Catalysis Science & Technology

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cy01030f

Recyclable $(PhSe)_2$-catalyzed selective oxidation of isatin by H_2O_2: a practical and waste-free access to isatoic anhydride under mild and neutral conditions†

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Received 8th July 2015,
Accepted 21st July 2015

DOI: 10.1039/c5cy01030f

www.rsc.org/catalysis

After a series of careful conditional optimizations and catalyst screenings, a methodology to prepare isatoic anhydrides through organoselenium-catalyzed selective oxidation of isatins by H_2O_2 under mild and neutral conditions was developed. The reactions were very practical because of the recyclability of the catalyst and solvent and the convenient isolation procedures of the products. This work reports the organoselenium-catalyzed oxidation of heterocycles that greatly expands the application scopes of organoselenium catalysis. It also indicates that the organoselenium catalysts are robust enough to be recycled in industrial production if suitable isolation procedures are developed.

Introduction

Isatoic anhydrides (1*H*-benzo[*d*][1,3]oxazine-2,4-diones) are significant intermediates for the construction of many useful organic skeletons, such as quinolones,[1a,b] 2,3-dihydroquinazolin-4(1*H*)-ones,[1c] benzodiazepinones,[1d] 2-aminobenzoic acid derivatives,[1e–g] 1,2-dihydro-2-thioxo-4*H*-3,1-benzothiazin-4-ones[1h] and others.[1i] In addition, isatoic anhydrides are also abundantly employed compounds in herbicide production,[2] natural product synthesis[3] and medicinal chemistry for the preparation of enzyme inhibitors, non-nucleoside inhibitors, antagonists, *etc.*[4] Therefore, synthesis of isatoic anhydrides is an important topic in synthetic organic chemistry research. Although isatoic anhydrides can be synthesized through a series of methodologies from smaller building blocks such as *N*-methylbenzenamines,[5a] 2-isocyanophenyl lithiums,[5b] indoles,[5c] 2-aminobenzoic acids,[5d–f] *etc.*, the oxidation of isatins should be a more concise and clean choice because isatins are cheap and accessible starting materials and this procedure does not require highly toxic and hazardous chemicals for laboratory preparation. But the currently reported oxidation procedures of isatins to isatoic anhydrides always employ oxidants that generate wastes, and require a large amount of acids, which are harmful from the viewpoint of industrial production due to corrosion of equipment.[6] In 2006, Deligeorgiev *et al.* reported a nice work on the ultrasound-promoted oxidation of isatin to prepare isatoic anhydride using urea/H_2O_2.[7] But since generation of ultrasound requires special sonication equipment and consumes huge power energy and the oxidant urea/H_2O_2 inevitably leads to urea as the massive solid waste, this technology is still far away from large scale production. In addition, the method also required an acidic solvent such as acetic acid or formic acid along with drops of sulfuric acid.[7] Thus, developing practical and waste-free oxidation procedures of isatins in neutral media are not only desirable but also timely for industrial applications.

On the other hand, selenium is an important and necessary trace element for human beings and has very wide applications in biochemistry, medicinal chemistry, organic synthesis and materials science.[8] Recently, the eco-friendly aspects of organoselenium chemistry have attracted much attention of chemists[9] and among the reported studies, organoselenium catalysis is an important topic because of its clean procedures, transition metal-free conditions and the metabolizable catalyst element that is safe to the environment,[10] providing potential alternatives of transition metal catalysts in drug synthesis. Also recently, researchers have reported a series of organoselenium-catalyzed reactions[11–13] and this field is still in rapid progress in recent years. During our continuous investigations on green organic reactions with industrial potential,[12,14] we also found that the organoselenium compounds were very good catalysts for the reactions using H_2O_2 as the clean oxidant.[12] Thus, it is envisioned that isatoic anhydrides might be synthesized

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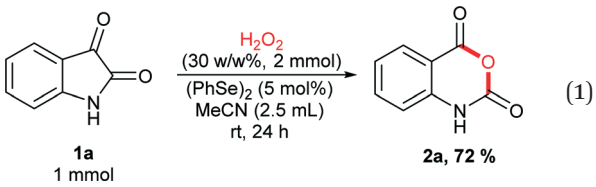
† Electronic supplementary information (ESI) available: Detailed conditional optimization tables and product NMR spectra. See DOI: 10.1039/c5cy01030f

through organoselenium-catalyzed clean oxidations under mild and neutral conditions as well. But this strategy faces tremendous challenges because of the multiple reaction points for the oxidation of the C–C bonds (paths *a* and *b*)[6f] and the possible organoselenium-catalyzed oxidation of the amidogen N–H (path *c*), as reported in the literature (Scheme 1).[13] Recently, after a series of careful conditional optimizations and catalyst screenings, we successfully overcame the above difficulties and developed an organoselenium-catalyzed selective oxidation procedure of isatins to prepare isatoic anhydrides (Scheme 1, path *b*). Herein, we wish to report our findings.

Results and discussion

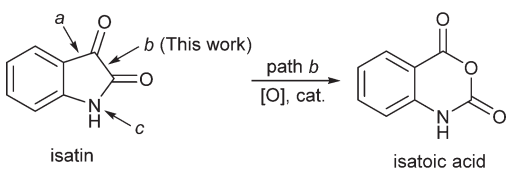
Based on our previous reports,[12] we initially stirred isatin **1a** and H_2O_2 in MeCN in the presence of $(PhSe)_2$ at room temperature (25 °C). After 24 h, the expected product isatoic anhydride **2a** could be obtained in 72% yield after purification with column chromatography (eqn (1)).



