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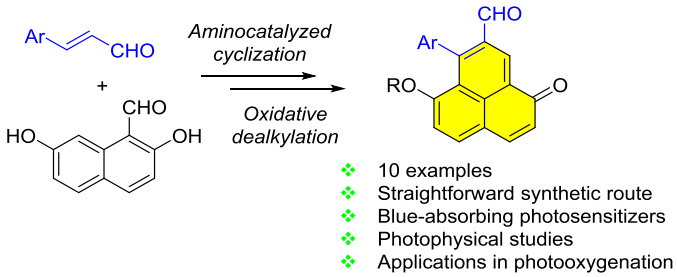


ABSTRACT: A series of functionalized 6-alkoxy phenalenones was prepared through an unprecedented oxidative dealkylation of readily available phenalene precursors. The starting phenalenes were efficiently synthesized *via* an aminocatalyzed annulation/*O*-alkylation strategy starting from simple substrates. The spectroscopic properties of some phenalenones were investigated in different solvents. Introducing an alkoxy substituent at the 6-position onto the phenalenone framework results in a redshift of the absorption. The synthesized phenalenones exhibit low fluorescence quantum yields and the fluorescence decay was studied in different solvents highlighting the presence of several lifetimes. The singlet oxygen ($^1O_2$) photosensitizing propensity of some phenalenones was investigated and the results showed the striking importance of the phenalenone molecular structure in generating singlet oxygen with high yields. The ability of phenalenones to generate singlet oxygen was then harnessed in three photooxygenation

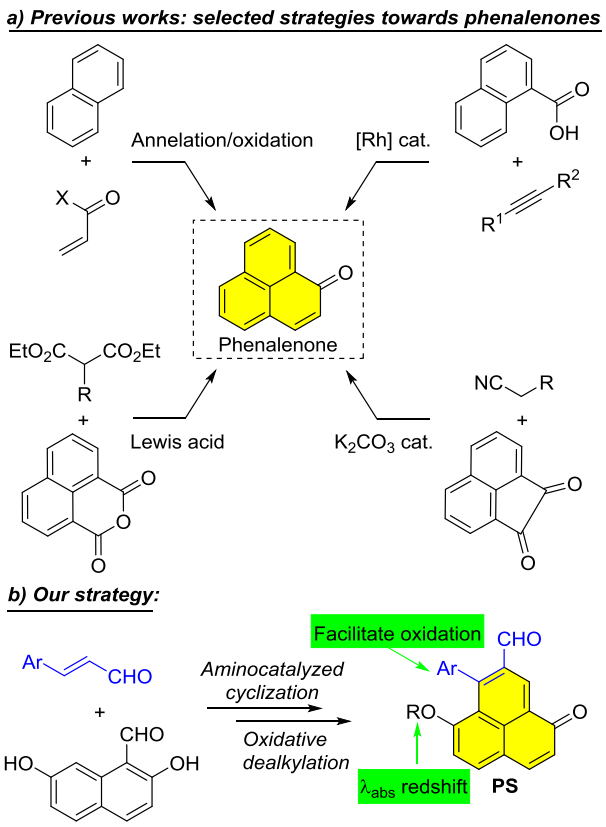
reactions: anthracene oxidation, oxy-functionalization of citronellol through Schenck-ene reaction and photooxidation of a diene.

■ INTRODUCTION

The light-induced production of reactive oxygen species lies at the heart of photodynamic therapy (PDT). Over the past decades, this research field has been thriving with applications ranging from the treatment of superficial cancers[1] to the destruction of bacteria,[2] fungi[3] or viruses.[4] The concept of photodynamic therapy is based on the combination of oxygen, light and a photosensitizer (PS). The classical mechanism starts by the activation of PS through light absorption to initially generate its excited singlet state which would then evolve to the excited triplet state by intersystem crossing.[5] The photosensitizer in its triplet state can subsequently react with molecular entities to form radical or radical ions leading to the oxidized and/or oxygenated products (Type I photooxygenation) or can generate singlet oxygen by triplet-triplet energy transfer (Type II photooxygenation).[6] One convenient strategy to enhance intersystem crossing lies in the incorporation of heavy atoms (*i.e.* Ir, Ru, Pd, I, Br) into the photosensitizer.[7] Nevertheless, the dark toxicity and cost of heavy atom containing photosensitizers are drawbacks to fully exploit the potential of PDT in clinical applications. Within this context, the cost-effective development of organic photosensitizers deprived of heavy atoms is of utmost importance to tackle the challenge of efficient production of singlet oxygen by sensitization of ground state oxygen.[8] One approach in which these demands can be achieved is through the use of phenalenone derivatives. Phenalenone is a type-II photosensitizer which is considered as a universal reference molecule for the determination of quantum yields of singlet oxygen sensitization.[9] Phenalenone possesses attractive features for singlet oxygen production such as its photostability in various solvents, an efficient intersystem crossing and a high quantum yield of singlet oxygen.[10] These interesting features have spurred interest in investigating phenalenone compounds as prospective PDT agents.[11]

In addition, the phenalenone framework is also found in biologically relevant products exhibiting anti-leishmanial,[12] anti-fungal,[13] and anti-malarial activities.[14] However, the drawbacks of phenalenones such as their tendency to aggregate,[11f,15] absorption in UVA regions and limited synthetic strategies to obtain functionalized structures still constitute important barriers to their widespread adoption. An approach to circumventing these issues lies in the molecular design of new visible-light absorbing phenalenone architectures thoroughly decorated with functional groups. From a synthetic standpoint, a convenient route towards phenalenones involves the reaction of naphthalene compounds with acrylic acid or derivatives followed by an oxidative protocol (Scheme 1).[16] The Lewis acid-promoted reaction of naphthalic anhydride and diethyl malonate compounds has also been reported as an efficient procedure to give access to phenalenones but this strategy remained limited in terms of substrate scope.[17]

Scheme 1. Designed phenalenone photosensitizers PS and synthetic strategies.



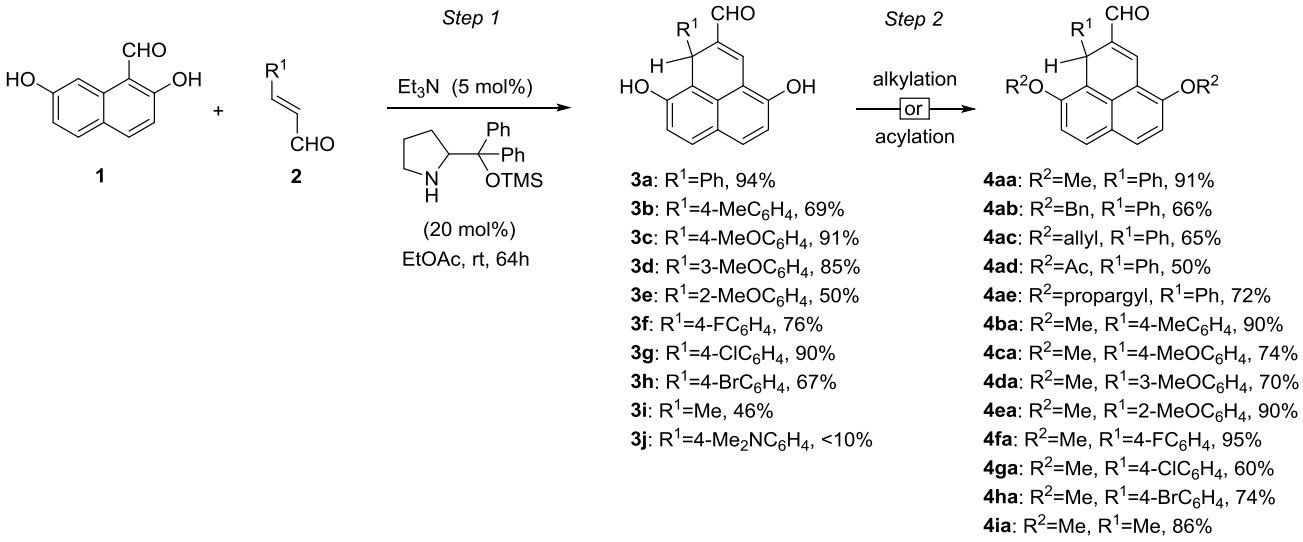
More recently, the group of Fukuyama described the preparation of phenalenones through a rhodium-catalyzed dehydrative annulation of 1-naphthoic acids with alkynes.[18] Methylene active compounds bearing a cyano group have also been used by Lebreton and co-workers for the preparation of phenalenones from acenaphthylene-1,2-dione.[19] Nevertheless, this attractive synthetic route was limited to unsubstituted naphthalene ring-containing substrates. In spite of substantial efforts towards the preparation of phenalenone architectures, the current strategies have several drawbacks such as lengthy multi-step routes or limited ability to introduce functional groups onto the phenalenone frameworks.[20] We described herein a synthetic strategy towards highly promising phenalenone photosensitizers with high singlet oxygen quantum yields *via* an oxidative dealkylation tactic.

■ RESULTS AND DISCUSSION

Synthesis. We began our study by preparing a series of phenalene derivatives **4** following the synthetic route depicted in Scheme 2. The reaction sequence started with the condensation of naphthol **1**[21] with a series of α,β-unsaturated aldehydes **2** in the presence of a catalytic amount of triethylamine (5 mol%) and a racemic mixture of diphenylprolinol silyl ether catalyst (20 mol%). This procedure is based on a slightly modified experimental protocol previously reported by our group.[22] The yields were improved by simply switching the solvent from toluene to ethyl acetate. Under these conditions, the products **3** were obtained in good-to-high yields regardless of the substituents. Nevertheless, the introduction of a dimethylamino group on the aryl ring of the α,β-unsaturated aldehyde **2j** had a dramatic impact on the reaction outcome and only a small amount of **3j** was detected in the crude product. It is worthwhile noting that aminocatalyzed transformation between **1** and *trans*-cinnamaldehyde **2a** (R^1=Ph) was scaled up to 10 mmol and proceeded with excellent yield (90%). With the compounds **3** in hand, the *O*-alkylation and *O*-acylation were investigated. Methylation, benzylation and allylation reactions gave rise to the *O*-protected phenalenes in

good-to excellent yields while **3a** was acylated in the presence of acetic anhydride in pyridine to give **4ad** in 50% yield.

Scheme 2. Synthetic route towards phenalene derivatives.



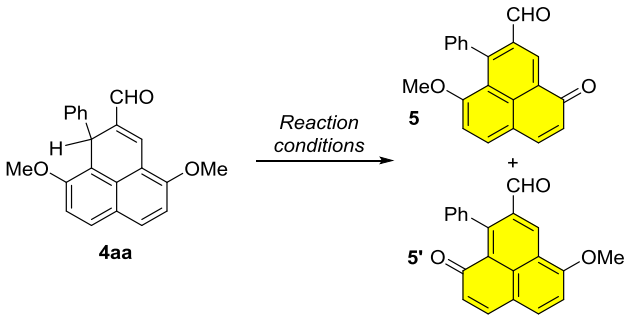
3a: R^1=Ph, 94%
3b: R^1=4-MeC_6H_4, 69%
3c: R^1=4-$MeOC_6H_4$, 91%
3d: R^1=3-$MeOC_6H_4$, 85%
3e: R^1=2-$MeOC_6H_4$, 50%
3f: R^1=4-FC_6H_4, 76%
3g: R^1=4-ClC_6H_4, 90%
3h: R^1=4-BrC_6H_4, 67%
3i: R^1=Me, 46%
3j: R^1=4-$Me_2NC_6H_4$, <10%

4aa: R^2=Me, R^1=Ph, 91%
4ab: R^2=Bn, R^1=Ph, 66%
4ac: R^2=allyl, R^1=Ph, 65%
4ad: R^2=Ac, R^1=Ph, 50%
4ae: R^2=propargyl, R^1=Ph, 72%
4ba: R^2=Me, R^1=4-MeC_6H_4, 90%
4ca: R^2=Me, R^1=4-$MeOC_6H_4$, 74%
4da: R^2=Me, R^1=3-$MeOC_6H_4$, 70%
4ea: R^2=Me, R^1=2-$MeOC_6H_4$, 90%
4fa: R^2=Me, R^1=4-FC_6H_4, 95%
4ga: R^2=Me, R^1=4-ClC_6H_4, 60%
4ha: R^2=Me, R^1=4-BrC_6H_4, 74%
4ia: R^2=Me, R^1=Me, 86%

Reaction conditions. *Step 1*, reactions were performed in ethyl acetate (5 mL, 0.20 mol.L^{-1}) at room temperature for 64h using 2 equiv. of **2**, 5 mol% of Et_3N and 20 mol% of diphenylprolinol silyl ether catalyst. *Step 2*, methylation: MeI (2.2 equiv.), K_2CO_3, DMF, rt, 5h. Benzylation: BnBr (2.5 equiv.), K_2CO_3, acetone, reflux, 5 h. Allylation: allyl bromide (4 equiv.), K_2CO_3, acetone, reflux, 5 h. Acylation: acetic anhydride (4 equiv.), pyridine, rt, 5h. Propargylation: propargyl bromide (5 equiv.), K_2CO_3, acetone, reflux, 16 h.

