Chemoselective Syntheses of Various Cyanofluoromethylene Compounds from Organic Bromides by Use of Sodium Triethylgermanate(IV) and Its Mechanistic Studies

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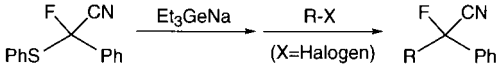
Abstract: The chemoselective syntheses of various cyanofluoromethylene compounds proceeded through the formation of the cyanofluoromethyl anion from 2-fluoro-2-phenyl-2-phenyl-thioacetonitrile by the use of sodium triethylgermanate(IV) (Et_3GeNa).

Key words: germanium reagents, fluorine derivatives, carbonitriles, mechanism

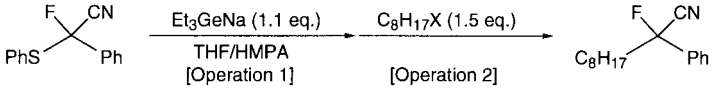
In recent years, the development of synthetic reactions of various fluorinated compounds has been important in organic synthesis, because these compounds have useful chemical and physical properties.[1] Particularly, the preparation of fluorinated compounds containing various functional groups is an attractive method owing to the potential utility of the fluorinated products as useful synthetic precursors. Among them, the synthesis of a cyanofluoromethylene compound is a challenging problem from the viewpoint of not only its role as a building block, but also its multifunctional carbon chemistry.[2] There are two strategies for the synthesis of cyanofluoromethylene compounds; the first is a stepwise introduction of cyano and fluoro groups,[3] and the second is the introduction of a cyanofluoromethylene unit to a substrate. The latter method is particularly suitable for the synthesis of the cyanofluoromethylene compound, because the target molecule can be formed more straightforwardly. However, investigation of the preparative method using direct cyanofluo-romethylation has been limited.[4] In this connection, we have already reported the germanate anion species promoted synthesis of a cyanofluoromethylene compound by use of 2-fluoro-2-phenyl-2-phenylthioacetonitrile as the cyanofluoromethylene source (Scheme 1).[5] This reaction was applied for the first and efficient syntheses of fluorinated homoallylic and homopropargylic cyanides.



Scheme 1

In continuation of our work, we introduce an effective and chemoselective transformation of organic bromides having various substituents such as chloro, ester units, and some protective groups to the desired fluorinated cyanides

Table 1 Cyanofluoromethylation of Organic Halide Under Various Reaction Conditions



Entry	Operation 1		Operation 2		Solvent	X	Yield[a] (%)
	Temp. (°C)	Time (h)	Temp. (°C)	Time (h)			
1	0	0.25	–80	0.5	THF	Br	78
2	–30	0.25	–80	0.5	THF	Br	97
3	–60	0.25	–80	0.5	THF	Br	97
4	–80	0.25	–80	0.5	THF	Br	86
5	–60	0.5	–80	0.5	THF	Br	97
6	–60	1.0	–80	0.5	THF	Br	97
7	–60	0.25	0	0.5	THF	Br	70
8	–60	0.25	–30	0.5	THF	Br	97
9	–60	0.25	–60	0.5	THF	Br	97
10	–60	0.25	–80	0.25	THF	Br	69
11	–60	0.25	–80	0.5	Et_2O	Br	96
12	–60	0.25	–80	0.5	hexane	Br	7.8
13	–60	0.25	–80	0.5	THF	Cl	NR

[a] Yield of isolated pure product.

by use of the foregoing method. This reaction proceeded smoothly to give the corresponding compound in excellent yield without decomposition of the substituent. We also report some mechanistic studies of the foregoing method.

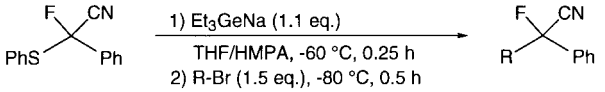
1-Halooctane was chosen as a model electrophile and Et_3GeNa promoted synthesis of a cyanofluoromethylene compound was examined under various conditions using 2-fluoro-2-phenyl-2-phenylthioacetonitrile (Table 1).

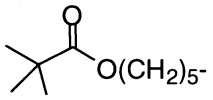
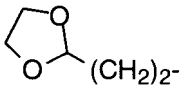
As expected, the treatment of 2-fluoro-2-phenyl-2-phenylthioacetonitrile with Et_3GeNa at 0 °C for 0.25 h (Operation 1) followed by the addition of 1-bromooctane at –80 °C for 0.5 h (Operation 2) afforded 2-fluoro-2-phenyldecanenitrile in 78% yield (entry 1). In this case, many unidentified byproducts were also obtained. The formation of these byproducts was suppressed by carrying out the Operation 1 at low temperature. The desired compound was given quantitatively when the first operation took place at –30 or –60 °C (entries 2 and 3). On the other hand, the starting fluorinated cyanide was treated at –80 °C and 1-bromooctane was added to give the target compound in moderate yield, because 10% of the starting material was recovered (entry 4). When Operation 1 was carried out over a prolonged period, the desired product was also obtained quantitatively (entries 5 and 6). These facts revealed that the active species of this reaction was formed effectively at –30 to –60 °C for 0.25 hours and this species was stable at the same reaction conditions. The reaction temperature and the period of Operation 2 are significant factors in this reaction. When Operation 2 took place at 0 °C, the desired compound was obtained in 70% yield, while at lower temperatures the corresponding cyanide was obtained quantitatively (entries 7 vs 3, 8 and 9). Moreover, when Operation 2 was carried out for 0.25 hours (–80 °C), the target cyanide and 1-fluoro-1-phenylacetonitrile were obtained in 69 and 28% yields, respectively (entry 10). The latter compound probably was generated by the quenching of an active species of this method. In this reaction, diethyl ether could be used as a solvent, but hexane was unfavorable (entries 11 and 12). Interestingly, 1-chlorooctane could not be transformed to the product at all and was almost recovered under the same conditions; nevertheless, allylic or propargylic chlorides were applicable as substrates (entry 13).[5] The results of entry 3 and 13 indicated that an organic bromide was more suitable for this reaction than an organic chloride and prompted us to try the chemoselective transformation of organic bromides having various functional groups to the desired cyanofluoromethylene compounds.

