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Domino [3+3] Annulation/Ring-Cleavage Reactions of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with 5-Aryl- and 5-Vinyl-3-acyl-4,5-dihydrofurans: Efficient Synthesis of 5-(4-Chlorobut-2-en-1-yl)- and 5-(2-Aryl-2-chloroethyl)salicylates

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Dedicated to Professor Dr. Uwe Rosenthal on the occasion of his 60th birthday

Keywords: Arenes / Regioselectivity / Annulation / Ring cleavage / Silyl enol ethers

The domino "[3+3] cyclization–ring-opening" reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-vinyl-4,5-dihydrofurans afforded 5-(4-halobut-2-en-1-yl)-salicylates. The reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-aryl-4,5-dihydrofurans gave 5-(2-aryl-2-chloroethyl)salicylates.

Introduction

1,3-Bis(trimethylsilyloxy)-1,3-butadienes represent useful synthetic building blocks.[1,2] They have been employed in the synthesis of butenolides,[3a] arenes,[3b] nitrogen heterocycles,[3c] biaryl lactones, azaxanthones and benzophenones,[3d] organofluorine compounds[3e] and tetrahydrofuran derivatives.[3f] Some years ago we reported[4] the synthesis of 5-(2-chloroethyl)salicylates by $TiCl_4$-mediated domino "[3+3] cyclization–cyclopropane-opening" reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 1,1-diacylcyclopropanes. Recently we reported[5] the cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-aryl-4,5-dihydrofurans. Herein, we report full details of these studies. With regard to our preliminary studies,[5] we have greatly extended the scope of this method, which provides a convenient approach to a variety of 5-(2-aryl-2-haloethyl)salicylates.

In addition, we report for the first time the synthesis of 5-(4-chlorobut-2-en-1-yl)salicylates by the domino "[3+3] cyclization–ring-opening" reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-vinyl-4,5-dihydrofurans. None of the products reported herein, which are highly functionalized arenes, are readily available by any other method.

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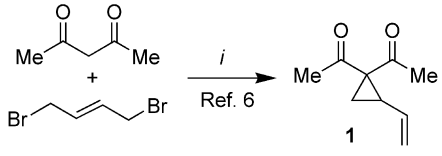
Results and Discussion

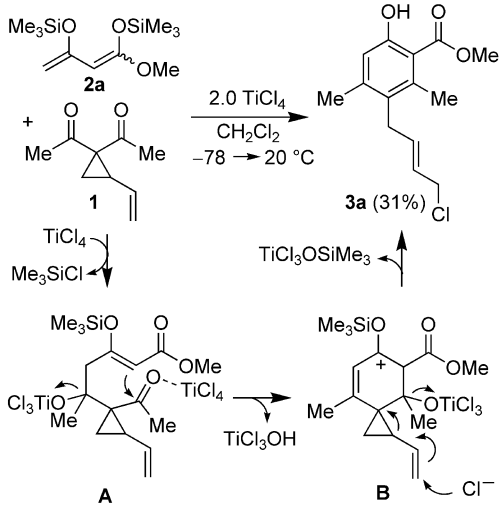
1,1-Diacetyl-2-vinylcyclopropane (**1**) was prepared, following a known procedure,[6] by K_2CO_3-mediated cyclization of acetylacetone with 1,4-dibromobut-2-ene (Scheme 1).



Scheme 1. Synthesis of **1**. Reagents and conditions: *i*) K_2CO_3, acetone, 14 h, reflux.

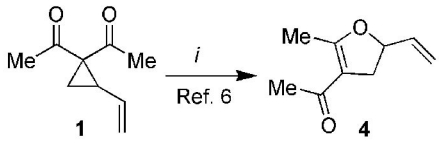
1,3-Bis(trimethylsilyloxy)-1,3-butadienes **2a**–**k** are readily available in two steps from the corresponding β-keto esters.[7,8] The $TiCl_4$-mediated cyclization of 1,3-bis(silyloxy)-1,3-butadiene **2a** with **1** afforded salicylate **3a** (Scheme 2). The formation of **3a** can be explained by $TiCl_4$-mediated attack of the terminal carbon atom of **2a** on **1** to give intermediate **A**, cyclization to intermediate **B**, attack of the $TiCl_4$-derived chloride ion on the vinylcyclopropyl double bond and cleavage of the spirocyclopropane moiety.

The best yield was obtained when 2 equiv. of $TiCl_4$ and 1.5 equiv. of diene **2a** were employed. In contrast to our original protocol for the reaction of **2a** with 1,1-diacetylcyclopropane, it proved advantageous to carry out the reaction in a highly concentrated solution [c(**1**) = 0.2 M]. The yield decreased to 23% when the reaction was carried out in a more dilute solution [c(**1**) = 0.02 M].



Scheme 2. Possible mechanism for the formation of **3a**.

1,1-Diacetyl-2-vinylcyclopropane (**1**) has previously been transformed[6] into 3-acetyl-5-vinyl-4,5-dihydrofuran **4** by a $[Ni(cod)_2]$-mediated reaction (Scheme 3). Compound **4** is also formed during the synthesis of **1** from 1,4-dibromobut-2-ene. We separated fractions of pure product **4** and used it in reactions with dienes **2**.

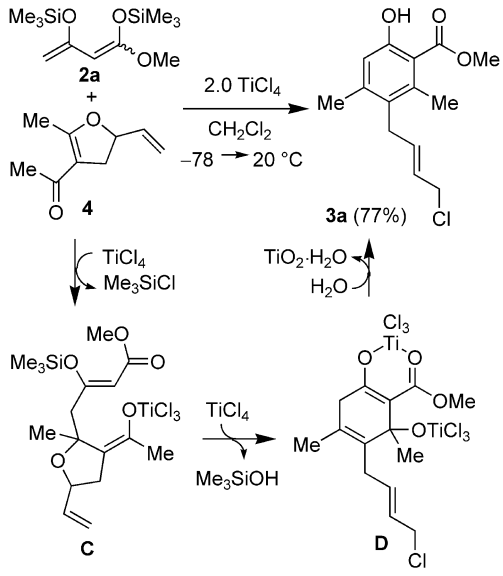


Scheme 3. Synthesis of **4**. Reagents and conditions: *i*) $[Ni(cod)_2]$, 2,2′-bipyridyl, acetonitrile, 15 min, 20 °C.

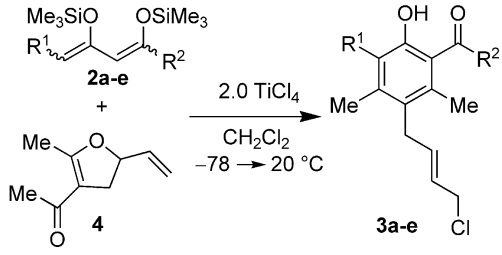
The reaction of diene **2a** with **4** afforded salicylate **3a** in 77% yield (Scheme 4). It is important to note that the yield is much higher than the yield of the same product prepared from **2a** and **1** (see Scheme 2). During the optimization it was found to be important to carry out the reaction in a relatively dilute solution [c(**4**) = 0.02 M]. The yield decreased to 48% when the reaction was carried out in a more concentrated solution [c(**4**) = 0.2 M]. The formation of **3a** can be explained by the conjugate addition of the terminal carbon atom of **2a** to **4** to give intermediate **C**, cyclization to intermediate **D** and aromatization (before or during the aqueous work-up).

The reactions of **4** with dienes **2b**–**e** following our optimized procedure afforded products **3b**–**e** (Scheme 5, Table 1). The best yields were obtained for the reactions of the C4-unsubstituted dienes **2a** and **2b**. The yield of product **3e** was relatively low (compared to products **3a**,**b**), which can be explained by the lower reactivity of 1,3-diketone-derived diene **2e** relative to the β-keto ester derived dienes **2a**–**d**.

The reactions of 1,3-diketones **5a**,**b** with styrenes **6a**–**h**, mediated by ceric ammonium nitrate (CAN) and following a known procedure[9] afforded products **7a**–**i** (Scheme 6, Table 2). The synthesis of **7a**–**c** and **7f** has been previously reported.[9]



Scheme 4. Possible mechanism for the cyclization of **2a** with **4**.

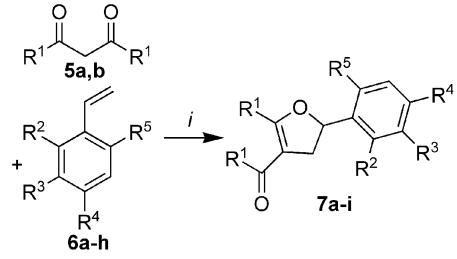


Scheme 5. Synthesis of **3a**–**e**.

Table 1. Synthesis of **3a**–**e** (see also Scheme 5).

2,**3**	R^1	R^2	Yield [%][a]
a	H	OMe	77
b	H	OEt	52
c	Me	OMe	51
d	OMe	OMe	31
e	H	Me	30

[a] Yields of isolated products.



Scheme 6. Synthesis of 5-aryl-4,5-dihydrofurans **7a**–**i**. Reagents and conditions: *i*) **6a**–**h** (4.4 equiv.), CAN (2.0 equiv.), 20 °C, 0.5–2 h.

Table 2. Synthesis of dihydrofurans **7a**–**i** (see also Scheme 6).

5	6	7	R^1	R^2	R^3	R^4	R^5	Yield of **7** [%][a]
a	**a**	**a**	Me	H	H	H	H	69[b]
a	**b**	**b**	Me	H	H	Me	H	63[b]
a	**c**	**c**	Me	H	H	Cl	H	74[b]
a	**d**	**d**	Me	H	H	Br	H	54
a	**e**	**e**	Me	H	H	F	H	43
a	**f**	**f**	Me	H	Cl	H	H	47[b]
a	**g**	**g**	Me	Cl	H	H	H	65
a	**h**	**h**	Me	Cl	H	H	Cl	28
b	**a**	**i**	Et	H	H	H	H	30

[a] Yields of isolated compounds. [b] Known compound (see ref.[9]).

The dihydrofurans **7** are rather unstable and can be stored only for a few days at –20 °C. However, we were able to grow crystals of **7h**. The crystal structure is shown in Figure 1.[10]

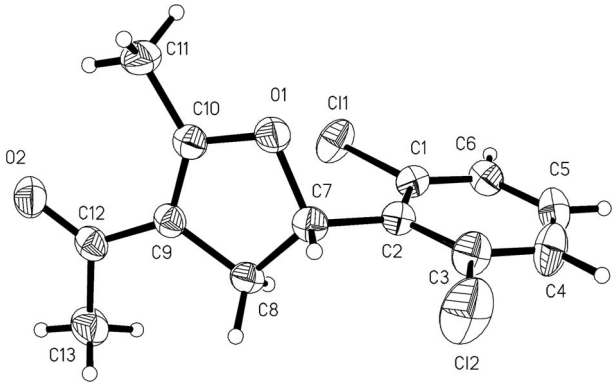
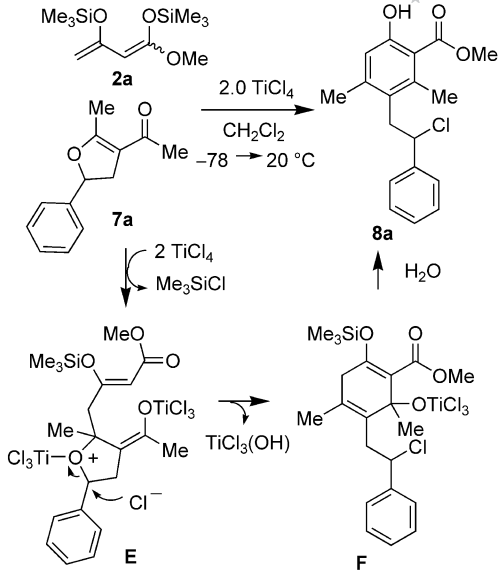


Figure 1. Crystal structure of **7h**.

