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光催化苯乙烯与 $BrCF_2CO_2Me$ 的 2：2 偶联反应：双-二氟乙酸酯己雌酚衍生物的合成

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摘要 报道了光催化苯乙烯与 $BrCF_2CO_2Me$ 的 2：2 偶联反应，通过原位生成的 β-CF_2CO_2Me 取代的苄基自由基完成偶联反应. 该反应官能团兼容性好，适用于多种底物类型，可以高产率合成双-二氟乙酸酯己雌酚衍生物.
关键词 光催化；自由基自偶联；己雌酚衍生物

Photocatalyzed 2：2 Coupling of Styrene and $BrCF_2CO_2Me$: A Facile Synthesis of Bis-difluoroacetylated Hexestrol Derivatives

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Abstract Photoredox-catalyzed 2：2 coupling of styrene and $BrCF_2CO_2Me$ is reported, which undergoes a homo-coupling of *in situ* generated β-CF_2CO_2Me substituted benzyl radical. The reaction features a wide substrate scope and functional group tolerance to afford bis-difluoroacetylated hexestrol derivatives with high yields.
Keywords photocatalysis; radical homo-coupling; hexestrol derivatives

1 Introduction

Fluorine-substituted compounds have been widely used in materials, agrochemicals, and pharmaceuticals due to the compatibility of fluorine with lipophilicity and unique stability in human metabolic system.[1] Difluoroacetylated compounds have shown prospective applications in direct regulation of molecular properties or further function group modification.[2] For instance, alkyl chain with 1,4-relationship of two CF_2 groups favors an extended conformation owing to the dipole-dipole interactions and steric hindrance of the two CF_2 groups.[1f,3] The introduction of two-difluoromethylene groups to hexestrol, known as non-steroidal estrogens,[4] has the potential to improve the drug performance. Classic hexestrol derivatives with alkyl chains could be obtained by coupling reaction of substituted styrene[5] with benzylic derivatives[6-7] through a metal-catalyzed process (Scheme 1a). Fluorine-substituted hexestrol was first synthesized by reductive coupling and hydrogenation of α-trifluoromethyl acetophenone[8] (Scheme 1b). Homo-coupling reaction of styrene derivatives mediated by the addition of CF_3 radical could also afford fluorine-substituted hexestrol, but it could only be observed by GC-MS or separated as one by-product.[9] Recently, Tlili and co-workers[10] reported a photocatalyzed strategy using R_FSO_2Na (R_F＝CF_3, CF_2H, CF_2H) and styrenes as substrates, which successfully afforded 1,4-$(CF_3)_2$ hexestrols, as well as 1,4-$(CF_2H)_2$ and 1,4-$(CFH_2)_2$ products (Scheme 1c). Method to efficiently introduce bis-difluoroacetate into the hexestrol skeletal is rarely reported, only one example obtaining diethyl 2,2,7,7-tetrafluoro-4,5-dimethyl-4,5-diphenyloctanedienoate in 60% yield with stoichiometric copper reagent and high temperature has been reported.[11]

Difluoroacetylation of alkenes has been widely exploited to introduce difluoroacetate into organic molecules, using difluoroacetate reagents XCF_2CO_2R with easy leaving groups (X＝Cl, Br, I, FSO_2). Among them, metal-

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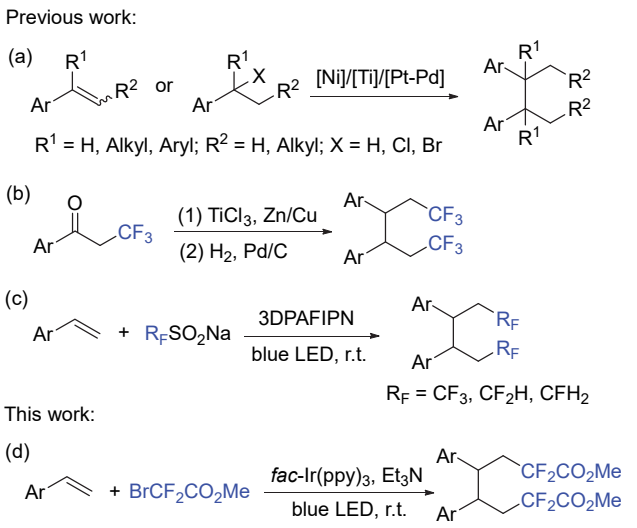


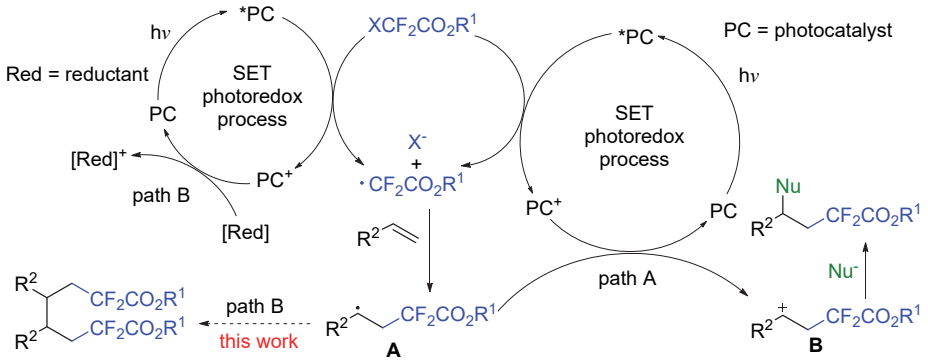
Scheme 1 Synthesis of hexestrol derivatives

catalyzed method has been well established to afford difluoroacetylated compounds by the difunctionalization of alkenes.[12] Meanwhile, photo-catalyzed difluoroacetylation of alkenes with XCF_2CO_2R has also been well-developed to synthesize similar products. The single-electron transfer (SET) between excited photocatalyst PC and XCF_2CO_2R generates the CF_2CO_2R radical and oxidized photocatalyst to PC^+ initially. Then the CF_2CO_2R radical attacks alkene to generate CF_2CO_2R substituted radical **A**, which can complete another SET process with PC^+ to afford CF_2CO_2R substituted carbocation **B** and realize subsequent conversion (Scheme 2, path A). The generated **B** could further combine with nucleophilic reagents to realize difunctionalization of alkenes such as halogenation,[13] oxydation,[14] thiolation,[15] amination,[15-16] cyanation,[17] alkenylation,[18] alkynylation,[19] arylation,[20] and ketonization.[21] We envisioned that direct coupling reaction of *in situ* generated CF_2CO_2R substituted radical **A** in the presence of additional reductant (Scheme 2, path B) could afford the bis-difluoroacetylated hexestrols. To the best of our knowledge, the direct transformation of the *in situ* generated CF_2CO_2R substituted radical **A** is rarely reported.[11] Herein, a photoredox-catalyzed strategy was developed to synthesize products with two CF_2CO_2Me groups located 1,4 in hexestrols through 2∶2 coupling of styrene derivatives and $BrCF_2CO_2Me$ under room temperature and irradiation of blue LEDs, in which the yield of desired product was up to 90% (Scheme 1d).

