DOI: 10.1002/ejoc.201101491

Efficient Synthesis of Arylated Flavones by Site-Selective Suzuki–Miyaura Cross-Coupling Reactions of the Bis(triflate) of 5,7- and 7,8-Dihydroxyflavone

Nadi Eleya,^[a] Imran Malik,^[a,b] Sebastian Reimann,^[a,c] Kai Wittler,^[d] Martin Hein,^[a] Tamás Patonay,^[b] Alexander Villinger,^[a] Ralf Ludwig,^[c,d] and Peter Langer^{*[a,c]}

Keywords: Synthetic methods / Natural products / Heterocycles / Flavones / Cross-coupling / Palladium / Regioselectivity

Suzuki–Miyaura reactions of the bis(triflate) of 5,7- and 7,8dihydroxyflavone proceed with very good site selectivity in favor of position 7 and allow the synthesis of various arylated flavones. The reaction of 5,7-dihydroxyflavone with one equivalent of triflic anhydride also proceeds with very good

Introduction

Flavones (2-arylchromones) are very important oxygenated heterocyclic compounds, which belong to the flavonoid group, and occur naturally as secondary metabolites in fruits, vegetables, seeds, and flowers. They play important roles in plant development, reproduction, and defense and possess a wide range of biological and pharmaceutical activities. This includes antiviral, anti-inflammatory, hepatoprotective, antioxidant, antithrombotic, vasodilating, and anticarcenogenic activity, combining high efficiency and low toxicity.^[1-6] The main synthetic methods include the Kostanecki reaction, Allan-Robinson synthesis, and the Baker-Venkataraman rearrangement.^[7-10] Despite the great pharmacological importance of flavones and chromones, relatively few applications of palladium-catalyzed cross-coupling reactions to their halides or triflates have been reported to date.^[11] Site-selective Suzuki-Miyaura reactions^[12] and related palladium-catalyzed cross-coupling reactions of polyhalogenated molecules^[13] or polytriflates^[14] have been extensively studied in recent years. Recently, we have reported the synthesis of 7,8-diarylflavones by site-selective Suzuki-Miyaura reactions of the bis(triflate) of 7,8dihydroxyflavone (9).^[15] Herein, we report full details of these studies. In addition, we report, for the first time, the synthesis of 5,7-diarylflavones by site-selective Suzuki-Miyaura reactions of the bis(triflate) of 5,7-dihydroxyflav-

Dr.-Lorenz-Weg 1, 18059 Rostock, Germany

site selectivity in favor of position 7. The subsequent Suzuki-Miyaura reaction of the product allows the synthesis of 7aryl-5-hydroxyflavones. The regioselectivity is discussed based on DFT calculations.

one (1). The regioselectivity observed in these reactions is discussed based on DFT calculations.

Results and Discussion

5,7-Dihydroxyflavone (1)

The reaction of **1** with triflic anhydride (Tf₂O; 2.4 equiv.) resulted in the formation of the mono-triflate **2** in 80% yield (Scheme 1). The expected bis-triflate was not formed. The yield of **2** slightly dropped when only 1.2 equiv. of triflic anhydride was employed. The synthesis of **2** and a Stille reaction of the latter has been previously reported.^[16] The difficulty in preparing the desired bis-triflate is in striking contrast to the facile synthesis of the bis(triflate) of **9**^[15] and might be explained by the formation of a stable intramolecular hydrogen bond in the case of **1**.



Scheme 1. Synthesis of **2**. Conditions: (i) (1) **1** (1.0 equiv.), pyridine (4.0 equiv.), CH₂Cl₂, 20 °C; (2) Tf₂O (2.4 equiv.), 20 °C, 4 h.

The Suzuki–Miyaura reaction of mono-triflate **2** with various arylboronic acids, **3a–I**, afforded the 7-aryl-5-hydroxyflavones **4a–I** in 75–90% yields (Scheme 2 and Table 1). The reactions were carried out under standard conditions [3 mol-% of [Pd(PPh₃)₄] as the catalyst, K₃PO₄ as the base, 1,4-dioxane, 80 °C]. Very good yields were obtained both for electron-rich and -poor arylboronic acids. The yields for arylboronic acids containing an *ortho* substituent were slightly lower than those of other arylboronic acids, presumably due to steric effects.



[[]a] Department of Chemistry, Organic Chemistry, University of Rostock,

Albert-Einstein-Str. 3a, 18059 Rostock, Germany

[[]b] Department of Organic Chemistry, University of Debrecen, 4032 Debrecen, Egyetem tér 1, Hungary

[[]c] Leibniz Institute for Catalysis at the University of Rostock e. V. (LIKAT), Albert-Einstein-Str. 29a, 18059 Rostock, Germany

 [[]d] Department of Chemistry, Physical and Theoretical Chemistry, University of Rostock,



Scheme 2. Synthesis of **4a–1**. Conditions: (i) **2** (1.0 equiv.), **3a–1** (1.0 equiv.), K_3PO_4 (1.5 equiv.), $[Pd(PPh_3)_4]$ (3 mol-%), 1,4-dioxane, 80 °C, 4 h.

Table 1. Synthesis of 4a-l.

3,4	Ar	4 [%] ^[a]		
a	$4 - MeC_6H_4$	90		
b	$3-MeC_6H_4$	85		
c	$3,5-Me_2C_6H_3$	80		
d	$2 - MeC_6H_4$	77		
e	$4-tBuC_6H_4$	80		
f	$4-(MeO)C_6H_4$	90		
g	$3,4-(MeO)_2C_6H_3$	85		
ĥ	$4-CF_3C_6H_4$	79		
i	$4-FC_6H_4$	80		
j	$4-ClC_6H_4$	86		
k	$2-ClC_6H_4$	75		
1	C ₆ H ₅	80		

[a] Yields of isolated products.

5,7-Bis(triflate)flavone (5) could be successfully prepared from 1 in 90% yield when the reaction was carried out at 40 °C instead of 20 °C (Scheme 3).



Scheme 3. Synthesis of 5. Conditions: (i) (1) 1 (1.0 equiv.), pyridine (4.0 equiv.), CH_2Cl_2 , 20 °C; (2) Tf_2O (2.4 equiv.), 20 \rightarrow 40 °C, 30 min.

The Suzuki–Miyaura reaction of bis-triflate **5** with 2.0 equiv. of various arylboronic acids **3** afforded the 5,7diarylflavones **6a–i** in 76–90% yields (Scheme 4 and Table 2). The reactions were carried out at a higher temperature (115 °C) than that used for the synthesis of products **4** to affect good yields. Very good yields were obtained for products derived from both electron-rich and -poor arylboronic acids.



Scheme 4. Synthesis of **6a**–i. Conditions: (i) **5** (1.0 equiv.), Ar-B(OH)₂ (2.0 equiv.), K_3PO_4 (3.0 equiv.), $[Pd(PPh_3)_4]$ (6 mol-%), 1,4-dioxane, 115 °C, 6 h.

The Suzuki–Miyaura reaction of bis-triflate **5** with 1.0 equiv. of arylboronic acids **3** afforded the 7-aryl-5-(triflate)flavones 7a-g in 71–85% yields (Scheme 5 and Table 3). The reactions were carried out at 70 °C instead of 115 °C to achieve good yields and to avoid the formation of 5,7-diarylflavones **6**.

Table 2. Synthesis of **6a–i**.

	-			
3	6	Ar	6 [%] ^[a]	
a	a	4-MeC ₆ H ₄	85	
b	b	$3-MeC_6H_4$	80	
c	с	$3,5-Me_2C_6H_3$	80	
e	d	$4-tBuC_6H_4$	77	
f	e	$4-(MeO)C_6H_4$	90	
h	f	$4-CF_3C_6H_4$	76	
i	g	$4-FC_6H_4$	83	
i	ĥ	$4-ClC_6H_4$	85	
ì	i	C ₆ H ₅	81	

[a] Yields of isolated products.



Scheme 5. Synthesis of **7a–g**. Conditions: (i) **5** (1.0 equiv.), ArB-(OH)₂ (1.0 equiv.), K_3PO_4 (1.5 equiv.), $[Pd(PPh_3)_4]$ (3 mol-%), 1,4-dioxane, 70 °C, 9 h.

Table 3. Synthesis of 7a-g.

3	7	Ar	7 [%] ^[a]	
b	a	3-MeC ₆ H ₄	85	
c	b	$3,5-Me_2C_6H_3$	85	
e	с	$4-tBuC_6H_4$	71	
f	d	$4-(MeO)C_6H_4$	83	
g	e	$2-(MeO)C_6H_4$	81	
ĭ	f	$4-FC_6H_4$	80	
j	g	$4-ClC_6H_4$	82	

[a] Yields of isolated products.

The structure of **7e** was independently confirmed by X-ray crystal-structure analysis (Figure 1).



Figure 1. Ortep plot of 7e. Ellipses are drawn at the 50% probability level. $^{\left[21\right] }$

The structure of compound **7g** was confirmed by a ¹H,¹H NOESY experiment. The *ortho* protons of the 4-chlorophenyl group correlate with protons H-6 and H-8 of the flavone moiety (Figure 2).



Figure 2. Diagnostic NOESY interactions of 7g.

The one-pot Suzuki–Miyaura reaction of bis-triflate **5** with two different arylboronic acids **3** (sequential addition of 1.0 equiv. of each boronic acid) afforded the 5,7-diaryl-flavones **8a,b** in 77–78% yields (Scheme 6 and Table 4). The reactions were carried out at 70 °C for the first step (to avoid double coupling) and at 115 °C in the second step.



Scheme 6. Synthesis of **8a,b**. Conditions: (i) (1) **5** (1.0 equiv.), $Ar^{1}B$ -(OH)₂ (1.0 equiv.), $K_{3}PO_{4}$ (1.5 equiv.), [Pd(PPh_{3})_{4}] (3 mol-%), 1,4-dioxane, 70 °C, 9 h; (2) $Ar^{2}B(OH)_{2}$ (1.0 equiv.), $K_{3}PO_{4}$ (1.5 equiv.), [Pd(PPh_{3})_{4}] (3 mol-%), 1,4-dioxane, 115 °C, 6 h.

Table 4. Synthesis of 8a,b.

3	8	Ar ¹	Ar ²	8 [%] ^[a]
c,j j,i	a b	$\begin{array}{c} 3,5\text{-}\text{Me}_2\text{C}_6\text{H}_3\\ 4\text{-}\text{ClC}_6\text{H}_4 \end{array}$	$\begin{array}{l} \text{4-ClC}_6\text{H}_4\\ \text{4-FC}_6\text{H}_4 \end{array}$	78 77

[a] Yields of isolated products.

7,8-Dihydroxyflavone

Bis(triflate) **10** was prepared from commercially available **9** in 76% yield (Scheme 7). The Suzuki–Miyaura reaction of **10** with arylboronic acids **3a,c,e,f,i,j,m** (2.6 equiv.) gave the 7,8-diarylflavones **11a**–g in 59–74% yield (Scheme 8 and Table 5). The reactions were carried out under conditions similar to the synthesis of 5,7-diarylflavones. Both electron-poor and -rich arylboronic acids could be successfully employed.



Scheme 7. Synthesis of 10. Conditions: (i) 9 (1.0 equiv.), Tf₂O (2.4 equiv.), pyridine (4.0 equiv.), CH₂Cl₂, $-78 \rightarrow 0$ °C, 4 h.



Scheme 8. Synthesis of **11a–g**. Conditions: (i) **10** (1.0 equiv.), **3a,c,e**, **f,i,j,m** (2.6 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%), K_3PO_4 (4.0 equiv.), 1,4-dioxane, 100 °C, 4 h.



Table 5. Synthesis of 11a-g.

3	11	R	11 [%] ^[a]
a	a	4-MeC ₆ H ₄	74
c	b	$3,5-Me_2C_6H_3$	71
e	c	$4-tBuC_6H_4$	59
f	d	$4-(MeO)C_6H_4$	68
i	e	$4-FC_6H_4$	62
j	f	$4-ClC_6H_4$	72
m	g	$4-EtC_6H_4$	70

[a] Yields of isolated products.

The Suzuki–Miyaura reaction of **10** with arylboronic acids **3a,h,j,m,n** (1.0 equiv.) afforded the 7-aryl-8-trifluorosulfonyloxyflavones **12a–e** in 66–76% yield (Scheme 9 and Table 6). The reaction had to be carried out at 70 °C instead of 100 °C to obtain a good site selectivity.



Scheme 9. Synthesis of **12a–e**. Reagents and conditions: (i) **10** (1.0 equiv.), **3a,h,j,m,n** (1.0 equiv.), K_3PO_4 (1.5 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%), 1,4-dioxane, 70 °C, 4 h.

Table 6. Synthesis of 12a-e.

3	12	R	12 [%] ^[a]
a	a	4-MeC ₆ H ₄	76
h	b	$4-(CF_3)C_6H_4$	69
i	с	$4-ClC_6H_4$	66
m	d	$4-\text{EtC}_6H_4$	72
n	e	$4-(HC=CH_2)C_6H_4$	74

[a] Yields of isolated products.

The Suzuki–Miyaura reaction of **12c** and **12a** with arylboronic acids **3f** and **3m**, respectively (1.3 equiv.) afforded the 7,8-diarylflavones **13a** and **13b**, respectively (Scheme 10 and Table 7). The reactions were carried out at 100 °C.



Scheme 10. Synthesis of **13a,b**. Reagents and conditions: (i) **12a,c** (1.0 equiv.), **3f,m** (1.3 equiv.), K_3PO_4 (1.5 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%), 1,4-dioxane, 100 °C, 4 h.

Table 7. Synthesis of 7,8-diarylflavones 13a,b.

3	12	13	Ar ¹	Ar ²	13 [%] ^[a]
f	c	a	$\begin{array}{c} \text{4-ClC}_6\text{H}_4\\ \text{4-MeC}_6\text{H}_4 \end{array}$	4-(MeO)C ₆ H ₄	73
m	a	b		4-EtC ₆ H ₄	66

[a] Yields of isolated products.

All products were characterized by spectroscopic methods. The constitutions of products **12a–e** and **13a,b** were proved by 2D NMR spectroscopy experiments (HMBC,

NOESY). The structure of **11a** was independently confirmed by X-ray crystal-structure analysis.^[15] Inspection of the X-ray structure shows that the flavone unit (including the phenyl group located at C2) is in the plane; the other two phenyl groups are twisted out of the plane for steric reasons.

The structure of **12d** was confirmed by 2D NMR spectroscopy correlations by using HMQC, HMBC, and NOESY. The chemical shift values of the carbon atoms were assigned with the help of an HMQC experiment, $\delta = 8.21$ (125.4, C-5), 7.44 ppm (127.4 ppm, C-6). In the HMBC spectrum, the aromatic proton of C-6 showed a strong coupling with C-5 (125.4), C-7 (131.6), C-1' (135.1 ppm). In the NOESY spectrum, the aromatic proton [$\delta = 7.44$ ppm (C-6)] showed an interaction with proton 5-H ($\delta = 8.18$ ppm). This information shows that the 4-(Et)-C₆H₄ moiety is attached to carbon atom C-7 (Figure 3).



Figure 3. HMBC (red arrows) and NOESY (blue arrows) correlations of **12d**.

Computational Studies

The regioselectivity observed in the Suzuki-Miyaura cross-coupling reactions of the bis(triflates) of 1 and 9 was investigated by DFT calculations at the B3LYP level of theory using a 6-31G* basis set. The first attack of siteselective palladium-catalyzed reactions usually occurs at the sterically less hindered or electronically more deficient position.^[19] Recently, we showed that the Suzuki-Miyaura reactions of the bis(triflates) of 1,2- and 1,3-dihydroxyanthraquinone proceed by initial attack at C1 (next to the carbonyl group), which can be explained by the fact that C1 is more electronically deficient than C3.^[14i,14j] However, considering the C-O bond lengths, the C1-O bond is assumed to be stronger than the C3–O bond (Table 8). These results were confirmed by computational calculations and NBO analysis (Tables 8 and 9). Furthermore, based on frontier molecular orbital (FMO) theory,^[20] the LUMO coefficient of the atom attacked by a nucleophile should be as large as possible. In case of the bis(triflate) of 1,3-dihydroxyanthraquinone, the corresponding coefficient of C1 is larger than that of C3 (Table 9). Therefore, the weaker binding strength of C3-O than C1-O appears to be irrelevant for regioselectivity.