(1)

We then tried to optimize the reaction conditions. The solvent effect was first examined and parallel reactions were performed in a series of solvents such as MeCN, alcohols, water, DMF, NMP, DMSO and THF for comparison (Fig. 1). It was shown that the alcohol solvents did not help to optimize the reaction (Fig. 1, runs 2–5 *vs.* 1) and water as a solvent also resulted in a very low product yield (run 6). The other polar solvents, such as DMF, NMP and DMSO were also tested (runs 7–9) and DMF was found to be the best one among them (run 7) while the other two led to reduced product yield (run 8) or even completely restrained the reaction (run 9). A low polar solvent, THF, was also employed but gave **2a** in a very low yield (run 10).

It was noticed that although the reaction in DMF afforded product **2a** in lower yield than in MeCN, the starting material **1a** dissolved well in it. Therefore, for further optimizations, we then tried to increase the starting material solubility by employing composite solvents of MeCN with DMF. The results of the reactions performed in solvents with different DMF/MeCN ratios are shown in Fig. 2 and it was found that



Scheme 1 Possible oxidation sites of isatin.

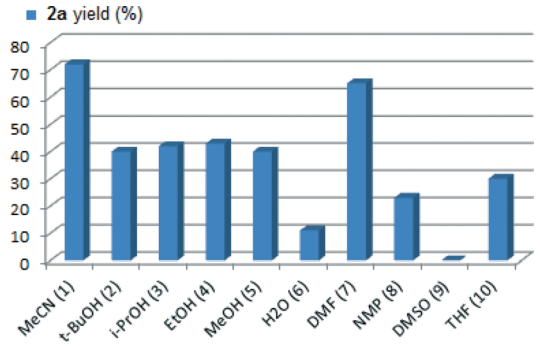


Fig. 1 Solvent effect test.[15]

the product yield reached its peak at 88% when 9 vol% DMF/MeCN was employed (Fig. 2).

Then, with the optimized solvent, the reaction temperature effect was tested, showing that room temperature (25 °C) should be the most suitable condition. The product yield decreased gradually when higher temperature was employed, probably due to the decomposition of H_2O_2 or the deep oxidation of the product (Fig. 3).

Since the reactions could not be completed and traces of the starting material were always observed by TLC even after 24 h, a series of parallel experiments were carried out in 9 vol% DMF/MeCN at 25 °C and stopped at 4 h, 6 h, 8 h, 12 h and 24 h to judge the termination of the reaction. Fig. 4 showed that the best reaction time should be 8 h and the product yield did not increase any more after then.

The effect of H_2O_2 dosage was also examined. Using 50–300 mol% of H_2O_2, five parallel reactions were performed under the screened out conditions respectively and their results are shown in Fig. 5. It was found that the product yield reached its peak when 200 mol% of H_2O_2 was employed and decreased with more H_2O_2, probably due to the deep oxidation of the product because a series of unidentified by-products were observed by TLC.

The catalyst loading effects were also investigated. Fortunately, the best catalyst loading is 5 mol% as employed initially. Lower catalyst loadings resulted in a reduced **2a** yield due to the slower reaction speed while a higher catalyst loading also gradually pulled down the product yield, probably

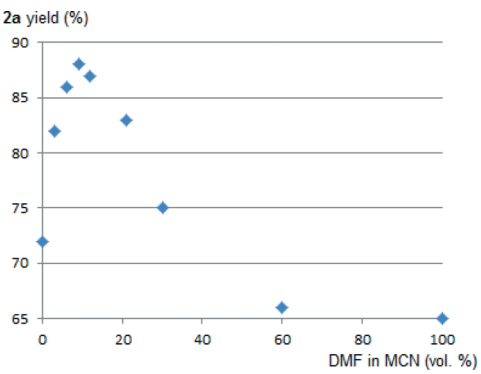


Fig. 2 DMF concentration effect test.[15]

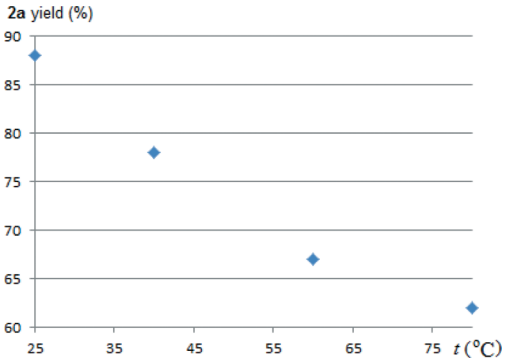


Fig. 3 Temperature effect test.[15]

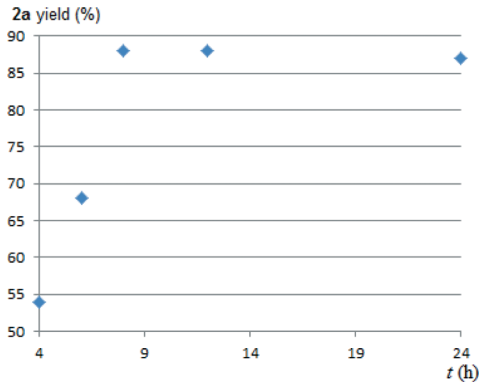


Fig. 4 Time effect test.[15]

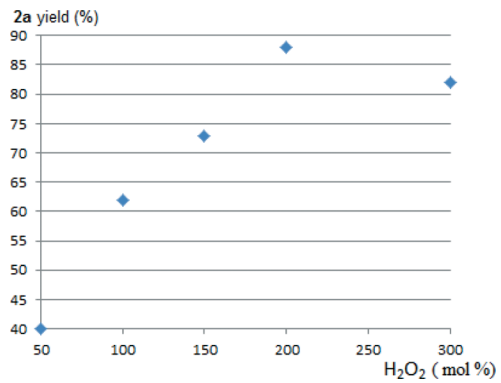


Fig. 5 H_2O_2 dosage effect test.[15]

due to the side reactions of the catalytic organoselenium species with the starting material or the product.

