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Synthesis of functionalized 2-alkoxybenzoates, 2-aryloxybenzoates and xanthones based on formal [3+3] cyclocondensations of 3-alkoxy- and 3-aryloxy-1-silyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones

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ABSTRACT

Functionalized 2-alkoxy- and 2-aryloxybenzoates were prepared by formal [3+3] cyclocondensations of 3-alkoxy- and 3-aryloxy-1-silyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones. The reaction of 2-aryloxybenzoates with concentrated sulfuric acid resulted in the formation of xanthones.

1. Introduction

Diaryl ethers occur in a great variety of pharmacologically important natural products. 2-Aryloxybenzoates, which can be regarded as diaryl ethers containing an ester or carboxylic acid function next to the ether linkage, constitute an important subgroup of naturally occurring diaryl ethers. Important examples include, for example, geodinhydrate methylester and methyl chloroasterrate,[1] 1-desgalloylsanguiin,[2] dehydrotrigallic acid,[3] epiphorellic acid,[4] jolkianin,[5] remurin A[6] and micareic acid.[7]

2-Aryloxybenzoates can be transformed, by treatment with acid, Lewis acid or other reagents, into xanthones.[8] Xanthones are widespread in nature[9] and represent very important lead structures in medicinal and agricultural chemistry. This includes, for example, the inhibition of baker's yeast glucosidase,[10] anticancer activity,[11] antifungal activity,[12] mitogenic activity,[13] antibacterial activity (including activity against multiresistant strains),[14] antioxidant activity,[15] protein binding activity,[16] inhibition of monoamine oxidase-B,[17] hepatoprotective activity,[18] cyctotoxic activity,[19] antihypotensive activity,[20] antiprotozoal activity,[21] or inhibition of sphingomyelinase.[22]

Diaryl ethers are available by the Ullmann reaction[23] and by various related transition metal-catalyzed C–O coupling reactions.[24] Despite their great synthetic usefulness, these methods often give unsatisfactory results for sterically encumbered or functionalized substrates. In addition, the synthesis of the required starting materials, functionalized aryl halides, can be a very difficult task, due to the poor regioselectivity of electrophilic aromatic substitutions (e.g., halogenation) or other drawbacks (such as the low reactivity of electron-poor arenes in electrophilic substitutions).

An alternative approach for the synthesis of diaryl ethers relies on the use appropriate building blocks in cyclocondensation reactions. Some years ago, Chan and co-workers reported[25] the synthesis of salicylates based on the cyclization of 1,3-bis(silyloxy)-1,3-butadienes[26] with 3-silyloxy-2-en-1-ones. In recent years, we have reported the application of this methodology to the synthesis of a variety of functionalized arenes.[27] Recently, we have reported the first formal [3+3] cyclocondensations of 3-alkoxy- and 3-aryloxy-1-silyloxy-1,3-butadienes with 3-silyloxy-2-en-1-ones.[28] Herein, we report full details of these studies and its application to the synthesis of xanthones. In contrast to the transition metal-catalyzed C–O coupling reactions outlined above, our method relies on the assembly of one of the two arene moieties with formation of two C–C bonds.

2. Results and discussion

3-Alkoxy-1-silyloxy-1,3-butadienes **1a–c** were prepared by phosphorus(V)chloride mediated chlorination of the respective β-ketoester, substitution of the chloride by an alkoxy group and subsequent silylation.[29] The $TiCl_4$-mediated cyclocondensation of 1,3-dimethoxy-1-trimethylsilyloxy-1,3-butadiene (**1a**, Brassard's diene) with 3-silyloxy-2-en-1-one **2a**, readily available from 3-methylacetylacetone,[25] afforded 2-methoxybenzoate **3a** (Scheme 1). The formation of **3a** might be explained as follows: The reaction of **2a** with $TiCl_4$ gave the allylic cation **A**. The attack of the terminal carbon atom of **1a** onto **A** afforded intermediate **B**. Cleavage of TMS-siloxane gave intermediate **C**, which underwent a $TiCl_4$-mediated cyclization to give intermediate **D**. Elimination and aromatization, before or

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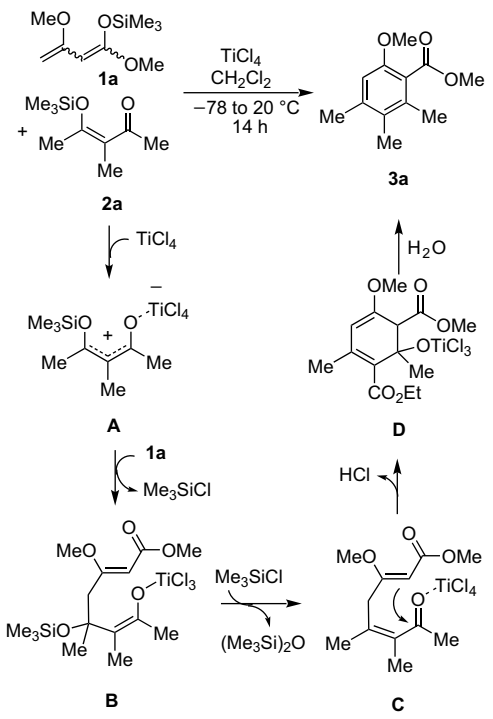
during the aqueous work-up, resulted in the formation of the final product **3a**.



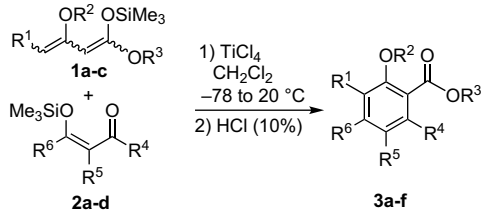
Scheme 1. Possible mechanism of the formation of **3a**.

During the optimization, the stoichiometry (**1a**/**2a**/$TiCl_4$=1:1:1), the concentration (c=0.2 M) and the temperature (−78 °C, warming during 14 h) were crucial parameters. Methyl 2-hydroxy-4,5,6-trimethylbenzoate was formed as a side-product by hydrolysis. This result suggests that the aromatization (transformation of **D** into **3a**) occurred during and not before the aqueous work-up. Due to its acidity, the unwanted side-product could be removed by washing the reaction mixture with an aqueous solution of sodium hydroxide. Therefore, the work-up procedure proved to be very important during the optimization of the reaction.

The $TiCl_4$-mediated cyclocondensation of **1a–c** with **2a–d** afforded 2-alkoxybenzoates **3a–f** (Scheme 2, Table 1). Products **3e** and **3f** were formed with very good regioselectivity.

The $TiCl_4$-mediated cyclization of 1,1,3,3-tetramethoxypropane (**4**) with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (Chan's diene) has been previously reported to give methyl salicylate.[25] The $TiCl_4$-mediated cyclocondensation of **4** with **1a** afforded the expected methyl 2-methoxybenzoate (**3g**), albeit, in only 25% yield (Scheme 3). Recently, the Me_3SiOTf-catalyzed cyclization of **4** with Chan's diene has been reported to give **3g**.[30] However, all attempts to induce a Me_3SiOTf-catalyzed cyclization of **4** with **1a** failed.

