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Synthesis of 1,4-diaryl-2-naphthoates based on site-selective Suzuki–Miyaura reactions

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ABSTRACT

The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of phenyl 1,4-dihydroxy-2-naphthoate afforded various 1,4-diaryl-2-naphthoates. The reactions proceeded with very good site-selectivity. Due to electronic reasons, the first attack occurred at the sterically more hindered position C-1.

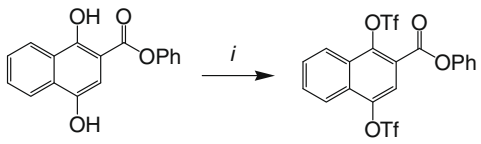
Functionalized naphthalene derivatives are of considerable pharmacological relevance and occur in a number of natural products. This includes, for example, 1,4-dihydroxy-2-naphthoates (e.g., the antitumor agent rhinacanthin N),[1] 4-aryl-2-naphthoates (e.g., eritrichin and globoidnan A),[2] and naphthyl-tetrahydroisoquinolines (e.g., the dioncophyllines C and michellamines) which show a very good activity against malaria or various cancer cell lines.[3]

Site-selective palladium-catalyzed reactions of polyhalogenated substrates are of considerable current interest.[4] The site-selectivity is influenced by electronic and steric parameters.[5] Palladium-catalyzed reactions of aromatic bis(triflates) have been previously reported. In most reactions reported to date there was no issue of site-selectivity.[6] Hosokawa et al. reported a site-selective Sonogashira reaction of a bis(triflate) prepared from a 1,3-dihydroxybenzene derivative.[7] Recently, we have observed that Suzuki–Miyaura (S–M) reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate proceed with very good site-selectivity in favour of position 5 which is presumably a result of steric effects.[8] It occurred to us that the site-selectivity might be different for benzoates and their naphthoate analogues, due to electronic reasons. We chose phenyl 1,4-dihydroxynaphthoate as a commercially available and inexpensive starting material. The latter can be regarded as a benzo-annulated analogue of methyl 2,5-dihydroxybenzoate. Transition metal-catalyzed cross-coupling reactions of this or related naphthoate derivatives (including the corresponding dihalides) have, to the best of our knowledge, not been reported to date. We have found that indeed a change of the site-selectivity is observed and the results of our studies are reported herein.

Phenyl 1,4-dihydroxynaphthoate (**1**) was transformed into the novel bis(triflate) **2** in 83% yield (Scheme 1).[9]

The S-M reaction of **2** with boronic acids **3a–e** (2.4 equiv) afforded the novel 1,4-diaryl-2-naphthoates **4a–e** in 61–85% yields (Scheme 2, Table 1). The best yields were obtained when $Pd(PPh_3)_4$ (3 mol %) was used as the catalyst, when 2.4 equiv of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (110 °C, 8 h) using K_3PO_4 as the base.[10,11] The use of $Pd(OAc)_2$ in the presence of XPhos[12] or SPhos[12] proved to be less efficient in terms of yield. The yields of the products **4a,b**, derived from arylboronic acids containing electron-withdrawing substituents, were higher than the yields of **4d,e** derived from electron-rich boronic acids.

The Suzuki reaction of **2** with boronic acids **3e–i** (1.1 equiv), in the presence of $Pd(PPh_3)_4$ (3 mol %), proceeded with very good site-selectivity at carbon atom C-1 and afforded the 1-aryl-4-(trifluoromethylsulfonyloxy)-2-naphthoates **5a–e** (Scheme 3, Table 2).[10,13] The products were isolated in pure form after chromatography. A small amount of the bis-coupled product could be detected



1 **2** (83%)

Scheme 1. Synthesis of **2**. Reagents and conditions: (i): 1) **1** (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, −78 °C, 10 min; 2) Tf_2O (2.4 equiv), −78 to 0 °C, 4 h.