It was notable that unlike many reported organoselenium-catalyzed oxidations,[11–13] this reaction did not require special organoselenium catalysts and the cheapest and most available pre-catalyst $(PhSe)_2$ was screened out to be the best one (Fig. 7), probably due to the high activity of isatin which bears two carboxyl groups on the ring and the insertion of an oxygen atom releases a portion of the ring tension. These phenomena were also observed during our previous research on the Baeyer–Villiger oxidation of 2-MCBones.[12c] Catalyst

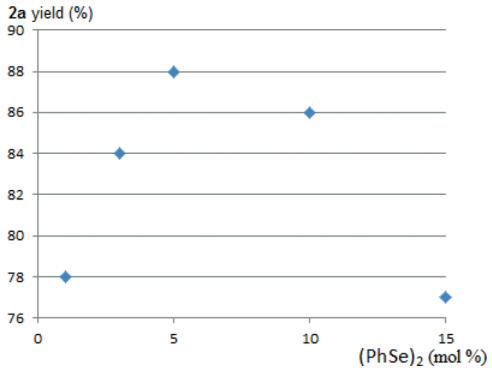


Fig. 6 $(PhSe)_2$ loading effect test.[15]

screenings showed that with most diselenides as catalysts, the reaction proceeded smoothly and gave product **2a** in moderate to good yields (Fig. 7, runs 1–7). Diselenides with a strong electron donating group {*e.g.* $[p\text{-}(CH_3)_2NC_6H_4Se]_2$, run 3} or a strong electron withdrawing group {*e.g.* $[3,5\text{-}(CF_3)_2C_6H_3Se]_2$, run 7} both led to **2a** in reduced yields. The former was probably due to the lower reaction speed while the latter was because of the too strong catalytic activity that caused over-oxidations because a series of unidentified by-products were observed by TLC. Selenides, such as EtSePh, i-PrSePh, *c*-C_6H_{11}SePh and PhSePh all resulted in decreased **2a** yields (runs 8–11). The first three were probably due to the delay of the catalytic species PhSe(O)OH generation through *syn*-selenoxide elimination with H_2O_2. For the PhSePh sample, although this compound cannot generate PhSe(O)OH *via* *syn*-selenoxide elimination, its selenoxide oxidation product also has some catalytic activities, as documented in the literature.[11n] Our previous studies have disclosed that in the presence of H_2O_2, $(PhSe)_2$ was converted to PhSe(O)OH in two steps, showing that PhSe(O)OH was the real catalytic species.[12c] However, when PhSe(O)OH was directly used (run 12), the **2a** yield was slightly reduced (run 12, 80% *vs.* run 1, 88%). This was because of the loading differences between these two catalysts, since 5 mol% of PhSe(O)OH was equivalent to only 2.5 mol% of $(PhSe)_2$, resulting in a **2a** yield similar to the case of 3 mol% $(PhSe)_2$ (84%, in Fig. 6). Similarly,

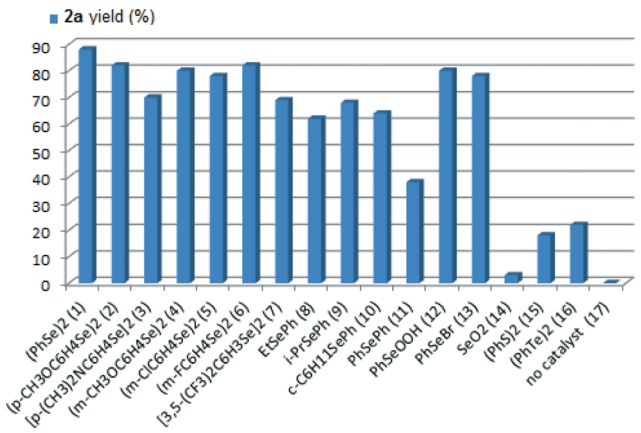


Fig. 7 Catalyst screenings.[15]

PhSeBr, which can rapidly generate PhSe(O)OH, also led to a reduced **2a** yield due to the half-cut of the real catalytic species (run 13). The inorganic selenium compound, SeO_2, only resulted in traces of product **2a** (run 14), showing that only organoselenium compounds are catalytically active for this reaction. The other chalcogen compounds, such as $(PhS)_2$ and $(PhTe)_2$, also showed some catalytic activities, but the yields of **2a** were very low (runs 15–16). Finally, a blank reaction confirmed that the reaction could not happen without a catalyst (run 17).

