DOI: 10.1002/ejoc.201001497

Site-Selective Arylation of Alizarin and Purpurin Based on Suzuki–Miyaura Cross-Coupling Reactions

Ahmed Mahal,[a] Alexander Villinger,[a] and Peter Langer*[a,b]

Keywords: Synthetic methods / Homogeneous catalysis / Palladium / Aromatic substitution / Cross-coupling / Regioselectivity

A variety of arylated anthraquinones were prepared by site-selective Suzuki–Miyaura cross-coupling reactions of the bis- and tris(triflates) of alizarin and purpurin, respectively. The site-selectivity is controlled by the electronic influence of the carbonyl group and by steric parameters.

Introduction

Anthraquinones are of considerable pharmacological relevance and represent an important core structure of many natural products.[1] They have been isolated both as *O*-glycosides and aglycons. For example, daunorubicin, adriamycin, saintopin, and aclarubicin, which belong to the class of the anthracyclines, exhibit strong anticancer and antibiotic activities. Structurally more simple anthraquinones are found, for example, in the natural products pulmatin, chrysophanic acid, vismiaquinone, anthragallol, questin, mumbaistatin, and several others (Figure 1).[2,3] A broad range of pharmacological activities, including cytotoxic, antimicrobial, anti-inflammatory or antimalaria activity, have been reported for substituted anthraquinones. Besides natural products and pharmaceutical chemistry, anthraquinones are important core structures in the field of analytical chemistry and material sciences. In fact, they show interesting redox, UV, and luminescence properties.[4]

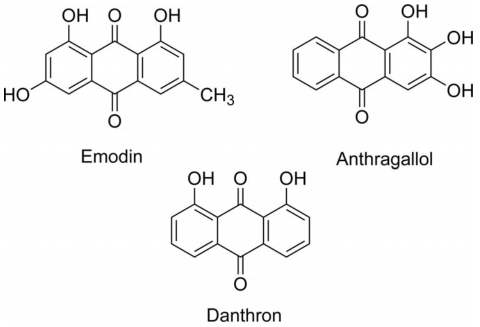


Figure 1. Structure of anthraquinone natural products.

Polyhalogenated molecules represent interesting substrates in palladium(0)-catalyzed cross-coupling reactions.[5] The site-selectivity is generally controlled by steric and electronic parameters. Recently, we have reported Suzuki and Heck reactions of tetrabromothiophene, tetrabromo-*N*-methylpyrrole, tetrabromoselenophene, and other polyhalogenated heterocycles.[6] We also reported site-selective Suzuki–Miyaura reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate and other arenes.[7] The first attack often occurs at the sterically less hindered carbon atom. Recently, we have reported Suzuki–Miyaura reactions of the bis(triflate) of 1,2-dihydroxy-anthraquinone (alizarin).[8] Interestingly, these reactions proceed with excellent site-selectivity in favor of the sterically more hindered position 1, for electronic reasons. Herein, we report full details of these studies and reveal, for the first time, site-selective reactions of purpurin (1,2,4-trihydroxyanthraquinone).

Results and Discussion

Alizarin

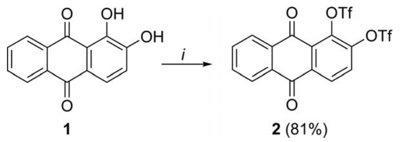
Alizarin (**1**) was transformed into the bis(triflate) **2** in 81% yield (Scheme 1). 1,2-Diarylanthraquinones **4a**–**f** were prepared by Suzuki reactions of **2** with 2.4 equiv. of arylboronic acids (Scheme 2, Table 1). The best yields were obtained when [Pd(PPh$_3$)$_4$] was used as the catalyst, K$_3$PO$_4$ as the base, and dioxane as the solvent (Table 2). The yields dropped when toluene or tetrahydrofuran (THF) was used. The use of [Pd(PPh$_3$)$_2$Cl$_2$] proved to be less successful in terms of yield, and an inseparable complex mixture was formed when [Pd(OAc)$_2$] was used in the presence of XPhos. The yield of **4b** was relatively low as a result of partial hydrolysis of **2** to give a monoaryl hydroxyanthraquinone, however, this side-reaction was observed only for the synthesis of **4b**, and was not seen for the other reactions.

---

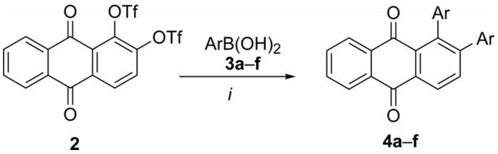
[a] Institut für Chemie der Universität Rostock,
Albert-Einstein-Straße 3a, 18059 Rostock, Germany
Fax: +49-381-498-6411
E-mail: peter.langer@uni-rostock.de
[b] Leibniz Institut für Katalyse e.V. an der Universität Rostock,
Albert-Einstein-Straße 29a, 18059 Rostock

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001497.

The moderate yield of **4f** can be explained by incomplete conversion and practical problems that occurred during the chromatographic purification. The use of 2-methylphenylboronic acid resulted in the formation of a complex mixture, presumably for steric reasons.



Scheme 1. Synthesis of **2**. Reagents and conditions: (i) CH_2Cl_2, **1** (1.0 equiv.), –78 °C, pyridine (4.0 equiv.), Tf_2O (2.4 equiv.), –78 → 20 °C, 14 h.



Scheme 2. Synthesis of **4a**–**f**. Reagents and conditions: (i) **2** (1.0 equiv.), **3a**–**f** (2.4 equiv.), $[Pd(PPh_3)_4]$ (6 mol-%), K_3PO_4 (3.0 equiv.), 1,4-dioxane (4 mL per 0.5 mmol of **2**), 110 °C, 10 h.

Table 1. Synthesis of **4a**–**f**.

3, **4**	Ar	% Yield of **4**[a]
a	4-$(F_3C)C_6H_4$	77
b	4-$(MeO)C_6H_4$	40
c	4-tBuC_6H_4	76
d	4-ClC_6H_4	81
e	4-MeC_6H_4	77
f	4-EtC_6H_4	59

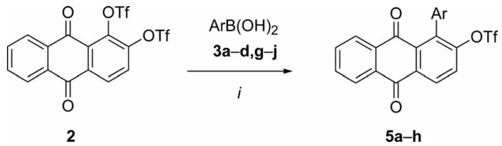
[a] Yield of isolated product.

Table 2. Optimization of the synthesis of **4d**.

Entry	Base[a,b]	Solvent[c]	Catalyst[d]	% Yield of **4d**[e]
1	K_2CO_3	dioxane	$[Pd(PPh_3)_2Cl_2]$	74
2	K_2CO_3	toluene	$[Pd(PPh_3)_2Cl_2]$	55
3	K_2CO_3	THF	$[Pd(PPh_3)_2Cl_2]$	61
4	K_3PO_4	dioxane	$[Pd(PPh_3)_4]$	81
5	K_3PO_4	toluene	$[Pd(PPh_3)_4]$	48
6	K_3PO_4	THF	$[Pd(PPh_3)_4]$	73

[a] 1 mL (2 M aqueous solution per 0.5 mmol of **2**). [b] K_3PO_4 (3.0 equiv. per 0.5 mmol of **2**). [c] 4 mL per 0.5 mmol of **2**. [d] 6 mol-% per 0.5 mmol of **2**. [e] Yield of isolated product.

The reaction of **2** with 1.0 equiv. of arylboronic acids gave rise to the issue of site-selectivity. The reaction of **2** with 1.0 equiv. of arylboronic acids **3a**–**d** or **3g**–**j** afforded 1-arylanthraquinones **5a**–**h**. The best yields were again obtained when $[Pd(PPh_3)_4]$ and K_3PO_4 were used and when the reaction was carried out at 90 °C instead of 110 °C (reaction time 10 h) (Scheme 3, Table 3). The electron-poor arylboronic acids **3d** and **3g** gave the best yields. The use of 2-methylphenylboronic acid resulted in the formation of a complex mixture, presumably for steric reasons. Only moderate yields were obtained in some cases, which can be explained by formation of bis-adducts **4** as the major side-reaction together with incomplete conversion (inspection of the crude product mixture by thin-layer chromatography).



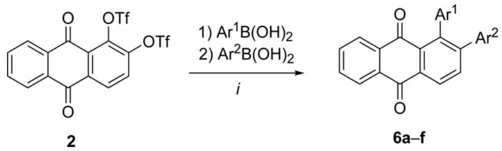
Scheme 3. Synthesis of **5a**–**h**. Reagents and conditions: (i) **2** (1.0 equiv.), **3a**–**d** or **3g**–**j** (1.0 equiv.), $[Pd(PPh_3)_4]$ (3 mol-%), K_3PO_4 (1.5 equiv.), 1,4-dioxane (3 mL per 0.5 mmol of **2**), 90 °C, 10 h.

Table 3. Synthesis of **5a**–**h**.

3	**5**	Ar	% Yield of **5**[a]
a	**a**	4-$(F_3C)C_6H_4$	74
b	**b**	4-$(MeO)C_6H_4$	67
c	**c**	4-tBuC_6H_4	61
d	**d**	4-ClC_6H_4	85
g	**e**	3-$(F_3C)C_6H_4$	84
h	**f**	3-$(MeO)C_6H_4$	79
i	**g**	4-FC_6H_4	50
j	**h**	4-$(CF_3O)C_6H_4$	52

[a] Yield of isolated product.

The possibilities of one-pot Suzuki coupling reactions of **2** with two different arylboronic acids were next studied. The boronic acids were added in a sequential manner. During the optimization, it proved to be important to carry out the first step of the one-pot reaction at 90 °C and the second step at 110 °C (Scheme 4). The one-pot reactions of **2** with various arylboronic acids afforded 1,2-diarylanthraquinones **6a**–**f** in 50–68% yields (Table 4). The moderate yields can be explained by formation of a small amount of bis-adducts **4**.



Scheme 4. Synthesis of **6a**–**f**. Reagents and conditions: (i) (1) **2** (1.0 equiv.), **3a**–**d** or **3g** (1.0 equiv.), $[Pd(PPh_3)_4]$ (3 mol-%), K_3PO_4 (1.5 equiv.), 1,4-dioxane, 90 °C, 10 h; (2) **3a** or **3c** (1.1 equiv.), K_3PO_4 (1.5 equiv.), 1,4-dioxane, 110 °C, 10 h.

Table 4. Synthesis of 1,2-diarylanthraquinones **6a**–**f**.

3	**6**	Ar^1	Ar^2	% Yield of **6**[a]
a,**c**	**a**	4-$(F_3C)C_6H_4$	4-tBuC_6H_4	65
b,**c**	**b**	4-$(MeO)C_6H_4$	4-tBuC_6H_4	50
c,**a**	**c**	4-tBuC_6H_4	4-$(F_3C)C_6H_4$	60
d,**c**	**d**	4-ClC_6H_4	4-tBuC_6H_4	61
g,**a**	**e**	3-$(F_3C)C_6H_4$	4-$(F_3C)C_6H_4$	68
g,**c**	**f**	3-$(F_3C)C_6H_4$	4-tBuC_6H_4	61

[a] Yield of isolated product.

The structure of product **5c** was confirmed by 2D NMR experiments (HMBC, NOESY) (see the Supporting Information). The structures of **4c**, **5b**, and **6a** were independently confirmed by X-ray crystal structure analyses (see Figures 2, 3, and 4).[9]

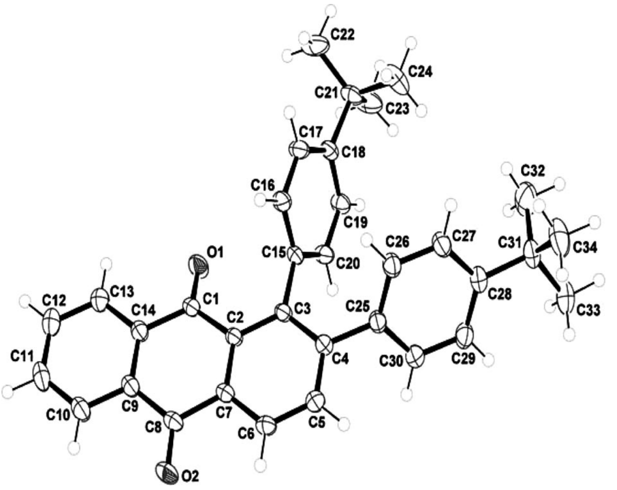


Figure 2. X-ray crystal structure of **4c**.

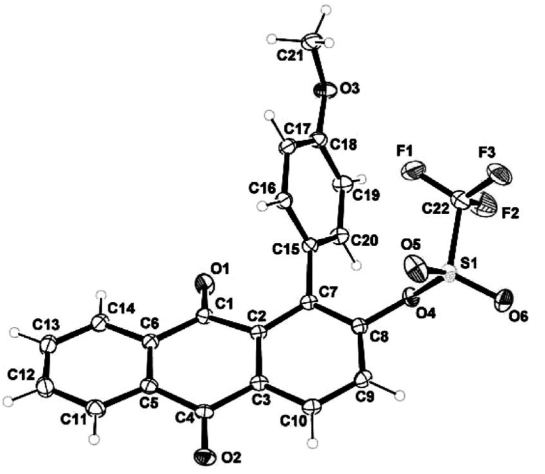


Figure 3. X-ray crystal structure of **5b**.

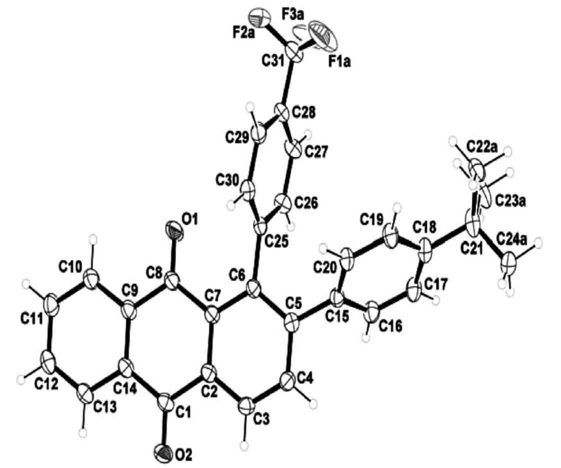


Figure 4. X-ray crystal structure of **6a**.

