Regioselective Synthesis of 5-(Arylsulfanyl)- and 5-(Benzylsulfanyl)-6-phenylsalicylates by One-Pot Cyclizations of 1,3-Bis(silyloxy)buta-1,3-dienes with 2-(Arylsulfanyl)- and 5-(Benzylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones

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5-(Arylsulfanyl)-6-phenylsalicylates were prepared by one-pot cyclizations of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes with 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones.

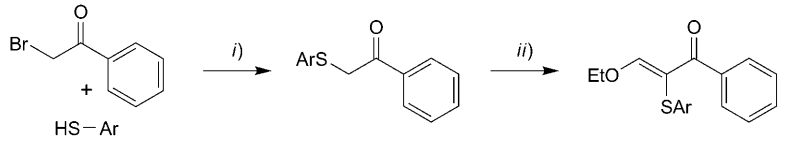
1. Introduction. – Natural and non-natural diaryl sulfides (diaryl thioethers) are of pharmacological relevance and have been isolated as natural products (for dibenzothiophenes, see [1a]; for lissoclinotoxins (varacins), see [1b][1c][1d]; for lissoclibadins, see [1e][1f]; for cyclo(penta-1,4-phenylenesulfide) and cyclotetra(*p*-phenylenesulfide), see [1g]; and for natural products isolated from *Streptomyces griseus*, see [1h]). For example, fluorinated diaryl sulfides have been reported to act as serotonin transporter ligands [2]. Diaryl sulfides have been prepared mainly by formation of a C–S bond. This includes, for example, the reaction of copper thiolates with aryl halides. An alternative relies on the reduction of aryl sulfones or aryl sulfoxides. All these methods are often limited by the harsh conditions, required by the formation of polysulfides, preparative scope, use of toxic reagents (such as HMPTA), or low regioselectivity (for the thermal reaction of arenes with sulfur, see, *e.g.*, [3a][3b]; for the trifluoromethanesulfonic acid-catalyzed sulfurization of cycloalkanes, see [3c]; for condensations of organometallic compounds with chlorophenyl sulfide, see, *e.g.*, [3d]; and for base-mediated reactions of chloroarenes with thiophenols, see [3e][3f][3g][3h]). Mild metal-catalyzed and metal-free reactions for the synthesis of diaryl sulfides have also been reported [4–6]. These methods are often limited by the fact that highly substituted and sterically encumbered products are not readily available. In addition, the synthesis of the starting materials, substituted arenes and thiophenols, can be difficult.

The use of S-containing building blocks in cyclization reactions (building-block approach) provides an alternative procedure to diaryl sulfides. This approach involves the assembly of the arene moiety by formation of two C–C bonds. *Hilt* and co-workers reported an efficient synthesis of diaryl sulfides by Co^{I}-catalyzed [4 + 2] cycloaddition

of alkynyl sulfides with buta-1,3-dienes [7]. Syntheses of 2-(arylsulfanyl)benzoates and related products by cyclization reactions of (arylsulfanyl)-1-(trimethylsilyloxy)buta-1,3-dienes were reported by *Chan* and *Prasad* [8], by us [9], and by others [10]. Recently, we reported [11] the synthesis of 3- and 5-(arylsulfanyl)salicylates based on formal [3 + 3] cyclizations [12] of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes with 3-(silyloxy)prop-2-en-1-ones and 1,1-diacetylcyclopropane [12]. Despite the usefulness of these reactions, they are limited by the fact that, in most cases, only symmetrical 1,3-dielectrophiles can be employed. In addition, a Me group must generally be present at 4-position. Here, we report, to the best of our knowledge, the first synthesis of 6-aryl-5-(arylsulfanyl)salicylates unsubstituted at C(4) by one-pot cyclizations of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes with 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones.

2. Results and Discussion. – The novel 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones **3a**–**3f** were prepared by reaction of α-bromoacetophenone with thiophenols **1a**–**1f** to give **2a**–**2f** (*Scheme 1* and *Table 1*). The reaction of the latter with triethyl orthoformate $HC(OEt)_3$ afforded the 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones **3a**–**3f**.

Scheme 1. *Synthesis of* **3a**–**3f**



1a – 1f **2a – 2f** **3a – 3f**

i) EtONa (1.0 equiv.), 2-bromoacetophenone (1.0 equiv.), **1a**–**1f** (1.0 equiv.). *ii*) **2a**–**2f** (1.0 equiv.), $HC(OEt)_3$ (3 equiv.), Ac_2O (3 equiv.), reflux, 15 h at 140°; products exist as mixtures of (*E*)- and (*Z*)-isomers.

Table 1. *Synthesis of* **3a**–**3f**

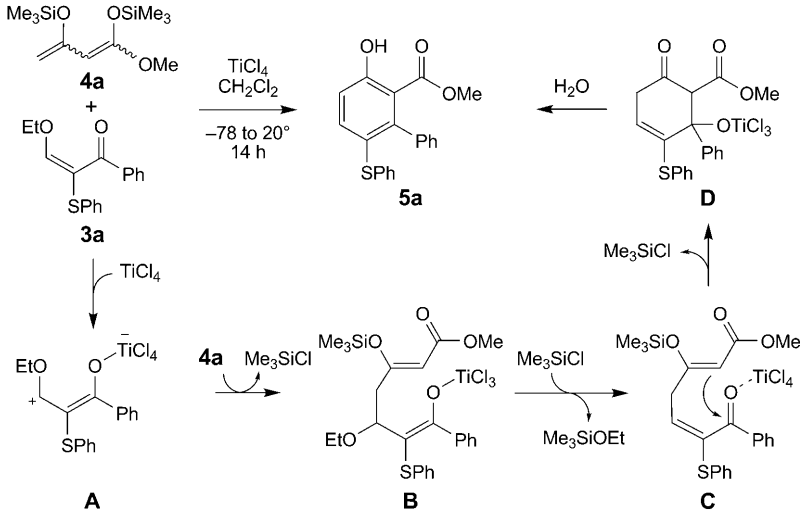
1–**3**	Ar	Yield [%][a])	
		2	**3**
a	Ph	95	41
b	4-Me–C_6H_4	98	54
c	4-F–C_6H_4	92	55
d	4-NO_2–C_6H_4	99	45
e	$PhCH_2$	99	42
f	Naphthalen-2-yl	96	50

[a]) Yields of isolated products.

The [3 + 3] cyclization of 1,3-bis(trimethylsilyloxy)buta-1,3-diene **4a**, prepared in two steps from methyl acetoacetate, with **3a** afforded the novel 5-(phenylsulfanyl)-6-phenylsalicylates **5a** in 44% yield (*Scheme 2*). The best yield was obtained when the reaction was carried out in highly concentrated solution, and when $TiCl_4$ was employed as *Lewis* acid. It is worthy to be noted that the cyclization proceeded with excellent

regioselectivity. The moderate yield of **5a** can be explained by practical problems during the chromatographic purification. The formation of the other regioisomer was not observed.

Scheme 2. *Possible Mechanism of the Formation of* **5a**



The formation of product **5a** can be explained by reaction of **3a** with $TiCl_4$ to give intermediate **A**, attack of the terminal C-atom of **4a** onto **A**, resulting in intermediate **B**, formation of intermediate **C**, cyclization *via* the central C-atom (intermediate **D**), and subsequent aromatization. The regioselectivity of the formation of **5a** might be explained by steric hindrance at the ketone CO group.

The [3 + 3] cyclization of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes **4a** – **4g**, prepared in two steps from the corresponding β-keto esters, with **3a** – **3f** afforded the novel 5-(arylsulfanyl)-6-phenylsalicylates **5a** – **5q** (*Scheme 3* and *Table 2*). The reactions could be successfully carried out with 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones containing electron-donating or electron-withdrawing groups. Cyclizations of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes **4b** – **4g**, containing a substituent at the terminal C-atom, gave slightly higher yields than the reactions of unsubstituted derivative **4a**. The synthesis of product **5p** showed that the method can be successfully applied for the preparation of 5-(benzylsulfanyl)salicylates.

The structures of all products were confirmed by spectroscopic methods (HMBC, NOESY). The structures of products **5a** and **5i**, which contain a H-atom at C(3), are evident by $J_o = 8.8$ and 8.7 Hz, respectively. The structure of **5j** was independently confirmed by an X-ray crystal structure analysis (*Fig.*) [13].

In conclusion, a variety of 5-(arylsulfanyl)-6-phenylsalicylates were prepared by one-pot cyclizations of 1,3-bis(trimethylsilyloxy)buta-1,3-dienes with 2-(arylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-ones. The products are not readily available by other methods.