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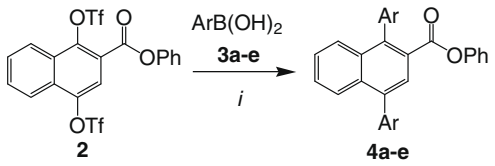
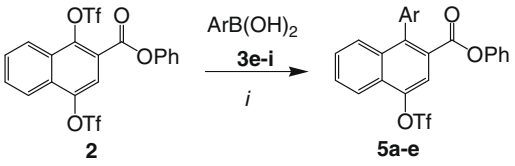


Scheme 2. Synthesis of **4a–e**. Reagents and conditions: (i), **2** (1.0 equiv), **3a–e** (2.4 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 8 h.

Table 1
Synthesis of **4a–e**

3,4	Ar	%[a] (**4**)
a	3-FC_6H_4	85
b	4-$(CF_3)C_6H_4$	80
c	4-MeC_6H_4	76
d	3-$(MeO)C_6H_4$	65
e	2-$(EtO)C_6H_4$	61

[a] Yields of isolated products.



Scheme 3. Synthesis of **5a–e**. Reagents and conditions: (i): **2** (1.0 equiv), **3e–i** (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 95 °C, 8 h.

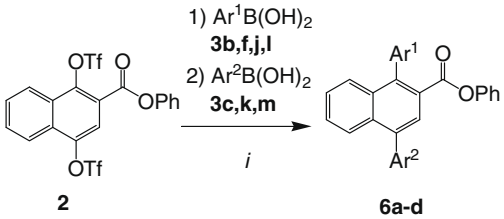
Table 2
Synthesis of **5a–e**

5	3	Ar	%[a] (**5**)
a	**e**	2-$(EtO)C_6H_4$	59
b	**f**	2,4-$(MeO)_2C_6H_3$	66
c	**g**	2,6-$(MeO)_2C_6H_3$	33
d	**h**	4-ClC_6H_4	73
e	**i**	4-*t*BuC_6H_4	71

[a] Yields of isolated products.

by ^1H NMR and GC–MS in the crude material before the purification. All products were isolated in good yields (except for **5c** which is derived from the sterically hindered 2,6-disubstituted arylboronic acid **3g**). During the optimization it proved to be important to employ only a slight excess of the arylboronic acid (1.1 equiv) and to carry out the reaction at 95 °C instead of 110 °C to avoid double coupling.

The one-pot reaction of **2** with two different arylboronic acids, which were sequentially added, afforded the unsymmetrical 1,4-diaryl-2-naphthoates **6a–d** in 51–67% yields (Scheme 4, Table 3).[14,15] During the optimization it proved to be important, for the



Scheme 4. Synthesis of **6a–d**. Reagents and conditions: (1) **2** (1.0 equiv), **3b**,**f**,**j**,**l** (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 95 °C, 7 h; (2) **3c**,**k**,**m** (1.3 equiv), K_3PO_4 (1.5 equiv), 110 °C, 8 h.

Table 3
Synthesis of **6a–d**

6	3	Ar^1	Ar^2	%[a] (**6**)
a	**j**,**k**	4-FC_6H_4	3,4-$(MeO)_2C_6H_3$	54
b	**f**,**c**	2,4-$(MeO)_2C_6H_3$	4-MeC_6H_4	63
c	**b**,**k**	4-$(CF_3)C_6H_4$	3,4-$(MeO)_2C_6H_3$	51
d	**l**,**m**	4-$(H_2C{=}CH)C_6H_4$	4-$(MeO)C_6H_3$	67

[a] Yields of isolated products.

first step of the one-pot protocol, to employ only a slight excess of the arylboronic acid (1.1 equiv) and to carry out the reaction at 95 °C instead of 110 °C.

