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Dialkylzinc-mediated allylic polyfluoroarylation reaction

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ABSTRACT

We present an allylic polyfluoroarylation reaction with broad substrate scope and excellent functional group tolerance, using organozinc reagents under mild conditions. A catalytic amount of triphenylphosphine oxide efficiently promotes iodine–zinc exchange reaction between polyfluoroaryl iodide and dimethylzinc, and the resulting phosphine oxide-activated polyfluoroarylzinc undergoes substitution reaction with allylic halides to afford the corresponding polyfluoroarylated products.

1. Introduction

Fluorine-containing substituents/molecules have unique properties[1] and have been widely applied in medicinal, agrochemical, and materials sciences.[2] Among them, multiply fluorinated arenes exhibit unusual interaction modes that are of interest in the fields of molecular organization and biological recognition.[3] They are promising structural units for organic n-type semiconductors due to their strong electron-withdrawing character and have been attracting attention as components of organic light-emitting diodes (OLEDs) and field-effect transistors (FETs) based on π-conjugated oligomers.[4] Fluorinated aromatics can also be utilized as sensitizers for photo-splitting of water.[5] From the viewpoint of synthetic methodologies, $C(sp^2)$–Ar_F forming reactions are well established,[4,6] but on the other hand, methods for formation of $C(sp^3)$–Ar_F bonds are still quite limited: to our knowledge, only a few transition metal-catalyzed allylic substitution,[7–9] benzylic substitution,[10] and substitution at primary/secondary carbons[11] have recently been reported. Miura et al. beautifully demonstrated deprotonative cupration of fluorinated benzenes with the aid of stoichiometric LiO^tBu and substitution reaction of the catalytically formed Ar_F-Cu species with allylic phosphates afforded allylated polyfluorobenzenes.[7] Simultaneously, Zhang et al. reported Tsuji–Trost type allylation of allylic carbonates with polyfluorinated benzenes and elegantly analyzed the mechanism.[8a] However, the scope of the reaction was limited to substrates with relatively robust functional groups, which are inert to transition metals, and indeed, metal-catalyzed double bond isomerization was observed in some cases.[8b] Moreover, the reaction conditions are quite harsh (e.g., high reaction temperature).[8]

Our solution to these problems is to utilize the mild reactivity and high chemoselectivity of organozinc reagents (Eq. 1). Organozinc reagents display high tunability of reactivity by selection of appropriate ligands, and they are often employed in synthesis due to their high functional group tolerance.[12] Knochel and co-workers reported that halogen–zinc exchange reaction between aryl iodides and dialkylzinc (R_2Zn) proceeds in the solvent mixture of Lewis basic NMP and Et_2O (10:1) to give ArZnR under very mild conditions.[13] Taking this into consideration, we hypothesized that (1) a catalytic amount of Lewis base might be enough to generate Ar_F–zinc in situ via halogen–zinc exchange reaction between R_2Zn and highly reactive polyfluoroaryl iodides[14] and (2) the activation of the resulting Ar_F–zinc species by Lewis base should enable polyfluoroarylation with good functional group tolerance. Therefore, we designed a sequential organocatalytic process, i.e., Lewis base-catalyzed zincation of polyfluoroaryl iodide by R_2Zn followed by allylic substitution reaction by in situ generated Ar_F–zinc species.

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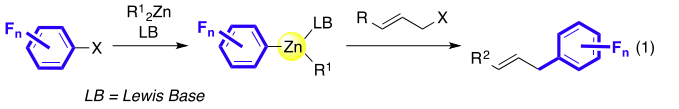
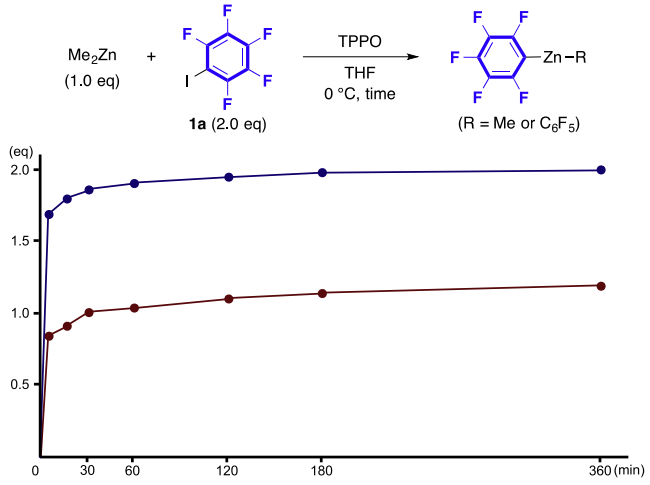


2. Results and discussion

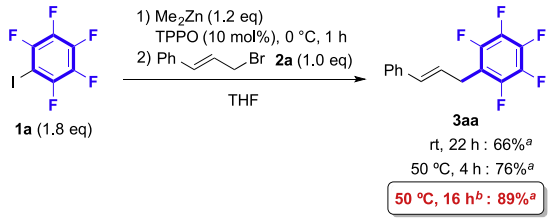
We began our studies by investigating the iodine–zinc exchange reaction between Me_2Zn and pentafluoroiodobenzene (Ar_FI: **1a**) using triphenylphosphine oxide (TPPO) as a Lewis basic activator at 0 °C (Scheme 1).[15] Consumption of **1a** was monitored by GC analysis and 1 equiv of TPPO was found to promote the reaction very efficiently: one methyl group was exchanged almost instantaneously. Even a catalytic amount of TPPO (10 mol %) was enough to exchange one methyl group within 1 h.



Vertical axis: consumption of **1a**. Horizontal axis: time. Run with 1.0 eq of TPPO in blue and run with 0.1 eq of TPPO in red.

Scheme 1. Rate of the iodine–zinc exchange reaction. Vertical axis: consumption of **1a**. Horizontal axis: time. Run with 1.0 equiv of TPPO in blue and run with 0.1 equiv of TPPO in red.

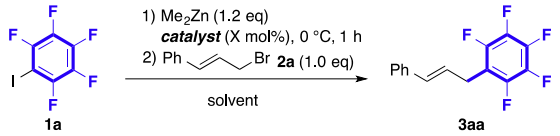
Encouraged by these results, we next tried nucleophilic substitution reaction of cinnamyl bromide (**2a**) with Ar_F–zinc (Scheme 2). Gratifyingly, the desired perfluoroarylated product **3aa** was obtained in 66% yield at room temperature. At 50 °C, the yield was improved to 89%; the thermal stability of this Ar_F–zinc species proved to be much higher than that of the lithium and magnesium counterparts.[16]



Scheme 2. Initial trials of the nucleophilic substitution reaction. [a]^{1}H NMR yields. [b]Compound **1a** (1.5 equiv) was used.

We commenced catalyst-screening studies to optimize the reaction (entries 1–8, Table 1). Use of triphenylphosphine resulted in a lower yield compared to the run with TPPO (entry 2). More electron-rich PCy_3 afforded the desired product in excellent yield (90%, entry 3). However, triethyl phosphite did not promote the reaction at all, presumably due to formation of the Arbuzov-type by-product (entry 4). Other Lewis bases such as DMPU and DMSO, and pyridine facilitated the reaction as well, albeit less efficiently than TPPO (entries 5–7). In the absence of catalyst, the reaction scarcely proceeded (entry 8). Based on these results, TPPO was chosen as the preferred catalyst due to its easy handling and low cost compared to PCy_3. Next, we briefly examined the effect of solvents. Less polar ethers such as Et_2O and 1,4-dioxane were less effective than THF (entry 1 vs entries 9 and 10). In these solvents, the iodine–zinc exchange reaction did not proceed smoothly. DMF gave the desired product in 86% yield (entry 11). No product formation was observed in a non-polar solvent, toluene (entry 12). Catalyst loading was next investigated (entries 1, 13, and 14). The catalyst loading of TPPO could be reduced to 10 mol % without decrease of the yield (entry 13), but further reduction of the loading to 5 mol % slowed the reaction slightly (entry 14). Finally, commercial $(C_6F_5)_2Zn$ was investigated as a C_6F_5 source. Reaction with 10 mol % TPPO gave the product **3aa** in significantly lower yield (~40%, entry 15), compared with in situ generated $(C_6F_5)ZnMe$ (92%, entry 13), and the yield was even lower without TPPO (~30%, entry 16). These results indicate that heteroleptic $(C_6F_5)ZnMe$ is the more reactive species, and catalytic activation by TPPO efficiently promotes the allylic perfluoroarylation reaction.