2 Results and discussion

During our study on a photoredox-catalyzed fluorodifluoroacetylation of alkene **1a** with $FSO_2CF_2CO_2Me$ (Chen's reagent) and Et_3N•3HF in dimethyl sulfoxide (DMSO),[13e] the product **3a** was obtained in a 40% NMR yield, where F source from Et_3N•3HF did not involve (Table 1, Entry 1). Thus, Et_3N, DBU, and $^iPr_2NEt$ were screened without HF, resulting in unsatisfactory yield of the desired product (Entries 2～4). Next, changing the solvent from DMSO to CH_3CN, and almost the same amount of desired product **3a** was obtained (Entry 5). Then the amount of Et_3N in CH_3CN (Entries 6～8) was screened and 3.0 equiv. of Et_3N was found to be the most proper amount (Entry 7). Generation of fluoride ion might be disadvantageous in CH_3CN. Thus, difluoroacetate sources substituted with various halogen were surveyed. When $ClCF_2CO_2Me$ and $BrCF_2CO_2Me$ were used (Entries 9～10), the coupling product **3a** was obtained in 80% and 90% yield, respectively, while employing ICF_2CO_2Et afforded **3a'** in 84% yield (Entry 11). The result might attribute to the dissociating ability of the substituted halogen, since the cleavage of C—Br or C—I bond was easier, compared with the cleavage of F—S and C—S bond in fluorosulfonyl substituted substrate.[22]

The substrate scope of this reaction was explored under the optimized condition (Table 1, Entry 10). Assorted alkenes with various electronic and steric effects on the aromatic ring could be converted into the target product **3** in good yields with a superb regioselectivity (Table 2). Substrates with electron-donating groups at the *para*-position of the phenyl ring were favourably transformed into desired products **3a**～**3e** in high yields. Substrates with electron-withdrawing groups at the *para*-position of the phenyl ring afforded the target compounds **3f**～**3k** in moderate yields, which might attribute to the instability of benzylic radical intermediate caused by the electron-with- drawing effect. Substrates with methyl at the *meta*-position afforded product **3l** in 69% isolated yield, while placing methyl at the *ortho*-position decreased the yield of product **3m** to



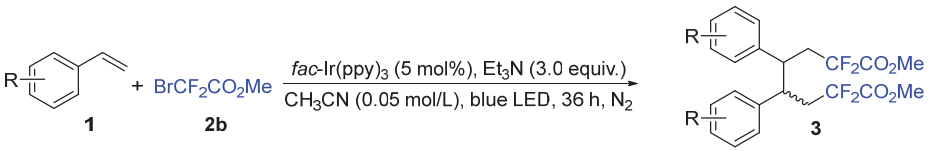
Scheme 2 Mechanism of photocatalyzed difluoroacetylation of alkenes with XCF_2CO_2R

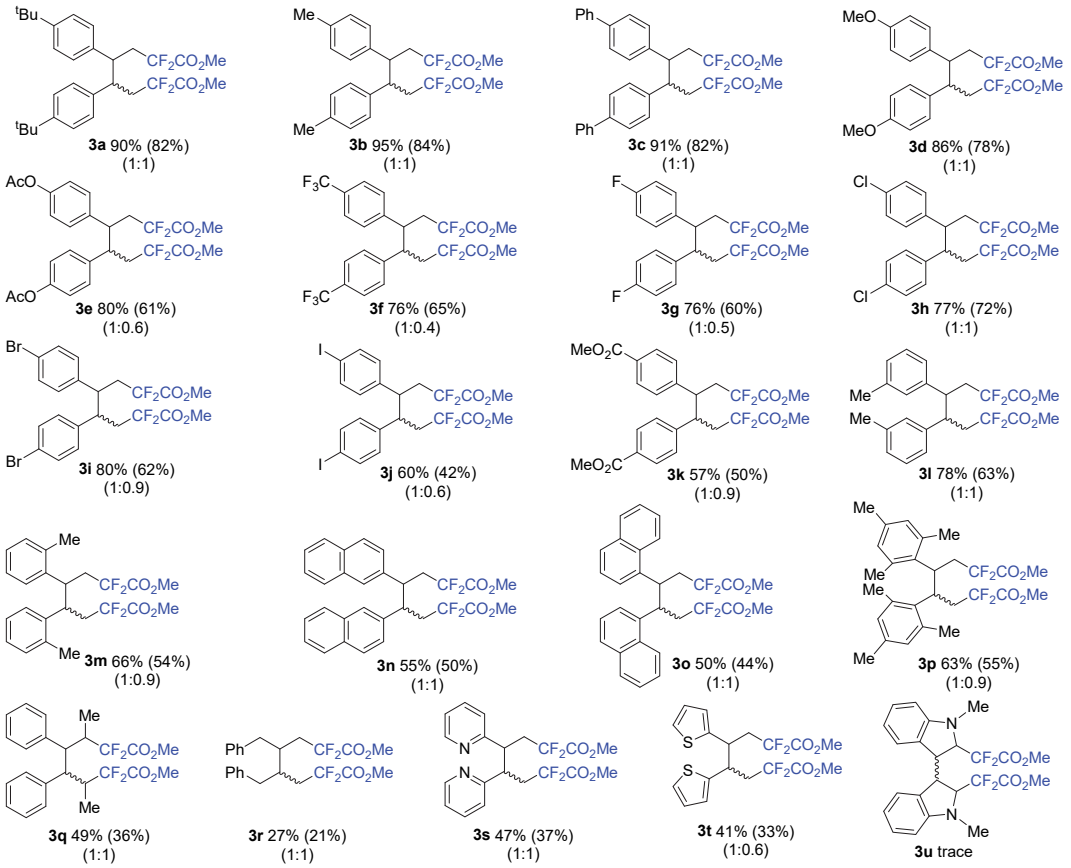
Table 1 Optimization of reaction conditions[a]

Entry	XCF_2CO_2R (equiv.)	Reductant (equiv.)	Solvent	Yield[d]/%
1[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N•3HF (5.0)	DMSO	61
2[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N (5.0)	DMSO	56
3[b]	$FSO_2CF_2CO_2Me$ (2.0)	DBU (5.0)	DMSO	n.d.
4[b]	$FSO_2CF_2CO_2Me$ (2.0)	$^iPr_2NEt$ (5.0)	DMSO	54
5[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N (5.0)	CH_3CN	55
6[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N (1.0)	CH_3CN	41
7[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N (3.0)	CH_3CN	60
8[b]	$FSO_2CF_2CO_2Me$ (2.0)	Et_3N (4.0)	CH_3CN	53
9[b]	$ClCF_2CO_2Me$ (2.0)	Et_3N (3.0)	CH_3CN	80
10[b]	$BrCF_2CO_2Me$ (2.0)	Et_3N (3.0)	CH_3CN	90 (82)
11[c]	ICF_2CO_2Et (2.0)	Et_3N (3.0)	CH_3CN	84

[a] Reaction conditions: **1a** (0.2 mmol), **2** (2.0 equiv.), *fac*-Ir(ppy)$_3$ (5.0 mol%), reductant (3.0 equiv.), solvent (4.0 mL), r.t.,, 36 h, N_2, 5 W blue LEDs. [b] R=Me. [c] R=Et. [d] Yields determined by ^{1}H NMR using CH_2Br_2 as the internal standard, isolated yield in parentheses.

Table 2 Substrate scope of alkenes[a]

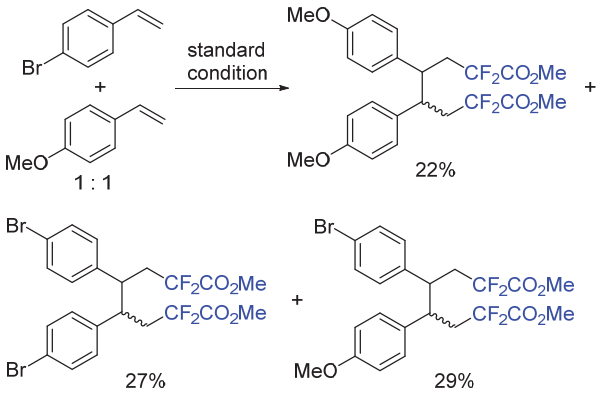




[a] Yields determined by ^{1}H NMR using CH_2Br_2 as the internal standard, isolated yield in parentheses, diastereoisomeric ratio (meso and racemic) calculated from crude ^{1}H-NMR.

54%, indicating that steric hindrance had notable effect on this coupling reaction. Both 2-vinylnaphthalene **1n** and 1-vinylnaphthalene **1o** were tolerated to transform into desired products **3n** and **3o** in moderate yield, due to the relative electron deficiency and steric hindrance of naphthalene. Fortunately, 2,4,6-trimethylstyrene was suitable in this reaction and the corresponding product **3p** was obtained in a decent yield of 55%. Asymmetrical internal alkene such as *β*-methylstyrene **1q** was explored and the product **3q** was obtained with obvious regioselectivity. Non-conjugated allylbenzene **1r** also showed high regioselectivity in this reaction, whereas the yield of product **3r** was inferior on account of the instability of alkyl radical and methyl 2,2-difluoro-5-phenylpentanoate as the main product. Heteroarenes were compatible as well, while 2-vinylpyridine and 2-vinylthiophene were successfully converted into products **3s** and **3t** in moderate yields, respectively. Unfortunately, 1-methylindole **1u** was not suitable for the coupling reaction, but dearomatization process by the attack of CF_2CO_2Me radical occurred and methyl 2,2-difluoro-2-(1-methylindol-2-yl)acetate was obtained.

