Efficient Synthesis of Fluoroalkenes via Diethylzinc-Promoted Wittig Reaction

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Abstract: The synthesis of α-fluoroacrylates and α-bromo-α-fluoroalkenes was achieved in very good yields using aldehydes and ketones, triphenylphosphine, diethylzinc as promoter, and ethyl dibromofluoroacetate or dibromofluoromethane, respectively. A change in the addition sequence was critical in order to obtain exclusively α-fluoroacrylates in good yields.

Key words: Wittig reaction, fluoroalkene, ketone, aldehyde, diethylzinc

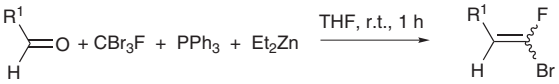
Organofluorine compounds have received considerable interest in recent years due to their increasing importance in the life sciences, especially for drug development and crop protection.[1] Modification of the physiological activity of bioactive compounds by introducing fluorine into molecules frequently leads to the discovery of novel and potent biochemical tools and medicinal agents.

α-Bromo-α-fluoroalkenes and α-fluoro-α,β-unsaturated esters (α-fluoroacrylates) have broad application as intermediates in the preparation of biologically active fluorinated compounds. Though other methods have been developed,[2] the main synthetic approaches to α-bromo-α-fluoroalkenes and α-fluoroacrylates and related compounds use the Wittig[2c] and the Horner–Wadsworth–Emmons reactions. Several efficient syntheses of α-fluoroacrylates have been recently reported using the latter approach, for example, an efficient one-pot version[3] and an efficient *Z*-selective Horner–Wadsworth–Emmons reaction.[4] Concerning the Wittig synthesis of α-fluoroacrylates, a one-pot sequence from (alkoxycarbonylmethyl)triphenylphosphonium bromides has been recently reported using Selectfluor as an electrophilic fluorinating agent.[5] For the synthesis of α-bromo-α-fluoroalkenes, the classical Wittig reaction using triphenylphosphine or zinc as a promoter usually gives low yields with unactivated ketones or aliphatic aldehydes.

Recently, our group has reported the synthesis of α-bromo-α-fluoroalkenes via the diethylzinc-promoted Wittig reaction.[6] It was, to our knowledge, the first report that diethylzinc can promote the Wittig reaction (Scheme 1).[7]

By optimizing the reaction conditions, that is, changing the solvent, the temperature, the nature of the phosphine, and the number of equivalents of reagents, the yield of 3-phenylpropanal could be increased to 88%. The optimized conditions used tetrahydrofuran as solvent at room temperature with a ratio of aldehyde/diethylzinc/tribromofluoromethane/triphenylphosphine of 1.0:1.2:1.2:1.2. This is the highest yield obtained for this particular aldehyde using this route.

Various aldehydes were subjected to these optimized reaction conditions, giving the corresponding α-bromo-α-fluoroalkenes in high yields (Table 1). Under the above conditions, even unactivated aldehydes could be converted into the corresponding α-bromo-α-fluoroalkenes (Table 1, entries 1–3). The reaction is general and can tolerate various functional groups, such as ester, nitro, protected alcohol, and others, with yields always around 80–90%.



Scheme 1 Synthesis of α-bromo-α-fluoroalkenes.

Table 1 Reaction with Aldehydes

Entry	Product	R^1	Yield[a] (%)	Ratio[b] *Z*/*E*
1	**1a**	CH_2CH_2Ph	88	49:51
2	**1b**	$CH_2CH_2OTBDPS$	90 (99[c])	53:47
3	**1c**	$CHMeCH_2OTBDPS$	83	42:58
4	**1d**	4-BrC_6H_4	74	55:45
6	**1e**	4-$O_2NC_6H_4$	85	58:42
7	**1f**	4-$MeOC_6H_4$	94[c]	49:51
8	**1g**	2-$O_2NC_6H_4$	87	70:30
9	**1h**	2-$MeOC_6H_4$	91	58:42
10	**1i**	3,4-$(OCH_2O)C_6H_3$	91	52:48
11	**1j**	4-$MeO_2CC_6H_4$	81	55:45
12	**1k**	2-naphthyl	78	52:48
13	**1l**	4-NCC_6H_4	84	56:44
14	**1m**	4-$F_3CC_6H_4$	70	56:44

[a] Isolated yield; ratio aldehyde/Et_2Zn/CBr_3F/PPh_3 = 1.0:1.2:1.2:1.2.
[b] Ratio determined by ^{19}F NMR or ^1H NMR.
[c] Ratio aldehyde/Et_2Zn/CBr_3F/PPh_3 = 1.0:1.5:1.5:1.5.

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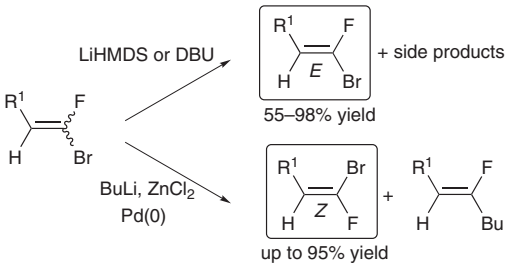
Unfortunately, regardless of the conditions or the aldehyde, the stereoselectivity was never better than 70:30. Pure *Z*- or *E*-isomer could be obtained via chemoselective transformation of one of the two isomers (Scheme 2).

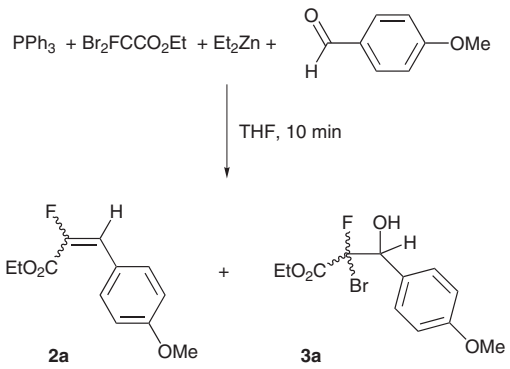


Scheme 2 Access to pure (*Z*)- or (*E*)-α-bromo-α-fluoroalkenes.

To broaden the scope of the reaction, we then subjected unactivated ketones to Wittig conditions with diethylzinc activation (Table 2). The yields of isolated α-bromo-α-fluoroalkenes from aromatic or aliphatic ketones were often moderate to good and the ketone could contain various functional groups such as amine, protected alcohol, etc. However, the reaction was not suitable for readily enolizable substrates such as *N*,*N*-diallyl-2-oxocyclopentanecarboxamide (Table 2, entry 10) or 3,4-dihydronaphthalen-2(1*H*)-one. In these particular cases, the α-hydrogen is probably too acidic and the ylide reacts first with it, instead of adding to the carbonyl group.

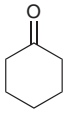
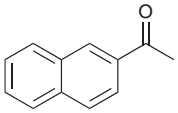
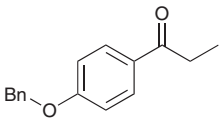
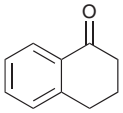
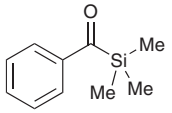
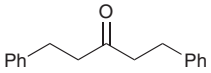
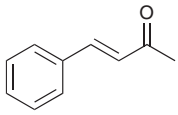
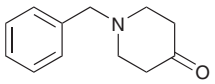
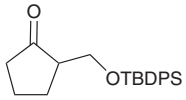
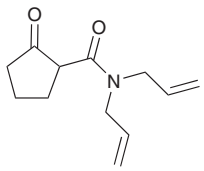
In a second step, we decided to investigate the generality of diethylzinc as a Wittig promoter and applied our process to the synthesis of α-fluoroacrylates.

Using standard conditions, as described for the synthesis of terminal α-bromo-α-fluoroalkenes, we studied the reaction between *p*-anisaldehyde (1 equiv), triphenylphosphine (1.2 equiv), and ethyl dibromofluoroacetate (1.2 equiv) in the presence of diethylzinc (added via syringe pump over 30 min) in dry tetrahydrofuran under argon. At the end of the reaction, the ^{19}F NMR spectra showed the presence of starting material (35%) and of four products identified as the two diastereomeric alcohols **3a** (60%) and two isomeric α-fluoroacrylates **2a** (less than 5%) (Scheme 3). No further reaction was then observed, even after 24 hours.



Scheme 3 Synthesis of fluoroacrylates.

Table 2 Reaction with Ketones

Entry	Starting ketone	Product	Yield[a] (%)	Ratio[b] *Z*/*E*
1		**1n**	66	–
2		**1o**	69	–c
3		**1p**	83	46:54
4		**1q**	78	41:59
5		**1r**	53	70:30
6		**1s**	66	–
7		**1t**	39	45:55
8		**1u**	76	–
9		**1v**	51d	44:56
10		**1w**	0	–

[a] Isolated yield; ratio ketone/Et_2Zn/CBr_3F/PPh_3 = 1.0:1.5:1.5:1.5.
[b] Ratio determined by ^{19}F NMR or ^{1}H NMR.
[c] Not determined.
[d] Ratio ketone/Et_2Zn/CBr_3F/PPh_3 = 1.0:3:3:3.

This disappointing result prompted us to fully reexamine the parameters of this reaction, especially the order of addition and the number of equivalents of each reaction partner used in this process.

In a first assay, *p*-anisaldehyde (1 equiv) was added dropwise to a tetrahydrofuran solution of triphenylphosphine, diethylzinc, and ethyl dibromofluoroacetate (1 equiv each), which had been introduced successively in this order at room temperature and stirred for 30 minutes. Under these conditions, after one hour, the ^{19}F NMR spectrum showed the presence of the starting aldehyde and of two

products identified as the two isomeric α-fluoroacrylates **2a**. No trace of alcohol was observed. Moreover the GC analysis of the reaction mixture showed a 67:33 ratio between *p*-anisaldehyde and **2a**. No further reaction was observed even after 24 hours.

