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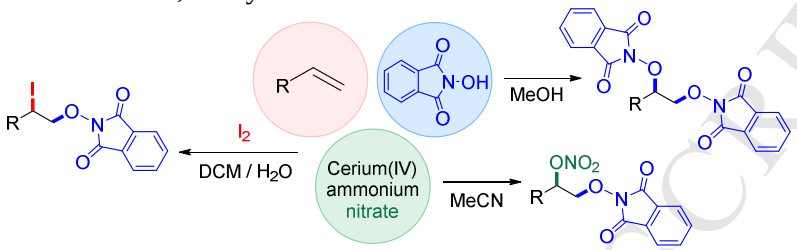

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Cerium(IV) ammonium nitrate: reagent for the versatile oxidative functionalization of styrenes using *N*-hydroxyphthalimide

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Dedicated to Corresponding Member of the Russian Academy of Sciences G. I. Nikishin on the occasion of his 90th birthday.

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ABSTRACT

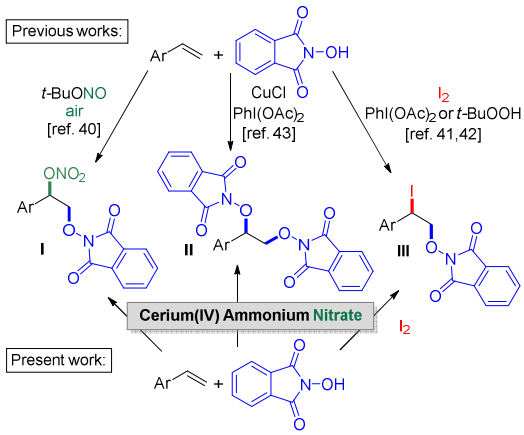
Cerium(IV) ammonium nitrate was found to be a versatile reagent for the oxidative functionalization of styrenes using *N*-hydroxyphthalimide and iodine affording three different types of products with oxyphthalimide, nitrate and iodide groups. It was shown that reaction of styrenes with *N*-hydroxyphthalimide and cerium(IV) ammonium nitrate can be selectively directed to oxynitro-oxyphthalimides and dioxyphthalimides depending on the reaction conditions, in particular a solvent. Reaction of styrenes with iodine under the action of *N*-hydroxyphthalimide and cerium(IV) ammonium nitrate leads to the formation of iodo-oxyphthalimides.

1. Introduction

Cerium(IV) compounds hold a special place among the variety of oxidants used in organic synthesis. The high redox potential (+1.61 V *vs* NHE), low toxicity, ease of handling, commercial availability and high solubility in organic solvents favorably distinguishes Ce(IV) and its compounds from other transition metals. Ce(IV) salts, especially cerium(IV) ammonium nitrate (CAN, $(NH_4)_2Ce(NO_3)_6$) are widely used as an effective single-electron oxidant in various oxidation[1-3] and oxidative coupling[4-9] reactions. Large number of papers is devoted to CAN-catalyzed processes.[10,11]

CAN is known to generate radicals from 1,3-dicarbonyl compounds,[12,13] azide anions,[14,15] thiocyano-anions[6,15] and sulfinates.[16] Under the action of CAN, *N*-hydroxyphthalimide (NHPI) is oxidized to the phthalimide-*N*-oxyl (PINO) radical,[17] which is the effective mediator of aerobic oxygenation and various processes of C-H functionalization.[18-22] The CAN/NHPI system was employed in the aerobic oxidation of aromatic alcohols,[23] Ritter-type amidation of alkanes and alkylarenes,[24] benzylic oxynitration[25] and oxyimidation[17].

Recently, *N*-hydroxyphthalimide has gained growing interest in PINO-mediated difunctionalization of styrenes to obtain oxygenated products.[26-39] The use of various oxidants allows to implement oxyimidation in conjunction with oxynitration,[40] iodination,[41,42] or double oxyimidation of styrenes[43] (Scheme 1).



Scheme 1. The present work is in the context of the oxidative oxynitration-oxyimidation (**I**), dioxyimidation (**II**) and iodo-oxyimidation (**III**) of styrenes using *N*-hydroxyphthalimide.

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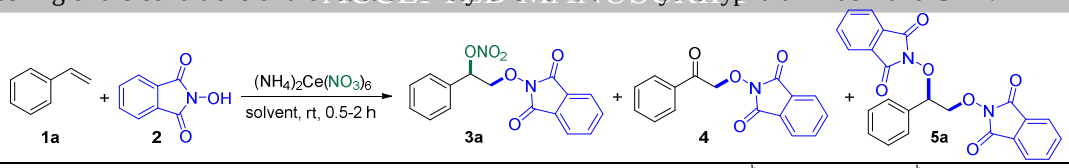
Table 1. Screening of the conditions of the reaction of styrene **1a** with *N*-hydroxyphthalimide **2** and CAN. [a]



Entry	Molar ratio **1a**/**2**	Molar ratio CAN/**2**	Solvent	Time, h	Yield of **3a** [b] (%)	Yield of **4** [b] (%)	Yield of **5a** [b] (%)
1	2	3	MeCN	2	26 (14)	<5	47
2 [c]	2	3	MeCN	2	40 (29)	12	15
3 [c]	2	2	MeCN	2	41 (31)	16	9
4 [c]	1	3	MeCN	2	30	13	10
5 [c]	1	2	MeCN	2	27	20	7
6 [c,d]	**2**	**2**	**MeCN**	**2**	**55 (45)**	**<5**	**10**
7	2	3	AcOH	2	10	8	46
8	2	3	acetone	2	9	<5	65
9	2	3	MeOH	2	5	<5	53 (42)
10	0.5	1	MeOH	2	<5	<5	56
11	0.5	1	MeOH	0.5	<5	<5	53
12	**0.5**	**1.5**	**MeOH**	**0.5**	**<5**	**<5**	**74 (65)**
13	2	3	EtOAc/H_2O (2/1)	0.5	<5	<5	68
14	2	3	PhMe/H_2O (2/1)	0.5	<5	<5	61
15	2	3	DCM/H_2O (2/1)	0.5	<5	<5	68
16	2	3	AcOH/H_2O (2/1)	0.5	14	<5	53
17	2	3	MeCN/H_2O (2/1)	0.5	12	<5	66
18	2	3	dioxane	2	10	21	32
19 [e]	2	3	dioxane	2	<5	32 (20)	5
20 [c,e]	2	3	MeCN	2	19	28	8

[a] General reaction conditions: CAN (1.0-3.0 mmol) was added to a mixture of styrene **1a** (0.5-2.0 mmol) and *N*-hydroxyphthalimide **2** (1.0 mmol) in a solvent (6.0 mL), and stirred at 20-25 °C for 0.5-2 h under air atmosphere. For entries with a mixture of solvents, v/v ratio is in parentheses.

[b] Yield was determined by ^{1}H NMR spectroscopy using *p*-methoxyacetophenone as an internal standard; isolated yields are given in parentheses.

[c] Solution of *N*-hydroxyphthalimide **2** in MeCN (15.0 mL) was added dropwise for 30 min to the mixture of styrene **1a** and CAN in MeCN (3.0 mL).

[d] At 0 °C, under argon atmosphere.

[e] Under O_2 atmosphere.

