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Suzuki–Miyaura reactions of the bis(triflates) of 1,3- and 1,4-dihydroxythioxanthone. Electronic and steric effects on the site-selectivity

Dhafer Saber Zinad [a], Holger Feist [a], Alexander Villinger [a], Peter Langer [a,b,*]

[a] Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
[b] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

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ABSTRACT

The palladium(0)-catalyzed Suzuki cross-coupling reactions of the bis(triflates) of 1,3- and 1,4-dihydroxythioxanthone afforded various aryl-substituted thioxanthones. While the Suzuki reactions of the bis(triflate) derived from 1,3-dihydroxythioxanthone proceeded by site-selective attack in favor of position 3, the reactions of the bis(triflate) of 1,4-dihydroxythioxanthone proceeded in favor of position 1. The site-selectivity is controlled by steric and electronic parameters.

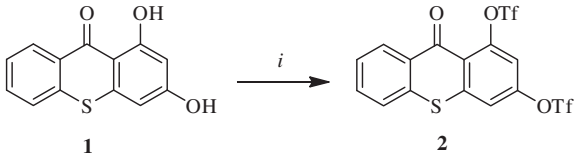
1. Introduction

Thioxanthones are present in various pharmacologically active natural products. For example, lucanthone and hycanthone have been reported to be active against murine pancreatic adenocarcinoma.[1] A number of plants, such as *Cartoxylum cochinchinense* (Lour.), contain thioxanthone-derived natural products and have been used as traditional medicines. Synthetic thioxanthones also exhibit a wide range of pharmacological activities including anti-tumor and antibiotic activity.[2] Thioxanthone-derived sulfones are known to be active against various tumors and inhibit monoamine oxidase activity (MAO).[3] In the field of material sciences, thioxanthones are used as activators in the photopolymerization of acrylates and as stabilizers of polyolefins.[4]

Classic syntheses of thioxanthones include the reaction of 2-chlorobenzoates with thiophenols and the reaction of thiosalicylic acids with benzene derivatives and subsequent intramolecular Friedel–Crafts acylation.[2] Despite their utility, these methods have several drawbacks, such as low yields or low regioselectivities. In recent years, site-selective Suzuki–Miyaura reactions of polyhalides[5] and polytriflates[6] have been extensively studied. Recently, we have reported the synthesis of arylated thioxanthones based on Suzuki–Miyaura reactions of the bis(triflate) of 1,3-dihydroxythioxanthone.[7] Herein, we report full details of this work and an extension of the preparative scope. In addition, we report, for the first time, Suzuki–Miyaura reactions of the bis(triflate) of 1,4-dihydroxythioxanthone. Interestingly, the Suzuki reactions of the bis(triflates) of 1,3- and 1,4-dihydroxythioxanthone proceed with different site-selectivities, which can be explained by a combination of steric and electronic reasons.

2. 1,3-Dihydroxythioxanthone

Bis(triflate) **2** was prepared by reaction of 1,3-dihydroxythioxanthone (**1**), prepared from thiosalicylic acid,[8] with triflic anhydride (Scheme 1).



1 2

Scheme 1. Synthesis of **2**. Reagents and conditions: (i) CH_2Cl_2, 1 (1.0 equiv), Et_3N (4.0 equiv), Tf_2O (2.4 equiv), −78 °C→20 °C, 8 h.

The Suzuki–Miyaura reaction of **2** with 2.4 equiv of arylboronic acids **3a**–**g** gave the 1,3-diarylthioxanthones **4a**–**g** (Scheme 2, Table 1). Good yields were obtained both for reactions of electron rich and poor arylboronic acids. The best yields were obtained

* Corresponding author. Fax: +49 381 4986412; e-mail address: peter.langer@uni-rostock.de (P. Langer).

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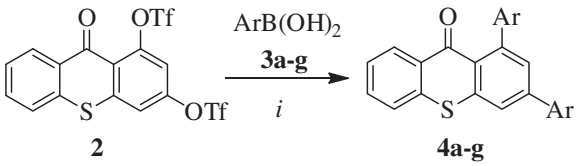


Scheme 2. Synthesis of **4a**–**g**. Reagents and conditions: (i) **2** (1.0 equiv), **3a**–**g** (2.4 equiv), $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (3.0 equiv), 1,4-dioxane, 90 °C, 8 h.

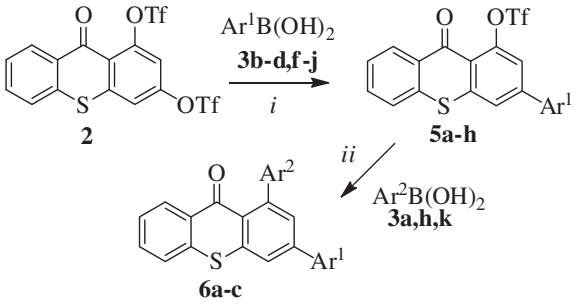
Table 1
Synthesis of **4a**–**g**

3,4	Ar	4[a] (%)
a	2-(MeO)C_6H_4	90
b	4-EtC_6H_4	81
c	4-*t*-BuC_6H_4	86
d	3,5-$Me_2C_6H_3$	77
e	4-MeC_6H_4	84
f	4-ClC_6H_4	70
g	3-(CF_3)C_6H_4	75

[a] Yields of isolated products.

when the reactions were carried out using $Pd(PPh_3)_4$ as the catalyst and K_3PO_4 as the base (dioxane, 90 °C, 8 h).

3-Aryl-1-(trifluorosulfonyloxy)-thioxanthones **5a**–**h** were prepared by reaction of **2** with 1.1 equiv of arylboronic acids **3b**–**d**,**f**–**j** (Scheme 3, Table 2). The first attack occurs at position 3. It proved to be important to carry out the reaction at 60 instead of 90 °C in order to induce a good site-selectivity and to avoid double attack. Good yields were again obtained for reactions of both electron rich and poor arylboronic acids.



Scheme 3. Synthesis of **5a**–**h** and **6a**–**c**. Reagents and conditions: (i) **2** (1.0 equiv), **3b**–**d**,**f**–**j** (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), THF, 60 °C, 8 h; (ii) **5b**,**c**,**f** (1.0 equiv), **3a**,**h**,**k** (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), 1,4-dioxane, 90 °C, 6 h.

Table 2
Synthesis of **5a**–**h** and **6a**–**c**

5	6	Ar[1]	5[a] (%)	Ar[2]	6[a] (%)
a		4-(MeO)C_6H_4	87		
b	**a**	4-EtC_6H_4	84	2-(MeO)C_6H_4	82
c	**b**	4-*t*-BuC_6H_4	75	4-(MeO)C_6H_4	79
d		3,5-$Me_2C_6H_3$	82		
e		C_6H_5	71		
f	**c**	4-ClC_6H_4	78	3,4-$(MeO)_2C_6H_3$	71
g		3-(CF_3)C_6H_4	81		
h		4-FC_6H_4	80		

[a] Yields of isolated products.

Products **5a** and **5f** were selected for optimization studies (Table 3). Thioxanthone **5a** is derived from an electron rich arylboronic acid, while **5f** is derived from an electron poor arylboronic acid. During the optimization, we have found that the best yields were obtained when the reactions were carried out at 60 °C. Higher temperatures led to the formation of significant amounts of bis-arylated products. The employment of potassium phosphate gave better yields than the use of an aqueous solution of potassium carbonate. The use of $Pd(PPh_3)_4$ gave higher yields than the use of $[Pd(PPh_3)_2Cl_2]$. In addition, it proved to be important to use exactly 1.1 equiv of the arylboronic acids. While the use of 1,4-dioxane as the solvent gave the best results in case of the synthesis of 1,3-diarylthioxanthones **4**, it was observed that employment of THF was advantageous in case of monoarylated products **5**. The diarylated products **6a**–**c** have been synthesized in two steps. Products **5b**,**c**,**f** were isolated from the first step and reacted with the second arylboronic acids **3a**,**h**,**k** (71–82%) yields (Scheme 3, Table 2).

Table 3
Optimization of the synthesis of **5a** and **5f** (all reactions were carried out at 60 °C for 8 h)

Entry	Base[a]	Solvent[b]	Catalyst[c]	5a[d] (%)	5f[d] (%)
1	K_2CO_3	Dioxane	$[Pd(PPh_3)_2Cl_2]$	35	24
2	K_2CO_3	THF	$[Pd(PPh_3)_2Cl_2]$	41	32
3	K_2CO_3	Dioxane	$[Pd(PPh_3)_4]$	46	37
4	K_2CO_3	THF	$[Pd(PPh_3)_4]$	41	33
5	K_3PO_4	Dioxane	$[Pd(PPh_3)_2Cl_2]$	55	47
6	K_3PO_4	THF	$[Pd(PPh_3)_2Cl_2]$	66	50
7	K_3PO_4	Dioxane	$[Pd(PPh_3)_4]$	63	57
8	K_3PO_4	THF	$[Pd(PPh_3)_4]$	87	78

[a] 1.5 equiv per 0.197 mmol of **2**.
[b] 5 mL per 0.197 mmol of **2**.
[c] 5 mol % per 0.197 mmol of **2**.
[d] Yields of isolated products.

The structure of **5c** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[9]

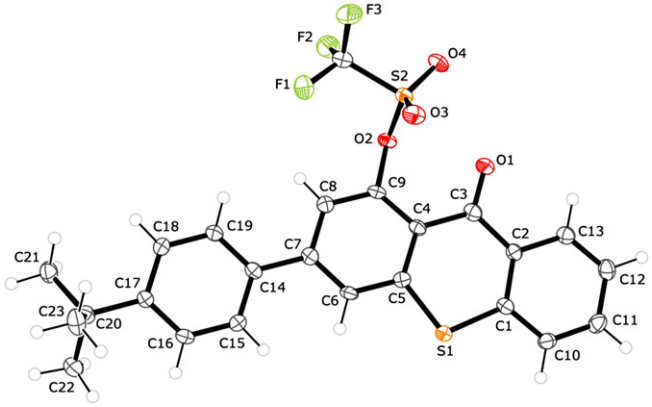
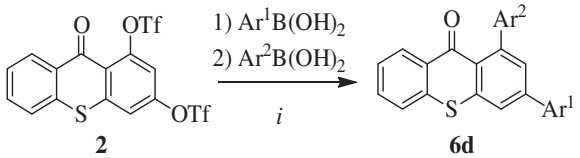


Fig. 1. Crystal structure of **5c**.

The sequential addition of two different arylboronic acids to **2** allowed for the direct synthesis of 1,3-diarylthioxanthone **6d** in only one step (75% yield) (Scheme 4, Table 4). Based on our findings related to the synthesis of monoarylated products **5**, the first step of the one-pot reaction was carried out at 60 °C while the second step was carried out at 90 °C. One portion of the catalyst (5 mol %) was added at the start of the reaction. It was not necessary to add a second portion later on.



Scheme 4. Synthesis of **6d**. Reagents and conditions: (i) (1) **2** (1.0 equiv), **3l** (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), 1,4-dioxane, 60 °C, 6 h; (2) **3h** (1.1 equiv), 90 °C, 6 h.

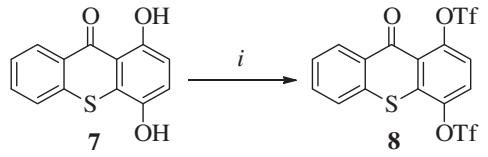
Table 4
Synthesis of **6d**

6	3	Ar[1]	Ar[2]	6[a] (%)
d	**l**, **h**	2-MeC_6H_4	4-(MeO)C_6H_4	75

[a] Yields of isolated products.

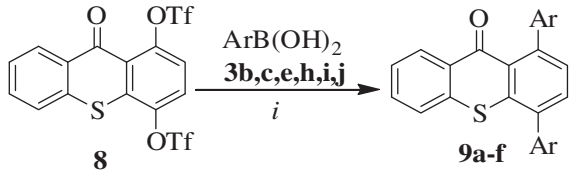
3. 1,4-Dihydroxythioxanthone

1,4-Dihydroxythioxanthone (**7**) was prepared, following a known procedure, by reaction of thiosalicylic acid with 1,4-benzoquinone.[10] Bis(triflate) **8** was prepared by reaction of **7** with triflic anhydride (Scheme 5).



Scheme 5. One-pot synthesis of **8**. Reagents and conditions: (i) CH_2Cl_2, 7 (1.0 equiv), NEt_3, pyridine, Tf_2O (2.4 equiv), −78 °C→20 °C, 8 h.

The Suzuki reaction of **8** with 2.4 equiv of arylboronic acids **3** gave the 1,4-diarylthioxanthones **9a**–**f** in 80–92% yields (Scheme 6, Table 5). The reactions were carried at the same conditions as reported for the synthesis of products **4**.



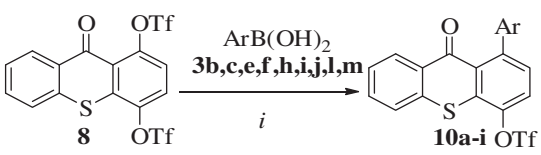
Scheme 6. Synthesis of **9a**–**f**. Reagents and conditions: (i) **2** (1.0 equiv), **3** (2.4 equiv), $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (3.0 equiv), THF, 90 °C, 8 h.

