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A cascade process for the synthesis of *ortho*-formyl allyl aryl ethers and 2*H*-chromen-2-ol derivatives from arynes *via* trapping of *o*-quinone methide with an activated alkene†

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A transition-metal free synthetic strategy has been developed for the direct synthesis of *ortho*-formyl substituted allyl aryl ethers *via* a cascade three-component coupling of arynes, activated alkene and *N*,*N*-dimethylformamide. The reaction proceeds *via* C–O and C–C bond cleavage as well as C–C and two new C–O bond formations in a single reaction vessel. The methodology provides a good yield of *ortho*-formyl substituted allyl aryl ethers. Moreover, the synthetic strategy has been utilized for the one-pot synthesis of 2*H*-chromen-2-ol derivatives.

Arynes are highly reactive transient intermediates and have emerged as potent synthons for exploring the new frontiers in organic synthesis.[1] This reactive intermediate, particularly Kobayashi's protocol for using *o*-silyl aryl triflate[2] as a versatile precursor, is widely used for the development of new-aryne based reactions for the atom-economical synthesis of various synthetic compounds and natural products.[3] Additionally, arynes have been used for the synthesis of *ortho*-disubstituted arenes *via* multicomponent reactions[1c] and dipolar cycloaddition.[1f] Recently, aryne-based sequential reactions have been utilized for the installation of important functional groups through the formation of carbon–carbon and carbon–heteroatom bonds into adjacent positions of the aromatic skeleton for the synthesis of 1,2-difunctionalized arenes in a straightforward manner. This synthetic strategy for the one-pot synthesis of *ortho*-disubstituted arenes has been studied extensively with or without a transition-metal catalyst.[4] However, most effort has been focused on the transition-metal-free reactions which avoid expensive metal-catalysts, ligands and harsh reaction conditions.

Synthetic strategies for the direct *ortho*-functionalization of arenes with two versatile functional groups *via* aryne insertion into a σ-bond and π-bond have gained priority over others. Regarding the aryne insertion into a C=C bond, Suzuki and co-workers have developed a highly stereoselective tandem [2 + 2] cycloaddition for the synthesis of benzocyclobutenes as relatively stable products, which could be used for the rapid construction of nitrogen heterocycles.[5] On the other hand, aryne insertion into the sigma bond[6] takes place when the nucleophile and the electrophile belong to the same molecule. In this regard, the Yoshida group pioneered a reaction of aryne and β-dicarbonyl compounds which involves aryne insertion into the methylene-carbonyl σ-bond to produce the corresponding *ortho*-disubstituted product.[3a] This synthetic strategy provides a powerful and useful tool for the rapid build-up of complex molecules in a highly atom-economical manner. Varieties of amine-containing *ortho*-disubstituted arenes[7] have been synthesized *via* aryne insertion into an amide, arylphosphoryl amide, and nitrogen-halide bonds or the nucleophilic attack of amines on arynes. In addition to these, the insertion of arynes into P–O bonds for the synthesis of *ortho*-hydroxy substituted arylphosphine oxides,[8] aryne insertion into the I–I bond for the synthesis of *o*-diiodoarenes,[9] and aryne double bond insertion/nucleophilic addition with vinylogous amides and carbodiimides[10] have been reported.

Regarding the synthesis of *ortho*-disubstituted arenes *via* a transition-metal-free three-component coupling reaction, solvents such as THF,[11] DMSO[12] and DMF[13] play a dual role as the reaction media and reactant. In this regard, the solvent THF has been used for the synthesis of functionalized bromoarenes. Whereas DMSO has been used for the synthesis of aryl-thioethers *via* aryne insertion into the S=O bond of DMSO.[12a] The aryne insertion into the π-bond of DMF proceeds *via* an interesting reactive intermediate *o*-quinone methide which subsequently reacts with suitable electrophiles for the synthesis of *ortho*-functionalized arenes (Fig. 1). Several synthetic strategies have been developed for the synthesis of

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†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR and HRMS spectra of all products. See DOI: 10.1039/c8ob02507j

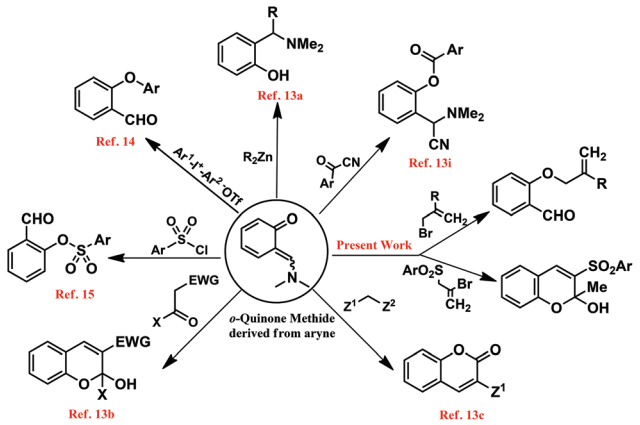
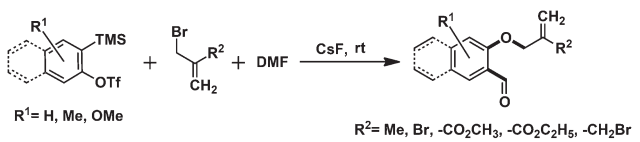


Fig. 1 Previous and present studies for the synthesis of *ortho*-disubstituted arenes *via* *o*-quinone methide derived from an aryne and DMF.

functionalized arenes *via* aryne insertion into the π-bond of DMF. Miyabe and co-workers developed a general method for the synthesis of *ortho*-disubstituted arene *via* aryne insertion into the C–heteroatom bond of DMF *via* the three-component coupling reaction of aryne, formamide and alkylzinc in a single reaction vessel.[13a] Later, they have also developed a multicomponent reaction *via* aryne insertion into DMF followed by trapping with activated methylenes.[13b] Furthermore, Yoshida and co-workers have reported the synthesis of diverse coumarins *via* the coupling of *ortho*-quinone methides generated from arynes and DMF with active methylene compounds.[13c] Recently, Jiang *et al.* have reported the synthesis of *ortho*-formyl diaryl ether by the three-component coupling of aryne, DMF and diaryliodonium salts.[14]

From our group, we have also reported the one-pot synthesis of 2-formylarylsulfonate from aryne, aryl sulfonyl chloride and DMF *via* *o*-quinone methide.[15] This interesting chemistry encouraged us to further investigate the synthetic utility of *o*-quinone methide for the synthesis of 1,2-disubstituted arenes. In continuation of our research on aryne chemistry,[16] we came up with an idea to use this highly reactive intermediate for the direct synthesis of *ortho*-formyl substituted allyl aryl ethers and 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol from arynes. To the best of our knowledge, there is no such synthetic method/strategy for the direct synthesis of *ortho*-formyl substituted allyl aryl ethers and 2*H*-chromen-2-ol derivatives from arynes. Here, we used an activated alkene to trap *o*-quinone methide derived from an aryne and DMF under mild conditions for the synthesis of *ortho*-formyl substituted allyl aryl ethers (Scheme 1). This synthetic method avoids the use of transition-metal and strong bases or Lewis acids for the introduction of an aldehyde functionality into an aromatic ring by conventional methods.[17]

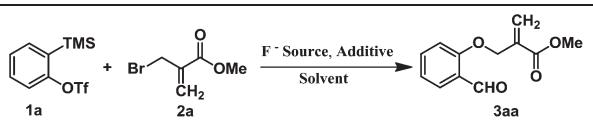


Scheme 1 Synthesis of *o*-formyl allyl aryl ether from arynes.

Our experiments were started with optimization studies by considering a common aryne precursor 2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1a** (0.5 mmol), activated alkene methyl-2-(bromomethyl)acrylate **2a** (0.75 mmol) and a well-established fluoride source CsF (1.5 mmol) in DMF (2 mL) at room temperature for 0.5 h. Under these reaction conditions, the desired product **3aa** was obtained in 68% yield (Table 1, entry 1). To improve the yield of **3aa**, some other fluoride sources were also screened (Table 1, entries 2 and 3). However, no significant enhancement of yield was observed. Additionally, KF along with 18-crown-6 (1 equiv.) were used as additives for the synthesis of **3aa**. Under these reaction conditions, the desired product **3aa** was isolated in 60% yield (Table 1, entry 4). From these optimization studies, CsF was found to be a suitable fluoride source for our cascade reaction. After optimizing our fluoride source, few more experiments were performed by changing the amount of CsF and the reaction time (Table 1, entries 5–7). To our delight, an improvement of yield (75%) was observed when the reaction was performed using 4 equivalents of CsF for 1 h (Table 1, entry 7), which were considered as the optimized reaction conditions for our generalization. In addition to these optimization studies, we also investigated the solvent effect by using a mixed solvent (1 : 1; DMF with CH_3CN and DMF with THF) for our cascade process (Table 1, entries 8 and 9). However, no significant improvements were observed. As a control experiment, when the reaction was performed in the absence of a fluoride source, product **3aa** was not observed (Table 1, entry 10).

