

Article

# NHC-Catalyzed Organocatalytic Asymmetric Approach to 2,2-Disubstituted Benzofuran-3(2*H*)-ones Containing Fully Substituted Quaternary Stereogenic Center

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Received: 21 December 2018; Accepted: 12 February 2019; Published: 20 February 2019

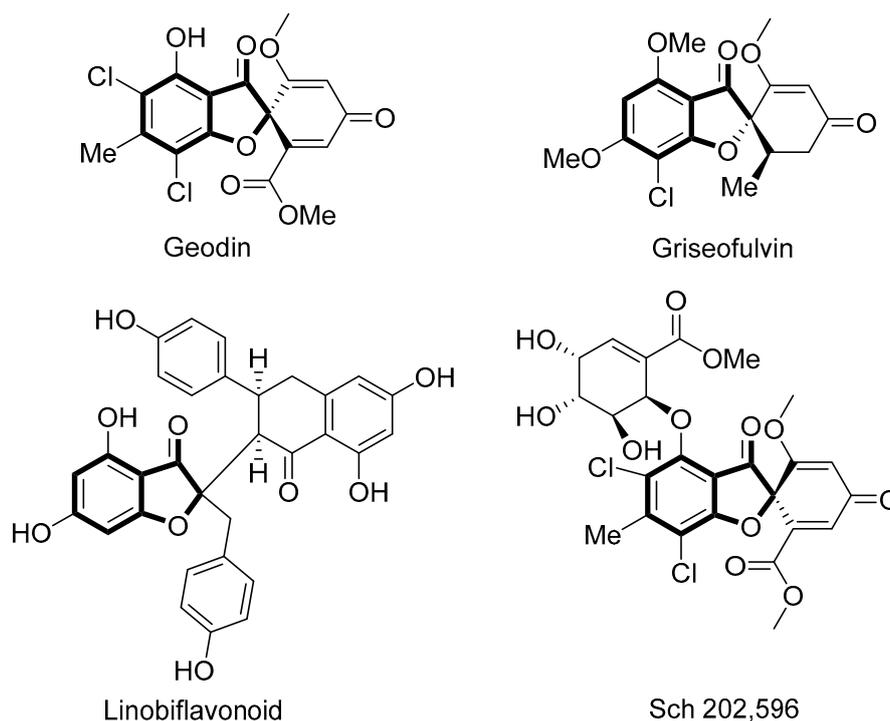


**Abstract:** A highly efficient and enantioselective approach to the synthesis of functionalized benzofuran-3(2*H*)-ones is presented. It proceeds via an intramolecular Stetter reaction using  $\beta,\beta$ -disubstituted Michael acceptors in the construction of five-membered rings with fully-substituted quaternary stereogenic centers and is promoted by terpene-derived triazolium salts. As a result, a series of chiral 2,2-disubstituted benzofuran-3(2*H*)-one derivatives with linear, branched, and cyclic aliphatic substitutions on the quaternary stereogenic center were obtained in high yields and with excellent enantioselectivities of up to 99% ee.

**Keywords:** *N*-Heterocyclic carbenes; organocatalysis; Stetter reaction

## 1. Introduction

The development of stereocontrolled strategies leading to molecules of biological interest is of vital importance in contemporary organic chemistry [1,2]. 3-Coumaranones (benzofuran-3(2*H*)-one) and naphthofuranone derivatives constitute an interesting class of heterocycles because of their presence in many naturally occurring and biologically interesting compounds and they are regarded as having a “privileged” structure in medicinal chemistry [3–9]. They have also been found to be important building blocks in the synthesis of valuable biologically active heterocycles and possess interesting cytotoxic and pharmacological properties such as antifungal, anticancer, and antipsychotic [10–15]. In one particularly valuable context, 2,2-disubstituted coumaranones bearing a fully substituted quaternary stereogenic center act as synthetic intermediates, since the core skeleton is present in several natural products, including pterocarpan, lignans, and other biologically active agents such as Geodin [16], griseofulvin (an antifungal agent) [17], linobiflavonoid (an anticancer agent) [18], and Sch 202,596 (which combats Alzheimer’s disease) [19] (Figure 1). The quaternary stereogenic centers are present in many natural products, but their construction represents a synthetic challenge, especially with the need for stereoselective synthesis [20]. Therefore, efficient and enantioselective methods to construct such scaffolds are desirable. Progress in this area has mainly come from transition-metal-catalyzed C–H bond activations [21–23]. Metal-free catalytic approaches have been much less explored.

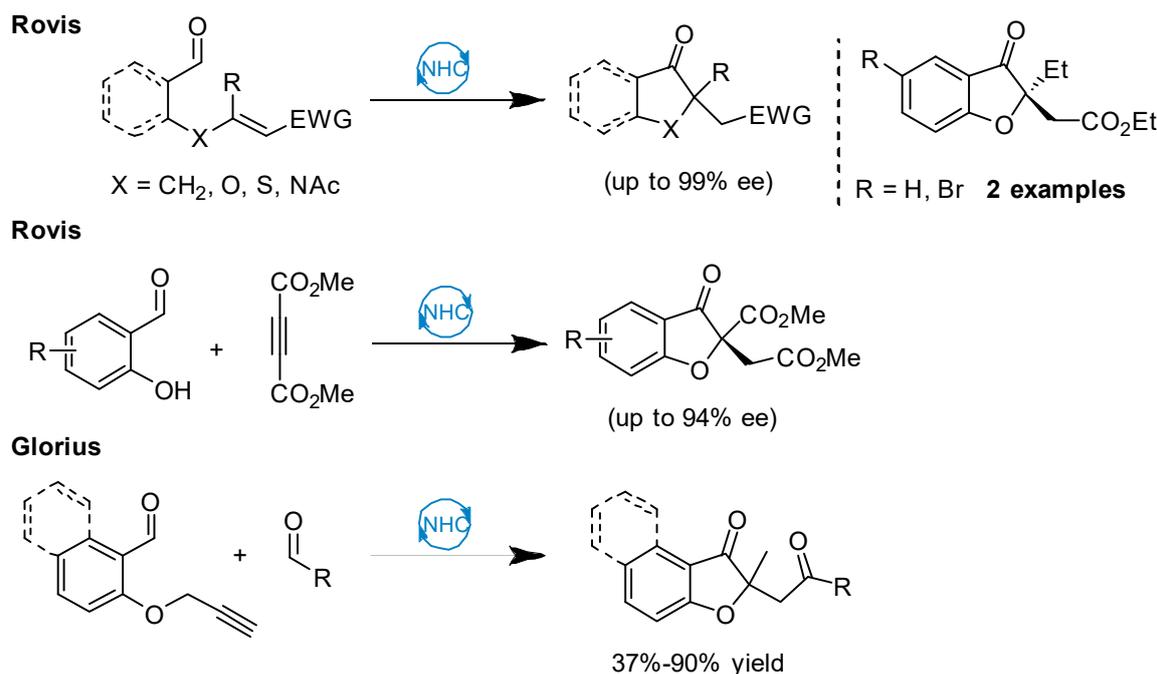


**Figure 1.** Selected benzofuran-3(2H)-one-derived natural products.

Over the past decade, *N*-heterocyclic carbene (NHC) organocatalysts have received considerable attention due to their unique ability to catalyze a wide range of synthetic transformations [24–29]. The ability of NHCs to reverse natural reactivity of a functional group has led to intensive research on them, leading to unprecedented access to designed target molecules and a set of umpolung reactions [30–32]. As a powerful carbon–carbon bond-forming reaction, the Stetter reaction is undoubtedly one of the most attractive and important umpolung processes and it enables access to many 1,4-dicarbonyl compounds through 1,4-addition to electron-deficient olefins [33–40]. *N*-Heterocyclic carbenes (NHCs) have been demonstrated to be useful catalysts for the synthesis of 2,2-disubstituted benzofuranone compounds [34,35,41,42]. The pioneering work by Rovis showcased how the Stetter reaction involves the addition of an aldehyde to a  $\beta,\beta$ -disubstituted Michael acceptor and is an excellent way to access five-membered rings with fully-substituted quaternary stereogenic centers. A series of enantioenriched thiobenzofuranones and aliphatic heterocycles have been obtained in this way. However, in the case of benzofuran-3-one analogues, this approach is so far limited to two examples [34,35].

Recently, Rovis and coworkers described an elegant procedure for the enantioselective preparation of benzofuran-3-one products, utilizing a one-pot Michael/Stetter protocol. However, their methodology only gave adequate enantioselectivity for dimethyl acetylenedicarboxylate [43]. Application of unsymmetrical alkynes significantly decreased yield and selectivity of the products. More recently, Glorius uncovered a non-enantioselective approach to the synthesis of 2,2-disubstituted benzofuran-3-ones using a multicatalytic process that involves intramolecular hydroacylation of unactivated alkynes, followed by an intermolecular Stetter reaction and a subsequent base-catalyzed rearrangement (Figure 2) [42]. Despite these elegant contributions, the asymmetric synthesis of chiral 2,2-disubstituted benzofuran-3-one derivatives is still in its infancy and novel catalytic processes are highly desirable.

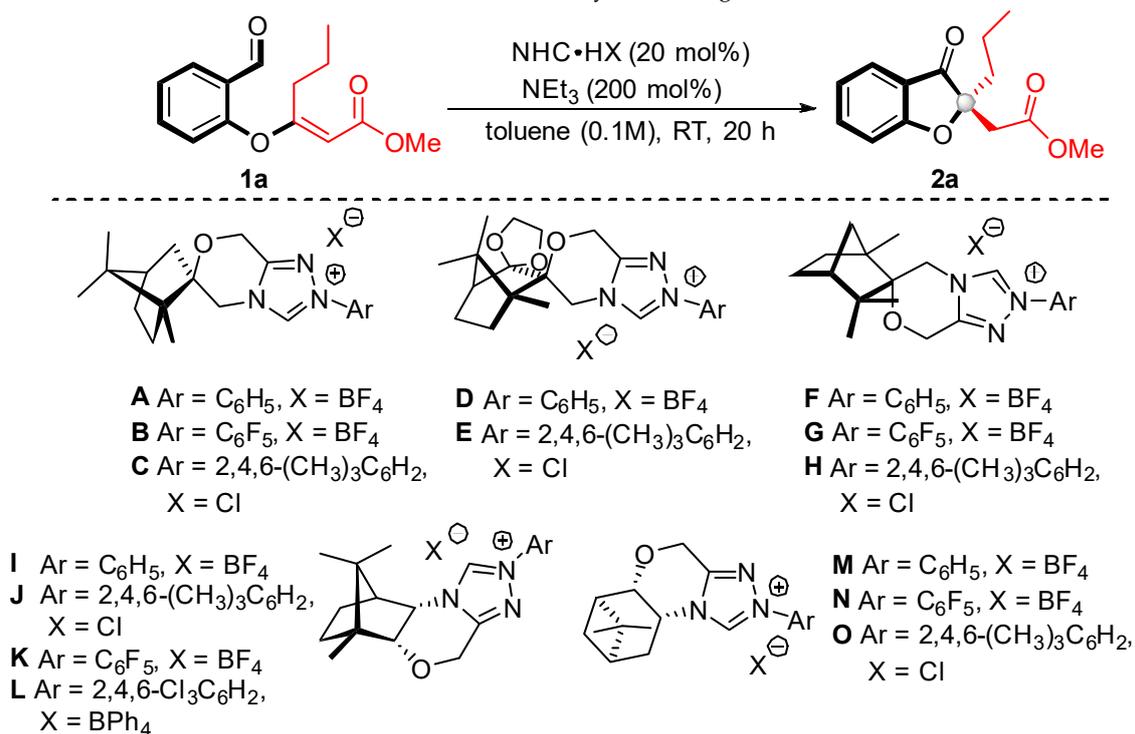
Due to the ongoing interest in the development of chiral terpene-based *N*-heterocyclic carbene catalysts and their applications to organocatalytic reactions [44–48], we report the NHC-catalyzed stereoselective synthesis of functionalized 3-coumaranones and naphthofuranones via an intramolecular Stetter reaction.