Several results of the transformation of organic bromides to fluorinated cyanides by use of 2-fluoro-2-phenyl-2-phenylthioacetonitrile/Et_3GeNa system are shown in Table 2.

When 1-bromo-3-chloropropane or 1-bromo-5-chloropentane was used as the substrate, the desired cyanofluoromethylene compounds were obtained in excellent yields without loss of the chloromethylene unit (entries 1 and 2).

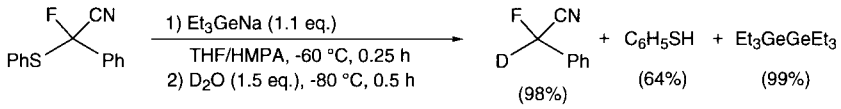
Table 2 Chemoselective Cyanofluoromethylation of Various Organic Bromides



Entry	R-	Yield[a] (%)
1	Cl-$(CH_2)_3$-	95
2	Cl-$(CH_2)_5$-	96
3	AcO-$(CH_2)_5$-	96
4	BzO-$(CH_2)_5$-	96
5		96
6	EtO_2C-$(CH_2)_5$-	98
7	MOMO-$(CH_2)_5$-	96
8	MEMO-$(CH_2)_5$-	96
9		96

[a] Yield of isolated pure product.

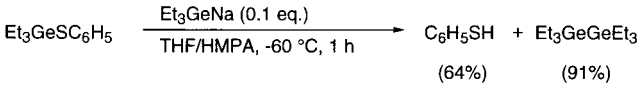
Some bromo esters were also employed as substrates of this reaction. When ω-acetoxy, ω-benzoyloxy, and ω-trimethylacetoxy bromides were applied to this reaction, the corresponding compounds were obtained perfectly without decomposition of their structures (entries 3, 4, and 5). Ethyl 6-bromohexanoate could be transformed to the fluorinated cyano ester quantitatively (entry 6). Moreover, some cyanofluoromethylene compounds which had protective groups on the hydroxy unit, such as a methoxymethyl (MOM) and 2-methoxyethoxymethyl (MEM) substituent, could be formed in excellent yields (entries 7 and 8). Furthermore, a five-membered cyclic acetal which is a known protective group of a carbonyl substituent was unaffected under these reaction conditions. The cyanofluoromethylene compound having the foregoing groups could be easily synthesized in excellent yields (entry 9). These results suggested that this reaction was favorable for the chemoselective transformation of organic bromides containing various substituents to the corresponding cyanofluoromethylene compounds. Fortunately, hexaethyldigermane ($Et_3GeGeEt_3$) was recovered quantitatively from the mixture. This compound could be reused for the formation of Et_3GeNa.[6] Generally, the organogermanium compound is too expensive to use in organic synthesis, but it can be employed as a useful synthetic reagent if it is recovered and reused.



Scheme 2

At the next stage, we tried to clarify the mechanism of this reaction. When the reaction of entry 3 (Table 1) was carried out in the presence of 2.1 equivalents of 1-bromooctane, the corresponding cyanofluoromethylene product, and octyl phenyl sulfide ($C_6H_5SC_8H_{17}$) and $Et_3GeGeEt_3$ were obtained in 97, 99, and 99% yields (based on 2-fluoro-2-phenyl-2-phenylthioacetonitrile), respectively. The same reaction was unaffected by 1-oxy-2,2,6,6-tetramethylpiperidine (TEMPO) which is well known as a radical scavenger, and the target compound was obtained in 95% yield. This fact suggested that the active intermediate of this reaction was not a radical species. On the other hand, treatment of 2-fluoro-2-phenyl-2-phenylthioacetonitrile with Et_3GeNa followed by D_2O (99.9%) trapping of the active intermediate afforded 98% of the desired deuteride, 64% of thiophenol,[7] and 99% (based on the starting cyanide) of $Et_3GeGeEt_3$ (Scheme 2).

Moreover, when phenyl triethylgermyl sulfide ($Et_3GeSC_6H_5$) was treated with a catalytic amount of Et_3GeNa, thiophenol (64%)[7] and $Et_3GeGeEt_3$ (91%, based on $Et_3GeSC_6H_5$ + Et_3GeNa) were obtained (Scheme 3).[8]



Scheme 3

Judging from all these results, the reaction mechanism was considered as follows. At first, 2-fluoro-2-phenyl-2-phenylthioacetonitrile was transformed to the corresponding α-cyano-α-fluoro carbanion and $Et_3GeSC_6H_5$ by Et_3GeNa. This fluorinated carbanion was stable at under –30 °C, but it was decomposed at 0 °C (Table 1, entries 2, 3, 8, and 9 vs 1 and 7). It was thought that this step progressed through one-electron transfer from a germanate anion to the starting sulfide or the nucleophilic attack of a germyl anion to the sulfur atom of a cyanide. It was clear that the driving force of this reaction was the thiophilicity of the germanium atom.[5,9] Thus, $Et_3GeSC_6H_5$ was formed easily by the thiophilic character of the germanium atom and α-cyano-α-fluoro carbanion was obtained effectively. In the second step, the former species (carbanion) reacted with an organic bromide to form the cyanofluoromethylene compound, and the latter compound was decomposed to thiophenol and $Et_3GeGeEt_3$ by a catalytic amount of a germanate anion. Furthermore, a phenyl sulfide was obtained from the reaction of thiophenol with an organic bromide.

In conclusion, we have reported a chemoselective cyanofluoromethylation of various organic bromides using Et_3GeNa. This reaction proceeded smoothly under mild conditions to give the desired compound in excellent yield. This method is very attractive not only in the area of organic synthesis, but also in the field of fluorine chemistry, because the active intermediate is an α-fluorinated carbanion which is difficult to form.[10] Further investigation is now in progress.