Table 8. LUMOs of optimized structures and their largest orbital coefficients for the reaction centers C5 and C7.



NBO analysis for compound 5 showed that position C7 was electronically less deficient than position C5 (Table 8); this can be explained by the proximity of C5 to the carbonyl group. The values of the largest LUMO orbital coefficients of C5 and C7 do not seem to be the main reason for regioselective attack at C7 (Table 9). The regiodirecting effect of the carbonyl group of 5 seems to be less effective than in the case of the bis(triflates) of 1,2- and 1,3-dihydroxyanthraquinone. When comparing the bond lengths, the C7-O bond is longer and therefore weaker than that of the C5-O bond (Table 8). The lower steric hindrance of position C7 and the weak C7–O bond might account for regioselective attack at position 7 (Figure 4). Although the thermodynamic stability of the products is unlikely to have an influence, it is interesting to note that the mono-coupling product derived from the Suzuki reaction of 5 with phenylboronic acid is thermodynamically more stable for attack at the 7- rather than the 5-position (Table 10).

Table 9. Partial charges at corresponding carbon atoms obtained by using natural bond orbital (NBO) population analysis at the B3LYP/6-31G* levels of theory.

Compound	5		10		1,3-Bis(anthrag	triflate)- Juinone
Reaction centers	C5	C7	C8	C7	C1	C3
Distance C(X)–O NBO charges [a.u.]	1.394 0.3371	1.402 0.3034	1.400 0.2342	1.402 0.2772	1.394 0.3297	1.400 0.3047



Figure 4. Possible explanation for the site selectivity of reactions of bis(triflate) **5**.

Similarly, the site-selective formation of **12** can be explained by the fact that the C7 position of **10** is sterically less hindered than position C8. Clearly, both C–O bond strengths are similar, because the bond lengths of C7–O and

Table 10. Calculated model products and energies, given in hartrees, of the structures optimized at the B3LYP/6-31G* levels of theory.



C8 are similar (Table 8). In addition, position C7 (located *meta* to the ether oxygen atom and *para* to the carbonyl group) is considerably more electron deficient than position 1 (located *ortho* to the ether oxygen atom and *meta* to the carbonyl group; Tables 8 and 10 and Figure 5). Although the thermodynamic stability of the products is unlikely to have an influence, it is again interesting to note that the mono-coupling product is thermodynamically slightly more stable for attack at the 7- rather than the 8-position (Table 10).



Figure 5. Possible explanation for the site selectivity of the reactions of bis(triflate) 10.

Conclusion

The 5,7 and 7,8-diarylflavones were prepared by Suzuki– Miyaura reactions of the bis(triflate) of **1** and **9**. The reactions proceeded with very good site selectivity: first attack proceeded at position 7, for electronic or steric reasons, and was confirmed by results of DFT calculations and NBO analysis. The reaction of **1** with one equivalent of triflic anhydride also proceeded with very good site selectivity and allowed the synthesis of 7-aryl-5-hydroxyflavones.

Experimental Section

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

Computations: Geometry optimizations and NBO^[17] population analysis were carried out by using the Gaussian 09 program pack-age.^[18] We used the B3LYP gradient-corrected hybrid density func-

tional^[22,23] to calculate the structures and vibrational frequencies of the molecules. No imaginary frequencies were found, indicating that all molecules and fragments represented at least local minimum structures on the potential energy surface. For all molecules, the calculations were performed with 6-31G* basis sets implemented in Gaussian 09. All calculations were carried out on the high-performance computing cluster at the physical chemistry section of the University of Rostock.

5-Hydroxy-4-oxo-2-phenyl-4H-chromen-7-yl Trifluoromethanesulfone (2): Pyridine (1.3 mL, 15.72 mmol) was added to a solution of 1 (1.0 g, 3.93 mmol) in CH_2Cl_2 (40 mL) and the solution was stirred at room temperature. Tf₂O (1.5 mL, 9.43 mmol) was then added to the solution at room temperature and it was stirred for 4 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The product 2 was isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc) as a yellow solid (1.2 g, 80%). M.p. 75–77 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.64 (d, J = 2.2 Hz, 1 H, ArH), 6.69 (s, 1 H), 6.88 (d, J = 2.2 Hz, 1 H,ArH), 7.44-7.52 (m, 3 H, ArH), 7.76-7.80 (m, 2 H, ArH), 12.84 (br. s, 1 H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 99.8, 104.0, 105.3 (CH), 109.3 (C), 117.6 (d, J_{F,C} = 320.9 Hz, CF₃), 125.2, 128.2 (CH), 129.3 (C), 131.5 (CH), 152.2, 155.6, 161.5, 164.2 (C), 181.5 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -72.64 (s, 3 F, CF₃) ppm. IR (KBr): \tilde{v} = 3099, 3082, 3063 (w), 1650 (m), 1614, 1582, 1485 (s), 1415 (m), 1420 (s), 1371, 1337 (m), 1324 (w), 1298 (m), 1282 (w), 1264 (m), 1253, 1242 (w), 1229 (m), 1208, 1185, 1128, 1096 (s), 1034 (w), 1020 (s), 1001, 992 (w), 973 (s), 935, 908 (w), 857 (s), 842 (w), 825, 769, 721, 684, 664, 650 (s), 635, 612 (m), 596 (s), 566, 540 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 387 (20) $[M + H]^+$, 386 (100) $[M]^+$, 225 (77), 207 (12), 123 (31), 77 (10). HRMS (EI, 70 eV): calcd. for C₁₆H₉O₆F₃S [M]⁺: 386.00664; found 386.006622.

General Procedure for Synthesis of 4a–l: A solution of 2, K_3PO_4 , [Pd(PPh₃)₄], and arylboronic acid 3 1,4-dioxane (3 mL) was stirred at 80 °C for 4 h. After cooling to 20 °C, distilled water was added, the organic and the aqueous layers were separated, and the latter was extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

5-Hydroxy-2-phenyl-7-(*p*-tolyl)-4*H*-chromen-4-one (4a): Starting with **2** (80 mg, 0.207 mmol), **3a** (28 mg, 0.207 mmol), $[Pd(PPh_3)_4]$ (7 mg, 3 mol-%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4a was isolated as a yellow solid (61 mg, 90%). M.p. 204–206 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.32 (s, 3 H, CH₃), 6.63 (s, 1 H), 6.95 (d, *J* = 1.5 Hz, 1 H, ArH), 7.11 (d, *J* = 1.5 Hz, 1 H, ArH), 7.16–7.20 (m, 2 H, ArH), 7.47 (m, 5 H, ArH), 7.81–7.84 (m, 2 H, ArH), 12.45 (br. s, 1 H,

OH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 21.2$ (CH₃), 104.2, 105.1 (CH), 108.5 (C), 108.8, 125.3, 126.0, 128.0, 128.7 (CH), 130.2 (C), 130.9 (CH), 135.3, 137.9, 147.4, 155.6, 159.7, 163.5 (C), 182.1 (CO) ppm. IR (KBr): $\tilde{v} = 3074$, 2918, 2855, 1894 (w), 1658, 1614, 1591 (s), 1564, 1556, 1538 (w), 1519, 1486 (m), 1450, 1430, 1409, 1359 (s), 1344, 1309, 1294 (w), 1272 (m), 1254, 1211, 1201, 1189, 1159, 1124 (w), 1093, 1051, 1031 (m), 998 (s), 957, 938 (w), 864 (s), 838 (w), 803 (s), 774 (w), 763 (s), 727, 684 (m), 674 (s), 654, 645, 633, 623, 600, 563 (m), 531 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 329 (22) [M + H]⁺, 328 (100) [M]⁺, 300 (12), 155 (10). HRMS (EI, 70 eV): calcd. for C₂₂H₁₆O₃ [M]⁺: 328.10940; found 328.109336.

5-Hydroxy-2-phenyl-7-(m-tolyl)-4H-chromen-4-one (4b): Starting with 2 (80 mg, 0.207 mmol), 3b (28 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4b was isolated as a yellow solid (57 mg, 85%). M.p. 186–188 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.33 (s, 3 H,CH₃), 6.62 (s, 1 H), 6.94 (d, J = 1.5 Hz, 1 H, ArH), 7.10 (d, J = 1.5 Hz, 1 H, ArH), 7.12–7.15 (m, 1 H, ArH), 7.23– 7.28 (m, 1 H, ArH), 7.35–7.39 (m, 2 H, ArH), 7.40–7.49 (m, 3 H, ArH), 7.79–7.83 (m, 2 H, ArH), 12.44 (br. s, 1 H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 20.4$ (CH₃), 104.5, 105.0 (CH), 108.6 (C), 109.0, 123.3, 125.3, 126.9, 127.8, 128.0, 128.5 (CH), 130.2 (C), 130.9 (CH), 137.6, 138.1, 147.6, 155.5 159.6, 163.5 (C), 182.1 (CO) ppm. IR (KBr): $\tilde{v} = 3067, 2916, 2850, 2791$ (m), 1652, 1615, 1591 (s), 1568, 1556, 1537, 1504 (w), 1494, 1482 (m), 1450, 1411, 1398, 1362 (s), 1342, 1312 (w), 1294 (m), 1270, 1254, 1237, 1205 (m), 1179, 1166, 1159 (w), 1120, 1094, 1054, 1032, 1011, 999 (m), 965, 938, 920 (w), 907, 899, 861, 827, 809, 793 (m), 761 (s), 725, 700, 691, 684 (w), 673 (s), 654, 643 (w), 634 (s), 619, 607, 576, 545 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 329 (22) [M + H_{1}^{+} , 328 (100) $[M_{1}^{+}$. HRMS (EI, 70 eV): calcd. for $C_{22}H_{16}O_{3}$ [M]⁺: 328.10940; found 328.109336.

7-(3,5-Dimethylphenyl)-5-hydroxy-2-phenyl-4*H*-chromen-4-one (4c): Starting with 2 (80 mg, 0.207 mmol), 3c (31 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4c was isolated as a yellow solid (56 mg, 80%). M.p. 169-171 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 2.29 \text{ (s, 6 H, 2CH}_3), 6.61 \text{ (s, 1 H)}, 6.93 \text{ (d,}$ J = 1.5 Hz, 1 H, ArH), 6.96 (s, 1 H, ArH), 7.10 (d, J = 1.5 Hz, ArH), 7.15 (br. s, 2 H, ArH), 7.40–7.45 (m, 3 H, ArH), 7.79–7.82 (m, 2 H, ArH), 12.4 (br. s, 1 H, OH) ppm. ¹³C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.4$ (2CH₃), 105.5, 106.1 (CH), 109.6 (C), 110.1, 125.1, 126.4, 129.1, 130.5 (CH), 131.2 (C), 131.9 (CH), 138.5, 139.2, 148.8, 156.5, 160.7, 164.5 (C), 183.1 (CO) ppm. IR (KBr): v = 3066, 3023, 2917, 2863, 2796 (w), 1657, 1619 (s), 1592 (m), 1556, 1537 (w), 1491 (m), 1449 (s), 1414 (m), 1384 (w), 1295 (m), 1260 (s), 1219 (w), 1200 (m), 1177, 1160 (w), 1119, 1095, 1033, 1022, 999 (m), 968, 950 (w), 903 (m), 891 (w), 845, 820, 795 (s), 780, 771 (w), 761 (s), 721, 701 (w), 672, 663, 635 (s), 585 (m), 558, 546 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 343 (28) [M + H]⁺, 342 (100) $[M]^+$, 314 (6). HRMS (EI, 70 eV): calcd. for $C_{23}H_{18}O_3$ $[M]^+$: 342.12505; found 342.125397.

5-Hydroxy-2-phenyl-7-(o-tolyl)-4H-chromen-4-one (4d): Starting with **2** (80 mg, 0.207 mmol), **3d** (28 mg, 0.207 mmol), $[Pd(PPh_3)_4]$ (7 mg, 3 mol-%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound **4d** was isolated as a yellow solid (52 mg, 77%). M.p. 150–152 °C. ¹H NMR (250 MHz, CDCl₃): δ = 2.33 (s, 3 H, CH₃), 6.60 (s, 1 H), 6.93 (d, J = 1.4 Hz, 1 H, ArH), 7.09 (d, J = 1.4 Hz, 1 H, ArH), 7.11–7.14 (m, 1 H, ArH), 7.22–7.28 (m, 1 H, ArH), 7.31–7.34 (m, 2 H, ArH), 7.41–7.43 (m, 3 H, ArH), 7.78–7.81 (m, 2 H, ArH), 12.4 (br. s, 1 H, OH) ppm. ¹³C

NMR (62.9 MHz, CDCl₃): δ = 105.5, 106.1 (CH), 109.6 (C), 110.1, 124.3, 126.3, 128.0, 128.8, 129.0, 129.6 (CH), 131.2 (C), 131.9 (CH), 138.6, 139.2, 148.6, 156.5, 160.7, 164.5 (C), 183.1 (CO) ppm. IR (KBr): \tilde{v} = 3068, 2916 (w), 1652, 1615 (s), 1591 (m), 1568, 1556, 1537, 1519, 1504 (w), 1494, 1482, 1450, 1411, 1362 (m), 1343, 1312, 1295 (w), 1271, 1255, 1237, 1206 (m), 1167, 1159, 1120, 1054, 1033 (w), 1011, 999 (m), 965, 938, 921 (w), 908, 899, 860, 827, 809, 794 (m), 761 (s), 725, 700, 691, 685 (w), 673 (s), 654, 643 (w), 634 (m), 619, 608, 576, 545 (w) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 329 (24) [M + H]⁺, 328 (100) [M]⁺, 300 (9). HRMS (EI, 70 eV): calcd. for C₂₂H₁₆O₃ [M]⁺: 328.10940; found 328.109232.

7-[4-(*tert*-Butyl)phenyl]-5-hydroxy-2-phenyl-4*H*-chromen-4-one (4e): Starting with 2 (80 mg, 0.207 mmol), 3e (37 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4e was isolated as a yellow solid (61 mg, 80%). M.p. 196-198 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.27 (s, 9 H, 3CH₃), 6.6 (s, 1 H), 6.95 (d, J = 1.5 Hz, ArH), 7.10 (d, J = 1.5 Hz, 1 H, ArH), 7.38–7.44 (m, 5 H, ArH), 7.47-7.50 (m, 2 H, ArH), 7.78-7.81 (m, 2 H, ArH), 12.45 (br. s, 1 H, OH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 31.3 (3CH₃), 34.7 (C), 105.3, 106.1 (CH), 109.5 (C), 109.9, 126.0, 126.4, 126.9, 129.1 (CH), 131.2 (C), 131.9 (CH), 136.2, 148.4, 152.1, 156.6, 160.7, 164.5 (C), 183.1 (CO) ppm. IR (KBr): $\tilde{v} = 3063, 2962, 2902, 2859$ (w), 1646 (m), 1608 (s), 1590 (m), 1558, 1522, 1505, 1494, 1472, 1464 (w), 1450 (m), 1428, 1397, 1362, 1352, 1313, 1294 (w), 1263, 1205 (s), 1159, 1118, 1096, 1075, 1050, 1032, 1017 (w), 1002, 997 (m), 985, 970, 926, 910 (w), 868 (m), 859, 849, 841 (w), 827, 822 (s), 791 (m), 760 (s), 743, 733 (m), 717, 685 (w), 676 (s), 657, 644, 634, 625, 619, 607, 591 (w), 551 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* $(\%) = 371 (20) [M + H]^+, 370 (100) [M]^+, 356 (26), 355 (100), 127$ (12). HRMS (EI, 70 eV): calcd. for $C_{25}H_{22}O_3$ [M]⁺: 370.15635; found 370.155853.