When the same amount of 4-methoxystyrene **1d** and 4-bromostyrene **1i** were employed in the standard condition, the homo-coupling product and the cross-coupling product were obtained with poor chemoselectivity, indicating that the electronic nature of substituents showed indistinctive impact on this reaction (Scheme 3).



Scheme 3 Exploration of cross-coupling reactions (yields determined by ^{1}H NMR using CH_2Br_2 as the internal standard)

To further elucidate the reaction mechanism, Stern-Volmer fluorescence quenching experiments were carried out with *fac*-Ir(ppy)$_3$, $BrCF_2CO_2Me$, Et_3N, and 4-(*tert*-butyl)styrene alone. As shown in Figure 1, the substrate 4-(*tert*-butyl)-styrene and the reductant Et_3N scarcely quenched the photocatalyst. $BrCF_2CO_2Me$ performed certain quenching effect, while the mixture of $BrCF_2CO_2Me$ and Et_3N showed prominent quenching effect, denoting that the excited photocatalyst reacted with $BrCF_2CO_2Me$ firstly and Et_3N could promote this process.

Adding 3.5 equiv. of 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) as a radical scavenger under the standard condition completely restrained the generation of the target

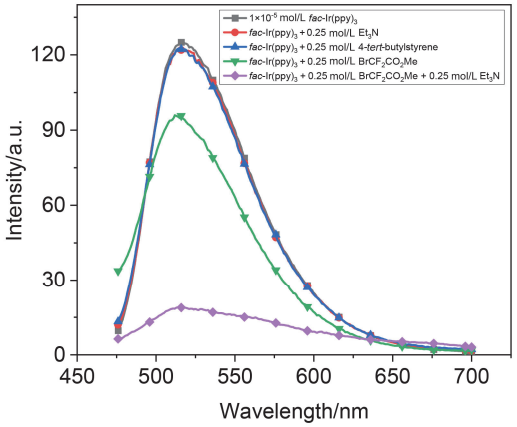
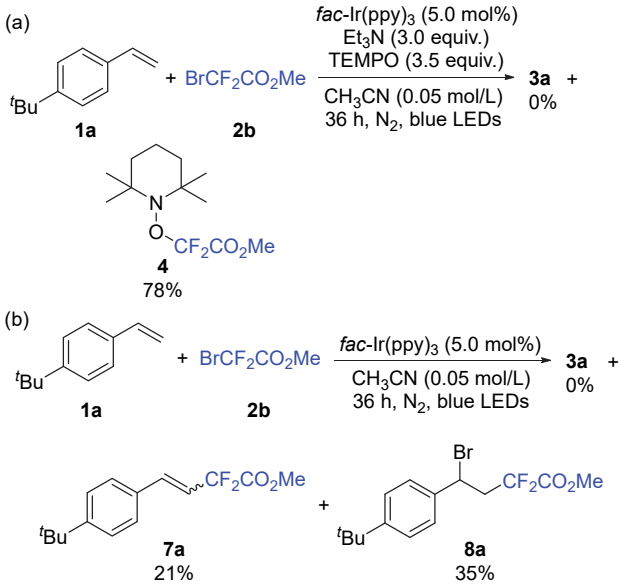


Figure 1 Fluorescence quenching experiment between photocatalyst and substrates

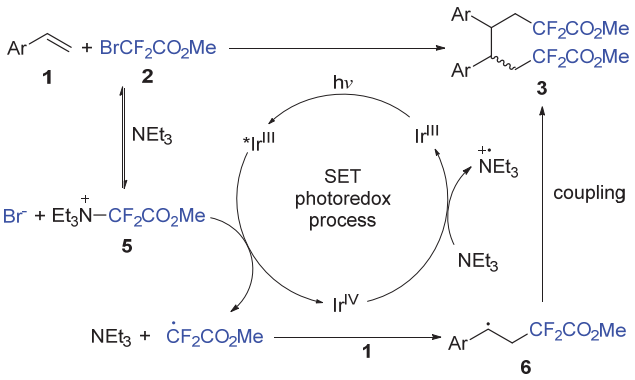
product **3a**. Meanwhile, the TEMPO-CF_2CO_2Me adduct **4** was procured in 78% isolated yield (Scheme 4a). The absence of Et_3N also inhibited the generation of **3a**, while products **7a** and **8a** were obtained (Scheme 4b), through proton elimination or bromination of the CF_2CO_2R substituted carbocation, indicating that Et_3N, as a reductant, might restrain the oxidation of the *in situ* formed CF_2CO_2R substituted radical.



Scheme 4 Control experiments. (a) with TEMPO; (b) without Et_3N

Based on the above results and related precedents,[13e,14c,21b] a plausible mechanism is proposed and shown in Scheme 5. Firstly, $BrCF_2CO_2Me$ experiences nucleophilic attack by Et_3N to generate **5**, while irradiation from blue LEDs excites the photocatalyst *fac*-Ir^{III}(ppy)$_3$ (Ir^{III}) to *fac*-*Ir^{III}(ppy)$_3$ (*Ir^{III}). The SET process between *Ir^{III} and **5** generates *fac*-Ir^{IV}(ppy)$_3$ (Ir^{IV}) and CF_2CO_2Me radical. Alkene **1** is then attacked by the CF_2CO_2Me radical and converts into intermediate **6**, which is capable of

the homo-coupling to afford product **3**. Another SET process between Ir^{IV} and Et_3N transforms the photocatalyst to ground state Ir^{III}, and the catalytical cycle is completed.



Scheme 5 A plausible mechanism of the reaction

3 Conclusions

A straightforward strategy has been developed to construct two difluoroacetylated hexestrol derivatives with a high regioselectivity based on the photoredox-catalyzed 2∶2 coupling reaction of alkenes and $BrCF_2CO_2Me$. The reaction features a broad substrate scope and respectable functional group tolerance with good yields.

4 Experimental section

4.1 General information

Unless otherwise noted, all the reactions were carried out in oven-dried sealed tube with Teflon-lined-septum under N_2 atmosphere. All materials were obtained from commercial sources and used as received. Super dry acetonitrile with molecular sieves in it was used in the reaction. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Japan Electron Optics Laboratory JNM-ECZ-400S/L1 spectrometer at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were referenced to the residual proton resonance of $CDCl_3$ (δ 7.25) and the carbon resonance of $CDCl_3$ (δ 77.10). The reaction progress was monitored by GC-MS if applicable. GC-MS was performed on a Shimadzu GCMS-QP2010 SE spectrometer. Column chromatography was performed with silica gel (200～300 meshes). Thin layer chromatography (TLC) was visualized using UV light. Fluorescence quenching experiments were measured on an Ahilent Technologies Cary Eclipse Fluorescence Spectrophotometer. Infrared spectra were recorded using a FT-IR spectrometer with KBr discs in the 4000～400 cm^{-1} region. HRMS analysis was performed on a Shimadzu LCMS-IT/TOF spectrometer.

4.2 General procedures for synthesis of products 3

A sealed tube equipped with a stirrer bar was charged with 9.9 mg *fac*-Ir(ppy)$_3$ (5.0 mol%), which was degassed and refilled with N_2 for 3 times. The alkenes **1a**～**1u** (0.3 mmol, 1.0 equiv.), $BrCF_2CO_2Me$ (113.4 mg, 0.6 mmol, 2.0 equiv.), Et_3N (91.1 mg, 0.9 mmol, 3.0 equiv.) and anhydrous CH_3CN (6 mL) were added under N_2. The reaction mixture was irradiated for 36 h under room temperature by 5 W blue LEDs. The reaction was quenched with 15 mL of H_2O and the aqueous layer was extracted with 6 mL of dichloromethane (CH_2Cl_2) for three times. The combined organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products **3a**～**3u**, which were identified by ^1H NMR, ^{13}C NMR, and ^{19}F NMR. Products **3a**, **3b**, **3o**, **3p**, and **3t** were isolated as two separate epimers and shown in two sets of ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra. Products **3a'**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3m**, **3n**, **3q**, **3r**, and **3s** were isolated as the mixture of the two epimers and shown in one set of ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra. Product **3u** was detected by GC-MS as trace amount.

