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Nickel-Catalyzed Decarbonylative Alkylation of Aroyl Fluorides Assisted by Lewis-Acidic Organoboranes

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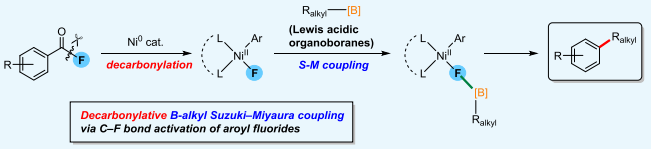
Supporting Information

ABSTRACT: Herein, nickel-catalyzed decarbonylative C−F bond alkylation of aroyl fluorides with organoboron reagents is reported. Aroyl fluorides are more chemically stable than the corresponding aroyl chlorides and can be readily synthesized from the corresponding carboxylic acids. The fluoronickel intermediate formed via oxidative addition interacts with Lewis-acidic trialkylboranes, and the subsequent decarbonylative alkylation proceeds. This new synthetic methodology allows 1,2-bifunctionalization of aromatic carboxylic acids via palladium-catalyzed *ortho*-C−H arylation. In addition, an unprecedented 1,4-nickel migration on *ortho*-arylated aroyl fluorides was observed. As a demonstration of the synthetic utility of the present reaction, the sequential 1-alkyl-2-arylation of 3-hydroxy-2-naphthoic acid was accomplished via chemoselective alkylation at a fluorocarbonyl moiety and the subsequent C−O bond arylation at an acetoxy group.



INTRODUCTION

In the past three decades, palladium-catalyzed alkylation of aroyl chlorides and anhydrides with organozinc,[1] aluminum,[2] tin,[3] and lead compounds[4] in a retentive manner (i.e., where the reaction proceeds without decarbonylation) has been utilized to afford unsymmetrical alkyl aryl ketones. In 2000, the first palladium-catalyzed Suzuki−Miyaura (S−M) alkylation reaction of aroyl chlorides with alkylboranes was reported.[5] Since then, transition-metal-catalyzed S−M alkylation reaction has been widely applied as one of the most reliable and versatile synthetic methods to construct $C(sp^2)-C(sp^3)$ bonds.[6] An example of the utility of these reactions is found in the total synthesis of epothilones.[7] In general, S−M alkylation requires a special palladium complex bearing a sterically hindered bidentate ligand because the target $C(sp^2)-C(sp^3)$ bond formation should occur prior to a competing β-hydride elimination.[8]

Decarbonylative cross-coupling of carboxylic acid derivatives has been developed as an alternative class of transition-metal-catalyzed cross-coupling reactions. Hence, development of S−M coupling reaction of carboxylic acid derivatives with alkylboron reagents is expected to be a new sustainable synthetic strategy of C−C bond formation because naturally abundant carboxylic acid derivatives could readily be synthesized and then be utilized as aryl electrophile equivalents. In general, decarbonylative coupling reaction requires relatively harsh conditions to overcome the high activation barrier to decarbonylation. Malanga reported a Ni-catalyzed decarbonylative reduction of aroyl chlorides with tin hydride into the corresponding simple arenes,[9] where decarbonylation of a (aroyl)(chloro)nickel complex predominates above 50 °C. In addition, previously reported density functional theory (DFT) studies indicated that a relatively high activation barrier of 20−30 kcal/mol exists for decarbonylation.[10]

Recent development of decarbonylative cross-couplings of aromatic carboxylic acid derivatives have been extensively reported. For example, Yu and co-workers reported Rh(I)-catalyzed decarbonylative C−H functionalization of aroyl chlorides.[11] Sanford demonstrated widespread functionalizations via decarbonylative chlorination of aroyl chlorides.[12] In the viewpoint of utilization of aromatic esters, Itami−Yamaguchi, Love, and Rueping independently have demonstrated a practical Ni- or Pd-catalyzed decarbonylative arylation of phenyl esters with organoboron or zinc compounds through C(aroyl)−OPh bond cleavages and sequential decarbonylation (Scheme 1a).[13] On the other hand, regarding the use of aroyl fluorides as substrates, there have been only one example, which is a catalytic Negishi coupling in a retentive manner, affording unsymmetrical alkyl aryl ketones, reported by Rovis (Scheme 1b),[14] but no precedent decarbonylative transformation of aroyl fluorides have been disclosed. Accordingly, we paid much attention to develop an unprecedented decarbonylative alkylation of aroyl fluorides. Herein, we report a first example of contrasting alkylation of aroyl fluorides with Lewis-acidic alkylboranes. In previous studies on alkylation in S−M coupling reaction, Lewis-acidic trialkylboranes have been applied to accelerate transmetalation of alkyl groups via interaction of oxygen in alkoxypalladium complexes with a boron center.[8,15] We herein describe a novel C−F bond functionalization strategy to construct alkyl−aryl scaffold starting from naturally abundant carboxylic acid (Scheme 1c).

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Scheme 1. Ni-Catalyzed Retentive vs Decarbonylative C−F Bond Functionalization

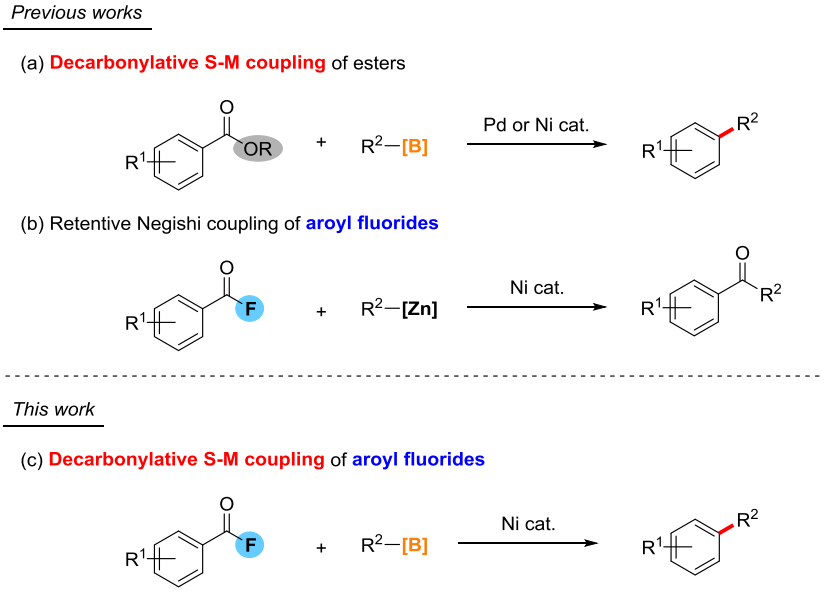
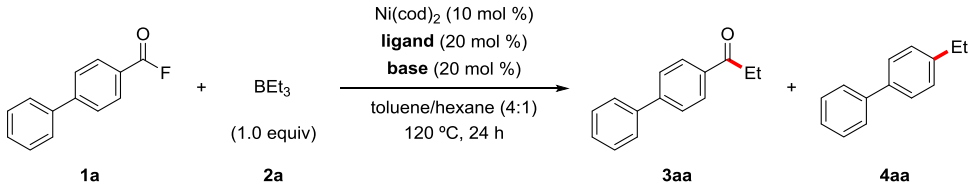


Table 1. Optimization of Reaction Conditions in Nickel(0)-Catalyzed C(aroyl)−F Bond Ethylation of Biphenyl-4-Carbonyl Fluoride (1a) with BEt_3 (2a)[a]



1a 2a 3aa 4aa

entry	ligand	base	yield (%)[b] 3aa	4aa
1	PPh_3	none	0	21
2	PCy_3	none	22	26
3[c]	DPPE	none	0	83 (78)
4[c]	DPPBz	none	0	45
5	ICy·HCl	pyridine	27	trace
6[c,d]	DPPE	none	0	85 (85)
7[c,e]	DPPE	none	0	77 (73)
8[c,f]	DPPE	none	0	28
9	none	none	0	0

[a]Reaction conditions: **1a** (0.125 mmol, 1.0 equiv), **2a** (0.125 mmol, 1.0 equiv), $Ni(cod)_2$ (0.0125 mmol, 10 mol %), ligand (0.025 mmol, 20 mol %), base (0.025 mmol, 20 mol %), solvent (0.5 mL, 0.25 M of **1a**), 120 °C, 24 h. [b]Determined by ^1H NMR analysis of the crude mixture, using dibromomethane as an internal standard. An isolated yield was shown in parentheses. [c]10 mol % of ligand was used. [d]At 130 °C for 24 h. [e]At 140 °C for 24 h. [f]At 110 °C for 24 h. DPPE, 1,2-bis(diphenylphosphino)ethane; DPPBz, 1,2-bis(diphenylphosphino)benzene; ICy·HCl, 1,3-dicyclohexylimidazolium chloride; $Ni(cod)_2$, bis(1,5-cyclooctadiene)nickel(0); PCy_3, tricyclohexylphosphine.