Table 5
Synthesis of **9a**–**f**

9	3	Ar	9[a] (%)
a	**b**	4-EtC_6H_4	80
b	**c**	*t*-BuC_6H_4	83
c	**e**	4-MeC_6H_4	84
d	**h**	4-(MeO)C_6H_4	92
e	**i**	C_6H_5	91
f	**j**	4-FC_6H_4	82

[a] Yields of isolated products.

The reaction of **8** with 1.1 equiv of arylboronic acids **3** afforded the 1-aryl-4-(trifluorosulfonyloxy)-thioxanthones **10a**–**i** (Scheme 7, Tables 6 and 7). The first attack occurred at position 1. As for the synthesis of products **5**, it proved to be important to carry out the reaction at 65 instead of 90 °C to induce a good site-selectivity. Good yields were again obtained both for reactions of electron rich and poor arylboronic acids.



Scheme 7. Synthesis of **10a**–**i**. Reagents and conditions: (i) **8** (1.0 equiv), **3b**,**c**,**e**,**f**,-**h**,**i**,**j**,**l**,**m** (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), THF, 65 °C, 8 h.

Table 6
Optimization of the synthesis of **10e** and **10d** at 65°C for 8 h

Entry	Base[a]	Solvent[b]	Catalyst[c]	**10e**[d] (%)	**10d**[d] (%)
1	K_2CO_3	Dioxane	$[Pd(PPh)_3Cl_2]$	33	22
2	K_2CO_3	THF	$[Pd(PPh)_3Cl_2]$	44	39
3	K_2CO_3	Dioxane	$[Pd(PPh_3)_4]$	41	40
4	K_2CO_3	THF	$[Pd(PPh_3)_4]$	42	33
5	K_3PO_4	Dioxane	$[Pd(PPh)_3Cl_2]$	51	48
6	K_3PO_4	THF	$[Pd(PPh)_3Cl_2]$	56	50
7	K_3PO_4	Dioxane	$[Pd(PPh_3)_4]$	60	52
8	K_3PO_4	THF	$[Pd(PPh_3)_4]$	81	84

[a] 1.5 equiv per 0.197 mmol of **8**.
[b] 5 mL per 0.197 mmol of **8**.
[c] 5 mol % (scale: 0.197 mmol of **8**).
[d] Yields of isolated products.

Table 7
Synthesis of **10a**–**i**

10	3	Ar	10[a] (%)
a	**b**	4-EtC_6H_4	90
b	**c**	4-*t*-BuC_6H_4	76
c	**e**	4-MeC_6H_4	87
d	**f**	4-ClC_6H_4	84
e	**h**	4-(MeO)C_6H_4	81
f	**i**	C_6H_5	88
g	**j**	4-FC_6H_4	82
h	**l**	2-MeC_6H_4	76
i	**m**	3-MeC_6H_4	79

[a] Yields of isolated products.

Compounds **10e** and **10d** have been used for the optimization of the reaction conditions for the synthesis of monoarylated thioxanthones (Table 6). The best yields were obtained when THF was used as the solvent and $Pd(PPh_3)_4$ (5 mol %) as the catalyst.

The structure of product **10e** was unambiguously confirmed by 2D NMR experiments (Fig. 2). In the NOESY spectrum, an interaction was observed between the aromatic proton 2-H and the aromatic protons 2′-H and 6′-H.

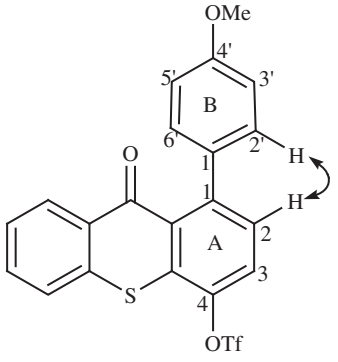


Fig. 2. Diagnostic NOESY correlation for **10e**.

The structure of **10a** was independently confirmed by X-ray crystal structure analysis (Fig. 3).[9]

The one-pot reaction of **8** with two different arylboronic acids allowed for the synthesis of 1,4-diarylthioxanthones **11a**–**d** in only one step and in very good yields (Scheme 8, Table 8). Based on our findings related to the synthesis of monoarylated products **5**, the first step of the one-pot reaction was carried out at 65 °C, while the second step was carried out at 90 °C. One portion of the catalyst (5 mol %) was added at the start of the reaction.

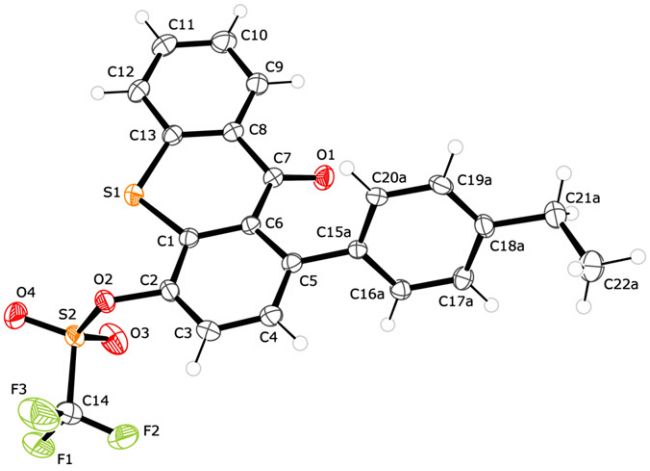
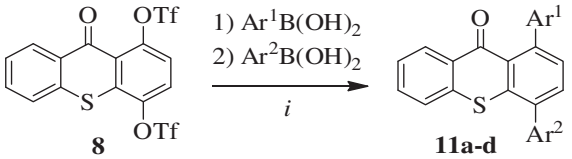


Fig. 3. Crystal structure of **10a**.



Scheme 8. Synthesis of **11a–d**. Reagents and conditions: (i) (1) **8** (1.0 equiv), **3h**,**j**,**h**,**h** (1.1 equiv), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (1.5 equiv), THF, 65 °C, 8 h; (2) **3e**,**h**,**c**,**n** (1.1 equiv), 90 °C, 6 h.

Table 8
Synthesis of **11a–d**

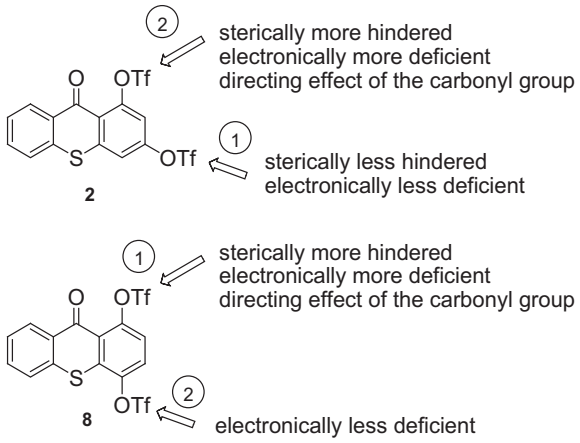
11	3	Ar^1	Ar^2	11[a] (%)
a	**h**,**e**	4-(MeO)C_6H_4	4-MeC_6H_4	90
b	**j**,**h**	4-FC_6H_4	4-(MeO)C_6H_4	88
c	**h**,**c**	4-(MeO)C_6H_4	4-*t*-BuC_6H_4	84
d	**h**,**n**	4-(MeO)C_6H_4	3-ClC_6H_4	89

[a] Yields of isolated products.

4. Conclusions

The site-selectivity of palladium catalyzed reactions of polyhalides or -triflates is generally controlled by steric and electronic parameters. The first attack usually occurs at the sterically less hindered or electronically more deficient position.[11] The Suzuki reaction of the bis(triflate) **2** proceeds by initial attack to the sterically less hindered position 3, while the reaction of bis(triflate) **8** proceeds by initial attack at the sterically more hindered position 1. This striking difference might be explained as follows: carbon atom 1 is the most electron deficient position, but it is sterically more hindered than positions 4 and 3. In addition, the carbonyl group may direct the catalyst to the *ortho* position 1. In case of compound **2**, the first attack occurs at the sterically less hindered position 3. The attack to carbon atom C-4 of thioxanthone **8** might be hindered by the lone pairs of the sulfur atom. In addition, position 3, located *para* to the carbonyl group, is expected to be more electronically deficient than position 4. Therefore, the attack occurs at position 1 in case of bis(triflate) **8**, but at position 3 in case of bis(triflate) **2** (Scheme 9).

The reactions reported herein provide a convenient and regioselective approach to a variety of arylated thioxanthones, which are not readily available by other methods.



Scheme 9. Possible explanation for the site-selectivity of the reactions of bis(triflates) **2** and **8**.

5. Experimental section

5.1. General

*5.1.1. Synthesis of 9-oxo-9H-thioxanthene-1,3-diyl bis(trifluoromethanesulfonate) (**2**).* To a solution of **1** (0.34 g, 1.39 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (0.77 mL, 5.56 mmol) at 20 °C under an argon atmosphere. After stirring for 10 min at −78 °C, Tf_2O (0.56 mL, 3.34 mmol) was added. The mixture was allowed to warm to 20 °C and stirred for further 8 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was chromatographed without work up (flash silica gel, heptanes/EtOAc) and **2** was isolated as a yellow solid (0.57 g, 80%). Mp 149–150 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.11(d, 1H, J=2.37 Hz, ArH), 7.45–7.51(m, 3H, ArH), 7.58–7.65 (m, 1H, ArH), 8.50 (dd, 1H, J=1.02, 8.5 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−72.3, −73.2. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=114.7 (CH), 118.6 (q, $J_{F,C}$=321.3 Hz, CF_3), 118.7 (q, $J_{F,C}$=320.9 Hz, CF_3), 118.9, 125.4, 127.7 (CH), 129.9 (C), 130.3, 133.3 (CH), 134.3, 142.7, 149.9, 150.8 (C), 177.8 (CO). IR (KBr): ν=3081, 3030, 2958, 2923, 2851, 1728 (w), 1602, 1599, 1590 (m), 1554, 1465 (w), 1426 (s), 1399 (m), 1317, 1295 (w), 1246 (m), 1198 (s), 1150 (m), 1133, 1099 (s), 1080 (m), 1033 (w), 989, 929, 904, 884, 819, 807, 798 (m), 768 (w), 751, 714 (m), 684, 666, 655, 635 (w), 590, 569, 542, 530 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=508 ($[M+H]^+$, 100), 347 (28), 283 (62), 255 (19). HRMS (EI): calcd for $C_{15}H_6F_6O_7S_3$ $[M]^+$: 507.91744; found: 507.916890.

5.2. General procedure for Suzuki–Miyaura reactions

A THF solution (4–5 mL) of K_3PO_4 (1.5 equiv per cross-coupling), $Pd(PPh_3)_4$ (5 mol% per cross-coupling), and arylboronic acid **3** (1.1 equiv per cross-coupling) was stirred at 65–90 °C for 8–10 h. After cooling to 20 °C, water was added. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptanes/EtOAc).

*5.2.1. Synthesis of 1,3-bis(2-methoxyphenyl)-9H-thioxanthen-9-one (**4a**).* Starting with **2** (100 mg, 0.197 mmol), 2-methoxyphenylboronic acid **3a** (72 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol%), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4a** was isolated as a light yellow solid (75 mg, 90%); reaction temperature: 90 °C for 8 h. Mp 163–165 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.72 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.87 (dd, 1H, J=0.71, 8.19 Hz, ArH), 6.93 (d, 1H, J=8.04 Hz, ArH), 6.97–7.02 (m, 2H, ArH), 7.19–7.36 (m, 6H, ArH), 7.46 (d, 2H, J=1.79 Hz, ArH), 7.68 (d, 1H, J=1.77 Hz, ArH),

8.23 (dt, 1H, J=0.96, 8.01 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.5 (OCH_3), 55.7 (OCH_3), 110.3, 111.4, 120.7, 121.0, 125.3, 125.9, 126.1 (CH), 127.0 (C), 128.4, 129.1, 129.4, 129.8, 130.9, 131.5 (CH), 131.6 (C), 131.8 (CH), 132.7, 136.2, 137.1, 141.2, 141.5, 156.1, 156.3 (C), 181.0 (CO). IR (KBr): ν=3377, 3056, 2997, 2930, 2833, 2247 (w), 1640, 1587 (s), 1536 (w), 1492, 1460, 1434 (s), 1485 (m), 1299, 1270 (m), 1238 (s), 1178, 1157, 1117 (m), 1074, 1057, 1047 (w), 1022 (s), 963 (w), 924 (m), 906, 877, 851(w), 834 (m), 807, 785, 771 (w), 746, 736, 722 (s), 678, 666 (m), 645, 615, 574, 552 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=423 ([M−H]$^+$, 100), 394 (29), 377 (39). HRMS (EI): calcd for $C_{27}H_{20}O_3S$ [M]$^+$: 424.11277; found: 424.11227.