The first attack of the arylboronic acid occurred at carbon atom C-1 of bis(triflate) **2**, which can be explained as follows. The first attack of palladium(0)-catalyzed cross-coupling reactions generally occurs at the electronically more deficient and sterically less hindered position.[5,10] Position 1 of bis(triflate) **2** is sterically more hindered than position 2 (Figure 5), however, position 1 (located in β-position to the carbonyl group) is more electron-deficient than position 2. Hand and Zhang reported a simple guide for the prediction of the site selectivity of palladium(0)-catalyzed cross-coupling reactions based on the ^{1}H NMR chemical shift values of the compound in which the triflate or halogen groups are replaced by hydrogen atoms.[10] In fact, the ^{1}H NMR signals of the aromatic proton located at position 1 of anthraquinone is shifted to lower field compared to the proton located at position 2. In addition, a neighboring group effect by the quinone carbonyl group (chelation of the approaching palladium complex) might play a role. In conclusion, the first attack occurs at the sterically more hindered position for electronic reasons.

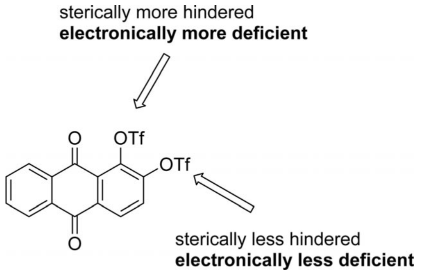
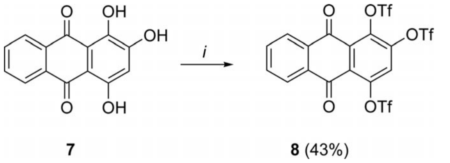


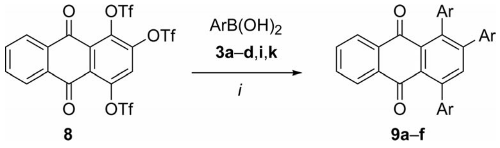
Figure 5. Possible explanation for the site-selective reaction of **2**.

The reaction of commercially available purpurin (**7**) with triflic anhydride, in the presence of pyridine, afforded tris(triflate) **8** in 43 % yield (Scheme 5).



Scheme 5. Synthesis of **8**. Reagents and conditions: (i) CH_2Cl_2, **7** (1.0 equiv.), –78 °C, pyridine (7.0 equiv.), Tf_2O (5.0 equiv.), –78 → 20 °C, 14 h.

The Suzuki–Miyaura reaction of **8** with 4.0 equiv. of boronic acid derivatives afforded 1,2,4-triarylanthraquinones **9a**–**f** (Scheme 6, Table 5). In these reactions $[Pd(PPh_3)_4]$ was used as the catalyst and K_3PO_4 as the base (Table 6). The best yields were obtained when the reaction was carried out at 120 °C. The electron-rich arylboronic acids **3b**, **3c**, and **3k** gave very good yields. In contrast, electron-poor arylboronic acids **3a**, **3d**, and **3i** provided only moderate to good yields. This result, which is in contrast to the corresponding reactions of alizarin-derived bis(triflate) **2**, might be explained by the fact that tris(triflate) **8** is more electron-poor than bis(triflate) **2**. The moderate yields of products **9a** and **9e** can be explained by incomplete conversion and practical problems that occurred during the chromatographic purification.



Scheme 6. Synthesis of **9a**–**f**. Reagents and conditions: (i) **8** (1.0 equiv.), **3a**–**d**, **3i**, or **3k** (4.0 equiv.), $[Pd(PPh_3)_4]$ (10 mol-%), K_3PO_4 (5.0 equiv.), 1,4-dioxane (5 mL per 0.15 mmol of **8**), 120 °C, 12 h.

Table 5. Synthesis of **9a**–**f**.

3	9	Ar	% Yield of 9[a]
a	**a**	4-$(F_3C)C_6H_4$	43
b	**b**	4-$(MeO)C_6H_4$	73
c	**c**	4-tBuC_6H_4	83
d	**d**	4-ClC_6H_4	60
i	**e**	4-FC_6H_4	57
k	**f**	C_6H_4	86

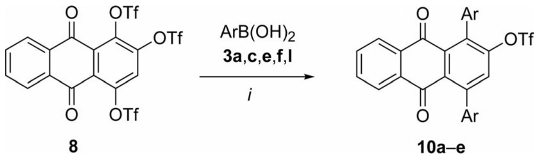
[a] Yield of isolated product.

Table 6. Optimization of the synthesis of **9c**.

Entry	Base[a,b]	Solvent[c]	Catalyst[d]	% Yield of 9c[e]
1	K_2CO_3	dioxane	$[Pd(PPh_3)_2Cl_2]$	70
2	K_2CO_3	toluene	$[Pd(PPh_3)_2Cl_2]$	39
3	K_2CO_3	THF	$[Pd(PPh_3)_2Cl_2]$	62
4	K_3PO_4	dioxane	$[Pd(PPh_3)_4]$	83
5	K_3PO_4	toluene	$[Pd(PPh_3)_4]$	66
6	K_3PO_4	THF	$[Pd(PPh_3)_4]$	74

[a] 1 mL (2 M aqueous solution) per 0.15 mmol of **8**. [b] K_3PO_4 (5.0 equiv. per 0.15 mmol of **8**). [c] 5 mL per 0.15 mmol of **8**. [d] 10 mol-% per 0.15 mmol of **8**. [e] Yield of isolated product.

The reaction of the **8** and 2.0 equiv. of arylboronic acid afforded 1,4-diaryl-2-[(trifluoromethyl)sulfonyloxy]anthraquinones **10a**–**e** (Scheme 7, Table 7). During the optimization, it proved to be important to carry out the reaction at 105 °C instead of 120 °C.



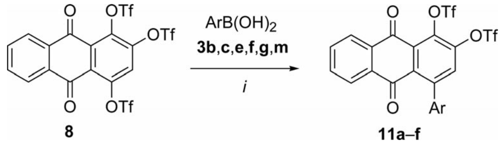
Scheme 7. Synthesis of **10a**–**e**. Reagents and conditions: (i) **2** (1.0 equiv.), **3** (2.0 equiv.), $[Pd(PPh_3)_4]$ (6 mol-%), K_3PO_4 (3.0 equiv.), 1,4-dioxane (4 mL per 0.15 mmol of **8**), 105 °C, 10 h.

Table 7. Synthesis of **10a**–**e**.

3	10	Ar	% Yield of 10[a]
a	**a**	4-$(CF_3)C_6H_4$	61
c	**b**	4-tBuC_6H_4	81
e	**c**	4-MeC_6H_4	51
f	**d**	4-EtC_6H_4	74
l	**e**	3,5-MeC_6H_4	60

[a] Yield of isolated product.

The site-selective Suzuki–Miyaura reactions of **8** with 1.0 equiv. of arylboronic acid afforded products **11a**–**f** (Scheme 8, Table 8). During the optimization, it proved to be important to carry out the reaction at 95 °C instead of 105 °C. The moderate yields can be explained by formation of bis- and tris-adducts **10** and **9** as the major side reactions and by incomplete conversion (reaction monitored by TLC).



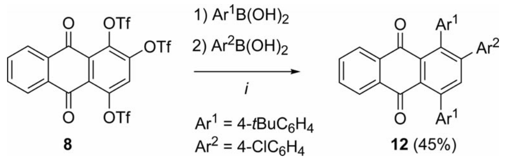
Scheme 8. Synthesis of **11a**–**f**. Reagents and conditions: (i) **8** (1.0 equiv.), **3** (1.0 equiv.), $[Pd(PPh_3)_4]$ (3.0 mol-%), K_3PO_4 (1.5 equiv.), 1,4-dioxane (3 mL per 0.15 mmol of **8**), 95 °C, 10 h.

Table 8. Synthesis of **11a**–**f**.

3	11	Ar	% Yield of 11[a]
b	**a**	4-$(MeO)C_6H_4$	38
c	**b**	4-tBuC_6H_4	41
e	**c**	4-MeC_6H_4	61
f	**d**	4-EtC_6H_4	65
g	**e**	3-$(CF_3)C_6H_4$	40
m	**f**	3-ClC_6H_4	56

[a] Yield of isolated product.

The one-pot reaction of **8** with different arylboronic acids afforded product **12** in 45% yield (Scheme 9). The first step of the reaction was carried out using 2.0 equiv. of arylboronic acid **3c** at 95 °C (10 h). The second step was carried out using **3d** at 110 °C (10 h).



Scheme 9. Synthesis of **12**. Reagents and conditions: (i) (1) **8** (1.0 equiv.), **3c** (2.0 equiv.), $[Pd(PPh_3)_4]$ (6 mol-%), K_3PO_4 (3.0 equiv.), 1,4-dioxane, 95 °C, 10 h; (2) **3d** (1.0 equiv.), $[Pd(PPh_3)_4]$ (3 mol-%), K_3PO_4 (1.5 equiv.), 1,4-dioxane, 110 °C, 10 h.

The structures of products **10e** and **11f** were confirmed by 2D NMR experiments (NOESY and HMBC) (see the Supporting Information). The structures of **10a** and **11e** were independently confirmed by X-ray crystal structure analyses (see Figures 6 and 7).[9]

The site-selectivity can be explained as follows. Positions 2 and 4 of **8** are sterically less hindered than position 1 (Figure 8), however, because positions 1 and 4 of **8** are more electron-deficient than position 2, the first attack occurs at the sterically less hindered and more electronically deficient position 4. The second attack occurs at position 1, which is sterically hindered, but electron deficient. The third attack occurs at position 2, which is not electron-deficient and not sterically hindered.

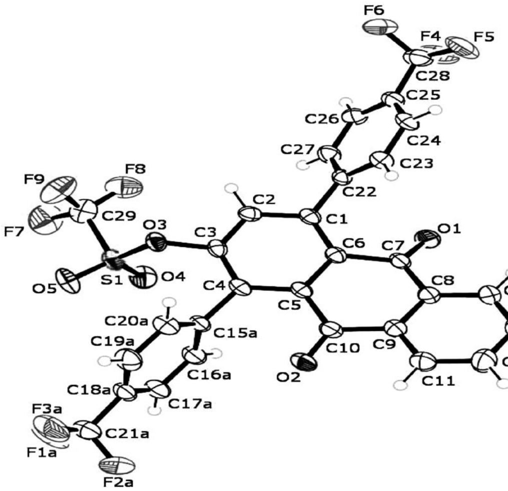


Figure 6. X-ray crystal structure of **10a**.

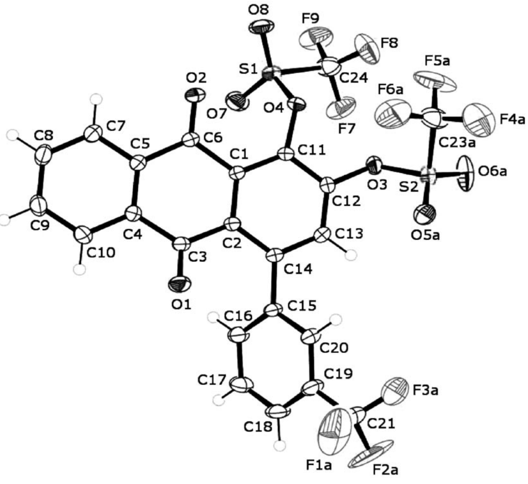


Figure 7. X-ray crystal structure of **11e**.

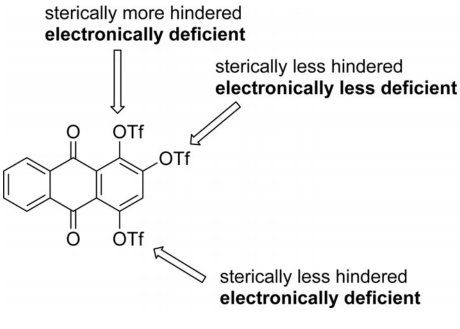


Figure 8. Possible explanation for the site selectivity of **8**.

Conclusions

A variety of arylated anthraquinones have been synthesized by site-selective Suzuki–Miyaura cross coupling reactions. For the triflates of alizarin and purpurin, the site-selectivity is controlled by electronic parameters.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. The deuterated solvents indicated were used for ^{1}H and ^{13}C NMR measurements. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane), or electrospray ionization (ESI). Silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used for preparative-scale chromatography.

1,2-Bis[(trifluoromethyl)sulfonyloxy]anthraquinone (2). General Procedure: To a solution of **1** (1.0 equiv.) in CH_2Cl_2 (10 mL/mmol) was added pyridine (4.0 equiv.) at room temperature under an argon atmosphere. After 10 min, Tf_2O (2.4 equiv.) was added at –78 °C and the mixture was warmed to room temperature and stirred overnight. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The products of the reaction mixture were isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc).

Starting with **1** (1.9 g, 8.0 mmol), pyridine (2.6 mL, 32.0 mmol), CH_2Cl_2 (80 mL), and Tf_2O (3.2 mL, 19.2 mmol), **2** was isolated as a yellow solid (3.25 g, 81%); m.p. 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.85 (m, 3 H, ArH), 8.23–8.26 (m, 1 H, ArH), 8.29–8.32 (m, 1 H, ArH), 8.46 (d, J = 8.76 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 118.5 (q, $J_{F,C}$ = 320.9 Hz, CF_3), 118.6 (d, $J_{F,C}$ = 320.7 Hz, CF_3), 127.4 (CH), 127.8 (C), 128.0, 128.1, 128.9 (CH), 132.0, 133.7, 134.1 (C), 135.1, 135.2 (CH), 139.2, 145.0 (C), 180.2, 180.5 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (q, J_F = 3.02, 6.02 Hz, 3 F, CF_3), –72.58 (q, J_F = 2.84, 5.83 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1674 (s), 1601, 1587, 1472 (w), 1427 (s), 1330, 1316, 1282, 1249 (w), 1208 (s), 1164, 1150 (m), 1124 (s), 1007, 998, 901, 856 (m), 807 (s), 795, 738 (m), 721, 708 (s), 684, 676, 655, 643 (w), 618, 606 (m), 589, 575, 569 (s), 543, 529 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 504 (36) $[M + H]^+$, 435 (05), 375 (08), 348 (23), 279 (100), 251 (76), 223 (26), 154 (26), 126 (60). HRMS (EI, 70 eV): calcd. for $C_{16}H_6O_8F_6S_2$ $[M]^+$ 503.94028; found 503.940108.

General Procedure for Suzuki–Miyaura Reactions: A 1,4-dioxane solution (4 mL per 3 mmol of **2**) of **2**, K_3PO_4, $[Pd(PPh_3)_4]$, and arylboronic acid **3** was stirred at 110 °C or 90 °C for 10 h. After cooling to 20 °C, distilled 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.