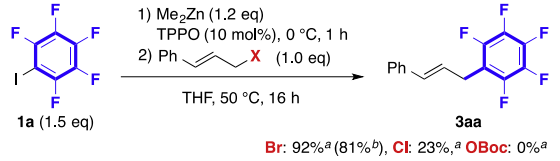
Table 1
Optimization of the reaction conditions



Entry	Catalyst	X [mol %]	Solvent	Yield[a] [%]
1	TPPO	20	THF	89 (84)
2	PPh_3	20	THF	63
3	PCy_3	20	THF	90 (87)
4	$P(OEt)_3$	20	THF	0
5	DMPU	20	THF	79
6	DMSO	20	THF	76
7	Pyridine	20	THF	50
8	None	—	THF	Trace
9	TPPO	20	Et_2O	28
10	TPPO	20	Dioxane	26
11	TPPO	20	DMF	86 (76)
12	TPPO	20	Toluene	0
13	TPPO	10	THF	92 (81)
14	TPPO	5	THF	78
15[b]	TPPO	10	THF	43 (36)
16[b]	None	—	THF	26 (22)

[a] NMR yields. Isolated yields are shown in parentheses.
[b] Commercially available $(C_6F_5)_2Zn$ (1.2 equiv) was used.

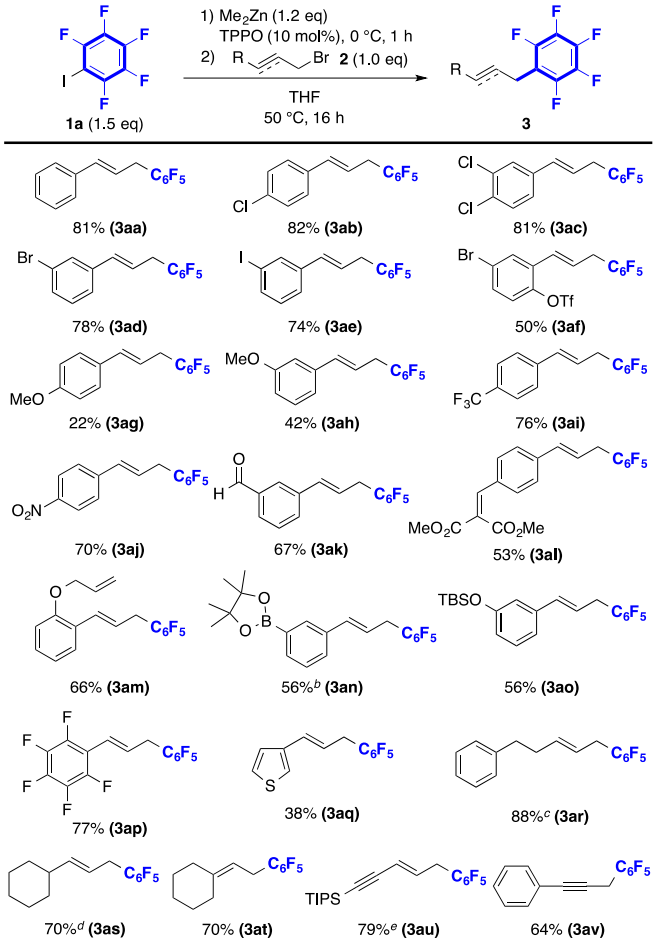
With optimal conditions in hand, the effect of the leaving group was examined (Scheme 3). Cinnamyl chloride gave the product **3aa** in 23% yield.[8b] Boc-protected cinnamyl alcohol, which is often used in palladium-catalyzed allylic alkylation reactions, did not react due to poor leaving ability of the OBoc group in the absence of transition metals.[8a]



Scheme 3. Effect of leaving group. [a]^{1}H NMR yields. [b]Isolated yield.

This reaction has a broad scope, being applicable to substrates bearing a variety of functional groups (Table 2). The Cl-substituted products **3ab** and **3ac** were obtained in 82% and 81% yields,

Table 2
Scope of electrophiles[a]



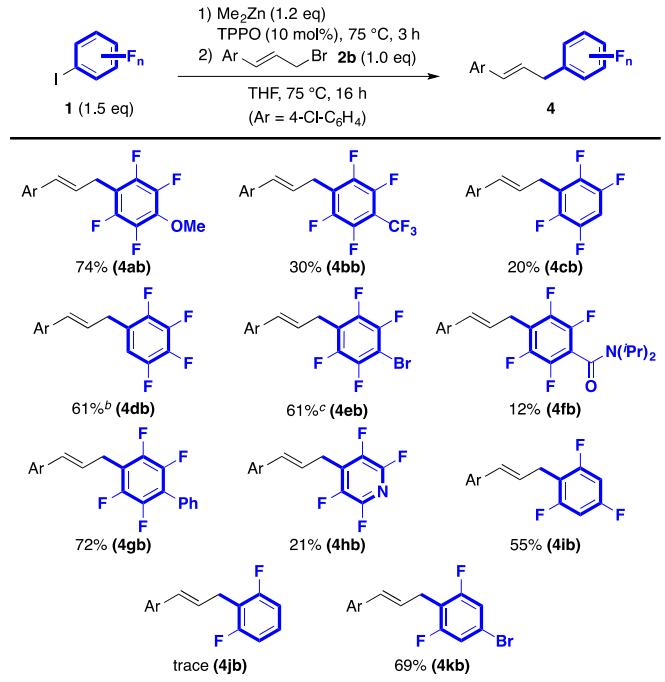
[a] Isolated yields. [b] A mixture of regioisomers (87 : 13). [c] A mixture of regioisomers (89 : 11). [d] A mixture of regioisomers (94 : 6). [e] A mixture of regioisomers (96 : 4).

respectively. No proto-debrominated by-product was observed, and the Br-containing product **3ad** was formed cleanly in 78% yield. It is worth emphasizing that even the C–I bond survived under these reaction conditions, and OTf was untouched (**3ae** and **3af**). These results clearly distinguish this methodology from other transition-metal-catalyzed processes.[7,8] An electron-donating methoxy group at the *para*-position had a detrimental effect on the product yield and significant amounts of methylated byproducts were formed (**3ag**). On the other hand, the substrate with a methoxy group at the *meta*-position afforded the desired arylated product **3ah** in 42% yield. Substrates with a strongly electron-withdrawing substituent via an inductive (**2ai**) or resonance (**2aj**) effect at the *para*-position gave the desired products in high yield (**3ai** and **3aj**). Surprisingly, a formyl group was inert under these reaction conditions, and perfluoroarylation occurred solely at the allylic position (**3ak**).

In addition, a benzylidene malonate moiety, which behaves as a highly reactive Michael acceptor, was also tolerated (**3al**). Substrates with an allyloxy group or a boronpinacolato group, which would be vulnerable to transition metals, were converted to the corresponding products **3am** and **3an** in 66% and 56% yields, respectively. Base-sensitive silyl ether was tolerated as well (**3ao**). 1,3-Bis-pentafluorophenylated product **3ap** was obtained in 77% yield. Allylic bromides possessing alkyl substituents underwent perfluoroarylation in satisfactory yields (**3ar**, **3as**, and **3at**). The enyne substrate **2au** afforded allylic substitution product **3au** with high regioselectivity in 79% yield. Further, the substrate scope is not limited to allylic bromides. Propagylic substitution reaction also proceeded smoothly to give **3av** in 64% yield.

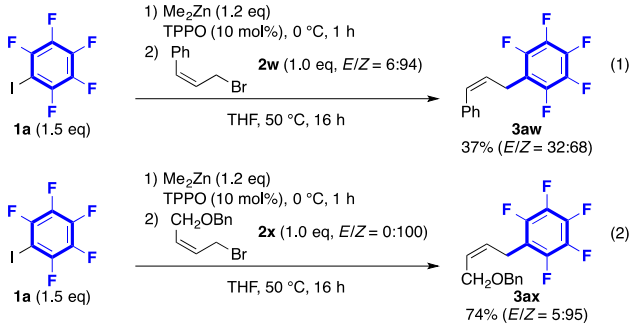
We next investigated the nucleophilic polyfluoroaryl part (Table 3). A 4-MeO-substituted tetrafluoroaryl group was installed in 74% yield (**4ab**). On the other hand, reaction of the 4-CF_3-substituted counterpart proceeded in only 30% yield (**4bb**). The striking contrast between 2,3,5,6- and 2,3,4,5-tetrafluorophenyl groups is intriguing (**4cb** vs **4db**): **4cb** was obtained in 20% yield, whereas **4db** was obtained in markedly higher yield (61%). Taking the first two examples into account, we consider that the reactivity of polyfluoroaryl zinc species is reduced in the absence of a mesomerically electron-donating substituent at the 4-position (MeO, F vs CF_3, H). A similar trend was seen with the reactions using 4-bromo- and 4-amido-substituted iodobenzenes as nucleophile precursors. While the former compound benefits from the electron-donating Br at the 4-position to give the product **4eb** in 61% yield, the latter was strongly deactivated by the electron-withdrawing amide substituent, resulting in poor yield (**4fb**). The 4-Ph-substituted product was obtained in good yield (**4gb**: 72%). The highly electron-deficient tetrafluoropyridyl zinc was presumably too stable and the reaction was sluggish (**4hb**). Installation of a 2,4,6-trifluorophenyl group was achieved in 55% yield (**4ib**).[17] 2,6-Difluoroiodobenzene was not reactive enough in the first iodine–zinc interconversion process and the desired product **4jb** was formed in only a trace amount. Introduction of Br at the 4-position greatly facilitated the iodine–zinc exchange process and the subsequent substitution reaction proceeded smoothly to give **4kb** in 69% yield.