To identify suitable conditions for the oxidative dealkylation,[23] the transformation of **4aa** into the corresponding phenalenones **5** and **5'** was investigated (Table 1).

Table 1. Oxidant screening.

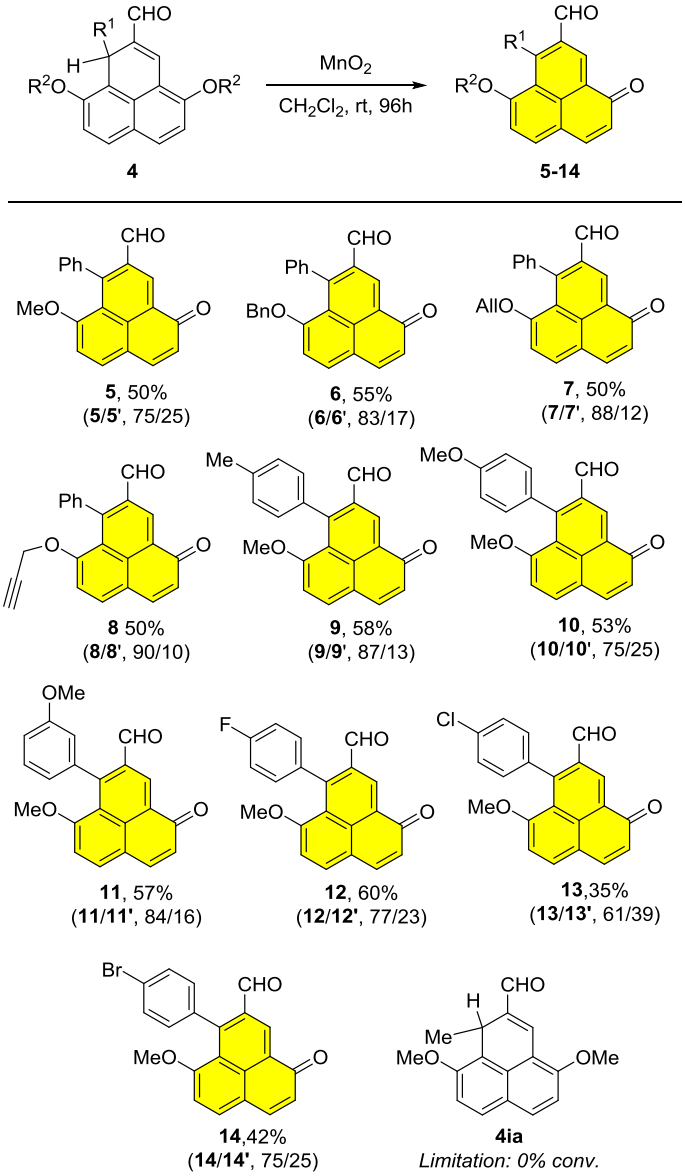


Entry	Reaction conditions	Yield **5/5'**[a]
1	DDQ (2 equiv.), CH_2Cl_2, 1h, rt	47%/49%
2	$NOBF_4$ (2 equiv.), MeCN, 1h, rt	32%/66%
3	MnO_2 (20 equiv.), CH_2Cl_2, 60h, rt	31%/8%
4	MnO_2 (20 equiv.), CH_2Cl_2, 96h, rt	50%/20%
5	MnO_2 (20 equiv.), CH_2Cl_2, 48h, reflux	27%/5%

[a] Isolated yield.

The oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been successfully used in oxidative dealkylation and therefore, we first explored this oxidant (entry 1).[23a] Oxidation of **4aa** in dichloromethane with 2 equiv. of DDQ led to the formation of two phenalenone compounds **5** and **5'** in 47% and 49% isolated yields respectively. It is important to note that full NMR analyses were carried out to unambiguously confirm the structures of **5** and **5'** which were easily separated by column chromatography. The promising results prompted us to explore some oxidants in order to improve the reaction selectivity. The use of nitrosyl tetrafluoroborate ($NOBF_4$) at room temperature provided **5'** as the major compound in 66% yield while **5** was isolated in 32% yield (entry 2). Nevertheless, recent studies have shown that 9-phenylsubstituted phenalenones such as **5'** were inefficient photocatalysts for oxygen sensitization due to a competitive reaction pathway.[24] Changing the oxidant to MnO_2 enhanced the selectivity towards the major formation of **5** (entries 3-5). The use of MnO_2 in dichloromethane at room temperature provided an effective balance between yield in **5** and selectivity (entry 4). Having identified suitable conditions for the phenalenone formation, the scope and limitations of the transformation were investigated (Scheme 3).

Scheme 3. Substrate scope.



Phenalene compounds **4** (R^1=Ph) bearing *O*-alkylated groups on the naphthalene ring were well tolerated and the desired phenalenones **5-8** were obtained in 50-55% isolated yields with good selectivities. In contrast, the oxidation of **4ad** (R^1=Ph, R^2=Ac) led to the formation of the corresponding phenalenone which was unstable upon purification by column chromatography on silica gel. A similar reaction outcome was observed by performing the oxidation of phenalene **4ea** (R^1=2-$MeOC_6H_4$, R^2=Me). The use of *O*-alkylated phenalene derivatives as substrates is crucial for the success of the reaction because running the reaction

with **3a** led to a complete degradation of the starting material. The phenalene substrates incorporating different substituents on the phenyl ring were prone to oxidation. The compounds **9-12** were isolated in 53-60% yields while products **13** and **14** were formed with moderate levels of yields. The methyl-derived phenalene **4ia** was subjected to the standard reaction conditions and no oxidation was observed. This result underscores the importance of the aromatic substituent R^1 to trigger the oxidative dealkylation. Although a comprehensive understanding of the mechanism should await further investigations, cyclic voltammetry of phenalene **4aa** was performed (Figure 1).

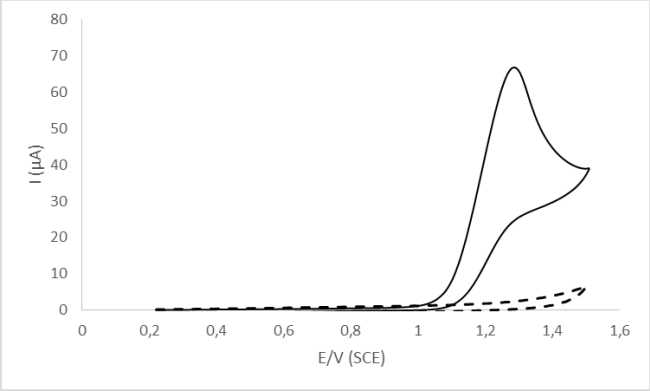
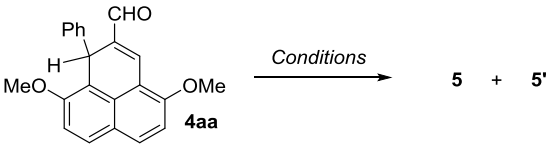


Figure 1. Cyclic voltammogram at a glassy carbon electrode in dichloromethane and Bu_4NPF_6, c = 0.1 mol.L^{-1} referenced to SCE *via* internal ferrocene (not shown) (---) and in the presence of **4aa** (□), c = 5.10^{-3} mol.L^{-1}, 100 mV.s^{-1}.

The cyclic voltammogram of **4aa** showed an irreversible electron oxidation process with a peak potential at $E_{p,a}$ = 1.27 V (vs SCE) which correlates with the oxidation ability of MnO_2.[25] A set of control experiments was performed in order to get a better understanding of the formation of phenalenones from phenalenes **4** (Scheme 4).

Scheme 4. Control experiments.



*t*BuLi or NaH (1.2 equiv.), THF, 0°C to RT: no reaction
Ph_3CBF_4 (1.2 equiv.), MeCN, RT to reflux: no reaction
NBS (2 equiv.), AIBN (0.1 equiv.), 1,2-DCE, reflux: **5** (2%), **5'** (2%)

First, phenalene **4aa** was treated with strong bases under inert atmosphere in order to assess if a phenalenyl anion could be an intermediate of the reaction.[26] No reaction occurred under these conditions and the starting material **4aa** was recovered. With the aim of preparing the phenalenyl cation, **4aa** was allowed to react with tritylium tetrafluoroborate according to a known procedure. [27] Even under reflux conditions, no traces of the desired phenalenones **5** and **5'** were detected. Gratifyingly, the expected phenalenones **5** and **5'** were detected by treating the phenalene **4aa** under radical conditions using *N*-bromosuccinimide (NBS) and azobisisobutyronitrile (AIBN). Therefore, the formation of phenalenones from phenalene **4** could proceed through a radical intermediate.

Spectroscopic properties of phenalenones **5** and **5'** were investigated in order to study the influence of the substitution pattern.

Spectroscopic characterization. ***A. Steady state absorption and emission spectra.*** The absorption spectra in MeOH of phenalenone (**PN**), **5** and **5'** as representative derivatives are presented in Figure 2. The absorption spectra of **5/5'** and **PN** show noticeable differences. The group of absorption band located between 330 and 360 nm, ascribed for phenalenone to a ππ* transition, are weak in derivatives **5/5'**. The band related to n* transition, was displaced to longer wavelength (430-450 nm) and these results are in agreement with previous studies dealing with photophysical analyses of 6-ethoxy and 6-hydroxy phenalenones.[28]

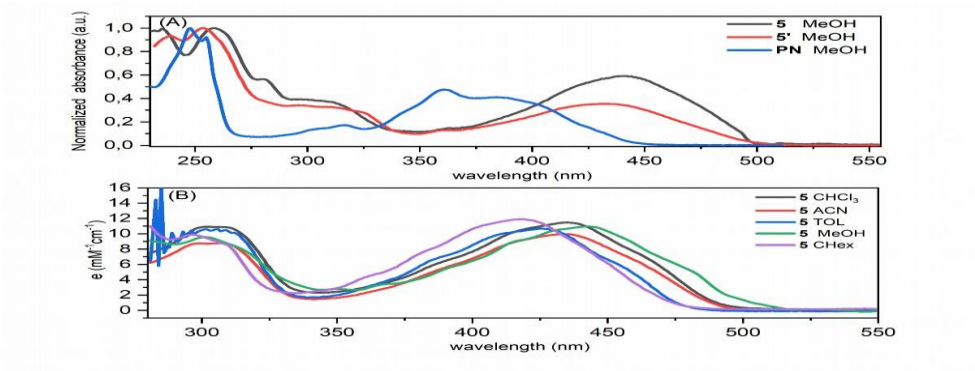


Figure 2. Absorption spectra of phenalenone (**PN**), **5** and **5'** in methanol.

