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Access to Vinyl Ethers and Ketones with Hypervalent Iodine Reagents as Oxy-Allyl Cation Synthetic Equivalents

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In the memory of Prof. Dr. Kilian Muñiz

Abstract: We report an Umpolung strategy of enol ethers to generate oxy-allyl cation equivalents based on the use of hypervalent iodine reagents. Under mild basic conditions, the addition of nucleophiles to aryloxy-substituted vinylbenziodoxolone (VBX) reagents, easily available in two steps from silyl alkynes, resulted in the stereoselective formation of substituted aryl enol ethers. The reaction was most efficient with phenols as nucleophiles, but preliminary results were also achieved for C- and N- nucleophiles. In absence of external nucleophiles, the 2-iodobenzoate group of the reagent was transferred. The obtained aryl enol ethers could then be transformed into α -difunctionalized ketones by oxidation. The described "allyl cation"-like reactivity contrast with the well-established "vinyl-cation" behavior of alkenyl iodonium salts.

In standard organic reactions, new bonds are formed between atoms of opposite polarity.^[1] First introduced by Seebach,^[2] the Umpolung approach -inverting the reactivity of one of the partners- allowed chemical transformations impossible based on the inherent polarity of the reactants. In this context, hypervalent iodine compounds are broadly used in organic synthesis as efficient group transfer reagents via Umpolung of nucleophiles.^[3] Enolates, enol ethers and enamines are among the most important nucleophilic synthons in synthetic chemistry.^[4] The Umpolung of enolates with hypervalent iodine reagents is well established,^[5] but it is only recently that the involved enolonium species could be characterized by Szpilman and co-workers.^[6] Nevertheless, controlling transformations involving highly reactive intermediates formed *in situ* is challenging, and an access to stable reagents would be highly desirable.

Cyclic benziodoxol(on)es (BX) reagents are more stable and especially useful for group transfer reactions.^[7] Recently, Miyake and co-workers^[8] and our group^[9a] reported the first synthesis of enol ethers and enamides-based vinyl benziodoxol(on)es (VBX) reagents by the reaction of nucleophiles with ethynyl benziodoxol(on)es (EBX)^[10] (Scheme 1A, left). The enhanced reactivity of the hypervalent bond allowed the use of VBX as electrophiles in palladium-catalyzed Stille cross-couplings at room temperature for the formation of aryl, vinyl, alkynyl, and alkyl-substituted Z-enamides and enol ethers.^[9a] Moreover, they reacted directly with thiol nucleophiles to form thio-enamides,

acting as vinyl cation equivalents,^[9a] a well established polarity for alkenyl iodonium salts.^[11]

Scheme 1. O-Vinylbenziodoxolones (VBXs) as vinyl and oxy-allyl cation equivalents (A) and application to the synthesis of functionalized ketones (B).

Herein, we report a new mode of reactivity of O-VBX reagents, allowing the Umpolung of enol ethers to give formal oxy-allyl cations instead of vinyl cations (Scheme 1A, right). Oxy-allyl cations have been used as transient electrophilic species for the reaction with nucleophiles^[12] or with dienes in [4 + 3] cycloadditions.^[13] They are also formed in the versatile Nazarov cyclization.^[14] Enantioselective processes have been recently developed.^[15] Access to this type of reactive intermediates from hypervalent iodine reagents has not been reported to the best of our knowledge. Hypervalent iodoallyl intermediates have been proposed in sigmatropic [2,3] and [3,3] rearrangements.^[16] Reactive allylic cation intermediates were accessed recently using diazo-substituted hypervalent iodine reagents by Suero.^[17] In our work, we now disclose a different approach based on the treatment of O-VBX reagents with base and nucleophiles for the formation of C-O, C-N and C-C bonds in allylic position. The obtained aryl enol ethers were transformed into α -difunctionalized ketones under oxidative conditions (Scheme 1B), resulting in a 3-4 steps synthesis from the corresponding silylated alkynes.

After having successfully used O-VBX reagents as vinyl cation equivalents with thiols,^[9a] we attempted to extend this reactivity to phenols as nucleophiles. However, the reaction of O-VBX (**1a**) and *para*-cresol (**2a**) under basic conditions led to the unexpected formation of allyl ether **3a** as main product (Table 1).^[18] In 1,2-dimethoxyethane (DME) as solvent with 1.2 equivalents of potassium *tert*-butoxide as base, **3a** could be obtained in 80% yield (entry 1). Other solvents gave a lower yield (See Supporting Information). When various bases were tested, cesium carbonate gave a similar NMR yield as KO^tBu, but with higher reproducibility (entry 2),^[19] whereas organic bases, such

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as pyridine and triethylamine gave no reactivity (entries 3-4). O-VBX **1a** was also recovered when performing the reaction without base (entry 5). Incomplete conversion of **1a** was observed when using a catalytic amount or one equivalent of base (entries 6 and 7). In the case of a larger excess of base (entry 8), formation of the allylic ester **4a** resulting from addition of 2-iodo benzoate was increased. In fact, small amounts of **4a** were always observed in this transformation. Allyl ester such as **4a** are valuable building blocks in synthetic chemistry. Furthermore, all the parts of reagent **1a** are incorporated in the product, resulting in high atom economy.^[20] Therefore, we optimized the formation of ester **4a** in absence of external nucleophiles (see Supporting Information for details). In presence of 20 mol% anisole as a non-participating nucleophilic additive, **4a** could be obtained as the only product in 65% yield (entry 9).

Table 1. Optimisation of the addition of *p*-cresol (**2a**) to O-VBX **1a**.

Entry	Base	Base equivalents	Yield of 3a (%) ^[a]	Yield of 4a (%) ^[a]
1	KOtBu	1.20	80	15%
2	Cs ₂ CO ₃	1.20	79	15%
3	Pyridine	1.20	NR	NR
4	Et ₃ N	1.20	NR	NR
5	none	-	NR	NR
6	Cs ₂ CO ₃	0.20	35	6%
7	Cs ₂ CO ₃	1.00	60	8%
8	Cs ₂ CO ₃	2.00	62	32%
9 ^[b]	Cs ₂ CO ₃	1.20	-	65%

Reactions conditions: Substrate **1a** (0.100 mmol), *para*-cresol (**2a**) (0.100 mmol), base (0.120 mmol) and DME (0.1 M) at 25 °C. NR = No reaction. ^[a]NMR yield determined by addition of 0.1 mmol of CH₂Br₂ as an internal standard after the reaction. When determined, the yield of **4a** is given in parenthesis.

^[b]Reaction performed without **2a** in presence of 0.20 equiv. anisole as additive.

To explore the scope of formation of aryl enol ethers and esters, two conditions were used: conditions **A**, starting from isolated O-VBX **1** and conditions **B**, using an one-pot two-step procedure from the corresponding EBX reagent **5** without isolation of the intermediate O-VBX **1** (Scheme 2). For the addition of external nucleophiles to give allyl ethers **3**, method **A** usually gave better yields. For allylic esters **4**, the yields were nearly identical for both methods, and the more practical method **B** was therefore preferred.

The scope of phenol nucleophiles was first investigated (Scheme 2A). On a 0.3 mmol scale, using conditions **A**, substrate

3a was obtained in 83% yield. When conditions **B** were employed, only 63% yield was observed. The difference came from the larger amount of allyl ester **4a** formed.^[21] 4-Bromo- and 4-iodo-phenols afforded the corresponding products **3b** and **3c** in respectively 75% and 73% yields. 4-Methoxyphenol ether **3d** was obtained in a reduced yield of 45%, due to increased formation of ester **4a**. Boronic acid pinacol ester **3e** was formed in 71% yield. A *meta*-methoxy group was also well tolerated (product **3f**). When an unprotected amine-containing substrate was employed, 35% of product **3g** was still obtained, but significant decomposition was observed. Aryl enol ether **3h** bearing an *ortho* ester group was obtained in 89% yield. A sterically highly hindered hydroxyacetophenone still afforded compound **3i** in 43% yield. 2-Naphthol was successfully converted into the corresponding aryl enol ether **3j** in 72% yield.

The scope of the reaction could be extended to more complex phenols (Scheme 2B). Protected tyrosine gave the desired product **3k** in 96% yield. Two natural products containing phenols -capsaicin and estradiol- could be used subsequently in the one-pot protocol **B** to give highly functionalized product **3l** in 41% yield. Under the optimized conditions, the reaction worked best with phenols. Nevertheless, promising results were obtained with several C- and N-nucleophiles (Scheme 2B). Diketone and ketoester-derived products **3m** and **3n** were obtained in 31 and 65% yield respectively, whereas tosyl amide **3o** was isolated in 33% yield.

Having explored the reactivity of various nucleophiles, we turned to the scope of O-VBX reagents with *para*-cresol (**2a**) as nucleophile (Scheme 2C). Propyl-substituted O-VBX **1b** led to formation of allylic ether **3p** in 65% yield with a complete *E*-stereoselectivity.^[22] The formation of **3p** also confirmed that the new C-O bond was formed at the position of the iodine atom. A longer alkyl chain was also well tolerated and product **3q** was obtained in 57% yield. A hypervalent iodine reagent bearing a free alcohol could be converted into allylic ether **3r**. Ethers **3s** and **3t** containing a protected alkyne and a phthalimide group could also be accessed. We could also perform this transformation with O-VBX bearing phenol with an iodide in *ortho* position to give products **3u-w** in 44-61% yield. An electron-donating group in *para* position was also well tolerated (products **3x** and **3y**). When the reaction was examined for N-VBX reagent **1l** bearing a sulfonamide group, the product **3z** could be observed by NMR in about 30% yield. However, isolation of the product always led to partial decomposition and isomerization to the more stable internal alkene.

We then examined the synthesis of allyl esters using conditions **B** (Scheme 2D). Primary alkyl chains were well tolerated on the EBX reagents, and products **4b-d** were obtained in good yield (Scheme 6A). EBXs bearing functional groups such as a protected alkyne, a phthalimide, an alkene or a chloride could be converted to the corresponding products **4e-h** in 60% to 82% yield. Halogen substituents were also tolerated. The *ortho*-iodo, *meta*-bromo and pentafluoro, derivatives **4i-m** were obtained in 40% to 70% yield. In addition, phenols bearing an electron-donating methoxy group in *para* position or an electron-withdrawing aldehyde in *ortho* position could also be used to give products **4n-p** in 58-64% yield.

Scheme 2. Scope of the reaction. For **A**, **B**, and **C**, the yield of ester product **4** is given in parenthesis. ^[a]Only partial conversion of **1a** was observed. ^[b]Reaction time was 24 h. ^[c]The reaction was performed on gram scale.

In some cases, formation of the O-VBX reagent **1** was successful, but the reaction stopped at this stage. In particular, this was the case for secondary alkyl groups, in absence of an allylic C-H bond, for sterically hindered O-VBX or for simple VBX lacking the ether group^[23] (see Scheme S1 in Supporting Information for more details). To highlight the efficiency of the transformation, gram scale syntheses were performed (Scheme 2C and 2D). Allylic ether **3x** was isolated in 63% yield using method **A**, while one-pot procedure **B** gave 66% of allylic ester **4e**. These yields are nearly identical to the one obtained on small scale, showing the robustness of the procedures.

We then examined further functionalization of the obtained aryl enol ethers (Scheme 3). The *ortho*-iodine substrate **3u** could

be used in a reported palladium oxidative cyclization^[24] to generate benzofuran **6** in high yield (Eq. 1). Under palladium-catalyzed hydrogenation conditions, ketone **7** resulting from cleavage of the aryl-O bond and reduction of the aryl iodide was obtained in 96% yield (Eq. 2). Finally, the electron-rich nature of the enol ether make it well-suited for oxidative modification, with the potential for accessing more highly functionalized ketones. Indeed, when using 1.2 equivalents of *meta*-chloroperbenzoic acid (*m*-CPBA) buffered with sodium bicarbonate, the epoxides **8a** and **8b** could be obtained in quantitative yield starting from the corresponding enol ethers (Eq. 3).^[25] Interestingly, the addition of the *in situ* generated *meta*-chlorobenzoic acid was observed in absence of buffer to give α -benzoylated ketones such as **9a** and

9b in moderate to good yields (Eq. 4).^[26] Treatment of the isolated epoxide **8a** with acetic acid lead to the same regioselective formation of α -acetoxo ketone **10** in 72% yield (Eq. 5). This straightforward oxidation method allows to make use of the formed enol ether resulting in an overall C-H functionalization of the initial propargylic C-H bond.

Scheme 3. Product modifications.

A speculative mechanism to rationalize the observed oxy-allyl cation-like reactivity would involve the isomerization of VBX **1** to the corresponding allyl iodane under basic conditions. The high leaving group ability of hypervalent iodine^[27] would then lead to the formation of an allyl cation. Indeed, ring-opening of an adjacent cyclopropane and a [4+3] reaction with furan in low yield were observed, supporting such an intermediate (See Scheme S5 and S6 in SI). However, the evidence does not allow to exclude a direct S_N2 pathway and further experiments will be needed to understand the observed transformations.

In conclusion, hypervalent iodine reagents have been used as oxy-allyl cation surrogates for the stereoselective synthesis of aryl enol ethers by reaction with phenols. In absence of external nucleophiles, the *in-situ* generated benzoate group reacted, resulting in the formation of allylic esters. The reaction most probably proceeds via an electrophilic allylic intermediate and both S_N1 or S_N2 pathways appear feasible at this stage. The obtained enol ethers could be transformed into α -difunctionalized ketones under oxidative conditions, demonstrating the synthetic utility of the transformation.

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Keywords: Hypervalent Iodine Reagents • Umpolung • Allyl Cation • Enol Ethers • Vinylbenziodoxolones

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Access to oxy-allyl cation equivalents from alkynes via hypervalent iodine reagents is described. The stereoselective transformation of Vinylbenziodoxolones (VBXs) gives aryl enol ethers bearing an allylic ether or ester group and corresponds to a Umpolung of the nucleophilic reactivity of enol ethers. The obtained products are easily transformed into α -difunctionalized ketones under oxidative conditions.

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Supporting Information

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1. Additional experiments and results

Limitations for the formation of allylic esters from EBX:

In some cases, formation of the O-VBX reagent **1** was successful, but the reaction stopped at this stage (Scheme S1). In particular, this was the case for secondary alkyl groups. For cyclopropyl and cyclohexyl groups, the corresponding O-VBXs **1m** and **1n** were recovered in 88% and 65% yield. Cyclopentyl-substituted O-vBX **1o** decomposed under the reaction conditions. The reaction cannot proceed in absence of allylic C-H bond and *t*-Butyl-VBX **1p** and phenyl-EBX **1q** were isolated in excellent yield. In contrast, the reaction proceeded for all O-VBX reagents bearing a primary alkyl group, with the exception of sterically hindered *ortho*-dichlorobenzene-substituted O-VBX **1r**, which could not be converted to the corresponding allylic ester. Finally, simple VBX **11**¹ lacking the ether group was engaged in the procedure, but no reaction occurred and the starting material was recovered.

Scheme S1: Scope of EBX **5** for the formation of allylic esters **4**: reaction stopping at VBX stage.

The analysis data of compounds **1m-1r** are described section 4.

Mechanistic investigations:

To gain insights into the reaction mechanism several control experiments were performed. We first wondered if allylic ester **4a** was just an intermediate for the formation of allylic ether **3a** via nucleophilic substitution (Scheme S2). When **4a** was resubmitted to the reaction conditions, no substitution was observed, showing that **4a** was not an intermediate in the synthesis of allylic ethers.

¹ E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan, B. Olofsson, *Chem. Eur. J.* **2016**, 22, 16066.

Scheme S2: Reaction of **4a** with *p*-cresol **2a**.

We then wondered if the formation of **4a** was an intramolecular process, which would explain why it was difficult to suppress completely. To check this hypothesis, a mixture of O-VBX reagents **1a** and **1t** bearing different groups on the benzene ring of the hypervalent iodine reagent and the one of the phenol was submitted to the reaction conditions. Four products **4q**, **4q'**, **4r** and **4r'** were obtained in a similar proportion, showing that rapid cross-over was occurring and not a selective intramolecular process (Scheme S3).

Scheme S3: Cross-over experiment.

We then investigated the nature of the reactive intermediate by attempting to trap it (Scheme S4). Addition of an equivalent of TEMPO or *para*-methoxystyrene to the reaction of O-VBX (**1a**) with *para*-cresol (**2a**) did not affect the result. These indicated that radical or carbene intermediates, if at all present, would be short-lived and difficult to intercept.

Scheme S4: Reaction of **1a** with *p*-cresol **2a** in presence of TEMPO or *p*-methoxystyrene.

We then wondered if the reaction could proceed through an oxy-allyl cation intermediate (Scheme S5). With furan as co-solvent starting from **1a**, **4a** was still obtained in 50% yield. Formation of (4+3) adduct **12** was observed by HRMS, but in too small amounts to be isolated.

Scheme S5: Reaction of **1a** with *p*-cresol **2a** in presence of furan as co-solvent.

In order to gain further insight into the nature of the reactive intermediate, we then prepared the new EBX reagent **5q** (Scheme S6). Under the one-pot reaction conditions, **5q** was converted to diene **13** as main product, together with small amounts of **4s** and ketone **14**. The formation of **13** could come from the regioselective nucleophilic attack of the in situ generated iodobenzoate on a putative oxy-allyl intermediate **I**, but a concerted mechanism with simultaneous cleavage of the C-I bond cannot be excluded. A control experiment showed that **4s** did not react with benzoate to give **13**.

Scheme S6: Reaction of **5ab** with *p*-cresol **2a**.

Proposed mechanism:

Based on the performed experiments, the following speculative mechanism can be proposed (Scheme S7). The formation of O-VBX **1** from EBX **5** was previously reported.² Then, several pathways are available for O-VBX **1**. Direct substitution, either via a vinyl cation intermediate or via a concerted/stepwise addition-elimination pathway as common for EBX reagents³ would lead to the vinylic product with thiol nucleophiles (Scheme S7 A).² In presence of a catalytic amount of cesium carbonate, deprotonation of the vinyl position would lead to vinyl anion **I**, which can fragment to give back EBX **5** and the phenolate (Scheme S7 B). In our previous work, this equilibrium was shown to be feasible and strongly in the favour of VBX **1**. In presence of an excess of base, a small amount of

² P. Caramenti, N. Declas, R. Tessier, M. D. Wodrich, J. Waser, *Chem. Sci.* **2019**, *10*, 3223.

³ a) R. Frei, M. D. Wodrich, D. P. Hari, P. A. Borin, C. Chauvier, J. Waser, *J. Am. Chem. Soc.* **2014**, *136*, 16563; b) M. D. Wodrich, P. Caramenti, J. Waser, *Org. Lett.* **2016**, *18*, 60.

deprotonation at the allylic position could also occur to give allylic anion **II**, which can be drawn as its resonance structure **II'** and reprotonated α to the iodine atom to give allylic hypervalent iodine intermediate **III** (Scheme S7 C).

Scheme S7: Speculative reaction mechanism. **A.** Vinyl cation reactivity. **B.** Equilibrium with EBX. **C.** Oxo-allyl cation reactivity.

In the deprotonation event, it would be important to minimize the strong $\text{A}^{1,2}$ strain with the aryl group on the ether in **TS^{1-II}**. The aryl group is expected to point away from the iodine atom to limit steric interactions, and potentially also allow a favourable overlap of the oxygen lone-pair with the "sigma-hole" of the hypervalent iodine. If reprotonation is significantly faster than bond rotation, the stereochemistry of the double-bond would be fixed. From allylic-I(III) intermediate **III**, two pathways could be envisaged. The well-known thermodynamic instability of alkyl-I(III)⁴ in general and allylic intermediates in particular⁵ would lead to an α -elimination of the aryl iodide to deliver oxy-allyl cation

⁴ a) J. B. Dence, J. D. Roberts, *J. Org. Chem.* **1968**, 33, 1251; b) G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1969**, 91, 2113; c) D. G. Morris, A. G. Shepherd, *J. Chem. Soc. Chem. Commun.* **1981**, 1250; d) A. Flores, E. Cots, J. Bergès, K. Muñiz, *Adv. Synth. Catal.* **2019**, 361, 2; f) A. E. Bosnidou, K. Muñiz, *Chem. Eur. J.* **2019**, 25, 13654.

⁵ Selected examples: a) K. Lee, D. Y. Kim, D. Y. Oh, *Tetrahedron Lett.* **1988**, 29, 667; b) H. R. Khatri, J. Zhu, *Chem. Eur. J.* **2012**, 18, 12232; c) H. Nguyen, H. R. Khatri, J. Zhu, *Tetrahedron Lett.* **2013**, 54, 5464; d) B. Xu, U. K. Tambar, *J. Am. Chem. Soc.* **2016**, 138, 12073; e) B. Xu, U. K. Tambar, *Angew. Chem., Int. Ed.* **2017**, 56, 9868; Reviews: f) A.

species **IV**. Nucleophilic attack by the generated iodobenzoate, or by an external phenolate, would provide the desired allylic products **3** and **4** via an overall S_{N}^1 pathway. However, an alternative S_{N}^2 pathway by direct reaction of the nucleophile with allylic intermediate **III** cannot be excluded at this stage, especially when considering that no very strong support could be gathered for a free oxy-allyl cation intermediate **IV**. Finally, it is difficult to propose a rationalization for the anisole additive effect. One highly speculative explanation may be that a donor could coordinate to the iodine atom to give iodonium **V**, resulting both in enhanced electrophilicity of the allylic system and enhanced nucleophilicity of the benzoate.

2. General methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 10 ppm, Karl-Fischer titration). The solvents were degassed through Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem, or Merck and used as such unless otherwise stated. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, with the solvents indicated as eluent under 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain, or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ¹H-NMR spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in CDCl₃, DMSO-d₆, CD₃OD, C₆D₆ and CD₂Cl₂, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm the internal methanol signal at 3.30 ppm, the internal dichloromethane signal at 5.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation). ¹³C-NMR spectra were recorded with ¹H-decoupling on a Bruker DPX-400 100 MHz spectrometer in CDCl₃, DMSO-d₆, CD₃OD or CD₂Cl₂, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm, the internal methanol signal at 49.0 ppm and the internal dichloromethane signal at 54.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. Optical rotations were measured on a Schmidt+Haensch (Polartronic M) polarimeter using a 10 cm cell with a Na 589 nm filter. The specific solvents and concentrations (in 10 mg/mL) are indicated.

3. Preparation of EBX reagents

The synthesis of the precursors for EBX reagents (except **5f**, **5o**, **5p** and **5q**) and their starting materials had been already described before in our group.^{6,7} The procedures here reported are taken from the cited publications to facilitate reproduction of the results by having all the data in the same file.

General procedure for the synthesis of EBX from boronic acid:

GP1: Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (1.00 equiv.), *para*-toluenesulfonic acid monohydrate (1.10 equiv.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 1.10 equiv.) were dissolved in dichloromethane and 2,2,2-trifluoroethanol (1:1 mixture, 0.27 M). The mixture was stirred at room temperature under nitrogen for 1 hour, after which the correspondent alkyl-1-boronic acid pinacol ester (1.40 equiv.) was added in one portion. The reaction mixture was stirred for 2.5 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. NaHCO₃ (30 mL) was added. The mixture was stirred for 15 minutes, the two layers were separated and the aqueous phase was extracted with additional portions of dichloromethane (3 x 25 mL). The combined organic layers were washed with brine (25 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (DCM:MeOH 9:1) to afford the desired compounds **5**.

Propynyl-1,2-benziodoxol-3(1*H*)-one (**5a**)

Following **GP1** on 4.30 mmol scale and using propynyl-1-boronic acid pinacol ester (4.85 g, 21.2 mmol, 1.40 equiv.), propynyl-1,2-benziodoxol-3(1*H*)-one **5a** (1.03 g, 3.60 mmol, 84%) was obtained as a white solid. *R*_f: 0.10 (EtOAc). *Mp* 124-150 °C (decomposition). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.41-8.35 (m, 1 H, ArH), 8.22-8.14 (m, 1 H, ArH), 7.79-7.68 (m, 2H, ArH), 2.27 (s, 3H, CCCH₃). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.7, 134.8, 132.5, 131.6, 126.4, 115.6, 105.1, 39.0, 5.7.⁹ IR ν 2183 (w), 1607 (s), 1559 (m), 1350 (m), 746 (m), 730 (m). HRMS (ESI) C₁₀H₈IO₂⁺ [M+H]⁺ 286.9564; found 286.9561.

(Pent-1-ynyl)-1,2-benziodoxol-3(1*H*)-one (**5b**)

Following **GP1** on 4.00 mmol scale and using 1-pentynyl-1-boronic acid pinacol ester (1.09 g, 4.60 mmol, 1.15 equiv.) (pent-1-ynyl)-1,2-benziodoxol-3(1*H*)-one **5b** (0.754 g, 2.40 mmol, 60%) was obtained as a white oil.¹⁰ ¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (ddd, *J* = 7.4, 3.8, 2.3 Hz, 1H, ArH), 8.26 – 8.09 (m, 1H, ArH), 7.75 (dddd, *J* = 6.0, 4.6, 2.8, 1.8 Hz, 2H, ArH), 2.58 (td, *J* = 7.1,

⁶ R. Frei, M. D. Wodrich, D. P. Hari, P.-A. Borin, C. Chauvier, J. Waser, *J. Am. Chem. Soc.* **2014**, *136*, 16563.

⁷ D. P. Hari, J. Waser, *J. Am. Chem. Soc.* **2016**, *138*, 2190.

⁸ M. J. Bouma, B. Olofsson, *Chem. – A Eur. J.* **2012**, *18*, 14242.

⁹ One aromatic carbon signal was not resolved.

¹⁰ NB: the compound was isolated as an extremely viscous oil and retains organic solvent.

1.6 Hz, 2H, CH_2), 1.68 (dtd, $J = 14.7, 7.2, 2.1$ Hz, 2H, CH_2), 1.08 (td, $J = 7.6, 2.1$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz) 166.8, 134.6, 132.1, 131.3, 126.2, 115.5, 109.5, 50.4, 38.8, 22.3, 21.6, 13.4. IR ν 2960 (w), 2875 (w), 2172 (w), 1732 (m), 1654 (s), 1465 (w), 1439 (w), 1342 (w), 1296 (m), 1252 (m), 1109 (w), 1016 (w), 832 (m), 743 (s). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{IO}_2^+$ $[\text{M}+\text{H}]^+$ 314.9877; found 314.9882.

(5-Chloropent-1-ynyl)-1,2-benziodoxol-3(1H)-one (5i)

Following **GP1** on 15.2 mmol scale and using 5-chloro-1-pentynyl-1-boronic acid pinacol ester (4.85 g, 21.2 mmol, 1.40 equiv.), (5-chloropent-1-ynyl)-1,2-benziodoxol-3(1H)-one **5i** (3.76 g, 10.8 mmol, 71%) was obtained as a white solid. **Mp**: 138.5–141.7 °C. **R_f**: 0.15 (EtOAc 100%).