Table 3
Scope of nucleophiles[a]



[a] Isolated yields. [b] A mixuture of regioisomers (88 : 12). [c] The reaction was performed under the same conditions as those of Table 2.

Then, we were interested in the stereospecificity of this transformation. The reaction with (*Z*)-cinnamyl bromide under the same reaction conditions as those of Table 2 and obtained the desired product **3aw** in 37% yield with a significant loss of stereoinformation (Scheme 4, Eq. 1). On the contrary, (*Z*)-allylic bromide



Scheme 4. Reactions with (*Z*)-configurated allylic bromides.

without phenyl group **2x** gave the product **3ax** with retension of configuration (Eq. 2). Currently, we are investigating the mechanism of the isomerization pathway with **2w**.

3. Conclusion

In summary, we have developed a method for generation of polyfluoroaryl zinc reagent from Me_2Zn and pentafluoroiodobenzene, catalyzed by triphenylphosphine oxide, and demonstrated its utility in nucleophilic substitution reactions with allylic bromides. It is noteworthy that this zinc reagent is more stable than conventional reagents, and has excellent functional group compatibility. Further applications of this method to the synthesis of functional molecules are in progress, together with work to elucidate the reaction pathway/mechanism with the help of theoretical and spectroscopic studies.

4. Experimental section

4.1. Instrumentation

NMR spectra were obtained on a Bruker AVANCE III HD 500 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, quint=quintet, m=multiplet, br s=broad singlet, and br d=broad doublet. Melting points were determined with a Yanaco micro melting point apparatus and uncorrected. IR spectra were obtained on a METLER TOLEDO ReactIR 4000 or a JASCO FT/IR-4700. ESI mass spectra were measured on a Bruker micrOTOF-II spectrometer and EI mass spectra were measured on a JEOL JMS-700V spectrometer.

4.2. Materials

Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Sigma–Aldrich Co., LLC., and other commercial suppliers. Diethylzinc in *n*-hexane was obtained from Kanto Chemical Co., Inc. Dimethylzinc in *n*-heptane and $(C_6F_5)_2Zn$ were purchased from Sigma–Aldrich Co., LLC. Cinnamyl bromide (**2a**) was purchased from Tokyo Chemical Industry Co., Ltd. Anhydrous THF was purchased from Kanto Chemical Co., Inc. All other chemicals were of reagent grade and used as received. Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques under argon atmosphere. Normal-phase column chromatography was performed with silica gel 60 (230–400 mesh) from Merck and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

4.3. General procedure for polyfluoroarylation reaction

Method A

A Schlenk tube was dried using heat gun under reduced pressure and filled with argon. The tube was charged with triphenylphosphine oxide (TPPO) (13.9 mg, 0.05 mmol) and then evacuated and refilled with argon (×3). To the tube were added THF (1 mL) and Me_2Zn (0.6 mL, 0.6 mmol, 1.0 M solution in hexane). Then, iodopentafluorobenzene **1a** (100 μL, 0.75 mmol) was added at 0 °C and the resultant mixture was stirred for 1 h at the same temperature. Followingly, allylic bromide (0.5 mmol) was added to the reaction mixture at 0 °C and then the tube was immersed in an oil bath. The reaction mixture was gradually warmed to 50 °C and stirred for 16 h. The reaction mixture was cooled to room temperature and quenched with saturated aq NH_4Cl solution followed by extraction with Et_2O (×3). Combined organic layer was washed with brine (×1), dried over Na_2SO_4, and filtered. Volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford analytically pure product.

Method B

The reaction set-up was the same as method A. After being cooled to room temperature, the reaction mixture was quenched with Me_2NH (1.25 mL, 2.5 mmol, 2 M solution in MeOH). The resultant mixture was stirred for 30 min, and then acidified with 1 N aq HCl followed by extraction with Et_2O (×3). Combined organic layer was washed with saturated aq $NaHCO_3$ and brine (×1), dried over Na_2SO_4, and filtered. Volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford analytically pure product.

Method C

A Schlenk tube was dried using heat gun under reduced pressure and filled with argon. The tube was charged with TPPO (69.5 mg, 0.25 mmol) and then the tube was evacuated and refilled with argon (×3). To the tube were added THF (1 mL), Me_2Zn (0.6 mL, 0.6 mmol, 1.0 M solution in hexane), and fluoroarene 1 (0.75 mmol) at room temperature and then the tube was immersed in an oil bath. The reaction mixture was gradually warmed to 75 °C and stirred for 3 h. The mixture was cooled to room temperature and allylic bromide (0.5 mmol) was added. The resultant mixture was warmed to 75 °C and stirred for 16 h. The reaction mixture was quenched with saturated aq NH_4Cl solution followed by extraction with Et_2O (×3). Combined organic layer was washed with brine (×1), dried over Na_2SO_4, and filtered. Volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford analytically pure product.

Pure regioisomers (>99:1) were obtained unless otherwise noted. In case regioisomers were obtained, the ratio was determined by the ^{1}H NMR spectrum of the crude mixture.

*4.3.1. (E)-1-Phenyl-3-pentafluorophenyl-prop-1-ene (**3aa**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 81% yield (115.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.28 (m, 4H), 7.24–7.21 (m, 1H), 6.47 (br d, *J*=15.5 Hz, 1H), 6.21 (dt, *J*=15.5, 7.0 Hz, 1H), 3.59 (dd, *J*=7.0, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.0 (m), 141.0–138.8 (m), 138.7–136.4 (m), 136.6, 132.5, 128.6, 127.7, 126.2, 124.3, 113.4–113.1 (m), 25.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=23.5, 9.4 Hz, 2F), −157.2 (t, *J*=23.5 Hz, 1F), −162.5 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[7]

*4.3.2. (E)-1-(4-Chlorophenyl)-3-pentafluorophenyl-prop-1-ene (**3ab**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 82% yield (131.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.23 (m, 4H), 6.42 (br d, *J*=16.0 Hz, 1H), 6.19 (dt, *J*=16.0, 6.5 Hz, 1H), 3.58 (dd, *J*=6.5, 1.5 Hz, 2H). ^{13}C NMR (125 MHz,

$CDCl_3$): δ 146.1–144.0 (m), 141.1–138.9 (m), 138.7–136.5 (m), 135.1, 133.3, 131.3, 128.7, 127.5, 125.0, 113.1–112.8 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=23.5, 9.4 Hz, 2F), −157.0 (t, *J*=23.5 Hz, 1F), −162.3 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[7]

*4.3.3. (E)-1-(3,4-Dichlorophenyl)-3-pentafluorophenyl-prop-1-ene (**3ac**). Method B* (eluent: hexane); the title compound was obtained as a white solid in 81% yield (142.2 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J*=2.0 Hz, 1H), 7.35 (d, *J*=8.5 Hz, 1H), 7.14 (dd, *J*=8.5, 2.0 Hz, 1H), 6.36 (br d, *J*=16.0 Hz, 1H), 6.22 (dt, *J*=16.0, 6.5 Hz, 1H), 3.59 (dd, *J*=6.5, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0–143.9 (m), 141.1–138.9 (m), 138.7–136.4 (m), 136.6, 132.7, 131.4, 130.5, 130.2, 128.0, 126.5, 125.4, 112.8–112.5 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.8 (dd, *J*=21.2, 7.1 Hz, 2F), −146.7 (t, *J*=21.2 Hz, 1F), −162.2 (dt, *J*=21.2, 7.1 Hz, 2F). IR (ATR-IR): 1504, 1472, 1112, 1065, 1027, 985, 957, 882, 812, 673, 557 cm^{-1}. Mp: 72.8–73.8 °C (recrystallized from hexane, white needles). HRMS (EI): *m*/*z*: calcd for $C_{15}H_7Cl_2F_5$ [M^+] 351.9845, found 351.9841. Anal. Calcd for $C_{15}H_7Cl_2F_5$: C, 51.02; H, 2.00. Found: C, 50.80; H, 2.18.

