Competing Pathways for Photoremovable Protecting Groups: The Effects of Solvent, Oxygen and Encapsulation

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Abstract: Extending the applications of Photoremovable Protecting Groups (PPGs) to "cage" phenols has generally met with unusually complex PPG byproducts. In this study, we demonstrate that the *p*–hydroxyphenacyl (pHP) cage for both simple and complex phenolics, e.g., tyrosine, dispense free phenols in accord with the pK_a of the released phenol, i.e., according to its Brønsted Leaving Group ability. However, significant features of these reactions involve non-Kekulé intermediates produced from the cage fragment that leave an imprint through identifiable byproducts that are sensitive to the photolysis conditions and the presence of O_2. The byproduct formed from the cage accords with several recent reports on other, related PPG release reactions with different leaving groups. Many of these findings, in fact, point to a common photochemical singlet-triplet crossing event that is sensitive to the influences of the medium and oxygen during the subsequent chemistry of the cage fragment. Competition between a closed-shell, non-Kekulé cation with its open-shell cationic diradical configuration involves very short-lived intermediates created upon the photorelease step. When initially formed within an octa acid (OA) supramolecular enclosure, the intermediates are released from the OA enclosure into the solvents containing exogenous dissolved reagents. The now available reactive agents probe the chemistry of the short-lived cage fragments. Their reactions reveal characteristic chemistry of singlet, closed-shell cation and open-shell triplet radical behavior.

Introduction

Photoremovable protecting groups (PPGs) have been employed to investigate temporal, spatial, and environmental influences on chemical and signaling events in fundamental mechanistic studies of biological processes.[1] Several groups,[2] including ours[3] have sought to pinpoint the role of specific functional groups within the multi-faceted molecular entities. The results of these investigations often serve as guidelines for molecular design for biological or pharmaceutical agents or to identify significant molecular barriers to chemical transformations. The unraveling of mechanistic pathways in chemical and biochemical transformations has been aided by applications of PPG or "caged" initiators.[4-8] PPGs are also employed to release reagents as specific spatially-occupied, functional group initiators in chemical or biochemical processes.[9-12]

To be effective in reaching these goals, PPGs require specific attributes such as rapid, efficient release of a functional group while also forming non-perturbing residues from the protecting group or "cage" portion of the PPG. Furthermore, an ideal PPG should be versatile and adaptable for the release of, or application in the presence of, a wide variety of important functional groups. Ideally, the release reaction should occur by a common, well-understood photolysis reaction that is unperturbed by exogenous agents such as oxygen, photochemical quenchers, solvent variations, variations in pH or phase changes[1,2,4] *p*-HydroxyPhenacyl (pHP) has been tested as a PPG and fulfills many of the qualifications of an ideal protecting group as evidenced by a growing array of biological[1] and biochemical applications[13-15] including neurotransmission,[13] enzyme catalysis[14, 15] and possibly drug delivery.[9, 16] While pHP has been developed for release of many familiar functional groups,[2] there remain several challenging targets that have not been thoroughly explored , e.g. amines,[3, 17] alcohols,[18] and phenols.[19-25] A factor that may distinguish these functional groups from the many successful examples cited here is their "leaving group ability", a parameter often cited in ground-state or solvolysis release reactions. The classical examples are described by Brønsted Leaving Group Ability[26] which has been explored for a few "caged" compound studies[27]. More recently, photosolvolysis reactions of caged substrates have been the subject of investigations regarding the nature of the bond breaking that occurs in the PPG excited state, thereby releasing the protected substrate from the

excited protecting group.[28-33] These examinations of both the more classical and photophysical studies are coupled with theoretical analysis of the photo release from caged substrates and are the subject of this investigation on pHP release of phenols.

Phenols, e.g., dopamine or tyrosine[15,20-22] and phosphorylated phenols[24] have been investigated, but those efforts have generally met with difficulty or were unrewarding, primarily due to their inherently poor leaving group ability. Low yields, poor release rates, and/or competing side reactions plagued these attempts. Modifications of the PPG of choice by inserting carbonate (OCO) or carbamate (OCONH) between the PPG and a poor, but desirable leaving group have given cleaner reactions but sidestepped only the poor yields. Low efficiencies and slower release rates[19] resulting from a slow ground-state decarboxylation to free the intended product, as well as lengthy syntheses to access the starting materials are the ongoing problems.

Modifying the PPG by adding halogens, extending the chromophore, or rearranging the key substituents frequently leads to lower release rates and efficacies or undesirable new side reactions. For example, Dore et al.[20] successfully modified their 7-hydroxyquinoline cage by incorporating Br or CN groups (e.g., 8-bromo-7-hydroxyquinolinyl (BHQ) and 8-cyano-7-hydroxyquinolinyl (CNHQ) PPG's[4, 20, 21] to enhance release of tyrosine with reasonable one photon excitation (1PE) (0.32 – 0.38) and 2PE (0.61 – 0.36 GM) efficiencies at 366 or 371 nm, respectively.[20, 21] The modified PPGs are reasonably efficient for the release of tyrosine and other phenols but the reactions are frequently accompanied by fragmentation and loss of the halogen (Br).

The currently reported limitations, e.g., poor leaving groups with low efficiencies, complex product mixtures and required carbonate/carbamate linkages, that plagued previous studies on phenol release, have encouraged us to expand our investigations of pHP cages to include phenols, one of which is the amino acid tyrosine. Advantages of other pHP caged functional groups vis-a-vis other PPGs, when compared by us and others,[1-4, 17, 23] suggest that extending the comparison to pHP phenol release, including their side reactions and efficiencies, are warranted and are reported here.

Experimental

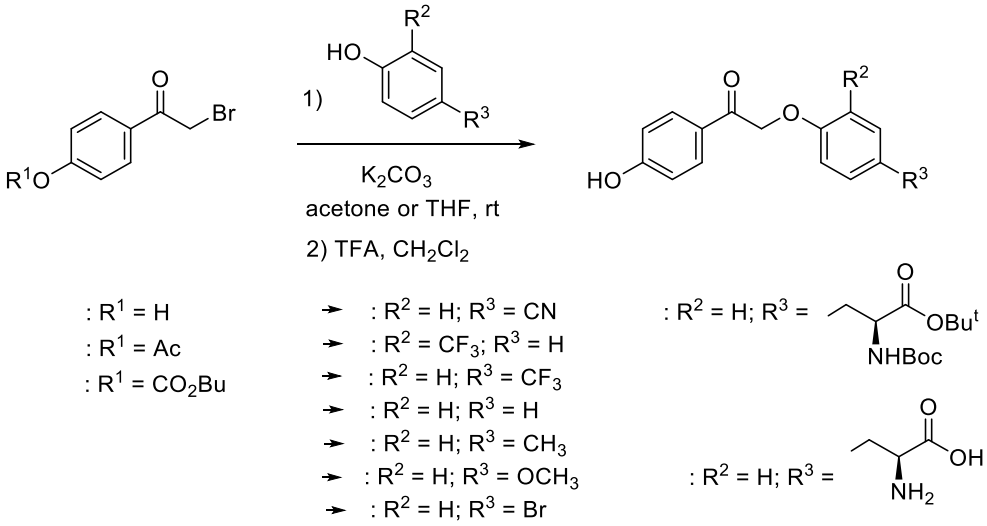
Detailed adopted methods for the synthesis of reactants (**SI** sections **1**-**3**), procedure used for irradiation (**SI** section **4**), of analysis of photoproducts and measurements of quantum yields

and instruments (**SI** section **7**) used for analyses are provided in the supporting information section.

Results

Synthesis

A series of seven representative pHP phenyl ethers (**3a** – **f**)[26] and pHP tyrosyl-O ether (**3i**) were synthesized by Williamson alkylation of substituted phenols **2a-h** by 2'-bromo-4-hydroxyacetophenone **1a** (**Scheme 1**). Occasionally, it was necessary to protect the phenolic moiety (**2c**, **h** and **i**) in the pHP bromide with acetyl (**1b**), or in the tyrosyl series, *t*-butoxycarbonyl group to also protect the amino acid groups on **1c**.[27] Upon completion of the alkylation step, the protecting groups were removed by treating the crude reaction mixtures with trifluoro acetic acid (TFA).

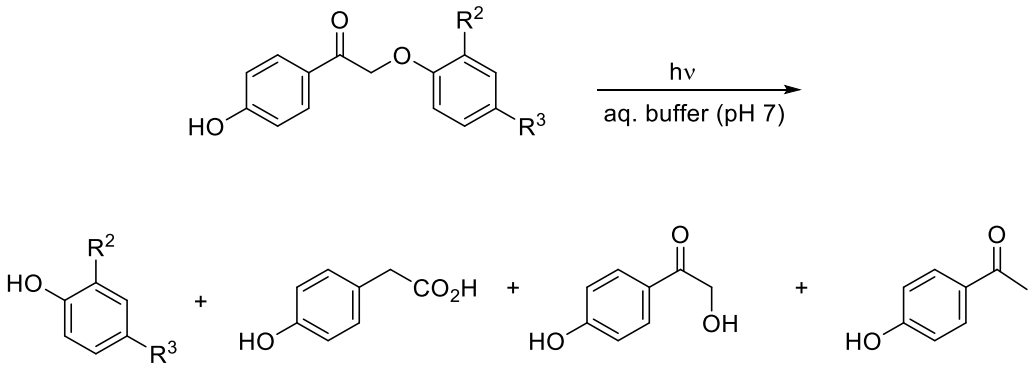


Scheme 1. Synthesis of *p*-hydroxyphenacyl phenyl ethers **3a** – **g**, **i**. (For details, see **S4)**

Photochemistry

Irradiation of caged ethers **3a-f** and **3i** was carried out at 300 or 350 nm in aqueous CH_3CN at pH 7 in either NMR tubes or Pyrex test tubes containing DMF as the internal standard (**Scheme 2**). The reaction mixtures were analyzed by ^1H NMR or HPLC and UV-vis

spectroscopy. Light output was determined by potassium ferrioxalate actinometry (see supporting information S11 and S15)[34].



Scheme 2. Photorelease of phenols **2a-2f**, **2i** from pHP phenyl ethers **3a–3f**, **3i**.

To explore the mechanism and environmental factors influencing the photorelease, our investigation of pHP phenols was conducted through the following fundamental studies: (a) the effects of varying substituents and their phenolic pK$_a$'s on the reaction and products, (b) the effects of quenchers, the solvent pH, and supramolecular encapsulation by the cavitand octa acid and (c) the role of oxygen on the photochemistry.

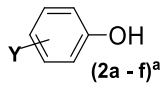
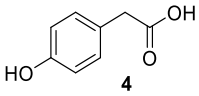
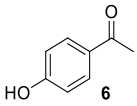
Substituent Effects by the Phenol Leaving Group on the Photochemistry

Irradiation of seven substituted pHP phenyl ethers and tyrosine released the phenols in good yields, as shown in **Table 1**. The pHP phenyl ethers are arranged according to increasing pK$_a$ of the leaving group's conjugate acid. Earlier studies on the relationship between pK$_a$ and rates[28, 29] or efficiencies[16] have reported linear Brønsted dependence for rates and efficiencies for a large range of acid leaving groups, including pHP esters.[25, 35-42]

For the yield of released phenol and byproducts, the initial studies were by photolysis of pHP ethers in 10 -20% aq. CH$_3$CN at 300 nm for 1 hr. For the less acidic phenols, yields of phenol were low, as well as the cage product **4** (the Favorskii rearrangement product). Furthermore, this was accompanied by increasing amounts of two other minor byproducts **5** and **6**, suggesting an increasing diversion from the established photo-Favorskii pathway. Ultimately,

the yield of Favorskii product **4** vanished while 5 and **6,** accompanied by new products were released with the phenol (**Table 1**; **Figure 1**).

Table 1. Yields of Phenols and Byproducts after 1 hr Photolysis of pHP Caged Phenyl Ether[a]

pHP Phenyl Ether **3**	Recovered **3** (%)	Released **2** (%)  (2a - f)[a]	Favorskii Product **4** (%)  4	Reduction Product **6** (%)  6
p-CN (**3a**)	0	98	94	n/o[b]
o-CF_3 (**3b**)	0	99	90	n/o
p-CF_3 (**3c**)	0	98	90	n/o
H (**3d**)	26	30	26	3.5
p-CH_3 (**3e**)	35	25	n/o	~ 10
p-OCH_3 (**3f**)	27	37	n/o	15

[a] after 1h photolysis at 300 nm in 33% aqueous CH_3CN; determined by ^1H NMR of the reaction mixture (DMF as internal standard). [b]n/o = not observed.

As anticipated, the appearance quantum yields for **2a** – **2f** (Φ_{phenol}, **Table 2**) monotonically decrease as the departing phenol pK_a increased. Interestingly, however, this trend is not observed for the pHP ether disappearance quantum yield (Φ_{dis}, **Table 2**; **Figure 1B**). This unusual result suggests that other, more complex processes are involved. The decreased phenol yield with increasing pK_a was reflected by the decrease in the quantum yield in accord with the Brønsted Leaving Group relationship employed for ground state S_N1 reactions. This correlation has been observed in a few other photochemical cage release reactions.

Table 2. Quantum Yields for pHP Phenol Ether **3a-f** Disappearance (Φ_{dis}) and Phenol **2a–f** Appearance (Φ_{phenol}) as a function of Phenol pK_a.

pHP Phenyl Ether **3**[a]	pKa of 2[18]	Φ_{dis} of **3**	Φ_{phenol} of **2**
p-CN (**3a**)[a]	7.17	0.11	0.09
o-CF_3 (**3b**)	8.11	0.085	0.078
p-CF_3 (**3c**)	8.51	0.093	0.074
H (**3d**)[a]	9.8	0.029	0.014
Tyrosine (**3i**)[b]	10.07	0.1	0.085
p-CH_3 (**3e**)	10.2	0.121	0.02
p-OCH_3 (**3f**)	10.4	0.13	0.027

[a] See ref. [24,25]

[b]Tyrosine not included in the Brønsted correlation. Its pK_a is influenced by contributions of its amine group.

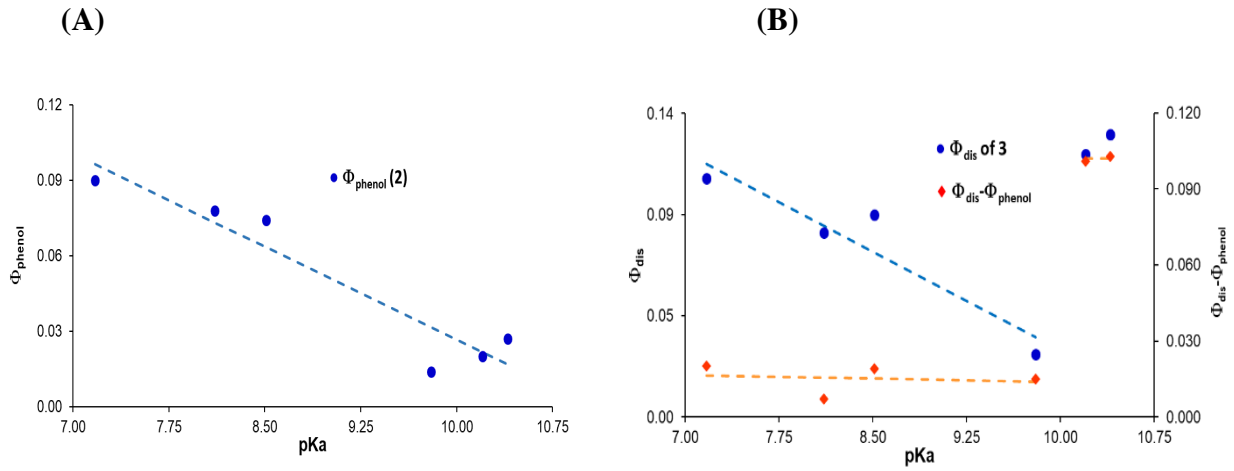


Figure 1. The effect of pK_a of the phenol leaving group on product yields. **A.** Quantum yield of phenol release versus its pK_a. **B**. Disappearance efficiency of pHP phenyl ether vs phenol pK_a corrected for reduction product **6** (blue). Note the deviations for the weakly acidic phenols (red) vs. phenol pK_a.

Effects of Quencher, pH, and Supramolecular Encapsulation by Octa Acid on the photochemistry

The photorelease of phenols **2a** – **f** occurs through the triplet excited state[1] as demonstrated by methyl sorbate quenching[21] in accord with our earlier studies.[2, 28, 29, 35] Photolysis of **3a** at 300 nm gave Stern-Volmer quenching ($K_{sv} = 10^6$ M^{-1}) and a typical triplet lifetime of $\tau^3 = 4.2$ ns (see S16 in SI), in accord with triplet lifetimes obtained for pHP phosphate release.[2,23]

In contrast to those results, under basic solution conditions (pH> 7.8), pHP absorption spectra changed to reflect its conversion to the pHP conjugate base and the photochemical reaction efficiency decreased as has been shown with other leaving groups.[35] The UV-vis absorption spectra of the pHP conjugate base dominates at pH 9 to 12.6 (Fig. S12 in SI) where the reaction efficiencies are significantly lower, likely due to the change in excited states of the conjugate bases (**Table 2**[35]). Here, Brønsted behavior was not reflected in our pHP disappearance or byproduct yields.

Particularly intriguing, however, were the changes in the nature of the caging group chemistry. The expected, well established Favorskii rearrangement photoproduct **4** is observed as the major product for the three most reactive ethers (**3a** – **c**) whereas its yield decreases dramatically for the remaining phenol leaving groups. In fact, the direct photohydrolysis and reduction of pHP moiety to form **5** and **6** emerge as more significant pathways (**Table 1**, **Figure 1**).

Based on this change in the reaction course, we turned our attention to another method to probe the photorelease process, i.e., the supramolecular encasement of the caged derivative, which had recently given promising results for a number of caged compounds,[22,26] including pHP esters.[4]

The phenol and byproduct yields in borate buffer (pH 8.7) within OA were determined by 1 hr photolyses at $\lambda \geq 300$ nm. Two of the pHP phenyl ethers (**3c** and **3f**) that represented the two extremes in pHP disappearance and product diversity were chosen for encapsulation within an octa acid capsule, i.e., @$(OA)_2$, as the host: **3c**@$(OA)_2$ and **3f**@$(OA)_2$. These two were studied earlier in conjunction with a series of pHP carboxylate esters for the release of caged carboxylic acids.[5, 6, 37] In those studies,[5] the release from the pHP esters was very efficient and free of

extraneous side reactions, in contrast to more complicated product arrays found with three other PPG's examined.[6, 37] Thus, when **3c,** encased in OA, was irradiated, the pHP caging chromophore was primarily converted to the Favorskii rearrangement product **4**. ^{1}H NMR absorptions were assigned to *p*-trifluoromethylphenol (**2c**) as the major product along with minor amounts of 2,4-dihydroxyacetophenone (**5**), a hydrolysis product, and *p*-hydroxyacetophenone (**6**), a reduction product, along with other minor, unidentified products. For **3f**, however, a more extended irradiation was required resulting in a decreased yield of phenol **2f** along with additional side products. The photoreaction was monitored by LC-DAD-MS, which provided quantitative assessment of small amounts of **5** and **6** (*vide infra,* **Figures 2** and **3**).

Effect of O_2 (Oxygen) in pHP Photochemistry.

Prompted by our earlier studies of the effect of oxygen on the reactions of the 7-diethylaminocoumarin-4-methyl (DEA) cage photochemistry[37] we turned our investigation to the effect of O_2 on the pHP release of phenols in the photolysis reaction in solution with and without OA enclosure.

Normally, for most cage compounds, hydration of the cationic cage fragment generated by the heterolytic release of the leaving group, yields the corresponding alcohol product. With *p*-hydroxyphenacyl (pHP), the fate of the pHP cage is directed through a Favorskii rearrangement to form a bicyclic dienedione **19** (*vide infra,* **Scheme 3**) that leads instead to *p*-hydroxyphenyl acetic acid (**4**). The analysis of the photolysis mixtures for **3c** and **3f** are shown in **Figures 2** and **3**. The blue traces are for decaging under normal (aerated) conditions that indicate the relative yields of the respective phenols **2**, the rearranged **4** along with the minor, but measurable amounts of (**5**) and (**6**). Solutions containing an excess of OA were prepared in aqueous borate buffer (pH 8.7) at 4:1 stoichiometry (400 μM OA:100 μM of **3f**). Oxygen removal was achieved by purging with N_2 for 5 min. Chromatographic separation was performed using a gradient of water and acetonitrile. As also observed for 2:1 stoichiometry (SI Figure S17) and in Figure 2 for **3c**, the photoproduction of **6** increases in the absence of O_2. The prominent peak at 10 min marked with an asterisks and the smaller adjacent peak are isomeric with **3f.** (See Fig S22 in SI).

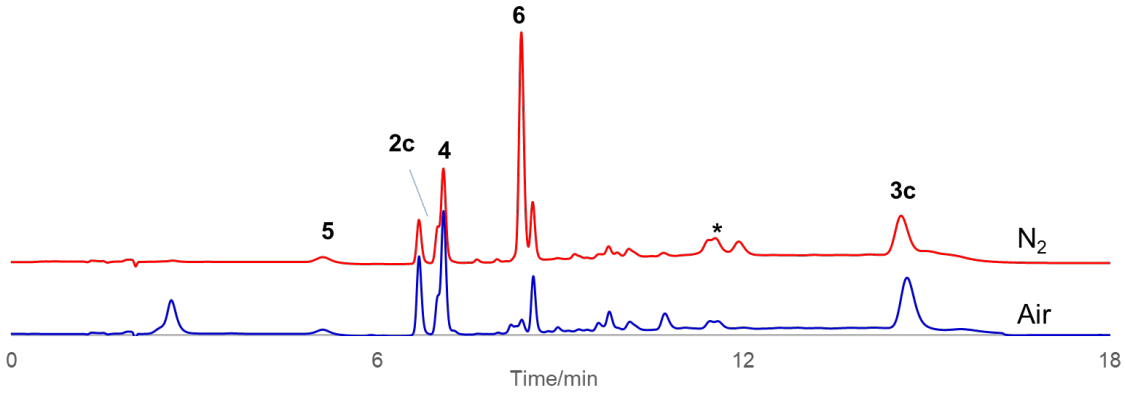


Figure 2. Effect of O_2 on photolysis of 3c@$(OA)_2$. LC-DAD profiles (280 nm) from irradiation of **3c**@OA_2 complexes at $\lambda > 300$ nm in air (blue trace) and after N_2 purging (red trace). Solutions of complexes were prepared in aqueous borate buffer (pH 8.7) at 1:2 **3c@**$(OA)_2$ stoichiometry (200 μM OA:100 μM of **3c**). Oxygen removal was achieved by purging with N_2 for 5 min. Chromatographic separation was performed using a gradient of water and acetonitrile. An asterisk denotes two photoproducts that are isomeric with the caged ether, **3c**. (See Fig. S21 in SI).

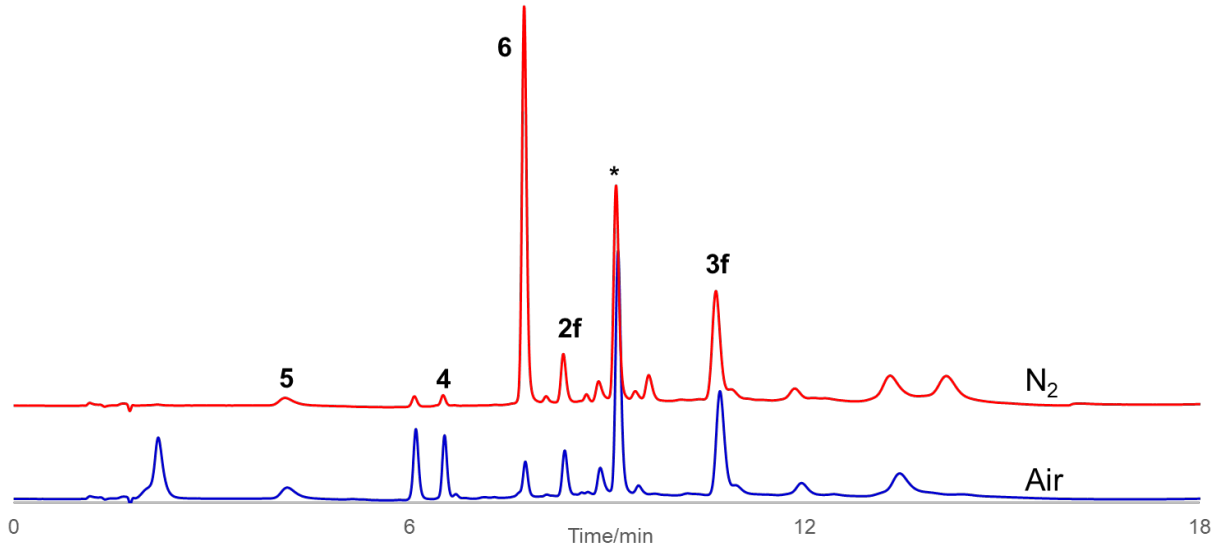


Figure 3. Effect of O2 on photolysis of 3f@$(OA)_2$. LC-DAD profiles (280 nm) from irradiation of **3f**@$(OA)_2$ complexes at $\lambda > 300$ nm) in air (blue trace) and after N_2 purging (red trace).

When the photoreactions are conducted after N_2 purging, the LC-DAD-MS analyses show a significant increase in formation of the reduction product **6** shown by the red traces in **Figures 2** and **3**. **Table 3** depicts the quantitative increase in reduction product for both **3c** and **3f** to be larger than 10-fold. Interestingly, there is a decrease in the major side product, the Favorskii fragment **4**, but little or no change in the relative amounts of hydrolysis product **5**. The main photoreaction of pHP phenyl ether to phenol progresses unperturbed for both protected phenols in the presence or absence of O_2.

Table 3. Relative product yields (%) after irradiation of **3c**@$(OA)_2$ and **3f**@$(OA)_2$ in air equilibrated and N_2 purged solutions.

Irradiation Conditions	3c converted	2c	4	5	6	3f converted	2f	4	5	6
OA, air equilibrated	89	25	79	1	2	89	31	29	4	3
OA N_2 purged	93	24	59	2	22	89	32	6	2	33

Errors are 5 -10 %. Concentration of the pHP ethers were 100 μM. Concentration of OA was 200 μM. Conversions and yields of products after 45 minutes irradiation (λ > 300 nm).

Discussion

The photorelease of phenols from caged phenyl ethers has been the objective of investigations by our group and others.[1, 2, 18, 19, 23, 26] We first demonstrated the efficacy of phenol release from pHP with two of the phenols, *p*-cyanophenol **3a** and unsubstituted phenol **3d**, which encouraged us to study the entire series, **3a** - **3f**, shown in **Scheme 1**. Two principal objectives were that the monosubstituted phenol leaving groups would provide a contiguous, monotonic pK_a gradient and thus be a quantifiable, systematic influence on the rates and

quantum efficiencies to probe the nature of the bond-breaking process from the excited state. Ultimately, we also became interested in another, more fundamental aspect than simply verifying e.g., the classical ground state Brønsted Leaving Group relationship for the photosolvolysis rates versus leaving group pK_a relationship.[26, 36-39] On the other hand, this series systemically subtends a few poor leaving groups that might explore alternate pathways at the reactivity limits. Unexpectedly, we also discovered valuable general mechanistic features of the cage release that may account for other, adventitious pHP cage products. These secondary byproducts from the pHP portion release may relate to unexpected products that occur with other cages. These discoveries expand our understanding and the intricacies of photorelease reactions.

Scheme 1 illustrates the synthetic approach to the series of pHP substituted-phenol ethers. Since pHP itself is a weakly acidic phenol (pK_a7.9), synthesis requires protection of the OH group, especially for phenols with a higher pK_a, e.g. tyrosine as shown in **Scheme 1** and detailed in SI (S9 and S10)**.** We have also examined pHP caged tyrosine, an important phenolic amino acid to demonstrate both ease of synthesis and efficiency of the photorelease.

To explore the photochemistry and limitations of the phenol as a leaving group, we evaluated the following variables: (a) the effect of increasing phenol pK_a vis-a-vis quantum yield and rate constant, i.e., Brønsted behavior, (b) the Supramolecular Encapsulation and O_2 Environmental Effects on Product Distribution, (c) Intermediates from cage release and chromophore degradation, and (d) Proposed pathways for reactions of the non-Kekulé cage fragment.

(a) Brønsted Behavior

The photorelease of phenols in aqueous acetonitrile solvents were quantitatively assayed for pHP phenyl ethers **3a** – **3f** (Table 2). As expected, these leaving groups were less efficient when compared with our previous studies using leaving groups with lower pK_a's as defined by Brønsted Leaving Group measures for solvolysis reactions.[1, 2] Thus, **3a** through **3f** quantum efficiencies were determined and were substantially lower than those reported for sulfonate, phosphate and carboxylate leaving groups.[2] The unsubstituted phenol **3d** and most acidic

member, **3a**, exhibit low rates conforming with the expected Brønsted Behavior, e.g., as shown in Figure **4** and **Table 4**.

Table 4: The triplet state quantum efficiencies and rate constants for disappearance (log k_r) for pHP sulfonate, phosphate, and carboxylate esters and for pHP phenol and *p*-cyanophenol ethers (this work) and the pK_a of the leaving group conjugate acids.

pHP Caged Leaving Groups	**Φ_{dis}**	**LG pK_a**	**Log (k)**
Mesylate (**7**)	0.932	1.54	9.7
Tosylate (**8**)	1.04	0.44	10
Diethyl phosphate (**9**)	0.40	0.71	9.06
Fluoride (**10**)[9]	0.84	3.17	9.3
p-CF_3 Benzoate (**11**)	0.288	3.69	8.51
Formate (**12**)	0.94	3.75	9.15
p-OCH_3 benzoate (**13**)	0.288	4.09	8.54
Benzoate (**14**)	0.316	4.21	8.44
GABA (**15**)	0.21	4.26	8.78
p-CN Phenoxy (**3a**)	0.11	7.17	7.88
ATP (**16**)	0.38	7.4	9.8
Phenoxy (**3d**)	0.03	10.02	7.02

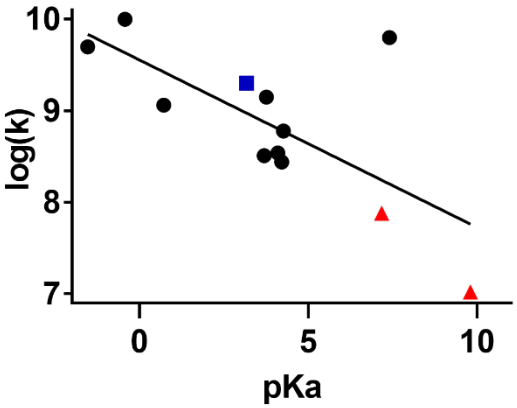


Figure 4. The Brønsted Linear Free Energy Relationship applied to rates of release from pHP derivatives versus the pK_a of the leaving group acid including pHP phenyl ethers **3a** and **3d** (red). The pK_a's of the leaving group conjugate acids are plotted versus the log k_r's for the rates of photorelease from the pHP triplet excited states. The values for log k_r and pK_a are given in **Table 4**. A 95% confidence interval for the fit includes **3a** and **3d** (this work) and pHP F (**10**)(fluoride release). The slope of the fit is -0.18 + 0.06 ($p < 0.05$l; Pearson Coefficient R2 = 0.49. (Further details are found in section **SI 4** and **Figure SI 5**)

(b) Supramolecular Encapsulation and O_2 Environmental Effects on Product Distribution

As described in the Results section, OA complexes of pHP phenyl ethers, **3c** and **3f** were dissolved in aqueous buffer (pH 8.7) and photolyzed to release the two phenols **2c** and **2f** along with side products of the cage, **4**, **5**, and **6** (*vide supra*).[5] As shown in **Table 1** and **Figure 1**, the side products dramatically change as the leaving group pK_a increases. The pHP chromophore no longer proceeds exclusively by its signature Favorskii rearrangement for the poorer leaving groups; rather the pHP moiety proceeds primarily through the reduction pathway of hydrogen abstraction to form **6**. Nevertheless, **3f** even with its very poor leaving group ejects phenol **2f** with a yield sufficient to maintain consistent Brønsted behavior for the series. This suggests that the bond cleavage continues to be sensitive to the leaving group's pK_a.[28,29]

However, there is an even greater decrease in the yield of Favorskii product **4**. Photolysis in OA of **3c,** with its very good leaving group, produces **2c** and byproduct **4**, whereas for **3f**, with a very poor leaving group, very little **4** is formed. When purged with nitrogen, **4** is a minor

component of the reaction mixture. Yet in both cases the pHP chromophore disappearance occurs with nearly the same efficiency (**Table 2**).

A series of pHP and pMeOHP esters were subjected to identical supramolecular OA confinement recently. Photolysis revealed a dramatic difference in the fate of the chromophore.[5] For pHP esters, the Favorskii rearranged product prevailed.[6] With the *p*-methoxyphenacyl ester, under identical conditions, a plethora of radical abstraction cage-derived products including attack on OA itself and very little Favorskii product, *p*-methoxyphenyl acetate, was detected. In contrast with the release of phenols,[1, 2] the same photolysis of all other pHP esters in the OA resulted in a clean release of the acid accompanied with the expected Favorskii product and the released acids.

For the oxygen effect, it appears to alter the reduction or radical pathway over the ionic pathway for the cage fragment, i.e., favoring formation of *p*-hydroxyacetophenone (reduction product) without affecting the phenol release. The hydrogen atom source for the reduction appears to be OA (SI Figures **S14 and S21**). The hydrogen may be abstracted from OA since, when it is in excess, more reduction products result (see Figures **S23** and **S24**).

(c) Intermediates from Cage Release and Chromophore Degradation.

There is a long history of photorelease studies of "cage" compounds and the broader field of photosolvolysis reactions which have been explored for the nature of the bond breaking process.[1, 2, 43, 44] The focus of many of these studies has been on the nature and product distribution of the bond breaking process, especially for the leaving group. For caged compounds, the primary interest has been the substrate released by photolysis with little attention given to the fate of the cage chromophore and its chemistry.

A recent survey of the photochemistry of a large number of cages by Winter et al.[32, 33] addressed this subject in detail, suggesting that heterolytic release of the chromophore-substrate bond was enhanced by conical surface crossing of the putative excited singlet state crossing with the ground state chromophore cation surface. The focus of his study centered on those chromophores that react only via their singlet states.

Since our cage release for pHP reactions occur exclusively within the triplet manifold,[2] we were faced with the question of accounting for the role of the spin state in the bond

fragmentation process and its effect on the reaction products. Furthermore, for cage release reactions it is the anion that accounts for the electrons of interest. The triplet caged ethers initially undergo homolysis to a tight radical pair. The radical pair experiences electron migration to the leaving group to form an ion pair. Thus, the cage is "released" as an electron deficient, unstable cation and these species are often non-Kekulé cations which have historical precedence.[45, 46] In addition, the general chemistry of non-Kekulé cations and their excited states are not well-understood. Here, the triplet pathway must be assessed not only, for product formation, but also, for the general stability of the cation, and for spin conservation.

The cage portion of pHP readily loses its acidic phenolic proton. This deprotonated pHP intermediate is a non-Kekulé triplet capable of spin relaxation to a singlet diradical that has zwitterionic character (**Figure 5**), similar in concept to the large array of caged compounds that react through their singlet manifolds. The role of the singlet state pathway in the release of the cation has been thoroughly established by Peters on photosolvolysis of arylmethyl acetates.[2, 8, 29] This replaced the original "meta effect" mechanism of the earlier, classical studies by Zimmerman,[38] which was challenged by Pincock,[39, 41, 47, 48] and also noted by us, and many others.

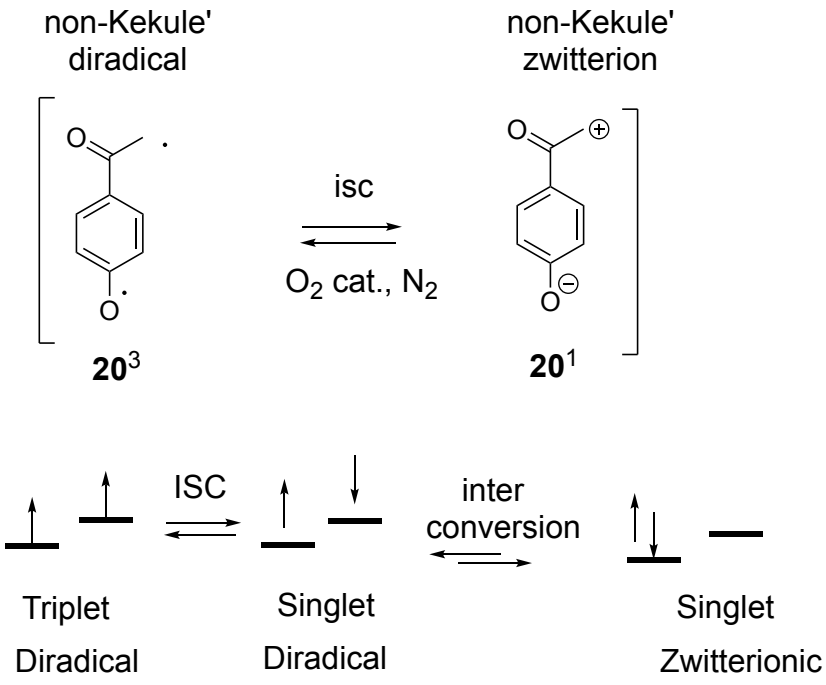


Figure 5. Inter System Crossing (triplet/singlet) of non-Kekulé Intermediate.

The triplet $^{-}OC_6H_4COCH_2^{\circ}$ (**20**^{3}, **Figure 5**) formed from the conjugate base of the pHP ether is a neutral non-Kekulé triplet (**Scheme 3**). Evidence for this behavior can be deduced by comparing the data on the photoproducts of the pHP chromophore under aq. CH_3CN photolysis conditions or with the supramolecular studies employing encapsulation. It appears that 7-substituted coumaryl and p-substituted phenacyl cations are, in fact, both members of a large class of non-Kekulé structures that have interconverting singlet closed shell and singlet-triplet open shell diradical character.

