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Synthesis of functionalized 2-(arylthio)benzoates by formal [3+3] cyclizations of 3-arylthio-1-silyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones and 1,3-diacylcyclopropanes

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ABSTRACT

Functionalized 2-(arylthio)benzoates are prepared by formal [3+3] cyclizations of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones and 1,1-diacylcyclopropanes.

1. Introduction

Functionalized diaryl sulfides are pharmacologically important molecules which occur in various natural products. For example, they are present in dibenzothiophenes,[1] varacins (lissoclinotoxins),[2] lissoclibadins,[3] cyclic sulfides,[4] and various other natural products isolated from *Streptomyces griseus*.[5] Diaryl sulfides are synthetically available by reaction of arenes with sulfur[6] and sulfur dichloride,[7] by condensation of organometallic reagents with chlorophenyl-sulfide[8] and by base-mediated reaction of chloroarenes with thiophenols.[9] These reactions often suffer from their low regioselectivity and from the formation of polysulfides, due to the harsh reaction conditions.

An alternative approach to diaryl sulfides is based on the use of sulfur-containing building blocks in cyclization reactions. Hilt and co-workers reported a convenient approach to diaryl sulfides by cobalt(I)-catalyzed [4+2] cycloaddition of alkynyl sulfides with 1,3-butadienes.[10] Recently, we have studied[11] the synthesis of 3- and 5-(arylthio)salicylates by $TiCl_4$-mediated formal [3+3] cyclizations[12] of 1,3-bis(silyloxy)-1,3-butadienes[13] with 3-silyloxy-2-en-1-ones.[14] Chan et al. reported the synthesis of methyl 4,6-dimethyl-2-(phenylthio)benzoate by $TiCl_4$-mediated [3+3] cyclization of 4-trimethylsilyloxy-3-penten-2-one with 1-methoxy-3-phenylthio-1-trimethylsilyloxy-1,3-butadiene.[15] Simple 2-(aryloxythio)benzoates have been prepared by catalytic cyclizations of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 1,1,3,3-tetramethoxypropane.[16] In addition, the synthesis of 6-alkyl- and 6-aryl-2-(arylthio)benzoates by cyclization of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 3-alkoxy-2-en-1-ones has been reported.[17] We have recently studied the synthesis of 5-chloroethyl-2-(arylthio)benzoates by $TiCl_4$-mediated domino '[3+3] cyclization/homo-Michael' reaction of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 1,1-diacylcyclopropanes.[18] Herein, we provide a full account of this work. In addition, we report a comprehensive study related to the formal [3+3] cyclization of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones. The reactions reported provide a convenient approach to substituted 2-(arylthio)benzoates and thioxanthones which are not readily available by other methods.

2. Results and discussion

3-Arylthio-1-trimethylsilyloxy-1,3-butadienes **3a–m** were prepared, as previously reported,[15,18] by reaction of methyl acetoacetate (**1a**), methyl 3-oxopentanoate (**1b**), and methyl 3-oxohexanoate (**1c**) with various thiophenols to give methyl 3-(arylthio)crotonates **2a–m** (Scheme 1). The latter were subsequently transformed into **3a–m** by deprotonation (LDA) and subsequent silylation.

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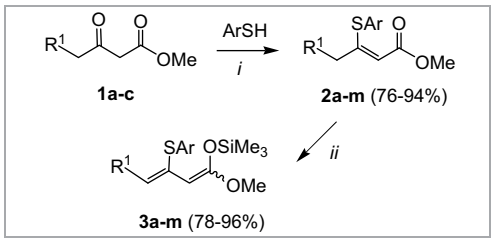
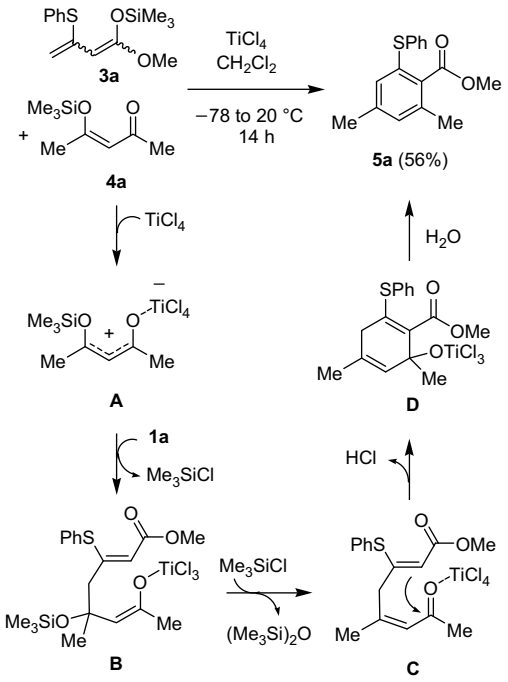


Scheme 1. Synthesis of **3a–m**. Conditions: (i) P_4O_{10}, CH_2Cl_2, 20 °C, 18 h; (ii) (1) LDA, THF, −78 °C, 1 h; (2) Me_3SiCl, −78→20 °C, 14 h.

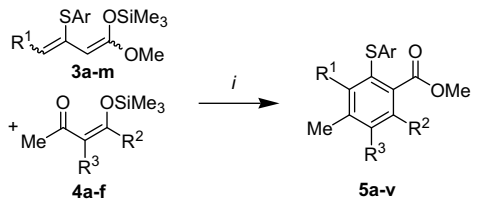
The $TiCl_4$-mediated cyclization of **3a** with 3-silyloxy-2-en-1-one **4a**, prepared from acetylacetone, afforded the 2-(phenylthio)benzoate **5a** (Scheme 2). The best yields were obtained when the reaction was carried out in a highly concentrated solution (stoichiometric ratio: **3a**/**4a**/$TiCl_4$=1.0/1.5/1.5). The solution was slowly warmed from −78 to 20 °C (20 h).



Scheme 2. Possible mechanism of the formation of **5a**.

The formation of **5a** can be explained by reaction of **4a** with $TiCl_4$ to give intermediate **A** (Scheme 2). The attack of the terminal carbon atom of **3a** onto **A** afforded intermediate **B**. The elimination of TMS-siloxane (intermediate **C**) and subsequent cyclization gave intermediate **D**. The elimination of titanium hydroxide (before or during the aqueous work-up) and aromatization resulted in the formation of product **5a**. Due to the symmetrical structure of **A**, the attack of **1a** on either terminal allylic carbon atom would result in the formation of the same product (**5a**).

The cyclization of dienes **3a–m** with 3-silyloxy-2-en-1-ones **4a–f** afforded the 2-(thioaryloxy)benzoates **5a–v** (Scheme 3, Table 1).



Scheme 3. Synthesis of **5a–v**.

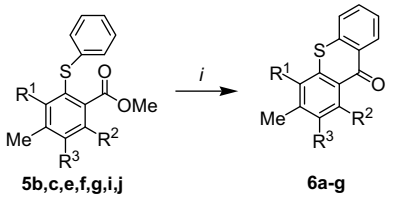
Table 1
Synthesis of **5a–v**

3	4	5	Ar	R^1	R^2	R^3	% (**5**)[a]
a	**a**	**a**	Ph	H	Me	H	56
a	**b**	**b**	Ph	H	Me	Me	43
a	**c**	**c**	Ph	H	Me	Cl	43
a	**d**	**d**	Ph	H	Me	PhS	63
a	**e**	**e**	Ph	H	*n*Pr	H	42
b	**b**	**f**	Ph	Me	Me	Me	55
b	**c**	**g**	Ph	Me	Me	Cl	49
b	**f**	**h**	Ph	Me	Ph	H	52
c	**b**	**i**	Ph	Et	Me	Me	55
c	**c**	**j**	Ph	Et	Me	Cl	51
c	**f**	**k**	Ph	Et	Ph	H	50
d	**a**	**l**	4-MeC_6H_4	H	Me	H	54
e	**a**	**m**	4-MeC_6H_4	Me	Me	H	39
f	**a**	**n**	3-MeC_6H_4	H	Me	H	57
g	**a**	**o**	4-EtC_6H_4	H	Me	H	49
h	**a**	**p**	4-EtC_6H_4	Me	Me	H	45
i	**a**	**q**	4-ClC_6H_4	H	Me	H	37
i	**c**	**r**	4-ClC_6H_4	H	Me	Cl	35
j	**a**	**s**	4-ClC_6H_4	Me	Me	H	36
k	**a**	**t**	3-ClC_6H_4	H	Me	H	37
l	**a**	**u**	4-FC_6H_4	H	Me	H	40
m	**a**	**v**	4-FC_6H_4	Me	Me	H	33

[a] Isolated yields.

Products **5h** and **5k** were formed with very good regioselectivity. Only the isomers containing the phenyl group located *ortho* to the ester group were isolated. The other isomers could not be isolated. However, the yields of **5h** and **5k** the isolated products were only moderate. This can be explained by practical reasons (loss of material during the chromatographic purification) and by hydrolysis of the diene (small amounts of methyl 3-(arylthio)-crotonates **2** were isolated in some cases). Inspection of the crude product mixture by ^1H NMR and TLC suggests that the reaction indeed proceeded with very good regioselectivity. The regioselectivity is in agreement with the regiochemical result of the reaction of **4f** with 1,3-bis(silyloxy)-1,3-butadienes and might be explained by steric reasons.[12,15] The regioselective formation of **5e** is surprising, since the effective sizes of *n*-propyl and methyl group are similar. The reaction of 1,3-bis(silyloxy)-1,3-butadienes with **4e** has not been previously studied. In general, the yields of products **5a–v** are only moderate (33–63%). This can be again explained by practical problems during the isolation and purification process.

Treatment of 2-(arylthio)benzoates **5b**,**c**,**e**,**f**,**g**,**i**,**j** with concd sulfuric acid resulted in an intramolecular Friedel–Crafts cyclization to give the thioxanthones **6a–g** in excellent yields (Scheme 4, Table 2).



Scheme 4. Synthesis of **6a–g**. Conditions: (i) concd H_2SO_4, 20 °C, 2 h.

Table 2
Synthesis of thioxanthones **6a–g**

5	8	R^1	R^2	R^3	% (**6**)[a]
b	**a**	H	Me	Me	98
c	**b**	H	Me	Cl	97
e	**c**	H	*n*-Pr	H	95
f	**d**	Me	Me	Me	97
g	**e**	Me	Me	Cl	97
i	**f**	Et	Me	Me	95
j	**g**	Et	Me	Cl	96

[a] Isolated yields.