*4.3.4. (E)-1-(3-Bromophenyl)-3-pentafluorophenyl-prop-1-ene (**3ad**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 78% yield (141.4 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, *J*=2.0, 1.5 Hz, 1H), 7.34 (br d, *J*=7.5 Hz, 1H), 7.23 (br d, *J*=7.5 Hz, 1H), 7.16 (dd *J*=7.5, 7.5 Hz, 1H), 6.39 (br d, *J*=15.5 Hz, 1H), 6.23 (dt, *J*=15.5, 6.5 Hz, 1H), 3.59 (dd, *J*=6.5 Hz, 1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6.1–144.0 (m), 141.1–138.9 (m), 138.7–136.4 (m), 138.7, 131.1, 130.6, 130.1, 129.2, 126.0, 124.9, 122.8, 113.0–112.7 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.8 (dd, *J*=23.5, 9.4 Hz, 2F), −156.9(t, *J*=23.5 Hz, 1F), −162.3 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1503, 1115, 1066, 959, 917, 780, 682 cm^{-1}. Mp: 73.2–74.0 °C (recrystallized from hexane, white needles). HRMS (pos. ESI): *m*/*z*: calcd for $C_{15}H_8BrF_5$ $[M+Ag]^+$ 468.8780, found 468.8773. Anal. Calcd for $C_{15}H_8BrF_5$: C, 49.62; H, 2.22. Found: C, 49.55; H, 2.50.

*4.3.5. (E)-1-(3-Iodophenyl)-3-pentafluorophenyl-prop-1-ene (**3ae**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 74% yield (151.8 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.55 (d, *J*=8.0 Hz, 1H), 7.28 (d, *J*=8.0 Hz, 1H), 7.02 (dd, *J*=8.0, 8.0 Hz, 1H), 6.36 (br d, *J*=16.0 Hz, 1H), 6.21 (dt, *J*=16.0, 6.0 Hz, 1H), 3.59 (d, *J*=6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–143.9 (m), 141.1–139.0 (m), 138.8, 138.6–136.5 (m), 136.5, 135.1, 131.0, 130.2, 125.8, 125.5, 113.0–112.7 (m), 94.6, 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.8 (dd, *J*=23.5, 9.4 Hz, 2F), −156.9 (t, *J*=23.5 Hz, 1F), −162.3 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1566, 1519, 1113, 1062, 958, 915, 848, 780, 686, 656 cm^{-1}. Mp: 77.4–78.4 °C (recrystallized from hexane, colorless prisms). HRMS (pos. ESI): *m*/*z*: calcd for $C_{15}H_8F_5I$ $[M+Ag]^+$ 516.8642, found: 516.8631. Anal. Calcd for $C_{15}H_8F_5I$: C, 43.93; H, 1.97. Found: C, 43.72; H, 2.16.

*4.3.6. (E)-1-[2-(Trifluoromethanesulfonyloxy)-5-bromophenyl]-3-pentafluorophenyl-prop-1-ene (**3af**). Method B* (eluent: hexane); the title compound was obtained as a colorless oil in 50% yield (127.3 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, *J*=2.5 Hz, 1H), 7.42 (dd, *J*=9.0, 2.5 Hz, 1H), 7.12 (d, *J*=9.0 Hz, 1H), 6.55 (br d, *J*=16.0 Hz, 1H), 6.35 (dt, *J*=16.0, 6.5 Hz, 1H), 3.66 (dd, *J*=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.0 (m), 145.5, 141.4–139.1 (m), 138.8–136.5 (m), 132.1, 131.9, 130.8, 130.3, 123.4, 123.3, 122.1, 118.5 (q, *J*=318.8 Hz), 111.8 (t, *J*=18.8 Hz), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −73.7 (s, 3F), −143.6 (dd, *J*=23.5, 4.7 Hz, 2F), −156.3 (t, *J*=23.5 Hz, 1F), −162.1 (dt, *J*=23.5, 4.7 Hz, 2F). IR (ATR-IR): 1520, 1503, 1471, 1212, 1138, 1092, 993, 960, 852, 820, 742, 610, 575 cm^{-1}. HRMS (pos. ESI): *m*/*z*: calcd for $C_{16}H_7BrF_8O_3S$ $[M+Ag]^+$ 616.8222, found: 616.8221. Anal. Calcd for $C_{16}H_7BrF_8O_3S$: C, 37.59; H, 1.38. Found: C, 37.66; H, 1.61.

*4.3.7. (E)-1-(4-Methoxyphenyl)-3-pentafluorophenyl-prop-1-ene (**3ag**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 22% yield (33.9 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J*=8.0 Hz, 2H), 6.82 (d, *J*=8.0 Hz, 2H), 6.41 (br d, *J*=15.5 Hz, 1H), 6.06 (dt, *J*=15.5, 7.0 Hz, 1H), 3.79 (s, 3H), 3.56 (dd, *J*=7.0 , 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 146.1–143.9 (m), 140.9–138.8 (m), 138.7–136.4 (m), 131.9, 129.4, 127.4, 122.1, 114.0, 113.7–113.4 (m), 55.3, 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −144.0 (dd, *J*=23.5, 9.4 Hz, 2F), −157.5 (t, *J*=23.5 Hz, 1F), −162.6 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[7]

*4.3.8. (E)-1-(3-Methoxyphenyl)-3-pentafluorophenyl-prop-1-ene (**3ah**). Method B* (eluent: hexane/AcOEt=25:1); the title compound was obtained as a colorless oil in 42% yield (66.0 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.21 (dd, *J*=8.0, 8.0 Hz, Hz, 1H), 6.92 (d, *J*=8.0 Hz, 1H), 6.85 (br s, 1H), 6.78 (dd, *J*=8.0, 2.5 Hz, 1H), 6.43 (br d, *J*=15.5 Hz, 1H), 6.20 (dt, *J*=15.5, 7.0 Hz, 1H), 3.80 (s, 3H), 3.59 (dd, *J*=7.0, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 146.1–143.9 (m), 141.0–138.8 (m), 138.6–136.5 (m), 138.0, 132.4, 129.6, 124.6, 118.9, 113.4, 113.4–113.0 (m), 111.5, 55.2, 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=23.5, 9.4 Hz, 2F), −157.2 (t, *J*=23.5 Hz, 1F), −162.5 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[8b]

*4.3.9. (E)-1-[4-(Trifluoromethyl)phenyl]-3-pentafluorophenyl-prop-1-ene (**3ai**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 76% yield (134.1 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J*=8.0 Hz, 2H), 7.41 (d, *J*=8.0 Hz, 2H), 6.49 (br d, *J*=15.5 Hz, 1H), 6.32 (dt, *J*=15.5, 7.0 Hz, 1H), 3.62 (d, *J*=7.0, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.0 (m), 141.1–139.1 (m), 140.0, 138.7–136.6 (m), 131.2, 129.5 (q, *J*=32.5 Hz), 127.1, 126.4, 125.5, 124.1 (q, *J*=270.0 Hz), 112.8–112.5 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.6 (s, 3F), −143.8 (dd, *J*=23.5, 9.4 Hz, 2F), −156.7 (t, *J*=23.5 Hz, 1F), −162.2 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[8a]

*4.3.10. (E)-1-(4-Nitrophenyl)-3-pentafluorophenyl-prop-1-ene (**3aj**). Method A* (eluent: hexane/AcOEt=13:1); the title compound was obtained as a yellow solid in 70% yield (115.7 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (br d, *J*=9.0 Hz, 2H), 7.46 (br d, *J*=9.0 Hz, 2H), 6.53 (br d, *J*=16.0 Hz, 1H), 6.42 (dt, *J*=16.0, 6.5 Hz 1H), 3.66 (dd, *J*=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 146.0–144.0 (m), 142.0, 141.2–139.2 (m), 138.7–136.6 (m), 130.6, 129.3, 126.8, 124.0, 112.4–112.1 (m), 25.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.6 (dd, *J*=23.5, 9.4 Hz, 2F), −156.3 (t, *J*=23.5 Hz, 1F), 161.9 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1596, 1503, 1337, 1109, 1069, 975, 956, 916, 861, 829, 751, 735, 690 cm^{-1}. Mp: 92.7–93.8 °C (recrystallized from hexane, yellow needles). HRMS (pos. ESI): *m*/*z*: calcd for $C_{15}H_8F_5NO_2$ $[M+Ag]^+$ 435.9526, found 435.9524. Anal. Calcd for $C_{15}H_8F_5NO_2$: C, 54.72; H, 2.45; N, 4.25. Found: C, 54.70; H, 2.68; N, 4.10.