We have suggested that the interconversion/intersystem crossover among these electronic states can be perturbed by the presence of triplet O_2. By altering the ratios of the singlet zwitterion state, which undergoes nucleophilic addition and the diradical-like open shell form for which hydrogen abstraction or coupling reactions dominate, two contrasting pathways are provided as signatures of their origin.

Two factors, the efficiency of intersystem crossing (100%) and the rapid rate of fragmentation of triplet pHP-leaving group bond cleavage (10^7 - 10^{10} s^{-1})[23] outpace other processes to the ion-pair/radical-pair intermediate. Brønsted behavior, illustrated in **Table 4** and **Figure 5**, furthermore suggests no ion pair return. Thus the non-Kekulé triplet diradical (**Figure 5**), must relax to a singlet diradical that has a zwitterionic character prior to nucleophilic attack (by water, **5**) or by a Favorskii rearrangement to **4.** The leaving group anion (a ground state singlet) would have little driving force toward rebonding to form a pHP phenoxy ether.

In addition, interconversion between singlet and triplet states of **20**^{1}, **20**^{3} should be facile when the energy difference is small, and there is a mechanism available for spin interconversion.[49] The singlet-triplet gap ([delta] E_{ST}) was calculated for compound **20** (Figure **5**) using UB3LYP/6-31G+(d,p)[50] with the spin-corrected singlet energy to be +0.27 kcal/mol. The singlet and triplet states of this intermediate are approximately degenerate, which supports fast interconversion between the two states which may be perturbed by the surrounding environment.[28]

The divergence in photoproducts from compound **4** to **6** with the poorer leaving groups further suggests a change in mechanism. While Brønsted-like behavior is still observed for **3c**, the reduction product **6** is observed and becomes more prominent when oxygen is absent. This points to the likely scenario that the compound is undergoing homolysis in the triplet excited state, as is expected for the pHP photo cage and electron transfer occurs after bond cleavage. The pHP phenol bond lengths were scanned on the triplet surface of **3a**, **3d**, and **3f** using UB3LYP/6-31+g(d,p)[50] with a SMD solvent model and the SOMOs were calculated sequentially (a) at the initial optimized structure, (b) at the transition state, and (c) at the initial bond cleavage stage. These calculations support a mechanism of complete photo homolysis for **3a**-**d**. Interestingly, the SOMOs of **3f** at the transition state tended to strongly favor homolysis. These may represent the variation in the transition states with these three photolysis pathways. However these calculations allow a variance in the degree of homolytic bond-breaking favoring the reduction pathway or possibly a rearrangement of pHP *p*-methoxyphenol ether products as the "Brønsted" leaving group influence diminishes.

(d) Proposed Pathways for non-Kekulé Cage Release.

Based on this study of phenol release from the *p*-hydroxyphenacyl protecting group and prior mechanistic studies on pHP photochemistry, we propose the reaction pathway shown in **Scheme 3**. The initial events, excitation to the pHP singlet, then quantitative intersystem crossing yields the reactive triplet. Rapid cleavage of the pHP-ether bond ($10^9 s^{-1}$) leads to a tight radical pair in accord with our earlier studies on pHP photorelease.[2] The relative rate of this cleavage process is controlled by the leaving group ability of each phenol according to the Brønsted Leaving Group paradigm as reflected in this study and several previous studies using other leaving groups.[25]

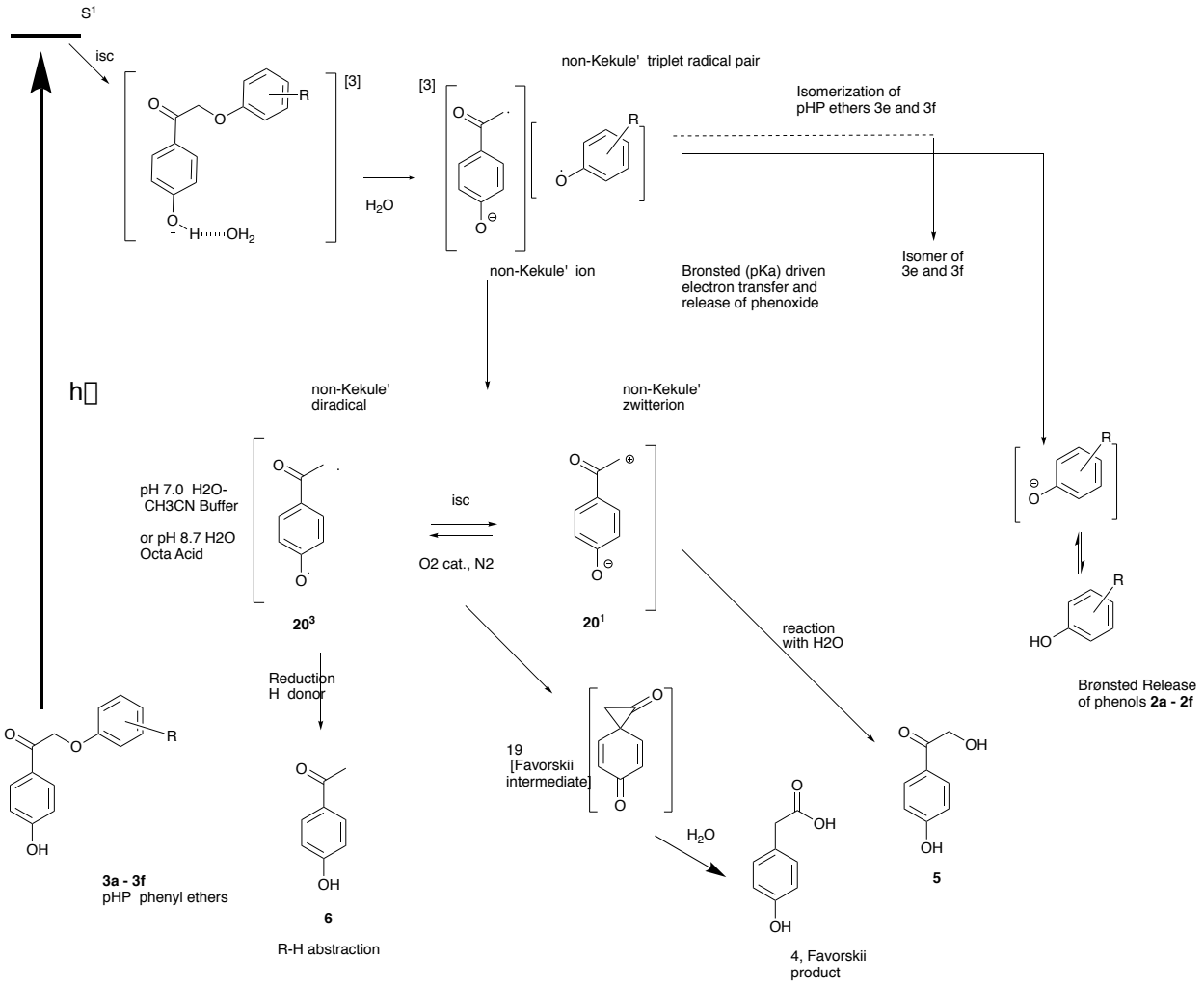
It also appears there is no competing radical pair return of the leaving group. [2, 16, 37] This observation contrasts with the work of Peters[28] and Pincock,[39, 40] where radical coupling was observed. Thus, the pHP release reaction lacks a competing coupling reaction of the phenoxy radicals fundamental for evaluating Marcus behavior from the radical versus ionic pathways.

We have based our proposed mechanism on several previous studies on pHP photochemistry and the results shown here. Earlier studies had shown that bond cleavage from the triplet is not reversible by the absence of isotope scrambling, e.g., oxygen labels (O^{18} vs. O^{16}) labeled carboxylate esters are not interchanged.[47, 48] and diastereomeric centers of chiral protecting groups are not compromised during photorelease reactions.[51] The subsequent events for pHP and the phenoxy tight radical pair are solvent, media, and substituent dependent. Whereas the Brønsted behavior is followed throughout the full series of phenols, the behavior of the protecting group pHP varies greatly with changes in the media, leaving group and physical environment. As shown in **Scheme 3**, electron transfer from the tight radical pair to free, solvated ions occurs readily for the better leaving groups (**3a** – **3c**) forming a pHP non-Kekulé cation which is very sensitive to solvent, encapsulation, and oxygen. Changes in solvent toward anhydrous environments result in reduction of the pHP radical rather than the rearrangement of the pHP cation via the Favorskii reaction. In OA enclosed ethers dissolved in aqueous media, the cation hydrates before rearrangement. Clearly, it is not obvious at what stage the non-Kekulé intermediate partitions between a Favorskii closure to form the spirodienedione intermediate **19** with hydrolysis to **4** or reacts directly with the solvent water to form the hydroxyketone **5**.

Even more surprisingly, for the poorer leaving groups **3e** and **3f**, is the appearance of a new isomeric form of the pHP ether. Rearrangement products of the caged ether (**Figures 2** and **3** and **S23** and **S24**) appear indicating a change in the role of the phenol leaving group.

A general observation for phenol release as well as other pHP leaving groups, is the lack of evidence of recombination of the cage and the ligand as found in our previous studies.[2] Thus, we conclude that this mechanism in **Scheme 3** is the best candidate for pHP release of all the leaving groups shown in **Table 4**.

Scheme 3. Overall mechanism for pHP release of phenols



The roles of solvent and oxygen do alter the chemistry of the pHP protecting group. Simply stated, in aqueous media, the deprotonation of the pHP cation is facilitated resulting in **20**[1,3]. Evidence for the reduction pathway was found when the photolysis of pHP phenols were irradiated in anhydrous acetonitrile. Mixtures of new products were formed along with reduction product **6** confirming our earlier studies on the critical influence of water on the pHP release reactions.

The H_2O concentration causes a change in the reactivity of the non-Kekulé **20**^{1} (**Figure 5**). This also alters the propensity of the cation to follow through on the Favorskii rearrangement and, instead, undergoes direct solvolysis to form **5**. These both appear to be results of the singlet-triplet behavior of the non-Kekulé cation. The triplet state of the non-Kekulé intermediate is susceptible to reduction in the presence of suitable H-atom donors. *p*-Hydroxyl acetophenone **6** becomes a dominant product of the change.

Likewise, O_2 plays a significant role in the product composition from **20**^{1,3}**.** When O_2 is absent, more reduction occurs whereas in its presence, solvolysis dominates. Thus, the presence of oxygen facilitates the intersystem crossing from the initially formed triplet to the singlet **20**^{1,3}**.**

This reduction pathway is also observed when the phenolic OH group on pHP is blocked by methylation or is absent. H-atom abstraction dominates, leading primarily to the reduction product **6** (*vide supra*),[5] established in earlier studies on the closely related caged *p*-methoxyphenacyl analogs[52] first pioneered by Sheehan and Umezawa[53] and later extensively reexamined by Phillips.[43, 44, 54-57]

A recent study by Phillips and Dore[20, 54] on phenol and ester release from 7-diethylaminocoumaryl-4-methyl cation ($DEACM^+$) cages also reported that photorelease occurred from its singlet excited state. Here, both the cationic and diradicaloid behavior through singlet-triplet interconversion was demonstrated by observation of the triplet intermediate.[54, 55]

In both cases, oxygen plays the role of catalyzing the singlet-triplet intersystem crossing of the non-Kekulé carbocation, from triplet to singlet for **20**^{3} to **20**^{1} (**Figure 5**) and the reverse for the $DEACM^+$ cation.

Similar behavior was also observed in our earlier studies with 7-methoxy-4-methylcoumaryl (also a singlet reaction) cage release in OA and O_2 environments with DEACM+ protected esters.[2] Thus, the triplet state release from pHP phenyl ethers compares favorably with that of the coumarin protected esters which occur from their singlet excited state, i.e., 4-methylcoumaryl phosphates and carboxylates, reported by us[1, 2] and by Schmidt, Bendig, et

al.[36, 42, 58] As in the case of the pHP series, the coumarylmethyl cation is also a non-Kekulé intermediate.

That both the excited triplet state and ground state bond cleavages maintain Brønsted behavior strongly implies enthalpic factors control the bond breaking process.

The subsequent chemistry of these reactive intermediate species are controlled by the environment that leads to a) carbocation-like nucleophilic attack (H_2O or ROH, e.g., outside the octa acid container) or b) diradicaloid behavior capable of H-abstraction and other radical-based processes.

There are several significant differences when comparing the triplet pHP cation, with the singlet coumaryl-4-methyl cation. The relative rates of release for both coumarylmethyl and pHP series are very similar, even though quantum efficiencies can be nearly an order of magnitude or more lower for coumarylmethyl cages. Cleavage of the coumaryl-4-methyl-substrate bond has to compete with singlet state fluorescence pathways and, to a lesser degree, with intersystem crossing. These two factors lower the *apparent* quantum efficiency for singlet state bond breaking for coumaryl cages.

Interestingly, in an earlier study we had shown that gas-phase thermal homolysis of several pHP esters including phenyl ethers **3a** and **3d** occurred by thermal, ground state processes, and surprisingly, displayed good Brønsted LG behavior.[26, 27]

Conclusions

Caged pHP phenols including tyrosine have been synthesized and their photochemistry examined. Upon photolysis the phenols are released in modest to good yields, but with poor quantum yields. Our investigations show that the *p*-hydroxyphenacyl caged phenyl ethers undergo initial homolysis of the pHP ether bond in the triplet excited state. This tight radical pair undergoes electron transfer of the pHP radical to the phenoxy radical to yield the phenol conjugate base. Concomitantly, the triplet pHP moiety sheds its acidic proton generating a neutral non-Kekulé intermediate (**20**^{3}), which is susceptable to intersystem crossing to its singlet states. The subsequent chemistry of **20** is controlled or strongly influenced by its environment, undergoing both nucleophilic attack by H_2O or ROH at the carbocation center (**20**^{1}) or diradicaloid H-abstraction and other radical reactions with adventitious H-atom sources (**20**^{3}).

These competing pathways are sensitive to the presence of oxygen, which appears to stimulate the intersystem crossing between the singlet and triplet states of **20**.

It is not clear at what stage or under what conditions $\mathbf{20}^{\mathbf{1}}$ partitions toward Favorskii closure eventually forming the rearrangement product, phenylacetic acid. For the more strongly acidic phenols **2a** – **2d,** the pHP protected phenol is easily released and does so according to the same predictable Brønsted leaving group behavior previously observed for a large array of leaving group acids. This same consistent predictable release behavior continues even with weakly acidic phenols, **2e** and **2f** with progressively less efficiency as predicted by Brønsted analysis. This lower reactivity supports our initial Brønsted-governed mechanism for this leaving group, in accord with most caged pHP photorelease reactions.

In fact, we suggest that the formation of the anion occurs through electron transfer from the pHP radical. There are a wide array of PPG's that may exhibit similar non-Kekulé mechanistic pathways to unleash their cargos. Future studies are necessary to discover whether other PPGs undergo the formation of non-Kekulé cation intermediates. Furthermore, the effects of solvent, presence of oxygen, confinement, pK_a and multiplicity influence the chemistry of the PPG and the released product.

Electronic Supplementary Information

Experimental procedures, ^{1}H NMR, UV and ESI-MS spectra for all new compounds. Irradiation procedures, ^{1}H NMR titration spectra of host-guest complexes, progress of photoreactions as monitored by ^{1}H NMR, LC-DAD-MS.

Conflicts of interest

The authors declare no competing financial interest.

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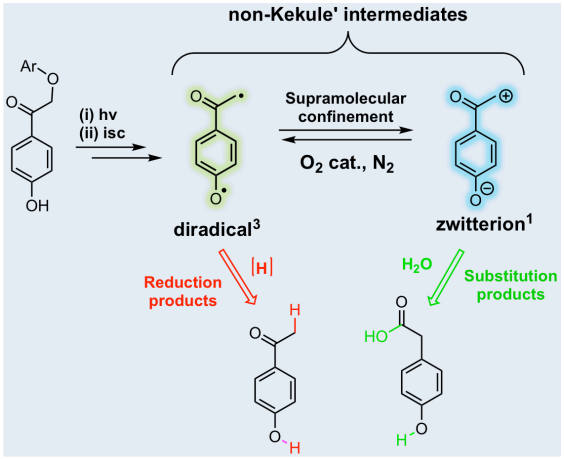
Table of Contents Graphic



Supporting Information

Competing Pathways for Photoremovable Protecting Groups: The Effects of Solvent, Oxygen and Encapsulation

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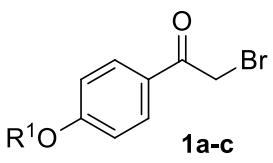
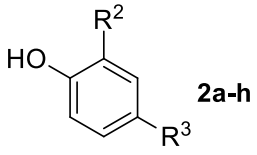
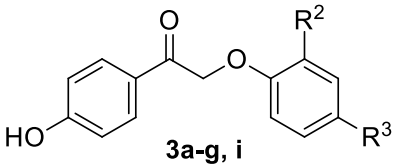
1. Structures of starting compounds, intermediates, pHP triggers (3a-3g and 3i) and octa acid (OA) host



1a-c



2a-h

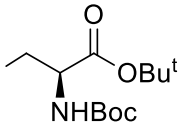


3a-g, i

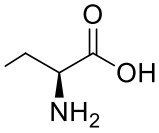
1a: R^1 = H
1b: R^1 = Ac
1c: R^1 = CO_2Bu^t

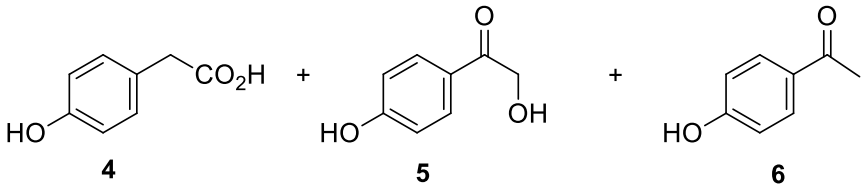
2a → **3a**: R^2 = H; R^3 = CN
2b → **3b**: R^2 = CF_3; R^3 = H
2c → **3c**: R^2 = H; R^3 = CF_3
2d → **3d**: R^2 = H; R^3 = H
2e → **3e**: R^2 = H; R^3 = CH_3
2f → **3f**: R^2 = H; R^3 = OCH_3
2g → **3g**: R^2 = H; R^3 = Br

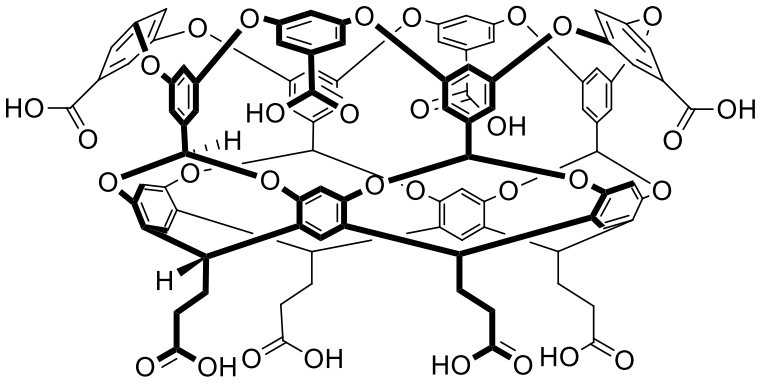
2h: R^2 = H; R^3 =



2i, 3i: R^2 = H; R^3 =







Octa acid (**OA**)

Scheme 1. Structures of starting compounds, intermediates, pHP triggers and octa acid (OA)[1] host.

2. Chemicals, materials and equipment.

2.1 Chemicals and materials.

Compounds di-*tert*-butyldicarbonate (DiBoc) and t-Boc protected ethyl tyrosyl esters, used for synthesis of pHP triggers, *p*-hydroxyacetophenone, 4-cyanophenol, *o*-trifluoromethylphenol, 4-methylphenol, *p*-bromophenol, *p*-hydroxyphenyl acetic acid, (*p*-hydroxybenzoyl)methanol, utilized for synthesis or for identification/quantification of triggers and photoproducts, potassium ferrioxalate, trifluoroacetic acid, 1,2,3-tribenzenetricarboxylic acid, phenanthroline, (Sigma-Aldrich/Alfa Aesar), utilized for determination of quantum yields, (Sigma-Aldrich/Alfa Aesar) were used as received.

Organic solvents acetonitrile, ether, dioxane, dichloromethane and ethyl acetate were p.a. grade and used as received while acetonitrile and formic acid used for chromatographic separations were HPLC gradient grade/LC-MS grade (VWR). TLC was carried out using 0.25 mm Merck silica gel plates (60F-254) and column chromatography was performed with 230-400 mesh Merck silica gel 60 for flash chromatography.

2.2 Equipment.

The melting points of synthetized compounds were taken on a micro melting point apparatus. IR spectra were obtained in liquid films or KBr disks on an FT-IR spectrometer and their UV-vis spectra recorded on a Cary-100. The synthetized compounds were analyzed by NMR, using 400 MHz and 500 MHz Bruker instruments, and by mass spectrometry, using a Bruker Daltonics micro TOFQ II.

Formation of host-guest complexes with OA and photoproducts was studied by NMR, using 400 MHz and 500 MHz Bruker instruments or using a 500 MHz JEOL system equipped with a Royal HFX probe. The formation of products was also followed by UV-Visible absorbance, using a Cary-100. The identification and quantification of photoproducts was performed by HPLC, by LC-DAD-MS (liquid chromatography coupled to mass spectrometry), using a Agilent LC coupled to a Bruker Daltonics HCT *ultra* mass spectrometer, and by UHPLC-HRMS (liquid chromatography coupled to high resolution mass spectrometry), using a Thermo Ultimate 3000 UHPLC coupled to a Orbitrap Elite mass spectrometer.

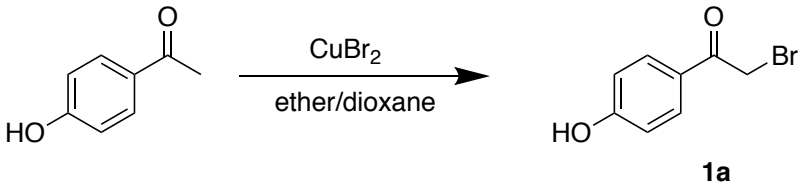
Irradiations were performed using two different setups. In one a Rayonet RPR-100 merry-go-round photochemical reactor was used at 300 nm (RPR 3000 Å) or 350 nm (RPR 3500 Å). In the second the irradiations were performed using a high-pressure xenon lamp in conjunction with a water filter to prevent heating of the sample solution. An additional Pyrex filter was inserted to remove UV light below 300 nm.

3. Synthetic procedures and spectral data for pHP phenol ethers.

Compounds **1a**, and **3a** to **3i** were synthesized according to reported procedures[2,3]. Octa Acid (OA) host was synthesized following literature procedure.[1]

3.1 Preparation of α-bromo-*p*-hydroxyacetophenone (1a) and hydroxyl protected pHP's acetoxy (1b) and Boc-protected (1c) pHPs.

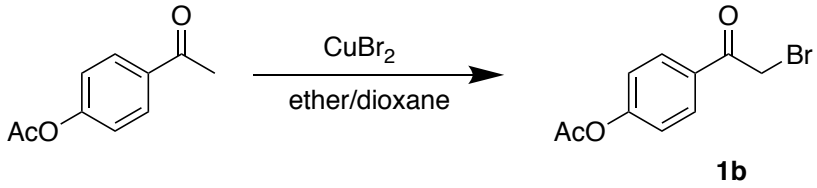
i. Preparation of α-bromo-*p*-hydroxyacetophenone (1a).[2]



1a

To an ice-cooled solution of 2.06 g (15.1 mmol) of p-hydroxyacetophenone in 20 mL 1:1(ether/dioxane), was added a solution of 4.8 g (1.3 times excess) $CuBr_2$ in 20 mL of 1:1 ether/dioxane mixture in dropwise manner. After the addition, the solution was stirred at room temperature for 12 h, and the product was extracted between water and EtOAc (20 mL, 2 times), and the combined organic layer was washed with saturated NaCl and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by crystallization from CH_2Cl_2 to give **1a** as a white solid (58% yield), mp 126-128 ^oC/130 ^oC.

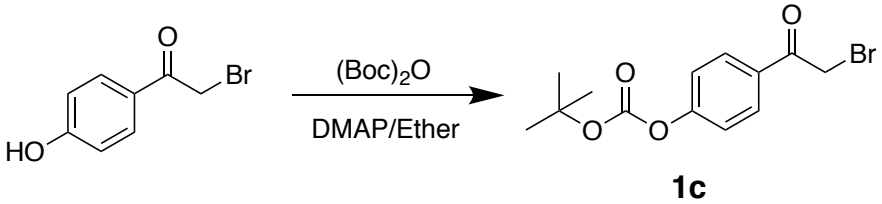
ii. Preparation of α-bromo-4'-acetoxyacetophenone (1b).



1b

To a solution of 5.6 g (32 mmol) of 4'-acetoxyacetophenone in 60 mL (1:1) dioxane/ether placed in an ice bath under nitrogen, was added 7.3 g (32 mmol) of $CuBr_2$ in 60 mL (1:1) dioxane/ether. The solution was stirred at room temperature for 4 h, then the solvent was removed *in vacuo*, and the product was separated between EtOAc and water, washed with 5% $NaHCO_3$ and saturated NaCl, dried over Na_2SO_4, and concentrated *in vacuo* to give crude **α**-bromo-4'-acetoxyacetophenone (**1b**). The crude product was crystallized from (1:1) hexane/EtOAc to give the product **1b** in 86% yield as a colorless solid. ^{1}H NMR ($CDCl_3$) δ 2.35(s, 3H), 4.45 (s, 2H), 7.26 (d, J = 8.8 Hz, 2H), 8.03(d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 21.57, 31.07, 122.58, 131.87, 132.03, 155.36, 169.17, 191.69.

iii. Preparation of DIBOC protected pHP Br (1c).



1c

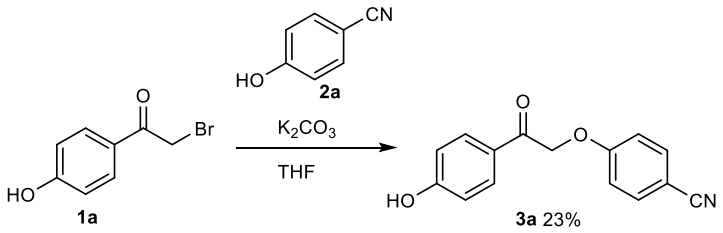
To a solution of 10.0 g (46.5 mmol) α-bromo-*p*-hydroxyacetophenone (α-bromo-pHP) and catalytic amount of DMAP in 200 mL of anhydrous ether in an ice bath under nitrogen was added 11.1 g (50.8 mmol) di-tert-butyldicarbonate ($(Boc)_2O$) in 50 mL ether over 15 min. The reaction was stirred for 4 h at room temperature, then was washed twice with water (10 mL), saturated NaCl, dried over Na_2SO_4, and concentrated *in vacuo* to give 14.1 g of **1c** (yield = 96%) as an colorless solid, mp: 63.5-64.2 ^{o}C. ^{1}H NMR ($CDCl_3$) δ: 1.57(s, 9H), 4.43 (s, 2H), 7.28 (d, J = 8.4

Hz, 2H), 8.11(d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 28.03, 31.07, 84.54, 121.78, 131.42, 130.80, 151.02, 155.38, 190.23. HRMS: Theoretical (M+H) 296.0923, Found 296.0925

3.2 Synthesis of pHP substituted phenyl ethers 3a, b, e, g and i.

Preparations of 1-(4-hydroxyphenyl)-2-(4-(trifluoromethyl) phenoxy)ethan-1-one (**3c**, pHP *p*-trifluoromethylphenyl ether), 1-(4-hydroxyphenyl)-2-phenoxyethan-1-one (**3d**, pHP phenol ether), and 1-(4-hydroxyphenyl)-2-(4-methoxyphenoxy)ethan-1-one (**3f**, pHP *p*-ansyl ether) have been reported previously.[3]

iv. Preparation of 4-(2-(4-hydroxyphenyl)-2-oxoethoxy)benzonitrile (3a, pHP *p*-cyanophenyl ether).



Using the same procedure employed for **3e** (*vide infra*)**,** pHP protected p-cyanophenol displayed the following physical and spectral data: mp 224-225 °C as crystalline needles. 272 (ε 5940), 249 (ε 5900), 218 (ε 3800); IR (KBr), 3276 (OH), 2229 (CN), 1693 (C=O). ^{1}H NMR ($CDCl_3$) δ: 5.48 (s, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.96 (s, OH). ^{13}C NMR ($CDCl_3$) δ: 68.50, 102.14, 114.23, 117.42, 124.19, 128.93, 132.35, 152.71, 160.16, 161.56, 189.83. HRMS: Theoretical (M+H) 254.0817, Found 254.0819.

The acetate protected pHP Br (**1b**) gave similar or better yields.

v. Preparation of 1-(4-hydroxyphenyl)-2-(2-(trifluoromethyl)phenoxy)ethan-1-one (3b, pHP *o*-trifluoromethylphenylether).

To a solution of 0.93 g (5.7 mmol) *o*-trifluoromethylphenol and 1.48g (5.7 mmol) of bromo ester **1b** in 50 mL acetone, 2 g of K_2CO_3 , was added. The mixture was stirred for 12 h, then filtered. The filtrate was concentrated *in vacuo* and the crude product was eluted through silica gel column using 4:1 hexane:EtOAc as the mobile phase to purify. 2'-2-trifluoromethylphenoxy-4-acetyloxyacetophenone (**3b**) was obtained as a white solid (yield 46%). ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 3H), 5.32 (s, 2H), 6.89 (d, *J* = 8.8 Hz, 1H), 7.06 (t, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.45 (t, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.60, 60.82, 113.31, 121.49, 119.56 (q, *J* = 32.4 Hz, 1C), 122.56, 127.80 (q, *J* = 5.2 Hz, 1C), 123.34 (q, *J* = 269 Hz, 1C) 130.37, 132.15, 133.72, 155.45, 169.15, 193.51. HRMS: Theoretical (M+ H) 339.0844, Found 339.0838.

To a solution of 0.90 g (2.7 mmol) 2'-(2-trifluoromethylphenoxy)-4-acetyloxyacetophenone in 30 mL methanol, was added the 1.5 g of KOH. The mixture was stirred for 12 h. The mixture was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by flash column with 3:1 hexane/EtOAc. The white solid obtained was 2'-(2-trifluoromethylphenoxy)-4-hydroxyacetophenone **(3c)** in 86% yield. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/DMSO) δ 5.31 (s, 2H), 6.83 (m, 3H), 6.96 (t, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 10.06 (s, OH); ^{13}C NMR ($CDCl_3$/ DMSO) δ 70.40, 112.64, 115.28, 118.09 (q, *J* = 30.6 Hz, 1C), 120.18, 122.07, 123.15(q, *J* = 270 Hz, 1C), 125.41, 126.60, 130.20, 132.90, 155.56, 162.63, 191.46. HRMS: Theoretical (M+H) 297.0739, Found 297.0753.

vi. Preparation of 1-(4-hydroxyphenyl)-2-(*p*-tolyloxy)ethan-1-one (3e, pHP *p*-toluyl ether).

To a cooled (ice bath) solution of 1.18 g (11 mmol) of 4-methylphenol in 20 mL of THF, was added 0.36 g (60% in mineral oil) NaH slowly. To this mixture, the solution of 1.8 g (8.7 mmol) of α-bromo-*p*-hydroxyacetophenone in 20 mL of THF was added drop wise through an additional funnel. After 2 h, the white solid was filtered and the remaining solution of the filtrate was stirred with a magnetic stir bar at room temperature for an additional 24h. The mixture was filtered and the filtrate was concentrated using a rotary evaporator. Flash column was used to

separate the mixture by using 3:1 hexane/EtOAc to obtain the product **3e** (0.8 g, yield = 30%), mp 154-156^{o}C as needle crystal, the spectral data were as follows: UV ε_{271}=18000, ε_{218}=19000. IR, 3211(OH), 1664 (C=O). ^{1}H NMR ($CDCl_3$) δ: 2.30 (s, 3H), 5.21 (s, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 20.70, 71.15,114.86, 115.79, 128.12, 130.22, 131.11, 156.17, 160.71, 193.58. HRMS, Theoretical (M+H) 243.1021, Found 243.1024.

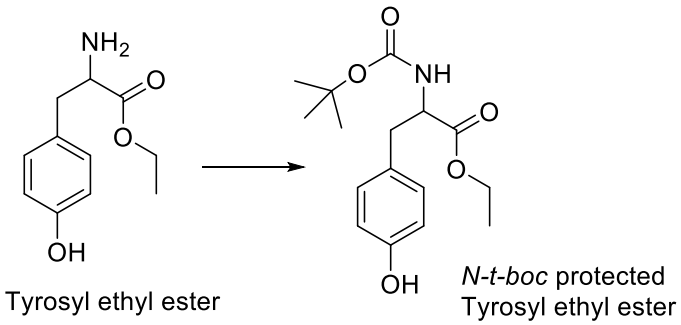
vii. Preparation of 2-(4-bromophenoxy)-1-(4-hydroxyphenyl)ethan-1-one (3g, pHP *p*-bromophenyl ether).

To an ice-cold solution of 0.55 g (3.2 mmol) of *p*-bromophenol (**2 g**) and 0.59 g (4.3 mmol) of K_2CO_3 in 20 mL of acetone, 0.45 g (2.1 mmol) of **1a** was added drop wise using an addition funnel. After 2 h, the white solid was filtered and the remaining filtrate was stirred at room temperature for an additional 24h. The resulting mixture was filtered and the filtrate was concentrated *in vacuo*. The mixture was purified by flash chromatography by using 3:1 hexane/EtOAc as the mobile phase to obtain the product as a solid (0.3 g, yield = 28%). The solid decomposed when the melting point was measured. The spectral data of **3g** were as follows: UV ε_{272} 940, 249 (ε 5900), 218 (ε 3800). IR (KBr), 3276(OH), 2229(CN), 1693 (C=O). ^{1}H NMR ($CDCl_3$) δ: 5.48 (s, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.96(s, OH). ^{13}C NMR ($CDCl_3$) δ: 69.71, 112.49, 115.40, 129.95, 131.62, 156.91, 162.55, 191.54. HRMS: Theoretical (M + Na) 328.9789, Found 328.9805.

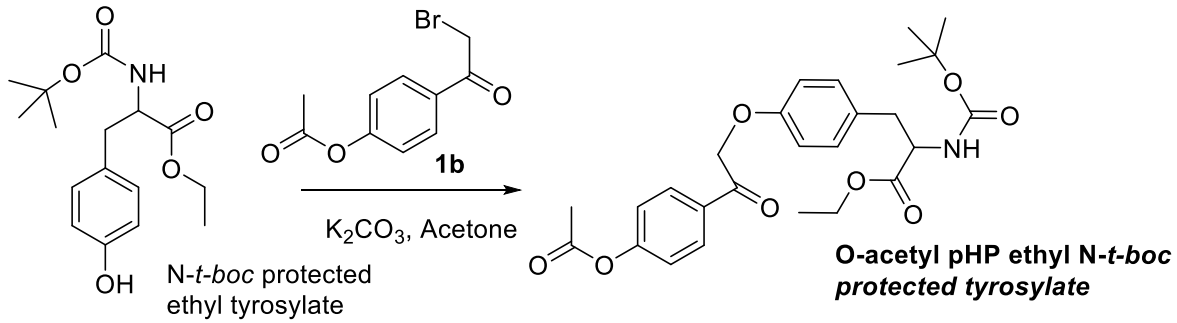
viii. Preparation of protected pHP tyrosyl ethyl ester, R = Et and pHP tyrosyl ether (3i).

Synthesis of pHP tyrosyl ether: The general method of Frechet, et al.[4] was employed to protect the amino acid moieties on the peptide. For the tyrosyl pHP derivative, it was necessary to first protect the amino acid functional groups. Using the sequence reported by Frechet[4] The model ethyl ester of tyrosine was first employed to protect both the amino and the pHP phenolic group. Then, selective removal of the *t*-butyl group on tyrosine and installation of *t*-Boc protected pHP Br was carried out. Finally, the N-*t*-butyl group was removed yielding the pHP tyrosyl ethyl ester.

This same sequence was repeated with tyrosine in which all the functional groups were protected with *t*-Boc, the phenol groups was deprotected, and the pHP group was installed. These procedures were then repeated on tyrosine to yield the desired final pHP tyrosine (**3i**).

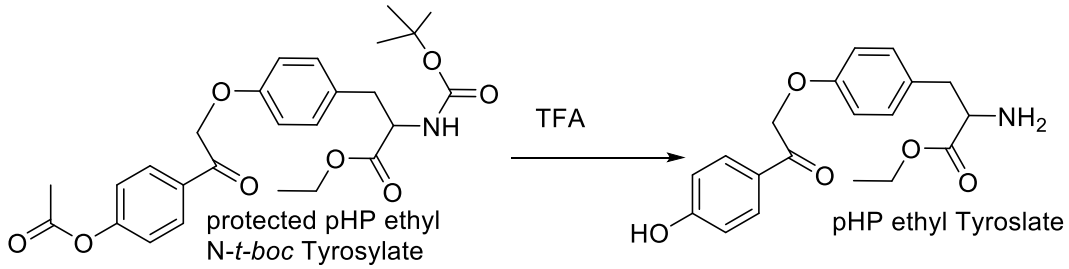


To a solution of 1.71 g (8.13 mmol) of tyrosine ethyl ester HCl and 1.78 g (8.13 mmol) of di-*tert*-butyldicarbonate in 50% of EtOAc in water, 5.0 g (36.2 mmol) of K_2CO_3 and 1.0 g of 18-Crown-6 was added. The mixture was stirred for 72 h. The crude product was separated between water and EtOAc. The combined organics *in vacuo*, the resulting solid was purified by column with 2:1 hexane/EtOAc. The spectral data *t*-Boc protected tyrosyl were as follows: ^{1}H NMR ($CDCl_3$) δ: 1.15 (t, *J* = 7.0 Hz, 3H), 1.40 (s, 9H), 3.08 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 4.56 (m, 1H), 5.08 (m, 1H), 6.30 (bs, OH), 6.74 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.54, 28.72, 37.99, 55.06, 61.8, 80.60, 115.85, 127.88, 130.82, 155.56, 155.76, 172.65.



