JOC*Note*

Novel Synthesis of 7-Fluoro-8-(trifluoromethyl)-1*H*-1,6-naphthyridin-4-one Derivatives: Intermolecular Cyclization of an *N*-Silyl-1-azaallyl Anion with Perfluoroalkene and Subsequent Intramolecular Skeletal Transformation of the Resulting Pentasubstituted Pyridines

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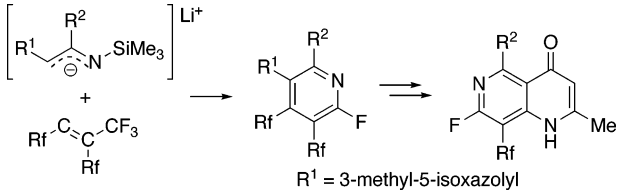
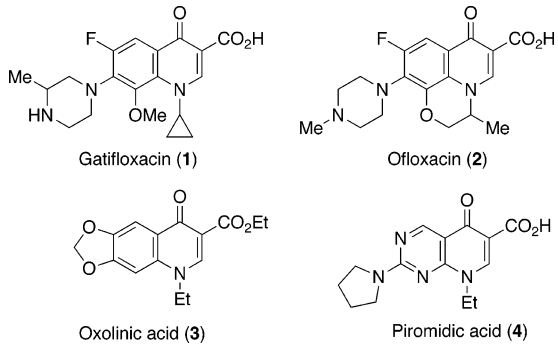


In this study, fluorine-containing pentasubstituted pyridine derivatives **9a**−**m** were prepared regioselectively in good yields by the intermolecular cyclization of a variety of *N*-silyl-1-azaallylic anion intermediates **7**, which were generated from a functionalized silane **5** and an aromatic/aliphatic nitrile **6** with perfluoroalkene **8**. Also, 7-fluoro-8-(trifluoromethyl)-1*H*-1,6-naphthyridin-4-one derivatives **11a**−**k** were synthesized in excellent yields by the subsequent base-promoted intramolecular skeletal transformation of the resulting pyridine derivatives **10a**−**k**.

A facile and practical synthesis of quinolone (1,4-dihydroquinolin-4-one) and its analogues has attracted considerable interest in the fields of pharmaceutical, medicinal, and organic chemistry, since most of those basic skeletons exhibit potent antimicrobial activity.[1,2] As shown in Scheme 1, the compounds of a new quinolone or a quinolone family, such as gatifloxacin (**1**), ofloxacin (**2**), oxolinic acid (**3**), and piromidic acid (**4**), have been especially successful as drugs both commercially and clinically.[3] Among them, it is well-known that new quinolone compounds, which contain a fluorine group on the 6-position, such as gatifloxacin and ofloxacin, showed potent biological

SCHEME 1. Fluoroquinolone Family



activity. Hence, a number of approaches for the general and efficient introduction of either a perfluoroalkyl (Rf) group or a fluoro group onto the ring of the quinolone skeleton have been explored,[1] and development of new Rf group-containing quinolone derivatives showing a more potent pharmaceutical activity is thus highly desirable.

In this context, we previously reported that the *N*-silyl-1-azaallyl anion,[4] which was prepared from an α-functionalized silane and an aromatic nitrile in the presence of a base,[5] reacts smoothly with the α,*β*-unsaturated carbonyl compounds to produce a variety of polysubstitued pyridine derivatives (paths a and b in Scheme 2).[6] During the ongoing investigation of the synthesis of the nitrogen-containing heterocycles, the cyclization of the azaallyl anion intermediate with a perfluoroalkene, producing a pyridine derivative containing a perfluoroalkyl group, was demonstrated.[7] Moreover, it was found that a reductive ring-opening reaction of the isoxazolyl group on the pyridine ring produced the amino group and a subsequent intramolecular ring-closing reaction between the resulting tethered amino group and the fluorocarbon group led to the production of a 1,6-naphthyridinone framework.[8] Hence, it was determined that development of the consecutive combined procedure of a former *intermolecular* cyclization procedure with the latter *intramolecular* skeletal transformation could be possible and the fluorine-containing 1,6-naphthyridin-4-one framework, which constitutes the key structure of biologically active agents as well as the fluoroquinolones as shown above,[3,9] would be easily and efficiently obtained (path c in Scheme 2).