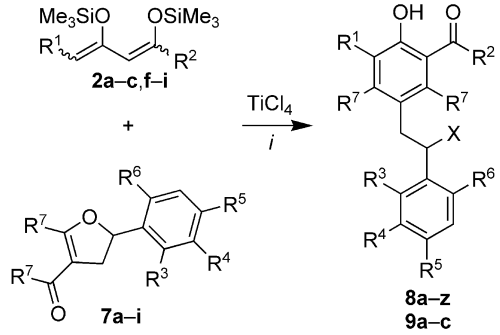
The reaction of diene **2a** with **7a** in the presence of $TiCl_4$ afforded the 5-(2-phenyl-2-chloroethyl)salicylate **8a** (Scheme 7). The best yields of **8a** were obtained when 1.0 equiv. of **7a**, 1.7 equiv. of **2a** and 2.0 equiv. of $TiCl_4$ were employed. The low concentration [c(**7a**) = 0.017 M] and the use of hydrochloric acid (10%) for the aqueous work-up also played an important role. The yield of **8a** decreased to 37% when an aqueous solution of NaOH was employed (c = 1 mol/L). The employment of $BF_3{\cdot}Et_2O$ instead of $TiCl_4$ resulted in the formation of a complex mixture from which only the starting material **7a** could be isolated in 28% yield. The formation of **8a** can be explained by attack of the terminal carbon atom of **2a** on **7a** to give intermediate **E**, ring cleavage, cyclization to give intermediate **F**, aromatization and formation of the final product **8a** after aqueous work-up.

The $TiCl_4$-mediated cyclization reactions of 1,3-bis(silyloxy)-1,3-butadienes **2a**–**c** and **2f**–**i** with 3-acetyl-5-aryl-4,5-dihydrofurans **7a**–**i** afforded the 5-(2-aryl-2-chloroethyl)salicylates **8a**–**z** (Scheme 8, Table 3).

In the reactions of dihydrofurans **7g** and **7h**, the alcohols **9a**–**c** were isolated. Their formation can be explained by hydrolysis of the chloride moiety. The yields of the products derived from halogenated 3-acetyl-5-aryl-4,5-dihydrofurans



Scheme 7. Possible mechanism for the formation of **8a**.



Scheme 8. Reaction of 5-aryl-4,5-dihydrofurans **7a**–**i** with 1,3-bis(silyloxy)-1,3-butadienes **2a**–**c** and **2f**–**i**. Reagents and conditions: *i*) $TiCl_4$ (2.0 equiv.), CH_2Cl_2, –78 → 20 °C.

tend to be slightly higher than those of the other products. This can be explained by the electron-withdrawing effect of the halogen atoms, which results in activation of the dihydrofuran moiety.

The structure of **8r** was independently confirmed by X-ray crystal structure analysis (Figure 2).[10]

Stilbenes are present in various plants,[11] including, for example, in the phytoestrogen rhaponthicin[12] or the phytoalexin resveratrol, which is found in grapes and possesses anti-mutagenic and possibly anticarcinogenic properties.[13] In addition, cytostatic activities have been reported.[14] Stilbene derivatives are also used as dyes and fluorescence dyes. Hence their synthesis is of considerable interest.

The thermal elimination of hydrogen chloride from salicylate **8a** afforded stilbene **10a** (Scheme 9, Table 4). Initially, the reactions were carried out without the addition of base. The best results with regard to *E* diastereoselectivity and yield (60%) were obtained when the reaction was carried out at 150 °C for 3 h. Both the yield and *E* diastereoselectiv-

Table 3. Synthesis of **8a**–**x** and **9a**–**c** (see also Scheme 8).

7	2	8	9	X	R^1	R^2	R^3	R^4	R^5	R^6	R^7	Yield of **8** [%][a]
a	**a**	**a**		Cl	H	OMe	H	H	H	H	Me	46
a	**b**	**b**		Cl	H	OEt	H	H	H	H	Me	44
a	**c**	**c**		Cl	Me	OMe	H	H	H	H	Me	36
a	**f**	**d**		Cl	Et	OMe	H	H	H	H	Me	51
a	**g**	**e**		Cl	H	O*i*Pr	H	H	H	H	Me	56
a	**h**	**f**		Cl	*n*Pr	OMe	H	H	H	H	Me	52
b	**a**	**g**		Cl	H	OMe	H	H	Me	H	Me	35
c	**a**	**h**		Cl	H	OMe	H	H	Cl	H	Me	38
c	**b**	**i**		Cl	H	OEt	H	H	Cl	H	Me	74
c	**c**	**j**		Cl	Me	OMe	H	H	Cl	H	Me	47
c	**f**	**k**		Cl	Et	OMe	H	H	Cl	H	Me	56
d	**a**	**l**		Cl	H	OMe	H	H	Br	H	Me	53
d	**c**	**m**		Cl	Me	OMe	H	H	Br	H	Me	62
d	**f**	**n**		Cl	Et	OMe	H	H	Br	H	Me	45
d	**g**	**o**		Cl	H	O*i*Pr	H	H	Br	H	Me	65
d	**i**	**p**		Cl	$Cl(CH_2)_3$	OMe	H	H	Br	H	Me	32
e	**a**	**q**		Cl	H	OMe	H	H	F	H	Me	45
e	**c**	**r**		Cl	Me	OMe	H	H	F	H	Me	51
e	**f**	**s**		Cl	Et	OMe	H	H	F	H	Me	22
f	**a**	**t**		Cl	H	OMe	H	Cl	H	H	Me	46
f	**c**	**u**		Cl	Me	OMe	H	Cl	H	H	Me	38
f	**f**	**v**		Cl	Et	OMe	H	Cl	H	H	Me	33
g	**a**	**w**	**a**	Cl (OH)[b]	H	OMe	Cl	H	H	H	Me	15 (36)[c]
g	**c**	**x**	**b**	Cl (OH)[b]	Me	OMe	Cl	H	H	H	Me	14 (47)[c]
h	**a**		**c**	Cl (OH)[b]	H	OMe	Cl	H	H	Cl	Et	0 (49)[c]
i	**a**	**y**		Cl	H	OMe	H	H	H	H	Et	39
i	**c**	**z**		Cl	Me	OMe	H	H	H	H	Et	70

[a] Yields of isolated products. [b] Substitutes in parentheses refer to **9a**–**c**. [c] Yields in brackets refer to **9a**–**c**.

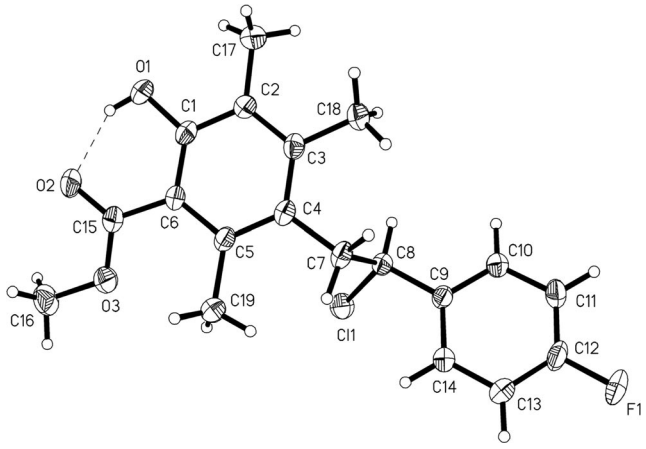
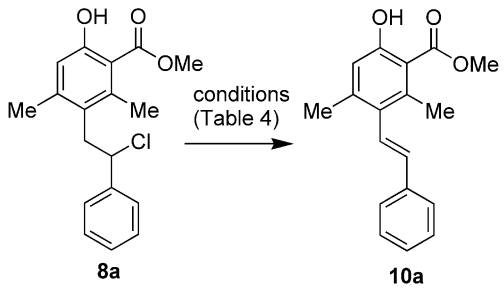


Figure 2. Crystal structure of **8r**.



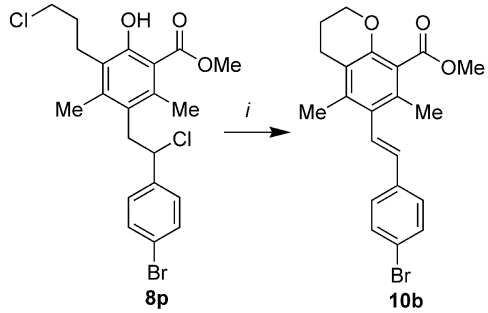
Scheme 9. Synthesis of stilbene **10a**.

ity decreased when the reaction time was prolonged or when the temperature was increased. Dramatic improvements in the yield and *E* diastereoselectivity were observed when the reactions were carried out in the presence of sodium hydride in DMF at 20 °C.

Table 4. Optimization of the synthesis of **10a** (see also Scheme 9).

Entry	*T* [°C]	*t* [h]	*E*/*Z*[a]	Yield [%][b]
1	200	3	4:1	38
2	150	3	11:1	60
3	150	7	6:1	45

[a] By ^{1}H NMR spectroscopy. [b] Yields of isolated products.



Scheme 10. Synthesis of **10b**. Reagents and conditions: *i*) NaH (3.0 equiv.), TBAI (3.6 equiv.), DMF, 20 °C, 20 h.

Treatment of **8p** with NaH and TBAI (tetrabutylammonium iodide) afforded, following a known procedure,[8b] the chromane **10b** in 76% yield as the pure *E* diastereomer (Scheme 10). The product was formed by base-mediated elimination and intramolecular Williamson reaction.

Conclusions

We have reported an efficient synthesis of 5-(4-halobut-2-en-1-yl)salicylates by domino "[3+3] cyclization–ring-opening" reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-vinyl-4,5-dihydrofurans. The domino reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-aryl-4,5-dihydrofurans gave 5-(2-aryl-2-chloroethyl)salicylates. The highly functionalized products reported are not readily available by other methods.

Experimental Section

General: 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 deuteriated 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.

General Procedure for the Synthesis of 3a–e, 8a–z and 9a–c: Diene **2** (1.5–1.7 equiv.) was added to a dichloromethane solution (50 mL) of **1**, **4** or **7** (1.0 equiv.) was added at –78 °C under argon. $TiCl_4$ (2.0 equiv.) was added to the mixture. The temperature of the solution was allowed to warm to 20 °C over 16 h with stirring. Hydrochloric acid (10%, 50 mL) was added to the mixture. The mixture was stirred for 10 min and was subsequently extracted with dichloromethane (3 × 50 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).

Methyl 5-[(*E*)-4-Chlorobut-2-enyl]-4,6-dimethylsalicylate (3a): Starting with **1** (see Scheme 2; 0.150 g, 0.97 mmol), **2a** (0.385 g, 1.48 mmol) and $TiCl_4$ (0.22 mL, 1.97 mmol), **3a** was isolated by chromatography (heptane/EtOAc, 10:1) as a slightly yellow solid (0.205 g, 77%); m.p. 55–57 °C; R_f = 0.62 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 3.36 (d, ^3J = 5.3 Hz, 2 H, CHCH_2), 3.94 (s, 3 H, OCH_3), 4.00 (d, ^3J = 7.0 Hz, 2 H, CHCH_2), 5.38 (dt, $^3J_{trans}$ = 15.2, $^3J_{CH,CH2}$ = 7.0 Hz, 1 H, CH_2C*H*), 5.84 (dt, $^3J_{trans}$ = 15.2, $^3J_{CH,CH2}$ = 5.3 Hz, 1 H, CH_2C*H*), 6.70 (s, 1 H, Ar), 10.64 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.5, 20.9 (CH_3), 31.6, 45.0 (CH_2), 52.0 (OCH_3), 111.8, 128.1, 138.9, 144.3, 159.9 (C_{Ar}), 116.9 (CH_{Ar}), 126.4, 132.6 (CH_{Olefin}), 171.9 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2984 (w), 1650 (m), 1600 (m), 1574 (m), 1441 (m), 1246 (m), 1211 (m), 1071 (m), 1033 (m), 920 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 270 (11) $[M]^+$ (^{37}Cl), 268 (31) $[M]^+$ (^{35}Cl), 238 (35), 236 (100), 201 (29). $C_{14}H_{17}ClO_3$ (268.74): calcd. C 62.57, H 6.38; found C 62.67, H 6.69.

