Syntheses of Mono-, Di-, and Trifluorinated Styrenic Monomers

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Abstract: Concise syntheses of gram quantities of three fluorinated α-methylstyrenic monomers suitable for polymerisation studies are disclosed, all based on the use of reasonably priced commercially available starting materials and reagents.

Key words: fluorination, nucleophilic fluoroalkylation, palladium catalysis, monomer synthesis, functional fluoropolymers

Fluoropolymers are performance materials with unique properties.[1] Key characteristics are their advantageously high thermostability and chemical inertness combined with low refractive index, friction coefficient, dielectric constant, dissipation factor, as well as low water absorptivity. These high value products have, therefore, found applications in various fields of advanced technology (e.g., chemical and automobile industries, fuel cell membranes, engineering, microelectronics, optics,[2,3] textile finishing,[3] and aeronautics[4]). Fluorinated aromatic polymers belong to a highly desirable subcategory of fluorinated polymers, but only few examples of the copolymerisation of fluorine-functionalised aromatic monomers with fluoroolefins have been reported to date.[5]

With the objective to prepare new functional fluoropolymers for fuel cell membranes, we have developed convenient and cost-effective routes to access various noncommercially available fluorinated styrenic monomers of increasing fluorine content. The α-(monofluoromethyl)styrene **I** (FMST), α-(difluoromethyl)styrene **II** (DFMST) and α-(trifluoromethyl)styrene **III** (TFMST), either unsubstituted at the aryl group or possessing a bromo substituent at the *para* position, were identified as prime candidates for further studies (Figure 1). (Co)polymerisation of these monomers could deliver material suitable for post-modification (e.g., sulfonylation or phosphonylation). Alternatively, if this strategy suffers from lack of control over the degree and location of functionalisation, these monomers can be manipulated prior to polymerisation.

The monofluorinated monomers FMST **3a** and 4-BrFMST **3b** were prepared following a two-step process (Scheme 1). In preliminary work, we studied the reactivity of allylsilanes **2a**,**b** (3–5 mmol scale), which are prone to electrophilic fluorination. A palladium-catalysed cross-coupling reaction of allyltrimethylsilane with the corresponding triflates **1a** or **1b** delivered the desired allylsilanes **2a**,**b** in good yields. Subsequent fluorodesilylation (S_E2') of these allylsilanes was conducted at room temperature with Selectfluor in acetonitrile and led within two hours to **3a** and **3b** in 93% and 76% isolated yield, respectively (Scheme 1, Table 1).[6] Studies aimed at probing the efficiency of this synthetic route for the preparation of larger quantities of material (up to 40 and 30 mmol scale) indicated that the overall yields for this sequence decreased significantly, with both the synthesis of allylsilane and the fluorodesilylation becoming more problematic (Table 1). Attempts to improve the synthesis of the allylphenylsilane derivatives **2a**,**b** using ionic-liquid-promoted palladium-catalysed coupling of halobenzenes with allyltrimethylsilane were not fruitful.[7] This limitation combined with the high cost of the aryl triflates **1a**,**b** and of the reagents necessary to prepare the corresponding allylsilanes prompted us to examine alternative routes.

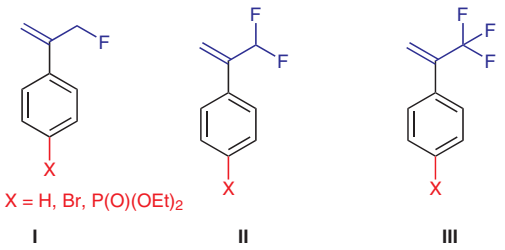
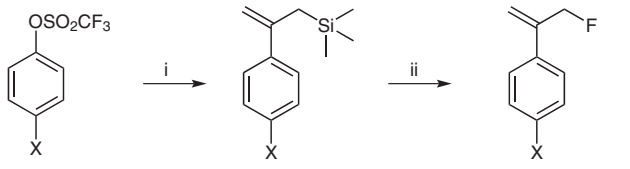


Figure 1 Three classes of fluorinated monomers: α-(monofluoromethyl)styrenes **I** (FMST), α-(difluoromethyl)styrenes **II** (DFMST), α-(trifluoromethyl)styrenes **III** (TFMST).



Scheme 1 Synthesis of α-(monofluoromethyl)styrenes **3** by electrophilic fluorodesilylation of allylsilanes **2** with Selectfluor. *Reagents and conditions:* (i) for **1a**: $Pd(OAc)_2$ (0.03 equiv) dppf (0.13 equiv), allylTMS (5 equiv), Et_3N (2 equiv), MeCN, 60 °C, 20 h; for **1b** $Pd(OAc)_2$ (0.03 equiv), dppf (0.13 equiv), allylTMS (5 equiv), K_2CO_3 (2 equiv), MeCN, 65 °C, 20 h; (ii) (b) Selectfluor (1.1 equiv), MeCN, r.t., 2 h.

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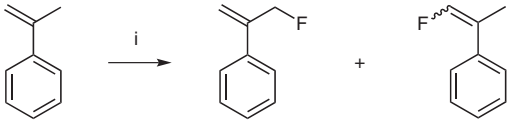
Table 1 Electrophilic Fluorination of **2a**,**b**

Entry	Triflate (mmol)	X	Silane[a] (yield)	Allylic fluoride (yield)	Overall yield[b] (%)
1	**1a** (3)	H	**2a** (84%)	**3a** (93%)	78
2	**1a** (6)	H	**2a** (83%)	**3a** (74%)	61
3	**1a** (20)	H	**2a** (72%)	**3a** (72%)	52
4	**1a** (40)	H	**2a** (60%)	**3a** (65%)	39
5	**1b** (5)	Br	**2b** (78%)	**3b** (76%)	59
6	**1b** (15)	Br	**2b** (67%)	**3b** (65%)	43
7	**1b** (30)	Br	**2b** (57%)	**3b** (63%)	36

[a] Isolated yield.
[b] Isolated overall yield over 2 steps.

