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Copper(I) Catalyzed Differential Peroxidation of Terminal and Internal Alkenes Using TBHP

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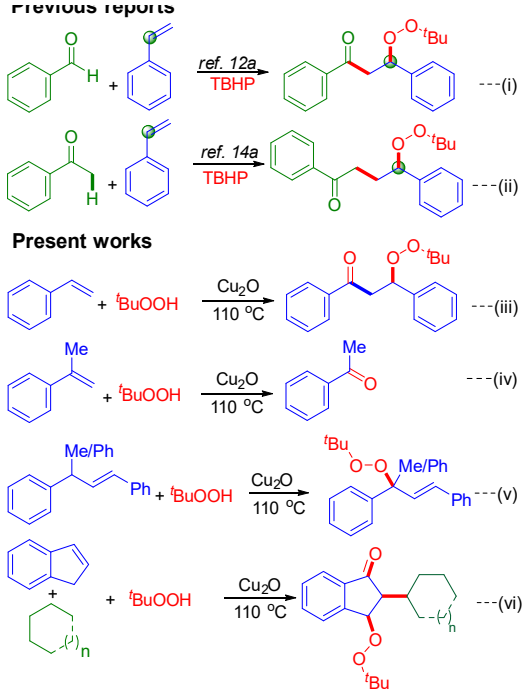
Abstract: Terminal and internal alkenes react contrarily with *tert*-butyl hydroperoxide (TBHP) giving different products. A Cu(I) catalyzed decarbonylative C–C bond formation followed by a carbonylation-peroxidation of vinyl arenes has been achieved using *tert*-butyl hydroperoxide (TBHP) as the oxidant in acetonitrile. Whereas, α–methyl styrenes yielded aryl methyl ketones and the α–substituted unsymmetrical internal alkenes afforded selective α–peroxidation under the identical reaction conditions. Concurrent peroxidation-carbonylation-cycloalkylation/cycloetherifiction of internal cyclic alkene such as indene is achieved by switching the solvent system from acetonitrile to cycloalkanes/cyclic ether. All these reactions proceed via radical paths generating interesting peroxo-compounds.

Keywords: Carbonylation; peroxidation; cycloalkylation/cycloetherification; terminal alkenes; internal alkenes.

Introduction

Difunctionalization of alkenes is significant in the synthetic transformation to build molecular complexity in a single operation. Both intra and intermolecular hetero-difunctionalizations of alkenes have received considerable attention. In contrast to intermolecular processes, intramolecular difunctionalizations are much more selective and thermodynamically favourable. The transition-metal-catalyzed intermolecular difunctionalizations such as carbohalogenation,[1] dihydroxylation,[2] oxyarylation,[3] oxyamination,[4] aminofluorination,[5] aminocyanation,[6] hydro-alkylation,[7] carboboration[8] and other difunctionalizations[9] are well explored. However, intermolecular difunctionalization of olefins has rarely been explored following the C–H bond functionalization strategy. Carbonylation of alkenes has been developed as one of the powerful methods for the synthesis of carbonyl compounds.[10] But the simultaneous introduction of a carbonyl group and another functional group such as alcohol, amine and peroxide into alkenes is not well explored.[11] Lately, organic peroxides are used as oxidizing agents and initiators for free-radical reactions both in academia and industry. These peroxo compounds are produced and used in various natural and biological processes such as preparation of antimalarial agents,[11d-f] anthelmintics,[11g] and antitumor drugs.[11h,i] A Fe(II)-catalyzed



Scheme 1. Strategies for difunctionalization via C–H functionalization.

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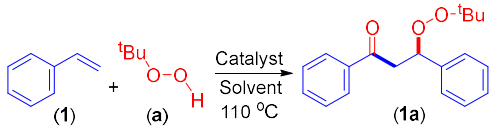
carbonylation–peroxidation of olefins is reported via the sp^2 C–H bond functionalization using aldehydes and *tert*-butyl hydroperoxide (TBHP) (Scheme 1).[12a] This carbonylation–peroxidation product has been utilised by Li group for the synthesis of (±) clavilactones A, B[12b] and D.[12c] MacMillan group demonstrated a complementary asymmetric carbofunctionalization of olefins using aldehydes following the concept of singly occupied molecular orbital (SOMO).[13] Klussmann group have reported an acid-catalyzed oxidative keto-peroxidation of olefins using ketones and TBHP (Scheme 1(i)).[14a] Recently, Chen and coworkers reported a vanadium catalyzed carbonylation-peroxidation of styrenes using aldehydes and TBHP (Scheme 1(ii)).[14b] On the other hand, in 2018 Wang *et al*. reported a *tetra*-n-butylammonium bromide (TBAB)-catalyzed carbonylation-peroxidation of styrenes using aldehydes and TBHP.[14c] In addition to this, Li group reported an Fe-catalyzed alkoxycarbonylation–peroxidation of alkenes with carbazates and T-Hydro.[14d] The application of readily available, nontoxic copper catalyst instead of expensive and sensitive catalysts is highly desirable for any chemical synthesis.[15] Of late, great progress has been made in exploring copper-catalyzed oxidative C–H bond transformation.[16] Our group and others have successfully employed a Cu (I or II)/peroxide catalytic system for the formation of C–C, and C–O bonds.[17]

We have also developed a directing group assisted *o*-benzoxylation (–OCOR) using Cu(II) catalyst, terminal aryl alkene (styrene) and oxidant TBHP. In this process, styrene serves as the synthetic equivalent of an aryl carboxy group.[17f] However, using Pd(II) as the catalyst, the same terminal aryl alkene serves as an aroyl (–COR) surrogate. Both these processes proceed through the *in situ* generation of an aryl carboxaldehyde intermediate. Earlier our group generated two coupling partners from the same precursor, where one half of alkylbenzene is converted to an aryl carboxyl intermediate and the other half into a benzyl cation leading to the formation of an ester.[18a] Thus, we envisaged that one half of the styrene can be converted to an arylcarboxaldehyde[17f-g] which can couple with the remaining half of the styrene in the presence of an oxidant TBHP leading to keto-peroxidation as shown in Scheme 1 (i).

Results and Discussion

To execute our strategy an initial reaction was carried out employing styrene (**1**) (1.0 mmol), *tert*-butyl hydroperoxide (**a**) (3.0 mmol), and $Cu(OAc)_2$ catalyst (10 mol %) in chlorobenzene (2 mL) at 110 °C (Table 1, entry 1).

Table 1. Optimization of the reaction conditions for the first step.[a-d]



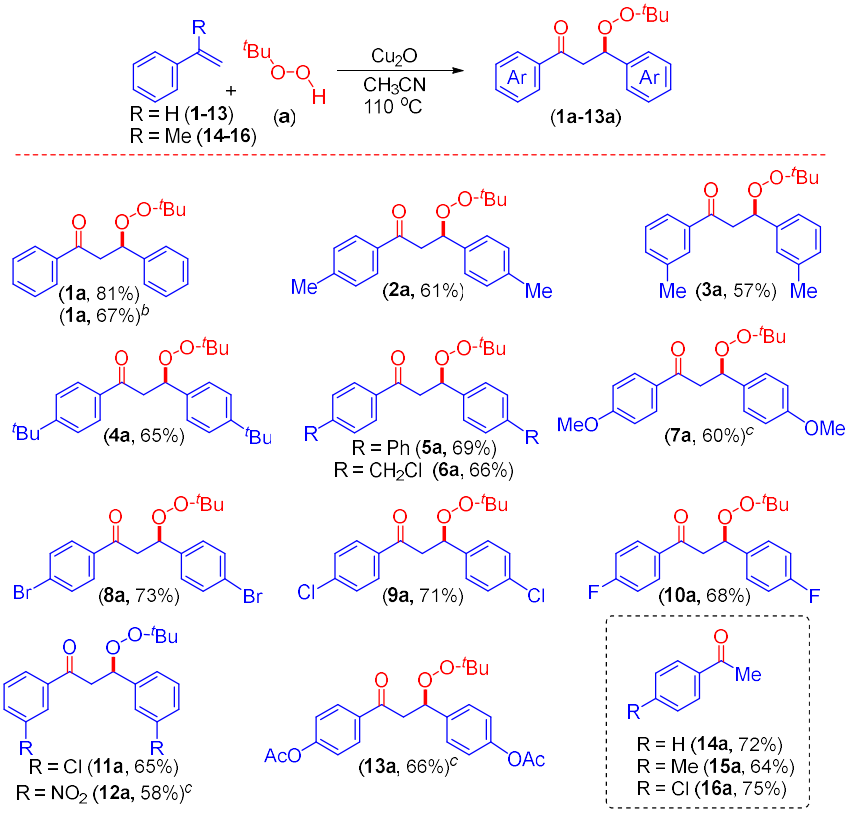
(1) (a) (1a)

