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Regioselective Alkoxycarbonylation of Allyl Phenyl Ethers Catalyzed by Pd/dppb Under Syngas Conditions

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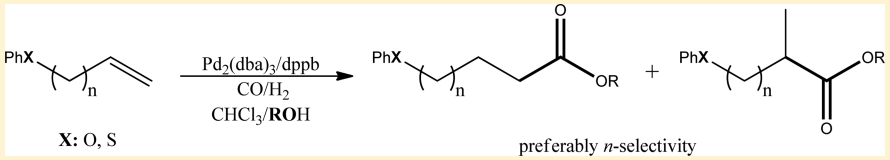
Supporting Information



ABSTRACT: A simple and regioselective synthesis of phenoxy esters and phenylthio esters is reported. The products are obtained by selective alkoxycarbonylation catalyzed by $Pd_2(dba)_3$, 1,4-bis(diphenylphisphino)butane (dppb), and syngas (CO/H_2) in chloroform/alcohol. This methodology affords bifunctional products in good yield with excellent n-selectivity and without the need to use additives.

INTRODUCTION

Phenoxy esters are important building blocks for the synthesis of certain biologically active molecules and thus are attractive synthetic targets. For example, the chlorolactone (CL) and chloro-thiolactone (CTL) exhibit quorum sensing inhibition (QSI), offering an alternative strategy in curbing bacterial infections, which do not respond to conventional antibiotics (Figure 1).[1] Moreover, these esters also are key intermediates

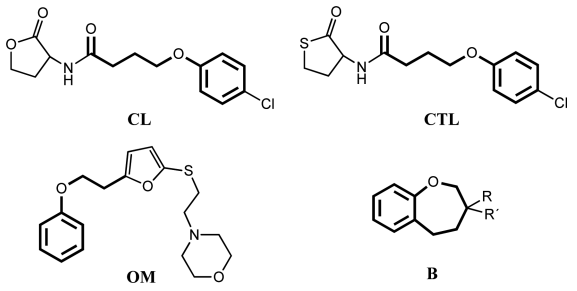


Figure 1. Important bioactive molecules containing a phenoxy motif.

for the synthesis of oxadiazole-morpholine derivatives (OM), which display antineoplastic properties in Dalton's lymphoma ascites (DLA).[2] On the other hand, fatty acids and benzoxepin derivatives (B) also can be obtained using the corresponding ester substrate.[3]

The conventional syntheses of phenoxy esters proceed by alkylation of a bromo ester with excess amounts of phenol under basic conditions. Surprisingly, a catalytic method for the synthesis of this kind of ester has never been developed, to our knowledge. Direct carbonylation (alkoxycarbonylation) of an appropriate substrate using CO and an alcohol can afford the desired compounds.

The alkoxycarbonylation reaction is a useful industrial process to produce materials for the synthesis of natural products, dyes, agrochemicals, pharmaceuticals, and fine chemicals.[4] Thanks to the versatility of this process, different synthetic strategies have been developed using a diversity of unsaturated compounds such as allenes,[5] alkenes,[4,6] alkynes,[6c,7] enyne oxiranes,[8] and enyne carbonates.[9]

Despite the increased attention, the regioselectivity to form linear or branched products in high selectivity is a challenge. In this context, it is well-known that bidentate ligands such as phosphines can give excellent linear selectivity.[4,6,10] Monodentate ligands can also be used,[11] but lead to a higher proportion of branched structures.[12] Another traditional strategy to solve the selectivity problem is to work with *para*-toluenesulfonic acid to improve the linear selectivity, but the acid additive makes that process corrosive.[13] One way to address this issue is to use a Lewis acid.[11,14] We have recently developed a protocol using $SnCl_2$ or $Ti(O^iPr)_4$ and monodentate phosphines, giving very good linear selectivity.[15] We now wish to report the carbonylation of allyl phenyl ethers and allyl phenyl sulfides using a $Pd_2(dba)_3$/dppb catalytic system and syngas, affording excellent linear selectivity.

RESULTS AND DISCUSSION

Initially, we investigated palladium-catalyzed alkoxycarbonylation using 1-phenoxy-2-propene **1a** and ethanol as the model reaction; the results are illustrated in the Table 1. First, different palladium sources were tested in the presence of dppb as the ligand, affording the desired product in low yield and moderate selectivity (entries 1−4). *para*-Toluenesulfonic acid (*p*-TsOH) is commonly used to enhance the conversion in the

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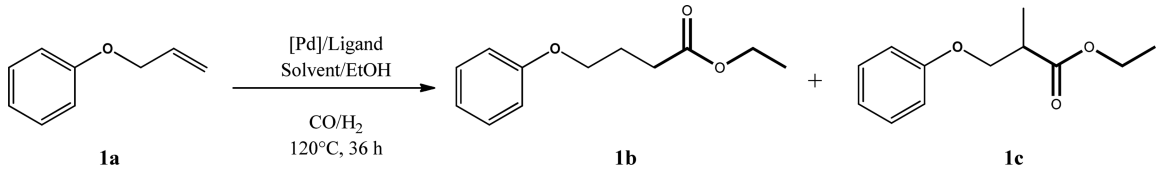
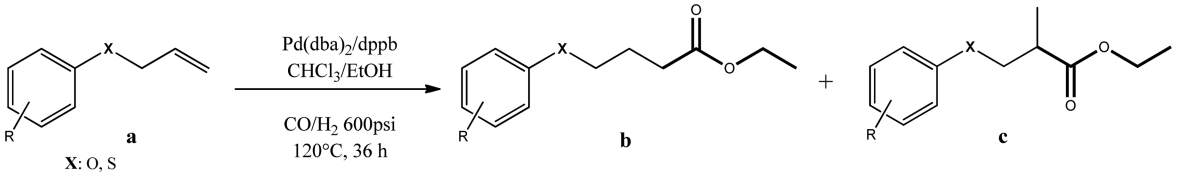
Table 1. Screening Reaction Conditions[a]



