enantiomer will be longer retained on the column than the S antipode, which is in agreement with experiment. We overestimate the magnitude of the computed separability factor by underestimating the dielectric of the medium but find the agreement between theory and experiment satisfactory. Information extracted from our simulations that are not amenable to experimentation include the following. (1) There are no well-defined binding sites on this CSP in contrast to earlier studies on Pirkle phases. The intermolecular PESs are extremely flat, allowing 1 to freely slide up and down 2. The reason for this slippery behavior is now clear: the CSP looks more like a ball of hydrocarbon than anything else. (2) Binding originates primarily from hydrophobic portions on the CSP with the analyte. Fully $^3/_4$ of the CSP's accessible surface area is nonpolar in nature. (3) The fragment most cognizant of differences between the chirality of analyte molecules is the amide attached to the spacer chain. We conclude that this part of the CSP is most responsible for enantiodifferentiation while the *tert*-butyl and isopropyl groups are most responsible for analyte binding.

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Registry No. (±)-1, 60686-64-8; (*R*)-1, 53531-34-3; (*S*)-1, 60646-30-2; 2, 122902-99-2.

Chemistry of Novel Compounds with Multifunctional Carbon Structure. 5.[1] Molecular Design of Versatile Building Blocks for Aliphatic Monofluoro Molecules by Manipulation of Multifunctional Carbon Structures

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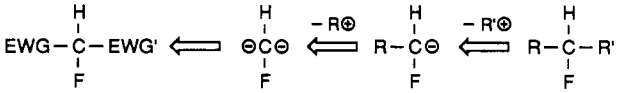
Three kinds of doubly functionalized monofluoromethylene fragments, 1-fluoro-1-nitro-1-(phenylsulfonyl)alkanes (10), 2-fluoro-2-(phenylsulfonyl)alkanoic esters (11), and 2-fluoro-2-nitroalkanoic esters (12), potentially versatile building blocks for the general synthesis of various aliphatic monofluoro molecules, were prepared from the corresponding difunctional compounds 1–3 by monoalkylations (R) and selective fluorinations. The interconversion or reductive removal of each functional group in 10–12 followed by the introduction of the second alkyl groups (R′) at the fluorine-bearing carbon atom was examined. Compounds 12 proved to be useful and practical building blocks for conversions to the various monofluoroalkanes 20–26.

Introduction

The synthesis of aliphatic organofluorine compounds, in contrast to aromatics, has been severely limited. The recent increasing interest in aliphatic fluorine compounds for new materials,[2] biological activity,[3] and mechanistic chemistry[4] led us to attempt to develop general synthetic methods for the preparation of structurally complex fluoroaliphatic compounds. Monofluoro molecules are extremely difficult to prepare because of the inherent problem of stereoselectivity and the high C–F bond reactivity.[5] Although some building blocks for monofluoro compounds have been developed,[6] only simple structures can be derived from them since only a small number of fluorinated starting materials are available.

Scheme I



With this situation in mind, we hoped to develop general synthetic pathways to a wide variety of deliberately designed secondary alkyl fluorides by the use of novel monofluoro building blocks that have multifunctionalized carbon structures.[7,8] The development of synthetic approaches and the investigation of the chemical behavior of such geminally functionalized fluorine compounds were also matters of our interest, since these compounds have been so far not investigated. This paper provides a full account of the molecular design of the building blocks and the interconversion of each functional group on the position α to the fluorine.[9]

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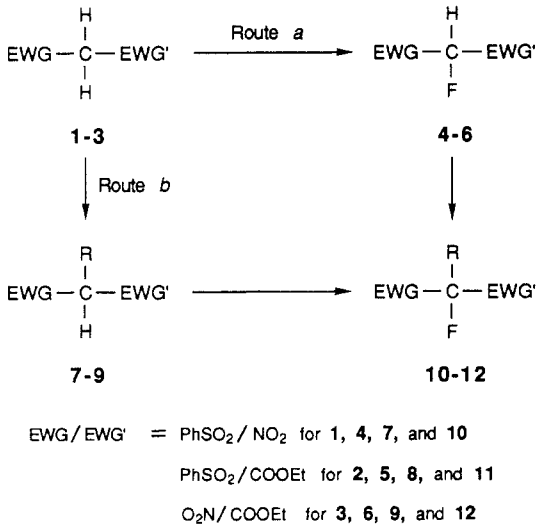
0022-3263/89/1954-5453$01.50/0

Scheme II



EWG/EWG' = $PhSO_2$/NO_2 for **1**, **4**, **7**, and **10**
$PhSO_2$/COOEt for **2**, **5**, **8**, and **11**
O_2N/COOEt for **3**, **6**, **9**, and **12**

Results and Discussion

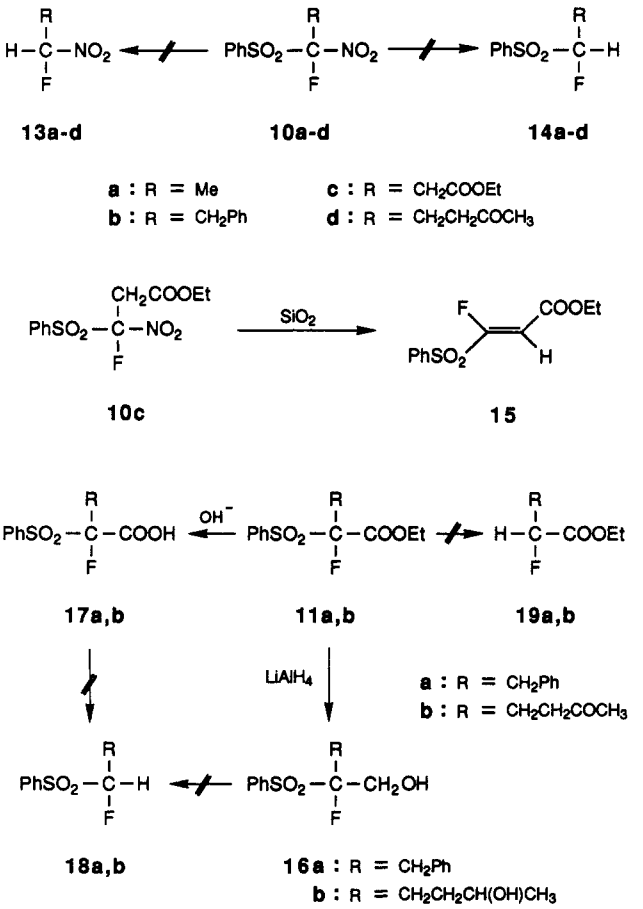
Molecular Designing of Versatile Building Blocks (Scheme I). Our basic strategy in designing these building blocks involved sequential introduction of two independent alkyl chains into the smallest fluorine-bearing carbon fragment (CHF) which is common to all secondary alkyl fluorides. If two kinds of alkyl groups, R and R′, are to be introduced one after another into the fragment, alkyl fluorides (R–CHF–R′) would be obtained that possess a fluorine atom at a position in an alkyl chain dependent on the choice of those two alkyl groups. Since electrophilic introduction of alkyl groups is far easier than the other modes of reaction from a synthetic viewpoint, the fragment should be an α-fluorocarbanion equivalent such as $^-$CHF(R) or $^-$CHF$^-$. However, these species are extremely destabilized because of electronic repulsion.[10]

To overcome this problem, we designed structures with two strong electron-withdrawing groups (EWG, EWG′) at the geminal position to fluorine, which we hoped would contribute to stabilizing the corresponding carbanions as well as being liable to reductive removal at some later stage. Three classes of compounds, 1-fluoro-1-nitro-1-(phenylsulfonyl)alkanes (**10**), 2-fluoro-2-(phenylsulfonyl)alkanoic esters (**11**), and 2-fluoro-2-nitroalkanoic esters (**12**), were finally chosen as potentially practical building blocks that could meet our criteria.