The structures of all products were elucidated by spectroscopic methods. The structure of **6f** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[19]

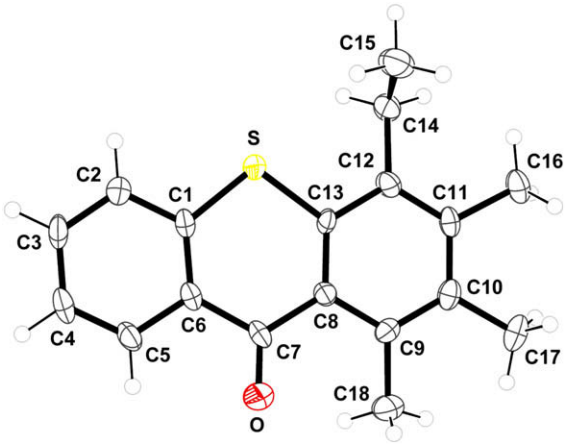
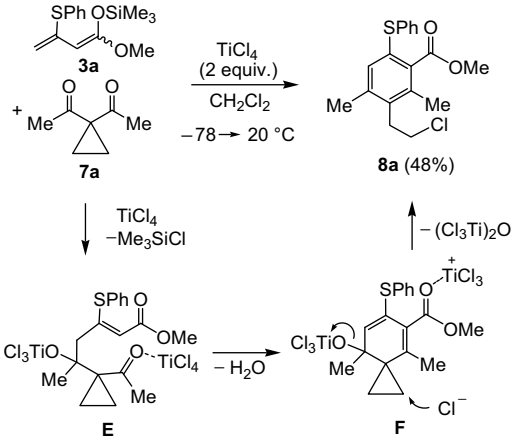


Figure 1. Ortep plot of **8f**.

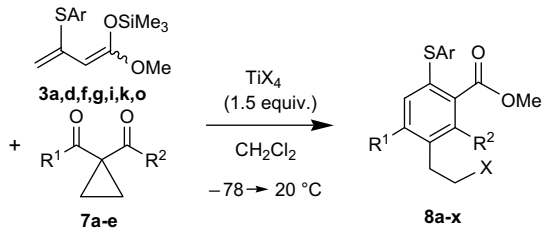
The $TiCl_4$-mediated cyclization of **3a** with 1,1-diacetylcyclopropane (**7a**) afforded the 2-(phenylthio)benzoate **8a** (Scheme 5). During the optimization, the stoichiometry (1.5 equiv of $TiCl_4$ and of **7a**) played an important role. The yields dropped when only 1.0 equiv of $TiCl_4$ and of **7a** were employed. The yield also decreased when an excess of **3a** was used. The concentration (30 mL per mmol of **3a**) also proved to be an important parameter. A complex mixture was obtained when the reaction was carried out in a highly concentrated solution (following the procedure given for the reaction of **3a** with 4-(trimethylsilyloxy)pent-3-en-2-one, vide supra).



Scheme 5. Possible mechanism of the formation of **8a**.

The formation of **8a** can be explained by a domino '[3+3] cyclization/homo-Michael' reaction. The $TiCl_4$-mediated attack of the terminal carbon atom of **3a** onto **7a** gave intermediate **E**, cyclization via the central carbon atom gave intermediate **F**, and $TiCl_4$-assisted cleavage of the spirocyclopropane moiety and aromatization led to the formation of the final product **8a**. Reactions of acceptor-substituted cyclopropanes have been classified by Danishefsky in terms of 'strictly nucleophilic ring openings', 'electrophilically assisted ring openings' and 'spiro-activations'.[20] In the present case, a 'spiro-activation' is combined with the activation by an electrophile.[21]

The cyclization of 1-trimethylsilyloxy-3-arylthio-1,3-butadienes **3a**,**d**,**f**,**g**,**i**,**k**,**o** with 1,1-diacylcyclopropanes **7a**–**e**, in the presence of $TiCl_4$ or $TiBr_4$, afforded the 5-haloethyl-2-(arylthio)benzoates **8a**–**x** (Scheme 6, Table 3). Products **8b**–**d**,**g**,**i**,**j**,**l**,**o**, derived from the unsymmetrical cyclopropanes **7b**–**d**, were formed with very good regioselectivity. This can be explained by regioselective attack of the terminal carbon atom of diene **3** onto the acetyl rather than the less reactive aroyl group of **7b**–**d**.



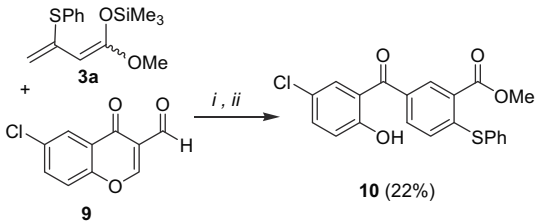
Scheme 6. Synthesis of **8a**–**x**. Reagents and conditions: (i) TiX_4, CH_2Cl_2, −78→20 °C, 14 h.

Table 3
Synthesis of **8a**–**x**

3	7	8	Ar	R^1	R^2	X	%[a]
a	**a**	**a**	Ph	Me	Me	Cl	48
a	**b**	**b**	Ph	Me	Ph	Cl	47
a	**c**	**c**	Ph	Ph	4-ClC_6H_4	Cl	43
a	**d**	**d**	Ph	Ph	4-FC_6H_4	Cl	40
a	**e**	**e**	Ph	Et	Et	Br	28
a	**a**	**f**	Ph	Me	Me	Br	58
a	**b**	**g**	Ph	Me	Ph	Br	40
d	**a**	**h**	4-MeC_6H_4	Me	Me	Cl	40
d	**b**	**i**	4-MeC_6H_4	Me	Ph	Cl	41
d	**b**	**j**	4-MeC_6H_4	Me	Ph	Br	45
i	**a**	**k**	4-ClC_6H_4	Me	Me	Cl	43
i	**b**	**l**	4-ClC_6H_4	Me	Ph	Cl	47
i	**a**	**m**	4-ClC_6H_4	Me	Me	Br	41
o	**a**	**n**	3-(MeO)C_6H_4	Me	Me	Cl	35
o	**b**	**o**	3-(MeO)C_6H_4	Me	Ph	Cl	33
o	**a**	**p**	3-(MeO)C_6H_4	Me	Me	Br	41
k	**a**	**q**	3-ClC_6H_4	Me	Me	Br	40
f	**a**	**r**	3-MeC_6H_4	Me	Me	Br	40
f	**a**	**s**	3-MeC_6H_4	Me	Me	Cl	43
d	**a**	**t**	4-MeC_6H_4	Me	Me	Br	40
g	**b**	**u**	4-EtC_6H_4	Me	Ph	Br	38
g	**a**	**v**	4-EtC_6H_4	Me	Me	Br	42
g	**a**	**w**	4-EtC_6H_4	Me	Me	Cl	44
g	**b**	**x**	4-EtC_6H_4	Me	Ph	Cl	40

[a] Isolated yields.

The Me_3SiOTf-catalyzed reaction of diene **3a** with 3-formylchromone **9** afforded the highly functionalized diaryl sulfide **10** (Scheme 7). The formation of product **10** can be explained by a domino 'Michael/retro-Michael/Mukaiyama–Aldol' reaction. This type of reaction has been earlier reported for 1,3-bis(silyloxy)-1,3-butadienes.[22]



Scheme 7. Synthesis of **10**: Reagents and conditions: (i) Me_3SiOTf (0.3 equiv) 20 °C, 10 min; (ii) (1) **3a** (1.3 equiv), CH_2Cl_2, 0→20 °C, 12 h; (2) HCl (10%).

In conclusion, we have reported the synthesis of substituted 2-(arylthio)benzoates and thioxanthones based on formal [3+3] cyclizations of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones and 1,1-diacylcyclopropanes.

3. Experimental section

3.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used.

3.2. General procedure for the synthesis of 2-(thiophenoxy)benzoates 5a–v

To a dichloromethane solution (5 mL/mmol of **3**) of **3** (1.0 mmol) and of **4** (1.5 mmol) was added $TiCl_4$ (1.5 mmol) at −78 °C. The solution was allowed to warm to 20 °C within 20 h. To the solution was added a saturated aqueous solution of $NaHCO_3$ (15 mL). The organic and the aqueous layer were separated and the latter was extracted with diethyl ether (3×20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, EtOAc/*n*-heptane=1:4).

3.2.1. 2,4-Dimethyl-6-phenylsulfanyl-benzoic acid methyl ester (**5a**)

Starting with **4a** (387 mg, 2.3 mmol), **3a** (420 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5a** was isolated as a highly viscous oil (229 mg, 56%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.05 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.67 (s, 3H, OCH_3), 6.75–7.12 (m, 7H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=19.6, 21.1 (CH_3), 52.0 (OCH_3), 126.9 (ArCH), 129.0 (2C, ArCH), 130.4 (ArCH), 130.8 (2C, ArCH), 131.0 (ArCH), 132.7, 134.0, 135.9, 136.1, 140.7 (ArC), 169.1 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2990 (w), 2947 (w), 2920 (w), 1726 (s), 1599 (m), 1581 (w), 1516 (w), 1476 (m), 1438 (s), 1378 (w), 1267 (s), 1257 (s), 1217 (m), 1188 (m), 1151 (s), 1078 (s), 1023 (m), 999 (w), 956 (w), 852 (m), 810 (m), 738 (s), 689 (s), 579 (m), 555 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 272 (60), 241 (41), 240 (21), 239 (M^+, 100), 198 (15), 197 (26), 165 (6), 91 (4). HRMS (EI): calcd for $C_{16}H_{16}O_2S$ 272.08655, found 272.086221.

3.2.2. Methyl 2,3,4-trimethyl-6-(phenylsulfanyl)benzoate (**5b**)

Starting with **4b** (558 mg, 3.0 mmol), **3a** (562 g, 2.0 mmol), $TiCl_4$ (0.32 mL, 3.0 mmol) and CH_2Cl_2 (10 mL), **5b** was isolated as a yellow highly viscous oil (250 mg, 43%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 6.76 (s, 1H, ArH), 7.0 (m, 2H, ArH), 7.06 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.7, 17.5, 20.6 (CH_3), 52.6 (OCH_3), 126.2 (ArCH), 127.2 (C), 128.8 (2C, ArCH), 129.5 (2C, ArCH), 133.3 (ArCH), 133.7, 136.0, 136.07, 137.2, 138.7, 169.7 (C). IR (neat): $\tilde{\nu}$ = 3382(w), 2940 (s), 1712 (m), 1609 (m), 1530 (m), 1481 (m), 1311 (m), 1213 (m), 1162 (m), 1010 (m), 758 (w), 730 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 286 (M^+, 58), 253 (100), 240 (8), 211 (15), 178 (6). HRMS (EI): calcd for $C_{17}H_{18}O_2S$ [M^+] 286.10220, found 286.10225.