Recently, Luo and Loh reported a one-step direct electrophilic fluorination of α-methylstyrene (**4**) with Selectfluor.[8] For this less reactive alkene, the fluorination required higher temperatures and extended reaction times to reach completion. Carried out on a 2 mmol scale, this reaction was found reproducible and delivered (3-fluoroprop-1-en-2-yl)benzene (**3a**) in 75% isolated yield. When using up to 38 mmol of α-methylstyrene (**4**), the fluorination led to the formation of significant amounts of byproducts identified as the isomerised fluoroalkenes (*E*)-**5** and (*Z*)-**5**. The subsequent purification proved difficult and this was directly reflected in the low isolated yield of the pure desired product **3a** (35%). This route was therefore abandoned (Scheme 2).



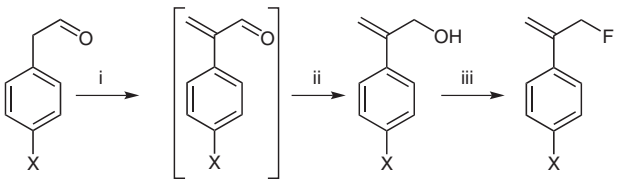
4 **3a** (35%) (*E*/*Z*)-**5** (9%)

Scheme 2 Direct electrophilic fluorination of α-methylstyrene.[8] *Reagents and conditions:* (i) Selectfluor (1.1 equiv), DMF, 75 °C, 18 h.

At this stage, the availability of both diethylaminosulfur trifluoride (DAST) and 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride (FLUOLEAD), two reagents suitable for nucleophilic fluorination, encouraged further work. The synthesis of allylic alcohols **8a**,**b** to be used as starting materials was first examined using metal-mediated coupling chemistry. Both ionic-liquid-promoted palladium-catalysed Heck coupling of various halobenzenes with allylic alcohols[9] and nickel-catalysed cross-coupling of 2-chloroallylic alcohol with Grignard reagents[10] were attempted, but these transformations were either poorly regioselective or low yielding.

The most convenient large-scale synthesis (up to 100 mmol) of **8a**,**b** began with the aldehydes **6a** and **6b**. α-Methylenation was performed by reacting these aldehydes with the Eschenmoser's salt [dimethyl(methylene)ammonium iodide] in the presence of a large excess of triethylamine. Without isolation, the resulting products were reduced, leading uneventfully to the desired allylic alcohols **8a** and **8b** in moderate to good yields over two steps. These alcohols were converted into the corresponding fluorides **3a** and **3b** by direct nucleophilic fluorination. In comparative studies, both DAST and FLUOLEAD, a more stable reagent used in combination with triethylamine trihydrofluoride, were employed.[11] The yields for the fluorination were consistent and comparable, independent of the reagent or the scale of the reaction, averaging 67% and 61% for **3a** and **3b**, respectively.

This three-step synthetic route to α-(monofluoromethyl)styrenes using direct nucleophilic fluorination was found to be easy to implement, selective, cost-effective, and easily scalable (up to 100 mmol) giving the desired allylic fluorides **3a** (X = H) and **3b** (X = Br) in 47% and 38% overall yield, respectively (Scheme 3, Table 2).



6a (X = H) 100 mmol scale
6b (X = Br) 70 mmol scale
7a (X = H)
7b (X = Br)
8a (X = H, 73%) over 2 steps
8b (X = Br, 66%) over 2 steps
3a (X = H, 65%)
3b (X = Br, 58%)

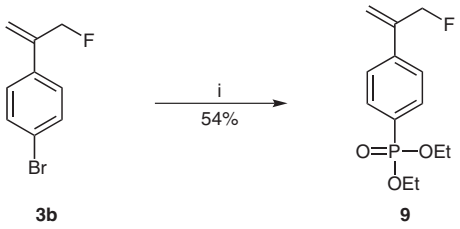
Scheme 3 Synthesis of α-(monofluoromethyl)styrenes **3** by direct nucleophilic deoxyfluorination of the allylic alcohols **8** with DAST or FLUOLEAD. *Reagents and conditions:* (i) $Me_2N^+{=}CH_2\ I^-$ (2 equiv), Et_3N (10 equiv), CH_2Cl_2, r.t., 30 min; (ii) $NaBH_4$ (1 equiv), $CeCl_3{\cdot}7\ H_2O$ (1 equiv), r.t., 1 h; (iii) DAST (1.5 equiv), CH_2Cl_2, r.t., 6 h or FLUOLEAD (1.25 equiv), $Et_3N{\cdot}3$ HF (1.25 equiv), CH_2Cl_2, r.t., 6 h.

The monofluorinated styrenic monomer **3b** was further manipulated taking advantage of the presence of the bromo substituent. The introduction of a phosphonate group was elected as a suitable post-modification since it is well documented that polymers substituted with phosphonic acid groups display advantageous characteristics for fuel cell membrane applications.[12] To form the necessary aryl–P bond, different approaches were considered inclusive of the classical Michaelis–Arbuzov or Michaelis–Becker reactions[13] as well as $NiCl_2$[14] or $Pd(PPh_3)_4$[15] mediated cross-coupling processes. However, metal–halogen exchange followed by P–C bond formation proved to be the most efficient protocol. Accordingly, the reaction of the in situ generated aryllithium intermediate derived from **3b** with diethyl chlorophosphate produced the desired arylphosphonate **9** (4-PFMST) in 54% isolated yield. This reaction was performed on a 25.7 mmol scale (Scheme 4).[16]

