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Diethylzinc-Mediated Addition of 2,2-Dibromo-2-fluoroacetamides to Carbonyl Compounds: Synthesis of α-Bromo-α-fluoro-β-hydroxy Amides and/or (*Z*)-Fluorovinyl Amides

Gérald Lemonnier,[a] Thomas Poisson,[a] Samuel Couve-Bonnaire,[a] Philippe Jubault,[a] and Xavier Pannecoucke*[a]

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We describe straightforward routes either to α-bromo-α-fluoro-β-hydroxy amides or to (*Z*)-α-fluoroacrylamides starting from aldehydes, ketones or imine and 2,2-dibromo-2-fluoroacetamides. Depending on the nature of the amide, these diethylzinc-mediated additions to aldehydes, ketones or imine afford selective access either to bromofluorohydrins or to (*Z*)-α-fluoroacrylamides. The corresponding products were obtained in moderate to very good yields and the configurations of both products were confirmed by X-ray analyses.

Introduction

Physical, chemical and biological properties of a molecule can be modulated by judicious introduction of a fluorine atom.[1] Consequently, for the past decades, fluorine-containing molecules have received considerable attention for the development of new technologies and biologically active compounds.[2] In view of the unique features of fluorine, it is not surprising that about 20% of pharmaceutical compounds and 40% of agrochemicals contain at least one fluorine atom.

Although fluorine is quite abundant on earth, fluoroorganic compounds are scarce in nature, and one of the most efficient means to access such compounds involves the use of fluorinated building blocks prepared from commercially available fluorinated precursors.[3] In that context, our group have developed several methodologies for the synthesis of monofluorinated scaffolds.[4] One of our approaches was based on Et_2Zn- or Zn-mediated addition of commercially available ethyl dibromofluoroacetate, affording straightforward access to fluoroacrylates,[4j] α-bromo-α-fluoro-β-hydroxy esters,[4h] fluoroepoxides[4i] and fluorocyclopropanes.[4c–4e]

In addition, α,β-unsaturated amides are valuable synthetic intermediates that can lead, through one-step reactions, to various functional groups such as allylic amines, allylic alcohols, α,β-unsaturated ketones, aldehydes or imines.[5] However, the direct olefination of carbonyl compounds to afford highly valuable α-fluorinated α,β-unsaturated amides has been scarcely reported to date.[6] The methods used have basically involved Pd-catalysed condensation of fluoroiodomethylpiperidino ketone on aldehydes,[7] a two-step addition of tetrafluoroethane (HFC-134a) onto aldehydes,[8] or Julia–Kocienski olefination of aldehydes and ketones with the aid of a well-designed presynthesized fluorinated reagent.[9] Nevertheless, despite their synthetic utility, these methodologies can suffer from several issues such as narrow substrate scope, the presence of inseparable *E*/*Z* isomers, moderate yields and/or the need for a multistep preparation of the fluorinated reagent. To overcome these major drawbacks, we turned our attention to 2,2-dibromo-2-fluoroacetamides as fluorinated precursors. Surprisingly, despite their potential to achieve more convergent access to α-fluorinated acetamide derivatives, only a single example of the use of such reagents has, to the best of our knowledge, been reported in the literature: Ando and co-workers described the preparation of α-bromo-α-fluoro-β-hydroxyamides as non-isolated intermediates through Et_2Zn-mediated addition of *N*-benzyl-2,2-dibromo-2-fluoroacetamide to a few aromatic aldehydes in the presence of Wilkinson's catalyst.[10] Inspired by our recent work dealing with the direct conversion of carbonyl compounds either into α-bromo-α-fluoro-β-hydroxy esters[4g] or into (*Z*)-acrylates,[4i] here we report the use of secondary and tertiary 2,2-dibromo-2-fluoroacetamides as fluorine sources, thus furnishing access to α-bromo-α-fluoro-β-hydroxy amides and/or fluorinated (*Z*)-acrylamide derivatives (Scheme 1).

[a] Normandie Univ., COBRA, UMR 6014 et FR 3038; Univ. Rouen, INSA Rouen, CNRS,
1 rue Tesnière, 76821 Mont Saint-Aignan Cedex, France
Fax: +33-2-35522959
E-mail: xavier.pannecoucke@insa-rouen.fr
Homepage: http://www.normandie-univ.fr

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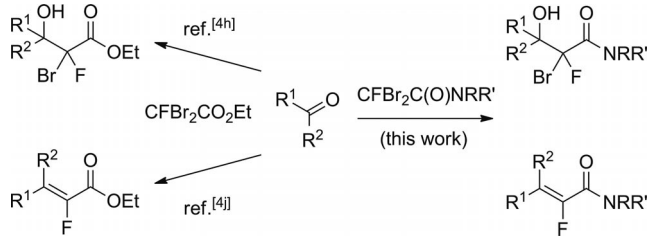
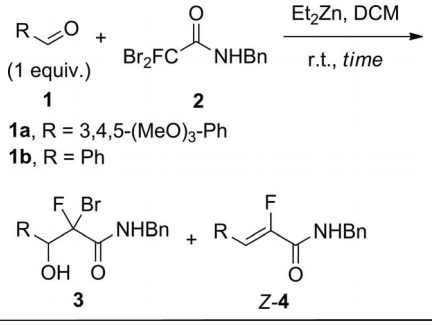


Scheme 1. Synthesis of fluorinated building blocks.

Results and Discussion

Initially, we examined the reactivity of the secondary amide **2** toward aromatic aldehydes **1a** and **1b** (Table 1). From our previous results with ethyl dibromofluoroacetate as a versatile fluorinated reagent,[4c–4j] we assumed that Et_2Zn-mediated addition of the amide **2** to a carbonyl compound might result in the formation of an alcohol of type **3** and/or an olefin of type **4**. With a slight excess of reactants,[11] the electron-rich aldehyde **1a** exclusively furnished the alcohol **3a**, albeit in low yield, as an equimolar mixture of diastereoisomers (Entry 1). An increase in reaction time was ineffective to improve the yield (Entry 2), whereas the use of a larger excess of Et_2Zn resulted in the partial formation of olefin **4a** (Entry 3). After a survey of the stoichiometry of the reaction, we were pleased to observe that the aldehyde **1a** was fully converted into **3a** with the use of 3 equivalents of amide **2** and 6 equiv. of Et_2Zn (Entries 4–6). In the case of a more electrophilic aldehyde such as benzaldehyde (**1b**), only 2 equiv. of amide **2** and 4 equiv. of Et_2Zn were required to ensure complete conversion into the alcohol **3b** (Entries 7–8).

Table 1. Reactivity of *N*-benzyl-2,2-dibromo-2-fluoroacetamide.

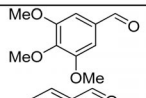
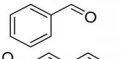
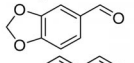
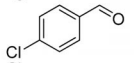
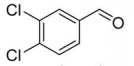
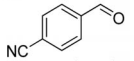
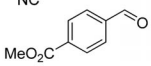
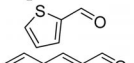
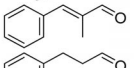
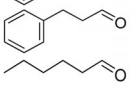
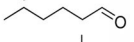
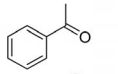
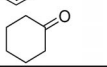


Entry		Amide equiv.	Et_2Zn equiv.	*t* [h]	**3/4** ratio[a]	*syn*-**3**/*anti*-**3** ratio[a]	Yield [%][b]
1	**1a**	1.1	2.2	2	100:0	56:44	43
2	**1a**	1.5	3.0	16	100:0	58:42	66
3	**1a**	2.0	5.0	16	72:28	n.d.	40
4	**1a**	1.5	3.0	2	100:0	56:44	60
5	**1a**	2.0	4.0	2	100:0	55:45	77
6	**1a**	3.0	6.0	2	100:0	55:45	99 (92)[c]
7	**1b**	2.0	4.0	2	100:0	57:43	99 (85)[c]
8	**1b**	3.0	6.0	2	100:0	57:43	99

[a] Determined by ^{19}F NMR examination of the crude mixtures. [b] Determined by ^{19}F NMR with trifluorotoluene as an internal standard. [c] Isolated yields.

Although the addition of the secondary amide **2** occurs without diastereoselectivity, this methodology can be successfully applied to a wide range of carbonyl compounds with good yields (Table 2). Electron-rich aromatic aldehydes were suitable partners in this process and the corresponding α-bromo-α-fluoro-β-hydroxy amides were isolated in excellent yields (Entries 1–3). Pleasingly, chlorinated aldehydes were compatible and afforded the corresponding adducts in fairly good yields (Entries 4–5). Aromatic aldehydes bearing electron-withdrawing groups such as ester or nitrile groups were also tolerated (Entries 6–7), as was a heteroaromatic backbone (Entry 8). Interestingly, substituted α,β-unsaturated aldehydes (Entry 9) and aliphatic aldehydes (Entries 10–11) afforded the corresponding fluorinated products in moderate to good yields. Finally, ketones were tolerated well in this process, thus giving straightforward access to fluorinated building blocks containing two contiguous quaternary centres (Entries 12 and 13).

Table 2. Synthesis of α-bromo-α-fluoro-β-hydroxy amides **3**.[a]

Entry	Substrate	Method	Product	*syn*/*anti*[b]	% Yield
1		**1a** B	**3a**	55:45	92
2		**1b** A	**3b**	57:43	85
3		**1c** A	**3c**	54:46	91
4		**1d** A	**3d**	59:41	86
5		**1e** A	**3e**	55:45	71
6		**1f** B	**3f**	56:44	84
7		**1g** A	**3g**	53:47	72
8		**1h** A	**3h**	56:44	82
9		**1i** A	**3i**	57:43	75
10		**1j** A	**3j**	68:32	71
11		**1k** A	**3k**	62:38	42[c]
12		**1l** B	**3l**	56:44	85
13		**1m** B	**3m**	–	43

[a] Reactions performed in CH_2Cl_2 at room temp. for 2 h; Method A: **1/2**/Et_2Zn 1:2:4; Method B: **1/2**/Et_2Zn 1:3:6. [b] Determined by ^{19}F NMR examination of the crude mixtures. [c] Only the *syn* diastereoisomer was isolated.

Moreover, this methodology was also successfully applied to the *N*-tosylimine **5** (Scheme 2). Although the adduct **6** was obtained with a modest yield and poor diastereoselectivity, this represents the first example of a one-step synthesis of an α-bromo-α-fluoro-β-amino amide.

Scheme 2. Synthesis of α-bromo-α-fluoro-β-amino amide **6**.

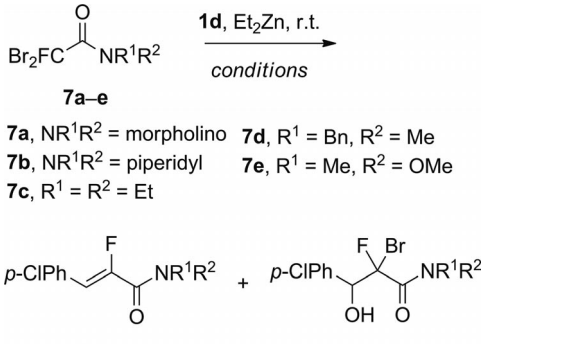
Despite numerous attempts to optimize the formation of the (*Z*)-olefin **4**, we were not able to find suitable conditions to favour the elimination step over the degradation of the alcohols *syn*-**3** and *anti*-**3**. Consequently, we turned our attention to tertiary amides, and in particular to *N*-dibromofluoroacetylmorpholine (**7a**, Table 3), to develop conditions for stereoselective preparation of fluorinated (*Z*)-acrylamide derivatives. Firstly, a screening of solvents was carried out with 4-chlorobenzaldehyde (**1d**) as a model substrate, 1.1 equiv. of amide **7a** and 4.4 equiv. of Et_2Zn (Entries 1–4). The best result was obtained with CH_2Cl_2 as a solvent, with a 74% yield of olefin (*Z*)-**8ad** and a 17% yield of alcohol *syn*-**9ad** being obtained. In order to enhance the degree of conversion of the alcohol *syn*-**9ad** into olefin (*Z*)-**8ad** we tested the use of additives. Unfortunately, the addition of TMEDA only enhanced the degradation of the alcohol *syn*-**9ad** (Entry 5), whereas the addition of molecular sieves had no effect on the outcome of the reaction (Entry 6). Finally, the amount of Et_2Zn was decreased to 2.5 equiv. A reaction time of 2 hours was then sufficient to achieve full consumption of the alcohol *anti*-**9ad**,[12] with an excellent global yield (96% isolated yield, Entry 7).

