

Copper-catalyzed tandem reaction of cyclic esterification/selenoxidation for 11-oxo-11H-5-oxa-11-selena-benzo[*a*] fluoren-6-ones synthesis

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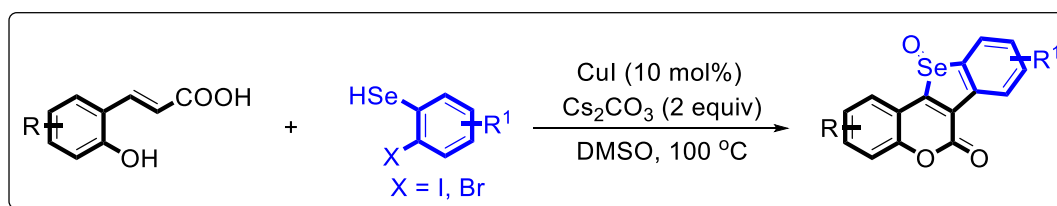
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Abstract

Organoselenium compounds have attracted much attention for their wide use in a variety of fields. A transition-metal-catalyzed cross-coupling reaction is the mostly commonly used methodology for incorporation of a Se atom into aromatic structures. A copper-catalyzed tandem reaction of cyclic esterification/selenoxidation has been developed. Starting from sample 3-(2-hydroxy-phenyl)-acrylic acids with 2-halide-benzeneselenols, 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-ones, with reported biological-activity importance, were efficiently synthesized in good-to-high yields. This new methodology provides an approach toward C(sp²)-Se bond formation.

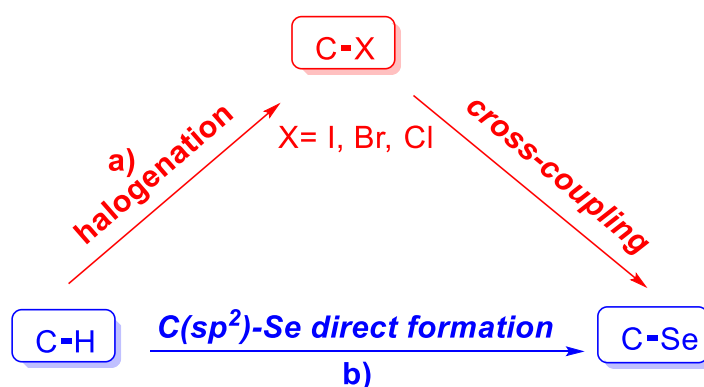


Keywords: Copper-catalyzed, tandem reaction, cyclic esterification, selenoxidation, C(sp²)-Se bond formation, organoselenium, organometallic

Introduction

Due to their important applications in the synthesis of materials,¹⁻³ pharmaceutical agents,^{4,5} fluorescent probes,⁶ and functional organic materials,⁷ organoselenium compounds syntheses have attracted extensive attention of synthetic chemists. It is known that a transition-metal-catalyzed cross-coupling reaction is the methodology used mostly for the incorporation of a Se atom into aromatic frameworks,^{8,9} however, pre-functionalization of the substrate is generally required. Simple methods of C-Se bonds formation have been scarcely described.¹⁰⁻¹²

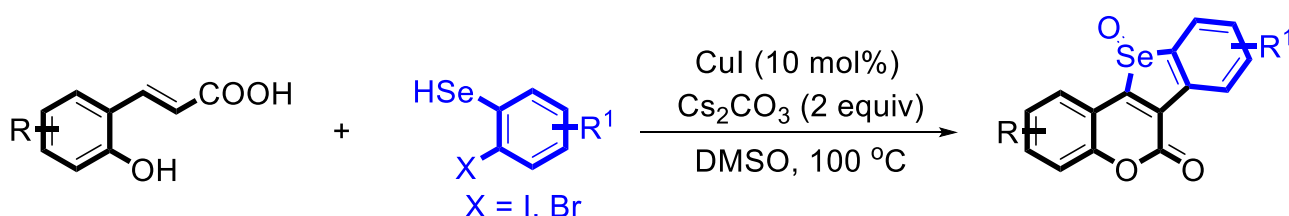
In recent decades, the activation of C-H bonds is considered to be one of the most useful C-Se bond-formation strategies (Scheme1, a). In comparison with the C-X (X = I, Br, Cl) cross-coupling reactions, however, the C(sp²)-Se bond selenoxidation direct-cross-coupling reactions need harsher conditions, and activated reaction systems (Scheme1, b).^{13,14} Given the present challenges, the development of more efficient, and environmentally friendly, chemical processes for drug discovery is required.^{15,16}



Scheme 1. C(sp²)-Se bond formation synthesis approaches.

