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Metal-free difunctionalization of alkynes to access tetrasubstituted olefins through spontaneous selenosulfonylation of vinylidene *ortho*-quinone methide (VQM)†

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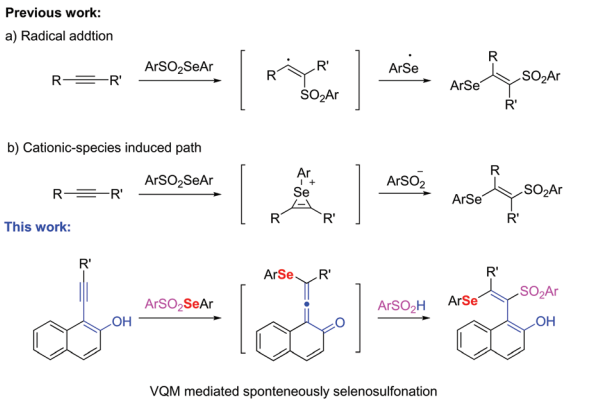
A metal-free difunctionalization of alkynes to access tetrasubstituted olefins through spontaneous selenosulfonylation of vinylidene *ortho*-quinone methide (VQM) was described herein. The reaction was conducted under mild conditions without any catalysts or additives. Preliminary mechanism studies revealed that the formation of VQM was the key for this alkyne di-functionalization reaction. The reaction could be applied in the enantioselective asymmetric synthesis of axially chiral styrene. Furthermore, the selenosulfonylation adducts can be transformed into useful naphtho[2,1-*b*]furan and benzofuran scaffolds.

Introduction

Tetrasubstituted olefins have been found as key structural units in a number of biologically active natural products such as Nileprost analogues and pharmaceutically important molecules such as Tamoxifen and Rofecoxib.[1] Tetrasubstituted olefins are also key substrates for various organic transformations such as hydrogenation and epoxidation.[2] As a result, synthetic approaches toward the construction of tetrasubstituted olefins have attracted considerable attention in organic chemistry research.[3] Nevertheless, a facile synthetic method for introducing two heteroatoms into tetrasubstituted olefins remains a challenge.[4] Among the heteroatom-substituted olefins, vinyl selenides are valuable synthetic intermediates and therapeutic entities that have been reported to exhibit a broad range of biological activities.[5] Moreover, selenium can be readily introduced, manipulated and removed from organic compounds in a variety of different ways.[6] Furthermore, vinyl sulfones are unique motifs in some biologically active molecules and useful precursors in organic synthesis.[7] As a remarkable combination of selenides and sulfone functionalities, β-(Seleno)vinyl sulfones can be readily converted into several useful products such as acetylenic, allenic and β-keto sulfones, thus proving the significance of synthetic approaches towards β-(Seleno)vinyl sulfones.[8]

The first method for the construction of β-(Seleno)vinyl sulfones has been established featuring a radical-type reaction as the favorite approach (Scheme 1a).[9] In this particular case, a radical initiator was required to promote the homolytic cleavage of the selenosulfonylation reagent. Recently, many elegant procedures have been developed for the selenosulfonylation of alkyne through the vinyl radical intermediate.[9a] For example, Liu and co-workers reported a copper-catalyzed regio- and stereo-specific selenosulfoylation of alkynes with arylsulfonohydrazides and diphenyl diselenide under mild



Scheme 1 Alkyne difunctionalization through selenosulfonylation.

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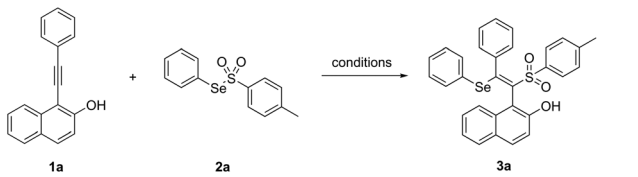
conditions.[9b] More recently, Sun and co-workers described an efficient multicomponent regio- and stereo-specific selenosulfonylation of alkynes with the insertion of sulfur dioxide.[9c] Despite this remarkable progress, vinyl radical species are commonly considered to be highly reactive and readily undergo hydrofunctionalization by proton abstraction.[9d] To develop a mechanistically new approach for the selenosulfonylation of alkynes, a metal-free method for the 1,2-selenosulfonylation of alkynes through a cationic-species-induced selenosulfonylation process was achieved by Sun and co-workers (Scheme 1b).[10] Taking all these precedents into consideration, the development of a novel reaction model with a facile procedure under mild reaction conditions is highly desirable.

As a precedent reaction intermediate, vinylidene *ortho*-quinone methide (VQM) has attracted much attention in a variety of synthetic transformations.[11] To further explore the application scope of this versatile intermediate in organic synthesis, herein we described the selenosulfonylation of the VQM intermediate to realize the difunctionalization of alkynes under mild conditions. Furthermore, the generated substituted alkene with an aromatic ring may restrict the rotation of the single bond between them and the enantiomers of axially styrene may exist.[12] Therefore, this method can be potentially used to prepare axially chiral styrene bearing selenium and sulfone moieties.

Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	Solvent	Additive	Yield[b] (%)	*E*/Z[c]
1	DCE	Et_3N	67	>99 : 1
2	DCE	K_2CO_3	69	>99 : 1
3	DCE	KF	73	>99 : 1
4	DCE	DABCO	70	>99 : 1
5	DCE	Malonic acid	72	>99 : 1
6	DCE	Benzoic acid	54	>99 : 1
7	DCE	Citric acid	57	>99 : 1
8	DCE	Cinnamic acid	49	>99 : 1
9	DCE	Boric acid	<5	>99 : 1
10	DCE	AIBN	48	>99 : 1
11	**DCE**	—	**85**	**>99 : 1**
12	CH_3OH	—	69	>99 : 1
13	CH_2Cl_2	—	73	>99 : 1
14	CH_3CN	—	54	>99 : 1
15	Toluene	—	63	>99 : 1
16[d]	Toluene	—	64	>99 : 1

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol), **2a** (0.1 mmol) and additive (0.1 mmol) in solvent (1.0 mL) at room temperature for 10 h. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis. [d] The reaction was carried out at 80 °C.

