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Note

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Three-Step Synthesis of Fluoranthenes through Pd-Catalyzed Inter and Intramolecular C−H Arylation

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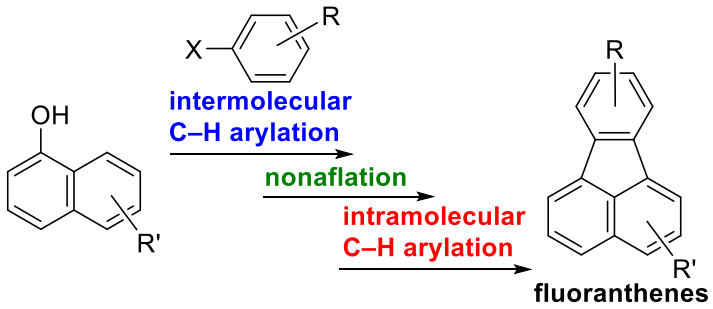


ABSTRACT: A three-step synthetic method for the preparation of fluoranthenes, involving Miura's intermolecular C−H arylation, nonaflation, and intramolecular C−H arylation has been

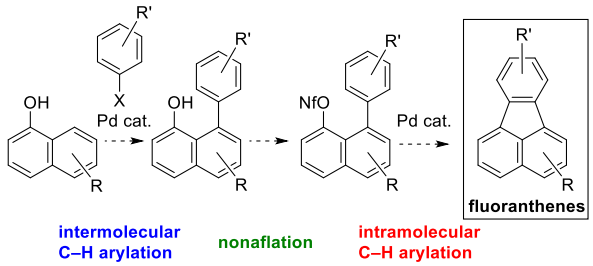
developed. Various 1-naphthols and haloarenes were successfully used as substrates. Reaction conditions that afford high site-selectivity have been developed for the intramolecular C−H arylation step.

Polycyclic aromatic hydrocarbons (PAHs) have attracted much attention because of their biological, electronic, and optical properties.[1−5] Fluoranthene is one of the smallest nonalternant PAHs, and its framework has often been utilized as a structural motif for many applications, such as in sensors[6] and organic field-effect transistors,[7] and as a key synthetic intermediate for bowl-shaped PAHs.[8,9] While various fluoranthene synthetic methods, many of which utilize cross-coupling reactions, have been reported,[10−17] it is still desirable to develop facile methods for the synthesis of substituted fluoranthenes from readily available compounds.

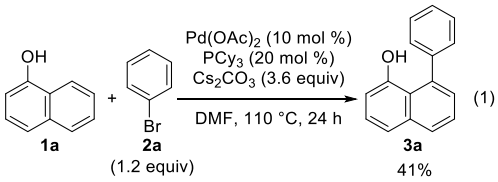
Recently, there have been many reports of C−H arylation, especially Pd-catalyzed C−H arylation with aryl halides, being used to replace conventional cross-coupling reactions to construct biphenyl units.[18–20] Direct arylation at the C−H groups does not require stoichiometric amounts of pre-formed organometallic compounds, thus making the synthesis of biphenyl structures easier and more atom-economical. Pd-catalyzed C−H arylation has also been used for efficient synthesis of PAHs.[21,22] We envisaged that a combination of inter and intramolecular C−H arylation would help realize a convenient synthetic route to fluoranthenes (Scheme 1). The first step is the Pd-catalyzed intermolecular C−H arylation of 1-naphthols with halobenzenes. This reaction, developed by Miura et al.,[23,24] site-selectively takes place at the C8 position of 1-naphthols. The second step is nonaflation of the hydroxy group through introduction of a nonafluorobutanesulfonyl (Nf) group,[25] which is more resistant to O−SO_2 cleavage than the

commonly used trifluoromethanesulfonyl group.[26,27] In addition, the nonaflating agent, NfF, is generally cheaper than the common triflating agent, Tf_2O. The third step is the Pd-catalyzed intramolecular C−H arylation of the corresponding nonaflates.[28−30] This step was designed based on the seminal work of fluoranthene synthesis by Rice and Cai.[10] Herein, we demonstrate the feasibility of this synthetic scheme, which provides a useful method for fluoranthene synthesis.

Scheme 1. Three-Step Synthesis of Fluoranthenes

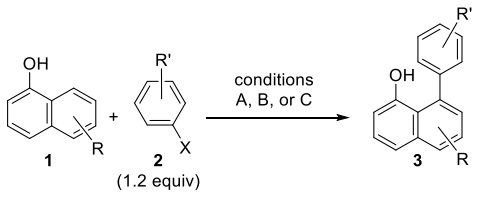


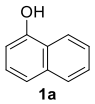
Miura's C−H arylation of 1-naphthols with halobenzenes is a convenient way of introducing an aryl group at the C8 position.[23,24] However, it was only successful with iodobenzenes; the use of bromobenzenes, which are cheaper and more easily available than iodobenzenes, resulted in poor yields (<5%).[24] To expand the scope of our fluoranthene synthesis, we first investigated the catalytic conditions of the reaction with bromobenzene. While Miura's conditions ($Pd(OAc)_2$, Cs_2CO_3, DMF) did not afford a significant amount of the desired product, PCy_3 was found to be effective as a ligand to Pd (Eq. 1).[31] Although the product yield was still modest, these catalytic conditions significantly expanded the substrate scope of halobenzenes, and bromobenzenes are now applicable to this C−H arylation.

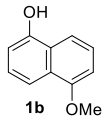
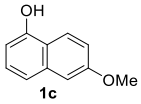
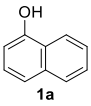
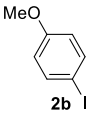
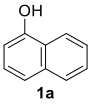
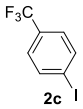
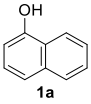
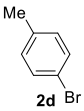
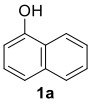
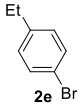
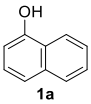
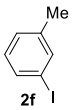
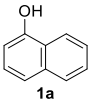
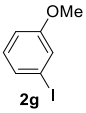
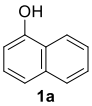
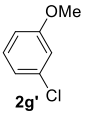
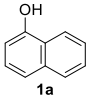
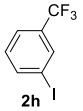


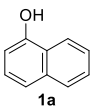
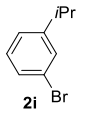
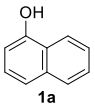
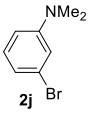
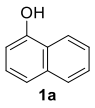
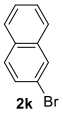
Intermolecular C−H arylation of other 1-naphthols **1** and halobenzenes **2** was carried out, and various 8-aryl-1-naphthols **3** were obtained (Table 1).[32] Both iodobenzenes and bromobenzenes were applicable, although the use of bromobenzenes often resulted in lower yields of **3**. Besides 1-naphthol (**1a**), substituted naphthols **1b** and **1c** also afforded the corresponding products in good yields (entries 2 and 3). Halobenzenes substituted at the *para*-(entries 4−7) or the *meta*-positions (entries 8−13) were used. As well as the catalytic system shown in Eq. 1, $PdCl_2(PCy_3)_2$ worked well for some bromobenzenes (condition C). Interestingly, less reactive 3-chloroanisole (**2g'**) also reacted under catalytic condition C to give **3i**, albeit in low yield (entry 10). Unfortunately, *ortho*-substituted halobenzenes, such as 2-iodotoluene, afforded the product only in very low yields (<5%).