After having the optimized reaction conditions in hand, the scope of our cascade process was further investigated and the

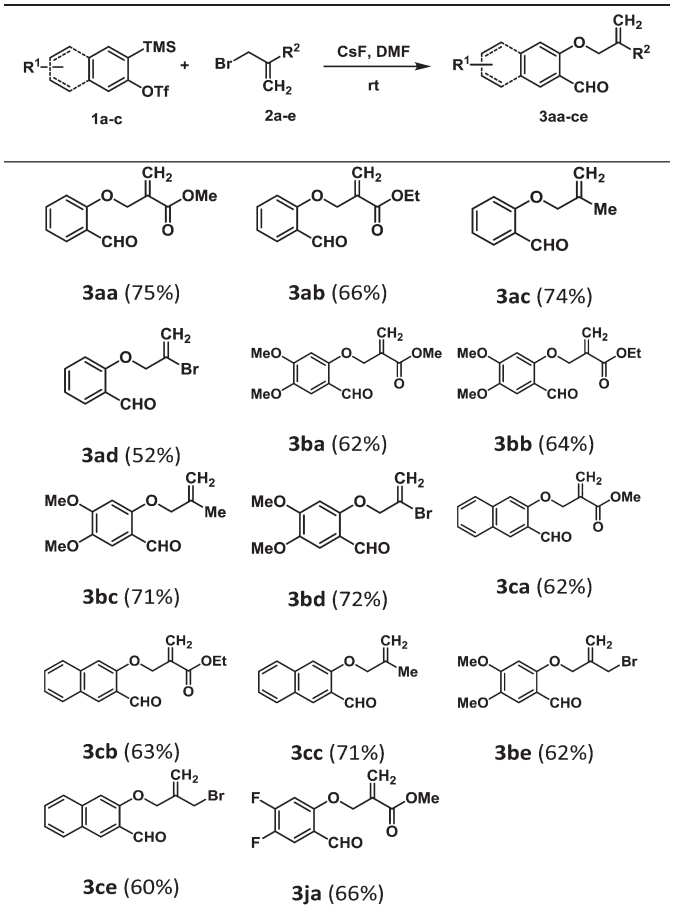
Table 1 Optimization studies[a]



Entry	F^- Source (equiv.)	Additive (1 equiv.)	Solvent	Time (h)	Temp. (°C)	Yield[b] (%)
1	CsF (3.0)	—	DMF	0.5	rt	68
2	KF (3.0)	—	DMF	0.5	rt	54
3	TBAF (3.0)	—	DMF	0.5	rt	Trace
4	KF (3.0)	18-Crown-6	DMF	0.5	rt	60
5	CsF (3.0)	—	DMF	1.0	rt	64
6	CsF (4.0)	—	DMF	0.5	rt	70
7	**CsF (4.0)**	**—**	**DMF**	**1**	**rt**	**75**
8	CsF (4.0)	—	DMF/CH_3CN (1 : 1)	1	rt	55
9	CsF (4.0)	—	DMF/THF (1 : 1)	1	rt	69
10	—	—	DMF	1	rt	ND

[a] Conditions: *o*-Silyl aryl triflate **1a** (0.5 mmol), methyl-2-(bromomethyl)acrylate **2a** (0.75 mmol), fluoride source (1.5 to 2 mmol), additive (0.5 mmol), DMF (2 mL) stirred at rt. [b] Isolated yield. ND: not detected.

Table 2 One-pot synthesis of *ortho*-formyl allyl aryl ether from benzyne precursors[a]



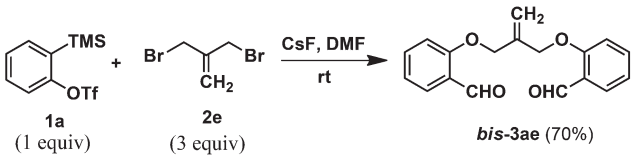
[a] Conditions: *o*-Silyl aryl triflate **1** (0.5 mmol), activated alkene **2** (0.75 mmol), fluoride source (2 mmol), DMF (2 mL) stirred at rt for 1 h.

results are presented in Table 2. As shown in Table 2, *o*-silyl aryl triflate **1a** was treated with a variety of activated alkenes, leading to our desired *ortho*-formyl allyl aryl ethers in good yields (Table 2, **3aa**–**3ad**).

Other symmetrical silyltriflates such as 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** and 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1c** were also examined as aryne precursors for our cascade process and a series of 2-formyl substituted allyl aryl ethers were synthesized in 62–72% yield (Table 2, **3ba**–**3cc**). Additionally, an aryne precursor bearing an electron-withdrawing group such as 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1j** is also used in our cascade process to form the corresponding 2-formyl substituted allyl aryl ether in 66% yield. Under our optimized reaction conditions, two interesting 2-formyl allyl aryl ethers **3ad** and **3bd** having an alkenyl bromide functionality were synthesized, which offer possibilities for further functionalization as well as the modification of the functional groups. Moreover, 3-bromo-2-bromomethyl-1-propene **2e** was also used as an activated alkene for the synthesis of *ortho*-formyl allyl aryl ethers and products **3be** and **3ce** were synthesized with good yields. Interestingly, when the activated alkene **2e** was treated with *o*-silyl aryl triflate **1a** under the optimized conditions, 2,2′-[(2-methylenepropane-1,3-diyl)bis(oxy)] dibenzaldehyde bis-**3ae** was obtained with 42% yield. However, the yield of bis-**3ae** could be increased up to 70% by increasing the amount of alkene **2e** (Scheme 2).

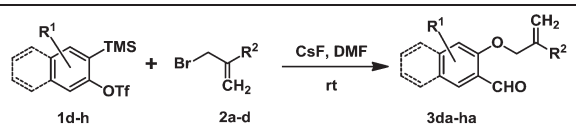
Additionally, unsymmetrical benzyne precursors *i.e.* 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1d**, 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **1e**, 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1f** and 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1g** were also investigated under our optimized reaction conditions (Table 3). Benzyne precursors **1d** and **1e** provided *ortho*-formyl allyl aryl ethers **3da**/**3d′a** and **3ec**/**3e′c** as mixtures of regioisomers. The regioisomers were not separated into individual isomers and their ratios were calculated from ^{1}H NMR. Furthermore, the unsymmetrical aryne derived from **1f** reacted with activated alkenes **2a** and **2b** to give exclusively **3fa** and **3fb** in 65% and 67% yield, respectively, with excellent regioselectivity. However, the unsymmetrical benzyne precursor **1g** when treated with methyl 2-(bromomethyl)acrylate **2a** furnished two seperate regioisomers **3ga** and **3g′a** which were isolable under flash chromatography and isolated into individual isomers with 29% and 37% yields, respectively (Table 3). Interestingly, when the unsymmetrical benzyne precursor 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1h** was used, a single regioisomer **3ha** was formed in 71% yield with excellent regioselectivity which could be rationalized by the electronic effect of the –OMe group, favoring the sterically hindered benzoxetene intermediate *via* aryne insertion into the C=O of DMF.

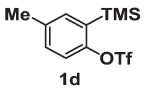
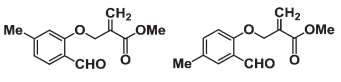
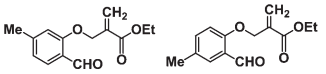
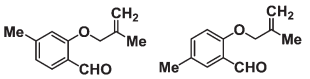
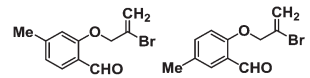
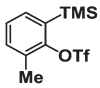
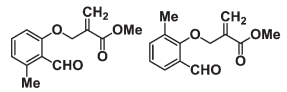
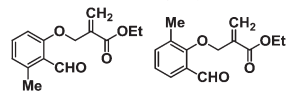
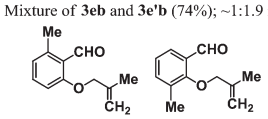
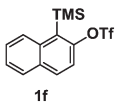
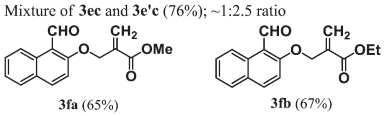
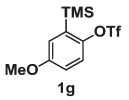
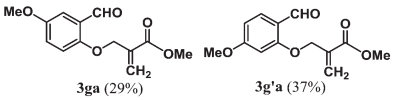
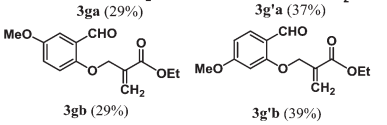
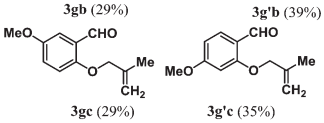
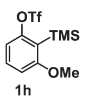
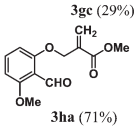
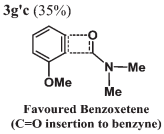
To explore the scope and synthetic utility of our cascade process, 2-bromoallylsulfone was considered as the activated alkene for our cascade process. In this regard, (2-bromoallylsulfonyl)benzene **2f** derived from 2,3-dibromopropene and sodium benzenesulfinate was treated with *o*-silyl aryl triflate **1a** under our optimized reaction conditions. An interesting cyclized product 2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol was isolated and characterized in 67% yield. As shown in Table 4, other symmetrical as well as unsymmetrical silyltriflates **1b**, **1c**, and **1h** and 5-(trimethylsilyl)benzo[*d*][1,3]-dioxol-6-yltrifluoromethane-sulfonate **1i** were also examined as aryne precursors to extend the scope of our synthetic utility, and a series of 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol were synthesized in 54–67% yields.



Scheme 2 Synthesis of bis(oxy)dibenzaldehyde from an aryne and 3-bromo-2-bromomethyl-1-propene.