Table 2 Nucleophilic Fluorination of **8a**,**b**

Entry	Aldehyde (mmol)	X	Allylic alcohol[a] (yield)	Allylic fluoride (yield)	Overall yield[b] (%)
1	**6a** (5)	H	**8a** (75%)	**3a** (68%)[c] **3a** (65%)[d]	51[c] 49[d]
2	**6a** (10)	H	**8a** (73%)	**3a** (69%)[c] **3a** (70%)[d]	50[c] 51[d]
3	**6a** (50)	H	**8a** (75%)	**3a** (67%)[c] **3a** (66%)[d]	50[c] 49[d]
4	**6a** (100)	H	**8a** (73%)	**3a** (65%)[c] **3a** (67%)[d]	47[c] 49[d]
5	**6b** (5)	Br	**8b** (67%)	**3b** (65%)[c] **3b** (65%)[d]	43[c] 43[d]
6	**6b** (10)	Br	**8b** (59%)	**3b** (61%)[c] **3b** (63%)[d]	36[c] 37[d]
7	**6b** (50)	Br	**8b** (63%)	**3b** (59%)[c] **3b** (57%)[d]	37[c] 36[d]
8	**6b** (70)	Br	**8b** (66%)	**3b** (58%)[c] **3b** (59%)[d]	38[c] 39[d]

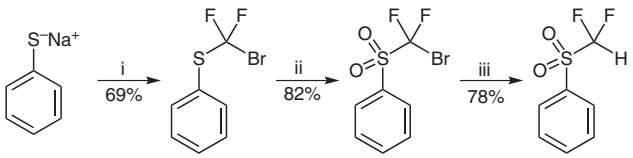
[a] Isolated yield over 2 steps.
[b] Isolated overall yield over 3 steps.
[c] Fluorination with DAST.
[d] Fluorination with FLUOLEAD.



3b **9**

Scheme 4 Synthesis of diethyl 4-(3-fluoroprop-1-en-2-yl)phenylphosphonate (**9**). *Reagents and conditions:* (i) *n*-BuLi (1.1 equiv), $(EtO)_2P(O)Cl$ (1.1 equiv), THF, –78 °C, 4 h.

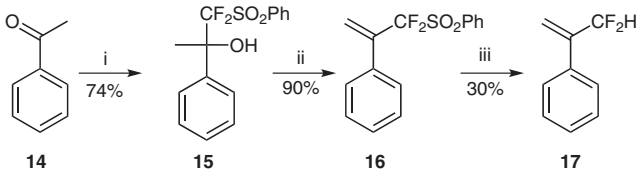
Our long-term objective is to examine the influence of the fluorine content of styrenic monomers on both reactivity and copolymer composition. Since the difluoromethyl group has been used extensively to modulate the physicochemical properties of organic molecules, we considered accessing the α-(difluoromethyl)styrene **17** for subsequent polymerisations.[17] Attempts to access this monomer by direct fluorination of the corresponding 1,3-dithiolane using DAST in the presence of either 1,3-dibromo-5,5-dimethylhydantoin or *N*-bromosuccinimide were not successful.[18] We, therefore, examined an alternative strategy based on a nucleophilic difluoromethylation process using the well-documented reagent difluoromethyl phenyl sulfone (**13**) (Scheme 5). This reagent was prepared by using a three-step literature protocol.[19] The reaction of sodium thiophenolate (**10**, 40 mmol scale) with dibromodifluoromethane in the presence of catalytic amount of dibenzo-18-crown-6 ether resulted in the formation of bromodifluoromethyl sulfide **11** in a good yield (69%). Oxidation of **11** with excess *m*-chloroperoxybenzoic acid gave the desired sulfone **12** in 82% yield (Lit. 83%).[19a] This bromodifluoromethyl phenyl sulfone (**12**) was converted into the corresponding difluoromethylating reagent **13** by treatment with chlorotrimethylsilane in the presence of *n*-butyllithium at –78 °C.[20] This three-step synthetic route to difluoromethyl phenyl sulfone (**13**) was found to be effective and easily scalable giving the desired product in 44% overall yield.



10 (40 mmol) **11** (27.6 mmol) **12** (22.6 mmol) **13** (17.7 mmol)

Scheme 5 Three-step synthesis of difluoromethyl phenyl sulfone (**13**). *Reagents and conditions:* (i) CF_2Br_2 (3 equiv), dibenzo-18-crown-6 (0.02 equiv), Et_2O, –40 °C, 8 h; (ii) MCPBA (3 equiv), CH_2Cl_2, 0–20 °C, 2 h; (iii) *n*-BuLi (1.8 equiv), TMSCl (1.5 equiv), THF, –78 °C, 1 h, silica gel purification.

The base-induced coupling of **13** with acetophenone **14** was performed in tetrahydrofuran at –78 °C.[21] The resulting carbinol **15** was isolated in 74% yield (Scheme 6). Dehydration of **15** was high yielding (90%) using phosphorus pentoxide in toluene at reflux. Reductive desulfonylation of the resulting difluorinated sulfone **16** afforded the desired α-(difluoromethyl)styrene **17**, albeit in low yield.[22] Despite the low yield of the last step, this synthetic route was found easy to implement and was applied

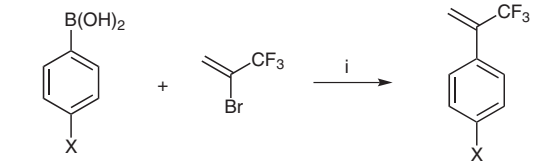


Scheme 6 Synthesis of α-(difluoromethyl)styrene **17** by nucleophilic difluoromethylation of acetophenone **14** with difluoromethyl phenyl sulfone (**13**). *Reagents and conditions:* (i) acetophenone (**14**, 2 equiv), $PhSO_2CF_2H$ (**13**, 1 equiv), LiHMDS (2 equiv), HMPA–THF, –78 °C, 2 h; (ii) P_2O_5 (3 equiv), toluene, reflux, 2 h; (iii) Mg (15 equiv), AcOH–NaOAc buffer, DMF, r.t., 2 h.

for the synthesis of gram quantities of **17** (20 mmol scale) allowing for polymerisation studies.