A change in the addition sequence was critical in order to obtain exclusively α-fluoroacrylates. If diethylzinc, triphenylphosphine, and ethyl dibromofluoroacetate are added prior to *p*-anisaldehyde, the expected compounds **2a** were obtained; otherwise bromofluoro alcohols **3a** are the major products. We next changed the number of equivalents of each partner (except *p*-anisaldehyde) in order to improve the conversion. The results obtained during this study are collected in Table 3.

When two equivalents of triphenylphosphine were used (Table 3, entry 2), a slight improvement in the conversion of aldehyde into **2a** was observed. Moreover, no trace of dibromofluoroacetate was detected in the ^{19}F NMR spectrum of the reaction mixture. However, when two equivalents of diethylzinc were used (Table 3, entry 3), the conversion did not improve. Addition of two equivalents of each component (relative to the aldehyde) led to a very interesting 85% conversion (Table 3, entry 4) into **2a**.

Table 3 Optimization of the Parameters

Entry	Number of equivalents[a]			GC Ratio[b]	
	PPh_3	Et_2Zn	Br_2FCCO_2Et	**2a**	4-MeC_6H_4CHO
1	1	1	1	33	67
2	2	1	1	50	50
3	1	2	1	22	77
4	2	2	2	85	15
5	3	2	2	70	30
6	3	3	3	85	15
7	4	4	2	100	0

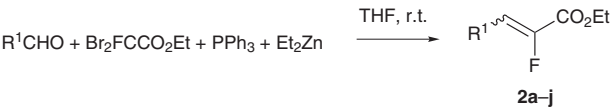
[a] 1 equiv of *p*-anisaldehyde was introduced.
[b] Determined on a DB1 column.

Finally the optimal conditions, resulting in complete conversion of the aldehyde into fluoroacrylate **2a** (Table 3, entry 7), were obtained when four equivalents of triphenylphosphine, four equivalents of diethylzinc and two equivalents of ethyl dibromofluoroacetate were used.

It should be noticed that when triphenylphosphine, diethylzinc, and ethyl dibromofluoroacetate were introduced in this order to a tetrahydrofuran solution, a slight exothermicity was observed (the internal temperature rose to 35 °C). The aldehyde was added when the temperature had gone down to 20 °C (ca. 10 min). The reaction was complete within ten minutes after addition of the aldehyde as indicated by GC analysis.

Various aldehydes were subjected to these optimized reaction conditions, giving the corresponding α-fluoroacrylates in high yields (Table 4). Under these conditions, even unactivated aldehydes could be converted into the corresponding α-fluoroacrylates **2a–j**. With yields always around 75–95%, the reaction is general and tolerates various functional groups such as ester or protected alcohol.

Table 4 Reaction with Aldehydes R^1CHO[a]



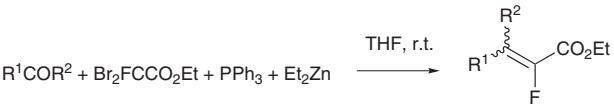
2a–j

Entry	R^1	Product	Yield[b] (%)	Ratio[c] *Z*/*E*
1	4-$MeOC_6H_4$	**2a**	91	85:15
2	$(CH_2)_4Me$	**2b**	98	70:30
3	$CH_2CH_2OTBDPS$	**2c**	83	65:35
4	Ph	**2d**	98	80:20
5	CH_2CH_2Ph	**2e**	94	68:32
6	4-$F_3CC_6H_4$	**2f**	98	75:25
7	4-BrC_6H_4	**2g**	77	80:20
8	4-pyridyl	**2h**	30 (96[d])	85:15
9	CH_2CHMe_2	**2i**	90	70:30
10	4-$MeO_2CC_6H_4$	**2j**	88	70:30

[a] Ratio aldehyde/Et_2Zn/Br_2FCCO_2Et/PPh_3 = 1.0:4.0:2.0:4.0.
[b] Isolated yield.
[c] Ratio determined by ^{19}F NMR.
[d] Conversion determined by GC analysis in the reaction mixture, rapid degradation occurred during purification on silica gel.

To broaden the scope of the reaction, we then subjected ketones to Wittig conditions as described above. We first tested an activated ketone, 2,2,2-trifluoroacetophenone and obtained the expected α-fluoroacrylate **2n** in 92% yield (ratio *Z*/*E* = 35:65). Others unactivated ketones were then engaged in this reaction and the obtained results are collected in Table 5.

Table 5 Reaction with Ketones R^1COR^2 [a]



2k–n

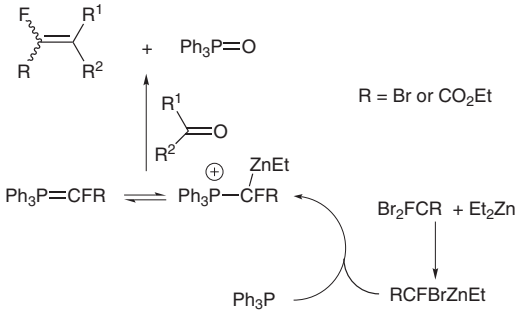
Entry	R^1	R^2	Product	Yield[b] (%)	Ratio[c] *Z*/*E*
1	Ph	Me	**2k**	77	60:40
2	CH_2CH_2Ph	Me	**2l**	98	60:40
3	$(CH_2)_5$		**2m**	80	–
4	Ph	CF_3	**2n**	92	35:65

[a] Ratio ketone/Et_2Zn/Br_2FCCO_2Et/PPh_3 = 1.0:4.0:2.0:4.0.
[b] Isolated yield.
[c] Ratio determined by ^{19}F NMR.

Concerning the mechanism of such a process (Scheme 4), we suggest that the first step is the reaction between diethylzinc and ethyl dibromofluoroacetate to generate the corresponding zinc carbenoid. The latter reacts with triphenylphosphine to form the key ylide intermediate, which reacts with the aldehyde or ketone leading to the expected α-fluoroacrylate **2**. Indeed, if diethylzinc was added to a solution containing ethyl dibromofluoroacetate, aldehyde, and triphenylphosphine, we obtained a mixture of alkene **2** and alcohol **3**, meaning that the reaction between zinc carbenoid and aldehyde is much more rapid than its reaction with triphenylphosphine.

In the case of the synthesis of α-bromo-α-fluoroalkenes (Scheme 4), the aldehyde can be added at the beginning of the reaction. Indeed, in this particular case, the tribromofluoromethane deriving zinc carbenoid is less nucleophilic (carbene character is more pronounced) than that prepared from ethyl dibromofluoroacetate, allowing the phosphine to react first.

In conclusion, we found that diethylzinc could act very efficiently as a Wittig promoter. Applied to the synthesis of α-bromo-α-fluoroalkenes and to α-fluoroacrylates, this procedure appears to be rapid, convenient, and high-yielding for aldehydes and ketones. Moreover, the reaction tolerates various functional groups. On-going studies include the determination of the exact mechanism (by NMR and IR spectroscopy), the use of supported triphenylphosphine-type reagents, and the replacement of triphenylphosphine by other nucleophiles.



Scheme 4 Proposed mechanism.

All commercial solvents were distilled before using. THF was distilled from sodium benzophenone ketyl under N_2. TLC was performed on Merck 60F-250 silica gel plates. Flash column chromatography purifications were carried out using silica gel (70–230 mesh). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR ($CFCl_3$ as external reference) were recorded at 300.13 MHz, 75.47 MHz, and 282.40 MHz respectively.

α-Bromo-α-fluoroalkenes from Aldehydes; General Procedure

To a soln of PPh_3 (1.2 mmol, 1.2 equiv), tribromofluoromethane (1.2 mmol, 1.2 equiv), and an appropriate aldehyde (1.0 mmol, 1.0 equiv) in anhyd THF (40 mL), was added a soln of 1 M Et_2Zn in hexanes (1.2 mmol, 1.2 equiv) dropwise via a syringe pump over 20 min at r.t. under argon. The mixture was stirred for 1 h. The resulting soln was then quenched with MeOH (10 mL), stirred for 15 min, and concentrated under reduced pressure. The residue was then chromatographed (silica gel, cyclohexane–EtOAc), affording the desired α-bromo-α-fluoroalkene.

(*Z*)- and (*E*)-(4-Bromo-4-fluorobut-3-enyl)benzene (1a)

Ratio *Z*/*E* = 49:51; R_f = 0.7 (cyclohexane–EtOAc, 98:2).

IR (neat): 3028, 2927, 1807, 1718, 1667, 1603, 1495, 1454, 1178, 1111, 1088, 1022, 1000, 747, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.1 (m, 5 H, H_6, H_7, H_8), 5.5 (dt, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-F}$ = 12.8 Hz, 0.5 H, H_{2Z}), 5.0 (dt, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-F}$ = 31.0 Hz, 0.5 H, H_{2E}), 2.7–2.6 (m, 2 H, H_4), 2.4–2.2 (m, 2 H, H_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.5, 134.5 (d, *J* = 314 Hz), 130.6 (d, *J* = 320 Hz), 127.2, 127.3, 125, 110.5 (d, *J* = 13 Hz), 107.9 (d, *J* = 16 Hz), 33.8 (d, *J* = 2 Hz), 33.5 (d, *J* = 2 Hz), 28.2, 28.1.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –71.7 (d, *J* = 13.1 Hz, 0.5 F), –75.4 (dt, *J* = 31.2 Hz, *J* = 2.6 Hz, 0.5 F).