11-Oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one constitutes the central core unit of a variety of natural polycyclic lactones with important biological activities including anticancer, antibacterial, antimyotoxic, and phytoalexine effects.^{17,18} A wide range of biological properties make 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-ones an interesting synthetic target for chemists. A number of synthetic methods have been developed for the construction of this privileged structural unit. Most of the reported procedures involve multiple steps with moderate overall yields. The starting materials are often not very readily available, and harsh reaction conditions are usually required. In view of these limitations, the development of an efficient strategy for the 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-ones synthesis is highly desirable.

Herein, we report on a novel copper-catalyzed tandem reaction of cyclic esterification/selenoxidation (Scheme 2). Versatile 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one compounds were efficiently synthesized in good-to-high yields under mild conditions. This new methodology provides an approach towards C(sp²)-Se bond formation.



Scheme 2. Copper-catalyzed tandem reaction for cyclic esterification/selenoxidation

Results and Discussion

First, reaction conditions were screened based on the model reaction of 3-(2-hydroxy-phenyl)-acrylic acid **1a** with 2-iodine-benzeneselenol **2a** (Table 1). The structure of **3a** was confirmed by NMR and MS analysis (Please see Supplementary Material). The copper catalysts displayed good catalytic activity in the presence of Cs_2CO_3 (entries 1-6). In addition, CuI exhibited superior catalytic efficiency over all of the other examined copper catalysts (entry 7). These results indicated that Cs_2CO_3 was the optimal base (entry 12), which produced the product **3a** in 84% overall yield. It was also noted that the product yield was decreased when the reaction temperature was less or greater than 100 °C (entries 13 and 14). Furthermore, the results also show that the reaction yield with DMSO as solvent is higher than that of other solvents (entries 15 and 16). Thus, the optimum reaction condition was determined to be a **1a**:**2a** ratio of 1:1.5 in the presence of CuI (10 mol%) and Cs_2CO_3 (2 equiv) in DMSO (5 mL) at 100 °C for 12 hours (Table 1, entry 12).

Table 1. Optimization of the reaction conditions^a

Reaction scheme: **1a** + **2a** $\xrightarrow[\text{base, DMSO}]{\text{Cu salt}}$ **3a**

Entry	Ni catalyst	Base	1a : 2a	3a (%) ^b
1	CuCl ₂	Cs ₂ CO ₃	1:1	nr
2	CuBr ₂	Cs ₂ CO ₃	1:1	39
3	CuSO ₄	Cs ₂ CO ₃	1:1	47
4	Cu(OAc) ₂	Cs ₂ CO ₃	1:1	42
5	CuI	Cs ₂ CO ₃	1:1	80
6	CuCl	Cs ₂ CO ₃	1:1	33
7	CuI	Na ₂ CO ₃	1:1	58
8	CuI	NaOH	1:1	68
9	CuI	Na ₂ SO ₄	1:1	55
10	CuI	NaOEt	1:1	56
11	CuI	NEt ₃	1:1	58
12	CuI	Cs ₂ CO ₃	1:1.5	84
13	CuI	Cs ₂ CO ₃	1:1.5	71 ^c
14	CuI	Cs ₂ CO ₃	1:1.5	78 ^d
15	CuI	Cs ₂ CO ₃	1:1.5	76 ^e
16	CuI	Cs ₂ CO ₃	1:1.5	57 ^f

^a Unless otherwise noted, reaction conditions were **1a** (0.5 mmol), **2a** (0.5 mmol), copper catalyst (10 mol%), base (2 equiv), DMSO (5 mL), 100 °C for 12 h.