1,2-Bis[4-(trifluoromethyl)phenyl]anthraquinone (4a): Starting with **2** (250 mg, 0.5 mmol), **3a** (225 mg, 1.2 mmol), $[Pd(PPh_3)_4]$ (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4a** was isolated as a yellow solid (190 mg, 77%); m.p. 208–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01–7.07 (m, 4 H, ArH), 7.35 (d, J = 8.12 Hz, 2 H, ArH), 7.42 (d, J = 8.12 Hz, 2 H, ArH), 7.62–7.71 (m, 3 H, ArH), 7.95–8.0 (m, 1 H, ArH), 8.18–8.21 (m, 1 H, ArH), 8.45 (d, J = 8.12 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 123.8 (q, $J_{F,C}$ = 272.2 Hz, CF_3), 124.1 (q, $J_{F,C}$ = 272.1 Hz, CF_3), 124.7 (C), 124.7, 124.8, 126.7, 127.4, 127.7 (CH), 128.8 (C), 129.5, 129.7 (CH), 131.5, 132.6 (C), 134.0 (CH), 134.3 (C), 134.4 (CH), 134.5 (C), 135.1 (CH), 140.6, 143.0, 143.2, 147.3 (C), 182.7, 183.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.69 (s, 3 F, CF_3), –62.37 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1670 (m), 1633, 1615, 1580, 1416, 1397 (w), 1324, 1299 (s), 1281, 1261, 1212, 1199 (m), 1158, 1108, 1078, 1061, 1016 (s), 977 (w), 958, 947 (m), 900, 866 (w), 835, 825 (s), 797 (m), 787, 768, 757, 747, 740 (w), 720, 711 (s), 679 (w), 672 (m), 648 (w), 636 (m), 606 (s), 545 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 496 (78) [M$^+$], 495 (100), 477 (09), 428 (25), 427 (86). HRMS (EI, 70 eV): calcd. for $C_{28}H_{13}O_2F_6$ [M – H]$^+$ 495.08143; found 495.081086.

1,2-Bis(4-methoxyphenyl)anthraquinone (4b): Starting with **2** (250 mg, 0.5 mmol), **3b** (180 mg, 1.2 mmol), [Pd(PPh$_3$)$_4$] (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4b** was isolated as red crystals (84 mg, 40%); m.p. 220–221 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 6.61 (d, *J* = 8.76 Hz, 2 H, ArH), 6.71 (d, *J* = 8.73 Hz, 2 H, ArH), 6.83 (d, *J* = 7.92 Hz, 4 H, ArH), 7.60–7.65 (m, 3 H, ArH), 7.97–8.0 (m, 1 H, ArH), 8.15–8.18 (m, 1 H, ArH), 8.30 (d, *J* = 8.07 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 54.0 (OCH_3), 54.1 (OCH_3), 112.1, 112.2, 125.4, 126.0, 126.3, 129.4, 129.6 (CH), 130.8, 131.0, 131.4, 131.7 (C), 132.4 (CH), 132.5 (C), 133.0 (CH), 134.0 (C), 134.2 (CH), 140.0, 148.0, 157.1, 157.5 (C), 182.3, 183.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2838 (w), 1671 (s), 1606 (m), 1588, 1550, 1516, 1464, 1451, 1440, 1412, 1394 (w), 1328, 1311 (m), 1297, 1240 (s), 1208, 1107, 1088, 1074 (m), 1027 (s), 977 (w), 954 (s), 858 (w), 840 (m), 828 (s), 811 (w), 800 (s), 767, 749 (w), 727 (m), 718 (s), 697 (m), 669, 649 (w), 640, 601, 588 (m), 537 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 420 (100) [M$^+$], 419 (49), 405 (11), 390 (12), 389 (45), 345 (14), 312 (09). HRMS (EI, 70 eV): calcd. for $C_{28}H_{20}O_4$ [M]$^+$ 420.13561; found 420.134505.

1,2-Bis(4-*tert*-butylphenyl)anthraquinone (4c): Starting with **2** (250 mg, 0.5 mmol), **3c** (213 mg, 1.2 mmol), [Pd(PPh$_3$)$_4$] (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4c** was isolated as orange crystals (180 mg, 76%); m.p. 234–236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9 H, 3 × CH_3), 1.20 (s, 9 H, 3 × CH_3), 6.75–6.83 (m, 4 H, ArH), 7.01–7.14 (m, 4 H, ArH), 7.60–7.65 (m, 2 H, ArH), 7.71 (d, *J* = 8.01 Hz, 1 H, ArH), 8.01–8.03 (m, 1 H, ArH), 8.17–8.23 (m, 1 H, ArH), 8.34 (d, *J* = 8.05 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.2 (3 × CH_3), 31.4 (3 × CH_3), 34.4, 34.4 (C), 124.2, 124.3, 126.6, 127.0, 127.5, 129.0, 129.0 (CH), 131.3, 132.9 (C), 133.5 (CH), 133.6 (C), 134.1, 134.9 (CH), 135.0, 136.9, 137.2, 142.7, 149.1, 149.8, 149.8 (C), 183.4, 183.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2959 (m), 2901, 2866 (w), 1675 (s), 1663, 1588 (m), 1575, 1566, 1548, 1513, 1475, 1456, 1410, 1394, 1360 (w), 1330, 1315 (m), 1298 (s), 1280, 1262, 1253, 1211, 1199 (m), 1185, 1160 (w), 1113 (m), 1072 (w), 1016 (m), 979 (w), 956 (m), 942, 904 (w), 860, 836 (m), 822 (s), 795 (m), 774, 768, 755, 745 (w), 719 (s), 690 (m), 682 (w), 662, 645 (m), 587 (s), 568, 559, 543 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 472 (45) [M$^+$], 457 (93), 439 (04), 415 (100), 401 (23), 383 (11). HRMS (EI, 70 eV): calcd. for $C_{34}H_{32}O_2$ [M]$^+$ 472.23968; found 472.238675.

1,2-Bis(4-chlorophenyl)anthraquinone (4d): Starting with **2** (250 mg, 0.5 mmol), **3d** (185 mg, 1.2 mmol), [Pd(PPh$_3$)$_4$] (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4d** was isolated as a yellow solid (174 mg, 81%); m.p. 208–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82–6.87 (m, 4 H, ArH), 7.06–7.16 (m, 4 H, ArH), 7.61–7.70 (m, 3 H, ArH), 7.95–8.02 (m, 1 H, ArH), 8.15–8.18 (m, 1 H, ArH), 8.34 (d, *J* = 8.01 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 126.7, 127.4, 127.5, 128.1, 128.2, 130.5, 130.7 (CH), 131.6, 132.6, 132.8, 133.6 (C), 133.8 (CH), 134.0 (C), 134.3 (CH), 134.6 (C), 135.1 (CH), 137.9, 138.1, 140.8, 147.7 (C), 183.0, 183.5 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 1673 (s), 1589 (m), 1576, 1551 (w), 1489 (m), 1478, 1451, 1410, 1388 (w), 1326 (m), 1308, 1297, 1267 (s), 1245, 1210 (m), 1181 (w), 1159 (m), 1091 (s), 1070 (m), 1014 (s), 972 (w), 954 (s), 938, 856, 846 (m), 834, 820 (s), 791, 774, 763, 729 (m), 714 (s), 698, 688 (m), 656 (w), 644 (m), 636, 573 (w), 559, 548 (m), 537 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 432 (2 × ^{37}Cl, 12) [M$^+$], 431 (^{37}Cl, 26) [M + H$^+$], 430 (^{37}Cl, 67) [M$^+$], 429 (^{35}Cl, 91) [M + H$^+$], 428 (^{35}Cl, 93) [M$^+$], 427 (100), 395 (30), 394 (24), 393 (91), 357 (17), 300 (26). HRMS (EI, 70 eV): calcd. for $C_{26}H_{13}Cl_2O_2$ ([M – H]$^+$, ^{35}Cl) 427.02871; found 427.028111.

1,2-Bis(4-methylphenyl)anthraquinone (4e): Starting with **2** (250 mg, 0.5 mmol), **3e** (162 mg, 1.2 mmol), [Pd(PPh$_3$)$_4$] (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4e** was isolated as a yellow solid (149 mg, 77%); m.p. 218–220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 6.82–7.00 (m, 4 H, ArH), 6.90 (d, *J* = 7.86 Hz, 2 H, ArH), 6.98 (d, *J* = 7.88 Hz, 2 H, ArH), 7.60–7.70 (m, 3 H, ArH), 8.00–8.03 (m, 1 H, ArH), 8.18–8.21 (m, 1 H, ArH), 8.34 (d, *J* = 8.01 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.1 (CH_3), 21.4 (CH_3), 126.5, 127.0, 127.4, 128.4, 128.5, 129.1, 129.3 (CH), 131.8, 132.8 (C), 133.5 (CH), 133.6 (C), 134.1 (CH), 135.1 (C), 135.3 (CH), 136.0, 136.7, 136.8, 137.2, 142.4, 149.2 (C), 183.4, 183.9 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2920, 2851 (w), 1672, 1662 (s), 1590, 1574, 1548, 1512, 1478, 1445, 1414, 1385 (w), 1327, 1313 (m), 1293, 1278, 1260 (s), 1241, 1208 (m), 1182, 1159, 1112, 1070, 1039 (w), 1018 (m), 965 (w), 952, 939 (m), 896, 854, 832 (w), 811 (s), 794 (m), 762, 749 (w), 723, 713, 701 (s), 669, 650 (w), 642 (m), 595 (w), 580, 549, 540 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 388 (49) [M$^+$], 374 (26). 373 (100), 371 (6). HRMS (EI, 70 eV): calcd. for $C_{28}H_{20}O_2$ [M]$^+$ 388.14578; found 388.144687.

1,2-Bis(4-ethylphenyl)anthraquinone (4f): Starting with **2** (250 mg, 0.5 mmol), **3f** (180 mg, 1.2 mmol), [Pd(PPh$_3$)$_4$] (34 mg, 6 mol-%, 0.03 mmol), K_3PO_4 (320 mg, 1.5 mmol), and 1,4-dioxane (4 mL), **4f** was isolated as a brown solid (124 mg, 60%); m.p. 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03–1.14 (m, 6 H, 2 × CH_3), 2.43–2.55 (m, 4 H, 2 × CH_2), 6.76–6.87 (m, 6 H, ArH), 6.95 (d, *J* = 8.07 Hz, 2 H, ArH), 7.54–7.64 (m, 3 H, ArH), 7.94–8.01 (m, 1 H, ArH), 8.11–8.14 (m, 1 H, ArH), 8.27 (d, *J* = 8.04 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.2, 14.4 (2 × CH_3), 27.3, 27.5 (2 × CH_2), 125.4, 125.8, 126.0 (d, *J* = 11.9 Hz), 126.3, 126.8, 128.1, 128.3 (CH), 130.5, 131.6 (C), 132.3 (CH), 132.5 (C), 133.0 (CH), 134.1 (C), 134.1 (CH), 136.0, 136.3, 141.2, 141.3, 142.0, 148.2 (C), 182.2, 182.6 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2962, 2849 (w), 1665 (s), 1630 (w), 1589 (m), 1572, 1512, 1478, 1470, 1454, 1434, 1409, 1392, 1358 (w), 1325, 1313 (m), 1294, 1288, 1262 (s), 1210, 1189, 1163, 1156 (m), 1114, 1089 (w), 1073 (m), 1051, 1041, 1017, 974 (w), 951, 943 (m), 889 (w), 871 (m), 832 (s), 791 (m), 761, 738 (w), 712 (s), 694, 669, 648, 583, 553, 533 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 416 (30) [M$^+$], 388 (30), 387 (100), 372 (5), 357 (4). HRMS (EI, 70 eV): calcd. for $C_{30}H_{24}O_2$ [M]$^+$ 416.17708; found 416.176631.

1-[4-(Trifluoromethyl)phenyl]-2-[(trifluoromethyl)sulfonyloxy]-anthraquinone (5a): Starting with **2** (250 mg, 0.5 mmol), **3a** (95 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5a** was isolated as a yellow solid (186 mg, 74%); m.p. 135–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.24 Hz, 2 H, ArH), 7.64–7.71 (m, 5 H, ArH), 7.94–7.96 (m, 1 H, ArH), 8.14–8.17 (m, 1 H, ArH), 8.43 (d, *J* = 8.57 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 117.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 123.1 (q, $J_{F,C}$ = 271.3 Hz, CF_3), 124.3 (q, *J* = 272.0 Hz), 125.4, 126.0, 126.5, 128.1, 129.1 (CH), 129.2, 129.6, 131.1, 132.2, 133.0 (d, *J* = 1.7 Hz, 1 C), 133.4, 133.7 (CH), 134.7, 136.7 (d, *J* = 1.1 Hz), 151.1 (C), 180.4, 180.8 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.03 (s, 3 F, CF_3), –62.57 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1674 (s), 1617, 1589, 1572, 1479, 1452, 1433, 1418 (w), 1402 (m), 1326 (s), 1301, 1273 (m), 1249 (w), 1219, 1165, 1125, 1107, 1085, 1061 (s), 1018 (m), 1000 (w), 946 (m), 793, 770, 743 (w), 723, 711 (s), 676, 651 (w), 601 (s), 572, 528 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 500 (48) [M$^+$], 499 (13), 431 (25), 368 (24), 367 (100), 366 (24), 298 (23). HRMS (EI, 70 eV): calcd. for $C_{22}H_{10}O_5F_6S$ [M]$^+$ 500.01476; found 500.013920.

1-(4-Methoxyphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5b): Starting with **2** (250 mg, 0.5 mmol), **3b** (76 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5b** was isolated as orange crystals (154 mg, 67%); m.p. 140–142 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.82 (s, 3 H, OCH$_3$), 6.94 (d, J = 8.76 Hz, 2 H, ArH), 7.07 (d, J = 8.76 Hz, 2 H, ArH), 7.60–7.67 (m, 3 H, ArH), 7.96–8.00 (m, 1 H, ArH), 8.11–8.14 (m, 1 H, ArH), 8.36 (d, J = 8.67 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 55.2 (OCH$_3$), 113.8 (CH), 118.2 (q, $J_{F,C}$ = 320.4 Hz, CF$_3$), 125.4 (C), 126.2, 126.8, 127.5, 129.2, 130.0 (CH), 132.3, 133.5 (C), 134.0 (CH), 134.1, 134.5 (C), 134.6 (CH), 137.3, 152.0, 159.6 (C), 182.0, 182.1 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –74.04 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 2838 (w), 1671 (s), 1606 (m), 1588, 1550, 1516, 1464, 1451, 1440, 1412, 1394 (w), 1328, 1311 (m), 1297, 1240 (s), 1208, 1107, 1088, 1074 (m), 1027 (s), 977 (w), 954 (s), 858 (w), 840 (m), 828 (s), 811 (w), 800 (s), 767, 749 (w), 727, 718 (s), 697 (m), 669, 649 (w), 640, 601, 588 (m), 537 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 462 (55) [M$^+$], 330 (23), 329 (100), 314 (17), 286 (11), 202 (14). HRMS (EI, 70 eV): calcd. for $C_{22}H_{13}O_6F_3S$ [M]$^+$ 462.03794; found 462.037734.