Preliminary efforts to access the trifluorinated monomers **20a**,**b** (TFMST) focused on palladium-catalysed cross-coupling reactions of both organoboron compounds with 3,3,3-trifluoroprop-1-en-2-yl tosylate,[23] and of halobenzenes with a 1:1 complex of 3,3,3-trifluoropropen-2-yl-zinc bromide and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[24] These reactions failed to deliver **20a** leading instead to complex mixture of products. Pleasingly, the Suzuki coupling of organoboron **18a** with 2-bromo-3,3,3-trifluoropropene (**19**) was successful affording the α-(trifluoromethyl)styrene derivatives **20a** in good chemical yield. The coupling was also successful with the *para*-brominated phenylboronic acid **18b** leading to **20b** in 54% yield. This chemistry was routinely performed on a 30 mmol scale (Scheme 7, Table 3).[25]

In conclusion, we have developed efficient routes to novel functional aromatic fluorinated monomers. Various α-mono-, α-di-, and α-trifluoromethyl-substituted styrene analogues were made available in gram quantities allowing for subsequent polymerisation studies. If superior polymers emerge, further improvement will be necessary to carry out the synthesis of these monomers on a much larger scale. The results of (co)polymerisation of these monomers with styrene or fluorinated olefins will be reported in due course.



Scheme 7 Synthesis of α-(trifluoromethyl)styrenes **20a**,**b** by Suzuki coupling of the phenylboronic acids **18a**,**b** with 2-bromo-3,3,3-trifluoropropene (**19**). *Reagents and conditions:* (i) $PdCl_2(PPh_3)_2$ (0.03 equiv), $AsPh_3$ (0.15 equiv), DME–THF (1:1), 2 M KOH, 74 °C, 16 h.

Table 3 Palladium-Catalysed Cross-Coupling of **18a**,**b** with **19**

Entry	Phenylboronic acid (mmol)	X	α-(Trifluoromethyl) styrene	Yield[a] (%)
1	**18a** (10)	H	**20a**	73
2	**18a** (30)	H	**20a**	84
3	**18b** (3)	Br	**20b**	54
4	**18b** (20)	Br	**20b**	54

[a] Isolated yield.

^{1}H NMR spectra were recorded in deuterated solvents using Bruker DPX200, AV400 spectrometers, calibrated using residual undeuterated solvent as an internal reference. ^{13}C NMR spectra were recorded in deuterated solvents using Bruker DPX200, AV400 spectrometers. ^{19}F and ^{31}P spectra were recorded on a AV400 spectrometer. Mass spectral data were recorded on Micromass GCT (CI) or Bruker FT-ICR-MS Apex III (EI) instruments. All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of N_2. Solvents were dried and purified before use according to standard procedures. Room temperature = 20 °C. All reactions were monitored by TLC using Merck Kiesegel 60 F254 plates. Visualisation of the reaction components was achieved using UV fluorescence (254 nm) and $KMnO_4$ stain. Column chromatography was carried out over Merck silica gel C60 (40–60 μm). Purification of large-scale reactions was performed on Biotage SP-4 System, using Biotage KP-SIL SNAP Flash Cartridges (10 g, 25 g, 50 g, 100 g, 340 g). Petroleum ethers PE 30-40 and PE 40-60 used refer to the fraction boiling in the ranges 30–40 °C and 40–60 °C, respectively.

Trimethyl(2-phenylallyl)silanes 2; General Procedure (GP1)

A mixture of triflate **1** (1 equiv), $Pd(OAc)_2$ (0.03 equiv), dppf (0.13 equiv), allyltrimethylsilane (5 equiv), base (2 equiv), and anhyd MeCN (4 mL) was placed in a pressure tube. The tube was sealed and the mixture was heated for 20 h with vigorous stirring. The resulting dark soln was allowed to cool to r.t. and the mixture was quenched with H_2O (8 mL) and extracted with Et_2O (3 × 8.5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, PE 40-60) or by Biotage SP-4 System (PE 40-60).

Trimethyl(2-phenylallyl)silane (2a)

Following GP1 using triflate **1** (9.05 g, 6.48 mL, 40.0 mmol), $Pd(OAc)_2$ (0.27 g, 1.20 mmol), dppf (2.96 g, 5.33 mmol), allyltrimethylsilane (22.8 g, 31.8 mL, 200 mmol), Et_3N (8.09 g, 11.2 mL, 80.0 mmol), and anhyd MeCN (160 mL), heated at 60 °C, with quenching with H_2O (320 mL) and extraction with Et_2O (3 × 350 mL) gave **2a**; yield: 4.57 g (24.0 mmol, 60%); R_f = 0.68 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.11 [s, 9 H, $Si(CH_3)_3$], 2.02 [m, 2 H, $CH_2Si(CH_3)_3$], 4.86 (m, 1 H, C=CH_2), 5.12 (m, 1 H, C=CH_2), 7.26–7.34 (m, 3 H, H_{Ar}), 7.38–7.43 (m, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4 [$Si(CH_3)_3$], 26.2 [$CH_2Si(CH_3)_3$], 110.1 (C=CH_2), 126.3 (C_{Ar}), 127.2 (C_{Ar}), 128.1 (C_{Ar}), 142.8 (C_{Ar}), 146.6 (C=CH_2).

HRMS (CI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{18}Si$: 190.1178; found: 190.1177.

