-0.057023000
H	-2.010013000	2.935979000	0.826963000
H	-2.027642000	2.896651000	-0.962628000
H	-3.525538000	3.260364000	-0.060507000
C	3.974987000	-1.082110000	-0.032589000
O	4.516841000	0.052248000	-0.063210000
H	4.627900000	-1.971908000	-0.019532000
O	3.380561000	2.538099000	0.027413000
H	3.207437000	2.648537000	0.969755000
H	3.796837000	1.647885000	-0.023984000
C	1.601767000	-0.330331000	-0.027989000
H	1.943994000	0.699342000	-0.055880000
C	2.578747000	-1.345139000	-0.013693000

H	2.291575000	-2.391532000	0.013010000

Trans-III

C	2.454455000	-1.145048000	-0.018623000
C	1.427064000	-2.105196000	-0.056035000
C	2.131801000	0.246141000	0.009788000
H	1.697421000	-3.154370000	-0.076835000
C	0.126028000	-1.693813000	-0.064815000
C	0.825366000	0.667758000	0.000457000
H	-0.674937000	-2.424617000	-0.093240000
H	0.597024000	1.723558000	0.023100000
C	-0.234642000	-0.291433000	-0.037545000
O	3.727122000	-1.528815000	-0.010321000
H	4.290081000	-0.733650000	0.015931000
O	3.230825000	1.023733000	0.044395000
C	3.069835000	2.439790000	0.072964000
H	2.544846000	2.783804000	-0.821973000
H	2.520366000	2.745101000	0.967314000
H	4.074767000	2.855231000	0.095691000
C	-3.491522000	1.677297000	-0.042912000
O	-4.433113000	0.843934000	-0.059629000
H	-3.744007000	2.751679000	-0.034533000
O	-4.348350000	-1.889174000	0.065562000
H	-4.213253000	-2.048825000	1.007105000

H	-4.389665000	-0.907993000	0.005148000
C	-1.600143000	0.056606000	-0.048772000
H	-2.318916000	-0.756287000	-0.072053000
C	-2.103004000	1.372412000	-0.034175000
H	-1.427032000	2.221858000	-0.017722000

Trans-IV

C	-2.330001000	1.268657000	-0.020284000
C	-1.085245000	1.910261000	-0.041131000
C	-2.393018000	-0.166294000	0.005737000
H	-1.061890000	2.993676000	-0.059530000
C	0.064570000	1.167965000	-0.038289000
C	-1.245661000	-0.917952000	0.007709000
H	1.020803000	1.674195000	-0.054819000
H	-1.292899000	-1.999043000	0.026372000
C	0.031127000	-0.284178000	-0.014662000
O	-3.455148000	1.976402000	-0.023971000
H	-4.211272000	1.362036000	-0.008241000
O	-3.655815000	-0.619367000	0.026494000
C	-3.883661000	-2.027949000	0.056441000
H	-3.462113000	-2.500820000	-0.833871000
H	-3.443828000	-2.465372000	0.956037000
H	-4.963439000	-2.155730000	0.069919000
C	3.661111000	-1.390949000	-0.033134000

O	4.853980000	-0.994251000	-0.044929000
H	3.467070000	-2.480168000	-0.023930000
O	4.898733000	1.741892000	0.013992000
H	4.802935000	1.923800000	0.956085000
H	4.955334000	0.759011000	-0.024280000
C	1.206755000	-1.061252000	-0.013675000
H	1.082651000	-2.141155000	0.001819000
C	2.517224000	-0.552237000	-0.030783000
H	2.713457000	0.515741000	-0.045822000

Cis-I

C	-2.213435000	-0.097291000	0.309129000
C	-2.241230000	-1.483560000	0.529903000
C	-1.097494000	0.495159000	-0.277042000
H	-3.140466000	-1.913857000	0.956477000
C	-1.148919000	-2.271412000	0.221709000
C	0.033863000	-0.273795000	-0.580951000
H	-1.174438000	-3.336241000	0.425161000
H	0.723261000	0.090411000	-1.329652000
C	0.028974000	-1.697725000	-0.286594000
O	-3.305929000	0.643204000	0.603344000
H	-3.113289000	1.560873000	0.353118000
O	-1.257704000	1.812997000	-0.556881000
C	-0.193123000	2.532520000	-1.174900000

