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Graphical Abstract

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Acid-Catalyzed C-O Coupling of Styrenes with N-hydroxyphthalimide: Trapping Alkenyl Radicals by TEMPO

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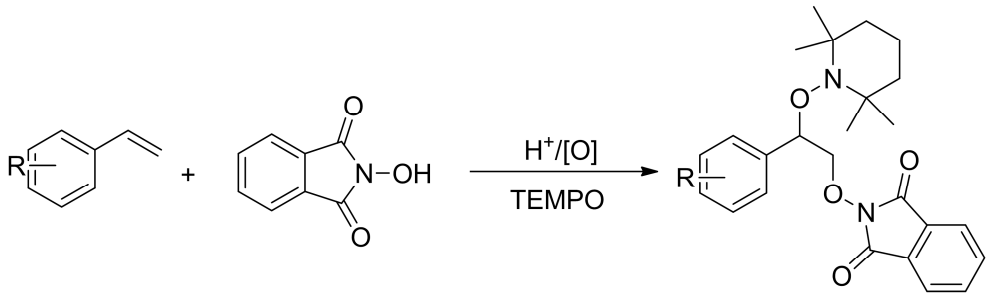

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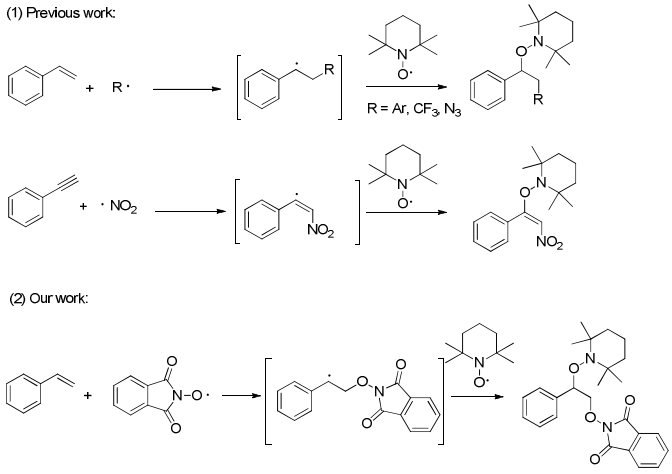
ABSTRACT

A mild metal-free acid-catalyzed 1,2-dihydroxylaminations of alkenes with N-hydroxyphthalimide and 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO) has been demonstrated under air conditions to furnish the dioxygenated products in good to excellent yields. The dioxygenated product can be easily transformed into ketone derivative using 3-chloroperbenzoic acid (*m*-CPBA) as the oxidant in a high yield.

1. Introduction

Alkenes are abundant simple chemical feedstocks and organic molecules, which have been widely applied in organic synthesis, and methods for their efficient, selective transformations are attractive to construct more complex molecules.[1] In these methodologies, direct 1,2-difunctionalization of alkenes has stimulated chemists' considerable attention, providing the most efficient strategy for the synthesis of functionalized organic compounds.[2] 1,2-Dioxygenated structures are present in many natural products and biologically active molecules, such as Myriocin and related immunosuppressive compounds.[3] In this context, in recent years, a series of metal-catalyzed 1,2-dioxygenation of alkenes have been developed,[4] however, metal-free conditions have not been seriously studied up to now.[5] On the other hand, as we all know, TEMPO is usually used as a radical scavenging to trap radicals or inhibit reactions in radical reactions. At the same time, olefins are undoubtedly one of the most important radical acceptors. When they are attacked by radicals, alkyl radicals are formed which can be easily trapped by TEMPO and give useful aminoxylative products. Indeed, some significant studies on intermolecular aminoxylative of olefins have been reported involving Ar, CF_3, NO_2 and N_3 radicals (Scheme 1-1).[6] Recently, our group and others found that N-hydroxyphthalimide (NHPI) can generate the phthalimide N-oxyl (PINO) radical under the oxidizing conditions, which is an active species to realize the radical addition of alkenes.[5b, 7] Herein, we envisioned that the PINO captured alkyl radicals from alkenes can be also trapped by TEMPO to give the 1,2-dioxygenated products (Scheme 1-2).