[2-(4-Bromophenyl)allyl]trimethylsilane (2b)

Following GP1 using triflate **1a** (9.15 g, 30.0 mmol), $Pd(OAc)_2$ (0.20 g, 0.90 mmol), dppf (2.16 g, 3.99 mmol), allyltrimethylsilane (17.1 g, 23.8 mL, 150 mmol), K_2CO_3 (8.29 g, 60.0 mmol), and anhyd MeCN (120 mL), heated at 65 °C, with quenching with H_2O (240 mL) and extraction with Et_2O (3 × 250 mL); yield: 4.61 g (17.1 mmol, 57%); R_f = 0.68 (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.09 [s, 9 H, Si(C*H*$_3$)$_3$], 1.99 [d, *J* = 0.9 Hz, 2 H, C*H*$_2$Si(CH$_3$)$_3$], 4.88 (m, 1 H, C=CH$_2$), 5.12 (d, *J* = 1.5 Hz, 1 H, C=CH$_2$), 7.28 (d, *J* = 8.7 Hz, 2 H, H$_{Ar}$), 7.43 (d, *J* = 8.7 Hz, 2 H, H$_{Ar}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4 [Si(*C*H$_3$)$_3$], 26.0 [*C*H$_2$Si(CH$_3$)$_3$], 110.6 (C=*C*H$_2$), 121.1 (C$_{Ar}$), 127.9 (C$_{Ar}$), 131.1 (C$_{Ar}$), 141.6 (C$_{Ar}$), 145.5 (C=*C*H$_2$).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{17}BrSi$: 268.0283; found: 268.0281.

2-Arylacrylaldehydes 7 and 2-Arylallylic Alcohols 8; General Procedure (GP2)

To a soln of aldehyde **6** (50 mmol, 1 equiv) and Et_3N in anhyd CH_2Cl_2 (500 mL), was added portion wise Me_2N^+=CH_2 I^- (100 mmol, 2 equiv). The mixture was stirred at r.t. until the starting material had been consumed (TLC monitoring). The mixture was then washed with sat. aq $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated under reduced pressure (note that the temperature of rotary evaporator bath should not exceed 20 °C). The crude residue of allylic aldehyde **7** was then submitted to the next step of synthesis without purification. To a soln of crude aldehyde **7** and $CeCl_3 \cdot 7\ H_2O$ (50 mmol, 1 equiv) in abs EtOH (500 mL) was added portionwise $NaBH_4$ (50 mmol, 1 equiv). The mixture was stirred at r.t. for 1 h. H_2O was slowly added and the mixture was extracted with CH_2Cl_2 (3 × 500 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Crude alcohol **8** was purified by column chromatography (silica gel, gradient PE 30-40–Et_2O) or by Biotage SP-4 System (gradient PE 30-40–Et_2O).

2-Phenylacrylaldehyde (7a)

Crude product; R_f = 0.65 (hexane–Et_2O, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.19 (m, 1 H, C=CH$_2$), 6.64 (m, 1 H, C=CH$_2$), 7.37–7.44 (m, 3 H, H$_{Ar}$), 7.45–7.50 (m, 2 H, H$_{Ar}$), 9.82 (s, 1 H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.0 (C$_{Ar}$), 128.3 (C$_{Ar}$), 128.7 (C$_{Ar}$), 133.6 (C=*C*H$_2$), 135.6 (C$_{Ar}$), 148.3 (*C*=CH$_2$), 192.9 (CHO).

2-(4-Bromophenyl)acrylaldehyde (7b)

Crude product; R_f = 0.65 (hexane–Et_2O, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.21 (s, 1 H, C=CH$_2$), 6.65 (s, 1 H, C=CH$_2$), 7.35 (d, *J* = 8.4 Hz, 2 H, H$_{Ar}$), 7.52 (d, *J* = 8.5 Hz, 2 H, H$_{Ar}$), 9.78 (s, 1 H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.6 (C$_{Ar}$), 129.7 (C$_{Ar}$), 131.5 (C$_{Ar}$), 131.8 (C=*C*H$_2$), 136.3 (C$_{Ar}$), 147.3 (*C*=CH$_2$), 192.6 (CHO).

2-Phenylprop-2-en-1-ol (8a)

Yield: 5.03 g (37.5 mmol, 75%, over 2 steps); R_f = 0.37 (hexane–Et_2O, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (br s, 1 H, OH), 4.54 (s, 2 H, C*H*$_2$OH), 5.36 (m, 1 H, C=CH$_2$), 5.48 (m, 1 H, C=CH$_2$), 7.31–7.39 (m, 3 H, H$_{Ar}$), 7.45–7.47 (m, 2 H, H$_{Ar}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.9 (CH$_2$OH), 112.5 (C=*C*H$_2$), 126.0 (C$_{Ar}$), 127.9 (C$_{Ar}$), 128.5 (C$_{Ar}$), 138.4 (C$_{Ar}$), 147.2 (*C*=CH$_2$).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_9H_{10}O$: 134.0732; found: 134.0735.

2-(4-Bromophenyl)prop-2-en-1-ol (8b)

Yield: 6.71 g (31.5 mmol, 63%, over 2 steps); R_f = 0.37 (hexane–Et_2O, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (br s, 1 H, OH), 4.50 (m, 2 H, C*H*$_2$OH), 5.36 (m, 1 H, C=CH$_2$), 5.47 (m, 1 H, C=CH$_2$), 7.32 (d, *J* = 8.6 Hz, 2 H, H$_{Ar}$), 7.47 (d, *J* = 8.6 Hz, 2 H, H$_{Ar}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.8 (CH$_2$OH), 113.3 (C=*C*H$_2$), 121.9 (C$_{Ar}$), 127.7 (C$_{Ar}$), 131.6 (C$_{Ar}$), 137.3 (C$_{Ar}$), 146.1 (*C*=CH$_2$).

HRMS (EI): *m*/*z* [M]$^+$ calcd for C_9H_9OBr: 211.9837; found: 211.9842.

2-Phenylallylic Fluorides 3 by Fluorodesilylation; General Procedure (GP3)

A soln of the allylsilane **2** (1 equiv) in anhyd MeCN (8 mL) was treated with Selectfluor (1.1 equiv). The mixture was stirred at r.t. for 2 h. When the reaction was complete, the mixture was poured into a separating funnel charged with sat. aq $NaHCO_3$ and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40), or by short-path distillation under reduced pressure.