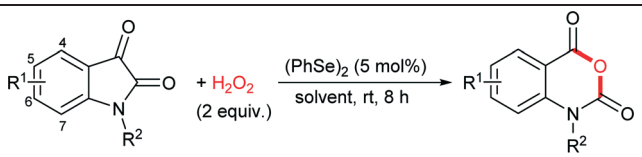
Under the optimized conditions, a series of isatins were employed, giving isatoic anhydrides in good yields (Table 1). This methodology has wide application scopes and isatins with different kinds of substituents including electron donating or electron withdrawing groups at different positions of the aromatic ring or nitrogen were all successfully oxidized to give the corresponding isatoic anhydrides, affording a convenient methodology for isatoic anhydride preparation. It was noticed that for the reactions using 9 vol% DMF/MeCN, the nitrogen-unsubstituted isatins generally afforded a higher product yield than the substituted ones (Table 1, entries 1–10 *vs.* 11–17), probably due to the higher polarity of the substrates, which led to the higher solubility in DMF/MeCN. These phenomena inspired us to perform reactions of nitrogen-substituted isatins in a lower polarity solvent, pure MeCN, which gave higher product yields than the isatins in DMF/MeCN (Table 1, entries 18–24 *vs.* 11–17).

On the basis of our previous studies as well as the references,[11–13] a plausible mechanism of this reaction is given. As proved by the ^{77}Se NMR studies in our previous reports,[12c] $(PhSe)_2$ was initially oxidized by H_2O_2 to organoselenium species $[PhSe(O)O]_2O$ (A), which afforded benzeneseleninoperoxoic acid (B) after hydrolysis. Nucleophilic addition of isatin **1** with B afforded **3**. Then, a ring breaking reaction happened[12c] in **3** and due to the higher activity of the C–C bond adjacent to the carboxyl group, path *a* was preferred, giving the final product isatoic anhydride **2** and the selenium species C. Oxidation of C by H_2O_2 regenerated B, which took part in the next cycle of reaction (Scheme 2).

To ensure that the methodology is practical for large-scale preparation, a magnified experiment for the oxidation of isatin **1a** in 50 mmol scale was performed in a 250 mL round bottom flask. It was noticed that the product precipitated at the bottom of the flask (Fig. 8). Thus, different from the previous small-scale preparations, the product could be easily isolated by simple filtration.

Because the organoselenium catalytic species were very stable and could be recycled and reused many times in our previous studies,[12a,b,d] we speculated that the mother liquid,

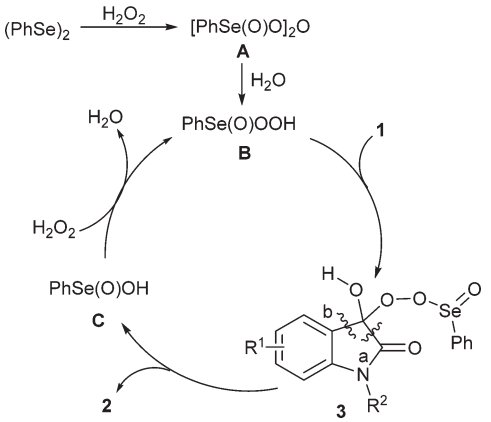
Table 1 Synthesis of isatoic anhydrides[a]



1 **2**

Entry	1: R^1, R^2	Solvent	2%[b]
1	**1a:** H, H	9 vol% DMF/MeCN	**2a:** 88
2	**1b:** 5-Me, H	9 vol% DMF/MeCN	**2b:** 86
3	**1c:** 5-MeO, H	9 vol% DMF/MeCN	**2c:** 85
4	**1d:** 5-F, H	9 vol% DMF/MeCN	**2d:** 89
5	**1e:** 5-Cl, H	9 vol% DMF/MeCN	**2e:** 80
6	**1f:** 7-Cl, H	9 vol% DMF/MeCN	**2f:** 84
7	**1g:** 4-Br, H	9 vol% DMF/MeCN	**2g:** 78
8	**1h:** 5-Br, H	9 vol% DMF/MeCN	**2h:** 81
9	**1i:** 6-Br, H	9 vol% DMF/MeCN	**2i:** 78
10	**1j:** 7-Br, H	9 vol% DMF/MeCN	**2j:** 88
11	**1k:** H, Bn	9 vol% DMF/MeCN	**2k:** 72
12	**1l:** 5-Me, Bn	9 vol% DMF/MeCN	**2l:** 73
13	**1m:** 5-Me, Bu^n	9 vol% DMF/MeCN	**2m:** 76
14	**1n:** 5-F, Bn	9 vol% DMF/MeCN	**2n:** 72
15	**1o:** 5-F, Bu^n	9 vol% DMF/MeCN	**2o:** 71
16	**1p:** 5-Cl, Bn	9 vol% DMF/MeCN	**2p:** 71
17	**1q:** 5-Cl, Bu^n	9 vol% DMF/MeCN	**2q:** 70
18	**1k:** H, Bn	MeCN	**2k:** 75
19	**1l:** 5-Me, Bn	MeCN	**2l:** 75
20	**1m:** 5-Me, Bu^n	MeCN	**2m:** 84
21	**1n:** 5-F, Bn	MeCN	**2n:** 76
22	**1o:** 5-F, Bu^n	MeCN	**2o:** 75
23	**1p:** 5-Cl, Bn	MeCN	**2p:** 80
24	**1q:** 5-Cl, Bu^n	MeCN	**2q:** 78

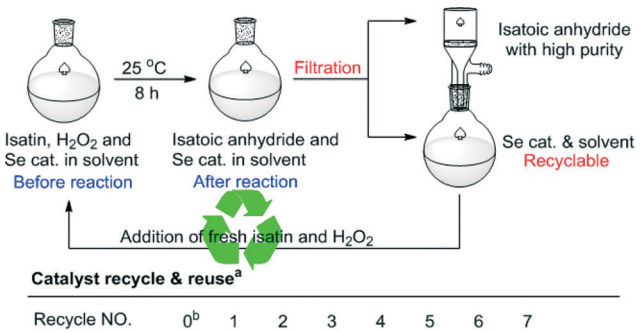
[a] 1 mmol of **1**, 2 equiv. H_2O_2, 0.05 mmol of $(PhSe)_2$, and 2.5 mL of solvent were stirred at rt (25 °C) for 8 h. [b] Isolated yields.