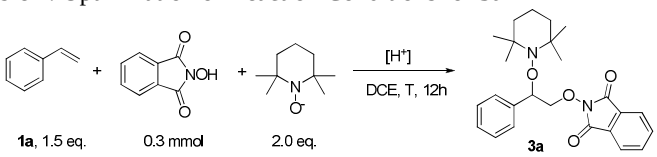
Scheme 1. Trapping alkyl radicals by TEMPO.

2. Results/Discussion

On the basis of our assumption, we began our study using our previous conditions [5b] by reacting styrene **1a** with NHPI **2a** and TEMPO using 10% 4-methylbenzenesulfonic acid (TsOH) as a catalyst, *t*-butylhydroperoxide (TBHP, 5.0 equiv.) as the oxidant in 1,2-dichloroethane (DCE) at room temperature, and **3a** was indeed sluggishly produced in 86% yield after 24 hours (Table 1, entry 1). When the oxidant was omitted, no reaction was detected, which meant that TEMPO was not the oxidant in this

reaction and TBHP was essential for this transformation. When oxygen gas (1 atm) was used as the oxidant, only trace amount of product was observed (entry 3). Interestingly, the loading of TBHP was decreased to 3 equivalents, and the yield was increased to 92% within 24 hours (entry 5). Then, the reaction temperature was increased to 60 °C, the yield reached up to 98% in a short time (4 hours). Other acids were also tried, and no better results were obtained (entries 7 and 8). When the loadings of **1a** and TEMPO were changed to 1.0 equiv., the yield of **3a** was decreased to 57%.

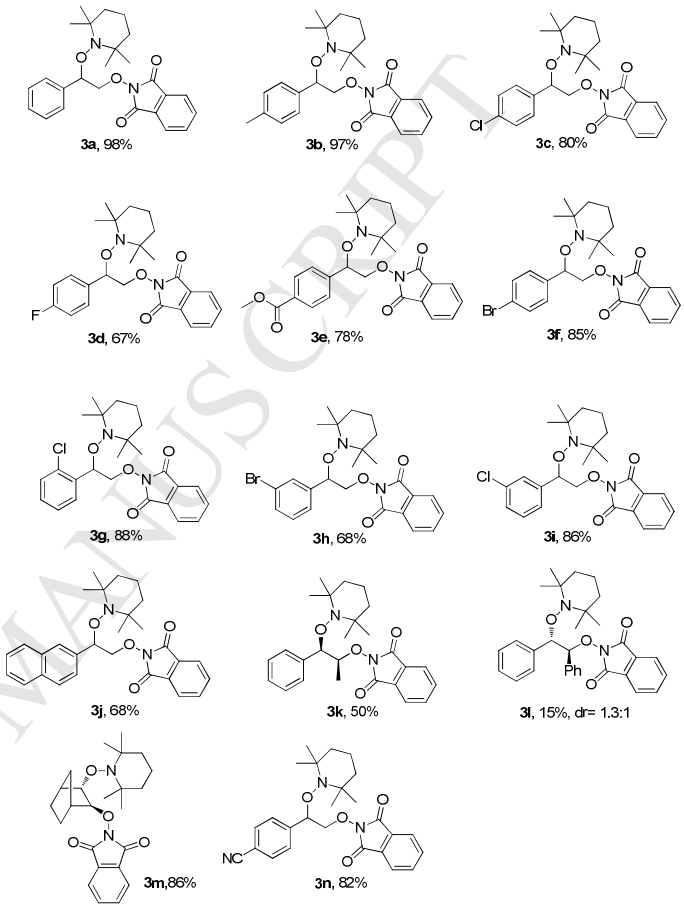
Table 1. Optimization of Reaction Conditions for **3a**[a]



