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tert-Butyl Nitrite Mediated Nitro-Nitratosation of Internal Alkenes

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Abstract: In an oxygen atmosphere *tert*-butyl nitrite (TBN) reacts with unsymmetrical internal benzylic alkenes giving nitro-nitratosation product exclusively. The γ-diaryl substituted styrenes provided better yields compared to γ-alkyl-aryl substituted styrenes. The higher yields for the former type of substrates is possible dictated by the additional stability of benzylic radical due to the anchimeric assistance imparted by the γ-substituted phenyl ring. During oxidative nitration, the nitro (NO_2) group adds at the non-benzylic site, whereas the nitrato group (ONO_2) is attached at the relatively stable benzylic position. Under similar reaction conditions, α,β-unsaturated carboxylic acids, afforded nitroalkenes as the sole product.

Keywords: *tert*-Butyl nitrite (TBN); oxidative nitration; nitro alkenes; internal alkenes, β-attack.

Introduction

The metal-free reagent, *tert*-butyl nitrite (TBN) is emerging as a multi-tasking reagent in various synthetic applications because of its easy availability, easy handling, low cost, and stability.[1] Thermolysis of TBN provides NO and ^{t}BuO radicals. The former can directly participate in a reaction, whereas both of these radicals can initiate several reactions. Due to the intrinsic ability of TBN to activate molecular oxygen it captures dioxygen generating a NO_2 radical, which prompts nitration and many other oxidation processes. Interestingly, the NO radical is a good acceptor of transient radicals thus serving as an efficient radical trapper and source of N and N-O synthons.[1]

Terminal alkenes such as styrene react differently with TBN depending upon the other additives present in the reaction. Styrenes react with TBN in the presence of Fe(II) catalyst and $NaBH_4$ to give corresponding oximes.[2] Treatment of styrene with TBN in an air atmosphere in toluene at room temperature provided β-nitroalcohol along with some nitrated products (Scheme 1c).[3] Styrenes undergo cross-coupling in the presence of metal-based carbene and NO radical (generated *in situ* from TBN) providing isooxazolines.[4] In this process, styrene serve as a dienophile and undergo [3+2]cycoaddition *in situ* generated nitrile oxide intermediate. Following the analogous [3+2] cycloaddition strategy our group obtained symmetrical isoxazolines from styrenes in the presence of TBN, $Sc(OTf)_3$ and quinoline.[5] While quinoline did not participate and serve only as a base during the formation of isoxazolines. However, in a Cu-catalyzed process, it took part along with the styrene and TBN providing imidazo[1,2-*a*]quinolines via a three-component process. Here, TBN serves the dual role of an N1 synthon as well as an oxidant.[6] In the absence of any other additives, styrene analogues react with TBN in DMSO providing 1,2,4-oxadiazole-5(4*H*)-ones.[7] Sulfonyl hydrazide as sulfonyl radical and TBN as the NO source adds across the styrene double bond to give a bi-functionalized product α-sulfonylethanone oximes, which is mediated by a base.[8] Similarly, α-sulfonylethanone oxime is obtained from styrene, where TOsMIC acts as the sulfonyl source and TBN as the NO source as well as an oxidant.[9] Using sulfinic acids as the sulfonating agent and TBN as the NO source as well as an oxidant a vicinal sulfoximation of styrene has been accomplished.[10a] TBN has also been employed for the stereoselective nitration,[10b] aerobic oxynitration of terminal olefins,[10c] metal-free nitration of 2-oxindoles,[10d] metal-free synthesis of isatins,[10e] synthesis of quinoxaline N-oxides,[10f] cascade nitration/cyclization of 1,7enynes,[10g] and nitration-peroxidation of styrenes, where the TBN serves as a NO source and TBHP as a ^{t}BuOO source (Scheme 1f).[10h] From the above

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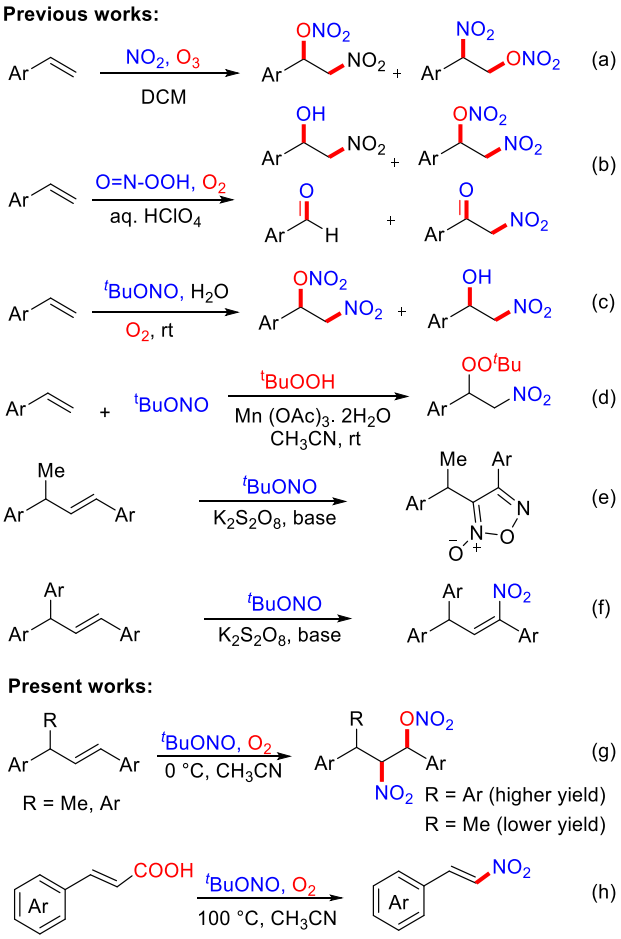
literature reports, it is evident that TBN reacts with styrenes in many ways depending on the reaction conditions and other additives present. On the other hand, internal benzylic and non-benzylic alkenes also react differently with TBN. An interesting synthesis of furoxane is accomplished from benzylic internal alkene using TBN, quinoline and $K_2S_2O_8$ (Scheme 1e). Under a similar condition α,β-unsaturated carboxylic acids and cyclic internal alkene afforded nitroalkenes.[11]



Scheme 1. Various methods for nitration of alkenes.

During the formation of isoxazoline,[4,5] imidazo[1,2-*a*]quinolines,[6] and 1,2,4-oxadiazole-5(4*H*)-ones[7] from styrenes and TBN, the *in situ* generated NO_2 radical attacks at the β-carbon while the NO radical attacks at the α-carbon even though both the radicals coexist in the medium. From the computational calculation, it was found that the attack of NO_2 radical at the terminal carbon that is at the β-carbon is stabilised by around 6 kcal/mole less than the attack by NO radical at the same site.[7] During the furoxane formation from internal alkenes *viz.* (*E*)-1,3-diphenyl-1-butenes, the NO_2 radical again attacks at the β-carbon while the NO radical at the benzylic position (i.e α-carbon) leading to the formation of furoxane (Scheme 1e).[11] However, in an analogous internal alkene *viz.* prop-2-ene-1,1,3-triyltriaryl system gave exclusively a mono nitro product where the nitro group is at the benzylic position (α-carbon) (Scheme 1f). Surprisingly, compared to all other previous results[5-7] this is an unusual attacking position for the nitro group as it always prefers to attack at the β-position (Scheme 1a-d).[11] Styrenes react with TBN in an oxygen atmosphere to give β-nitro alcohols and their nitrate derivatives, where the exclusive attack of the NO_2 group is at the terminal carbon of the styrene (Scheme 1c).[3] Thus, instead of a terminal alkene (styrene) if an internal alkene such as γ-diaryl substituted or γ-alkyl-aryl substituted styrene is treated with TBN under an oxygen atmosphere will they react similarly or behave differently giving different products? Further, if mono-nitration takes place will it be at the α or at the β-position of the internal benzylic alkenes? Therefore, we were curious to investigate the reaction of various internal alkenes with TBN in an oxygen atmosphere.