The structures of all products were proved by 2D NMR experiments (NOESY, HMBC). The structures of **5c** and **6c** were independently confirmed by X-ray crystal structure analyses (Figs. 1 and 2).[16]

The S-M reaction of methyl 2,5-bis(trifluoromethylsulfonyloxy)benzoate **7** occurs first at the sterically less hindered carbon atom C-5. In contrast, naphthoate **2** is first attacked at the sterically more hindered position C-1. This might be explained by electronic effects (Scheme 5). The oxidative addition of the electron-rich palladium species usually occurs first at the most electron deficient carbon atom.[4] In case of **7**, carbon atom C-2 is more electron deficient than C-5, due to its location *ortho* to the ester group. For naphthoate **2**, carbon atom C-1 is also more electron deficient than C-4, but this difference is more pronounced than for benzoate **7**. The nonsubstituted benzene moiety of naphthoate **2** represents a stable 6π aromatic system. In contrast, the aromaticity of the other benzene moiety of **2** is considerably disturbed, because of the presence of the ester and the triflate groups. The aromaticity of the substituted benzene moiety should be more disturbed than the aromaticity of the benzene moiety of **7**. The substituted benzene moiety of **2** might thus be regarded as a cross-conjugated diene

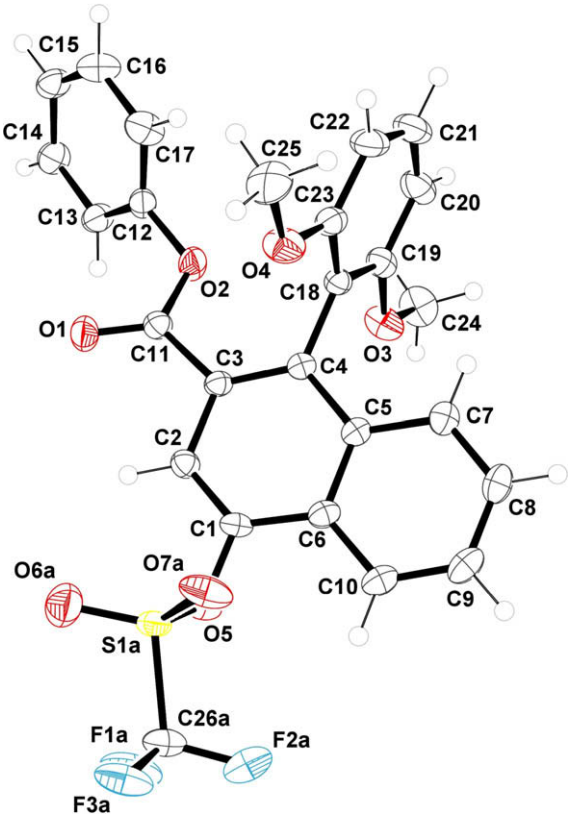


Figure 1. Crystal structure of **5c**.

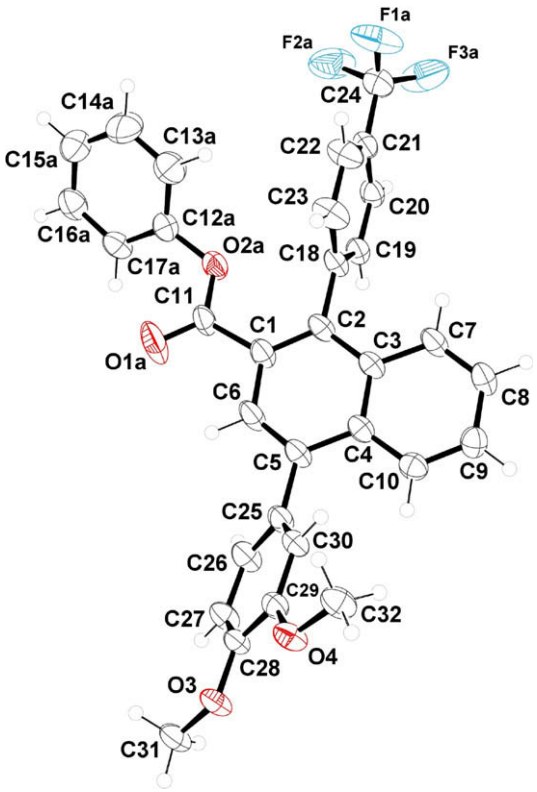
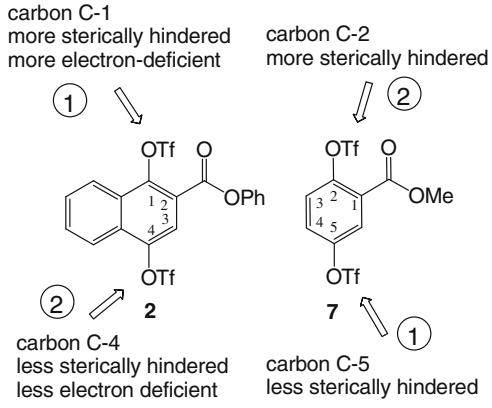
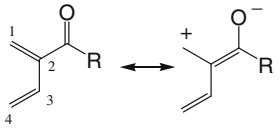


