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Ni-catalyzed Dimerization and Hydroperfluoroarylation of 1,3-Dienes

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ABSTRACT

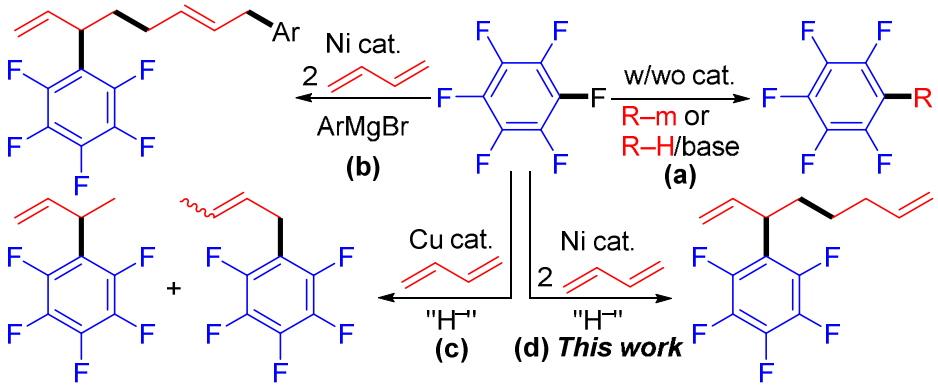
A nickel-catalyzed three-component coupling reaction between perfluoroarenes and two molecules of a 1,3-diene in the presence of an alkyl Grignard reagent, which acted as a hydride source, provided 3-perfluoroarylated-1,7-octadienes via 1,3-diene dimerization and subsequent perfluoroarylation upon C–F bond cleavage. The reaction proceeded smoothly in a regioselective manner by simply combining of $NiCl_2$ and PPh_3 as a catalyst and tolerated various functional groups on the perfluoroarenes. When substituted perfluoroarenes were employed, the reaction selectively occurred at the *para*-position. Mechanistic studies revealed that an anionic Ni complex, generated upon the reaction of Ni(0) with two molecules of a 1,3-diene and an alkyl Grignard reagent, played an important role in the C–C bond forming step with perfluoroarenes. The C–F bond cleavage was found to be a relatively fast step in the catalytic cycle.

INTRODUCTION

Perfluorinated arenes have received much attention in medicinal and material science due to their characteristic properties such as high metabolic stability, low LUMO energies, and unique intermolecular interactions with aromatic rings and polar bonds.[1] For the synthesis of more complex fluoroarenes, the functionalization of easily accessible perfluoroarenes provides reliable routes.[2] Among the C–C bond forming reactions available to introduce a perfluoroaryl group into organic molecules,[3] the S_NAr reaction with carbanions represents a useful method owing to the facile accessibility of perfluoroarenes in comparison to mono- or partially fluorinated arenes (Scheme 1a).[4] Transition-metal-catalyzed cross-coupling reactions also provide promising

methods for the arylation,[5] alkenylation,[6] alkynylation,[7] and methylation[8] of perfluoro(hetero)arenes via C–F bond cleavage (Scheme 1a).[9] Multicomponent coupling reactions[10] are useful approaches since they allow the concomitant construction of more than one chemical bonds. In this context, we recently reported a Ni-catalyzed four-component coupling reaction of perfluoroarenes with two molecules of 1,3-butadiene and aryl Grignard reagents to produce 1,6-octadienes bearing aryl and perfluoroaryl groups at the 8- and 3-position, respectively (Scheme 1b).[11] When a Cu catalyst was employed along with EtMgCl, the hydroarylation of 1,3-dienes with perfluoroarenes occurred to give allylperfluoroarenes as mixtures of regioisomers: in this case, EtMgCl acted as a hydride source (Scheme 1c).[12] These successful results prompted us to examine the use of alkyl Grignard reagents instead of aryl Grignard reagents in the Ni-catalyzed reaction of perfluoroarenes with 1,3-butadiene. It was found that bis-terminal octadienes (1,7-octadienes) bearing a perfluoroaryl group at the 3-position were formed under mild conditions (Scheme 1d). This umpolung telomerization[13] enabled the dimerization and functionalization of 1,3-butadiene by perfluoroarenes owing to an electrophilic carbon and hydride deriving from Grignard reagents.

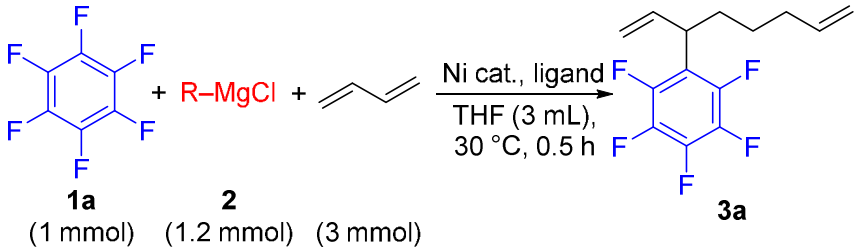
Scheme 1. C–C bond formation of perfluoroarenes via C–F bond cleavage.



RESULTS AND DISCUSSION

We initiated our study on this three-component coupling reaction using perfluorobenzene (**1a**), 1,3-butadiene, and different alkyl Grignard reagents (Table 1). When **1a** was treated with 1.2 equiv of *n*-BuMgCl (**2a**) and 3 equiv of 1,3-butadiene in the presence of 10 mol % of $NiCl_2$ and 20 mol % of PPh_3 at room temperature for 30 min, 3-pentafluorophenyl-1,7-octadiene (**3a**) was obtained in 80% yield (Table 1, entry 1). Reducing the amount of PPh_3 to 10 mol % improved the efficiency of the reaction affording a nearly quantitative yield of **3a**, while no reaction occurred in the absence of PPh_3, suggesting a crucial role of PPh_3 in the catalytic reaction (entries 2 and 3). Under the same conditions, other group 10 metals, such as Pd and Pt, and first row transition metals did not lead to the formation of **3a**.[14] Among the ligands tested, PPh_3 gave the best results, while electron-rich and electron-deficient phosphine ligands resulted in somewhat lower yields (entries 4 and 5). Trialkylphosphines, such as PCy_3 (entry 6) and $P(n\text{-}Bu)_3$ were not effective.[14] Furthermore, the catalyst loading could be reduced to 5 mol % without significant loss of efficiency (entry 7). When *i*-BuMgCl (**2b**) was used, **3a** was obtained in a comparable yield (entry 8). Acyclic and cyclic secondary alkyl Grignard reagents (**2c** and **2d**) also promoted the reaction, albeit less efficiently (entries 9 and 10). When cyclopropyl Grignard reagent was employed, **3a** was not obtained, resulting in a low conversion of **1a** (34% conv.). The use of *t*-BuMgCl (**2e**) afforded only the direct coupling product **4ae** in 11% yield, and 82% of unreacted **1a** was recovered (entry 11). MeMgCl, which has no β-hydrogens, did not afford **3a**; conversely, a four-component coupling reaction took place to give 3-pentafluorophenyl-1,6-nonadiene **5af** in 50% yield (Scheme 2, see also Scheme 6 for mechanistic discussion).

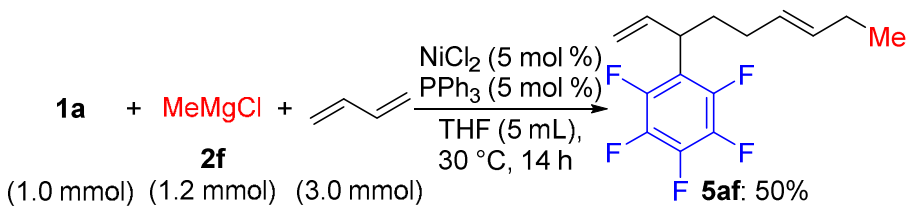
Table 1. Nickel-catalyzed three-component coupling reaction of **1a** with 1,3-butadiene in the presence of alkyl Grignard reagents.[a]



entry	cat. (mol %)	ligand (mol %)	RMgCl **2**	**3a** (%)[b]
1	$NiCl_2$ (10)	PPh_3 (20)	*n*-BuMgCl (**2a**)	80
2	$NiCl_2$ (10)	PPh_3 (10)	*n*-BuMgCl (**2a**)	99
3	$NiCl_2$ (10)	none	*n*-BuMgCl (**2a**)	n.d.
4	$NiCl_2$ (10)	P(*p*-tol)$_3$ (10)	*n*-BuMgCl (**2a**)	37
5	$NiCl_2$ (10)	P(*p*-FC_6H_4)$_3$ (10)	*n*-BuMgCl (**2a**)	70
6	$NiCl_2$ (10)	PCy_3 (10)	*n*-BuMgCl (**2a**)	5
7[c]	$NiCl_2$ (5)	PPh_3 (5)	*n*-BuMgCl (**2a**)	92(74)
8[d]	$NiCl_2$ (5)	PPh_3 (5)	*i*-BuMgCl (**2b**)	81
9[d]	$NiCl_2$ (5)	PPh_3 (5)	*s*-BuMgCl (**2c**)	50
10[d]	$NiCl_2$ (5)	PPh_3 (5)	CyMgCl (**2d**)	49
11[d]	$NiCl_2$ (5)	PPh_3 (5)	*t*-BuMgCl (**2e**)	n.d.[e]

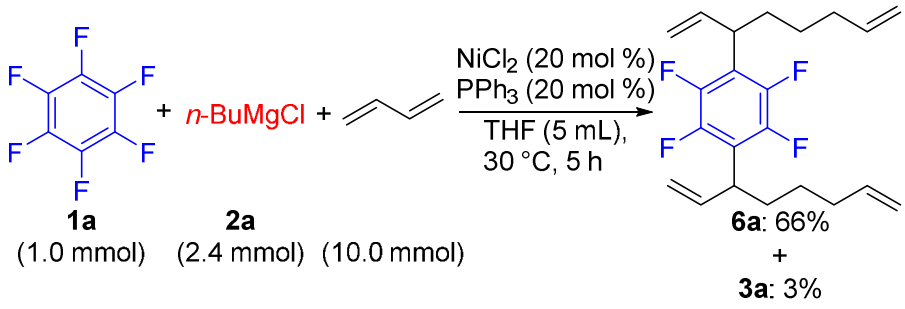
[a]Reaction conditions: A mixture of **1a** (1.0 mmol), RMgCl (**2**) (1.2 mmol), 1,3-butadiene (3 mmol), and catalyst in THF was stirred at 30 °C for 30 min. [b]GC yield. Yield is in parentheses. [c]At 30 °C for 40 min. [d]At 30 °C for 14-16 h. [e]C_6F_5–*t*-Bu (**4ae**) was solely obtained in 11% yield. Cy = cyclohexyl.

Scheme 2. Reaction of **1a** with MeMgCl in the presence of 1,3-butadiene.



Under the optimized conditions shown in entry 7 (Table 1), 4% of disubstitution product **6a** was detected by GC analysis. Therefore, in order to selectively obtain **6a**, the reaction was conducted using excess amounts of Grignard reagent and 1,3-butadiene. When **1a** was treated with 2.4 equiv of *n*-BuMgCl (**2a**) and 10 equiv of 1,3-butadiene in the presence of 20 mol % of catalyst, the disubstitution pathway predominated to afford 1,2,4,5-tetrafluoro-3,6-bis(1,7-octadien-3-yl)benzene (**6a**) in 66% yield with exclusive *para*-selectivity along with 3% of **3a** (Scheme 3).