The structures of all products **3** were elucidated by spectroscopic methods. The structure of **3f** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[31] The structure of **3e** was independently confirmed as follows: Treatment of **3e** with

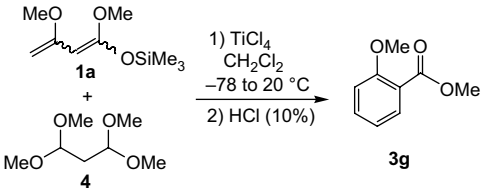


Scheme 2. Synthesis of **3a–f**.

Table 1
Synthesis of **3a–f**

1	2	3	R^1	R^2	R^3	R^4	R^5	R^6	% (**3**)[a]
a	**a**	**a**	H	Me	Me	Me	Me	Me	40
b	**b**	**b**	H	Et	Et	Me	H	Me	48
b	**a**	**c**	H	Et	Et	Me	Me	Me	34
c	**a**	**d**	Et	Et	Et	Me	Me	Me	36[b]
a	**c**	**e**	H	Me	Me	Ph	H	Me	43
a	**d**	**f**	H	Me	Me	$-(CH_2)_4-$		Me	28

[a] Yields of isolated products.
[b] A small amount of ethyl 3-ethyl-4,5,6-trimethylsalicylate could not be separated.



Scheme 3. Synthesis of **3g**.

concentrated sulfuric acid, following conditions earlier reported by us,[32] resulted in the formation of the novel fluorenone **5** in 90% yield (Scheme 4). This result indicates that the phenyl group of **3e** is located on the same site as the ester group. The structure of **5** was unambiguously confirmed by X-ray crystal structure analysis (Fig. 2).[31]

Some years ago, we have reported the synthesis of 5-(chloroethyl)salicylates by cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 1,1-diacetylcyclopropane.[33] Unfortunately, all attempts to induce a cyclization of 1,1-diacetylcyclopropane with **1a** failed.

1-Aryloxy-3-siloxy-1,3-butadienes **6a–e** were prepared in three steps: The reaction of the parent β-ketoesters with phosphorus(V)chloride afforded the corresponding 3-chlorocrotonates, which were transformed, by reaction with various phenols, into 3-(aryloxy)crotonates. Deprotonation (by means of LDA) and subsequent silylation afforded **6a–e**. The $TiCl_4$-mediated formal [3+3] cyclocondensation of **6a–e** with 3-silyloxy-2-en-1-ones **2a–c**,**e**,**f** afforded the 2-aryloxybenzoates **7a–k** (Scheme 5).

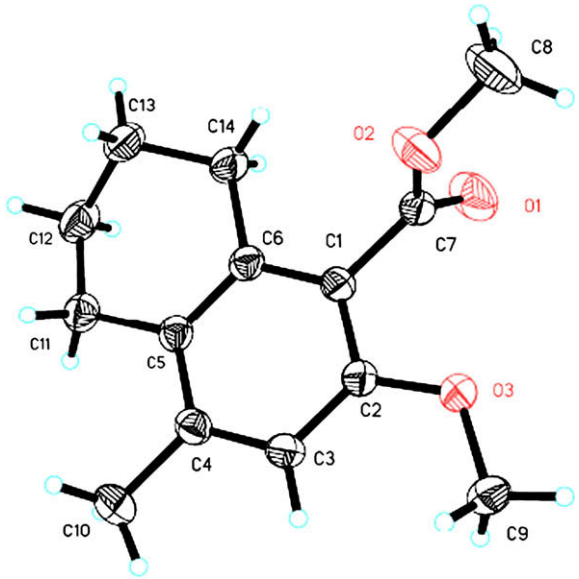
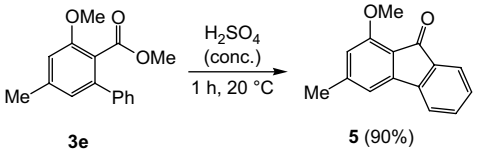


Figure 1. ORTEP plot of **3f** (50% probability level).



Scheme 4. Synthesis of **5**.

The best yields were obtained in the reactions of the alkyl-substituted 3-silyloxy-2-en-1-ones **2a**,**b**. In general, the purification of 2-aryloxybenzoates **7** was considerably more difficult than the purification of 2-alkoxybenzoates **3**, because significant amounts of salicylate side-products were formed. This can be explained by the better leaving group ability of phenols compared to aliphatic alcohols. Therefore, the intermediates formed during the synthesis of **7** are more prone towards hydrolysis than those leading to products **3**. Therefore, the (isolated) yields of products **7** were, in some cases, relatively low. The best yield was obtained for **7a**. The lowest yields were observed for products

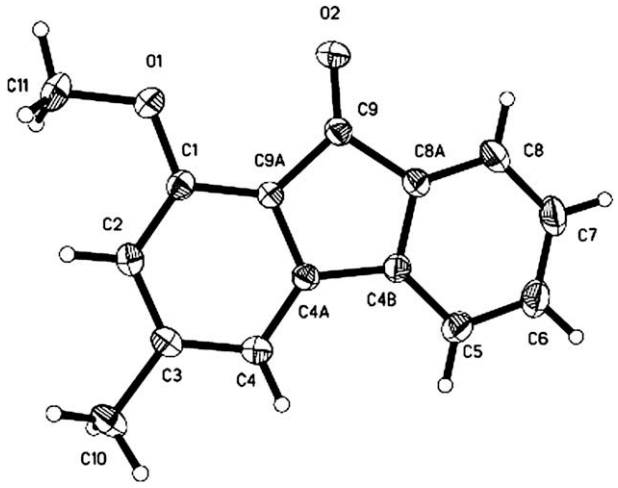


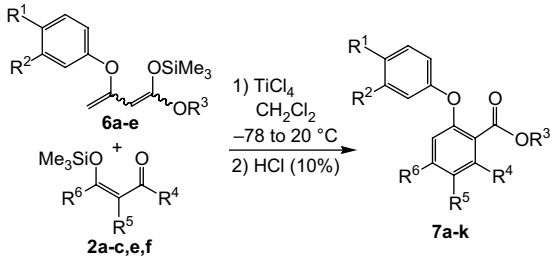
Figure 2. ORTEP plot of **5** (50% probability level).

7i–**k** containing a methoxy group located in *para* position of the aryloxy moiety (Table 2).

Treatment of diaryl ethers **7a**–**c** and **7e**–**g** with concentrated sulfuric acid afforded the xanthones **8a**–**f** in excellent yields (Scheme 6, Table 3). During the optimization, the reaction time proved to be an important parameter (TLC control).

The structures of xanthones **8b** and **8c** were independently confirmed by X-ray crystal structure analysis (Figs. 3 and 4).[31]

In case of the formation of products **8c** and **8e** it becomes apparent that the formation of the xanthones is favoured over the

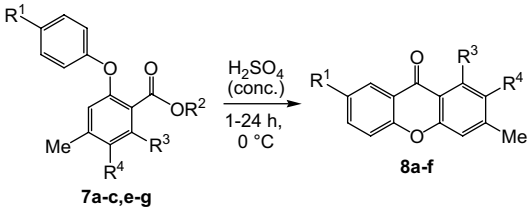


Scheme 5. Synthesis of **7a**–**k**.