MS (EI): *m*/*z* = 228–230 (M^+), 149 (M^+ – Br), 91 ($PhCH_2^+$).

Anal. Calcd for $C_{10}H_{10}BrF$: C, 52.43; H, 4.40. Found: C, 52.22; H, 4.51.

(*Z*)- and (*E*)-(4-Bromo-4-fluorobut-3-enyloxy)*tert*-butyldiphenylsilane (1b)

Ratio *Z*/*E* = 53:47; R_f = 0.7 (cyclohexane–EtOAc, 98:2).

IR (neat): 3448, 3072, 2958, 2859, 1792, 1742, 1671, 1590, 1473, 1428, 1113, 1024, 822, 701, 613, 509 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.6 (m, 4 H, H_8), 7.5–7.3 (m, 6 H, H_9, H_{10}), 5.6 (dt, $^3J_{H-F}$ = 13.3 Hz, $^3J_{H-H}$ = 7.8 Hz, 0.5 H, H_{2Z}), 5.1 (dt, $^3J_{H-F}$ = 31.2 Hz, $^3J_{H-H}$ = 7.8 Hz, 0.5 H, H_{2E}), 3.7–3.6 (m, 2 H, H_4), 2.4–2.2 (m, 2 H, H_3), 1.1 (s, 9 H, H_6).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.7 (d, *J* = 277 Hz), 132.5 (d, *J* = 255 Hz), 136.0, 134.0, 130.0, 128.1, 110.0 (d, *J* = 13 Hz), 107.0 (d, *J* = 10 Hz), 62.0 (dd, *J* = 2 Hz, *J* = 2 Hz), 31.5 (d, *J* = 4 Hz), 30.0 (d, *J* = 2 Hz), 27.0, 19.6.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –70.6 (d, *J* = 13.2 Hz, 0.5 F), –75.0 (dt, *J* = 31.2 Hz, *J* = 2.1 Hz, 0.5 F).

MS (EI): *m*/*z* = 349–351 (M^+ – C_4H_9).

Anal. Calcd for $C_{20}H_{24}BrFOSi$: C, 58.96; H, 5.94. Found: C, 58.73; H, 6.08.

(*Z*)- and (*E*)-(4-Bromo-4-fluoro-2-methylbut-3-enyloxy)*tert*-butyldiphenylsilane (1c)

Ratio *Z*/*E* = 42:58; R_f = 0.7 (cyclohexane).

IR (neat): 3399, 3071, 2960, 2858, 1667, 1472, 1427, 1126, 1028, 824, 740, 702, 613, 505 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.6 (m, 4 H, H_9), 7.6–7.4 (m, 6 H, H_{10}, H_{11}), 5.5 (dd, $^3J_{H-H}$ = 9.7 Hz, $^3J_{H-F}$ = 13.3 Hz, 0.4 H, H_{2Z}), 5.0 (dd, $^3J_{H-H}$ = 9.7 Hz, $^3J_{H-F}$ = 31.7 Hz, 0.6 H, H_{2E}), 3.7–3.5 (m, 2 H, H_4), 3.0–2.8 (m, 0.6 H, H_{3E}), 2.7–2.5 (m, 0.4 H, H_{3Z}), 1.2 (s, 9 H, H_6), 1.2–1.1 (m, 3 H, H_7).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.6 (d, *J* = 315 Hz), 136.1, 134.0, 133.5, 132.2 (d, *J* = 316 Hz), 128.1, 116.0 (d, *J* = 12 Hz), 113.3 (d, *J* = 14 Hz), 68.0 (d, *J* = 2 Hz), 67.8 (d, *J* = 3 Hz), 36.7 (d, *J* = 4 Hz), 34.8, 27.4, 27.3, 19.73, 19.71, 10.8.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –71.7 (d, *J* = 13.3 Hz, 0.6 F), –74.7 (d, *J* = 31.7 Hz, 0.4 F).

MS (EI): *m*/*z* = 363–365 (M^+ – C_4H_9).

Anal. Calcd for $C_{21}H_{26}BrFOSi$: C, 59.85; H, 6.22. Found: C, 59.97; H, 6.24.

(*Z*)- and (*E*)-1-Bromo-4-(2-bromo-2-fluorovinyl)benzene (1d)
Ratio *Z*/*E* = 55:45; R_f = 0.8 (cyclohexane).

IR (neat): 3064, 3026, 2924, 1650, 1487, 1400, 1107, 1085, 1046, 1010, 866, 853, 808, 794 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.4 (m, 2 H, H_5), 7.3 (2 d, *J* = 8.5 Hz, *J′* = 8.7 Hz, 2 H, H_4), 6.6 (d, $^3J_{H-F}$ = 17.0 Hz, 0.5 H, H_{2Z}), 5.9 (d, $^3J_{H-F}$ = 32.0 Hz, 0.5 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 133.8 (d, *J* = 317 Hz), 132.8 (d, *J* = 331 Hz), 132.2, 131.7 (d, *J* = 7 Hz), 130.8 (d, *J* = 8 Hz), 130.1 (d, *J* = 3 Hz), 130.1 (d, *J* = 4 Hz), 122.0, 112.1 (d, *J* = 6 Hz), 111.0 (d, *J* = 25 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –64.0 (d, *J* = 17.0 Hz, 0.5 F), –67.2 (d, *J* = 32.0 Hz, 0.5 F).

MS (EI): *m*/*z* = 278–282 (M^+), 199–201 (M^+ – Br).

Anal. Calcd for $C_8H_5Br_2F$: C, 34.33; H, 1.80. Found: C, 34.41; H, 1.86.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-4-nitrobenzene (1e)
Ratio *Z*/*E* = 58:42; mp 47–49 °C; R_f = 0.3 (cyclohexane–EtOAc, 98:2).

IR (KBr): 3069, 3022, 2833, 1642, 1594, 1510, 1341, 1286, 1108, 1081, 875, 841, 748, 689, 489 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.2 (2 d, *J* = 8.7 Hz, *J′* = 8.7 Hz, 2 H, H_5), 7.5 (2 d, *J* = 8.7 Hz, *J′* = 8.7 Hz, 2 H, H_4), 6.7 (d, $^3J_{H-F}$ = 14.4 Hz, 0.6 H, H_{2Z}), 6.0 (d, $^3J_{H-F}$ = 31.9 Hz, 0.4 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 145.9, 145.6, 134.3 (d, *J* = 320 Hz), 137.6 (d, *J* = 5 Hz), 137.2 (d, *J* = 9 Hz), 134.0 (d, *J* = 334 Hz), 127.9 (d, *J* = 3 Hz), 127.5 (d, *J* = 8 Hz), 122.9, 122.4 (d, *J* = 24 Hz), 110.5 (d, *J* = 6 Hz), 109.4 (d, *J* = 26 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –59.3 (d, *J* = 14.4 Hz, 0.6 F), –62.3 (d, *J* = 31.9 Hz, 0.4 F).

MS (EI): *m*/*z* = 245–247 (M^+), 215–217 (M^+ – NO), 199–201 (M^+ – NO_2).

Anal. Calcd for $C_8H_5BrFNO_2$: C, 39.05; H, 2.05; N, 5.69. Found: C, 39.09; H, 2.07; N, 5.87.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-4-methoxybenzene (1f)
Ratio *Z*/*E* = 49:51; R_f = 0.6 (5% EtOAc–cyclohexane).

IR (neat): 3060, 3004, 2934, 2837, 1651, 1608, 1513, 1463, 1253, 1180, 1083, 1037, 853, 808, 590 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.3 (2 d, *J* = 8.7 Hz, *J′* = 8.4 Hz, 2 H, H_4), 6.8 (2 d, *J* = 8.7 Hz, *J′* = 8.4 Hz, 2 H, H_5), 6.5 (d, $^3J_{H-F}$ = 15.0 Hz, 0.5 H, H_{2Z}), 5.8 (d, $^3J_{H-F}$ = 33.3 Hz, 0.5 H, H_{2E}), 3.7 (2 s, 3 H, H_7).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.0 (d, *J* = 3 Hz), 133.9 (d, *J* = 314 Hz), 133.4 (d, *J* = 329 Hz), 129.0 (d, *J* = 7 Hz), 128.5 (d, *J* = 23 Hz), 125.0 (d, *J* = 8 Hz), 123.0 (d, *J* = 4 Hz), 115.2 (d, *J* = 3 Hz), 114.4 (d, *J* = 5 Hz), 113.1 (d, *J* = 7 Hz), 111.1 (d, *J* = 24 Hz), 56.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –68.2 (d, *J* = 15.0 Hz, 0.5 F), –71.4 (d, *J* = 33.3 Hz, 0.5 F).

MS (EI): *m*/*z* = 230–232 (M^+), 215–217 (M^+ – CH_3).

Anal. Calcd for C_9H_8BrFO: C, 46.78; H, 3.49. Found: C, 46.58; H, 3.67.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-2-nitrobenzene (1g)
Ratio *Z*/*E* = 70:30; mp 44–46 °C; R_f = 0.3 (cyclohexane).

IR (KBr): 3052, 2922, 2853, 1651, 1524, 1344, 1105, 785, 742, 682 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.0 (m, 1 H, H_5), 7.5 (m, 3 H, H_6, H_7, H_8), 7.0 (d, $^3J_{H-F}$ = 11.8 Hz, 0.7 H, H_{2Z}), 6.5 (d, $^3J_{H-F}$ = 30.1 Hz, 0.3 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.3, 146.6, 134.9 (d, *J* = 319 Hz), 133.7, 133.3 (d, *J* = 332 Hz), 133.8, 132.4 (d, *J* = 2 Hz), 131.5 (d, *J* = 9 Hz), 128.8, 128.3, 127.1 (d, *J* = 9 Hz), 126.0 (d, *J* = 4 Hz), 124.0, 107.7 (d, *J* = 5 Hz), 108.8 (d, *J* = 28 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –64.3 (d, *J* = 11.8 Hz, 0.7 F), –67.6 (d, *J* = 30.1 Hz, 0.3 F).