In order to evaluate the influence of amide substituents on this process, various dibromofluoroacetamides were synthesized[13] and engaged in reaction with 4-chlorobenzaldehyde (**1d**, Table 3). *N*-Dibromofluoroacetylpiperidine (**7b**, Entry 8) and the corresponding diethylamide **7c** (Entry 9) gave the corresponding olefin (*Z*)-**8d** and alcohol *syn*-**9d** in good but somewhat lower yields. Surprisingly, the corresponding *N*-benzylmethyl amide **7d** and Weinreb amide **7e** gave poorer results. Indeed, these two substrates either were unreactive or fully decomposed under the standard conditions (Entries 10–11). For comparison with fluorinated esters, when **1d** was engaged in the olefination reaction with ethyl dibromofluoroacetate under these optimized conditions, the corresponding (*Z*)-acrylate and *syn*-α-bromo-α-fluoro-β-hydroxy ester were obtained in only 22% and 19% yields, respectively. In fact, 2 equiv. of ethyl dibromofluoroacetate and 4 equiv. of diethylzinc were necessary to achieve the full conversion of the aldehyde,[4j] thus highlighting the advantage of using *N*-dibromofluoroacetylmorpholine to prepare such α-carbonylated fluorinated olefins.

Furthermore, these optimization results showed that *syn* and *anti* isomers of the α-bromo-α-fluoro-β-hydroxy amides **9** exhibit different reactivities towards excess diethylzinc. ^{19}F NMR monitoring of the reactions showed that the *anti* isomers were rapidly converted into the corresponding (*Z*)-olefins whereas – as can be seen from Entry 7 (3 h reaction time, 62% yield of (*Z*)-olefin, 96% global yield) and Entry 6 (72 h reaction time, 74% yield of (*Z*)-olefin, 91% global yield) – the conversion of the *syn* isomers is slower and slight degradation occurs.

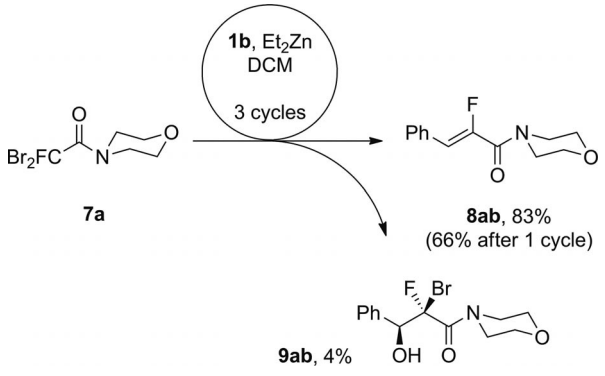
We thus examined the kinetics of the reaction between the α-bromo-α-fluoro-β-hydroxy amide *syn*-**9ad** and Et_2Zn. In the first 2 h we observed the rapid formation of the (*Z*)-olefin **8ad**, and the elimination then slowed down to reach about 50% conversion. This reactivity pattern clearly showed that a significant amount of *syn*-α-bromo-α-fluoro-β-hydroxy amide affords the corresponding α-fluoroacrylamide. However, all our attempts to increase the molecular ratio between (*Z*)-**8ad** and *syn*-**9ad** were unsuccessful and the use of more equivalents of diethylzinc resulted in the degradation of *syn*-**9ad**.

Table 3. Reactivity of fluorinated acetamides.



Entry		Solv.	Equiv.		*t* [h]	% Yield[b]			
	7		**7**	Et_2Zn		**8**	(*Z*)-**8**	**9**	*syn*-**9**
1	**7a**	THF	1.1	4.4	18	**8ad**	58	**9ad**	14
2	**7a**	Et_2O	1.1	4.4	18	**8ad**	62	**9ad**	9
3	**7a**	C_6H_{12}	1.1	4.4	18	**8ad**	47	**9ad**	2
4	**7a**	CH_2Cl_2	1.1	4.4	72	**8ad**	74	**9ad**	17
5[b]	**7a**	CH_2Cl_2	1.1	4.4	3	**8ad**	44	**9ad**	2
6[c]	**7a**	CH_2Cl_2	1.1	4.4	72	**8ad**	71	**9ad**	17
7	**7a**	CH_2Cl_2	1.1	2.5	3	**8ad**	62[d]	**9ad**	34[d]
8	**7b**	CH_2Cl_2	1.1	2.5	3	**8bd**	32[d]	**9bd**	54[d]
9	**7c**	CH_2Cl_2	1.1	2.5	3	**8cd**	39[d]	**9cd**	38[d]
10	**7d**	CH_2Cl_2	1.1	2.5	3	**8dd**	0	**9dd**	19[d]
11	**7e**	CH_2Cl_2	1.1	2.5	3	**8ed**	trace	**9ed**	0

[a] Determined by ^{19}F NMR with trifluorotoluene as internal standard. [b] TMEDA (5 equiv.) was added. [c] MS (4 Å) were added. [d] Isolated yields.

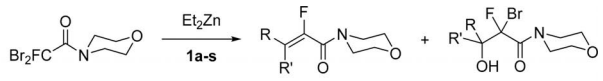


Scheme 3. Multi-cycle reaction.

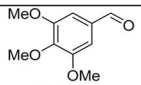
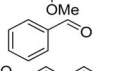
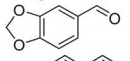
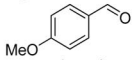
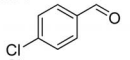
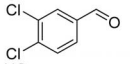
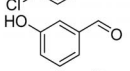
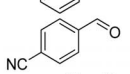
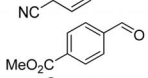
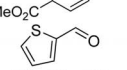
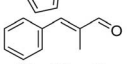
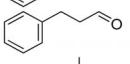
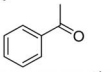
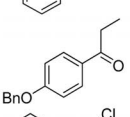
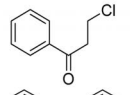
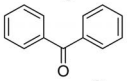
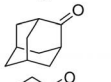
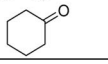
To obtain the α-fluoroacrylamide in better yield, we next sought to perform several cycles of reactions. We hypothesized that the residual *syn*-α-bromo-α-fluoro-β-hydroxy amide might be re-engaged in another elimination reaction to improve the level of conversion into the desired fluoroacrylamide. We were pleased to observe that after three cycles the *syn*-α-bromo-α-fluoro-β-hydroxy amide had been converted into the corresponding α-fluoroacrylamide in good overall yield (83%, Scheme 3).

Under our optimized conditions, this methodology was successfully applied to a wide variety of carbonyl compounds (Table 4). Aromatic aldehydes bearing either an electron-withdrawing or -donating group were nicely converted into the corresponding α-fluoroacrylamides (Entries 1–10). Aliphatic (Entry 12) and α,β-unsaturated aldehydes (Entry 11) were also converted into the desired fluoroalkenes with excellent global yields. In all cases, the α,β-unsaturated amide (*Z*)-**8a** and the α-bromo-α-fluoro-β-hydroxy amide *syn*-**9a** were obtained stereoselectively and were easily separated by flash chromatography. Additionally, ketones were successfully tested in this process (Entries 13–18). Interestingly, in these cases, the olefins were the exclusive reaction products, obtained in excellent yields. Moreover, unsymmetrical ketones gave the tetrasubstituted olefins with complete stereoselectivity (Entries 13–15).[14] Finally, this method showed good chemical tolerance, with an ester function (Entry 9), an alcohol function (Entry 7) and an aliphatic chlorinated compound (Entry 15) being well tolerated in this process.

Table 4. Synthesis of olefins **8** and compounds *syn*-**9**.



7a 8aa-as 9aa-as

Entry	Substrate		Products 8	% 8	*Z*/*E*[a]	9	% *syn*-9
1		**1a**	**8aa**	54	>95:5	**9aa**	41
2		**1b**	**8ab**	66	>95:5	**9ab**	28
3		**1c**	**8ac**	52	>95:5	**9ac**	44
4		**1n**	**8an**	59	>95:5	**9an**	32
5		**1d**	**8ad**	61	>95:5	**9ad**	34
6		**1e**	**8ae**	65	>95:5	**9ae**	34
7		**1o**	**8ao**	61	>95:5	**9ao**	33
8		**1f**	**8af**	58	>95:5	**9af**	33
9		**1g**	**8ag**	69	>95:5	**9ag**	18
10		**1h**	**8ah**	40	>95:5	**9ah**	42
11		**1i**	**8ai**	42	>95:5	**9ai**	21
12		**1j**	**8aj**	53	>95:5	**9aj**	23
13		**1l**	**8al**	99	8:92	**9al**	0
14		**1p**	**8ap**	85	>5:95	**9ap**	0
15		**1q**	**8aq**	85	>5:95	**9aq**	0
16		**1r**	**8ar**	96	–	**9ar**	0
17		**1s**	**8as**	63	–	**9as**	0
18		**1m**	**8am**	92	–	**9am**	0

[a] Determined by ^{19}F NMR examination of the crude mixtures.

The configurations of the compounds were confirmed by X-ray analyses (Figure 1).[15] We were able to obtain crystal structures of (*Z*)-**8ad** and *syn*-**9ac**.

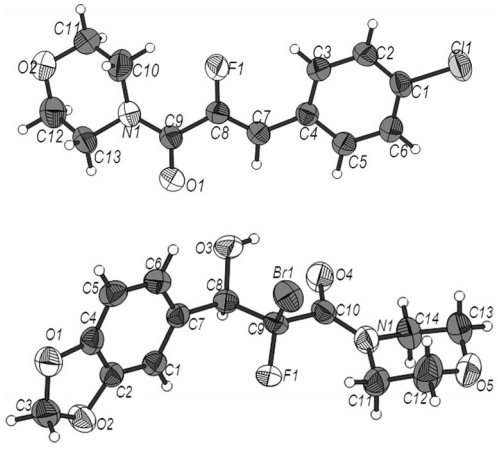
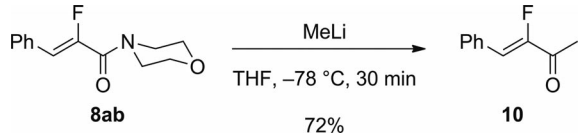


Figure 1. X-ray structures of (*Z*)-**8ad** and *syn*-**9ac**.

Morpholine acrylamides are versatile intermediates, being transformable into various functional groups such as acids, aldehydes or ketones.[5a] In this context, to highlight the synthetic utility of fluorinated morpholine acrylamides, we prepared the α,β-unsaturated ketone **10** (Scheme 4) in 72% yield by addition of MeLi to acrylamide **8ab**.



Scheme 4. Synthesis of fluorinated α,β-unsaturated ketone **10**.

Conclusions

In summary, we have described selective and straightforward routes either to *syn*-α-bromo-α-fluoro-β-hydroxy amides or to (*Z*)-α-fluoroacrylamides. The developed methodologies, based on Et_2Zn-mediated addition of 2,2-di-

bromo-2-fluoroacetamides to aldehydes or ketones, afford the products in good to excellent yields. It is worth mentioning that aromatic and aliphatic substrates bearing either electron-donating or electron-withdrawing group are suitable for these reactions. The stereochemical outcome of the reaction has been unambiguously determined by X-ray analysis of the products. Finally, the versatility of our products was highlighted through a useful synthetic transformation. Deeper mechanistic studies to elucidate the elimination process are currently underway in our laboratory.

Experimental Section

General Methods: Residual $CHCl_3$ served as internal standard (δ = 7.26 ppm) for ^1H NMR, $CFCl_3$ served as internal standard (δ = 0.0 ppm) for ^{19}F NMR, and $CDCl_3$ served as internal standard (δ = 77.16 ppm) for ^{13}C NMR spectroscopy. Chemical shifts are quoted in parts per million (ppm) and the following abbreviations have been used: δ (chemical shift), J (coupling constant), br (broad), s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), q (quartet), dq (doublet of quartets), m (multiplet). Flash chromatography was performed with silica gel (0.063–0.200 mm). Analytical thin layer chromatography (TLC) was performed with silica gel aluminium plates (F-254 indicator) and visualized by UV fluorescence and/or staining with $KMnO_4$ or PMA. THF, Et_2O and hexane were distilled from Na/benzophenone prior to use. CH_2Cl_2 was distilled from CaH_2 prior to use. HRMS analyses were performed under ESI conditions with a micro-TOF detector. IR spectra were recorded with a Perkin–Elmer Spectrum 100 instrument. All experiments were conducted under nitrogen in oven-dried glassware with magnetic stirring and use of standard Schlenk techniques. All aldehydes and ketones were recrystallized, distilled or filtered through basic alumina prior to use.

Product **10** has been described previously and gave satisfactory spectroscopic and physical data. It was prepared from acrylamide **8ab** by known procedure.[5a]

***N*-Benzyl-2,2-dibromo-2-fluoroacetamide (2):** Benzylamine (9.86 mL, 90 mmol, 2 equiv.) was added to a solution of Me_2AlCl (0.9 N in hexanes, 100 mL, 90 mmol, 2 equiv.) in dry CH_2Cl_2 (200 mL) and the mixture was stirred at room temperature for 45 min. The reaction mixture was cooled to 0 °C, after which ethyl dibromofluoroacetate (6.27 mL, 45 mmol, 1 equiv.) was added slowly. After 16 h stirring at room temperature, the reaction was quenched by slow addition of HCl (4 N, 25 mL). The organic layer was separated, the aqueous layer was extracted with Et_2O (2× 50 mL), the combined organic layers were concentrated, and the desired amide **2** was recrystallized from cyclohexane (12.4 g, 85% yield, 97% purity by ^{19}F NMR): R_f (cyclohexane/EtOAc 8:2) = 0.48, white solid, m.p. 77–80 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.41–7.28 (m, 5 H), 6.52 (br. s, 1 H), 4.55 [d, ^3J(H,H) = 5.8 Hz, 2 H] ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.5 (d, $^2J_{C,F}$ = 18 Hz), 136.3, 128.6 (2 C), 127.7, 127.5 (2 C), 86.9 (d, $^1J_{C,F}$ = 328 Hz), 44.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –66.0 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3264, 1678, 1537, 1085, 812 cm^{-1}. $C_9H_8Br_2FNO$ (324.97): calcd. C 33.26, H 2.48, N 4.31; found C 33.51, H 2.61, N 4.53.