Table 2
Synthesis of **7a**–**k**

2	6	7	R^1	R^2	R^3	R^4	R^5	R^6	% (**7**)[a]
b	**a**	**a**	H	H	Et	Me	H	Me	63
a	**a**	**b**	H	H	Et	Me	Me	Me	44
c	**a**	**c**	H	H	Et	Ph	H	Me	37[b]
e	**b**	**d**	H	Me	Me	Me	Cl	Me	20
a	**c**	**e**	Me	H	Me	Me	Me	Me	56
c	**c**	**f**	Me	H	Me	Ph	H	Me	22
a	**d**	**g**	Cl	H	Me	Me	Me	Me	47
c	**d**	**h**	Cl	H	Me	Ph	H	Me	30
b	**e**	**i**	OMe	H	Me	Et	H	Et	15
a	**e**	**j**	OMe	H	Me	Me	Me	Me	20
f	**e**	**k**	OMe	H	Me	Me	OAr[c]	Me	20

[a] Yields of isolated products.
[b] A small amount of ethyl 4-methyl-6-phenylsalicylate could not be separated.
[c] Ar=4-EtC_6H_4.



Scheme 6. Synthesis of xanthones **8a**–**f**.

Table 3
Synthesis of **8a**–**f**

7	8	R^1	R^3	R^4	% (**8**)[a]
a	**a**	H	Me	H	95
b	**b**	H	Me	Me	83
c	**c**	H	Ph	H	88
e	**d**	Me	Me	Me	95
f	**e**	Me	Ph	H	93
g	**f**	Cl	Me	Me	96

[a] Yields of isolated products.

(theoretically also possible) formation of the isomeric fluorenones (Scheme 7). This can be explained by thermodynamic effects.

In conclusion, functionalized 2-alkoxy- and 2-aryloxybenzoates were prepared by formal [3+3] cyclocondensations of 3-alkoxy- and 3-aryloxy-1-silyloxy-1,3-butadienes with 3-silyloxy-2-en-1-

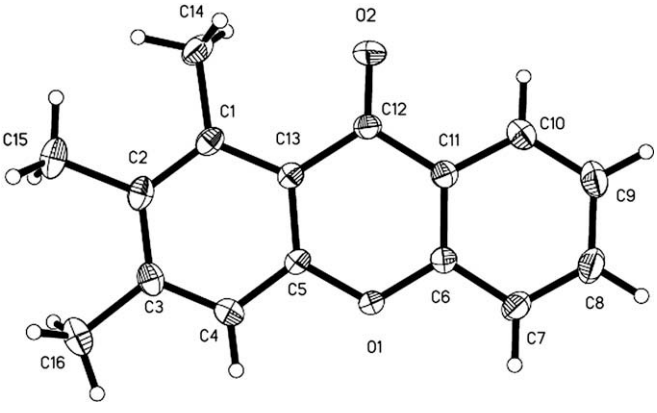


Figure 3. ORTEP plot of **8b** (50% probability level).

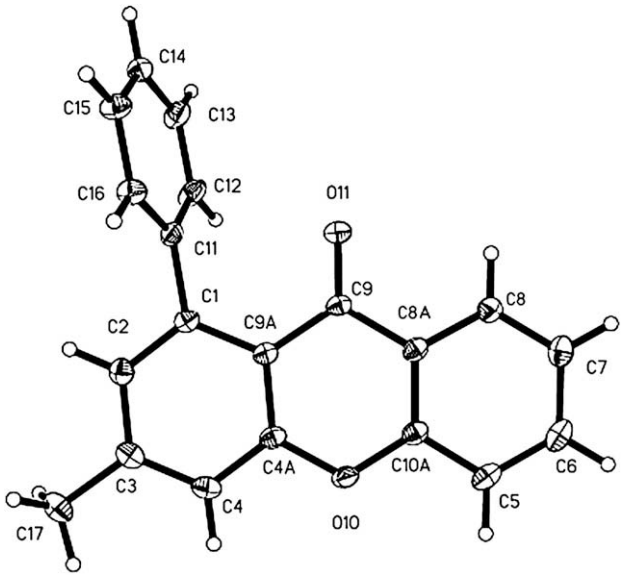
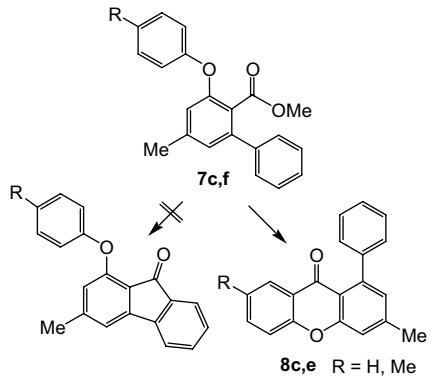


Figure 4. Synthesis of **8c** (50% probability level).



Scheme 7. Selective formation of xanthones **8c**,**e** at the expense of isomeric fluorenones.

ones. The reaction of 2-aryloxybenzoates with concentrated sulfuric acid resulted in the formation of xanthones.

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 ^{1}H 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, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

3.2. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H 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.

3.3. Typical procedure for the synthesis of arylalkyl and diaryl ethers 3a–g and 7a–k

To a dichloromethane solution (9 mL) of **2** or **4** (2.0 mmol) and of **1** or **6** (2.0 mmol) was added a dichloromethane solution (1 mL) of $TiCl_4$ (0.23 mL, 2.0 mmol) at −78 °C. The solution was allowed to warm to ambient temperature within 14 h. To the solution were added dichloromethane (25 mL) and hydrochloric acid (10%, 30 mL). The organic and the aqueous layer were separated and the latter was extracted with dichloromethane (3×15 mL). The combined organic layers were washed four times with an aqueous solution of sodium hydroxide (2 M), dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, EtOAc/heptanes=1:20, column length=30 cm, diameter=4 cm).

*3.3.1. Methyl 6-methoxy-2,3,4-trimethylbenzoate (**3a**)*

Starting with **2a** (0.186 g, 1.0 mmol) and **1a** (0.202 g, 1.00 mmol) in CH_2Cl_2 (5 mL), **3a** was isolated as a colourless oil (0.092 g, 44%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.11 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.60 (s, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.7, 17.2, 21.3 (CH_3), 52.1, 55.8 (OCH_3), 110.4 (CH, Ar), 122.1, 127.4, 134.0, 138.6, 153.6 (C, Ar), 169.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3435 (w), 2948 (m), 2838 (w), 1726 (s), 1598 (m), 1463 (m), 1432 (m), 1409 (m), 1312 (m), 1263 (s), 1228 (m), 1190 (m), 1154 (s), 1098 (s), 1076 (m), 1046 (s), 1005 (m). MS (EI, 70 eV): *m*/*z* (%)=208 (M^+, (56)), 177 (100), 176 (32), 119 (24), 118 (35), 91 (23). HRMS (EI): calcd for $C_{12}H_{16}O_3$ (M^+): 208.1094, found: 208.1088.