5-Hydroxy-7-(4-methoxyphenyl)-2-phenyl-4*H*-chromen-4-one (4f): Starting with 2 (80 mg, 0.207 mmol), 3f (31 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4f was isolated as a yellow solid (64 mg, 90%). M.p. 173-175 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3 H, OCH₃), 6.63 (s, 1 H), 6.89– 6.92 (m, 3 H, ArH), 7.09 (d, J = 1.5 Hz, 1 H, ArH), 7.42–7.45 (m, 3 H, ArH), 7.45 (d, J = 6.7 Hz, 2 H, ArH), 7.80–7.90 (m, 2 H, ArH), 12.45 (br. s, 1 H, OH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 55.4 (OCH_3), 104.9, 106.1 (CH), 109.3 (C), 109.5, 114.4, 126.3,$ 128.4, 129.1 (CH), 131.3, 131.5 (C), 131.9 (CH), 148.1, 156.4, 160.4, 160.7, 164.5 (C), 183.1 (CO) ppm. IR (KBr): $\tilde{v} = 3068, 3046,$ 2995, 2978, 1941, 2914, 2894, 1836 (w), 1656, 1606, 1592 (s), 1572, 1558 (m), 1539 (w), 1519, 1490, 1450, 1433, 1417, 1402, 1361, 1345, 1294, 1272 (m), 1253 (s), 1214, 1203 (w), 1177 (s), 1122, 1115, 1095, 1051 (w), 1034 (s), 1013 (w), 999 (m), 955, 929 (w), 858 (m), 842 (w), 821, 797, 764 (s), 728, 722, 685 (w), 675 (s), 655, 643, 619 (w), 603 (m), 566 (w), 534 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 345 (24) [M + H]⁺, 344 (100) [M]⁺, 301 (8). HRMS (EI, 70 eV): calcd. for C₂₂H₁₆O₄ [M]⁺: 344.10431; found 344.104996.

5-Hydroxy-7-(3,4-dimethoxyphenyl)-2-phenyl-*4H***-chromen-4-one** (**4g**): Starting with **2** (80 mg, 0.207 mmol), **3g** (38 mg, 0.207 mmol), $[Pd(PPh_3)_4]$ (7 mg, 3 mol-%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound **4g** was isolated as a yellow solid (65 mg, 85%). M.p. 198–200 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3 H, OCH₃), 3.87 (s, 3 H, OCH₃), 6.62 (s, 1 H), 6.87 (d, *J* = 8.3 Hz, 1 H, ArH), 6.92 (d, *J* = 1.4 Hz, 1 H, ArH), 7.05–7.08 (m, 2 H, ArH), 7.13 (dd, *J* = 2.0, 8.3 Hz, 1 H, ArH), 7.43–7.47 (m, 3 H, ArH), 7.80–7.84 (m, 2 H, ArH), 12.4 (br. s, 1 H, OH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 56.0, 56.0 (2OCH₃), 105.0, 106.1 (CH), 109.3 (C), 109.6, 110.2, 111.4, 119.9, 126.4, 129.1 (CH), 131.2, 131.9 (C), 132.0 (CH), 148.3, 149.3, 149.9, 156.6, 160.7, 164.5 (C), 183.1 (CO) ppm. IR (KBr): $\bar{\nu}$ = 3436, 3070, 3000, 2937, 2916, 2837 (w), 1651, 1608, 1587 (s), 1522 (m), 1492 (s), 1468 (w), 1450, 1434 (s), 1398 (w), 1347 (s), 1322, 1301, 1291 (w), 1252, 1247 (s), 1218, 1203, 1192 (w), 1170 (m), 1129, 1096 (s), 1049 (w), 1018, 1006, 999 (7), 973, 949, 923, 904 (w), 864, 837 (m), 820, 802, 769 (s), 726 (w), 682, 672 (s), 663, 650, 621, 607, 580, 569 (w) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 375 (20) [M + H]⁺, 374 (100) [M]⁺, 332 (13), 331 (26), 238 (11). HRMS (EI, 70 eV): calcd. for C₂₃H₁₈O₅ [M]⁺: 374.11488; found 374.1143136.

5-Hydroxy-2-phenyl-7-[4-(trifluoromethyl)phenyl]-4H-chromen-4one (4h): Starting with 2 (80 mg, 0.207 mmol), 3h (39 mg, 0207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4h was isolated as a yellow solid (62 mg, 79%). M.p. 215-217 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 6.67 \text{ (s, 1 H)}, 6.95 \text{ (br. s, 1 H, ArH)}, 7.13$ (br. s, 1 H, ArH), 7.45–7.48 (m, 3 H, ArH), 7.65 (br. s, 4 H, ArH), 7.82-7.85 (m, 2 H, ArH), 12.51 (br. s, 1 H, OH) ppm. ¹³C NMR $(75.4 \text{ MHz}, \text{CDCl}_3)$: $\delta = 105.8$, 106.2 (CH), 110.2 (C), 110.3 (CH), 122.2 [q, J(F,C) = 320.3 Hz, CF_3], 125.9 (q, J = 3.7 Hz, CH), 126.4, 129.1 (CH), 130.5, 131.0 (C), 142.8, 146.8, 156.6, 161.0, 164.8 (C), 183.1 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -62.60 ppm. IR (KBr): $\tilde{v} = 3060, 2922, 2850, 2803$ (w), 1650, 1611, 1589 (s), 1557, 1523 (w), 1484, 1450, 1433, 1410, 1355, 1325, 1296, 1284, 1267 (s), 1249, 1214, 1203 (m), 1167, 1108, 1098, 1068 (s), 1049, 1032, 1015, 997 (m), 975, 958, 930, 906 (w), 845 (m), 822, 766 (s), 754, 724, 699 (w), 686, 676, 656, 633 (s), 611, 593, 580 (w), 531 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 383 (18) [M + H]⁺, 382 (100) $[M]^+$, 252 (10), 177 (8). HRMS (EI, 70 eV): calcd. for $C_{22}H_{13}F_3O_3$ [M]⁺: 382.08113; found 382.080944.

(4i): 7-(4-Fluorophenyl)-5-hydroxy-2-phenyl-4H-chromen-4-one Starting with 2 (80 mg, 0.207 mmol), 3i (29 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4i was isolated as a yellow solid (55 mg, 80%). M.p. 214-216 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.66 (s, 1 H), 6.92 (d, J = 1.5 Hz, 1 H, ArH), 7.06-7.12 (m, 3 H, ArH), 7.45-7.50 (m, 3 H, ArH), 7.51-7.56 (m, 2 H, ArH), 7.83–7.86 (m, 2 H, ArH), 12.4 (br. s, 1 H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 105.4, 106.2 (CH), 109.6 (C), 110.0, 116.0 (d, *J* = 21.6 Hz, CH), 126.4, 129.0 (d, *J* = 8.2 Hz, CH), 129.1 (CH), 131.1 (C), 132.0 (CH), 135.4 (d, J = 3.2 Hz, 1 C), 147.4, 156.6, 160.8 (C), 163.2 (d, J_{EC} = 248.9 Hz) (CF), 164.6 (C), 183.1 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -112.90 ppm. IR (KBr): $\tilde{v} = 3074$, 3056, 1885 (w), 1657, 1619, 1600 (s), 1568, 1556 (w), 1517, 1490, 1450, 1434, 1410 (s), 1398 (w), 1359 (m), 1346, 1300, 1293 (w), 1270 (m), 1254 (w), 1235, 1215, 1202, 1163 (m), 1123, 1095, 1050, 1032, 1015 (w), 999 (s), 952, 937 (w), 909, 862 (s), 842 (w), 817, 807, 798 (s), 775 (w), 764 (s), 727, 718, 684 (w), 674 (s), 654 (m), 641, 632, 618 (w), 600 (m), 561 (w), 533 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 333 (20) [M + H]⁺, 332 (100) [M]⁺, 304 (11), 202 (10), 152 (12). HRMS (EI, 70 eV): calcd. for C₂₁H₁₃FO₃ [M]⁺: 332.08432; found 332.084347.

7-(4-Chlorophenyl)-5-hydroxy-2-phenyl-4H-chromen-4-one (4): Starting with **2** (80 mg, 0.207 mmol), **3j** (32 mg, 0.207 mmol), $[Pd(PPh_3)_4]$ (7 mg, 3 mol-%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound **4j** was isolated as a yellow solid (62 mg, 86%). M.p. 217–219 °C. ¹H NMR (250 MHz, CDCl₃): $\delta = 6.68$ (s, 1 H), 6.94 (d, J = 1.5 Hz, 1 H, ArH), 7.12 (d, J = 1.5 Hz, 1 H, ArH), 7.35–7.40 (m, 2 H, ArH), 7.48–7.52 (m, 5 H, ArH), 7.83–7.87 (m, 2 H, ArH), 12.5 (br. s, 1



H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 105.4$, 106.2 (CH), 109.8 (C), 109.9, 126.4, 128.5, 129.1, 129.2 (CH), 131.1 (C), 132.1 (CH), 135.0, 137.7, 147.2, 156.6, 160.9, 164.7 (C), 183.1 (CO) ppm. IR (KBr): $\tilde{v} = 3071$, 3053, 1900 (w), 1656, 1619 (s), 1593 (m), 1572, 1557 (w), 1504, 1494, 1485, 1477, 1450, 1430, 1408 (m), 1393 (w), 1356, 1294, 1267, 1216, 1203 (m), 1188, 1160, 1123, 1108 (m), 1093 (s), 1052, 1032, 1015, 1000 (m), 969, 956, 943 (w), 909 (m), 889 (w), 862 (s), 840 (w), 814 (s), 790 (m), 764 (s), 737, 720, 715 (w), 673 (s), 655, 639, 631, 618 (m), 607 (w), 584, 534 (s) cm⁻¹. GC– MS (EI, 70 eV): m/z (%) = 350 (³⁷Cl, 34) [M]⁺, 349 (³⁵Cl, 24) [M + H]⁺, 348 (³⁵Cl, 100) [M]⁺, 155 (11). HRMS (EI, 70 eV): calcd. for C₂₁H₁₃³⁷ClO₃ [M]⁺: 348.05477 found 348.055573.

5-Hydroxy-7-(2-chlorophenyl)-2-phenyl-4H-chromen-4-one (4k): Starting with 2 (80 mg, 0.207 mmol), 3k (32 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4k was isolated as a yellow solid (54 mg, 75%). M.p. 186-188 °C. ¹H NMR (250 MHz, CDCl₃): δ = 6.68 (s, 1 H), 6.80 (d, J = 1.4 Hz, 1 H, ArH), 7.02 (d, J = 1.4 Hz, 1 H, ArH), 7.25–7.29 (m, 3 H, ArH), 7.43-7.46 (m, 4 H, ArH), 7.81-7.85 (m, 2 H, ArH), 12.50 (br. s, 1 H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 106.2, 108.3 (CH), 110.0 (C), 112.8, 126.4, 127.0, 129.1, 129.5, 130.2, 130.9, 131.1 (CH), 132.0, 132.1, 138.9, 146.7, 155.9, 160.2, 164.7 (C), 183.3 (CO) ppm. IR (KBr): $\tilde{v} = 2956$, 2851 (w), 1657, 1609, 1591 (s), 1573, 1556, 1503, 1492, 1462 (m), 1450, 1421, 1396, 1359 (s), 1341 (w), 1296 (s), 1268 (w), 1255, 1246, 1211, 1196, 1186 (s), 1156, 1119, 1095 (m), 1078, 1067 (w), 1043 (s), 1034 (w), 998 (m), 970, 954, 921, 907, 869, 861 (w), 844 (s), 828, 817, 766, 751 (s), 734, 727, 713 (m), 690, 681, 673, 656, 627 (m), 579 (w), 545 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 350 (³⁷Cl, 35) [M]⁺, 349 (³⁵Cl, 20) [M + H]⁺, 348 (³⁵Cl, 100) [M]⁺, 218 (10), 155 (14). HRMS (EI, 70 eV): calcd. for C₂₁H₁₃³⁷ClO₃ [M]⁺: 350.05182; found 350.052314, calcd. for C₂₁H₁₃³⁵ClO₃ [M]⁺: 348.05477 found 348.054378.

5-Hydroxy-2,7-diphenyl-4H-chromen-4-one (4I): Starting with 2 (80 mg, 0.207 mmol), 31 (25 mg, 0.207 mmol), [Pd(PPh₃)₄] (7 mg, 3 mol-%, 0.006 mmol), K₃PO₄ (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), compound 4I was isolated as a yellow solid (mg, 80%). M.p. 186–188 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.62 (s, 1 H), 6.94 (d, J = 1.5 Hz, 1 H, ArH), 7.11 (d, J = 1.5 Hz, 1 H, ArH), 7.30-7.36 (m, 3 H, ArH), 7.41-7.48 (m, 3 H, ArH), 7.52-7.55 (m, 2 H, ArH), 7.79–7.782 (m, 2 H, ArH), 12.46 (br. s, 1 H, OH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 105.6, 106.1 (CH), 109.7 (C), 110.1; 126.4, 127.3, 128.8, 129.0, 129.1 (CH), 131.2 (C), 132.0 (CH), 139.2, 148.5, 156.6, 160.8, 164.6 (C), 183.1 (CO) ppm. IR (KBr): $\tilde{v} = 3075$, 3053, 3032, 2926, 2852, 2797 (w), 1656, 1651, 1613, 1593 (s), 1537 (w), 1508 (m), 1496 (w), 1482, 1450, 1420, 1402, 1361, 1346 (s), 1296 (m), 1270 (s), 1251 (w), 1217, 1207, 1199, 1186 (m), 1160 (w), 1121, 1094, 1075, 1052, 1032, 1002, 997 (m), 946 (w), 910, 903 (m), 872 (w), 850 (s), 835, 825, 794 (m), 752, 727, 684, 674, 654, 639, 630 (s), 616, 575 (w), 535 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 315 (20) [M + H]⁺, 314 (100) [M]⁺, 184 (8). HRMS (EI, 70 eV): calcd. for C₂₁H₁₄O₃ [M]⁺: 314.09375; found 314.093679.

4-Oxo-2-phenyl-4H-chromene-5,7-diyl Bis(trifluoromethanesulfonate) (5): Pyridine (0.6 mL, 7.86 mmol) was added to a solution of **1** (0.5 g, 1.96 mmol) in CH_2Cl_2 (20 mL) and the solution was stirred at room temperature. Tf_2O (0.8 mL, 4.72 mmol) was then added to the solution and the solution was stirred at room temperature for 10 min. Subsequently, the solution was stirred at 40 °C for 30 min. After cooling, the reaction mixture was concentrated in vacuo. Product **5** was isolated by rapid column chromatography

(flash silica gel, heptanes/EtOAc) as a white solid (0.90 g, 90%). M.p. 182–184 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.76$ (s, 1 H), 7.07 (d, J = 2.2 Hz, 1 H, ArH), 7.47–7.52 (m, 3 H, ArH), 7.55 (d, J = 2.2 Hz, 1 H, ArH), 7.80–7.83 (m, 2 H, ArH) ppm. ¹³C NMR $(75.4 \text{ MHz}, \text{CDCl}_3): \delta = 109.0, 112.3, 113.2 \text{ (CH)}, 117.7 \text{ (C)}, 118.6$ $(q, J_{C,F} = 320 \text{ Hz}, \text{CF}_3)$, 118.7 $(q, J_{C,F} = 320 \text{ Hz}, \text{CF}_3)$, 126.4, 129.3 (CH), 130 (C), 132.5 (CH), 147.8, 150.8, 157.4, 163.4 (C), 174.6 (CO) ppm. ¹⁹F NMR (282.4 MHz. CDCl₃): $\delta = -72.27$ (3 F, CF₃), -72.96 (3 F, CF₃) ppm. IR (KBr): $\tilde{v} = 3111, 3093, 3068, 2958, 2924,$ 2855 (w), 1651, 1617 (s), 1572, 1496, 1467, 1450 (w), 1427, 1363 (s), 1338, 1301, 1279 (w), 1248, 1216, 1202, 1135, 1129, 1097 (s), 1067, 1035 (m), 1006, 972 (s), 929 (w), 892, 872, 848, 812 (s), 782 (w), 773 (s), 761, 713, 705, 689 (m), 680 (w), 661 (m), 650, 641 (w), 612 (s), 596 (w), 586 (s), 569, 545 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 519 (23) [M + H]⁺, 518 (100) [M]⁺, 454 (12). HRMS (EI, 70 eV): calcd. for C₁₇H₈F₆O₈S₂ [M]⁺: 517.95593; found 517.95651.