Table 1. Intermolecular C−H Arylation of 1-Naphthols with Halobenzenes



entry	**1**	**2**	condition[a]	**3**	yield (%)
1			A	**3a**	47[b]

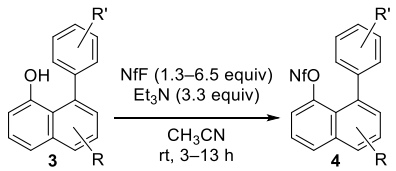
2	 1b	 2a'	A	**3b**	77[b]
3	 1c	 2a'	A	**3c**	51
4	 1a	 2b	A	**3d**	40[b]
5	 1a	 2c	A	**3e**	49
6	 1a	 2d	B	**3f**	32
7	 1a	 2e	B	**3g**	18
8	 1a	 2f	A	**3h**	65
9	 1a	 2g	A	**3i**	56
10	 1a	 2g'	C	**3i**	13
11	 1a	 2h	A	**3j**	43

12			C	**3k**	37
13			C	**3l**	38
14			B	**3m**	43

[a]A: $Pd(OAc)_2$ (2.5 mol %), Cs_2CO_3 (2.0 equiv), DMF, 110 ºC, 19−24 h. B: $Pd(OAc)_2$ (10 mol %), PCy_3 (20 mol %), Cs_2CO_3 (3.6 equiv), DMF, 110 ºC, 24 h. C: $PdCl_2(PCy_3)_2$ (10 mol %), Cs_2CO_3 (3.6 equiv), DMF, 110 ºC, 18−24 h. [b]This combination of **1** and **2** was also reported by Miura et al.[24] The yield shown here is based on our experimental results.[32]

We next performed nonaflation of **3** using NfF and Et_3N in CH_3CN (Table 2). Nonaflates **4**, the substrates for the subsequent intramolecular C−H arylation, were successfully obtained in high yields (81−98%).

Table 2. Nonaflation of 3



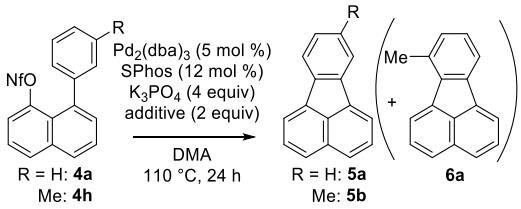
entry	**3**	**4**	yield (%)

1	**3a**	**4a**	84
2	**3b**	**4b**	98
3	**3c**	**4c**	81
4	**3d**	**4d**	90
5	**3e**	**4e**	98
6	**3f**	**4f**	86
7	**3g**	**4g**	94
8	**3h**	**4h**	94
9	**3i**	**4i**	86
10	**3j**	**4j**	93
11	**3k**	**4k**	89
12	**3l**	**4l**	97
13	**3m**	**4m**	81

We then studied the reaction conditions of another key step, the intramolecular C−H arylation of nonaflates **4** (Table 3). The initial screening of the catalytic conditions for the intramolecular C−H arylation of **4a** led to a combination of $Pd_2(dba)_3$ as the Pd source, SPhos[33] as the ligand, K_3PO_4 as the base, and DMA as the solvent. Fluoranthene (**5a**) was obtained in good yield (entry 1). To our delight, the use of 1-adamantanecarboxylic acid (1-$AdCO_2H$)[34−38] as an additive greatly improved the yield (entry 2). We also tested a *meta*-substituted substrate **4h** to identify the selectivity between **5b** and **6a**. Site-selective intramolecular C−H arylation[39−45]

proceeded to give **5b** as the main product (**5b**:**6a** = 50:1, entry 3) probably due to steric effects. The use of pivalic acid instead of 1-$AdCO_2H$ resulted in slight decreases in yield and selectivity (entry 4).

Table 3. Conditions for Intramolecular C−H Arylation



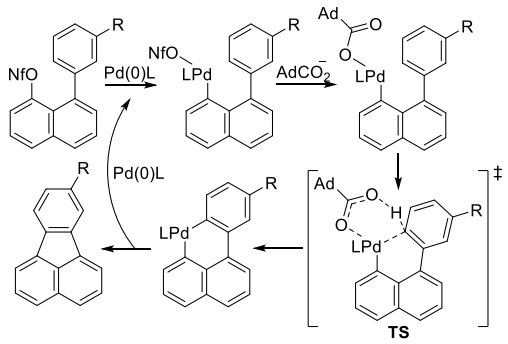
entry	**4**	additive	yield (%)[a]
1	**4a** (R = H)	−	<68[b]
2	**4a** (R = H)	1-$AdCO_2H$	98
3	**4h** (R = Me)	1-$AdCO_2H$	91 (50:1)
4	**4h** (R = Me)	*t*-$BuCO_2H$	86 (45:1)

[a]For entries 3 and 4, the products were obtained as a mixture of **5b** and **6a**. The ratio of **5b** to **6a** was determined by ^{1}H NMR and is shown in parentheses. [b]A small amount of impurity was included.

The concerted metalation−deprotonation mechanism[34-36] is assumed for the intramolecular C−H arylation (Scheme 2). The high site-selectivity is attributed to transition state **TS**, in which

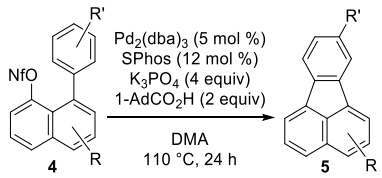
the sterically less hindered position is involved in the six-membered transition state.

Scheme 2. Assumed mechanism of intramolecular C−H arylation

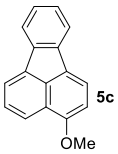
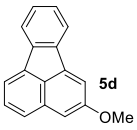
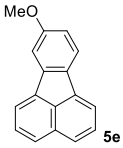
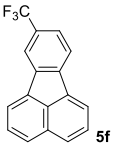
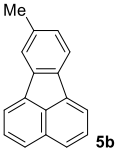
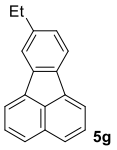
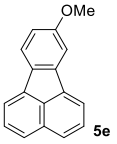
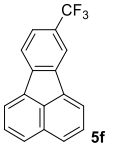
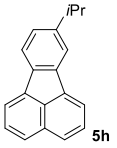


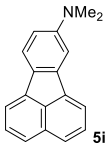
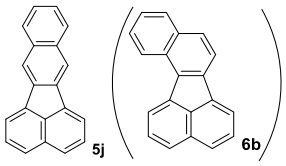
With the effective conditions in hand, we applied them to the synthesis of various substituted fluoranthenes (Table 4). In most cases, good yields were obtained. For fluoranthene synthesis using *meta*-substituted substrates (**4i−l**, entries 7−10), excellent site-selectivities (>99:1) were observed. Unfortunately, naphthyl-substituted nonaflate **4m** gave benzo[*k*]fluoranthene (**5j**) in lower yield and selectivity under these conditions (entry 11).

Table 4. Intramolecular C−H Arylation of Nonaflates



entry	**4**	**5**	yield (%)[a]

1	**4b**	 **5c**	91
2	**4c**	 **5d**	89
3	**4d**	 **5e**	73
4	**4e**	 **5f**	98
5	**4f**	 **5b**	84
6	**4g**	 **5g**	79
7	**4i**	 **5e**	92 (>99:1)
8	**4j**	 **5f**	80 (>99:1)
9	**4k**	 **5h**	70 (>99:1)

10	**4l**	 **5i**	81 (>99:1)
11	**4m**	 **5j** **6b**	26 (8)[b]

[a]The ratio of the isomers was determined by ^{1}H NMR and is shown in parentheses. [b]Yield of **6b**.