H	0.688283000	2.555806000	-0.529617000
H	0.054977000	2.101950000	-2.149517000
H	-0.568225000	3.544497000	-1.319806000
C	2.651888000	-0.585487000	0.199469000
O	1.669299000	0.112534000	0.695119000
H	3.639889000	-0.117308000	0.217555000
O	2.395193000	2.771871000	1.076428000
H	3.042106000	2.874949000	0.368406000
H	2.117873000	1.837706000	1.003252000
C	1.224692000	-2.441586000	-0.458735000
H	1.151001000	-3.518308000	-0.580257000
C	2.487401000	-1.846751000	-0.363253000
H	3.376446000	-2.385756000	-0.671610000

Cis-II

C	-1.942986000	1.342333000	-0.230076000
C	-0.619197000	1.641346000	-0.560120000
C	-2.317553000	-0.012056000	0.061295000
H	-0.362249000	2.666554000	-0.800034000
C	0.322541000	0.643439000	-0.575587000
C	-1.383397000	-1.014546000	0.039593000
H	1.334743000	0.872604000	-0.877669000
H	-1.663794000	-2.035956000	0.262846000

C	-0.020175000	-0.726541000	-0.264129000
O	-2.863053000	2.300744000	-0.181198000
H	-3.716655000	1.900072000	0.063657000
O	-3.625287000	-0.129624000	0.344153000
C	-4.148886000	-1.419049000	0.658638000
H	-4.010558000	-2.102482000	-0.182828000
H	-3.662084000	-1.821169000	1.550670000
H	-5.209712000	-1.272903000	0.848092000
C	3.175351000	-0.632624000	-0.010171000
O	4.429738000	-0.681673000	-0.111304000
H	2.714716000	0.288578000	0.381665000
O	4.990859000	1.812544000	0.787776000
H	5.015590000	1.679231000	1.742105000
H	4.925200000	0.897927000	0.429528000
C	0.917266000	-1.784772000	-0.300851000
H	0.493085000	-2.785252000	-0.276752000
C	2.323046000	-1.716969000	-0.354657000
H	2.847615000	-2.626495000	-0.640300000

Molecular structures in the target triplet nπ* state.

Van T_2

C	-2.020534000	-0.454581000	0.106237000
C	-1.714943000	-1.805926000	0.146856000
C	-0.986244000	0.483955000	-0.045854000
H	-2.522481000	-2.519744000	0.268126000
C	-0.399582000	-2.234787000	0.032106000
C	0.330211000	0.077594000	-0.160727000
H	-0.173205000	-3.294793000	0.062233000
H	1.128308000	0.805111000	-0.242670000
C	0.637183000	-1.301705000	-0.126519000
O	-3.309374000	-0.032681000	0.214686000
H	-3.299245000	0.935057000	0.156646000
O	-1.419521000	1.776746000	-0.059622000
C	-0.462167000	2.801245000	-0.279273000
H	0.303542000	2.803627000	0.502303000
H	0.021436000	2.682404000	-1.253988000
H	-1.010879000	3.741392000	-0.255747000
C	1.994647000	-1.755858000	-0.250743000
O	2.992787000	-0.945985000	-0.453277000
H	2.282634000	-2.801073000	-0.127350000
O	3.173540000	1.769029000	0.524911000
H	2.813176000	1.775533000	1.420334000
H	3.496798000	0.864212000	0.415348000