General Procedure for the Synthesis of α-Bromo-α-fluoro-β-hydroxy Amides 3: Et_2Zn (1.0 N in hexanes. Method A: 1.2 mL, 1.2 mmol, 4 equiv. Method B: 1.8 mL, 1.8 mmol, 6 equiv.) was added to a solution of an aldehyde **1** (0.3 mmol, 1 equiv.) and an amide **2** (Method A: 200 mg, 0.6 mmol, 2 equiv; Method B: 300 mg, 0.9 mmol, 3 equiv.) and the reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched by the dropwise addition of a saturated solution of NH_4Cl (50 μL). After the addition of silica gel, solvents were evaporated, and the crude residue was adsorbed on silica gel and purified by column chromatography to afford the desired product **3** as a mixture of diastereoisomers.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-3-(3,4,5-trimethoxyphenyl)-propanamide (3a):** Yield 122 mg, 92%, R_f (cyclohexane/EtOAc 6:4) = 0.28, white solid, m.p. 132–135 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29–7.13 (m, 3 H), 7.11–7.03 (m, 1 H), 6.98–6.84 (m, 1.5 H), 6.79–6.66 (m, 0.5 H), 6.59 (s, 1 H), 6.58 (s, 1 H), 5.15 (d, $^3J_{H,F}$ = 18.4 Hz, 1 H), 4.51–4.28 (m, 1 H), 4.39 (dd, $^2J_{H,H}$ = 5.6, $^3J_{H,H}$ = 12.9 Hz, 0.5 H), 4.20 (dd, $^2J_{H,H}$ = 5.6, $^3J_{H,H}$ = 15.0 Hz, 0.5 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.68 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.5 (d, $^2J_{C,F}$ = 23 Hz), 165.9 (d, $^2J_{C,F}$ = 21 Hz), 152.7, 152.6, 138.0 (2 C), 136.4, 136.3, 131.3, 130.3, 128.7 (2 C), 128.6 (2 C), 127.7 (2 C), 127.2 (2 C), 127.1 (2 C), 105.4, 105.2 (d, $^4J_{C,F}$ = 1 Hz), 103.0 (d, $^1J_{C,F}$ = 275 Hz), 100.2 (d, $^1J_{C,F}$ = 276 Hz), 77.7 (d, $^2J_{C,F}$ = 22 Hz), 77.2 (d, $^2J_{C,F}$ = 19 Hz), 60.7 (2 C), 55.9 (4 C), 43.4, 43.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –130.8 (d, $^3J_{F,H}$ = 17 Hz, 0.56 F), –132.5 (d, $^3J_{F,H}$ = 16 Hz, 0.44 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3302, 1674, 1540, 700 cm^{-1}. $C_{19}H_{21}BrFNO_5$ (442.28): calcd. C 51.60, H 4.79, N 3.17; found C 51.64, H 4.64, N 3.56.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-3-phenylpropanamide (3b):** Yield 90 mg, 85%, R_f (cyclohexane/EtOAc 8:2) = 0.26, white solid, m.p. 129–132 °C. ^1H NMR (300 MHz, MeOD/$CDCl_3$, 25 °C): δ = 7.54–7.43 (m, 1 H), 7.43–7.35 (m, 1 H), 7.35–7.18 (m, 6 H), 7.17–7.07 (m, 2 H), 6.84–6.73 (m, 1 H), 5.27 (d, $^3J_{H,F}$ = 23.0 Hz, 0.5 H), 5.26 (d, $^3J_{H,F}$ = 23.8 Hz, 0.5 H), 4.52 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H), 4.46 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H), 4.36 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.08 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H) ppm. ^{13}C NMR (75 MHz, MeOD/$CDCl_3$, 25 °C): δ = 168.2 (d, $^2J_{C,F}$ = 23 Hz), 167.5 (d, $^2J_{C,F}$ = 21 Hz), 138.8, 138.3, 138.0, 137.4, 129.8 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 129.5, 129.4, 129.3 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 129.3 (2 C), 129.1 (2 C), 129.0 (2 C), 128.6 (2 C), 128.1 (2 C), 128.0, 127.81, 127.78 (2 C), 105.6 (d, $^1J_{C,F}$ = 278 Hz), 102.0 (d, $^1J_{C,F}$ = 276 Hz), 77.92 (d, $^2J_{C,F}$ = 20 Hz), 77.86 (d, $^2J_{C,F}$ = 18 Hz), 44.0, 43.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –135.1 (d, $^3J_{F,H}$ = 23 Hz, 0.56 F), –138.8 (d, $^3J_{F,H}$ = 16 Hz, 0.44 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3322, 1676, 1537, 696, 672 cm^{-1}. $C_{16}H_{15}BrFNO_2$ (352.20): calcd. C 54.56, H 4.29, N 3.98; found C 54.48, H 4.59, N 4.20.

3-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-benzyl-2-bromo-2-fluoro-3-hydroxy-propanamide (3c): Yield 108 mg, 91%, R_f (cyclohexane/EtOAc 8:2) = 0.20, yellow solid, m.p. 136–140 °C. ^1H NMR (300 MHz, MeOD, 25 °C): δ = 7.28–7.01 (m, 3.5 H), 6.95–6.63 (m, 4 H), 6.57 (d, $^3J_{H,H}$ = 7.9 Hz, 0.5 H), 5.86–5.77 (m, 2 H), 5.10 (d, $^3J_{H,F}$ = 23.1 Hz, 0.5 H), 5.07 (d, $^3J_{H,F}$ = 23.9 Hz, 0.5 H), 4.42 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.36 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.33 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H), 3.97 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 168.5 (d, $^2J_{C,F}$ = 24 Hz), 167.8 (d, $^2J_{C,F}$ = 21 Hz), 149.32, 149.28, 149.0, 148.7, 139.3, 138.9, 132.3, 131.5, 129.5 (2 C), 129.3 (2 C), 128.3 (2 C), 128.2 (2 C), 128.0 (2 C), 124.2, 123.7, 110.0 (d, $^4J_{C,F}$ = 3 Hz), 109.6 (d, $^4J_{C,F}$ = 3 Hz), 108.8, 108.3, 105.0 (d, $^1J_{C,F}$ = 277 Hz), 103.5 (d, $^1J_{C,F}$ = 277 Hz), 102.5, 102.4, 78.1 (d, $^2J_{C,F}$ = 17 Hz), 78.0 (d, $^2J_{C,F}$ = 19 Hz), 44.1, 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –135.8 (d, $^3J_{F,H}$ = 24 Hz, 0.56 F), –139.3 (d, $^3J_{F,H}$ = 23 Hz, 0.44 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3328, 1670, 1531, 690, 660 cm^{-1}. $C_{17}H_{15}BrFNO_4$ (396.21): calcd. C 51.53, H 3.82, N 3.54; found C 51.89, H 4.06, N 3.60.

***N*-Benzyl-2-bromo-3-(4-chlorophenyl)-2-fluoro-3-hydroxypropanamide (3d):** Yield 100 mg, 86%, R_f (cyclohexane/EtOAc 8:2) = 0.23, white solid, m.p. 124–127 °C. ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 7.39 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H), 7.28–7.04 (m, 8 H), 6.76–6.69 (m, 1 H), 5.18 (d, $^3J_{H,F}$ = 23.2 Hz, 0.5 H), 5.14 (d, $^3J_{H,F}$ = 23.7 Hz, 0.5 H), 4.42 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.35 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.30 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H), 3.94 (d, $^2J_{H,H}$ = 15.0 Hz, 0.5 H) ppm. ^{13}C NMR (75 MHz, DMSO, 25 °C): δ = 165.4 (d, $^2J_{C,F}$ = 23 Hz), 164.9 (d, $^2J_{C,F}$ = 22 Hz), 138.7, 138.2, 136.9, 136.2, 133.0 (2 C), 130.9 (2 C), 130.2 (2 C), 128.3 (2 C), 128.0 (4 C), 127.7 (2 C), 127.0 (2 C), 126.7 (2 C), 103.2 (d, $^1J_{C,F}$ = 278 Hz), 102.4 (d, $^1J_{C,F}$ = 279 Hz), 75.1 (d, $^2J_{C,F}$ = 18 Hz), 74.9 (d, $^2J_{C,F}$ = 19 Hz), 42.3, 41.8 ppm. ^{19}F NMR (282 MHz, MeOD, 25 °C): δ = –136.1 (d, $^3J_{F,H}$ = 24 Hz, 0.59 F), –139.6 (d, $^3J_{F,H}$ = 23 Hz, 0.41 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 3330, 1665, 1537, 696, 530 cm^{-1}. $C_{16}H_{14}BrClFNO_2$ (386.64): calcd. C 49.70, H 3.65, N 3.62; found C 49.92, H 3.76, N 3.54.

***N*-Benzyl-2-bromo-3-(3,4-dichlorophenyl)-2-fluoro-3-hydroxypropanamide (3e):** Yield 82 mg, 71%, R_f (cyclohexane/EtOAc 8:2) = 0.28, white solid, m.p. 116–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.58 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H), 7.42 (d, $^3J_{H,H}$ = 8.5 Hz, 0.5 H), 7.38 (d, $^3J_{H,H}$ = 8.7 Hz, 0.5 H), 7.36–7.25 (m, 4 H), 7.18–7.11 (m, 1 H), 7.11–7.05 (m, 1 H), 6.72 (br. s, 0.5 H), 6.63 (br. s, 0.5 H), 5.28 (dd, $^3J_{H,F}$ = 17.2, $^3J_{H,H}$ = 6.8 Hz, 0.5 H), 5.17 (d, $^3J_{H,F}$ = 13.2 Hz, 0.5 H), 4.60–4.31 (m, 2 H), 4.27–4.16 (m, 0.5 H), 4.21 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.2 (d, $^2J_{C,F}$ = 21 Hz, 2 C), 136.2, 136.1, 135.8, 135.0, 133.2, 133.1, 132.4 (2 C), 130.4 (d, $^4J_{C,F}$ = 2 Hz), 130.2 (d, $^4J_{C,F}$ = 2 Hz), 130.0 (2 C), 128.9 (4 C), 128.04, 128.00, 127.8 (d, $^4J_{C,F}$ = 2 Hz), 127.7 (d, $^4J_{C,F}$ = 2 Hz), 127.5 (2 C), 127.4 (2 C), 101.9 (d, $^1J_{C,F}$ = 273 Hz), 99.6 (d, $^1J_{C,F}$ = 276 Hz), 76.6 (d, $^2J_{C,F}$ = 21 Hz), 75.1 (d, $^2J_{C,F}$ = 21 Hz), 43.6, 43.5 ppm. ^{19}F NMR (282 MHz, MeOD, 25 °C): δ = –129.8 (d, $^3J_{F,H}$ = 13 Hz, 0.55 F), –133.3 (d, $^3J_{F,H}$ = 17 Hz, 0.45 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3321, 2925, 1669, 1537, 1024, 700 cm^{-1}. $C_{16}H_{13}BrCl_2FNO_2$ (421.09): calcd. C 45.64, H 3.11, N 3.33; found C 45.85, H 3.44, N 3.47.

***N*-Benzyl-2-bromo-3-(4-cyanophenyl)-2-fluoro-3-hydroxypropanamide (3f):** Yield 95 mg, 84%, R_f (cyclohexane/EtOAc 8:2) = 0.21, white solid, m.p. 142–146 °C. ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 7.77 (s, 2 H), 7.59 (s, 2 H), 7.47–7.25 (m, 5 H), 7.09–6.96 (m, 1 H), 5.47 (d, $^3J_{H,F}$ = 22.5 Hz, 0.5 H), 5.42 (d, $^3J_{H,F}$ = 22.3 Hz, 0.5 H), 4.63 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.58 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.51 (d, $^2J_{H,H}$ = 14.7 Hz, 0.5 H), 4.20 (d, $^2J_{H,H}$ = 14.7 Hz, 0.5 H) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 167.3 (d, $^2J_{C,F}$ = 23 Hz), 166.7 (d, $^2J_{C,F}$ = 21 Hz), 143.3, 142.5, 138.3, 137.9, 132.4 (2 C), 132.2 (2 C), 130.5 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 129.8 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 129.1 (2 C), 129.0 (2 C), 128.0 (2 C), 127.9 (4 C), 119.2, 119.1, 112.7, 112.6, 103.6 (d, $^1J_{C,F}$ = 276 Hz), 102.3 (d, $^1J_{C,F}$ = 277 Hz), 76.81 (d, $^2J_{C,F}$ = 18 Hz), 76.79 (d, $^2J_{C,F}$ = 20 Hz), 43.9, 43.5 ppm. ^{19}F NMR (282 MHz, MeOD, 25 °C): δ = –134.8 (d, $^3J_{F,H}$ = 22 Hz, 0.56 F), –138.8 (d, $^3J_{F,H}$ = 22 Hz, 0.44 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3321, 1664, 1453, 798 cm^{-1}. $C_{17}H_{14}BrFN_2O_2$ (377.21): calcd. C 54.13, H 3.74, N 7.43; found C 54.33, H 4.04, N 7.36.