Preparation of the Building Blocks 10–12 (Scheme II). Initial access to the key compounds **10–12** was by fluorination followed by alkylation of the corresponding difunctional compounds **1–3** (route a).[11] However, the yields in the fluorination step were unsatisfactory because of formation of difluorinated byproducts. Also, alkylation of **4–6** using alkyl halides often failed because, contrary to our expectations, the combined carbanion-stabilizing abilities of the two strong EWGs were not sufficient to overcome the well-known carbanion destabilization by the gem fluorine.

The alternative approach of reversing the order of functionalization avoids the problematic step of fluoro-

Scheme III



carbanion generation (route b). Thus, the compounds **1–3** were alkylated with alkyl halides or active olefins by using appropriate bases and solvents to give **7–9** (54–93%). Fluorination of **7–9** was achieved according to our method, using diluted $FClO_3$ freshly generated in ordinary glassware at room temperature, to give the key compounds **10–12** in more than 90% yield. This direct fluorination is noteworthy because of its safety,[12] handiness, selectivity, and excellent yield.

Functional Group Interconversion of 10 and 11 (Scheme III). Attempted conversion of **10a–d** into **13a–d** by desulfonylation with Na–Hg,[13] 1-benzyl-1,4-dihydronicotinamide (BNAH),[14] or 1,3-dimethyl-2-phenylbenzimidazole (DMBI)[15] resulted either in recovery of the starting materials or in formation of decomposed products. Denitration of **10a–d** with n-Bu_3SnH,[16] NaTeH,[17] MeSNa,[18] or BNAH[19] did not give the desired compounds

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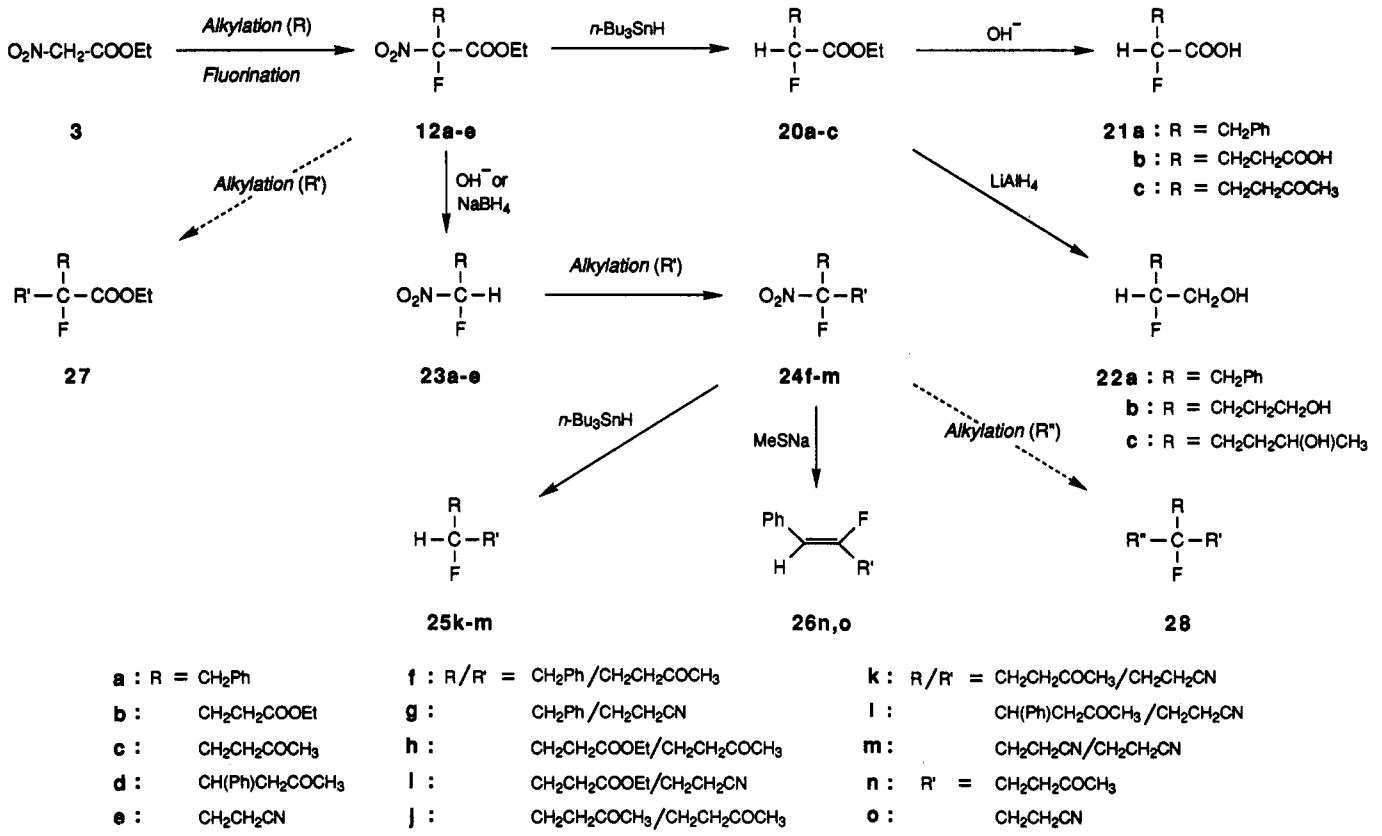
Scheme IV



14a–d. These results were presumably due to a perturbation in chemistry caused by the presence of the several functional groups.[5] Interestingly, however, **10c** gave selectively the (*E*)-fluoroalkene **15** (65%) by simple treatment with silica gel. Compound **15** can be a useful intermediate for the preparation of various monofluoro molecules since it is a good Michael acceptor,[20] a good Diels–Alder dienophile,[20] and a good 1,3-dipolarophile.[21]

Treatment of **11a,b** with $LiAlH_4$ gave the 2-fluoroalkanols **16a,b**[22] (90–94%). Saponificative hydrolysis (aqueous NaOH) of **11a,b** produced the corresponding acids **17a,b** (92–98%). However, attempted conversion of **16a,b** or **17a,b** into **18a,b** and direct decarbethoxylation (LiI/DMSO)[23] of **11a,b** into **18a,b** failed, probably because of poor stabilizability of the fluorocarbanion by the α-sulfonyl group.[24] Since the desulfonylation of **11a,b** under the above conditions[13–15] was also unsuccessful, we next focused on the nitroacetate structure **12**, which is far more susceptible to decarboxylation and deformylation.[25]

Functional Group Interconversion of 12 (Scheme IV). Denitration of **12a–c** with *n*-Bu_3SnH[16] successfully produced the 2-fluoroalkanoic esters **20a–c** (68–88%). Compounds **20a–c** were readily converted to the 2-fluoroalkanoic acids **21a–c**[26] and the 2-fluoroalkanols **22a–c**[22] in excellent yield by the usual manner, happily without any of the anticipated defluorination. The compounds **20–22** can be further transformed into various monofluorinated compounds by manipulating the functional groups still present.

Decarbethoxylation of **12a–e** was performed either by saponificative hydrolysis (aqueous NaOH) and subsequent decarboxylation or by treatment with 1 mol equiv of $NaBH_4$ to give the 1-fluoro-1-nitroalkanes **23a–e** (70–95%). The latter reaction is mechanistically a direct decarbethoxylation rather than an initial formation of the β-fluoro alcohol followed by deformylation.[27] Successive introduction of the second alkyl groups (R′) into **23a–e** was accomplished by Michael-type additions to give the desired dialkylated derivatives **24f–m** (43–82%).

Denitration of **24k–m**, the final stage of our pathway to the desired secondary alkyl fluorides, was successfully achieved by the use of *n*-Bu_3SnH,[16] affording **25k–m**[28] (52–96%). Dehydronitration using MeSNa[18] was successful for those compounds that contained a benzyl structure, **24f,g**. The (*Z*)-fluoroalkenes **26n,o** were produced in a regio- and stereoselective manner in 75 and 55% yields, respectively.