Thus, in this paper we report a detailed investigation to extend the scope of the intermolecular cyclization of a variety of

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(1) Mitscher, L. A. *Chem. Rev.* **2005**, *105*, 559 and references cited therein.
(2) Joule, J. A.; Mills, K. *Heterocyclic Chemistry*, 4th ed.; Blackwell Science Ltd.: Oxford, U.K., 2000; pp 121−150.
(3) (a) Chen, Y.-L.; Chen, I.-L.; Wang, T.-C.; Han, C.-H.; Tzeng, C.-C. *Eur. J. Med. Chem.* **2005**, *40*, 928. (b) Butenschön, I.; Möller, K.; Hänsel, W. *J. Med. Chem.* **2001**, *44*, 1249. (c) Campbell, W. E.; Davidowitz, B.; Jackson, G. E. *Phytochemistry* **1990**, *29*, 1303.
(4) For a recent review on 1-azaallyl anions, see: Mangelinckx, S.; Giubellina, N.; De Kimpe, N. *Chem. Rev.* **2004**, *104*, 2353 and references cited therein.
(5) (a) Konakahara, T.; Kurosaki, Y. *J. Chem. Res., Synop.* **1989**, 130. (b) Konakahara, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1241.
(6) (a) Konakahara, T.; Sugama, N.; Yamada, A.; Kakehi, A.; Sakai, N. *Heterocycles* **2001**, *55*, 313. (b) Konakahara, T.; Ogawa, R.; Tamura, S.; Kakehi, A.; Sakai, N. *Heterocycles* **2001**, *55*, 1737. (c) Hojahmat, M.; Konakahara, T.; Tamura, S. *Heterocycles* **2000**, *53*, 629. (d) Konakahara, T.; Hojahmat, M.; Tamura, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2803. (e) Konakahara, T.; Mojahmat, M.; Sujimoto, K. *Heterocycles* **1997**, *45*, 271. (f) Konakahara, T.; Sugama, N.; Sato, K. *Heterocycles* **1992**, *33*, 157.
(7) Konakahara, T.; Satoh, M.; Haruyama, T.; Sato, K. *Nippon Kagaku Kaishi* **1990**, 466.
(8) Sakai, N.; Aoki, Y.; Sasada, T.; Konakahara, T. *Org. Lett.* **2005**, *7*, 4705.

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SCHEME 2

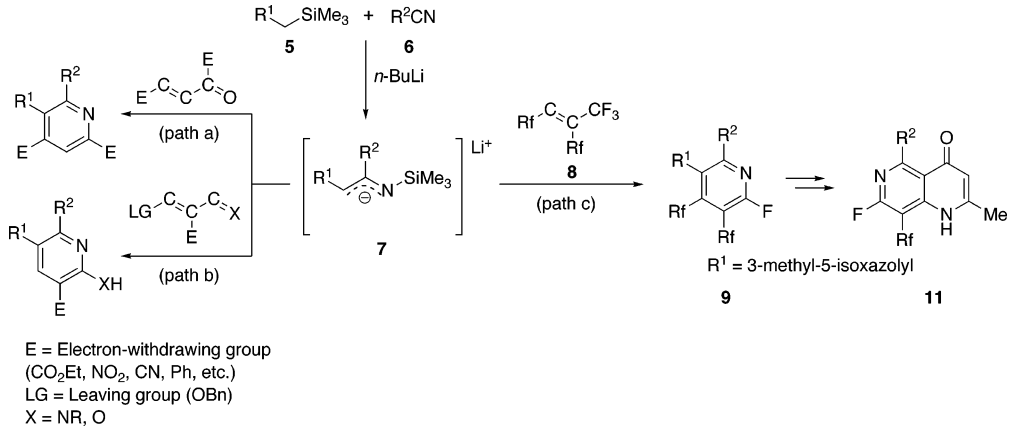
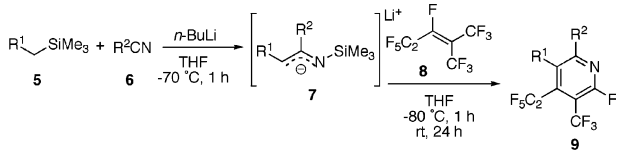
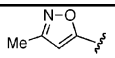


TABLE 1. Cyclization of 1-Azaallylic Anion 7 with Fluoroalkene 8 Leading to the Preparation of Fluoro-Containing Pyridine Derivatives



entry	silane **5** (R^1)		nitrile **6** (R^2)		yield (%)[a]	
1		**5a**	Ph	**6a**	82	**9a**
2			4-Me-C_6H_4	**6b**	55	**9b**
3			4-MeO-C_6H_4	**6c**	70	**9c**
4			4-Me_2N-C_6H_4	**6d**	56	**9d**
5			4-Cl-C_6H_4	**6e**	51	**9e**
6			4-CF_3-C_6H_4	**6f**	65	**9f**
7			2-Py	**6g**	67	**9g**
8			4-Py	**6h**	55	**9h**
9				**6i**	58	**9i**
10				**6j**	67	**9j**
11			Et	**6k**	16	**9k**
12		**5b**	Ph	**6l**	32	**9l**
13			4-Cl-C_6H_4	**6m**	43	**9m**

[a] Isolated yields.