Entry	Catalyst (mol %)	Oxidant (equiv)	Solvent	Yield (%)[b]
1	$Cu(OAc)_2$ (10)	TBHP (6)	PhCl	58
2	$Cu(OTf)_2$ (10)	TBHP (6)	PhCl	51
3	CuI (10)	TBHP (6)	PhCl	67
4	CuCl (10)	TBHP (6)	PhCl	65
5	Cu_2O (10)	TBHP (6)	PhCl	73
6	Cu_2O (10)	**TBHP (6)**	**CH_3CN**	81
7	Cu_2O (10)	TBHP (6)	DCE	55
8	Cu_2O (10)	TBHP (6)	Cyclohexane	49
9	Cu_2O (10)	TBHP (6)	DMSO	00
10	Cu_2O (10)	TBHP (6)	DMF	00
11[c]	Cu_2O (10)	TBHP (6)	CH_3CN	78
12[d]	Cu_2O (10)	TBHP (6)	CH_3CN	72
13	Cu_2O (10)	TBHP (8)	CH_3CN	81
14	Cu_2O (10)	TBHP (4)	CH_3CN	64
15	Cu_2O (15)	TBHP (6)	CH_3CN	82
16	Cu_2O (5)	TBHP (6)	CH_3CN	66
17	-	TBHP (6)	CH_3CN	07

[a]Reaction condition: Styrene (**1**) (1.0 mmol) and *tert*-butyl hydroperoxide (**a**) (3.0 mmol) at 110 °C for 2 h.
[b]Isolated yields. [c]Temperature 120 °C. [d]Temperature 100 °C.

A new product (**1a**) was isolated in 58 % yield which was subjected to spectroscopic analysis (^{1}H and ^{13}C NMR) and comparison of the spectra with the literature,[12] the structure of the product was revealed to be 3-(*tert*-butylperoxy)-1,3-diphenylpropan-1-one (**1a**) (Scheme 1). Having successfully implemented our strategy, to further improve the yield of the desired product various parameters such as catalysts, solvents, temperatures were varied. As can be seen from Table 1, among various Cu(I) and Cu(II) catalysts tested (Table 1, entries 2–5) the catalyst Cu_2O was found to be best in terms of yield in chlorobenzene solvent. Keeping the catalyst Cu_2O and its quantity fixed, screening of various solvents such as CH_3CN, DCE, cyclohexane, DMSO and DMF (Table 1, entries 6–10) the former (Table 1, entry 6) was found to be the best. The reaction when carried out at higher (120 °C) or a lower (100 °C) temperature (Table 1, entries 11–12) reduced the yield of the product (**1a**) marginally compared to the reaction at 110 °C. Keeping the catalyst, solvent and temperature fixed, the yield remained unchanged (81 %) using 8 equiv of TBHP, but the yield dropped to 64 % using 4 equiv of TBHP (Table 1, entries 13–14). Similarly, keeping all other parameters identical, a marginal improvement in the yield (82 %) was observed when the catalyst loading was increased to 15 mol % (Table 1, entry 15) but the yield reduced to 66 % using 5 mol % of the catalyst (Table 1, entry 16). A control experiment in the absence of catalyst delivered a trace amount of the desired product (Table 1, entry 17). Thus, it was found that the use of styrene (**1**) (1.0 mmol), *tert*-butyl hydroperoxide (TBHP) (**a**) (3.0 mmol), Cu_2O (10 mol %) in acetonitrile (2 mL) at 110 °C for 2 h (Table 1, entry 6) is the ideal reaction condition to achieve (**1a**).

After successful carbonylation-peroxidation, various styrenes were investigated under the optimized reaction condition. Styrenes possessing moderately electron-donating groups such as *p*-Me (**2**), *m*-Me (**3**), *p*-^{t}Bu (**4**), *p*-Ph (**5**) and *p*-CH_2Cl (**6**) provided their corresponding products (**2a**, 61 %), (**3a**, 57 %), (**4a**, 65 %), (**5a**, 69 %) and (**6a**, 66 %) in the modest yields (Scheme 2). Styrene possessing a strongly electron-donating group such as *p*-OMe reacted successfully providing the corresponding product (**7a**) in 60 % yield. On the other hand, the presence of moderately electron-withdrawing groups on styrenes such as *p*-Br (**8**), *p*-Cl (**9**), *p*-F (**10**) and *m*-Cl (**11**) yielded their respective products (**8a**, 73 %), (**9a**, 71 %), (**10a**, 68 %) and (**11a**, 65 %) in moderate yields (Scheme 2). Styrenes having strong electron-withdrawing *m*-NO_2 (**12**) and *p*-OAc (**13**) groups reacted successfully giving their corresponding keto-peroxidation products in moderate yields. The yield of the product (**1a**) dropped to (67 %) when a gram scale (1.99 g, 20 mmol) reaction was performed under an identical reaction condition (Scheme 2).

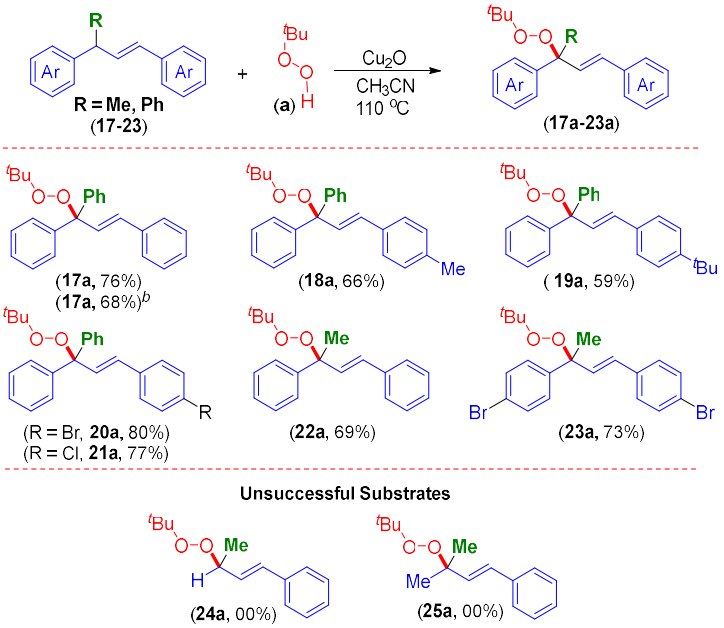


[a]Reaction conditions: alkene **1**–**16** (1.0 mmol), and *tert*-butylhydroperoxide (**a**) (3.0 mmol) at 110 °C for 2 h in CH_3CN.
[b]Yield reported for 20 mmol scale. [c] Freshly prepared styrenes were used.

Scheme 2. Selective-peroxidation of substrates.[a]

To check whether α-methyl styrene (**14**) would undergo similar carbonylation-peroxidation, it was subjected to an identical reaction condition. The reaction did not provide any carbonylation-peroxidation product rather yielded acetophenone in 72 % yield, suggesting the essential requirement of benzylic sp^2 C–H bond for the process. Thus, this is one of the useful method for the preparation of aryl methyl ketone. Two other α-methyl styrenes namely, one possessing an electron-donating *p*-Me (**15**) and the other an electron-withdrawing group *p*-Cl (**16**) both provided their aryl methyl ketones (**15a**, 64 %) and (**16a**, 75 %) in moderate yields (Scheme 2). This result is not surprising and similar transformation has been observed using TBHP in the presence of other catalysts.[19]

After the successful carbonylation-peroxidation of styrenes, we were curious to investigate the fate of substituted internal alkenes such as (*E*)-prop-2-ene-1,1,3-triyltribenzene (**17**) under the present reaction condition. The HRMS analysis of the product suggests the loss of a proton and addition of 88 mass unit indicating a possible peroxidation (-OO^{t}Bu). Further, the spectroscopic (^{1}H and ^{13}C NMR) analysis of the new product revealed its structure to be (*E*)-(1-(*tert*-butylperoxy)prop-2-ene-1,1,3-triyl)tribenzene (**17a**) which was isolated in 76 % yield (Scheme 3). Here, the peroxidation is not at the double bond, rather it is taking place at the tertiary benzylic site. The radical generated at this tertiary site is benzylic as well as allylic and also α-to the other phenyl group, thus is expected to be much more stable than the other possible secondary benzylic radical. Thus in spite of steric hindrance, the peroxidation is taking place regioselectively at this benzylic tertiary position. This trend in the regioselective peroxidation was demonstrated with four other substrates. The substrate possessing a moderately electron-donating groups such as *p*-Me (**18**) and *p*-^{t}Bu (**19**) in the phenyl ring and the other two substrates having moderately electron-withdrawing groups such as *p*-Br (**20**), *p*-Cl (**21**) all provided their peroxo products (**18a**, 66 %), (**19a**, 59 %), (**20a**, 80 %) and (**21a**, 77 %) in modest to good yields. This strategy was equally successful even when the phenyl group is replaced with a methyl group as has been demonstrated for substrates (**22**) and (**23**) yielding their peroxo products (**22a**, 69 %) and (**23a**, 73 %) respectively. When the phenyl group at the allylic position is replaced with a hydrogen (a mono-methyl) or methyl (*i.e* a di-methyl part), the peroxidation was completely unsuccessful giving numerous products (Scheme 3). The yield of the product (**17a**) dropped to 68 % when a gram scale (1.22 g, 5 mmol) reaction was performed under an identical reaction condition (Scheme 3).