Mps are uncorrected. ^{1}H NMR Spectra were recorded at 400 MHz (Varian UNITY-INOVA-400). ^{13}C NMR Spectra were recorded at 100 MHz (Varian UNITY-INOVA-400). Chemical shifts were reported as δ values (ppm) downfield from TMS. ^{19}F NMR Spectra were recorded at 376 MHz (Varian UNITY-INOVA-400). Chemical shifts were reported as δ values (ppm) upfield from $CFCl_3$. IR Spectra were recorded with Shimadzu FTIR-4200. MS and HRMS were recorded with Jeol JMS DX-303. Et_3GeNa was prepared from $Et_3GeGeEt_3$ in HMPA according to the literature.[6] 2-Phenyl-2-phenylthioacetonitrile, 5-bromopentyl acetate, 5-bromopentyl benzoate and $Et_3GeSC_6H_5$ were synthesized according to the literature procedures.[11] Commercially available 1-fluoropyridinium trifluoromethanesulfonate, 5-bromopentan-1-ol, trimethylacetyl chloride, DMAP, chloroform, dimethoxymethane, P_2O_5, 2-methoxyethoxymethyl chloride, iPr_2NEt, 1-chlorooctane, 1-bromooctane, TEMPO, 3-bromo-1-chloropropane, 3-bromo-1-chloropentane, ethyl 6-bromohexanoate, 2-(2-bromoethyl)-1,3-dioxolane and D_2O (99.9%) were used without further treatment. Silica gel, Wakogel C-200 was obtained from Wako Pure Chemical Industries, Ltd. and Silica Gel 60, from Merck. Solvents were purified before use: Et_2O and THF were distilled from sodium benzophenone ketyl; hexane, HMPA, dichloroethane, benzene and CH_2Cl_2 were distilled from CaH_2. All reactions were carried out under argon. Reaction temperatures were bath temperature (MeOH/liq N_2). All reactions were monitored by TLC on 0.25 mm E. Merck silica gel plates (60F-254), where materials were detected by a UV lamp and applying the 5% ethanolic solution of phosphomolybdenic acid and heat.

2-Fluoro-2-phenyl-2-phenylthioacetonitrile

To a solution of 2-phenyl-2-phenylthioacetonitrile (6.0 g, 26.6 mmol) in dichloroethane (100 mL) was added 1-fluoropyridinium trifluoromethanesulfonate (11.8 g, 47.7 mmol). After stirring for 3.5 h at reflux temperature, the mixture was poured on to ice-water and was extracted with Et_2O. The dried, concentrated organic phase was passed through a short column of silica gel (Wakogel C-200) and eluted with Et_2O. Concentration of this eluate followed by crystallization in hexane afforded the product as white crystals; yield: 5.0 g (77%); mp 73–74 °C.

^{1}H NMR: δ = 7.69–7.76 (m, 4 H), 7.44–7.55 (m, 6 H).

^{13}C NMR: δ = 136.37 (s), 133.55 (d, $J_{C,F}$ = 23.4 Hz), 130.94 (d, $J_{C,F}$ = 15.4 Hz), 129.47 (s), 128.95 (s), 128.71 (d, $J_{C,F}$ = 1.5 Hz), 125.28 (d, $J_{C,F}$ = 2.3 Hz), 114.28 (d, $J_{C,F}$ = 43.7 Hz), 97.36 (d, $J_{C,F}$ = 227.5 Hz).

^{19}F NMR: δ = –118.37 (s).

IR (KBr): ν = 3070, 2235, 1572, 1390, 1457, 1219, 1026, 976, 864, 762, 691 cm^{-1}.

MS (70 eV): *m/z* (%) = 243 (M^+, 100), 224 (M^+ – F, 5), 217 (M^+ – CN, 5), 198 (M^+ – CN – F, 5), 166 (M^+ – Ph, 5), 134 (M^+ – SPh, 100), 115 (M^+ – F – SPh, 3), 109, (SPh, 100), 108 (M^+ – CN – SPh, 55), 77 (Ph, 32).

HRMS: *m/z* calcd for $C_{14}H_{10}FNS$: 243.0518; found: 243.0559.

5-Bromopentyl Trimethylacetate

To a solution of 5-bromopentan-1-ol (2.5 g, 15.0 mmol) in benzene (30 mL) were added trimethylacetyl chloride (1.9 g, 15.7 mmol), a catalytic amount of DMAP and pyridine (1.4 g, 17.7 mmol) at r.t. After stirring for 17 h, the mixture was poured on to ice-water and was extracted with Et_2O. The dried, concentrated organic phase was purified by column chromatography [silica gel (Silica Gel 60), hexane/Et_2O 10:1] to give the product as a clear oil; yield: 1.5 g (40%).

^1H NMR: δ = 4.07 (t, 2 H, *J* = 6.4 Hz), 3.42 (t, 2 H, *J* = 6.8 Hz), 1.90 (tt, 2 H, *J* = 7.1 and 6.8 Hz), 1.70–1.63 (m, 2 H), 1.56–1.49 (m, 2 H), 1.20 (s, 9 H).

^{13}C NMR: δ = 178.32 (s), 63.78 (s), 38.57 (s), 33.32 (s), 32.11 (s), 27.64 (s), 27.06 (s), 24.44 (s).

IR (neat): ν = 2967, 1728, 1284, 1153, 1457, 580 cm^{-1}.

MS (70 eV): *m/z* (%) = 252 (M^{+81}[Br], 28), 250 (M^{+79}[Br], 28), 171 (M^+ – Br, 5), 167 (M^{+81}[Br] – C_5H_9O, 1), 165 (M^{+79}[Br] – C_5H_9O, 1), 151 (M^{+81}[Br] – $C_5H_9O_2$, 100), 149 (M^{+79}[Br] – $C_5H_9O_2$, 100), 101, ($C_5H_9O_2$, 2), 85 (C_5H_9O, 100).

HRMS: *m/z* calcd for $C_{10}H_{19}{}^{81}BrO_2$: 252.0548; found: 252.0591 and calcd for $C_{10}H_{19}{}^{79}BrO_2$: 250.0568; found: 250.0567.

5-Bromopentyl Methoxymethyl Ether

To a solution of 5-bromopentan-1-ol (2.5 g, 15.0 mmol) in $CHCl_3$ (60 mL) were added dimethoxymethane (3.4 g, 44.7 mmol) and a catalytic amount of P_2O_5 at r.t. After stirring for 3 h, the mixture was poured on to ice-water and was extracted with Et_2O. The dried, concentrated organic phase was purified by column chromatography [silica gel (Silica Gel 60), hexane/Et_2O 7:1] to give the product as a clear oil; yield: 1.7 g (54%).

