Cluster

Diphenyl Diselenide Catalyzed Oxidative Degradation of Benzoin to Benzoic Acid

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Abstract The diphenyl diselenide catalyzed oxidative degradation of benzoin to benzoic acid is reported. As this reaction can convert the malodorous compound into an odorless and innocuous product under mild conditions, it might be useful for pollutant disposal. The reaction does not require a transition-metal catalyst or a chemical oxidant, so that it can be performed at low cost and without generation of wastes. This is believed to be the first example of the use of organoselenium catalysis technology in pollutant destruction, thereby expanding its range of applications.

Key words diphenyl diselenide, organoselenium catalysis, green chemistry, benzoin, pollutant destruction, benzoin

Benzoin (2-hydroxy-1,2-diphenylethanone) is a wellknown flavoring agent that has been widely used for many years. Owing to its unique biological and chemical activities, this compound is now widely used in many areas, both in the laboratory and in industry, for example, in organic synthesis, medicinal chemistry, food chemistry, and materials science.¹ Although benzoin has a low toxicity, its strong smell can cause pollution in large-scale applications. Currently, benzoin can be eliminated by oxidation methods, but these reactions usually require transition-metal catalysts and chemical oxidants, which can be expensive and might lead the production of large quantities of hazardous solid wastes.² Therefore, the development of a transitionmetal-free and waste-free method for degrading benzoin to form odorless and innocuous small molecules is of practical interest, as this issue needs to be resolved from the point of view of environmental protection.



First example of pollutant degradation through Se catalysis

Selenium is a ubiquitous element with distinctive properties. Selenium compounds can serve as building blocks in organic syntheses, as bioactive components in the development of medicines, and as unique active sites in materials science.³ Recently, the catalytic activities of selenium compounds have begun to attract the attention of chemists.⁴ Organoselenium-catalyzed reactions can be used to construct a series of complex organic skeletons that are difficult to be built through conventional methods.⁵ Organoselenium-catalyzed asymmetric synthesis has been used to prepare chiral compounds.⁶ Organoselenium compounds are also widely used in waste-free procedures for green syntheses,⁷ and such techniques have become useful because heterogeneous Se catalysts have been developed and successfully applied in several cases.8 Our group aims to develop green catalysis technologies,9,10 including organoselenium-catalyzed green reactions.¹⁰ We recently found that benzoin can be oxidized by H₂O₂ to produce benzoic acid in good yield in the presence of diphenyl diselenide as a catalyst. The Se catalyst is sufficiently robust to permit its reuse at least six times without deactivation. This reaction might provide a new method for eliminating of benzoin in environmental-protection projects. We report our findings below.

As calculated from the chemical equation, the oxidation of benzoin (**1a**) to benzoic acid (**2a**) should consume two equivalents of H_2O_2 (200 mol% based on **1a**). Therefore, on the basis of our experience in previous investigations, we stirred 1 mmol of benzoin (**1a**), 2 mmol of H_2O_2 , and 0.05 mmol of (PhSe)₂ in 2 mL of MeCN at room temperature (~25 °C) for 24 hours. After purification, the benzoic acid (**2a**) was obtained in 68% yield (Table 1, entry 1). Because thin-layer chromatography (TLC) indicated that the reaction was incomplete, and because the starting material **1a**

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was recovered in 23% yield, we considered that H₂O₂ might partially decompose during the reaction process. Therefore, an excess of H₂O₂ was required, and we initially tested the reaction with a 50 mol% excess of H_2O_2 ; in this case, the product yield increased to 72%, but unreacted benzoin (1a) was still recovered in 11% yield (entry 2). The use of 200 mol% of H₂O₂ increased the product yield to 82%, and benzoin (1a) was completely converted in the reaction (entry 3). However, a further increase in the amount of oxidant decreased the yield, and a series of unidentified byproducts were generated (entries 4 and 5). Therefore, the optimal dosage of H₂O₂ is 400 mol% versus **1a** (i.e., a 100 mol% excess). The effect of the catalyst loading on the reaction was also investigated. The yield of benzoic acid (2a) decreased on reducing the amount of catalyst (entries 6 and 7) because of the lower reaction rate; unreacted starting material 1a remained, as shown by TLC, and could be isolated to calculate the conversion ratios of **1a** shown in Table 1. The use of more catalyst resulted in a reduced product yield, due to the generation of the unidentified byproducts (entries 8 and 9). Therefore, the best catalyst loading for this reaction is 5 mol%, as we initially used (entry 3).