^1H NMR (400 MHz, Chloroform- d) δ 8.41–8.34 (m, 1H, ArH), 8.22–8.13 (m, 1H, ArH), 7.82–7.68 (m, 2H, ArH), 3.71 (t, $J = 6.1$ Hz, 2H, ClCH_2CH_2), 2.82 (t, $J = 6.9$ Hz, 2H, CCCH_2CH_2), 2.18–2.05 (m, 2H, ClCH_2CH_2). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.8, 134.9, 132.5, 131.6, 131.6, 126.4, 115.8, 107.1, 43.4, 41.2, 30.7, 18.0. IR ν 2942 (w), 2866 (w), 2171 (w), 2091 (w), 1727 (w), 1617 (s), 1556 (w), 1441 (w), 1339 (m), 1213 (w), 1023 (w), 846 (w), 742 (s). The characterization data corresponded to the reported values.⁸

2-Cyclopropylethynyl-1,2-benziodoxol-3(1H)-one (5j)

Following **GP1** on 25.8 mmol scale and using 5-chloro-1-pentynyl-1-boronic acid pinacol ester (4.85 g, 21.2 mmol, 1.40 equiv.), (cyclopropylethynyl)trimethylsilane (5.00 g, 36.2 mmol, 1.40 equiv.) 2-cyclopropylethynyl-1,2-benziodoxol-3(1H)-one **5j** (2.11 g, 6.76 mmol, 26%) was obtained as a white solid. **Mp**: 174.2–177.6 °C (Dec.). **R_f**: 0.46 (EtOAc:MeOH, 9:1).

^1H NMR (400 MHz, Chloroform- d) δ 8.34 (dd, $J = 7.0, 2.1$ Hz, 1H, ArH), 8.18–8.09 (m, 1H, ArH), 7.81–7.63 (m, 2H, ArH), 1.59 (tt, $J = 8.2, 5.0$ Hz, 1H, CH), 1.07–0.85 (m, 4H, CH_2CH_2). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7, 134.7, 132.3, 131.7, 131.4, 126.2, 115.9, 113.3, 35.0, 9.8, 1.1. IR ν 3464 (w), 3077 (w), 3012 (w), 2238 (w), 2159 (m), 1607 (s), 1559 (m), 1438 (m), 1338 (m), 1298 (m), 833 (m), 744 (s), 691 (m). HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{10}\text{IO}_2^+$ $[\text{M}+\text{H}]^+$ 312.9720; found 312.9719. Data reported in literature.⁶

2-Cyclohexylethynyl-1,2-benziodoxol-3(1H)-one (5k)

Following **GP1** on 4.00 mmol scale and using ethynylcyclohexane (0.732 g, 5.60 mmol, 1.40 equiv) 2-cyclohexylethynyl-1,2-benziodoxol-3(1H)-one **5k** (0.850 g, 2.40 mmol, 60%) was obtained as a white amorphous solid. **R_f**: 0.44 (DCM:MeOH 9:1).

^1H NMR (400 MHz, Chloroform- d) δ 8.28 (t, $J = 6.0$ Hz, 1H, ArH), 8.10 (t, $J = 5.8$ Hz, 1H, ArH), 7.65 (dp, $J = 12.9, 6.6$ Hz, 2H, ArH), 2.68 (h, $J = 4.7, 4.2$ Hz, 1H, CH), 1.82 (d, $J = 12.5$ Hz, 2H, CH_2), 1.67 (d, $J = 10.7$ Hz, 2H, CH_2), 1.46 (t, $J = 10.4$ Hz, 3H, CH_2), 1.29 (d, $J = 10.2$ Hz, 3H, CH_2). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7, 134.3, 131.9, 131.4, 130.9, 126.1, 115.5, 113.4, 38.7, 31.9, 30.4, 25.3, 24.4. IR ν 2899 (m), 2877 (m), 1634 (s), 1579 (s), 1494 (w), 1307 (s), 1241 (w), 1049 (w), 980 (w), 876 (w), 817 (w). HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{IO}_2^+$ $[\text{M}+\text{H}]^+$ 355.0190; found 355.0192.

2-Cyclopentylethynyl-1,2-benziodoxol-3(1H)-one (5l)

Following **GP1** on 4.00 mmol scale and using ethynylcyclopentane (0.649 g, 5.60 mmol, 1.40 equiv.) at 50 °C, 2-cyclopentylethynyl-1,2-benziodoxol-3(1H)-one **5l** (0.950 g, 2.79 mmol, 70%) was obtained as a white amorphous solid. **R_f**: 0.40 (DCM:MeOH 9:1). ^1H NMR (400 MHz, Chloroform- d) δ 8.28 (t,

$J = 6.0$ Hz, 1H, ArH), 8.08 (t, $J = 6.4$ Hz, 1H, ArH), 7.66 (tt, $J = 13.4$, 7.0 Hz, 2H, ArH), 2.91 (q, $J = 6.7$ Hz, 1H, CH), 1.96 (dd, $J = 13.6$, 7.5 Hz, 2H, CH₂), 1.68 (d, $J = 13.9$ Hz, 4H, CH₂), 1.63 – 1.48 (m, 2H, CH₂). ¹³C NMR (CDCl₃, 100 MHz) δ 166.7, 134.4, 131.9, 131.5, 131.0, 126.1, 115.5, 113.7, 38.3, 33.5, 31.3, 24.9. IR ν 2960 (w), 2868 (w), 2165 (w), 1649 (s), 1610 (s), 1560 (m), 1439 (m), 1333 (m), 1295 (m), 1222 (w), 1008 (m), 833 (w), 752 (m). HRMS (ESI) calcd for C₁₄H₁₄IO₂⁺ [M+H]⁺ 341.0033; found 341.0036.

Preparation of hydroxy-BX:

GP2: Following a reported procedure,⁶ NaIO₄ (1.05 equiv.) and 2-iodobenzoic acid **15** (1.00 equiv.) were suspended in 30% (v/v) aq. AcOH (48 mL for 33.8 mmol). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product **16**.

1-Hydroxy-5-methyl-1,2-benziodoxol-3-(1H)-one (16a)

Following **GP2** on 33.8 mmol scale, 1-hydroxy-1,2-benziodoxol-3-(1H)-one **16a** (8.3 g, 31 mmol, 98%) was obtained as a white solid. ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.02 (dd, $J = 7.7$, 1.4 Hz, 1H, ArH), 7.97 (m, 1H, ArH), 7.85 (dd, $J = 8.2$, 0.7 Hz, 1H, ArH), 7.71 (td, $J = 7.6$, 1.2 Hz, 1H, ArH). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. IR ν 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 834 (m), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m). The values of the NMR spectra are in accordance with reported literature data.⁶

1-Hydroxy-5-methyl-1,2-benziodoxol-3-(1H)-one (16b)

Following **GP2** on 1.91 mmol scale, 1-hydroxy-5-methyl-1,2-benziodoxol-3-(1H)-one **16b** (0.402 g, 1.45 mmol, 76%) was obtained as a white amorphous solid. ¹H NMR (400 MHz, Dimethyl Sulfoxide-*d*₆) δ 7.96 (s, 1H, OH), 7.84 (s, 1H, ArH), 7.78 (d, $J = 8.0$ Hz, 1H, ArH), 7.69 (d, $J = 8.0$ Hz, 1H, ArH), 2.47 (s, 3H, ArCH₃). δ 8.00 (s, 1H, ArH), 7.72 – 7.61 (m, 1H, ArH), 7.59 – 7.47 (m, 1H, ArH), 3.88 (s, 3H, OCH₃). ¹³C NMR (100 MHz, Dimethyl Sulfoxide-*d*₆) δ 168.2, 141.0, 135.7, 131.9, 126.4, 117.2, 20.6. The values of the NMR spectra are in accordance with reported literature data.¹¹

1-Hydroxy-5-methoxy-1,2-benziodoxol-3-(1H)-one (16c)

Following **GP2** on 3.60 mmol scale, 1-hydroxy-5-methoxy-1,2-benziodoxol-3-(1H)-one **16c** (0.838 g, 2.85 mmol, 79%) was obtained as a white amorphous solid. ¹H NMR (400 MHz, Dimethyl Sulfoxide-*d*₆) δ 8.00 (s, 1H, ArH), 7.72 – 7.61 (m, 1H, ArH), 7.59 – 7.47 (m, 1H, ArH), 3.88 (s, 3H, OCH₃). ¹³C NMR (100 MHz, Dimethyl

Sulfoxide- d_6) δ 167.9, 162.0, 133.5, 127.6, 122.0, 115.4, 109.5, 56.4. The values of the NMR spectra are in accordance with reported literature data.¹¹

General procedure for the synthesis of EBX from hydroxy-BX:

GP3: Following a reported procedure,¹² to a solution of 2-iodosylbenzoic acid **16** (1.00 equiv.) in dry DCM ($c = 0.2 \text{ M}$) was added trimethylsilyl trifluoromethanesulfonate (1.10 equiv.) dropwise at room temperature and the reaction mixture was stirred for 1 h. After this time, the corresponding trimethylethynylsilane **17** (1.10 equiv.) was added and the mixture was stirred for 6 h at room temperature. The reaction mixture was then quenched with saturated aqueous NaHCO_3 solution and extracted with dichloromethane (3 times). The combined organic extracts were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/methanol as eluent to give the corresponding EBX reagent **5**.

1-[Phenylethynyl]-1,2-benziodoxol-3(1H)-one (5n)

Following **GP2** on 41.5 mmol scale, 1-[phenylethynyl]-1,2-benziodoxol-3(1H)-one **5n** (6.08 g, 17.4 mmol, 46 %) as a white solid. **Mp** (Dec.) 155.0–160.0 °C (lit 153–155 °C). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.46 (m, 1H, ArH), 8.28 (m, 1H, ArH), 7.80 (m, 2H, ArH), 7.63 (m, 2H, ArH), 7.48 (m, 3H, ArH). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.9, 134.9, 132.9, 132.5, 131.6, 131.3, 130.8, 128.8, 126.2, 120.5, 116.2, 106.6, 50.2. Data reported in literature.¹²

5-Methyl-propynyl-1,2-benziodoxol-3(1H)-one (5o)

Following **GP3** on 1.44 mmol scale, 5-methyl-propynyl-1,2-benziodoxol-3(1H)-one **5o** (0.235 g, 783 μmol , 54% - about 85% purity) was obtained as a white solid **Rf**: 0.57 (DCM:MeOH 9:1). **Mp**: 137 °C. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.15 (s, 1H, ArH), 7.98 (d, $J = 8.4 \text{ Hz}$, 1H, ArH), 7.52 (dd, $J = 8.5, 2.2 \text{ Hz}$, 1H, ArH), 2.46 (s, 3H, ArCH_3), 2.23 (s, 3H, CH_3). $^{13}\text{C NMR}$ (100 MHz, Chloroform- d) δ 167.4, 142.3, 135.7 (2 Carbon signals are overlapping), 132.9, 126.3, 111.7, 105.1, 37.7, 20.8, 5.6. **IR** ν 2979 (m), 2913 (w), 2245 (w), 2175 (w), 1625 (s), 1574 (m), 1456 (m), 1404 (m), 1316 (m), 1253 (m), 1067 (m), 1004 (m), 909 (s), 786 (m), 730 (s), 645 (m). **HRMS** (ESI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2^+$ 300.9720; Found 300.9724.

5-Methoxy-propynyl-1,2-benziodoxol-3(1H)-one (5p)

Following **GP3** on 2.72 mmol scale, 5-methoxy-propynyl-1,2-benziodoxol-3(1H)-one **5aa** (0.273 g, 864 μmol , 32%) was obtained as a white solid **Rf**: 0.51 (DCM:MeOH 9:1). **Mp**: 176 °C. $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 7.97 (d, $J = 9.1 \text{ Hz}$, 1H, ArH), 7.91 (d, $J = 3.0 \text{ Hz}$, 1H, ArH), 7.30 (dd, $J = 9.1, 3.0 \text{ Hz}$, 1H, ArH),

¹¹ S. Bertho, R. Rey-Rodriguez, C. Colas, P. Retailleau, I. Gillaizeau, *Chem. – Eur. J.* **2017**, 23, 17674–17677.

¹² S. Nicolai, C. Piemontesi, J. Waser, *Angew. Chem. Int. Ed.* **2011**, 50, 4680.

3.93 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.6, 163.3, 133.2, 127.0, 123.1, 115.5, 104.7, 103.3, 56.4, 38.5, 5.7. IR ν 2175 (w), 1631 (s), 1577 (s), 1464 (m), 1418 (m), 1317 (s), 1231 (m), 1031 (m), 1000 (w), 907 (m), 789 (m), 734 (s). HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₁H₁₀IO₃⁺ 316.9669; Found 316.9676.

One pot procedure for the synthesis of EBX:

Octynyl-1,2-benziodoxol-3(1*H*)-one (**5c**)

Following a slightly modified procedure,¹³ a solution of 1-octyne **18** (747 mg, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL) was cooled to -78 °C, at which temperature 1.6 M *n*BuLi in hexanes (4.24 mL, 6.78 mmol, 1.00 eq.) was added dropwise. The mixture was stirred at -78 °C for 90 minutes and then cannulated into a to -78 °C pre-cooled solution consisting of triisopropyl borate (1.56 mL, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL). The reaction mixture was stirred at -78 °C for 2 hours, after which 2.0 M HCl in diethyl ether (3.73 mL, 7.46 mmol, 1.10 eq.) was added. The cooling bath was removed and the mixture was stirred for an additional 60 minutes. After filtration and solvent removal, Kugelrohr distillation (75 °C at 0.6 mbar) furnished pure diisopropyloct-1-ynylboronate (**19**, 940 mg, 3.95 mmol, 58% yield) as a colorless liquid. ¹H NMR (CDCl₃, 400 MHz): δ 4.55 (sept, 2 H, *J* = 6.2 Hz, ⁱPr-CH), 2.27 (t, 2 H, *J* = 7.0 Hz, propargyl CH₂), 1.60-1.48 (m, 2 H, CH₂), 1.45-1.24 (m, 6 H, CH₂), 1.19 (d, 12 H, *J* = 6.2 Hz, ⁱPr-CH₃), 0.89 (t, 3 H, *J* = 6.9 Hz, alkyl CH₃). The values of the ¹H NMR spectrum are in accordance with reported literature data.¹⁴

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (692 mg, 2.79 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH·H₂O, 531 mg, 2.79 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 756 mg, 3.07 mmol, 1.10 eq.) were dissolved in dichloromethane (4.5 mL) and 2,2,2-trifluoroethanol (4.5 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which diisopropyloct-1-ynylboronate (**19**, 930 mg, 3.90 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 2 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. NaHCO₃ (30 mL) was added. The mixture was stirred for 15 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl

¹³ H. C. Brown, N. G. Bhat, M. Srebnik, *Tetrahedron Lett.* **1988**, 29, 2631.

¹⁴ R. Morita, E. Shirakawa, T. Tsuchimoto, Y. Kawakami, Y. *Org. Biomol. Chem.* **2005**, 3, 1263.

acetate) to afford **5c** (940 mg, 2.64 mmol, 95%) as a white solid. R_f (EtOAc) = 0.25. **Mp** 50-63 °C. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.42-8.35 (m, 1 H, ArH), 8.20-8.13 (m, 1 H, ArH), 7.78-7.69 (m, 2 H, ArH), 2.59 (t, 2 H, J = 7.1 Hz, CCCH_2), 1.70-1.58 (m, 2 H), 1.51-1.39 (m, 2 H), 1.38-1.26 (m, 4 H), 0.94-0.86 (m, 3 H, CH_2CH_3). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 166.7, 134.7, 132.5, 131.7, 131.6, 126.3, 115.7, 109.9, 39.4, 31.3, 28.7, 28.3, 22.6, 20.6, 14.1. **IR** ν 2930 (w), 2858 (w), 2166 (w), 1619 (s), 1561 (w), 1439 (w), 1331 (m), 1297 (m), 832 (w), 748 (m). **HRMS** (ESI) $\text{C}_{15}\text{H}_{18}\text{IO}_2^+$ $[\text{M}+\text{H}]^+$ calc. = 357.0346; $[\text{M}+\text{H}]^+$ obs. = 357.0339.

5-Pentanoethynyl-1,2-benziodoxol-3(1H)-one (**5d**)

Following a slightly modified procedure,¹⁵ 2.5 M $n\text{BuLi}$ in hexanes (39.2 mL, 98.0 mmol, 2.20 eq.) was added at -78 °C under nitrogen to a mixture of hept-6-yn-1-ol **20** (5.00 g, 44.6 mmol, 1.00 eq.) and dry THF (150 mL), followed by 4-dimethylaminopyridine (DMAP, 1.36 g, 11.1 mmol, 0.25 eq.). The mixture was stirred at -78 °C for 60 minutes, after which trimethylsilyl chloride (TMS-Cl, 20.4 mL, 156 mmol, 3.50 eq.) was added dropwise. The cooling bath was removed and the reaction stirred for 2 hours. Next, 1.0 N aq. HCl (50 mL) was added and the solution was stirred vigorously for 30 minutes at room temperature. The mixture was diluted with EtOAc (200 mL) and extracted. The aqueous layer was extracted with additional portions of EtOAc (3 x 50 mL). The combined organic layers were washed with sat. aq. NaHCO_3 (100 mL), brine (50 mL), dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (pentane:EtOAc 4:1) to afford 7-(trimethylsilyl)hept-6-yn-1-ol (**21**, 8.22 g, 43.5 mmol, 97%) as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.61 (t, 2 H, J = 6.5 Hz, CH_2OH), 2.21 (t, 2 H, J = 7.0 Hz, CCCH_2), 1.73 (bs, 1 H, CH_2OH), 1.61-1.48 (m, 4 H), 1.48-1.38 (m, 2 H), 0.11 (s, 9 H, TMS). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 107.4, 84.6, 62.8, 32.3, 28.5, 25.1, 19.9, 0.3. The values of the $^1\text{H NMR}$ spectrum are in accordance with reported literature data.¹⁶

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (7.69 g, 31.0 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate ($\text{TsOH} \cdot \text{H}_2\text{O}$, 5.90 g, 31.0 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 8.41 g, 34.1 mmol, 1.10 eq.) were dissolved in dichloromethane (57 mL) and 2,2,2-trifluoroethanol (57 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which 7-(trimethylsilyl)hept-6-yn-1-ol (**21**, 8.00 g, 43.4 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 18 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (500 mL) and under vigorous stirring, saturated aq. NaHCO_3 (500 mL) was added. The mixture was stirred for 60 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 150 mL). The combined organic layers were dried over

¹⁵ P. A. Peixoto, J. A. Richard, R. Severin, D. Y. Chen, *Org. Lett.* **2011**, 13, 5724.

¹⁶ F. Rodier, M. Rajzmann, J. L. Parrain, G. Chouraqui, L. Commeiras, *Chem. Eur. J.* **2013**, 19, 2467.

MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (EtOAc:MeOH 95:5) to afford **5d** (3.56 g, 9.94 mmol, 32%) as a white solid. *R_f* (EtOAc:MeOH 9:1) = 0.24. *Mp* 115–120 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.33 (dd, 1 H, *J* = 7.2, 2.0 Hz, *ArH*), 8.15 (d, 1 H, *J* = 8.0 Hz, *ArH*), 7.79–7.64 (m, 2 H, *ArH*), 3.66 (t, 2 H, *J* = 5.9 Hz, CH₂OH), 2.59 (t, 2 H, *J* = 6.9 Hz, CCCH₂), 1.73–1.49 (m, 7 H, CH₂ and OH). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 134.8, 132.3, 131.6, 131.5, 126.5, 115.7, 109.7, 62.3, 39.2, 32.1, 28.0, 25.3, 20.6. IR ν 3351 (w), 2934 (w), 2170 (w), 1623 (s), 1585 (m), 1561 (w), 1439 (w), 1333 (m), 1300 (w), 1058 (w), 911 (m), 832 (w), 732 (s), 689 (m). HRMS (ESI) C₁₄H₁₆IO₃⁺ [M+H]⁺ calc. = 359.0139; [M+H]⁺ obs. = 359.0136.

8-(Trimethylsilyl)octa-1,7-diyn-1-yl-1,2-benziodoxol-3(1*H*)-one (**5e**)

Following a slightly modified procedure,⁶ to a solution of 1,7-octadiyne **22** (10.6 g, 100 mmol, 1.00 equiv) in dry THF (150 mL) was added at -78 °C under nitrogen 1 M lithium bis(trimethylsilyl)amide in THF (LiHMDS, 100 mL, 100 mmol, 1.00 equiv.). The solution was stirred at -78 °C for 30 minutes, after which trimethylsilyl chloride (TMSCl, 13.0 mL, 100 mmol, 1.00 equiv.) was added dropwise. The reaction was warmed to room temperature and stirred for 2 h. The reaction was cooled to 0 °C and quenched by adding water (10 mL). The mixture was diluted with 1 M HCl (200 mL) and extracted with diethyl ether (100 mL and 2 x 75 mL). The combined organic layers were washed with brine (200 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by vacuum distillation using a 20 cm Vigreux column (oil bath set to 98 °C at 0.3 mbar) furnishing pure trimethyl(octa-1,7-diyn-1-yl)silane **23** (8.37 g, 46.9 mmol, 47%) as a colorless liquid. *R_f*: 0.2 (Pentane). ¹H NMR (CDCl₃, 400 MHz) δ 2.28–2.17 (m, 4H), 1.93 (t, *J* = 2.7 Hz, 1H, CCH), 1.68–1.57 (m, 4H), 0.13 (s, 9H, TMS). ¹³C NMR (CDCl₃, 100 MHz) δ 107.0, 84.9, 84.2, 68.6, 27.7, 27.6, 19.5, 18.1, 0.3. IR ν 3309 (w), 2951 (w), 2175 (w), 1250 (m), 912 (w), 841 (s), 761 (m), 734 (m). Data reported in literature.⁶

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (8.43 g, 33.3 mmol, 1.00 equiv.), *para*-toluenesulfonic acid monohydrate (TsOH.H₂O, 6.40 g, 33.3 mmol, 1.00 equiv.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 9.04 g, 36.7 mmol, 1.10 equiv.) were dissolved in CH₂Cl₂ (60 mL) and 2,2,2-trifluoroethanol (60 mL). The mixture was stirred at room temperature under nitrogen for 1 h, after which trimethyl(octa-1,7-diyn-1-yl)silane **23** (8.32 g, 46.7 mmol, 1.40 equiv.) was added. The reaction mixture was stirred for 15 h at room temperature and then filtered and concentrated *in vacuo*. The resulting light being solid was dissolved in CH₂Cl₂ (500 mL) and under vigorous stirring, saturated solution of NaHCO₃ (500 mL) was added. The mixture was stirred for 1 h, the two layers were separated and the aqueous layer was extracted with additional portions of CH₂Cl₂ (3 x 150 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography using ethyl acetate to afford **5e** (4.20 g, 9.90 mmol, 30%) as a white solid. *Mp*: 152.3–155.6 °C. *R_f*: 0.59 (EtOAc:MeOH 9:1). ¹H NMR (CDCl₃, 400 MHz)

δ 8.37 (dd, J = 6.7, 2.3 Hz, 1H, ArH), 8.17 (dd, J = 7.8, 1.5 Hz, 1H, ArH), 7.82-7.66 (m, 2H, ArH), 2.63 (t, J = 6.8 Hz, 2H), 2.29 (t, J = 6.7 Hz, 2H), 1.83-1.62 (m, 4H), 0.13 (s, 9H, TMS). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7, 134.8, 132.4, 131.7, 131.5, 126.3, 115.7, 109.1, 106.4, 85.4, 40.0, 27.7, 27.3, 20.2, 19.4, 0.3. IR ν 2955 (w), 2170 (w), 1647 (m), 1621 (s), 1439 (w), 1329 (m), 1296 (w), 1249 (m), 840 (s), 746 (s). HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{IO}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$ 425.0428; found 425.0433. Data reported in literature.⁶

2-(6-(3-Oxo-1,2-benziodoxol-3(1H)-yl)hex-5-yn-1-yl)isoindoline-1,3-dione (5f)

To a stirring solution of 6-(trimethylsilyl)hex-5-yn-1-ol **25** (852 mg, 5.00 mmol, 1.00 equiv.) in THF (16.7 mL) was added triphenylphosphine (1.44 g, 5.50 mmol, 1.10 equiv.) and DIAD (1.15 mL, 5.50 mmol, 1.10 equiv.) at 0°C . The reaction mixture was stirred at this temperature for 15 min and then, phthalimide (**24**) (750 mg, 5.10 mmol, 1.02 equiv.) was added. The reaction was continued at room temperature for 5 h, then cold water (20 mL) was added and the product was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using Et₂O/pentane 10:90 as eluent to furnish 2-(6-(trimethylsilyl)hex-5-yn-1-yl)isoindoline-1,3-dione (**26**) as a white solid (1.37 g, 4.58 mmol, 92%). **M.p.** 68–70 $^\circ\text{C}$; **R_f** = 0.26 (Et₂O/pentane 10:90); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (dd, J = 5.4, 3.1 Hz, 2H, ArH), 7.70 (dd, J = 5.4, 3.1 Hz, 2H, ArH), 3.70 (t, J = 7.0 Hz, 2H, CH_2NPhth), 2.27 (t, J = 7.1 Hz, 2H, $\text{C}\equiv\text{CCH}_2$), 1.85–1.74 (m, 2H, CH_2), 1.61–1.49 (m, 2H, CH_2), 0.12 (s, 9H, TMS); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 134.0, 132.3, 123.3, 106.7, 85.1, 37.6, 27.8, 25.9, 19.6, 0.3; IR (ν_{max} , cm^{-1}) 2955 (w), 2931 (w), 2170 (w), 1770 (w), 1705 (m), 1440 (w), 1390 (s), 1352 (m), 1324 (m), 1247 (m), 1035 (m), 904 (m), 841 (s), 761 (s), 718 (s), 638 (m); HRMS (ESI/QTOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{17}\text{H}_{22}\text{NO}_2\text{Si}^+$ 300.1414; Found 300.1413.

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (496 mg, 2.00 mmol, 1.00 equiv.), *para*-toluenesulfonic acid monohydrate ($\text{TsOH} \cdot \text{H}_2\text{O}$, 380 mg, 2.00 mmol, 1.00 equiv.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 493 mg, 2.20 mmol, 1.10 equiv.) were dissolved in CH_2Cl_2 (3 mL) and 2,2,2-trifluoroethanol (3 mL). The mixture was stirred at room temperature under nitrogen for 1 h, after which 2-(6-(trimethylsilyl)hex-5-yn-1-yl)isoindoline-1,3-dione **26** (599 mg, 2.00 mmol, 1.00 equiv.) was added. The reaction mixture was stirred for 15 h at room temperature and then filtered and concentrated in vacuo. The resulting light beige solid was dissolved in CH_2Cl_2 (30 mL) and under vigorous stirring, a saturated solution of NaHCO_3 (30 mL) was added. The mixture was stirred for 1 h, the two layers were separated and the aqueous layer was extracted with additional portions of CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated

in vacuo. The crude product was purified by flash column chromatography using ethyl acetate to afford 2-(6-(3-oxo-1,2-benziodoxol-3(1*H*)-yl)hex-5-yn-1-yl)isoindoline-1,3-dione **5f** (300 mg, 634 μ mol, 32%) as a white solid. **R_f**: 0.54 (DCM:MeOH 9:1). **Mp**: 168-172 °C. **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.40 (dd, *J* = 7.3, 1.9 Hz, 1H, Ar*H*), 8.16 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar*H*), 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 7.82 – 7.69 (m, 4H, Ar*H*), 3.76 (t, *J* = 7.0 Hz, 2H, CH₂), 2.67 (t, *J* = 7.0 Hz, 2H, CH₂), 1.95 – 1.83 (m, 2H, CH₂), 1.78 – 1.67 (m, 2H, CH₂). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 168.6, 166.6, 135.0, 134.3, 132.5, 132.1, 131.6, 131.6, 126.3, 123.5, 115.7, 108.6, 40.7, 37.3, 27.8, 25.4, 20.1. **IR** ν 2937 (w), 2164 (w), 1768 (m), 1710 (s), 1647 (s), 1619 (s), 1441 (m), 1398 (m), 1329 (m), 1181 (w), 1031 (w), 914 (m), 835 (w), 727 (s), 687 (w). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₁₇INO₄⁺ 474.0197; Found 474.0203.