Results and discussion

We initiated our study with 1-(phenylethynyl)naphthalen-2-ol (**1a**) and selenosulfonate (**2a**) as model substrates to optimize the reaction conditions. First, we screened a series of bases (1.0 equiv.) as additives. Pleasingly, the selenosulfonylation product **3a** was obtained with high levels of regio- and stereoselectivity at room temperature by using 1,2-dichloroethane (DCE) as the solvent (Table 1, entries 1–4).

Nevertheless, the reaction output was not satisfactory from the reaction with bases as additives. We envisioned that an acid might contribute to the activation of selenosulfonate to increase the reaction yield. Thus, we tried malonic acid (Table 1, entry 5) as the additive. As expected, the reaction went smoothly, albeit the reaction yield was not improved compared to that with basic conditions. Other acids as additives caused the decrease in reaction yields (Table 1, entries 6–9). Inspirited by Kobayashi's work,[9a] we then evaluated azodiisobutyronitrile (AIBN) as the radical initiator in this transformation. Unfortunately, the reaction yield was not improved (Table 1, entry 10).

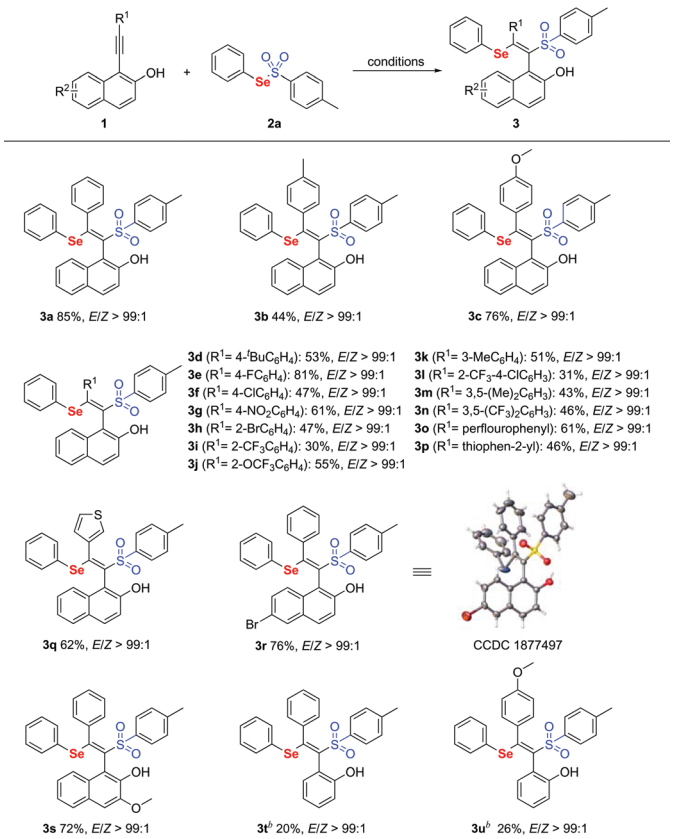
Next, we performed a reaction in the absence of any additives or catalysts. Intriguingly, the reaction went smoothly to give **3a** with an improved yield after simply mixing two reagents at room temperature. Then, several solvents were screened, including methanol, dichloromethane, acetonitrile and toluene. These solvents did not increase the reaction yield compared to DCE (Table 1, entries 12–15). Notably, after increasing the temperature to 80 °C, with toluene as the solvent, the reaction rate and yield were not changed.

With the optimized reaction conditions in our hand, we then investigated the substrate scope of this alkyne selenosulfonylation reaction. Various tetrasubstituted olefins could be constructed by this straightforward methodology (Table 2). R^1 groups with both electron-donating and -withdrawing substitution groups at the *para*-position of phenyl were well tolerated, thus leading to expected products **3a–3g** in good yields with excellent *E*-selectivity (>99 : 1).

Next, the substrates with a series of substitution groups at the *ortho*-position of phenyl were examined under standard conditions. Notably, compared to *para*-substituted R^1 groups, the *ortho*-substituted counterparts decreased the reaction yields (Table 2, **3h–3j**). The substrate with *meta*-substituted R^1 groups was also tolerant to our reaction system and gave the desired product in moderate yield (Table 2, **3k**).

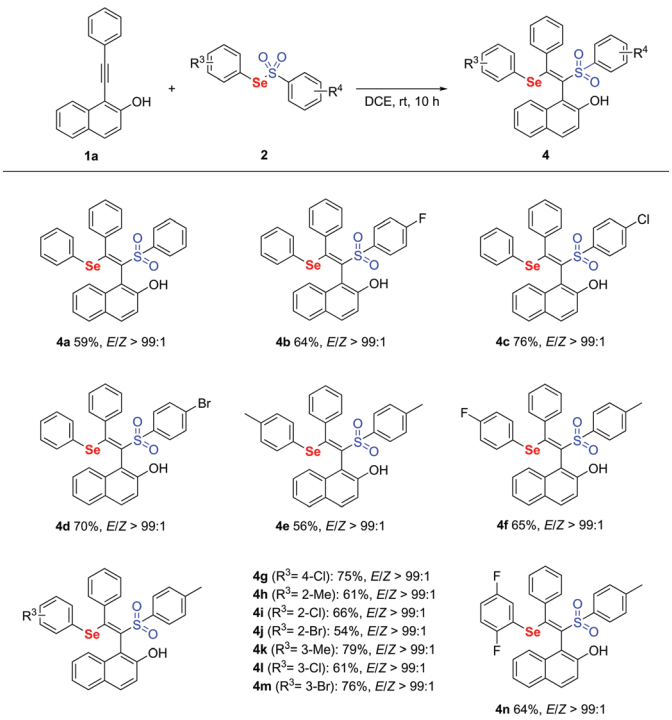
Moreover, the substrates with 2,4 or 3,5-disubstituted groups proceeded smoothly under standard reaction conditions (Table 2, **3l–3n**). The substrate with the pentafluorophenyl group also gave desired product **3o** in good yield. In particular, heterocyclic rings, such as thiophenes, were also tolerated and afforded the desired products in good yields and excellent stereoselectivities (Table 2, **3p–3q**). Electron-donating or -withdrawing groups on the different positions of the naphthalene ring did not influence the reaction output and the products **3r** and **3s** were obtained with good yields and stereoselectivities. It is noteworthy that 2-(phenylethynyl)

Table 2 Substrate scope[a,c]



[a] Unless otherwise noted, all reactions were carried out with **1** (0.2 mmol) and **2a** (0.2 mmol) in 2.0 mL DCE loading at room temperature for 10 h. [b] The reactions were carried out with **1** (1.0 mmol), **2a** (1.0 mmol) and Et_3N (1.0 mmol) in 10.0 mL toluene reflux for 16 h. [c] Isolated yield.