1-(4-*tert*-Butylphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5c): Starting with **2** (250 mg, 0.5 mmol), **3c** (90 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5c** was isolated as yellow crystals (149 mg, 61%); m.p. 160–162 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.31 (s, 9 H, 3 × CH$_3$), 7.07 (d, J = 8.4 Hz, 2 H, ArH), 7.42 (d, J = 8.51 Hz, 2 H, ArH), 7.58–7.67 (m, 3 H, ArH), 7.96–8.0 (m, 1 H, ArH), 8.11–8.14 (m, 1 H, ArH), 8.36 (d, J = 8.81 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 31.3 (3 × CH$_3$), 34.7 (C), 118.2 (q, $J_{F,C}$ = 318.5 Hz, CF$_3$), 125.2, 126.3, 126.9, 127.7, 128.3, 129.3 (CH), 130.5, 132.4, 133.4 (C), 134.1 (CH), 134.1 (C), 134.5 (CH), 134.6, 137.6, 151.2, 151.8 (C), 181.9, 182.0 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –74.2 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 2960, 2930, 2869, 1675, 1665, 1590, 1580, 1573, 1429 (w), 1410 (m), 1362, 1329, 1316, 1297 (w), 1267 (m), 1205 (s), 1165 (m), 1129 (s), 1079, 1040, 1017, 997 (w), 946, 879, 843 (m), 820 (s), 792, 775, 767, 757, 745 (w), 725 (m), 713 (s), 683, 671 (w), 642 (m), 603 (s), 573 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 488 (18) [M$^+$], 473 (100), 431 (31), 325 (58), 299 (26), 239 (08). HRMS (EI, 70 eV): calcd. for $C_{25}H_{19}O_5F_3S$ [M]$^+$ 488.08998; found 488.090070.

1-(4-Chlorophenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5d): Starting with **2** (250 mg, 0.5 mmol), **3d** (78 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5d** was isolated by as a yellow solid (199 mg, 85%); m.p. 160–162 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.08–7.11 (m, 2 H, ArH), 7.38–7.40 (m, 2 H, ArH), 7.62–7.71 (m, 3 H, ArH), 7.96–8.00 (m, 1 H, ArH), 8.14–8.17 (m, 1 H, ArH), 8.41 (d, J = 8.68 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 118.1 (q, $J_{F,C}$ = 320.5 Hz, CF$_3$), 126.3, 127.0, 127.6, 128.7, 129.9, 130.0 (CH), 132.1, 132.3, 133.3, 134.1, 134.2 (C), 134.3 (CH), 134.5 (C), 134.7 (CH), 136.1, 151.4 (C), 181.6, 182.0 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –73.92 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 1676 (s), 1589, 1579, 1570, 1492, 1477, 1453 (w), 1408 (m), 1327, 1314, 1300 (w), 1270 (m), 1253 (w), 1212, 1170, 1132 (s), 1089, 943 (m), 883 (s), 854 (w), 827 (s), 793, 775 (w), 713 (s), 640 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 468 (^{37}Cl, 21) [M + H$^+$], 467 (^{37}Cl, 14) [M$^+$], 466 (^{35}Cl, 53) [M + H$^+$], 465 (^{35}Cl, 09) [M$^+$], 431 (09), 335 (32), 334 (25), 333 (100), 332 (14), 298 (35), 297 (15), 270 (19). HRMS (EI, 70 eV): calcd. for $C_{21}H_{10}ClF_3O_5S$ ([M]$^+$, ^{35}Cl) 465.98841; found 465.987508.

1-(3-Trifluoromethylphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5e): Starting with **2** (250 mg, 0.5 mmol), **3g** (95 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5e** was isolated as a yellow solid (209 mg, 84%); m.p. 115–117 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.35 (d, J = 7.62 Hz, 1 H, ArH), 7.42 (s, 1 H, ArH), 7.52 (t, J = 7.76 Hz, 1 H, ArH), 7.60–7.73 (m, 4 H, ArH), 7.89–7.92 (m, 1 H, ArH), 8.08–8.10 (m, 1 H, ArH), 8.38 (d, J = 8.64 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 117.0 (q, $J_{F,C}$ = 320.6 Hz, CF$_3$), 123.0 (q, $J_{F,C}$ = 272.2 Hz, CF$_3$), 124.1 (q, J = 3.8 Hz), 124.6 (q, J = 3.8 Hz), 125.4, 126.0, 126.5, 127.8 (d, J = 4.0 Hz), 129.1 (CH), 129.5, 130.0 (C), 131.2 (CH), 132.2, 133.0 (d, J = 5.5 Hz, 1 C), 133.3 (CH), 133.6 (C), 133.7 (d, J = 4.4 Hz, CH), 134.4, 144.0, 150.2 (C), 180.4, 180.7 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –74.10 (s, 3 F, CF$_3$), –62.70 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 1673 (s), 1589, 1568, 1492, 1479 (w), 1418, 1308 (m), 1277, 1274 (w), 1250 (m), 1213, 1167, 1121, 1099, 1069 (s), 1001 (w), 955 (m), 883, 839, 804 (s), 770 (w), 727, 712, 702 (s), 689, 652 (w), 628, 598 (s), 572 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 500 (34) [M$^+$], 431 (12), 368 (21), 367 (100), 266 (16), 347 (24). HRMS (EI, 70 eV): calcd. for $C_{22}H_{10}O_5F_6S$ [M]$^+$ 500.01476; found 500.015351.

1-(3-Methoxyphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5f): Starting with **2** (250 mg, 0.5 mmol), **3h** (76 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **4f** was isolated as a yellow solid (183 mg, 79%); m.p. 115–116 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.72 (s, 3 H, OCH$_3$), 6.69–6.73 (m, 2 H, ArH), 6.91–6.95 (m, 1 H, ArH), 7.31 (t, J = 8.76 Hz, 1 H, ArH), 7.58–7.66 (m, 3 H, ArH), 7.94–8.01 (m, 1 H, ArH), 8.10–8.13 (m, 1 H, ArH), 8.36 (d, J = 8.70 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 55.2 (OCH$_3$), 113.8, 114.3 (CH), 118.2 (q, $J_{F,C}$ = 320.5 Hz, CF$_3$), 120.8, 126.1, 126.8, 127.5, 129.4, 129.5 (CH), 132.2, 133.3, 134.0 (C), 134.1 (CH), 134.3 (C), 134.6 (CH), 135.0, 137.1, 151.5, 159.5 (C), 181.7, 181.8 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –74.02 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 1679 (m), 1606, 1571, 1488, 1455 (w), 1422 (s), 1327, 1300 (w), 1270 (m), 1250 (w), 1210, 1166, 1152, 1132 (s), 1096, 1076 (w), 1038 (m), 1000 (w), 959 (m), 892, 848 (s), 825, 810, 780, 769 (m), 742 (w), 725 (m), 707, 701 (s), 671 (m), 627, 597 (s), 571 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 462 (40) [M$^+$], 330 (21), 329 (100), 314 (28), 298 (10), 286 (14), 202 (13). HRMS (EI, 70 eV): calcd. for $C_{22}H_{13}O_6F_3S$ [M]$^+$ 462.03794; found 462.038112.

1-(4-Fluorophenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (5g): Starting with **2** (250 mg, 0.5 mmol), **3i** (70 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5g** was isolated as a yellow solid (113 mg, 50%); m.p. 136–138 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.11–7.14 (m, 4 H, ArH), 7.63–7.72 (m, 3 H, ArH), 7.97–8.00 (m, 1 H, ArH), 8.16–8.20 (m, 1 H, ArH), 8.42 (d, J = 8.70 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 115.4, 115.7 (CH), 118.1 (q, $J_{F,C}$ = 318.3 Hz, CF$_3$), 126.3, 127.0, 127.5 (CH), 129.4 (d, $J_{F,C}$ = 3.7 Hz, 1 C), 129.7, 130.4, 130.5 (CH), 132.2, 133.4, 134.1 (C), 134.2 (CH), 134.3 (C), 134.6 (CH), 136.3, 151.5 (C), 162.7 (d, $J_{F,C}$ = 247.7 Hz, CF), 181.7, 182.0 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –113.01 (s, 1 F, CF), –74.00 (s, 3 F, CF$_3$) ppm. IR (KBr): ṽ = 1674 (m), 1589, 1568, 1510. 1479, 1450 (w), 1420 (m), 1329, 1315, 1298, 1271, 1249 (w), 1206 (s), 1162 (m), 1130 (s), 1096 (m), 1080, 1038, 1015, 999, 974, 945 (w), 879 (s), 856 (m), 832, 809 (s), 770, 752 (w), 729 (m), 717, 708 (s), 681, 669 (w), 646 (m), 637, 621 (w), 603, 578 (s), 541 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 450 (46) [M$^+$], 449 (09), 318 (23), 317 (100), 316 (14), 260 (10), 233 (20), 231 (14). HRMS (EI, 70 eV): calcd. for $C_{21}H_{10}O_5F_4S$ [M]$^+$ 450.01796; found 450.017099.

1-(4-Trifluoromethoxyphenyl)-2-[(trifluoromethyl)sulfonyloxy]-anthraquinone (5h): Starting with **2** (250 mg, 0.5 mmol), **3j** (102 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (160 mg, 0.75 mmol), and 1,4-dioxane (3 mL), **5h** was isolated as a yellow solid (135 mg, 52%); m.p. 108–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.28 (m, 4 H, ArH), 7.66–7.70 (m, 3 H, ArH), 7.96–8.00 (m, 1 H, ArH), 8.16–8.18 (m, 1 H, ArH), 8.43 (d, J = 8.65 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 118.1 (q, $J_{F,C}$ = 320.6 Hz, CF_3), 120.5 (q, $J_{F,C}$ = 257.6 Hz, OCF_3), 120.8, 126.4, 127.0, 127.6, 129.9, 130.1 (CH), 132.3, 133.3, 134.1, 134.2 (C), 134.3, 134.7 (CH), 135.8, 149.2, 149.3, 151.3 (C), 181.6, 182.0 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.10 (s, 3 F, CF_3), –57.78 (s, 3 F, OCF_3) ppm. IR (KBr): ṽ = 1681 (m), 1609, 1588, 1570, 1510, 1450 (w), 1425 (m), 1409, 1329, 1315, 1298 (w), 1250, 1204, 1167, 1152, 1131, 1105 (s), 1081 (m), 1038 (w), 1019 (m), 999 (w), 946 (m), 920 (w), 877 (s), 852 (m), 820 (s), 805 (m), 771 (w), 722, 711 (s), 681, 668, 655 (w), 628 (m), 599 (s), 571, 553, 527 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 516 (43) [M$^+$], 431 (10), 384 (22), 383 (100), 382 (13). HRMS (EI, 70 eV): calcd. for $C_{22}H_{10}O_6F_6S$ [M]$^+$ 416.00968; found 416.010762.

General Procedure for the Synthesis of 6a–f: The reaction was carried out in a pressure tube. To a suspension of **2** (0.5 mmol), Ar^1-B(OH)$_2$ (0.5 mmol), and [Pd(PPh$_3$)$_4$] (3 mol-%) in dioxane (3 mL), was added K_3PO_4 (0.75 mmol), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 90 °C under an argon atmosphere for 10 h, then the mixture was cooled to 20 °C. Ar^{2}B(OH)$_2$ (0.55 mmol), [Pd(PPh$_3$)$_4$] (3 mol-%), K_3PO_4 (0.75 mmol), and dioxane (2 mL) were added and the reaction mixture was heated under an argon atmosphere for 10 h at 110 °C. The reaction mixture was diluted with H_2O, extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (flash silica gel, heptanes/EtOAc).

1-[4-(Trifluoromethyl)phenyl]-2-(4-*tert*-butylphenyl)anthraquinone (6a): Starting with **2** (252 mg, 0.5 mmol), **3a** (95 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3c** (98 mg, 0.55 mmol), **6a** was isolated as yellow crystals (157 mg, 65%); m.p. 225–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9 H, 3 × CH_3), 6.76–6.80 (m, 2 H, ArH), 7.03–7.10 (m, 4 H, ArH), 7.38 (d, J = 8.1 Hz, 2 H, ArH), 7.61–7.66 (m, 2 H, ArH), 7.70 (d, J = 8.01 Hz, 1 H, ArH), 7.94–7.98 (m, 1 H, ArH), 8.16–8.20 (m, 1 H, ArH), 8.36 (d, J = 8.04 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.2 (3 × CH_3), 34.4 (C), 124.3 (q, $J_{F,C}$ = 272.3 Hz, CF_3), 124.4 (dq, $J_{F,C}$ = 7.6, 2.2 Hz), 124.7, 126.7, 127.4, 127.6 (CH), 128.5 (q, J = 32.8 Hz, 1 C), 129.0, 129.7 (CH), 131.3, 132.8, 133.6 (C), 133.8, 134.3 (CH), 134.6 (C), 135.4 (CH), 136.3, 140.8, 144.0 (d, J = 1.7 Hz), 149.1, 150.5 (C), 183.0, 183.6 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.3 (s, 3 F, CF_3) ppm. IR (KBr): ṽ = 2962, 2905, 2869 (w), 1672 (m), 1613, 1588, 1552, 1513, 1462, 1409, 1399, 1363 (w), 1321 (s), 1300, 1278, 1263 (m), 1213, 1186 (w), 1158 (s), 1118 (m), 1105 (s), 1087, 1075, 1059, 1016 (m), 976 (w), 954 (m), 899, 864 (w), 837, 824 (m), 796, 784, 767, 758, 744 (w), 718 (s), 688, 671, 662, 640, 605 (w), 584 (m), 566, 564, 532 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 484 (43) [M$^+$], 469 (100), 449 (10), 427 (08), 383 (02), 357 (03). HRMS (EI, 70 eV): calcd. for $C_{31}H_{23}O_2F_3$ [M]$^+$ 484.16447; found 484.164850.