MS (EI): *m*/*z* = 245–247 (M^+), 166 (M^+ – Br).

Anal. Calcd for $C_8H_5BrFNO_2$: C, 39.05; H, 2.05; N, 5.69. Found: C, 39.27; H, 2.13; N, 5.75.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-2-methoxybenzene (1h)
Ratio *Z*/*E* = 58:42; R_f = 0.6 (cyclohexane).

IR (neat): 3079, 2936, 2837, 1651, 1600, 1486, 1464, 1437, 1273, 1251, 1123, 1080, 1029, 820, 750, 632 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.6 (d, *J* = 8.0 Hz, 1 H, H_6), 7.3–7.1 (m, 1 H, H_4), 6.9–6.8 (m, 1 H, H_5), 6.8 (d, *J* = 8.1 Hz, 1 H, H_7), 6.7 (d, $^3J_{H-F}$ = 15.1 Hz, 0.6 H, H_{2Z}), 6.3 (d, $^3J_{H-F}$ = 34.3 Hz, 0.4 H, H_{2E}), 3.7 (s, 3 H, H_9).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.2 (d, *J* = 4 Hz), 156.1, 133.4 (d, *J* = 315 Hz), 131.5 (d, *J* = 331 Hz), 129.8, 129.7, 129.5 (d, *J* = 2 Hz), 129.3 (d, *J* = 2 Hz), 121.7 (d, *J* = 5 Hz), 121.1, 120.8 (d, *J* = 8 Hz), 120.7, 111.0, 110.8, 107.6 (d, *J* = 25 Hz), 107.3 (d, *J* = 5 Hz), 55.9.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –65.6 (d, *J* = 15.1 Hz, 0.6 F), –69.5 (d, *J* = 34.3 Hz, 0.4 F).

MS (EI): *m*/*z* = 230–232 (M^+), 151 (M^+ – Br).

Anal. Calcd for C_9H_8BrFO: C, 46.78; H, 3.49. Found: C, 46.98; H, 3.48.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-3,4-(methylenedioxy)benzene (1i)
Ratio *Z*/*E* = 52:48; R_f = 0.5 (cyclohexane).

IR (neat): 3480, 3046, 2897, 1651, 1504, 1488, 1257, 1041, 930, 866 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.1 (d, *J* = 1.5 Hz, 0.5 H, H_{4Z}), 7.0 (d, *J* = 1.0 Hz, 0.5 H, H_{4E}), 6.9–6.7 (m, 2 H, H_7, H_8), 6.6 (d, $^3J_{H-F}$ = 15.4 Hz, 0.5 H, H_{2Z}), 6.0 (2 s, 2 H, H_9), 5.9 (d, $^3J_{H-F}$ = 32.5 Hz, 0.5 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.3, 148.1, 147.8, 147.6 (d, *J* = 3 Hz), 134.4 (d, *J* = 314 Hz), 133.0 (d, *J* = 329 Hz), 127.1 (d, *J* = 5 Hz), 125.5 (d, *J* = 9 Hz), 123.3 (d, *J* = 4 Hz), 122.8 (d, *J* = 6 Hz), 108.8, 113.1 (d, *J* = 6 Hz), 111.8 (d, *J* = 24 Hz), 108.5 (2 d), 101.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –67.6 (d, *J* = 15.4 Hz, 0.5 F), –70.6 (d, *J* = 32.5 Hz, 0.5 F).

MS (EI): *m*/*z* = 244–246 (M^+), 165 (M^+ – Br).

Anal. Calcd for $C_9H_6BrFO_2$: C, 44.11; H, 2.47. Found: C, 44.38; H, 2.65.

Methyl (*Z*)- and (*E*)-4-(2-Bromo-2-fluorovinyl)benzoate (1j)
Ratio *Z*/*E* = 55:45; mp 48–50 °C; R_f = 0.6 (cyclohexane–EtOAc, 9:1).

IR (KBr): 3026, 2954, 1943, 1714, 1641, 1609, 1439, 1278, 1114, 870, 765, 698, 589 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.1–7.9 (br s, 2 H, H_5), 7.6 (d, *J* = 8.4 Hz, 1.1 H, H_{4Z}), 7.5 (d, *J* = 8.5 Hz, 0.9 H, H_{4E}), 6.7 (d,

$^3J_{H-F}$ = 14.9 Hz, 0.55 H, H_{2Z}), 6.0 (d, $^3J_{H-F}$ = 32.3 Hz, 0.45 H, H_{2E}), 4.0 (s, 1.35 H, H_{8E}), 3.8 (s, 1.65 H, H_{8Z}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.9, 167.9, 138.1 (d, *J* = 5 Hz), 135.5 (d, *J* = 318 Hz), 137.4 (d, *J* = 9 Hz), 134.9 (d, *J* = 334 Hz), 131.3, 131.0, 130.7, 130.5 (d, *J* = 3 Hz), 129.6 (d, *J* = 3 Hz), 129.2 (d, *J* = 8 Hz), 113.8 (d, *J* = 6 Hz), 112.4 (d, *J* = 25 Hz), 53.5.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –62.2 (d, *J* = 14.9 Hz, 0.6 F), –64.5 (d, *J* = 32.3 Hz, 0.4 F).

MS (EI): *m*/*z* = 258–260 (M^+), 227–229 (M^+ – OMe), 199–201 (M^+ – CO_2Me), 120.

Anal. Calcd for $C_{10}H_8BrFO_2$: C, 46.36; H, 3.11. Found: C, 46.57; H, 3.34.

(*Z*)- and (*E*)-2-(2-Bromo-2-fluorovinyl)naphthalene (1k)
Ratio *Z*/*E* = 52:48; mp 83–85 °C; R_f = 0.6 (cyclohexane–EtOAc, 98:2).

IR (KBr): 3102, 2879, 1645, 1505, 1281, 1252, 1082, 908, 868, 825, 744, 481 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.7 (m, 4 H), 7.7–7.3 (m, 3 H), 6.8 (d, $^3J_{H-F}$ = 15.1 Hz, 0.5 H, H_{2Z}), 6.1 (d, $^3J_{H-F}$ = 32.8 Hz, 0.5 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 133.5 (d, *J* = 316 Hz), 132.3 (d, *J* = 332 Hz), 133.7, 133.6, 133.2, 133.1 (d, *J* = 2 Hz), 130.4 (d, *J* = 5 Hz), 129.3 (d, *J* = 9 Hz), 128.8, 128.6, 128.5, 128.4, 128.3 (d, *J* = 4 Hz), 128.1, 128.0, 127.8 (d, *J* = 7 Hz), 126.9, 126.8, 126.3 (d, *J* = 3 Hz), 126.0 (d, *J* = 8 Hz), 113.7 (d, *J* = 6 Hz), 112.3 (d, *J* = 24 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –65.1 (d, *J* = 15.1 Hz, 0.5 F), –67.9 (d, *J* = 32.8 Hz, 0.5 F).

MS (EI): *m*/*z* = 250–252 (M^+), 170 (M^+ – Br).

Anal. Calcd for $C_{12}H_8BrF$: C, 57.40; H, 3.21. Found: C, 57.69; H, 3.35.

(*Z*)- and (*E*)-4-(2-Bromo-2-fluorovinyl)benzonitrile (1l)
Ratio *Z*/*E* = 56:44; mp 79–81 °C; R_f = 0.4 (cyclohexane–EtOAc, 95:5).

IR (KBr): 3466, 2298, 1645, 1605, 1503, 1412, 1281, 1068, 866, 550 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.4 (m, 4 H, H_4, H_5), 6.6 (d, $^3J_{H-F}$ = 14.6 Hz, 0.6 H, H_{2Z}), 6.0 (d, $^3J_{H-F}$ = 32.0 Hz, 0.4 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.6 (d, *J* = 320 Hz), 137.2 (d, *J* = 334 Hz), 137.2, 136.7 (d, *J* = 9 Hz), 132.9, 132.6, 129.3 (d, *J* = 4 Hz), 128.9 (d, *J* = 8 Hz), 119.0, 112.4 (d, *J* = 6 Hz), 111.9, 111.5, 111.1 (d, *J* = 26 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –60.3 (d, *J* = 14.6 Hz, 0.6 F), –63.1 (d, *J* = 32.0 Hz, 0.4 F).

MS (EI): *m*/*z* = 225–227 (M^+), 146 (M^+ – Br).

Anal. Calcd for C_9H_5BrFN: C, 47.82; H, 2.23; N, 6.20. Found: C, 47.98; H, 2.25; N, 6.19.

(*Z*)- and (*E*)-1-(2-Bromo-2-fluorovinyl)-4-(trifluoromethyl)benzene (1m)
Ratio *Z*/*E* = 56:44; R_f = 0.6 (5% EtOAc–cyclohexane).