Ethyl 5-[(*E*)-4-Chlorobut-2-enyl]-2,4-dimethylsalicylate (3b): Starting with **1** (0.180 g, 1.18 mmol), **2b** (0.487 g, 1.77 mmol) and $TiCl_4$ (0.26 mL, 2.37 mmol), **3b** was isolated by chromatography (heptane/EtOAc, 10:1) as a yellow oil (0.174 g, 52%). R_f = 0.58 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.41 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.25 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.32–3.39 (m, ^3J = 5.4 Hz, 2 H, CHCH_2), 3.96–4.03 (m, ^3J = 7.0 Hz, 2 H, CHCH_2), 4.42 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.30–5.48 (m, $^3J_{trans}$ = 15.2, $^3J_{CHCH2}$ = 7.0 Hz, 1 H, C*H*CH_2), 5.77–5.92 (m, $^3J_{trans}$ = 15.2, $^3J_{CHCH2}$ = 5.4 Hz, 1 H, C*H*CH_2), 6.70 (s, 1 H, Ar), 10.68 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.2, 18.6, 20.9 (CH_3), 31.7, 45.0, 61.5 (CH_2), 116.9 (CH_{Ar}), 126.4, 132.7 (CH_{Olefin}), 111.9, 128.0, 138.9, 144.1, 159.9 (C_{Ar}), 171.5 (*C*O-OCH_2CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2981 (m), 1658 (s), 1603 (m), 1574 (m), 1467 (m), 1373 (m), 1243 (s), 1155 (m), 1016 (w), 861 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 284 (26) $[M]^+$ (^{37}Cl), 282 (75) $[M]^+$ (^{35}Cl), 247 (63), 236 (100), 201 (71). HRMS (EI): calcd. for $C_{15}H_{19}ClO_3$ $[M]^+$ (^{35}Cl) 282.10165; found 282.10172.

Methyl 5-[(*E*)-4-Chlorobut-2-enyl]-3,4,6-trimethylsalicylate (3c): Starting with **1** (0.135 g, 0.89 mmol), **2c** (0.365 g, 1.33 mmol) and $TiCl_4$ (0.20 mL, 1.77 mmol), **3c** was isolated by chromatography (heptane/EtOAc, 20:1) as a colourless solid (0.129 g, 51%); m.p. 54–57 °C; R_f = 0.82 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.19 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 3.38–3.43 (m, ^3J = 5.3 Hz, 2 H, CHCH_2), 3.93 (s, 3 H, OCH_3), 3.97–4.03 (m, ^3J = 7.1 Hz, 2 H, CHCH_2), 5.30–5.46 (m, $^3J_{trans}$ = 15.2, $^3J_{CHCH2}$ = 7.1 Hz, 1 H, C*H*CH_2), 5.81–5.94 (m, $^3J_{trans}$ = 15.2, ^3JCHCH_2 = 5.3 Hz, 1 H, C*H*CH_2), 10.87 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.2, 16.8, 18.6 (CH_3), 32.2, 45.1 (CH_2), 52.0 (OCH_3), 126.5, 135.4 (CH_{Olefin}), 111.2, 122.6, 127.6, 135.6, 142.5, 157.5 (C_{Ar}), 172.6 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2953 (w), 1652 (s), 1596 (m), 1437 (m), 1349 (m), 1313 (m), 1248 (s), 1205 (s), 1178 (s), 1097 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 284 (11) $[M]^+$ (^{37}Cl), 282 (33) $[M]^+$ (^{35}Cl), 250 (100), 222 (13), 215 (95). $C_{15}H_{19}ClO_3$ (282.76): calcd. C 63.71, H 6.77; found C 63.41, H 6.86.

Methyl 5-[(*E*)-4-Chlorobut-2-enyl]-3-methoxy-4,6-dimethylsalicylate (3d): Starting with **1** (0.170 g, 1.12 mmol), **2d** (0.487 g, 1.68 mmol) and $TiCl_4$ (0.25 mL, 2.24 mmol), **3d** was isolated by chromatography (heptane/EtOAc, 10:1) as a slightly yellow solid (0.104 g, 31%); m.p. 43–45 °C; R_f = 0.57 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 3.34–3.40 (m, ^3J = 5.4 Hz, 2 H, CHCH_2), 3.79 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 3.96–4.03 (m, ^3J = 7.1 Hz, 2 H, CHCH_2), 5.31–5.47 (m, $^3J_{trans}$ = 15.3, $^3J_{CHCH2}$ = 7.1 Hz, 1 H, C*H*CH_2), 5.77–5.90 (m, $^3J_{trans}$ = 15.3, $^3J_{CHCH2}$ = 5.4 Hz, 1 H, C*H*CH_2), 10.20 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.8, 18.0 (CH_3), 32.1, 45.0 (CH_2), 52.2, 60.2 (OCH_3), 126.5, 132.5 (CH_{Olefin}), 113.4, 128.1, 133.0, 136.2, 144.6, 152.5 (C_{Ar}), 171.7 (*C*OOCH$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2954 (m), 1654 (s), 1598 (w), 1438 (s), 1414 (m), 1359 (m), 1321 (s), 1217 (m), 1071 (m), 968 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 300 (8) $[M]^+$ (^{37}Cl), 298 (24) $[M]^+$ (^{35}Cl), 266 (70), 238 (12), 231 (100). $C_{15}H_{19}ClO_4$ (298.77): calcd. C 60.30, H 6.41; found C 60.10, H 6.52.

5-[(*E*)-4-Chlorobut-2-enyl]-4,6-dimethylacetophenone (3e): Starting with **1** (0.155 g, 1.02 mmol), **2e** (0.373 g, 1.53 mmol) and $TiCl_4$ (0.22 mL, 2.04 mmol), **3e** was isolated by chromatography (heptane/EtOAc, 10:1) as a slightly yellow solid (0.077 g, 30%); m.p. 47–50 °C; R_f = 0.57 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 3.32–3.39 (m, ^3J = 5.4 Hz, 2 H, CHCH_2), 3.96–4.03 (m, ^3J = 7.0 Hz, 2 H, CHCH_2), 5.32–5.47 (m, $^3J_{trans}$ = 15.2, $^3J_{CHCH2}$ = 7.0 Hz, 1 H, C*H*CH_2), 5.78–5.91 (m, $^3J_{trans}$ = 15.2, $^3J_{CHCH2}$ = 5.4 Hz, 1 H, C*H*CH_2), 6.68 (s, 1 H, Ar), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.5, 20.7, 32.8 (CH_3), 31.5, 44.9 (CH_2), 117.3 (CHAr), 126.5, 132.3 (CH_{Olefin}), 122.6, 128.1, 136.9, 144.4, 158.4 (C_{Ar}), 206.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2966 (w),

1625 (s), 1559 (m), 1450 (m), 1442 (s), 1205 (s), 1058 (m), 1025 (m), 979 (m), 839 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 254 (6) $[M]^+$ (^{37}Cl), 252 (17) $[M]^+$ (^{35}Cl), 237 (23), 217 (100), 175 (16). HRMS (EI): calcd. for $C_{14}H_{17}ClO_2$ $[M]^+$ (^{35}Cl) 252.09116; found 252.091036.

General Procedure for the Synthesis of Dihydrofurans 7a–i: Ceric ammonium nitrate (CAN; 2.0 equiv.) was dissolved in acetonitrile. An acetonitrile solution (10 mL) of **5a**,**b** (1.0 equiv.) and **6** (4.4 equiv.) was added to the mixture and the solution was stirred at 20 °C until the reaction was complete (TLC control). Water (250 mL) was added to the mixture and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (300 mL), dried (Na_2SO_4) and filtered. The solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc). Compounds **7a**–**c** and **7f** have been previously reported.[9]

1-[5-(4-Bromophenyl)-2-methyl-4,5-dihydrofuran-3-yl]ethanone (7d): Starting with **5a** (0.51 mL, 4.99 mmol), **6d** (2.87 mL, 21.97 mmol) and CAN (5.476 g, 9.99 mmol) in acetonitrile (100 mL), **7d** was isolated by chromatography (heptane/EtOAc, 15:1) to give **7d** as a yellow oil (0.763 g, 54%). R_f = 0.17 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 2.26–2-32 (m, 3 H, CH_3), 2.83–2.97 (m, 1 H, H_a), 3.31–3.45 (m, 1 H, H_b), 5.47–5.60 (m, 1 H, H_x), 7.14–7.23 (m, ^3J = 8.4 Hz, 2 H, Ar), 7.44–7.55 (m, ^3J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.9, 29.4 (CH_3), 38.7 (CH_2), 82.4 (*C*HCH_2), 111.9, 122.1, 140.3, 167.3 ($C_{Ar,Olefin}$), 127.3, 131.9 (CH_{Ar}), 194.3 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2921 (w), 2866 (w), 1591 (s), 1487 (m), 1381 (m), 1360 (m), 1216 (s), 1068 (m), 1010 (m), 930 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 282 (81) $[M]^+$ (^{81}Br), 280 (82) $[M]^+$ (^{79}Br), 263 (17), 186 (52), 115 (36). HRMS (EI): calcd. for $C_{13}H_{13}BrO_2$ $[M]^+$ (^{79}Br) 280.00896; found 280.00934.

1-[5-(4-Fluorophenyl)-2-methyl-4,5-dihydrofuran-3-yl]ethanone (7e): Starting with **5a** (0.62 mL, 5.99 mmol), **6e** (3.15 mL, 26.37 mmol) and CAN (6.571 g, 11.99 mmol) in acetonitrile (100 mL), **7e** was isolated by chromatography (heptane/EtOAc, 15:1) as a yellow oil (0.563 g, 43%). R_f = 0.44 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.26–2.31 (m, 3 H, CH_3), 2.85–3.00 (m, 1 H, H_a), 3.29–3.45 (m, 1 H, H_b), 5.48–5.64 (m, 1 H, H_x), 6.94–7.15 (m, 2 H, Ar), 7.22–7.39 (m, 2 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.0, 29.4 (CH_3), 38.8 (CH_2), 82.5 (*C*HCH_2), 112.0, 167.3 (C_{Olefin}), 115.6 (d, ^2J = 21.8 Hz, CH_{Ar}), 127.5 (d, ^3J = 8.3 Hz, CH_{Ar}), 137.0 (d, ^4J = 3.2 Hz, C_{Ar}), 162.5 (d, ^1J = 246.9 Hz, C_{Ar}), 194.4 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1712 (br), 1599 (m), 1510 (s), 1372 (m), 1222 (s), 1157 (m), 1099 (m), 1126 (m), 1014 (m), 835 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 220 (68) $[M]^+$, 201 (18), 159 (27), 133 (26). HRMS (EI): calcd. for $C_{13}H_{13}FO_2$ $[M]^+$ 220.08987; found 220.08941.

1-[5-(2-Chlorophenyl)-2-methyl-4,5-dihydrofuran-3-yl]ethanone (7g): Starting with **5a** (0.62 mL, 5.99 mmol), **6g** (3.35 mL, 26.37 mmol) and CAN (6.571 g, 11.99 mmol) in acetonitrile (100 mL), **7g** was isolated by chromatography (heptane/EtOAc, 20:1) as a yellow oil (0.918 g, 65%). R_f = 0.35 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.33–2.37 (m, 3 H, CH_3), 2.72–2.84 (m, 1 H, H_a), 3.48–3.61 (m, 1 H, H_b), 5.82–5.95 (m, 1 H, H_x), 7.22–7.41 (m, 4 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.8, 29.5 (CH_3), 38.3 (CH_2), 80.0 (*C*HCH_2), 111.6, 131.2, 139.3, 167.2 ($C_{Ar,Olefin}$), 125.9, 127.1, 129.0, 129.6 (CH_{Ar}), 194.5 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2922 (w), 2867 (w), 1602 (s), 1476 (m), 1383 (m), 1360 (m), 1219 (s), 1130 (s), 922 (m), 752 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 238 (44) $[M]^+$ (^{37}Cl), 236 (91) $[M]^+$ (^{35}Cl), 221 (22), 141 (24), 43 (100). HRMS (EI): calcd. for $C_{13}H_{13}ClO_2$ $[M]^+$ (^{35}Cl) 236.06002; found 236.05986.