*5.2.2. Synthesis of 1,3-bis(4-ethylphenyl)-9H-thioxanthen-9-one (**4b**).* Starting with **2** (100 mg, 0.197 mmol), 4-ethylphenylboronic acid **3b** (70 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4b** was isolated as a light yellow solid (67 mg, 81%); reaction temperature: 90 °C for 8 h. Mp 179–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.18 (t, 3H, J=7.59 Hz, CH_3), 1.21 (t, 3H, J=7.59 Hz, CH_3), 2.60 (q, 2H, J=7.59 Hz, CH_2), 2.67 (q, 2H, J=7.59 Hz, CH_2), 7.17–7.22 (m, 6H, ArH), 7.26–7.32 (m, 1H, ArH), 7.40 (d, 1H, J=1.86 Hz, ArH), 7.40–7.46 (m, 2H, ArH), 7.50 (d, 2H, J=8.25 Hz, ArH), 7.64 (d, 1H, J=1.86 Hz, ArH), 8.26 (dd, 1H, J=0.75, 8.49 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=15.3 (CH_3), 15.5 (CH_3), 28.6 (CH_2), 28.7 (CH_2), 122.9, 125.2 (CH), 125.9 (C), 126.1, 127.3, 127.4, 127.9, 128.6, 129.4, 129.8 (CH), 131.6 (C), 131.8 (CH), 135.9, 136.0, 138.9, 140.9, 142.6, 143.4, 145.1, 140.8 (C), 180.7 (CO). IR (KBr): ν=3050, 3022, 2961, 2927, 2891, 2871, 2853 (w), 1644 (s), 1612 (w), 1588 (s), 1556, 1537 (w), 1510 (m), 1469, 1455 (w), 1432 (m), 1380, 1316 (w), 1298 (s), 1286 (m), 1231, 1184, 1162 (w), 1152, 1115, 1074 (m), 1051 (w), 1031 (m), 1017, 966 (w), 924 (m), 892, 875(w), 833 (m), 821 (s), 770 (w), 749, 720 (s), 672 (m), 659, 651, 640, 615, 591, 574, 566 (w), 553 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=420 ([M]$^+$, 53), 419 ([M−H]$^+$, 100), 404 (11). HRMS (EI): calcd for $C_{29}H_{23}OS$ [M−H]$^+$: 419.14641; found: 419.14579.

*5.2.3. Synthesis of 1,3-bis(4-(tert-butyl)phenyl)-9H-thioxanthen-9-one (**4c**).* Starting with **2** (100 mg, 0.197 mmol), 4-*tert*-butylphenylboronic acid **3c** (84 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4c** was isolated as a light yellow solid (80 mg, 86%); reaction temperature: 90 °C for 8 h. Mp 123–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.28 (s, 9H, $3CH_3$), 1.33 (s, 9H, $3CH_3$), 7.20 (d, 2H, 8.49 Hz, ArH), 7.28–7.33 (m, 1H, ArH), 7.35–7.40 (m, 3H, ArH), 7.42–7.48 (m, 4H, ArH), 7.54 (d, 2H, J=8.6 Hz, ArH), 7.66 (d, 1H, J=1.89 Hz, ArH), 8.27 (d, 1H, J=7.80 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.3 (CH_3), 30.5 (CH_3), 33.4, 33.5 (C), 121.9, 123.8, 124.2, 124.9, 125.1 (CH), 125.6 (C), 126.0, 126.7, 128.6, 128.8 (CH), 130.6 (C), 130.7 (CH), 134.7, 134.9, 137.9, 139.5, 142.3, 145.7, 148.3, 151.0 (C), 179.7 (CO). IR (KBr): ν=3389, 3051, 3030, 2952, 2901, 2865 (w), 1638 (s), 1611 (w), 1588 (s), 1556, 1537 (w), 1511 (m), 1475 (w), 1461, 1434 (m), 1416 (w), 1381, 1360 (m), 1317 (w), 1299 (s), 1267 (m), 1231, 1201 (w), 1157, 1109 (m), 1175, 1144, 1032, 1014, 961 (w), 924 (m), 890, 867 (w), 822, 754 (s), 746 (m), 719 (s), 697, 671, 671, 656, 646, 613 (w), 581 (s), 563, 549, 541 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=476 ([M]$^+$, 64), 475 ([M−H]$^+$, 100), 462 (15), 461 (46). HRMS (ESI): calcd for $C_{33}H_{33}OS$ [M+H]$^+$: 477.22470; found: 477.22430.

*5.2.4. Synthesis of 1,3-bis(3,5-dimethylphenyl)-9H-thioxanthen-9-one (**4d**).* Starting with **2** (100 mg, 0.197 mmol), 3,5-dimethylphenylboronic acid **3d** (71 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4d** was isolated as a light yellow solid (64 mg, 77%); reaction temperature: 90 °C for 8 h. Mp 159–161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31 (s, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 6.88 (br s, 2H, ArH), 6.98 (d, 2H, J=6.39 Hz, ArH), 7.22 (br s, 2H, ArH), 7.30–7.36 (m, 1H, ArH), 7.40 (d, 1H, J=1.83 Hz, ArH), 7.48–7.49 (m, 2H, ArH), 7.66 (d, 1H, J=1.86 Hz, ArH), 8.27 (d, 1H, J=7.80 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.3 (CH_3), 20.5 (CH_3), 122.1 (CH), 124.1 (C), 124.2, 124.7 (CH), 125.0 (C), 125.1, 127.6, 128.3, 128.7, 129.3, 130.6, 130.7 (CH), 134.9, 136.2, 137.6, 137.7, 138.0, 142.5, 142.6, 145.8 (C), 179.7 (CO). IR (KBr): ν=3269, 3004, 2914, 2854, 2729 (w), 1640 (s), 1601 (m), 1587 (s), 1540 (m), 1503, 1494, 1468 (w), 1432 (m), 1398 (w), 1382, 1373 (m), 1332, 1315 (w), 1300 (s), 1279 (m), 1245, 1204, 1185, 1168 (w), 1150 (m), 1137, 1117, 1100, 1080 (w), 1034 (m), 1011, 966, 940 (w), 912, 889, 875 (m), 842 (s), 813, 806 (m), 769 (w), 752, 744, 719 (s), 703, 697, 692, 672, 651, 643 (m), 603 (w), 591 (m), 569, 540 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=420 ([M]$^+$, 54), 419 ([M−H]$^+$, 100), 405 (39). HRMS (ESI): calcd for $C_{29}H_{25}OS$ [M+H]$^+$: 421.16210; found: 421.16300.

*5.2.5. Synthesis of 1,3-di-(p-tolyl)-9H-thioxanthen-9-one (**4e**).* Starting with **2** (100 mg, 0.197 mmol), 4-methylphenylboronic acid **3e** (64 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4e** was isolated as a light yellow solid (65 mg, 84%); reaction temperature: 90 °C for 8 h. Mp 175–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31(s, 3H, CH_3), 2.36 (s, 3H, CH_3), 7.15–7.19 (m, 6H, ArH), 7.27–7.32 (m, 1H, ArH), 7.39 (d, 1H, J=1.89 Hz, ArH), 7.44 (d, 1H, J=1.17 Hz, ArH), 7.48 (d, 3H, J=8.25 Hz, ArH), 7.63 (d, 1H, J=1.89 Hz, ArH), 8.27 (dd, 1H, J=0.78, 8.61 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.2 (CH_3), 20.4 (CH_3), 121.9, 124.2 (CH), 124.9 (C), 125.1, 126.2, 126.8, 127.6, 128.2, 128.7, 128.8 (CH), 130.5 (C), 130.7 (CH), 134.7, 134.9, 135.3, 137.8, 137.9, 139.7, 142.3, 145.7 (C), 179.7 (CO). IR (KBr): ν=3044, 3022, 2952, 2919, 2857 (w), 1631 (s), 1613 (w), 1588 (s), 1556, 1537 (w), 1511 (m), 1462 (w), 1433 (m), 1415, 1380, 1316, 1192 (w), 1256 (m), 1116, 1107, 1075 (m), 1044 (w), 1031 (m), 1017 (w), 983, 961, 945 (w), 923 (s), 888, 877, 848, 837 (w), 811, 803 (s), 787 (m), 768 (w), 757, 748 (s), 725, 717, 675 (m), 659, 649, 631, 612, 586 (w), 568, 536 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=392 ([M]$^+$, 49), 391 ([M−H]$^+$, 100). HRMS (ESI): calcd for $C_{27}H_{21}OS$ [M+H]$^+$: 393.13080; found: 393.13090.

*5.2.6. Synthesis of 1,3-bis(4-chlorophenyl)-9H-thioxanthen-9-one (**4f**).* Starting with **2** (100 mg, 0.197 mmol), 4-chloro phenylboronic acid **3f** (73 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4f** was isolated as a light yellow solid (60 mg, 70%); reaction temperature: 90 °C for 8 h. Mp 230–231 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.19 (d, 2H, J=3.72 Hz, ArH), 7.32 (d, 2H, J=1.86 Hz, ArH), 7.35–7.39 (m, 4H, ArH), 7.41–7.49 (m, 2H, ArH), 7.53 (d, 2H, J=8.46 Hz, ArH), 7.67 (d, 1H, J=1.77 Hz, ArH), 8.27 (d, 1H, J=7.71 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=122.6, 124.3 (CH), 125.1 (C), 125.4, 127.1, 127.6, 127.9, 128.2, 128.3, 129.7 (CH), 130.2 (C), 131.1 (CH), 131.9, 134.2, 134.8, 135.9, 138.4, 140.8, 141.3, 144.6 (C), 179.4 (CO). IR (KBr): ν=3064, 3041, 2920, 2851 (w), 1640, 1589 (s), 1537 (w), 1490 (s), 1470 (w), 1434 (m), 1414, 1397, 1375 (w), 1317, 1298 (m), 1284, 1263, 1234, 1186 (w), 1158 (m), 1107 (w), 1090 (s), 1076 (m), 1032, 1031 (w), 1012 (s), 926 (m), 892, 873, 844 (w), 832 (m), 816, 806, 747 (s), 727, 713 (m), 693 (w), 680, 651 (m), 643, 626, 602 (w), 567, 553 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=433 ([M+H]$^+$, 44), 432 ([M]$^+$, 27), 431 ([M−H]$^+$, 56), 199 (100), 181 (49), 165 (16). HRMS (EI): calcd for $C_{25}H_{14}Cl_2OS$ [M]$^+$: 432.01369; found: 432.01221.

*5.2.7. Synthesis of 1,3-bis(3-(trifluoromethyl)phenyl)-9H-thioxanthen-9-one (**4g**).* Starting with **2** (100 mg, 0.197 mmol), 3-(trifluoromethyl)phenylboronic acid **3g** (89 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **4g** was isolated as a light yellow solid (74 mg, 75%); reaction temperature: 90 °C for 8 h. Mp 167–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.32–7.38 (m, 2H, ArH), 7.42–7.54 (m, 6H, ArH), 7.56–7.62 (m, 1H, ArH), 7.58–7.59 (m, 1H, ArH), 7.73 (d, 1H, J=1.90 Hz, ArH), 7.77 (d, 1H, J=7.68 Hz, ArH), 7.83 (br s, 1H, ArH),

8.22–8.26 (m, 1H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.6, −62.3. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=122.7 (q, $J_{F,C}$=3.7 Hz, CH), 122.9 (q, $J_{F,C}$=272.5 Hz, CF_3), 123.2 (q, $J_{F,C}$=272.5 Hz, CF_3),123.2 (q, $J_{F,C}$=3.9 Hz, CH), 123.3 (CH), 123.6 (q, $J_{F,C}$=3.9 Hz, CH), 124.4 (CH), 124.5 (q, $J_{F,C}$=3.9 Hz, CH), 125.4 (C), 125.6, 127.2, 128.0, 128.6, 128.7 (CH), 129.5 (q, $J_{F,C}$=32.2 Hz, C−CF_3), 129.7 (CH), 130.1 (C), 130.3 (CH), 130.9 (q, $J_{F,C}$=32.5 Hz, C−CF_3), 131.2 (CH), 134.7, 138.3, 138.7, 141.2, 142.9, 144.4 (C), 179.3 (CO). IR (KBr): ν=3270, 3063, 2959, 2852 (w), 1641 (s), 1615 (w), 1588 (s), 1547, 1496, 1486, 1462, 1455 (w), 1435 (m), 1380 (w), 1326, 1304 (s), 1268, 1251, 1226 (m), 1195 (w), 1174 (m), 1154, 1112, 1095, 1069, 1052 (s), 1033, 1000, 961, 928, 897, 887, 871, 859 (m), 797, 755 (s), 748 (m), 720, 698 (m), 686, 672, 654 (s), 627, 611, 562, 542 (m) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=500 ([M]$^+$, 45), 499 ([M−H]$^+$, 100), 356 (19), 277 (07), 240 (08). HRMS (EI): calcd for $C_{27}H_{13}F_6OS$ [M−H]$^+$: 499.05858; found: 499.058160.