Results and Discussion

Our initial investigation started by reacting γ-diaryl substituted internal alkene (**1**) with *tert*-butyl nitrite (**a**). Initially, alkene (**1**) was treated with *tert*-butyl nitrite (**a**) (2 equiv.) in chlorobenzene (2.0 mL) at room temperature for 24 h in an air atmosphere. A new product (**1a**) was isolated in 39% yield after column chromatographic separation (Table 1, entry 1). Spectroscopic (IR, ^{1}H and ^{13}C NMR) analysis of the product (**1a**) revealed the disappearance of both alkene protons at 6.60 ppm and 6.40 ppm. However, the appearance of two doublets one at 5.87 ppm and another at 4.88 ppm along with a multiplet at 5.69 ppm suggests that the PhCH(Ph)- part is intact thereby confirming di-functionalization across the double bond of (**1**). Further, HRMS analysis of the product indicates the loss of two protons and the addition of NO_2 and ONO_2 groups. Eventually, the exact structure of the product was confirmed by X-ray crystallographic analysis of one of its derivative (**10a**) as shown in Figure 1.

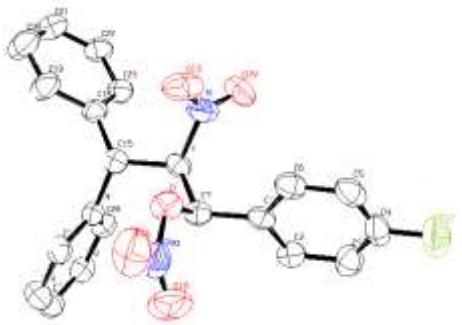
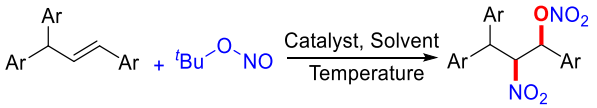


Figure 1. ORTERP molecular diagram of (**10a**)[12]

Fascinated by the formation of this oxidative nitration product (**1a**), this reaction was further screened by varying various other solvents. Among the solvents screened such as CH_3CN, DCE, DMSO, DMF, MeOH and THF (Table 1, entries 2–6) the polar

aprotic solvent CH_3CN (Table 1, entry 2) was found to give the best yield of (**1a**) in 48% under otherwise identical condition. Gratifyingly, when the same reaction was performed in an oxygen atmosphere, the product (**1a**) was obtained in an improved yield of 65% (Table 1, entry 7). To see if the use of a metal catalyst can help improve the yield, various metal catalysts such as $Cu(OAc)_2$, $CuCl_2$, $Cu(acac)_2$, CuO, Cu_2O, $FeCl_3$ were employed but none provided any improved yield of the product (**1a**) compared to the uncatalyzed reaction (Table 1, entries 8–14). Interestingly, when the reaction was performed at 0 °C under otherwise identical reaction conditions provided the desired product (**1a**) in improved yield of 74% (Table 1, entry 15). On the other hand, when the reaction was performed at 50 °C, the yield of (**1a**) dropped drastically to 11%, possibly due to competitive side reactions among various radicals (Table 1, entry 16).

Table 1. Screening of reaction conditions[a]



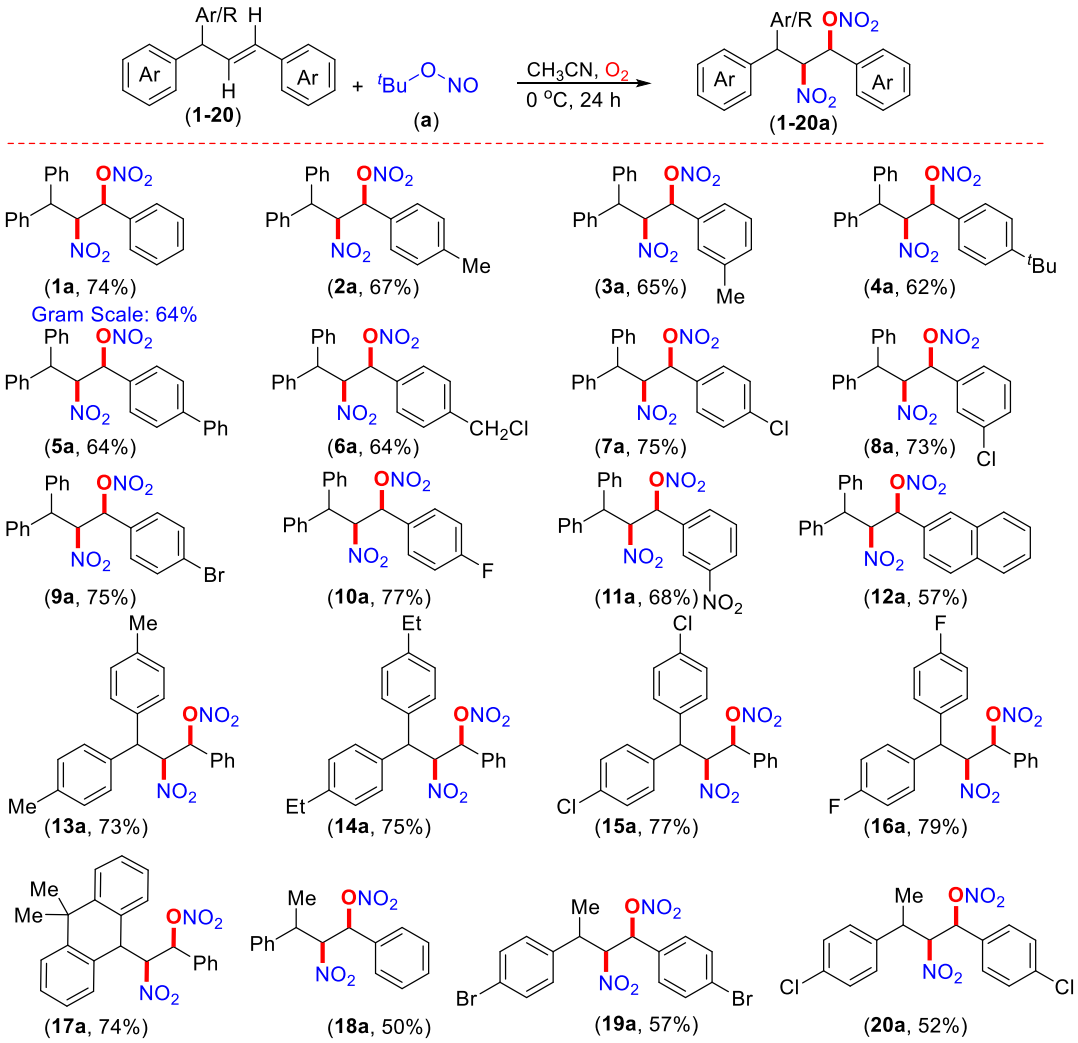
(**1**) (**a**) (**1a**)

Entry	Catalyst (10 mol %)	Solvent	Yield (%)[b]
1.		PhCl	39[c]
2.		CH_3CN	**48**[c]
3.		DCE	23[c]
4.		DMSO	38[c]
5.		DMF	14[c]
6.		MeOH	18[c]
7.		CH_3CN	65[d]
8.	$Cu(OAc)_2$	CH_3CN	27[d]
9.	$CuCl_2$	CH_3CN	23[d]
10.	$Cu(acac)_2$	CH_3CN	24[d]
11.	CuO	CH_3CN	22[d]
12.	$Cu(OTf)_2$	CH_3CN	45[d]
13.	Cu_2O	CH_3CN	34[d]
14.	$FeCl_3$	CH_3CN	11[d]
15.		**CH_3CN**	**74**[d,e]
16.		CH_3CN	11[e,f]

[a]Reaction conditions: **1** (0.5 mmol), *tert*-butyl nitrite (1.0 mmol) solvent (2.0 mL). [b]Yield after 24 h. [c]Under an air atmosphere. [d]In the presence of O_2 (balloon). [e]Temperature 0 ˚C. [f]Temperature 50 ˚C.