Methyl 4-[3-(Benzylamino)-2-bromo-2-fluoro-1-hydroxy-3-oxopropyl]benzoate (3g): Yield 89 mg, 72%, R_f (cyclohexane/EtOAc 8:2) = 0.18, yellow solid, m.p. 145–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.97 (t, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.51 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.35–7.21 (m, 3 H), 7.18–7.10 (m, 1 H), 7.07–6.98 (m, 1 H), 6.84 (br. s, 1 H), 6.71 (br. s, 1 H), 5.36 (dd, $^3J_{H,F}$ = 17.6, $^3J_{H,H}$ = 6.6 Hz, 0.5 H), 5.29 (d, $^3J_{H,F}$ = 14.9 Hz, 0.5 H), 4.56–4.24 (m, 3 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.8, 166.7, 166.3 (d, $^2J_{C,F}$ = 23 Hz), 166.2 (d, $^2J_{C,F}$ = 21 Hz), 140.5, 139.8, 136.3, 136.2, 130.54, 130.51, 129.3 (4 C), 128.8 (2 C), 128.7 (2 C), 128.5 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 128.4 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 127.90 (2 C), 127.88 (2 C), 127.50 (2 C), 127.46 (2 C), 102.3 (d, $^1J_{C,F}$ = 274 Hz), 99.8 (d, $^1J_{C,F}$ = 275 Hz), 77.3 (d, $^2J_{C,F}$ = 21 Hz), 75.9 (d, $^2J_{C,F}$ = 21 Hz), 52.2 (2 C), 43.5, 43.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –130.0 (d, $^3J_{F,H}$ = 14 Hz, 0.53 F), –133.4 (d, $^3J_{F,H}$ = 17 Hz, 0.47 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3473, 3334, 1700, 1670, 1531, 1275, 533 cm^{-1}. $C_{18}H_{17}BrFNO_4$ (410.23): calcd. C 52.70, H 4.18, N 3.41; found C 52.74, H 4.54, N 3.54.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-3-(thiophen-2-yl)propanamide (3h):** Yield 88 mg, 82%, R_f (cyclohexane/EtOAc 8:2) = 0.29, brown solid, m.p. 101–103 °C. ^{1}H NMR (300 MHz, MeOD, 25 °C): δ = 7.32 (d, $^3J_{H,H}$ = 5.0 Hz, 0.5 H), 7.28 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 0.9 Hz, 0.5 H), 7.25–7.19 (m, 2 H), 7.19–7.06 (m, 3 H), 6.94–6.86 (m, 1 H), 6.86–6.78 (m, 2 H), 5.49 (d, $^3J_{H,F}$ = 23.4 Hz, 0.5 H), 5.47 (d, $^3J_{H,F}$ = 23.6 Hz, 0.5 H), 4.42 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.36 (d, $^2J_{H,H}$ = 15.1 Hz, 0.5 H), 4.30 (d, $^2J_{H,H}$ = 15.2 Hz, 0.5 H), 4.06 (d, $^2J_{H,H}$ = 15.2 Hz, 0.5 H) ppm. ^{13}C NMR (75 MHz, MeOD, 25 °C): δ = 168.1 (d, $^2J_{C,F}$ = 23 Hz), 167.7 (d, $^2J_{C,F}$ = 22 Hz), 140.9, 140.2, 139.2, 138.8, 129.5 (2 C), 129.4 (2 C), 129.2, 128.6, 128.3 (2 C), 128.2, 128.1 (2 C), 128.0, 127.5, 127.43, 127.38, 127.1, 103.7 (d, $^1J_{C,F}$ = 277 Hz), 102.9 (d, $^1J_{C,F}$ = 277 Hz), 74.6 (d, $^2J_{C,F}$ = 20 Hz), 74.3 (d, $^2J_{C,F}$ = 19 Hz), 44.1, 43.7 ppm. ^{19}F NMR (282 MHz, MeOD, 25 °C): δ = –135.3 (d, $^3J_{F,H}$ = 23 Hz, 0.56 F), –138.9 (d, $^3J_{F,H}$ = 23 Hz, 0.44 F) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3325, 1669, 1438, 1118 cm^{-1}. $C_{14}H_{13}BrFNO_2S$ (358.23): calcd. C 46.94, H 3.66, N 3.91, S 8.95; found C 47.33, H 3.97, N 4.08, S 8.71.

(*E*)-*N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-4-methyl-5-phenylpent-4-enamide (3i): Yield 88 mg, 75%, R_f (cyclohexane/EtOAc 8:2) = 0.29, yellow solid, m.p. 144–148 °C. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29–7.25 (m, 2 H), 7.24–7.22 (m, 1 H), 7.20–7.14 (m, 4 H), 7.14–7.11 (m, 3 H), 6.72 (br. s, 1 H), 6.62 (s, 1 H), 4.73 (d, $^3J_{H,F}$ = 18.8 Hz, 1 H), 4.48 (dd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 6.3 Hz, 1 H), 4.32 (dd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 5.5 Hz, 1 H), 3.56 (s, 1 H), 1.87 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.1 (d, $^2J_{C,F}$ = 21 Hz), 136.5, 132.1, 132.0, 129.2 (2 C), 128.8 (2 C), 128.1 (2 C), 127.82, 127.76, 127.6 (2 C), 127.0, 104.5 (d, $^1J_{C,F}$ = 276 Hz), 79.0 (d, $^2J_{C,F}$ = 19 Hz), 43.6, 14.8 (d, $^4J_{C,F}$ = 4 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –128.4 (d, $^3J_{F,H}$ = 18 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3405, 2925, 1669, 1533, 883, 728 cm^{-1}. HRMS (ESI+): calcd. for $C_{19}H_{20}BrFNO_2$ [M + H]$^+$ 392.0661; found 392.0664. Minor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29–7.25 (m, 2 H), 7.24–7.19 (m, 8 H), 6.76 (br. s, 1 H), 6.60 (s, 1 H), 4.82 (d, $^3J_{H,F}$ = 18.8 Hz, 1 H), 4.54–4.41 (m, 2 H), 3.76–3.45 (br. s, 1 H), 1.88 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.7 (d, $^2J_{C,F}$ = 22 Hz), 136.6, 136.5, 132.8, 132.4, 129.2 (2 C), 128.8 (2 C), 128.1 (2 C), 127.9, 127. 6 (2 C), 127.1, 101.4 (d, $^1J_{C,F}$ = 276 Hz), 80.8 (d, $^2J_{C,F}$ = 20 Hz), 43.7, 14.4 (d, $^4J_{C,F}$ = 4 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –132.0 (d, $^3J_{F,H}$ = 19 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3405, 2925, 1670, 1533, 1053, 752 cm^{-1}. $C_{19}H_{19}BrFNO_2$ (392.26): calcd. C 58.18, H 4.88, N 3.57; found C 57.89, H 5.15, N 3.94.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-5-phenylpentanamide (3j):** Yield 81 mg, 71%, R_f (cyclohexane/EtOAc 8:2) = 0.27, yellow solid, m.p. 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.26 (m, 7 H), 7.24–7.16 (m, 3 H), 6.74 (br. s, 1 H), 4.61–4.49 (m, 1.5 H), 4.44 (dd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 5.6 Hz, 0.5 H), 4.34–4.17 (m, 0.5 H), 4.02–3.90 (m, 0.5 H), 3.79 (br. s, 0.5 H), 3.17 (d, $^3J_{H,H}$ = 7.0 Hz, 0.5 H), 3.04–2.89 (m, 1 H), 2.80–2.66 (m, 1 H), 2.36–2.22 (m, 0.5 H), 2.02–1.86 (m, 1.5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.9 (d, $^2J_{C,F}$ = 23 Hz), 166.4 (d, $^2J_{C,F}$ = 22 Hz), 141.1,

141.0, 136.6, 136.5, 128.9 (2 C), 128.8 (2 C), 128.50 (2 C), 128.47 (2 C), 128.45 (2 C), 128.42 (2 C), 128.0, 127.9, 127.7 (2 C), 127.6 (2 C), 126.1, 126.0, 103.3 (d, $^1J_{C,F}$ = 271 Hz), 103.6 (d, $^1J_{C,F}$ = 274 Hz), 74.7 (d, $^2J_{C,F}$ = 22 Hz), 73.3 (d, $^2J_{C,F}$ = 23 Hz), 43.5 (2 C), 32.1, 31.8, 31.3, 31.1 (d, $^4J_{C,F}$ = 3 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –127.2 (d, $^3J_{F,H}$ = 8 Hz), –134.5 (d, $^3J_{F,H}$ = 19 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3302, 2925, 1674, 1537, 892, 747 cm^{-1}. $C_{18}H_{19}BrFNO_2$ (380.25): calcd. C 56.86, H 5.04, N 3.68; found C 56.87, H 5.37, N 3.93.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxyoctanamide (3k):** Yield 44 mg, 42%, R_f (cyclohexane/EtOAc 8:2) = 0.29, yellow solid, m.p. 85–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26–7.41 (m, 5 H), 6.78 (br. s, 1 H), 4.54 (dd, $^2J_{H,H}$ = 14.8, $^3J_{H,H}$ = 5.9 Hz, 1 H), 4.48 (dd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 4.6 Hz, 1 H), 3.56 (s, 1 H), 4.09–3.88 (m, 1 H), 3.56 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H), 1.66–1.59 (m, 2 H), 1.36–1.24 (m, 6 H), 0.91–0.86 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.8 (d, $^2J_{C,F}$ = 23 Hz), 136.7, 128.8 (2 C), 127.9, 127.6 (2 C), 102.8 (d, $^1J_{C,F}$ = 271 Hz), 74.4 (d, $^2J_{C,F}$ = 22 Hz), 43.4, 31.4, 30.5, 25.2, 22.4, 13.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –127.7 (d, $^3J_{F,H}$ = 10 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3307, 2921, 1669, 1645, 1448, 1076 cm^{-1}. $C_{15}H_{21}BrFNO_2$ (346.24): calcd. C 52.03, H 6.11, N 4.05; found C 52.37, H 6.43, N 3.90.

***N*-Benzyl-2-bromo-2-fluoro-3-hydroxy-3-phenylbutanamide (3l):** Yield 93 mg, 85%, R_f (cyclohexane/EtOAc 8:2) = 0.19, colourless oil. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55–7.42 (m, 2 H), 7.41–7.28 (m, 5 H), 7.22–7.11 (m, 3 H), 6.63 (d, $^3J_{H,H}$ = 6.1 Hz, 1 H), 5.29 (s, 1 H), 4.42 (dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 7.3 Hz, 1 H), 4.06 (dd, $^2J_{H,H}$ = 15.2, $^3J_{H,H}$ = 4.6 Hz, 1 H), 1.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.4 (d, $^2J_{C,F}$ = 21 Hz), 139.7, 136.0, 128.7 (2 C), 128.3 (2 C), 128.0, 127.7, 127.1 (2 C), 126.6 (d, $^4J_{C,F}$ = 3 Hz, 2 C), 104.5 (d, $^1J_{C,F}$ = 276 Hz), 77.4 (d, $^2J_{C,F}$ = 24 Hz), 24.6 (d, $^4J_{C,F}$ = 2 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.7 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 3305, 1640, 1110 cm^{-1}. $C_{17}H_{18}BrFNO_2$ (366.22): calcd. C 55.75, H 4.68, N 3.82; found C 55.57, H 4.43, N 3.70. Minor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.66–7.55 (m, 2 H), 7.42–7.31 (m, 6 H), 7.31–7.25 (m, 2 H), 6.81 (br. s, 1 H), 5.12 (s, 1 H), 4.55 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H), 1.73 (d, $^4J_{H,H}$ = 1.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.9 (d, $^2J_{C,F}$ = 22 Hz), 139.9, 136.4, 129.0 (2 C), 128.13, 128.06, 127.7 (2 C), 127.6 (2 C), 127.3 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 104.0 (d, $^1J_{C,F}$ = 274 Hz), 77.1 (d, $^2J_{C,F}$ = 21 Hz), 43.7, 24.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –124.6 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3330, 2980, 1665, 1434, 690, 660 cm^{-1}. $C_{17}H_{18}BrFNO_2$ (366.22): calcd. C 55.75, H 4.68, N 3.82; found C 55.57, H 4.43, N 3.70.