 Table 1
 Optimization of the H2O2 Dosage and Amount of Catalyst^a

		H ₂ O ₂ → MeCN, rt, 24 h	H_{2a}	0
Entry	H ₂ O ₂ ^b (mol%)	(PhSe) ₂ ^b (mol%)	Conversion ^c (%)	Yield ^d (%)
1	200	5	77	68
2	300	5	89	72
3	400	5	100	82
4	500	5	100	75
5	600	5	100	71
6	400	1	64	48
7	400	3	70	60
8	400	10	100	65
9	400	20	100	51

^a Reaction conditions: 1a (1 mmol), MeCN (2 mL), r.t., 24 h.

^b Molar dosage based on benzoin (**1a**). ^c Conversion ratio of **1a**.

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^d Isolated yield of **2a** based on benzoin (**1a**).

Next, a series of solvents were tested to optimize the reaction. Water, as the most ecofriendly solvent, was our first choice but, unfortunately, it gave a lower yield of **2a**, and the starting material **1a** was incompletely converted (Table 2, entry 1). Reactions in alcohols or acetone also resulted in poor product yields (entries 2–4). For ether-type solvents, the reaction in THF afforded benzoic acid (**2a**) in 73% yield, whereas in 1,4-dioxane, the yield fell to 45% (entries 5 and 6). In the highly polar solvents DMF, DMSO, and NMP, the product yields were rather low (entries 7–9), so MeCN was finally selected as the best solvent among the candidates examined (entry 10). The effect of the reaction temperature was also investigated. When the reaction was performed at ice–water temperature, although fewer byproducts were formed, the reaction was markedly retarded and product **2a** was obtained in only 28% yield, and more than 60% of the starting material was not recovered (entry 11). However, elevating the reaction temperature did not improve the reaction and, despite producing higher reaction rates, higher reaction temperatures resulted in increased generation of byproducts and reduced the product yield (entries 12–14).

Table 2 Optimization of the Reaction temperature and Solvent^a

	Ph Ph H 20 OH 400 m 1a	5 mol% (PhS 00% solvent, 24	$\stackrel{e)_2}{\longrightarrow} \stackrel{O}{\underset{Ph}{\longrightarrow}} \stackrel{O}{\underset{OH}{\longrightarrow}} + H$	l ₂ O
Entry	Solvent	Temp (°C)	Conversion ^b (%)	Yield⁰ (%
1	H ₂ O	r.t.	64	56
2	EtOH	r.t.	68	32
3	MeOH	r.t.	70	35
4	acetone	r.t.	74	66
5	THF	r.t.	94	73
6	1,4-dioxane	r.t.	61	45
7	DMF	r.t.	35	27
8	DMSO	r.t.	52	40
9	NMP	r.t.	8	5
10	MeCN	r.t.	100	82
11	MeCN	0	39	28
12	MeCN	40	100	70

^a Reaction conditions: **1a** (1 mmol), H₂O (4 mmol), (PhSe)₂ (0.05 mmol),

100

100

54

37

60

80

MeCN (2 mL), r.t., 24 h.

MeCN

MeCN

13

14

^b Conversion ratio of benzoin (**1a**). ^c Isolated yield of **2a** based on benzoin (**1a**).

Our previous studies had shown that the use of functionalized organoselenium compounds as catalysts might improve the catalytic reaction,¹⁰ so we screened various organoselenium catalysts. The results shown in Table 3 indicate that electron-rich diselenides had poor catalytic activities and led to decreased yields of benzoic acid (**2a**) and residual unreacted starting material **1a**, as observed by TLC (Table 3, entries 1–3). Unlike many reported cases, the use of diaryl diselenides with electron-withdrawing substituents also resulted in poor product yields because of the generation of unidentified byproducts (entries 4–7). Bulky benzyl and alkyl diselenides were also tested but failed to give any improvement in the reaction (entries 8–10). When PhSeBr, PhSeO₂H, EtSePh, or *i*-PrSePh was employed, the yield of **2a** decreased to 52–60% (entries 11–14), a similar

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result to that obtained by the reaction in the presence of 3 mol% of (PhSe)₂ (entry 7). This is possibly due to the halving of the amount of the actual catalytic species, PhSeO₂H (see below).