Table 3 Synthesis of *ortho*-formyl allyl aryl ether from unsymmetrical benzyne precursors[a]

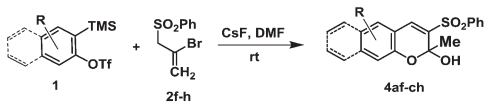


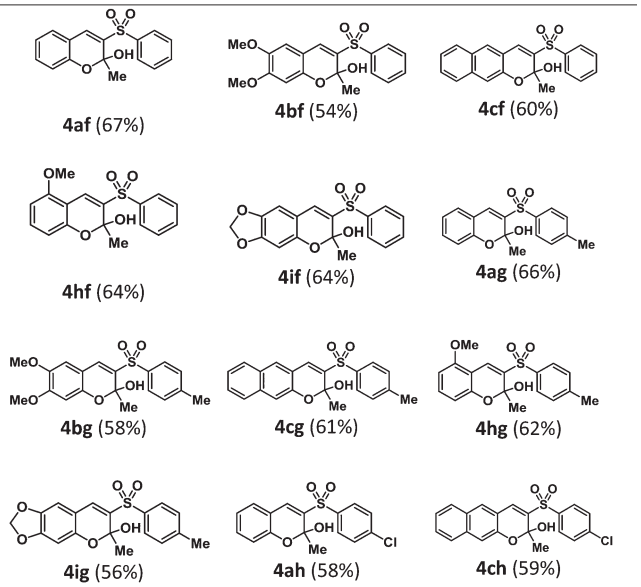
Entry	Aryne precursor (**1d–h**)	*o*-Formyl allyl aryl ether (**3da–3ha**)
1	 **1d**	 Mixture of **3da** and **3d'a** (73%); ~1:1.4 ratio  Mixture of **3db** and **3d'b** (76%); ~1:1.4 ratio  Mixture of **3dc** and **3d'c** (78%); ~1:1.4 ratio  Mixture of **3dd** and **3d'd** (63%); ~1:3.3 ratio
2	 **1e**	 Mixture of **3ea** and **3e'a** (68%); ~1:1.6 ratio  Mixture of **3eb** and **3e'b** (74%); ~1:1.9 ratio  Mixture of **3ec** and **3e'c** (76%); ~1:2.5 ratio
3	 **1f**	 **3fa** (65%) **3fb** (67%)
4	 **1g**	 **3ga** (29%) **3g'a** (37%)  **3gb** (29%) **3g'b** (39%)  **3gc** (29%) **3g'c** (35%)
5	 **1h**	 **3ha** (71%)  Favoured Benzoxetene (C=O insertion to benzyne)

[a] Conditions: *o*-Silyl aryl triflate **1** (0.5 mmol), activated alkene **2** (0.75 mmol), fluoride source (2 mmol), DMF (2 mL) stirred at rt for t1 h.

Based on previous reports,[13,14,16] a plausible reaction mechanism for the one-pot synthesis of *ortho*-formyl allyl aryl ether is proposed in Scheme 3. As shown in Scheme 3, the

Table 4 Synthesis of 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol[a]

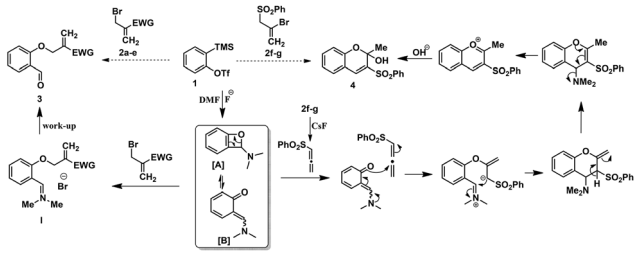




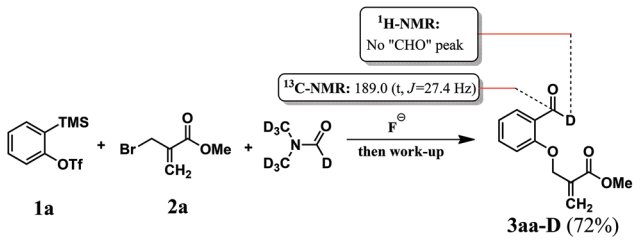
[a] Conditions: *o*-Silyl aryl triflate **1** (0.5 mmol), bromoallyl sulfones **2f–h** (0.75 mmol), fluoride source (2 mmol), DMF (2 mL) stirred at rt for 3 h.

in-generated aryne undergoes insertion into the C=O π-bond of formamide to form benzoxetene **A** and its isomer *ortho*-quinone methide **B**. The reactive intermediate **B** was trapped by the activated alkene to afford intermediate **I**. Finally, the reactive intermediate **I** leads to *ortho*-substituted arylaldehyde **3** after the aqueous work-up. Regarding the formation of 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol from aryne and 2-bromoallylsulfone, it is presumed that in the presence of CsF, 2-bromoallylsulfone forms sulfonyl allene,[18] which undergoes a conjugate addition with *o*-quinone methide followed by an intramolecular nucleophilic addition to form the cyclized product **4**.

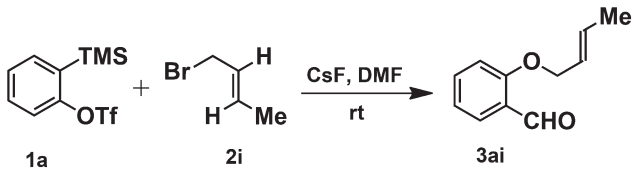
In order to explore the reaction mechanism, a deuterium-labelling study was performed using DMF-d_7 (Scheme 4). Under the optimized reaction conditions, the corresponding



Scheme 3 Plausible reaction mechanism for the synthesis of *ortho*-formyl allyl aryl ether and 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol.



Scheme 4 Isotopic tracer experiment.



Scheme 5 Independent experiment.

isotope labelled product **3aa-D** was isolated in 72% yield. Complete deuterium incorporation at the hydrogen of the aldehyde moiety was observed by ^{1}H-NMR analysis, which reveals that DMF serves as a source of the aldehyde functionality. Reasonably, this observation reveals that our one-pot sequential reaction proceeded *via* [2 + 2] cycloaddition of the aryne with DMF solvent.

Additionally, another independent experiment was performed to know the regioselectivity of nucleophilic substitution. In this regard, gamma-substituted allylic bromide namely crotyl bromide was used for our cascade process under the optimized conditions and the 2-formyl substituted allyl aryl ether **3ai** was isolated and characterized (Scheme 5).[23]

In summary, we have developed a transition-metal-free synthetic strategy for *ortho*-difunctionalization of an arene *via* trapping of an activated alkene by *in situ* generated *ortho*-quinone methide. A series of *ortho*-formyl allyl aryl ether derivatives have been synthesized by using our one-pot synthetic strategy in good yields. Remarkably, this synthetic strategy has been accomplished through C–O and C–C bond cleavage as well as C–C and two new C–O bond formations in a single reaction vessel. Additionally, our cascade synthetic strategy has been demonstrated for the one-pot synthesis of 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol.

Experimental section

General

All reactions involving oxygen- or moisture-sensitive compounds were carried out under an argon atmosphere using oven-dried or flame-dried glassware. All other solvents and reagents were purified according to standard procedures or were used as received from TCI, Aldrich, Merck and Spectrochem. The reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized with ultraviolet light (254 nm). Flash column chromatography was performed with silica gel 60 (100–200 or 200–400 mesh). HRMS data were recorded *via* electrospray ionization with a Q-TOF mass analyzer.

General procedure for the synthesis of *o*-formyl allyl aryl ether derivatives

An oven-dried round bottom flask (50 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. *o*-Silyl aryl triflate (0.5 mmol, 1 equiv.), activated alkene (0.75 mmol, 1.5 equiv.), CsF (2 mmol, 4 equiv.) and DMF (2 mL) were added successively at room temperature. The reaction mixture was stirred at room temperature for 1 h. Water (10 mL) was added to the reaction mixture and the organic layer was extracted with EtOAc (20 × 2 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

Methyl 2-[(2-formylphenoxy)methyl]acrylate (3aa)[19]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), methyl-2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[(2-formylphenoxy)methyl]acrylate **3aa** was obtained as a light brown gummy product (0.083 g, 75% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, CDCl$_3$):** δ 10.52 (s, 1H), 7.85 (dd, J_1 = 1.4 Hz, J_2 = 7.7 Hz, 1H), 7.48–7.61 (m, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.46 (s, 1H), 6.06 (s, 1H), 4.87 (s, 2H), 3.82 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$):** δ 189.5, 165.6, 160.5, 135.9, 135.1, 128.8, 126.9, 125.1, 121.3, 112.9, 66.6, 52.1; **IR (CHCl$_3$):** 2923, 2855, 1719, 1687, 1598, 1483, 1456, 1284, 1192, 759, 666 cm^{-1}; **HRMS (+ESI) Calcd for C$_{12}$H$_{12}$O$_4$Na [M + Na]$^+$:** 243.0633; found: 243.0638.

Ethyl 2-[(2-formylphenoxy)methyl]acrylate (3ab)

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), ethyl-2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), ethyl 2-[(2-formylphenoxy)methyl]acrylate **3ab** was obtained as a light yellow gummy product (0.078 g, 66% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, CDCl$_3$):** δ 10.52 (s, 1H), 7.84 (dd, J_1 = 1.7 Hz, J_2 = 7.7 Hz, 1H), 7.45–7.60 (m, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.45 (s, 1H), 6.02 (s, 1H), 4.87 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, CDCl$_3$):** δ 189.4, 165.1, 160.4, 135.8, 135.3, 128.6, 126.6, 125.0, 121.1, 112.8, 66.6, 61.0, 14.1; **IR (CHCl$_3$):** 2922, 2903, 1714, 1687, 1483, 1456, 1177, 759, 665 cm^{-1}; **HRMS (+ESI) Calcd for C$_{13}$H$_{14}$O$_4$Na [M + Na]$^+$:** 257.0790; found: 257.0792.