Figure 2. Crystal structure of **6c**.



Scheme 5. Possible explanation for the site-selective reactions of **2**.



Scheme 6. Diene character of **2**.

system (Scheme 6). Due to the π-acceptor effect of the ester group, the nucleophilic attack occurs at carbon atom C-1 of the diene system (conjugate addition).

In conclusion, we have reported site-selective Suzuki–Miyaura reactions of the bis(triflate) of phenyl 1,4-dihydroxynaphthoate. The first attack occurred at the sterically more hindered position C-1.

Acknowledgments

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9. *Phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate (**2**):* To a solution of **1** (1.0 equiv) in CH_2Cl_2 (10 mL per 1 mmol of **1**), was added pyridine (4.0 equiv) at −78 °C under an argon atmosphere. After stirring for 10 min, Tf_2O (2.4 equiv) was added at −78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 h. 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** (2.800 g, 10.0 mmol), pyridine (3.2 mL, 40.0 mmol), **2** was isolated as a white solid (4.515 g, 83%); mp = 100–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.27 (m, 3H, ArH), 7.36–7.41 (m, 2H, ArH), 7.75–7.85 (m, 2H, ArH), 8.08 (s, 1H, ArH), 8.12 (dd, J = 7.1, 1.8 Hz, 1H, ArH), 8.24 (d, J = 7.9 Hz, 1H, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 118.5 (CH), 118.6 (q, $^1J_{CF}$ = 321 Hz, CF_3), 118.7 (q, $^1J_{CF}$ = 321 Hz, CF_3), 121.2 (C), 121.4 (2CH), 121.5 (CH), 123.1 (CH), 126.6 (CH), 127.9 (C), 129.6 (C), 129.7 (2CH), 129.9 (CH), 131.4 (CH), 144.0 (C), 144.2 (C), 150.2 (C), 161.9 (C=O); ^{19}F NMR (282.4 MHz. $CDCl_3$): δ = −72.27 (3F, CF_3), −72.96 (3F, CF_3); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 1733(m), 1589 (w), 1482 (w), 1427 (s), 1358 (m), 1347 (m), 1247 (m), 1203 (s), 1130 (s), 1045 (m), 1018 (m), 936 (m), 873 (s), 761 (s), 641 (s), 597 (s); MS (EI, 70 eV): m/z (%): 544 (M^+, 10), 453 (16), 452 (22), 451 (100), 318 (64), 234 (3), 186 (19), 185 (97), 157 (47), 129 (16), 101 (18), 75 (5), 69 (8), 64 (9), 51 (3); HRMS (EI) calcd for $C_{19}H_{10}O_8F_6S_2$ [M^+]: 543.97158; found 543.97051.
10. *General procedure for Suzuki–Miyaura reactions*: A 1,4-dioxane solution (4 mL per 0.5 mmol of **2**) of **2**, K_3PO_4, $Pd(PPh_3)_4$ and arylboronic acid **3** was stirred at 110 or 95 °C for 8 or 7 h. After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer 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.
11. *Phenyl 1,4-di(p-tolyl)-2-naphthoate (**4c**):* Starting with **2** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **3c** (163 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **4c** was isolated as a colourless solid (163 mg, 76%), mp = 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.70–6.74(m, 2H, ArH), 7.02–7.08 (m, 1H, ArH), 7.15–7.26 (m, 8H, ArH), 7.31–7.43 (m, 4H, ArH), 7.65 (dd, J = 8.1, 1.2 Hz, 1H, ArH), 7.89 (s, 1H, ArH), 7.91 (dd, J = 7.6, 1.2 Hz, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.3 (CH_3), 21.4 (CH_3), 121.5 (2CH), 125.7 (CH), 126.3 (2CH), 126.5 (CH), 127.5 (C), 127.6 (CH), 128.3 (CH), 128.9 (2CH), 129.2 (2CH), 129.3 (2CH), 129.9 (2CH), 130.0 (2CH), 133.2 (C), 133.4 (C), 135.9 (C), 137.0 (C), 137.2 (C), 137.5 (C), 140.2 (C), 141.0 (C), 150.8 (C), 167.1 (C=O). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3022 (w), 2921 (w), 2865 (w), 1711(s), 1591 (w), 1511 (w), 1485 (m), 1378 (m), 1367 (m), 1241 (s), 1220 (s), 1192 (s), 1099 (m), 1020 (m), 926 (m), 814 (s), 746 (s), 687 (m), 595 (m). MS (EI, 70 eV): m/z (%): 428 (M^+, 3), 336 (27), 335 (100), 292 (7), 289 (6), 276 (6), 145 (3), 65 (2). HRMS (EI): calcd for $C_{31}H_{24}O_2$ [M^+]: 428.17708; found 428.17783.