Table 3 Screening of Se Catal	ystsª
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Ph	5 mol% Se cat.	0
$H = H_2O_2$ OH 400 mol%	MeCN, rt, 24 h	Ph OH $+ H_2O$
1a		2a

Entry	Se catalyst	Conversion ^b (%)	Yield ^c (%)
1	(PhSe) ₂	100	82
2	$(4-MeC_6H_4Se)_2$	83	76
3	$(4-MeOC_6H_4Se)_2$	62	56
4	$(4-FC_6H_4Se)_2$	89	64
5	$(3-FC_6H_4Se)_2$	87	66
6	$(2-FC_6H_4Se)_2$	82	61
7	$[3,5-(F_3C)_2C_6H_3Se]_2$	91	44
8	(1-C ₁₀ H ₈ Se)	85	72
9	(BnSe) ₂	87	80
10	(CySe) ₂	84	78
11	PhSeBr	64	56
12	PhSeO ₂ H	67	58
13	EtSePh	72	60
14	<i>i</i> -PrSePh	66	52

^a Reaction conditions: 1a (1 mmol), H₂O (4 mmol), Se catalyst (0.05 mmol), MeCN (2 mL), r.t., 24 h.

^b Conversion ratio of benzoin (1a).

^c Isolated yield of **2a** based on benzoin (**1a**).

The scalability of the reaction was next examined, and a 100 mmol-scale reaction was tested. We were pleased to find that in this large-scale preparation, the dosage of H_2O_2 could be reduced to 120% without a decrease in the product vield. Product 2a was purified by distillation rather than preparative TLC, as used in the small-scale reaction, affording a much higher yield [88% compared with 82% (Table 3, entry 1)]. Because the reaction system is simple and the organoselenium species is stable, it was possible to recover the catalytic Se-contained mixtures after distillation and to reuse it merely by adding fresh starting material, solvent, and H₂O₂ for the next run of the reaction. The results in Figure 1 show that the catalyst could be reused at least six times without an obvious decrease in the product yield.

A series of benzoin derivatives 1 were employed as substrates for the reaction under the optimized conditions (Table 3, entry 1).¹¹ The reactions were efficient and gave the corresponding carboxylic acids 2 in good yields (Table 4, entries 1-7). Generally, electron-rich substrates gave higher product yields and higher conversion ratios of the substrate



Figure 1 Catalyst recycling and reuse

Table 4 Substrate Extension^a

	0 R H H2O2 0H 400 mol%	5 mol% (PhSe) ₂	О Р ОН + Н 2	I ₂ O
Entry	R	Conversion ^b (%)	Product	Yield ^c (%)
1	Ph	100	2a	82
2	4-Tol	100	2b	85
3	4-MeOC ₆ H ₄	100	2c	88
4	4-FC ₆ H ₄	80	2d	72
5	$4-CIC_6H_4$	83	2e	76
6	$4-BrC_6H_4$	85	2f	78
7	Bn	98	2g	80

^a Reaction conditions: 1 (1 mmol), H₂O (4 mmol), (PhSe)₂ (0.05 mmol), MeCN (2 mL), r.t., 24 h.

^b Conversion ratio of **1**

^c Isolated yield based on benzoin derivative **1**.

than electron-deficient ones (Table 4, entries 1-3 and 7 versus entries 4–6).

To identify a reasonable mechanism for the reaction, we performed several experiments. First, an experiment using 10 mol% of PhSeO₂H as catalyst was performed, and it gave 2a in 78% yield (Scheme 1, Equation 1), which was similar to that produced by the reaction in the presence of 5 mol% of (PhSe)₂ (Table 1, entry 3), indicating that PhSeO₂H might be the actual catalytic species.¹⁰ Then, to examine whether the reaction proceeds through a benzil-generation step, the oxidation of benzil (3) with H₂O₂ was performed under similar conditions, giving the same product, 2a, in 73% yield as expected (Scheme 2, Equation 2).