2-[(2-Methylallyl)oxy]benzaldehyde (3ac)[20]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-[(2-methylallyl)oxy]benzaldehyde **3ac** was obtained as a light yellow gummy product (0.065 g, 74% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.54 (s, 1H), 7.84 (m, 1H), 7.42–7.63 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 5.12 (s, 1H), 5.03 (s, 1H), 4.54 (s, 2H), 1.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.7, 161.0, 139.9, 135.8, 128.3, 124.9, 120.7, 113.2, 112.6, 71.9, 19.4; **IR ($CHCl_3$):** 2925, 2858, 1690, 1483, 1454, 1283, 1220, 758, 649 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_{13}O_2$ $[M + H]^+$:** 177.0916; found: 177.0919.

2-[(2-Bromoallyl)oxy]benzaldehyde (3ad)[21]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), 2,3-dibromopropene (0.07 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-[(2-bromoallyl)oxy]benzaldehyde **3ad** was obtained as a colourless oil (0.063 g, 52% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.55 (s, 1H), 7.86 (dd, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 1H), 7.51–7.57 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 5.95–6.07 (m, 1H), 5.66–5.80 (m, 1H), 4.76 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.4, 159.9, 135.8, 128.7, 126.1, 125.2, 121.7, 118.6, 113.0, 71.9; **IR ($CHCl_3$):** 2919, 2851, 1684, 1599, 1481, 1458, 1287, 1237, 758, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{10}H_{10}BrO_2$ $[M + H]^+$:** 240.9864; found: 240.9855.

Methyl 2-[(2-formyl-4,5-dimethoxyphenoxy)methyl]acrylate (3ba)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[(2-formyl-4,5-dimethoxyphenoxy)methyl]acrylate **3ba** was obtained as a yellow gummy product (0.087 g, 62% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.36 (s, 1H), 7.33 (s, 1H), 6.54 (s, 1H), 6.46 (brs, 1H), 6.06 (brs, 1H), 4.84 (brs, 2H), 3.96 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 187.7, 165.7, 157.2, 155.7, 144.1, 135.2, 127.3, 117.8, 108.9, 97.5, 67.5, 56.3, 56.1, 52.2; **IR ($CHCl_3$):** 2917, 2850, 1663, 1605, 1513, 1410, 1275, 1218, 773, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{16}O_6Na$ $[M + Na]^+$:** 303.0845; found: 303.0848.

Ethyl-2-[(2-formyl-4,5-dimethoxyphenoxy)methyl]acrylate (3bb)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), ethyl 2-[(2-formyl-4,5-dimethoxyphenoxy)methyl]acrylate **3bb** was obtained as a light brown gummy product (0.095 g, 64% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.36 (s, 1H), 7.33 (s, 1H), 6.54 (s, 1H), 6.45 (s, 1H), 6.04 (s, 1H), 4.84 (s, 2H), 4.28 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.88 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 187.8, 165.3, 157.3, 155.7, 144.1, 135.6, 126.9, 117.9, 108.9, 97.6, 67.7, 61.2, 56.3, 56.2, 14.2; **IR ($CHCl_3$):** 2976, 2935, 1670, 1606, 1514, 1411, 1277, 1220, 757, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{19}O_6$ $[M + H]^+$:** 295.1182; found: 295.1181.

4,5-Dimethoxy-2-[(2-methylallyl)oxy]benzaldehyde (3bc)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 4,5-dimethoxy-2-[(2-methylallyl)oxy]benzaldehyde **3bc** was obtained as a yellow gummy product (0.084 g, 71% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.38 (s, 1H), 7.32 (s, 1H), 6.51 (s, 1H), 5.14 (s, 1H), 5.05 (s, 1H), 4.54 (s, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 1.86 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 187.9, 157.8, 155.6, 143.6, 140.3, 117.6, 113.4, 108.6, 97.2, 73.0, 56.1, 19.4 (one peak is missing due to overlapping); **IR ($CHCl_3$):** 2925, 2850, 1667, 1606, 1513, 1452, 1276, 1219, 756, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{17}O_4$ $[M + H]^+$:** 237.1127; found: 237.1134.

2-[(2-Bromoallyl)oxy]-4,5-dimethoxybenzaldehyde (3bd)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), 2,3-dibromopropene (0.07 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-[(2-bromoallyl)oxy]-4,5-dimethoxybenzaldehyde **3bd** was obtained as a colourless oil (0.108 g, 72% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.39 (s, 1H), 7.33 (s, 1H), 6.45 (s, 1H), 6.04 (d, J = 1.6 Hz, 1H), 5.74 (d, J = 1.2 Hz, 1H), 4.73 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 187.8, 156.5, 155.5, 144.3, 126.3, 118.9, 118.0, 108.8, 97.7, 73.1, 56.2, 56.1; **IR ($CHCl_3$):** 2920, 2855, 1660, 1607, 1520, 1450, 1268, 1220, 759, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{14}BrO_4$ $[M + H]^+$:** 301.0075; found: 301.0076.

Methyl 2-[{(3-formylnaphthalen-2-yl)oxy}methyl]acrylate (3ca)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[{(3-formylnaphthalen-2-yl)oxy}methyl]acrylate **3ca** was obtained as a yellow gummy product (0.084 g,

62% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.95 (s, 1H), 9.27 (d, J = 8.7 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.63 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 9.1 Hz, 1H), 6.48 (s, 1H), 6.06 (s, 1H), 5.01 (s, 2H), 3.84 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.7, 165.6, 162.6, 137.5, 135.2, 131.5, 129.9, 128.8, 128.2, 127.4, 125.1, 124.9, 117.3, 113.7, 67.8, 52.2; **IR ($CHCl_3$):** 2921, 2848, 1671, 1590, 1509, 1435, 1268, 1243, 773, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{16}H_{14}O_4Na$ [M + Na]$^+$:** 293.0790; found: 293.0794.

Ethyl 2-[{(3-formylnaphthalen-2-yl)oxy}methyl]acrylate (3cb)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), ethyl 2-[{(3-formylnaphthalen-2-yl)oxy}methyl] acrylate **3cb** was obtained as a light yellow gummy product (0.090 g, 63% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.61 (s, 1H), 8.37 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.23 (s, 1H), 6.48 (d, J = 0.9 Hz, 1H), 6.10 (d, J = 0.9 Hz, 1H), 4.96 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.8, 165.3, 156.1, 137.4, 135.4, 131.3, 129.8, 129.3, 127.9, 126.7, 126.5, 125.6, 124.9, 107.7, 66.5, 61.1, 14.2; **IR ($CHCl_3$):** 2928, 2870, 1690, 1625, 1598, 1449, 1338, 1309, 1153, 772, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{16}O_4Na$ [M + Na]$^+$:** 307.0946; found: 307.0948.

3-[(2-Methylallyl)oxy]-2-naphthaldehyde (3cc)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 3-[(2-methylallyl)oxy]-2-naphthaldehyde **3cc** was obtained as a yellow gummy product (0.080 g, 71% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.65 (s, 1H), 8.37 (s, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.33–7.57 (m, 2H), 7.19 (s, 1H), 5.20 (s, 1H), 5.07 (s, 1H), 4.64 (s, 2H), 1.91 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 190.1, 156.6, 140.0, 137.4, 130.6, 129.8, 129.1, 127.7, 126.5, 125.6, 124.6, 113.1, 107.4, 71.9, 19.4; **IR ($CHCl_3$):** 2918, 2850, 1686, 1624, 1597, 1451, 1337, 772, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{15}O_2$ [M + H]$^+$:** 227.1072; found: 227.1072.

2,2′-[(2-Methylenepropane-1,3-diyl)bis(oxy)]dibenzaldehyde (3ae)[22]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-bromomethyl-1-propene (0.172 mL; 1.5 mmol, 3 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2,2′-[(2-methylenepropane-1,3-diyl)bis (oxy)]dibenzaldehyde **3ae** was obtained as a light yellow gummy product (0.104 g, 70% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.48 (d, J = 0.7 Hz, 2H), 7.84 (dd, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 2H), 7.48–7.59 (m, 2H), 6.99–7.09 (m, 4H), 5.52 (brs, 2H), 4.79 (s, 4H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.2, 160.4, 138.8, 135.8, 128.8, 124.9, 121.2, 116.9, 112.6, 68.8; **IR ($CHCl_3$):** 2923, 2852, 1683, 1598, 1483, 1455, 1286, 1235, 757, 664 cm^{-1}; **HRMS (+ESI) Calcd for $C_{18}H_{16}O_4Na$ [M + Na]$^+$:** 319.0946; found: 319.0941.

2-[(2-(Bromomethyl)allyl)oxy]-4,5-dimethoxybenzaldehyde (3be)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-bromomethyl-1-propene (0.086 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-[(2-(bromomethyl)allyl) oxy]-4,5-dimethoxybenzaldehyde **3be** was obtained as a light brown gummy product (0.098 g, 62% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.36 (s, 1H), 7.32 (s, 1H), 6.56 (s, 1H), 5.47 (s, 1H), 5.38 (s, 1H), 4.77 (s, 2H), 4.11 (s, 2H), 3.95 (s, 3H), 3.87 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 187.7, 157.3, 155.7, 143.9, 140.3, 118.1, 117.7, 108.8, 97.3, 69.3, 56.4, 56.2, 32.5; **IR ($CHCl_3$):** 2925, 2852, 1665, 1605, 1513, 1450, 1276, 1219, 756, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{16}BrO_4$ [M + H]$^+$:** 315.0232; found: 315.0237.

3-[((2-Bromomethyl)allyl)oxy]-2-naphthaldehyde (3ce)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-bromomethyl-1-propene (0.086 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 3-[((2-bromomethyl)allyl)oxy]-2-naphthaldehyde **3ce** was obtained as a light yellow gummy product (0.092 g, 60% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.61 (s, 1H), 8.38 (s, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.48–7.61 (m, 1H), 7.37–7.43 (m, 1H), 7.25 (s, 1H), 5.51 (d, J = 0.6 Hz, 1H), 5.47 (d, J = 0.5 Hz, 1H), 4.88 (s, 2H), 4.17 (s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.9, 156.2, 140.3, 137.4, 131.2, 129.9, 129.3, 127.9, 126.7, 125.6, 124.9, 118.2, 107.6, 68.5, 32.6; **IR ($CHCl_3$):** 2926, 2852, 1687, 1625, 1449, 1247, 1211, 748, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{15}H_{14}BrO_2$ [M + H]$^+$:** 305.0177; found: 305.0162.