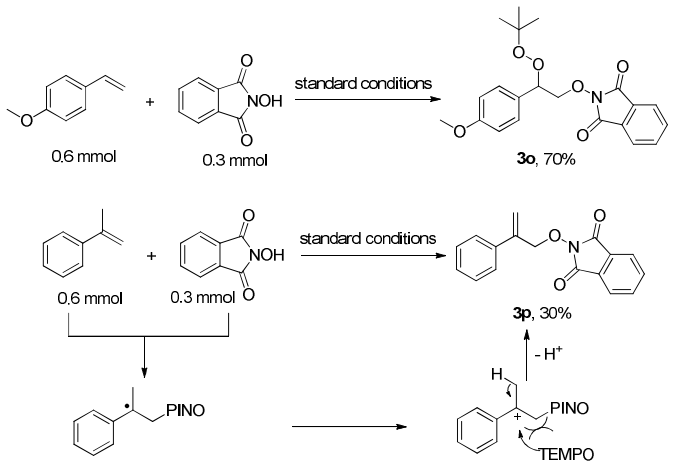
Entry	Catalyst	Oxidant	Solvent	T/ (°C)	Yield (%)[b]
1	10% TsOH	5.0 equiv. TBHP	DCE	r.t.	86%
2	10% TsOH	—	DCE	r.t.	0%
3	10% TsOH	O_2	DCE	r.t.	<5%
4	10% TsOH	2.0 equiv. TBHP	DCE	r.t.	69%
5	10% TsOH	3.0 equiv. TBHP	DCE	r.t.	92%
6	***10% TsOH***	***3.0 equiv. TBHP***	***DCE***	***60***	***98%***[c]
7	10% PhCOOH	3.0 equiv. TBHP	DCE	60	70%[c]
8	10% HOAc	3.0 equiv. TBHP	DCE	60	68%[c]
9[d]	10% TsOH	3.0 equiv. TBHP	DCE	60	57%

[a] Reaction conditions: **1a** (0.45 mmol), N-hydroxyphthalimide (0.3 mmol), TEMPO (0.6 mmol), catalyst (0.03 mmol, 10%), oxidant, and solvent (2.0 mL), 12 h. [b] Isolated yield. [c] 4h. [d] **1a**:NHPI:TEMPO= 1:1:1.

With the optimal reaction condition in hand (Table 1, entry 6), we subsequently investigated the substrate scope of this highly selective method (Scheme 2). A series of substituted styrenes including fluoro, chloro, bromo, methoxyl, ester, cyano and methyl substituents, can readily be converted into the corresponding products in good to excellent yields, where 1-methyl-4-vinylbenzene gave the product **3b** in 97% yield. Electron-withdrawing substituents on the *para* position gave a slightly lower yield (**3c**, **3d**, **3e**, **3f**, **3l**). When a sterically demanding *ortho* substituted Cl was imbedded in styrene, a slightly lower yield was obtained (**3g**). 3-Bromostyrene delivered the product **3h** in 68% yield, while 3-chlorostyrene gave a higher yield (**3i**, 86%). 2-Vinylnaphthalene gave a moderate yield (**3j**, 68%). (E)-Prop-1-enylbenzene can be well tolerated in this reaction, providing **3k** in 50% yield in a single isomer. (E)-1,2-Diphenylethene was also tolerated, but unfortunately, a very low yield was obtained due to the steric hindrance (**3l**, 15%, dr=1.3:1). When norbornene was used as substrate under the standard conditions, the target product **3m** was obtained in 86% yield. Cyano substituent was also well retained during the reaction (**3n**). When the olefin with an expanded pi-system such as (1E, 3E)-1,4-diphenylbuta-1,3-diene was used in our reaction conditions, a mixture was obtained. Interestingly, when 4-methoxylstyrene was submitted to the reaction conditions, a peroxide product **3o** was separated in 70% yield, which was difficult to be synthesized in our previous work. α-Methyl styrene did not yield the corresponding product, but an allyl product **3p** (Scheme 3). In our opinion, when NHPI radical added to α-methyl styrene, a benzyl radical was obtained, which underwent further oxidation to give benzyl ion. Due to the steric hindrance of TEMPO, an easily proton elimination was occurred to give the product **3p**.



Scheme 2. The scope of the reaction

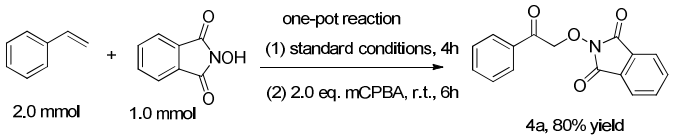


Scheme 3. The special scope of the reaction

In view of the reactive N−O bond, the dioxygenated product can be easily transformed into the ketone derivative **4a** in 90% yield using *m*-CPBA as the oxidant at room temperature (Scheme 4).