1-(4-Methoxyphenyl)-2-(4-*tert*-butylphenyl)anthraquinone (6b): Starting with **2** (252 mg, 0.5 mmol), **3b** (76 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3c** (98 mg, 0.55 mmol), **6b** was isolated as a red solid (111 mg, 50%); m.p. 221–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 9 H, 3 × CH_3), 3.71 (s, 3 H, OCH_3), 6.70 (d, J = 8.58 Hz, 2 H, ArH), 6.84 (d, J = 7.26 Hz, 4 H, ArH), 7.10 (d, J = 8.58 Hz, 2 H, ArH), 7.58–7.68 (m, 3 H, ArH), 7.98–8.01 (m, 1 H, ArH), 8.16–8.20 (m, 1 H, ArH), 8.32 (d, J = 8.58 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.2 (3 × CH_3), 33.4 (C), 54.0 (OCH_3), 112.1, 123.5, 125.4, 125.9, 126.3, 128.1, 129.4 (CH), 130.8, 130.9, 131.7 (C), 132.4 (CH), 132.6 (C), 133.0 (CH), 134.1 (C), 134.2 (CH), 136.1, 141.0, 148.3, 149.0, 157.2 (C), 182.3, 183.0 (CO) ppm. IR (KBr): ṽ = 2956, 2865, 2839, 2042 (w), 1671 (s), 1658, 1609, 1586 (w), 1573 (m), 1547 (w), 1513 (m), 1477, 1465, 1451, 1439, 1415, 1405, 1390, 1361 (w), 1329, 1315 (m), 1297, 1277, 1241 (s), 1206 (m), 1176 (s), 1159, 1115 (m), 1088, 1071 (w), 1024 (s), 1014 (m), 977 (w), 953 (m), 941, 931, 901, 859 (w), 836 (m), 823 (s), 795 (m), 767, 752, 747 (w), 718 (s), 686, 661 (w), 648 (m), 634 (w), 597, 578, 569 (m), 540 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 446 (100) [M$^+$], 445 (12), 432 (16), 431 (40), 416 (10), 415 (23), 390 (13). 389 (18). HRMS (EI, 70 eV): calcd. for $C_{31}H_{26}O_3$ [M]$^+$ 446.18765; found 446.187401.

1-(4-*tert*-Butylphenyl)-2-[4-(trifluoromethyl)phenyl]anthraquinone (6c): Starting with **2** (252 mg, 0.5 mmol), **3c** (90 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3a** (104 mg, 0.55 mmol), **6c** was isolated as a yellow solid (143 mg, 60%); m.p. 220–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9 H, 3 × CH_3), 6.81 (d, J = 8.59 Hz, 2 H, ArH), 6.98 (d, J = 8.12 Hz, 2 H, ArH), 7.14 (d, J = 8.59 Hz, 2 H, ArH), 7.28 (d, J = 8.12 Hz, 2 H, ArH), 7.60–7.68 (m, 3 H, ArH), 8.00–8.02 (m, 1 H, ArH), 8.17–8.20 (m, 1 H, ArH), 8.36 (d, J = 8.12 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 30.2 (3 × CH_3), 33.4 (C), 122.9 (q, J = 272.2 Hz, CF_3), 123.3 (q, $J_{F,C}$ = 7.4, 3.7 Hz), 123.5, 125.6, 126.1, 126.5 (CH), 127.7 (C), 127.8 (CH), 128.2 (C), 128.7 (CH), 130.4, 131.7 (C), 132.6, 133.2, 133.6 (CH), 133.8, 135.1, 141.5, 142.8 (d, J = 1.3 Hz), 146.9, 148.7 (C), 182.1, 182.4 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.68 (s, 3 F, CF_3) ppm. IR (KBr): ṽ = 1674 (s), 1615, 1587, 1576, 1551, 1511, 1461, 1456, 1415, 1393, 1364, 1359 (w), 1323, 1300 (s), 1283, 1258 (m), 1210, 1198, 1184 (w), 1155, 1109 (s), 1085 (m), 1073, 1061, 1014 (s), 978, 967 (w), 956, 941 (m), 903, 861 (m), 837, 823 (s), 796 (m), 780, 766, 753, 739 (w), 720, 714, 700 (s), 678 (w), 646 (m), 632 (w), 605, 585, 563, 545 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 485 (10) [M + H$^+$], 484 (29) [M$^+$], 470 (34), 469 (100), 428 (22), 427 (65). HRMS (EI, 70 eV): calcd. for $C_{31}H_{24}F_3O_2$ [M + H]$^+$ 485.1723; found 485.1713.

1-(4-Chlorophenyl)-2-(4-*tert*-butylphenyl)anthraquinone (6d): Starting with **2** (252 mg, 0.5 mmol), **3d** (78 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3c** (98 mg, 0.55 mmol), **6d** was isolated as a yellow solid (137 mg, 61%); m.p. 245–246 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, 3 × CH_3), 6.92–7.00 (m, 4 H, ArH), 7.21–7.26 (m, 4 H, ArH), 7.75–7.82 (m, 3 H, ArH), 8.09–8.12 (m, 1 H, ArH), 8.30–8.33 (m, 1 H, ArH), 8.48 (d, J = 7.46 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.2 (3 × CH_3), 34.5 (C), 124.7, 126.6, 127.3, 127.4, 128.0, 129.1, 130.7 (CH), 131.6, 132.5, 132.7, 133.6 (C), 133.7, 134.2 (CH), 134.8 (C), 135.5 (CH), 136.6, 138.4, 141.0, 149.1, 150.3 (C), 183.1, 183.8 (CO) ppm. IR (KBr): ṽ = 1667 (s), 1588, 1575, 1549, 1513, 1492, 1477, 1461, 1409, 1391, 1360 (w), 1332 (m), 1316 (w), 1298 (m), 1277 (w), 1261 (m), 1247, 1212, 1184, 1159, 1112, 1087, 1071 (w), 1013 (m), 981 (w), 954 (m), 941, 905, 858, 842 (w), 832, 825 (m), 794, 774, 763, 746 (w), 720 (s), 697, 691, 679, 643, 630 (w), 583, 576 (m), 549, 533 (w) $\mathrm{cm^{-1}}$. GC-MS (EI, 70 eV): *m*/*z* (%) = 452 (^{37}Cl, 16) [M$^+$], 451 (^{35}Cl, 19) [M + H$^+$], 450 (^{35}Cl, 46) [M$^+$], 437 (38), 436 (31), 435 (100), 393 (14), 207 (10). HRMS (EI, 70 eV): calcd. for $C_{30}H_{24}ClO_2$ ([M + H]$^+$, ^{35}Cl) 451.1459; found 451.1459.

1-(3-Trifluoromethylphenyl)-2-[4-(trifluoromethyl)phenyl]anthraquinone (6e): Starting with **2** (252 mg, 0.5 mmol), **3g** (95 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3a** (104 mg, 0.55 mmol), **6e** was isolated as a yellow solid (169 mg, 68%); m.p. 255–256 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, J = 8.23 Hz, 2 H, ArH), 7.14 (d, J = 7.65 Hz, 1 H, ArH), 7.27–7.45 (m, 5 H, ArH), 7.65–7.77 (m, 3 H, ArH), 8.00–8.03 (m, 1 H, ArH), 8.23–8.26 (m, 1 H, ArH), 8.46 (d, J = 8.10 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 122.8 (q, $J_{F,C}$ = 321.2 Hz, CF_3), 123.1 (q, $J_{F,C}$ = 272.0 Hz, CF_3), 123.6 (d, J = 4.1 Hz), 124.8 (d, J = 3.7 Hz), 126.2 (d, J = 3.8 Hz), 126.8, 127.4, 127.8, 128.2, 129.7 (CH), 130.0, 130.5, 131.5 (C), 132.5 (CH), 132.6 (C), 134.0 (CH), 134.3 (C), 134.4 (CH), 134.6 (C), 134.9 (CH), 140.1, 140.5, 143.0, 147.6 (C), 182.8, 183.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.79 (s, 3 F, CF_3), –62.78 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1669 (s), 1617, 1589, 1574, 1533, 1490, 1432, 1414, 1399 (w), 1328, 1302 (s), 1285, 1263, 1244, 1291, 1212 (w), 1161, 1109, 1081, 1066 (s), 1018 (m), 1002, 981 (w), 961 (m), 923, 893, 863 (w), 849 (m), 836 (w), 825, 805 (m), 792, 767, 752, 746, 725 (w), 712, 706 (s), 686 (w), 675 (m), 655, 629, 605, 567, 542 (w) $\mathrm{cm^{-1}}$. GC-MS (EI, 70 eV): *m*/*z* (%) = 496 (80) [M$^+$], 495 (100), 477 (09), 428 (21), 427 (72), 407 (08). HRMS (EI, 70 eV): calcd. for $C_{28}H_{13}O_2F_6$ [M – H]$^+$ 495.08143; found 495.080798.

1-(3-Trifluoromethylphenyl)-2-(4-*tert*-butylphenyl)anthraquinone (6f): Starting with **2** (252 mg, 0.5 mmol), **3g** (95 mg, 0.5 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 3 mol-%, 0.015 mmol), K_3PO_4 (320 mg, 1.5 mmol), 1,4-dioxane (3 mL), and **3c** (98 mg, 0.55 mmol), **6f** was isolated as a yellow solid (148 mg, 61%); m.p. 227–229 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (s, 9 H, 3×CH_3), 6.75 –6.77 (m, 2 H, ArH), 7.07–7.10 (m, 3 H, ArH), 7.17 (d, J = 8.34 Hz, 1 H, ArH), 7.27 (t, J = 7.68 Hz, 1 H, ArH), 7.40 (d, J = 7.86 Hz, 1 H, ArH), 7.60–7.70 (m, 2 H, ArH), 7.73 (d, J = 7.86 Hz, 1 H, ArH), 7.96–8.00 (m, 1 H, ArH), 8.18–8.21 (m, 1 H, ArH), 8.37 (d, J = 8.04 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 30.1 (3×CH_3), 33.4 (C), 122.2 (q, $J_{F,C}$ = 3.84 Hz, CH), 122.9 (q, J = 272.4 Hz, CF_3), 123.6, 125.3 (q, J = 3.8 Hz), 125.6, 126.3, 126.5, 126.7, 128.0 (CH), 128.7, 129.1, 130.4, 131.7 (C), 131.9 (CH), 132.6 (C), 132.7, 133.2 (CH), 133.7 (C), 134.2 (CH), 135.2, 139.6 (d, J = 9.8 Hz), 148.3, 149.4 (C), 182.0, 182.6 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.68 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2957, 2907, 2872, 2134 (w), 1671 (s), 1589, 1574, 1549, 1513, 1479, 1460, 1433, 1407, 1393, 1365 (w), 1329, 1316, 1302 (s), 1279 (m), 1258, 1245 (s), 1211, 1183 (w), 1159, 1116, 1100, 1068 (s), 1017 (m), 1001, 986, 973 (w), 961 (m), 917, 892 (w), 861, 838 (m), 824, 801 (s), 792 (m), 768, 751, 744 (w), 715, 702 (s), 688 (w), 679, 666, 652 (m), 628 (w), 580, 566, 545 (m) $\mathrm{cm^{-1}}$. GC-MS (EI, 70 eV): *m*/*z* (%) = 484 (43) [M$^+$], 470 (33), 469 (100). HRMS (EI, 70 eV): calcd. for $C_{31}H_{23}O_2F_3$ [M]$^+$ 484.16447; found 484.164011.

1,2,4-Tris[(trifluoromethyl)sulfonyloxy]anthraquinone (8): To a solution of **7** (1.0 equiv.) in CH_2Cl_2 (10 mL/mmol), was added pyridine (7.0 equiv.) at room temperature under an argon atmosphere. After 10 min, Tf_2O (5.0 equiv.) was added at –78 °C and the mixture was warmed to room temperature and stirred overnight. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The products of the reaction mixture were isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc).

1,2,4-Tris[(trifluoromethyl)sulfonyloxy]anthraquinone (8): Starting with 1,2,4-trihydroxyanthraquinone **7** (1.00 g, 3.90 mmol), pyridine (2.2 mL, 27.3 mmol), CH_2Cl_2 (40 mL), Tf_2O (3.3 mL, 19.5 mmol), **8** was isolated as a yellow solid (1.10 g, 43%); m.p. 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1 H, ArH), 7.80–7.86 (m, 2 H, ArH), 8.22–8.36 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.3 (d, $J_{F,C1}$ = 313.5 Hz, CF_3), 118.4 (d, $J_{F,C}$ = 316.0 Hz, CF_3), 118.6 (d, $J_{F,C}$ = 319.0 Hz, CF_3), 123.3 (CH), 126.8 (C), 127.7, 127.8 (CH), 129.6, 132.5, 132.6 (C), 135.5, 135.6 (CH), 138.9, 144.5, 146.6 (C), 178.4, 179.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.02 (q, J_F = 2.82, 5.28 Hz, 3 F, CF_3), –72.83 (s, 3 F, CF_3), –72.24 (q, J_F = 2.73, 5.07 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3100 (w), 1682 (s), 1589 (m), 1440, 1428 (s), 1310 (m), 1278 (w), 1208, 1182, 1170, 1127 (s), 1071, 1039, 1018 (m), 974 (w), 929, 904, 851, 812, 780, 763 (s), 756, 740 (m), 719 (s), 712, 695, 674 (m), 653, 635 (s), 623 (m), 597, 534 (s) $\mathrm{cm^{-1}}$. GC-MS (EI, 70 eV): *m*/*z* (%) = 652 (100) [M$^+$], 583 (13), 519 (11), 455 (46), 427 (16), 391 (14), 363 (85), 336 (11), 335 (74). HRMS (EI, 70 eV): calcd. for $C_{17}H_5F_9O_{11}S_3$ [M]$^+$ 651.88448; found 651.883916.

General Procedure for Suzuki–Miyaura Reactions: A 1,4-dioxane solution (4 mL per 3 mmol of **8**) of **8**, K_3PO_4, [Pd(PPh$_3$)$_4$], and arylboronic acid **3**, was stirred at 110 °C or 90 °C for 10 h. After cooling to 20 °C, distilled 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).

