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Facile Synthesis of Quaternary α-Fluoronitriles by Cobalt-Catalyzed Hydrocyanation of Monofluoroalkenes

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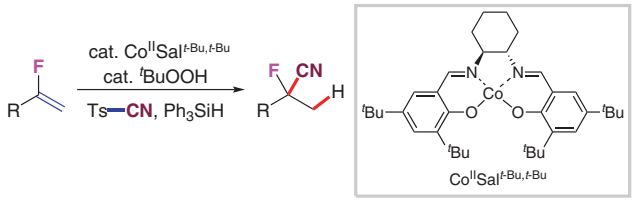

* *Co-catalyzed hydrocyanation of monofluoroalkenes*
* *19 new examples, up to 82% yield*
* *good substrate scope and wide functional group compatibilities*

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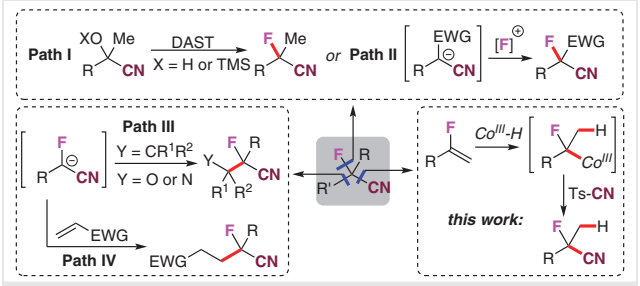
Abstract An exclusively regioselective hydrocyanation of monofluoroalkenes has been developed, with which a series of aliphatic quaternary α-fluoronitriles were synthesized in a facile and efficient manner. This novel method is featured with mild conditions, good functional groups compatibilities, and high reactivity.

Key words quaternary α-fluoronitriles, hydrocyanation, monofluoroalkenes, cobalt catalysis, radical

The fluorine atom has a tiny atomic radius and the strongest electronegativity of the periodic table of elements.[1] These natural characters make the introduction of fluorine into organic structure dramatically change its properties, such as metabolic stability, lipophilicity, bioavailability, and binding affinity.[2] Meanwhile, nitriles have been extensively used as one of the most versatile intermediates in organic synthesis, enabling diverse chemical transformations. As one of the alternative precursors of β-fluoroamines, which serves as the key moieties in bioactive and pharmaceutical compounds,[3] the efficient synthesis of α-fluoronitriles have inspired wide attentions of organofluorine chemists. Despite the importance of α-fluoronitriles, there are only few synthetic methods reported so far, especially for the quaternary α-fluoronitriles. The common method to afford quaternary α-fluoronitriles is direct fluorination by the construction of C–F bonds, via either dehydroxylate fluorination of cyanohydrins[4] (Scheme 1, Path I) or electrophilic fluorination of in situ generated carbanion[5] (Scheme 1, Path II). However, the instability of cyanohydrins for the dehydroxylate fluorination and the requirement of electron-drawing group (EWG) adjacent to the cyano group for the electrophilic fluorination definitely hampered their utility for synthetic applications. Thus, an alternative method has been developed by C–C bond formation via nucleophilic addition of tertiary α-fluoronitrile carbanion to electrophiles[6] (Scheme 1, Path III–IV), in which the reaction types and substrate scope was correspondingly limited. Indeed, the diverse construction of quaternary α-fluoronitriles, especially bearing no other activating group on the quaternary carbon center, remains still an unsolved issue to be addressed.



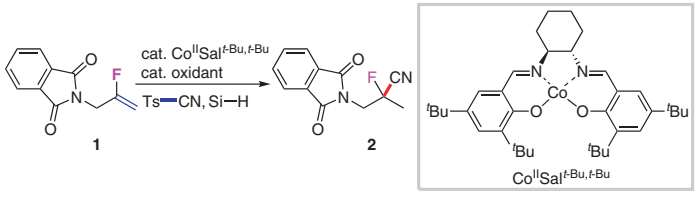
Scheme 1 Synthesis of quaternary α-fluoronitriles

As we are very much inspired by the exploration for facile synthetic methods for the various monofluorinated compounds with new molecular platforms, the construction of quaternary α-fluoronitrile has accordingly aroused our research interests.[7] Considering that alkenes served normally as one kind of simple and basal materials for further transformation to diverse complex molecules, we envisioned that monofluoroalkenes may play as a potential molecular platform to construct various monofluorine-containing compounds.[8] As is known, the metal-hydride hydrogen atom transfer (MHAT) process is used as a strong strategy for the hydrofunctionalization of alkenes by an in situ generation of hydrogenated carbon radical or metal species, followed by various radical captures or metal-catalyzed functionalizations.[9] Accordingly, we speculated that a

Co^{III}–H-promoted radical hydrocyanation of monofluoroalkenes would pave a new approach for effective construction of quaternary α-fluoronitriles, by a strategical cleavage of C–CN bonds. Herein, we describe an exclusively regioselective hydrocyanation of monofluoroalkenes, with which a series of aliphatic quaternary α-fluoronitriles were synthesized in a facile and efficient manner. This novel method is featured with mild conditions, well functional groups compatibilities, and high reactivity.

At the beginning, our study commenced with methyl 2-(2-fluoroallyl)isoindoline-1,3-dione (**1**) as the initial substrate, tosyl cyanide (0.15 mmol, 1.5 equiv) as the cyano source, and $PhSiH_3$ as the hydride source in the presence of a catalytic amount of $Co^{II}Sal^{t\text{-}Bu,t\text{-}Bu}$ (10 mol%) in EtOH. To our delight, the desired quaternary α-fluoronitrile **2** was obtained smoothly in 47% yield when 0.3 equivalent of *t*-BuOO*t*-Bu was added to the reaction as oxidant to generate the active catalyst (Table 1, entry 1). Considering this metal-hydride hydrogen atom transfer (MHAT) process was initiated only by Co^{III}–H species, different kinds of oxidants were examined under such reaction conditions at first (entries 2–6). The resulting data show that a number of added oxidants, including *t*-BuOOH, $PhCO_2Ot$-Bu, Selectfluor, NFSI, and BIOH, could start this radical reaction and provide the desired product **2** in tolerable yields, but *t*-BuOOH favored the hydrocyanation of monofluoroalkene with a slightly higher yield (entry 2). In order to adjust the rate of Co–H species generation to match the rate of radical capture, various Si–H reagents, including, activated $HSi(OEt)_3$, $HSiMe(OEt)_2$, and PMHS or non-activated PhSiMeH and Ph_2SiH_2 were carefully investigated in this cobalt catalytic system (entries 7–11). The results revealed that the non-activated Si–H reagents adapted this reaction conditions better, and $PhSiH_3$ still gave the best yield of aliphatic qua-