*3.3.2. Ethyl 2-ethoxy-4,6-dimethylbenzoate (**3b**)*

Starting with **2b** (0.344 g, 2.0 mmol) and **1b** (0.460 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **3b** was isolated as a colourless, viscous oil (0.650 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.36 (t, ^{3}J=7.1 Hz, 6H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.02 (q, ^{3}J=6.9 Hz, 2H, OCH_2CH_3), 4.37 (q, ^{3}J=7.1 Hz, 2H, OCH_2CH_3), 6.54 (s, 1H, Ar), 6.59 (s, 1H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.2, 14.6 (CH_3), 19.0, 21.5 (CH_2CH_3), 60.7, 64.1 (CH_2CH_3), 110.4, 121.5, 122.9 (CH, Ar), 136.0, 140.2, 155.8 (C, Ar), 168.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2980 (m), 2930 (w), 1727 (s), 1612 (m), 1581 (m), 1446 (m), 1393 (w), 1317 (s), 1267 (s), 1173 (s), 1115 (m), 1086 (s). MS (EI, 70 eV): *m*/*z* (%)=222 (M^+, (80)), 178 (12), 177 (74), 176 (57), 175 (16), 149 (51), 148 (100), 120 (26), 91 (26). HRMS (EI): calcd for $C_{13}H_{18}O_3$ (M^+): 222.1250, found: 222.1242.

*3.3.3. Ethyl 6-ethoxy-2,3,4-trimethylbenzoate (**3c**)*

Starting with **2a** (0.372 g, 2.0 mmol) and **1b** (0.460 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **3c** was isolated as a slightly yellow, viscous oil (0.160 g, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.34 (t, ^{3}J=6.9 Hz, 3H, OCH_2CH_3), 1.36 (t, ^{3}J=7.1 Hz, 3H, OCH_2CH_3), 2.09 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.01 (q, ^{3}J=6.9 Hz, 2H, OCH_2CH_3), 4.37 (q, ^{3}J=7.1 Hz, 2H, OCH_2CH_3), 6.58 (s, 1H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.3, 14.7, 14.8 (CH_3), 17.1, 21.2 (OCH_2CH_3), 60.8, 64.3 (OCH_2CH_3), 111.8, 122.2 (CH, Ar), 127.4, 133.8, 138.4, 153.0 (C, Ar), 169.2 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2979 (m), 2903 (w), 1728 (s), 1599 (m), 1472 (m), 1415 (w), 1393 (w), 1314 (s), 1265 (s), 1158 (s), 1116 (m), 1094 (s), 1048 (m), 1010 (w). MS (EI, 70 eV): *m*/*z* (%)=236 (M^+, (27)), 191 (42), 190 (25), 163 (33), 162 (100), 134 (31), 119 (24), 105 (16). HRMS (EI): calcd for $C_{14}H_{20}O_3$ (M^+): 236.1407, found: 236.1404.

*3.3.4. Ethyl 2-ethoxy-3-ethyl-4,5,6-trimethylbenzoate (**3d**)*

Starting with **2a** (0.372 g, 2.0 mmol) and **1c** (0.516 g, 2.00 mmol) in CH_2Cl_2 (5 mL), **3d** was isolated as a yellowish oil (0.093 g, 36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, ^{3}J=7.4 Hz, 3H, CH_2CH_3), 1.38 (tt, 6H, OCH_2CH_3), 2.14 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.23 (s, 3H,

CH_3), 3.90 (q, ^3J=7.0 Hz, 2H, CH_2CH_3), 4.38 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 4.41 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0, 14.6, 15.0 (CH_3), 16.5, 17.0 (OCH_2CH_3), 17.6 (CH_2CH_3), 61.4, 61.7 (OCH_2CH_3), 71.6 (CH_2CH_3), 112.3, 128.5, 131.1, 131.9, 133.9, 157.4 (C, Ar), 169.0 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2975 (s), 2932 (m), 2874 (m), 1727 (s), 1652 (m), 1598 (w), 1573 (w), 1445 (m), 1390 (m), 1373 (m), 1311 (m), 1273 (s), 1241 (w), 1189 (s), 1104 (m), 1036 (m). MS (EI, 70 eV): *m*/*z* (%)=264 (M^+, (47)), 236 (20), 219 (44), 218 (19), 191 (33), 190 (99), 189 (23), 176 (23), 175 (21), 163 (18), 162 (100), 148 (35), 147 (30). HRMS (EI): calcd for $C_{16}H_{24}O_3$ (M^+): 264.1720, found: 264.1721.

3.3.5. Methyl 5-methoxy-3-methylbiphenyl-4-carboxylate (**3e**)

Starting with **2c** (0.468 g, 2.0 mmol) and **1a** (0.404 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **3e** was isolated as a yellowish oil (0.220 g, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.40 (s, 3H, CH_3), 3.59 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.75 (s, 1H, CH, Ar), 6.80 (q, ^4J=0.7 Hz, 1H, CH, Ar), 7.31–7.38 (m, 5H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=21.8 (CH_3), 52.0, 56.0 (OCH_3), 110.7 (CH, Ar), 118.2 (C, Ar), 122.7, 127.7, 128.1, 128.2 (CH, Ar), 140.3, 140.8, 141.4, 156.0 (C, Ar), 169.2 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3058 (w), 3927 (w), 3001 (w), 2948 (m), 2840 (w), 1732 (s), 1606 (s), 1571 (s), 1498 (m), 1461 (s), 1429 (m), 1409 (m), 1334 (s), 1264 (s), 1188 (m), 1150 (s), 1089 (s), 1048 (s), 1028 (m). MS (EI, 70 eV): *m*/*z* (%)=256 (M^+, (33)), 226 (17), 225 (100), 210 (10), 182 (15), 180 (15), 165 (30), 153 (25), 152 (34). HRMS (EI): calcd for $C_{16}H_{16}O_3$ (M^+): 256.1094, found: 256.1092.

3.3.6. Methyl 3-methoxy-1-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylate (**3f**)

Starting with **2d** (0.424 g, 2.0 mmol) and **1a** (0.404 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **3f** was isolated (0.125 g, 28%) as a colourless solid, mp=49–51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.71–1.80 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.21 (s, 3H, CH_3), 2.55 (t, ^3J=6.0 Hz, 2H, $CH_2(CH_2)_2CH_2$), 2.66 (t, ^3J=6.0 Hz, 2H, $CH_2(CH_2)_2CH_2$), 3.78 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.60 (s, 1H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=20.1 (CH_3), 22.3, 22.8, 26.2, 27.1 (CH_2), 55.7, 55.8 (OCH_3), 110.5 (CH, Ar), 121.0, 127.9, 134.8, 139.0, 153.5 (C, Ar), 169.2 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3448 (br), 2944 (s), 2930 (s), 2861 (m), 2836 (w), 1735 (s), 1598 (s), 1585 (m), 1479 (m), 1466 (s), 1429 (m), 1335 (w), 1304 (s), 1255 (s), 1211 (m), 1194 (m), 1154 (s), 1095 (s), 1075 (m). MS (EI, 70 eV): *m*/*z* (%)=234 (M^+, (39)), 203 (35), 202 (100), 201 (16), 144 (11). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.56; H, 7.78.