^b Isolated yield. ^c At 90 °C. ^d At 110 °C. ^e In CHCl₃. ^f In DMF

Next, a wide array of 3-(2-hydroxy-phenyl)-acrylic acids **1** and 2-iodine-benzeneselenols **2** were subjected to this reaction conditions, providing the products **3** in good-to-excellent yields (71-90%, Table 2). 3-(2-

Hydroxy-phenyl)-acrylic acids **1** bearing an electron-donating group (Me and MeO) demonstrated better activity than those bearing an electron-withdrawing group (F, Cl, and Br). It was notable that very strong electron-withdrawing groups, e.g., the trifluoromethyl and nitro groups, failed to obtain the corresponding products.

Table 2. Copper-catalyzed tandem reaction of cyclic esterification/selenoxidation^a

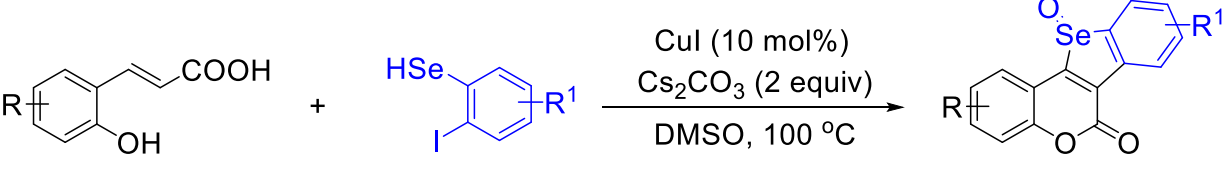
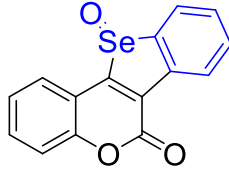
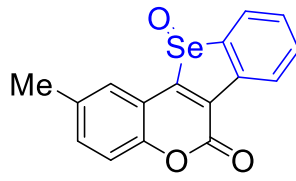
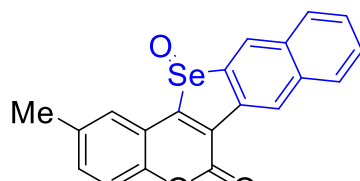
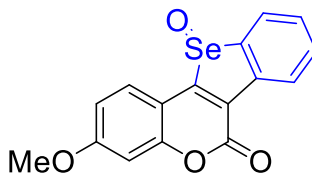
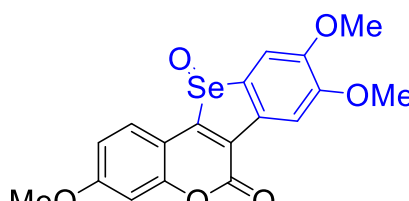
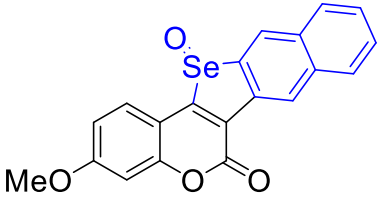
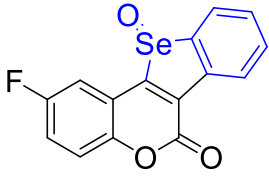
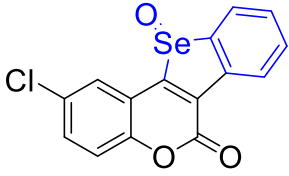
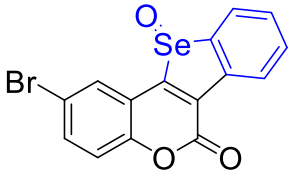
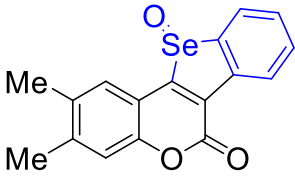
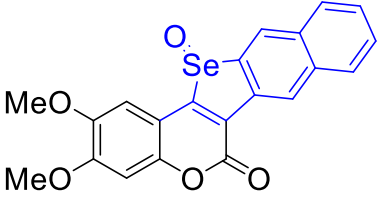
				
Entry	R	R ¹	3	Yield ^b
1	H	H	 3a	85
2	5-CH ₃	H	 3b	86
3	5-CH ₃	Acene	 3c	88
4	4-CH ₃ O	H	 3d	90
5	4-CH ₃ O	4,5-diCH ₃ O	 3e	78