Table 3 Substrate scope[a,b]



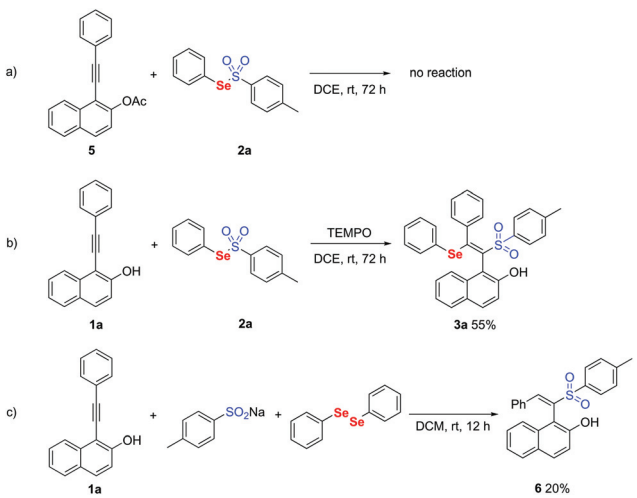
[a] Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol) and **2** (0.2 mmol) in 2.0 mL DCE loading at room temperature for 10 h. [b] Isolated yield.

phenol cannot be tolerant to our reaction system under standard conditions, probably due to the fact that the formation of the Vinylidene *ortho*-Quinone Methide (VQM) analogue from phenol derivatives is much more difficult than from naphthol derivatives. Nevertheless, after condition screening (for details, please see ESI Table 3†), products **3t** and **3u** could be formed in the presence of triethyl amine by refluxing in toluene for 16 hours.

Encouraged by these results, we further investigated the substrate scope of selenosulfonates in this transformation. First, different substitution groups at R^4 were evaluated. The substrate without substitution groups on the phenyl ring slightly decreased the reaction yield (Table 3, **4a**). Compared to the *para*-methyl phenyl group on the sulfone moiety, fluoro, chloro or bromo at the *para*-position did not influence the reaction yields and *E*/*Z* selectivities (Table 3, **4b–4d**).

Next, we investigated the substitution groups on the benzene ring of phenyl selenide. With *para*-methyl-, -fluoro- and -chloro-substituted phenyl selenide, the desired products were obtained in good yields (Table 3, **4e–4g**). Meanwhile, substrates bearing methyl, bromo, chloro substitution groups at *ortho*- and *meta*-positions proceeded smoothly to give desired products (Table 3, **4h–4m**) with good yields and *E*/*Z* selectivities. Furthermore, the adduct with 2,5-difluoro substitution at the phenyl selenide moiety (Table 3, **4n**) could also be successfully formed under standard reaction conditions.

In order to gain insight into the reaction mechanism, we conducted some control experiments (Scheme 2). First, we per-



Scheme 2 Mechanistic studies.

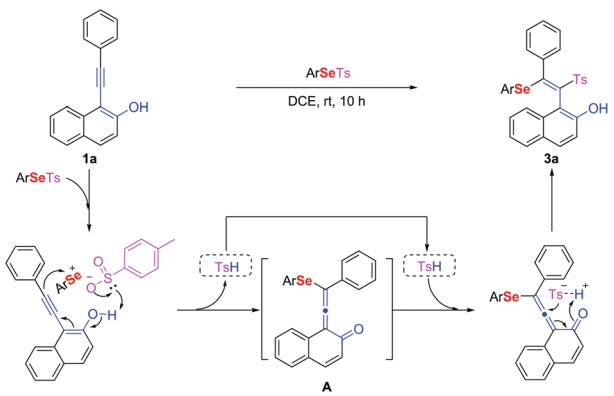
formed the reaction by using acetyl protected substrate **5** to prevent the formation of the VQM intermediate. The reaction did not proceed under standard conditions, indicating that the formation of the VQM intermediate was the key for this spontaneous selenosulfonylation protocol. Next, (2,2,6,6-tetramethyl-1-piperidinyl)oxyl (TEMPO) was added to the reaction mixture of **1a** and **2a** under standard conditions. After 72 h, product **3a** was isolated with 55% yield (Scheme 2b). This result therefore dismisses the possibility of a radical pathway.

Furthermore, the reaction by substituting selenosulfonate with diphenyl diselenide and sodium *p*-tolylsulfinate (Scheme 2c) delivered the mono-functionalized sulfonylation product **6** in 20% yield within 12 h, indicating that the spontaneous cleavage of selenosulfonate was required for the reaction and played a key role in activating 1-(phenylethynyl) naphthalen-2-ol to form the VQM as the key intermediate.

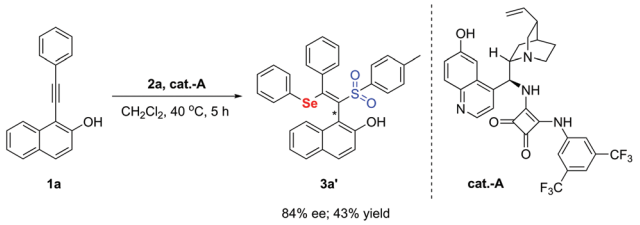
Based on the mechanism experiments and previous reports,[11a] we proposed a plausible mechanism (Scheme 3). First, selenosulfonate was cleaved by 1-(phenylethynyl) naphthalen-2-ol; thus, the VQM intermediate **A** was formed along with the release of one molecule of *p*-toluenesulfinic acid (TsH). According to the theoretical calculation and previous reports, the terminal carbon of VQM was nucleophilic and enabled the addition of the selenium cation to form intermediate **A**.[11e] Finally, intermediate **A** was attacked by the previously formed TsH to afford the desired adduct **3a**.