We have thus developed the versatile building blocks **12** for general synthetic pathways leading to a wide variety of secondary alkyl fluorides. These building blocks are equivalent to the synthon of monofluoromethylene dicarbanion, $^-CH(F)^-$.

We also wished to develop a synthetic route capable of producing certain tertiary alkyl fluorides. A successful general synthetic scheme leading to this class of organo-

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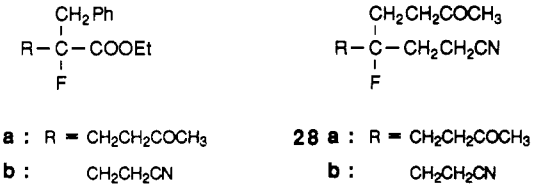
(22) The carbonyl group on the side chain was also reduced to the alcohol for **11b** and **20b,c**.
(23) Kristensen, J.; Lawesson, S.-O. *Tetrahedron* **1979**, *35*, 2075.
(24) The pπ(C)–dπ(S) interaction of the C–SO_2 bond is not enough to stabilize the α-fluorocarbanion in contrast to the pπ(C)–pπ(N) interaction of the C–NO_2 bond, which can form the stable aci form of FCH=N-(O⁻M⁺)→O.
(25) Shipchandler, M. T. *Synthesis* **1979**, 666.
(26) The ester group on the side chain was also hydrolyzed to the carboxylic acid for **20b**.
(27) Reaction of **12a** with $LiAlH_4$ gave the alcohol $PhCH_2CF(NO_2)CH_2OH$, which did not give **23a**. Reaction of **12c** with $NaBH_4$ produced $CH_3CH(OCOOEt)CH_2CH_2CHF(NO_2)$ as a byproduct.
(28) In the case of **24j**, defluorination occurred to give 5-nitro-2,8-nonanediene.

fluorine compounds has not yet been published. Reaction of **12a** with n-Bu_3SnH in the presence of a large excess of the Michael acceptors methyl vinyl ketone and acrylonitrile[29] produced the alkylated products **27a,b** in 14 and



27 a : R = $CH_2CH_2COCH_3$ **28 a** : R = $CH_2CH_2COCH_3$

b : CH_2CH_2CN **b** : CH_2CH_2CN

10% yields, respectively. However, attempted denitrative introduction of the third alkyl groups into **24j,k** using the above Michael acceptors gave **28a,b** in extremely low yield (ca. 4%). The major undesired byproducts were the hydrogenated derivatives **20b** in the former reaction and **25j,k** in the latter reaction. Further studies for optimizing the reaction conditions using n-Bu_3GeH[30] or n-$Bu_3SnCH_2CH{=}CH_2$[31] or employing carbon electrophiles in the presence of a Lewis acid[32] are under way.

Conclusion

We have presented a new general and practical methodology in which deliberately designed building blocks are used for the synthesis of various kinds of monofluorinated aliphatic molecules.

Experimental Section

All melting points were determined on a Yanagimoto micro-melting-point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrometer. ^1H NMR spectra were measured in $CDCl_3$ with $SiMe_4$ as internal standard and were recorded on JEOL PMX-60 (60 MHz), Varian XL-200 (200 MHz), or JEOL GX-270 (270 MHz) spectrometers. ^{19}F NMR spectra were measured in $CDCl_3$ with $CFCl_3$ as internal standard and were taken with a JEOL GX-270 (254 MHz) spectrometer. Upfield shifts are quoted as negative δ values. Coupling constants (J) are given in hertz. EI mass spectra (including high-resolution mass spectra) were taken with a JEOL JMS-D300 spectrometer. Column chromatography and preparative TLC were performed on Kieselgel 60 (Merck, Art. 9385 and Art. 7748, respectively). The purity of all title compounds was judged to be ≥90% by ^1H NMR spectral determinations.

General Procedure for Preparation of 1-Nitro-1-(phenylsulfonyl)alkanes (7). A solution of (phenylsulfonyl)nitromethane[11] (0.201 g, 1.0 mmol) in THF (5 mL) was added at 0 °C to a stirred suspension of NaH (48 mg, 60% dispersion, 1.2 mmol) in THF–HMPA (10 mL), and the mixture was stirred for 15 min. To the solution was added alkyl halide (1.1 mmol), and the resultant mixture was stirred at room temperature for 10–24 h. Water (20 mL) was added and acidified with 1 N HCl and then extracted with CH_2Cl_2 (10 mL × 3), washed with brine, and dried ($MgSO_4$). Evaporation of the solvent gave an oil which was purified by silica gel chromatography to afford the compounds **7** (70–85%). A catalytic amount of KF was employed when an active olefin was used as a Michael acceptor.

General Procedure for Preparation of 2-(Phenylsulfonyl)alkanoic Acid Ethyl Esters (8). A solution of alkyl halide (2.0 mmol) in THF (2 mL) was added dropwise to a mixture of NaH (80 mg, 60% dispersion, 2.0 mmol) and ethyl (phenylsulfonyl)acetate[11] (0.228 g, 2.0 mmol) in THF or sulfolane (10 mL) at 0 °C, and the whole mixture was stirred at room temperature for 8–10 h. The mixture was poured into 0.5 N HCl (30 mL) and extracted with Et_2O (10 mL × 3). The ethereal layer was washed with brine, dried ($MgSO_4$), and concentrated to give a crude product. Purification using silica gel column chromatography afforded the compounds **8** (70–93%). A catalytic amount of KF was employed as a base when an active olefin was used as a Michael acceptor.

General Procedure for Preparation of 2-Nitroalkanoic Acid Ethyl Esters (9). To a suspension of NaOEt (0.476 g, 7.0 mmol) in dry EtOH (10 mL) was added a solution of ethyl nitroacetate (1.064 g, 8.0 mmol) and alkyl halide (7.0 mmol) in dry DMAC (30 mL) under an argon atmosphere, and the mixture was stirred at room temperature for 1–3 days. Evaporation of the solvent gave a crude product which was purified by silica gel column chromatography to yield the compounds **9** (54–72%). A catalytic amount of KF as a base and sulfolane for a solvent were employed when an active olefin was used as an alkylating agent. The yields were usually higher (70–90%) than when using alkyl halides.

General Procedure for Preparation of 1-Fluoro-1-nitro-1-(phenylsulfonyl)alkanes (10) or 2-Fluoro-2-nitroalkanoic Acid Ethyl Esters (12). To a solution of **7** or **9** (1.0 mmol) in dry MeOH (15 mL) was added spray-dried KF[33] (116 mg, 2.0 mmol), and the mixture was stirred at room temperature for 0.5 h. The solvent was evaporated to dryness, and the residual salt was dissolved in dry THF (50 mL). To the solution was introduced diluted perchloryl fluoride [$FClO_3$, generated from $KClO_4$ (6.0 g) and FSO_3H (36 mL)[34]] at 0 °C for 1 h. Evaporation of the solvent gave a solid which was dissolved in AcOEt (50 mL) and washed with water (10 mL). The organic layer was dried ($MgSO_4$) and concentrated to give the compounds **10** or **12** (87–100%).

General Procedure for Preparation of 2-Fluoro-2-(phenylsulfonyl)alkanoic Acid Ethyl Esters (11). To a solution of **8** (1.0 mmol) in dry THF (5 mL) was added dropwise n-BuLi (0.64 mL, 1.58 M in hexane, 1 mmol) at 0 °C under an argon atmosphere. The resulting solution was stirred for 0.5 h and chilled to −20 °C. To the solution was introduced diluted $FClO_3$ gas as mentioned above. After the usual workup, compounds **11** were obtained (80–95%).