**Figure 2.** *N*-heterocyclic carbene (NHC)-catalyzed approach to the 2,2-disubstituted benzofuran-3-ones.

## 2. Results and Discussion

To examine the feasibility of the envisaged intramolecular Stetter reaction, we started by surveying a variety of chiral terpene-derived triazolium salts, **A–O**, as *N*-heterocyclic carbene precursors, with the use of salicylaldehyde-derived **1a** as a model substrate. It was found that the devised strategy is possible under umpolung activation by using different terpene-derived carbene precursors. To our delight, in most cases, the reaction product **2a** could be obtained. Catalysts with an *N*-phenyl substituent were ineffective (Table 1, entries 1, 4, 6, 9, and 13), likely due to the orthosubstitution effects [49]. Similar observations with NHCs lacking orthosubstituted aromatics were reported in several studies [50,51]. We were encouraged to find that, in the presence of spirocyclic camphor-derived pre-NHCs (**C**, **D**), the desired coumaranone with fully substituted quaternary stereogenic centers **2a** could be obtained with moderate yield and selectivity (Table 1, entries 3 and 5). Replacing the *N*-mesityl substituent of the NHC catalyst **C** with a pentafluorophenyl unit led to the formation of **2a** with excellent yield, though slight erosion of enantiomeric excess was observed (Table 1, entry 2). Similar results were obtained using fenchone-derived NHCs (**F**, **G**, **H**) (Table 1, entries 6–8). We next evaluated triazolium NHC catalysts derived from camphor **J–L**, which displayed significantly better outcomes (Table 1, entries 10–12). Gratifyingly, the desired product **2a** was obtained in 98% yield with 84% ee when the precatalyst **L**, bearing a 2,4,6-trichlorophenyl *N*-substituent, was employed (entry 12). Pinene-derived triazolium salt **N** with a pentafluorophenyl moiety promoted the intramolecular Stetter reaction to give 2,2-disubstituted coumaranone **2a** with excellent control of the enantioselectivity of the process (Table 1, entry 14).

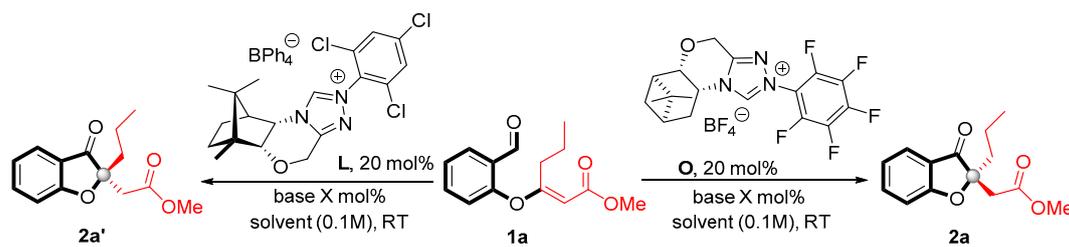
Table 1. NHC catalyst screening <sup>a</sup>.

Entry	NHC Precat.	Yield (%) <sup>b</sup>	ee <sup>c</sup>
1	A	<5	ND
2	B	97	38
3	C	37	48
4	D	<5	ND
5	E	31	42
6	F	<5	ND
7	G	98	20
8	H	24	28
9	I	<5	ND
10	J	27	-80
11	K	98	-74
12	L	98	-84
13	M	<5	ND
14	N	97	94
15	O	<5	ND

<sup>a</sup> Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol), triethylamine 200 mol%, toluene 1 mL (0.1 M). <sup>b</sup> Isolated yields. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase.

Taking into account the very promising results in terms of stereoselectivity and the fact that precatalysts **L** and **O** gave products with opposite stereochemical configurations, further work was carried out using camphor-derived NHC **L** and **O** pinene-derived NHC precursors.

With the catalyst screening accomplished, further optimization studies were undertaken (Table 2). Various reaction parameters, including base (Table 2, entries 1–23), solvent (entries 24–37), and reaction time, were evaluated.

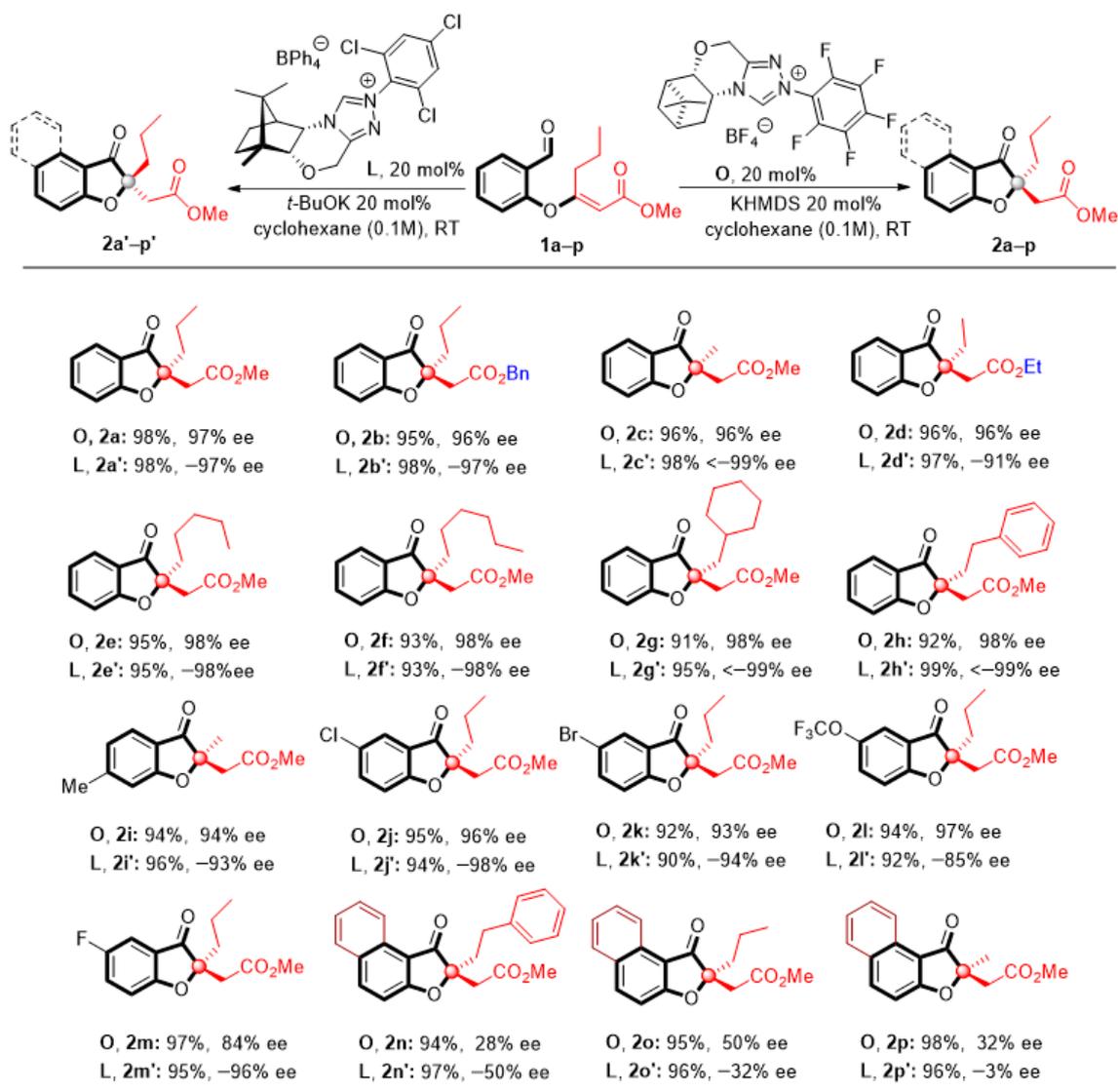
Table 2. Optimization of the reaction conditions <sup>a</sup>.


Entry	NHC Precat.	Solvent	Base	mol%	Time (h)	Yield (%) <sup>b</sup>	ee <sup>c</sup>
1	L	Toluene	NEt <sub>3</sub>	200	20	98	−84
2	O	Toluene	NEt <sub>3</sub>	200	20	98	94
3	L	Toluene	NEt <sub>3</sub>	20	20	98	−84
4	O	Toluene	NEt <sub>3</sub>	20	20	96	94
5	L	Toluene	DIPEA	20	20	97	−89
6	O	Toluene	DIPEA	20	20	98	89
7	L	Toluene	DCyEA	20	20	97	−90
8	O	Toluene	DCyEA	20	20	97	93
9	L	Toluene	DMAP	20	20	91	−88
11	O	Toluene	DMAP	20	20	89	92
12	L	Toluene	TBD	20	0.5	98	−92
13	O	Toluene	TBD	20	20	51	92
14	L	Toluene	P <sub>2</sub> -Et	20	0.5	99	−92
15	O	Toluene	P <sub>2</sub> -Et	20	0.5	99	92
16	L	Toluene	KHMDS	20	0.5	99	−89
17	O	Toluene	KHMDS	20	0.5	99	94
18	L	Toluene	<i>t</i> -BuOK	20	0.5	98	−94
19	O	Toluene	<i>t</i> -BuOK	20	20	98	94
20	L	Toluene	BEMP	20	0.3	98	−86
21	O	Toluene	BEMP	20	0.3	98	92
22	L	Toluene	PEMP	20	3	99	−92
23	O	Toluene	PEMP	20	20	98	93
24	L	<i>o</i> -Xylene	<i>t</i> -BuOK	20	20	99	−92
25	O	<i>o</i> -Xylene	KHMDS	20	20	90	84
26	L	THF	<i>t</i> -BuOK	20	24	84	−93
27	O	THF	KHMDS	20	24	82	92
28	L	CPME	<i>t</i> -BuOK	20	0.5	99	−94
29	O	CMPE	KHMDS	20	0.5	99	94
30	L	TAME	<i>t</i> -BuOK	20	0.5	98	−93
31	O	TAME	KHMDS	20	0.5	98	96
32	L	Cyclohexane	<i>t</i> -BuOK	20	0.5	98	−97
33	O	Cyclohexane	KHMDS	20	0.5	98	97
34	L	MTBE	<i>t</i> -BuOK	20	0.5	96	−95
35	O	MTBE	KHMDS	20	0.5	97	96
36	L	EtOH	<i>t</i> -BuOK	20	48	–	–
37	O	EtOH	KHMDS	20	48	–	–

<sup>a</sup> Unless otherwise noted, all reactions were carried out with the **1a** (0.1 mmol), precatalyst **L**, **O** 20 mol%, base 20 mol% in 0.1 M in solvent (1 mL), and at room temperature. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase. BEMP: 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; DCyEA: dicyclohexylethylamine; CMPE: cyclopentyl methyl ether; TAME: *tert*-amyl methyl ether.

As can be seen from Table 2, all bases used in this model reaction were well tolerated, giving the benzofuran-3(2*H*)-one derivative **2a** and **2a'** in high yields with excellent enantioselectivities. Initially, the reaction was conducted with 200 mol% of triethylamine. The reaction product **2a** was formed in full conversion after 6 h for the precatalyst **L** and after 20 h for the precatalyst **O** (Table 1, entry 1, 2). Fortunately, for both triazolium salts, **L** and **O**, the base loading could be reduced to 20 mol% and so undesired reactions with bases stronger than triethylamine were avoided. The corresponding benzofuranones, **2a** and **2a'**, were obtained with the same level of yield and enantioselectivity (Table 2, entries 3 and 4). It is worth noting that for both triazolium salts, the use of organic bases (such as  $P_2$ -Et, KHMDS, BEMP, *t*-BuOK) had a significant effect on reaction time, affording the desired Stetter products, **2a** and **2a'**, within 30 min, without erosion of the ee value (Table 2, entries 14–21). Among the various solvents screened, the reactions in nonpolar solvents, such as TAME, MTBE, and CMPE, resulted in comparable results (entries 28–31, 34, 35), whereas after reaction in polar ethanol, the desired coumaranone-type products were not observed. Gratifyingly, the enantioselectivity slightly increased to 97% ee for both NHC precatalysts with cyclohexane as a solvent. These observations enabled us to identify the final reaction parameters (Table 2, entries 32, 33).

Next, the generalizability of the reaction was verified by engaging a variety of coumarone-type products. Generally, the reaction reached completion within 3 h and gave the products in high yields, with good to excellent enantioselectivity at room temperature. As shown in Table 3 (**2a–2h**, **2a'–2h'**), a wide range of aliphatic substituents located in the double bonds of the substrates could be converted into products of uniformly high efficiency and selectivity. In addition, different ester groups, such as benzyl and ethyl, were also accommodated (Table 3, **2b**, **2b'**, **2d**, **2d'**). Furthermore, various substituted salicylaldehyde-derived substrates **1i–1m**, including those bearing electron-withdrawing and electron-donating substituents at different positions on the aromatic ring, could be tolerated and gave the corresponding compounds **2i–2m**, **2i'–2m'** in high yields and with excellent enantioselectivities. The electronic effects of the substituents did not have much influence on the outcome of the reaction. Of particular interest is the fact that simply changing the carbenes generated in situ from triazolium salts **L** or **O**, it is possible to affect chirality switching and select the product with the desired stereochemical configuration. We were surprised to find that, despite the structural differences between the camphor-derived **L** and pinene-derived **O** triazolium salts, both catalyzed the Stetter reaction and promoted opposite but high enantiofacial selectivity. The catalytic system also proved to be efficient when **2n–p**, **2n'–p'** contained a naphthyl substituent, producing distinct naphthofuranones with high yields (94–98%), albeit with reduced enantioselectivity. Interestingly, for the NHC precatalyst **L**, reduction of the enantiomeric excess occurred along with a decrease in the substituent at the double bond. In particular, 3% ee was observed where the product **2p'** had a methyl substituent. This method represents a unique NHC-catalyzed asymmetric intramolecular Stetter reaction with the use of  $\beta,\beta$ -disubstituted Michael acceptors to access enantioenriched all-carbon quaternary 2,2-disubstituted coumaranones and naphthofuranones.