RESULTS AND DISCUSSION

In an initial study, we optimized reaction conditions for the nickel-catalyzed C(aroyl)−F bond ethylation of biphenyl-4-carbonyl fluoride (**1a**) with BEt_3 (**2a**, 1.0 equiv) (Table 1). We first elucidated the ligand effect (entries 1−5). To our delight, the reaction with an air-stable and moderately electron-donating 1,2-bis(diphenylphosphino)ethane (DPPE) ligand selectively delivered the target decarbonylative cross-coupled product 4-ethylbiphenyl (**4aa**), in 83% yield (entry 3). Very recently, Rueping and co-workers have reported decarbonylative coupling of aromatic ethers, and the related nickel/bidentate phosphine catalysis could accelerate this decarbonylative coupling.[13d,e] In contrast, results with a strong σ-donating *N*-heterocyclic carbene, ICy·HCl, ligand gave the retentive product of 4-phenylacetophenone (**3aa**) in 27% yield (entry 5). This result is notable because the reaction proceeds in a completely retentive manner in spite of the fast oxidative addition obtained with the strong σ-donating ICy·HCl ligand. We also optimized reaction temperature; **4aa** was obtained in 85% yield at 130 °C (entry 6), but in only 28% at 110 °C (entry 8). We finally performed the reaction without any ligand, but no product was formed (entry 9).

We then also examined the reaction with an array of catalysts and aromatic carboxylic acid derivatives (see Supporting Information). As a result, we identified that the current decarbonylative alkylation was possible with the economical and air-stable $Ni(OAc)_2{\cdot}4H_2O$ precatalyst (80% NMR yield of **4aa** at 130 °C), while $NiCl_2$ showed no activity

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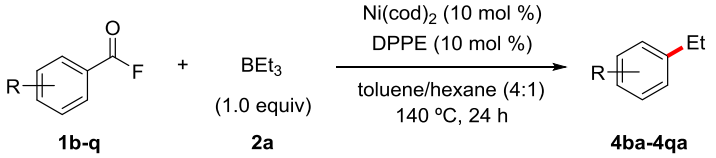
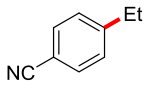
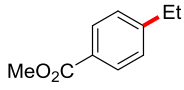
Table 2. Scope of (Hetero)aroyl Fluorides for Decarbonylative C((hetero)aroyl)−F Bond Alkylation[a]



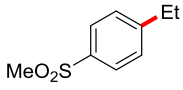
1b-q + **2a** → **4ba-4qa**



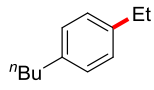
4ba: 68%



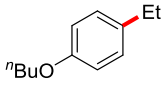
4ca: 54%



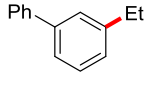
4da: 51%



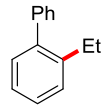
4ea: 61%



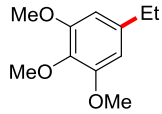
4fa: 52%



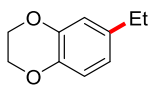
4ga: 71%



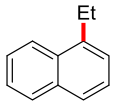
4ha: 36%



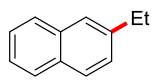
4ia: 68%



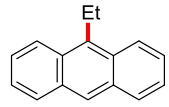
4ja: 69%



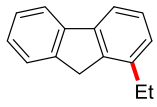
4ka: 70%



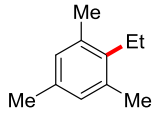
4la: 74%



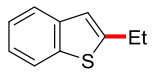
4ma: 56%



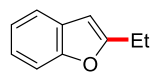
4na: 78%



4oa: <1%[a]



4pa: 70%



4qa: 28%

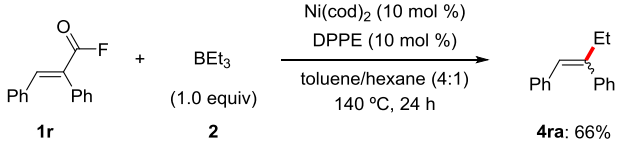
[a]NMR yield based on 1,4-dioxane as an internal standard.

(Table S4). Notably, alternative carboxylic acid derivatives, such as aroyl chlorides, esters, and thioesters, did not participate in the reaction (Table S5). These results clearly indicate that the nickel-catalyzed decarbonylative alkylation is specific transformation for aroyl fluorides.

Our investigations on the scope of aroyl fluorides substrates for decarbonylative C(aroyl)−F bond ethylation are presented in Table 2. For this screen, we employed a higher reaction temperature of 140 °C to obtain better results. We established that products bearing electron-withdrawing 4-cyano (**4ba**, 68%), 4-methoxycarbonyl (**4ca**, 54%), 4-methylsulfonyl (**4da**, 51%), and electron-donating 4-butyl (**4ea**, 61%) and 4-butoxy (**4fa**, 52%) groups were formed in moderate to good yields. Biphenyl-3-carbonyl fluoride, in which phenyl group is installed in the *meta*-position, was also readily transformed to 3-ethylbiphenyl (**4ga**) as the target product in 71% yield. However, aroyl fluorides bearing a substituent in the *ortho*-position, such as biphenyl-2-carbonyl fluoride, gave lower yields (**4ha**, 36%). Decarbonylative ethylation of aroyl fluorides bearing multiple substituents (**4ia**, 68% and **4ja**, 69%) or a fused ring (**4ka**−**na**; 56−78%) at the *meta*- and *para*-positions were also demonstrated. However, a substrate having a sterically hindered mesityl group did not afford any corresponding product at all (**4oa**, <1%), as predicted by a previous DFT study.[9] Finally, we evaluated heterocyclic substituents. Benzo[*b*]thiophene-substituted aroyl fluoride afforded a good yield of the target product **4pa** in 70% yield. However, benzo[*b*]furan-substituted aroyl fluoride gave low yield (**4qa**, 28%). During this substrate screening process, protonated products from *β*-hydride elimination were also detected (**4**/*β*-hydride elimination >10:1).

To expand the scope of the reaction, we examined the reaction with *α*-phenylcinnamoyl fluoride (**1r**), which proceeds via C(alkenyl)−F bond cleavage. Under the same reaction conditions, an *E*/*Z* mixture of products (**4ra**, 66% combined yield, *E*/*Z* = 0.93:1) was obtained. This result implies that decarbonylation and *E*/*Z* isomerization sequences are much faster than reductive elimination after the initial oxidative addition (Scheme 2).

Scheme 2



1r + **2** → **4ra**: 66% (*E*/*Z* = 0.93 : 1)

In the field of pharmaceuticals and natural product synthesis, methylation is the most common alkylation. However, trimethylborane is difficult to handle because it is a highly flammable gaseous substance at room temperature (rt). We thus evaluated the other reaction with alternative methyl-containing organoboranes (see Supporting Information, Table S3). Pleasingly, we show that use of trimethylboroxine (**2b**) in the presence of an equimolar amount of CsF efficiently afforded the target 4-methylbiphenyl (**4ac**), whereas excess CsF retarded the reaction. Finally, by employing a 2-fold greater amount of all of the reagents, we succeeded in obtaining **4ac** in 49% yield (Scheme 3). Other methylating

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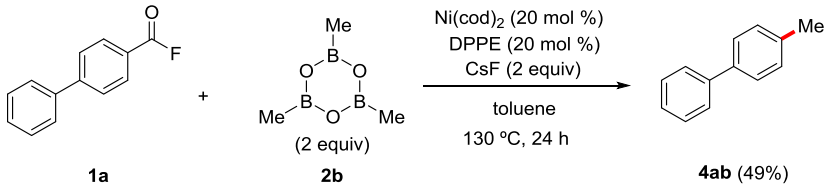
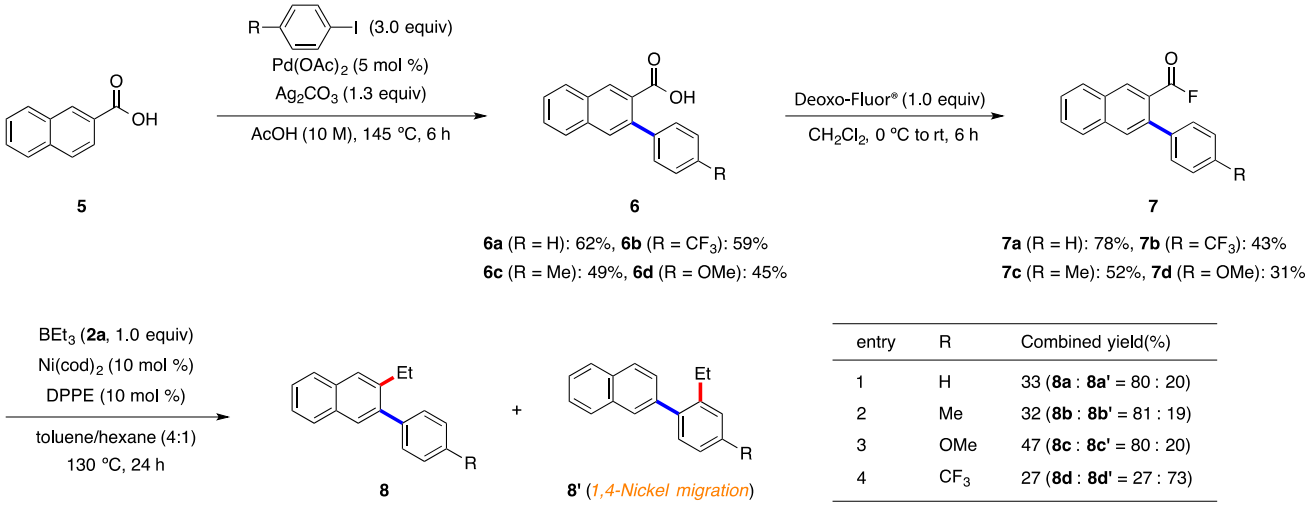
Scheme 3