In conclusion, we developed a strategy for the three-step synthesis of fluoranthenes consisting of Pd-catalyzed inter and intramolecular C−H arylation. Fluoranthenes were produced in acceptable yields without using stoichiometric amounts of organometallic reagents. Various 1-naphthols and halobenzenes, including bromobenzenes, were successfully used as the starting materials. While only mono-substituted fluoranthenes were synthesized in this work, this three-step procedure is expected to be easily applied to the synthesis of multi-substituted fluoranthenes. Considering the wide availability of 1-naphthols and halobenzenes together with the highly site-selective intramolecular C−H arylation step, this synthetic method will provide a useful route to various fluoranthenes. Furthermore, the strategy could be applied to the synthesis of other PAHs.

EXPERIMENTAL SECTION:

All reactions were conducted under an argon atmosphere. All of the starting materials, catalysts, and reagents are commercially available and were used as purchased without further purification. DMF, CH_3CN, and DMA were purchased as anhydrous solvents. Melting points are uncorrected. For ^1H NMR, tetramethylsilane (TMS) ($\delta = 0$) in $CDCl_3$ was used as the internal standard. For ^{13}C NMR, $CDCl_3$ ($\delta = 77.0$) served as an internal standard. Compounds **1b**[46] and **1c**[47,48] were prepared according to procedures reported in the literature.

General procedure for intermolecular C−H arylation (condition A).[24] To a suspension of 1-naphthol, Cs_2CO_3 (2 equiv), and $Pd(OAc)_2$ (2.5 mol %) in DMF (5.0 mL/1 mmol 1-naphthol) was added an iodoarene (1.2 equiv) at rt. The mixture was heated at 110 ºC and stirred for 19−24 h. After cooling to rt, the mixture was diluted with EtOAc, washed with 1 M aq. HCl, water, and brine, dried over Na_2SO_4, and concentrated under vacuum. Purification by chromatography gave the desired product.

General procedure for intermolecular C−H arylation (condition B). To a suspension of 1-naphthol, Cs_2CO_3 (3.6 equiv), $Pd(OAc)_2$ (10 mol %), and PCy_3 (20 mol %) in DMF (8.0 mL/1 mmol 1-naphthol) was added a bromoarene (1.2 equiv) at rt. The mixture was heated at 110 ºC and stirred for 24 h. After cooling to rt, the mixture was diluted with EtOAc, washed with 1 M aq. HCl, water, and brine, dried over Na_2SO_4, and concentrated under vacuum. Purification by

chromatography gave the desired product.

General procedure for intermolecular C−H arylation (condition C). To a suspension of 1-naphthol, Cs_2CO_3 (3.6 equiv), and $PdCl_2(PCy_3)_2$ (10 mol %) in DMF (8.0 mL/1 mmol 1-naphthol) was added a bromoarene (1.2 equiv) at rt. The mixture was heated at 110 ºC and stirred for 18−24 h. After cooling to rt, the mixture was diluted with EtOAc, washed with 1 M aq. HCl, water, and brine, dried over Na_2SO_4, and concentrated under vacuum. Purification by chromatography gave the desired product.

8-Phenylnaphthalen-1-ol (3a)[24] (Eq. 1 and Table 1, entry 1). 1-Naphthol (**1a**) (72.1 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition B for 24 h. After column chromatography twice (SiO_2, hexane/EtOAc = 100/1−25/1 and SiO_2, hexane/$CHCl_3$ = 20/1), **3a** (45.6 mg, 41%) was obtained as a yellow oil. Alternatively, 1-naphthol (**1a**) (72.1 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under conditions A for 19 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1), **3a** (51.2 mg, 47%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (1H, s), 6.92 (1H, dd, J = 1.5, 7.3 Hz), 7.21 (1H, dd, J = 1.5, 7.3 Hz), 7.40 (1H, t, J = 7.8 Hz), 7.44 (1H, t, J = 8.3 Hz), 7.49−7.51 (6H, m), 7.86 (1H, dd, J = 1.5, 8.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 111.8, 121.0, 121.3, 124.2, 126.8, 128.5, 128.6, 128.7, 128.9, 129.4, 135.7, 136.1, 141.3, 153.0 ppm.

5-Methoxy-8-phenylnaphthalen-1-ol (3b) (Table 1, entry 2). Naphthol **1b** (256 mg, 1.5

mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1), **3b** (289 mg, 77%) was obtained as a brown solid. Mp. 95.3−96.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (3H, s), 5.44 (1H, s), 6.81 (1H, d, *J* = 8.0 Hz), 6.94 (1H, d, *J* = 7.6 Hz), 7.11 (1H, d, *J* = 7.6 Hz), 7.40 (1H, t, *J* = 8.0), 7.44−7.54 (5H, m), 7.96 (1H, d, *J* = 8.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.6, 103.0, 112.6, 114.6, 122.0, 126.3, 127.5, 128.26, 128.28, 128.4, 128.9, 129.8, 141.4, 152.9, 155.4 ppm; IR (ATR) 615, 698, 750, 1042, 1244, 3429, 3472 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{15}O_2$ ([M+H]$^+$) 251.1067; found: 251.1079.

6-Methoxy-8-phenylnaphthalen-1-ol (3c) (Table 1, entry 3). Naphthol **1c** (321 mg, 1.4 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1) and preparative TLC twice (SiO_2, hexane/EtOAc = 8/1 and 4/1), **3c** (183 mg, 51%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (3H, s), 5.33 (1H, s), 6.77 (1H, d, *J* = 6.8 Hz), 6.90 (1H, d, *J* = 2.4 Hz), 7.18 (1H, d, *J* = 2.4 Hz), 7.32-7.45 (2H, m), 7.52 (5H, s) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.3, 106.6, 109.8, 116.9, 119.9, 120.9, 127.6, 128.7, 129.0, 129.3, 137.3, 138.0, 140.9, 153.3, 156.2 ppm; IR (ATR): 602, 619, 768, 812, 1458, 2926, 2963, 3044 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{15}O_2$ ([M+H]$^+$) 251.1067; found: 251.1074.

8-(4-Methoxyphenyl)naphthalen-1-ol (3d) (Table 1, entry 4). 1-Naphthol (**1a**) (145 mg,

1.0 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1), **3d** (100 mg, 40%) was obtained as a yellow solid. Mp. 114.1−114.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 5.73 (1H, s), 6.96 (1H, d, *J* = 7.8 Hz), 7.07 (2H, d, *J* = 8.3 Hz), 7.22 (1H, t, *J* = 6.8), 7.39−7.50 (4H, m), 7.50−7.58 (1H, m), 7.88 (1H, d, *J* = 8.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ ppm 55.3, 111.6, 114.4, 120.8, 121.5, 124.8, 126.8, 128.5, 128.7, 130.7, 133.0, 135.7, 135.8, 153.2, 159.8 ppm; IR (ATR): 563, 768, 827, 1177, 1233, 3460 cm^{-1}; HRMS (DRAT-TOF): *m/z* calcd for $C_{17}H_{15}O_2$ ([M+H]$^+$) 251.1067; found: 251.1083.

8-(4-(Trifluoromethyl)phenyl)naphthalen-1-ol (3e) (Table 1, entry 5). 1-Naphthol (**1a**) (72.2 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1) and preparative TLC (SiO_2, hexane/CH_2Cl_2 = 1/1), **3e** (70.9 mg, 49%) was obtained as a white solid. Mp. 72.8−74.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (1H, s), 5.91 (1H, d, *J* = 7.8 Hz), 7.23 (1H, d, *J* = 6.8 Hz), 7.43 (1H, t, *J* = 8.1 Hz), 7.50 (1H, t, *J* = 7.5 Hz), 7.57 (1H, d, *J* = 8.3 Hz) , 7.63 (2H, d, *J* = 7.8 Hz), 7.76 (2H, d, *J* = 8.3 Hz), 7.92 (1H, d, *J* = 8.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 112.0, 121.2, 121.5, 124.1 (q, $^1J_{CF}$ = 272.0 Hz), 125.0, 125.3 (q, $^3J_{CF}$ = 3.3 Hz), 126.9, 128.8, 129.1, 129.8, 130.1 (q, $^2J_{CF}$ = 33.0 Hz), 135.4, 135.8, 146.2, 152.4 ppm; IR (ATR): 615, 758, 820, 1061, 1074, 1107, 1321, 3051 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{12}F_3O$ ([M+H]$^+$)

289.0835; found: 289.0837.