Table 2. Continued

Entry	R	R ¹	3	Yield ^b
6	4-CH ₃ O	Acene	 3f	83
7	5-F	H	 3g	73
8	5-Cl	H	 3h	77
9	5-Br	H	 3i	71
10	4,5-diCH ₃	H	 3j	76
11	4,5-diCH ₃ O	Acene	 3k	75

^a Unless otherwise noted, reaction conditions were **1** (0.5 mmol), **2** (0.75 mmol), CuI (10 mol%), Cs₂CO₃ (2 equiv), DMSO (5 mL), 100 °C for 12 h. ^b Isolated yield

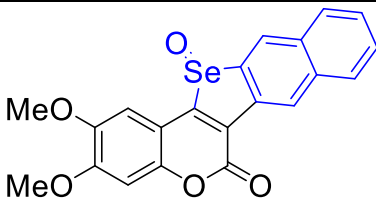
Other 3-(2-hydroxy-phenyl)-acrylic acids **1** and 2-bromo-benzeneselenols **4** also successfully provided the corresponding products in 54-77% yields, respectively (Table 3). The 3-(2-hydroxy-4,5-dimethoxy-phenyl)-acrylic acid displayed a moderate reactivity with 2-bromo-benzeneselenol with 66% yield (entry 4).

Furthermore, to our delight, reactants with more substituents also performed smoothly which displayed a moderate reactivity with 54% yield (entry 6).

Table 3. Copper-catalyzed tandem reaction of cyclic esterification/selenoxidation^a

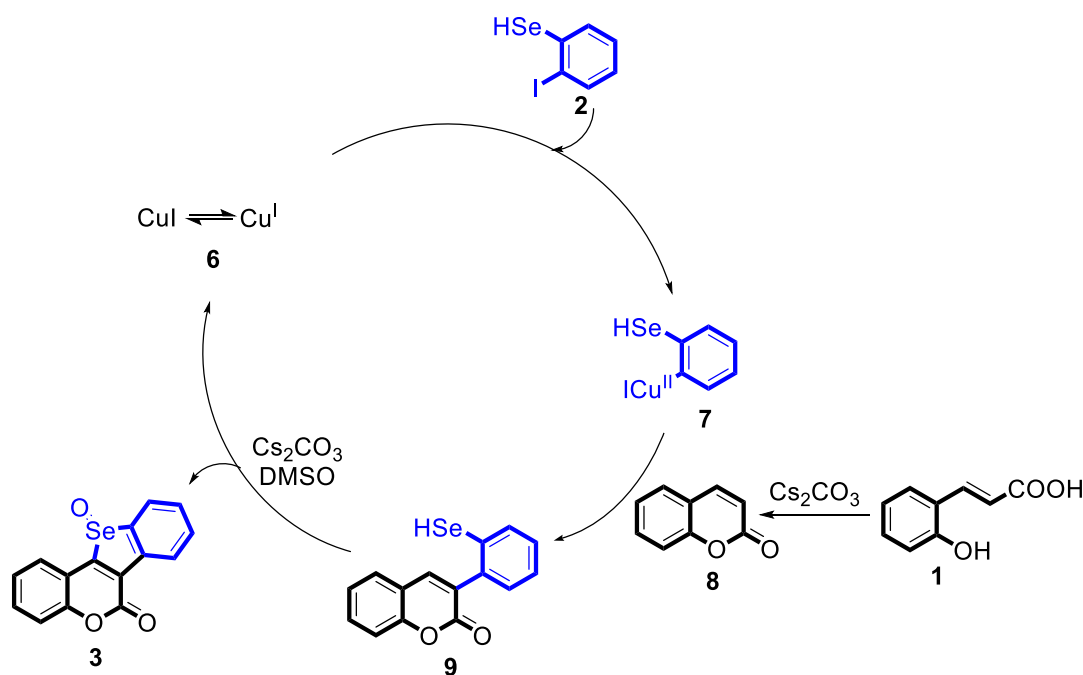
Entry	R	R ²	3	Yield ^b
1	H	H	 3a	75
2	4-CH ₃ O	H	 3b	71
3	5-Cl	H	 3h	77
4	4,5-diCH ₃	H	 3j	66
5	4,5-diCH ₃ O	H	 3l	62

