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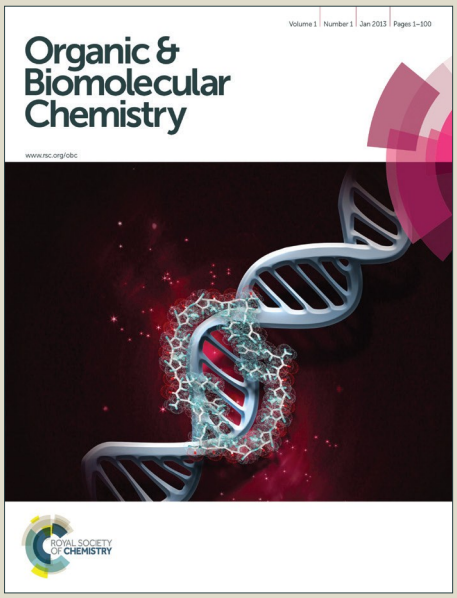

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ARTICLE

Geminal Difunctionalization of α-Diazo Arylmethylphosphonates: Synthesis of Fluorinated Phosphonates

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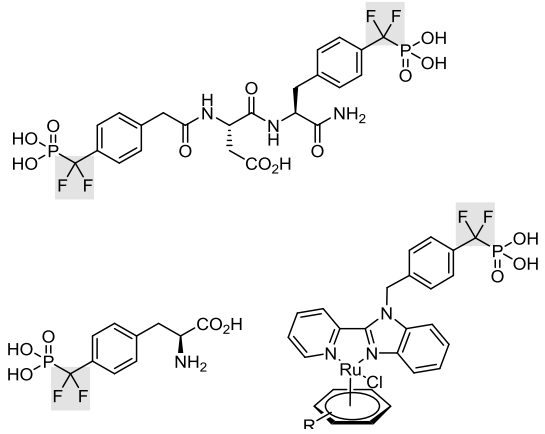
A general approach towards diverse fluorinated phosphonates *via* geminal difunctionalization reactions of α-diazo arylmethylphosphonates is described. Diazo functionality (RR'C=N_2) is successfully converted to RR'CF_2, RR'CHF, RR'CFBr or RR'CFNR"$_2$ groups by employing different fluorination reagents. A variety of fluorinated organophosphorus compounds were readily accessed in good to excellent yields from a common type of precursors.

Introduction

Fluorine-substituted molecules have showed wide applications in bioactive compounds and pharmaceuticals because the introduction of fluorine atoms leads to significant alternations in physical, chemical and biological properties of a molecule.[1] In particular, arenes bearing fluoromethylphosphonate fragments are extremely appealing.[2] They can be regarded as stable surrogates of the corresponding phosphates because they are more resistant to the potential metabolic hydrolysis.

Protein tyrosine phosphatase inhibitors

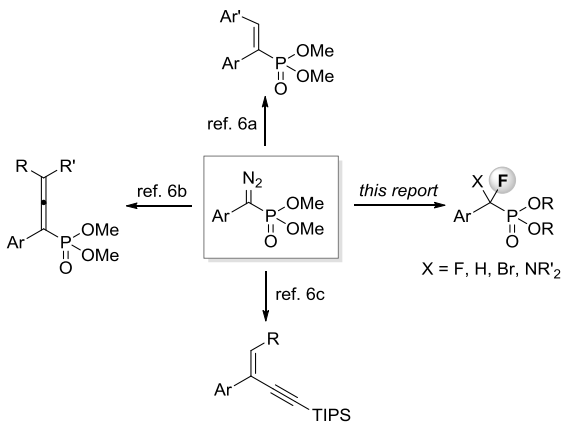


Scheme 1 Examples of bioactive fluorinated phosphonates

As presented in Scheme 1, there are several bioactive compounds containing a difluoromethylphosphinic acid motif that already show their applications as protein tyrosine phosphatase inhibitors.[3]

Due to their importance, the synthetic routes towards difluoromethylated phosphonate scaffolds have been actively pursued and some methods have been well established. Traditionally, they can be achieved *via* deoxofluorination reactions of relevant ketones or difluorination reactions of benzylic phosphonates.[3d,4] In recent years, transition-metal-catalyzed or -mediated cross-coupling reactions have emerged as efficient methods for accessing difluorinated compounds.[5] However, no general strategies are available for the synthesis of other fluoromethylated phosphonates, especially from a common type of precursors. In this context, the development of a straightforward method for accessing diverse fluorinated phosphonates is highly desirable.

Recently, we have disclosed several methods for the synthesis of phosphonate motifs as well as their subsequent transformations from diazo compounds.[6] α-Diazo arylmethylphosphonates, which are relatively stable and



Scheme 2 Transformations of α-diazo arylmethyl phosphonates

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† *Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of diazo substrates and products. See DOI: 10.1039/x0xx00000x*

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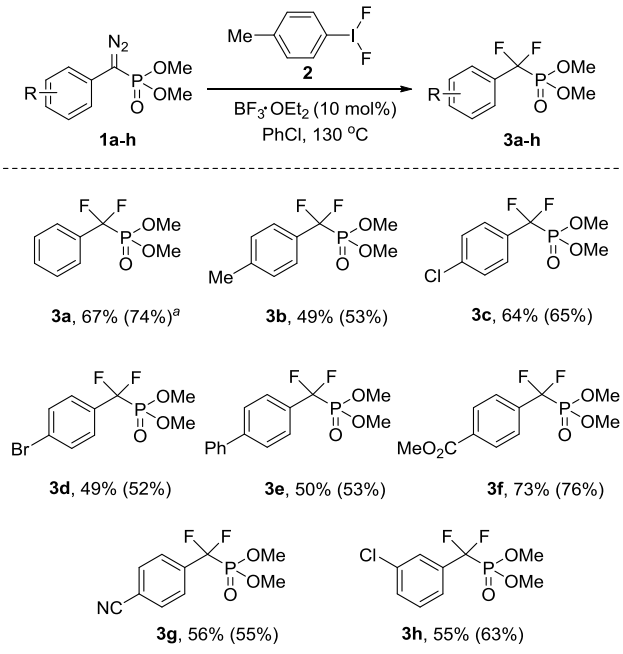
readily accessible, turned out to be good substrates to introduce phosphorus functionality into target molecules (Scheme 2). Based on our continuous interests in the application of diazo compounds in organic synthesis, we herein report successful fluoro-functionalization of α-diazo arylmethylphosphonates, which provide a straightforward and efficient route to a range of fluorinated phosphonate compounds.

Results and discussion

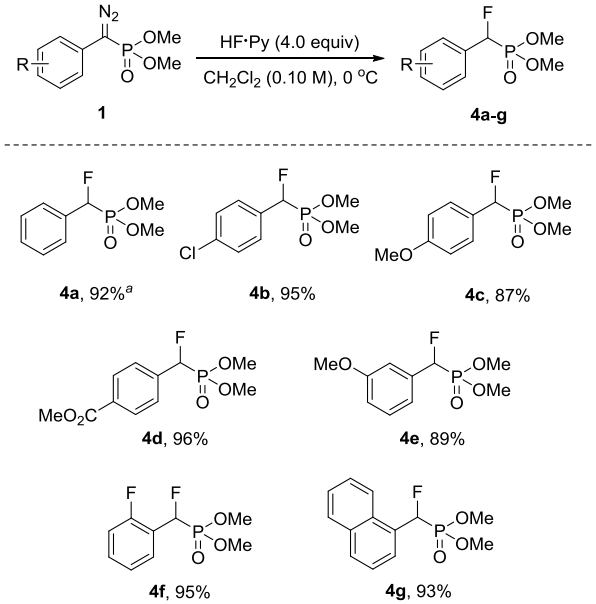
In the preliminary investigations, we evaluated the difluorination reaction of α-diazo arylmethylphosphonates by employing the hypervalent iodine compound **2** as the fluorination reagent. Compound 2 is a hypervalent iodine reagent that can be used to transfer two fluorine atoms at the same time. The similar transformation has been reported in the previous literature.[7] When diazo compound **1a** (R = H) was subjected to the previously reported conditions (5 mol% $BF_3{\cdot}OEt_2$, 1.1 equivalent of *p*-TolIF$_2$, 110 °C),[7] the desired phenyl difluoromethylphosphonate **3a** was only obtained in 31% NMR yield. Considering the lower nucleophilicity of α-diazo phosphonates compared to their carboxylic acid ester analogues,[8] we conceived that raising the reaction temperature and the loading of Lewis acid may increase the concentration of activated hypervalent iodine reagent, thus improving the efficiency. Upon extensive attempts, the desired product could be generated in 67% isolated yield. Subsequently, we explored the substrate scope of diazo compounds (Scheme 3). The results elucidated good functional group compatibility of this method and the reactions were complete within only 15 minutes. It is worth mentioning that bromide substrate was also successfully converted to the corresponding product (**3d**), which was not compatible in the catalytic systems of cross-coupling reactions with transition-metal catalysts. However, the substrates containing methoxyl group or *ortho* substituents did not provide satisfying results. In most cases, the difluorinated phosphonates were only afforded in moderate yields, and this limitation may due to the instability of hypervalent iodine reagent under the present conditions.