Scheme 3. *Synthesis* of **5a**–**5q**

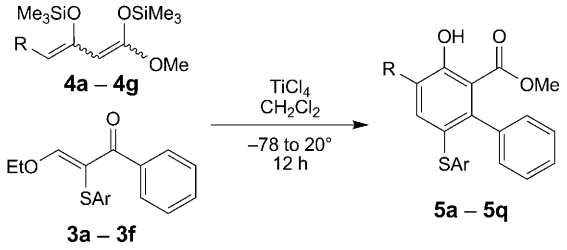


Table 2. *Synthesis of* **5a**–**5q**

3	4	5	Ar	R	Yield of 5[a]) [%]
a	**a**	**a**	Ph	H	44
a	**c**	**b**	Ph	Et	48
a	**f**	**c**	Ph	Octyl	51
a	**g**	**d**	Ph	Decyl	52
b	**c**	**e**	4-Me–C_6H_4	Et	37
b	**g**	**f**	4-Me–C_6H_4	Decyl	38
c	**b**	**g**	4-F–C_6H_4	Me	43
c	**g**	**h**	4-F–C_6H_4	Decyl	45
d	**a**	**i**	4-NO_2–C_6H_4	H	35
d	**b**	**j**	4-NO_2–C_6H_4	Me	48
d	**c**	**k**	4-NO_2–C_6H_4	Et	40
d	**d**	**l**	4-NO_2–C_6H_4	Pentyl	48
d	**e**	**m**	4-NO_2–C_6H_4	Hexyl	42
d	**f**	**n**	4-NO_2–C_6H_4	Octyl	45
d	**g**	**o**	4-NO_2–C_6H_4	Decyl	50
e	**c**	**p**	$PhCH_2$	Et	47
f	**c**	**q**	Naphthalen-2-yl	Et	52

[a]) Yields of isolated products.

Experimental Part

General. All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. Prep. scale column chromatography (CC): silica gel (SiO_2; 60–200 mesh, *Merck*) with heptane/AcOEt as eluent were used. M.p.: Microheating table *HMK 67/1825 Kuestner* (*Büchi* apparatus); uncorrected. IR Spectra: *Nicolet 380* FT-IR spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AVANCE 300 III* and *Bruker AVANCE 250 II* spectrometer; in $CDCl_3$ at 300 and 75 MHz, resp. EI-MS and HR-EI-MS: *MAT 95-XP* instrument; in *m*/*z*.

General Procedure for the Synthesis of **2a**–**2f** (*GP 1*). To a suspension of EtONa (1.0 equiv.) in EtOH (0.7 ml per 1 mmol of EtONa) was added **1** (1.0 equiv.) at 25°, followed by portionwise addition of 2-bromoacetophenone (1.0 equiv.). The mixture was heated to reflux for 10 min and poured into 2 l of ice-water. Filtration of the suspension gave the respective product **2**.

1-Phenyl-2-(phenylsulfanyl)ethanone (**2a**). *GP 1* with EtONa (1.361 g, 20.0 mmol), **1a** (2.20 g, 20.0 mmol), and 2-bromoacetophenone (4.00 g, 20.0 mmol): **2a** (4.286 g, 93%). Brown semi-solid. IR (KBr): 3339*w*, 3057*w*, 2902*w*, 1675*s*, 1596*m*, 1579*m*, 1480*m*, 1447*m*, 1438*m*, 1412*w*, 1394*w*, 1317*m*, 1273*s*, 1197*m*, 1158*m*, 1088*m*, 1024*m*, 999*m*, 932*w*, 906*w*, 843*w*, 736*s*, 685*s*, 641*s*, 616*m*, 555*m*. ^1H-NMR: 4.20 (*s*,

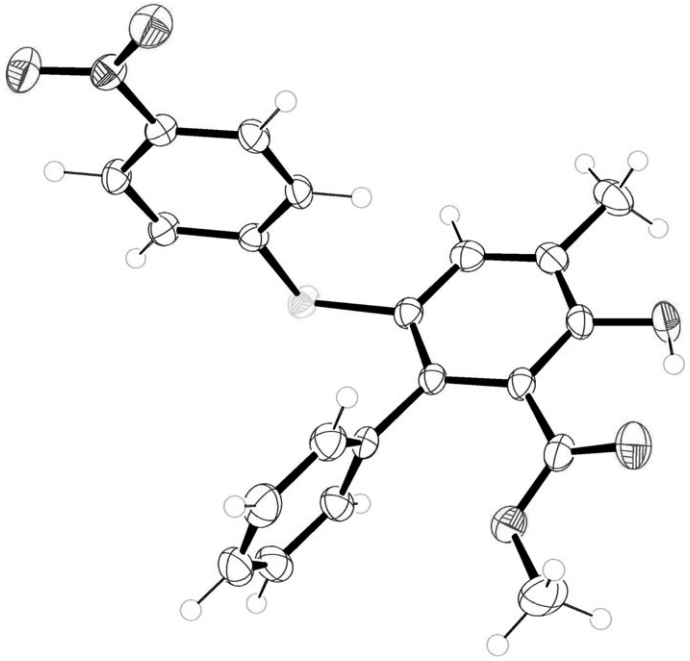


Figure. *Crystal structure of* **5j**

CH_2); 7.13–7.24 (*m*, 3 arom. H); 7.29–7.33 (*m*, 2 arom. H); 7.36–7.41 (*m*, 2 arom. H); 7.48–7.53 (*m*, 1 arom. H); 7.85–7.89 (*m*, 2 arom. H). ^{13}C-NMR: 41.2 (CH_2); 127.1 (arom. CH); 128.7 (4 arom. CH); 129.1 (2 arom. CH); 130.6 (2 arom. CH); 133.5 (arom. CH); 134.8, 135.4 (arom. C); 194.1 (CO). GC/EI-MS (70 eV): 228 (39, M^+), 123 (8), 105 (100), 77 (32), 65 (6), 51 (10). HR-EI-MS: 228.0603 (M^+, $C_{14}H_{12}OS^+$; calc. 228.0603).

2-[(4-Methylphenyl)sulfanyl]-1-phenylethanone (**2b**). *GP 1* with EtONa (1.361 g, 20.0 mmol), **1b** (2.484 g, 20.0 mmol), and 2-bromoacetophenone (4.00 g, 20.0 mmol): **2b** (4.773 g, 98%). Brown semi-solid. IR (neat): 3340*w*, 3055*w*, 2918*w*, 2732*w*, 1675*s*, 1593*m*, 1475*m*, 1447*m*, 1317*m*, 1273*s*, 1195*m*, 1134*m*, 1035*w*, 987*m*, 854*m*, 748*m*, 685*s*, 641*m*, 623*w*, 610*w*, 557*m*. ^{1}H-NMR: 2.22 (*s*, Me); 4.19 (*s*, CH_2); 6.94–6.96 (*m*, 1 arom. H); 7.09–7.13 (*m*, 3 arom. H); 7.35–7.40 (*m*, 2 arom. H); 7.47–7.52 (*m*, 1 arom. H); 7.85–7.88 (*m*, 2 arom. H). ^{13}C-NMR: 21.3 (Me); 41.3 (CH_2); 127.5, 128.0 (arom. CH); 128.6 (2 arom. CH); 128.7 (2 arom. CH); 128.9, 131.2, 133.4 (arom. CH); 134.5, 135.5, 138.9 (arom. C); 194.1 (CO). GC/EI-MS (70 eV): 242 (45, M^+), 137 (14), 105 (100), 91 (9), 77 (30), 65 (7), 51 (7). HR-EI-MS: 242.0765 (M^+, $C_{15}H_{14}OS^+$; calc. 242.0760).

2-[(4-Fluorophenyl)sulfanyl]-1-phenylethanone (**2c**). *GP 1* with EtONa (1.361 g, 20.0 mmol), **1c** (2.563 g, 20.0 mmol), and 2-bromoacetophenone (4.00 g, 20.0 mmol): **2c** (4.554 g, 92%). Slightly brown oil. IR (neat): 3338*w*, 3062*w*, 2905*w*, 1675*s*, 1589*m*, 1580*m*, 1489*s*, 1448*m*, 1396*m*, 1274*m*, 1221*s*, 1196*s*, 1156*m*, 1090*m*, 1000*m*, 932*w*, 826*m*, 748*m*, 687*s*, 646*m*, 625*m*, 557*m*. ^{1}H-NMR: 4.22 (*s*, CH_2); 6.97–7.03 (*m*, 2 arom. H); 7.39–7.44 (*m*, 2 arom. H); 7.46–7.52 (*m*, 2 arom. H); 7.59–7.64 (*m*, 1 arom. H); 7.93–7.96 (*m*, 2 arom. H). ^{13}C-NMR: 42.1 (CH_2); 116.2 (*d*, ^2J(C,F) = 22.0); 128.7 (4 arom. CH); 129.4 (arom. C); 133.5 (arom. CH); 133.9 (*d*, ^3J(C,F) = 8.2); 135.3 (arom. C); 162.5 (*d*, ^1J(C,F) = 247.8); 193.9 (CO). ^{19}F-NMR (285 MHz, $CDCl_3$): −113.5. GC/EI-MS (70 eV): 246 (30, M^+), 141 (4), 127 (5), 105 (100), 83 (6), 77 (33), 51 (8). HR-EI-MS: 246.0509 (M^+, $C_{14}H_{11}FOS^+$; calc. 246.0509).