^1H NMR: δ = 4.62 (s, 2 H), 3.54 (t, 2 H, *J* = 6.2 Hz), 3.42 (t, 2 H, *J* = 6.8 Hz), 3.36 (s, 3 H), 1.90 (tt, 2 H, *J* = 7.1 and 6.8 Hz), 1.66–1.58 (m, 2 H), 1.57–1.49 (m, 2 H).

^{13}C NMR: δ = 96.26 (s), 67.27 (s), 55.00 (s), 33.53 (s), 32.43 (s), 28.76 (s), 24.81 (s).

IR (neat): ν = 2984, 1456, 1281, 1252, 1246, 1144, 1111, 1078, 1042, 939, 644, 565 cm^{-1}.

MS (70 eV): *m/z* (%) = 212 (M^{+81}[Br], 2), 210 (M^{+79}[Br], 2), 181 (M^{+81}[Br] – CH_3O, 10), 179 (M^{+79}[Br] – CH_3O, 11), 151 (M^{+81}[Br] – $C_2H_5O_2$, 100), 149 (M^{+79}[Br] – $C_2H_5O_2$, 100), 131 (M^+ – Br, 2).

HRMS: *m/z* calcd for $C_7H_{15}{}^{81}BrO_2$: 212.0235; found: 212.0280 and calcd for $C_{10}H_{19}{}^{79}BrO_2$: 210.0255; found: 210.0253.

5-Bromopentyl 2-Methoxyethoxymethyl Ether

To a solution of 5-bromopentan-1-ol (2.5 g, 15.0 mmol) in CH_2Cl_2 (70 mL) were added 2-methoxyethoxymethyl chloride (4.1 g, 32.9 mmol) and iPr_2NEt (4.5 g, 34.8 mmol) at r.t.. After stirring for 2 h, the mixture was poured on to ice-water and was extracted with Et_2O. The dried, concentrated organic phase was purified by column chromatography [silica gel (Silica Gel 60), hexane/Et_2O 3:1] to give the product as a clear oil; yield: 1.8 g (47%).

^1H NMR: δ = 4.72 (s, 2 H), 3.71–3.68 (m, 2 H), 3.58–3.56 (m, 2 H), 3.56 (t, 2 H, *J* = 6.2 Hz), 3.42 (t, 2 H, *J* = 6.8 Hz), 3.40 (s, 3 H), 1.89 (tt, 2 H, *J* = 7.3 and 6.8 Hz), 1.66–1.58 (m, 2 H), 1.57–1.47 (m, 2 H).

^{13}C NMR: δ = 95.24 (s), 71.59 (s), 67.24 (s), 66.50 (s), 58.80 (s), 33.46 (s), 32.33 (s), 28.63 (s), 24.71 (s).

IR (neat): ν = 2940, 1471, 1281, 1244, 1200, 1119, 1046, 1042, 936, 851, 642, 561 cm^{-1}.

MS (70 eV): *m/z* (%) = 256 (M^{+81}[Br], 1), 254 (M^{+79}[Br], 1), 225 (M^{+81}[Br] – CH_3O, 10), 223 (M^{+79}[Br] – CH_3O, 11), 181 (M^{+81}[Br] – $C_3H_7O_2$, 42), 179 (M^{+79}[Br] – $C_3H_7O_2$, 43), 151 (M^{+81}[Br] – $C_4H_9O_3$, 100), 149 (M^{+79}[Br] – $C_4H_9O_3$, 100), 105 ($C_4H_9O_3$, 100).

HRMS: *m/z* calcd for $C_9H_{19}{}^{81}BrO_3$: 256.0497; found: 256.0496 and calcd for $C_9H_{19}{}^{79}BrO_3$: 254.0518; found: 254.0526.

2-Fluoro-2-phenyldecanenitrile; Typical Procedure

To a solution of 2-fluoro-2-phenyl-2-phenylthioacetonitrile (37.7 mg, 0.155 mmol) in THF (2 mL) was slowly added 0.42 N Et_3GeNa in HMPA (0.4 mL) at –60 °C. After stirring for 0.25 h at –60 °C, the temperature was lowered to –80 °C, and 1-bromooctane (44.9 mg, 0.233 mmol) was added to the mixture. The mixture was stirred for 0.5 h at –80 °C and then was passed through a short column of silica gel (Wakogel C-200) and eluted with Et_2O. Concentration of this eluate followed by column chromatographic purification (Silica Gel 60, hexane/Et_2O 15:1) afforded the title compound; yield: 37.1 mg (97%). Moreover, 16.0 mg (46%) of octyl phenyl sulfide and 24.6 mg (99%, based on 2-fluoro-2-phenyl-2-phenylthioacetonitrile) of $Et_3GeGeEt_3$ were obtained as byproducts.

When this reaction was carried out on a ten-times scale, the desired compound was obtained in 97% yield (371 mg).

When this reaction was carried out using 2.1 equiv amount of 1-bromooctane (62.8 mg, 0.325 mmol), the corresponding compound, octyl phenyl sulfide and $Et_3GeGeEt_3$ were obtained in 97% (37.0 mg), 99% (34 mg), and 99% (24.6 mg, based on 2-fluoro-2-phenyl-2-phenylthioacetonitrile) yields, respectively.

When this reaction was carried out in the presence of TEMPO (24.2 mg, 0.155 mmol), the corresponding compound was obtained in 95% yield (36.5 mg).

^1H NMR: δ = 7.51–7.42 (m, 5 H), 2.27–2.07 (m, 2 H), 1.60–1.43 (m, 2 H), 1.35–1.43 (m, 10 H), 0.87 (t, 3 H, *J* = 6.8 Hz).

^{13}C NMR: δ = 136.34 (d, $J_{C,F}$ = 23.0 Hz), 129.78 (d, $J_{C,F}$ = 1.9 Hz), 128.86 (s), 125.59 (d, $J_{C,F}$ = 6.1 Hz), 117.38 (d, $J_{C,F}$ = 34.1 Hz), 92.06 (d, $J_{C,F}$ = 183.8 Hz), 41.68 (d, $J_{C,F}$ = 25.3 Hz), 31.73 (s), 29.17 (s), 29.05 (s), 28.98(s), 23.78 (d, $J_{C,F}$ = 3.5 Hz), 22.58 (s), 14.05 (s).