The molar extinction coefficients (ε) determined for **5** and **5'** in several solvents are shown in Table 2. A longer wavelength absorption and higher ε values were determined for **5**. Additionally, a bathochromic shift is observed in the absorption wavelength with the increase of solvent polarity for this compound.

Table 2. Molar extinction coefficients determined in selected solvents (ε, 10^3 $M^{-1}.cm^{-1}$)

Solvent	**5** ε /10^3 $M^{-1}cm^{-1}$ (λ_{max} /nm)	**5'** ε /10^3 $M^{-1}cm^{-1}$ (λ_{max} / nm)
Cyclohexane	12.23 (419)	8.29 (412)
Toluene	10.49 (425)	8.06 (426)
Chloroform	11.86 (436)	8.19 (431)
Acetonitrile	10.11 (435)	8.74 (426)
Methanol	11.31 (442)	8.31 (431)

Normalized emission spectra of **5** and **5'** in several solvents are shown in Figure 3. The maximun emission wavelength is dependent on the solvent polarity in both derivatives, the higher shift is observed in protic polar media. Emission intensity of compound **5'** was lower than that observed for **5** in all solvents. Investigations of excited singlet state properties in apolar solvents was not carried out because emission was very low.

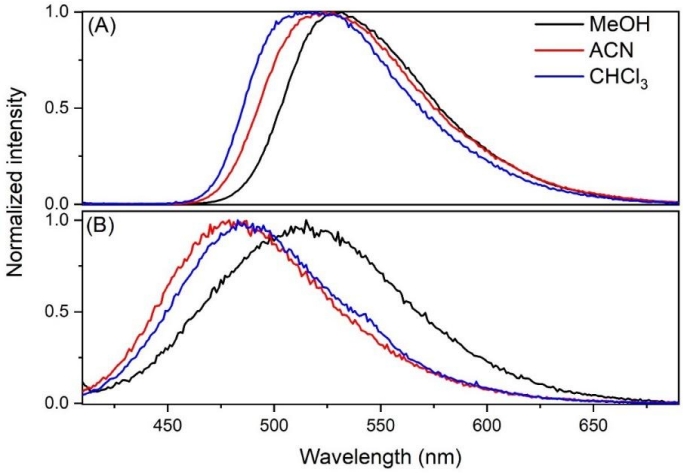


Figure 3. Normalized emission spectra in several solvents for **5** (A) and **5'** (B). λ_{exc} = 360 nm.

Fluorescence quantum yields measured under air ($\Phi_{F,air}$) and under Argon ($\Phi_{F,Ar}$) for **5** and **5'** are shown in Table 3. Besides being low, the similarity between values indicates that oxygen is not able to quench appreciably the singlet states of these derivatives. Both the emission quantum yields and emission maximum wavelengths are sensitive to polarity solvent, the bathochromic effect observed indicates nπ* character for the transition involved.

Table 3. Quantum yields of fluorescence in selected solvents

Solvent	**5**		**5'**	
	$\Phi_{F,air}$	$\Phi_{F,Ar}$	$\Phi_{F,air}$	$\Phi_{F,Ar}$
Chloroform	0.034±0.003	0.030±0.001	0.003±0.0005	0.004±0.001
Acetonitrile	0.031±0.006	0.042±0.003	0.004±0.001	0.004±0.0007
Methanol	0.225±0.010	0.280±0.007	0.007±0.002	0.009±0.001

B. Time resolved measurements. Fluorescence lifetimes data were analyzed by global fitting of a set of decays acquired at different emission wavelengths. A representative data analysis showing a biexponential fit for phenalenone **5** in methanol is shown in Figure 4, inset of the figure shows time resolved emission spectra (TRES) with two bands centered around 540 nm. Three bands (two centered around 530 nm and one centred at 490 nm) were observed in the TRES for **5'** in methanol (see Figure S3 in supporting information).

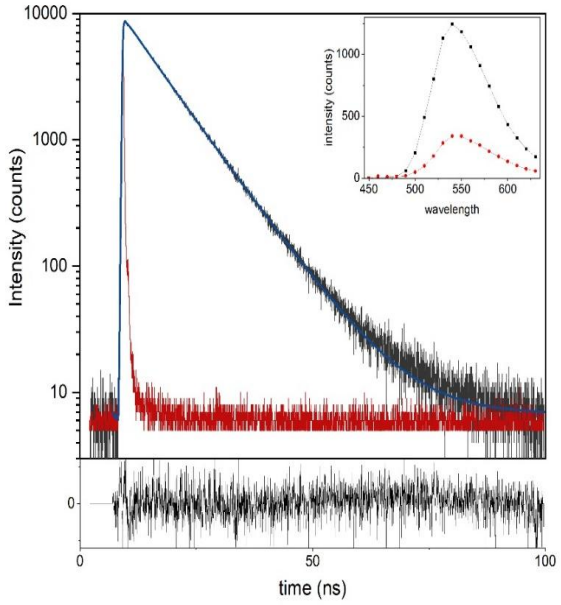


Figure 4. Emission decay of **5** in methanol at 520 nm (λ_{exc} = 375 nm) under air. Inset corresponds to time resolved fluorescence spectra (Pre-exponential factors obtained from a global fit of fluorescence intensity time traces).

Regardless of the solvent, phenalenone **5** shows two fluorescent lifetimes (Table 4) while **5'** has three lifetimes (see Table S2 in Supporting Information). In all cases, saturation of solution with argon did not influence the lifetime values even if a small change in lifetimes was observed in some cases.

Table 4. Fluorescence lifetime of **5** in selected solvents. The values in brackets corresponds to fractional intensities of lifetimes.

Solvent	**5**			
	$\tau_{1,air}$/ns	$\tau_{2,air}$/ns	$\tau_{1,Ar}$/ns	$\tau_{2,Ar}$/ns
Chloroform	5.88 (1.2)	0.85 (98.8)	8.35 (7.4)	0.77 (92.3)
Acetonitrile	7.71 (5.7)	1.07 (94.3)	8.46 (6.8)	1.06 (93.2)
Methanol	8.80 (76.1)	6.12 (23.9)	8.56	-

The presence of multiexponential decays observed for the emission of both compounds **5** and **5'** can be explained through the participation of rotamers involving both the aldehyde moiety

and the phenyl ring (Figure 5). DFT and TD-DFT calculations were performed on phenalenones **5** and **5'**at the B3LYP and CAM-B3LYP levels, respectively.

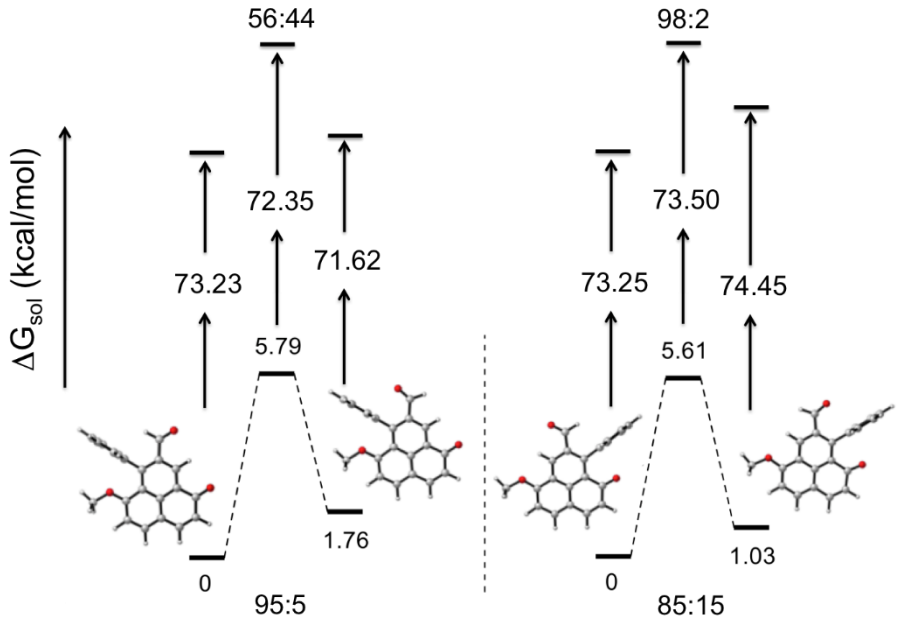


Figure 5. DFT (TD-DFT) computed energy surfaces for the conformational change of **5** (left) and **5'** (right) in their ground (excited) states. Vertical excitation energies provided by TD-DFT calculations were also depicted on the figure.

The interconversion between the stable conformers is kinetically and thermodynamically feasible in both cases accordingly with the activation free energy and the thermodynamic driving force values at the ground and excited states. By taking into account the thermodynamic driving force data the following ratio between the stable conformers of 95:5 (56:44) and 85:15 (98:2) are computed for **5** and **5'** derivatives in their ground (excited) states. These data suggest that both isomers would be present in solution under the experimental conditions and both of them could be prone to be excited. This result could explain the two lifetimes measured in methanol for both phenalenone derivatives.[29]

C. Singlet oxygen generation. Singlet oxygen quantum yields (Φ_Δ) were determined by observing the 1270 nm emission of $^1O_2$ of air-saturated samples excited at 355 nm. The results indicate that the solvent highly modulates the capacity of the studied compounds **5** and **5'** to generate $O_2(^1\Delta_g)$ (Table 5).

Table 5. Singlet oxygen quantum yields of compounds **5** and **5'**. The values were determined using phenalenone as actinometer. λ_{exc}= 355 nm.

Solvent	**5**	**5'**
	$\Phi_{\Delta,air}$	$\Phi_{\Delta,air}$
Cyclohexane	1.09	0.52
Toluene	1.17	0.21
Chloroform	0.53	0.13
Acetonitrile	0.72	0.22
Methanol	0.38	0.22

For phenalenone **5**, the lowest singlet oxygen quantum yield values was obtained in methanol and chloroform. Particularly, in methanol, hydrogen bonding interactions could promote a lowered ISC, as reported by Martinez *et al* for *9H*-Fluoren-9-one.[30] This result is fully consistent with the higher fluorescence quantum yield and singlet excited state lifetime determined in this solvent. On the other hand, the compound **5'** presents lower singlet oxygen quantum yields, and with exception of cyclohexane almost independent of solvent. In light of the very low singlet oxygen quantum yield for this compound the main deactivation path would correspond to internal conversion.

D. Laser flash photolysis absorption experiments. Triplet-triplet absorption experiments in Argon-saturated acetonitrile and cyclohexane solutions were performed for both derivatives. The transient decays for **5** were mono-exponential in both solvents studied (decays followed at 550 nm in acetonitrile and 530 nm in cyclohexane). This result is consistent with the absorption of only one species, which additionally is strongly quenched by oxygen, and almost disappeared when oxygen was admitted to the samples. Therefore, the observed transient absorptions should be attributed to the excited triplet state of **5**. For both derivatives, the transient spectra are similar showing four absorption bands and a ground depletion (Figure

6). For phenalenone **5**, three absorption maxima appear, at 350, 540 and 650 nm with a lifetime of 4.7 +/- 0.06 μs in acetonitrile and 3.8 +/- 0.07 μs in cyclohexane. Additionally ground depletion and emission are observed at 410 nm and 469 nm. Estimation of ε cannot be done for the absorption bands below 500 nm due to the ground state absorption. For compound **5'**, similar absorption peaks and ground depletion/emission were observed in acetonitrile. Nevertheless, the signals are clearly of lower magnitude, indicating (if extinction coefficients of transients are similar), a lower production of transient states, compatible with the behavior described previously for singlet oxygen quantum yields. The decay at 540 nm in acetonitrile fits to a biexponential, where probably the longer component (2.0 μs corresponds to the triplet state), while in cyclohexane there are three components, and the triplet state could have a lifetime of 0.7 μs or 8.7 μs. All components disappear in the presence of oxygen regardless of the solvents.