*5.2.8. Synthesis of 3-(4-methoxyphenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5a**).* Starting with **2** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5a** was isolated as a light yellow solid (80 mg, 87%); reaction temperature: 60 °C for 8 h. Mp 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.81 (s, 3H, OCH_3), 6.96 (d, 2H, J=8.85 Hz, ArH), 7.33 (d, 1H, J=1.10 Hz, ArH), 7.41–7.58 (m, 5H, ArH), 7.64 (d, 1H, J=1.74 Hz, ArH), 8.53 (dd, 1H, J=1.10, 8.2 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.4. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.5 (OCH_3), 114.9 (CH), 118.9 (q, $J_{F,C}$=321.3 Hz, CF_3), 119.1 (CH), 120.3 (C), 123.4, 125.4, 126.9, 128.5 (CH), 129.2 (C), 130.1 (CH), 130.2 (C), 132.6 (CH), 135.3, 141.0, 145.4, 150.4, 161.0 (C), 178.5 (CO). IR (KBr): ν=3082, 3063, 2841, 1651 (w), 1635, 1594 (s), 1558 (w), 1523 (m), 1471, 1460 (w), 1435 (m), 1425 (s), 1404 (w), 1389 (m), 1328, 1317, 1307 (w), 1286, 1256, 1242, 1219 (m), 1191 (s), 1135, 1126, 1111(m), 1060 (w), 1030 (m), 1007 (w), 958, 904, 889, 881 (m), 848 (w), 832 (s), 811, 799 (m), 782, 759 (w), 745 (s), 725 (w), 712, 661, 653, 637 (m), 595 (s), 582, 567, 527 (m) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=466 ([M]$^+$, 100), 334 (13), 305 (44), 262 (17). HRMS (EI): calcd for $C_{21}H_{13}F_3O_5S_2$ [M]$^+$: 466.01510; found: 466.015129.

*5.2.9. Synthesis of 3-(4-ethylphenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5b**).* Starting with **2** (100 mg, 0.197 mmol), 4-ethylphenylboronic acid **3b** (32 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5b** was isolated as a yellow solid (77 mg, 84%); reaction temperature: 60 °C for 8 h. Mp 158–160 °C (CH_2Cl_2/EtOH 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.21 (t, 3H, J=7.59 Hz, CH_3), 2.65 (q, 2H, J=7.59 Hz, CH_2), 7.27 (d, 2H, J=8.34 Hz, ArH), 7.35 (d, 1H, J=0.96 Hz, ArH), 7.38–7.48 (m, 4H, ArH), 7.50–7.56 (m, 1H, ArH), 7.66 (d, 1H, J=1.74 Hz, ArH), 8.52 (dd, 1H, J=1.05, 8.13 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.4. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.4 (CH_3), 27.6 (CH_2), 117.4 (q, $J_{F,C}$=321.1 Hz, CF_3), 118.4 (CH), 120.4 (C), 122.9, 124.4, 125.9, 126.1, 127.9, 129.0 (CH), 129.1 (C), 131.6 (CH), 133.5, 134.3, 139.9, 144.8, 145.3, 149.3 (C), 177.5 (CO). IR (KBr): ν=3052, 2960, 2929, 2871 (w), 1641, 1602, 1589 (s), 1524 (m), 1454, 1444 (w), 1422 (s), 1386, 1316, 1303, 1240 (m), 1221, 1186 (s), 1157 (w), 1134, 1123 (s), 1110 (m), 1080, 1060, 1033, 1018 (w), 955, 899 (s), 862 (w), 839 (m), 811, 798 (s), 759 (w), 745 (s), 714 (m), 666, 659, 637 (w), 595, 577, 569 (s), 531 (w) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=464 ([M]$^+$, 100), 332 (14), 303 (39), 275 (17), 260 (19). HRMS (EI): calcd for $C_{22}H_{15}F_3O_4S_2$ [M]$^+$: 464.03584; found: 464.03590.

*5.2.10. Synthesis of 3-(4-(tert-butyl)phenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5c**).* Starting with **2** (100 mg, 0.197 mmol), 4-*tert*-butyl phenylboronic acid **3c** (39 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5c** was isolated as a yellow solid (73 mg, 75%); reaction temperature: 60 °C for 8 h. Mp 170–172 °C (CH_2Cl_2/EtOH 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.30 (s, 9H, $3CH_3$), 7.36 (d, 1H, J=0.90 Hz, ArH), 7.38–7.46 (m, 3H, ArH), 7.48 (d, 3H, J=1.77 Hz, ArH), 7.50–7.57 (m, 1H, ArH), 7.68 (d, 1H, J=1.68 Hz, ArH), 8.52 (dd, 1H, J=1.08, 8.10 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.4. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=31.2 (CH_3), 31.9 (C), 118.9 (q, $J_{F,C}$=321.0 Hz, CF_3), 119.5 (CH), 120.7 (C), 124.0, 125.4, 126.4, 126.9, 130.1 (CH), 130.2 (C), 132.7 (CH), 134.1, 135.3, 141.0, 145.8, 150.4, 153.2 (C), 178.6 (CO). IR (KBr): ν=3087, 3050, 3022, 2966, 2920, 2872, 2854 (w), 1630, 1602, 1589 (s), 1524 (m), 1480 (w), 1465, 1437 (m), 1424 (s), 1384 (m), 1362, 1325 (w), 1305 (m), 1278 (w), 1241 (m), 1217, 1193 (s), 1171 (m), 1131, 1105 (s), 1078, 1059, 1035, 1024, 1014 (w), 958, 903 (s), 890 (m), 829 (s), 810 (m), 801 (s), 760 (m), 753 (s), 712 (m), 666, 658, 651, 637 (w), 588 (s), 568, 537, 529 (w) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=493 ([M+H]$^+$, 17), 492 ([M]$^+$, 59), 478 (28), 477 (100), 316 (36). HRMS (EI): calcd for $C_{24}H_{19}F_3O_4S_2$ [M]$^+$: 492.06714; found: 492.06645.

*5.2.11. Synthesis of 3-(3,5-dimethylphenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5d**).* Starting with **2** (100 mg, 0.197 mmol), 3,5-dimethylphenylboronic acid **3d** (33 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5d** was isolated as a yellow solid (75 mg, 82%); reaction temperature: 60 °C for 8 h. Mp 221–223 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.34 (s, 6H, $2CH_3$), 7.04 (br s, 1H, ArH), 7.14 (br s, 2H, ArH), 7.35 (d, 1H, J=0.96 Hz, ArH), 7.39–7.48 (m, 2H, ArH), 7.52–7.58 (m, 1H, ArH), 7.67 (d, 1H, J=1.71 Hz, ArH), 8.53 (dd, 1H, J=1.02, 7.68 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.4. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.4 (CH_3), 117.9 (q, $J_{F,C}$=321.1 Hz, CF_3), 118.7 (CH), 119.7 (C), 123.3, 124.0, 124.4, 125.9, 129.1 (CH), 129.2 (C), 130.3, 131.6 (CH), 134.3, 136.0, 138.1, 139.9, 145.2, 149.2 (C), 177.6 (CO). IR (KBr): ν=3152, 3115, 3059, 2951, 2917, 2849 (w), 1631, 1601, 1588 (s), 1555 (w), 1534 (m), 1503, 1483 (w), 1427 (s), 1408 (w), 1375, 1302, 1248 (m), 1217, 1197, 1186, 1130 (s), 1081 (m), 1031, 1004 (w), 964, 911 (m), 894, 888 (s), 871 (m), 842, 813, 803 (s), 760 (w), 727 (w), 715, 686, 660 (m), 630 (w), 609 (m), 589 (s), 568 (m), 545, 537 (w) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=464 ([M]$^+$, 100), 303 (46), 275 (27). HRMS (EI): calcd for $C_{22}H_{15}F_3O_4S_2$ [M]$^+$: 464.03584; found: 464.03623.

*5.2.12. Synthesis of 9-oxo-3-phenyl-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5e**).* Starting with **2** (100 mg, 0.197 mmol), phenylboronic acid **3i** (26 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5e** was isolated as a yellow solid (61 mg, 71%); reaction temperature: 60 °C for 8 h. Mp 163–165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.36 (d, 1H, J=0.87 Hz, ArH), 7.39–7.47 (m, 5H, ArH), 7.50–7.56 (m, 3H, ArH), 7.67 (d, 1H, J=1.68 Hz, ArH), 8.50 (dd, 1H, J=1.11, 8.16 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=118.9 (q, $J_{F,C}$=321.0 Hz, CF_3), 119.6 (CH), 120.9 (C), 124.3, 125.4, 127.0, 127.2, 129.4, 129.7, 130.0 (CH), 130.1 (C), 132.7 (CH), 135.3, 137.0, 141.1, 145.8, 150.4 (C), 178.5 (CO). IR (KBr): ν=3083, 3062, 3023, 2917, 2848 (w), 1635, 1606, 1588 (s), 1531 (m), 1506, 1463, 1448 (w), 1423 (s), 1404 (w), 1388 (m), 1345, 1321 (w), 1306 (m), 1277 (w), 1242, 1218 (m), 1189 (s), 1169, 1157 (m), 1135, 1124, 1109 (s), 1081, 1032 (m), 999 (w), 956, 902, 876 (s), 843 (w), 810, 802, 761, 748 (s), 716, 684, 673, 666 (m), 622 (w), 637 (w), 597, 585 (s), 568 (m), 530 (w) cm^{-1}. GC−MS (EI, 70 eV): m/z (%)=436 ([M]$^+$, 100), 275 (49), 247 (48), 245 (16). HRMS (ESI): calcd for $C_{20}H_{12}F_3O_4S_2$ [M+H]$^+$: 437.01240; found: 437.01280.

*5.2.13. Synthesis of 3-(4-chlorophenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5f**).* Starting with **2** (100 mg, 0.197 mmol), 4-chlorophenylboronic acid **3f** (34 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5f** was isolated as a yellow solid (72 mg, 78%); reaction temperature: 60 °C for 8 h. Mp 133–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.34 (d, 1H, J=0.80 Hz, ArH), 7.42–7.51 (m, 6H, ArH), 7.57

(d, 1H, J=8.25 Hz, ArH), 7.67 (d, 1H, J=1.67 Hz, ArH), 8.45 (dd, 1H, J=1.01, 7.95 Hz, ArH). ^{19}F NMR (282.4 MHz,$CDCl_3$): δ=−73.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=118.7 (q, $J_{F,C}$=321.1 Hz, CF_3), 119.5 (CH), 121.1 (C), 124.2, 125.4, 127.1, 128.5(CH), 129.6 (C), 129.7, 130.2, 132.8 (CH), 135.2, 135.5, 136.1, 141.2, 144.5, 150.4 (C), 178.5 (CO). IR (KBr): ν=3087, 3060, 3023, 2956, 2918, 2849 (w), 1714, 1673, 1668 (w), 1639, 1606, 1590 (s), 1531 (w), 1503 (m), 1463, 1456 (w), 1426 (s), 1380 (m), 1319 (w), 1303 (m), 1276, 1262 (w), 1242 (m), 1219, 1190 (s), 1167, 1159 (w), 1135, 1126 (s), 1112 (w), 1090 (s), 1049, 1033 (w), 1010 (m), 955 (s), 928 (w), 902, 890 (s), 845 (w), 832 (m), 811, 799 (s), 760 (m), 748 (s), 717, 712 (m), 692 (w), 666, 659, 654, 630 (m), 595, 586 (s), 567 (m), 558, 537 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=470 ([M+H]$^+$, 100), 338 (11), 311 (19), 310 (12), 309 (47), 281 (41), 274 (12), 245 (22). HRMS (ESI): calcd for $C_{20}H_{11}ClF_3O_4S_2$ [M+H]$^+$: 470.97340; found: 470.97450.

*5.2.14. Synthesis of 9-oxo-3-(3-(trifluoromethyl)phenyl)-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5g**).* Starting with **2** (100 mg, 0.197 mmol) 3-(trifluoromethyl)phenylboronic acid **3g** (41 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5g** was isolated as a yellow solid (80 mg, 81%); reaction temperature: 60 °C for 8 h. Mp 176–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.35 (d, 1H, J=1.14 Hz, ArH), 7.40–7.48 (m, 2H, ArH), 7.54–7.62 (m, 2H, ArH), 7.67–7.74 (m, 3H, ArH), 7.77 (br s, 1H, ArH), 8.52 (dd, 1H, J=1.11, 8.16 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.3, −62.7. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=118.9 (q, $J_{F,C}$=323.9 Hz, CF_3), 119.7 (CH), 121.4 (C), 123.7 (q, $J_{F,C}$=272.5 Hz, CF_3), 124.0 (q, $J_{F,C}$=3.79 Hz, CH), 124.6, 125.4 (CH), 126.3 (q, $J_{F,C}$=3.66 Hz, CH), 127.2, 130.0 (CH), 130.1 (C), 130.2, 130.6 (CH), 131.9 (q, $J_{F,C}$=32.5 Hz, C–CF_3), 132.9 (CH), 135.1, 137.9, 141.4, 144.2, 150.4 (C), 178.4 (CO). IR (KBr): ν=3083, 3062, 3023, 2918, 2851 (w), 1630, 1609, 1589 (s), 1537, 1502, 1461 (w), 1424 (s), 1386 (m), 1336 (s), 1303, 1267, 1240, 1224 (m), 1204 (s), 1166 (m), 1123 (s), 1078, 1066 (m), 1033, 1000 (w), 963 (s), 906, 877 (m), 814, 801 (s), 777 (w), 761, 750 (m), 734 (w), 717, 661 (m), 685 (s), 566, 657, 647, 633, 623 (w), 595 (s), 568 (m), 533 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=503 ([M]$^+$, 46), 375 (42), 311 (100), 283 (15), 242 (27), 214 (16), 186 (29), 158 (13). HRMS (EI): calcd for $C_{21}H_{10}F_6O_4S_2$ [M]$^+$: 503.99192; found: 503.99228.

