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Sunlight Induced Oxidative Photoactivation of *N*-Hydroxyphthalimide Mediated by Naphthalene Imides

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Abstract: We report the aerobic photoactivation of *N*-hydroxyphthlimide (NHPI) to the phthalimido-*N*-oxyl (PINO) radical mediated by naphthalene monoimides (NI) for promoting the selective oxidation of alkylaromatics and allylic compounds to the corresponding hydroperoxides. In the absence of either NI or NHPI no oxidation was observed, meaning that the two molecules operate in a synergistic way. Sunlight as well as artificial UV-light irradiation was necessary in order to perform the process at low temperature (30–35 °C). EPR spectroscopy confirmed the role of NI and oxygen in promoting the formation of the superoxide radicals $O_2^{\bullet -}$ which, in turn, increased the concentration of PINO radicals during the UV light irradiation of NI/NHPI mixtures in MeCN. The investigation was extended to NI bearing different substituents on the naphthalene moiety. Finally, the synthesis and application of a unique photocatalyst including the NI and NHPI moieties linked by a suitable spacer was also considered. In this case the photocatalyst showed a substrate-dependent behaviour with some peculiarities in comparison to the system where NI and NHPI are independent units in the same reacting system. This photocatalytic system paves the way to a non-thermal, metal-free approach for C–H bond activation towards aerobic oxidation under very mild conditions.

Keywords: hydroperoxides; *N*-hydroxyphthalimide; naphthalene imides; oxidation; oxygen; photoactivation

Introduction

N-Hydroxyphthalimide (NHPI) is a good hydrogen donor acting as precursor of the phthalimide *N*-oxyl (PINO) radical, which in turn is able to activate the C–H bond by hydrogen abstraction.[1] For this reason, in the last decade the combination of NHPI with metals or other initiators was proposed as a valuable catalytic system for the aerobic oxidation and functionalization of a large number of organic substrates.[2]

The aerobic oxidation of alkylaromatic hydrocarbons to the corresponding hydroperoxides has attracted increasing interest due to the considerable importance of this transformation both in the chemical industry and in organic synthesis.[3] In this context, activation of molecular oxygen in the presence of NHPI allows one to operate at lower temperatures compared to the non-catalyzed processes, and under metal-free conditions, overcoming the two main drawbacks which affect the selectivity in hydroperoxides for classical protocols, namely the high temperature and the use of metals as co-catalysts. Nevertheless, in all the proposed approaches the combined use of NHPI with different initiators was mandatory in order to operate under the required mild conditions. We have recently shown how acetaldehyde can be used as sacrificial initiator for the NHPI-catalyzed aerobic oxidation of cumene (CU)[4a] and ethylbenzene[4b] to the corresponding cumyl hydroperoxide (CH) and ethylbenzene hydroperoxide, respectively, at temperatures lower than 50 °C. However, despite the good conversions (up to 40%), the formation of by-products [mainly cumyl alcohol (CA) and acetophenone (AP)] was still observed.

On the basis of these considerations, the introduction of new oxidation methods for the production of hydroperoxides, combining the catalytic efficiency of NHPI with mild process conditions, still requires the development of new metal-free initiation protocols capable of limiting the formation of secondary products.

In this context, we decided to investigate the possibility of activating NHPI by photo-irradiation.

The very first example of light-induced *in situ* generation of PINO radical was reported in 2007 by Lucarini and co-workers.[5] Following this approach, irradiation promoted the selective homolysis of the O–C bond of *N*-alkoxyphthalimides, leading to the formation of the *N*-oxyl radical. However, this valuable procedure cannot be applied directly to NHPI. More recently, Zhang et al. successfully proposed the metal-free oxidation of allylic compounds using NHPI in combination with graphitic carbon nitride (g-C_3N_4) as visible-light photo-activated catalyst.[6] According to the reported mechanism, visible-light irradiated g-C_3N_4 was able to activate O_2 to the more reactive $O_2^{\bullet -}$ species. In turn, $O_2^{\bullet -}$ effected hydrogen abstraction from NHPI generating the PINO radical and finally promoting the chain oxidation mechanism. Nevertheless, it was also reported how g-C_3N_4 promotes the hydroperoxide decomposition, making this system useless for our purposes. Moreover, most of the reported data were collected at 60 °C, a temperature at which the partial superimposition of classical thermal autoxidation process cannot be ignored.

Due to their commercial availability, low cost, chemical stability and excellent optical and electric performances, naphthalene monoimides (NI) and diimides (NDI) have been intensely investigated in the last years as valuable candidates for the preparation of organic thin-film transistors, photovoltaic cells and chemical sensors.[7] In particular, NI are valuable candidates for applications in photo-oxidative processes due to their electron donor behaviour.[8]

For this reason, we wanted to verify the possible mediation of NI in promoting the photo-activation of NHPI under aerobic conditions.

In this work we report, for the first time, the photo-assisted metal-free aerobic activation of NHPI mediated by NI (Figure 1). The NI/NHPI catalytic system was successfully applied for the selective sunlight induced oxidation of different hydrocarbons (including alkylaromatics and cyclic alkenes) to the corresponding hydroperoxides under very mild conditions. Moreover, we investigated the photoactivity of substituted NI bearing different functional groups introduced on the naphthalene moiety. Finally we also considered the synthesis and application of a photocatalyst having the NI and NHPI groups linked by a suitable spacer. The combined action of O_2, NI and NHPI during the photo-oxidative process was supported by an in depth EPR investigation.

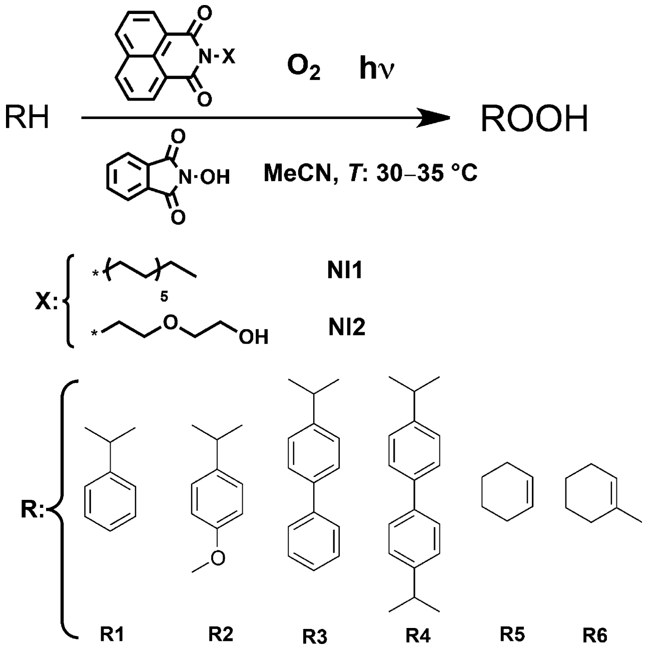


Figure 1. Reaction scheme.