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13. *Phenyl 1-(2,6-dimethoxyphenyl)-4-(trifluoromethylsulfonyloxy)-2-naphthoate* (**5c**)*:* Starting with **2** (272 mg, 0.5 mmol), K_3PO_4 (160 mg, 0.75 mmol), $Pd(PPh_3)_4$ (3 mol %), **3g** (100 mg, 0.55 mmol) and 1,4-dioxane (4 mL), **5c** was isolated as colourless crystals (88 mg, 33%), mp = 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.53 (s, 6H, OCH_3), 6.62 (d, *J* = 8.4 Hz, 2H, ArH), 6.79–6.84(m, 2H, ArH), 7.06–7.12 (m, 1H, ArH), 7.20–7.26 (m, 2H, ArH), 7.33 (t, *J* = 8.26, 1H, ArH), 7.41–7.48 (m, 1H, ArH), 7.55 (d, *J* = 8.1 Hz, 1H, ArH), 7.64 (dt, *J* = 7.8, 1.3 Hz, 1H, ArH), 8.07 (d, *J* = 8.3 Hz, 1H, ArH), 8.08 (s, 1H, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 104.1 (2CH), 114.8 (C), 118.3 (CH), 118.8 (q, $^1J_{CF}$ = 321 Hz, CF_3), 120.9 (CH), 121.3 (2CH), 125.7 (CH), 127.7 (C), 127.9 (CH), 128.0 (CH), 128.2 (C), 129.3 (2CH), 129.5 (CH), 130.1 (CH), 134.3 (C), 137.0 (C), 144.9 (C), 150.7 (C), 157.8 (2C), 164.7 (C=O); IR (ATR, cm^{-1}): $\bar{\nu}$ = 3014 (w), 2937 (w), 2839 (w), 1723 (m), 1589 (w), 1510 (w), 1470 (m), 1413 (m), 1336 (m), 1247 (m), 1192 (s), 1109 (s), 1011 (m), 956 (m), 828 (m), 747 (m), 687 (m), 599 (m). MS (EI, 70 eV): *m*/*z* (%): 532 (M^+, 4), 441 (7), 440 (21), 439 (100), 306 (17), 275 (25), 263 (20), 248 (4), 220 (6) 176 (2), 94 (3), 69 (4), 43 (5). HRMS (EI) calcd for $C_{26}H_{19}O_7F_3S$ [M^+]: 532.07981; found 532.08011.
14. *General procedure for the synthesis of* **6a–d**: The reaction was carried out in a pressure tube. To a dioxane suspension (4 mL) of **2** (272 mg, 0.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and K_3PO_4 (159 mg, 0.75 mmol) was added $Ar^1B(OH)_2$ (0.55 mmol)and the solution was degassed by bubbling argon through the solution for 10 min. The reaction mixture was heated at 95 °C under argon atmosphere for 7 h. The reaction mixture was cooled to 20 °C and $Ar^2B(OH)_2$ (0.65 mmol) and K_3PO_4 (159 mg, 0.75 mmol) were added. The reaction mixture was heated under Argon atmosphere for 8 h at 110 °C. They were diluted with water 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 (silica gel, EtOAc/heptanes).