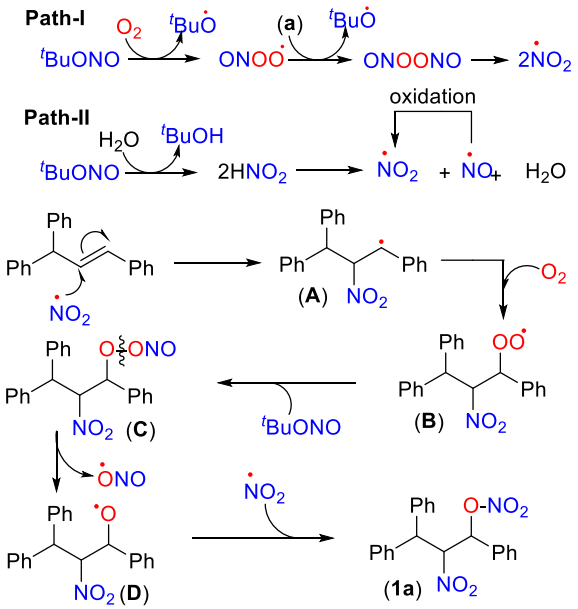
After a series of screening experiments, it was found that this *bis*-functionalization is best achieved using alkene (**1**) (0.5 mmol), TBN (2 equiv.) at 0 °C for 24 h. After establishing the optimized reaction condition for this oxidative nitration as shown in (Table 1), we explored the reaction of various (*E*)-prop-2-ene-1,1,3-triyltribenzenes (**1**–**17**) with TBN (**a**). This reaction proceeds well with a variety of internal alkenes (**1**–**17**) bearing electron-donating as well as electron-withdrawing groups in their phenyl ring attached directly to the double bond. Phenyl rings of these internal benzylic alkenes possessing moderately electron-donating groups such as *p*-Me (**2**), *m*-Me (**3**), *p*-^{t}Bu (**4**), *p*-Ph (**5**), *p*-CH_2Cl (**6**) gave their corresponding oxidative nitration products (**2a**, 67%), (**3a**, 65%), (**4a**, 62%), (**5a**, 64%), (**6a**, 64%) in moderate yields (Scheme 2). Internal benzylic alkenes bearing moderately electron-withdrawing groups such as *p*-Cl (**7**), *m*-Cl (**8**), *p*-Br (**9**) and *p*-F (**10**) in their phenyl rings, provided their corresponding products (**7a**, 75%), (**8a**, 73%), (**9a**, 75%) and (**10**, 77%), in good yields as shown in (Scheme 2). Alkene possessing strongly electron-withdrawing group such as *m*-NO_2 (**11**) also underwent oxidative nitration and provided the corresponding product (**11a**) in 68% yield. As can be seen from the pattern in the yield obtained, phenyl ring possessing moderately electron-withdrawing groups provided better yields than substrates having electron-donating groups. This yield trend is not pronounced for a substrate having strongly electron-withdrawing groups such as nitro suggesting some additional factors may be responsible for it. Alkene having a polycyclic ring such as 2-naphthyl (**12**) at the double also delivered the desired oxidative nitration product (**12a**) in moderate yield (Scheme 2). In addition to simple phenyl rings at the γ-position (**1**-**12**) substituted phenyl rings (**13**–**16**) all reacted efficiently. γ-Phenyl rings having electron-donating *p*-Me (**13**), *p*-Et (**14**) as well as electron-withdrawing *p*-Cl (**15**), *p*-F (**16**) all reacted successfully and provided their corresponding oxidative nitration products (**13a**, 73%), (**14a**, 75%) and (**15a**, 77%), (**16a**, 79%) in good yields (Scheme 2). An alkene (**17**) where both the γ-phenyl rings are locked through the $C(CH_3)_2$ unit also reacted successfully and provided the expected product (**17a**) in a good yield of 74%. As can be seen from Scheme 2, γ-diaryl substituted styrene (**1**) provided the better yield of the product compared to γ-alkyl-aryl substituted styrene (**18**) even though the benzylic radical formed is away. The higher yield of the product (**1a**) obtained for the substrate (**1**) may be due to additional stability of the benzylic radical imparted by the γ-phenyl ring through anchimeric assistance. However, such type of assistance is missing for substrate (**18**). The same trend was also observed for two other substrates (**19**) and (**20**) providing their products (**19a**, 57%) and (**20a**, 52%) in lesser yields. Under the present reaction conditions when this method was applied to other terminal alkenes such as styrene or vinylcyclopentane none provided nitro-nitrosation product. Interestingly, both gave their respective isooxazolines, which is consistent with our earlier report.[5,11]

To check whether the reaction is proceeding *via* a radical path, alkene (**1**) was reacted with *tert*-butyl nitrite (**a**) in the presence of an equimolar quantity of radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO). Formation of (<8%) of the product (**1a**), suggests a possible radical pathway. In order to ascertain, whether molecular oxygen is



Scheme 2. Substrate scope for nitro-nitratosation. Reaction conditions: **1**–**17** (0.50 mmol), *tert*-butyl nitrite (1.0 mmol) in CH_3CN (2.0 mL) at 0 °C for 24 h. Isolated yields.

involved in the product formation or not, a reaction was performed under an atmosphere of nitrogen keeping all other parameters identical. Under a nitrogen atmosphere the reaction did not yield the desired product (**1a**) and most of the starting material remained unreacted thereby, suggesting the involvement of molecular oxygen in the product formation. No ^{18}O labelled product was obtained when the reaction was carried out in the presence of an equivalent of ^{18}O labelled water. Taking cues from the above reactions and on the basis of the literature reports,[13] a plausible mechanism has been proposed for this nitro nitratosation. Initially, *tert*-butyl nitrite reacts with molecular oxygen to generate NO_2 radical *via* peroxynitrite radical ($ONOO^{\bullet}$) intermediate (Scheme 4, path-I).[13] Alternatively, the nitro radical can also be obtained by the reaction of TBN with water generating HNO_2, decomposition of which would give NO_2 radical (Scheme 4, path-II).[3,13d-f] The NO_2 radical so generated then attacks at the nonbenzylic carbon of the internal



Scheme 3. Plausible mechanism for nitro nitratosation.

alkene (**1**) to form a nitroalkane benzyl radical intermediate (**A**) (Scheme 3). The benzylic radical intermediate (**A**) then reacts with the molecular O_2 to generate a peroxy radical intermediate (**B**). The intermediate (**B**) reacts further with TBN (**a**) to give intermediate (**C**) via the transfer of NO radical. The O-O bond cleavage of intermediate (**C**) generates an oxyradical intermediate (**D**) *via* the loss of a NO_2 radical (Scheme 3). The intermediate (**D**) reacts with NO_2 radical where the electron is localized at the N atom to give the product (**1a**) (Scheme 3). This proposed mechanism is well supported by DFT calculations as shown in Figure 2. Based on experimental results, we have considered a credible mechanistic design which has been studied using Density Functional Theory (DFT) in order to verify our findings. This plausible mechanistic approach is depicted in Figure 2. All DFT calculations have been accomplished using 6-31+G(d,p) basis set for the atoms present in the system at M06[14a] level of theory.