Dimethyl 4,5-bis(4-(*tert*-butyl)phenyl)-2,2,7,7-tetrafluorooctanedioate (**3a**): White solid, 65.4 mg (82% yield). Eluent for the flash chromatography with silica gel: *V*(petroleum ether, PE)∶*V*(ethyl acetate, EA)=40∶1.

Dimethyl (4*R*,5*S*)-4,5-bis(4-(*tert*-butyl)phenyl)-2,2,7,7-tetrafluorooctanedioate (**3a-1**): m.p. 102～104 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J=8.4 Hz, 4H), 6.73 (d, J=8.4 Hz, 4H), 3.32 (s, 6H), 3.17～3.11 (m, J=8.4 Hz, 2H), 2.53～2.36 (m, 4H), 1.25 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.3 (t, J=33.3 Hz), 150.0, 134.9, 129.4, 124.6, 115.9 (t, J=251.5 Hz), 52.9, 44.3 (d, J=6.4 Hz), 38.6 (t, J=23.2 Hz), 34.5, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.2 (dt, J=256.2, 12.8 Hz), −106.4～−107.4 (m); IR (KBr) ν: 3528, 3349, 3092, 2961, 2907, 2870, 1970, 1773, 1613, 1512, 1459, 1442, 1418, 1394, 1363, 1308, 1270, 1222, 1200, 1083, 1019, 962, 920, 827 cm^{-1}; HRMS (ESI^+) calcd for $C_{30}H_{38}F_4O_4Na$ $[M+Na]^+$ 561.2598, found 561.2596.

Dimethyl (4*R*,5*R*)/(4*S*,5*S*)-4,5-bis(4-(*tert*-butyl)phenyl)-2,2,7,7-tetrafluorooctanedioate (**3a-2**): m.p. 190～193 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=8.1 Hz, 4H), 7.11 (d, J=8.2 Hz, 4H), 3.23 (s, 6H), 2.95～2.88 (m, 2H), 2.36～2.22 (m, 2H), 2.01 (td, J=15.2, 10.6 Hz, 2H), 1.31 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.9 (t, J=40.4 Hz), 150.5, 136.7, 128.4, 125.7, 115.8 (t, J=254.5), 52.7, 45.4 (d, J=6.7 Hz), 38.9 (t, J=24.2 Hz), 34.6, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −97.0～−98.2 (m), −108.2 (ddd, J=261.7, 26.9, 10.8 Hz); IR (KBr) ν: 3541, 3357, 3182, 2958, 2922, 2869, 1921, 1774, 1658, 1509, 1443, 1412, 1394, 1360, 1350, 1326, 1300, 1281, 1269, 1221, 1203, 1090, 1064, 1010, 963, 913, 824 cm^{-1}; HRMS (ESI^+) calcd for $C_{30}H_{38}F_4O_4Na$ $[M+Na]^+$ 561.2598, found 561.2596.

Diethyl 4,5-bis(4-(*tert*-butyl)phenyl)-2,2,7,7-tetrafluorooctanedioate (**3a'**): White solid, 41.9 mg (74% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=40∶1. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J=8.2 Hz, 4H), 7.14 (d, J=8.3 Hz, 4H), 7.11 (d, J=8.3 Hz, 2H), 6.73 (d, J=8.2 Hz), 3.73～3.63 (m, 4H), 3.59～3.54 (m, 4H), 3.16～3.11 (m, 2H), 2.97～2.88 (m, 2H),

2.55～2.45 (m, 2H), 2.44～2.23 (m, 2H), 2.07～1.99 (m, 2H), 1.98～1.95 (m, 2H), 1.31 (s, 18H), 1.24 (s, 18H), 1.09～1.06 (m, 6H), 1.06～1.02 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.6 (t, J=32.3 Hz), 163.5 (t, J=33.3 Hz), 150.4, 150.0, 136.9, 135.2, 129.4, 128.5, 125.6, 124.5, 115.8 (t, J=247.5 Hz), 115.7 (t, J=244.4 Hz), 62.6, 62.4, 45.5 (d, J=6.9 Hz), 44.3 (d, J=5.5 Hz), 38.8 (t, J=23.2 Hz), 38.5 (t, J=23.2 Hz), 34.6, 34.4, 31.4, 31.4, 29.8, 29.4, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −97.5～−99.7 (m), −106.4～−108.4 (m); IR (KBr) ν: 3522, 3357, 3185, 2957, 2920, 2851, 1766, 1659, 1632, 1509, 1469, 1411, 1374, 1346, 1325, 1270, 1216, 1089, 1018, 919, 848, 833 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{32}H_{42}F_4O_4Na$ [M+Na]$^+$ 589.2912, found 589.2908.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di-*p*-tolyloctanedioate (**3b**): White solid, 57.3 mg (84% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=30∶1.

Dimethyl (4*R*,5*S*)-2,2,7,7-tetrafluoro-4,5-di-*p*-tolyloctanedioate (**3b-1**): m.p. 74～77 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, J=8.0 Hz, 4H), 6.70 (d, J=8.0 Hz, 4H), 3.19～3.14 (m, 2H), 2.56～2.37 (m, 4H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ:164.2 (t, J=33.3 Hz), 136.8, 135.0, 129.6, 128.5, 116.0 (t, J=249.5 Hz), 53.0, 44.2 (d, J=5.6 Hz), 38.7 (t, J=23.2 Hz), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.4 (t, J=13.2 Hz), −100.1 (t, J=13.0 Hz), −106.0 (dd, J=21.6, 15.2 Hz), −106.7 (dd, J=21.7, 15.2 Hz); IR (KBr) ν: 3520, 3210, 3131, 3094, 3024, 2957, 2926, 2858, 2730, 2594, 1906, 1766, 1653, 1614, 1579, 1515, 1443, 1346, 1306, 1277, 1222, 1197, 1083, 1021, 960, 914, 823, 779 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{24}H_{26}F_4O_4Na$ [M+Na]$^+$ 477.1660, found 477.1657.

Dimethyl (4*R*,5*R*)/(4*S*,5*S*)-2,2,7,7-tetrafluoro-4,5-di-*p*-tolyloctanedioate (**3b-2**): m.p. 81～84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (d, J=8.0 Hz, 4H), 7.07 (d, J=7.9 Hz, 4H), 3.32 (s, 6H), 2.94～2.87 (m, 2H), 2.33 (s, 6H), 2.31～2.25 (m, 2H), 2.08～1.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (t, J=33.3 Hz), 137.2, 137.0, 129.5, 128.6, 115.8 (t, J=248.5 Hz), 52.8, 45.6 (d, J=6.1 Hz), 38.8 (t, J=24.2 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.7 (ddd, J=261.6, 15.3, 8.7 Hz), −107.3 (ddd, J=260.3, 23.8, 12.0 Hz); IR (KBr) ν: 3516, 3359, 3188, 3031, 2961, 2921, 2852, 2735, 2588, 1913, 1767, 1659, 1633, 1515, 1444, 1354, 1324, 1303, 1275, 1226, 1202, 1115, 1091, 1077, 1014, 959, 913, 824, 779 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{24}H_{26}F_4O_4Na$ [M+Na]$^+$ 477.1660, found 477.1657.

Dimethyl 4,5-di([1,1'-biphenyl]-4-yl)-2,2,7,7-tetrafluorooctanedioate (**3c**): White solid, 71.1 mg (82% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=30∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64～7.61 (m, 10H), 7.57～7.54 (m, 4H), 7.48～7.44 (m, 8H), 7.40～7.30 (m, 12H), 6.94 (d, J=8.2 Hz, 2H), 3.44 (s, 6H), 3.33 (s, 6H), 3.32～3.31 (m, 2H), 3.12～3.07 (m, 2H), 2.66～2.37 (m, 6H), 2.20～2.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (t, J=21.2 Hz), 163.9 (t, J=21.2 Hz), 140.6, 140.4, 140.1, 139.0, 137.2, 130.2, 129.2, 129.0, 128.9, 128.8, 127.6, 127.5, 127.4, 127.0, 127.0, 126.5, 115.7 (t, J=250.5 Hz), 115.7 (t, J=247.5 Hz), 53.1, 53.0, 45.6, 45.5, 44.4, 44.3, 39.0 (t, J=6.1 Hz), 38.7 (t, J=12.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.1～−98.9 (m), −99.0～−100.3 (m), −106.0～−106.9 (m), −106.9～−107.7 (m); IR (KBr) ν: 3527, 3030, 2955, 2920, 2851, 1912, 1768, 1682, 1601, 1518, 1487, 1441, 1411, 1351, 1305, 1222, 1197, 1085, 1007, 959, 914, 842, 826, 767, 735, 698 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{34}H_{30}F_4O_4Na$ [M+Na]$^+$ 601.1973, found 601.1972.

