Tetrahedron 68 (2012) 6305–6313

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of aryl-substituted naphthalenes by chemoselective Suzuki–Miyaura reactions of bromo-trifluoromethanesulfonyloxy-naphthalenes. Influence of steric and electronic parameters

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ARTICLE INFO

Article history:
Received 5 February 2012
Received in revised form 23 April 2012
Accepted 7 May 2012
Available online 19 May 2012

Keywords:
Catalysis
Palladium
Tetralone
Suzuki–Miyaura reaction
Naphthalene
Naphthaquinones
Chemoselectivity

ABSTRACT

Chemoselective Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene, 1-bromo-2-(trifluoromethanesulfonyloxy) naphthalene and 2-acetyl-4-bromo-1-(trifluoromethanesulfonyloxy)naphthalene, which are all readily available from the corresponding tetralone derivatives, afforded a variety of mono- and diarylnaphthalenes. The reactions generally proceed with excellent chemoselectivity in favour of the bromide position, no matter whether the bromide is located at position 1 or 2 of the naphthalene or whether the carbon attached to the triflate group is electronically more deficient by the presence of a neighbouring acetyl group.

1. Introduction

Arylated naphthalenes occur in a wide range of pharmacologically active natural products. Examples include the naphthylisoquinolines, such as the michellamines, such as **1** (Chart 1), which exhibit anti-malarial and anti-HIV activity.[1–3] 2-Arylated naphthalenes can be regarded as rigid stilbene derivatives. The rigidity can be advantageous with regard to biological activity. For example, the stilbene resveratrol (**2**) is a natural product, which shows antitumour activity. However, the applicability of the molecule is limited by its chemical and metabolic instability.[4,5] Naphthalene derivatives have been proved very good activity against human breast cancer cell line B with good bioavailability and stability. It has been also reported that aryl-substituted naphthalenes can be efficiently used as fungicides.[6] 1,2-Diphenylnaphthalenes are synthetically available by reaction of α-phenyltetralone with phenyl magnesium bromide and subsequent elimination.[7] An alternative approach to arylated naphthalenes relies on palladium catalyzed cross-coupling reactions of brominated naphthalenes and a number of mono-coupling reactions have been reported.[3] This approach heavily relies on the availability of the starting materials and on the fact that the bromination of naphthalenes usually occurs at

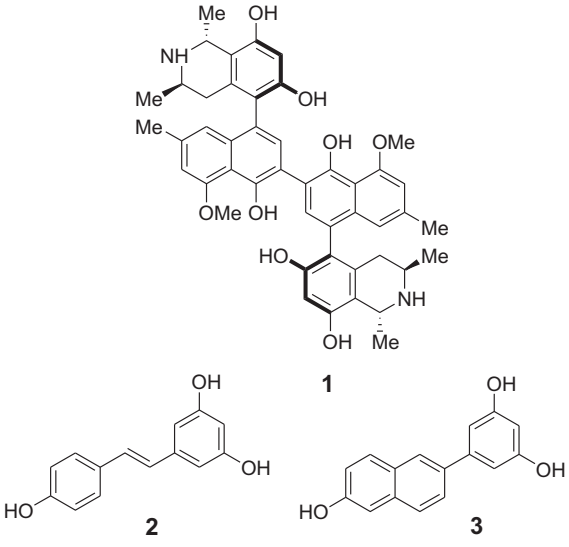

Chart 1. Pharmacologically important naphthalene derivatives.

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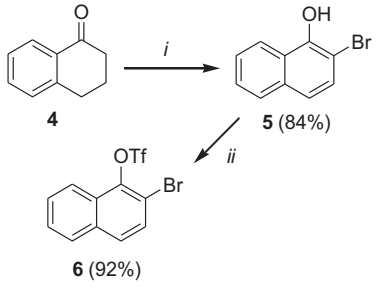
doi:10.1016/j.tet.2012.05.026

position 1. In recent years, site-selective cross-coupling reactions of polyhalogenated substrates have been studied.[8,9] Arenes containing both a bromide and a triflate group represent interesting substrates for chemoselective cross-coupling reactions and it is known that several parameters influence the selectivity of such reactions.[10] It occurred to us that naphthalenes containing both a bromide and a triflate group might be attractive substrates for chemoselective cross-coupling reactions as they are readily available from the corresponding tetralones. Recently, we have reported chemoselective Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene.[11] Herein, we report the extension of our concept to 1-bromo-2-(trifluoromethanesulfonyloxy)naphthalene and to 2-acetyl-4-bromo-1-(trifluoromethanesulfonyloxy)naphthalene. Our results show that the reactions generally proceed with excellent chemoselectivity in favour of the bromide position, no matter whether the bromide is located at position 1 or 2 of the naphthalene or whether the carbon attached to the triflate group is electronically more deficient by the presence of a neighbouring acetyl group. The reactions provide a convenient approach to various arylated naphthalene derivatives, which are not readily available by other methods.

2. Results and discussion

In 2005, Bekaert et al. described[12] the selective synthesis of 2-bromonaphth-1-ol (**5**) by reaction of 1-tetralone (**4**) with *N*-methylpyrrolidin-2-one hydrotribromide (MPHT, $[NMP]_2HBr_3$). We have found an alternative approach to **5**, which is based on the bromination[13] of **4** using NBS (2.2 equiv) and $(PhCOO)_2$ (5 mol %) (Scheme 1). Inexpensive reagents are used and the product is obtained in good yield (84%). The structure of **5** was confirmed by 2D NMR techniques (HMBC and NOESY) (Fig. 1). It is noteworthy that, although free radical conditions were applied, bromination at position 4 was not observed. However, by increasing the amount of NBS to up 4.0 equiv, further bromination was observed at C-4 to give a small amount of 2,4-dibromonaphthalen-1-ol (10%). 2-Bromonaphth-1-ol (**5**) was transformed to its triflate **6** in very good yield 92% (Scheme 2).



Scheme 1. Synthesis of **5** and **6**. Conditions: i, **4** (1.0 equiv), NBS (2.2 equiv), $(PhCOO)_2$ (5 mol %), benzene, reflux, 5 h; ii, **5** (1.0 equiv), Tf_2O (1.2 equiv), pyridine (2.0 equiv), CH_2Cl_2, 20 °C, 12 h.

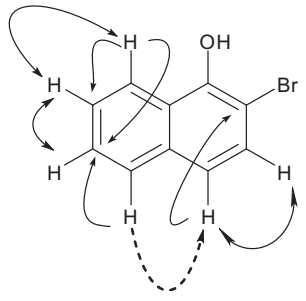
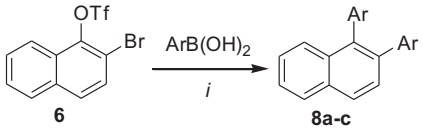


Fig. 1. Important HMBC (single pointed arrow), NOESY (dashed arrow) and COSY (double pointed arrow) correlations of compound **5**.



Scheme 2. Synthesis of **8a**–**c**. Conditions: i, **6** (1.0 equiv), $ArB(OH)_2$ (2.2 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (3.0 equiv), dioxane, 110 °C, 4 h.

The Suzuki–Miyaura reaction[14] of **6** with arylboronic acids **7** (2.2 equiv) provided the 1,2-diarylnaphthalenes **8a**–**c** in 62–94% yield (Scheme 2, Table 1). Both electron-poor and electron-rich arylboronic acids could be successfully employed. Better yields were observed with electron-poor arylboronic acids as compared to electron-rich arylboronic acids. The best yields were obtained using $Pd(PPh_3)_4$ (5 mol %) as the catalyst and K_3PO_4 (3.0 equiv) as the base. 1,4-Dioxane was used as solvent and reactions were carried out at 110 °C.

Table 1
Synthesis of 1,2-diarylnaphthalenes **8a**–**c**

7,8	Ar	% (**8**)[a]
a	2-(MeO)C_6H_4	62
b	4-MeC_6H_4	79
c	4-ClC_6H_4	94

[a] Yields of isolated compounds.