Scheme 2 Possible mechanisms.

Fig. 8 The round bottom flask after reaction.

which contained the organoselenium catalyst, could be directly reused in the next turn of reaction by adding fresh isatin **1a** and H_2O_2 (Fig. 9). It was shown that the recycled mother liquid resulted in even higher **2a** yield than its first use, possibly because of the fact that part of the product **2a** of the first turn experiment saturated the mother liquid and thus reduced the loss of the product caused by its partial dissolution in the next cycles. The product yield began to decrease after recycling of the mother liquid three times, possibly because for each reaction, some water was introduced from aqueous H_2O_2 and the accumulated water finally changed the solvent properties and thus reduced the product yield. It was shown that the mother liquid could be reused for at least seven times with satisfactory **2a** yield (77–94%) and high purity, which was confirmed by the ^{1}H NMR spectrum (Fig. 10).



Catalyst recycle & reuse[a]

Recycle NO.	0[b]	1	2	3	4	5	6	7
2a weight (g)	6.9	7.1	7.5	7.7	7.3	7.1	6.8	6.3
2a yield (%)[c]	84	87	92	94	89	87	83	77

[a] Reaction scale: 50 mmol; [b] First use; [c] Isolated yields based on isatin.

Fig. 9 Catalyst recycle & reuse.

Conclusions

In conclusion, we developed a concise method for the synthesis of isatoic anhydrides from available isatins through organoselenium-catalyzed oxidation. Compared with the known methodologies, this method is waste-free and can be performed under mild and neutral conditions, which are more preferable for large-scale preparation. The reaction is metal-free and the catalytic element selenium is eco-friendly. In addition, the easily recyclable catalyst and solvent and the convenient isolation procedures made this method more practical than the previously reported studies on isatoic anhydride synthesis and organoselenium catalysis. To the best of our knowledge, this reaction is the first example of the organoselenium-catalyzed Baeyer–Villiger oxidation of heterocycles and expands the application scopes of organoselenium catalysis. More research studies on the applications of organoselenium catalysis are on the way in our laboratory.

Experimental section

General methods

The isatins were purchased from reagent merchant with their purities more than 98% and were directly used as received. The organoselenium catalysts were commercially available or prepared according to the literature.[12d] The solvents were

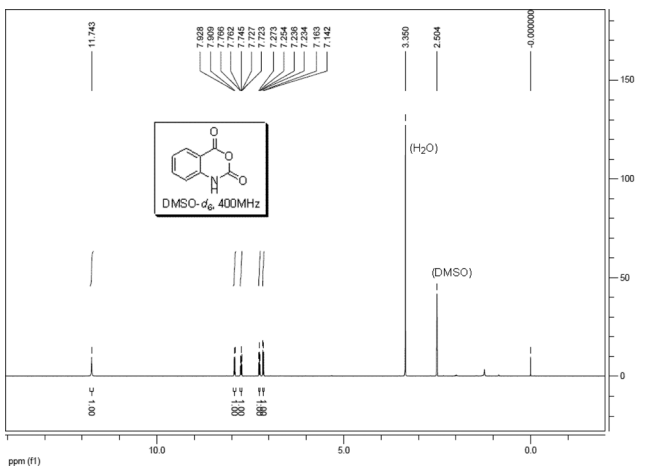


Fig. 10 Product ^{1}H NMR spectrum of the 7th catalyst recycle & reuse reaction.

analytically pure (AR) and directly used without any special treatment. All reactions were carried out in open air in Schlenk tubes and monitored by GC-MS and/or TLC. In small-scale experiments (1 mmol), the products were all purified by column chromatography on silica gel using petroleum ether and ethyl acetate (ratio 2/1) as the eluent. The melting points were measured by a WRS-2A digital instrument. The IR spectra were measured on a Bruker Tensor 27 infrared spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 600/400 instrument (600 or 400 MHz for ^{1}H and 150 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ as the solvent and Me_4Si as the internal standard. The chemical shifts for ^{1}H and ^{13}C NMR were referenced to internal Me_4Si (0 ppm) and the *J*-values were shown in Hz. The mass spectra were measured on a Shimadzu GCMS-QP2010 Ultra spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker microTOF-Q II instrument.

Typical procedure for the synthesis of 2a

1 mmol of **1a** (147.1 mg) and 0.05 mmol of $(PhSe)_2$ (5 mol%, 15.6 mg) were added. A solution of 2 mmol of H_2O_2 (30 w/w%, 226.0 mg) in 2.5 mL of 9 vol% DMF/MeCN was injected by a syringe. The mixture was stirred at 25 °C for 8 h and the solvent was evaporated by vacuum. The residue was purified by column chromatography (eluent: petroleum ether/EtOAc 2/1) to give 143.5 mg of **2a** (yield 88%). Other isatoic anhydrides **2** were prepared in a similar way.