1-azaallyl anion intermediates with the perfluoroalkene. A further consecutive intramolecular cyclization leading to the preparation of the perfluoroalkyl group containing 1,6-naphthyridine derivatives is also disclosed.

On the basis of previous work, we initially performed the synthesis of a pyridine derivative having a fluorocarbon group by a three-component coupling reaction of a functional silane, **5**, an aryl/alkyl nitrile, **6**, and perfluoro-2-methyl-2-pentene (**8**). The results are summarized in Table 1. For example, the reaction of silane **5a** having an isoxazolyl group with benzonitrile (**6a**) was carried out in THF at −70 °C in the presence of a base, in situ generating the active species 1-azaallyl anion **7a**, followed by the reaction with additional fluorine-substituted alkene **8** to afford fluorine-containing pentasubstituted pyridine derivative **9a** as a sole product in 82% yield. The structure of **9a** was determined by the spectroscopic data and combustion analysis data, and the locations of each substituted group were unambiguously determined by the X-ray crystallographic analysis of the crystalline **9k**.[10] The cyclization reaction was found to proceed along with preservation of a high regioselectivity. When conducted with 2-cyanopyridine **(6g)**, methoxyacetonitrile (**6i**), and 2-cyano-1,3-dioxolane (**6j**), the reaction also proceeded cleanly to produce the corresponding pyridine derivatives **9** in moderate to good yields. On the other hand, the use of propionitrile (**6k**) provided a poor yield of the desired product **9k**, presumably due to an extraction of an α-proton by the strong base 1-azaallyl anion **7**, leading to the formation of byproducts. To extend the scope of the present method, the cyclization with silane **5b**, having an amide group instead of the isoxazolyl group, was also performed under the above conditions. The corresponding derivatives **9l**,**m** were obtained in moderate yields.

As stated above, generally, it is known that the isoxazolyl group acts as a masked β-aminoenone group.[11] Thus, the reductive ring-opening reaction of the group on the resulting pyridines prepared was carried out (Table 2). When the use of PtO_2 under a H_2 atmosphere was initially examined at room temperature, the desired reductive reaction clearly proceeded to produce the corresponding pyridine derivatives **10** tethered with the aminoenone group in good to excellent yields (entries 1−5). On the other hand, in the hope of decreasing the cost of the catalyst and simplifying the experimental procedure, other catalytic systems were sought for the reduction of the isoxazole ring. As a result, referring to the literature,[12] it was found that the refluxing acetonitrile aqueous solution in the presence of 50 mol % $Mo(CO)_6$ could be applied to the products, affording the desired pyridine involving the β-aminoenone group in good yield. The results of reductive ring-opening reaction of com-

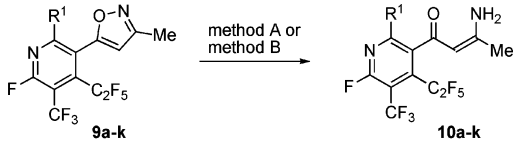
(9) (a) Falardeau, G.; Chan, L.; Stefanac, T.; May, S.; Jin, H.; Lavallée, J.-F. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2769. (b) Chan, L.; Jin, H.; Stefanac, T.; Lavallée, J.-F.; Falardeau, G.; Wang, W.; Bédard, J.; May, S.; Yuen, L. *J. Med. Chem.* **1999**, *42*, 3023. (c) Hawes, E. M.; Gorecki, D. K. J. *J. Med. Chem.* **1973**, *16*, 849.

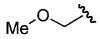
(10) Crystal data for **9k**: $C_{14}H_9F_9N_2O$, M = 392.23, monoclinic, a = 10.563(4) Å, b = 9.543(4) Å, c = 15.602(6) Å, U = 1504.2(10) Å^3, T = 273 K, space group $P2(1)/n$, Z = 4, μ(Mo Kα) = 0.710 mm^{-1}, 8879 reflections measured, 3401 independent reflections (R_{int} = 0.0631), R_1 = 0.1017, wR_2 = 0.2729. Also see the details in the Supporting Information.

(11) (a) Calle, M.; Calvo, L. A.; Gonzalez-Ortega, A.; Gonzalez-Nogal, A. M. *Tetrahedron* **2006**, *62*, 611. (b) Singh, V.; Saxena, R.; Batra, S. *J. Org. Chem.* **2005**, *70*, 353. (c) Churykau, D. H.; Zinovich, V. G.; Kulinkovich, O. G. *Synlett* **2004**, 1949.

(12) Li, C.-S.; Lacasse, E. *Tetrahedron Lett.* **2002**, *43*, 3565.