The structures of **8b** and **8c** were confirmed independently by X-ray crystallography (Figs. 2 and 3).[15]

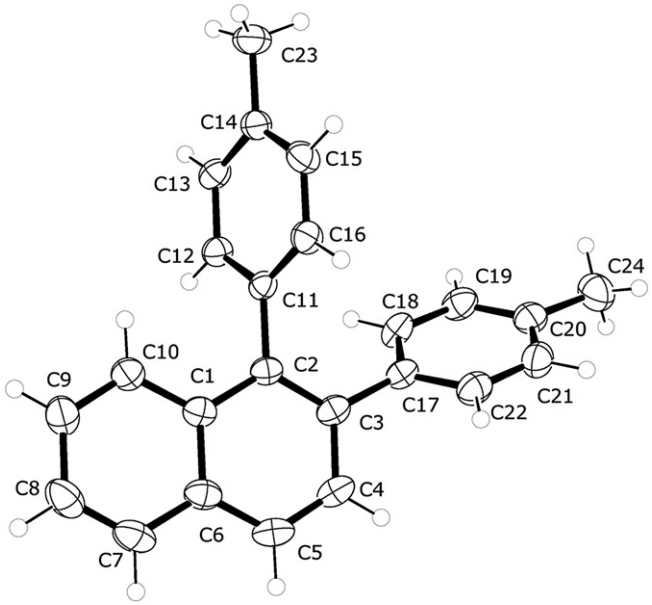


Fig. 2. Crystal structure of **8b**.

The Suzuki–Miyaura reaction of **6** with arylboronic acids **7** (1.0 equiv) afforded the 2-arylnaphth-1-yl-trifluoromethanesulfonates **9a**–**e** in 60–88% yields (Scheme 3, Table 2). The reactions proceeded with very good chemoselectivity in favour of the bromide position, while the triflate remained unattacked. During the optimization, it proved to be important to use exactly equimolar quantities of the arylboronic acid and $Pd(PPh_3)_4$ (5 mol %) as the catalyst. The temperature played an imperative role as well. A good selectivity was attained only when the reaction was carried out at 90 °C (instead of 110 °C) because the reaction of the triflate was slow at this temperature. The reactions were successful for both electron-rich and electron-poor arylboronic acids, but again electron-poor boronic acids provided better yields.

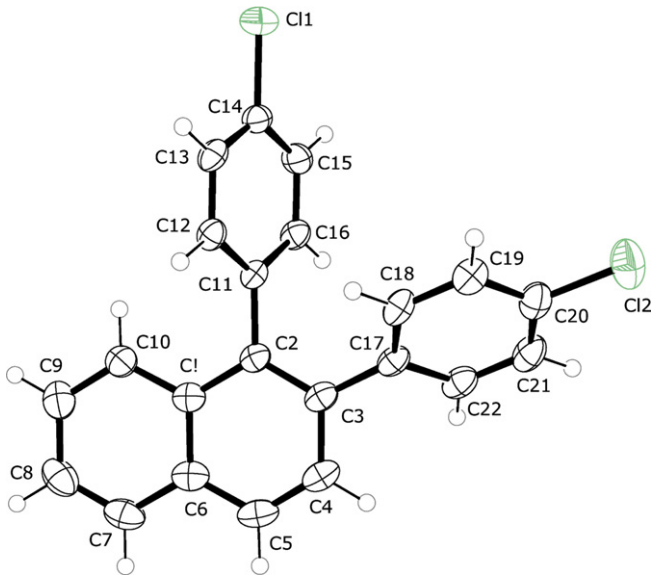
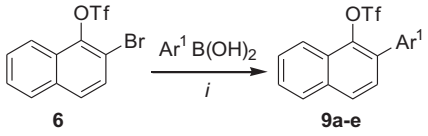


Fig. 3. Crystal structure of **8c**.



Scheme 3. Synthesis of **9a**–**e**. Conditions: i, **6** (1.0 equiv), $Ar^1B(OH)_2$ (1.0 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), dioxane, 90 °C, 4 h.

Table 2
Synthesis of **9a**–**e**

7	9	Ar^1	% (**9**)[a]
a	**a**	2-(MeO)C_6H_4	60
b	**b**	4-MeC_6H_4	73
c	**c**	4-ClC_6H_4	88
d	**d**	C_6H_5	77
e	**e**	4-FC_6H_4	85

[a] Yields of isolated compounds.

The structure of **9e** was independently confirmed by X-ray crystallography (Fig. 4).[15]

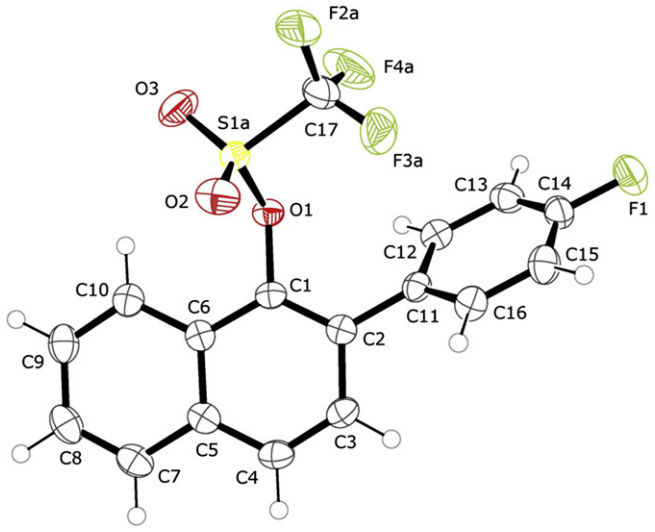
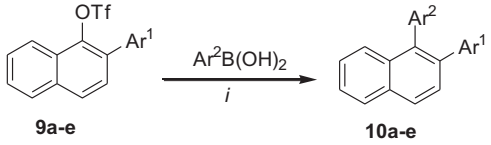


Fig. 4. Molecular structure of **9e**.

The Suzuki–Miyaura reaction of **9a**–**e** with arylboronic acids **7** (1.1 equiv) afforded the 1,2-diarylnaphthalenes **10a**–**e** containing two different aryl groups (Scheme 4, Table 3). The reactions were carried out at 110 °C. The application of a one-pot synthesis of products **10** by sequential addition of two different arylboronic acids to **6** resulted in a decrease of the yield (with respect to the stepwise protocol). Therefore, this strategy was not further studied.



Scheme 4. Synthesis of **10a**–**e**. Conditions: i, **9a**–**e** (1.0 equiv), $Ar^2B(OH)_2$ (1.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), dioxane, 110 °C, 4 h.

Table 3
Synthesis of **10a**–**e**

10	7	9	Ar^1	Ar^2	% (**10**)[a]
a	**j**	**a**	2-(MeO)C_6H_4	4-*t*BuC_6H_4	66
b	**i**	**b**	4-MeC_6H_4	2,5-$(MeO)_2C_6H_3$	65
c	**g**	**c**	4-ClC_6H_4	3,5-$(Me)_2C_6H_3$	72
d	**a**	**d**	C_6H_5	2-(MeO)C_6H_4	69
e	**h**	**e**	4-FC_6H_4	3-(Me)C_6H_4	77

[a] Yields of isolated compounds.

The structure of **10d** was independently confirmed by X-ray crystallography (Fig. 5).[15]

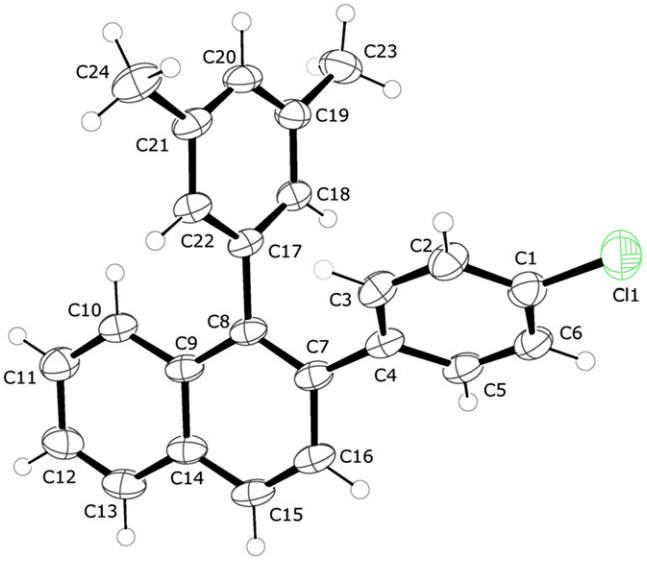
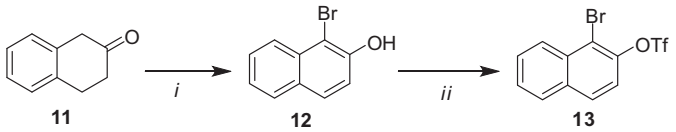


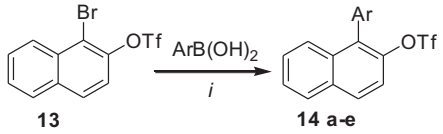
Fig. 5. Molecular structure of **10c**.