15. *Phenyl 4-(3,4-dimethoxyphenyl)-1-(4-(trifluoromethyl)phenyl)-2-naphthoate* (**6c**)*:* Starting with **2** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **3b** (104 mg, 0.55 mmol), 1,4-dioxane (4 mL), and **3k** (118 mg, 0.65 mmol), **6c** was isolated as colourless crystals (134 mg, 51%), mp = 163–165 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.70–6.73(m, 2H, ArH), 6.96 (d, *J* = 8.2 Hz, 1H, ArH), 7.01–7.11 (m, 3H, ArH), 7.17–7.24 (m, 2H, ArH), 7.40 (dd, *J* = 7.3, 2.4 Hz, 1H, ArH), 7.44–7.50 (m, 4H, ArH), 7.68–7.71 (m, 2H, ArH), 7.95–7.99 (m, 1H, ArH), 8.0 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 56.0 (OCH_3), 56.1 (OCH_3), 111.3 (CH), 113.3 (CH), 121.2 (2CH), 122.4 (CH), 124.3 (q, $^1J_{CF}$ = 272 Hz, CF_3), 125.2 (q, $^3J_{CF}$ = 3.8 Hz, 2CH), 125.9 (CH), 126.4 (CH), 126.5 (CH), 126.8 (C), 126.9 (CH), 127.8 (CH), 128.1 (CH), 129.4 (2CH), 129.9 (d, $^2J_{CF}$ = 32.5 Hz, C), 130.3 (2CH), 132.3 (C), 132.8 (C), 133.7 (C), 139.7 (C), 140.9 (C), 143.1 (C), 148.9 (C), 149.0 (C), 150.5 (C), 166.2 (C=O). ^{19}F NMR (282.4 MHz. $CDCl_3$): δ = −62.38 (3F, CF_3). IR (ATR, cm^{-1}): $\bar{\nu}$ = 3065 (w), 2966 (w), 2838 (w), 1712 (m), 1597 (w), 1515 (m), 1406 (w), 1320 (m), 1239 (m), 1212 (m), 1159 (s), 1101 (s), 1023 (m), 923 (w), 775 (m), 744 (m), 685 (m), 623 (m), 549 (w). MS (EI, 70 eV): *m*/*z* (%): 528 (M^+, 18), 436 (27), 435 (100), 376 (4), 333 (4), 252 (3), 207 (3), 153 (3), 94 (18), 69 (13), 60 (25), 43 (29). HRMS (EI) calcd for $C_{32}H_{23}O_4F_3$ [M^+]: 528.15430; found 528.15443.
16. CCDC 760147 and 760148 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.