1-[5-(2,6-Dichlorophenyl)-2-methyl-4,5-dihydrofuran-3-yl]ethanone (7h): Starting with **5a** (0.62 mL, 5.99 mmol), **6h** (3.60 mL, 26.37 mmol) and CAN (6.571 g, 11.99 mmol) in acetonitrile (100 mL), **7h** was isolated by chromatography (heptane/EtOAc, 20:1) as a colourless solid (0.450 g, 28%); m.p. 61–62 °C; R_f = 0.45 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 2.31–2-34 (m, 3 H, CH_3), 3.13–3.40 (m, 2 H, H_a, H_b), 6.28–6.41 (m, 1 H, H_x), 7.21–7.32 (m, 1 H, Ar), 7.35–7.42 (m, 2 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.7, 29.5 (CH_3), 36.0 (CH_2), 79.4 (*C*HCH_2), 112.6, 134.1, 135.4, 167.4 ($C_{Ar,Olefin}$), 129.3, 129.9 (CH_{Ar}), 194.4 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2873 (w), 1668 (m), 1586 (s), 1435 (m), 1358 (m), 1330 (m), 1223 (s), 1135 (m), 1068 (m), 932 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 272 (53) $[M]^+$ (^{35}Cl, ^{37}Cl), 270 (87) $[M]^+$ (^{35}Cl, ^{35}Cl), 255 (25), 111 (50). HRMS (EI): calcd. for $C_{13}H_{12}Cl_2O_2$ $[M]^+$ (^{35}Cl, ^{35}Cl) 270.02074; found 270.02089.

1-(2-Ethyl-5-phenyl-4,5-dihydrofuran-3-yl)propan-1-one (7i): Starting with **5b** (0.63 mL, 4.68 mmol), **6a** (2.37 mL, 20.60 mmol) and CAN (5.133 g, 9.36 mmol) in acetonitrile (100 mL), **7i** was isolated by chromatography (heptane/EtOAc, 20:1) as a yellow oil (0.327 g, 30%). R_f = 0.62 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.20 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 2.36–2.50 (m, ^3J = 7.3 Hz, 2 H, CH_2CH_3), 2.68–2.84 (m, ^3J = 7.3 Hz, 2 H, CH_2CH_3), 2.88–3.02 (m, 1 H, H_a), 3.32–3.47 (m, 1 H, H_b), 5.53–5.64 (m, 1 H, H_x), 7.24–7.44 (m, 5 H, Ph) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 7.9, 11.1 (CH_3), 22.0, 34.7, 38.8 (CH_2), 82.9 (*C*HCH_2), 109.6, 141.7, 172.0 ($C_{Ph,Olefin}$), 125.5, 128.1, 128.7 (CH_{Ph}), 197.4 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2978 (w), 2940 (w), 1703 (br), 1589 (m), 1596 (m), 1450 (m), 1377 (m), 1207 (m), 903 (m), 757 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 230 (52) $[M]^+$, 201 (24), 131 (35), 105 (57), 57 (100). HRMS (EI): calcd. for $C_{15}H_{18}O_2$ $[M]^+$ 230.13026; found 230.13013.

Methyl 5-(2-Chloro-2-phenylethyl)-4,6-dimethylsalicylate (8a): Starting with **7a** (0.198 g, 0.98 mmol), **2a** (0.383 g, 1.47 mmol) and $TiCl_4$ (0.21 mL, 1.96 mmol), **8a** was isolated by chromatography (heptane/EtOAc, 20:1) as a colourless solid (0.143 g, 46%); m.p. 79–80 °C; R_f = 0.62 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.12, 2.41 (s, 3 H, CH_3), 3.26 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.3 Hz, 1 H, H_a), 3.49 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.3 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.95 (t, $^3J_{Hx,Hab}$ = 7.3 Hz, 1 H, CHCl), 6.64 (s, 1 H, Ar), 7.30 (s, 5 H, Ph), 10.70 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.0, 21.4 (CH_3), 40.3 (CH_2CHCl), 52.1 (OCH_3), 63.2 (CHCl), 111.9, 127.2, 139.4, 141.1, 144.9, 160.2 ($C_{Ph,Ar}$), 117.2, 126.9, 128.3, 128.4 ($CH_{Ph,Ar}$), 171.9 (*C*$OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2991 (w), 1661 (s), 1569 (m), 1442 (m), 1202 (m), 1154 (m), 1072 (m), 1055 (w), 915 (m), 820 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 320 (3) $[M]^+$ (^{37}Cl), 318 (9) $[M]^+$ (^{35}Cl), 193 (93), 178 (11), 161 (100). HRMS (EI): calcd. for $C_{18}H_{19}ClO_3$ $[M]^+$ (^{35}Cl) 318.10153; found 318.10172. $C_{18}H_{19}ClO_3$ (318.79): calcd. C 67.82, H 6.01; found C 67.47, H 5.91.

Ethyl 5-(2-Chloro-2-phenylethyl)-4,6-dimethylsalicylate (8b): Starting with **7a** (0.167 g, 0.83 mmol), **2b** (0.340 g, 1.5 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol), **8b** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.120 g, 44%); m.p. 66–68 °C; R_f = 0.67 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.42 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 2.12, 2.42 (s, 3 H, CH_3), 3.26 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.3 Hz, 1 H, H_a), 3.50 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.3 Hz, 1 H, H_b), 4.41 (q, ^3J = 7.1 Hz, 2 H, CH_2CH_3), 4.96 (t, $^3J_{Hx,Hab}$ = 7.3 Hz, 1 H, CHCl), 6.64 (s, 1 H, Ar), 7.30 (s, 5 H, Ph), 10.78 (s, 1 H, OH) ppm. ^{13}C

NMR (62.9 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 19.1, 21.4 (CH_3), 40.3 (CH_2CHCl), 61.6 (OCH_2CH_3), 63.2 (CHCl), 112.0, 127.1, 139.4, 141.2, 144.8, 160.2 ($C_{Ph,Ar}$), 117.2, 126.9, 128.3, 128.4 ($CH_{Ph,Ar}$), 171.5 ($COOCH_2CH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2977 (w), 1650 (w), 1468 (m), 1373 (m), 1313 (m), 1246 (s), 1232 (s), 1161 (m), 1072 (m), 920 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 334 (0.8) $[M]^+$ (^{37}Cl), 268 (2) $[M]^+$ (^{35}Cl), 250 (7), 207 (65), 161 (100). $C_{19}H_{21}ClO_3$ (332.82): calcd. C 68.57, H 6.36; found C 68.67, H 6.36.

Methyl 5-(2-Chloro-2-phenylethyl)-3,4,6-trimethylsalicylate (8c): Starting with **7a** (0.160 g, 0.79 mmol), **2c** (0.366 g, 1.35 mmol) and $TiCl_4$ (0.17 mL, 1.58 mmol), **8c** was isolated by chromatography (heptane/EtOAc, 50:1) as a slightly yellow solid (0.098 g, 36%); m.p. 78–79 °C; R_f = 0.62 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.12, 2.15, 2.34 (s, 3 H, CH_3), 3.32 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Ha,Hx}$ = 7.2 Hz, 1 H, H_a), 3.56 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hb,Hx}$ = 7.3 Hz, 1 H, H_b), 3.92 (s, 3 H, OCH_3), 4.94 ("t", $^3J_{Hx,Ha}$ = 7.2, $^3J_{Hx,Hb}$ = 7.3 Hz, 1 H, CHCl), 7.29 (s, 5 H, Ar), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 17.4, 19.1 (CH_3), 40.5 (CH_2CHCl), 52.1 (OCH_3), 63.6 (CHCl), 111.4, 122.8, 126.7, 135.9, 141.2, 143.0, 158.0 (C_{Ar}), 127.0, 128.2, 128.4 (CH_{Ar}), 172.6 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3033 (w), 2958 (w), 1646 (s), 1435 (m), 1350 (m), 1264 (s), 1205 (s), 1174 (s), 1009 (m), 951 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 334 (1) $[M]^+$ (^{37}Cl), 332 (3) $[M]^+$ (^{35}Cl), 264 (4), 207 (58), 175 (100). HRMS (EI): calcd. for $C_{19}H_{21}ClO$ $[M]^+$ (^{35}Cl) 332.11817; found 332.11737. $C_{19}H_{21}ClO_3$ (332.12): calcd. C 68.57, H 6.36; found C 68.33, H 6.41.

Methyl 5-(2-Chloro-2-phenylethyl)-3-ethyl-4,6-dimethylsalicylate (8d): Starting with **7a** (0.167 g, 0.83 mmol), **2f** (0.405 g, 1.40 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol), **8d** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.147 g, 51%); m.p. 72–73 °C; R_f = 0.70 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 2.10, 2.35 (s, 3 H, CH_3), 2.60–2.76 (m, ^3J = 7.5 Hz, 2 H, CH_3CH_2), 3.32 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.4 Hz, 1 H, H_a), 3.56 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 7.1 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.94 ("t", $^3J_{Hx,Ha}$ = 7.4, $^3J_{Hx,Hb}$ = 7.1 Hz, 1 H, CHCl), 7.28 (s, 5 H, Ph), 10.85 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.2 16.5, 19.0 (CH_3), 19.9 (CH_3CH_2) 40.6 (CH_2CHCl), 52.1 (OCH_3), 63.5 (CHCl), 111.6, 128.9, 136.0, 141.2, 142.3, 157.9 ($C_{Ph,Ar}$), 127.0, 128.2, 128.4 ($CH_{Ph,Ar}$), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2962 (w), 2871 (w), 1648 (s), 1436 (m), 1357 (m), 1205 (s), 1171 (m), 1032 (m), 952 (m), 807 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 348 (5) $[M]^+$ (^{37}Cl), 346 (14) $[M]^+$ (^{35}Cl), 315 (9), 221 (99), 189 (100). HRMS (EI): calcd. for $C_{20}H_{23}ClO_3$ $[M]^+$ (^{35}Cl) 346.13267; found 346.13302.

Isopropyl 5-(2-Chloro-2-phenylethyl)-4,6-dimethylsalicylate (8e): Starting with **7a** (0.200 g, 0.99 mmol), **2g** (0.428 g, 1.48 mmol) and $TiCl_4$ (0.22 mL, 1.98 mmol), **8e** was isolated by chromatography (heptane/EtOAc, 50:1) as a yellow solid (0.192 g, 56%); m.p. 73–74 °C; R_f = 0.63 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36–1.43 (m, ^3J = 6.3 Hz, 3 H, CH_3CHCH_3), 2.12, 2.40 (s, 3 H, CH_3), 3.26 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.3 Hz, 1 H, H_a), 3.49 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.2 Hz, 1 H, H_b), 4.96 ("t", $^3J_{Hx,Ha}$ = 7.3, $^3J_{Hx,Hb}$ = 7.2 Hz, 1 H, CHCl), 5.31 (sept., ^3J = 6.3 Hz, 1 H, CH_3CHCH_3), 6.64 (s, 1 H, Ar), 7.30 (br. s, 5 H, Ph), 10.78 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.1, 21.4, 21.9 (CH_3), 40.4 (CH_2CHCl), 63.3, 69.7 (CH), 112.4, 127.1, 139.4, 141.2, 144.6, 160.1 ($C_{Ph,Ar}$), 117.2, 126.9, 128.2, 128.4 ($CH_{Ph,Ar}$), 171.0 (COO) ppm. IR (ATR): $\tilde{\nu}$ = 2980 (w), 2935 (w), 1650 (s), 1595 (m), 1455 (m), 1367 (s), 1303 (m), 1243 (s), 1102 (s), 912 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 348 (1) $[M]^+$ (^{37}Cl), 346 (3) $[M]^+$ (^{35}Cl), 250 (34), 221 (77), 161 (100). HRMS (EI): calcd. for $C_{20}H_{23}ClO_3$ $[M]^+$ (^{35}Cl) 346.13344; found 346.13302. $C_{20}H_{23}ClO_3$ (346.13): calcd. C 69.26, H 6.68; found C 68.84, H 6.77.