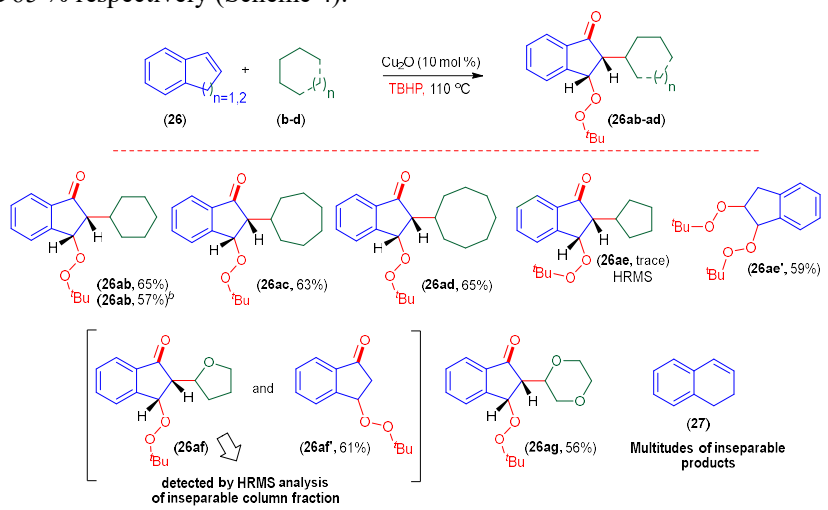
[a]Reaction conditions: alkene **17**–**23** (0.5 mmol), and *tert*-butyl hydroperoxide (**a**) (1.5 mmol) at 110 °C for 2 h in CH_3CN. [b]Yield reported for 5 mmol scale.

Scheme 3. Selective-peroxidation of substrates.[a]

As can be seen from Scheme 2 and Scheme 3, terminal and internal alkenes react differently giving two types of products. The non-cyclic benzylic internal alkenes underwent successful peroxidation at the available allylic position which however is dictated by the stability of the radicals formed (Scheme 3). Thus, the query arises what will happen if a cyclic benzylic internal alkene such as indene (**26**) which has a benzylic/vinylic position? With this objective indene (**26**) was subjected to the present condition. The substrate indene (**26**) was fully consumed but gave a multitude of inseparable products in CH_3CN solvent. Interestingly, by switching the solvent from CH_3CN to

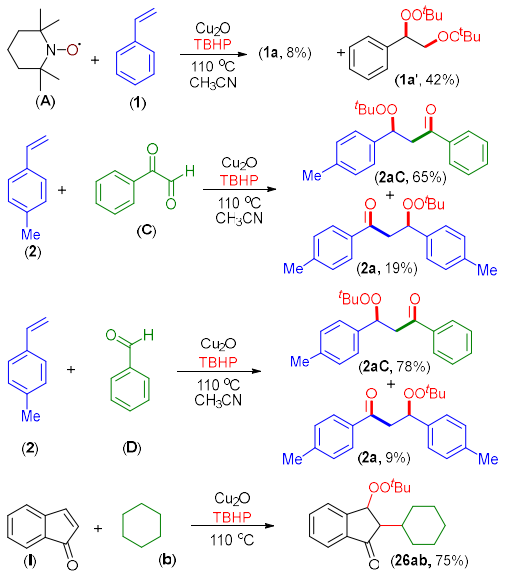
cyclohexane (**b**) under otherwise identical reaction condition gave cyclohexylation-peroxidation-benzylic oxidation product (**26ab**) in 35 % yield. The structure along with the regioselectivity of the product (**26ab**) has been confirmed by ^{1}H, ^{13}C, COSY, NOESY, and NOE NMR spectroscopic techniques (see the Supporting Information, SI). After a series of optimization, it was found that by changing the number of TBHP equiv from 3 to 6 resulted in the formation of an improved yield (66 %) of the product (Scheme 4). This type of cycloalkane functionalization is in agreement with our previous work, where substituted coumarin undergoes cycloalkylation-peroxidation under a similar condition.[17l] This trifunctionalization strategy was successfully extended to higher cycloalkanes such as cycloheptane (**c**), cyclooctane (**d**). Both the cycloalkanes coupled successfully with indene (**26**) affording tri-functionalized products (**26ac**) and (**26ad**) in moderate yields of 63 % and 65 % respectively (Scheme 4).

However, when an indene (**26**) was treated with cyclopentane (**e**), the desired tri-functionalized cyclopentynalated product (**26ae**) was formed in trace amount which was detected only by HRMS analysis (see Supporting Information, Figure S3). However, a diperoxy product of indene (**26ae´**) could be isolated in 59 % yield (Scheme 4). Similar to cycloalkanes, cyclic ethers are amenable to form radical adjacent to an oxygen atom. Thus, when this strategy was extended to a cyclic ether such as THF (**f**), the trifunctionalized product (**26af**) could not be isolated due to the formation of a multitude of uncharacterized products but was detected by HRMS analysis of the inseparable column fraction (see Supporting Information, Figure S4). Interestingly, a keto-peroxidation product (**26af´**) was isolated in 64 % yield. However, another cyclic ether dioxane (**g**) gave the trifunctionalized product (**26ag**) in 57 % isolated yield (Scheme 4).



[a]Reaction conditions: alkene **26** (0.5 mmol), and *tert*-butyl hydroperoxide (**a**) (3.0 mmol) at 110 °C for 3 h in cyclohexane.
[b]Yield reported for 10 mmol scale.

Scheme 4. Indene trifunctionalization.[a]

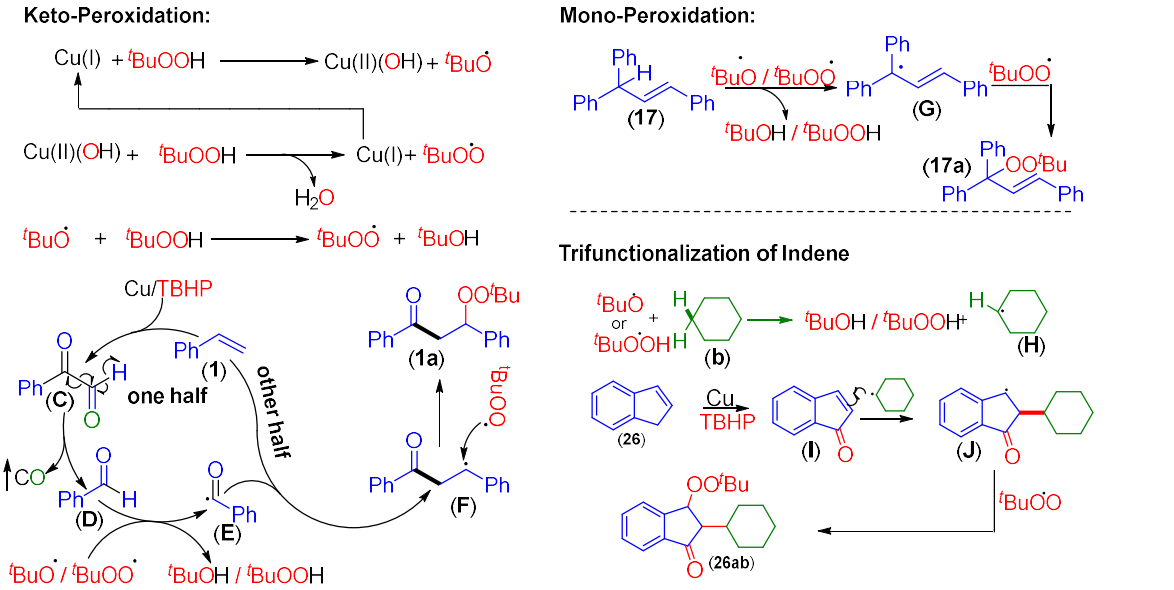


Scheme 5. Some controlled experiments

Several control experiments were conducted to elucidate a plausible reaction mechanism for these transformations. When a typical reaction between styrene (**1**) and TBHP (**a**) was carried out under an identical condition, but in the presence of a radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (**A**) (TEMPO, 1 equiv), only a trace amount of the product (**1a**) was obtained along with the formation a substantial amount of side product (**1a'**) (Scheme 5). It seems the reaction is proceeding via a radical mechanism, that is the generation of *tert*-butoxy radical (^{t}Bu-OO$^{\bullet}$), which on reaction with styrene (**1**). gave product (**1a'**). Similar di-peroxidation product (**1a'**) is well known in the literature.[18b] The *tert*-butoxy radical (^{t}BuOO$^{\bullet}$) cannot be trapped with TEMPO as it will result in the formation of a species having three consecutive oxygen which will be unstable under the reaction temperature (110 °C). Reaction of styrene with TBHP gives phenyl glyoxal (**C**), and benzyhaldehyde (**D**),[17f,g] which decomposed in the presence of metal catalyst to an aroyl radical (ArCO$^{\bullet}$) which perhaps couple with the styrene to give