Methyl 2-[(4,5-difluoro-2-formylphenoxy)methyl]acrylate (3ja)

On applying the general experimental procedure using 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), methyl-2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[(4,5-difluoro-2-formylphenoxy)methyl]acrylate **3ja** was obtained as a white solid (0.085 g, 66% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; mp: 151–153 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.37 (s, 1H), 7.66 (t, J = 9.5 Hz, 1H),

6.86 (dd, J_1 = 5.9 Hz, J_2 = 11.5 Hz, 1H), 6.48 (s, 1H), 6.02 (s, 1H), 4.82 (s, 2H), 3.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 186.9, 165.3, 157.4 (dd, J_1 = 1.5 Hz, J_2 = 8.3 Hz), 155.9 (d, J = 14.4 Hz), 153.8 (d, J = 14.5 Hz), 146.3 (d, J = 13.1 Hz), 144.4 (d, J = 13.1 Hz), 134.4, 127.7, 121.4 (t, J = 3.5 Hz), 116.5 (dd, J_1 = 2.8 Hz, J_2 = 18.7 Hz), 103.1 (d, J = 21.5 Hz), 67.6, 52.3; **IR ($CHCl_3$):** 2922, 2849, 1718, 1677, 1625, 1604, 1436, 1292, 1208, 959, 890 cm^{-1}; **HRMS (−ESI) Calcd for $C_{12}H_9F_2O_4$ $[M - H]^+$:** 255.0469; found: 255.0470.

Methyl 2-[(2-formyl-5-methylphenoxy)methyl]acrylate and methyl 2-[(2-formyl-4-methylphenoxy)methyl]acrylate (3da) and (3d′a)

On applying the general experimental procedure using 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of methyl 2-[(2-formyl-5-methylphenoxy)methyl]acrylate and methyl 2-[(2-formyl-4-methylphenoxy)methyl]acrylate (**3da** and **3d′a**) was obtained as a yellow gummy product (0.086 g, 73% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.48 (s, 1H), 10.43 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 1.7 Hz, 1H), 7.34 (dd, J_1 = 2.1 Hz, J_2 = 8.5 Hz, 1H), 6.90 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 6.45 (s, 1H), 6.44 (s, 1H), 6.05 (s, 1H), 6.03 (s, 1H), 4.84 (s, 2H), 4.83 (s, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 2.39 (s, 3H), 2.31 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.6, 189.1, 165.7, 160.5, 158.5, 147.5, 136.6, 135.2, 135.1, 130.7, 128.8, 128.7, 126.9, 126.8, 124.7, 122.8, 122.2, 113.4, 112.9, 66.7, 66.4, 52.1, 52.0, 22.3, 20.2; **IR ($CHCl_3$):** 2922, 2854, 1686, 1607, 1390, 1259, 1151, 772, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{14}O_4Na$ $[M + Na]^+$:** 257.0790; found: 257.0796.

Ethyl 2-[(2-formyl-5-methylphenoxy)methyl]acrylate and ethyl 2-[(2-formyl-4-methylphenoxy)methyl]acrylate (3db) and (3d′b)

On applying the general experimental procedure using 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of ethyl 2-[(2-formyl-5-methylphenoxy)methyl]acrylate and ethyl 2-[(2-formyl-4-methylphenoxy)methyl]acrylate (**3db** and **3d′b**) was obtained as a light yellow gummy product (0.095 g, 76% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.48 (s, 1H), 10.44 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.34 (dd, J_1 = 2.4 Hz, J_2 = 8.5 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.86 (dd, J_1 = 0.6 Hz, J_2 = 7.9 Hz, 1H), 6.80 (s, 1H), 6.40–6.46 (m, 2H), 5.98–6.06 (m, 2H), 4.80 (m, 4H), 4.21–4.33 (m, 4H), 2.39 (s, 3H), 2.31 (s, 3H), 1.26–1.38 (m, 6H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.6, 189.1, 165.2, 160.6, 158.6, 147.5, 136.6, 135.6, 135.4, 130.7, 128.7, 128.6, 126.6, 126.5, 124.8, 122.9, 122.2, 113.4, 113.0, 66.8, 66.5, 61.1, 61.0, 22.3, 20.2, 15.1; **IR ($CHCl_3$):** 2921, 2848, 1685, 1607, 1497, 1259, 1153, 811, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{16}O_4Na$ $[M + Na]^+$:** 271.0946; found: 271.0948.

4-Methyl-2-[(2-methylallyl)oxy]benzaldehyde and 5-methyl-2-[(2-methylallyl)oxy]benzaldehyde (3dc) and (3d′c)

On applying the general experimental procedure using 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of 4-methyl-2-[(2-methylallyl)oxy]benzaldehyde and 5-methyl-2-[(2-methylallyl)oxy]benzaldehyde (**3dc** and **3d′c**) was obtained as a yellow gummy product (0.074 g, 78% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.51 (s, 1H), 10.48 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.31 (dd, J_1 = 2.2 Hz, J_2 = 8.3 Hz, 1H), 6.86 (d, J = 8.6 Hz, 1H), 6.82 (d, J = 7.4 Hz, 1H), 6.76 (s, 1H), 4.94–5.19 (m, 4H), 4.51 (s, 2H), 4.50 (s, 2H), 2.38 (s, 3H), 2.29 (s, 3H), 1.85 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.9, 189.3, 161.1, 159.1, 147.3, 140.3, 140.1, 136.5, 130.1, 128.3, 128.2, 124.6, 122.7, 121.8, 113.2, 113.0, 112.8, 72.0, 71.8, 22.3, 20.2, 19.4; **IR ($CHCl_3$):** 2992, 2859, 1683, 1606, 1497, 1280, 1257, 771, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{15}O_2$ $[M + H]^+$:** 191.1072; found: 191.1074.

2-[(2-Bromoallyl)oxy]-4-methylbenzaldehyde and 2-[(2-bromoallyl)oxy]-5-methylbenzaldehyde (3dd) and (3d′d)

On applying the general experimental procedure using 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), 2,3-dibromopropene (0.07 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of 2-[(2-bromoallyl)oxy]-4-methylbenzaldehyde and 2-[(2-bromoallyl)oxy]-5-methylbenzaldehyde (**3dd** and **3d′d**) was obtained as a colourless oil (0.080 g, 63% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.52 (s, 1H), 10.47 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 2.1 Hz, 1H), 7.34 (dd, J_1 = 2.2 Hz, J_2 = 8.3 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.73 (s, 1H), 5.96–6.06 (m, 2H), 5.65–5.75 (m, 2H), 4.74 (m, 4H), 2.40 (s, 3H), 2.32 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.6, 189.0, 159.8, 157.9, 147.3, 136.4, 131.1, 128.6, 128.5, 126.2, 126.0, 124.7, 122.8, 122.6, 118.4, 118.3, 113.4, 112.9, 71.9, 71.7, 22.2, 20.2; **IR ($CHCl_3$):** 2923, 2854, 1683, 1607, 1496, 1284, 1257, 771, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_{12}BrO_2$ $[M + H]^+$:** 255.0021; found: 255.0020.

Methyl 2-[(2-formyl-3-methylphenoxy)methyl]acrylate and methyl 2-[(2-formyl-6-methylphenoxy)methyl]acrylate (3ea) and (3e′a)

On applying the general experimental procedure using 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of methyl 2-[(2-formyl-3-methylphenoxy)methyl]acrylate and methyl 2-[(2-formyl-6-

methylphenoxy)methyl]acrylate (**3ea** and **3e′a**) was obtained as a yellow gummy product (0.080 g, 68% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.69 (s, 1H), 10.33 (s, 1H), 7.69 (dd, J_1 = 1.7 Hz, J_2 = 7.7 Hz, 1H), 7.45 (m, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.47 (d, J = 0.9 Hz, 1H), 6.44 (d, J = 1.0 Hz, 1H), 6.12 (d, J = 1.4 Hz, 1H), 6.02 (d, J = 0.9 Hz, 1H), 4.83 (t, J = 1.5 Hz, 2H), 4.64 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.57 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.9, 190.3, 165.7, 161.7, 159.9, 142.2, 137.6, 135.7, 135.2, 134.4, 132.4, 129.4, 127.7, 126.9, 126.5, 124.7, 124.6, 110.3, 73.4, 66.7, 52.1, 52.0, 21.4, 15.6; **IR ($CHCl_3$):** 2925, 2855, 1719, 1686, 1588, 1471, 1438, 1274, 1247, 779, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{14}O_4Na$ $[M + Na]^+$:** 257.0790; found: 257.0792.