The mechanism for geminal difluorination reaction is probably similar to the proposed mechanism for dichlorination reaction.[7a] However, it is also possible that diazo compounds undergo electrophilic fluorination reaction with the activated hypervalent iodine reagent in the first step.

Next, we turned our attention to the synthesis of mono-fluoro-substituted arylmethylphosphonates. In this context, it has been well-established that hydrofluorination reaction of diazo compounds can be realized *via* an H-F insertion process.[7b,9] To our delight, the simple combination of α-diazo arylmethylphosphonates and Olah's reagent (HF·pyridine) at 0 °C led to the generation of mono-fluorinated phosphonates in excellent yields. Diazo substrates bearing different functional groups in *ortho*-, *meta*- or *para*-positions were all efficiently transferred to the desired products (Scheme 4).



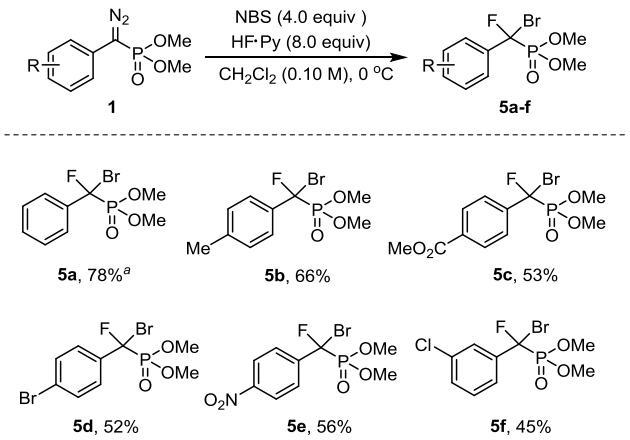
Scheme 3 Difluorination reactions of α-diazo arylmethyl phosphonates. The reactions were carried out with **1** (0.30 mmol, 1.0 equiv), *p*-TolIF$_2$ (0.60 mmol), $BF_3{\cdot}OEt_2$ (10 mol%) in PhCl (4.5 mL) under N_2 atmosphere at 130 °C for 15 min. [a]Isolated yield. ^{19}F NMR yield is given in the parentheses.



Scheme 4 Hydrofluorination reactions of α-diazo arylmethyl phosphonates. The reactions were carried out with **1** (0.20 mmol), HF·Py (0.80 mmol) in CH_2Cl_2 (2.0 mL) under N_2 atmosphere at 0 °C for 15 min. [a]Isolated yield.

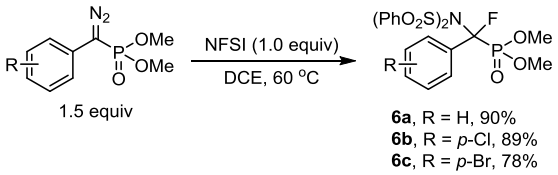
If *N*-bromosuccinimide (NBS) was added to the aforementioned reaction system, the bromofluorinated compounds were obtained instead (Scheme 5).[7b,10] The model

substrate **1a** provided the corresponding product **5a** in 78% isolated yield, while other substrates bearing *para* or *meta* substituents resulted in slightly diminished yields (ranging from 45 to 66%). Nitro, ester and halogen groups were well tolerated under the standard conditions. The mechanism for bromofluorination reaction is similar to that proposed in the previous paper.[10] We use an excess amount of NBS because it tends to decompose during the reaction.



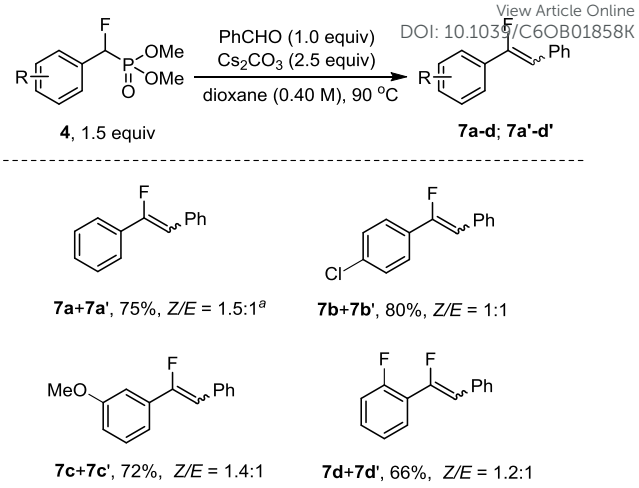
Scheme 5 Bromofluorination reactions of α-diazo arylmethylphosphonates. The reactions were carried out with **1** (0.20 mmol, 1.0 equiv), NBS (0.80 mmol), HF·Py (1.60 mmol) in CH_2Cl_2 (2.0 mL) under N_2 atmosphere at 0 °C for 5 min. [a]Isolated yield.

Furthermore, we studied the aminofluorination reactions of α-diazo arylmethylphosphonates.[11] The desired transformation could be realized by employing *N*-fluorobenzenesulfonimide (NFSI) as the key reagent (eq. 1). Chloride and bromide substrates led to the generation of aminofluorinated products in high yields, but diazo compounds with other substitution pattern resulted in low conversion under the current conditions. Further condition optimization is necessary to expand the scope of this reaction. The mechanism for aminofluorination reaction has been studied in detail in the previous report.[11]



(1)

Finally, to further demonstrate the utility of mono-fluorinated products, compounds **4** were converted to related alkenes through a Horner-Wadsworth-Emmons protocol.[6c] Thus, fluorinated olefins were generated smoothly in good yields in the presence of Cs_2CO_3. However, the *Z*/*E* ratio of newly formed double bond is close to 1:1 (Scheme 6).



Scheme 6 Synthesis of fluorinated alkenes *via* HWE reaction of compound **4**. The reactions were carried out with **4** (0.60 mmol), PhCHO (0.40 mmol, 1.0 equiv), Cs_2CO_3 (1.0 mmol) in dioxane (1.0 mL) under N_2 atmosphere for 12 h. [a]Combined yield of both isomers. *Z*/*E* ratio was determined by the isolated yield of each isomer.

Conclusion

In conclusion, we have demonstrated a series of geminal difunctionalization reactions of α-diazo arylmethyl phosphonates. The strategy employs easily accessible starting materials, and diverse fluoromethylated phosphonates can be readily achieved with high efficiency. The successful implement of these reactions not only provides practical synthetic methods for a range of fluorinated phosphonates, but also grants possibility for further study of their bioactivity and potential applications.

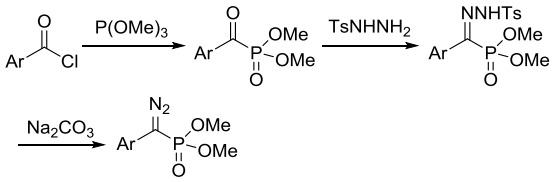
Experimental

General methods.

All the reactions were performed under nitrogen atmosphere in 10 mL or 50 mL Schlenk tubes. Some solvents were distilled prior to use. Toluene, 1,4-dioxane and THF were dried over Na with benzophenone-ketyl intermediate as indicator. DCE was dried over CaH_2. Super dry chlorobenzene is commercially available. DCM was used without distillation. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on Brucker ARX 400 spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). IR spectra were recorded on Nicolet iS10 in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. Unless otherwise noted, starting materials obtained from commercial suppliers were used directly without further purification. *p*-ABSA: *p*-acetamidobenzenesulfonyl azide.

General procedure for the preparation of *α*-aryldiazo phosphonates 1a-m.

Method A:[12]

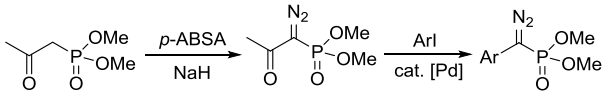


To a 25 mL flask was added acid chloride (10 mmol, 1.0 equiv) under N_2 at 0 °C. Then trimethyl phosphite (1.24 g, 10 mmol, 1.0 equiv) was added dropwise and the mixture was stirred at room temperature for 4 h. The resulting pale yellow oil was used in the next step without further purification.

A suspension of $TsNHNH_2$ (1.86 g, 10 mmol, 1.0 equiv) in THF (10 mL, 1 M) in a 25 mL flask was chilled to 0 °C and concentrated HCl (0.37 mL, 5 mmol, 0.5 equiv) was added. The resulting solution was stirred at 0 °C while dimethyl benzoyl phosphonate was added dropwise. The flask was stoppered and the mixture was allowed to warm to room temperature and stirred for 12 h. The resulting white precipitate was filtered and washed with hexane to give the corresponding *N*-tosylhydrazone.