***N*-Benzyl-2-bromo-2-fluoro-2-(1-hydroxycyclohexyl)acetamide (3m):** Yield 44 mg, 42%, R_f (cyclohexane/EtOAc 8:2) = 0.28, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.41–7.26 (m, 5 H), 6.81 (br. s, 1 H), 4.52 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H), 3.93 (s, 1 H), 2.13–1.98 (m, 1 H), 1.76–1.40 (m, 8 H), 1.20–1.04 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.6 (d, $^2J_{C,F}$ = 23 Hz), 136.6, 129.0 (2 C), 128.1, 127.7 (2 C), 106.3 (d, $^1J_{C,F}$ = 277 Hz), 75.0 (d, $^2J_{C,F}$ = 20 Hz), 43.5, 31.2, 30.9, 25.2, 21.4, 20.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –125.1 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3337, 1669, 1076, 916, 794 cm^{-1}. HRMS (mode): calcd. for $C_{15}H_{20}BrFNO_2$ [M + H]$^+$ 344.0661; found 344.0657.

***N*-Benzyl-2-bromo-3-(4-chlorophenyl)-2-fluoro-3-(4-methylphenylsulfonamido)propanamide (6):** Mixture of rotamers of both diastereoisomers. Yield 71 mg, 44%, R_f (cyclohexane/EtOAc 8:2) = 0.27, white solid, m.p. 120–126 °C. ^{1}H NMR (300 MHz, DMSO, 25 °C): δ = 7.41–6.86 (m, 13 H), 6.57 (br. s, 0.5 H), 6.55 (br. s, 0.5 H), 5.30–5.11 (m, 0.5 H), 5.11–4.94 (m, 0.5 H), 4.45 (d, $^2J_{H,H}$ = 15.4 Hz, 0.5 H), 4.30 (d, $^2J_{H,H}$ = 15.5 Hz, 0.5 H), 4.28 (d, $^2J_{H,H}$ = 15.4 Hz, 0.5 H), 3.90 (d, $^2J_{H,H}$ = 15.5 Hz, 0.5 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (75 MHz, DMSO, 25 °C): δ = 164.6 (d, $^2J_{C,F}$ = 23 Hz, 0.5 C), 164.5 (d, $^2J_{C,F}$ = 23 Hz, 0.5 C), 164.2 (d, $^2J_{C,F}$ = 21 Hz, 0.5 C), 164.1 (d, $^2J_{C,F}$ = 21 Hz, 0.5 C), 142.39, 142.36, 138.5, 138.4, 137.9, 137.6, 133.2, 133.1, 132.9, 132.1, 131.2 (2 C), 130.9 (2 C), 129.0 (2 C), 128.8 (2 C), 128.3 (2 C), 127.94 (2 C), 127.88 (2 C), 127.6 (2 C), 127.0 (2 C), 126.9 (2 C), 126.7 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 126.43 (2 C), 126.38 (2 C), 103.1 (d, $^1J_{C,F}$ = 273 Hz), 101.7 (d, $^1J_{C,F}$ = 276 Hz), 63.1 (d, $^2J_{C,F}$ = 17 Hz), 62.2 (d, $^2J_{C,F}$ = 19 Hz), 42.5 (0.5 C), 42.3 (0.5 C), 41.9 (0.5 C), 41.8 (0.5 C), 20.8 (2 C) ppm. ^{19}F NMR (282 MHz, DMSO, 25 °C): δ = –129.62 (d, $^3J_{F,H}$ = 29 Hz), –129.65 (d, $^3J_{F,H}$ = 28 Hz), –132.1 (d, $^3J_{F,H}$ = 32 Hz), –132.2 (d, $^3J_{F,H}$ = 34 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3358, 3195, 1670, 563, 533 cm^{-1}. $C_{23}H_{21}BrClFN_2O_3S$ (539.84): calcd. C 51.17, H 3.92, N 5.19, S 5.94; found C 51.30, H 4.27, N 3.60, S 5.68.

General Procedure for the Synthesis of Dibromofluoroacetamides 7: The appropriate amine (2 equiv.) was added to a solution of Me_2AlCl (1.0 N in hexanes, 2 equiv.) in dry CH_2Cl_2 (1 N) and the mixture was stirred at room temperature for 3 h. Ethyl dibromofluoroacetate (1 equiv.) was added and the mixture was stirred at reflux for 14 h. The reaction was quenched by slow addition of HCl (4 N). The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 ×), the combined organic layers were concentrated, and the desired amides **7a**–**e** were either recrystallized (**7a**) or purified by silica gel chromatography (**7b**–**e**).

2,2-Dibromo-2-fluoro-1-morpholinoethanone (7a): 100 mmol scale, recrystallized from cyclohexane. Yield 11.9 g, 78%, white solid, m.p. 58–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.70 (s, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.4 (d, $^3J_{C,F}$ = 23 Hz), 85.8 (d, $^1J_{C,F}$ = 323 Hz), 66.4, 65.7, 48.2, 44.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –55.9 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2848, 1665, 1434, 1116, 1094, 1036, 802 cm^{-1}. $C_6H_8Br_2FNO_2$ (304.94): calcd. C 26.63, H 2.64, N 4.59; found C 26.82, H 2.82, N 4.74.

2,2-Dibromo-2-fluoro-1-(piperidin-1-yl)ethanone (7b): 1 mmol scale. Yield 239 mg, 79%, R_f (PE/EtOAc 6:4) = 0.82, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.78–3.35 (br. m, 4 H), 1.62 (br. s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.2 (d, $^2J_{C,F}$ = 22 Hz), 86.3 (d, $^1J_{C,F}$ = 324 Hz), 48.6, 45.7, 25.4 (2 C), 23.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –54.1 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3440, 1765, 1689 cm^{-1}. HRMS (ESI+): calcd. for $C_7H_{12}Br_2FNO$ [M + H]$^+$ 301.9191; found 301.9195.

2,2-Dibromo-*N*,*N*-diethyl-2-fluoroacetamide (7c): 1 mmol scale. Yield 270 mg, 93%, R_f (PE/EtOAc 6:4) = 0.77, yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.40 (dq, $^3J_{H,H}$ = 7.0, $^2J_{H,H}$ = 2.2 Hz, 2 H), 3.23 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 1.07 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H), 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.6 (d, $^2J_{C,F}$ = 22 Hz), 88.2 (d, $^1J_{C,F}$ = 327 Hz), 43.1 (d, $^4J_{C,F}$ = 5 Hz), 42.4, 13.1, 11.3 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –55.9 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3440, 1763; 1688 cm^{-1}. HRMS (ESI+): calcd. for $C_6H_{12}Br_2FNO$ [M + H]$^+$ 289.9191; found 289.9188.

***N*-Benzyl-2,2-dibromo-2-fluoro-*N*-methylacetamide (7d):** 1 mmol scale. Yield 296 mg, 87%, R_f (PE/EtOAc 6:4) = 0.82, colourless oil, mixture (3:1) of rotamers; only major rotamer is described. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43–7.23 (m, 5 H), 4.66 (br. s, 2 H), 3.19 (br. s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.9 (d, $^2J_{C,F}$ = 22 Hz), 135.4, 128.7 (2 C), 127.7 (2 C), 126.9, 87.6 (d, $^1J_{C,F}$ = 326 Hz), 53.7, 36.6 (d, $^4J_{C,F}$ = 6 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –55.3 (s) ppm. IR (neat): $\tilde{\nu}_{max}$

= 3440, 1762, 1688 cm^{-1}. HRMS (ESI+): calcd. for $C_{10}H_{11}Br_2FNO$ [M + H]$^+$ 337.9191; found 337.9187.

2,2-Dibromo-2-fluoro-*N*-methoxy-*N*-methylacetamide (7e): 1 mmol scale. Standard procedure was followed with 3 equiv. of both Me_2AlCl and amine. Yield 221 mg, 81%, R_f (cyclohexane/EtOAc 95:5) = 0.18, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 3 H), 3.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.3 (d, $^2J_{C,F}$ = 22 Hz), 86.2 (d, $^1J_{C,F}$ = 322 Hz), 61.6, 35.0 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –60.2 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3440, 1763, 1689 cm^{-1}. $C_4H_6Br_2FNO_2$ (278.90): calcd. C 17.23, H 2.17, N 5.02; found C 17.37, H 2.09, N 4.71.

General Procedure for the Synthesis of α,β-Unsaturated Amides (*Z*)-8 and α-Bromo-α-fluoro-β-hydroxy Amides *syn*-9: Et_2Zn (1.0 N in hexanes, 1 mL, 1.00 mmol, 2.5 equiv.) was added to a solution of an aldehyde **1** (0.40 mmol, 1 equiv.) and an amide **7** (135 mg, 0.44 mmol, 1.1 equiv.) in dry CH_2Cl_2 (1 mL) and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then quenched by dropwise addition of HCl (4 N, 25 μL). After the addition of silica gel, solvents were evaporated and the crude residue, adsorbed on silica gel, was purified by column chromatography to furnish the desired products **8** and **9** as single stereoisomers.

(*Z*)-2-Fluoro-1-morpholino-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (8aa): Yield 70 mg, 54%, R_f (PE/EtOAc 6:4) = 0.12, white solid, m.p. 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.77 (s, 2 H), 6.49 (d, $^3J_{H,F}$ = 38.1 Hz, 1 H), 3.81 (s, 9 H), 3.72–3.59 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.6 (d, $^2J_{C,F}$ = 28 Hz), 152.9 (2 C), 150.0 (d, $^1J_{C,F}$ = 278 Hz), 138.6, 126.7, 115.9 (d, $^3J_{C,F}$ = 4 Hz), 106.8 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 66.6, 60.6, 55.8 (2 C), 45.8 (br), 44.3 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –116.0 (d, $^3J_{F,H}$ = 39 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2925, 1641, 1415, 1250, 1133, 1104 cm^{-1}. $C_{16}H_{20}FNO_5$ (325.33): calcd. C 59.07, H 6.20, N 4.31; found C 59.31, H 6.60, N 4.18.

***syn*-2-Bromo-2-fluoro-3-hydroxy-1-morpholino-3-(3,4,5-trimethoxyphenyl)propan-1-one (9aa):** Yield 69 mg, 41%, R_f (PE/EtOAc 6:4) = 0.21, yellow solid, m.p. 115–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.72 (s, 2 H), 5.07 (dd, $^3J_{H,F}$ = 3.8, $^3J_{H,H}$ = 2.3 Hz, 1 H), 4.95 (br. m, 1 H), 3.85 (s, 6 H), 3.83 (s, 3 H), 3.81–3.51 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.3 (d, $^2J_{C,F}$ = 22 Hz), 152.5 (2 C), 138.1, 130.7, 105.8 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 102.6 (d, $^1J_{C,F}$ = 275 Hz), 75.4 (d, $^2J_{C,F}$ = 25 Hz), 66.5, 66.1, 60.7, 56.0 (2 C), 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.0 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3424, 2925, 1627, 1114, 1081 cm^{-1}. $C_{16}H_{21}BrFNO_6$ (422.24): calcd. C 45.51, H 5.01, N 3.32; found C 46.71, H 4.41, N 3.36.

(*Z*)-2-Fluoro-1-morpholino-3-phenylprop-2-en-1-one (8ab): Yield 62 mg, 66%, R_f (cyclohexane/EtOAc 8:2) = 0.17, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.60–7.53 (m, 2 H), 7.43–7.26 (m, 3 H), 6.60 (d, $^3J_{H,F}$ = 38.5 Hz, 1 H), 3.77–3.69 (m, 4 H), 3.69–3.62 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.3 (d, $^2J_{C,F}$ = 28 Hz), 150.1 (d, $^1J_{C,F}$ = 279 Hz), 131.1 (d, $^3J_{C,F}$ = 3 Hz), 129.3 (d, $^4J_{C,F}$ = 8 Hz, 2 H), 128.6 (d, $^6J_{C,F}$ = 3 Hz), 128.3 (2 C), 115.4 (d, $^2J_{C,F}$ = 5 Hz), 66.3 (2 C), 46.0 (br), 43.4 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –114.53 (d, $^3J_{F,H}$ = 39 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2916, 1640, 833 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{15}FNO_2$ [M + H]$^+$ 236.1087; found 236.1093.

***syn*-2-Bromo-2-fluoro-3-hydroxy-1-morpholino-3-phenylpropan-1-one (9ab):** Yield 37 mg, 28%, R_f (cyclohexane/EtOAc 8:2) = 0.27, colourless solid, m.p. 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.44 (m, 2 H), 7.42–7.32 (m, 3 H), 5.16 (dd, $^3J_{H,F}$ = 3.8, $^3J_{H,H}$ = 2.3 Hz, 1 H), 4.93 (br. m, 1 H), 3.95–3.50 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.3 (d, $^2J_{C,F}$ = 23 Hz), 135.3, 128.8, 128.7 (2 C), 127.6 (2 C), 102.8 (d, $^1J_{C,F}$ = 276 Hz), 75.5 (d, $^2J_{C,F}$ = 26 Hz), 66.5, 66.1, 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.4 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3437, 2862, 1634, 1059, 611 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{16}BrFNO_3$ [M + H]$^+$ 332.0298; found 332.0299.