Aryl bromides generally undergo Suzuki–Miyaura reactions faster than aryl triflates.[10] This reactivity order is different for other palladium catalyzed cross-coupling reactions. One of the justifications for, that is, based on the high borane-halide affinity. Nevertheless, other parameters control the selectivity as well.[10e] To investigate whether the selectivity for naphthalene **6** is based on the type of leaving group or on steric effects, we decided to study 1-bromonaphthalen-2-yl trifluoromethanesulfonate (**13**), which is an isomer of **6**. Bromination of 2-tetralone (**11**) with NBS (3.0 equiv) afforded the known product **12**.[16] Subsequent reaction with triflic anhydride provided **13** (Scheme 5).

The Suzuki–Miyaura reaction of **13** with arylboronic acids **7** (1.0 equiv) afforded the 1-arylnaphth-2-yl-trifluoromethanesulf onates **14a**–**e** (Scheme 6, Table 4). This proves that the bromine-halide affinity plays the decisive role to control the selectivity of



Scheme 5. Reaction conditions: i, **11** (1.0 equiv), NBS (3.0 equiv), $(PhCOO)_2$ (5 mol %), benzene, reflux, 5 h; ii, (1.0 equiv), Tf_2O (1.2 equiv), pyridine (2.0 equiv), CH_2Cl_2, 20 °C, 6 h.



Scheme 6. Synthesis of **14a**–**e**. Conditions: i, **13** (1.0 equiv), $ArB(OH)_2$ (1.0 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), dioxane, 90 °C, 4 h.

Table 4
Synthesis of **14a**–**e**

7	14	Ar[1]	(**14**) %[a]
b	**a**	4-MeC_6H_4	73
k	**b**	2-(MeO)-5-ClC_6H_4	60
d	**c**	C_6H_5	74
e	**d**	4-FC_6H_4	54
g	**e**	3,5-$(Me)_2C_6H_3$	76

[a] Yields of isolated compounds.

the reactions of compounds **6** and **13**. The steric or electronic difference of positions 1 and 2 of the naphthalene moiety has no influence.

We have previously reported that the Suzuki–Miyaura reaction of phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate **15** (Fig. 6) proceeds regioselectively at position 1, which is more electron deficient, but also more sterically hindered, than position 4.[17] Therefore, we decided to study Suzuki–Miyaura reactions of 2-acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate **19**. In this substrate the reactivity of the triflate group should be enhanced, due to the proximity of the electron-withdrawing acetyl group. 2-Acetyl-3,4-dihydronaphthalen-1(2*H*)-one **16** is a commercially available substrate, which was successfully brominated using NBS (3.0 equiv) and $(PhCOO)_2$ (5 mol %) to give a separable mixture of product **17** (82%) and **18** (11%) (Scheme 7). 1-(4-Bromo-1-hydroxynaphthalen-2-yl)ethanone (**17**) was transformed to its corresponding triflate **19** in high yield 88% (Scheme 7). The structure of **17** was independently confirmed by X-ray crystal structure analysis (Fig. 7).

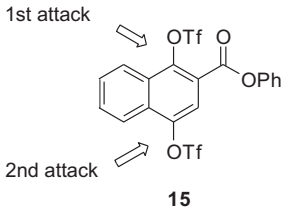
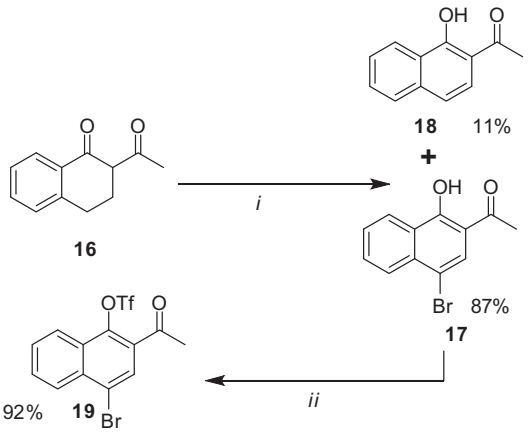


Fig. 6. Regioselectivity of the Suzuki–Miyaura reactions of **15**.

The Suzuki–Miyaura reaction of **19** with arylboronic acids **7** (2.2 equiv) afforded the 1,2-diarylnaphthalenes **21a**,**b** in 78–85% yield (Scheme 8, Table 6). The Suzuki–Miyaura reaction of **19** with arylboronic acids **7** (1.0 equiv) provided the 4-aryl-2-acetylnaphthalen-1-yl-trifluoromethanesulfonates **20a**,**b** in 72–86% yields (Scheme 8, Table 5). The reactions proceeded with very good chemoselectivity in favour of the bromide position, while the C-1 triflate remained unattacked. This was confirmed by 2D NMR experiments of compound **20a** (Fig. 8). The regioselectivity observed is opposite to the one observed for the Suzuki–Miyaura



Scheme 7. Reaction conditions: i, **16** (1.0 equiv), NBS (3.0 equiv), $(PhCOO)_2$ (5 mol %), benzene, reflux, 4 h; ii, **17** (1.0 equiv), Tf_2O (1.2 equiv), pyridine (2.0 equiv), CH_2Cl_2, 20 °C, 6 h.

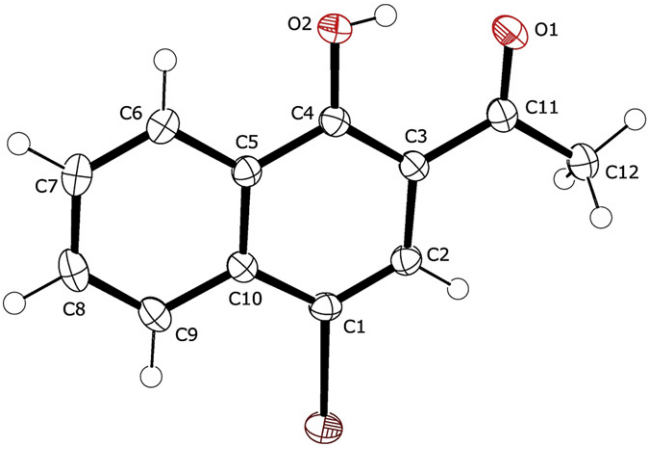
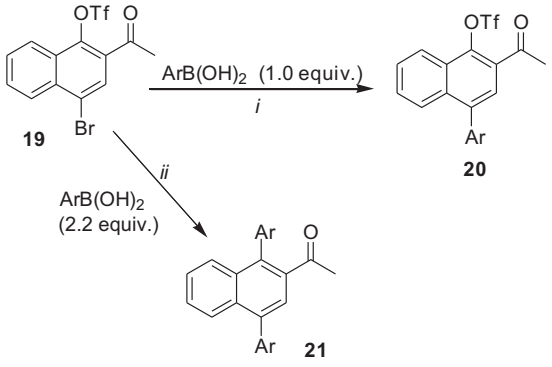


Fig. 7. Crystal structure of **17**.

reactions of phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate **15**.[15] The first attack occurs at the bromide position, despite the electron deficient character of the triflate located close to the acetyl group.



Scheme 8. Synthesis of **20a**,**b** and **21a**,**b**. Conditions: i, **19** (1.0 equiv), $Ar^1B(OH)_2$ (1.0 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (1.5 equiv), dioxane, 90 °C, 4 h; ii, **20** (1.0 equiv), $ArB(OH)_2$ (2.2 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (3.0 equiv), dioxane, 110 °C, 4 h.

Table 5
Synthesis of **20a**,**b**

20	7	Ar	% (**20**)[a]
a	**l**	4-(MeO)C_6H_4	72
b	**c**	4-ClC_6H_5	86

[a] Yields of isolated compounds.

Table 6
Synthesis of **21a**,**b**

21	7	Ar	% (**21**)[a]
a	**l**	4-$MeOC_6H_4$	83
b	**c**	4-ClC_6H_4	85

[a] Yields of isolated compounds.

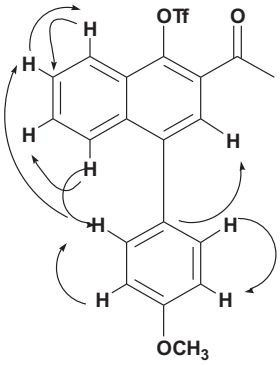


Fig. 8. Important HMBC (single headed arrows), NOESY (dashed arrows) and COSY (double headed arrows) correlations of **20a**.