1-Fluoro-1-nitro-1-(phenylsulfonyl)ethane (10a): mp 65.0–66.0 °C (hexane–Et_2O); IR (KBr) 1575, 1350, 1170 cm^{-1}; ^1H NMR δ 2.30 (d, 3 H, J(H–F) = 19.8, CH_3), 7.43–8.10 (m, 5 H, Ph); ^{19}F NMR δ −118.18 (q, J = 19.6); MS, m/z 233 (M^+), 187 ($M^+ - NO_2$). Anal. Calcd for $C_8H_8FNO_4S$: C, 41.20; H, 3.46; N, 6.01. Found: C, 41.19; H, 3.57; N, 5.87.

1-Fluoro-1-nitro-2-phenyl-1-(phenylsulfonyl)ethane (10b): mp 71.0–72.0 °C (Et_2O–hexane–$CHCl_3$); IR (KBr) 1580, 1360, 1160 cm^{-1}; ^1H NMR δ 3.80 (dd, 1 H, J = 15.1, 8.3 (H–F), CH_aH_bPh), 4.14 (dd, 1 H, J = 34.7 (H–F), 15.1, CH_aH_bPh), 7.16–7.33 (m, 5 H, CH_2Ph), 7.63–7.96 (m, 5 H, SO_2Ph); ^{19}F NMR δ −125.52 (dd, J = 34.9, 9.1); MS, m/z 309 (M^+), 263 ($M^+ - NO_2$), 168 ($M^+ - SO_2Ph$). Anal. Calcd for $C_{14}H_{12}FNO_4S$: C, 54.36; H, 3.91; N, 4.53. Found: C, 54.40; H, 3.99; N, 4.35.

Ethyl 3-fluoro-3-nitro-3-(phenylsulfonyl)propionate (10c): mp 88.0–89.0 °C (Et_2O–hexane); IR (KBr) 1740, 1580, 1340, 1160 cm^{-1}; ^1H NMR δ 1.24 (t, 3 H, J = 7.2, CH_3), 3.52 (dd, 1 H, J = 17.6, 5.4 (H–F), CH_aH_bCOO), 4.14 (dd, 1 H, J = 34.9 (H–F), 17.6, CH_aH_bCOO), 4.19 (q, 2 H, J = 7.2, CH_2CH_3), 7.62–7.93 (m, 5 H, Ph); ^{19}F NMR δ −125.61 (dd, J = 35.0, 3.7); MS, m/z 306 ($M^+ + 1$), 260 ($M^+ + 1 - NO_2$). Anal. Calcd for $C_{11}H_{12}FNO_6S$: C, 43.27; H, 3.96; N, 4.59. Found: C, 43.42; H, 3.78; N, 4.60.

5-Fluoro-5-nitro-5-(phenylsulfonyl)-2-pentanone (10d): mp 108.5–110.0 °C (hexane–CH_2Cl_2); IR (KBr) 1720, 1570, 1340, 1160 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H, CH_3), 2.40–3.33 (m, 4 H, CH_2CH_2), 7.40–8.03 (m, 5 H, Ph); ^{19}F NMR δ −125.89 (dd, J = 27.6, 9.2); MS, m/z 289 (M^+), 148 ($M^+ - SO_2Ph$). Anal. Calcd for $C_{11}H_{12}FNO_5S$: C, 45.67; H, 4.18; N, 4.84. Found: C, 45.75; H, 4.20; N, 4.62.

Ethyl 2-fluoro-3-phenyl-2-(phenylsulfonyl)propionate (11a): mp 81.5–82.0 °C (Et_2O–hexane); IR (KBr) 1750, 1330, 1160 cm^{-1}; ^1H NMR δ 1.05 (t, 3 H, J = 7.1, CH_3), 3.51 (dd, 1 H, J = 14.7, 12.0 (H–F), CH_aH_bPh), 3.81 (dd, 1 H, J = 38.6 (H–F), 14.7, CH_aH_bPh), 4.04 (m, 2 H, CH_2CH_3), 7.18–7.28 (m, 5 H, CH_2Ph),

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7.56–7.98 (m, 5 H, SO_2Ph); ^{19}F NMR δ –156.89 (dd, J = 38.6, 11.0); MS, m/z 336 (M^+), 291 (M^+ – OEt), 195 (M^+ – SO_2Ph). Anal. Calcd for $C_{17}H_{17}FO_4S$: C, 60.70; H, 5.10. Found: C, 60.91; H, 5.13.

Ethyl 2-fluoro-5-oxo-2-(phenylsulfonyl)hexanoate (11b): mp 66.0–67.0 °C ($CHCl_3$–hexane); IR (KBr) 1740, 1720, 1330, 1160 cm^{-1}; ^1H NMR δ 1.27 (t, 3 H, J = 7.0, CH_2CH_3), 2.13 (s, 3 H, $COCH_3$), 2.47–3.00 (m, 4 H, CH_2CH_2), 4.23 (q, 2 H, J = 7.0, CH_2CH_3), 7.58–8.07 (m, 5 H, Ph); MS, m/z 317 (M^+ + 1), 271 (M^+ – OEt), 175 (M^+ – SO_2Ph). Anal. Calcd for $C_{14}H_{17}FO_5S$: C, 53.15; H, 5.42. Found: C, 53.40; H, 5.31.

Ethyl 2-fluoro-2-nitro-3-phenylpropionate (12a): IR (film) 1765, 1580 cm^{-1}; ^1H NMR δ 1.38 (t, 3 H, J = 7.0, CH_2CH_3), 3.75 (d, 2 H, J = 23.0 (H–F), CH_2Ph), 4.37 (q, 2 H, J = 7.5, CH_2CH_3), 7.35 (m, 5 H, Ph); ^{19}F NMR δ –127.99 (t, J = 23.2); MS, m/z 241 (M^+); exact mass, calcd for $C_{11}H_{12}FNO_4$ (M^+) 241.0745, found 241.0729, calcd for $C_{11}H_{12}FO_2$ (M^+ – NO_2) 195.0822, found 195.0839.

Diethyl 2-fluoro-2-nitroglutarate (12b): IR (film) 1765, 1735, 1580 cm^{-1}; ^1H NMR δ 1.20 (t, 3 H, J = 7.5, $CH_2COOCH_2CH_3$), 1.30 (t, 3 H, J = 7.5, $CHFCOOCH_2CH_3$), 2.50 (3H, m, $CH_aH_bCH_2COO$), 2.90 (m, 1 H, $CH_aH_bCH_2COO$), 4.20 (q, 2 H, J = 7.5, CH_2COOCH_2), 4.45 (q, 2 H, J = 7.5, $CHFCOOCH_2$); ^{19}F NMR δ –128.55 (dd, J = 23.2, 18.3); MS, m/z 252 (M^+ + 1); exact mass, calcd for $C_9H_{14}O_4F$ (M^+ – NO_2) 205.0877, found 205.0982, calcd for $C_7H_9NO_5F$ (M^+ – OC_2H_5) 206.0465, found 206.0491.

Ethyl 2-fluoro-2-nitro-5-oxohexanoate (12c): IR (film) 1762, 1720, 1580 cm^{-1}; ^1H NMR δ 1.35 (t, 3 H, J = 7.5, CH_2CH_3), 2.18 (s, 3 H, $COCH_3$), 2.43–3.13 (m, 4 H, CH_2CH_2), 4.42 (q, 2 H, J = 7.5, CH_2CH_3); ^{19}F NMR δ –129.25 (t, J = 19.9); MS, m/z 221 (M^+); exact mass, calcd for $C_8H_{12}FNO_5$ (M^+) 221.0699, found 221.0681, calcd for $C_8H_{12}FO_3$ (M^+ – NO_2) 175.0770, found, 175.0806.