Ethyl 2-[(2-formyl-3-methylphenoxy)methyl]acrylate and ethyl 2-[(2-formyl-6-methylphenoxy)methyl]acrylate (3eb) and (3e′b)

On applying the general experimental procedure using 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of ethyl 2-[(2-formyl-3-methylphenoxy)methyl]acrylate and ethyl 2-[(2-formyl-6-methylphenoxy)methyl]acrylate (**3eb** and **3e′b**) was obtained as a light yellow gummy product (0.092 g, 74% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.69 (s), 10.34 (s), 7.69 (dd, J_1 = 1.6 Hz, J_2 = 7.7 Hz), 7.45 (d, J = 6.6 Hz), 7.37 (t, J = 8.0 Hz), 7.15 (d, J = 7.6 Hz), 6.86 (d, J = 8.4 Hz), 6.83 (d, J = 7.6 Hz), 6.46 (d, J = 0.7 Hz), 6.43 (d, J = 1.1 Hz), 6.11 (d, J = 1.4 Hz), 5.99 (d, J = 0.9 Hz), 4.83 (s), 4.64 (s), 4.19–4.33 (m), 2.57 (s), 2.33 (s), 1.30 (t, J = 7.4 Hz); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.5, 190.3, 165.3, 165.2, 161.8, 160.0, 142.1, 137.6, 136.1, 135.4, 134.4, 132.4, 129.4, 127.5, 126.6, 126.5, 124.6, 124.5, 123.6, 110.4, 73.4, 66.8, 61.1, 21.4, 15.6, 14.2, 14.1; **IR ($CHCl_3$):** 2924, 2843, 1719, 1686, 1555, 1472, 772, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{16}O_4Na$ $[M + Na]^+$:** 271.0946; found: 271.0941.

2-Methyl-6-[(2-methylallyl)oxy]benzaldehyde and 3-methyl-2-[(2-methylallyl)oxy]benzaldehyde (3ec) and (3e′c)

On applying the general experimental procedure using 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), a mixture of 2-methyl-6-[(2-methylallyl)oxy]benzaldehyde and 3-methyl-2-[(2-methylallyl)oxy]benzaldehyde (**3ec** and **3e′c**) was obtained as a yellow gummy product (0.072 g, 76% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.72 (d, J = 0.5 Hz), 10.36 (d, J = 0.7 Hz), 7.69 (dd, J_1 = 1.3 Hz, J_2 = 7.7 Hz), 7.32–7.47 (m), 7.14 (t, J = 7.6 Hz), 6.81 (t, J = 8.1 Hz), 4.96–5.20 (m), 4.51 (s), 4.32 (s), 2.57 (s), 2.34 (s), 1.90 (s), 1.84 (s); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 192.2, 190.5, 162.2, 160.6, 141.9, 140.4, 137.5, 134.3, 132.3, 129.3, 126.1, 124.3, 124.1, 113.4, 110.1, 79.4, 72.1, 21.5, 19.6, 19.3, 15.7; **IR ($CHCl_3$):** 2927, 2859, 1687, 1588, 1471, 1261, 1248, 779, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{15}O_2$ $[M + H]^+$:** 191.1072; found: 191.1074.

Methyl 2-[{(1-formylnaphthalen-2-yl)oxy}methyl]acrylate (3fa)

On applying the general experimental procedure using 1-(trimethylsilyl)-2-naphthyltrifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[{(1-formylnaphthalen-2-yl)oxy}methyl]acrylate **3fa** was obtained as a yellow gummy product (0.088 g, 65% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.95 (s, 1H), 9.26 (d, J = 8.7 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.63 (m, 1H), 7.44 (m, 1H), 7.29 (d, J = 9.1 Hz, 1H), 6.48 (d, J = 0.8 Hz, 1H), 6.06 (d, J = 0.7 Hz, 1H), 5.01 (s, 2H), 3.84 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.6, 165.6, 162.6, 137.5, 135.1, 131.4, 129.9, 128.7, 128.1, 127.3, 124.9, 124.8, 117.1, 113.6, 67.6, 52.1; **IR ($CHCl_3$):** 2951, 2877, 1673, 1619, 1602, 1591, 1269, 1245, 775, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{16}H_{15}O_4$ $[M + H]^+$:** 271.0970; found: 271.0963.

Ethyl 2-[{(1-formylnaphthalen-2-yl)oxy}methyl]acrylate (3fb)

On applying the general experimental procedure using 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1equiv), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), ethyl 2-[{(1-formylnaphthalen-2-yl)oxy}methyl]acrylate **3fb** was obtained as a yellow gummy product (0.095 g, 67% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.95 (s, 1H), 9.26 (dd, J_1 = 0.7 Hz, J_2 = 8.7 Hz, 1H), 8.05 (d, J = 9.1 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63 (m, 1H), 7.43 (m, 1H), 7.30 (d, J = 9.2 Hz, 1H), 6.47 (d, J = 0.9 Hz, 1H), 6.04 (d, J = 0.9 Hz, 1H), 5.01 (t, J = 1.4 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 191.7, 165.2, 162.7, 137.5, 135.5, 131.5, 129.9, 128.8, 128.2, 127.1, 125.0, 124.9, 117.3, 113.8, 67.8, 61.2, 14.2; **IR ($CHCl_3$):** 2927, 2874, 1675, 1619, 1591, 1509, 1269, 1245, 775, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{17}O_4$ $[M + H]^+$:** 285.1127; found: 285.1121.

Methyl 2-[(2-formyl-4-methoxyphenoxy)methyl]acrylate (3ga) and methyl 2-[(2-formyl-5-methoxyphenoxy)methyl]acrylate (3g′a)

On applying the general experimental procedure using 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[(2-formyl-4-methoxyphenoxy)methyl]acrylate **3ga** was obtained as a light yellow gummy product (0.037 g, 29% yield), and methyl 2-[(2-formyl-5-methoxyphenoxy)methyl]acrylate **3g′a** as a yellow gummy product (0.046 g; 37% yield) and were isolated by flash chromatography using hexane/EtOAc (4 : 1) as the eluent:

For 3ga: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.47 (s, 1H), 7.33 (d, J = 3.2 Hz, 1H), 7.12 (dd, J_1 = 3.3 Hz, J_2 = 9.1 Hz, 1H), 6.96 (d, J = 9.1 Hz, 1H), 6.44 (d, J = 1.0 Hz, 1H), 6.01 (d, J = 1.0 Hz, 1H), 4.82 (t, J = 1.4 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.2, 165.6, 155.2, 153.9, 135.2, 126.9, 125.3, 123.4, 114.9, 110.3, 67.3, 55.7, 52.0; **IR ($CHCl_3$):** 2921, 2837, 1676, 1637, 1492, 1277, 1218, 772, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{14}O_5Na$ $[M + Na]^+$:** 273.0739; found: 273.0733.

For 3g′a: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.33 (d, J = 0.7 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 6.57 (m, 1H), 6.47 (d, J = 2.2 Hz, 1H), 6.46 (dd, J_1 = 1.3 Hz, J_2 = 2.3 Hz, 1H), 6.06 (dd, J_1 = 1.7 Hz, J_2 = 2.6 Hz, 1H), 4.83 (t, J = 1.5 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 188.0, 166.1, 165.6, 162.2, 134.9, 130.9, 127.0, 119.2, 106.4, 99.0, 66.4, 55.7, 52.1; **IR ($CHCl_3$):** 2923, 2851, 1677, 1599, 1439, 1259, 1200, 772, 666 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{15}O_5$ $[M + H]^+$:** 251.0919; found: 251.0913.

Ethyl 2-[(2-formyl-4-methoxyphenoxy)methyl]acrylate (3gb) and ethyl 2-[(2-formyl-5-methoxyphenoxy)methyl]acrylate (3g′b)

On applying the general experimental procedure using 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), ethyl 2-(bromomethyl)acrylate (0.10 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), ethyl 2-[(2-formyl-4-methoxyphenoxy)methyl]acrylate **3gb** was obtained as a light yellow gummy product (0.038 g, 29% yield) and ethyl 2-[(2-formyl-5-methoxyphenoxy)methyl]acrylate **3g′b** as a yellow gummy product (0.052 g; 39% yield) and were isolated by flash chromatography using hexane/EtOAc (4 : 1) as the eluent:

For 3gb: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.47 (s, 1H), 7.32 (d, J = 3.2 Hz, 1H), 7.11 (dd, J_1 = 3.3 Hz, J_2 = 9.1 Hz, 1H), 6.97 (d, J = 9.1 Hz, 1H), 6.42 (d, J = 0.8 Hz, 1H), 5.98 (s, 1H), 4.81 (s, 2H), 4.62 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.3, 165.2, 155.3, 153.9, 135.6, 126.7, 125.4, 123.4, 114.9, 110.4, 67.5, 61.1, 55.7, 14.1; **IR ($CHCl_3$):** 2927, 2854, 1686, 1555, 1494, 1277, 1217, 772, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{16}O_5Na$ $[M + Na]^+$:** 287.0895; found: 287.0898.

For 3g′b: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.33 (d, J = 1.0 Hz, 1H), 7.82 (dd, J_1 = 1.7 Hz, J_2 = 8.7 Hz, 1H), 6.57 (d, J = 8.7 Hz, 1H), 6.47 (s, 1H), 6.44 (s, 1H), 6.04 (s, 1H), 4.83 (d, J = 1.4 Hz, 2H), 4.23–4.31 (m, 2H), 3.87 (d, J = 1.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 188.0, 166.1, 165.2, 162.2, 135.2, 130.8, 126.7, 119.2, 106.4, 99.1, 66.5, 61.1, 55.7, 14.2; **IR ($CHCl_3$):** 2923, 2854, 1681, 1602, 1561, 1261, 1200, 772, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{14}H_{17}O_5$ $[M + H]^+$:** 265.1076; found: 265.1078.