3. Conclusions

In conclusion, we have reported chemoselective Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy) naphthalene, 1-bromo-2-(trifluoromethanesulfonyloxy)naphthalene and 2-acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate. For all substrates the first attack was observed at the brominated carbon (C–Br) while the triflate was attacked later on. The strategy outlined herein provides a convenient approach to 1,2-diarylnaphthalenes and 2-acetyl 1,4-diarylnaphthalenes, which are not readily available by other methods.

4. Experimental section

4.1. General procedure A for the synthesis of 5, 12 and 17

A benzene suspension (30 mL) of 1-tetralone **4**, **11**, **16** (1.0 equiv), *N*-bromosuccinimide (NBS) (2.2 equiv) and $(PhCOO)_2$ (5 mol %) was refluxed under Argon atmosphere for 4 h and then cooled to 20 °C. To the reaction mixture was added triethylamine (1 mL) and the solvent was removed in vacuo. The reaction mixture was 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, heptane/EtOAc) to give **5**, **12** and **17**.

4.2. Synthesis of 2-bromonaphth-1-ol (5)

Starting with 1-tetralone (**4**) (1.8 mL, 13.7 mmol), *N*-bromosuccinimide (NBS) (5.4 g, 30.2 mmol) and $(PhCOO)_2$ (0.17 g, 5 mol %), following *general procedure A*, **5** was isolated as colourless solid (2.57 g, 84%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=5.89 (s, 1H, OH), 7.24 (d, J=8.8 Hz, 1H), 7.38–7.46 (m, 3H), 7.66–7.75 (m, 1H), 8.12–8.19 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=104.0 (C), 121.3, 122.2, 124.1 (CH), 124.4 (C), 124.8, 127.5, 128.3 (CH), 133.7, 148.1 (C). IR (KBr): ν=3400 (s), 3051, 1958, 1931, 1883, 1877, 1624 (w), 1586, 1574 (m), 1504 (w), 1453, 1396, 1384, 1347, 1240, 1212, 1202, 1140, 1126, 1054, 1021, 876, 856 (m), 829, 792, 768, 736 (s), 716, 641, 600, 561 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=222 ([M]$^+$ 98), 115 (92). HRMS (EI, 70 eV): calcd for $C_{10}H_7BrO$ [M]$^+$ 221.9680; found: 221.9679. The spectroscopic data were in agreement with those reported in the literature.[12]

4.3. General procedure B for the synthesis of triflate 6, 13 and 19

To a solution of **5**, **12** or **17** (1.0 equiv) in CH_2Cl_2 (2.5 mL/mmol) was added pyridine (2.0 equiv) at 20 °C under an argon atmosphere. After stirring for 10 min at 0 °C, Tf_2O (1.5 equiv) was added. The mixture was allowed to warm to 20 °C and stirred for further 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was directly purified by chromatography without aqueous work up (flash silica gel, heptane/EtOAc).

*4.3.1. 2-Bromonaphth-1-yl trifluoromethanesulfonate (**6**).* Starting with **5** (2.4 g, 10.8 mmol) in CH_2Cl_2 (25 mL), pyridine (1.8 mL, 21.6 mmol) and Tf_2O (2.7 mL, 16.4 mmol), following the general procedure B, **6** was isolated as a light yellow oil (3.53 g, 92%). R_f=0.71 (heptane/EtOAC system; 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.56–7.69 (m, 4H), 7.83 (d, J=7.8 Hz, 1H), 8.13 (d, J=8.1 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.0. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=114.1 (C), 118.5 (q, $J_{C,F}$=321.0 Hz, CF_3), 121.2, 127.5 (CH), 127.9 (C), 128.1, 128.5, 129.4, 129.9 (CH), 133.7, 142.6 (C). IR (KBr): ν=1589, 1501, 1457 (m), 1408 (s), 1370, 1365 (m), 1203, 1181, 1124 (s), 1032 (m) 1018, 890, 801, 761 (s), 743, 703, 665, 616, 587 (m) cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=354 ([M]$^+$, 100), 223 (52). HRMS (EI, 70 eV): calcd for $C_{11}H_6BrF_3O_3S$: 353.9173 [M]$^+$; found: 353.9171.

4.4. General procedure C for Suzuki–Miyaura reactions

A 1,4-dioxane (5 mL) solution of K_3PO_4 (1.5 equiv per cross-coupling step), $Pd(PPh_3)_4$ (5 mol %) and arylboronic acid **7** (1.0–1.1 equiv per cross-coupling step) was stirred at 90–110 °C for 4 h. After cooling to 20 °C, the organic layer was dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo without aqueous workup. The residue was purified by column chromatography (flash silica gel, heptane/EtOAc 9:1).

*4.4.1. 1,2-Bis(2-methoxyphenyl)naphthalene (**8a**).* Starting with **6** (258 mg, 0.73 mmol), 2-methoxyphenylboronic acid (244 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **8a** was isolated as a light yellow solid (154 mg, 62%), mp 105–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.46 (s, 3H, OCH_3),3.52 (s, 3H, OCH_3), 6.64–6.78 (m, 4H), 6.96–7.13 (m, 4H), 7.23–7.29 (m, 1H), 7.33–7.38 (m, 1H), 7.43 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.3 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=55.1 (OCH_3), 55.2 (OCH_3), 110.1, 110.2, 111.1, 119.6, 119.7, 120.3, 125.3, 125.7, 126.6, 127.1, 127.9, 128.1, 128.4, 128.6 (CH), 131.1, 131.4, 132.6, 132.8, 135.2, 135.9, 156.4, 157.3 (C). IR (KBr): ν=3060, 3026, 2940, 2837 (m), 1605, 1597, 1581, 1495, 1465, 1436, 1405 (s), 1343, 1296, 1270, 1254 (m), 1201, 1132, 1079, 1048, 1026, 1007, 895, 866, 812, 748, 708, 686, 634, 602, 588, 574 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=341 (M$^+$, 98), 309 (57), 234 (47). HRMS (EI, 70 eV): calcd for $C_{24}H_{20}O_2$ [M]$^+$: 340.1534; found: 340.1531.

*4.4.2. 1,2-Bis(4-methylphenyl)naphthalene (**8b**).* Starting with **6** (258 mg, 0.73 mmol), *p*-tolylboronic acid (219 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 mL), following the general procedure C, **8b** was isolated as a white crystalline solid (177 mg, 79%), mp 103–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.21 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 6.91 (d, J=8.1 Hz, 2H), 6.96–7.03 (m, 6H), 7.26–7.31 (m, 1H), 7.41 (d, J=8.4 Hz, 2H), 7.54 (d, J=8.4 Hz, 1H), 7.80 (d, J=8.3 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 21.3 (2-CH_3), 125.2, 126.1, 126.9, 127.3, 127.8, 128.4, 128.5, 128.6, 130.1, 131.2 (CH), 132.7, 132.9, 135.6, 136.1, 136.2, 137.5, 138.2, 139.2 (C). IR (KBr): ν=3051, 3028, 2918, 2862 (m), 1513, 1498, 1425, 1415, 1336, 1308, 1265, 1242, 1208, 1222, 1208, 1110, 1089, 1023, 1008, 958 (m), 807, 790, 783, 749, 722, 683 (s), 589,

573, 552 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=308 (M^+, 100), 293 (34), 178 (27), 252 (15), 138 (25). HRMS (EI, 70 eV): calcd for $C_{24}H_{20}$ $[M]^+$: 308.1559; found: 308.1558. Anal. Calcd for C, 93.46; H, 6.54; found: C, 93.41; H, 6.52.

*4.4.3. 1,2-Bis(4-chlorophenyl)naphthalene (**8c**).* Starting with **6** (258 mg, 0.73 mmol), *p*-chloroboronic acid (251 mg, 1.61 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (464 mg, 2.19 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **8c** was isolated as a white crystalline solid (239 mg, 94%), mp 170–180 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=6.95–6.98 (m, 2H), 7.01–7.03 (m, 2H), 7.07–7.11 (m, 2H), 7.19–7.22 (m, 2H), 7.30–7.35 (m, 1H), 7.38–7.44 (m, 2H), 7.56 (d, *J*=8.5 Hz, 1H), 7.73 (d, *J*=3.1 Hz, 1H), 7.89 (d, *J*=3.0 Hz, 1H).^{13}C NMR (62.9 MHz, $CDCl_3$): δ=126.1, 126.4, 126.6 (CH), 127.4 (C), 127.9, 128.1, 128.2, 128.3 (CH), 129.1 (C), 131.3 (CH), 132.4, 132.5 (C), 132.6 (CH), 132.9 (C), 133.1 (CH), 136.3, 137.2, 140.1 (C). IR (KBr): *v*=3050, 2923, 2852 (w), 1487, 1459, 1395, 1374, 1259, 1209 (m), 1086, 1013, 961, 801, 840, 824, 810 (s), 752, 739, 730, 718, 679, 657, 636, 608 (m), 573, 559, 540, 531 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=348 (M^+, 100), 278 (58), 138 (36), 69 (26). HRMS (EI, 70 eV): calcd for $C_{22}H_{14}Cl_2$ $[M]^+$: 348.0467; found: 348.0466. Anal. Calcd for C, 75.66; H, 4.04; found: C, 75.64; H, 4.01.