On the basis of these experimental results and reports in the literature,^{10,12} we proposed the plausible mechanism shown in Scheme 2. Oxidation of (PhSe)₂ with H₂O₂ initially gives the peroxide 4, which we previously characterized by means of ⁷⁷Se NMR analysis;^{10g} this subsequently affords

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the organoselenium species 5 on standing or vigorous stirring. Benzoin (1a) is readily oxidized to benzil (3) by H_2O_2 in the presence of the organoselenium catalyst (Scheme 1, Equation 2).¹² Nucleophilic addition of **5** to a carbonvl group of **3** affords the organoselenium intermediate **6**, in which, two possible C-C bond-cleavage reactions are possible. However, position *a* is obviously much more active than b, due to the adjacent carbonyl group, and the reaction at this position generates benzoic anhydride (7) and benzeneseleninic acid (8) (Scheme 1, Equation 1). The former is hvdrated to give benzoic acid (2a), whereas the latter is oxidized by H_2O_2 to regenerate the catalytic species 5. Because of its reactivity with H₂O₂, the MeCN solvent might participate in the reaction, but none of the possible resulting byproducts were detected by GC-MS; this is probably due to the mild reaction conditions, which also ensured high yields of the desired major product.



In conclusion, we have reported an organoselenium-catalyzed degradation of benzoin to benzoic acid for the first time. The method does not require a transition-metal catalyst and employs H_2O_2 as a green oxidant. The catalyst was so robust that it could be recycled and reused, without deactivation. As a first example of the use of organoselenium catalysis technology for pollutant disposal, this work markedly expands the scope of this field and should attract broad attention from chemists, not only in synthetic organic chemistry, but also in related fields, such as the environment protection.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611761.

References and Notes

- For selected articles, see: (a) Niu, Z.-Q.; Cui, F.; Kuttner, E.; Xie, C.-L.; Chen, H.; Sun, Y.-C.; Dehestani, A.; Schierle-Arndt, K.; Yang, P.-D. *Nano Lett.* **2018**, *18*, 5329. (b) Haghshenas, P.; Langdon, S. M.; Gravel, M. *Synlett* **2017**, *28*, 542. (c) Burger, P.; Casale, A.; Kerdudo, A.; Michel, T.; Laville, R.; Chagnaud, F.; Fernandez, X. Food Chem. **2016**, *210*, 613.
- (2) (a) Urgoitia, G.; SanMartin, R.; Herrero, M. T.; Domínguez, E. *Chem. Commun.* **2015**, *51*, 4799. (b) Fukuda, N.; Kajiwara, T.; Katou, T.; Majima, K.; Ikemoto, T. *Synlett* **2013**, *24*, 1438. (c) Jain, S. L.; Sharma, V. B.; Sain, B. *Synth. Commun.* **2003**, *33*, 3875. (d) Imanzadeh, G. H.; Zamanloo, M. R.; Mansoori, Y.; Khodayari, A. Chin. J. Chem. **2007**, *25*, 836.
- (3) (a) Casola, K. K.; Gomes, M. R.; Back, D. F.; Zeni, G. J. Org. Chem. 2018, 83, 6706. (b) Jing, X.-B.; Chen, C.-Z.; Deng, X.; Zhang, X.; Wei, D.; Yu, L. Appl. Organomet. Chem. 2018, 32, e4332. (c) Liu, M.; Li, Y.; Yu, L.; Xu, Q.; Jiang, X. Sci. China: Chem. 2018, 61, 294. (d) Kodama, S.; Saeki, T.; Mihara, K.; Higashimae, S.; Kawaguchi, S.-i.; Sonoda, M.; Nomoto, A.; Ogawa, A. J. Org. Chem. 2017, 82, 12477. (e) Wei, D.; Hang, M.-T.; Yu, L. Sci. Rep. 2017, 7, 6376. (f) Tamai, T.; Yoshikawa, M.; Higashimae, S.; Nomoto, A.; Ogawa, A. J. Org. Chem. 2016, 81, 324. (g) Sancineto, L.; Mariotti, A.; Bagnoli, L.; Marini, F.; Desantis, J.; Iraci, N.; Santi, C.; Pannecouque, C.; Tabarrini, O. J. Med. Chem. 2015, 58, 9601. (h) Wang, Y.; Zhu, B.; Xu, Q.; Zhu, Q.; Yu, L. RSC Adv. 2014, 4, 49170. (i) Yu, L.; Wu, Y.; Chen, T.; Pan, Y.; Xu, Q. Org. Lett. 2013, 15, 144. (j) Yu, L.; Ren, L.; Yi, R.; Wu, Y.; Chen, T.; Guo, R. J. Organomet. Chem. 2011, 696, 2228. (k) Yu, L.; Ren, L.; Guo, R.; Chen, T. Synth. Commun. 2011, 41, 1958. (1) Yu, L.; Meng, J.; Xia, L.; Guo, R. J. Org. Chem. 2009, 74, 5087. (m) Yu, L.; Meng, B.; Huang, X. Synth. Commun. 2008, 38, 3142. (n) Yu, L.; Meng, B.; Huang, X. Synlett 2007, 2919. (o) Yu, L.; Huang, X. Synlett 2007, 1371. (p) Yu, L.; Chen, B.; Huang, X. Tetrahedron Lett. 2007, 48, 925. (q) Yu, L.; Huang, X. Synlett 2006, 2136.