3.3.7. Methyl 2-methoxybenzoate (**3g**)

Starting with **4** (0.164 g, 1.0 mmol) and **1a** (0.202 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **3g** was isolated as a colourless oil (0.045 g, 25%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.89 (s, 6H, OCH_3), 6.94–7.01 (m, 2H, CH, Ar), 7.43–7.50 (m, 1H, CH, Ar), 7.79 (dd, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=51.9, 55.9 (OCH_3), 112.0 (C, Ar), 120.1, 131.7, 133.5 (CH, Ar), 159.0 (C, Ar), 166.9 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3003 (w), 2951 (w), 2840 (w), 1728 (s), 1600 (m), 1583 (w), 1492 (m), 1436 (m), 1304 (m), 1254 (s), 1182 (w), 1130 (w), 1085 (m), 1023 (w). MS (EI, 70 eV): *m*/*z* (%)=166 (M^+, (33)), 135 (100), 133 (45), 105 (19). HRMS (EI): calcd for $C_9H_{10}O_3$ (M^+): 166.0624, found: 166.0627.

3.3.8. Ethyl 2,4-dimethyl-6-phenoxybenzoate (**7a**)

Starting with **2b** (0.344 g, 2.0 mmol) and **6a** (0.556 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **7a** was isolated as a yellowish oil (0.170 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.20 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.26 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 6.57 (s, 1H, CH, Ar), 6.80 (s, 1H, CH, Ar), 6.94–7.10 (m, 3H, CH, Ph), 7.27–7.33 (m, 2H, CH, Ph). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0 (OCH_2CH_3), 19.3, 21.2 (CH_3), 61.0 (OCH_2CH_3), 117.4, 118.3, 118.8, 122.9 (CH, Ar, Ph), 123.9 (C, Ar), 129.5 (CH, Ph), 137.1, 140.9, 157.2, 157.6 (C, Ar), 167.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3064 (w), 3039 (w), 2980 (w), 2925 (w), 2870 (w), 1728 (s), 1616 (m), 1590 (m), 1575 (m), 1489 (s), 1455 (m), 1412 (w), 1365 (w), 1303 (s), 1270 (s), 1216 (s), 1159 (m), 1068 (s). MS (EI, 70 eV): *m*/*z* (%)=270 (M^+, (88)), 225 (100), 223 (73), 181 (15), 170 (98), 169 (18), 149 (33), 148 (44), 142 (39), 141 (57). Anal. Calcd for $C_{17}H_{18}O_3$: C, 25.03; H, 6.76. Found: C, 25.08; H, 6.57.

3.3.9. Ethyl 2,3,4-trimethyl-6-phenoxybenzoate (**7b**)

Starting with **2a** (0.372 g, 2.0 mmol) and **6a** (0.556 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **7b** was isolated (0.252 g, 44%) as a yellowish solid, mp=136–139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.19 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 2.15 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.26 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 6.62 (s, 1H, CH, Ar), 6.94–7.07 (m, 3H, CH, Ph), 7.24–7.31 (m, 2H, CH, Ph). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0 (OCH_2CH_3), 15.1, 17.2, 20.9 (CH_3), 61.1 (OCH_2CH_3), 118.0, 118.6, 122.6 (CH, Ar, Ph), 126.4 (C, Ar), 129.4 (CH, Ph), 134.9, 139.1, 148.5, 151.4, 157.5 (C, Ar), 168.2 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3064 (w), 3039 (w), 2980 (w), 2930 (w), 2871 (w), 1728 (s), 1653 (w), 1589 (m), 1489 (s), 1470 (m), 1412 (m), 1386 (w), 1300 (s), 1268 (s), 1217 (s), 1154 (m), 1050 (s). MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, (95)), 240 (26), 239 (100), 238 (46), 237 (98), 224 (15), 223 (21), 195 (22), 163 (49), 162 (55). HRMS (EI): calcd for $C_{18}H_{20}O_3$ (M^+): 284.1407, found: 284.1400.

3.3.10. Ethyl 5-methyl-3-phenoxybiphenyl-2-carboxylate (**7c**)

Starting with **2c** (0.468 g, 2.0 mmol) and **6a** (0.556 g, 2.0 mmol) in CH_2Cl_2 (5 mL), **7c** was isolated as a yellowish oil (0.244 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 2.32 (s, 3H, CH_3), 4.03 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 6.72 (q, ^4J=0.7 Hz, 1H, CH, Ar), 6.96 (q, ^4J=0.7 Hz, 1H, CH, Ar), 7.04–7.14 (m, 3H, CH, Ph), 7.31–7.43 (m, 7H, CH, Ph). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0 (OCH_2CH_3), 21.8 (CH_3), 61.4 (OCH_2CH_3), 118.6, 119.3, 123.7, 125.9 (CH, Ar, Ph), 126.0 (C, Ar), 127.8, 128.6, 128.7, 130.0 (CH, Ph), 141.2, 142.2, 143.5, 154.7, 158.0 (C, Ar), 168.3 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3059 (w), 3031 (w), 2981 (w), 2926 (w), 2871 (w), 1731 (s), 1659 (w), 1610 (m), 1568 (m), 1490 (s), 1454 (m), 1408 (m), 1324 (w), 1264 (s), 1236 (m), 1214 (s), 1165 (m), 1129 (m), 1081 (s). MS (EI, 70 eV): *m*/*z* (%)=332 (M^+, (4)), 256 (24), 211 (17), 210 (100), 182 (38), 153 (13). HRMS (EI): calcd for $C_{22}H_{20}O_3$ (M^+): 332.1407, found: 332.1405.

3.3.11. Methyl 3-chloro-2,4-dimethyl-6-(3-tolyloxy)benzoate (**7d**)

Starting with **2e** (0.206 g, 1.0 mmol) and **6c** (0.278 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7d** was isolated as a colourless oil (0.060 g, 20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.30 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.62 (s, 1H, CH, Ar), 6.78 (d, ^3J=8.0 Hz, 2H, CH, Ar), 6.90 (d, ^3J=7.5 Hz, 1H, CH, Ar), 7.19 (dd, ^3J=7.6 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=13.0, 20.3, 20.8 (CH_3), 51.3 (OCH_3), 114.0, 117.5, 118.5, 123.4 (CH, Ar), 124.6 (C, Ar), 128.3 (CH, Ar), 128.4, 133.7, 137.9, 138.9, 151.0, 155.9 (C, Ar), 166.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2953 (w), 2924 (m), 2854 (w), 1736 (s), 1603 (w), 1568 (w), 1486 (m), 1451 (m), 1438 (m), 1393 (m), 1313 (m), 1259 (s), 1196 (m), 1149 (m), 1103 (s), 1053 (m), 1012 (m). MS (EI, 70 eV): *m*/*z* (%)=306 (M^+, ^{37}Cl, (34)), 304 (M^+, ^{35}Cl, (100)), 275 (20), 273 (80), 272 (17), 271 (63), 259 (27), 258 (14), 257 (81). HRMS (EI): calcd for $C_{17}H_{17}O_3Cl$ (M^+): 304.0860, found: 304.0868.