*4.4.4. (2-Methoxyphenyl)naphthalen-1-yl trifluoromethanesulfonate (**9a**).* Starting with **6** (258 mg, 0.73 mmol), 2-methoxyphenylboronic acid (111 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **9a** was isolated as a yellow solid (167 mg, 60%), mp 73–75 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.71 (s, 3H, OCH_3), 6.90 (d, *J*=8.4 Hz, 1H), 7.01 (td, *J*=8.4, 1.2 Hz, 1H), 7.35–7.41 (m, 1H), 7.21 (d, *J*=8.4 Hz, 1H), 7.47–7.52 (m, 1H), 7.42 (d, *J*=8.4 Hz, 1H), 7.54–7.61 (m, 1H), 7.83 (t, *J*=8.1 Hz, 2H), 8.14 (d, *J*=8.4, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−74.1. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.5 (OCH_3), 111.9 (CH), 118.0 (q, $J_{F,C}$=316.2 Hz, CF_3), 120.6, 121.6 (CH), 126.4, 126.7 (C), 127.4, 127.9, 128.8, 129.2, 129.6, 130.2, 131.8 (CH), 129.8, 134.4, 142.6, 156.9 (C). IR (KBr): *v*=3060, 3026, 3004, 2939, 2837 (w) 1605, 1597, 1581, 1494, 1466, 1436, 1405, 1361, 1343, 1270, 1254 (m), 1200, 1132, 1079, 1048, 1026, 1007, 895, 866, 811, 748 (s), 708, 686, 634, 602, 588, 574 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=382 (M^+, 93), 249 (100), 234 (43), 218 (35), 189 (12). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_4S$ $[M]^+$: 382.0481; found: 382.0481. Anal. Calcd for C, 56.54; H, 3.43; found; C, 56.41; H, 3.19.

*4.4.5. (4-Methylphenyl)naphthalen-1-yl trifluoromethanesulfonate (**9b**).* Starting with **6** (258 mg, 0.73 mmol), *p*-tolylboronic acid (100 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **9b** was isolated as a brown solid (195 mg, 73%), mp 71–73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 7.21 (d, *J*=8.1 Hz, 2H), 7.37 (d, *J*=8.1 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 1H), 7.51–7.54 (m, 1H), 7.57–7.62 (m, 1H), 7.83 (dd, *J*=8.1, 4.8 Hz, 2H), 8.09 (d, *J*=8.4 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1 (CH_3), 119.9 (q, $J_{F,C}$=314.2 Hz, CF_3), 120.6, 126.0 (CH), 126.4 (C), 126.8, 126.9, 127.4, 127.5, 128.2, 128.5 (CH), 131.8, 132.4, 132.9, 137.2, 140.9 (C). IR (KBr): *v*=3051, 3028, 2918, 2862 (m), 1513, 1498, 1425, 1415, 1336, 1308, 1265, 1242, 1208, 1222, 1208, 1110, 1089, 1023, 1008, 958 (m), 807, 790, 783, 749, 722, 683 (s), 589, 573, 552 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=366 (M^+, 78), 275 (64), 204 (27), 138 (25). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_3S$ $[M]^+$: 366.0559; found: 366.0556. Anal. Calcd for C, 59.01; H, 3.58; found: C, 59.02; H, 3.55.

*4.4.6. 2-(4-Chlorophenyl)naphthalen-1-yl trifluoromethanesulfonate (**9c**).* Starting with **6** (258 mg, 0.73 mmol), phenylboronic acid (114 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **9d** was isolated as a yellow solid (248 mg, 88%), mp 82–84 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.38–7.41 (m, 5H), 7.51–7.56 (m, 1H), 7.57–7.63 (m, 1H), 7.84 (dd, *J*=8.1, 3.2 Hz, 2H), 8.09 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.8. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=117.1 (q, $J_{C,F}$=263.0 Hz, CF_3), 120.6 (CH), 126.3 (C), 126.4, 126.9, 127.0, 127.1, 127.6, 127.8, 130.1 (CH), 130.6, 133.1, 133.6, 133.8, 140.8 (C). IR (KBr): *v*=3073, 2954, 2922, 2852 (m), 1493, 1402, 1341, 1240, 1212, 1145, 1130, 1094 (s), 1028, 1018, 1006 (m), 894, 864, 837, 811, 765, 750 (s), 734, 698, 680, 634, 626, 597, 574, 549, 538 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=386 (M^+, 83), 253 (49), 218 (100), 189 (23). HRMS (EI, 70 eV): calcd for $C_{17}H_{10}ClF_3O_3S$ $[M]^+$: 385.9985; found: 385.9988. Anal. Calcd for C, 52.79; H, 2.61; found: C, 52.76; H, 2.58.

*4.4.7. 2-Phenylnaphthalen-1-yl trifluoromethanesulfonate (**9d**).* Starting with **6** (258 mg, 0.73 mmol), phenylboronic acid (89 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **9c** was isolated as a light yellow solid (197 mg, 77%), mp 75–77 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.34–7.52 (m, 7H), 7.55–7.61 (m, 1H), 7.81 (dd, *J*=8.2, 3.4 Hz, 2H), 8.05 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=117.1 (q, $J_{C,F}$=316.2 Hz, CF_3), 120.6, 126.1 (CH), 126.3 (C), 126.9, 127.0, 127.3, 127.4, 127.5, 127.6, 128.7 (CH), 131.7, 133.0, 135.3, 140.9 (C). IR (KBr): *v*=2931, 2865 (m), 1578, 1518, 1485, 1437, 1395, 1321 (s), 1253, 1237, 1202, 1198, 1073, 958 (m), 837, 756, 719, 637 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=352 (M^+, 98), 275 (60). HRMS (EI, 70 eV): calcd for $C_{17}H_{11}F_3O_3S$ $[M]^+$: 352.0412; found: 352.0411. Anal. Calcd for C, 56.54; H, 3.45; found: C, 56.52; H, 3.44.

*4.4.8. 2-(4-Fluorophenyl)naphthalen-1-yl trifluoromethanesulfonate (**9e**).* Starting with **6** (258 mg, 0.73 mmol), *p*-fluorophenylboronic acid (102 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol %), K_3PO_4 (232 mg, 1.1 mmol) and 1,4-dioxane (5 mL), following the general procedure C, **9c** was isolated as a light yellow solid (229 mg, 85%), mp 75–77 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.05–7.15 (m, 2H), 7.38–7.45 (m, 3H), 7.49–7.62 (m, 2H), 7.80–7.59 (m, 2H), 8.09 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−113.2, −74.0. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=115.6 (d, $J_{C,F}$=21.4 Hz, CH), 117.1 (q, $J_{C,F}$=316.2 Hz, CF_3), 119.7 (C), 121.7, 127.3, 128.0 (CH), 128.2 (d, $J_{F,C}$=2.6 Hz, CH), 128.6, 131.4, 131.6 (CH), 132.3, 132.4, 134.1, 141.9 (C), 161.9 (d, $J_{F,C}$=248.5 Hz, CF). IR (KBr): *v*=2961, 1606 (w), 1513, 1498 (m), 1405, 1341, 1201 (s), 1159 (m), 1132 (s), 1088, 1018, 1007 (m), 894 (s), 867 (m), 816, 804 (s), 764 (m), 749 (s), 703, 683, 622, 598, 556 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=370 (M^+, 19), 237 (100), 209 (51), 183 (12). HRMS (EI, 70 eV): calcd for $C_{17}H_{10}F_4O_3S$ $[M]^+$: 370.0271; found: 370.0273. Anal. Calcd for C, 55.14; H, 2.72; found: C, 54.11; H, 2.71.