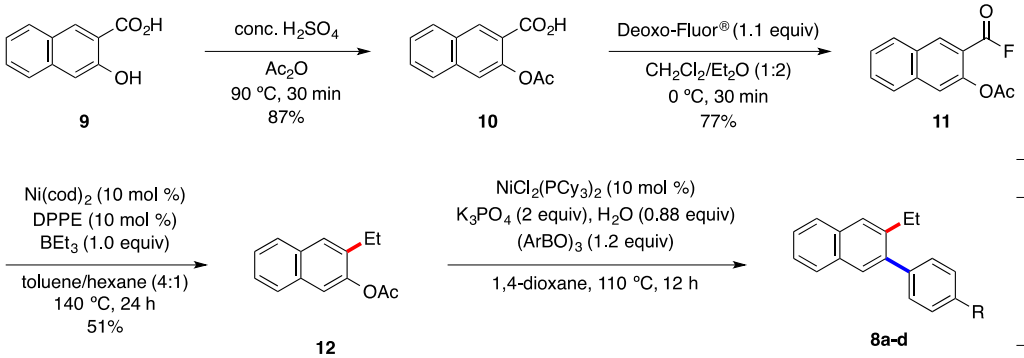


Scheme 4. *ortho*-Arylation, Fluorination, and *ipso*-Alkylation Sequences, Starting from 2-Naphthoic Acid (5)



entry	R	Combined yield(%)
1	H	33 (**8a** : **8a'** = 80 : 20)
2	Me	32 (**8b** : **8b'** = 81 : 19)
3	OMe	47 (**8c** : **8c'** = 80 : 20)
4	CF_3	27 (**8d** : **8d'** = 27 : 73)

Scheme 5. Chemoselective Alkylation−Arylation Sequences, Starting from *ortho*-Hydroxy Carboxylic Acid 9



entry	R	yield(%)
1	H	63
2	Me	75
3	OMe	64
4	CF_3	44

reagents such as $SnMe_4$ and $SiMe_4$ proved unsuitable for the present reaction.

To apply this decarbonylative C−F bond alkylation, we developed a novel *ortho*-arylation/*ipso*-alkylation sequences since aroyl fluorides can be directly synthesized from the corresponding carboxylic acids. Several research groups have independently reported the palladium-catalyzed *ortho*-C−H bond arylation of carboxylic acids.[16] We thus combined the *ortho*-C−H arylation protocol of carboxylic acid with the sequential fluorination[17] and the present decarbonylative C−F bond alkylation (Scheme 4). As the first step, we synthesized 3-aryl-2-naphthoic acids (**6a−d**) in 45−62% yields under modified conditions of Daugulis' procedure.[16b] Next, the corresponding aroyl fluorides (**7a−d**) were readily prepared by fluorination with nucleophilic fluorinating reagent (Deoxo-Fluor) in 31−78% yields. Finally, we carried out the nickel-catalyzed decarbonylative alkylation of the C−F bond. Notably, we detected a mixture of the target 2-ethyl-3-arylnaphtalenes (**8a−d**) and 2-(2-ethyl-4-substituted phenyl)-naphthalenes (**8a′−d′**). As the possible reaction mechanism for the formation of unexpected regioisomers of **8a′−d′**, we herein propose the unprecedented 1,4-nickel migration whose analogous phenomena have been well known for palladium,[18] rhodium,[19] cobalt,[20] iridium,[19m,21] platinum,[18j] and ruthenium.[22] Only one example of 1,4-nickel migration has been reported, albeit in a bimetallic system.[23] However, to the best of our knowledge, a monometallic 1,4-nickel migration has not been reported to date.

As an additional application, we planned more straightforward alkylation and arylation sequences. Previously, Itami reported the orthogonal couplings of different esters; decarbonylative coupling of phenyl ester containing C(aroyl)−O bond cleavage predominantly occurred prior to C(aryl)−O/C−H coupling.[13a] Hence, we next examined whether the present decarbonylative coupling can proceed prior to C(aryl)−O bond cross-coupling to realize a straightforward 1-alkyl-2-arylation. To investigate this strategy, we conducted the nickel-catalyzed C(aryl)−O bond arylation

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with triarylboroxines under the standard conditions reported by Shi.[24] On the basis of the synthetic procedure, we started the chemoselective functionalization of the substrate having both fluorocarbonyl and acetoxy groups with organoboron under nickel catalysis (Scheme 5). 3-Acetoxy-2-(fluorocarbonyl)naphthalene (**11**) was readily synthesized in 62% overall yield through acid-catalyzed acetoxylation of 3-hydroxy-2-naphthoic acid (**9**) and the subsequent nucleophilic fluorination with Deoxo-Fluor. Subsequently, we examined the nickel-catalyzed decarbonylative alkylation of **11**. To our delight, the desired 3-acetoxy-2-ethylnaphthalene (**12**) could be obtained in 51% yield without any C(aryl)−O bond-cleaved byproduct. Finally, we conducted the nickel-catalyzed arylation via C(aryl)−O bond cleavage and isolated **8a−d** as the target products in 44−75% yield. Through this synthetic scheme, we accomplished a straightforward 1-alkyl-2-arylation sequence of a naturally abundant hydroxy carboxylic acid scaffold.

CONCLUSIONS

In summary, we have developed a new protocol for decarbonylative C(aroyl)−F bond alkylation with Lewis-acidic organoboranes. Lewis acidity of organoboranes is required due to the acceleration of transmetalation in S−M reaction. Synthetically significant methylation was also demonstrated by applying trimethylboroxine. A thermodynamic driving force derived from B−F bond formation provides a nexus for the specific transformation of aroyl fluorides over aroyl halides. We are currently further investigating the mechanism of this novel monometallic 1,4-nickel migration.

EXPERIMENTAL SECTION

General. All of the reactions were carried out under Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 °C) and heated under reduced pressure prior to use. Solvents were employed as eluents for all other routine operations, and dehydrated solvents were purchased from commercial suppliers and employed without any further purification. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40−100 μm) from Kanto Chemicals Co., Ltd. The ^{1}H, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on Varian INOVA-600 (600 MHz) spectrometers. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. Gas chromatography (GC) analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. GC−mass spectrometry (MS) analyses were carried out on a SHIMADZU GC-17A equipped with a Shimadzu QP-5050 GC−MS system. Elemental analyses were carried out with a PerkinElmer 2400 CHN elemental analyzer at Okayama University. Compounds **1b**,[25,26] **1c**,[27] **1k**,[28] **1l**,[27] and **1o**,[29] were prepared according to the reported literature methods.

Representative Procedure for the Synthesis of Aroyl Fluorides from Acid Chlorides. To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, aroyl chlorides **1-Cl** (2.0 mmol), 18-crown-6 (26.4 mg, 0.1 mmol, 5 mol %), KF (1.16 g, 20 mmol, 10 equiv), and tetrahydrofuran (10 mL) were successively added. After the reaction was stirred at 40 °C for 24 h, the insoluble inorganic solid (KF or KCl) was filtered and the volatiles were concentrated using a rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding aroyl fluorides **1** in 30−72% yields.

*Biphenyl-4-carbonyl Fluoride (**1a**).* Yield was 64%. mp: 42−45 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.43−7.46 (m, 1H), 7.48−7.51 (m, 2H), 7.63−7.65 (m, 2H), 7.77 (d, J = 7.8 Hz, 2H), 8.11−8.13 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 123.6 (d, $^{2}J_{C-F}$ = 61 Hz), 127.5, 127.8, 128.9, 129.2, 132.1 (d, $^{3}J_{C-F}$ = 3 Hz), 139.4, 148.3, 157.5 (d, $^{1}J_{C-F}$ = 343 Hz); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 18.1. Fourier transform infrared (FT-IR) (neat, cm^{-1}): 1803 (s), 1607 (s), 1450 (w), 1408 (m), 1256 (s), 1180 (w), 1030 (s), 1003 (s), 853 (m), 743 (s), 691 (m). Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53%. Found: C, 77.91; H, 4.48%.

*4-Butylbenzoyl Fluoride (**1e**).* Yield was 30%. bp: 140 °C/80 mmHg. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 0.94 (t, J = 7.2 Hz, 3H), 1.36 (sext, J = 7.6 Hz, 2H), 1.60−1.65 (m, 2H), 2.70 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 14.0, 22.4, 33.2, 36.0, 122.4 (d, $^{2}J_{C-F}$ = 60 Hz), 129.3, 131.7 (d, $^{3}J_{C-F}$ = 5 Hz), 151.6, 157.7 (d, $^{1}J_{C-F}$ = 343 Hz); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 17.4. FT-IR (neat, cm^{-1}): 2959 (s), 2932 (s), 2866 (m), 1807 (s), 1773 (m), 1609 (s), 1462 (w), 1418 (w), 1256 (s), 1177 (m), 1107 (m), 1007 (s), 878 (m), 845 (m), 737 (m), 694 (w). Anal. Calcd for $C_{11}H_{13}FO$: C, 73.31; H, 7.27%. Found: C, 73.29; H, 7.41%.