IR (KBr): 3070, 1651, 1619, 1415, 1325, 1170, 1130, 1069, 1018, 842, 598 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.5 (m, 4 H, H_4, H_5), 6.8 (d, $^3J_{H-F}$ = 14.5 Hz, 0.6 H, H_{2Z}), 6.1 (d, $^3J_{H-F}$ = 32.3 Hz, 0.4 H, H_{2E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.9 (d, *J* = 318 Hz), 136.7 (d, *J* = 335 Hz), 137.8 (d, *J* = 11 Hz), 135.7 (d, *J* = 9 Hz), 134.4, 134.1, 130.4 (d, *J* = 4 Hz), 130.3 (d, *J* = 3 Hz), 128.7, 128.6, 126.0 (q, *J* = 3.45 Hz), 125.7 (q, *J* = 3.45 Hz), 112.5 (d, *J* = 6 Hz), 111.2 (d, *J* = 25 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –62.2 (d, *J* = 15.1 Hz, 0.6 F), –63.2 (3 F), –65.1 (d, *J* = 32.2 Hz, 0.4 F).

MS (EI): *m*/*z* = 268–270 (M^+), 249–251 (M^+ – F), 189 (M^+ – Br), 169, 120.

α,α-Bromofluoroalkenes from Ketones; General Procedure
To a soln of PPh_3 (1.5 mmol, 1.5 equiv), tribromofluoromethane (1.5 mmol, 1.5 equiv), and an appropriate ketone (1.0 mmol, 1.0 equiv) in anhyd THF (40 mL), was added a soln of 1 M Et_2Zn in hexanes (1.5 mmol, 1.5 equiv) dropwise via a syringe pump over 20 min at r.t. under argon. The mixture was stirred for 1 h. The resulting soln was then quenched with MeOH (10 mL), stirred for 15 min, and concentrated under reduced pressure. The residue was then chromatographed (silica gel, cyclohexane–EtOAc), affording the desired α-bromo-α-fluoroalkene.

(Bromofluoromethylene)cyclohexane (1n)
R_f = 0.8 (cyclohexane–EtOAc, 95:5).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.2 (m, 2 H, H_3 or H_7), 2.1 (m, 2 H, H_3 or H_7), 1.5 (m, 6 H, H_4, H_5).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 126.9 (d, *J* = 302 Hz), 120.7 (d, *J* = 10 Hz), 31.1, 27.5 (d, *J* = 6 Hz), 27.0 (d, *J* = 6 Hz), 26.9.

^{19}F NMR (282.5 MHz, $CDCl_3$, decoupled): δ = –82.8.

(*Z*)- and (*E*)-2-(2-Bromo-2-fluoro-1-methylvinyl)naphthalene (1o)
R_f = 0.7 (cyclohexane–EtOAc, 98:2).

IR (neat): 3056, 1651, 1589, 1505, 1121, 1013, 857, 817, 747 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.9–7.6 (m, 4 H, H_7, H_8, H_9, H_{10}), 7.5–7.3 (m, 3 H, H_4, H_5, H_{12}), 2.2–2.0 (m, 3 H, H_{13}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 136.7, 133.6, 134.3, 133.6, 133.1, 133.0, 130.9 (d, *J* = 317 Hz), 129.3 (d, *J* = 322 Hz), 128.6, 128.5, 128.4, 128.2, 128.1, 128.0 (d, *J* = 3 Hz), 127.4 (d, *J* = 4 Hz), 126.8, 126.7, 126.6 (d, *J* = 3 Hz), 126.2 (d, *J* = 5 Hz), 120.0 (d, *J* = 7 Hz), 118.2 (d, *J* = 4 Hz), 21.1 (d, *J* = 3 Hz), 18.3 (d, *J* = 4 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –74.4 (could not be resolved).

MS (EI): *m*/*z* = 264–266 (M^+), 183 (M^+ – Br).

Anal. Calcd for $C_{13}H_{10}BrF$: C, 58.89; H, 3.80. Found: C, 58.78; H, 3.71.

(*Z*)- and (*E*)-1-Benzyloxy-4-[1-(Bromofluoromethylene)propyl]benzene (1p)
Ratio *Z*/*E* = 46:54; mp 65–67 °C; R_f = 0.5 (cyclohexane).

IR (KBr): 3035, 2968, 2874, 1660, 1607, 1511, 1454, 1386, 1239, 1177, 1133, 1013, 835, 815, 744, 696, 550 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.2 (m, 5 H, H_{11}, H_{12}, H_{13}), 7.2–7.0 (m, 2 H, H_6), 7.0–6.8 (m, 2 H, H_5), 5.0 (s, 2 H, H_9), 2.5–2.3 (m, 2 H, H_2), 0.9 (q, *J* = 7.8 Hz, 3 H, H_1).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.7, 137.2, 129.3 (d, *J* = 316 Hz), 130.4 (d, *J* = 3 Hz), 129.8 (d, *J* = 3 Hz), 128.1 (d, *J* = 195 Hz), 129.0, 128.7, 128.4, 128.0, 127.9, 125.6, 123.5 (d, *J* = 6 Hz), 115.0, 114.9, 70.9, 28.2, 25.5 (d, *J* = 4 Hz), 12.9 (d, *J* = 2 Hz,), 12.5 (d, *J* = 4 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –76.5 (s, 0.5 F), –76.7 (t, *J* = 3.6 Hz, 0.5 F).

MS (EI): *m*/*z* = 334–336 (M^+), 240 (M^+ – Br).

Anal. Calcd for $C_{17}H_{16}BrFO$: C, 60.91; H, 4.81. Found: C, 61.07; H, 4.88.

(*Z*)- and (*E*)-1-(Bromofluoromethylene)-1,2,3,4-tetrahydronaphthalene (1q)
Ratio *Z*/*E* = 41:59; R_f = 0.8 (cyclohexane–EtOAc, 98:2).

IR (neat): 3429, 3061, 2934, 1686, 1451, 1253, 1199, 783, 745, 660 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.9–7.7 (m, 1 H, H_8), 7.4–7.1 (m, 3 H, H_9, H_{10}, H_{11}), 2.9–2.7 (m, 3 H, 1 H_3 and 2 H_5), 2.6–2.5 (m, 1 H, 1 H_3), 2.0–1.8 (m, 2 H, H_4).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.3 (d, *J* = 5 Hz), 133.4 (d, *J* = 3 Hz), 131.4 (d, *J* = 7 Hz), 131.6 (d, *J* = 10 Hz), 123.8 (d, *J* = 221 Hz), 127.6 (d, *J* = 326 Hz), 129.2, 129.1, 129.0, 128.5, 128.1, 127.9 (d, *J* = 1 Hz), 126.6, 125.8, 119.0 (d, *J* = 17 Hz), 116.0 (d, *J* = 14 Hz), 31.1, 30.6, 30.6, 26.0 (d, *J* = 6 Hz), 23.2 (d, *J* = 1 Hz), 22.7 (d, *J* = 2 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –69.0 (t, *J* = 3.6 Hz, 0.4 F), –72.6 (s, 0.6 F).

MS (EI): *m*/*z* = 240–242 (M^+).

Anal. Calcd for $C_{11}H_{10}BrF$: C, 54.80; H, 4.18. Found: C, 54.62; H, 4.31.

(*Z*)- and (*E*)-(2-Bromo-2-fluoro-1-phenylvinyl)trimethylsilane (1r)
Ratio *Z*/*E* = 70:30; R_f = 0.5 (cyclohexane).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.0 (m, 3 H, H_4, H_6), 7.0–6.8 (m, 2 H, H_5), 0.1–0 (m, 9 H, H_7).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.8 (d, *J* = 11 Hz), 138.6, 136.1 (d, *J* = 315 Hz), 134.1 (d, *J* = 332 Hz), 129.3, 129.1, 128.9 (d, *J* = 3 Hz), 128.5 (d, *J* = 1 Hz), 127.4, 127.3, 124.6 (d, *J* = 28 Hz), 122.4 (d, *J* = 9 Hz), 0.0 (d, *J* = 3 Hz), –0.1 (d, *J* = 2 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –39.61 (0.7 F), –39.64 (0.3 F).

MS (EI): *m*/*z* = 272–274 (M^+), 257–259 ($M^+ - CH_3$).

Anal. Calcd for $C_{11}H_{14}BrFSi$: C, 48.36; H, 5.16. Found: C, 48.97; H, 5.37; large error due to rapid decomposition.

3-(Bromofluoromethylene)-1,5-diphenylpentane (1s)
R_f = 0.5 (cyclohexane).

IR (neat): 3085, 3026, 2928, 2861, 1663, 1496, 1454, 1182, 1099, 1073, 748, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.0 (m, 10 H, H_6, H_7, H_8, H_{12}, H_{13}, H_{14}), 2.8–2.6 (m, 4 H, H_4, H_{10}), 2.6–2.4 (m, 2 H, H_3 or H_9), 2.4–2.2 (m, 2 H, H_3 or H_9).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.5, 141.4, 129.6 (d, *J* = 313 Hz), 129.0, 128.9, 128.8, 128.7, 126.6, 126.5, 120.5 (d, *J* = 10 Hz), 34.7, 34.5 (d, *J* = 7 Hz), 33.9 (d, *J* = 4 Hz), 31.3 (d, *J* = 5 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$, decoupled): δ = –77.6.

MS (EI): *m*/*z* = 332–334 (M^+), 253 ($M^+ - Br$), 105 ($PhCH_2CH_2^+$).

Anal. Calcd for $C_{18}H_{18}BrF$: C, 64.88; H, 5.44. Found: C, 64.83; H, 5.37.

(*Z*)- and (*E*)-1-[(1*E*)-4-Bromo-4-fluoro-3-methylbuta-1,3-dienyl]benzene (1t)
Ratio *Z*/*E* = 45:55; R_f = 0.8 (cyclohexane–EtOAc, 95:5).