*5.2.15. Synthesis of 3-(4-fluorophenyl)-9-oxo-9H-thioxanthen-1-yl trifluoromethanesulfonate (**5h**).* Starting with **2** (100 mg, 0.197 mmol), 4-flourophenylboronic acid **3j** (30 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **5h** was isolated as a yellow solid (71 mg, 80%); reaction temperature: 60 °C for 8 h. Mp 179–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.13 (t, 2H, J=8.52 Hz, ArH), 7.30 (d, 1H, J=1.02 Hz, ArH), 7.38–7.45 (m, 2H, ArH), 7.49–7.58 (m, 3H, ArH), 7.63 (d, 1H, J=1.74 Hz, ArH), 8.50 (dd, 1H, J=0.90, 7.80 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−111.1, −73.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=116.5 (d, $J_{F,C}$=21.9 Hz, CH), 118.9 (q, $J_{F,C}$=321.2 Hz, CF_3), 119.5 (CH), 120.9 (C), 124.1, 125.4, 127.0 (CH), 129.1 (d, $J_{F,C}$=8.46 Hz, CH), 130.1, 132.8 (CH), 133.1, 133.2, 135.2, 141.2, 144.7, 150.4 (C), 163.8 (d, $J_{F,C}$=250.9 Hz, C–F), 178.8 (CO). IR (KBr): ν=3070, 2953, 2921, 2851 (w), 1637(m), 1591 (s), 1531 (w), 1514 (m), 1488, 1435 (w), 1421 (s), 1383 (m), 1321 (w), 1302 (m), 1281 (w), 1241(m), 1207, 1191 (s), 1163 (m), 1137, 1116 (s), 1079 (m), 1034, 1014, 993 (w), 957, 903 (s), 876 (m), 854 (w), 838, 810, 792, 754, 741 (s), 715, 665, 659 (m), 636 (w), 590 (s), 569 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=454 ([M]$^+$, 100), 294 (10), 293 (49), 265 (52), 263 (14). HRMS (ESI): calcd for $C_{20}H_{11}F_4O_4S_2$ [M+H]$^+$: 455.00290; found: 455.00300.

*5.2.16. Synthesis of 3-(4-ethylphenyl)-1-(2-methoxyphenyl)-9H-thioxanthen-9-one (**6a**).* Starting with **5b** (77 mg, 0.166 mmol), 2-methoxyphenylboronic acid **3a** (28 mg, 0.182 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol %), K_3PO_4 (53 mg, 0.25 mmol), and 1,4-dioxane (5 mL), **6a** was isolated as a yellow solid (57 mg, 82%); reaction temperature: 90 °C for 6 h. Mp 185–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.20 (t, 3H, J=7.59 Hz, CH_3), 2.63 (s, 2H, J=7.59 Hz, CH_2), 3.58 (s, 3H, OCH_3), 6.88 (dd, 1H, J=0.66, 8.19 Hz, ArH), 7.02 (td, 1H, J=1.02, 7.44 Hz, ArH), 7.23 (d, 3H, J=7.68 Hz, ArH), 7.28–7.35 (m, 2H, ArH), 7.42 (d, 1H, J=1.86 Hz, ArH), 7.46–7.48 (m, 2H, ArH), 7.53 (d, 2H, J=8.25 Hz, ArH), 7.66 (d, 1H, J=1.86 Hz, ArH), 8.23 (dt, 1H, J=0.96, 8.10 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.5 (CH_3), 28.6 (CH_2), 55.5 (OCH_3), 110.3, 120.7, 123.2, 125.3, 126.1 (CH), 127.0 (C), 127.3, 128.5, 128.9, 129.1, 129.4, 131.4, 131.5 (CH), 132.7, 136.0, 136.2, 138.0, 142.2, 143.7, 144.9, 156.0 (C), 180.9 (CO). IR (KBr): ν=3272, 3109, 3061, 3012, 2964, 2865, 2238, 1922, 1899 (w), 1643, 1589 (s), 1538, 1514, 1494, 1461, 1452, 1435 (m), 1385 (w), 1301 (s), 1278 (m), 1241 (s), 1228, 1189, 1180 (w), 1156, 1117, 1074, 1052 (m), 1032 (w), 1020 (s), 964, 938 (w), 925 (m), 896, 871, 838 (w), 826 (s), 802(m), 769 (w), 751, 741, 719 (s), 677, 660 (m), 647, 636, 629, 623, 593, 577, 552 (w), 536 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=422 ([M]$^+$, 4), 391 ([M]$^+$, 100), 376 (65). HRMS (EI): calcd for $C_{28}H_{22}O_2S$ [M]$^+$: 422.13350; found: 422.13464.

*5.2.17. Synthesis of 3-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)-9H-thioxanthen-9-one (**6b**).* Starting with **5c** (73 mg, 0.148 mmol), 4-methoxyphenylboronic acid **3h** (25 mg, 0.163 mmol), $Pd(PPh_3)_4$ (9 mg, 5 mol %), K_3PO_4 (47 mg, 0.22 mmol), and 1,4-dioxane (5 mL), **6b** was isolated as a yellow solid (53 mg, 79%); reaction temperature: 90 °C for 6 h. Mp 178–180 °C (CH_2Cl_2/EtOH 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.28 (s, 9H, $3CH_3$), 3.79 (s, 3H, OCH_3), 6.89 (d, 2H, 8.70 Hz, ArH), 7.19 (d, 2H, J=8.70 Hz, ArH), 7.29–7.34 (m, 1H, ArH), 7.40–7.48 (m, 5H, ArH), 7.54 (d, 2H, J=8.52 Hz, ArH), 7.65 (d, 1H, J=1.83 Hz, ArH), 8.27 (dd, 1H, J=0.75, 8.52 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.3 (CH_3), 34.7 (C), 55.2 (OCH_3), 113.4, 122.9, 125.2 (CH), 125.9 (C), 126.0, 126.2, 127.0, 129.1, 129.4, 129.7 (CH), 131.6 (C), 131.7 (CH), 135.7, 135.8, 136.0, 139.0, 143.0, 146.0, 152.0, 158.6 (C), 180.9 (CO). IR (KBr): ν=3092, 3051, 3005, 2950, 2902, 2865, 2830 (w), 1642 (s), 1607 (m), 1587 (s), 1557, 1537 (w), 1507 (s), 1460, 1432 (m), 1415, 1379, 1359, 1316 (w), 1297 (s), 1279 (m), 1238 (s), 1176 (m), 1163 (w), 1152, 1111, 1074, 1028 (m), 1015, 961 (w), 923 (m), 891, 867 (w), 818 (s), 769 (w), 754 (s), 730, 722 (m), 709 (w), 675 (m), 653, 633, 611 (w), 573, 542 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=450 ([M]$^+$, 77), 449 ([M−H]$^+$, 100). HRMS (ESI, 70 eV): calcd for $C_{30}H_{27}O_2S$ [M+H]$^+$: 451.17260; found: 451.17250.

*5.2.18. Synthesis of 3-(4-chlorophenyl)-1-(3,4-dimethoxyphenyl)-9H-thioxanthen-9-one (**6c**).* Starting with **5f** (72 mg, 0.153 mmol), 3,4-dimethoxyphenylboronic acid **3k** (31 mg, 0.168 mmol), $Pd(PPh_3)_4$ (9 mg, 5 mol %), K_3PO_4 (49 mg, 0.23 mmol), and 1,4-dioxane (5 mL), **6c** was isolated as a yellow solid (50 mg, 71%); reaction temperature: 90 °C for 6 h. Mp 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.79 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.77 (d, 1H, J=1.86 Hz, ArH), 6.81 (dd, 1H, J=1.92, 8.16 Hz, ArH), 6.88 (d, 1H, J=8.16 Hz, ArH), 7.32–7.39 (m, 4H, ArH), 7.48–7.55 (m, 4H, ArH), 7.62 (d, 1H, J=1.9 Hz, ArH), 8.25 (dd, 1H, J=0.84, 8.70 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=54.8, 54.9 (OCH_3), 109.7, 110.7, 119.1, 122.0, 124.3, 125.4, 127.6, 128.1, 128.3, 128.6 (CH), 130.7 (C), 130.9 (CH), 134.0, 134.7, 134.8, 136.1, 138.1, 141.1, 145.5, 147.2, 147.5 (C), 179.8 (CO). IR (KBr): ν=3052, 2989, 2957, 2925, 2850, 2829, 2247 (w), 1643 (s), 1609 (w), 1589 (m), 1537(w), 1513, 1491, 1469, 1462, 1454, 1434, 1417 (m), 1401, 1372, 1331 (w), 1296 (m), 1281 (w), 1257, 1240, 1216, 1185, 1170, 1153, 1136, 1122, 1102, 1092, 1077, 1056 (m), 1027, 1013 (s), 952, 932 (w), 909, 894, 875, 863 (m), 841 (w), 825 (m), 816 (s), 804, 789, 761 (m), 747, 721 (s), 683, 662, 652, 646, 629, 618, 600, 583, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=458 ([M]$^+$, 100), 457 ([M−H]$^+$, 74), 443 (24), 371 (17), 214 (14). HRMS (EI): calcd for $C_{27}H_{19}ClO_3S$ [M]$^+$: 458.07379; found: 458.074006.

*5.2.19. Synthesis of 1-(4-methoxyphenyl)-3-(o-tolyl)-9H-thioxanthen-9-one (**6d**).* Starting with **2** (100 mg, 0.197 mmol), 2-

methylphenylboronic acid **3l** (29 mg, 0.22 mmol), 4-methoxyphenylboronic acid **3h** (34 mg, 0.22 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and 1,4-dioxane (5 mL), **6d** was isolated as a yellow solid (60 mg, 75%); reaction temperature: at 60 °C for 8 h, at 90 °C for 6 h. Mp 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.88 (d, 2H, J=8.73 Hz, ArH), 7.17–7.23 (m, 7H, ArH), 7.31–7.36 (m, 1H, ArH), 7.42 (d, 1H, J=1.74 Hz, ArH), 7.47–7.52 (m, 2H, ArH), 8.28 (dd, 1H, J=0.84, 8.64 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.4 (CH_3), 55.2 (OCH_3), 113.4, 125.2, 125.4 (CH), 125.9 (C), 126.1, 126.3, 128.3, 129.2, 129.5, 129.7, 130.7 (CH), 131.7 (C), 131.8, 131.9 (CH), 135.3, 135.5, 135.9, 138.4, 139.6, 144.8, 145.6, 158.6 (C), 181.2 (CO). IR (KBr): ν=3399, 3057, 2950, 2928, 2861, 2834 (w), 1641 (s), 1607 (m), 1588 (s), 1536(w), 1508 (s), 1489, 1461 (w), 1435 (m), 1409, 1384, 1316 (w), 1295 (m), 1241 (s), 1175, 1156 (m), 1115, 1077, 1053 (w), 1032 (m), 962 (w), 923 (m), 879, 894(w), 826 (s), 808, 786, 769 (w), 755, 723 (s), 680, 667 (m), 643, 613 (w), 573 (m), 556, 536 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=408 ($[M]^+$, 70), 407 ($[M-H]^+$, 100). HRMS (EI): calcd for $C_{27}H_{20}O_2S$ $[M]^+$: 408.11785; found: 408.11643.

*5.2.20. Synthesis of 9-oxo-9H-thioxanthene-1,4-diyl bis(trifluoromethanesulfonate) (**8**).* To a solution of **7** (0.40 g, 1.63 mmol) in CH_2Cl_2 (20 mL) was added a 1:2 mixture of Et_3N and pyridine (0.34 mL, 2.46 mmol of Et_3N, and 0.40 mL, 4.10 mmol of pyridine) at 20 °C under an argon atmosphere. After stirring for 10 min at −78 °C, Tf_2O (0.66 mL, 3.91 mmol) was added. The mixture was allowed to warm to 20 °C and stirred for further 8 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was chromatographed without work up (flash silica gel, heptanes/EtOAc) and **8** was isolated as a yellow solid (0.72 g, 87%). Mp 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.29 (d, 1H, J=8.91 Hz, ArH), 7.48–7.58 (m, 2H, ArH), 7.62–7.67 (m, 2H, ArH), 8.50 (dd, 1H, J=1.41, 8.1 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.2, −73.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=118.5, 118.7 (q, $J_{F,C}$=317.6, 321.0 Hz, CF_3), 120.9 (CH), 124.2 (C), 124.8, 126.1, 128.0 (CH), 129.5 (C), 130.2 (CH), 133.2 (C), 133.5 (CH), 135.2, 143.4, 148.7 (C), 178.0 (CO). IR (KBr): ν=3080, 2961, 2904 (w), 1649, 1592 (w), 1429 (m), 1412, 1388, 1318, 1302 (w), 1257 (s), 1236, 1216, 1199 (m), 1078, 1010 (s), 907, 882, 850 (m), 789, 758 (s), 740 (m), 691, 673, 660, 646, 620, 607 (w), 589 (m), 569, 529 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=508 ($[M+H]^+$, 43), 375 (40), 311 (100), 311 (100), 283 (14), 242 (27). HRMS (EI): calcd for $C_{15}H_6F_6O_7S_3$ $[M]^+$: 507.91744; found: 507.91799.