Table 1 Optimization of the Reaction Conditions[a]

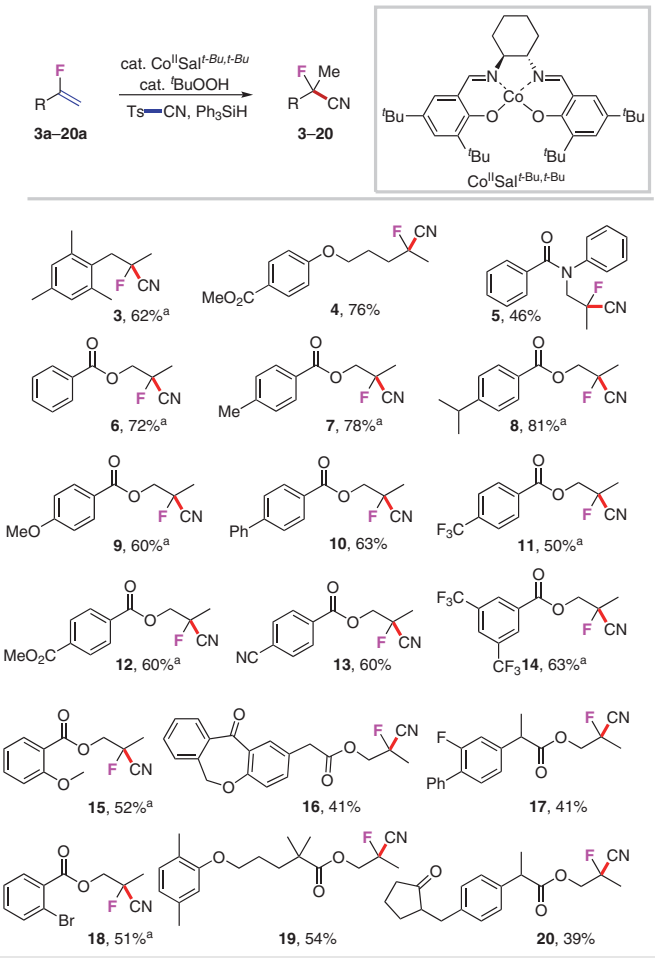


Entry	Si–H	Oxidant	Solvent (mL)	Yield (%)
1	$PhSiH_3$	*t*-BuOO*t*-Bu	EtOH	47
2	$PhSiH_3$	*t*-BuOOH	EtOH	49
3	$PhSiH_3$	$PhCO_2Ot$-Bu	EtOH	41
4	$PhSiH_3$	Selectfluor	EtOH	37
5	$PhSiH_3$	NFSI	EtOH	32
6	$PhSiH_3$	BIOH	EtOH	45
7	$HSi(OEt)_3$	*t*-BuOOH	EtOH	2
8	$HSiMe(OEt)_2$	*t*-BuOOH	EtOH	9
9	PMHS	*t*-BuOOH	EtOH	6
10	$PhSiMeH_2$	*t*-BuOOH	EtOH	45
11	Ph_2SiH_2	*t*-BuOOH	EtOH	45
12	$PhSiH_3$	*t*-BuOOH	acetone (0.9)/EtOH (0.1)	34
13	$PhSiH_3$	*t*-BuOOH	DCE (0.9)/EtOH (0.1)	45
14	$PhSiH_3$	*t*-BuOOH	DME (0.9)/EtOH (0.1)	38
15	$PhSiH_3$	*t*-BuOOH	MeCN (0.9)/EtOH (0.1)	15
16[b]	$PhSiH_3$	*t*-BuOOH	EtOH	34
17[b,c]	$PhSiH_3$	*t*-BuOOH	EtOH	60
18[b,d]	$PhSiH_3$	*t*-BuOOH	EtOH	84 (82)

[a] Reaction conditions: **1** (0.1 mmol, 1.0 equiv), TsCN (1.5 equiv), $Co^{II}Sal^{t\text{-}Bu,t\text{-}Bu}$ (10 mol%), Si–H (1.0 equiv), oxidant (0.3 equiv), solvent (1 mL), r.t., 12 h. Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard; numbers in parentheses were yields of isolated products. PMHS = Poly(methylhydrosiloxane).
[b] TsCN (3.0 equiv) was used.
[c] $PhSiH_3$ (1.5 equiv) was used.
[d] $PhSiH_3$ (2.5 equiv) was used.

ternary α-fluoronitrile **2**. Meanwhile, the optimization of solvents indicated mixed solvents were unhelpful for this reaction (entries 12–15), and only DCM (0.9 mL)/EtOH (0.1 mL) gave a similar yield as in entry 2. While increasing the loading of TsCN to 0.3 mmol slightly decreased the yield (entry 16), to our satisfaction, the enhancement of the equivalent of both Ts–CN (0.3 mmol) and $PhSiH_3$ (0.15 mmol) could clearly improve the yield of target product to 60% (entry 17). This result indicated that the loading of Si–H reagent should be closely related to Ts–CN and was crucial for the transformation. Finally, further increasement of the loading of $PhSiH_3$ to 2.5 equivalents furnished the aliphatic quaternary α-fluoronitriles **2** in 82% isolated yield (entry 18).

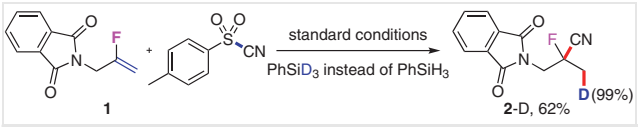
With the optimized reaction conditions in hand, we next explored the compatibilities with various monofluoroalkenes in this cobalt catalytic system (Scheme 2). As expected, the monofluoroalkenes with a longer carbon chain could adapt this radical reaction well affording **4**, which indicated that a directing group was not necessary for this transformation. Furthermore, the monofluoroalkenes installed with benzamide group were also compatible with the optimized conditions, affording the desired products **2** and **5** in acceptable to good yields. Meanwhile, the benzoate-derived monofluoroalkenes were also suitable substrates for this transformation (**6**–**15**, **18**). Notably, diverse monofluoroalkenes containing different phenyl rings which were equipped with various functional groups, such as methyl (**7**), isopropyl (**8**), methoxy (**9**), phenyl (**10**), ester (**12**), cyano (**13**), and trifluoromethyl (**11**, **14**), could all provide the corresponding products in moderate to good yields. To our interests, the substrates installed with *ortho*-functional groups on the phenyl rings, no matter methoxy (**15**) or bromo (**18**), could also furnish the desired quaternary α-fluoronitrile smoothly, albeit in slightly decreased yields. Inspired by these interesting results, this novel transformation has also been explored for late-stage modification of complex bioactive molecules. Accordingly, several monofluoroalkenes containing diversified pharmaceutical structures have been synthesized and subjected into the



Scheme 2 Scope of monofluoroalkenes. *Reagents and conditions*: monofluoroalkene (0.1 mmol, 1.0 equiv), TsCN (3.0 equiv), $Co^{II}Salt^{t\text{-}Bu,t\text{-}Bu}$ (10 mol%), $PhSiH_3$ (2.5 equiv), *t*-BuOOH (0.3 equiv), EtOH (1 mL), r.t., 12 h. Isolated yields are shown. [a] Reactions run with 0.5 mmol of **1**.