*4-Butoxylbenzoyl Fluoride (**1f**).* Yield was 44%. bp: 140 °C/80 mmHg. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 0.98 (t, J = 7.5 Hz, 3H), 1.50 (sext, J = 7.4 Hz, 2H), 1.77−1.82 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 13.9, 19.2, 31.1, 68.3, 114.9, 116.6 (d, $^{2}J_{C-F}$ = 62 Hz), 133.8 (d, $^{3}J_{C-F}$ = 5 Hz), 157.4 (d, $^{1}J_{C-F}$ = 339 Hz), 165.0; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 15.7. FT-IR (neat, cm^{-1}): 2961 (s), 2938 (s), 2873 (m), 1803 (s), 1605 (s), 1510 (s), 1470 (m), 1319 (m), 1254 (s), 1171 (s), 1109 (m), 1024 (s), 999 (s), 968 (m), 846 (s), 691 (m). Anal. Calcd for $C_{11}H_{13}FO_2$: C, 67.33; H, 6.68%. Found: C, 66.96; H, 6.89%.

*1,2,3-Trimethoxy-5-benzoyl Fluoride (**1i**).* Yield was 34%. mp: 77−79 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 3.88 (s, 6H), 3.92 (s, 3H) 7.24 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 56.4, 61.2, 108.7 (d, $^{3}J_{C-F}$ = 2 Hz), 119.4 (d, $^{2}J_{C-F}$ = 62 Hz), 144.4, 153.4, 157.3 (d, $^{1}J_{C-F}$ = 342 Hz); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 16.5. FT-IR (neat, cm^{-1}): 1809 (s), 1591 (s), 1503 (m), 1462 (s), 1416 (s), 1339 (s), 1238 (s), 1167 (s), 1126 (s), 1070 (s), 995 (m), 891 (s), 858 (w), 748 (m), 681 (m). Anal. Calcd for $C_{10}H_{11}FO_4$: C, 56.08; H, 5.18%. Found: C, 56.11; H, 5.24%.

*Benzo[b]thiophene-2-carbonyl Fluoride (**1p**).* Yield was 46%. mp: 79−81 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.48 (ddd, J = 8.1, 7.2, 0.9 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.91 (dd, J = 8.4, 0.6 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.21 (s, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 123.0, 125.8, 126.5, 126.9 (d, $^{2}J_{C-F}$ = 75 Hz), 128.6, 135.3 (d, $^{3}J_{C-F}$ = 2 Hz), 138.3, 143.8 (d, $^{3}J_{C-F}$ = 2 Hz), 153.3 (d, $^{1}J_{C-F}$ = 335 Hz); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 25.1. FT-IR (neat, cm^{-1}): 1796 (s), 1680 (m), 1512 (s), 1165 (m), 962 (m), 756 (m), 714 (m). Anal. Calcd for C_9H_5FOS: C, 59.99; H, 2.80%. Found: C, 60.00; H, 2.55%.

Representative Procedure for the Synthesis of Aroyl Fluorides from Carboxylic Acids. To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, carboxylic acids **1-**

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OH (3.0 mmol) and CH_2Cl_2 (15 mL) were successively added. After the mixture was stirred at 0 °C, Deoxo-Fluor reagent (1.1 equiv, 608 μL, 3.3 mmol) was slowly added to the reaction mixture. After the reaction mixture was stirred at 0 °C for 30 min, the solution was slowly poured into saturated $NaHCO_3$, and after CO_2 evolution ceased, it was extracted into CH_2Cl_2 (3 × 15 mL) and dried over $MgSO_4$. The crude product was purified by flash chromatography (CH_2Cl_2 (**1d**), Hex/Et_2O = 10:1 (others)) to afford the corresponding aroyl fluorides **1** in 39−91% yields.

*4-(Methylsulfonyl)benzoyl Fluoride (**1d**).* Yield was 50%. mp: 124−125 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 3.11 (s, 3H), 8.12 (d, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 44.3, 128.3, 129.8 (d, $^2J_{C-F}$ = 62 Hz), 132.5 (d, $^3J_{C-F}$ = 3 Hz), 146.6, 155.9 (d, $^1J_{C-F}$ = 347 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 20.9. FT-IR (neat, cm^{-1}): 1802 (s), 1406 (m), 1325 (m), 1296 (m), 1252 (s), 1153 (s), 1040 (m), 1007 (w), 957 (w), 737 (s), 681 (s). Anal. Calcd for $C_8H_7FO_3S$: C, 47.52; H, 3.49%. Found: C, 47.46; H, 3.10%.

*Biphenyl-3-carbonyl Fluoride (**1g**).* Yield was 50%. mp: 43−45 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.42 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.60−7.62 (m, 3H), 7.92−7.94 (m, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.28 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 125.6 (d, $^2J_{C-F}$ = 60 Hz), 127.3, 128.4, 129.2, 129.7, 130.1 (d, $^3J_{C-F}$ = 5 Hz), 130.2 (d, $^3J_{C-F}$ = 3 Hz), 134.0, 139.3, 142.5, 157.6 (d, $^1J_{C-F}$ = 345 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 18.6. FT-IR (neat, cm^{-1}): 1809 (s), 1477 (w), 1452 (w), 1416 (w), 1294 (s), 1217 (s), 1064 (m), 1036 (m), 1007 (m), 816 (m), 770 (m), 733 (s), 692 (m), 644 (m). Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53%. Found: C, 77.99; H, 4.50%.

*Biphenyl-2-carbonyl Fluoride (**1h**).* Yield was 90%. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.41−7.46 (m, 4H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.68 (td, *J* = 7.5, 1.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 124.3 (d, $^2J_{C-F}$ = 57 Hz), 127.8, 128.0, 128.4, 128.5, 131.9 (d, $^{3\text{ or }4}J_{C-F}$ = 2 Hz), 132.3 (d, $^{3\text{ or }4}J_{C-F}$ = 3 Hz), 134.0, 140.2, 145.6 (d, $^{3\text{ or }4}J_{C-F}$ = 2 Hz), 159.2 (d, $^1J_{C-F}$ = 348 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 34.9. FT-IR (neat, cm^{-1}): 3063 (m), 3028 (m), 1821 (s), 1597 (s), 1568 (m), 1475 (s), 1450 (m), 1261 (s), 1225 (s), 1126 (m), 1067 (s), 995 (s), 777 (s), 748 (s), 698 (s). Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53%. Found: C, 78.27; H, 4.30%.

*1,4-Benzodioxane-6-carbonyl Fluoride (**1j**).* Yield was 89%. mp: 88−89 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 4.29−4.30 (m, 2H), 4.34−4.36 (m, 2H), 6.95 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.55−7.57 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 64.1, 64.9, 117.7 (d, $^2J_{C-F}$ = 62 Hz), 118.0, 120.9 (d, $^3J_{C-F}$ = 5 Hz), 125.7 (d, $^3J_{C-F}$ = 3 Hz), 143.8, 150.0, 157.2 (d, $^1J_{C-F}$ = 340 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 16.5. FT-IR (neat, cm^{-1}): 1792 (s), 1609 (m), 1585 (m), 1506 (m), 1456 (m), 1436 (m), 1336 (m), 1304 (s), 1180 (m), 1123 (m), 1064 (m), 1040 (s), 1005 (m), 895 (s), 878 (m), 826 (w), 748 (s), 716 (m), 660 (w). Anal. Calcd for $C_9H_7FO_3$: C, 59.35; H, 3.87%. Found: C, 59.38; H, 3.71%.

*9-Anthracenecarbonyl Fluoride (**1m**).* Yield was 57%. mp: 106−108 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.55−7.57 (m, 2H), 7.65−7.68 (m, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.32 (dd, *J* = 9.0, 0.6 Hz, 2H), 8.69 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 120.2 (d, $^2J_{C-F}$ = 54 Hz), 120.8 (d, $^3J_{C-F}$ = 3 Hz), 126.0, 128.7, 129.1, 130.3, 130.9, 133.3, 158.6 (d, $^1J_{C-F}$ = 354 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 59.6. FT-IR (neat, cm^{-1}): 2361 (w), 1819 (s), 1798 (s), 1159 (m), 1115 (m), 1096 (s), 941 (m), 922 (m), 901 (m), 735 (s), 719 (m). Anal. Calcd for $C_{15}H_9FO$: C, 80.35; H, 4.05%. Found: C, 80.11; H, 3.91%.

*9H-Fluorene-1-carbonyl Fluoride (**1n**).* Yield was 39%. mp: 88−90 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 4.21 (s, 2H), 7.37−7.43 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.96 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 38.5 (d, $^4J_{C-F}$ = 2 Hz), 120.2, 121.7 (d, $^2J_{C-F}$ = 60 Hz), 125.2, 126.3, 127.2, 127.8, 128.0, 129.8 (d, $^{3\text{ or }4}J_{C-F}$ = 2 Hz), 139.8, 143.3 (d, $^{3\text{ or }4}J_{C-F}$ = 2 Hz), 143.8 (d, $^{3\text{ or }4}J_{C-F}$ = 2 Hz), 147.8 (d, $^{3\text{ or }4}J_{C-F}$ = 6 Hz), 157.0 (d, $^1J_{C-F}$ = 346 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 25.2. FT-IR (neat, cm^{-1}): 1794 (s), 1582 (w), 1427 (w), 1254 (s), 1171 (w), 1119 (s), 1092 (m), 1065 (w), 1024 (m), 1005 (s), 856 (m), 766 (w), 739 (s). Anal. Calcd for $C_{14}H_9FO$: C, 79.23; H, 4.27%. Found: C, 79.14; H, 4.18%.