Methyl 5-(2-Chloro-2-phenylethyl)-4,6-dimethyl-3-propylsalicylate (8f): Starting with **7a** (0.167 g, 0.83 mmol), **2h** (0.375 g, 1.24 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol), **8f** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.154 g, 52%); m.p. 67–68 °C; R_f = 0.71 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.3 Hz, 3 H, CH_3CH_2), 1.36–1.53 (m, 2 H, CH_2), 2.09, 2.35 (s, 3 H, CH_3), 2.56–2.68 (m, 2 H, CH_2), 3.32 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.5 Hz, 1 H, H_a), 3.56 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 7.0 Hz, 1 H, H_b), 4.93 ("t", $^3J_{Hx,Ha}$ = 7.5, $^3J_{Hx,Hb}$ = 7.0 Hz, 1 H, CHCl), 7.28 (s, 5 H, Ar), 10.85 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.3, 16.8, 19.1 (CH_3), 22.2, 28.7, 40.6 (CH_2), 52.1 (OCH_3), 63.5 (CHCl), 111.5, 126.9, 127.5, 136.0, 141.1, 142.6, 158.1 (C_{Ar}), 127.0, 128.2, 128.4 (CH_{Ar}), 172.6 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2949 (m), 2866 (m), 1651 (s), 1586 (m), 1437 (s), 1402 (m), 1321 (s), 1169 (s), 1110 (s), 1039 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 362 (1) $[M]^+$ (^{37}Cl), 360 (2) $[M]^+$ (^{35}Cl), 264 (36), 235 (87), 203 (100). HRMS (EI): calcd. for $C_{21}H_{25}ClO_3$ $[M]^+$ (^{35}Cl) 360.14919; found 360.14867.

Methyl 5-[2-Chloro-2-(*p*-tolyl)ethyl]-4,6-dimethylsalicylate (8g): Starting with **7b** (0.121 g, 0.56 mmol), **2a** (0.248 g, 0.95 mmol) and $TiCl_4$ (0.12 mL, 1.12 mmol), **8g** was isolated by chromatography (heptane/EtOAc, 50:1) as a yellow oil (0.065 g, 35%). R_f = 0.43 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.14, 2.34, 2.43 (s, 3 H, CH_3), 3.25 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.0 Hz, 1 H, H_a), 3.49 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.5 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.94 ("t", $^3J_{Hx,Ha}$ = 7.0, $^3J_{Hx,Hb}$ = 7.5 Hz, 1 H, CHCl), 6.65 (s, 1 H, Ar), 7.07–7.24 (m, 4 H, Ar), 10.68 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.1, 21.1, 21.5 (CH_3), 40.2 (CH_2CHCl), 52.1 (OCH_3), 63.3 (CHCl), 111.9, 127.3, 138.1, 138.3, 139.4, 144.9, 160.1 (C_{Ar}), 117.2, 126.8, 129.1 (CH_{Ar}), 171.9 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2952 (w), 2860 (w), 1658 (s), 1572 (m), 1437 (m), 1347 (m), 1312 (m), 1235 (s), 1207 (s), 1072 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 334 (1) $[M]^+$ (^{37}Cl), 332 (3) $[M]^+$ (^{35}Cl), 264 (18), 193 (78), 161 (100). HRMS (EI): calcd. for $C_{19}H_{21}ClO_3$ $[M]^+$ (^{35}Cl) 332.11765; found 332.11737.

Methyl 5-[2-Chloro-2-(4-chlorophenyl)ethyl]-4,6-dimethylsalicylate (8h): Starting with **7c** (0.170 g, 0.72 mmol), **2a** (0.318 g, 1.22 mmol) and $TiCl_4$ (0.16 mL, 1.44 mmol), **8h** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.146 g, 38%); m.p. 91–93 °C; R_f = 0.65 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.11, 2.37 (s, 3 H, CH_3), 3.23 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.46 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.0 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.91 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 7.0 Hz, 1 H, CHCl), 6.65 (s, 1 H, Ar), 7.18–7.30 (m, 4 H, Ar), 10.68 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.0, 21.4 (CH_3), 40.3 (CH_2CHCl), 52.1 (OCH_3), 62.2 (CHCl), 111.9, 126.8, 134.0, 139.3, 139.6, 144.8, 160.2 (C_{Ar}), 117.3, 128.4, 128.6 (CH_{Ar}), 171.8 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3026 (w), 2980 (w), 1661 (s), 1568 (m), 1432 (br), 1312 (s), 1202 (br), 1150 (m), 1072 (m), 825 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 354 (2) $[M]^+$ (^{37}Cl, ^{35}Cl), 252 (3) $[M]^+$ (^{35}Cl, ^{35}Cl), 284 (6), 193 (92), 161 (100). HRMS (EI): calcd. for $C_{18}H_{18}Cl_2O_3$ $[M]^+$ (^{35}Cl, ^{35}Cl) 352.06352; found 352.06275. $C_{18}H_{18}Cl_2O_3$ (353.24): calcd. C 61.20, H 5.14; found C 61.29, H 5.30.

Ethyl 5-[2-Chloro-2-(4-chlorophenyl)ethyl]-4,6-dimethylsalicylate (8i): Starting with **7c** (0.179 g, 0.76 mmol), **2b** (0.353 g, 1.29 mmol) and $TiCl_4$ (0.17 mL, 1.51 mmol), **8i** was isolated by chromatography (heptane/EtOAc, 50:1) as a slightly yellow solid (0.205 g, 74%); m.p. 93–94 °C; R_f = 0.76 (heptane/EtOAc, 1:1). ^1H NMR

(250 MHz, $CDCl_3$): δ = 1.41 (t, ^3J = 7.1 Hz, 3 H, CH_3CH_2), 2.12, 2.37 (s, 3 H, CH_3), 3.23 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.46 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 6.9 Hz, 1 H, H_b), 4.41 (q, ^3J = 7.1 Hz, 2 H, CH_3CH_2), 4.91 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 6.9 Hz, 1 H, CHCl), 6.45 (s, 1 H, Ar), 7.17–7.30 (m, 4 H, Ar), 10.75 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2 19.1, 21.4 (CH_3), 40.3 (CH_2CHCl), 61.6 (OCH_2CH_3), 62.2 (CHCl), 112.1, 126.7, 134.0, 139.4, 139.6, 144.6, 160.3 (C_{Ar}), 117.3, 128.4, 128.6 (CH_{Ar}), 171.4 ($COOCH_2CH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2989 (w), 2935 (w), 1656 (s), 1570 (m), 1470 (m), 1309 (s), 1197 (s), 1014 (s), 914 (m), 831 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 368 (3) $[M]^+$ (^{37}Cl, ^{35}Cl), 366 (4) $[M]^+$ (^{35}Cl, ^{35}Cl), 321 (9), 207 (100), 161 (99). HRMS (ESI): calcd. for $C_{19}H_{20}Cl_2NaO_3$ $[M + Na]^+$ (^{35}Cl, ^{35}Cl) 389.06817; found 389.06729. $C_{19}H_{20}Cl_2O_3$ (367.27): calcd. C 62.14, H 5.49; found C 62.07, H 5.47.

Methyl 5-[2-Chloro-2-(4-chlorophenyl)ethyl]-3,4,6-trimethylsalicylate (8j): Starting with **7c** (0.151 g, 0.64 mmol), **2c** (0.296 g, 1.09 mmol) and $TiCl_4$ (0.14 mL, 1.28 mmol), **8j** was isolated by chromatography (heptane/EtOAc, 40:1) as a colourless solid (0.109 g, 47%); m.p. 100–101 °C; R_f = 0.73 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.12, 2.15, 2.30 (s, 3 H, CH_3), 3.29 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Ha,Hx}$ = 7.6 Hz, 1 H, H_a), 3.53 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hb,Hx}$ = 7.0 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.89 ("t", $^3J_{Hx,Ha}$ = 7.6, $^3J_{Hx,Hb}$ = 7.0 Hz, 1 H, CHCl), 7.16–7.32 (m, 4 H, Ar), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 17.4, 19.1 (CH_3), 40.5 (CH_2CHCl), 52.1 (OCH_3), 62.6 (CHCl), 111.4, 122.9, 126.2, 134.0, 135.9, 139.6, 142.8, 158.1 (C_{Ar}), 128.4, 128.5 (CH_{Ar}), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2992 (w), 2945 (w), 1660 (s), 1588 (m), 1437 (m), 1314 (s), 1166 (s), 1089 (s), 1114 (m), 919 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 368 (6) $[M]^+$ (^{35}Cl, ^{37}Cl), 366 (9) $[M]^+$ (^{35}Cl, ^{35}Cl), 207 (100), 175 (98). HRMS (EI): calcd. for $C_{19}H_{20}Cl_2O_3$ $[M]^+$ (^{35}Cl, ^{35}Cl) 366.07804; found 366.07840. $C_{19}H_{20}Cl_2O_3$ (366.08): calcd. C 62.14, H 5.49; found C 62.01, H 5.38.

Methyl 5-[2-Chloro-2-(4-chlorophenyl)ethyl]-3-ethyl-4,6-dimethylsalicylate (8k): Starting with **7c** (0.146 g, 0.62 mmol), **2f** (0.303 g, 1.05 mmol) and $TiCl_4$ (0.14 mL, 1.23 mmol), **8k** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.131 g, 56%); m.p. 98–99 °C; R_f = 0.71 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 2.10, 2.31 (s, 3 H, CH_3), 2.59–2.76 (m, ^3J = 7.5 Hz, 2 H, CH_3CH_2), 3.29 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.52 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 6.8 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.89 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 6.8 Hz, 1 H, CHCl), 7.15–7.30 (m, 4 H, Ar), 10.84 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.2, 16.5, 19.1 (CH_3), 19.9 (CH_3CH_2), 40.6 (CH_2CHCl), 52.1 (OCH_3), 62.4 (CHCl), 111.6, 126.5, 129.1, 134.0, 136.0, 139.6, 142.1, 158.0 (C_{Ar}), 128.4, 128.5 (CH_{Ar}), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2965 (w), 2930 (w), 1651 (s), 1587 (m), 1441 (s), 1319 (s), 1202 (s), 1168 (s), 1034 (m), 821 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 380 (1) $[M]^+$ (^{35}Cl) ^{35}, 278 (4), 221 (91), 189 (100), 161 (27). HRMS (EI): calcd. for $C_{20}H_{22}Cl_2O_3$ $[M]^+$ (^{35}Cl, ^{35}Cl) 380.09330; found 380.09405.

Methyl 5-[2-(4-Bromophenyl)-2-chloroethyl]-4,6-dimethylsalicylate (8l): Starting with **7d** (0.155 g, 0.51 mmol), **2a** (0.244 g, 0.94 mmol) und $TiCl_4$ (0.12 mL, 1.10 mmol), **8l** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.116 g, 53%); m.p. 94–95 °C; R_f = 0.56 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.11, 2.37 (s, 3 H, CH_3), 3.23 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.6 Hz, 1 H, H_a), 3.46 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 7.0 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.89 ("t", $^3J_{Hx,Ha}$ = 7.6, $^3J_{Hx,Hb}$ = 7.0 Hz, 1 H, CHCl), 6.65 (s, 1 H, Ar), 7.11–7.19 (m, 2 H, Ar), 7.38–7.46 (m, 2 H, Ar), 10.68 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.1, 21.4 (CH_3), 40.2 (CH_2CHCl), 52.2 (OCH_3), 62.2 (CHCl), 112.0, 122.2, 126.7, 139.4, 140.1, 144.8, 160.3 (C_{Ar}), 117.3, 128.7, 131.6 (CH_{Ar}), 171.8 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2977 (w), 2951 (w), 1666 (s), 1568 (m), 1464 (m), 1315 (s), 1192 (s), 1152 (s), 1071 (s), 911 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 398 (1) $[M]^+$ (^{37}Cl/^{79}Br, ^{35}Cl/^{81}Br), 193 (90), 178 (6), 161 (100). HRMS (EI): calcd. for $C_{18}H_{18}BrClO_3$ $[M]^+$ (^{35}Cl, ^{79}Br) 396.01201; found 396.01224. $C_{18}H_{18}BrClO_3$ (396.01): calcd. C 54.36, H 4.56; found C 54.28, H 4.63.