Ethyl 2-fluoro-2-nitro-5-oxo-3-phenylhexanoate (12d, as a mixture of two diastereomers): IR (film) 1765, 1720, 1580 cm^{-1}. ^1H NMR Data for isomer A: δ 1.08 (t, 3 H, J = 7.0, CH_2CH_3), 2.05 (s, 3 H, $COCH_3$), 2.77 (dd, 1 H, J = 17.7, 3.0, CH_aH_bCO), 3.11 (dd, 1 H, J = 17.7, 10.3, CH_aH_bCO), 4.10 (q, 2 H, J = 7.0, CH_2CH_3), 4.70 (ddd, 2 H, J = 29.7 (H–F), 10.3, 3.0, CHPh), 7.29 (s, 5 H, Ph). ^1H NMR Data for isomer B: δ 1.35 (t, 3 H, J = 7.0, CH_2CH_3), 2.08 (s, 3 H, $COCH_3$), 3.06 (dd, 1 H, J = 18.9, 5.1, $COCH_aH_b$), 3.08 (dd, 1 H, J = 18.9, 7.7, $COCH_aH_b$), 4.37 (q, 2 H, J = 7.0, CH_2CH_3), 4.63 (ddd, 1 H, J = 31.0 (H–F), 7.7, 5.1, CHPh), 7.29 (s, 5 H, Ph); ^{19}F NMR δ –134.81 (d, J = 31.3), –135.47 (d, J = 29.4); MS, m/z 297 (M^+); exact mass, calcd for $C_{14}H_{16}FNO_5$ (M^+) 297.1011, found 297.0993, calcd for $C_{14}H_{16}FO_3$ (M^+ – NO_2) 251.1083, found 251.1110.

Ethyl 4-cyano-2-fluoro-2-nitrobutyrate (12e): IR (film) 2250, 1765, 1580 cm^{-1}; ^1H NMR δ 1.37 (t, 3 H, J = 7.0, CH_2CH_3), 2.37–3.20 (m, 4 H, CH_2CH_2), 4.43 (q, 2 H, J = 7.0, CH_2CH_3); ^{19}F NMR δ –129.84 (t, J = 18.4); MS, m/z 204 (M^+); exact mass, calcd for $C_7H_9FN_2O_4$ (M^+) 204.0547, found 204.0558, calcd for $C_7H_9FNO_2$ (M^+ – NO_2) 158.0617, found 158.0572.

Ethyl (*E*)-3-Fluoro-3-(phenylsulfonyl)acrylate (15). Compound **10c** (26.4 mg, 0.087 mmol) was adsorbed on a column of silica gel (Merck Art. 9385, 2 g) in Et_2O and allowed to stand at room temperature overnight. Elution with Et_2O gave 14.4 mg (65%) of compound **15**: IR (film) 1725, 1670, 1350, 1160 cm^{-1}; ^1H NMR δ 1.30 (t, 3 H, J = 7.1, CH_3), 4.40 (q, 2 H, J = 7.1, CH_2), 6.50 (d, 1 H, J = 28.8 (H–F), C=CH), 7.61–8.00 (m, 5 H, Ph); ^{19}F NMR δ –105.43 (d, J = 27.6); MS, m/z 258 (M^+), 213 (M^+ – OEt), 117 (M^+ – SO_2Ph); exact mass, calcd for $C_{11}H_{11}FO_4S$ (M^+) 258.0363, found 258.0369, calcd for $C_9H_6FO_3S$ (M^+ – OEt) 213.0022, found 213.0065.

Reaction of Esters 11 with $LiAlH_4$. To a stirred suspension of $LiAlH_4$ (7.6 mg, 0.2 mmol) in dry Et_2O (2 mL) was syringed a solution of **11** (0.1 mmol) in dry Et_2O (0.5 mL) at –70 °C under argon atmosphere and the resultant mixture was allowed to stand at room temperature for 0.5 h. To the mixture was added 0.5 N HCl (1 mL), and the whole mixture was extracted with AcOEt (5 mL × 2). The combined organic layer was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the alcohols **16** (90–94%).

2-Fluoro-3-phenyl-2-(phenylsulfonyl)-1-propanol (16a): IR (film) 3520, 1320, 1150, 1075 cm^{-1}; ^1H NMR δ 2.32 (br s, 1 H, OH), 3.25–3.80 (m, 4 H, CH_2 × 2), 7.55–8.08 (m, 5 H, Ph); ^{19}F NMR δ –159.44 (dddd, J = 38.6, 23.9, 20.2, 11.0); MS, m/z 294 (M^+), 276 (M^+ – H_2O), 264 (M^+ – CH_2O).

2-Fluoro-2-(phenylsulfonyl)-1,5-hexanediol (16b) (as a mixture of two diastereomers): IR ($CHCl_3$) 3400, 1305, 1150 cm^{-1}; ^1H NMR δ 1.21 (d, 6 H, J = 6.6, CH_3 × 2), 1.54–2.29 (m, 8 H, CH_2CH_2 × 2), 3.82 (m, 4 H, CH_2O × 2), 4.06 (m, 2 H, $CHCH_3$ × 2), 7.58–7.95 (m, 10 H, Ph × 2); ^{19}F NMR δ –157.58 (sextet, J = 13.0), –158.77 (septet, J = 10.7); MS, m/z 276 (M^+), 259 (M^+ – OH).

Alkaline Hydrolysis of Esters 11. A solution of **11** (0.3 mmol) in EtOH (1 mL) and 1 N NaOH (0.3 mL) was stirred at room temperature for 0.5 h. Most of the EtOH was evaporated, water (6 mL) was added, and the resultant solution was washed with Et_2O. The aqueous layer was acidified with 1 N HCl and extracted with AcOEt (6 mL × 3), and the extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the carboxylic acids **17** (92–98%).

2-Fluoro-3-phenyl-2-(phenylsulfonyl)propionic acid (17a): IR (film) 3300–2700, 1735, 1330, 1160 cm^{-1}; ^1H NMR δ 3.44 (dd, 1 H, J = 14.7, 11.8 (H–F), CH_aH_bPh), 3.78 (dd, 1 H, J = 38.1 (H–F), 14.7, CH_aH_bPh), 5.89 (br s, 1 H, COOH), 7.18–7.25 (m, 5 H, CH_2Ph), 7.54–7.95 (m, 5 H, SO_2Ph); ^{19}F NMR δ –156.89 (dd, J = 38.1, 12.2); MS, m/z 309 (M^+ + 1), 308 (M^+), 167 (M^+ – SO_2Ph).

2-Fluoro-5-oxo-2-(phenylsulfonyl)hexanoic acid (17b): IR (film) 3600–3200, 1740, 1710 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H, CH_3), 2.34–2.87 (m, 4 H, CH_2CH_2), 6.27 (br s, 1 H, COOH), 7.58–7.97 (m, 5 H, Ph); ^{19}F NMR δ –158.11 (dd, J = 34.0, 8.3); MS, m/z 288 (M^+), 271 (M^+ – OH).

General Procedure for Preparation of 2-Fluoroalkanoic Esters 20 by Denitration of 2-Fluoro-2-nitroalkanoic Esters 12. To a solution of **12** (1.0 mmol) in dry benzene (5 mL) were successively added AIBN (0.5 mmol) and n-Bu_3SnH (1.5 mmol), and the whole was heated at reflux for 2 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography to give the fluoro esters **20** as a colorless oil (68–88%).

Ethyl 2-fluoro-3-phenylpropionate (20a): IR (film) 1760 cm^{-1}; ^1H NMR δ 1.25 (t, 3 H, J = 7.1, CH_2CH_3), 3.16 (ddd, 1 H, J = 24.2 (H–F), 14.7, 7.3, CH_aH_bPh), 3.23 (ddd, 1 H, J = 28.1 (H–F), 14.7, 4.4, CH_aH_bPh), 4.22 (q, 2 H, J = 7.1, CH_2CH_3), 5.08 (ddd, 1 H, J = 49.1 (H–F), 7.3, 4.4, CFH), 7.22–7.34 (m, 5 H, Ph); ^{19}F NMR δ –190.38 (ddd, J = 48.8, 28.5, 23.9); MS, m/z 177 (M^+ – F), 149 (M^+ – F – CH_2=CH_2), 91 ($PhCH_2^+$).