2-[(4-Nitrophenyl)sulfanyl]-1-phenylethanone (**2d**). *GP 1* with EtONa (1.361 g, 20 mmol), **1d** (3.104 g, 20 mmol), and 2-bromoacetophenone (4.00 g, 20 mmol): **2d** (5.438 g, 99%). Brown solid.

M.p. 150–152°. IR (neat): 3370*w*, 3094*w*, 3062*w*, 2918*w*, 2850*w*, 1677*m*, 1594*m*, 1575*s*, 1502*s*, 1448*m*, 1392*m*, 1334*s*, 1276*m*, 1196*m*, 1108*m*, 1069*m*, 988*m*, 906*w*, 852*m*, 755*m*, 737*s*, 680*s*, 623*m*, 610*m*, 566*m*, 537*m*. ^{1}H-NMR: 4.37 (*s*, CH_2); 7.33–7.36 (*m*, 2 arom. H); 7.41–7.46 (*m*, 3 arom. H); 7.90–7.93 (*m*, 2 arom. H); 8.03–8.06 (*m*, 2 arom. H). ^{13}C-NMR: 39.1 (CH_2); 124.0 (2 arom. CH); 127.2 (2 arom. CH); 128.6 (2 arom. CH); 128.9 (2 arom. CH); 134.0 (arom. CH); 134.9, 145.4, 145.7 (arom. C); 192.7 (CO). GC/EI-MS (70 eV): 273 (8, M^+), 105 (100), 77 (30), 51 (6). HR-EI-MS: 273.0457 (M^+, $C_{14}H_{11}NO_3S^+$; calc. 273.0454).

2-(Benzylsulfanyl)-1-phenylethanone (**2e**). *GP 1* with EtONa (1.361 g, 20.0 mmol), **1e** (2.484 g, 20.0 mmol), and 2-bromoacetophenone (4.00 g, 20.0 mmol): **2e** (4.828 g, 99%). Semi-brown solid. IR (neat): 3648*w*, 3327*w*, 3083*w*, 3059*w*, 3027*w*, 2919*w*, 2626*w*, 2321*w*, 1964*w*, 1900*w*, 1813*w*, 1766*w*, 1670*s*, 1596*m*, 1579*m*, 1493*m*, 1447*m*, 1417*w*, 1315*m*, 1275*s*, 1197*m*, 1130*m*, 1071*m*, 1013*m*, 932*w*, 803*w*, 748*m*, 698*s*, 686*s*, 645*m*, 618*w*, 588*w*, 561*m*. ^{1}H-NMR: 3.70 (*s*, CH_2); 3.79 (*s*, CH_2); 7.28–7.32 (*m*, 2 arom. H); 7.34–7.38 (*m*, 3 arom. H); 7.46–7.52 (*m*, 2 arom. H); 7.57–7.62 (*m*, 1 arom. H); 7.94–7.98 (*m*, 2 arom. H). ^{13}C-NMR: 35.9, 36.1 (CH_2); 127.3 (arom. CH); 128.5 (2 arom. CH); 128.6 (2 arom. CH); 128.7 (2 arom. CH); 129.3 (2 arom. CH); 133.3 (arom. CH); 135.4, 137.3 (arom. C); 194.5 (CO). GC/EI-MS (70 eV): 242 (15, M^+), 120 (70), 105 (100), 91 (45), 77 (39), 65 (12), 51 (11). HR-EI-MS: 242.0763 (M^+, $C_{15}H_{14}OS^+$; calc. 242.0760).

2-[(Naphthalen-2-yl)sulfanyl]-1-phenylethanone (**2f**). *GC 1* with EtONa (1.361 g, 20.0 mmol), **1f** (3.205 g, 20.0 mmol), and 2-bromoacetophenone (4.00 g, 20.0 mmol): **2f** (5.389 g, 96%). Semi-brown solid. IR (neat): 3328*w*, 3104*w*, 3052*w*, 2985*w*, 2943*w*, 2902*w*, 2853*w*, 1971*w*, 1954*w*, 1916*w*, 1828*w*, 1686*m*, 1668*m*, 1621*m*, 1578*m*, 1498*m*, 1446*m*, 1417*w*, 1338*w*, 1270*m*, 1194*m*, 1130*m*, 1068*m*, 1012*m*, 941*m*, 846*m*, 814*s*, 738*s*, 686*s*, 651*m*, 626*m*, 599*w*, 553*m*. ^{1}H-NMR: 4.29 (*s*, CH_2); 7.35–7.40 (*m*, 5 arom); 7.63–7.75 (*m*, 5 arom); 7.86–7.89 (*m*, 2 arom. H). ^{13}C-NMR: 41.2 (CH_2); 126.2, 126.6, 127.4, 127.7, 128.0, 128.6 (arom. CH); 128.7 (4 arom. CH); 128.9 (arom. CH); 132.2 (arom. C); 133.5 (arom. CH); 133.7, 134.0, 135.5 (arom. C); 194.1 (CO). GC/EI-MS (70 eV): 278 (88, M^+), 173 (29), 129 (11), 115 (20), 105 (100), 77 (26), 51 (6). HR-EI-MS: 278.0762 (M^+, $C_{18}H_{14}OS^+$; calc. 278.076).

General Procedure for the Synthesis of **3a**–**3f** (*GP 2*). To a soln. of **2a**–**2f** (1 equiv.) in Ac_2O (3 equiv.) was added $HC(OEt)_3$ (3.0 equiv.). The mixture was heated for 15 h at 140°. The mixture was dried *in vacuo* and was purified by chromatography (SiO_2) to give **3**.

3-Ethoxy-1-phenyl-2-(phenylsulfanyl)prop-2-en-1-one (**3a**). *GP 2* with **2a** (2.00 g, 8.8 mmol), $HC(OEt)_3$ (3.90 g, 26.3 mmol), and Ac_2O (2.68 g, 26.3 mmol): **3a** (1.013 g, 41%). Yellowish oil. IR (neat): 3057*w*, 2981*w*, 2935*w*, 2895*w*, 1644*m*, 1588*s*, 1475*m*, 1439*m*, 1390*m*, 1297*m*, 1212*s*, 1178*m*, 1089*m*, 1009*m*, 892*m*, 822*m*, 737*m*, 688*s*, 657*s*, 616*m*, 577*m*, 541*m*. ^{1}H-NMR: 1.25 (*t*, $^3J = 7.1$, *Me*CH_2O); 4.09 (*q*, $^3J = 7.1$, MeCH_2O); 6.99–7.04 (*m*, 1 arom. H); 7.09–7.12 (*m*, 1 arom. H); 7.13–7.19 (*m*, 3 arom. H); 7.28–7.34 (*m*, 2 arom. H); 7.38–7.44 (*m*, 1 arom. H); 7.55–7.58 (*m*, 3 arom. H). ^{13}C-NMR: 15.3 (Me); 71.8 (CH_2O); 112.3 (C); 125.7 (arom. CH); 128.1 (4 arom. CH); 128.7 (2 arom. CH); 128.8 (2 arom. CH); 131.5 (arom. CH); 135.8, 138.9 (arom. C); 166.4 (C); 193.5 (CO). GC/EI-MS (70 eV): 284 (100, M^+), 255 (6), 149 (10), 135 (6), 121 (15), 105 (90), 77 (46), 51 (10). HR-EI-MS: 284.0860 (M^+, $C_{17}H_{16}O_2S^+$; calc. 284.0866).

3-Ethoxy-2-[(4-methylphenyl)sulfanyl]-1-phenylprop-2-en-1-one (**3b**). *GP 2* with **2b** (2.00 g, 8.3 mmol), $HC(OEt)_3$ (3.67 g, 24.7 mmol), and Ac_2O (2.53 g, 24.7 mmol): **3b** (1.333 g, 54%). Yellowish oil. ^{1}H-NMR: 1.25 (*t*, $^3J = 7.1$, *Me*CH_2O); 2.18 (*s*, Me); 4.10 (*q*, $^3J = 7.1$, MeCH_2O); 6.96–7.00 (*m*, 2 arom. H); 7.28–7.34 (*m*, 2 arom. H); 7.38–7.43 (*m*, 2 arom. H); 7.53–7.58 (*m*, 3 arom. H); 7.82–7.85 (*m*, 1 arom. H). ^{13}C-NMR: 15.4, 21.3 (Me); 71.7 (CH_2O); 112.3 (C); 125.1, 126.6, 127.7, 128.1, 128.6, 128.8, 128.9, 131.5, 133.9 (arom. CH); 135.4, 138.4, 139.0 (arom. CH); 166.3 (CH); 192.1 (CO). IR (neat): 3057*w*, 2980*w*, 2930*w*, 1749*m*, 1703*m*, 1645*m*, 1591*s*, 1447*m*, 1370*m*, 1272*m*, 1214*s*, 1180*m*, 1085*m*, 1011*m*, 893*m*, 822*m*, 755*m*, 687*s*, 658*m*, 617*w*, 562*m*, 542*w*. GC/EI-MS (70 eV): 298 (100, M^+), 149 (12), 135 (11), 123 (9), 105 (88), 91 (9), 77 (40), 51 (6). HR-EI-MS: 298.1016 (M^+, $C_{18}H_{18}O_2S^+$; calc. 298.1022).