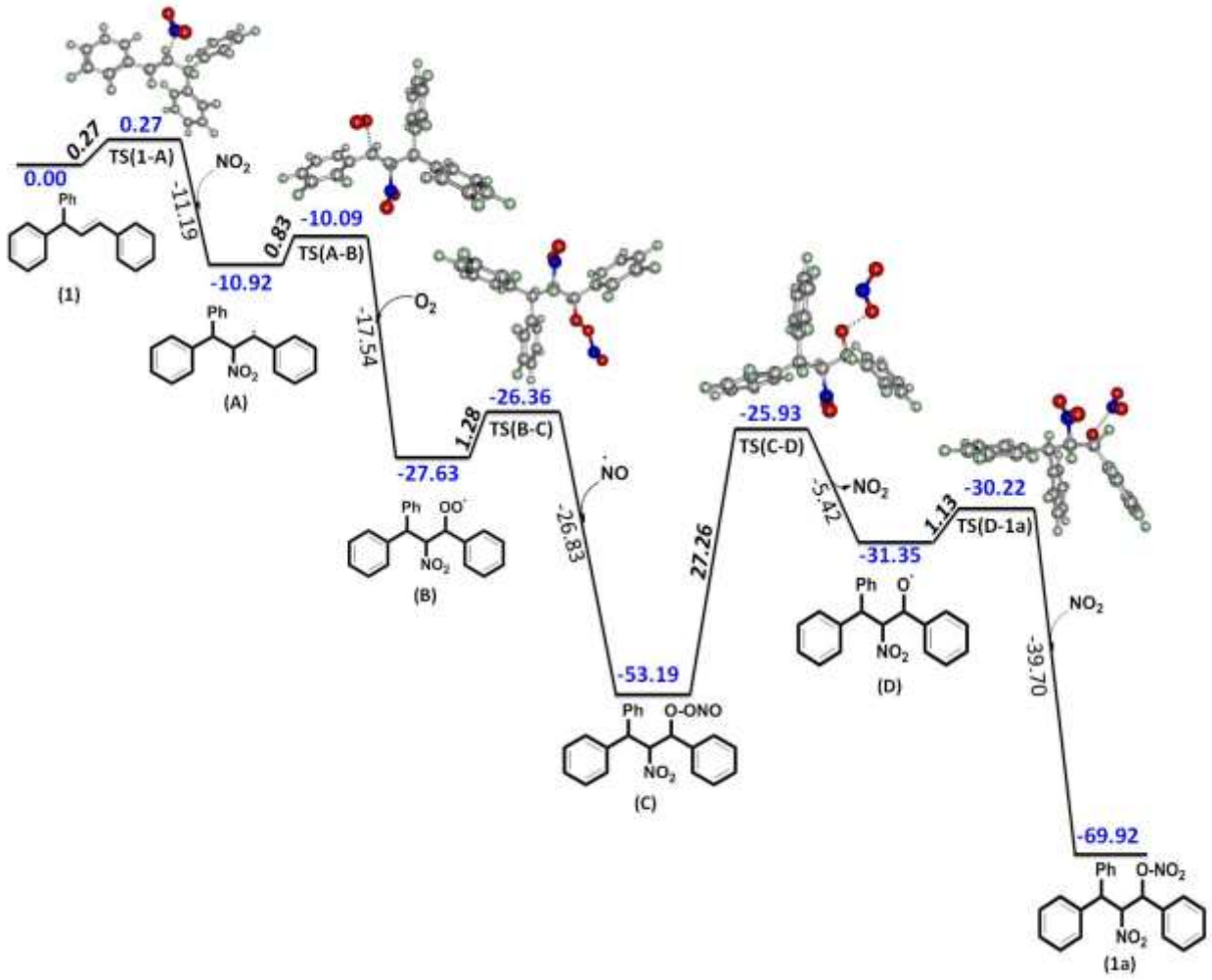
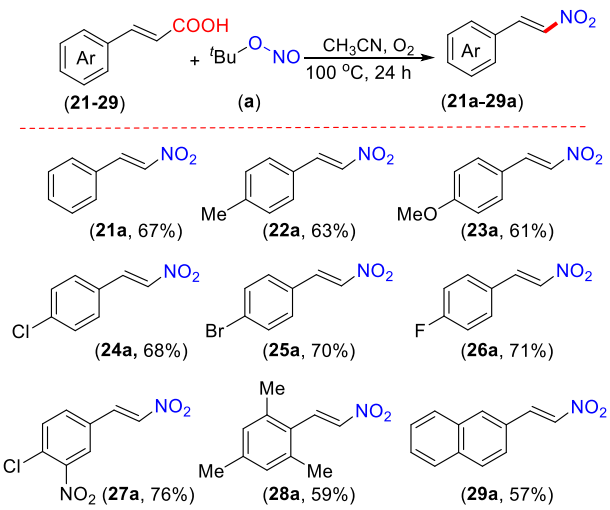


Figure 2. Calculated energy profile diagram for the nitro-nitratosation nitration reaction. The relative energies from DFT calculations are in kcal.mol^{-1} at M06/6-31g+(d,p) level of theory. The relative energies are shown in blue color, activation barrier in italic bold and stabilization energy in normal font are given in kcal.mol^{-1}.

GAUSSIAN 09 program package has been utilized to perform the calculation.[14b,c] Frequency calculations have been done on all modelled structures with the same level of theory. The reaction coordinates of all the species involved {i.e. reactants, intermediates, transition states (TSs) and products} along with the energy values are provided in the supporting information. The optimized geometries of the various structures involved in the reaction, as well as selected bond lengths are provided in Figure S1 of the supporting information. The reaction starts with the attack of NO_2 radical at the internal C=C thereby generating another free radical (**A**) at the benzylic position; which is stabilized by releasing an energy of 11.19 kcal.mol^{-1} and formed by crossing a barrier height of 0.27 kcal.mol^{-1}. The intermediate benzylic radical attack a molecular oxygen forming a peroxy radical intermediate (**B**) involving a barrier of 0.83 kcal.mol^{-1} and releasing 17.54 kcal.mol^{-1} of energy. At this stage, the NO radical generated from TBN attacks the

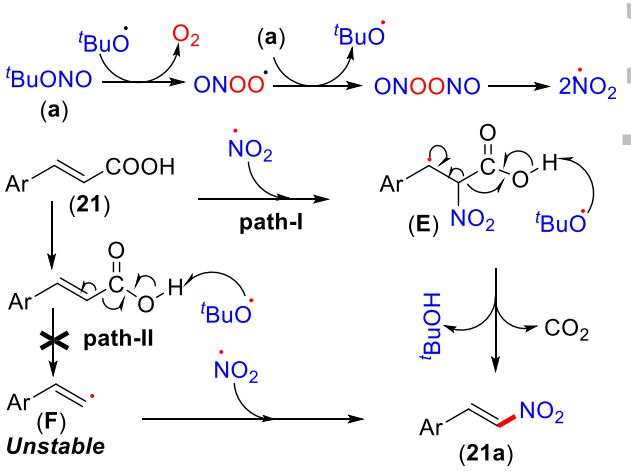
intermediate (**B**) forming an intermediate (**C**) in which the transition state is associated with a barrier of 1.28 kcal.mol^{-1} and releases energy of 26.83 kcal.mol^{-1}. The intermediate (**C**) upon decomposition generates an unstable oxy-radical intermediate (**D**) by crossing energy barrier of 27.26 kcal.mol^{-1} and releasing energy of 5.42 kcal.mol^{-1} which is the rate determining step in the proposed reaction mechanism. The radical intermediate (**D**) readily gets attached to the *N*-site of the NO_2 radical and the process is stabilized by releasing 39.70 kcal.mol^{-1} of energy and formed by crossing a height of 1.13 kcal.mol^{-1}. In the case of intermediate (**C**), the NO_2 is linked to the O-atom of the benzylic position with O-site of NO_2; whereas, in the final product (**1a**) the NO_2 group is attached through its *N*-site. Further, from the energy profile diagram, we could see that the final product (**1a**) is energetically more favourable as compared to intermediate (**C**) by 38.57 kcal.mol^{-1} of energy. The overall reaction is found to be exothermic in nature. Thus, the theoretical findings are in good agreement with the proposed mechanism.



Scheme 4. Nitration of *α,β*-Unsaturated carboxylic acids. Reaction conditions: **21**–**29** (0.50 mmol), *tert*-butyl nitrite (1.0 mmol) in CH_3CN (2.0 mL) at 100 °C for 24 h. Isolated yield.

Further, to check whether this nitro nitratosation strategy is applicable to other internal alkenes such as *α,β*-unsaturated acids or not? *trans*-cinnamic acid (**21**) was reacted with TBN (**a**) at 100 °C otherwise under identical reaction conditions. The reaction proceeded well and provided a new product (**21a**). Spectroscopic (IR, ^{1}H and ^{13}C NMR) analysis of the isolated product (**21a**) showed the absence of COOH group. The HRMS analysis of the new product revealed the loss of a COOH group and incorporation of a NO_2 group. The reaction of corresponding ester (ethyl cinnamate) with TBN did not yield any trace of the nitroalkene nor any oxidative nitration product. Thus the *tert*-butyl nitrite (**a**) is serving as a decarboxylative nitrating agent. Prior to this report, there are reports on decarboxylative nitration of *trans*-cinnamic acid using HNO_3[15a-c] ^{t}BuONO in combination with CuCl,[15d] TEMPO,[15e] and $K_2S_2O_8$.[11] These decarboxylations have been achieved either using metal catalyst or the use of harsh reaction conditions such as high temperature, highly acidic conditions stoichiometric amounts of metal nitrates or stoichiometric amounts of additives.[15] Compared to all the methods reported our present method is the mildest as it is achieved in the absence of any other additives.

To explore the generality of this strategy, the reaction of *trans*-cinnamic acid having moderately electron-donating such as *p*-Me (**22**) and strongly electron-donating group such as *p*-OMe (**23**) both provided their corresponding products (**22a**, 63%), (**23a**, 61%), in moderate yields. The moderately electron-withdrawing groups such as *p*-Cl (**24**), *p*-Br (**25**), *p*-F (**26**) and strongly electron-withdrawing groups such as *p*-Cl-*m*-NO_2 (**27**) cinnamic acids all reacted successfully and delivered their corresponding nitroalkenes (**24a**, 68%), (**25a**, 70%), (**26a**, 71%), (**27a**, 76%), in moderate to good yields. This strategy is equally successful even for a sterically crowded (**28**), and multinuclear (**29**) alkene carboxylic acids both provided their corresponding products (**28a**, 59%) and (**29a**, 57%) in moderate yields (Scheme 4).