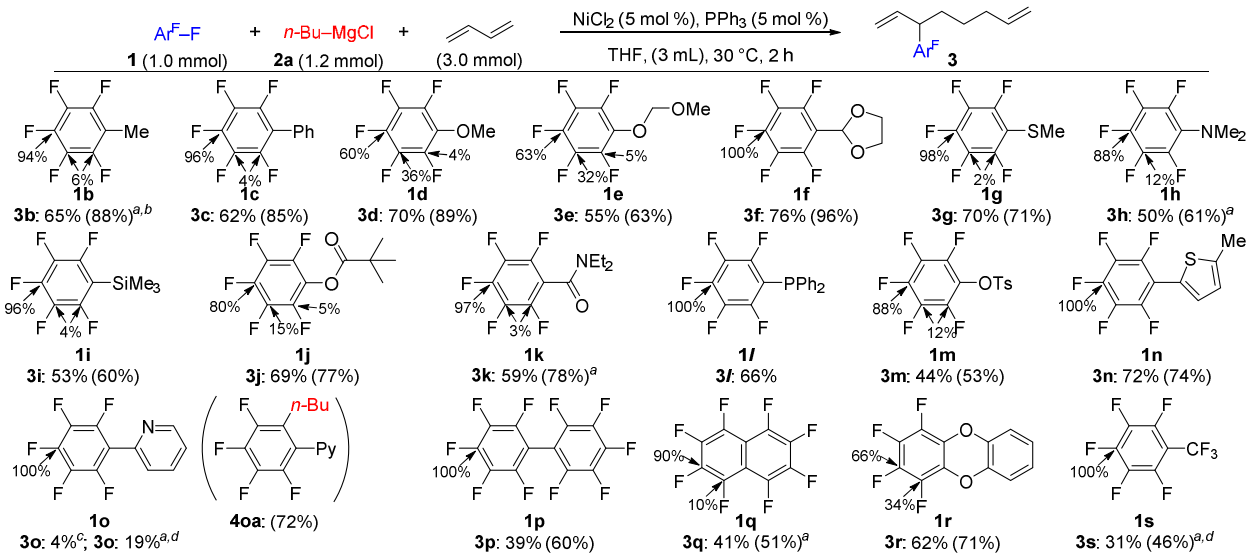
Scheme 3. Disubstitution reaction of **1a**.



Next, the scope of the reaction was investigated across a range of perfluoroarenes (Scheme 4). The reaction of pentafluorotoluene (**1b**) and pentafluorobiphenyl (**1c**) predominantly occurred at the *para*-position to give **3b** and **3c** in 65% and 62% yields with a 94% and 96% *para*-position selectivity, respectively. The structure of product **3c** was irrefutably determined by X-ray crystallography.[14,15] Functional groups including ether (**1d**), acetal (**1e** and **1f**), thioether (**1g**), amino (**1h**), and silyl (**1i**) groups remained intact affording the corresponding products **3d-i** in moderate to good yields with an excellent *para*-selectivity, except for **1d** and **1e**. Similar poor *para*-position selectivities were also observed in previous studies when **1d** and **1e** were used,[11,12] and could be explained by electronic effects, i.e., the present reaction occurred preferentially at the more electron-deficient position (*vide infra*). Ester, amide, and phosphine groups, which

might possibly serve as directing groups for *ortho*-substitution, also gave predominantly the corresponding *para*-substituted products **3j**, **3k**, and **3l** in good yields. Aryl tosylates are widely employed as useful substrates in Ni-catalyzed coupling reactions; however, the presence of tosylate moiety as in **1m** afforded **3m** in a moderate yield under the present reaction conditions. A thiophene moiety was well tolerated, and **3n** was obtained in 74% yield. However, the presence of a pyridine substituent largely affected the reaction, directing the substitution at the *ortho*-position that predominated to give **4oa** in 72% yield, probably due to the coordination ability of the pyridine moiety towards the Grignard reagent. Perfluorobiphenyl (**1p**) and perfluoronaphthalene (**1q**) selectively reacted at the 4- and 2-position, respectively, furnishing the desired products in slightly lower yields. The position selectivity of **1r** was low giving rise to a ca 2:1 mixture of the three-component coupling products. The reaction of highly electron-deficient perfluorotoluene (**1s**) resulted in a 15% yield, which could be increased to 31% yield upon slow addition of *i*-BuMgCl.

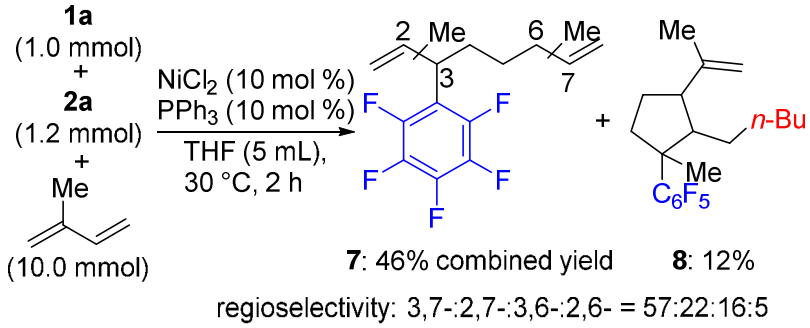
Scheme 4. Ni-catalyzed three-component coupling reaction of perfluoroarenes, 1,3-butadiene, and alkyl Grignard reagents.



Reaction conditions: $NiCl_2$ (5 mol %), PPh_3 (5 mol %), perfluoroarene **1** (1 mmol), *n*-BuMgCl (1.2 mmol), and 1,3-butadiene (3 mmol) in THF (3 mL) at 30 °C for 2 h. GC yields are given in parenthesis. Position-selectivities were determined by GC and NMR (see the experimental section for details) and are shown in percent. [a]10 mol % of $NiCl_2$ and PPh_3 were used. [b]1.5 mmol of *n*-BuMgCl was used. [c]72% of direct-coupling product **4oa** was formed. [d]*i*-BuMgCl (1.5 mmol) was slowly added.

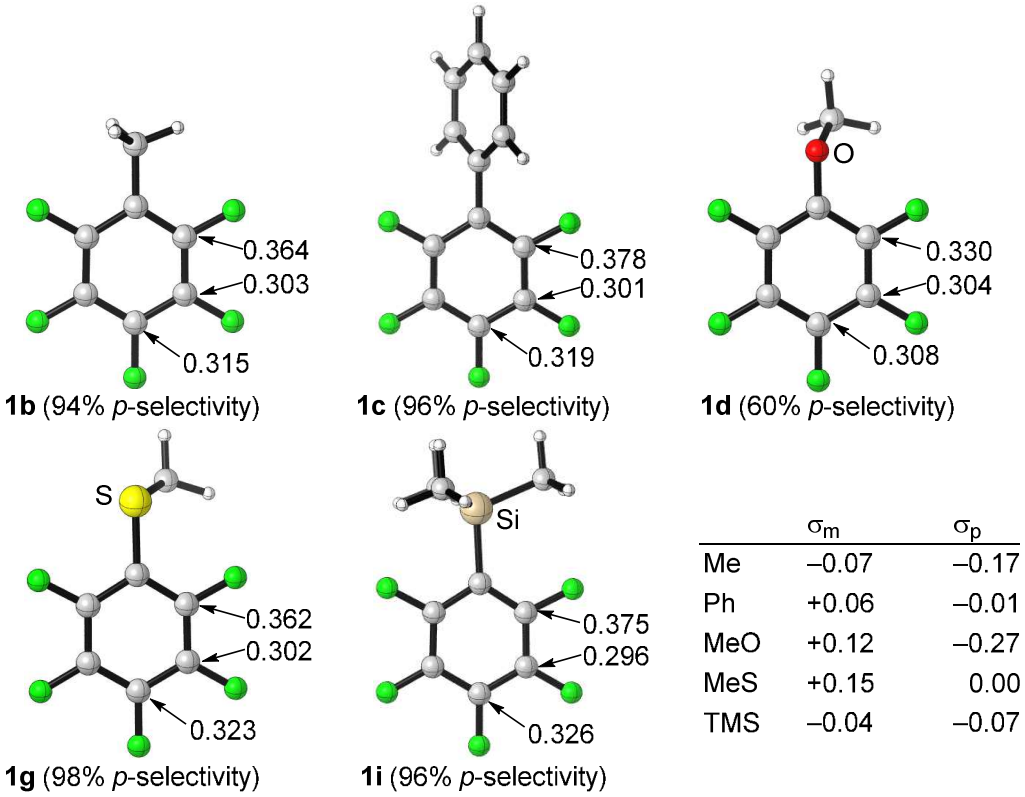
When isoprene was employed instead of 1,3-butadiene, the corresponding three-component coupling product **7** was obtained as a mixture of four regioisomers along with 12% of cyclized product **8** (Scheme 5).[14] In contrast to isoprene, 1,3-pentadiene, an analogue of mono substituted 1,3-butadiene, did not give three-component coupling products.

Scheme 5. Reaction of isoprene with **1a** and **2a**.



In order to determine the origin of the observed position-selectivities on the perfluoroarenes, we performed density functional theory (DFT) calculations. The structure of perfluoroarenes **1b-d**, **1g**, and **1i** were optimized with Gaussian 09[16] at the B3LYP[17]/6-31+G(d) level of theory, followed by frequency calculations at the same level of theory. The natural bond orbital (NBO)[18] analysis of these optimized structures was conducted at the B3LYP/6-311++G(d,p) level of theory. Figure 1 shows the results of the NBO population analysis of perfluoroarenes **1b-d**, **1g**, and **1i** along with the Hammett constants for these substituents. In all cases, *ortho*-carbon is the most electron-deficient but could not react due to steric effects. The atomic charge difference between the *meta*- and *para*-positions of pentafluoroanisole **1d** is 0.004, which is much smaller

than those of pentafluorotoluene **1b** (0.012) and pentafluorobiphenyl **1c** (0.018). In the case of perfluoroarenes bearing an SMe (**1g**) and TMS (**1i**) group, the *para*-position was found to be much more electro-positive than the *meta*-position. These results are in good agreement with the observed high *para*-selectivity mentioned above.



1b (94% *p*-selectivity) **1c** (96% *p*-selectivity) **1d** (60% *p*-selectivity)

1g (98% *p*-selectivity) **1i** (96% *p*-selectivity)

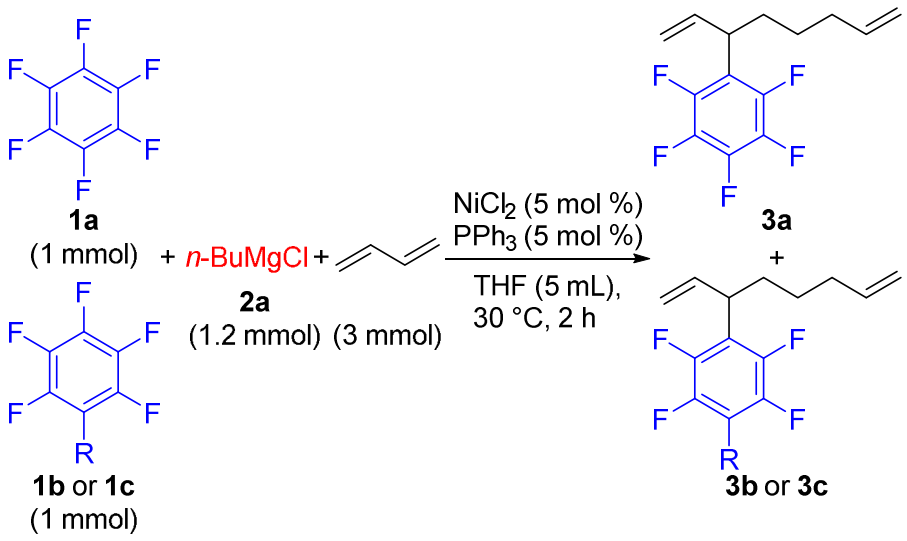
	σ_m	σ_p
Me	–0.07	–0.17
Ph	+0.06	–0.01
MeO	+0.12	–0.27
MeS	+0.15	0.00
TMS	–0.04	–0.07

Figure 1. Atomic charges by NBO population analysis of **1b-d**, **1g**, and **1i** and Hammett constants of these substituents. The atomic charge values for *ortho*- and *meta*-positions are the average of two equivalent carbons.