Results and Discussion

NI1 and **NI2** were synthesized to be tested as photo-activators of NHPI under aerobic conditions. The presence of a dodecyl alkyl chain on the nitrogen atom of **NI1** guarantees high solubility of the compound in classical organic mediums. The introduction of a different chain, leading to the formation of compound **NI2**, had the scope to verify the eventual effect of the chain on the overall activity.

Initial experiments were conducted using CU as substrate in order to verify the feasibility of the process and to set the experimental conditions. Table 1

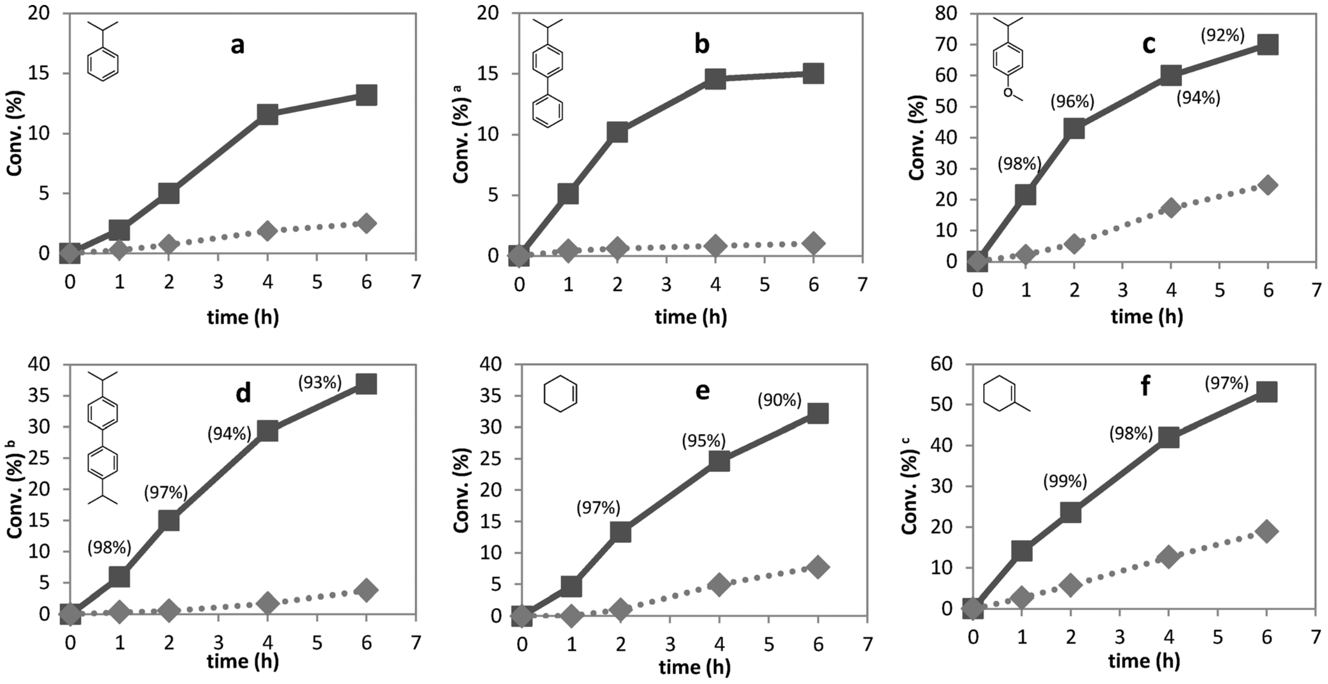
Table 1. Cumene oxidation under sunlight using compound **NI1**. *Conditions:* 5 mmol cumene in 10 mL MeCN under O_2 (1 atm) for 6 h, *T*: 30–35 °C. Total sunlight exposure: 5 h.

Entry	NHPI	NI	CH yield [%]	Selectivity [%]
1	2%	5%	8.48	100
2[a]	2%	5%	7.99	100
3	2%	none	1.40	100
4	none	5%	0.00	–
5	5%	5%	13.14	100
6	5%	5%	13.34	100
7	5%	none	3.29	100
8	5%	none	3.49	100
9	5%	none	2.93	100
10[b]	5%	5%	0.00	–
11[c]	2%	5%	8.72	100

[a] Cumene:water = 1:1 (mol:mol).

[b] Reaction in the dark.

[c] Compound **NI2** in place of **NI1**.



[a] Performed using 1 mmol of substrate and 5 mL of MeCN.

[b] Conversion of isopropyl groups and selectivity in total hydroperoxides (see Supporting Information, Table SI1 for details).

[c] Selectivity in total hydroperoxides (see Supporting Information, Table SI1 for details).

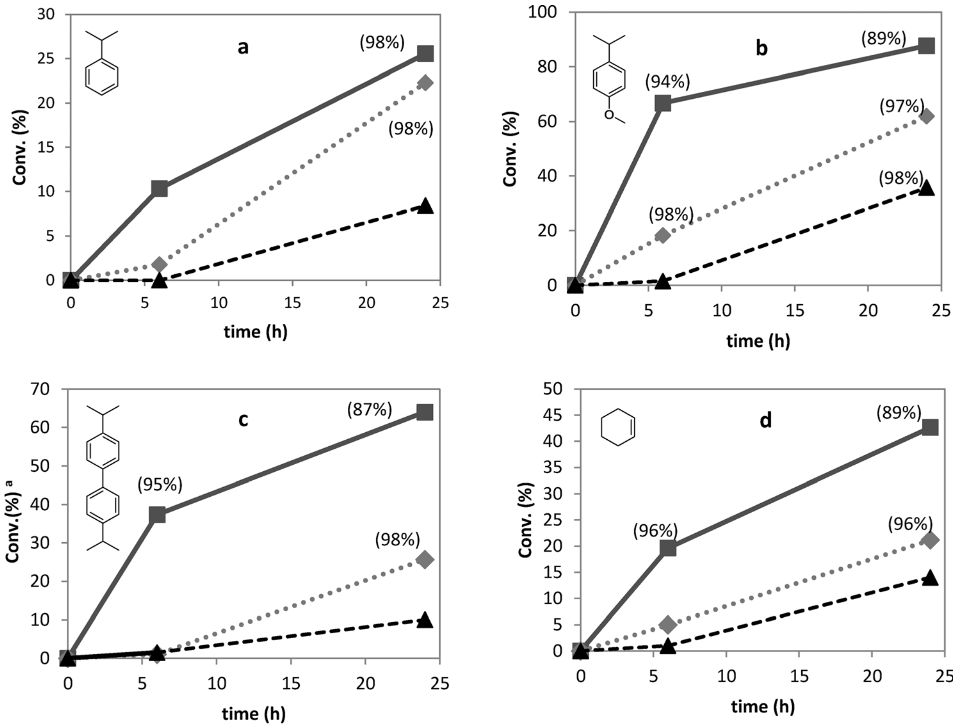
Figure 2. Hydrocarbon oxidation under sunlight. ■ **NI1** (5%)+NHPI (5%); ◆ NHPI (5%). *Conditions:* 5 mmol of hydrocarbon in 10 mL of MeCN under O_2 (1 atm), *T*: 30–35 °C. Hydroperoxide selectivity is reported in brackets if lower than 100%.