Methyl 5-[2-(4-Bromophenyl)-2-chlorethyl]-3,4,6-trimethylsalicylate (8m): Starting with **7d** (0.147 g, 0.52 mmol), **2c** (0.242 g, 0.89 mmol) and $TiCl_4$ (0.11 mL, 1.05 mmol), **8m** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.133 g, 62%); m.p. 105–107 °C; R_f = 0.63 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.12, 2.15, 2.29 (s, 3 H, CH_3), 3.29 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.6 Hz, 1 H, H_a), 3.52 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 7.0 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.87 ("t", $^3J_{Hx,Ha}$ = 7.6, $^3J_{Hx,Hb}$ = 7.0 Hz, 1 H, CHCl), 7.11–7.19 (m, 2 H, Ar), 7.37–7.46 (m, 2 H, Ar), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 17.4, 19.1 (CH_3), 40.4 (CH_2CHCl), 52.1 (OCH_3), 62.6 (CHCl), 111.5, 122.1, 123.0, 126.2, 135.9, 140.1, 142.8, 158.1 (C_{Ar}), 128.7, 131.5 (CH_{Ar}), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2996 (w), 2948 (w), 1662 (s), 1588 (m), 1436 (m), 1313 (s), 1256 (s), 1166 (s), 1008 (s), 918 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 412 (5) $[M]^+$ (^{37}Cl/^{79}Br, ^{35}Cl/^{81}Br), 344 (4), 207 (100), 175 (95). $C_{19}H_{20}BrClO_3$ (411.72): calcd. C 55.43, H 4.90; found C 55.58, H 4.90.

Methyl 5-[2-(4-Bromophenyl)-2-chloroethyl]-3-ethyl-4,6-dimethylsalicylate (8n): Starting with **7d** (0.152 g, 0.54 mmol), **2f** (0.265 g, 0.92 mmol) and $TiCl_4$ (0.12 mL, 1.08 mmol), **8n** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.104 g, 45%); m.p. 102–103 °C; R_f = 0.53 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 2.11, 2.31 (s, 3 H, CH_3), 2.60–2.75 (m, ^3J = 7.5 Hz, 2 H, CH_3CH_2), 3.28 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.8 Hz, 1 H, H_a), 3.52 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 6.8 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.87 ("t", $^3J_{Hx,Ha}$ = 7.8, $^3J_{Hx,Hb}$ = 6.8 Hz, 1 H, CHCl), 7.09–7.17 (m, 2 H, Ar), 7.37–7.45 (m, 2 H, Ar), 10.84 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.2, 16.5, 19.1 (CH_3), 19.9 (CH_3CH_2), 40.5 (CH_2CHCl), 52.1 (OCH_3), 62.5 (CHCl), 111.7, 122.1, 126.5, 129.1, 136.0, 140.1, 142.1, 158.0 (C_{Ar}), 128.7, 131.5 (CH_{Ar}), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2949 (w), 2870 (w), 1660 (m), 1588 (m), 1436 (s), 1317 (s), 1202 (s), 1152 (s), 1103 (s), 919 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 426 (3) $[M]^+$ (^{37}Cl/^{79}Br, ^{35}Cl/^{81}Br), 358 (3), 221 (93), 189 (100). $C_{20}H_{22}BrClO_3$ (424.04): calcd. C 56.42, H 5.21; found C 56.40, H 5.26.

Isopropyl 5-[2-(4-Bromophenyl)-2-chloroethyl]-4,6-dimethylsalicylate (8o): Starting with **7d** (0.195 g, 0.69 mmol), **2g** (0.340 g, 1.18 mmol) and $TiCl_4$ (0.15 mL, 1.34 mmol), **8o** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.192 g, 65%); m.p. 101–102 °C; R_f = 0.74 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (d, ^3J = 6.2 Hz, 6 H, CH_3CHCH_3), 2.12, 2.33 (s, 3 H, CH_3), 3.22 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.45 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 6.9 Hz, 1 H, H_b), 4.88 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 6.9 Hz, 1 H, CHCl), 5.30 (sept., ^3J = 6.2 Hz, 1 H, CH_3CHCH_3), 6.65 (s, 1 H, Ar), 7.10–7.19 (m, 2 H, Ar), 7.37–7.47 (m, 2 H, Ar), 10.78 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.1, 21.3, 21.9, 21.9 (CH_3), 40.3 (CH_2CHCl), 62.2 (CHCl), 69.7 (CH_3CHCH_3), 112.4, 122.1, 126.6, 139.3, 140.1, 144.4, 160.2 (C_{Ar}), 117.3, 128.7, 131.5 (CH_{Ar}), 170.9

(*C*OO*i*Pr) ppm. IR (ATR): ṽ = 2981 (w), 2932 (w), 1650 (s), 1569 (m), 1467 (m), 1363 (s), 1224 (m), 1203 (s), 1103 (s), 914 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 426 (3) [M]$^+$ (^{37}Cl/^{79}Br, ^{35}Cl/^{81}Br), 221 (95), 179 (83), 161 (100). $C_{20}H_{22}BrClO_3$ (411.72): calcd. C 56.42, H 5.21; found C 56.40, H 5.32.

Methyl 5-[2-(4-Bromophenyl)-2-chloroethyl]-3-(3-chloropropyl)-4,6-dimethylsalicylate (8p): Starting with **7d** (0.198 g, 0.70 mmol), **2i** (0.403 g, 1.20 mmol) and $TiCl_4$ (0.15 mL, 1.41 mmol), **8p** was isolated by chromatography (heptane/EtOAc, 100:1) as a colourless solid (0.106 g, 32%); m.p. 101–102 °C; R_f = 0.47 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84–1.97 (m, 2 H, CH_2), 2.13, 2.33 (s, 3 H, CH_3), 2.72–2.88 (m, 2 H, CH_2), 3.20–3.65 (m, 4 H, CH_2, H_a, H_b), 3.94 (s, OCH_3), 4.80–4.93 (m, 1 H, H_x), 7.09–7.17 (m, ^3J = 8.4 Hz, 2 H, Ar), 7.38–7.45 (m, ^3J = 8.4 Hz, 2 H, CH_2), 10.92 (s, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.9, 19.2 (CH_3), 24.2, 31.9, 40.5, 45.1 (CH_2), 52.2 (OCH_3), 62.4 (CHCl), 111.7, 122.2, 126.0, 126.7, 136.7, 140.1, 142.5, 158.3 (C_{Ar}), 128.7, 131.5 (CH_{Ar}), 172.4 (*C*OOCH$_3$) ppm. IR (ATR): ṽ = 2949 (w), 1650 (m), 1587 (m), 1485 (m), 1435 (s), 1317 (s), 1192 (s), 1165 (s), 1142 (s), 1009 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 474 (2) [M]$^+$ (^{35}Cl/^{35}Cl/^{81}Br), 371 (3), 269 (87), 237 (100). HRMS (EI): calcd. for $C_{21}H_{23}BrCl_2O_3$ [M]$^+$ (^{35}Cl, ^{35}Cl, ^{81}Br) 474.01817; found 474.01733.

Methyl 5-[2-Chloro-2-(4-fluorophenyl)ethyl]-4,6-dimethylsalicylate (8q): Starting with **7e** (0.161 g, 0.73 mmol), **2a** (0.324 g, 1.24 mmol) and $TiCl_4$ (0.16 mL, 1.46 mmol), **8q** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.111 g, 45%); m.p. 120–121 °C; R_f = 0.59 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.11, 2.38 (s, 3 H, CH_3), 3.24 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.47 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 6.9 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.93 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 6.9 Hz, 1 H, CHCl), 6.65 (s, 1 H, Ar), 6.91–7.05 (m, 2 H, Ar), 7.19–7.32 (m, 2 H, Ar), 10.69 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.9, 21.4 (CH_3), 40.5 (*C*H_2CHCl), 52.2 (OCH_3), 62.3 (CHCl), 111.9, 126.9, 139.4, 144.8, 160.3 (C_{Ar}), 137.0 (d, ^4J = 3.3 Hz, C_{Ar}), 162.4 (d, ^1J = 247.5 Hz, C_{Ar}), 115.3 (d, ^2J = 22.0 Hz, CH_{Ar}), 117.3 (CH_{Ar}), 128.7 (d, ^3J = 8.3 Hz, CH_{Ar}), 171.9 (*C*OOCH$_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = 113.5 (CF) ppm. IR (ATR): ṽ = 2991 (w), 2950 (w), 1661 (s), 1601 (m), 1506 (m), 1442 (s), 1335 (s), 1201 (s), 1071 (m), 914 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 336 (1) [M]$^+$ (^{35}Cl), 300 (7), 193 (60), 161 (100). HRMS (EI): calcd. for $C_{18}H_{18}ClFO_3$ [M]$^+$ (^{35}Cl) 336.09215; found 336.09230. $C_{18}H_{18}ClFO_3$ (336.09): calcd. C 64.19, H 5.39; found C 64.20, H 5.66.

Methyl 5-[2-Chloro-2-(4-fluorophenyl)ethyl]-3,4,6-trimethylsalicylate (8r): Starting with **7e** (0.152 g, 0.69 mmol), **2c** (0.320 g, 1.17 mmol) and $TiCl_4$ (0.15 mL, 1.38 mmol), **8r** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.098 g, 51%); m.p. 103–104 °C; R_f = 0.69 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11, 2.15, 2.30 (s, 3 H, CH_3), 3.30 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.7 Hz, 1 H, H_a), 3.54 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 6.9 Hz, 1 H, H_b), 3.92 (s, 3 H, OCH_3), 4.91 ("t", $^3J_{Hx,Ha}$ = 7.7, $^3J_{Hx,Hb}$ = 6.9 Hz, 1 H, CHCl), 6.92–7.02 (m, 2 H, Ar), 7.20–7.30 (m, 2 H, Ar), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.3, 17.4, 19.0 (CH_3), 40.7 (*C*H_2CHCl), 52.1 (OCH_3), 62.7 (CHCl), 111.4, 122.9, 126.4, 135.9, 142.8, 158.1 (C_{Ar}), 137.0 (d, ^4J = 3.3 Hz, C_{Ar}), 162.4 (d, ^1J = 247.7 Hz, C_{Ar}), 115.3 (d, ^2J = 21.6 Hz, CH_{Ar}), 128.7 (d, ^3J = 8.2 Hz, CH_{Ar}), 172.5 (*C*OOCH$_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.7 (CF) ppm. IR (ATR): ṽ = 2997 (w), 2949 (w), 1651 (s), 1603 (m), 1508 (m), 1439 (m), 1345 (m), 1303 (m), 1204 (s), 1097 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 352 (1) [M]$^+$ (^{37}Cl), 350 (3) [M]$^+$ (^{35}Cl), 282 (36), 207 (53), 175 (100). HRMS (EI): calcd. for $C_{19}H_{20}ClFO_3$ [M]$^+$ (^{35}Cl) 350.10876; found 350.10795.

Methyl 5-[2-Chloro-2-(4-fluorophenyl)ethyl]-3-ethyl-4,6-dimethylsalicylate (8s): Starting with **7e** (0.132 g, 0.60 mmol), **2f** (0.294 g, 1.02 mmol) and $TiCl_4$ (0.13 mL, 1.20 mmol), **8s** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.048 g, 22%); m.p. 68–69 °C; R_f = 0.73 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3 H, C*H*$_3$CH$_2$), 2.10, 2.32 (s, 3 H, CH_3), 2.57–2.77 (m, ^3J = 7.5 Hz, 3 H, CH$_3$C*H*$_2$), 3.29 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.8 Hz, 1 H, H_a), 3.53 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 6.8 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.91 ("t", $^3J_{Hx,Ha}$ = 7.8, $^3J_{Hx,Hb}$ = 6.8 Hz, 1 H, CHCl), 6.90–7.03 (m, 2 H, Ar), 7.17–7.29 (m, 2 H, Ar), 10.85 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.2, 16.5, 19.0 (CH_3), 19.9 (CH$_3$*C*H$_2$), 40.7 (*C*H$_2$CHCl), 52.1 (OCH_3), 62.6 (CHCl), 111.6, 126.6, 129.0, 136.0, 142.1, 158.0 (C_{Ar}), 136.9 (d, ^4J = 3.3 Hz, C_{Ar}), 162.4 (d, ^1J = 247.3 Hz, C_{Ar}), 115.2 (d, ^2J = 21.0 Hz, CH_{Ar}), 128.7 (d, ^3J = 8.3 Hz, CH_{Ar}), 172.5 (*C*OOCH$_3$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.7 (CF) ppm. IR (ATR): ṽ = 2960 (w), 2870 (w), 1659 (s), 1589 (m), 1506 (s), 1436 (s), 1317 (s), 1200 (s), 1103 (s), 917 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 364 (2) [M]$^+$ (^{35}Cl), 296 (24), 221 (52), 189 (100). HRMS (EI): calcd. for $C_{20}H_{22}ClFO_3$ [M]$^+$ (^{35}Cl) 364.12359; found 364.12360. $C_{20}H_{22}ClFO_3$ (364.12): calcd. C 65.84, H 6.08; found C 66.09, H 6.42.