(3-Fluoroprop-1-en-2-yl)benzene (3a)

According to GP3 using **2a** (4.57 g, 24.0 mmol) in anhyd MeCN (190 mL) and Selectfluor (9.35 g, 26.4 mmol) with extraction with Et_2O (3 × 480 mL); yield: 2.12 g (15.6 mmol, 65%); bp 80–81 °C/17 mbar; R_f = 0.4 (pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (d, *J* = 47.1 Hz, 2 H, CH$_2$F), 5.44 (s, 1 H, C=CH$_2$), 5.63 (m, 1 H, C=CH$_2$), 7.32–7.41 (m, 3 H, H$_{Ar}$), 7.46–7.48 (m, 2 H, H$_{Ar}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.3 (d, *J* = 169.4 Hz, CH$_2$F), 115.3 (d, *J* = 11.2 Hz, H$_2$*C*=CCH$_2$F), 125.9 (C$_{Ar}$), 128.2 (C$_{Ar}$), 128.5 (C$_{Ar}$), 137.2 (C$_{Ar}$), 143.0 (d, *J* = 15.2 Hz, H$_2$C=*C*CH$_2$F).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –212.7 (t, *J* = 47.0 Hz, 1 F, CH$_2$F).

HRMS (CI): *m*/*z* [M]$^+$ calcd for C_9H_9F: 136.0688; found: 136.0685.

1-Bromo-4-(3-fluoroprop-1-en-2-yl)benzene (3b)

According to GP3 using **2b** (4.61 g, 17.1 mmol) in anhyd MeCN (140 mL) and Selectfluor (6.66 g, 18.8 mmol) with extraction with Et_2O (3 × 350 mL); yield: 2.32 g (10.8 mmol, 63%); R_f = 0.4 (pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.21 (d, *J* = 47.1 Hz, 2 H, CH$_2$F), 5.45 (d, *J* = 3.1 Hz, 1 H, C=CH$_2$), 5.62 (m, 1 H, C=CH$_2$), 7.33 (d, *J* = 8.5 Hz, 2 H, H$_{Ar}$), 7.50 (d, *J* = 8.5 Hz, 2 H, H$_{Ar}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.1 (d, *J* = 169.1 Hz, CH$_2$F), 116.2 (d, *J* = 10.3 Hz, H$_2$*C*=CCH$_2$F), 122.2 (C$_{Ar}$), 127.5 (C$_{Ar}$), 131.6 (C$_{Ar}$), 136.1 (d, *J* = 2.3 Hz, C$_{Ar}$), 142.0 (d, *J* = 14.9 Hz, H$_2$C=*C*CH$_2$F).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –212.3 (dt, *J* = 47.1 Hz, *J* = 3.1 Hz, 1 F, CH$_2$F).

HRMS (EI): *m*/*z* [M]$^+$ calcd for C_9H_8BrF: 213.9793; found: 213.9789.

(3-Fluoroprop-1-en-2-yl)benzene (3a) by Direct Electrophilic Fluorination

To a soln of α-methylstyrene **4** (4.55 g, 5.00 mL, 38.0 mmol) in DMF (200 mL) was added portionwise Selectfluor (14.9 g, 41.8 mmol). The mixture was stirred at 75 °C for 18 h and then allowed to cool to r.t. and poured into a separating funnel charged with sat. aq $NaHCO_3$ (400 mL) and extracted with Et_2O (3 × 250 mL). The combined organic layers were washed with H_2O, brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40); yield: 1.81 g (13.3 mmol, 35%).

α-(Monofluoromethyl)styrenes 3 by Nucleophilic Fluorination; General Procedure (GP4)

Fluorination Procedure Using DAST: To a soln of allylic alcohol **8** (1 equiv) in anhyd CH_2Cl_2 (4 mL) at 0 °C was added dropwise DAST (1.5 equiv). The mixture was then warmed to r.t. and stirred for 6 h (TLC monitoring). Sat. aq $NaHCO_3$ was then slowly added and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40), or by short-path distillation under reduced pressure.

Fluorination Procedure Using FLUOLEAD: To a soln of FLUOLEAD (1.25 equiv) and $Et_3N{\cdot}3$ HF (1.25 equiv) in anhyd CH_2Cl_2 (2 mL) at 0 °C was added dropwise a soln of allylic alcohol **8** (1 equiv) in anhyd CH_2Cl_2 (2 mL). The mixture was then warmed to r.t. and stirred for 6 h (TLC monitoring). Sat. aq K_2CO_3 (5 mL) was then slowly added, the mixture was additionally stirred for 1 h, and then extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40), or by short-path distillation under reduced pressure.

(3-Fluoroprop-1-en-2-yl)benzene (3a)

According to GP4-DAST using **8a** (5.03 g, 37.5 mmol) in anhyd CH_2Cl_2 (150 mL) and DAST (6.54 g, 5.40 mL, 56.3 mmol) then sat. aq $NaHCO_3$ (200 mL) and extraction with CH_2Cl_2 (3 × 200 mL); yield: 3.42 g (25.1 mmol, 67%).

1-Bromo-4-(3-fluoroprop-1-en-2-yl)benzene (3b)

According to GP4-DAST using **8b** (6.71 g, 31.5 mmol) in anhyd CH_2Cl_2 (120 mL) and DAST (7.62 g, 6.25 mL, 47.3 mmol) then sat. aq $NaHCO_3$ (150 mL) and extraction with CH_2Cl_2 (3 × 200 mL); yield: 4.00 g (18.6 mmol, 59%).

(3-Fluoroprop-1-en-2-yl)benzene (3a)

According to GP4-FLUOLEAD using **8a** (5.03 g, 37.5 mmol) in anhyd CH_2Cl_2 (75 mL) and FLUOLEAD (11.7 g, 46.9 mmol) and $Et_3N{\cdot}3$ HF (7.56 g, 7.68 mL, 46.9 mmol) in anhyd CH_2Cl_2 (75 mL) and then sat. aq K_2CO_3 (190 mL) and extraction with CH_2Cl_2 (3 × 120 mL); yield: 3.37 g (24.8 mmol, 66%).