Hexadecynyl-1,2-benziodoxol-3(1*H*)-one (**5g**)

To a mixture of trimethylsilylacetylene (8.33 g, 85.0 mmol, 1.20 eq.) and dry THF (46 mL) was added at -78 °C under nitrogen 2.5 M *n*BuLi in hexanes (33.9 mL, 85.0 mmol, 1.20 eq.) over a 10 minute time period. The resulting light yellow solution was stirred at -78 °C for 60 minutes, after which a mixture consisting of 1-bromotetradecane **27** (19.6 g, 70.7 mmol, 1.00 eq.), hexamethylphosphoramide (HMPA, 14.2 mL, 78.0 mmol, 1.10 eq.) and dry THF (23 mL) was slowly added *via* cannula over a 20 minute time period. The reaction mixture was stirred for 60 minutes at -78 °C, followed by 24 hours of stirring at room temperature. The reaction was quenched at 0 °C with saturated aq. NH₄Cl (50 mL) and diluted with water (10 mL) and EtOAc (50 mL). The two layers were separated and the aq. layer was extracted with additional portions of EtOAc (3 x 50 mL). The combined organic layers were washed with water (2 x 100 mL), brine (100 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The light brown crude liquid was finally pushed through a small plug of silica gel with pentane as eluent to afford pure hexadec-1-yn-1-yltrimethylsilane (**28**, 19.3 g, 65.5 mmol, 92.7% yield) as a colorless liquid. **R_f** (pentane) = 0.78. **¹H NMR** (CDCl₃, 400 MHz): δ 2.19 (t, 2 H, *J* = 7.1 Hz, CCCH₂), 1.54-1.44 (m, 2 H, CH₂), 1.42-1.18 (m, 22 H, CH₂), 0.87 (t, 3 H, *J* = 6.7 Hz, CH₂CH₃), 0.13 (s, 9 H, TMS). **¹³C NMR** (CDCl₃, 100 MHz): ¹⁷ δ 107.7, 84.3, 32.2, 29.9, 29.8, 29.7, 29.6, 29.3, 29.0, 28.9, 22.9, 20.0, 14.3, 0.3. **IR** ν 2924 (m), 2854 (m), 2175 (w), 1461 (w), 1249 (w), 910 (w), 841 (s), 761 (w), 736 (m). **HRMS** (ESI) C₁₉H₃₈AgSi⁺ [M+Ag]⁺ calc. = 401.1794; [M+Ag]⁺ obs. = 401.1798.

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (8.00 g, 32.2 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH·H₂O, 6.13 g, 32.2 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 8.74 g, 35.5 mmol, 1.10 eq.) were dissolved in dichloromethane (60 mL) and 2,2,2-trifluoroethanol (60 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which hexadec-1-yn-1-yltrimethylsilane (**28**, 13.3 g, 45.1

¹⁷ Some signals were not resolved at 100 MHz.

mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 14 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (400 mL) and under vigorous stirring, saturated aq. NaHCO₃ (400 mL) was added. The mixture was stirred for 60 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 100 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **5g** (6.02 g, 12.9 mmol, 40%) as a white solid. *R_f* (EtOAc) = 0.36. *Mp* 102.6-105.3 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.44-8.37 (m, 1 H, ArH), 8.21-8.14 (m, 1 H, ArH), 7.80-7.70 (m, 2 H, ArH), 2.59 (t, 2 H, *J* = 7.1 Hz, CCCH₂), 1.65 (p, 2 H, *J* = 7.1 Hz, CCCH₂CH₂), 1.52-1.40 (m, 2 H), 1.39-1.19 (m, 20 H, CH₂), 0.86 (t, 3 H, *J* = 6.7 Hz, CH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 166.6, 134.7, 132.5, 131.7, 131.6, 126.2, 115.7, 109.9, 39.5, 32.1, 29.8, 29.7, 29.6, 29.5, 29.2, 29.1, 28.3, 22.8, 20.6, 14.3. IR ν 2924 (s), 2853 (m), 2166 (w), 1649 (m), 1623 (m), 1439 (w), 908 (m), 736 (s). HRMS (ESI) C₂₃H₃₄IO₂⁺ [M+H]⁺ calc. = 469.1598; [M+H]⁺ obs. = 469.1614.

(Oct-6-en-1-ynyl)-1,2-benziodoxol-3(1H)-one (5h)

To a mixture of trimethylsilylacetylene (7.23 g, 73.6 mmol, 1.20 eq.) and dry THF (40 mL) was added at -78 °C under nitrogen 2.5 M *n*BuLi in hexanes (31.9 mL, 80.0 mmol, 1.30 eq.) over a 10 minute time period. The resulting light yellow solution was stirred at -78 °C for 60 minutes, after which a mixture consisting of 6-bromohexene **29** (10.0 g, 61.3 mmol, 1.00 eq.), hexamethylphosphoramide (HMPA, 12.0 mL, 67.5 mmol, 1.10 eq.) and dry THF (20 mL) was slowly added *via* cannula over a 20 minute time period. The reaction mixture was stirred for 60 minutes at -78 °C, followed by 24 hours of stirring at room temperature. The reaction was quenched at 0 °C with saturated aq. NH₄Cl (50 mL) and diluted with water (5 mL) and EtOAc (50 mL). The two layers were separated and the aq. layer was extracted with additional portions of EtOAc (3 x 50 mL). The combined organic layers were washed with water (2 x 100 mL), brine (100 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The light brown crude liquid was finally pushed through a small plug of silica gel with pentane as eluent to afford pure trimethyl(oct-7-en-1-yn-1-yl)silane (**30**, 10.6 g, 58.8 mmol, 95.9% yield) as a colorless liquid. ¹H NMR (CDCl₃, 400 MHz): δ 5.79 (ddt, 1 H, *J* = 16.9, 10.2, 6.7 Hz, CH₂CHCH₂), 5.04-4.91 (m, 2 H, CH₂CHCH₂), 2.22 (t, 2 H, *J* = 6.9 Hz, CH₂), 2.11-2.01 (m, 2 H, CH₂), 1.58-1.43 (m, 4 H, CH₂), 0.14 (s, 9 H, TMS). ¹³C NMR (CDCl₃, 100 MHz): δ 138.8, 114.7, 107.6, 84.5, 33.3, 28.2, 28.1, 19.9, 0.3. The values of the NMR spectra are in accordance with reported literature data.¹⁸

¹⁸ H. Urabe, F. Sato, *J. Am. Chem. Soc.* **1999**, 121, 1245.

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (9.82 g, 39.6 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH·H₂O, 7.53 g, 39.6 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 10.7 g, 43.6 mmol, 1.10 eq.) were dissolved in dichloromethane (73 mL) and 2,2,2-trifluoroethanol (73 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which trimethyl(oct-7-en-1-yn-1-yl)silane (**30**, 10.0 g, 55.4 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 14 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (700 mL) and under vigorous stirring, saturated aq. NaHCO₃ (700 mL) was added. The mixture was stirred for 1 hour, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 200 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **5h** (2.60 g, 7.34 mmol, 19%) as a white solid. In addition, starting trimethyl(oct-7-en-1-yn-1-yl)silane (**77**, 3.20 g, 17.7 mmol) was recovered and re-submitted to the above described conditions to afford additional **11m** (1.18 g, 3.33 mmol, 28%) as a white solid, giving an overall yield of 27% brsm. *R*_f (EtOAc) = 0.34. *Mp* 48-58 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.43-8.36 (m, 1 H, ArH), 8.21-8.13 (m, 1 H, ArH), 7.80-7.69 (m, 2 H, ArH), 5.81 (ddt, 1 H, *J* = 17.0, 10.2, 6.7 Hz, CH₂CHCH₂), 5.10-4.95 (m, 2 H, CH₂CHCH₂), 2.61 (t, 2 H, *J* = 7.0 Hz), 2.17-2.07 (m, 2 H), 1.73-1.51 (m, 4 H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.7, 138.1, 134.8, 132.5, 131.6, 131.6, 126.2, 115.7, 115.2, 109.5, 39.7, 33.2, 28.1, 27.7, 20.4. IR ν 3294 (w), 2912 (w), 2869 (w), 1731 (w), 1650 (w), 1625 (w), 1447 (m), 1250 (w), 1101 (s), 1018 (m), 747 (s). HRMS (ESI) C₁₅H₁₆IO₂⁺ [M+H]⁺ calc. = 355.0189; [M+H]⁺ obs. = 355.0182.

3,3-Dimethylbutynyl-1,2-benziodoxol-3(1*H*)-one (**5m**)

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (1.64 g, 6.59 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH·H₂O, 1.25 g, 6.59 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 1.79 g, 7.25 mmol, 1.10 eq.) were dissolved in dichloromethane (12 mL) and 2,2,2-trifluoroethanol (12 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which diisopropyl (3,3-dimethylbut-1-yn-1-yl)boronate (**31**, 1.94 g, 9.23 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 1 hour at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (120 mL) and under vigorous stirring, saturated aq. NaHCO₃ (120 mL) was added. The mixture was stirred for 60 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **5m** (2.06 g, 6.28 mmol, 95%) as a white solid. *R*_f (EtOAc) = 0.36. *Mp* 189-192 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.39-8.33 (m, 1 H, ArH), 8.13-8.07 (m, 1 H, ArH), 7.78-7.66 (m, 2 H, ArH), 1.34 (s, 9 H, *t*Bu). ¹³C NMR (CDCl₃, 100 MHz): δ 166.7, 134.7, 132.4, 131.6, 131.5, 126.0, 117.5, 115.7, 38.2, 30.6, 29.7. IR ν 3463 (w), 2971 (w), 2171 (w), 1646 (s), 1622 (s), 1440 (w), 1332 (m), 1248 (m), 913 (w), 832 (m), 745 (s). HRMS (ESI) C₁₃H₁₄IO₂⁺ [M+H]⁺ calc. = 329.0033; [M+H]⁺ obs. = 329.0023.

1-(3-Cyclopropylprop-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one (5q)

To a mixture of trimethylsilylacetylene (2.36 g, 24.0 mmol, 1.20 eq.) and dry THF (20 mL) was added at -78 °C under nitrogen 2.5 M *n*BuLi in hexanes (10.4 mL, 26.0 mmol, 1.30 eq.) over a 10 minute time period. The resulting light yellow solution was stirred at -78 °C for 60 minutes, after which a mixture consisting of (bromomethyl)cyclopropane **32** (2.70 g, 20.0 mmol, 1.00 eq.), hexamethylphosphoramide (HMPA, 3.83 mL, 22.0 mmol, 1.10 eq.) and dry THF (2 mL) was slowly added *via* cannula over a 20 minute time period. The reaction mixture was stirred for 60 minutes at -78 °C, followed by 24 hours of stirring at room temperature. The reaction was quenched at 0 °C with saturated aq. NH₄Cl (20 mL) and diluted with water (5 mL) and Et₂O (20 mL). The two layers were separated and the aq. layer was extracted with additional portions of Et₂O (3 x 20 mL). The combined organic layers were washed with water (2 x 20 mL), brine (20 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The light brown crude liquid was finally pushed through a small plug of silica gel with pentane as eluent to afford the (3-cyclopropylprop-1-yn-1-yl)trimethylsilane **33** (2.72 g, 17.9 mmol, 89%).

Following a slightly modified procedure,⁸ 2-iodobenzoic acid **15** (2.33 g, 9.38 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH·H₂O, 1.78 g, 9.38 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 2.31 g, 10.3 mmol, 1.10 eq.) were dissolved in dichloromethane (16 mL) and 2,2,2-trifluoroethanol (16 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which (3-cyclopropylprop-1-yn-1-yl)trimethylsilane (**33**, 2.00 g, 13.1 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 14 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. NaHCO₃ (30 mL) was added. The mixture was stirred for 1 hour, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 20 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (DCM/methanol) to afford **5q** (1.08 g, 3.31 mmol, 35%) as a white solid. **Rf**: 0.61 (DCM:MeOH 9:1). **Mp**: 132-137 °C. ¹H NMR (400 MHz, Methylene Chloride-*d*₂) δ 8.34 – 8.28 (m, 1H, ArH), 8.27 – 8.22 (m, 1H, ArH), 7.77 (m, 2H, ArH), 2.61 (d, *J* = 6.3 Hz, 2H, CH₂), 1.08 (t, *J* = 8.0, 6.3, 4.8 Hz, 1H, CH), 0.66 – 0.53 (m, 2H, CH₂), 0.35 – 0.27 (m, 2H, CH₂). ¹³C NMR (101 MHz, Methylene Chloride-*d*₂) δ 166.7, 135.1, 132.4, 132.2, 131.9, 126.9, 116.3, 108.5, 40.3, 25.4, 9.9, 4.7. **IR** ν 3425 (m), 3073 (m), 3005 (m), 2921 (m), 2167 (m), 1616 (s), 1560 (s), 1514 (m), 1443 (s), 1328 (s), 1296 (s), 1243 (m), 1011 (s), 950 (m), 833 (s), 751 (s), 681 (m), 643 (m). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₂IO₂⁺ 326.9877; Found 326.9879.

Preparation of (*E*)-1-(Pent-1-en-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one **11**:

1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (**81**)

Following a reported procedure,¹⁹ 2-iodosylbenzoic acid **16a** (20.8 g, 79.0 mmol, 1.00 equiv.) was suspended in acetic anhydride (75.0 mL, 788 mmol, 10.0 equiv.) and heated to reflux (140 °C) until complete dissolution (about 15 min). The resulting clear solution was allowed to cool to room temperature and then cooled to 5 °C overnight. The white crystals were filtered, washed with pentane (3 x 30 mL) and dried under reduced pressure to afford 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one **34** as a white solid (22.3 g, 73.0 mmol, 92%). ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (dd, *J* = 7.6, 1.6 Hz, 1H, ArH), 8.00 (dd, *J* = 8.3, 1.0 Hz, 1H, ArH), 7.92 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H, ArH), 7.71 (td, *J* = 7.3, 1.1 Hz, 1H, ArH), 2.25 (s, 3 H, COCH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 176.5, 168.2, 136.2, 133.3, 131.4, 129.4, 129.1, 118.4, 20.4. The values of the NMR spectra are in accordance with reported literature data.²⁰

(*E*)-1-(Pent-1-en-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**11**)

Following the reported procedure²¹, a solution of the corresponding *trans*-1-penten-1-ylboronic acid **35** (1.30 mmol, 1.00 equiv.) in dry DCM (13 mL) was added BF₃·OEt₂ (0.198 mL, 1.56 mmol, 1.20 equiv.) dropwise at 0 °C. After 15 minutes, 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one **34** (477 mg, 1.56 mmol, 1.20 equiv.) was added in one portion at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred until the reaction was completed (4 to 24 h, monitored by TLC using MeOH/DCM 5:95). The reaction was then quenched with a saturated solution of NaHCO₃ (13 mL) and stirred vigorously for 1 h. The resulting suspension was filtered and the filtrate was extracted with DCM (3 x 20 mL). The combined organic layers were washed with water (3 x 20 mL), dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The resulting solid was dissolved in DCM (minimum amount until dissolution) and precipitated in Et₂O (ca. 150 mL). After precipitation at 4 °C for 2 h, the solid was filtered and washed with Et₂O to afford (*E*)-1-(pent-1-en-1-yl)-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (**11**) as a white solid (115 mg, 0.364 mmol, 28%). M.p. (dec.) 154-160 °C; *R*_f = 0.15 (MeOH/DCM 5:95); ¹H NMR (400 MHz, MeOD) δ 8.34 - 8.22 (m, 1H, ArH), 7.80 - 7.63 (m, 3H, ArH), 7.16 (dt, *J* = 14.9, 7.0 Hz, 1H, ICHCHCH₂), 6.87 (dt, *J* = 15.0, 1.4 Hz, 1H, ICHCHCH₂), 2.49 (qd, *J* = 7.2, 1.5 Hz, 2H, CHCH₂CH₂), 1.65 (h, *J* = 7.4 Hz, 2H, CH₂CH₂CH₃), 1.05 (t, *J* = 7.4 Hz, 3H, CH₂CH₃); ¹³C NMR (101 MHz, MeOD) δ 169.7, 160.4, 134.9, 133.1, 131.6, 128.7, 114.7, 100.1, 38.6, 22.2, 13.7; IR (ν_{max}, cm⁻¹) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for C₁₂H₁₄IO₂ + [M+H]⁺ 317.0033; found 317.0033.

¹⁹ P. Caramenti, S. Nicolai, J. Waser, *Chem. Eur. J.* **2017**, *23*, 14702–14706.

²⁰ P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579.

²¹ G. Pisella, A. Gagnebin, J. Waser, *ChemRxiv. Preprint*, **2019**, <https://doi.org/10.26434/chemrxiv.7892513.v1>

4. Synthesis of O-VBX reagents

General Procedure for the Synthesis O-VBX.

In a glass vial, the correspondent sulfonamide or phenol (1.00 equiv.) was dissolved in EtOH (0.08 M). Cs_2CO_3 (10 mol%) was added and the mixture stirred vigorously for 5 minutes. Then the corresponding EBX **5** was added in one portion (1.00 equiv.) and the reaction was left stirring for 12 hours if not specifically specified otherwise. The reaction was stopped, the EtOH removed under reduced pressure and the crude purified via column chromatography using DCM:MeOH (20:1) as eluent to provide **1**.

(Z)-(1-Prop-1-en-2-yl-2-oxy)-4-methylbenzene-1,2-benziodoxol-3-(1H)-one (**1a**)

Starting from EBX **5a** (286 mg, 1.00 mmol), (Z)-(1-prop-1-en-2-yl-2-oxy)-4-methylbenzene-1,2-benziodoxol-3-(1H)-one **1a** (226 mg, 0.572 mmol, 57% yield) was obtained, as a white amorphous solid. **Rf**: 0.48 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.40 – 8.34 (m, 1H, ArH), 7.64 – 7.52 (m, 3H, ArH), 7.11 – 7.04 (m, 2H, ArH), 6.77 (d, J = 8.5 Hz, 2H, ArH), 5.80 (d, J = 1.1 Hz, 1H, vinylH), 2.27 (s, 3H, CH_3), 2.18 (d, J = 0.9 Hz, 3H, CH_3). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 167.1, 166.8, 151.2, 135.4, 133.7, 133.1, 132.7, 130.4, 130.3, 125.3, 120.0, 113.7, 77.3 (1 Carbon signal overlaps with Chloroform-*d*), 20.7, 19.2. **IR** ν 1603 (s), 1559 (w), 1505 (s), 1437 (w), 1357 (w), 1275 (w), 1211 (m), 837 (w).

HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{IO}_3^+$ $[\text{M}+\text{H}]^+$ 395.0139; found 395.0148. The olefin geometry was assigned by analogy to NMR data of compound **1l**. The values of the NMR spectra are in accordance with reported literature data.²

(Z)-(1-Pent-1-en-2-yl-2-oxy)-4-methylbenzene-1,2-benziodoxol-3-(1H)-one (**1b**)

Starting from EBX **5b** (314 mg, 1.00 mmol), (Z)-(1-pent-1-en-2-yl-2-oxy)-4-methylbenzene-1,2-benziodoxol-3-(1H)-one **1b** (172 mg, 0.407 mmol, 41% yield) was obtained as a white amorphous solid. **Rf**: 0.50 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.49 – 8.31 (m, 1H, ArH), 7.60 (m, 3H, ArH), 7.09 (d, J = 7.9 Hz, 2H, ArH), 6.78 (d, J = 7.9 Hz, 2H, ArH), 5.85 (s, 1H, vinylH), 2.48 (t, J = 7.6 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.60 (q, J = 7.5 Hz, 2H, CH_2), 0.96 (t, J = 7.4 Hz, 3H, CH_3). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 170.4, 166.5, 151.5, 134.9, 133.8, 133.1, 132.9, 130.6, 130.5, 125.1, 119.1, 113.9, 80.1, 34.4, 20.7, 20.4, 13.5. **IR** ν 1601 (w), 1505 (w), 1430 (w), 1266 (m), 1205 (m), 1143 (w), 740 (s), 703 (m), 660 (m).

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{IO}_3^+$ $[\text{M}+\text{H}]^+$ 423.0452; found 423.0452. The olefin geometry was assigned by analogy to NMR data of compound **1l**. The values of the NMR spectra are in accordance with reported literature data.²

(Z)-1-(2-(p-tolyloxy)oct-1-en-1-yl)-1,3-benziodoxol-3-(1H)-one (1c)

Starting from EBX **5c** (0.107 g, 0.300 mmol), (Z)-1-(2-(p-tolyloxy)oct-1-en-1-yl)-1,3-benziodoxol-3-(1H)-one **1c** (80.0 mg, 0.172 mmol, 57% yield) was obtained, as a white amorphous solid. **Rf**: 0.50 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.48 – 8.42 (m, 1H, ArH), 7.67 – 7.60 (m, 3H, ArH), 7.14 – 7.07 (m, 2H, ArH), 6.86 – 6.79 (m, 2H, ArH), 5.90 (s, 1H, vinylH), 2.51 (t, *J* = 7.6 Hz, 2H, CCH₂CH₂CH₂CH₂CH₂CH₃), 2.31 (s, 3H, ArCH₃), 1.58 (p, *J* = 7.5 Hz, 2H, CCH₂CH₂CH₂CH₂CH₂CH₃), 1.39 – 1.19 (m, 6H, CCH₂CH₂CH₂CH₂CH₂CH₃), 0.88 (t, *J* = 6.8 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 167.2, 151.7, 135.2, 133.5, 133.5, 133.2, 130.8, 130.6, 125.7, 119.5, 114.5, 79.8, 32.6, 31.5, 28.8, 27.1, 22.6, 20.9, 14.1. **IR** ν 3056 (m), 2929 (m), 2858 (m), 1605 (s), 1505 (s), 1340 (m), 1272 (s), 1206 (s), 1117 (m), 1008 (m), 927 (m), 832 (s), 748 (s), 693 (m). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₆IO₃⁺ 465.0921; Found 465.0921. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(7-hydroxy-2-(p-tolyloxy)hept-1-en-1-yl)-1,3-benziodoxol-3-(1H)-one (1d)

Starting from EBX **5d** (0.107 g, 0.300 mmol), (Z)-1-(7-hydroxy-2-(p-tolyloxy)hept-1-en-1-yl)-1,3-benziodoxol-3-(1H)-one **1d** (0.110 g, 0.237 mmol, 79% yield) was obtained, as a white solid. **Rf**: 0.27 (DCM:MeOH 9:1). **Mp**: 151-172 °C. **¹H NMR** (400 MHz, Methanol-*d*₄) δ 8.29 (dd, *J* = 7.5, 1.9 Hz, 1H, ArH), 7.89 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 7.78 (td, *J* = 8.1, 7.6, 1.9 Hz, 1H, ArH), 7.75 – 7.69 (m, 1H, ArH), 7.18 (d, *J* = 8.2 Hz, 2H, ArH), 6.97 – 6.90 (m, 2H, ArH), 6.28 (s, 1H, vinylH), 3.55 (t, *J* = 6.2 Hz, 2H, CH₂CH₂CH₂CH₂CH₂OH), 2.65 (t, *J* = 7.6 Hz, 2H, CH₂CH₂CH₂CH₂CH₂OH), 2.32 (s, 3H, CH₃), 1.66 (p, *J* = 7.5 Hz, 2H, CH₂CH₂CH₂CH₂CH₂OH), 1.49 (m, 4H, CH₂CH₂CH₂CH₂CH₂OH). **¹³C NMR** (101 MHz, Methanol-*d*₄) δ 172.3, 170.2, 153.0, 136.4, 135.2, 134.7, 133.4, 131.8, 131.5, 128.5, 120.8, 114.3, 79.7, 62.6, 33.1, 33.0, 27.9, 26.3, 20.7. **IR** ν 3334 (m), 2946 (m), 2833 (w), 2518 (w), 2224 (w), 2042 (w), 1667 (w), 1454 (w), 1029 (s), 740 (m). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₄IO₄⁺ 467.0714; Found 467.0718. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(p-tolyloxy)-8-(trimethylsilyl)oct-1-en-7-yn-1-yl)-1,3-benziodoxol-3-(1H)-one (1e)

Starting from EBX **5e** (0.127 g, 0.300 mmol), (Z)-1-(2-(p-tolyloxy)-8-(trimethylsilyl)oct-1-en-7-yn-1-yl)-1,3-benziodoxol-3-(1H)-one **1e** (78.0 mg, 0.146 mmol, 49% yield) was obtained, as a white solid. **Rf**: 0.42 (DCM:MeOH 9:1). **Mp**: 116-119 °C. **¹H NMR** (400 MHz, Methylene Chloride-*d*₂) δ 8.35 (dq, *J* = 5.6, 2.3, 1.8 Hz, 1H, ArH), 7.66 (d, *J* = 3.1 Hz, 3H, ArH), 7.14 (d, *J* = 8.1 Hz, 2H, ArH), 6.83 (d, *J* = 8.1 Hz, 2H, ArH), 5.89 (s, 1H, vinylH), 2.54 (t, *J* = 7.5 Hz, 2H, CH₂), 2.31 (s, 3H, ArCH₃), 2.23 (t, *J* = 6.9 Hz, 2H, CH₂), 1.70 (d, *J* = 8.0 Hz, 2H, CH₂), 1.54 (p, *J* = 7.1 Hz, 2H, CH₂), 0.13 (d, *J* = 1.1 Hz, 9H, Si(CH₃)₃). **¹³C NMR** (101 MHz, Methylene Chloride-*d*₂) δ 170.9, 166.6, 152.1, 135.7, 134.5, 133.7, 133.0, 131.1, 131.0, 125.9, 119.8, 114.6, 106.9, 85.5, 80.9, 32.5, 28.3, 26.6, 21.0, 19.9, 0.4. **IR** ν 3001 (w), 2817 (w), 2170 (w), 1598 (s), 1503 (m), 1356 (m), 1248

(m), 1205 (m), 1136 (m), 984 (m), 840 (s), 746 (s), 687 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{25}H_{30}IO_3Si^+$ 533.1003; Found 533.1008. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-2-(6-(3-Oxo-1,2-benziodoxol-3-(1H)-yl)-5-(p-tolyloxy)hex-5-en-1-yl)isoindoline-1,3-dione (1f)

Starting from EBX **5f** (300 mg, 634 μ mol), (Z)-2-(6-(3-Oxo-1,2-benziodoxol-3-(1H)-yl)-5-(p-tolyloxy)hex-5-en-1-yl)isoindoline-1,3-dione **1f** (180 mg, 310 μ mol, 49% yield) was obtained, as a white solid. **Rf**: 0.68 (DCM:MeOH 9:1). **Mp**: 87–92 °C. **1H NMR** (400 MHz, Chloroform- d) δ 8.45 – 8.37 (m, 1H, ArH), 7.88 – 7.77 (m, 2H, ArH), 7.77 – 7.68 (m, 2H, ArH), 7.66 – 7.53 (m, 3H, ArH), 7.04 (d, J = 8.2 Hz, 2H, ArH), 6.75 (d, J = 8.5 Hz, 2H, ArH), 5.91 (s, 1H, vinylH), 3.67 (t, J = 6.9 Hz, 2H, CH_2), 2.57 (t, J = 7.5 Hz, 2H, CH_2), 2.26 (s, 3H, CH_3), 1.72 (tt, J = 13.0,