*4.3.11. (E)-1-(3-Formylphenyl)-3-pentafluorophenyl-prop-1-ene (**3ak**). Method A* (eluent: hexane/AcOEt=25:1); the title compound was obtained as a white solid in 67% yield (104.0 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 10.0 (s, 1H), 7.84 (s, 1H), 7.73 (d, *J*=7.5 Hz, 1H), 7.57 (d, *J*=7.5 Hz, 1H), 7.47 (dd, *J*=7.5, 7.5 Hz, 1H), 6.53 (br d, *J*=16.0 Hz, 1H), 6.33 (dt, *J*=16.0, 6.5 Hz, 1H), 3.63 (dd, *J*=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 146.1–144.0 (m), 141.1–138.9 (m), 138.7–136.5 (m), 137.6, 136.6, 132.1, 131.2, 129.3, 129.0, 127.1, 126.4, 112.9–112.6 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.8 (dd, *J*=23.5, 9.4 Hz, 2F), −156.7 (t, *J*=23.5 Hz, 1F), −162.2 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1694, 1520, 1498, 1146,

1119, 970, 956, 795, 687, 648 cm^{-1}. Mp: 53.2–54.1 °C (recrystallized from hexane, colorless prisms). HRMS (pos. ESI): *m/z*: calcd for $C_{16}H_9F_5O$ $[M+Ag]^+$ 418.9624, found: 418.9619. Anal. Calcd for $C_{16}H_9F_5O$: C, 61.55; H, 2.91. Found: C, 61.85; H, 3.15.

*4.3.12. Dimethyl 2-{4-(E)-[3-(pentafluorophenyl)prop-1-en-1-yl] benzylidene}malonate (**3al**). Method A* (eluent: hexane/AcOEt=25:1); the title compound was obtained as a white solid in 53% yield (113.2 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.37–7.32 (m, 4H), 6.46 (br d, *J*=15.5 Hz, 1H), 6.30 (dt, *J*=15.5, 6.5 Hz, 1H), 3.84 (s, 6H), 3.61 (dd, *J*=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 163.5, 145.0–142.9 (m), 141.3, 140.1–138.0 (m), 138.0, 137.7–135.4 (m), 131.0, 130.5, 128.8, 124.0, 111.9–111.6 (m), 51.7, 51.7, 24.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.8 (dd, *J*=23.5, 9.4 Hz, 2F), −156.8 (t, *J*=23.5 Hz, 1F), −162.2 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1728, 1623, 1523, 1503, 1436, 1259, 1205, 1125, 1069, 1004, 972, 918, 852, 792, 760, 715, 515 cm^{-1}. Mp: 74.8–76.1 °C (recrystallized from hexane/EtOAc, colorless prisms). HRMS (pos. ESI): *m/z*: calcd for $C_{21}H_{15}F_5O_4$ $[M+Ag]^+$ 532.9941, found: 532.9944. Anal. Calcd for $C_{21}H_{15}F_5O_4+1/3H_2O$: C, 58.34; H, 3.65. Found: C, 58.50; H, 3.65.

*4.3.13. (E)-1-[2-(Allyloxy)phenyl]-3-pentafluorophenyl-prop-1-ene (**3am**). Method A* (eluent: hexane); the title compound was obtained as a pale yellow oil in 66% yield (112.3 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J*=7.5, 1.5 Hz, 1H), 7.17 (ddd, *J*=7.5, 7.5, 1.5 Hz, 1H), 6.89 (dd, *J*=7.5, 7.5 Hz, 1H), 6.84–6.81 (m, 2H), 6.23 (dt, *J*=16.0 Hz, *J*=6.5 Hz, 1H), 6.09–6.03 (m, 1H), 5.39 (dd, *J*=17.0, 1.5 Hz, 1H), 5.28 (dd, *J*=10.8, 1.5 Hz, 1H), 4.53 (dd, *J*=5.0, 1.5, 1.5 Hz, 2H), 3.60 (dd, *J*=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 146.1–144.0 (m), 140.9–138.8 (m), 138.5–136.5 (m), 133.3, 128.6, 127.4, 126.8, 126.0, 124.9, 120.9, 117.1, 113.6–113.4 (m), 112.4, 69.1, 26.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=18.8, 9.4 Hz, 2F), −157.6 (t, *J*=18.8 Hz, 1F), −162.8 (dt, *J*=18.8, 9.4 Hz, 2F). IR (ATR-IR): 1599, 1520, 1501, 1452, 1240, 1119, 960, 916, 750 cm^{-1}. HRMS (pos. ESI): *m/z*: calcd for $C_{18}H_{13}F_5O$ $[M+Ag]^+$ 446.9937, found: 446.9940. Anal. Calcd: C, 63.53; H, 3.85. Found: C, 63.81; H, 4.07.

*4.3.14. 4,4,5,5-Tetramethyl-2-{3-(E)-[3-(pentafluorophenyl)prop-1-en-1-ylphenyl]}-1,3,2-dioxaborolane (**3an**). Method B* (eluent: hexane/AcOEt=25:1); the title compound was obtained as a mixture of **3an** and its S_N2' isomer **3an′** (87:13) as a white solid in 56% yield (115.2 mg). ^1H NMR (500 MHz, $CDCl_3$) for **3an**: δ 7.73 (s, 1H), 7.65 (d, *J*=7.5 Hz, 1H), 7.40 (d, *J*=7.5 Hz, 1H), 7.31–7.26 (m, 1H), 6.44 (d, *J*=15.5 Hz, 1H), 6.23 (dt, *J*=15.5, 6.5 Hz, 1H), 3.56 (dd, *J*=6.5, 1.5 Hz, 2H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) for **3an**: δ 145.0–142.9 (m), 139.9–137.8 (m), 137.6–135.5 (m), 134.9, 133.0, 131.6, 131.3, 128.0, 127.0, 123.3, 112.4–112.1 (m), 82.9, 23.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ −141.1 (dd, *J*=23.5, 9.4 Hz, 0.12×2F for **3an′**), −143.9 (dd, *J*=23.5, 9.4 Hz, 2F for **3an**), −156.6 (t, *J*=23.5 Hz, 0.12×1F for **3an′**), −157.3 (t, *J*=23.5 Hz, 1F for **3an**), −162.0 (dt, *J*=23.5, 9.4 Hz, 0.12×2F for **3an′**), −162.6 (dt, *J*=23.5, 9.4 Hz, 2F for **3an**). IR (ATR-IR): 2977, 1504, 1418, 1358, 1262, 1207, 1143, 1117, 1079, 959, 920, 887, 852, 797, 676, 704 cm^{-1}. Mp: 59.3–61.0 °C (recrystallized from hexane, colorless prisms). HRMS (pos. ESI): *m/z*: calcd for $C_{21}H_{20}BF_5O_2$ $[M+Ag]^+$ 517.0527, found: 517.0534. Anal. Calcd for $C_{21}H_{20}BF_5O_2+1/2H_2O$: C, 60.17; H, 5.05. Found: C, 60.15; H, 5.23.

*4.3.15. (E)-1-[3-(tert-Butyldimethylsilyloxy)phenyl]-3-pentafluorophenyl-prop-1-ene (**3ao**). Method A* (eluent: hexane, followed by preparative TLC (eluent: hexane)), the title compound was obtained as a colorless oil in 56% yield (115.6 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, *J*=8.0, 8.0 Hz, 1H), 6.92 (d, *J*=8.0 Hz, 1H), 6.80 (s, 1H), 6.71 (br d, *J*=8.0 Hz, 1H), 6.41 (d, *J*=15.5 Hz, 1H), 6.17 (dt, *J*=15.5, 6.5 Hz, 1H), 3.57 (d, *J*=6.5 Hz, 2H), 0.99 (d, *J*=1.0 Hz, 9H), 0.19 (d, *J*=1.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 146.1–144.0 (m), 140.9–138.9 (m), 138.7–136.5 (m), 138.1, 136.4, 132.4, 129.5, 124.3, 119.4, 117.9, 113.4–113.1 (m), 25.7, 25.6, 18.2, −4.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=23.5, 9.4 Hz, 2F), −157.3 (t, *J*=23.5 Hz, 1F), −162.5 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 2931, 1578, 1520, 1502, 1281, 1254, 1158, 1119, 1000, 958, 910, 838, 780, 688 cm^{-1}. HRMS (pos. ESI): *m/z*: calcd for $C_{21}H_{23}F_5OSi$ $[M+Ag]^+$ 521.0489, found: 521.0485. Anal. Calcd for $C_{21}H_{23}F_5OSi$: C, 60.85; H, 5.59. Found: C, 61.01; H, 5.58.