*5.2.21. Synthesis of 1,4-bis(4-ethylphenyl)-9H-thioxanthen-9-one (**9a**).* Starting with **8** (100 mg, 0.197 mmol), 4-ethylphenylboronic acid **3b** (71 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9a** was isolated as a yellow solid (66 mg, 80%); reaction temperature: 90 °C for 8 h. Mp 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25–1.31 (m, 6H, $2CH_3$), 2.64–2.75 (m, 4H, $2CH_2$), 7.02–7.17 (m, 1H, ArH), 7.21–7.32 (m, 5H, ArH), 7.35 (d, 4H, J=8.40 Hz, ArH), 7.40–7.48 (m, 2H, ArH), 7.50–7.78 (m, 1H, ArH), 8.19 (dd, 1H, J=1.20, 8.19 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=14.2, 14.4 ($2CH_3$), 27.6, 27.7 ($2CH_2$), 124.5, 125.1 (CH), 125.9 (C), 126.5, 126.9, 127.1, 128.2, 128.6, 128.8 (CH), 130.2 (C), 130.6, 131.0 (CH), 134.8, 135.4, 136.5, 137.7, 139.7, 141.4, 143.7, 143.8 (C), 181.2 (CO). IR (KBr): ν=3270, 3053, 3024, 2961, 2929, 2872 (w), 1730 (m), 1642 (s), 1610 (w), 1589 (m), 1547, 1511, 1494, 1474, 1462 (w), 1433 (s), 1408, 1377, 1358 (w), 1304, 1273, 1250, 1215 (m), 1184, 1160, 1137, 1115 (w), 1080, 1072 (m), 1045, 1027 (w), 1013 (m), 970, 934, 886 (w), 822, 757, 734 (s), 717, 690 (m), 651 (w), 640 (m), 612, 602 (w), 534 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=420 ($[M]^+$, 61), 419 ($[M-H]^+$, 100), 404 (12), 391 (13). HRMS (EI): calcd for $C_{29}H_{23}OS$ $[M-H]^+$: 419.14641; found: 419.14575.

*5.2.22. Synthesis of 1,4-bis(4-(tert-butyl)phenyl)-9H-thioxanthen-9-one (**9b**).* Starting with **8** (100 mg, 0.197 mmol), 4-*tert*-butylphenylboronic acid **3c** (84 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9b** was isolated as a yellow solid (78 mg, 83%); reaction temperature: 90 °C for 8 h. Mp 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.33 (s, 9H, $3CH_3$), 1.35 (s, 9H, $3CH_3$), 7.20 (d, 2H, J=10.5 Hz, ArH), 7.26 (d, 2H, J=9.15 Hz, ArH), 7.35–7.45 (m, 7H, ArH), 7.47 (d, 2H, J=10.1 Hz, ArH), 8.19 (dd, 1H, J=1.17, 9.57 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=30.4, 30.5 (CH_3), 33.5, 33.8 (C), 123.9, 124.4, 124.6, 125.0, 126.6 (CH), 127.1 (C), 128.1, 128.2, 128.9 (CH), 130.2 (C), 130.6, 131.0 (CH), 134.6, 135.4, 136.4, 137.6, 139.4, 143.7, 148.2, 150.5 (C), 181.2 (CO). IR (KBr): ν=3025, 2959, 2902, 2866, 2712, 2257, 1909, 1726 (w), 1638 (s), 1614 (w), 1589 (m), 1563, 1543 (w), 1509, 1461 (m), 1433 (s), 1392, 1360 (w), 1308 (m), 1289 (w), 1267, 1256 (m), 1237 (w), 1212, 1203 (m), 1168, 1161, 1138 (w), 1112 (m), 1105, 1080, 1047, 1025 (w), 1014 (m), 973, 961, 935 (w), 917, 905, 847 (m), 835 (w), 821 (s), 801, 759, 748 (m), 724 (s), 700, 687, 666 (w), 648 (m), 625, 611, 604, 590 (w), 568 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=477 ($[M+H]^+$, 28), 476 ($[M]^+$, 81), 475 ($[M-H]^+$, 100), 461 (51), 419 (14). HRMS (EI): calcd for $C_{33}H_{31}OS$ $[M-H]^+$: 475.20901; found: 475.20877.

*5.2.23. Synthesis of 1,4-di-p-tolyl-9H-thioxanthen-9-one (**9c**).* Starting with **8** (100 mg, 0.197 mmol), 4-methylphenylboronic acid **3e** (64 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9c** was isolated as a yellow solid (65 mg, 84%); reaction temperature: 90 °C for 8 h. Mp 160–162 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ=2.35 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 7.13–7.15 (m, 3H, ArH), 7.22 (d, 2H, J=7.63 Hz, ArH), 7.27–7.32 (m, 5H, ArH), 7.35 (d, 2H, J=7.63 Hz, ArH), 7.40 (dd, 1H, J=1.37, 6.93 Hz, ArH), 8.18 (dd, 1H, J=1.18, 7.93 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.3, 20.4 ($2CH_3$), 124.4, 125.1, 126.8 (CH), 127.1 (C), 127.7, 128.1, 128.4, 128.5, 128.7 (CH), 130.2 (C), 130.6, 130.9 (CH), 134.6, 135.2, 135.4, 136.5, 137.4, 137.7, 139.6, 143.8 (C), 181.1 (CO). IR (KBr): ν=3271, 3027, 2961, 2914, 2859, 2726, 2253 (w), 1642 (s), 1615 (w), 1589 (s), 1574, 1557, 1494, 1547 (w), 1512 (m), 1463 (w), 1434 (s), 1378, 1358 (w), 1305 (s), 1285 (w), 1250, 1234, 1204 (m), 1183, 1159, 1139 (w), 1107 (m), 1080, 1070, 1045, 1033 (w), 1016 (m), 971, 956, 934, 917, 896, 864, 848, 838 (w), 805 (s), 773 (w), 758, 736, 728 (s), 688, 661, 650 (w), 642 (m), 627, 621, 613, 601, 585 (w), 556 (m), 544 (w), 530 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=392 ($[M]^+$, 56), 391 ($[M-H]^+$, 100). HRMS (EI): calcd for $C_{27}H_{19}OS$ $[M-H]^+$: 391.11511; found: 391.11509.

*5.2.24. Synthesis of 1,4-bis(4-methoxyphenyl)-9H-thioxanthen-9-one (**9d**).* Starting with **8** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (72 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9d** was isolated as a yellow solid (77 mg, 92%); reaction temperature: 90 °C for 8 h. Mp 193–194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.83 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.89 (d, 2H, J=8.67 Hz, ArH), 6.98 (d, 2H, J=8.70 Hz, ArH), 7.17–7.25 (m, 3H, ArH), 7.28–7.38 (m, 5H, ArH), 7.44 (td, 1H, J=1.41, 8.19 Hz, ArH), 8.19 (dd, 1H, J=1.02, 8.01 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.2, 55.4 ($2OCH_3$), 113.5, 114.0, 125.5, 126.2 (CH), 128.1(C), 129.1, 129.2, 129.8 (CH), 130.8 (C), 130.9 (CH), 131.3 (C), 131.7, 132.1(CH), 135.8, 136.4, 137.8, 138.4, 144.4, 158.5, 159.8 (C), 182.4 (CO). IR (KBr): ν=3061, 3031, 3004, 2952, 2921, 2852, 2834, 2537, 2350, 2285, 2252, 2052, 1907 (w), 1634, 1606, 1589 (s), 1575 (m), 1556, 1547 (w), 1509 (s), 1462 (m), 1432 (s), 1409, 1377, 1358 (w), 1310, 1302, 1287 (m), 1239 (s), 1193 (m), 1174 (s), 1117 (w), 1105 (m), 1081, 1049 (w), 1026 (s), 1008, 965, 935, 927, 918, 903, 877, 864, 832 (w), 815 (s), 788, 773 (w), 759, 724 (s), 689 (w), 662, 651, 644 (m), 629, 609, 594 (w), 569 (m), 542 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=425 ($[M+H]^+$, 51), 424 ($[M]^+$, 99), 423 ($[M-H]^+$, 100), 380 (11). HRMS (EI): calcd for $C_{27}H_{20}O_3S$ $[M]^+$: 424.11277; found: 424.11145.

*5.2.25. Synthesis of 1,4-diphenyl-9H-thioxanthen-9-one (**9e**).* Starting with **8** (100 mg, 0.197 mmol), phenylboronic acid **3i**

(57 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9e** was isolated as a yellow solid (65 mg, 91%); reaction temperature: 90 °C for 8 h. Mp 193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.27(t, 4H, J=7.50 Hz, ArH), 7.31–7.36 (m, 4H, ArH), 7.38–7.47 (m, 7H, ArH), 8.18 (dd, 1H, J=1.05, 8.04 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=124.5, 125.2, 125.5, 126.8, 126.9 (CH), 127.0 (C), 127.6, 127.7, 128.2, 128.6, 128.7 (CH), 130.1 (C), 130.7, 130.9 (CH), 135.3, 136.5, 137.5, 137.9, 142.5, 144.0 (C), 180.9 (CO). IR (KBr): ν=3269, 3077, 3055, 3045, 3023, 2917, 2849 (w), 1638 (s), 1622 (m), 1589 (s), 1574 (w), 1548 (m), 1519, 1514 (w), 1491 (m), 1462 (w), 1441 (m), 1429 (s), 1358 (w), 1313, 1306 (s), 1286, 1251, 1235 (m), 1177 (w), 1163, 1115, 1076, 1069, 1049 (m), 1033 (w), 1022 (m), 1001, 975, 961 (w), 934 (m), 908, 875, 717, 690, 852 (w), 838, 823 (m), 811, 767 (w), 752, 730, 692 (s), 652, 638, 619, 609, 604 (m), 548 (w), 530 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=364 ([M]$^+$, 50), 363 ([M–H]$^+$, 100). HRMS (EI): calcd for $C_{25}H_{15}OS$ [M–H]$^+$: 363.08381; found: 363.08337.

*5.2.26. Synthesis of 1,4-bis(4-fluorophenyl)-9H-thioxanthen-9-one (**9f**).* Starting with **8** (100 mg, 0.197 mmol), 4-flourophenylboronic acid **3j** (66 mg, 0.47 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **9f** was isolated as a yellow solid (65 mg, 82%); reaction temperature: 90 °C for 8 h. Mp 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.04 (t, 2H, J=8.76 Hz, ArH), 7.14 (d, 2H, J=8.70 Hz, ArH), 7.17–7.23 (m, 3H, ArH), 7.27–7.51 (m, 6H, ArH), 8.18 (dd, 1H, J=1.05, 8.61 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−115.9, −112.6. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=113.9 (d, $J_{F,C}$=21.5 Hz, CH), 114.8 (d, $J_{F,C}$=21.7 Hz, CH), 124.5, 125.4 (CH), 127.1 (C), 128.2 (CH), 128.4 (d, $J_{F,C}$=7.87 Hz, CH), 128.7 (CH), 129.9 (C), 130.4 (d, $J_{F,C}$=8.27 Hz, CH), 130.9, 131.0 (CH), 133.3 (d, $J_{F,C}$=3.35 Hz, C), 135.0, 136.8, 137.1 (C), 138.3 (d, $J_{F,C}$=3.61 Hz, C), 143.1 (C), 160.7 (d, $J_{F,C}$=245.5 Hz, C–F), 161.9 (d, $J_{F,C}$=248.6 Hz, C–F), 180.8 (CO). IR (KBr): ν=3072, 3045, 2961, 2920, 2850 (w), 1639 (s), 1600 (m), 1590 (s), 1558, 1550 (w), 1506 (s), 1463 (w), 1434 (s), 1406, 1359 (w), 1307 (m), 1288, 1279, 1259 (w), 1220 (s), 1168 (w), 1157, 1090 (m), 1070, 1043, 1033 (w), 1013 (m), 961 (w), 931 (m), 866 (w), 845 (m), 823, 797 (s), 785 (m), 760, 738 (s), 688 (w), 660, 650, 641 (m), 630, 608 (w), 591 (m), 553, 533 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=400 ([M]$^+$, 59), 399 ([M–H]$^+$, 100). HRMS (EI): calcd for $C_{25}H_{31}F_2OS$ [M–H]$^+$: 399.06497; found: 399.06452.