Table 3. Scope of coumaranones and naphthofuranones <sup>a</sup>.

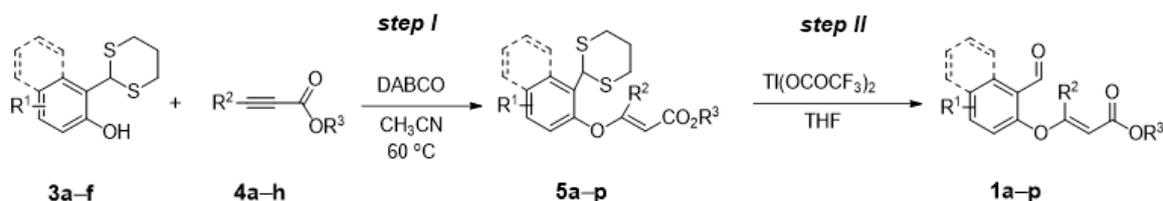
<sup>a</sup> Unless otherwise noted, all reactions were carried out with the substrate (0.2 mmol), NHC precatalyst **L** 20 mol%, potassium tert-butoxide 20 mol% in cyclohexane (2 mL) at RT for 3 h. NHC precatalyst **O** 20 mol%, KHMDS 20 mol% in cyclohexane (2 mL) at RT for 3 h. Yields of isolated product after column chromatography. The ee values were determined by HPLC analysis using a chiral stationary phase.

### 3. Materials and Methods

Reactions involving moisture-sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques. All glassware used was flame-dried and cooled under a vacuum. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System (INERT) and degassed via three freeze-pump-thaw cycles. All other commercial reagents were used as supplied without further purification, unless stated otherwise. The crude compounds were purified by a Combiflash Rf chromatography system (Teledyne Technologies, Inc., Thousand Oaks, CA, USA) unless specified otherwise. Analytical thin-layer chromatography was performed on pre-coated aluminum plates (Kieselgel 60 F<sub>254</sub> silica). TLC visualization was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous KMnO<sub>4</sub> solution. NMR spectra were recorded on Bruker AMX 400 and 700 (Bruker, Karlsruhe, Germany) spectrometers and referenced to the solvent residual peak. Elemental analyses were performed on a Vario MACRO CHN analyzer (Elementar Analysensysteme GmbH, Langensfeld, Germany). Optical rotations ([ $\alpha$ ]<sub>D</sub>) were measured on

a PolAAR 3000 (Optical Activity Ltd., Cambridgeshire, UK) polarimeter. IR spectra were recorded on a Bruker Alfa spectrometer and are reported in terms of frequency of absorption  $\text{cm}^{-1}$ . Mass spectra were collected on a Shimadzu HPLC Chromatograph/Mass Spectrometer LCMS-8030 (Shimadzu, Kyoto, Japan), (ESI, operating in positive mode). Enantiomeric excesses were determined by HPLC analysis on chiral stationary phase using 4.6 mm  $\times$  250 mm Phenomenex Lux Cellulose-1 and Luz Amylose-1 with *n*-hexane, 2-propanol as eluent.

All other reagents were purchased from commercial suppliers. Catalysts A–O were prepared according to the known method [44–47]. Salicylaldehyde-derived substrates 1a–1p were prepared by using two-step procedure (Scheme 1). The spectra of NMR and HPLC are in Supplementary Materials.



**Scheme 1.** Synthesis of salicylaldehyde-derived substrates 1a–p.

### 3.1. General Procedure for the Preparation of Compounds 1a–p

**Step I:** To a solution of dithiane [52] (5.2 mmol) in acetonitrile (52 mL), DABCO (0.58 g, 5.2 mmol) was added. After stirring for 10 min, alkyne derivative (10.4 mmol, 2 equiv.) was added and the mixture was stirred at 60 °C overnight. After completion (monitored by TLC), most of the acetonitrile was evaporated, then water was added to the solution and the mixture was extracted with ethyl acetate. The combined ethyl acetate extract was washed with brine, dried over anhydrous  $\text{MgSO}_4$  and then concentrated under reduced pressure. The crude product was purified by flash chromatography.

**Step II:** To a solution of dithane (3.0 mmol) in tetrahydrofuran (25 mL), thallium trifluoroacetate (3.3 g, 6.0 mmol, 2 equiv.) was added and the resulting cloudy solution was stirred until reaction was judged to be complete by TLC. The reaction mixture was then filtered through a Cellite pad and the resulting solution was concentrated in vacuo. The desired product was purified by decanting from a solution of petroleum ether, or a mixture of pentane and diethyl ether.

**Methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (5a).** The title compound was prepared according to the general procedure (Step I) using 2-(1,3-dithian-2-yl)phenol (3a) (5.0 g, 21.2 mmol) and methyl hex-2-ynoate (4a). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give 5a (4.60 g, 64%) as a white solid. M.p. = 63–65 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.13 (t,  $J$  = 8.0 Hz, 3H), 1.81–1.90 (m, 2H), 1.92–1.99 (m, 1H), 2.15–2.20 (m, 1H), 2.88–2.90 (m, 1H), 2.92–2.94 (m, 1H), 3.00–3.07 (m, 4H), 3.63 (s, 3H), 4.85 (s, 1H), 5.30 (s, 1H), 6.97 (dd,  $J$  = 8.0, 4.0 Hz, 1H), 7.20 (dt,  $J$  = 7.2, 1.6 Hz, 1H), 7.33 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 7.71 (dd,  $J$  = 7.6, 1.6 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.9, 21.0, 25.1, 32.3 (2C), 33.0, 44.2, 50.8, 96.1, 122.1, 126.4, 129.7, 129.9, 131.6, 149.6, 167.6, 175.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2958, 2933, 2896, 1710, 1632, 1484, 1432, 1373, 1276, 1246, 1129, 1088, 1041, 938, 830, 822, 750, 670. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{17}\text{H}_{22}\text{O}_3\text{S}_2\text{Na}$ : 361.1; found 361.2. Anal. Calcd. for  $\text{C}_{17}\text{H}_{22}\text{O}_3\text{S}_2$ : C, 60.32; H, 6.55; found: C, 60.37; H, 6.63.

**Benzyl (E)-3-(2-(1,3-dithian-2-yl)-5-phenoxy)but-2-enoate (5b).** The title compound was prepared according to the general procedure (Step I) using 2-(1,3-dithian-2-yl)phenol (3a) (5.0 g, 21.2 mmol) and benzyl hex-2-ynoate (4b). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give 5b (4.67 g, 53%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.16 (t,  $J$  = 8.0 Hz, 3H), 1.86–1.95 (m, 3H), 2.12–2.18 (m, 1H), 2.90 (dt,  $J$  = 13.6, 4.0 Hz, 2H), 2.99–3.09 (m, 4H), 4.97 (s, 1H), 5.12 (s, 2H), 5.34 (s, 1H), 7.00 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.26 (dt,  $J$  = 6.4, 1.2 Hz, 1H), 7.29–7.36 (m, 6H), 7.74 (dd,  $J$  = 1.6 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 21.0, 25.2, 32.4 (2C), 33.2, 44.3, 65.5, 96.3, 122.1, 126.5, 128.0, 128.2 (2C), 128.5 (2C), 129.8, 130.0, 131.6, 136.4, 149.6, 167.1, 175.9. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2959,

2932, 1709, 1629, 1484, 1451, 1383, 1258, 1223, 1121, 1090, 1023, 833, 732, 696. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{23}H_{26}O_3S_2Na$ : 437.1; found 437.2. Anal. Calcd. for  $C_{23}H_{26}O_3S_2$ : C, 66.63; H, 6.32; found: C, 66.71; H, 6.42.

*Ethyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)pent-2-enoate (5d)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)phenol (**3a**) (5.0 g, 21.2 mmol) and ethyl pent-2-ynoate (**4d**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5d** (5.53 g, 77%) as a yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 1.22 (t,  $J = 7.2$  Hz, 3H), 1.38 (t,  $J = 7.6$  Hz, 3H), 1.88–1.98 (m, 1H), 2.14–2.19 (m, 1H), 2.88–2.93 (m, 2H), 3.00–3.07 (m, 4H), 4.10 (q,  $J = 7.2$  Hz, 2H), 4.84 (s, 1H), 5.31 (s, 1H), 6.99 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.25 (dt,  $J = 7.6, 1.2$  Hz, 1H), 7.32 (dt,  $J = 7.6, 1.6$  Hz, 1H), 7.71 (dd,  $J = 8.0, 1.6$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 12.1, 14.3, 24.8, 25.1, 32.3 (2C), 44.3, 59.6, 95.8, 122.1, 126.4, 129.7, 129.9, 131.6, 149.7, 167.2, 176.7. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2975, 2936, 1706, 1629, 1448, 1378, 1275, 1227, 1211, 1127, 1086, 1041, 1003, 832. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{17}H_{22}O_3S_2Na$ : 361.1; found 361.3. Anal. Calcd. for  $C_{17}H_{22}O_3S_2$ : C, 60.32; H, 6.55; found: C, 60.41; H, 6.50.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)oct-2-enoate (5e)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)phenol (**3a**) (5.0 g, 21.2 mmol) and methyl oct-2-ynoate (**4e**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5e** (3.96 g, 51%) as a yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 0.97 (t,  $J = 8.0$  Hz, 3H), 1.41–1.52 (m, 4H), 1.78–1.86 (m, 2H), 1.88–1.98 (m, 1H), 2.14–2.19 (m, 1H), 2.87–2.93 (m, 2H), 2.99–3.06 (m, 4H), 3.62 (s, 3H), 4.84 (s, 1H), 5.30 (s, 1H), 6.97 (dd,  $J = 8.0, 4.0$  Hz, 1H), 7.25 (dt,  $J = 8.0, 1.6$  Hz, 1H), 7.31 (dt,  $J = 7.6, 1.6$  Hz, 1H), 7.70 (dd,  $J = 7.6, 1.6$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 14.0, 22.6, 25.1, 27.4, 31.2, 31.6, 32.3 (2C), 44.2, 50.9, 95.6, 122.1, 126.4, 129.7, 129.9, 131.6, 149.7, 167.7, 176.0. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2953, 2928, 2854, 1711, 1634, 1428, 1367, 1244, 1213, 1134, 1093, 825. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{19}H_{26}O_3S_2Na$ : 389.1; found 389.3. Anal. Calcd. for  $C_{19}H_{26}O_3S_2$ : C, 58.59; H, 6.73; found: C, 58.66; H, 6.82.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)non-2-enoate (5f)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)phenol (**3a**) (5.0 g, 21.2 mmol) and methyl non-2-ynoate (**4f**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5f** (3.53 g, 41%) as a yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 0.93 (t,  $J = 8.0$  Hz, 3H), 1.37–1.41 (m, 4H), 1.48–1.55 (m, 2H), 1.77–1.85 (m, 2H), 1.92–1.98 (m, 1H), 2.14–2.20 (m, 1H), 2.88–2.93 (m, 2H), 2.99–3.06 (m, 4H), 3.62 (s, 3H), 4.83 (s, 1H), 5.29 (s, 1H), 6.96 (dd,  $J = 8.0, 4.0$  Hz, 1H), 7.25 (dt,  $J = 8.0, 1.6$  Hz, 1H), 7.31 (dt,  $J = 7.6, 1.6$  Hz, 1H), 7.70 (dd,  $J = 7.6, 1.6$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 14.0, 22.6, 25.1, 27.4, 31.2, 31.6, 32.3 (2C), 44.2, 50.9, 95.6, 122.1, 126.4, 129.7, 129.9, 131.6, 149.7, 167.7, 176.0. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2950, 2924, 2850, 1709, 1636, 1427, 1366, 1240, 1212, 1134, 1093, 825. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{20}H_{28}O_3S_2Na$ : 403.1; found 403.2. Anal. Calcd. for  $C_{20}H_{28}O_3S_2$ : C, 63.12; H, 7.42; found: C, 63.27; H, 7.58.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)-4-cyclohexylbut-2-enoate (5g)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)phenol (**3a**) (5.0 g, 21.2 mmol) and methyl 4-cyclohexylbut-2-ynoate (**4g**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5g** (3.53 g, 41%) as a yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 1.19–1.36 (m, 5H), 1.68–1.74 (m, 2H), 1.78–1.84 (m, 2H), 1.89–1.99 (m, 3H), 2.15–2.21 (m, 1H), 2.88–3.06 (m, 6H), 3.62 (s, 3H), 4.89 (s, 1H), 5.31 (s, 1H), 6.97 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.26 (dt,  $J = 7.6, 1.6$  Hz, 1H), 7.30 (dt,  $J = 7.6, 1.6$  Hz, 1H), 7.72 (dd,  $J = 7.6, 1.6$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 25.1, 26.4, 26.4 (2C), 32.3 (2C), 33.0 (2C), 36.7, 38.4, 44.1, 50.8, 96.4, 122.1, 126.4, 129.8, 130.0, 131.6, 149.6, 167.7, 174.7. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2920, 2850, 1713, 1630, 1447, 1430, 1373, 1274, 1258, 1194, 1170, 1134, 1104, 1040, 830. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{21}H_{28}O_3S_2Na$ : 415.1; found 415.3. Anal. Calcd. for  $C_{21}H_{28}O_3S_2$ : C, 64.25; H, 7.19; found: C, 64.31; H, 7.27.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)-5-phenylpent-2-enoate (5h)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)phenol (**3a**) (5.0 g, 21.2 mmol) and methyl 5-phenylpent-2-ynoate (**4h**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5h** (3.65 g, 43%) as a yellow solid. M.p. = 97–99 °C. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ: 1.90 (m, 1H), 2.13 (dspt, *J* = 14.2, 2.4 Hz, 1H), 2.87 (ddd, *J* = 14.6, 3.2, 0.9 Hz, 2H), 2.97 (m, 2.5 Hz, 2H), 3.10–3.14 (m, 2H), 3.28–3.40 (m, 2H), 3.63 (s, 3H), 4.86 (s, 1H), 5.24 (s, 1H), 6.87 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.22–7.26 (m, 2H), 7.28–7.31 (m, 1H), 7.32–7.35 (m, 2H), 7.36–7.39 (m, 2H), 7.70 (dd, *J* = 7.7, 1.7 Hz, 1H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ: 24.68, 31.86, 32.59, 33.18, 43.75, 50.60, 96.11, 121.64, 125.82, 126.14, 128.09, 128.19, 129.40, 129.60, 131.21, 140.49, 149.22, 167.16, 174.33. IR (ATR) ν (cm<sup>-1</sup>): 2920, 2850, 1713, 1630, 1447, 1430, 1373, 1274, 1258, 1194, 1170, 1134, 1104, 1040, 830. LRMS (ESI): Mass calcd. for [M + Na]<sup>+</sup> C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub>Na: 423.1; found 423.0. Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub>: C, 65.97; H, 6.04; found: C, 66.01 H, 6.11.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)-5-methylphenoxy)but-2-enoate (5i)*. The title compound was prepared according to the general procedure (*Step I*) using 2-(1,3-dithian-2-yl)-5-methylphenol (**3b**) (5.0 g, 21.2 mmol) and methyl but-2-ynoate (**4c**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5i** (6.17 g, 85%) as a yellow solid. M.p. = 108–109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.88–1.99 (m, 1H), 2.15–2.22 (m, 1H), 2.36 (s, 3H), 2.55 (s, 3H), 2.88–2.93 (m, 2H), 3.02–3.10 (m, 2H), 3.64 (s, 3H), 4.96 (s, 1H), 5.24 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 7.10–7.12 (m, 1H), 7.50 (d, *J* = 2.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 18.2, 20.8, 25.2, 32.4 (2C), 44.3, 50.9, 96.6, 121.8, 130.3, 130.4, 131.0, 136.3, 147.4, 168.0, 172.4. IR (ATR) ν (cm<sup>-1</sup>): 2949, 2927, 2822, 1706, 1629, 1493, 1434, 1383, 1340, 1257, 1122, 1094, 1041, 1004, 933, 876, 822. LRMS (ESI): Mass calcd. for [M + Na]<sup>+</sup> C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub>Na: 347.1; found 347.2. Anal. calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>S<sub>2</sub>: C, 59.23; H, 6.21; found: C, 59.31; H, 6.34.