3.2.3. Methyl 3-chloro-2,4-dimethyl-6-(phenylsulfanyl)-benzoate (**5c**)

Starting with **4c** (621 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiCl_4$ (0.32 mL, 3.0 mmol) and CH_2Cl_2 (11 mL), **5c** was isolated as a highly viscous oil (350 mg, 57%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 7.01 (s, 1H, ArH), 7.16 (m, 2H, ArH), 7.33 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.1, 20.8 (CH_3), 52.3 (OCH_3), 127.0 (ArCH), 129.1 (2C, ArCH), 130.0 (C), 130.5 (2C, ArCH), 133.0 (ArCH), 135.0, 135.7, 135.8, 136.6, 138.4, 168.3 (C). IR (neat): $\tilde{\nu}$ = 3382(w), 2898 (s), 1722 (m), 1663 (s), 1534 (m), 1434 (m), 1321 (s), 1223 (s), 1123 (m), 1024 (m), 768 (w), 713 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 308 (M^+, ^{37}Cl, 37), 306 (M^+, ^{35}Cl, 41), 267 (100), 105 (89), 77 (34). HRMS (EI): calcd for $C_{15}H_{17}O_2ClS$ [M^+, ^{35}Cl]: 306.06127, found 306.06139.

3.2.4. Methyl 2,4-dimethyl-3,6-bis(phenylsulfanyl)benzoate (**5d**)

Starting with **4d** (840 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiCl_4$ (0.32 mL, 3.0 mmol), and CH_2Cl_2 (11 mL), **5d** was isolated as a highly viscous oil (485 mg, 63%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.87 (s, 1H, ArH), 7.03 (m, 3H, ArH), 7.11 (m, 2H, ArH), 7.23 (m, 3H, ArH), 7.34 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.1, 22.1 (CH_3), 52.1 (OCH_3), 125.1 (ArCH), 125.9 (2C, ArCH), 127.7 (ArCH), 129.0 (2C, ArCH), 129.3 (2C, ArCH), 130.0 (C), 131.2 (ArCH), 132.0 (2C, ArCH), 134.5, 134.9, 135.1, 136.9, 141.1, 145.8, 168.8 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2938 (w), 1721 (s), 1685 (m), 1512 (m), 1423 (m), 1236 (s), 1149 (s), 1056 (s), 728 (s), 681 (s), 538 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 380 (100), 213 (26), 182 (25), 153 (16), 139 (20), 108 (8). HRMS (EI): calcd for $C_{22}H_{20}O_2S_2$ ([M^+]): 380.06225, found 380.06228.

3.2.5. Methyl 4-methyl-6-(phenylsulfanyl)-6-propylbenzoate (**5e**)

Starting with **4e** (600 mg, 3.0 mmol), **3a** (562 g, 2.0 mmol), $TiCl_4$ (0.32 mL, 3.0 mmol), and CH_2Cl_2 (11 mL), **5e** was isolated as a highly viscous oil (255 mg, 42%). ^1H NMR (250 MHz, $CDCl_3$): δ=0.85 (t, 3H, *J*=7.1 Hz, CH_3), 1.47 (m, 2H, CH_2), 2.11 (q, 2H, *J*=6.4 Hz, CH_3), 2.24 (s, 3H, CH3), 3.80 (s, 3H, OCH3), 6.91 (s, 1H, ArH), 7.16 (m, 2H, ArH), 7.33 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.5, 19.7 (CH_3), 24.3, 36.7 (CH_2), 52.0 (OCH_3), 126.8 (ArCH), 129.0 (2C, ArCH), 129.5 (C), 130.0 (ArCH), 131.3 (2C, ArCH), 135.5 (ArCH), 136.1, 139.9, 144.8, 160.2, 165.8 (C). IR (neat): $\tilde{\nu}$ = 3045(w), 2978 (w), 1714 (s), 1675 (m), 1590 (s), 1460 (m), 1369 (s), 1269 (m), 1171 (m), 1024 (m), 751 (s), 690 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 300 (40), 287 (46), 211 (23), 139 (23), 105 (23). HRMS (EI): calcd for $C_{18}H_{20}O_2S$ [M^+]: 300.03177, found 300.03156.

3.2.6. Methyl 2,3,4,5-tetramethyl-6-(phenylsulfanyl)benzoate (**5f**)

Starting with **4b** (450 mg, 2.4 mmol), **3b** (859 mg, 2.9 mmol), $TiCl_4$ (0.37 mL, 3.6 mmol), and CH_2Cl_2 (14 mL), **5f** was isolated as a highly viscous oil (400 mg, 55%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.15 (s, 3H, CH_3), 2.17 (s, 2×3H, CH_3), 2.24 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 6.99 (m, 2H, ArH), 7.12 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.5, 17.3, 17.8, 19.9 (CH_3), 51.1 (OCH_3), 124.0 (C), 125.1 (ArCH), 126.8 (2C, ArCH), 128.7 (2C, ArCH), 130.5, 137.5, 137.7, 138.0, 139.1, 139.6, 170.1 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2946 (w), 1729 (s), 1598 (m), 1580 (m), 1422 (s), 1306 (m), 1232 (m), 1172 (s), 1068 (m), 737 (s), 688 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 300 (M^+, 86), 267 (100), 253 (12), 239 (10), 225 (7), 110 (89). HRMS (EI): calcd for $C_{18}H_{20}O_2S$ [M^+]: 300.11785, found 300.11812.

3.2.7. Methyl 3-chloro-2,4,5-trimethyl-6-(phenylsulfanyl)-benzoate (**5g**)

Starting with **4c** (550 mg, 2.6 mmol), **3b** (943 mg, 3.1 mmol), $TiCl_4$ (0.42 mL, 3.9 mmol) and CH_2Cl_2 (11 mL), **5g** was isolated as a highly viscous oil (417 mg, 49%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 7.00 (m, 2H, ArH), 7.14 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=17.2, 17.3, 17.5 (CH_3), 51.2 (OCH_3), 123.6 (C), 125.5 (ArCH), 126 (C), 127.1 (2C, ArCH), 128.9 (2C, ArCH), 129.6, 136.0, 136.7, 139.4, 139.9, 166.2 (C). IR (neat): $\tilde{\nu}$ = 3010(w), 2953 (w), 1722 (s), 1601 (m), 1580 (m), 1434 (m), 1383 (s), 1234 (s), 1151 (s), 1009 (s), 732 (s), 685 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 322 (M^+, ^{37}Cl, 28), 320 (M^+, ^{35}Cl, 74), 287 (100), 253 (17), 211 (10), 178 (20), 115. HRMS (EI): calcd for $C_{17}H_{17}O_2ClS$ [M^+, ^{35}Cl]: 320.06323, found 320.06363.

*3.2.8. Methyl 2-phenyl-4,5-dimethyl-6-(phenylsulfanyl)-benzoate (**5h**)*

Starting with **4f** (500 mg, 2.0 mmol), **1b** (743 mg, 2.0 mmol), $TiCl_4$ (0.34 mL, 3.1 mmol), and CH_2Cl_2 (12.5 mL), **5h** was isolated as a highly viscous oil (380 mg, 52%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.48 (s, 3H, OCH_3), 7.12 (m, 3H, ArH), 7.26 (m, 3H, ArH), 7.36 (s, 1H, ArH), 7.42 (m, 4H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.6, 18.0 (CH_3), 50.1 (OCH_3), 124.0 (C), 125.9 (ArCH), 126.4 (2C, ArCH), 126.3 (C), 127.2 (2C, ArCH), 127.4 (2C, ArCH), 127.5 (2C, ArCH), 127.8 (ArCH), 131.5, 132.2 (C), 136.2 (ArCH), 137.5, 138.1, 138.7, 139.9, 166.2 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2946 (w), 1730 (s), 1580 (m), 1476 (m), 1456 (s), 1384 (w), 1246 (s), 1146 (s), 1023 (m), 697 (s), 688 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 348 (M^+, 100), 315 (89), 373 (26), 39 (9), 165 (18), 105 (7). HRMS (EI): calcd for $C_{22}H_{20}O_2S$ [M^+]: 348.11785, found 348.11834.

*3.2.9. Methyl 5-ethyl-2,4-dimethyl-6-(phenylsulfanyl)benzoate (**5i**)*

Starting with **4b** (700 mg, 3.8 mmol), **3c** (1.40 g, 4.5 mmol), $TiCl_4$ (0.61 mL, 5.6 mmol), and CH_2Cl_2 (19 mL), **5i** was isolated as a highly viscous oil (650 mg, 55%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80 (t, 3H, *J*=7.4 Hz, CH_3), 2.13 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.76 (q, 2H, *J*=7.3 Hz, CH_2), 3.67 (s, 3H, OCH_3), 6.97 (m, 3H, ArH), 7.10 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.5, 16.6, 16.9, 17.8 (CH_3), 24.9 (CH_2), 51.9 (OCH_3), 123.2 (C), 125.0 (ArCH), 126.6 (2C, ArCH), 128.9 (2C, ArCH), 134.2, 137.0, 138.5, 140.3, 142.7, 145.1, 170.0 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2946 (w), 1729 (s), 1580 (m), 1477 (m), 1434 (m), 1294 (m), 1224 (m), 1171 (s), 1024 (m), 736 (s), 688 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 314 (M^+, 100), 281 (56), 267 (21), 239 (16), 211 (12), 177 (23), 105 (27). HRMS (EI): calcd for $C_{19}H_{22}O_2S$ [M^+]: 314.13351, found 314.13418.