Diethyl 2-fluoroglutarate (20b): IR (film) 1760, 1730 cm^{-1}; ^1H NMR δ 1.26 (t, 3 H, J = 7.0, $CH_2COOCH_2CH_3$), 1.32 (t, 3 H, J = 7.0, $CFHCOOCH_2CH_3$), 2.20 (m, 2 H, $CFHCH_2$), 2.50 (m, 2 H, CH_2COO), 4.16 (q, 2 H, J = 7.0, CH_2COOCH_2), 4.27 (q, 2 H, J = 7.0, $CHFCOOCH_2$), 4.90 (ddd, 1 H, J = 48.4 (H–F), 7.0, 4.4, CHF); MS, m/z 206 (M^+), 161 (M^+ – OEt), 133 (M^+ – COOEt).

Ethyl 2-fluoro-5-oxohexanoate (20c): IR (film) 1760, 1720 cm^{-1}; ^1H NMR δ 1.30 (t, 3 H, J = 7.0, CH_2CH_3), 1.90–2.90 (m, 4 H, CH_2CH_2), 2.15 (s, 3 H, $COCH_3$), 4.27 (q, 2 H, J = 7.0, CH_2CH_3), 4.95 (dt, 1 H, J = 49.2 (H–F), 6.2, CHF); MS, m/z 176 (M^+), 161 (M^+ – CH_3), 103 (M^+ – COOEt).

General Procedure for Preparation of 2-Fluoroalkanoic Acids 21 by Saponification of 2-Fluoroalkanoic Esters 20. A solution of **20** (0.1 mmol) in 0.1 N NaOH (1.5–3.0 mL) was stirred at room temperature for 3 h. The solution was acidified with 1 N HCl and extracted with AcOEt (2 mL × 3), and the extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the acids **21** as a colorless solid (84–96%).

2-Fluoro-3-phenylpropionic acid (21a): IR ($CHCl_3$) 3050, 1735 cm^{-1}; ^1H NMR δ 3.21 (ddd, 1 H, J = 25.0 (H–F), 15.0, 7.5, CH_aH_bPh), 3.32 (ddd, 1 H, J = 29.0 (H–F), 15.0, 4.0, CH_aH_bPh), 5.18 (ddd, 1 H, J = 49.0 (H–F), 7.5, 4.0, CFH), 7.32 (m, 5 H, Ph), 7.90 (br s, 1 H, COOH); exact mass, calcd for $C_9H_9O_2F$ (M^+) 168.0586, found 168.0570, calcd for C_8H_8F (M^+ – COOH) 123.0610, found 123.0608.

2-Fluoroglutaric acid (21b): mp 112.0–112.5 °C (AcOEt); IR (KBr) 2950, 1720 cm^{-1}; ^1H NMR (CD_3OD) δ 1.80–2.70 (m, 4 H, CH_2CH_2), 5.10 (dt, 1 H, J = 51.2 (H–F), 6.4, CHF); exact mass, calcd for $C_5H_7O_4F$ (M^+) 150.0328, found 150.0288, calcd for $C_5H_6O_3F$ (M^+ – OH) 133.0301, found 133.0272.

2-Fluoro-5-oxohexanoic acid (21c): IR (film) 3600–2800, 1740, 1710 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H, $COCH_3$), 2.30–2.90 (m, 4 H, CH_2CH_2), 5.00 (dt, 1 H, J = 49.0 (H–F), 6.4, CFH), 6.57 (s,

1 H, COOH); exact mass, calcd for $C_6H_9FO_3$ (M^+) 148.0535, found 148.0496, calcd for $C_5H_6FO_3$ ($M^+ - CH_3$) 133.0301, found 133.0272.

General Procedure for Preparation of 2-Fluoro Alcohols 22 by Reaction of 2-Fluoro Carboxylic Esters 20 with $LiAlH_4$. To a stirred solution of **20** (0.1 mmol) in dry Et_2O (1.0 mL) was added $LiAlH_4$ (0.1–0.2 mmol) at −70 °C, and the solution was allowed to warm to room temperature and remained there for 1 h. Water (2 mL) was added and acidified with 1 N HCl, and the organic layer was separated. The aqueous layer was extracted with AcOEt (2 mL × 3), and the combined organic layer was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the fluoro alcohols **22** as a colorless oil (82–96%).

2-Fluoro-3-phenyl-1-propanol (22a): IR (film) 3370, 1050 cm^{-1}; ^1H NMR δ 1.90 (br s, 1 H, OH), 2.95 (m, 2 H, CH_2Ph), 3.69 (ddd, 1 H, J = 23.0 (H–F), 12.5, 6.0, CH_aH_bOH), 3.77 (ddd, 1 H, J = 25.5 (H–F), 12.5, 3.0, CH_aH_bOH), 4.79 (dm, 1 H, J = 49.6 (H–F), CFH), 7.30 (m, 5 H, Ph); exact mass, calcd for $C_9H_{11}FO$ (M^+) 154.0793, found 154.0808, calcd for C_8H_8F ($M^+ - CH_2OH$) 123.0609, found 123.0594.

2-Fluoro-1,5-pentanediol (22b): IR ($CHCl_3$) 3400, 1040 cm^{-1}; ^1H NMR δ 1.60–1.80 (m, 4 H, $CFHCH_2CH_2$), 1.92 (br s, 2 H, OH × 2), 3.84–3.90 (m, 4 H, CH_2OH × 2), 4.66 (m, 1 H, CFH); MS, m/z 122 (M^+), 105 (M^+ − OH); exact mass, calcd for $C_5H_{11}FO_2$ (M^+) 122.0740, found 122.0746, calcd for $C_5H_{10}FO$ (M^+ − OH) 105.0713, found 105.0701.

2-Fluoro-1,5-hexanediol (22c) (as a mixture of two diastereomers): IR ($CHCl_3$) 3650, 1050 cm^{-1}; ^1H NMR δ 1.23 (d, 3 H, J = 6.4, CH_3), 1.55–2.32 (m, 4 H, CH_2CH_2), 3.61–3.92 (m, 5 H, CH_3CH, CH_2OH, and OH × 2), 4.93 (m, 1 H, CHF); ^{19}F NMR δ −189.96 (m), −192.44 (m); MS, m/z 105 ($M^+ - CH_2OH$), 92 ($M^+ - CH_3CHO$); exact mass, calcd for $C_6H_{13}FO_2$ (M^+) 136.0896, found 136.0901, calcd for $C_5H_{10}FO$ ($M^+ - CH_2OH$) 105.0713, found 105.0715.

General Procedure for Preparation of 1-Fluoro-1-nitroalkanes 23 by Decarbethoxylation of Esters 12 with $NaBH_4$. To a stirred solution of **12** (0.5 mmol) in EtOH (15 mL) was slowly added in portions $NaBH_4$ (0.5 mmol) at −20 °C, and the resulting mixture was allowed to warm to room temperature and remained there for 1 h. The solvent was evaporated. Water (4 mL) was added to the residue and acidified with 1 N HCl. The aqueous solution was extracted with ether (4 mL × 3), and the extract was washed with brine (2 mL) and dried ($MgSO_4$). Evaporation of the solvent gave a crude product which was purified by silica gel column chromatography with Et_2O–hexane as eluant to afford the fluoronitroalkanes **23** as a colorless oil or crystals (70–88%).