5-[2-Chloro-2-(3-chlorophenyl)ethyl]-4,6-dimethylsalicylate (8t): Starting with **7f** (0.159 g, 0.67 mmol), **2a** (0.297 g, 1.14 mmol) and $TiCl_4$ (0.15 mL, 1.34 mmol), **8t** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.110 g, 46%); m.p. 76–77 °C; R_f = 0.64 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.15, 2.39 (s, 3 H, CH_3), 3.23 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.2 Hz, 1 H, H_a), 3.46 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 7.4 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.89 ("t", $^3J_{Hx,Ha}$ = 7.2, $^3J_{Hx,Hb}$ = 7.4 Hz, 1 H, CHCl), 6.66 (s, 1 H, Ar), 7.07–7.15 (m, 1 H, Ar), 7.17–7.30 (m, 2 H, Ar), 7.33–7.38 (m, 1 H, Ar), 10.71 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.0, 21.4 (CH_3), 40.1 (*C*H_2CHCl), 51.1 (OCH_3), 62.1 (CHCl), 111.9, 126.7, 134.4, 139.3, 143.1, 144.8, 160.3 (C_{Ar}), 117.3, 125.1, 127.1, 128.4, 129.7 (CH_{Ar}), 171.8 (*C*OOCH$_3$) ppm. IR (ATR): ṽ = 2989 (w), 2949 (w), 1660 (s), 1571 (m), 1441 (m), 1333 (m), 1315 (m), 1206 (s), 1073 (m), 916 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = (1) [M]$^+$ (^{35}Cl, ^{35}Cl), 284 (7), 193 (58), 161 (100). HRMS (EI): calcd. for $C_{18}H_{18}Cl_2O_3$ [M]$^+$ (^{35}Cl) 352.06334; found 352.06275. $C_{18}H_{18}Cl_2O_3$ (352.06): calcd. C 61.20, H 5.14; found C 61.48, H 5.15.

Methyl 5-[2-Chloro-2-(3-chlorophenyl)ethyl]-3,4,6-trimethylsalicylate (8u): Starting with **7f** (0.151 g, 0.64 mmol), **2c** (0.296 g, 1.09 mmol) and $TiCl_4$ (0.14 mL, 1.28 mmol), **8u** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.088 g, 38%); m.p. 65–66 °C; R_f = 0.73 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13, 2.16, 2.33 (s, 3 H, CH_3), 3.29 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Ha,Hx}$ = 7.2 Hz, 1 H, H_a), 3.53 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hb,Hx}$ = 7.3 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.87 ("t", $^3J_{Hx,Ha}$ = 7.2, $^3J_{Hx,Hb}$ = 7.3 Hz, 1 H, CHCl), 7.08–7.14 (m, 1 H, Ar), 7.17–7.30 (m, 2 H, Ar), 7.32–7.36 (m, 1 H, Ar), 10.91 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.3, 17.4, 19.1 (CH_3), 40.3 (*C*H_2CHCl), 52.1 (OCH_3), 62.5 (CHCl), 111.5, 123.0, 126.2, 134.3, 135.9, 142.8, 143.1, 158.1 (C_{Ar}), 125.2, 127.2, 128.4, 129.6 (CH_{Ar}), 172.5 (*C*OOCH$_3$) ppm. IR (ATR): ṽ = 2958 (w), 2924 (w), 1651 (s), 1595 (m), 1432 (s), 1351 (m), 1312 (s), 1203 (s), 1094 (m), 952 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 368 (1) [M]$^+$ (^{35}Cl, ^{37}Cl), 366 (2) [M]$^+$ (^{35}Cl, ^{35}Cl), 330 (3), 207 (53), 175 (100). HRMS (EI): calcd. for $C_{19}H_{20}Cl_2O_3$ [M]$^+$ (^{35}Cl) 366.07927; found 366.07840. $C_{19}H_{20}Cl_2O_3$ (366.08): calcd. C 62.14, H 5.49; found C 61.87, H 5.48.

Methyl 5-[2-Chloro-2-(3-chlorophenyl)ethyl]-3-ethyl-4,6-dimethylsalicylate (8v): Starting with **7f** (0.150 g, 0.63 mmol), **2f** (0.311 g,

1.08 mmol) and $TiCl_4$ (0.14 mL, 1.27 mmol), **8v** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless oil (0.080 g, 33%); R_f = 0.74 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3CH$_2$), 2.11, 2.35 (s, 3 H, CH_3), 2.59–2.77 (m, ^3J = 7.5 Hz, 2 H, CH$_3$CH_2), 3.28 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hx,Ha}$ = 7.4 Hz, 1 H, H_a), 3.53 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hb,Hx}$ = 7.1 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.87 ("t", $^3J_{Hx,Ha}$ = 7.4, $^3J_{Hx,Hb}$ = 7.1 Hz, 1 H, CHCl), 7.06–7.13 (m, 1 H, Ar), 7.16–7.29 (m, 2 H, Ar), 7.31–7.36 (m, 1 H, Ar), 10.87 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.2, 16.5, 19.1 (CH_3), 19.9 (CH$_3$CH_2), 40.4 (CH_2CHCl), 52.1 (OCH_3), 62.4 (CHCl), 111.6, 126.4, 129.1, 134.3, 136.0, 142.1, 143.1, 152.0 (C_{Ar}), 125.2, 127.2, 128.3, 129.6 (CH_{Ar}), 172.5 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2953 (w), 2872 (w), 1653 (s), 1573 (m), 1435 (m), 1348 (m), 1316 (m), 1268 (s), 1201 (s), 1034 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 382 (1) $[M]^+$ (^{35}Cl, ^{37}Cl), 380 (2) $[M]^+$ (^{35}Cl, ^{35}Cl), 312 (7), 221 (83), 189 (100). HRMS (EI): calcd. for $C_{20}H_{22}Cl_2O_3$ $[M]^+$ (^{35}Cl) 380.09446; found 380.09405. $C_{20}H_{22}Cl_2O_3$ (380.09): calcd. C 63.00, H 5.82; found C 62.79, H 5.33.

Methyl 5-[2-Chloro-2-(2-chlorophenyl)ethyl]-4,6-dimethylsalicylate (8w): Starting with **7g** (0.165 g, 0.70 mmol), **2a** (0.272 g, 1.05 mmol) and $TiCl_4$ (0.15 mL, 1.39 mmol), **8w** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.037 g, 15%); m.p. 119–120 °C; R_f = 0.71 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.26, 2.49 (s, 3 H, CH_3), 3.27 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 6.3 Hz, 1 H, H_a), 3.47 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 8.5 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 5.60 (dd, $^3J_{Hx,Ha}$ = 6.3, $^3J_{Hx,Hb}$ = 8.5 Hz, 1 H, CHCl), 6.67 (s, 1 H, Ar), 7.17–7.40 (m, 3 H, Ar), 7.74–7.82 (m, 1 H, Ar), 10.87 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2, 21.6 (CH_3), 38.9 (CH_2CHCl), 52.1 (OCH_3), 58.6 (CHCl), 111.9, 126.6, 132.4, 139.1, 139.7, 145.0, 160.3 (C_{Ar}), 117.2, 127.4, 129.2, 129.4, 129.4 (CH_{Ar}), 172.0 (*C*O-OCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2961 (w), 2928 (w), 1665 (m), 1566 (m), 1438 (m), 1315 (m), 1260 (m), 1190 (m), 1070 (m), 911 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 354 (2) $[M]^+$ (^{35}Cl, ^{37}Cl), 352 (3) $[M]^+$ (^{35}Cl, ^{35}Cl), 193 (99), 161 (100). HRMS (EI): calcd. for $C_{18}H_{18}Cl_2O_3$ $[M]^+$ (^{35}Cl, ^{35}Cl) 352.06306; found 352.06275.

Methyl 5-[2-Chloro-2-(2-chlorophenyl)ethyl]-3,4,6-trimethylsalicylate (8x): Starting with **7g** (0.175 g, 0.74 mmol), **2c** (0.304 g, 1.11 mmol) and $TiCl_4$ (0.16 mL, 1.48 mmol), **8x** was isolated by chromatography (heptane/EtOAc, 100:1) as a colourless solid (0.038 g, 14%); m.p. 132–133 °C; R_f = 0.65 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.17, 2.25, 2.45 (s, 3 H, CH_3), 3.32 (dd, $^2J_{Ha,Hb}$ = 15.1, $^3J_{Ha,Hx}$ = 6.1 Hz, 1 H, H_a), 3.56 (dd, $^2J_{Ha,Hb}$ = 15.1, $^3J_{Hb,Hx}$ = 8.6 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 5.58 (dd, $^3J_{Hx,Ha}$ = 6.1, $^3J_{Hx,Hb}$ = 8.6 Hz, 1 H, CHCl), 7.177.40 (m, 3 H, Ar), 7.73–7.82 (m, 1 H, Ar), 10.91 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 17.6, 19.3 (CH_3), 39.1 (CH_2CHCl), 52.1 (OCH_3), 59.0 (CHCl), 111.4, 122.8, 126.1, 132.4, 136.2, 139.2, 143.1, 158.2 (C_{Ar}), 127.4, 129.3, 129.3, 129.5 (CH_{Ar}), 172.6 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2961 (w), 1660 (m), 1658 (s), 1587 (w), 1435 (m), 1375 (w), 1310 (m), 1257 (s), 1092 (s), 1009 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 368 (1) $[M]^+$ (^{35}Cl, ^{37}Cl), 366 (2) $[M]^+$ (^{35}Cl, ^{35}Cl), 298 (7), 207 (52), 175 (100). HRMS (EI): calcd. for $C_{19}H_{20}Cl_2O_3$ $[M]^+$ (^{35}Cl, ^{35}Cl) 366.07917; found 366.07840.

Methyl 5-[2-(2-Chlorophenyl)-2-hydroxyethyl]-4,6-dimethylsalicylate (9a): Starting with **7g** (0.165 g, 0.70 mmol), **2a** (0.272 g, 1.05 mmol) and $TiCl_4$ (0.15 mL, 1.39 mmol), **9a** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.085 g, 36%); m.p. 116–117 °C; R_f = 0.53 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.82 (br. s, 1 H, OH), 2.37, 2.58 (s, 3 H, CH_3), 2.98 (dd, $^2J_{Ha,Hb}$ = 14.6, $^3J_{Ha,Hx}$ = 9.5 Hz, 1 H, H_a), 3.10 (dd, $^2J_{Ha,Hb}$ = 14.6, $^3J_{Hb,Hx}$ = 4.5 Hz, 1 H, H_b), 3.95 (s, 3 H, OCH_3), 5.29 (dd, $^3J_{Hx,Ha}$ = 9.5, $^3J_{Hx,Hb}$ = 4.5 Hz, 1 H, CHCl), 6.72 (s, 1 H, Ar), 7.16–7.40 (m, 3 H, Ar), 7.65–7.77 (m, 1 H, Ar), 10.62 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2, 21.8 (CH_3), 37.3 (CH_2CHOH), 52.1 (OCH_3), 70.3 (CHOH), 112.0, 126.9, 131.6, 140.0, 141.8, 145.6, 160.0 (C_{Ar}), 117.2, 127.2, 127.3, 128.6, 129.3 (CH_{Ar}), 172.0 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3479 (w), 2956 (w), 1657 (m), 1573 (m), 1440 (m), 1348 (m), 1306 (m), 1236 (m), 1209 (s), 1028 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 334 (1) $[M]^+$ (^{35}Cl), 194 (41), 161 (100). HRMS (EI): calcd. for $C_{18}H_{19}ClO_4$ $[M]^+$ (^{35}Cl) 334.09680; found 334.09664.