the product (**1a**). When *p*-Me styrene (**2**) was reacted with phenyl glyoxal (**C**) under the present reaction condition it gave two coupled keto-peroxo products (**2aC**, 65 %) and (**2a**, 19 %) (Scheme 5). The product **2aC** was obtained in higher percentage (65 %) because of the coupling of aroyl radical (ArCO$^{\bullet}$) generated by the easy decomposition of phenyl glyoxal (**C**) with *p*-Me styrene (**2**), thereby supporting the intermediacy of (**C**). Further, when *p*-Me styrene (**2**) was reacted with benzaldehyde (**D**) it again gave two keto-peroxo products (**2aC**, 78 %) and (**2a**, 9 %) (Scheme 5). The product **2aC** was yet again obtained in higher percentage (78 %) because of the coupling of aroyl (ArCO$^{\bullet}$) obtained by the C–H bond cleavage of benzaldehyde (**C**) with *p*-Me styrene (**2**), there by confirming the intermediacy of benzaldehyde (**D**).[17m] Phenyl glyoxal (**C**), on decomposition gives benzaldehyde with concurrent release of CO.[17n-p] Here, the release of CO from the reaction has been confirmed by spot test using $PdCl_2$-phosphomolybdic acid (PMA) strip, supporting the decarbonylation path (see Supporting Information, Figure S1, S2).

The results of the above experiments and related literature reports,[17f,g] convey the operation of the following path for the carbonylation-peroxidation (Scheme 6).



Scheme 6. Plausible reaction mechanism.

The Cu(I)-assisted cleavage of *tert*-butyl hydroperoxide (TBHP) generates ^{t}BuO$^{\bullet}$ radical and Cu(II) species in the medium. The Cu(II) species on reaction with another equivalent of TBHP produce ^{t}BuOO$^{\bullet}$ radical and Cu(I) for further reaction.[17e] This ^{t}BuOO$^{\bullet}$ radical can also be generated by the action of TBHP and ^{t}BuO$^{\bullet}$ radical. On the other hand, styrene (**1**) in the presence of Cu/TBHP is converted to benzaldehyde (**D**) via the intermediacy of phenyl glyoxal (**C**) (Scheme 6).[17f,g,m] The PhCO$^{\bullet}$ radical (**E**) generated from benzaldehyde (**D**) reacts with the unreacted part of styrene (**a**) to give a benzylic radical intermediate (**F**), which subsequently couples with ^{t}BuOO$^{\bullet}$ radical to provide the desired product (**1a**). So far as mono-peroxidation of internal alkene, but-1-ene-1,3-diylbenzene (**16**) is concerned, the peroxidation is not taking place at the double bond, rather it is happening at the tertiary benzylic site (Scheme 6). Here, the ^{t}BuO$^{\bullet}$ or ^{t}BuOO$^{\bullet}$ radical species abstract the tertiary proton of (**17**) to generate a radical intermediate (**G**) which is doubly benzylic as well as allylic, thus is much more stable than the other possible secondary benzylic radical that may form by the direct attack of ^{t}BuOO$^{\bullet}$ radical at the double bond. Thus, preferential peroxidation is taking place regioselectively at this benzylic tertiary position in spite of steric hindrance to give product (**17a**). The mechanism for the formation of tri-functionalization of indene is depicted in Scheme 6. The *in situ* generated radical species ^{t}BuO$^{\bullet}$ or ^{t}BuOO$^{\bullet}$ as shown in Scheme (6) abstract a proton from the cycloalkane to generate a cycloalkyl radical species (**H**). The benzylic CH_2 of the indene (**26**) is oxidized to C=O in the presence of Cu/TBHP to give α,β-unsaturated ketone (**I**). The cyclohexyl radical (**H**) attacks at the α-carbon of (**I**) generating a benzylic radical (**J**).[17c]. This has been confirmed when a 1*H*-inden-1-one (**I**) was reacted with cyclohexane and TBHP under the optimised reaction condition, it resulted in the exclusive formation of product (**26ab**) in an improved yield of 75 % thereby suggesting its intermediacy (Scheme 5). Finally, a radical cross-coupling between ^{t}BuOO$^{\bullet}$ benzylic radical (**J**) furnish the cycloalkyl–peroxy product (**26ab**) (Scheme 6). Similar peroxidation at the α- and cyclohexylation at the β-positions has been documented in literature.[17c,q] This mechanism can also account for the formation of other products and by products obtained in Scheme 4.

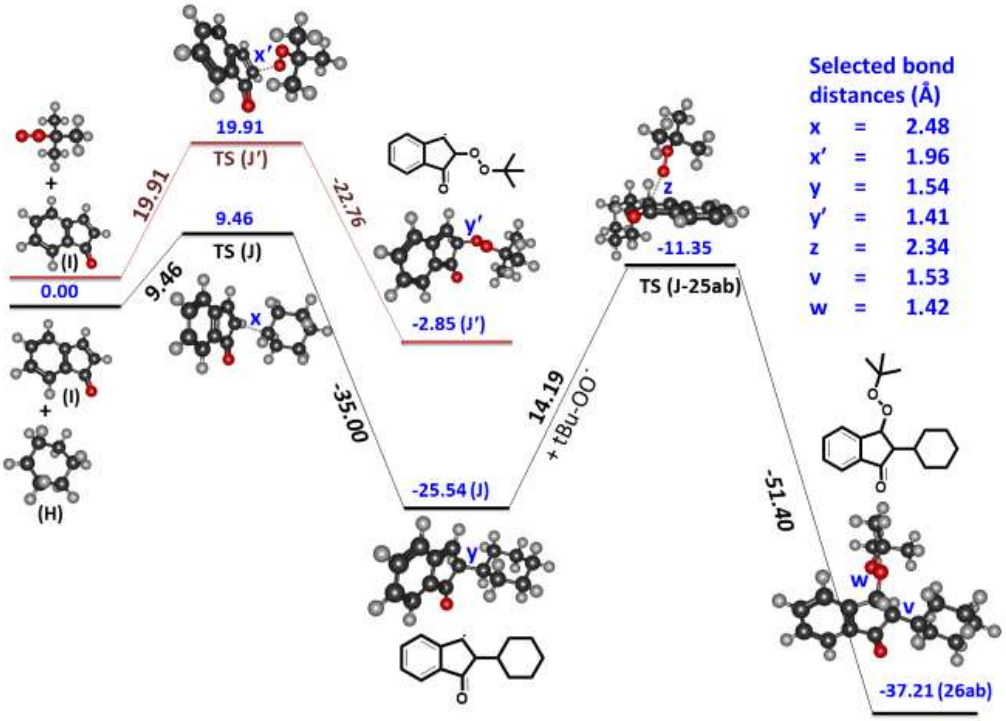


Figure 1. Calculated energy profile diagram for the reaction with two paths considered. The relative energies from DFT calculations are in kcal.mol^{-1}and bond lengths in Å, done at M06/6-31g+(d,p) level of theory.