General Procedure for Synthesis of 6a–i and 7a–g: A solution of 5, K_3PO_4 , [Pd(PPh_3)_4], and arylboronic acid 3 in 1,4-dioxane (3 mL) was stirred at 70 or 115 °C for 6–9 h. After cooling to 20 °C, distilled water was added, the organic and the aqueous layers were separated, and the latter was extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

2-Phenyl-5,7-di(p-tolyl)-4H-chromen-4-one (6a): Starting with 5 (75 mg, 0.145 mmol), 3a (39 mg, 0.29 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol-%, 0.009 mmol), K₃PO₄ (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6a was isolated as a white solid (49 mg, 85%). Reaction temperature: 115 °C for 6 h. M.p. 236-238 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.32 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 6.6 (s, 1 H), 7.13-7.16 (m, 3 H, ArH), 7.19-7.22 (m, 3 H, ArH), 7.36 (d, J = 1.8 Hz, 1 H, ArH), 7.42–7.44 (m, 3 H, ArH), 7.52 (d, J = 8.1 Hz, 2 H, ArH), 7.66 (d, J = 1.8 Hz, 1 H, ArH), 7.83–7.86 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 21.2, 21.3 (CH₃), 108.9, 114.9 (CH), 119.8 (C), 126.1, 127.1, 127.1, 128.2, 128.6, 128.9, 129.8, 131.3 (CH), 131.7, 135.8, 136.8, 138.8, 143.5, 145.1, 157.9, 161.7 (C), 178.0 (CO) ppm. IR (KBr): \tilde{v} = 3063, 2915, 2858 (w), 1643, 1605 (s), 1574, 1552, 1537 (w), 1519, 1495, 1484, 1463, 1448, 1423 (w), 1372 (s), 1311, 1286, 1271, 1225, 1203, 1191 (w), 1138, 1108 (m), 1081, 1064 (w), 1033, 1023, 1015, 965, 941 (w), 929, 909, 877, 861 (m), 843 (w), 809, 773 (s), 725, 711 (w), 692, 678 (s), 645, 616, 603, 596 (m), 568 (w), 546 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 403 (11) [M + H]⁺, 402 (43) [M]⁺, 401 (100). HRMS (EI, 70 eV): calcd. for $C_{29}H_{21}O_2$ [M - H]⁺: 401.15361; found 401.1534321.

2-Phenyl-5,7-di(m-tolyl)-4H-chromen-4-one (6b): Starting with 5 (75 mg, 0.145 mmol), **3b** (39 mg, 0.29 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol-%, 0.009 mmol), K₃PO₄ (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6b was isolated as a white solid (46 mg, 80%). Reaction temperature: 115 °C for 6 h. M.p. 122-124 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.33 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 6.60 (s, 1 H), 7.09–7.16 (m, 5 H, ArH), 7.20–7.30 (m, 2 H, ArH), 7.36 (d, J = 1.8 Hz, 1 H, ArH), 7.40–7.44 (m, 5 H, ArH), 7.69 (d, J = 1.8 Hz, 1 H, ArH), 7.83–7.86 (m, 2 H, ArH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 21.5, 21.5 (2CH₃), 108.9, 115.4, 124.4, 126.0, 126.2, 127.3, 127.9, 128.1, 129.0, 129.3, 129.56, 131.4 (CH), 131.7, 137.0, 138.7, 138.7, 141.3, 143.7, 145.3, 157.8, 161.8 (C), 178.0 (CO) ppm. IR (KBr): $\tilde{v} = 3068$, 3060, 3033, 2952 (m), 2920, 2852 (m), 1642 (s), 1622 (w), 1602 (s), 1574, 1557 (w), 1495, 1462, 1447 (m), 1371 (s), 1302, 1286, 1260, 1193, 1169 (w), 1130 (m), 1106, 1091, 1078, 1063, 1041, 1028, 998, 971, 948, 928, 900 (w), 876, 862, 854, 820, 790 (m), 780, 770 (s), 717 (m) 687, 676 (s)

646, 635, 631 (m), 612, 587, 578, 556 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 403 (12) [M + H]⁺, 402 (38) [M]⁺, 401 (100), 201 (18), 185 (10). HRMS (EI, 70 eV): calcd. for C₂₉H₂₁O₂ [M – H]⁺: 401.15361; found 401.153486.

5,7-Bis(3,5-dimethylphenyl)-2-phenyl-4H-chromen-4-one (6c): Starting with 5 (75 mg, 0.145 mmol), 3c (93 mg, 0.29 mmol), [Pd-(PPh₃)₄] (10 mg, 6 mol-%, 0.009 mmol), K₃PO₄ (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6c was isolated as a white solid (49 mg, 80%). Reaction temperature: 115 °C for 6 h. M.p. 171–173 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.29 (s, 6 H, 2CH₃), 2.30 (s, 6 H, 2CH₃), 6.62 (s, 1 H), 6.93-6.97 (m, 4 H, ArH), 7.23 (br. s, 2 H, ArH), 7.35 (d, J = 1.8 Hz, 1 H, ArH), 7.41– 7.45 (m, 3 H, ArH), 7.67 (d, J = 1.8 Hz, 1 H, ArH), 7.84–7.87 (m, 2 H, ArH) ppm. $^{13}\mathrm{C}$ NMR (74.5 MHz, CDCl₃): δ = 21.3, 21.4 (4 CH₃), 108.9, 115.2 (CH), 119.9 (C), 125.2, 126.1, 126.5, 127.4, 128.9, 129.0, 130.3, 131.3 (CH), 131.7, 136.8, 138.6, 138.7, 141.3, 143.7, 145.4, 157.7 (C), 161.7 (CO) ppm. IR (KBr): v = 3062, 3006, 2914, 2858, 2732 (w), 1645, 1597 (s), 1574, 1557 (w), 1483 (m), 1463 (w), 1447 (m), 1433 (w), 1371 (s), 1304, 1284, 1262, 1246, 1231, 1188, 1157 (w), 1137, 1110, 1062 (m), 1029, 1012, 998, 983, 954, 925, 911, 901, 868 (w), 846 (s), 790 (m), 765 (s), 746 (m), 707 (w), 690, 680 (s), 645, 637, 617, 586 (m), 563, 541, 531 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 430 (25) [M]⁺, 429 (100), 416 (9), 199 (43). HRMS (EI, 70 eV): calcd. for $C_{31}H_{25}O_2 [M - H]^+$: 429.18491; found 429.184637.

5,7-Bis[4-(tert-butyl)phenyl]-2-phenyl-4H-chromen-4-one (6d): Starting with 5 (75 mg, 0.145 mmol), 3e (52 mg, 0.29 mmol), [Pd- $(PPh_3)_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6d was isolated as a white solid (54 mg, 77%). Reaction temperature: 115 °C for 6 h. M.p. 204–206 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.29 (s, 9 H, $3CH_3$), 1.31 (s, 9 H, $3CH_3$), 6.62 (s, 1 H), 7.25 (d, J = 8.4 Hz, 2 H, ArH), 7.36 (d, J = 8.4 Hz, 2 H, ArH), 7.41 (d, J = 1.8 Hz, 1 H, ArH), 7.55 (d, J = 8.5 Hz, 2 H, ArH), 7.69 (d, J = 1.7 Hz, 1 H, ArH), 7.84-7.87 (m, 2 H, ArH) ppm. 13C NMR (75.4 MHz, CDCl₃): δ = 31.3, 31.4 (CH₃), 34.6, 34.7 (C), 108.8, 115.0, 124.4 (CH), 125.6 (C), 126.0, 126.2, 127.0, 127.4, 128.5, 129.0, 131.4 (CH), 131.7, 135.8, 138.3, 143.6, 145.1, 149.8, 152.0, 157.9, 161.9 (C), 178.1 (CO) ppm. IR (KBr): $\tilde{v} = 3071$, 3039 (w), 2957, 2947 (m), 2900, 2863 (w), 1644, 1604 (s), 1576, 1548 (w), 1520 (m), 1496 (w), 1462, 1449, 1422 (m), 1402 (w), 1375 (s), 1318, 1309, 1287 (w), 1268 (m), 1211, 1193, 1157, 1144 (w), 1108 (m), 1081, 1064, 1034, 1023, 1012, 999, 970, 942 (w), 929, 909, 873, 863, 843 (m), 825 (s), 815 (m), 769 (s), 750, 740, 729 (w), 693, 679 (s), 659, 644, 613, 604, 588 (w), 566 (m), 545, 535 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) $= 487 (17) [M + H]^+, 486 (57) [M]^+, 485 (100), 471 (26), 455 (12).$ HRMS (EI, 70 eV): calcd. for $C_{35}H_{33}O_2$ [M - H]⁺: 485.24751; found 485.247625.

5,7-Bis(4-methoxyphenyl)-2-phenyl-4*H***-chromen-4-one (6e):** Starting with **5** (75 mg, 0.145 mmol), **3f** (44 mg, 0.29 mmol), $[Pd(PPh_3)_4]$ (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound **6e** was isolated as a white solid (56 mg, 90%). Reaction temperature: 115 °C for 6 h. M.p. 211–212 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.75 (s, 3 H, OCH₃), 3.77 (s, 3 H, OCH₃), 6.57 (s, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H, ArH), 6.90 (d, *J* = 8.8 Hz, 2 H, ArH), 7.40–7.43 (m, 3 H, ArH), 7.55 (d, *J* = 8.8 Hz, 2 H, ArH), 7.60 (d, *J* = 1.8 Hz, 1 H, ArH), 7.40–7.43 (m, 2 H, ArH), 7.81–7.84 (m, 2 H, ArH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 55.2, 55.4 (OCH₃), 108.9, 113.0, 114.4, 114.5 (CH), 119.5 (C), 126.1, 127.0, 128.4, 129.0, 130.0 (CH), 131.1 (C), 131.3 (CH), 131.7, 133.6, 143.2, 144.7, 158.0, 158.9, 160.3, 161.6 (C), 178.1 (CO) ppm. IR

 $\begin{array}{l} ({\rm KBr}): \tilde{v} = 3066, \ 3011, \ 2957, \ 2933, \ 2904, \ 2836 \ (w), \ 1643, \ 1600 \ (s), \\ 1576, \ 1552 \ (m), \ 1511 \ (s), \ 1461, \ 1448, \ 1427 \ (m), \ 1371 \ (s), \ 1346, \ 1313 \\ (w), \ 1291, \ 1282, \ 1254 \ (m), \ 1236 \ (s), \ 1205 \ (m), \ 1183, \ 1176 \ (s), \ 1157 \\ (w), \ 1139 \ (m), \ 1116 \ (w), \ 1106 \ (m), \ 1080, \ 1062 \ (w), \ 1028, \ 1018 \ (s), \\ 954 \ (w), \ 927, \ 907, \ 878, \ 857, \ 838 \ (m), \ 825 \ (s), \ 807, \ 793 \ (m), \ 770 \ (s), \\ 730 \ (m), \ 693, \ 677 \ (s), \ 645, \ 616, \ 596, \ 550, \ 535 \ (m) \ cm^{-1}. \ GC-MS \\ (EI, \ 70 \ eV): \ m/z \ (\%) = \ 435 \ (15) \ [M + H]^+, \ 434 \ (61) \ [M]^+, \ 433 \ (100), \\ 390 \ (10), \ 217 \ (7). \ HRMS \ (EI, \ 70 \ eV): \ calcd. \ for \ C_{29}H_{21}O_4 \ [M - H] \\ ^+: \ 433.14344; \ found \ 433.1143348. \end{array}$

2-Phenyl-5,7-bis(4-trifluoromethylphenyl)-4H-chromen-4-one (6f): Starting with 5 (75 mg, 0.145 mmol), 3h (55 mg, 0.29 mmol), $[Pd(PPh_3)_4]$ (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6f was isolated as a yellow solid (56 mg, 76%). Reaction temperature: 115 °C for 6 h. M.p. 308–310 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.64 (s, 1 H), 7.35 (br. s, 1 H, ArH), 7.41–7.49 (m, 5 H, ArH), 7.62 (d, J = 7.8 Hz, 2 H, ArH), 7.68-7.76 (m, 4 H, ArH), 7.80 (br. s, 1 H, ArH), 7.88-7.89 (br. m, 2 H, ArH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 108.8, 116.7 (CH), 120.6 (q, $J_{C,F}$ = 270 Hz, CF₃), 120.8 (q, J_{CF} = 270 Hz, CF₃), 124.5 (q, J_{CF} = 3.7 Hz, CH), 126.1 (q, $J_{C,F}$ = 3.7 Hz, CH), 126.3, 127.1, 127.7, 129.0, 129.1 (CH), 131.8 (C), 131.8 (CH), 136.2, 138.9, 142.0, 144.1, 149.8, 152.0, 157.9, 162.5 (C), 177.7 (CO) ppm. ¹⁹F NMR (282.4 MHz. CDCl₃): $\delta = -62.39$ (3 F, CF_3) , -62.63 (3 F, CF_3) ppm. IR (KBr): $\tilde{v} = 3069$ (w), 1645, 1606 (s), 1578, 1556 (m), 1536, 1498 (w), 1470, 1452, 1427 (m), 1406 (w), 1375, 1320 (s), 1291, 1260, 1195 (w), 1170, 1163, 1152, 1102, 1066 (s), 1035 (w), 1012 (s), 955, 948 (w), 929 (m), 909, 884 (w), 871, 854 (m), 831, 773 (s), 740 (w), 693, 681, 671 (s), 650, 641, 621 (w), 598, 584 (m), 533 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) $= 511 (9) [M + H]^+, 510 (44) [M]^+, 509 (100).$ HRMS (EI, 70 eV): calcd. for $C_{29}H_{16}F_6O_2$ [M – H]⁺: 510.11541; found 510.117632.

5,7-Bis(4-fluorophenyl)-2-phenyl-4H-chromen-4-one (6g): Starting with 5 (75 mg, 0.145 mmol), 3i (41 mg, 0.29 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol-%, 0.009 mmol), K₃PO₄ (92 mg, 0.345 mmol), and 1,4-dioxane (3 mL), compound 6g was isolated as a white solid (49 mg, 83%). Reaction temperature: 115 °C for 6 h. M.p. 213-215 °C. ¹H NMR (250 MHz, CDCl₃): δ = 6.63 (s, 1 H), 7.06 (dt, J = 8.7, 17.2 Hz, 4 H, ArH), 7.23–7.29 (m, 3 H, ArH), 7.44–7.47 (m, 3 H, ArH), 7.59 (dd, J = 5.2, 8.8 Hz, 2 H, ArH), 7.67 (d, J = 1.6 Hz, 1 H, ArH), 7.83-7.87 (m, 2 H, ArH) ppm. ¹³C NMR $(62.9 \text{ MHz}, \text{CDCl}_3)$: $\delta = 108.9, 114.5 \text{ (d}, J = 21.5 \text{ Hz}, \text{CH}), 115.6,$ 115.2 (d, J = 21.4 Hz, CH), 119.9 (C), 126.1, 127.2, 129.0 (CH), 129.1 (d, J = 8.0 Hz, CH), 130.4 (d, J = 8.0 Hz, CH), 131.4 (C), 131.5 (CH), 134.8 (d, J = 3.3 Hz, 1 C), 136.9 (d, J = 3.3 Hz, 1 C), 142.6, 144.2, 157.8, 162.0 (C), 162.3 (d, J_{F,C} = 245.9 Hz, CF), 163.3 (d, $J_{\rm F,C}$ = 249.1 Hz, CF), 175.8 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -115.4, -112.7$ ppm. IR (KBr): $\tilde{v} = 3065, 2919, 2852,$ 1894, 1743 (w), 1644 (s), 1621 (m), 1606 (s), 1576, 1555 (m), 1509 (s), 1466, 1448, 1425 (m), 1402 (w), 1369 (s), 1346, 1305, 1287, 1271, 1260 (w), 1216 (s), 1189 (w), 1157, 1138 (s), 1108, 1092, 1081, 1054, 1034, 1020, 1012, 1000, 984, 965 (w), 927 (m), 908, 895 (w), 873 (m), 858 (w), 829 (s), 790 (m), 771 (s), 742, 730, 721 (w), 694, 685, 674 (s), 647, 636 (w), 616, 603, 594, 566, 547 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 411 (9) [M + H]⁺, 410 (44) [M]⁺, 409 (100), 251 (7). HRMS (EI, 70 eV): calcd. for $C_{27}H_{15}F_2O_2$ [M – H] +: 409.10346; found 409.103561.