*Benzofuran-2-carbonyl Fluoride (**1q**).* Yield was 72%. mp: 94−96 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.38 (td, *J* = 7.5, 1.0 Hz, 1H), 7.56 (td, *J* = 7.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.75−7.77 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 112.8, 119.5, 123.7, 124.7, 126.4, 129.6, 140.1 (d, $^2J_{C-F}$ = 90 Hz), 149.6 (d, $^1J_{C-F}$ = 330 Hz), 157.0 (d, $^3J_{C-F}$ = 2 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 17.3. FT-IR (neat, cm^{-1}): 1801 (s), 1612 (w), 1556 (s), 1477 (w), 1329 (w), 1298 (s), 1163 (s), 1134 (s), 1049 (s), 928 (m), 883 (w), 750 (s), 731 (m), 700 (w). Anal. Calcd for $C_9H_5FO_2$: C, 65.86; H, 3.07%. Found: C, 65.93; H, 2.85%.

*α-Phenylcinnamoyl Fluoride (**1r**).* Yield was 91%. mp: 47−50 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.14 (d, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.30−7.33 (m, 3H), 7.44−7.46 (m, 3H), 7.99 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 127.4 (d, $^2J_{C-F}$ = 54 Hz), 128.6, 128.8, 129.2, 129.7, 130.6, 131.2, 133.5, 133.9, 146.5 (d, $^3J_{C-F}$ = 2 Hz), 158.3 (d, $^1J_{C-F}$ = 346 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 18.9. FT-IR (neat, cm^{-1}): 1790 (s), 1620 (m), 1493 (w), 1445 (m), 1223 (s), 1207 (m), 1138 (s), 1105 (w), 1074 (w), 949 (m), 907 (m), 781 (m), 762 (m), 698 (s). Anal. Calcd for $C_{15}H_{11}FO$: C, 79.63; H, 4.90%. Found: C, 79.55; H, 4.96%.

Representative Procedure for Decarbonylative Ethylation of 1a. *Synthesis of 4-Ethylbiphenyl (**4aa**).*[30] To a 20 mL Schlenk tube, Ni(cod)$_2$ (10 mol %, 3.4 mg, 0.0125 mmol), DPPE (10 mol %, 5.0 mg, 0.0125 mmol), and toluene (500 μL) were added. After stirring for a short time, BEt_3 (**2a**) (1.0 M hexane solution, 125 μL, 0.125 mmol) and biphenyl-4-carbonyl fluoride (**1a**) (25.0 mg, 0.125 mmol) were added, and resulting mixture was heated at 130 °C. After 24 h, the reaction was quenched with 1 M HCl solution, extracted with EtOAc, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was purified by column chromatography (hexane/Et_2O = 10:1) to afford the desired product of 4-ethylbiphenyl (**4aa**) (17.7 mg, 0.0971 mmol) in 78% yield. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.29 (t, *J* = 7.8 Hz, 3H), 2.71 (q, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.32−7.35 (m, 1H), 7.42−7.45 (m, 2H), 7.52−7.54 (m, 2H), 7.59−7.60 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 15.7, 28.7, 127.10, 127.16, 127.22, 128.4, 128.8, 138.8, 141.3, 143.5.

*4-Ethylbenzonitrile (**4ba**).*[31] Yield was 68% (11.1 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.25 (t, *J* = 7.8 Hz, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0

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Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.2, 29.2, 109.6, 119.3, 128.8, 132.3, 149.9.

*Methyl 4-Ethylbenzoate (**4ca**).*[31] Yield was 54% (11.0 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.25 (t, J = 7.8 Hz, 3H), 2.70 (q, J = 7.4 Hz, 2H), 3.90 (s, 3H), 7.26 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4, 29.1, 52.1, 127.6, 128.0, 129.8, 149.9, 167.4.

*1-Ethyl-4-(methylsulfonyl)benzene (**4da**).*[32] Yield was 51% (11.8 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.27 (t, J = 7.8 Hz, 3H), 2.75 (q, J = 7.6 Hz, 2H), 3.04 (s, 3H), 7.39 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.3, 29.0, 44.8, 127.6, 129.0, 138.0, 150.9.

*1-n-Butyl-4-ethylbenzene (**4ea**).*[33] Yield was 61% (12.4 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 0.92 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.5 Hz, 3H), 1.36 (sext, J = 7.4 Hz, 2H), 1.55−1.63 (m, 2H), 2.58 (t, J = 7.8 Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H), 7.09−7.12 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 14.1, 15.8, 22.6, 28.6, 33.9, 35.4, 127.8, 128.5, 140.2, 141.5.

*1-n-Butoyl-4-ethylbenzene (**4fa**).*[34] Yield was 52% (11.6 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 0.97 (t, J = 7.5 Hz, 3H), 1.21 (t, J = 7.8 Hz, 3H), 1.43−1.51 (m, 2H), 1.74−1.77 (m, 2H), 2.59 (q, J = 7.6 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 7.10 (d, J = 9.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 14.0, 16.0, 19.4, 28.1, 31.6, 67.8, 114.5, 128.8, 136.3, 157.3.

*3-Ethylbiphenyl (**4ga**).*[30] Yield was 71% (16.2 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.30 (t, J = 7.8 Hz, 3H), 2.73 (q, J = 7.6 Hz, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.33−7.38 (m, 2H), 7.41−7.46 (m, 4H), 7.60 (dd, J = 8.4, 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.8, 29.1, 124.7, 127.0, 127.28, 127.31, 127.35, 127.39, 128.83, 128.87, 128.89, 141.4, 141.6, 144.9.

*2-Ethylbiphenyl (**4ha**).*[30] Yield was 36% (8.2 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.10 (t, J = 7.8 Hz, 3H), 2.60 (q, J = 7.6 Hz, 2H), 7.18−7.42 (m, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.8, 26.3, 125.7, 126.9, 127.3, 127.4, 127.6, 128.1, 128.7, 128.9, 129.4, 130.1, 141.75, 141.77.

*5-Ethyl-1,2,3-trimethoxybenzene (**4ia**).*[35] Yield was 68% (16.6 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.24 (t, J = 7.5 Hz, 3H), 2.60 (q, J = 7.6 Hz, 2H), 3.82 (s, 3H), 3.86 (s, 6H), 6.42 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.8, 29.4, 56.2, 61.0, 104.8, 128.9, 136.0, 153.2.

*6-Ethyl-1,4-benzodioxane (**4ja**).*[36] Yield was 69% (14.2 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.20 (t, J = 7.8 Hz, 3H), 2.55 (q, J = 7.6 Hz, 2H), 4.24 (m, 4H), 6.67 (dd, J = 8.1, 2.1 Hz, 1H), 6.71 (d, J = 1.8 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.9, 28.3, 64.5, 64.6, 116.6, 117.1, 120.9, 137.8, 141.6, 143.4.

*1-Ethylnaphthalene (**4ka**).*[30] Yield was 70% (13.7 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.39 (t, J = 7.5 Hz, 3H), 3.12 (q, J = 7.2 Hz, 2H), 7.34 (d, J = 6.6 Hz, 1H), 7.41 (t, J = 6.9 Hz, 1H), 7.46−7.53 (m, 2H), 7.71 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.2, 26.0, 123.9, 125.0, 125.5, 125.8 (2C), 126.5, 128.9, 131.9, 133.9, 140.4.

*2-Ethylnaphthalene (**4la**).*[30] Yield was 74% (14.5 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.33 (t, J = 7.5 Hz, 3H), 2.82 (q, J = 7.6 Hz, 2H), 7.35 (dd, J = 8.4, 1.8 Hz, 1H), 7.39−7.46 (m, 2H), 7.63 (s, 1H), 7.76−7.81 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.7, 29.2, 123.6, 125.1, 125.7, 126.0, 127.2, 127.5, 127.7, 127.9, 131.0, 133.8, 141.9.

*9-Ethylanthracene (**4ma**).*[37] Yield was 56% (14.4 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.45 (t, J = 7.8 Hz, 3H), 3.65 (q, J = 7.8 Hz, 2H), 7.45−7.47 (m, 2H), 7.49−7.52 (m, 2H), 8.01 (d, J = 7.8 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 8.34 (s, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.7, 21.3, 124.5, 124.9, 125.5, 125.6, 129.3, 129.4, 131.8, 136.8.

*1-Ethyl-9H-fluorene (**4na**).*[38] Yield was 78% (19.0 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.32 (t, J = 7.5 Hz, 3H), 2.79 (q, J = 7.6 Hz, 2H), 3.85 (s, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.30 (td, J = 7.2, 1.2 Hz, 1H), 7.34−7.38 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 14.4, 26.4, 35.6, 117.6, 120.1, 125.1, 126.1, 126.7, 126.8, 127.4, 140.5, 141.5, 141.6, 142.2, 143.2.

*2-Ethylbenzo[b]thiophene (**4pa**).*[39] Yield was 70% (14.1 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.38 (t, J = 7.5 Hz, 3H), 2.94 (qd, J = 7.6, 1.2 Hz, 2H), 7.01 (d, J = 0.6 Hz, 1H), 7.23−7.26 (m, 1H), 7.28−7.32 (m, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.76 (dd, J = 7.8, 0.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.6, 24.3, 119.8, 122.3, 122.8, 123.5, 124.2, 139.3, 140.4, 148.5.

*2-Ethylbenzofuran (**4qa**).*[36] Yield was 28% (5.1 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.34 (t, J = 7.8 Hz, 3H), 2.80 (qd, J = 7.5, 0.9 Hz, 2H), 6.38 (d, J = 0.6 Hz, 1H), 7.16−7.22 (m, 2H), 7.41 (dd, J = 7.8, 0.6 Hz, 1H), 7.48 (dd, J = 6.3, 0.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 12.0, 21.9, 101.1, 110.8, 120.3, 122.5, 123.2, 129.1, 154.8, 161.1.