*Methyl (E)-3-(4-chloro-2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (5j)*. The title compound was prepared according to the general procedure (*Step I*) using 4-chloro-2-(1,3-dithian-2-yl)phenol (**3c**) (5.0 g, 21.2 mmol) and methyl hex-2-ynoate (**4a**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5j** (6.17 g, 85%) as a white solid. M.p. 103–104 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.11 (t, *J* = 7.2 Hz, 3H), 1.78–1.87 (m, 2H), 1.91–1.99 (m, 1H), 2.14–2.20 (m, 1H), 2.86–2.94 (m, 2H), 2.97–3.05 (m, 4H), 3.65 (s, 3H), 4.84 (s, 1H), 5.23 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.69 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 13.8, 21.0, 25.0, 32.2 (2C), 32.9, 43.7, 51.0, 96.5, 123.4, 129.9, 130.0, 131.8, 133.4, 148.2, 167.4, 175.4. IR (ATR) ν (cm<sup>-1</sup>): 2954, 2888, 1711, 1625, 1479, 1436, 1370, 1226, 1210, 1126, 1102, 1080, 1037, 936, 828. LRMS (ESI): Mass calcd. for [M + Na]<sup>+</sup> C<sub>17</sub>H<sub>21</sub>ClO<sub>3</sub>S<sub>2</sub>Na: 395.0; found 395.1. Anal. Calcd. for C<sub>17</sub>H<sub>21</sub>ClO<sub>3</sub>S<sub>2</sub>: C, 54.75; H, 5.68; found: C, 54.88; H, 5.72.

*Methyl (E)-3-(4-bromo-2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (5k)*. The title compound was prepared according to the general procedure (*Step I*) using 4-bromo-2-(1,3-dithian-2-yl)phenol (**3d**) (5.0 g, 21.2 mmol) and methyl hex-2-ynoate (**4a**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5k** (6.19 g, 70%) as a white solid. M.p. 87–89 °C. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ: 1.12 (t, *J* = 7.7 Hz, 3H), 1.82–1.97 (m, 1H), 2.18–2.20 (m, 1H), 2.92–2.95 (m, 2H), 3.00–3.05 (m, 4H), 3.65 (s, 3H), 4.85 (s, 1H), 5.24 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.44–7.46 (m, 1H), 7.85 (d, *J* = 2.1 Hz, 1H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ: 14.9, 22.0, 26.0, 33.2 (2C), 33.9, 44.6, 52.0, 97.6, 120.4, 124.8, 133.8, 134.0, 134.8, 149.8, 168.4, 176.4. IR (ATR) ν (cm<sup>-1</sup>): 2957, 2933, 1710, 1626, 1477, 1436, 1369, 1226, 1209, 1125, 1102, 1079, 1035, 934, 829. LRMS (ESI): Mass calcd. for [M + Na]<sup>+</sup> C<sub>17</sub>H<sub>21</sub>BrO<sub>3</sub>S<sub>2</sub>Na: 439.0; found 439.1. Anal. Calcd. for C<sub>17</sub>H<sub>21</sub>BrO<sub>3</sub>S<sub>2</sub>: C, 49.92; H, 5.07; found: C, 50.02; H, 5.17.

*Methyl (E)-3-(2-(1,3-dithian-2-yl)-4-(trifluoromethoxy)phenoxy)hex-2-enoate (5l)*. The title compound was prepared according to the general procedure (*Step I*) using 4-trifluoromethoxy-2-(1,3-dithian-2-yl)phenol (**3e**) (5.0 g, 21.2 mmol) and methyl hex-2-ynoate (**4a**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5l** (3.77 g, 42%) as a white solid. M.p. 57–60 °C. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ: 1.13 (t, *J* = 7.7 Hz, 3H), 1.82–1.88 (m, 2H), 1.92–1.96 (m, 1H), 2.17–2.20

(m, 1H), 2.91–2.94 (m, 2H), 3.00–3.06 (m, 4H), 3.65 (s, 3H), 4.86 (s, 1H), 5.27 (s, 1H), 7.01 (d,  $J = 8.4$  Hz, 1H), 7.18–7.20 (m, 1H), 7.59 (d,  $J = 2.1$  Hz, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.8, 22.0, 25.9, 33.1 (2C), 33.9, 44.6, 52.0, 97.6, 121.0 (q,  $J = 258$  Hz), 123.2, 123.7, 124.3, 134.6, 147.8, 148.9, 168.4, 176.4. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2959, 2934, 2901, 1714, 1634, 1490, 1434, 1372, 1255, 1208, 1164, 1128, 1093, 1038, 937, 883, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{18}\text{H}_{21}\text{F}_3\text{O}_4\text{S}_2\text{Na}$ : 445.1; found 445.1. Anal. Calcd. for  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{O}_4\text{S}_2$ : C, 51.17; H, 5.01; found: C, 51.27; H, 5.10.

*Methyl (E)-3-(4-fluoro-2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (5m)*. The title compound was prepared according to the general procedure (*Step I*) using 4-fluoro-2-(1,3-dithian-2-yl)phenol (**3g**) (5.0 g, 21.1 mmol) and methyl hex-2-ynoate (**4a**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5m** (3.56 g, 47%) as a white solid. M.p. 75–78 °C.  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.11 (t,  $J = 7.2$  Hz, 3H), 1.78–1.87 (m, 2H), 1.91–1.99 (m, 1H), 2.14–2.20 (m, 1H), 2.86–2.94 (m, 2H), 2.97–3.05 (m, 4H), 3.65 (s, 3H), 4.84 (s, 1H), 5.23 (s, 1H), 6.92 (d,  $J = 8.8$  Hz, 1H), 7.28 (dd,  $J = 8.4, 2.4$  Hz, 1H), 7.69 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.8, 21.0, 25.0, 32.2 (2C), 32.9, 43.7, 51.0, 96.5, 123.4, 129.9, 130.0, 131.8, 133.4, 148.2, 167.4, 175.4. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2956, 2915, 1714, 1622, 1490, 1432, 1221, 1206, 1163, 1125, 1085, 1071, 1036, 1002, 965, 933, 874, 831. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{17}\text{H}_{21}\text{FO}_3\text{S}_2\text{Na}$ : 379.1; found 379.2. Anal. Calcd. for  $\text{C}_{17}\text{H}_{21}\text{FO}_3\text{S}_2$ : C, 57.28; H, 5.94; found: C, 57.40; H, 5.99.

*Methyl (E)-3-((1-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)-5-phenylpent-2-enoate (5n)* The title compound was prepared according to the general procedure (*Step I*) using 1-(1,3-dithian-2-yl)naphthalen-2-ol (**3f**) (5.0 g, 19.1 mmol) and methyl 5-phenylpent-2-ynoate (**4h**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5n** (3.93 g, 53%) as a white solid. M.p. 140–144 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.05–2.10 (m, 1H), 2.21–2.25 (m, 1H), 2.97 (t,  $J = 2.0$  Hz, 1H), 2.99 (t,  $J = 2.0$  Hz, 1H), 3.05–3.08 (m, 2H), 3.23–3.25 (m, 2H), 3.44–3.46 (m, 2H), 3.65 (s, 3H), 4.90 (s, 1H), 5.96 (s, 1H), 7.03 (d,  $J = 5.3$  Hz, 1H), 7.30 (t,  $J = 4.4$  Hz, 1H), 7.39–7.41 (m, 2H), 7.46 (m, 2H), 7.53–7.55 (m, 1H), 7.63–7.65 (m, 1H), 7.82 (d,  $J = 5.2$  Hz, 1H), 7.85 (d,  $J = 4.4$  Hz, 1H), 9.24 (d,  $J = 4.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 25.7, 33.0, 33.2 (2C), 33.8, 45.4, 51.0, 97.4, 120.7, 125.7, 126.0, 126.1, 126.3, 127.4, 128.4, 128.5 (2C), 128.6 (2C), 130.9, 132.4, 132.5, 140.8, 147.0, 167.5, 174.2. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 3026, 2980, 2899, 1710, 1632, 1432, 1365, 1232, 1215, 1185, 1161, 1150, 1113, 1046, 1008, 931, 838, 828. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{26}\text{H}_{26}\text{O}_3\text{S}_2\text{Na}$ : 473.1; found 473.3. Anal. Calcd. for  $\text{C}_{26}\text{H}_{26}\text{O}_3\text{S}_2$ : C, 69.30; H, 5.82; found: C, 69.41; H, 5.87.