Scheme 4. Transformation of the product **3a**

Last, a one-pot two-steps reaction was also tried using the standard reaction conditions, and the product **4a** was obtained in 80% yield (Scheme 5).



Scheme 5. One pot reaction

3. Conclusion

In conclusion, we have developed an efficient acid-catalyzed highly 1,2-dihydroxylation of olefins with N-hydroxyphthalimide and TEMPO. A radical addition process was involved in this transformation with the formation of two C-O bonds in one step. The product can be further easily transformed into ketone derivative using *m*-CPBA as the oxidant. Further investigations on the synthetic application of these reactions are ongoing in our group.

4. Experimental section

4.1 General Remarks:

Column chromatography was carried out on silica gel. Unless noted, ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

4.2 Typical procedure for the synthesis of products 3

To a solution of N-hydroxyphthalimide (**2**, 0.3 mmol, 48.9 mg) and TEMPO (0.6 mmol, 93.6 mg) in DCE (2.0 mL) was added styrene (**1**, 0.45 mmol), TsOH (10%, 0.03 mmol, 5.2 mg), TBHP (3.0 equiv., 150 uL, 5-6 M in decane). The reaction mixture was then stirred for 4 h at 60 ^{o}C in air. After the reaction, the resulting mixture was quenched with water and extracted twice with EtOAc (10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the product **3 (**petroleum ether/ethyl acetate as eluent (10:1)).

2-(2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxy)-isoindolin-1,3-dione, **3a**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.67-7.77 (m, 4 H), 7.46-7.47 (m, 2 H), 7.33-7.35 (m, 2 H), 7.25-7.31 (m, 1 H), 5.13-5.16 (m, 1 H), 4.73-4.75 (m, 1 H), 4.48-4.52 (m, 2 H), 1.20-1.46 (m, 13 H), 1.05 (m, 3 H), 0.72 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 140.0, 134.2, 128.3, 127.7, 123.2, 83.2, 80.1, 60.0, 40.3, 33.9, 20.2, 17.0; HRMS (ESI) m/z: calcd for $C_{25}H_{30}N_2O_4Na^+$: [M+Na$^+$]= 445.2103; found: 445.2104. IR (cm^{-1}): 3063, 2972, 2931, 1790, 1732, 1467, 1454, 1375, 1362, 1187, 1132, 1018, 996, 877, 784;

2-(2-(2,2,6,6,-tetramethylpiperidin-1-yloxy)-2-p-tolylethoxy)-isoindoline-1,3-dione, **3b**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.68-7.78 (m, 4 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 5.08-5.11 (m, 1 H), 4.71-4.74 (m, 1 H), 4.47-4.51 (m, 1 H), 2.3 (s, 3 H), 1.04-1.46 (m, 16 H), 0.74 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.1, 137.3, 137.0, 134.2, 128.8, 128.7, 127.8, 123.2, 82.9, 79.9, 59.9, 40.3, 34.1, 33.9, 21.1, 20.2, 17.1; IR (cm^{-1}): 2972, 2930, 1790, 1731, 1514, 1468, 1375, 1361, 1186, 1131, 1081, 1017, 876, 817, 701; HRMS (ESI) m/z: calcd for $C_{26}H_{32}N_2O_4Na^+$: [M+Na$^+$]= 459.2260; found:459.2282.

2-(2-(4-chlorophenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethoxy)isoindoline-1,3-dione, **3c**, M.P.= 86-88 ^{o}C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.71-7.79 (m, 4 H), 7.43 (d, *J*= 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.08-5.11 (m, 1 H), 4.69-4.72 (m, 1 H), 4.45-4.49 (m, 1 H), 1.03-1.47 (m, 16 H), 0.73 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.9, 138.5, 134.2, 133.3, 129.1, 128.5, 127.9, 123.1, 82.4, 79.5, 59.8, 40.1, 33.9, 33.8, 20.0, 16.8; IR (cm^{-1}): 2973, 2932, 1791, 1731, 1491, 1467, 1375, 1362, 1187, 1131, 1082, 1015, 876, 830, 701; HRMS (ESI) m/z: calcd for $C_{25}H_{29}ClN_2O_4Na^+$: [M+Na$^+$]= 479.1714; found: 479.1714.