In this work, the combination of CAN and NHPI is proposed as a versatile system for selective difunctionalization of styrenes, opening the direct way to three different types of products.

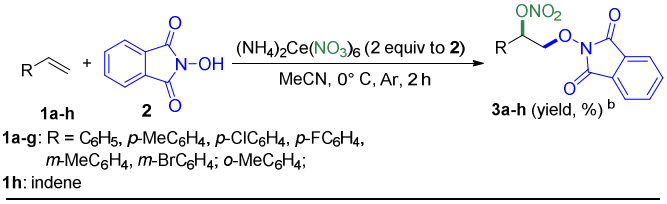
2. Results and discussion

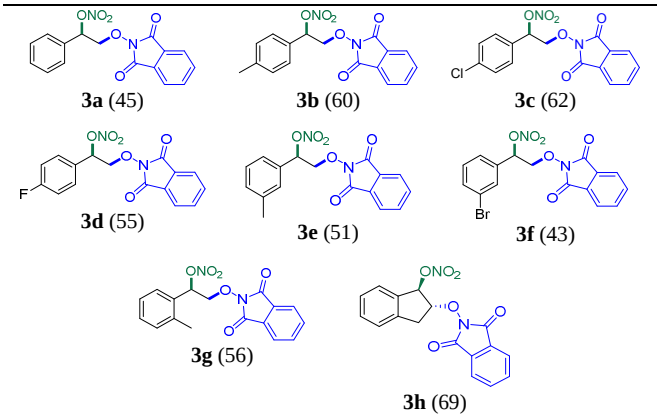
In the present work, the oxidative difunctionalization of styrenes under the action of *N*-hydroxyphthalimide **2** and cerium(IV) ammonium nitrate was carried out. At the first stage the model reaction of styrene **1a** with *N*-hydroxyphthalimide **2** and CAN was examined (Table 1). In the experiment (Table 1, entry 1, in MeCN) with the molar ratio styrene **1a**:NHPI **2**:CAN = 2:1:3 dioxyphthalimide **5a** was identified as the main product with the 47% yield along with the high amount of nitrate ester **3a** (26% yield). The goal of our research was to find the optimal condition for the selective synthesis of the products **3a** and **5a**.

The influence of reaction parameters on the yield of nitrate ester **3a** was evaluated in entries 2-6. In order to decrease the yield of dioxyphthalimide **5a** a solution of *N*-hydroxyphthalimide **2** was added dropwise to the mixture of styrene **1a** and CAN in MeCN. Slow addition of *N*-hydroxyphthalimide improved the yield of **3a** to 40% (Table 1, entry 2). Molar ratio of styrene **1a**, *N*-hydroxyphthalimide **2** and CAN was optimized in entries 3-6. The optimal molar ratio of styrene **1a**, *N*-hydroxyphthalimide **2** and CAN, allowing to obtain the product **3a** with the yield of 41%, was 2:1:2 (Table 1, entry 3). In these conditions the yields of side-products were 16% for **4** and 9% for **5a**. Carrying out the reaction in an inert atmosphere at 0 °C allowed to almost completely avoid the formation of side-products **4** and **5a**, and thereby the yield of nitrate ester **3a** increased to 55% (Table 1, entry 6).

When using AcOH, acetone or MeOH (Table 1, entries 7-12), as well as binary single- or two-phase systems (EtOAc, PhMe, DCM, AcOH and MeCN mixed with H_2O, Table 1, entries 13-17) as a solvent with the ratio of styrene **1a**:NHPI **2**:CAN = 2:1:3 the main pathway of the reaction was the double addition of *N*-hydroxyphthalimide **2** to the C=C bond of styrene **1a** with the formation of dioxyimide **5a**. The highest yield (74%) of **5a** was achieved by carrying out the reaction in MeOH with the molar ratio of styrene **1a**, NHPI **2** and CAN 0.5:1:1.5 (Table 1, entry 12). In the reaction of styrene **1a** with *N*-hydroxyphthalimide **2** in dioxane (Table 1, entries 18 and 19) keto-oxyimide **4** was observed as one of the major product, and in the reaction under oxygen atmosphere (Table 1, entry 19) the yield of **4** was 32%. Comparable yield of the product **4** (28%) was obtained using MeCN as the solvent (Table 1, entry 20).

Table 2. Scope of the oxynitration-oxyimidation of vinylarenes **1a-h** with *N*-hydroxyphthalimide **2** under the action of CAN. [a]





[a] Reaction conditions: solution of *N*-hydroxyphthalimide **2** in MeCN (15.0 mL) was added dropwise for 30 min to a mixture of vinylarene **1a-h** (2.0 mmol) and CAN (2.0 mmol) in MeCN (3.0 mL), and then stirred at 0 °C for 2 h under argon atmosphere. [b] Isolated yield.

In order to study the scope of the developed method vinylarenes **1b-h** were involved in the reaction under optimized conditions for the synthesis of **3a** (Table 1, entry 6) to obtain nitrate esters **3b-i** with yield from 43% to 69% (Table 2).

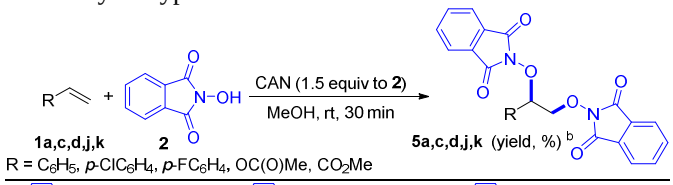
The obtained results show that the reaction has general character, and successfully proceeds with styrenes bearing both electron-withdrawing substituents in the aromatic ring – Cl (**3c**, 62%), F (**3d**, 55%) and Br (**3f**, 43%), and electron-donating methyl group (**3b**, **3e**, **3g**, 51-60%). Reaction with indene **1h** gave product **3h** with the yield of 69%.

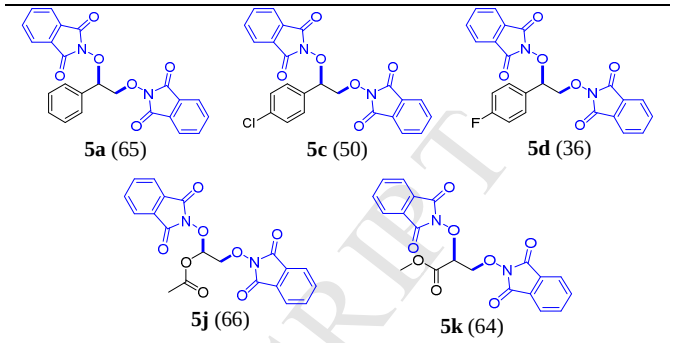
Treatment of terminal olefins – 1-hexene, 1-octene, and allylbenzene with NHPI/CAN system led to a complex mixture of products presumably due to the numerous side processes of oxidation of the allylic methylene fragment.[18]

Using optimized conditions for the synthesis of **5a** (Table 1, entry 12), dioxyimides **5c,d** were obtained from styrenes **1c,d** with the yields of 50% and 36%, respectively (Table 3). It was found that the reaction scope was not limited to the vinylarenes. In the reaction of vinyl acetate **1j** and methyl acrylate **1k** with *N*-hydroxyphthalimide **2** and CAN under the optimal conditions for dioxyimidation (Table 1, entry 12), as well as using the conditions for oxynitration-oxyimidation (Table 1, entry 6) only dioxyimides **5j** and **5k** were isolated with 66% (dioxyimidation conditions; 78% – oxynitration-oxyimidation conditions) and 64% (dioxyimidation conditions; 36% – oxynitration-oxyimidation conditions) yields.