*4.3.16. (E)-1,3-Bis(pentafluorophenyl)prop-1-ene (**3ap**). Method B* (eluent: hexane); the title compound was obtained as a white solid in 77% yield (144.6 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 6.58 (dt, *J*=16.5 Hz, *J*=6.8 Hz, 1H), 6.40 (d, *J*=16.5 Hz, 1H), 3.66 (d, *J*=6.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.1 (m), 145.7–143.6 (m), 141.0–138.9 (m), 138.8–136.6 (m), 133.9–133.8 (m), 116.9, 112.0–111.9 (m), 111.4–111.2 (m), 26.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ −142.9 (dd, *J*=18.8, 9.4 Hz, 2F), −143.5 (dd, *J*=23.5, 9.4 Hz, 2F), −155.9 (t, *J*=18.8 Hz, 1F), −156.1 (t, *J*=23.5 Hz, 1F), −162.0 (dt, *J*=18.8, 9.4 Hz, 2F), −162.8 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[8c]

*4.3.17. (E)-1-(3-Thienyl)-3-pentafluorophenyl-prop-1-ene (**3aq**). Method A* (eluent: hexane); the title compound was obtained as a white solid in 38% yield (55.1 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (dd, *J*=5.0, 2.5 Hz, 1H), 7.15 (dd, *J*=5.0, 1.0 Hz, 1H), 7.11 (br d, *J*=2.5 Hz, 1H), 6.47 (br d, *J*=16.0 Hz, 1H), 6.07 (dt, *J*=16.0, 7.0 Hz, 1H), 3.55 (dd, *J*=7.0, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–143.9 (m), 140.9–138.7 (m), 139.0, 138.5–136.4 (m), 126.7, 126.2, 124.8, 124.2, 122.0, 113.4–113.1 (m), 25.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.9 (dd, *J*=23.5, 9.4 Hz, 2F), −157.2 (t, *J*=23.5 Hz, 1F), −162.5 (dt, *J*=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1497, 1119, 1065, 984, 958, 938, 904, 870, 775, 596, 560 cm^{-1}. Mp: 63.6–64.9 °C (recrystallized from hexane, colorless prisms). HRMS (pos. ESI): *m/z*: calcd for $C_{13}H_7F_5S$ $[M+Ag]^+$ 396.9240, found: 396.9237. Anal. Calcd for $C_{13}H_7F_5S$: C, 53.80; H, 2.43. Found: C, 53.57; H, 2.58.

*4.3.18. 1-(E)-(Pentafluorophenyl)-5-phenylpent-2-ene (**3ar**). Method A* (eluent: hexane); the title compound was obtained as a mixture of **3ar** and its regioisomers (89:11) as a colorless oil in 88% yield (137.2 mg). The structures of minor isomers were not identified. ^1H NMR (500 MHz, $CDCl_3$): δ 7.28–7.11 (m, 5H), 5.57–5.52 (m, 1H), 5.47–5.42 (m, 1H), 3.34 (d, *J*=6.5 Hz, 2H), 2.65 (t, *J*=8.0 Hz, 2H), 2.32–2.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.9–143.8 (m), 141.6, 140.7–138.7 (m), 138.6–136.3 (m), 132.5, 128.5, 128.2, 125.8, 125.1, 114.0–113.7 (m), 35.6, 34.1, 25.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ −144.2 (dd, *J*=18.8, 9.4 Hz, 2F), −158.0 (t, *J*=18.8 Hz, 1F), −162.9 (dt, *J*=18.8, 9.4 Hz, 2F). IR (ATR-IR): 1519, 1500, 1120, 957, 746, 698, 568 cm^{-1}. HRMS (pos. ESI): *m/z*: calcd for $C_{17}H_{13}F_5$ $[M+Ag]^+$ 418.9988, found: 418.9988. Anal. Calcd for $C_{17}H_{13}F_5$: C, 65.39; H, 4.20. Found: C, 65.11; H, 4.25.

*4.3.19. 1-(E)-(Pentafluorophenyl)-3-cyclohexyl-prop-2-ene (**3as**). Method A* (eluent: hexane, followed by recycle GPC); the title compound was obtained as a mixture of **3as** and its S_N2' isomer **3as′** (94:6) as a colorless oil in 70% yield (101.1 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 5.50 (dd, *J*=15.5, 6.5 Hz, 1H), 5.43–5.37 (dt, *J*=15.5, 6.0 Hz, 1H), 3.36 (d, *J*=6.0 Hz, 2H), 1.93–1.87 (m, 1H), 1.72–1.61 (m, 5H), 1.28–1.19 (m, 2H), 1.17–1.09 (m, 1H), 1.07–0.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0–143.9 (m), 140.7–138.6 (m), 139.4, 138.7–136.5 (m), 121.8, 114.3–114.0 (m), 40.4, 32.7, 26.1, 26.0, 25.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ −144.3 (dd, *J*=23.5, 9.4 Hz, 2F), −158.1 (t, *J*=23.5 Hz, 1F), −163.0 (dt, *J*=23.5, 9.4 Hz, 2F). The spectral data are in agreement with the literature.[8c]

*4.3.20. 2-Cyclohexylidene-1-(pentafluorophenyl)ethane (**3at**). Method A* (eluent: hexane); the title compound was obtained

as a colorless oil in 70% yield (96.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.09 (t, J=7.5 Hz, 1H), 3.39 (d, J=7.5 Hz, 2H), 2.26 (t, J=5.5 Hz, 2H), 2.05 (t, J=5.5 Hz, 2H), 1.58–1.50 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.0–143.9 (m), 142.6, 150.5–138.5 (m), 138.6–136.4 (m), 115.6, 115.1–114.8 (m), 37.0, 28.6, 28.4, 27.5, 26.7, 20.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ −144.4 (dd, J=23.5, 9.4 Hz, 2F), −158.6 (t, J=23.5 Hz, 1F), −163.1 (dt, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 2930, 1519, 1500, 1448, 1308, 1120, 1003, 958, 913, 849, 609 cm^{-1}. HRMS (pos. ESI): m/z: calcd for $C_{14}H_{13}F_5$ $[M+Ag]^+$ 382.9988, found: 382.9984. Anal. Calcd for $C_{14}H_{13}F_5$: C, 60.87; H, 4.74. Found: C, 61.11; H, 5.04.

*4.3.21. (E)-1-Triisopropylsilyl-5-(pentafluorophenyl)-pent-3-en-1-yne (**3au**). Method A* (eluent: hexane); the title compound was obtained as a mixture of **3au** and its regioisomers (96:4) as a colorless oil in 79% yield (153.5 mg). The structures of minor isomers were not identified. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.18 (dt, J=16.0, 6.5 Hz, 1H), 5.59 (br d, J=16.0 Hz, 1H), 3.48 (dd, J=6.5, 1.5 Hz, 2H), 1.06 (s, 21H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0–144.0 (m), 141.2–139.1 (m), 138.5–136.5 (m), 138.2, 112.9, 112.2–111.9 (m), 104.3, 91.5, 25.4, 18.6, 11.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −143.6 (dd, J=23.5, 9.4 Hz, 2F), −156.6 (t, J=23.5 Hz, 1F), −162.2 (dt, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 2944, 2866, 1520, 1503, 1464, 1122, 1074, 983, 951, 882, 666 cm^{-1}. HRMS (pos. ESI): m/z: calcd for $C_{20}H_{25}F_5Si$ $[M+Ag]^+$ 495.0697, found: 495.0705. Anal. Calcd for $C_{20}H_{25}F_5Si$: C, 61.83; H, 6.49. Found: C, 61.72; H, 6.51.

*4.3.22. 1-Phenyl-3-(pentafluorophenyl)prop-1-yne (**3av**). Method B* (eluent: hexane); the title compound was obtained as a mixture of **3av** and its regioisomer (89:11) in 72% yield (101.1 mg). The pure isomer was obtained as a white solid in 64% yield (90.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H), 7.30–7.26 (m, 3H), 3.82 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.0 (m), 141.5–139.5 (m), 138.7–136.6 (m), 131.7, 128.3 (2C), 122.8, 110.9–110.6 (m), 83.5, 81.5, 13.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ −142.9 (dd, J=23.5, 9.4 Hz, 2F), −156.1 (t, J=23.5 Hz, 1F), −162.1 (dt, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1504, 1323, 1120, 1000, 941, 900, 757, 693, 666, 604, 528 cm^{-1}. Mp: 60.8–61.8 °C (recrystallized from hexane, colorless prisms). HRMS (pos. ESI): m/z: calcd for $C_{15}H_7F_5$ $[M+Ag]^+$ 388.9519, found: 388.9515. Anal. Calcd for $C_{15}H_7F_5$: C, 63.84; H, 2.50. Found: C, 63.92; H, 2.77.