Detailed procedure for the large scale synthesis and the catalyst recycle and reuse

To a 250 mL round bottom flask, 7.35 g of isatin **1a** (50 mmol), 0.78 g of $(PhSe)_2$ (2.5 mmol), 91 mL of MeCN and 9 mL of DMF were added in that order. 10.2 mL of H_2O_2 (30 w/w%, d = 1.11 g mL^{-1}, 100 mmol) was then dropped into the stirred solution. The mixture was stirred for 8 h at room temperature. The precipitated product isatoic anhydride **2a** and the mother liquid were isolated by simple filtration. The product **2a** was washed with a small amount of EtOH and dried in air. The mother liquid was directly reused both as a solvent and a catalyst in the next cycle. The detailed results are summarized in Fig. 9.

Characterization of the products

1*H*-Benzo[*d*][1,3]oxazine-2,4-dione 2a. Yellow solid. M.p. 231.3–232.2 °C (lit. 233–234 °C). IR (KBr): 3240, 3104, 2939, 1767, 1617, 1513, 1487, 1438, 1362, 1327, 1264, 1152,1121, 1011, 904, 792, 763 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.73 (s, 1H, NH), 7.92 (dd, J = 1.2 Hz, J = 7.8 Hz, 1H, ArH), 7.74 (dt, J = 2.4 Hz, J = 7.2 Hz, 1H, ArH), 7.25 (dt, J = 2.4 Hz, J = 7.2 Hz, 1H, ArH), 7.16 (d, J = 7.8Hz, 1H, ArH). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 159.8, 147.1, 141.4, 136.9, 128.9, 123.5, 115.3, 110.2. MS (EI, 70 eV): m/z (%) 163(22) [M$^+$], 119(100) [M$^+$ − CO_2], 92(70). Known compound (118-48-9).[5b]

6-Methyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2b. Yellow solid. M.p. 248.6–249.8 °C (lit. 249–250 °C). IR (KBr): 3109, 2010, 1781, 1728, 1622, 1514, 1422, 1349, 1269, 1145, 1030, 1001,916, 825, 780, 728 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.64 (s, 1H, NH), 7.71 (s, 1H, ArH), 7.56 (d, J = 8.4 Hz, 1H, ArH), 7.06 (d, J = 8.4 Hz, 1H, ArH), 2.33 (s, 3H, CH_3). ^{13}CNMR (150 MHz, DMSO-d_6) δ (ppm): 159.9, 147.1, 139.2, 137.9, 132.9, 128.3, 115.3, 110.0, 20.0. MS (EI, 70 eV): m/z (%) 177(20) [M$^+$], 133(100), 104(58). Known compound (4692-99-3).[16a]

6-Methoxy-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2c. Yellow solid. M.p. 242.5–243.3 °C (lit. 242–244 °C). IR (KBr): 3246, 3183, 1782, 1733, 1623, 1507, 1422, 1360, 1334, 1257, 1157, 1016, 920, 838, 753 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.6 (s, 1H, NH), 7.38 (dd, J = 2.4 Hz, J = 9.0 Hz, 1H, ArH), 7.33 (d, J = 2.4 Hz, 1H, ArH), 7.11 (d, J = 9.0 Hz, 1H, ArH), 3.81 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 159.8, 155.2, 146.9, 135.5, 125.7, 116.9, 110.6, 109.8, 55.7. MS (EI, 70 eV): m/z (%) 193(25) [M$^+$], 149(88), 106(100). Known compound (37795-77-0).[16b]

6-Fluoro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2d. Yellow solid. M.p. 263.7–264.6 °C (lit. 265–268 °C). IR (KBr): 3188, 2932, 1941, 1760, 1696, 1426, 1259, 1224, 1119, 1040, 1002, 933, 893 847, 735 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.80 (s, 1H, NH), 7.70–7.64 (m, 2H, ArH), 7.20–7.17 (m, 1H, ArH). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 159.2 (d, J_{C-F} = 3.2 Hz), 157.5 (d, J_{C-F} = 239.9 Hz), 146.8, 138.1, 124.8 (d, J_{C-F} = 24.2 Hz), 117.5 (d, J_{C-F} = 7.8 Hz), 114.0 (d, J_{C-F} = 24.2 Hz), 111.4 (d, J_{C-F} = 8.1 Hz). MS (EI, 70 eV): m/z (%) 181(22) [M$^+$], 137(100), 109(53). Known compound (321-69-7).[6f]

6-Chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2e. Yellow solid. M.p. 277.0–278.6 °C (lit. 278–281 °C). IR (KBr): 3098, 1772, 1698, 1619, 1495, 1419, 1343, 1272, 1243, 1186, 1038, 999, 909 846, 811, 751 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.85 (s, 1H, NH), 7.86 (d, J = 8.4 Hz, 1H, ArH), 7.80–7.78 (m, 1H, ArH), 7.16 (d, J = 8.4 Hz, 1H, ArH). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 158.9, 146.7, 140.3, 136.6, 127.6, 127.1, 117.4, 112.0. MS (EI, 70 eV): m/z (%) 197(20) [M$^+$], 153(100), 125(35). Known compound (4743-17-3).[16c]