Even though both *tert*-butylperoxy and cyclohexyl radicals exist in the medium in this regioselective cycloalkylation-peroxidation process, the peroxidation is preferentially taking place at the benzylic position and the cycloalkylation at the C2 position. No reverse attack is observed in any of the cases. To understand the origin of regioselectivity, Density Functional (DFT) studies were carried out which is depicted in figure 1. Theoretical calculations have been performed at the M06 level of theory using a 6-31+G(d,p) basis set for the atoms present in the system as implemented in GAUSSIAN 09 program package. Frequency calculations have been performed on all the modelled structures using the same level of theory The optimised structures for transition states, intermediates and the products are depicted in the energy profile diagram with some selected geometric parameters (Figure 1) Two possible ways to proceed with the reaction have been investigated: the C2 position of the indene can be attacked by an in *situ* generated cyclohexyl radical (**H**) which passes through a barrier height of 9.46 kcal.mol^{-1} and forms intermediate (**J**). Alternately, the attack of *tert*-butylperoxyradical at the non- benzylic position (C2) passes through a barrier height of 19.91 kcal.mol^{-1}, forming intermediate(J′). It could be seen from Figure 1, the energy of activation required to proceed with ^{t}BuOO· is 10.45 kcal.mol^{-1} higher as compared to one attacked by cyclohexyl radical (**H**). Intermediate (**J**) is more stable than (**J′**) by 12.24 kcal.mol^{-1}. Thus, the reaction proceeding with ^{t}BuOO· as attacking nucleophile is less favourable and its possibility has been ruled out. The length of bonds (x,y) shown in Figure 1, reveals the formation of a bond between the reactant and the incoming cyclohexyl radical. In the transition state, the bond length of x is of 2.48 Å indicating interaction with the incoming moiety. This bond (y) has shortened to a length of 1.54 Å in species (J), indicating the formation of a C–C bond. Subsequently, the incoming radical ^{t}BuOO· attack at position C3 of the intermediate (**J**), forming a stable product (**26ab**) with an energy release of -51.40 kcal.mol^{-1} after crossing a barrier height of 14.19 kcal.mol.[20] (Figure 1).

Conclusion

In conclusion, we have demonstrated the differential reactivity of terminal and internal alkenes. A carbonylation-peroxidation of vinyl arenes is achieved in the absence of any carbonyl source. Vinyl arenes undergo decarbonylative C–C bond formation followed by a concurrent carbonylation-peroxidation catalyzed by Cu(I) and *tert*-butyl hydroperoxide (TBHP) but α–methyl styrenes yielded aryl methyl ketones as the only product. A α–substituted unsymmetrical internal alkene such as but-1-ene-1,3-diylbenzene afforded selective α–peroxidation at the tertiary carbon and not across the double bond under the identical reaction conditions which is governed by stability of tertiary radical. An internal cyclic alkene such as indene provided peroxidation-carbonylation-cycloalkylation/cycloetherification by switching the solvent system from acetonitrile to cycloalkanes/cyclic ether. Plausible reaction mechanisms have been proposed for each of these

transformations. Thus a variety of organic peroxy compounds can be generated via radical mediated peroxidation of internal and terminal alkenes which may find useful applications in medicinal chemistry.

Experimental Section

General Information:

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (100-200 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 and 600 MHz) and in for ^{13}C NMR (101 and 151 MHz) $CDCl_3$ as the internal standard. HRMS spectra were recorded using +ESI (TOF) mode. IR spectra were recorded in KBr or neat.

General Procedure for the Synthesis of 3-(*tert*-Butylperoxy)-1,3-diphenylpropan-1-one (1a) from Styrene (1) and *tert*-Butyl hydroperoxide (a):
To an oven-dried 10 mL round bottom flask fitted with a reflux condenser was added styrene (**1**) (114.4 µL, 1.0 mmol), *tert*-butyl hydroperoxide (**a**) (600 µL, 3.0 mmol), Cu_2O (14.0 mg, 0.1 mmol), and acetonitrile (2.0 mL). The reaction mixture was refluxed in a preheated oil bath at 110 °C for 2 h. The reaction mixture was cooled to room temperature, admixed with ethyl acetate (25 mL) and the organic layer was washed with water (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel (hexane / ethyl acetate, 99.5:0.5) to give pure 3-(*tert*-butylperoxy)-1,3-diphenylpropan-1-one (**1a**) (121 mg, yield 81 %). The identity and purity of the product was confirmed by spectroscopic analysis.

General Procedure for the Synthesis of (*E*)-(3-(*tert*-Butylperoxy)but-1-ene-1,3-diyl)dibenzene (22a) from (*E*)-but-1-ene-1,3-diyldibenzene (22) and *tert*-Butyl hydroperoxide (a)
To an oven-dried 10 mL round bottom flask fitted with a reflux condenser was added (*E*)-but-1-ene-1,3-diyldibenzene (**22**) (104 mg, 0.5 mmol), *tert*-butyl hydroperoxide (**a**) (600 µL, 3.0 mmol), Cu_2O (7.0 mg, 0.05 mmol), and acetonitrile (2.0 mL). The reaction mixture was refluxed in a preheated oil bath at 110 °C for 2 h. The reaction mixture was cooled to room temperature, admixed with ethyl acetate (25 mL) and the organic layer was washed with water (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel (hexane / ethyl acetate, 99.5:0.5) to give pure (*E*)-(3-(*tert*-butylperoxy)but-1-ene-1,3-diyl)dibenzene (**22a**) (102 mg, yield 69 %). The identity and purity of the product was confirmed by spectroscopic analysis.

General Procedure for the Synthesis of 3-(*tert*-butylperoxy)-2-cyclohexyl-2,3-dihydro-1*H*-inden-1-one (26ab) from indene (26) and *tert*-Butyl hydroperoxide (a)
To an oven-dried 10 mL round bottom flask fitted with a reflux condenser was added indene (**26**) (58 µL, 0.5 mmol), *tert*-butyl hydroperoxide (**a**) (600 µL, 3.0 mmol), Cu_2O (7.0 mg, 0.05 mmol), and cyclohexane (2.0 mL). The reaction mixture was refluxed in a preheated oil bath at 110 °C for 3 h. The reaction mixture was cooled to room temperature, admixed with ethyl acetate (25 mL) and the organic layer was washed with water (2 x 10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel (hexane / ethyl acetate, 99:1.0) to give pure 2-(*tert*-butylperoxy)-3-cyclohexyl-2,3-dihydro-1*H*-inden-1-one (**26ab**) (100 mg, yield 66 %). The identity and purity of the product was confirmed by spectroscopic analysis.

3-(*tert*-Butylperoxy)-1,3-diphenylpropan-1-one (1a): Colourless oil, (121 mg, 81 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 2H, J = 7.2 Hz), 7.55 (t, 1H, J = 7.4 Hz), 7.47–7.42 (m, 4H), 7.35 (t, 2H, J = 7.4 Hz), 7.30 (d, 1H, J = 7.2 Hz), 5.60 (t, 1H, J = 6.4 Hz), 3.77 (dd, 1H, J = 16.4, 7.2 Hz), 3.21 (dd, 1H, J = 16.0, 6.0 Hz), 1.16 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 197.64, 140.17, 137.35, 133.21, 128.68, 128.54, 128.40, 128.24, 127.25, 82.47, 80.92, 44.17, 26.49 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 1687, 1450, 1360, 1198, 751, 694 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}NaO_3$ 321.1461; Found 321.1466.

3-(*tert*-Butylperoxy)-1,3-di-*p*-tolylpropan-1-one (2a): Yellow gummy, (100 mg, 61 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.15 (d, 2H, J = 7.6 Hz), 5.55 (t, 1H, J = 6.6 Hz), 3.76 (dd, 1H, J = 16.0, 6.8 Hz), 3.19 (dd, 1H, J = 16.0, 6.0 Hz), 2.40 (s, 3H), 2.33 (s, 3H), 1.16 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 197.40, 143.98, 137.99, 137.06, 134.86, 129.34, 129.24, 128.52, 127.27, 82.45, 80.88, 43.91, 26.50, 21.78, 21.35 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 2928, 1684, 1606, 1512, 1362, 1271, 1195, 1019, 810, 756 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_3$ 349.1774; Found 349.1783.

3-(*tert*-Butylperoxy)-1,3-di-*m*-tolylpropan-1-one (3a): Gummy, (93 mg, 57 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, 2H, J = 7.6 Hz), 7.35–7.23 (m, 3H), 7.23 (d, 3H, J = 3.6 Hz,), 5.59–5.53 (m, 1H), 3.76 (dd, 1H, J = 16.3, 7.1 Hz), 3.18 (dd, 1H, J = 16.0, 6.8 Hz), 2.40 (s, 3H), 2.35 (s, 3H), 1.17 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 197.89, 140.03, 138.41, 138.11, 137.33, 133.94, 129.04, 128.92, 128.52, 128.42, 127.94, 125.61, 124.32, 82.55, 80.94, 44.23, 26.49, 21.61, 21.47 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 2927, 1683, 1654, 1606, 1362, 1195, 783, 702 cm^{-1}. HRMS

(ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_3$ 349.1774; Found 349.1778.