8-(4-Methylphenyl)naphthalen-1-ol (3f) (Table 1, entry 6). 1-Naphthol (**1a**) (72.2 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition B for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1, and then NH Silica, hexane/$CHCl_3$ = 20/1−10/1), **3f** (39.9 mg, 32%) was obtained as a yellow solid. Mp. 81.4−83.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (3H, s), 5.59 (1H, s), 6.93 (1H, d, *J* = 7.3 Hz), 7.21 (1H, d, *J* = 6.8 Hz), 7.35 (2H, d, *J* = 8.0 Hz), 7.39−7.49 (4H, m), 7.52 (1H, d, *J* = 8.3 Hz), 7.87 (1H, d, *J* = 8.3 Hz) ppm; ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ 21.3, 111.7, 120.9, 121.4, 124.8, 126.8, 128.5, 128.6, 129.3, 129.7, 135.7, 136.2, 138.2, 138.6, 153.2 ppm; IR (ATR): 617, 764, 820, 1233, 1389, 3478 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{15}O$ ($[M+H]^+$) 235.1117; found: 235.1116.

8-(4-Ethylphenyl)naphthalen-1-ol (3g) (Table 1, entry 7). 1-Naphthol (**1a**) (144 mg, 1.0 mmol) was subjected to the intermolecular C−H arylation under condition B for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−50/1, and then NH Silica, hexane/$CHCl_3$ = 1/0−10/1) and preparative TLC (SiO_2, hexane/$CHCl_3$ = 1/1), **3g** (32.2 mg, 18%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (3H, t, *J* = 7.6 Hz), 2.77 (2H, q, *J* = 7.3 Hz), 5.99 (1H, s), 6.92 (1H, d, *J* = 7.8 Hz), 7.21 (1H, d, *J* = 6.8 Hz), 7.32−7.48 (6H, m), 7.51 (1H, d, *J* = 7.8 Hz), 7.86 (1H, d, *J* = 8.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.4, 28.6, 111.7, 120.9, 121.4, 124.8, 126.8, 128.47, 128.50, 128.6, 129.4, 135.7, 136.2, 138.3, 144.9, 153.2 ppm;

IR (ATR): 764, 819, 1233, 1389, 1454, 3497 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{18}H_{17}O$ ($[M+H]^+$) 249.1274; found: 249.1278.

8-(3-Methylphenyl)naphthalen-1-ol (3h) (Table 1, entry 8). 1-Naphthol (**1a**) (721 mg, 5.0 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−50/1), **3h** (761 mg, 65%) was obtained as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (3H, s), 5.54 (1H, s), 6.91 (1H, dd, *J* =1.2, 7.6 Hz), 7.19 (1H, dd, *J* =1.2, 7.1 Hz), 7.32−7.44 (4H, m), 7.49 (1H, dd, *J* =1.2, 8.0Hz), 7.84 (1H, dd, *J* = 8.3, 1.0 Hz) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.4, 111.7, 120.9, 121.3, 124.7, 126.4, 126.8, 128.2, 128.6, 128.8, 129.3, 130.1, 125.7, 136.2, 138.8, 141.2, 153.1 ppm; IR (ATR): 712, 764, 822, 1186, 1233, 1387, 3497 cm^{-1}; HRMS (ESI-TOF): *m/z* calcd for $C_{17}H_{13}O$ ($[M-H]^-$) 233.0972; found: 233.0974.

8-(3-Methoxyphenyl)naphthalen-1-ol (3i) (Table 1, entries 9 and 10). 1-Naphthol (**1a**) (72.2 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−20/1), **3i** (70.1 mg, 56%) was obtained as a yellow oil. Alternatively, 1-naphthol (**1a**) (72.1 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under conditions C for 24 h. After column chromatography three times (SiO_2, hexane/EtOAc = 100/1, NH Silica, hexane/$CHCl_3$ = 10/3, and NH Silica, hexane/$CHCl_3$ = 10/1) and preparative TLC (SiO_2, hexane/EtOAc = 3/1), **3i** (16.2 mg, 13%) was

obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (3H, s), 5.58 (1H, s), 6.92 (1H, dd, J = 7.3, 1.0), 7.03−7.09 (3H, m), 7.22 (1H, dd, J = 6.8, 1.5 Hz), 7.38−7.46 (3H, m), 7.50 (1H, dd, J = 8.0, 1.5), 7.86 (1H, dd, J = 8.3, 1.5 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.4, 111.9, 114.5, 114.8, 121.0, 121.3, 121.5, 124.8, 126.9, 128.2, 128.8, 130.1, 135.6, 136.0, 142.7, 153.0, 159.7 ppm; IR (ATR): 708, 766, 822, 1038, 1219, 1578, 2942, 3482 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{15}O_2$ ($[M+H]^+$) 251.1067; found: 251.1078.

8-(3-(Trifluoromethyl)phenyl)naphthalen-1-ol (3j) (Table 1, entry 11). 1-Naphthol (**1a**) (72.3 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition A for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−30/1) and preparative TLC (SiO_2, hexane/$CHCl_3$ = 1/1), **3j** (61.7 mg, 43%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (1H, s), 6.90 (1H, d, J = 7.3 Hz), 7.24 (1H, d, J = 6.8 Hz), 7.42 (1H, t, J = 8.0 Hz), 7.49 (1H, t, J = 7.6 Hz), 7.55 (1H, d, J = 7.8 Hz), 7.58−7.66 (1H, m), 7.70 (1H, d, J = 4.0 Hz), 7.74 (1H, d, J = 8.0 Hz), 7.79 (1H, s), 7.91 (1H, d, J = 8.2 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 111.9, 121.1, 121.3, 124.5 (q, $^1J_{CF}$ = 273.1 Hz), 124.7 (q, $^3J_{CF}$ = 4.0 Hz), 125.1, 126.3 (q, $^3J_{CF}$ = 4.0 Hz), 126.9, 128.8, 129.0, 129.2, 130.7 (q, $^2J_{CF}$ = 32.1 Hz), 132.7, 135.4, 135.9, 143.3, 152.5 ppm; IR (ATR): 507, 704, 766, 1067, 1096, 1119, 1161, 3049, 3539 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{12}F_3O$ ($[M+H]^+$) 289.0835; found: 289.0851.

8-(3-Isopropylphenyl)naphthalen-1-ol (3k) (Table 1, entry 12). 1-Naphthol (**1a**) (72.1

mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition C for 18 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1) and preparative TLC (SiO_2, hexane/EtOAc = 8/1), **3k** (48.7 mg, 37%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (6H, d, *J* = 6.8 Hz), 3.01 (1H, spt, *J* = 6.8 Hz), 5.60 (1H, s), 6.95 (1H, dd, *J* = 7.3 1.0 Hz), 7.25 (1H, dd, *J* = 6.8, 1.0 Hz), 7.32−7.51 (6H, m), 7.53 (1H, d, *J* = 7.8 Hz), 7.89 (1H, d, *J* = 7.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.9, 34.1, 111.7, 120.9, 121.3, 124.8, 126.76, 126.82, 126.84, 127.5, 128.3, 128.6, 129.0, 135.7, 136.5, 141.2, 149.8, 153.2 ppm; IR (ATR): 712, 766, 826, 1233, 1389, 2959, 3497 cm^{-1}; HRMS (ESI-TOF): *m/z* calcd for $C_{19}H_{17}O$ ([M−H]$^-$) 261.1274; found: 261.1277.