(*Z*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-1-morpholinoprop-2-en-1-one (8ac): Yield 58 mg, 52%, R_f (PE/EtOAc 6:4) = 0.47, white solid, m.p. 131–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.14 (d, $^5J_{H,F}$ = 1.3 Hz, 1 H), 6.98 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 6.78 (d, $^5J_{H,F}$ = 8.1 Hz, 1 H), 6.52 (d, $^3J_{H,F}$ = 38.2 Hz, 1 H), 5.96 (s, 2 H), 3.74–3.67 (m, 4 H), 3.67–3.61 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.9 (d, $^2J_{C,F}$ = 28 Hz), 150.0 (d, $^1J_{C,F}$ = 276 Hz), 148.0 (d, $^6J_{C,F}$ = 3 Hz), 147.9, 125.5 (d, $^3J_{C,F}$ = 3 Hz), 124.8 (d, $^4J_{C,F}$ = 7 Hz), 116.0 (d, $^2J_{C,F}$ = 4 Hz), 109.2 (d, $^4J_{C,F}$ = 10 Hz), 66.8 (2 C), 47.6–42.5 (br, 2 C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –117.1 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 1634, 1259, 672, 635 cm^{-1}. $C_{14}H_{14}FNO_4$ (279.26): calcd. C 60.21, H 5.05, N 5.02; found C 60.42, H 5.14, N 4.79.

***syn*-3-(Benzo[*d*][1,3]dioxol-5-yl)-2-bromo-2-fluoro-3-hydroxy-1-morpholinopropan-1-one (9ac):** Yield 66 mg, 44%, R_f (PE/EtOAc 6:4) = 0.28, white solid, m.p. 79–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.04 (s, 1 H), 6.93 (d, $^2J_{H,H}$ = 8.1 Hz, 1 H), 6.78 (d, $^2J_{H,H}$ = 8.1 Hz, 1 H), 5.96 (s, 2 H), 5.06 (dd, $^3J_{H,F}$ = 3.8, $^3J_{H,H}$ = 1.8 Hz, 1 H), 4.92 (br. s, 1 H), 3.94–3.47 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.3 (d, $^2J_{C,F}$ = 23 Hz), 147.8, 147.1, 129.1, 122.5 (d, $^4J_{C,F}$ = 2 Hz), 109.1 (d, $^4J_{C,F}$ = 2 Hz), 107.5, 102.8 (d, $^1J_{C,F}$ = 275 Hz), 75.2 (d, $^2J_{C,F}$ = 26 Hz), 66.5, 66.1, 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.1 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2917, 2862, 1646, 1446, 1101 cm^{-1}. $C_{14}H_{15}BrFNO_5$ (376.18): calcd. C 44.70, H 4.02, N 3.72; found C 44.57, H 4.34, N 3.59.

(*Z*)-3-(4-Chlorophenyl)-2-fluoro-1-morpholinoprop-2-en-1-one (8ad): Yield 66 mg, 61%, R_f (PE/EtOAc 6:4) = 0.33, white solid, m.p. 111–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.47 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 7.30 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 6.54 (d, $^3J_{H,F}$ = 38.1 Hz, 1 H), 3.77–3.67 (m, 4 H), 3.66–3.59 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.4 (d, $^2J_{C,F}$ = 28 Hz), 152.3 (d, $^1J_{C,F}$ = 280 Hz), 134.6 (d, $^6J_{C,F}$ = 3 Hz), 130.8 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 129.8 (d, $^3J_{C,F}$ = 3 Hz), 128.8 (2 C), 114.7 (d, $^2J_{C,F}$ = 5 Hz), 66.7 (2 C), 46.3 (br), 43.6 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –113.8 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2862, 1646, 1610, 1114, 1083, 817 cm^{-1}. $C_{13}H_{13}ClFNO_2$ (269.70): calcd. C 57.89, H 4.86, N 5.19; found C 57.95, H 5.26, N 5.08.

***syn*-2-Bromo-3-(4-chlorophenyl)-2-fluoro-3-hydroxy-1-morpholinopropan-1-one (9ad):** Yield 50 mg, 34%, R_f (PE/EtOAc 6:4) = 0.50, white solid, m.p. 77–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.33 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 5.12 (br. s, 1 H), 5.0 (br. s, 1 H), 3.96–3.46 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.1 (d, $^2J_{C,F}$ = 23 Hz), 134.6, 133.8, 130.1 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 127.8 (2 C), 102.4 (d, $^1J_{C,F}$ = 275 Hz), 74.8 (d, $^2J_{C,F}$ = 26 Hz), 66.5, 66.1, 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.7 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 2862, 1640, 1114, 1078, 575 cm^{-1}. $C_{13}H_{14}BrClFNO_3$ (366.61): calcd. C 42.59, H 3.85, N 3.82; found C 42.91, H 4.19, N 3.73.

(*Z*)-3-(3,4-Dichlorophenyl)-2-fluoro-1-morpholinoprop-2-en-1-one (8ae): Yield 79 mg, 65%, R_f (PE/EtOAc 6:4) = 0.77, white solid, m.p. 82–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H), 7.40 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.34 (dd, $^3J_{H,H}$

= 8.3, $^4J_{H,H}$ = 1.6 Hz, 1 H), 6.50 (d, $^3J_{H,F}$ = 37.4 Hz, 1 H), 3.74–3.67 (m, 4 H), 3.67–3.59 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.1 (d, $^2J_{C,F}$ = 27 Hz), 152.1 (d, $^1J_{C,F}$ = 282 Hz), 132.84 (d, $^6J_{C,F}$ = 3 Hz), 132.78, 131.3 (d, $^3J_{C,F}$ = 3 Hz), 131.1 (d, $^4J_{C,F}$ = 3 Hz), 130.5, 128.8 (d, $^4J_{C,F}$ = 3 Hz), 113.8 (d, $^2J_{C,F}$ = 5 Hz), 66.7 (2 C), 47.8 (br), 43.7 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –111.9 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2962, 1624, 1110, 833 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{13}Cl_2FNO_2$ [M + H]$^+$ 304.0307; found 304.0310.

***syn*-2-Bromo-3-(3,4-dichlorophenyl)-2-fluoro-3-hydroxy-1-morpholinopropan-1-one (9ae):** Yield 55 mg, 34%, R_f (PE/EtOAc 6:4) = 0.57, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.61 (s, 1 H), 7.43 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.32 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 5.10 (s, 1 H), 5.06 (s, 1 H), 3.92–3.52 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.0 (d, $^2J_{C,F}$ = 22 Hz), 135.6, 132.8, 131.9, 130.7 (d, $^4J_{C,F}$ = 2 Hz), 129.6, 128.0 (d, $^4J_{C,F}$ = 3 Hz), 102.0 (d, $^1J_{C,F}$ = 276 Hz), 74.4 (d, $^2J_{C,F}$ = 26 Hz), 66.5, 66.1, 47.6 (d, $^4J_{C,F}$ = 10 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.8 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 2916, 1640, 840, 532 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{14}BrCl_2FNO_3$ [M + H]$^+$ 399.9518; found 399.9524.

(*Z*)-4-(2-Fluoro-3-morpholino-3-oxoprop-1-enyl)benzonitrile (8af): Yield 60 mg, 58%, R_f (PE/EtOAc 6:4) = 0.19, white solid, m.p. 120–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.62 (s, 4 H), 6.57 (d, $^3J_{H,F}$ = 37.3 Hz, 1 H), 3.89–3.46 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.8 (d, $^2J_{C,F}$ = 28 Hz), 153.0 (d, $^1J_{C,F}$ = 275 Hz), 135.8 (d, $^3J_{C,F}$ = 3 Hz), 132.3 (2 C), 129.9 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 118.3, 114.0 (d, $^2J_{C,F}$ = 4 Hz), 112.0 (d, $^6J_{C,F}$ = 3 Hz), 66.6 (2 C), 46.9 (br), 43.5 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.8 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2917, 1622, 1259, 1107, 842, 533 cm^{-1}. $C_{14}H_{13}FN_2O_2$ (260.26): calcd. C 64.61, H 5.03, N 10.76; found C 64.25, H 5.39, N 10.49.

4-(*syn*-2-Bromo-2-fluoro-1-hydroxy-3-morpholino-3-oxopropyl)-benzonitrile (9af): Yield 47 mg, 33%, R_f (PE/EtOAc 6:4) = 0.30, white solid, m.p. 147–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.66 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.63 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 5.20 (br. s, 1 H), 5.11 (br. s, 1 H), 3.89–3.51 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.9 (d, $^2J_{C,F}$ = 23 Hz), 140.5, 131.4 (2 C), 129.5 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 118.6, 112.5, 101.9 (d, $^1J_{C,F}$ = 276 Hz), 74.6 (d, $^2J_{C,F}$ = 25 Hz), 66.5, 66.0, 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –123.0 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3431, 2850, 1640, 1083, 660, 570 cm^{-1}. $C_{14}H_{14}BrFN_2O_3$ (357.17): calcd. C 47.08, H 3.95, N 7.84; found C 47.25, H 4.33, N 7.73.

Methyl (*Z*)-4-(2-Fluoro-3-morpholino-3-oxoprop-1-enyl)benzoate (8ag): Yield 81 mg, 69%, R_f (PE/EtOAc 6:4) = 0.27, orange oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.96 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.55 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 6.55 (d, $^3J_{H,F}$ = 38.0 Hz, 1 H), 3.84 (s, 3 H), 3.74–3.53 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.3, 161.3 (d, $^2J_{C,F}$ = 28 Hz), 152.3 (d, $^1J_{C,F}$ = 283 Hz), 135.6 (d, $^3J_{C,F}$ = 3 Hz), 130.0 (d, $^3J_{C,F}$ = 2 Hz), 129.7 (2 C), 129.5 (d, $^4J_{C,F}$ = 6 Hz), 114.7 (d, $^2J_{C,F}$ = 4 Hz), 66.7 (2 C), 52.1, 46.8 (br), 43.6 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –111.2 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2862, 1715, 1646, 1114 cm^{-1}. HRMS (ESI+): calcd. for $C_{15}H_{17}FNO_4$ [M + H]$^+$ 294.1142; found 294.1146.

Methyl *syn*-4-(2-Bromo-2-fluoro-1-hydroxy-3-morpholino-3-oxopropyl)benzoate (9ag): Yield 28 mg, 18%, R_f (PE/EtOAc 6:4) = 0.43, orange oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.58 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 5.20 (br. s, 1 H), 5.05 (br. s, 1 H), 3.88–3.50 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.8, 165.1 (d, $^2J_{C,F}$ = 22 Hz), 140.3, 130.4, 128.83 (2 C), 128.80 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 102.4 (d, $^1J_{C,F}$ = 276 Hz), 75.1 (d, $^2J_{C,F}$ = 25 Hz), 66.5, 66.1, 52.1, 47.6 (d, $^4J_{C,F}$ = 10 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.7 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3424, 2958, 1720, 1622, 830, 530 cm^{-1}. HRMS (ESI+): calcd. for $C_{15}H_{18}BrFNO_5$ [M + H]$^+$ 390.0352; found 390.0359.

(*Z*)-2-Fluoro-1-morpholino-3-(thiophen-2-yl)prop-2-en-1-one (8ah): Yield 39 mg, 40%, R_f (PE/EtOAc 6:4) = 0.38, brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H), 7.19 (d, $^3J_{H,H}$ = 3.1 Hz, 1 H), 7.04–6.97 (m, 1 H), 6.94 (d, $^3J_{H,F}$ = 37.1 Hz, 1 H), 3.73–3.56 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.1 (d, $^2J_{C,F}$ = 27 Hz), 149.6 (d, $^1J_{C,F}$ = 277 Hz), 133.6 (d, $^4J_{C,F}$ = 4 Hz), 130.3 (d, $^6J_{C,F}$ = 4 Hz), 129.0 (d, $^3J_{C,F}$ = 10 Hz), 127.2, 111.2 (d, $^2J_{C,F}$ = 9 Hz), 66.8 (2 C), 47.4–43.3 (br, 2 C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –113.8 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2862, 1644, 1104, 833 cm^{-1}. HRMS (ESI+): calcd. for $C_{11}H_{13}FNO_2S$ [M + H]$^+$ 242.0651; found 242.0654.