Since the addition of selenosulfonate to 1-(phenylethynyl) naphthalen-2-ol had been developed as a preparation method for β-(Seleno)vinyl sulfones, we envisaged that this process might be carried out in an enantioselective fashion for the construction of axially chiral styrene. Inspirited by the methodology recently developed by Liu,[11d] we used easily accessible **cat.-A** as the catalyst and CH_2Cl_2 as the solvent. Gratifyingly, the reaction gave axially chiral **3a′** in moderate yield and 84% enantiomeric excess (Scheme 4). The further exploration of a new catalyst and substrate scope is ongoing in our laboratory.

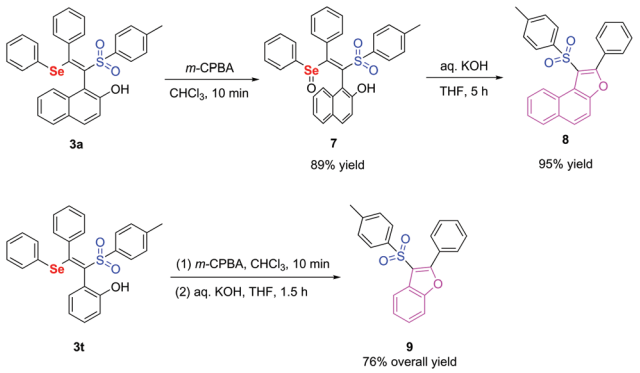
As mentioned above, apart from the asymmetric synthetic attempts of the reaction, we evaluated the application of the selenosulfonylation product by further transformation of the



Scheme 3 Plausible mechanism.



Scheme 4 Enantioselective synthesis of β-(Seleno)vinyl sulfones.



Scheme 5 Synthetic transformations.

adduct to the desired heterocyclic compound. Product **3a** could be oxidized into selenoxide with 3-chloroperoxybenzoic acid (*m*-CPBA) and then gave a naphtho[2,1-*b*]furan derivative in high yield under basic conditions. With a similar procedure, product **3t** could be successfully transformed to benzofuran derivative **9** with good yield (Scheme 5).

Conclusion

In summary, we have developed a metal-free difunctionalization of alkynes to access tetrasubstituted olefins through spontaneous selenosulfonylation of the vinylidene *ortho*-quinone methide (VQM) intermediate. The reaction was conducted under mild conditions without any catalysts or additives. The preliminary mechanism investigation indicated that the formation of VQM was the key for this selenosulfonylation process. The application prospect of this reaction was demonstrated by the enantioselective asymmetric synthesis of axially chiral styrene and further transformation of the adducts to naphtho[2,1-*b*]furan and benzofuran derivatives.

Experimental section

General information

^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400MR DD2 (400 MHz) spectrometer and an Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual

solvent peak was used as an internal reference: $CDCl_3$ (^1H NMR δ 0.00, ^{13}C NMR δ 77.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on a Bruker Solarix 7.0T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-ray diffractometer. Melting points were measured using a SGWX-4A Microscopic melting point meter and are uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis on a Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6 mm Φ × 250 mmL. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

General procedure for the synthesis of compounds 3 or 4

The substrate **1** (0.2 mmol) and selenosulfonate **2** (0.2 mmol) were added to a 10 mL flame-dried Schlenk tube with a magnetic stirring bar. DCE (2.0 mL) was injected into the tube. After stirring at room temperature for 10 h, the mixture was evaporated and purified by column chromatography on silica gel (PE : EA = 4 : 1) to afford the products **3** or **4**.

General procedure for the synthesis of compounds 3t and 3u

Et_3N (1.0 mmol) was added to a solution of substrate **1t** or **1u** (1.0 mmol) and selenosulfonate **2a** (1.0 mmol) in toluene (10 mL). After refluxing for 16 h, the mixture was evaporated and purified by column chromatography on silica gel (PE : EA = 4 : 1) to afford the products **3t** or **3u**.

3a: Yield 85% (94.4 mg); white solid; mp 171–173 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 8.3 Hz, 1H), 7.38–7.24 (m, 6H), 7.14–6.96 (m, 8H), 6.93–6.84 (m, 4H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.15, 153.19, 144.00, 137.11, 135.87, 135.77, 135.11, 132.19, 132.12, 130.41, 130.27, 128.96, 128.87, 128.58, 128.49, 128.30, 127.86, 127.14, 127.01, 123.55, 122.95, 119.32, 114.29, 21.38; HRMS (ESI) m/z calcd for $[C_{31}H_{24}NaO_3SSe, M + Na]^+$: 579.0504, found: 579.0508.

3b: Yield 44% (50.1 mg); white solid; mp 188–190 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.36–7.23 (m, 6H), 7.09–6.97 (m, 5H), 6.94–6.83 (m, 6H), 2.23 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.55, 153.12, 143.95, 137.82, 136.99, 135.79, 132.22, 132.06, 130.11, 128.92, 128.78, 128.50, 128.45, 128.26, 127.81, 127.18, 126.95, 123.52, 123.00, 119.28, 114.43, 21.37, 21.28; HRMS (ESI) m/z calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, found: 593.0658.

3c: Yield 76% (89.0 mg); white solid; mp 189–190 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.35–7.24 (m, 6H), 7.12–6.97 (m, 5H), 6.97–6.85 (m, 4H), 6.62 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.23, 159.35, 153.04, 143.89, 136.91, 136.01, 132.29, 132.04, 130.53, 130.22, 128.94, 128.79, 128.47, 128.44, 128.34, 128.27, 127.48, 127.38, 126.99, 123.55, 123.08, 119.20, 114.61, 112.66, 55.18, 21.37; HRMS (ESI) m/z calcd for $[C_{32}H_{26}NaO_4SSe, M + Na]^+$: 609.0609, found: 609.0613.

3d: Yield 53% (61.4 mg); white solid; mp 212–213 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.40–7.23 (m, 6H), 7.02 (t, 3H), 6.98–6.89 (m, 4H), 6.85 (q, 4H), 2.20 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.70, 153.11, 150.88, 143.75, 137.15, 136.19, 132.27, 132.07, 131.93, 130.17, 129.02, 128.81, 128.47, 128.31, 128.29, 128.12, 127.34, 127.06, 123.98, 123.59, 123.14, 119.20, 114.25, 34.39, 31.20, 21.39; HRMS (ESI) m/z calcd for $[C_{35}H_{32}NaO_3SSe, M + Na]^+$: 635.1130, found: 635.1126.