IsoVan T_2

C	1.534265000	-0.443568000	-0.419210000
C	0.387812000	-1.202385000	-0.237993000
C	1.438638000	0.959121000	-0.403593000
H	0.484852000	-2.282875000	-0.263517000
C	-0.852470000	-0.610567000	-0.038690000
C	0.213415000	1.567998000	-0.196097000
H	-1.741147000	-1.220330000	0.083679000
H	0.150740000	2.652175000	-0.182906000
C	-0.948135000	0.792084000	-0.007722000
O	2.734793000	-1.062675000	-0.665733000
O	2.586410000	1.661135000	-0.605643000
C	-2.203550000	1.453524000	0.208646000
O	-3.318641000	0.816000000	0.401078000
H	-2.313733000	2.539222000	0.184337000
O	-4.029611000	-1.927950000	0.177696000
H	-4.084036000	-1.776846000	1.129547000
H	-4.257710000	-1.067271000	-0.195999000
C	3.666846000	-1.000067000	0.411633000
H	3.257390000	-1.478685000	1.307967000
H	4.555281000	-1.543552000	0.087933000
H	3.936666000	0.033932000	0.641583000
H	2.400200000	2.607720000	-0.553817000

4HBA T_2

C	2.185836000	-0.422182000	0.003268000
C	2.112752000	0.971121000	0.078674000
C	1.014537000	-1.169288000	-0.084563000
C	0.886361000	1.605263000	0.064277000
C	-0.222588000	-0.540108000	-0.099576000
H	0.842095000	2.687973000	0.122912000
H	-1.128349000	-1.134790000	-0.163876000
C	-0.308418000	0.862628000	-0.026687000
O	3.425554000	-0.987820000	0.020622000
H	3.343730000	-1.948395000	-0.038053000
C	-1.571945000	1.546595000	-0.043884000
O	-2.711047000	0.923800000	-0.127759000
H	-1.660638000	2.631396000	0.029993000
O	-3.395785000	-1.883306000	0.051627000
H	-3.217186000	-1.984930000	0.994752000
H	-3.670249000	-0.960868000	-0.028342000
H	1.067533000	-2.253140000	-0.140921000
H	3.031777000	1.542859000	0.147955000

Syr T_3

C	-1.207379000	1.064745000	0.017478000
C	-1.825490000	-0.190590000	0.043567000

C	0.182758000	1.143760000	-0.087616000
C	-1.058539000	-1.345395000	-0.041513000
C	0.970874000	0.004797000	-0.173373000
H	-1.528076000	-2.319692000	-0.024280000
H	2.049961000	0.073833000	-0.218706000
C	0.342139000	-1.253714000	-0.154004000
O	-1.964477000	2.194265000	0.096148000
H	-1.349071000	2.942147000	0.052487000
O	0.650273000	2.425226000	-0.092385000
C	2.042562000	2.630074000	-0.277694000
H	2.623483000	2.159259000	0.520922000
H	2.372109000	2.233086000	-1.242909000
H	2.197077000	3.707652000	-0.254143000
C	1.115474000	-2.459863000	-0.249397000
O	2.407285000	-2.456225000	-0.402151000
H	0.684071000	-3.452551000	-0.110418000
O	4.227017000	-0.463461000	0.636869000
H	3.919115000	-0.204331000	1.514134000
H	3.891781000	-1.364750000	0.533862000
O	-3.179665000	-0.166538000	0.154811000
C	-3.863429000	-1.407411000	0.177277000
H	-3.696528000	-1.973725000	-0.745073000
H	-3.558781000	-2.017605000	1.034106000

H	-4.922418000	-1.167876000	0.265333000

ConAld T_3

Trans-I

C	-2.904970000	-0.517591000	-0.040519000
C	-2.500317000	-1.839552000	-0.032650000
C	-1.934505000	0.500257000	-0.017633000
H	-3.254693000	-2.618617000	-0.050454000
C	-1.143960000	-2.152247000	-0.002491000
C	-0.588636000	0.190626000	0.012383000
H	-0.839664000	-3.194083000	0.003206000
H	0.141886000	0.988927000	0.029641000
C	-0.164571000	-1.154633000	0.020471000
O	-4.224810000	-0.192105000	-0.070059000
H	-4.280085000	0.775976000	-0.070885000
O	-2.468482000	1.756652000	-0.028434000
C	-1.583655000	2.864575000	-0.010131000
H	-0.970204000	2.864682000	0.896439000
H	-0.931429000	2.863155000	-0.889216000
H	-2.209624000	3.755417000	-0.024446000
C	3.650912000	-1.134511000	0.102634000
O	4.679182000	-0.342960000	0.122588000
H	3.929097000	-2.193289000	0.108466000
O	3.797278000	2.163039000	0.117559000