3-Ethoxy-2-[(4-fluorophenyl)sulfanyl]-1-phenylprop-2-en-1-one (**3c**). *GP 2* with **2c** (2.00 g, 8.1 mmol), $HC(OEt)_3$ (3.61 g, 24.4 mmol), and Ac_2O (2.49 g, 24.4 mmol): **3c** (1.351 g, 55%). Brownish oil. IR (neat): 3062*w*, 2982*w*, 2936*w*, 2896*w*, 2816*w*, 1749*w*, 1704*w*, 1644*m*, 1586*s*, 1487*s*, 1445*m*, 1392*m*, 1334*w*, 1272*m*, 1212*s*, 1153*m*, 1086*m*, 1010*s*, 928*w*, 822*m*, 755*w*, 657*m*, 625*m*, 562*w*. ^{1}H-NMR: 1.26 (*t*, $^3J =$ 7.1, *Me*CH_2O); 4.09 (*q*, $^3J = 7.1$, MeCH_2O); 6.79–6.85 (*m*, 2 arom. H); 7.16–7.21 (*m*, 2 arom. H); 7.29–

7.34 (*m*, 2 arom. H); 7.39–7.44 (*m*, 1 arom. H); 7.48 (*s*, CH); 7.52–7.56 (*m*, 2 arom. H). ^{13}C-NMR: 15.4 (Me); 71.8 (CH_2O); 113.2 (C); 115.8 (*d*, ^2J(C,F) = 22.0); 128.2 (2 arom. CH); 128.8 (2 arom. CH); 131.1 (*d*, ^3J(C,F) = 8.1); 130.7 (arom. C); 131.6 (arom. CH); 138.9 (arom. C); 161.6 (*d*, ^1J(C,F) = 245.5); 165.9 (CH); 193.3 (CO). ^{19}F-NMR (285 MHz, $CDCl_3$): −116.5. GC/EI-MS (70 eV): 302 (100, M^+), 273 (5), 127 (12), 105 (94), 77 (43), 51 (7). HR-EI-MS: 302.0774 (M^+, $C_{17}H_{15}FO_2S^+$; calc. 302.0771).

3-Ethoxy-2-[(4-nitrophenyl)sulfanyl]-1-phenylprop-2-en-1-one (**3d**). *GP 2* with **2d** (2.00 g, 7.3 mmol), $HC(OEt)_3$ (3.25 g, 22.0 mmol), and Ac_2O (2.24 g, 22.0 mmol): **3d** (1.078 g, 45%). Yellowish oil. IR (neat): 3272*w*, 3092*w*, 3011*w*, 2951*w*, 2891*w*, 2605*w*, 2440*w*, 1672*m*, 1643*m*, 1592*m*, 1574*s*, 1558*s*, 1500*s*, 1471*m*, 1386*m*, 1332*s*, 1314*s*, 1217*s*, 1175*s*, 1109*m*, 1013*s*, 934*m*, 910*s*, 844*s*, 794*m*, 717*s*, 697*s*, 681*s*, 659*m*, 645*s*, 625*m*, 565*m*, 541*m*. ^{1}H-NMR: 1.27 (*t*, ^3J = 7.1, *Me*CH_2O); 4.15 (*q*, ^3J = 7.1, MeCH_2O); 7.19–7.22 (*m*, 2 arom. H); 7.34–7.39 (*m*, 2 arom. H); 7.43–7.48 (*m*, 1 arom. H); 7.58–7.61 (*m*, 2 arom. H); 7.74 (*s*, 1 arom. H); 7.97–8.00 (*m*, 2 arom. H). ^{13}C-NMR: 15.4 (Me); 72.5 (CH_2O); 109.3 (C); 123.9 (2 arom. CH); 126.2 (2 arom. CH); 128.4 (2 arom. CH); 128.8 (2 arom. CH); 132.0 (arom. CH); 138.4, 145.2, 146.4 (arom. C); 168.7 (CH); 192.6 (CO). GC/EI-MS (70 eV): 329 (68, M^+), 300 (8), 255 (6), 197 (6), 165 (6), 105 (100), 77 (27), 50 (7). HR-EI-MS: 329.0718 (M^+, $C_{17}H_{15}NO_4S^+$); calc. 329.0716).

2-(Benzylsulfanyl)-3-ethoxy-1-phenylprop-2-en-1-one (**3e**). *GP 2* with **2e** (2.00 g, 8.3 mmol), $HC(OEt)_3$ (3.67 g, 24.8 mmol), and Ac_2O (2.53 g, 24.8 mmol): **3e** (1.033 g, 42%). Yellowish oil. IR (neat): 3060*w*, 3028*w*, 2978*w*, 2924*w*, 1750*w*, 1704*w*, 1672*m*, 1596*m*, 1492*m*, 1447*m*, 1340*m*, 1275*m*, 1217*m*, 1179*m*, 1071*m*, 1014*m*, 967*m*, 843*m*, 765*m*, 696*s*, 687*s*, 646*m*, 618*m*, 563*m*, 540*m*. ^{1}H-NMR: 1.19 (*t*, ^3J = 7.1, *Me*CH_2O); 3.90–3.97 (*m*, CH_2, MeCH_2O); 7.13–7.19 (*m*, 5 arom. H); 7.26–7.28 (*m*, 4 arom. H); 7.36–7.41 (*m*, 2 arom. H). ^{13}C-NMR: 15.3 (Me); 36.7 (CH_2); 71.3 (CH_2O); 112.3 (C); 126.8 (arom. CH); 128.0 (2 arom. CH); 128.1 (2 arom. CH); 128.8 (2 arom. CH); 129.3 (2 arom. CH); 131.2 (arom. CH); 138.3, 139.3 (arom. C); 166.1 (CH); 193.6 (CO). GC/EI-MS (70 eV): 298 (M^+, 34); 252 (30), 147 (51), 131 (10), 105 (79), 91 (100), 77 (49), 65 (13), 51 (8), 39 (8). HR-EI-MS: 298.1026 (M^+, $C_{18}H_{18}O_2S^+$; calc. 298.1022).

3-Ethoxy-2-[(naphthalen-2-yl)sulfanyl]-1-phenylprop-2-en-1-one (**3f**). *GP 2* with **2f** (2.00 g, 7.2 mmol), $HC(OEt)_3$ (3.19 g, 21.5 mmol), and Ac_2O (2.20 g, 21.5 mmol): **3f** (1.201 g, 50%). Yellowish oil. IR (neat): 3053*w*, 2979*w*, 2930*w*, 1749*m*, 1703*m*, 1644*m*, 1587*m*, 1500*m*, 1446*m*, 1339*m*, 1268*m*, 1215*s*, 1132*m*, 1086*m*, 1012*m*, 940*m*, 847*m*, 811*s*, 743*m*, 688*s*, 632*m*, 617*m*, 601*m*, 575*m*, 541*m*. ^{1}H-NMR: 1.24 (*t*, ^3J = 7.1, *Me*CH_2O); 4.11 (*q*, ^3J = 7.1, MeCH_2O); 7.26–7.43 (*m*, 7 arom. H); 7.58–7.67 (*m*, 6 arom. H). ^{13}C-NMR: 15.4 (Me); 71.8 (CH_2O); 112.1 (C); 125.4, 126.2, (arom. CH); 126.3 (2 arom. CH); 127.1, 127.6 (arom. CH); 128.1 (2 arom. CH); 128.3 (arom. CH); 128.8 (2 arom. CH); 131.5 (arom. CH); 131.7, 133.3, 133.7, 138.9 (arom. C); 166.5 (CH); 193.5 (CO). GC/EI-MS (70 eV): 334 (100, M^+), 159 (12), 115 (16), 105 (76), 77 (31). HR-EI-MS: 334.1022 (M^+; $C_{21}H_{18}O_2S^+$; calc. 334.1022).

General Procedure for the Synthesis of **5a**–**5q** (*GP 3*). To a CH_2Cl_2 soln. (3 ml per 1 mmol of **3a**–**3f**) of **3a**–**3f** was added **4a**–**4g** (1.1 mmol) and, subsequently, $TiCl_4$ (1.1 mmol) at −78°. The soln. was allowed to warm to 20° during 14 h with stirring. HCl (10%, 20 ml) was added to the soln., and the org. and the aq. layer were separated. The latter was extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by CC (SiO_2) to give **5a**–**5q**.