1-Bromo-4-(3-fluoroprop-1-en-2-yl)benzene (3b)

According to GP4-FLUOLEAD using **8b** (6.71 g, 31.5 mmol) in anhyd CH_2Cl_2 (65 mL) and FLUOLEAD (9.86 g, 39.4 mmol) and $Et_3N{\cdot}3$ HF (6.35 g, 6.40 mL, 39.4 mmol) in anhyd CH_2Cl_2 (65 mL) and then sat. aq K_2CO_3 (160 mL) and extraction with CH_2Cl_2 (3 × 100 mL); yield: 3.86 g (18.0 mmol, 57%).

Diethyl 4-(3-Fluoroprop-1-en-2-yl)phenylphosphonate (9)

To a soln of 1-bromo-4-(3-fluoroprop-1-en-2-yl)benzene (**3b**, 5.53 g, 25.7 mmol, 1 equiv) in anhyd THF (180 mL) cooled to –78 °C was added dropwise 2.5 M *n*-BuLi (12.0 mL, 28.3 mmol, 1.1 equiv). The residue was stirred at –78 °C for 1 h and $(EtO)_2P(O)Cl$ (4.88 g, 4.10 mL, 28.3 mmol, 1.1 equiv) was then added. The mixture was stirred at –78 °C for an additional 1 h until the starting material had been consumed (TLC monitoring), then allowed to warm up to r.t. and Et_2O and sat. aq $NaHCO_3$ were added. The mixture was extracted with Et_2O (3 × 200 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2–EtOAc) or by Biotage SP-4 System (CH_2Cl_2–EtOAc); yield: 3.78 g (13.9 mmol, 54%); R_f = 0.27 (CH_2Cl_2–EtOAc, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 4.11 (m, 4 H, OCH_2CH_3), 5.23 (d, *J* = 47.1 Hz, 2 H, CH_2F), 5.52 (m, 1 H, C=CH_2), 5.70 (m, 1 H, C=CH_2), 7.54 (dd, *J* = 8.0 Hz, *J* = 3.8 Hz, 2 H, H_{Ar}), 7.80 (dd, *J* = 13.0 Hz, *J* = 8.0 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3 (d, *J* = 6.6 Hz, OCH_2CH_3), 62.1 (d, *J* = 5.3 Hz, OCH_2CH_3), 84.0 (d, *J* = 169.2 Hz, CH_2F), 117.7 (d, *J* = 10.1 Hz, H_2C=CCH_2F), 125.9 (d, *J* = 15.4 Hz, C_{Ar}), 128.0 (d, *J* = 189.4 Hz, C_{Ar}), 132.1 (d, *J* = 10.1 Hz, C_{Ar}), 141.2 (C_{Ar}), 142.2 (d, *J* = 15.4 Hz, H_2C=CCH_2F).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –212.5 (dt, *J* = 47.1 Hz, *J* = 3.1 Hz, 1 F, CH_2F).

^{31}P NMR (376 MHz, $CDCl_3$): δ = 18.5 [m, 1 P, $(O)P(OCH_2CH_3)_2$].

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{18}FO_3P$: 272.0978; found: 272.0980.

1,1-Difluoro-2-phenyl-1-(phenylsulfonyl)propan-2-ol (15)

To a soln of $PhSO_2CF_2H$ (**13**, 3.84 g, 20.0 mmol) and acetophenone (**14**, 4.81 g, 4.67 mL, 40.0 mmol) in THF–HMPA (110 mL; 10:1 v/v) cooled to –78 °C was added dropwise 1 M LiHMDS (40 mL, 40 mmol). The mixture was stirred at –78 °C for 2 h. Sat. aq NaCl (200 mL) was then added at –78 °C and the residue was brought to r.t. and extracted with Et_2O (3 × 400 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE 40-60–CH_2Cl_2) or by Biotage SP-4 System (PE 40-60–CH_2Cl_2); yield: 4.62 g (14.8 mmol, 74%); R_f = 0.21 (hexane–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (m, 3 H, CH_3), 3.91 (br s, 1 H, OH), 7.37 (m, 3 H, H_{Ar}), 7.56 (m, 4 H, H_{Ar}), 7.71 (t, *J* = 7.6 Hz, 1 H, H_{Ar}), 7.89 (d, *J* = 8.0 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 76.8 [t, *J* = 19 Hz, $(OH)CCF_2$], 120.8 (t, *J* = 299 Hz, CF_2), 126.6 (C_{Ar}), 128.2 (C_{Ar}), 128.6 (C_{Ar}), 129.3 (C_{Ar}), 130.4 (C_{Ar}), 133.8 (C_{Ar}), 135.3 (C_{Ar}), 138.9 (C_{Ar}).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.3 (s, 2 F, CF_2).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{14}F_2O_3S$: 312.0632; found: 312.0633.

3,3-Difluoro-2-phenyl-3-(phenylsulfonyl)prop-1-ene (16)

To a soln of **15** (4.62 g, 14.8 mmol) in toluene (120 mL) was added P_2O_5 (6.30 g, 44.4 mmol) and the mixture was stirred at reflux for 2 h. The mixture was then allowed to cool to r.t. and poured into a separating funnel charged with H_2O (200 mL) and extracted with Et_2O (3 × 300 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE 40-60–CH_2Cl_2) or by Biotage SP-4 System (PE 40-60–CH_2Cl_2); yield: 3.92 g (13.3 mmol, 90%); R_f = 0.33 (hexane–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (s, 1 H, C=CH_2), 6.13 (s, 1 H, C=CH_2), 7.31 (m, 2 H, H_{Ar}), 7.51 (m, 3 H, H_{Ar}), 7.60 (t, *J* = 7.7 Hz, 2 H, H_{Ar}), 7.75 (t, *J* = 7.2 Hz, 1 H, H_{Ar}) 8.02 (d, *J* = 7.7 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.2 (t, *J* = 288 Hz, CF_2), 125.3 (C_{Ar}), 127.9 (C_{Ar}), 128.2 (C_{Ar}), 128.7 (t, *J* = 9 Hz, H_2C=CCF_2), 128.9 (C_{Ar}), 129.0 (C_{Ar}), 129.2 (C_{Ar}), 130.6 (C_{Ar}), 135.2 (C_{Ar}), 137.7 (t, *J* = 21 Hz, H_2C=CCF_2).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.7 (s, 2 F, CF_2).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{12}F_2O_2S$: 294.0526; found: 294.0528.