reports the yields in CH after 6 h of sunlight irradiation in the presence of **NI1**, NHPI and under an O_2 atmosphere. On increasing the NHPI concentration (from 2 to 5% on a molar base, Table 1, entries 1 to 6) the CH yield increased up to about 13%, while in the absence of the photo-activator the yield did not exceed 3% (entries 3, 7, 8 and 9). The reaction conducted in the presence of **NI1** (5%) and NHPI (5%), but in the dark, did not show any CH formation, confirming the key role of the light irradiation in the oxidative process (entry 10). Finally, **NI2** gave results analogous to those obtained with **NI1** (entry 11).

Encouraged by these preliminary data we decided to extend the investigation to different alkylaromatics and cyclic alkenes. Figure 2 reports the conversion of the selected hydrocarbons under sunlight *versus* time by operating in the presence of: a) **NI1** (5%) and NHPI (5%) (continuous line, square markers); b) only NHPI (5%) (dotted line, rhomboid markers). The selectivity in hydroperoxide is reported in brackets if lower than 100%.

The data clearly show a significant increase of the oxidation rate for all the substrates when using **NI1** in combination with NHPI. Moreover, the process is characterized by high selectivity in hydroperoxides (> 90%). In the case of alkylaromatic hydrocarbons, alcohols are the main by-products while the corresponding ketones are formed in very small amounts. In the case of cyclohexene, apart the formation of 3-hydroperoxycyclohex-1-ene as main product, we observed only the formation of cyclohex-2-enone as secondary product. Finally, the oxidation of 1-methylcyclohex-1-ene gave a mixture of hydroperoxides – 3-hydroperoxy-3-methylcyclohex-1-ene and 3-hydroperoxy-1-methylcyclohex-1-ene being the predominant ones. No formation of ketones was detected. The complete distribution of the product for all the investigated substrates is reported in Table SI1 in the Supporting Information. For all the substrates no conversion was observed in the dark.

Similar experiments were performed under artificial light irradiation ($\lambda = 365$ nm) focusing the attention on the substrates **R1**, **R2**, **R4** and **R5**. The experimental observations are reported in Figure 3. In Figure 3 we also report the data obtained when performing the oxidation at 40 °C without irradiation and without **NI1** but in presence of NHPI (5%) in order to verify how much the temperature can affect the experimental results. It is worth noting that in all the photo-assisted experiments (both under sunlight and artificial light) the temperature of the reacting mixtures never exceeded 35 °C (30–35 °C). These data



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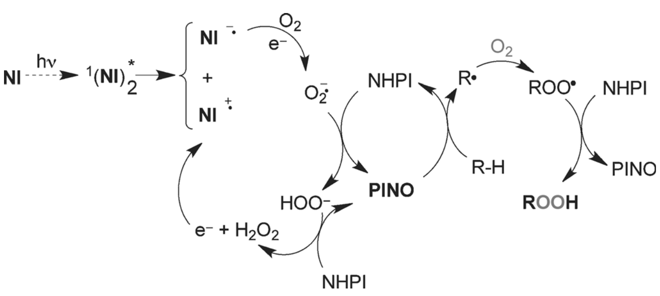
[a] Conversion of isoproyl groups and selectivity in total hydroperoxides.

Figure 3. Hydrocarbon oxidation under UV light irradiation ($\lambda = 365$ nm). ■ **NI1** (5%)+NHPI (5%); ◆ NHPI (5%); ▲ NHPI (5%) at 40 °C without irradiation. *Conditions:* 5 mmol of hydrocarbon in 10 mL of MeCN under O_2 (1 atm), *T*: 30–35 °C. Hydroperoxide selectivity is reported in brackets if lower than 100%.

clearly highlight how the presence of **NI1** is extremely advantageous for the activation of the oxidative process due to the significant increase of the reaction rate (continuous line – square markers). This allows us to reduce the delay times generally observed both in the absence of **NI1** (dotted line – rhomboid markers) and during the classical thermally assisted oxidation (dashed line – triangular markers). In this last case, the substrate conversion after 6 h at 40 °C was practically negligible. Only after a prolonged time (24 h) did we observe a certain conversion of the substrates that was, in any case, below the values measured under UV irradiation. Moreover, a comparison between the three curves reported in each graph of Figure 3 evidences that, by itself, UV light is beneficial for the oxidation process but only after the formation of a minimum amount of hydroperoxide. Once formed, tiny amounts of hydroperoxides can undergo light-induced decomposition, becoming a further source of radicals. Hence NHPI, playing its fundamental role of H-donor, reduces the effects of the termination reactions, while the PINO radical promotes the generation of carbon centered radicals enhancing the propagation of chain length by the formation of other hydroperoxide molecules. However, the amount of hydroperoxide decomposed by the UV light is sufficiently low in our temperature conditions that the selectivity is still high even after prolonged irradiation times.

In order to justify the higher conversions obtained with the NI/NHPI system, we hypothesized that NI could be able to increase the concentration of PINO radical through the generation of the superoxide radical $O_2^{\bullet -}$ by a photo-activated electron transfer under aerobic conditions, according to the Scheme 1.[9] We found evidence of our assumption by means of electron spin resonance (EPR) spectroscopy. Room temperature irradiation of an aerobic MeCN solution of NHPI (25 mM) with filtered light ($\lambda > 300$ nm) of



Scheme 1. Possible role of NI in the photoactivation of the NHPI-based hydrocarbons oxidation. See ref.[9]