^{19}F NMR: δ = –146.94 (dd, $J_{F,H}$ = 25.2 and 16.6 Hz).

IR (neat): ν = 2957, 2250, 1495, 1466, 1379, 1334, 1225, 1098, 1001, 931, 764, 714 cm^{-1}.

MS (70 eV): *m/z* (%) = 247 (M^+, 8), 221 (M^+ – CN, 5), 135 (M^+ – C_8H_{16}, 100), 134 (M^+ – C_8H_{17}, 46), 113 (C_8H_{17}, 1), 77 (Ph, 13).

HRMS: *m/z* calcd for $C_{16}H_{22}FN$: 247.1736; found: 247.1784.

5-Chloro-2-fluoro-2-phenylpentanenitrile

This compound (clear oil) was synthesized in 95% yield (31.1 mg, Table 2, entry 1) from 1-bromo-3-chloropropane in a similar manner (column chromatographic purification: hexane/Et_2O 30:1) to that described in the Typical Procedure.

^1H NMR: δ = 7.53–7.45 (m, 5 H), 3.62–3.57 (m, 2 H), 2.45–2.29 (m, 2 H), 2.13–2.01 (m, 2 H).

^{13}C NMR: δ = 135.69 (d, $J_{C,F}$ = 22.6 Hz), 130.11 (d, $J_{C,F}$ = 1.5 Hz), 129.06 (s), 124.54 (d, $J_{C,F}$ = 6.1 Hz), 116.98 (d, $J_{C,F}$ = 34.1 Hz), 91.41 (d, $J_{C,F}$ = 184.5 Hz), 43.69 (s), 39.07 (d, $J_{C,F}$ = 25.3 Hz), 26.91 (d, $J_{C,F}$ = 3.1 Hz).

^{19}F NMR: δ = –148.08 (dd, $J_{F,H}$ = 25.2 and 16.1 Hz).

IR (neat): ν = 2946, 2240, 1495, 1451, 1317, 1292, 1234, 1069, 1001, 931, 856, 829, 760, 715, 654 cm^{-1}.

MS (70 eV): *m/z* (%) = 213 (M^{+37}[Cl], 33), 211 (M^{+35}[Cl], 100), 194 (M^{+37}[Cl] – F, 0.3), 192 (M^{+35}[Cl] – F, 1), 187 (M^{+37}[Cl] – CN, 1), 185 (M^{+35}[Cl] – F, 3), 176 (M^+ – Cl, 75), 157 (M^+ – Cl – F, 2), 150 (M^+ – Cl – CN, 2), 148 (M^+ – Cl – C_2H_4, 30), 136 (M^{+37}[Cl] – Ph, 66), 134 (M^{+35}[Cl] – Ph, 100), 117 (M^{+37}[Cl] – F – Ph, 6), 115 (M^{+35}[Cl] – F – Ph, 32), 110 (M^{+37}[Cl] – CN – Ph, 30), 108 (M^{+35}[Cl] – CN – Ph, 100), 77 (Ph, 100).

HRMS: *m/z* calcd for $C_{11}H_{11}{}^{37}ClFN$: 213.0534; found: 213.0491 and calcd for $C_{11}H_{11}{}^{35}ClFN$: 211.0563; found: 211.0576.

7-Chloro-2-fluoro-2-phenylheptanenitrile

This compound (clear oil) was synthesized in 96% yield (35.6 mg, Table 2, entry 2) from 1-bromo-5-chloropentane in a similar manner (column chromatographic purification: hexane/Et_2O 30:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.52–7.44 (m, 5 H), 3.52 (t, 2 H, *J* = 6.6 Hz), 2.27–2.10 (m, 2 H), 1.79 (tt, 2 H, *J* = 13.9 and 6.6 Hz), 1.66–1.43 (m, 4 H).

^{13}C NMR: δ = 136.10 (d, $J_{C,F}$ = 23.1 Hz), 129.91 (d, $J_{C,F}$ = 1.9 Hz), 128.95 (s), 124.54 (d, $J_{C,F}$ = 6.5 Hz), 117.23 (d, $J_{C,F}$ = 34.1 Hz), 91.85 (d, $J_{C,F}$ = 184.1 Hz), 44.61 (s), 41.52 (d, $J_{C,F}$ = 25.3 Hz), 32.12 (s), 26.24 (s), 23.20 (d, $J_{C,F}$ = 3.5 Hz).

^{19}F NMR: δ = –147.37 (dd, $J_{F,H}$ = 25.2 and 16.1 Hz).

IR (neat): ν = 3094, 2955, 2240, 1495, 1464, 1317, 1271, 1223, 1094, 1001, 952, 843, 764, 734, 698, 652 cm^{-1}.

MS (70 eV): *m/z* (%) = 241 (M^{+37}[Cl], 47), 239 (M^{+35}[Cl], 100), 222 (M^{+37}[Cl] – F, 0.3), 220 (M^{+35}[Cl] – F, 1), 215 (M^{+37}[Cl] – CN, 1), 213 (M^{+35}[Cl] – F, 4), 204 (M^+ – Cl, 13), 185 (M^+ – Cl – F, 1), 178 (M^+ – Cl – CN, 1), 164 (M^{+37}[Cl] – Ph, 1), 162 (M^{+35}[Cl] – Ph, 4), 159 (M^+ – Cl – CN, 1), 137 (M^{+37}[Cl] – CN – C_6H_6, 33), 135 (M^{+35}[Cl] – CN – C_6H_6, 100), 118 (M^{+37}[Cl] – CN – F – C_6H_6, 2), 116 (M^{+35}[Cl] – CN – F – C_6H_6, 25), 77 (Ph, 60).

HRMS: *m/z* calcd for $C_{13}H_{15}{}^{37}ClFN$: 241.0847; found: 241.0802 and calcd for $C_{13}H_{15}{}^{35}ClFN$: 239.0876; found: 239.0837.