Based on the literature data[40,41] we assumed that the reaction of styrenes with *N*-hydroxyphthalimide and cerium(IV) ammonium nitrate proceeds through the formation of stable benzylic radical. Aiming to expand synthetic applicability of this process with the radical formation I_2 was introduced into the reaction with styrenes under the action of NHPI and CAN.

Table 3. Dioxyimidation of styrenes **1a,c,d** and esters **1j,k** with *N*-hydroxyphthalimide **2** under the action of CAN. [a]





[a] Reaction conditions: vinyl substrate **1a,c,d,j,k** (0.5 mmol), *N*-hydroxyphthalimide **2** (1.0 mmol), CAN (1.5 mmol), MeOH (6.0 mL), at 20-25 °C for 30 min under air atmosphere. [b] Isolated yield.

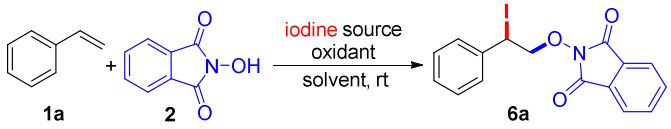
It was found, that the formation of products containing iodine atom in the benzylic position occurred. The influence of the nature of a solvent, as well as oxidant and a source of iodine on the yield of iodo-oxyimide **6a** was studied in the model reaction of styrene **1a** with iodine under the action of *N*-hydroxyphthalimide **2** (Table 4).

The direction of the process is highly dependent on the nature of a solvent. Thus, carrying out the reaction in MeOH, MeCN, DCM, H_2O or MeCN/H_2O mixture (Table 4, entries 1-5) resulted in the formation of product **6a** with the yield of 11-42%. Two-phase DCM/H_2O system permitted to increase the yield of compound **6a** to 70% (Table 4, entry 6). With the use of DCM/H_2O system molar ratio of starting reagents and the iodine source were optimized (Table 4, entries 7-11). The optimal ratio of CAN to NHPI is 1.5; the reaction with 1.2 equivalents of CAN (Table 4, entry 7) led to the formation of product **6a** with the decreased yield (64% *vs* 70% with 1.5 equiv. of CAN). Employing NaI•2H_2O, TBAI or NH_4I as the iodine source (Table 4, entries 8-10) product **6a** was obtained with the yields comparable to the reaction with molecular iodine, but in these cases, it was necessary to use a large amount of oxidizing agent. The introduction of twofold molar excess of styrene **1a** allowed us to obtain **6a** in 86% yield (Table 4, entry 11).

Among the other tested metal-based oxidants $(NH_4)_4Ce(SO_4)_4$•2H_2O, $Ce(SO_4)_2$ and $Mn(OAc)_3$•2H_2O showed good results (Table 4, entries 12, 13 and 16, yield of **6a** 60-66%). Catalytic oxidative system of Ce(IV)/$KBrO_3$ (Table 4, entry 14, yield of **6a** 10%)[44] and Ce(IV)/Ag(II)/$(NH_4)_2S_2O_8$ (Table 4, entry 15, yield of **6a** 43%)[45] exhibited poor efficacy in the iodo-oxyimidation of styrene **1a**. When $Fe(ClO_4)_3$•8H_2O and $Pb(OAc)_4$ were used the yield of the desired product **6a** did not exceed 34% (Table 4, entries 17-19).

With the optimal conditions (Table 4, entry 11) for the synthesis of **6a** in hands, we obtained iodo-oxyimides **6b-i** with the yields from 62% to 72% in the reactions with vinylarenes **1b-h** and vinyl acetate **1i** (Table 5). The reaction was successful with styrenes bearing Cl, F and Br atoms (products **6c**, **6d**, **6f**, yield 70-72%).

Table 4. Optimization of the iodo-oxyimidation of styrene **1a** under the action of the *N*-hydroxyphthalimide **2**, iodine and oxidant with the formation of product **6a**. [a]



Entry	Oxidant (molar ratio: mol/mol of **2**)	Solvent	Yield of **6a** [b] (%)
1	$(NH_4)_2Ce(NO_3)_6$ (1.5)	MeOH	14
2	$(NH_4)_2Ce(NO_3)_6$ (1.5)	MeCN	42
3	$(NH_4)_2Ce(NO_3)_6$ (1.5)	DCM	11
4	$(NH_4)_2Ce(NO_3)_6$ (1.5)	H_2O	27
5	$(NH_4)_2Ce(NO_3)_6$ (1.5)	MeCN/H_2O (2/1)	32
6	$(NH_4)_2Ce(NO_3)_6$ (1.5)	DCM/H_2O (2/1)	70
7	$(NH_4)_2Ce(NO_3)_6$ (1.2)	DCM/H_2O (2/1)	64
8 [c]	$(NH_4)_2Ce(NO_3)_6$ (3.0)	DCM/H_2O (2/1)	71
9 [d]	$(NH_4)_2Ce(NO_3)_6$ (3.0)	DCM/H_2O (2/1)	70
10 [e]	$(NH_4)_2Ce(NO_3)_6$ (3.0)	DCM/H_2O (2/1)	48
11 [f]	**$(NH_4)_2Ce(NO_3)_6$ (1.5)**	**DCM/H_2O (2/1)**	**86**
12	$(NH_4)_4Ce(SO_4)_4$•$2H_2O$ (1.5)	DCM/H_2O (2/1)	66
13	$Ce(SO_4)_2$ (1.5)	DCM/H_2O (2/1)	60
14 [g]	$(NH_4)_2Ce(NO_3)_6$ (0.1) $KBrO_3$ (1.0)	DCM/H_2O (2/1)	10
15 [h]	$(NH_4)_4Ce(SO_4)_4$•$2H_2O$ (0.05) $[Ag(bipy)_2]S_2O_8$ (0.1) $(NH_4)_2S_2O_8$ (3.0)	DCM/H_2O (2/1)	43
16	$Mn(OAc)_3$•$2H_2O$ (1.5)	AcOH	65
17	$Fe(ClO_4)_3$•$8H_2O$ (1.5)	MeCN	13
18	$Fe(ClO_4)_3$•$8H_2O$ (1.5)	DCM/H_2O (2/1)	ND
19	$Pb(OAc)_4$ (0.6)	DCM	34

[a] General reaction conditions: oxidant (0.6-3.0 mmol) was added to a mixture of styrene **1a** (1.0 mmol), *N*-hydroxyphthalimide **2** (1.0 mmol) and I_2 (0.5 mmol) in a solvent (6.0 mL), and stirred at 20-25 °C for 30 min under air atmosphere. For entries with mixture of solvents, v/v ratio is in the parentheses. ND = Not detected.

[b] Isolated yield.

[c] NaI•$2H_2O$ (1.0 mmol) was employed.

[d] TBAI (1.0 mmol) was employed.

[e] NH_4I (1.0 mmol) was employed.

[f] Styrene **1a** (2.0 mmol) was employed.