Methyl 5-[2-(2-Chlorophenyl)-2-hydroxyethyl]-3,4,6-trimethylsalicylate (9b): Starting with **7g** (0.175 g, 0.74 mmol), **2c** (0.304 g, 1.11 mmol) and $TiCl_4$ (0.16 mL, 1.48 mmol), **9b** was isolated by chromatography (heptane/EtOAc, 100:1) as a colourless solid (0.120 g, 47%); m.p. 86–88 °C; R_f = 0.50 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 1 H, OH), 2.21, 2.36, 2.55 (s, 3 H, CH_3), 3.05 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Ha,Hx}$ = 9.5 Hz, 1 H, H_a), 3.15 (dd, $^2J_{Ha,Hb}$ = 14.8, $^3J_{Hb,Hx}$ = 4.6 Hz, 1 H, H_b), 3.95 (s, 3 H, OCH_3), 5.28 (dd, $^3J_{Hx,Ha}$ = 9.5, $^3J_{Hx,Hb}$ = 4.6 Hz, 1 H, C*H*OH), 7.17–7.39 (m, 3 H, Ar), 7.66–7.76 (m, 1 H, Ar), 10.82 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 17.6, 19.3 (CH_3), 37.5 (CH_2CHOH), 52.1 (OCH_3), 70.5 (CHOH), 111.6, 122.9, 126.3, 131.6, 136.5, 141.9, 143.7, 157.9 (C_{Ar}), 127.2, 127.3, 128.5, 129.3 (CH_{Ar}), 172.6 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2952 (w), 2925 (w), 1593 (br. m), 1438 (m), 1381 (m), 1358 (m), 1211 (m), 1222 (s), 1030 (m), 753 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 350 (2) $[M]^+$ (^{37}Cl), 348 (5) $[M]^+$ (^{35}Cl), 317 (6), 207 (90), 175 (100). HRMS (EI): calcd. for $C_{19}H_{21}ClO_4$ $[M]^+$ (^{35}Cl) 348.11224; found 348.11229. $C_{19}H_{21}ClO_4$ (348.11): calcd. C 65.42, H 6.07; found C 65.34, H 6.11.

Methyl 5-[2-(2,6-Dichlorophenyl)-2-hydroxyethyl]-4,6-diethylsalicylate (9c): Starting with **7h** (0.152 g, 0.56 mmol), **2a** (0.219 g, 0.84 mmol) and $TiCl_4$ (0.12 mL, 1.12 mmol), **9c** was isolated by chromatography (heptane/EtOAc, 100:1) as a colourless solid (0.102 g, 49%); m.p. 149–150 °C; R_f = 0.29 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.29, 2.51 (s, 3 H, CH_3), 3.19 (dd, $^2J_{Ha,Hb}$ = 14.5, $^3J_{Ha,Hx}$ = 6.5 Hz, 1 H, H_a), 3.53 (dd, $^2J_{Ha,Hb}$ = 14.5, $^3J_{Hb,Hx}$ = 8.2 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 5.55 (dd, $^3J_{Hx,Ha}$ = 6.5, $^3J_{Hx,Hb}$ = 8.2 Hz, 1 H, CHCl), 6.67 (s, 1 H, Ar), 7.09–7.18 (m, 1 H, Ar), 7.23–7.32 (m, 2 H, Ar), 10.63 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.2, 21.6 (CH_3), 34.6 (CH_2CHOH), 52.1 (OCH_3), 71.9 (CHOH), 111.9, 126.7, 134.5, 137.2, 139.8, 145.2, 160.0 (C_{Ar}), 117.1, 129.1, 129.4 (CH_{Ar}), 172.0 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3500 (w), 2921 (w), 1651 (s), 1573 (m), 1433 (s), 1352 (s), 1241 (s), 1194 (m), 1072 (s), 767 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 370 (4) $[M]^+$ (^{35}Cl, ^{37}Cl), 368 (7) $[M]^+$ (^{35}Cl, ^{35}Cl), 337 (13), 194 (100), 162 (81). HRMS (EI): calcd. for $C_{18}H_{18}Cl_2O_4$ $[M]^+$ (^{35}Cl, ^{35}Cl) 368.05825; found 368.05767. $C_{18}H_{18}Cl_2O_4$ (368.06): calcd. C 58.55, H 4.91; found C 58.52, H 5.24.

Methyl 5-(2-Chloro-2-phenylethyl)-4,6-diethylsalicylate (8y): Starting with **7i** (0.165 g, 0.72 mmol), **2a** (0.280 g, 1.08 mmol) and $TiCl_4$ (0.16 mL, 1.43 mmol), **8y** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.096 g, 39%); m.p. 72–73 °C; R_f = 0.60 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.3 Hz, 3 H, CH_3CH$_2$), 1.12 (t, ^3J = 7.5 Hz, 3 H, CH_3CH$_2$), 2.34–2.58 (m, 2 H, CH$_3$CH_2), 2.72–3.03 (m, 2 H, CH$_3$CH_2), 3.25 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Ha,Hx}$ = 7.3 Hz, 1 H, H_a), 3.48 (dd, $^2J_{Ha,Hb}$ = 14.9, $^3J_{Hb,Hx}$ = 7.2 Hz, 1 H, H_b), 3.94 (s, 3 H, OCH_3), 4.94 ("t", $^3J_{Hx,Ha}$ = 7.3, $^3J_{Hx,Hb}$ = 7.2 Hz, 1 H,

CHCl), 6.70 (s, 1 H, Ar), 7.29 (s, 5 H, Ar), 10.58 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.5, 15.8 (CH_3), 24.1, 26.5, 38.8 (CH_2), 52.2 (OCH_3), 64.2 (CHCl), 111.1, 125.7, 141.1, 145.8, 150.9, 160.4 ($C_{Ph/Ar}$), 115.5, 126.9, 128.3, 128.4 ($CH_{Ph/Ar}$), 171.7 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2965 (w), 2872 (w), 1658 (s), 1572 (m), 1435 (m), 1346 (m), 1309 (m), 1242 (s), 1206 (s), 1081 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 348 (1) $[M]^+$ (^{37}Cl), 346 (3) $[M]^+$ (^{35}Cl), 278 (100), 221 (69), 189 (83). HRMS (EI): calcd. for $C_{20}H_{23}ClO_3$ $[M]^+$ (^{35}Cl) 346.13247; found 346.13302. $C_{20}H_{23}ClO_3$ (346.13): calcd. C 69.26, H 6.68; found C 68.73, H 6.46.

Methyl 5-(2-Chloro-2-phenylethyl)-4,6-diethyl-3-methylsalicylate (8z): Starting with **7i** (0.165 g, 0.72 mmol), **2c** (0.295 g, 1.08 mmol) and $TiCl_4$ (0.16 mL, 1.43 mmol), **8z** was isolated by chromatography (heptane/EtOAc, 100:1) as a yellow solid (0.180 g, 70%); m.p. 83–84 °C; R_f = 0.71 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 1.07 (t, ^3J = 7.3 Hz, 3 H, CH_3CH_2), 2.36–2.99 (m, 4 H, CH_3CH_2), 3.10 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Ha,Hx}$ = 7.1 Hz, 1 H, H_a), 3.49 (dd, $^2J_{Ha,Hb}$ = 15.0, $^3J_{Hb,Hx}$ = 7.3 Hz, 1 H, H_b), 3.93 (s, 3 H, OCH_3), 4.95 ("t", $^3J_{Hx,Ha}$ = 7.1, $^3J_{Hx,Hb}$ = 7.3 Hz, 1 H, CHCl), 7.30 (s, 5 H, Ar), 10.81 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.7, 13.9, 15.9 (CH_3), 23.5, 24.1, 39.1 (CH_2), 52.2 (OCH_3), 64.7 (CHCl), 110.8, 122.5, 125.0, 141.2, 142.7, 149.0, 158.5 ($C_{Ph/Ar}$), 126.9, 128.2, 128.4 (CH_{Ph}), 172.3 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2948 (w), 2871 (w), 1651 (s), 1597 (m), 1434 (m), 1405 (m), 1308 (s), 1201 (s), 1173 (s), 952 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 360 (2) $[M]^+$ (^{35}Cl), 292 (25), 235 (49), 203 (100), 175 (7). HRMS (EI): calcd. for $C_{21}H_{25}ClO_3$ $[M]^+$ (^{35}Cl) 360.14902; found 360.14876. $C_{21}H_{25}ClO_3$ (360.15): calcd. C 69.89, H 6.98; found C 69.82, H 7.24.

Methyl 6-[(*E*)-2-(4-Bromophenyl)vinyl]-5,7-dimethylchromane-8-carboxylate (10b): To a DMF solution (20 mL per 1 mmol of **8p**) of **8p** (1.0 equiv.) was added TBAI (2.2 equiv.) under argon. The mixture was cooled to –78 °C and NaH (60% dispersion in mineral oil, 1.5 equiv.) was added at 0 °C. After stirring for 20 h at 20 °C, ethyl acetate (5 mL) and ice-cold water (5 mL) were added and the mixture was subsequently neutralized by addition of hydrochloric acid (10%). The mixture was extracted with EtOAc (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. Starting with **8p** (0.050 g, 0.11 mmol), sodium hydride (0.013 g, 0.32 mmol) and TBAI (0.140 g, 0.38 mmol), **10b** was isolated by chromatography (heptane/EtOAc, 50:1) as a colourless solid (0.032 g, 76%); m.p. 145–147 °C; R_f = 0.75 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99–2.09 (m, ^3J = 6.6 Hz, 2 H, CH_2), 2.18 (br. s, 6 H, 2 CH_3), 2.64 (t, ^3J = 6.6 Hz, 2 H, CH_2), 3.89 (s, 3 H, OCH_3), 4.10–4.18 (m, 2 H, CH_2), 6.36 (d, ^3J = 16.6 Hz, 1 H, CH), 7.00 (d, ^3J = 16.6 Hz, 1 H, CH), 7.29–7.38 (m, ^3J = 8.4 Hz, 2 H, Ar), 7.42–7.52 (m, ^3J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.6, 17.7 (CH_3), 22.3, 23.0, 66.1 (CH_2), 52.1 (OCH_3), 119.1, 121.3, 121.6, 129.6, 131.3, 136.3, 136.9, 150.6 (C_{Ar}), 127.7, 131.7 (CH_{Ar}), 127.7, 133.4 (CH_{Olefin}), 169.4 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2947 (w), 2872 (w), 1728 (s), 1574 (m), 1486 (m), 1436 (m), 1274 (s), 1191 (m), 1114 (s), 937 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 402 (99) $[M]^+$ (^{81}Br), 400 (100) $[M]^+$ (^{79}Br), 369 (25), 342 (39), 306 (36). HRMS (EI): calcd. for $C_{23}H_{19}BrO_3$ $[M]^+$ (^{79}Br) 400.06686; found 400.06657.

Methyl 4,6-Dimethyl-5-[(*E*)-styryl]salicylate (10a): Heating of neat **8a** (0.045 g, 0.14 mmol) at 150 °C for 3 h afforded **10a**, which was isolated by chromatography (heptane/EtOAc, 150:1) as a colourless oil (0.24 g, 60%, *E*/*Z* = 11:1); R_f = 0.73 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30, 2.53 (s, 3 H, CH_3), 3.96 (s, 3 H, OCH_3), 6.46 (d, $^3J_{trans}$ = 16.6 Hz, 1 H, CH_{Olefin}), 6.76 (s, 1 H, Ar), 7.00 (d, $^3J_{trans}$ = 16.6 Hz, 1 H, CH_{Olefin}), 7.23–7.43 (m, 3 H, Ph), 7.45–7.55 (m, 2 H, Ph), 10.91 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.6, 21.8 (CH_3), 52.1 (OCH_3), 111.2, 130.6, 137.3, 138.7, 144.1, 160.6 ($C_{Ph,Ar}$), 116.6, 126.2, 127.6, 128.7 ($CH_{Ph,Ar}$), 126.8, 134.8 (CH_{Olefin}), 172.1 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3024 (w), 2952 (w), 1657 (s), 1571 (m), 1438 (m), 1348 (m), 1310 (m), 1216 (s), 1156 (m), 1073 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 282 (58) $[M]^+$, 250 (100), 235 (37), 178 (29). HRMS (EI): calcd. for $C_{18}H_{18}O_3$ $[M]^+$ 282.12537; found 282.12505. $C_{18}H_{18}O_3$ (282.13): calcd. C 76.57, H 6.43; found C 76.67, H 6.45.

Acknowledgments

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After publication in Early View, erroneous Scheme 3 was replaced by the correct version.