(E)-[40] *and (Z)-1,2-Diphenyl-1-butene (**4ra**).*[41] Yield was 66% (E/Z = 0.93:1) (17.2 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.05−1.08 (m, (E) and (Z)), 2.51 (qd, J = 7.4, 1.5 Hz, (Z)), 2.75 (q, J = 7.6 Hz, (E)), 6.43 (s, (Z)), 6.69 (s, (E)), 6.92 (d, J = 7.2 Hz, (Z)), 7.04−7.10 (m, (Z)), 7.15 (d, J = 7.2 Hz, (Z)), 7.24−7.48 (m, (E) and (Z)); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 13.0 (Z), 13.6 (E), 23.4 (E), 33.7 (Z), 125.2 (Z), 126.2 (Z), 126.7 (E), 126.8 (Z), 126.9 (E), 127.3 (E), 127.7 (Z), 127.9 (E), 128.4 (Z), 128.5 (E), 128.6 (E), 128.7 (Z), 128.9 (E), 129.1 (Z), 137.7 (Z), 138.4 (E), 141.6 (Z), 142.8 (E), 144.6 (E), 145.1 (Z).

Decarbonylative C(aroyl)−F Bond Methylation of 1a with Trimethylboroxine: Synthesis of 4-Methylbiphenyl (4ab).[42] To a 20 mL Schlenk tube, $Ni(cod)_2$ (20 mol %, 6.9 mg, 0.025 mmol), DPPE (20 mol %, 10.0 mg, 0.025 mmol), and toluene (500 μL) were added. Subsequently, CsF (38.0 mg, 0.25 mmol, 2 equiv), $(MeBO)_3$ (**2b**) (34.9 μL, 0.25 mmol, 2 equiv), and biphenyl-4-carbonyl fluoride (**1a**) (25.0 mg, 0.125 mmol) were added, and the resulting mixture was heated at 130 °C. After 24 h, the reaction mixture was quenched with 1 M HCl, extracted with EtOAc, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was purified by column chromatography (hexane/Et_2O = 10:1) to afford **4ab** (10 mg, 0.061 mmol) in 49% yield.

^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 2.40 (s, 3H), 7.26 (d, J = 7.8 Hz, 2H), 7.31−7.34 (m, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 8.4, 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 21.2, 127.12, 127.14, 127.3, 128.9, 129.6, 137.2, 138.5, 141.3.

Representative Procedure for Palladium-Catalyzed *ortho*-C−H Arylation of 2-Naphthoic Acid (5). *Synthesis of 3-Phenyl-2-naphthoic Acid (**6a**).*[43] To an oven-dried 20 mL Schlenk tube, $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5 mol %), Ag_2CO_3 (358 mg, 1.3 mmol, 1.3 equiv), 2-naphthoic acid (**5**) (172 mg, 1.0 mmol), iodobenzene (336 μL, 3.0 mmol, 3.0

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equiv), and AcOH (100 μL) were added under argon atmosphere. After the reaction mixture was stirred at 145 °C for 6 h, it was cooled to room temperature and quenched with 1 M HCl. The mixture was filtrated by Celite, extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. After the volatiles were evaporated, the crude mixture was purified by column chromatography (CH_2Cl_2/EtOAc = 10:1) and the high-boiling starting material 2-naphthoic acid (**5**) was removed by bulb-to-bulb distillation (2 mmHg, 200 °C) to afford **6a** in 62% yield.

^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.41−7.46 (m, 5H), 7.56 (td, *J* = 7.5, 1.2 Hz, 1H), 7.62 (td, *J* = 7.6, 1.4 Hz, 1H), 7.82 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 8.55 (s, 1H). The signal of carboxylic acid was not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 126.9, 127.3, 127.5, 127.8, 128.1, 128.78, 128.81, 128.9, 130.3, 131.5, 132.6, 134.8, 139.2, 141.2, 173.9.

*3-(p-Tolyl)-2-naphthoic Acid (**6b**).*[44] Yield was 49% (129 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 2.44 (s, 3H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.55 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.82 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 8.56 (s, 1H). The signal of carboxylic acid was not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 21.4, 126.8, 127.7, 127.9, 128.7, 128.8, 128.9, 129.0, 130.3, 131.5, 132.5, 134.9, 137.0, 138.3, 139.1, 173.9.

*3-(p-Anisoyl)-2-naphthoic Acid (**6c**).*[44] Yield was 45% (125 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 3.78 (s, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.55 (td *J* = 7.5, 0.8 Hz, 1H), 7.61 (td, *J* = 7.6, 1.0 Hz, 1H), 7.81 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.56 (s, 1H). The signal of carboxylic acid was not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 55.3, 113.7, 126.8, 127.7, 127.8, 128.7, 128.9, 129.9, 130.2, 131.3, 132.5, 133.6, 134.9, 138.8, 159.0, 174.0.

*3-(p-Trifluoromethylphenyl)-2-naphthoic Acid (**6d**).*[44] Yield was 59% (187 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.66 (td, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.78 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 8.64 (s, 1H). The signal of carboxylic acid was not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 124.5 (q, $^1J_{C-F}$ = 272 Hz), 125.0 (q, $^2J_{C-F}$ = 4 Hz), 126.7, 127.5, 128.0, 129.1, 129.2, 129.3, 129.5, 130.7, 131.9, 133.3, 134.9, 138.1, 145.2, 172.6; ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ −62.3.

Representative Procedure for the Direct Fluorination of 3-Aryl-2-naphthoic Acids with Deoxo-Fluor. *Synthesis of 3-Phenyl-2-naphthoyl Fluoride (**7a**).* To a 20 mL Schlenk tube charged with a magnetic stirrer bar, Deoxo-Fluor reagent (32.3 μL, 0.175 mmol, 1.1 equiv) was slowly added to the solution of 3-phenyl-2-naphthoic acid (**6a**) (39.4 mg, 0.159 mmol) in CH_2Cl_2 (0.8 mL) at 0 °C. After the addition, the solution was allowed to warm to room temperature. After 30 min, the reaction mixture was quenched with sat. $NaHCO_3$ aq, extracted with CH_2Cl_2, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was subjected to column chromatography (Hex/Et_2O = 10:1) to afford 3-phenyl-2-naphthoyl fluoride (**7a**) (31.1 mg) in 78% yield. mp: 76−78 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.41−7.48 (m, 5H), 7.61−7.63 (m, 1H), 7.68−7.71 (m, 1H), 7.86 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 8.66 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 122.3 (d, $^2J_{C-F}$ = 57 Hz), 127.5, 127.8, 128.0, 128.4, 128.9, 129.3, 130.1, 131.0 (d, $^3J_{C-F}$ = 2 Hz), 131.4, 135.0 (d, $^3J_{C-F}$ = 2 Hz), 135.6, 140.1 (d, *J* = 2 Hz), 140.4, 157.5 (d, $^1J_{C-F}$ = 347 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 33.4. FT-IR (neat, cm^{-1}): 1801 (s), 1273 (m), 1252 (m), 1186 (s), 1128 (m), 1055 (m), 1011 (m), 949 (s), 916 (m), 893 (m), 764 (s), 698 (m). Anal. Calcd for $C_{17}H_{11}FO$: C, 81.59; H, 4.43%. Found: C, 81.91; H, 4.64%.

*3-(p-Tolyl)-2-naphthoyl Fluoride (**7b**).* Yield was 52%. mp: 81−83 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 2.44 (s, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.60 (m, 1H), 7.68 (m, 1H), 7.84 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 8.63 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 21.4, 122.4 (d, $^2J_{C-F}$ = 57 Hz), 127.4, 128.0, 128.7, 129.1, 129.2, 130.0, 130.9 (d, $^3J_{C-F}$ = 2 Hz), 131.3, 134.9 (d, $^3J_{C-F}$ = 2 Hz), 135.7, 137.5, 137.6, 140.0, 157.6 (d, $^1J_{C-F}$ = 347 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 33.6. FT-IR (neat, cm^{-1}): 1811 (s), 1626 (m), 1441 (m), 1275 (m), 1258 (s), 1186 (s), 1125 (m), 1055 (s), 1015 (s), 951 (s), 897 (s), 812 (s), 766 (s), 750 (s). Anal. Calcd for $C_{18}H_{13}FO$: C, 81.80; H, 4.96%. Found: C, 81.55; H, 5.20%.

*3-(p-Anisoyl)-2-naphthoyl Fluoride (**7c**).* Yield was 31%. mp: 97−99 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 3.88 (s, 3H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.60 (m, 1H), 7.68 (m, 1H), 7.83 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 8.62 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 55.3, 113.8, 122.3 (d, $^2J_{C-F}$ = 55 Hz), 127.3, 127.8, 129.1, 129.9, 130.0, 130.8 (d, $^3J_{C-F}$ = 2 Hz), 131.1, 132.6, 134.8 (d, $^3J_{C-F}$ = 2 Hz), 135.6, 139.6, 157.6 (d, $^1J_{C-F}$ = 347 Hz), 159.4; ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ 33.8. FT-IR (neat, cm^{-1}): 1811 (s), 1607 (m), 1516 (s), 1458 (m), 1285 (m), 1248 (s), 1182 (s), 1126 (m), 1013 (m), 957 (m), 837 (m), 756 (m). Anal. Calcd for $C_{18}H_{13}FO_2$: C, 77.13; H, 4.68%. Found: C, 77.04; H, 4.43%.