1,2,4-Tris[4-(trifluoromethyl)phenyl]anthraquinone (9a): Starting with **8** (100 mg, 0.15 mmol), **3a** (114 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9a** was isolated as a yellow solid (43 mg, 43%); m.p. 237–238 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03–7.12 (m, 4 H, ArH), 7.35–7.47 (m, 6 H, ArH), 7.48 (s, 1 H, ArH), 7.64–7.67 (m, 4 H, ArH), 7.94–8.02 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 123.7 (q, $J_{F,C}$ = 272.3 Hz, CF_3), 124.0 (q, $J_{F,C}$ = 272.1 Hz, CF_3), 124.2 (q, $J_{F,C}$ = 272.1 Hz, CF_3), 124.9 (t, J = 3.5 Hz), 125.0, 125.2 (d, J = 3.8 Hz), 126.8, 127.0, 128.3 (CH), 128.9 (C), 129.4, 129.6 (CH), 129.8, 130.1, 132.1, 133.4, 133.7, 133.9 (C), 134.1, 134.2, 138.0 (CH), 140.8, 142.4, 143.0, 143.1, 145.4, 146.2 (C), 183.2, 183.7 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.77 (s, 3 F, CF_3), –62.41 (s, 3 F, CF_3), –62.38 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3067, 2929, 2581 (w), 1673 (m), 1616, 1592, 1531, 1407, 1372 (w), 1323 (s), 1285, 1251 (m), 1211 (w), 1167, 1108 (s), 1089 (m), 1081, 1060, 1017 (s), 966 (m), 937, 919, 866 (w), 839 (m), 801, 766, 746 (w), 726 (m), 711, 684, 660, 644, 622, 604, 551, 539 (w) $\mathrm{cm^{-1}}$. GC-MS (EI, 70 eV): *m*/*z* (%) = 640 (98) [M$^+$], 639 (100), 638 (13), 621 (15), 572 (28), 571 (81), 570 (36). HRMS (EI, 70 eV): calcd. for $C_{35}H_{16}F_9O_2$ [M – H]$^+$ 639.10011; found 639.099492.

1,2,4-Tris(4-methoxyphenyl)anthraquinone (9b): Starting with **8** (100 mg, 0.15 mmol), **3b** (91 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9b** was isolated as an orange solid (59 mg, 73%); m.p. 240–242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 6.61–6.64 (m, 2 H, ArH), 6.72–6.75 (m, 2 H, ArH), 6.85–6.90 (m, 6 H, ArH), 7.21–7.24 (m, 2 H, ArH), 7.49 (s, 1 H, ArH), 7.58–7.61 (m, 2 H, ArH), 7.93–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.0, 55.1, 55.2 (OCH_3), 113.2, 113.3, 113.6, 126.5, 126.6, 129.3, 130.5, 130.7 (CH), 131.3, 132.1, 132.2 (C), 133.5, 133.6 (CH), 134.0, 134.3, 134.4, 134.5 (C), 138.8 (CH), 141.2, 143.3, 147.5, 158.2, 158.6, 158.9 (C), 184.1, 185.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3318, 3068, 3033, 3012, 2952, 2918, 2849, 2833, 2539 (w), 1665, 1606 (s), 1592, 1575 (m), 1508 (s), 1461, 1454, 1435 (m), 1410, 1368 (w), 1330, 1310 (m), 1289, 1239, 1173 (s), 1107, 1085, 1076 (m), 1027, 1010, 963 (s), 938 (m), 917, 907, 862 (w), 829, 802, 796 (s), 773, 763 (m), 749 (w), 736 (m), 722 (s), 686 (w), 653, 645, 628, 621 (m), 594 (w), 572 (m), 548 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 526 (100) [M$^+$], 525 (40), 495 (15), 285 (12). HRMS (EI, 70 eV): calcd. for $C_{35}H_{26}O_5$ [M]$^+$ 526.17748; found 526.176367.

1,2,4-Tris(4-*tert*-butylphenyl)anthraquinone (9c): Starting with **8** (100 mg, 0.15 mmol), **3c** (107 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9c** was isolated as an orange solid (77 mg, 83%); m.p. 244–246 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.13 (s, 9 H, 3×CH$_3$), 1.20 (s, 9 H, 3×CH$_3$), 1.31 (s, 9 H, 3×CH$_3$), 6.75–6.76 (m, 2 H, ArH), 6.84–6.87 (m, 2 H, ArH), 6.99–7.02 (m, 2 H, ArH), 7.12–7.15 (m, 2 H, ArH), 7.21–7.24 (m, 2 H, ArH), 7.36–7.39 (m, 2 H, ArH), 7.53 (s, 1 H, ArH), 7.55–7.58 (m, 2 H, ArH), 7.93–8.03 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 31.2, 31.4, 31.5 (9×CH$_3$), 34.3, 34.4, 34.6, 124.2, 124.4, 125.0, 126.6, 126.8, 127.7, 127.9, 128.6 (C), 129.0 (CH), 131.4 (C), 133.5, 133.5 (CH), 133.6, 134.0, 134.4, 136.8, 137.1 (C), 138.8 (CH), 139.3, 142.0, 143.7, 148.2, 149.1, 149.8 (C), 184.1, 184.6 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2952 (s), 2902, 2864 (m), 1677, 1669 (s), 1607 (w), 1592 (m), 1574, 1512, 1504, 1475 (w), 1462 (m), 1440, 1392 (w), 1360 (m), 1327 (s), 1309, 1301, 1279, 1266 (m), 1241 (s), 1212, 1201, 1165, 1155 (w), 1114, 1081, 1016, 966 (m), 944, 934, 918, 898, 863 (w), 831 (s), 796 (m), 772, 764, 740 (w), 725 (s), 705, 681 (w), 651, 625 (m), 615 (w), 580 (m), 567 (s), 551 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 604 (31) [M$^+$], 590 (11), 589 (24), 548 (14), 547 (33), 532 (03), 490 (04), 287 (11), 69 (06), 57 (100). HRMS (EI, 70 eV): calcd. for $C_{44}H_{44}O_2$ [M]$^+$ 604.33358; found 604. 33345.

1,2,4-Tris(4-chlorophenyl)anthraquinone (9d): Starting with **8** (100 mg, 0.15 mmol), **3d** (94 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9d** was isolated as a yellow solid (50 mg, 60%); m.p. 293–295 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.84–6.92 (m, 4 H, ArH), 7.07–7.11 (m, 2 H, ArH), 7.18–7.23 (m, 4 H, ArH), 7.34–7.38 (m, 2 H, ArH), 7.44 (s, 1 H, ArH), 7.62–7.65 (m, 2 H, ArH), 7.93–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$): δ = 126.7, 126.8, 128.2, 128.2, 128.4, 129.3, 130.5, 130.6 (CH), 131.9, 132.9, 133.5, 133.7, 133.8 (C), 133.9, 134.0 (CH), 134.1, 137.5, 138.0 (C), 138.3 (CH), 141.2, 140.2, 140.7, 142.9, 145.5 (C), 183.8, 184.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3320, 3065, 2923, 2853 (w), 1670 (s), 1650, 1644, 1632 (w), 1591 (m), 1524 (w), 1492 (s), 1470, 1441, 1397, 1370 (w), 1328 (m), 1311 (s), 1282 (m), 1247 (s), 1209, 1158 (w), 1089, 1013, 962 (s), 935, 918, 862 (w), 818 (s), 810, 766 (m), 733 (s), 718 (m), 700, 687, 671, 656 (w), 647 (m), 636, 618, 593 (w), 551 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 542 (2×^{37}Cl, 29) [M$^+$], 541 (^{37}Cl, 50) [M + H$^+$], 540 (^{37}Cl, 92) [M$^+$], 539 (^{35}Cl, 100) [M + H$^+$], 538 (^{35}Cl, 93) [M$^+$], 537 (78), 505 (24), 504 (26), 503 (37), 502 (25). HRMS (EI, 70 eV): calcd. for $C_{32}H_{17}Cl_3O_2$ ([M]$^+$, ^{37}Cl) 540.02591; found 540.024908, $C_{32}H_{17}Cl_3O_2$ ([M]$^+$, 2×^{37}Cl): 542.02296; found 542.023142.

1,2,4-Tris(4-fluorophenyl)anthraquinone (9e): Starting with **8** (100 mg, 0.15 mmol), **3i** (84 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9e** was isolated as orange crystals (43 mg, 57%); m.p. 204–206 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.77–6.83 (m, 2 H, ArH), 6.86–6.93 (m, 6 H, ArH), 7.04–7.11 (m, 2 H, ArH), 7.23–7.27 (m, 2 H, ArH), 7.47 (s, 1 H, ArH), 7.61–7.64 (m, 2 H, ArH), 7.93–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 114.7, 114.8, 115.0, 115.1, 115.2, 115.3, 126.6, 126.8, 129.6, 129.7, 130.7, 130.8, 131.0, 131.1 (CH), 131.8, 133.8 (C), 133.8, 133.9 (CH), 133.9, 134.2, 135.2 (d, *J* = 3.3 Hz), 135.5 (d, *J* = 3.6 Hz), 137.7 (d, *J* = 3.6 Hz, 1 C), 138.5 (CH), 140.9, 143.0, 146.9, 161.7 (d, $J_{F,C}$ = 246.4 Hz), 161.9 (d, $J_{F,C}$ = 248.0 Hz), 162.2 (d, $J_{F,C}$ = 246.6 Hz, CF), 183.7, 184.3 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –115.07 (s, 1 F, CF), –114.85 (s, 1 F, CF), –114.14 (s, 1 F, CF) ppm. IR (KBr): $\tilde{\nu}$ = 3069, 3041, 2920, 2852 (w), 1673 (s), 1604 (w), 1592 (m), 1530 (w), 1510 (s), 1442, 1402, 1370 (w), 1328, 1308 (m), 1278 (w), 1245 (m), 1222, 1157 (s), 1092, 1083, 1073, 1014 (w), 963 (m), 945, 927, 866 (w), 829, 817 (s), 804 (m), 786, 766, 745 (w), 734, 721 (m), 709, 701, 686, 658, 650, 642, 624, 617, 587, 560 (w), 551 (m), 534 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 490 (83) [M$^+$], 489 (100), 488 (18), 394 (18). HRMS (EI, 70 eV): calcd. for $C_{32}H_{17}O_2F_3$ [M$^+$] 490.11752; found 490.116052.

1,2,4-Triphenylanthraquinone (9f): Starting with **8** (100 mg, 0.15 mmol), **3k** (73 mg, 0.6 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (159 mg, 0.75 mmol), and 1,4-dioxane (5 mL), **9f** was isolated as a yellow solid (58 mg, 86%); m.p. 228–230 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.92–7.00 (m, 4 H, ArH), 7.06 (t, *J* = 2.61 Hz, 3 H, ArH), 7.16–7.18 (m, 3 H, ArH), 7.28–7.38 (m, 5 H, ArH), 7.52 (s, 1 H, ArH), 7.57–7.60 (m, 2 H, ArH), 7.93–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 126.5, 126.6, 126.8, 127.1, 127.2, 127.6, 127.7, 128.0, 128, 129.3, 129.4 (CH), 131.6 (C), 133.6, 133.7 (CH), 133.8, 133.9, 134.4 (C), 138.6 (CH), 139.6, 139.9, 141.8, 142.2, 143.8, 147.7 (C), 183.8, 184.5 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3329, 3065, 3054, 3022, 2953, 2919, 2850 (w), 1677 (s), 1633 (w), 1590 (m), 1557, 1537, 1524, 1494, 1455, 1443, 1431, 1370 (w), 1322, 1302 (s), 1277 (m), 1243 (s), 1206, 1160 (w), 1085, 1077, 1071 (m), 1034 (w), 1024 (m), 1001, 975 (w), 959 (m), 938, 915, 899, 857, 842, 825 (w), 801, 774, 760, 750, 742 (m), 728 (s), 711 (m), 691 (s), 671 (m), 652 (s), 637, 614, 570 (m), 554 (w), 541 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 436 (78) [M$^+$], 435 (100), 434 (18), 358 (19), 218 (19), 217 (44). HRMS (EI, 70 eV): calcd. for $C_{32}H_{19}O_2$ [M – H]$^+$ 435.13796; found 435.137591.

1,4-Bis[4-(trifluoromethyl)phenyl]-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (10a): Starting with **8** (100 mg, 0.15 mmol), **3a** (57 mg, 0.3 mmol), [Pd(PPh$_3$)$_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (96 mg, 0.45 mmol), and 1,4-dioxane (4 mL), **10a** was isolated as an orange solid (61 mg, 61%); m.p. 168–170 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.32–7.40 (m, 4 H, ArH), 7.48 (s, 1 H, ArH), 7.66–7.72 (m, 6 H, ArH), 7.94–8.00 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 118.0 (q, $J_{F,C}$ = 320.4 Hz, CF$_3$), 119.7 (q, $J_{F,C}$ = 272.2 Hz, CF$_3$), 125.4 (t, *J* = 3.8 Hz), 127.0, 127.1, 128.1 (CH), 128.5 (q, $J_{F,C}$ = 286.2 Hz, CF$_3$), 128.9, 129.2 (CH), 129.9, 130.2, 130.4, 132.2, 133.2, 133.3 (C), 134.5, 134.6 (CH), 135.3, 135.7, 137.7, 143.9, 145.6, 149.6 (C), 182.2, 182.2 (CO) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –73.86 (s, 3 F, CF$_3$), –62.59 (s, 3 F, CF$_3$), –62.51 (s, 3 F, CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2917 (w), 1675 (m), 1618, 1591, 1541, 1428, 1408 (w), 1321 (s), 1241 (m), 1217 (s), 1190 (w), 1163 (m), 1122, 1108, 1080, 1059 (s), 1040 (w), 1017, 948, 900 (m), 854 (w), 834, 823, 799, 786, 763, 753, 744 (s), 731 (m), 713, 692, 682, 662, 641, 630 (w), 599 (s), 571, 535 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 644 (100) [M$^+$], 643 (68), 625 (11), 576 (14), 575 (48), 512 (21), 511 (56), 510 (29), 509 (13). HRMS (EI, 70 eV): calcd. for $C_{29}H_{13}F_9O_5S$ [M]$^+$ 644.03345; found 644.03239.

1,4-Bis(4-*tert*-butylphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (10b): Starting with **8** (100 mg, 0.15 mmol), **3c** (54 mg, 0.3 mmol), [Pd(PPh$_3$)$_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (96 mg, 0.45 mmol), and 1,4-dioxane (4 mL), **10b** was isolated as a yellow solid (77 mg, 81%); m.p. 245–247 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.59 (s, 9 H, 3×CH$_3$), 0.60 (s, 9 H, 3×CH$_3$), 6.37–

6.40 (m, 2 H, ArH), 6.46–6.48 (m, 2 H, ArH), 6.68–6.74 (m, 4 H, ArH), 6.74 (s, 1 H, ArH), 6.86–6.90 (m, 2 H, ArH), 7.21–7.27 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.3, 31.4 (6×CH_3), 34.7, 34.8 (C), 117.5 (q, $J_{F,C}$ = 318.5 Hz, CF_3), 125.2, 125.3, 126.8, 127.0, 127.6, 128.3, 129.5 (CH), 130.8, 132.3, 133.7, 133.8 (C), 133.9, 134.0 (CH), 135.5, 136.5, 137.5, 146.5, 150.1, 150.8, 151.0 (C), 182.8, 182.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.69 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2965 (m), 2867 (w), 1677 (s), 1590, 1536, 1531, 1513, 1462 (w), 1425 (s), 1404, 1360 (w), 1319 (s), 1268 (m), 1239, 1214 (s), 1177 (m), 1159 (w), 1137, 1115 (s), 1040, 1015, 1004, 977, 966 (w), 947, 900, 844, 825, 812, 803 (s), 776 (w), 746 (m), 732, 722 (s), 699 (w), 686 (m), 661 (w), 642 (m), 608 (s), 597 (m), 566 (s), 528 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 620 (06) [M^+], 606 (13), 605 (34), 565 (10), 564 (32), 563 (100), 571 (09), 457 (10). HRMS (EI, 70 eV): calcd. for $C_{35}H_{31}F_3O_5S$ $[M]^+$ 620.18388; found 620.183785.