5,7-Bis(4-chlorophenyl)-2-phenyl-4*H***-chromen-4-one (6h):** Starting with **5** (75 mg, 0.145 mmol), **3j** (45 mg, 0.29 mmol), $[Pd(PPh_3)_4]$ (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound **6h** was isolated as a yellow solid (54 mg, 85%). Reaction temperature: 115 °C for 6 h. M.p. 280–282 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.66 (s, 1 H), 7.23 (d, *J*



= 8.6 Hz, 2 H, ArH), 7.29–7.33 (m, 3 H, ArH), 7.40 (d, J = 8.6 Hz, 2 H, ArH), 7.44–7.49 (m, 3 H, ArH), 7.55 (d, J = 8.6 Hz, 2 H, ArH), 7.7 (d, J = 1.8 Hz, 1 H, ArH), 7.83–7.87 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 108.9, 115.8, 126.2, 127.0, 127.7, 128.6, 129.1, 129.3, 130.1, 131.6 (CH), 131.6, 133.4, 135.2, 137.0, 139.4, 142.5, 144.1, 157.8, 162.2 (C), 177.8 (CO) ppm. IR (KBr): $\tilde{v} = 3061$, 2954, 2922, 2852 (w), 1639, 1605 (s), 1574, 1552 (w), 1503, 1496, 1463, 1448, 1423 (m), 1398 (w), 1372 (s), 1311, 1287, 1257, 1212, 1190, 1110 (w), 1087 (s), 1064, 1033, 1019, 1014 (w), 1008 (m), 964, 937 (w), 927, 908, 878, 865 (m), 845, 834 (w), 818, 808, 775 (s), 732, 712 (w), 692, 678, 650 (s), 634, 609, 601, 585, 538 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 445 ([³⁵Cl] [³⁷Cl], 12) $[M + H]^+$, 444 ([³⁵Cl] [³⁷Cl], 23) $[M]^+$, 443 ([³⁵Cl] [³⁵Cl], 68) [M +H]⁺, 442 ([³⁵Cl] [³⁵Cl], 36) [M]⁺, 441 (100). HRMS (EI, 70 eV): calcd. for C₂₇H₁₅Cl₂O₂ ([M - H]⁺, [³⁵Cl] [³⁷Cl]): 443.04141; found 443.041464, calcd. for $C_{27}H_{15}$ Cl_2O_2 ([M - H]⁺, [³⁵Cl] [³⁵Cl]): 441.04436; found 441.044306.

2,5,7-Triphenyl-4-H-chromen-4-one (6i): Starting with 5 (75 mg, 0.145 mmol), 31 (35 mg, 0.29 mmol), [Pd(PPh₃)₄] (10 mg, 6 mol-%, 0.009 mmol), K₃PO₄ (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), compound 6i was isolated as a white solid (43 mg, 81%). Reaction temperature: 115 °C for 6 h. M.p. 194–195 °C.¹H NMR (300 MHz, $CDCl_3$): $\delta = 6.60$ (s, 1 H), 7.30–7.45 (m, 12 H, ArH), 7.60–7.63 (m, 2 H, ArH), 7.71 (d, J = 1.8 Hz, 1 H, ArH), 7.84–7.87 (m, 2 H, ArH) ppm. ¹³C NMR (75.4 MHz, CDCl₃): δ = 108.9, 115.5 (CH), 120.0 (C), 126.2, 127.2, 127.3, 127.5, 128.7, 128.8, 129.0, 129.1, 131.4 (CH), 131.6, 138.7, 141.3, 143.6, 145.2, 157.8, 161.9 (C), 178.0 (CO) ppm. IR (KBr): $\tilde{v} = 3059$, 3030 (w), 1644, 1606, 1598 (s), 1574, 1556 (m), 1537 (w), 1503, 1495, 1464, 1448 (s), 1440 (m), 14150, 1393 (w), 1372 (s), 1310, 1287, 1207, 1192, 1157 (w), 1139, 1109 (m), 1079, 1072, 1064, 1039, 1030 (w), 1016 (m), 999, 975 (w), 929, 906, 872 (m), 843, 789 (w), 760 (s), 710 (m), 690 (s), 646, 627, 614, 604, 583 (w), 569, 534 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 374 (38) [M]⁺, 373 (100), 215 (5). HRMS (EI, 70 eV): calcd. for C₂₄H₁₇F₃O₅S [M]⁺: 373.12231; found 373.121759.

4-Oxo-2-phenyl-7-(m-tolyl)-4H-chromen-5-yl Trifluoromethanesulfonate (7a): Starting with 5 (75 mg, 0.145 mmol), 3b (22 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7a was isolated as a white solid (58 mg, 85%). Reaction temperature: 70 °C for 9 h. M.p. 218–221 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.38 (s, 3 H, CH₃), 6.70 (s, 1 H), 7.21–7.24 (m, 1 H, ArH), 7.30–7.36 (m, 4 H, ArH), 7.44–7.48 (m, 3 H, ArH), 7.72 (J = 1.8 Hz, 1 H, ArH), 7.81-7.84 (m, 2 H, ArH) ppm. 13C NMR (75.4 MHz, CDCl₃): δ = 108.8 (CH), 116.1 (C), 116.6, 117.7 (CH), 118.9 (q, $J_{\rm F,C}$ = 320.1 Hz, CF₃), 124.3, 126.3, 127.9, 129.1, 129.3, 130.4 (CH), 130.8 (C), 132.0, 137.2 (CH), 139.2, 147.0, 157.3, 162.8 (C), 175.8 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.3 ppm. IR (KBr): $\tilde{v} = 3061, 2955$ (w), 2921 (m), 2852 (w), 1647, 1626, 1614 (s), 1579, 1552 (w), 1495 (m), 1468 (w), 1449 (m), 1430 (s), 1392 (m), 1368 (s), 1348, 1303, 1287 (w), 1246 (m), 1217, 1193, 1137 (s), 1112 (m), 1080 (w), 1066, 1033 (m), 981 (s), 938, 926, 905, 886 (w), 867, 834, 796, 786, 768, 760 (s), 711 (w), 687 (s), 666, 647 (m), 637 (w), 609, 585, 577 (s), 533 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) $= 461 (25) [M + H]^+, 460 (100) [M]^+, 368 (32), 299 (26), 228 (9).$ HRMS (EI, 70 eV): calcd. for C₂₃H₁₅F₃O₅ S [M]⁺: 460.06346; found 460.063561.

7-(3,5-Dimethylphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl Trifluoromethanesulfonate (7b): Starting with 5 (75 mg, 0.145 mmol), 3c (22 mg, 0.145 mmol), [Pd(PPh_3)4] (5 mg, 3 mol-%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7b was isolated as a white solid (58 mg, 85%). Reaction temperature: 70 °C for 9 h. M.p. 218–221 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.34 (s, 3 H, 6CH₃), 6.70 (s, 1 H), 7.05 (br., 1 H, ArH), 7.15 (br., 2 H, ArH), 7.32 (br., 1 H, ArH), 7.45–7.49 (m, 3 H, ArH), 7.72 (d, J = 1.6 Hz, 1 H, ArH), 7.821–7.85 (m, 2 H, ArH) ppm. ¹³C NMR (74.5 MHz, CDCl₃): δ = 21.3 (2 CH₃), 108.7 (CH), 116.0 (C), 116.3 (CH), 117.3 (q, $J_{F,C} = 320.1 \text{ Hz}$, CF₃), 117.7, 125.0, 126.2, 129.1 (CH), 130.8 (C), 131.3, 132.0 (CH), 137.2, 139.1, 146.9, 147.2, 157.3, 162.8 (C), 175.8 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.3 ppm. IR (KBr): \tilde{v} = 3063, 2916, 2859 (w), 1639, 1630, 1611 (s), 1579, 1493 (w), 1449 (m), 1425 (s), 1394 (w), 1369 (s), 1348, 1298, 1284, 1249 (w), 1231 (m), 1201, 1138 (s), 1116 (m), 1077 (w), 1064, 1031, 1008 (m), 978 (s), 949, 924, 908, 895, 868, 857, 850 (w), 828, 768, 758 (s), 734, 711, 701 (w), 685, 675, 665 (m), 653 (w), 614, 588 (s), 569, 541 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 475 (25) [M + H]⁺, 474 (100) [M]⁺, 382 (29), 313 (25). HRMS (EI, 70 eV): calcd. for C₂₄H₁₇F₃O₅S [M]⁺: 474.07433; found 474.072983.

7-[4-(tert-Butyl)phenyl]-4-oxo-2-phenyl-4H-chromen-5-yl Trifluoromethanesulfonate (7c): Starting with 5 (75 mg, 0.145 mmol), 3e (26 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7c was isolated as a white solid (51 mg, 71%). Reaction temperature: 70 °C for 9 h. M.p. 185–188 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.30$ (s, 9 H, 3 CH₃), 6.71 (s, 1 H), 7.35 (br. s, 1 H, ArH), 7.45– 7.54 (m, 7 H, ArH), 7.74 (d, J = 1.5 Hz, 1 H, ArH), 7.83–7.86 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 31.21 (3CH₃), 34.8 (C), 108.3, 116.2, 117.5 (CH), 118.7 (q, J_{EC} = 322.1 Hz, CF₃), 126.3, 126.4, 126.9, 129.1 (CH), 130.9 (C), 131.9 (CH), 134.3, 146.7, 147.0, 153.1, 157.4, 162.8 (C), 175.8 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.3 ppm. IR (KBr): \tilde{v} = 3063, 2962, 2866, 2252 (w), 1643, 1630, 1613 (s), 1577, 1546, 1523, 1494, 1474 (w), 1449 (m), 1242 (s), 1400 (m), 1369 (s), 1346, 1301, 1285, 1269 (w), 1242 (m), 1230 (w), 1205, 1137 (s), 1117, 1106, 1065, 1055, 1031 (m), 1016, 1001 (w), 981, 903 (s), 879 (w), 833, 810, 767, 761 (s), 746 (w), 730, 721, 707, 686, 676, 647 (m), 613, 595, 588 (s), 569, 558, 546, 527 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 503 (11) $[M + H]^+$, 502 (40) $[M]^+$, 487 (27), 488 (100), 326 (10). HRMS (EI, 70 eV): calcd. for C₂₆H₂₁ F₃O₅S [M]⁺: 502.10563; found 502.105916.

7-(4-Methoxyphenyl)-4-oxo-2-phenyl-4H-chromen-5-yl Trifluoromethanesulfonate (7d): Starting with 5 (75 mg, 0.145 mmol), 3f (22 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7d was isolated as a white solid (57 mg, 83%). Reaction temperature: 70 °C for 9 h. M.p. 214-216 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3 H, OCH₃), 6.71 (s, 1 H), 6.98 (d, J = 8.8 Hz, ArH), 730 (br., 1 H, ArH), 7.46–7.53 (m, 5 H, ArH), 7.70 (d, J = 1.5 Hz, 1 H, ArH), 7.82–7.85 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, $CDCl_3$): $\delta = 55.4$ (OCH₃), 108.7, 114.8, 115.6, 117.1 (CH), 118.7 $(q, J_{F,C} = 320.1 \text{ Hz}, CF_3), 126.2, 128.4, 129.1 (CH), 129.9, 130.9$ (C), 131.9 (CH), 146.4, 147.1, 157.4, 160.9, 162.7 (C), 175.8 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.3 ppm. IR (KBr): \tilde{v} = 3062, 3006, 2963, 2836 (w), 1647, 1629, 1604 (s), 1578, 1549 (w), 1523 (s), 1495, 1476, 1450 (w), 1429 (s), 1402 (m), 1371 (s), 1346, 1298, 1285 (w), 1257, 1244, 1212, 1201, 1192, 1182 (m), 1161 (w), 1139 (s), 1116, 1090, 1078, 1065, 1054, 1031 (m), 1009, 1001 (w), 982 (s), 923 (w), 904 (s), 877, 866 (w), 822 (s), 797, 789, 766 (m), 732, 713 (w), 686, 676 (m), 657, 645, 613 (w), 604, 586 (s), 569, 549, 528 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 477 (26) [M + H]⁺, 476 (100) [M]⁺, 369 (12), 315 (22). HRMS (EI, 70 eV): calcd. for C₂₃H₁₅F₃O₆S [M]⁺:476.05359; found 476.052814.

7-(2-Methoxyphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl Trifluoromethanesulfonate (7e): Starting with 5 (75 mg, 0.145 mmol), 3g (22 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7e was isolated as a white solid (55 mg, 81%). Reaction temperature: 70 °C for 9 h. M.p. 218–220 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.79 (s, 3 H, OCH₃), 6.71 (s, 1 H, CH), 6.95–6.98 (m, 1 H, ArH), 6.99-7.04 (m, 1 H, ArH), 7.29-7.33 (m, 1 H, ArH), 7.36-7.39 (m, 2 H, ArH), 7.42–7.49 (m, 3 H, ArH), 7.70 (d, J = 1.8 Hz, 1 H, ArH), 7.81–7.84 (m, 2 H, ArH) ppm. ¹³C NMR (74.5 MHz, $CDCl_3$): $\delta = 55.5$ (OCH₃), 108.8, 111.5 (CH), 116.0 (C), 118.2 (q, $J_{\rm EC} = 285.2 \, \text{Hz}, \, \text{CF}_3$, 119.1, 120.5, 121.2, 126.3 (CH), 126.5 (C), 129.1, 130.4, 130.9 (CH); 131.0 (C), 131.9 (CH), 144.6, 146.1, 156.4, 156.8, 162.7 (C), 175.9 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -73.4$ ppm. IR (KBr): $\tilde{v} = 3075$, 3061, 3011 (w), 2922 (m), 2851 (w), 1647, 1627, 1613, 1598 (s), 1598, 1579 (m), 1544 (w), 1495, 1467, 1450 (m), 1440 (w), 1420, 1405, 1369 (s), 1308 (w), 1266 (m), 1238, 1201, 1190 (s), 1166 (w), 1143, 1134, 1110 (s), 1072, 1066, 1058, 1044 (w), 1029, 1022 (m), 1000 (w), 979 (s), 941 (w), 899, 877 (s), 861, 852 (w), 814 (s), 786, 779, 769 (w), 752 (s), 713 (w), 690 (s), 672, 647, 623 (w), 611, 587 (s), 568, 551 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 478 (9) [M + 1]⁺, 477 (26) [M]⁺, 476

7-(4-Fluorophenyl)-4-oxo-2-phenyl-4H-chromen-5-yl Trifluoromethanesulfonate (7f): Starting with 5 (75 mg, 0.145 mmol), 3i (20 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7f was isolated as a white solid (53 mg, 80%). Reaction temperature: 70 °C for 9 h. M.p. 188–189 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.71$ (s, 1 H, CH), 7.12–7.15 (m, 1 H, ArH), 7.29 (br., 1 H, ArH), 7.45– 7.50 (m, 4 H, ArH), 7.52–7.57 (m, 2 H, ArH), 7.70 (d, J = 1.5 Hz, 1 H ArH), 7.81–7.84 (m, 2 H, ArH) ppm. ¹³C NMR (74.5 MHz, CDCl₃): δ = 108.8, 116.3 (d, J = 21.6 Hz), 116.4, 117.5 (CH), 118.2 (q, $J_{F,C}$ = 321.1 Hz, CF₃), 126.3, 129.1 (d, J = 8.2 Hz), 129.2 (CH), 130.7 (C), 132.1 (CH), 133.4 (d, J = 3.3 Hz), 145.7, 147.1, 157.4, 162.8 (C), 163.7 (d, $J_{F,C}$ = 248.9 Hz) (CF), 175.6 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -111.2, -73.3$ ppm. IR (KBr): $\tilde{v} =$ 3067, 2956, 2922, 2852 (w), 1648, 1627, 1613 (s), 1601 (m), 1578, 1549 (w), 1518 (s), 1495, 1473, 1451 (w), 1431, 1420 (s), 1394 (m), 1372 (s), 1344, 1306, 1288 (w), 1241 (m), 1199 (s), 1161 (m), 1140, 1134 (s), 1116 (m), 1103, 1081 (w), 1068, 1054, 1030 (m), 1014, 1001 (w), 984 (s), 930 (w), 904 (s), 882, 873 (w), 833, 821, 800 (s), 777, 770, 760 (m), 722, 709, 695, 688, 678, 649, 637, 614 (w), 602, 586 (s), 569, 546, 528 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 465 (25) [M + H]⁺, 464 (100) [M]⁺, 400 (9), 372 (40), 303 (25), 246 (10). HRMS (EI, 70 eV): calcd. for C₂₂H₁₂F₄O₅S [M]⁺:464.03359; found 464.033814.