8-Chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2f. Yellow solid. M.p. 212.4–214.6 °C (lit. 210–215 °C). IR (KBr): 3482, 3368, 3058, 1796, 1670, 1608, 1586, 1548, 1455, 1420, 1338, 1312, 1272, 1251, 1164, 1077, 1014, 892, 752 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 7.74 (dd, J = 1.2 Hz, J = 7.8 Hz, 1H, ArH), 7.48 (dd, J = 1.8 Hz, J = 7.2 Hz, 1H, ArH), 6.58 (t, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.1, 146.9, 133.7, 130.3, 119.0, 115.1, 111.7. MS (EI, 70 eV): m/z (%) 197(13) [M$^+$], 153(88), 44(100). Known compound (63497-60-9).[6f,16d]

5-Bromo-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2g. Yellow solid. M.p. 218.3–220.6 °C. IR (KBr): 3182, 3102, 2995, 2916, 1771, 1700, 1608, 1588, 1506, 1465, 1428, 1362, 1305, 1257, 1215, 1181, 1031, 801, 751 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.82 (s, 1H), 7.57–7.50 (m, 2H), 7.14 (d, J = 7.8

Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 156.8, 146.5, 144.0, 136.7, 129.3, 123.3, 115.1, 109.2. MS (EI, 70 eV): *m*/*z* (%) 241(18) [M^+], 197(100), 170(50). Known compound (77603-45-3).[5e]

6-Bromo-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2h. Yellow solid. M.p. 233.6–234.9 °C (lit. 235 °C). IR (KBr): 3491, 3240, 3179, 3094, 1772, 1701, 1615, 1496, 1474, 1417, 1340, 1272, 1184, 1138, 1035, 998, 907, 845, 764 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.85 (s, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 2.4 Hz, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 158.8, 146.7, 140.6, 139.3, 130.6, 117.6, 114.6, 112.4. MS (EI, 70 eV): *m*/*z* (%) 241(19) [M^+], 197(100), 170(26). Known compound (4692-98-2).[16e]

7-Bromo-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2i. Yellow solid. M.p. 220.1–222.5 °C. IR (KBr): 3179, 3104, 1780, 1706, 1612, 1485, 1403, 1341, 1246, 1072, 1025, 922, 892, 785, 760 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.81 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 1.8 Hz, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 159.3, 146.8, 142.4, 130.7, 130.3, 126.5, 117.7, 109.7. MS (EI, 70 eV): *m*/*z* (%) 241(20) [M^+], 197(100), 170(56). Known compound (76561-16-5).[5e]

8-Bromo-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2j. Yellow solid. M.p. 191.8–193.0 °C (lit. 192–194 °C). IR (KBr): 3243, 3215, 3131, 1792, 1721, 1608, 1494, 1459, 1346, 1308, 1252, 1213, 1136, 1023, 815, 788, 745 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.07 (s, 1H), 8.02 (dd, *J* = 1.2 Hz, *J* = 8.4 Hz, 1H), 7.95 (dd, *J* = 1.2 Hz, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 159.1, 146.5, 140.1, 139.5, 128.6, 124.5, 112.9, 107.9. MS (EI, 70 eV): *m*/*z* (%) 241(17) [M^+], 197(100), 169(13). Known compound (331646-98-1).[16f]

1-Benzyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2k. Yellow solid, yield: 72%. M.p. 138.8–140.6 °C (lit. 139–141 °C). IR (KBr): 3028, 2921, 1662, 1575, 1516, 1440, 1410, 1362, 1324, 1279,1250, 1160, 1108, 1075, 1028, 898 834, 789 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 7.8Hz, 1H, ArH), 7.36–7.32 (m, 5H, ArH), 7.28–7.26 (m, 1H, ArH), 6.64–6.61 (m, 2H, ArH), 4.49 (s, 2H, NCH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 151.6, 138.7, 135.6, 132.6, 129.1, 128.7, 128.2, 127.2, 127.0, 115.1, 111.9, 46,9. MS (EI, 70 eV): *m*/*z* (%) 253(35) [M^+], 180(85), 91(100). Known compound (35710-05-5).[1d]

1-Benzyl-6-methyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2l. Yellow solid. M.p. 147.3–148.8 °C. IR (KBr): 2917, 2861, 1780, 1619, 1574, 1445, 1384, 1317, 1280, 1063, 1048,912, 892, 808, 775 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.96 (s, 1H, ArH), 7.43 (d, *J* = 9.0 Hz, 1H, ArH), 7.37–7.34 (m, 2H, ArH), 7.31–7.28 (m, 3H, ArH), 7.00 (d, *J* = 8.4 Hz, 1H, ArH), 5.29 (s, 2H, NCH_2), 2.37 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 158.5, 148.5, 139.2, 138.2, 134.6, 134.2, 130.5, 129.1, 128.1, 126.6, 114.7, 111.7, 48.5, 20.4. MS (EI, 70 eV): *m*/*z* (%) 267(27) [M^+], 194(59), 91(100). Known compound (35710-11-3).[16g]

1-Butyl-6-methyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2m. Yellow solid. M.p. 142.1–143.3 °C. IR (KBr): 2957, 2862, 2370, 1720, 1655, 1568,1512, 1476, 1440, 1406, 1383, 1221, 1162, 1126,801, 745 cm^{-1}. ^{1}H NMR (600 MHz, CDCl3) δ (ppm): 7.96 (s, 1H, ArH), 7.55 (dd, *J* = 1.2 Hz, *J* = 9.0 Hz, 1H, ArH), 7.06 (d, *J* = 8.4Hz, 1H, ArH), 4.04 (t, *J* = 7.8 Hz, 2H, NCH_2), 2.41 (s, 3H, CH_3), 1.76–1.71 (m, 2H, CH_2), 1.48–1.45 (m, 2H, CH_2), 1.0 (t, *J* = 7.5Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 158.8, 147.8, 139.2, 138.3, 133.9, 130.5, 113.9, 111.6, 44.7, 28.9, 20.4, 19.9, 13.7. MS (EI, 70 eV): *m*/*z* (%) 233(22) [M^+], 146(100), 133(78). HRMS calcd. for $C_{13}H_{16}NO_3$ ([M + H]$^+$): 234.1125; found: 234.1130.