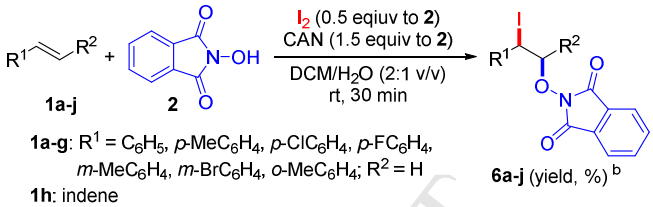
[g] Reaction time 1 h.

[h] Reaction time 2 h.

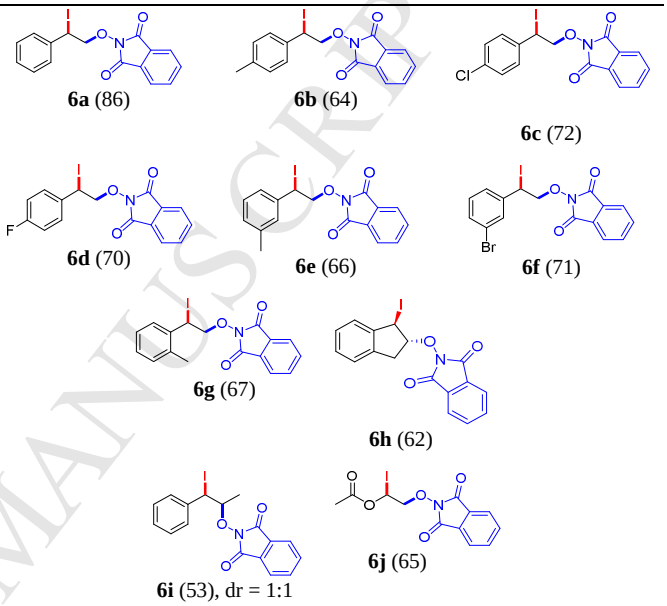
The iodo-oxyimidation of styrenes with methyl group in the aromatic ring proceeds with slightly lower yields, products **6b**, **6e** and **6g** were isolated with yields from 64% to 67%. When indene **1h** was introduced into the reaction, product **6h** was obtained with the yield of 62%; *β*-methyl styrene **1i** gave equimolar mixture of diastereomeric iodo-oxyimides with the total yield of 53% (Table 5, **6i**). Vinyl acetate **1j** gave the product of iodo-oxyimidation **6j** in 65% yield.

On the basis of our previous experience[41] and literature data describing the reaction of *N*-hydroxyphthalimide with CAN[17] and the addition of resulting O-centered radical to styrenes,[40,41] a mechanism of the interaction of styrenes with *N*-hydroxyphthalimide, cerium(IV) ammonium nitrate and I_2 was proposed (Scheme 3).

Table 5. Scope of the iodo-oxyimidation of vinylarenes **1a-i** and vinyl acetate **1j** with *N*-hydroxyphthalimide **2** under the action of I_2 and CAN. [a]

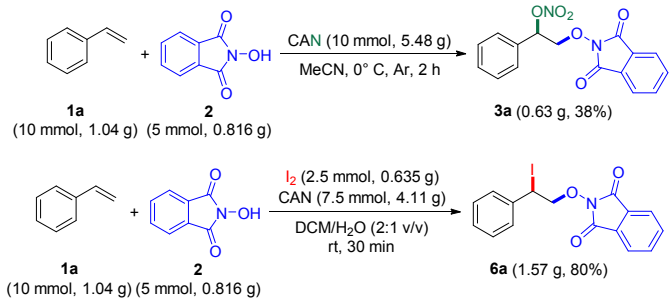


1a-g: R^1 = C_6H_5, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-FC_6H_4, *m*-MeC_6H_4, *m*-BrC_6H_4, *o*-MeC_6H_4; R^2 = H
1h: indene
1i: R^1 = C_6H_5; R^2 = Me
1j: R^1 = OC(O)Me



[a] Reaction conditions: vinyl substrate **1a-j** (2.0 mmol), *N*-hydroxyphthalimide **2** (1.0 mmol), I_2 (0.5 mmol), CAN (1.5 mmol), DCM/H_2O (2:1 v/v, 6.0 mL), at 20-25 °C for 30 min under air atmosphere. [b] Isolated yield.

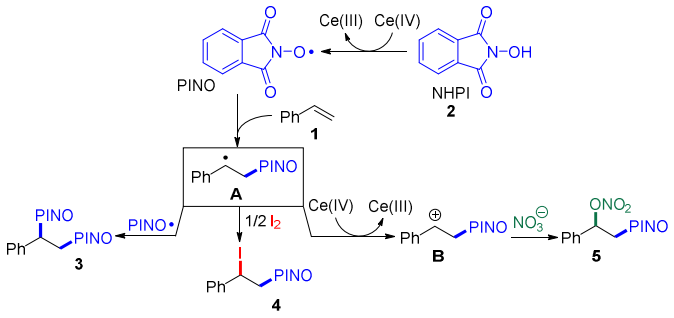
The applicability of the developed method for carrying out synthesis on a gram scale was demonstrated by the preparation of compounds **3a** and **6a** with the yields of 38% and 80%, respectively (Scheme 2).



Scheme 2. Gram-scale synthesis of the compounds **3a** and **6a**.

At the first stage, *N*-hydroxyphthalimide **2** is oxidized by CAN to form phthalimide-*N*-oxyl radical (PINO), which adds to a terminal carbon atom of the double C=C bond of styrene **1** giving benzylic radical **A**, which can undergo further transformations, depending on the solvent and order of addition of reagents, by radical or ionic routes. In the presence of the large amount of NHPI in a solution PINO is generated more efficiently and it traps intermediate **A** with the formation of product **3**. When I_2 is in the reaction medium, it traps radical **A** to form product **4**.[41,42] In the case when NHPI is added dropwise to the

mixture of styrene **1** and CAN, concentration of PINO is low and radical **A** undergo oxidation by Ce(IV) to form carbocation **B**, which reacts with NO_3^- anion yielding nitrate ester **5**.[46]



Scheme 3. Mechanism of oxidative difunctionalization of styrene **1** under the action of *N*-hydroxyphthalimide **2**, cerium(IV) ammonium nitrate and I_2.

3. Conclusion

Tunable difunctionalization of styrenes using cerium(IV) ammonium nitrate/*N*-hydroxyphthalimide system was developed. Depending on the reaction conditions, such as nature of a solvent, molar ratio of starting reagents and temperature, vicinal oxynitro-oxyphthalimides or dioxyphthalimides were synthesized. Reaction of styrenes with iodine in the presence of *N*-hydroxyphthalimide and cerium(IV) ammonium nitrate affords iodo-oxyimides. Besides styrenes, electron-deficient and electron-rich vinyl-containing substrates, such as vinyl acetate and methyl acrylate were successfully introduced in the reaction with NHPI/CAN system. The proposed mechanism involves the generation of phthalimide-*N*-oxyl radical, its addition to a terminal carbon atom of the double C=C bond resulting C-centered benzyl radical, which transformations *via* ionic or radical path determine the structure of the reaction product.

4. Experimental part

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE II 300 spectrometer (300.13 MHz and 75.47 MHz, respectively) in $CDCl_3$. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^{1}H ($CDCl_3$ δ=7.26 ppm), ^{13}C ($CDCl_3$ δ=77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), m (multiplet).