***syn*-2-Bromo-2-fluoro-3-hydroxy-1-morpholino-3-(thiophen-2-yl)-propan-1-one (9ah):** Yield 57 mg, 42%, R_f (PE/EtOAc 6:4) = 0.52, brown solid, m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H), 7.13 (br. s, 1 H), 7.02 (bt, $^3J_{H,H}$ = 5.0 Hz, 1 H), 5.43 (dd, $^3J_{H,F}$ = 5.0, $^3J_{H,H}$ = 2.6 Hz, 1 H), 4.96 (dd, $^4J_{H,F}$ = 1.4, $^3J_{H,H}$ = 2.6 Hz, 1 H), 3.93–3.45 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.8 (d, $^2J_{C,F}$ = 23 Hz), 138.2, 127.1 (d, $^4J_{C,F}$ = 3 Hz), 126.3, 126.2, 101.4 (d, $^1J_{C,F}$ = 276 Hz), 73.2 (d, $^2J_{C,F}$ = 27 Hz), 66.5, 66.1, 47.6 (d, $^4J_{C,F}$ = 11 Hz), 43.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.5 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3361, 2927, 1622, 1112, 993, 892, 776 cm^{-1}. $C_{11}H_{13}BrFNO_3S$ (338.19): calcd. C 39.07, H 3.87, N 4.14, S 9.48; found C 39.47, H 4.17, N 4.24, S 9.03.

(2*Z*,4*E*)-2-Fluoro-4-methyl-1-morpholino-5-phenylpenta-2,4-dien-1-one (8ai): Yield 46 mg, 42%, R_f (PE/EtOAc 6:4) = 0.35, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38–7.12 (m, 5 H), 6.65 (s, 1 H), 6.27 (d, $^3J_{H,F}$ = 38.7 Hz, 1 H), 3.80–3.49 (m, 8 H), 2.11 (dd, $^4J_{H,H}$ = 2.8, 1.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.2 (d, $^2J_{C,F}$ = 29 Hz), 149.3 (d, $^1J_{C,F}$ = 278 Hz), 136.6, 135.7 (d, $^4J_{C,F}$ = 6 Hz), 131.1 (d, $^5J_{C,F}$ = 5 Hz, 2 H), 129.2 (2 C), 128.2 (2 C), 127.3, 120.7 (d, $^2J_{C,F}$ = 4 Hz), 66.8 (2 C), 48.6–41.7 (br, 2 C), 16.6 (d, $^4J_{C,F}$ = 7 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –116.6 (d, $^3J_{F,H}$ = 39 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2856, 1634, 1440, 1259, 1120, 751, 702 cm^{-1}. HRMS (ESI+): calcd. for $C_{16}H_{19}FNO_2$ [M + H]$^+$ 276.1400; found 276.1405.

***syn*-(*E*)-2-Bromo-2-fluoro-3-hydroxy-4-methyl-1-morpholino-5-phenylpent-4-en-1-one (9ai):** Yield 31 mg, 21%, R_f (PE/EtOAc 6:4) = 0.45, white solid, m.p. 74–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.23 (m, 4 H), 7.23–7.10 (m, 1 H), 6.74 (s, 1 H), 4.75 (br. s, 1 H), 4.58 (br. s, 1 H), 3.95–3.60 (m, 7 H), 3.60–3.39 (m, 1 H), 1.94 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.6 (d, $^2J_{C,F}$ = 23 Hz), 137.0, 132.2, 131.5, 129.2 (2 C), 128.0 (2 C), 126.8, 103.8 (d, $^1J_{C,F}$ = 276 Hz), 75.6 (d, $^1J_{C,F}$ = 27 Hz), 66.5, 66.2, 47.7 (d, $^2J_{C,F}$ = 11 Hz), 43.6, 16.9 (d, $^4J_{C,F}$ = 5 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –121.6 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3429, 3307, 2855, 1631, 1250, 1114, 751 cm^{-1}. HRMS (ESI+): calcd. for $C_{16}H_{20}BrFNO_3$ [M + H]$^+$ 372.0611; found 372.0614.

(*Z*)-2-Fluoro-1-morpholino-5-phenylpent-2-en-1-one (8aj): Yield 56 mg, 53%, R_f (PE/EtOAc 6:4) = 0.27, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.16 (m, 2 H), 7.16–7.06 (m, 3 H), 5.60 (dt, $^3J_{H,F}$ = 36.1, $^3J_{H,H}$ = 7.8 Hz, 1 H), 3.74–3.09 (m, 8 H), 2.68 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H), 2.68 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.5 (d, $^2J_{C,F}$ = 30 Hz), 151.5 (d,

$^1J_{C,F}$ = 267 Hz), 140.6, 128.4 (2 C), 128.3 (2 C), 126.0, 116.1 (d, $^2J_{C,F}$ = 8 Hz), 66.7 (2 C), 46.6 (br), 42.9 (br), 34.5 (d, $^4J_{C,F}$ = 2 Hz), 25.4 (d, $^3J_{C,F}$ = 3 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –118.4 (d, $^3J_{F,H}$ = 36 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2917, 1622, 1107, 530 cm^{-1}. HRMS (ESI+): calcd. for $C_{15}H_{19}FNO_2$ [M + H]$^+$ 264.1400; found 264.1403.

***syn*-2-Bromo-2-fluoro-3-hydroxy-1-morpholino-5-phenylpentan-1-one (9aj):** Yield 33 mg, 23%, R_f (PE/EtOAc 6:4) = 0.52, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.28–7.08 (m, 5 H), 4.34 (br. s, 1 H), 3.90–3.76 (m, 2 H), 3.76–3.58 (m, 6 H), 3.54–3.39 (m, 1 H), 2.92 (ddd, $^3J_{H,H}$ = 13.9, 5.7, $^2J_{H,H}$ = 8.5 Hz, 1 H), 2.68 (ddd, $^3J_{H,H}$ = 16.8, 8.5, $^2J_{H,H}$ = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.1 (d, $^2J_{C,F}$ = 24 Hz), 141.5, 128.6 (2 C), 128.4 (2 C), 125.9, 103.9 (d, $^1J_{C,F}$ = 276 Hz), 73.1 (d, $^1J_{C,F}$ = 26 Hz), 66.5, 66.2, 47.6 (d, $^2J_{C,F}$ = 11 Hz), 43.4, 32.0 (d, $^4J_{C,F}$ = 1.1 Hz), 31.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –123.6 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 2920, 1622, 1120 cm^{-1}. HRMS (ESI+): calcd. for $C_{15}H_{20}BrFNO_3$ [M + H]$^+$ 360.0611; found 360.0617.

(*E*)-2-Fluoro-1-morpholino-3-phenylbut-2-en-1-one (8al): Yield 99 mg, 99%, R_f (PE/EtOAc 6:4) = 0.32, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.24 (m, 3 H), 7.24–7.16 (m, 2 H), 3.51–3.27 (m, 4 H), 3.13–3.00 (m, 2 H), 2.97–2.85 (m, 2 H), 2.05 (d, $^4J_{H,F}$ = 4.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.0 (d, $^2J_{C,F}$ = 34 Hz), 145.5 (d, $^1J_{C,F}$ = 256 Hz), 136.6 (d, $^3J_{C,F}$ = 7 Hz), 128.7 (2 C), 128.5, 127.8 (d, $^4J_{C,F}$ = 3 Hz), 120.4 (d, $^2J_{C,F}$ = 16 Hz), 66.0, 65.9, 46.7, 41.8, 15.4 (d, $^3J_{C,F}$ = 15 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –113.2 (q, $^4J_{F,H}$ = 5 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2858, 1622, 1444, 1110, 832, 533 cm^{-1}. HRMS (ESI+): calcd. for $C_{14}H_{17}FNO_2$ [M + H]$^+$ 250.1243; found 250.1250.

2-Cyclohexylidene-2-fluoro-1-morpholinoethanone (8am): Yield 84 mg, 92%, R_f (PE/EtOAc 6:4) = 0.42, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.74–3.52 (m, 6 H), 3.51–3.33 (br. m, 2 H), 2.28–2.16 (br. m, 2 H), 2.16–2.05 (br. m, 2 H), 1.50 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.8 (d, $^2J_{C,F}$ = 34 Hz), 142.2 (d, $^1J_{C,F}$ = 252 Hz), 124.4 (d, $^2J_{C,F}$ = 10 Hz), 66.8, 66.5, 46.9 (d, $^4J_{C,F}$ = 4 Hz), 42.0, 27.5 (d, $^4J_{C,F}$ = 4 Hz), 27.0 (d, $^4J_{C,F}$ = 2 Hz), 26.4 (d, $^3J_{C,F}$ = 2 Hz), 25.8, 25.4 (d, $^3J_{C,F}$ = 7 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –123.8 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2855, 1624, 1100 cm^{-1}. HRMS (ESI+): calcd. for $C_{12}H_{19}FNO_2$ [M + H]$^+$ 228.1400; found 228.1410.

(*Z*)-2-Fluoro-3-(4-methoxyphenyl)-1-morpholinoprop-2-en-1-one (8an): Yield 63 mg, 59%, R_f (PE/EtOAc 6:4) = 0.25, white solid, m.p. 72–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 6.88 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H), 6.56 (d, $^3J_{H,F}$ = 38.9 Hz, 1 H), 3.80 (s, 3 H), 3.75–3.57 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.0 (d, $^2J_{C,F}$ = 28 Hz), 159.9 (d, $^6J_{C,F}$ = 3 Hz), 149.8 (d, $^1J_{C,F}$ = 275 Hz), 131.2 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 124.0 (d, $^3J_{C,F}$ = 3 Hz), 115.8 (d, $^2J_{C,F}$ = 5 Hz), 114.0 (2 C), 66.7 (2 C), 47.7–42.5 (br, 2 C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –117.9 (d, $^3J_{F,H}$ = 39 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3424, 2925, 1598, 1429, 1250, 1118, 1020 cm^{-1}. $C_{14}H_{16}FNO_3$ (265.28): calcd. C 63.39, H 6.08, N 5.28; found C 63.21, H 6.16, N 4.94.

***syn*-2-Bromo-2-fluoro-3-hydroxy-3-(4-methoxyphenyl)-1-morpholinopropan-1-one (9an):** Yield 36 mg, 32%, R_f (PE/EtOAc 6:4) = 0.30, white solid, m.p. 142–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 6.90 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 5.11 (dd, $^3J_{H,F}$ = 3.8, $^3J_{H,H}$ = 2.3 Hz, 1 H), 4.89 (br. m, 1 H), 3.95–3.47 (m, 8 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.4 (d, $^2J_{C,F}$ = 22 Hz), 159.9, 129.9 (d, $^4J_{C,F}$ = 2 Hz, 2 C), 127.4, 113.1 (2 C), 103.1 (d, $^1J_{C,F}$ = 275 Hz), 75.2 (d, $^2J_{C,F}$ = 26 Hz), 66.5, 66.1, 55.2, 47.7 (d, $^4J_{C,F}$ = 11 Hz), 43.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.3 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2921, 2860, 1645, 1260, 1109 cm^{-1}. $C_{14}H_{17}BrFNO_4$ (362.19): calcd. C 46.43, H 4.73, N 3.87; found C 46.80, H 5.05, N 3.94.

(*Z*)-2-Fluoro-3-(4-hydroxyphenyl)-1-morpholinoprop-2-en-1-one (8ao): Yield 61 mg, 61%, R_f (PE/EtOAc 6:4) = 0.25, white solid, m.p. 94–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (br. s, 1 H), 7.21 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.12–7.05 (m, 2 H), 6.89–6.79 (m, 1 H), 6.44 (d, $^3J_{H,F}$ = 38.3 Hz, 1 H), 3.80–3.62 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.2 (d, $^2J_{C,F}$ = 28 Hz), 156.4, 150.6 (d, $^1J_{C,F}$ = 278 Hz), 132.3 (d, $^4J_{C,F}$ = 3 Hz), 129.9, 121.8 (d, $^3J_{C,F}$ = 8 Hz), 116.7 (2 C), 116.6 (d, $^4J_{C,F}$ = 2 Hz), 66.7 (2 C), 47.3 (br), 43.8 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –114.2 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2925, 1644, 1438, 1095, 752 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{15}FNO_3$ [M + H]$^+$ 252.1036; found 252.1035.

***syn*-2-Bromo-2-fluoro-3-hydroxy-3-(4-hydroxyphenyl)-1-morpholinopropan-1-one (9ao):** Yield 46 mg, 33%, R_f (PE/EtOAc 6:4) = 0.26, white solid, m.p. 133–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.20 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H), 7.03 (s, 1 H), 6.99 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 6.83 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.8 Hz, 1 H), 6.13 (br. s, 1 H), 5.13 (d, $^3J_{H,F}$ = 4.9 Hz, 1 H), 5.12 (br. s, 1 H), 3.93–3.39 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.3 (d, $^2J_{C,F}$ = 24 Hz), 155.3, 136.9, 128.9, 121.0 (d, $^4J_{C,F}$ = 3 Hz), 115.8, 115.7 (d, $^4J_{C,F}$ = 3 Hz), 102.6 (d, $^1J_{C,F}$ = 276 Hz), 75.3 (d, $^2J_{C,F}$ = 25 Hz), 66.5, 66.1, 47.7 (d, $^4J_{C,F}$ = 11 Hz), 43.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.6 (d, $^3J_{F,H}$ = 4 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3283, 2925, 1627, 110, 949, 700 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{16}BrFNO_4$ [M + H]$^+$ 348.0247; found 348.0253.