*3-(p-Trifluoromethylphenyl)-2-naphthoyl Fluoride (**7d**).* Yield was 43%. mp: 102−105 °C. ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.65−7.67 (m, 1H), 7.71−7.74 (m, 3H), 7.83 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.71 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt) δ 121.6 (d, $^2J_{C-F}$ = 58 Hz), 122.5 (q, $^1J_{C-F}$ = 272 Hz), 125.3 (q, $^3J_{C-F}$ = 4 Hz), 128.0, 128.1, 129.3, 129.4, 130.0 (q, $^2J_{C-F}$ = 32 Hz), 130.5, 131.2 (d, $^3J_{C-F}$ = 2 Hz), 131.7, 135.5, 135.6, 138.7, 144.1, 157.0 (d, $^1J_{C-F}$ = 346 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$, 564 MHz, rt) δ −62.5, 31.7. FT-IR (neat, cm^{-1}): 1807 (s), 1325 (s), 1184 (s), 1109 (s), 1069 (m), 1018 (m), 955 (m), 845 (m), 760 (m). Anal. Calcd for $C_{18}H_{10}F_4O$: C, 67.93; H, 3.17%. Found: C, 67.58; H, 3.04%.

Representative Procedure for Decarbonylative Ethylation of 7a.[46] *Synthesis of **8a**[45] and **8a′**.*[46] To a 20 mL Schlenk tube, Ni(cod)$_2$ (10 mol %, 3.4 mg, 0.0125 mmol), DPPE (10 mol %, 5.0 mg, 0.0125 mmol), and toluene (500 μL) were added. Subsequently, BEt_3 (**2a**) (1.0 M hexane solution, 125 μL, 0.125 mmol) and 3-phenyl-2-naphthoyl fluoride (**7a**) (31.3 mg, 0.125 mmol) were added, and the resulting mixture was heated at 130 °C. After 24 h, the reaction was quenched with 1 M HCl, extracted with EtOAc, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was purified by column chromatography (hexane/Et_2O = 10:1) and high-performance liquid chromatography (eluent: $CHCl_3$) to give a mixture of **8a** and **8a′**. Combined yield was 33% in an NMR ratio of 83:17 (**8a**:**8a′**). ^{1}H NMR ($CDCl_3$, 600 MHz, rt): δ 1.10 (t, *J* = 7.5 Hz, **8a′**), 1.15 (t, *J* = 7.5 Hz, **8a**), 2.64 (q, *J* = 7.6 Hz, **8a′**), 2.75

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(q, J = 7.6 Hz, **8a**), 7.34−7.90 (m, **8a** and **8a′**); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.3 (**8a**), 15.8 (**8a′**), 26.4 (**8a′**), 26.7 (**8a**), 125.6 (**8a**), 125.7 (**8a′**), 125.96 (**8a′**), 125.98 (**8a**), 126.3 (**8a′**), 126.6 (**8a**), 127.0 (**8a**), 127.3 (**8a**), 127.6 (**8a′**), 127.70 (**8a**), 127.75 (**8a′**), 127.8 (**8a′**), 127.9 (**8a′**), 128.0 (**8a′**), 128.1 (**8a′**), 128.2 (**8a**), 128.7 (**8a**), 129.0 (**8a′**), 129.5 (**8a**), 130.3 (**8a′**), 131.9 (**8a**), 132.4 (**8a′**), 133.1 (**8a**), 133.4 (**8a′**), 139.7 (**8a′**), 140.3 (**8a**), 140.9 (**8a**), 141.7 (**8a′**), 141.96 (**8a**), 141.97 (**8a′**).

*Synthesis of **8b** and **8b′***. Combined yield was 32% in an NMR ratio of 81:19 (**8b**:**8b′**). ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.09 (t, J = 7.5 Hz, **8b′**), 1.15 (t, J = 7.5 Hz, **8b**), 2.41 (s, **8b′**), 2.43 (s, **8b**), 2.61 (q, J = 7.6 Hz, **8b′**), 2.75 (q, J = 7.4 Hz, **8b**), 7.08−7.10 (m, **8b′**), 7.17 (s, **8b′**), 7.19 (d, J = 7.8 Hz, **8b′**), 7.24−7.29 (m, **8b** and/or **8b′**), 7.41−7.51 (m, **8b** and/or **8b′**), 7.65 (s, **8b**), 7.73 (s, **8b**), 7.75 (s, **8b′**), 7.79 (d, J = 8.4 Hz, **8b**), 7.82 (d, J = 7.8 Hz, **8b**), 7.84−7.89 (m, **8b** and **8b′**); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4 (**8b**), 15.9 (**8b′**), 21.4 (**8b**), 26.3 (**8b′**), 26.7 (**8b**), 29.8 (**8b′**), 125.5 (**8b**), 125.87 (**8b**), 125.88 (**8b′**), 126.2 (**8b′**), 126.50 (**8b**), 126.52 (**8b′**), 127.3 (**8b**), 127.5 (**8b′**), 127.7 (**8b**), 127.8 (**8b′**), 128.0 (**8b′**), 128.1 (**8b′**), 128.2 (**8b′**), 128.8 (**8b**), 128.9 (**8b**), 129.38 (**8b**), 129.39 (**8b′**), 129.5 (**8b′**), 130.3 (**8b′**), 131.9 (**8b**), 133.1 (**8b**), 133.4 (**8b′**), 136.7 (**8b**), 137.4 (**8b′**), 138.1 (**8b′**), 139.0 (**8b**), 139.7 (**8b′**), 140.4 (**8b**), 140.9 (**8b**).

*Synthesis of **8c** and **8c′***. Combined yield was 47% in an NMR ratio of 80:20 (**8c**:**8c′**). ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.11 (t, J = 7.5 Hz, **8c′**), 1.16 (t, J = 7.5 Hz, **8c**), 2.63 (q, J = 7.4 Hz, **8c′**), 2.76 (q, J = 7.4 Hz, **8c**), 3.87 (s, **8c′**), 3.88 (s, **8c**), 6.83 (dd, J = 8.4, 2.4 Hz, **8c′**), 6.90 (d, J = 2.4 Hz, **8c′**), 6.98 (d, J = 9.0 Hz, **8c**), 7.23 (d, J = 8.4 Hz, **8c′**), 7.32 (d, J = 8.4 Hz, **8c**), 7.41−7.51 (m, **8c** and/or **8c′**), 7.66 (s, **8c**), 7.73 (s, **8c**), 7.74 (s, **8c′**), 7.79 (d, J = 7.8 Hz, **8c**), 7.82 (d, J = 7.8 Hz, **8c**), 7.84−7.89 (m, **8c′**); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4 (**8c**), 15.7 (**8c′**), 26.6 (**8c′**), 26.8 (**8c**), 55.4 (**8c′**), 55.5 (**8c**), 110.9 (**8c′**), 113.6 (**8c**), 114.3 (**8c′**), 125.5 (**8c**), 125.8 (**8c′**), 125.9 (**8c**), 126.2 (**8c′**), 126.5 (**8c**), 127.2 (**8c**), 127.5 (**8c′**), 127.6 (**8c**), 127.8 (**8c′**), 128.1 (**8c′**), 128.3 (**8c′**), 128.8 (**8c**), 130.5 (**8c**), 131.3 (**8c′**), 131.4 (**8c′**), 131.9 (**8c**), 132.3 (**8c′**), 133.1 (**8c**), 133.4 (**8c′**), 134.35 (**8c**), 134.37 (**8c′**), 139.4 (**8c′**), 140.53 (**8c**), 140.58 (**8c**), 143.4 (**8c′**), 158.8 (**8c**), 159.2 (**8c′**).

*Synthesis of **8d** and **8d′***. Combined yield was 27% in an NMR ratio of 27:73 (**8d**:**8d′**). ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.12 (t, J = 7.8 Hz, **8d′**), 1.15 (t, J = 7.5 Hz, **8d**), 2.69 (q, J = 7.6 Hz, **8d′**), 2.73 (q, J = 7.8 Hz, **8d**), 7.38−7.55 (m, **8d** and/or **8d′**), 7.60 (s, **8d′**), 7.65 (s, **8d**), 7.70−7.91 (m, **8d** and/or **8d′**); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4 (**8d**), 15.5 (**8d′**), 26.4 (**8d′**), 26.7 (**8d**), 122.5 (q, $^3J_{C-F}$ = 3.8 Hz, **8d′**), 123.6 (**8d′**), 124.5 (q, $^1J_{C-F}$ = 272 Hz, **8d**), 125.2 (q, $^3J_{C-F}$ = 3.8 Hz, **8d**), 125.5 (q, $^3J_{C-F}$ = 3.8 Hz, **8d′**), 125.9 (**8d**), 126.38 (**8d′**), 126.40 (**8d**), 126.6 (**8d′**), 126.9 (**8d**), 127.2 (**8d′**), 127.29 (**8d′**), 127.34 (**8d**), 127.7 (**8d′**), 127.75 (**8d**), 127.76 (**8d′**), 127.80 (**8d′**), 127.9 (**8d′**), 128.0 (**8d′**), 128.2 (**8d′**), 128.8 (**8d**), 129.2 (**8d′**), 129.3 (q, $^2J_{C-F}$ = 32 Hz, **8d**), 129.87 (**8d**), 129.9 (q, $^2J_{C-F}$ = 32 Hz, **8d′**), 130.7 (**8d′**), 131.8 (**8d**), 132.6 (**8d′**), 133.3 (**8d′**), 133.4 (**8d**), 138.3 (**8d′**), 139.4 (**8d**), 139.7 (**8d**), 142.9 (**8d′**), 145.2 (**8d′**), 145.7 (**8d**); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ −62.38 (**8d′**), −62.37 (**8d**).