Dimethyl 2,2,7,7-tetrafluoro-4,5-bis(4-methoxyphenyl)-octanedioate (**3d**): Yellow solid, 56.9 mg (78% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=5∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (d, J=8.0 Hz, 4H), 6.86 (d. J=8.0 Hz, 4H), 6.70 (s, 8H), 3.79 (s, 6H), 3.74 (s, 6H), 3.44 (s, 6H), 3.34 (s, 6H), 3.16～3.11 (m, 2H), 2.87～2.84 (m, 2H), 2.49～2.30 (m, 6H), 2.04～1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.2 (t, J=33.3 Hz), 163.9 (t, J=34.3 Hz), 159.0, 158.7, 131.9, 130.7, 129.9, 129.7, 115.9 (t, J=249.5 Hz), 115.8 (t, J=248.5 Hz), 114.2, 113.1, 55.3, 55.2, 53.1, 52.9, 45.3 (d, J=6.6 Hz), 43.9 (d, J=5.7 Hz), 38.9 (t, J=22.2 Hz), 38.8 (t, J=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.7 (ddd, J=262.1, 15.3, 8.7 Hz), −99.6 (dt, J=258.2, 13.4 Hz), −106.1～−107.0 (m), −107.1～−108.0 (m); IR (KBr) ν: 3528, 3003, 2958, 2938, 2840, 2598, 2555, 2060, 1888, 1768, 1679, 1612, 1584, 1513, 1458, 1443, 1305, 1261, 1222, 1181, 1083, 1033, 960, 913, 833, 792, 779, 738 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{24}H_{26}F_4O_6Na$ [M+Na]$^+$ 509.1558, found 509.1563.

Dimethyl 4,5-bis(4-acetoxyphenyl)-2,2,7,7-tetrafluorooctanedioate (**3e**): White solid, 49.6 mg (61% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=3∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, J=8.6 Hz, 2H), 7.07 (d, J=8.6 Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 6.80 (d, J=8.6 Hz, 2H), 3.45 (s, 6H), 3.37 (s, 6H), 3.24～3.16 (m, 2H), 3.02～2.96 (m, 2H), 2.60～2.39 (m, 4H), 2.38～2.36 (m, 2H), 2.27 (s, 6H), 2.23 (s, 6H), 2.09～2.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.3, 164.1 (t, J=33.3 Hz), 164.0 (t, J=33.3 Hz), 150.2, 149.9, 137.2, 135.6, 130.4, 129.6, 122.1, 121.1, 115.6 (t, J=250.5 Hz), 115.4 (t, J=251.5 Hz), 53.3, 53.2, 45.3 (d, J=5.3 Hz), 44.1 (d, J=5.2 Hz), 38.8 (t, J=23.2 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.1～−99.8 (m), −106.4～−108.0 (m); IR (KBr) ν: 3662, 3512, 3358, 3040, 3009, 2959, 2922, 2852, 2591, 2411, 2126, 2022, 1905, 1760, 1606, 1580, 1508, 1443, 1371, 1305, 1270, 1203, 1085, 1045, 1017, 949, 913, 851, 828, 780, 736, 703 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{26}F_4O_8Na$ [M+Na]$^+$ 565.1457, found 565.1450.

Dimethyl 2,2,7,7-tetrafluoro-4,5-bis(4-(trifluoromethyl)-phenyl)octanedioate (**3f**): White solid, 54.8 mg (65% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=10∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J=8.0 Hz, 4H), 7.42 (d, J=8.1 Hz, 4H), 7.34 (d, J=8.1 Hz, 4H), 6.95 (d, J=8.2 Hz, 4H), 3.53 (s, 6H), 3.41

(s, 6H), 3.36～3.30 (m, 2H), 3.20～3.13 (m, 2H), 2.67～2.47 (m, 4H), 2.46～2.43 (m, 2H), 2.09～2.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (t, J=32.3 Hz), 163.7 (t, J=33.3 Hz), 144.0, 142.7, 130.0, 129.6, 129.3, 129.1, 126.0 (q, J=3.4 Hz), 125.1 (q, J=4.1 Hz), 123.9 (q, J=273.2 Hz), 115.5 (t, J=252.5 Hz), 115.4 (t, J=252.5 Hz), 53.3, 53.1, 45.4, 44.4, 38.5 (t, J=24.2 Hz), 38.4 (t, J=24.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.5 (s), −62.6 (s), −99.7～−101.3 (m), −105.8 (dt, J=262.4, 17.4 Hz); IR (KBr) ν: 3533, 2960, 2920, 2850, 1923, 1770, 1619, 1443, 1421, 1355, 1326, 1221, 1196, 1163, 1069, 1017, 957, 912, 843, 826, 778, 739 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{24}H_{20}F_{10}O_4K$ $[M+K]^+$ 601.0834, found 601.0828.

Dimethyl 2,2,7,7-tetrafluoro-4,5-bis(4-fluorophenyl)-octanedioate (**3g**): Light yellow solid, 41.5 mg (60% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=15∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07～7.02 (m, 4H), 6.99～6.94 (m, 4H), 6.87～6.83 (m, 4H), 6.77～6.74 (m, 4H), 3.51 (s, 6H), 3.42 (s, 6H), 3.20～3.14 (m, 2H), 2.99～2.96 (m, 2H), 2.60～2.36 (m, 4H), 2.35～2.26 (m, 2H), 2.04～1.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1 (t, J=33.3 Hz), 164.0 (t, J=31.3 Hz), 163.1, 163.0, 160.6, 160.5, 135.6 (d, J=2.9 Hz), 134.2 (d, J=3.4 Hz), 130.9 (d, J=7.8 Hz), 130.2 (d, J=7.7 Hz), 115.8 (d, J=26.3 Hz), 115.8 (t, J=238.4 Hz), 115.7 (t, J=224.2 Hz), 114.9 (d, J=21.2 Hz), 53.2, 53.0, 45.2 (d, J=5.5 Hz), 44.0 (d, J=5.3 Hz), 38.8 (t, J=23.2 Hz), 38.7 (t, J=22.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.1～−100.5 (m), −105.9～−107.2 (m), −114.1 (s), −114.8 (s); IR (KBr) ν: 3684, 3532, 3358, 3196, 3045, 3010, 2959, 2920, 2852, 2263, 1895, 1770, 1658, 1632, 1605, 1511, 1443, 1352, 1306, 1222, 1199, 1161, 1083, 1016, 961, 912, 839, 826, 796, 779, 735 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{22}H_{20}F_6O_4K$ $[M+K]^+$ 501.0898, found 501.0894.

Dimethyl 4,5-bis(4-chlorophenyl)-2,2,7,7-tetrafluoro-octanedioate (**3h**): Light yellow solid, 53.5 mg (72% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=15∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J=8.2 Hz, 4H), 7.15～7.10 (m, 8H), 6.74 (d, J=8.2 Hz, 4H), 3.52 (s, 6H), 3.43(s, 6H), 3.20～3.15 (m, 2H), 3.01～2.94 (m, 2H), 2.53 (q, J=14.7 Hz, 2H), 2.45～2.22 (m, 4H), 2.01 (q, J=14.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.8 (t, J=27.3 Hz), 163.7 (t, J=33.3 Hz), 138.4, 136.8, 133.7, 133.3, 130.7, 123.0, 129.1, 128.2, 115.5 (t, J=254.5 Hz), 115.3 (t, J=254.5 Hz), 53.3, 53.1, 45.2 (d, J=5.8 Hz), 43.9 (d, J=6.0 Hz), 38.6 (t, J=23.2 Hz), 38.6 (t, J=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.3～−101.1 (m), −105.3～−107.2 (m); IR (KBr) ν: 3533, 3036, 3013, 2959, 2924, 2853, 1920, 1773, 1689, 1595, 1493, 1445, 1412, 1354, 1305, 1276, 1219, 1199, 1183, 1093, 1071, 1012, 962, 913, 833, 776, 740, 726 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{22}H_{20}Cl_2F_4O_4K$ $[M+K]^+$ 533.0306, found 533.0287.