High-resolution mass spectra (HR-MS) were measured on a Bruker maXis instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from *m*/*z* 50 to *m*/*z* 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for all acetonitrile solutions (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

The TLC analysis was carried out on standard silica gel chromatography plates (ALUGRAMR Xtra SIL G/UV254). Column chromatography was performed using silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9, Acros).

Column chromatography was performed using silica gel (0.060-0.200 mm, 60 Å, Acros).

Dichloromethane (DCM) was distilled over K_2CO_3. Acetonitrile (MeCN) and ethyl acetate (EtOAc) were distilled over P_2O_5. Methanol (MeOH) was distilled over magnesium turnings. Toluene (PhMe) was distilled over sodium metal. Acetone was distilled over $KMnO_4$. Glacial acetic acid (AcOH) and dioxane were used as is from commercial sources.

Vinylarenes **1a-i**, vinyl acetate **1j**, methyl acrylate **1k**, *N*-hydroxyphthalimide (NHPI) **2**, cerium(IV) ammonium nitrate (CAN, $(NH_4)_2Ce(NO_3)_6$), cerium(IV) ammonium sulfate dihydrate ($(NH_4)_4Ce(SO_4)_4•2H_2O$), cerium(IV) sulfate ($Ce(SO_4)_2$), potassium bromate ($KBrO_3$), ammonium peroxydisulfate ($(NH_4)_2S_2O_8$), manganese(III) acetate dihydrate ($Mn(OAc)_3•2H_2O$), iron(III) perchlorate hydrate ($Fe(ClO_4)_3•nH_2O$) (anhydrous basis purity ca. 65%), lead(IV) tetraacetate ($Pb(OAc)_4$), sodium iodide dihydrate ($NaI•2H_2O$), tetrabutylammonium iodide (TBAI) and ammonium iodide (NH_4I) were commercial reagents (Acros, Sigma, Alfa Aesar). Tetrakis(bipyridine)silver(II) peroxydisulfate ($[Ag(bipy)_2]S_2O_8$) was synthesized according to the literature.[47]

All the new compounds (**3d**, **5j**, **5k** and **6j**) were characterized using ^{1}H and ^{13}C NMR spectroscopy, FT-IR spectroscopy, HR-MS and/or elemental analysis. Compounds **3d** and **5d** were characterized using ^{19}F spectroscopy. ^{1}H and ^{13}C NMR spectra of the known compounds (**3a-c**, **3e-i**, **4**, **5a,c,d** and **6a-i**) were in agreement with the literature data.[31,40,41,43]

4.2. Experimental procedure for Table 1

N-hydroxyphthalimide **2** (163 mg, 1.0 mmol) and CAN (548-1644 mg, 1.0-3.0 mmol) were added to a stirred solution of styrene **1a** (52-208 mg, 0.5-2.0 mmol) in MeCN, AcOH, acetone, EtOAc/H_2O, PhMe/H_2O, DCM/H_2O, AcOH/H_2O or dioxane (6.0 mL; for the mixture of solvents the ratio was 2:1 v/v) at 20-25 °C under air atmosphere. In the entries 2-6 solution of *N*-hydroxyphthalimide **2** (163 mg, 1.0 mmol) in MeCN (15 mL) was added dropwise for 30 min to the mixture of styrene **1a** (104-208 mg, 1.0-2.0 mmol) and CAN (1096-1644 mg, 2.0-3.0 mmol) in MeCN (3 mL). In the entry 6 reaction was carried out at 0 °C under argon atmosphere. After stirring the reaction mixture at 20-25 °C for 0.5-2 h, aqueous solution of $Na_2S_2O_4$ (200 mg in 30 mL of water) was added and the mixture was extracted with DCM (3×10 mL), combined extracts were washed with saturated aqueous $NaHCO_3$ solution (20 mL), then with water (20 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 40-45 °C under reduced pressure (20-30 mmHg). The yields of products **3a**, **4** and **5a** were determined by ^{1}H NMR spectroscopy using *p*-methoxyacetophenone as the internal standard. In the selected entries (1, 2, 3, 6, 9, 12 and 19) desired product was isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 0% to 3%).

*4.2.1. 2-((1,3-dioxoisoindolin-2-yl)oxy)-1-phenylethyl nitrate (**3a**)*

White solid: 45% yield (148 mg); mp = 112-114 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.90-7.73 (m, 4H), 7.42-7.35 (m, 5H), 6.30 (dd, J_1 = 9.4 Hz, J_2 = 3.0 Hz, 1H), 4.55 (dd, J_1 = 12.6 Hz, J_2 = 9.4 Hz, 1H), 4.35 (dd, J_1 = 12.6 Hz, J_2 = 3.0 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 134.9, 133.6, 129.9, 129.2, 128.8, 126.9, 123.9, 82.7, 77.3.

*4.2.2. 2-(2-oxo-2-phenylethoxy)isoindoline-1,3-dione (**4**)*

White solid: 20% yield (56 mg); mp = 177-178 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.03-7.94 (m, 2H), 7.87-7.70 (m, 4H), 7.65-7.56 (m, 1H), 7.54-7.44 (m, 2H), 5.44 (s, 2H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 192.3, 163.1, 134.8, 134.5, 134.2, 129.0, 128.7, 128.4, 123.8, 78.6.

*4.2.3. 2,2'-((1-phenylethane-1,2-diyl)bis(oxy))bis(isoindoline-1,3-dione) (**5a**)*

White solid: 65% yield (139 mg); mp = 179-180 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.84-7.65 (m, 8H), 7.61-7.53 (m, 2H), 7.41-7.32 (m, 3H), 5.86 (dd, J_1 = 7.4 Hz, J_2 = 3.7 Hz, 1H), 4.94 (dd, J_1 = 11.5 Hz, J_2 = 7.4 Hz, 1H), 4.57 (dd, J_1 = 11.5 Hz, J_2 = 3.7 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.6, 163.3, 134.6, 134.4, 134.3, 129.9, 129.1, 129.0, 128.8, 128.3, 123.7, 123.6, 85.9, 79.6.

*4.3. General procedure for synthesis of compounds **3a-i** (experimental for Table 2)*

Solution of *N*-hydroxyphthalimide **2** (163 mg, 1.0 mmol) in MeCN (15.0 mL) was added dropwise for 30 min to a stirred mixture of vinylarene **1a-h** (208-366 mg, 2.0 mmol) and CAN (1096 mg, 2.0 mmol) in MeCN (3.0 mL) at 0 °C under argon atmosphere. After stirring at 0 °C under argon atmosphere for 2 h reaction mixture was concentrated on a rotary evaporator to a volume of 5 mL at 40-45 °C under reduced pressure (20-30 mmHg) and aqueous solution of $Na_2S_2O_4$ (200 mg in 20 mL of water) was added. The mixture was extracted with DCM (3×10 mL), combined extracts were washed with saturated aqueous $NaHCO_3$ solution (20 mL), then with water (20 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 40-45 °C under reduced pressure (20-30 mmHg). Products **3a-h** were isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 0% to 3%).

*4.3.1. 2-((1,3-dioxoisoindolin-2-yl)oxy)-1-(p-tolyl)ethyl nitrate (**3b**)*

White solid: 60% yield (205 mg); mp = 128-130 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.76 (m, 4H), 7.30 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 6.29 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 4.56 (dd, J_1 = 12.6 Hz, J_2 = 9.5 Hz, 1H), 4.35 (dd, J_1 = 12.6 Hz, J_2 = 3.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 140.0, 134.9, 130.6, 129.9, 128.9, 126.9, 123.9, 82.8, 77.3, 21.3.