To reveal substituent effects, we conducted competitive reactions of perfluorobenzene (**1a**) and substituted perfluoroarenes to reveal the effect of substituents (Table 2). When a 1:1 mixture of **1a** and **1b** (R = Me) was reacted with 1,3-butadiene and *n*-BuMgCl under the optimized conditions, **3a** and **3b** were formed in 40:1 ratio, indicating that *p*-methyl group largely retarded the reaction. A similar competitive reaction of **1a** with **1c** (R = Ph) resulted in formation of **3a**

and **3c** in 2.1:1 ratio. Hammett constant σ_p of Me, Ph, and F substituents is –0.17, +0.02, and +0.06, respectively. These results indicate that the present reaction prefers electron-deficient perfluoroarenes rather than electron-rich ones, suggesting the S_NAr mechanism.

Table 2. Competitive reaction of perfluoroarenes.



R	σ_p	**3a** (mmol)[a]	**3b** or **3c** (mmol)[a]	**3a**/**3b** or **3c**
Me (**1b**)	–0.17	0.80	0.02	40
Ph (**1c**)	+0.02	0.56	0.27	2.1

[a]Determined by GC. σ_p of F is +0.06.

Subsequently, we conducted kinetic studies using **1a** as model substrate. Initially, we attempted to determine the rate law using a conventional Schlenk technique; however, the reaction was too fast to trace. Since a time course within 1 min is required to determine the initial rates, for these kinetic studies, we employed a flow reactor[19] in the presence of $Ni(acac)_2$ (Figure 2).[14,20] The kinetic study results suggested that the reaction obeyed an almost zeroth-order kinetics with respect to 1,3-butadiene, whereas the concentrations of *n*-BuMgCl and catalyst exerted significant effects on the rates.[14] The rate law for the present catalytic reaction can be

expressed as $d[\mathbf{3a}]/dt = k[Ni(acac)_2/PPh_3]^{0.64}[\mathbf{1a}]^{0.25}[n\text{-BuMgCl}]^{0.65}[1,3\text{-butadiene}]^{-0.03}$. The relatively small rate order of 0.25 for **1a** might suggest that the reaction of a perfluoroarene with an anionic bis(π-allyl)nickel complex[14] is a fast process, and thus it is not the rate-determining step. This is in striking contrast with the four-component coupling reaction between a perfluoroarene, aryl Grignard reagent, and two molecules of 1,3-butadiene catalyzed by a Ni catalyst, where the reaction of a Ni intermediate with the perfluoroarene is the rate-determining step.[11]

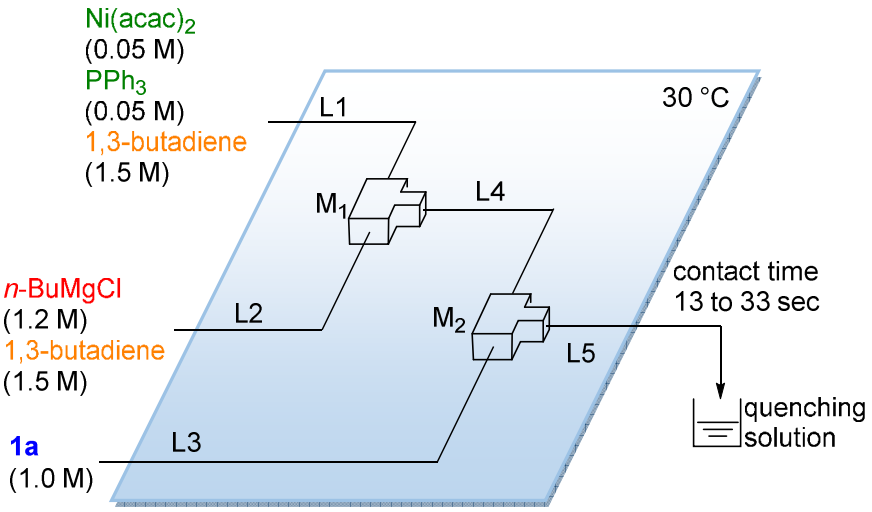
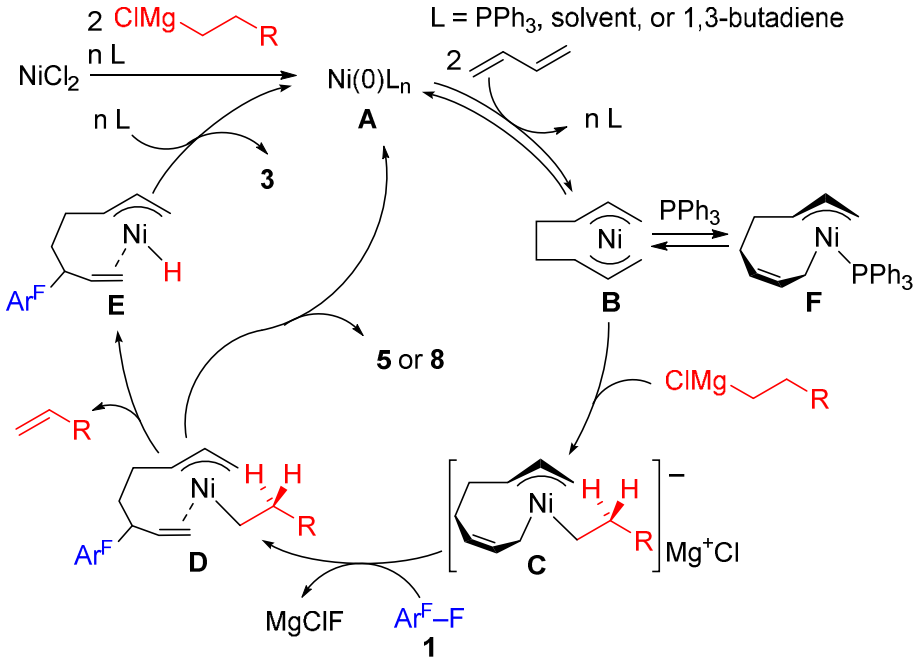


Figure 2. A flow reactor used for kinetic studies and the standard conditions.

A proposed catalytic cycle is shown in Scheme 6. Initially, a Ni(II) salt is reduced by a Grignard reagent to form Ni(0) species **A**, which then undergoes an oxidative dimerization with 1,3-butadiene to form bis(π-allyl)nickel complex **B**. As reported by Wilke and co-workers,[21] triphenylphosphine coordinates with complex **B** to form complex **F** as a resting state of the present reaction. Complexation of **B** with an alkyl Grignard reagent leads to the formation of anionic complex **C**,[14,22-24] which selectively reacts with perfluoroarene **1** at the γ-carbon of the σ-allyl group. Reductive elimination of the alkyl and allyl groups of Ni in complex **D** most likely generates alkylperfluoroarylation product **5**; however, this is a slow process, and the more facile

β-hydrogen elimination proceeds selectively[25] giving rise to three-component coupling product **3** via hydride complex **E**.[26] When Grignard reagents carrying no β-hydrogens are employed, the reductive elimination of complex **D** occurs to form alkylperfluoroarylation product **5** as shown in Scheme 2.[27] When the reductive elimination is slow, the insertion of the terminal C–C double bond into the allyl or alkyl C–Ni bond proceeds to give cyclic compound **8**, as in the case of isoprene (Scheme 5).[14,28]

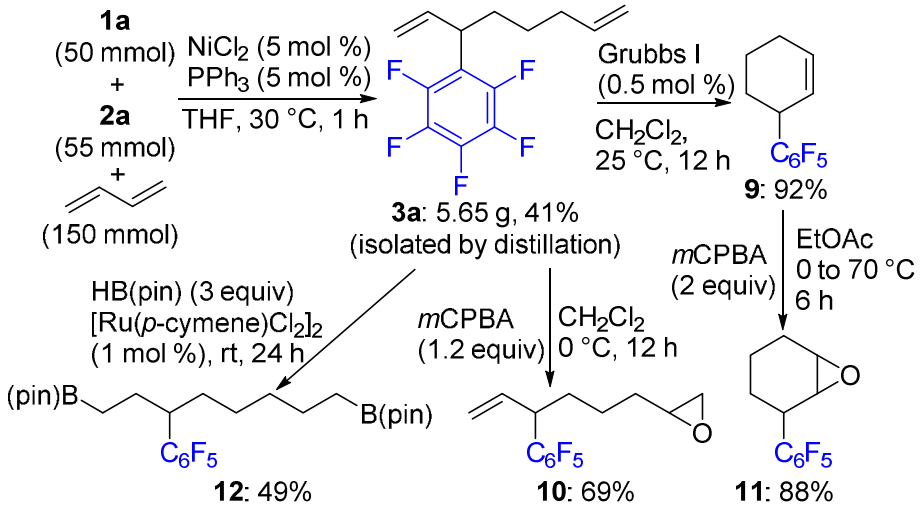
Scheme 6. Proposed catalytic cycle.



Finally, we investigated derivatization of the hydroperfluoroarylated products (Scheme 7). The gram-scale synthesis of **3a** using 5 mol % of catalyst afforded 5.65 g of product after simple vacuum distillation. Ring-closing metathesis between both terminal alkene moieties of **3a** afforded cyclized compound **9** in the presence of first generation Grubbs' catalyst in CH_2Cl_2. Epoxidation of **3a** and **9** afforded the corresponding epoxides **10** and **11** in 69 and 88% yields,

respectively. Furthermore, the treatment of **3a** with HB(pin) provided diborylated product **12** in 49% yield.[29]

Scheme 7. Synthetic manipulation of **3a**.



CONCLUSIONS

In conclusion, we developed a Ni-catalyzed three-component coupling reaction for the preparation of synthetically useful 1,7-dienes bearing a perfluoroaryl moiety at the 3-position via C–F bond cleavage of easily accessible perfluoroarenes. Mechanistic studies revealed that the reaction involved an anionic Ni complex as key intermediate, and the C–F bond cleavage of perfluoroarenes was a relatively fast step in the catalytic cycle. In this reaction, an alkyl Grignard reagent acted not only as a hydride source but also as activator of the Ni intermediates by forming anionic Ni complexes. This activation of the catalytic intermediates enabled the facile cleavage of the aromatic C–F bonds without the assistance of an electron-withdrawing or directing group.

EXPERIMENTAL SECTION

Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR) spectra were recorded at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR), and 162 MHz (^{31}P NMR) in 5 mm NMR tubes. All ^{1}H NMR chemical shifts were reported in ppm relative to an internal reference tetramethylsilane at δ 0.00. All ^{13}C NMR chemical shifts were reported in ppm relative to the carbon of chloroform-*d*$_1$ as δ 77.00. ^{19}F NMR and ^{31}P NMR chemical shifts were reported in ppm relative to external references of α,α,α-trifluorotoluene as δ –63.90 and 85% H_3PO_4 aq. as δ 0.00, respectively. Infrared spectra were recorded using ATR. HPLC separations were performed on a recycling preparative HPLC equipped with Shodex K2001 and 2002 columns (GPC) using $CHCl_3$ as an eluent. GC analyses were performed with a GL Sciences InertCap 5 capillary column (I.D. 0.25 mm, Length 30 m, df 0.25 μm) using an internal standard. Conventional and high resolution mass spectra were recorded with a double-focusing magnetic sector mass instrument or with a time-of-flight mass instrument. Melting points were measured using a glass capillary. Single crystallographic analysis was made on a diffractometer with a 2-D area detector using graphite-monochromated Cu-Kα radiation (λ = 1.54187 Å).