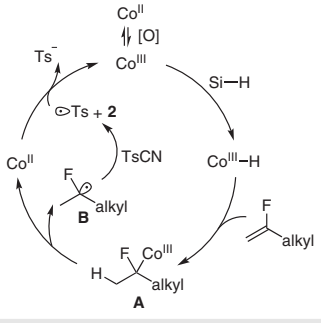
hydrocyanation conditions. To our excitement, such monofluoroalkenes derived from diverse drugs, such as isoxepac (**16**), flurbiprofen (**17**), gemfibrozil (**19**), and loxoprofen (**20**), all were compatible well with this transformation in acceptable yields.

In order to confirm the hydride source of this hydrocyanation reaction, $PhSiD_3$ has been used as hydride source to subject into the standard conditions by replacement of $PhSiH_3$, affording the corresponding product **2**-D in 62% yield with 99% deuterium incorporation (Scheme 3). This result clearly indicated that the hydrogen atom for hydrocyanation comes from the Si–H species via a MHAT process.



Scheme 3 Deuterium experiment

Based on previous reports[9] and the above deuterium experiment result, a possible mechanism is proposed as shown in Scheme 4. Initially, the Co^{II} species is oxidized to the active Co^{III} species,[9i–k] which generates the Co^{III}–H species by interaction with $PhSiH_3$. Subsequently, the insertion of monofluoroalkene into the Co^{III}–H bond affords alkylated cobalt species **A**. The following homolytic cleavage of C–Co^{III} bond provides carbon radical **B**, followed by a radical capture by TsCN to furnish the final product **2** and produces Ts• radical. Finally, the Ts• (or *t*-BuOOH) oxidizes Co^{II} species to Co^{III} species and completes the catalytic cycle.



Scheme 4 Proposed mechanism

In summary, we have reported an exclusively regioselective hydrocyanation of monofluoroalkenes. This method paves a novel way to construct a series of aliphatic quaternary α-fluoronitriles, and featured with mild conditions, good functional groups compatibilities, and high reactivity. Further explorations for regio- and stereoselective construction of monofluorine-containing quaternary carbon center are underway in our laboratory.

Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$ δ_H = 7.26, δ_C = 77.16. Standard abbreviations were used to indicate multiplicities. Coupling constants were reported in hertz (Hz). High-resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight). The monofluoroalkenes were synthesized according to following methods. Anhydrous solvents and commercially available reagents were purchased and used without further purification. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes.

2-(2-Fluoroallyl)isoindoline-1,3-dione (1); Typical Procedure 1 (TP 1)

The starting material 2-fluoroprop-2-en-1-ol was synthesized according to a reported procedure[10] from methyl 2-fluoroacrylate (5.2 g, 50 mmol). After removing the solvent carefully, the crude 2-fluoroprop-2-en-1-ol was dissolved in THF (0.5 M). At 0 °C, to the solution was added NaH (60% in mineral oil, 1.2 equiv) slowly and the mixture was stirred for 5 min. Then TsCl (1.1 equiv) in THF was added dropwise and the reaction was stirred overnight. H_2O (100 mL) and EtOAc (100 mL) were added to the reaction mixture, then the aqueous phase was extracted with EtOAc (3 × 100 mL) and the organic layers were combined, washed with brine, and dried (Na_2SO_4). The organic layer was concentrated for flash column chromatography on silica gel with an eluent of PE and EtOAc (10:1) to obtain the crude 2-furoprop-2-enyl toslate. Next, phthalimide (7.36 g, 50 mmol) was dissolved in THF, followed by the addition of NaH (60% in mineral oil, 1.2 equiv) at 0 °C. After stirring for 5 min, the tosylate from the last step was added to the reaction mixture and allowed to stay overnight at r.t. After quenching with H_2O (100 mL), EtOAc (100 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (3 × 100 mL). The organic layers were combined, washed with brine, and dried (Na_2SO_4). The mixture was concentrated for column chromatography on silica gel with an eluent of PE and EtOAc to obtain the final product **1**; total yield: 3.6 g (35%).

Similarly, **5a** was prepared from *N*-phenylbenzamide and 2-fluoroprop-2-en-1-ol.

2-Fluoroallyl Benzoate (6a); Typical Procedure 2 (TP 2)

The starting material 2-fluoroprop-2-en-1-ol was synthesized according to a reported procedure[10] from methyl 2-fluoroacrylate (5.2.g, 50 mmol), and then the crude 2-fluoroprop-2-en-1-ol was stirred with PhCOCl (7.03 g, 50 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 M) at 0 °C. NEt_3 (10.1 g, 100 mmol, 2 equiv) was added to the reaction mixture and the mixture was stirred overnight. After total consumption of the starting material, the mixture was concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EtOAc 10:1) to give the target product **6a**; yield: 6.5 g (72%).

Vinyl fluorides **7a**–**20a** were prepared from suitable starting materials based on the above typical procedure 2.

2-(2-Fluoroallyl)-1,3,5-trimethylbenzene (3a)

2,4,6-Trimethylphenylmagnesium bromide (1 M in THF, 2.23 g, 10 mmol, 1 equiv) was stirred at r.t. Anhyd THF (30 mL) and 2-fluoroallyl 4-methylbenzenesulfonate (2.3 g, 10 mmol, 1 equiv) were added sequentially to the reaction mixture. The mixture was stirred at 60 °C for 4 h. Afterwards, the mixture was quenched with aq 1 M HCl. The organic phase was washed with aq 1 M HCl, and the aqueous phase was extracted with EtOAc (3 × 50 mL). The organic layers were com-

bined, and concentrated under vacuum. The residue was purified by flash column chromatography (PE) to give the target product **3a**; yield: 540 mg (30%).

2-(2-Fluoroallyl)isoindoline-1,3-dione (1)

Purified by silica gel chromatography (PE/EtOAc 5:1); white solid; mp 82.8–84.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.4, 3.1 Hz, 2 H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2 H), 4.75 (dd, *J* = 16.1, 3.5 Hz, 1 H), 4.56 (dd, *J* = 47.6, 3.4 Hz, 1 H), 4.39 (d, *J* = 12.1 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.50, 159.68 (d, *J* = 260.0 Hz), 134.37, 132.00, 123.69, 93.06 (d, *J* = 17.1 Hz), 37.99 (d, *J* = 34.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –103.71 (ddt, *J* = 48.2, 15.3, 12.2 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{11}H_8FNO_2Na^+$: 228.0431; found: 228.0427.