2-(2-(4-fluorophenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxy)isoindoline-1,3-dione, **3d**, M.P.=75-77 ^{o}C**,** ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.70-7.79 (m, 4 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.01-7.05 (m, 2 H), 5.09-5.12 (m, 1 H), 4.70-4.73 (m, 1 H), 4.45-4.49 (m, 1 H), 1.03-1.47 (m,16 H), 0.71 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 163.0, 161.1, 135.9, 134.3, 129.6, 128.7, 123.3, 114.9, 114.7, 82.4, 79.8, 60.1, 59.9, 40.3, 33.9, 20.2, 16.9; IR (cm^{-1}): 2973, 2932, 1791, 1732, 1605, 1509, 1375, 1361, 1187, 1131, 1071, 877, 836; HRMS (ESI) m/z: calcd for $C_{25}H_{29}FN_2O_4Na^+$: [M+ Na$^+$]= 463.2009; found: 463.2010.

Methyl 4-(2-(1,3-dioxoisoindolin-2-yloxy)-1-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl)benzoate, **3e**, M.P.=100-102 ^{o}C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.70-7.78 (m, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 5.14-5.17 (m, 1 H), 4.72-4.74 (m, 1 H), 4.44-4.49 (m, 1 H), 2.3 (s, 3 H), 1.05-1.47 (m, 16 H), 0.74 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 169.0, 163.0, 150.1, 137.5, 134.3, 128.8, 128.6, 123.2, 120.9, 82.4, 79.9, 59.9, 40.2, 33.9, 33.8, 20.9, 20.1, 16.9; IR (cm^{-1}): 2973, 2933, 1790, 1731, 1506, 1467, 1372, 1131, 1081, 1017, 877, 701; HRMS (ESI) m/z: calcd for $C_{27}H_{32}N_2O_6Na^+$: [M+Na$^+$]= 503.2158; found: 503.2156.

2-(2-(4-bromophenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxy)isoindoline-1,3-dione, **3f**, M.P.= 95-97 ^{o}C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.70-7.79 (m, 4 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 5.06-5.09 (m, 1 H), 4.69-4.71 (m, 1 H), 4.44-4.49 (m, 1 H), 1.03-1.47 (m, 16 H), 0.73 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 139.2, 134.4, 128.7, 123.3, 121.7, 82.6, 79.6, 60.0, 40.3, 34.1, 33.9, 20.2, 17.0; IR (cm^{-1}): 2973, 2932, 1790, 1731, 1487, 1468, 1374, 1361, 1186, 1131, 1081, 1072, 876, 826; HRMS (ESI) m/z: calcd for $C_{25}H_{29}BrN_2O_4Na^+$: [M+Na$^+$]= 523.1208; found: 523.1239.

2-(2-(2-chlorophenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)

ethoxy)isoindoline-1,3-dione, **3g**, M.P.= 85-87 °C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.68-7.77 (m,5 H), 7.21-7.34 (m, 3 H), 5.50-5.52 (m, 1 H), 4.70-4.74 (m, 1 H), 4.57-4.60 (m, 1 H), 1.06-1.49 (m, 16 H), 0.78 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.9, 137.7, 134.2, 132.3, 128.6, 126.4, 123.2, 81.3, 78.7, 60.0, 40.3, 34.0, 33.1, 20.2, 17.0; IR (cm^{-1}): 3062, 2973, 2932, 1791, 1732, 1468, 1187, 1131, 1081, 1034, 876, 759; HRMS (ESI) m/z: calcd for $C_{25}H_{29}ClN_2O_4Na^+$: [M+Na^+]= 479.1714; found: 479.1710.

2-(2-(3-bromophenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)

ethoxy)isoindoline-1,3-dione, **3h**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.70-7.80 (m, 4 H), 7.63 (s, 1 H), 7.38-7.44 (m, 2 H), 7.20-7.24 (m, 1 H), 5.07-5.10 (m, 1 H), 4.69-4.71 (m, 1 H), 4.45-4.49 (m, 1 H), 1.05-1.47 (m, 16 H), 0.74 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 142.5, 134.3, 130.9, 130.7, 129.6, 128.7, 126.5, 123.3, 122.1, 82.6, 79.6, 60.1, 40.3, 33.9, 20.2, 17.0; IR (cm^{-1}): 3070, 2972, 1790, 1730, 1570, 1374, 1361, 1186, 1131, 1081, 876, 785; HRMS (ESI) m/z: calcd for $C_{25}H_{29}BrN_2O_4Na^+$: [M+Na^+]= 523.1208; found: 523.1230.