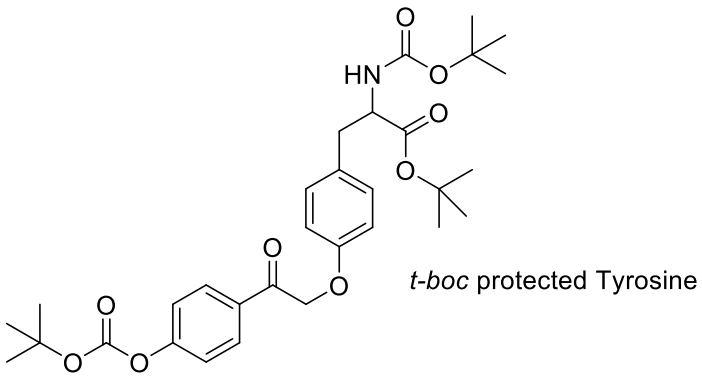
About 0.8 g (2.6 mmol) of *t*-Boc protected ethyl tyrosine, 1.0 g of K_2CO_3 and 0.7 g of *t*-Boc protected *p*-hydroxyphenacyl bromide (**1b**) and 50 mL of acetone were added and stirred at room temperature for 72 h. The mixture was filtered and the solvent was removed *in vacuo*. The residue

was purified by flash chromatography using 2:1 Hexane/EtOAc as the mobile phase to obtain **5a** as a solid (0.6 g, yield = 50%). ^{1}H NMR ($CDCl_3$) δ: 1.24 (t, *J* = 7.0 Hz, 3H), 1.44 (s, 9H), 2.30 (s, 3H), 3.04 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 4.53 (m, 1H), 4.98 (m, H), 5.33 (s, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 8.34 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$/ DMSO) δ: 14.40, 21.37, 28.51, 37.67, 54.69, 61.54, 71.11, 80.06, 115.02, 122.31, 129.46, 130.12, 132.31, 155.11, 155.31, 168.97, 172.08, 193.59. HRMS: Theoretical (M + H) 486.2142, Found 486.2128.



Deprotection of *t*-Boc group was performed by following the same procedure as the *t*-Boc tyrosine pHP, followed by the hydrolysis of the phenolate ester by KOH. The product was separated between water and EtOAc, washed with brine, and dried over Na_2SO_4 to give a white solid.

ix. Preparation of protected pHP tyrosine (3i) from *t*-butyl ester, R_2 = *t*-Bu.



To a solution of 1.45 g (5.6 mmol) of α-bromo-4'-*t*-butoxyacetophenone (**1c**) and 5.6 mmol of *t*-Boc protected tyrosine in 20 mL of acetone was added 1.0 g (7.4 mmol) potassium carbonate and a catalytic amount of KI. The mixture was refluxed at 60 °C for 24 h, the solid was filtered, and the filtrate was concentrated *in vacuo*. Flash column chromatography was used to separate the mixture with a 7:3 hexane/EtOAc to obtain *t*-Boc protected pHP *t*-butyl tyrosine ester (yield = 87%) as a colorless solid (mp: 90-92 °C). UV ε =12000, ε =13000. ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H), 1.44 (s, 9H), 1.59 (s, 9H), 3.01 (d, *J* = 5.6 Hz, 2H), 4.41(q, *J* = 8.0 Hz, 1H), 4.98 (*d*, *J* = 7.60 Hz, 1H), 5.22 (s, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 7.32 (*d*, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 28.06, 28.37, 28.73, 84.50, 82.44, 80.05, 71.35,55.26, 37.99, 115.03, 122.04, 129.98, 130.32, 131.10, 132.35, 151.34, 155.48, 155.59,157.36, 171.36, 193.83. HRMS: Theoretical (M + Na) 594.2679, Found 594.2691.

A solution of 0.5 g (0.87 mmol) of the *t*-Boc protected pHP *t*-butyl tyrosine ester in 2 mL of TFA and 20 mL of CH_2Cl_2 was stirred for 60 min at room temperature. Then TFA solution was removed *in vacuo*. A white solid of pHP tyrosine **3i** was obtained: ^{1}H NMR (DMSO) δ: 3.17 (m, 2H), 4.12 (m, 1H), 5.38 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.19 (*d*, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (DMSO) δ: 34.78, 53.46, 69.49, 114.36, 115.12, 125.81, 126.57, 130.00, 130.34, 157.32, 162.69, 169.36, 192.23. HRMS: Theoretical (M + H) 316.1185, Found 316.1181.

4. General photolysis procedure and quantum yield determination in solution

4.1. Photolysis of pHP triggers 3a-g

Photolysis of pHP phenol ethers **3a–g** were carried out in a Rayonet RPR-100 photochemical reactor using 300 nm (RPR 3000 Å) or 350 nm (RPR 3500 Å) lamps fitted with an RPR merry-go-round apparatus. The experiments were carried out using NMR tubes or 20 × 180 mm Pyrex test tubes with samples of 20 – 100 mg of the ethers dissolved in appropriate solvents (2 – 5 mL) with internal standards of either 1,2,3-benzenetricarboxylic acid or DMF. The pH was adjusted with either Tris or phosphate buffer solution by addition of TFA, HCl and NaOH. For 300 nm irradiations, the reactor was fitted with only 4 or 8 lamps and turned on before sample placement

to warm up the lamps for 15 min prior to removing an opaque sleeve to start the photolysis. A counter recorded the time of irradiation. The light output for the determination of quantum efficiencies was measured using potassium ferrioxalate, *vide infra*.[1] Photolysis times ranged up to 10 hours, depending on the conversion desired, the efficiency of the reaction, and the size of the sample. The progress of the reaction was monitored by ^{1}H NMR. Product yields were determined by ^{1}H NMR using DMF as the internal standard. After completion of the photolysis, the products were isolated by HPLC or standard flash column chromatography. Compounds **3c** and **3f** were also irradiated in mixtures D_2O:acetonitrile-d_3 20:80 using a high-pressure xenon lamp in conjunction with water and Pyrex filters. Figures S1 and S2 show the ^{1}H NMR obtained for these compounds before and after irradiation.

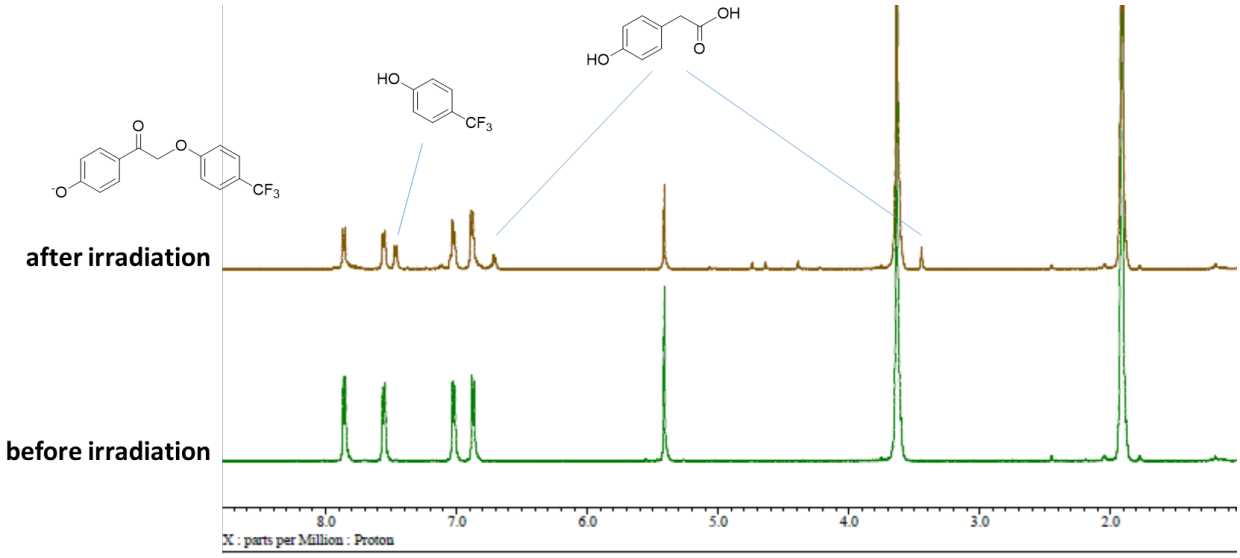


Figure S1. ^{1}H NMR spectra of **3c** in D_2O:acetonitrile-d_3 20:80 before and after irradiation.

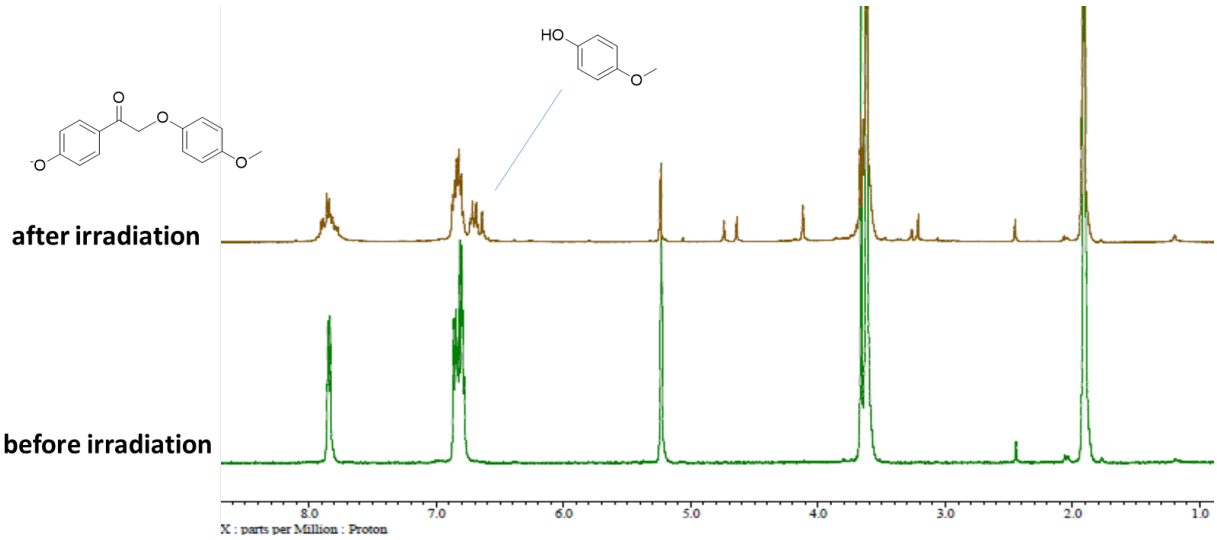


Figure S2. ^{1}H NMR spectra of **3f** in D_2O:acetonitrile-d_3 20:80 before and after irradiation.

Additional monitoring of the reaction by UV-vis spectroscopic analysis was accomplished by the following general procedures with ether **3b**, a sample of 5 mg 2,4-cyanophenoxy-4-hydroxyacetophenone was dissolved in 5 mL of 20% aqueous acetonitrile, buffered at pH 7.4 with a phosphate buffer and the solution transferred to a Pyrex test tube. The sample was irradiated with eight 300 nm lamps and samples were periodically removed in 50 µL aliquots and diluted to 2 mL for UV analysis. The UV-vis spectra were recorded every 3 min of irradiation. The phototransformation of ethers **3c** and **3f** was also studied in dry acetonitrile and mixtures of acetonitrile:water 20:80 and 80:20. In this case, the irradiations were performed using a high-pressure xenon lamp in conjunction with water and Pyrex filters. Figures S3-S6 show the UV spectra before and after irradiation of **3c** and **3f** in dry acetonitrile and acetonitrile:water 20:80.

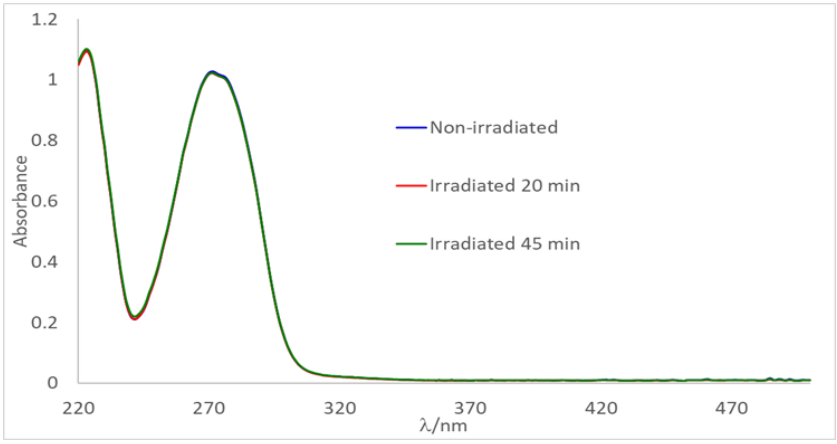


Figure S3. UV-vis traces obtained before and after photolysis of **3c** in dry CH_3CN. [**3c**] ~ 50 μM.

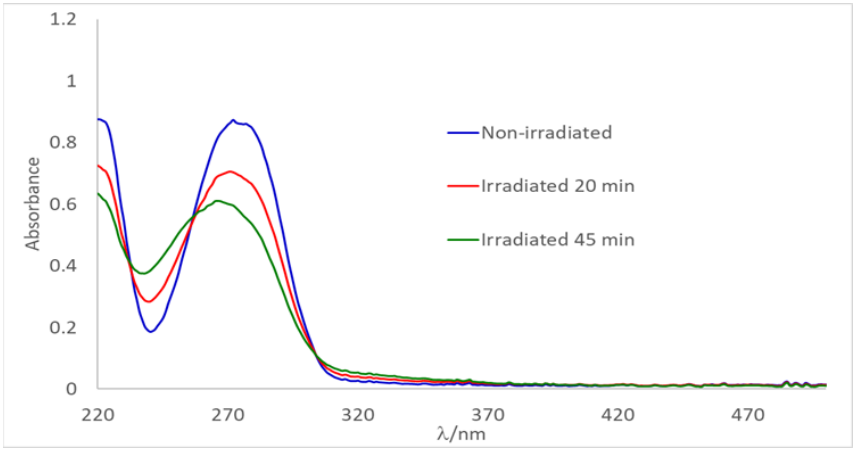


Figure S4. UV-vis traces obtained before and after photolysis of **3f** in dry CH_3CN. [**3f**] ~ 50 μM.

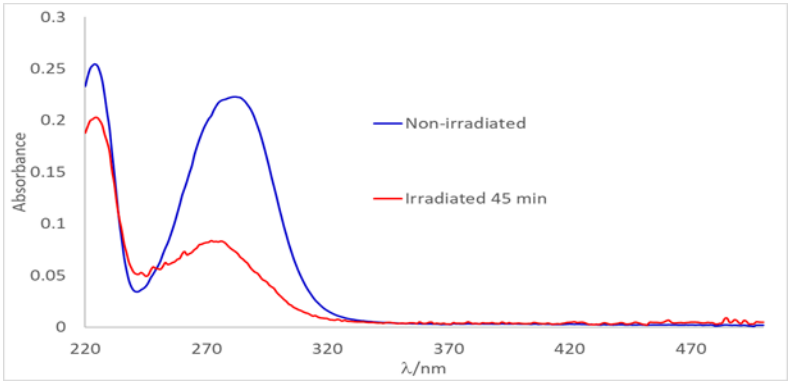


Figure S5. UV-vis traces obtained before and after photolysis of **3c** in water:acetonitrile mixture (80:20). [**3c**] ~ 12 μM.

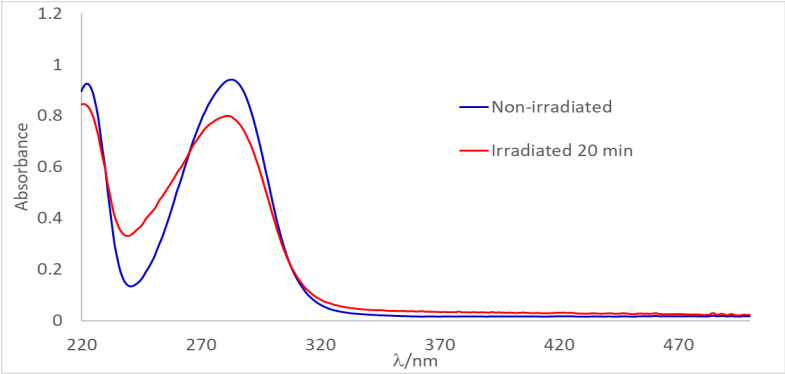


Figure S6. UV-vis traces obtained before and after photolysis of **3f** in water:acetonitrile mixture (80:20). [**3f**] ~ 50 μM.

4.2. Photolysis of pHP tyrosyl ether 3i.

A 4 mM solution of pHP caged tyrosine **3i** was dissolved in 30% aqueous phosphate buffer (pH ~7.0)/CH_3CN was photolyzed at 300 nm. The initial optical density of the sample solution was >4.0 over the emission range of the 300 nm RPR lamps, assuring the complete absorption by the sample for quantum yield measurements at low conversions. Higher conversion (1 hour photolysis) gave 82%, released tyrosine at 80% conversion.

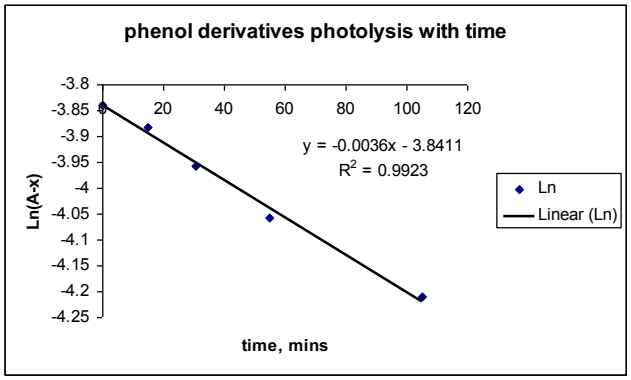
The quantum yield determinations gave $\Phi_{dis} = 0.1$ for pHP tyrosine disappearance and $_{app} = 0.085$ for the appearance of uncaged tyrosine. Stern-Volmer quenching constants (K_{SV}) were carried out using methyl sorbate. Light output was determined using potassium ferrioxalate method of Parker and Hatchard.[1] See quenching studies below for details.

4.3. Actinometry

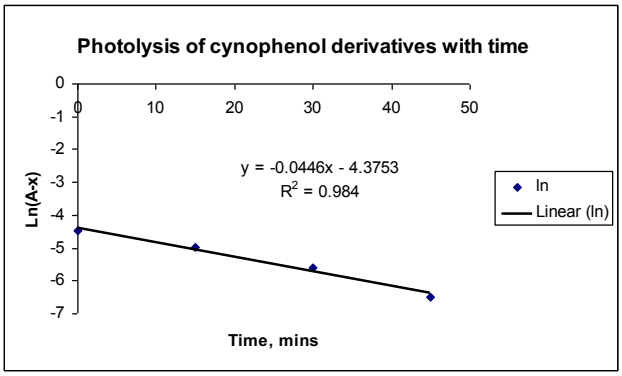
A solution of 0.6 mM of potassium ferrioxalate in 0.05 M H_2SO_4 was irradiated under identical conditions as the pHP ethers, i.e., with the same lamps, test tubes, and volumes. The procedure of preparation and handling of actinometer as well as calibration curve are detailed Hatchard and Packer.[5] To a 10 mL volumetric flask was added 0.5 mL buffer, 2 mL 0.1% phenanthroline, 0.9 mL 0.05 M sulfuric acid, and 0.1mL of the irradiated solution. Absorbance was recorded. The difference in optical density was converted to concentration using a calibration curve. The change in concentration was converted to mol/min and light output was determined by dividing this number by 1.24.[5] The optical density was measured at 510 nm.

4.4 Quantum yield determinations.

Quantum yields of reactant ether disappearance, Φ_{dis} (**3a** – **f**, **i**), and product appearance, Φ_{ArOH} (**2a** – **f**, **i**) were determined by reverse phase HPLC using the internal standard method. The quantum yields for photorearrangement product of pHP, *p*-hydroxyphenylacetic acid (**4**) along with products 2',4-dihydroxyacetophenone (**5**) and *p*-hydroxyacetophnone (**6**) were determined by the relative percentages of the differences between Φ_{ArOH} from Φ_{dis}. Figures S7**a** and **b** show the photolysis of **3d** and **3a** unsubstituted phenol and (*p*-cyanophenyl release) l vs time. Note the extended time necessary fo the unsubstituted phenol release vs. *p*-cyanophenyl.



(a)



(b)

Figure S7. Photolysis of pHP phenyl ether **3d** (a) and *p*-cyanophenyl ether **3a** (b) in CH_3CN/H_2O.

4.5 Quenching experiments with methyl sorbate, RPR 310 nm and 350 nm excitation.

The Stern-Volmer expression for quenching of the release of *p*-cyanophenol from pHP *p*-cynophenol ether **3a** is quenched by methyl sorbate is $\Phi_0 / \Phi = 1 + K\text{sv}\,[Q]$. Photolysis at 310 nm gave $K\text{sv} = 105.5$ for the Stern-Volmer slope in the equation $\Phi_0 / \Phi = 1 + k_q\tau^3\,[Q]$ and τ^0, the lifetime of the excited triplet state in the absence of the quencher Q (methyl sorbate) is obtained for this reaction when $k_q = k_d$. Therefore, the lifetime $\tau^3 = k\text{sv}/k\text{d} = 4.2 \times 10^{-9}$ s or τ^0 4.2 ns, the lifetime of the reactive excited triplet state. Figures S8 and S9 show the Stern-Volmer plots for the quenching of the photoreaction of **3a** by methyl sorbate.

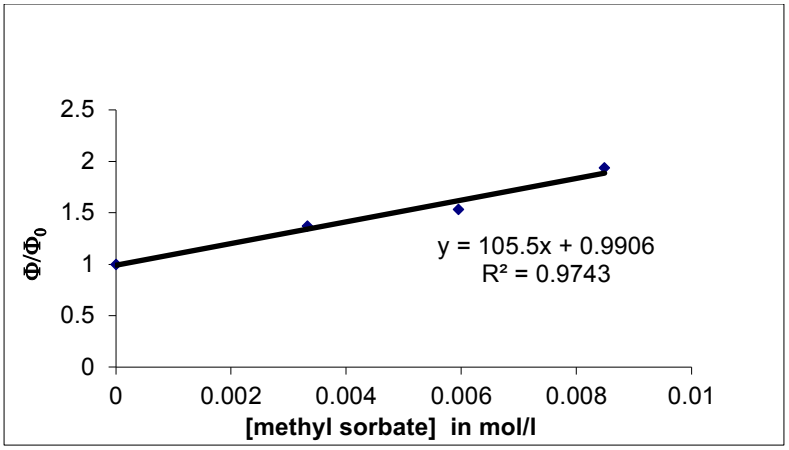


Figure S8. Stern-Volmer quenching by methyl sorbate of pHP *p*-cyanophenyl ether (**3a**) by photolysis at 320 nm.

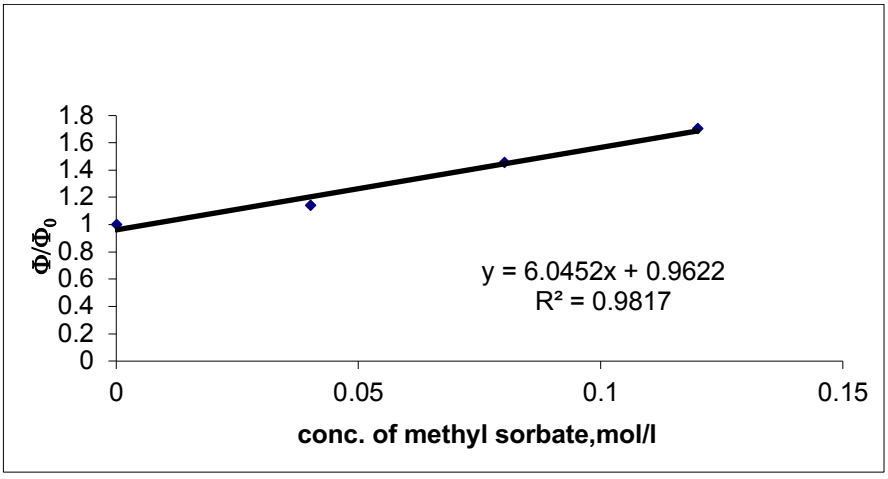


Figure S9. Stern-Volmer Plot for quenching of **3a** with methyl sorbate for photolysis at 350 nm.

For photolysis at 350 nm, methyl sorbate quenching gave a Stern-Volmer quenching constant of Ksv = 6.045 for $\Phi_0 / \Phi = 1 + k_q\tau^3$ [Q]. The τ^3 (the lifetime of the triplet in the absence of quencher Q) obtained was $k_q = k_d$, $\tau^3 = k_{sv}/k_d$ = 0.24 ns.

5. pH effect on pHP phenyl ether photochemistry

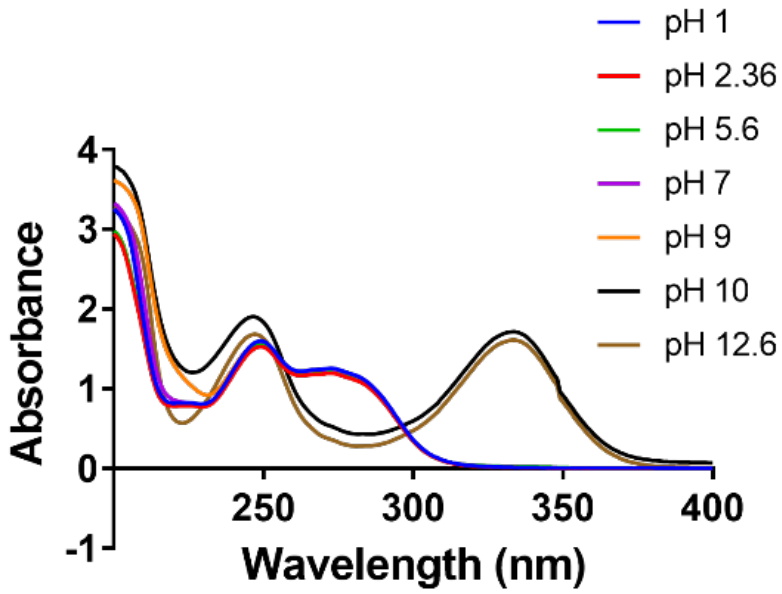


Figure S10. UV-vis spectra of pHP *p*-cyanophenyl ether (**3a**) (a) UV-vis spectrum as a function of pH. pH effect on the absorption spectra of **3a** at pH 1.0 (HCl aq.) to 12.6 in phosphate buffer. The UV-vis spectra were measured for solutions of 2.1 × 10^{-4} mol/L of pHP *p*-cyanophenyl ether (**3a**) at pH 1.0 (aq. HCl) and over a range of pH from 2.4 to 12.8 in aq. phosphate buffer solutions of pHP *p*-cyanophenyl ether (2.1 × 10^{-4} mol/L) NaOD/D_2O.

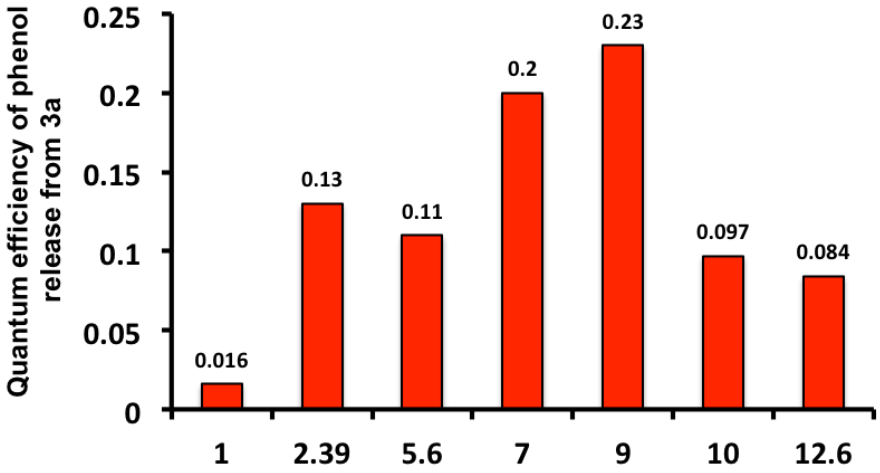


Figure S11. Effect of pH on the quantum efficiency of phenol release from pHP *p*-cyanophenyl ether (**3a**) in 20% aq. CH_3CN. pHP cyanophenol ether **1a** (4.2×10^{-3} mol) with 0.0275 g of biphenyl is used as internal standard.

6. Supramolecular encapsulation and photochemistry of pHP phenyl ethers 3c and 3f.

6.1 Spectral data for OA enclosed pHP phenol ethers.

Procedure for 1-(4-hydroxyphenyl)-2-(4-(trifluoromethyl) phenoxy)ethan-1-one (3c, pHP *p*-triflouromethylphenyl ether).

A 1 mM solution of OA in borate buffer (pH = 8.7) was prepared in a Pyrex NMR tube after which a solution of 2.5 μL of a 60 mM solution of **3c** in DMSO-d_6 was added incrementally. The ^{1}H NMR spectra were recorded after each addition until the ratio of **3c** to OA was 1:2 as indicated by the appearance of free, excess **3c** by ^{1}H NMR (*vide infra* for **1g** irradiations). The solution was then irradiated for 1 h using a 450 W medium pressure mercury lamp with Pyrex jacket. The ^{1}H NMR spectra showed a new peak at 3.3 ppm assigned to the methylene group of 4-hydroxyphenylacetic acid, the Favorskii rearrangement product. In addition, ^{1}H NMR absorptions for each of the two ether photoproducts were assigned to *p*-trifluoromethylphenol (**2c**) and *p*-

methoxyphenol (**2f**), respectively, as well as the reduction product 4-dihydroxyacetophenone (**6**). The photoreaction was also monitored by LC UV-vis (*vide infra)*. The phenol yields decrease with extended irradiation, reflecting the instabilty of the phenol to the photolysis conditions. Examination of the photorelease of phenols for the corresponding ethers **3c**, **3g** and **3c** are shown in Figure 2 for **3c**; Figure 3 for **3f**) gave the reduction product **6** from the cage (see Figures 2 and 3).

6.2 UV-vis spectral data for OA enclosed pHP phenol ether 3c.

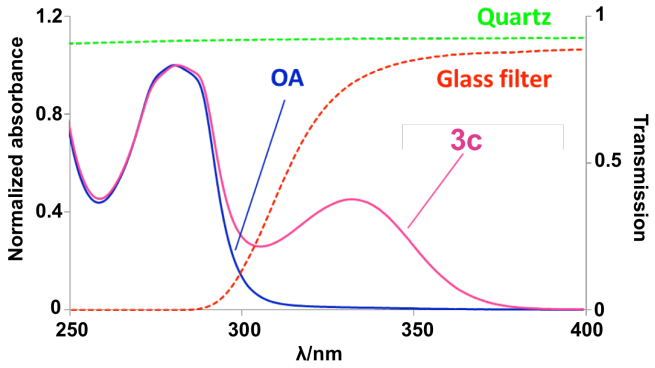


Figure S12. UV-vis spectra as a function of supramolecular encapsulation. Absorption spectra of **3c** (purple trace) in OA container and OA alone (blue trace) dissolved in aqueous borate buffer (pH 8.7). The dotted red and green lines are the transmission profiles of Pyrex and quartz glass filters, respectively.

6.3 Procedure for photolysis of OA encapsulated pHP ethers for NMR studies.

1-(4-hydroxyphenyl)-2-(4-(trifluoromethyl) phenoxy)ethan-1-one (3c, pHP *p*-triflouromethylphenyl ether).

^{1}H NMR titration experiment: A 1 mM solution of OA in borate buffer (pH = 8.7) placed in a Pyrex NMR tube to which was added 2.5 μL of a 60 mM of **3c** in DMSO-d_6. ^{1}H NMR was employed to assure that the pHP ether (**3c**) forms a 1:2 complex with OA (**3c**:OA).

UV-light irradiation experiment (monitored by ^{1}H NMR): A 1 mM solution of OA in borate buffer (pH = 8.7) was prepared in a Pyrex NMR tube after which a solution of 5 μL of a 60 mM solution of **3c** in DMSO-d_6 was added. The ^{1}H NMR spectra were recorded before and after the addition of **3c** to OA to form 1:2 complex **3c**@$(OA)_2$. The solution was then irradiated for 1 h using a 450 W medium pressure mercury lamp with Pyrex jacket. The ^{1}H NMR spectra showed a new peak at 3.3 ppm assigned to the methylene group of 4-hydroxyphenylacetic acid (**4**), the Favorskii rearrangement product. In addition, proton peaks of *p*-trifluorophenol (**2c**) and 2', 4-dihydroxyacetophenone (**5**) were also observed (See Figure 3). The photoreaction was also monitored by LC UV-vis. The phenol yield then decreases reflecting the instabilty of the phenol to the photolysis conditions. Examination of the photorelease of phenols for the corresponding ethers **3c** and **3f** gave the additional product **4** from the cage attributed to a Favorskii rearrangement of the chromophore (see Figure 3 in the text).

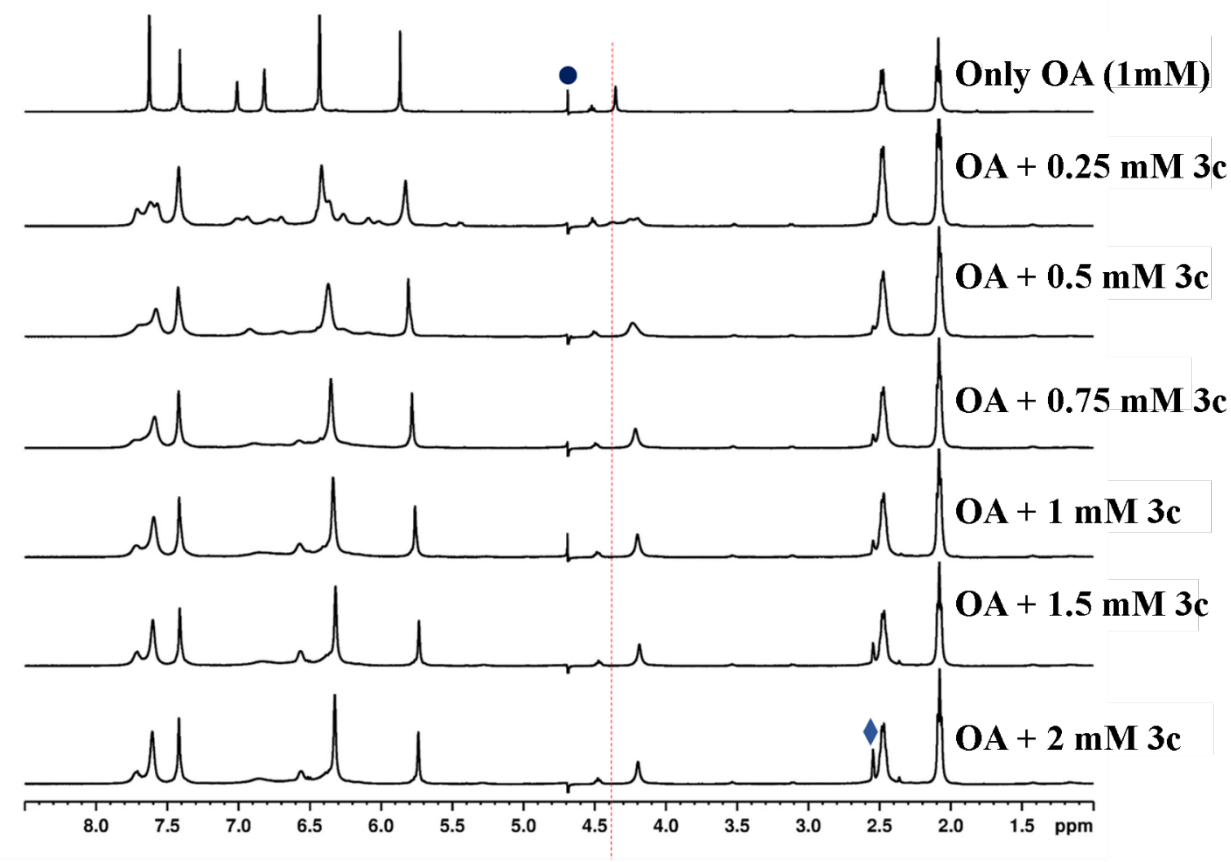


Figure S13. ^{1}H NMR titration spectra of **3c**@OA in borate buffer solution. The "●" and "◆" represent the residual solvent peaks for D_2O and DMSO-d_6, respectively.