2-(2-Fluoroallyl)-1,3,5-trimethylbenzene (3a)

Purified by silica gel chromatography (PE); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 2 H), 4.65–4.49 (m, 1 H), 4.07–3.82 (m, 1 H), 3.54 (d, *J* = 6.7 Hz, 2 H), 2.35 (s, 6 H), 2.33 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.82 (d, *J* = 259.2 Hz), 137.15, 136.46, 129.70 (d, *J* = 8.8 Hz), 129.11, 89.84 (d, *J* = 19.5 Hz), 31.89 (d, *J* = 29.2 Hz), 20.99, 19.79.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –93.03 (ddt, *J* = 50.1, 17.3, 6.7 Hz).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{15}F^+$: 178.1152; found: 178.1152.

Methyl 4-[(4-Fluoropent-4-en-1-yl)oxy]benzoate (4a)[11]

Purified by silica gel chromatography (PE/EtOAc 10:1); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.56 (dd, *J* = 17.4, 2.8 Hz, 1 H), 4.27 (dd, *J* = 50.0, 2.7 Hz, 1 H), 4.05 (t, *J* = 6.1 Hz, 2 H), 3.88 (s, 3 H), 2.48–2.30 (m, 2 H), 2.02 (p, *J* = 6.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.00, 165.79 (d, *J* = 257.1 Hz), 162.78, 131.74, 122.78, 114.18, 90.51 (d, *J* = 20.2 Hz), 66.80, 52.00, 28.60 (d, *J* = 28.0 Hz), 25.81.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –95.57 (dq, *J* = 50.4, 16.8 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{13}H_{16}FO_3^+$: 239.1078; found: 239.1083.

***N*-(2-Fluoroallyl)-*N*-phenylbenzamide (5a)**

Purified by silica gel chromatography (PE/EtOAc 5:1); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.30 (m, 2 H), 7.25–7.19 (m, 3 H), 7.19–7.12 (m, 3 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 4.74 (dd, *J* = 16.5, 3.2 Hz, 1 H), 4.64 (d, *J* = 13.3 Hz, 2 H), 4.54 (dd, *J* = 48.4, 3.1 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.64, 161.31 (d, *J* = 260.1 Hz), 143.32, 135.56, 130.02, 129.28, 128.89, 127.90, 127.57, 127.08, 93.51 (d, *J* = 18.0 Hz), 50.38 (d, *J* = 32.2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –99.39 to –113.03 (m).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{16}H_{15}FNO^+$: 256.1132; found: 256.1140.

2-Fluoroallyl Benzoate (6a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.02 (m, 2 H), 7.60–7.53 (m, 1 H), 7.49–7.39 (m, 2 H), 4.86 (dd, *J* = 15.9, 3.3 Hz, 1 H), 4.84 (dd, *J* = 13.9, 0.5 Hz, 2 H), 4.71 (dd, *J* = 47.3, 3.3 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.91, 160.44 (d, *J* = 257.9 Hz), 133.44, 129.8, 129.58, 128.57, 94.53 (d, *J* = 17.0 Hz), 61.80 (d, *J* = 34.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.33 (ddt, *J* = 47.3, 15.8, 13.9 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{10}H_{10}FO_2^+$: 181.0659; found: 181.0662.

2-Fluoroallyl 4-Methylbenzoate (7a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 4.86 (dd, *J* = 15.9, 3.3 Hz, 1 H), 4.83 (d, *J* = 13.8 Hz, 2 H), 4.71 (dd, *J* = 47.4, 3.2 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.94, 160.55 (d, *J* = 258.1 Hz), 144.17, 129.89, 129.25, 126.80, 94.33 (d, *J* = 17.0 Hz), 61.58 (d, *J* = 34.1 Hz), 21.73.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.30 (ddt, *J* = 47.4, 15.9, 13.9 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{11}H_{11}FO_2Na^+$: 217.0635; found: 217.0652.

2-Fluoroallyl 4-Isopropylbenzoate (8a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 4.86 (dd, *J* = 16.0, 3.2 Hz, 1 H), 4.84 (d, *J* = 13.7 Hz, 2 H), 4.71 (dd, *J* = 47.4, 3.2 Hz, 1 H), 2.97 (hept, *J* = 6.9 Hz, 1 H), 1.27 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.93, 160.58 (d, *J* = 258.1 Hz), 154.93, 130.06, 127.16, 126.68, 94.28 (d, *J* = 16.9 Hz), 61.57 (d, *J* = 34.2 Hz), 34.38, 23.76.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.34 (ddt, *J* = 47.3, 15.8, 13.7 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{13}H_{16}FO_2^+$: 223.1129; found: 223.1137.

2-Fluoroallyl 4-Methoxybenzoate (9a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.7 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 4.88–4.77 (m, 3 H), 4.69 (dd, *J* = 47.4, 3.2 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.69, 163.81, 160.68 (d, *J* = 257.7 Hz), 131.99, 121.96, 113.85, 94.32 (d, *J* = 17.3 Hz), 61.55 (d, *J* = 34.5 Hz), 55.58.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –105.33 (dq, *J* = 46.9, 14.5 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{11}H_{11}FO_3Na^+$: 233.0584; found: 233.0591.

2-Fluoroallyl [1,1′-Biphenyl]-4-carboxylate (10a)

Purified by silica gel chromatography (PE/EtOAc 30:1); white solid; mp 43.8–45.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.7 Hz, 2 H), 7.68 (d, *J* = 7.7 Hz, 2 H), 7.63 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.44–7.36 (m, 1 H), 4.91–4.85 (m, 3 H), 4.74 (dd, *J* = 47.3, 2.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.89, 160.53 (d, *J* = 257.9 Hz), 146.26, 140.06, 130.47, 129.10, 128.40, 128.35, 127.45, 127.30, 94.59 (d, *J* = 17.1 Hz), 61.87 (d, *J* = 34.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.31 (dq, *J* = 48.9, 14.9 Hz).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}FO_2^+$: 256.0894; found: 256.0896.

2-Fluoroallyl 4-(Trifluoromethyl)benzoate (11a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H), 4.90 (dd, *J* = 15.7, 3.3 Hz, 1 H), 4.88 (d, *J* = 14.6 Hz, 2 H), 4.74 (dd, *J* = 47.0, 3.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.81, 160.05 (d, *J* = 258.3 Hz), 134.99 (q, *J* = 32.9 Hz), 132.86, 130.34, 125.67 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 273.4 Hz), 95.17 (d, *J* = 17.2 Hz), 62.38 (d, *J* = 33.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.21, –105.40 (dq, *J* = 47.5, 14.9 Hz).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{11}H_9F_4O_2^+$: 249.0533; found: 249.0514.