IR (neat): 3048, 3024, 2926, 1802, 1763, 1701, 1633, 1616, 1495, 1447, 1281, 1116, 1030, 958, 749, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.2 (m, 5 H, H_6, H_7, H_8), 7.2 (d, *J* = 16.0 Hz, 1 H, H_3), 6.9 (d, *J* = 16.0 Hz, 1 H, H_4), 2.0–1.8 (m, 3 H, H_9).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.4, 132.8 (d, *J* = 349 Hz), 132.7 (d, *J* = 351 Hz), 131.4 (d, *J* = 12 Hz), 129.8 (d, *J* = 5 Hz), 129.1, 128.3, 127.0, 126.9 (d, *J* = 1 Hz), 126.1 (d, *J* = 1 Hz), 121.8 (d, *J* = 6 Hz), 117.4–117.0, 15.5, 12.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –72.5 (d, *J* = 3.8 Hz, 0.5 F), –74.4 (d, *J* = 4.3 Hz, 0.5 F).

MS (EI): *m*/*z* = 240–242 (M^+), 161 ($M^+ - Br$).

1-Benzyl-4-(bromofluoromethylene)piperidine (1u)
R_f = 0.5 (cyclohexane).

IR (neat): 3341, 3028, 2964, 2906, 2803, 2761, 1681, 1494, 1455, 1439, 1364, 1338, 1298, 1231, 1103, 1079, 985, 862, 738, 698, 586, 465 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.1 (m, 5 H, H_9, H_{10}, H_{11}), 3.4 (s, 2 H, H_7), 2.5–2.3 (m, 6 H, H_4, H_5, H_3 or H_6), 2.3–2.1 (m, 2 H, H_3 or H_6).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 138.5, 129.5, 128.7, 127.5, 128.1 (d, *J* = 310 Hz), 117.7 (d, *J* = 12 Hz), 63.2, 53.6 (dd, *J* = 2 Hz, *J* = 2 Hz), 30.5, 27.2 (d, *J* = 5 Hz).

^{19}F NMR (282.5 MHz, $CDCl_3$, decoupled): δ = –82.1.

MS (EI): *m*/*z* = 283–285 (M^+), 204 ($M^+ - Br$).

Anal. Calcd for $C_{13}H_{15}BrFN$: C, 54.95; H, 5.32; N, 4.93. Found: C, 54.98; H, 5.36; N, 4.90.

(*Z*)- and (*E*)-{[(2-(Bromofluoromethylene)cyclopentyl]methoxy}*tert*-butyldiphenylsilane (1v)
Ratio *Z*/*E* = 44:56; R_f = 0.7 (cyclohexane–EtOAc, 98:2).

IR (neat): 3394, 3071, 2958, 2857, 1682, 1471, 1428, 1111, 1092, 823, 701, 504 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.6 (m, 4 H, H_{11}), 7.3 (m, 6 H, H_{12}, H_{13}), 3.6 (m, 1 H, H_7), 3.5–3.4 (m, 1 H, H_7), 3.0–2.9 (m, 0.4 H, H_{6Z}), 2.7–2.6 (m, 0.6 H, H_{6E}), 2.4–2.2 (m, 1.1 H, H_{3E}), 2.2–2.1 (m, 0.9 H, H_{3Z}), 2.0–1.5 (br m, 4 H, H_4, H_5), 1.0 (s, 9 H, H_9).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 142.9 (d, *J* = 249 Hz), 136.4, 135.2, 134.4, 131.0, 130.4, 128.7, 128.4, 125.3 (2 d, *J* = 10 Hz), 64.9, 64.2, 46.3, 45.3, 32.8, 31.3, 30.2, 29.8, 27.6, 26.7, 25.3, 24.7, 20.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –74.0 (m, 0.4 F), –77.3 (m, 0.6 F).

MS (EI): *m*/*z* = 447 (M^+), 201, 181, 135, 109, 91, 81, 57 (*t*-Bu^+).

Anal. Calcd for $C_{23}H_{28}BrFOSi$: C, 61.74; H, 6.31. Found: C, 61.57; H, 6.42.

α-Fluoroacrylates from Aldehydes or Ketones; General Procedure
To an anhyd THF soln (10 mL) of PPh_3 (4 mmol, 4 equiv) and ethyl bromodifluoroacetate (2 mmol, 2 equiv) was rapidly added 1 M Et_2Zn in hexane (4 mmol, 4 equiv) under argon. The mixture was stirred for 10 min (until the internal temperature returned to r.t.), then the appropriate carbonyl compound was rapidly added. The mixture was stirred for 10 min. The resulting soln was then quenched with EtOH (15 mL), stirred for 15 min, and concentrated under reduced pressure. The residue was taken up in Et_2O (5 mL) and filtered through Celite and then it was chromatographed (silica gel, cyclohexane–EtOAc) to afford the expected α-fluoroacrylate.

Ethyl (*Z*)- and (*E*)-2-Fluoro-3-(4-methoxyphenyl)acrylate (2a)
Ratio *Z*/*E* = 85:15; R_f = 0.3 (cyclohexane–EtOAc, 9:1).

IR (neat): 2983, 1726, 1660, 1607, 1514, 1371, 1256, 1179, 1098, 1030, 830 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.5 (d, 2 H, H_6), 6.8–6.7 (m, 3 H, H_3, H_5), 4.2 (2 q, *J* = 7.2 Hz, 2 H, H_9), 3.7 (2 s, 3 H, H_8), 1.3 (t, *J* = 7.0 Hz, 2.55 H, H_{10Z}), 1.2 (t, *J* = 7.0 Hz, 0.45 H, H_{10E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.5 (d, *J* = 34 Hz), 160.7 (d, *J* = 36 Hz), 160.5 (d, *J* = 3 Hz), 160.1 (d, *J* = 1 Hz), 145.0 (d, *J* = 263 Hz), 132.4 (d, *J* = 9 Hz), 132.1 (d, *J* = 3 Hz), 123.7 (d, *J* = 5 Hz), 123.0 (d, *J* = 10 Hz), 121.9 (d, *J* = 27 Hz), 117.3 (d, *J* = 5 Hz), 114.2, 113.4, 61.6, 61.4, 55.6, 55.5, 14.2, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –119.5 (d, *J* = 23.6 Hz, 0.1 F), –129.2 (d, *J* = 35.5 Hz, 0.9 F).

MS (EI): *m*/*z* = 224 (M^+), 195 (M^+ – Et).

Anal. Calcd for $C_{12}H_{13}FO_3$: C, 64.28; H, 5.84. Found: C, 63.71; H, 6.02.

Ethyl (*Z*)- and (*E*)-2-Fluorooct-2-enoate (2b)
Ratio *Z*/*E* = 70:30; R_f = 0.5 (cyclohexane–EtOAc, 9:1).

IR (neat): 2960, 2932, 1732, 1678, 1467, 1373, 1309, 1261, 1201, 1148, 1089, 765 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.0 (dt, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-F}$ = 33.3 Hz, 0.7 H, H_{3Z}), 5.8 (dt, $^3J_{H-H}$ = 8.3 Hz, $^3J_{H-F}$ = 21.6 Hz, 0.3 H, H_{3E}), 4.2–4.1 (m, 2 H, H_9), 2.4 (dq, *J* = 1.7 Hz, *J* = 8.6 Hz, 0.6 H, H_{4E}), 2.1 (dq, *J* = 2.2 Hz, *J* = 7.2 Hz, 1.4 H, H_{4Z}), 1.4–1.2 (m, 9 H, H_5, H_6, H_7, H_8), 0.8 (t, *J* = 6.8 Hz, 3 H, H_{10}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.1 (d, *J* = 36 Hz), 161.0 (d, *J* = 26 Hz), 148.0 (d, *J* = 255 Hz), 147.0 (d, *J* = 250 Hz), 123.8 (d, *J* = 18 Hz), 121.0 (d, *J* = 12 Hz), 61.5, 61.3, 31.4, 29.0 (d, *J* = 2 Hz), 29.0 (d, *J* = 2 Hz), 25.5 (d, *J* = 5 Hz), 24.2 (d, *J* = 2 Hz), 22.5, 22.4, 14.1, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –123.2 (d, *J* = 21.5 Hz, 0.3 F), –131.6 (d, *J* = 33.3 Hz, 0.7 F).

MS (EI): *m*/*z* = 188 (M^+), 91, 41.

Ethyl (*Z*)- and (*E*)-5-(*tert*-Butyldiphenylsilyloxy)-2-fluoropent-2-enoate (2c)
Ratio *Z*/*E* = 65:35; R_f = 0.4 (cyclohexane–EtOAc, 9:1).

IR (neat): 3071, 2932, 2958, 1738, 1681, 1473, 1428, 1314, 1215, 1112, 1027, 939, 824, 741, 703, 614, 505 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.3 (m, 10 H, H_{arom}), 6.2 (dt, $^3J_{H-H}$ = 7.8 Hz, $^3J_{H-F}$ = 21.4 Hz, 0.7 H, H_{3Z}), 6.0 (dt, $^3J_{H-H}$ = 7.9 Hz, $^3J_{H-F}$ = 21.4 Hz, 0.3 H, H_{3E}), 4.3 (q, *J* = 7.2 Hz, 1.3 H, H_{12Z}), 4.3 (q, *J* = 7.2 Hz, 0.7 H, H_{12E}), 3.7 (t, *J* = 6.4 Hz, 2 H, H_5), 2.8–2.7 (m, 0.7 H, H_{4E}), 2.5–2.4 (m, 1.3 H, H_{4Z}), 1.3 (t, *J* = 7.2 Hz, 3 H, H_{13}), 1.0 (s, 9 H, H_7).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.1 (d, *J* = 36 Hz), 160.5 (d, *J* = 36.0 Hz), 149.1 (d, *J* = 256 Hz), 148.1 (d, *J* = 252 Hz), 137.5 (d, *J* = 10 Hz), 136.0, 134.1, 130.1, 120.4 (d, *J* = 19 Hz), 117.9 (d, *J* = 12 Hz), 61.5, 61.3, 31.4, 29.0 (d, *J* = 2 Hz), 29.0 (d, *J* = 1.7 Hz), 25.5 (d, *J* = 5.2 Hz), 24.2 (d, *J* = 2.3 Hz), 22.5, 22.4, 14.1, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –121.4 (d, *J* = 21.5 Hz, 0.3 F), –129.7 (d, *J* = 33.3 Hz, 0.7 F).