3e: Yield 81% (92.9 mg); white solid; mp 182–184 °C; ^1H NMR (400 MHz, $CDCl_3$): 7.81 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.36–7.26 (m, 6H), 7.12–7.05 (m, 3H), 7.02 (d, J = 7.1 Hz, 2H), 6.98–6.86 (m, 4H), 6.78 (t, J = 8.3 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.20 (d, J = 258.0 Hz), 158.78, 153.13, 144.17, 137.09, 135.74, 132.20, 132.10, 131.21, 131.18, 128.95, 128.90, 128.82, 128.51, 128.43, 128.34, 127.07, 126.90, 123.61, 122.86, 119.28, 114.40, 114.18, 21.39; HRMS (ESI) m/z calcd for $[C_{31}H_{23}FNaO_3SSe, M + Na]^+$: 597.0409, found: 597.0412.

3f: Yield 47% (55.5 mg); white solid; mp 171–172 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.9 Hz, 1H), 7.73 (q, J = 9.2 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.41–7.20 (m, 7H), 7.16–7.00 (m, 6H), 6.99–6.84 (m, 4H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.40, 158.40, 153.13, 144.75, 144.29, 137.11, 135.52, 133.93, 133.75, 132.26, 132.06, 131.15, 128.94, 128.58, 128.49, 128.35, 128.26, 127.41, 127.08, 126.69, 123.63, 122.78, 119.34, 118.98, 114.09, 21.42; HRMS (ESI) m/z calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, found: 613.0118.

3g: Yield 61% (73.3 mg); yellow solid; mp 120–123 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 2H), 7.85 (d, J = 8.5 Hz, 1H), 7.78–7.70 (m, 1H), 7.40 (s, 1H), 7.36–7.22 (m, 8H), 7.14–7.00 (m, 3H), 6.99–6.84 (m, 4H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.40, 153.25, 146.83, 144.79, 142.40, 137.25, 134.74, 132.54, 131.83, 131.57, 129.42, 129.11, 128.95, 128.84, 128.56, 128.44, 127.18, 125.95, 123.74, 122.43, 119.53, 113.54, 21.43; HRMS (ESI) m/z calcd for $[C_{31}H_{23}NNaO_5SSe, M + Na]^+$: 624.0354, found: 624.0355.

3h: Yield 47% (59.6 mg); white solid; mp 175–177 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.9 Hz, 1H), 7.73–7.61 (m, 3H), 7.43–7.28 (m, 4H), 7.26–7.15 (m, 5H), 7.15–7.07 (m, 2H), 6.94 (t, J = 7.5 Hz, 3H), 6.87 (d, J = 8.0 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.79, 153.18, 144.45, 137.58, 136.00, 134.24, 132.40, 132.33, 131.90, 131.10, 129.62, 129.28, 129.07, 128.97, 128.80, 128.24, 127.97, 126.72, 126.45, 125.86, 123.62, 123.58, 121.32, 119.71, 113.73, 21.38; HRMS (ESI) m/z calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, found: 656.9614.

3i: Yield 30% (37.4 mg); white solid; mp 201–204 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 9.4 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 8.9 Hz, 2H), 7.34–7.26 (m, 4H), 7.26–7.15 (m, 3H), 7.09 (t, J = 8.3 Hz, 3H), 6.93 (t, J = 7.5 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.55, 153.12, 144.52, 137.77,

133.98, 133.25, 132.53, 132.47, 131.27, 130.84, 129.95, 129.11, 129.01, 128.83, 128.76, 128.34, 128.22, 127.93, 126.93, 126.18 (q, J = 30.0 Hz), 126.15 (q, J = 5.0 Hz), 125.90, 124.06 (q, J = 272.0 Hz), 123.64, 122.78, 122.77, 119.80, 113.90, 21.34; HRMS (ESI) m/z calcd for $[C_{32}H_{23}F_3NaO_3SSe, M + Na]^+$: 647.0377, found: 647.0374.

3j: Yield 55% (70.4 mg); white solid; mp 161–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 10.0 Hz, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.9 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.24–7.19 (m, 1H), 7.19–7.06 (m, 6H), 7.05–6.98 (m, 2H), 6.94 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.24, 153.36, 144.79, 144.53, 137.35, 134.12, 132.41, 132.04, 131.26, 130.69, 129.51, 129.09, 128.85, 128.82, 128.75, 128.41, 127.94, 126.75, 126.39, 126.08, 124.56, 123.60, 123.16, 120.56 (q, J = 258.0 Hz), 119.62, 115.77, 113.71, 21.35; HRMS (ESI) m/z calcd for $[C_{32}H_{23}F_3NaO_4SSe, M + Na]^+$: 663.0327, found: 663.0330.

3k: Yield 51% (56.7 mg); white solid; mp 175–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.59–7.50 (m, 1H), 7.39–7.25 (m, 6H), 7.09–6.93 (m, 5H), 6.93–6.79 (m, 5H), 6.67 (s, 1H), 2.20 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.21, 153.21, 143.80, 137.11, 136.55, 136.20, 134.73, 132.04, 130.34, 128.97, 128.82, 128.55, 128.46, 128.29, 128.08, 127.17, 127.04, 123.54, 123.08, 119.20, 114.21, 21.37, 21.02; HRMS (ESI) m/z calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, found: 593.0657.

3l: Yield 31% (40.8 mg); white solid; mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.79 (m, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.43 (s, 1H), 7.38–7.31 (m, 2H), 7.31–7.07 (m, 9H), 6.97 (t, J = 7.4 Hz, 2H), 6.85 (d, J = 7.8 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.00, 153.04, 144.72, 137.74, 134.31, 133.74, 132.63, 132.55, 132.37, 131.97, 130.94, 130.79, 129.44, 128.99, 128.90, 128.75, 128.60, 127.99, 127.63 (q, J = 31.0 Hz), 126.99, 126.48 (q, J = 5.0 Hz), 125.62, 123.70, 123.20 (q, J = 273.0 Hz) 122.59, 119.82, 113.73, 21.35; HRMS (ESI) m/z calcd for $[C_{32}H_{22}ClF_3NaO_3SSe, M + Na]^+$: 680.9988, found: 680.9989.