General Procedure for Preparation of 1-Fluoro-1-nitroalkanes 23 by Saponification and Concomitant Decarboxylation of Esters 12. To a solution of **12** (0.5 mmol) in EtOH (0.1 mL) was added 1 N NaOH (0.6 mL), and the mixture was stirred at room temperature for 3 h. The resulting solution was acidified with 1 N HCl and extracted with Et_2O (5 mL × 3). The organic layer was washed with brine (2 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the fluoronitroalkanes **23** as a colorless oil (81–95%).

1-Fluoro-1-nitro-2-phenylethane (23a): IR (film) 1570, 1120 cm^{-1}; ^1H NMR δ 3.38 (ddd, 1 H, J = 22.5 (H–F), 12.0, 6.5, CH_aH_bPh), 3.44 (ddd, 1 H, J = 24.0 (H–F), 12.0, 4.0, CH_aH_bPh), 5.92 (ddd, 1 H, J = 50.5 (H–F), 6.5, 4.0, CFH), 7.20–7.40 (m, 5 H, Ph); MS, m/z 169 (M^+), 123 ($M^+ - NO_2$).

Ethyl 4-fluoro-4-nitrobutyrate (23b): IR (film) 1730, 1570, 1370 cm^{-1}; ^1H NMR δ 1.30 (t, 3 H, J = 7.0, CH_3), 2.20–3.80 (m, 4 H, CH_2CH_2), 4.25 (q, 2 H, J = 7.0, CH_2CH_3), 6.05 (dt, 1 H, J = 52.2 (H–F), 6.4, CFH); MS, m/z 180 ($M^+ + 1$), 134 ($M^+ + 1 - NO_2$).

5-Fluoro-5-nitro-2-pentanone (23c): IR (film) 1720, 1570 cm^{-1}; ^1H NMR δ 2.20 (s, 3 H, $COCH_3$), 2.50–2.90 (m, 4 H, CH_2CH_2), 5.90 (dt, 1 H, J = 51.0 (H–F), 6.2, CFH); MS, m/z 149 (M^+), 129 (M^+ − HF), 103 ($M^+ - NO_2$).

5-Fluoro-5-nitro-4-phenyl-2-pentanone (23d). Data for the less polar isomer: IR (KBr) 1710, 1570, 1360 cm^{-1}; ^1H NMR δ 2.15 (s, 3 H, $COCH_3$), 3.04 (dd, 1 H, J = 17.8, 7.3, $CH_aH_bCOCH_3$), 3.07 (dd, 1 H, J = 17.8, 6.4, $CH_aH_bCOCH_3$), 4.11 (dddd, 1 H, J = 23.2 (H–F), 7.3, 6.4, 3.2, CHPh), 5.97 (dd, 1 H, J = 50.0 (H–F), 3.2, CFH), 7.24–7.36 (m, 5 H, Ph); ^{19}F NMR δ −150.98 (dd, J = 50.6, 23.0); MS, m/z 225 (M^+), 179 ($M^+ - NO_2$). Data for the more polar isomer: IR (KBr) 1710, 1570, 1360 cm^{-1}; ^1H NMR δ 2.20 (s, 3 H, $COCH_3$), 3.00 (dd, 1 H, J = 18.6, 5.6, $CH_aH_bCOCH_3$), 3.15 (dd, 1 H, J = 18.6, 9.1, $CH_aH_bCOCH_3$), 4.13 (dddd, 1 H, J = 29.8 (H–F), 9.1, 5.6, 3.4, CHPh), 6.19 (dd, 1 H, J = 50.8 (H–F), 3.4, CFH), 7.16–7.40 (m, 5 H, Ph); ^{19}F NMR δ −156.96 (dd, J = 50.6, 30.4); MS, m/z 225 (M^+), 179 ($M^+ - NO_2$).

4-Fluoro-4-nitrobutanenitrile (23e): IR (film) 2250, 1580, 1370, 1140 cm^{-1}; ^1H NMR δ 2.20–2.87 (m, 4 H, CH_2CH_2), 6.00 (dm, 1 H, J = 50.0 (H–F), CHF); MS, m/z 133 ($M^+ + 1$), 86 ($M^+ - NO_2$).

General Procedure for Preparation of Dialkylated Fluoronitroalkanes 24 by Alkylation of 1-Fluoro-1-nitroalkanes 23. To a solution of **23** (1.0 mmol) in either acetonitrile (1.0 mL) or sulfolane (0.5 mL) was added spray-dried KF[33] (1.0 mmol), and the mixture was stirred at room temperature for 30 min. Methyl vinyl ketone or acrylonitrile (2 mmol) was syringed into the mixture, and stirring was continued at room temperature for 6 h. Water (8 mL) was added, and the whole was extracted with Et_2O (6 mL × 3). The organic layer was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave a crude product which was purified by silica gel column chromatography (Et_2O/hexane = 2/1) to give the fluoroalkanes **24** as a colorless oil or crystals (43–82%).

5-Fluoro-5-nitro-6-phenyl-2-hexanone (24f): IR (KBr) 1705, 1540 cm^{-1}; ^1H NMR δ 2.15 (s, 3 H, $COCH_3$), 2.31–2.73 (m, 4 H, CH_2CH_2), 3.40 (dd, 1 H, J = 18.1 (H–F), 14.6, CH_aH_bPh), 3.50 (dd, 1 H, J = 24.9 (H–F), 14.6, CH_aH_bPh), 7.15–7.37 (m, 5 H, Ph); ^{19}F NMR δ −129.16 (m); MS, m/z 193 ($M^+ - NO_2$), 91 ($PhCH_2^+$). Anal. Calcd for $C_{12}H_{14}FNO_3$: C, 60.23; H, 5.90; N, 5.86. Found: C, 60.05; H, 6.06; N, 6.03.

4-Fluoro-4-nitro-5-phenylpentanenitrile (24g): IR (film) 2250, 1560 cm^{-1}; ^1H NMR δ 2.26–2.85 (m, 4 H, CH_2CH_2), 3.42 (dd, 1 H, J = 20.0 (H–F), 14.6, CH_aH_bPh), 3.50 (dd, 1 H, J = 23.5, 14.6, CH_aH_bPh), 7.15–7.38 (m, 5 H, Ph); exact mass, calcd for $C_{11}H_{11}FN_2O_2$ (M^+) 222.0804, found 222.0832, calcd for $C_{11}H_{11}FN$ ($M^+ - NO_2$) 176.0875, found 176.0861.

Ethyl 4-fluoro-4-nitro-7-oxooctanoate (24h): IR (film) 1740, 1730, 1570, 1360 cm^{-1}; ^1H NMR δ 1.27 (t, 3 H, J = 7.0, CH_2CH_3), 2.17 (s, 3 H, $COCH_3$), 2.28–2.83 (m, 8 H, CH_2CH_2 × 2), 4.17 (q, 2 H, J = 7.0, CH_2CH_3); ^{19}F NMR δ −130.57 (m); MS, m/z 203 ($M^+ - NO_2$); exact mass, calcd for $C_{10}H_{16}FNO_5$ (M^+) 249.1012, found 249.1034, calcd for $C_{10}H_{16}FO_3$ ($M^+ - NO_2$) 203.1082, found 203.1082, calcd for $C_{10}H_{15}O_3$ ($M^+ - NO_2 - HF$) 183.1021, found 183.1021.

Ethyl 6-cyano-4-fluoro-4-nitrohexanoate (24i): IR (film) 2250, 1730, 1570 cm^{-1}; ^1H NMR δ 1.27 (t, 3 H, J = 7.0, CH_3), 2.20–3.27 (m, 8 H, CH_2CH_2 × 2), 4.17 (q, 2 H, J = 7.0, CH_2CH_3); exact mass, calcd for $C_9H_{13}FN_2O_4$ (M^+) 232.0856, found 232.1022, calcd for $C_9H_{13}FNO_2$ ($M^+ - NO_2$) 186.0927, found 186.0919.