2-(2-(3-chlorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)

ethoxy)isoindoline-1,3-dione, **3i**, oil, ^{1}H NMR (400 MH_Z, $CDCl_3$): 7.72-7.79 (m, 4 H), 7.48 (s, 1 H), 7.37-7.39 (m, 1 H), 7.23-7.30 (m, 2 H), 5.08-5.11 (m, 1 H), 4.69-4.71 (m, 1 H), 4.45-4.49 (m, 1 H), 1.05-1.47 (m, 16 H), 0.74 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.1, 142.2, 134.4, 133.8, 129.3, 128.7, 128.0, 127.8, 126.1, 123.3, 82.7, 79.7, 65.8, 60.1, 40.3, 34.0, 20.2, 17.0, 15.2; IR (cm^{-1}): 2973, 2932, 1791, 1732, 1468, 1362, 1187, 1131, 1081, 1018, 998, 876, 786, 699; HRMS (ESI) m/z: calcd for $C_{25}H_{29}ClN_2O_4H^+$: [M+H^+]=457.1894; found: 457.1896.

2-(2-(naphthalen-2-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)

ethoxy)isoindoline-1,3-dione, **3j**, M.P.=108-109 °C, ^{1}H NMR (400 MH_Z, $CDCl_3$): 7.92 (s, 1 H), 7.76-7.86 (m, 3 H), 7.68-7.71 (m, 2 H), 7.58-7.62 (m, 3 H), 7.39-7.46 (m, 2 H), 5.28-5.31 (m, 1 H), 4.80-4.84 (m, 1 H), 4.58-4.62 (m, 1 H), 1.05-1.49 (m, 16 H), 0.69 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 137.4, 132.9, 128.0, 127.7, 127.5, 127.3, 125.7, 125.6, 125.4, 123.1, 83.5, 79.7, 40.3, 17.0; IR (cm^{-1}): 3058, 2976, 2932, 1788, 1734, 1465, 1369, 1183, 1129, 994, 874, 818, 742; HRMS (ESI) m/z: calcd for $C_{29}H_{32}N_2O_4H^+$:[M+H^+]=473.2440; found: 473.2440.

2-(1-phenyl-1-(2,2,6,6-tetramethylpiperidin-1-yloxy)propan-2-yloxy)isoindoline-1,3-dione, **3k**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.79-7.82 (m, 2 H), 7.71-7.74 (m, 2 H), 7.62-7.64 (m, 2 H), 7.28-7.35 (m, 3 H), 5.05-5.11 (m, 1 H), 4.83 (d, *J* = 3.2 Hz, 1 H), 1.27-1.40 (m, 15 H), 1.10 (m, 2 H), 1.00 (m, 2 H), 0.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.7, 138.6, 134.2, 129.8, 129.0, 127.5, 123.1, 89.8, 85.4, 60.4, 59.5, 40.6, 34.4, 33.9, 20.2, 17.0, 16.4; IR (cm^{-1}): 3070, 2932, 1791, 1731, 1467, 1455, 1376, 1362, 1187, 1131, 1081, 1016, 878; HRMS (ESI) m/z: calcd for $C_{26}H_{32}N_2O_4Na^+$: [M+Na^+]= 459.2260; found: 459.2260.

2-(1,2-diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxy)

isoindoline-1,3-dione, **3l**, dr=1.3:1, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.61-7.73 (m, 4 H), 7.06-7.34 (m, 10 H), 6.01-6.20 (d, *J* = 5.2, 6.8 Hz, 1 H), 5.04-5.45 (d, *J* = 6.8, 5.2 Hz, 1 H), 1.26-1.67 (m, 15 H), 1.01-1.02 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 138.9, 137.3, 136.1, 135.3, 134.1, 128.2, 127.1, 123.2, 123.1, 89.8, 88.8, 88.6, 88.0, 60.7, 40.9, 34.5, 33.8, 31.5, 30.1, 29.7, 22.7, 20.4, 17.1; IR (cm^{-1}): 2930, 1790, 1737, 1455, 1374, 1187, 1132, 976, 876, 699; HRMS (ESI) m/z: calcd for $C_{31}H_{34}N_2O_4Na^+$: [M+Na^+] = 521.2416; found: 521.2417.