*4.4.9. 1-(4-tert-Butylphenyl)-2-(2-methoxyphenyl)naphthalene (**10a**).* Starting with **9a** (100 mg, 0.26 mmol), 4-*tert*-butylphenylboronic acid (40 mg, 0.31 mmol), $Pd(PPh_3)_4$ (15 mg, 5 mol %), K_3PO_4 (85 mg, 0.52 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **10a** was isolated as a viscous solid (124 mg, 66%), ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (s, 9H, CH_3), 3.51 (s, 3H, OCH_3), 6.96–7.13 (m, 3H), 7.23–7.29 (m, 2H), 7.33–7.37 (m, 1H), 7.39 (d, *J*=8.63 Hz, 2H), 7.43 (d, *J*=8.4 Hz, 2H), 7.57 (d, *J*=8.61 Hz, 2H), 7.76 (d, *J*=8.3 Hz, 2H). 13C NMR (75.5 MHz, $CDCl_3$): δ=30.1 (3-CH_3), 33.7 (C) 55.2 (OCH_3), 116.6, 119.3, 120.3, 125.5, 125.6, 126.2, 127.3, 128.0, 128.2, 128.5, 128.7, 129.3 (CH), 131.4, 131.7, 132.4, 132.7, 134.7, 136.5, 149.4, 156.4 (C). IR (KBr): *v*=3052, 3016, 2924, 2904, 2873 (m), 1625, 1577, 1551, 1493, 1454, 1413 (s), 1296, 1267, 1243 (m), 1172, 1077, 1038, 897, 826, 812, 651, 624, 574 (s) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%)=366 (M+, 98), 335 (64), 278 (58). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}O$ [M]+: 366.4136; found: 366.4132.

*4.4.10. 2-(4-Methylphenyl)-1-(2,5-dimethoxyphenyl)naphthalene (**10b**).* Starting with **9b** (100 mg, 0.27 mmol), 2,5-

dimethoxyphenylboronic acid (55 mg, 0.30 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (86 mg, 0.41 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **10b** was isolated as a highly viscous oil (62 mg, 65%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.21 (s, 3H, CH_3), 3.41 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 6.56 (d, J=2.7 Hz, 1H), 6.73–6.74 (m, 2H), 6.91 (d, J=7.8 Hz, 2H), 7.02 (d, J=7.9 Hz, 2H), 7.29–7.32 (m, 1H), 7.34–7.41 (m, 1H), 7.48 (d, J=8.4 Hz, 2H), 7.81 (dd, J=4.7, 4.4 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.7 (CH_3), 54.6 (OCH_3), 54.8 (OCH_3), 110.8, 112.6, 117.1, 124.3, 125.1, 125.6, 126.6, 126.8 (CH), 127.1 (2-CH), 128.0 (2-CH), 128.2 (CH), 128.3, 131.5, 131.7, 132.8, 134.7, 137.8, 138.2, 151.1, 152.2 (C). IR (KBr): ν=2934, 2872 (w), 1476, 1454, 1361, 1259 (m), 1166, 1043, 975, 843, 834 (s), 742, 729, 708, 679, 647, 626 (m), 571, 542, 537 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=354 (M^+, 100), 323 (57), 263 (31), 216 (18). HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_2$ $[M]^+$: 354.1623; found: 354.1621. Anal. Calcd for C, 84.72H, 6.26; found: C, 84.69; H, 6.21.

*4.4.11. 2-(4-Chlorophenyl)-1-(3,5-dimethylphenyl)naphthalene (**10c**).* Starting with **9d** (100 mg, 0.26 mmol), 3,5-dimethylphenylboronic acid (44 mg, 0.29 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (83 mg, 0.39 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **10d** was isolated as a reddish crystalline solid (64 mg, 72%), mp 106–109 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.19 (s, 6H, $2CH_3$) 6.71 (br s, 2H), 6.84 (br s, 1H), 7.01–7.12 (m, 4H), 7.29–7.35 (m, 1H), 7.38–7.44 (m, 2H), 7.42 (d, J=8.4 Hz, 1H), 7.59 (d, J=8.4 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.3 (2 CH_3), 125.1 (C), 125.7, 126.2, 127.1, 127.4, 127.7, 127.8, 127.9, 128.4, 129.1, 131.3, 132.1 (CH), 132.1, 132.7, 132.8, 136.7, 137.2, 138.1, 138.4, 140.6 (C). IR (KBr): ν=2978, 2853 (w), 1477, 1458, 1375, 1276, 1254 (m), 1037, 1003, 987, 821, 834, 817 (s), 739, 721, 718, 673, 665, 608 (m), 573, 543, 537 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=342 (M^+, 100), 307 (58), 238 (36). HRMS (EI, 70 eV): calcd for $C_{24}H_{19}Cl$ $[M]^+$: 342.1271; found: 342.1269. Anal. Calcd for C, 84.26; H, 5.59; found: C, 84.23; H, 5.58.

*4.4.12. 2-(Phenyl)-1-(2-methoxyphenyl)naphthalene (**10d**).* Starting with **9c** (100 mg, 0.28 mmol), 2-methoxyphenylboronic acid (48 mg, 0.31 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol %), K_3PO_4 (89 mg, 0.42 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **10c** was isolated as a brown highly viscous oil (60 mg, 69%). ^1H NMR (300 MHz, $CDCl_3$): δ=3.39 (s, 3H, OCH_3), 6.82–7.21 (m, 4H), 7.34–7.45 (m, 6H), 7.47–7.54 (m, 1H), 7.57–7.63 (m, 1H), 7.81–7.85 (m, 2H), 8.09 (d, J=8.4 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=54.6 (OCH_3), 111.2, 120.7, 121.6 (CH), 124.6 (C), 127.0, 127.8, 128.1, 128.5, 128.6, 129.2, 129.6 (CH), 129.8 (C), 130.2, 131.5, 131.8 (CH), 134.2, 142.6, 156.9 (C). GC–MS (EI, 70 eV): m/z (%)=310 (M^+, 98), 279 (53), 233 (69). HRMS (EI, 70 eV): calcd for $C_{23}H_{18}O$ $[M]^+$: 310.1431; found: 310.1430. Anal. Calcd for C, 89.00H, 5.85; found: C, 89.01; H, 5.81.

*4.4.13. 2-(4-Fluorophenyl)-1-(m-tolyl)naphthalene (**10e**).* Starting with **9e** (200 mg, 0.54 mmol), 3-methylphenylboronic acid (81 mg, 0.59 mmol), $Pd(PPh_3)_4$ (32 mg, 5 mol %), K_3PO_4 (173 mg, 0.81 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **10e** was isolated as a colourless solid (130 mg, 77%), mp 109–111 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 6.75–6.91 (m, 4H), 7.00–7.05 (m, 3H), 7.10 (t, J=7.4 Hz, 1H), 7.28–7.40 (m, 2H), 7.43 (d, J=8.6 Hz, 1H), 7.58 (d, J=8.5 Hz, 1H), 7.81 (d, J=8.2 Hz 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−116.6. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=114.5 (d, $J_{C,F}$=21.3 Hz, CH), 125.8, 126.3, 126.9, 127.6, 127.8, 127.9, 128.1, 128.5, 131.5, 131.6, 132.1 (CH), 132.7, 132.8, 137.2, 137.4, 137.9, 138.1 (d, $J_{C,F}$=3.3 Hz, C), 138.7 (C), 161.5 (d, $J_{C,F}$=245.6 Hz, CF). IR (KBr): ν=3050, 2920 (m), 2852 (w), 1601 (m), 1499 (s), 1457 (m), 1234 (w), 1218 (s), 1155, 1092, 1023 (m), 962 (w), 863, 841 (m), 817, 803, 778, 743, 713, 693 (s), 653, 544 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=312 (M^+, 100), 222 (55), 204 (7). HRMS (EI, 70 eV): calcd for $C_{23}H_{17}F$ $[M]^+$: 312.1314; found: 312.1313.

4.5. Synthesis of 1-bromonaphth-2-ol (12)

Starting with 1-tetralone (**11**) (0.6 mL, 4.6 mmol), *N*-bromosuccinimide (NBS) (1.8 g, 10.1 mmol) and $(PhCOO)_2$ (0.056 g, 5 mol %), following *general procedure A*, **12** was isolated as colourless solid (0.81 g, 82%). The spectroscopic data were in agreement with those reported in the literature.[15]

*4.5.1. 1-Bromonaphthalen-2-yl trifluoromethanesulfonate (**13**).* Starting with **12** (0.80 g, 3.6 mmol) in CH_2Cl_2 (20 mL), pyridine (0.5 mL, 7.0 mmol) and Tf_2O (0.9 mL, 5.4 mmol), following *general procedure B*, **13** was isolated as a light yellow oil (1.20 g, 92%).