All manipulations involving air- and moisture-sensitive compounds were carried out by the standard Schlenk techniques under a nitrogen atmosphere. Dehydrated THF was purified by SPS[30] prior to use. Perfluoroarenes **1e**, **1g-i**, **1k**, **1m**, and **1r** were prepared according to the literature.[11] CyMgCl was prepared by a standard procedure from the corresponding chlorocyclohexane and Mg. Other THF solutions of Grignard reagents were purchased and used after titration using I_2. $NiCl_2$ (Wako), 1,3-butadiene (TCI), PPh_3 (Kishida), and all other commercially available reagents were used as received.

Synthesis of Substrates

*2,3,4,5,6-Pentafluoro-1,1'-biphenyl (**1c**)*.[31] A mixture of hexafluorobenzene (2.79 g, 15 mmol) and PhMgBr (22.5 mmol. 0.82 M in THF) in THF (15 mL) was stirred at 60 °C for 67 h. The resulting mixture was carefully quenched by H_2O. The product was extracted by Et_2O, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (pentane as an eluent) to give **1c** as a white solid (1.32 g, 5.4 mmol, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.51 (m, 5H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –143.1 (dd, J = 22.5, 7.9 Hz, 2F), –155.7 (t, J = 21.0 Hz, 1F), –162.0-–162.2 (m, 2F).

*2-(Pentafluorophenyl)-1,3-dioxolane (**1f**)*.[32] A mixture of pentafluorobenzaldehyde (1.96 g, 10.0 mmol), ethylene glycol (14.0 mL, 250 mmol), and pyridinium *p*-toluenesulfonate (PPTS) (0.25 g, 1.0 mmol) in benzene (70 mL) was stirred at 80 °C for 20 h. The resulting mixture was washed with K_2CO_3 aq. and brine, dried over Na_2SO_4, and concentrated to give **1f** as white powder (2.40 g, 9.99 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (s, 1H), 4.03-4.23 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 66.0, 96.4, 140.5, 143.0, 146.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ –143.6-–143.7 (m, 2F), –152.3-–152.4 (tt, J = 20.5, 2.6 Hz, 1F), –161.7-–161.8 (m, 2F).

*Pentafluorophenyl pivalate (**1j**)*.[33] *N,N'*-Dicyclohexylcarbodiimide (DCC) (2.34 g, 11.3 mmol) was added to a stirred solution of pivalic acid (1.04 g, 10.2 mmol) and pentafluorophenol (2.32 g, 12.6 mmol) in 1,4-dioxane (40 mL) under dry nitrogen atmosphere. Stirring was continued for 12 h, by which time a colorless precipitate had formed. The mixture was filtered, evaporated, and purified by silica gel column chromatography (EtOAc/hexane = 5/95) to yield the product as a colorless oil (2.08 g, 7.8 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 9H); ^{19}F NMR

(376 MHz, $CDCl_3$): δ –153.4 (d, *J* = 21.4 Hz, 2F), –158.4 (d, *J* = 21.6 Hz, 1F), –162.4-–162.6 (m, 2F).

*2-Pentafluorophenyl-5-methylthiophene (**1n**).* The compound **1n** was prepared by a similar procedure reported by Tilley.[34] A solution of 2-methylthiophene (0.98 g, 10 mmol) in THF (20 mL) was added *n*-BuLi (1.55 M in hexane, 6.45 mL, 10 mmol) at –78 °C and then stirred at 0 °C for 1 h. The resulting solution was slowly cannulated into a solution of hexafluorobenzene (2.79 g, 15 mmol) in THF (20 mL) held in a dry-ice/ethanol bath cooling. The cooling bath was removed, and the stirring was continued for 8 h at rt. The reaction was carefully quenched by slow addition of water. The product was extracted by CH_2Cl_2, dried over Na_2SO_4, and purified by silica gel column chromatography (hexane as an eluent) to give **1n** as a white solid (1.21 g, 4.6 mmol, 46%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 3.6 Hz, 1H), 6.83-6.82 (m, 1H), 2.55 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ –140.3 (dd, *J* = 22.6, 7.1 Hz, 2F), –156.8 (t, *J* = 21.2 Hz, 1F), –162.2-–162.4 (m, 2F). These data matched with previously reported data for this compound.[35]

General procedure for Ni-catalyzed three-component coupling of perfluorobenzene, *n*-BuMgCl, and 1,3-butadiene (Table 1). An oven-dried test tube was charged with catalyst, ligand, and stirring bar and closed with a septum cap in a glove box. Undecane (50 μL) as an internal standard and THF (2.3 mL) were added at ambient temperature via a syringe and then the mixture was cooled with dry-ice/ethanol bath. Into this solution were added 1,3-butadiene (67 mL as gas, 3.0 mmol), *n*-BuMgCl (**2a**) (1.74 M in THF, 0.69 mL, 1.2 mmol), and perfluorobenzene (**1a**) (116 μL, 1.0 mmol) in this order. The reaction mixture was stirred at 30 ºC. After 0.5 h, the reaction mixture was diluted with Et_2O, carefully quenched by 1N HCl aq., and analyzed by GC.

General procedure for Ni-catalyzed three-component coupling of perfluoroarenes, *n*-BuMgCl, and 1,3-butadiene (Scheme 4). An oven-dried test tube was charged with $NiCl_2$ (7 mg, 0.05 mmol), PPh_3 (13 mg, 0.05 mmol), and stirring bar and closed with a septum cap in a glove box. THF (2.3 mL) was added at ambient temperature via a syringe and then the mixture was cooled with dry-ice/ethanol bath. Into this solution were added 1,3-butadiene (67 mL as gas, 3.0 mmol), *n*-BuMgCl (**2a**) (1.55 M in THF, 0.77 mL, 1.2 mmol), and perfluoroarene **1** (1.0 mmol) in this order. The reaction mixture was stirred at 30 ºC. After 2 h, the reaction mixture was diluted with Et_2O and carefully quenched by 1N HCl aq. The products were extracted by Et_2O for three times, dried over Na_2SO_4, concentrated, filtered through a short pad of silica gel (hexane or Et_2O as an eluent), and purified by GPC ($CHCl_3$ as an eluent) to give the desired product.

*1,2,3,4,5-Pentafluoro-6-(octa-1,7-dien-3-yl)benzene (**3a**).* The representative general procedure was followed using hexafluorobenzene (116 μL, 1.010 mmol) and butylmagnesium chloride (in THF, 1.85 M, 0.65 mL, 1.2 mmol). Purification by GPC gave the desired product as a colorless oil (203.4 mg, 74%); IR (neat): 1521, 1499, 1118, 977, 919, 652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.07-5.98 (m, 1H), 5.81-5.71 (m, 1H), 5.13-5.09 (m, 2H), 5.02-4.94 (m, 2H), 3.72 (q, J = 8.0 Hz, 1H), 2.06 (q, J = 7.2 Hz, 2H), 1.88-1.72 (m, 2H), 1.47-1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9 (dm, $^1J_{C\text{-}F}$ = 245.1 Hz, *o*-), 139.6 (dm, $^1J_{C\text{-}F}$ = 250.8 Hz, *p*-), 137.6 (dm, $^1J_{C\text{-}F}$ = 251.3 Hz, *m*-), 117.2 (m, *ipso*-), 38.1, 137.7, 116.5, 114.9, 40.0, 33.3, 32.7, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.2 (dd, J = 22.6, 7.1 Hz, 2F), –157.4 (t, J = 21.1 Hz, 1F), –162.3 (ddd, J = 22.6, 21.1, 7.1 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{14}H_{13}F_5$: 276.0937; Found 276.0936.

*Procedure for large-scale synthesis of **3a**.* To a 1000 mL three-neck flask equipped with a magnetic stirring bar was added $NiCl_2$ (324.0 mg, 2.5 mmol), PPh_3 (656.0 mg, 2.5 mmol), and THF (200 mL). The mixture was cooled with a dry ice/ethanol bath and were added 1,3-btuadiene (3350 mL as gas, 150 mmol) followed by adding *n*-butylmagnesium chloride (50 mL, 1.1 M in THF, 55 mmol) and hexafluorobenzene (9.41g, 50 mmol) in this order. After stirring at 30 °C for 1 h, the reaction was quenched by 1 N HCl aq. (200 mL), and extracted by Et_2O (200 mL x 3). The mixture was dried by Na_2SO_4 and concentrated by rotary evaporator to obtain a yellow oil. The desired product was obtained as a colorless oil (5.65 g, 41%) by vacuum distillation (at 0.6 kPa, bp = 100–103 °C).

*1,2,4,5-Tetrafluoro-3-methyl-6-(octa-1,7-dien-3-yl)benzene (**3b**).* The representative general procedure was followed using 2,3,4,5,6-pentafluorotoluene (180.0 mg, 0.989 mmol) and butylmagnesium chloride (in THF, 1.95 M, 0.77 mL, 1.5 mmol). Purification by GPC gave **3b** as a mixture of two isomers in *p*:*m* or *o* = 94:6 ratio (determined by GC and ^{19}F NMR, but the substitution pattern of the minor isomer could not be identified) as a colorless oil (175.6 mg, 65%): ^1H NMR (400 MHz, $CDCl_3$): δ 6.10–6.01 (m, 1H), 5.80–5.71 (m, 1H), 5.12–4.92 (m, 4H), 3.74 (q, *J* = 8.0 Hz, 1H), 2.23 (s, 3H), 2.06 (dt, *J* = 7.6, 7.4 Hz, 2H), 1.80 (q, *J* = 8.0 Hz, 2H), 1.47–1.22 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.1 (dm, $^1J_{C\text{-}F}$ = 224.0 Hz), 144.4 (dm, $^1J_{C\text{-}F}$ = 244.0 Hz), 138.4, 138.3, 116.0, 114.7, 40.2, 33.4, 32.8, 27.0, 7.4 (m) (carbon signals from two ipso carbons of the perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –144.4 (m, 4F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{15}H_{16}F_4$: 272.1188; Found 272.1190.

*2,3,5,6-Tetrafluoro-4-(octa-1,7-dien-3-yl)-1,1'-biphenyl (**3c**).* The representative general procedure was followed using 2,3,4,5,6-pentafluoro-1,1'-biphenyl (245.0 mg, 1.00 mmol) and

butylmagnesium chloride (in THF, 1.55 M, 0.77 mL, 1.2 mmol). Purification by GPC gave **3c** as a mixture of two isomers in *p*:*m* or *o* = 96:4 ratio (determined by GC and ^{19}F NMR, but the substitution pattern of the minor isomer could not be identified) as a white powder (208.0 mg, 62%): m.p. = 51–54 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.42 (m, 5H), 6.13–6.08 (m, 1H), 5.82–5.76 (m, 1H), 5.19–4.95 (m, 4H), 3.82 (q, J = 7.6 Hz, 1H), 2.09 (q, J = 6.8 Hz, 2H), 1.86 (dt, J = 8.0, 7.6 Hz, 2H), 1.53–1.42 (m, 1H), 1.40–1.31 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.9 (dm, $^{1}J_{C\text{-}F}$ = 237.4 Hz), 143.8 (dm, $^{1}J_{C\text{-}F}$ = 240.3 Hz), 138.3, 138.0, 130.1 (t, $^{4}J_{C\text{-}F}$ = 1.9 Hz), 128.9, 128.5, 121.3 (m), 118.3 (m), 116.4, 40.5, 33.4, 32.7 (d, $^{3}J_{C\text{-}F}$ = 1.9 Hz), 27.0 (carbon signals from two ipso carbons of the perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –143.1 (dd, J = 22.4, 12.2 Hz, 2F), –144.6 (dd, J = 22.4, 12.2 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{20}H_{18}F_4$: 334.1345; Found 334.1341. Single crystals of **3c** suitable for X-ray crystallography were obtained by recrystallization from Et_2O. X-ray data for **3c** (CCDC 1836311): The structure was solved by direct method (SIR2008)[36]. The structure was refined on F^2 by full-matrix least-squares method using SHELXL-97[37]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using riding model. C1 and C4 carbons of octa-1,7-diene moiety and hydrogens on C5 and C3 were refined as disorder model (0.643(17):0.367(17) ratio). $C_{20}H_{18}F_4$, T = 123(1) K, M = 334.36, colorless, monoclinic, $P2/c$ (#13), a = 13.0228(4) Å, b = 5.7000(2) Å, c = 22.0772(8) Å, β = 95.7060(19)°, V = 1630.66(10) Å^3, Z = 4, D_{calcd} = 1.362 g/cm^3, R_{int} = 0.0862, R_1 = 0.1007, wR_2 = 0.2756 for $I > 2\sigma(I)$, R_1 = 0.1354, wR_2 = 0.3210 for all data.