To a 50 mL flask was added *N*-tosylhydrazone (10 mmol, 1.0 equiv) and Na_2CO_3 (1.2 g, 11 mmol, 1.1 equiv). Then water was added (15 mL) and the mixture was stirred at room temperature for 24 h. When the stirring was complete, the mixture was extracted with Et_2O for three times, washed with water and brine, dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by chromatography (silica gel, petroleum ether: EtOAc = 1:1) to give the final product.

Method B:[13]



The diazo compounds were prepared according to our previously reported method of palladium-catalyzed cross-coupling of dimethyl (1-diazo-2-oxopropyl)phosphonate with aryl iodide.[13a] The dimethyl (1-diazo-2-oxopropyl)phosphonate was prepared following a literature procedure.[13b] A solution of dimethyl 2-oxopropylphosphonate (3.32 g, 20.0 mmol) in toluene (85 mL) and THF (18 mL) was stirred and cooled to 0 °C by ice-water bath for 30 min, and sodium hydride (60% in oil, 0.88 g, 22.0 mmol) was slowly added into the flask. The mixture was stirred at 0 °C under N_2 for 1 hour, and *p*-ABSA (5.28 g, 22.0 mmol) was then added. The reaction was warmed to room temperature and stirring was continued overnight under N_2. The mixture was filtered through a *Celite* pad, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified by chromatography (silica gel, petroleum ether: EtOAc = 1:1) to give the product as a pale yellow oil.

$Pd(PPh_3)_4$ (116 mg, 5 mol%), K_2CO_3 (552 mg, 4.0 mmol, 2.0 equiv) and aryl iodide (2.0 mmol, 1.0 equiv) were suspended in methanol (5 mL) and toluene (5 mL) in a 25 mL flask under ambient atmosphere. Dimethyl (1-diazo-2-oxopropyl) phosphonate (499 mg, 2.6 mmol, 1.3 equiv) was then added, and the resulting solution was stirred at room temperature for 5 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified by column chromatography (silica gel, petroleum ether: EtOAc = 1:1) to afford the final products.

*Dimethyl (diazo(phenyl)methyl)phosphonate (**1a**).*[6a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.38 (m, 2H), 7.13-7.17 (m, 3H), 3.81 (d, *J* = 11.9 Hz, 6H).

*Dimethyl (diazo(p-tolyl)methyl)phosphonate (**1b**).*[6a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.80 (d, *J* = 11.6 Hz, 6H), 2.33 (s, 3H).

*Dimethyl ((4-chlorophenyl)(diazo)methyl)phosphonate (**1c**).*[6a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.34 (m, 2H), 7.08-7.11 (m, 2H), 3.82 (d, *J* = 12.0 Hz, 6H).

*Dimethyl ((4-bromophenyl)(diazo)methyl)phosphonate (**1d**).*[6a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 3.81 (d, *J* = 11.9 Hz, 6H).

*Dimethyl ([1,1'-biphenyl]-4-yl(diazo)methyl)phosphonate (**1e**).*[6a] Method B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.42-7.45 (m, 2H), 7.32-7.36 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.84 (d, *J* = 12.0 Hz, 6H).

*Methyl 4-(diazo(dimethoxyphosphoryl)methyl)benzoate (**1f**).*[13a] Method B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H), 3.84 (d, *J* = 12.0 Hz, 6H).

*Dimethyl ((4-cyanophenyl)(diazo)methyl)phosphonate (**1g**).*[13a] Method B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.84 (d, *J* = 11.9 Hz, 6H).

*Dimethyl ((3-chlorophenyl)(diazo)methyl)phosphonate (**1h**).* Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.11-7.14 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 12.0 Hz, 6H).

*Dimethyl (diazo(4-methoxyphenyl)methyl)phosphonate (**1i**).*[6a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.12 (m, 2H), 6.92-6.94 (m, 2H), 3.81 (d, *J* = 12.0 Hz, 6H), 3.80 (s, 3H).

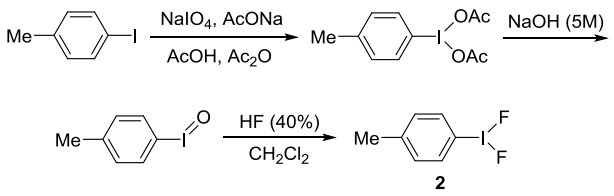
*Dimethyl (diazo(3-methoxyphenyl)methyl)phosphonate (**1j**).*[13a] Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.71-6.68 (m, 2H), 3.81 (d, *J* = 11.9 Hz, 6H), 3.80 (s, 3H).

*Dimethyl (diazo(2-fluorophenyl)methyl)phosphonate (**1k**).* Method A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.05-7.21 (m, 3H), 3.82 (d, *J* = 12.0 Hz, 6H).

*Dimethyl (diazo(naphthalen-1-yl)methyl)phosphonate (**1l**).* Method B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.60-7.65 (m, 2H), 7.48-7.57 (m, 2H), 3.80 (d, *J* = 11.6 Hz, 6H)

*Dimethyl (diazo(4-nitrophenyl)methyl)phosphonate (**1m**).*[13a] Method B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 3.86 (d, *J* = 11.9 Hz, 6H).

Preparation of (difluoroiodo)toluene (*p*-TolIF$_2$) 2



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(Difluoroiodo)toluene (*p*-TolIF$_2$) was prepared according to the previously reported literature.[14] A stirred suspension of $NaIO_4$ (4.40 g, 20.6 mmol, 1.03 equiv) and NaOAc (3.60 g, 44 mmol, 2.2 equiv) in glacial AcOH (30 mL) and Ac_2O (3 mL) at room temperature was treated with 4-iodotoluene (4.32 g, 20 mmol, 1.0 equiv). The reaction mixture was refluxed for 4 h. Then the mixture was poured into water (50 mL), extracted with DCM for three times, washed with water and brine, dried with Na_2SO_4 and concentrated under reduced pressure. Hexane was added to the obtained residue to collect the solid product. The product was filtered and washed with hexane to provide the (diacetoxyiodo)toluene.

A suspension of (diacetoxyiodo)toluene (1.0 g, 3 mmol) in 5 M NaOH (5 mL) was stirred at room temperature for 2 h. The yellow solid was collected by suction and washed with water and $CHCl_3$. The collect solid was dried by suction and then transferred to a 50 mL Teflon flask. DCM (15 mL) was added, followed by dropwise addition of 40% HF (3 mL). The mixture was stirred for 30 min, and then extracted with DCM for three times, washed with water and brine and dried with Na_2SO_4. The solvent was removed under atmospheric pressure through nitrogen flow to obtain an off white solid. The final product was transferred to the glove box and kept in a freezer.

*(Difluoroiodo)toluene (**2**).*[7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 2.47 (s, 3H).

General procedure for the difluorination reaction of α-diazo arylmethylphosphonates.[7] A 50 mL oven-dried Schlenk tube was charged with a magnetic stir bar and flushed with N_2. Then the tube was taken into the glove box and charged with *p*-TolIF$_2$ (0.60 mmol, 2.0 equiv, 154 mg). The tube was sealed and removed from the glove box. Then a solution of α-diazo arylmethylphosphonate (0.30 mmol, 1.0 equiv) in PhCl (4.5 mL) was added, and the mixture was allowed to stir at 130 ^{o}C for 1 min. $BF_3{\cdot}OEt_2$ (10 mol%) was then added as a solution in DCM (5% v/v), and the mixture was allowed to stir at 130 ^{o}C for another 15 min. It was subsequently cooled down to room temperature and the crude mixture was purified by column chromatography (silica gel, petroleum ether: EtOAc = 1:1) to afford the final products.

*Dimethyl (difluoro(phenyl)methyl)phosphonate (**3a**).* Colorless oil; yield 67% (47 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.8 Hz, 2H), 7.45-7.51 (m, 3H), 3.82 (d, J = 10.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (td, J = 21.6 Hz, J = 13.6 Hz), 130.9 (d, J = 2.0 Hz), 128.4 (d, J = 1.1 Hz), 126.0 (td, J = 7.0 Hz, J = 2.3 Hz), 118.1 (td, J = 261.6 Hz, J = 217.2 Hz), 54.8 (d, J = 6.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.0 (d, J_{PF} = 116.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.63 (t, J_{PF} = 116.0 Hz); IR (film) 1453, 1279, 1260, 1052, 844, 758, 734, 701 cm^{-1}; EI-MS (*m/z*, relative intensity): 236 (15), 218 (8), 127 (100), 109 (10); HRMS (ESI) calcd for $C_9H_{12}F_2O_3P$ [(M+H)$^+$] 237.0487, found: 237.0486.