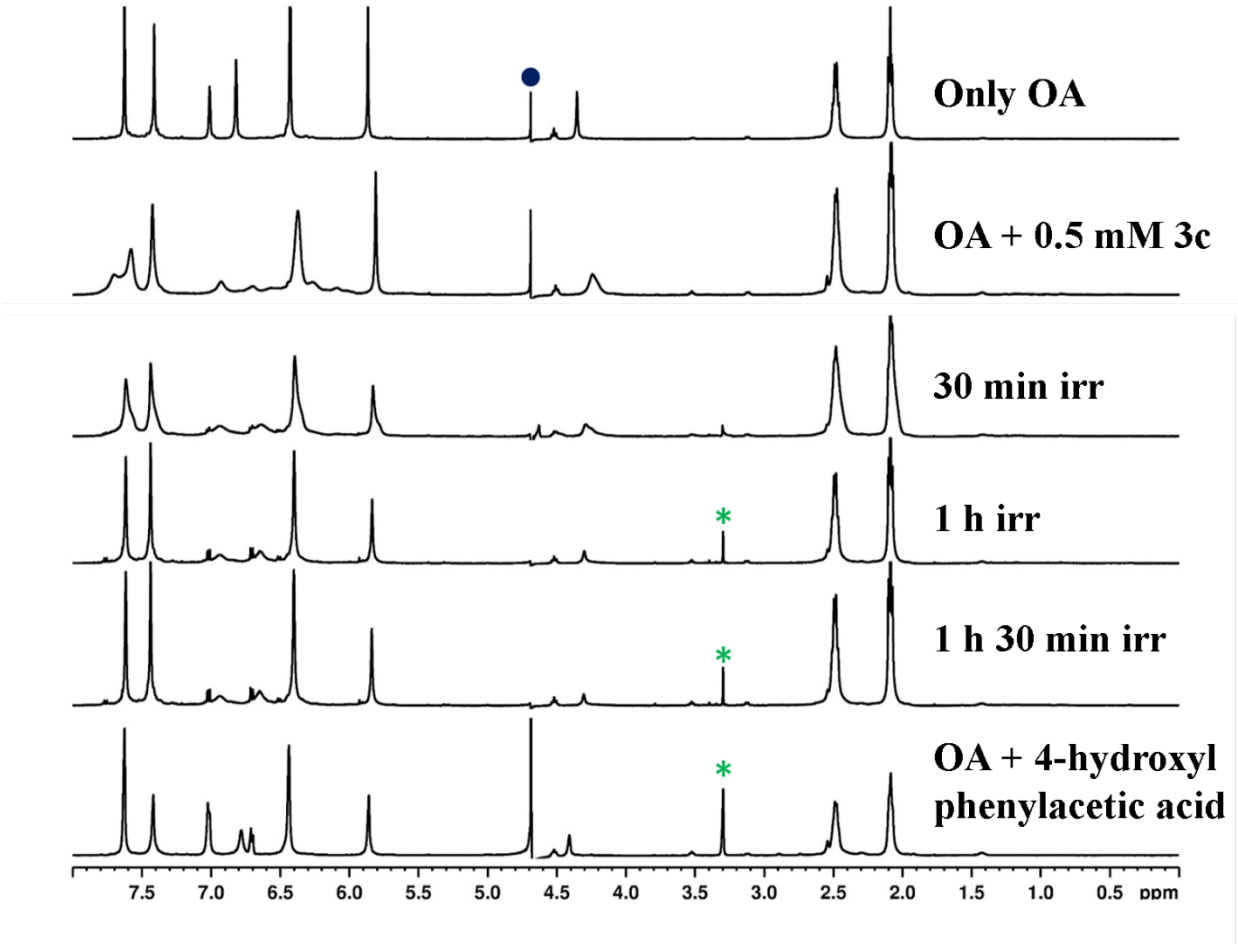


Figure S14. ^{1}H NMR spectra of **3c**@$(OA)_2$ in borate buffer solution(before and after irradiation). The "*" indicates the aliphatic proton peak of 4-hydroxyphenylacetic acid and "●" represents the residual solvent peak for D_2O. The reaction is much more efficient vis-à-vis **3f** (*p*-methoxyphenol release) (1.5:48 or ~1:32 more efficient) With respect to the releases of carboxylate, the phenols are slower, even the ***p*-CF$_3$**phenol.

1-(4-hydroxyphenyl)-2-(4-methoxyphenoxy)ethan-1-one (3f). pHP *p*-methoxyphenyl ether) in Octa Acid.

^{1}H NMR titration experiment: A 1 mM solution of OA in borate buffer (pH = 8.7) was prepared in a Pyrex NMR tube after which a solution of 2.5 μL of a 60 mM solution of **3f** in DMSO-d_6 was added incrementally. The ^{1}H NMR spectrum was recorded after each addition of the **3f** solution. The upfield shift of the aliphatic proton peaks of the -OMe group of **3f** indicating that the guest molecule was forming a complex with OA. This observation was accompanied by the disappearance of the guest OMe peak at -0.8 ppm. Further increase of **3f** concentration indicated that the excess guests did not enter the complex except by exchange with the fully complexed guest (the NMR titration experiment suggests that **3f** forms a 2:1 complex with OA (**3f**@$(OA)_2$). (See Figure S17 ans S18 for **3f** irradiations).

UV-light irradiation experiment (monitored by ^{1}H NMR): A 1 mM solution of OA in borate buffer (pH = 8.7) was prepared in a Pyrex NMR tube after which a solution of 5 μL of a 60 mM solution of **3f** in DMSO-d_6 was added. The ^{1}H NMR spectra were recorded before and after the addition of **3f** to OA to form 1:2 complex **3f**@$(OA)_2$. The solution was then irradiated for 1 h using a 450 W medium pressure mercury lamp with Pyrex jacket. The ^{1}H NMR spectra showed a new peak at 3.3 ppm assigned to the methylene group of 4-hydroxyphenylacetic acid, the Favorskii rearrangement product. In addition, ^{1}H NMR absorptions were assigned to *p*-methoxyphenol (**2f**) and 2', 4-dihydroxyacetophenone (**6**) were observed. The photoreaction was also monitored by LC UV-vis. The phenol yield then decreases reflecting the instabilty of the phenol to the photolysis conditions. Examination of the photorelease of phenols for the corresponding ethers **3c** and **3f** were done.

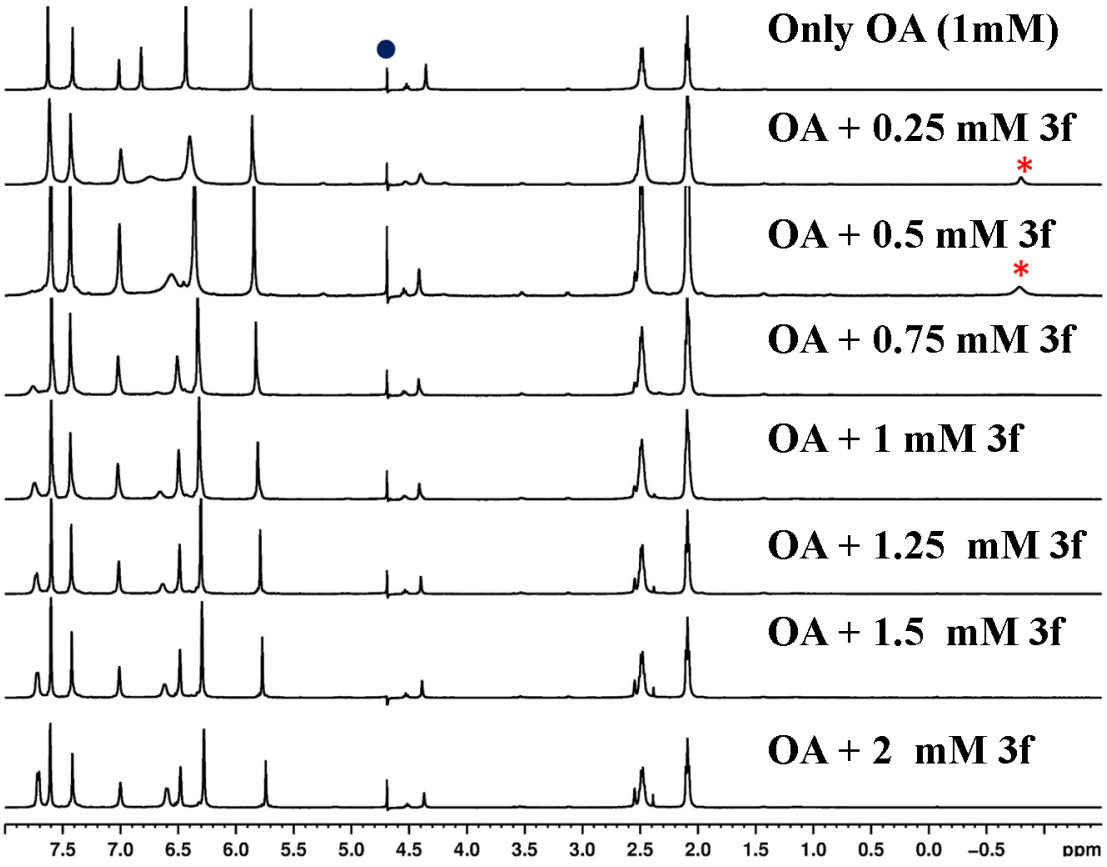


Figure S15. ^{1}H NMR titration spectra of **3f**@OA in borate buffer solution. "*" indicates the –OMe proton peaks of **3f** are inside the OA cavity. The "●" represents the residual solvent peak for D_2O. A 2:1 OA:**3f** complex formed.

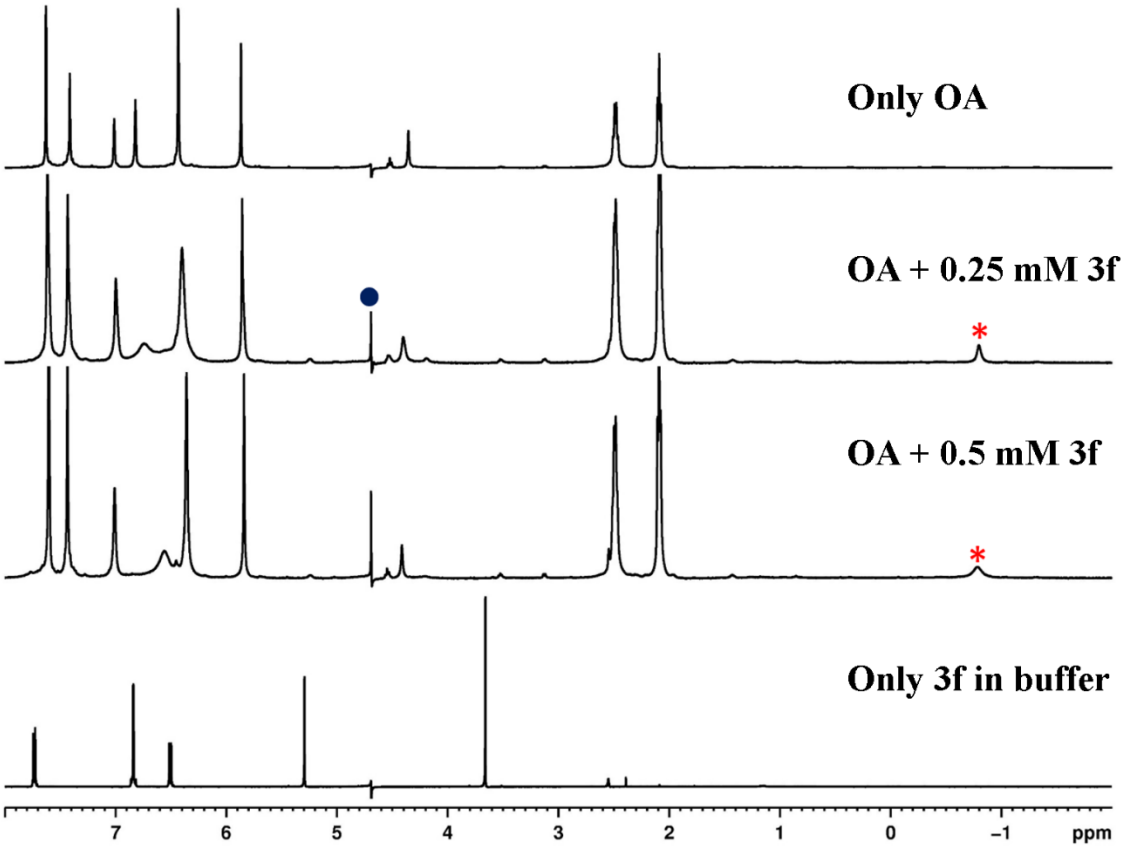


Figure S16. ^{1}H NMR titration spectra of **3f**@OA in borate buffer solution. "*" indicates the –OMe proton peaks of **3f** are initially inside OA cavity. The "●" represents the residual solvent peak for D_2O. [OA] = 1 mM.

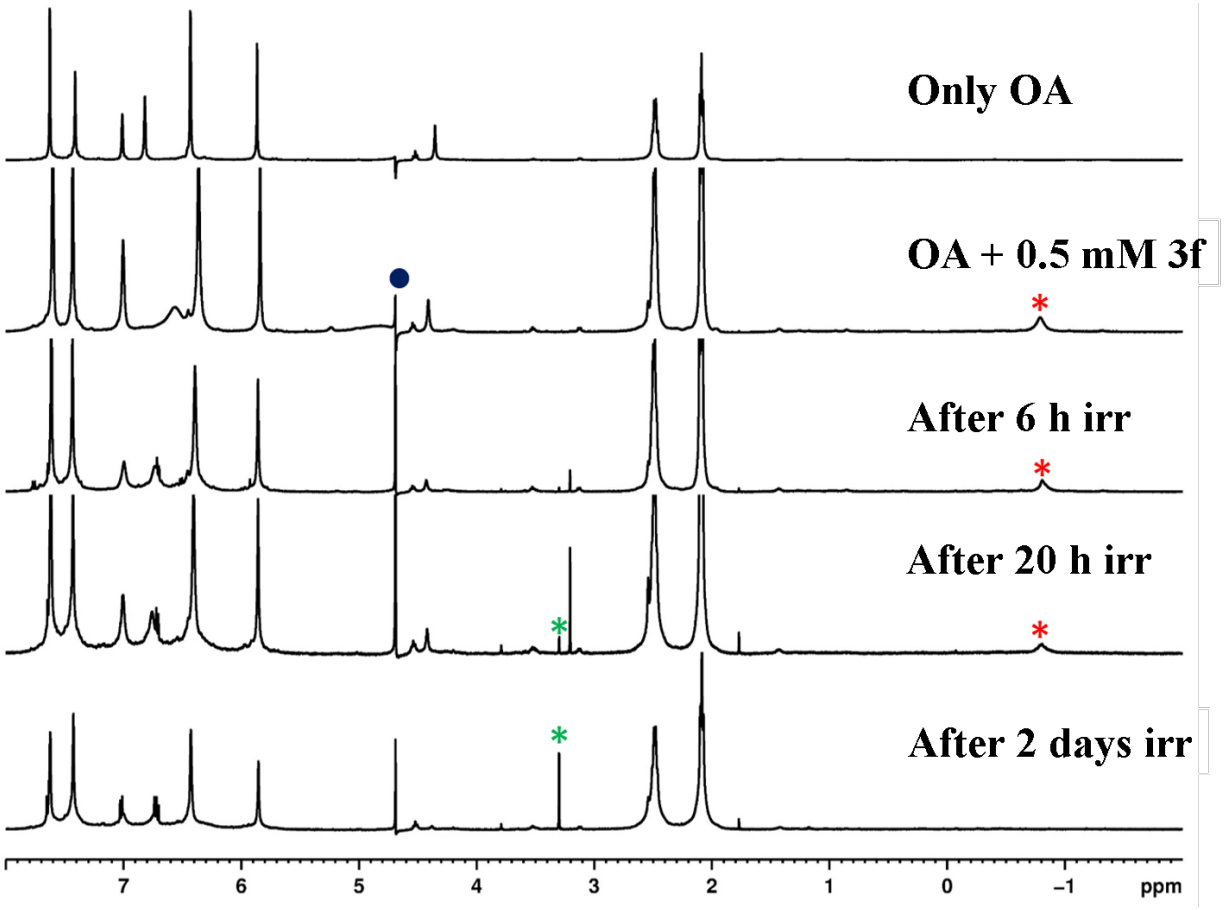


Figure S17. ^{1}H NMR spectra of **3f**@$(OA)_2$ in borate buffer solution (before and after irradiation). The "*" and "*" indicate the aliphatic proton peaks of **3f** are inside the OA cavity and 4-hydroxyphenylacetic acid, respectively **(4)**, respectively**.** The "●" represents the residual solvent peak for D_2O. [OA] = 1 mM.

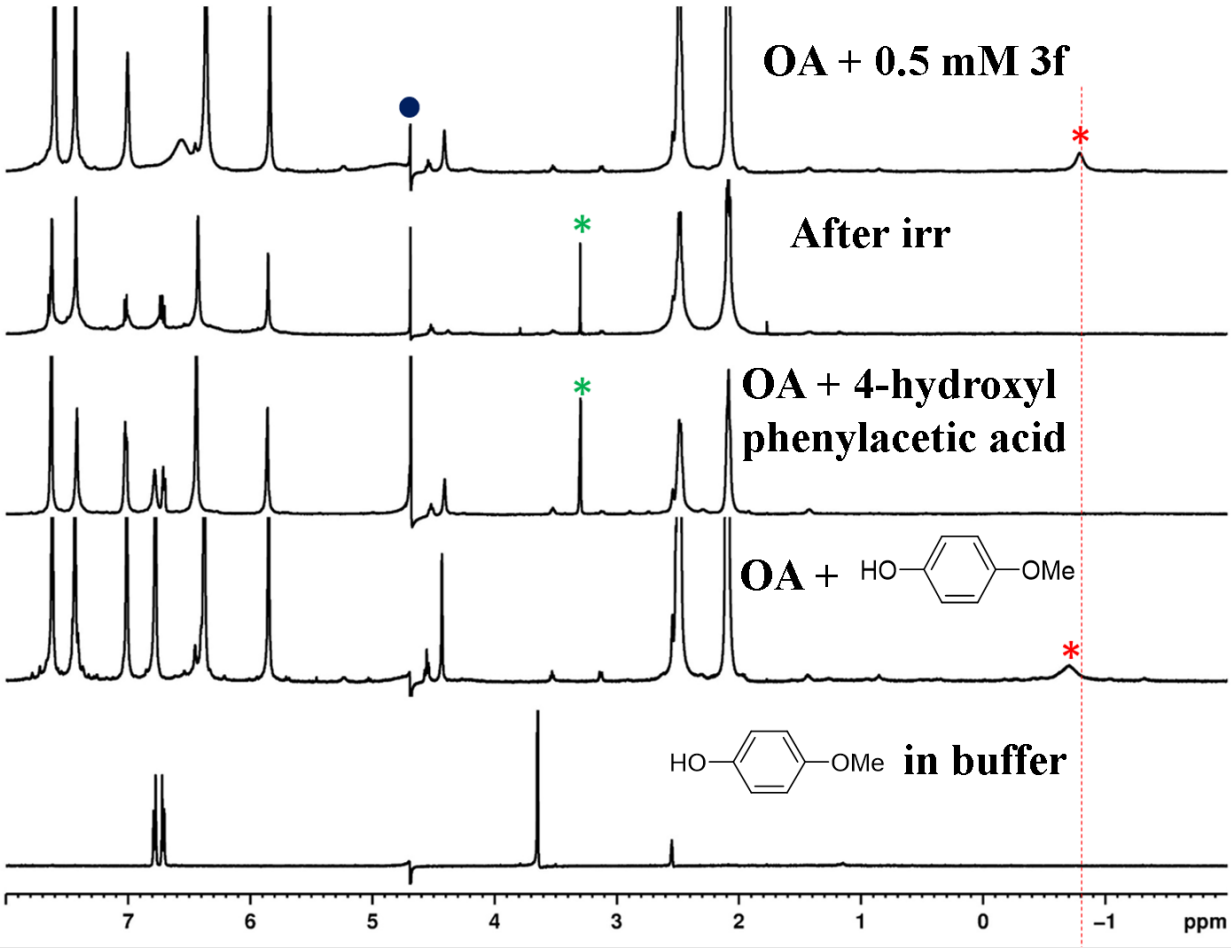


Figure S18. ^{1}H NMR spectra of **3f**@$(OA)_2$ in borate buffer solution (before and after irradiation). The "*" and "*" indicate the aliphatic proton peaks of **3f** are inside the OA cavity and 4-hydroxyphenylacetic acid **(4)**, respectively. "●" represents the residual solvent peak for D_2O, [OA] = 1 mM.

About 5 mM solution of Octa Acid (OA) in borate buffer (pH = 8.7) was prepared in an NMR tube. To this solution, 25 μL of a 60 mM solution of **3f** in DMSO-d_6 was added and the 2D-NOESY spectrum recorded. The correlation peak corresponding to the methyl protons of **3f** and 'g' protons of OA indicate the complex formation. This also suggests that the guest molecule methyl protons are closer to the 'g' proton of OA.

7. LC-DAD-MS and UHPLC-HR-MSn for pHP phenyl ethers 3c and 3f.

7.1 Sample preparation and irradiation conditions.

Host-guest complexes **3c**@OA_2 and **3f**@OA_2 were prepared in borate buffer ($Na_2B_4O_7$, 10 mM, pH = 8.7) using 100 μM of guest and 200 μM of OA. Air equilibrated and N_2 purged solutions (gas bubbling for 5 min) were irradiated for different times and the decrease of trigger and formation of products followed by LC-DAD-MS. The irradiations were performed using a high-pressure xenon lamp in conjunction with a water filter to prevent heating of the sample solution and a Pyrex filter to remove UV radiation below 300 nm.

7.2 Instrumentation and analysis conditions.

The LC-DAD-MS traces were obtained using an Agilent Technologies 1200 Series LC, equipped with a diode array detector, coupled to a Bruker Daltonics HCT *ultra* mass spectrometer. The MS analyses were performed using the following experimental conditions: ionization mode, negative polarity; capillary voltage, 4.0 kV; capillary exit voltage, -300 V; skimmer voltage, -15 V; drying gas, 320 ºC at 8 L min^{-1}; nebulizer gas pressure, 45 psi.

Depending on the sample and trigger, different columns and mobile phase gradient conditions were used. For analytical separation of OA, triggers and products, a mobile phase comprising water (A) and CH_3CN (B), both with 0.1 % of formic acid, and ethyl acetate (C) was used. The gradient started with 52 % of A, 38 % of B and 10 % of C. The mobile phase composition was changed to 2 % of A, 73 % of B and 25 % of C in 5 min and kept at this composition for an additional 7 min. Finally, the system was allowed to return to the initial mobile phase composition (52 % of A, 38 % of B and 10 % of C) in 1 min and then stabilized for additional 5 min before the next run.

When better separation of photoproducts was necessary, as was the case for products of compound **3c**, a gradient with A and B, both with 0.1 % of formic acid was used, followed by a cleaning step to remove OA, using a mixture of A, B and C. In this case the gradient started with 85 % of A and 15 % of B. The mobile phase composition was changed to 10 % of A, 90 % of B in 5 min and then changed to 100 % of B in additional 6 min. The compositions were kept for 3 min in the case of **3f** and for 5 min in the case of **3c**. Then the column was washed with 2 % of A,

73 % of B and 25 % of C for 3 min to remove OA. Finally, the system was allowed to return to the initial mobile phase composition in 1 min and then stabilized for additional 5 min before the next run.

Three different columns were used: a) an Agilent PLRP-S LC column with 15.0 cm length, 2.1 mm internal diameter and 5 μm particle diameter; a b) silica based Grace RP-18, with 10.0 cm length, 2.1 mm internal diameter and 3 μm particle diameter and c) an Agilent RP-18 with 15.0 cm length, 4.6 mm internal diameter and 5 μm particle diameter. The flow was 0.35 mL/min when the former two were used and 1.0 mL/min when the last one was used. Column a) was mainly used for analysis of OA samples, column b) when better separation of products was required and column c) for LC-DAD operation (no MS). All columns were stabilized at 25 °C.

The non-irradiated and irradiated solutions were directly injected into the LC-DAD-MS system without further processing. In the analysis of samples containing borate buffer the mobile phase was sent to waste during the first 2 min to prevent contamination of the ion source with this non-volatile salt.

The UHPLC-HR-MSn studies were performed using a Thermo Scientific *ultimate* 3000 coupled to an Orbitrap Elite mass spectrometer. The HR-MSn analyses were achieved using the following experimental conditions: ionization mode, negative polarity; heater temperature, 300 ºC; capillary temperature, 350 ºC; spray voltage, 3.7 kV; S-Lenses RF level 68%. Fragmentation spectra of triggers and products were obtained by running the system in data dependent mode. A Thermo Accucore RP-18 column with 10.0 cm length, 2.1 mm internal diameter and 2.6 μm particle diameter was utilized. A mobile phase comprising water (A) and CH_3CN (B), both with 0.1 % of formic acid, was used. The gradient started with 100 % of A. The mobile phase composition was changed to 30 % of B in 15 min and then raised to 100% of B in 16 min. This mobile phase composition (100 of % B) was kept for 4 min. Finally, the system was allowed to return to the initial mobile phase composition in 1 min and then stabilized for additional 4 min before the next run.

7.3 Identification and quantification studies on non-irradiated and irradiated samples by LC-DAD-MS.

The identification of products was achieved by injecting authentic standards and comparing the retentions times, m/z values and fragmentation patterns of these standards with the observed formed compounds. Photoproducts of **3c** and **3f** were followed by LC-DAD with UV analysis at 280, 320, 350, 380 nm and by LC-MS/UHPLC-HRMSn under negative polarity. Quantitative analyses of triggers and photo-products were performed using calibrations curves prepared from DAD traces obtained at 280 nm.

Figures S23 and S24 show the fragmentation spectra (CID) of compounds **3c** and **3f** and of the correspondent observed isomers. Figures S25 and S26 show the transformation of compounds **3c** and **3f** and correspondent products yields OA.

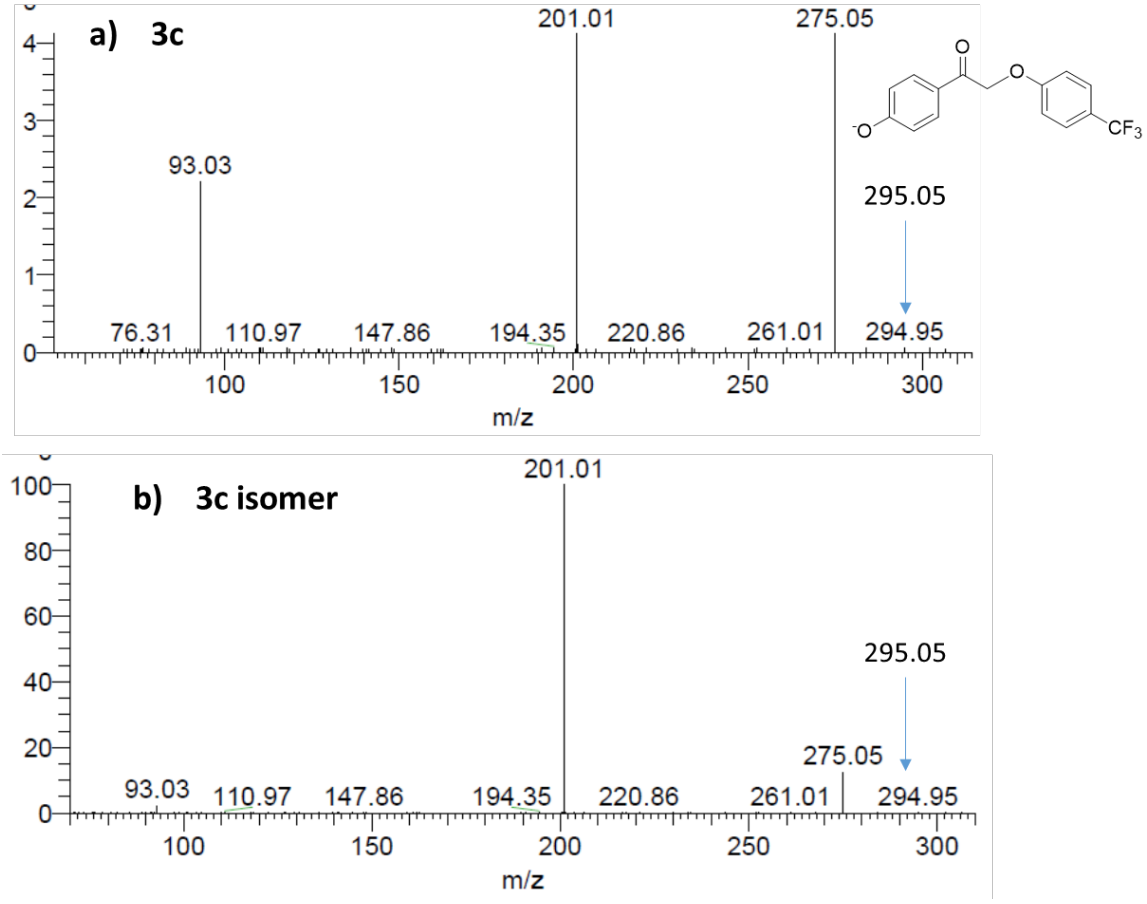


Figure S19. Fragmentation (CID) of compound **3c** (a), and of the correspondent isomer (b). The arrow indicates the fragmented peak.

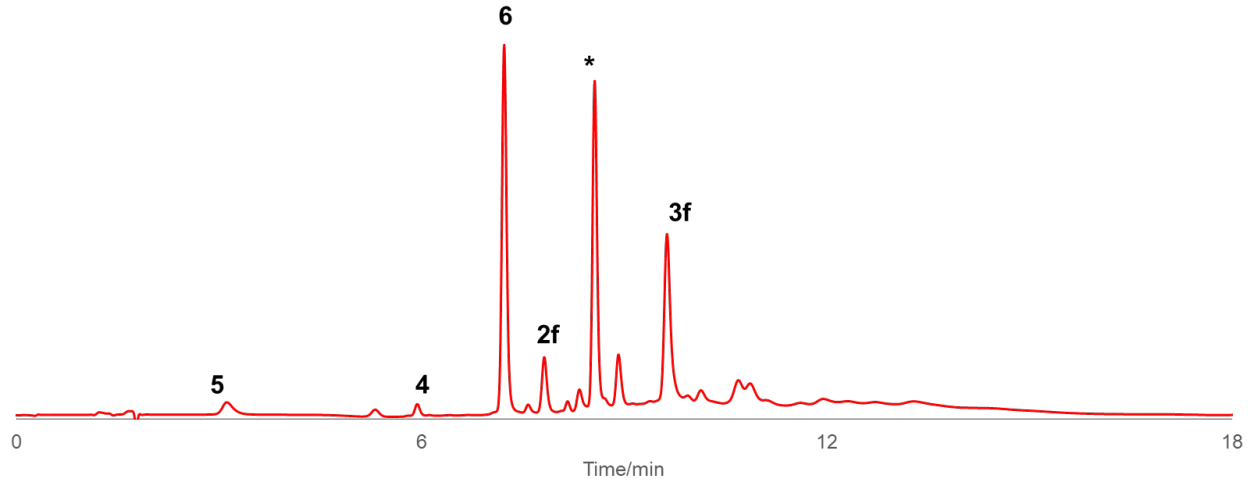


Figure S20. LC-DAD profile (280 nm) from irradiated **3f**@$(OA)_2$ complexes at $\lambda > 300$ nm after N_2 purging. Solutions of complexes were prepared in aqueous borate buffer (pH 8.7) at 2:1 stoichiometry (200 μM OA:100 μM of **3f**). Oxygen removal was achieved by purging with N_2 for 5 min. The prominent peak at 8.59 min, marked with an asterisks, and the smaller adjacent peak are isomeric with **3f**. (See Fig S23 in SI).

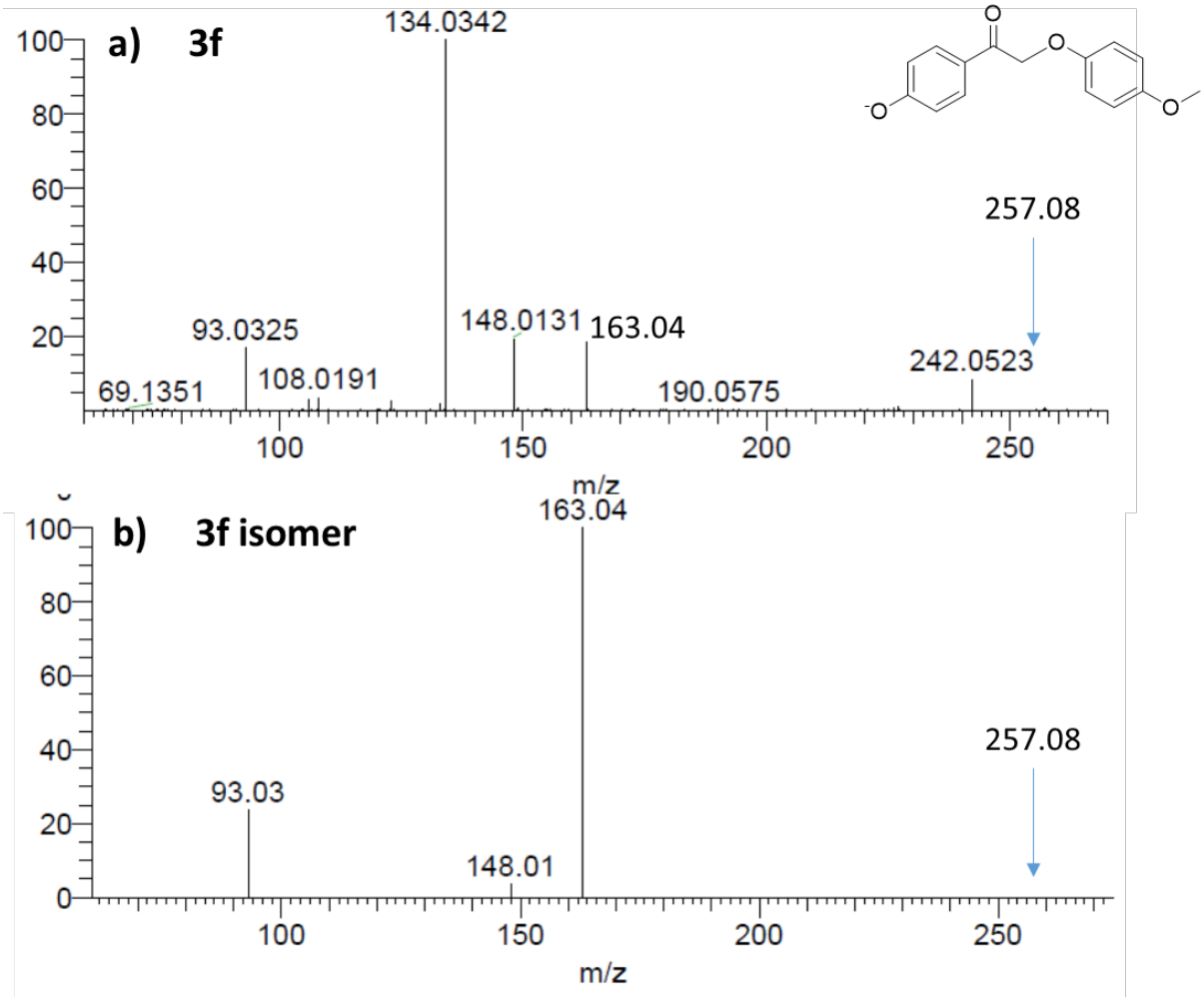


Figure S21. Fragmentation (CID) of compound **3c** (a), and of the correspondent isomer (b).). The arrow indicates the fragmented peak.

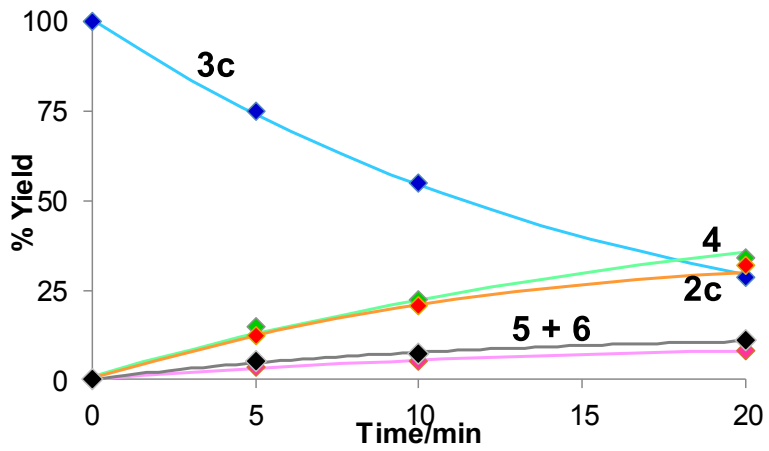


Figure S22. Reaction progress curves for the photolysis (λ > 300 nm) of **3c** encapsulated in OA (**3c**@$(OA)_2$). Disappearance of **3c** (blue), appearance of 4-methoxyphenol, **2c** (red), along with *p*-hydroxyphenylacetic acid, **4** (green), 2,4'-dihydroxyacetophenone, **5** (cyan), and acetophenone, **6** (black), from the cage portion of **3c**. Solutions of complexes were prepared in aqueous borate buffer (pH = 8.7) at 2:1 stoichiometry (50 μM OA:100 μM of **3c**).

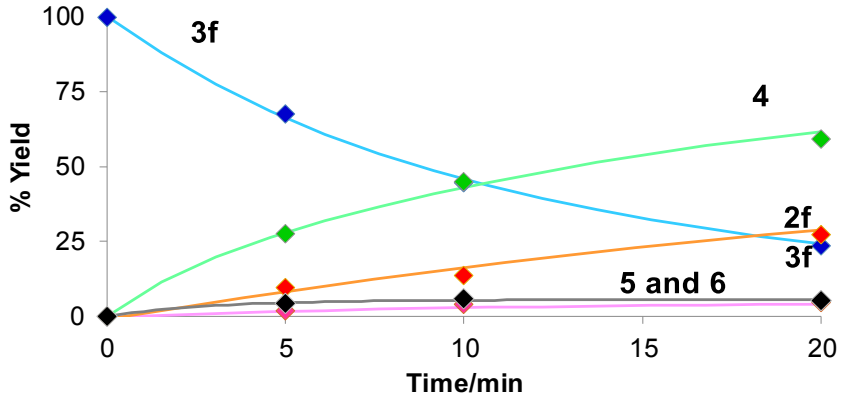


Figure S23. Reaction progress curves for the photolysis (λ > 300 nm) of **3f** encapsulated in OA (**3f**@$(OA)_2$). Disappearance of **3f** (blue), appearance of 4-methoxyphenol (**2f**, red), along with *p*-hydroxyphenylacetic acid (**4**, green), 2,4'-dihydroxyacetophenone (**5**, cyan), and acetophenone (**6**, black) from the cage portion of **3f**. Solutions of complexes were prepared in aqueous borate buffer (pH = 8.7) at 2:1 stoichiometry (50 μM OA:100 μM of **3f**).