*3.2.10. Methyl 3-chloro-2,4-dimethyl-5-ethyl-6-(phenylsulfanyl)-benzoate (**5j**)*

Starting with **4c** (650 mg, 3.1 mmol), **3c** (1.10 g, 3.7 mmol), $TiCl_4$ (0.51 mL, 4.6 mmol), and CH_2Cl_2 (15.5 mL), **5j** was isolated as a highly viscous oil (524 mg, 50%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.74 (t, 3H, *J*=7.1 Hz, CH_3), 2.11 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.65 (q, 2H, *J*=7.4 Hz, CH_2), 3.55 (s, 3H, OCH_3), 6.92 (m, 3H, ArH), 7.10 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.6, 18.9, 19.7 (CH_3), 24.3 (CH_2), 52.1 (OCH_3), 126.1 (C), 126.6 (ArCH), 128.2 (2C, ArCH), 131.0 (2C, ArCH), 133.6, 136.9, 139.0, 139.2, 142.3, 148.1, 170.0 (C). IR (neat): $\tilde{\nu}$ = 3053(w), 297 (w), 1727 (s), 1575 (m), 1431 (m), 1404 (m), 1280 (s), 1224 (s), 1152 (s), 1022 (s), 735 (s), 685 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 336 (M^+, ^{37}Cl, 39), 334 (M^+, ^{35}Cl, 100), 301 (52), 287 (21), 224 (10), 197 (23), 105 (34). HRMS (EI): calcd for $C_{16}H_{15}O_2ClS$ [M^+, ^{35}Cl]: 334.07888, found 334.07942.

*3.2.11. Methyl 2-methyl-3-phenyl-5-ethyl-6-(phenylsulfanyl)-benzoate (**5k**)*

Starting with **4f** (717 mg, 3.0 mmol), **3c** (618 g, 2.0 mmol), $TiCl_4$ (0.32 mL, 3.0 mmol), and CH_2Cl_2 (10 mL), **5k** was isolated as a highly viscous oil (362 mg, 50%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.88 (t, 3H, *J*=7.1 Hz, CH_3), 2.25 (s, 3H, CH_3), 2.73 (q, 2H, *J*=6.4 Hz, CH_2), 3.80 (s, 3H, OCH_3), 7.10 (m, 3H, ArH), 7.26 (m, 5H, ArH), 7.34 (s, 1H, ArH), 7.67 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 (CH_3), 20.1 (CH_2), 24.4 (CH_3), 51.8 (OCH_3), 123.0 (2C, ArCH), 124.4 (ArCH), 125.3 (2C, ArCH), 127.7 (ArCH), 128.4 (2C, ArCH), 130.3 (2C, ArCH), 130.2, 133.7, 134.9 (C), 136.3 (ArCH), 137.1, 139.1, 140.6, 144.2, 148.2, 165.8 (C). IR (neat): $\tilde{\nu}$ = 3058(w), 2947 (w), 1730 (m), 1597 (m), 1579 (m), 1453 (m), 1271 (s), 1191 (s), 739 (s), 698 (s), 618 (m), 556 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 362 (M^+, 100), 331 (19), 315 (20), 271 (16), 225 (20), 178 (13). HRMS (EI): calcd for $C_{23}H_{22}O_2S$ [M^+]: 362.13350, found 362.13303.

*3.2.12. 2,4-Dimethyl-6-(4-tolylsulfanyl)benzoic acid methyl ester (**5l**)*

Starting with **4a** (387 mg, 2.3 mmol), **3d** (441 g, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5l** was isolated as a highly viscous oil (232 mg, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH3), 2.22 (s, 3H, CH3), 2.25 (s, 3H, CH3), 3.79 (s, 3H, OCH3), 6.80–7.19 (m, 6H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=19.6, 21.1, 21.3 (CH_3), 52.0 (OCH_3), 129.8 (ArCH), 129.9, 131.8 (2C, ArCH), 131.9 (ArCH), 133.1, 134.1, 135.9, 137.4, 137.9, 139.9 (ArC), 169.1 (C). IR (neat): $\tilde{\nu}$ = 3018(w), 2947 (w), 2919 (w), 2863 (w), 2733 (w), 1726 (s), 1598 (m), 1560 (m), 1490 (m), 1435 (m), 1378 (w), 1267 (s), 1257 (s), 1217 (m), 1188 (m), 1151 (s), 1078 (s), 1023 (m), 999 (w), 956 (w), 852 (m), 810 (m), 738 (s), 689 (s), 579 (m), 553 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 286 (100), 255 (55), 255 (55), 254 (20), 253 (76), 240 (15), 239 (56), 212 (17), 211 (23), 197 (11), 165 (5), 91 (4). HRMS (EI): calcd for $C_{17}H_{18}O_2S$: 286.10220, found 286.101944.

*3.2.13. 3,4,6-Trimethyl-2-(4-tolylsulfanyl)benzoic acid methyl ester (**5m**)*

Starting with **4a** (387 mg, 2.3 mmol), **3e** (462 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5m** was isolated as a highly viscous oil (176 mg, 39%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.16 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 6.87–7.16 (m, 5H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.9, 18.9, 20.9, 21.0 (CH_3), 52.0 (OCH_3), 127.5 (2C, ArCH), 128.4 (ArCH), 129.6. (2C, ArCH), 131.8, 132.7, 133.9, 135.3, 138.8, 139.0, 139.3 (ArC), 169.6 (C). IR (neat): $\tilde{\nu}$ = 2946(w), 2919 (w), 2863 (w), 1728 (s), 1596 (m), 1490 (m), 1434 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 557 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 300 (96), 269 (33), 268 (12), 267 (43), 253 (M^+, 100), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 65 (4). HRMS (EI): calcd for $C_{18}H_{20}O_2S$: 300.11767, found 300.117653.

*3.2.14. 2,4-Dimethyl-6-(m-tolylsulfanyl)benzoic acid methyl ester (**5n**)*

Starting with **4a** (387 mg, 2.3 mmol), **3f** (441 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5n** was isolated as a highly viscous oil (232 mg, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 6.80–7.19 (m, 6H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=19.6, 21.1, 21.3 (CH_3), 52.0 (OCH_3), 129.8 (ArCH), 129.9, 131.8 (2C, ArCH), 131.9 (ArCH), 133.1, 134.1, 135.9, 137.4, 137.9, 139.9 (ArC), 169.1 (C). IR (neat): $\tilde{\nu}$ = 3018(w), 2947 (w), 2919 (w), 2863 (w), 2733 (w), 1726 (s), 1598 (m), 1560 (m), 1490 (m), 1435 (m), 1378 (w), 1267 (s), 1257 (s), 1217 (m), 1188 (m), 1151 (s), 1078 (s), 1023 (m), 999 (w), 956 (w), 852 (m), 810 (m), 738 (s), 689 (s), 579 (m), 553 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 286 (100), 255 (55), 255 (55), 254 (20), 253 (76), 240 (15), 239 (56), 212 (17), 211 (23), 197 (11), 165 (5), 91 (4). HRMS (EI): calcd for $C_{17}H_{18}O_2S$: 286.10220, found 286.101944.

*3.2.15. 2-(4-Ethylphenylsulfanyl)-4,6-dimethyl-benzoic acid methyl ester (**5o**)*

Starting with **4a** (387 mg, 2.3 mmol), **3g** (462 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5o** was isolated as a highly viscous oil (221 mg, 49%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (t, 3H, *J*=7.2 Hz, CH3), 2.12 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.56 (q, 2H, *J*=7.2 Hz, CH_2), 3.79 (s, 3H, OCH_3), 6.82–7.21 (m, 6H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.4, 19.6, 21.6 (CH_3), 28.4 (CH_2), 52.0 (OCH_3), 128.7 (2C, ArCH), 129.4, 129.9 (ArCH), 131.8 (2C, ArCH), 132.1, 133.2, 133.9, 135.9, 139.9, 143.6 (ArC), 169.2 (C). IR (neat): $\tilde{\nu}$ = 3018(w), 2963 (w), 2928 (w), 2871 (w), 1727 (s), 1599 (m), 1491 (m), 1435 (m), 1404 (w), 1377 (w), 1266 (s), 1257 (s), 1217 (m), 1187 (m), 1152 (s), 1078 (s), 1016 (m), 965 (w), 947 (w), 849 (m), 810 (m), 778 (w), 738 (m), 579 (m), 555 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 300 (M^+, 100), 284 (5), 283 (26), 282 (10), 281 (27), 267 (7),

254 (20), 253 (97), 239 (7), 225 (15), 178 (5), 134 (4), 121 (19). HRMS (EI): calcd for $C_{18}H_{20}O_2S$: 300.11785, found 300.117168.

3.2.16. 2-(4-Ethylphenylsulfanyl)-3,4,6-trimethyl-benzoic acid methyl ester (**5p**)

Starting with **4a** (387 mg, 2.3 mmol), **3h** (483 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5p** was isolated as a highly viscous oil (212 mg, 45%). ^1H NMR (250 MHz, $CDCl_3$): δ=1.09 (t, 3H, J=7.2 Hz, CH_3), 2.16 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.47 (q, 2H, J=7.2 Hz, CH_2), 3.74 (s, 3H, OCH_3), 6.93–7.17 (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.4, 16.9, 18.9 (CH_3), 28.3 (CH_2), 52.0 (OCH_3), 127.6 (2C, ArCH), 128.4 (2C, ArCH), 128.5, 131.9 (ArC), 132.8 (ArCH), 134.1, 138.7, 139.0, 141.6 (ArC), 169.7 (C). IR (neat): $\tilde{\nu}$ = 3016(w), 2963 (w), 2948 (w), 2928 (w), 2871 (w), 1729 (s), 1596 (m), 1491 (m), 1433 (m), 1404 (w), 1383 (w), 1285 (s), 1242 (m), 1223 (m), 1187 (m), 1142 (s), 1119 (m), 1087 (m), 1052 (m), 1014 (m), 1004 (m), 821 (s), 789 (m), 751 (w), 721 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 314 (M^+, 100), 284 (5), 283 (26), 182 (10), 281 (27), 267 (7), 254 (20), 253 (97), 239 (7), 225 (15), 178 (5), 134 (4), 121 (19). HRMS (EI): calcd for $C_{19}H_{22}O_2S$: 314.13350, found 314.133456.