H	4.390741000	1.963397000	0.852520000
H	4.342008000	1.999616000	-0.662616000
C	1.240046000	-1.541466000	0.050874000
H	1.427250000	-2.612696000	0.053768000
C	2.307481000	-0.698006000	0.074409000
H	2.194986000	0.381888000	0.073774000

Trans-II

C	-2.634811000	-0.962460000	-0.024672000
C	-1.803075000	-2.069780000	-0.015021000
C	-2.070898000	0.322998000	-0.008266000
H	-2.250810000	-3.057631000	-0.026399000
C	-0.421880000	-1.910460000	0.010165000
C	-0.697542000	0.481884000	0.016841000
H	0.202044000	-2.796986000	0.019912000
H	-0.263196000	1.474558000	0.028735000
C	0.158829000	-0.637350000	0.025435000
O	-3.985962000	-1.109726000	-0.048873000
H	-4.370416000	-0.219511000	-0.051240000
O	-2.996812000	1.326120000	-0.019774000
C	-2.533598000	2.666434000	-0.006290000
H	-1.952410000	2.873942000	0.897754000
H	-1.921296000	2.881083000	-0.887853000
H	-3.421479000	3.296641000	-0.019233000

C	3.953054000	-1.088195000	0.061569000
O	4.451832000	0.109218000	0.122711000
H	4.711531000	-1.872357000	0.026235000
O	3.225268000	2.644187000	0.043788000
H	3.593237000	2.426053000	0.909234000
H	3.821790000	2.192132000	-0.566114000
C	1.596893000	-0.398730000	0.050452000
H	1.902229000	0.643765000	0.079455000
C	2.568829000	-1.356917000	0.031203000
H	2.327885000	-2.413669000	-0.012723000

Trans-III

C	2.489587000	-1.145914000	-0.016988000
C	1.462820000	-2.071569000	-0.003739000
C	2.181837000	0.227098000	-0.001592000
H	1.709041000	-3.127721000	-0.015118000
C	0.139077000	-1.640994000	0.023688000
C	0.868900000	0.654235000	0.025935000
H	-0.659392000	-2.376016000	0.032826000
H	0.654474000	1.714942000	0.041554000
C	-0.186501000	-0.281374000	0.037501000
O	3.787996000	-1.545609000	-0.043183000
H	4.334181000	-0.744275000	-0.047828000
O	3.286614000	1.028373000	-0.014655000

C	3.098976000	2.433949000	-0.000762000
H	2.539245000	2.765692000	-0.880982000
H	2.573173000	2.752584000	0.904858000
H	4.094386000	2.874953000	-0.016361000
C	-3.449546000	1.708440000	0.078904000
O	-4.398394000	0.824647000	0.152697000
H	-3.815186000	2.735806000	0.033739000
O	-4.330448000	-2.000888000	-0.038826000
H	-4.537953000	-1.808740000	0.884156000
H	-4.710641000	-1.249233000	-0.510992000
C	-1.591681000	0.102882000	0.063597000
H	-2.301360000	-0.719854000	0.088609000
C	-2.078485000	1.377929000	0.044745000
H	-1.422302000	2.240338000	-0.003514000

Trans-IV

C	-2.397577000	1.283169000	-0.034924000
C	-1.171380000	1.926097000	-0.036602000
C	-2.438380000	-0.119686000	-0.006441000
H	-1.151634000	3.010367000	-0.059879000
C	0.008516000	1.190152000	-0.010152000
C	-1.265786000	-0.852284000	0.020233000
H	0.952616000	1.722816000	-0.014169000
H	-1.301089000	-1.935125000	0.042517000