7-Acetoxy-2-fluoro-2-phenylheptanenitrile

This compound (clear oil) was synthesized in 96% yield (39.1 mg Table 2, entry 3) from 5-bromopentyl acetate in a similar manner (column chromatographic purification: hexane/Et_2O 6:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.51–7.43 (m, 5 H), 4.04 (t, 2 H, *J* = 6.6 Hz), 2.30–2.09 (m, 2 H), 2.04 (s, 3 H), 2.03–1.49 (m, 4 H), 1.46–1.38 (m, 2 H).

^{13}C NMR: δ = 171.13 (s), 136.13 (d, $J_{C,F}$ = 23.0 Hz), 129.88 (d, $J_{C,F}$ = 1.9 Hz), 128.93 (s), 124.54 (d, $J_{C,F}$ = 6.1 Hz), 117.25 (d, $J_{C,F}$ = 34.1 Hz), 91.86 (d, $J_{C,F}$ = 183.8 Hz), 64.13 (s), 41.54 (d, $J_{C,F}$ = 24.9 Hz), 28.25 (s), 25.48 (s), 23.54 (d, $J_{C,F}$ = 3.1 Hz), 20.94 (s).

^{19}F NMR: δ = –147.31 (dd, $J_{F,H}$ = 24.1 and 14.9 Hz).

IR (neat): ν = 2953, 2250, 1738, 1464, 1367, 1244, 1037, 766, 698 cm^{-1}.

MS (30 eV): *m/z* (%) = 263 (M^+, 1), 244 (M^+ – F, 2), 220 (M^+ – C_2H_3O, 1), 204 (M^+ – $C_2H_3O_2$, 5), 201 (M^+ – F – C_2H_3O, 20), 192 (M^+ – CN – C_2H_3O, 1), 185, (M^+ – F – $C_2H_3O_2$, 2), 178 (M^+ – CN – $C_2H_3O_2$, 13), 177 (M^+ – CN – $C_2H_4O_2$, 100), 158 (M^+ – CN – F – $C_2H_4O_2$, 1), 157 (M^+ – CN – F – $C_2H_3O_2$, 10), 129 ($C_7H_{13}O_2$, 78).

HRMS: *m/z* calcd for $C_{15}H_{18}FNO_2$: 263.1322; found: 263.1345.

7-Benzoyloxy-2-fluoro-2-phenylheptanenitrile

This compound (clear oil) was synthesized in 96% yield (48.4 mg, Table 2, entry 4) from 5-bromopentyl benzoate in a similar manner (column chromatographic purification: hexane/Et_2O 5:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 8.05–8.02 (m, 2 H), 7.58–7.37 (m, 8 H), 4.31 (t, 2 H, *J* = 6.6 Hz), 2.28–2.12 (m, 2 H), 1.79 (tt, 2 H, *J* = 14.5 and 6.6 Hz), 1.70–1.50 (m, 4 H).

^{13}C NMR: δ = 166.52 (s), 136.10 (d, $J_{C,F}$ = 22.6 Hz), 132.88 (s), 130.26 (s), 129.87 (d, $J_{C,F}$ = 1.9 Hz), 129.50 (s), 128.92 (s), 128.33 (s), 124.53 (d, $J_{C,F}$ = 6.1 Hz), 117.26 (d, $J_{C,F}$ = 34.1 Hz), 91.86 (d, $J_{C,F}$ = 184.1 Hz), 64.61 (s), 41.57 (d, $J_{C,F}$ = 24.9 Hz), 28.44 (s), 25.63 (s), 23.60 (d, $J_{C,F}$ = 3.5 Hz).

^{19}F NMR: δ = –147.31 (dd, $J_{F,H}$ = 24.1 and 14.9 Hz).

IR (neat): ν = 2953, 2250, 1719, 1603, 1464, 1387, 1316, 1275, 1115, 1071, 1026, 763, 714 cm^{-1}.

MS (30 eV): *m/z* (%) = 325 (M^+, 1), 306 (M^+ – F, 1), 204 (M^+ – $C_7H_5O_2$, 2), 203 (M^+ – $C_7H_6O_2$, 15), 178 (M^+ – F – $C_7H_5O_2$, 5), 177 (M^+ – F – $C_7H_6O_2$, 45), 123 (M^+ – CN – F – $C_9H_{10}O_2$, 46), 105 (C_7H_5O, 100), 77 (Ph, 3).

HRMS: *m/z* calcd for $C_{20}H_{20}FNO_2$: 325.1478; found: 325.1470.

2-Fluoro-2-phenyl-7-(trimethylacetoxy)heptanenitrile

This compound (clear oil) was synthesized in 92% yield (43.6 mg, Table 2, entry 5) from 5-bromopentyl trimethylacetate in a similar manner (column chromatographic purification: hexane/Et_2O 6:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.51–7.44 (m, 5 H), 4.03 (t, 2 H, *J* = 6.6 Hz), 2.23–2.09 (m, 2 H), 1.68–1.53 (m, 4 H), 1.46–1.34 (m, 2 H), 1.18 (s, 9 H).

^{13}C NMR: δ = 178.52 (s), 136.12 (d, $J_{C,F}$ = 22.6 Hz), 129.86 (d, $J_{C,F}$ = 1.5 Hz), 128.91 (s), 124.53 (d, $J_{C,F}$ = 6.1 Hz), 117.24 (d, $J_{C,F}$ = 34.1 Hz), 91.85 (d, $J_{C,F}$ = 184.1 Hz), 63.97 (s), 41.58 (d, $J_{C,F}$ = 24.9 Hz), 38.69 (s), 28.31 (s), 27.15 (s), 25.52 (s), 23.55 (d, $J_{C,F}$ = 3.5 Hz).

^{19}F NMR: δ = –147.33 (dd, $J_{F,H}$ = 24.1 and 14.9 Hz).

IR (neat): ν = 2940, 2240, 1726, 1480, 1453, 1398, 1365, 1284, 1159, 1034, 1001, 937, 765, 698 cm^{-1}.

MS (30 eV): *m/z* (%) = 305 (M^+, 4), 286 (M^+ – F, 4), 204 (M^+ – $C_5H_9O_2$, 69), 178 (M^+ – CN – $C_5H_9O_2$, 14), 177 (M^+ – CN – $C_5H_{10}O_2$, 100), 158 (M^+ – CN – F – $C_5H_{10}O_2$, 100), 85 ($C_5H_9O_2$, 100).