8-(3-(*N*,*N*-Dimethylamino)phenyl)naphthalen-1-ol (3l) (Table 1, entry 13). 1-Naphthol (**1a**) (72.1 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition C for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1−40/1), **3l** (50.4 mg, 38%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (6H, s), 5.97 (1H, s), 6.76−6.83 (3H, m), 6.91 (1H, d, *J* = 8.0 Hz), 7.24 (1H, dd, *J* = 8.0, 4.0 Hz), 7.35 (1H, t, *J* = 6.0), 7.46 (1H, d, *J* = 8.0), 7.42 (1H, d, *J* = 8.0), 7.48 (1H, d, *J* = 8.0 Hz), 7.84 (1H, dd, *J* = 8.0, 6.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 40.3, 111.7, 112.3, 112.8, 116.8, 120.7, 121.4, 124.8, 126.8, 127.9, 128.5, 129.8, 135.6, 137.1, 142.1, 150.5, 153.4 ppm; IR (ATR): 422, 455, 492, 706, 764, 1234, 1593, 3460 cm^{-1}; HRMS (DRAT-TOF): *m/z* calcd for $C_{18}H_{18}NO$ ([M+H]$^+$) 264.1383;

found: 264.1388.

[1,2'-Binaphthalen]-8-ol (3m) (Table 1, entry 14). 1-Naphthol (**1a**) (72.1 mg, 0.50 mmol) was subjected to the intermolecular C−H arylation under condition B for 24 h. After column chromatography (SiO_2, hexane/EtOAc = 100/1) and preparative TLC (SiO_2, hexane/$CHCl_3$ = 1/1), **3m** (58.5 mg, 43%) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (1H, s), 6.93 (1H, d, *J* = 7.3 Hz), 7.30 (1H, d, *J* = 7.3 Hz),7.39−7.46 (1H, m), 7.49 (1H, t, *J* = 7.6 Hz), 7.51 (1H, d, *J* = 8.3), 7.58−7.66 (3H, m), 7.88−7.93 (2H, m), 7.94−8.04 (3H, m) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 111.8, 121.1, 121.5, 124.9, 126.8, 126.9, 127.1, 127.3, 127.9, 128.2, 128.6, 128.76, 128.83, 132.9, 133.0, 135.8, 136.2, 138.9, 153.1 ppm (One carbon signal is overlapped.); IR (ATR): 741, 756, 818, 1260, 1325, 1580, 3530 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{20}H_{15}O$ ($[M+H]^+$) 271.1117; found: 271.1126.

General procedure for nonaflation. To a solution of an 8-aryl-1-naphthol in CH_3CN (2.6 mL/1 mmol 8-aryl-1-naphthol) was added Et_3N (3.3 equiv) at rt. After cooling to 0 ºC, NfF (1.3−6.5 equiv) was added dropwise for 1 min. The reaction mixture was allowed to warm to rt and was then stirred for 3−13 h, after which 1 M aq. HCl was added. The mixture was extracted with EtOAc, washed with water and brine, dried over Na_2SO_4, and concentrated under vacuum. Purification by chromatography gave the desired product.

8-Phenylnaphthalen-1-yl nonafluorobutanesulfonate (4a) (Table 2, entry 1). Naphthol

3a (110 mg, 0.50 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 4 h. After column chromatography twice (SiO_2, hexane/EtOAc = 100/1−40/1 and hexane/EtOAc = 100/1), **4a** (211 mg, 84%) was obtained as a pale yellow solid. Mp.77.7−78.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.50 (8H, m), 7.60 (1H, t, *J* = 7.6 Hz), 7.92 (1H, dd, *J* = 8.3, 1.0 Hz), 7.97 (1H, dd, *J* = 8.3, 1.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.7, 124.5, 125.0, 126.5, 127.4, 127.8, 128.0, 129.6, 129.7, 132.2, 136.3, 137.4, 161.6, 146.0 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 527, 563, 588, 696, 764, 1140, 1192 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{20}H_{12}F_9O_3S$ ($[M+H]^+$) 503.0358; found: 503.0344.

5-Methoxy-8-phenylnaphthalen-1-yl nonafluorobutanesulfonate (4b) (Table 2, entry 2). Naphthol **3b** (228 mg, 0.91 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 5 h. After column chromatography twice (SiO_2, hexane/EtOAc = 50/1), **4b** (475 mg, 98%) was obtained as a yellow solid. Mp. 107.8−109.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (3H, s), 6.97 (1H, d, *J* = 8.3 Hz), 7.31−7.69 (8H, m), 8.49 (1H, dd, *J* = 7.3, 2.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.8, 104.7, 120.3, 123.5, 124.3, 125.4, 127.0, 127.7, 128.3, 129.4, 129.8, 132.3, 141.8, 145.9, 154.7 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 511, 571, 733, 766, 1020, 1140, 1194, 1425 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_4S$ ($[M+H]^+$) 533.0464; found: 533.0459.

6-Methoxy-8-phenylnaphthalen-1-yl nonafluorobutanesulfonate (4c) (Table 2, entry 3).

Naphthol **3c** (227 mg, 0.91 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 7 h. After preparative TLC three times (SiO_2, hexane/EtOAc = 8/1, hexane/CH_2Cl_2 = 1/1 twice), **4c** (393 mg, 81%) was obtained as a pale yellow solid. Mp. 111.3−112.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 (3H, s), 7.19 (1H, d, *J* = 2.4 Hz), 7.23 (1H, d, *J* = 2.4 Hz), 7.31 (1H, d, *J* = 7.8 Hz), 7.39−7.52 (6H, m), 7.85 (1H, d, *J* = 8.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.4, 106.1, 117.2, 120.1, 124.5, 125.6, 127.5, 127.8, 128.3, 129.5, 138.0, 139.3, 141.2, 146.3, 157.4 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 563, 839, 1003, 1136, 1177, 1192, 1425 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_4S$ ([M+H]$^+$) 533.0464; found: 533.0487.

8-(4-Methoxyphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4d) (Table 2, entry 4). Naphthol **3d** (83.3 mg, 0.33 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 7 h. After preparative TLC (SiO_2, hexane/EtOAc = 5/1), **4d** (159 mg, 90%) was obtained as a pale yellow solid. Mp. 115.4−116.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (3H, s), 7.01 (2H, d, *J* = 8.7 Hz), 7.36 (2H, d, *J* = 8.7 Hz), 7.43−7.56 (3H, m), 7.60 (1H, t, *J* = 7.8 Hz), 7.91 (1H, d, *J* = 7.8 Hz), 7.97 (1H, d, *J* = 7.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.3, 113.4, 119.8, 124.7, 124.9, 126.5, 127.6, 129.7, 130.8, 132.1, 134.1, 136.4, 137.2, 146.0, 159.4 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 561, 584, 766, 820, 1136, 1180, 1242 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_4S$ ([M+H]$^+$) 533.0464; found: 533.0453.