5-Methoxy-2-[(2-methylallyl)oxy]benzaldehyde (3gc) and 4-methoxy-2-[(2-methylallyl)oxy]benzaldehyde (3g′c)

On applying the general experimental procedure using 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), 3-bromo-2-methylpropene (0.075 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 5-methoxy-2-[(2-methylallyl)oxy]benzaldehyde **3gc** was obtained as a light yellow gummy product (0.030 g, 29% yield) and 4-methoxy-2-[(2-methylallyl)oxy]benzaldehyde **3g′c** as a yellow gummy product (0.036 g; 35% yield) and were isolated by flash chromatography using hexane/EtOAc (4 : 1) as the eluent:

For 3gc: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.50 (s, 1H), 7.32 (d, J = 3.3 Hz, 1H), 7.10 (dd, J_1 = 3.3 Hz, J_2 = 9.1 Hz, 1H), 6.93 (d, J = 9.1 Hz, 1H), 5.00–5.11 (m, 2H), 4.49 (s, 2H), 3.79 (s, 3H), 1.83 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.5, 155.9, 153.6, 140.2, 125.2, 123.5, 114.7, 113.1, 110.1, 72.7, 55.7, 19.4; **IR ($CHCl_3$):** 2927, 2864, 1684, 1613, 1492, 1276, 1217, 772, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{15}O_3$ $[M + H]^+$:** 207.1021;found: 207.1024.

For 3g′c: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.81 (d, J = 8.7 Hz, 1H), 6.54 (dd, J_1 = 2.2 Hz, J_2 = 8.7 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 5.12 (s, 1H), 5.03 (s, 1H), 4.51 (s, 2H), 3.85 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 188.2, 166.0, 162.8, 139.9, 130.4, 119.2, 113.3, 106.0, 98.9, 72.0, 55.6, 19.3; **IR ($CHCl_3$):** 2927, 2850, 1678, 1602, 1500, 1297, 1261, 770, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{12}H_{15}O_3$ $[M + H]^+$:** 207.1021; found: 207.1024.

Methyl 2-[(2-formyl-3-methoxyphenoxy)methyl]acrylate (3ha)

On applying the general experimental procedure using 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), methyl 2-(bromomethyl) acrylate (0.09 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), methyl 2-[(2-formyl-3-methoxyphenoxy)methyl]acrylate **3ha** was obtained as a light yellow gummy product (0.089 g, 71% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.55 (s, 1H), 7.44 (t, J = 8.5 Hz, 1H), 6.61 (s, 1H), 6.59 (s, 1H), 6.45 (m, 1H), 6.26 (m, 1H), 4.81 (t, J = 1.8 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.1, 165.7, 162.3, 160.5, 135.9, 134.8, 126.9, 114.5, 104.9, 104.3, 66.7, 56.1, 52.0; **IR ($CHCl_3$):** 2922, 2843, 1683, 1596, 1474, 1256, 773, 665 cm^{-1}; **HRMS (+ESI) Calcd for $C_{13}H_{14}O_5Na$ $[M + Na]^+$:** 273.0739; found: 273.0740.

Methyl 2-[(2-(formyl-d)phenoxy)methyl]acrylate {3aa(D)}

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), methyl 2-(bromomethyl)acrylate (0.045 mL; 0.375 mmol, 1.5 equiv.), and CsF (0.152 g; 2 mmol, 4 equiv.) in DMF-d_7 (0.75 mL), methyl 2-[(2-(formyl-*d*)phenoxy) methyl]acrylate **3aa(D)** was obtained as a light yellow gummy product (0.040 g, 72% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.84 (dd, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 1H), 7.51–7.57 (m, 1H), 7.03–7.08 (m, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 1.0 Hz, 1H), 6.04 (d, J = 0.9 Hz, 1H), 4.86 (t, J = 1.6 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.0 (t, J = 27.4 Hz), 165.6, 160.4, 135.9, 135.0, 128.7, 126.9, 125.0 (t, J = 3.2 Hz), 121.2, 112.8, 66.6, 52.1; **IR ($CHCl_3$):** 2913, 2839, 1644, 1595, 1481, 1446, 1283, 1231, 758, 666 cm^{-1}; **HRMS**

(+ESI) Calcd for $C_{12}H_{12}DO_4$ $[M + H]^+$: 222.0877; found: 222.0876.

General procedure for the synthesis of 2-methyl-3-(arylsulfonyl)-2*H*-chromen-2-ol derivatives (4)

An oven-dried round bottom flask (50 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. *o*-Silyl aryl triflate (0.5 mmol, 1 equiv.), 2-bromoallyl arylsulfones **2f–h** (0.75 mmol, 1.5 equiv.), CsF (2 mmol, 4 equiv.) and DMF (2 mL) were added successively at room temperature. The reaction mixture was stirred at room temperature for 3 h. Water (10 mL) was added to the reaction mixture and the organic layer was extracted with EtOAc (20 × 2 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

2-Methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol (4af)[18]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), (2-bromoallylsulfonyl)benzene (0.195 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol **4af** was obtained as a yellow solid (0.101 g, 67% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 138–141 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.93–7.98 (m, 2H), 7.81 (s, 1H), 7.62 (m, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.32–7.38 (m, 2H), 7.04 (m, 1H), 6.96 (d, J = 8.7 Hz, 1H), 3.64 (brs, 1H), 1.61 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 152.7, 140.3, 135.2, 133.9, 133.5, 133.2, 129.4, 129.1, 128.1, 122.2, 118.2, 116.9, 97.4, 26.5; **IR ($CHCl_3$)**: 3440, 3060, 2945, 1690, 1620, 1450, 1300, 1123, 860, 750, 680, 640 cm^{-1}; **HRMS (+ESI) Calcd for $C_{16}H_{13}O_3S$ $[M - H_2O]^+$**: 285.0585; found: 285.0580.

6,7-Dimethoxy-2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol (4bf)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), (2-bromoallylsulfonyl)benzene (0.195 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 6,7-dimethoxy-2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol **4bf** was obtained as a light brown gummy product (0.098 g, 54% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.91–7.96 (m, 2H), 7.76 (s, 1H), 7.59–7.62 (m, 1H), 7.50–7.55 (m, 2H), 6.79 (s, 1H), 6.52 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 1.58 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 153.6, 148.4, 144.6, 140.8, 135.4, 133.3, 130.5, 129.1, 128.0, 110.6, 109.9, 100.6, 97.6, 56.4, 56.2, 26.2; **IR ($CHCl_3$)**: 3445, 3058, 2940, 1691, 1617, 1453, 1297, 1123, 857, 750, 681, 639 cm^{-1}; **HRMS (+ESI) Calcd for $C_{18}H_{17}O_5S$ $[M - H_2O]^+$**: 345.0797; found: 345.0787.

2-Methyl-3-(phenylsulfonyl)-2*H*-benzo[*g*]chromen-2-ol (4cf)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), (2-bromoallylsulfonyl)benzene (0.195 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-methyl-3-(phenylsulfonyl)-2*H*-benzo[*g*]chromen-2-ol **4cf** was obtained as a light yellow solid (0.106 g, 60% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 120–123 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.96–8.00 (m, 2H), 7.94 (s, 1H), 7.83 (s, 1H), 7.79 (dd, J_1 = 0.6 Hz, J_2 = 8.2 Hz, 1H), 7.67 (dd, J_1 = 0.5 Hz, J_2 = 8.2 Hz, 1H), 7.61 (m, 1H), 7.51–7.56 (m, 2H), 7.46 (m, 1H), 7.37 (m, 1H), 7.29 (s, 1H), 1.61 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 149.3, 140.2, 137.0, 136.0, 135.2, 133.6, 130.3, 129.3, 129.1, 128.6, 128.3, 128.2, 126.9, 124.9, 119.5, 112.6, 97.6, 26.6; **IR ($CHCl_3$)**: 3435, 3056, 2940, 1688, 1630, 1456, 1300, 1123, 867, 750, 683, 640 cm^{-1}; **HRMS (+ESI) Calcd for $C_{20}H_{15}O_3S$ $[M - H_2O]^+$**: 335.0742; found: 335.0732.

5-Methoxy-2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol (4hf)

On applying the general experimental procedure using 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), (2-bromoallylsulfonyl)benzene (0.195 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 5-methoxy-2-methyl-3-(phenylsulfonyl)-2*H*-chromen-2-ol **4hf** was obtained as a yellow solid (0.106 g, 64% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 123–125 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.18 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.49–7.53 (m, 2H), 7.22–7.30 (m, 1H), 6.55 (d, J = 8.2 Hz, 1H), 6.50 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H), 1.77 (brs, 1H), 1.54 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 157.4, 153.6, 140.7, 133.7, 133.3, 131.6, 130.7, 129.1, 128.1, 109.4, 108.6, 103.6, 97.3, 55.8, 26.2; **IR ($CHCl_3$)**: 3422, 3058, 2926, 1718, 1606, 1469, 1305, 1148, 1099, 746, 688 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{15}O_4S$ $[M - H_2O]^+$**: 315.0691; found: 315.0673.

6-Methyl-7-(phenylsulfonyl)-6*H*-[1,3]dioxolo[4,5*g*]chromen-6-ol (4if)

On applying the general experimental procedure using 5-(trimethylsilyl)benzo[*d*][1,3]-dioxol-6-yltrifluoromethanesulfonate (0.10 mL; 0.5 mmol, 1 equiv.), (2-bromoallylsulfonyl)benzene (0.195 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 6-methyl-7-(phenylsulfonyl)-6*H*-[1,3]dioxolo[4,5*g*]chromen-6-ol **4if** was obtained as a yellow solid (0.111 g, 64% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 162–164 °C; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.93 (d, J = 7.2 Hz, 2H), 7.69 (s, 1H), 7.55 (dt, J_1 = 1.6 Hz, J_2 = 2.5 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 6.74 (s, 1H), 6.48 (s, 1H), 5.97 (dd, J_1 = 1.2 Hz, J_2 = 5.3 Hz, 2H), 3.67 (s, 1H), 1.57 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 151.8, 149.7, 143.0, 140.7, 135.4, 133.4, 130.4, 129.1, 128.0, 111.2, 107.1, 101.8, 99.0, 97.7, 26.1; **IR ($CHCl_3$)**: 3418, 3060, 2922, 1746, 1619, 1479, 1303, 1219, 1146, 931, 770, 686 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{13}O_5S$ $[M - H_2O]^+$**: 329.0484; found: 329.0490.