(*E*)-3-[4-(Benzyloxy)phenyl]-2-fluoro-1-morpholinopent-2-en-1-one (8ap): Yield 126 mg, 85%, R_f (PE/EtOAc 6:4) = 0.47, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.36–7.17 (m, 5 H), 7.08 (d, $^3J_{H,H}$ = 8.8 Hz), 6.85 (d, $^3J_{H,H}$ = 8.8 Hz), 4.97 (s, 2 H), 3.39–3.26 (m, 4 H), 3.08–2.99 (m, 2 H), 2.96–2.86 (m, 2 H), 2.46 (dq, $^3J_{H,H}$ = 7.4, $^4J_{H,F}$ = 3.6 Hz, 2 H), 0.89 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.0 (d, $^2J_{C,F}$ = 34 Hz), 158.6, 144.3 (d, $^1J_{C,F}$ = 255 Hz), 136.4, 129.3 (d, $^4J_{C,F}$ = 3 Hz, 2 C), 128.4 (2 C), 127.3, 127.2 (2 C), 125.6 (d, $^2J_{C,F}$ = 15 Hz), 114.9 (2 C), 69.7, 65.9, 65.8, 46.5, 41.5, 22.4 (d, $^3J_{C,F}$ = 5 Hz), 12.2 (d, $^4J_{C,F}$ = 2 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –116.2 (bm) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2958, 1646, 1114, 840, 636, 532 cm^{-1}. HRMS (ESI+): calcd. for $C_{22}H_{25}FNO_3$ [M + H]$^+$ 370.1818; found 3701824.

(*E*)-5-Chloro-2-fluoro-1-morpholino-3-phenylpent-2-en-1-one (8aq): Yield 100 mg, 84%, R_f (PE/EtOAc 6:4) = 0.41, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.36–7.26 (m, 3 H), 7.26–7.16 (m, 2 H), 3.46 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 3.39 (br. s, 4 H), 3.24–3.17 (m, 2 H), 3.10–3.03 (m, 2 H), 2.95 (dt, $^3J_{H,H}$ = 7.0, $^4J_{H,F}$ = 3.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.3 (d, $^2J_{C,F}$ = 33 Hz), 147.6 (d, $^1J_{C,F}$ = 262 Hz), 134.1 (d, $^3J_{C,F}$ = 7 Hz), 128.91 (2 C), 128.88, 128.4 (d, $^4J_{C,F}$ = 3 Hz), 120.0 (d, $^2J_{C,F}$ = 14 Hz), 66.2, 66.0, 46.7, 41.8, 41.6 (d, $^4J_{C,F}$ = 3 Hz), 32.7 (d, $^4J_{C,F}$ = 4 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –111.7 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2858, 1622, 986, 540 cm^{-1}. HRMS (ESI+): calcd. for $C_{15}H_{18}ClFNO_2$ [M + H]$^+$ 298.1010; found 297.0999.

2-Fluoro-1-morpholino-3,3-diphenylprop-2-en-1-one (8ar): Yield 120 mg, 96%, R_f (PE/EtOAc 6:4) = 0.43, white solid, m.p. 162–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31–7.18 (m, 8 H), 7.18–7.09 (m, 2 H), 3.48–3.33 (m, 4 H), 3.28–3.19 (m, 2 H), 3.08–2.98 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ =

161.7 (d, $^2J_{C,F}$ = 33 Hz), 145.2 (d, $^1J_{C,F}$ = 266 Hz), 135.6 (d, $^3J_{C,F}$ = 5 Hz), 135.2 (d, $^3J_{C,F}$ = 2 Hz), 129.8 (d, $^4J_{C,F}$ = 3 Hz, 2 C), 129.7 (d, $^3J_{C,F}$ = 4 Hz), 128.6, 128.5 (2 C), 128.2, 128.0 (2 C), 125.2 (d, $^2J_{C,F}$ = 12 Hz), 65.9, 65.8, 46.5, 41.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –112.2 (s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2862, 1622, 745, 696 cm^{-1}. $C_{19}H_{18}FNO_2$ (311.35): calcd. C 73.29, H 5.83, N 4.50; found C 73.11, H 5.96, N 4.52.

2-Fluoro-1-morpholino-2-(tricyclo[3.3.1.1^{3,7}]dec-2-ylidene)prop-2-en-1-one (8as): Yield 70 mg, 63%, R_f (PE/EtOAc 6:4) = 0.57, white solid, m.p. 67–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.76–3.55 (m, 6 H), 3.55–3.39 (br. m, 2 H), 3.08–2.97 (br. m, 1 H), 2.64–2.77 (br. m, 1 H), 2.04–1.66 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.8 (d, $^2J_{C,F}$ = 34 Hz), 139.6 (d, $^1J_{C,F}$ = 251 Hz), 132.7 (d, $^2J_{C,F}$ = 9 Hz), 66.9, 66.6, 47.0 (d, $^4J_{C,F}$ = 4 Hz), 42.0, 38.6 (d, $^4J_{C,F}$ = 3 Hz, 2 C), 38.04 (2 C), 36.4, 30.8 (d, $^3J_{C,F}$ = 5 Hz), 28.6 (d, $^4J_{C,F}$ = 7 Hz), 27.6 (2 C) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –128.5 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2911, 2856, 1640, 1440 cm^{-1}. $C_{16}H_{22}FNO_2$ (279.35): calcd. C 68.79, H 7.94, N 5.01; found C 68.64, H 8.16, N 5.00.

(*Z*)-3-(4-Chlorophenyl)-2-fluoro-1-(piperidin-1-yl)prop-2-en-1-one (8bd): Yield 47 mg, 32%, R_f (PE/EtOAc 6:4) = 0.53, white solid, m.p. 76–79 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.50 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 7.33 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 6.44 (d, $^3J_{H,F}$ = 38.1 Hz, 1 H), 3.56 (br. s, 4 H), 1.74–1.53 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.6 (d, $^2J_{C,F}$ = 28 Hz), 152.3 (d, $^1J_{C,F}$ = 281 Hz), 134.4 (d, $^6J_{C,F}$ = 3 Hz), 130.8 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 130.3 (d, $^3J_{C,F}$ = 3 Hz), 128.9 (2 C), 113.6 (d, $^2J_{C,F}$ = 5 Hz), 47.8 (br), 44.3 (br), 26.4 (br), 25.6 (br), 24.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –111.8 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2935, 2850, 1603, 1443, 827 cm^{-1}. $C_{14}H_{15}ClFNO$ (267.73): calcd. C 62.81, H 5.65, N 5.23; found C 62.47, H 5.85, N 5.09.

***syn*-2-Bromo-3-(4-chlorophenyl)-2-fluoro-3-hydroxy-1-(piperidin-1-yl)propan-1-one (9bd):** Yield 58 mg, 54%, R_f (PE/EtOAc 6:4) = 0.72, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.49–7.41 (m, 2 H), 7.38–7.30 (m, 2 H), 5.24 (br. s, 1 H), 5.11 (br. s, 1 H), 3.80–3.65 (m, 2 H), 3.65–3.51 (m, 2 H), 1.78–1.49 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.9 (d, $^2J_{C,F}$ = 22 Hz), 134.5, 134.2, 130.1 (d, $^3J_{C,F}$ = 2 Hz, 2 C), 128.7 (2 C), 102.6 (d, $^1J_{C,F}$ = 274 Hz), 75.0 (d, $^2J_{C,F}$ = 26 Hz), 48.0 (d, $^4J_{C,F}$ = 11 Hz), 44.7, 25.7, 25.5, 24.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –121.7 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3425, 1631, 1363, 1175, 1024, 944 cm^{-1}. $C_{14}H_{16}BrClFNO_2$ (364.64): calcd. C 46.11, H 4.42, N 3.84; found C 46.00, H 4.15, N 3.64.

(*Z*)-3-(4-Chlorophenyl)-*N*,*N*-diethyl-2-fluoroacrylamide (8cd): Yield 40 mg, 39%, R_f (PE/EtOAc 6:4) = 0.57, white solid, m.p. 56–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.49 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 7.32 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 6.56 (d, $^3J_{H,F}$ = 37.9 Hz, 1 H), 3.42 (q, $^3J_{H,F}$ = 7.0 Hz, 4 H), 1.31–1.06 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.9 (d, $^2J_{C,F}$ = 28 Hz), 152.5 (d, $^1J_{C,F}$ = 282 Hz), 134.4 (d, $^6J_{C,F}$ = 3 Hz), 130.8 (d, $^4J_{C,F}$ = 8 Hz, 2 C), 130.3 (d, $^3J_{C,F}$ = 3 Hz), 128.8 (2 C), 113.6 (d, $^2J_{C,F}$ = 5 Hz), 42.9 (br), 41.2 (br), 14.6 (br), 12.5 (br) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –113.9 (d, $^3J_{F,H}$ = 38 Hz) ppm. IR (neat): $\tilde{\nu}_{max}$ = 2973, 1613, 1438, 1278, 794 cm^{-1}. $C_{13}H_{15}ClFNO$ (255.72): calcd. C 61.06, H 5.91, N 5.48; found C 60.94, H 6.21, N 5.26.

***syn*-2-Bromo-3-(4-chlorophenyl)-*N*,*N*-diethyl-2-fluoro-3-hydroxypropanamide (9cd):** Yield 54 mg, 38%, R_f (PE/EtOAc 6:4) = 0.76, colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.33 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 5.32 (br. s, 1 H), 5.11 (br. s, 1 H), 4.00–3.78 (m, 1 H), 3.67–3.48 (m, 1 H), 3.33–3.11 (m, 2 H), 1.20 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H), 1.18 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.2 (d, $^2J_{C,F}$ = 22 Hz), 134.5, 134.2, 130.1 (d, $^3J_{C,F}$ = 2 Hz, 2 C), 127.8 (2 C), 102.7 (d, $^1J_{C,F}$ = 276 Hz), 75.2 (d, $^2J_{C,F}$ = 26 Hz), 43.2 (d, $^4J_{C,F}$ = 10 Hz), 42.1, 13.8, 11.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.9 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3424, 1640, 1617, 1391, 1029, 878 cm^{-1}. HRMS (ESI+): calcd. for $C_{13}H_{17}BrClFNO_2$ [M + H]$^+$ 352.0115; found 352.0120.

***N*-Benzyl-2-bromo-3-(4-chlorophenyl)-2-fluoro-3-hydroxy-*N*-methylpropanamide (9dd):** Yield 30 mg, 19%, R_f (PE/EtOAc 6:4) = 0.80, colourless oil. Mixture of *syn* and *anti* diastereoisomers; only major diastereoisomer is described. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.42 (m, 2 H), 7.42–7.27 (m, 5 H), 7.24–7.13 (m, 2 H), 5.22 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,F}$ = 4.6 Hz, 1 H), 5.10 (br. m, 1 H), 4.78 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H), 5.22 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H), 3.15 (d, $^4J_{H,F}$ = 4.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.9 (d, $^2J_{C,F}$ = 23 Hz), 135.4, 134.7, 134.0, 130.2 (d, $^3J_{C,F}$ = 3 Hz, 2 C), 128.9 (2 C), 127.9 (2 C), 127.7 (2 C), 127.1, 103.0 (d, $^1J_{C,F}$ = 276 Hz), 75.3 (d, $^2J_{C,F}$ = 25 Hz), 52.8, 36.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.8 (br. s) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3424, 2961, 1642, 1106, 957, 833, 546 cm^{-1}. $C_{17}H_{17}BrClFNO_2$ (400.67): calcd. C 50.96, H 4.03, N 3.50; found C 51.27, H 4.33, N 3.66.

Multi-Cycle Procedure for the Preparation of Pure 8ab: The standard procedure was followed for the preparation of **8ab** and *syn*-**9ab** from **1b** (0.6 mL, 6 mmol). The recovered pure *syn*-α-bromo-α-fluoro-β-hydroxy amide **9ab** was then dissolved in dry CH_2Cl_2 (3 mL) and Et_2Zn (2 equiv.) was added. The mixture was for stirred 2 h at room temperature. Standard workup and purification gave pure **8ab** and remaining *syn*-**9ab**. Repeating this procedure once again finally gave a total of 1.17 g (83%) of **8ab**.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra.

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[11] At the outset of the project we found that carrying out the reaction at room temperature with a 2:1 Et_2Zn/amide ratio was crucial to ensure complete conversion of the amide **2**.

[12] When 2.2 equiv. of Et_2Zn were used, *anti*-**9ad** (9%) remained at the end of the reaction.

[13] Dibromofluoroacetamides were readily synthesized by a one-step procedure from the corresponding amines and ethyl dibromofluoroacetate; see Exp. Section for details.

[14] The relative configurations of olefins **8al** and **8ap** were determined by ^1H-^{19}F HOESY. See the Supporting Information for details.

[15] CCDC-919940 (for **9ac**) and CCDC-919939 (for **8ad**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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