1,3-*bis*(4-(*tert*-Butyl)phenyl)-3-(*tert*-butylperoxy)propan-1-one (4a): Gummy, (124 mg, 65 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, J = 8.4 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.35 (bs, 4H), 5.59 (t, 1H, J = 6.4 Hz), 3.77 (dd, 1H, J = 16.4, 6.8 Hz), 3.21 (dd, 1H, J = 16.4, 10.4 Hz), 1.33 (s, 9H), 1.30 (s, 9H), 1.18 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 197.45, 156.91, 151.05, 137.02, 134.82, 128.35, 126.97, 125.59, 125.46, 82.33, 80.91, 44.01, 35.24, 34.69, 31.48, 31.23, 26.53 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 1759, 1685, 1601, 1452, 1361, 1198, 1019, 831, 752, 696 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + K]^+$ Calcd for $C_{27}H_{38}KO_3$ 449.2453; Found 449.2441.

1,3-di([1,1'-Biphenyl]-4-yl)-3-(*tert*-Butylperoxy)propan-1-one (5a): Yellow solid, (311 mg, 69 %); m. p. 100-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.58-7.64 (m, 6H), 7.52 (d, J = 8.4 Hz, 2H), 7.49-7.40 (m, 5H), 7.35 (t, J = 7.2 Hz, 1H), 5.67 (t, J = 6.4 Hz, 1H), 3.85 (dd, J = 16.4, 6.8 Hz, 1H), 3.29 (dd, J = 16.0, 6.0 Hz, 1H), 1.21 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.19, 145.92, 141.17, 140.97, 139.96, 139.15, 135.98, 129.09, 129.01, 128.87, 128.38, 127.70, 127.43, 127.40, 127.35, 127.33, 127.26, 82.29 , 81.05, 44.12, 26.54 ppm. IR (KBr): $\tilde{\nu}$ = 2974, 2924, 1664, 1599, 1484, 1405, 1360, 1196, 870, 760, 690 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}NaO_3$ 473.2187; Found 473.2192.

3-(*tert*-Butylperoxy)-1,3-*bis*(4-(chloromethyl)phenyl)propan-1-one (6a): Brownish gummy, (130 mg, 66 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, 2H, J = 8.3 Hz), 7.47 (d, 2H, J = 8.3 Hz), 7.40 (dd, 4H, J = 20.1, 8.2 Hz), 5.59 (t, 1H, J = 6.5 Hz), 4.61 (s, 2H), 4.58 (s, 2H), 3.74 (dd, 1H, J = 16.3, 7.1 Hz), 3.18 (dd, 1H, J = 16.3, 5.9 Hz), 1.16 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 196.79, 142.63, 140.49, 137.43, 137.09, 128.84, 128.83, 128.81, 127.58, 81.97, 81.05, 46.08, 45.39, 44.18, 26.49 ppm. IR (KBr): $\tilde{\nu}$ = 2982, 2881, 1691, 1362, 1267, 1196 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{24}Cl_2NaO_3$ 417.0995; Found 417.0968.

3-(*tert*-Butylperoxy)-1,3-*bis*(4-ethoxyphenyl)propan-1-one(7a): Gummy, (215 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.2 Hz 2H), 7.35 (d, 2H, J = 8.8 Hz), 6.94–6.86 (m, 4H), 5.52 (t, 1H, J = 6.6 Hz), 3.86 (s, 3H), 3.79 (s, 3H), 3.75 (dd, 1H, J = 16.0, 6.4 Hz), 3.19 (dd, 1H, J = 16.0, 6.0 Hz), 1.17 (s, 9H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 163.61, 159.57, 132.10, 130.67, 130.46, 128.68, 113.9, 113.8, 82.34, 80.83, 55.60, 55.36, 43.51, 26.51 ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2839, 1675, 1602, 1512, 1255, 1174, 1030, 831, 739 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_5$ 381.1672; Found 381.1679.

1,3-*bis*(4-Bromophenyl)-3-(*tert*-butylperoxy)propan-1-one (8a): Gummy, (167 mg, 73 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, 2H, J = 8.8 Hz), 7.43 (d, 2H, J = 7.2 Hz), 7.37–7.31 (m, 4H), 5.53 (t, 1H, J = 6.6 Hz), 3.70 (dd, 1H, J = 16.0, 6.8 Hz), 3.12 (dd, 1H, J = 16.4, 6.0 Hz), 1.15 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 196.10, 139.90, 138.60, 135.50, 134.09, 129.80, 129.08, 128.79, 128.60, 81.65, 81.10, 43.93, 26.47 ppm. IR (KBr): $\tilde{\nu}$ = 2980, 2880, 1689, 1589, 1490, 1401, 1362, 1091, 823 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + K]^+$ Calcd for $C_{19}H_{20}Br_2KO_3$ 492.9411; Found 492.9418.

3-(*tert*-Butylperoxy)-1,3-*bis*(4-chlorophenyl)propan-1-one (9a): Gummy, (130 mg, 71 %). δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 4.8 Hz), 7.59 (d, 2H, J = 8.8 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.4 Hz), 5.52 (t, 1H, J = 6.6 Hz), 3.68 (dd, 1H, J = 16.4, 7.2 Hz), 3.11 (dd, 1H, J = 16.4, 6.0 Hz), 1.15 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 196.20, 139.12, 135.86, 132.15, 132.05, 131.71, 130.73, 129.87, 128.90, 122.23, 81.64, 81.08, 43.85, 26.45 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 2881, 1691, 1585, 1486, 1362, 1195, 1071, 1009 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}Cl_2NaO_3$ 389.0682; Found 389.0678.

3-(*tert*-Butylperoxy)-1,3-*bis*(4-fluorophenyl)propan-1-one (10a): Gummy, (114 mg, 68 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93–7.92 (m, 1H), 7.82 (d, 1H, J = 8.0 Hz), 7.55–7.52 (m, 1H), 7.42–7.38 (m, 3H), 7.31–7.29 (m, 2H), 5.54 (dd, 1H, J = 7.2, 5.6 Hz), 3.69 (dd, 1H, J = 20.4, 32.0 Hz), 3.12 (dd, 1H, J = 16.4, 5.6 Hz), 1.16 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.87, 167.23, 164.70, 163.93, 161.48, 135.83 (d, J = 3.2 Hz), 133.68 (d, J = 3.0 Hz), 131.87 (d, J = 9.4 Hz), 131.03 (d, J = 9.3 Hz), 128.98 (d, J = 8.2 Hz), 115.94, 115.72 (d, J = 15.0 Hz), 115.36, 81.76, 81.01, 43.93, 26.47 ppm. ^{19}F NMR ($CDCl_3$, 377 MHz) δ -105.59–105.81 (m), 114.52–114.78 (m). IR (KBr): $\tilde{\nu}$ = 2979, 2932, 1724, 1687, 1600, 1509, 1411, 1364, 1226, 1156, 834 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}F_2NaO_3$ 357.1273; Found 357.1283.

3-(*tert*-Butylperoxy)-1,3-*bis*(3-chlorophenyl)propan-1-one (11a): Yellow gummy, (119 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, 1H, J = 1.8 Hz), 7.83–7.81 (m, 1H), 7.55–7.52 (m, 1H), 7.42–7.38 (m, 2H), 7.31–7.27 (m, 3H), 5.54 (t, 1H J = 6.4 Hz), 3.69 (dd, 1H, J = 19.6, 7.2 Hz), 3.12 (dd, 1H, J = 17.6, 5.6 Hz), 1.16 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 195.89, 142.18, 138.59, 135.11, 134.47, 133.33, 130.08, 129.89, 128.53, 128.47, 127.27, 126.46, 125.37, 81.51, 81.21, 44.10, 26.44 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 2683, 1687, 1609, 1414, 1363, 1195, 1017, 680 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}Cl_2KO_3$ 389.0682; Found 389.0686.

3-(*tert*-Butylperoxy)-1,3-*bis*(3-nitrophenyl)propan-1-one (12a): Gummy, (225 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.45 (d, 1H, J = 8.0 Hz), 8.33 (s, 1H), 8.30 (d, 1H, J = 8.0 Hz), 8.19 (d, 1H, J = 8.4 Hz), 7.80 (d, 1H, J = 7.6 Hz), 7.71 (t, 1H, J = 8.0

Hz), 7.57 (t, 1H, *J* = 8.0 Hz), 5.69 (t, 1H, *J* = 6.6 Hz), 3.82 (dd, 1H, *J* = 16.4, 6.8 Hz), 3.25 (dd, 1H, *J* = 16.8, 5.6 Hz), 1.16 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.56, 142.24, 138.09, 133.87, 133.42, 130.17, 129.66, 127.87, 123.41, 123.33, 122.16, 81.52, 80.91, 44.00, 26.44 ppm. IR (KBr): $\tilde{\nu}$ = 3088, 1700, 1689, 1530, 1351 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_7$ 389.1343; Found 389.1349.