entry	[Pd]	ligand	solvent	yield %[b]	L/B %[c]
1[d]	$PdCl_2$	dppb	DCM	25	53/47
2[d]	$Pd(OAc)_2$	dppb	DCM	12	60/40
3[d]	$Pd(acac)_2$	dppb	DCM	trace	–
4[d]	$Pd_2(dba)_3$	dppb	DCM	37	56/44
5[d,e]	$Pd_2(dba)_3$	dppb	DCM	41	60/40
6[d,f]	$Pd_2(dba)_3$	PPh_3	DCM	–	–
7	$Pd_2(dba)_3$	dppb	DCM	40	90/10
8	$Pd_2(dba)_3$	dppb	toluene	47	79/21
9	$Pd_2(dba)_3$	dppb	THF	52	68/32
10	$Pd_2(dba)_3$	dppb	MeCN	trace	–
11	$Pd_2(dba)_3$	dppb	$CHCl_3$	75	100/0
12	$Pd_2(dba)_3$	dppb	DCE	68	73/27
13	$PdCl_2$	dppb	$CHCl_3$	trace	–
14	$Pd(OAc)_2$	dppb	$CHCl_3$	trace	–
15	$Pd(acac)_2$	dppb	$CHCl_3$	trace	–
16	$Pd(PPh_3)_4$	dppb	$CHCl_3$	56	100/0
17	$Pd_2(dba)_3$	binap	$CHCl_3$	40	77/23
18	$Pd_2(dba)_3$	dppf	$CHCl_3$	61	81/19
19	$Pd_2(dba)_3$	dppp	$CHCl_3$	–	–
20	$Pd_2(dba)_3$	dppe	$CHCl_3$	–	–

[a]Reactions were carried out with **1a** (1.2 mmol), 2 mol % [Pd]/Ligand, 0.2 mL of ethanol, 600 psi CO/H_2 (1:1), at 120 °C in 10 mL of solvent for 36h. [b]After column chromatography. [c]The ratio of linear/branched [L/B] products was determined by ^1H NMR spectroscopy. [d]300 psi of CO was used. [e]*p*-TsOH 10 mol % was used. [f]*p*-TsOH 20 mol % was used.

Table 2. Substrate Scope[a]



entry	R/X	products	yield %[b]	L/B ratio[c]
1	*p*-Me/O	**2b**	72	100/0
2	*p*-OMe/O	**3b**	69	100/0
3	*p*-^{t}Bu/O	**4b**	70	100/0
4	*p*-Cl/O	**5b**	71	98/2
5	*p*-Ph/O	**6b, 6c**	67	89/11
6	*m*-Me/O	**7b**	68	100/0
7	*m*-OMe/O	**8b**	70	100/0
8	*m*-Cl/O	**9b**	72	100/0
9	*o*-Me/O	**10b**	69	100/0
10	*o*-OMe/O	**11b**	69	100/0
11	*o*-Cl/O	**12b**	71	100/0
12	*o*−OH/O	**13b**	72	100/0
13	1-Naphthyl/O	**14b**	73	99/1
14	2-Naphthyl/O	**15b**	71	99/1
15	H/S	**16b**	70	100/0
16	*p*-OMe/S	**17b**	69	100/0
17	*p*-F/S	**18b**	71	100/0
18	2-Naphthyl/S	**19b**	70	100/0

[a]Reactions were carried out with **2a**−**19a** (1.2 mmol), 2 mol % $Pd_2(dba)_3$ (0.024 mmol), 4 mol % of dppb (0.048 mmol), 0.3 mL of ethanol, 600 psi CO/H_2 (1:1), at 120 °C in 10 mL of chloroform for 36 h. [b]After column chromatography. [c]The ratio of linear/branched [L/B] products was determined by ^1H NMR spectroscopy.

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Scheme 1. Examination of Oxygen Absence in the Substrate

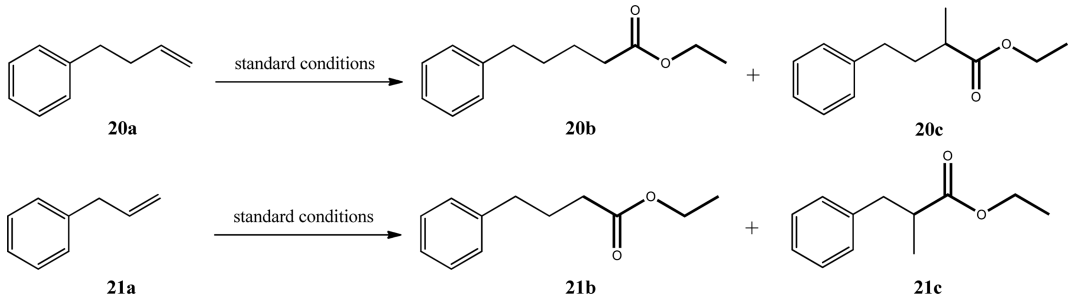
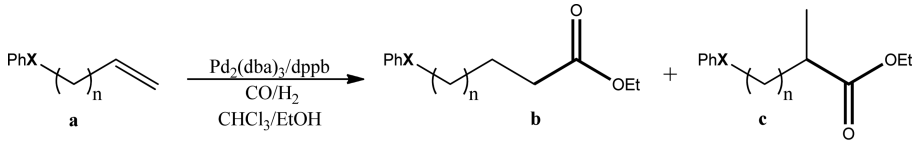


Table 3. Scope of the Alkoxycarbonylation Reaction Using Long Chain Substrates[a]



entry	substrate (X/*n*)	products	yield %[b]	L/B ratio[c]
1	O/2	**22b**	76	100/0
2	O/3	**23b**	70	99/1
3	O/4	**24b**	35	85/15
4	O/6	**25b**	45	90/10
5	O/8	–	trace	–
6	S/2	**26b**, **26c**	68	75/25
7	S/3	**27b**, **27c**	70	87/13
8	S/4	**28b**, **28c**	46	86/14
9	S/6	**29b**	62	95/5
10	S/8	**30b**	21	98/2