3.3.12. Methyl 2,3,4-trimethyl-6-(4-tolyloxy)benzoate (**7e**)

Starting with **2a** (0.186 g, 1.0 mmol) and **6c** (0.278 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7e** was isolated as a yellowish oil (0.160 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.14 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.56 (s, 1H, CH, Ar), 6.88 (d, ^3J=8.5 Hz, 2H, CH, Ar), 7.09 (d, ^3J=8.5 Hz, 2H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0, 16.3, 19.6, 19.9 (CH_3), 51.1 (OCH_3), 116.8, 117.5 (CH, Ar), 123.7 (C, Ar), 128.9 (CH, Ar), 129.4,

131.4, 133.5, 138.1, 150.5, 154.4 (C, Ar), 167.9 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3028 (w), 2949 (m), 2924 (m), 2865 (w), 1733 (s), 1602 (m), 1582 (m), 1506 (s), 1457 (m), 1435 (m), 1410 (m), 1380 (w), 1267 (s), 1219 (s), 1154 (s), 1104 (w), 1050 (s). MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, (100)), 254 (14), 253 (75), 252 (18), 237 (48), 162 (28). HRMS (EI): calcd for $C_{18}H_{20}O_3$ (M^+): 284.1407, found: 284.1403.

*3.3.13. Methyl 5-methyl-3-(4-tolyloxy)biphenyl-2-carboxylate (**7f**)*

Starting with **2c** (0.234 g, 1.0 mmol) and **6c** (0.278 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7f** was isolated as a colourless oil (0.072 g, 22%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.30 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.59 (s, 3H, OCH_3), 6.67 (s, 1H, CH, Ar), 6.93 (s, 1H, CH, Ar), 6.97 (d, ^3J=8.5 Hz, 2H, CH, Ar), 7.15 (s, ^3J=8.0 Hz, 2H, CH, Ar), 7.35–7.45 (m, 5H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=20.7, 21.4 (*C*H_3), 52.1 (OCH_3), 117.4, 119.3 (CH, Ar), 123.2 (C, Ar), 125.1, 127.6, 128.2, 128.3, 130.2 (CH, Ar), 133.2, 140.0, 140.9, 141.2, 149.8, 155.0 (C, Ar), 168.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3058 (w), 3029 (w), 2994 (w), 2948 (w), 2923 (w), 2857 (w), 1733 (s), 1609 (m), 1570 (m), 1505 (s), 1455 (m), 1430 (m), 1408 (m), 1326 (s), 1265 (s), 1236 (s), 1216 (s), 1167 (m), 1129 (m), 1082 (s). MS (EI, 70 eV): *m*/*z* (%)=332 (M^+, (88)), 302 (22), 301 (100), 210 (36), 165 (10). HRMS (EI): calcd for $C_{22}H_{20}O_3$ (M^+): 332.1407, found: 332.1407.

*3.3.14. Methyl 6-(4-chlorophenoxy)-2,3,4-trimethylbenzoate (**7g**)*

Starting with **2a** (0.186 g, 1.0 mmol) and **6d** (0.298 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7g** was isolated as a colourless oil (0.144 g, 47%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.16 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.58 (s, 1H, CH, Ar), 6.88 (d, ^3J=9.0 Hz, 2H, CH, Ar), 7.23 (d, ^3J=9.0 Hz, 2H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=15.1, 17.4, 21.0 (*C*H_3), 52.2 (OCH_3), 118.6, 119.4 (CH, Ar), 125.5, 128.2 (C, Ar), 129.4 (CH, Ar), 132.4, 135.7, 139.8, 151.2, 154.4 (C, Ar), 168.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2950 (w), 2925 (w), 2856 (w), 1733 (s), 1603 (w), 1580 (m), 1486 (s), 1435 (m), 1409 (w), 1302 (m), 1270 (s), 1224 (s), 1154 (m), 1094 (m). MS (EI, 70 eV): *m*/*z* (%)=306 (M^+, ^{37}Cl, (33)), 304 (M^+, ^{35}Cl, (93)), 275 (28), 274 (18), 273 (100), 272 (15), 271 (64), 237 (20), 162 (55). Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67.00; H, 5.62. Found: C, 67.25; H, 5.88.

*3.3.15. Methyl 3-(4-chlorophenoxy)-5-methylbiphenyl-2-carboxylate (**7h**)*

Starting with **2c** (0.187 g, 0.8 mmol) and **6d** (0.238 g, 0.8 mmol) in CH_2Cl_2 (5 mL), **7h** was isolated as a colourless oil (0.085 g, 30%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.33 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 6.70 (s, 1H, CH, Ar), 6.97–7.00 (m, 3H, CH, Ar), 6.57 (s, 1H, CH, Ar), 6.88 (d, ^3J=9.0 Hz, 2H, CH, Ar), 7.24 (d, ^3J=9.0 Hz, 2H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=15.0, 21.1 (*C*H_3), 52.2 (OCH_3), 118.6, 119.4 (CH, Ar), 125.5, 128.2 (C, Ar), 129.4 (CH, Ar), 132.4, 135.7, 139.8, 151.2, 154.4 (C, Ar), 168.6 (C=O). MS (EI, 70 eV): *m*/*z* (%)=354 (M^+, ^{37}Cl, (27)), 352 (M^+, ^{35}Cl, (78)), 323 (34), 322 (22), 321 (100), 285 (12), 210 (68). HRMS (EI): calcd for $C_{21}H_{17}O_3Cl$ (M^+): 352.0860, found: 352.0860.

*3.3.16. Methyl 2,4-diethyl-6-(4-methoxyphenoxy)benzoate (**7i**)*

Starting with **2b** (0.200 g, 1.0 mmol) and **6e** (0.294 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7i** was isolated as a colourless oil (0.045 g, 15%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.14 (t, ^3J=7.6 Hz, 3H, CH_2CH_3), 1.23 (t, ^3J=7.5 Hz, 3H, CH_2CH_3), 2.52 (q, ^3J=7.6 Hz, 2H, CH_2CH_3), 2.64 (q, ^3J=7.6 Hz, 2H, CH_2CH_3), 3.79 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.48 (s, 1H, CH, Ar), 6.78 (s, 1H, CH, Ar), 6.85 (d, ^3J=9.2 Hz, 2H, CH, Ar), 6.97 (d, ^3J=9.2 Hz, 2H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.2, 15.1 (CH_2CH_3), 25.6, 27.8 (CH_2CH_3), 51.1, 54.6 (OCH_3), 113.5, 113.6, 119.5 (CH, Ar), 121.0 (C, Ar), 121.5 (CH, Ar), 142.1, 146.3, 149.5, 154.2, 154.7 (C, Ar), 167.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2965 (m), 2934 (m), 2874 (m), 2837 (w), 1732 (s), 1660 (w), 1612 (m), 1575 (m), 1504 (s), 1462 (m), 1426 (m), 1375 (w), 1334 (w), 1278 (s), 1249 (s), 1208 (s), 1155 (m), 1090 (s), 1035 (m), 1006 (m). MS (EI, 70 eV): *m*/*z* (%)=314 (M^+, (100)), 283 (33), 281 (50), 267 (56). HRMS (EI): calcd for $C_{19}H_{22}O_4$ (M^+): 314.1512, found: 314.1514.