3m: Yield 43% (50.2 mg); white solid; mp 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.44–7.37 (m, 1H), 7.36–7.24 (m, 5H), 7.04 (t, J = 7.3 Hz, 1H), 7.01–6.95 (m, 2H), 6.91 (d, J = 7.8 Hz, 4H), 6.63 (s, 1H), 6.57 (s, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.28, 153.24, 143.62, 137.11, 136.57, 136.40, 134.46, 132.36, 131.94, 130.42, 129.17, 128.97, 128.75, 128.50, 128.45, 128.29, 127.87, 127.29, 127.06, 125.90, 123.52, 123.19, 119.12, 114.17, 21.35, 20.92; HRMS (ESI) m/z calcd for $[C_{33}H_{28}NaO_3SSe, M + Na]^+$: 607.0817, found: 607.0818.

3n: Yield 46% (63.6 mg); white solid; mp 179–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (t, J = 7.8 Hz, 2H), 7.57–7.50 (m, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.40–7.30 (m, 5H), 7.22 (d, J = 8.9 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.00–6.89 (m, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.88, 153.39, 144.80, 137.39, 137.27, 135.91, 133.70, 132.44, 131.96, 130.46 (q, J = 33.0 Hz), 129.36, 129.29, 129.03, 128.88, 128.55, 128.26, 127.48, 126.18, 123.82, 123.29 (q, J = 270.0 Hz), 122.71, 121.13 (t, J = 4.0 Hz), 118.75, 113.32, 21.39; HRMS (ESI) m/z calcd for $[C_{33}H_{22}F_6NaO_3SSe, M + Na]^+$: 715.0251, found: 715.0249.

3o: Yield 61% (78.8 mg); white solid; mp 211–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.43–7.14 (m, 10H), 7.11 (t, J = 7.4 Hz, 2H), 6.93 (d, J = 7.9 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.23, 145.19, 143.37, 137.00, 134.15, 133.54, 132.88, 131.26, 130.16, 129.20, 128.99, 128.83, 128.21, 127.23, 125.57, 123.74, 122.53, 119.49, 112.45, 21.43; HRMS (ESI) m/z calcd for $[C_{31}H_{19}F_5NaO_3SSe, M + Na]^+$: 669.0032, found: 669.0030.

3p: Yield 46% (51.7 mg); white solid; mp 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.45–7.34 (m, 3H), 7.33–7.26 (m, 2H), 7.25–7.20 (m, 1H), 7.16 (d, J = 4.5 Hz, 1H), 7.15–7.06 (m, 3H), 7.03–6.93 (m, 3H), 6.90 (d, J = 7.5 Hz, 2H), 6.77–6.70 (m, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.99, 150.76, 143.93, 136.39, 135.89, 135.38, 134.57, 132.29, 132.04, 130.64, 128.83, 128.58, 128.44, 128.42, 128.29, 128.05, 127.73, 127.18, 126.16, 123.61, 123.16, 119.02, 114.63, 21.40; HRMS (ESI) m/z calcd for $[C_{29}H_{22}NaO_3SSe, M + Na]^+$: 585.0068, found: 585.0070.

3q: Yield 62% (69.6 mg); white solid; mp 188–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 8.1, 4.6 Hz, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 8.0 Hz, 3H), 7.31 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 6.3 Hz, 1H), 7.20 (d, J = 8.9 Hz, 1H), 7.16–7.00 (m, 4H), 7.01–6.84 (m, 5H), 6.67 (d, J = 4.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.16, 153.04, 143.73, 136.56, 136.51, 134.52, 132.63, 132.27, 131.97, 128.93, 128.84, 128.49, 128.42, 128.38, 128.32, 128.17, 127.45, 127.15, 125.97, 124.15, 123.59, 123.25, 118.96, 114.31, 21.40; HRMS (ESI) m/z calcd for $[C_{29}H_{22}NaO_3SSe, M + Na]^+$: 585.0068, found: 585.0071.

3r: Yield 76% (94.4 mg); white solid; mp 172–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.69 (d, J = 8.9 Hz, 1H), 7.52 (s, 1H), 7.46–7.38 (m, 2H), 7.32–7.23 (m, 3H), 7.15–7.00 (m, 6H), 6.99 (d, J = 7.5 Hz, 2H), 6.95–6.80 (m, 4H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.42, 153.67, 144.17, 137.04, 135.91, 134.80, 131.04, 130.84, 130.25, 130.22, 130.11, 130.04, 129.01, 128.66, 128.38, 128.35, 127.91, 127.13, 126.80, 124.86, 120.48, 117.22, 114.41, 21.45; HRMS (ESI) m/z calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, found: 656.9607.

3s: Yield 72% (84.3 mg); white solid; mp 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.47 (t, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 7.7 Hz, 2H), 7.25 (s, 2H), 7.07–6.94 (m, 5H), 6.94–6.78 (m, 6H), 6.56 (s, 1H), 4.06 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.06, 146.81, 144.91, 142.92, 138.53, 136.94, 134.93, 133.52, 129.46, 129.00, 128.54, 128.33, 128.23, 128.21, 127.80, 127.52, 127.35, 127.08, 126.81, 125.34, 124.40, 123.94, 114.54, 107.61, 55.99, 21.46; HRMS (ESI) m/z calcd for $[C_{32}H_{26}NaO_4SSe, M + Na]^+$: 609.0609, found: 609.0605.

3t: Yield 20% (101.2 mg); white solid; mp 76–78 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (s, 4H), 7.40 (s, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 7.7 Hz, 2H), 7.10–7.05 (m, 3H), 6.95–6.88 (m, 3H), 6.58 (d, J = 8.1 Hz, 1H), 6.54 (d, J = 7.5 Hz, 1H), 6.50 (t, J = 7.4 Hz, 1H), 5.62 (s, 1H), 2.35 (s, 3H); ^{13}C NMR

(150 MHz, $CDCl_3$): δ 151.88, 151.78, 143.78, 139.38, 137.47, 136.91, 134.33, 129.88, 129.79, 129.59, 129.11, 128.86, 128.77, 128.30, 128.12, 127.13, 123.62, 119.96, 116.95, 21.55; HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{22}NaO_3SSe, M + Na]^+$: 529.0347, found: 529.0351.