Synlett

H. Cao et al.

- (4) For selected reviews, please see: (a) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. Angew. Chem. Int. Ed. 2009, 48, 8409. (b) Santi, C.; Santoro, S.; Battistelli, B. Curr. Org. Chem. 2010, 14, 2442. (c) Santoro, S.; Azeredo, J. B.; Nascimento, V.; Sancineto, L.; Braga, A. L.; Santi, C. RSC Adv. 2014, 4, 31521. (d) Młochowski, J.; Wójtowicz-Młochowska, H. Molecules 2015, 20, 10205. (e) Breder, A.; Ortgies, S. Tetrahedron Lett. 2015, 56, 2843. (f) Guo, R.; Liao, L.; Zhao, X. Molecules 2017, 22, 835. (g) Zheng Y., Wu A., Ke Y., Cao H., Yu L.; Chin. Chem. Lett.; DOI: 10.1016/j.cclet.2019.01.012.
- (5) For selected articles, see: (a) Depken, C.; Krätzschmar, F.; Rieger, R.; Rode, K.; Breder, A. Angew. Chem. Int. Ed. 2018, 57, 2459.
 (b) Rode, K.; Palomba, M.; Ortgies, S.; Rieger, R.; Breder, A. Synthesis 2018, 50, 3875. (c) Guo, R.; Huang, J.; Zhao, X. ACS Catal. 2018, 8, 926. (d) Ortgies, S.; Rieger, R.; Rode, K.; Koszinowski, K.; Kind, J.; Thiele, C. M.; Rehbein, J.; Breder, A. ACS Catal. 2017, 7, 7578. (e) Liao, L.; Guo, R.; Zhao, X. Angew. Chem. Int. Ed. 2017, 56, 3201. (f) Ortgies, S.; Depken, C.; Breder, A. Org. Lett. 2016, 18, 2856. (g) Guo, R.; Huang, J.; Huang, H.; Zhao, X. Org. Lett. 2016, 18, 504. (h) Cresswell, A. J.; Eey, S. T.-C.; Denmark, S. E. Nat. Chem. 2015, 7, 146. (i) Ortgies, S.; Breder, A. Org. Lett. 2015, 17, 2748. (j) Deng, Z.; Wei, J.; Liao, L.; Huang, H.; Zhao, X. Org. Lett. 2015, 17, 1834. (k) Trenner, J.; Depken, C.; Weber, T.; Breder, A. Angew. Chem. Int. Ed. 2013, 52, 8952.
- (6) (a) Luo, J.; Cao, Q.; Cao, X.; Zhao, X. Nat. Commun. 2018, 9, 527.
 (b) Liu, X.; Liang, Y.; Ji, J.; Luo, J.; Zhao, X. J. Am. Chem. Soc. 2018, 140, 4782. (c) Chen, F.; Tan, C. K.; Yeung, Y.-Y. J. Am. Chem. Soc. 2013, 135, 1232.
- (7) For selected articles on organoselenium-catalyzed green reactions, see: (a) Jing, X.; Yuan, D.; Yu, L. Adv. Synth. Catal. 2017, 359, 1194. (b) Jing, X.; Wang, T.; Ding, Y.; Yu, L. Appl. Catal., A 2017, 541, 107. (c) Wang, F.; Xu, L.; Sun, C.; Xu, Q.; Huang, J.; Yu, L. Chin. J. Org. Chem. 2017, 37, 2115. (d) Yu, L.; Chen, F.; Ding, Y. ChemCatChem 2016, 8, 1033. (e) Sancineto, L.; Tidei, C.; Bagnoli, L.; Marini, F.; Lenardão, E. J.; Santi, C. Molecules 2015, 20, 10496. (f) Yu, L.; Wang, J.; Chen, T.; Wang, Y.; Xu, Q. Appl. Organomet. Chem. 2014, 28, 652. (g) Yu, L.; Wang, J.; Chen, T.; Ding, K.; Pan, Y. Youji Huaxue 2013, 33, 1096. (h) Santi, C.; Di Lorenzo, R.; Tidei, C.; Bagnoli, L.; Wirth, T. Tetrahedron 2012, 68, 10530. (i) Santoro, S.; Santi, C.; Sabatini, M.; Testaferri, L.; Tiecco, M.