*3.3.17. Methyl 6-(4-methoxyphenoxy)-2,3,4-trimethylbenzoate (**7j**)*

Starting with **2a** (0.186 g, 1.0 mmol) and **6e** (0.294 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7j** was isolated as a colourless oil (0.060 g, 20%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.13 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.50 (s, 1H, CH, Ar), 6.77–6.99 (m, 4H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=13.9, 16.3, 20.0 (CH_3), 51.3, 54.7 (OCH_3), 113.7, 114.9, 119.2 (CH, Ar), 120.2, 123.2, 129.0, 133.4, 149.9, 151.2, 154.4 (C, Ar), 168.0 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2957 (m), 2928 (m), 2854 (w), 1733 (m), 1719 (m), 1635 (w), 1603 (w), 1504 (s), 1463 (m), 1439 (m), 1389 (w), 1378 (w), 1266 (s), 1207 (s), 1153 (s), 1132 (s), 1100 (m), 1040 (s), 1009 (m). MS (EI, 70 eV): *m*/*z* (%)=300 (M^+, (100)), 269 (37), 253 (24), 138 (22), 123 (22). HRMS (EI): calcd for $C_{18}H_{20}O_4$ (M^+): 300.1356, found: 300.1360.

*3.3.18. Methyl 3-(4-ethylphenoxy)-6-(4-methoxyphenoxy)-2,4-dimethylbenzoate (**7k**)*

Starting with **2f** (0.291 g, 1.0 mmol) and **6e** (0.294 g, 1.0 mmol) in CH_2Cl_2 (5 mL), **7k** was isolated as a yellow oil (0.081 g, 20%). ^1H NMR (300 MHz, $CDCl_3$): δ=1.21 (t, ^3J=7.6 Hz, 3H, CH_2CH_3), 2.03 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.69 (q, ^3J=7.6 Hz, 2H, CH_2CH_3), 3.80 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.56 (s, 1H, CH, Ar), 6.68 (d, ^3J=8.7 Hz, 2H, CH, Ar), 6.87 (d, ^3J=9.2 Hz, 2H, CH, Ar), 7.00 (d, ^3J=9.2 Hz, 2H, CH, Ar), 7.07 (d, ^3J=8.7 Hz, 2H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=12.5, 14.6 (CH_3), 15.7 (CH_2CH_3), 26.9 (CH_2CH_3), 51.3, 54.6 (OCH_3), 113.3, 113.7, 116.8, 119.4 (CH, Ar), 123.8 (C, Ar), 127.9 (CH, Ar), 129.6, 133.5, 136.2, 145.3, 149.6, 150.7, 154.6, 154.8 (C, Ar), 166.7 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2997 (w), 2961 (m), 2930 (m), 2871 (w), 2836 (w), 1734 (s), 1610 (m), 1504 (s), 1440 (m), 1410 (m), 1319 (m), 1266 (s), 1209 (s), 1101 (m), 1055 (s), 1036 (s). MS (EI, 70 eV): *m*/*z* (%)=406 (M^+, (100)), 268 (41), 123 (10). HRMS (EI): calcd for $C_{25}H_{26}O_5$ (M^+): 406.1774, found: 406.1776.

3.4. Synthesis of xanthones 8a–f and of fluorenone 5

Concentrated sulfuric acid (3 mL) was added to compound **7a–c**,**e–g** or **3e** (0.25 mmol) at 0 °C and the mixture was stirred for 1–24 h at 0 °C (TLC control). The mixture was poured into ice water (50 mL) and subsequently extracted with dichloromethane (3×10 mL). The combined organic layers were dried (sodium sulfate), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, EtOAc/heptanes=1:5, length=5 cm, diameter=1 cm).

*3.4.1. 1,3-Dimethylxanth-9-one (**8a**)*

Starting with **7a** (0.050 g, 0.18 mmol), **8a** was isolated (0.038 g, 95%) as a brownish solid, mp=81–82 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.44 (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 6.94 (s, 1H, CH, Ar), 7.14 (s, 1H, CH, Ar), 7.26–7.70 (m, 3H, CH, Ar), 8.27 (d, ^3J=7.9 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=21.6, 23.1 (CH_3), 115.8, 117.3 (CH, Ar), 122.8 (C, Ar), 123.5, 126.6, 129.5 (CH, Ar), 129.5 (C, Ar), 134.1 (CH, Ar), 141.7, 144.9, 155.2, 157.6 (C, Ar), 178.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3030 (w), 2967 (w), 2952 (w), 2915 (w), 2849 (w), 2729 (w), 1725 (w), 1649 (s), 1620 (m), 1605 (s), 1479 (s), 1461 (s), 1446 (s), 1404 (m), 1371 (m), 1351 (s), 1351 (s), 1336 (m), 1304 (s), 1336 (m), 1304 (s), 1274 (s), 1304 (s), 1274 (s), 1231 (s), 1212 (s), 1174 (s), 1135 (s), 1086 (m), 1054 (m), 1031 (m), 1026 (m). MS (EI, 70 eV): *m*/*z* (%)=224 (M^+, (100)), 223 (53). HRMS (EI): calcd for $C_{15}H_{12}O_2$ (M^+): 224.0831, found: 224.0828.

*3.4.2. 1,2,3-Trimethylxanth-9-one (**8b**)*

Starting with **7b** (0.180 g, 0.63 mmol), **8b** was isolated (0.125 g, 83%) as a colourless solid, mp=124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.27 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 7.15 (s, 1H, CH, Ar), 7.28–7.40 (m, 2H, CH, Ar), 7.61–7.68 (m, 1H, CH, Ar), 8.27 (d, ^3J=8.0 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=15.2, 17.7, 21.8 (CH_3), 116.2, 117.1 (CH, Ar), 118.3 (C, Ar), 123.2, 126.8 (CH, Ar), 129.4, 131.9 (C, Ar), 133.8 (CH, Ar), 139.3, 144.2, 155.0, 155.5 (C, Ar), 178.9 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3282 (w), 3072 (w), 3044 (w), 2970 (w), 2946 (w), 2917 (w), 2859 (w), 2726 (w), 1726 (w), 1644 (s), 1599 (s), 1462 (s), 1454 (s), 1410 (s), 1371 (s), 1340 (m), 1326 (m), 1297 (s), 1267 (s), 1229 (m), 1214 (m), 1202 (m), 1187 (m), 1187 (m), 1148 (m), 1118 (m), 1109 (m), 1083 (m), 1048 (s), 1023 (s), 1003 (s). MS (EI, 70 eV): *m*/*z* (%)=238 (M^+, (100)), 223 (64). HRMS (EI): calcd for $C_{16}H_{14}O_2$ (M^+): 238.0988, found: 238.0986.