(3,3-Difluoroprop-1-en-2-yl)benzene (17)

To a soln of sulfone **16** (3.92 g, 13.3 mmol) in DMF (130 mL) at r.t. was added AcOH–NaOAc (1:1) buffer soln (70 mL, 8 mol/L). Mg turnings (4.85 g, 199 mmol) were added in portions. The mixture was stirred at r.t. for 3 h followed by addition of H_2O (400 mL). The mixture was extracted with Et_2O (3 × 300 mL) and the combined or-

ganic phases were washed with sat. $NaHCO_3$ soln and brine and dried ($MgSO_4$). Et_2O was removed and the crude product was purified by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40); yield: 0.62 g (4.0 mmol, 30%); R_f = 0.53 (pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 (s, 1 H, C=CH_2), 5.75 (s, 1 H, C=CH_2), 6.42 (t, J = 55.4 Hz, 1 H, CF_2H), 7.40 (m, 3 H, H_{Ar}), 7.51 (m, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.4 (t, J = 239.7 Hz, CF_2H), 118.9 (t, J = 9.7 Hz, H_2C=CCF_2H), 126.9 (C_{Ar}), 128.5 (C_{Ar}), 128.6 (C_{Ar}), 134.7 (C_{Ar}), 141.9 (t, J = 20.0 Hz, H_2C=CCF_2H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.2 (d, J = 56.0 Hz, 2 F, CF_2H).

HRMS (CI): m/z $[M]^+$ calcd for $C_9H_8F_2$: 154.0594; found: 154.0593.

α-(Trifluoromethyl)styrenes 20; General Procedure (GP5)

To a soln of **19** (1.5 equiv) in DME–THF (1:1, 3 mL) and aq 2 M KOH (2 mL) was added phenylboronic acid **18** (1 equiv), $PdCl_2(PPh_3)_2$ (0.03 equiv), and $AsPh_3$ (0.15 equiv) under an inert atmosphere in a pressure tube. The mixture was sealed and stirred at 74 °C for 12 h.[25] The mixture was cooled to r.t., H_2O (10 mL) was added, and the mixture was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried ($MgSO_4$). The solvent was removed and the residue was purified by short-path distillation under reduced pressure or by column chromatography (silica gel, PE 30-40) or by Biotage SP-4 System (PE 30-40).

(3,3,3-Trifluoroprop-1-en-2-yl)benzene (20a)

According to GP5 using **19** (7.87 g, 45.0 mmol) in DME–THF (1:1, 90 mL) and aq 2 M KOH (60 mL) and phenylboronic acid (**18a**, 3.66 g, 30.0 mmol), $PdCl_2(PPh_3)_2$ (0.63 g, 0.90 mmol), and $AsPh_3$ (1.38 g, 4.50 mmol); workup used H_2O (300 mL), extraction with Et_2O (2 × 300 mL), and washing with brine (3 × 300 mL); yield: 4.34 g (25.2 mmol, 84%); bp 55–57 °C/17 mbar; R_f = 0.6 (pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.79 (m, 1 H, C=CH_2), 5.98 (m, 1 H, C=CH_2), 7.41 (s, 3 H, H_{Ar}), 7.48 (s, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.4 (q, J = 5.7 Hz, H_2C=CCF_3), 123.4 (q, J = 274.1 Hz, H_2C=CCF_3), 127.4 (C_{Ar}), 128.6 (C_{Ar}), 129.0 (C_{Ar}), 133.7 (C_{Ar}), 139.0 (q, J = 29.1 Hz, H_2C=CCF_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –64.8 (s, 3 F, CF_3).

HRMS (CI): m/z $[M]^+$ calcd for $C_9H_7F_3$: 172.0500; found: 172.0504.

1-Bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (20b)

According to GP5 using **19** (5.25 g, 30.0 mmol) in DME–THF (1:1, 60 mL) and aq 2 M KOH (40 mL), and 4-bromophenylboronic acid (**18b**, 4.02 g, 20.0 mmol), $PdCl_2(PPh_3)_2$ (0.42 g, 0.60 mmol), and $AsPh_3$ (0.92 g, 3.00 mmol); workup used H_2O (300 mL), extraction with Et_2O (2 × 200 mL), and washing with brine (3 × 200 mL); yield: 2.71 g (10.8 mmol, 54%); bp 86–88 °C/17 mbar; R_f = 0.58 (pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (m, 1 H, C=CH_2), 5.98 (m, 1 H, C=CH_2), 7.33 (d, J = 8.5 Hz, 2 H, H_{Ar}), 7.52 (d, J = 8.5 Hz, 2 H, H_{Ar}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.9 (q, J = 5.8 Hz, H_2C=CCF_3), 123.0 (q, J = 273.8 Hz, H_2C=CCF_3), 123.3 (C_{Ar}), 127.0 (C_{Ar}), 131.8 (C_{Ar}), 132.5 (C_{Ar}), 138.0 (q, J = 30.7 Hz, H_2C=CCF_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –64.9 (s, 3 F, CF_3).

HRMS (EI): m/z $[M]^+$ calcd for $C_9H_6BrF_3$: 249.9605; found: 249.9608.

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