1-Benzyl-6-fluoro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2n. Yellow solid. M.p. 136.6–138.3 °C. IR (KBr): 2917, 2600, 1669, 1581, 1523, 1493, 1342, 1310, 1284, 1260, 1226, 1145, 1025, 938, 886, 753 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (dd, *J* = 3.0 Hz, *J* = 7.8 Hz, 1H, ArH), 7.37–7.28 (m, 6H, ArH), 7.10 (dd, *J* = 3.6 Hz, *J* = 9.0 Hz, 1H, ArH), 5.30 (s, 2H, NCH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 158.5 (d, J_{C-F} = 245.9 Hz), 157.5 (d, J_{C-F} = 2.9 Hz), 148.1, 137.9, 134.1, 129.3, 128.3, 126.6, 125.0 (d, J_{C-F} = 23.7 Hz), 117.0 (d, J_{C-F} = 7.7 Hz), 116.3 (d, J_{C-F} = 24.2 Hz), 113.2 (d, J_{C-F} = 8.0 Hz), 48.9. MS (EI, 70 eV): *m*/*z* (%) 271(20) [M^+], 198(43), 91(100). Known compound (749865-71-2).[16h]

1-Butyl-6-fluoro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2o. Yellow solid. M.p.129.6–131.2 °C. IR (KBr): 2923, 2858, 2724, 2547, 1659, 1579, 1518, 1388, 1306, 1224, 1146, 1021, 935, 807 768 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.66–7.64 (m, 1H, ArH), 7.17–7.14 (m, 1H, ArH), 6.65–6.63 (m, 1H, ArH), 3.19(t, *J* = 7.2 Hz, 2H, NCH_2), 1.69–1.65 (m, 2H, CH_2), 1.48–1.44 (m, 2H, CH_2), 0.98 (t, *J* = 7.5Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 151.8 (d, J_{C-F} = 231.6 Hz), 147.8, 127.2, 122.3 (d, J_{C-F} = 22.8 Hz), 116.4 (d, J_{C-F} = 23.0), 111.5 (d, J_{C-F} = 6.9 Hz), 107.3, 42.0, 30.2, 19.3, 12.9. MS (EI, 70 eV): *m*/*z* (%) 237(19) [M^+], 150(100), 137(79). HRMS calcd. for $C_{12}H_{12}FNNaO_3$ ([M + Na]$^+$): 260.0693; found: 260.0699.

1-Benzyl-6-chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2p. Yellow solid. M.p. 147.0–148.8 °C (lit. 147–149 °C). IR (KBr): 2922, 2852, 2541, 1668, 1571, 1443, 1338, 1312, 1280, 1228, 1158, 1117, 1024, 917, 894, 873 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 2.4 Hz, 1H, ArH), 7.36–7.32 (m, 4H, ArH), 7.29 (d, *J* = 5.4 Hz, 1H, ArH), 7.24 (d, *J* = 2.4 Hz, 1H, ArH), 6.58 (d, *J* = 9.0 Hz, 1H, ArH), 4.47 (s, 2H,NCH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.1, 138.2, 135.5, 131.7, 129.0, 128.8, 128.2, 127.4, 126.9, 119.7, 113.4, 109.7, 47.0. MS (EI, 70 eV): *m*/*z* (%) 243 [(M − 44)$^+$, 100], 288 [(M + 1)$^+$, 30]. Known compound (57384-84-6).[16i]

1-Butyl-6-chloro-1*H*-benzo[*d*][1,3]oxazine-2,4-dione 2q. Yellow solid. M.p. 140.8–142.2 °C. IR (KBr): 2956, 2924, 2854, 2389, 2318, 1654, 1566, 1383, 1307, 1216, 1157, 1017, 907, 871 772 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.12 (d, *J* = 2.4 Hz, 1H, ArH), 7.70 (dd, *J* = 2.4 Hz, *J* = 9.0Hz, 1H, ArH), 7.13 (d, *J* = 9.0 Hz, 1H, ArH), 4.05 (t, *J* = 7.8 Hz, 2H, NCH_2), 1.76–1.71 (m, 2H, CH_2), 1.50–1.44 (m, 2H, CH_2), 1.01 (t, *J* = 7.2Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 157.6, 147.3, 139.9, 137.3, 130.1, 129.6, 115.7, 113.0, 45.1, 28.9, 19.9, 13.8. MS (EI, 70 eV): *m*/*z* (%) 253(24) [M^+], 166(100), 111(40). Known compound (144155-83-9).[16j]

Acknowledgements

This work was supported by the NNSFC (21202141, 21173182), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions and the Yangzhou Nature Science Foundation (YZ2014040) and the Opening Foundation of the Key Laboratory of Environmental Materials and Engineering of Jiangsu Province (K14010). We thank Prof. Mark Lautens for suggestions and Miss Hongyan Li and the analysis centre of Yangzhou University for assistance.

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