8. Effect of oxygen on the Photochemistry of pHP phenyl ethers 3c and 3f in acetonitrile and mixtures acetonitrile-water (20%-80%)

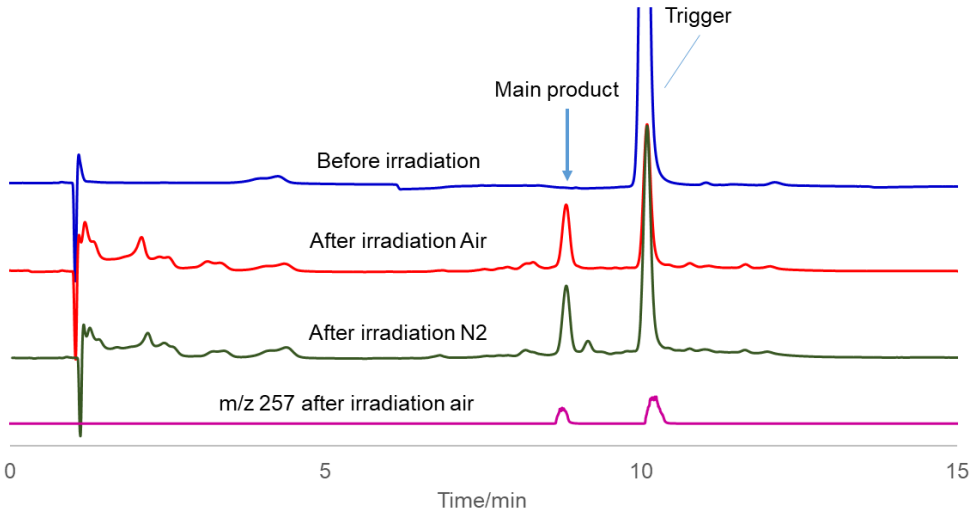


Figure S24. LC-DAD-MS profiles obtained after photolysis of **3f** in dry air equilibrated and N_2 purged CH_3CN.

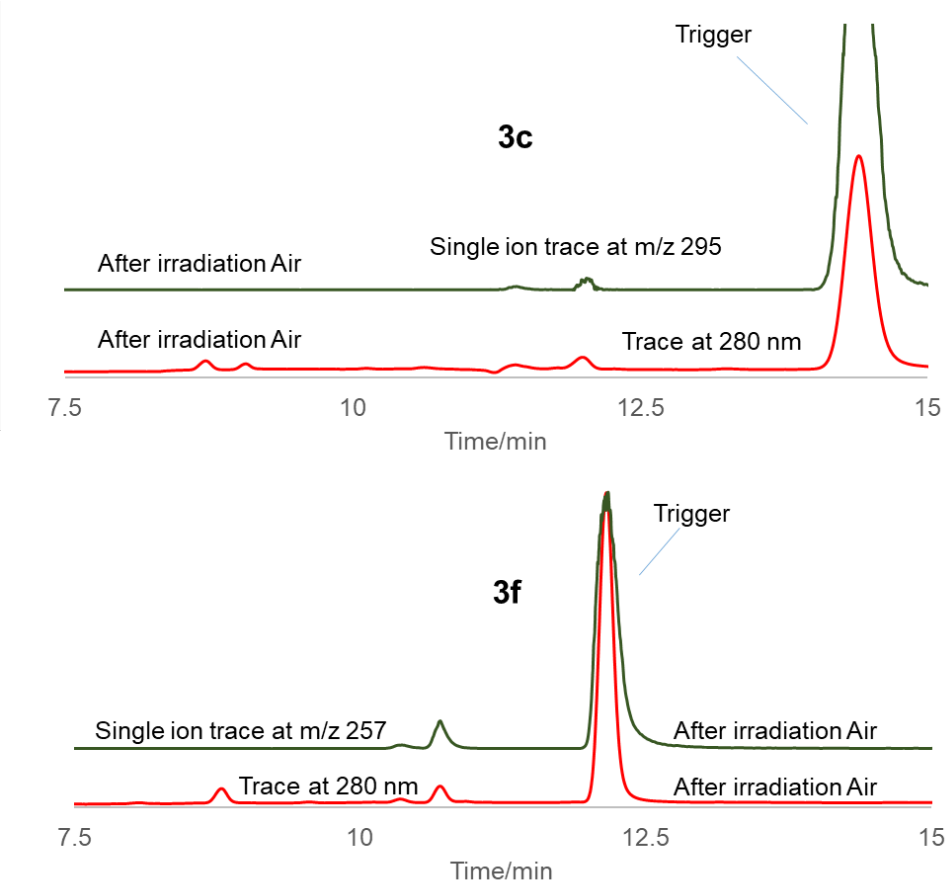


Figure S25. Detail of the LC-DAD-MS profiles obtained after photolysis of **3c** and **3f** in air equilibrated water:CH3CN mixture (80:20) showing the formation of rearrangement products.

9. Calculations

Compound **20** was optimized on the singlet and triplet state using uB3LYP/6-31+G(d,p) on G09 software.[6-10] The singlet energy was corrected for spin contamination using the following equation.

$$E_{singlet} = \frac{2E_{<S_z>=0} - < S^2 > E_{<S_z>=1}}{2 - < S^2 >}$$

Where E_{singlet} is the spin-corrected singlet energy, $E_{<S_z>=0}$ is the unrestricted singlet state energy, $< S^2 >$ is the expectation value of the total-spin operator for the broken-symmetry singlet calculation, and $E_{<S_z>=1}$ is the energy of the triplet state at the singlet geometry.

Compound **20** (optimized singlet state geometry)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.087836	-1.223191	0.059299
2	6	0	-1.460755	-1.226204	0.068643
3	6	0	-2.211401	0.020827	0.004404
4	6	0	-1.440155	1.253116	-0.069627
5	6	0	-0.064930	1.227307	-0.071772
6	1	0	0.480087	-2.146673	0.099487
7	1	0	-2.032911	-2.147076	0.122793
8	1	0	-1.995832	2.183710	-0.125315
9	1	0	0.477696	2.163930	-0.139512
10	6	0	0.640413	-0.004264	-0.004283
11	6	0	2.140063	-0.098150	-0.017113
12	6	0	2.934053	1.091240	0.141959
13	8	0	2.696541	-1.203398	-0.144098
14	1	0	2.519072	2.083097	0.273048
15	1	0	4.011942	0.973393	0.149181
16	8	0	-3.466137	0.034088	0.013005

Singlet Energy: -458.84345547 Hartrees
Spin-corrected Energy: -458.843453521 Hartrees

Compound **20** (optimized triplet state geometry)

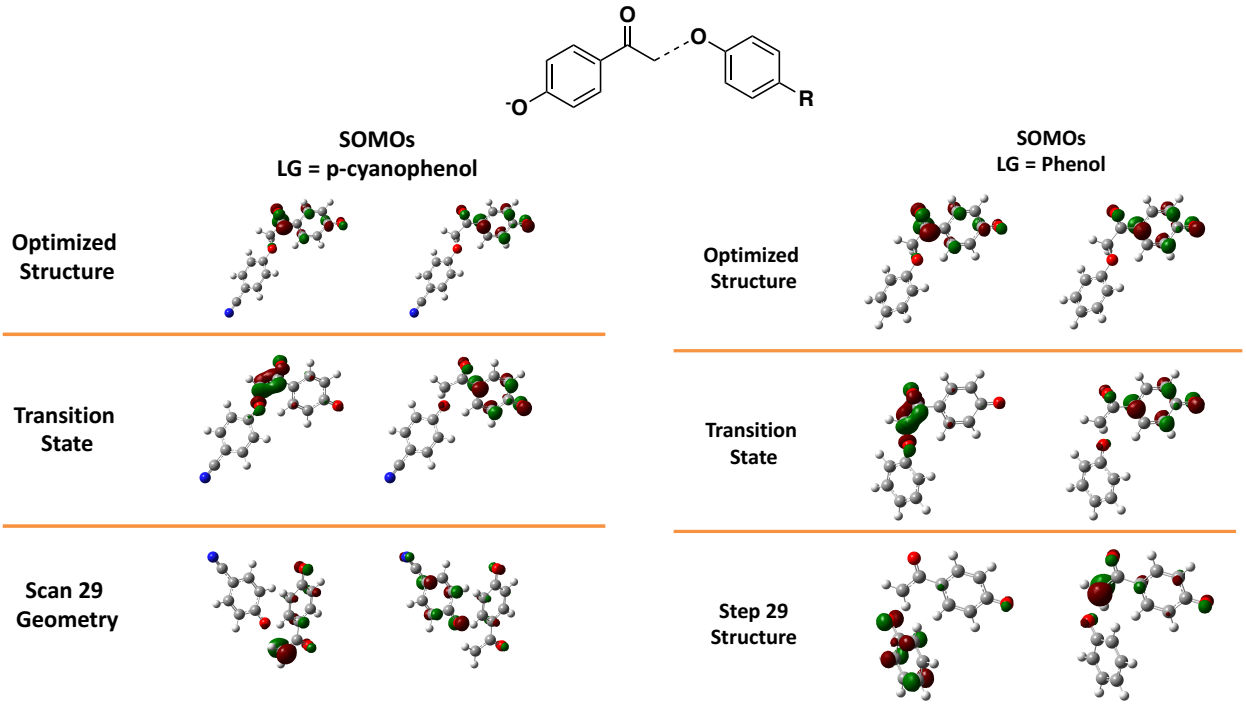
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.091350	-1.224794	0.060773
2	6	0	1.464705	-1.224184	0.072363
3	6	0	2.212238	0.022290	0.006383
4	6	0	1.437993	1.253142	-0.076142
5	6	0	0.062627	1.224767	-0.080604
6	1	0	-0.470972	-2.151232	0.104407
7	1	0	2.037826	-2.144071	0.130360
8	1	0	1.992146	2.184348	-0.137279
9	1	0	-0.484883	2.158461	-0.156161
10	6	0	-0.639284	-0.007330	-0.005257
11	6	0	-2.132181	-0.084714	-0.013834
12	6	0	-2.954559	1.078344	0.150062

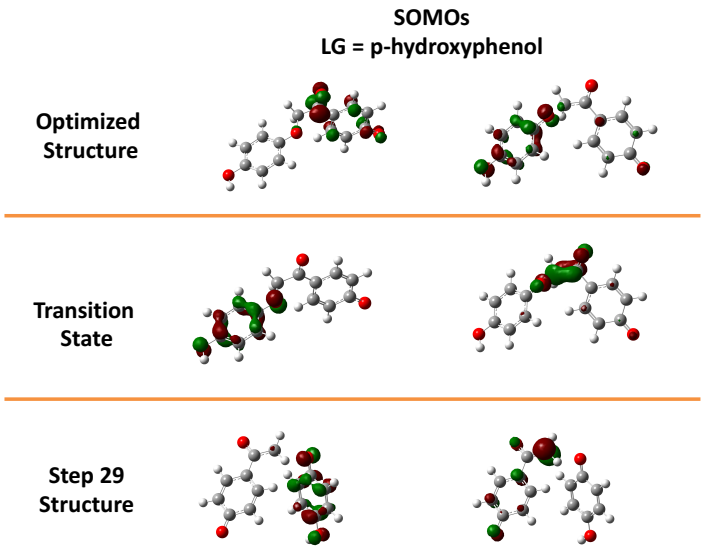
13	8	0	-2.685053	-1.202407	-0.151308
14	1	0	-2.563627	2.065383	0.366211
15	1	0	-4.028209	0.941744	0.093147
16	8	0	3.467601	0.042437	0.015914

Triplet Energy: -458.84387534 Hartrees

B. Relaxed scans of C-O bond

A relaxed scan on the bond length between the deprotonated pHP and phenolic leaving groups (as shown below) was done using B3LYP(6-31+G(d,p)) with SMD water solvent model using Gaussian 09.





p-hydroxyphenol leaving group

Geometry 1:
Energy: -841.11284323 Hartrees

C	4.49765200	-1.31436700	-0.06382400
C	3.14894900	-1.67174200	-0.44695600
C	2.12260500	-0.75371000	-0.44282300
C	2.34891800	0.62102600	-0.07895800
C	3.68443000	0.97890500	0.32777400
C	4.70825000	0.05601800	0.32988100
H	2.96458500	-2.70477400	-0.73139300
H	1.12412500	-1.07727100	-0.71688100
H	3.86237300	2.00610300	0.62452200
H	5.71232800	0.34412500	0.63234900
O	5.44961000	-2.18313800	-0.06373200
C	-0.07292800	1.30156300	-0.57989900
H	-0.58022600	2.22908500	-0.86680800
H	-0.07612600	0.61183000	-1.43405900
O	1.55861600	2.83466500	0.32507500
C	1.30890800	1.63315100	-0.10209200
O	-0.83374200	0.67070400	0.50623900
C	-2.12109100	0.26982200	0.25675300
C	-2.77870700	-0.38857400	1.30833200
C	-2.80527000	0.47557300	-0.95046000

C	-4.09144200	-0.83378300	1.16092900
H	-2.24884000	-0.54761800	2.24249900
C	-4.12308300	0.02501000	-1.09669300
H	-2.33328700	0.98270000	-1.78292800
C	-4.76914900	-0.62881200	-0.04789600
H	-4.65110400	0.18399100	-2.03197200
H	-4.58449900	-1.34126100	1.98660100
O	-6.06642600	-1.04890800	-0.25529000
H	-6.40203300	-1.49396700	0.53533400

Geom 2:
Energy: -841.11202221 Hartrees

C	4.50547900	-1.31738200	-0.05908500
C	3.15755100	-1.67601100	-0.44422900
C	2.13216100	-0.75670000	-0.44601200
C	2.35870400	0.61775000	-0.08782400
C	3.69134300	0.97696700	0.32080900
C	4.71573500	0.05458800	0.32970200
H	2.97334400	-2.71006300	-0.72465600
H	1.13410300	-1.08089200	-0.72080300
H	3.86809300	2.00543000	0.61383700
H	5.71897400	0.34373400	0.63357700
O	5.45601200	-2.18554000	-0.05300400
C	-0.05442300	1.30840400	-0.59973500
H	-0.57002600	2.22767300	-0.89056500
H	-0.07471200	0.59046000	-1.42664800
O	1.56849600	2.83094600	0.32364500
C	1.31798400	1.63341900	-0.11675600
O	-0.85132300	0.68395500	0.53202600
C	-2.13225100	0.27760200	0.27125900
C	-2.80082500	-0.37748600	1.31952600
C	-2.80796300	0.47306500	-0.94353400
C	-4.11123000	-0.82683400	1.16232800
H	-2.28037000	-0.53040500	2.26006500
C	-4.12303200	0.01795400	-1.09988300
H	-2.33068500	0.97668300	-1.77511200
C	-4.77811200	-0.63109400	-0.05381300
H	-4.64211600	0.17011200	-2.04138100
H	-4.61060800	-1.33080100	1.98648800
O	-6.07287400	-1.05581000	-0.27146400
H	-6.41522100	-1.49578700	0.51905600

Geom 3:
Energy: -841.11025175 Hartrees

C	4.50280600	-1.32788000	-0.05856200
C	3.15349800	-1.68133600	-0.44449500
C	2.13335400	-0.75602200	-0.44967000
C	2.36702100	0.61623200	-0.09539100
C	3.69863000	0.97064500	0.31324900
C	4.71961300	0.04444300	0.32644800
H	2.96456000	-2.71517300	-0.72211900
H	1.13388500	-1.07570800	-0.72452000
H	3.87892500	1.99933100	0.60332400
H	5.72377100	0.32979500	0.63041900
O	5.44785300	-2.19930900	-0.04908300
C	-0.03451100	1.32821900	-0.61374900
H	-0.55773100	2.24251900	-0.90007100
H	-0.07537500	0.58915800	-1.41817000
O	1.58710600	2.83144000	0.32908000
C	1.32940600	1.64070700	-0.12732400
O	-0.86755400	0.70457400	0.55984600
C	-2.14013300	0.28908200	0.28789800
C	-2.81437100	-0.37768400	1.32681900
C	-2.81144000	0.48543100	-0.93052000
C	-4.12105800	-0.83431800	1.15799300
H	-2.30036800	-0.53334900	2.27053800
C	-4.12217200	0.02235700	-1.09897200
H	-2.33285300	0.99749900	-1.75622000
C	-4.78095200	-0.63637100	-0.06135300
H	-4.63538500	0.17650300	-2.04345600
H	-4.62274400	-1.34619700	1.97600400
O	-6.07208300	-1.06826000	-0.29058000
H	-6.41740600	-1.51296600	0.49594400

Geom 4:
Energy: -841.10806812 Hartrees

C	4.48738700	-1.34770600	-0.06349900
C	3.13324900	-1.68918000	-0.44432400
C	2.12354600	-0.75229500	-0.44949700

C	2.37345000	0.61630200	-0.10090300
C	3.70730500	0.95941200	0.30147600
C	4.71999200	0.02418600	0.31559400
H	2.93295300	-2.72191300	-0.71757600
H	1.11978300	-1.06187900	-0.72015500
H	3.89769800	1.98769300	0.58657500
H	5.72786200	0.30057600	0.61498400
O	5.42208500	-2.22714100	-0.05366900
C	-0.01286800	1.36307400	-0.62069800
H	-0.54102000	2.27608500	-0.89600600
H	-0.07854100	0.60804800	-1.40597400
O	1.61640300	2.83639600	0.34169800
C	1.34365000	1.65564300	-0.13221800
O	-0.88371800	0.73794900	0.59190700
C	-2.14491500	0.30729200	0.30783400
C	-2.81773000	-0.38957500	1.32962800
C	-2.81646900	0.51659300	-0.90986900
C	-4.11838600	-0.85861400	1.14644600
H	-2.30667900	-0.55772000	2.27291200
C	-4.12018300	0.03996100	-1.09346300
H	-2.34199700	1.05163700	-1.72341700
C	-4.77571600	-0.64605400	-0.07155700
H	-4.63112800	0.20565800	-2.03733200
H	-4.61707800	-1.39220100	1.95249500
O	-6.06115800	-1.08959500	-0.31480700
H	-6.40460500	-1.55108300	0.46278200

Geom 5:
Energy: -841.10590293 Hartrees

C	4.43093700	-1.39531400	-0.08241500
C	3.06395700	-1.70242400	-0.44805300
C	2.08059400	-0.73779800	-0.44490900
C	2.37181600	0.62191600	-0.10296200
C	3.71565700	0.93185100	0.28378800
C	4.70446600	-0.02845900	0.29044700
H	2.83353900	-2.73007500	-0.71616600
H	1.06571100	-1.01997900	-0.70369900
H	3.93494500	1.95584600	0.56365500
H	5.72247300	0.22164200	0.57787200
O	5.34084300	-2.29690200	-0.08040200
C	0.01190900	1.44102100	-0.61185600
H	-0.51076400	2.36205700	-0.86418500

H	-0.09288700	0.67950700	-1.38455600
O	1.67461000	2.85642400	0.36594400
C	1.36607700	1.69264600	-0.12620700
O	-0.89846100	0.81374800	0.63781500
C	-2.13926700	0.34853800	0.33761700
C	-2.78344200	-0.43351500	1.31727600
C	-2.82890200	0.60510200	-0.86269700
C	-4.07001800	-0.93302300	1.11317700
H	-2.26132400	-0.64156700	2.24656200
C	-4.11635100	0.09556000	-1.06920300
H	-2.37900600	1.20665800	-1.64339400
C	-4.74229300	-0.67121200	-0.08664500
H	-4.63893800	0.29971700	-1.99919200
H	-4.54553300	-1.52993500	1.88840500
O	-6.01469400	-1.14257500	-0.34976700
H	-6.33742600	-1.65877300	0.40183200

Geom 6:
Energy: -841.10424111 Hartrees

C	4.15325700	-1.57130200	-0.12480800
C	2.74181400	-1.74717400	-0.39848200
C	1.86614100	-0.68395400	-0.37866200
C	2.31753200	0.64588900	-0.11063300
C	3.70442100	0.82886800	0.18461900
C	4.58922200	-0.22738100	0.17473300
H	2.39173100	-2.75406400	-0.60888400
H	0.81261500	-0.86388300	-0.56314000
H	4.04374500	1.83355900	0.40922000
H	5.64327400	-0.07607100	0.39189800
O	4.96324000	-2.55992500	-0.13676800
C	0.04645600	1.69516100	-0.56275700
H	-0.41356000	2.65567000	-0.78124100
H	-0.16797300	0.93896500	-1.31634600
O	1.86265800	2.94229700	0.35865100
C	1.42059400	1.81771200	-0.11821400
O	-0.91635400	1.12941300	0.74345800
C	-2.08338500	0.52433700	0.41497700
C	-2.56175300	-0.50040400	1.25658200
C	-2.86510400	0.87552200	-0.70477100
C	-3.77842700	-1.13723700	1.00350600
H	-1.96891800	-0.78700000	2.12036800
C	-4.07535700	0.22581400	-0.96767600

H	-2.53954500	1.66631100	-1.37180500
C	-4.53821500	-0.77866300	-0.11567800
H	-4.66849300	0.50466200	-1.83390200
H	-4.12838200	-1.91916700	1.67403400
O	-5.74396600	-1.37996700	-0.42426300
H	-5.95229300	-2.05665200	0.23475100

Geom 7:
Energy: -841.1032706 Hartrees

C	4.04489000	-1.62305800	-0.13275200
C	2.61933900	-1.75700100	-0.35610600
C	1.78364400	-0.66207700	-0.33977200
C	2.29134600	0.65461500	-0.12438000
C	3.69041300	0.79871900	0.12010500
C	4.53841300	-0.28677600	0.11281400
H	2.22836700	-2.75640900	-0.52549200
H	0.71856800	-0.80670100	-0.48475500
H	4.06966400	1.79749600	0.30459200
H	5.60366800	-0.16758700	0.29090900
O	4.81805700	-2.63750800	-0.14179100
C	0.06054200	1.78423600	-0.56345400
H	-0.38481500	2.75220700	-0.77331000
H	-0.20540200	1.01537000	-1.28538100
O	1.92204500	2.96574200	0.33799700
C	1.43205500	1.86186500	-0.13332500
O	-0.94231900	1.26033300	0.79574400
C	-2.06806100	0.59301700	0.46066900
C	-2.40513500	-0.58464400	1.15974400
C	-2.95094200	1.02998600	-0.55105800
C	-3.58361800	-1.28191100	0.88203200
H	-1.73385200	-0.94180700	1.93551800
C	-4.12044100	0.32319000	-0.84316600
H	-2.72680000	1.93615600	-1.10508300
C	-4.44355200	-0.83159000	-0.12559900
H	-4.79221600	0.67056300	-1.62304300
H	-3.82570200	-2.18131500	1.44424200
O	-5.61729600	-1.48447900	-0.45252400
H	-5.72873600	-2.26211100	0.11189500

Geom 8:

Energy: -841.10282543 Hartrees

C	3.97335900	-1.65378600	-0.12559500
C	2.53815200	-1.76180100	-0.29974500
C	1.72957600	-0.64673500	-0.29177700
C	2.27536500	0.66094400	-0.13347700
C	3.68221700	0.78167400	0.06427000
C	4.50577400	-0.32198500	0.06393900
H	2.11996300	-2.75655000	-0.42507100
H	0.65693900	-0.76792100	-0.39755000
H	4.08829900	1.77685300	0.20752700
H	5.57856900	-0.22347700	0.20457900
O	4.72212900	-2.68356600	-0.12853800
C	0.07610200	1.83750200	-0.58367400
H	-0.36831900	2.80543200	-0.79099900
H	-0.22074800	1.05155500	-1.27261300
O	1.95859500	2.98209600	0.30873500
C	1.43987000	1.89132400	-0.15329200
O	-0.96749200	1.34905100	0.82320300
C	-2.06216400	0.64028400	0.48909200
C	-2.29269800	-0.62318000	1.07571600
C	-3.02352000	1.11530600	-0.43277800
C	-3.44109600	-1.36370900	0.78255500
H	-1.56221700	-1.01239800	1.77953800
C	-4.16294500	0.36919600	-0.74151100
H	-2.87746800	2.08503900	-0.89953900
C	-4.37828300	-0.87062200	-0.13174800
H	-4.89500200	0.74779000	-1.44942700
H	-3.60065700	-2.32821600	1.26007100
O	-5.52767600	-1.56090100	-0.46879200
H	-5.56205600	-2.39800600	0.01477400

Geom 9:
Energy: -841.10292376 Hartrees

C	3.93066600	-1.67570800	-0.11941500
C	2.49034500	-1.76463400	-0.26436700
C	1.70070000	-0.63623700	-0.26242700
C	2.27135600	0.66299300	-0.13758600
C	3.68186400	0.76677800	0.03187000
C	4.48862200	-0.34874500	0.03581300
H	2.05478700	-2.75479800	-0.36324700

H	0.62425400	-0.73980100	-0.34593800
H	4.10531300	1.75806400	0.15041700
H	5.56534200	-0.26555700	0.15362100
O	4.66250100	-2.71529500	-0.11828600
C	0.09883200	1.87364900	-0.60683800
H	-0.34879800	2.84134600	-0.80380700
H	-0.21784800	1.07749100	-1.27314900
O	1.98648800	2.98731700	0.30186300
C	1.45184400	1.90948600	-0.16283100
O	-0.98762200	1.39948800	0.83750000
C	-2.06129600	0.66880600	0.50340000
C	-2.24853600	-0.62249400	1.04814400
C	-3.05242200	1.14370000	-0.38966300
C	-3.37933500	-1.38601800	0.74574800
H	-1.49783600	-1.01411700	1.72916100
C	-4.17486200	0.37641500	-0.70655700
H	-2.93891100	2.13228000	-0.82558700
C	-4.34493500	-0.88958800	-0.13666700
H	-4.92882200	0.75693500	-1.39018500
H	-3.50391400	-2.37062900	1.19176000
O	-5.47964000	-1.60131700	-0.48019600
H	-5.48443100	-2.45317400	-0.02184000

Geom 10:
Energy: -841.10339413 Hartrees

C	3.86687900	-1.71078600	-0.11624700
C	2.42242800	-1.76805800	-0.23905100
C	1.66047400	-0.62095400	-0.24156200
C	2.26438400	0.66415200	-0.14040200
C	3.67823000	0.73848400	0.00660900
C	4.45910700	-0.39487200	0.01285800
H	1.96257100	-2.74888700	-0.31818600
H	0.58069500	-0.69828700	-0.30886800
H	4.12626000	1.72107200	0.10635300
H	5.53914700	-0.33608500	0.11280700
O	4.57381700	-2.76565900	-0.11235300
C	0.13038700	1.92673200	-0.63113700
H	-0.31210600	2.89923000	-0.81140600
H	-0.20888400	1.12922700	-1.28305200
O	2.02630700	2.99018700	0.31030900
C	1.47136900	1.93185500	-0.16619300
O	-1.00559800	1.46382400	0.84396600
C	-2.05496400	0.70717600	0.51111000

C	-2.21683600	-0.58941700	1.05676500
C	-3.05445800	1.15432000	-0.39004100
C	-3.32730200	-1.37994000	0.74930300
H	-1.46203700	-0.96219200	1.74390600
C	-4.15673100	0.36060100	-0.71075000
H	-2.96012500	2.14399100	-0.82844200
C	-4.30003100	-0.90824800	-0.13900000
H	-4.91587000	0.72149300	-1.39939500
H	-3.43114600	-2.36651800	1.19640400
O	-5.41599900	-1.64738200	-0.48681700
H	-5.40432800	-2.49707100	-0.02451600

Geom 11:
Energy: -841.10413741 Hartrees

C	3.77290700	-1.75984200	-0.11344700
C	2.32623200	-1.77077200	-0.22649100
C	1.60313200	-0.59898500	-0.23470300
C	2.25039200	0.66492000	-0.14540500
C	3.66629000	0.69515500	-0.01004300
C	4.40992400	-0.46260200	-0.00072800
H	1.83382700	-2.73649200	-0.29370100
H	0.52099500	-0.64013500	-0.29492700
H	4.14699300	1.66331200	0.07853400
H	5.49206400	-0.43894800	0.08991100
O	4.44458800	-2.83614100	-0.10457900
C	0.17016500	1.99954700	-0.65939900
H	-0.25737900	2.98166900	-0.81902800
H	-0.19680500	1.20857600	-1.30285700
O	2.07912200	2.99172100	0.32525100
C	1.49733100	1.95987300	-0.16897000
O	-1.02183100	1.55039800	0.84141300
C	-2.04117700	0.75986700	0.51394100
C	-2.17742800	-0.53228200	1.08215900
C	-3.04218300	1.16005700	-0.41047000
C	-3.26090900	-1.35859200	0.77438100
H	-1.42349600	-0.87149200	1.78744800
C	-4.11748400	0.33064700	-0.73019700
H	-2.96718500	2.14288000	-0.86784700
C	-4.23386200	-0.93112200	-0.13608900
H	-4.87641300	0.65683500	-1.43624600
H	-3.34436400	-2.33903000	1.23890600
O	-5.32367700	-1.70768900	-0.48460100

H	-5.29383500	-2.54869200	-0.00730200

Geom 12:
Energy: -841.10506675 Hartrees

C	3.72318200	-1.78610500	-0.11079300
C	2.27748200	-1.77039800	-0.23745000
C	1.57657500	-0.58543500	-0.25154600
C	2.24598500	0.66552800	-0.15105100
C	3.66046500	0.67032500	-0.00385000
C	4.38310200	-0.50044500	0.00927000
H	1.76803700	-2.72678500	-0.31014600
H	0.49452900	-0.60652200	-0.32228700
H	4.15773600	1.62951800	0.09120700
H	5.46466400	-0.49669500	0.10898000
O	4.37502900	-2.87367100	-0.09744500
C	0.20381100	2.04148800	-0.69136900
H	-0.22115100	3.02696700	-0.83323700
H	-0.18101600	1.25178500	-1.32459400
O	2.10769100	2.99056000	0.33767000
C	1.51645700	1.97574300	-0.17359000
O	-1.03394900	1.59298300	0.83872000
C	-2.03575100	0.78677200	0.51646400
C	-2.15568900	-0.50639900	1.09158400
C	-3.04228700	1.16524600	-0.41440700
C	-3.22495200	-1.35027500	0.78496500
H	-1.39909800	-0.83027500	1.80121600
C	-4.10361300	0.31847100	-0.73157100
H	-2.97944200	2.14607200	-0.87795500
C	-4.20223300	-0.94220300	-0.13049200
H	-4.86575600	0.62851400	-1.44143900
H	-3.29529100	-2.32946500	1.25426300
O	-5.27879400	-1.73644000	-0.47738000
H	-5.23821900	-2.57445100	0.00449300

Geom 13:
Energy: -841.10615105 Hartrees

C	3.67881500	-1.80923300	-0.10991900
C	2.24007300	-1.76693400	-0.29504500

C	1.55910900	-0.57065000	-0.31564600
C	2.24129500	0.66750200	-0.15977800
C	3.64817000	0.64597700	0.04351100
C	4.35204600	-0.53621000	0.06225400
H	1.71860000	-2.71310100	-0.40616200
H	0.48074700	-0.57486200	-0.43055100
H	4.15576200	1.59507300	0.17811600
H	5.42861000	-0.55116000	0.20579800
O	4.31351100	-2.90670300	-0.09211200
C	0.23904000	2.08028000	-0.73309700
H	-0.18527600	3.06828000	-0.85563400
H	-0.16214900	1.29303500	-1.35778500
O	2.12852300	2.99150700	0.34730300
C	1.53496500	1.99052000	-0.18224000
O	-1.03618000	1.61888100	0.82884100
C	-2.02584500	0.80478000	0.51714200
C	-2.13632100	-0.48728700	1.10414800
C	-3.03774600	1.16648300	-0.41909200
C	-3.19695800	-1.34161500	0.80394500
H	-1.37643400	-0.79836100	1.81583200
C	-4.09093700	0.30922000	-0.72777100
H	-2.98121200	2.14348200	-0.89126400
C	-4.17826000	-0.94819300	-0.11536300
H	-4.85636600	0.60549000	-1.43987200
H	-3.25995000	-2.31784800	1.28022400
O	-5.24669300	-1.75252000	-0.45518600
H	-5.20029100	-2.58717800	0.03224900

Geom 14:
Energy: -841.10998290 Hartrees

C	4.32421500	-1.53918200	-0.01750700
C	3.06475600	-1.63637100	-0.71182300
C	2.17277300	-0.57904900	-0.77454400
C	2.43944800	0.67015500	-0.15640200
C	3.67309200	0.78252100	0.53256800
C	4.57757000	-0.26194200	0.60366400
H	2.82345200	-2.58127200	-1.19440300
H	1.24020700	-0.73044300	-1.31075600
H	3.90178900	1.72856900	1.01556200
H	5.51616700	-0.13894000	1.14076000
O	5.15764600	-2.51493000	0.04544900
C	0.29561600	1.74379900	-0.93637600

H	-0.29288400	2.64737600	-1.03282200
H	0.08146600	0.93247100	-1.61793600
O	1.78901000	2.89219300	0.44381200
C	1.51802600	1.82409800	-0.19604800
O	-1.04741200	0.97826200	0.51217800
C	-2.19204400	0.44863200	0.33612400
C	-2.85102900	-0.25517300	1.41811300
C	-2.88977800	0.51602600	-0.93225600
C	-4.08163400	-0.84209800	1.24409400
H	-2.33744200	-0.30719700	2.37252000
C	-4.11975000	-0.07208700	-1.09563400
H	-2.42173800	1.04829500	-1.75256100
C	-4.72681200	-0.75879600	-0.01433300
H	-4.64762500	-0.02371400	-2.04248500
H	-4.56461700	-1.36979600	2.06191800
O	-5.93092700	-1.31563800	-0.24855700
H	-6.27201100	-1.76765800	0.53929800

Geom 15:
Energy: -841.11243024 Hartrees

C	4.32675700	-1.54633100	-0.01794200
C	3.07843200	-1.62906200	-0.73435500
C	2.19184400	-0.56763800	-0.79689600
C	2.45337500	0.67177400	-0.15666200
C	3.67586300	0.76970900	0.55457300
C	4.57461500	-0.27901400	0.62625800
H	2.84235300	-2.56591000	-1.23482600
H	1.26837100	-0.70716800	-1.35158100
H	3.89950900	1.70803600	1.05463500
H	5.50444200	-0.16803900	1.18084800
O	5.15544900	-2.52532100	0.04453100
C	0.32541300	1.76386600	-0.95422200
H	-0.26667200	2.66613300	-1.03826600
H	0.10074800	0.95053200	-1.62968100
O	1.80827000	2.89223300	0.45194000
C	1.53907100	1.83018100	-0.19691400
O	-1.06356600	0.98090300	0.51551900
C	-2.20628600	0.44993200	0.34069000
C	-2.86509300	-0.25943500	1.41985000
C	-2.90515400	0.52086900	-0.92760700
C	-4.09505800	-0.84711100	1.24319300
H	-2.35183200	-0.31478600	2.37429500

C	-4.13430700	-0.06815000	-1.09364700
H	-2.43626700	1.05668900	-1.74530900
C	-4.74035900	-0.75965300	-0.01486700
H	-4.66218900	-0.01714300	-2.04039100
H	-4.57764500	-1.37874200	2.05874600
O	-5.94405700	-1.31740200	-0.25105500
H	-6.28425500	-1.77252700	0.53535100

Geom 16:
Energy: -841.11461604 Hartrees

C	4.32770400	-1.55516700	-0.02193300
C	3.08688200	-1.62383200	-0.75320100
C	2.20663700	-0.55749900	-0.81365800
C	2.46755500	0.67343500	-0.15642800
C	3.68250400	0.75732300	0.56995100
C	4.57478300	-0.29641400	0.63999900
H	2.85241300	-2.55366100	-1.26723800
H	1.28934000	-0.68554700	-1.38107500
H	3.90480800	1.68887600	1.08306600
H	5.49886800	-0.19699100	1.20616400
O	5.15091000	-2.53809200	0.03808000
C	0.35376800	1.78473200	-0.96443900
H	-0.24028400	2.68658800	-1.03651900
H	0.11692800	0.96977000	-1.63353600
O	1.83153900	2.89328400	0.46155200
C	1.56115900	1.83701600	-0.19491300
O	-1.08152000	0.98636700	0.52698400
C	-2.22141900	0.45287600	0.34963600
C	-2.87660100	-0.27402800	1.41990300
C	-2.92334900	0.53788400	-0.91675000
C	-4.10492200	-0.86342200	1.23686000
H	-2.36188200	-0.34097200	2.37286800
C	-4.15072100	-0.05298800	-1.08916500
H	-2.45627700	1.08622900	-1.72733500
C	-4.75263600	-0.76089300	-0.01878800
H	-4.68029200	0.00871100	-2.03436700
H	-4.58457200	-1.40800300	2.04563000
O	-5.95524600	-1.31948900	-0.26045600
H	-6.29259400	-1.78570400	0.52062100

Geom 17:
Energy: -841.11655503 Hartrees

C	4.36853300	-1.53867800	-0.03585500
C	3.13022800	-1.60967400	-0.77156300
C	2.24203000	-0.54993900	-0.82358100
C	2.49165600	0.67624900	-0.15268400
C	3.70441300	0.76264400	0.57754800
C	4.60462000	-0.28437300	0.63912400
H	2.90469600	-2.53603900	-1.29566900
H	1.32731300	-0.67925600	-1.39477400
H	3.91801500	1.69077100	1.10043600
H	5.52677800	-0.18354300	1.20809400
O	5.19855400	-2.51559500	0.01712500
C	0.37227100	1.77921300	-0.95660600
H	-0.23628800	2.67259700	-1.01049800
H	0.13441800	0.96378800	-1.62467600
O	1.83489500	2.88334300	0.48742700
C	1.57595000	1.83184700	-0.18024100
O	-1.09451600	0.92622800	0.54907800
C	-2.24288500	0.41652000	0.36342300
C	-2.89756400	-0.34949100	1.40703600
C	-2.95786200	0.56861600	-0.88984800
C	-4.13698900	-0.91143600	1.21196900
H	-2.37357200	-0.46762900	2.34996300
C	-4.19602200	0.00478100	-1.07444500
H	-2.49008500	1.14542300	-1.68008500
C	-4.79700600	-0.74138600	-0.02992300
H	-4.73507700	0.11669800	-2.00964900
H	-4.61656100	-1.48522200	2.00060700
O	-6.01144700	-1.26930700	-0.28248900
H	-6.34774900	-1.76428800	0.48100700

