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

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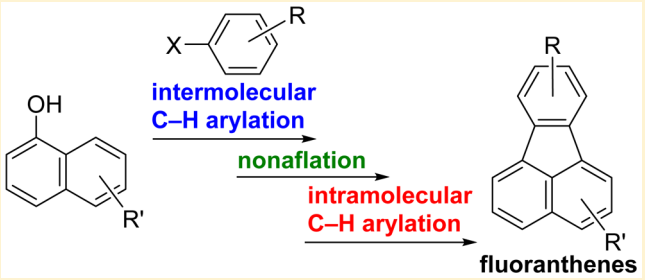
Supporting Information

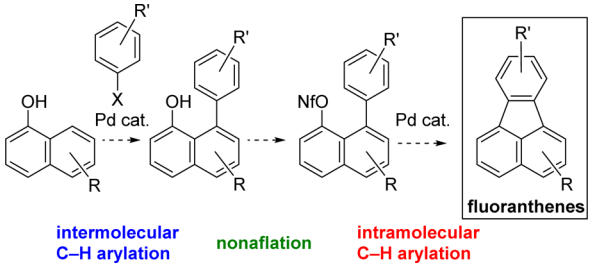
ABSTRACT: A three-step synthetic method for the preparation of fluoranthenes, involving Miura's intermolecular C−H arylation, nonaflation, and intramolecular C−H arylation, has been developed. Various 1-naphthols and haloarenes were successfully used as substrates. Reaction conditions that afford high site selectivity have been developed for the intramolecular C−H arylation step.



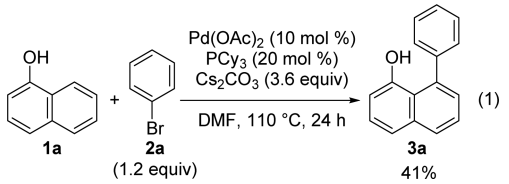
Polycyclic aromatic hydrocarbons (PAHs) have attracted much attention because of their biological, electronic, and optical properties.[1−5] Fluoranthene is one of the smallest nonalternant PAHs, and its framework has often been utilized as a structural motif for many applications, such as in sensors[6] 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 preformed 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**

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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%).

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%).

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).

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.

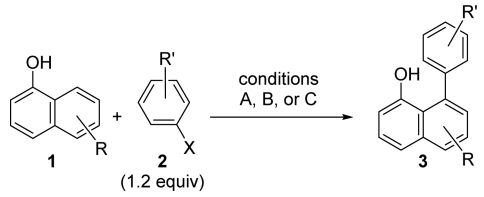
With the effective conditions in hand, we applied them to the synthesis of various substituted fluoranthenes (Table 4). In most cases, good yields were obtained. For fluoranthene synthesis using *meta*-substituted substrates (**4i**−**l**, entries 7−10), excellent site selectivities (>99:1) were observed.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

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 monosubstituted fluoranthenes were synthesized in this work, this three-step procedure is expected to be easily applied to the synthesis of multisubstituted 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)

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



entry	1	2	condition[a]	3	yield (%)
1			A	**3a**	47[b]
2			A	**3b**	77[b]
3			A	**3c**	51
4			A	**3d**	40[b]
5			A	**3e**	49
6			B	**3f**	32
7			B	**3g**	18
8			A	**3h**	65
9			A	**3i**	56
10			C	**3i**	13
11			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 °C, 19−24 h. B: $Pd(OAc)_2$ (10 mol %), PCy_3 (20 mol %), Cs_2CO_3 (3.6 equiv), DMF, 110 °C, 24 h. C: $PdCl_2(PCy_3)_2$ (10 mol %), Cs_2CO_3 (3.6 equiv), DMF, 110 °C, 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]

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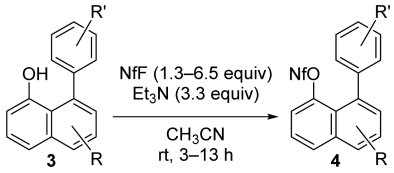
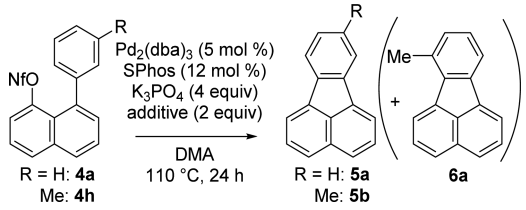
Table 2. Nonaflation of 3