7.1 Hz, 2H, CH_2), 1.59 (dq, J = 9.7, 7.3 Hz, 2H, CH_2). **^{13}C NMR** (101 MHz, Chloroform- d) δ 169.8, 168.5, 166.7, 151.5, 135.3, 134.3, 133.9, 133.4, 133.2, 132.1, 130.8, 130.7, 125.3, 123.5, 119.2, 114.1, 80.8, 37.2, 32.0, 27.9, 24.3, 20.9. **IR** ν 3067 (w), 2939 (m), 1768 (m), 1710 (s), 1607 (s), 1506 (m), 1442 (m), 1397 (m), 1347 (m), 1208 (m), 1178 (m), 1119 (w), 996 (w), 917 (m), 825 (m), 728 (s), 687 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{28}H_{25}INO_5^+$ 582.0772; Found 582.0778. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(2-iodophenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1g)

Starting from EBX **5a** (86.0 mg, 0.300 mmol), (Z)-1-(2-(2-iodophenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1g** (50.5 mg, 0.100 mmol, 33% yield) was obtained, as an off-white sticky solid. **Rf**: 0.45 (DCM:MeOH 9:1). **1H NMR** (400 MHz, Chloroform- d) δ 8.45 – 8.38 (m, 1H, ArH), 7.78 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.75 – 7.67 (m, 1H, ArH), 7.64 – 7.55 (m, 2H, ArH), 7.33 (td, J = 7.7, 1.6 Hz, 1H, ArH), 7.04 – 6.90 (m, 2H, ArH), 5.86 (d, J = 1.1 Hz, 1H, vinylH), 2.16 (d, J = 0.9 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, Chloroform- d) δ 167.1, 166.3, 153.4, 140.1, 133.8,

133.4, 133.0, 130.8, 130.1, 128.0, 126.1, 122.1, 114.1, 90.3, 77.7, 19.9. **IR** ν 3060 (m), 2778 (m), 1604 (s), 1348 (m), 1261 (m), 1218 (m), 1125 (m), 1069 (m), 1011 (s), 912 (s), 832 (s), 739 (s). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{13}I_2O_3^+$ 506.8949; Found 506.8956. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(2-iodophenoxy)pent-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1h)

Starting from EBX **5b** (500 mg, 1.60 mmol), (Z)-1-(2-(2-iodophenoxy)pent-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1h** (0.450 mg, 0.842 mmol, 53% yield) was obtained, as a white solid. **Rf**: 0.53 (DCM:MeOH 9:1). **Mp**: 176–177 °C. **1H NMR** (400 MHz, Chloroform- d) δ 8.48 – 8.42 (m, 1H, ArH), 7.80 (dd, J = 7.9, 1.5 Hz, 1H, ArH), 7.70 – 7.59 (m, 3H, ArH), 7.31 (ddd, J = 8.1, 7.5, 1.6 Hz, 1H, ArH), 6.99 – 6.88 (m, 2H, ArH), 5.90 (d, J = 1.0 Hz, 1H, vinylH), 2.44 – 2.35 (m, 2H, CH_2), 1.71 – 1.58 (m, 2H, CH_2), 1.00 (t, J = 7.4 Hz, 3H, CH_3). **^{13}C NMR**

(101 MHz, Chloroform- d) δ 169.6, 166.7, 153.3, 140.3, 133.9, 133.4, 133.1, 130.8, 129.9, 127.5, 125.7, 120.5, 114.1, 89.5, 80.0, 34.7, 20.4, 13.8. **IR** ν 3062 (w), 2966 (m), 2872 (w), 1722 (w), 1604 (s), 1578 (m), 1559 (m), 1506 (w), 1465 (s), 1438 (m), 1342 (m), 1300 (m), 1258 (m), 1221 (s), 1124 (m), 1043

(m), 1019 (m), 908 (m), 829 (m), 741 (s), 687 (m), 644 (w). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{17}I_2O_3^+$ 534.9262; Found 534.9266. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(2-Iodophenoxy)oct-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1i)

Starting from EBX **5c** (0.142 g, 0.400 mmol), (Z)-1-(2-(2-Iodophenoxy)oct-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1i** (0.190 g, 0.330 mmol, 82% yield) was obtained, as a white solid. **Rf**: 0.51 (DCM:MeOH 9:1). **Mp**: 130-133.5 °C. **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.48 – 8.41 (m, 1H, ArH), 7.79 (dd, J = 7.8, 1.6 Hz, 1H, ArH), 7.70 – 7.66 (m, 1H, ArH), 7.62 (hept, J = 5.1 Hz, 2H, ArH), 7.36 – 7.27 (m, 1H, ArH), 6.94 (td, J = 8.5, 2.9 Hz, 2H, ArH), 5.94 (s, 1H, vinylH), 2.43 (t, J = 7.6 Hz, 2H, CH_2), 1.59 (p, J = 7.6 Hz, 2H, CH_2), 1.41 – 1.22 (m, 6H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 169.9, 167.1, 153.3, 140.3, 133.6, 133.5, 133.1, 130.8, 129.9, 127.4, 126.0, 120.6, 114.3, 89.5, 80.0, 32.7, 31.5, 28.8, 27.0, 22.6, 14.1. **IR** ν 3061 (w), 2925 (m), 2859 (m), 1601 (s), 1460 (m), 1341 (s), 1219 (s), 1119 (m), 1011 (m), 920 (w), 825 (m), 745 (s), 681 (m), 641 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{21}H_{23}I_2O_3^+$ 576.9731; Found 576.9742. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(4-Methoxyphenoxy)pent-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1j)

Starting from EBX **5b** (2.00 g, 6.40 mmol), (Z)-1-(2-(4-methoxyphenoxy)pent-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1j** (2.10 g, 4.80 mmol, 75% yield) was obtained, as a white solid. **Rf**: 0.53 (DCM:MeOH 9:1). **Mp**: 175.8-180.9 °C. **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.49 – 8.41 (m, 1H, ArH), 7.66 – 7.57 (m, 3H, ArH), 6.83 (s, 4H, ArH), 5.79 (d, J = 0.9 Hz, 1H, vinylH), 3.77 (s, 3H, OCH₃), 2.46 (t, J = 7.6 Hz, 2H, CH_2), 1.61 (h, J = 7.4 Hz, 2H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 170.9, 166.7, 157.2, 147.2, 134.0, 133.3, 133.1, 130.8, 125.1, 120.8, 115.1, 114.0, 79.0, 55.8, 34.5, 20.6, 13.7. **IR** ν 3667 (m), 2975 (s), 2904 (s), 2355 (w), 2233 (w), 1607 (s), 1503 (s), 1445 (m), 1348 (s), 1294 (m), 1245 (s), 1207 (s), 1055 (s), 909 (s), 836 (m), 736 (s), 648 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{19}H_{20}IO_4^+$ 439.0401; Found 439.0403. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(4-Methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1k)

Starting from EBX **5a** (86.0 mg, 0.300 mmol), (Z)-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1k** (63.0 mg, 0.154 mmol, 51% yield) was obtained, as an off-white sticky solid. **Rf**: 0.46 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.47 – 8.39 (m, 1H, ArH), 7.74 – 7.66 (m, 1H, ArH), 7.67 – 7.60 (m, 2H, ArH), 6.96 – 6.89 (m, 2H, ArH), 6.89 – 6.74 (m, 2H, ArH), 5.86 (d, J = 1.2 Hz, 1H, vinylH), 3.77 (s, 3H, OCH₃), 2.21 (s, 3H, CH_3). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 167.6, 167.4, 157.5, 147.1, 133.6, 133.5, 133.2, 130.7, 125.7, 121.7, 115.0, 114.3, 76.4, 55.8, 19.5. **IR** ν 3620 (s), 3041 (s), 2778 (s), 1610 (s), 1507 (s), 1208 (s), 1127 (s), 1070 (s), 977 (s), 908 (s), 844 (s), 736 (s). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{17}H_{16}IO_4^+$

411.0088; Found 411.0092. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-N-(1-Prop-1-en-2-yl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide-1,2-benziodoxol-3-(1H)-one (1l)

Starting from EBX **5a** (286 mg, 1.00 mmol), (Z)-N-(1-prop-1-en-2-yl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide-1,2-benziodoxol-3-(1H)-one **1l** (383 mg, 0.680 mmol, 68% yield) was obtained, as a white solid. **Rf**: 0.30 (DCM:MeOH 9:1). **Mp**: 92.4 °C– 96.3 °C. **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (dd, *J* = 7.4, 1.8 Hz, 1H, ArH), 7.62 – 7.55 (m, 3H, ArH), 7.51 (ddd, *J* = 9.0, 7.2, 1.9 Hz, 1H, ArH), 7.35 (dd, *J* = 8.1, 1.1 Hz, 1H, ArH), 7.31 – 7.27 (m, 2H, ArH), 6.99 – 6.93 (m, 2H, ArH), 6.80 (d, *J* = 1.4 Hz, 1H, vinylH), 6.77 – 6.71 (m, 2H, ArH), 3.73 (s, 3H, OMe), 2.43 (s, 3H, CH₃), 2.21 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.9, 160.0, 152.6, 145.2, 135.4, 133.8, 133.3, 132.78, 130.6, 130.3, 129.9, 129.8, 128.0, 126.1, 114.8, 114.6, 105.4, 55.5, 22.9, 21.6. **IR** ν 2970 (m), 1757 (w), 1654 (s), 1575 (s), 1481 (s), 1230 (m), 1195 (w), 1170 (w), 1081 (w). **HRMS** (ESI) calcd for C₂₄H₂₃INO₅S⁺ [M+H]⁺ 564.0336; found 564.0339. The structure of the obtained regioisomer was confirmed by crystal structure. The values of the NMR spectra are in accordance with reported literature data. **Error! Bookmark not defined.**

(Z)-1-(2-Cyclopropyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one (1m)

Starting from EBX **5j** (31.0 mg, 0.100 mmol), (Z)-1-(2-cyclopropyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one **1m** (37.0 mg, 88.0 μmol, 88% yield) was obtained, as a white amorphous solid. **Rf**: 0.43 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.51 – 8.35 (m, 1H, ArH), 7.64 – 7.58 (m, 2H, ArH), 7.56 – 7.51 (m, 1H, ArH), 7.16 – 7.01 (m, 2H, ArH), 6.92 – 6.77 (m, 2H, ArH), 5.72 (s, 1H, vinylH), 2.29 (s, 3H, CH₃), 1.67 (tt, *J* = 8.2, 5.3 Hz, 1H, CH), 1.02 – 0.88 (m, 4H, CH₂). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 172.7, 166.8, 152.5, 135.0, 133.9, 133.3, 133.0, 130.7, 130.6, 125.2, 119.2, 114.4, 75.5, 20.8, 14.3, 9.7. **IR** ν 3672 (m), 3059 (m), 2805 (m), 1603 (s), 1504 (s), 1344 (m), 1203 (s), 1141 (s), 1065 (s), 1012 (s), 932 (s), 824 (s), 737 (s). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₈IO₃⁺ 421.0295; Found 421.0296. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-Cyclohexyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one (1n)

Starting from EBX **5k** (35.0 mg, 0.100 mmol), (Z)-1-(2-cyclohexyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one **1n** (30.0 mg, 65.0 μmol, 65% yield) was obtained, as a white amorphous solid. **Rf**: 0.34 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.48 – 8.32 (m, 1H, ArH), 7.64 – 7.58 (m, 2H, ArH), 7.58 – 7.52 (m, 1H, ArH), 7.14 – 7.01 (m, 2H, ArH), 6.88 – 6.69 (m, 2H, ArH), 6.04 (s, 1H, vinylH), 2.42 (tt, *J* = 11.7, 3.3 Hz, 1H, CH), 2.29 (s, 3H, CH₃), 2.11 – 2.00 (m, 2H, CH₂), 1.85 – 1.75 (m, 2H, CH₂), 1.74 – 1.65 (m, 1H, CH₂), 1.39 (qd, *J* = 12.0, 3.3 Hz, 2H, CH₂), 1.28 – 1.11 (m, 3H, CH₂, CH₂). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 174.9, 167.2, 152.4, 134.5, 133.6, 133.4, 133.1, 130.7, 130.7, 125.6, 118.4, 114.5, 81.7, 41.2, 31.8, 26.0, 25.9, 20.8. **IR** ν 3052 (w), 2931 (m), 2857 (w), 1604 (m), 1504 (m), 1444 (w), 1342 (m), 1202 (m), 1173 (w), 1116 (w), 1010 (w), 906 (s), 826 (m),

728 (s), 687 (w), 644 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{22}H_{24}IO_3^+$ 463.0765; Found 463.0768. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(3,3-dimethyl-2-(p-tolyloxy)but-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1p)

Starting from EBX **5m** (33.0 mg, 0.100 mmol), (Z)-1-(3,3-dimethyl-2-(p-tolyloxy)but-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1p** (35.0 mg, 80.0 μ mol, 80% yield) was obtained, as a white amorphous solid. **Rf**: 0.43 (DCM:MeOH 9:1). **1H NMR** (400 MHz, Chloroform- d) δ 8.40 (dd, J = 5.9, 3.4 Hz, 1H, ArH), 7.67 – 7.58 (m, 2H, ArH), 7.53 – 7.42 (m, 1H, ArH), 7.12 – 7.01 (m, 2H, ArH), 6.80 (d, J = 8.6 Hz, 2H, ArH), 6.13 (s, 1H, vinylH), 2.27 (s, 3H, CH_3), 1.37 (s, 9H, $C(CH_3)_3$). **^{13}C NMR** (101 MHz, Chloroform- d) δ 177.3, 166.8, 155.2, 134.2, 133.6, 133.4, 133.2, 131.3, 130.8, 125.4, 116.8, 115.2, 80.9, 40.4, 28.8, 20.8. **IR** ν 3246 (m), 2994 (m), 1739 (s), 1658 (s), 1631 (s), 1583 (s), 1552 (s), 1508 (s), 1394 (s), 1363 (s), 1320 (s), 1263 (s), 1214 (s), 1173 (s), 1072 (m), 1021 (s), 972 (m), 848 (s), 829 (s), 752 (s). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{20}H_{22}IO_3^+$ 437.0608; Found 437.0595. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-phenyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one (1q)

Starting from EBX **5n** (35.0 mg, 0.100 mmol), (Z)-1-(2-phenyl-2-(p-tolyloxy)vinyl)-1,2-benziodoxol-3-(1H)-one **1q** (45.3 mg, 99.0 μ mol, 99% yield) was obtained, as a white amorphous solid. **Rf**: 0.31 (DCM:MeOH 9:1). **1H NMR** (400 MHz, Chloroform- d) δ 8.51 – 8.41 (m, 1H, ArH), 7.69 – 7.57 (m, 5H, ArH), 7.42 (dq, J = 8.9, 7.1, 6.6 Hz, 3H, ArH), 6.98 (d, J = 8.4 Hz, 2H, ArH), 6.80 – 6.72 (m, 2H, ArH), 6.66 (s, 1H, vinylH), 2.21 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, Chloroform- d) δ 167.2, 165.6, 153.6, 133.9, 133.7, 133.3, 133.2, 131.7, 131.5, 130.9, 130.6, 129.3, 128.1, 126.1, 117.2, 115.0, 86.4, 20.7. **IR** ν 3066 (w), 1604 (s), 1505 (m), 1442 (w), 1347 (m), 1283 (m), 1201 (m), 1033 (w), 1016 (w), 911 (m), 824 (m), 737 (s), 697 (m), 649 (w). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{22}H_{18}IO_3^+$ 457.0295; Found 457.0287. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-1-(2-(2,6-dichlorophenoxy)oct-1-en-1-yl)-1,3-benziodoxol-3(1H)-one (1r)

Starting from EBX **5c** (36.0 mg, 0.100 mmol), (Z)-1-(2-(2,6-dichlorophenoxy)oct-1-en-1-yl)-1,3-benziodoxol-3(1H)-one **1r** (43.0 mg, 83.0 μ mol, 83% yield) was obtained, as a white solid. **Rf**: 0.46 (DCM:MeOH 9:1). **1H NMR** (400 MHz, Chloroform- d) δ 8.45 (dd, J = 7.2, 2.0 Hz, 1H, ArH), 7.69 (dd, J = 7.7, 1.5 Hz, 1H, ArH), 7.67 – 7.56 (m, 2H, ArH), 7.34 (d, J = 8.1 Hz, 2H, ArH), 7.15 (dd, J = 8.6, 7.7 Hz, 1H, ArH), 5.81 (t, J = 1.1 Hz, 1H, vinylH), 2.38 – 2.25 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.62 (t, J = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.45 – 1.19 (m, 6H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.88 (t, J = 6.9 Hz, 3H, CH_3). **^{13}C NMR** (101 MHz, Chloroform- d) δ 170.1, 167.1, 145.7, 133.6, 133.4, 133.1, 130.8, 129.4, 129.3, 127.6, 126.1, 114.0, 76.1, 32.1, 31.4, 28.8, 26.7, 22.6, 14.1. **IR** ν 3067 (m), 2935 (m), 2864 (m), 1738 (m), 1665 (m), 1597 (s), 1562 (m), 1442 (s), 1336 (m), 1246 (s), 1124 (m), 1006 (m), 916 (m), 830 (m), 734 (s), 725 (s),

678 (m), 643 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{21}H_{22}Cl_2IO_3^+$ 518.9985; Found 518.9993. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-5-Methyl-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1s)

Starting from EBX **5o** (90.0 mg, 0.300 mmol), (Z)-5-methyl-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1s** (83.0 mg, 0.196 mmol, 65% yield) was obtained, as an off-white solid. **Rf**: 0.53 (DCM:MeOH 9:1). **Mp**: 168 °C. **¹H NMR** (400 MHz, Methylene chloride- d_2) δ 8.19 (d, J = 2.2 Hz, 1H, ArH), 7.55 – 7.44 (m, 2H, ArH), 6.92 – 6.81 (m, 4H, ArH), 5.68 (d, J = 1.1 Hz, 1H, vinylH), 3.77 (s, 3H, OCH₃), 2.48 (s, 3H, CH₃), 2.17 (d, J = 1.0 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Methylene chloride- d_2) δ 168.0, 166.9, 158.0, 147.7, 141.9, 134.5, 134.3, 133.6, 125.6, 122.1, 115.3, 110.7, 77.0, 56.2, 21.0, 19.7. **IR** ν 3667 (m), 2979 (s), 2903 (s), 1615 (m), 1499 (m), 1400 (m), 1241 (m), 1212 (m), 1059 (s), 901 (w), 790 (w), 712 (w), 677 (w). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{18}O_4^+$ 425.0244; Found 425.0244. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

(Z)-5-Methoxy-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1t)

Starting from EBX **5p** (158 mg, 0.500 mmol), (Z)-5-Methoxy-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one **1t** (133 mg, 0.302 mmol, 60% yield) was obtained, as a white solid. **Rf**: 0.50 (DCM:MeOH 9:1). **Mp**: 180 °C. **¹H NMR** (400 MHz, Methylene chloride- d_2) δ 7.91 (d, J = 3.0 Hz, 1H, ArH), 7.50 (d, J = 9.0 Hz, 1H, ArH), 7.21 (dd, J = 8.9, 3.1 Hz, 1H, ArH), 6.93 – 6.81 (m, 4H, ArH), 5.68 (d, J = 1.1 Hz, 1H, vinylH), 3.92 (s, 3H, OCH₃), 3.77 (s, 3H, OCH₃), 2.17 (d, J = 1.0 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Methylene chloride- d_2) δ 168.1, 166.6, 162.9, 158.0, 147.6, 136.2, 126.5, 122.1, 121.3, 116.4, 115.4, 102.5, 76.7, 56.6, 56.2, 19.7. **IR** ν 3676 (w), 2979 (s), 2903 (s), 1618 (m), 1571 (m), 1498 (m), 1461 (m), 1403 (m), 1342 (m), 1214 (m), 1058 (s), 953 (w), 902 (w), 712 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{18}IO_5^+$ 441.0193; Found 441.0191. The olefin geometry was assigned by analogy to NMR data of compound **1l**.

5. Nucleophilic additions onto O-VBX

Optimization procedure and table for the synthesis of 3a:

In a round-bottom flask were added *p*-cresol (10.8 mg, 0.100 mmol, 1.00 equiv.) and cesium carbonate (39.0 mg, 0.120 mmol, 1.20 equiv.). Anhydrous DME (1.00 mL, 0.1 M) was introduced at 0 °C and the solution was stirred at room temperature for 10 min. O-VBX **1a** (39.0 mg, 0.100 mmol, 1.00 equiv.) was added to the reaction mixture under open air and the reaction mixture was stirred at room temperature for 16 h.

Table S1: Optimisation studies of the addition of *p*-cresol (**2a**) to O-VBX **1a**.

Reaction scheme: O-VBX **1a** + *p*-cresol (**2a**) $\xrightarrow[\text{solvent 0.1 M, 0 °C to rt}]{\text{x equiv. base}}$ **3a** + **4a**

Entry	Base	Equivalent	Solvent ^[a]	Yield (%) ^[b]
1	KOtBu	1.20	DME	80
2	KOtBu	1.20	THF	48
3	KOtBu	1.20	1,4-dioxane	33
4	KOtBu	1.20	Et ₂ O	40
5	KOtBu	1.20	DCM	40
6	KOtBu	1.20	CH ₃ CN	34
7	KOtBu	1.20	MeOH	22
8	KOtBu	1.20	EtOH	29
9	KOtBu	1.20	TFE	8
10	KOtBu	1.20	HFIP	NR
11	Cs₂CO₃	1.20	DME	79^[c]
12	Pyridine	1.20	DME	NR
13	Et ₃ N	1.20	DME	NR
14	none	-	DME	NR
15	Cs ₂ CO ₃	0.20	DME	35
16	Cs ₂ CO ₃	1.00	DME	60
17	Cs ₂ CO ₃	2.00	DME	62

Reactions were performed on 0.1 mmol scale: Substrate **1a** (0.100 mmol), *para*-cresol (**2a**) (0.100 mmol), base (0.120 mmol) and solvent (0.1 M) at 25 °C. NR = No reaction. ^[a]Concentration based on **1a**: 0.1 M; ^[b]NMR yield determined by addition of 0.1 mmol of CH₂Br₂ as an internal standard after the reaction. ^[c]**3a** was obtained with 10% (NMR yield) of **4a**.

Cesium carbonate effect: The reaction is heterogeneous. The size of the particles is not influencing the reaction. When the reaction was performed with finely grinded salt, same isolated yield was obtained for **3p**. Also, two batches of Cs_2CO_3 were tested for the synthesis of **3p** and the same yield was obtained.

One-pot two-step procedure for the synthesis of **3a:**

To increase the efficiency of the new aryl allyl ether synthesis, a one-pot two-step procedure was examined, starting from EBX **5a**. Using the optimized conditions previously developed for the synthesis of O-VBXs, but replacing EtOH with DME, Me-EBX (**5a**) was efficiently converted into O-VBX **1a**. Then another equivalent of cresol **2a** and an excess of base were added. After 16 hours, allyl ether **3a** was obtained in 63% yield, together with 36% allyl ester **4a**. Therefore, the one-pot procedure is efficient, but leads to the formation of a larger amount of allyl ester **4a**.

General procedure for nucleophilic additions onto O-VBX:

Nucleophile (0.300 mmol, 1 equiv.) and cesium carbonate (0.117 g, 0.360 mmol, 1.20 equiv.) were added to a round-bottom flask. Anhydrous DME (3.00 mL, 0.1 M) was introduced at 0 °C and the solution was stirred at room temperature for 10 min. O-VBX reagent **1** (0.300 mmol, 1equiv.) was added to the reaction mixture under open air and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane:ethyl acetate 9:1) to provide **3** as a sticky solid.

4,4'-(Prop-2-ene-1,2-diylbis(oxy))bis(methylbenzene) (**3a**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), 4,4'-(prop-2-ene-1,2-diylbis(oxy))bis(methylbenzene) **3a** (63.0 mg, 0.248 mmol, 83% yield) and **4a** (15.3 mg, 38.8 μ mol, 13%) were obtained, as a colorless amorphous solids. **Rf**: 0.70 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.2 Hz, 2H, ArH), 7.12 – 7.07 (m, 2H, ArH), 7.00 – 6.95 (m, 2H, ArH), 6.92 – 6.87 (m, 2H, ArH), 4.61 (s, 2H, CCH₂O), 4.57 – 4.50 (m, 1H, CH₂CO), 4.19 (d, *J* = 2.2 Hz, 1H, CH₂CO), 2.33 (s, 3H, CH₃), 2.30 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 158.8, 156.5, 152.8, 134.1, 130.6, 130.3, 130.0, 120.8, 115.0, 90.4, 67.9, 20.9, 20.7. **IR** ν 3027 (w), 2925 (m), 2849 (w), 1650 (w), 1612 (w), 1586 (w), 1510 (s), 1459 (w), 1370 (w), 1294 (m), 1224 (s), 1180 (w), 1072 (w), 1040 (w), 958 (w), 907 (w), 818 (m), 729 (m), 660 (w). **HRMS** (ESI) calcd for C₁₇H₁₈NaO₂⁺ [M+Na]⁺ 277.1199; found 277.1189.

1-Bromo-4-((2-(*p*-tolyl)oxy)allyl)oxy)benzene (**3b**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and 4-bromophenol **2b** (51.9 mg, 0.300 mmol), 1-bromo-4-((2-(*p*-tolyl)oxy)allyl)oxy)benzene **3b** (71.3 mg, 0.223 mmol, 75% yield) and **4a** (20.1 mg, 51.0 μ mol, 17%) were obtained, as a colorless amorphous solids. **Rf**: 0.67 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.33 (m, 2H, ArH), 7.18 – 7.09 (m, 2H, ArH), 7.00 – 6.92 (m, 2H, ArH), 6.92 – 6.83 (m, 2H, ArH), 4.61 (s, 2H, CCH₂O), 4.51 (dd, *J* = 2.3, 1.1 Hz, 1H, CH₂CO), 4.20 (d, *J* = 2.3 Hz, 1H, CH₂CO), 2.34 (s, 3H, ArCH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 158.3, 157.7, 152.6, 134.3, 132.4, 130.3, 120.8, 117.0, 113.6, 90.7, 68.0, 20.9. **IR** ν 3033 (w), 2929 (w), 1650 (w), 1587 (w), 1507 (m), 1488 (s), 1455 (w), 1388 (w), 1288 (m), 1227 (s), 1167 (w), 1064 (w), 1011 (w), 963 (w), 908 (m), 828 (m), 734 (m). **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₆H₁₅⁷⁹BrO₂⁺ 318.0250; Found 318.0240.

1-Iodo-4-((2-(*p*-tolyl)oxy)allyl)oxy)benzene (**3c**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and 4-iodophenol **2c** (66.0 mg, 0.300 mmol), 1-iodo-4-((2-(*p*-tolyl)oxy)allyl)oxy)benzene **3c** (80.0 mg, 0.218 mmol, 73% yield) and **4a** (16.5 mg, 41.9 μ mol, 14%) were obtained, as a colorless amorphous solids. **Rf**: 0.42 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H, ArH), 7.18 – 7.13 (m, 2H, ArH), 6.98 – 6.93 (m, 2H, ArH), 6.81 – 6.75 (m, 2H, ArH), 4.60 (d, *J* = 0.8 Hz, 2H, CCH₂O), 4.51 (dd, *J* = 2.2, 1.1 Hz, 1H, CH₂CO), 4.20 (d, *J* = 2.4 Hz, 1H, CH₂CO), 2.34 (s, 3H, ArCH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 158.5, 158.2, 152.6, 138.4, 134.3, 130.3, 120.8, 117.6, 90.7, 83.5, 67.9, 20.9. **IR** ν 3051 (w), 2958 (w), 2928 (w), 1739 (w), 1494 (w), 1265 (m), 1231 (w), 827 (w), 735 (s), 702 (s). **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₆H₁₅IO₂⁺ 366.0111; Found 366.0108.