3u: Yield 26% (139.3 mg); white solid; mp 183–184 °C; ^{1}H NMR (600 MHz, CDCl3): δ 7.42–7.29 (m, 2H), 7.27–7.23 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 3H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.92 (dt, *J* = 18.7, 7.1 Hz, 3H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.50 (q, *J* = 7.7 Hz, 2H), 5.52 (s, 1H), 3.88 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, CDCl3): δ 160.54, 151.99, 151.75, 143.68, 139.20, 137.59, 136.92, 131.83, 129.86, 129.79, 129.10, 128.75, 128.30, 128.07, 127.27, 126.30, 123.78, 120.01, 116.99, 114.32, 55.30, 21.56; HRMS (ESI) *m*/*z* calcd for $[C_{28}H_{24}NaO_4SSe, M + Na]^+$: 559.0453, found: 559.0449.

4a: Yield 59% (63.9 mg); white solid; mp 121–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.50–7.38 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30–7.22 (m, 3H), 7.18–6.94 (m, 10H), 6.89 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.49, 153.27, 138.97, 137.06, 134.97, 132.92, 132.16, 130.32, 128.93, 128.58, 128.38, 128.31, 128.22, 127.89, 127.17, 127.11, 126.96, 123.60, 122.89, 119.21, 114.02; HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{22}NaO_3SSe, M + Na]^+$: 565.0347, found: 565.0349.

4b: Yield 64% (71.6 mg); white solid; mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63–7.57 (m, 1H), 7.48–7.37 (m, 3H), 7.36–7.28 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18–6.95 (m, 8H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.20 (d, *J* = 254.0 Hz), 160.49, 153.24, 137.04, 135.32 (d, *J* = 2.0 Hz), 134.89, 132.24, 132.11, 131.21, 131.11, 130.51, 128.95, 128.63, 128.48, 128.34, 127.98, 127.32, 127.20, 126.90, 123.76, 122.84, 119.06, 115.43 (d, *J* = 22.0 Hz), 113.81; HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{21}FNaO_3SSe, M + Na]^+$: 583.0253, found: 583.0250.

4c: Yield 76% (87.6 mg); white solid; mp 166–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38–7.30 (m, 3H), 7.27–7.23 (m, 1H), 7.18 (s, 1H), 7.13–7.03 (m, 7H), 7.01 (d, *J* = 7.7 Hz, 3H), 6.90 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.00, 153.20, 139.58, 137.82, 137.07, 134.85, 132.33, 132.10, 130.27, 129.79, 129.01, 128.68, 128.52, 128.46, 128.38, 128.05, 127.38, 127.22, 126.88, 123.82, 122.84, 119.07, 113.75; HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{21}ClNaO_3SSe, M + Na]^+$: 598.9957, found: 598.9960.

4d: Yield 70% (86.9 mg); white solid; mp 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (t, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32–7.26 (m, 3H), 7.25–7.19 (m, 3H), 7.13–6.92 (m, 8H), 6.88 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.78, 153.31, 138.66, 137.03, 134.78, 132.24, 132.17, 131.43, 130.64, 129.79, 128.97, 128.63, 128.51, 128.34, 128.10, 127.99, 127.41, 127.17, 126.90, 123.77, 122.91, 118.98, 113.63; HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{21}BrNaO_3SSe, M + Na]^+$: 642.9452, found: 642.9449.

4e: Yield 56% (63.8 mg); white solid; mp 179–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.45 (s, 1H), 7.36–7.23 (m, 5H), 7.07 (s, 5H), 6.86 (d, *J* = 7.6 Hz, 4H), 6.68 (d, *J* = 7.7 Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.30, 153.22, 143.84, 138.68, 136.93, 136.03, 135.15, 132.22, 131.98, 130.30, 129.07, 129.07, 128.89, 128.82, 128.40, 128.40, 128.24, 127.74, 127.05, 126.97, 123.48, 123.41, 123.02, 119.19, 114.21, 21.36, 21.04; HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, found: 593.0659.

4f: Yield 65% (74.6 mg); white solid; mp 159–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.48 (s, 1H), 7.38–7.26 (m, 4H), 7.24 (s, 1H), 7.19–6.99 (m, 5H), 6.99–6.92 (m, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 8.5 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.91 (d, *J* = 248.0 Hz), 159.30, 153.29, 143.93, 139.13, 139.05, 136.01, 134.91, 132.16, 132.07, 131.01, 128.87, 128.39, 128.30, 127.94, 127.21, 127.06, 123.53, 122.91, 121.95 (d, *J* = 3.0 Hz), 119.18, 115.49 (d, *J* = 22.0 Hz), 115.38, 113.97, 21.36; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}FNaO_3SSe, M + Na]^+$: 597.0409, found: 597.0411.

4g: Yield 75% (88.5 mg); white solid; mp 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.56–7.47 (m, 2H), 7.37–7.22 (m, 5H), 7.18–7.00 (m, 5H), 6.99–6.78 (m, 6H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.98, 153.28, 144.02, 138.22, 135.89, 135.19, 134.94, 132.16, 132.14, 131.17, 128.89, 128.48, 128.45, 128.32, 128.12, 127.30, 127.08, 125.22, 123.57, 122.87, 119.24, 114.03, 21.38; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, found: 613.0115.

4h: Yield 61% (69.5 mg); white solid; mp 188–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.34–7.22 (m, 5H), 7.15–7.01 (m, 6H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 3H), 6.71 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 153.16, 143.91, 142.74, 138.89, 135.88, 135.28, 132.37, 131.97, 130.95, 129.48, 128.89, 128.83, 128.43, 128.27, 128.03, 127.94, 126.98, 126.93, 125.79, 123.52, 123.02, 119.27, 114.54, 23.21, 21.37; HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, found: 593.0662.

4i: Yield 66% (77.9 mg); white solid; mp 197–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.36–7.17 (m, 7H), 7.17–7.01 (m, 5H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.25, 153.23, 143.97, 140.06, 139.59, 135.82, 134.96, 132.25, 132.12, 131.43, 130.57, 129.04, 128.84, 128.44, 128.23, 128.15, 127.79, 127.02, 126.48, 123.60, 123.13, 119.17, 114.11, 21.38; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, found: 613.0113

4j: Yield 54% (68.5 mg); white solid; mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.37–7.23 (m, 9H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.12–7.05 (m, 3H), 6.87 (d, *J* = 7.9 Hz, 3H), 6.82 (t, *J* = 7.5 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 159.42, 153.18, 144.03, 139.59, 135.75, 134.97, 132.42, 132.29, 132.16, 131.72, 131.32, 130.51, 130.28, 128.90, 128.85, 128.49, 128.25, 128.21, 127.12, 127.06, 127.00, 123.61, 123.19, 119.23, 114.12, 21.38; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, found: 656.9610.