*1,2,4,5-Tetrafluoro-3-methoxy-6-(octa-1,7-dien-3-yl)benzene (**3d**).* The representative general procedure was followed using 2,3,4,5,6-pentafluoroanisole (199.0 mg, 1.005 mmol) and butylmagnesium chloride (in THF, 1.85 M, 0.65 mL, 1.2 mmol). Purification by GPC gave **3d** as

a mixture of three isomers in *p*:*m*:*o* = 60:36:4 ratio (determined by ^{19}F NMR) as a colorless oil (200.6 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08–6.00 (m, 1H), 5.80–5.71 (m, 1H), 5.12–4.93 (m, 4H), 4.05 (t, *J* = 1.8 Hz, 1.8H), 3.97 (s, 1.0H), 4.05 (t, *J* = 1.2 Hz, 0.2H), 3.70 (q, *J* = 7.6 Hz, 1H), 2.06 (dt, *J* = 7.2, 6.8 Hz, 2H), 1.83–1.79 (m, 2H), 1.45–1.37 (m, 1H), 1.31–1.26 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.0 (dm, $^{1}J_{C\text{-}F}$ = 230.8 Hz), 141.0 (dm, $^{1}J_{C\text{-}F}$ = 228.8 Hz), 138.3, 138.2, 116.0, 114.8, 62.4 (t, $^{3}J_{C\text{-}F}$ = 2.8 Hz), 62.1 (t, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 39.9, 33.3, 32.8 (m), 26.9 (carbon signals from two ipso carbons of the perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.6 (d, *J* = 7.9 Hz, 0.6F), –142.3 (dd, *J* = 22.6, 7.1 Hz, 0.08F), –143.6 (d, *J* = 22.2 Hz, 0.6F), –144.0 (dd, *J* = 21.6, 8.1 Hz, 2F), –152.9 (d, *J* = 20.7 Hz, 0.6F), –156.2 (dd, *J* = 20.3, 8.6 Hz, 0.08F), –158.2 (dd, *J* = 21.8, 8.6 Hz, 2F), –159.0 (t, *J* = 20.9 Hz, 0.08F), –163.6 (t, *J* = 21.6 Hz, 0.08F), –164.0 (m, 0.6F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{15}H_{16}F_4O$: 288.1137; Found 288.1135.

1,2,4,5-Tetrafluoro-3-(methoxymethoxy)-6-(octa-1,7-dien-3-yl)benzene ***(3e)***. The representative general procedure was followed using 1,2,3,4,5-pentafluoro-6-(methoxymethoxy) benzene (225.8 mg, 0.990 mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3e** as a mixture of three isomers in *p*:*m*:*o* = 63:32:5 ratio (determined by ^{19}F NMR) as a colorless oil (171.8 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06–6.01 (m, 1H), 5.80–5.73 (m, 1H), 5.18–4.93 (m, 6H), 3.70 (q, *J* = 7.6 Hz, 1H), 3.60 (d, *J* = 2.8 Hz, 3H), 2.09–2.03 (m, 2H), 1.84–1.76 (m, 2H), 1.44–1.39 (m, 1H), 1.31–1.25 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.9 (dm, $^{1}J_{C\text{-}F}$ = 247.9 Hz), 141.8 (dm, $^{1}J_{C\text{-}F}$ = 245.1 Hz), 138.3, 138.2, 138.1, 116.2, 116.1, 114.8 (d, $^{2}J_{C\text{-}F}$ = 2.8 Hz), 99.2 (t, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 99.1 (t, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 57.3 (d, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 40.1 (d, $^{3}J_{C\text{-}F}$ = 1.9 Hz), 39.9, 33.3 (d, $^{3}J_{C\text{-}F}$ = 2.8 Hz), 32.7 (d, $^{3}J_{C\text{-}F}$ = 1.9 Hz), 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –135.6 (d, *J* = 8.6 Hz, 0.5F), –141.2 (dd, *J*

= 21.4, 7.9 Hz, 0.08F), –142.1 (d, *J* = 22.6 Hz, 0.5F), –143.8 (dd, *J* = 21.8, 9.0 Hz, 2F), –151.5 (d, *J* = 21.1 Hz, 0.5F), –154.8 (dd, *J* = 20.9, 8.8 Hz, 0.08F), –156.8 (dd, *J* = 21.8, 9.0 Hz, 2F), –158.8 (t, *J* = 20.9 Hz, 0.08F), –162.6 (t, *J* = 21.6 Hz, 0.08F), –163.9 (m, 0.5F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{16}H_{18}F_4O_2$: 318.1243; Found 318.1249.

*2-(2,3,5,6-Tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl)-1,3-dioxolane (**3f**).* The representative general procedure was followed using 2-(perfluorophenyl)-1,3-dioxolane (242.5 mg, 1.010 mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3f** (*p*-only) as a colorless oil (254.7 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 (s, 1H), 6.06–5.99 (m, 1H), 5.79–5.72 (m, 1H), 5.12–5.08 (m, 2H), 5.02–4.93 (m, 2H), 4.23–4.20 (m, 2H), 4.06–4.03 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 2.05 (dt, *J* = 7.2, 7.0 Hz, 2H), 1.84–1.77 (m, 2H), 1.44–1.37 (m, 1H), 1.31–1.23 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.1 (dm, $^1J_{C\text{-}F}$ = 245.0 Hz), 144.6 (dm, $^1J_{C\text{-}F}$ = 248.9 Hz), 138.2, 137.6, 123.5 (t, $^3J_{C\text{-}F}$ = 16.7 Hz), 116.5, 114.9, 114.7 (t, $^2J_{C\text{-}F}$ = 12.9 Hz), 96.7 (m), 66.0, 40.4 (d, $^4J_{C\text{-}F}$ = 1.9 Hz), 33.3, 32.6 (d, $^3J_{C\text{-}F}$ =1.9 Hz), 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.9 (dd, *J* = 21.2, 12.6 Hz, 2F), –145.1 (dd, *J* = 21.4, 12.8 Hz, 2F); HRMS (CI+) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{19}F_4O_2$: 331.1321; Found 331.1308.

*2,3,5,6-Tetrafluoro-1-methylthio-4-(octa-1,7-dien-3-yl)benzene (**3g**).* The representative general procedure was followed using methyl perfluorophenyl sulfide (215.8 mg, 1.008 mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3g** as a mixture of two isomers in *p*:*m* or *o* = 98:2 ratio (determined by GC and ^{19}F NMR, but the substitution pattern of the minor isomer could not be identified) as a colorless oil (213.6 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07–6.00 (m, 1H), 5.80–5.73 (m, 1H), 5.14–5.08 (m, 2H), 5.02–4.93 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 2.50 (s, 3H), 2.06 (dt, *J* = 7.4, 6.8 Hz, 2H), 1.87–1.81 (m, 2H), 1.46–1.38 (m, 1H), 1.32–1.26 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.6

(dm, $^1J_{C\text{-}F}$ = 244.1 Hz), 144.7 (dm, $^1J_{C\text{-}F}$ = 246.0 Hz), 138.2, 137.8, 116.5, 114.8, 40.5, 33.3, 32.7, 26.9, 17.70 (carbon signals from two ipso carbons of the perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –135.4 (dd, *J* = 23.3, 11.7 Hz, 2F), –142.4 (dd, *J* = 23.7, 12.0 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{15}H_{16}F_4S$: 304.0909; Found 304.0916.

*2,3,5,6-Tetrafluoro-N,N-dimethyl-4-(octa-1,7-dien-3-yl)aniline (**3h**).* The representative general procedure was followed using 2,3,4,5,6-pentafluoro-*N,N*-dimethylaniline (211.8 mg, 1.003 mmol) and butylmagnesium chloride (in THF, 1.95 M, 0.62 mL, 1.2 mmol). Purification by GPC gave **3h** as a mixture of two isomers in *p*:*m* = 88:12 ratio (determined by ^{19}F NMR) as a colorless oil (149.5 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07–6.02 (m, 1H), 5.80–5.74 (m, 1H), 5.11–4.92 (m, 4H), 3.67 (q, *J* = 8.0 Hz, 1H), 2.92 (t, *J* = 2.2 Hz, 5.2H), 2.86 (t, *J* = 1.6 Hz, 0.8H), 2.06 (dt, *J* = 7.2, 7.0 Hz, 2H), 1.78 (dt, *J* = 8.0, 7.8 Hz, 2H), 1.44–1.25 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.1 (dm, $^1J_{C\text{-}F}$ = 242.2 Hz), 142.6 (dm, $^1J_{C\text{-}F}$ = 249.8 Hz), 138.6, 138.4, 115.7, 114.7, 43.4, 39.9, 33.4, 32.9, 27.0 (carbon signals from two ipso carbons of the perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –127.9 (d, *J* = 7.1 Hz, 0.14F), –143.5 (d, *J* = 22.9 Hz, 0.13F), –144.9 (dd, *J* = 20.3, 8.6 Hz, 2F), –145.6 (d, *J* = 21.1 Hz, 0.14F), –151.5–-151.6 (m, 2F), –165.0 (m, 0.13F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{16}H_{19}F_4N$: 301.1454; Found 301.1456.

*Trimethyl(2,3,5,6-tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl)silane (**3i**).* The representative general procedure was followed using trimethyl(perfluorophenyl)silane (241.8 mg, 1.006 mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3i** as a mixture of two isomers in *p*:*m* or *o* = 96:4 ratio (determined by GC and ^{19}F NMR, but the substitution pattern of the minor isomer could not be identified) as a colorless oil (175.9 mg, 53%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09–6.02 (m, 1H), 5.80–5.72 (m, 1H), 5.14–5.07 (m, 2H),

5.02–4.94 (m, 2H), 3.76 (q, J = 7.6 Hz, 1H), 2.06 (q, J = 7.2 Hz, 2H), 1.82 (dt, J = 8.4, 7.4 Hz, 2H), 1.48–1.37 (m, 1H), 1.35–1.25 (m, 1H), 0.38 (t, J = 1.4 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.5 (dm, $^1J_{C\text{-}F}$ = 240.3 Hz), 145.0 (dm, $^1J_{C\text{-}F}$ = 246.0 Hz), 138.4, 138.1, 123.7 (t, $^2J_{C\text{-}F}$ = 16.6 Hz), 116.3, 114.8, 40.7, 33.4, 32.7 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 27.0, 0.0 (t, $^4J_{C\text{-}F}$ = 2.9 Hz) (a carbon signal from ipso carbon of the perfluoroaryl ring was not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –128.7 (dd, J = 23.8, 9.4 Hz, 2F), –143.1 (dd, J = 23.9, 9.4 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{17}H_{22}F_4Si$: 330.1427; Found 330.1432.