[a]Reactions were carried out with **22a**–**30a** (1.2 mmol), 2 mol % $Pd_2(dba)_3$ (0.024 mmol), 4 mol % of dppb (0.048 mmol), 0.3 mL of ethanol, 600 psi CO/H_2 (1:1), at 120 °C in 10 mL of chloroform for 36 h. [b]After column chromatography. [c]The ratio of linear/branched [L/B] regioisomers was determined by ^1H NMR spectroscopy.

alkoxycarbonylation reaction, but in our case, did not lead to any noticeable improvement (entries 5–6). Surprisingly, working under hydroformylation conditions (CO/H_2) the alkoxycarbonylation products were obtained in excellent regioselectivity (90/10 [L/B]), but in only moderate yield 40% (entry 7). Additionally, different temperatures, pressures, and ratios between gases were also explored (see Supporting Information, Table S1). In general, two pathways are commonly proposed to explain the alkoxycarbonylation of olefins using alcohols, i.e., via an alkoxy or hydride mechanisms.[6c,7b,16] The results above clearly showed that the presence of H_2 is crucial for the reaction, indicating that the hydride path may be involved in the reaction, via a palladium hydride intermediate (H-Pd-dppb).

To improve the efficiency of this reaction, different solvents were screened. Chloroform gave the best results in comparison with the other solvents, with the product isolated in 75% yield and excellent linear selectivity 100% (entries 8–11). When another chlorinated solvent was used, a slightly lower yield with low regioselectivity was obtained (entry 12). On the other hand, the use of Pd(II) precursors under these conditions resulted in negligible conversion. In contrast, the Pd(0) source gave the product in moderate yield and 100% linear isomer (entries 13–16). The striking difference between Pd(II) and Pd(0) could be due to their different propensities to form the catalytically active species in the presence of dppb under syngas conditions. Therefore, $Pd_2(dba)_3$ was selected as the Pd source to complete this study. Other bidentate phosphine ligands such as binap, dppp, dppe, dppf were also investigated, and they did not show any advantage compared with dppb. These results indicate the possible importance of the bite angle for the catalytic system (entries 17–20).

Using the optimized reaction conditions, the scope of the alkoxycarbonylation reaction for the synthesis of phenoxy esters was investigated; the results are summarized in Table 2. In general, the reaction worked well with excellent regioselectivity, affording the linear isomer as the major product; additionally, the presence or the position of the electron-donating or -withdrawing group in the aromatic ring did not have a significant impact on the yield or selectivity. Thus, –Me, –OMe, or –^{t}Bu substituents in the *para* position gave the desired product in quite good yield (up to 72%) with a selectivity of 100/0 (L/B) (entries 1–3). The presence of a halogen such a –Cl had a minimal effect on the regioselectivity 98/2 (L/B), while a weak electron-withdrawing group (–Ph) provided moderate selectivity 89/11 (L/B) (entries 4–5). Also, *meta* and *ortho* substituents performed well, giving the corresponding linear isomer in good yield (entries 6–12). Moreover, when the phenyl group was changed to a naphthyl substituent, essentially the same selectivity was obtained (entries 13–14). It was also found that when the oxygen is replaced by sulfur, the reaction outcome was similar, providing the corresponding thioester in comparable yield and in excellent regioselectivity 100/0 (L/B) (entries 15–18).

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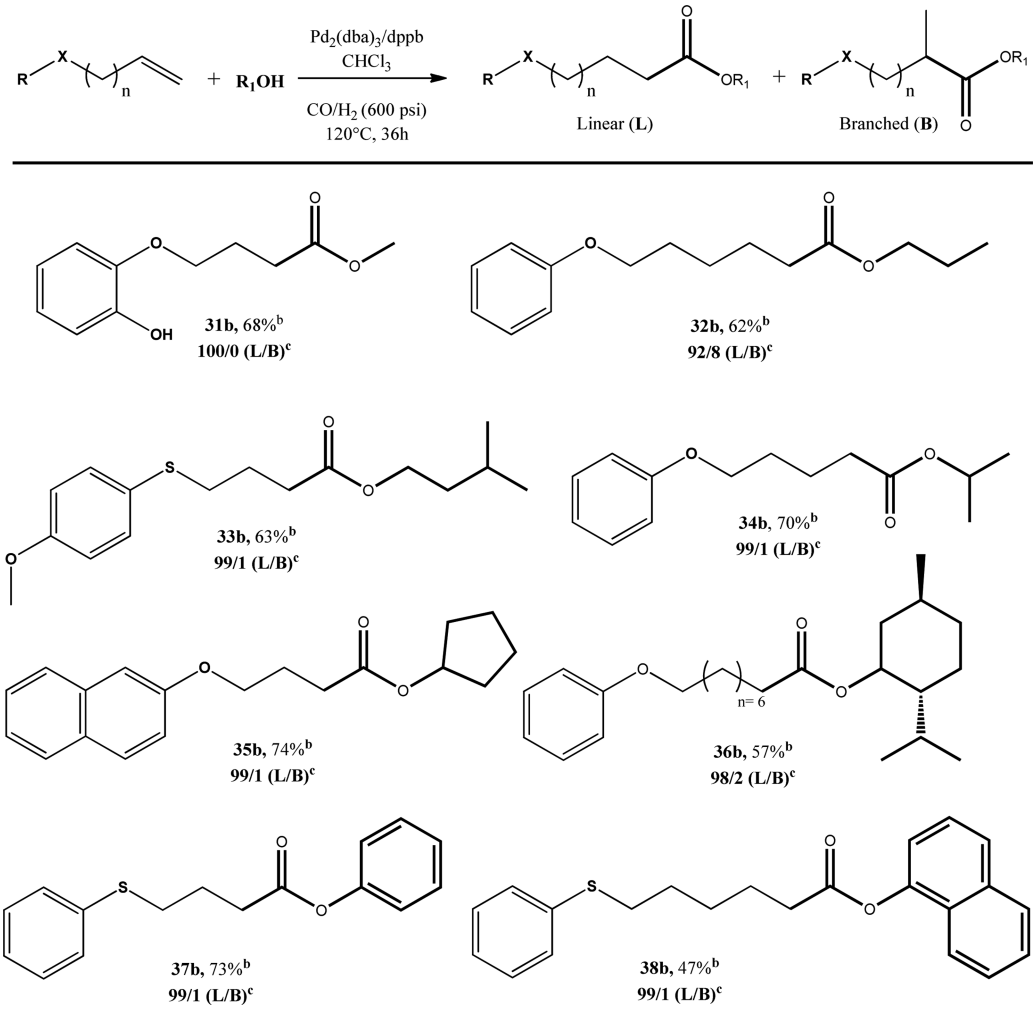
Scheme 2. Scope of Different Substrates and Alcohols[a]