2-Fluoroallyl Methyl Terephthalate (12a)

Purified by silica gel chromatography (PE/EtOAc 20:1); colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.07 (m, 4 H), 4.89 (dd, *J* = 15.7, 3.3 Hz, 1 H), 4.86 (d, *J* = 14.5 Hz, 2 H), 4.73 (dd, *J* = 47.1, 3.3 Hz, 1 H), 3.95 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.33, 165.20, 160.10 (d, *J* = 258.2 Hz), 134.41, 133.34, 129.90, 129.77, 95.11 (d, *J* = 17.2 Hz), 62.27 (d, *J* = 33.8 Hz), 52.63.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –102.76 to –113.92 (m).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{12}H_{12}FO_4^+$: 239.0714; found: 239.0716.

2-Fluoroallyl 4-Cyanobenzoate (13a)

Purified by silica gel chromatography (PE/EtOAc 20:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.5 Hz, 2 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 4.94–4.87 (m, 1 H), 4.87 (d, *J* = 14.9 Hz, 2 H), 4.73 (dd, *J* = 46.9, 3.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.35, 159.75 (d, *J* = 258.3 Hz), 133.36, 132.42, 130.39, 117.96, 116.89, 95.50 (d, *J* = 16.9 Hz), 62.58 (d, *J* = 33.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.37.

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{11}H_9FNO_2^+$: 206.0612; found: 206.0611.

2-Fluoroallyl 3,5-Bis(trifluoromethyl)benzoate (14a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (s, 2 H), 8.09 (s, 1 H), 4.94 (dd, *J* = 15.4, 3.4 Hz, 1 H), 4.92 (d, *J* = 15.3 Hz, 2 H), 4.77 (dd, *J* = 46.7, 3.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.45, 159.56 (d, *J* = 258.6 Hz), 132.51 (q, *J* = 34.1 Hz), 131.82 , 130.07 (d, *J* = 3.2 Hz), 126.89 (pent, *J* = 3.6 Hz), 122.95 (q, *J* = 272.9 Hz), 95.96 (d, *J* = 17.3 Hz), 62.98 (d, *J* = 32.5 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.04, –105.35 (dq, *J* = 48.7, 17.2, 16.6 Hz).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_7F_7O_2^+$: 316.0334; found: 316.0330.

2-Fluoroallyl 2-Methoxybenzoate (15a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 7.9, 1.7 Hz, 1 H), 7.52–7.42 (m, 1 H), 6.98 (dt, *J* = 7.2, 3.0 Hz, 2 H), 4.87–4.78 (m, 3 H), 4.72 (dd, *J* = 47.6, 3.1 Hz, 1 H), 3.90 (s, 3 H).

^{3}C NMR (126 MHz, $CDCl_3$): δ = 165.25, 160.59 (d, *J* = 257.4 Hz), 159.63, 134.14, 131.99, 120.27, 119.19, 112.19, 94.12 (d, *J* = 16.7 Hz), 61.50 (d, *J* = 35.0 Hz), 56.07.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –94.99 to –129.78 (m).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{11}H_{12}FO_3^+$: 211.0765; found: 211.0771.

2-Fluoroallyl 2-(11-Oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (16a)

Purified by silica gel chromatography (PE/EtOAc 5:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.1 Hz, 1 H), 7.85 (d, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.1 Hz, 1 H), 7.45–7.37 (m, 2 H), 7.31 (d, *J* = 7.4 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 5.13 (s, 2 H), 4.78 (dd, *J* = 15.9, 3.3 Hz, 1 H), 4.61 (d, *J* = 14.3 Hz, 2 H), 4.58 (dd, *J* = 47.4, 3.2 Hz, 1 H), 3.68 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.68, 170.65, 160.52, 159.98 (d, *J* = 257.8 Hz), 140.35, 136.28, 135.49, 132.78, 132.49, 129.42, 129.22, 127.82, 127.23, 125.10, 121.13, 94.59 (d, *J* = 17.0 Hz), 73.54, 61.65 (d, *J* = 33.8 Hz), 39.79.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.39 (dq, *J* = 47.3, 14.4 Hz).

HRMS (EI): *m*/*z* [M + H$^+$] calcd for $C_{19}H_{16}FO_4^+$: 327.1027; found: 327.1040.

2-Fluoroallyl 2-(2-Fluoro-[1,1′-biphenyl]-4-yl)propanoate (17a)

Purified by silica gel chromatography (PE/EtOAc 10:1); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.8 Hz, 2 H), 7.49–7.35 (m, 4 H), 7.22–7.14 (m, 2 H), 4.81 (dd, *J* = 15.9, 3.3 Hz, 1 H), 4.74–4.45 (m, 3 H), 3.85 (q, *J* = 7.2 Hz, 1 H), 1.60 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 173.30, 160.11 (d, *J* = 258.0 Hz), 159.78 (d, *J* = 248.4 Hz), 141.34 (d, *J* = 7.5 Hz), 135.50, 130.96 (d, *J* = 3.8 Hz), 129.03 (d, *J* = 2.7 Hz), 128.55, 128.08 (d, *J* = 13.6 Hz), 127.80, 123.67 (d, *J* = 3.4 Hz), 115.37 (d, *J* = 23.8 Hz), 94.44 (d, *J* = 16.9 Hz), 61.70 (d, *J* = 34.2 Hz), 44.90, 18.40.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –105.48 (dq, *J* = 47.9, 15.1, 14.6 Hz), –113.24 to –132.27 (m).

HRMS (EI): *m*/*z* [M + H$^+$] calcd for $C_{18}H_{17}F_2O_2^+$: 303.1191; found: 303.1205.

2-Fluoroallyl 2-Bromobenzoate (18a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 7.3, 2.1 Hz, 1 H), 7.65 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.42–7.29 (m, 2 H), 4.93–4.66 (m, 4 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.26, 159.96 (d, *J* = 258.0 Hz), 134.57, 133.04, 131.65, 131.29, 127.30, 122.04, 95.06 (d, *J* = 16.8 Hz), 62.26 (d, *J* = 33.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.19 (dq, *J* = 47.0, 14.7 Hz).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{10}H_9BrFO_2$: 258.9764; found: 258.9771.