Table 3. Continued

Entry	R	R ²	3	Yield ^b
6	4,5-diCH ₃ O	Acene	 3k	54

^a Unless otherwise noted, reaction conditions were **1** (0.5 mmol), **3** (0.75 mmol), CuI (10 mol%), NaOEt (2 equiv), DMSO (5 mL), 100 °C for 12 h. ^b Isolated yield

We propose a possible reaction mechanism in Scheme 3. At the beginning of the reaction, the CuI generated a Cu^I intermediate **6**. Next, intermediate **7** was provided from **2** via an oxidation addition step. Intermediate **8** was then provided from **1** via intramolecular esterification. Finally, through the oxidation reaction by DMSO and CS₂CO₃, intermediate **9** generated the desired products **3**, and, concomitantly, formed intermediate **6**, which then re-entered the catalytic cycle.



Scheme 3. Proposed mechanism.

Conclusions

In summary, we report a copper-catalyzed tandem reaction of cyclic esterification/selenoxidation. Starting from sample 3-(2-hydroxy-phenyl)-acrylic acids with 2-halide-benzeneselenols, a number of 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-ones were efficiently synthesized in good-to-high yields. This new methodology provides an economical approach toward C(sp²)-Se bond formation for biologically-active 11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one compounds.

Experimental Section

General. All reagents used in the experiment were obtained from commercial sources and used without further purification. Solvents for chromatography were of technical grade and distilled prior to use. Solvent mixtures are understood to be volume/volume. Chemical yields refer to pure isolated substances. Catalysts were purchased from Alfa Aesar (analytical reagent). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with an F-254 indicator, visualized by irradiation with UV light. The NMR spectra were recorded on a Bruker AVANCE III-400 spectrometer at 400 MHz and 100 MHz for ^1H and ^{13}C NMR, respectively, in CDCl_3 . The NMR chemical shifts were reported in ppm relative to 7.26 and 77 ppm of CDCl_3 as internal standards for ^1H and ^{13}C NMR, respectively. The mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer equipped with an ESI interface and ion trap analyzer. The ESI-HRMS was tested on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

General synthesis methods of 3a-3l

A solution of 3-(2-hydroxy-phenyl)-acrylic acids **1** (0.5 mmol), 2-halide-benzeneselenols **2** or **4** (0.75 mmol), CuI (10 mol%) and Cs_2CO_3 (2 equiv) in DMSO (5 mL) was stirred under air. After stirring at 100 °C for 12 h, it was cooled to room temperature. The reaction mixture was then quenched with a saturated salt-water solution (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product **3** or **5** was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate).

11-Oxo-11H-5-oxa-11-selena-benzo[a]fluoren-6-one (3a) white solid, mp 171-172 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 3:1); ^1H NMR (500 MHz, CDCl_3): δ 8.15 (dd, J_1 2.4 Hz, J_2 6.6 Hz, 1H), 8.05 (dd, J_1 1.5 Hz, J_2 7.8 Hz, 1H), 7.68 (dd, J_1 1.7 Hz, J_2 6.9 Hz, 1H), 7.60-7.64 (m, 1H), 7.41-7.52 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.0, 158.1, 155.6, 153.7, 131.9, 126.8, 125.2, 124.7, 123.5, 121.9, 117.5, 112.7, 111.8, 105.9 (one peak is missing due to overlap); HRMS (+ESI) Calcd for $\text{C}_{15}\text{H}_9\text{O}_3\text{Se}$ $[\text{M}+\text{H}]^+$: 316.9717, found 316.9719.

2-Methyl-11-oxo-11H-5-oxa-11-selena-benzo[a]fluoren-6-one (3b) yellow solid, mp 153-154 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ^1H NMR (500 MHz, CDCl_3): δ 8.07-8.18 (m, 1H), 7.80 (br s, 1H), 7.59-7.70 (m, 1H), 7.32-7.51 (m, 4H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 160.0, 158.2, 155.5, 151.9, 134.5, 133.0, 126.6, 125.1, 123.5, 121.8, 121.5, 117.2, 112.3, 111.7, 105.8, 20.9; HRMS (+ESI) Calcd for $\text{C}_{16}\text{H}_{11}\text{O}_3\text{Se}$ $[\text{M}+\text{H}]^+$: 330.9873, found 330.9875.