3.2.17. 2-(4-Chlorophenylsulfanyl)-4,6-dimethyl-benzoic acid methyl ester (**5q**)

Starting with **4a** (387 mg, 2.3 mmol), **3i** (470 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.3 mmol) and CH_2Cl_2 (9 mL), **5q** was isolated as a highly viscous oil (170 mg, 37%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.17 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.90–7.34 (m, 6H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=18.1, 20.1 (CH_3), 49.9 (OCH_3), 127.0, 128.1 (ArCH), 129.0 (2C, ArCH), 130.3 (ArC), 135.7 (2C, ArCH), 137.1, 137.3, 139.2, 164.5 (ArC), 167.9 (C). IR (neat): $\tilde{\nu}$ = 2945(w), 2918 (w), 2853 (w), 1728 (s), 1596 (m), 1491 (m), 1435 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 554 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 308 (M^+, 25), 306 (M^+, 100), 266 (12), 262 (43), 253 (100), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 63 (4). HRMS (EI): calcd for $C_{16}H_{15}O_2ClS$: 306.58923, found 306.587603.

3.2.18. 3-Chloro-6-(4-chlorophenylsulfanyl)-2,4-dimethyl-benzoic acid methyl ester (**5r**)

Starting with **4c** (460 mg, 2.3 mmol), **3i** (470 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5r** was isolated as a highly viscous oil (179 mg, 35%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.31 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.90–7.19 (m, 5H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=18.1, 20.9 (CH3), 52.4 (OCH3), 129.1 (2C, ArCH), 129.2 (ArCH), 131.5 (2C, ArCH), 133.0, 133.8, 134.1, 135.5, 137.0, 138.7 (ArC), 168.2 (C). IR (neat): $\tilde{\nu}$ = 2946(w), 2919 (w), 2863 (w), 1728 (s), 1596 (m), 1490 (m), 1434 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 557 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 344 (25, M^+), 342 (50, M^+), 340 (100, M^+), 268 (12), 267 (43), 253 (100), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 65 (4). HRMS (EI): calcd for $C_{16}H_{14}O_2Cl_2S$: 341.01787, found 341.017653.

3.2.19. 2-(4-Chlorophenylsulfanyl)-3,4,6-trimethyl-benzoic acid methyl ester (**5s**)

Starting with **4a** (387 mg, 2.3 mmol), **3j** (490 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5s** was isolated as a highly viscous oil (188 mg, 36%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.90–7.34 (m, 5H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=18.1, 18.3, 20.1 (CH_3), 50.6 (OCH_3), 127.0, 128.1 (ArCH), 129.0 (2C, ArCH), 130.3. (ArC), 135.7 (2C, ArCH), 137.1, 137.3, 139.2, 164.5 (ArC), 167.9 (C). IR (neat): $\tilde{\nu}$ = 2945(w), 2918 (w), 2853 (w), 1728 (s), 1596 (m), 1491 (m), 1435 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 554 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 322 (M^+, 25), 320 (M^+, 100), 266 (12), 262 (43), 253 (10), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 63 (4). HRMS (EI): calcd for $C_{17}H_{17}O_2ClS$: 320.58923, found 320.587603.

3.2.20. 2-(3-Chlorophenylsulfanyl)-4,6-dimethyl-benzoic acid methyl ester (**5t**)

Starting with **4a** (387 mg, 2.3 mmol), **3k** (470 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5t** was isolated as a highly viscous oil (171 mg, 37%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.90–7.34 (m, 6H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=18.1, 20.1 (CH_3), 50.6 (OCH_3), 127.0, 128.1 (ArCH), 129.0 (2C, ArCH), 130.3 (ArC), 135.7 (2C, ArCH), 137.1, 137.3, 139.2, 164.5 (ArC), 167.9 (C). IR (neat): $\tilde{\nu}$ = 2945(w), 2918 (w), 2853 (w), 1728 (s), 1596 (m), 1491 (m), 1435 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 554 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 308 (M^+, 25), 306 (M^+, 100), 266 (12), 262 (43), 253 (100), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 63 (4). HRMS (EI): calcd for $C_{16}H_{15}O_2ClS$: 306.58923, found 306.587603.

3.2.21. 2(4-Fluorophenylsulfanyl)-4,6-dimethyl-benzoic acid methyl ester (**5u**)

Starting with **4a** (387 mg, 2.3 mmol), **3l** (447 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5u** was isolated as a highly viscous oil (174 mg, 40%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.14 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.79–7.29 (m, 6H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=19.6, 21.1 (CH_3), 52.0 (OCH_3), 130.2 (2C, ArCH), 130.8, 133.3 (ArCH), 133.7 (2C, ArCH), 136.1, 137.2, 137.9, 140.2 (ArCH), 169.1 (C). IR (neat): $\tilde{\nu}$ = 2949(w), 2921 (w), 2737 (w), 1726 (s), 1599 (m), 1588 (m), 1561 (w), 1487 (s), 1436 (m), 1396 (w), 1378 (w), 1267 (s), 1219 (s), 1189 (m), 1152 (s), 1078 (s), 1012 (m), 965 (w), 947 (w), 827 (m), 810 (m), 738 (s), 689 (s), 579 (m), 554 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 290 (66, M^+), 259 (46), 258 (22), 257 (100), 216 (17), 215 (28), 91 (4), 75 (2). HRMS (EI): calcd for $C_{16}H_{15}O_2FS$: 290.07713, found 290.077041.

3.2.22. 2-(4-Fluorophenylsulfanyl)-3,4,6-trimethylbenzoic acid methyl ester (**5v**)

Starting with **4a** (387 mg, 2.3 mmol), **3m** (468 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (9 mL), **5v** was isolated as a highly viscous oil (161 mg, 33%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.19 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 6.90–7.34 (m, 5H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$): δ=18.3, 18.6, 20.9 (CH_3), 51.5 (OCH_3), 127.0, 128.1 (ArCH), 129.0 (2C, ArCH), 130.3 (ArC), 135.7 (2C, ArCH), 137.1, 137.3, 139.2, 164.5 (ArC), 167.9 (C). IR (neat): $\tilde{\nu}$ = 2945(w), 2918 (w), 2853 (w), 1728 (s), 1596 (m), 1491 (m), 1435 (m), 1383 (w), 1285 (s), 1223 (m), 1189 (m), 1140 (s), 1085 (m), 1015 (m), 965 (w), 948 (w), 853 (m), 803 (m), 751 (m), 626 (m), 554 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 304 (M^+, 100), 266 (12), 262 (43), 226 (14), 225 (20), 211 (13), 192 (4), 91 (9), 63 (4). HRMS (EI): calcd for $C_{16}H_{15}O_2ClS$: 304.04523, found 304.045603.

3.3. General procedure for the synthesis of thioxanthones 6a–g

To **5** (1.0 mmol) was added concd sulfuric acid (98%, 12 mL/mmol of **5**) at 20 °C and the solution was stirred for 2 h. To the solution was added ice water (50 mL). The organic and the aqueous layer were separated and the latter was extracted with dichloromethane (3×15 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc).

*3.3.1. 1,2,3-Trimethylthioxanthone (**6a**)*

Starting with **5b** (114 mg, 1.0 mmol) and concd sulfuric acid, **6a** was isolated as a highly viscous oil (270 mg, 98%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.21 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 7.31 (m, 1H, ArH), 7.40 (m, 3H, ArH), 8.30 (dd, 1H, ^3J=7.4 Hz, ^4J=2.1 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.9, 19.1, 21.4 (CH_3), 124.2, 125.0, 125.7 (ArCH), 127.0 (C), 129.4, 131.0 (ArCH), 132.4, 134.9, 135.4, 135.7, 141.0, 141.1, 183.3 (C). IR (neat): $\tilde{\nu}$ = 3023(w), 2918 (w), 1712 (m), 1671 (s), 1530 (m), 1493 (s), 1329 (m), 1216 (s), 1166 (m), 1019 (m), 7546 (w), 645 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 254 (100), 239 (46), 225 (34), 211 (12), 178 (13), 165 (15), 91 (8). HRMS (EI): calcd for $C_{16}H_{14}OS$ [M$^+$]: 254.07799, found 254.07586.

*3.3.2. 2-Chloro-1,3-dimethylthioxanthone (**6b**)*

Starting with **5c** (114 mg, 0.4 mmol) and cond sulfuric acid, **6b** was isolated as a highly viscous oil (114 mg, 97%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.38 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 7.16 (s, 1H, ArH), 7.45 (m, 3H, ArH), 8.31 (dd, 1H, ^3J=7.9 Hz, ^4J=2.0 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=19.8, 21.4 (CH_3), 125.1 (2C, ArCH), 126.2 (ArCH), 127.3 (C), 129.6, 131.7 (ArCH), 131.8, 135.0, 135.3, 136.7, 141.7, 141.9, 182.4 (C). IR (neat): $\tilde{\nu}$ = 3375(w), 2978 (s), 1734 (m), 1675 (m), 1590 (m), 1490 (m), 1319 (m), 1219 (m), 1176 (m), 1029 (m), 751 (w), 690 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 276 (M$^+$, ^{37}Cl, 37), 274 (M$^+$, ^{35}Cl, 41), 267 (100), 105 (89), 77 (34). HRMS (EI): calcd for $C_{15}H_{11}OClS$ [M$^+$, ^{35}Cl]: 274.06127, found 274.06139.

*3.3.3. 1-Propyl-3-methylthioxanthone (**6c**)*

Starting with **5e** (50 mg, 0.16 mmol) and concd sulfuric acid, **6c** was isolated as a highly viscous oil (42 mg, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.90 (t, 3H, *J*=7.4 Hz, CH_3), 1.60 (m, 2H, CH_2), 2.55 (t, H, *J*=7.4 Hz, CH_2), 2.81 (m, 3H, CH_3), 7.10 (s, 1H, ArH), 7.38 (m, 3H, ArH), 8.25 (dd, 1H, ^3J=7.2 Hz, ^4J=1.87 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.8, 23.4 (CH_3), 24.8, 37.6 (CH_2), 123.6, 125.1, 125.9 (ArCH), 127.2 (C), 129.6, 131.0, 131.5 (ArCH), 132.1, 135.4, 139.2, 143.8, 146.5, 182.2 (C). IR (neat): $\tilde{\nu}$ = 3056(w), 2973 (w), 1732 (m), 1625 (s), 1560 (m), 1460 (s), 1329 (s), 1249 (2), 1186 (s), 1029 (m), 723 (w), 690 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 268 (100), 253 (7), 239 (34), 211 (36), 178 (10), 120 (7), 77 (8). HRMS (EI): calcd for $C_{17}H_{16}OS$ [M$^+$]: 268.09164, found 268.09153.