Methyl 3-Hydroxy-6-(phenylsulfanyl)-1,1′-biphenyl-2-carboxylate (**5a**). *GC 3* with **3a** (0.427 g, 1.5 mmol) and **4a** (0.430 g, 1.65 mmol): **5a** (0.222 g, 44%). Yellowish oil. IR (neat): 3056*w*, 3021*w*, 2950*w*, 2850*w*, 2659*w*, 2536*w*, 1943*w*, 1880*w*, 1739*w*, 1663*s*, 1582*m*, 1496*w*, 1435*s*, 1335*m*, 1288*m*, 1208*s*, 1155*m*, 1094*m*, 1024*m*, 964*m*, 828*m*, 737*s*, 698*s*, 688*s*, 612*m*, 575*m*. ^{1}H-NMR: 3.23 (*s*, MeO); 6.83 (*d*, ^3J = 8.8, 1 arom. H); 6.92–6.95 (*m*, 4 arom. H); 6.99–7.05 (*m*, 3 arom. H); 7.14–7.17 (*m*, 3 arom. H); 7.28 (*d*, ^3J = 8.8, 1 arom. H); 10.67 (*s*, OH). ^{13}C-NMR: 52.0 (MeO); 113.9 (*C*COOMe); 118.2 (arom. CH); 126.1 (arom. C); 126.4, 127.0 (arom. CH); 127.4 (2 arom. CH); 128.5 (2 arom. CH); 128.9 (2 arom. CH); 130.0 (2 arom. CH); 137.3 (arom. C); 139.1 (arom. CH); 140.7, 146.1 (arom. C); 161.1 (COH); 171.0 (CO). GC/EI-MS (70 eV): 336 (46, M^+), 304 (100), 275 (8), 247 (17), 215 (8), 171 (17), 139 (10). HR-EI-MS: 336.0811 (M^+, $C_{20}H_{16}O_3S^+$; calc. 336.0815).

Methyl 4-Ethyl-3-hydroxy-6-(phenylsulfanyl)-1,1′-biphenyl-2-carboxylate (**5b**). *GP 3* with **3a** (0.427 g, 1.5 mmol) and **4c** (0.476 g, 1.65 mmol): **5b** (0.263 g, 48%). Yellowish oil. IR (neat): 3057*w*, 3023*w*, 2963*m*, 2951*m*, 2933*w*, 2874*w*, 1933*w*, 1701*m*, 1661*s*, 1598*m*, 1477*m*, 1436*s*, 1409*m*, 1338*m*, 1290*m*,

1229*s*, 1196*s*, 1161*s*, 1065*m*, 1024*m*, 968*m*, 907*m*, 841*m*, 815*m*, 737*s*, 697*s*, 689*s*, 628*m*, 569*w*, 530*m*. ^{1}H-NMR: 1.02 (*t*, $^3J = 7.5$, *Me*CH$_2$); 2.50 (*q*, $^3J = 7.7$, MeC*H*$_2$); 3.19 (*s*, MeO); 6.84–6.90 (*m*, 4 arom. H); 6.96–7.03 (*m*, 2 arom. H); 7.08–7.12 (*m*, 5 arom); 10.89 (*s*, OH). ^{13}C-NMR: 14.7 (Me); 24.1 (CH$_2$); 53.1 (MeO); 114.6 (*C*COOMe); 125.6 (arom. C); 127.1, 128.0 (arom. CH); 128.5 (2 arom. CH); 129.8 (2 arom. CH); 130.0 (2 arom. CH); 130.3 (2 arom. CH); 134.4, 139.3 (arom. C); 140.2 (arom. CH); 142.2, 145.6 (arom. C); 160.7 (COH); 172.7 (CO). GC/EI-MS (70 eV): 364 (34, M^+), 332 (100), 223 (37), 205 (11), 184 (7), 165 (14), 110 (9), 78 (11), 63 (9), 40 (31). HR-EI-MS: 364.1127 (M^+; $C_{22}H_{20}O_3S^+$; calc. 364.1128).

Methyl 3-Hydroxy-4-octyl-6-(phenylsulfanyl)-1,1′-biphenyl-2-carboxylate (**5c**). *GP 3* with **3a** (0.427 g, 1.5 mmol) and **4f** (0.615 g, 1.65 mmol): **5c** (0.344 g, 51%). Yellowish oil. IR (neat): 3058*w*, 3024*w*, 2952*m*, 2923*m*, 2853*m*, 1934*w*, 1703*m*, 1663*m*, 1598*w*, 1477*w*, 1437*s*, 1410*m*, 1340*m*, 1234*s*, 1197*m*, 1161*m*, 1024*m*, 905*w*, 842*m*, 813*m*, 749*m*, 698*s*, 629*m*, 616*w*, 596*w*, 572*w*, 532*w*. ^{1}H-NMR: 0.70 (*t*, $^3J = 7.5$, *Me*(CH$_2$)$_7$); 1.07–1.12 (*m*, 5 CH$_2$); 1.39–1.43 (*m*, CH$_2$); 2.45 (*t*, $^3J = 7.5$, Me(CH$_2$)$_6$C*H*$_2$); 3.19 (*s*, MeO); 6.84–6.90 (*m*, 4 arom. H); 6.95–7.03 (*m*, 3 arom. H); 7.08–7.11 (*m*, 4 arom. H); 10.87 (*s*, OH). ^{13}C-NMR: 15.3 (Me); 23.9, 30.2, 30.3, 30.5, 30.6, 30.9, 33.1 (CH$_2$); 53.0 (MeO); 114.6 (*C*COOMe); 125.4 (arom. C); 127.0, 128.0 (arom. CH); 128.4 (2 arom. CH); 129.8 (2 arom. CH); 130.0 (2 arom. CH); 130.2 (2 arom. CH); 133.1, 139.4 (arom. C); 141.1 (arom. CH); 142.2, 145.6 (arom. C); 160.7 (COH); 172.7 (CO). GC/EI-MS (70 eV): 448 (21, M^+), 416 (15), 340 (72), 308 (81), 291 (10), 210 (100), 181 (16), 152 (28), 129 (17), 116 (37), 71 (9), 57 (16), 43 (15). HR-EI-MS: 448.2068 (M^+, $C_{28}H_{32}O_3S^+$; calc. 448.2067).

Methyl 4-Decyl-3-hydroxy-6-(phenylsulfanyl)-1,1′-biphenyl-2-carboxylate (**5d**). *GP 3* with **3a** (0.427 g, 1.5 mmol) and **4g** (0.661 g, 1.65 mmol): **5d** (0.372 g, 52%). Yellowish oil. IR (neat): 3058*w*, 3024*w*, 2951*m*, 2922*s*, 2852*m*, 1938*w*, 1745*w*, 1663*m*, 1598*w*, 1582*w*, 1477*m*, 1437*s*, 1410*m*, 1340*m*, 1292*m*, 1234*m*, 1197*m*, 1162*m*, 1072*m*, 1024*m*, 999*m*, 909*w*, 842*w*, 813*m*, 737*s*, 698*s*, 689*s*, 631*w*, 596*w*, 572*w*, 531*w*. ^{1}H-NMR: 0.71 (*t*, $^3J = 7.1$, *Me*(CH$_2$)$_9$); 1.07–1.10 (*m*, 7 CH$_2$); 1.37–1.43 (*m*, CH$_2$); 2.45 (*t*, $^3J = 7.5$, Me(CH$_2$)$_8$C*H*$_2$); 3.19 (*s*, MeO); 6.84–6.90 (*m*, 4 arom. H); 7.00–7.12 (*m*, 7 arom. H); 10.87 (*s*, OH). ^{13}C-NMR: 14.1 (Me); 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.9, 31.9 (CH$_2$); 51.9 (MeO); 113.4 (*C*COOMe); 124.2 (arom. C); 125.8, 126.7, 127.2, 127.6, 128.1, 128.6 (arom. CH); 128.8 (2 arom. CH); 129.0 (2 arom. CH); 131.9, 138.2 (arom. C); 139.9 (arom. CH); 141.0, 144.4 (arom. C); 159.5 (COH); 171.5 (CO). GC/EI-MS (70 eV): 476 (14, M^+), 444 (11), 368 (35), 336 (77), 318 (9), 304 (52), 210 (100), 182 (18), 152 (16), 129 (11), 116 (22), 43 (17). HR-EI-MS: 476.2385 (M^+, $C_{30}H_{36}O_3S^+$; calc. 476.2380).

Methyl 4-Ethyl-3-hydroxy-6-[(4-methylphenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5e**). *GP 3* with **3b** (0.448 g, 1.5 mmol) and **4c** (0.476 g, 1.65 mmol): **5e** (0.210 g, 37%). Yellowish oil. IR (neat): 3054*w*, 3025*w*, 2963*m*, 2932*m*, 2908*w*, 2873*w*, 1934*w*, 1731*m*, 1662*s*, 1592*m*, 1574*m*, 1436*s*, 1413*m*, 1342*m*, 1289*m*, 1231*s*, 1197*m*, 1163*m*, 1080*m*, 1027*m*, 970*m*, 907*w*, 845*m*, 815*m*, 774*m*, 750*m*, 699*s*, 689*m*, 629*w*. ^{1}H-NMR: 1.01 (*t*, $^3J = 7.5$, *Me*CH$_2$); 2.07 (*s*, Me); 2.49 (*q*, $^3J = 7.5$, MeC*H*$_2$); 3.20 (*s*, MeO); 6.65–6.73 (*m*, 2 arom. H); 6.87–6.91 (*m*, 3 arom. H); 7.08 (*s*, 1 arom. H); 7.10–7.13 (*m*, 4 arom. H); 10.87 (*s*, OH). ^{13}C-NMR: 14.8, 22.5 (Me); 24.1 (CH$_2$); 53.1 (MeO); 114.5 (*C*COOMe); 125.9 (arom. C); 127.6, 128.0, 128.1 (arom. CH); 128.5 (2 arom. CH); 128.8, 129.2 (arom. CH); 129.9 (2 arom. CH); 134.3, 134.8, 139.8 (arom. C); 140.0 (arom. CH); 142.2, 145.3 (arom. C); 160.6 (*C*OH); 172.8 (CO). GC/EI-MS (70 eV): 378 (38, M^+), 346 (100), 254 (17), 223 (62), 205 (13), 184 (9), 165 (25), 124 (12), 105 (11), 91 (31), 77 (16), 44 (30). HR-EI-MS: 378.1282 (M^+, $C_{23}H_{22}O_3S^+$; calc. 378.1284).