MS (EI): *m*/*z* = 343 (M^+ – *t*-Bu).

Anal. Calcd for $C_{23}H_{29}FO_3Si$: C, 68.97; H, 7.30. Found: C, 68.93; H, 7.16.

Ethyl (*Z*)- and (*E*)-2-Fluoro-3-phenylacylate (2d)
Ratio *Z*/*E* = 80:20; R_f = 0.6 (cyclohexane–EtOAc, 9:1).

IR (neat): 2984, 1732, 1660, 1450, 1372, 1283, 1202, 1100, 1020, 768, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.3 (m, 5 H, H_5, H_6, H_7), 6.9 (d, *J* = 35.2 Hz, 0.8 H, H_{3Z}), 6.9 (d, *J* = 22.2 Hz, 0.2 H, H_{3E}), 4.3 (q, *J* = 7.2 Hz, 1.6 H, H_{8Z}), 4.2 (q, *J* = 7.2 Hz, 0.2 H, H_{8E}), 1.4 (t, *J* = 7.2 Hz, 2.4 H, H_{9Z}), 1.2 (t, *J* = 7.2 Hz, 0.6 H, H_{9E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 35 Hz), 160.6 (d, *J* = 36 Hz), 147.2 (d, *J* = 267 Hz), 142.0 (d, *J* = 258 Hz), 133.9 (d, *J* = 20 Hz), 131.3 (d, *J* = 5 Hz), 130.4 (d, *J* = 8 Hz), 129.8 (d, *J* = 3 Hz), 129.7 (d, *J* = 3 Hz), 128.9, 128.2, 121.6 (d, *J* = 26 Hz), 117.6 (d, *J* = 5 Hz), 62.0, 61.8, 14.4, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –117.6 (d, *J* = 22.5 Hz, 0.2 F), –125.7 (d, *J* = 35.5 Hz, 0.8 F).

MS (EI): *m*/*z* = 194 (M^+), 165 (M^+ – Et), 101.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{11}FO_2$: 194.2075; found: 194.2067 and 194.2080.

Ethyl (*Z*)- and (*E*)-2-Fluoro-5-phenylpent-2-enoate (2e)
Ratio *Z*/*E* = 68:32; R_f = 0.3 (cyclohexane–EtOAc, 9:1).

IR (neat): 2984, 2935, 1732, 1678, 1455, 1373, 1314, 1270, 1241, 1184, 1105, 746, 698, 502 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.3 (m, 5 H, H_{arom}), 6.2 (dt, $^3J_{H-F}$ = 33.1 Hz, $^3J_{H-F}$ = 7.9 Hz, 0.7 H, H_{3Z}), 6.0 (dt, $^3J_{H-F}$ = 21.0 Hz, $^3J_{H-F}$ = 7.9 Hz, 0.3 H, H_{3E}), 4.4–4.3 (m, 2 H, H_{10}), 2.9–2.6 (m, 4 H, H_{4-5}), 1.4–1.3 (m, 3 H, H_{11}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.7 (d, *J* = 36 Hz), 160.5 (d, *J* = 35.0 Hz), 148.1 (d, *J* = 256 Hz), 147.2 (d, *J* = 252 Hz), 140.5 (d, *J* = 12 Hz), 137.1 (d, *J* = 12 Hz), 133.5 (d, *J* = 19 Hz), 129.2, 126.7, 122.8 (d, *J* = 18 Hz), 120.0 (d, *J* = 12 Hz), 61.9, 61.7, 35.7, 34.9, 27.7, 26.4, 14.6, 14.5.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –122.1 (d, *J* = 21.5 Hz, 0.3 F), –130.1 (d, *J* = 33.3 Hz, 0.7 F).

MS (EI): *m*/*z* = 222 (M^+), 202, 91 ($PhCH_2^+$).

HRMS-EI: *m*/*z* [M]$^+$ calcd for $C_{13}H_{15}FO_2$: 222.1056; found: 222.1058 and 222.1032.

Ethyl (*Z*)- and (*E*)-2-Fluoro-3-[4-(trifluoromethyl)phenyl]acrylate (2f)
Ratio *Z*/*E* = 75:25; R_f = 0.5 (cyclohexane–EtOAc, 9:1).

IR (neat): 2987, 1736, 1325, 1126, 1068, 1018, 829 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.6–7.1 (m, 4 H, H_5, H_6), 6.8 (d, *J* = 34.6 Hz, 0.8 H, H_{3Z}), 6.8 (d, *J* = 17.0 Hz, 0.2 H, H_{3E}), 4.2 (q, *J* = 7.0 Hz, 1.5 H, H_{9Z}), 4.1 (q, *J* = 7.4 Hz, 0.5 H, H_{9E}), 1.3 (t, *J* = 7 Hz, 2.3 H, H_{10Z}), 1.1 (t, *J* = 7.0 Hz, 0.7 H, H_{10E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 35 Hz), 160.5 (d, *J* = 36 Hz), 148.6 (d, *J* = 272 Hz), 148.3 (d, *J* = 260 Hz), 132.1, 131.6 (d, *J* = 11 Hz), 131.3 (d, *J* = 4 Hz), 131.3, 130.6 (d, *J* = 8 Hz), 130.2 (d, *J* = 3 Hz), 126.1 (q, *J* = 4 Hz), 120.2 (d, *J* = 27 Hz), 116.1 (d, *J* = 5 Hz), 62.6, 62.3, 14.5, 14.1.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –63.3 (0.7 F), –63.4 (2.3 F), –115.1 (d, *J* = 21.5 Hz, 0.2 F), –122.5 (d, *J* = 34.4 Hz, 0.8 F).

MS (EI): *m*/*z* = 262 (M^+).

Anal. Calcd for $C_{12}H_{10}F_4O_2$: C, 54.97; H, 3.84. Found: C, 54.76; H: 3.90.

Ethyl (*Z*)- and (*E*)-3-(4-Bromophenyl)-2-fluoroacrylate (2g)
Ratio *Z*/*E* = 80:20; R_f = 0.3 (cyclohexane–EtOAc, 9:1).

IR (neat): 2981, 1732, 1670, 1489, 1373, 1286, 1234, 1204, 1095, 1070, 1010, 828, 762, 472 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.3 (m, 4 H, H_5, H_6), 6.8 (d, *J* = 34.7 Hz, 0.8 H, H_{3Z}), 6.8 (d, *J* = 21.9 Hz, 0.2 H, H_{3E}), 4.3 (q, *J* = 7.2 Hz, 1.6 H, H_{8Z}), 4.2 (q, *J* = 7.0 Hz, 0.4 H, H_{8E}), 1.4 (t, *J* = 7.2 Hz, 2.4 H, H_{9Z}), 1.2 (t, *J* = 7.2 Hz, 0.6 H, H_{9E}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.2 (d, *J* = 34 Hz), 160.3 (d, *J* = 35 Hz), 147.4 (d, *J* = 265 Hz), 147.2 (d, *J* = 254 Hz), 132.1, 131.6 (d, *J* = 11 Hz), 131.3 (d, *J* = 4 Hz), 131.3, 130.0 (d, *J* = 5 Hz), 129.9 (d, *J* = 10 Hz), 124.0, 122.9, 120.5 (d, *J* = 27 Hz), 116.3 (d, *J* = 5 Hz), 62.1, 61.8, 14.2, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –116.3 (d, *J* = 22.5 Hz, 0.2 F), –124.4 (d, *J* = 35.5 Hz, 0.8 F).

MS (EI): *m*/*z* = 272–274 (M^+), 148, 120.

Anal. Calcd for $C_{11}H_{10}BrFO_2$: C, 48.38; H, 3.69. Found: C, 48.59; H, 3.78.

Ethyl (*Z*)- and (*E*)-2-Fluoro-3-(4-pyridyl)acrylate (2h)
Ratio *Z*/*E* = 85:15; R_f = 0.4 (cyclohexane–EtOAc, 9:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.6–7.3 (m, 4 H, H_5, H_6), 6.9 (d, *J* = 35.2 Hz, 0.9 H, H_{3Z}), 6.9 (d, *J* = 22.1 Hz, 0.1 H, H_{3E}), 4.3 (q, *J* = 7.2 Hz, 1.7 H, H_{7Z}), 4.2 (q, *J* = 7.2 Hz, 0.3 H, H_{7E}), 1.4 (t, *J* = 7.2 Hz, 2.55 H, H_{8Z}), 1.2 (t, *J* = 7.2 Hz, 0.45 H, H_{8E}).

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –117.7 (d, *J* = 22.5 Hz, 0.15 F), –125.8 (d, *J* = 35.5 Hz, 0.85 F).

Ethyl (*Z*)- and (*E*)-2-Fluoro-5-methylhex-2-enoate (2i)
Ratio *Z*/*E* = 70:30; R_f = 0.5 (cyclohexane–EtOAc, 9:1).