*2,3,5,6-Tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl pivalate (**3j**).* The representative general procedure was followed using perfluorophenyl pivalate (267.1 mg, 0.996 mmol) and butylmagnesium chloride (in THF, 1.55 M, 0.77 mL, 1.2 mmol). Purification by GPC gave **3j** as a mixture of three isomers in *p*:*m*:*o* = 80:15:5 ratio (determined by GC and ^{19}F NMR) as a yellow oil (273.4 mg, 69%): ^1H NMR (400 MHz, $CDCl_3$): δ 6.08–6.00 (m, 1H), 5.80–5.71 (m, 1H), 5.14–4.94 (m, 4H), 3.74 (q, J = 7.8 Hz, 1H), 2.07 (dt, J = 7.4, 7.2 Hz, 2H), 1.87–1.76 (m, 2H), 1.39 (s, 9H), 1.35–1.23 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.7, 144.7 (dm, $^1J_{C\text{-}F}$ = 244.1 Hz), 140.7 (dm, $^1J_{C\text{-}F}$ = 247.0 Hz), 138.2, 137.8, 119.3 (t, $^2J_{C\text{-}F}$ =16.6 Hz), 116.5, 114.9, 45.2, 40.2, 39.4, 33.3, 32.7, 26.9 (a carbon signal from ipso carbon of the perfluoroaryl ring was not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –143.2 (dd, J = 22.2, 8.6 Hz, 2F), –154.5 (dd, J =21.8, 8.6 Hz, 2F); HRMS (CI+) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{23}F_4O_2$: 359.1634; Found 359.1635.

*N,N-Diethyl-2,3,5,6-tetrafluoro-4-(octa-1,7-dien-3-yl)benzamide (**3k**).* The representative general procedure was followed using *N*,*N*-diethyl-2,3,4,5,6-pentafluorobenzamide (268.6 mg, 1.005 mmol) and butylmagnesium chloride (in THF, 1.95 M, 0.62 mL, 1.2 mmol). Purification by GPC gave **3k** as a mixture of two isomers in *p*:*m* or *o* = 97:3 ratio (determined by GC and ^{19}F

NMR, but the substitution pattern of the minor isomer could not be identified) as a colorless oil (210 mg, 59%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08–6.01 (m, 1H), 5.80–5.72 (m, 1H), 5.17–5.09 (m, 2H), 5.02–4.94 (m, 2H), 3.77 (q, J = 7.6 Hz, 1H), 3.59 (q, J = 7.4 Hz, 2H), 3.24 (dt, J = 7.4 Hz, 2H), 2.07 (q, J = 7.2 Hz, 2H), 1.90–1.76 (m, 2H), 1.50–1.30 (m, 2H), 1.27 (t, J = 7.4 Hz, 3H), 1.14 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 144.5 (dm, $^{1}J_{C\text{-}F}$ = 243.1 Hz), 142.2 (dm, $^{1}J_{C\text{-}F}$ = 246.9 Hz), 138.0, 137.4, 123.3 (t, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 116.7, 114.8, 114.6 (t, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 43.1, 40.5, 39.5, 33.2, 32.5, 26.8, 13.9, 12.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –141.1 (dd, J = 22.7, 12.6 Hz, 1F), –141.4 (dd, J = 23.1, 13.0 Hz, 1F), –142.6-–142.8 (m, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{19}H_{23}F_4NO$: 357.1716; Found 357.1715;

*Diphenyl(2,3,5,6-tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl)phosphane (**3l**).* The representative general procedure was followed using (perfluorophenyl)diphenylphosphane (351.5 mg, 0.998 mmol) and butylmagnesium chloride (in THF, 1.85 M, 0.65 mL, 1.2 mmol). Purification by GPC gave **3l** (*p*-only) as a white powder (293.3 mg, 66%): m.p. = 38–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.42 (m, 4H), 7.36–7.35 (m, 6H), 6.10–6.01 (m, 1H), 5.79–5.73 (m, 1H), 5.16–5.09 (m, 2H), 5.02–4.94 (m, 2H), 3.76 (q, J = 7.8 Hz, 1H), 2.06 (dt, J = 7.2, 7.0 Hz, 2H), 1.89–1.74 (m, 2H), 1.50–1.39 (m, 1H), 1.35–1.26 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.0 (dm, $^{1}J_{C\text{-}F}$ = 243.1 Hz), 144.7 (dm, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 138.2, 137.6, 133.8 (d, J = 10.5 Hz), 133.0 (d, J = 21.0Hz) 129.1, 128.6 (d, J = 6.7 Hz), 124.9 (t, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 116.8, 114.9, 113.5 (m), 40.8, 33.3, 32.6, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –128.6-–128.8 (m, 2F), –141.6 (dd, J = 22.7, 12.6 Hz, 2F); ^{31}P NMR (162 MHz, $CDCl_3$): δ –24.6 (t, J = 37.2 Hz); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{26}H_{23}F_4P$: 442.1474; Found 442.1465.

*2,3,5,6-Tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl 4-methylbenzenesulfonate (**3m**).* The representative general procedure was followed using 4-methylbenzenesulfonate (338.3 mg, 1.000

mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3m** as a mixture of two isomers in *p*:*m* or *o* = 88:12 ratio (determined by GC and ^{19}F NMR, but the substitution pattern of the minor isomer could not be identified) as a yellow oil (190.6 mg, 44%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.06–5.97 (m, 1H), 5.80–5.71 (m, 1H), 5.15–5.10 (m, 2H), 5.02–4.94 (m, 2H), 3.73 (q, *J* = 7.4 Hz, 1H), 2.50 (s, 3H), 2.09–2.04 (m, 2H), 1.85–1.75 (m, 2H), 1.46–1.39 (m, 1H), 1.31–1.25 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.7 (dm, $^{1}J_{C\text{-}F}$ = 242.2 Hz), 141.6 (dm, $^{1}J_{C\text{-}F}$ = 252.7 Hz), 146.4, 138.1, 137.3, 132.0, 130.0, 128.5, 121.2 (t, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 116.9, 114.9, 40.4 (d, $^{3}J_{C\text{-}F}$ = 1.9 Hz), 33.2, 32.6 (t, $^{4}J_{C\text{-}F}$ = 1.9 Hz), 26.9, 21.8 (a carbon signal from ipso carbon of the perfluoroaryl ring was not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –141.7 (dd, *J* = 20.9, 8.1 Hz, 2F), –151.6 (m, 2F); HRMS (CI+) *m/z* $[M+H]^+$ Calcd for $C_{21}H_{21}F_4O_3S$: 429.1148; Found 429.1142.

2-Methyl-5-(2,3,5,6-tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl)thiophene ***(3n)***. The representative general procedure was followed using 2-methyl-5-(perfluorophenyl)thiophene (264.9 mg, 1.003 mmol) and butylmagnesium chloride (in THF, 1.55 M, 0.77 mL, 1.2 mmol). Purification by GPC gave **3n** (*p*-only) as a colorless oil (256.9 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 3.6 Hz, 1H), 6.82 (d, *J* = 2.8 Hz, 1H), 6.12–6.03 (m, 1H), 5.81–5.74 (m, 1H), 5.16–4.96 (m, 4H), 3.77 (q, *J* = 7.6 Hz, 1H), 2.54 (s, 3H), 2.07 (q, *J* = 7.2 Hz, 2H), 1.84 (dt, *J* = 8.4, 7.6 Hz, 2H), 1.50–1.39 (m, 1H), 1.37–1.26 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.1 (dm, $^{1}J_{C\text{-}F}$ = 236.5 Hz), 143.5 (dm, $^{1}J_{C\text{-}F}$ = 247.9 Hz), 142.8 (t, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 138.3, 138.0, 130.1 (t, $^{4}J_{C\text{-}F}$ = 5.7 Hz), 125.6, 125.4 (m), 120.0 (t, $^{2}J_{C\text{-}F}$ = 16.7 Hz), 116.3, 114.8, 112.6 (t, $^{2}J_{C\text{-}F}$ = 14.7 Hz), 40.3, 33.4, 32.7, 27.0, 15.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ –141.3 (dd, *J* =

23.9, 11.7 Hz, 2F), –143.4 (dd, J = 21.4, 11.7 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{19}H_{18}F_4S$: 354.1065; Found 354.1064.

*2-(2,3,5,6-Tetrafluoro-4-(octa-1,7-dien-3-yl)phenyl)pyridine (**3o**).* When *n*-BuMgCl was used under the standard conditions, **4oa** was yielded in 72% yield along with 4% of **3o**. The representative general procedure was followed using 2-(perfluorophenyl)pyridine (246.8 mg, 1.007 mmol) and 10 mol % of catalyst components, and *i*-BuMgCl (in THF, 1.55 M, 0.97 mL, 1.5 mmol) was added slowly. Purification by GPC gave **3o** (*p*-only) as a colorless oil (64 mg, 19%) along with a cross-coupling compound **4ob** (111 mg, 39%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 8.0 Hz, 1H), 7.86–7.81 (m, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.39–7.36 (m, 1H), 6.14–6.05 (m, 1H), 5.81–5.75 (m, 1H), 5.17–5.11 (m, 2H), 5.03–4.95 (m, 2H), 3.82 (q, J = 7.6 Hz, 1H), 2.11–2.04 (m, 2H), 1.86 (dt, J = 7.8, 8.0 Hz, 2H), 1.46–1.40 (m, 1H), 1.36–1.25 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.0, 138.3, 137.8, 136.6, 125.9, 123.5, 116.5, 114.9, 40.4, 33.4, 32.7, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.7 (dd, J = 21.8, 12.4 Hz, 2F), –144.6 (dd, J = 22.4, 12.2 Hz, 2F); HRMS (DART) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{18}F_4N$ 336.1375; Found 336.1378.

*2-(2-Butyl-3,4,5,6-tetrafluorophenyl)pyridine (**4oa**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75–8.73 (m, 1H), 7.83–7.79 (m, 1H), 7.38–7.34 (m, 2H), 2.57–2.52 (m, 2H), 1.39–1.31 (m, 2H), 1.21–1.11 (m, 2H), 0.76–0.71 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.8, 145.9 (dm, $^1J_{C\text{-}F}$ = 240.3 Hz), 145.0 (dm, $^1J_{C\text{-}F}$ = 245.1 Hz), 140.3 (dm, $^1J_{C\text{-}F}$ = 251.7 Hz), 138.6 (dm, $^1J_{C\text{-}F}$ = 237.4 Hz), 136.5, 125.7, 123.1, 31.9, 25.2, 22.3, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.4 (dd, J = 22.4, 12.2 Hz, 1F), –143.3 (dd, J = 20.9, 12.2 Hz, 1F), –156.5–156.6 (m, 1F), –159.7 (dt, J = 21.3, 5.8 Hz, 1F); HRMS (DART) *m/z* $[M]^+$ Calcd for $C_{15}H_{13}F_4N$ 283.0984; Found 283.1004.