Methyl 4-Decyl-3-hydroxy-6-[(4-methylphenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5f**). *GP 3* with **3b** (0.448 g, 1.5 mmol) and **4g** (0.661 g, 1.65 mmol): **5f** (0.280 g, 38%). Yellowish oil. IR (neat): 3055*w*, 3025*w*, 2951*m*, 2922*s*, 2852*m*, 1934*w*, 1749*w*, 1716*w*, 1704*w*, 1662*s*, 1592*m*, 1574*w*, 1437*s*, 1412*m*, 1339*m*, 1291*m*, 1234*s*, 1197*m*, 1162*m*, 1073*w*, 998*m*, 908*w*, 844*m*, 813*m*, 767*m*, 749*m*, 698*s*, 631*w*, 595*w*, 542*w*. ^{1}H-NMR: 0.70 (*t*, $^3J = 7.1$, *Me*(CH$_2$)$_9$); 1.07–1.10 (*m*, 7 CH$_2$); 1.38–1.47 (*m*, CH$_2$); 2.06 (*s*, Me); 2.45 (*t*, $^3J = 7.6$, Me(CH$_2$)$_8$C*H*$_2$); 3.19 (*s*, MeO); 6.65–6.69 (*m*, 2 arom. H); 6.87–6.90 (*m*, 3 arom. H); 7.07–7.12 (*m*, 5 arom); 10.86 (*s*, OH). ^{13}C-NMR: 15.3, 22.5 (Me); 23.9, 30.3, 30.5, 30.6, 30.7, 30.8, 30.9, 31.1, 33.1 (CH$_2$); 53.0 (MeO); 114.5 (*C*COOMe); 125.7 (arom. C); 127.5, 128.0 (arom. CH); 128.4 (2 arom. CH); 128.8, 129.3 (arom. CH); 129.8 (2 arom. CH); 131.0 (arom. CH); 133.0, 138.9, 139.7 (arom. C); 140.8 (arom. CH); 142.2, 145.3 (arom. C); 160.6 (COH); 172.7 (CO). GC/EI-MS (70 eV): 490 (5, M^+), 458 (6), 336 (32), 223 (11), 210 (100), 181 (19), 152 (29), 129 (14), 116 (31), 91 (16), 71 (16), 43 (33). HR-EI-MS: 490.2541 (M^+, $C_{31}H_{38}O_3S^+$; calc. 490.2536).

Methyl 6-[(4-Fluorophenyl)sulfanyl]-3-hydroxy-4-methyl-1,1′-biphenyl-2-carboxylate (**5g**). *GP 3* with **3c** (0.454 g, 1.5 mmol) and **4b** (0.453 g, 1.65 mmol): **5g** (0.238 g, 43%). Yellowish oil. IR (neat): 3059*w*, 3025*w*, 2951*w*, 2926*w*, 2902*w*, 2854*w*, 1729*w*, 1664*m*, 1613*w*, 1599*w*, 1488*m*, 1437*m*, 1408*m*, 1338*m*, 1280*m*, 1243*s*, 1228*s*, 1197*m*, 1155*m*, 1086*m*, 1013*m*, 943*w*, 827*s*, 809*s*, 760*m*, 698*s*, 678*m*, 628*m*, 595*w*, 564*w*, 548*w*. ^{1}H-NMR: 2.17 (*s*, Me); 3.30 (*s*, MeO); 6.94–6.99 (*m*, 4 arom. H); 7.18–7.25 (*m*, 6 arom. H); 10.98 (*s*, OH). ^{13}C-NMR: 14.9 (Me); 50.9 (MeO); 112.2 (*C*COOMe); 115.0 (*d*, ^2J(C,F) = 21.9); 125.9, 126.3 (arom. CH); 126.4 (arom. C); 126.6, 127.1, 127.7 (arom. CH); 131.1 (*d*, ^3J(C,F) = 8.1); 138.4 (arom. CH); 139.8, 141.3, 141.9, 142.6 (arom. C); 158.6 (COH); 160.7 (*d*, ^1J(C,F) = 246.5); 170.4 (CO). ^{19}F-NMR (285 MHz, $CDCl_3$): −115.6. GC/EI-MS (70 eV): 368 (28, M^+), 336 (100), 240 (11), 209 (26), 184 (10), 152 (15), 128 (7). HR-EI-MS: 368.0880 (M^+, $C_{21}H_{17}FO_3S^+$; calc. 368.0877).

Methyl 4-Decyl-6-[(4-fluorophenyl)sulfanyl]-3-hydroxy-1,1′-biphenyl-2-carboxylate (**5h**). *GP 3* with **3c** (0.454 g, 1.5 mmol) and **4g** (0.661 g, 1.65 mmol): **5h** (0.334 g, 45%). Yellowish oil. IR (neat): 3058*w*, 3025*w*, 2951*m*, 2922*s*, 2852*m*, 1935*w*, 1873*w*, 1746*w*, 1704*w*, 1663*m*, 1589*m*, 1556*w*, 1488*s*, 1437*s*, 1409*m*, 1339*m*, 1292*m*, 1227*s*, 1197*m*, 1155*s*, 1085*w*, 1012*w*, 999*m*, 883*w*, 822*m*, 749*m*, 698*s*, 626*m*, 598*w*, 573*w*. ^{1}H-NMR: 0.71 (*t*, ^3J = 7.1, *Me*$(CH_2)_9$); 1.07–1.10 (*m*, 7 CH_2); 1.38–1.42 (*m*, CH_2); 2.44 (*t*, ^3J = 7.4, $Me(CH_2)_8CH_2$); 3.19 (*s*, MeO); 6.69–6.74 (*m*, 2 arom. H); 6.83–6.89 (*m*, 4 arom. H); 7.11–7.13 (*m*, 4 arom. H); 10.84 (*s*, OH). ^{13}C-NMR: 15.3 (Me); 23.9, 30.3, 30.5, 30.6, 30.7 (CH_2); 30.8 (2 CH_2); 30.9, 33.1 (CH_2); 53.1 (MeO); 114.6 (*C*COOMe); 117.1 (*d*, ^2J(C,F) = 22.0); 126.3 (arom. C); 127.8 (arom. CH); 128.5 (2 arom. CH); 129.9 (2 arom. CH); 131.1 (*d*, ^3J(C,F) = 8.0); 133.8, 134.9 (arom. C); 140.1 (arom. CH); 142.1, 144.8 (arom. C); 160.5 (COH); 162.9 (*d*, ^1J(C,F) = 246.0); 172.7 (CO). ^{19}F-NMR (285 MHz, $CDCl_3$): −115.7. GC/EI-MS (70 eV): 494 (100, M^+), 462 (79), 377 (12), 335 (29), 240 (26), 209 (99), 152 (6), 128 (6). HR-EI-MS: 494.2292 (M^+, $C_{30}H_{35}FO_3S^+$; calc. 494.2286).

Methyl 3-Hydroxy-6-[(4-nitrophenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5i**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4a** (0.430 g, 1.65 mmol): **5i** (0.200 g, 35%). Yellowish oil. IR (neat): 3093*w*, 3060*w*, 3024*w*, 2959*w*, 2924*w*, 2852*w*, 1737*w*, 1666*m*, 1574*m*, 1510*m*, 1476*w*, 1437*m*, 1334*s*, 1259*m*, 1214*m*, 1083*m*, 1012*m*, 902*w*, 852*m*, 796*m*, 741*m*, 700*m*, 643*w*, 625*w*, 613*w*, 575*w*, 544*w*. ^{1}H-NMR: 3.33 (*s*, MeO); 6.88–6.93 (*m*, 4 arom. H); 7.06 (*d*, ^3J = 8.7, 1 arom. H); 7.17–7.19 (*m*, 3 arom. H); 7.60 (*d*, ^3J = 8.7, 1 arom. H); 7.91–7.94 (*m*, 2 arom. H); 11.03 (*s*, OH). ^{13}C-NMR: 51.2 (MeO); 113.6 (*C*COOMe); 118.0 (arom. CH); 120.1 (arom. C); 122.8 (2 arom. CH); 125.1 (2 arom. CH); 126.3 (arom. CH); 126.4 (2 arom. CH); 127.0 (2 arom. CH); 139.3 (arom. C); 141.1 (arom. CH); 144.1, 148.2, 148.5 (arom. C); 161.9 (COH); 169.7 (CO). GC/EI-MS (70 eV): 381 (39, M^+), 349 (100), 319 (24), 303 (7), 274 (7), 247 (10), 202 (6), 171 (23), 139 (13). HR-EI-MS: 381.0669 (M^+, $C_{20}H_{15}O_5NS^+$; calc. 381.0665).