4k: Yield 79% (90.0 mg); white solid; mp 187–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.39 (s, 1H), 7.36–7.22 (m, 5H), 7.07 (s, 5H), 6.92–6.71 (m, 6H), 2.18 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.27, 153.20, 143.90, 137.99, 137.73, 135.94, 135.04, 133.87, 132.18, 132.04, 130.25, 129.25, 128.92, 128.84, 128.44, 128.25, 128.05, 127.77, 126.97, 126.94, 126.73, 123.51, 123.00, 119.23, 114.18, 21.36, 20.79; HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{26}NaO_3SSe, M + Na]^+$: 593.0660, found: 593.0663.

4l: Yield 61% (72.0 mg); white solid; mp 183–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 6.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 7.35–7.25 (m, 5H), 7.18–7.07 (m, 5H), 7.02 (d, 1H), 6.96 (s, 1H), 6.89 (t, J = 8.4 Hz, 3H), 6.83 (t, J = 7.8 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.03, 153.28, 144.11, 136.68, 135.74, 134.97, 134.72, 133.54, 132.24, 132.08, 131.02, 129.29, 128.93, 128.76, 128.49, 128.37, 128.34, 128.17, 127.26, 127.12, 123.62, 122.82, 119.29, 113.95, 21.40; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}ClNaO_3SSe, M + Na]^+$: 613.0114, found: 613.0113

4m: Yield 76% (96.4 mg); white solid; mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 6.9 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.38 (s, 1H), 7.34–7.25 (m, 5H), 7.24–7.05 (m, 7H), 6.96 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.78 (t, J = 7.8 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.13, 153.26, 144.15, 139.48, 135.65, 135.36, 134.71, 132.27, 132.06, 131.63, 130.87, 129.60, 128.94, 128.66, 128.52, 128.34, 128.22, 127.28, 127.11, 123.63, 122.80, 121.67, 119.34, 113.97, 21.41; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{23}BrNaO_3SSe, M + Na]^+$: 656.9609, found: 656.9610.

4n: Yield 64% (75.7 mg); white solid; mp 203–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.42–7.24 (m, 6H), 7.24–7.07 (m, 5H), 6.89 (d, J = 7.9 Hz, 2H), 6.82–6.69 (m, 2H), 6.69–6.60 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.58 (d, J = 241.0 Hz), 158.30, 157.28 (d, J = 244.0 Hz), 153.34, 144.21, 135.52, 134.77, 132.37, 132.01, 131.55, 128.94, 128.54, 128.39, 128.30, 124.98, 124.74, 123.70, 122.83, 119.31, 118.31 (d, J = 8.0 Hz), 118.08 (d, J = 7.0 Hz), 115.97 (d, J = 8.0 Hz), 115.70 (d, J = 8.0 Hz), 113.86, 21.41; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{22}F_2NaO_3SSe, M + Na]^+$: 615.0315, found: 615.0313.

General procedure for the synthesis of compound 7

m-CPBA (0.6 mmol, 1.2 equiv.) was dissolved in 5.0 mL of $CHCl_3$ and added to a solution of **3a** (0.5 mmol, 1.0 equiv.) in 20.0 mL of $CHCl_3$. After allowing to stand for 10 min at room temperature, the solvent $CHCl_3$ was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE : EA = 1 : 10) to afford compound 7 as a white solid with a yield of 89% (254.0 mg); mp 123–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.48–7.30 (m, 7H), 7.30–7.20 (m, 5H), 6.94 (d, J = 8.0 Hz, 3H), 6.80 (d, J = 7.7 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.60, 154.16, 146.43, 143.96, 137.63, 136.64, 134.25, 132.34, 131.66, 130.73, 129.34, 129.13, 128.68, 128.47, 128.32, 127.88, 127.66, 127.14, 126.78, 126.05, 124.35, 123.55, 118.61, 111.07, 21.52; HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{24}NaO_4SSe, M + Na]^+$: 595.0453, found: 595.0458.

General procedure for the synthesis of compound 8

A solution of 355.8 mg of KOH (6.34 mmol) in 5.0 mL of water was added dropwise to 7 (0.2 mmol) in 10.0 mL of THF. After 5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (PE : EA = 4 : 1) to afford **8** as a white solid with a yield of 95% (76.0 mg); mp 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.80–7.68 (m, 4H), 7.66 (d, J = 8.9 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.55–7.44 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.35, 151.91, 143.89, 139.45, 131.43, 130.82, 130.41, 129.55, 129.15, 129.01, 128.41, 127.74, 127.07, 126.99, 126.61, 126.11, 125.25, 119.95, 118.93, 111.82, 21.47; HRMS (ESI) *m*/*z* calcd for $[C_{25}H_{18}NaO_3S, M + Na]^+$: 421.0869, found: 421.0862.

General procedure for the synthesis of compound 9

m-CPBA (1.2 mmol, 2.4 equiv.) was dissolved in 5 mL of $CHCl_3$ and added to a solution of **3t** (0.5 mmol, 1 equiv.) in 20 mL of $CHCl_3$. After allowing to stand for 10 min at room temperature, the solvent was removed under reduced pressure to afford a residue. The residue was dissolved in 20 mL of THF, and then 5 mL of 1 M aqueous KOH solution was added dropwise to the reaction mixture. After 1.5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (PE : EA = 15 : 1) to afford **9** as a white solid with a yield of 76% (132 mg); mp 112–114 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–8.03 (m, 1H), 7.82 (d, J = 7.1 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.43–7.37 (m, 4H), 7.29–7.25 (m, 2H), 7.05 (d, J = 8.1 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.70, 153.16, 144.08, 139.43, 130.78, 130.05, 129.51, 128.14, 128.10, 126.66, 125.87, 125.47, 124.51, 121.62, 118.72, 111.36, 21.44; HRMS (ESI) *m*/*z* calcd for $[C_{21}H_{16}NaO_3S, M + Na]^+$: 371.0712, found: 371.0717.

Conflicts of interest

There are no conflicts to declare.

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