2-Fluoroallyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (19a)

Purified by silica gel chromatography (PE/EtOAc 30:1); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 7.5 Hz, 1 H), 6.72 (d, *J* = 7.5 Hz, 1 H), 6.67 (s, 1 H), 4.85 (dd, *J* = 15.9, 3.2 Hz, 1 H), 4.66 (dd, *J* = 47.4, 3.2 Hz, 1 H), 4.66 (d, *J* = 13.8 Hz, 2 H), 4.03–3.86 (m, 2 H), 2.37 (s, 3 H), 2.25 (s, 3 H), 1.96–1.68 (m, 4 H), 1.32 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.07, 160.61 (d, *J* = 258.2 Hz), 157.03, 136.52, 130.39, 123.68, 120.80, 112.02, 94.02 (d, *J* = 17.1 Hz), 67.90, 61.23 (d, *J* = 34.0 Hz), 42.28, 37.16, 25.22, 25.17, 21.48, 15.83.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –105.24 to –105.65 (m).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{18}H_{26}FO_3^+$: 309.1860; found: 309.1864.

2-Fluoroallyl 2-{4-[(2-Oxocyclopentyl)methyl]phenyl}propanoate (20a)

Purified by silica gel chromatography (PE/EtOAc 10:1), colorless oil; dr = 1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.1 Hz, 2 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 4.70 (dd, *J* = 16.1, 3.3 Hz, 1 H), 4.61–4.36 (m, 3 H), 3.73 (q, *J* = 7.2 Hz, 1 H), 3.10 (dd, *J* = 13.9, 4.1 Hz, 1 H), 2.49 (dd, *J* = 13.9, 9.5 Hz, 1 H), 2.37–2.27 (m, 2 H), 2.13–2.00 (m, 2 H), 1.97–1.87 (m, 1 H), 1.70 (dtdd, *J* = 12.8, 10.6, 8.4, 6.4 Hz, 1 H), 1.59–1.40 (m, 1 H), 1.48 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 220.31, 173.84, 160.20 (d, *J* = 257.5 Hz), 139.07, 137.83, 129.20, 127.56, 93.89 (d, *J* = 17.0 Hz), 61.29 (d, *J* = 34.9 Hz), 50.95, 44.93, 38.18, 35.18, 29.17, 20.55, 18.39 (d, *J* = 1.3 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –88.67 to –129.99 (m).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{18}H_{22}FO_3^+$: 305.1547; found: 305.1556.

Cobalt-Catalyzed Hydrocyanation of Monofluoroalkenes; General Procedure (GP)

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with the respective monofluoroalkene (0.1 mmol or 0.5 mmol), tosyl cyanide (0.3 mmol or 1.5 mmol), and $Co^{II}Sal^{t\text{-}Bu,t\text{-}Bu}$ (0.01 mmol or 0.05 mmol), EtOH (1 mL or 5 mL). Then the $PhSiH_3$ (0.25 mmol or 1.25 mmol) and TBHP (0.03 mmol or 0.15 mmol) were added dropwise in sequence. The reaction mixture was stirred at r.t. for 12 h. Then the mixture was concentrated directly in vacuo for purification by column chromatography on silica gel (eluent: PE/EtOAc) to provide the respective products **2**–**20**.

3-(1,3-Dioxoisoindolin-2-yl)-2-fluoro-2-methylpropanenitrile (2)

Prepared by following GP using **1** (20.5 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 10:1); white solid; yield: 19.0 mg (82%); mp 120.0–123.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 5.5, 3.1 Hz, 2 H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2 H), 4.29–4.08 (m, 2 H), 1.83 (d, *J* = 21.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.44 , 134.76 , 131.67 , 124.08 , 116.70 (d, *J* = 33.6 Hz), 86.97 (d, *J* = 186.7 Hz), 44.13 (d, *J* = 26.2 Hz), 23.93 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –145.09 to – 155.55 (m).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{12}H_{10}FN_2O_2^+$: 233.0721; found: 233.0731.

2-Fluoro-3-mesityl-2-methylpropanenitrile (3)

Prepared by following GP using **3a** (89 mg, 0.5 mmol) as substrate. Purification by silica gel chromatography (PE); colorless oil; yield: 63.5 mg (62%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.94 (s, 2 H), 3.54–3.17 (m, 2 H), 2.39 (s, 6 H), 2.31 (s, 3 H), 1.83 (d, *J* = 21.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.13, 137.30, 129.59, 127.11, 118.66 (d, *J* = 35.0 Hz), 89.27 (d, *J* = 182.1 Hz), 38.47 (d, *J* = 23.5 Hz), 26.14 (d, *J* = 25.4 Hz), 20.92, 20.90.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –134.04 to – 145.79 (m).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{13}H_{16}FN^+$: 205.1267; found: 205.1261.

Methyl 4-[(4-Cyano-4-fluoropentyl)oxy]benzoate (4)

Prepared by following GP using **4a** (23.8 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 10:1); colorless oil; yield: 20.2 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.9 Hz, 2 H), 4.09 (qt, *J* = 9.7, 5.2 Hz, 2 H), 3.89 (s, 3 H), 2.38–1.99 (m, 4 H), 1.80 (d, *J* = 21.1 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.94, 162.49, 131.79, 123.01, 118.14 (d, *J* = 34.8 Hz), 114.13, 88.31 (d, *J* = 180.2 Hz), 66.81, 52.06, 36.84 (d, *J* = 23.1 Hz), 25.94 (d, *J* = 24.8 Hz), 24.02 (d, *J* = 3.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –146.15 (dddd, *J* = 27.3, 20.9, 13.4, 5.8 Hz).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{14}H_{17}FNO_3^+$: 266.1187; found: 266.1195.

N-(2-Cyano-2-fluoropropyl)-*N*-phenylbenzamide (5)

Prepared by following GP using **5a** (25.5 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 10:1); colorless oil; yield: 13.0 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.21 (m, 5 H), 7.20–7.10 (m, 5 H), 4.66–4.30 (m, 2 H), 1.86 (d, *J* = 21.5 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.55, 143.21, 134.92, 130.27, 129.51, 128.83, 127.98, 127.55, 117.12 (d, *J* = 34.2 Hz), 88.65 (d, *J* = 183.7 Hz), 55.68 (d, *J* = 23.8 Hz), 29.84, 24.07 (d, *J* = 24.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –143.61 (dq, *J* = 43.4, 21.6 Hz).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{17}H_{16}FN_2O^+$: 283.1241; found: 283.1254.

2-Cyano-2-fluoropropyl Benzoate (6)

Prepared by following GP using **6a** (90 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 74.5 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25–7.81 (m, 2 H), 7.55 (tt, *J* = 7.0, 1.3 Hz, 1 H), 7.47–7.34 (m, 2 H), 4.73–4.29 (m, 2 H), 1.79 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.42, 133.95, 130.06, 128.76, 128.70, 116.36 (d, *J* = 34.4 Hz), 86.31 (d, *J* = 184.7 Hz), 66.62 (d, *J* = 25.7 Hz), 22.59 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –152.39 (pd, *J* = 21.3, 14.8 Hz).