Scheme 5. Plausible mechanism for decarboxylative nitration.

To account for the formation of nitroalkenes from *α,β*-unsaturated carboxylic acids, a mechanism as depicted in Scheme 5 (path I) has been suggested which is similar to previously proposed one. The *trans*-cinnamic acid reacts with ^{t}BuO radical and form a nitro benzylic intermediate (**E**), which upon decarboxylation gives nitroalkene (**21a**) (Scheme 5).[15e] Alternatively, a sequence of CO_2 elimination followed by a radical (NO_2) coupling cannot be ruled out (path II). To validate the later path a Density Functional Theory (DFT) calculation was attempted but unfortunately the desired transition state could not

be obtained even after repeated attempts. This may be possibly due to the formation of an extremely unstable vinylradical intermediate (**F**), thus ruling out the later path.

Conclusion

In conclusion, we have demonstrated the differential reactivity of TBN with internal benzylic alkenes in an oxygen atmosphere, which provided nitro-nitrosation products. This result is in contrast to the furoxane formation for the same substrate with TBN but in the presence of $K_2S_2O_8$. The *γ*-diaryl substituted styrenes provided better yields compared to *γ*-alkyl-aryl substituted styrenes possibly due to anchimeric assistance imparted by the *γ*-phenyl ring. While *α,β*-unsaturated esters are inert to TBN but *α,β*-unsaturated acids provided corresponding nitroalkenes via decarboxylation. Even though other radical species coexist in the medium the nitro radical attacks exclusively at the *β*-carbon in internal benzylic alkenes. A plausible mechanism has been proposed which is supported by DFT calculation.

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 2-Nitro-1,3,3-triphenylpropyl nitrate (1a)

To an oven-dried 25 mL round bottom flask was added (*E*)-prop-2-ene-1,1,3-triyltribenzene (135 mg, 0.5 mmol) and subjected to the vacuum for 10 minutes. Next, CH_3CN (2 mL) and *tert*-butyl nitrite (0.119 mL, 1.0 mmol) were introduced to the flask through a syringe under an oxygen atmosphere (balloon). Then the reaction mixture was stirred at 0 °C for 24 h. After the completion of the reaction excess solvent was evacuated under reduced pressure. The reaction mixture was admixed with dichloromethane (20 mL) and washed with water (2 x 10 mL) and organic layer was separated. The separated organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), and evaporated under reduced pressure. The crude product so obtained was purified by silica gel column chromatography using hexane as the eluent to give pure 2-nitro-1,3,3-triphenylpropyl nitrate (**1a**, 140 mg, 74% yield). The identity and purity of the product was confirmed by spectroscopic analysis.

General Procedure for the Synthesis of *E*-(2-Nitrovinyl)benzene (21a)

To an oven-dried 25 mL double neck round bottom flask were added *trans*-cinnamic acid (74 mg, 0.5 mmol) and fitted with reflux condenser. The reaction setup was subjected to the vacuum for 10 minutes. *tert*-Butyl nitrite (0.119 mL, 1.0 mmol) was purged into 2.0 mL of acetonitrile, the TBN containing acetonitrile was introduced into the reaction setup in an oxygen atmosphere. Then the reaction mixture was refluxed at 100 °C for 24 h. After the completion of the reaction excess solvent was evacuated under reduced pressure. The reaction mixture was admixed with ethyl acetate 20 mL washed with water (2 x 10 mL). The separated organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), and evaporated under reduced pressure. The crude product so obtained was purified by silica gel column chromatography using hexane as the eluent to give pure *E*-(2-nitrovinyl)benzene (**21a**, 49 mg, 67% yield). The identity and purity of the product was confirmed by spectroscopic analysis.

2-Nitro-1,3,3-triphenylpropyl nitrate (1a): Yellow gummy, (140 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36–7.31 (m, 10H), 7.28 (bs, 1H), 7.25–7.19 (m, 4H), 5.87 (d, *J* = 5.0 Hz, 1H), 5.69 (dd, *J* = 11.4, 5.0 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.14, 138.12, 133.04, 130.02, 129.78, 129.33, 129.23, 128.25, 128.10, 127.87, 127.63, 126.08, 93.51, 80.40, 52.09 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2913, 1646, 1556, 1493, 1453, 1363, 1272, 1031, 903, 828, 746, 695 cm^{-1}. HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{18}N_2NaO_5$ 401.1108, Found 401.1116.

2-Nitro-3,3-diphenyl-1-(*p*-tolyl)propyl nitrate (2a): Yellow solid, (131 mg, 67%); m.p. 110–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 4.4 Hz, 5H), 7.28–7.21 (m, 4H), 7.11 (d, *J* = 4.0 Hz, 3H), 5.83 (d, *J* = 5.2 Hz, 1H), 5.67 (dd, *J* = 11.6, 5.2 Hz, 2H), 4.87 (d, *J* = 11.6 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) *δ* 140.12, 138.16, 138.13, 130.10, 129.92, 129.73, 129.22, 128.15, 128.07, 127.86, 127.64, 126.00, 93.52, 80.41, 52.01, 21.35 ppm. IR (KBr): $\tilde{\nu}$ = 3031, 2915, 1653, 1552, 1492, 1450, 1363, 1270, 1087, 1031, 823, 751, 704, 588, 532 cm^{-1}. HRMS (ESI/Q-TOF) m/z: [M + NH_4]$^+$ Calcd for $C_{22}H_{24}N_3O_5$ 410.1710, Found 410.1739.

2-Nitro-3,3-diphenyl-1-(*m*-tolyl)propyl nitrate (3a): Yellow solid, (128 mg, 65%); m.p. 116–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.28–7.19 (m, 5H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 5.84 (d, *J* = 5.1 Hz, 1H), 5.68 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 2.29 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) *δ* 139.14, 138.15, 138.12, 132.86, 130.82, 129.69, 129.21, 128.18, 128.07, 127.84, 127.63, 126.72, 123.06, 93.43, 80.56, 52.13,

21.45 ppm. IR (KBr): $\tilde{\nu}$ = 3031, 2915, 1645, 1556, 1492, 1452, 1364, 1272, 1036, 836, 748, 696, 613 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{24}N_3O_5$ 410.1710, Found 410.1735.

1-(4-(*tert*-Butyl)phenyl)-2-nitro-3,3-diphenylpropyl nitrate (4a): Yellow gummy, (135 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 11H), 7.23–7.19 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.90 (d, J = 5.6 Hz, 1H), 5.69 (dd, J = 11.2, 5.6 Hz, 1H), 4.81 (d, J = 11.2 Hz, 1H), 1.26 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 153.12, 138.23, 138.14, 129.73, 129.62, 129.20, 128.08, 128.05, 127.88, 127.67, 126.19, 93.17, 80.94, 52.40, 31.26 ppm. IR (KBr): $\tilde{\nu}$ = 3034, 2961, 1645, 1556, 1493, 1453, 1363, 1272, 1107, 1029, 831, 749, 698, 610 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{25}H_{30}N_3O_5$ 452.2180, Found 452.2209.

1-([1,1'-Biphenyl]-4-yl)-2-nitro-3,3-diphenylpropyl nitrate (5a): Yellow gummy, (145 mg, 64%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.53–7.50 (m, 3H), 7.43 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.8 Hz, 3H), 7.30–7.27 (m, 9H), 7.25–7.21 (m, 2H), 5.94 (d, J = 5.4 Hz, 1H), 5.74 (dd, J = 11.4, 5.4 Hz, 1H), 4.88 (d, J = 11.4 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.92, 140.07, 138.10, 138.05, 131.71, 129.72, 129.24, 129.00, 128.13, 128.12, 127.97, 127.88, 127.63, 127.25, 126.71, 93.31, 80.56, 52.26 ppm. IR (KBr): $\tilde{\nu}$ = 3035, 2961, 1646, 1556, 1489, 1451, 1362, 1270, 1025, 828, 749, 695 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{27}H_{26}N_3O_5$ 472.1867, Found 472.1870.