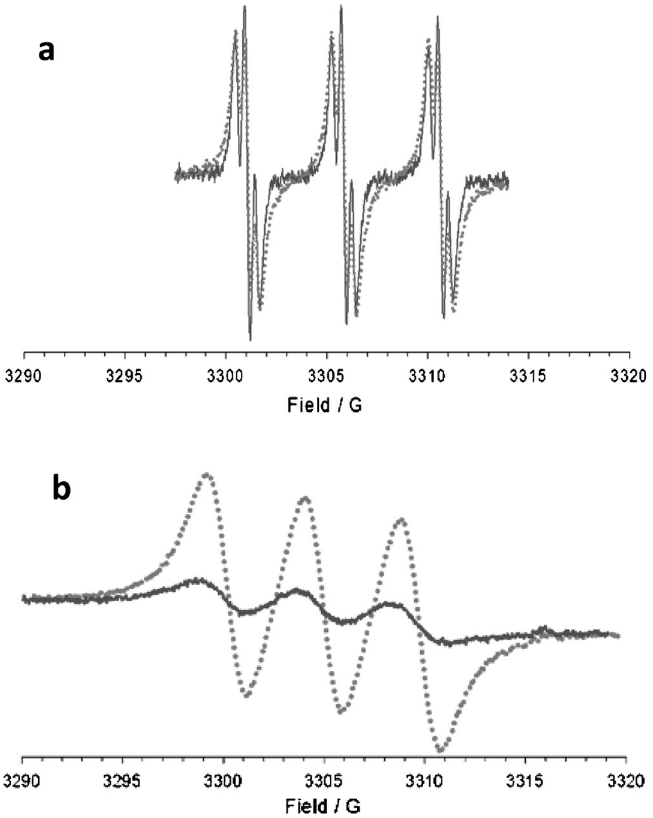


Figure 4. Room temperature EPR spectra of PINO radicals produced by UV irradiation ($\lambda > 300$ nm) of NHPI (35 mM); **a**) absence of oxygen; **b**) presence of oxygen. Solid and dotted lines correspond to spectra recorded in the absence and in the presence of **NI1** (35 mM), respectively.

a mercury lamp, resulted in the formation of an EPR signal whose spectroscopic parameters are consistent with those of PINO nitroxide radical [a(N) = 4.3 G, $g = 2.0073$, see Figure 4b].[5] Due to the presence of oxygen, severe broadening of the EPR lines was evident, this making it impossible to resolve the coupling of the unpaired electron with hydrogen atoms.

When the NHPI solution was irradiated under the same experimental conditions in the presence of an equimolar amount of **NI1** (35 mM) a significant increase of the EPR signal due to PINO radicals was observed (Figure 4b). By comparison of the corresponding doubly integrated signals, a 6 times increase in the radical concentration was calculated in the presence of **NI1** (from 0.01 to 0.06 mM). On the contrary, in the absence of oxygen no differences in the EPR signal intensity were observed when NHPI was irradiated in the absence and in the presence of **NI1** (Figure 4a). Because of the absence of oxygen in the solution, the coupling of the unpaired electron with two hydrogen atoms is clearly visible [a(2H) = 0.45 G]. Similar results were also obtained in the presence of the photo-activator **NI2** (data not shown). According to the well-known photo-oxidation type I mechanism,[10] it is conceivable that a photo-assisted transfer of an electron from the NI to the oxygen molecule occurs under irradiation leading to the formation of superoxide radical anion ($O_2^{\bullet -}$) which is able to abstract a hydrogen atom from NHPI forming the PINO radical.

The involvement of $O_2^{\bullet -}$ possibly formed *via* the reduction of O_2 by the photoexcited **NI1**, was checked by a spin trapping experiment in the presence of DMPO (5,5-dimethyl-1-pyrroline *N*-oxide).[11]

When an MeCN solution of **NI1** (16 mM) and DMPO (0.1 M) was irradiated in the presence of O_2 a strong EPR spectrum became visible (Figure 5b).

This spectrum was attributed to the spin adduct resulting from addition of $O_2^{\bullet -}$ to DMPO, as suggested by the values of the EPR coupling constants [a(N) = 13.0 G, a(H) = 10.3 G] that are similar to those reported in the literature for the same adduct.[12] Prolongation of light irradiation produced a significant narrowing of the EPR lines, this being further evidence that the O_2 in the EPR tube was rapidly consumed (Figure 5d). Under this condition, the increased spectrum

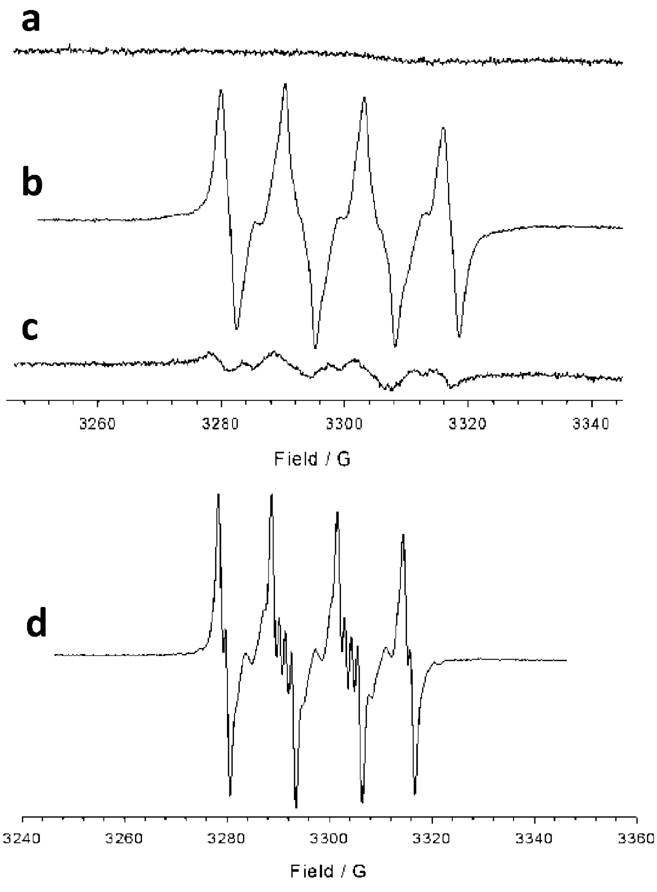


Figure 5. Room temperature EPR spectra under UV irradiation ($\lambda > 300$ nm) of oxygenated MeCN solutions containing: a) DMPO 0.1 M; b) **NI1** (16.0 mM) + DMPO (0.1 M); c) DMPO (0.1 M) + NHPI (50 mM); d) **NI1** (16.0 mM) + DMPO (0.1 M) after 20 min of UV irradiation.

resolution allows measurement of the small coupling with a γ-hydrogen [a(H) = 1.05 G]. A blank experiment performed in the presence of oxygen and in the absence of **NI1** gave no EPR signals (see Figure 5a).