*Methyl (E)-3-((1-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)hex-2-enoate (5o)*. The title compound was prepared according to the general procedure (*Step I*) using 1-(1,3-dithian-2-yl)naphthalen-2-ol (**3f**) (5.0 g, 19.1 mmol) and methyl hex-2-ynoate (**4a**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5o** (2.37 g, 32%) as a yellow solid. M.p. 108–109 °C.  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.19 (t,  $J = 7.7$  Hz, 3H), 1.95–1.97 (m, 2H), 2.08–2.12 (m, 1H), 2.26–2.28 (m, 1H), 2.98–3.02 (m, 2H) 3.08–3.13 (m, 4H), 3.62 (s, 3H), 4.86 (s, 1H), 5.97 (s, 1H), 7.11 (d,  $J = 9.1$  Hz, 1H), 7.51–7.54 (m, 1H), 7.61–7.63 (m, 1H), 7.82 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 8.4$  Hz, 1H), 9.20 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 15.0, 22.2, 26.7, 34.0, 34.2 (2C), 46.4, 51.9, 98.0, 121.8, 126.7, 127.0, 127.1, 128.4, 129.4, 131.9, 133.4, 133.5, 148.0, 168.6, 176.2. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2967, 2939, 1710, 1625, 1509, 1431, 1368, 1273, 1257, 1129, 1080, 830. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{21}\text{H}_{24}\text{O}_3\text{S}_2\text{Na}$ : 411.1; found 411.2. Anal. Calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_3\text{S}_2$ : C, 64.92; H, 6.23; found: C, 65.01; H, 6.37.

*Methyl (E)-3-((3-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)but-2-enoate (5p)*. The title compound was prepared according to the general procedure (*Step I*) using 1-(1,3-dithian-2-yl)naphthalen-2-ol (**3f**) (5.0 g, 19.1 mmol) and methyl but-2-ynoate (**4c**). The product was purified by flash chromatography (petroleum ether/EtOAc 8:2) to give **5p** (3.02 g, 44%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.03–2.13 (m, 1H), 2.21–2.29 (m, 1H), 2.62 (s, 3H), 2.96–3.02 (m, 2H), 3.10–3.16 (m, 2H), 3.63 (s, 3H), 4.96 (s, 1H), 5.94 (s, 1H), 7.12 (d,  $J = 8.8$  Hz, 1H), 7.49–7.53 (m, 1H), 7.59–7.63 (m, 1H), 7.80–7.84 (m, 2H), 9.21 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.2, 25.7, 33.3 (2C), 45.5, 50.9, 97.7, 120.8, 125.6,

125.9, 126.0, 127.4, 128.4, 130.8, 132.3, 132.4, 147.2, 167.9, 171.6. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2951, 2908, 1706, 1638, 1620, 1508, 1345, 1248, 1213, 1144, 1128, 1016, 930 856, 831. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{19}\text{H}_{20}\text{O}_3\text{S}_2\text{Na}$ : 383.1; found 383.2. Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{S}_2$ : C, 63.31; H, 5.59; found: C, 63.40; H, 5.70.

**Methyl (E)-3-(2-formylphenoxy)hex-2-enoate (1a).** The title compound was prepared according to the general procedure (*Step II*) using methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (**5a**) (1.0 g, 3.0 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 94% yield (0.70 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.09 (t,  $J = 8.0$  Hz, 3H), 1.77–1.86 (m, 2H), 2.99–3.03 (m, 2H), 3.62 (s, 3H), 4.81 (s, 1H), 7.10 (dd,  $J = 8.0, 0.8$  Hz, 1H), 7.35–7.39 (m, 1H), 7.65 (dddd,  $J = 15.6, 9.2, 7.6, 2.0$  Hz, 1H), 7.95 (dd,  $J = 8.0, 2.0$  Hz, 1H), 10.16 (d,  $J = 0.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.9, 20.8, 33.0, 51.0, 97.3, 122.8, 126.2, 128.4, 129.0, 135.9, 155.7, 167.0, 176.4, 188.1. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2951, 2929, 1715, 1696, 1629, 1600, 1455, 1434, 1371, 1236, 1187, 1097, 1042, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}$ : 271.1; found 271.2. Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 67.73; H, 6.50; found: C, 67.82; H, 6.66.

**Benzyl (E)-3-(2-formylphenoxy)hex-2-enoate (1b).** The title compound was prepared according to the general procedure (*Step II*) using benzyl (E)-3-(2-(1,3-dithian-2-yl)-5-phenoxy)but-2-enoate (**5b**) (1.2 g, 3.0 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 90% yield (0.70 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.08 (t,  $J = 7.4$  Hz, 4H), 1.81 (sxtt,  $J = 7.6, 1.7$  Hz, 2H), 2.99–3.03 (m, 2H), 4.84 (s, 1H), 5.07 (s, 2H), 7.08 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.29–7.34 (m, 6H), 7.63 (ddd,  $J = 8.2, 7.3, 1.7$  Hz, 1H), 7.94 (ddd,  $J = 7.7, 1.8, 0.3$  Hz, 1H), 10.15 (d,  $J = 0.8$  Hz, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.6, 20.5, 32.8, 65.4, 96.9, 122.5, 125.9, 127.8, 128.0, 128.2, 128.7, 135.6, 135.7, 155.2, 166.1, 176.4, 187.6, 187.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2946, 2932, 1711, 1692, 1633, 1598, 1455, 1430, 1373, 1235, 1189, 1100, 1042, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Na}$ : 347.1; found 347.2. Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{O}_4$ : C, 74.06; H, 6.22; found: C, 74.15; H, 6.34.

**Methyl (E)-3-(2-formylphenoxy)but-2-enoate (1c).** The title compound was prepared according to the general procedure (*Step II*) using methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)but-2-enoate (**5c**) (0.93 g, 3.0 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 95% yield (0.63 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.57 (d,  $J = 0.6$  Hz, 3H), 3.63 (s, 3H), 4.84 (d,  $J = 0.6$  Hz, 1H), 7.11 (dd,  $J = 8.2, 1.0$  Hz, 1H), 7.36–7.39 (m, 1H), 7.65 (ddd,  $J = 8.1, 7.4, 1.7$  Hz, 1H), 7.94 (dd,  $J = 7.7, 1.8$  Hz, 1H), 10.12–10.14 (m, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 17.7, 50.7, 97.2, 122.4, 126.0, 127.8, 128.9, 135.5, 155.0, 166.9, 172.5, 187.7, 187.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2946, 1713, 1694, 1636, 1602, 1457, 1428, 1375, 1232, 1189, 1100, 1045, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Na}$ : 243.1; found 243.2. Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{O}_4$ : C, 65.45; H, 6.49; found: C, 65.54; H, 6.48.

**Ethyl (E)-3-(2-formylphenoxy)pent-2-enoate (1d).** The title compound was prepared according to the general procedure (*Step II*) using ethyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)pent-2-enoate (**5d**) (1.0 g, 3.0 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 92% yield (0.68 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.19–1.22 (m, 3H), 1.31–1.35 (m, 3H), 3.03 (q,  $J = 7.5$  Hz, 2H), 4.08 (q,  $J = 7.1$  Hz, 2H), 4.74 (s, 1H), 7.10 (dd,  $J = 8.2, 0.9$  Hz, 1H), 7.35–7.39 (m, 1H), 7.65 (ddd,  $J = 8.2, 7.3, 1.7$  Hz, 1H), 7.95 (dd,  $J = 7.7, 1.7$  Hz, 1H), 10.16 (d,  $J = 0.9$  Hz, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.4, 13.8, 24.4, 59.4, 96.6, 122.4, 125.9, 128.0, 128.5, 135.6, 155.4, 166.2, 177.1, 187.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2940, 1710, 1691, 1629, 1600, 1453, 1428, 1373, 1232, 1189, 1110, 1045, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}$ : 271.1; found 271.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 67.73; H, 6.50; found: C, 67.70; H, 6.59.

**Methyl (E)-3-(2-formylphenoxy)oct-2-enoate (1e).** The title compound was prepared according to the general procedure (*Step II*) using methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)oct-2-enoate (**5e**) (1.0 g, 2.72 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 85% yield (0.64 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.93 (t,  $J = 7.2$  Hz, 3H), 1.37–1.47 (m, 4H), 1.74–1.79 (m, 2H), 2.98–3.02 (m, 2H), 3.61 (s, 3H), 4.78 (s, 1H), 7.08 (dd,  $J = 8.2, 1.0$  Hz, 1H), 7.35–7.38 (m, 1H), 7.64 (ddd,  $J = 8.2, 7.4,$

1.8 Hz, 1H), 7.95 (dd,  $J = 7.8, 1.8$  Hz, 1H), 10.15 (d,  $J = 0.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 22.4, 27.1, 31.2, 31.6, 51.0, 97.1, 122.8, 126.3, 128.4, 128.9, 135.9, 155.8, 167.0, 176.8, 188.1. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2951, 2929, 2857, 1715, 1696, 1629, 1600, 1455, 1434, 1371, 1272, 1236, 1187, 1110, 1045, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{16}\text{H}_{20}\text{O}_4\text{Na}$ : 299.1; found 299.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 69.55; H, 7.30; found: C, 69.60; H, 7.42.

**Methyl (E)-3-(2-formylphenoxy)non-2-enoate (1f).** The title compound was prepared according to the general procedure (*Step II*) using methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)non-2-enoate (**5f**) (1.0 g, 2.63 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 82% yield (0.63 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.93 (t,  $J = 7.1$  Hz, 3H), 1.35–1.40 (m, 4H), 1.43–1.53 (m, 2H), 1.73–1.82 (m, 2H), 2.99–3.05 (m, 2H), 3.63 (s, 3H), 4.80 (s, 1H), 7.10 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.35–7.40 (m, 1H), 7.66 (ddd,  $J = 8.2, 7.3, 1.8$  Hz, 1H), 7.96 (dd,  $J = 7.8, 1.7$  Hz, 1H), 10.17 (d,  $J = 0.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 22.6, 27.4, 29.1, 31.2, 31.6, 51.0, 97.2, 122.8, 126.2, 128.4, 129.0, 135.9, 155.8, 167.0, 176.8, 188.1. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2950, 2929, 2855, 1717, 1694, 1632, 1602, 1455, 1434, 1374, 1272, 1236, 1187, 1113, 1045, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{17}\text{H}_{22}\text{O}_4\text{Na}$ : 313.1; found 313.2. Anal. Calcd. for  $\text{C}_{17}\text{H}_{22}\text{O}_4$ : C, 70.32; H, 7.64; found: C, 70.28; H, 7.74.

**Methyl (E)-4-cyclohexyl-3-(2-formylphenoxy)but-2-enoate (1g).** The title compound was prepared according to the general procedure (*Step II*) methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)-4-cyclohexylbut-2-enoate (**5g**) (1.0 g, 2.55 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 87% yield (0.67 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.90 (t,  $J = 7.0$  Hz, 3H), 1.13–1.30 (m, 5H), 1.65–1.89 (m, 5H), 2.93 (d,  $J = 7.0$  Hz, 2H), 3.60 (s, 3H), 4.85 (s, 1H), 7.07 (d,  $J = 7.0$  Hz, 1H), 7.34 (m, 1H), 7.63 (m, 1H), 7.93 (dd,  $J = 14.0, 7.0$  Hz, 1H), 10.01 (s, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 25.8 (2C), 25.9, 32.7 (2C), 36.2, 37.8, 50.6, 97.8, 122.3, 125.8, 127.9, 128.5, 135.5, 155.4, 166.7, 175.0, 187.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2950, 2929, 1710, 1691, 1632, 1602, 1457, 1435, 1372, 1274, 1236, 1187, 1113, 1047, 830. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Na}$ : 325.1; found 325.3. Anal. Calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_4$ : C, 71.50; H, 7.33; found: C, 71.56; H, 7.45.

**Methyl (E)-3-(2-formylphenoxy)-5-phenylpent-2-enoate (1h).** The title compound was prepared according to the general procedure (*Step II*) methyl (E)-3-(2-(1,3-dithian-2-yl)phenoxy)-5-phenylpent-2-enoate (**5h**) (1.0 g, 2.50 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 93% yield (0.72 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.11 (dd,  $J = 9.0, 6.6$  Hz, 8H), 3.36 (dd,  $J = 9.8, 6.6$  Hz, 8H), 3.65 (s, 3H), 4.81 (s, 1H), 6.97 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.23–7.28 (m, 1H), 7.33–7.40 (m, 5H), 7.64 (ddd,  $J = 8.2, 7.3, 1.8$  Hz, 1H), 7.95 (dd,  $J = 7.8, 1.7$  Hz, 1H), 10.00 (d,  $J = 0.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 33.0, 33.4, 51.1, 97.6, 122.8, 126.3, 126.4, 128.5, 128.6, 129.1, 136.0, 140.5, 155.5, 166.9, 175.5, 188.1. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2954, 2932, 1714, 1689, 1634, 1600, 1455, 1433, 1373, 1272, 1236, 1187, 1111, 1044, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$ : 333.1; found 333.1. Anal. Calcd. for  $\text{C}_{19}\text{H}_{18}\text{O}_4$ : C, 73.53; H, 5.85; found: C, 73.61; H, 5.89.