*4.5.2. 1-p-Tolylnaphthalen-2-yl trifluoromethanesulfonate (**14a**).* Starting with **13** (70 mg, 0.20 mmol), *p*-tolylboronic acid (27 mg, 0.20 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **14a** was isolated as a brown solid (54 mg, 73%), mp 70–72 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.33 (s, 3H, CH_3), 7.21 (d, J=8.2 Hz, 2H), 7.24 (d, J=8.4 Hz, 1H), 7.39–7.46 (m, 1H), 7.49–7.56 (m, 1H), 7.68 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.5 Hz, 2H), 8.15 (d, J=8.5 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.2. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1 (CH_3), 119.9 (q, $J_{F,C}$=314.2 Hz, CF_3), 119.8, 126.8, 127.3, 127.6, 127.7, 128.1 (CH), 128.3 (C), 129.1, 130.6 (CH), 132.8, 132.6, 133.4, 138.3, 144.3 (C). IR (KBr): ν=3019, 2927, 2869 (m), 1541, 1498, 1438, 1423, 1301, 1285, 1245, 1211, 1108, 1093, 1073, 967 (m), 817, 793, 771, 758, 712, 653 (s), 574, 542 (m), cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=366 (M^+, 98), 275 (57), 217 (44), 138 (37). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_3S$ $[M]^+$: 366.0519; found: 366.0516. Anal. Calcd for C, 59.01; H, 3.58; found: C, 59.02; H, 3.55.

*4.5.3. 1-(5-Chloro-2-methoxyphenyl)naphthalen-2-yl trifluorome thanesulfonate (**14b**).* Starting with **13** (70 mg, 0.20 mmol, 1.0 equiv), 5-chloro-2-methoxyphenylboronic acid (37 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **14b** was isolated as a white solid (50 mg, 60%), mp 75–77 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.69 (s, OCH_3), 6.79 (d, J=8.4 Hz, 2H), 6.98 (d, J=8.2 Hz, 1H), 7.10–7.11 (m, 1H), 7.16–7.21 (m, 2H), 7.33–7.47 (m, 2H), 7.80–7.89 (m, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−74.5. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=54.7 (OCH_3), 117.5 (q, $J_{F,C}$=316.2 Hz, CF_3), 120.1, 121.3 (CH), 126.1, 126.4 (C), 127.2, 127.6, 128.5, 128.8, 129.2, 130.0, 131.6 (CH), 132.7, 134.0, 137.8, 142.3, 155.1 (C). IR (KBr): ν=3014, 2941, 2872 (w) 1655, 1572, 1581, 1466, 1436, 1405, 1361, 1343, 1270, 1254 (m), 1200, 1132, 1079, 1048, 1026, 1007, 895, 866, 811, 748 (s), 708, 686, 634, 602, 588, 574 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=416 (M^+, 81), 274 (76), 267 (43), 141 (29). HRMS (EI, 70 eV): calcd for $C_{18}H_{12}ClF_3O_4S$ $[M]^+$: 416.0135; found: 416.0131. Anal. Calcd for C, 51.87; H, 2.90; found; C, 51.86; H, 2.88.

*4.5.4. 1-Phenylnaphthalen-2-yl trifluoromethanesulfonate (**14c**).* Starting with **13** (86 mg, 0.24 mmol), phenylboronic acid (30 mg, 0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (14 mg, 5 mol %), K_3PO_4 (77 mg, 0.36 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **14c** was isolated as a white solid (61 mg, 74%), mp 72–74 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.24–7.34 (m, 3H), 7.49–7.62 (m, 3H), 7.68 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.5 Hz, 2H), 8.15 (d, J=8.5 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−73.7. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=^{13}C NMR (62.9 MHz, $CDCl_3$): δ=117.8 (q, $J_{F,C}$=314.2 Hz, CF_3), 119.8, 126.8, 127.3, 127.6, 127.7, 128.1, 129.0, 129.3, 130.6 (CH), 132.8, 132.6, 133.4, 135.3, 140.7 (C). IR (KBr): ν=2956, 2891 (m), 1573, 1511, 1483, 1422, 1255, 1219, 1213, 1173, 1133, 983 (m), 819, 781, 784, 765 (s),

547, 514 (m), cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=352 (M^+, 97), 273 (57), 217 (34). HRMS (EI, 70 eV): calcd for $C_{17}H_{11}F_3O_3S$ $[M]^+$: 352.0412; found: 352.0410.

*4.5.5. 1-(4-Fluorophenyl)naphthalen-2-yl trifluoromethanesulfonate (**14d**).* Starting with **13** (86 mg, 0.24 mmol), 4-fluorophenylboronic acid (34 mg, 0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (14 mg, 5 mol %), K_3PO_4 (77 mg, 0.36 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **14d** was isolated as a solid (70 mg, 54%), mp 71–73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.03–7.11 (m, 2H), 7.36–7.41 (m, 3H), 7.51–7.59 (m, 2H), 7.61–7.64 (m, 2H), 8.11 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−113.1, −73.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=115.3 (d, $J_{C,F}$=21.2 Hz, CH), 117.1 (q, $J_{C,F}$=315.7 Hz, CF_3), 119.5 (C), 122.0, 127.1, 127.8 (CH), 128.0 (d, $J_{F,C}$=2.4 Hz, CH), 128.2, 130.7, 131.3 (CH), 132.0, 132.2, 133.8, 140.9 (C), 162.1 (d, $J_{F,C}$=248.7 Hz, CF). IR (KBr): *v*=2926, 1626 (w), 1572, 1521 (m), 1463, 1344, 1227 (s), 1167 (m), 1144 (s), 1081, 1018 (m), 894 (s), 866 (m), 824, 814 (s), 754 (m), 747 (s), 703, 622, 556 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=370 (M^+, 19), 237 (100), 209 (51), 183 (12). HRMS (EI, 70 eV): calcd for $C_{17}H_{10}F_4O_3S$ $[M]^+$: 370.0271; found: 370.0273.

*4.5.6. 1-(3,5-Dimethylphenyl)naphthalen-2-yl trifluoromethane sulfonate (**14e**).* Starting with **13** (86 mg, 0.24 mmol), 3,5-dimethylphenylboronic acid (43 mg, 0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (14 mg, 5 mol %), K_3PO_4 (67 mg, 0.36 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **14e** was isolated as a brown solid (73 mg, 76%), mp 81–83 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.27 (s, 6H, $2CH_3$) 6.68 (s, 2H), 6.77 (br s, 1H), 7.16–7.21 (m, 3H), 7.33–7.47 (m, 1H), 7.76 (d, *J*=8.6 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.4 (2-CH_3), 125.3 (C), 124.9, 126.0, 126.8, 127.1, 127.3, 127.7, 128.0, 128.5, 129.0, 130.7, 132.0, (CH), 132.3, 133.0, 133.3, 136.0, 136.6, 138.0, 138.3, 140.2 (C). IR (KBr): *v*=2966, 2873 (w), 1481, 1468, 1355, 1327, 1264, 1244 (m), 1036, 978, 822, 831, 827 (s), 733, 715, 663, 605 (m), 543, 531 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=380 (M^+, 100), 274 (68), 231 (46). HRMS (EI, 70 eV): calcd for $C_{19}H_{15}F_3O_3S$ $[M]^+$: 380.2821; found: 380.218.

4.6. Synthesis of 1-(4-bromo-1-hydroxynaphthalen-2-yl) ethanone (17)

Starting with 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (**16**) (3.00 g, 13.7 mmol), *N*-bromosuccinimide (NBS) (5.4 g, 30.2 mmol) and $(PhCOO)_2$ (0.17 g, 5 mol %), following *general procedure A*, **17** was isolated as green crystalline solid, mp 124–126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.59 (s, 3H, CH_3), 7.47–7.53 (m, 1H), 7.63–7.68 (m, 1H), 7.87 (s, 1H), 8.03 (d, *J*=8.4 Hz, 1H), 8.38 (d, *J*=8.3 Hz, 1H), 13.83 (s, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=26.8 (CH_3), 111.1, 113.9 (C), 124.8, 126.41 (CH), 126.7 (C), 127.1, 128.2, 131.2 (CH), 135.7, 161.9, 203.3 (C). IR (KBr): *v*=3130, 3071, 3033 (m), 1731, 1712, 1620, 1614, 1574, 1565, 1502, 1447, 1406, 1363, 1314, 1265, 1236, 1211, 1137 (s), 1082, 1025, 979, 871, 862, 837, 862, 837 (m), 754, 720, 686, 643, 588, 565 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=364 (M^+, 100), 251 (76), 195 (20), 114 (23). HRMS (EI, 70 eV): calcd for $C_{12}H_9BrO_2$ $[M]^+$: 263.9780; found: 263.9778. Anal. Calcd for C, 54.37; H, 3.42; found: C, 54.31; H, 3.41.