Methyl 3-Hydroxy-4-methyl-6-[(4-nitrophenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5j**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4b** (0.453 g, 1.65 mmol): **5j** (0.285 g, 48%). Crystalline solid. M.p. 124–126°. IR (neat): 3101*w*, 3088*w*, 3059*w*, 3021*w*, 2952*w*, 2922*w*, 2903*w*, 2855*w*, 1723*w*, 1713*w*, 1668*m*, 1592*m*, 1572*m*, 1499*m*, 1475*m*, 1439*m*, 1398*m*, 1326*s*, 1243*s*, 1196*s*, 1158*s*, 1108*m*, 1018*m*, 945*m*, 884*m*, 846*s*, 810*s*, 743*s*, 678*s*, 624*m*, 542*m*. ^{1}H-NMR: 2.20 (*s*, Me); 3.26 (*s*, MeO); 6.81–6.87 (*m*, 4 arom. H); 7.08–7.13 (*m*, 3 arom. H); 7.43 (*s*, 1 arom. H); 7.83–7.88 (*m*, 2 arom. H); 11.20 (*s*, OH). ^{13}C-NMR: 14.8 (Me); 51.1 (MeO); 112.7 (*C*COOMe); 118.8 (arom. C); 122.8 (2 arom. CH); 124.9 (2 arom. CH); 126.0 (arom. CH); 126.2 (2 arom. CH); 127.1 (2 arom. CH); 127.5, 139.5 (arom. C); 141.5 (arom. CH); 144.0, 146.0, 148.7 (arom. C); 160.5 (COH); 170.2 (CO). GC/EI-MS (70 eV): 395 (27, M^+), 363 (100), 333 (25), 316 (5), 219 (38), 209 (21), 184 (9), 152 (10), 129 (10), 93 (6), 73 (12). HR-EI-MS: 395.0754 (M^+, $C_{21}H_{17}NO_5S^+$; calc. 395.0755). The structure of **5j** was secured by an X-ray crystal-structure analysis (*cf. Fig.*)[1])

Methyl 4-Ethyl-3-hydroxy-6-[(4-nitrophenyl)sulfanyl]-1-1′-biphenyl-2-carboxylate (**5k**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4c** (0.476 g, 1.65 mmol): **5k** (0.246 g, 40%). Yellowish oil. IR (neat): 3107*w*, 3089*w*, 3062*w*, 3025*w*, 2961*w*, 2929*w*, 2851*w*, 1659*m*, 1593*m*, 1575*m*, 1556*w*, 1504*m*, 1476*m*, 1434*m*, 1407*m*, 1353*m*, 1332*s*, 1260*m*, 1197*m*, 1109*m*, 1016*m*, 926*m*, 853*m*, 787*m*, 740*s*, 699*s*, 650*m*, 625*m*, 565*m*, 542*m*. ^{1}H-NMR: 1.19 (*t*, ^3J = 7.5, *Me*CH_2); 2.68 (*q*, ^3J = 7.4, MeCH_2); 3.32 (*s*, MeO); 6.86–6.93 (*m*, 4 arom. H);

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[1]) CCDC-769128 contains all crystallographic details of this publication which are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: *Cambridge Crystallographic Data Centre*, 12 Union Road, GB-Cambridge CB21EZ; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

7.13 – 7.19 (*m*, 3 arom. H); 7.48 (*s*, 1 arom. H); 7.88 – 7.94 (*m*, 2 arom. H); 11.25 (*s*, OH). ^{13}C-NMR: 12.5 (Me); 21.9 (CH_2); 51.1 (MeO); 113.0 (*C*COOMe); 119.0 (arom. C); 122.8 (2 arom. CH); 124.9 (2 arom. CH); 126.1 (arom. CH); 126.2 (2 arom. CH); 127.1 (2 arom. CH); 133.2, 139.6 (arom. C); 140.0 (arom. CH); 143.9, 146.0, 148.7 (arom. C); 160.1 (COH); 170.2 (CO). GC/EI-MS (70 eV): 409 (30, M^+), 377 (100), 347 (49), 254 (15), 223 (70), 205 (31), 184 (12), 165 (26), 129 (12), 93 (12), 69 (8). HR-EI-MS: 409.0988 (M^+, $C_{22}H_{19}NO_5S^+$; calc. 409.0978).

Methyl 3-Hydroxy-6-[(4-nitrophenyl)sulfanyl]-4-pentyl-1,1′-biphenyl-2-carboxylate (**5l**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4d** (0.546 g, 1.65 mmol): **5l** (0.325 g, 48%). Yellowish oil. IR (neat): 3058*w*, 3024*w*, 2952*w*, 2926*w*, 2857*w*, 1746*w*, 1711*w*, 1662*m*, 1632*w*, 1594*m*, 1577*m*, 1512*m*, 1438*m*, 1409*m*, 1333*s*, 1296*m*, 1233*m*, 1198*m*, 1162*m*, 1109*m*, 1011*m*, 952*w*, 852*m*, 812*m*, 750*m*, 699*m*, 681*m*, 626*w*, 543*w*. ^{1}H-NMR: 0.83 (*t*, $^3J = 7.1$, *Me*(CH_2)$_4$); 1.26 – 1.30 (*m*, 2 CH_2); 1.56 – 1.61 (*m*, CH_2); 2.63 (*t*, $^3J = 7.5$, Me(CH_2)$_3$CH_2); 3.31 (*s*, MeO); 6.86 – 6.93 (*m*, 4 arom. H); 7.15 – 7.19 (*m*, 3 arom. H); 7.46 (*s*, 1 arom. H); 7.89 – 7.92 (*m*, 2 arom. H); 11.23 (*s*, OH). ^{13}C-NMR: 13.0 (Me); 21.5, 27.8, 28.7, 30.6 (CH_2); 51.1 (MeO); 113.0 (*C*COOMe); 118.9 (arom. C); 122.8 (2 arom. CH); 124.9 (2 arom. CH); 126.1 (arom. CH); 126.3 (2 arom. CH); 127.1 (2 arom. CH); 132.0, 139.6 (arom. C); 140.8 (arom. CH); 143.9, 146.0, 148.8 (arom. C); 160.1 (COH); 170.2 (CO). GC/EI-MS (70 eV): 451 (64, M^+), 419 (70), 402 (10), 389 (40), 363 (11), 346 (46), 265 (25), 240 (22), 209 (100), 152 (11). HR-EI-MS: 451.1457 (M^+, $C_{25}H_{25}NO_5S^+$; calc. 451.1448).

Methyl 4-Hexyl-3-hydroxy-6-[(4-nitrophenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5m**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **3e** (0.569 g, 1.65 mmol): **5m** (0.293 g, 42%). Yellowish oil. IR (neat): 3059*w*, 3024*w*, 2953*w*, 2926*m*, 2855*w*, 2258*w*, 1932*w*, 1664*m*, 1594*w*, 1578*m*, 1514*w*, 1438*m*, 1409*m*, 1333*s*, 1234*m*, 1198*m*, 1161*m*, 1110*w*, 1085*m*, 1010*w*, 907*m*, 851*m*, 839*m*, 768*m*, 729*s*, 698*s*, 681*m*, 648*m*, 626*w*, 544*w*. ^{1}H-NMR: 0.71 (*t*, $^3J = 6.8$, *Me*(CH_2)$_5$); 1.08 – 1.19 (*m*, 3 CH_2); 1.40 – 1.50 (*m*, CH_2); 2.53 (*t*, $^3J = 7.5$, Me(CH_2)$_4$CH_2); 3.21 (*s*, MeO); 6.76 – 6.83 (*m*, 4 arom. H); 7.03 – 7.08 (*m*, 3 arom. H); 7.36 (*s*, 1 arom. H); 7.79 – 7.83 (*m*, 2 arom. H); 11.13 (*s*, OH). ^{13}C-NMR: 15.3 (Me); 23.8, 30.3, 30.4, 31.0, 32.8 (CH_2); 53.3 (MeO); 115.2 (*C*COOMe); 121.1 (arom. C); 125.0 (2 arom. CH); 127.1 (2 arom. CH); 128.3 (arom. CH); 128.5 (2 arom. CH); 129.3 (2 arom. CH); 134.2, 141.8 (arom. C); 143.0 (arom. CH); 146.1, 148.2, 151.0 (arom. C); 162.3 (COH); 172.4 (CO). GC/EI-MS (70 eV): 465 (100, M^+), 403 (24), 346 (80), 316 (9), 279 (22), 209 (96), 152 (11). HR-EI-MS: 465.1679 (M^+, $C_{26}H_{27}NO_5S^+$; calc. 465.1683).