(100). HRMS (EI, 70 eV): calcd. for C₂₃H₁₅F₃O₆S: 476.05359;

found 476.053485.

7-(4-Chlorophenyl)-4-oxo-2-phenyl-4H-chromen-5-yl Trifluoromethanesulfonate (7g): Starting with 5 (75 mg, 0.145 mmol), 3j (22 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), compound 7g was isolated as a white solid (57 mg, 82%). Reaction temperature: 70 °C for 9 h. M.p. 249–252 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.72$ (s, 1 H), 7.30 (br., 1 H, ArH), 7.42–7.52 (m, 7 H, ArH), 7.72 (d, J = 1.6 Hz, 1 H, ArH), 7.82–7.85 (m, 2 H, ArH) ppm. ¹³C NMR $(62.9 \text{ MHz}, \text{CDCl}_3): \delta = 108.8, 116.3, 116.5, 117.5 \text{ (CH)}, 118.2 \text{ (q,})$ $J_{\rm EC} = 320.7 \,\text{Hz}, \,\text{CF}_3$, 126.2, 128.4, 129.1, 129.6 (CH), 130.7 (C), 132.1 (CH), 135.6, 136.0, 145.5, 147.2, 157.4, 162.9 (C), 175.6 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.32 ppm. IR (KBr): \tilde{v} = 3116, 3063, 2956, 2922, 2852 (w), 1647, 1626, 1614 (s), 1593, 1579, 1574, 1548 (w), 1505, 1494 (m), 1470, 1449 (w), 1432 (s), 1413, 1388 (m), 1367 (s), 1343, 1301, 1282, 1257 (w), 1244, 1214, 1202, 1192, 1183, 1140 (s), 1116, 1091, 1077, 1065, 1053, 1035, 1011, 1001 (m), 982 (s), 922 (w), 901, 870 (s), 842 (w), 820 (s), 779



(w), 767 (s), 730 (w), 711, 686, 678, 664 (m), 654, 645, 633 (w), 612, 588 (s), 565, 532 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 483 (³⁷Cl, 8) [M + H]⁺, 482 (³⁷Cl, 41) [M]⁺, 481 (³⁵Cl, 24) [M + H]⁺, 480 (³⁵Cl, 100) [M]⁺, 390 (13), 319 (23). HRMS (EI, 70 eV): calcd. for C₂₂H₁₂³⁵ClF₃O₅S [M]⁺: 480:00406; found 480.003734.

General Procedure for the Synthesis of 8a,b: The reaction was carried out in a pressure tube. K_3PO_4 (46 mg, 0.217 mmol) was added to a suspension of 5 (75 mg, 0.145 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.145 mmol), and [Pd(PPh_3)_4] (3 mol-%) in dioxane (3 mL), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 70 °C under an argon atmosphere for 9 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.145 mmol), [Pd(PPh_3)_4] (3 mol-%), K_3PO_4 (46 mg, 0.75 mmol), and dioxane (2 mL) were added. The reaction mixtures were heated under an argon atmosphere for 6 h at 115 °C. They were diluted with H₂O and extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptane/ EtAOc).

5-(4-Chlorophenyl)-7-(3,5-dimethylphenyl)-2-phenyl-4H-chromen-4one (8a): Starting with 5 (75 mg, 0.145 mmol), 3c (22 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), 1,4-dioxane (3 mL), 3j (23 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (2 mL), compound 8a was isolated as a white solid (49 mg, 78%). M.p. 226-227 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.33 (s, 6 H, 2CH₃), 6.64 (s, 1 H), 7.01 (br. s, 1 H, ArH), 7.23-7.27 (m, 4 H, ArH), 7.29-7.31 (m, 2 H, ArH), 7.33 (d, J = 1.8 Hz, 1 H, ArH), 7.45–7.47 (m, 3 H, ArH), 7.73 (d, J = 1.8 Hz, 1 H, ArH), 7.86–7.89 (m, 2 H, ArH) ppm. ¹³C NMR $(74.5 \text{ MHz}, \text{CDCl}_3)$: $\delta = 21.3 (2\text{CH}_3), 107.7, 114.7 (CH), 118.7 (C),$ 124.1, 125.2, 126.3, 126.6, 128.0, 129.1, 129.5, 130.5 (CH), 132.2, 137.4, 137.7, 138.7, 141.1, 144.7, 156.7, 161.0 (C), 177.0 (CO) ppm. IR (KBr): $\tilde{v} = 3058$, 2961, 2915, 2852 (w), 1640, 1606 (s), 1575, 1557 (w), 1495 (m), 1480 (w), 1447 (m), 1401 (w), 1371 (s), 1324, 1303 (w), 1288, 1261 (m), 1203, 1187, 1140, 1109, 1101 (w), 1085, 1055 (m), 1029 (w), 1014 (m), 999, 949 (w), 920, 880, 872 (m), 850, 823 (s), 788 (w), 767 (s), 733, 713 (w), 690, 680, 638 (s), 599, 283 (w), 537 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 438 (³⁷Cl, 16) $[M]^+$, 437 (³⁵Cl, 41) $[M + H]^+$, 436 (³⁵Cl, 46) $[M]^+$, 435 (100). HRMS (EI, 70 eV): calcd. for $C_{29}H_{20}^{35}Cl O_2 [M - H]^+$: 435.11463; found 435.11470.

7-(4-Chlorophenyl)-5-(4-fluorophenyl)-2-phenyl-4H-chromen-4-one (8b): Starting with 5 (75 mg, 0.145 mmol), 3j (20 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), 1,4-dioxane (3 mL), 3i (23 mg, 0.145 mmol), [Pd(PPh₃)₄] (5 mg, 3 mol-%, 0.004 mmol), K₃PO₄ (46 mg, 0.217 mmol), and 1,4-dioxane (2 mL), compound 8b was isolated as a white solid (47 mg, 77%). M.p. 256-258 °C. ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 6.63$ (s, 1 H), 6.99–7.06 (m, 2 H, ArH), 7.24–7.28 (m, 2 H, ArH), 7.30 (d, J = 1.8 Hz, 1 H, ArH), 7.38 (d, J = 7.5 Hz, 2 H, ArH), 7.43–7.47 (m, 3 H, ArH), 7.55 (d, J =8.6 Hz, 2 H, ArH), 7.68 (d, J = 1.8 Hz, 1 H, ArH), 7.84–7.87 (m, 2 H, ArH) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 108.9, 114.5 (d, $J_{F,C} = 21.5 \text{ Hz}$), 115.6 (CH), 120.3 (C), 126.2, 127.1, 128.5, 129.0, 129.3, 130.4 (d, $J_{\rm F,C}$ = 8.0 Hz) (CH), 131.4 (C), 131.6 (CH), 135.1, 136.9 (d, $J_{\rm F,C}$ = 3.4 Hz), 137.0, 142.7, 144.0, 157.8, 162.0 (C), 162.3 (d, $J_{\rm EC}$ = 246.1 Hz, CF), 177.9 (CO) ppm. IR (KBr): \tilde{v} = 3062 (m), 1639 (s), 1622 (w), 1606 (s), 1575, 1553 (m), 1503, 1463, 1449, 1424 (m), 1374 (s), 1311 (w), 1288, 1272 (m), 1257 (w), 1215 (s), 1189 (m), 1157 (s), 1140, 1110, 1091 (s), 1065, 1034, 1021

(w), 1009 (s), 999, 982, 958 (w), 934, 929, 909 (m), 872, 830, 821 (s), 811 (m), 797 (w), 775 (s), 733, 723 (w), 693, 679 (s), 656, 648, 638, 621, 600 (w), 585, 553, 541 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 428 (³⁷Cl, 15) [M]⁺, 427 (³⁵Cl, 46) [M + H]⁺, 426 (³⁵Cl, 49) [M]⁺, 425 (100), 388 (11), 386 (17), 384 (23). HRMS (EI, 70 eV): calcd. for C₂₇H₁₅ClF O₂ ([M – H]⁺, ³⁵Cl): 425.07391; found 425.073196.

4-Oxo-2-phenyl-4H-chromene-7,8-diyl Bis(trifluoromethanesulfonate) (10): pyridine (0.32 mL, 4.0 mmol) was added to a solution of 9 (254 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) at -78 °C under argon atmosphere. After stirring for 10 min, Tf₂O (0.40 mL, 2.4 mmol) was added at -78 °C. The mixture was warmed to 0 °C and stirred for 4 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. Product 10 was isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc) as a white solid (393 mg, 76%). M.p. 142–143 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.82 (s, 1 H), 7.43–7.52 (m, 4 H, ArH), 7.88–7.91 (m, 2 H, ArH), 8.25 (d, J = 9.4 Hz, 1 H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): $\delta =$ 108.3 (CH), 118.6 (q, $J_{\rm FC}$ = 321.6 Hz, CF₃), 118.7 (q, $J_{\rm FC}$ = 320.4 Hz, CF₃), 118.9 (CH), 124.7 (C), 126.6, 126.7, 129.3 (CH), 129.9, 130.2 (C), 132.6 (CH), 143.9, 149.5, 164.5, 175.3 (C) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -72.6, -72.8 ppm. IR (KBr): \tilde{v} = 3080 (w), 1660 (s), 1613 (m), 1427 (s), 1359 (m), 1210 (s), 1126 (s), 1053 (m), 996 (m), 955 (m), 836 (m), 794 (m), 756 (m), 733 (w), 684 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 518 (95) [M]⁺ 385 (7), 357 (15), 321 (29), 293 (100), 219 (66), 191 (79). HRMS (EI, 70 eV): calcd. for C₁₇H₈F₆O₈S₂ [M⁺]: 517.95700; found 517.95651.

General Procedure for Synthesis of 11a–g, 12a–e, and 13a,b: A solution of 10 (1.0 equiv.), arylboronic acid 3 (1.0–1.3 equiv. per desired cross-coupling reaction), K_3PO_4 (1.5–2.0 equiv. per desired cross-coupling reaction), and [Pd(PPh_3)_4] (5 mol-%) in 1,4-dioxane (3–4 mL) was heated at 70–100 °C for 4 h. After cooling to 20 °C, a sat. aq. solution of NH₄Cl was added, the organic and aqueous layers were separated, and the latter was extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

2-Phenyl-7,8-di(p-tolyl)-4H-chromen-4-one (11a): Starting with 10 (259 mg, 0.5 mmol), K₃PO₄ (424 mg, 2.0 mmol), [Pd(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), 3a (177 mg, 1.3 mmol), and 1,4dioxane (5 mL), compound 11a was isolated as a crystalline light yellow solid (148 mg, 74%). Reaction temperature: 100 °C for 4 h. M.p. 248–249 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.19 (s, 3 H, CH₃), 2.29 (s, 3 H, CH₃), 6.75 (s, 1 H), 6.90-7.04 (m, 8 H, ArH), 7.24–7.33 (m, 3 H, ArH), 7.39 (d, J = 8.2 Hz, 1 H, ArH), 7.48– 7.51 (m, 2 H, ArH), 8.16 (d, J = 8.2 Hz, 1 H, ArH) ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 21.2, 21.4 (CH_3), 106.7 (CH), 122.8 (C),$ 124.4, 126.2, 127.4, 128.6, 128.7, 128.9, 129.7 (CH), 130.2 (C), 131.0, 131.4 (CH), 131.6, 131.7, 137.0, 137.1, 146.7, 153.9, 163.2 (C), 178.6 (CO) ppm. IR (KBr): $\tilde{v} = 2917$ (w), 1631 (m), 1592 (w), 1446 (m), 1371 (m), 1238 (w), 1145 (m), 1016 (m), 917 (w), 816 (s), 773 (s), 690 (s), 665 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 402 (100) [M]⁺, 387 (34), 359 (03), 331 (4), 299 (4), 285 (07), 243 (09), 229 (12). HRMS (EI): calcd. for $C_{29}H_{22}O_2$ [M⁺]: 402.16143; found 402.161442.

7,8-Bis(3,5-dimethylphenyl)-2-phenyl-4*H***-chromen-4-one (11b): Starting with 10** (259 mg, 0.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), $[Pd(PPh_3)_4]$ (28.8 mg, 5 mol-%, 0.025 mmol), **3c** (195 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound **11b** was isolated as a colorless crystalline (152 mg, 71%). Reaction temperature: 100 °C for 4 h. M.p. 233–235 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.13 (s, 6 H, 2CH₃), 2.19 (s, 6 H, 2CH₃), 6.73 (br. s, 2 H, ArH), 6.77

(br. s, 1 H), 6.80 (br. s, 2 H, ArH), 6.82 (s, 1 H, ArH), 6.87 (br. s, 1 H, ArH), 7.28–7.37 (m, 3 H, ArH), 7.43 (d, J = 8.2 Hz, 1 H, ArH), 7.56–7.59 (m, 2 H, ArH), 8.24 (d, J = 8.2 Hz, 1 H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): $\delta = 21.2$, 21.3 (4CH₃), 106.5 (CH), 122.7 (C), 124.2, 126.2, 127.3, 127.7, 128.8, 128.9, 129.0 (CH), 130.4 (C), 131.4 (CH), 131.7, 134.4, 137.0, 137.2, 139.8, 147.0, 153.8, 163.2 (C), 178.8 (CO) ppm. IR (KBr): $\tilde{v} = 2951$ (w), 1709 (m), 1663 (m), 1629 (s), 1593 (m), 1435 (m), 1366 (m), 1332 (m), 1272 (m), 1190 (s), 1024 (m), 849 (w), 819 (m), 764 (m), 680 (m) cm⁻¹. GC–MS (EI, 70 eV): *m*/*z* (%) = 430 (100) [M]⁺, 415 (73), 402 (07), 355 (05), 313 (09), 285 (06), 239 (07), 164 (17). HRMS (EI): calcd. for C₃₁H₂₆O₂ [M⁺]: 430.19273; found 430.19366.

7,8-Bis(4-tert-butylphenyl)-2-phenyl-4H-chromen-4-one (11c): Starting with 10 (259 mg, 0.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), [Pd(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), 3e (231 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound 11c was isolated as a white solid (143 mg, 59%). Reaction temperature: 100 °C for 4 h. M.p. 162–164 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.20 (s, 9 H, 3CH₃), 1.28 (s, 9 H, 3CH₃), 6.80 (s, 1 H), 7.03–7.17 (m, 7 H, ArH), 7.23–7.30 (m, 4 H, ArH), 7.44–7.51 (m, 3 H, ArH), 8.18 (d, J =8.1 Hz, 1 H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 31.2, 31.4 (CH₃), 34.4, 34.6 (C), 106.6 (CH), 122.7 (C), 124.3, 124.7, 124.8, 126.2, 127.2, 128.8, 129.5 (CH), 130.4 (C), 130.8, 131.4 (CH), 131.6, 131.8, 136.8, 146.5, 150.3, 150.4, 154.0, 163.0, 178.7 (C) ppm. IR (KBr): $\tilde{v} = 3059$ (w), 2958 (m), 1635 (s), 1372 (m), 1258 (m), 1142 (w), 1090 (m), 1014 (m), 919 (w), 794 (s), 684 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 486 (95) [M]⁺, 471 (100), 455 (02), 429 (06), 415 (86), 387 (05), 373 (19), 339 (04), 313 (07), 228 (14), 200 (08), 177 (15). HRMS (EI): calcd. for C₃₅H₃₄O₂ [M⁺]: 486.25533; found 486.25569.