*4.3.23. (E)-1-(4-Chlorophenyl)-3-(2,3,5,6-tetrafluoro-4-methoxyphenyl)prop-1-ene (**4ab**). Method C* (quenched by 2 M Me_2NH, eluent: hexane); the title compound was obtained as a white solid in 74% yield (122.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 4H), 6.41 (br d, J=16.0 Hz, 1H), 6.21 (dt, J=16.0, 6.5 Hz, 1H), 4.05 (s, 3H), 3.56 (dd, J=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3–144.1 (m), 142.1–139.9 (m), 137.0–136.8 (m), 135.3, 133.1, 130.8, 128.7, 127.4, 125.7, 111.5–111.2 (m), 62.2 (t, rJ=3.8 Hz), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −145.6 (dd, J=18.8, 9.4 Hz, 2F), −158.2 (dd, J=18.8, 9.4 Hz, 2F). IR (ATR-IR): 1655, 1488, 1188, 1125, 1091, 1067, 1004, 984, 969, 923, 837, 791, 709, 681, 613 cm^{-1}. Mp: 67.0–68.8 °C (recrystallized from hexane, white needles). HRMS (EI): m/z: calcd for $C_{16}H_{11}ClF_4O$ $[M^+]$ 330.0435, found 330.0440. Anal. Calcd for $C_{16}H_{11}ClF_4O+1/10H_2O$: C, 57.80; H, 3.40. Found: C, 58.07; H, 3.51.

*4.3.24. (E)-1-(4-Chlorophenyl)-3-[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]prop-1-ene (**4bb**). Method C* (quenched by Me_2NH, eluent: hexane); the title compound was obtained as a white solid in 30% yield (54.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.24 (m, 4H), 6.47 (br d, J=16 Hz, 1H), 6.18 (dt, J=16, 7.0 Hz, 1H), 3.67 (dd, J=7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.2–144.0 (m), 145.1–142.9 (m), 134.8, 133.5, 132.1, 128.8, 127.5, 123.8, 123.0 (t, J=18.8 Hz), 120.9 (q, J=272.5 Hz), 26.3. ^{19}F NMR (500 MHz, $CDCl_3$): δ −56.2 (t, J=18.8 Hz, 3F), −140.8 to −141.0 (m, 2F), −141.9 to −142.0 (m, 2F). IR (ATR-IR): 1486, 1334, 1217, 1177, 1142, 1091, 1010, 987, 968, 911, 873, 836, 796, 714, 607 cm^{-1}. Mp: 57.2–58.5 °C (recrystallized from hexane, colorless prisms). HRMS (EI): m/z: calcd for $C_{15}H_8ClF_7$ $[M^+]$ 368.0203, found 368.0196. Anal. Calcd for $C_{15}H_8ClF_7$: C, 52.13; H, 2.19. Found: C, 51.85; H, 2.45.

*4.3.25. (E)-1-(4-Chlorophenyl)-3-(2,3,5,6-tetrafluorophenyl)prop-1-ene (**4cb**). Method C* (eluent: hexane, followed by preparative TLC (eluent: hexane)); the title compound was obtained as a white solid in 20% yield (30.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.25 (m, 4H), 6.99–6.92 (m, 1H), 6.43 (br d, J=15.5 Hz, 1H), 6.22 (dt, J=15.5, 7.0 Hz, 1H), 3.62 (dd, J=7.0, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.9–144.8 (m), 145.8–143.7 (m), 135.2, 133.2, 131.2, 128.7, 127.5, 125.2, 119.0 (t, J=18.8 Hz), 100.1 (t, J=22.5 Hz), 26.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −139.40 to −139.49 (m, 2F), −144.36 to −144.45 (m, 2F). IR (ATR-IR): 1491, 1384, 1244, 1172, 1090, 1008, 968, 867, 841, 825, 796, 711, 684, 506 cm^{-1}. Mp: 69.0–70.1 °C (recrystallized from hexane, colorless prisms). HRMS (EI): m/z: calcd for $C_{15}H_9ClF_4$ $[M^+]$ 300.0329, found 300.0338. Anal. Calcd for $C_{15}H_9ClF_4+1/3H_2O$: C, 58.75; H, 3.18. Found: C, 58.95; H, 3.31.

*4.3.26. (E)-1-(4-Chlorophenyl)-3-(2,3,4,5-tetrafluorophenyl)prop-1-ene (**4db**). Method C* (eluent: hexane); the title compound was obtained as mixture of **4db** and its regioisomer (88:12) as a colorless oil in 61% yield (91.0 mg). The structures of minor isomers were not identified. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.25 (m, 4H), 6.87–6.82 (m, 1H), 6.42 (d, J=16.0 Hz, 1H), 6.20 (dt, J=16.0, 7.0 Hz, 1H), 3.53 (d, J=7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0–146.0 (m), 146.6–144.6 (m), 141.9–139.6 (m), 140.3–138.0 (m), 135.2, 133.3, 131.6, 128.8, 127.4, 126.1, 111.3–111.1 (m), 31.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ −139.67 to −139.77 (m, 1F), −143.55 to −143.63 8 (m, 1F), −155.72 to −155.80 (m, 1F), −158.34 to −158.44 (m, 1F). IR (ATR-IR): 1523, 1486, 1365, 1218, 1093, 1033, 1012, 966, 934, 798, 714, 683 cm^{-1}. HRMS (EI): m/z: calcd for $C_{15}H_9ClF_4$ $[M^+]$ 300.0329, found 300.0339.

*4.3.27. (E)-1-(4-Chlorophenyl)-3-(2,3,5,6-tetrafluoro-4-bromophenyl)prop-1-ene (**4eb**). Method A* (eluent: hexane, followed by preparative TLC (eluent: hexane)); the title compound was obtained as a white solid in 61% yield (114.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.23 (m, 4H), 6.43 (br d, J=15.5 Hz, 1H), 6.19 (dt, J=15.5, 7.0 Hz, 1H), 3.61 (dd, J=7.0, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–143.8 (m), 135.1, 133.3, 131.4, 128.7, 127.5, 124.7, 117.9 (t, J=18.8 Hz), 97.9 (t, J=22.5 Hz), 26.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −133.65 to −133.73 (m, 2F), −142.47 to −142.53 (m, 2F). IR (ATR-IR): 1480, 1089, 970, 900, 853, 797, 680, 516 cm^{-1}. Mp: 78.9–79.9 °C (recrystallized from hexane, white needles). HRMS (EI): m/z: calcd for $C_{15}H_8ClBrF_4$ $[M^+]$ 377.9434, found 377.9416. Anal. Calcd for $C_{15}H_8ClBrF_4+1/3H_2O$: C, 46.73; H, 2.27. Found: C, 46.84; H, 2.34.

*4.3.28. (E)-4-[3-(4-Chlorophenyl)prop-2-enyl]-2,3,5,6-tetrafluoro-N,N-diisopropylbenzamide (**4fb**). Method C* (quenched by Me_2NH, eluent: hexane/AcOEt=15:1, followed by preparative TLC (eluent: hexane/CH_2Cl_2=1:1)); the titled compound was obtained as a white solid in 12% yield (25.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 4H), 6.47 (br d, J=16.0 Hz, 1H), 6.21 (dt, J=16.0, 7.0 Hz, 1H), 3.72 (hept, J=6.5 Hz, 1H), 3.62 (dd, J=7.0, 1.0 Hz, 2H), 3.57 (hept, J=6.5 Hz, 1H), 1.55 (d, J=6.5 Hz, 6H), 1.19 (d, J=6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 145.8–143.7 (m), 143.2–141.1 (m), 135.2, 133.3, 131.4, 128.8, 127.5, 124.9, 118.4 (t, J=18.8 Hz), 116.4 (t, J=22.5 Hz), 51.8, 46.7, 26.2, 20.9, 20.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ −142.9 (dd, J=23.5, 9.4 Hz, 2F), −143.6 (dd, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1643, 1476, 1372, 1336, 1090, 977, 918, 807, 782, 739, 682, 619 cm^{-1}. Mp: 156.4–158.2 °C (recrystallized from hexane/EtOAc, colorless prisms). HRMS (EI): m/z: calcd for $C_{22}H_{22}ClF_4NO$ $[M^+]$

427.1326, found: 427.1322. Anal. Calcd for $C_{22}H_{22}ClF_4NO$: N, 3.27; C, 61.76; H, 5.18. Found: N, 3.41; C, 61.52; H, 5.30.