When NHPI was added under the same experimental conditions to this system (50 mM) in the presence of O_2, a much weaker EPR signal for the adduct was observed (Figure 5c). This result clearly indicates that the oxidation of NHPI to PINO radical by $O_2^{\cdot-}$ competes with DMPO trapping of this activated oxygen species.

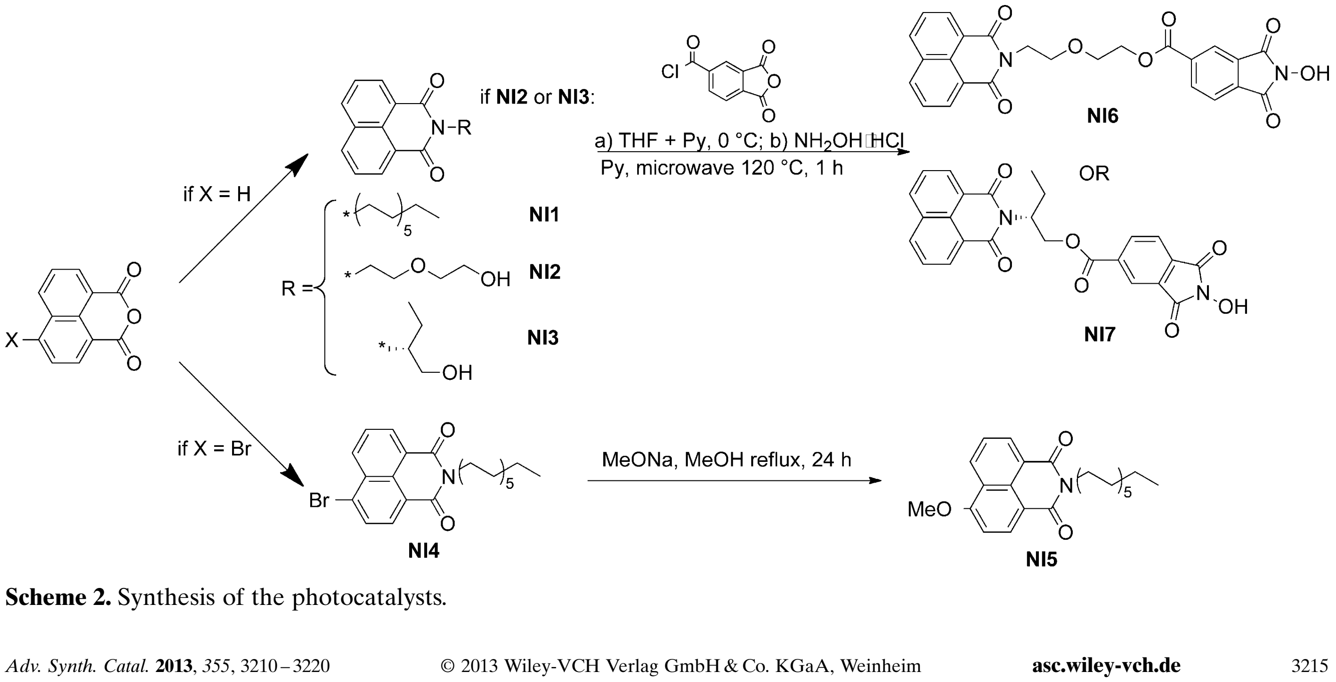
Our EPR results are in agreement with those reported by Reszka et al.[13] that investigated the photochemistry of different NI and NDI. In particular they found that under UV light exposure, NDI generate the corresponding radical anions $NDI^{\cdot-}$ in N_2-saturated methanol solutions. Moreover, using DMPO, they even observed the adducts DMPO/$^{\cdot}CH_2OH$ and DMPO/$^{\cdot}OCH_3$. While using O_2-containing solutions they observed mainly the adduct DMPO/$O_2^{\cdot-}$. In the case of NI, no radical anion $NI^{\cdot-}$ was detected by them in N_2-saturated MeOH/MeCN solutions while a significant formation of $O_2^{\cdot-}$ was observed in the presence of O_2. This last point gave them an indirect confirmation that also NI can give the formation of the corresponding radical anion $NI^{\cdot-}$ under UV light exposure. Anyway, due to the lower reduction potential of NI with respect to NDI,[14] once formed this radical is rapidly quenched by O_2 (even when present in low concentration like in deaerated solutions) hindering the detection of its EPR signal. In the case of NDI, a possible mechanism for the generation of the $NDI^{\cdot-}$ suggests a charge transfer from singlet state excimers according to Eq. (1):[13,14]

$$^{1}(NDI)_2^{*} \rightarrow NDI^{\cdot-} + NDI^{\cdot+} \tag{1}$$

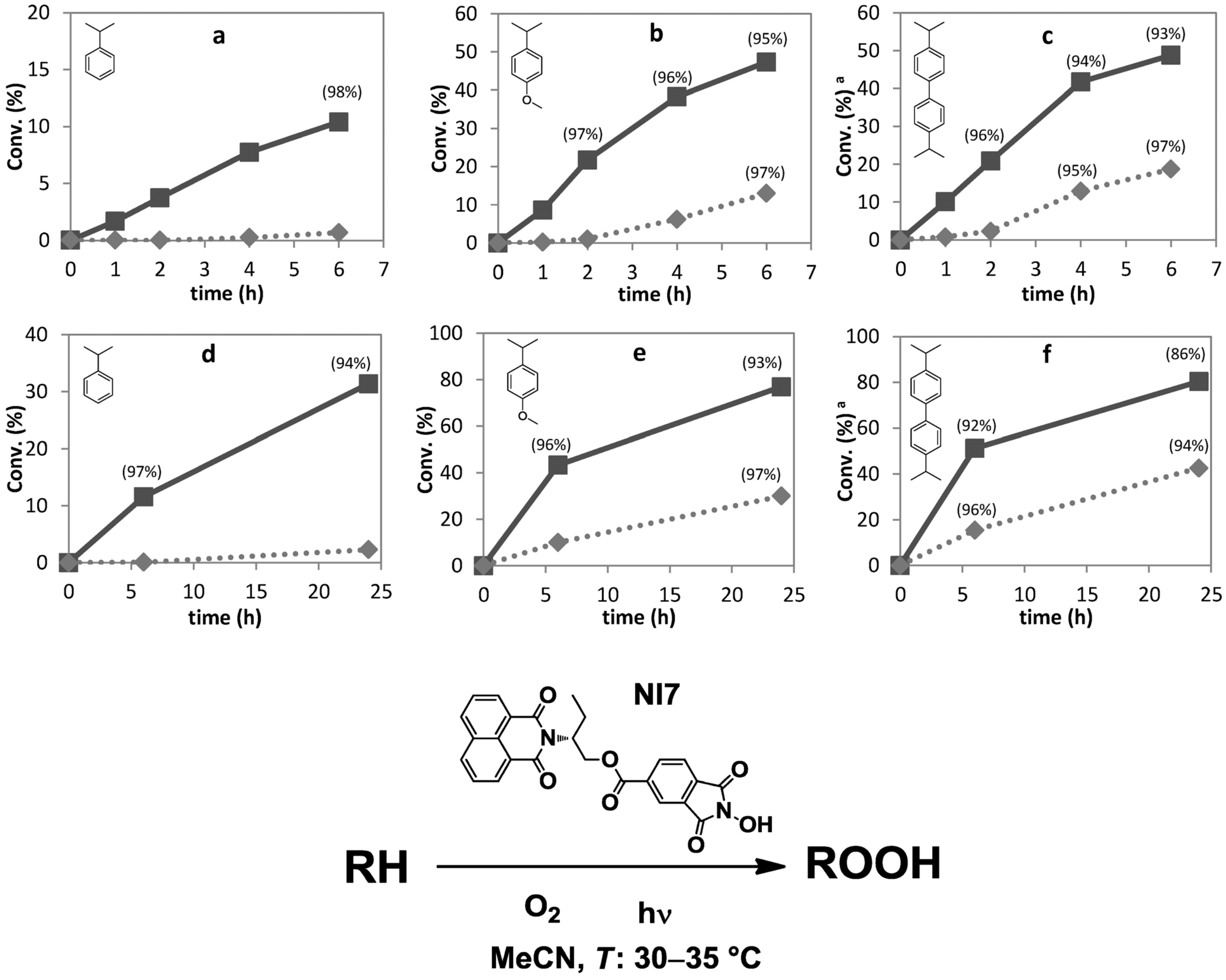
Such a mechanism seems to be effective when [NDI] > 50 μM. According to the above reported considerations we would assume that Eq. (1) could be applied also to NI.