[a]Reaction conditions: Substrate (1.2 mmol), 2 mol % $Pd_2(dba)_3$ (0.024 mmol), 4 mol % of dppb (0.048 mmol), alcohol (2.0 mmol), 600 psi CO/H_2 (1:1), 120 °C, 36h. [b]After column chromatography. [c]The ratio of linear/branched [L/B] regioisomers was determined by ^1H NMR spectroscopy.

Unfortunately, using a nitrogen (e.g., −NH or −NMe) based heteroatom as the substrate did not lead to the desired product. This result may be due to hydrogenolysis of the substrate, with aniline and *N*-methylaniline observed as byproducts.

In order to confirm whether the heteroatom present in the substrate has an important influence on the selectivity, the alkoxycarbonylation reaction was applied to **20a** and **21a**; under standard conditions the corresponding esters **20b**/**20c** and **21b**/**21c** were obtained, with selectivities of 65/35 and 80/20 (L/B), respectively (Scheme 1). The results indicate that the heteroatom has a direct influence on the n-selectivity, and this behavior might be due in part to electronic effects.

To explore the effect of chain extension on the alkene and to probe the role of the heteroatom, a series of long-chain substrates were employed as reactants. Allyl phenyl ethers and sulfides ranging from C_4 to C_{10} were compatible with these reaction conditions, giving the expected products in low to moderate yields (Table 3). In general, increasing the carbon chain affects the yield and selectivity of the reaction. For example, in the case of ethers, when the reaction was carried out with substrates ranging from a C_4 to C_8 chain, a reduction of the yield occurred accompanied by a decrease in selectivity (entries 1−4). With a long chain substrate (C_{10}), the formation of the corresponding esters takes place in trace quantities (entry 5). Similarly, the desired products from allyl phenyl sulfides were obtained from different chain lengths (entries 6−10). Noteworthy, the linear product is favored by increasing the carbon chain. These results make it clear that the electronic influence exerted by the heteroatom helps to control the selectivity for the reaction.

Different alcohols were investigated to determine the versatility of this approach, (Scheme 2). Nucleophiles aliphatic and aromatic are compatible with these reaction conditions, giving the expected products in good yield and excellent linear selectivity. Primary alcohols participated in the alkoxycarbonylation reaction to afford linear esters in excellent regioselectivity. Similar results were achieved using secondary alcohols. In addition, an aromatic alcohol was also compatible, affording the expected product in fine selectivity.

In summary, we have developed an efficient regioselective alkoxycarbonylation reaction of allyl phenyl ethers and sulfides, using a simple catalytic method [$Pd_2(dba)_3$/dppb] in the presence of syngas (CO/H_2). A variety of esters can be obtained in good yields. This methodology does not require any extra additive to improve the product selectivity.

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EXPERIMENTAL SECTION

Preparation of Allyl Substrates. Allyl substrates were prepared from the corresponding phenol and allyl bromide in high yield in two steps. Allyl bromide (3.0 mmol) was added to a suspension of the phenol derivate (2.5 mmol) and potassium carbonate (5.0 mmol, 691.1 mg) in acetone (100 mL). The reaction mixture was heated to 66 °C for 12 h, cooled to room temperature, diluted with ether (100 mL), and quenched with water (100 mL). The organic layer was separated, and the aqueous layer was extracted twice with ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography using hexane/ethyl acetate.

Procedure for the Alkoxycarbonylation Reaction. In a Schlenk tube under nitrogen atmosphere, a solution of the substrate (1.2 mmol), $Pd_2(dba)_3$ (0.024 mmol), dppb (0.048 mmol), and 0.3 mL of ethanol in 10 mL of chloroform (stabilized with 2-methyl-2-butene) was placed in a 45 mL autoclave equipped with a magnetic stirring bar. At room temperature, the autoclave was flushed with CO three times and pressurized with CO and H_2 to 600 psi in a 1:1 ratio. The reaction was performed for 36h at 120 °C. After the reaction finished, the autoclave was cooled to room temperature, and the pressure was carefully released. Finally, the reaction mixture was purified by column chromatography using hexane and ethyl acetate as eluent.

*Ethyl 4-Phenoxybutanoate (**1b**).*[1a] Light-yellow oil, 177.2 mg, 75% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.54−7.03 (m, 2H), 6.86−6.94 (m, 3H), 4.13 (d, J = 7.1 Hz, 2H), 3.99 (t, J = 6.1 Hz, 2H), 2.50 (t, J = 7.3 Hz, 2H), 2.26−1.92 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 158.8, 129.4, 120.7, 114.4, 66.6, 60.4, 30.8, 24.6, 14.2. MS (EI) m/z 282.2.