8-(4-(Trifluoromethyl)phenyl)naphthalen-1-yl nonafluorobutanesulfonate (4e) (Table 2, entry 5). Naphthol **3e** (199 mg, 0.69 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 7 h. After preparative TLC twice (SiO_2, hexane/EtOAc = 8/1 twice) and column chromatography (SiO_2, hexane/CH_2Cl_2 = 1/0−20/1), **4e** (387 mg, 98%) was obtained as a pale yellow solid. Mp. 108.1−108.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.60 (5H, m), 7.64 (1H, t, J = 7.6 Hz), 7.72 (2H, d, J = 8.3 Hz), 8.00 (2H, t, J = 7.3 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 120.1, 124.35, 124.39 (q, $^1J_{CF}$ = 270.8 Hz), 124.8 (q, $^3J_{CF}$ = 4.2 Hz), 125.4, 126.5, 128.7, 129.2, 129.86 (q, $^2J_{CF}$ = 23.1 Hz), 129.90, 132.0, 135.9, 136.3, 145.3, 145.4 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 727, 764, 826, 1136, 1323, 1431 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{10}F_{12}O_3S$ ($M^{+\cdot}$) 570.0154; found: 570.0186.

8-(4-Methylphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4f) (Table 2, entry 6). Naphthol **3f** (47.8 mg, 0.20 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 7 h. After preparative TLC twice (SiO_2, hexane/EtOAc = 8/1, hexane/EtOAc = 5/1), **4f** (90.8 mg, 86%) was obtained as a pale yellow solid. Mp. 97.1−98.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (3H, s), 7.28 (2H, d, J = 8.0 Hz), 7.33 (2H, d, J = 8.0 Hz), 7.44−7.57 (3H, m), 7.61 (1H, t, J = 7.6 Hz), 7.92 (1H, d, J = 7.8 Hz), 7.99 (1H, d, J = 4.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.1, 119.8, 124.7, 124.9, 126.5, 127.7, 128.5, 129.5, 129.6, 132.1, 136.3, 137.2, 137.5, 138.7, 146.0 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 571, 764, 814, 1136,

1188, 1431 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_3S$ ($[M+H]^+$) 517.0514; found: 517.0502.

8-(4-Ethylphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4g) (Table 2, entry 7). Naphthol **3g** (33.7 mg, 0.14 mmol) was subjected to the nonaflation with 1.3 equiv of NfF for 7 h. After preparative TLC (SiO_2, hexane/$CHCl_3$ = 2/1), **4g** (67.6 mg, 94%) was obtained as a pale yellow solid. Mp. 111.1−112.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (3H, t, *J* = 7.8 Hz), 2.75 (2H, q, *J* = 7.8 Hz), 7.31 (4H, m), 7.47 (1H, d, *J* = 8.0 Hz), 7.52 (2H, t, *J* = 8.0 Hz), 7.60 (1H, t, *J* = 8.0 Hz), 7.92 (1H, d, *J* = 8.3 Hz), 7.97 (1H, d, *J* = 7.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.6, 28.7, 119.7, 124.7, 124.9, 126.5, 127.3, 127.7, 129.55, 129.57, 132.0, 136.3, 137.6, 138.9, 143.6, 145.8 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 569, 698, 725, 764, 824, 1136, 1186, 1204, 1431 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{22}H_{16}F_9O_3S$ ($[M+H]^+$) 531.0671; found: 531.0659.

8-(3-Methylphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4h) (Table 2, entry 8). Naphthol **3h** (116 mg, 0.50 mmol) was subjected to the nonaflation with 2.0 equiv of NfF for 8 h. After preparative TLC (SiO_2, hexane/EtOAc = 8/1), **4h** (240 mg, 94%) was obtained as a yellow solid. Mp. 55.6−56.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s), 7.22 (3H, m), 7.34 (1H, t, *J* = 3.8, 8.0 Hz), 7.48 (3H, m), 7.56 (1H, t, *J* = 7.8, 8.0 Hz), 7.88 (1H, dd, *J* = 1.6, 8.4 Hz) , 7.92 (1H, t, *J* = 4.3, 4.6 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.3, 119.6, 124.6, 124.9,

126.5, 126.7, 127.7, 127.9, 128.0, 130.0, 130.4, 132.0, 136.3, 137.4, 137.6, 141.6, 146.0 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 569, 583, 762, 1126, 1140, 1192, 1425 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_3S$ ($[M+H]^+$) 517.0514; found: 517.0498.

8-(3-Methoxyphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4i) (Table 2, entry 9). Naphthol **3i** (71.0 mg, 0.28 mmol) was subjected to the nonaflation with 6.5 equiv of NfF for 6 h. After preparative TLC (SiO_2, hexane/EtOAc = 8/1), **4i** (129 mg, 86%) was obtained as a yellow solid. Mp. 67.8−69.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (3H, s), 6.95-6.99 (3H, m), 7.35 (1H, t, *J* = 8.0 Hz), 7.46−7.52 (3H, m), 7.59 (1H, t, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 8.0 Hz) , 7.97 (1H, d, *J* = 4.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.3, 113.0, 115.6, 119.7, 122.3, 124.5, 125.0, 126.5, 128.1, 128.8, 129.6, 131.9, 136.2, 137.2, 142.9, 145.9, 159.2 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 573, 586, 698, 727, 766, 1140, 1192, 1422 cm^{-1}; HRMS (ESI-TOF): *m/z* calcd for $C_{21}H_{14}F_9O_4S$ ($[M+H]^+$) 533.0464; found: 533.0495.

8-(3-(Trifluoromethyl)phenyl)naphthalen-1-yl nonafluorobutanesulfonate (4j) (Table 2, entry 10). Naphthol **3j** (236 mg, 0.82 mmol) was subjected to the nonaflation with 2.0 equiv of NfF for 6 h. After preparative TLC (SiO_2, hexane/EtOAc = 10/1), **4j** (433 mg, 93%) was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.65 (6H, m), 7.71 (2H, s), 8.00 (2H, t, *J* = 8.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 120.0, 124.2 (q, $^3J_{CF}$ = 3.3 Hz), 124.27 (q,

$^{1}J_{CF}$ = 270.8 Hz), 124.29, 125.4, 126.5, 128.4, 128.7, 129.7, 130.3 (q, $^{2}J_{CF}$ = 32.1 Hz), 132.2, 132.8, 135.7, 136.3, 142.5, 145.5 ppm (One aromatic carbon signal is overlapped. The perfluorobutyl carbons were not observed.); IR (ATR): 586, 762, 827, 1009, 1125, 1198, 1331 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{21}H_{10}F_{12}O_3S$ ($M^{+\cdot}$) 570.0154; found: 570.0144.

8-(3-Isopropylphenyl)naphthalen-1-yl nonafluorobutanesulfonate (4k) (Table 2, entry 11). Naphthol **3k** (57.0 mg, 0.22 mmol) was subjected to the nonaflation with 2.0 equiv of NfF for 8 h. After preparative TLC (SiO_2, hexane/EtOAc = 10/1), **4k** (106 mg, 89%) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (3H, d, *J* = 1.3 Hz), 1.32 (3H, d, *J* = 2.4 Hz), 2.95 (1H, spt, *J* = 6.8 Hz), 7.23 (1H, dd, *J* = 1.6, 1.8 Hz), 7.27 (2H, dd, *J* = 1.6, 7.0 Hz), 7.37 (1H, d, *J* = 8.0 Hz), 7.40−7.55 (3H, m), 7.58 (1H, t, *J* = 7.6, 7.8 Hz) , 7.89 (1H, dd, *J* = 1.6, 8.4 Hz), 7.94 (1H, dd, *J* = 1.2, 8.0 Hz) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 23.8, 24.0, 34.2, 119.7, 124.6, 124.9, 125.5, 126.5, 127.1, 127.7, 127.8, 128.0, 129.6, 132.0, 136.3, 137.8, 141.5, 146.1, 148.3 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 584, 764, 826, 1009, 1142, 1196, 1227, 2963 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{23}H_{18}F_9O_3S$ ($[M+H]^+$) 545.0827; found: 545.0810.