7,8-Bis(4-methoxyphenyl)-2-phenyl-4H-chromen-4-one (11d): Starting with 10 (259 mg, 0.5 mmol), K₃PO₄ (424 mg, 2.0 mmol), [Pd(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), 3f (197 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound 11d was isolated as a white crystalline (147 mg, 68%). Reaction temperature: 100 °C for 4 h. M.p. 172–174 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.71 (s, 3 H, OCH₃), 3.77 (s, 3 H, OCH₃), 6.70 (d, J = 8.8 Hz, 2 H, ArH), 6.80 (s, 1 H), 6.82 (d, J = 8.8 Hz, 2 H, ArH), 7.02 (d, J = 8.8 Hz, 2 H, ArH), 7.10 (d, J = 8.8 Hz, 2 H, ArH), 7.32–7.36 (m, 3 H, ArH), 7.42 (d, J = 8.2 Hz, 1 H, ArH), 7.54–7.58 (m, 2 H, ArH) 8.17 (d, J = 8.2 Hz, 1 H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 55.2, 55.3 (OCH₃), 106.7, 113.4, 113.5 (CH), 121.7, 123.3 (C), 124.3 (CH), 126.0 (C), 126.2, 127.3, 128.9 (CH), 130.4, 130.7 (C), 131.0, 131.4, 132.4 (CH), 145.5, 153.0, 157.8, 157.9, 162.2, 177.7 (C) ppm. IR (KBr): $\tilde{v} = 2922$ (w), 1635 (s), 1512 (m), 1423 (m), 1372 (m), 1285 (m), 1243 (s), 1177 (m), 1112 (w), 1017 (m), 916 (w), 822 (s), 769 (s), 687 (s) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 434 (100) [M]⁺, 403 (07), 331 (04), 281 (09), 253 (05), 207 (17), 189(11). HRMS (EI): calcd. for C₂₇H₁₄O₆ [M⁺]: 434.07849; found 434.07952.

7,8-Bis(4-fluorophenyl)-2-phenyl-*4H***-chromen-4-one (11e):** Starting with **10** (259 mg, 0.5 mmol), K₃PO₄ (424 mg, 2.0 mmol), [Pd-(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), **3i** (182 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound **11e** was isolated as a white solid (127 mg, 62%). Reaction temperature: 100 °C for 4 h. M.p. 233–235 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.84 (s, 1 H), 6.89 (d, *J* = 8.7 Hz, 2 H, ArH), 7.01–7.07 (m, 4 H, ArH), 7.12–7.18 (m, 2 H, ArH), 7.34 (d, *J* = 8.1 Hz, 2 H, ArH), 7.42 (d, *J* = 8.2 Hz, 2 H, ArH) 7.50–7.53 (m, 2 H, ArH), 8.22 (d, *J* = 8.2 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, CDCl₃): δ = 107.0 (CH), 115.2 (d, *J*_{C,F} = 21.3 Hz, CH), 123.1 (C), 125.0, 126.1, 127.2, 129.0, (CH), 129.3 (C), 130.4 (d, *J*_{C,F} = 3.5 Hz, 1 C), 131.3 (CH), 131.4 (C), 131.5 (d,

$$\begin{split} J_{\rm C,F} &= 20~{\rm Hz},~{\rm CH}),~132.7,~132.8~({\rm CH}),~135.6~({\rm d},~J_{\rm C,F} = 3.2~{\rm Hz},~1~{\rm C}),~145.8,~153.7,~163.4~({\rm C}),~162.8~({\rm d},~J_{\rm C,F} = 247~{\rm Hz},~{\rm CF}),~162.9~({\rm d},~J_{\rm C,F} = 247~{\rm Hz},~{\rm CF}),~162.9~({\rm d},~J_{\rm C,F} = 247~{\rm Hz},~{\rm CF}),~162.9~({\rm d},~J_{\rm C,F} = 247~{\rm Hz},~{\rm CF}),~178.3~({\rm C})~{\rm ppm}.~^{19}{\rm F}~{\rm NMR}~(282~{\rm MHz},~{\rm CDCl}_3):~\delta = -113.3~({\rm ArF}),~-112.4~({\rm ArF})~{\rm ppm}.~{\rm IR}~({\rm KBr}):~\tilde{\nu} = 3062~({\rm w}),~1630~({\rm s}),~1602~({\rm m}),~1509~({\rm s}),~1449~({\rm m}),~1415~({\rm m}),~1373~({\rm s}),~1219~({\rm s}),~1159~({\rm s}),~1093~({\rm m}),~1014~({\rm m}),~834~({\rm s}),~771~({\rm s})~{\rm cm}^{-1}.~{\rm GC}-{\rm MS}~({\rm EI},~70~{\rm eV}):~m/z~(\%) = 410~(100)~[{\rm M}]^+,~382~(16),~351~(02),~307~(17),~280~(06),~262~(09),~251~(40),~225~(03).~{\rm HRMS}~({\rm EI}):~{\rm calcd}.~{\rm for}~{\rm C}_{27}{\rm H}_{16}~{\rm F_2O_2}~[{\rm M}^+]:~410.11129;~{\rm found}~410.11046. \end{split}$$

7,8-Bis(4-chlorophenyl)-2-phenyl-4H-chromen-4-one (11f): Starting with 10 (259 mg, 0.5 mmol), K₃PO₄ (424 mg, 2.0 mmol), [Pd-(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), **3**j (203 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound 11f was isolated as a light yellow solid (160 mg, 72%). Reaction temperature: 100 °C for 4 h. M.p. 192–194 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.82 (s, 1 H), 7.01 (d, J = 8.8 Hz, 2 H, ArH) 7.10–7.18 (m, 5 H, ArH), 7.29 (d, J = 8.6 Hz, 2 H, ArH) 7.37–7.43 (m, 3 H, ArH), 7.48–7.53 (m, 2 H, ArH), 8.23 (d, J = 8.2 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, $CDCl_3$): $\delta = 107.0$ (CH), 123.2 (C), 125.2, 126.1, 127.1, 128.4, 128.5, 129.1, 131.0 (CH), 131.3 (C), 131.6, 132.4 (CH), 132.8, 133.8, 133.9, 137.9, 143.0, 145.4, 154.0, 163.4 (C), 178.2 (CO) ppm. IR (KBr): $\tilde{v} = 3055$ (w), 1682 (w), 1587 (w), 1486 (m), 1248 (w), 1088 (m), 1009 (m), 940 (m), 820 (m), 742 (s), 723 (s) cm⁻¹. GC– MS (EI, 70 eV): *m*/*z* (%) = 442 (100) [M]⁺, 407 (23), 378 (01), 339 (09), 305 (12), 249 (27), 213 (27), 172 (14). HRMS (EI): calcd. for C₂₇H₁₆³⁵Cl₂O₂ [M⁺]: 442.05219; found 442.05234.

7,8-Bis(4-ethylphenyl)-2-phenyl-4H-chromen-4-one (11g): Starting with 10 (259 mg, 0.5 mmol), K₃PO₄ (424 mg, 2.0 mmol), [Pd-(PPh₃)₄] (28.8 mg, 5 mol-%, 0.025 mmol), 3m (195 mg, 1.3 mmol), and 1,4-dioxane (5 mL), compound 11g was isolated as a crystalline white solid (150 mg, 70%). Reaction temperature: 100 °C for 4 h. M.p. 148–150 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.11 (t, J = 7.8 Hz, 3 H, CH₃), 1.18 (t, J = 7.4 Hz, 3 H, CH₃), 2.50 (q, J = 7.4,15.3 Hz, 2 H, CH₂), 2.59 (q, J = 7.4,15.3 Hz, 2 H, CH₂), 6.76 (s, 1 H), 6.93-7.07 (m, 8 H, ArH), 7.22-7.35 (m, 3 H, ArH), 7.41 (d, J = 8.3 Hz, 1 H, ArH), 7.46–7.50 (m, 2 H, ArH), 8.16 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, CDCl₃): δ = 15.3, 15.8 (CH₃), 28.4, 28.7 (CH₂), 106.6 (CH), 122.7 (C), 124.3, 126.2, 127.3, 127.4, 127.5, 128.8, 129.7 (CH), 130.3 (C), 131.1, 131.4 (CH), 131.6, 132.0, 137.2, 143.3, 143.5, 146.6, 154.0, 163.1, 178.7 (C) ppm. IR (KBr): $\tilde{v} = 3064$ (w), 2966 (w), 1643 (s), 1510 (m), 1394 (m), 1370 (m), 1147 (m), 1016 (m), 919 (m), 823 (s), 772 (s), 689 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 430 (100) [M]⁺, 415 (09), 401 (51), 373 (03), 344 (02), 313 (09), 239 (09), 156 (03). HRMS (EI): calcd. for C₃₁H₂₆O₂ [M⁺]: 430.19273; found 430.19288.

4-Oxo-2-phenyl-7-p-tolyl-4H-chromen-8-yl Trifluoromethanesulfonate (12a): Starting with 10 (156 mg, 0.30 mmol), K₃PO₄ (96 mg, 0.45 mmol), [Pd(PPh₃)₄] (17.3 mg, 5 mol-%, 0.015 mmol), 3a (41 mg, 0.30 mmol), and 1,4-dioxane (3 mL), compound 12a was isolated as an amorphous white solid (105 mg, 76%). Reaction temperature: 70 °C for 4 h. M.p. 156-158 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.37 (s, 3 H, CH₃), 6.78 (s, 1 H), 7.26–7.30 (m, 3 H, ArH), 7.42–7.49 (m, 4 H, ArH), 7.74 (d, J = 8.3 Hz, 1 H, ArH), 7.84–7.88 (m, 2 H, ArH) 8.24 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): *δ* = 21.3 (CH₃), 107.8, 116.4 (CH), 118.2 (q, J_{C,F} = 320 Hz, CF₃), 124.7 (C), 126.4, 126.5, 128.9, 129.2, 129.8 (CH), 130.6 (C), 131.7 (CH), 131.8, 132.7, 135.0, 145.1, 149.6, 164.0, 176.8 (C) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -74.3$ ppm. IR (KBr): v = 2917 (m), 1623 (s), 1389 (m), 1248 (m), 1167 (s), 1019 (m), 811 (m), 767 (m), 682 (s) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 460 (40) [M]⁺, 418 (03), 380 (02), 355 (14), 328 (100),

300 (04), 262 (02), 226 (73), 211 (22), 198 (10). HRMS (EI): calcd. for $C_{23}H_{15}F_3O_5S$ [M⁺]: 460.06230; found 460.06350.

4-Oxo-2-phenyl-7-[4-(trifluoromethyl)phenyl]-4H-chromen-8-yl Trifluoromethanesulfonate (12b): Starting with 10 (156 mg, 0.30 mmol), K₃PO₄ (96 mg, 0.45 mmol), [Pd(PPh₃)₄] (17.3 mg, 5 mol-%, 0.015 mmol), 3h (57 mg, 0.30 mmol), and 1,4-dioxane (3 mL), compound 12b was isolated as a white solid (107 mg, 69%). Reaction temperature: 70 °C for 4 h. M.p. 176–178 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.85 (s, 1 H), 7.42 (d, J = 8.3 Hz, 2 H, ArH), 7.49–7.51 (m, 2 H, ArH), 7.60 (d, J = 8.0 Hz, 2 H, ArH), 7.72 (d, J = 8.2 Hz, 2 H, ArH), 7.94–7.97 (m, 2 H, ArH) 8.24 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, CDCl₃): $\delta =$ 108.3, (CH), 118.3 (q, J_{C,F} = 319 Hz, CF₃), 124.2 (q, J_{C,F} = 280 Hz, CF₃), 125.1 (C), 125.5 (q, J_{C,F} = 3.6 Hz, CH), 125.8, 126.7, 127.0, 129.2, 129.7 (CH), 130.1 (q, $J_{C,F}$ = 34.2 Hz, 1 C), 130.6, 132.0 (C), 132.3 (CH), 139.0, 145.3, 149.2, 164.1, 176.4 (C) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -74.2$, -62.8 ppm. IR (KBr): $\tilde{v} = 2923$ (w), 1649 (m), 1421 (m), 1326 (m), 1205 (m), 1115 (s), 1070 (m), 1017 (m), 963 (m), 829 (m), 802 (s), 763 (m), 682 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 514 (19) [M]⁺, 381 (100), 325 (02), 279 (08), 251 (08), 223 (13), 183 (06). HRMS (EI): calcd. for $C_{23}H_{12}F_6O_5S [M^+]$: 514.03041; found 514.03132.

7-(4-Chlorophenyl)-4-oxo-2-phenyl-4H-chromen-8-yl Trifluoromethanesulfonate (12c): Starting with 10 (156 mg, 0.30 mmol), K₃PO₄ (96 mg, 0.45 mmol), [Pd(PPh₃)₄] (17.3 mg, 5 mol-%, 0.015 mmol), **3i** (47 mg, 0.30 mmol), and 1,4-dioxane (3 mL), compound **12c** was isolated as a light-yellow amorphous solid (95 mg, 66%). Reaction temperature: 70 °C for 4 h. M.p. 143–145 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.84 (s, 1 H), 7.39–7.43 (m, 5 H, ArH), 7.48–7.52 (m, 3 H, ArH), 7.93–7.96 (m, 2 H, ArH), 8.20 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, CDCl₃): δ = 108.2 (CH), 118.2 (q, $J_{C,F} = 321 \text{ Hz}, \text{ CF}_3$, 124.7 (C), 125.4, 126.7, 127.0, 129.1, 129.2, 130.6 (CH), 130.7 (C), 132.2 (CH), 132.8, 135.8, 139.2, 145.5, 149.0, 164.0, 176.5 (C) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -74.1 ppm. IR (KBr): $\tilde{v} = 2928$ (w), 1656 (s), 1426 (m), 1359 (m), 1212 (s), 1134 (s), 1090 (m), 1015 (m), 966 (m), 880 (w), 803 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 480 (16) [M]⁺ 347 (100), 332 (02), 284 (05), 345 (08), 210 (08), 189 (10). HRMS (EI): calcd. for C₂₂H₁₂³⁵ClF₃O₅S [M⁺]: 480.00406; found 480.00345.

7-(4-Ethylphenyl)-4-oxo-2-phenyl-4H-chromen-8-yl Trifluoromethanesulfonate (12d): Starting with 10 (156 mg, 0.30 mmol), K₃PO₄ (96 mg, 0.45 mmol), [Pd(PPh₃)₄] (17.3 mg, 5 mol-%, 0.015 mmol), 3m (45 mg, 0.30 mmol), and 1,4-dioxane (3 mL), compound 12d was isolated as a white solid (102 mg, 72%). Reaction temperature: 70 °C for 4 h. M.p. 167–168 °C. ¹H NMR (500 MHz, CDCl₃): δ = 1.22 (t, J = 7.7 Hz, 3 H, CH₃), 2.66 (q, J = 7.5 Hz, 2 H, CH₂), 6.83 (s, 1 H), 7.27 (d, J = 8.0 Hz, 2 H, ArH), 7.38 (d, J = 8.3 Hz, 2 H, ArH), 7.44 (d, J = 8.3 Hz, 1 H, ArH), 7.46–7.50 (m, 3 H, ArH), 7.95–7.97 (m, 2 H, ArH), 8.18 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (125.76 MHz, CDCl₃): δ = 15.5 (CH₃), 28.7 (CH₂), 108.2 (CH), 118.0 (q, J_{F,C} = 320 Hz, CF₃), 124.2 (C), 125.4, 126.7, 127.4, 128.3, 129.1, 129.2 (CH), 130.8, 131.6 (C), 132.1 (CH), 135.1, 140.7, 145.9, 149.0, 163.8 (C), 176.7 (CO) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -74.3$ ppm. IR (KBr): $\tilde{v} = 2916$ (w), 2850 (w), 1622 (m), 1568 (m), 1447 (m), 1386 (s), 1271 (m), 1164 (s), 1041 (m), 906 (w), 811 (s), 767 (s), 681 (s), 634 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 474 (40) [M]⁺, 410 (28), 395 (18), 366 (03), 341 (100), 326 (08), 313 (20), 281 (04). HRMS (EI): calcd. for C₂₄H₁₇F₃O₅S [M⁺]: 474.07471; found 474.07492.