2-Methyl-13-oxo-13H-5-oxa-13-selena-dibenzo[a,h]fluoren-6-one (3c) yellow solid, mp 141-143 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ^1H NMR (500 MHz, CDCl_3): δ 8.59 s, 1H), 7.94-8.06 (m, 3H), 7.86 (s, 1H), 7.42-7.56 (m, 4H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 162.4, 158.3, 153.9, 152.4, 35.7, 134.7, 133.7, 132.1, 128.5, 127.9, 126.2, 125.3, 123.4, 121.8, 20.4, 117.3, 112.1, 107.7, 105.2, 20.9; HRMS (+ESI) Calcd for $\text{C}_{20}\text{H}_{13}\text{O}_3\text{Se}$ $[\text{M}+\text{H}]^+$: 381.0030, Found 381.0032.

3-Methoxy-11-oxo-11H-5-oxa-11-selena-benzo[a]fluoren-6-one (3d) yellow solid, mp 178-179 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ^1H NMR (500 MHz, CDCl_3): δ 8.04-8.14 (m, 1H), 7.91 (dd, J_1 1.9 Hz, J_2 7.3 Hz, 1H), 7.57-7.67 (m, 1H), 7.39-7.47 (m, 2H), 6.94-7.02 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 163.0, 160.6, 158.3, 155.5, 155.2, 126.0, 125.0, 23.5, 122.8, 121.4, 113.0, 111.4, 105.8, 103.3, 101.3, 55.7; HRMS (+ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{O}_4\text{Se}$ $[\text{M}+\text{H}]^+$: 346.9823, found 346.9825.

3,8,9-Trimethoxy-11-oxo-11H-5-oxa-11-selena-benzo[a]fluoren-6-one (3e) yellow solid, mp 130-133 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ^1H NMR (500 MHz,

CDCl₃): δ 7.85 (d, *J* 8.4 Hz, 1H), 7.51 (s, 1H), 7.13 (s, 1H), 6.94–7.04 (m 2H), 4.00 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 162.4, 159.7, 158.8, 154.9, 149.9, 149.0, 147.9, 122.3, 115.5, 113.0, 106.3, 103.8, 102.2, 101.4, 95.5, 56.5, 56.4, 55.8; HRMS (+ESI) Calcd for C₁₈H₁₅O₆Se [M+H]⁺: 407.0034, found 407.0036.

3-Methoxy-13-oxo-13H-5-oxa-13-selena-dibenzo[*a,h*]fluoren-6-one (3f) yellow solid, mp: 157–159 °C m, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.55 (s, 1H), 7.87–8.12 (m, 4H), 7.43–7.60 (m, 2H), 6.92–7.10 (m, 2H), 3.93 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 163.5, 162.9, 158.2, 156.1, 153.8, 131.8, 131.4, 128.3, 127.9, 125.9, 125.2, 123.4, 123.2, 119.8, 113.2, 107.5, 105.6, 102.6, 101.4, 55.8; HRMS (+ESI) Calcd for C₂₀H₁₃O₄Se [M+H]⁺: 396.9979, found 396.9979.

2-Fluoro-11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one (3g) yellow solid, mp 178–180 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* 7.4 Hz, 1H), 7.62–7.74 (m, 2H), 7.45–7.55 (m, 3H), 7.29–7.34 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 159.0 (d, *J* 2.8 Hz), 158.9 (d, *J* 245.7 Hz), 157.6, 155.7, 149.8 (d, *J* 1.6 Hz), 127.2, 126.4, 123.2, 122.0, 119.4 (d, *J* 34.7 Hz), 119.3, 113.4 (d, *J* 9.8 Hz), 111.8, 107.4 (d, *J* 25.8 Hz), 106.6; HRMS (+ESI) Calcd for C₁₅H₈FO₃Se [M+H]⁺: 334.9623, found 334.9625.