1-(4-(Chloromethyl)phenyl)-2-nitro-3,3-diphenylpropyl nitrate (6a): Yellow solid, (137 mg, 64%); m.p. 120–125 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 4H), 7.31–7.28 (m, 5H), 7.27–7.20 (m, 5H), 5.87 (d, J = 5.2 Hz, 1H), 5.68 (dd, J = 11.6, 5.2 Hz, 1H), 4.87 (d, J = 11.6 Hz, 1H), 4.52 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.94, 138.09, 136.14, 136.08, 129.75, 127.72, 127.23, 127.00, 126.12, 125.97, 125.90, 125.65, 125.25, 124.75, 91.33, 78.61, 50.30, 27.83 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2960, 1654, 1554, 1492, 1451, 1360, 1275, 1032, 899, 828, 748, 698, 671, 617, 591, 552 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{23}ClN_3O_5$ 444.1321, Found 444.1334.

1-(4-Chlorophenyl)-2-nitro-3,3-diphenylpropyl nitrate (7a): Yellow solid, (155 mg, 75%); m.p. 140–144 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.31–7.27 (m, 8H), 7.25–7.22 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.83 (d, J = 5.2 Hz, 1H), 5.66 (dd, J = 11.6, 5.6 Hz, 1H), 4.86 (d, J = 11.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.94, 137.88, 136.15, 131.52, 129.83, 129.61, 129.28, 128.30, 128.18, 127.83, 127.54, 93.29, 79.77, 52.11 ppm. IR (KBr): $\tilde{\nu}$ = 3029, 2912, 1658, 1598, 1554, 1491, 1452, 1410, 1365, 1273, 1196, 1091, 1033, 900, 826, 755, 707, 674 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{21}ClN_3O_5$ 430.1164, Found 430.1180.

1-(3-Chlorophenyl)-2-nitro-3,3-diphenylpropyl nitrate (8a): Yellow solid, (151 mg, 73%); m.p. 116–119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.6 Hz, 2H), 7.32–7.22 (m, 10H), 7.17 (s, 1H), 7.12 (d, J = 7.6 Hz, 1H), 5.83 (d, J = 5.2 Hz, 1H), 5.67 (dd, J = 11.6, 5.2 Hz, 1H), 4.86 (d, J = 11.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.14, 138.15, 138.12, 132.86, 130.82, 129.69, 129.21, 128.18, 128.07, 127.84, 127.63, 126.72, 123.06, 93.43, 80.56, 52.13, 21.45 ppm. IR (KBr): $\tilde{\nu}$ = 3029, 2958, 1658, 1554, 1491, 1361, 1275, 1098, 1079, 1032, 820, 787, 747, 696, 614 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{21}ClN_3O_5$ 430.1164, Found 430.1176.

1-(4-Bromophenyl)-2-nitro-3,3-diphenylpropyl nitrate (9a): Yellow gummy, (171 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.36–7.26 (m,10H), 7.08 (d, J = 8.4 Hz, 2H), 5.82 (d, J = 5.2 Hz, 1H), 5.65 (dd, J = 11.6, 5.2 Hz, 1H), 4.85 (d, J = 11.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 137.94, 137.89, 132.57, 129.84, 129.29, 128.31, 128.19, 127.84, 127.78, 127.56, 124.38, 93.24, 79.83, 52.12 ppm. IR (KBr): $\tilde{\nu}$ = 3029, 2958, 1658, 1554, 1491, 1361, 1275, 1098, 1079, 1032, 820, 787, 747, 698, 616 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{21}BrN_3O_5$ 476.0642, Found 476.0658.

1-(4-Fluorophenyl)-2-nitro-3,3-diphenylpropyl nitrate (10a): Colourless solid, (153 mg, 77 %); m.p 128–131 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.2 Hz, 2H), 7.31–7.29 (m, 5H), 7.27–7.18 (m, 5H), 7.00 (t, J = 8.6 Hz, 2H), 5.86 (d, J = 5.2 Hz, 1H), 5.66 (dd, J = 11.2, 5.2 Hz, 1H), 4.85 (d, J = 11.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49 (d, J = 251.49 Hz), 137.97 (d, J = 5.1 Hz), 129.80, 129.27, 128.87 (d, J = 3.3 Hz), 128.28, 128.20, 128.17, 127.83, 127.57, 116.5 (d, J = 22.2 Hz), 93.39, 79.89, 52.17 ppm. ^{19}F NMR ($CDCl_3$, 377 MHz) δ -110.42. IR (KBr): $\tilde{\nu}$ = 3031, 2958, 1654, 1601, 1551, 1508, 1492, 1364, 1270, 1228, 1158, 1092, 1031, 825, 752, 703, 674 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{21}FN_3O_5$ 414.1460, Found 414.1480.

2-Nitro-1-(3-nitrophenyl)-3,3-diphenylpropyl nitrate (11a): Yellow gummy, (144 mg, 68%). ^1H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 8.05 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.32–7.29 (m, 6H), 7.25–7.22 (m, 2H), 5.98 (d, J = 5.4 Hz, 1H), 5.74 (dd, J = 12.0, 5.4 Hz, 1H), 4.88 (d, J = 11.4 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.45, 137.72, 137.54, 135.31, 131.80, 130.65, 129.93, 129.36, 128.44, 128.30, 127.81, 127.46, 126.64, 124.91, 121.85, 92.94, 79.45, 52.32 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2922, 1658, 1554, 1524, 1451, 1349, 1274, 1090, 1031, 825, 736, 700, 592, 551 cm^{-1}. HRMS (ESI/Q-

TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}N_3NaO_7$ 446.0959, Found 446.0965.

1-(Naphthalen-2-yl)-2-nitro-3,3-diphenylpropyl nitrate (12a): Yellow gummy, (122 mg, 57%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.79 (m, 3H), 7.69 (s, 1H), 7.52–7.50 (m, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 7.31–7.27 (m, 5H), 7.24–7.19 (m, 2H), 6.04 (d, J = 5.4 Hz, 1H), 5.80 (dd, J = 11.4, 5.4 Hz, 1H), 4.92 (d, J = 11.4 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.08, 138.06, 133.81, 133.03, 130.22, 129.73, 129.50, 129.25, 128.34, 128.21, 128.12, 127.94, 127.86, 127.64, 127.32, 127.04, 126.11, 122.71, 93.35, 80.64, 52.17 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 2853, 1646, 1555, 1493, 1453, 1364, 1273, 1029, 824, 747, 698 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{20}N_2NaO_5$ 451.1264, Found 451.1273.

2-Nitro-1-phenyl-3,3-di-*p*-tolylpropyl nitrate (13a): Yellow gummy, (148 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.31 (m, 3H), 7.23–7.18 (m, 6H), 7.11–7.06 (m, 4H), 5.85 (d, J = 4.8 Hz, 1H), 5.64 (dd, J = 11.6, 4.8 Hz, 1H), 4.82 (d, J = 11.6 Hz, 1H), 2.28 (s, 3H), 2.25 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.96, 137.71, 135.34, 135.31, 133.20, 130.42, 129.87, 129.30, 127.40, 126, 93.74, 80.32, 51.28, 21.13, 21.11 ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2919, 1646, 1656, 1511, 1365, 1273, 1037, 906, 832, 732, 697 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{23}H_{26}N_3O_5$ 424.1867, Found 424.1875.

3,3-*bis*(4-Ethylphenyl)-2-nitro-1-phenylpropyl nitrate (**14a**): Yellow gummy, (163 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.21 (m, 3H), 7.18 (d, J = 8.4 Hz, 2H), 7.44–7.12 (m, 4H), 7.03 (t, J = 8.2 Hz, 4H), 5.79 (d, J = 4.8 Hz, 1H), 5.58 (dd, J = 11.6, 4.8 Hz, 1H), 4.75 (d, J = 11.2 Hz, 1H), 2.53–2.44 (m, 4H), 1.12–1.05 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.17, 143.92, 135.57, 135.48, 133.21, 129.89, 129.26, 129.18, 128.64, 127.73, 127.47, 126.08, 93.70, 80.49, 51.48, 28.49, 28.45, 15.41, 15.41 ppm. IR (KBr): $\tilde{\nu}$ = 3031, 2966, 1646, 1557, 1510, 1455, 1365, 1273, 1125, 1034, 905, 829, 744, 696 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{25}H_{30}N_3O_5$ 452.2180, Found 452.2192.

3,3-*bis*(4-Chlorophenyl)-2-nitro-1-phenylpropyl nitrate (15a): Yellow gummy, (171 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 3H), 7.28–7.25 (m, 6H), 7.22–7.17 (m, 4H), 5.89 (d, J = 5.6 Hz, 1H), 5.60 (dd, J = 10.8, 5.6 Hz, 1H), 4.79 (d, J = 11.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.15, 136.05, 134.45, 134.41, 132.59, 130.26, 129.99, 129.58, 129.43, 129.11, 128.95, 126.34, 92.83, 80.62, 50.95.ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2916, 1900, 1654, 1648, 1557, 1490, 1410, 1364, 1273, 1091, 1013, 906, 819, 730, 696 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{20}Cl_2N_3O_5$ 464.0775, Found 464.0782.