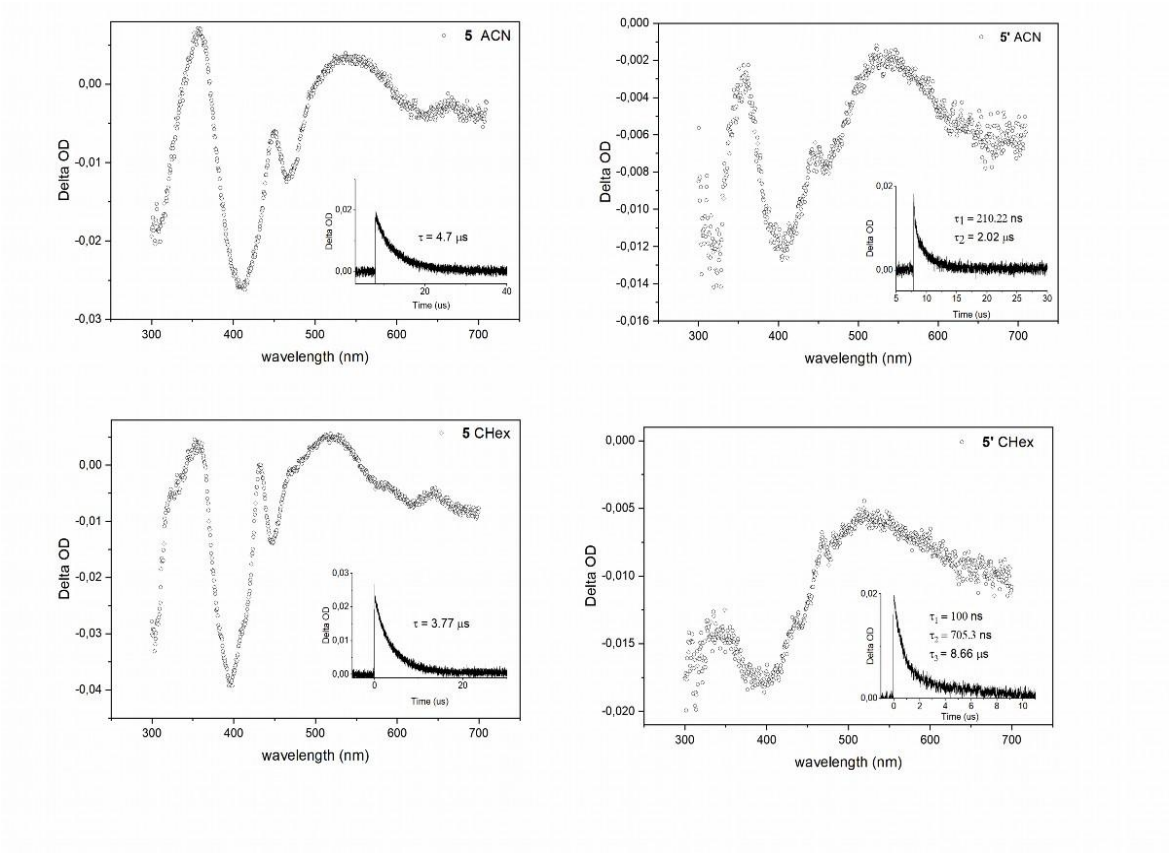
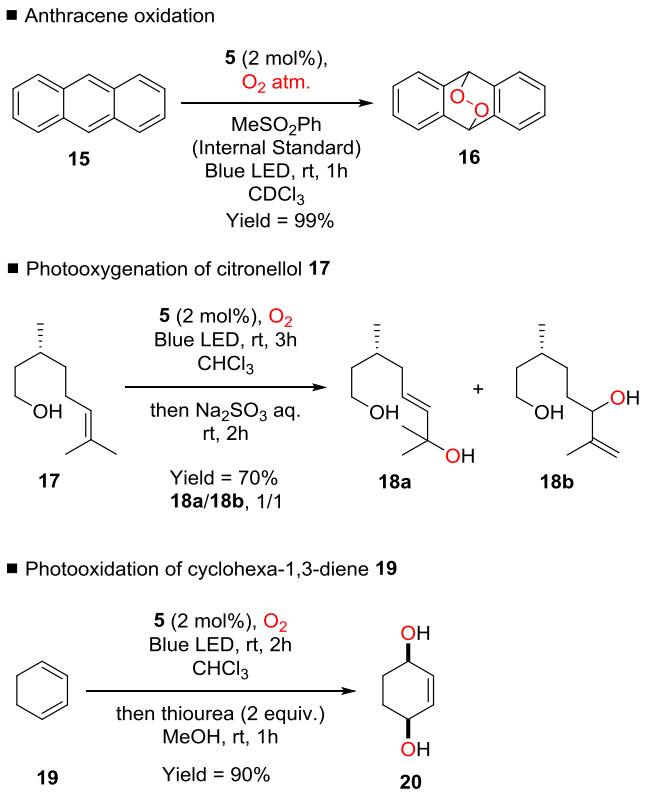


Figure 6. Triplet-triplet absorption spectra for **5** and **5'** in acetonitrile and cyclohexane

acquired after 100 ns pulse. The insets show the kinetic traces at around 530nm.

Photooxygenation. Phenalenones have been scarcely investigated as photosensitizers in synthetic transformations in spite of their ability to generate singlet oxygen in high yields. In light of the photophysical studies, the phenalenone compound **5** has been tested as a photosensitizer (Scheme 5). The photooxygenation reactions have been performed under oxygen bubbling or under atmospheric pressure of oxygen by utilizing blue light (LED, λ=470 nm).

Scheme 5. Application of PS **5** in singlet oxygen-mediated transformations.



Photooxygenation of anthracene **15** which is a singlet oxygen trap was first investigated.[31] Irradiation of **15** in the presence of 2 mol% of **5** led to the quantitative production of anthracene-9,10-endoperoxide **16** and **5** turned out to be stable under the reaction conditions. Other photosensitizers such as **10** or **12** (2 mol%) were tested in the photooxygenation of **15**

and full conversions into **16** were also observed after 1h. Photooxidation of citronellol **17** which is a key step in the industrial production of the fragrance rose oxide was then explored. Singlet oxygen Schenck-ene reaction of **17** was performed in chloroform under blue light using 2 mol% of phenalenone **5**. Subsequent reductive work led to an equimolar mixture of allylic alcohols **18a** and **18b** in 70% overall yield. The photosensitizer **5** was also effective for the formation of endoperoxides through [4+2] cycloaddition. Photooxygenation of cyclohexa-1,3-diene **19** in the presence of a catalytic amount of **5** followed by reduction with thiourea led to the formation of the diol **20** in 90% yield.

■ CONCLUSION

In summary, functionalized phenalenone derivatives were prepared based on an unusual oxidative dealkylation as a key step. A protocol has been implemented to synthesize functionalized phenalenones from readily available phenalenes with a simple oxidant and practically straightforward reaction conditions. A redshift absorption was observed owing to the insertion of an alkoxy group at the 6-position on the phenalenone ring. Singlet excited state deactivation of these derivatives is mainly controlled by non-radiative processes: Intersystem crossing to triplet excited state or internal conversion to ground state singlet. Transients with triplet character were observed by flash photolysis for all compounds studied, determining their lifetimes. The phenalenone derivatives studied, show deactivation pathways dependent on substituent position, keeping in one case a high capacity of singlet oxygen generation which is the most remarkable property of phenalenone. Computational study predicts a feasible rotameric equilibrium in both derivatives in methanol. The propensity of phenalenone motifs to generate singlet oxygen under light irradiation prompted us to investigate their use as photosensitizer in photooxygenation reactions. Under blue light LED, phenalenone photosensitizers were successfully applied to endoperoxide formation and

Schenck-ene reactions. Investigations are ongoing to further harness the biological and synthetic potential of these phenalenones as photosensitizers.

■ EXPERIMENTAL SECTION

Materials and methods. ^{1}H NMR and ^{13}C spectra were recorded at room temperature on samples dissolved in $CDCl_3$. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Structural assignments were made with additional information from gCOSY, gHSQC and gHMBC experiments. High-resolution mass spectrometry (HRMS) analyses was performed using electrospray ionization (ES) and ASAP. FTIR spectra were obtained from neat samples using the attenuated total reflection (ATR) technique. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel. Column chromatography separations were performed using silica gel. All reagents were used without purification. All solvents were of HPLC grade or were distilled using standard drying agents prior to use. Starting chemical substrates and reagents were used as commercially provided unless otherwise indicated.

Synthetic procedures. Synthesis of phenalene derivatives 3a-i. The naphthalene substrate (1 equiv.) was introduced into a capped flask. Ethyl acetate (0.2 $mol.L^{-1}$), a racemic mixture of diphenylprolinol silyl ether catalyst (20 mol%), and the α,β-unsaturated aldehyde (2 equiv.) were successively added into the flask. Et_3N (5 mol%) was then added, and the resulting mixture was stirred at room temperature for 64 hours at which point the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel to afford the corresponding product.

*4,9-dihydroxy-1-phenyl-1H-phenalene-2-carbaldehyde **3a***. According to the described general procedure, 1.51 g (94%) of **3a** (orange solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (5.32 mmol, 1 g), catalyst (1.06 mmol, 345 mg), cinnamaldehyde (10.62

mmol, 1.34 mL), and Et_3N (0.27 mmol, 37 µL). The compound was purified by column chromatography on silica gel (6/4 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

4,9-dihydroxy-1-(p-tolyl)-1H-phenalene-2-carbaldehyde ***3b***. According to the described general procedure, 350 mg (69%) of **3b** (orange solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (1.59 mmol, 300 mg), catalyst (0.32 mmol, 104 mg), *(E)*-3-(p-tolyl)acrylaldehyde (3.18 mmol, 465 mg), and Et_3N (79.5 µmol, 11 µL). The compound was purified by column chromatography on silica gel (8/2 PE/EtOAc). R_f = 0.31 (PE/EtOAc 8/2). mp 210-212 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ 2.16 (s, 3H), 5.65 (s, 1H), 6.91–6.88 (m, 2H), 6.97 (d, J = 8.7 Hz, 1H), 7.05 (d, J = 8.9 Hz, 1H), 7.13–7.10 (m, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 8.9 Hz, 1H), 8.00 (s, 1H), 9.60 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, Acetone-d_6) δ 20.9, 38.8, 113.2, 115.9, 116.8, 119.3, 123.8, 128.5, 129.0, 129.1 (2C), 132.0 (2C), 133.9, 135.9, 139.0, 139.2, 143.1, 154.9, 155.2, 192.1. IR (ATR, cm^{-1}) 3498, 3187, 2917, 1735, 1277, 1157. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}NaO_3$ 339.0997; Found 339.1001.