1-Methoxy-4-((2-(*p*-tolylloxy)allyl)oxy)benzene (3d)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and 4-methoxyphenol **2d** (37.2 mg, 0.300 mmol), 1-methoxy-4-((2-(*p*-tolylloxy)allyl)oxy)benzene **3d** (36.2 mg, 0.134 mmol, 45% yield) and **4a** (56.8 mg, 0.144 mmol, 48%) were obtained, as a colorless amorphous solids. **Rf**: 0.61 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 2H, ArH), 7.00 – 6.91 (m, 4H, ArH), 6.88 – 6.82 (m, 2H, ArH), 4.59 (d, J = 0.9 Hz, 2H, CCH₂O), 4.52 (dd, J = 2.1, 1.0 Hz, 1H, CH₂CO), 4.18 (d, J = 2.2 Hz, 1H, CH₂CO), 3.78 (s, 3H, OCH₃), 2.33 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 158.9, 154.3, 152.7 (2 Carbon signals are overlapping), 134.1, 130.3, 120.8, 116.3, 114.7, 90.5, 68.6, 55.9, 20.9. **IR** ν 3056 (w), 2927 (w), 2842 (w), 1589 (w), 1507 (s), 1461 (w), 1276 (m), 1226 (s), 1159 (w), 1111 (w), 1026 (w), 964 (w), 929 (w), 831 (m), 747 (m), 714 (m). **HRMS** (APPI/LTQ-Orbitrap) m/z : [M]⁺ Calcd for C₁₇H₁₈O₃⁺ 270.1250; Found 270.1252.

4,4,5,5-Tetramethyl-2-(4-((2-(*p*-tolylloxy)allyl)oxy)phenyl)-1,3,2-dioxaborolane (3e)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol **2e** (66.0 mg, 0.300 mmol), 4,4,5,5-tetramethyl-2-(4-((2-(*p*-tolylloxy)allyl)oxy)phenyl)-1,3,2-dioxaborolane **3e** (78.3 mg, 0.214 mmol, 71% yield) and **4a** (30.7 mg, 77.9 μ mol, 26%) were obtained, as a colorless amorphous solids. **Rf**: 0.51 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Methylene Chloride-*d*₂) δ 7.74 – 7.69 (m, 2H, ArH), 7.21 – 7.14 (m, 2H, ArH), 7.02 – 6.94 (m, 4H, ArH), 4.66 (s, 2H, CCH₂O), 4.53 (dt, J = 2.0, 0.9 Hz, 1H, CH₂CO), 4.18 (d, J = 2.3 Hz, 1H, CH₂CO), 2.33 (s, 3H, ArCH₃), 1.32 (s, 12H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 161.1, 158.5, 152.7, 136.6, 134.1, 130.3 (2 Carbon signals are overlapping), 120.8, 114.4, 90.6, 83.7, 67.4, 25.0, 20.9. **IR** ν 3034 (w), 2987 (w), 2253 (w), 1722 (w), 1604 (m), 1505 (m), 1360 (s), 1323 (w), 1217 (m), 1159 (m), 1143 (m), 1087 (m), 905 (s), 829 (w), 734 (s), 652 (m). **HRMS** (APPI/LTQ-Orbitrap) m/z : [M]⁺ Calcd for C₂₂H₂₇BO₄⁺ 366.1997; Found 366.2000.

1-Methoxy-3-((2-(*p*-tolylloxy)allyl)oxy)benzene (3f)

Starting from O-VBX **1a** (0.118 mg, 0.300 mmol) and 3-methoxyphenol **2f** (37.2 mg, 0.300 mmol), 1-methoxy-3-((2-(*p*-tolylloxy)allyl)oxy)benzene **3f** (49.0 mg, 0.181 mmol, 60% yield) and **4a** (42.5 mg, 0.108 mmol, 36%) were obtained, as a colorless amorphous solids. **Rf**: 0.58 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 7.24 - 7.15 (m, 3H, ArH), 6.99 - 6.93 (m, 2H, ArH), 6.62 - 6.53 (m, 3H, ArH), 4.63 (d, J = 0.8 Hz, 2H, CH₂CO), 4.55 (dd, J = 2.1, 1.0 Hz, 1H, CCH₂O), 4.14 (d, J = 2.1 Hz, 1H, CCH₂O), 3.77 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 161.9, 160.6, 159.8, 153.6, 135.2, 131.2, 131.0, 121.4, 107.9, 107.7, 102.1, 91.6, 68.4, 55.9, 20.7. **IR** ν 3665 (m), 3091 (m), 2989 (m), 2906 (m), 2601 (m), 2262 (s), 1886 (w), 1799 (w), 1639 (w), 1581 (w), 1489 (s), 1404 (w), 1334 (w), 1192 (m), 1149 (m), 1040 (s), 841 (s), 777 (s), 689 (s). **HRMS** (APCI/QTOF) m/z : [M + H]⁺ Calcd for C₁₇H₁₉O₃⁺ 271.1329; found 271.1329.

3-((2-(*p*-Tolyloxy)allyl)oxy)aniline (**3g**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and 3-aminophenol **2g** (33.0 mg, 0.300 mmol), 3-((2-(*p*-tolyloxy)allyl)oxy)aniline **3g** (27.0 mg, 0.106 mmol, 35% yield) was obtained, as a orange amorphous solid and **4a** (24.7 mg, 62.6 μ mol, 21%) was obtained as a colorless amorphous solid. **Rf**: 0.62 (Pentane:EtOAc 7:3). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, J = 8.2 Hz, 2H, ArH), 7.13 – 7.07 (m, 1H, ArH), 7.00 – 6.94 (m, 2H, ArH), 6.48 (ddd, J = 8.2, 2.3, 0.9 Hz, 1H, ArH), 6.44 – 6.39 (m, 2H, ArH), 4.61 – 4.58 (m, 2H, CCH₂O), 4.54 (dt, J = 2.0, 1.0 Hz, 1H, CH₂CO), 4.19 (d, J = 2.3 Hz, 1H, CH₂CO), 2.33 (s, 3H, ArCH₃). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 158.7, 152.8, 145.9, 134.1, 130.3, 130.3, 120.8, 109.4, 106.3, 103.2, 90.5, 67.6, 20.9. **IR** ν 3464 (w), 3378 (m), 3221 (w), 2929 (m), 1823 (m), 1607 (s), 1501 (s), 1459 (m), 1294 (m), 1219 (m), 1188 (s), 1166 (s), 1158 (s), 1071 (w), 1029 (w), 966 (w), 910 (m), 840 (m), 735 (m). **HRMS** (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₁₆H₁₈NO₂⁺ 256.1332; Found 256.1325.

Methyl 2-((2-(*p*-tolyloxy)allyl)oxy)benzoate (**3h**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and methyl 2-hydroxybenzoate **2h** (46.1 mg, 0.300 mmol), methyl 2-((2-(*p*-tolyloxy)allyl)oxy)benzoate **3h** (80.1 mg, 0.268 mmol, 89% yield) and **4a** (8.00 mg, 20.3 μ mol, 7%) were obtained, as a colorless amorphous solids. **Rf**: 0.41 (Pentane:EtOAc 9:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, J = 7.7, 1.9 Hz, 1H, ArH), 7.47 (ddd, J = 8.4, 7.3, 1.8 Hz, 1H, ArH), 7.18 – 7.12 (m, 2H, ArH), 7.06 – 7.00 (m, 2H, ArH), 7.00 – 6.96 (m, 2H, ArH), 4.72 (dt, J = 2.3, 1.1 Hz, 1H, CH₂CO), 4.70 (s, 2H, CCH₂O), 4.23 (d, J = 2.2 Hz, 1H, CH₂CO), 3.90 (s, 3H, OCH₃), 2.34 (s, 3H, ArCH₃). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 158.1, 158.0, 152.7, 134.1, 133.6, 132.0, 130.3, 121.0, 120.9, 120.7, 114.0, 90.2, 68.2, 52.2, 20.9. **IR** ν 2952 (m), 1726 (s), 1654 (m), 1602 (m), 1499 (m), 1456 (m), 1389 (m), 1301 (s), 1244 (s), 1134 (m), 1085 (s), 1054 (m), 964 (m), 909 (m), 840 (m), 750 (s). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₁₈H₁₈NaO₄⁺ 321.1097; Found 321.1100.

1-(3,5-Di-*tert*-butyl-4-((2-(*p*-tolyloxy)allyl)oxy)phenyl)ethan-1-one (**3i**)

Starting from O-VBX **1a** (39.4 mg, 0.100 mmol) and 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethanone **2i** (24.8 mg, 0.100 mmol), 1-(3,5-di-*tert*-butyl-4-((2-(*p*-tolyloxy)allyl)oxy)phenyl)ethan-1-one **3i** (17.0 mg, 43.0 μ mol, 43% yield) and **4a** (35.4 mg, 89.8 μ mol, 30%) were obtained, as a colorless amorphous solids. **Rf**: 0.54 (Pentane:EtOAc 9:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (s, 2H, ArH), 7.15 – 7.09 (m, 2H, ArH), 6.92 – 6.87 (m, 2H, ArH), 4.16 (d, J = 1.6 Hz, 1H, CH₂CO), 4.01 (d, J = 1.8 Hz, 1H, CH₂CO), 3.56 – 3.51 (m, 2H, CCH₂O), 2.34 (s, 3H, COCH₃), 2.32 (s, 3H, ArCH₃), 1.35 (s, 18H, C(CH₃)₃). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 162.8, 153.2, 146.6, 142.2, 134.8, 133.7, 130.1, 127.0, 120.9, 89.9, 40.7, 35.5, 31.6, 22.9, 20.9. **IR** ν 2962 (s), 2921 (m), 2877 (m), 1761 (s), 1640 (m), 1604 (m), 1506 (s), 1476 (m), 1428 (m), 1365 (s), 1268 (s), 1222 (s), 1195 (s), 1185 (s), 1109 (s), 1011 (m), 961 (m), 905 (m), 822 (s), 742 (m), 700 (m), 635 (m). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₂₆H₃₄NaO₃⁺ 417.2400; Found 417.2405.

2-((2-(*p*-Tolyloxy)allyl)oxy)naphthalene (**3j**)

Starting from O-VBX **1a** (0.118 g, 0.300 mmol) and naphthalene-2-ol **2j** (43.3 mg, 0.300 mmol), 2-((2-(*p*-tolyloxy)allyl)oxy)naphthalene **3j** (62.4 mg, 0.215 mmol, 72% yield) and **4a** (30.6 mg, 77.6 μ mol, 26%) were obtained, as a colorless amorphous solids. **Rf**: 0.66 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (td, J = 8.7, 6.0 Hz, 3H, ArH), 7.47 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H, ArH), 7.37 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H, ArH), 7.31 – 7.26 (m, 2H, ArH), 7.21 – 7.15 (m, 2H, ArH), 7.05 – 7.00 (m, 2H, ArH), 4.78 (s, 2H, CCH₂O), 4.64 (dd, J = 2.2, 1.1 Hz, 1H, CH₂CO), 4.27 (d, J = 2.3 Hz, 1H, CH₂CO), 2.36 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 158.5, 156.5, 152.7, 134.6, 134.2, 130.3, 129.6, 129.3, 127.8, 127.0, 126.5, 124.0, 120.8, 119.1, 107.6, 90.8, 67.8, 20.9. IR ν 3051 (w), 2923 (w), 1830 (w), 1637 (m), 1602 (m), 1506 (s), 1463 (w), 1393 (w), 1259 (s), 1216 (s), 1182 (m), 1127 (w), 1024 (w), 963 (w), 839 (m), 741 (s), 714 (m). **HRMS** (APPI/LTQ-Orbitrap) m/z : [M]⁺ Calcd for C₂₀H₁₈O₂⁺ 290.1301; Found 290.1295.

Ethyl (S)-2-acetamido-3-(4-((2-(*p*-tolyloxy)allyl)oxy)phenyl)propanoate (**3k**)

Starting from O-VBX **1a** (0.118 mg, 0.300 mmol) and (S)-ethyl 2-acetamido-3-(4-hydroxyphenyl)propanoate hydrate **2k** (81.0 mg, 0.300 mmol), ethyl (S)-2-acetamido-3-(4-((2-(*p*-tolyloxy)allyl)oxy)phenyl)propanoate **3k** (0.115 g, 0.289 mmol, 96% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.45 (DCM:MeOH 9:1). *Mixture of rotamers not identified yet.* **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 7.23 – 7.17 (m, 2H, ArH), 7.17 – 7.11 (m, 2H, ArH), 6.99 – 6.89 (m, 4H, ArH), 6.66 (d, J = 7.8 Hz, 1H, NH), 4.63 (s, 2H, OCH₂CO), 4.58 – 4.50 (m, 2H, vinylH, ArCH₂CHNH), 4.13 (d, J = 2.1 Hz, 1H, vinylH), 4.09 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 3.02 (dd, J = 13.9, 6.0 Hz, 1H, ArCH₂CHNH), 2.95 – 2.85 (m, 1H, ArCH₂CHNH), 2.31 (s, 3H, ArCH₃), 1.85 (s, 3H, COCH₃), 1.17 (t, J = 7.1 Hz, 3H, OCH₂CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 172.6, 170.6, 159.8, 158.3, 153.6, 135.1, 131.3, 131.2, 130.5, 121.4, 115.7, 91.6, 68.3, 61.8, 54.9, 37.4, 22.7, 20.7, 14.4. IR ν 3332 (w), 2991 (w), 2931 (w), 2866 (w), 2254 (w), 1737 (m), 1664 (m), 1614 (w), 1505 (s), 1442 (w), 1377 (w), 1221 (s), 1127 (m), 1024 (w), 910 (m), 822 (m), 736 (s), 656 (w), 612 (w). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₂₃H₂₇NNaO₅⁺ 420.1781; found 420.1781. [α]_D²⁰ = + 46.8 (c = 1.00, CHCl₃).

(*E*)-N-(4-((3-(((8*R*,9*S*,13*S*,14*S*,17*S*)-17-Hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)prop-1-en-2-yl)oxy)-3-methoxybenzyl)-8-methylnon-6-enamide (**3l**)

One pot procedure: In a glass vial, Capsaicin **2l** (31.0 mg, 0.100 mmol, 1.00 equiv.) was dissolved in DME (0.1 M). Cesium carbonate (3.26 mg, 10.0 μ mol, 0.10 equiv.) was added and the mixture stirred vigorously for 5 min. Then EBX **5a** was added in one portion (29.0 mg, 0.100 mmol, 1.00 equiv.) and the reaction was left stirring for 16 hours at room temperature. Then cesium carbonate (39.0 mg, 0.120 mmol, 1.20 equiv.) and Estradiol **2l'** (27.0 mg, 0.100 mmol, 1.00 equiv.) were added and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography

(pentane:ethyl acetate 9:1) to provide compound **3l** (25.0 mg, 41.0 μ mol, 41% yield), as a white amorphous solid. **Rf**: 0.57 (DCM:MeOH 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 7.21 (d, *J* = 8.6 Hz, 1H, ArH), 6.97 (d, *J* = 8.2 Hz, 2H, ArH), 6.83 (dd, *J* = 8.1, 1.9 Hz, 1H, ArH), 6.76 (dd, *J* = 8.4, 2.9 Hz, 1H, ArH), 6.71 (d, *J* = 2.9 Hz, 1H, ArH), 5.46–5.31 (m, 2H, vinylH), 4.62 (s, 2H, OCH₂CO), 4.39 (d, *J* = 2.2 Hz, 1H, OCCH₂), 4.30 (d, *J* = 6.1 Hz, 2H, ArCH₂NH), 3.92 (d, *J* = 2.2 Hz, 1H, OCCH₂), 3.81 (d, *J* = 4.8 Hz, 1H, OH), 3.77 (s, 3H, OCH₃), 3.61 (td, *J* = 8.5, 4.2 Hz, 1H, CH), 2.91–2.74 (m, 2H, CH₂), 2.64 (d, *J* = 6.4 Hz, 1H, NH), 2.31 (dq, *J* = 12.3, 3.7 Hz, 1H, CH₂), 2.26–2.16 (m, 2H, CH + CH), 2.15 (s, 2H, CH₂), 2.03–1.95 (m, 1H, CH₂), 1.87 (ddt, *J* = 13.3, 8.3, 3.0 Hz, 2H, CH₂), 1.67 (ddt, *J* = 12.2, 5.1, 2.6 Hz, 1H, CH₂), 1.61–1.55 (m, 2H, CH₂), 1.55–1.46 (m, 1H, CH₂), 1.45–1.40 (m, 1H, CH₂), 1.40–1.22 (m, 6H, CH₂ + CH₂ + CH₂ + CH₂ + CH₂ + CH₂), 1.17 (ddd, *J* = 14.5, 11.3, 5.5 Hz, 2H, CH₂ + CH₂), 0.94 (d, *J* = 6.8 Hz, 4H, CH + CHCH₃), 0.86 (d, *J* = 6.6 Hz, 3H, CHCH₃), 0.73 (s, 3H, CCH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 173.7, 159.7, 157.2, 152.5, 142.9, 139.1, 138.8, 138.7, 134.3, 127.8, 127.4, 123.3, 120.5, 115.8, 113.3, 113.2, 89.2, 82.0, 68.1, 56.5, 50.9, 44.9, 44.1, 43.1, 39.9, 37.7, 36.7, 32.9, 31.8, 30.9, 30.5, 30.0, 28.0, 27.3, 26.1, 23.8, 23.0, 22.9, 11.7. **IR** ν 3062 (m), 2924 (s), 2851 (m), 1648 (s), 1542 (s), 1507 (s), 1460 (m), 1355 (m), 1274 (s), 1221 (s), 1156 (s), 1068 (w), 1025 (s), 966 (m), 826 (m), 735 (m). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₃₉H₅₃NNaO₅⁺ 638.3816; Found 638.3830. [α]_D²⁰ = +41.7 (*c* = 0.66, CHCl₃).

2-Methyl-2-(2-(*p*-tolylloxy)allyl)cyclopentane-1,3-dione (**3m**)

Starting from O-VBX **1a** (39.4 mg, 0.100 mmol) and 2-methylcyclopentane-1,3-dione **2m** (11.2 mg, 0.100 mmol), 2-methyl-2-(2-(*p*-tolylloxy)allyl)cyclopentane-1,3-dione **3m** (8.00 mg, 31.0 μ mol, 31% yield) was obtained, as a colorless amorphous solid. The allyl ester **4a** was formed in 15% NMR yield, but not isolated. **Rf**: 0.20 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.1 Hz, 2H, ArH), 6.81–6.75 (d, *J* = 8.1 Hz, 2H, ArH), 4.11 (dd, *J* = 2.3, 1.1 Hz, 1H, CH₂CO), 3.81 (d, *J* = 2.4 Hz, 1H, CH₂CO), 2.83 (s, 2H, CCH₂C), 2.81–2.69 (m, 4H, OCCH₂CH₂CO), 2.31 (s, 3H, ArCH₃), 1.16 (s, 3H, CCH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 216.0, 158.1, 151.8, 134.6, 130.4, 120.8, 89.0, 54.1, 39.9, 34.9, 20.9, 20.9. **IR** ν 3465 (m), 3038 (m), 2925 (m), 2867 (m), 1724 (s), 1644 (m), 1506 (s), 1451 (m), 1422 (m), 1378 (m), 1277 (m), 1215 (s), 1159 (m), 1067 (m), 958 (m), 894 (m), 838 (m), 739 (m), 617 (m). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₆H₁₈NaO₃⁺ 281.1148; Found 281.1148.

Ethyl 2-acetyl-2-methyl-4-(*p*-tolylloxy)pent-4-enoate (**3n**)

Starting from O-VBX **1a** (39.4 mg, 0.100 mmol) and ethyl 2-methyl-3-oxobutanoate **2n** (15.2 mg, 0.100 mmol), ethyl 2-acetyl-2-methyl-4-(*p*-tolylloxy)pent-4-enoate **3n** (19.0 mg, 65.0 μ mol, 65% yield) was obtained, as a colorless amorphous solid. The allyl ester **4a** was formed in 15% NMR yield, but not isolated. **Rf**: 0.42 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.15–7.08 (m, 2H, ArH), 6.89–6.84 (m, 2H, ArH), 4.18 (q, *J* = 7.1 Hz, 2H, OCH₂CH₃), 4.07 (d, *J* = 1.9 Hz, 1H, CH₂CO), 3.87 (d, *J* = 2.0 Hz, 1H,

CH₂CO), 2.95 – 2.78 (m, 2H, CCH₂C), 2.31 (s, 3H, ArCH₃), 2.20 (s, 3H, COCH₃), 1.46 (s, 3H, CCH₃), 1.23 (t, *J* = 7.1 Hz, 3H, OCH₂CH₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 204.5, 172.5, 159.5, 152.2, 134.1, 130.1, 121.1, 90.2, 61.5, 58.5, 39.4, 26.1, 20.8, 18.7, 14.0. IR ν 3039 (m), 2990 (m), 2935 (w), 1714 (s), 1640 (m), 1507 (m), 1452 (m), 1359 (m), 1293 (m), 1252 (s), 1220 (s), 1182 (s), 1107 (m), 1020 (m), 971 (m), 932 (m), 836 (m), 740 (m), 655 (m). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₂₂NaO₄⁺ 313.1410; Found 313.1414.

***N*-(4-Methoxyphenyl)-4-nitro-*N*-(2-(*p*-tolylloxy)allyl)benzenesulfonamide (3o)**

Starting from O-VBX **1a** (39.4 mg, 0.100 mmol) and *N*-(4-methoxyphenyl)-4-nitrobenzenesulfonamide **2o** (31.0 mg, 0.100 mmol), *N*-(4-methoxyphenyl)-4-nitro-*N*-(2-(*p*-tolylloxy)allyl) benzene sulfonamide **3o** (15.0 mg, 33.0 μmol, 33% yield) was obtained, as a colorless amorphous solid. The allyl ester **4a** was formed in 15% NMR yield, but not isolated.

Rf: 0.33 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Methylene Chloride-*d*₂) δ 8.30 – 8.21 (m, 2H, ArH), 7.89 – 7.79 (m, 2H, ArH), 7.14 – 7.07 (m, 2H, ArH), 7.06 – 6.98 (m, 2H, ArH), 6.92 – 6.79 (m, 2H, ArH), 6.76 – 6.66 (m, 2H, ArH), 4.37 (s, 2H, CCH₂N), 4.16 (d, *J* = 2.3 Hz, 1H, CH₂CO), 3.91 (d, *J* = 2.3 Hz, 1H, CH₂CO), 3.81 (s, 3H, OCH₃), 2.30 (s, 3H, ArCH₃). ¹³C NMR (101 MHz, Methylene Chloride-*d*₂) δ 160.2, 157.9, 152.6, 150.6, 145.4, 135.0, 131.1, 131.0, 130.7, 129.6, 124.5, 121.1, 114.9, 92.1, 56.0, 54.7, 21.0. IR ν 3340 (m), 2970 (m), 2880 (m), 1435 (s), 1307 (m), 1091 (s), 1046 (s), 880 (s), 777 (s). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₂N₂NaO₆S⁺ 477.1091; Found 477.1091.

(*E*)-4,4'-(Pent-1-ene-2,3-diylbis(oxy))bis(methylbenzene) (3p)

Starting from O-VBX **1b** (0.127 g, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-4,4'-(pent-1-ene-2,3-diylbis(oxy))bis(methylbenzene) **3p** (55.0 mg, 0.195 mmol, 65% yield) and **4b** (40.5 mg, 95.6 μmol, 32%) were obtained, as a colorless amorphous solids. Rf: 0.65 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.13 (dd, *J* = 7.4, 1.4 Hz, 2H, ArH), 7.11 – 7.06 (m, 2H, ArH), 6.90 – 6.86 (m, 2H, ArH), 6.86 – 6.81 (m, 2H, ArH), 5.05 (t, *J* = 7.9 Hz, 1H, CCHO), 4.61 (s, 2H, CH₂CO), 2.28 (s, 3H, ArCH₃), 2.25 (s, 3H, ArCH₃), 2.13 (p, *J* = 7.5 Hz, 2H, CHCH₂CH₃), 0.95 (t, *J* = 7.5 Hz, 3H, CHCH₂CH₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.6, 154.0, 149.6, 132.5, 130.3, 130.0, 129.8, 119.1, 116.8, 115.0, 64.4, 20.7, 20.5, 20.0, 14.8. IR ν 3665 (m), 3408 (m), 2968 (s), 2929 (s), 1722 (m), 1611 (m), 1512 (s), 1441 (m), 1385 (m), 1239 (s), 1170 (m), 1061 (s), 890 (m), 820 (s), 738 (m). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₉H₂₂NaO₂⁺ 305.1512; Found 305.1514.

(*E*)-4,4'-(Oct-2-ene-1,2-diylbis(oxy))bis(methylbenzene) (3q)

Starting from O-VBX **1c** (0.139 g, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-4,4'-(oct-2-ene-1,2-diylbis(oxy))bis(methylbenzene) **3q** (55.0 mg, 0.170 mmol, 57% yield) and **4c** (44.6 mg, 95.3 μmol, 32%) were obtained, as a colorless amorphous solids. Rf: 0.8 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.16 – 7.11 (m, 2H, ArH), 7.11 – 7.06 (m, 2H, ArH), 6.90 – 6.85 (m, 2H, ArH), 6.85 – 6.81 (m, 2H, ArH), 5.05 (t, *J* = 8.0 Hz, 1H, OCCHCH₂), 4.61

(s, 2H, OCH₂CO), 2.28 (s, 3H, ArCH₃), 2.25 (s, 3H, ArCH₃), 2.10 (q, *J* = 7.5 Hz, 2H, CH₂), 1.40 – 1.30 (m, 2H, CH₂), 1.30 – 1.23 (m, 4H, CH₂CH₂), 0.87 (t, *J* = 6.8 Hz, 3H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 157.5, 155.1, 150.7, 133.4, 131.3, 131.0, 130.8, 119.6, 116.9, 115.8, 64.7, 32.0, 30.3, 26.9, 23.1, 20.6, 20.4, 14.3. IR ν 3669 (m), 2976 (s), 2912 (s), 1506 (s), 1388 (s), 1220 (s), 1057 (s), 890 (m), 815 (m), 723 (m). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₈NaO₂⁺ 347.1982; Found 347.1972.

(*E*)-6,7-bis(*p*-Tolyloxy)hept-5-en-1-ol (**3r**)

Starting from O-VBX **1d** (0.140 g, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), and following the general procedure with 24 h reaction time, (*E*)-6,7-bis(*p*-tolyloxy)hept-5-en-1-ol **3r** (63.0 mg, 0.193 mmol, 64% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.8 (DCM:MeOH 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.16 – 7.09 (m, 2H, ArH), 7.11 – 7.06 (m, 2H, ArH), 6.90 – 6.86 (m, 2H, ArH), 6.86 – 6.81 (m, 2H, ArH), 5.05 (t, *J* = 8.0 Hz, 1H, OCCHCH₂), 4.61 (s, 2H, OCH₂CO), 3.46 (t, *J* = 6.4 Hz, 2H, CH₂OH), 2.28 (s, 3H, ArCH₃), 2.26 (s, 3H, ArCH₃), 2.13 (q, *J* = 7.5 Hz, 2H, CH₂), 1.51 – 1.42 (m, 2H, CH₂), 1.41 – 1.34 (m, 2H, CH₂). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 157.5, 155.1, 150.9, 133.5, 131.3, 131.0, 130.8, 119.6, 116.6, 115.8, 64.7, 62.3, 32.9, 27.0, 26.8, 20.6, 20.4. IR ν 3001 (m), 2944 (m), 1608 (m), 1507 (s), 1224 (s), 1063 (m), 1013 (s), 916 (m), 821 (s), 741 (m). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₂₆NaO₃⁺ 349.1774; Found 349.1771.