2-(3-(2,2,6,6-tetramethylpiperidin-1-yloxy)bicycle[2.2.1]heptan-2-yloxy)isoindoline-1,3-dione, **3m**, M.P.= 104-106 °C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.80-7.82 (m, 2 H), 7.73-7.75 (m, 2 H), 4.35-4.46 (m, 1 H), 4.10-4.23 (m, 1 H), 2.65 (m, 1 H), 2.25-2.26 (m, 1 H), 1.98-2.00 (m, 1 H), 1.81-1.83 (m, 1 H), 1.53-1.60 (m, 2 H), 1.44 (m, 7 H), 1.26-1.34 (m, 3 H), 1.11-1.19 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 134.1, 128.9, 123.1, 94.9, 90.8, 89.8, 59.9, 59.1, 40.4, 40.2, 39.9, 39.5, 33.9, 33.7, 33.6, 32.7, 25.4, 24.0, 23.5, 20.0, 17.0; IR (cm^{-1}): 2971, 2933, 1790, 1731, 1461, 1374, 1361, 1185, 1131, 1082, 1045, 876, 733; HRMS (ESI) m/z: calcd for $C_{24}H_{32}N_2O_4Na^+$: [M+Na^+]= 435.2260; found: 435.2263.

4-(2-((1,3-dioxoisoindolin-2-yl)oxy-1-((2,2,6,6-tetramethyl-

piperidin-1-yl)oxy)ethyl)benzonitrile, **3n**, M.P.=119-120 °C, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.79-7.81 (m, 4 H), 7.63-7.75 (m, 4 H), 5.14-5.17 (m, 1 H), 4.70-4.73 (m, 1 H), 4.47-4.52 (m, 1 H), 1.43-1.49 (m, 5 H), 1.05-1.40 (m, 10 H), 0.73 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.9, 145.4, 134.4, 131.7, 128.4, 123.3, 118.7, 111.3, 82.6, 79.2, 60.0, 40.1, 33.8, 20.1, 16.8; IR(cm^{-1}): 2937, 2229, 1791, 1733, 1467, 1374, 1187, 1130, 1020, 996, 877, 840; HRMS (ESI) m/z: calcd for $C_{26}H_{29}N_3O_4Na^+$: [M+Na^+]= 470.2056; found: 470.2086.

2-(2-(tert-butylperoxy)-2-(4-methoxyphenyl)ethoxy)isoindoline-1,3-dione, **3o**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.71-7.81 (m, 4 H), 7.35-7.38 (m, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 5.30-5.33 (m, 1 H), 4.62-4.65 (m, 1 H), 4.44-4.48 (m, 1 H), 3.77 (s, 3 H), 1.17 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.1, 159.7, 134.3, 128.9, 128.8, 123.3, 113.7, 82.8, 80.6, 78.2, 55.1, 28.5, 26.2; IR (cm^{-1}): 2977, 2933, 1790, 1731, 1612, 1407, 1364, 1249, 1186, 1130, 1018, 996, 877, 830, 701; HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO_6Na^+$: [M+ Na^+]= 408.1423; found: 408.1415.

2-(2-phenylallyloxy)isoindoline-1,3-dione, **3p**, oil, ^{1}H NMR (400 M H_Z, $CDCl_3$): 7.81-7.83 (m, 2 H), 7.72-7.75 (m, 2 H), 7.66-7.68 (m, 2 H), 7.38-7.40 (m, 2 H), 7.33-7.37 (m, 1 H), 5.73 (s, 1 H), 5.51 (s, 1 H), 5.09 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.4, 141.2, 137.8, 134.4, 128.4, 127.9, 126.2, 123.4, 119.6, 79.7; IR (cm^{-1}): 3060, 2970, 1790, 1731, 1645, 1465, 1180, 1130, 1080, 1034, 876.

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