*4.3.2. 1-(4-chlorophenyl)-2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl nitrate (**3c**)*

White solid: 62% yield (224 mg); mp = 127-128 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.74 (m, 4H), 7.44-7.32 (m, 4H), 6.28 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H), 4.54 (dd, J_1 = 12.5 Hz, J_2 = 9.2 Hz, 1H), 4.35 (dd, J_1 = 12.5 Hz, J_2 = 3.2 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 136.0, 135.0, 132.2, 129.5, 128.8, 128.4, 124.0, 81.9, 77.1.

*4.3.3. 1-(4-fluorophenyl)-2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl nitrate (**3d**)*

White solid: 55% yield (190 mg); mp = 136-137 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.91-7.74 (m, 4H), 7.41 (dd, J_1 = 8.5 Hz, J_2 = 5.2 Hz, 2H), 7.22 (t, J = 8.5 Hz, 2H), 6.28 (dd, J_1 = 9.1 Hz, J_2 = 3.2 Hz, 1H), 4.54 (dd, J_1 = 12.5 Hz, J_2 = 9.1 Hz, 1H), 4.34 (dd, J_1 = 12.5 Hz, J_2 = 3.2 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.52 (d, J = 249.5 Hz), 163.46, 135.0, 129.6 (d, J = 3.3 Hz), 129.1 (d, J = 8.6 Hz), 128.8, 124.0, 116.4 (d, J = 21.9 Hz), 81.9, 77.2. ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.57. IR (KBr) ν(cm^{-1}): 1792, 1734, 1644, 1607, 1513, 1469, 1377, 1275, 1187, 1128, 1081, 1020, 1020, 1001, 877, 853, 840, 699, 530, 517. Anal. Calcd for $C_{16}H_{11}FN_2O_6$: C, 55.50; H, 3.20; N, 8.09. Found: C, 55.54; H, 3.09; N, 8.03.

*4.3.4. 2-((1,3-dioxoisoindolin-2-yl)oxy)-1-(m-tolyl)ethyl nitrate (**3e**)*

White solid: 51% yield (174 mg); mp = 119-120 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.76 (m, 4H), 7.34-7.18 (m, 4H), 6.29 (dd, J_1 = 9.4 Hz, J_2 = 2.9 Hz, 1H), 4.56 (dd, J_1 = 12.6 Hz, J_2 = 9.4 Hz, 1H), 4.36 (dd, J_1 = 12.6 Hz, J_2 = 2.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 139.2, 134.9, 133.6, 130.6, 129.2, 128.9, 127.5, 124.0, 82.9, 77.5, 21.5.

*4.3.5. 1-(3-bromophenyl)-2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl nitrate (**3f**)*

White solid: 43% yield (175 mg); mp = 124-125 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.93-7.74 (m, 4H), 7.60-7.48 (m, 2H), 7.40-7.23 (m, 2H), 6.25 (dd, J_1 = 9.1 Hz, J_2 = 3.2 Hz, 1H), 4.52 (dd, J_1 = 12.6 Hz, J_2 = 9.1 Hz, 1H), 4.34 (dd, J_1 = 12.6 Hz, J_2 = 3.2 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 136.0, 135.0, 133.1, 130.9, 130.0, 128.8, 125.5, 124.0, 123.3, 81.7.

*4.3.6. 2-((1,3-dioxoisoindolin-2-yl)oxy)-1-(o-tolyl)ethyl nitrate (**3g**)*

White solid: 56% yield (192 mg); mp = 110-111 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.76 (m, 4H), 7.38-7.18 (m, 4H), 6.58 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 4.53 (dd, J_1 = 12.7 Hz, J_2 = 9.5 Hz, 1H), 4.28 (dd, J_1 = 12.7 Hz, J_2 = 2.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.5, 135.6, 134.9, 132.1, 131.2, 129.6, 128.9, 127.0, 125.8, 124.0, 80.2, 76.8, 19.1. HRMS (ESI): *m/z* $[M+NH_4]^+$ calcd for $C_{17}H_{14}N_2O_6$: 360.1190; found 360.1198.

*4.3.7. 2-((1,3-dioxoisoindolin-2-yl)oxy)-2,3-dihydro-1H-inden-1-yl nitrate (**3h**)*

White solid: 69% yield (235 mg); mp = 162-163 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.74 (m, 4H), 7.53-7.28 (m, 4H), 6.65 (m, 1H), 5.18-5.11 (m, 1H), 3.62 (dd, J_1 = 17.8 Hz, J_2 = 7.1 Hz, 1H), 3.41-3.28 (m, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.9, 142.1, 134.9, 134.1, 131.1, 128.8, 128.1, 126.9, 125.4, 124.0, 90.2, 89.5, 36.1.

*4.4. General procedure for synthesis of compounds **5a,c,d,i,j** (experimental for Table 3)*

CAN (822 mg, 1.5 mmol) was added to a stirred mixture of vinyl substrate **1a,c,d,i,j** (43-70 mg, 0.5 mmol) and *N*-hydroxyphthalimide **2** (163 mg, 1.0 mmol) in MeOH (6.0 mL) at 20-25 °C. After stirring the reaction mixture under air atmosphere at 20-25 °C for 30 min, aqueous solution of $Na_2S_2O_4$ (200 mg in 30 mL of water) was added and the mixture was extracted with DCM (3×10 mL), combined extracts were washed with saturated aqueous $NaHCO_3$ solution (20 mL), then with water (20 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 40-45 °C under reduced pressure (20-30 mmHg). Products **5a,c,d,i,j** were isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 0% to 3%).

*4.4.1. 2,2'-((1-(4-chlorophenyl)ethane-1,2-diyl)bis(oxy))bis(isoindoline-1,3-dione) (**5c**)*

White solid: 50% yield (116 mg); mp = 106-107 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.85-7.67 (m, 8H), 7.55 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.81 (dd, J_1 = 7.0 Hz, J_2 = 4.3 Hz, 1H), 4.88 (dd, J_1 = 11.3 Hz, J_2 = 7.0 Hz, 1H), 4.55 (dd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.6, 163.3, 135.9, 134.7, 134.6, 132.9, 129.8, 129.1, 129.01, 128.96, 123.8, 123.7, 85.1, 79.1.

*4.4.2. 2,2'-((1-(4-fluorophenyl)ethane-1,2-diyl)bis(oxy))bis(isoindoline-1,3-dione) (**5d**)*

White solid: 36% yield (80 mg); mp = 108-109 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.88-7.65 (m, 8H), 7.64-7.54 (m, 2H), 7.12-7.01 (m, 2H), 5.82 (dd, J_1 = 7.0 Hz, J_2 = 4.3 Hz, 1H), 4.89 (dd, J_1 = 11.3 Hz, J_2 = 7.0 Hz, 1H), 4.57 (dd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.6, 163.3,

134.7, 134.5, 130.5 (d, J = 8.5 Hz), 130.3 (J = 3.2 Hz), 129.01, 128.96, 123.8, 123.7, 115.9 (J = 21.6 Hz), 85.1, 79.2. ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.96.