*Ethyl 4-(4-Methylphenoxy)butanoate (**2b**).*[1a] Light-red oil, 198.1 mg, 72% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.16−6.95 (m, 2H), 6.77 (d, J = 8.6 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.96 (t, J = 6.1 Hz, 2H), 2.50 (t, J = 7.3 Hz, 2H), 2.27 (s, 3H), 2.16−1.98 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.3, 156.7, 129.9, 129.8, 114.3, 66.8, 60.4, 30.8, 24.7, 20.4, 14.2. MS (EI) m/z 222.1.

*Ethyl 4-(4-Methoxyphenoxy)butanoate (**3b**).*[1a] Yellow oil, 199.2 mg, 69% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.80 (s, 4H), 4.12 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 6.1 Hz, 2H), 3.74 (s, 3H), 2.48 (t, J = 7.3 Hz, 2H), 2.19−1.97 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.31, 153.85, 153.01, 115.45, 114.65, 67.40, 60.42, 55.74, 30.87, 24.77, 14.24. MS (EI) m/z 238.2.

*Ethyl 4-(4-tert-Butylphenoxy)butanoate (**4b**).*[1a] Yellow oil, 217.6 mg, 70% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.30−7.25 (m, 2H), 6.84−6.78 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.1 Hz, 2H), 2.49 (t, J = 7.3 Hz, 2H), 2.15−1.98 (m, 2H), 1.28 (s, 9H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 156.6, 143.3, 126.2, 113.9, 66.6, 60.4, 34.0, 31.5, 30.8, 24.7, 14.2. MS (EI) m/z 264.2.

*Ethyl 4-(4-Chlorophenoxy)butanoate (**5b**).*[2] Yellow oil, 201.5 mg, 71% yield, L/B = 98/2. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.22−7.13 (m, 2H), 6.88−6.73 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.95 (t, J = 6.1 Hz, 2H), 2.48 (t, J = 7.3 Hz, 2H), 2.16−1.98 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.1, 157.4, 129.3, 125.5, 115.7, 67.0, 60.4, 30.7, 24.5, 14.2. MS (EI) m/z 244.1.

*Ethyl 4-(4-Phenylphenoxy)butanoate (**6b**).*[1a] Light-yellow oil, 221.9 mg, 67% yield, L/B = 89/11. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.52 (m, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 4.04 (t, J = 6.0 Hz, 2H), 2.53 (t, J = 7.3 Hz, 2H), 2.22−2.03 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 158.4, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.7, 66.8, 60.4, 30.8, 24.7, 14.2. MS (EI) m/z 284.1.

*Ethyl 2-Methyl-3-(4-phenylphenoxy)propanoate (**6c**).* Light-yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.57−7.47 (m, 4H), 7.39 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.00−6.92 (m, 2H), 4.20 (m, 3H), 4.02 (dd, J = 9.1, 6.2 Hz, 1H), 3.00−2.88 (m, 1H), 1.30 (d, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 174.2, 158.2, 140.8, 134.0, 128.7, 128.1, 126.7, 126.6, 114.9, 69.7, 60.6, 39.9, 14.2, 14.0. MS (EI) m/z 284.1; HRMS (EI-MS) calcd for $C_{18}H_{20}O_3$ 284.1412, found 284.1413.

*Ethyl 4-(3-Methylphenoxy)butanoate (**7b**).*[1d] Yellow oil, 192.6 mg, 68% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.14 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 7.5 Hz, 1H), 6.75−6.66 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.1 Hz, 2H), 2.49 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 2.14−2.02 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.3, 158.8, 139.4, 129.1, 121.5, 115.3, 111.3, 66.5, 60.4, 30.8, 24.7, 21.5, 14.2. MS (EI) m/z 222.1.

*Ethyl 4-(3-Methoxyphenoxy)butanoate (**8b**).*[1a] Yellow oil, 201.6 mg, 70% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.15 (t, J = 8.2 Hz, 1H), 6.59−6.39 (m, 4H), 3.97 (t, J = 6.1 Hz, 1H), 3.77 (s, 3H), 2.49 (t, J = 7.3 Hz, 2H), 2.12−2.05 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 160.8, 160.1, 129.8, 106.6, 106.3, 100.9, 66.7, 60.4, 55.2, 30.8, 24.6, 14.2. MS (EI) m/z 238.2.

*Ethyl 4-(3-Chlorophenoxy)butanoate (**9b**).*[1a] Yellow oil, 203.3 mg, 72% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.16 (t, J = 8.1 Hz, 1H), 6.90 (ddd, J = 7.9, 1.9, 0.9 Hz, 1H), 6.86 (t, J = 2.2 Hz, 1H), 6.75 (ddd, J = 8.4, 2.4, 0.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.1 Hz, 2H), 2.49 (t, J = 7.3 Hz, 2H), 2.16−2.02 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 159.5, 134.8, 130.2, 120.9, 114.8, 113.0, 66.9, 60.5, 30.7, 24.5, 14.2. MS (EI) m/z 244.1.

*Ethyl 4-(2-Methylphenoxy)butanoate (**10b**).*[2] Yellow oil, 189.9 mg, 69% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.12 (t, J = 7.1 Hz, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.99 (t, J = 6.0 Hz, 2H), 2.52 (t, J = 7.4 Hz, 2H), 2.20 (s, 3H), 2.16−2.04 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.3, 156.9, 130.6, 126.8, 126.7, 120.3, 110.8, 66.6, 60.4, 30.9, 24.7, 16.1, 14.2. MS (EI) m/z 222.1.

*Ethyl 4-(2-Methoxyphenoxy)butanoate (**11b**).* Yellow oil, 200.1 mg, 69% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.94−6.83 (m, 4H), 4.12 (q, J = 7.1 Hz, 2H), 4.04 (t, J = 6.3 Hz, 2H), 3.83 (s, 3H), 2.52 (t, J = 7.3 Hz, 2H), 2.13 (p, J = 6.8 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 149.6, 148.3, 121.2, 120.8, 113.5, 111.9, 67.9, 60.4, 55.9, 30.8, 24.6, 14.2. MS (EI) m/z 238.1; HRMS (EI-MS) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1310.