4,9-dihydroxy-1-(4-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***3c***. According to the described general procedure, 800 mg (91%) of **3c** (red solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (2.65 mmol, 500 mg), catalyst (0.53 mmol, 173 mg), *(E)*-3-(4-methoxyphenyl)acrylaldehyde (5.31 mmol, 860 mg), and Et_3N (0.13 mmol, 18 µL). The compound was purified by column chromatography on silica gel (6/4 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

4,9-dihydroxy-1-(3-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***3d***. According to the described general procedure, 810 mg (85%) of **3d** (red solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (2.65 mmol, 500 mg), catalyst (0.53 mmol, 173 mg), *(E)*-3-(3-methoxyphenyl)acrylaldehyde (5.3 mmol, 860 mg), and Et_3N (0.13 mmol, 18 µL). The

compound was purified by column chromatography on silica gel (6/4 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

4,9-dihydroxy-1-(2-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***3e***. According to the described general procedure, 132 mg (50%) of **3e** (red solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (0.78 mmol, 147 mg), catalyst (0.16 mmol, 52 mg), *(E)*-3-(2-methoxyphenyl)acrylaldehyde (1.56 mmol, 253 mg), and Et_3N (39 µmol, 5 µL). The compound was purified by column chromatography on silica gel (6/4 PE /EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

1-(4-fluorophenyl)-4,9-dihydroxy-1H-phenalene-2-carbaldehyde ***3f***. According to the described general procedure, 389 mg (76%) of **3f** (orange solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (1.59 mmol, 300 mg), catalyst (0.32 mmol, 104 mg), *(E)*-3-(4-fluorophenyl)acrylaldehyde (3.18 mmol, 0.42 mL), and Et_3N (79.5 µmol, 11 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

1-(4-chlorophenyl)-4,9-dihydroxy-1H-phenalene-2-carbaldehyde ***3g***. According to the described general procedure, 482 mg (90%) of **3g** (orange solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (1.59 mmol, 300 mg), catalyst (0.32 mmol, 104 mg), *(E)*-3-(4-chlorophenyl)acrylaldehyde (3.18 mmol, 530 mg), and Et_3N (79.5 µmol, 11 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

1-(4-bromophenyl)-4,9-dihydroxy-1H-phenalene-2-carbaldehyde ***3h***. According to the described general procedure, 294 mg (67%) of **3h** (orange solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (1.16 mmol, 218 mg), catalyst (0.23 mmol, 75 mg), *(E)*-3-(4-bromophenyl)acrylaldehyde (2.32 mmol, 490 mg), and Et_3N (58 µmol, 8 µL). The compound

was purified by column chromatography on silica gel (7/3 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

*4,9-dihydroxy-1-methyl-1H-phenalene-2-carbaldehyde **3i***. According to the described general procedure, 586 mg (46%) of **3i** (red solid) was obtained from 2,7-dihydroxy-1-naphthtaldehyde (5.32 mmol, 1 g), catalyst (1.06 mmol, 345 mg), *(E)*-but-2-enal (10.62 mmol, 0.91 mL) and Et_3N (0.27 mmol, 37 µL). The compound was purified by column chromatography on silica gel (6/4 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

Synthesis of dimethoxy phenalene derivatives 4aa-ia. Under argon atmosphere, the naphthol derivative (1 equiv.) was dissolved in anhydrous DMF (0.6 $mol.L^{-1}$). K_2CO_3 (2 equiv.) and then MeI (2.2 equiv.) were added. The reaction mixture was stirred at room temperature for 5 hours and then diluted with Et_2O. This resulting mixture was filtered and washed with Et_2O. The filtrate was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude compound was purified by column chromatography on silica gel to afford the corresponding product.

*4,9-dimethoxy-1-phenyl-1H-phenalene-2-carbaldehyde **4aa***. According to the described general procedure, 1.86 g (91%) of **4aa** (orange solid) was obtained from 4,9-dihydroxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **3a** (6.25 mmol, 1.5 g), K_2CO_3 (12.50 mmol, 1.73 g), and MeI (13.75 mmol, 0.86 mL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). All the physical and spectroscopic data were in complete agreement with the reported ones.[22]

*4,9-dimethoxy-1-(p-tolyl)-1H-phenalene-2-carbaldehyde **4ba***. According to the described general procedure, 269 mg (90%) of **4ba** (orange solid) was obtained from 4,9-dihydroxy-1-(p-tolyl)-1*H*-phenalene-2-carbaldehyde **3b** (0.87 mmol, 275 mg), K_2CO_3 (1.74 mmol,

240 mg), and MeI (1.91 mmol, 120 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). R_f = 0.34 (PE/EtOAc 7/3). mp 283-285 °C. ^{1}H NMR (300 MHz, Acetone-d_6) δ 2.16 (s, 3H), 3.82 (s, 3H), 4.09 (s, 3H), 5.60 (s, 1H), 6.91–6.88 (m, 2H), 7.08–7.04 (m, 2H), 7.22 (d, J = 8.9 Hz, 1H), 7.32 (d, J = 9.2 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.98 (s, 1H), 9.60 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, Acetone-d_6) δ 20.9, 39.0, 56.3, 56.8, 111.8, 112.8, 115.0, 121.8, 124.5, 128.9 (3C), 129.2 (2C), 130.9, 134.2, 136.1, 138.2, 139.9, 142.8, 156.8, 157.0, 192.1. IR (ATR, cm^{-1}) 2938, 2712, 1661, 1263, 1252, 1158, 1055. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_3$ 367.1310; Found 367.1310.

4,9-dimethoxy-1-(4-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***4ca***. According to the described general procedure, 241 mg (74%) of **4ca** (orange solid) was obtained from 4,9-dihydroxy-1-(4-methoxyphenyl)-1*H*-phenalene-2-carbaldehyde **3c** (0.90 mmol, 300 mg), K_2CO_3 (1.80 mmol, 249 mg), and MeI (1.98 mmol, 285 µL). The compound was purified by column chromatography on silica gel (9/1 PE/EtOAc). R_f = 0.26 (PE/EtOAc 9/1). mp 183-185 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.79 (s, 3H), 4.05 (s, 3H), 5.65 (s, 1H), 6.68–6.63 (m, 2H), 7.07 (d, J = 8.9 Hz, 1H), 7.11 (d, J = 9.1 Hz, 1H), 7.16–7.14 (m, 2H), 7.63 (d, J = 8.9 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.94 (s, 1H), 9.58 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 37.9, 55.1, 56.0, 56.3, 110.5, 112.1, 113.2 (2C), 114.5, 121.6, 123.5, 127.7, 129.2 (2C), 130.1, 133.1, 137.0, 138.1, 139.0, 156.0, 155.6, 157.8, 192.2. IR (ATR, cm^{-1}) 3006, 2934, 2743, 1718, 1505, 1244, 1165. HRMS (ASAP+) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}O_4$ 361.1440; Found 361.1429.

4,9-dimethoxy-1-(3-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***4da***. According to the described general procedure, 566 mg (70%) of **4da** (yellow solid) was obtained from 4,9-dihydroxy-1-(3-methoxyphenyl)-1*H*-phenalene-2-carbaldehyde **3d** (2.08 mmol, 750 mg), K_2CO_3 (4.16 mmol, 574 mg), and MeI (4.58 mmol, 260 µL). The compound was purified by

column chromatography on silica gel (7/3 PE/EtOAc). R_f = 0.4 (PE/EtOAc 7/3). mp 155-157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.79 (s, 3H), 4.04 (s, 3H), 5.70 (s, 1H), 6.61 (ddd, J = 8.2, 2.5, 1.1 Hz, 1H), 6.85–6.82 (m, 2H), 7.05–7.01 (m, 1H), 7.07 (d, J = 8.9 Hz, 1H), 7.11 (d, J = 9.1 Hz, 1H), 7.64 (d, J = 8.9 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.95 (s, 1H), 9.59 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 38.0, 55.2, 56.1, 56.4, 110.6, 112.2, 113.2 (2C), 114.6, 121.7, 123.6, 127.8, 129.3 (2C), 130.3, 133.3, 137.1, 138.2, 139.2, 155.7, 156.2, 157.9, 192.3. IR (ATR, cm^{-1}) 2949, 2834, 1667, 1584, 1279, 1256, 1160, 1040. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_4$ 383.1259; Found 383.1247.

4,9-dimethoxy-1-(2-methoxyphenyl)-1H-phenalene-2-carbaldehyde ***4ea***. According to the described general procedure, 120 mg (90%) of **4ea** (yellow solid) was obtained from 4,9-dihydroxy-1-(2-methoxyphenyl)-1*H*-phenalene-2-carbaldehyde **3e** (0.37 mmol, 124 mg), K_2CO_3 (0.74 mmol, 102 mg), and MeI (0.81 mmol, 48 µL). The compound was purified by column chromatography on silica gel (6/4 PE/EtOAc). R_f = 0.33 (PE/EtOAc 6/4). mp 191-193 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (s, 6H), 4.04 (s, 3H), 5.99 (s, 1H), 6.71 (td, J = 14.6, 8.5, 4.6 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 7.13 – 7.00 (m, 4H), 7.59 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.97 (s, 1H), 9.55 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 34.0, 56.1 (2C), 56.3, 110.5, 111.7, 112.3, 114.9, 120.4, 122.1, 123.5, 127.2, 127.4, 130.5, 130.9, 132.7, 133.3, 138.1, 138.7, 155.2, 156.0, 157.1, 192.3. IR (ATR, cm^{-1}) 3020, 2949, 1656, 1595, 1205, 1292, 1103, 1090. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_4$ 383.1530; Found 383.1515.

1-(4-fluorophenyl)-4,9-dimethoxy-1H-phenalene-2-carbaldehyde ***4fa***. According to the described general procedure, 400 mg (95%) of **4fa** (yellow solid) was obtained from 4,9-dihydroxy-1-(4-fluorophenyl)-1*H*-phenalene-2-carbaldehyde **3f** (1.21 mmol, 389 mg), K_2CO_3 (2.42 mmol, 334 mg), and MeI (2.66 mmol, 170 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). R_f = 0.37 (PE/EtOAc 7/3). mp 195-197 °C. ^{1}H

NMR (300 MHz, Acetone-d_6) δ 3.83 (s, 3H), 4.10 (s, 3H), 5.62 (s, 1H), 6.90–6.82 (m, 2H), 7.21–7.15 (m, 2H), 7.23 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 8.01 (s, 1H), 9.61 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, Acetone-d_6) δ 38.7, 56.3, 56.8, 111.9, 112.8, 114.7, 114.9, 115.2, 121.3, 124.5, 129.2, 130.6, 130.7, 134.4, 138.5, 139.5, 141.9, 143.5, 157.0, 161.1, 164.5, 192.2. IR (ATR, cm^{-1}) 3011, 2940, 2841, 1657, 1631, 1505, 1264, 1157, 1046. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}FO_3$ 349.1240; Found 349.1235.

1-(4-chlorophenyl)-4,9-dimethoxy-1H-phenalene-2-carbaldehyde ***4ga***. According to the described general procedure, 302 mg (60%) of **4ga** (yellow solid) was obtained from 4,9-dihydroxy-1-(4-chlorophenyl)-1*H*-phenalene-2-carbaldehyde **3g** (1.38 mmol, 465 mg), K_2CO_3 (2.76 mmol, 381 mg), and MeI (3.04 mmol, 189 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). R_f = 0.34 (PE/EtOAc 7:3). mp 201-203 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.06 (s, 3H), 5.66 (s, 1H), 7.11–7.05 (m, 3H), 7.18–7.14 (m, 3H), 7.66 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 9.1 Hz, 1H), 7.96 (s, 1H), 9.57 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 38.3, 55.9, 56.3, 110.5, 111.9, 114.2, 120.8, 123.5, 127.9 (2C), 128.1, 129.7 (2C), 130.1, 131.6, 133.4, 138.3, 138.5, 143.1, 155.8, 156.0, 191.9. IR (ATR, cm^{-1}) 3008, 2934, 2744, 1662, 1632, 1260, 1163, 815. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{17}ClNaO_3$ 387.0764; Found 387.0760.

1-(4-bromophenyl)-4,9-dimethoxy-1H-phenalene-2-carbaldehyde ***4ha***. According to the described general procedure, 234 mg (74%) of **4ha** (yellow solid) was obtained from 4,9-dihydroxy-1-(4-bromophenyl)-1*H*-phenalene-2-carbaldehyde **3h** (0.77 mmol, 294 mg), K_2CO_3 (1.54 mmol, 213 mg), and MeI (1.69 mmol, 105 µL). The compound was purified by column chromatography on silica gel (7/3 PE/EtOAc). R_f = 0.41 (PE/EtOAc 7/3). mp 196-198 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.10 (s, 3H), 5.69 (s, 1H), 7.11 (d, J = 8.9 Hz, 1H), 7.18–7.14 (m, 3H), 7.31–7.26 (m, 2H), 7.71 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 9.2 Hz,

1H), 8.01 (s, 1H), 9.61 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 37.9, 55.5, 55.9, 110.1, 111.5, 113.8, 120.3, 123.0, 127.5 (2C), 127.7, 129.3 (2C), 129.7, 131.2, 133.0, 137.9, 138.1, 142.7, 155.4, 155.6, 191.5. IR (ATR, cm^{-1}) 2932, 2856, 1665, 1632, 1503, 1252, 1161, 579. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}BrO_3$ 409.0439; Found 409.0421.