The formation of NI excimers could be guaranteed by the high concentration of NI in our oxidative system ([NI] = 0.025 M). The overall hypothetical mechanism that includes the oxygen photo-activation *via* NI and the NHPI catalytic cycle is reported in Scheme 1.

It is widely established in the literature how the photo-physical properties of the NI can be modulated through the introduction of suitable functional groups on the naphthalene moiety.[15] Accordingly we synthesized two substituted NI, **NI4** and **NI5**, bearing respectively a bromo and a methoxy group in the C-4 position of the naphthalene moiety (Scheme 2). As expected, the presence of these functional groups modified the UV-vis absorption spectra compared to the original molecule **NI1** (see the Supporting Information Figure SI10). In accord with the literature,[16] the bromo substituent red shifts the spectrum by about 10 nm in MeCN with a maximum peak at 340 nm and a shoulder at 353 nm. Whereas **NI1** produces a blue fluorescence under UV light exposure at 365 nm, **NI4**, both crystalline and in MeCN solution, shows a remarkably low fluorescence. On the other hand the presence of the methoxy group in **NI5** significantly modifies the spectral properties of the compound. Indeed, a broad absorption band having a peak at 364 nm is observed and the material emits an intense blue light under irradiation at 365 nm. The absorption and emission spectra of **NI1**, **NI4** and **NI5** are reported in the Supporting Information, Figure SI10 and Figure SI12.



Scheme 2. Synthesis of the photocatalysts.



[a] Conversion of isopropyl groups and selectivity in total hydroperoxide.

Figure 6. Hydrocarbon oxidation using the photocatalyst **NI7**, under sunlight (a–c) and UV light irradiation ($\lambda = 365$ nm, d–f). ■ **NI7** (5%); ◆ carb-NHPI (5%). *Conditions:* 5 mmol of hydrocarbon in 10 mL of MeCN under O_2 (1 atm), *T*: 30–35 °C. Hydroperoxide selectivity is reported in brackets if lower than 100%.

The photoactivities of the three NIs were comparatively investigated by EPR spectroscopy evaluating the capability of **NI4** and **NI5** for increasing the concentration of the PINO radical under aerobic UV irradiation. In terms of PINO radical generation, **NI4** gave results almost similar to **NI1** and **NI2** (data not shown). On the contrary, with the derivative **NI5** a reduction of the EPR signal of PINO was observed (about 60% less) indicating a lower activity of this photocatalyst in the electron transfer process to oxygen.

The need of having two catalysts, NI as oxygen photo-activator and NHPI as promoter of the oxidative radical chain, working at the same time in a synergic way, prompted us to combine the two molecules in one assembly through a suitable spacer. Initially we attempted the synthesis of the molecule **NI6** where the NI unit was linked to the NHPI moiety *via* esterification with a linear spacer (Scheme 2). Anyway, the solubility of **NI6** in our reaction system at room temperature was not complete. By changing the spacer (**NI3**) we obtained **NI7** that was nicely soluble in all the RH:MeCN mixtures.[17] So **NI7** (5% mol respect to the substrate) was used for the oxidation of **R1**, **R2**, **R4** and **R5** under both sunlight and under UV light irradiation at 365 nm. Comparative experiments were performed under the same conditions using a substituted NHPI having an ester group on the aromatic ring (in the next indicated as carb-NHPI – see the Supporting Informations). The data reported in Figure 6 again clearly indicate that **NI7** effectively increased the oxidation rate of the three alkylaromatics in both irradiation conditions. Moreover, the selectivity in hydroperoxides was always quite high and generally above 90% depending on the reaction time and the reactivity of the substrate. The corresponding alkylaromatic alcohols resulted to be the main by-products found during the course of the reactions while ketones were observed in traces only after a prolonged time (24 h) as in the case of the UV light-assisted experiments. The analogous experiments performed with **NI7** but in the dark did not show any conversion of the substrates indicating that light was, once again, necessary for the effectiveness of the process.

However, and quite surprisingly, **NI7** did not exhibit the same performance during the oxidation of cyclohexene, in spite of the fact that this substrate was oxidized with satisfactory results by using **NI1** and NHPI (about 32% conversion after 6 h – see Figure 2). A very slow oxidation kinetics was indeed observed under sunlight irradiation (data not reported) with a final conversion of about 12% after 6 h. Such a result is slightly higher than that obtained with NHPI only (~8%, Figure 2e) indicating that **NI7** worked as a simple NHPI during the oxidation of cyclohexene.