*Ethyl 4-(2-Chlorophenoxy)butanoate (**12b**).*[2] Yellow oil, 202.5 mg, 71% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33 (dd, J = 7.8, 1.6 Hz, 1H), 7.18 (ddd, J = 8.3, 7.5, 1.6 Hz, 1H), 6.94−6.83 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 6.1 Hz, 2H), 2.56 (t, J = 7.3 Hz, 2H), 2.22−2.07 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 154.3, 130.2, 127.6, 122.9, 121.4, 113.4, 67.8, 60.4, 30.6, 24.5, 14.2. MS (EI) m/z 244.1.

*Ethyl 4-(2-Hydroxyphenoxy)butanoate (**13b**).* Light-yellow oil, 188.2 mg, 72% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.93−6.77 (m, 4H), 5.82 (br, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 2.50 (t, J = 7.0 6 Hz, 2H), 2.22−2.07 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 146.0, 145.7, 121.7, 120.0, 114.8, 111.9, 68.1, 60.7, 31.2, 24.6, 14.1. MS (EI) m/z 224.1; HRMS (EI-MS) calcd for $C_{12}H_{16}O_4$ 224.1049, found 224.1029.

*Ethyl 4-(1-Naphthyloxy)butanoate (**14b**).*[1a] Yellow oil, 218.7 mg, 73% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.35−8.18 (m, 1H), 7.78 (dd, J = 6.6, 2.7 Hz, 1H), 7.59−7.39 (m, 3H), 7.35 (t, J = 7.9 Hz, 1H), 6.79 (d, J = 7.5 Hz, 1H), 4.19−4.16 (m, 4H), 2.62 (t, J = 7.3 Hz, 2H), 2.33−2.18 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.3, 154.5, 134.5, 127.4, 126.4, 125.8, 125.6, 125.1, 122.0, 120.2, 104.5, 66.9, 60.5, 31.1, 24.7, 14.2. MS (EI) m/z 258.3.

*Ethyl 4-(2-Naphthyloxy)butanoate (**15b**).*[1a] Yellow oil, 216.3 mg, 71% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.80−7.69 (m, 3H), 7.48−7.40 (m, 1H), 7.37−7.30 (m, 1H), 7.17−7.10 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 4.12 (t, J = 6.1 Hz, 2H), 2.56 (t, J = 7.3 Hz, 2H), 2.27−2.10 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR

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(100 MHz, $CDCl_3$, δ ppm): 173.2, 156.8, 134.6, 129.4, 129.0, 127.6, 126.7, 126.3, 123.6, 118.9, 106.6, 66.7, 60.5, 30.9, 24.6, 14.2. MS (EI) *m*/*z* 258.3.

*Ethyl 4-(Phenylthio)butanoate (**16b**).*[17] Yellow oil, 186.6 mg, 70% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.36−7.22 (m, 4H), 7.20−7.13 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.94 (p, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 172.9, 136.1, 129.3, 128.9, 126.0, 60.4, 32.9, 32.9, 24.4, 14.2. MS (EI) *m*/*z* 224.3.

*Ethyl 4-(4-Methoxyphenylthio)butanoate (**17b**).*[18] Yellow oil, 209.9 mg, 69% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.83 (t, *J* = 7.1 Hz, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.86 (p, *J* = 7.3 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.0, 159.0, 133.3, 126.0, 114.6, 60.3, 55.3, 35.1, 32.8, 24.5, 14.2. MS (EI) *m*/*z* 254.3.

*Ethyl 4-(4-Fluorophenylthio)butanoate (**18b**).* Yellow oil, 207.1 mg, 71% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.35−7.31 (m, 2H), 7.00−7.95 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.89 (p, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 172.9, 163.0, 160.6 (d, 1JC-F = 245 Hz), 132.5, 132.4, 130.8, 116.1, 115.9, 60.4, 34.3, 32.8, 24.3, 14.2. MS (EI) *m*/*z* 242.1; HRMS (EI-MS) calcd for $C_{12}H_{15}O_2SF$ 242.0777, found 242.0759.

*Ethyl 4-(2-Naphthalenylthio)butanoate (**19b**).*[19] Yellow oil, 228.8 mg, 70% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.78−7.72 (m, 4H), 7.49−7.37 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.99 (p, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 172.9, 133.8, 133.6, 131.7, 128.4, 127.7, 127.4, 127.0, 127.0, 126.5, 125.6, 60.4, 32.9, 32.8, 24.3, 14.2. MS (EI) *m*/*z* 274.4.

*Ethyl 5-Phenylpentanoate (**20b**) and Ethyl 2-Methyl-4-phenylbutanoate (**20c**).* The mixture cannot be distinguished in ^{1}H NMR. Yellow oil, 176.7 mg, 74% yield, L/B = 65/35. ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 176.1, 173.5, 166.5, 141.4, 139.4, 129.0, 128.6, 128.5, 128.3, 128.3, 126.2, 125.9, 60.2, 41.5, 39.7, 35.1, 33.7, 26.5, 16.8, 14.2, 14.1.

*Ethyl 4-Phenylbutanoate (**21b**).* Yellow oil, 207.1 mg, 71% yield, L/B = 80/20. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.38−7.22 (m, 3H), 7.22−7.09 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.70−2.58 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.03−1.82 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.5, 141.4, 128.5, 128.3, 125.9, 60.2, 35.1, 33.7, 26.5, 14.2.

*Ethyl 5-(Phenoxy)pentanoate (**22b**).* Yellow oil, 201.7 mg, 76% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.34−7.20 (m, 2H), 6.98−6.83 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.96 (t, *J* = 5.6 Hz, 2H), 2.37 (t, *J* = 5.9 Hz, 2H), 1.82−1.79 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.5, 158.9, 129.4, 120.6, 114.4, 67.2, 60.3, 33.9, 28.7, 21.6, 14.2. MS (EI) *m*/*z* 222.1; HRMS (EI-MS) calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1248.