4,9-dimethoxy-1-methyl-1H-phenalene-2-carbaldehyde ***4ia***. According to the described general procedure, 337 mg (86%) of **4ia** (yellow solid) was obtained from 4,9-dihydroxy-1-methyl-1*H*-phenalene-2-carbaldehyde **3i** (1.46 mmol, 350 mg), K_2CO_3 (2.92 mmol, 404 mg), and MeI (3.21 mmol, 200 µL). The compound was purified by column chromatography on silica gel (9/1 Cyclohexane/EtOAc). R_f = 0.33 (Cyclohexane/EtOAc 9/1). mp 148-149 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (d, J = 6.7 Hz, 3H), 3.96 (s, 3H), 4.01 (s, 3H), 4.61 (q, J = 6.7 Hz, 1H), 7.06 (d, J = 9.1 Hz, 1H), 7.15 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 9.1 Hz, 1H), 7.85 (s, 1H), 9.65 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 22.5, 27.9, 55.9, 56.3, 110.5, 111.6, 114.8, 123.0, 123.7, 127.1, 130.2, 132.9, 138.9, 140.9, 155.1, 155.4, 192.7. IR (ATR, cm^{-1}) 2977, 2938, 2839, 1654, 1510, 1255, 1169, 1044. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}O_3$ 269.1178; Found 269.1173.

Synthesis of 4,9-bis(benzyloxy)-1-phenyl-1*H*-phenalene-2-carbaldehyde 4ab. Under argon atmosphere, 4,9-dihydroxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **3a** (0.99 mmol, 300 mg, 1 equiv.) and 4 mL of anhydrous acetone were added into a flask. K_2CO_3 (2.5 mmol, 346 mg, 2.5 equiv.) and benzyl bromide (2.5 mmol, 0.30 mL, 2.5 equiv.) were then added. The reaction was left to stir at reflux using a round bottom flask heating block for 5 hours at which point the mixture was cooled down to room temperature and 10 mL of dichloromethane was then added. The resulting mixture was then filtered through a pad of celite and washed with dichloromethane. The filtrate was evaporated under reduced pressure. The compound was purified by column chromatography on silica gel (8/2 PE/EtOAc) to afford the corresponding product **4ab** as a yellow solid (316 mg, 66%). R_f = 0.28 (PE/EtOAc

8/2). mp 222-224 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (d, J = 12.0 Hz, 1H), 5.11 (d, J = 12.0 Hz, 1H), 5.30 (d, J = 11.9 Hz, 1H), 5.35 (d, J = 11.9 Hz, 1H), 5.74 (s, 1H), 7.14–7.05 (m, 6H), 7.21–7.16 (m, 3H), 7.32–7.27 (m, 3H), 7.52–7.39 (m, 5H), 7.59 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.97 (s, 1H), 9.55 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 39.1, 70.2, 71.3, 112.1, 112.8, 115.3, 121.6, 123.6, 126.0, 127.4 (2C), 127.5 (2C), 127.7, 127.8 (2C), 127.9, 128.3, 128.4 (2C), 128.7 (2C), 128.8 (2C), 130.5, 133.0, 136.5, 136.7, 138.2, 139.0, 144.3, 154.8, 154.9, 192.1. IR (ATR, cm^{-1}) 2848, 1633, 1472, 1442, 1046. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{34}H_{27}O_3$ 483.1960; Found 483.1964.

Synthesis of 4,9-bis(allyloxy)-1-phenyl-1*H*-phenalene-2-carbaldehyde 4ac. Under argon atmosphere, 4,9-dihydroxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **3a** (0.99 mmol, 300 mg, 1 equiv.) and 4 mL of anhydrous acetone were added into a flask. K_2CO_3 (2.50 mmol, 345 mg, 2.5 equiv.) and allyl bromide (3.96 mmol, 0.37 mL, 4 equiv.) were then added. The reaction was left to stir at reflux using a round bottom flask heating block for 5 hours. The solvent was removed under reduced pressure. The crude compound was purified by chromatography on silica gel (6/4 PE/EtOAc) to afford the corresponding product **4ac** as a yellow solid (250 mg, 65%). R_f = 0.42 (PE/EtOAc 6/4). mp 147-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.58–4.41 (m, 2H), 4.80–4.78 (m, 2H), 5.19–5.17 (m, 1H), 5.25–5.20 (m, 1H), 5.40–5.36 (m, 1H), 5.54–5.48 (m, 1H), 5.74 (s, 1H), 5.87 (ddt, J = 17.3, 10.4, 5.2 Hz, 1H), 6.16 (ddt, J = 17.3, 10.4, 5.2 Hz, 1H), 7.14–7.01 (m, 6H), 7.27–7.24 (m, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.98 (s, 1H), 9.59 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 39.0, 69.3, 69.9, 111.8, 113.0, 115.0, 117.5, 118.2, 121.8, 123.6, 126.1, 127.6, 127.7 (2C), 128.5 (2C), 130.4, 133.0 (2C), 133.1, 138.3, 139.0, 144.4, 154.7, 155.0, 192.1. IR (ATR, cm^{-1}) 3060, 2862, 1665, 1631, 1262, 910. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}O_3$ 383.1647; Found 383.1648.

Synthesis of 2-formyl-1-phenyl-1*H*-phenalene-4,9-diyl diacetate 4ad. Under argon atmosphere, 4,9-dihydroxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **3a** (0.99 mmol, 300 mg, 1 equiv.) and 8 mL of anhydrous pyridine were added into a flask. Acetic anhydride (3.96 mmol, 0.37 mL, 4 equiv.) was then added. The reaction was left to stir at room temperature for 5 hours. The reaction mixture was poured into 100 mL of water and filtered. The solid was solubilised in 20 mL of ethyl acetate. The organic layer was then washed with 10 mL of 1N HCl aq., 20 mL of a saturated Na_2CO_3 aq., and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the product **4ad** as a yellow solid (192 mg, 50%). R_f = 0.42 (PE/EtOAc 7/3). mp 175-177 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.48 (s, 3H), 5.57 (s, 1H), 7.18–7.12 (m, 5H), 7.23 (d, J = 8.8 Hz, 1H), 7.30 (d, J= 9.0 Hz, 1H), 7.57 (s, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 9.59 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 20.9, 21.1, 40.0, 120.2, 121.7, 123.2, 127.0, 127.2, 127.6, 128.3 (2C), 128.4 (2C), 129.1, 129.5, 132.1, 135.4, 140.9, 142.4, 146.9, 147.8, 168.5, 169.1, 191.5. IR (ATR, cm^{-1}) 3030, 2837, 1757, 1667, 1449, 1366, 1158, 1008. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}O_5$ 387.1232; Found 387.1229.

Synthesis of 1-phenyl-4,9-bis(prop-2-yn-1-yloxy)-1*H*-phenalene-2-carbaldehyde 4ae. Under argon atmosphere, 4,9-dihydroxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **3a** (4.3 mmol, 1.3 g, 1 equiv.) and 19.5 mL of acetone were introduced into a flask. K_2CO_3 (8.6 mmol, 1.19 g, 2 equiv.) and then propargyl bromide (22 mmol, 1.6 mL, 5 equiv.) were added. The mixture was refluxed using a round bottom flask heating block and stirred for 16 hours. After cooling to room temperature, 20 mL of dichloromethane was added. The organic layer was washed with NaOH 1M aq. and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the product **4ae** as a yellow solid (1.17 g, 72%). R_f = 0.33 (PE/EtOAc 6/4). mp 147-148 °C. ^{1}H NMR (400 MHz, Acetone-d_6) □ 3.06 (t, J = 2.4 Hz, 1H), 3.20 (t, J = 2.4 Hz, 1H), 4.74 (dd, J = 15.8, 2.4 Hz, 1H), 4.83 (dd, J = 15.9, 2.4 Hz, 1H), 5.11

(d, J = 2.4 Hz, 2H), 5.67(s, 1H), 7.13 – 7.00 (m, 3H), 7.24–7.21 (m, 2H), 7.32 (d, J = 8.9 Hz, 1H), 7.42 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 8.03 (s, 1H), 9.64 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, Acetone-d_6) δ 39.6, 57.1, 57.8, 77.1, 77.9, 79.5, 79.6, 113.7, 114.3, 116.3, 122.9, 125.3, 126.9, 128.6 (2C), 128.8, 129.1 (2C), 130.8, 133.9, 138.0, 140.2, 145.2, 154.9, 155.2, 192.2. IR (ATR, cm^{-1}) 3262, 2124, 1660, 1634. HRMS (ASAP+) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}O_3$ 379.1334; Found 379.1336.

Synthesis of phenalenone derivatives 5-14. The protected compound **4** (1 equiv.) and dichloromethane (0.02 $mol.L^{-1}$) were introduced into a flask. MnO_2 (20 equiv.) was then added. The reaction was left to stir at room temperature for 96 hours. The reaction mixture was filtered through a pad of celite, washed with dichloromethane, and the filtrate was then evaporated under reduced pressure. The crude compound was purified by column chromatography on silica gel (95/5 DCM/Et_2O) to afford the two isomers.

6-methoxy-1-oxo-7-phenyl-1H-phenalene-8-carbaldehyde ***5*** *and 6-methoxy-1-oxo-9-phenyl-1H-phenalene-8-carbaldehyde* ***5'***. According to the described general procedure, 707 mg (50%) of **5** (yellow solid) and 283 mg (20%) of **5'** (orange solid) were obtained from 4,9-dimethoxy-1-phenyl-1*H*-phenalene-2-carbaldehyde **4aa** (4.5 mmol, 1.5 g) and MnO_2 (90 mmol, 7.8 g). For **5**, R_f = 0.38 (DCM/Et_2O 95/5). mp 232-234 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 3H), 6.66 (d, J = 9.7 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.30–7.27 (m, 2H), 7.46–7.43 (m, 3H), 7.72 (d, J = 9.7 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 9.20 (s, 1H), 9.78 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 55.7, 107.0, 121.1, 123.4, 126.3, 127.5 (3C), 128.5, 128.6 (2C), 129.5, 131.5, 133.2, 135.6, 138.4, 142.5, 149.8, 162.2, 185.0, 191.5. IR (ATR, cm^{-1}) 3049, 2864, 1679, 1638, 1572, 1449, 1391, 1263, 1221, 1052, 1007**.** HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}O_3$ 315.1021; Found 315.1025. For **5'**, R_f = 0.58 (DCM/Et_2O 95/5). mp decomposition. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (s, 3H). 6.45 (d, J = 9.7 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.31–7.28 (m, 2H), 7.53–7.46 (m, 3H), 7.61 (d, J = 9.7 Hz, 1H), 7.81 (d, J

= 8.0 Hz, 1H), 9.30 (s, 1H), 9.80 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 56.3, 105.1, 121.5, 124.5, 126.9, 127.5, 128.2 (3C), 128.5 (2C), 128.6, 131.5, 133.3, 135.6, 137.7, 140.2, 148.2, 160.7, 185.5, 191.7. IR (ATR, cm^{-1}) 3020, 2949, 2861, 1725, 1629, 1560, 1490, 1463, 1378, 1225, 1152. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}O_3$ 315.1021; Found 315.1027.