Dimethyl 4,5-bis(4-bromophenyl)-2,2,7,7-tetrafluoro-octanedioate (**3i**): Light yellow solid, 54.3 mg (62% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J=8.2 Hz, 4H), 7.30 (d, J=8.6 Hz, 4H), 7.05 (d, J=8.3 Hz, 4H), 6.69 (d, J=8.5 Hz, 4H), 3.53 (s, 6H), 3.43 (s, 6H), 3.22～3.14 (m, 2H), 3.01～2.93 (m, 2H), 2.58～2.45 (m, 2H), 2.44～2.31 (m, 2H), 2.30～2.21 (m, 2H), 2.07～1.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1 (t, J=37.4 Hz), 164.0 (t, J=33.3 Hz), 138.9, 137.3, 132.1, 131.2, 131.0, 130.3, 121.7, 121.4, 115.5 (t, J=251.5 Hz), 115.4 (t, J=250.5 Hz), 53.3, 53.1, 45.2 (d, J=3.0 Hz), 43.9 (d, J=4.1 Hz), 38.5 (t, J=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.4～−100.9 (m), −105.5～−106.8 (m); IR (KBr) ν: 3658, 3516, 3027, 2957, 2927, 2853, 2596, 1905, 1768, 1654, 1591, 1489, 1442, 1410, 1305, 1274, 1222, 1197, 1082, 1010, 959, 914, 827, 778, 738, 724 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{22}H_{20}Br_2F_4O_4K$ $[M+K]^+$ 620.9296, found 620.9290.

Dimethyl 2,2,7,7-tetrafluoro-4,5-bis(4-iodophenyl)octanedioate (**3j**): White solid, 42.7 mg (42% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=15∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, J=8.4 Hz, 4H), 6.56 (d, J=8.3 Hz, 4H), 3.53 (s, 6H), 3.20～3.13 (m, 2H), 2.58～2.32 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (t, J=33.3 Hz), 137.9, 137.2, 131.3, 115.5 (t, J=253.5 Hz), 93.0, 53.3, 43.9 (d, J=4.1 Hz), 38.5 (t, J=23.2 Hz), 27.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −100.0～−100.8 (m), −105.6～−106.4 (m); IR (KBr) ν: 3395, 3022, 2955, 2919, 2849, 1909, 1767, 1645, 1633, 1587, 1539, 1485, 1441, 1408, 1305, 1221, 1195, 1083, 1006, 956, 912, 825, 784, 722 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{22}H_{20}I_2F_4O_4K$ $[M+K]^+$ 716.9019, found 716.9017.

Dimethyl 2,2,7,7-tetrafluoro-4,5-bis(4-(methoxycarbonyl)phenyl)octanedioate (**3k**): White solid, 40.7 mg (50% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=2∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J=8.2 Hz, 4H), 7.80 (d, J=8.3 Hz, 4H), 7.27 (d, J=8.3 Hz, 4H), 6.89 (d, J=8.3 Hz, 4H), 3.92 (s, 6H), 3.86 (s, 6H), 3.50 (s, 6H), 3.40 (s, 6H), 3.31～3.25 (m, 2H), 3.16～3.09 (m, 2H), 2.65～2.49 (m, 4H), 2.41～2.32 (m, 2H), 2.08～1.94 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 163.7 (t, J=33.3 Hz), 161.3 (t, J=31.3 Hz), 145.2, 144.0, 137.2, 136.0, 130.2, 129.3, 129.2, 128.7, 115.2 (t, J=117.2 Hz), 115.2 (t, J=116.2 Hz), 53.3, 53.1, 52.3, 52.2, 45.6, 44.6, 38.5 (t, J=23.2 Hz), 38.4 (t, J=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −100.1～−101.1 (m), −105.5～−106.4 (m); IR (KBr) ν: 3359, 3197, 3005, 2956, 2920, 2850, 1769, 1722, 1660, 1633, 1612, 1576, 1438, 1283, 1221, 1190, 1113, 1084, 1019, 964, 913, 859, 827, 774, 710 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{26}F_4O_8Na$ $[M+Na]^+$ 565.1457, found 565.1460.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di-*m*-tolyl-octanedioate (**3l**): White solid, 42.9 mg (63% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25～7.21 (m, 3H), 7.08～7.04 (m, 3H), 6.99～6.96 (m, 6H), 6.63～6.56 (m, 2H), 6.56 (s, 2H), 3.41 (s, 6H), 3.31 (s, 6H), 3.19～3.15 (m, 2H), 2.96～2.87 (m, 2H), 2.45～2.26 (m, 6H), 2.36 (s,

6H), 2.23 (s, 6H), 2.06～1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ:163.9 (t, J=33.3 Hz), 140.0, 138.4, 137.9, 137.2, 130.4, 129.5, 128.7, 128.4, 128.0, 127.6, 126.9, 125.7, 115.9 (t, J=253.5 Hz), 115.7 (t, J=253.5 Hz), 53.0, 52.8, 45.8 (d, J=6.8 Hz), 44.5 (d, J=5.0 Hz), 38.8 (t, J=23.2 Hz), 38.5 (t, J=23.2 Hz), 21.6, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.1～−100.0 (m), −106.1～−107.9 (m); IR (KBr) ν: 3529, 3025, 2957, 2923, 2853, 1939, 1772, 1685, 1607, 1589, 1490, 1442, 1350, 1304, 1280, 1222, 1197, 1082, 964, 876, 826, 778, 708 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{26}F_4O_8Na$ [M + Na]$^+$ 477.1660, found 477.1657.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di-*o*-tolyloctanedioate (**3m**): Light yellow solid, 36.8 mg (54% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=30∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, J=5.9 Hz, 2H), 7.19～7.13 (m, 8H), 7.03 (t, J=7.5 Hz, 2H), 6.91 (t, J=7.6 Hz, 2H), 6.81 (d, J=7.7 Hz, 2H), 3.36 (s, 6H), 3.35～3.29 (m, 2H), 3.26 (s, 6H), 3.28～3.22 (m, 2H), 2.74～2.64 (m, 4H), 2.51～2.35 (m, 2H), 2.34 (s, 6H), 2.01 (s, 6H), 2.06～1.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ:163.9 (t, J=33.3 Hz), 163.8 (t, J=33.3 Hz), 138.6, 138.5, 137.9, 136.9, 130.8, 130.2, 127.5, 127.2, 126.7, 126.3, 125.4, 115.8 (t, J=250.5 Hz), 115.7 (t, J=248.5 Hz), 53.0, 52.9, 40.4 (d, J=5.8 Hz), 39.6 (d, J=4.1 Hz), 39.4 (t, J=25.2 Hz), 37.8 (t, J=23.5 Hz), 20.0, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −97.6～−99.0 (m), −106.8～−107.8 (m); IR (KBr) ν: 3529, 3358, 3020, 2959, 2936, 2852, 1920, 1772, 1493, 1443, 1307, 1278, 1229, 1195, 1085, 959, 912, 826, 804, 770, 732 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{26}F_4O_8Na$ [M + Na]$^+$ 477.1660, found 477.1656.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di(naphthalen-2yl)octanedioate (**3n**): Light yellow solid, 39.5 mg (50% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=10∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92～7.84 (m, 6H), 7.75～7.72 (m, 4H), 7.68～7.61 (m, 4H), 7.53～7.50 (m, 4H), 7.43～7.40 (m, 6H), 7.33 (s, 2H), 6.98～6.95 (m, 2H), 3.58～3.51 (m, 2H), 3.35～3.28 (m, 2H), 3.22 (s, 6H), 3.02 (s, 6H), 2.76～2.46 (m, 6H), 2.12 (q, J=14.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.9 (t, J=33.3 Hz), 163.8 (t, J=31.3 Hz), 137.3, 135.6, 133.4, 132.9, 132.8, 132.6, 128.9, 128.8, 128.6, 128.5, 127.9, 127.8, 127.6, 127.4, 126.6, 126.3, 126.2, 126.1, 125.6, 125.5, 116.0 (t, J=241.2 Hz), 115.7 (t, J=248.5 Hz), 53.0, 52.7, 45.8 (d, J=5.0 Hz), 44.7 (d, J=5.2 Hz), 38.8 (t, J=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −98.4～−100.0 (m), −106.0～−107.6 (m); IR (KBr) ν: 3515, 3055, 3021, 2955, 2924, 2851, 1916, 1768, 1600, 1508, 1441, 1352, 1305, 1272, 1222, 1198, 1127, 1085, 963, 895, 859, 823, 779, 749 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{30}H_{26}F_4O_4Na$ [M+Na]$^+$ 549.1660, found 549.1659.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di(naphthalen-1-yl)octanedioate (**3o**): Light yellow solid, 34.7 mg (44% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=10∶1.