3,3-*bis*(4-Fluorophenyl)-2-nitro-1-phenylpropyl nitrate (16a): Yellow solid, (164 mg, 79%); m.p. 130–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.19 (m, 9H), 7.02–6.96 (m, 4H), 5.89 (d, J = 5.6 Hz, 1H), 5.60 (dd, J = 11.2, 5.6 Hz, 1H), 4.82 (d, J = 11.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 162.46 (d, J = 248.46 Hz), 162.35 (d, J = 249.47 Hz), 133.72 (d, J = 3.8 Hz), 132.70, 130.22, 129.51, 129.42, 129.41, 129.35, 129.27, 126.33, 116.68 (d, J = 47.47 Hz), 116.45 (d, J = 47.47 Hz), 93.29, 80.63 50.72 ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.10, -113.61 IR (KBr): $\tilde{\nu}$ = 3065, 2917, 1661, 1603, 1564, 1508, 1453, 1418, 1366, 1230, 1161, 1109, 1033, 905, 833, 777, 750, 700, 677 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{21}H_{20}F_2N_3O_5$ 432.1366, Found 432.1371.

1-(10,10-Dimethyl-9,10-dihydroanthracen-9-yl)-2-nitro-2-phenylethyl nitrate (17a): Gummy, (155 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 15.2, 8.0 Hz, 2H), 7.44–7.33 (m, 7H), 7.26 (d, J = 4.4 Hz, 3H), 7.18 (d, J = 7.6 Hz, 1H), 6.02 (d, J = 7.2 Hz, 1H), 5.02 (t, J = 6.9 Hz, 1H), 4.72 (d, J = 6.8 Hz, 1H), 1.68 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.60, 144.86, 132.92, 131.54, 130.57, 130.40, 129.70, 128.70, 128.67, 128.04, 127.99, 127.40, 127.15, 127.08, 126.67, 97.10, 80.83, 45.18, 38.87, 35.53, 32.77 ppm. IR (KBr): $\tilde{\nu}$ = 3036, 2971, 1658, 1599, 1448, 1322, 1264, 1167, 1039, 932, 735, 700 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}NaN_2O_5$ 441.1421, Found 441.1432.

2-Nitro-1,3-diphenylbutyl nitrate (18a): Gummy, (79 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 3H), 7.38–7.36 (m, 2H), 7.27–7.25 (m, 3H), 7.01–6.99 (m, 2H), 6.20 (d, J = 9.6 Hz, 1H), 5.11 (dd, J = 9.6, 6.0 Hz, 1H), 3.27–3.17 (m, 1H), 1.33 (d, J = 7.2 Hz, 3H). ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.45, 132.29, 130.68, 129.45, 128.78, 128.30, 128.18, 127.84, 92.88, 82.29, 40.17, 18.86 ppm. IR (KBr): $\tilde{\nu}$ = 3037, 2979, 1694, 1640, 1552, 1494, 1452, 1270, 1199, 1084, 1040, 745, 695 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}NaN_2O_5$ 339.0951, Found 339.0959.

1,3-*bis*(4-Bromophenyl)-2-nitrobutyl nitrate (19a): Yellow solid, m.p. 183–187 °C, (135 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.05 (d, J = 9.0 Hz, 1H), 4.96 (dd, J = 9.0, 6.0 Hz, 1H), 3.17–3.11 (m, 1H), 1.28 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.27, 132.86, 132.11, 131.20, 129.81, 129.53, 125.32, 122.43, 92.44, 81.16, 39.74, 18.61 ppm. IR (KBr): $\tilde{\nu}$ = 3049, 2925, 2854, 1644, 1555, 1460, 1375, 1274, 1016, 801, 723 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{16}H_{18}Br_2N_3O_5$ 491.9588, Found 491.9595.

1,3-*bis*(4-Chlorophenyl)-2-nitrobutyl nitrate (20a): Gummy, (100 mg, 52 %). ^{1}H NMR (600 MHz, $CDCl_3$)

δ 7.45 (d, *J* = 6.6 Hz, 2H), 7.39–7.37 (m, 2H), 7.28–7.25 (m, 2H), 7.00–6.98 (m, 2H), 6.19 (d, *J* = 9.6 Hz, 1H), 5.10 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.23–3.19 (m, 1H), 1.36 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.44, 132.39, 130.74, 129.51, 128.85, 128.40, 128.27, 127.90, 92.88, 82.28, 40.22, 18.99 ppm. IR (KBr): $\tilde{\nu}$ = 3036, 2924, 2848, 1653, 1558, 1449, 1366, 1275, 1092, 1014, 749 cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{16}H_{18}Cl_2N_3O_5$ 402.0618, Found 402.0625.

***(E)-(*2-Nitrovinyl)benzene (21a):** Yellow solid, (49 mg, 67%), m.p. 57–61 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.56–7.54 (m, 2H), 7.52–7.49 (m, 1H), 7.47–7.44 (m, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.21, 137.24, 132.27, 130.19, 129.52, 129.27 ppm. IR (KBr): $\tilde{\nu}$ = 3109, 2923, 1632, 1577, 1513, 1449, 1344, 1262, 967, 764, 750 cm^{-1}. HRMS (ESI/Q-TOF) Calcd for $C_8H_7NaNO_2$ $[M + Na]^+$ 172.0369, Found 172.0382.

(*E*)-1-Methyl-4-(2-nitrovinyl)benzene (22a): Yellow solid, (51 mg, 63%); m.p. 106–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 13.6 Hz, 1H), 7.57 (d, *J* = 13.7 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.24, 139.30, 136.42, 130.28 , 129.32, 127.41, 21.79 ppm. IR (KBr): $\tilde{\nu}$ = 3109, 2923, 2853, 1632, 1496, 1341, 1265, 965, 810, 741 cm^{-1}. HRMS ESI/Q-TOF) m/z: Calcd for $C_9H_{10}NO_2$ $[M + H]^+$ 164.0706, found 164.0712.

***(E)*-1-Methoxy-4-(2-nitrovinyl)benzene (23a):** Yellow solid, (55 mg, 61%); m.p. 85–88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 13.6 Hz, 1H), 7.54–7.48 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.03, 139.18, 135.07, 131.29, 122.60, 115.01, 55.64 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 1605, 1498, 1339, 1256, 1176, 1031, 973, 809 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_9H_{10}NO_3$ $[M + H]^+$ 180.0655, Found 180.0669.

(*E*)-1-Chloro-4-(2-nitrovinyl)benzene (24a): Yellow solid, (62 mg, 68%), m.p. 102–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 14.0 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.46, 137.85, 137.52, 130.40, 129.89, 128.63 ppm. IR (KBr): $\tilde{\nu}$ = 3107, 2924, 2852, 1721, 1642, 1601, 1529, 1344, 1201, 1048, 965, 832, 753, 677 cm^{-1}. HRMS (ESI/Q-TOF) m/z: calcd for $C_8H_6ClNaNO_2$ $[M + Na]^+$ 205.9979, Found 205.9991.

***(E)*-1-Bromo-4-(2-nitrovinyl)benzene (25a):** Yellow solid, (80 mg, 70%); m.p. 151–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 13.7 Hz, 2H), 7.61–7.56 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.93, 137.58, 132.87, 130.52, 129.06, 126.92 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2849, 1633, 1517, 1341, 1073, 812 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_8H_6BrNaNO_2$ $[M + Na]^+$ 249.9474, Found 249.9480.

(*E*)-1-Fluoro-4-(2-nitrovinyl)benzene (26a): Yellow solid, (59 mg, 71%); m.p. 102–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.59–7.52 (m, 3H), 7.16 (t, *J* = 8.6 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06 (d, *J* = 255.83 Hz), 137.96, 136.99, 131.41 (d, *J* = 8.9 Hz), 126.46, 116.91 (d, *J* = 22.32 Hz) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.81. IR (KBr): $\tilde{\nu}$ = 3109, 2973, 1630, 1554, 1514, 1449, 1338, 1261, 1189, 1072, 964, 762, 699 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_8H_6FNaNO_2$ $[M + Na]^+$ 190.0275, Found 190.0287.