*Ethyl 6-(Phenoxy)hexanoate (**23b**).*[20] Yellow oil, 193.4 mg, 70% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.30−7.22 (m, 2H), 6.95−6.84 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.86−1.74 (m, 2H), 1.73−1.65 (m, 2H), 1.56−1.44 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 159.0, 129.4, 120.5, 114.4, 67.5, 60.2, 34.2, 28.9, 25.6, 24.7, 14.2. MS (EI) *m*/*z* 236.3.

*Ethyl 7-(Phenoxy)heptanoate (**24b**).* Yellow oil, 83.7 mg, 35% yield, L/B = 85/15. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.28−7.24 (m, 2H), 7.05−6.76 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.86−1.71 (m, 2H), 1.69−1.61 (m, 2H), 1.52−1.34 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 159.1, 129.4, 120.5, 114.5, 67.6, 60.1, 34.2, 29.1, 28.9, 25.7, 24.9, 14.2. MS (EI) *m*/*z* 250.2; HRMS (EI-MS) calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1550.

*Ethyl 9-(Phenoxy)nonanoate (**25b**).* Yellow oil, 147.7 mg, 45% yield, L/B = 90/10. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.32−7.21 (m, 2H), 6.98−6.81 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.83−1.70 (m, 2H), 1.66−1.53 (m, 2H), 1.50−1.28 (m, 8H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.8, 159.1, 129.4, 120.4, 114.5, 67.8, 60.1, 34.3, 29.2, 29.2, 29.1, 29.0, 26.0, 24.9, 14.2. MS (EI) *m*/*z* 278.2; HRMS (EI-MS) calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1886.

*Ethyl 5-(Phenylthio)pentanoate (**26b**).* Yellow oil, 192.3 mg, 68% yield, L/B = 75/25. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33−7.22 (m, 4H), 7.19−7.12 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.99−2.84 (m, 2H), 2.29 (t, *J* = 7.3 Hz, 2H), 1.84−1.59 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.3, 136.5, 129.2, 129.1, 128.8, 125.8, 60.3, 33.8, 33.2, 28.5, 24.0, 14.2. MS (EI) *m*/*z* 238.1; HRMS (EI-MS) calcd for $C_{13}H_{18}O_2S$ 238.1028, found 238.1027.

*Ethyl 2-Methyl-4-(phenylthio)butanoate (**26c**).* Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.34−7.25 (m, 4H), 7.19−7.12 (m, 1H), 4.11. (q, *J* = 7.1 Hz, 2H), 3.03−2.81 (m, 2H), 2.65−2.56 (m, 1H), 2.08−1.91 (m, 1H), 1.75−1.66 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 175.9, 136.2, 129.2, 128.9, 125.9, 60.4, 38.5, 33.0, 31.3, 17.0, 14.2. MS (EI) *m*/*z* 238.1; HRMS (EI-MS) calcd for $C_{13}H_{18}O_2S$ 238.1028, found 238.1066.

*Ethyl 6-(Phenylthio)hexanoate (**27b**).* Yellow oil, 207.9 mg, 70% yield, L/B = 87/13. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33−7.22 (m, 4H), 7.18−7.11 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.71−1.55 (m, 4H), 1.51−1.38 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 136.7, 129.0, 128.8, 125.8, 60.2, 34.1, 33.4, 28.8, 28.2, 24.5, 14.2. MS (EI) *m*/*z* 252.1; HRMS (EI-MS) calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1164.

*Ethyl 2-Methyl-5-(phenylthio)pentanoate (**27c**).* Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.34−7.22 (m, 4H), 7.19−7.11 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.46−2.34 (m, 1H), 1.83−1.70 (m, 1H), 1.69−1.48 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 176.4, 136.5, 129.1, 128.8, 125.8, 60.2, 39.1, 33.5, 32.8, 26.8, 17.1, 14.2. MS (EI) *m*/*z* 252.1; HRMS (EI-MS) calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1192.

*Ethyl 6-(Phenylthio)heptanoate (**28b**).* Yellow oil, 145.8 mg, 46% yield, L/B = 86/14. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33−7.21 (m, 4H), 7.18−7.11 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.77−1.54 (m, 4H), 1.51−1.27 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 136.9, 128.9, 128.8, 125.7, 60.2, 34.2, 33.5, 28.9, 28.6, 28.4, 24.8, 14.2.

*Ethyl 9-(Phenylthio)nonanoate (**29b**).* Yellow oil, 206.8 mg, 62% yield, L/B = 95/5. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33−7.20 (m, 4H), 7.18−7.11 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.92−2.86 (m, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.68−1.54 (m, 4H), 1.41−1.36 (m, 2H), 1.28−1.21 (m, 9H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.8, 137.0, 128.8, 128.8, 125.6, 60.1, 34.3, 33.5, 29.1, 29.0, 28.9, 28.7, 24.9, 14.2. MS (EI) *m*/*z* 294.2; HRMS (EI-MS) calcd for $C_{17}H_{26}O_2S$ 294.1654, found 294.1648.

*Ethyl 11-(Phenylthio)undecanoate (**30b**).* Yellow oil, 73.8 mg, 21% yield, L/B = 98/2. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.31−7.23 (m, 4H), 7.18−7.11 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.97−2.80 (m, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.68−1.54 (m, 5H), 1.45−1.18 (m, 14H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.9, 137.0, 128.8, 128.8, 125.6, 60.1, 34.3, 33.5, 29.4, 29.3, 29.2, 29.1, 28.8, 24.9, 14.2. MS (EI) *m*/*z* 322.2; HRMS (EI-MS) calcd for $C_{19}H_{30}O_2S$, 322.1967 found 322.1964.