The anomalous substrate-depending behaviour of **NI7** induced us to verify whether such a molecule was still able to induce oxygen photo-activation and hence to induce the PINO radical formation. Using **NI7** MeCN solutions (35 mM) under oxygen exposure we performed the same EPR experiments conducted with **NI1**. In line with the results obtained with cyclohexene, a very weak EPR signal due to PINO radicals was observed during UV light irradiation. On the other hand, the signal of the PINO radical was significantly increased by irradiating the same solution containing 10% (v/v) of di-*tert*-butyl peroxide, thus confirming that the NHPI moiety was still effectively active as proton donor. The reason for the different behaviour could be ascribed to a reduced ability of **NI7** in activating oxygen to $O_2^{\bullet -}$ by the electron transfer mechanism. In other words the presence of the NHPI moiety directly linked to the NI units could modify the spectral properties of the molecule to such an extent that the superoxide radical is no longer favourably generated.

The modification of the photophysical properties is, perhaps, also witnessed by the reduced fluorescence emission of **NI7** under UV light irradiation both in the solid phase and in MeCN solution (Supporting Information, Figure SI13). On the contrary by simply substituting the hydroxy group with an alkyl group as in **NI8** (see the Supporting Information) the molecule was again remarkably fluorescent (Supporting Information, Figure SI13). This suggested that the NHPI moiety through the N−OH group worked as a fluorescence quencher. We ascribe this behaviour to an intramolecular interaction between the NHPI and the naphthalene units in **NI7**. Indeed, equimolar solutions of **NI1** and NHPI did not show a significant reduction of fluorescence emission (Supporting Information, Figure SI14). Despite the results obtained with cyclohexene and confirmed by the EPR investigation, the data reported in Figure 6 related to the alkylaromatics **R1**, **R2** and **R4** without any doubt indicate that in the presence of **NI7** all the substrates undergo oxidation faster than by operating with carb-NHPI only.

It is well reported in the literature that, for NHPI-catalyzed aerobic oxidations, the conversion rate of the substrate as well as the oxygen consumption is a function of the PINO radical concentration according to Eq. (2):[1a] where the k_H value depends on the

$$\mathrm{PINO} + \mathrm{RH} \xrightarrow{k_H} R^{\cdot} + \mathrm{NHPI} \tag{2}$$

specific substrate RH. In the case of cumene, for example, k_H has a value of $3.25\,M^{-1}s^{-1}$ at 25 °C in benzene-MeCN solutions.[1a] According to Eq. (2) exogenous sources of PINO radicals, like **NI1** in the presence of NHPI, oxygen and UV light, are beneficial in order to increase the conversion rate of the substrate. As the positive results reported in Figure 6 (perhaps being comparable with those related to **NI1**) cannot be explained without considering Eq. (2), our idea is that **NI7** molecules, in the presence of a comparatively high concentration of alkylaromatics (0.5 M in our conditions), are again able to induce oxygen photo-activation and consequentially increase the concentration of the **NI7**-PINO radical. Probably some interactions between the alkyaromatic molecules and **NI7** could play either a role in reducing the intramolecular effects of the N−OH unit on the performances of the photocatalyst, or a role in improving the electron transfer process from **NI7** to the oxygen. Anyway, these hypotheses could be the starting point for future investigations, for example, by performing quantum mechanical calculations that, however, are beyond the purposes of this work.

Conclusions

In conclusion, we have investigated the photo-assisted metal-free aerobic oxidation of different hydrocarbons, including tertiary alkyaromatics and cyclic alkenes, to the corresponding hydroperoxides using simple naphthalene imides (NI) as oxygen photo-activator and *N*-hydroxyphthalimide (NHPI) as catalyst in extremely mild conditions (*T*: 30–35 °C). Experiments were performed both under sunlight and artificial light irradiation ($\lambda = 365$ nm), providing clear evidence about the beneficial effect of NI as well as the UV light activity in increasing the oxidation rate of the process. EPR spectroscopy confirmed the role of NI in increasing the concentration of PINO radicals during the irradiation of NI/NHPI mixtures in MeCN under oxygen exposure. In the absence of oxygen no significant changes in the PINO radical concentration were observed. In particular, NI promotes the production of superoxide radicals $O_2^{\bullet -}$during the UV light irradiation under aerobic exposure. In presence of NHPI the superoxide radicals undergo hydrogen abstraction, leading to the formation of PINO, which in turn is able to promote proton transfer from benzylic and allylic C–H bonds, following the well-known NHPI-catalyzed oxidation process. The introduction of substituents (Br and MeO) on the naphthalene moiety was also investigated: while the bromo derivative (**NI4**) had activity comparable with the unsubstituted NI (**NI1**), the MeO derivative (**NI5**) showed reduced performance.

On the base of the synergic action of NI and NHPI we synthesised a photocatalyst bearing both moieties linked by a suitable spacer. We observed that the new catalyst (**NI7**) was still effective in increasing the oxidation rate of different alkylaromatic hydrocarbons with activity comparable to the system NI/NHPI. Nevertheless when used for the oxidation of cyclohexene, **NI7** showed reduced photocatalytic performances.

Finally we believe that the proposed approach opens the way for the development of new attractive metal-free strategies for the oxygen activation having particular relevance for the production of hydroperoxides under very mild conditions.

Experimental Section

All reagents used in this work are commercially available and were used as received without further purification unless otherwise stated. The compound **R2** (4-methoxycumene, Alfa Aeser) was purified by column chromatography on silica gel using *n*-hexane as eluent.

^{1}H and ^{13}C NMR spectra of the products were recorded at room temperature with a Bruker Avance-400 NMR spectrometer. Conversions and yields for **R1**, **R2** and **R3** were determined by HPLC analysis (reverse phase column; MeCN/MeOH/H_2O, 35/5/60), with 2-phenylethanol added as internal standard, and confirmed by ^{1}H NMR. With regard to **R4**, conversion and yields were based on the isopropyl groups and were determined by ^{1}H NMR. For **R5** and **R6** conversion and yields were determined by ^{1}H NMR according to literature by comparison with authentic products.[18]

EPR spectra were recorded at room temperature using an ELEXYS E500 spectrometer equipped with an NMR gaussmeter for the calibration of the magnetic field and a frequency counter for the determination of *g*-factors.

UV-vis and fluorescence spectra were recorded using a Perkin–Elmer 8354 spectrophotometer and a Jasco FP 6600 spectrophotometer respectively with MeCN as solvent.

Catalysts Preparation

Compound **NI1** was prepared from 1,8-naphthalic anhydride (10 mmol) and dodecylamine (10 mmol) using pyridine (40 mL) as solvent. The reaction was performed in a microwave reactor with the automatic control of power (MicroSYNTH Labstation – Milestone Inc., USA) under reflux for 1 h. After evaporating the solvent under vacuum, the solid was extensively washed with a 0.5 M HCl solution, water and finally dried in air. The purification was achieved by chromatography on silica-gel using hexane:EtOAc 8:2 (v:v) as eluent (R_f: 0.43 (**NI1**); yield: 92% (pale yellow crystals); mp 53.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.51$ (d, 2H), 8.12 (d, 2H), 7.67 (t, 2H), 4.13 (t,2H), 1.71 (m, 2H), 1.45–1.15 (m, 18H), 0.85 (t, 3H).