Dimethyl (4*R*,5*S*)-2,2,7,7-tetrafluoro-4,5-di(naphthalen-1-yl)octanedioate (**3o-1**): m.p. 126～128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (m, 2H), 7.74～7.65 (m, 2H), 7.55～7.46 (m, 4H), 7.44～7.39 (m, 2H), 7.18 (s, 4H), 4.31～4.25 (m, 2H), 3.05 (s, 6H), 2.99～2.73 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (t, J=34.3 Hz), 135.8, 133.7, 131.9, 128.8, 127.7, 126.1, 125.8, 125.5, 124.5, 123.3, 115.8 (t, J=92.9 Hz), 52.7, 38.6, 38.1 (d, J=6.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.5～−99.8 (m), −105.8～−106.6 (m); IR (KBr) ν: 3515, 3358, 3191, 3047, 3008, 2956, 2919, 2850, 1767, 1655, 1632, 1512, 1441, 1351, 1309, 1222, 1197, 1101, 1079, 826, 778, 734 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{30}H_{26}F_4O_4Na$ [M+Na]$^+$ 549.1660, found 549.1656.

Dimethyl (4*R*,5*R*)/(4*S*,5*S*)-2,2,7,7-tetrafluoro-4,5-di(naphthalen-1-yl)octanedioate (**3o-2**): m.p. 152～154 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J=8.4 Hz, 2H), 7.89 (dd, J=7.9, 1.6 Hz, 2H), 7.80 (dd, J=7.8, 1.6 Hz, 2H), 7.59～7.52 (m, 8H), 4.24～4.18 (m, 2H), 2.99 (s, 6H), 2.69～2.54 (m, 2H), 2.16～2.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.8 (t, J=32.3 Hz), 137.0, 133.9, 133.0, 129.1, 128.1, 126.7, 126.0, 125.5, 124.5, 122.7, 118.1 (t, J=85.9 Hz), 52.6, 39.5 (d, J=4.2 Hz), 39.0 (t, J=24.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.7～−99.5 (m), −106.5～−107.3 (m); IR (KBr) ν: 3530, 3359, 3193, 3048, 3009, 2955, 2920, 2850, 1768, 1659, 1597, 1512, 1441, 1397, 1348, 1304, 1221, 1197, 1100, 1073, 826, 801, 779, 735 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{30}H_{26}F_4O_4Na$ [M+Na]$^+$ 549.1660, found 549.1656.

Dimethyl 2,2,7,7-tetrafluoro-4,5-dimesityloctanedioate (**3p**): White solid, 42.1 mg (55% yield). Eluent for the flash chromatography with silica gel: V(PE)∶V(EA)=30∶1.

Dimethyl (4*R*,5*S*)-2,2,7,7-tetrafluoro-4,5-dimesityloctanedioate (**3p-1**): m.p. 149～152 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.76 (d, J=1.9 Hz, 2H), 6.50 (d, J=1.9 Hz, 2H), 3.83～3.74 (m, 2H), 3.38 (s, 6H), 3.00～2.85 (m, 2H), 2.67～2.55 (m, 2H), 2.46 (s, 6H), 2.14 (s, 6H), 1.52 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.9 (t, J=33.0 Hz), 138.2, 136.4, 136.0, 135.3, 130.9, 129.0, 116.3 (t, J=254.5 Hz), 53.0, 36.5 (d, J=6.1 Hz), 36.3 (t, J=22.2 Hz), 21.1, 20.7, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −97.5～−98.3 (m), −107.7～−108.5 (m); IR (KBr) ν: 3532, 3007, 2957, 2924, 2872, 2734, 1774, 1611, 1573, 1443, 1348, 1303, 1223, 1195, 1143, 1092, 966, 900, 853, 827, 779, 737 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{28}H_{34}F_4O_4Na$ [M+Na]$^+$ 533.2286, found 533.2284.

Dimethyl (4*R*,5*R*)/(4*S*,5*S*)-2,2,7,7-tetrafluoro-4,5-dimesityloctanedioate (**3p-2**): m.p. 189～191 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.83 (d, J=4.3 Hz, 4H), 4.00～3.93 (m, 2H), 3.25 (s, 6H), 2.84～2.68 (m, 2H), 2.51 (s, 6H), 2.37 (s, 6H), 2.23 (s, 6H), 1.93～1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.8 (t, J=33.3 Hz), 139.0, 136.7, 136.4, 132.4, 131.9, 130.0, 116.3 (t, J=246.4 Hz), 52.8, 36.5 (d, J=6.9 Hz), 34.6 (t, J=23.2 Hz), 22.3, 21.4, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.1～−97.9 (m), −107.4～−108.2 (m); IR (KBr) ν: 3536, 3359, 3009, 2955, 2920, 2850, 1778, 1659, 1633, 1610, 1573, 1539,

1442, 1350, 1326, 1272, 1228, 1201, 1181, 1141, 1088, 1069, 1007, 849, 822, 777, 739 cm^{-1}; HRMS (ESI^+) calcd for $C_{28}H_{34}F_4O_4Na$ $[M+Na]^+$ 533.2286, found 533.2284.

Dimethyl 2,2,7,7-tetrafluoro-3,6-dimethyl-4,5-diphenyloctanedioate (**3q**): Colorless oily liquid, 24.5 mg (36% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=20∶1. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.34～7.31 (m, 8H), 7.30～7.26 (m, 4H), 7.16～7.10 (m, 4H), 6.81～6.75 (m, 2H), 3.49 (s, 6H), 3.48～3.43 (m, 2H), 3.40 (s, 6H), 2.88～2.72 (m, 2H), 2.68～2.56 (m, 2H), 2.55～2.32 (m, 2H), 1.39 (d, *J*=6.6 Hz, 6H), 0.97 (d, *J*=7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.5 (t, *J*=33.2 Hz), 164.3 (t, *J*=33.3 Hz), 138.5, 136.8, 131.3, 129.6, 128.2, 127.4, 127.2, 53.0, 52.9, 51.8, 47.4, 39.4 (t, *J*=21.2 Hz), 39.1 (t, *J*=20.2 Hz), 14.6 (t, *J*=5.7 Hz), 13.0 (t, *J*=4.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −101.7～−103.2 (m), −107.1～−108.9 (m); IR (KBr) *ν*: 3527, 3031, 2956, 2923, 2852, 1957, 1888, 1763, 1654, 1602, 1496, 1453, 1439, 1386, 1298, 1250, 1191, 1040, 912, 812, 762, 739, 704 cm^{-1}; HRMS (ESI^+) calcd for $C_{24}H_{26}F_4O_4Na$ $[M+Na]^+$ 477.1660, found 477.1656.