(*E*)-(7,8-bis(*p*-Tolyloxy)oct-6-en-1-yn-1-yl)trimethylsilane (**3s**)

Starting from O-VBX **1e** (0.160 g, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-(7,8-bis(*p*-tolyloxy)oct-6-en-1-yn-1-yl)trimethylsilane **3s** (75.0 mg, 0.191 mmol, 64% yield) and **4e** (41.5 mg, 77.9 μmol, 26%) were obtained, as a colorless amorphous solids. **Rf**: 0.8 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.16 – 7.11 (m, 2H, ArH), 7.11 – 7.07 (m, 2H, ArH), 6.91 – 6.86 (m, 2H, ArH), 6.86 – 6.82 (m, 2H, ArH), 5.00 (t, *J* = 8.0 Hz, 1H, OCCHCH₂), 4.63 (s, 2H, OCH₂CO), 2.28 (s, 3H, ArCH₃), 2.25 (s, 3H, ArCH₃), 2.20 (td, *J* = 7.3, 3.3 Hz, 4H, CH₂CH₂), 1.50 (p, *J* = 7.1 Hz, 2H, CH₂), 0.08 (s, 9H, Si(CH₃)₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 157.5, 154.9, 151.7, 133.6, 131.3, 131.1, 130.8, 119.8, 115.9, 115.1, 108.1, 85.5, 64.8, 29.5, 25.9, 20.6, 20.5, 19.5, 0.1. IR ν 3621 (w), 3096 (w), 2964 (w), 2602 (w), 2262 (s), 1633 (m), 1514 (m), 1227 (m), 1187 (m), 1038 (s), 841 (s), 681 (w). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₃₂NaO₂Si⁺ 415.2064; Found 415.2070.

(*E*)-2-(5,6-bis(*p*-Tolyloxy)hex-4-en-1-yl)isoindoline-1,3-dione (**3t**)

Starting from O-VBX **1f** (174 mg, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-2-(5,6-bis(*p*-tolyloxy)hex-4-en-1-yl)isoindoline-1,3-dione **3t** (86.3 mg, 0.195 mmol, 65% yield with 10% impurities) and **4f** (50.6 mg, 86.7 μmol, 29%) were obtained, as a colorless amorphous solids. **Rf**: 0.40 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.81 – 7.74 (m, 4H, ArH), 7.11 (dd, *J* = 7.4, 1.4 Hz, 2H, ArH), 7.07 – 7.03 (m, 2H, ArH), 6.90 – 6.84 (m, 2H, ArH), 6.82 – 6.76 (m, 2H, ArH), 5.03 (t, *J* = 8.0 Hz, 1H, OCCH), 4.59 (s, 2H, OCH₂CO), 3.60 (t, *J* = 7.0 Hz, 2H, CH₂), 2.28

(s, 3H, CH₃), 2.24 (s, 3H, CH₃), 2.16 (q, *J* = 7.7 Hz, 2H, CH₂), 1.69 (p, *J* = 7.2 Hz, 2H, CH₂). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 169.3, 157.4, 154.8, 151.5, 135.0, 133.6, 133.2, 131.3, 131.0, 130.8, 123.7, 119.7, 115.8, 115.1, 64.9, 38.1, 29.4, 24.5, 20.6, 20.4. IR ν 2934 (m), 1770 (m), 1712 (s), 1609 (m), 1508 (s), 1459 (m), 1397 (m), 1364 (m), 1221 (s), 1173 (m), 1114 (m), 1020 (m), 899 (m), 815 (m), 720 (m). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₂₇NNaO₄⁺ 464.1832; Found 464.1840.

1-Iodo-2-((3-(*p*-tolylloxy)prop-1-en-2-yl)oxy)benzene (3u)

Starting from O-VBX **1g** (152 mg, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), 1-iodo-2-((3-(*p*-tolylloxy)prop-1-en-2-yl)oxy)benzene **3u** (66.5 mg, 0.182 mmol, 61% yield) was obtained, as a yellow amorphous solid and **4i** (11.8 mg, 29.9 μmol, 10%) was obtained, as a colorless amorphous solid. **Rf**: 0.7 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H, ArH), 7.42 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H, ArH), 7.18 – 7.08 (m, 3H, ArH), 6.99 (td, *J* = 7.6, 1.5 Hz, 1H, ArH), 6.95 – 6.89 (m, 2H, ArH), 4.68 (d, *J* = 0.9 Hz, 2H, OCH₂CO), 4.57 (dt, *J* = 2.5, 1.0 Hz, 1H, OCCH₂), 4.00 (d, *J* = 2.5 Hz, 1H, OCCH₂), 2.27 (s, 3H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 158.7, 157.2, 155.3, 140.8, 131.5, 131.0, 130.8, 127.7, 123.0, 115.8, 91.3, 90.5, 68.1, 20.4. IR ν 3667 (m), 2991 (s), 2908 (s), 1512 (m), 1401 (m), 1231 (s), 1068 (s), 1028 (s), 905 (m), 825 (m), 742 (m). HRMS (APPI/QTOF) *m/z*: [M]⁺ Calcd for C₁₆H₁₅IO₂⁺ 366.0111; Found 366.0111.

(*E*)-1-Iodo-2-((1-(*p*-tolylloxy)pent-2-en-2-yl)oxy)benzene (3v)

Starting from O-VBX **1h** (160 mg, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-1-iodo-2-((1-(*p*-tolylloxy)pent-2-en-2-yl)oxy)benzene **3v** (70.0 mg, 0.178 mmol, 59% yield) and **4j** (51.9 mg, 0.121 mmol, 41%) were obtained, as a colorless amorphous solids. **Rf**: 0.61 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.82 (dd, *J* = 7.9, 1.5 Hz, 1H, ArH), 7.34 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H, ArH), 7.13 – 7.06 (m, 2H, ArH), 7.04 (dd, *J* = 8.2, 1.4 Hz, 1H, ArH), 6.93 – 6.79 (m, 3H, ArH), 5.04 (t, *J* = 7.9 Hz, 1H, OCCH), 4.66 (s, 2H, OCH₂CO), 2.25 (s, 3H, ArCH₃), 2.14 (q, *J* = 7.8 Hz, 2H, CH₂), 0.97 (t, *J* = 7.5 Hz, 3H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 157.4, 156.6, 149.6, 140.6, 131.4, 130.8, 130.7, 126.0, 119.9, 119.1, 115.9, 88.9, 64.7, 20.5, 20.5, 14.9. IR ν 3671 (w), 2969 (m), 2872 (w), 2604 (w), 2360 (w), 1758 (w), 1680 (w), 1612 (m), 1580 (m), 1510 (s), 1465 (s), 1439 (m), 1393 (w), 1259 (m), 1227 (s), 1174 (m), 1119 (m), 1108 (m), 1041 (m), 1020 (s), 939 (m), 887 (m), 817 (m), 752 (m), 718 (w), 687 (w), 645 (w). HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₈H₁₉IO₂⁺ 417.0322; Found 417.0323.

(*E*)-1-Iodo-2-((1-(*p*-tolylloxy)oct-2-en-2-yl)oxy)benzene (3w)

Starting from O-VBX **1i** (173 mg, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), (*E*)-1-iodo-2-((1-(*p*-tolylloxy)oct-2-en-2-yl)oxy)benzene **3w** (57.0 mg, 0.131 mmol, 44% yield) and **4k** (48.7 mg, 0.105 μmol, 35%) were obtained, as a colorless amorphous solids. **Rf**: 0.86 (Pentane:EtOAc 9:1). ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H, ArH), 7.35 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 1H, ArH), 7.12 – 7.07 (m, 2H, ArH), 7.03 (dd, *J* = 8.2, 1.5 Hz, 1H, ArH), 6.90 – 6.82 (m, 3H, ArH), 5.01 (t, *J* = 8.0 Hz, 1H, OCCH), 4.66 (s, 2H, OCH₂CO), 2.26 (s, 3H, ArCH₃), 2.18 – 2.08 (m, 2H, CH₂), 1.39 – 1.22 (m, 6H, CH₂), 0.91 – 0.83 (m, 3H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃) δ 157.4,

156.7, 150.0, 140.6, 131.4, 130.8, 130.7, 126.1, 120.0, 117.4, 116.0, 89.0, 64.8, 31.9, 30.2, 26.9, 23.1, 20.4, 14.3. **IR** ν 3666 (m), 2979 (s), 2902 (s), 2322 (w), 2261 (m), 2069 (w), 1643 (w), 1443 (w), 1401 (m), 1238 (m), 1056 (s), 888 (m), 840 (m), 687 (w). **HRMS** (ESI/QTOF) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{25}INaO_2^+$ 459.0791; Found 459.0794.

(E)-1-Methoxy-4-((1-(*p*-tolyl)oxy)pent-2-en-2-yl)oxy)benzene (3x)

Starting from O-VBX **1j** (1 g, 2.28 mmol) and *p*-cresol **2a** (0.247 g, 2.28 mmol), (*E*)-1-methoxy-4-((1-(*p*-tolyl)oxy)pent-2-en-2-yl)oxy)benzene **3x** (0.427 g, 1.43 mmol, 63% yield) and **4n** (0.164 g, 0.340 mmol, 15%) were obtained, as a colorless amorphous solids. **Rf**: 0.57 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile- d_3) δ 7.13 – 7.07 (m, 2H, ArH), 6.95 – 6.81 (m, 6H, ArH), 4.94 (t, J = 7.9 Hz, 1H, OCCH), 4.62 (s, 2H, OCH₂CO), 3.75 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃), 2.11 (p, J = 7.6 Hz, 2H, CH₂), 0.93 (t, J = 7.5 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile- d_3) δ 157.5, 156.7, 151.4, 150.4, 131.3, 130.8, 121.4, 116.4, 115.8, 115.6, 64.8, 56.1, 20.4 (2C), 15.1. **IR** ν 3666 (m), 2979 (s), 2902 (s), 2333 (m), 2260 (m), 1938 (w), 1617 (m), 1506 (m), 1445 (m), 1400 (m), 1240 (m), 1056 (s), 874 (m), 839 (m), 742 (w), 687 (m). **HRMS** (APPI/QTOF) m/z : $[M]^+$ Calcd for $C_{19}H_{22}O_3^+$ 298.1563; Found 298.1551.

1-Methoxy-4-((3-(*p*-tolyl)oxy)prop-1-en-2-yl)oxy)benzene (3y)

Starting from O-VBX **1k** (123 mg, 0.300 mmol) and *p*-cresol **2a** (32.4 mg, 0.300 mmol), 1-methoxy-4-((3-(*p*-tolyl)oxy)prop-1-en-2-yl)oxy)benzene **3y** (45.1 mg, 0.167 mmol, 56% yield) and **4o** (48.3 mg, 0.122 mmol, 41%) were obtained, as a colorless amorphous solids. **Rf**: 0.60 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile- d_3) δ 7.14 – 7.09 (m, 2H, ArH), 7.02 – 6.96 (m, 2H, ArH), 6.95 – 6.87 (m, 4H, ArH), 4.61 (d, J = 0.8 Hz, 2H, OCH₂CO), 4.47 (dd, J = 2.0, 1.0 Hz, 1H, OCCH₂), 4.04 (d, J = 2.1 Hz, 1H, OCCH₂), 3.77 (s, 3H, OCH₃), 2.27 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile- d_3) δ 160.6, 157.5, 157.2, 149.1, 131.4, 130.8, 122.9, 115.8, 115.7, 90.4, 68.5, 56.2, 20.4. **IR** ν 2962 (s), 2921 (s), 1647 (m), 1615 (m), 1508 (s), 1456 (m), 1394 (m), 1289 (m), 1217 (s), 1039 (s), 963 (m), 916 (m), 832 (s). **HRMS** (APPI/QTOF) m/z : $[M]^+$ Calcd for $C_{17}H_{18}O_3^+$ 270.1250; Found 270.1239.

6. Allylic esters formation from EBX

Optimization procedure and table for the synthesis of **4a**:

In a glass vial, phenol (0.100 mmol, 1.00 equiv.) was dissolved in 1.00 mL of DME (0.1 M). Cesium carbonate (10.0 μ mol, 0.10 equiv.) was added and the mixture stirred vigorously for 5 min. Then the corresponding EBX **5** was added in one portion (0.100 mmol, 1.00 equiv.) and the reaction was left stirring for 16 hours at room temperature. Then cesium carbonate (0.120 mmol, 1.20 equiv.) and anisole (20.0 μ mol, 0.20 equiv.) were added and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane : ethyl acetate 9:1) to provide product **4** as a sticky solid.

Table S2: Optimisation studies for the transformation of **1a** into **4a**.

Entry	Additive	Equiv.	Temperature (°C)	Remaining 1a (%) ^[a]	Yield (%) ^[a]
1	-	-	25 °C	36	0-30
2	Anisole	1.0	25 °C	<5	45
3	Anisole	1.0	0-25 °C	9-60	34-87
4	Anisole	0.20	25 °C	<5	65
5	Anisole	0.20	0-25 °C	34	61
6 ^[b]	Anisole	1.00	25 °C	>95	NR
7 ^[b]	DMAP	2.00	25 °C	>95	NR

Reaction conditions: Substrate **1a** (0.100 mmol), Cs₂CO₃ (0.120 mmol), additive (xx equiv.) and DME (0.1 M). NR: no reaction. ^[a]NMR yield given, calculated using 7.0 μ L of dibromomethane as internal standard. ^[b]The reaction was performed without Cs₂CO₃.

In absence of external nucleophiles, formation of **4a** was sometimes observed, together with decomposition of **1a** (entry 1). However, the yield was never higher than 30% and this result was not reproducible. During screening of nucleophiles, electron-rich phenols have led to increased amount of ester **4a**. Anisole was then tested as additive to promote the reaction as an electron-rich arene lacking the free OH group. Indeed, compounds **4a** was now obtained, but with low reproducibility in yield and conversion (entry 2), in moderate yield. At 0 °C, the yield was improved in some instance, but the transformation still suffered of low reproducibility, with yields between 34 and 87% (entry 3). A better reproducibility was obtained using 0.20 equivalents of anisole at room temperature, giving **4a** in 65% yield (entry 4). Starting at 0 °C, a similar yield was obtained but no full conversion was observed (entry 5). Furthermore, to confirm the role of Cs₂CO₃, the reaction was performed in absence of base and with 1.00 equivalent of anisole (entry 6). No product was formed and **1a** was recovered. Thereby, for

the reaction to proceed efficiently, a base and an additive seem to be required. We then wonder if DMAP could play both roles (entry 7), but no conversion was observed.

One-pot two-step procedure for the synthesis of 4a:

With the optimized conditions in hand, a one-pot two-step procedure was applied to the synthesis of **4a**. After conversion of Me-EBX (**5a**) to O-VBX **1a**, anisole and an excess of base were added to the reaction mixture. The product **4a** could be isolated in the same yield as when starting from isolated **1a**.

General procedure for allylic esters formation from EBX:

In a glass vial, phenol (0.100 mmol, 1.00 equiv.) was dissolved in 1.00 mL of DME (0.1 M). Cesium carbonate (10.0 μmol, 0.10 equiv.) was added and the mixture stirred vigorously for 5 min. Then the corresponding EBX **5** was added in one portion (0.100 mmol, 1.00 equiv.) and the reaction was left stirring for 16 hours at room temperature. Then cesium carbonate (0.120 mmol, 1.20 equiv.) and anisole (20.0 μmol, 0.20 equiv.) were added and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane : ethyl acetate 9:1) to provide product **4** as a sticky solid.

2-(*p*-Tolyloxy)allyl 2-iodobenzoate (**4a**)

Starting from EBX **5a** (0.118 mg, 0.300 mmol), 2-(*p*-tolyloxy)allyl 2-iodobenzoate **4a** (77.0 mg, 0.195 mmol, 65% yield) was obtained, as a colorless amorphous solid. **R_f**: 0.58 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.20 – 7.12 (m, 3H, ArH), 7.02 – 6.96 (m, 2H, ArH), 4.94 (d, *J* = 0.6 Hz, 2H,

CCH₂O), 4.55 (d, *J* = 2.3 Hz, 1H, CH₂CO), 4.23 (d, *J* = 2.3 Hz, 1H, CH₂CO), 2.33 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 157.5, 152.6, 141.6, 134.8, 134.2, 133.0, 131.4, 130.3, 128.1, 120.8, 94.5, 92.1, 65.0, 20.9. **IR** ν 3463 (w), 3030 (w), 2929 (w), 1736 (s), 1729 (s), 1651 (w), 1588 (w), 1505 (m), 1457 (w), 1430 (m), 1373 (w), 1289 (s), 1243 (s), 1134 (s), 1101 (s), 1045 (w), 1017 (m), 964 (w), 839 (m), 741 (s), 697 (w). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₅INaO₃⁺ 416.9958; Found 416.9964.

2-(*p*-Tolyloxy)pent-1-en-3-yl 2-iodobenzoate (**4b**)

Starting from EBX **5b** (42.2 mg, 0.100 mmol), 2-(*p*-tolyloxy)pent-1-en-3-yl 2-iodobenzoate **4b** (25.0 mg, 59.0 μ mol, 59% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.60 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.73 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.37 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.14 (td, J = 7.7, 1.7 Hz, 1H, ArH), 7.12 – 7.08 (m, 2H, ArH), 6.95 – 6.90 (m, 2H, ArH), 5.12 (t, J = 7.9 Hz, 1H, CCHO), 4.99 (s, 2H, CH₂CO), 2.31 (s, 3H, ArCH₃), 2.21 (p, J = 7.6 Hz, 2H, CH₂CH₃), 1.01 (t, J = 7.5 Hz, 3H, CH₂CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 154.1, 148.3, 141.5, 134.9, 132.8, 132.7, 131.3, 130.2, 128.0, 119.1, 118.1, 94.4, 60.9, 20.8, 20.2, 15.0. **IR** ν 3464 (w), 3030 (w), 2957 (w), 2256 (w), 1728 (m), 1607 (w), 1590 (w), 1517 (w), 1462 (w), 1427 (w), 1372 (w), 1286 (m), 1254 (m), 1123 (m), 1017 (m), 904 (m), 821 (w), 741 (s), 649 (w). **HRMS** (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₁₉H₂₀IO₃⁺ 423.0452; Found 423.0449.

(*E*)-2-(*p*-Tolyloxy)oct-2-en-1-yl 2-iodobenzoate (**4c**)

Starting from EBX **5c** (46.4 mg, 0.100 mmol), (*E*)-2-(*p*-tolyloxy)oct-2-en-1-yl 2-iodobenzoate **4c** (27.8 mg, 60.0 μ mol, 60% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.69 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.73 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.36 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 – 7.07 (m, 3H, ArH), 7.00 – 6.87 (m, 2H, ArH), 5.14 (t, J = 8.0 Hz, 1H, CCHCH₂), 4.99 (s, 2H, CCH₂O), 2.31 (s, 3H, ArCH₃), 2.18 (q, J = 7.5 Hz, 2H, CHCH₂CH₂CH₂CH₂CH₃), 1.38 (t, J = 7.1 Hz, 2H, CHCH₂CH₂CH₂CH₂CH₃), 1.34 – 1.21 (m, 4H, CHCH₂CH₂CH₂CH₂CH₃), 0.95 – 0.80 (m, 3H, CH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 154.2, 148.5, 141.5, 134.9, 132.8, 132.7, 131.3, 130.2, 128.0, 119.0, 117.0, 94.4, 60.9, 31.5, 29.8, 26.7, 22.6, 20.8, 14.2. **IR** ν 3458 (w), 3038 (w), 2929 (m), 2861 (w), 2254 (w), 1731 (m), 1610 (w), 1505 (s), 1456 (w), 1369 (w), 1282 (m), 1246 (m), 1216 (s), 1170 (m), 1128 (m), 1105 (m), 1016 (m), 958 (w), 904 (m), 820 (w), 741 (s), 648 (w). **HRMS** (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₂₂H₂₆IO₃⁺ 465.0921; Found 465.0923.

(*E*)-2-(*p*-Tolyloxy)hexadec-2-en-1-yl 2-iodobenzoate (**4d**)

Starting from EBX **5g** (47.0 mg, 0.100 mmol), (*E*)-2-(*p*-tolyloxy)hexadec-2-en-1-yl 2-iodobenzoate **4d** (39.5 mg, 69.0 μ mol, 69% yield) was obtained, as a colorless amorphous solid. **¹H NMR** (400 MHz, Methylene Chloride-*d*₂) δ 8.00 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.71 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.40 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 (td, J = 7.7, 1.7 Hz, 1H, ArH), 7.13 – 7.08 (m, 2H, ArH), 6.96 – 6.85 (m, 2H, ArH), 5.14 (t, J = 8.0 Hz, 1H, CCHCH₂), 4.96 (s, 2H, CCH₂O), 2.30 (s, 3H, ArCH₃), 2.18 (q, J = 7.5 Hz, 2H, CH₂), 1.43 – 1.33 (m, 2H, CH₂), 1.33 – 1.22 (m, 20H, CH₂), 0.92 – 0.83 (m, 3H, CH₃). **¹³C NMR** (101 MHz, Methylene Chloride-*d*₂) δ 166.6, 154.6, 148.9, 141.8, 135.6, 133.2, 133.2, 131.5, 130.6, 128.5, 119.2, 117.7, 94.4, 61.3, 32.5, 30.6, 30.3, 30.3, 30.2, 30.2, 30.2, 30.0, 29.9, 29.7, 27.1, 23.3, 20.9, 14.5. **IR** ν 2959 (m), 2923 (m), 1732 (s), 1503 (s), 1400 (s), 1256 (s), 1075 (s), 1069 (s), 741 (s). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₃₀H₄₁IO₃⁺ 599.1993; Found 599.2001.

(E)-2-(p-Tolyloxy)-8-(trimethylsilyl)oct-2-en-7-yn-1-yl 2-iodobenzoate (4e)

Starting from EBX **5e** (42.0 mg, 0.100 mmol), (*E*)-2-(*p*-tolylloxy)-8-(trimethylsilyl)oct-2-en-7-yn-1-yl 2-iodobenzoate **4e** (37.3 mg, 70.0 μ mol, 70% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.64 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.74 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.14 (td, *J* = 7.8, 1.9 Hz, 1H, ArH), 7.10 (d, *J* = 8.3 Hz, 2H, ArH), 6.95 – 6.89 (m, 2H, ArH), 5.04 (t, *J* = 8.0 Hz, 1H, CCHCH₂), 5.01 (s, 2H, CCH₂O), 2.30 (d, *J* = 7.2 Hz, 5H, CHCH₂CH₂CH₂C, ArCH₃), 2.25 (t, *J* = 7.1 Hz,

2H, CHCH₂CH₂CH₂C), 1.60 (p, *J* = 7.2 Hz, 2H, CHCH₂CH₂CH₂C), 0.14 (s, 9H, Si(CH₃)₃). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 166.3, 153.9, 149.8, 141.4, 135.0, 133.0, 132.8, 131.3, 130.3, 128.0, 119.3, 114.7, 106.8, 94.3, 85.3, 60.9, 28.9, 25.7, 20.8, 19.3, 0.3. **IR** ν 3669 (w), 2978 (s), 2902 (s), 2172 (w), 1734 (m), 1676 (w), 1589 (w), 1506 (m), 1399 (m), 1249 (s), 1232 (s), 1221 (s), 1054 (s), 1028 (s), 901 (m), 842 (s), 741 (s), 642 (w). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₉INaO₃Si⁺ 555.0823; Found 555.0834.

(E)-6-(1,3-Dioxoisindolin-2-yl)-2-(p-tolyloxy)hex-2-en-1-yl 2-iodobenzoate (4f)

Starting from EBX **5f** (47.0 mg, 0.100 mmol), (*E*)-6-(1,3-dioxoisindolin-2-yl)-2-(*p*-tolylloxy)hex-2-en-1-yl 2-iodobenzoate **4f** (35.0 mg, 60.0 μ mol, 60% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.28 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Acetonitrile-*d*₃) δ 7.99 (dd, *J* = 7.9, 1.1 Hz, 1H, ArH), 7.77 (tdd, *J* = 8.8, 5.4, 3.9 Hz, 4H, ArH), 7.64 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.44 (td, *J* = 7.6, 1.1 Hz, 1H, ArH), 7.21 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 7.14 – 7.09 (m, 2H, ArH), 6.91 – 6.86 (m, 2H,

ArH), 5.11 (t, *J* = 7.9 Hz, 1H, OCCH), 4.94 (s, 2H, OCH₂CO), 3.63 (t, *J* = 7.0 Hz, 2H, CH₂), 2.26 (d, *J* = 11.3 Hz, 5H, CH₂, CH₃), 1.74 (p, *J* = 7.2 Hz, 2H, CH₂). $^{13}\text{C NMR}$ (101 MHz, Acetonitrile-*d*₃) δ 169.3, 167.2, 154.9, 150.0, 142.0, 136.5, 135.0, 133.8, 133.7, 133.2, 131.5, 131.1, 129.2, 123.7, 119.6, 116.5, 94.0, 61.5, 38.1, 29.4, 24.7, 20.6. **IR** ν 2942 (w), 1769 (w), 1705 (s), 1611 (w), 1583 (w), 1503 (m), 1465 (w), 1434 (w), 1394 (m), 1369 (m), 1283 (m), 1244 (m), 1219 (m), 1169 (m), 1129 (m), 1099 (m), 1041 (m), 1015 (m), 954 (w), 919 (w), 888 (w), 823 (w), 747 (w), 718 (s). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₂₄INNaO₅⁺ 604.0591; Found 604.0589.

(E)-2-(p-Tolyloxy)octa-2,7-dien-1-yl 2-iodobenzoate (4g)

Starting from EBX **5h** (35.0 mg, 0.100 mmol), (*E*)-2-(*p*-tolylloxy)octa-2,7-dien-1-yl 2-iodobenzoate **4g** (38.0 mg, 82.0 μ mol, 82% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.66 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.73 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.18 – 7.07 (m, 3H, ArH), 6.95 – 6.89 (m, 2H, ArH), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH₂CHCH₂), 5.10 (t, *J* = 7.9 Hz, 1H, OCCHCH₂), 5.04 – 4.93 (m, 4H, CCH₂O, CH₂CHCH₂), 2.31 (s, 3H, ArCH₃), 2.20 (q, *J*

= 7.6 Hz, 2H, CHCH₂CH₂CH₂CH), 2.14 – 2.03 (m, 2H, CHCH₂CH₂CH₂CH), 1.49 (p, *J* = 7.4 Hz, 2H, CHCH₂CH₂CH₂CH). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 166.4, 154.0, 148.9, 141.5, 138.5, 134.9, 132.8, 132.8, 131.3, 130.2, 128.0, 119.1, 116.1, 115.0, 94.4, 61.0, 33.3, 29.3, 26.1, 20.8. **IR** ν 2927 (m), 1728

(s), 1585 (w), 1505 (s), 1458 (w), 1436 (w), 1287 (s), 1249 (s), 1219 (s), 1168 (w), 1127 (m), 1096 (s), 1044 (m), 1015 (s), 949 (w), 914 (m), 821 (m), 741 (s). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{22}H_{24}IO_3^+$ 463.0765; Found 463.0768.