*4.6.1. 2-Acetyl-4-bromonaphthalen-1-yl trifluoromethanesulfonate (**19**).* Starting with **17** (2.00 g, 7.54 mmol) in CH_2Cl_2 (25 mL), pyridine (1.5 mL, 20 mmol) and Tf_2O (1.8 mL), following *general procedure B*, **19** was isolated as a light green oil (2.75 g, 88%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.59 (s, 3H, CH_3), 7.46–7.51 (m, 1H), 7.62–7.71 (m, 2H), 7.92 (s, 1H), 8.11 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−72.7. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.6 (CH_3), 117.5 (q, $J_{C,F}$=321 Hz, CF_3), 121.7 (C), 122.18 (CH), 126.5, 126.6 (C), 127.0, 128.1, 129.2, 130.3 (CH), 133.3, 140.3, 195.6 (C). IR (KBr): *v*=3076, 3002, 2962, 2929 (m), 1699, 1620, 1594, 1494, 1426, 1403 (s), 1370, 1351, 1318, 1266, 1243 (m), 1203, 1130, 1171, 1037, 867, 818, 760, 720, 647, 629, 603, 571, 551 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=396 (M^+, 97), 265 (95), 248 (20), 237 (73), 128 (36). HRMS (EI, 70 eV): calcd for $C_{13}H_8BrF_3O_4S$ $[M]^+$: 395.9273; found: 395.9269. Anal. Calcd for C, 39.31; H, 2.02; found: C, 39.29; H, 2.01.

*4.6.2. 2-Acetyl-4-(4-methoxyphenyl)naphthalen-1-yl trifluorometh anesulfonate (**20a**).* Starting with **19** (79 mg, 0.20 mmol), 4-methoxyphenylboronic acid (30 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **20a** was isolated as a **s**light brown oil (53 mg, 62%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.64 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.96–7.01 (m, 2H), 7.18 (s, 1H), 7.31–7.34 (m, 1H), 7.50–7.55 (m, 2H), 7.59–7.64 (m, 1H), 7.87 (d, *J*=8.5 Hz, 1H), 8.16 (d, *J*=8.5 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−72.8. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.7 (CH_3), 55.4 (OCH_3), 114.1 (CH), 117.5 (q, $J_{C,F}$=321 Hz, CF_3), 122.5, 125.0, 126.6 (CH), 126.9 (C), 128.1, 128.7 (CH), 129.5, 130.7 (C), 131.0 (CH), 134.5, 140.9, 141.1, 159.6 (C), 198.3 (CO). IR (KBr): *v*=3073, 3003, 2957, 2929, 2838 (m), 1697, 1607, 1572, 1515, 1499, 1456, 1423, 1404, 1366 (s), 1290, 1256 (w), 1244, 1204, 1177, 1149, 1134, 1028 (s), 978, 943, 937, 886 (m), 831, 793, 764, 721, 707, 636, 604, 588, 574 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=424 (M^+, 81), 291 (98), 277 (17), 263 (36), 235 (12), 149 (29). HRMS (EI, 70 eV): calcd for $C_{20}H_{15}F_3O_5S$ $[M]^+$: 424.0678; found: 424.0668 Anal. Calcd for C, 56.61; H, 3.56; found: C, 56.59; H, 3.54.

*4.6.3. 2-Acetyl-4-(4-chlorophenyl)naphthalen-1-yl trifluoromethane sulfonate (**20b**).* Starting with **19** (79 mg, 0.20 mmol), 4-chlorophenylboronic acid (31 mg, 0.20 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (64 mg, 0.30 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **20b** was isolated as a highly viscous oil (74 mg, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.61 (s, 3H, CH_3), 6.91–6.97 (m, 2H), 7.13 (s, 1H), 7.28–7.332 (m, 1H), 7.47–7.52 (m, 2H), 7.56–7.61 (m, 1H), 7.81 (d, *J*=8.4 Hz, 1H), 8.14 (d, *J*=8.4 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−72.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.4 (CH_3), 113.8 (CH), 116.9 (q, $J_{C,F}$=321 Hz, CF_3), 121.7, 121.8, 121.4 (CH), 125.6 (C), 127.7, 127.9 (CH), 128.2, 129.8 (C), 131.0 (CH), 133.7, 140.0, 141.1, 158.9 (C), 198.0 (CO). IR (KBr): *v*=3067, 3023, 2975, 2883 (m), 1687, 1636, 1552, 1423, 1404, 1386 (s), 1266 (w), 1231, 1209, 1176, 1141 (s), 972, 934, 874 (m), 831, 773, 761, 709, 570 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=428 (M^+, 98), 317 (76), 279 (37), 168 (09). HRMS (EI, 70 eV): calcd for $C_{19}H_{12}ClF_3O_4S$ $[M]^+$: 428.0156; found: 428.0154. Anal. Calcd for C, 53.22; H, 2.82; found: C, 53.19; H, 2.79.

*4.6.4. 1-(1,4-Di-p-tolylnaphthalen-2-yl)ethanone (**21a**).* Starting with **19** (79 mg, 0.20 mmol), *p*-tolylboronic acid (60 mg, 0.44 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (127 mg, 0.60 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **21a** was isolated as a slight yellow highly viscous oil (60 mg, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ=2.1 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 7.21–7.27 (m, 6H), 7.33–7.41 (m, 4H), 7.50 (s, 1H), 7.63–7.72 (m, 1H), 7.88–7.91 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.2, 21.3, 30.8 (CH_3), 125.1, 126.2, 126.4, 127.1, 127.6, 129.1, 129.2, 129.9, 130.6 (CH), 132.5, 132.8, 135.3, 137.1, 137.3, 137.6, 137.7, 137.9, 140.1 (C), 204.9 (CO). IR (KBr): 3022, 2921, 2865 (w), 1711 (s), 1591, 1511 (w), 1485, 1378, 1367 (m), 1241, 1220, 1192 (s), 1099, 1020, 926 (m), 814, 746 (s), 687, 595 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=350 (M^+, 99), 259 (66), 91 (07). HRMS (EI, 70 eV): calcd for $C_{26}H_{22}O$ $[M]^+$: 350.1745; found: 350.1741. Anal. Calcd for C, 89.11; H, 6.33; found: C, 89.09; H, 6.31.

*4.6.5. 1-(1,4-Bis(2-chlorophenyl)naphthalen-2-yl)ethanone (**21b**).* Starting with **19** (79 mg, 0.20 mmol), 2-chlorophenylboronic acid (69 mg, 0.44 mmol), $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_3PO_4 (127 mg,

0.60 mmol) and 1,4-dioxane (5 mL), following *general procedure C*, **21b** was isolated as a slight yellow highly viscous oil (229 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.10 (s, 3H, CH_3), 7.17–7.21 (m, 1H), 7.31–7.33 (m, 5H), 7.38–7.39 (m, 2H), 7.41–7.43 (m, 2H), 7.50 (s, 1H), 7.59 (dd, J=7.1, 1.5 Hz, 1H), 7.80 (dd, J=7.2, 1.5 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.7 (CH_3), 120.6, 124.1, 124.8, 125.9, 126.4, 126.7, 127.1, 127.3, 127.8, 128.6, 128.8, 128.9, 129.4 (CH), 131.2, 131.4, 133.3, 133.5, 135.6, 136.2, 138.2, 139.0, 140.5 (C), 202.3 (CO). IR (KBr): ν=3063 (w), 2929, 2857, 1714 (m), 1588 (w), 1498, 1362, 1353, 1244 (m), 1218, 1192, 1087 (s), 1013, 907 (m), 823, 764, 740, 690 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=390 (M^+, 99), 347 (23), 279 (61). HRMS (EI, 70 eV): calcd for $C_{26}H_{16}Cl_2O$ $[M]^+$: 390.0651; found: 390.0648. Anal. Calcd for C, 73.67; H, 4.12; found: C, 73.64; H, 4.09.

Acknowledgements

Financial support by the State of Mecklenburg-Vorpommern is gratefully acknowledged.

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