C	-0.011792000	-0.209089000	0.019635000
O	-3.556050000	1.995528000	-0.061196000
H	-4.284578000	1.355725000	-0.056696000
O	-3.705217000	-0.629219000	-0.008104000
C	-3.862474000	-2.038251000	0.010642000
H	-3.404120000	-2.498338000	-0.870500000
H	-3.424639000	-2.472404000	0.915096000
H	-4.935015000	-2.226155000	0.001180000
C	3.603333000	-1.426094000	0.099120000
O	4.831729000	-1.008787000	0.123135000
H	3.525057000	-2.518054000	0.104275000
O	4.806849000	1.646240000	0.116023000
H	5.264134000	1.299169000	0.892267000
H	5.313328000	1.287012000	-0.623352000
C	1.189728000	-1.034771000	0.049562000
H	1.022073000	-2.109236000	0.055331000
C	2.472312000	-0.580390000	0.071684000
H	2.711819000	0.478527000	0.070568000

CIS-I

C	-2.833481000	-0.323507000	-0.285997000
C	-2.548685000	-1.679404000	-0.413049000
C	-1.770888000	0.576359000	0.137382000
H	-3.334472000	-2.350562000	-0.741605000

C	-1.273317000	-2.149177000	-0.149585000
C	-0.504242000	0.096794000	0.444599000
H	-1.055956000	-3.205680000	-0.259910000
H	0.265942000	0.775736000	0.776711000
C	-0.216170000	-1.261317000	0.303243000
O	-4.055936000	0.178828000	-0.572743000
H	-4.031836000	1.138261000	-0.433070000
O	-2.154978000	1.852190000	0.183922000
C	-1.205300000	2.857226000	0.547808000
H	-0.883569000	2.715798000	1.581940000
H	-0.342129000	2.819510000	-0.120771000
H	-1.723011000	3.807642000	0.444121000
C	2.750305000	-0.112028000	-0.166416000
O	2.000771000	0.610543000	-0.872213000
H	3.828891000	0.119364000	-0.127056000
O	6.222423000	0.741184000	-0.283051000
H	6.164233000	0.240797000	-1.106326000
H	5.854382000	1.602028000	-0.517801000
C	1.074170000	-1.802881000	0.732755000
H	1.023479000	-2.756608000	1.255728000
C	2.356969000	-1.239678000	0.594886000
H	3.159642000	-1.742565000	1.126971000

Cis-II

C	-1.629902000	1.402391000	-0.024398000
C	-0.303850000	1.613990000	-0.352087000
C	-2.093865000	0.086930000	0.152645000
H	0.042711000	2.630759000	-0.502639000
C	0.568055000	0.536449000	-0.496881000
C	-1.230479000	-0.981561000	0.011825000
H	1.587600000	0.745218000	-0.788826000
H	-1.590174000	-1.994194000	0.152118000
C	0.130240000	-0.777475000	-0.304208000
O	-2.488383000	2.446572000	0.118644000
H	-3.356050000	2.074071000	0.339123000
O	-3.421729000	0.014564000	0.461219000
C	-3.995976000	-1.267285000	0.655346000
H	-3.914666000	-1.877100000	-0.250012000
H	-3.518223000	-1.791223000	1.489291000
H	-5.046721000	-1.099537000	0.886575000
C	3.324978000	-1.093807000	-0.130789000
O	4.584294000	-1.368272000	-0.068944000
H	3.131269000	-0.038377000	0.137144000
O	3.346419000	1.936904000	0.418321000
H	3.011539000	2.048647000	1.317280000
H	4.303415000	2.039690000	0.503417000
C	0.980262000	-1.956139000	-0.432659000

H	0.441818000	-2.888483000	-0.578932000
C	2.338288000	-2.080896000	-0.382086000
H	2.743294000	-3.078576000	-0.526147000