*Dimethyl (difluoro(p-tolyl)methyl)phosphonate (**3b**).* Pale yellow oil; yield 53% (40 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.82 (d, J = 10.4 Hz, 6H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (d, J = 2.1 Hz), 129.4 (td, J = 22.0 Hz, J = 13.7 Hz), 129.2 (d, J = 1.0 Hz), 126.0 (td, J = 6.6 Hz, J = 2.2 Hz), 118.3 (td, J = 261.6 Hz, J = 218.2 Hz), 54.8 (d, J = 6.6 Hz), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.3 (d, J_{PF} = 118.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.83 (t, J_{PF} = 118.6 Hz); IR (film) 1275, 1263, 1094, 844, 817, 764, 732 cm^{-1}; EI-MS (*m/z*, relative intensity): 250 (13), 141 (100), 91 (10); HRMS (ESI) calcd for $C_{10}H_{14}F_2O_3P$ [(M+H)$^+$] 251.0643, found: 251.0635.

*Dimethyl ((4-chlorophenyl)difluoromethyl)phosphonate (**3c**).* Pale yellow oil; yield 64% (52 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 3.84 (d, J = 10.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3 (d, J = 2.2 Hz), 130.8 (td, J = 22.2 Hz, J = 13.9 Hz), 128.8, 127.6 (td, J = 6.6 Hz, J = 2.1 Hz), 117.7 (td, J = 261.8 Hz, J = 218.0 Hz), 54.9 (d, J = 6.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.9 (d, J_{PF} = 115.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.17 (t, J_{PF} = 115.7 Hz); IR (film) 1492, 1277, 1258, 1092, 1045, 846, 826, 773, 735 cm^{-1}; EI-MS (*m/z*, relative intensity): 270 (18), 161 (100), 109 (12); HRMS (ESI) calcd for $C_9H_{11}ClF_2O_3P$ [(M+H)$^+$] 271.0097, found: 271.0095.

*Dimethyl ((4-bromophenyl)difluoromethyl)phosphonate (**3d**).* Pale yellow oil; yield 49% (46 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 3.84 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 131.3 (td, J = 22.2 Hz, J = 13.8 Hz), 127.8 (td, J = 6.7 Hz, J = 2.2 Hz), 125.6 (d, J = 2.6 Hz), 117.8 (td, J = 261.9 Hz, J = 217.7 Hz), 54.9 (d, J = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.1 (d, J_{PF} = 115.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.08 (t, J_{PF} = 115.5 Hz); IR (film) 1596, 1488, 1399, 1277, 1257, 1128, 1048, 1015, 966, 845, 821, 772, 731 cm^{-1}; EI-MS (*m/z*, relative intensity): 316 (15), 235 (12), 205 (100), 126 (25), 109 (17); HRMS (ESI) calcd for $C_9H_{11}BrF_2O_3P$ [(M+H)$^+$] 314.9592, found: 314.9598.

*Dimethyl ([1,1'-biphenyl]-4-yldifluoromethyl)phosphonate (**3e**).* Pale yellow solid; yield 50% (47 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.71 (m, 4H), 7.60 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36-7.41 (m, 1H), 3.86 (d, J = 10.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8 (d, J = 1.8 Hz), 139.9, 131.1 (td, J = 21.7 Hz, J = 13.5 Hz), 128.9, 128.0, 127.2, 127.2, 126.6 (td, J = 6.6 Hz, J = 2.2 Hz), 118.3 (td, J = 261.6 Hz, J = 217.8 Hz), 54.9 (d, J = 6.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.5 (d, J_{PF} = 116.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.66 (t, J_{PF} = 117.4 Hz); IR (film) 1270, 1121, 1038, 847, 778, 749, 731, 698 cm^{-1}; EI-MS (*m/z*, relative intensity): 312(16), 203(100), 152(7); HRMS (ESI) calcd for $C_{15}H_{16}F_2O_3P$ [(M+H)$^+$] 313.0800, found: 313.0802.

*Methyl 4-((dimethoxyphosphoryl)difluoromethyl)benzoate (**3f**).* Pale yellow solid; yield 73% (64 mg); R_f = 0.40 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 3.95 (s, 3H), 3.84 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 136.6 (td, J = 21.6

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Hz, *J* = 13.6 Hz), 132.4 (d, *J* = 1.5 Hz), 129.7, 126.3 (td, *J* = 6.6 Hz, *J* = 2.1 Hz), 117.8 (td, *J* = 262.2 Hz, *J* = 216.0 Hz), 55.0 (d, *J* = 6.6 Hz), 52.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.6 (d, J_{PF} = 113.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.02 (t, J_{PF} = 113.6 Hz); IR (film) 1729, 1280, 1186, 1113, 1047, 756, 733, 720, 697 cm^{-1}; EI-MS (*m/z*, relative intensity): 294 (30), 263 (15), 185 (100), 157 (14), 126 (20), 109 (18); HRMS (ESI) calcd for $C_{11}H_{17}F_2NO_5P$ [$(M+NH_4)^+$] 312.0807, found: 312.0803.

*Dimethyl ((4-cyanophenyl)difluoromethyl)phosphonate (**3g**).* Pale yellow oil; yield 56% (44 mg); R_f = 0.40 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.79 (m, 4H), 3.88 (d, *J* = 10.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (td, *J* = 22.0 Hz, *J* = 13.9 Hz), 132.3 (d, *J* = 1.1 Hz), 127.1 (td, *J* = 6.7 Hz, *J* = 2.2 Hz), 117.8, 117.3 (td, *J* = 262.6 Hz, *J* = 215.9 Hz), 115.0 (d, *J* = 1.9 Hz), 55.1 (d, *J* = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4 (d, J_{PF} = 112.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.51 (t, J_{PF} = 111.9 Hz); IR (film) 2234, 1279, 1257, 1042, 848, 833, 733 cm^{-1}; EI-MS (*m/z*, relative intensity): 261 (38), 152 (63), 109 (100); HRMS (ESI) calcd for $C_{10}H_{11}NF_2O_3P$ [$(M+H)^+$] 262.0439, found: 262.0439.

*Dimethyl ((3-chlorophenyl)difluoromethyl)phosphonate (**3h**).* Pale yellow oil; yield 55% (45 mg); R_f = 0.50 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.39-7.53 (m, 3H), 3.86 (d, *J* = 10.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7 (d, *J* = 1.1 Hz), 134.2 (td, *J* = 22.3 Hz, *J* = 14.0 Hz), 131.1 (d, *J* = 1.9 Hz), 129.9, 126.3 (td, *J* = 7.0 Hz, *J* = 2.3 Hz), 124.4 (td, *J* = 6.8 Hz, *J* = 2.2 Hz), 117.4 (td, *J* = 262.3 Hz, *J* = 217.2 Hz), 55.0 (d, *J* = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.0 (d, J_{PF} = 114.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.02 (t, J_{PF} = 113.9 Hz); IR (film) 1278, 1247, 1034, 842, 793, 746, 689 cm^{-1}; EI-MS (*m/z*, relative intensity): 270 (22), 161 (100), 109 (38); HRMS (ESI) calcd for $C_9H_{11}ClF_2O_3P$ [$(M+H)^+$] 271.0097, found: 271.0102.

General procedure for the hydrofluorination reaction of α-diazo phosphonates.[7b] To a solution of α-diazo phenylemthylphosphonate (0.20 mmol, 1.0 equiv) in DCM (2.0 mL) in a 10 mL Schlenk tube was added HF·pyridine (0.80 mmol, 4.0 equiv) at 0 °C. The mixture was allowed to stir at 0 °C and the reaction was deemed to complete until it had decolorized (5-15 min). Then the mixture was quenched with a saturated solution of $NaHCO_3$. The crude product was extracted with DCM for three times, washed with HCl (1 M), water and brine, dried with Na_2SO_4 and concentrated under reduced pressure. The crude mixture was then purified by column chromatography (silica gel, petroleum ether: EtOAc = 1:1) to afford the final products.

*Dimethyl(fluoro(phenyl)methyl)phosphonate (**4a**).* Colorless oil; yield 92% (40 mg); R_f = 0.25 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.50 (m, 5H), 5.72 (dd, J_{FH} = 44.8 Hz, J_{PH} = 8.0 Hz, 1H), 3.74 (d, *J* = 10.8 Hz, 3H), 3.73 (d, *J* = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, *J* = 17.7 Hz), 129.2 (t, *J* = 2.4 Hz), 128.5 (d, *J* = 2.1 Hz), 126.7 (t, *J* = 6.2 Hz), 89.1 (dd, *J* = 182.9 Hz, *J* = 169.0 Hz), 54.1 (d, *J* = 6.8 Hz), 53.7 (d, *J* = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -202.6 (dd, J_{PF} = 85.0 Hz, J_{FH} = 44.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.28 (d, J_{PF} = 85.5 Hz); IR (film) 1267, 1062, 1040, 839, 736, 700 cm^{-1}; EI-MS (*m/z*, relative intensity): 218 (21), 109 (100); HRMS (ESI) calcd for $C_9H_{13}FO_3P$ [$(M+H)^+$] 219.0581, found: 219.0587.