*3.3.4. 1,2,3,4-Tetramethylthioxanthone (**6d**)*

Starting with **5f** (118 mg, 0.39 mmol) and concd sulfuric acid, **6d** was isolated as a colourless solid (102 mg, 97%), mp=221 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.32 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 7.40 (m, 1H, ArH), 7.52 (m, 2H, ArH), 8.30 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.5, 16.7, 17.6, 19.4 (CH_3), 125.3, 125.8 (ArCH), 127.4, 128.4 (C), 128.9, 131.1 (ArCH), 132.2, 134.4, 134.8, 135.8, 138.0, 139.4, 184.6 (C). IR (neat): $\tilde{\nu}$ = 3064(w), 2916 (w), 1622 (s), 1587 (s), 1433 (s), 1490 (m), 1301 (s), 1204 (m), 1093 (s), 952 (m), 743 (s), 643 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 268 (100), 253 (82), 239 (34), 184 (10), 119 (7), 69 (12). HRMS (EI): calcd for $C_{17}H_{16}O_2S$ [M$^+$]: 268.09164, found 268.09113.

*3.3.5. 2-Chloro-1,3,4-trimethylthioxanthone (**6e**)*

Starting with **5g** (90 mg, 0.28 mmol) and concd sulfuric acid, **6e** was isolated as a colourless solid (78 mg, 97%), mp=194 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.50 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 7.45 (m, 1H, ArH), 7.57 (m, 2H, ArH), 8.34 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.8, 18.7, 20.2 (CH_3), 125.3, 126.3, 129.0 (ArCH), 130.0 (C), 131.6 (ArCH), 131.6, 132.3, 132.7, 134.0, 134.1, 137.8, 138.7, 183.9 (C). IR (neat): $\tilde{\nu}$ = 3063(w), 2918 (s), 1732 (m), 1624 (s), 1588 (m), 1432 (m), 1378 (m), 1229 (m), 1155 (s), 1009 (s), 741 (s), 615 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 290 (M$^+$, ^{37}Cl, 45), 288 (M$^+$, ^{35}Cl, 100), 253 (16), 225 (26), 208 (8), 119 (13), 69 (9). HRMS (EI): calcd for $C_{16}H_{13}OClS$ [M$^+$, ^{35}Cl]: 288.03701, found 288.03628.

*3.3.6. 1,2,3-Trimethyl-4-ethylthioxanthone (**6f**)*

Starting with **5i** (181 mg, 0.57 mmol) and concd sulfuric acid, **6f** was isolated as a colourless solid (102 mg, 97%), mp=221 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 (t, 3H, *J*=7.5 Hz, CH_3), 2.23 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.90 (q, 2H, *J*=7.4 Hz, CH_2), 7.30 (m, 1H, ArH), 7.44 (m, 2H, ArH), 8.22 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=12.9, 16.6, 16.8, 19.5 (CH_3), 23.7 (CH_2), 125.2, 125.8 (ArCH), 127.8 (C), 128.8 (ArCH), 131.1 (ArCH), 132.2, 133.7, 134.5, 135.3, 135.6, 136.1, 139.0, 184.9 (C). IR (neat): $\tilde{\nu}$ = 3064(w), 2927 (s), 1624 (s), 1585 (m), 1431 (m), 1382 (s), 1366 (s), 1203 (m), 1085 (s), 1028 (m), 748 (s), 643 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 282 (M$^+$, 89), 267 (100), 253 (21), 224 (10), 126 (9), 113 (9), 69 (16). HRMS (EI): calcd for $C_{18}H_{18}OS$ [M$^+$]: 282.10729, found 282.10724.

*3.3.7. 2-Chloro-1,3-dimethyl-4-ethylthioxanthone (**6g**)*

Starting with **5j** (302 mg, 0.92 mmol) and concd sulfuric acid, **6g** was isolated as a colourless solid (270 mg, 96%), mp=81 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (t, 3H, *J*=7.5 Hz, CH_3), 2.03 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.85 (q, 2H, *J*=7.2 Hz, CH_2), 7.28–7.40 (m, 2H, ArH), 7.47–7.89 (m, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=12.5, 18.0, 20.3 (CH_3), 24.1 (CH_2), 125.3 (ArCH), 126.3 (2C, ArCH), 129.0 (ArCH), 130.8, 131.7, 134.4, 136.3, 136.6, 137.6, 138.4, 139.4, 184.2 (C). IR (neat): $\tilde{\nu}$ = 3045(w), 2938 (w), 1711 (w), 1624 (s), 1587 (s), 1432 (s), 1373 (w), 1214 (s), 1174 (s), 1027 (s), 751 (m), 637 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 304 (M$^+$, ^{37}Cl, 30), 302 (M$^+$, ^{35}Cl, 100), 267 (23), 251 (12), 221 (10), 210 (8), 97 (15), 57 (27). HRMS (EI): calcd for $C_{17}H_{15}OClS$ [M$^+$, ^{35}Cl]: 302.05268, found 302.05282.

3.4. General procedure for the synthesis of diaryl sulfides 8a–x

To a dichloromethane solution (30 mL/mmol) of 3-arylthio-1-trimethylsilyloxy-1,3-butadienes **3** (1.0 mmol) and 1,1-diacyclopropane **7** (1.5 mmol) was added TiX_4 (1.5 mmol) at −78 °C. The solution was allowed to warm to ambient temperature within 14 h. To the solution was added a diluted aqueous solution of HCL (25 mL). The organic and the aqueous layer were separated and the latter was extracted with dichloromethane (3×20 mL). The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, EtOAc/*n*-heptane).

*3.4.1. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(phenylsulfanyl)benzoate (**8a**)*

Starting with **7a** (378 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiCl_4$ (0.33 mL, 3.0 mmol) and CH_2Cl_2 (60 mL), **8a** was isolated as a highly viscous oil (322 mg, 48%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.19 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.09 (t, 2H, *J*=7.5 Hz, CH_2), 3.43 (t, 2H, *J*=7.1 Hz, CH_2), 3.76 (s, 3H, OCH_3), 6.96 (s, 1H, ArH), 7.11–7.21 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.8, 20.1 (CH_3), 33.0, 41.6 (CH_2), 52.2 (CH_3), 126.9.0 (CH), 129.04 (2C, CH), 130.3 (C), 130.5 (2C, CH), 133.1 (CH), 134.1, 135.1, 136.0, 136.6, 138.9 (C), 169.3 (C=O). IR (ATR): $\tilde{\nu}$ = 2948(w), 2871 (w), 1727 (s), 1579 (m), 1437 (m), 1268 (s), 1148 (s), 1039 (m), 1023 (m), 933 (w), 777 (w), 738 (s), 689 (s), 557 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 336 (M$^+$, ^{37}Cl, 37), 334 (M$^+$, ^{35}Cl, 100), 301 (61), 285 (56), 267 (36), 253 (66), 210 (13), 115 (8), 77 (9). Anal. Calcd (%) for $C_{18}H_{19}ClO_2S$ (334.86): C, 64.56; H, 5.72. Found: C, 64.59; H, 5.84.

*3.4.2. Methyl 4-methyl-5-(2-chloroethyl)-6-phenyl-2-(phenylsulfanyl)benzoate (**8b**)*

Starting with **7b** (564 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiCl_4$ (0.33 mL, 3.0 mmol) and CH_2Cl_2 (60 mL), **8b** was isolated as a highly viscous oil (278 mg, 47%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 2.83 (t, 2H, *J*=7.5 Hz, CH_2), 3.22 (t, 2H, *J*=7.4 Hz, CH_2), 3.31 (s, 3H, OCH_3), 7.03 (s, 1H, ArH), 7.11–7.18 (m, 5H, ArH),

7.23–7.30 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.6 (CH_3), 32.1, 42.2 (CH_2), 51.7 (CH_3), 128.5, 128.7 (CH), 128.9 (2C, CH), 129.0 (2C, CH), 129.2 (2C, CH), 130.8 (C), 131.2 (2C, CH), 133.5 (CH), 133.9,135.2, 136.3,137.1, 138.5, 140.0 (C), 168.1 (C=O). IR (ATR): $\tilde{\nu}$ = 3022(w), 2947 (w), 1729 (s), 1573 (m), 1438 (s), 1270 (s), 1137 (s), 1023 (m), 739 (s), 699 (s), 595 (m), 557 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 398 (M^+, ^{37}Cl, 28), 396 (M^+, ^{35}Cl, 75), 365 (7), 315 (100), 300 (10), 271 (23), 178 (8), 156 (6), 77 (2). HRMS (EI) calcd for $C_{23}H_{21}O_2ClS$ [M^+, ^{35}Cl]: 396.09453, found 396.09453.

3.4.3. Methyl 4-methyl-5-(2-chloroethyl)-6-(4-chlorophenyl)-2-(phenylsulfanyl)benzoate (**8c**)

Starting with **7c** (333 mg, 1.5 mmol), **3a** (281 mg, 1.0 mmol), $TiCl_4$ (0.16 mL, 1.5 mmol) and CH_2Cl_2 (100 mL), **8c** was isolated as a highly viscous oil (185 mg, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.14 (s, 3H, CH_3), 2.71 (t, 2H, *J*=7.5 Hz, CH_2), 3.14 (t, 2H, *J*=7.5 Hz, CH_2), 3.28 (s, 3H, O*C*H_3), 6.94 (s, 1H, ArH), 6.99 (d, 2H, *J*=8.4 Hz, ArH), 7.08–7.22 (m, 7H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 33.1, 42.3 (CH_2), 51.9 (CH_3), 127.4 (CH), 128.3 (2C, CH), 129.1 (2C, CH), 130.6 (2C, CH), 131.4 (C), 131.5 (2C, CH), 133.7 (CH), 133.9, 134.0, 134.9, 135.3, 136.4, 139.3, 139.5 (C), 168.0 (C=O). IR (ATR): $\tilde{\nu}$ = 2996(w), 2947 (w), 1729 (s), 1574 (m), 1438 (s), 1271 (s), 1191 (m), 1087 (s), 1001 (m), 836 (m), 739 (s), 598 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 435 ([M]$^+$, [2×^{37}Cl], 3), 433 ([M]$^+$, [^{37}Cl], [^{35}Cl], 15), 370 ([M]$^+$, [2×^{35}Cl], 23), 349 (100), 314 (16), 285 (10), 271 (24), 156 (10), 77 (3). Anal. Calcd (%) for $C_{23}H_{20}ClO_2S$ (431.37): C, 64.04; H, 4.67. Found: C, 63.79; H, 4.86.