Adv. Synth. Catal. **2008**, 350, 2881. (j) ten Brink, G.-J.; Fernandes, B. C. M.; van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 224. (k) ten Brink, G.-J.; Vis, J.-M.; Arends, I. W. C. E.; Sheldon, R. A. *J. Org. Chem.* **2001**, 66, 2429. (l) Syper, L. *Tetrahedron* **1987**, 43, 2853.

- (8) (a) Yang, Y.; Fan, X.; Cao, H.; Chu, S.; Zhang, X.; Xu, Q.; Yu, L. Catal. Sci. Technol. 2018, 8, 5017. (b) Wang, Y.; Yu, L.; Zhu, B.; Yu, L. J. Mater. Chem. A 2016, 4, 10828.
- (9) Cao, H.; Zhu, B.; Yang, Y.; Xu, L.; Yu, L.; Xu, Q. Chin. J. Catal. 2018, 39, 899.
- (10) For our works on Se catalysis, see: (a) Chen, C.; Zhang, X.; Cao, H.; Wang, F.; Yu, L.; Xu, Q. Adv. Synth. Catal. 2019, 361, 603.
 (b) Cao, H.; Liu, M.; Qian, R.; Zhang, X.; Yu, L. Appl. Organomet. Chem. 2019, 33, e4599. (c) Yu, L.; Bai, Z.; Zhang, X.; Zhang, X.; Ding, Y.; Xu, Q. Catal. Sci. Technol. 2016, 6, 1804. (d) Yu, L.; Ye, J.; Zhang, X.; Ding, Y.; Xu, Q. Catal. Sci. Technol. 2015, 5, 4830.
 (e) Zhang, X.; Sun, J.; Ding, Y.; Yu, L. Org. Lett. 2015, 17, 5840.
 (f) Zhang, X.; Ye, J.; Yu, L.; Shi, X.; Zhang, M.; Xu, Q.; Lautens, M. Adv. Synth. Catal. 2015, 357, 955. (g) Yu, L.; Wu, Y.; Cao, H.; Zhang, X.; Shi, X.; Luan, J.; Chen, T.; Pan, Y.; Xu, Q. Green Chem. 2014, 16, 287. (h) Yu, L.; Li, H.; Zhang, X.; Ye, J.; Liu, J.; Xu, Q.; Lautens, M. Org. Lett. 2014, 16, 1346.
- (11) Oxidation of Benzoin (1a) to Benzoic Acid (2a); Typical Procedure
 - A reaction tube was charged with benzoin (**1a**; 212.2 mg, 1 mmol), (PhSe)₂ (15.6 mg, 0.05 mmol), and a magnetic stirrer bar. A 30% aq solution of H₂O₂ (453.5 mg, 4 mmol) in MeCN (2 mL) was then injected into the tube from a syringe, and the mixture was stirred at r.t. for 24 h. The solvent was then evaporated under vacuum, and the residue was purified by preparative TLC (PE–EtOAc, 10:1) to give benzoic acid (**2a**) as a white solid; yield: 200.2 mg (82%); mp 122.0–122.4 °C (Lit.^{12a} 122.13 °C). IR (KBr): 1915, 1680, 1485, 1455, 1398, 1324, 1291, 1181, 933, 805 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ = 8.13 (d, *J* = 8.9 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 133.7, 130.2, 129.2, 128.5.
- (12) (a) Wang, T.; Jing, X.; Chen, C.; Yu, L. J. Org. Chem. 2017, 82, 9342. (b) Kang, S.; Joo, C.; Kim, S. M.; Han, H.; Yang, J. W. Tetrahedron Lett. 2011, 52, 502.