**Methyl (E)-3-(2-formyl-5-methoxyphenoxy)but-2-enoate (1i).** The title compound was prepared according to the general procedure (*Step II*) methyl (E)-3-(2-(1,3-dithian-2-yl)-5-methoxyphenoxy)but-2-enoate (**5i**) (1.0 g, 2.94 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 95% yield (0.70 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.42 (s, 3H), 2.57 (d,  $J = 0.5$  Hz, 3H), 3.64 (s, 3H), 4.84 (d,  $J = 0.5$  Hz, 1H), 7.01 (d,  $J = 8.3$  Hz, 1H), 7.41–7.50 (m, 1H), 7.74 (d,  $J = 2.2$  Hz, 1H), 10.10 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.1, 20.7, 51.0, 97.3, 122.7, 127.8, 129.3, 136.4, 136.7, 153.3, 167.4, 173.2, 188.4. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2955, 2931, 1711, 1691, 1632, 1601, 1456, 1433, 1373, 1269, 1234, 1187, 1113, 1045, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{13}\text{H}_{14}\text{O}_5\text{Na}$ : 273.1; found 273.1. Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{O}_5$ : C, 62.39; H, 5.64; found: C, 62.47; H, 5.72.

**Methyl (E)-3-(4-chloro-2-formylphenoxy)hex-2-enoate (1j).** The title compound was prepared according to the general procedure (*Step II*) methyl (E)-3-(4-chloro-2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (**5j**) (1.0 g, 2.68 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 91% yield (0.69 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.08 (t,  $J = 7.0$  Hz, 3H), 1.77 (m, 2H), 2.97–2.99 (m, 2H),

3.62 (s, 3H), 4.80 (s, 1H), 7.03 (d,  $J = 7.0$  Hz, 1H), 7.58 (dd,  $J = 9.1, 3.5$  Hz, 1H), 7.89 (d,  $J = 2.1$  Hz, 1H), 10.07 (s, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.4, 20.4, 32.5, 50.7, 97.4, 123.9, 128.2, 128.9, 131.9, 131.8, 135.4, 153.7, 166.4, 175.8, 186.4. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2953, 2930, 1705, 1690, 1632, 1600, 1456, 1433, 1373, 1265, 1230, 1187, 1113, 1045, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{14}\text{H}_{15}\text{ClO}_4\text{Na}$ : 305.1; found 305.2. Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{ClO}_4$ : C, 59.48; H, 5.35; found: C, 59.56; H, 5.41.

*Methyl (E)-3-(4-bromo-2-formylphenoxy)hex-2-enoate (1k)*. The title compound was prepared according to the general procedure (*Step II*) methyl (*E*)-3-(4-bromo-2-(1,3-dithian-2-yl)phenoxy)hex-2-enoate (**5k**) (1.0 g, 2.40 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 90% yield (0.70 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.08 (t,  $J = 7.3$  Hz, 3H), 1.80 (dq,  $J = 15.0, 7.5$  Hz, 1H), 2.97–3.03 (m, 2H), 4.83 (s, 1H), 3.65 (s, 3H), 7.01 (d,  $J = 8.6$  Hz, 1H), 7.75 (dd,  $J = 8.7, 2.6$  Hz, 1H), 8.07 (d,  $J = 2.4$  Hz, 1H), 10.09 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.8, 20.8, 32.9, 51.1, 97.9, 119.7, 124.6, 129.6, 131.7, 138.7, 154.6, 166.8, 176.1, 186.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2953, 1701, 1692, 1632, 1600, 1456, 1433, 1371, 1263, 1232, 1184, 1110, 1044, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{14}\text{H}_{15}\text{BrO}_4\text{Na}$ : 349.0; found 349.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{BrO}_4$ : C, 51.40; H, 4.62; found: C, 51.48; H, 4.70.

*Methyl (E)-3-(2-formyl-4-(trifluoromethoxy)phenoxy)hex-2-enoate (1l)*. The title compound was prepared according to the general procedure (*Step II*) methyl (*E*)-3-(2-(1,3-dithian-2-yl)-4-(trifluoromethoxy)phenoxy)hex-2-enoate (**5l**) (1.0 g, 2.37 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 85% yield (0.67 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.10 (t,  $J = 7.3$  Hz, 3H), 1.81 (sxt,  $J = 7.5$  Hz, 1H), 2.97–3.04 (m, 2H), 3.66 (s, 3H), 4.85 (s, 1H), 7.17 (d,  $J = 8.8$  Hz, 1H), 7.50 (ddd,  $J = 8.9, 3.1, 0.7$  Hz, 1H), 7.80 (dd,  $J = 2.9, 1.0$  Hz, 1H), 10.13 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.8, 20.8, 32.9, 51.1, 98.1, 120.7, 124.4, 128.3, 129.4, 146.7–146.8 (m), 153.8, 166.7, 176.0, 186.5. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2950, 1704, 1690, 1635, 1603, 1458, 1431, 1370, 1262, 1231, 1184, 1110, 1044, 831. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_5\text{Na}$ : 355.1; found 355.1. Anal. Calcd. for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_5$ : C, 54.22; H, 4.55; found: C, 54.30; H, 4.67.

*Methyl (E)-3-(4-fluoro-2-formylphenoxy)hex-2-enoate (1m)*. The title compound was prepared according to the general procedure (*Step II*) methyl (*E*)-3-(2-(1,3-dithian-2-yl)-4-fluorophenoxy)hex-2-enoate (**5m**) (1.0 g, 2.80 mmol) and thallium (III) trifluoroacetate. The product was obtained as a colorless oil in 94% yield (0.70 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.09 (t,  $J = 8.0$  Hz, 3H), 1.78–1.84 (m, 2H), 2.98–3.02 (m, 2H), 3.64 (s, 3H), 4.79 (s, 1H), 7.10 (dd,  $J = 12.0, 8.0$  Hz, 1H), 7.34–7.39 (m, 1H), 7.62 (dd,  $J = 8.0, 4.0$  Hz, 1H), 10.08 (d,  $J = 4.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.8, 20.8, 32.9, 51.1, 97.5, 114.7 (d,  $J = 23.1$  Hz), 123.0 (d,  $J = 25.2$  Hz), 124.7 (d,  $J = 8.0$  Hz), 129.6 (d,  $J = 6.0$  Hz), 151.6 (d,  $J = 2.0$  Hz), 160.2 (d,  $J = 248.5$  Hz), 166.8, 176.6, 186.9 (d,  $J = 2.0$  Hz). IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2954, 1700, 1693, 1636, 1606, 1454, 1429, 1371, 1262, 1231, 1184, 1112, 1046, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{14}\text{H}_{15}\text{FO}_4\text{Na}$ : 289.1; found 289.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{FO}_4$ : C, 63.15; H, 5.68; found: C, 63.21; H, 5.79.

*Methyl (E)-3-((1-formylnaphthalen-2-yl)oxy)-5-phenylpent-2-enoate (1n)*. The title compound was prepared according to the general procedure (*Step II*) methyl (*E*)-3-((1-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)-5-phenylpent-2-enoate (**5n**) (1.0 g, 2.22 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 85% yield (0.68 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.12–3.19 (m, 2H), 3.38–3.45 (m, 2H), 3.64 (s, 3H), 4.88 (s, 1H), 7.02 (d,  $J = 9.0$  Hz, 1H), 7.23–7.33 (m, 1H), 7.34–7.44 (m, 4H), 7.59 (ddd,  $J = 8.1, 7.0, 1.2$  Hz, 1H), 7.71 (ddd,  $J = 8.6, 7.0, 1.3$  Hz, 1H), 7.88 (d,  $J = 8.1$  Hz, 1H), 8.09 (d,  $J = 8.8$  Hz, 1H), 9.27 (dd,  $J = 8.8, 0.7$  Hz, 1H), 10.44 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 32.9, 33.4, 51.1, 98.8, 120.8, 121.7, 125.6, 126.4, 126.8, 128.4, 128.5, 128.6, 129.9, 131.0, 131.6, 137.3, 140.4, 157.9, 166.8, 175.2, 190.6. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2951, 1703, 1690, 1635, 1604, 1456, 1429, 1371, 1262, 1231, 1184, 1110, 1048, 835. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{23}\text{H}_{20}\text{O}_4\text{Na}$ : 383.1; found 383.2. Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{O}_4$ : C, 76.65; H, 5.59; found: C, 76.76; H, 5.70.

*Methyl (E)-3-((1-formylnaphthalen-2-yl)oxy)hex-2-enoate (1o)*. The title compound was prepared according to the general procedure (*Step II*) methyl (*E*)-3-((1-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)hex-2-enoate

(**5o**) (1.0 g, 2.57 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 90% yield (0.69 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.13 (t,  $J = 7.5$  Hz, 3H), 1.86 (sxt,  $J = 7.5$  Hz, 2H), 3.05 (ddd,  $J = 8.5, 6.1, 1.4$  Hz, 2H), 3.63 (s, 3H), 4.88 (s, 1H), 7.19 (d,  $J = 8.8$  Hz, 1H), 7.60 (ddd,  $J = 8.1, 6.9, 1.1$  Hz, 1H), 7.72 (ddd,  $J = 8.6, 7.0, 1.3$  Hz, 1H), 7.89 (d,  $J = 8.1$  Hz, 1H), 8.13 (d,  $J = 8.8$  Hz, 1H), 9.28 (dd,  $J = 8.6, 1.0$  Hz, 1H), 10.57 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.9, 20.8, 33.0, 51.1, 98.6, 120.8, 125.6, 126.8, 128.4, 130.0, 131.0, 131.5, 137.4, 158.2, 167.1, 176.2, 190.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2947, 1715, 1694, 1638, 1600, 1456, 1429, 1374, 1263, 1231, 1184, 1111, 1045, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}$ : 321.1; found 321.2. Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_4$ : C, 72.47; H, 6.08; found: C, 72.55; H, 6.18.

*Methyl (E)-3-((1-formylnaphthalen-2-yl)oxy)but-2-enoate (1p)*. The title compound was prepared according to the general procedure (*Step II*) methyl (E)-3-((1-(1,3-dithian-2-yl)naphthalen-2-yl)oxy)hex-2-enoate (**5p**) (1.0 g, 2.77 mmol) and thallium (III) trifluoroacetate. The product was obtained as a yellow oil in 93% yield (0.70 g).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.61 (s, 3H), 3.61 (s, 3H), 4.90 (s, 1H), 7.19 (d,  $J = 7.0$  Hz, 1H), 7.56–7.59 (m, 1H), 7.68–7.71 (m, 1H), 7.87 (dd,  $J = 7.7, 1.4$  Hz, 1H), 8.1 (d,  $J = 9.1$  Hz, 1H), 9.24 (m, 1H), 10.56 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.1, 51.1, 98.8, 120.9, 121.6, 125.6, 126.8, 128.4, 129.9, 131.1, 131.6, 137.3, 157.8, 167.2, 172.5, 190.5. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2942, 1713, 1690, 1631, 1604, 1456, 1429, 1374, 1263, 1231, 1184, 1112, 1044, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{16}\text{H}_{14}\text{O}_4\text{Na}$ : 293.1; found 293.2. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_4$ : C, 71.10; H, 5.22; found: C, 71.17; H, 5.31.

### 3.2. General Procedure for Enantioselective Intramolecular Stetter Reaction Using Triazolium Salts **O** and **L**

A flame dried round bottom flask was charged with triazolium salt **O** (19.0 mg, 20 mol%) and 1.0 mL of cyclohexane. To this solution, KHMDs (0.5M in toluene 80  $\mu\text{L}$ , 0.04 mmol, 20 mol%) was added via syringe and the solution was allowed to stir at ambient temperature for 20 min. A solution of the substrate (0.20 mmol) in 1.0 mL of cyclohexane was added. The resulting solution was allowed to stir at ambient temperature and monitored by TLC. The reaction mixture was placed directly onto a silica gel column and eluted with a suitable solution of hexane and ethyl acetate (80:20). Evaporation of solvent allowed analytically pure product.

A flame dried round bottom flask was charged with triazolium salt **L** (28.8 mg, 20 mol%) and 1.0 mL of cyclohexane. To this solution, potassium tert-butoxide (1.0 M in THF 40  $\mu\text{L}$ , 0.04 mmol, 20 mol%) was added via syringe and the solution was allowed to stir at ambient temperature for 20 min. A solution of the substrate (0.20 mmol) in 1.0 mL of cyclohexane was added. The resulting solution was allowed to stir at ambient temperature and monitored by TLC. The reaction mixture was placed directly onto a silica gel column and eluted with a suitable solution of hexane and ethyl acetate (80:20). Evaporation of solvent allowed analytically pure product.

*Methyl (R)-2-(3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2a)*. Yellow oil (98% yield, 97% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 14.0 min,  $t$  (minor) = 12.6 min.  $[\alpha]_{\text{D}}^{20} = -19.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.87 (t,  $J = 8.0$  Hz, 3H), 1.14–1.23 (m, 1H), 1.30–1.37 (m, 1H), 1.84 (m, 2H), 2.96 (d,  $J = 16.0$  Hz, 1H), 3.03 (d,  $J = 16.0$  Hz, 1H), 3.53 (s, 3H), 7.09–7.11 (m, 2H), 7.59–7.64 (m, 1H), 7.69–7.72 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 16.2, 38.7, 40.6, 51.7, 88.8, 112.9, 121.8, 124.1, 137.7, 169.0, 171.5, 202.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2961, 2936, 2875, 1720, 1602, 1462, 1436, 1268, 1211, 1171, 1120, 993, 820. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+$   $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}$ : 271.1; found 271.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 67.73; H, 6.50; found: C, 67.80; H, 6.61.