*2,2',3,3',4,5,5',6,6'-Nonafluoro-4'-(octa-1,7-dien-3-yl)-1,1'-biphenyl (**3p**).* The representative general procedure was followed using decafluorobiphenyl (336.0 mg, 1.006 mmol) and butylmagnesium chloride (in THF, 1.81 M, 0.66 mL, 1.2 mmol). Purification by GPC gave **3p** (*p*-only) as a colorless oil (165 mg, 39%) along with a disubstituted compound **6p** (colorless oil, 46.5 mg, 9%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14–6.05 (m, 1H), 5.82–5.75 (m, 1H), 5.21–5.15 (m, 2H), 5.04–4.96 (m, 2H), 3.85 (q, *J* = 8.0 Hz, 1H), 2.10 (dt, *J* = 7.4, 6.8 Hz, 2H), 1.92–1.84 (m, 2H), 1.53–1.43 (m, 1H), 1.40–1.31 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.8 (dm, $^{1}J_{C\text{-}F}$ = 237.4 Hz), 144.7 (dm, $^{1}J_{C\text{-}F}$ = 231.7 Hz), 144.6 (dm, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 144.1 (dm, $^{1}J_{C\text{-}F}$ = 234.6 Hz), 142.3 (dm, $^{1}J_{C\text{-}F}$ = 243.1 Hz), 138.2, 137.3, 125.1 (t, $^{2}J_{C\text{-}F}$ = 16.2 Hz), 117.1, 115.0, 103.9 (m), 102.6 (m), 40.8, 33.3, 32.6, 27.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –137.3 (m, 2F), –138.8 (m, 2F), –141.4 (dd, *J* = 21.2, 11.8 Hz, 2F), –150.6 (m, 1F), –160.7 (m, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{20}H_{13}F_9$: 424.0874; Found 424.0867.

*4,4'-Bis(octa-1,7-dien-3-yl)-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (**6p**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14–6.05 (m, 2H), 5.84–5.74 (m, 2H), 5.21–4.96 (m, 8H), 3.83 (q, *J* = 7.6 Hz, 2H), 2.10 (dt, *J* = 7.2, 6.8 Hz, 4H), 1.91–1.83 (m, 4H), 1.52–1.31 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 137.4, 117.0, 115.0, 40.8, 33.3, 32.6, 27.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –138.8–138.9 (m, 4F), –141.8–142.0 (m, 4F); HRMS (DART) *m/z* $[M+H]^+$ Calcd for $C_{28}H_{27}F_8$ 515.1985; Found 515.1989.

*1,2,3,4,5,6,8-Heptafluoro-7-(octa-1,7-dien-3-yl)naphthalene (**3q**).* The representative general procedure was followed using perfluoronaphthalene (271.0 mg, 0.996 mmol) and butyl-magnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3q** as a mixture of two isomers in *7*:*8* = 90:10 ratio (determined by GC and ^{19}F NMR) as a colorless oil (149.4 mg, 41%) along with a cross-coupling compound **4qa** (white powder, 19.8 mg, 6%): ^{1}H

NMR (400 MHz, $CDCl_3$): δ 6.17–6.08 (m, 1H), 5.80–5.72 (m, 1H), 5.18–5.12 (m, 2H), 5.02–4.93 (m, 2H), 3.93 (q, *J* = 7.6 Hz, 1H), 2.08 (dt, *J* = 7.6, 6.8 Hz, 2H), 1.94–1.86 (m, 2H), 1.50–1.41 (m, 1H), 1.35–1.25 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.9 (dm, $^1J_{C\text{-}F}$ = 235.5 Hz), 146.7 (dm, $^1J_{C\text{-}F}$ = 246.9 Hz), 141.3 (dm, $^1J_{C\text{-}F}$ = 232.7 Hz), 141.0 (dm, $^1J_{C\text{-}F}$ = 245.1 Hz), 140.7 (dm, $^1J_{C\text{-}F}$ = 247.9 Hz), 139.3 (dm, $^1J_{C\text{-}F}$ = 253.6 Hz), 138.6 (dm, $^1J_{C\text{-}F}$ = 225.2 Hz), 138.2, 137.7, 116.9, 114.9, 110.2 (m), 107.9 (m), 40.4, 33.3, 32.6 (t, $^3J_{C\text{-}F}$ = 1.9 Hz), 27.0 (a carbon signal from ipso carbon of the perfluoroaryl ring was not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –120.8 (dd, *J* = 70.3, 17.5 Hz, 1F), –136.4 (d, *J* = 15.0, 1F), –144.3–144.6 (m, 1F), –146.4–146.6 (m, 1F), –148.9–149.1 (m, 1F), –154.4–154.5 (m, 1F), –156.1 (m, 1F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{18}H_{13}F_7$: 362.0905; Found 362.0906

*2-Butyl-1,3,4,5,6,7,8-heptafluoronaphthalene (**4qa**).* ^1H NMR (400 MHz, $CDCl_3$): δ 2.86 (t, *J* = 7.8 Hz, 2H), 1.68–1.61 (m, 2H), 1.50–1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.2 (dm, $^1J_{C\text{-}F}$ = 252.6 Hz), 146.9 (dm, $^1J_{C\text{-}F}$ = 253.8 Hz), 141.1 (dm, $^1J_{C\text{-}F}$ = 268.9 Hz), 140.3 (dm, $^1J_{C\text{-}F}$ = 270.8 Hz), 139.1 (dm, $^1J_{C\text{-}F}$ = 268.8 Hz), 138.5 (dm, $^1J_{C\text{-}F}$ = 319.4 Hz), 110.0 (m), 107.8 (m), 31.4, 22.7, 22.4, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –123.0 (dd, *J* = 68.1, 18.8 Hz, 1F), –138.7 (d, *J* = 17.7, 1F), –144.8–145.1 (m, 1F), –146.6–146.8 (m, 1F), –149.7–149.9 (m, 1F), –155.1–155.2 (m, 1F), –156.5 (m, 1F); HRMS (DART) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{10}F_7$ 311.0671; Found 311.0683.

*1,2,4-Trifluoro-3-(octa-1,7-dien-3-yl)dibenzo[b,e][1,4]dioxine (**3r**).* The representative general procedure was followed using 1,2,3,4-tetrafluorodibenzo[*b*,*e*][1,4]dioxine (257.0 mg, 1.003 mmol) and butylmagnesium chloride (in THF, 1.41 M, 0.85 mL, 1.2 mmol). Purification by GPC gave **3r** as a mixture of two isomers in *3*:*4* = 66:34 ratio (determined by ^{19}F NMR) as a colorless oil (216.7 mg, 62%): ^1H NMR (400 MHz, $CDCl_3$): δ 6.97–6.93 (m, 4H), 6.08–6.01 (m, 1H),

5.80–5.73 (m, 1H), 5.08–4.93 (m, 4H), 3.78 (q, J = 8.0 Hz, 0.35H), 3.67 (q, J = 8.0 Hz, 0.7H), 2.07–2.04 (m, 2H), 1.85–1.76 (m, 2H), 1.43–1.40 (m, 1H), 1.33–1.26 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.0 (dm, $^1J_{C\text{-}F}$ = 227.0 Hz), 144.5 (dm, $^1J_{C\text{-}F}$ = 230.8 Hz), 143.9 (dm, $^1J_{C\text{-}F}$ = 247.9 Hz), 140.9, 140.6 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 140.2, 138.5, 138.4 (d, $^4J_{C\text{-}F}$ = 1.9 Hz), 132.1, 132.0, 131.9 (d, $^3J_{C\text{-}F}$ = 1.9 Hz), 128.5, 128.4, 125.0, 124.8, 124.7 (d, $^4J_{C\text{-}F}$ = 1.9 Hz), 116.8 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 116.5 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 115.9, 115.7, 114.7 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 39.8, 39.5, 33.3 (d, $^3J_{C\text{-}F}$ = 5.7 Hz), 32.7 (d, $^3J_{C\text{-}F}$ = 1.9 Hz), 32.5 (d, $^3J_{C\text{-}F}$ = 1.9 Hz), 27.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.3 (d, J = 9.4 Hz, 1F), –144.7 (d, J = 22.2 Hz, 0.5F), –145.3 (d, J = 22.6 Hz, 1F), –158.1 (d, J = 21.0 Hz, 0.5F), –163.4 (dd, J = 21.6, 9.2 Hz, 1F), –165.8 (t, J = 21.8 Hz, 0.5F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{20}H_{17}F_3O_2$: 346.1181; Found 346.1182.

*1,2,4,5-Tetrafluoro-3-(octa-1,7-dien-3-yl)-6-(trifluoromethyl)benzene (**3s**).* The representative general procedure was followed using octafluorotoluene (236.4 mg, 1.001 mmol) and *iso*-butylmagnesium chloride (in THF, 1.72 M, 0.87 mL, 1.5 mmol). Purification by GPC gave **3s** (*p*-only) as a yellow oil (102.9 mg, 31%): ^1H NMR (400 MHz, $CDCl_3$): δ 6.08–5.99 (m, 1H), 5.79–5.71 (m, 1H), 5.17–5.13 (m, 2H), 5.03–4.94 (m, 2H), 3.81 (q, J = 7.8 Hz, 1H), 2.08 (dt, J = 7.4, 6.8 Hz, 2H), 1.90–1.79 (m, 2H), 1.47–1.41 (m, 1H), 1.32–1.26 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.9 (dm, $^1J_{C\text{-}F}$ = 240.3 Hz), 144.1 (dm, $^1J_{C\text{-}F}$ = 239.3 Hz), 138.0, 136.8, 127.2 (t, $^2J_{C\text{-}F}$ = 16.2 Hz), 117.4, 115.1, 40.7, 33.2, 32.5, 26.9 (carbon signals of an ipso carbon of perfluoroaryl ring and the CF_3 group were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –56.2 (t, J = 21.2 Hz, 3F), –140.3–140.5 (m, 2F), –140.8–141.0 (m, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{15}H_{13}F_7$: 326.0905; Found 326.0902.

*(E)-1,2,3,4,5-Pentafluoro-6-(nona-1,6-dien-3-yl)benzene (**5af**).* The representative general procedure was followed using hexafluorobenzene (116 μL, 1.010 mmol) and methylmagnesium

chloride (in THF, 2.52 M, 0.48 mL, 1.2 mmol). Purification by GPC gave the desired product as a colorless oil (146.3 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04–5.99 (m, 1H), 5.44–5.29 (m, 2H), 5.11–5.07 (m, 2H), 3.75 (q, *J* = 7.6 Hz, 1H), 2.02–1.84 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.0 (dm, $^1J_{C\text{-}F}$ = 246.1 Hz), 139.6 (dm, $^1J_{C\text{-}F}$ = 250.7 Hz), 137.7, 137.6 (dm, $^1J_{C\text{-}F}$ = 250.8 Hz), 133.4, 127.4, 116.5, 39.3, 32.9, 30.5, 25.6,13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.1 (dd, *J* = 22.2, 7.5 Hz, 2F), –157.4 (t, *J* = 20.9 Hz, 1F), –162.5 (td, *J* = 21.6, 7.6 Hz, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{15}H_{15}F_5$: 290.1094; Found 290.1089.

*1,2,4,5-Tetrafluoro-3,6-bis(octa-1,7-dien-3-yl)benzene (**6a**).* The representative general procedure was followed using hexafluorobenzene (116 μL, 1.010 mmol), butylmagnesium chloride (in THF, 1.83 M, 1.31 mL, 2.4 mmol), 1,3-butadiene (224 mL as gas, 10.0 mmol) and 20 mol % of catalyst. Purification by GPC gave the desired product as a colorless oil (241.8 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10–6.01 (m, 2H), 5.80–5.73 (m, 2H), 5.13–5.01 (m, 8H), 3.72 (q, *J* = 7.6 Hz, 2H), 2.06 (dt, *J* = 7.2, 7.2 Hz, 4H), 1.82–1.78 (m, 4H), 1.44–1.26 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.6 (dm, $^1J_{C\text{-}F}$ = 253.2 Hz), 138.3, 138.1, 116.2, 114.8, 40.3, 33.4, 32.7, 26.9 (a carbon signal of ipso carbons of perfluorophenylene ring was not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ –143.5 (s); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{22}H_{26}F_4$: 366.1971; Found 366.1968.