HRMS: *m/z* calcd for $C_{18}H_{24}FNO_2$: 305.1791; found: 305.1776.

Ethyl 7-Cyano-7-fluoro-7-phenylheptanoate

This compound (clear oil) was synthesized in 98% yield (42.0 mg, Table 2, entry 6) from ethyl 6-bromohexanoate in a similar manner (column chromatographic purification: hexane/Et_2O 6:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.51–7.44 (m, 5 H), 4.12 (q, 2 H, *J* = 7.1 Hz), 2.28 (t, 2 H, *J* = 7.3 Hz), 2.27–2.12 (m, 2 H), 1.67–1.46 (m, 4 H), 1.43–1.37 (m, 2 H), 1.25 (t, 3 H, *J* = 7.1 Hz).

^{13}C NMR: δ = 173.42 (s), 136.16 (d, $J_{C,F}$ = 22.6 Hz), 129.85 (d, $J_{C,F}$ = 1.5 Hz), 128.91 (s), 124.55 (d, $J_{C,F}$ = 6.1 Hz), 117.27 (d, $J_{C,F}$ = 34.1 Hz), 91.90 (d, $J_{C,F}$ = 183.8 Hz), 60.27 (s), 41.46 (d, $J_{C,F}$ = 25.3 Hz), 33.98 (s), 28.42 (s), 24.49(s), 23.50 (d, $J_{C,F}$ = 3.5 Hz), 14.21 (s).

^{19}F NMR: δ = –147.29 (dd, $J_{F,H}$ = 24.1 and 16.1 Hz).

IR (neat): ν = 2940, 2250, 1732, 1464, 1375, 1259, 1183, 1115, 1030, 920, 766, 698 cm^{-1}.

MS (30 eV): *m/z* (%) = 277 (M^+, 1), 258 (M^+ – F, 10), 249 (M^+ – CN, 3), 248 (M^+ – C_2H_5, 22), 232 (M^+ – OC_2H_5, 5), 230 (M^+ – CN – F, 3), 214 (M^+ – F – C_2H_5O, 14), 204 (M^+ – $C_3H_5O_2$, 6), 185, (M^+ – F – $C_3H_5O_2$, 8), 177 (M^+ – CN – $C_3H_4O_2$, 100), 176 (M^+ – CN – $C_3H_5O_2$, 13), 171 (M^+ – F – $C_4H_7O_2$, 4), 143 (M^+ – CN – F – $C_4H_7O_2$, 17), 73 ($C_3H_5O_2$, 2).

HRMS: *m/z* calcd for $C_{16}H_{20}FNO_2$: 277.1478; found: 277.1432.

2-Fluoro-7-(methoxymethoxy)-2-phenylheptanenitrile
This compound (clear oil) was synthesized in 96% yield (39.5 mg, Table 2, entry 7) from 5-bromopentyl methoxymethyl ether in a similar manner (column chromatographic purification: hexane/Et_2O 3:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.51–7.42 (m, 5 H), 4.60 (s, 2 H), 3.50 (t, 2 H, *J* = 6.4 Hz), 3.34 (s, 3 H), 2.30–2.08 (m, 2 H), 1.69–1.40 (m, 6 H).

^{13}C NMR: δ = 136.21 (d, $J_{C,F}$ = 23.0 Hz), 129.84 (d, $J_{C,F}$ = 1.5 Hz), 128.90 (s), 124.58 (d, $J_{C,F}$ = 5.6 Hz), 117.31 (d, $J_{C,F}$ = 34.1 Hz), 96.37 (s), 91.93 (d, $J_{C,F}$ = 183.8 Hz), 67.30 (s), 55.12 (s), 41.63 (d, $J_{C,F}$ = 25.3 Hz), 29.33 (s), 25.73 (s), 23.61 (d, $J_{C,F}$ = 3.5 Hz).

^{19}F NMR: δ = –147.09 (dd, $J_{F,H}$ = 25.1 and 14.9 Hz).

IR (neat): ν = 2957, 2250, 1495, 1466, 1379, 1334, 1225, 1098, 1001, 931, 764, 714 cm^{-1}.

MS (30 eV): *m/z* (%) = 265 (M^+, 5), 234 ($M^+ – OCH_3$, 2), 233 ($M^+ – CH_4O$, 5), 220 ($M^+ – CN – F$, 1), 204 ($M^+ – C_2H_5O_2$, 21), 190 ($M^+ – C_3H_7O_2$, 100), 171 ($M^+ – F – C_3H_7O_2$, 6), 169 ($M^+ – F – Ph$, 1), 164 ($M^+ – CN – C_3H_7O_2$, 1), 162 ($M^+ – CN – Ph$, 1), 145 ($M^+ – CN – F – C_3H_7O_2$, 3), 143 ($M^+ – CN – F – Ph$, 13), 129 ($M^+ – CN – F – Ph – CH_2$, 89), 113 (C_8H_{17}, 1), 77 (Ph, 3), 75 ($C_3H_7O_2$, 25), 61 ($C_2H_5O_2$, 12).

HRMS: *m/z* calcd for $C_{15}H_{20}FNO_2$: 265.1478; found: 265.1519.

2-Fluoro-7-(2-methoxyethoxymethoxy)-2-phenylheptanenitrile
This compound (clear oil) was synthesized in 96% yield (46.0 mg, Table 2, entry 8) from 5-bromopentyl 2-methoxyethoxymethyl ether in a similar manner (column chromatographic purification: hexane/Et_2O 3:2) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.51–7.44 (m, 5 H), 4.69 (s, 2 H), 3.68–3.66 (m, 2 H), 3.56–3.54 (m, 2 H), 3.53 (t, 2 H, *J* = 6.4 Hz), 3.39 (s, 3 H), 2.26–2.09 (m, 2 H), 1.66–1.41 (m, 6 H).