Geom 18:
Energy: -841.11827007 Hartrees

C	4.37236100	-1.54601600	-0.04165300
C	3.13956800	-1.60448000	-0.78806400
C	2.25693900	-0.54039800	-0.83709800
C	2.50710400	0.67832500	-0.15231200
C	3.71430900	0.75218300	0.58893000
C	4.60893100	-0.29927300	0.64774100
H	2.91448300	-2.52470500	-1.32296700

H	1.34667500	-0.65968700	-1.41741300
H	3.92756100	1.67430100	1.12245800
H	5.52695700	-0.20854200	1.22494600
O	5.19744800	-2.52656400	0.00817300
C	0.39941300	1.79804100	-0.96233800
H	-0.21114500	2.69064000	-1.00510600
H	0.15104100	0.98175300	-1.62544800
O	1.85771600	2.88403400	0.49909600
C	1.59794800	1.83828900	-0.17649300
O	-1.11248300	0.92620600	0.56395100
C	-2.25909500	0.41620300	0.37371500
C	-2.90896300	-0.37273700	1.40361600
C	-2.97878500	0.59078600	-0.87435200
C	-4.14759700	-0.93395900	1.20089300
H	-2.38207400	-0.50840000	2.34260400
C	-4.21594900	0.02740700	-1.06672400
H	-2.51372200	1.18431600	-1.65385300
C	-4.81177500	-0.74084900	-0.03539300
H	-4.75811300	0.15616600	-1.99798700
H	-4.62351100	-1.52459600	1.97931800
O	-6.02592400	-1.26680300	-0.29486600
H	-6.35866900	-1.77736600	0.45981300

Geom 19:
Energy: -841.11977473 Hartrees

C	4.37845100	-1.55210500	-0.04553200
C	3.15098900	-1.59957200	-0.80183200
C	2.27334400	-0.53166500	-0.84887000
C	2.52357200	0.68048400	-0.15197700
C	3.72546000	0.74340900	0.59928600
C	4.61510300	-0.31193500	0.65623000
H	2.92657700	-2.51447800	-1.34598500
H	1.36730900	-0.64219700	-1.43738600
H	3.93812800	1.66032800	1.14191800
H	5.52917600	-0.22998400	1.24089400
O	5.19908200	-2.53587800	0.00215400
C	0.42756600	1.81525800	-0.96966300
H	-0.18559100	2.70656800	-1.00193800
H	0.17135700	0.99894600	-1.62972300
O	1.87904600	2.88412200	0.51059800
C	1.61999800	1.84409700	-0.17340900
O	-1.12908900	0.92035400	0.57494200
C	-2.27531500	0.41248100	0.38122800

C	-2.92420200	-0.39053900	1.40119400
C	-2.99729500	0.60393200	-0.86336100
C	-4.16357700	-0.94825000	1.19278300
H	-2.39615700	-0.53917500	2.33760000
C	-4.23490700	0.04365100	-1.06166600
H	-2.53195100	1.20743300	-1.63511000
C	-4.82946700	-0.73805900	-0.03978900
H	-4.77840000	0.18485400	-1.99036900
H	-4.63881600	-1.54888300	1.96402300
O	-6.04449700	-1.25987800	-0.30461000
H	-6.37627900	-1.78029400	0.44366300

Geom 20:
Energy: -841.12108797 Hartrees

C	4.39055400	-1.55554700	-0.04790300
C	3.16787300	-1.59498800	-0.81271300
C	2.29349900	-0.52469300	-0.85849900
C	2.54250700	0.68232500	-0.15181500
C	3.73968200	0.73728600	0.60795400
C	4.62607600	-0.32046800	0.66371700
H	2.94494800	-2.50576700	-1.36427600
H	1.39129500	-0.62882500	-1.45396200
H	3.95093500	1.65015000	1.15790800
H	5.53662800	-0.24489300	1.25463500
O	5.20815700	-2.54135300	-0.00142800
C	0.45532400	1.82754000	-0.97603500
H	-0.16096500	2.71706800	-0.99948500
H	0.19312700	1.01077100	-1.63317700
O	1.89974500	2.88356800	0.51999100
C	1.64247500	1.84806100	-0.17104300
O	-1.14694500	0.90812300	0.58492400
C	-2.29401200	0.40497800	0.38767900
C	-2.94579400	-0.40598400	1.39978200
C	-3.01566800	0.61045600	-0.85514300
C	-4.18729200	-0.95710600	1.18613400
H	-2.41838000	-0.56551500	2.33478100
C	-4.25517400	0.05639000	-1.05889300
H	-2.54706000	1.21924700	-1.62084900
C	-4.85249100	-0.73267500	-0.04430100
H	-4.79813700	0.20793300	-1.98629800
H	-4.66476000	-1.56326000	1.95171400
O	-6.06967200	-1.24742900	-0.31397500

H	-6.40327200	-1.77362100	0.42938800

Geom 21:
Energy: -841.12223247 Hartrees

C	4.39874500	-1.56243800	-0.05107900
C	3.17946100	-1.59300200	-0.82202300
C	2.30998800	-0.51900900	-0.86650600
C	2.56101000	0.68350300	-0.15236600
C	3.75494500	0.72973300	0.61345800
C	4.63636700	-0.33185100	0.66814900
H	2.95568100	-2.50005000	-1.37928700
H	1.41050400	-0.61610500	-1.46718000
H	3.96721300	1.63906200	1.16883600
H	5.54445100	-0.26333900	1.26365200
O	5.21181700	-2.55150500	-0.00588000
C	0.48152700	1.84028800	-0.97848200
H	-0.13473600	2.73006700	-0.99577100
H	0.20976400	1.02155800	-1.62929400
O	1.92700000	2.88584700	0.52379000
C	1.66671300	1.85312600	-0.16993500
O	-1.16884600	0.90708000	0.60231800
C	-2.31448100	0.40452500	0.39858100
C	-2.96587800	-0.42176000	1.39874900
C	-3.03608300	0.62620400	-0.84174900
C	-4.20660200	-0.97140100	1.17666000
H	-2.43890900	-0.59359200	2.33184200
C	-4.27462800	0.07326300	-1.05412600
H	-2.56692300	1.24605800	-1.59828300
C	-4.87136000	-0.73066700	-0.05093100
H	-4.81726900	0.23672900	-1.97971000
H	-4.68390300	-1.58864100	1.93346800
O	-6.08787000	-1.24325100	-0.32847900
H	-6.42103200	-1.78018900	0.40731500

Geom 22:
Energy: -841.12322945 Hartrees

C	4.34857100	-1.59701500	-0.07973700
C	3.12437300	-1.59469400	-0.84383300
C	2.27913300	-0.50152400	-0.87512300

C	2.56166700	0.68989700	-0.15346000
C	3.76102500	0.70384200	0.60573000
C	4.61821800	-0.37753700	0.64779300
H	2.87808300	-2.49239500	-1.40667300
H	1.37472800	-0.57352200	-1.47189400
H	3.99689500	1.60416900	1.16624000
H	5.53089700	-0.33427600	1.23865300
O	5.13927100	-2.60381500	-0.04731900
C	0.49874200	1.89470200	-0.94984300
H	-0.10087000	2.79604800	-0.95236300
H	0.19184400	1.07859200	-1.58822800
O	1.98878600	2.90594500	0.53224400
C	1.69519400	1.87998100	-0.15792500
O	-1.18389300	0.95027400	0.66870000
C	-2.31671400	0.43048800	0.44056100
C	-2.91362900	-0.51912900	1.36242500
C	-3.07737400	0.75306300	-0.75362200
C	-4.13999600	-1.08821100	1.11097200
H	-2.35721200	-0.76771200	2.26053200
C	-4.30115400	0.17984300	-0.99578800
H	-2.64883100	1.46530500	-1.45071400
C	-4.84378700	-0.74581400	-0.06982900
H	-4.87273100	0.41847200	-1.88701600
H	-4.57615300	-1.79831800	1.80898100
O	-6.04890000	-1.27111200	-0.37316100
H	-6.34437600	-1.89405600	0.30885000

Geom 23:
Energy: -841.1237670 Hartrees

C	3.39197200	-2.03208000	-0.10538400
C	2.23425200	-1.67454800	-0.89338800
C	1.73844700	-0.38448700	-0.92792900
C	2.33600200	0.67319900	-0.18880900
C	3.47439400	0.33996100	0.59226800
C	3.98604700	-0.94181200	0.63904600
H	1.75205800	-2.46138000	-1.46918200
H	0.86307700	-0.19120200	-1.54052600
H	3.94586200	1.13328600	1.16535000
H	4.86050600	-1.16434700	1.24692700
O	3.86111100	-3.22933500	-0.06642500
C	0.69985000	2.41159500	-0.99474000
H	0.35430600	3.43770100	-0.97601300
H	0.18727300	1.71616400	-1.64441700

O	2.40791700	2.97047800	0.52410600
C	1.83997800	2.06232500	-0.18900400
O	-1.24371500	1.91233200	0.60854600
C	-2.13193400	1.01330700	0.42527000
C	-2.34734500	-0.05195400	1.39128200
C	-2.96966600	0.99662700	-0.76370000
C	-3.29611000	-1.02641600	1.18516300
H	-1.73008800	-0.05553200	2.28402200
C	-3.91566400	0.01958700	-0.95882400
H	-2.82531300	1.78602100	-1.49433000
C	-4.08739800	-1.00089200	0.01008000
H	-4.54237500	0.00592500	-1.84494500
H	-3.44552500	-1.81912500	1.91364100
O	-5.03237400	-1.93169000	-0.24561800
H	-5.08024600	-2.58826500	0.46661700

Geom 24:
Energy: -841.12511548 Hartrees

C	3.38455600	-2.03725500	-0.10238000
C	2.23565400	-1.67105500	-0.89694300
C	1.74803200	-0.37933100	-0.93011300
C	2.34690000	0.67122200	-0.18195500
C	3.47723500	0.32808700	0.60645300
C	3.98002600	-0.95573500	0.65111400
H	1.75360400	-2.45304200	-1.47924800
H	0.87864400	-0.17836800	-1.54848500
H	3.94907900	1.11612000	1.18632800
H	4.84860300	-1.18672200	1.26406300
O	3.84382900	-3.23031700	-0.06568700
C	0.73603700	2.42489800	-0.99162100
H	0.39883400	3.45378800	-0.96790600
H	0.21811300	1.73717800	-1.64497400
O	2.42299700	2.94986400	0.53365800
C	1.86146300	2.06068600	-0.18000900
O	-1.32668800	1.97921400	0.55857900
C	-2.17661600	1.05440400	0.39670000
C	-2.36361300	0.01123900	1.38913200
C	-3.00331000	0.98042900	-0.79515200
C	-3.27963400	-0.99775300	1.20410900
H	-1.75297200	0.05175100	2.28555200
C	-3.91621900	-0.03045500	-0.97058000
H	-2.87706400	1.75448000	-1.54537500

C	-4.06244600	-1.02930400	0.02395500
H	-4.53534200	-0.08780300	-1.86020200
H	-3.40900900	-1.77429000	1.95364300
O	-4.97459100	-1.99590400	-0.21330100
H	-5.00525900	-2.63641200	0.51436800

Geom 25:
Energy: -841.12585075 Hartrees

C	3.38285500	-2.04534800	-0.10483500
C	2.24572300	-1.66692700	-0.91063500
C	1.76745800	-0.37181800	-0.94233200
C	2.36492600	0.67054500	-0.18139900
C	3.48370500	0.31529500	0.61823100
C	3.97694600	-0.97210500	0.66173400
H	1.76534600	-2.44242900	-1.50287700
H	0.90713900	-0.16138700	-1.57014800
H	3.95402100	1.09692500	1.20791400
H	4.83659100	-1.21260600	1.28352200
O	3.83357000	-3.24148800	-0.06956300
C	0.77228000	2.43839200	-0.99553100
H	0.44040900	3.46911600	-0.96803400
H	0.24848700	1.75494800	-1.64882800
O	2.45253800	2.94596000	0.54298400
C	1.88974000	2.06326700	-0.17755600
O	-1.34962900	1.98775800	0.55861400
C	-2.19584700	1.05989100	0.39653200
C	-2.36966700	0.00815600	1.38239400
C	-3.03249100	0.99135700	-0.78875100
C	-3.28342200	-1.00296100	1.19780900
H	-1.75158400	0.04445500	2.27388400
C	-3.94267800	-0.02194500	-0.96400900
H	-2.91550000	1.77150100	-1.53417200
C	-4.07640300	-1.02872100	0.02433400
H	-4.56905700	-0.07536600	-1.84878000
H	-3.40341100	-1.78546600	1.94269100
O	-4.98681900	-1.99708900	-0.21225600
H	-5.00847600	-2.64330000	0.51066600

Geom 26:
Energy: -841.12648067 Hartrees

C	3.33964100	-2.06642300	-0.10876700
C	2.23776400	-1.65677900	-0.94764100
C	1.78217500	-0.35357600	-0.97577300
C	2.37003200	0.66721800	-0.17880800
C	3.45461800	0.28128800	0.65324800
C	3.92433900	-1.01485500	0.69443100
H	1.76596100	-2.41507100	-1.56833100
H	0.94839000	-0.11932200	-1.63038000
H	3.91704900	1.04602900	1.27069800
H	4.75737800	-1.27934100	1.34217400
O	3.76901000	-3.27030100	-0.07643900
C	0.82857600	2.47104800	-1.01188600
H	0.51264600	3.50683000	-0.97898300
H	0.30409500	1.80248500	-1.68007400
O	2.47681200	2.93211400	0.57489200
C	1.91855500	2.06747800	-0.17035400
O	-1.35547500	2.01169300	0.54027500
C	-2.19468500	1.07648000	0.38545900
C	-2.36529600	0.03469800	1.38245700
C	-3.02717300	0.98969800	-0.80159100
C	-3.27312300	-0.98333600	1.20687900
H	-1.75006300	0.08451100	2.27527400
C	-3.93125300	-0.03049400	-0.96790800
H	-2.91183200	1.76190400	-1.55550600
C	-4.06267300	-1.02654900	0.03159000
H	-4.55468900	-0.09754400	-1.85382400
H	-3.39085200	-1.75785700	1.96043500
O	-4.96762700	-2.00201600	-0.19662100
H	-4.98884100	-2.63990200	0.53366400

Geom 27:
Energy: -841.12733872 Hartrees

C	3.15927100	-1.98837600	-0.23767500
C	2.21797400	-1.43385800	-1.18220400
C	1.76084200	-0.13468400	-1.08506100
C	2.18969500	0.73933200	-0.04777300
C	3.11505600	0.20936100	0.89074800
C	3.58328800	-1.08535400	0.81013700
H	1.87017800	-2.07779800	-1.98677800
H	1.05321200	0.21332600	-1.83131000
H	3.45341600	0.85998300	1.69211500
H	4.29215500	-1.46276400	1.54412000

O	3.58817800	-3.18980500	-0.31876000
C	0.78983000	2.67328400	-0.83795700
H	0.46469600	3.69752500	-0.70222600
H	0.38553000	2.12126600	-1.67431200
O	2.14851700	2.86044400	1.05176400
C	1.73022600	2.12874900	0.10036900
O	-1.92436400	2.38793900	-0.37280100
C	-2.40613900	1.23915700	-0.14944800
C	-2.28416000	0.60390200	1.15065300
C	-3.09744400	0.48846500	-1.18333300
C	-2.79619200	-0.65045000	1.38612100
H	-1.77112600	1.15240900	1.93409900
C	-3.60469700	-0.76373000	-0.93914900
H	-3.19817900	0.95112800	-2.16004500
C	-3.45784100	-1.34649800	0.34467900
H	-4.11910000	-1.32821400	-1.71033000
H	-2.69807700	-1.11527800	2.36371500
O	-3.97573300	-2.58113500	0.51420500
H	-3.82374400	-2.90693300	1.41504200

Geom 28:
Energy: -841.12784551 Hartrees

C	3.18441100	-1.98448500	-0.22897000
C	2.23199400	-1.44132500	-1.16909100
C	1.77152700	-0.14299000	-1.07883500
C	2.20823100	0.74169400	-0.05375300
C	3.14505500	0.22319500	0.87994700
C	3.61615000	-1.07077900	0.80654800
H	1.87879400	-2.09335900	-1.96471500
H	1.05613800	0.19645300	-1.82159200
H	3.48954000	0.88226900	1.67172700
H	4.33313700	-1.43961200	1.53696400
O	3.61600100	-3.18520100	-0.30345300
C	0.78411000	2.65934000	-0.83931800
H	0.45562000	3.68338400	-0.70938100
H	0.36150500	2.09339100	-1.65728400
O	2.18236600	2.87699800	1.01836800
C	1.74714400	2.13131500	0.08573100
O	-1.97869000	2.40130000	-0.34500700
C	-2.44563100	1.24428400	-0.13346200
C	-2.32434100	0.60161300	1.16305400
C	-3.11922800	0.49150400	-1.17749300
C	-2.82232900	-0.66052600	1.38658800

H	-1.82355800	1.15119700	1.95366000
C	-3.61301800	-0.76829000	-0.94503700
H	-3.21847100	0.95919300	-2.15196200
C	-3.46884600	-1.35735000	0.33622600
H	-4.11496400	-1.33392700	-1.72354800
H	-2.72491400	-1.13095300	2.36154300
O	-3.97431600	-2.59859400	0.49465600
H	-3.82709300	-2.92726800	1.39526300

Geom 29:
Energy: -841.12828776 Hartrees

C	3.20411100	-1.98400900	-0.22124700
C	2.24126800	-1.45034900	-1.15632500
C	1.78052800	-0.15177800	-1.07316900
C	2.22771500	0.74290000	-0.06118300
C	3.17540000	0.23405800	0.86698300
C	3.64623200	-1.06030300	0.80111200
H	1.88074700	-2.10986000	-1.94242200
H	1.05782100	0.18053300	-1.81204900
H	3.52792700	0.90100400	1.64854700
H	4.37078400	-1.42201600	1.52759500
O	3.63570000	-3.18493600	-0.28900600
C	0.78200900	2.64678000	-0.83972000
H	0.45123000	3.67071500	-0.71404500
H	0.34031800	2.06786300	-1.63842600
O	2.22308800	2.89268200	0.98174000
C	1.76810800	2.13371500	0.06956500
O	-2.02749900	2.41539300	-0.30918700
C	-2.48184000	1.25087300	-0.11232200
C	-2.35393300	0.59349700	1.17611700
C	-3.14779600	0.50424500	-1.16564900
C	-2.84030800	-0.67574000	1.38439700
H	-1.85808600	1.13807100	1.97328900
C	-3.63037300	-0.76256000	-0.94828300
H	-3.25112600	0.98263100	-2.13448900
C	-3.48130700	-1.36542800	0.32598300
H	-4.12728800	-1.32325500	-1.73356900
H	-2.73817700	-1.15708500	2.35347900
O	-3.97688200	-2.61238900	0.46989800
H	-3.82828400	-2.95002200	1.36697400

Geom 30:
Energy: -841.12867072 Hartrees

C	3.22717600	-1.97799500	-0.21773000
C	2.25104500	-1.45442700	-1.14483400
C	1.78673300	-0.15702200	-1.06537200
C	2.24341100	0.74661200	-0.06551200
C	3.20475700	0.24802400	0.85424600
C	3.67893900	-1.04521100	0.79225900
H	1.88356200	-2.12075400	-1.92187400
H	1.05437600	0.16765200	-1.79811600
H	3.56475100	0.92200100	1.62629500
H	4.41339200	-1.39926300	1.51251800
O	3.66164000	-3.17793000	-0.28179000
C	0.77392300	2.63612700	-0.83345800
H	0.43942600	3.65925100	-0.71012500
H	0.31716800	2.04637900	-1.61571400
O	2.25185900	2.90713300	0.95490900
C	1.78142500	2.13696900	0.06023400
O	-2.08645800	2.42657800	-0.29308500
C	-2.52246200	1.25408400	-0.10251700
C	-2.38107100	0.59046300	1.18130700
C	-3.18077000	0.50458500	-1.15861200
C	-2.84946800	-0.68651900	1.38325100
H	-1.89015700	1.13685300	1.98029500
C	-3.64575200	-0.76979500	-0.94745600
H	-3.29334400	0.98733900	-2.12425000
C	-3.48511000	-1.37807500	0.32284100
H	-4.13754700	-1.33238900	-1.73460400
H	-2.73731500	-1.17258000	2.34885700
O	-3.96460600	-2.63192400	0.46104900
H	-3.81044500	-2.97226400	1.35616200

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p-cyanophenol leaving group

Geom 1:
C-O Bond Length: 1.48072 Angstrom
Energy: -858.14463 Hartrees

C	4.70748900	-1.39588200	-0.04214500
C	3.35363700	-1.73331300	-0.41826300
C	2.35365900	-0.78794300	-0.43866000
C	2.61805000	0.58493900	-0.10583500
C	3.96018300	0.92253600	0.28630400
C	4.96068500	-0.02464600	0.31360200
H	3.14182600	-2.76722100	-0.67782000
H	1.34881900	-1.09200900	-0.71059400
H	4.17657500	1.95031700	0.55348000
H	5.97195400	0.24650100	0.60596900
O	5.64025900	-2.29287900	-0.01799800
C	0.21008500	1.31784100	-0.62480700
H	-0.27440000	2.24467700	-0.94509800
H	0.18422300	0.59001600	-1.44192300
O	1.86703200	2.82487900	0.27993400
C	1.59309900	1.61690600	-0.14648700
O	-0.58121100	0.75635200	0.49372900
C	-1.87128300	0.38891400	0.27131000
C	-2.54322700	-0.18357100	1.36992900
C	-2.54052500	0.54874800	-0.95529300
C	-3.86103900	-0.59233900	1.24860100
H	-2.01239100	-0.29971500	2.30919000
C	-3.86507400	0.13654800	-1.07527300
H	-2.04606400	0.98902800	-1.81156800
C	-4.53608000	-0.43626600	0.01900600
H	-4.37509400	-1.03380500	2.09597400
H	-4.38276300	0.25959400	-2.02091900
C	-5.89230700	-0.85743500	-0.11275400
N	-7.00363400	-1.20348900	-0.21963100

Geom 2:
Bond Length: 1.53072 Angstrom
Energy: -858.144 Hartrees

C	4.72254500	-1.39188400	-0.03589800
C	3.37077200	-1.73495700	-0.41471900
C	2.36884900	-0.79156000	-0.44196800

C	2.62922200	0.58170100	-0.11491200
C	3.96704400	0.92512200	0.27990600
C	4.97106200	-0.01826800	0.31475700
H	3.16257000	-2.77054300	-0.67011000
H	1.36546500	-1.09932700	-0.71506800
H	4.17901600	1.95481400	0.54322300
H	5.98056900	0.25707300	0.60892400
O	5.65665600	-2.28496400	-0.00537500
C	0.22882800	1.31618400	-0.64909600
H	-0.26946700	2.23394000	-0.96836100
H	0.18954400	0.56537000	-1.44169500
O	1.86835900	2.81778200	0.28098400
C	1.59986600	1.61400900	-0.16265500
O	-0.59577900	0.75456900	0.51182000
C	-1.88179500	0.38796200	0.28251800
C	-2.56601000	-0.17409600	1.38079700
C	-2.54437400	0.53653400	-0.95047400
C	-3.88364100	-0.58106900	1.25352000
H	-2.04323400	-0.28300600	2.32550000
C	-3.86853600	0.12602900	-1.07652000
H	-2.04351100	0.96751100	-1.80776200
C	-4.54986800	-0.43522000	0.01774300
H	-4.40476000	-1.01351500	2.10133000
H	-4.37859900	0.24135300	-2.02733600
C	-5.90574200	-0.85424500	-0.12015600
N	-7.01726000	-1.19860200	-0.23216000

Geom 3:
Bond length: 1.58072 Angstrom
Energy: -858.1426 Hartrees

C	4.73595000	-1.38884200	-0.03200600
C	3.38477700	-1.73699200	-0.40878100
C	2.38181100	-0.79460600	-0.44113400
C	2.64073300	0.57896400	-0.12263900
C	3.97549500	0.92773600	0.27014500
C	4.98229500	-0.01250000	0.31085800
H	3.17848300	-2.77441700	-0.65774700
H	1.37862900	-1.10521400	-0.71168400
H	4.18466300	1.95954300	0.52741000
H	5.99120000	0.26647000	0.60324800
O	5.67049300	-2.27853900	0.00340900
C	0.24879600	1.31728700	-0.67017800
H	-0.26459300	2.22710100	-0.98309600

H	0.19637800	0.54775900	-1.44134600
O	1.87139000	2.81062500	0.28703600
C	1.60710100	1.61285700	-0.17578000
O	-0.60963700	0.75014300	0.52987500
C	-1.89158300	0.38544700	0.29457900
C	-2.58781000	-0.17021100	1.39055300
C	-2.54824700	0.52780900	-0.94386800
C	-3.90543200	-0.57443100	1.25631700
H	-2.07274900	-0.27566700	2.33994500
C	-3.87212500	0.11994500	-1.07696800
H	-2.04094200	0.95286800	-1.80036500
C	-4.56338600	-0.43377600	0.01535500
H	-4.43346600	-1.00084200	2.10301500
H	-4.37512700	0.23134500	-2.03208100
C	-5.91905000	-0.84965900	-0.12954900
N	-7.03091500	-1.19156400	-0.24732700

Geom 4:
Bond Length: 1.63072 Angstrom
Energy -858.1409 Hartrees

C	4.73924800	-1.39383000	-0.03280100
C	3.38580400	-1.74111600	-0.40309400
C	2.38613500	-0.79506900	-0.43748900
C	2.65119900	0.57730000	-0.12839600
C	3.98551200	0.92578100	0.25751800
C	4.99099200	-0.01566600	0.30103600
H	3.17605100	-2.77942600	-0.64488100
H	1.38082700	-1.10362600	-0.70241500
H	4.19727400	1.95883300	0.50768300
H	6.00156900	0.26231900	0.58804600
O	5.67019100	-2.28394700	0.00459200
C	0.27049500	1.33077100	-0.68453700
H	-0.25637600	2.23573500	-0.98434400
H	0.20185200	0.54758700	-1.43837800
O	1.88426400	2.80717400	0.29791200
C	1.61705900	1.61794800	-0.18383000
O	-0.62257800	0.75330800	0.55167400
C	-1.89891400	0.38783400	0.31019400
C	-2.60444800	-0.17428500	1.39913600
C	-2.55181500	0.53365500	-0.93171700
C	-3.92079200	-0.57878900	1.25537800
H	-2.09580700	-0.28381100	2.35161000
C	-3.87405400	0.12534800	-1.07443900

H	-2.04034400	0.96314800	-1.78359100
C	-4.57226100	-0.43372000	0.01127300
H	-4.45343100	-1.00916200	2.09729000
H	-4.37148000	0.24047300	-2.03212500
C	-5.92631400	-0.84970600	-0.14326800
N	-7.03746200	-1.19186900	-0.26887200

Geom 5:
Bond length: 1.68072 Angstrom
Energy: -858.1393 Hartrees

C	4.73187200	-1.40716300	-0.03831000
C	3.37307200	-1.74742000	-0.39678000
C	2.38117800	-0.79297900	-0.42984500
C	2.66036100	0.57677900	-0.13180500
C	3.99716500	0.91911300	0.24212800
C	4.99688600	-0.02814000	0.28510900
H	3.15416300	-2.78564300	-0.63014300
H	1.37118000	-1.09428700	-0.68510600
H	4.21704900	1.95248300	0.48406600
H	6.01152100	0.24389400	0.56283300
O	5.65515200	-2.30163600	-0.00217600
C	0.29422400	1.35655100	-0.69319100
H	-0.24372900	2.25944400	-0.97482500
H	0.20659500	0.56366000	-1.43292900
O	1.90691400	2.80738300	0.31301100
C	1.62998000	1.62920800	-0.18642000
O	-0.63476300	0.76577600	0.57676900
C	-1.90375000	0.39580400	0.32892100
C	-2.61527000	-0.18573200	1.40619900
C	-2.55519800	0.55380000	-0.91444500
C	-3.92894000	-0.59390200	1.25070700
H	-2.11147700	-0.30639400	2.36000600
C	-3.87428600	0.14154700	-1.06903000
H	-2.04204800	0.99764900	-1.75804300
C	-4.57607100	-0.43527900	0.00569900
H	-4.46352300	-1.03802400	2.08433300
H	-4.36784100	0.26749400	-2.02747400
C	-5.92710300	-0.85461900	-0.16065000
N	-7.03643400	-1.19969600	-0.29618300

Geom 6:
Bond length: 1.73072
Energy: -858.13807

C	4.71207800	-1.42958300	-0.04886000
C	3.34533000	-1.75535200	-0.39229700
C	2.36637300	-0.78739600	-0.42066300
C	2.66784300	0.57767700	-0.13289500
C	4.00971900	0.90671400	0.22613000
C	4.99856100	-0.05157500	0.26497100
H	3.11146300	-2.79192100	-0.61780600
H	1.34949500	-1.07512600	-0.66403500
H	4.24338800	1.93886400	0.46059600
H	6.01924800	0.20854700	0.53111800
O	5.62313800	-2.33300400	-0.01737200
C	0.32010900	1.39620600	-0.69675000
H	-0.22517900	2.30035000	-0.95517200
H	0.21040000	0.59773000	-1.42576900
O	1.93991100	2.81131100	0.33294600
C	1.64643400	1.64711600	-0.18309000
O	-0.64599200	0.78946800	0.60475700
C	-1.90563800	0.41005400	0.35015900
C	-2.61736200	-0.20748400	1.40976800
C	-2.55976500	0.59157000	-0.89103100
C	-3.92683600	-0.62314200	1.24090300
H	-2.11527600	-0.34850800	2.36180100
C	-3.87395200	0.17122300	-1.05926300
H	-2.04934300	1.06251400	-1.72166900
C	-4.57375200	-0.43901300	-0.00103800
H	-4.45903300	-1.09328100	2.06182700
H	-4.36692400	0.31716900	-2.01530300
C	-5.92034900	-0.86504300	-0.18065200
N	-7.02678000	-1.21576700	-0.32722900

Geom 7:
Bond length: 1.78072

Energy: -858.13738

C	4.67881200	-1.46193200	-0.06291000
C	3.30155800	-1.76619700	-0.38599900
C	2.34091300	-0.77989200	-0.40763700

C	2.67276200	0.57883300	-0.13247400
C	4.02252600	0.88782400	0.20686800
C	4.99510200	-0.08664100	0.23893300
H	3.04672000	-2.79977500	-0.60174900
H	1.31529900	-1.04852000	-0.63559800
H	4.27605300	1.91740200	0.43225700
H	6.02384400	0.15603100	0.48952300
O	5.57301300	-2.37888300	-0.03865300
C	0.34734000	1.44851500	-0.69618400
H	-0.19933700	2.35718000	-0.93051800
H	0.21073200	0.64616800	-1.41485100
O	1.98391800	2.81896400	0.35182600
C	1.66658300	1.67028000	-0.17604100
O	-0.65781700	0.83098000	0.63771600
C	-1.90538900	0.43483600	0.37517500
C	-2.61038100	-0.23399800	1.41055100
C	-2.56599600	0.64781300	-0.86012000
C	-3.91324700	-0.66320600	1.22625400
H	-2.10696000	-0.40175200	2.35766500
C	-3.87253300	0.21285200	-1.04430500
H	-2.06321400	1.15778300	-1.67241900
C	-4.56388300	-0.44541600	-0.00865200
H	-4.43811000	-1.17052800	2.02972600
H	-4.36799300	0.38527000	-1.99478100
C	-5.90346300	-0.88454700	-0.20379500
N	-7.00488200	-1.24607100	-0.36347700

Geom 8:
Bond length: 1.83072

Energy: -858.13734

C	4.15022300	-1.79714700	-0.10599600
C	2.71439600	-1.84745400	-0.28288000
C	1.95941500	-0.69614100	-0.29300700
C	2.56791700	0.58292900	-0.14786600
C	3.97740200	0.64615200	0.04543000
C	4.74948500	-0.49323000	0.06196600
H	2.25062900	-2.82283000	-0.39729700
H	0.88360900	-0.77102000	-0.40702900
H	4.44050300	1.61845700	0.17058200
H	5.82555200	-0.44138400	0.20012600
O	4.85248300	-2.86498200	-0.09001300

C	0.43210900	1.86026500	-0.65202100
H	0.02471600	2.84574600	-0.85095400
H	0.12067600	1.08750300	-1.34736600
O	2.31999000	2.91350500	0.32718800
C	1.77745300	1.84629200	-0.17485900
O	-0.64792800	1.40243600	0.75349000
C	-1.79892200	0.79639900	0.46995300
C	-2.30093500	-0.17590600	1.37526300
C	-2.55986000	1.08771200	-0.69203300
C	-3.50701100	-0.81553900	1.14083700
H	-1.72257000	-0.40676600	2.26472800
C	-3.76264400	0.43818200	-0.93278300
H	-2.20727700	1.83516900	-1.39401700
C	-4.25356100	-0.51950100	-0.02142600
H	-3.87978000	-1.55180100	1.84631600
H	-4.33591900	0.67338100	-1.82428800
C	-5.48910300	-1.18007500	-0.26955100
N	-6.50495500	-1.72453700	-0.47318500

Geom 9:
Bond length: 1.88072

Energy: -858.13783

C	4.06200300	-1.84601300	-0.10558100
C	2.62179600	-1.85465600	-0.25622000
C	1.90371600	-0.68022300	-0.27030300
C	2.55577800	0.57884900	-0.15261700
C	3.96869800	0.60306400	0.01484100
C	4.70574500	-0.55880600	0.03314000
H	2.12661500	-2.81672100	-0.34862800
H	0.82419300	-0.72042300	-0.36490500
H	4.46251000	1.56279400	0.11869100
H	5.78523700	-0.53957500	0.15060800
O	4.73029900	-2.93341200	-0.08776000
C	0.46855600	1.92355100	-0.67144800
H	0.07621100	2.91725700	-0.85513800
H	0.12373900	1.15138800	-1.35030000
O	2.37492200	2.91191200	0.32664300
C	1.80221600	1.86832300	-0.18087400
O	-0.65746900	1.49009100	0.77122300
C	-1.78588300	0.85215900	0.48748300
C	-2.25484000	-0.15831900	1.37105200
C	-2.56369600	1.14380000	-0.66564900

C	-3.44276900	-0.82779500	1.12776100
H	-1.66562200	-0.39246900	2.25263600
C	-3.74725200	0.46467700	-0.91593200
H	-2.23443500	1.91687300	-1.35167100
C	-4.20502300	-0.52785600	-0.02360000
H	-3.78976500	-1.59092500	1.81780300
H	-4.33219800	0.70193000	-1.79937800
C	-5.42187300	-1.21839800	-0.27954700
N	-6.42307700	-1.78757200	-0.48937100

Geom 10:
Bond length: 1.93072

Energy: -858.13863

C	3.97781600	-1.88912700	-0.10502500
C	2.53615400	-1.85925500	-0.24360800
C	1.85192100	-0.66499300	-0.26282800
C	2.54119100	0.57443700	-0.15961400
C	3.95492900	0.56232400	-0.00438600
C	4.65958400	-0.61897200	0.01722100
H	2.01390400	-2.80792700	-0.32368800
H	0.77104100	-0.67391400	-0.34945800
H	4.47520300	1.50926600	0.08717600
H	5.74015400	-0.62977400	0.12467400
O	4.61544700	-2.99310400	-0.08444900
C	0.50048600	1.98092500	-0.69341400
H	0.12413200	2.98255600	-0.86366300
H	0.12167300	1.21041400	-1.35473000
O	2.42316500	2.90869900	0.31985100
C	1.82307500	1.88675500	-0.19007200
O	-0.66897800	1.57681800	0.78872800
C	-1.77517000	0.90783600	0.50641300
C	-2.19586900	-0.15366800	1.35609300
C	-2.58324500	1.21320000	-0.62421300
C	-3.36381400	-0.85451400	1.10457500
H	-1.58537000	-0.40080000	2.21960800
C	-3.74605800	0.50361500	-0.88353400
H	-2.28892800	2.02266400	-1.28417100
C	-4.15503500	-0.53804200	-0.02285200
H	-3.67303900	-1.65552300	1.76928600
H	-4.35306300	0.75285400	-1.74869700
C	-5.35119400	-1.26042900	-0.28639500

N	-6.33591700	-1.85566600	-0.50279300

Geom 11:
Bond length: 1.98072

Energy: -858.13962

C	3.90421200	-1.92536400	-0.10217800
C	2.46449000	-1.86093100	-0.25316600
C	1.81061800	-0.65012300	-0.28024900
C	2.52975700	0.57098200	-0.17024400
C	3.94118300	0.52597000	-0.00462800
C	4.61665500	-0.67177400	0.02382100
H	1.92018200	-2.79674900	-0.33667300
H	0.73080300	-0.63173000	-0.37720600
H	4.48273500	1.46056700	0.09021400
H	5.69569500	-0.70949000	0.13962700
O	4.51450800	-3.04329500	-0.07535000
C	0.53192600	2.03160200	-0.71902600
H	0.16804300	3.04021300	-0.87136400
H	0.12303600	1.26626000	-1.36733400
O	2.46532700	2.90447600	0.31224000
C	1.84355200	1.90225300	-0.20222000
O	-0.67666300	1.64396300	0.80160400
C	-1.76490600	0.95177200	0.52155400
C	-2.14547200	-0.14740000	1.34415300
C	-2.59940400	1.26618100	-0.58912500
C	-3.29728300	-0.87242300	1.08741900
H	-1.51648100	-0.40331100	2.19180200
C	-3.74592300	0.53343100	-0.85383700
H	-2.33353000	2.10190600	-1.22857100
C	-4.11369400	-0.54476600	-0.01894800
H	-3.57494100	-1.70137400	1.73160300
H	-4.37210700	0.79070500	-1.70289200
C	-5.29274700	-1.29243900	-0.28721700
N	-6.26380000	-1.90856900	-0.50768800