*4.4.3. 1,2-bis((1,3-dioxoisoindolin-2-yl)oxy)ethyl acetate (**5j**)*

White solid: 66% yield (135 mg); mp = 176-178 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.87-7.72 (m, 8H), 6.66 (dd, J_1 = 7.4 Hz, J_2 = 3.5 Hz, 1H), 4.76 (dd, J_1 = 12.2, J_2 = 3.5 Hz, 1H), 4.44 (dd, J_1 = 12.2, J_2 = 7.4 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 169.9, 163.3, 163.1, 134.83, 134.80, 128.83, 128.79, 124.0, 123.9, 96.1, 75.0, 20.9. IR (KBr) ν(cm^{-1}): 1798, 1779, 1740, 1375, 1360, 1207, 1185, 1128, 985, 877, 698. Anal. Calcd for $C_{20}H_{14}N_2O_8$: C, 58.54; H, 3.44; N, 6.83. Found: C, 58.49; H, 3.43; N, 6.81.

*4.4.4. Methyl 2,3-bis((1,3-dioxoisoindolin-2-yl)oxy)propanoate (**5k**)*

White solid: 64% yield (131 mg); mp = 134-136 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.89-7.72 (m, 8H), 5.29-5.23 (m, 1H), 4.88-4.72 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 166.6, 163.3, 163.1, 134.7, 128.9, 123.9, 123.8, 82.7, 53.3. IR (KBr) ν(cm^{-1}): 1795, 1747, 1466, 1422, 1375, 1310, 1272, 1187, 1131, 1080, 1063, 1016, 984, 875, 780, 696, 517. HRMS (ESI): *m/z* $[M+NH_4]^+$ calcd for $C_{20}H_{14}N_2O_8$: 428.1088; found 428.1074.

4.5. Experimental procedure for Table 4

Iodine (127 mg, 0.5 mmol) was added to a stirred mixture of styrene **1a** (104 mg, 1.0 mmol) and *N*-hydroxyphthalimide **2** (163 mg, 1.0 mmol) in MeOH, MeCN, DCM, H_2O, MeCN/H_2O, DCM/H_2O or AcOH (6.0 mL; for the mixture of solvents the ratio was 2:1 v/v) at 20-25 °C. Then, oxidant ($(NH_4)_2Ce(NO_3)_6$, $(NH_4)_4Ce(SO_4)_4$•$2H_2O$, $Ce(SO_4)_2$, $(NH_4)_2Ce(NO_3)_6$/$KBrO_3$, $(NH_4)_4Ce(SO_4)_4$•$2H_2O$/$[Ag(bipy)_2]S_2O_8$/$(NH_4)_2S_2O_8$, $Mn(OAc)_3$•$2H_2O$, $Fe(ClO_4)_3$•$8H_2O$ or $Pb(OAc)_4$, 222-1644 mg, 1.5-3.0 mmol) was added. In the entries 8-10 NaI•$2H_2O$, TBAI or NH_4I (145-369 mg, 1.0 mmol) were employed instead of I_2. In the entry 11 styrene **1a** (208 mg, 2.0 mmol) was employed. After stirring the reaction mixture under air atmosphere at 20-25 °C for 30 min, DCM (30 mL) was added. The mixture was washed with aqueous solution of $Na_2S_2O_3$•$5H_2O$ (200 mg in 20 mL of water), saturated aqueous $NaHCO_3$ solution (20 mL), then with water (20 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 20-25 °C under reduced pressure (20-30 mmHg). Product **6a** was isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 0% to 5%).

*4.5.1. 2-(2-iodo-2-phenylethoxy)isoindoline-1,3-dione (**6a**)*

White solid: 86% yield (338 mg); mp = 135-136 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.85-7.68 (m, 4H), 7.54 (d, J = 7.4 Hz, 2H), 7.36-7.17 (m, 3H), 5.53 (dd, J_1 = 9.8 Hz, J_2 = 5.7 Hz, 1H), 5.00-4.88 (m, 1H), 4.71 (dd, J_1 = 10.7 Hz, J_2 = 5.7 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.3, 139.8, 134.7, 128.9, 128.7, 128.6, 127.9, 123.7, 81.4, 25.2.

*4.6. General procedure for synthesis of compounds **6a-j** (experimental for Table 5)*

Iodine (127 mg, 0.5 mmol) was added to a stirred mixture of vinyl substrate **1a-i** (172-366 mg, 2.0 mmol) and *N*-hydroxyphthalimide **2** (163 mg, 1.0 mmol) in DCM/H_2O (6.0 mL, 2:1 v/v) at 20-25 °C. Then, CAN (822 mg, 1.5 mmol) was added. After stirring the reaction mixture under air atmosphere at 20-25 °C for 30 min, DCM (30 mL) was added and the mixture was washed with aqueous solution of $Na_2S_2O_3$•$5H_2O$ (200 mg in 20 mL of water), saturated aqueous $NaHCO_3$ solution (20 mL), then with water (20 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 20-25 °C under reduced pressure (20-30 mmHg) Products **6a-i** were isolated by column chromatography on silica gel using DCM/EtOAc as eluent (with the volume part of EtOAc gradually increased from 0% to 5%).

*4.6.1. 2-(2-iodo-2-(p-tolyl)ethoxy)isoindoline-1,3-dione (mixture of regioisomers 4:1) (**6b**)*

White solid: 64% yield (260 mg); mp = 135-136 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.84-7.66 (m, 4H), 7.47-7.35 (m, 2H), 7.17 (d, J = 7.8 Hz, 0.4H), 7.09 (d, J = 7.9 Hz, 1.6H), 5.56-5.45 (m, 1H), 4.97-4.87 (m, 0.8H), 4.67 (dd, J_1 = 10.7 Hz, J_2 = 5.6 Hz, 0.8H), 3.73 (dd, J_1 = 10.4 Hz, J_2 = 6.2 Hz, 0.2H), 3.57 (dd, J_1 = 10.4 Hz, J_2 = 8.0 Hz, 0.2H), 2.33 (s, 0.6H), 2.25 (s, 2.4H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.3, 138.7, 136.8, 134.7, 129.7, 128.8, 127.7, 123.7, 81.3, 25.6, 21.3.

*4.6.2. 2-(2-(4-chlorophenyl)-2-iodoethoxy)isoindoline-1,3-dione (**6c**)*

White solid: 72% yield (307 mg); mp = 137-138 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.87-7.70 (m, 4H), 7.50 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 5.50 (dd, J_1 = 10.2 Hz, J_2 = 5.3 Hz, 1H), 4.97-4.86 (m, 1H), 4.68 (dd, J_1 = 10.7 Hz, J_2 = 5.3 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.3, 138.5, 134.8, 134.4, 129.3, 129.2, 128.8, 123.7, 81.2, 23.7.

*4.6.3. 2-(2-(4-fluorophenyl)-2-iodoethoxy)isoindoline-1,3-dione (**6d**)*

White solid: 70% yield (288 mg); mp = 153-154 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.87-7.68 (m, 4H), 7.57-7.48 (m, 2H), 7.00 (t, J = 8.5 Hz, 2H), 5.50 (dd, J_1 = 10.1 Hz, J_2 = 5.4 Hz, 1H), 4.98-4.80 (m, 1H), 4.66 (dd, J_1 = 10.7 Hz, J_2 = 5.4 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.3, 162.5 (d, J = 248.6 Hz), 135.8 (d, J = 3.4 Hz), 134.8, 129.8 (d, J = 8.4 Hz), 128.8, 123.7, 115.9 (d, J = 21.8 Hz), 81.5, 24.1.