1-(*tert*-Butylperoxy)-3-oxopropane-1,3-diyl)*bis*(4,1-phenylene) diacetate (13a): Colorless solid, (273 mg, 66 %); m. p. 90-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 2H, *J* = 8.4 Hz), 7.44 (d, 2H, *J* = 8.4 Hz), 7.19 (d, 2H, *J* = 8.4 Hz), 7.08 (d, 2H, *J* = 8.4 Hz), 5.59 (t, 1H, *J* = 6.4 Hz), 3.73 (dd, *J* = 16.4, 6.2 Hz, 1H), 3.16 (dd, 1H, *J* = 16.4, 6.0 Hz), 2.32 (s, 3H), 2.29 (s, 3H), 1.16 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.22, 169.59, 168.96, 154.55, 150.53, 137.72, 134.79, 130.01, 128.30, 121.91, 121.65, 81.73, 81.07, 44.12, 26.47, 21.29 ppm. IR (KBr): $\tilde{\nu}$ = 3439, 2924, 2853, 1383, 1022, 742 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{23}H_{30}NO_7$ 432.2017; Found 432.2027.

Acetophenone (**14a**): Colorless liquid, (87 mg, 72 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 2H, *J* = 8.0 Hz), 7.53 (t, 1H, *J* = 7.8 Hz), 7.44 (t, 2H, *J* = 7.6 Hz,), 2.58 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.09, 137.13, 133.09, 128.57, 128.29, 26.57 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 1685, 1594, 1444, 1359, 1263, 1179, 1021, 760, 690, 589 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_8H_{12}NO$ 138.0913; Found 138.0921.

1-(*p*-Tolyl)than-1-one (15a): Colorless liquid, (86 mg, 64 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, *J* = 8.2 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 2.56 (s, 3H), 2.40 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 197.82, 143.88, 134.76, 129.27, 128.46, 26.51, 21.63 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 1683, 1596, 1447, 1361, 1263, 1179, 1021, 760, 690, 592 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{11}O$ 135.0804; Found 135.0814.

1-(4-Chlorophenyl)ethan-1-one (16a): Colorless liquid, (120 mg, 75 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2H, *J* = 8.5 Hz), 7.42 (d, 2H, *J* = 8.5 Hz), 2.58 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 196.84, 139.60, 135.51, 129.79, 128.94, 26.58 ppm. IR (KBr): $\tilde{\nu}$ = 3069, 1686, 1589, 1451, 1363, 1264, 1182, 1021, 764, 693, 595 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + K]^+$ Calcd for C_8H_7ClKO 192.9817; Found 192.9830.

***E*-(1-(*tert*-Butylperoxy)prop-2-ene-1,1,3-triyl)tribenzene (17a):** Yellow gummy, (133 mg, 74 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 1H, *J* = 7.2 Hz), 7.58 (t, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 8.0 Hz), 7.39–7.36 (m, 4H), 7.33–7.32 (m 3H), 7.25 (d, 5H, *J* = 4.8 Hz), 6.34 (d, 1H, *J* = 9.6 Hz), 5.41 (d, 1H, *J* = 9.6 Hz), 1.18 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.65, 141.63, 140.05, 139.45, 132.55, 130.20, 130.11, 128.89, 128.73, 128.57, 128.42, 128.28, 128.27, 128.03, 127.78, 127.61, 127.57, 127.45, 83.24, 80.45, 26.59 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 3028, 2977, 2928, 1661, 1598, 1492, 1477, 1385, 1362, 1276, 1195, 758, 697, 638 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}O_2$ 359.2006; Found 359.2015.

(*E*)-(1-(*tert*-Butylperoxy)-3-(*p*-tolyl)prop-2-ene-1,1-diyl)dibenzene (18a): Yellow gummy, (123 mg, 66 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.34 (m, 4H), 7.24–7.21 (m, 7H), 7.14 (d, 3H, *J* = 8.0 Hz), 6.36 (d, 1H, *J* = 9.6 Hz), 5.37 (d, 1H, *J* = 9.6 Hz), 2.34 (s, 3H), 1.17 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.35, 141.69, 139.49, 137.86, 136.89, 130.13, 129.31, 128.24, 127.72, 127.68, 127.60, 127.51, 127.41, 83.11, 80.44, 26.59, 21.37 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2925, 1663, 1493, 1446, 1360, 1273, 1194, 1015, 812, 762, 699 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{28}NaO_2$ 395.1982; Found 395.1998.

***E*-(3-(4-(*tert*-Butyl)phenyl)-1-(*tert*-butylperoxy)prop-2-ene-1,1-diyl)dibenzene (19a):** Gummy, (116 mg, 56 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.33 (m, 5H), 7.29–7.23 (m, 9H), 6.37 (d, 1H, *J* = 9.6 Hz), 5.40 (d, 1H, *J* = 9.6 Hz), 1.31 (s, 9H), 1.18 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.97, 143.10, 141.68, 139.48, 136.62, 130.17, 128.23, 127.79, 127.70, 127.59, 127.48, 127.11, 125.55, 82.99, 80.52, 34.70, 31.47, 26.58 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 2923, 1669, 1486, 1442, 1365, 1273, 1199, 1015, 818, 752, 689 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{29}H_{38}NO_2$ 432.2897; Found 432.2913.

***E*-(3-(4-Bromophenyl)-1-(*tert*-butylperoxy)prop-2-ene-1,1-diyl)dibenzene (20a):** Gummy, (173 mg, 79 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, 3H, *J* = 8.4 Hz), 7.37 (d, 3H, *J* = 7.6 Hz), 7.26 (bs, 2H), 7.23–7.17 (m, 6H), 6.24 (d, 1H, *J* = 9.6 Hz), 5.35 (d, 1H, *J* = 9.5 Hz), 1.17 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.23, 141.40, 139.42, 139.26, 131.69, 129.98, 129.10, 128.38, 128.33, 127.97, 127.74, 127.61, 126.52, 121.91, 82.64, 80.54, 26.58 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 1656, 1587, 1527, 1492, 1452, 1333, 1070, 1012, 732, 698 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{25}BrNaO_2$ 459.0930; Found 459.0947.

***E*-(1-(*tert*-Butylperoxy)-3-(4-chlorophenyl)prop-2-ene-1,1-diyl)dibenzene (21a):** Reddish gummy, (151 mg, 77 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, 3H, *J* = 7.2 Hz), 7.30 (d, 4H, *J* = 8.4 Hz), 7.25 (bs, 3H), 7.24–7.21 (m, 4H), 6.25 (d, 1H, *J* = 9.6 Hz), 5.37 (d, 1H, *J* = 9.6 Hz), 1.17 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.16, 141.38, 139.24, 138.82, 133.73, 129.97, 128.76, 128.74, 128.37, 128.32, 127.96, 127.72, 127.60, 126.57, 82.58, 80.56, 26.56 ppm. IR (KBr): $\tilde{\nu}$ = 3031, 1653, 1604, 1559, 1511, 1333, 1232, 1161, 835, 704 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{25}ClNaO_2$ 415.1435; Found 415.1449.

3-(*tert*-Butylperoxy)but-1-ene-1,3-diyl)dibenzene (22a): Colourless oil, (102 mg, 69 %). δ ^{1}H NMR (600

MHz, $CDCl_3$) δ 7.49 (d, 2H, J = 7.2 Hz), 7.40 (d, 2H, J = 7.2 Hz), 7.35–7.30 (m, 4H), 7.28–7.21 (m, 2H), 6.52 (dd, 2H, J = 39.6, 16.2 Hz), 1.79 (s, 3H), 1.25 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 151 MHz) δ 144.30, 137.16, 134.03, 129.96, 128.67, 128.09, 127.68, 127.25, 126.69, 126.53, 83.76, 79.42, 26.88, 24.70 ppm. IR (KBr): $\tilde{\nu}$ = 2988, 2935, 1891, 1736, 1677, 1578, 1486, 1394, 1263, 1072, 1026, 1007, 927, 913, 861, 807, 757, 735, 731, 718, 667, 645 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + K]^+$ Calcd for $C_{20}H_{24}KO_2$ 335.1408; Found 335.1416.