*5.2.27. Synthesis of 1-(4-ethylphenyl)-9-oxo-9H-thioxanthen-4-yltrifluoromethanesulfonate (**10a**).* Starting with **8** (100 mg, 0.197 mmol), 4-ethylphenylboronic acid **3b** (32 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10a** was isolated as a yellow solid (82 mg, 90%); reaction temperature: 65 °C for 8 h. Mp 196–198 °C (CH_2Cl_2/EtOH 1:1). ^{1}H NMR(300 MHz, $CDCl_3$): δ=1.23 (t, 3H, J=7.6 Hz, CH_3), 2.67 (q, 2H, J=7.6 Hz, CH_2), 7.10 (d, 2H, J=8.20 Hz, ArH), 7.15–7.20 (m, 2H, ArH), 7.25 (d, 1H, J=8.4 Hz, ArH), 7.27–7.41 (m, 1H, ArH), 7.49–7.54 (m, 3H, ArH), 8.19 (dd, 1H, J=0.99, 8.10 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=14.2 (CH_3), 27.6 (CH_2), 117.6 (q, $J_{F,C}$=318.7 Hz, CF3), 122.1, 124.8, 126.1, 126.6, 126.7 (CH), 128.2 (C), 128.6, 129.1 (CH), 130.0 (C), 131.4 (CH), 132.8, 138.1, 142.2, 142.4, 145.0, 179.3 (CO). IR (KBr): ν=3060, 3028, 2960, 2928, 2870, 2852 (w), 1644 (s), 1614 (w), 1593, 1580 (m), 1555, 1511, 1454 (w), 1430 (s), 1372, 1316 (w), 1303 (m), 1274, 1260 (w), 1247 (m), 1219, 1205, 1186 (s), 1160 (m), 1134 (s), 1114, 1079, 1049, 1034, 1017, 971 (m), 883 (s), 857, 836, 831 (m), 802, 756, 739 (s), 724 (m), 693, 666, 652 (w), 640 (s), 632 (m), 603, 590 (s), 566, 535 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=464 ([M]$^+$, 26), 331 (100), 302 (89), 274 (24). HRMS (EI): calcd for $C_{22}H_{15}F_3O_4S_2$ [M]$^+$: 464.03584; found: 464.03664.

*5.2.28. Synthesis of 1-(4-(tert-butyl)phenyl)-9-oxo-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10b**).* Starting with **8** (100 mg, 0.197 mmol), 4-*tert*-butylphenylboronic acid **3c** (39 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10b** was isolated as a yellow solid (74 mg, 76%); reaction temperature: 65 °C for 8 h. Mp 181–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.32 (s, 9H, $3CH_3$), 7.13 (d, 2H, J=8.49 Hz, ArH), 7.27 (d, 1H, J=8.43 Hz, ArH), 7.35–7.39 (m, 3H, ArH), 7.51–7.60 (m, 3H, ArH), 8.22 (dd, 1H, J=0.99, 8.07 Hz, ArH). ^{19}F NMR (282.4 MHz,$CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=30.4 ($3CH_3$), 33.6 (C), 117.6 (q, $J_{F,C}$=320.8 Hz, CF_3), 122.1, 123.9, 124.8, 126.1, 126.5 (CH), 128.2 (C), 128.6, 129.3 (CH), 130.1 (C), 131.4 (CH), 132.8, 137.8, 142.4, 145.0, 149.1 (C), 179.4 (CO). IR (KBr): ν=3106, 3071, 3027, 2959, 2903, 2865 (w), 1643 (s), 1614 (w), 1591, 1582 (m), 1507, 1474, 1461 (w), 1419 (s), 1373, 1316 (w), 1305 (m), 1283, 1263, 1247, 1238 (w), 1214 (s), 1187 (m), 1269, 1160 (w), 1130 (s), 1115 (m), 1078, 1052, 1035, 1014 (w), 972 (m), 906 (w), 884 (s), 854 (w), 844, 821 (m), 796 (s), 765 (w), 758 (m), 747 (w), 735 (s), 720 (m), 686, 666, 653, 632 (w), 603 (s), 593 (m), 573, 564 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=492 ([M]$^+$, 41), 477 (13), 359 (68), 344 (23), 303 (63), 302 (100), 274 (15). HRMS (EI): calcd for $C_{24}H_{19}F_3O_4S_2$ [M]$^+$: 492.06714; found: 492.06628.

*5.2.29. Synthesis of 9-oxo-1-(p-tolyl)-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10c**).* Starting with **8** (100 mg, 0.197 mmol), 4-methylphenylboronic acid **3e** (30 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10c** was isolated as a yellow solid (77 mg, 87%); reaction temperature: 65 °C for 8 h. Mp 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 7.09 (d, 2H, J=8.1 Hz, ArH), 7.17 (d, 2H, J=7.95 Hz, ArH), 7.25 (d,1H, J=8.43 Hz, ArH), 7.35–7.42 (m, 1H, ArH), 7.52–7.57 (m, 3H, ArH), 8.22 (d, 1H, J=7.89 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.37 (CH_3), 118.6 (q, $J_{F,C}$=320.7 Hz, CF_3), 123.1, 125.9, 127.2, 127.7, 128.9 (CH), 129.2 (C), 129.6, 130.1 (CH), 131.1 (C), 132.4 (CH), 132.5, 133.8, 137.1, 138.9, 143.4, 146.1 (C), 180.4 (CO). IR (KBr): ν=3290, 3090, 3055, 3028, 2953, 2921, 2850, 2666 (w), 1652 (s), 1614 (w), 1589, 1582 (m), 1552, 1515, 1463 (w), 1436 (m), 1424 (s), 1407 (m), 1312 (w), 1301, 1294, 1248 (m), 1206, 1190 (s), 1166 (w), 1157 (m), 1137, 1131 (s), 1109 (m), 1076, 1050, 1034, 1017 (w), 968 (m), 945, 934 (w), 883 (s), 872 (m), 851 (w), 834, 801 (s), 780 (m), 760, 732 (s), 689, 675, 649, 639 (w), 618, 601, 590 (s), 571 (m), 563, 552 (w), 533 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=450 ([M]$^+$, 43), 317 (100), 302 (78), 274 (17). HRMS (EI): calcd for $C_{21}H_{13}F_3O_4S_2$ [M]$^+$: 450.02019; found: 450.01967.

*5.2.30. Synthesis of 1-(4-chlorophenyl)-9-oxo-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10d**).* Starting with **8** (100 mg, 0.197 mmol), 4-chlorophenylboronic acid **3f** (34 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10d** was isolated as a yellow solid (78 mg, 84%); reaction temperature: 65 °C for 8 h. Mp 133–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.12 (d, 2H, J=8.31 Hz, ArH), 7.22 (d, 1H, J=8.46 Hz, ArH), 7.33 (d, 2H, J=8.31 Hz, ArH), 7.38–7.43 (m, 1H, ArH), 7.54–7.61 (m, 3H, ArH), 8.22 (dd, 1H, J=0.90, 8.01 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=118.6 (q, $J_{F,C}$=320.8 Hz, CF_3), 123.3, 126.0, 127.3, 128.4, 129.1, 129.7, 129.9 (CH), 130.7, 131.2 (C), 132.7 (CH), 132.9, 133.4, 133.8, 140.4, 143.8, 144.7 (C), 180.1 (CO). IR (KBr): ν=3281, 3097, 3066, 2922, 2853, 2667, 2554 (w), 1649 (s), 1614 (w), 1588 (m), 1568, 1551, 1492, 1464, 1455 (w), 1424 (s), 1407, 1397 (m), 1377, 1315 (w), 1302, 1294 (m), 1277, 1247, 1238 (w), 1223, 1205, 1209, 1188 (s), 1158 (m), 1135, 1129 (s), 1090, 1077 (m), 1048, 1035 (w), 1012, 971 (m), 881 (s), 871 (m), 847, 834 (m), 815, 805, 759 (s), 739 (w), 734 (s), 711, 686, 665 (w), 647, 631 (m), 615, 601 (s), 588 (m), 568, 555, 538 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 470 ([M+H]$^+$, 38), 337 (100), 302 (68), 274 (26), 245 (14). HRMS (EI): calcd for $C_{20}H_{10}F_3ClO_4S_2$ [M]$^+$: 469.96556; found: 469.96474.

*5.2.31. Synthesis of 1-(4-methoxyphenyl)-9-oxo-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10e**).* Starting with **8** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol),

and THF (5 mL), **10e** was isolated as a yellow solid (74 mg, 81%); reaction temperature: 65 °C for 8 h. Mp 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.79 (s, 3H, OCH_3), 6.89 (d, 2H, J=8.76 Hz, ArH), 7.12 (d, 2H, J=8.73 Hz, ArH), 7.25 (d, 1H, J=8.40 Hz, ArH), 7.35–7.41 (m, 1H, ArH), 7.50–7.56 (m, 3H, ArH), 8.20 (d, 1H, 8.01 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=54.2 (OCH_3), 112.6 (CH),117.6 (q, $J_{F,C}$=320.9 Hz, CF_3), 122.1, 124.8, 126.1, 128.0 (CH), 128.1 (C), 128.6, 129.1 (CH), 130.1 (C), 131.4 (CH), 131.5, 132.8, 133.0, 142.3, 144.7, 158.0 (C), 179.5 (CO). IR (KBr): ν=3290, 3104, 3071, 3034, 2996, 2950, 2934, 2907, 2853, 2833, 1682 (w), 1652 (s), 1607 (w), 1589, 1589 (m), 1567, 1552 (w), 1513 (m), 1464, 1455 (w), 1424 (s), 1375, 1353, 1314 (w), 1303, 1295 (m), 1271 (w), 1248, 1241 (m), 1224, 1202, 1191, 1178 (s), 1164, 1157 (w), 1131 (s), 1108 (m), 1078, 1055, 1035 (w), 1026, 972 (m), 885 (s), 846 (m), 832 (w), 819, 807 (s), 779 (w), 761, 734 (s), 690, 673 (w), 650, 643 (m), 619, 599, 592 (s), 574, 544 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=466 ([M]$^+$, 36), 333 (100), 302 (31), 274 (10). HRMS (EI): calcd for $C_{21}H_{13}F_3O_5S_2$ [M]$^+$: 466.01510; found: 466.05129.

*5.2.32. Synthesis of 9-oxo-1-phenyl-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10f**).* Starting with **8** (100 mg, 0.197 mmol), phenylboronic acid **3i** (27 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10f** was isolated as a yellow solid (76 mg, 88%); reaction temperature: 65 °C for 8 h. Mp 178–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.17–7.21 (m, 1H, ArH), 7.26 (d, 2H, J=8.37 Hz, ArH), 7.35–7.42 (m, 4H, ArH), 7.53–7.57 (m,3H, ArH), 8.21 (dd, 1H, J=0.90, 8.01 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=117.6 (q, $J_{F,C}$=318.8 Hz, CF_3), 122.1, 124.9, 126.2, 126.3, 126.7, 127.1 (CH), 128.2 (C), 128.6, 129.0 (CH), 129.9 (C), 131.5 (CH), 131.6, 132.8, 140.9, 142.5, 145.0 (C), 179.2 (CO). IR (KBr): ν=3274, 3064, 2960, 1901 (w), 1667 (w), 1645 (s), 1622 (w), 1587 (m), 1552, 1493, 1461 (m), 1427 (s), 1409 (m), 1315, 1305 (w), 1292 (m), 1260, 1251 (w), 1227, 1207, 1187 (s), 1158 (m), 1129 (s), 1112, 1079, 1054, 1034, 1020, 971 (m), 912 (w), 879 (s), 861 (w), 842 (s), 821 (w), 799 (s), 768 (m), 756 (s), 738, 732, 701, 695, 680 (m), 651 (w), 637 (m), 616 (w), 598 (s), 569, 554 (w), 535 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=436 ([M]$^+$, 36), 303 (100), 302 (45), 274 (38), 245 (12). HRMS (EI): calcd for $C_{20}H_{11}F_3O_4S_2$ [M]$^+$: 436.00454; found: 436.00406.

*5.2.33. Synthesis of 1-(4-fluorophenyl)-9-oxo-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10g**).* Starting with **8** (100 mg, 0.197 mmol), 4-flourophenylboronic acid **3j** (31 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10g** was isolated as a yellow solid (73 mg, 82%); reaction temperature: 65 °C for 8 h. Mp 157–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.05 (t, 2H, J=8.73 Hz, ArH), 7.12–7.18 (m, 2H, ArH), 7.23 (d, 1H, J=8.37 Hz, ArH), 7.37–7.43 (m, 1H, ArH), 7.52–7.61 (m, 3H, ArH), 8.20 (dd, 1H, J=0.90, 7.83 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−114.9, −73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=114.1 (d, $J_{F,C}$=21.6 Hz, CH), 117.6 (q, $J_{F,C}$=320.9 Hz, CF_3), 122.2, 124.9, 126.3 (CH), 128.1(C), 128.4(d, $J_{F,C}$=7.98 Hz, CH), 128.6, 129.0 (CH), 129.7 (C), 131.6 (CH), 131.8, 132.8 (C), 136.7 (d, $J_{F,C}$=3.45 Hz, C), 142.7, 143.9 (C), 161.2 (d, $J_{F,C}$=245.4 Hz, C–F), 179.1 (CO). IR (KBr): ν=3068, 3044, 2957, 2917, 2848 (w), 1649 (s), 1620, 1601 (w), 1589 (m), 1567, 1551 (w), 1510 (m), 1463 (w), 1429 (s), 1408 (m), 1370, 1316, 1303, 1293, 1248 (w), 1213 (s), 1188, 1156 (m), 1129 (s), 1092, 1078, 1048, 1034, 1012 (w), 972 (m), 883 (s), 871, 843 (m), 832 (s), 815 (m), 804 (s), 791 (m), 761 (s), 741 (w), 733 (m), 690, 674 (w), 650, 639 (m), 617, 598 (s), 588, 571 (m), 563, 549 (w), 537 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=454 ([M+H]$^+$, 33), 321 (100), 292 (42), 263 (13). HRMS (EI): calcd for $C_{20}H_{10}F_4O_4S_2$ [M]$^+$: 453.99511; found: 453.99530.