HRMS (ESI): *m*/*z* [M + H$^+$] calcd for $C_{11}H_{11}FNO_2^+$: 208.0768; found: 208.0775.

2-Cyano-2-fluoropropyl 4-Methylbenzoate (7)

Prepared by following GP using **7a** (97 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 86.2 mg (78%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 4.88–4.28 (m, 2 H), 2.43 (s, 3 H), 1.86 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.49, 144.85, 130.11, 129.81, 129.48, 116.42 (d, *J* = 34.5 Hz), 86.36 (d, *J* = 184.5 Hz), 66.47 (d, *J* = 25.9 Hz), 22.60 (d, *J* = 24.2 Hz), 21.89.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –152.39 (pd, *J* = 21.0, 15.0 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{12}H_{13}FNO_2^+$: 222.0925; found: 222.0938.

2-Cyano-2-fluoropropyl 4-Isopropylbenzoate (8)

Prepared by following GP using **8a** (111 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 101.0 mg (81%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 4.81–4.34 (m, 2 H), 2.97 (dq, *J* = 13.7, 6.9 Hz, 1 H), 1.86 (d, *J* = 20.9 Hz, 3 H), 1.27 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.48, 155.58, 130.29, 126.90, 126.28, 116.42 (d, *J* = 34.4 Hz), 86.37 (d, *J* = 184.8 Hz), 66.45 (d, *J* = 25.8 Hz), 34.47, 23.80, 22.61 (d, *J* = 24.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –152.41 (pd, *J* = 20.9, 15.3 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{14}H_{17}FNO_2^+$: 250.1238; found: 250.1245.

2-Cyano-2-fluoropropyl 4-Methoxybenzoate (9)

Prepared by following GP using **9a** (105 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); colorless oil; yield: 71.1 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25–7.93 (m, 2 H), 7.05–6.68 (m, 2 H), 4.83–4.14 (m, 2 H), 3.88 (s, 3 H), 1.85 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.14, 164.18, 132.22, 121.02, 116.46 (d, *J* = 34.2 Hz), 114.04, 86.42 (d, *J* = 184.6 Hz), 66.39 (d, *J* = 25.9 Hz), 55.65, 22.62 (d, *J* = 24.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –152.35 (dtd, *J* = 41.8, 20.8, 11.3 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{12}H_{13}FNO_3^+$: 238.0874; found: 238.0884.

2-Cyano-2-fluoropropyl [1,1′-Biphenyl]-4-carboxylate (10)

Prepared by following GP using **10a** (25.6 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); white solid; yield: 17.8 mg (63%); mp 105.9–107.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.09 (m, 2 H), 7.72–7.67 (m, 2 H), 7.65–7.59 (m, 2 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.42 (t, *J* = 7.3, 6.4, 3.2 Hz, 1 H), 4.75–4.49 (m, 2 H), 1.88 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.34, 146.72, 139.87, 130.62, 129.13, 128.51, 127.45, 127.43, 127.39, 116.40 (d, *J* = 34.6 Hz), 86.36 (d, *J* = 184.8 Hz), 66.64 (d, *J* = 25.7 Hz), 22.62 (d, *J* = 24.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –152.30 (pd, *J* = 21.5, 15.0 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{17}H_{14}FNO_2Na^+$: 306.0901; found: 306.0905.

2-Cyano-2-fluoropropyl 4-(Trifluoromethyl)benzoate (11)

Prepared by following GP using **11a** (124 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 68.8 mg (50%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 4.90–4.12 (m, 2 H), 1.88 (d, *J* = 20.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.28, 135.38 (q, *J* = 32.8 Hz), 131.93, 130.50, 125.84 (q, *J* = 3.7 Hz), 123.59 (q, *J* = 273.0 Hz), 116.18 (d, *J* = 34.4 Hz), 86.21 (d, *J* = 185.4 Hz), 67.05 (d, *J* = 25.5 Hz), 22.52 (d, *J* = 23.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.24, –152.35 (pd, *J* = 21.1, 14.3 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{12}H_9F_4NO_2Na^+$: 298.0462; found: 298.0459.

2-Cyano-2-fluoropropyl Methyl Terephthalate (12)

Prepared by following GP using **12a** (119 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); colorless oil; yield: 79.5 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28–7.99 (m, 4 H), 4.80–4.37 (m, 2 H), 3.96 (s, 3 H), 1.88 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.18, 164.66, 134.82, 132.40, 130.04, 129.88, 116.23 (d, *J* = 34.5 Hz), 86.22 (d, *J* = 185.0 Hz), 66.95 (d, *J* = 25.5 Hz), 52.68, 22.56 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –152.35 (pd, *J* = 20.9, 14.6 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{13}H_{13}FNO_4^+$: 266.0823; found: 266.0833.

2-Cyano-2-fluoropropyl 4-Cyanobenzoate (13)

Prepared by following GP using **13a** (20.5 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); white solid; yield: 14.0 mg (60%); mp 91.0–92.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54–8.03 (m, 2 H), 8.02–7.56 (m, 2 H), 5.22–4.23 (m, 2 H), 1.87 (d, *J* = 20.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.76, 132.49, 132.38, 130.46, 117.75, 117.29, 115.99 (d, *J* = 34.7 Hz), 86.05 (d, *J* = 185.5 Hz), 67.13 (d, *J* = 24.9 Hz), 22.40 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –148.37 to –156.53 (m),

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{12}H_{10}FN_2O_2^+$: 233.0721; found: 233.0720.

2-Cyano-2-fluoropropyl 3,5-Bis(trifluoromethyl)benzoate (14)

Prepared by following GP using **14a** (158 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 108.1 mg (63%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 8.13 (s, 1H), 4.81–4.47 (m, 2 H), 1.89 (d, *J* = 20.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.95, 132.69 (q, *J* = 34.3 Hz), 130.95, 130.12 (d, *J* = 3.2 Hz), 127.72–126.99 (m), 122.82 (q, *J* = 273.0 Hz), 115.95 (d, *J* = 34.4 Hz), 86.10 (d, *J* = 185.6 Hz), 67.42 (d, *J* = 24.9 Hz), 22.44 (d, *J* = 24.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.24, –152.35 (pd, *J* = 21.1, 14.3 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{13}H_8F_7NO_2Na^+$: 366.0335; found: 366.0365.