Compound **NI4** was prepared in similar way starting from 4-bromo-1,8-naphthalic anhydride; yield: 95% (yellow crystals); mp 63.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.56$ (d, 1H), 8.45 (d, 1H), 8.31 (d, 1H), 7.94 (d, 1H), 7.75 (t, 1H), 4.11 (t, 2H), 1.70 (q, 2H), 1.46–1.13 (m, 18H), 0.85 (t, 3H).

Compounds **NI2** and **NI3** were obtained as **NI1** using 2-(2-aminoethoxy)ethanol and (*R*)-(−)-2-amino-1-butanol, respectively (10 mmol). **NI2** and **NI3** were purified by chromatography on silica-gel using $CHCl_3$:MeOH 9:1 (v:v) as eluent (R_f: 0.67). Yield: 95% (white crystals); mp 127.5 °C (**NI2**), 150.0 °C (**NI3**); ^{1}H NMR of **NI2** (400 MHz, $CDCl_3$): $\delta = 8.44$ (d, 2H), 8.06 (d, 2H), 7.61 (t, 2H), 4.35 (t, 2H), 3.80 (t, 2H), 3.70–3.58 (m, 4H), 2.75 (s, 1H); ^{1}H NMR of **NI3** (400 MHz, $CDCl_3$): $\delta = 8.46$ (d, 2H), 8.11 (d, 2H), 7.64 (t, 2H), 5.25 (m, 1H), 4.20 (dd, 1H), 3.96 (dd, 1H), 3.40 (s broad, 1H), 2.15–1.89 (m, 2H), 0.91 (t, 3H).

Compound **NI5** was prepared by reacting 1 mmol of **NI4** with 5 mmol of MeONa in MeOH under reflux for 24 h. A yellow solid precipitated on cooling to room temperature that was filtered and finally purified by chromatography on silica-gel using hexane:EtOAc 8:2 (v:v) as eluent (R_f: 0.46); mp 59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.55$ (d, 1H), 8.50 (d, 2H), 7.66 (t, 1H), 6.99 (t, 1H), 4.14 (t, 2H), 4.11 (s, 3H), 1.72 (q, 2H), 1.50–1.05 (m, 18H), 0.87 (t, 3H).

Compound **NI7** was obtained adding, by dropwise addition (~30 min) and under stirring at 0 °C, of 20 mL of **NI3** (10 mmol) solution in anhydrous THF to 20 mL of a solution of trimellitic anhydride chloride (10 mmol) in anhydrous THF containing 4 mL of anhydrous pyridine. The mixture was kept at 0 °C for 6 h then overnight at room tempearture. After filtration of the white precipitate, the clear liquid was vacuum evaporated, so obtaining a white solid that was dissolved in pyridine (~40 mL) and reacted with $NH_2OH{\cdot}HCl$ (50 mmol) in microwave for 1 h under reflux. The evaporation of the solvent and the washing of the mixture with HCl (0.1 M) at 0 °C resulted in a white solid that was purified by chromatography on silica-gel using $CHCl_3$:MeOH 9:1 (v:v) as eluent (R_f: 0.60 – orange coloured spot if TLC is exposed to NH_3); yield: 90%; mp 115.0 °C. ^{1}H NMR (400 MHz, DMSO): $\delta = 10.91$ (s, 1H), 8.49 (d, 2H), 8.42 (d, 2H), 8.18 (d, 1H), 8.01 (s, 1H), 7.84 (m, 1H+2H), 5.43 (s, 1H), 4.95 (dd, 1H), 4.76 (dd, 1H), 2.21 (m, 1H), 2.018 (m, 1H), 0.97 (t, 3H).

Compound **NI6** was prepared similarly to **NI7** but using **NI2** in place of **NI3**. Purified by chromatography on silica gel using $CHCl_3$:MeOH 9:1 (v:v) as eluent (R_f: 0.60 – orange coloured spot if TLC is exposed to NH_3); yield: 92%; mp 125.0 °C. ^{1}H NMR (400 MHz, DMSO): $\delta = 9.88$

(broad s, 1H), 8.34 (d, 2H), 8.21 (d, 2H), 8.14 (d, 1H), 7.99 (s, 1H), 7.69 (t, 2H), 7.67 (s, 1H), 4.47 (t, 2H), 4.33 (t, 2H), 3.90 (t, 2H), 3.86 (t, 2H)

The compound **NI8** was obtained with the same procedure as for **NI7** but using $EtNH_2$ in place of $NH_2OH·HCl$. Purified by chromatography on silica gel using hexane:EtOAc 7:3 (v:v) as eluent (R_f: 0.42); yield: 90%; mp 129 °C. ^1H NMR (400 MHz, DMSO): $\delta = 8.56$ (d, 2H), 8.31 (s, 1H), 8.24 (dd, 1H), 8.204 (d, 2H), 7.76 (d, 1H), 7.74 (3, 2H), 5.54 (m, 1H), 5.03 (dd, 1H), 4.85 (dd, 1H), 3.69 (q, 2H), 2.31 (m, 1H), 2.07 (m, 1H), 1.23 (t, 3H), 0.99 (t, 3H).

Carb-NHPI was synthesized similarly to **NI7**, by preparing the ester from MeOH and trimellitic anhydride chloride and then forming the *N*-hydroxyimide using $NH_2OH·HCl$. Purified by chromatography on silica gel using $CHCl_3$:MeOH 9:1 (v:v) as eluent (R_f: 0.60 – orange-coloured spot if TLC is exposed to NH_3); yield: 94%; mp 172.0 °C. ^1H NMR (400 MHz, acetone-d_6): $\delta = 9.95$ (broad s, 1H), 8.43 (d, 1H), 8.28 (s, 1H), 7.96 (d, 1H), 3.98 (s, 3H).

Photo-assisted Oxidations

The sunlight aerobic oxidations were performed by dissolving 5 mmol of hydrocarbon in 10 mL of MeCN with 5% NHPI and 5% NI (molar basis) (more details in the figures and tables) using a glass test tube with an oxygen balloon and a thermometer. The apparatus was exposed to the solar light (behind a glass window) under stirring and using a fan as cooling system in order to minimize the heating effects.[19] Similar experiments were repeated under artificial light irradiation using a quartz test tube (Φ: 20 mm) and a ventilated Rayonet reactor equipped with 4 lamps Philips Blacklight Blue TL8W/08F8T5/BLB emitting in the UV range (maximum at 365 nm).

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