(E)-5-Chloro-2-(*p*-tolxyloxy)pent-2-en-1-yl 2-iodobenzoate (4h)

Starting from EBX **5i** (35.0 mg, 0.100 mmol), (*E*)-5-chloro-2-(*p*-tolxyloxy)pent-2-en-1-yl 2-iodobenzoate **4h** (32.0 mg, 70.0 μ mol, 70% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.45 Pentane : EtOAc 9:1. **1H NMR** (400 MHz, Chloroform- d) δ 8.00 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.77 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.39 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.20 – 7.05 (m, 3H, ArH), 7.00 – 6.88 (m, 2H, ArH), 5.02 (d, J = 2.5 Hz, 3H, CCH₂O, OCCHCH₂), 3.53 (t, J = 6.7 Hz, 2H, CH₂CH₂Cl), 2.66 (dt, J = 8.1, 6.7 Hz, 2H, CH₂CH₂Cl), 2.32 (s, 3H, ArCH₃). **^{13}C NMR** (101 MHz, Chloroform- d) δ 166.2, 153.2, 151.7, 141.4, 134.7, 133.3, 132.8, 131.2, 130.2, 127.9, 119.6, 109.9, 94.3, 60.8, 44.3, 30.0, 20.7. **IR** ν 3666 (w), 2979 (s), 2902 (s), 1401 (m), 1253 (w), 1064 (s), 886 (w), 767 (w), 717 (w). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{19}H_{19}ClIO_3^+$ 457.0062; Found 457.0062.

2-(2-Iodophenoxy)allyl 2-iodobenzoate (4i)

Starting from EBX **5a** (29.0 mg, 0.100 mmol) and 2-iodophenol (22.0 mg, 0.100 mmol), 2-(2-iodophenoxy)allyl 2-iodobenzoate **4i** (35.6 mg, 70.0 μ mol, 70% yield) was obtained, as a yellow amorphous solid. **Rf**: 0.62 (Pentane:EtOAc 9:1). **1H NMR** (400 MHz, Acetonitrile- d_3) δ 8.05 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.89 (ddd, J = 7.8, 2.8, 1.6 Hz, 2H, ArH), 7.50 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.43 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H, ArH), 7.30 – 7.22 (m, 1H, ArH), 7.19 (dd, J = 8.1, 1.5 Hz, 1H, ArH), 6.99 (ddd, J = 8.0, 7.3, 1.5 Hz, 1H, ArH), 4.99 (d, J = 0.6 Hz, 2H, OCH₂CO), 4.66 (dt, J = 2.7, 0.7 Hz, 1H, OCCH₂), 4.07 (d, J = 2.7 Hz, 1H, OCCH₂). **^{13}C NMR** (101 MHz, Acetonitrile- d_3) δ 167.0, 157.3, 155.2, 142.2, 140.9, 136.0, 134.0, 131.9, 131.1, 129.3, 127.8, 122.9, 94.2, 93.4, 90.3, 65.2. **IR** ν 3666 (s), 3091 (m), 2995 (s), 2905 (s), 2261 (s), 1625 (m), 1401 (m), 1230 (m), 1068 (s), 1027 (s), 909 (m), 839 (s), 748 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{13}I_2O_3^+$ 506.8949; Found 506.8949.

(E)-2-(2-Iodophenoxy)pent-2-en-1-yl 2-iodobenzoate (4j)

Starting from EBX **5b** (31.0 mg, 0.100 mmol), (*E*)-2-(2-iodophenoxy)pent-2-en-1-yl 2-iodobenzoate **4j** (37.0 mg, 69.0 μ mol, 69% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.43 (Pentane:EtOAc 9:1). **1H NMR** (400 MHz, Acetonitrile- d_3) δ 8.05 – 7.96 (m, 1H, ArH), 7.83 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.73 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.45 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.35 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H, ArH), 7.23 (td, J = 7.7, 1.7 Hz, 1H, ArH), 7.07 (dd, J = 8.2, 1.5 Hz, 1H, ArH), 6.87 (td, J = 7.6, 1.5 Hz, 1H, ArH), 5.09 (t, J = 7.9 Hz, 1H, OCCH), 5.02 (s, 2H, OCH₂CO), 2.23 (p, J = 7.5 Hz, 2H, CH₂), 1.01 (t, J = 7.5 Hz, 3H, CH₃). **^{13}C NMR** (101 MHz, Acetonitrile- d_3) δ 167.0, 156.4, 148.1, 142.1, 140.7, 136.2, 133.9, 131.8, 130.8, 129.2, 126.2, 120.0, 119.8, 94.2, 89.0, 61.2, 20.6, 14.9. **IR** ν 3672 (m), 3091 (w), 3062 (w), 2969 (s), 2872 (m), 2604 (w), 1881 (w), 1873 (w), 1730 (s), 1680 (w), 1581 (m), 1511 (w), 1465 (s), 1437 (m), 1391 (m), 1345 (w), 1307 (w), 1281 (m), 1246 (s), 1228 (s), 1181 (m), 1124 (m), 1095 (s), 1066 (m), 1042 (s), 1017 (s), 944 (m), 884 (w), 848 (w), 833 (m), 803 (w), 743 (s), 717 (w), 687 (w), 640 (m). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{17}I_2O_3^+$ 534.9262; Found 534.9271.

(E)-2-(2-Iodophenoxy)oct-2-en-1-yl 2-iodobenzoate (4k)

Starting from EBX **5c** (36.0 mg, 0.100 mmol) and 2-iodophenol (22.0 mg, 0.100 mmol), (E)-2-(2-iodophenoxy)oct-2-en-1-yl 2-iodobenzoate **4k** (33.0 mg, 57.0 μ mol, 57% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.80 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Acetonitrile- d_3) δ 8.02 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.83 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.74 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.46 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.35 (ddd, J = 8.2, 7.3, 1.5 Hz, 1H, ArH), 7.23 (td, J = 7.7, 1.7 Hz, 1H, ArH), 7.07 (dd, J = 8.2, 1.5 Hz, 1H, ArH), 6.88 (td, J = 7.6, 1.5 Hz, 1H, ArH), 5.05 (t, J = 8.0 Hz, 1H, OCCH), 5.02 (s, 2H, OCH₂CO), 2.20 (q, J = 7.3 Hz, 2H, CH₂), 1.44 – 1.36 (m, 2H, CH₂), 1.32 – 1.28 (m, 4H, CH₂), 0.91 – 0.83 (m, 3H, CH₃). $^{13}\text{C NMR}$ (101 MHz, Acetonitrile- d_3) δ 167.0, 156.4, 148.6, 142.1, 140.7, 136.2, 133.9, 131.8, 130.8, 129.2, 126.3, 120.0, 118.3, 94.2, 89.1, 61.2, 32.0, 30.2, 27.0, 23.1, 14.3. **IR** ν 3666 (m), 2979 (s), 2903 (s), 2351 (w), 2260 (m), 1613 (w), 1459 (w), 1400 (m), 1250 (m), 1050 (s), 883 (w), 838 (m), 751 (w), 686 (w). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₂₁H₂₂I₂NaO₃⁺ 598.9551; Found 598.9560.

(E)-2-(3-Bromophenoxy)-5-chloropent-2-en-1-yl 2-iodobenzoate (4l)

Starting from EBX **5i** (52.2 mg, 0.100 mmol), (E)-2-(3-bromophenoxy)-5-chloropent-2-en-1-yl 2-iodobenzoate **4l** (27.0 mg, 52.0 μ mol, 52% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.55 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.00 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.73 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.39 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.25 – 7.13 (m, 4H, ArH), 7.00 (ddd, J = 7.5, 2.3, 1.5 Hz, 1H, ArH), 5.22 (t, J = 8.0 Hz, 1H, vinylH), 5.00 (s, 2H, OCH₂C), 3.59 (t, J = 6.5 Hz, 2H, CH₂CH₂Cl), 2.72 (dt, J = 8.0, 6.5 Hz, 2H, CH₂CH₂Cl). $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 166.2, 157.0, 150.5, 141.6, 134.5, 133.1, 131.4, 131.0, 128.1, 126.6, 123.0, 122.3, 117.7, 113.9, 94.4, 60.6, 44.2, 30.0. **IR** ν 3667 (m), 3062 (m), 3011 (m), 2948 (w), 1731 (m), 1583 (m), 1469 (m), 1432 (w), 1247 (s), 1218 (m), 1132 (m), 1065 (s), 1017 (s), 912 (s), 861 (m), 822 (w), 781 (m), 736 (s). **HRMS** (ESI/QTOF) m/z : [M + H]⁺ Calcd for C₁₈H₁₆⁷⁹Br³⁵ClIO₃⁺ 520.9011; Found 520.9011.

2-(Perfluorophenoxy)pent-1-en-3-yl 2-iodobenzoate (4m)

Starting from EBX **5b** (49.8 mg, 0.100 mmol), 2-(perfluorophenoxy)pent-1-en-3-yl 2-iodobenzoate **4m** (20.1 mg, 40.0 μ mol, 40% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.65 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 8.02 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.87 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 (td, J = 7.6, 1.7 Hz, 1H, ArH), 5.07 (s, 2H, CH₂CO), 4.82 (tt, J = 7.8, 1.3 Hz, 1H, CCHO), 2.25 – 2.14 (m, 2H, CHCH₂CH₃), 0.99 (t, J = 7.5 Hz, 3H, CHCH₂CH₃). $^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 166.1, 149.1, 141.6, 134.5, 133.1, 131.4, 128.1, 112.9, 94.5, 60.2, 19.9, 14.8. The carbon signals of the pentafluorobenzene ring could not be resolved. $^{19}\text{F NMR}$ (376 MHz, Chloroform- d) δ -153.70 – -154.37 (m), -160.23 (t, J = 21.9 Hz), -161.98 – -162.63 (m). **IR** ν 3060 (w), 2970 (w), 2939 (w), 2876 (w), 1738 (m), 1685 (w), 1577 (w), 1516 (s), 1470 (m), 1437 (w), 1386 (w), 1245 (m), 1183 (m), 1094 (m), 996 (s), 741 (s). **HRMS** (ESI/QTOF) m/z : [M + Na]⁺ Calcd for C₁₈H₁₂F₅IO₃⁺ 520.9644; Found 520.9651.

(E)-2-(4-Methoxyphenoxy)pent-2-en-1-yl 2-iodobenzoate (4n)

Starting from EBX **5b** (31.0 mg, 0.100 mmol) and 4-methoxyphenol (12.0 mg, 0.100 mmol), (E)-2-(4-methoxyphenoxy)pent-2-en-1-yl 2-iodobenzoate **4n** (28.0 mg, 64.0 μ mol, 64% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.52 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 8.02 (dd, *J* = 7.9, 1.1 Hz, 1H, ArH), 7.68 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.23 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 6.98 – 6.93 (m, 2H, ArH), 6.90 – 6.85 (m, 2H, ArH), 5.03 (t, *J* = 7.9 Hz, 1H, OCCH), 4.97 (s, 2H, OCH₂CO), 3.74 (s, 3H, OCH₃), 2.19 (p, *J* = 7.6 Hz, 2H, CH₂), 0.98 (t, *J* = 7.5 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 167.3, 156.7, 150.4, 149.9, 142.0, 136.7, 133.8, 131.5, 129.2, 121.2, 117.8, 115.6, 94.0, 61.5, 56.2, 20.6, 15.1. **IR** ν 2963 (m), 1730 (s), 1672 (m), 1582 (m), 1504 (s), 1460 (m), 1280 (s), 1247 (s), 1214 (s), 1123 (m), 1105 (m), 1025 (m), 946 (m), 837 (m), 745 (m). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₀IO₄⁺ 439.0401; Found 439.0404.

2-(4-Methoxyphenoxy)allyl 2-iodobenzoate (4o)

Starting from EBX **5a** (29.0 mg, 0.100 mmol) and 4-methoxyphenol (12.0 mg, 0.100 mmol), 2-(4-methoxyphenoxy)allyl 2-iodobenzoate **4o** (23.8 mg, 58.0 μ mol, 58% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.50 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.17 (td, *J* = 7.6, 1.7 Hz, 1H, ArH), 7.06 – 6.99 (m, 2H, ArH), 6.91 – 6.85 (m, 2H, ArH), 4.94 (s, 2H, OCH₂CO), 4.51 (d, *J* = 2.4 Hz, 1H, OCCH₂), 4.16 (d, *J* = 2.4 Hz, 1H, OCCH₂), 3.79 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 158.0, 156.6, 148.2, 141.6, 134.8, 133.0, 131.3, 128.1, 122.2, 114.8, 94.4, 91.2, 65.0, 55.7. **IR** ν 3667 (m), 2994 (m), 2907 (m), 1732 (s), 1649 (m), 1588 (w), 1505 (s), 1436 (w), 1388 (w), 1290 (m), 1219 (s), 1105 (m), 1027 (s), 963 (m), 908 (m), 841 (m), 745 (s). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₆IO₄⁺ 411.0088; Found 411.0094.

(E)-2-(2-Formylphenoxy)oct-2-en-1-yl 2-iodobenzoate (4p)

Starting from EBX **5c** (36.0 mg, 0.100 mmol) and 2-hydroxybenzaldehyde (10.7 μ L, 0.100 mmol), (E)-2-(2-formylphenoxy)oct-2-en-1-yl 2-iodobenzoate **4p** (28.0 mg, 59.0 μ mol, 59% yield) was obtained, as a colorless amorphous solid. **Rf**: 0.55 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 10.35 (d, *J* = 0.8 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.80 (dd, *J* = 8.0, 1.8 Hz, 1H, ArH), 7.64 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.60 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H, ArH), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.26 – 7.15 (m, 3H, ArH), 5.26 (t, *J* = 8.0 Hz, 1H, OCCH), 5.06 (s, 2H, OCH₂CO), 2.23 (q, *J* = 7.4 Hz, 2H, CH₂), 1.48 – 1.37 (m, 2H, CH₂), 1.30 (ddd, *J* = 7.2, 4.4, 3.1 Hz, 4H, CH₂), 0.93 – 0.80 (m, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 190.0, 167.1, 159.9, 149.0, 142.1, 136.9, 136.3, 133.9, 131.5, 129.2, 128.9, 127.8, 124.4, 120.7, 119.7, 94.1, 61.3, 32.0, 30.1, 27.1, 23.1, 14.3. **IR** ν 3646 (s), 2938 (s), 2260 (s), 1875 (s), 1733 (s), 1686 (s), 1593 (s), 1467 (s), 1282 (s), 1253 (s), 1038 (s), 903 (s), 840 (s), 755 (s). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₃IO₄⁺ 501.0533; Found 501.0538.

7. Crystal Structure

Crystal structure of **3a**:

A single crystal was grown by slow diffusion of the solution of **3a** in ethyl acetate and pentane mixture. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (**1989749**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure of **3p**:

A single crystal was grown by slow diffusion of the solution of **3p** in ethyl acetate and pentane mixture. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (**1989757**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

8. NOE experiments

NOE experiment on compound 4c:

NOE experiment on compound 4m:

9. Gram scale synthesis

(*E*)-2-(*p*-Tolyloxy)-8-(trimethylsilyl)oct-2-en-7-yn-1-yl 2-iodobenzoate (**4e**)

In a round-bottom flask, *p*-cresol (0.255 g, 2.36 mmol, 1.00 equiv.) was dissolved in 23.5 mL of DME (0.1 M). Cesium carbonate (77.0 mg, 0.236 mmol) was added and the mixture stirred vigorously for 5 min. Then the corresponding EBX **5e** was added in one portion (1.00 g, 2.36 mmol, 1.00 equiv.) and the reaction was left stirring for 16 hours at room temperature. Then cesium carbonate (0.921 g, 2.83 mmol, 1.20 equiv.) and anisole (0.471 mmol, 51.0 μ L) were added and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, the solvent was removed under reduced pressure and the crude material was purified by column chromatography using phosphate buffered silica (Na₂HPO₄) and pentane/ethyl acetate as eluent. (*E*)-2-(*p*-tolyloxy)-8-(trimethylsilyl)oct-2-en-7-yn-1-yl 2-iodobenzoate **4e** (0.825 g, 1.55 mmol, 66% yield) was obtained, as a colorless sticky solid.

(*E*)-1-Methoxy-4-((1-(*p*-tolyloxy)pent-2-en-2-yl)oxy)benzene (**3x**)

In a round-bottom flask, *p*-cresol (0.247 g, 2.28 mmol, 1 equiv.) and cesium carbonate (0.892 g, 2.74 mmol, 1.20 equiv.) were added. Anhydrous DME (23 mL, 0.1 M) was introduced at 0 °C and the solution was stirred at room temperature for 10 min. O-VBX reagent **1j** (1.00 g, 2.28 mmol, 1 equiv.) was added to the reaction mixture under open air and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was filtrated, the solvent was removed under reduced pressure and the crude material was purified by column chromatography using Pentane:EtOAc (9:1). (*E*)-1-Methoxy-4-((1-(*p*-tolyloxy)pent-2-en-2-yl)oxy)benzene **3x** (0.427 g, 1.43 mmol, 63% yield) was obtained, as a colorless sticky solid.

10. Product modifications

Palladium oxidation cyclization:

2-((*p*-Tolyloxy)methyl)benzofuran (**6**)

Following a reported procedure,²² to a microwave vial charged with 1-iodo-2-((3-(*p*-tolyloxy)prop-1-en-2-yl)oxy)benzene **3u** (36.6 mg, 0.1 mmol), Pd(dppf)Cl_2 (7.32 mg, 10.0 μmol) and triethylamine (0.028 mL, 0.20 mmol) was added dry MeCN (0.27 mL) under N_2 . The reaction mixture was stirred at 82 °C for 72 hours to go to complete conversion. The solution was then filtrated and concentrated under reduced pressure. The crude was purified by preparative TLC (Pentane:EtOAc 80:20) to provide 2-((*p*-tolyloxy)methyl)benzofuran **6** (21.6 mg, 91.0 μmol , 91 % yield) as a white solid. **Rf**: 0.7 (Pentane:EtOAc 9:1). **Mp**: 78 °C. **¹H NMR** (400 MHz, Methylene Chloride- d_2) δ 7.61 – 7.54 (m, 1H, *ArH*), 7.49 (dq, J = 8.4, 1.0 Hz, 1H, *ArH*), 7.30 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H, *ArH*), 7.24 (td, J = 7.5, 1.1 Hz, 1H, *ArH*), 7.15 – 7.07 (m, 2H, *ArH*), 6.94 – 6.86 (m, 2H, *ArH*), 6.79 (d, J = 0.9 Hz, 1H, *OCCH*), 5.13 (d, J = 0.7 Hz, 2H, *OCH₂C*), 2.29 (s, 3H, *CH₃*). **¹³C NMR** (101 MHz, Methylene Chloride- d_2) δ 156.7, 155.7, 153.9, 131.4, 130.5, 128.6, 125.1, 123.4, 121.6, 115.3, 111.8, 106.5, 63.6, 20.7. **IR** ν 3112 (m), 3045 (s), 2925 (s), 2861 (s), 1735 (s), 1612 (s), 1513 (s), 1458 (s), 1377 (s), 1287 (s), 1247 (s), 1182 (s), 1017 (s), 950 (s), 858 (s), 816 (s), 747 (s), 710 (s). **HRMS** (APPI/QTOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2^+$ 237.0910; Found 237.0902.

Palladium reduction:

2-Oxopentyl benzoate (**7**)

2-((*p*-Tolyloxy)pent-1-en-3-yl 2-iodobenzoate **4b** (42.2 mg, 0.100 mmol), Pd/C (loading 5 wt. %, 11.8 mg, 5 mol%) and EtOH (2.90 mL, 0.035 M) were added into a flame dried test tube equipped with a teflon coated stir bar. The tube was placed under hydrogen atmosphere using an autoclave (10 bar) and the solution was stirred at room temperature for 24 h. 2-Oxopentyl benzoate **7** (19.9 mg, 96.0 μmol , 96% yield) was obtained, as a colorless sticky solid. **Rf**: 0.51 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile- d_3) δ 8.09 – 8.02 (m, 2H, *ArH*), 7.70 – 7.62 (m, 1H, *ArH*), 7.57 – 7.48 (m, 2H, *ArH*), 4.91 (s, 2H, *OCH₂CO*), 2.48 (t, J = 7.3 Hz, 2H, *COCH₂CH₂CH₃*), 1.61 (h, J = 7.3 Hz, 2H, *COCH₂CH₂CH₃*), 0.93 (t, J = 7.4 Hz, 3H, *COCH₂CH₂CH₃*). **¹³C NMR** (101 MHz, Acetonitrile- d_3) δ 205.0, 166.5, 134.4, 130.5, 130.4, 129.7, 69.4, 41.0, 17.5, 13.8. **IR** ν 2963 (w), 2878 (w), 2261 (m), 1726 (s), 1719 (s), 1458 (w), 1415 (m), 1375 (m), 1275 (s), 1116 (m), 1056 (m), 1031 (m), 984 (w), 840 (m), 713 (s). **HRMS** (APCI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_3^+$ 229.0835; Found 229.0833.

²² L. Zhou, Y. Shi, X. Zhu, P. Zhang, *Tetrahedron Lett.* **2019**, 60, 2005–2008.

Epoxidation:

To a solution of **3** (0.300 mmol, 1.0 equiv.) in DCM (3.0 mL) was added NaHCO₃ (3.0 mL) and then 3-chloroperbenzoic acid (0.360 mmol, 1.2 equiv.). The resulting mixture was stirred at room temperature for 5 h. A saturated aqueous solution of NaHCO₃ (3 mL) was added to the reaction mixture and stirred for 10 min. The organic layers were extracted with dichloromethane three times. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The sulfate was removed by filtration and the filtrate was concentrated under reduced pressure to provide product **8** as a yellowish oil.

3-Ethyl-2-((p-tolyloxy)-2-((p-tolyloxy)methyl)oxirane (**8a**)

Starting from **3p** (85.0 mg, 0.300 mmol), 3-ethyl-2-((p-tolyloxy)-2-((p-tolyloxy)methyl)oxirane **8a** (90.0 mg, 0.300 mmol, quant. yield) was obtained, as a yellowish oil. **Rf**: 0.81 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 7.15 – 7.04 (m, 4H, ArH), 7.00 – 6.92 (m, 2H, ArH), 6.86 – 6.76 (m, 2H, ArH), 4.44 (dd, *J* = 11.2, 0.8 Hz, 1H, OCH₂C), 4.09 (d, *J* = 11.2 Hz, 1H, OCH₂C), 3.21 – 3.15 (m, 1H, OCHCH₂), 2.27 (s, 3H, ArCH₃), 2.25 (s, 3H, ArCH₃), 1.71 – 1.56 (m, 2H, CH₂CH₃), 1.04 (t, *J* = 7.5 Hz, 3H, CH₂CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 157.3, 152.9, 133.9, 131.7, 130.9, 130.9, 120.4, 115.5, 86.7, 66.8, 64.0, 22.1, 20.6, 20.4, 10.4. **IR** ν 3032 (m), 2972 (m), 2928 (m), 2878 (m), 1612 (m), 1587 (m), 1510 (s), 1462 (m), 1289 (m), 1221 (s), 1175 (m), 1127 (m), 1108 (m), 1051 (m), 1016 (m), 930 (m), 843 (m), 818 (s), 768 (m), 737 (m), 701 (m). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₉H₂₂NaO₃⁺ 321.1461; Found 321.1464.

3-Ethyl-2-(4-methoxyphenoxy)-2-((p-tolyloxy)methyl)oxirane (**8b**)

Starting from **3x** (30.0 mg, 0.100 mmol), 3-ethyl-2-(4-methoxyphenoxy)-2-((p-tolyloxy)methyl)oxirane **8b** (31.0 mg, 0.100 mmol, quant. yield) was obtained, as a yellowish oil. **Rf**: 0.55 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 7.12 – 7.06 (m, 2H, ArH), 7.03 – 6.98 (m, 2H, ArH), 6.87 – 6.81 (m, 4H, ArH), 4.41 (dd, *J* = 11.2, 0.9 Hz, 1H, OCH₂C), 4.06 (d, *J* = 11.1 Hz, 1H, OCH₂C), 3.73 (s, 3H, OCH₃), 3.17 (td, *J* = 6.6, 0.8 Hz, 1H, OCHCH₂), 2.25 (d, *J* = 0.8 Hz, 3H, ArCH₃), 1.62 (qd, *J* = 7.5, 6.4 Hz, 2H, CH₂CH₂), 1.02 (t, *J* = 7.5 Hz, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 157.3, 157.0, 148.4, 131.7, 130.9, 122.2, 115.5, 115.4, 87.2, 66.9, 63.8, 56.1, 22.1, 20.4, 10.3. **IR** ν 2979 (w), 2940 (w), 2880 (w), 1732 (w), 1613 (w), 1588 (w), 1507 (s), 1469 (w), 1439 (w), 1393 (w), 1291 (m), 1242 (s), 1211 (s), 1178 (m), 1126 (w), 1106 (m), 1038 (m), 1012 (w), 930 (m), 823 (m), 736 (m), 705 (w). **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M]⁺ Calcd for C₁₉H₂₂O₄⁺ 314.1513; Found 314.1513.

Oxidation with *m*-CPBA:

To a solution of **3** (0.300 mmol, 1.0 equiv.) in DCM (3.0 mL) was added 3-chloroperbenzoic acid (0.390 mmol, 1.3 equiv.). The resulting mixture was stirred at room temperature for 17 h. A saturated aqueous solution of NaHCO_3 (3 mL) was added to the reaction mixture and stirred for 10 min. The organic layers were extracted with dichloromethane three times. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The sulfate was removed by filtration and the filtrate was concentrated under reduced pressure. The crude was purified by column chromatography (pentane:ethyl acetate 9:1) to provide product **9** as a colorless sticky solid.

2-Oxo-1-(*p*-tolylloxy)pentan-3-yl 3-chlorobenzoate (9a**)**

Starting from **3p** (85.0 mg, 0.300 mmol), 2-oxo-1-(*p*-tolylloxy)pentan-3-yl 3-chlorobenzoate **9a** (66.5 mg, 0.19 mmol, 64% yield) was obtained, as a colorless oil. **Rf**: 0.43 (Pentane:EtOAc 9:1). **^1H NMR** (400 MHz, Acetonitrile- d_3) δ 8.05 (t, $J = 1.9$ Hz, 1H, ArH), 8.01 (dt, $J = 7.8, 1.4$ Hz, 1H, ArH), 7.68 (ddd, $J = 8.1, 2.3, 1.1$ Hz, 1H, ArH), 7.52 (t, $J = 7.9$ Hz, 1H, ArH), 7.14 – 7.07 (m, 2H, ArH), 6.85 – 6.77 (m, 2H, ArH), 5.43 (dd, $J = 7.8, 4.4$ Hz, 1H, OCH₂CO), 4.98 – 4.82 (m, 2H, OCH₂CO), 2.26 (s, 3H, ArCH₃), 2.08 (ddd, $J = 14.6, 7.3, 3.8$ Hz, 1H, CH₂), 1.99 (dd, $J = 15.0, 7.6$ Hz, 1H, CH₂), 1.07 (t, $J = 7.4$ Hz, 3H, CH₃).

^{13}C NMR (101 MHz, Acetonitrile- d_3) δ 203.7, 165.6, 156.7, 135.2, 134.4, 132.3, 131.8, 131.4, 130.9, 130.2, 129.0, 115.3, 79.3, 71.6, 24.5, 20.4, 9.9. **IR** ν 3673 (m), 3093 (m), 2978 (s), 2878 (m), 2604 (w), 1934 (w), 1746 (m), 1720 (m), 1592 (w), 1512 (m), 1472 (w), 1427 (w), 1392 (m), 1302 (m), 1244 (m), 1181 (w), 1070 (s), 1043 (s), 957 (w), 897 (w), 870 (w), 847 (m), 832 (m), 751 (m), 687 (w), 673 (w), 632 (w). **HRMS** (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{ClNaO}_4^+$ 369.0864; Found 369.0863.