*3.4.3. 1-Methyl-3-phenylxanth-9-one (**8c**)*

Starting with **7c** (0.110 g, 0.33 mmol), **8c** was isolated (0.083 g, 88%) as a yellow solid, mp=106–108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.43 (s, 3H, CH_3), 6.92 (s, 1H, CH, Ar), 7.21–7.41 (m, 8H, CH, Ar), 7.53–7.63 (m, 1H, CH, Ar), 8.11 (d, ^3J=8.2 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=21.7 (CH_3), 114.2 (C, Ar), 117.3, 117.4 (CH, Ar), 122.7 (C, Ar), 123.6, 126.8, 126.9, 127.5, 128.3, 128.7, 134.2 (CH, Ar), 141.9, 143.9, 144.7, 155.3, 157.3 (C, Ar), 176.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3316 (w), 3103 (w), 3075 (m), 3058 (m), 3023 (m), 2951 (m), 2920 (m), 2851 (m), 1660 (s), 1603 (s), 1563 (s), 1537 (m), 1494 (m), 1469 (s), 1462 (s), 1440 (s), 1402 (m), 1351 (s), 1335 (m), 1324 (m), 1306 (s), 1297 (s), 1229 (s), 1215 (m), 1173 (m), 1142 (m), 1114 (m), 1103 (m), 1070 (m), 1029 (m), 1013 (m). MS (EI, 70 eV): *m*/*z* (%)=285 (M^+, (100)). HRMS (EI): calcd for $C_{20}H_{14}O_2$ (M^+): 285.0910, found: 285.0906.

*3.4.4. 1,2,3,7-Tetramethylxanth-9-one (**8d**)*

Starting with **7e** (0.120 g, 0.42 mmol), **8d** was isolated (0.101 g, 95%) as a yellow solid, mp=143–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 7.14 (s, 1H, CH, Ar), 7.29 (d, ^3J=8.5 Hz, 1H, CH, Ar), 7.45 (d, ^3J=8.2 Hz, 1H, CH, Ar), 8.06 (d, ^4J=1.4 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=15.2, 17.8, 20.8, 21.8 (CH_3), 116.2, 116.9 (CH, Ar), 118.3, 122.7 (C, Ar), 126.1 (CH, Ar), 131.6, 132.8 (C, Ar), 135.0 (CH, Ar), 139.3, 144.0, 153.2, 155.5 (C, Ar), 179.0 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3027 (w), 2920 (w), 2859 (w), 2738 (w), 1644 (s), 1604 (s), 1592 (s), 1557 (m), 1489 (s), 1456 (s), 1428 (s), 1375 (m), 1329 (m), 1288 (s), 1268 (m), 1228 (s), 1268 (m), 1228 (s), 1195 (m), 1154 (m), 1136 (m), 1078 (w), 1047 (w), 1005 (w). MS (EI, 70 eV): *m*/*z* (%)=252 (M^+, (100)), 251 (29), 237 (55). HRMS (EI): calcd for $C_{17}H_{16}O_2$ (M^+): 252.1144, found: 252.1147.

*3.4.5. 3,7-Dimethyl-1-phenylxanth-9-one (**8e**)*

Starting with **7f** (0.030 g, 0.09 mmol), **8e** was isolated (0.025 g, 93%) as a yellow solid, mp=117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.32 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.90 (s, 1H, CH, Ar), 7.30–7.50 (m, 8H, CH, Ar), 7.95 (s, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=20.7, 21.7 (CH_3), 116.9 (C, Ar), 117.1, 117.4 (CH, Ar), 122.3 (C, Ar), 126.2, 126.9, 127.5, 128.3, 128.5 (CH, Ar), 133.3 (C, Ar), 135.4 (CH, Ar), 141.9, 143.8, 144.5, 153.5, 157.3 (C, Ar), 176.7 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3303 (w), 3079 (w), 3056 (w), 3028 (w), 2922 (w), 2854 (w), 1655 (s), 1608 (s), 1563 (m), 1482 (s), 1468 (s), 1441 (s), 1423 (s), 1402 (m), 1343 (s), 1288 (s), 1231 (m), 1218 (m), 1201 (m), 1168 (m), 1132 (m), 1121 (s), 1071 (m), 1029 (w), 1012 (w). MS (EI, 70 eV): *m*/*z* (%)=300 (M^+, (38)), 299 (100). HRMS (EI): calcd for $C_{21}H_{15}O_2$ (M^+): 299.1066, found: 299.1069.

*3.4.6. 7-Chloro-1,2,3-trimethylxanth-9-one (**8f**)*

Starting with **7g** (0.065 g, 0.21 mmol), **8f** was isolated (0.056 g, 96%) as a yellow solid, mp=164–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.26 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.88 (s, 3H, CH_3), 7.13 (s, 1H, CH, Ar), 7.34 (d, ^3J=8.9 Hz, 1H, CH, Ar), 7.56 (d, ^3J=8.9 Hz, 1H, CH, Ar), 8.22 (d, ^4J=2.6 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=16.2, 17.7, 21.8 (CH_3), 116.2 (CH, Ar), 117.9 (C, Ar), 118.9 (CH, Ar), 123.9 (C, Ar), 126.1 (CH, Ar), 128.9, 132.3 (C, Ar), 133.9 (CH, Ar), 139.4, 144.6, 153.3, 155.3 (C, Ar), 177.6 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3094 (w), 3071 (w), 3030 (w), 2958 (w), 2921 (w), 2852 (w), 2730 (w), 1644 (s), 1599 (s), 1557 (m), 1470 (m), 1455 (s), 1429 (s), 1373 (m), 1326 (m), 1276 (s), 1265 (s), 1224 (m), 1184 (m), 1130 (m), 1057 (m), 1045 (m), 1006 (m). MS (EI, 70 eV): *m*/*z* (%)=274 (M^+, ^{37}Cl, (34)), 272 (M^+, ^{35}Cl, (100)), 271 (23), 257 (53). HRMS (EI): calcd for $C_{16}H_{13}O_2Cl$ (M^+): 272.0598, found: 272.0598.

*3.4.7. 1-Methoxy-3-methylfluoren-9-one (**5**)*

Starting with **3e** (0.151 g, 0.58 mmol), **5** was isolated (0.120 g, 90%) as a yellow solid, mp=130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 6.62 (s, 1H, CH, Ar), 6.95 (s, 1H, CH, Ar), 7.24–7.48 (m, 3H, CH, Ar), 7.63 (d, ^3J=7.2 Hz, 1H, CH, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=22.4 (CH_3), 55.7 (OCH_3), 113.3, 114.0 (CH, Ar), 117.8 (C, Ar), 119.9, 123.6, 129.0, 133.5 (CH, Ar), 135.0, 143.0, 146.5, 148.3, 158.2 (C, Ar), 191.4 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3040 (w), 3006 (w), 2969 (w), 2940 (w), 2846 (w), 1730 (w), 1693 (s), 1600 (s), 1581 (s), 1485 (m), 1454 (s), 1415 (s), 1377 (m), 1334 (m), 1303 (s), 1275 (s), 1239 (s), 1185 (s), 1172 (s), 1155 (m), 1131 (s), 1087 (m), 1038 (s), 1011 (m). MS (EI, 70 eV): *m*/*z* (%)=224 (M^+, (86)), 209 (24), 195 (100), 181 (21), 166 (18), 165 (96), 152 (33). HRMS (EI): calcd for $C_{15}H_{12}O_2$ (M^+): 224.0831, found: 224.0831.

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