8-(3-(*N*,*N*-Dimethylamino)phenyl)naphthalen-1-yl nonafluorobutanesulfonate (4l) (Table 2, entry 12). Naphthol **3l** (83.4 mg, 0.32 mmol) was subjected to the nonaflation with 3.0 equiv of NfF for 13 h. After preparative TLC (SiO_2, hexane/EtOAc = 4/1), **4l** (167 mg, 97%) was

obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (6H, s), 6.75 (1H, d, *J* = 8.0 Hz), 6.80 (2H, dd, *J* = 8.0, 1.2 Hz), 7.28 (1H, t, *J* = 8.0 Hz), 7.43−7.58 (4H, m), 7.88 (1H, dd, *J* = 8.0, 4.0 Hz), 7.93 (1H, dd, *J* = 8.0, 4.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 40.8, 112.1, 114.7, 118.7, 119.5, 124.7, 124.8, 126.5, 127.7, 128.4, 129.5, 131.8, 136.3, 138.3, 142.4, 146.1, 150.5 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 571, 584, 698, 826, 1011, 1142, 1196 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{22}H_{17}F_9NO_3S$ ($[M+H]^+$) 546.0780; found: 546.0784.

[1,2'-Binaphthalen]-8-yl nonafluorobutanesulfonate (4m) (Table 2, entry 13). Naphthol **3m** (37.0 mg, 0.14 mmol) was subjected to the nonaflation with 3.0 equiv of NfF for 4 h. After preparative TLC (SiO_2, hexane/EtOAc = 4/1), **4m** (61.5 mg, 81%) was obtained as a pale yellow solid. Mp. 120.1−121.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.54 (5H, m), 7.56 (1H, dd, *J* = 7.0, 1.2 Hz), 7.61 (1H, t, *J* = 8.0 Hz), 7.86−7.90 (4H, m), 7.93 (1H, dd, *J* = 8.2, 1.2 Hz), 7.97 (1H, dd, *J* = 8.0, 1.2 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 119.8, 124.7, 125.1, 125.9, 126.1, 126.6, 127.2, 127.6, 127.1, 128.0, 128.1, 128.4, 129.6, 132.4, 132.7, 133.3, 136.3, 137.4, 139.2, 145.9 ppm (The perfluorobutyl carbons were not observed.); IR (ATR): 584, 725, 746, 764, 822, 1138, 1188, 1429 cm^{-1}; HRMS (ESI-TOF): *m/z* calcd for $C_{24}H_{12}F_9O_3S$ ($[M-H]^-$) 551.0369; found: 551.0343.

General procedure for intramolecular C−H arylation. A suspension of an

8-aryl-1-naphthyl nonaflate, $Pd_2(dba)_3$ (5 mol %), SPhos (12 mol %), K_3PO_4 (4.0 equiv), and 1-$AdCO_2H$ (2.0 equiv) in DMA (4.0 mL/1 mmol 8-aryl-1-naphthyl nonaflate) was heated at 110 °C for 24 h. After cooling to rt, 1 M aq. HCl was added. The mixture was extracted with EtOAc three times, and the combined organic phases were washed with water and brine, dried over Na_2SO_4, and concentrated under vacuum. Purification by chromatography gave the desired product.

Fluoranthene (5a)[15] **(Table 3, entry 2).** Nonaflate **4a** (50.2 mg, 0.10 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1), **5a** (19.9 mg, 98%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (2H, dd, *J* =5.2, 2.8 Hz), 7.62 (2H, t, *J* =8.4 Hz), 7.83 (2H, d, *J* =8.4 Hz), 7.89−7.94 (4H, m) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 120.0, 121.5, 126.6, 127.5, 127.9, 130.0, 132.4, 136.9, 139.4 ppm.

8-Methylfluoranthene (5b)[49] **(Table 3, entry 3 and Table 4, entry 5).** Nonaflate **4h** (103 mg, 0.20 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC three times (SiO_2, hexane/EtOAc = 10/1, three times), methylfluoranthenes (39.3 mg, 91%) were obtained as an orange solid. The ratio of **5b** to **6a** was determined by ^{1}H NMR to be 50:1. Alternatively, nonaflate **4f** (58.0 mg, 0.11 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1), **5b** (20.5 mg, 84%) was obtained as a yellow solid. **5b**:[49] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (3H, s), 7.18 (1H, dd, *J* = 8.0, 8.4

Hz), 7.60 (1H, dd, *J* = 2.8, 6.2 Hz), 7.62 (1H, t, *J* = 2.8, 6.2 Hz), 7.73 (1H, s), 7.80 (3H, m), 7.88 (1H, d, *J* = 2.8 Hz), 7.90 (1H, d, *J* = 2.8 Hz) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.8, 119.5, 119.8, 121.2, 122.3, 126.1, 126.5, 127.85, 127.93, 128.3, 130.0, 132.6, 136.9, 137.07, 137.08, 137.5, 139.7 ppm. **6a**:[49] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (3H, s), 7.19 (1H, d, *J* = 7.6 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 7.52−7.54 (2H, m), 7.62−7.72 (2H, m), 7.80 (1H, d, *J* = 7.2 Hz), 7.85 (1H, dd, *J* = 3.2, 8.4 Hz), 7.96 (1H, d, *J* = 6.8 Hz), 8.00 (1H, d, *J* = 6.8 Hz) ppm.

3-Methoxyfluoranthene (5c) (Table 4, entry 1). Nonaflate **4b** (347 mg, 0.65 mmol) was subjected to the intramolecular C−H arylation. After column chromatography (SiO_2, hexane/$CHCl_3$ = 20/1−10/1) and preparative TLC (SiO_2, hexane/$CHCl_3$ = 1/1), **5c** (138 mg, 91%) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.06 (3H, s), 6.88 (1H, d, *J* = 7.8 Hz), 7.30−7.44 (2H, m), 7.64 (1H, dd, *J* = 8.1, 7.1 Hz), 7.80−7.88 (2H, m), 7.92 (1H, d, *J* = 6.8 Hz), 7.98 (1H, d, *J* = 6.8 Hz), 8.13 (1H, d, *J* = 8.3 Hz) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 55.8, 105.6, 120.4, 120.6, 121.1, 121.4, 121.7, 122.7, 126.2, 126.9, 127.4, 129.4, 133.7, 136.3, 139., 139.3, 157.0 ppm; IR (ATR): 748, 756, 775, 1069, 1150, 1238, 1422 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{13}O$ ($[M+H]^+$) 233.0961; found: 233.0976.

2-Methoxyfluoranthene (5d) (Table 4, entry 2). Nonaflate **4c** (107 mg, 0.20 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 8/1), **5d** (41.5 mg, 89%) was obtained as a yellow solid. Mp. 75.3−76.4 ºC; ^{1}H NMR (400 MHz,

$CDCl_3$): δ 4.00 (3H, s), 7.16 (1H, s), 7.36−7.44 (2H, m), 7.57−7.66 (2H, m), 7.74 (1H, d, *J* = 7.8 Hz), 7.81 (1H, d, *J* = 6.8 Hz), 7.90 (2H, d, *J* = 6.8 Hz) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.8, 104.7, 113.1, 117.8, 121.4, 121.75, 125.6, 127.4, 127.9, 128.3, 128.5, 130.5, 136.6, 138.3, 138.8, 140.4, 160.5 ppm; IR (ATR): 509, 615, 723, 741, 773, 835, 1032, 1466 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{13}O$ ($[M+H]^+$) 233.0961; found: 233.0969.