1,4-Bis(4-methyllphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (10c): Starting with **8** (100 mg, 0.15 mmol), **3e** (41 mg, 0.3 mmol), [$Pd(PPh_3)_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (96 mg, 0.45 mmol), and 1,4-dioxane (4 mL), **10c** was isolated as a yellow solid (42 mg, 51%); m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 7.07–7.10 (m, 2 H, ArH), 7.14–7.17 (m, 2 H, ArH), 7.22–7.26 (m, 4 H, ArH), 7.46 (s, 1 H, ArH), 7.59–7.66 (m, 2 H, ArH), 7.94–7.98 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.4, 21.5 (CH_3), 118.1 (q, $J_{F,C}$ = 320.7 Hz, CF_3), 126.9, 127.0, 127.8, 128.5, 129.1, 129.2, 129.3 (CH), 130.8, 132.4, 133.7, 133.8 (C), 134.0, 134.1 (CH), 135.5, 136.7, 137.6, 137.8, 137.9, 146.5, 150.1 (C), 182.8, 182.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.96 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3022, 2960, 2920, 2860 (w), 1675 (s), 1651, 1592, 1538, 1515, 1446 (w), 1420 (s), 1403, 1379 (w), 1312 (m), 1272, 1261 (w), 1239 (m), 1220, 1205 (s), 1161 (w), 1131 (s), 1037, 1019, 1005, 962 (w), 946, 896 (s), 848 (m), 829, 819, 810, 798 (s), 769 (w), 752 (m), 729 (s), 715 (m), 689, 659, 650, 631 (w), 599 (s), 570, 558, 538, 530 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 536 (85) [M^+], 535 (23), 523 (10), 522 (26), 521 (100), 404 (10), 403 (48), 402 (33), 401 (20), 389 (18), 388 (77), 387 (61), 386 (27). HRMS (EI, 70 eV): calcd. for $C_{29}H_{19}F_3O_5S$ $[M]^+$ 536.08998; found 536.090080.

1,4-Bis(4-ethyllphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (10d): Starting with **8** (100 mg, 0.15 mmol), **3f** (45 mg, 0.3 mmol), [$Pd(PPh_3)_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (96 mg, 0.45 mmol), and 1,4-dioxane (4 mL), **10d** was isolated as a yellow solid (64 mg, 74%); m.p. 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.62 Hz, 3 H, CH_3), 1.26 (t, J = 7.60 Hz, 3 H, CH_3), 2.70 (q, J = 15.18, 7.59 Hz, 4 H, 2×CH_2), 7.08–7.12 (m, 2 H, ArH), 7.17–7.20 (m, 2 H, ArH), 7.24–7.28 (m, 4 H, ArH), 7.47 (s, 1 H, ArH), 7.60–7.63 (m, 2 H, ArH), 7.94–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.2, 15.3 (CH_3), 28.6, 28.7 (CH_2), 118.1 (q, $J_{F,C}$ = 320.1 Hz, CF_3), 126.9, 127.0, 127.8, 127.9, 128.2, 128.5, 129.4 (CH), 131.0, 132.4, 133.7, 133.8 (C), 134.0, 134.1 (CH), 135.5, 136.7, 137.8, 143.9, 144.2, 146.6, 150.1 (C), 182.8, 182.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.01 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3024, 2962, 2932, 2874 (w), 1677 (s), 1641, 1610, 1591, 1536, 1514, 1460 (w), 1427 (s), 1410, 1373 (w), 1320, 1311 (m), 1260 (w), 1206 (s), 1173, 1160 (w), 1133 (s), 1050, 1038 (w), 1018 (m), 1005, 977 (w), 946, 899 (s), 846 (m), 823, 802 (s), 766 (w), 752 (m), 729 (s), 703, 688, 663, 642 (m), 631 (w), 599, 569 (s), 541 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 564 (43) [M^+], 563 (11), 537 (11), 536 (32), 535 (100), 403 (17), 402 (50), 401 (28), 387 (16), 386 (11), 374 (25), 373 (86). HRMS (EI, 70 eV): calcd. for $C_{31}H_{23}F_3O_5S$ $[M]^+$ 564.12128; found 564.121848.

1,4-Bis(3,5-dimethylphenyl)-2-[(trifluoromethyl)sulfonyloxy]anthraquinone (10e): Starting with **8** (100 mg, 0.15 mmol), **3l** (45 mg, 0.3 mmol), [$Pd(PPh_3)_4$] (10 mg, 6 mol-%, 0.009 mmol), K_3PO_4 (96 mg, 0.45 mmol), and 1,4-dioxane (4 mL), **10e** was isolated as a yellow solid (52 mg, 60%); m.p. 211–213 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6 H, 2×CH_3), 2.32 (s, 6 H, 2×CH_3), 6.79 (br. m, 2 H, ArH), 6.86 (br. m, 2 H, ArH), 7.03 (br. m, 2 H, ArH), 7.44 (s, 1 H, ArH), 7.61–7.64 (m, 2 H, ArH), 7.96–7.99 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.4, 21.4 (4×CH_3), 118.1 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 125.5, 126.2, 126.9, 127.0, 129.1, 129.6, 129.8 (CH), 132.2, 133.7, 133.7, 133.8 (C), 134.0, 134.1 (CH), 135.3, 136.8, 137.7, 137.9, 140.5, 146.7, 149.9 (C), 182.7, 182.8 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.51 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3005, 2916, 2861 (w), 1674 (s), 1593, 1537, 1442, 1427 (w), 1405 (m), 1371 (w), 1331, 1294 (m), 1267 (w), 1240 (m), 1206 (s), 1173, 1162 (m), 1134, 1026, 1010 (s), 968 (m), 920, 898, 883 (w), 848, 814, 796 (s), 771, 752 (w), 729, 723 (s), 708 (w), 692, 648, 631, 604 (s), 570, 552, 530 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 564 (66) [M^+], 550 (22), 549 (80), 432 (14), 431 (49), 430 (21), 417 (34), 416 (86), 415 (36), 402 (16), 401 (57), 387 (14), 215 (14), 208 (100), 207 (15). HRMS (EI, 70 eV): calcd. for $C_{31}H_{23}F_3O_5S$ $[M]^+$ 564.12128; found 564.122443.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(4-methoxyphenyl)anthraquinone (11a): Starting with **8** (100 mg, 0.15 mmol), **3b** (23 mg, 0.15 mmol), [$Pd(PPh_3)_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11a** was isolated as a red solid (36 mg, 38%); m.p. 87–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 6.91–6.93 (m, 1 H, ArH), 6.94–6.96 (m, 1 H, ArH), 7.13–7.14 (m, 1 H, ArH), 7.16–7.18 (m, 1 H, ArH), 7.59 (s, 1 H, ArH), 7.69–7.78 (m, 2 H, ArH), 7.99–8.01 (m, 1 H, ArH), 8.21–8.24 (m, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.0 (CH), 115.9 (q, $J_{F,C}$ = 318.4 Hz, CF_3), 121.0 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 127.2, 127.4, 129.2 (CH), 129.3 (C), 131.1 (CH), 131.2, 131.9, 132.9, 133.4 (C), 134.5, 135.0 (CH), 138.1, 143.1, 146.2, 159.9 (C), 181.1, 181.4 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.33 (q, J_F = 5.33, 2.45 Hz, 3 F, CF_3), –72.56 (q, J_F = 5.70, 2.79 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2916, 2840 (w), 1680 (s), 1607, 1593, 1579, 1513 (w), 1432 (s), 1323 (m), 1303 (w), 1243, 1204, 1177, 1168, 1126 (s), 1044, 1030 (m), 1013, 996 (s), 905 (w), 865, 830, 805, 784, 760, 723 (s), 684, 654, 644, 622 (m), 593, 579 (s), 534 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 610 (100) [M + H^+], 479 (10), 478 (27), 477 (82), 385 (10), 346 (12), 345 (24), 317 (28), 316 (93), 315 (10). HRMS (EI, 70 eV): calcd. for $C_{23}H_{12}F_6O_9S_2$ $[M]^+$ 609.98214; found 609.981630.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(4-*tert*-butylphenyl)anthraquinone (11b): Starting with **8** (100 mg, 0.15 mmol), **3c** (27 mg, 0.15 mmol), [$Pd(PPh_3)_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11b** was isolated as a yellow solid (40 mg, 41%); m.p. 80–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 9 H, 3×CH_3), 7.13–7.17 (m, 2 H, ArH), 7.41–7.44 (m, 2 H, ArH), 7.60 (s, 1 H, ArH), 7.69–7.78 (m, 2 H, ArH), 7.99–8.02 (m, 1 H, ArH), 8.22–8.25 (m, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.31 (3×CH_3), 33.75 (C), 115.0 (q, $J_{F,C}$ = 319.4 Hz, CF_3), 120.0 (q, $J_{F,C}$ = 321.7 Hz, CF_3), 124.5, 126.2, 126.4, 126.5 (CH), 128.2 (C), 130.2 (CH), 131.0, 132.0, 132.4 (C), 133.5, 134.0 (CH), 135.1, 137.2, 142.1, 145.5, 150.5 (C), 180.1, 180.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = 73.32 (q, J_F = 5.31, 2.52 Hz, 3 F, CF_3), –72.56 (q, J_F = 6.09, 2.97 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2963 (m), 2870 (w), 1684 (s), 1594, 1577 (w), 1436 (s), 1364 (w), 1325 (m), 1303 (w), 1245, 1218 (s), 1169 (w), 1135 (s), 1105, 1045, 1018, 1000, 906 (w), 870 (m), 839 (w), 806 (m), 783, 763, 727, 703, 685, 655, 644, 624 (w), 598 (m), 575

(w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 636 (53) [M$^+$], 623 (12), 622 (27), 621 (90), 581 (14), 580 (27), 579 (100), 447 (26). HRMS (EI, 70 eV): calcd. for $C_{26}H_{18}F_6O_8S_2$ [M]$^+$ 636.03418; found 636.033895.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(4-methylphenyl)anthraquinone (11c): Starting with **8** (100 mg, 0.15 mmol), **3e** (20 mg, 0.15 mmol), [Pd(PPh$_3$)$_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11c** was isolated as a yellow solid (56 mg, 61%); m.p. 79–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 7.09–7.11 (m, 2 H, ArH), 7.20–7.23 (m, 2 H, ArH), 7.58 (s, 1 H, ArH), 7.67–7.76 (m, 2 H, ArH), 7.97–8.00 (m, 1 H, ArH), 8.20–8.23 (m, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.36 (CH_3), 113.4 (q, $J_{F,C}$ = 318.8 Hz, CF_3), 123.6 (q, $J_{F,C}$ = 319.1 Hz, CF_3), 127.2, 127.4, 127.6 (CH), 128.3 (C), 129.3, 131.1 (CH), 132.0, 132.9, 133.4 (C), 134.6, 135.0 (CH), 136.2, 138.3, 138.4, 143.1, 146.5 (C), 181.1, 181.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.33 (q, J_F = 5.13, 2.34 Hz, 3 F, CF_3), –72.58 (d, J_F = 2.88 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3070, 3027, 2924, 2871 (w), 1680 (s), 1593, 1578, 1513 (w), 1432 (s), 1322 (m), 1303 (w), 1243 (m), 1203 (s), 1168 (m), 1126 (s), 1044, 1021, 1015 (w), 998 (m), 946, 905 (w), 865, 818, 805 (s), 783, 760 (m), 723 (s), 708, 684, 645, 627 (w), 593, 576 (s), 532 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 594 (17) [M + H$^+$], 579 (14), 461 (19), 369 (10), 330 (19), 329 (32), 316 (10), 315 (45), 301 (19), 300 (31), 215 (31), 64 (100), 48 (58). HRMS (EI, 70 eV): calcd. for $C_{23}H_{12}F_6O_8S_2$ [M]$^+$ 593.98723; found 593.985244.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(4-ethylphenyl)anthraquinone (11d): Starting with **8** (100 mg, 0.15 mmol), **3f** (22 mg, 0.15 mmol), [Pd(PPh$_3$)$_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11d** was isolated as an orange solid (61 mg, 65%); m.p. 101–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.65 Hz, CH_3), 2.69 (q, *J* = 14.94, 7.62 Hz, 2 H, CH_2), 7.12–7.15 (m, 2 H, ArH), 7.24–7.26 (m, 2 H, ArH), 7.59 (s, 1 H, ArH), 7.68–7.77 (m, 2 H, ArH), 7.98–8.01 (m, 1 H, ArH), 8.21–8.24 (m, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.2 (CH_3), 28.6 (CH_2), 113.2 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 121.7 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 126.2, 126.4, 126.7, 127.0 (CH), 128.2, 130.1 (C), 131.0 (CH), 131.9, 132.4 (C), 133.5, 134.0 (CH), 135.4, 137.3, 142.1, 143.6, 145.5 (C), 180.1, 180.3 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.32 (q, J_F = 5.31, 2.76 Hz, 3 F, CF_3), –72.56 (q, $J_{C,F}$ = 6.09, 2.94 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3075, 3027, 2965, 2931, 2874 (w), 1681 (s), 1611, 1593, 1577, 1512 (w), 1433 (s), 1323 (m), 1303 (w), 1243 (m), 1205 (s), 1168 (m), 1128 (s), 1044 (w), 1015, 998 (m), 905 (w), 865 (s), 826 (m), 803 (s), 783, 760, 754 (m), 723 (s), 684, 654, 645, 626 (w), 594 (s), 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 608 (32) [M$^+$], 581 (11), 580 (20), 579 (85), 475 (14), 447 (14), 383 (12), 382 (12), 354 (25), 344 (13), 343 (23), 316 (18), 315 (100), 314 (36), 313 (14) cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{24}H_{14}F_6O_8S_2$ [M]$^+$ 608.00288; found 608.003921.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(3-trifluoromethylphenyl)anthraquinone (11e): Starting with **8** (100 mg, 0.15 mmol), **3g** (28 mg, 0.15 mmol), [Pd(PPh$_3$)$_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11e** was isolated as yellow crystals (40 mg, 40%); m.p. 169–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.71 Hz, 1 H, ArH), 7.47 (b, 1 H, ArH), 7.54 (d, *J* = 7.80 Hz 1 H, ArH), 7.59 (s, 1 H, ArH), 7.68–7.71 (m, 1 H, ArH), 7.73–7.81 (m, 2 H, ArH), 7.97–8.00 (m, 1 H, ArH), 8.23–8.26 (m, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 117.5 (q, $J_{F,C}$ = 321.3 Hz, CF_3), 121.2 (q, $J_{F,C}$ = 272.3 Hz, CF_3), 123.5 (d, *J* = 3.8 Hz), 124.2 (d, *J* = 3.7 Hz), 126.3, 126.6 (CH), 127.3 (q, $J_{F,C}$ = 265.5 Hz, CF_3), 128.0 (CH), 128.4 (C), 129.8 (d, *J* = 5.1 Hz), 129.9, 130.3, 131.0 (C), 131.9, 132.0, 133.9, 134.2 (CH), 138.0, 138.8, 142.4, 143.3 (C), 179.8, 179.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.25 (q, J_F = 5.78, 2.84 Hz, 3 F, CF_3), –72.48 (q, J_F = 5.16, 2.25 Hz, 3 F, CF_3), –62.59 (s, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2852 (w), 1690 (m), 1676 (s), 1612, 1593, 1578, 1570, 1489 (w), 1446, 1429 (s), 1412 (m), 1389, 1334 (w), 1306, 1242, 1208, 1180, 1163, 1118, 1049, 1071, 1046, 1007 (s), 927, 909 (w), 879, 841 (s), 828 (m), 811, 802, 782 (s), 773 (w), 759, 741, 724, 717, 701, 680 (s), 657, 650, 624 (m), 603, 591, 571 (s), 530 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 647 (17) [M$^+$], 579 (10), 516 (15), 515 (49), 451 (29), 424 (25), 423 (100), 395 (13), 384 (26), 383 (50), 312 (12), 355 (37), 354 (71). HRMS (EI, 70 eV): calcd. for $C_{23}H_9F_9O_8S_2$ [M]$^+$ 647.95896; found 647.958459.