*Methyl (S)-2-(3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2a')*. Yellow oil (98% yield, 97% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 12.7 min,  $t$  (minor) = 14.2 min.  $[\alpha]_{\text{D}}^{20} = +19.4$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Benzyl (R)-2-(3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2b)*. Yellow oil (95% yield, 96% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 95:5  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 19.1 min,  $t$  (minor) = 21.1 min.  $[\alpha]_D^{20} = -1.4$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.86 (t,  $J = 8.0$  Hz, 1H), 1.18–1.20 (m, 1H), 1.31–1.35 (m, 1H), 1.80–1.85 (m, 2H), 3.01 (d,  $J = 16.0$  Hz, 1H), 3.09 (d,  $J = 16.0$  Hz, 1H), 4.96 (s, 1H), 7.03–7.08 (m, 2H), 7.15–7.18 (m, 2H), 7.28–7.31 (m, 3H), 7.56–7.60 (m, 1H), 7.63 (dd,  $J = 8.0, 4.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 16.2, 38.9, 40.8, 66.7, 88.8, 112.9, 121.7, 121.8, 124.2, 128.2, 128.3 (2C), 128.5 (2C), 135.2, 137.7, 168.5, 171.5, 202.7. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2953, 2935, 2874, 1726, 1482, 1437, 1250, 1213, 1163, 1123, 1010, 836. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{20}\text{H}_{20}\text{O}_4\text{Na}$ : 347.1; found 347.2. Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{O}_4$ : C, 74.06; H, 6.22; found: C, 74.12; H, 6.34.

*Benzyl (S)-2-(3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2b')*. Yellow oil (98% yield, 97% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 14.7 min,  $t$  (minor) = 13.2 min.  $[\alpha]_D^{20} = +1.5$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(2-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2c)*. Yellow oil (96% yield, 96% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 15.6 min,  $t$  (minor) = 14.0 min.  $[\alpha]_D^{20} = -12.6$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.96 (d,  $J = 16.0$  Hz, 1H), 3.05 (d,  $J = 16.0$  Hz, 1H), 3.56 (s, 3H), 7.09–7.13 (m, 2H), 7.61–7.65 (m, 1H), 7.71–7.74 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.3, 41.2, 51.8, 86.3, 113.3, 120.4, 121.9, 124.6, 137.8, 169.1, 170.9, 202.6. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2958, 2940, 2870, 1722, 1601, 1473, 1434, 1262, 1210, 1163, 1123, 1011, 836. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{12}\text{H}_{12}\text{O}_4\text{Na}$ : 243.1; found 243.1. Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{O}_4$ : C, 65.45; H, 5.49; found: C, 65.52; H, 5.56.

*Methyl (S)-2-(2-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2c')*. Yellow oil (98% yield, <99% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 14.2 min,  $t$  (minor) = 15.6 min.  $[\alpha]_D^{20} = +13.4$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Ethyl (R)-2-(2-ethyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2d)*. Yellow oil (96% yield, 96% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 98:2,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 23.5 min,  $t$  (minor) = 26.0 min.  $[\alpha]_D^{20} = -19.5$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.85 (t,  $J = 7.5$  Hz, 3H), 0.97 (t,  $J = 7.2$  Hz, 3H), 1.89 (q,  $J = 7.3$  Hz, 2H), 2.99 (dd,  $J = 16.1, 16.1$  Hz, 2H), 3.95 (m, 2H), 7.04–7.14 (m, 2H), 7.61 (ddd,  $J = 8.4, 7.2, 1.5$  Hz, 1H), 7.69 (ddd,  $J = 7.6, 1.5, 0.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.3, 13.7, 29.9, 40.7, 60.8, 89.1, 112.9, 121.7, 122.0, 124.1, 137.7, 168.6, 171.7, 202.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2952, 2930, 2874, 1720, 1482, 1434, 1256, 1211, 1168, 1120, 1012, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{14}\text{H}_{16}\text{O}_4\text{Na}$ : 271.1; found 271.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 67.73; H, 6.50; found: C, 67.80; H, 6.61.

*Ethyl (S)-2-(2-ethyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2d')*. Yellow oil (98% yield, 91% ee). HPLC (Phenomenex Lux Amylose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 10.0 min,  $t$  (minor) = 9.5 min.  $[\alpha]_D^{20} = +18.8$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(3-oxo-2-pentyl-2,3-dihydrobenzofuran-2-yl)acetate (2e)*. Yellow oil (95% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 14.0 min,  $t$  (minor) = 11.6 min.  $[\alpha]_D^{20} = -27.8$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.83 (t,  $J = 7.1$  Hz, 3H), 0.88–1.03 (m, 2H), 1.19–1.25 (m, 4H), 1.80–1.87 (m, 2H), 2.97 (d,  $J = 16.4$  Hz, 1H), 3.00 (d,  $J = 16.4$  Hz, 1H), 3.52 (s, 3H), 7.06–7.11 (m, 2H), 7.61 (ddd,  $J = 8.4, 7.2, 1.5$  Hz, 1H), 7.69 (dd,  $J = 7.9, 1.6$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.9, 22.2, 22.4, 31.7, 36.5, 40.6, 51.8, 88.8, 112.9, 121.8, 124.2, 137.7, 169.1, 171.6, 202.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2950, 2934, 2870, 1725, 1480, 1438, 1257, 1209, 1171, 1122, 1012, 833. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{16}\text{H}_{20}\text{O}_4\text{Na}$ : 299.1; found 299.2. Anal. Calcd. for  $\text{C}_{16}\text{H}_{20}\text{O}_4$ : C, 69.55; H, 7.30; found: C, 69.64; H, 7.38.

*Methyl (S)-2-(3-oxo-2-pentyl-2,3-dihydrobenzofuran-2-yl)acetate (2e')*. Yellow oil (95% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 11.6 min, t (minor) = 14.6 min.  $[\alpha]_D^{20} = +27.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(2-hexyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2f)*. Yellow oil (93% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 13.7 min, t (minor) = 10.9 min.  $[\alpha]_D^{20} = -28.3$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.86 (t,  $J = 7.0$  Hz, 3H), 1.17–1.26 (m, 7H), 1.27–1.32 (m, 2H), 1.82–1.90 (m, 2H), 2.97 (d,  $J = 14.0$  Hz, 1H), 3.02 (d,  $J = 14.0$  Hz, 1H), 3.54 (s, 3H), 7.11 (m, 2H), 7.62–7.64 (m, 1H), 7.69 (dd,  $J = 7.0, 2.0$  Hz, 1H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.9, 23.4, 23.6, 30.2, 32.4, 37.6, 41.6, 52.7, 89.8, 113.9, 122.7, 122.8, 125.2, 138.7, 170.1, 172.6, 203.8. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2958, 2940, 2870, 1722, 1601, 1473, 1434, 1262, 1210, 1163, 1123, 1011, 836. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{17}\text{H}_{22}\text{O}_4\text{Na}$ : 313.1; found 313.2. Anal. Calcd. for  $\text{C}_{17}\text{H}_{22}\text{O}_4$ : C, 70.32; H, 7.64; found: C, 70.39; H, 7.72.

*Methyl (S)-2-(2-hexyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2f')*. Yellow oil (93% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 10.6 min, t (minor) = 13.6 min.  $[\alpha]_D^{20} = +28.3$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(2-(cyclohexylmethyl)-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2g)*. Yellow oil (91% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 15.3 min, t (minor) = 12.2 min.  $[\alpha]_D^{20} = -19.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.87–1.01 (m, 3H), 1.04–1.17 (m, 4H), 1.24–1.36 (m, 3H), 1.67 (dd,  $J = 14.7, 6.8$  Hz, 3H), 1.79 (dd,  $J = 14.7, 5.1$  Hz, 1H), 3.00 (s, 2H), 3.50 (s, 3H), 7.07–7.12 (m, 2H), 7.61 (ddd,  $J = 8.4, 7.2, 1.5$  Hz, 1H), 7.71 (dd,  $J = 8.1, 1.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 26.0, 26.1, 33.1, 34.2, 34.7, 40.8, 43.6, 51.7, 89.1, 113.0, 121.8, 124.2, 137.7, 169.1, 171.3, 203.0. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2952, 2944, 2876, 1709, 1607, 1466, 1430, 1267, 1212, 1155, 1123, 1006, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{18}\text{H}_{22}\text{O}_4\text{Na}$ : 325.1; found 325.2. Anal. Calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_4$ : C, 66.45; H, 6.82; found: C, 66.54; H, 6.88.

*Methyl (S)-2-(2-(cyclohexylmethyl)-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2g')*. Yellow oil (95% yield, <99% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 12.0 min, t (minor) = 14.6 min.  $[\alpha]_D^{20} = +20.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(3-oxo-2-phenethyl-2,3-dihydrobenzofuran-2-yl)acetate (2h)*. Yellow oil (92% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 18.4 min, t (minor) = 15.2 min.  $[\alpha]_D^{20} = -38.0$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.19 (ddd,  $J = 11.3, 6.1, 2.9$  Hz, 2H), 2.47 (ddd,  $J = 13.4, 11.0, 6.4$  Hz, 1H), 2.63 (ddd,  $J = 13.4, 11.0, 6.3$  Hz, 1H), 2.98–3.10 (m, 2H), 3.55 (s, 3H), 7.09–7.21 (m, 5H), 7.22–7.28 (m, 2H), 7.64 (ddd,  $J = 8.5, 7.2, 1.5$  Hz, 1H), 7.73 (ddd,  $J = 7.6, 1.5, 0.7$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 29.2, 38.3, 40.7, 51.8, 88.4, 113.1, 121.7, 122.0, 124.2, 126.2, 128.3 (2C), 128.4 (2C), 137.9, 140.6, 169.0, 171.6, 202.3. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2953, 2939, 2870, 1701, 1604, 1459, 1433, 1271, 1215, 1148, 1119, 1012, 834. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{19}\text{H}_{18}\text{O}_4\text{Na}$ : 333.1; found 333.1. Anal. Calcd. for  $\text{C}_{19}\text{H}_{18}\text{O}_4$ : C, 73.53; H, 5.85; found: C, 73.60; H, 5.94.

*Methyl (S)-2-(3-oxo-2-phenethyl-2,3-dihydrobenzofuran-2-yl)acetate (2h')*. Yellow oil (92% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 15.6 min, t (minor) = 18.6 min.  $[\alpha]_D^{20} = +38.4$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(6-methyl-2-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2i)*. Yellow oil (94% yield, 94% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 23.3 min, t (minor) = 20.3 min.  $[\alpha]_D^{20} = -1.6$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.44 (s, 3H), 2.34 (s, 3H), 2.90 (d,  $J = 14.0$  Hz, 1H), 3.00 (d,  $J = 14.0$  Hz, 1H), 3.53 (s, 3H), 6.96 (d,  $J = 7.0$  Hz, 1H), 7.40 (d,  $J = 2.1$  Hz, 1H), 7.47 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 20.2, 22.0, 40.8, 51.4, 86.0, 112.5, 119.9, 123.6, 131.1, 138.7, 168.8, 169.0, 202.3. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2956, 2941,

2869, 1715, 1609, 1462, 1433, 1270, 1212, 1155, 1123, 1006, 833. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{13}H_{14}O_5Na$ : 273.1; found 273.2. Anal. Calcd. for  $C_{13}H_{14}O_5$ : C, 62.39; H, 5.64; found: C, 62.47; H, 5.70.

*Methyl (S)-2-(6-methyl-2-methyl-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate (2i')*. Yellow oil (96% yield, 93% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 20.2 min,  $t$  (minor) = 23.5 min.  $[\alpha]_D^{20} = +1.7$  (c 1.0,  $CH_2Cl_2$ ).

*Methyl (R)-2-(5-chloro-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2j)*. Yellow oil (95% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 9.5 min,  $t$  (minor) = 7.6 min.  $[\alpha]_D^{20} = -24.8$  (c 1.0,  $CH_2Cl_2$ ).  $^1H$  NMR (700 MHz,  $CDCl_3$ )  $\delta$ : 0.89 (t,  $J = 7.0$  Hz, 3H), 1.20 (m, 1H), 1.34 (m, 1H), 1.81 (dtd,  $J = 17.6, 13.9, 5.6$  Hz, 2H), 3.00 (d,  $J = 14.0$  Hz, 1H), 3.06 (d,  $J = 14.0$  Hz, 1H) 3.56 (s, 3H), 7.02 (d,  $J = 7.0$  Hz, 1H), 7.56 (dd,  $J = 8.4, 2.1$  Hz, 1H), 7.67 (d,  $J = 1.4$  Hz, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$ : 15.0, 17.2, 39.8, 41.6, 52.8, 90.9, 115.2, 124.0, 124.5, 128.2, 138.4, 170.0, 170.8, 202.6. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2961, 2878, 1722, 1620, 1482, 1247, 1210, 1155, 1123, 1009, 829. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{14}H_{15}ClO_4Na$ : 305.1; found 305.2. Anal. Calcd. for  $C_{14}H_{15}ClO_4$ : C, 59.48; H, 5.35; found: C, 59.55; H, 5.43.