*4.3.29. (E)-4-[3-(4-Chlorophenyl)prop-2-enyl]-2,3,5,6-tetrafluoro-1,1′-biphenyl (**4gb**). Method C* (eluent: hexane); the title compound was obtained as a white solid in 72% yield (135.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.44 (m, 5H), 7.29–7.25 (m, 4H), 6.48 (br d, J=16.0 Hz, 1H), 6.27 (dt, J=16.0, 7.0 Hz, 1H), 3.67 (dd, J=7.0, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1–144.0 (m), 144.9–142.7 (m), 135.3, 133.2, 131.2, 130.2, 129.0, 128.7, 128.6, 127.6, 127.5, 125.4, 118.9 (t, J=17.5 Hz), 117.1 (t, J=17.5 Hz), 26.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −144.5 (dd, J=23.5, 9.4 Hz, 2F), −144.8 (dd, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1481, 1437, 1305, 1091, 1010, 979, 966, 902, 800, 768, 689 cm^{-1}. Mp: 141.7–143.4 °C (recrystallized from hexane, white needles). HRMS (EI): m/z: calcd for $C_{21}H_{13}ClF_4$ [M$^+$] 376.0642, found 376.0641. Anal. Calcd for $C_{21}H_{13}ClF_4$+1/3H_2O: C, 65.89; H, 3.60. Found: C, 65.75; H, 3.68.

*4.3.30. (E)-4-[3-(4-Chlorophenyl)prop-2-enyl]-2,3,5,6-tetrafluoropyridine (**4hb**). Method C* (eluent: hexane/AcOEt=20:1, followed by preparative TLC (eluent: hexane/AcOEt=10:1)); the title compound was obtained as a colorless solid in 21% yield (32.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.24 (m, 4H), 6.49 (br d, J=16.5 Hz, 1H), 6.18 (dt, J=16.5, 7.0 Hz, 1H), 3.70 (dd, J=7.0, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ143.3–142.3 (m), 141.5–139.2 (m), 134.7, 133.7, 132.6, 128.8, 127.5, 122.9, 26.9. ^{19}F NMR (470 MHz, $CDCl_3$): δ −90.91 to −91.05 (m, 2F), −144.96 to −145.10 (m, 2F). IR (ATR-IR): 1648, 1466, 1405, 1253, 1093, 1047, 1002, 979, 946, 837, 783, 707, 651, 574 cm^{-1}. Mp: 70.4–71.5 (recrystallized from hexane/EtOAc, white needles). HRMS (EI): m/z: calcd for $C_{14}H_8ClF_4N$ [M$^+$] 301.0281, found: 301.0281.

*4.3.31. (E)-1-(4-Chlorophenyl)-3-(2,4,6-trifluorophenyl)prop-1-ene (**4ib**). Method C* (eluent: hexane, followed by preparative TLC (eluent: hexane)); the title compound was obtained as a white solid in 55% yield (77.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.24 (m, 4H), 6.68–6.63 (m, 1H), 6.36 (d, J=15.5 Hz, 1H), 6.22 (dt, J=15.5, 6.5 Hz, 1H), 3.50 (d, J=6.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5–160.2 (m), 135.6, 132.9, 130.2, 128.7, 127.4, 126.7, 111.8–111.4 (m), 100.3–99.9 (m), 25.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ −110.67 to −110.73 (m, 1F), −112.7 (t, J=9.4 Hz, 2F). IR (ATR-IR): 1606, 1491, 1438, 1164, 1113, 1093, 1070, 1012, 997, 968, 835, 802, 768, 676, 612, 532, 512 cm^{-1}. Mp: 47.9–49.3 °C (recrystallized from hexane, colorless prism). HRMS (EI): m/z: calcd for $C_{15}H_{10}ClF_3$ [M$^+$] 282.0423, found 282.0416. Anal. Calcd for $C_{15}H_{10}ClF_3$+1/6H_2O: C, 63.06; H, 3.65. Found: C, 63.30; H, 3.82.

*4.3.32. (E)-1-(4-Chlorophenyl)-3-(4-bromo-2,6-difluorophenyl) prop-1-ene (**4kb**). Method C* (eluent: hexane, followed by preparative TLC (eluent: hexane/AcOEt=10:1)); the title compound was obtained as a white solid in 69% yield (118.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.20 (m, 4H), 7.08–7.04 (m, 2H), 6.35 (br d, J=16.0 Hz, 1H), 6.19 (dt, J=16.0, 6.5 Hz, 1H), 3.49 (dd, J=6.5, 1.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2 (dd, J=250.0 Hz, 10.0 Hz), 135.5, 133.0, 130.4, 128.7, 127.4, 126.2, 119.7 (t, J=12.5 Hz), 115.4–114.7 (m), 25.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ −113.6 (d, J=4.7 Hz, 2F). IR (ATR-IR): 1619, 1474, 1415, 1183, 1092, 1032, 1012, 965, 874, 840, 767, 589, 511 cm^{-1}. Mp: 43.9–45.0 °C (recrystallized from hexane, colorless prisms). HRMS (EI): m/z: calcd for $C_{15}H_{10}BrClF_2$ [M$^+$] 341.9622, found: 341.9622. Anal. Calcd for $C_{15}H_{10}BrClF_2$+1/4H_2O: C, 51.76; H, 3.04. Found: C, 52.01; H, 3.18.

*4.3.33. (E)-1-(4-Chlorophenyl)-3-(3,4,5-trifluorophenyl)prop-1-ene (**4lb**). Method C* (solvent: NMP/THF=10:1,[11] without TPPO, eluent: hexane, followed by preparative TLC (eluent: hexane)); the title compound was obtained as a colorless oil in 9% yield (39% NMR yield) (12.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.26 (m, 4H), 6.86–6.81 (m, 2H), 6.40 (dt, J=16.0, 1.5 Hz, 1H), 6.22 (dt, J=16.0, 7.0 Hz), 3.47 (br d, J=7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ152.2–150.1 (m), 139.5–137.3 (m), 136.1–136.0 (m), 135.3, 133.2, 131.3, 128.8, 127.7, 127.4, 112.5–112.4 (m), 38.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ −134.61 to −134.67 (m, 2F), −163.77 to −163.88 (m, 1F). IR (ATR-IR): 1621, 1525, 1489, 1446, 1341, 1229, 1092, 1037, 1011, 973, 846, 832, 778, 704, 679, 606, 578, 507 cm^{-1}. HRMS (EI): m/z: calcd for $C_{15}H_{10}ClF_3$ [M$^+$] 282.0423, found: 282.0428. Anal. Calcd for $C_{15}H_{10}ClF_3$: C, 63.73; H, 3.57. Found: C, 63.53; H, 3.85.

*4.3.34. (E)-1-Phenyl-3-pentafluorophenyl-prop-1-ene (**3aw**). Method A* (eluent: hexane), the title compound was obtained as a mixture of stereoisomers (E/Z=32:68) as a white solid in 37% yield (52.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) for (Z)-**3aw**: δ 7.40–7.22 (m, 5H), 6.58 (br d, J=6.5 Hz, 1H), 5.62 (dt, J=6.5, 7.0 Hz, 1H), 3.70 (dd, J=7.0, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) for (Z)-**3aw**: δ 146.1––144.0 (m), 141.0–138.8 (m), 138.7–136.5 (m), 136.5, 131.5, 128.6, 128.4, 127.2, 126.2, 114.0–113.7 (m), 21.9. ^{19}F NMR (470 MHz, $CDCl_3$) for (Z)-3aw: δ −143.4 (dd, J=18.8, 9.4 Hz, 2F), −157.4 (t, J=18.8 Hz, 1F), −162.6 (dt, J=18.8, 9.4 Hz, 2F). HRMS (pos. ESI): m/z: calcd for $C_{15}H_9F_5$ [M+Ag]$^+$ 390.9675, found: 390.9676.

*4.3.35. (Z)-(4-Pentafluorophenyl)-(but-2-en-1-yloxymethyl)-benzene (**3ax**). Method B* (eluent: hexane/AcOEt=25:1), the title compound was obtained as a mixture of stereoisomers (E/Z=5:95) as a colorless oil in 74% yield (121.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) for (Z)-3ax: δ 7.36–7.28 (m, 4H), 5.77–5.72 (m, 1H), 5.62–5.58 (m, 1H), 4.55 (s, 2H), 4.21 (d, J=6.0 Hz, 2H), 3.45 (d, J=7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) for (Z)-**3ax**: δ 146.1–143.9 (m), 141.0–138.7 (m), 138.6–136.4 (m), 138.1, 129.1, 128.4, 127.8, 127.7, 127.2, 113.6–113.2 (m), 72.5, 65.4, 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) for (Z)-**3ax**: δ −143.9 (dd, J=23.5, 9.4 Hz, 2F), −157.3 (t, J=23.5 Hz, 1F), −162.5 (td, J=23.5, 9.4 Hz, 2F). IR (ATR-IR): 1520, 1501, 1313, 1118, 1000, 904, 735, 697 cm^{-1}. HRMS (pos. ESI): m/z: calcd for $C_{17}H_{13}F_5O$ [M+Ag]$^+$ 434.9937, found: 434.9946. Anal. Calcd for $C_{17}H_{13}F_5O$: C, 62.20; H, 3.99. Found: C, 61.99; H, 4.06.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.05.107.

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