(*E*)-1-Chloro-2-nitro-4-(2-nitrovinyl)benzene (27a): Yellow solid, (87 mg, 76%); m.p. 131–135 °C. ^{1}H NMR (600 MHz, $CDCl_3$ + DMSO-d_6) δ 8.33 (d, *J* = 6.0 Hz, 1H), 8.10–7.96 (m, 2H), 7.93–7.83 (m, 1H), 7.73–7.61 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$ + DMSO-d_6) δ 147.68, 139.39, 134.85, 132.77, 132.10, 129.96, 128.80, 125.34 ppm. IR (KBr): $\tilde{\nu}$ = 3103, 3039, 2924, 2852, 1734, 1633, 1591, 1518, 1404, 1339, 1259, 1086, 970, 819, 742 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_8H_5ClNaN_2O_4$ $[M + Na]^+$ 250.983, Found 250.989.

(*E*)-1,3,5-Trimethyl-2-(2-nitrovinyl)benzene (28a): Yellow solid, (56 mg, 59%); m.p. 122–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 13.9 Hz, 1H), 7.31 (d, *J* = 13.9 Hz, 1H), 6.95 (s, 2H), 2.39 (s, 6H), 2.31 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.01, 139.82, 138.61, 136.72, 130.02, 125.88, 21.67, 21.34 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1627, 1604, 1500, 1329, 1149, 1032, 967, 922, 799, 751, 716 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_{11}H_{13}NaNO_2$ $[M + Na]^+$ 214.0838, Found 214.0847.

(*E*)-2-(2-Nitrovinyl)naphthalene (29a): Yellow solid, (57 mg, 57%); m.p. 129–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 13.6 Hz, 1H), 7.99 (s, 1H), 7.89–7.85 (m, 3H), 7.68 (d, *J* = 13.6 Hz, 1H), 7.63–7.53 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.34, 137.25, 135.03, 133.26, 132.39, 129.48, 128.95, 128.51, 128.06, 127.66, 127.40, 123.44 ppm. IR (KBr): $\tilde{\nu}$ = 3106, 1625, 1503, 1328, 1267, 1169, 960, 872, 821, 750, 710 cm^{-1}. HRMS (ESI/Q-TOF) m/z: Calcd for $C_{12}H_9NaNO_2$ $[M + Na]^+$ 222.0525, Found 222.0531.

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References

[1] a) P. Li, X. Jia, *Synthesis* **2018**, *50*, 711-722; b) A. Dahiya, A. K. Sahoo, T. Alam, B. K. Patel, *Chem. Asian J.* **2019**, *14*, 4454-4492.

[2] S. Prateeptongkum, I. Jovel, R. Jackstell, N. Vogl, C. Weckbeckerb, M. Beller, *Chem. Commun*. **2009**, 1990-1992.

[3] T. Taniguchi, A. Yajima, H. Ishibashi, *Adv. Synth. Catal.* **2011**, *353*, 2643-2647.

[4] R. Chen, Y. Zhao, S. Fang, W. Long, H. Sun, X. Wan, *Org. Lett.* **2017**, *19*, 5896-5899.

[5] P. Sau, S. K. Santra, A. Rakshit, B. K. Patel, *J. Org. Chem.* **2017**, *82*, 6358-6365.

[6] P. Sau, A. Rakshit, A. Modi, A. Behera, B. K. Patel, *J. Org. Chem.* **2018**, *83*, 1056-1064.

[7] P. Sau, A. Rakshit, T. Alam, H. K. Srivastava, B. K. Patel, *Org. Lett.* **2019**, *21*, 4966-4970.

[8] B. Wang, L. Tang, L. Liu, J. Wang, Z. Zha, Z. Wang, *Green Chem.* **2017**, *19*, 5794-5799.

[9] X. -Q. Chu, D. Ge, T. –P. Loh, Z. –L. Shen, *Org. Chem. Front.* **2019**, *6*, 835-840.

[10] a) F. Chen, N. -N. Zhou, J. -L. Zhan, B. Han, W. Yu, *Org. Chem. Front.* **2017**, *4*, 135-139; b) S. Maity, T. Naveen, U. Sharma, D. Maiti, *Org. Lett.* **2013**, *15*, 3384-3387; c) U. Dutta, S. Maity, R. Kancherla, D. Maiti, *Org. Lett*. **2014**, *16*, 6302-6305; d) W.-T. Wei,W.-M. Zhu,W.-W. Ying, Y.-N. Wang, W.-H. Bao, L.-H. Gao, Y.-J. Luo, H. Lianga, *Adv. Synth. Catal*. **2017**, *359*, 3551-3554; e) W.-T. Wei, W.-M. Zhu, W.-W. Ying, Y. Wu, Y.-L. Huang H. Liang, *Org. Biomol. Chem.* **2017**, *15*, 5254-5257; f) F. Chen, X. Huang, X. Li, T. Shen, M. Zou, N. Jiao, *Angew. Chem. Int. Ed.* **2014**, *53*, 10495-10499; g) Y. Liu, J.-L. Zhang, R.-J. Song, P.-C. Qian, J.-H. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 9017-9020; h) Y. Chen, Y. Ma, L. Li, H. Jiang, Z. Li, *Org. Lett.* **2019**, *21*, 1480-1483.

[11] B. A. Mir, S. J. Singh, R. Kumar, B. K. Patel, *Adv. Synth. Catal*. **2018**, *360*, 3801-3809.

[12] CCDC 1979947 (**10a**) contains the supplementary crystallographicdata for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] For autoxidation of nitrogen monoxide: a) S. Goldstein, G. Czapski, *J. Am. Chem. Soc.* **1995**, *117*, 12078-12084; b) L.Grossi, S. Strazzari, *J. Org. Chem.* **1999**, *64*, 8076-8079; c) B. Galliker, R. Kissner, T. Nauser, W. H. Koppenol, *Chem. Eur. J.* **2009**, *15*, 6161-6168; d) M. P. Doyle, J. W. Terpstra, R. A. Pickering, D. M. LePoire, *J. Org. Chem.* **1983**, *48*, 3379-3382; e) J.- Y. Park, Y.- N. Lee, *J. Phy. Chem.* **1988**, *92*, 6294-6302; f) S. Ranganathan, S. K. Kar, *J. Org. Chem.* **1970**, *35*, 3962-3964.

[14] a) Y. Zhao, D. G. Truhlar, The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements *Theor. Chem. Acc.* **2008**, *120*, 215-241; b) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Gaussian, Inc., Wallingford CT, **2009**); c) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[15] a) J. P. Das, P. Sinha, S. A. Roy, *Org. Lett*. **2002**, *4*, 3055-3058; b) A. K. Bose, S. N. Ganguly and M. S. Manhas, W. He, J. Speck, *Tetrahedron*. *Lett*. **2006**, *47*, 3213-3215; c) K. C. Rajanna, K. Ramesh, S. Ramgopal, S. Shylaja, P. G. Reddy, P. K. Saiprakash, *Green Sustainable Chem*. **2011**, *1*, 132-148; d) B. V. Rokade, K. R. Prabhu, *Org. Biomol. Chem*. **2013**, *11*, 6713-6716; e) S. Manna, S. Jana, T. Saboo, A. Maji, D. Maiti, *Chem. Commun.*, **2013**, *49*, 5286-5288; f) L. C. R. Henry, *Acad. Sci. Ser. C*, **1895**, *120*, 1265-1268; g) S. Maity, S. Manna, S. Rana, T. Naveen, A. Mallick, D. Maiti, *J. Am. Chem. Soc*. **2013**, *135*, 3355-3358; h) G. Bachman, T. Biermann, *J. Org. Chem*. **1970**, *35*, 4229-4231; i) M. S. Kumar, P. Venkanna, S. Ramgopal, K. Ramesh, M. Venkateswarlu, K. C. Rajanna, *Org. Commun*. **2012**, *5*, 42-49; j) A. Messere, A. Gentili, I. Garella, F. Temussi, B. D. Blasio, A. Fiorentino, *Synth. Commun*. **2004**, *34*, 3317-3324; k) S. Ramgopal, K. A. Ramesh, N. Chakradhar, Reddy, Maasi, K. C. Rajanna, *Tetrahedron Lett*. **2007**, *48*, 4043-4045; l) A. S. Rao, P. V. Srinivas, K. S. Babu, J. M. Rao, *Tetrahedron Lett*. **2005**, *46*, 8141-8143.

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