6-(benzyloxy)-1-oxo-7-phenyl-1H-phenalene-8-carbaldehyde ***6*** *and 6-(benzyloxy)-1-oxo-9-phenyl-1H-phenalene-8-carbaldehyde* ***6'***. According to the described general procedure, 71 mg (55%) of **6** (yellow solid) and 12.9 mg (10%) of **6'** (yellow solid) were obtained from 4,9-bis(benzyloxy)-1-phenyl-1*H*-phenalene-2-carbaldehyde **4ab** (0.33 mmol, 134 mg) and MnO_2 (6.6 mmol, 574 mg). For **6**, R_f = 0.39 (DCM/Et_2O 95/5). mp decomposition. ^{1}H NMR (300MHz, $CDCl_3$) δ 4.85 (s, 2H), 6.67 (d, J = 9.7 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.99–6.96 (m, 2H), 7.13–7.08 (m, 1H), 7.25–7.17 (m, 5H), 7.29–7.28 (m, 2H), 7.72 (d, J = 9.7 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 9.20 (s, 1H), 9.67 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 71.2, 108.0, 121.1, 123.3, 126.3, 127.4 (2C), 127.6, 128.1 (2C), 128.2, 128.5 (5C), 129.5, 131.6, 133.4, 134.5, 135.5, 138.0, 142.5, 149.8, 161.2, 185.0, 191.5. IR (ATR, cm^{-1}) 3038, 2870, 1675, 1633, 1568, 1513, 1338, 1220, 1139. HRMS (ES+) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{18}NaO_3$ 413.1154; Found 413.1150. For **6'**, R_f = 0.63 (DCM/Et_2O 95/5). ^{1}H NMR (300MHz, $CDCl_3$) δ 5.41 (s, 2H), 6.45 (d, J = 9.7 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.31–7.28 (m, 2H), 7.47–7.40 (m, 5H), 7.55–7.48 (m, 3H), 7.60 (d, J = 9.7 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 9.35 (s, 1H), 9.80 (s, 1H).

6-(allyloxy)-1-oxo-7-phenyl-1H-phenalene-8-carbaldehyde ***7*** *and 6-(allyloxy)-1-oxo-9-phenyl-1H-phenalene-8-carbaldehyde* ***7'***. According to the described general procedure, 178 mg (50%) of **7** (yellow solid) and 29 mg (8%) of **7'** (yellow solid) were obtained from 4,9-bis(allyloxy)-1-phenyl-1*H*-phenalene-2-carbaldehyde **4ac** (0.83 mmol, 400 mg) and MnO_2 (16.6 mmol, 1.4 g). For **7**, R_f = 0.35 (DCM/Et_2O 95/5). mp 167-169 °C. ^{1}H NMR

(300MHz, $CDCl_3$) δ 4.30 (d, J = 5.5 Hz, 2H), 5.11–5.04 (m, 2H), 5.31–5.18 (m, 1H), 6.64 (d, J = 9.7 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 7.29–7.27 (m, 2H), 7.44–7.41 (m, 3H), 7.70 (d, J = 9.7 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 9.18 (s, 1H), 9.73 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) □ 53.4, 69.7, 107.8, 118.4, 121.1, 123.4, 126.2, 127.5, 127.7 (2C), 128.4, 128.7 (2C), 129.5, 131.6, 133.2, 135.6, 138.5, 142.5, 149.8, 161.1, 184.9, 191.5. IR (ATR, cm^{-1}) 3057, 2876, 2780, 1675, 1631, 1567, 1629, 1228, 1056, 1025. HRMS (ASAP+) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}O_3$ 341.1178; Found 341.1178. For **7**', R_f = 0.55 (DCM/Et_2O 95/5). ^1H NMR (300MHz, $CDCl_3$) δ 4.87-4.85 (m, 2H), 5.43 (dd, J = 10.5, 1.2 Hz, 1H), 5.56 (dd, J = 10.5, 1.2 Hz, 1H), 6.20 (ddt, J = 17.2, 10.5, 5.3 Hz, 1H), 6.45 (d, J = 9.6 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 7.29 (d,d, J = 7.1, 1.6 Hz, 2H), 7.54-7.46 (m, 3H), 7.60 (d, J = 9.6 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 9.32 (s, 1H), 9.80 (s, 1H).

1-oxo-7-phenyl-6-(prop-2-yn-1-yloxy)-1H-phenalene-8-carbaldehyde ***8*** *and 1-oxo-9-phenyl-6-(prop-2-yn-1-yloxy)-1H-phenalene-8-carbaldehyde* ***8'***. According to the described general procedure, 206.6 mg (50%) of **8** (yellow solid) and 18.6 mg (5%) of **8'** (orange solid) were obtained from 1-phenyl-4,9-dipropynyl-1*H*-phanelene-2-carbaldehyde **4ae** (2.65 mmol, 1 g) and MnO_2 (53 mmol, 4.6 g). For **8**, R_f = 0.32 (DCM/Et_2O 95/5). mp 188-191 °C. ^1H NMR (400MHz, $CDCl_3$) □ 2.41 (t, J = 2.4 Hz, 1H), 4.37 (d, J = 2.4 Hz, 2H), 6.65 (d, J = 9.7 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 7.31-7.28 (m, 2H), 7.46-7.43 (m, 3H), 7.71(d, J = 9.7 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 9.16 (s, 1H), 9.76 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) □ 56.2, 76.4, 77.0, 108.9, 122.0, 123.8, 126.8, 127.8 (3C), 128.6, 128.9 (2C), 129.6, 131.7, 133.6, 135.1, 138.3, 142.4, 149.8, 159.8, 185.0, 191.5. IR (ATR, cm^{-1}) 3304, 2133, 1675, 1630, 1566, 1268. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{23}H_{15}O_3$ 339.1021; Found 339.1021. For **8**', R_f = 0.47 (DCM/Et_2O 95/5). ^1H NMR (300MHz, $CDCl_3$) □ 2.63 (t, J = 2.4 Hz, 1H), 5.04 (d, J = 2.4 Hz, 2H), 6.46 (d, J = 9.6Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.30-7.27 (m, 2H), 7.52-7.47 (m, 3H), 7.62 (d, J = 9.6 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 9.28 (s, 1H), 9.80 (s, 1H).

6-methoxy-1-oxo-7-(p-tolyl)-1H-phenalene-8-carbaldehyde ***9*** *and 6-methoxy-1-oxo-9-(p-tolyl)-1H-phenalene-8-carbaldehyde* ***9'***. According to the described general procedure, 135 mg (58%) of **9** (orange solid) and 33 mg (14%) of **9'** (orange solid) were obtained from 4,9-dimethoxy-1-(p-tolyl)-1*H*-phenalene-2-carbaldehyde **4ba** (0.71 mmol, 244 mg) and MnO_2 (14.2 mmol, 1.23 g). For **9**, R_f = 0.35 (DCM/Et_2O 95/5). mp 256-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.54 (s, 3H), 6.66 (d, J = 9.7 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.17–7.15 (m, 2H), 7.27–7.26 (m, 2H), 7.72 (d, J = 9.7 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 9.19 (s, 1H), 9.78 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 21.3, 55.7, 107.0, 121.1, 123.6, 126.3, 128.1 (2C), 128.5, 128.6 (2C), 129.4, 131.5, 133.5, 135.3, 135.5, 137.1, 142.4, 150.1, 162.3, 185.0, 191.7. IR (ATR, cm^{-1}) 3042, 2960, 2936, 1681, 1639, 1569, 1546, 1453, 1392. HRMS (ASAP+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}O_3$ 329.1178; Found 329.1176. For **9'**, R_f = 0.52 (DCM/Et_2O 95/5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 4.14 (s, 3H), 6.44 (d, J = 9.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 7.20–7.16 (m, 2H), 7.34–7.30 (m, 2H), 7.60 (d, J = 9.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 9.27 (s, 1H), 9.83 (s, 1H).

6-methoxy-7-(4-methoxyphenyl)-1-oxo-1H-phenalene-8-carbaldehyde ***10*** *and 6-methoxy-9-(4-methoxyphenyl)-1-oxo-1H-phenalene-8-carbaldehyde* ***10'***. According to the described general procedure, 53 mg (53%) of **10** (yellow solid) and 22 mg (22%) of **10'** (orange solid) were obtained from 4,9-dimethoxy-1-(4-methoxyphenyl)-1*H*-phenalene-2-carbaldehyde **4ca** (0.29 mmol, 104 mg) and MnO_2 (5.8 mmol, 504 mg). For **10**, R_f = 0.32 (DCM/Et_2O 95/5). mp 228-230 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 3.91 (s, 3H), 6.62 (d, J = 9.7 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.01–6.96 (m, 2H), 7.21–7.16 (m, 2H), 7.69 (d, J = 9.7 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 9.15 (s, 1H), 9.79 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 55.4, 55.8, 107.0, 112.9 (2C), 121.0, 123.6, 126.1, 128.5, 129.3, 130.0 (2C), 130.4, 131.5, 133.7, 135.6, 142.5, 149.7, 159.1, 162.4, 185.0, 191.8. IR (ATR, cm^{-1}) 3031, 2954, 2873, 1726, 1676, 1568, 1512, 1448, 1390, 1229, 1174. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}O_4$ 345.1127;

Found 345.1149. For **10**', R_f = 0.65 (DCM/Et_2O 95/5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H), 4.13 (s, 3H), 6.45 (d, J = 9.6 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 7.07–7.02 (m, 2H), 7.24–7.19 (m, 2H), 7.59 (d, J = 9.6 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 9.25 (s, 1H), 9.85 (s, 1H).

*6-methoxy-7-(3-methoxyphenyl)-1-oxo-1H-phenalene-8-carbaldehyde **11** and 6-methoxy-9-(3-methoxyphenyl)-1-oxo-1H-phenalene-8-carbaldehyde **11'**.* According to the described general procedure, 397 mg (57%) of **11** (yellow solid) and 84 mg (12%) of **11'** (orange solid) were obtained from 4,9-dimethoxy-1-(3-methoxyphenyl)-1*H*-phenalene-2-carbaldehyde **4da** (1.03 mmol, 400 mg) and MnO_2 (20.6 mmol, 1.79 g). For **11**, R_f = 0.4 (95/5 DCM/Et_2O). mp 170-172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3H), 3.83 (s, 3H), 6.63 (d, J = 9.7 Hz, 1H), 6.88–6.81 (m, 3H), 6.98 (ddd, J = 8.3, 2.6, 0.8 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.70 (d, J = 9.7 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 9.16 (s, 1H), 9.78 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 55.4, 55.8, 107.0, 113.0, 114.5, 121.0, 121.4, 123.3, 126.2, 128.3, 128.6, 129.5, 131.4, 133.1, 135.6, 139.7, 142.5, 149.4, 159.0, 162.2, 184.9, 191.5. IR (ATR, cm^{-1}) 2947, 2843, 1683, 1635, 1570, 1221, 1169, 1096, 1041. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}O_4$ 345.1127; Found 345.1118. For **11**', R_f = 0.65 (95/5 DCM/Et_2O). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.14 (s, 3H), 6.45 (d, J = 9.6 Hz, 1H), 6.83–6.82 (m, 1H), 6.88 (dt, J = 7.4, 1.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.00 (ddd, J = 8.4, 2.6, 1.2 Hz, 1H), 7.44–7.40 (m, 1H), 7.61 (d, J = 9.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 9.28 (s, 1H), 9.81 (s, 1H).