*Dimethyl ((4-chlorophenyl)fluoromethyl)phosphonate (**4b**).* Colorless oil; yield 95% (48 mg); R_f = 0.30 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.44 (m, 4H), 5.70 (dd, J_{FH} = 44.4 Hz, J_{PH} = 8.0 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 3H), 3.75 (d, *J* = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (t, *J* = 2.8 Hz), 131.2 (dd, *J* = 18.9 Hz, *J* = 1.2 Hz), 128.8 (d, *J* = 2.2 Hz), 128.0 (t, *J* = 6.2 Hz), 88.5 (dd, *J* = 183.3 Hz, *J* = 169.5 Hz), 54.2 (d, *J* = 6.8 Hz), 53.7 (d, *J* = 6.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -203.0 (dd, J_{PF} = 84.2 Hz, J_{FH} = 44.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.71 (d, J_{PF} = 84.2 Hz); IR (film) 1493, 1266, 1093, 1062, 1039, 847, 728 cm^{-1}; EI-MS (*m/z*, relative intensity): 252 (17), 143 (100), 109 (16); HRMS (ESI) calcd for $C_9H_{12}ClFO_3P$ [$(M+H)^+$] 253.0191, found: 253.0186.

*Dimethyl (fluoro(4-methoxyphenyl)methyl)phosphonate (**4c**).* Colorless oil; yield 87% (43 mg); R_f = 0.20 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.64 (dd, J_{FH} = 44.8 Hz, J_{PH} = 7.2 Hz, 1H), 3.82 (s, 3H), 3.77 (d, *J* = 10.8 Hz, 3H), 3.71 (d, *J* = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 128.8 (t, *J* = 6.0 Hz), 124.5 (d, *J* = 19.7 Hz), 114.1 (d, *J* = 1.2 Hz), 89.0 (dd, *J* = 181.5 Hz, *J* = 172.0 Hz), 55.3, 54.1 (d, *J* = 6.8 Hz), 53.7 (d, *J* = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -197.4 (dd, J_{PF} = 90.2 Hz, J_{FH} = 44.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.72 (d, J_{PF} = 90.2 Hz); IR (film) 1613, 1516, 1254, 1180, 1061, 1035, 842, 765, 732 cm^{-1}; EI-MS (*m/z*, relative intensity): 248 (10), 230 (4), 207 (7), 139 (100), 121 (16); HRMS (ESI) calcd for $C_{10}H_{18}FNO_4P$ [$(M+NH_4)^+$] 266.0952, found: 266.0956.

*Methyl 4-((dimethoxyphosphoryl)fluoromethyl)benzoate (**4d**).* Pale yellow oil; yield 96% (53 mg); R_f = 0.20 (petroleum ether: EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 5.81 (dd, J_{FH} = 44.8 Hz, J_{PH} = 8.8 Hz, 1H), 3.93 (s, 3H), 3.78 (d, *J* = 10.8 Hz, 3H), 3.72 (d, *J* = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.5 (dd, *J* = 18.2 Hz, *J* = 1.4 Hz), 130.8, 129.7 (d, *J* = 2.1 Hz), 126.3 (t, *J* = 6.2 Hz), 88.7 (dd, *J* = 184.6 Hz, *J* = 167.4 Hz), 54.3 (d, *J* = 6.8 Hz), 53.8 (d, *J* = 6.8 Hz), 52.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -205.7 (dd, J_{PF} = 81.2 Hz, J_{FH} = 44.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.37 (d, J_{PF} = 81.3 Hz); IR (film) 1726, 1285, 1114, 1062, 1040, 838, 773, 715 cm^{-1}; EI-MS (*m/z*, relative intensity): 276 (65), 245 (20) 233 (26), 167 (100), 136 (24), 109 (37); HRMS (ESI) calcd for $C_{11}H_{15}FO_5P$ [$(M+H)^+$] 277.0636, found: 277.0640.

*Dimethyl (fluoro(3-methoxyphenyl)methyl)phosphonate (**4e**).* Colorless oil; yield 89% (44 mg); R_f = 0.20 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.70 (dd, J_{FH} = 44.8 Hz, J_{PH} = 7.6 Hz, 1H), 3.83 (s, 3H), 3.75 (d, *J* = 10.8 Hz, 3H), 3.74 (d, *J* = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, *J* = 2.1 Hz), 134.0 (d, *J* = 18.0 Hz), 129.6 (d, *J* = 2.1 Hz), 118.8 (t, *J* = 6.2 Hz), 115.0 (t, *J* = 2.1 Hz), 111.9 (dd, *J* = 6.9 Hz, *J* = 5.7 Hz), 89.0 (dd, *J* = 183.2 Hz, *J* = 168.7 Hz), 55.2, 54.1 (d, *J* = 6.8 Hz), 53.7 (d, *J* = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -202.5 (dd, J_{PF} = 84.2 Hz, J_{FH} = 44.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.17 (d, J_{PF} = 84.6 Hz); IR (film) 1603, 1490, 1264, 1037, 7344, 656 cm^{-1}; EI-MS (*m/z*, relative intensity):

248 (32), 139 (100), 109 (18); HRMS (ESI) calcd for $C_{10}H_{15}FO_4P$ [$(M+H)^+$] 249.0686, found: 249.0685.

Dimethyl (fluoro(2-fluorophenyl)methyl)phosphonate ***(4f)***. Colorless oil; yield 95% (45 mg); R_f = 0.30 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, J = 7.6 Hz, 1H), 7.37-7.42 (m, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 8.8 Hz, 1H), 6.07 (dd, J_{FH} = 44.0 Hz, J_{PH} = 8.0 Hz, 1H), 3.85 (d, J = 10.8 Hz, 3H), 3.74 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (ddd, J = 247.6 Hz, J = 7.0 Hz, J = 5.0 Hz), 131.2 (dd, J = 8.1 Hz, J = 2.7 Hz), 128.9 (m), 124.5 (t, J = 2.8 Hz), 120.3 (dd, J = 19.7 Hz, J = 13.1 Hz), 115.4 (dd, J = 21.2 Hz, J = 1.6 Hz), 82.7 (ddd, J = 180.6 Hz, J = 174.1 Hz, J = 3.5 Hz), 54.1 (d, J = 6.6 Hz), 53.7 (d, J = 6.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.0 (s, 1F), -204.8 (ddd, J_{PF} = 89.5 Hz, J_{FH} = 44.4 Hz, J = 16.5 Hz, 1F); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.13 (d, J_{PF} = 88.3 Hz); IR (film) 1494, 1458, 1267, 1237, 1038, 840, 817, 761, 736 cm^{-1}; EI-MS (*m/z*, relative intensity): 236 (18), 127 (100), 109 (36); HRMS (ESI) calcd for $C_9H_{12}F_2O_3P$ [$(M+H)^+$] 237.0487, found: 237.0486.

Dimethyl (fluoro(naphthalen-1-yl)methyl)phosphonate ***(4g)***. Colorless oil; yield 93% (50 mg); R_f = 0.25 (petroleum ether: EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.88-7.91 (m, 2H), 7.80 (dd, J = 6.8 Hz, J = 2.4 Hz, 1H), 7.50-7.59 (m, 3H), 6.51 (dd, J_{FH} = 44.0 Hz, J_{PH} = 8.0 Hz, 1H), 3.74 (d, J = 10.4 Hz, 3H), 3.64 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (d, J = 1.7 Hz), 130.2 (dd, J = 5.2 Hz, J = 2.8 Hz), 130.0 (t, J = 2.8 Hz), 128.8, 128.5 (d, J = 17.9 Hz), 126.7, 126.0, 125.9 (dd, J = 9.9 Hz, J = 6.1 Hz), 125.2 (d, J = 3.0 Hz), 123.2, 87.0 (dd, J = 181.5 Hz, J = 170.7 Hz), 54.2 (d, J = 6.7 Hz), 53.7 (d, J = 6.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.9 (dd, J_{PF} = 87.2 Hz, J_{FH} = 44.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.56 (d, J_{PF} = 87.8 Hz); IR (film) 1262, 1058, 1044, 838, 815, 779 cm^{-1}; EI-MS (*m/z*, relative intensity): 268 (21), 159 (100), 133 (10); HRMS (ESI) calcd for $C_{13}H_{15}FO_3P$ [$(M+H)^+$] 269.0737, found: 269.0735.