*5.2.34. Synthesis of 9-oxo-1-(o-tolyl)-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10h**).* Starting with **8** (100 mg, 0.197 mmol), 2-methylphenylboronic acid **3l** (30 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10h** was isolated as a yellow solid (67 mg, 76%); reaction temperature: 65 °C for 8 h. Mp 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.95 (s, 3H, CH_3), 6.97 (d, 1H, J=7.53 Hz, ArH), 7.16–7.28 (m, 4H, ArH), 7.33–7.39 (m, 1H, ArH), 7.54–7.58 (m, 3H, ArH), 8.22 (dd, 1H, J=0.90, 8.10 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.2 (CH_3), 118.6 (q, $J_{F,C}$=320.9 Hz, CF_3), 123.4, 125.6, 126.0, 127.2, 127.3, 127.4 (CH), 129.4 (C), 129.5, 129.6, 129.8 (CH), 130.3, 132.4 (C), 132.6 (CH), 133.9, 134.6, 141.9, 143.6, 145.5 (C), 179.6 (CO). IR (KBr): ν=3292, 3063, 3018, 2953, 2922, 2857 (w), 1650 (s), 1592 (m), 1554, 1489 (w), 1425 (s), 1377 (w), 1301 (m), 1271 (w), 1261 (w), 1248 (m), 1209, 1188 (s), 1161 (m), 1133, 1118 (s), 1078, 1055, 1035 (w), 974 (m), 884 (s), 838 (m), 800 (s), 785 (w), 752, 737, 729 (s), 693, 675 (w), 650 (m), 602 (s), 568, 536 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=450 ([M]$^+$, 30), 435 (16), 317 (68), 302 (100), 274 (30). HRMS (EI): calcd for $C_{21}H_{13}F_3O_4S_2$ [M]$^+$: 450.02019; found: 450.02029.

*5.2.35. Synthesis of 9-oxo-1-(m-tolyl)-9H-thioxanthen-4-yl trifluoromethanesulfonate (**10i**).* Starting with **8** (100 mg, 0.197 mmol), 3-methylphenylboronic acid **3m** (30 mg, 0.22 mmol), $Pd(PPh_3)_4$ (11 mg, 5 mol %), K_3PO_4 (63 mg, 0.29 mmol), and THF (5 mL), **10i** was isolated as a yellow solid (70 mg, 79%); reaction temperature: 65 °C for 8 h. Mp 151–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 6.99 (t, 2H, J=7.47 Hz, ArH), 7.15 (d, 1H, J=7.59 Hz, ArH), 7.25 (t, 2H, J=7.35 Hz, ArH), 7.36–7.43 (m, 1H, ArH), 7.52–7.57 (m, 3H, ArH), 8.21 (dd, 1H, J=0.87, 7.95 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=20.5 (CH_3), 117.6 (q, $J_{F,C}$=320.7 Hz, CF_3), 122.1, 123.9, 124.9, 126.2, 126.9, 127.1, 127.4 (CH), 128.2 (C), 128.6, 129.0 (CH), 130.0 (C), 131.5 (CH), 132.8, 136.7, 140.8, 142.5, 145.1 (C), 179.2 (CO). IR (KBr): ν=3283, 3061, 2961, 2922, 2859, 2736, 2668, 2554 (w), 1651 (s), 1613, 1605 (w), 1589 (m), 1568, 1552, 1537, 1484, 1463 (w), 1426 (s), 1387, 1314 (w), 1300, 1292 (m), 1261 (w), 1249 (m), 1230, 1202 (s), 1183, 1167, 1158 (m), 1131 (s), 1119 (m), 1094, 1078, 1035 (w), 970 (m), 900 (w), 880 (s), 864 (w), 840, 806, 792, 774 (s), 763 (w), 751 (s), 740 (w), 727, 702 (m), 692, 679, 653 (w), 634 (m), 600 (s), 568, 551 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=450 ([M]$^+$, 33), 317 (100), 302 (37), 288 (12). HRMS (EI): calcd for $C_{21}H_{13}F_3O_4S_2$ [M]$^+$: 450.02019; found: 450.01998.

*5.2.36. Synthesis of 1-(4-methoxyphenyl)-4-(p-tolyl)-9H-thioxanthen-9-one (**11a**).* Starting with **8** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), 4-methylphenylboronic acid **3e** (29 mg, 0.22 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **11a** was isolated as a yellow solid (72 mg, 90%); reaction temperature: at 65 °C for 8 h, at 90 °C for 6 h. Mp 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.39 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 6.89 (d, 2H, J=8.76 Hz, ArH), 7.19 (d, 2H, J=8.76 Hz, ArH), 7.23 (d, 2H, J=7.56 Hz, ArH), 7.27–7.37 (m, 6H, ArH), 7.39–7.44 (m, 1H, ArH), 8.18 (dd, 1H, J=1.08, 8.04 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.44 (CH_3), 55.2 (OCH_3), 113.5, 125.5, 126.2 (CH), 128.1 (C), 129.1, 129.2, 129.4, 129.6, 129.8 (CH), 131.4 (C), 131.7, 132.0 (CH), 135.7, 135.8, 136.4, 137.5, 138.5, 138.6, 144.5, 158.6 (C), 182.4 (CO). IR (KBr): ν=3055, 3029, 3008, 2955, 2918, 2857, 2835 (w), 1635 (s), 1606, 1591 (m), 1576, 1548 (w), 1512 (m), 1461 (w), 1434 (s), 1410, 1384, 1359 (w), 1318, 1307, 1290 (m), 1271 (w), 1254 (m), 1241 (s), 1172 (m), 1161, 1118, 1105, 1080, 1073 (w), 1149, 1026, 1019 (m), 973, 964, 935 (w), 920 (m), 902, 865, 854, 834 (w), 825 (m), 813 (s), 772 (w), 758, 731, 719 (s), 687, 660 (w), 651, 644 (m), 634, 609, 593 (w), 563 (m), 547 (w), 537 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=409 ([M+H]$^+$, 23), 408 ([M]$^+$, 76), 407 ([M−H]$^+$, 100). HRMS (ESI): calcd for $C_{27}H_{21}O_2S$ [M+H]$^+$: 409.12568; found: 409.12630.

*5.2.37. Synthesis of 1-(4-fluorophenyl)-4-(4-methoxyphenyl)-9H-thioxanthen-9-one (**11b**).* Starting with **8** (100 mg, 0.197 mmol), 4-

flourophenylboronic acid **3j** (30 mg, 0.22 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **11b** was isolated as a yellow solid (71 mg, 88%); reaction temperature: at 65 °C for 8 h, at 90 °C for 6 h. Mp 194–196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.80 (s, 3H, OCH_3), 7.05 (q, 4H, J=8.76 Hz, ArH), 7.19–7.24 (m, 3H, ArH), 7.28–7.48 (m, 6H, ArH), 8.19 (dd, 1H, J=1.05, 8.01 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−116.2. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=54.3 (OCH_3), 113.1 (CH), 113.9 (d, $J_{F,C}$=21.5 Hz, CH), 124.5, 125.2 (CH), 127.0 (C), 128.2 (CH), 128.4 (d, $J_{F,C}$=7.99 Hz, CH), 128.7 (CH), 129.6 (C), 129.8 (CH), 129.9 (C), 130.8, 131.1 (CH) 135.4, 137.1, 137.9 (C), 138.5 (d, $J_{F,C}$=3.42 Hz, C), 142.7, 158.9 (C), 160.8 (d, $J_{F,C}$=245.4 Hz, C–F), 180.9 (CO). IR (KBr): ν=3057, 3031, 2954, 2920, 2850, 2251 (w), 1633 (s), 1601 (m), 1589 (s), 1574, 1548 (w), 1509 (s), 1461 (m), 1434 (s), 1359 (w), 1305, 1307, 1290 (m), 1245, 1219 (s), 1174, 1157 (m), 1105, 1092, 1081, 1045 (w), 1022 (s), 965, 931, 914, 896, 877, 867 (w), 844 (m), 828, 821 (s), 795 (m), 777 (w), 760, 731, 725 (s), 700, 689 (w), 662, 649, 641 (m), 628 (w), 607, 593 (m), 561, 550 (m), 535 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=413 ($[M+H]^+$, 23), 412 ($[M]^+$, 78), 411 ($[M-H]^+$, 100), 368 (14). HRMS (EI): calcd for $C_{26}H_{16}FO_2S$ $[M-H]^+$: 411.08496; found: 411.08493.

*5.2.38. Synthesis of 4-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)-9H-thioxanthen-9-one (**11c**).* Starting with **8** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), 4-*tert*-butylphenylboronic acid **3c** (39 mg, 0.22 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **11c** was isolated as a yellow solid (75 mg, 84%); reaction temperature: at 65 °C for 8 h, at 90 °C for 6 h. Mp 212–214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.35 (s, 9H, $3CH_3$), 3.80 (s, 3H, OCH_3), 6.89 (d, 2H, J=8.64 Hz, ArH), 7.18 (d, 2H, J=8.70 Hz, ArH), 7.22–7.43 (m, 7H, ArH),7.47 (d, 2H, J=8.31 Hz, ArH), 8.18 (dd, 1H, J=0.90, 7.89 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=30.4 (CH_3), 33.8 (C), 54.2 (OCH_3), 112.5, 124.5, 124.6, 125.1 (CH), 127.0 (C), 128.1, 128.3, 128.8, 129.8 (CH), 130.3 (C), 130.6, 131.0 (CH), 134.5, 134.8, 135.4, 136.5, 137.6, 143.4, 150.5, 157.5 (C), 181.4 (CO). IR (KBr): ν=3059, 2997, 2959, 2931, 2903, 2866, 2834, 2248 (w), 1640, 1633 (s), 1606, 1589 (m), 1575, 1558, 1544 (w), 1510 (s), 1461 (m), 1350 (w), 1433 (s), 1410, 1360 (w), 1306 (m), 1290, 1271 (w), 1240 (s), 1174 (m), 1139 (w), 1113, 1105 (m), 1081 (w), 1049 (m), 1026, 1015 (m), 972, 935, 918, 907, 888, 863, 847, 838 (w), 817 (s), 779 (w), 759 (m), 744 (w), 729 (s), 688 (w), 649 (m), 630, 621, 607, 594 (w), 568, 545 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=451 ($[M+H]^+$, 28), 450 ($[M]^+$, 91), 449 ($[M-H]^+$, 100), 435 (12). HRMS (EI): calcd for $C_{30}H_{25}O_2S$ $[M-H]^+$: 449.15698; found: 449.15660.

*5.2.39. Synthesis of 4-(3-chlorophenyl)-1-(4-methoxyphenyl)-9H-thioxanthen-9-one (**11d**).* Starting with **8** (100 mg, 0.197 mmol), 4-methoxyphenylboronic acid **3h** (33 mg, 0.22 mmol), 3-chlorophenylboronic acid **3n** (34 mg, 0.22 mmol), $Pd(PPh_3)_4$ (23 mg, 10 mol %), K_3PO_4 (125 mg, 0.59 mmol), and THF (5 mL), **11d** was isolated as a yellow solid (75 mg, 89%); reaction temperature: at 65 °C for 8 h, at 90 °C for 6 h. Mp 190–191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.79 (s, 3H, OCH_3), 6.88 (d, 2H, J=8.73 Hz, ArH), 7.17 (d, 2H, J=8.73 Hz, ArH), 7.24 (d, 1H, J=7.62 Hz, ArH), 7.28–7.46 (m, 8H, ArH), 8.18 (dd, 1H, J=1.08, 8.04 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.2 (OCH_3), 113.6, 125.5, 126.4, 128.0 (CH), 128.2 (C), 128.7, 129.2, 129.3, 129.8, 129.9, 130.0 (CH), 131.3 (C), 131.9 (CH), 134.6, 135.5, 135.9, 137.1, 137.3, 140.3, 145.2, 158.7 (C), 182.2 (CO). IR (KBr): ν=3100, 3070, 3053, 2998, 2947, 2931, 2902, 2831 (w), 1650 (s), 1633 (s), 1605 (w), 1588 (m), 1575, 1564, 1546 (w), 1510 (m), 1462, 1454 (w), 1432 (s), 1407, 1365 (w), 1307, 1299 (m), 1288 (w), 1237 (s), 1178 (m), 1165, 1155, 1121 (w), 1106, 1074, 1049, 1025 (m), 963 (w), 941 (m), 928, 898, 885, 866 (w), 841 (m), 819 (s), 783, 779 (m), 762 (s), 748 (w), 734 (s), 715, 692 (m), 665, 645, 623, 609, 583, 571 (w), 546 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=429 ($[M+H]^+$, 55), 428 ($[M]^+$, 72), 427 ($[M-H]^+$, 100), 413 (10). HRMS (EI): calcd for $C_{26}H_{16}ClO_2S$ $[M-H]^+$: 427.05540; found: 427.05524.

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