Geom 12:
Bond length: 2.03072

Energy: -858.14066

C	3.84895900	-1.95265700	-0.09954500
C	2.41230500	-1.86072700	-0.26803600
C	1.78275000	-0.63743000	-0.30167900
C	2.52420300	0.56858700	-0.17889200
C	3.93228600	0.49741900	0.00262400
C	4.58429400	-0.71281800	0.03690800
H	1.85138600	-2.78585800	-0.35972200
H	0.70491300	-0.59755600	-0.41270100
H	4.48994900	1.42161500	0.10567300
H	5.66093300	-0.77181800	0.16516200
O	4.43743100	-3.08107000	-0.06763800
C	0.56287000	2.07060200	-0.74520400
H	0.20631600	3.08395600	-0.88010700
H	0.13110000	1.30952400	-1.38273400
O	2.49881700	2.90039400	0.30823500
C	1.86328700	1.91386800	-0.21251800
O	-0.68256900	1.68842600	0.81257100
C	-1.75734800	0.98110700	0.53311100
C	-2.11155900	-0.14217600	1.33692100
C	-2.60947300	1.30012000	-0.56458200
C	-3.25264900	-0.88242100	1.07666400
H	-1.47025100	-0.40339000	2.17375500
C	-3.74522100	0.55278900	-0.83275100
H	-2.36229100	2.15176200	-1.19073800
C	-4.08598600	-0.54804400	-0.01522200
H	-3.50955500	-1.72859200	1.70702200
H	-4.38401000	0.81452700	-1.67104000
C	-5.25407800	-1.31107500	-0.28653000
N	-6.21653700	-1.93986200	-0.50964700

Geom 13:
Bond length: 2.08072

Energy: -858.14169

C	3.78504900	-1.98346300	-0.09613600
C	2.35390300	-1.86029600	-0.29202200
C	1.75171600	-0.62366100	-0.33197700
C	2.51646600	0.56499700	-0.18698600
C	3.91883600	0.46374900	0.02072100
C	4.54415500	-0.76004300	0.06113500
H	1.77554300	-2.77286100	-0.39956300
H	0.67747900	-0.56002200	-0.46469700

H	4.49360600	1.37551400	0.13939900
H	5.61657000	-0.84297900	0.20973100
O	4.34886200	-3.12347400	-0.05946900
C	0.59696000	2.11080100	-0.77530500
H	0.25028000	3.12915600	-0.89563300
H	0.14252200	1.35443000	-1.40178900
O	2.53464700	2.89560500	0.30227000
C	1.88481700	1.92500200	-0.22461400
O	-0.68656000	1.73897500	0.81960300
C	-1.74711000	1.01487000	0.54195800
C	-2.07807800	-0.12422600	1.33549900
C	-2.61235500	1.32853300	-0.54864200
C	-3.20745100	-0.88138800	1.07381400
H	-1.42766400	-0.38299500	2.16612900
C	-3.73629100	0.56468800	-0.81808100
H	-2.38162300	2.18985700	-1.16811200
C	-4.05337500	-0.55039500	-0.00968500
H	-3.44618100	-1.73840000	1.69670900
H	-4.38426500	0.82316000	-1.65036200
C	-5.20956500	-1.33058700	-0.28173200
N	-6.16256000	-1.97359900	-0.50553300

Geom 14:
Bond length: -858.14169

Energy: -858.14267

C	3.72592700	-2.01120400	-0.09333900
C	2.30184300	-1.85904600	-0.31990400
C	1.72504100	-0.61070700	-0.36571300
C	2.50957900	0.56140000	-0.19503000
C	3.90478000	0.43208200	0.04233500
C	4.50527300	-0.80362400	0.08843900
H	1.70853500	-2.75952500	-0.44613900
H	0.65557600	-0.52549500	-0.52246300
H	4.49420000	1.33182900	0.17953600
H	5.57231900	-0.90850600	0.25993000
O	4.26677900	-3.16150700	-0.05209900
C	0.63056200	2.14759500	-0.80526600
H	0.29330400	3.17059600	-0.91090600
H	0.15548100	1.39711200	-1.42279000
O	2.56777000	2.89016500	0.29698200
C	1.90572200	1.93439700	-0.23663700
O	-0.68850700	1.78116600	0.82745300
C	-1.73702000	1.04373600	0.55098200

C	-2.04857300	-0.10835900	1.33554300
C	-2.61334800	1.35305500	-0.53351800
C	-3.16793400	-0.87940000	1.07234100
H	-1.39058500	-0.36509900	2.16089700
C	-3.72714300	0.57561200	-0.80431200
H	-2.39651300	2.22230900	-1.14715700
C	-4.02431000	-0.55124700	-0.00405700
H	-3.39138300	-1.74527800	1.68867800
H	-4.38270000	0.83128000	-1.63155000
C	-5.17035400	-1.34545000	-0.27724200
N	-6.11526400	-2.00012200	-0.50206400

Geom 15:
Bond length: 2.18072

Energy: -858.14358

C	3.68424800	-2.03047500	-0.09093500
C	2.26676600	-1.85747100	-0.34365500
C	1.70842600	-0.60106800	-0.39483000
C	2.50595500	0.55880700	-0.20278500
C	3.89454800	0.40923700	0.05994800
C	4.47698000	-0.83464600	0.11131900
H	1.66361700	-2.74902300	-0.48551200
H	0.64350200	-0.50073800	-0.57182600
H	4.49356500	1.30010700	0.21262600
H	5.53903600	-0.95521900	0.30222500
O	4.20830700	-3.18786200	-0.04543900
C	0.65887000	2.17548000	-0.83242500
H	0.32805000	3.20178400	-0.92493600
H	0.16604200	1.42958000	-1.44108700
O	2.59322400	2.88569600	0.29081600
C	1.92301300	1.94101100	-0.24807400
O	-0.69418600	1.81233400	0.83877800
C	-1.73290300	1.06517200	0.56189700
C	-2.02364400	-0.10399400	1.33085500
C	-2.62329400	1.37821500	-0.51136300
C	-3.13452800	-0.88583900	1.06451000
H	-1.35570400	-0.36460800	2.14701200
C	-3.72863900	0.59037700	-0.78509900
H	-2.42164100	2.25895400	-1.11392100
C	-4.00433600	-0.55277000	0.00019600

H	-3.34157000	-1.76405700	1.66906500
H	-4.39415000	0.84926800	-1.60337400
C	-5.14172600	-1.35791300	-0.27604300
N	-6.07970200	-2.02173300	-0.50351500

Geom 16:
Bond length: 2.23072

Energy: -858.14440847

C	3.66577500	-2.03941300	-0.08897700
C	2.25175400	-1.85530300	-0.35388200
C	1.70384700	-0.59459200	-0.40955700
C	2.50890400	0.55857400	-0.20921200
C	3.89403000	0.39838900	0.06532200
C	4.46631100	-0.84980800	0.12078800
H	1.64298400	-2.74207600	-0.50141300
H	0.64138200	-0.48597900	-0.59597200
H	4.49848200	1.28458400	0.22367800
H	5.52571300	-0.97889900	0.32054600
O	4.18042300	-3.20043500	-0.03987800
C	0.68046900	2.19161900	-0.85266200
H	0.35004800	3.21900800	-0.93393900
H	0.17401100	1.44665300	-1.45092700
O	2.61206000	2.88476600	0.28201500
C	1.93769600	1.94562200	-0.25779800
O	-0.70348600	1.82413200	0.85782100
C	-1.73584300	1.07336000	0.57633600
C	-2.00692500	-0.11818300	1.31932000
C	-2.64273000	1.40269100	-0.47927800
C	-3.11293600	-0.90438000	1.04634200
H	-1.32721400	-0.39206400	2.12133500
C	-3.74333000	0.61099800	-0.75945100
H	-2.45580300	2.29955400	-1.06267900
C	-3.99871000	-0.55404100	0.00071600
H	-3.30441400	-1.79922900	1.63138500
H	-4.42079400	0.88279100	-1.56364200
C	-5.13128100	-1.36337000	-0.28198400
N	-6.06550900	-2.03071900	-0.51488300

Geom 17:
Bond length: 2.28072

Energy: -858.14516801

C	3.80641900	-1.97274600	-0.08524500
C	2.37541200	-1.84896500	-0.28723700
C	1.77738500	-0.61160800	-0.34681700
C	2.54625700	0.57518100	-0.21241900
C	3.94765200	0.47522600	0.00075300
C	4.56962500	-0.74879400	0.05824100
H	1.79533400	-2.76152600	-0.38395600
H	0.70382400	-0.54645600	-0.48407100
H	4.52382300	1.38741900	0.10910400
H	5.64134300	-0.83331000	0.21025100
O	4.36689500	-3.11181700	-0.03290500
C	0.64290700	2.12388700	-0.84415000
H	0.26358600	3.13428300	-0.92485100
H	0.14948800	1.34625700	-1.41095700
O	2.56462300	2.90963800	0.24480800
C	1.91879000	1.93697300	-0.26676700
O	-0.73875900	1.71844600	0.92455500
C	-1.78458500	0.99964100	0.61781300
C	-2.01930900	-0.26976900	1.23489900
C	-2.74596500	1.44159500	-0.34513300
C	-3.13949800	-1.02478900	0.93324000
H	-1.29915800	-0.62983500	1.96431100
C	-3.86192400	0.68306600	-0.65352500
H	-2.58704800	2.39874400	-0.83355000
C	-4.07898300	-0.56165300	-0.01740800
H	-3.30200200	-1.98071700	1.42272200
H	-4.58079300	1.04166300	-1.38447100
C	-5.22672700	-1.33778200	-0.32988000
N	-6.17360100	-1.97763500	-0.58776900

Geom 18:
Bond length: 2.33072

Energy: -858.1458

C	3.78363100	-1.98619800	-0.08152200
C	2.35551700	-1.84778700	-0.29502400
C	1.77071600	-0.60440000	-0.35880900
C	2.55071500	0.57418300	-0.21676200
C	3.94921000	0.46014100	0.00809700
C	4.55817600	-0.77004300	0.06946800

H	1.76703600	-2.75434700	-0.39713500
H	0.69904500	-0.52825700	-0.50490800
H	4.53366200	1.36641000	0.12183800
H	5.62770500	-0.86567100	0.23001700
O	4.33223700	-3.13058900	-0.02611700
C	0.66944700	2.14254100	-0.86595000
H	0.29400900	3.15505700	-0.93911300
H	0.16452600	1.36667400	-1.42487400
O	2.58918600	2.90874400	0.23769700
C	1.93793200	1.94218000	-0.27578400
O	-0.74973200	1.73649300	0.93774900
C	-1.78847000	1.01201200	0.62726500
C	-2.01114100	-0.26668200	1.23129400
C	-2.75772100	1.45559400	-0.32814600
C	-3.12584700	-1.02766200	0.92518400
H	-1.28566500	-0.62854400	1.95456200
C	-3.86839600	0.69136000	-0.64044200
H	-2.60788500	2.41904200	-0.80712600
C	-4.07293500	-0.56212900	-0.01695500
H	-3.27871700	-1.99016400	1.40482900
H	-4.59293100	1.05160600	-1.36498800
C	-5.21539800	-1.34414700	-0.33325600
N	-6.15813300	-1.98896700	-0.59424000

Geom 19:
Bond length: 2.38072

Energy: -858.14632

C	3.67529300	-2.03925800	-0.07967000
C	2.26280000	-1.84769300	-0.34928500
C	1.72417700	-0.58384300	-0.41749600
C	2.53757600	0.56454900	-0.22401800
C	3.92094200	0.39798500	0.05572000
C	4.48428700	-0.85327900	0.12234000
H	1.64821800	-2.73146200	-0.49022400
H	0.66286400	-0.46926700	-0.60679300
H	4.53108800	1.28140000	0.20781200
H	5.54233600	-0.98843200	0.32497100
O	4.18177900	-3.20248700	-0.02054800
C	0.72893100	2.20704600	-0.90056900
H	0.38577500	3.23196800	-0.96067600
H	0.19752500	1.45325500	-1.46492200
O	2.65193000	2.89381700	0.24504700

C	1.97680700	1.95451600	-0.28554400
O	-0.74582700	1.81400600	0.92657400
C	-1.76795700	1.06614300	0.62314500
C	-1.98127200	-0.19904900	1.25984700
C	-2.73157500	1.46832000	-0.35714800
C	-3.08082000	-0.98407400	0.96088800
H	-1.26063400	-0.53008800	2.00248800
C	-3.82692000	0.67970100	-0.66194400
H	-2.58867900	2.42002100	-0.86120000
C	-4.02209300	-0.55896400	-0.00608600
H	-3.22644300	-1.93477600	1.46566600
H	-4.54677900	1.00884000	-1.40570900
C	-5.14909200	-1.36592700	-0.31410400
N	-6.07926200	-2.03159500	-0.56806600

Geom 20:
Bond length: 2.43072

Energy: -858.14673

C	3.62620300	-2.06315100	-0.07385400
C	2.21781600	-1.84821100	-0.34781400
C	1.70081500	-0.57551600	-0.41961400
C	2.53324800	0.55883700	-0.22513200
C	3.91250600	0.36960200	0.06067500
C	4.45451900	-0.89072700	0.13016200
H	1.58887100	-2.72168900	-0.48943900
H	0.64220200	-0.44318500	-0.61244200
H	4.53676400	1.24294500	0.21374700
H	5.50950000	-1.04358400	0.33607500
O	4.11306500	-3.23441000	-0.01280000
C	0.76455200	2.23296600	-0.92947500
H	0.43656000	3.26295700	-0.98953600
H	0.21980500	1.48506900	-1.48914300
O	2.68199500	2.88594200	0.24313800
C	1.99779600	1.95802900	-0.29368600
O	-0.76798100	1.87729900	0.92343100
C	-1.77362000	1.10811000	0.62350400
C	-1.95393900	-0.16648800	1.25306800
C	-2.75392100	1.49398600	-0.34766100
C	-3.03626800	-0.97520300	0.95519500
H	-1.22073600	-0.48588900	1.98848900
C	-3.83260900	0.68231100	-0.65045900

H	-2.63606500	2.45215600	-0.84605700
C	-3.99397700	-0.56562300	-0.00254900
H	-3.15603300	-1.93275700	1.45376500
H	-4.56521000	0.99954100	-1.38694100
C	-5.10323100	-1.39684800	-0.30980500
N	-6.01880500	-2.08266500	-0.56342800

Geom 21:
Bond length: 2.48072

Energy: -858.14708607

C	3.57973300	-2.08399000	-0.06567400
C	2.17523000	-1.84771100	-0.34254200
C	1.67858700	-0.56723900	-0.42005100
C	2.52898400	0.55410600	-0.22835300
C	3.90439700	0.34420500	0.06170400
C	4.42631000	-0.92418300	0.13629400
H	1.53269100	-2.71160500	-0.48180500
H	0.62249300	-0.41892200	-0.61510500
H	4.54200500	1.20818600	0.21287700
H	5.47836300	-1.09307800	0.34453700
O	4.04780200	-3.26245400	-0.00037000
C	0.79552200	2.25588400	-0.95535700
H	0.48268300	3.29063400	-1.01666300
H	0.23706600	1.51352100	-1.50901200
O	2.71220700	2.87981700	0.23258800
C	2.01741200	1.96136200	-0.30522700
O	-0.79337000	1.93956600	0.92330100
C	-1.78249100	1.14949300	0.62656100
C	-1.91941800	-0.14111900	1.23524000
C	-2.78870000	1.52582400	-0.32237100
C	-2.98256300	-0.97445600	0.93672100
H	-1.16650900	-0.45389900	1.95338500
C	-3.84901000	0.69036200	-0.62471700
H	-2.70472300	2.49608400	-0.80405300
C	-3.96552900	-0.57411300	0.00063100
H	-3.06798300	-1.94451200	1.41784800
H	-4.60119100	1.00063400	-1.34424400
C	-5.05445600	-1.43099500	-0.30846400
N	-5.95315100	-2.13815200	-0.56404000

Geom 22:
Bond length: 2.53072

Energy: -858.14736

C	3.55389600	-2.09484600	-0.06001400
C	2.15466300	-1.84582400	-0.35245500
C	1.67055000	-0.56096100	-0.43608200
C	2.52909600	0.55253800	-0.23518400
C	3.89929200	0.33021800	0.07024900
C	4.40882200	-0.94271900	0.15099600
H	1.50585900	-2.70388000	-0.49849000
H	0.61803900	-0.40357400	-0.64292400
H	4.54291300	1.18845900	0.22832700
H	5.45691000	-1.12105900	0.37094900
O	4.01017200	-3.27742200	0.01080100
C	0.81873300	2.27178900	-0.97921400
H	0.51362600	3.30921400	-1.03711000
H	0.25051000	1.53367000	-1.52871200
O	2.73233100	2.87723100	0.22107300
C	2.03248700	1.96441700	-0.31822900
O	-0.80233500	1.95811200	0.93867800
C	-1.78503600	1.16273700	0.63856900
C	-1.90185600	-0.14048600	1.22528900
C	-2.80568500	1.54419600	-0.29347800
C	-2.95768200	-0.98088900	0.92119500
H	-1.13842800	-0.45736900	1.93041700
C	-3.85898100	0.70197700	-0.60080900
H	-2.73801800	2.52413300	-0.75788400
C	-3.95441800	-0.57538100	0.00186500
H	-3.02683600	-1.96075600	1.38474700
H	-4.62173800	1.01634500	-1.30733200
C	-5.03550000	-1.43966600	-0.31349600
N	-5.92778200	-2.15302000	-0.57451700

Geom 23:
Bond length: 2.58072
Energy: -858.14757

C	3.52876200	-2.10464900	-0.05414900
C	2.13729700	-1.84421800	-0.37280400
C	1.66454300	-0.55555700	-0.46274800
C	2.52753200	0.55085500	-0.24261400

C	3.88995100	0.31726000	0.08855800
C	4.38820500	-0.95957200	0.17615500
H	1.48499800	-2.69695200	-0.53361800
H	0.61739700	-0.39048900	-0.68966700
H	4.53676200	1.17024100	0.26122600
H	5.43046400	-1.14631900	0.41587000
O	3.97439800	-3.29075300	0.02231100
C	0.84062300	2.28618600	-1.00666800
H	0.54380400	3.32625500	-1.06327600
H	0.26417300	1.55240600	-1.55351900
O	2.74797300	2.87466800	0.20962300
C	2.04498000	1.96689400	-0.33263400
O	-0.81119100	1.97833700	0.95212500
C	-1.78709900	1.17673100	0.64962100
C	-1.88307800	-0.13758700	1.21601800
C	-2.82216400	1.56094800	-0.26587000
C	-2.93124300	-0.98580200	0.90763300
H	-1.10894100	-0.45678100	1.90831800
C	-3.86809200	0.71117900	-0.57690800
H	-2.77116000	2.54938100	-0.71419600
C	-3.94191200	-0.57744900	0.00473000
H	-2.98371100	-1.97428200	1.35482600
H	-4.64161000	1.02790700	-1.27058600
C	-5.01480400	-1.44993300	-0.31548700
N	-5.90037300	-2.17015600	-0.58069100

Geom 24:
Bond length: 2.63072
Energy: -858.14772

C	3.47729200	-2.12507400	-0.05151400
C	2.10430300	-1.84011300	-0.42461000
C	1.65496300	-0.54364800	-0.52152000
C	2.52441300	0.54770700	-0.25547500
C	3.86918500	0.28961500	0.12660000
C	4.34403200	-0.99537900	0.22311100
H	1.44640900	-2.68113000	-0.62044200
H	0.62052200	-0.36231300	-0.78989300
H	4.52129200	1.13090300	0.33307100
H	5.37277300	-1.20010100	0.50313500
O	3.90070300	-3.31856500	0.03289800
C	0.87646000	2.31707300	-1.03342300
H	0.59647700	3.36246500	-1.08096800
H	0.28611400	1.59724700	-1.58390100

O	2.78033900	2.86676600	0.20301200
C	2.06813400	1.97207900	-0.34772200
O	-0.79767700	1.98559600	0.96860000
C	-1.77222900	1.18467700	0.66306700
C	-1.85856300	-0.13824600	1.21171200
C	-2.81668800	1.57712700	-0.23876800
C	-2.90538200	-0.98652200	0.89947400
H	-1.07763000	-0.46378100	1.89336600
C	-3.86134200	0.72734200	-0.55334900
H	-2.77345800	2.57204000	-0.67342100
C	-3.92503000	-0.56989400	0.01040200
H	-2.94999200	-1.98155900	1.33278100
H	-4.64173500	1.05041200	-1.23634300
C	-4.99645200	-1.44248000	-0.31391400
N	-5.88089800	-2.16287800	-0.58255600

Geom 25:
Bond length: 2.68072
Geometry: -858.14791

C	2.60898600	-2.39654000	-0.09890600
C	1.73211000	-1.78755200	-1.08131600
C	1.62494700	-0.41956100	-1.17877900
C	2.37323100	0.43208700	-0.32345600
C	3.24695200	-0.14567500	0.63867900
C	3.36480000	-1.50809400	0.76214100
H	1.16815700	-2.44515000	-1.73563800
H	0.96858600	0.00511100	-1.92947400
H	3.81535700	0.51272300	1.28610900
H	4.02153600	-1.95499900	1.50225500
O	2.71024400	-3.65846500	0.00008600
C	1.20639100	2.54981200	-1.08534000
H	1.17166900	3.63359800	-1.09952700
H	0.43263700	2.00228700	-1.60467400
O	3.17836800	2.61695600	0.16553700
C	2.28401200	1.92311300	-0.40697200
O	-0.33848300	2.03423600	1.04393800
C	-1.34920600	1.28505800	0.73127700
C	-1.49006800	-0.04382500	1.25534400
C	-2.38196900	1.74372200	-0.15334300
C	-2.57921500	-0.83511000	0.93933500
H	-0.71933500	-0.41775800	1.92342100

C	-3.46821500	0.95025200	-0.47171700
H	-2.29448800	2.74316900	-0.57015600
C	-3.58650900	-0.35277300	0.06996400
H	-2.66690500	-1.83522400	1.35380900
H	-4.23943400	1.32150800	-1.14033300
C	-4.70227200	-1.16724900	-0.25749800
N	-5.62323800	-1.83901100	-0.52839400

Geom 26:
Bond length: 2.73072
Energy: -858.14804

C	2.37536800	-2.46463700	-0.11588900
C	1.56734200	-1.78237100	-1.10896000
C	1.57148300	-0.40971100	-1.20024500
C	2.36903500	0.37553700	-0.32671600
C	3.17926300	-0.27519400	0.64441200
C	3.18633300	-1.64315200	0.76134000
H	0.96419900	-2.38943100	-1.77704900
H	0.96438500	0.06941300	-1.95985000
H	3.78701700	0.33358000	1.30468400
H	3.79345600	-2.14429900	1.50908300
O	2.37146700	-3.73123500	-0.02112200
C	1.37455100	2.57544000	-1.08805200
H	1.41317900	3.65935800	-1.08913800
H	0.57039600	2.08622600	-1.61942000
O	3.32535400	2.49076000	0.19614700
C	2.39371900	1.86780800	-0.39710800
O	-0.21820200	2.02248000	1.06002200
C	-1.24941100	1.30627500	0.74171700
C	-1.42458000	-0.02589300	1.24873000
C	-2.27307200	1.80585500	-0.13207400
C	-2.53769300	-0.78127300	0.92885300
H	-0.66111300	-0.42995900	1.90738400
C	-3.38293800	1.04800500	-0.45404400
H	-2.15906000	2.80780000	-0.53618200
C	-3.53518200	-0.25819200	0.07193900
H	-2.65217800	-1.78391300	1.33039900
H	-4.14715300	1.44931000	-1.11320600
C	-4.67645000	-1.03539000	-0.25890300
N	-5.61838500	-1.67611000	-0.53244100

Geom 27:
Bond length: 2.78072

Energy: -858.14822

C	2.14132100	-2.52360100	-0.14855800
C	1.36869300	-1.75971900	-1.10913400
C	1.48754800	-0.39115300	-1.18476900
C	2.36896000	0.31388100	-0.32348500
C	3.14540600	-0.42015400	0.61653800
C	3.04197000	-1.78560100	0.71436900
H	0.69599700	-2.30233300	-1.76627400
H	0.89626500	0.14467500	-1.91797500
H	3.81948000	0.12356000	1.26918200
H	3.62583300	-2.34622600	1.43816300
O	2.02989200	-3.78706400	-0.06812400
C	1.59241500	2.59872200	-1.09617800
H	1.71173300	3.67620800	-1.05845500
H	0.79243600	2.19017000	-1.69780500
O	3.45000300	2.34286400	0.29358600
C	2.51056000	1.79866500	-0.36212400
O	-0.07733200	1.97826000	1.03909500
C	-1.13992200	1.30923800	0.72885800
C	-1.36440200	-0.01844100	1.23099000
C	-2.15204200	1.85840000	-0.12987300
C	-2.51306000	-0.72303700	0.92164500
H	-0.61049100	-0.45739500	1.87788400
C	-3.29699900	1.15094100	-0.44049900
H	-1.99946300	2.85677300	-0.52984200
C	-3.49721000	-0.15105600	0.08110200
H	-2.66623800	-1.72218600	1.31868600
H	-4.05248600	1.58763600	-1.08694800
C	-4.67585700	-0.87586500	-0.23883500
N	-5.64826400	-1.47295300	-0.50333500

Geom 28:
Bond length: 2.83072
Energy: -858.14838

C	2.08289500	-2.52915800	-0.15156800
C	1.33597200	-1.75310200	-1.12241200
C	1.48107900	-0.38705200	-1.19990600
C	2.36462700	0.30401800	-0.32979800
C	3.11650500	-0.44255400	0.62053500
C	2.98650100	-1.80551800	0.72014200
H	0.66145900	-2.28460300	-1.78677100
H	0.90855900	0.15780900	-1.94135600
H	3.79305000	0.08981900	1.28004100
H	3.55140700	-2.37486300	1.45217900
O	1.94758000	-3.79060400	-0.06989500
C	1.63610300	2.60126800	-1.11230700
H	1.77846400	3.67615900	-1.07844300
H	0.82557800	2.20776400	-1.71021700
O	3.48146200	2.31387700	0.28677100
C	2.53523600	1.78445700	-0.37094500
O	-0.02785600	1.92249700	1.07481700
C	-1.10370000	1.28143000	0.75445500
C	-1.34786500	-0.05658500	1.21957400
C	-2.11185200	1.87347700	-0.08079700
C	-2.50988200	-0.73239400	0.89611800
H	-0.59797500	-0.52654200	1.84899100
C	-3.27004600	1.19489000	-0.40489200
H	-1.94413400	2.88042900	-0.45206700
C	-3.48845300	-0.11901700	0.07877900
H	-2.67782500	-1.74016400	1.26420300
H	-4.02200700	1.66294400	-1.03320500
C	-4.68048600	-0.81463400	-0.25662600
N	-5.66369500	-1.38743700	-0.53414400

Geom 29:
Bond length: 2.88072
Energy: -858.14874

C	1.02816200	-2.62037600	-0.24951800
C	0.79716300	-1.66578000	-1.31504800
C	1.43472700	-0.44631900	-1.32638000
C	2.33599400	-0.08248300	-0.29189700
C	2.58858100	-1.01287200	0.75378400
C	1.95807100	-2.23247300	0.79125600
H	0.10895800	-1.94581000	-2.10692100
H	1.24114500	0.23854200	-2.14423300
H	3.27898200	-0.73297100	1.54220600
H	2.13913000	-2.93570100	1.59883900

O	0.44151300	-3.75022100	-0.23223600
C	2.51751100	2.32347600	-1.03824400
H	3.00331300	3.28900600	-0.94300000
H	1.68239700	2.23013400	-1.71915200
O	4.00931600	1.41260500	0.51091800
C	3.01184400	1.24095700	-0.25312200
O	0.47002400	1.96554500	0.95631200
C	-0.67812000	1.44898900	0.67526200
C	-1.15458400	0.26939100	1.34724500
C	-1.54198500	2.02904600	-0.31724300
C	-2.40274600	-0.25931900	1.07605600
H	-0.51426700	-0.18935800	2.09458400
C	-2.78576700	1.49546400	-0.58827600
H	-1.19524000	2.91101500	-0.84782500
C	-3.23676800	0.34524700	0.10663000
H	-2.75044800	-1.14248000	1.60333500
H	-3.42831100	1.95246800	-1.33482100
C	-4.52000600	-0.19800400	-0.17197500
N	-5.57784900	-0.64399200	-0.40202200

Geom 30:
Bond length: 2.93072
Energy: -858.14895

C	0.98950800	-2.61180400	-0.24798800
C	0.76885300	-1.65299200	-1.31177100
C	1.42659500	-0.44416400	-1.32612400
C	2.33891500	-0.09554400	-0.29627700
C	2.58053900	-1.02993900	0.74842500
C	1.92988300	-2.23884700	0.78878600
H	0.07266900	-1.92134800	-2.10071800
H	1.24087900	0.24330600	-2.14361800
H	3.27930200	-0.76167100	1.53356500
H	2.10312600	-2.94503400	1.59552000
O	0.38593500	-3.73288400	-0.22897300
C	2.56040700	2.30658600	-1.04563300
H	3.06877600	3.26117600	-0.95798900
H	1.71358800	2.23128200	-1.71445600
O	4.04536800	1.36850100	0.49339900
C	3.03920200	1.21462200	-0.26297100
O	0.47679200	1.95835000	0.98572600

C	-0.67149400	1.44909900	0.69495200
C	-1.15814300	0.26789900	1.35746100
C	-1.52621500	2.03901700	-0.30018800
C	-2.40674600	-0.25350400	1.07468300
H	-0.52501800	-0.19768000	2.10667500
C	-2.77033500	1.51270600	-0.58257500
H	-1.17149800	2.92222500	-0.82335400
C	-3.23111000	0.36046700	0.10291700
H	-2.76223800	-1.13792800	1.59454500
H	-3.40591500	1.97652500	-1.33086000
C	-4.51471800	-0.17564200	-0.18785400
N	-5.57275200	-0.61576400	-0.42794000

Phenol as a leaving group:

Geom 1:
Energy: -765.88607390

C	4.16179100	-1.16285900	-0.05917800
C	2.83965600	-1.59067600	-0.46214100
C	1.76274000	-0.73246100	-0.45571900
C	1.90666100	0.64700400	-0.06947100
C	3.21542200	1.07443600	0.35605700
C	4.29011700	0.21128500	0.35618900
H	2.71723200	-2.62809100	-0.76344000
H	0.78704400	-1.10823000	-0.74459500
H	3.33189900	2.10570900	0.66858600
H	5.27331700	0.55117500	0.67316700
O	5.16168100	-1.97577000	-0.06106700
C	-0.54503800	1.19455100	-0.58757700
H	-1.10390400	2.09570200	-0.86056500
H	-0.49898000	0.52272700	-1.45421300
O	0.98360100	2.80426300	0.36202000
C	0.80942700	1.59742700	-0.08728300
O	-1.27997500	0.49746700	0.47779700
C	-2.54364100	0.04654100	0.22138400
C	-3.17284200	-0.64673400	1.27191500
C	-3.22713900	0.23461300	-0.99055300
C	-4.46495300	-1.14189600	1.11112100
H	-2.63233900	-0.78536400	2.20349600
C	-4.52620500	-0.27101800	-1.13666500
H	-2.76815600	0.76633400	-1.81492800
C	-5.15365700	-0.95837200	-0.09648100
H	-4.93688500	-1.67448200	1.93222700
H	-5.04523400	-0.11906400	-2.07913400
H	-6.16048100	-1.34513700	-0.22019400

Geom 2:
Energy: -765.88532846

C	4.16179100	-1.16285900	-0.05917800
C	2.83965600	-1.59067600	-0.46214100
C	1.76274000	-0.73246100	-0.45571900

C	1.90666100	0.64700400	-0.06947100
C	3.21542200	1.07443600	0.35605700
C	4.29011700	0.21128500	0.35618900
H	2.71723200	-2.62809100	-0.76344000
H	0.78704400	-1.10823000	-0.74459500
H	3.33189900	2.10570900	0.66858600
H	5.27331700	0.55117500	0.67316700
O	5.16168100	-1.97577000	-0.06106700
C	-0.54503800	1.19455100	-0.58757700
H	-1.10390400	2.09570200	-0.86056500
H	-0.49898000	0.52272700	-1.45421300
O	0.98360100	2.80426300	0.36202000
C	0.80942700	1.59742700	-0.08728300
O	-1.27997500	0.49746700	0.47779700
C	-2.54364100	0.04654100	0.22138400
C	-3.17284200	-0.64673400	1.27191500
C	-3.22713900	0.23461300	-0.99055300
C	-4.46495300	-1.14189600	1.11112100
H	-2.63233900	-0.78536400	2.20349600
C	-4.52620500	-0.27101800	-1.13666500
H	-2.76815600	0.76633400	-1.81492800
C	-5.15365700	-0.95837200	-0.09648100
H	-4.93688500	-1.67448200	1.93222700
H	-5.04523400	-0.11906400	-2.07913400
H	-6.16048100	-1.34513700	-0.22019400

Geom 3:
Energy: -765.88365468

C	4.17183400	-1.17184800	-0.05212100
C	2.84978200	-1.59823400	-0.45813700
C	1.77698500	-0.73446500	-0.45982200
C	1.92583400	0.64317700	-0.08241200
C	3.22966200	1.06907100	0.34620500
C	4.30337700	0.20446600	0.35651900
H	2.72492600	-2.63681300	-0.75358400
H	0.80051500	-1.10789200	-0.74902500
H	3.34629200	2.10184300	0.65372000
H	5.28603900	0.54315400	0.67561700
O	5.16670600	-1.98566700	-0.04574800
C	-0.50669300	1.21852700	-0.62247100
H	-1.08459000	2.10446800	-0.89108900

H	-0.49069100	0.49918000	-1.44510800
O	1.00696600	2.79946200	0.37101700
C	0.82817100	1.60385200	-0.10969300
O	-1.31390300	0.51150600	0.52366500
C	-2.56467200	0.05564400	0.24405200
C	-3.21891800	-0.63505800	1.28454000
C	-3.22959200	0.23086700	-0.98276600
C	-4.50625000	-1.13489200	1.10078400
H	-2.69881400	-0.76744200	2.22875000
C	-4.52344900	-0.27975100	-1.15237200
H	-2.75778300	0.75910100	-1.80219000
C	-5.17167300	-0.96236700	-0.12141900
H	-4.99282700	-1.66358500	1.91612400
H	-5.02302300	-0.13522300	-2.10666500
H	-6.17458400	-1.35313200	-0.26335000

Geom 4:
Energy: -765.88159396

C	4.15741700	-1.19160900	-0.05576900
C	2.82852200	-1.60710600	-0.45174100
C	1.76587100	-0.73071900	-0.45287300
C	1.93293800	0.64541900	-0.08615300
C	3.24074700	1.06094300	0.33203000
C	4.30637800	0.18645900	0.34284800
H	2.69112300	-2.64621700	-0.73913200
H	0.78330200	-1.09461100	-0.73334500
H	3.36897000	2.09469800	0.63162100
H	5.29427400	0.51692800	0.65376300
O	5.14208800	-2.01426200	-0.04962700
C	-0.48574500	1.25589000	-0.62889100
H	-1.06939300	2.13930700	-0.88748300
H	-0.49153400	0.51864600	-1.43320700
O	1.03524500	2.80679200	0.38750500
C	0.84199600	1.62139600	-0.11298600
O	-1.33233100	0.54270500	0.55401200
C	-2.56974500	0.07077100	0.25974200
C	-3.22652100	-0.64318300	1.28492500
C	-3.22930000	0.24950600	-0.97122500
C	-4.50501200	-1.15885200	1.08334200
H	-2.71406200	-0.78042000	2.23272800
C	-4.51355900	-0.27787400	-1.15924700

H	-2.75898400	0.79557700	-1.77986400
C	-5.16207500	-0.98216000	-0.14280800
H	-4.99114500	-1.70423500	1.88806000
H	-5.00627200	-0.12900100	-2.11657100
H	-6.15777700	-1.38584600	-0.29885600

Geom 5:
Energy: -765.87958217 Hartrees

C	4.11939700	-1.22718700	-0.06805900
C	2.77850800	-1.61856800	-0.44938000
C	1.73486600	-0.71944700	-0.44548100
C	1.93502800	0.65227800	-0.08827400
C	3.25205200	1.04495600	0.31378800
C	4.30095700	0.15076500	0.32039400
H	2.61767100	-2.65627600	-0.72902200
H	0.74192300	-1.06336100	-0.71428800
H	3.40231500	2.07816300	0.60513800
H	5.29826600	0.46302700	0.61916200
O	5.08551200	-2.06775900	-0.06598800
C	-0.46434600	1.32273100	-0.62486700
H	-1.04769500	2.21020400	-0.86403900
H	-0.50099200	0.57428300	-1.41583800
O	1.08075900	2.82400900	0.41605400
C	0.85989600	1.65438100	-0.10800600
O	-1.35179300	0.60191300	0.59249300
C	-2.56745300	0.09782700	0.28063400
C	-3.20721300	-0.67500000	1.27574600
C	-3.23247700	0.29799900	-0.94611200
C	-4.46870900	-1.22235300	1.05104500
H	-2.69405300	-0.83121000	2.22036800
C	-4.49814600	-0.26313200	-1.15854300
H	-2.77878900	0.88991900	-1.73193900
C	-5.12779900	-1.02366000	-0.17069400
H	-4.93959100	-1.81118900	1.83410700
H	-4.99259800	-0.09542300	-2.11200600
H	-6.10965200	-1.45297600	-0.34525300

Geom 6:

Energy: -765.87792966 Hartrees

C	4.03012600	-1.29020500	-0.09666000
C	2.67152200	-1.62893400	-0.46780200
C	1.66462400	-0.68896600	-0.45156100
C	1.92239200	0.66972500	-0.09043100
C	3.25427300	1.01150500	0.30020100
C	4.26909200	0.07919000	0.29480900
H	2.46862900	-2.65846500	-0.74981100
H	0.65653800	-0.99160700	-0.71341000
H	3.44470400	2.03735400	0.59448500
H	5.28024500	0.35153000	0.58537900
O	4.96145300	-2.16529000	-0.10611700
C	-0.44615400	1.44423200	-0.60425800
H	-1.01649200	2.34685600	-0.80920500
H	-0.53465700	0.69424100	-1.38797800
O	1.15595200	2.86475600	0.44930800
C	0.88259300	1.71749900	-0.09480500
O	-1.37209300	0.71661900	0.64946800
C	-2.54739500	0.14700500	0.31575100
C	-3.10955400	-0.76592500	1.23849700
C	-3.25612600	0.41360900	-0.87560800
C	-4.33497100	-1.37825500	0.98168400
H	-2.56546500	-0.97615500	2.15505700
C	-4.48181100	-0.21598500	-1.12356600
H	-2.86421200	1.11495400	-1.60317600
C	-5.03383800	-1.11239200	-0.20461400
H	-4.74539300	-2.07248400	1.71078900
H	-5.00892000	0.00641300	-2.04806400
H	-5.98612100	-1.59392500	-0.40516600

Geom 7:
Energy: -765.87687198 Hartrees

C	3.95108200	-1.34271600	-0.11282500
C	2.57349200	-1.64387400	-0.44720900
C	1.59950300	-0.67003000	-0.42446400
C	1.91164100	0.68247300	-0.09230400
C	3.26000500	0.98890600	0.26109100
C	4.24458600	0.02541500	0.24923700
H	2.33118000	-2.67077000	-0.70624600
H	0.57549600	-0.94128500	-0.65719000
H	3.48845900	2.01312700	0.53340200
H	5.27074000	0.26864000	0.51104500

O	4.85181100	-2.24551700	-0.12820900
C	-0.42627100	1.53957600	-0.59445200
H	-0.98752900	2.45125700	-0.77716800
H	-0.55586600	0.78173600	-1.36316000
O	1.21936000	2.89670200	0.46316900
C	0.90173700	1.76752900	-0.08812400
O	-1.39551700	0.81502800	0.69733300
C	-2.53137600	0.18945500	0.34635200
C	-3.03150500	-0.81290200	1.21262300
C	-3.26977700	0.48329500	-0.82296800
C	-4.22267200	-1.47863200	0.92692000
H	-2.46764700	-1.04732300	2.11140300
C	-4.45771600	-0.20132500	-1.10266200
H	-2.92608700	1.25270900	-1.50553000
C	-4.94776500	-1.18333500	-0.23643500
H	-4.58495500	-2.23890200	1.61473100
H	-5.00651300	0.04522000	-2.00840000
H	-5.87230400	-1.70711700	-0.45991600

Geom 8:
Energy: -765.87638027 Hartrees

C	3.80919700	-1.42252900	-0.12916100
C	2.40231400	-1.66414800	-0.38247300
C	1.48318700	-0.63859500	-0.35361500
C	1.88298000	0.70483800	-0.09424400
C	3.25922900	0.95529600	0.17952500
C	4.19199600	-0.05749700	0.15988600
H	2.09524700	-2.68633400	-0.58445200
H	0.43492600	-0.86041900	-0.52131800
H	3.55311100	1.97604900	0.39697500
H	5.24150600	0.14023300	0.35922800
O	4.65978900	-2.36932800	-0.15029800
C	-0.40725700	1.67764600	-0.58011500
H	-0.94671300	2.60545900	-0.73977000
H	-0.59036000	0.91470300	-1.33129700
O	1.30590900	2.94906400	0.46656400
C	0.92436800	1.84273000	-0.08220100
O	-1.42811800	0.97580900	0.75326100
C	-2.49668300	0.25879800	0.38319100
C	-2.88411100	-0.84844000	1.17855400
C	-3.28119400	0.55721700	-0.75724500
C	-4.01183500	-1.60415400	0.85832500
H	-2.28548700	-1.09024000	2.05280700
C	-4.40077200	-0.21804000	-1.07529000

H	-3.02099500	1.40509100	-1.38279200
C	-4.78025600	-1.30098900	-0.27473500
H	-4.28914200	-2.44185100	1.49394600
H	-4.98588600	0.03538300	-1.95623100
H	-5.65381200	-1.89523600	-0.52572900

Geom 9:
Energy: -765.87642591 Hartrees

C	3.72362500	-1.46464300	-0.13441300
C	2.30350700	-1.67023600	-0.34562800
C	1.41736200	-0.61621400	-0.31784800
C	1.86530700	0.71777000	-0.09891400
C	3.25338900	0.93470600	0.13376500
C	4.15547300	-0.10487200	0.11297400
H	1.96182700	-2.68715100	-0.51555900
H	0.35839600	-0.80710700	-0.45305600
H	3.58237800	1.95074100	0.32137400
H	5.21536800	0.06485900	0.27981700
O	4.54432600	-2.43493400	-0.15602800
C	-0.39085800	1.75950200	-0.58623800
H	-0.92132700	2.69423300	-0.72868200
H	-0.60902100	0.98941000	-1.31917000
O	1.35408700	2.97578200	0.46267700
C	0.93717800	1.88626600	-0.08547200
O	-1.45718600	1.06944600	0.78631500
C	-2.47897600	0.29814700	0.40884300
C	-2.78141300	-0.87247200	1.15114700
C	-3.30392000	0.59875100	-0.70459800
C	-3.86508100	-1.68217900	0.80983100
H	-2.15364700	-1.11918000	2.00350900
C	-4.37669100	-0.22962100	-1.04585900
H	-3.10603600	1.49295800	-1.28794500
C	-4.67179000	-1.37365700	-0.29484500
H	-4.07734400	-2.56673000	1.40601200
H	-4.99301000	0.02822900	-1.90409400
H	-5.51007200	-2.01009000	-0.56238900

Geom 10:
Energy: -765.87685288 Hartrees

C	3.61102000	-1.51668300	-0.13152700
C	2.18131000	-1.67378100	-0.32229800

C	1.33544100	-0.58717400	-0.30082700
C	1.83592100	0.73065600	-0.10615200
C	3.23257800	0.90154800	0.10733700
C	4.09629100	-0.16970000	0.09070800
H	1.80127000	-2.67999700	-0.47277200
H	0.26846900	-0.73961700	-0.42146500
H	3.60028100	1.90749500	0.27713800
H	5.16365800	-0.03692900	0.24193800
O	4.39479900	-2.51517600	-0.14955700
C	-0.37124500	1.85889100	-0.61531400
H	-0.88025900	2.80565200	-0.75079000
H	-0.62597800	1.08222600	-1.32790700
O	1.40490200	3.00465700	0.45059700
C	0.94952000	1.93560500	-0.09882700
O	-1.50372400	1.21039100	0.79308100
C	-2.45795800	0.35983900	0.42329500
C	-2.66887200	-0.83635000	1.15926500
C	-3.30576600	0.59693900	-0.69064600
C	-3.68562700	-1.72723700	0.81352500
H	-2.02475600	-1.03740300	2.01152800
C	-4.30953000	-0.31102600	-1.03679900
H	-3.17411800	1.50703700	-1.26894500
C	-4.51389500	-1.47843400	-0.29030800
H	-3.82819200	-2.62854600	1.40551300
H	-4.94400000	-0.09959000	-1.89462200
H	-5.29931100	-2.17786000	-0.56117300

Geom 11:
Energy: -765.87753698 Hartrees

C	3.52591400	-1.55009900	-0.12987400
C	2.09147000	-1.67108400	-0.31468000
C	1.27531300	-0.56204600	-0.29938300
C	1.81222100	0.74196000	-0.11444100
C	3.21291800	0.87870800	0.09311000
C	4.04833500	-0.21443600	0.08082700
H	1.68466000	-2.66804200	-0.45613900
H	0.20421500	-0.68643200	-0.41567400
H	3.60711300	1.87591500	0.25534400
H	5.11942000	-0.10947100	0.22700900
O	4.28246000	-2.56797200	-0.14359100
C	-0.35409200	1.93417700	-0.64574800
H	-0.85202500	2.88800200	-0.76744500

H	-0.63671300	1.15489000	-1.34365800
O	1.43636900	3.02280200	0.44746500
C	0.95690700	1.97240300	-0.11010500
O	-1.54154900	1.30497700	0.79480700
C	-2.44239700	0.40018600	0.43374000
C	-2.56725400	-0.81972200	1.15295700
C	-3.32113700	0.59713100	-0.66605300
C	-3.53097500	-1.76780800	0.80750200
H	-1.89909000	-0.99246700	1.99301000
C	-4.27094800	-0.36635400	-1.01210000
H	-3.25058300	1.52181500	-1.23256900
C	-4.39008400	-1.55546300	-0.28034900
H	-3.60824200	-2.68515900	1.38699400
H	-4.93002100	-0.18382300	-1.85801700
H	-5.13410700	-2.29900500	-0.55071600

Geom 12:
Energy: -765.87835337 Hartrees

C	3.48734800	-1.56601500	-0.12931900
C	2.05012700	-1.66881400	-0.30607000
C	1.24984700	-0.54838300	-0.29450100
C	1.80630600	0.74808400	-0.11876700
C	3.20930200	0.86810900	0.08035800
C	4.02987700	-0.23591600	0.06989200
H	1.62915400	-2.66105900	-0.43864800
H	0.17646500	-0.65780000	-0.40459600
H	3.61765600	1.86092400	0.23469300
H	5.10315000	-0.14517900	0.20897400
O	4.22956400	-2.59328300	-0.14045600
C	-0.33410600	1.97433900	-0.66907300
H	-0.83376000	2.92870300	-0.77452800
H	-0.63289600	1.19156400	-1.35527900
O	1.45470100	3.02890600	0.45380200
C	0.96654300	1.99140100	-0.11406000
O	-1.56364300	1.33973200	0.80271500
C	-2.43895200	0.41516200	0.44244700
C	-2.51765900	-0.82309000	1.13948600
C	-3.34067500	0.60404800	-0.64201100
C	-3.45803800	-1.79268500	0.79001800
H	-1.83267500	-0.99144300	1.96690100
C	-4.26684600	-0.38004900	-0.99205000
H	-3.30309100	1.54038100	-1.19271200
C	-4.33969400	-1.58586500	-0.28088900

H	-3.49997600	-2.72256600	1.35304700
H	-4.94362900	-0.20229100	-1.82496800
H	-5.06565000	-2.34604500	-0.55412900

Geom 13:
Energy: -765.87921030 Hartrees

C	3.46716400	-1.57567700	-0.12839500
C	2.02936400	-1.66639600	-0.30921500
C	1.23917000	-0.53899300	-0.30134800
C	1.80667900	0.75194900	-0.12294800
C	3.20975100	0.86081800	0.07971600
C	4.02104400	-0.24984300	0.07137900
H	1.60031300	-2.65510600	-0.44208500
H	0.16520700	-0.63865200	-0.41475700
H	3.62603600	1.85021600	0.23507400
H	5.09473400	-0.16842200	0.21269500
O	4.20042400	-2.60856400	-0.13709500
C	-0.31300600	2.00126500	-0.69378300
H	-0.81758200	2.95418200	-0.78468700
H	-0.62383200	1.21419200	-1.36876200
O	1.46736300	3.03135000	0.45965800
C	0.97698100	2.00337400	-0.11841000
O	-1.58008000	1.35600300	0.81064900
C	-2.44035600	0.42236400	0.45023900
C	-2.48998300	-0.82937300	1.12854400
C	-3.36028800	0.61067300	-0.62085700
C	-3.41798400	-1.80931700	0.77573100
H	-1.79225800	-0.99862200	1.94510300
C	-4.27399600	-0.38318800	-0.97402800
H	-3.34373400	1.55558000	-1.15799700
C	-4.31707900	-1.60117500	-0.28050400
H	-3.43723300	-2.74835000	1.32469900
H	-4.96444500	-0.20485400	-1.79557500
H	-5.03363300	-2.36937000	-0.55613100

Geom 14:
Energy: -765.88005752 Hartrees

C	3.45518900	-1.58038700	-0.12704000
C	2.01878200	-1.66222000	-0.32393100
C	1.23525800	-0.53033600	-0.32046100

C	1.80801100	0.75611100	-0.12849000
C	3.20919000	0.85659400	0.08952200
C	4.01449000	-0.25828400	0.08447800
H	1.58562100	-2.64790200	-0.46553600
H	0.16217000	-0.62350100	-0.44646000
H	3.62911400	1.84299600	0.25406000
H	5.08706800	-0.18358100	0.23730900
O	4.18271100	-2.61677800	-0.13264300
C	-0.29397100	2.02192400	-0.72148300
H	-0.80430200	2.97256300	-0.80083400
H	-0.61544200	1.22914100	-1.38390100
O	1.47479100	3.03462900	0.46034100
C	0.98553400	2.01313600	-0.12587700
O	-1.59578500	1.36615800	0.81796800
C	-2.44392700	0.42575600	0.45853700
C	-2.45696400	-0.84322100	1.10894800
C	-3.39245000	0.62015200	-0.58818800
C	-3.37519400	-1.83129900	0.75455700
H	-1.73845000	-1.01806900	1.90603300
C	-4.29668700	-0.38112000	-0.94256000
H	-3.40291100	1.57681000	-1.10443200
C	-4.30225800	-1.61525500	-0.27586800
H	-3.36581900	-2.78279200	1.28191500
H	-5.00916700	-0.19733000	-1.74385600
H	-5.01163400	-2.38971800	-0.55248800

Geom 15:
Energy: -765.88087636 Hartrees

C	3.43678600	-1.58781700	-0.12513400
C	2.00389500	-1.65686600	-0.35105200
C	1.22905100	-0.51918600	-0.35284700
C	1.80674000	0.76089300	-0.13546300
C	3.20400900	0.84883600	0.11048900
C	4.00131100	-0.27168300	0.11001000
H	1.56621700	-2.63783800	-0.51034100
H	0.15825600	-0.60389600	-0.50150900
H	3.62758500	1.83056900	0.29284400
H	5.07123300	-0.20627400	0.28420500
O	4.15685400	-2.62907400	-0.12679900
C	-0.27379000	2.04705800	-0.75325000
H	-0.78692500	2.99683400	-0.82256700
H	-0.60677200	1.24999700	-1.40405800
O	1.48306100	3.03961700	0.45909500

C	0.99444300	2.02477200	-0.13569900
O	-1.61308700	1.38375500	0.82011600
C	-2.44573400	0.43257500	0.46515500
C	-2.42184400	-0.84741900	1.09666500
C	-3.41884200	0.62247900	-0.56167900
C	-3.32679200	-1.84785200	0.74464400
H	-1.68496600	-1.01951200	1.87734500
C	-4.31008700	-0.39056100	-0.91292500
H	-3.45599100	1.58596200	-1.06387100
C	-4.27826400	-1.63438300	-0.26424300
H	-3.28899600	-2.80691800	1.25672500
H	-5.04174500	-0.20990200	-1.69744700
H	-4.97781400	-2.41848200	-0.53864400

Geom 16:
Energy: -765.88166393 Hartrees

C	3.36308900	-1.61765500	-0.12526100
C	1.94845700	-1.64240800	-0.45229600
C	1.20055900	-0.48706500	-0.46297300
C	1.78711100	0.76983500	-0.15306300
C	3.16622600	0.81365900	0.18826400
C	3.93750200	-0.32488300	0.19891100
H	1.50121600	-2.60533400	-0.68023400
H	0.14207900	-0.54344100	-0.69049400
H	3.59689800	1.77790600	0.43565300
H	4.99395500	-0.29134000	0.44840900
O	4.05895400	-2.67521800	-0.11801600
C	-0.24365700	2.11476100	-0.80537300
H	-0.74448200	3.07213200	-0.85815700
H	-0.59770200	1.32639900	-1.45481200
O	1.50239400	3.04961800	0.46197200
C	1.00664000	2.05307300	-0.15454700
O	-1.62907000	1.44513600	0.79491000
C	-2.42611300	0.46062900	0.46497800
C	-2.36949900	-0.79968500	1.13675100
C	-3.39643400	0.58928600	-0.57633500
C	-3.23972400	-1.83689200	0.80782200
H	-1.63382100	-0.92490300	1.92743100
C	-4.25265200	-0.46035800	-0.90289600
H	-3.45635100	1.53550500	-1.10815300
C	-4.18799700	-1.68250600	-0.21545700
H	-3.17810500	-2.77875700	1.34851500

H	-4.98236100	-0.32748300	-1.69859500
H	-4.86060800	-2.49572900	-0.47165400

Geom 17:
Energy: -765.88248976 Hartrees

C	3.30661400	-1.63554200	-0.12987400
C	1.94314200	-1.60577600	-0.62704700
C	1.21688500	-0.43688300	-0.64842100
C	1.77272900	0.78541300	-0.18140900
C	3.10287500	0.77473600	0.31964900
C	3.85213400	-0.37831700	0.34669000
H	1.51352400	-2.54043400	-0.97528100
H	0.19530500	-0.46107200	-1.00965500
H	3.51429000	1.71118900	0.68058800
H	4.87079400	-0.38184800	0.72363600
O	3.98291800	-2.70635800	-0.10941200
C	-0.21699600	2.17466400	-0.85893700
H	-0.71940100	3.13280000	-0.87793800
H	-0.59029400	1.39850500	-1.51124000
O	1.50925300	3.06288800	0.46047000
C	1.01826300	2.08098100	-0.18022200
O	-1.57472900	1.41980200	0.79633400
C	-2.38042400	0.44588000	0.48039700
C	-2.30587800	-0.82591900	1.13464300
C	-3.38491100	0.59284700	-0.52948700
C	-3.18936900	-1.85400800	0.81990100
H	-1.54391000	-0.96282700	1.89768100
C	-4.25484800	-0.44808000	-0.83988900
H	-3.45619400	1.54661000	-1.04571400
C	-4.17072300	-1.67975700	-0.16967700
H	-3.11500300	-2.80424300	1.34358000
H	-5.01076700	-0.30398700	-1.60838200
H	-4.85483300	-2.48678900	-0.41429800

Geom 18:
Energy: -765.88437447 Hartrees

C	3.16117800	-1.68217100	-0.14444700
C	1.92506700	-1.52430000	-0.88616700
C	1.25284000	-0.32299400	-0.91328000
C	1.73705400	0.81491100	-0.21143900

C	2.94868400	0.67929200	0.51974900
C	3.64014100	-0.50941300	0.56143800
H	1.54395800	-2.38977500	-1.42065700
H	0.32991800	-0.25924300	-1.47808900
H	3.31597100	1.54992500	1.05262900
H	4.56436500	-0.60326000	1.12492400
O	3.78686500	-2.78535300	-0.11367600
C	-0.17470300	2.29504400	-0.91042600
H	-0.66100400	3.26186100	-0.88304900
H	-0.57891200	1.54784400	-1.57711200
O	1.53548000	3.08641200	0.48134100
C	1.04011600	2.13530300	-0.19902500
O	-1.50875900	1.43094200	0.77963600
C	-2.29925500	0.44728800	0.49146800
C	-2.20028600	-0.81512800	1.16982300
C	-3.31705200	0.56637700	-0.51475600
C	-3.06905500	-1.85851900	0.87713400
H	-1.42956400	-0.92613500	1.92768600
C	-4.17298900	-0.48996200	-0.79851900
H	-3.40426400	1.51168000	-1.04311900
C	-4.06111200	-1.70998000	-0.10798900
H	-2.97873400	-2.80056600	1.41206800
H	-4.93919500	-0.37224400	-1.56067600
H	-4.73500000	-2.53058800	-0.33439200

Geom 19:
Energy: -765.88454213 Hartrees

C	3.08624000	-1.71964000	-0.15468700
C	1.89474800	-1.50045300	-0.94962200
C	1.25730800	-0.27943800	-0.97140100
C	1.73429100	0.82398100	-0.21206500
C	2.90393800	0.62781600	0.57167400
C	3.55888200	-0.58209500	0.60946900
H	1.51629600	-2.33597100	-1.53199300
H	0.36736100	-0.17358800	-1.58147200
H	3.27014400	1.46920100	1.15076400
H	4.45062000	-0.71803300	1.21562300
O	3.68030700	-2.84233200	-0.12773200
C	-0.12064300	2.36138000	-0.93043100
H	-0.59296200	3.33468400	-0.88344500
H	-0.53919300	1.63031700	-1.60619900
O	1.57351400	3.09095400	0.51085100

C	1.07564500	2.15804400	-0.19183300
O	-1.50140100	1.45092000	0.76714400
C	-2.27878700	0.46187100	0.49038100
C	-2.17809600	-0.79004100	1.19456500
C	-3.28720500	0.55823900	-0.53227500
C	-3.03343000	-1.84329400	0.90742500
H	-1.41552900	-0.87990300	1.96297600
C	-4.13029200	-0.50801800	-0.80711000
H	-3.37303000	1.49465000	-1.07590200
C	-4.01441100	-1.71570100	-0.09335700
H	-2.94439200	-2.77671100	1.45684900
H	-4.88896600	-0.41159100	-1.57926600
H	-4.67882900	-2.54529500	-0.31444300

Geom 20:
Energy: -765.88558920 Hartrees

C	3.06288900	-1.74267700	-0.15876300
C	1.88622600	-1.49597300	-0.96577600
C	1.26661000	-0.26502600	-0.98413000
C	1.74766100	0.82535200	-0.20862400
C	2.90316100	0.60145400	0.58827600
C	3.53967800	-0.61893000	0.62205900
H	1.50209200	-2.31899800	-1.56245500
H	0.38689200	-0.14176700	-1.60610700
H	3.27544600	1.43035200	1.18174500
H	4.42131900	-0.77238400	1.23911600
O	3.64165800	-2.87519100	-0.13524400
C	-0.07223900	2.39450000	-0.94345400
H	-0.53561300	3.37187200	-0.88794500
H	-0.49839500	1.67150000	-1.62335600
O	1.60519800	3.08889400	0.53208000
C	1.10977600	2.16491400	-0.18392700
O	-1.51430100	1.45884800	0.75998700
C	-2.28787400	0.47193900	0.48853000
C	-2.19903800	-0.77227000	1.21326300
C	-3.28304900	0.55810900	-0.55178200
C	-3.05007300	-1.82676700	0.92595900
H	-1.44764500	-0.85108300	1.99352100
C	-4.12222600	-0.50960000	-0.82430700
H	-3.35773400	1.48819800	-1.10737400
C	-4.01598700	-1.70829300	-0.09198700
H	-2.97205500	-2.75409600	1.48674700

H	-4.86994500	-0.42444100	-1.60803300
H	-4.67790200	-2.53995700	-0.31245600

Geom 21:
Energy: -765.88656523 Hartrees

C	3.04603200	-1.76491700	-0.16105000
C	1.87745700	-1.49671300	-0.97152100
C	1.27428000	-0.25700700	-0.98725100
C	1.76484400	0.82430300	-0.20494600
C	2.91278300	0.57880600	0.59627500
C	3.53260200	-0.65074200	0.62659700
H	1.48382900	-2.31078000	-1.57458500
H	0.39939200	-0.12028200	-1.61358300
H	3.29473700	1.39868500	1.19645300
H	4.40936800	-0.81772400	1.24741400
O	3.61033900	-2.90621600	-0.14007000
C	-0.02331200	2.42231800	-0.95368000
H	-0.47678200	3.40420300	-0.89278100
H	-0.45704200	1.70654300	-1.63667800
O	1.64036700	3.08497900	0.55002400
C	1.14552000	2.16908100	-0.17675100
O	-1.53486400	1.47098100	0.75259500
C	-2.30401900	0.48454200	0.48553700
C	-2.22800400	-0.75033000	1.23174600
C	-3.28367000	0.55783500	-0.57346600
C	-3.07398500	-1.80724000	0.94473300
H	-1.48937800	-0.81680700	2.02504600
C	-4.11797300	-0.51250100	-0.84390600
H	-3.34710200	1.48046000	-1.14249900
C	-4.02287800	-1.70075500	-0.09163500
H	-3.00729900	-2.72723500	1.51854100
H	-4.85300600	-0.43993400	-1.64053400
H	-4.68152800	-2.53516500	-0.31127500

Geom 22:
Energy: -765.88745030 Hartrees

C	2.97500500	-1.80893400	-0.16680700
C	1.83046100	-1.49407300	-0.99368900
C	1.26527400	-0.23612600	-1.00468800

C	1.77371300	0.82128700	-0.20152700
C	2.89918300	0.52999300	0.61592200
C	3.48051900	-0.71871100	0.64159500
H	1.42178400	-2.28763400	-1.61400000
H	0.40627900	-0.06630200	-1.64503200
H	3.29653800	1.33009400	1.23285500
H	4.34092200	-0.91879100	1.27562100
O	3.50376300	-2.96827400	-0.14906600
C	0.04855800	2.48007900	-0.96488700
H	-0.37905800	3.47329800	-0.89715800
H	-0.39982800	1.78270000	-1.65759200
O	1.70096400	3.07651800	0.57754300
C	1.19499500	2.18140100	-0.16737500
O	-1.56423500	1.52764700	0.72107900
C	-2.30881500	0.52171900	0.47150800
C	-2.23169100	-0.68522900	1.26499700
C	-3.26260500	0.54096900	-0.61542000
C	-3.05130900	-1.76562000	0.99400600
H	-1.51269900	-0.70933800	2.07837000
C	-4.07050500	-0.55246700	-0.86824200
H	-3.32556500	1.44187800	-1.21822400
C	-3.97424800	-1.71127100	-0.07039400
H	-2.98527100	-2.66395500	1.60100000
H	-4.78545800	-0.52273600	-1.68545100
H	-4.61278800	-2.56444300	-0.27683400

Geom 23:
Energy: -765.88825040 Hartrees

C	2.88540900	-1.85358000	-0.17483000
C	1.79299100	-1.47853300	-1.04527300
C	1.27097300	-0.20176500	-1.04985100
C	1.77661400	0.81862800	-0.19845000
C	2.85162200	0.46793400	0.66232800
C	3.38772000	-0.80116800	0.68369800
H	1.38791100	-2.24168700	-1.70502500
H	0.45062200	0.01293700	-1.72661100
H	3.24634900	1.23813500	1.31796900
H	4.20882800	-1.04650100	1.35310000
O	3.37345200	-3.03131200	-0.16203600
C	0.12717400	2.54462900	-0.97855100
H	-0.27178500	3.54930600	-0.90234700
H	-0.33532200	1.86928300	-1.68388100

O	1.76035800	3.06489600	0.61058400
C	1.24466100	2.19581600	-0.15824500
O	-1.59190200	1.59321800	0.67819600
C	-2.30538700	0.56203000	0.45237700
C	-2.20863600	-0.61653100	1.28745500
C	-3.24402700	0.52121600	-0.64858300
C	-2.99576500	-1.72565100	1.04067100
H	-1.50094200	-0.59463900	2.11067000
C	-4.01950400	-0.60015500	-0.87580400
H	-3.32024300	1.40021200	-1.28141800
C	-3.90443300	-1.72912600	-0.03791700
H	-2.91610200	-2.60216000	1.67707800
H	-4.72312900	-0.61686200	-1.70303700
H	-4.51793100	-2.60491800	-0.22460200

Geom 24:
Energy: -765.88896209 Hartrees

C	2.90713200	-1.85380000	-0.16883800
C	1.80986500	-1.48293200	-1.03439800
C	1.28653300	-0.20649000	-1.04204400
C	1.79594600	0.81897100	-0.19877300
C	2.87579700	0.47219200	0.65741400
C	3.41292300	-0.79662200	0.68143600
H	1.40119900	-2.24904100	-1.68861200
H	0.46250000	0.00390200	-1.71587200
H	3.27412600	1.24525400	1.30759800
H	4.23803900	-1.03766500	1.34759300
O	3.39644800	-3.03156500	-0.15305700
C	0.14364300	2.54120900	-0.98195300
H	-0.25298000	3.54725700	-0.91061800
H	-0.32687700	1.86032100	-1.67675900
O	1.78067300	3.06933800	0.60000400
C	1.26381300	2.19490600	-0.16234300
O	-1.65542500	1.61376600	0.68175600
C	-2.35009200	0.57245500	0.45460300
C	-2.23626900	-0.60511100	1.29089000
C	-3.28408900	0.51622400	-0.65119000
C	-3.00163800	-1.72748500	1.03931800
H	-1.53299000	-0.57033000	2.11736600
C	-4.03772900	-0.61832500	-0.88243300
H	-3.37226900	1.39448500	-1.28341900
C	-3.90512200	-1.74565200	-0.04412900

H	-2.90971700	-2.60335600	1.67479800
H	-4.73724600	-0.64804500	-1.71267000
H	-4.50163200	-2.63233000	-0.23438400

Geom 25:
Energy: -765.88959630 Hartrees

C	2.93068900	-1.85145200	-0.16404500
C	1.83250100	-1.48477500	-1.02984600
C	1.30599200	-0.20954500	-1.04044300
C	1.81318700	0.81972900	-0.20025100
C	2.89433500	0.47705400	0.65594600
C	3.43420500	-0.79063900	0.68287000
H	1.42522000	-2.25308200	-1.68243200
H	0.48167500	-0.00292900	-1.71521800
H	3.29176300	1.25237000	1.30406100
H	4.26021900	-1.02776400	1.34941300
O	3.42277500	-3.02839100	-0.14514400
C	0.15522000	2.53542300	-0.98596600
H	-0.24043200	3.54232600	-0.91986000
H	-0.32312700	1.84772500	-1.66881200
O	1.79696400	3.07439800	0.58695900
C	1.27943600	2.19411800	-0.16827900
O	-1.68860900	1.60898400	0.70850600
C	-2.38031500	0.57028900	0.46790500
C	-2.25836900	-0.62116600	1.28443300
C	-3.31934700	0.52938500	-0.63533500
C	-3.01950800	-1.74205800	1.01630600
H	-1.55226100	-0.59692900	2.10881700
C	-4.06857400	-0.60409800	-0.88298400
H	-3.41328500	1.41812500	-1.25183200
C	-3.92705200	-1.74508200	-0.06433300
H	-2.92175000	-2.62854500	1.63589000
H	-4.77126400	-0.62322800	-1.71077800
H	-4.52020500	-2.63109700	-0.26767100

Geom 26:
Energy: -765.89015720 Hartrees

C	2.94985800	-1.85303900	-0.15968000

C	1.84684100	-1.48962600	-1.02042900
C	1.32036600	-0.21434200	-1.03366200
C	1.83241300	0.81900100	-0.20119000
C	2.91847500	0.47944500	0.65002900
C	3.45822600	-0.78831500	0.67928300
H	1.43540200	-2.26049300	-1.66742700
H	0.49234800	-0.01083200	-1.70493600
H	3.32023700	1.25731500	1.29244600
H	4.28818200	-1.02231600	1.34208900
O	3.44205100	-3.03016800	-0.13830700
C	0.17190900	2.53183800	-0.98762300
H	-0.21988700	3.54072700	-0.92723700
H	-0.31552200	1.83893500	-1.65883600
O	1.82193300	3.07815200	0.57381300
C	1.30033600	2.19325900	-0.17328700
O	-1.72022600	1.60579900	0.73313700
C	-2.41004000	0.57017600	0.47975400
C	-2.28182900	-0.63390600	1.27767000
C	-3.35374400	0.54433100	-0.62080600
C	-3.04043500	-1.75235600	0.99438600
H	-1.57299700	-0.62014800	2.09991200
C	-4.10025700	-0.58710900	-0.88354600
H	-3.45215000	1.44260800	-1.22255700
C	-3.95185700	-1.74051200	-0.08328300
H	-2.93822400	-2.64843800	1.59918600
H	-4.80598700	-0.59568100	-1.70886800
H	-4.54303800	-2.62500200	-0.29860700

Geom 27:
Energy: -765.89005537 Hartrees

C	2.93481100	-1.87734600	-0.16059900
C	1.85134400	-1.48962800	-1.03814100
C	1.34257300	-0.20562500	-1.04942400
C	1.85386100	0.81459300	-0.19956200
C	2.92038800	0.45256300	0.66742000
C	3.44236900	-0.82403300	0.69624900
H	1.44071400	-2.24893900	-1.69942300
H	0.53006500	0.01526000	-1.73437500
H	3.32200800	1.21949800	1.32311600
H	4.25693800	-1.07439800	1.37224300
O	3.41366000	-3.06994000	-0.13983200
C	0.22037100	2.55365200	-1.00107500

H	-0.15887300	3.56759500	-0.94360500
H	-0.27232800	1.86631600	-1.67480600
O	1.87165000	3.08737700	0.59503400
C	1.34023200	2.19867000	-0.17102900
O	-1.73486800	1.62501000	0.72748100
C	-2.42849600	0.58259000	0.47559000
C	-2.30953100	-0.61755000	1.28521500
C	-3.36558800	0.54857700	-0.63354700
C	-3.06881900	-1.73631000	1.00506500
H	-1.60711000	-0.59878200	2.11283600
C	-4.11241300	-0.58365600	-0.89205100
H	-3.45729800	1.44181600	-1.24376000
C	-3.97238100	-1.73085200	-0.08019600
H	-2.97385300	-2.62782900	1.61779300
H	-4.81198400	-0.59826400	-1.72255200
H	-4.56413800	-2.61572800	-0.29241300

Geom 28:
Energy: -765.891166206 Hartrees

C	3.01846200	-1.88999000	-0.15853900
C	1.95137700	-1.48086600	-1.04269500
C	1.44420700	-0.19753300	-1.03256500
C	1.94235100	0.80155400	-0.15047300
C	2.99133300	0.41567600	0.72695900
C	3.51142400	-0.86093800	0.73205000
H	1.55013900	-2.22380300	-1.72790100
H	0.64216600	0.03936300	-1.72450900
H	3.38244900	1.16500400	1.40895800
H	4.31460700	-1.12866700	1.41501400
O	3.49418600	-3.07495200	-0.16024800
C	0.36372700	2.57659000	-0.96798000
H	-0.00982300	3.59134600	-0.89241100
H	-0.09981100	1.91931300	-1.68994000
O	1.92051500	3.02897400	0.71351400
C	1.43233300	2.18139900	-0.09756400
O	-2.04875100	1.79600800	0.26627500
C	-2.63792900	0.67448600	0.24083900
C	-2.50833300	-0.27048000	1.33562200
C	-3.46503700	0.28359400	-0.88657300
C	-3.15641500	-1.48775900	1.29526300
H	-1.88816700	0.01760400	2.17877300
C	-4.10231500	-0.94001100	-0.90179300

H	-3.56263100	0.98731700	-1.70746300
C	-3.95526600	-1.83282600	0.18273300
H	-3.05501900	-2.18818000	2.11868800
H	-4.72034800	-1.22380300	-1.74822100
H	-4.46067300	-2.79312000	0.16098700

Geom 29:
Energy: -765.89156951 Hartrees

C	2.96938900	-1.91692100	-0.15541700
C	1.90835300	-1.49047200	-1.03873800
C	1.42657400	-0.19742500	-1.03275700
C	1.94637500	0.79537300	-0.15604700
C	2.98995600	0.39257900	0.72036100
C	3.48454200	-0.89403800	0.72981000
H	1.49095900	-2.22813200	-1.71998500
H	0.62810100	0.05236600	-1.72428800
H	3.39767000	1.13683500	1.39820700
H	4.28370300	-1.17465100	1.41231900
O	3.42190000	-3.11090100	-0.15352300
C	0.39826500	2.59652800	-0.97482800
H	0.04693200	3.61970100	-0.90426200
H	-0.08584500	1.94307000	-1.68684200
O	1.97376700	3.02776200	0.69478700
C	1.46434700	2.18517000	-0.10825600
O	-2.02678600	1.80324100	0.33935400
C	-2.62131500	0.68622100	0.27648000
C	-2.51529800	-0.28568800	1.35006600
C	-3.43161900	0.32767500	-0.87374800
C	-3.16969400	-1.49758000	1.26966000
H	-1.90766100	-0.02156000	2.21001000
C	-4.07547300	-0.89129600	-0.92908200
H	-3.51130100	1.05152200	-1.67891900
C	-3.95176100	-1.81072800	0.13597700
H	-3.08621100	-2.21828700	2.07745100
H	-4.68089500	-1.15101800	-1.79217400
H	-4.46234400	-2.76704600	0.08265000

Geom 30:

Energy: -765.89192519 Hartrees

C	2.96029200	-1.92820700	-0.15352000
C	1.90200700	-1.49447500	-1.03661000
C	1.43074600	-0.19759500	-1.03231200
C	1.95921500	0.79242100	-0.15751700
C	3.00015600	0.38241100	0.71873100
C	3.48423300	-0.90813400	0.72984400
H	1.47821300	-2.22971500	-1.71652700
H	0.63399300	0.05754700	-1.72387400
H	3.41442200	1.12435500	1.39513500
H	4.28154600	-1.19405600	1.41232100
O	3.40333100	-3.12570200	-0.15032800
C	0.42458900	2.60446700	-0.97740700
H	0.08406900	3.63166500	-0.91059600
H	-0.06992500	1.95193400	-1.68323900
O	2.00808400	3.02687700	0.68697900
C	1.48945300	2.18623800	-0.11212600
O	-2.04317500	1.81070100	0.36678000
C	-2.63485900	0.69337300	0.28957100
C	-2.53079500	-0.28980200	1.35321500
C	-3.44018300	0.34564200	-0.86761500
C	-3.18245400	-1.50196000	1.25734500
H	-1.92683100	-0.03361300	2.21813200
C	-4.08130900	-0.87389800	-0.93839400
H	-3.51819400	1.07802100	-1.66518900
C	-3.95966300	-1.80436200	0.11734600
H	-3.10063200	-2.23120000	2.05759800
H	-4.68301400	-1.12561800	-1.80642700
H	-4.46813400	-2.76105200	0.05191000

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