3.4.4. Methyl 4-methyl-5-(2-chloroethyl)-6-(4-fluorophenyl)-2-(phenylsulfanyl)benzoate (**8d**)

Starting with **7d** (618 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiCl_4$ (0.33 mL, 1.5 mmol) and CH_2Cl_2 (60 mL), **8d** was isolated as a highly viscous oil (331 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.25 (s, 3H, CH_3), 2.82 (t, 2H, *J*=7.5 Hz, CH_2), 3.23 (t, 2H, *J*=7.4 Hz, CH_2), 3.37 (s, 3H, O*C*H_3), 7.01 (s, 1H, ArH), 7.10 (d, 2H, *J*=8.6 Hz, ArH), 7.14–7.33 (m, 7H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 33.3, 42.0 (CH_2), 51.8 (CH_3), 115.0, 115.3, 127.4 (CH), 129.2 (2C, CH), 130.9, 131.0 (CH), 131.3 (C), 131.5 (2C, CH), 133.6 (CH), 133.6, 134.3, 135.0, 135.5, 139.3, 139.7 (C), 162.1 (d, *J*=274.2 Hz, CF), 168.1 (C=O). IR (ATR): $\tilde{\nu}$ = 2948(w), 2923 (w), 1730 (s), 1590 (s), 1508 (s), 1438 (s), 1156 (s), 1023 (m), 785 (m), 690 (s), 605 (m), 558 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 416 (M^+, ^{37}Cl, 24), 414 (M^+, ^{35}Cl, 74), 383 (5), 333 (100), 318 (9), 289 (15), 197 (6), 163 (13), 57 (21). HRMS (EI) calcd for $C_{23}H_{20}O_2ClFS$ [M^+, ^{35}Cl]: 414.08518, found 141.08511.

3.4.5. Methyl 4,6-dimethyl-5-(2-bromoethyl)-2-(phenylsulfanyl)-benzoate (**8e**)

Starting with **7a** (378 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiBr_4$ (1.101 g, 3.0 mmol) and CH_2Cl_2 (60 mL), **8e** was isolated as highly viscous oil (439 mg, 58%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.17 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.10 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 3.76 (s, 3H, O*C*H_3), 6.95 (s, 1H, ArH), 7.07–7.19 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.8, 20.0 (CH_3), 28.8, 33.5 (CH_2), 52.2 (CH_3), 126.9.0 (CH), 129.04 (2C, CH), 130.4 (C), 130.5 (2C, CH), 133.1 (CH), 133.9, 136.0, 136.1, 136.6, 138.7 (C), 169.3 (C=O). IR (ATR): $\tilde{\nu}$ = 2947(w), 2923 (w), 1727 (s), 1579 (m), 1436 (m), 1267 (s), 1147 (s), 1129 (m), 1045 (m), 812 (m), 738 (s), 688 (s), 591 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 380 (M^+, ^{81}Br, 100), 378 (M^+, ^{79}Br, 98), 347 (68), 345 (53), 299 (20), 285 (50), 253 (68), 115 (12), 77 (9). Anal. Calcd (%) for $C_{18}H_{19}BrO_2S$ (379.31): C, 57.00; H, 5.05. Found: C, 57.24; H, 5.13.

3.4.6. Methyl 4,6-diethyl-5-(2-bromoethyl)-2-(phenylsulfanyl)-benzoate (**8f**)

Starting with **7e** (462 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiBr_4$ (1.10 g, 3.0 mmol) and CH_2Cl_2 (60 mL), **8f** was isolated as a highly viscous oil (228 mg, 30%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.06 (t, 3H, *J*=7.4 Hz, CH_3), 1.13 (t, 3H, *J*=7.5 Hz, CH_3), 2.54 (m, 4H, 2×CH_2), 312 (m, 2H, CH_2), 329 (m, 2H, CH_2), 3.78 (s, 3H, O*C*H_3), 6.98 (s, 1H, ArH), 7.12–7.21 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=15.3, 15.9 (CH_3), 24.4, 25.9, 30.1, 32.5 (CH_2), 52.1 (CH_3), 126.8 (CH), 129.0 (2C, CH), 130.4 (2C, CH), 130.9 (C), 131.6 (CH), 134.6, 136.0, 136.1, 140.2, 145.0 (C), 169.3 (C=O). IR (ATR): $\tilde{\nu}$ = 2967(w), 2874 (w), 1728 (s), 1578 (m), 1438 (m), 1476 (m), 1271 (s), 1145 (s), 1023 (m), 983 (w), 739 (s), 688 (s), 579 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 408 (M^+, ^{81}Br, 70), 406 (M^+, ^{79}Br, 69), 375 (100), 378 (88), 313 (19), 295 (37), 221 (8), 128 (13), 91 (5). Anal. Calcd (%) for $C_{20}H_{23}BrO_2S$ (407.06): C, 58.97; H, 5.69. Found: C, 59.55; H, 6.04.

3.4.7. Methyl 4-methyl-5-(2-bromoethyl)-6-phenyl-2-(phenylsulfanyl)benzoate (**8g**)

Starting with **7b** (564 mg, 3.0 mmol), **3a** (562 mg, 2.0 mmol), $TiBr_4$ (1.101 g, 3.0 mmol) and CH_2Cl_2 (60 mL), **8g** was isolated as a highly viscous oil (353 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.22 (s, 3H, CH_3), 2.85 (m, 2H, CH_2), 3.07 (m, 2H, CH_2), 3.31 (s, 3H, O*C*H_3), 7.03 (s, 1H, ArH), 7.11–7.19 (m, 5H, ArH), 7.25–7.32 (m, 4H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.1 (CH_3), 29.5, 33.7 (CH_2), 51.7 (CH_3), 127.3, 127.8 (C), 128.1 (CH), 129.1 (2C, CH), 129.2 (2C, CH), 131.5 (2C, CH), 133.5 (C), 133.6 (2C, CH), 135.2, 135.3 (CH), 135.5, 137.9, 139.0, 140.7 (C), 168.2 (C=O). IR (ATR): $\tilde{\nu}$ = 3021(w), 2846 (w), 1730 (s), 1573 (m), 1438 (m), 1268 (s), 1136 (s), 1089 (m), 1023 (m), 929 (w), 702 (s), 688 (s), 579 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 442 (M^+, ^{81}Br, 67), 440 (M^+, ^{79}Br, 64), 329 (15), 315 (100), 300 (10), 271 (24), 178 (11), 156 (10), 77 (3). Anal. Calcd (%) for $C_{18}H_{19}BrO_2S$ (441.38): C, 62.59; H, 4.80. Found: C, 62.73; H, 4.98.

3.4.8. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(4-methylphenylsulfanyl)benzoate (**8h**)

Starting with **7a** (283 mg, 2.25 mmol), **3d** (441 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8h** was isolated as a highly viscous oil (208 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.44 (t, *J*=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, O*C*H_3), 6.93–7.07 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.8 (CH_3), 20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 350 (M^+, ^{37}Cl, 38), 348 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_2ClS$ [M^+] 348.09453, found 348.094465.

3.4.9. Methyl 4-methyl-5-(2-chloroethyl)-2-(4-methylphenylsulfanyl)-6-phenylbenzoate (**8i**)

Starting with **7b** (283 mg, 2.25 mmol), **3d** (441 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8i** was isolated as a highly viscous oil (252 mg, 41%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.44 (t, *J*=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, O*C*H_3), 6.96–7.28 (m, 10H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.6 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 40.2 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 350 (M^+, ^{37}Cl, 38), 348 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_2ClS$ [M^+] 348.09453, found 348.094465.

*3.4.10. Methyl 4-methyl-5-(2-bromoethyl)-2-(4-methylphenylsulfanyl)-6-phenylbenzoate (**8j**)*

Starting with **7b** (283 mg, 2.25 mmol), **3d** (441 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8j** was isolated as a highly viscous oil (306 mg, 45%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.39 (t, J=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.96–7.66 (m, 10H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 40.2 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 350 (M^+, ^{81}Br, 100), 348 (M^+, ^{79}Br, 75), 317 (87), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{24}H_{23}O_2BrS$ [M^+] 454.05966, found 454.059387.

*3.4.11. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(4-chlorophenylsulfanyl)benzoate (**8k**)*

Starting with **7a** (283 mg, 2.25 mmol), **3i** (472 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8k** was isolated as a highly viscous oil (237 mg, 43%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.46 (t, J=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1327 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 645 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 372 (M^+, ^{37}Cl, ^{37}Cl, 14), 371 (M^+, ^{35}Cl, ^{37}Cl, 70), 370 (M^+, ^{35}Cl, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{18}H_{18}O_2Cl_2S$ [M^+] 368.03991, found 368.040296.

*3.4.12. Methyl 4-methyl-5-(2-chloroethyl)-2-(4-chlorophenylsulfanyl)-6-phenylbenzoate (**8l**)*

Starting with **7b** (283 mg, 2.25 mmol), **3i** (472 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8l** was isolated as a highly viscous oil (303 mg, 47%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.44 (t, J=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.93–7.26 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1577 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 434 (M^+, ^{37}Cl, ^{37}Cl, 12), 432 (M^+, ^{35}Cl, ^{37}Cl, 61), 430 (M^+, ^{35}Cl, ^{35}Cl, 85), 349 (100), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{23}H_{20}O_2Cl_2S$ [M^+] 430.09453, found 430.094465.

*3.4.13. Methyl 4,6-dimethyl-5-(2-bromooethyl)-2-(4-chlorophenylsulfanyl)benzoate (**8m**)*

Starting with **7a** (283 mg, 2.25 mmol), **3i** (472 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8m** was isolated as a highly viscous oil (252 mg, 41%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.46 (t, J=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w). MS (EI, 70 eV): m/z (%): 416 (29), 415 (20), 414 (100), 413 (16), 412 (M^+, 74), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{18}H_{18}O_2BrClS$ [M^+] 411.98939, found 411.989037.

*3.4.14. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(3-methoxyphenyl-sulfanyl)benzoate (**8n**)*

Starting with **7a** (283 mg, 2.25 mmol), **3o** (466 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8n** was isolated as a highly viscous oil (191 mg, 35%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.44 (t, J=8.3 Hz, 2H, CH_2), 3.66 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.93–7.07 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 51.2 (OCH_3), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 366 (M^+, ^{37}Cl, 39), 364 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_3ClS$ [M^+] 364.09453, found 364.094465.