2-Cyano-2-fluoropropyl 2-Methoxybenzoate (15)

Prepared by following GP using **15a** (105 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); colorless oil; yield: 61.6 mg (52%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.8 Hz, 1 H), 7.53 (t, *J* = 7.8 Hz, 1 H), 7.01 (t, *J* = 7.8 Hz, 2 H), 4.75–4.38 (m, 2 H), 3.93 (s, 3 H), 1.86 (d, *J* = 21.0 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.86, 159.92, 134.74, 132.29, 120.39, 118.17, 116.55 (d, *J* = 34.2 Hz), 112.22, 86.35 (d, *J* = 184.1 Hz), 66.43 (d, *J* = 26.5 Hz), 56.05, 22.68 (d, *J* = 23.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –152.34 (pd, *J* = 20.9, 14.7 Hz).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{12}H_{12}FNO_3Na^+$: 260.0693; found: 260.0705.

2-Cyano-2-fluoropropyl 2-(11-Oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (16)

Prepared by following GP using **16a** (32.6 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 10:1); colorless oil; yield: 14.5 mg (41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.3 Hz, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.56 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.50–7.41 (m, 2 H), 7.37 (d, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 8.4 Hz, 1 H), 5.19 (s, 2 H), 4.63–4.15 (m, 2 H), 3.76 (s, 2 H), 1.76 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 190.90, 170.35, 160.81, 140.51, 136.40, 135.60, 132.97, 132.70, 129.61, 129.43, 127.97, 126.79, 125.31, 121.42, 116.19 (d, *J* = 34.2 Hz), 86.09 (d, *J* = 184.8 Hz), 73.76, 66.49 (d, *J* = 25.7 Hz), 39.78, 22.46 (d, *J* = 23.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –152.60 (pd, *J* = 21.3, 15.3 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{20}H_{17}FNO_4^+$: 354.1136; found: 354.1145.

2-Cyano-2-fluoropropyl 2-(2-Fluoro-[1,1′-biphenyl]-4-yl)propanoate (17)

Prepared by following GP using **17a** (30.2 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 10:1); colorless oil; yield: 13.5 mg (41%); dr = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 2 H), 7.51–7.42 (m, 2 H), 7.41–7.33 (m, 2 H), 7.21–7.09 (m, 2 H), 4.61–4.15 (m, 2 H), 3.88 (q, *J* = 7.2 Hz, 1 H), 1.72 (d, *J* = 20.8 Hz, 3 H), 1.61 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.94, 172.89, 159.84 (d, *J* = 248.8 Hz), 140.75 (d, *J* = 2.3 Hz), 140.69 (d, *J* = 2.4 Hz), 135.46, 131.11, 131.08, 129.09, 129.07, 128.60, 128.35 (d, *J* = 13.5 Hz), 127.89, 123.78 (t, *J* = 3.6 Hz), 116.15 (dd, *J* = 34.4, 2.1 Hz), 115.42 (dd, *J* = 23.9, 1.7 Hz), 86.14 (dd, *J* = 184.9, 8.4 Hz), 66.39 (dd, *J* = 25.6, 4.0 Hz), 44.82, 22.44 (d, *J* = 23.9 Hz), 22.33 (d, *J* = 24.3 Hz), 18.21 (d, *J* = 8.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.46 to – 121.80 (m), –148.93 to – 154.51 (m).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{19}H_{17}F_2NO_2Na^+$: 352.1120; found: 352.1130.

2-Cyano-2-fluoropropyl 2-Bromobenzoate (18)

Prepared by following GP using **18a** (129 mg, 0.5 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 30:1); colorless oil; yield: 72.7 mg (51%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 7.1, 2.3 Hz, 1 H), 7.76–7.65 (m, 1 H), 7.48–7.33 (m, 2 H), 4.78–4.24 (m, 2 H), 1.88 (d, *J* = 20.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.45, 134.60, 133.37, 131.80, 130.03, 127.29, 122.20, 116.07 (d, *J* = 34.1 Hz), 85.84 (d, *J* = 184.9 Hz), 66.79 (d, *J* = 25.9 Hz), 22.43 (d, *J* = 23.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –152.34 (pd, *J* = 20.9, 14.7 Hz).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{12}H_9BrFNO_2^+$: 285.9873; found: 285.9876.

2-Cyano-2-fluoropropyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (19)

Prepared by following GP using **19a** (30.8 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); colorless oil; yield: 18.1 mg (54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (d, *J* = 7.5 Hz, 1 H), 6.66 (d, *J* = 7.3 Hz, 1 H), 6.60 (s, 1 H), 4.48–4.21 (m, 2 H), 4.00–3.85 (m, 2 H), 2.30 (s, 3 H), 2.17 (s, 3 H), 1.84–1.70 (m, 7 H), 1.28 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.53, 156.85, 136.48, 130.29, 123.57, 120.71, 116.18 (d, *J* = 34.5 Hz), 111.92, 86.18 (d, *J* = 184.5 Hz), 67.69, 66.00 (d, *J* = 25.5 Hz), 42.34, 36.94, 25.10, 25.02, 22.40 (d, *J* = 24.0 Hz), 21.42, 15.78.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –146.08 to – 162.75 (m).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{19}H_{27}FNO_3^+$: 336.1969; found: 336.1971.

2-Cyano-2-fluoropropyl 2-{4-[(2-Oxocyclopentyl)methyl]phenyl}propanoate (20)

Prepared by following GP using **20a** (30.4 mg, 0.1 mmol) as substrate. Purification by flash column chromatography (silica gel, PE:EtOAc 20:1); colorless oil; yield: 12.9 mg (39%); dr = 1:1:1.6.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 4.32 (ddt, *J* = 26.4, 20.2, 13.8 Hz, 2 H), 3.80 (q, *J* = 7.1 Hz, 1 H), 3.12 (dd, *J* = 13.9, 3.9 Hz, 1 H), 2.51 (dd, *J* = 13.8, 9.6 Hz, 1 H), 2.33 (dd, *J* = 17.3, 7.5 Hz, 2 H), 2.13–2.04 (m, 2 H), 2.02–1.89 (m, 1 H), 1.78–1.70 (m, 1 H), 1.66 (d, *J* = 21.1 Hz, 3 H), 1.54 (d, *J* = 7.1 Hz, 3 H), 1.57–1.49 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 220.28, 173.50 (d, *J* = 5.0 Hz), 139.45, 137.39, 129.41, 127.74, 116.20 (d, *J* = 32.4 Hz), 86.16 (dd, *J* = 184.8, 9.1 Hz), 66.15 (dd, *J* = 26.2, 2.3 Hz), 51.08, 44.96, 38.32, 35.31, 29.28, 22.37 (dd, *J* = 24.0, 15.7 Hz), 20.68, 18.22 (dd, *J* = 8.6, 2.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –147.81 to –162.94 (m).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{19}H_{23}FNO_3^+$: 332.1656; found: 332.1664.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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