8-Methoxyfluoranthene (5e) (Table 4, entries 3 and 7). Nonaflate **4d** (97.3 mg, 0.18 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 8/1), **5e** (30.9 mg, 73%) was obtained as a yellow solid. Alternatively, nonaflate **4i** (107 mg, 0.20 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 5/1), **5e** (42.7 mg, 92%, >99:1) was obtained as a yellow solid. Mp. 120.2−122.3 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 6.89 (1H, dd, *J* = 8.0, 4.0 Hz), 7.45 (1H, d, *J* = 4.0 Hz), 7.55−7.61 (2H, m), 7.86 (2H, t, *J* = 8.0 Hz), 7.80 (2H, t, *J* = 8.0 Hz), 7.89 (1H, d, *J* = 4.0 Hz) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.6, 107.7, 112.8, 119.0, 119.9, 122.2, 125.4, 126.9, 127.7, 128.0, 130.0, 132.5, 132.9, 136.8, 137.0, 141.3, 160.0 ppm; IR (ATR): 546, 596, 623, 772, 816, 1024, 1223 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{13}O$ ($[M+H]^+$) 233.0961; found: 233.0976.

8-(Trifluoromethyl)fluoranthene (5f) (Table 4, entries 4 and 8). Nonaflate **4e** (114 mg, 0.20 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2,

hexane/EtOAc = 10/1), **5f** (52.9 mg, 98%) was obtained as a pale yellow solid. Alternatively, nonaflate **4j** (104 mg, 0.18 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1), **5f** (39.3 mg, 80%, >99:1) was obtained as a pale yellow solid. Mp. 64.2−65.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60−7.73 (3H, m), 7.90 (1H, d, J = 8.0 Hz), 7.92 (1H, d, J = 8.0 Hz), 7.94 (1H, d, J = 8.0 Hz), 7.96 (1H, d, J = 8.0 Hz), 7.98 (1H, d, J = 8.0 Hz), 8.12 (1H, s) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 118.2 (q, $^3J_{CF}$ = 4.1 Hz), 120.8, 121.2, 121.3, 123.3, 124.4 (q, $^3J_{CF}$ = 4.1 Hz), 125.7, 127.4, 127.7, 128.0, 128.1, 129.3 (q, $^2J_{CF}$ = 32.2 Hz), 129.5 (q, $^1J_{CF}$ = 275.3 Hz), 135.5, 139.6, 142.26, 142.28 ppm; IR (ATR): 775, 818, 1055, 1099, 1109, 1263, 1323 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{17}H_{10}F_3$ ($[M+H]^+$) 271.0729; found: 271.0726.

8-Ethylfluoranthene (5g) (Table 4, entry 6). Nonaflate **4g** (67.2 mg, 0.13 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1 and then hexane/$CHCl_3$ = 2/1), **5g** (23.0 mg, 79%) was obtained as a yellow solid. Mp. 38.3−39.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (3H, t, J = 7.6 Hz), 2.82 (2H, q, J = 7.8 Hz), 7.21-7.29 (1H, m), 7.64 (2H, td, J = 7.6, 4.4 Hz), 7.78 (1H, s), 7.84 (4H, td, J = 7.8, 3.9 Hz), 7.93 (3H, dd, J = 14.2, 6.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.9, 29.2, 119.5, 119.8, 121.1, 121.3, 126.1, 126.5, 127.2, 127.8, 127.9, 130.0, 132.7, 137.09, 137.12, 137.14, 139.8, 144.0 ppm; IR (ATR): 704, 754, 1022, 1161, 1171, 1356 cm^{-1}; HRMS (DART-TOF): *m/z* calcd

for $C_{18}H_{15}$ ([M+H]$^+$) 231.1168; found: 231.1181.

8-Isopropylfluoranthene (5h) (Table 4, entry 9). Nonaflate **4k** (100 mg, 0.18 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1) and then gel permeation chromatography (JAIGEL-1H and 2H, Japan Analytical Industry, $CHCl_3$), **5h** (31.4 mg, 70%, >99:1) was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (6H, d, *J* = 7.3 Hz), 3.05 (1H, sep, *J* = 6.8 Hz), 7.23 (1H, d, *J* = 6.4 Hz), 7.62 (1H, d, *J* = 8.0 Hz), 7.64 (1H, d, *J* = 4.0 Hz), 7.66 (1H, d, *J* = 4.0 Hz), 7.82 (2H, d, *J* = 8.0 Hz), 7.85 (1H, s), 7.88 (1H, d, *J* = 6.8 Hz), 7.93 (1H, d, *J* = 6.8 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 24.2, 34.5, 119.55, 119.62, 119.8, 121.3, 125.9, 126.1, 126.5, 127.8, 127.9, 130.0, 132.7, 137.1, 137.2, 137.3, 139.7, 148.7 ppm; IR (ATR): 606, 772, 814, 1427, 1456, 2957, 3042 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{19}H_{17}$ ([M+H]$^+$) 245.1325; found: 245.1339.

8-(*N*,*N*-Dimethylamino)fluoranthene (5i) (Table 4, entry 10). Nonaflate **4l** (103 mg, 0.19 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC three times (SiO_2, hexane/EtOAc = 8/1, 8/1, 4/1), **5i** (38.7 mg, 81%, >99:1) was obtained as an orange solid. Mp. 94.4−96.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10 (6H, s), 6.73 (1H, dd, *J* = 8.0, 4.0 Hz), 7.33 (1H, d, *J* = 4.0 Hz), 7.53−7.61 (2H, m), 7.68 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 2.4 Hz), 7.75 (1H, d, *J* = 4.4 Hz), 7.79 (1H, d, *J* = 8.0 Hz), 7.90 (1H, d, *J* = 4.0 Hz) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 41.0, 106.1, 111.4, 117.9, 119.3, 122.2, 124.4, 126.5, 127.6, 128.1, 128.4,

130.0, 133.0, 137.6, 137.8, 141.1, 150.8 ppm; IR (ATR): 567, 596, 623, 768, 802, 1092, 1179, 1607 cm^{-1}; HRMS (DART-TOF): *m/z* calcd for $C_{18}H_{16}N$ ($[M+H]^+$) 246.1277; found: 246.1287.

Benzo[k]fluoranthene (5j)[10] **(Table 4, entry 11).** Nonaflate **4m** (59.6 mg, 0.11 mmol) was subjected to the intramolecular C−H arylation. After preparative TLC (SiO_2, hexane/EtOAc = 10/1, hexane/CH_2Cl_2 = 2/1) and then gel permeation chromatography (JAIGEL-1H and 2H, Japan Analytical Industry, $CHCl_3$), **5j** (7.0 mg, 26%) was obtained as a pale yellow solid, and **6b** (2.1 mg, 8%) was obtained as an yellow solid. **5j**:[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (2H, dd, *J* = 6.6, 2.8 Hz), 7.67 (2H, dd, *J* = 7.8, 6.8 Hz), 7.84 (2H, d, *J* = 3.6 Hz), 7.94 (2H, dd, *J* = 6.0, 3.2 Hz), 8.01 (2H, d, *J* = 6.8 Hz), 8.31 (2H, s) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 119.2, 120.2, 126.0, 126.2, 128.2, 128.7, 130.5, 133.5, 135.3, 136.9, 137.8 ppm. **6b**:[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (3H, s), 7.19 (1H, d, *J* = 7.6 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 7.52−7.54 (2H, m), 7.62−7.72 (2H, m), 7.80 (1H, d, *J* = 7.2 Hz), 7.85 (1H, dd, *J* = 3.2, 8.4 Hz), 7.96 (1H, d, *J* = 6.8 Hz), 8.00 (1H, d, *J* = 6.8 Hz) ppm.

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Notes

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SUPPORTING INFORMATION: ^{1}H- and ^{13}C-NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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