Dimethyl 4,5-dibenzyl-2,2,7,7-tetrafluorooctanedioate (**3r**): White solid, 14.3 mg (36% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=25∶1. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.29 (t, *J*=7.4 Hz, 4H), 7.23～7.17 (m, 4H), 7.07 (d, *J*=7.0 Hz, 2H), 6.95 (d, *J*=6.3 Hz, 2H), 3.77 (s, 6H), 3.68 (s, 6H), 2.80～2.75 (m, 2H), 2.64～2.58 (m, 5=6H), 2.25～2.10 (m, 8H), 2.02～1.91 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.6 (t, *J*=33.3 Hz), 164.3 (t, *J*=33.3 Hz), 139.1, 139.0, 129.1, 129.0, 128.6, 128.5, 126.6, 126.3, 116.7 (t, *J*=252.5 Hz), 116.6 (t, *J*=251.5 Hz), 53.4, 53.3, 36.8, 36.4, 35.1, 34.8, 34.4 (t, *J*=22.2Hz), 34.3 (t, *J*=22.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −101.1～−102.1 (m), −102.6～−103.8 (m); IR (KBr) *ν*: 3532, 3359, 3196, 3063, 3028, 2957, 2921, 2850, 1766, 1658, 1633, 1602, 1496, 1442, 1341, 1303, 1236, 1194, 1083, 1001, 958, 823, 777, 743, 699 cm^{-1}; HRMS (ESI^+) calcd for $C_{24}H_{26}F_4O_4Na$ $[M+Na]^+$ 477.1660, found 477.1658.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di(pyridin-2-yl)octanedioate (**3s**): Orange oily liquid, 23.8 mg (37% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)∶*V*(Et_3N)=2.5∶1∶1. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.63～8.51 (m, 2H), 8.47～8.44 (m, 2H), 7.62 (td, *J*=7.6, 1.9 Hz, 2H), 7.28 (td, *J*=7.6, 1.9 Hz, 2H), 7.20～7.15 (m, 4H), 6.98～6.93 (m, 2H), 6.71 (d, *J*=7.7 Hz, 2H), 3.58 (s, 6H), 3.54 (s, 6H), 3.47～3.42 (m, 2H), 3.40～3.37 (m, 2H), 3.20～3.08 (m, 2H), 2.82～2.72 (m, 2H), 2.71～2.60 (m, 2H), 1.93～1.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.3 (t, *J*=33.3 Hz), 164.1 (t, *J*=33.3 Hz), 160.4, 160.0, 150.0, 149.0, 136.5, 135.9, 125.5, 124.6, 122.4, 121.7, 115.9 (t, *J*=252.5 Hz), 115.7 (t, *J*=252.5 Hz), 53.2, 53.1, 45.9, 45.8, 37.3 (t, *J*=23.2 Hz), 35.5 (t, *J*=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −101.9～−103.0 (m), −104.0～−105.6 (m); IR (KBr) *ν*: 3530, 3010, 2957, 2918, 2849, 1765, 1590, 1570, 1471, 1438, 1301, 1219, 1196, 1150, 1077, 995, 826, 800, 776, 749 cm^{-1}; HRMS (ESI^+) calcd for $C_{20}H_{20}F_4N_2O_4Na$ $[M+Na]^+$ 451.1252, found 451.1247.

Dimethyl 2,2,7,7-tetrafluoro-4,5-di(thiophen-2-yl)octanedioate (**3t**): Light yellow oily liquid, 21.7 mg (33% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=15∶1.

Dimethyl (4*R*,5*S*)-2,2,7,7-tetrafluoro-4,5-di(thiophen-2-yl)octanedioate (**3t-1**): ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.17 (dd, *J*=5.1, 1.2 Hz, 2H), 6.89 (dd, *J*=5.1, 3.4 Hz, 2H), 6.63 (dd, *J*=3.4, 1.1 Hz, 2H), 3.60～3.55 (m, 8H), 2.66～2.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.1 (t, *J*=33.3 Hz), 141.0, 127.0, 126.5, 124.7, 115.5 (t, *J*=253.5 Hz), 53.3, 40.4 (d, *J*=2.8 Hz), 39.6 (t, *J*=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −100.2～−101.0 (m), −105.9～−106.6 (m); IR (KBr) *ν*: 3530, 3359, 3193, 3007, 2956, 2920, 2850, 1767, 1646, 1632, 1441, 1356, 1301, 1219, 1195, 1074, 957, 850, 826, 778, 701 cm^{-1}; HRMS (ESI^+) calcd for $C_{18}H_{18}F_4O_4S_2Na$ $[M+Na]^+$ 461.0475, found 461.0473.

Dimethyl (4*R*,5*R*)/(4*S*,5*S*)-2,2,7,7-tetrafluoro-4,5-di(thiophen-2-yl)octanedioate (**3t-2**): ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.26 (d, *J*=5.1 Hz, 2H), 6.94 (dd, *J*=5.2, 3.5 Hz, 2H), 6.84 (d, *J*=3.3 Hz, 2H), 3.50 (s, 6H), 3.37～3.29 (m, 2H), 2.44～2.20 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 163.8 (t, *J*=33.3 Hz), 143.2, 127.3, 126.8, 125.3, 115.4 (t, *J*=254.5 Hz), 53.2, 42.4 (d, *J*=4.2 Hz), 39.9 (t, *J*=23.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −99.4～−100.2 (m), −106.8～−107.6 (m); IR (KBr) *ν*: 3521, 3358, 3187, 3112, 3007, 2957, 2921, 2851, 1768, 1646, 1633, 1539, 1441, 1357, 1300, 1248, 1220, 1195, 1074, 1006, 957, 903, 850, 826, 779, 702 cm^{-1}; HRMS (ESI^+) calcd for $C_{18}H_{18}F_4O_4S_2Na$ $[M+Na]^+$ 461.0475, found 461.0473.

4.3 General procedures for synthesis of products 4

A sealed tube equipped with a stirrer bar was charged with *fac*-Ir(ppy)$_3$ (9.9 mg, 5.0 mol%) and TEMPO (164.1 mg, 1.05 mmol, 3.5 equiv.), which was degassed and refilled with N_2 for 3 times. 1-(*tert*-Butyl)-4-vinylbenzene (**1a**, 0.3 mmol, 1.0 equiv.), $BrCF_2CO_2Me$ (113.4 mg, 0.6 mmol, 2.0 equiv.), Et_3N (91.1 mg, 0.9 mmol, 3.0 equiv.) and anhydrous CH_3CN (6 mL) were added under N_2. The reaction mixture was irradiated for 36 h under room temperature by 5 W blue LEDs. The reaction was quenched with 15 mL of H_2O and the aqueous layer was extracted with 6 mL of dichloromethane (CH_2Cl_2) for three times. The combined organic layer was dried by Na_2SO_4 and concentrated *in vacuo*, then the residue was purified by chromatography on silica gel to afford product **4** in 78% isolated yield.

Methyl 2,2-difluoro-2-(2,2,6,6-tetramethylpiperidin-1-yl)acetate (**4**)[13e,14c]: Colorless oil liquid, 124.2 mg (78% yield). Eluent for the flash chromatography with silica gel: *V*(PE)∶*V*(EA)=30∶1. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 3.88 (s, 3H), 1.58～1.51 (m, 5H), 1.37～1.31 (m, 1H), 1.17～1.15 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 161.3 (t, *J*=42.4 Hz), 115.6 (t, *J*=271.7 Hz), 61.5, 53.5,

40.3, 33.5 (t, J=4.5 Hz), 20.8, 17.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −72.9 (s); IR (KBr) ν: 3539, 3003, 2979, 2938, 2877, 2294, 1779, 1667, 1462, 1441, 1384, 1368, 1334, 1246, 1195, 1171, 1130, 995, 977, 957, 895, 870, 840, 802, 791, 689 cm^{-1}.

4.4 General procedures for exploration of cross-coupling

A sealed tube equipped with a stirrer bar was charged with 9.9 mg of *fac*-Ir(ppy)$_3$ (5.0 mol%), which was degassed and refilled with N_2 for 3 times. The alkenes **1d** (0.15 mmol, 0.5 equiv.), **1i** (0.15 mmol, 0.5 equiv.), $BrCF_2CO_2Me$ (113.4 mg, 0.6 mmol, 2.0 equiv.), Et_3N (91.1 mg, 0.9 mmol, 3.0 equiv.) and anhydrous CH_3CN (6 mL) were added under N_2. The reaction mixture was irradiated for 36 h under room temperature by 5 W blue LEDs. The reaction was quenched with 15 mL of H_2O and the aqueous layer was extracted with 6 mL of dichloromethane (CH_2Cl_2) for three times. The combined organic layer was dried by Na_2SO_4 and concentrated *in vacuo*. Yields of the crude products were determined by ^{1}H NMR using CH_2Br_2 as the internal standard.

Supporting Information Experiments of mechanism studies, analysis of by-products **3m** and **9m**, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of products **3a**～**3t** and **4**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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