Methyl 3-Hydroxy-6-[(4-nitrophenyl)sulfanyl]-4-octyl-1,1′-biphenyl-2-carboxylate (**5n**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4f** (0.615 g, 1.65 mmol): **4n** (0.333 g, 45%). Yellowish oil. IR (neat): 2953*m*, 2923*m*, 2853*m*, 1746*w*, 1714*w*, 1664*m*, 1627*w*, 1595*w*, 1579*w*, 1516*m*, 1438*m*, 1408*m*, 1334*s*, 1233*m*, 1198*m*, 1162*m*, 1085*m*, 1011*m*, 909*w*, 852*m*, 814*m*, 741*m*, 699*m*, 681*m*, 626*w*, 543*w*. ^{1}H-NMR: 0.81 (*t*, $^3J = 6.9$, *Me*(CH_2)$_7$); 1.17 – 1.22 (*m*, 5 CH_2); 1.53 – 1.60 (*m*, CH_2); 2.63 (*t*, $^3J = 7.5$, Me(CH_2)$_6$CH_2); 3.31 (*s*, MeO); 6.86 – 6.93 (*m*, 3 arom. H); 7.15 – 7.19 (*m*, 4 arom. H); 7.46 (*s*, 1 arom. H); 7.90 – 7.93 (*m*, 2 arom. H); 11.23 (*s*, OH). ^{13}C-NMR: 13.1 (Me); 21.6, 28.1, 28.3, 28.4, 28.6, 28.7, 30.8 (CH_2); 51.1 (MeO); 113.0 (*C*COOMe); 118.8 (arom. C); 122.8 (2 arom. CH); 124.9 (2 arom. CH); 126.1 (arom. CH); 126.3 (2 arom. CH); 127.1 (2 arom. CH); 132.0, 139.6 (arom. C); 140.8 (arom. CH); 143.9, 146.0, 148.8 (arom. C); 160.1 (COH); 170.2 (CO). GC/EI-MS (70 eV): 493 (6, M^+), 463 (90), 431 (100), 405 (10), 374 (12), 333 (16), 307 (23), 253 (16), 240 (89), 221 (23), 209 (98), 184 (22), 152 (35), 124 (55), 105 (22), 93 (56), 55 (51). HR-EI-MS: 493.1849 (M^+, $C_{28}H_{31}NO_5S^+$; calc. 493.1850).

Methyl 4-Decyl-3-hydroxy-6-[(4-nitrophenyl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5o**). *GP 3* with **3d** (0.494 g, 1.5 mmol) and **4g** (0.661 g, 1.65 mmol): **5o** (0.391 g, 50%). Yellowish oil. IR (neat): 2952*w*, 2922*m*, 2852*m*, 1934*w*, 1748*w*, 1704*w*, 1664*m*, 1594*w*, 1578*m*, 1515*m*, 1438*m*, 1408*m*, 1334*s*, 1233*m*, 1198*m*, 1163*m*, 1085*m*, 1010*m*, 909*w*, 851*m*, 814*m*, 741*m*, 698*m*, 681*m*, 626*w*, 543*w*. ^{1}H-NMR: 0.70 (*t*, $^3J = 6.8$, *Me*(CH_2)$_9$); 1.07 – 1.11 (*m*, 7 CH_2); 1.40 – 1.50 (*m*, CH_2); 2.53 (*t*, $^3J = 7.4$, Me(CH_2)$_8$CH_2); 3.21 (*s*, MeO); 6.76 – 6.82 (*m*, 4 arom. H); 7.05 – 7.09 (*m*, 3 arom. H); 7.36 (*s*, 1 arom. H); 7.79 – 7.82 (*m*, 2 arom. H); 11.12 (*s*, OH). ^{13}C-NMR: 15.3 (Me); 23.9, 30.3, 30.5, 30.6, 30.7, 30.8, 30.9, 31.0, 33.1 (CH_2); 53.3 (MeO); 115.2 (*C*COOMe); 121.0 (arom. C); 125.0 (2 arom. CH); 127.1 (2 arom. CH); 128.3 (arom. CH); 128.5 (2 arom. CH); 129.3 (2 arom. CH); 134.2, 141.8 (arom. C); 143.0 (arom. CH); 146.1, 148.2, 151.0 (arom. C); 162.3 (COH); 172.4 (CO). GC/EI-MS (70 eV): 521 (97, M^+), 489 (50), 472 (11), 459 (22), 404 (13), 362 (29), 346 (44), 335 (19), 240 (17), 209 (100), 180 (7), 152 (9), 116 (21), 101 (9). HR-EI-MS: 521.2303 (M^+, $C_{30}H_{35}NO_5S^+$; calc. 521.2309).

Methyl 6-(Benzylsulfanyl)-4-ethyl-3-hydroxy-1,1′-biphenyl-2-carboxylate (**5p**). *GP 3* with **3e** (0.448 g, 1.5 mmol) and **4c** (0.476 g, 1.65 mmol): **5p** (0.267 g, 47%). Yellowish oil. IR (neat): 3060*w*, 3027*w*, 2963*w*, 2932*w*, 2873*w*, 1935*w*, 1728*w*, 1662*m*, 1597*m*, 1494*w*, 1435*m*, 1337*m*, 1276*m*, 1230*m*, 1196*m*, 1160*m*, 1069*m*, 1013*m*, 969*m*, 843*m*, 748*m*, 696*s*, 646*m*, 629*m*, 562*m*. ^{1}H-NMR: 1.10 (*t*, $^3J = 7.5$, *Me*CH$_2$); 1.48 (*s*, CH$_2$); 2.57 (*q*, $^3J = 7.3$, MeC*H*$_2$); 3.28 (*s*, MeO); 6.93–6.97 (*m*, 4 arom. H); 7.18–7.23 (*m*, 7 arom. H); 10.85 (*s*, OH). ^{13}C-NMR: 12.5 (Me); 21.8, 39.2 (CH$_2$); 50.8 (MeO); 112.1 (*C*COOMe); 125.7, 125.9 (arom. CH); 126.2 (2 arom. CH); 126.6, 127.1 (arom. C); 127.3 (2 arom. CH); 127.5 (arom. CH); 127.9 (2 arom. CH); 128.4 (arom. CH); 136.4, 136.5 (arom. C); 137.0 (arom. CH); 140.1 (arom. C); 157.7 (COH); 170.5 (CO). GC/EI-MS (70 eV): 378 (2, M^+), 346 (5), 255 (8), 120 (50), 105 (100), 91 (94), 77 (51), 65 (22), 51 (18). HR-EI-MS: 378.1283 (M^+, $C_{23}H_{22}O_3S^+$; calc. 378.1284).

Methyl 4-Ethyl-3-hydroxy-6-[(naphthalen-2-yl)sulfanyl]-1,1′-biphenyl-2-carboxylate (**5q**). *GP 3* with **3f** (0.502 g, 1.5 mmol) and **4c** (0.476 g, 1.65 mmol): **5q** (0.324 g, 52%). Yellowish oil. IR (neat): 3052*w*, 3024*w*, 2963*w*, 2950*w*, 2932*w*, 2873*w*, 1932*w*, 1698*w*, 1660*s*, 1591*m*, 1499*w*, 1435*m*, 1337*m*, 1290*m*, 1229*s*, 1195*m*, 1161*m*, 1063*m*, 967*m*, 847*m*, 743*s*, 697*s*, 628*m*, 600*m*, 529*m*. ^{1}H-NMR: 1.00 (*t*, $^3J = 7.5$, *Me*CH$_2$); 2.47 (*q*, $^3J = 7.5$, MeC*H*$_2$); 3.20 (*s*, MeO); 6.89–6.99 (*m*, 3 arom. H); 7.07–7.10 (*m*, 3 arom. H); 7.22–7.28 (*m*, 4 arom. H); 7.45–7.49 (*m*, 2 arom. H); 7.55–7.58 (*m*, 1 arom. H); 10.93 (*s*, OH). ^{13}C-NMR: 14.8 (Me); 24.2 (CH$_2$); 53.1 (MeO); 114.6 (*C*COOMe); 125.5 (arom. C); 126.9, 127.7, 128.1, 128.4 (arom. CH); 128.5 (2 arom. CH); 128.8, 128.9, 129.4, 129.6, (arom. CH); 129.8 (2 arom. CH); 133.0, 134.6, 134.9, 136.7 (arom. C); 140.2 (arom. CH); 142.2, 145.6 (arom. C); 160.8 (COH); 172.7 (CO). GC/EI-MS (70 eV): 414 (37, M^+), 382 (100), 254 (35), 223 (40), 160 (31), 128 (47), 77 (9), 63 (7), 44 (8). HR-EI-MS: 414.1286 (M^+, $C_{26}H_{22}O_3S^+$; calc. 414.1284).

Financial support from the *State of Mecklenburg-Vorpommern* (scholarship for *M. S.* and to *M. H.*) is gratefully acknowledged.

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Received November 9, 2009