5-Fluoro-5-nitro-2,8-nonanedione (24j): mp 61.5–62.5 °C; IR (KBr) 1710, 1550, 1350 cm^{-1}; ^1H NMR δ 2.13 (s, 6 H, CH_3 × 2), 2.28–2.87 (m, 8 H, CH_2CH_2 × 2); MS, m/z 173 ($M^+ - NO_2$), 140 ($M^+ - NO_2 - COCH_3$). Anal. Calcd for $C_9H_{14}FNO_4$: C, 49.29; H, 6.44; N, 6.39. Found: C, 49.54; H, 6.54; N, 6.62.

4-Fluoro-4-nitro-7-oxooctanenitrile (24k): IR ($CHCl_3$) 2250, 1720, 1560 cm^{-1}; ^1H NMR δ 2.19 (s, 3 H, CH_3), 2.30–3.00 (m, 8 H, CH_2CH_2 × 2); exact mass, calcd for $C_8H_{11}FNO$ ($M^+ - NO_2$) 156.0824, found 156.0830.

4-Fluoro-4-nitro-7-oxo-5-phenyloctanenitrile (24l). Data for the less polar isomer: IR (film) 2250, 1720, 1570, 1360 cm^{-1}; ^1H NMR δ 2.05 (s, 3 H, CH_3), 2.22–3.50 (m, 6 H, CH_2CH_2 and CH_2COCH_3), 4.18 (ddd, 1 H, J = 29.5 (H–F), 9.0, 4.5, CHPh), 7.28–7.48 (m, 5 H, Ph); MS, m/z 278 (M^+), 232 ($M^+ - NO_2$); exact mass, calcd for $C_{14}H_{15}FN_2O_3$ (M^+) 278.1065, found 278.1082, calcd for $C_{14}H_{15}FNO$ ($M^+ - NO_2$) 232.1137, found 232.1098. Data for the more polar isomer: IR (film) 2250, 1720, 1575, 1355 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H, CH_3), 2.30–2.70 (m, 4 H, CH_2CH_2), 3.00–3.20 (m, 2 H, CH_2COCH_3), 4.20 (dd, 1 H, J = 24.0 (H–F), 6.0, CHPh), 7.40 (m, 5 H, Ph); MS, m/z 278 (M^+), 232 ($M^+ - NO_2$); exact mass, calcd for $C_{14}H_{15}FN_2O_3$ (M^+) 278.1065, found 278.1077, calcd for $C_{14}H_{15}FNO$ ($M^+ - NO_2$) 232.1137, found 232.1104.

1,5-Dicyano-3-fluoro-3-nitropentane (24m): mp 60.5–62.0 °C (hexane–AcOEt); IR (KBr) 2250, 1550, 1350, 1170 cm^{-1}; ^1H NMR δ 2.43–3.00 (m, 8 H, CH_2CH_2 × 2); MS, m/z 185 (M^+), 139 ($M^+ - NO_2$). Anal. Calcd for $C_7H_8FN_3O_2$: C, 45.39; H, 4.36; N, 22.70. Found: C, 45.62; H, 4.52; N, 22.49.

General Procedure for Preparation of Fluoroalkanes 25 by Denitration of Fluoronitroalkanes 24. To a solution of

24 (0.2 mmol) in dry benzene (2 mL) were successively added AIBN (0.06 mmol) and n-Bu_3SnH (0.3 mmol), and the whole mixture was heated at reflux for 2 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane = 2/1) to give the fluoroalkanes **25** as a colorless oil (52–96%).

4-Fluoro-7-oxooctanenitrile (25k): IR (film) 2240, 1710 cm^{-1}; ^1H NMR δ 1.80–2.08 (m, 4 H, CH_2CHFCH_2), 2.20 (s, 3 H, CH_3), 2.53 (t, 2 H, J = 6.5, CH_2CN), 2.66 (t, 2 H, J = 6.5, CH_2CO), 4.62 (dm, 1 H, J = 49.0 (H–F), CHF); MS, m/z 157 (M^+); exact mass, calcd for $C_8H_{12}FNO$ (M^+) 157.0902, found 157.0903.

4-Fluoro-7-oxo-5-phenyloctanenitrile (25l). Data for the less polar isomer: IR (film) 2250, 1715 cm^{-1}; ^1H NMR δ 1.58–1.88 (m, 2 H, CH_2CHF), 2.12 (s, 3 H, CH_3), 2.40 (t, 2 H, J = 7.5, CH_2CN), 2.78–3.16 (m, 2 H, CH_2CO), 3.44 (m, 1 H, $CHPh$), 4.78 (ddt, 1 H, J = 50.0 (H–F), 10.3, 2.8, CHF), 7.15–7.35 (m, 5 H, Ph); exact mass, calcd for $C_{14}H_{16}FNO$ (M^+) 233.1215, found 233.1218. Data for the more polar isomer: IR (film) 2250, 1715 cm^{-1}; ^1H NMR δ 1.58–1.86 (m, 2 H, CH_2CHF), 2.07 (s, 3 H, CH_3), 2.43 (t, 2 H, J = 7.5, CH_2CN), 2.78–3.16 (m, 2 H, CH_2CO), 3.35 (m, 1 H, $CHPh$), 4.65 (ddt, 1 H, J = 49.7 (H–F), 8.6, 2.6, CHF), 7.15–7.35 (m, 5 H, Ph); exact mass, calcd for $C_{14}H_{16}FNO$ (M^+) 233.1215, found 233.1171.

1,5-Dicyano-3-fluoropentane (25m): IR (film) 2250 cm^{-1}; ^1H NMR δ 1.85–2.10 (m, 4 H, CH_2CFHCH_2), 2.35–2.85 (m, 4 H, $CH_2CN \times 2$), 4.70 (dm, 1 H, J = 49.6 (H–F), CHF); exact mass, calcd for $C_7H_9N_2F$ (M^+) 140.0749, found 140.0702.

General Procedure for Preparation of (*Z*)-Fluoroolefins 26 by Dehydronitration of Fluoronitroalkanes 24 with Sodium Thiomethoxide. A solution of **24** (0.1 mmol) and NaSMe (0.6 mmol) in DMF (1.0 mL) was stirred at 0 °C for 2 h. Water (20 mL) was added, and the whole was extracted with Et_2O (2 mL × 5). The organic layer was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave a crude product which was purified by silica gel chromatography (Et_2O/hexane = 2/1) to give the (*Z*)-fluoroolefins **26** as a colorless oil (55–70%).

(*Z*)-5-Fluoro-6-phenyl-5-hexen-2-one (26n): IR ($CHCl_3$) 1710, 1690 cm^{-1}; ^1H NMR δ 2.20 (s, 3 H, CH_3), 2.57–2.80 (m, 4 H, CH_2CH_2), 5.52 (d, 1 H, J = 39.2 (H–F), CH=CF), 7.19–7.50 (m, 5 H, Ph); ^{19}F NMR δ –103.35 (dt, J = 38.6, 18.4); MS, m/z 192 (M^+), 172 (M^+ – HF), 157 (M^+ – HF – CH_3); exact mass, calcd for $C_{12}H_{13}FO$ (M^+) 192.0950, found 192.0955.

(*Z*)-4-Fluoro-5-phenyl-4-pentenenitrile (26o): IR ($CHCl_3$) 2250, 1690 cm^{-1}; ^1H NMR δ 2.66–2.74 (m, 4 H, CH_2CH_2), 5.65 (d, 1 H, J = 38.8 (H–F), CH=CF), 7.26–7.49 (m, 5 H, Ph); ^{19}F NMR δ –106.88 (dt, J = 38.6, 18.8); MS, m/z 175 (M^+); exact mass, calcd for $C_{11}H_{10}FN$ (M^+) 175.0797, found 175.0814.

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Supplementary Material Available: ^1H NMR spectra of selected compounds (28 pages). Ordering information is given on any current masthead page.