*7-(4-fluorophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde **12** and 9-(4-fluorophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde **12'**.* According to the described general procedure, 114 mg (60%) of **12** (yellow solid) and 21 mg (11%) of **12'** (orange solid) were obtained from 1-(4-fluorophenyl)-4,9-dimethoxy-1*H*-phenalene-2-carbaldehyde **4fa** (0.57 mmol, 200 mg) and MnO_2 (11.4 mmol, 991 mg). For **12**, R_f = 0.35 (DCM/Et_2O 95/5). mp 240-241 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3H), 6.66 (d, J = 9.7 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.21–7.13 (m, 2H), 7.29–7.24 (m, 2H), 7.71 (d, J = 9.7

Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 9.18 (s, 1H), 9.80 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 55.8, 107.1, 114.5, 114.8, 121.2, 123.5, 126.3, 128.5, 129.7, 130.3, 130.4, 131.5, 133.4, 134.2, 134.3, 135.6, 142.4, 148.5, 162.0, 184.8, 191.1. IR (ATR, cm^{-1}) 3066, 1682, 1634, 1220, 1094. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}FO_3$ 333.0927; Found 333.0929. For **12**', R_f = 0.61 (DCM/Et_2O 95/5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (s, 3H), 6.42 (d, J = 9.6 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 7.16-7.12 (m, 2H), 7.63-7.58 (m, 3H), 7.80 (d, J = 8.1 Hz, 1H), 9.27 (s, 1H), 9.80 (s, 1H).

7-(4-chlorophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde ***13*** *and 9-(4-chlorophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde* ***13'***. According to the described general procedure, 83 mg (35%) of **13** (yellow solid) and 47 mg (20%) of **13'** (orange solid) were obtained from 1-(4-chlorophenyl)-4,9-dimethoxy-1*H*-phenalene-2-carbaldehyde **4ga** (0.75 mmol, 250 mg) and MnO_2 (15 mmol, 1.3 g). For **13**, R_f = 0.38 (DCM/Et_2O 95/5). mp decomposition. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 6.67 (d, J = 9.7 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.25–7.22 (m, 2H), 7.48–7.43 (m, 2H), 7.73 (d, J = 9.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 9.19 (s, 1H), 9.80 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 55.8, 107.1, 121.1, 123.3, 126.3, 127.8 (2C), 128.4, 129.7 (2C), 130.0, 131.4, 133.1, 133.6, 135.7, 136.9, 142.5, 148.1, 161.9, 184.8, 190.9. IR (ATR, cm^{-1}) 3042, 1681, 1639, 1223, 829. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}ClO_3$ 349.0631; Found 349.0629. For **13**', R_f = 0.55 (DCM/Et_2O 95/5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (s, 3H), 6.45 (d, J = 9.7 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 7.25–7.21 (m, 2H), 7.51–7.47 (m, 2H), 7.63 (d, J = 9.7 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 9.30 (s, 1H), 9.82 (s, 1H).

7-(4-bromophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde ***14*** *and 9-(4-bromophenyl)-6-methoxy-1-oxo-1H-phenalene-8-carbaldehyde* ***14'***. According to the described general procedure, 54 mg (42%) of **14** (yellow solid) and 19 mg (15%) of **14'** (orange solid) were obtained from 1-(4-bromophenyl)-4,9-dimethoxy-1*H*-phenalene-2-

carbaldehyde **4ha** (0.33 mmol, 134 mg) and MnO_2 (6.6 mmol, 574 mg). For **14**, R_f = 0.32 (DCM/Et_2O 95/5). mp decomposition. ^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 6.67 (d, J = 9.8 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.21–7.16 (m, 2H), 7.63–7.59 (m, 2H), 7.72 (d, J = 9.8 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 9.19 (s, 1H), 9.80 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 55.8, 107.1, 121.2, 121.6, 123.3, 126.4, 128.5, 129.7, 130.3 (2C), 130.7 (2C), 131.5, 133.1, 135.6, 137.4, 142.5, 148.1, 161.9, 184.8, 190.9. IR (ATR, cm^{-1}) 3054, 2948, 1731, 1681, 1569, 1486, 1223, 1174, 1096, 805. HRMS (ES+) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}BrO_3$ 393.0126; Found 393.0115. For **14**', R_f = 0.64 (DCM/Et_2O 95/5). ^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (s, 3H), 6.45 (d, J = 9.7 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 7.20–7.15 (m, 2H), 7.65–7.61 (m, 3H), 7.83 (d, J = 8.1 Hz, 1H), 9.30 (s, 1H), 9.82 (s, 1H).

Photooxygenation of anthracene 15. To a Schlenk flask was added anthracene **15** (0.28 mmol, 50 mg, 1 equiv.), 6-methoxy-1-oxo-7-phenyl-1*H*-phenalene-8-carbaldehyde **5** (5.6 µmol, 1.76 mg, 2 mol%), methyl phenyl sulfone as an internal standard (0.14 mmol, 21.9 mg, 0.5 equiv.) and $CDCl_3$ (3.5 mL) to give a yellow solution. The reaction medium was bubbled for 5 minutes with dioxygen and was then left under atmospheric pressure of dioxygen throughout the reaction time. The homogenous solution was irradiated with one blue LED (1 W, 25 lm, 470 nm typical wavelength). The distance from light source irradiation and the Schlenk vessel was 3 cm without the use of any filters. The reaction was left to stir at room temperature, an aliquot (0.2 mL) was taken from the reaction mixture at different reaction times. The aliquot was diluted with $CDCl_3$ (0.2 mL) nitrogen was bubbled through the solution to remove oxygen. The samples were analyzed by ^1H NMR to determine the yield and product formation.

Photooxidation of citronellol 17. To a Schlenk flask was added citronellol **17** (0.52 mmol, 95 µL, 1 equiv.), 6-methoxy-1-oxo-7-phenyl-1*H*-phenalene-8-carbaldehyde **5** (10.40 µmol, 3.27 mg, 2 mol%) and $CHCl_3$ (2 mL) to give a yellow solution. The reaction

medium was gently bubbled with dioxygen throughout the reaction time and the homogenous solution was irradiated with one blue LED (1 W, 25 lm, 470 nm typical wavelength). The distance from light source irradiation and the Schlenk vessel was 3 cm without the use of any filters. The reaction was left to stir at room temperature for 3 hours at which point a saturated solution of $Na_2S_2O_3$ aq. was added. Then the reaction medium was left to stir at room temperature for 2 hours. The solvent was removed under reduced pressure. The crude compound was purified by chromatography on silica gel (98/2 DCM/MeOH) to afford a 1:1 mixture of products **18a** and **18b** as a colourless oil (63 mg, 70%). *R_f = 0.4 (mixture **18a** + **18b,** DCM/MeOH 98/2).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91–0.88 (m, 6H), 1.27–1.02 (m, 2H), 1.30 (s, 6H, **18a**), 1.48–1.33 (m, 4H), 1.66–1.49 (m, 6H), 1.69–1.68 (m, 1H, **18a**), 1.71 (s, 3H, **18b**), 1.92 (dd, J = 6.6, 5.5 Hz) and 1.89–1.85 (m) (1H, **18a**), 2.05 (t, J = 5.5 Hz) and 2.02–1.99 (m) (1H, **18a**), 3.73–3.60 (m, 4H), 4.05–4.00 (m, 1H, **18b**), 4.82–4.81 (m, 1H, **18b**), 4.93–4.92 (m, 1H, **18b**), 5.60–5.57 (m, 2H, **18a**). All the physical and spectroscopic data were in complete agreement with the reported ones.[32]

Photooxidation of cyclohexa-1,3-diene 19. To a Schlenk flask was added cyclohexa-1,3-diene **19** (1 mmol, 80 mg, 1 equiv.), 6-methoxy-1-oxo-7-phenyl-1*H*-phenalene-8-carbaldehyde **5** (20 µmol, 6.29 mg, 2 mol%) and $CHCl_3$ (4 mL) to give a yellow solution. The reaction medium was gently bubbled with dioxygen throughout the reaction time and the homogenous solution was irradiated with one blue LED (1 W, 25 lm, 470 nm typical wavelength). The distance from light source irradiation and the Schlenk vessel was 3 cm without the use of any filters. The reaction was left to stir at room temperature for 2 hours at which point thiourea (1.26 mmol, 96 mg, 1 equiv.) in 2 mL of MeOH was added. Then the reaction middle was vigorously left to stir at room temperature for 1 hour. The reaction mixture was filtered through a pad of celite and washed with MeOH. The solvent was removed under reduced pressure. The crude compound was purified by chromatography on

silica gel (EtOAc) to afford the corresponding product **20** as white solid (103 mg, 90%). R_f = 0.3 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85–1.75 (m, 4H), 4.15 (s, 2H), 5.86 (s, 2H). All the physical and spectroscopic data were in complete agreement with the reported ones.[33]

Spectroscopic and photophysical measurements. UV-Vis spectra were recorded on an Agilent 8453 Diode-Array spectrophotometer in the range of 250-700 nm. Emission spectra were measured in an ISS PC1 spectrofluorometer at room temperature. Luminescence lifetime measurements were carried out using a PicoQuant FluoTime 200 fluorescence lifetime spectrometer with a multichannel scaler (PicoQuant's Timeharp 250) with the time correlated single photon counting (TCSPC) method. LEDs or lasers of adequate wavelength were employed as excitation source. Fluorescence quantum yields were determined using equation (1) and 6-ethoxy-phenalenone in chloroform (Φ_F = 0.049) as reference.[28]

$$\Phi_{F,sample} = \Phi_{F,reference} \frac{A_{reference}}{A_{sample}} \frac{I_{sample}}{I_{reference}} \left(\frac{\eta_{sample}}{\eta_{reference}}\right)^2 \quad (1)$$

Φ_F is the fluorescence quantum yields. A: is the absorbance in the wavelength of excitation, I correspond to area of the emission spectra and η is the refractive index of the solvent.

Lifetime decays singlet oxygen, $O_2(^1\Delta_g)$, were acquired with a FluoTime 200 consisting in a multichannel scaler Nanoharp 200. Excitation at 355 nm was achieved with a laser FTSS355-Q3, (Crystal Laser, Berlin, Germany) working at 1 kHz repetition rate. For the detection at 1270 nm a NIR PMT H10330A (Hamamatsu) was employed. The $O_2(^1\Delta_g)$ quantum yields (Φ_Δ) were determined by comparing the intensity at zero time of the 1270 nm signals to those of optically-matched solutions of phenalenone as reference, according to the following equation.[34]

$$\emptyset_\Delta = \frac{I_\Delta\,(t=0)}{I'_\Delta(t=0)}\ \emptyset'_\Delta \text{The transient difference absorption}$$

Computational methods. All calculations reported here are based on density functional theory (DFT). Full gas-phase geometry optimizations of both phenalenone derivatives

(namely as **5** and **5'**) were performed using the hybrid B3LYP[35] exchange-correlation functional in conjunction with the split-valence double-ζ quality Def2SVP basis set for all atoms. Conformation analysis was also carried out in each derivative identifying the most stables rotamers and the respective transition state connecting them. These stationary states were confirmed as local minima or first-order saddle-points through an harmonic vibrational analysis in accord with the number of imaginary frequencies, zero or one, respectively. Using the rigid-rotor-harmonic-oscillator (RRHO) approximation at a given temperature, frequencies calculations also provide the thermal and entropic corrections for the free Gibbs energies ($G^{T}_{RRHO}(B3LYP/Def2SVP)$). Additionally, more accurate electronic energies (E) for the rotameric changes were also computed at the same level of theory by single-point energy calculations combined with Def2TZVP. In those studies solute-solvent interactions were described through the implicit SMD solvation model,[36] using methanol as solvent. Therefore, the free Gibbs energy for each stationary state is given by: $G = E + G^{T}_{solv} + G^{T}_{RRHO}$. The excited features were investigated using TD-DFT framework using the range-separated hybrid CAM-B3LYP[37] exchange-correlation functional combined with the split-valence triple-ζ quality Def2TZVP basis set at the gas-phase optimized geometries. All calculations were done employing the Gaussian09 suite of programs.[38] CYLview program was used for molecular representations.[39]

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications web site.

Additional UV-vis, TRES spectra and fluorescence lifetimes for **5'** and computational details. Copies of ^{1}H and ^{13}C spectra as well as full characterization (2D-NMR spectra) for **5** and **5'** were provided.

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