General procedure for the bromofluorination reaction of *α*-diazo arylmethylphosphonates.[7b] To a suspension of *N*-bromosuccinimide (0.80 mmol, 4.0 equiv) in DCM (1.0 mL) in a 10 mL Schlenk tube was added HF·pyridine (1.6 mmol, 8.0 equiv) at 0 °C. The mixture was allowed to stir at 0 °C for 3 min. Then a solution of *α*-diazo phenylmethylphosphonate (0.20 mmol, 1.0 equiv) in DCM (1.0 mL) was added and the mixture was allowed to stir at the same temperature. The reaction was deemed to complete until it had decolorized (5-15 min). Then the mixture was quenched with a saturated solution of $NaHCO_3$. The crude product was extracted with DCM for three times, washed with water and brine, dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was then purified by column chromatography (silica gel, petroleum ether:EtOAc = 1:1) to afford the final products.

Dimethyl (bromofluoro(phenyl)methyl)phosphonate ***(5a)***. Colorless oil; yield 78% (43 mg); R_f = 0.65 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.72 (m, 2H), 7.41-7.44 (m, 3H), 4.01 (d, J = 10.4 Hz, 3H), 3.64 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7 (dd, J = 19.4 Hz, J = 5.7 Hz), 130.1, 128.4, 125.9 (dd, J = 8.9 Hz, J = 3.1 Hz), 100.0 (dd, J = 267.1 Hz, J = 191.1 Hz), 56.1 (d, J = 7.2 Hz), 55.3 (d, J = 6.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.2 (d, J_{PF} = 82.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.84 (d, J_{PF} = 82.6 Hz); IR (film) 1460, 1274, 1068, 1039, 732, 694 cm^{-1}; EI-MS (*m/z*, relative intensity): 217 (83), 189 (20), 187 (20), 105 (50), 93 (100); HRMS (ESI) calcd for $C_9H_{12}FBrO_3P$ [$(M+H)^+$] 296.9686, found: 296.9685.

Dimethyl (bromofluoro(p-tolyl)methyl)phosphonate ***(5b)***. Colorless oil; yield 66% (41 mg); R_f = 0.65 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.00 (d, J = 10.8 Hz, 3H), 3.64 (d, J = 10.8 Hz, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.7 (dd, J = 19.7 Hz, J = 5.9 Hz), 129.1, 125.8 (dd, J = 8.8 Hz, J = 3.3 Hz), 100.4 (dd, J = 267.2 Hz, J = 192.6 Hz), 56.1 (d, J = 7.0 Hz), 55.3 (d, J = 6.9 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.6 (d, J_{PF} = 83.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.87 (d, J_{PF} = 84.1 Hz); IR (film) 1275, 1188, 1076, 1038, 832, 745 cm^{-1}; EI-MS (*m/z*, relative intensity): 231 (86), 203 (16), 201 (16), 119 (74), 93 (100); HRMS (ESI) calcd for $C_{10}H_{14}FBrO_3P$ [$(M+H)^+$] 310.9842, found: 310.9842.

Methyl 4-(bromo(dimethoxyphosphoryl)fluoromethyl) benzoate ***(5c)***. Colorless oil; yield 52% (37 mg); R_f = 0.60 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.78 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 4.03 (d, J = 10.4 Hz, 3H), 3.94 (s, 3H), 3.67 (d, J = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 141.2 (dd, J = 19.8 Hz, J = 5.8 Hz), 131.6, 129.6, 125.9 (dd, J = 8.8 Hz, J = 3.3 Hz), 99.0 (dd, J = 267.7 Hz, J = 189.8 Hz), 56.3 (d, J = 7.1 Hz), 55.4 (d, J = 7.1 Hz), 52.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.0 (d, J_{PF} = 81.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.42 (d, J_{PF} = 82.5 Hz); IR (film) 1726, 1437, 1279, 1187, 1113, 1073, 1039, 837, 739 cm^{-1}; EI-MS (*m/z*, relative intensity): 275 (43), 163 (22), 107 (12), 93 (100); HRMS (ESI) calcd for $C_{11}H_{14}FBrO_5P$ [$(M+H)^+$] 354.9741, found: 354.9733.

Dimethyl (bromo(4-bromophenyl)fluoromethyl)phosphonate ***(5d)***. Colorless oil; yield 52% (39 mg); R_f = 0.65 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 4.02 (d, J = 10.4 Hz, 3H), 3.68 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (dd, J = 20.0 Hz, J = 5.9 Hz), 131.6, 127.5 (dd, J = 8.8 Hz, J = 3.4 Hz), 124.6, 99.3 (dd, J = 267.5 Hz, J = 191.6 Hz), 56.3 (d, J = 7.1 Hz), 55.4 (d, J = 7.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.6 (d, J_{PF} = 82.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.37 (d, J_{PF} = 82.0 Hz); IR (film) 1487, 1274, 1185, 1074, 1034, 1011, 833, 803, 751 cm^{-1}; EI-MS (*m/z*, relative intensity): 297 (55), 295 (55), 267 (20), 185 (15), 183 (15), 107 (25), 93 (100); HRMS (ESI) calcd for $C_9H_{11}FBr_2O_3P$ [$(M+H)^+$] 374.8791, found: 374.8789.

Dimethyl (bromofluoro(4-nitrophenyl)methyl)phosphonate ***(5e)***. Colorless oil; yield 56% (38 mg); R_f = 0.60 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 2H), 7.90 (dd, J = 8.8 Hz, J = 1.6 Hz, 2H), 4.07 (d, J = 10.4 Hz, 3H), 3.74 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.3 (dd, J = 20.0 Hz, J = 5.9 Hz), 127.1 (dd, J = 9.0 Hz, J = 3.1 Hz), 123.5, 98.0 (dd, J = 267.8 Hz, J = 189.0 Hz), 56.6 (d, J = 7.2 Hz), 55.4 (d, J = 7.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.4 (d, J_{PF} = 80.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.01 (d, J_{PF} = 80.4 Hz); IR (film) 1527, 1350, 1277, 1075, 1043, 733 cm^{-1}; EI-MS (*m/z*, relative intensity): 262 (45), 233 (10), 109 (58), 93

(100); HRMS (ESI) calcd for $C_9H_{14}FBrN_2O_5P$ [$(M+NH_4)^+$] 358.9802, found: 358.9810.

*Dimethyl (bromo(3-chlorophenyl)fluoromethyl)phosphonate (**5f**).* Colorless oil; yield 45% (30 mg); R_f = 0.65 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 1H), 7.60-7.61 (m, 1H), 7.35-7.41 (m, 2H), 4.03 (d, J = 10.8 Hz, 3H), 3.79 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7 (dd, J = 20.0 Hz, J = 5.9 Hz), 134.5 (t, J = 1.5 Hz), 130.2, 129.7, 125.8 (dd, J = 10.1 Hz, J = 2.5 Hz), 124.3 (dd, J = 8.3 Hz, J = 3.1 Hz), 98.8 (dd, J = 267.7 Hz, J = 191.0 Hz), 56.3 (d, J = 7.1 Hz), 55.4 (d, J = 7.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.6 (d, J_{PF} = 82.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.43 (d, J_{PF} = 81.6 Hz); IR (film) 1278, 1071, 1041, 842, 755, 730, 709, 684 cm^{-1}; EI-MS (*m/z*, relative intensity): 251 (30), 233 (10), 221 (10), 139 (14), 107 (21), 93 (100); HRMS (ESI) calcd for $C_9H_{11}FClBrO_3P$ [$(M+H)^+$] 330.9296, found: 330.9293.

General procedure for the aminofluorination reaction of *α*-diazo arylmethylphosphonates.[11] A 10 mL oven-dried Schlenk tube was charged with NFSI (32 mg, 0.10 mmol, 1.0 equiv). The tube was sealed and then evacuated and backfilled with N_2 for three times. Then a solution of *α*-diazo arylmethylphosphonate (0.15 mmol, 1.5 equiv) in DCE (1.0 mL) was added, and the mixture was allowed to stir at 60 ^{o}C for 24 h. The mixture was cooled down to room temperature and filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated *in vacuo* to remove the volatile materials. The crude residue was purified via column chromatography (silica gel, petroleum ether:EtOAc = 1:1) to give the final products.

*Dimethyl (fluoro(phenyl)(N-(phenylsulfonyl)phenyl sulfonamido)methyl)phosphonate (**6a**).* Colorless oil; yield 90% (46 mg); R_f = 0.55 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.93 (m, 4H), 7.56-7.61 (m, 2H), 7.42-7.49 (m, 6H), 7.29-7.33 (m, 1H), 7.21 (t, J = 8.0 Hz, 2H), 3.78 (d, J = 10.8 Hz, 3H), 3.41 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 134.2 (dd, J = 22.9 Hz, J = 2.2 Hz), 133.7, 129.3, 128.7, 128.5, 127.7 (dd, J = 6.9 Hz, J = 3.3 Hz), 127.6, 105.9 (dd, J = 226.8 Hz, J = 192.5 Hz), 55.1-55.3 (m, OMe); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.4 (d, J_{PF} = 95.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.68 (d, J_{PF} = 95.7 Hz); IR (film) 1450, 1390, 1272, 1179, 1082, 1043, 734, 686 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}FNO_7PS_2$ [$(M+H)^+$] 514.0554, found: 514.0556.