*4.6.4. 2-(2-iodo-2-(m-tolyl)ethoxy)isoindoline-1,3-dione (**6e**)*

White solid: 66% yield (269 mg); mp = 123-124 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.82-7.67 (m, 4H), 7.34-7.27 (m, 2H), 7.20-7.13 (m, 1H), 6.98 (d, J = 7.4 Hz, 1H), 5.48 (dd, J_1 = 9.7 Hz, J_2 = 5.7 Hz, 1H), 4.97-4.88 (m, 1H), 4.67 (dd, J_1 = 10.7 Hz, J_2 = 5.7 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.2, 139.7, 138.6, 134.7, 129.5, 128.9, 128.8, 128.4, 125.0, 123.6, 81.3, 25.5, 21.45.

*4.6.5. 2-(2-(3-bromophenyl)-2-iodoethoxy)isoindoline-1,3-dione (**6f**)*

White solid: 71% yield (334 mg); mp = 134-135 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.84-7.70 (m, 4H), 7.69-7.64 (m, 1H), 7.50-7.44 (m, 1H), 7.36-7.29 (m, 1H), 7.22-7.14 (m, 1H), 5.42 (dd, J_1 = 5.4 Hz, J_2 = 10.1 Hz, 1H), 4.93-4.84 (m, 1H), 4.65 (dd, J_1 = 10.8 Hz, J_2 = 5.4 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.2, 142.1, 134.8, 131.7, 131.0, 130.5, 128.7, 126.7, 123.8, 122.7, 81.2, 23.2.

*4.6.6. 2-(2-iodo-2-(o-tolyl)ethoxy)isoindoline-1,3-dione (**6g**)*

White solid: 67% yield (273 mg); mp = 112-113 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.82-7.69 (m, 4H), 7.59 (d, J = 7.5 Hz, 1H), 7.21-7.09 (m, 3H), 5.69 (dd, J_1 = 9.7 Hz, J_2 = 5.9 Hz, 1H), 5.11-5.02 (m, 1H), 4.75 (dd, J_1 = 10.6 Hz, J_2 = 5.9 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.2, 137.5, 136.3, 134.7, 131.3, 128.8 128.6, 126.8, 126.1, 123.7, 80.4, 22.4, 19.3.

*4.6.7. 2-((1-iodo-2,3-dihydro-1H-inden-2-yl)oxy)isoindoline-1,3-dione (**6h**)*

White solid: 62% yield (251 mg); mp = 164-165 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.91-7.76 (m, 4H), 7.52-7.45 (m, 1H), 7.31-7.25 (m, 3H), 5.95 (m, 1H), 5.36 (dt, J_1 = 5.6 Hz, J_2 = 1.4 Hz, 1H), 3.55 (dd, J_1 = 17.6 Hz, J_2 = 5.6 Hz, 1H), 3.33 (d, J = 17.6 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 164.1, 143.0, 139.6, 134.9, 129.2, 128.9, 128.1, 125.9, 125.2, 123.9, 96.2, 36.0, 29.5.

*4.6.8. 2-((1-iodo-1-phenylpropan-2-yl)oxy)isoindoline-1,3-dione (**6i**)*

White solid: 53% yield (215 mg), mixture of diastereomers 1:1; mp = 118-119 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.92-7.66 (m, 4H), 7.60-7.48 (m, 2H), 7.37-7.11 (m, 3H), 5.42 (d, J = 7.5 Hz, 0.5H), 5.32 (d, J = 6.8 Hz, 0.5H), 4.84-4.68 (m, 1H), 1.69 (d, J = 6.1 Hz, 1.5H), 1.32 (d, J = 6.3 Hz, 1.5H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 164.1, 163.8, 140.3, 139.9, 134.8, 134.6, 129.13, 129.07, 128.9, 128.74, 128.67, 128.6, 128.50, 128.3, 123.8, 123.6, 87.4, 85.5, 34.3, 32.2, 19.4, 16.8.

*4.6.9. 2-((1,3-dioxoisoindolin-2-yl)oxy)-1-iodoethyl acetate (**6j**)*

White solid: 65% yield (244 mg); mp = 132-133 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.88-7.74 (m, 4H), 7.02 (dd, J_1 = 10.3 Hz, J_2 = 2.4 Hz, 1H), 4.72 (dd, J_1 = 12.7 Hz, J_2 = 10.3 Hz, 1H), 4.56 (dd, J_1 = 12.7 Hz, J_2 = 2.4 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 168.7, 163.4, 135.0, 128.8, 123.9, 81.3, 48.8, 21.2. IR (KBr) ν(cm^{-1}): 1792, 1759, 1734, 1466, 1439, 1376, 1209, 1186, 1134, 1111, 1081, 1038, 1013, 986, 940, 901, 877, 842, 785, 702, 669, 517. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{10}INO_5$: 375.9676; found 375.9668.

*4.7. Gram scale synthesis of compound **3a** (experiment for Scheme 2)*

Solution of *N*-hydroxyphthalimide **2** (0.816 g, 5.0 mmol) in MeCN (75.0 mL) was added dropwise for 30 min to a stirred mixture of styrene **1a** (1.04 g, 10.0 mmol) and CAN (5.48 g, 10.0 mmol) in MeCN (15.0 mL) at 0 °C under argon atmosphere. After the stirring at 0 °C for 2 h reaction mixture was concentrated on a rotary evaporator to a volume of 10 mL at 40-45 °C under reduced pressure (20-30 mmHg) and aqueous solution of $Na_2S_2O_4$ (200 mg in 100 mL of water) was added. The mixture was extracted with DCM (3×30 mL), combined extracts were washed with saturated aqueous $NaHCO_3$ solution (50 mL), then with water (50 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated under reduced pressure (20-30 mmHg). Product **3a** was isolated by column chromatography on silica gel using DCM/EtOAc mixture as eluent (with the volume part of EtOAc gradually increased from 0% to 5%). Yield of **3a** was 0.63 g (38%).

*4.8. Gram scale synthesis of compound **6a** (experiment for Scheme 2)*

Iodine (0.635 g, 2.5 mmol) was added to a stirred mixture of styrene **1a** (1.04 g, 10.0 mmol) and *N*-hydroxyphthalimide **2** (0.816 g, 5.0 mmol) in DCM/H_2O (90 mL, 2:1 v/v) at 20-25 °C. Then, CAN (4.11 g, 7.5 mmol) was added. After stirring the reaction mixture under air atmosphere at 20-25 °C for 30 min the mixture was washed with aqueous solution of $Na_2S_2O_3$•$5H_2O$ (200 mg in 50 mL of water), saturated aqueous $NaHCO_3$ solution (50 mL), then with water (50 mL), dried over anhydrous Na_2SO_4 and filtered. DCM was rotary evaporated at 20-25 °C under reduced pressure (20-30 mmHg). Product **6a** was isolated by column chromatography on silica gel using DCM/EtOAc as eluent (with the volume part of EtOAc gradually increased from 0% to 5%). Yield of **6a** was 1.57 g (80%).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/xxxx.

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