Acetylation of 3-Hydroxy-2-naphthoic Acid (9): Synthesis of 3-Acetoxy-2-naphthoic Acid (10).[47] To a 50 mL Schlenk tube, 3-hydroxy-2-naphthoic acid (**9**) (27 g, 143.5 mmol) and acetic anhydride (Ac_2O) (40 mL) were added. Subsequently, a small amount of conc. H_2SO_4 (20−30 drops) was added, and the resulting mixture was vigorously stirred and heated at 90 °C. After 30 min, the completion of reaction was checked by GC−MS, subsequently quenched by water, extracted with CH_2Cl_2/acetone (∼10:1), washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was washed with hexane and collected **10** by filtration. Isolated yield of the target 3-acetoxy-2-naphthoic acid (**10**) was 87% (28.8 g, 125.1 mmol). ^1H NMR (acetone-d_6, 600 MHz, rt): δ 2.30 (s, 3H), 7.59−7.62 (m, 1H), 7.66−7.69 (m, 2H), 7.96 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.69 (s, 1H). The signal of −COO*H* was not observed. $^{13}C\{^1H\}$ NMR (acetone-d_6, 151 MHz, rt) δ 21.1, 121.8, 123.5, 127.5, 128.0, 129.8, 129.9, 131.5, 134.4, 136.6, 148.2, 165.9, 170.3.

Fluorination of 10 with Deoxo-Fluor Reagent: Synthesis of 3-Acetoxy-2-naphthoyl Fluoride (11). To a 20 mL Schlenk tube equipped with a magnetic stirrer bar, 3-acetoxy-2-naphthoic acid (**10**) (230 mg, 1.0 mmol), CH_2Cl_2 (25 mL), and Et_2O (10 mL) were successively added. After the mixture was stirred at 0 °C, Deoxo-Fluor reagent (1.1 equiv, 203 μL, 1.1 mmol) was slowly added to the reaction mixture. After the reaction was stirred at 0 °C for 30 min, the solution was slowly poured into saturated $NaHCO_3$. After CO_2 evolution ceased, the reaction mixture was extracted into CH_2Cl_2 (3 × 15 mL) and dried over $MgSO_4$. The crude product was purified by flash chromatography (Hex/Et_2O = 10:1) to afford **11** in 77% yield. mp: 77−79 °C. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 2.43 (s, 3H), 7.58 (m, 2H), 7.67−7.70 (m, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.4, 0.6 Hz, 1H), 8.65 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 21.1, 116.7 (d, $^2J_{C-F}$ = 60 Hz), 122.0 (d, $^3J_{C-F}$ = 3 Hz), 127.4, 127.6, 129.6, 130.5, 130.6, 136.5, 136.9, 147.2 (d, $^3J_{C-F}$ = 5 Hz), 154.2 (d, $^1J_{C-F}$ = 342 Hz), 170.1; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ 26.8. FT-IR (neat, cm^{-1}): 1809 (s), 1763 (s), 1209 (s), 1153 (m), 1121 (m), 978 (s), 905 (m), 764 (s). Anal. Calcd for $C_{13}H_9FO_3$: C, 67.24; H, 3.91%. Found: C, 67.13; H, 3.92%.

Chemoseletive C(aroyl)−F Bond Ethylation of 11: Synthesis of 3-Acetoxy-2-ethylnaphthalene (12). To a 20 mL Schlenk tube, $Ni(cod)_2$ (10 mol %, 3.4 mg, 0.0125 mmol), DPPE (10 mol %, 5.0 mg, 0.0125 mmol), and toluene (500 μL) were added. Subsequently, BEt_3 (**2a**) (1.0 M hexane solution, 125 μL, 0.125 mmol) and 3-acetoxy-2-naphthoyl fluoride (**11**) (29.0 mg, 0.125 mmol) were added, and resulting mixture was heated at 130 °C. After 24 h, the reaction mixture was quenched with 1 M HCl, extracted with EtOAc, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was purified by column chromatography (hexane/Et_2O = 10:1) and high-performance liquid chromatography (eluent: $CHCl_3$) to afford **12** (14 mg, 0.065 mmol) in 51% yield. mp: 48−50 °C. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.31 (t, J = 7.5 Hz, 3H), 2.39 (s, 3H), 2.71 (q, J = 7.6 Hz, 2H), 7.41−7.45 (m, 2H), 7.50 (s, 1H), 7.71 (s, 1H), 7.75−7.81 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 14.1, 21.1, 23.7, 119.4, 125.8, 125.9, 127.4, 127.9, 132.1, 132.5, 135.3, 147.7, 169.8. FT-IR (neat, cm^{-1}): 1753 (s), 1053 (m), 1439 (m), 1366 (s), 1339 (s), 1211 (s), 1146 (s), 1121 (m), 1092 (s), 1051 (m), 1013 (m), 988 (m), 959 (m), 930 (s), 899 (s), 756 (s). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%. Found: C, 78.10; H, 6.61%.

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C−O Bond Arylation of 12.[48] *Synthesis of 2-Ethyl-3-phenylnaphthalene (**8a**).*[48] To a 20 mL Schlenk tube, $NiCl_2(PCy_3)_2$ (10 mol %, 17.3 mg, 0.025 mmol), K_3PO_4 (2 equiv, 106 mg, 0.5 mmol), $(PhBO)_3$ (1.2 equiv, 94 mg, 0.3 mmol), 3-acetoxy-2-ethylnaphthalene (**12**) (54 mg, 0.25 mmol), and 1,4-dioxane (2 mL) were added. Subsequently, water (4 μL) was added and resulting mixture was heated at 110 °C. After 12 h, the reaction was quenched with 1 M HCl, extracted with EtOAc, washed by brine, and dried over $MgSO_4$. After the volatiles were removed under vacuum, the crude product was purified by column chromatography (hexane/Et_2O = 10:1) and high-performance liquid chromatography (eluent: $CHCl_3$) to afford **8a** (36.5 mg, 0.157 mmol) in 63% yield without the formation of any regioisomer. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.19 (t, *J* = 7.5 Hz, 3H), 2.79 (q, *J* = 7.4 Hz, 2H), 7.40−7.51 (m, 7H), 7.71 (s, 1H), 7.78 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4, 26.7, 125.6, 126.0, 126.6, 127.0, 127.3, 127.7, 128.2, 128.7, 129.5, 131.9, 133.1, 140.3, 140.9, 142.0.

*2-Ethyl-3-(p-tolyl)naphthalene (**8b**).* Yield was 75%. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.19 (t, *J* = 7.5 Hz, 3H), 2.47 (s, 3H), 2.79 (q, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.44−7.50 (m, 2H), 7.69 (s, 1H), 7.77 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4, 21.4, 26.7, 125.5, 125.9, 126.5, 127.2, 127.7, 128.8, 128.9, 129.4, 131.9, 133.1, 136.6, 139.0, 140.4, 140.9. FT-IR (neat, cm^{-1}): 1514 (m), 1493 (s), 1456 (s), 1020 (m), 887 (s), 826 (s), 785 (m), 746 (s), 727 (m). Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37%. Found: C, 92.58; H, 7.42%.

*2-Ethyl-3-(4-methoxyphenyl)naphthalene (**8c**).* Yield was 64%. mp: 85−87 °C. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.17 (t, *J* = 7.5 Hz, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.42−7.48 (m, 2H), 7.67 (s, 1H), 7.75 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.4, 26.8, 55.5, 113.6, 125.5, 125.9, 126.5, 127.3, 127.6, 128.8, 130.5, 131.9, 133.1, 134.3, 140.5, 140.6, 158.8. FT-IR (neat, cm^{-1}): 1512 (s), 1493 (m), 1460 (m), 1240 (s), 1179 (m), 1036 (m), 837 (m), 752 (s). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92%. Found: C, 86.80; H, 6.93%.

*2-Ethyl-3-(4-trifluoromethylphenyl)naphthalene (**8d**).* Yield was 44%. mp: 98−100 °C. ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 1.17 (t, *J* = 7.8 Hz, 3H), 2.74 (q, *J* = 7.4 Hz, 2H), 7.46−7.51 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.78 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 15.3, 26.6, 124.5 (q, $^1J_{C-F}$ = 272 Hz), 125.2 (q, $^3J_{C-F}$ = 3.5 Hz), 125.9, 126.4, 126.9, 127.3, 127.7, 128.8, 129.3 (q, $^2J_{C-F}$ = 32 Hz), 129.9, 131.8, 133.4, 139.4, 139.7, 145.7; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 564 MHz, rt) δ −62.35. FT-IR (neat, cm^{-1}): 1323 (s), 1159 (s), 1128 (s), 1105 (s), 1065 (s), 1018 (m), 895 (m), 849 (m), 750 (s). Anal. Calcd for $C_{19}H_{15}F_3$: C, 75.99; H, 5.03%. Found: C, 75.66; H, 4.99%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02155.

More detailed results of nickel-catalyzed reactions and the ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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