2-Methyl-3-tosyl-2*H*-chromen-2-ol (4ag)[18]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL;

0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-methylbenzene (0.206 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-methyl-3-tosyl-2*H*-chromen-2-ol **4ag** was obtained as a yellow solid (0.104 g, 66% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 158–160 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.82 (d, J = 8.4 Hz, 2H), 7.78 (s, 1H), 7.28–7.35 (m, 4H), 7.03 (m, 1H), 6.95 (dd, J_1 = 0.8 Hz, J_2 = 7.9 Hz, 1H), 3.62 (brs, 1H), 2.43 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 152.7, 144.7, 137.4, 134.7, 134.4, 133.1, 129.8, 129.4, 128.3, 122.3, 118.4, 117.0, 97.5, 26.5, 21.6; **IR ($CHCl_3$):** 3451, 3055, 2955, 1694, 1619, 1454, 1296, 1139, 865, 767, 680, 638 cm^{-1}; **HRMS (+ESI) Calcd for $C_{17}H_{15}O_3S$ [M − H_2O]$^+$**: 299.0742; found: 299.0746.

6,7-Dimethoxy-2-methyl-3-tosyl-2*H*-chromen-2-ol (4bg)

On applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl) trifluoromethanesulfonate (0.146 mL; 0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-methylbenzene (0.206 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 6,7-dimethoxy-2-methyl-3-tosyl-2*H*-chromen-2-ol **4bg** was obtained as a light brown gummy product (0.110 g, 58% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.81 (d, J = 8.4 Hz, 2H), 7.72 (s, 1H), 7.31 (d, J = 7.9 Hz, 2H), 6.78 (s, 1H), 6.52 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.42 (s, 3H), 1.58 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 153.5, 148.4, 144.5, 144.4, 137.8, 134.9, 130.8, 129.7, 128.1, 110.6, 110.0, 100.6, 97.6, 56.4, 56.1, 26.2, 26.1; **IR ($CHCl_3$):** 3444, 3057, 2940, 1685, 1610, 1440, 1297, 1145, 865, 746, 682, 643 cm^{-1}; **HRMS (+ESI) Calcd for $C_{19}H_{19}O_5S$ [M − H_2O]$^+$**: 359.0953; found: 359.0950.

2-Methyl-3-tosyl-2*H*-benzo[*g*]chromen-2-ol (4cg)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL; 0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-methylbenzene (0.206 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-methyl-3-tosyl-2*H*-benzo[*g*]chromen-2-ol **4cg** was obtained as a light yellow solid (0.112 g, 61% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 155–157 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.92 (s, 1H), 7.87 (s, 1H), 7.85 (d, J = 6.0 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.48 (m, 1H), 7.38 (m, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.31 (s, 1H), 3.74 (brs, 1H), 2.44 (s, 3H), 1.59 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 149.3, 144.8, 137.4, 137.1, 136.1, 134.7, 130.2, 129.8, 129.4, 128.5, 128.4, 128.3, 126.9, 124.9, 119.6, 112.6, 97.7, 26.6, 21.7; **IR ($CHCl_3$):** 3440, 3064, 2951, 1690, 1630, 1450, 1299, 1211, 860, 770, 682, 640 cm^{-1}; **HRMS (+ESI) Calcd for $C_{21}H_{17}O_3S$ [M − H_2O]$^+$**: 349.0898; found: 349.0890.

5-Methoxy-2-methyl-3-tosyl-2*H*-chromen-2-ol (4hg)

On applying the general experimental procedure using 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.13 mL; 0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-methylbenzene (0.206 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 5-methoxy-2-methyl-3-tosyl-2*H*-chromen-2-ol **4hg** was obtained as a yellow solid (0.108 g, 62% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 129–131 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.15 (s, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.26 (t, J = 8.3 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 6.49 (d, J = 8.3 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H), 1.76 (brs, 1H), 1.54 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.4, 153.6, 144.4, 137.6, 133.6, 131.9, 130.3, 129.7, 128.2, 109.3, 108.6, 103.5, 97.3, 55.7, 26.1, 21.6; **IR ($CHCl_3$):** 3431, 3055, 2926, 1694, 1606, 1469, 1299, 1144, 1097, 865, 776, 673 cm^{-1}; **HRMS (+ESI) Calcd for $C_{18}H_{17}O_4S$ [M − H_2O]$^+$**: 329.0848; found: 329.0844.

6-Methyl-7-tosyl-6*H*-[1,3]dioxolo[4,5*g*]chromen-6-ol (4ig)

On applying the general experimental procedure using 5-(trimethylsilyl)benzo[*d*][1,3]-dioxol-6-yltrifluoromethanesulfonate (0.10 mL; 0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-methylbenzene (0.206 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 6-methyl-7-tosyl-6*H*-[1,3]dioxolo[4,5*g*]chromen-6-ol **4ig** was obtained as a yellow solid (0.101 g, 56% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 166–168 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.80 (d, J = 8.3 Hz, 2H), 7.65 (s, 1H), 7.32 (d, J = 7.9 Hz, 2H), 6.73 (s, 1H), 6.48 (s, 1H), 5.97 (dd, J_1 = 1.2 Hz, J_2 = 5.1 Hz, 2H), 3.65 (s, 1H), 2.42 (s, 3H), 1.56 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 151.7, 149.6, 144.5, 142.9, 137.7, 134.9, 130.8, 129.8, 128.1, 111.2, 107.1, 101.8, 99.0, 97.7, 26.1, 21.6; **IR ($CHCl_3$):** 3422, 3051, 2922, 1744, 1623, 1479, 1385, 1262, 1144, 815, 772, 680 cm^{-1}; **HRMS (+ESI) Calcd for $C_{18}H_{15}O_5S$ [M − H_2O]$^+$**: 343.0640; found: 343.0650.

3-[(4-Chlorophenyl)sulfonyl]-2-methyl-2*H*-chromen-2-ol (4ah)

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-chlorobenzene (0.221 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 3-[(4-chlorophenyl)sulfonyl]-2-methyl-2*H*-chromen-2-ol **4ah** was obtained as a yellow solid (0.098 g, 58% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 135–137 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.88 (d, J = 8.7 Hz, 2H), 7.81 (s, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.32–7.39 (m, 2H), 7.05 (dt, J_1 = 1.0 Hz, J_2 = 7.5 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 3.57 (s, 1H), 1.65 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 152.8, 140.2, 139.1, 135.7, 133.6, 133.4, 129.7, 129.6, 129.5, 122.4, 118.2, 117.1, 97.5, 26.8; **IR ($CHCl_3$):** 3431, 3055, 2918, 1694, 1619, 1453, 1312, 1150, 942, 770, 755, 707 cm^{-1}; **HRMS (+ESI) Calcd for $C_{16}H_{12}ClO_3S$ [M − H_2O]$^+$**: 319.0196; found: 319.0201.

3-[(4-Chlorophenyl)sulfonyl]-2-methyl-2*H*-benzo[*g*]chromen-2-ol (4ch)

On applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl-trifluoromethanesulfonate (0.14 mL;

0.5 mmol, 1 equiv.), 1-(2-bromoallylsulfonyl)-4-chlorobenzene (0.221 g; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 3-[(4-chlorophenyl)sulfonyl]-2-methyl-2*H*-benzo[*g*]chromen-2-ol **4ch** was obtained as a light yellow solid (0.114 g, 59% yield) after purification by flash chromatography using hexane/EtOAc (4 : 1) as the eluent; mp: 157–159 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.94 (s, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.84 (s, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.45–7.52 (m, 3H), 7.36–7.41 (m, 1H), 7.30 (s, 1H), 1.67 (brs, 1H), 1.65 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 149.2, 140.3, 138.8, 136.6, 136.1, 135.7, 130.5, 129.8, 129.5, 129.4, 128.6, 128.4, 126.9, 125.0, 119.4, 112.7, 97.7, 26.9; **IR ($CHCl_3$):** 3422, 3056, 2922, 1742, 1632, 1475, 1316, 1211, 929, 763, 705, 680 cm^{-1}; **HRMS (+ESI) Calcd for $C_{20}H_{14}ClO_3S$ $[M - H_2O]^+$**: 369.0352; found: 369.0360.

2-(But-2-en-1-yloxy)benzaldehyde (3ai)[23]

On applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.12 mL; 0.5 mmol, 1 equiv.), crotyl bromide (0.077 mL; 0.75 mmol, 1.5 equiv.), and CsF (0.304 g; 2 mmol, 4 equiv.) in DMF (2 mL), 2-(but-2-en-1-yloxy)benzaldehyde **3ai** was obtained as a colourless oil (0.058 g, 66% yield) after purification by flash chromatography using hexane/EtOAc (9 : 1) as the eluent; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.50 (s, 1H), 7.83 (dd, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 1H), 7.52 (m, 1H), 6.93–7.02 (m, 2H), 5.70–5.92 (m, 2H), 4.57 (m, 2H), 1.77 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 189.9, 161.1, 135.8, 130.9, 128.3, 125.2, 124.9, 120.6, 112.8, 69.1, 17.8; **IR ($CHCl_3$):** 2920, 2850, 1688, 1483, 1456, 1285, 1218, 756, 645 cm^{-1}; **HRMS (+ESI) Calcd for $C_{11}H_{13}O_2$ $[M + H]^+$**: 177.0916; found: 177.0923.

Conflicts of interest

There are no conflicts to declare.

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