2-Chloro-11-oxo-11H-5-oxa-11H-selena-benzo[*a*]fluoren-6-one (3h) yellow solid, mp 189–191 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.14 (dd, *J*₁ 1.2 Hz, *J*₂ 7.9 Hz, 1H), 8.01 (d, *J* 2.5 Hz, 1H), 7.68 (d, *J* 7.6 Hz, 1H), 7.55 (dd, *J*₁ 2.5 Hz, *J*₂ 8.9 Hz, 1H), 7.47–7.52 (m, 2H), 7.45 (d, *J* 8.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 158.5, 157.4, 155.6, 151.8, 131.8, 130.2, 127.1, 125.4, 123.1, 121.9, 121.2, 118.8, 113.6, 111.8, 106.5; HRMS (+ESI) Calcd for C₁₅H₈ClO₃Se [M+H]⁺: 350.9327, found 350.9329.

2-Bromo-11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one (3i) yellow solid, mp 176–178 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.18 (d, *J* 2.3 Hz, 1H), 8.13–8.16 (m, 1H), 7.67–7.71 (m, 2H), 7.46–7.55 (m, 2H), 7.40 (d, *J* 8.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 158.4, 157.3, 155.6, 152.3, 134.6, 127.2, 125.4, 124.3, 123.1, 121.9, 119.1, 117.4, 114.1, 111.8, 106.5; HRMS (+ESI) Calcd for C₁₅H₈BrO₃Se [M+H]⁺: 394.8822, found 394.8824.

2,3-Dimethyl-11-oxo-11H-5-oxa-11-selena-benzo[*a*]fluoren-6-one (3j) yellow solid, mp 195–197 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.03–8.14 (m, 1H), 7.67 (s, 1H), 7.56–7.64 (m, 1H), 7.36–7.50 (m, 2H), 7.21 (s, 1H), 2.34 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 160.2, 158.3, 155.2, 152.1, 142.1, 133.5, 126.2, 124.9, 123.6, 121.6, 121.5, 117.8, 111.5, 109.9, 104.8, 20.4, 19.2; HRMS (+ESI) Calcd for C₁₇H₁₃O₃Se [M+H]⁺: 345.0030, found 345.0032.

2,3-Dimethoxy-13-oxo-13H-5-oxa-13-selena-dibenzo[*a,h*]fluoren-6-one (3k) yellow solid, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.54 (s, 1H), 7.94–8.05 (m, 3H), 7.50–7.55 (m, 2H), 7.39 (s, 1H), 7.00 (s, 1H), 4.04 (s, 3H), 3.99 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 162.9, 158.5, 153.8, 153.6, 150.4, 146.9, 131.8, 131.5, 128.4, 127.9, 126.0, 125.3, 123.6, 119.9, 114.1, 107.5, 104.4, 102.0, 100.6, 56.6, 56.6; HRMS (+ESI) Calcd for C₂₁H₁₅O₅Se [M+H]⁺: 427.0085, found 427.0087.

2,3-Dimethoxy-11-oxo-11H-5-oxa-11H-selena-benzo[*a*]fluoren-6-one (3l) yellow solid, mp 207–209 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1); ¹H NMR (500 MHz, CDCl₃): δ 8.09 (dd, *J*₁ 3.4 Hz, *J*₂ 5.7 Hz, 1H), 7.62 (dd, *J*₁ 3.0 Hz, *J*₂ 6.2 Hz, 1H), 7.44 (d, *J* 3.3 Hz, 1H), 7.43 (d, *J* 3.1 Hz, 1H), 7.35 (s, 1H), 6.99 (s, 1H), 4.02 (s, 3H), 3.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 160.5, 158.4, 155.1, 152.9, 149.6, 146.7, 126.1, 125.0, 123.6, 121.5, 111.3, 104.5, 103.6, 101.7, 100.5, 56.3, 56.3; HRMS (+ESI) Calcd for C₁₇H₁₃O₅Se [M+H]⁺: 376.9928, found 376.9930.

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Supplementary Material

Supplementary material, consisting of ^1H and ^{13}C NMR spectra for compounds **3a-3l**, can be found in the online version of the text.

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