*Dimethyl ((4-chlorophenyl)fluoro(N-(phenylsulfonyl)phenyl sulfonamido)methyl)phosphonate (**6b**).* Colorless oil; yield 89% (49 mg); R_f = 0.60 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 8.0 Hz, 4H), 7.40 (dd, J = 8.4 Hz, J = 1.2 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.78 (d, J = 10.8 Hz, 3H), 3.50 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 135.6, 133.9, 133.0 (dd, J = 23.7 Hz, J = 2.2 Hz), 129.1 (dd, J = 6.9 Hz, J = 3.4 Hz), 128.6, 127.7, 123.8 (d, J = 4.4 Hz), 105.4 (dd, J = 226.7 Hz, J = 192.8 Hz), 55.2-55.4 (m, OMe); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.4 (d, J_{PF} = 95.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.46 (d, J_{PF} = 95.9 Hz); IR (film) 1449, 1391, 1272, 1180, 1042, 745, 722, 685 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}ClFNO_7PS_2$ [$(M+H)^+$] 548.0164, found: 548.0159.

*Dimethyl ((4-bromophenyl)fluoro(N-(phenylsulfonyl)phenyl sulfonamido)methyl)phosphonate (**6c**).* Colorless oil; yield 78% (46 mg); R_f = 0.60 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 4H), 7.62 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 8.0 Hz, 4H), 7.29-7.34 (m, 4H), 3.79 (d, J = 10.8 Hz, 3H), 3.50 (d, J = 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 133.8, 133.5 (dd, J = 23.4 Hz, J = 2.1 Hz), 130.7, 129.3 (dd, J = 6.9 Hz, J = 3.4 Hz), 128.6, 128.6, 123.9, 105.4 (dd, J = 227.2 Hz, J = 193.1 Hz), 55.2-55.4 (m, OMe); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.7 (d, J_{PF} = 95.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.31 (d, J_{PF} = 96.2 Hz); IR (film) 1449, 1391, 1272, 1180, 1075, 1044, 721, 685 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}BrFNO_7PS_2$ [$(M+H)^+$] 591.9659, found: 591.9670.

General procedure for the synthesis of fluorinated alkenes. A 10 mL oven-dried Schlenk tube was charged with Cs_2CO_3 (1.0 mmol, 2.5 equiv, 325 mg). The tube was sealed and then evacuated and backfilled with N_2 for three times. Then a solution of *α*-fluoro phosphonate (0.60 mmol, 1.5 equiv) in 1,4-dioxane (1.0 mL) and PhCHO (42 mg, 0.40 mmol, 1.0 equiv) was successively added, and the mixture was allowed to stir at 90 ^{o}C for 24 h. The mixture was cooled down to room temperature and filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified via preparative thin-layer chromatography (silica gel, petroleum ether) to give the final products.

*(Z)-(1-Fluoroethene-1,2-diyl)dibenzene (**7a**).*[15] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.66 (m, 4H), 7.34-7.43 (m, 5H), 7.25-7.28 (m, 1H), 6.32 (d, J = 39.6 Hz, 1H).

*(E)-(1-Fluoroethene-1,2-diyl)dibenzene (**7a'**).*[15] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.2 Hz, 2H), 7.27-7.35 (m, 3H), 7.15-7.22 (m, 5H), 6.45 (d, J = 21.6 Hz, 1H).

*(Z)-1-Chloro-4-(1-fluoro-2-phenylvinyl)benzene (**7b**).*[16] Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.35-7.39 (m, 4H), 7.23-7.28 (m, 1H), 6.27 (d, J = 39.6 Hz, 1H).

*(E)-1-Chloro-4-(1-fluoro-2-phenylvinyl)benzene (**7b'**).*[17] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.35 (m, 9H), 6.47 (d, J = 21.6 Hz, 1H).

*(Z)-1-(1-Fluoro-2-phenylvinyl)-3-methoxybenzene (**7c**).* Colorless oil. R_f = 0.15 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.2 Hz, 2H), 7.22-7.38 (m, 5H), 7.16 (t, J = 2.0 Hz, 1H), 6.89-6.91 (m, 1H), 6.30 (d, J = 39.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J = 2.2 Hz), 157.0 (d, J = 257.2 Hz), 134.2 (d, J = 27.7 Hz), 133.6 (d, J = 2.9 Hz), 129.6 (d, J = 2.0 Hz), 128.9 (d, J = 7.9Hz), 128.6, 127.3 (d, J = 2.4 Hz), 116.8 (d, J = 7.3 Hz), 114.6, 109.8 (d, J = 7.9 Hz), 106.1 (d, J = 10.5 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6 (d, J = 39.1 Hz); IR (film) 1607, 1581, 1489, 1290, 1223, 1172, 1052, 1025, 778, 750, 690 cm^{-1}; EI-MS (*m/z*, relative intensity): 228 (100), 212 (19), 196 (30), 183 (28), 165 (20); HRMS (ESI) calcd for $C_{15}H_{14}FO$ [$(M+H)^+$] 229.1023, found: 229.1030.

*(E)-1-(1-Fluoro-2-phenylvinyl)-3-methoxybenzene (**7c'**).* Colorless oil. R_f = 0.20 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.25 (m, 6H), 7.01 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.87 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), 6.46 (d, J = 21.6 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 157.6 (d, J =

245.0 Hz), 133.7 (d, *J* = 12.4 Hz), 133.0 (d, *J* = 28.9 Hz), 129.3, 128.9 (d, *J* = 2.8 Hz), 128.4, 127.1, 120.6 (d, *J* = 5.1 Hz), 115.8 (d, *J* = 1.0 Hz), 113.1 (d, *J* = 5.1 Hz), 109.4 (d, *J* = 30.8 Hz), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.3 (d, *J* = 21.4 Hz); IR (film) 1581, 1489, 1290, 1251, 1161, 1042, 790, 754, 695 cm^{-1}; EI-MS (*m/z*, relative intensity): 228 (100), 212 (19), 196 (25), 183 (24), 165 (18); HRMS (ESI) calcd for $C_{15}H_{14}FO$ [$(M+H)^+$] 229.1023, found: 229.1022.

(Z)-1-Fluoro-2-(1-fluoro-2-phenylvinyl)benzene ***(7d)***. Colorless solid; R_f = 0.55 (petroleum ether); melting point 48-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.65 (m, 3H), 7.10-7.39 (m, 6H), 6.52 (d, *J* = 41.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (dd, *J* = 250.6 Hz, *J* = 5.6 Hz), 151.9 (dd, *J* = 254.9 Hz, *J* = 6.0 Hz), 133.6 (d, *J* = 2.5 Hz), 130.2 (d, *J* = 8.8 Hz), 129.3 (d, *J* = 8.0 Hz), 128.5, 127.6 (d, *J* = 2.3 Hz), 127.2 (dd, *J* = 9.1 Hz, *J* = 1.9 Hz), 124.3 (dd, *J* = 3.6 Hz, *J* = 1.1 Hz), 121.0 (dd, *J* = 29.7 Hz, *J* = 10.7 Hz), 116.3 (dd, *J* = 22.7 Hz, *J* = 2.6 Hz), 111.5 (dd, *J* = 13.7 Hz, *J* = 8.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3 (dd, J_{HF} = 41.4 Hz, J_{FF} = 8.6 Hz, 1F), -111.7 (m, 1F); IR (film) 1497, 1454, 1016, 848, 757, 692 cm^{-1}; EI-MS (*m/z*, relative intensity): 216 (100), 196 (42); HRMS (EI) calcd for $C_{14}H_{10}F_2$ [M^+] 216.0745, found: 216.0739.

(E)-1-Fluoro-2-(1-fluoro-2-phenylvinyl)benzene (7d'). Colorless oil. R_f = 0.45 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.42 (m, 2H), 7.03-7.18 (m, 7H), 6.58 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 251.6 Hz), 153.1 (d, *J* = 246.5 Hz), 133.1 (d, *J* = 10.9 Hz), 131.8 (dd, *J* = 8.1 Hz, *J* = 2.0 Hz), 131.3 (t, *J* = 2.6 Hz), 128.3, 128.2(d, *J* = 2.8 Hz), 127.2, 124.2 (d, *J* = 3.6 Hz), 120.4 (dd, *J* = 28.5 Hz, *J* = 14.6 Hz), 116.3 (d, *J* = 21.1 Hz), 112.4 (d, *J* = 29.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.0 (dd, J_{HF} = 19.9 Hz, J_{FF} = 8.6 Hz, 1F), -111.0 (m, 1F); IR (film) 1494, 1454, 1229, 1177, 1106, 1048, 1027, 869, 828, 762, 695 cm^{-1}; EI-MS (*m/z*, relative intensity): 216(100), 196(35); HRMS (EI) calcd for $C_{14}H_{10}F_2$ [M^+] 216.0745, found: 216.0740.