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

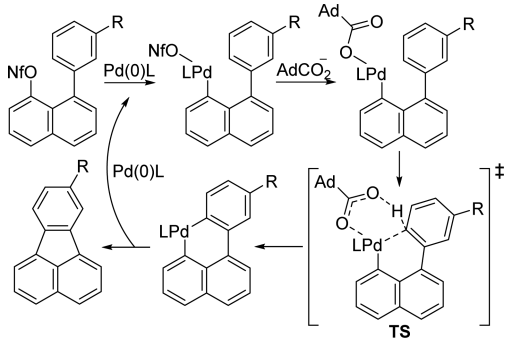
Table 3. Conditions for Intramolecular C−H Arylation



entry	4	additive	yield (%)[a]
1	**4a** (R = H)		<68[b]
2	**4a** (R = H)	1-AdCO$_2$H	98
3	**4h** (R = Me)	1-AdCO$_2$H	91 (50:1)
4	**4h** (R = Me)	*t*-BuCO$_2$H	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.

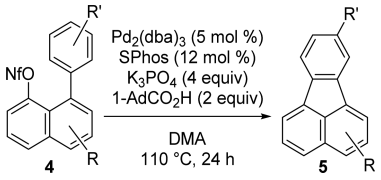
Scheme 2. Assumed Mechanism of Intramolecular C−H Arylation

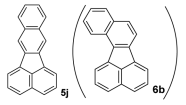


(δ = 0) in $CDCl_3$ was used as the internal standard. For ^{13}C NMR, $CDCl_3$ (δ = 77.0) served as an internal standard. Compounds **1b**[46] and **1c**[47,48] were prepared according to procedures reported in the literature.

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 °C 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.

Table 4. Intramolecular C−H Arylation of Nonaflates



entry	4	5	yield (%)[a]
1	**4b**		91
2	**4c**		89
3	**4d**		73
4	**4e**		98
5	**4f**		84
6	**4g**		79
7	**4i**		92 (>99:1)
8	**4j**		80 (>99:1)
9	**4k**		70 (>99:1)
10	**4l**		81 (>99:1)
11	**4m**		26 (8)[b]

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

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

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1-naphthol) was added a bromoarene (1.2 equiv) at rt. The mixture was heated at 110 °C 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 °C 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 °C; ^{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 °C; ^{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 °C; ^{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 °C; ^{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. ^{1}H 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, 8.0 Hz), 7.84 (1H, dd, J = 8.3, 1.0 Hz) ppm; ^{13}C{^{1}H} 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

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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 °C, 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 °C; ^{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 °C; ^{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 °C; ^{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 °C; ^{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 °C; ^{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 °C; ^{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

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(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 °C; ^1H 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; $^{13}C\{^1H\}$ 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 °C; ^1H 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; $^{13}C\{^1H\}$ 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 °C; ^1H 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; $^{13}C\{^1H\}$ 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. ^1H 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; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 120.0, 124.2 (q, $^3J_{CF}$ = 3.3 Hz), 124.27 (q, $^1J_{CF}$ = 270.8 Hz), 124.29, 125.4, 126.5, 128.4, 128.7, 129.7, 130.3 (q, $^2J_{CF}$ = 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. ^1H 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; $^{13}C\{^1H\}$ 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. ^1H 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; $^{13}C\{^1H\}$ 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 °C; ^1H 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; $^{13}C\{^1H\}$ 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. ^1H 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; $^{13}C\{^1H\}$ 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 ^1H 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] ^1H 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; $^{13}C\{^1H\}$ 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] ^1H 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. ^1H 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; $^{13}C\{^1H\}$ 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;

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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 °C; ^1H 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 °C; ^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 °C; ^1H 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; $^{13}C\{^1H\}$ 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 °C; ^1H 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; $^{13}C\{^1H\}$ 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. ^1H 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; $^{13}C\{^1H\}$ 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 °C; ^1H 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; $^{13}C\{^1H\}$ 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 a yellow solid. **5j**:[10] ^1H 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] ^1H 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00553.

^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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