2-Oxo-3-(*p*-tolylloxy)propyl 3-chlorobenzoate (9b**)**

Starting from **3a** (25.0 mg, 0.100 mmol), 2-oxo-3-(*p*-tolylloxy)propyl 3-chlorobenzoate **9b** (15.0 mg, 47.0 μmol , 47% yield) was obtained, as a colorless oil. **Rf**: 0.29 (Pentane:EtOAc 9:1). **^1H NMR** (400 MHz, Acetonitrile- d_3) δ 8.04 (t, $J = 1.9$ Hz, 1H, ArH), 7.99 (dt, $J = 7.8, 1.3$ Hz, 1H, ArH), 7.68 (ddd, $J = 8.1, 2.2, 1.1$ Hz, 1H, ArH), 7.52 (t, $J = 7.9$ Hz, 1H, ArH), 7.18 – 7.09 (m, 2H, ArH), 6.88 – 6.80 (m, 2H, ArH), 5.16 (s, 2H, CH₂), 4.82 (s, 2H, CH₂), 2.27 (s, 3H, ArCH₃).

^{13}C NMR (101 MHz, Acetonitrile- d_3) δ 201.3, 165.4, 156.7, 135.2, 134.4, 132.3, 131.9, 131.5, 130.9, 130.2, 128.9, 115.3, 72.0, 68.3, 20.4. **IR** ν 2975 (m), 2926 (m), 1732 (s), 1613 (m), 1576 (m), 1511 (s), 1457 (w), 1431 (m), 1411 (m), 1379 (m), 1290 (s), 1255 (s), 1244 (s), 1123 (m), 1109 (m), 1065 (m), 1053 (m), 985 (w), 898 (w), 818 (m), 752 (m), 719 (w), 676 (m), 629 (m). **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{ClNaO}_4^+$ 341.0551; Found 341.0554.

2-Oxo-1-(*p*-tolyl)oxypentan-3-yl acetate (**10**)

A solution of 3-ethyl-2-(*p*-tolyl)oxy-2-((*p*-tolyl)oxymethyl)oxirane **8a** (0.200 mmol, 1.0 equiv.) in acetic acid (1.0 mL) was stirred at room temperature for 30 minutes. The excess of acetic acid was removed by co-evaporation with toluene. The crude was purified by preparative TLC (pentane:ethyl acetate 9:1) to provide the 2-oxo-1-(*p*-tolyl)oxypentan-3-yl acetate **10** (36.0 mg, 0.144 mmol, 72% yield) as a colorless oil. **Rf**: 0.32 (Pentane:EtOAc 9:1). $^1\text{H NMR}$ (400 MHz, Methylene Chloride- d_2) δ 7.14 – 7.06 (m, 2H, ArH), 6.81 – 6.76 (m, 2H, ArH), 5.20 (dd, J = 8.0, 4.3 Hz, 1H, OCCHO), 4.79 – 4.65 (m, 2H, OCH₂CO), 2.28 (s, 3H, ArCH₃), 2.13 (s, 3H, OCCH₃), 2.00 – 1.87 (m, 1H, CH₂CH₃), 1.81 (ddt, J = 15.3, 14.5, 7.4 Hz, 1H, CH₂CH₃), 1.00 (t, J = 7.4 Hz, 3H, CH₃). $^{13}\text{C NMR}$ (101 MHz, Methylene Chloride- d_2) δ 203.7, 171.1, 156.2, 131.7, 130.6, 114.9, 78.0, 71.7, 24.3, 20.9, 20.7, 10.0. **IR** ν 3469 (w), 2974 (w), 2926 (w), 1736 (s), 1612 (w), 1588 (w), 1511 (s), 1459 (w), 1433 (w), 1374 (m), 1294 (m), 1227 (s), 1177 (w), 1096 (m), 1057 (m), 1019 (m), 970 (m), 902 (w), 816 (m), 717 (w), 678 (w). **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for C₁₄H₁₈NaO₄⁺ 273.1097; Found 273.1085.

The regioselectivity of the addition can be explained by acid activation of the epoxide (**I**) to form oxonium **II**, followed by addition of the carboxylic acid to give **III** and finally acyl migration (Scheme S8). This mechanism is well-established for structurally similar epoxides derived from alkyl vinyl ethers.²³

Scheme S8: Speculative mechanism for the epoxide opening with acid.

Oxidation with Oxone®:

To a solution of **4a** (20 mg, 0.050 mmol, 1.0 equiv.) in CH₃CN (0.50 mL) and H₂O (0.50 mL) was added Oxone® (92 mg, 0.15 mmol, 3.0 equiv.). The resulting mixture was stirred at room temperature for 5 h

²³ a) C. L. Stevens, W. Malik, R. Pratt, *J. Am. Chem. Soc.* **1950**, 72, 4758; b) C. L. Stevens, S. J. Dykstra, *J. Am. Chem. Soc.* **1953**, 75, 5975; Review: c) A. Kirrmann, P. Duhamel, R. Nouri-Bimorghi, *Justus Liebigs Ann. Chem.* **1966**, 691, 33.

and at 85 °C for 2 h. According to TLC, HRMS and NMR no reaction occurred and the starting **4a** was recovered.

Oxidation with Selectfluor™:

To a solution of **4a** (20 mg, 0.050 mmol, 1.0 equiv.) in CH₃CN (0.50 mL) was added Selectfluor™ (54 mg, 0.15 mmol, 3.0 equiv.). The resulting mixture was stirred at room temperature. After 1 h, full consumption of **4a** was observed. According to NMR, decomposition occurred and a complex product mixture was recovered.

11. Mechanistic investigations

Nature of 4a:

In a round-bottom flask were added *p*-cresol (10.8 mg, 0.100 mmol, 1.00 equiv.) and cesium carbonate (39.0 mg, 0.120 mmol, 1.20 equiv.). Anhydrous DME (3.00 mL, 0.1 M) was added and the solution was stirred at room temperature for 10 min. Allyl-ester **4a** (39.4 mg, 0.100 mmol, 1.00 equiv.) was added to the reaction mixture under open air and the reaction mixture was stirred at room temperature for 16 h.

Cross-over experiment:

O-VBX **1a** (0.020 g, 50.0 μmol , 0.5 equiv.), O-VBX **1t** (0.022 g, 0.050 mmol, 0.5 equiv.) and cesium carbonate (0.039 g, 0.12 mmol, 1.2 equiv.) were added to a 5 mL microwave vial. Anhydrous DME (1.0 mL) was introduced to the vial by syringe. Then anisole (2.17 μL , 20.0 μmol , 0.2 equiv.) was added and the reaction mixture was stirred at room temperature, for 16 h. The solution was then concentrated under reduced pressure. The crude material was purified by column chromatography (Pentane:Ethyl acetate 9:1) and 2-(*p*-tolxyloxy)allyl 2-iodobenzoate **4q** (0.013 g, 0.032 mmol, 32 % yield), 2-(4-methoxyphenoxy)allyl 2-iodobenzoate **4q'** (0.010 g, 0.024 mmol, 24 % yield), 2-(*p*-tolxyloxy)allyl 2-iodo-5-methoxybenzoate **4r'** (0.009 g, 0.021 mmol, 21 % yield) and 2-(4-methoxyphenoxy)allyl 2-iodo-5-methoxybenzoate **4r** (0.010 g, 0.023 mmol, 23 % yield) were obtained as a colorless oils.

2-(*p*-Tolyloxy)allyl 2-iodobenzoate (**4q**)

4q: ^1H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dd, $J = 8.0, 1.2$ Hz, 1H, ArH), 7.87 (dd, $J = 7.8, 1.7$ Hz, 1H, ArH), 7.41 (td, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.23 – 7.12 (m, 3H, ArH), 7.06 – 6.94 (m, 2H, ArH), 4.94 (s, 2H, CCH_2O), 4.55 (d, $J = 2.4$ Hz, 1H, CH_2CO), 4.23 (d, $J = 2.3$ Hz, 1H, CH_2CO), 2.33 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 157.5, 152.6, 141.6, 134.8, 134.2, 133.0, 131.4, 130.3, 128.1, 120.8, 94.5,

92.1, 65.0, 20.9.

2-(4-Methoxyphenoxy)allyl 2-iodobenzoate (4q')

4q': $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.02 (dd, $J = 7.9, 1.2$ Hz, 1H, ArH), 7.88 (dd, $J = 7.8, 1.7$ Hz, 1H, ArH), 7.42 (td, $J = 7.5, 1.2$ Hz, 1H, ArH), 7.17 (td, $J = 7.7, 1.7$ Hz, 1H, ArH), 7.06 – 6.97 (m, 2H, ArH), 6.92 – 6.84 (m, 2H, ArH), 4.94 (s, 2H, CCH₂O), 4.51 (d, $J = 2.3$ Hz, 1H, CH₂CO), 4.16 (d, $J = 2.4$ Hz, 1H, CH₂CO), 3.80 (s, 3H, OCH₃). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 166.1, 158.1, 156.6, 148.3, 141.6, 134.8, 133.0, 131.4, 128.1, 122.2, 114.9, 94.5, 91.2, 65.0, 55.7.

2-(4-Methoxyphenoxy)allyl 2-iodo-5-methoxybenzoate (4r)

4r: $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.85 (d, $J = 8.7$ Hz, 1H, ArH), 7.42 (d, $J = 3.1$ Hz, 1H, ArH), 7.08 – 6.98 (m, 2H, ArH), 6.92 – 6.83 (m, 2H, ArH), 6.77 (dd, $J = 8.8, 3.1$ Hz, 1H, ArH), 4.93 (s, 2H, CCH₂O), 4.51 (d, $J = 2.4$ Hz, 1H, CH₂CO), 4.16 (d, $J = 2.4$ Hz, 1H, CH₂CO), 3.81 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 165.9, 159.7, 158.0, 156.6, 148.3, 142.1, 135.6, 122.2, 119.6, 116.9, 114.9, 91.3, 82.8, 65.0, 55.7, 55.7.

2-(*p*-Tolyloxy)allyl 2-iodo-5-methoxybenzoate (4r')

4r': $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.85 (d, $J = 8.7$ Hz, 1H, ArH), 7.42 (d, $J = 3.1$ Hz, 1H, ArH), 7.20 – 7.11 (m, 2H, ArH), 7.05 – 6.94 (m, 2H, ArH), 6.77 (dd, $J = 8.7, 3.1$ Hz, 1H, ArH), 4.93 (s, 2H, CCH₂O), 4.56 (d, $J = 2.3$ Hz, 1H, CH₂CO), 4.23 (d, $J = 2.3$ Hz, 1H, CH₂CO), 3.80 (s, 3H, OCH₃), 2.33 (s, 3H, CH₃). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 165.9, 159.6, 157.4, 152.7, 142.1, 135.6, 134.2, 130.3, 120.8, 119.6, 116.9, 92.2, 82.8, 65.0, 55.7, 20.9.

Tentative to trap intermediate:

p-Cresol (10.8 mg, 0.100 mmol, 1.0 equiv.) and cesium carbonate (39.0 mg, 0.120 mmol, 1.2 equiv.) were added to a round-bottom flask. Anhydrous DME (0.1 M) was introduced at 0 °C and the solution was stirred at room temperature for 10 min. O-VBX reagent (39.0 mg, 0.100 mmol, 1.0 equiv.) and TEMPO or *p*-methoxystyrene (0.100 mmol, 1.0 equiv.) was added to the reaction mixture under open air and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane: ethyl acetate 9:1). The 4,4'-(prop-2-ene-1,2-

diylbis(oxy))bis(methylbenzene) **3a** (20.0 mg, 80.0 μmol , 80% yield) and the 2-(*p*-tolylxy)allyl 2-iodobenzoate **4a** (7.80 mg, 20.0 μmol , 20% yield) were obtained as a colorless amorphous solids.

To a solution of O-VBX **1a** (39.0 mg, 0.100 mmol, 1.00 equiv.) in DME and furan (0.1 M) were added cesium carbonate (39.0 mg, 0.120 mmol, 1.20 equiv.) and anisole (20.0 μL , 20.0 μmol , 0.20 equiv.) and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane:ethyl acetate 9:1). The 2-(*p*-tolylxy)allyl 2-iodobenzoate **4a** (19.6 mg, 50.0 μmol , 50% yield) was obtained as a colorless amorphous solid and the 3-(*p*-tolylxy)-8-oxabicyclo[3.2.1]octa-2,6-diene **12** was observed by mass analysis. **HRMS** (APPI/QTOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2^+$ 215.1067; Found 215.1063.

In a round-bottom flask, *p*-cresol (0.108 g, 1.00 mmol, 1.00 equiv.) was dissolved in 10 mL of DME (0.1 M). Cesium carbonate (33.0 mg, 0.100 mmol, 0.10 equiv.) was added and the mixture stirred vigorously for 5 min. Then EBX **5q** was added in one portion (0.326 g, 1.00 mmol, 1.00 equiv.) and the reaction was left stirring for 16 hours at room temperature. Then cesium carbonate (0.391 g, 1.20 mmol, 1.20 equiv.) and anisole (22 μL , 0.20 mmol, 0.20 equiv.) were added and the solution was stirred at room temperature for 16 hours. The reaction mixture was filtrated, solvent was removed under reduced pressure and the crude material was purified by column chromatography (pentane:ethyl acetate 9:1). The (*E*)-5-(*p*-tolylxy)hexa-3,5-dien-1-yl 2-iodobenzoate (**13**) (0.232 g, 0.534 mmol, 53% yield), the (*E*)-3-cyclopropyl-2-(*p*-tolylxy)allyl 2-iodobenzoate (**4s**) (78.0 mg, 0.178 mmol, 18% yield) and the 3-

Cyclopropyl-2-oxopropyl 2-iodobenzoate (**14**) (36.0 mg, 36.0 μ mol, 4% yield) were obtained as sticky solids.

(E)-5-(p-tolyloxy)hexa-3,5-dien-1-yl 2-iodobenzoate (13)

Rf: 0.29 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 8.03 – 7.98 (m, 1H, ArH), 7.70 (dd, *J* = 7.7, 1.7 Hz, 1H, ArH), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.23 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 7.16 – 7.11 (m, 2H, ArH), 6.93 – 6.88 (m, 2H, ArH), 6.19 (q, *J* = 1.9 Hz, 2H, OCCHCH), 4.47 (d, *J* = 1.6 Hz, 1H, OCCH₂), 4.38 (t, *J* = 6.4 Hz, 2H, CHCH₂CH₂O), 4.14 (d, *J* = 1.6 Hz, 1H, OCCH₂), 2.60 (tdd, *J* = 6.3, 3.9, 1.7 Hz, 2H, CHCH₂CH₂O),

2.29 (s, 3H, CH₃). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 167.6, 159.2, 154.7, 141.9, 137.2, 134.2, 133.6, 131.3, 131.1, 129.2, 128.8, 128.5, 120.4, 95.1, 93.8, 65.4, 32.2, 20.7. **IR** ν 2987 (m), 2888 (w), 1729 (s), 1679 (w), 1611 (w), 1584 (m), 1563 (w), 1507 (m), 1473 (w), 1427 (m), 1392 (m), 1288 (m), 1263 (s), 1219 (m), 1169 (w), 1135 (m), 1103 (w), 1044 (m), 1016 (m), 740 (s), 704 (m). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₀H₁₉INaO₃⁺ 457.0271; Found 457.0268.

(E)-3-cyclopropyl-2-(p-tolyloxy)allyl 2-iodobenzoate (4s)

Rf: 0.50 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 8.02 (dd, *J* = 7.9, 1.2 Hz, 1H, ArH), 7.74 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 7.19 (d, *J* = 8.2 Hz, 2H, ArH), 7.00 – 6.94 (m, 2H, ArH), 4.96 (d, *J* = 9.1 Hz, 1H, OCCHCH), 4.62 (d, *J* = 2.3 Hz, 1H, OCH₂CO), 4.11 (d, *J* = 2.3 Hz, 1H, OCH₂CO), 2.31 (s, 3H, ArCH₃), 1.50 (dtt, *J* = 9.5, 8.1, 4.9 Hz, 1H,

CH), 0.76 – 0.64 (m, 2H, CH₂), 0.56 (tddd, *J* = 13.1, 8.7, 6.8, 3.5 Hz, 2H, CH₂). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 167.0, 161.4, 153.8, 142.0, 137.1, 135.1, 133.7, 131.3, 131.2, 129.3, 121.3, 93.8, 91.5, 80.0, 20.7, 14.3, 4.7, 3.6. **IR** ν 3655 (w), 3546 (w), 3087 (m), 3006 (m), 2870 (w), 2602 (w), 1929 (w), 1884 (w), 1728 (s), 1646 (m), 1609 (m), 1584 (m), 1506 (s), 1464 (m), 1430 (m), 1281 (s), 1247 (s), 1223 (s), 1167 (w), 1129 (m), 1098 (s), 1041 (s), 1016 (s), 959 (s), 907 (m), 833 (s), 742 (s), 687 (m), 638 (w). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₀H₁₉INaO₃⁺ 457.0271; Found 457.0274.

3-Cyclopropyl-2-oxopropyl 2-iodobenzoate (14)

Rf: 0.56 (Pentane:EtOAc 9:1). **¹H NMR** (400 MHz, Acetonitrile-*d*₃) δ 8.06 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.52 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.27 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 4.99 (s, 2H, OCH₂C), 2.40 (d, *J* = 7.0 Hz, 2H, CCH₂C), 1.09 – 0.93 (m, 1H, CH), 0.62 – 0.47 (m, 2H, CH₂), 0.21 – 0.13 (m, 2H, CH₂). **¹³C NMR** (101 MHz, Acetonitrile-*d*₃) δ 204.3, 166.6, 142.3,

135.6, 134.2, 132.0, 129.3, 94.3, 69.6, 44.6, 6.4, 4.8. **IR** ν 2990 (m), 2941 (w), 2886 (w), 1729 (s), 1672 (w), 1611 (w), 1584 (m), 1564 (m), 1508 (s), 1473 (w), 1415 (m), 1369 (m), 1289 (m), 1253 (s), 1211 (w), 1134 (m), 1107 (m), 1072 (m), 1045 (m), 1018 (m), 952 (w), 826 (w), 740 (s), 704 (m), 639 (w). **HRMS** (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₃INaO₃⁺ 366.9802; Found 366.9810.

12. Spectra of new compounds

12.1. EBX

2-(6-(3-Oxo-1,2-benziodoxol-3(1H)-yl)hex-5-yn-1-yl)isoindoline-1,3-dione (5f)

^1H NMR (400 MHz, Chloroform- d)

^{13}C NMR (101 MHz, Chloroform- d)

5-Methyl-propynyl-1,2-benziodoxol-3(1*H*)-one (5o)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

5-Methoxy-propynyl-1,2-benziodoxol-3(1H)-one (5p)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

1-(3-cyclopropylprop-1-yn-1-yl)-1,2-benziodoxol-3(1H)-one (5q)

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Methylene Chloride-*d*₂)

12.2. O-VBX

(Z)-1-(7-hydroxy-2-(*p*-tolylloxy)hept-1-en-1-yl)-1,3-benziodoxol-3-(1*H*)-one (1c)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(7-hydroxy-2-(*p*-tolylloxy)hept-1-en-1-yl)-1,3-benziodoxol-3-(1*H*)-one (1d)

¹H NMR (400 MHz, Methanol-*d*₄)

¹³C NMR (101 MHz, Methanol-*d*₄)

(Z)-1-(2-(p-tolyloxy)-8-(trimethylsilyl)oct-1-en-7-yn-1-yl)-1,3-benziodoxol-3-(1H)-one (1e)

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Methylene Chloride-*d*₂)

(Z)-2-(6-(3-Oxo-1,2-benziodoxol-3-(1H)-yl)-5-(p-tolxyloxy)hex-5-en-1-yl)isoindoline-1,3-dione (1f)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

¹H NMR (400 MHz, Chloroform-*d*)

(Z)-1-(2-(2-Iodophenoxy)oct-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1i)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-(4-Methoxyphenoxy)pent-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1j)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1k)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-cyclopropyl-2-(*p*-tolxyloxy)vinyl)-1*H*-benzodioxol-3-one (1m)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-cyclohexyl-2-(p-tolxy)vinyl)-1,2-benziodoxol-3-(1H)-one (1n)

¹H NMR (400 MHz, Chloroform-d)

¹³C NMR (101 MHz, Chloroform-d)

(Z)-1-(3,3-dimethyl-2-(p-tolyloxy)but-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1p)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-phenyl-2-(*p*-tolylloxy)vinyl)-1,2-benziodoxol-3-(1*H*)-one (1q)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-1-(2-(2,6-dichlorophenoxy)oct-1-en-1-yl)-1,3-benziodoxol-3(1H)-one (1r)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(Z)-5-Methyl-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1s)

^1H NMR (400 MHz, Methylene chloride- d_2)

^{13}C NMR (101 MHz, Methylene chloride- d_2)

(Z)-5-Methoxy-1-(2-(4-methoxyphenoxy)prop-1-en-1-yl)-1,2-benziodoxol-3-(1H)-one (1t)

¹H NMR (400 MHz, Methylene chloride-*d*₂)

¹³C NMR (101 MHz, Methylene chloride-*d*₂)

12.3. Allylic alcohols

4,4'-(prop-2-ene-1,2-diylbis(oxy))bis(methylbenzene) (3a)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

1-bromo-4-((2-(*p*-tolxyloxy)allyl)oxy)benzene (3b)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

1-iodo-4-((2-(p-tolyloxy)allyl)oxy)benzene (3c)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

1-Methoxy-4-((2-(*p*-tolxyloxy)allyl)oxy)benzene (3d)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

4,4,5,5-tetramethyl-2-(4-((2-(*p*-tolxyloxy)allyl)oxy)phenyl)-1,3,2-dioxaborolane (3e)

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Chloroform-*d*)

1-Methoxy-3-((2-(*p*-tolxyloxy)allyl)oxy)benzene (3f)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

3-((2-(*p*-tolxy)allyl)oxy)aniline (3g)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

Methyl 2-((2-(*p*-tolxyloxy)allyl)oxy)benzoate (3h)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

1-(3,5-di-*tert*-butyl-4-((2-(*p*-tolxyloxy)allyl)oxy)phenyl)ethan-1-one (3i)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

2-((2-(*p*-tolxy)allyl)oxy)naphthalene (3j)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

Ethyl (S)-2-acetamido-3-(4-((2-(*p*-tolyl)oxy)allyl)oxy)phenyl)propanoate (3k)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-N-(4-((3-(((8R,9S,13S,14S,17S)-17-Hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)prop-1-en-2-yl)oxy)-3-methoxybenzyl)-8-methylnon-6-enamide (3I)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

2-methyl-2-(2-(p-tolyloxy)allyl)cyclopentane-1,3-dione (3m)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

Ethyl 2-acetyl-2-methyl-4-(p-tolyloxy)pent-4-enoate (3n)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

***N*-(4-methoxyphenyl)-4-nitro-*N*-(2-(*p*-tolylloxy)allyl)benzenesulfonamide (3o)**

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Methylene Chloride-*d*₂)

4,4'-(pent-1-ene-2,3-diylbis(oxy))bis(methylbenzene) (3p)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

(*E*)-4,4'-(Oct-2-ene-1,2-diylbis(oxy))bis(methylbenzene) (3q)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-6,7-bis(p-tolyloxy)hept-5-en-1-ol (3r)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-(7,8-bis(p-tolyloxy)oct-6-en-1-yn-1-yl)trimethylsilane (3s)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-1-iodo-2-((1-(p-tolyloxy)pent-2-en-2-yl)oxy)benzene (3v)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-1-iodo-2-((1-(p-tolyloxy)oct-2-en-2-yl)oxy)benzene (3w)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-1-Methoxy-4-((1-(p-tolyloxy)pent-2-en-2-yl)oxy)benzene (3x)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

1-Methoxy-4-((3-(p-tolyloxy)prop-1-en-2-yl)oxy)benzene (3y)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

12.4. Allylic esters

2-(*p*-tolxyloxy)allyl 2-iodobenzoate (4a)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

2-(*p*-tolylxy)pent-1-en-3-yl 2-iodobenzoate (4b)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(E)-2-(p-Tolyloxy)oct-2-en-1-yl 2-iodobenzoate (4c)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(E)-2-(p-tolyloxy)hexadec-2-en-1-yl 2-iodobenzoate (4d)

¹H NMR (400 MHz, Methylene Chloride-d₂)

¹³C NMR (101 MHz, Methylene Chloride-d₂)

(E)-6-(1,3-Dioxoisindolin-2-yl)-2-(p-tolyloxy)hex-2-en-1-yl 2-iodobenzoate (4f)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

(E)-2-(*p*-toloxy)octa-2,7-dien-1-yl 2-iodobenzoate (4g)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(E)-5-chloro-2-(*p*-tolxyloxy)pent-2-en-1-yl 2-iodobenzoate (4h)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

2-(2-Iodophenoxy)allyl 2-iodobenzoate (4i)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

(E)-2-(2-iodophenoxy)pent-2-en-1-yl 2-iodobenzoate (4j)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-2-(2-iodophenoxy)oct-2-en-1-yl 2-iodobenzoate (4k)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-2-(3-bromophenoxy)-5-chloropent-2-en-1-yl 2-iodobenzoate (4l)

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

2-(perfluorophenoxy)pent-1-en-3-yl 2-iodobenzoate (4m)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

^{19}F NMR (376 MHz, Chloroform-*d*)

(E)-2-(4-Methoxyphenoxy)pent-2-en-1-yl 2-iodobenzoateiodobenzoate (4n)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

2-(4-Methoxyphenoxy)allyl 2-iodobenzoate (4o)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

(E)-2-(2-formylphenoxy)oct-2-en-1-yl 2-iodobenzoate (4p)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

12.5. Product modifications

2-((*p*-Tolyloxy)methyl)benzofuran (6)

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Methylene Chloride-*d*₂)

2-oxopentyl benzoate (7)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

3-ethyl-2-((p-tolyloxy)-2-((p-tolyloxy)methyl)oxirane (8a)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

3-ethyl-2-(4-methoxyphenoxy)-2-((p-tolyloxy)methyl)oxirane (8b)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

2-oxo-1-(p-tolyloxy)pentan-3-yl 3-chlorobenzoate (9a)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

2-oxo-3-(p-tolyloxy)propyl 3-chlorobenzoate (9b)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

2-oxo-1-(*p*-tolylloxy)pentan-3-yl acetate (10)

¹H NMR (400 MHz, Methylene Chloride-*d*₂)

¹³C NMR (101 MHz, Methylene Chloride-*d*₂)

12.6. Mechanistic investigations

2-(*p*-Tolyloxy)allyl 2-iodobenzoate (4q)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

2-(4-Methoxyphenoxy)allyl 2-iodobenzoate (4q')

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

2-(4-Methoxyphenoxy)allyl 2-iodo-5-methoxybenzoate (4r)

^1H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (101 MHz, Chloroform-*d*)

2-(*p*-Tolyloxy)allyl 2-iodo-5-methoxybenzoate (4r')

¹H NMR (400 MHz, Chloroform-*d*)

¹³C NMR (101 MHz, Chloroform-*d*)

(E)-5-(p-tolyloxy)hexa-3,5-dien-1-yl 2-iodobenzoate (13)

¹H NMR (400 MHz, Acetonitrile-*d*₃)

¹³C NMR (101 MHz, Acetonitrile-*d*₃)

(E)-3-cyclopropyl-2-(p-tolyloxy)allyl 2-iodobenzoate (4s)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)

3-cyclopropyl-2-oxopropyl 2-iodobenzoate (14)

^1H NMR (400 MHz, Acetonitrile- d_3)

^{13}C NMR (101 MHz, Acetonitrile- d_3)