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Notes and references

1 For selected reviews, see: (*a*) J. A. Gladysz, D. P. Curran, I. T. Horváth, *Handbook of Fluorous Chemistry*; Wiley-VCH: Weinheim, 2005; (*b*) T. Umemoto, In *Fluorine-Containing Synthons*; V. A. Soloshonok, Ed.; American Chemical Society: Washington, DC, 2005; (*c*) M.; Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.,* 2005, **44**, 214-231; (*d*) K. Müller, C. Faeh, F. Diederich, *Science,* 2007, **317**, 1881-1886; (*e*) T. Furuya, A. S. Kamlet, T. Ritter, *Nature,* 2011, **473**, 470-477; (*f*) C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.,* 2015, **54**, 3216-3221.

2 For selected publications, see: (*a*) G. M. Blackburn, D. E. Kent, F. Kolkmann, *J. Chem. Soc. Chem. Commun.,* 1981, 1188-1190; (*b*) G. M. Blackburn, D. E. Kent, F. Kolkmann, *J. Chem. Soc. Perkin Trans., 1* 1984, 1119-1125; (*c*) W. Howson, J. M. Hills, G. M. Blackburn, M. Broekman, *Bioorg. Med. Chem. Lett.,* 1991, **1**, 501-502; (*d*) Z.-Y. Zhang, *Acc. Chem. Res.,* 2003, **36**, 385-392; (*e*) P. A. Cole, A. D. Courtney, K. Shen, Z. Zhang, Y. Qiao, W. Lu, D. M. Williams, *Acc. Chem. Res.*, 2003, **36**, 444-452; (*f*) V. D. Romanenko, V. P. Kukhar, *Chem. Rev.*, 2006, **106**, 3868-3935.

3 (*a*) T. R. Burke, M. S. Smyth, A. Otaka, M. Nomizu, P. P. Roller, G. Wolf, R. Case, S. E. Shoelson, *Biochemistry,* 1994, **33**, 6490-6494; (*b*) T. R. Burke, B. Ye, X. Yan, S. Wang, Z. Jia, L. Chen, Z.-Y. Zhang, D. Barford, *Biochemistry,* 1996, **35**, 15989-15996; (*c*) K. Shen, Y. Keng, L. Wu, X. Guo, D. S. Lawrence, Z. Zhang, *J. Biol. Chem.,* 2001, **276**, 47311-47319; (*d*) I. G. Boutselis, X. Yu, Z.-Y. Zhang, R. F. Borch, *J. Med. Chem.,* 2007, **50**, 856-864; (*e*) P. K. Mandal, W. S.-L. Liao, J. S. McMurray, *Org. Lett.,* 2009, **11**, 3394-3397; (*f*) S. Hikishima, M. Hashimoto, L. Magnowska, A. Bzowska, T. Yokomatsu, *Bioorg. Med. Chem.,* 2010, **18**, 2275-2284; (*g*) J.-X. Ong, C.-W. Yap, W.-H. Ang, *Inorg. Chem.,* 2012, **51**, 12483-12492.

4 (*a*) D. Solas, R. L. Hale, D. V. Patel, *J. Org. Chem.,* 1996, **61**, 1537-1539; (*b*) Z. Lian, H. Yin, S. D. Friis, T. Skrydstrup, *Chem. Commun.,* 2015, **51**, 7831-7834; (*c*) S. D. Taylor, A. N. Dinaut, A. N. Thadani, Z. Huang, *Tetrahedron Lett.,* 1996, **37**, 8089-8092; (*d*) S. D. Taylor, C. C. Kotoris, A. N. Dinaut, M.-J. Chen, *Tetrahedron,* 1998, **54**, 1691-1714; (*e*) B. Zagipa, A. Hidaka, Y. Cao, T. Fuchigami, *J. Fluorine Chem.,* 2006, **127**, 552-557.

5 For representative publications, see: (*a*) T. Yokomatsu, T. Murano, K. Suemune, S. Shibuya, *Tetrahedron,* 1997, **53**, 815-822; (*b*) X. Jiang, L. Chu, F. Qing, *New J. Chem.,* 2013, **37**, 1736-1741; (*c*) Z. Feng, Q.-Q. Min, Y.-L. Xiao, B. Zhang, X. Zhang, *Angew. Chem. Int. Ed.,* 2014, **53**, 1669-1673; (*d*) L. Wang, X.-J. Wei, W.-L. Lei, H. Chen, L.-W. Wu, Q. Liu, *Chem. Commun.,* 2014, **50**, 15916-15919; (*e*) A. Bayle, C. Cocaud, C. Nicolas, O. R. Martin, T. Poisson, X. Pannecoucke, *Eur. J. Org. Chem.,* 2015, 3787-3792; (*f*) M. V. Ivanova, A. Bayle, T. Besset, T. Poisson, X. Pannecoucke, *Angew. Chem. Int. Ed.,* 2015, **54**, 13406-13410.

6 (*a*) Y. Zhou, F. Ye, X. Wang, S. Xu, Y. Zhang, J. Wang, *J. Org. Chem.,* 2015, **80**, 6109-6118; (*b*) C. Wu, F. Ye, G. Wu, S. Xu, G. Deng, Y. Zhang, J. Wang, *Synthesis,* 2016*,* **48***,* 751-760; (*c*) Y. Zhou, F. Ye, Q. Zhou, Y. Zhang, J. Wang, *Org. Lett.,* 2016, **18**, 2024-2027.

7 (*a*) J. Tao, R. Tran, G. K. Murphy, *J. Am. Chem. Soc.,* 2013, **135**, 16312-16315; (*b*) E. Emer, J. Twilton, M. Tredwell, S. Calderwood, T. L. Collier, B. Liégault, M. Taillefer, V. Gouverneur, *Org. Lett.,* 2014, **16**, 6004-6007. (*c*) G. S. Sinclair, R. Tran, J. Tao, W. S Hopkins, G. K. Murphy, *Eur. J. Org. Chem.,* 2016, doi/10.1002/ejoc.201600773.

8 G. G. Cox, D. J. Miller, C. J. Moody, R.-E. H. B. Sie, *Tetrahedron,* 1994, **50**, 3195-3212.

9 For selected publications, see: (*a*) R. Pasceri, H. E. Bartrum, C. J. Hayes, C. J. Moody, *Chem. Commun.,* 2012, **48**, 12077-12079; (*b*) A. K. Yadav, V. P. Srivastava, L. D. S. Yadav, *Chem. Commun.,* 2013, **49**, 2154-2156; (*c*) C. Qin, H. M. L. Davies, *Org. Lett.,* 2013, **15**, 6152-6154.

10 G. A. Olah, J. Welch, *Synthesis,* 1974, 896-898.

11 G. Chen, J. Song, Y. Yu, X. Luo, C. Li, X. Huang, *Chem. Sci.,* 2016, **7**, 1786-1790.

12 (*a*) R. S. Marmor, D. Seyferth, *J. Org. Chem.,* 1971*,* **36***,* 128-136; (*b*) D. Seyferth, R. S. Marmor, P. Hilbert, *J. Org. Chem.,* 1971, **36**, 1379-1386.

13 (*a*) F. Ye, C. Wang, Y. Zhang, J. Wang, *Angew. Chem., Int. Ed.,* 2014, **53**, 11625-11628; (*b*) J. Pietruszka, A. Witt, *Synthesis,* 2006, 4266-4268.

14 (*a*) M. A. Arrica, T. Wirth, *Eur. J. Org. Chem.,* 2005, 395-403; (*b*) K. P. Landge, K. S. Jang, S. Y. Lee, D. Y. Chi, *J. Org. Chem.,* 2012, **77**, 5705-5713.

15 O. A. Wong, Y. Shi, *J. Org. Chem.,* 2009, **74**, 8377-8380.

16 C. Chen, K. Wilcoxen, Y. -F. Zhu, K. Kim, J. R. McCarthy, *J. Org. Chem.,* 1999, **64**, 3476-3482.

17 C. Chen, K. Wilcoxen, C. Q. Huang, N. Strack, J. R. McCarthy, *J. Fluorine Chem.,* 2000, **101**, 285-290.

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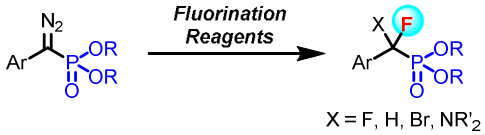

A general approach towards diverse fluorinated phosphonates *via* geminal difunctionalization reactions of *α*-diazo arylmethylphosphonates is reported.