4-Oxo-2-phenyl-7-(4-vinylphenyl)-4*H*-chromen-8-yl Trifluoromethanesulfonate (12e): Starting with 10 (156 mg, 0.30 mmol), K_3PO_4 (96 mg, 0.45 mmol), $[Pd(PPh_3)_4]$ (17.3 mg, 5 mol-%, 0.015 mmol),



3n (44 mg, 0.30 mmol), and 1,4-dioxane (3 mL), compound **12e** was isolated as a amorphous white solid (105 mg, 74%). Reaction temperature: 70 °C for 4 h. M.p. 113–115 °C. ¹H NMR (300 MHz, $CDCl_3$): $\delta = 5.30$ (d, J = 11.6 Hz, 1 H), 5.80 (d, J = 16.9 Hz, 1 H), 6.71 (dd, J = 10.8, 17.6 Hz, 1 H), 6.84 (s, 1 H), 7.42–7.50 (m, 8 H, ArH), 7.94–7.97 (m, 2 H, ArH), 8.19 (d, J = 8.4 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, CDCl₃): δ = 115.4 (CH₂), 108.2 (CH), 117.8 (q, J_{CF} = 319 Hz, CF₃), 124.4 (C), 125.2, 126.6, 126.7, 127.2, 129.1, 129.5 (CH), 130.8 (C), 132.1 (CH), 133.6, 135.0 (C), 136.0 (CH), 138.6, 140.2, 149.5, 163.9, 176.7 (C) ppm. ¹⁹F NMR (282 MHz, CDCl₃): $\delta = -74.2$ ppm. IR (KBr): $\tilde{v} = 2923$ (w), 1645 (s), 1484 (w), 1423 (s), 1354 (s), 1216 (s), 1128 (s), 1017 (m), 963 (m), 803 (m), 763 (m), 681 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) $= 472 (16) [M]^+$, 339 (100), 311 (01), 383 (11), 237 (07), 210 (03), 181 (07). HRMS (EI): calcd. for C₂₄H₁₅F₃O₅S [M⁺]: 472.05868; found 472.05988.

7-(4-Chlorophenyl)-8-(4-methoxyphenyl)-2-phenyl-4H-chromen-4one (13a): Starting with 12c (101 mg, 0.22 mmol), K₃PO₄ (93 mg, 0.44 mmol), [Pd(PPh₃)₄] (12.7 mg, 5 mol-%, 0.011), 4-methoxyphenylboronic acid (44 mg, 0.29 mmol), and 1,4-dioxane (3 mL), compound 13a was isolated as a yellow solid (60 mg, 73%). Reaction temperature: 100 °C for 4 h. M.p. 152-154 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.81 (s, 3 H, OCH₃), 6.82 (s, 1 H), 6.96 (d, J = 8.8 Hz, 2 H, ArH), 7.01–7.10 (m, 3 H, ArH), 7.40 (d, J =8.5 Hz, 5 H, ArH), 7.47-7.49 (m, 2 H, ArH), 7.93-7.97 (m, 2 H, ArH), 8.16 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (62 MHz, $CDCl_3$): $\delta = 55.4$ (OCH₃), 108.1, 114.3 (CH), 124.0 (C), 125.0, 126.2, 126.7, 127.2, 128.3, 129.1 (CH), 129.5 (C), 130.6 (CH), 130.8, 131.3 (C), 132.1 (CH), 135.0, 140.3, 145.5, 149.1, 160.6, 163.8, 176.7 ppm. IR (KBr): \tilde{v} = 3066 (w), 1649 (s), 1519 (m), 1438 (s), 1357 (m), 1246 (m), 1216 (s), 1134 (m), 963 (m), 802 (s), 684 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 438 (100) [M]⁺, 407 (05), 360 (02), 335 (05), 301 (03), 249 (03), 202 (16). HRMS (EI): calcd. for C₂₈H₁₉³⁵ClO₃ [M⁺]: 438.10230; found 438.10250.

8-(4-Ethylphenyl)-2-phenyl-7-(p-tolyl)-4H-chromen-4-one (13b): Starting with 12a (101 mg, 0.22 mmol), K₃PO₄ (93 mg, 0.44 mmol), $[Pd(PPh_3)_4]$ (12.7 mg, 5 mol-%, 0.011 mmol), **3m** (44 mg, 0.29 mmol), and 1,4-dioxane (3 mL), compound 13b was isolated as a yellow solid (60 mg, 66%). Reaction temperature: 100 °C for 4 h. M.p. 197–199 °C. ¹H NMR (500 MHz, CDCl₃): δ = 1.20 (t, J = 7.9 Hz, 3 H, CH₃), 2.23 (s, 3 H, CH₃), 2.62 (q, J = 7.5 Hz, 2 H, CH₂), 6.79 (s, 1 H), 6.95–7.01 (m, 4 H, ArH), 7.07–7.12 (m, 4 H, ArH), 7.26–7.38 (m, 3 H, ArH), 7.43 (dd, J = 3.4, 8.3 Hz, 1 H, ArH), 7.50–7.54 (m, 2 H, ArH), 8.18 (d, J = 8.3 Hz, 1 H, ArH) ppm. ¹³C NMR (125.75 MHz, CDCl₃): δ = 15.8, 21.1 (CH₃), 28.7 (CH₂), 122.8 (C), 124.3, 126.2, 127.4, 128.6, 128.7, 128.8, 128.9, 129.6, 131.0, 131.3 (CH), 131.6, 131.7, 132.0, 137.0, 143.5, 146.5, 146.7, 153.9, 136.1, 178.7 (C) ppm. IR (KBr): $\tilde{v} = 2962$ (s), 2923 (s), 1644 (s), 1597 (w), 1371 (m), 1202 (w), 1096 (w), 1016 (w), 815 (m), 771 (m), 688 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 416 (100) [M]⁺, 402 (16), 387 (49), 313 (06), 285 (14), 271 (05), 253 (06), 239 (09). HRMS (EI): calcd. for C₃₀H₂₄O₂ [M⁺]: 416.17783; found 416.17762.

Acknowledgments

Financial support by the Deutscher Akademischer Austauschdienst (DAAD) (scholarship to N. E.) and by the State of Pakistan (HEC scholarship to I. M.) is gratefully acknowledged. S. R. would like to acknowledge gratefully the University of Rostock (scholarship of the interdisciplinary faculty of the University of Rostock/Department LLM) and the State of Mecklenburg-Vorpommern for financial support.

- a) V. M. Malikov, M. P. Yuldashev, Chem. Nat. Compd. 2002, 38, 358; b) Römpp Lexikon Naturstoffe (Eds.: W. Steglich, B. Fugmann, S. Lang-Fugmann), Thieme, Stuttgart, Germany, 1997; c) J. B. Harborne, H. Baxter, The Handbook of Natural Flavonoids, vol. 1, Wiley, Chichester, 1999; d) G. R. Beecher, J. Nutr. 2003, 133, 3248S; e) B. H. Havsteen, Pharmacol. Ther. 2002, 96, 67; f) E. Middleton Jr, C. Kandaswami, T. C. Theoharides, Pharmacol. Rev. 2000, 52, 673; g) W. F. Hodnick, W. J. Roettger, F. S. Kung, C. W. Bohmant, R. S. Pardini, in: Plant Flavonoids in Biology and Medicine (Ed.: A. R. Liss), National Academy Press, Washington, 1986, pp. 249–252.
- [2] C. W. Huck, C. G. Huber, K.-H. Ongania, G. K. Bonn, J. Chromatogr. A 2000, 453.
- [3] T. Nagao, F. Abe, J. Kinjo, H. Okabe, *Biol. Pharm. Bull.* 2002, 250, 875.
- [4] a) J.-B. Daskiewicz, F. Depeint, L. Viornery, C. Bayet, C.-S. Geraldine, G. Comte, J.-M. Gee, I.-T. Johnson, K. Ndjoko, K. Hostettmann, D. Barron, J. Med. Chem. 2005, 48, 2790; b) Y. K. Rao, S.-H. Fang, Y.-M. Tzeng, Bioorg. Med. Chem. 2005, 13, 6850; c) S. F. Wang, Q. Jiang, Y. H. Ye, Y. Li, R. X. Tan, Bioorg. Med. Chem. 2005, 13, 4880; d) H. Gao, J. Kawabata, Bioorg. Med. Chem. 2005, 13, 1661; e) G.-Y. Gao, D.-J. Li, W. M. Keung, J. Med. Chem. 2001, 44, 3320.
- [5] a) B. Su, J. C. Hackett, E. S. Diaz-Cruz, Y.-W. Kim, R. W. Brueggemeier, *Bioorg. Med. Chem.* 2005, *13*, 6571; b) Y.-W. Kim, J. C. Hackett, R. W. Brueggemeier, *J. Med. Chem.* 2004, *47*, 4032; c) P. Traxler, J. Green, H. Mett, U. Séquin, P. Furet, *J. Med. Chem.* 1999, *42*, 1018; d) M. Cushman, H. Zhu, R. L. Geahlen, A. J. Kraker, *J. Med. Chem.* 1994, *37*, 3353.
- [6] a) C. S. Yang, S. Prabhu, S. Landau, J. Drug Metab. Rev. 2001, 33, 237; b) M. Haghiac, T. Walle, Nutr. Cancer 2005, 53, 220.
- [7] A. Banerji, N.-C. Goomer, Synthesis 1980, 874.
- [8] J. Allan, R. Robinson, J. Chem. Soc. 1924, 20, 2192.
- [9] a) M. S. Khanna, O. V. Singh, C. P. Garg, R. P. Kapoor, J. Chem. Soc. Perkin Trans. 1 1992, 2565; b) T. Patonay, D. Molnár, Z. Murányi, Bull. Soc. Chim. Fr. 1995, 132, 233.
- [10] a) J. H. Looker, W. W. Hanneman, J. Org. Chem. 1962, 27, 381;
 b) H. S. Mahal, H. S. Rai, K. Venkataraman, J. Chem. Soc. 1935, 866; c) S. Matsuura, M. Iinuma, K. Ishikawa, K. Kagei, Chem. Pharm. Bull. 1978, 26, 305; d) C. G. Shanker, B. V. Mallaiah, G. Srimannarayana, Synthesis 1983, 310; e) J. Haginawa, Y. Higuchi, T. Kawashima, H. Shinokawa, Yakugaku Zasshi 1976, 96, 195; f) Y. Maki, K. Shimada, M. Sako, K. Hirota, Tetrahedron 1988, 44, 3187; g) J. Massicot, Compt. Rend. Acad. Sci. Fr. 1955, 240, 94; h) R. S. Varma, M. Varma, Synth. Commun. 1982, 12, 927; i) N. Hans, S. K. Grover, Synth. Commun. 1993, 23, 1021; j) T. Patonay, J.A. S. Cavaleiro, A. Lévai, A. M. S. Silva, Heterocycl. Commun. 1997, 3, 223.
- [11] a) D.-E. Zembower, H. Zhang, J. Org. Chem. 1998, 63, 9300; b) X. Zheng, W.-D. Meng, F.-L. Qing, Tetrahedron Lett. 2004, 45, 8083; c) X. Huang, E. Tang, W.-M. Xu, J. Cao, J. Comb. Chem. 2005, 7, 802; d) W.-J. Peng, X.-W. Han, B. Yu, Chin. J. Chem. 2006, 24, 1154; e) S. G. Davies, B. E. Mobbs, J. Chem. Soc. Perkin Trans. 1 1987, 2597; f) K. M. Dawood, Tetrahedron 2007, 63, 9642; g) A. S. Klymchenko, Y. Mély, Tetrahedron Lett. 2004, 45, 8391; h) A. S. Klymchenko, H. Stoeckel, K. Takeda, Y. Mély, J. Phys. Chem. B 2006, 110, 13624; i) K. Dahlén, M. Grøtli, K. Luthman, Synlett 2006, 897; j) K. Dahlén, E. A. A. Wallén, M. Grøtli, K. Luthman, J. Org. Chem. 2006, 71, 6863; k) K. Tatsuta, S. Kasai, Y. Amano, T. Yamaguchi, M. Seki, S. Hosokawa, Chem. Lett. 2007, 36, 10; 1) T. Patonay, A. Vasas, A. Kiss-Szikszai, A. M. S. Silva, J. A. S. Cavaleiro, Aust. J. Chem. 2010, 63, 1592; m) A. Vasas, T. Patonay, K. Kónya, A. M. S. Silva, J. A. S. Cavaleiro, Aust. J. Chem. 2011, 64, 647.

- [12] For reviews of the Suzuki–Miyaura reaction, see: a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) N. Miyaura, *Top. Curr. Chem.* **2002**, *219*, 11.
- [13] For reviews of cross-coupling reactions of polyhalogenated heterocycles, see: a) S. Schröter, C. Stock, T. Bach, *Tetrahedron* 2005, 61, 2245; b) M. Schnürch, R. Flasik, A. F. Khan, M. Spina, M. D. Mihovilovic, P. Stanetty, *Eur. J. Org. Chem.* 2006, 3283; c) overview of the Suzuki protocol: A. Suzuki, in: *Organopalladium Chemistry for Organic Synthesis* (Ed.: E. Negishi), Wiley, New York, 2002, chapter III.2.
- [14] For Suzuki-Miyaura reactions of the bis(triflates) of benzene derivatives and other arenes, see for example: a) M. Takeuchi, T. Tuihiji, J. Nishimura, J. Org. Chem. 1993, 58, 7388; b) H. Sugiura, Y. Nigorikawa, Y. Saiki, K. Nakamura, M. Yamaguchi, J. Am. Chem. Soc. 2004, 126, 14858; c) K. Akimoto, H. Suzuki, Y. Kondo, K. Endo, U. Akiba, Y. Aoyama, F. Hamada, Tetrahedron 2007, 63, 6887; d) K. Akimoto, Y. Kondo, K. Endo, M. Yamada, Y. Aoyama, F. Hamada, Tetrahedron Lett. 2008, 49, 7361; e) S. Hosokawa, H. Fumiyama, H. Fukuda, T. Fukuda, M. Seki, K. Tatsuta, Tetrahedron Lett. 2007, 48, 7305; f) M. Nawaz, M. Farooq Ibad, O.-U.-R. Abid, R. A. Khera, A. Villinger, P. Langer, Synlett 2010, 150; g) A. Mahal, A. Villinger, P. Langer, Synlett 2010, 1085; h) M. Nawaz, R.A. Khera, I. Malik, M. F. Ibad, O.-U. R. Abid, A. Villinger, P. Langer, Synlett 2010, 979; i) O.-U. R. Abid, M. F. Ibad, M. Nawaz, A. Ali, M. Sher, N. H. Rama, A. Villinger, P. Langer, Tetrahedron Lett. 2010, 51, 1541; j) O. A. Akrawi, M. Hussain, P. Langer, Tetrahedron Lett. 2011, 52, 1093.
- [15] I. Malik, M. Hussain, N. T. Hung, A. Villinger, P. Langer, Synlett 2010, 2244.
- [16] A. M. Echavarren, J. K. Stille, J. Am. Chem. Soc. 1987, 109, 5478.
- [17] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.
- [18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision A.1, Gaussian, Inc., Wallingford CT, 2009.
- [19] For a simple guide for the prediction of the site-selectivity of palladium(0) catalyzed cross-coupling reactions based on the ¹H NMR chemical shift values, see: S. T. Handy, Y. Zhang, *Chem. Commun.* 2006, 299.
- [20] For discussion of the FMO-theory, see: a) I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, New York, 1976; b) F. Jensen, Introduction to Computational Chemistry, Wiley, New York, 1999, chapter 15.
- [21] CCDC-852502 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [22] A.-D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [23] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B: Solid State 1988, 37, 785.

Received: October 12, 2011

Published Online: January 30, 2012