^{13}C NMR: δ = 136.18 (d, $J_{C,F}$ = 23.0 Hz), 129.82 (d, $J_{C,F}$ = 1.5 Hz), 128.88 (s), 124.55 (d, $J_{C,F}$ = 6.5 Hz), 117.28 (d, $J_{C,F}$ = 34.1 Hz), 95.42 (s), 91.91 (d, $J_{C,F}$ = 183.8 Hz), 71.75 (s), 67.41 (s), 66.69 (s), 58.99 (s), 41.59 (d, $J_{C,F}$ = 25.3 Hz), 29.27 (s), 25.69 (s), 23.60 (d, $J_{C,F}$ = 3.5 Hz).

^{19}F NMR: δ = –147.09 (dd, $J_{F,H}$ = 24.4 and 16.0 Hz).

IR (neat): ν = 2936, 2240, 1452, 1366, 1242, 1171, 1115, 1053, 934, 766, 698 cm^{-1}.

MS (30 eV): *m/z* (%) = 309 (M^+, 2), 290 ($M^+ – F$, 1), 289 ($M^+ – HF$, 3), 234 ($M^+ – C_3H_7O_2$, 10), 233 ($M^+ – C_3H_8O_2$, 3), 232 ($M^+ – Ph$, 10), 214 ($M^+ – F – C_3H_8O_2$, 29), 185 ($M^+ – F – C_4H_9O_3$, 30), 184 ($M^+ – F – C_4H_{10}O_3$, 100), 159 ($M^+ – CN – F – C_4H_9O_3$, 1), 158 ($M^+ – CN – F – C_4H_{10}O_3$, 7), 105 ($C_4H_9O_3$, 20), 89 ($C_4H_9O_2$, 45).

HRMS: *m/z* calcd for $C_{17}H_{24}FNO_3$: 309.1740; found: 309.1727.

2-(3-Cyano-3-fluoro-3-phenylpropyl)-1,3-dioxolane
This compound (clear oil) was synthesized in 96% yield (35.0 mg, Table 2, entry 9) from 2-(2-bromoethyl)-1,3-dioxolane in a similar manner (column chromatographic purification: hexane/Et_2O 4:1) to that described in the Typical Procedure.

^{1}H NMR: δ = 7.52–7.43 (m, 5 H), 4.94 (t, 1 H, *J* = 4.2 Hz), 3.97–3.91 (m, 2 H), 3.90–3.84 (m, 2 H), 2.45–2.17 (m, 2 H), 1.99–1.86 (m, 2 H).

^{13}C NMR: δ = 135.90 (d, $J_{C,F}$ = 22.6 Hz), 129.93 (d, $J_{C,F}$ = 1.5 Hz), 128.95 (s), 124.60 (d, $J_{C,F}$ = 6.1 Hz), 117.10 (d, $J_{C,F}$ = 34.1 Hz), 102.70 (s), 91.55 (d, $J_{C,F}$ = 184.5 Hz), 76.68 (s), 65.06 (d, $J_{C,F}$ = 1.9 Hz), 35.52 (d, $J_{C,F}$ = 25.7 Hz) 28.10 (d, $J_{C,F}$ = 2.7 Hz)

^{19}F NMR: δ = –148.22 (dd, $J_{F,H}$ = 24.1 and 17.2 Hz).

IR (neat): ν = 3545, 2973, 2250, 1736, 1668, 1495, 1412, 1217, 1143, 1032, 976, 947, 883, 763, 698 cm^{-1}.

MS (70 eV): *m/z* (%) = 235 (M^+, 1), 234 ($M^+ – H$, 3), 215 ($M^+ – HF$, 2), 157 ($M^+ – C_6H_6$, 18), 130 ($M^+ – HCN – C6H6$, 5), 129 ($M^+ – H – HCN – C_6H_6$, 36), 77 (Ph, 3), 73 ($C_3H_5O_2$, 100).

HRMS: *m/z* calcd for $C_{13}H_{14}FNO_2$: 235.1009; found: 235.0993.

Trapping Experiment of an Active Intermediate by Use of D_2O (Scheme 2)
This experiment was carried out by use of D_2O in a similar manner (column chromatographic purification: hexane/Et_2O 30:1) to that described in the Typical Procedure. 2-Deutero-2-fluoro-2-phenylacetonitrile, thiophenol and $Et_3GeGeEt_3$ were obtained in 98% (21.1 mg), 64% (11 mg), and 99% (24.6 mg, based on 2-fluoro-2-phenyl-2-phenylthioacetonitrile) yields, respectively.

2-Deutero-2-fluoro-2-phenylacetonitrile
^{1}H NMR: δ = 7.57–7.54 (m, 5 H).

^{13}C NMR: δ = 131.22 (d, $J_{C,F}$ = 3.1 Hz), 129.34 (s), 129.32 (s), 127.51 (d, $J_{C,F}$ = 4.2 Hz), 115.21 (d, $J_{C,F}$ = 33.8 Hz), 79.88 (dt, $J_{C,D}$ = 24.6 Hz, $J_{C,F}$ = 180.7 Hz).

^{19}F NMR: δ = –168.53 (t, $J_{F,D}$ = 6.9 Hz).

IR (neat): ν = 3069, 2260, 1497, 1455, 1250, 1092, 1071, 939, 858, 760, 696, 637 cm^{-1}.

MS (70 eV): *m/z* (%) = 136 (M^+, 100), 117 ($M^+ – F$, 45), 110 ($M^+ – CN$, 100), 91 ($M^+ – CN – F$, 88), 77 (Ph, 34).

HRMS: *m/z* calcd for C_8H_5DFN: 136.0547; found: 136.0529.

Reaction of $Et_3GeSC_6H_5$ with a Catalytic Amount of Et_3GeNa (Scheme 3)
To a solution of $Et_3GeSC_6H_5$ (41.7 mg, 0.155 mmol) in THF (2 mL)/HMPA (0.36 mL) was slowly added a solution of Et_3GeNa in HMPA (0.037 mL, 0.43 N) at –60 °C. The mixture was stirred for 1 h at –60 °C and then was passed through a short column of silica gel (Wakogel C-200), and eluted with Et_2O. Concentration of this eluate followed by column chromatographic purification (Silica Gel 60, hexane) afforded 24.8 mg (91%, based on $Et_3GeSC_6H_5$ + Et_3GeNa) of $Et_3GeGeEt_3$. Moreover, 11.0 mg (64%) of thiophenol was obtained.

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