*The reaction of isoprene with **1a** and **2a**.* The representative general procedure was followed using hexafluorobenzene (116 μL, 1.010 mmol) and butylmagnesium chloride (in THF, 1.83 M, 0.66 mL, 1.2 mmol). Purification by GPC gave **7** as a mixture of four isomers in 3,7-:2,7-:3,6-:2,6- = 57:22:16:5 ratio (determined by ^{1}H NMR) as a colorless oil (141.1 mg, 46%) along with **8** as a yellow oil (43.6 mg, 12%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19–6.11 (m, 1.3H), 5.67–5.58

(m, 0.4H), 5.06–4.91 (m, 4.4H), 4.69 (s, 1.3H), 4.63 (s, 1.3H), 3.67 (t, J = 7.8 Hz, 0.4H), 3.62 (t, J = 7.6 Hz, 0.1H), 2.05–1.93 (m, 5.3H), 1.75–1.66 (m, 6.8H), 1.57–1.53 (m, 4.2H), 1.50–1.39 (m, 1.2H), 1.32–1.17 (m, 1.6H), 1.10–1.03 (m, 0.2H), 0.98–0.95 (m, 1.0H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0 (dm, $^1J_{C\text{-}F}$ = 247.9 Hz), 145.4 (dm, $^1J_{C\text{-}F}$ = 241.3 Hz), 145.3 (d, $^2J_{C\text{-}F}$ = 2.9 Hz), 145.2, 144.1, 144.0, 143.8, 139.6 (dm, $^1J_{C\text{-}F}$ = 219.6 Hz), 139.4 (dm, $^1J_{C\text{-}F}$ = 261.6 Hz), 137.9 (dm, $^1J_{C\text{-}F}$ = 234.8 Hz), 137.7 (dm, $^1J_{C\text{-}F}$ = 263.0 Hz), 113.0 (d, $^2J_{C\text{-}F}$ = 2.9 Hz), 112.1, 111.5, 110.2, 45.5, 42.2, 40.0 (t, $^3J_{C\text{-}F}$ = 3.8 Hz), 38.2 (d, $^3J_{C\text{-}F}$ = 1.9 Hz), 37.9, 37.8, 37.4, 35.0, 31.7, 30.1, 25.9, 25.7 (t, $^3J_{C\text{-}F}$ = 5.7 Hz), 22.8, 22.2, 21.5, 20.2 (d, $^3J_{C\text{-}F}$ = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –136.5 (d, J = 20.3 Hz, 2F), –141.5 (dd, J = 22.2, 7.1 Hz, 0.6F), –157.0–157.1 (m, 0.3F), –157.2–157.3 (m, 1F), –162.4–162.5 (m, 0.6F), –162.6–162.7 (m, 2F); HRMS (EI+) *m/z* $[M]^+$ Calcd for $C_{16}H_{17}F_5$: 304.1250; Found 304.1249.

*1,2,3,4,5-Pentafluoro-6-(1-methyl-2-pentyl-3-(prop-1-en-2-yl)cyclopentyl)benzene (**8**).* ^1H NMR (400 MHz, $CDCl_3$): δ 4.85 (s, 1H), 4.75 (s, 1H), 2.37–2.29 (m, 3H), 2.07–2.00 (m, 2H), 1.80 (s, 3H), 1.74–1.66 (m, 1H), 1.32 (s, 3H), 1.20–0.90 (m, 8H), 0.83 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.2, 145.6 (dm, $^1J_{C\text{-}F}$ = 246.0 Hz), 139.1 (dm, $^1J_{C\text{-}F}$ = 249.8 Hz), 137.7 (dm, $^1J_{C\text{-}F}$ = 247.9 Hz), 108.7, 50.9, 50.3 (t, $^3J_{C\text{-}F}$ = 2.4 Hz), 37.0 (t, $^4J_{C\text{-}F}$ = 6.7 Hz), 35.1, 31.9, 29.3 (t, $^4J_{C\text{-}F}$ = 2.0 Hz), 27.8, 26.8, 22.5, 22.1, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –137.9 (s, 2F), –158.0 (t, J = 21.6 Hz, 1F), –162.8 (td, J = 21.1, 5.4 Hz, 2F); HRMS (DART) *m/z* $[M]^+$ Calcd for $C_{20}H_{25}F_5$ 360.1876; Found 360.1875.

General procedure for kinetic study using a flow reactor (Figure 2).

Preparation of solutions for standard conditions. THF solutions of catalyst and reagents were prepared in a flame dried 100 mL vial under N_2. 1,3-Butadiene was condensed in to the solutions with cooling. Solution A: $Ni(acac)_2$ (257 mg, 1.00 mmol), PPh_3 (262 mg, 1.00 mmol), and

undecane (740 mg) were dissolved in THF (20 mL) and then 1,3-butadiene (672 mL as gas, 30.0 mmol) was added with cooling. Solution B: *n*-BuMgCl (**2a**) (1.75 M in THF, 13.7 mL, 24.0 mmol) and dodecane (742 mg) were dissolved in THF (6.3 mL, total 20 mL) and then 1,3-butadiene (672 mL as gas, 30.0 mmol) was added with cooling. Solution C: Perfluorobenzene (**1a**) (18.60 g, 100 mmol) and decane (3.70 g) were dissolved in THF (100 mL).

Device for flow reactor. Stainless steel tube (SUS316, 1/16 ϕ = 0.5 mm) was purchased from GL Sciences. Comet X-01 was obtained from Techno Applications Co. Ltd. KeyChem-L (YMC) equipped with gas tight syringes was used. A flow reactor system consisting a T-shaped micromixer (ϕ = 0.4 mm) for M1, Comet X-01 micromixer for M2, and stainless tubes was used. Flow channels are as follows: L1, L2, L3 = 300 mm, L4 = 50 mm, and L5 = 2,000 mm.

Procedure for kinetic study. The flow reactor was immersed in a water bath at 30 °C and solutions **A**, **B**, and **C** were introduced from L1, L2, and L3, respectively. The outflow was collected by a sample tube containing 1N HCl aq. for several seconds. The sample was extracted by Et_2O and analyzed by GC. Reaction time was changed by changing flow rate of all solutions from 0.8 to 2.5 mL/min. The results obtained by the reactions with various concentration of catalyst and substrates are plotted against reaction times in Figures S2-S7, and reaction rates were determined from the slope of the plots.

*Ring-closing metathesis of **3a**.* To a 100 mL flask equipped with a magnetic stirring bar was added **3a** (2.24 g, 8.1 mmol), Grubbs 1st catalyst (36.0 mg, 0.04 mmol, 0.5 mol %), and $CHCl_3$ (5 mL). The reaction mixture was vigorously stirred at 25 °C for 12 h. The reaction mixture was diluted with EtOAc and passed through a short pad of silica gel to give analytically pure **9** as a colorless oil (1.85 g, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87–5.84 (m, 1H), 5.55 (d, J = 10 Hz, 1H), 3.84 (m, 1H), 2.12–2.11 (m, 2H), 1.95–1.89 (m, 2H), 1.79–1.69 (m, 2H); ^{13}C{^{1}H}

NMR (100 MHz, $CDCl_3$): δ 145.3 (dm, $^1J_{C\text{-}F}$ = 247.9 Hz), 139.6 (dm, $^1J_{C\text{-}F}$ = 212.6 Hz), 137.5 (dm, $^1J_{C\text{-}F}$ = 232.7 Hz), 128.4 (dm, $^4J_{C\text{-}F}$ = 2.0 Hz), 127.1, 32.4, 28.8, 24.4, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.9–143.0 (m, 2F), –157.9–158.0 (m, 2F), –162.9–163.0 (m, 2F); HRMS (DART) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{10}F_5$ 249.0703; Found 249.0713.

*Epoxidation of **3a** with mCPBA.* To a solution of **3a** (220.6 mg, 0.80 mmol) in CH_2Cl_2 (1 mL), a solution of *m*CPBA (165.5 mg, 1.2 equiv.) in CH_2Cl_2 (1 mL) was added dropwise with an ice bath cooling. After addition of *m*CPBA, the reaction mixture was allowed to warm to rt and stirred at ambient temperature for 12 h. The reaction mixture was evaporated and diluted with 10 mL of $CHCl_3$. The organic layer was washed with 1N NaOH aq. and brine, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane as an eluate) to obtain **10** as colorless oil (160.1 mg, 69%). ^{1}H and ^{13}C NMR spectra of compound **10** showed a single diastereomer. However, the stereochemistry of the compound **10** could not be determined; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99-6.07 (m, 1H), 5.10-5.14 (m, 2H), 3.73 (q, *J* = 7.8 Hz, 1H), 2.86-2.90 (m, 1H), 2.73-2.76 (m, 1H), 2.45-2.47 (m, 1H), 1.78-1.93 (m, 2H), 1.28-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 139.6, 137.6, 137.4, 116.8, 52.0, 47.0, 40.1, 33.0, 32.1, 24.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –142.4, –157.3, –162.3; HRMS (DART) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{14}F_5O$ 293.0965; Found 293.0956.

*Epoxidation of **9** with mCPBA.* To a solution of **9** (1.81 g, 7.26 mmol) in EtOAc (5 mL), *m*-CPBA (2.53 g, 2 equiv.) was added in portions with an ice bath cooling. Then the mixture was stirred at 70 °C for 6 h. The reaction mixture was quenched with 1 N NaOH aq. and extracted with EtOAc. The organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane as an eluate) to obtain **11** as colorless oil (1.71 g, 88%). ^{1}H and ^{13}C NMR spectra of compound **11** showed a single diastereomer. However, the stereochemistry

of the compound **11** could not be determined; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51 (q, *J* = 6.0 Hz, 1H), 3.34 (d, *J* = 1.8 Hz, 1H), 3.13 (d, *J* = 2.7 Hz, 1H), 2.21 (d, *J* = 15.1 Hz, 1H), 1.74-1.89 (m, 2H), 1.45-1.58 (m, 2H), 1.27-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.8, 52.6, 31.6, 27.6, 24.3, 17.4 (carbon signals of perfluoroaryl ring were not observed); ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.81 (dd, J = 21.7, 7.2 Hz, 2F), -156.34 (t, J = 21.0 Hz, 1F), -161.79 (td, J = 21.3, 7.2 Hz, 2F); HRMS (DART) *m*/*z* $[M+H]^+$, Calcd for $C_{12}H_{10}F_5O$ 265.0652; Found 265.0665.

Diborylation of ***3a***.[29] $[Ru(p\text{-cymene})Cl_2]_2$ (32 mg, 1 mol %), **3a** (0.5 mmol), and pinacol borane (1.5 mmol) were charged to a screw cap vial in a glove box. The reaction mixture was stirred at room temperature for 24 h. Purification by silica gel column chromatography (hexane as an eluent) gave **12** as a colorless oil (131.0 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94-3.02 (m, 1H), 1.65-1.84 (m, 4H), 1.01-1.37 (m, 30H), 0.54-0.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 145.4, 139.2, 137.4, 83.1, 82.8, 38.7, 33.4, 32.1, 28.1, 27.8, 24.8, 24.8, 24.7, 23.8, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –141.9-–141.6 (m, 2F), –158.2-–158.0 (m, 1F), –163.2-–162.9 (m, 2F); HRMS (DART) *m*/*z* $[M+H]^+$ Calcd for $C_{26}H_{40}B_2F_5O_4$ 533.3033; Found 533.3027.

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Notes

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ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Additional results, Cartesian coordinates, and NMR spectra (PDF)

Crystallographic data for **3c** (CIF)

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