*Methyl 4-(2-Hydroxyphenoxy)butanoate (**31b**).*[21] Yellow oil, 169.3 mg, 68% yield, L/B = 100/0. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.95−6.75 (m, 4H), 5.83 (s, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 3.69 (s, 3H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.21−2.10 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 174.1, 146.0, 145.7, 121.7, 120.0, 114.8, 111.9, 68.0, 51.8, 31.0, 24.6. MS (EI) *m*/*z* 210.2.

*Propyl 6-(Phenoxy)hexanoate (**32b**).* Yellow oil, 195.9 mg, 62% yield, L/B = 92/8. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.28−7.23 (m, 2H), 6.96−6.83 (m, 3H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.87−1.44 (m, 8H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 159.0, 129.4, 120.5, 114.4, 67.5, 65.9, 34.2, 28.9, 25.7, 24.7, 22.0, 10.4. MS

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(EI) m/z 250.2; HRMS (EI-MS) calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1566.

*Isopentyl 4-(4-Methoxyphenylthio)butanoate (**33b**).* Yellow oil, 220.3 mg, 63% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.33 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.07 (t, J = 6.9 Hz, 2H), 3.77 (s, 3H), 2.82 (t, J = 7.1 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 1.89−1.82 (m, 2H), 1.68−1.60 (m, 1H), 1.48 (q, J = 6.9 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.1, 159.0, 133.4, 126.0, 114.6, 63.1, 55.3, 37.3, 35.2, 32.8, 25.0, 24.5, 22.4. MS (EI) m/z 296.1; HRMS (EI-MS) calcd for $C_{16}H_{24}O_3S$ 296.1446, found 296.1445.

*Isopropyl 5-(Phenoxy)pentanoate (**34b**).* Yellow oil, 194.4 mg, 70% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.30−7.20 (m, 2H), 6.96−6.80 (m, 3H), 5.04−4.95 (m, 1H), 4.00−3.92 (m, 2H), 2.40−2.28 (m, 2H), 1.82−1.78 (m, 4H), 1.21 (d, J = 6.3 Hz, 6H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.0, 158.9, 129.4, 120.6, 114.4, 67.5, 67.2, 34.3, 28.7, 21.8, 21.7. MS (EI) m/z 236.1; HRMS (EI-MS) calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1415.

*Cyclopentyl 4-(Naphthalen-2-yloxy)butanoate (**35b**).* Red oil, 267.9 mg, 74% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76−7.70 (m, 3H), 7.44−7.40 (m, 1H), 7.34−7.30 (m, 1H), 7.17−7.09 (m, 2H), 5.21−5.18 (m, 1H), 4.11 (t, J = 6.1 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 2.22−2.10 (m, 2H), 1.93−1.80 (m, 2H), 1.77−1.51 (m, 6H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.0, 156.8, 134.5, 129.3, 128.9, 127.6, 126.7, 126.3, 123.6, 118.9, 106.6, 77.1, 66.8, 32.7, 31.2, 24.7, 23.7. MS (EI) m/z 298.2; HRMS (EI-MS) calcd for $C_{19}H_{22}O_3$ 298.1569, found 298.1564.

*(−)-Menthol 9-(Phenoxy)nonanoate (**36b**).* Yellow oil, 201.7 mg, 57% yield, L/B = 98/2. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.40−7.14 (m, 2H), 6.92−6.86 (m, 3H), 4.66 (td, J = 10.9, 4.4 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 2.26 (t, J = 7.5 Hz, 2H), 1.96 (d, J = 11.6 Hz, 1H), 1.91−1.54 (m, 8H), 1.52−1.25 (m, 10H), 0.89−0.87 (m, 8H), 0.74 (d, J = 7.0 Hz, 3H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 173.4, 159.1, 129.4, 120.4, 114.5, 73.9, 67.8, 47.0, 40.9, 34.7, 34.3, 31.3, 29.2, 29.2, 29.2, 29.0, 26.2, 26.0, 25.1, 23.4, 22.0, 20.7, 16.3. MS (EI) m/z 388.2; HRMS (EI-MS) calcd for $C_{25}H_{40}O_3$ 388.2977, found 388.2980

*Phenyl 4-(Phenylthio)butanoate (**37b**).* Yellow oil, 236.7 mg, 73% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.39 (s, 5H), 7.36−7.32 (m, 2H), 7.30−7.26 (m, 2H), 7.20−7.16 (m, 1H), 2.98 (t, J = 7.1 Hz, 2H), 2.82 (t, J = 7.2 Hz, 2H), 2.05−1.98 (m, 2H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 196.8, 135.7, 134.5, 129.6, 129.4, 129.2, 129.0, 127.6, 126.2, 42.0, 32.9, 24.8. MS (EI) m/z 272.1; HRMS (EI-MS) calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0874

*1-Naphthalenyl 6-(Phenylthio)hexanoato (**38b**).* Yellow oil, 342.4 mg, 47% yield, L/B = 99/1. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.94−7.80 (m, 2H), 7.73 (d, J = 8.3 Hz, 1H), 7.57−7.41 (m, 3H), 7.39−7.11 (m, 6H), 2.97 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 1.95−1.82 (m, 2H), 1.79−1.72 (m, 2H), 1.70−1.57 (m, 2H).^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, δ ppm): 172.0, 146.6, 136.6, 134.6, 129.1, 128.9, 128.0, 126.8, 126.4, 126.4, 125.9, 125.8, 125.4, 121.1, 118.0, 34.2, 33.5, 28.8, 28.3, 24.6. MS (EI) m/z 350.1; HRMS (EI-MS) calcd for $C_{22}H_{22}O_2S$ 350.1341, found 350.1329.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00522.

^{1}H and ^{13}C spectra, spectral data and table of screening data (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Jochanan Blum, who was a wonderful educator, researcher, and lovely person. May his memory be a blessing.

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