1,2-Bis[(trifluoromethyl)sulfonyloxy]-4-(3-chlorophenyl)anthraquinone (11f): Starting with **8** (100 mg, 0.15 mmol), **3m** (23 mg, 0.15 mmol), [Pd(PPh$_3$)$_4$] (5 mg, 3 mol-%, 0.0045 mmol), K_3PO_4 (48 mg, 0.225 mmol), and 1,4-dioxane (3 mL), **11f** was isolated as yellow crystals (53 mg, 56%); m.p. 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.58 (dt, *J* = 7.17, 1.65 Hz, 1 H, ArH), 6.68–6.70 (m, 1 H, ArH), 6.81–6.90 (m, 2 H, ArH), 7.06 (s, 1 H, ArH), 7.19–7.28 (m, 2 H, ArH), 7.47–7.50 (m, 1 H, ArH), 7.71–7.74 (m, 1 H, ArH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 114.0 (q, $J_{F,C}$ = 316.2 Hz, CF_3), 120.0 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 124.8, 126.3, 126.5, 126.6, 127.5 (CH), 128.3 (C), 128.8, 129.8 (CH), 130.9, 131.9, 132.0 (C), 133.5 (CH), 133.8 (C), 134.1 (CH), 137.8, 139.8, 142.2, 143.5 (C), 179.8, 179.9 (CO) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.90 (q, J_F = 4.99, 2.85 Hz, 3 F, CF_3), –73.11 (q, $J_{F,C}$ = 5.53, 2.99 Hz, 3 F, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3070, 2961 (w), 1680 (s), 1592, 1577 (w), 1433 (s), 1323 (m), 1303 (w), 1244, 1205 (s), 1169 (m), 1127, 1093, 1080 (s), 1045 (m), 1008, 876, 837, 799, 784, 761, 711, 689, 654 (s), 623 (m), 593, 572 (s), 535 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 617 (2 × ^{37}Cl, 07) [M$^+$], 616 (^{37}Cl, 32) [M + H$^+$], 615 (^{37}Cl, 24) [M$^+$], 614 (^{35}Cl, 82) [M + H$^+$], 613 (^{35}Cl, 16) [M$^+$], 579 (15), 483 (12), 482 (12), 481 (29), 446 (16), 382 (18), 355 (18), 354 (100), 350 (12), 349 (20). HRMS (EI, 70 eV): calcd. for $C_{22}H_9ClF_6O_8S_2$ ([M]$^+$, ^{35}Cl) 613.93261; found 613.932573. HRMS (EI, 70 eV): calcd. for $C_{22}H_9ClF_6O_8S_2$ ([M]$^+$, ^{37}Cl) 615.92966; found 615.931303.

General Synthesis of 1,4-Bis(4-*tert*-butylphenyl)-2-(4-chlorophenyl)anthraquinone (12): The reaction was carried out in a pressure tube. To a suspension of **8** (100 mg, 0.15 mmol), $Ar^1B(OH)_2$ (0.3 mmol), and [Pd(PPh$_3$)$_4$] (6 mol-%) in dioxane (4 mL), was added K_3PO_4 (96 mg, 0.45 mmol), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 95 °C under an argon atmosphere for 10 h, then the mixture was cooled to 20 °C. $Ar^2B(OH)_2$ (0.15 mmol), [Pd(PPh$_3$)$_4$] (3 mol-%), K_3PO_4 (48 mg, 0.225 mmol), and dioxane (2 mL) were added and the reaction mixture was heated under an argon atmosphere for 10 h at 110 °C. The mixture was diluted with H_2O and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (flash silica gel, EtOAc/heptanes).

Compound 12a: Starting with **8** (100 mg, 0.15 mmol), **3c** (54 mg, 0.3 mmol), [Pd(PPh$_3$)$_4$] (17 mg, 10 mol-%, 0.015 mmol), K_3PO_4 (143 mg, 0.675 mmol), 1,4-dioxane (5 mL), and **3d** (23 mg, 0.15 mmol), **12a** was isolated as a yellow solid (40 mg, 45%); m.p. 288–290 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, 3 × CH_3), 1.32 (s, 9 H, 3 × CH_3), 6.80–6.83 (m, 2 H, ArH), 6.84–6.88 (m, 2 H, ArH), 6.98–7.01 (m, 2 H, ArH), 7.17–7.24 (m, 4 H, ArH), 7.39–7.41 (m, 2 H, ArH), 7.48 (s, 1 H, ArH), 7.58–7.62 (m, 2 H, ArH), 7.94–8.01 (m, 2 H, ArH) ppm. ^{13}C NMR (62.9 MHz,

$CDCl_3$): δ = 31.3, 31.4 ($6\times CH_3$), 34.5, 34.6 (C), 124.7, 125.1, 126.6, 126.8, 127.6, 127.8 (CH), 128.2 (C), 128.9, 130.7 (CH), 131.8, 133.1 (C), 133.5, 133.6 (CH), 133.9, 134.4, 136.5, 138.2 (C), 138.6 (CH), 139.0, 141.7, 143.8, 146.5, 149.5, 150.0 (C), 183.9, 184.5 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3076, 3025 (w), 2958 (m), 2902, 2865 (w), 1677 (s), 1591 (m), 1523, 1512, 1490, 1471, 1462, 1443, 1423, 1400, 1358 (w), 1329, 1306, 1269, 1248, 1217 (m), 1158, 1137, 1115 (w), 1092 (m), 1039 (w), 1013 (m), 964, 946, 935, 915, 899, 863, 846, 836 (w), 822 (s), 800 (m), 768, 746 (w), 730 (s), 721 (m), 697, 669, 658, 647, 631, 621, 608 (w), 575, 568 (m), 531 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 585 (^{37}Cl, 08) [M + H$^+$], 584 (^{37}Cl, 22) [M$^+$], 583 (^{35}Cl, 22) [M + H$^+$], 582 (^{35}Cl, 46) [M$^+$], 581 (10), 570 (15), 569 (30), 568 (40), 567 (63), 566 (10), 565 (10), 528 (20), 527 (44), 526 (56), 525 (100), 524 (11), 513 (10), 512 (23), 511 (27), 510 (43). HRMS (EI, 70 eV): calcd. for $C_{40}H_{35}ClO_2$ [M]$^+$ 582.23201; found 582.231833.

Supporting Information (see footnote on the first page of this article): Copies of 2D NMR spectra.

Acknowledgments

Financial support by the Deutscher Akademischer Austauschdienst (DAAD) (PhD fellowship to A. M.) is gratefully acknowledged. The authors are grateful to Dr. Dirk Michalik for his valuable support with regard to the 2D NMR experiments.

---

[1] W. Steglich, B. Fugmann, S. Lang-Fugmann (Eds.), *Römpp Lexikon Naturstoffe*, Thieme, Stuttgart, Germany, **1997**. For a review, see: K. Krohn, *Angew. Chem.* **1986**, *98*, 788; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 790.

[2] a) D. Ishiyama, K. Futamata, M. Futamata, O. Kasuya, S. Kamo, *J. Antibiot.* **1998**, *51*, 1069; b) A. A. El-Beih, T. Kawabata, K. Koimaru, T. Ohta, S. Tsukamoto, *Chem. Pharm. Bull.* **2007**, *55*, 1097; c) J. R. Nguemeving, A. G. B. Azebaze, V. Kuete, N. N. E. Carly, V. P. Beng, M. Meyer, A. Blond, B. Bodo, A. E. Nkengfack, *Phytochemistry* **2006**, *67*, 1341; d) M. R. Dhananjeyan, Y. P. Milev, M. A. Kron, M. G. Nair, *J. Med. Chem.* **2005**, *48*, 2822; e) R. Liu, W. Zhu, Y. Zhang, T. Zhu, H. Liu, Y. Fang, Q. Gu, *J. Antibiot.* **2006**, *59*, 362; f) T.-S. Wu, D.-M. Lin, L.-S. Shi, A. G. Damu, P.-C. Kuo, Y.-H. Kuo, *Chem. Pharm. Bull.* **2003**, *51*, 948; g) Z.-M. Feng, J.-S. Jiang, Y.-H. Wang, P.-C. Zhang, *Chem. Pharm. Bull.* **2005**, *53*, 1330; h) K. C. Nicolaou, H. L. Yee, J. L. Piper, C. D. Papageorgiou, *J. Am. Chem. Soc.* **2007**, *129*, 4001; i) A. A. El-Gamal, K. Takeya, H. Itokawa, A. F. Halim, M. M. Amer, *Phytochemistry* **1995**, *40*, 245; j) F. Diaz, H.-B. Chai, Q. Mi, B.-N. Su, J. S. Vigo, J. G. Graham, F. Cabieses, N. R. Farnsworth, G. A. Cordell, J. M. Pezzuto, S. M. Swanson, A. D. Kinghorn, *J. Nat. Prod.* **2004**, *67*, 352; k) L. Vertesy, M. Kurz, E. F. Paulus, D. Schummer, P. Hammann, *J. Antibiot.* **2001**, *54*, 354; l) M.-T. Huang, R. L. Chang, A. W. Wood, H. L. Newmark, J. M. Sayer, H. Yagi, D. M. Jerina, A. H. Conney, *Carcinogenecis* **1985**, *6*, 237; m) J. Schuhmacher, W. Maier-Borst, H. N. Wellman, *J. Nucl. Med.* **1980**, *21*, 983; n) R. W. Winter, K. A. Cornell, L. L. Johnson, L. M. Isabelle, D. J. Hinrichs, M. K. Riscoe, *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1927.

[3] a) Y.-C. Yang, M.-Y. Lim, H.-S. Lee, *J. Agric. Food Chem.* **2003**, *51*, 7629; b) L. Rafaelly, S. Heron, W. Nowik, A. Tchapla, *Dyes Pigm.* **2008**, *77*, 191.

[4] a) J. E. Gautrot, P. Hodge, D. Cupertino, M. Helliwell, *New J. Chem.* **2006**, *30*, 1801–1807; b) H. D. H. Showalter, E. M. Berman, J. L. Johnson, W. E. Hunter, *Tetrahedron Lett.* **1985**, *26*, 157–160; c) N. A. Shcheglova, D. N. Shigorin, N. S. Dokunikhin, *Zh. Fiz. Khim.* **1966**, *40*, 1048–1055 [*Chem. Abstr.* **1966**, *65*, 9958b]; d) N. A. Shcheglova, D. N. Shigorin, N. S. Dokunikhin, *Zh. Fiz. Khim.* **1965**, *39*, 3039–3043 [*Chem. Abstr.* **1965**, *64*, 12058f]; e) D. A. Orser, General Electric Company, Schenectady, USA, N. Y., *US Pat. 3764549*, Oct. 9, **1973** [*Chem. Abstr.* **1973**, *79*, 141431j].

[5] 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.

[6] a) T. T. Dang, T. T. Dang, R. Ahmad, H. Reinke, P. Langer, *Tetrahedron Lett.* **2008**, *49*, 1698; b) T. T. Dang, A. Villinger, P. Langer, *Adv. Synth. Catal.* **2008**, *350*, 2109; c) M. Hussain, T. H. Nguyen, P. Langer, *Tetrahedron Lett.* **2009**, *50*, 3929; d) S.-M. Tengho Toguem, M. Hussain, I. Malik, A. Villinger, P. Langer, *Tetrahedron Lett.* **2009**, *50*, 4962; e) T. T. Dang, T. T. Dang, N. Rasool, A. Villinger, P. Langer, *Adv. Synth. Catal.* **2009**, *351*, 1595; f) I. Ullah, R. A. Khera, M. Hussain, P. Langer, *Tetrahedron Lett.* **2009**, *50*, 4651.

[7] a) M. Nawaz, M. Farooq Ibad, A. Obaid-Ur-Rahman, R. A. Khera, A. Villinger, P. Langer, *Synlett* **2010**, 150; b) M. Nawaz, R. A. Khera, I. Malik, M. F. Ibad, A. Villinger, P. Langer, *Synlett* **2010**, 979; c) A. Obaid-Ur-Rahman, M. Farooq Ibad, M. Nawaz, M. Sher, N. H. Rama, A. Villinger, P. Langer, *Tetrahedron Lett.* **2010**, *51*, 1541.

[8] A. Mahal, A. Villinger, P. Langer, *Synlett* **2010**, 1085.

[9] CCDC-766105 (for **4c**), -766106 (for **5b**), -766107 (for **6a**), -805201 (for **10a**), and -805202 (for **11e**) contain 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.

[10] S. T. Handy, Y. Zhang, *Chem. Commun.* **2006**, 299.

Received: November 7, 2010