*3.4.15. Methyl 4-methyl-5-(2-chloroethyl)-2-(3-methoxyphenyl-sulfanyl)-6-phenylbenzoate (**8o**)*

Starting with **7b** (283 mg, 2.25 mmol), **3o** (466 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8o** was isolated as a highly viscous oil (211 mg, 33%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.44 (t, J=8.3 Hz, 2H, CH_2), 3.42 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.96–7.28 (m, 10H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1324 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 428 (M^+, ^{37}Cl, 38), 426 (M^+, ^{35}Cl, 100), 318 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{24}H_{23}O_3ClS$ [M^+] 426.09453, found 426.094465.

*3.4.16. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(3-methoxyphenyl-sulfanyl)benzoate (**8p**)*

Starting with **7a** (283 mg, 2.25 mmol), **3o** (466 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8p** was isolated as a highly viscous oil (251 mg, 41%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.44 (t, J=8.3 Hz, 2H, CH_2), 3.66 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.93–7.07 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 51.2 (OCH_3), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 410 (M^+, ^{81}Br, 79), 408 (M^+, ^{79}Br, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_3ClS$ [M^+] 408.09853, found 408.094465.

*3.4.17. Methyl 4,6-dimethyl-5-(2-bromooethyl)-2-(3-chlorophenyl-sulfanyl)benzoate (**8q**)*

Starting with **7a** (283 mg, 2.25 mmol), **3k** (472 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8q** was isolated as highly viscous oil (221 mg, 40%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.03 (t, J=8.3 Hz, 2H, CH_2), 3.46 (t, J=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1,

132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w). MS (EI, 70 eV): *m*/*z* (%): 416 (M^+, 29), 415 (M^+, 20), 414 (M^+, 100), 413 (M^+, 16), 412 (M^+, 74), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{18}H_{18}O_2BrClS$ [M^+] 411.98939, found 411.989037.

3.4.18. Methyl 4,6-dimethyl-5-(2-bromooethyl)-2-(3-methylphenylsulfanyl)benzoate (**8r**)

Starting with **7a** (283 mg, 2.25 mmol), **3f** (441 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8r** was isolated as a highly viscous oil (235 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.46 (t, *J*=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.6 (CH_3), 21.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w). MS (EI, 70 eV): *m*/*z* (%): 394 (100), 392 (M^+, 74), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_2BrS$ [M^+] 391.98939, found 391.989037.

3.4.19. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(3-methylphenylsulfanyl)benzoate (**8s**)

Starting with **7a** (283 mg, 2.25 mmol), **3f** (441 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8s** was isolated as a highly viscous oil (224 mg, 43%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.44 (t, *J*=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.07 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=16.8 (CH_3), 20.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 350 (M^+, ^{37}Cl, 38), 348 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_2ClS$ [M^+] 348.09453, found 348.094465.

3.4.20. Methyl 4,6-dimethyl-5-(2-bromooethyl)-2-(4-methylphenylsulfanyl)benzoate (**8t**)

Starting with **7a** (283 mg, 2.25 mmol), **3d** (441 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8t** was isolated as a highly viscous oil (235 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.46 (t, *J*=8.3 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.6 (CH_3), 21.1 (CH_3), 21.3 (CH_3), 33.1 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w). MS (EI, 70 eV): *m*/*z* (%): 394 (100), 392 (M^+, 74), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{19}H_{21}O_2BrS$ [M^+] 391.98939, found 391.989037.

3.4.21. Methyl 4-methyl-5-(2-bromoethyl)-2-(4-ethylphenylsulfanyl)-6-phenylbenzoate (**8u**)

Starting with **7b** (283 mg, 2.25 mmol), **3g** (460 mg, 1.5 mmol), $TiBr_4$ (0.826 g, 2.25 mmol) and CH_2Cl_2 (45 mL), **8u** was isolated as a highly viscous oil (266 mg, 38%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 2.13 (s, 3H, CH_3), 2.54 (q, *J*=7.5 Hz, 2H, CH_2CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.39 (t, *J*=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.96–7.66 (m, 10H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 28.5 (CH_2CH_3), 33.1 (CH_2), 40.2 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 470 (M^+, ^{81}Br, 100), 468 (M^+, ^{79}Br, 75), 317 (87), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{25}H_{25}O_2BrS$ [M^+] 468.98939, found 468.989037.

3.4.22. Methyl 4,6-dimethyl-5-(2-bromoethyl)-2-(4-ethylphenylsulfanyl)benzoate (**8v**)

Starting with **7a** (283 mg, 2.25 mmol), **3g** (441 mg, 1.5 mmol), $TiBr_4$ (0.826, 2.25 mmol) and CH_2Cl_2 (45 mL), **8v** was isolated as a highly viscous oil (170 mg, 42%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 2.13 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.54 (q, *J*=7.5 Hz, 2H, CH_2CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.39 (t, *J*=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.7 (CH_3), 20.1 (CH_3), 21.3 (CH_3), 28.5 (CH_2CH_3), 33.1 (CH_2), 40.2 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w). MS (EI, 70 eV): *m*/*z* (%): 408 (100), 406 (M^+, 74), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{20}H_{23}O_2BrS$ [M^+] 405.98939, found 405.989037.

3.4.23. Methyl 4,6-dimethyl-5-(2-chloroethyl)-2-(4-ethylphenylsulfanyl)benzoate (**8w**)

Starting with **4a** (283 mg, 2.25 mmol), **3g** (441 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8w** was isolated as highly viscous oil (239 mg, 44%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 2.13 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.54 (q, *J*=7.5 Hz, 2H, CH_2CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.39 (t, *J*=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.93–7.29 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=18.7 (CH_3), 20.1 (CH_3), 21.3 (CH_3), 28.5 (CH_2CH_3), 33.3 (CH_2), 40.1 (CH_2), 52.1 (OCH_3), 111.3 (C), 127.9 (2CH), 128.9 (CH), 130.7 (C), 131.1, 132.8 (CH), 133.0, 134.0, 134.8, 135.5, 138.9, 169.3 (C). IR (ATR): $\tilde{\nu}$ = 2947(w), 2926 (w), 2736 (w), 2249 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%): 364 (M^+, ^{37}Cl, 38), 362 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{20}H_{23}O_2ClS$ [M^+] 362.09453, found 362.094465.

3.4.24. Methyl 4-methyl-5-(2-chloroethyl)-2-(4-ethylphenylsulfanyl)-6-phenylbenzoate (**8x**)

Starting with **7b** (283 mg, 2.25 mmol), **3g** (460 mg, 1.5 mmol), $TiCl_4$ (0.25 mL, 2.25 mmol) and CH_2Cl_2 (45 mL), **8x** was isolated as a highly viscous oil (248 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.15 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 2.13 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.54 (q, *J*=7.5 Hz, 2H, CH_2CH_3), 3.03 (t, *J*=8.3 Hz, 2H, CH_2), 3.39 (t, *J*=8.3 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.96–7.66 (m, 10H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 21.3 (CH_3), 28.5 (CH_2CH_3), 33.1 (CH_2), 40.2 (CH_2), 52.1 (OCH_3), 127.8 (CH), 128.0, 128.8, 129.2 (2CH), 131.2, 132.3 (C), 132.4 (2CH), 132.5 (CH), 133.6, 134.7, 138.0, 139.1, 140.7, 144.1, 168.3 (C). IR (ATR): $\tilde{\nu}$ = 2948(w), 2921 (w), 2734 (w), 2249 (w), 1728 (s), 1588 (m), 1573 (m), 1473 (m), 1435 (m), 1392 (m), 1377 (m), 1325 (m), 1270 (sd), 1190 (s), 1140 (s), 1040 (s), 907 (s), 777 (s), 728 (s), 691 (s), 646 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%): 426 (M^+, ^{37}Cl, 38), 424 (M^+, ^{35}Cl, 100), 317 (29), 315 (37), 303 (10), 301 (10), 281 (24), 268 (13), 267 (63), 225 (12), 224 (10). HRMS (EI): calcd for $C_{20}H_{23}O_2ClS$ [M^+] 424.09453, found 424.094465.

3.4.25. Methyl 5-(2hydroxy-5-chlorobenzoyl)-2-(thiophenoxy)-benzoate (**10**)

Me_3SiOTf (0.3 equiv) was added to 3-formylchromone **9** (1.0 equiv) at 20 °C. After stirring for 10 min, CH_2Cl_2 (8 mL) was added, the solution was cooled to 0 °C and diene **3a** (1.3 equiv) was addd. The mixture was stirred at 20 °C for 12 h and was subsequently poured into an

aqueous solution of HCl (10%). The organic and the aqueous layer was separated and the latter was extracted 3 times with 15 mL of CH_2Cl_2. The combined filtrate was washed with 25 mL and dried over Na_2SO_4. The solvent was removed under reduced pressure and crude product was purified by chromatography (silica gel, EtOAc/*n*-heptane). Starting with 3-formylchromone **9** (417 mg, 2.0 mmol), 1-trimethylsilyloxy-3-thioaryloxy-1,3-butadiene **3a** (562 mg, 2.0 mmol), and Me_3SiOTf (0.11 mL, 0.65 mmol), **10** was isolated as a highly viscous oil (174 mg, 22%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.92 (s, 3H, OC*H*$_3$), 6.82 (d, *J*=8.5 Hz, 1H, ArH), 6.95 (d, *J*=8.2 Hz, 1H, ArH), 7.35–7.47 (m, 6H, ArH), 7.53–7.57 (m, 2H, ArH), 8.28 (d, *J*=2.0 Hz, 1H, ArH), 11.64 (s, 1H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=52.5 (CH_3), 119.5 (C), 120.2 (CH), 123.5, 125.9 (C), 126.6, 129.9 (CH), 130.1 (2C, CH), 130.8 (C), 131.7. 132.2, 132.3 (CH), 132.7 (C), 136.0 (2C, CH), 136.2 (CH), 150.1, 161.5, 165.8, 198.4 (C). IR (ATR): $\tilde{\nu}$ = 2952 (w), 2922 (w), 1720 (s), 1629 (s), 1582 (s), 1463 (s), 1310 (m), 1263 (s), 1046 (s), 952 (m), 722 (s), 643 (m), 536 (w) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 400 (M^+, ^{37}Cl, 40), 398 (M^+,^{35}Cl, 100), 365 (44), 337 (33), 244 (33), 184 (23), 155 (27), 99 (13); HRMS (EI) calcd for $C_{21}H_{15}ClO_4S$ [M^+, ^{35}Cl]: 398.03687, found 398.03741.

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