***E*-4,4'-(3-(*tert*-Butylperoxy)but-1-ene-1,3-diyl)*bis*(bromobenzene) (23a):** Yellow gummy, (161 mg, 71 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64–7.42 (m, 4H), 7.34 (d, 2H, J = 6.0 Hz), 7.25 (d, 2H, J = 5.6Hz), 6.43 (dd, 2H, J = 36.0, 11.2 Hz), 1.75 (s, 3H), 1.23 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.09, 135.78, 133.99, 131.80, 131.20, 129.29, 128.43, 128.22, 121.64, 121.34, 83.39, 79.65, 26.82, 24.63 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 2930, 1900, 1726, 1687, 1588, 1486, 1394, 1263, 1072, 1026, 1009, 930, 909, 858, 803, 755, 745, 739, 718, 681, 668, 644 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{20}H_{26}Br_2O_2$ 470.0325; Found 470.0337.

3-(*tert*-Butylperoxy)-2-cyclohexyl-2,3-dihydro-1*H*-inden-1-one (26ab): Yellow gummy, (98 mg, 65 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, 1H, J = 8.0 Hz), 7.73 (d, 1H, J = 7.6 Hz), 7.64 (t, 1H, J = 7.6, 1.1 Hz), 7.49 (t, 1H, J = 7.4 Hz), 5.45 (d, 1H, J = 2.4 Hz), 2.66 (dd, 1H, J = 4.4, 2.8 Hz), 2.11–2.04 (m, 1H), 1.79–1.74 (m, 2H), 1.66 (d, 2H, J = 7.6 Hz), 1.41 (d, 1H, J = 11.2 Hz), 1.35–1.30 (m, 2H), 1.27 (s, 9H), 1.22 (d, 1H, J = 3.6 Hz), 1.15–1.10 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.88, 151.09, 138.00, 134.87, 129.91, 127.84, 123.23, 82.21, 80.56, 58.32, 38.94, 31.32, 29.23, 26.75, 26.69, 26.47, 26.35 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 1717, 1601, 1449, 1362, 1194, 751 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}O_3$ 303.1955; Found 303.1981.

3-(*tert*-Butylperoxy)-2-cycloheptyl-2,3-dihydro-1*H*-inden-1-one (26ac): Gummy, (100 mg, 63 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, 1H, J = 8.0 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.64 (t, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 7.6 Hz), 5.45 (d, 1H, J = 2.4 Hz), 2.69 (t, 1H, J = 3.2 Hz), 2.33–2.27 (m, 1H), 1.80–1.71 (m, 2H), 1.53–1.47 (m, 3H), 1.41–1.29 (m, 5H), 1.28 (s, 9H), 1.27 (d, 2H, J = 2.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.67, 151.43, 138.06, 134.87, 129.84, 127.86, 123.28, 82.36, 80.58, 59.37, 40.34, 33.31, 30.82, 28.00, 27.76, 27.49, 27.33, 26.70 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2858, 1602, 1460, 1362, 1254, 1021, 754 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{29}O_3$ 317.2111; Found 317.2129.

3-(*tert*-Butylperoxy)-2-cyclooctyl-2,3-dihydro-1*H*-inden-1-one (26ad): Red gummy, (107 mg, 65 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, 1H, J = 7.6 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.64 (t, 1H, J = 7.0 Hz), 7.48 (t, 1H, J = 7.4 Hz), 5.43 (d, 1H, J = 2.8 Hz), 2.68 (t, 1H, J = 3.2 Hz), 2.45–2.38 (m, 1H), 1.76–1.68 (m, 4H), 1.54–1.51 (m, 3H), 1.44–1.31 (m, 5H), 1.28 (s, 9H), 1.26 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.67, 151.54, 138.17, 134.84, 129.81, 127.85, 123.26, 82.48, 80.58, 59.97, 37.84, 32.49, 30.06, 26.72, 26.64, 26.59, 26.21, 26.02 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 1718, 1602, 1464, 1362, 1195, 1021, 754 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{31}O_3$ 331.2268; Found 331.2273.

1,2-bis(*tert*-Butylperoxy)-2,3-dihydro-1*H*-indene (26ae'): Yellow gummy, (88 mg, 59 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 6.0 Hz), 7.22 (t, 2H, J = 6.0 Hz), 5.52 (d, 1H, J = 1.6 Hz), 4.99–4.96 (m, 1H), 3.36 (dd, 1H, J = 17.2, 6.8 Hz), 2.95 (dd, 1H, J = 17.2, 2.4 Hz), 1.28 (s, 9H), 1.26 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.81, 138.27, 129.49, 126.92, 126.87, 125.20, 89.61, 86.61, 80.68, 80.56, 35.85, 26.59 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 1717, 1466, 1341, 1195, 1020, 874, 751 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{17}H_{30}NO_4$ 312.2169; Found 312.2143.

2-(*tert*-Butylperoxy)-2,3-dihydro-1*H*-inden-1-one (26af'): Brownish gummy, (67 mg, 61 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, 1H, J = 7.6 Hz), 7.59 (t, 1H, J = 7.6 Hz), 7.38 (dd, 2H, J = 16.0, 8.0 Hz), 4.38 (dd, 1H, J = 7.6, 4.8 Hz), 3.48 (dd, 1H, J = 16.8, 8.0 Hz), 2.99 (dd, 1H, J = 16.4, 4.8 Hz), 1.34 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.08, 150.80, 135.41, 134.92, 127.85, 126.63, 124.30, 75.33, 74.26, 36.77, 28.49 ppm. IR (KBr): $\tilde{\nu}$ = 2971, 2925, 1723, 1664, 1606, 1366, 1265, 1193, 951, 752 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}O_3$ 221.1172; Found 221.1199.

3-*(tert*-Butylperoxy)-2-(1,4-dioxan-2-yl)-2,3-dihydro-1*H*-inden-1-one (26ag): Brownish gummy, (86 mg, 56 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81–7.75 (m, 2H), 7.67 (t, 1H, J = 7.4 Hz), 7.50 (t, 1H, J = 7.6 Hz), 5.80 (d, 1H, J = 2.4 Hz), 3.90–3.84 (m, 2H), 3.73–3.59 (m, 5H), 2.73 (t, 1H, J = 2.6 Hz), 1.29 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 202.76, 150.94, 137.38, 135.21, 129.92, 127.42, 123.60, 80.79, 80.30, 74.20, 69.77, 67.27, 66.54, 54.61, 26.69 ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2858, 1722, 1604, 1461, 1362, 1286, 1195, 1119, 876, 756, 616 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}O_5$ 307.1540; Found 307.1555.

3-(*tert*-Butylperoxy)-1-phenyl-3-(*p*-tolyl)propan-1-one (2aC): Gummy, (102 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, J = 7.2 Hz), 7.56 (t, 1H, J = 7.4 Hz), 7.44 (t, 2H, J = 7.6 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 5.56 (t, 1H, J = 6.6 Hz), 3.79 (dd, 1H, J = 16.4, 7.2 Hz), 3.21 (dd, 1H, J = 16.0, 6.0 Hz), 2.33 (s, 3H), 1.16 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.77, 138.02, 137.32, 136.95, 133.16, 129.24, 128.75, 128.63, 128.37, 127.26, 82.40, 80.86, 44.05, 26.47, 26.38, 21.32 ppm. IR (KBr) $\tilde{\nu}$ = 2979, 2933, 1608, 1518, 1372, 1261, 1199, 1014, 815,

766 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}NaO_3$ 335.1618; Found 335.1645.

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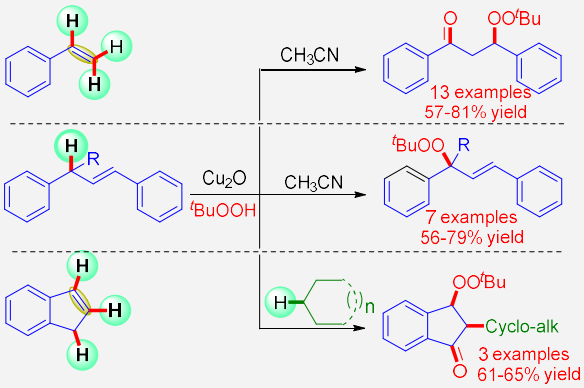
FULL PAPER

Graphical Abstract



A TBHP mediated carbonylation-peroxidation of styrene, α-peroxidation of α–substituted unsymmetrical internal alkenes and concurrent peroxidation-carbonylation-cycloalkylation/cycloetherifiction of internal cyclic alkene (indene) have been developed.

C–H Functionalization and Carbonylation-Peroxidation.

B. A. Mir, S. Rajamanickam, P. Begum and B. K. Patel*
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Copper(I) Catalyzed Differential Peroxidation of Terminal and Internal Alkenes Using TBHP

Keywords: Carbonylation; peroxidation; cycloalkylation/ cycloetherification; terminal alkenes; internal alkenes.