IR (neat): 2961, 2873, 1732, 1678, 1467, 1373, 1324, 1293, 1227, 1152, 1085, 1050, 764 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.1 (dt, $^3J_{H–H}$ = 8.0 Hz, $^3J_{H–F}$ = 33.3 Hz, 0.7 H, H_{3Z}), 5.9 (dt, $^3J_{H–H}$ = 8.2 Hz, $^3J_{H–F}$ = 22.1 Hz, 0.3 H, H_{3E}), 4.3–4.2 (m, 2 H, H_7), 2.4 (t, *J* = 7.3 Hz, 0.6 H, H_{4E}), 2.1 (dt, *J* = 1.6 Hz, *J* = 7.2 Hz, 1.4 H, H_{4Z}), 1.8–1.3 (m, 1 H, H_5), 1.3 (m, 3 H, H_8), 0.9 (d, *J* = 6.6 Hz, 6 H, H_6, $H_{6'}$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.3 (d, *J* = 36 Hz), 161.2 (d, *J* = 36 Hz), 148.4 (d, *J* = 255 Hz), 147.4 (d, *J* = 251 Hz), 122.6 (d, *J* = 18 Hz), 119.6 (d, *J* = 12 Hz), 61.6, 61.3, 34.2 (d, *J* = 5 Hz), 33.2 (d, *J* = 2 Hz), 28.7 (d, *J* = 2 Hz), 28.0 (d, *J* = 2 Hz), 22.3, 14.5.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –122.2 (d, *J* = 21.5 Hz, 0.3 F), –131.1 (d, *J* = 33.3 Hz, 0.7 F).

MS (EI): *m*/*z* = 174 (M^+), 104.

Ethyl (*Z*)- and (*E*)-3-[4-(Methoxycarbonyl)phenyl]-2-fluoroacrylate (2j)
Ratio *Z*/*E* = 70:30; R_f = 0.3 (cyclohexane–EtOAc, 9:1).

IR (neat): 2955, 1731, 1667, 1609, 1436, 1372, 1279, 1204, 1111, 1019, 861, 816, 769 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.2–7.9 (m, 4 H, H_5, H_6), 6.9 (d, $^3J_{H–F}$ = 34.4 Hz, 0.7 H, H_{3Z}), 6.8 (d, *J* = 21.4 Hz, 0.3 H, H_{3E}), 4.3 (q, *J* = 7.2 Hz, 1.4 H, H_{10Z}), 4.2 (q, *J* = 7.2 Hz, 0.6 H, H_{10E}), 3.8 (s, 2.1 H, H_{9Z}), 3.8 (s, 0.9 H, H_{9E}), 1.3 (t, *J* = 7.2 Hz, 2.1 H, H_{11}), 1.1 (t, *J* = 7.2 Hz, 0.9 H, H_{11}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.9, 166.7, 161.3 (d, *J* = 36 Hz), 160.5 (d, *J* = 36 Hz), 148.4 (d, *J* = 256 Hz), 147.5 (d, *J* = 252 Hz), 137.3 (d, *J* = 9 Hz), 136.1 (d, *J* = 8 Hz), 131.0 (d, *J* = 3 Hz), 130.5, 130.4, 130.3, 129.9 (d, *J* = 3 Hz), 129.6, 120.6 (d, *J* = 26 Hz), 116.6 (d, *J* = 5 Hz), 62.5, 62.2, 52.5, 14.5, 14.2.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –115.0 (d, *J* = 21.4 Hz, 0.3 F), –122.3 (d, *J* = 34.8 Hz, 0.7 F).

MS (EI): *m*/*z* = 252 (M^+), 221, 193.

Ethyl (*Z*)- and (*E*)-2-Fluoro-3-phenylbut-2-enoate (2k)
Ratio *Z*/*E* = 60:40; R_f = 0.6 (cyclohexane–EtOAc, 9:1).

IR (neat): 2988, 1746, 1666, 1306, 1265, 1231, 1185, 1137, 1017, 952, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.1 (m, 5 H, H_5, H_6, H_7), 4.2 (q, *J* = 7.2 Hz, 0.8 H, H_{9E}), 3.9 (q, *J* = 7.2 Hz, 1.2 H, H_{9Z}), 2.3 (d, *J* = 3.6 Hz, 1.2 H, H_{8E}), 2.0 (d, *J* = 4.4 Hz, 1.8 H, H_{8Z}), 1.3 (t, *J* = 7.2 Hz, 1.2 H, H_{10E}), 1.3 (t, *J* = 7.2 Hz, 1.8 H, H_{10Z}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 35 Hz), 161.0 (d, *J* = 36 Hz), 145.6 (d, *J* = 252 Hz), 143.5 (d, *J* = 254 Hz), 129.5 (d, *J* = 30 Hz), 129.6, 129.5, 128.7, 128.4, 138.9, 138.0, 131.8, 131.1, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 61.7, 61.4, 19.7, 19.6, 14.6, 14.0.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –124.4 (q, *J* = 4.3 Hz, 0.4 F), –126.3 (q, *J* = 3.2 Hz, 0.6 F).

MS (EI): *m*/*z* = 208 (M^+), 162.

Anal. Calcd for $C_{12}H_{13}FO_2$: C, 69.22; H 6.29. Found: C, 69.24; H: 6.09.

Ethyl 2-Fluoro-3-methyl-5-phenylpent-2-enoate (2l)
Ratio *Z*/*E* = 60:40; R_f = 0.5 (cyclohexane–EtOAc, 9:1).

IR (neat): 2983, 1722, 1664, 1455, 1299, 1127, 699, 543 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.2 (m, 5 H, H_7, H_8, H_9), 4.3 (m, 2 H, H_{11}), 2.8 (m, 3 H, H_4, H_5), 2.5–2.4 (m, 1 H, H_4), 2.0 (d, *J* = 3.2 Hz, 1.2 H, H_{10E}), 1.8 (d, *J* = 4.3 Hz, 1.8 H, H_{10Z}), 1.2 (m, 3 H, H_{12}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.8 (d, *J* = 35 Hz), 161.4 (d, *J* = 35 Hz), 144.7 (d, *J* = 249 Hz), 144.3 (d, *J* = 246.9 Hz), 133.1 (d, *J* = 13 Hz), 133.0 (d, *J* = 14 Hz), 141.6, 141.4, 134.3, 134.0, 128.8, 128.5, 61.4, 34.9, 34.8, 34.7, 33.9, 17.4 (d, *J* = 2 Hz), 17.2 (d, *J* = 9 Hz), 14.6.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –126.9 (q, *J* = 11 Hz, 0.6 F), –128.6 (q, *J* = 11 Hz, 0.4 F).

MS (EI): *m*/*z* = 236 (M^+), 216, 91 ($PhCH_2^+$).

HRMS-EI: *m*/*z* [M^+] calcd for $C_{14}H_{17}FO_2$: 236.1213; found: 236.1227 and 236.1220.

Ethyl (*Z*)- and (*E*)-Cyclohexylidenefluoroacetate (2m)
R_f = 0.6 (cyclohexane–EtOAc, 9:1).

IR (neat): 2922, 1722, 1661, 1437, 1264, 1183, 1119, 722, 541 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.2 (q, *J* = 7.1 Hz, 2 H, H_7), 2.7 (m, 2 H, H_4, $H_{4'}$), 2.3 (dd, *J* = 2.0 Hz, *J* = 4.1 Hz, 2 H, H_4, $H_{4'}$), 1.5 (m, 6 H, H_5, H_6), 1.3 (t, *J* = 7.1 Hz, 3 H, H_8).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.64 (d, *J* = 35 Hz), 139.95 (d, *J* = 245 Hz), 135.48 (d, *J* = 12 Hz), 59.9, 26.8, 26.6, 26.5, 26.4, 26.1, 13.2.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –131.8.

MS (EI): *m*/*z* = 186 (M^+), 158.

HRMS-EI: *m*/*z* [M^+] calcd for $C_{10}H_{15}FO_2$: 186.1056; found: 186.1054.

Ethyl (*Z*)- and (*E*)-2,4,4,4-Tetrafluoro-3-phenylbut-2-enoate (2n)
Ratio *Z*/*E* = 35:65; R_f = 0.5 (cyclohexane–EtOAc, 9:1).

IR (neat): 2988, 1746, 1656, 1446, 1373, 1306, 1265, 1231, 1185, 1137, 1017, 952, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.3–7.2 (m, 5 H, H_5, H_6, H_7), 4.3 (q, *J* = 7.2 Hz, 1.3 H, H_{9E}), 3.9 (q, *J* = 7.2 Hz, 0.7 H, H_{9Z}), 1.3 (t, *J* = 7.2 Hz, 2.0 H, H_{10E}), 0.9 (t, *J* = 7.2 Hz, 1.0 H, H_{10Z}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.6 (d, *J* = 35 Hz), 159.3 (d, *J* = 34 Hz), 152.0 (d, *J* = 284 Hz), 149.6 (d, *J* = 284 Hz), 137.8 (d, *J* = 30 Hz), 133.8 (d, *J* = 74 Hz), 129.6–128.4 (m), 125–117 (m), 63.5, 62.8, 14.1, 13.7.

^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –58.8 (d, *J* = 9.7 Hz, 1.95 F), –60.9 (d, *J* = 24.7 Hz, 1.05 F), –107.2 (q, *J* = 9.7 Hz, 0.35 F), –108.9 (q, *J* = 24.7 Hz, 0.65 F).

MS (EI): *m*/*z* = 262 (M^+), 233 (M^+ – Et).

HRMS-EI: *m*/*z* [M^+] calcd for $C_{12}H_{10}F_4O_2$: 262.0617; found: 262.0643 and 262.0608.

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