*Methyl (S)-2-(5-chloro-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2j')*. Yellow oil (94% yield, 98% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 7.6 min,  $t$  (minor) = 9.6 min.  $[\alpha]_D^{20} = +25.6$  (c 1.0,  $CH_2Cl_2$ ).

*Methyl (R)-2-(5-bromo-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2k)*. Yellow oil (90% yield, 93% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 13.0 min,  $t$  (minor) = 9.5 min.  $[\alpha]_D^{20} = -28.3$  (c 1.0,  $CH_2Cl_2$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 0.87 (t,  $J = 7.3$  Hz, 3H), 1.10–1.24 (m, 1H), 1.26–1.38 (m, 1H), 1.81 (dtd,  $J = 17.6, 13.9, 5.6$  Hz, 2H), 2.99 (d,  $J = 16.6$  Hz, 1H), 3.04 (d,  $J = 16.6$  Hz, 1H), 3.54 (s, 3H), 7.00 (d,  $J = 8.8$  Hz, 1H), 7.68 (dd,  $J = 8.8, 2.2$  Hz, 1H), 7.81 (dd,  $J = 2.2, 0.5$  Hz, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$ : 14.01, 16.22, 38.80, 40.63, 51.89, 89.80, 114.30, 114.65, 123.63, 126.69, 140.15, 168.99, 170.24, 201.38. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2955, 2870, 1715, 1622, 1478, 1244, 1211, 1156, 1123, 1009, 831. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{14}H_{15}BrO_4Na$ : 349.0; found 349.1. Anal. Calcd. for  $C_{14}H_{15}BrO_4$ : C, 51.40; H, 4.62; found: C, 51.49; H, 4.70.

*Methyl (S)-2-(5-bromo-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2k')*. Yellow oil (90% yield, 94% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 9.5 min,  $t$  (minor) = 12.7 min.  $[\alpha]_D^{20} = +28.7$  (c 1.0,  $CH_2Cl_2$ ).

*Methyl (R)-2-(3-oxo-2-propyl-5-(trifluoromethoxy)-2,3-dihydrobenzofuran-2-yl)acetate (2l)*. Yellow oil (94% yield, 97% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 9.5 min,  $t$  (minor) = 10.7 min.  $[\alpha]_D^{20} = -17.3$  (c 1.0,  $CH_2Cl_2$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 0.88 (t,  $J = 7.2$  Hz, 1H), 1.17–1.24 (m, 1H), 1.31–1.39 (m, 1H), 1.78–1.87 (m, 2H), 2.99 (d,  $J = 16.8$  Hz, 1H), 3.07 (d,  $J = 16.8$  Hz, 1H), 3.55 (s, 3H), 7.11 (d,  $J = 8.8$  Hz, 1H), 7.46 (dd,  $J = 9.2, 2.8$  Hz, 1H), 7.54 (m, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$ : 14.0, 16.2, 38.7, 40.5, 51.8, 90.3, 114.0, 116.3, 120.5 (d,  $J = 257.6$  Hz), 122.4, 130.9, 143.5 (d,  $J = 2.0$  Hz), 169.2 (d,  $J = 52.3$  Hz), 201.8. IR (ATR)  $\nu$  ( $cm^{-1}$ ): 2961, 2878, 1722, 1620, 1482, 1247, 1210, 1195, 1155, 1116, 1009, 829. LRMS (ESI): Mass calcd. for  $[M + Na]^+$   $C_{15}H_{15}F_3O_5Na$ : 355.1; found 355.2. Anal. Calcd. for  $C_{15}H_{15}F_3O_5$ : C, 54.22; H, 4.55; found: C, 54.31; H, 4.65.

*Methyl (S)-2-(3-oxo-2-propyl-5-(trifluoromethoxy)-2,3-dihydrobenzofuran-2-yl)acetate (2l')*. Yellow oil (92% yield, 85% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 10.7 min,  $t$  (minor) = 9.6 min.  $[\alpha]_D^{20} = +15.9$  (c 1.0,  $CH_2Cl_2$ ).

*Methyl (R)-2-(5-fluoro-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2m)*. Yellow oil (97% yield, 86% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $v = 0.7$  mL/min,  $\lambda = 254$  nm)  $t$  (major) = 12.2 min,  $t$  (minor) = 9.5 min.  $[\alpha]_D^{20} = -33.9$  (c 1.0,  $CH_2Cl_2$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 0.87 (t,  $J = 7.3$  Hz, 3H), 1.11–1.26 (m, 1H), 1.28–1.38 (m, 1H), 1.81 (dtd,  $J = 17.3, 13.0, 5.6$  Hz, 2H), 2.99 (d,  $J = 16.6$  Hz, 1H), 3.03 (d,  $J = 16.6$  Hz, 1H), 3.54 (s, 3H), 7.05 (dd,  $J = 9.7, 3.5$  Hz, 1H), 7.31–7.37

(m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 16.2, 38.8, 40.7, 51.8, 90.0, 109.2 (d,  $J = 23.1$  Hz), 113.9 (d,  $J = 8.1$  Hz), 122.3 (d,  $J = 7.0$  Hz), 125.2 (d,  $J = 26.1$  Hz), 156.4, 158.8, 168.2 (d,  $J = 134.8$  Hz), 202.5. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2953, 2935, 1726, 1482, 1437, 1250, 1213, 1163, 1123, 1084, 1009, 837. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{14}\text{H}_{15}\text{FO}_4\text{Na}$ : 289.1; found 289.1. Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{FO}_4$ : C, 58.13; H, 5.23; found: C, 58.20; H, 5.33.

*Methyl (S)-2-(5-fluoro-3-oxo-2-propyl-2,3-dihydrobenzofuran-2-yl)acetate (2m')*. Yellow oil (95% yield, 96% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 9.6 min, t (minor) = 12.0 min.  $[\alpha]_{\text{D}}^{20} = +36.5$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(1-oxo-2-phenethyl-1,2-dihydronaphtho [2,1-b]furan-2-yl)acetate (2n)*. Yellow oil (94% yield, 28% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 28.2 min, t (minor) = 28.0 min.  $[\alpha]_{\text{D}}^{20} = -4.3$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.26–2.35 (m, 2H), 2.48–2.56 (m, 1H), 2.61–2.68 (m, 1H), 3.04 (d,  $J = 16.0$  Hz, 1H), 3.10 (d,  $J = 16.0$  Hz, 1H), 3.55 (s, 3H), 7.11–7.14 (m, 2H), 7.15–7.18 (m, 1H), 7.22–7.26 (m, 2H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.51 (ddd,  $J = 8.0, 6.8, 1.2$  Hz, 1H), 7.70 (ddd,  $J = 8.4, 7.2, 1.6$  Hz, 1H), 7.87 (d,  $J = 8.4$  Hz, 1H), 8.12 (d,  $J = 8.8$  Hz, 1H), 8.80–8.82 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 29.2, 38.2, 40.5, 51.8, 89.4, 113.6, 113.7, 123.2, 125.4, 126.1, 128.3 (2C), 128.4 (2C), 128.5, 129.2, 129.3, 129.8, 140.0, 140.6, 169.0, 174.3, 201.6. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 3081, 3060, 3023, 2948, 1713, 1683, 1585, 1509, 1430, 1366, 1234, 1207, 1163, 1151, 1117, 1073, 1061, 1044, 1002, 1482, 1437, 1250, 1213, 1163, 1123, 1084, 1009, 837. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{23}\text{H}_{20}\text{O}_4\text{Na}$ : 383.1; found 383.2. Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{O}_4$ : C, 76.65; H, 5.59; found: C, 76.77; H, 5.68.

*Methyl (S)-2-(1-oxo-2-phenethyl-1,2-dihydronaphtho[2,1-b]furan-2-yl)acetate (2n')*. Yellow oil (90% yield, 50% ee). HPLC (Phenomenex Lux Amylose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 19.2 min, t (minor) = 26.8 min.  $[\alpha]_{\text{D}}^{20} = +9.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(1-oxo-2-propyl-1,2-dihydronaphtho[2,1-b]furan-2-yl)acetate (2o)*. Yellow oil (94% yield, 50% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 22.0 min, t (minor) = 15.8 min.  $[\alpha]_{\text{D}}^{20} = -7.7$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.85 (t,  $J = 7.0$  Hz, 3H), 1.88–1.96 (m, 2H), 2.99 (d,  $J = 16.0$  Hz, 1H), 3.04 (d,  $J = 16.0$  Hz, 1H), 3.51 (s, 3H), 7.24 (d,  $J = 9.0$  Hz, 1H), 7.47 (m, 1H), 7.66 (m, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 8.06 (d,  $J = 9.0$  Hz, 1H), 8.75 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.0, 16.3, 22.7, 29.7, 38.6, 40.5, 51.8, 89.9, 113.6, 123.2, 125.2, 128.5, 129.2, 129.7, 139.7, 169.1, 174.2, 202.0. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2949, 2928, 1734, 1688, 1630, 1578, 1515, 1437, 1359, 1288, 1211, 1163, 1151, 1123, 1076, 991, 912, 837. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}$ : 321.1; found 321.2. Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_4$ : C, 72.47; H, 6.08; found: C, 72.55; H, 6.17.

*Methyl (S)-2-(1-oxo-2-propyl-1,2-dihydronaphtho[2,1-b]furan-2-yl)acetate (2o')*. Yellow oil (94% yield, 32% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 22.0 min, t (minor) = 15.8 min.  $[\alpha]_{\text{D}}^{20} = +5.7$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

*Methyl (R)-2-(2-methyl-1-oxo-1,2-dihydronaphtho[2,1-b]furan-2-yl)acetate (2p)*. Yellow oil (98% yield, 32% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 18.8 min, t (minor) = 24.0 min.  $[\alpha]_{\text{D}}^{20} = -6.2$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.59 (s, 3H), 2.99 (d,  $J = 16.0$  Hz, 1H), 3.06 (d,  $J = 16.0$  Hz, 1H), 3.57 (s, 3H), 7.25 (d,  $J = 9.2$  Hz, 1H), 7.45 (m, 1H), 7.68 (m, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 8.09 (d,  $J = 9.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.3, 41.0, 51.8, 87.3, 112.1, 113.9, 123.2, 125.3, 128.5, 129.3, 129.5, 129.8, 139.8, 169.1, 173.6, 202.0. IR (ATR)  $\nu$  ( $\text{cm}^{-1}$ ): 2940, 2924, 1730, 1680, 1634, 1580, 1510, 1430, 1355, 1285, 1209, 1163, 1151, 1128, 1070, 991, 912, 837. LRMS (ESI): Mass calcd. for  $[\text{M} + \text{Na}]^+ \text{C}_{16}\text{H}_{14}\text{O}_4\text{Na}$ : 293.1; found 293.2. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_4$ : C, 71.10; H, 5.22; found: C, 71.18; H, 5.31.

*Methyl (S)-2-(2-methyl-1-oxo-1,2-dihydronaphtho[2,1-b]furan-2-yl)acetate (2p')*. Yellow oil (98% yield, 3% ee). HPLC (Phenomenex Lux Cellulose-1, hexanes/2-propanol 90:10,  $\nu = 0.7$  mL/min,  $\lambda = 254$  nm) t (major) = 18.8 min, t (minor) = 24.0 min.  $[\alpha]_{\text{D}}^{20} = +1.8$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).

## 4. Conclusions

In conclusion, camphor-derived **L** and pinene-derived **O** triazolium salts as *N*-heterocyclic carbene precursors have been found to be efficient for the enantioselective intramolecular Stetter reaction with varied  $\beta,\beta$ -substituted Michael acceptors. In general, with 20 mol% of the NHC catalysts **L** or **O**, the desired 2,2-disubstituted coumaranone and naphthofuranone derivatives bearing fully-substituted quaternary stereogenic centers could be obtained with excellent yields of up to 99% ee. Through a simple change of the terpene-derived triazolium salts, NHCs **L** and **O** promote very high but opposite enantiofacial selectivity. Further applications of these terpene-derived triazolium salts in other asymmetric reactions are currently underway.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/9/2/192/s1>.

**Funding:** This project was financed by the National Science Center (Poland) as part of the SONATA BIS program (UMO-2016/22/E/ST5/00469).

**Conflicts of Interest:** The author declares no conflict of interest.

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