TABLE 2. Reductive Ring-Opening Reaction of the Isoxazolyl Group on the Pyridine Ring



entry	R^1	method [a]	yield (%) [b]	
1	Ph	A	**10a**	99
2	4-Me-C_6H_4	A	**10b**	91
3	4-MeO-C_6H_4	A	**10c**	95
4	4-Me_2N-C_6H_4	A	**10d**	93
5	4-Cl-C_6H_4	A	**10e**	80
6	4-CF_3-C_6H_4	A	**10f**	83
7	2-Py	B	**10g**	78
8	4-Py	A	**10h**	72
9		B	**10i**	81
10		B	**10j**	78
11	Et	B	**10k**	71

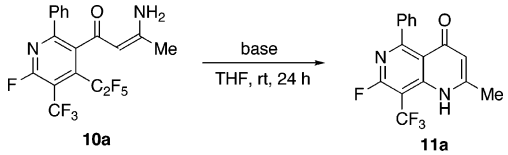
[a] Method A: PtO_2/H_2 (1 atm), EtOH, rt, 12 h. Method B: $Mo(CO)_6$, $MeCN/H_2O$, reflux, 2 h. [b] Isolated yields.

pounds **9a**−**k** are summarized in Table 2. Without exception, all cases show good to excellent results. However, other reductive catalysts, such as Raney Ni/H_2 and EtMgBr/Ti(O*i*-Pr)$_4$, are not suitable for the present product, resulting in a decrease of the product yield and the formation of side products.

Next, to illustrate a skeletal transformation from a pyridine derivative to a 1,6-naphthyridin-4-one derivative, the intramolecular cyclization of a series of pyridine **10** by the formed amino group was studied in the presence of various bases in THF at room temperature (Scheme 3). For example, when the cyclization reaction was conducted in 3 N NaOH aqueous solution, the corresponding 1,6-napthyridine derivative **11a** was obtained in nearly quantitative yield. Similarly, an equimolar amount of Triton B also produced **11a** in high yield (88%), and a series of organic bases, such as DBU (81%), sodium amide (85%), and *n*-butyllithium (88%) functioned well. The use of *N*,*N*-diisopropylethylamine, however, did not undergo the cyclization to recover the starting material, even refluxing of the mixture. Thus, it was found that sodium hydroxide is an effective and economical base for the desired cyclization.

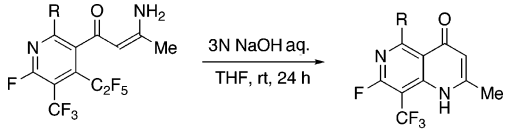
The structure of **11a** was determined by analysis of the spectroscopic data as well as combustion data. For example, IR absorption of **11a** at 1622 cm^{-1} showed the presence of a carbonyl group. In ^{19}F NMR, two peaks at −65.2 and −56.1 ppm were also assigned to the corresponding fluorine and trifluoromethyl group, respectively. HRMS indicated the molecular formula of the product **11a** to be $C_{16}H_{10}F_4N_2O$. Moreover, the crystalline product **11k** was subjected to an X-ray crystallographic analysis, and the structure of 1,6-naphthyridine was unambiguously established.[13] In all other cases involving not only a phenyl group but also a heterocycle and an aliphatic group, a desired intramolecular cyclization was cleanly com-

SCHEME 3. Examination of a Base



3N NaOH aq.	99%
Triton B	88%
DBU	81%
$NaNH_2$	85%
n-BuLi	88%
i-Pr_2EtN	—

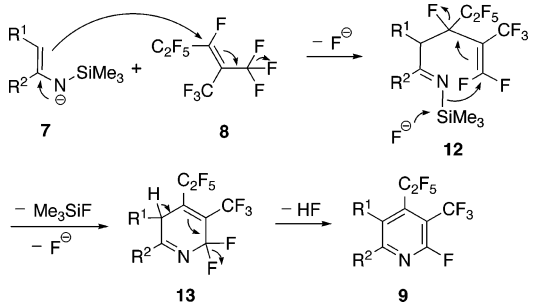
SCHEME 4. Intramolecular Cyclization Leading to the 1,6-Naphthyridin-4-one Framework[a,b]



11a: R = Ph	99%	**11g**: R = 2-Py	81%
11b:R = 4-Me-C_6H_4	83%	**11h**: R = 4-Py	87%
11c: R = 4-MeO-C_6H_4	81%	**11i**: R = MOM[a]	88%
11d: R = 4-Me_2N-C_6H_4	80%	**11j**: R = DIOX[b]	71%
11e: R = *p*-Cl-C_6H_4	84%	**11k**: R = Et	73%
11f: R = *p*-CF_3-C_6H_4	85%		

[a] MOM = methoxymethyl. [b]DIOX = 1,3-dioxolan-2-yl.

SCHEME 5

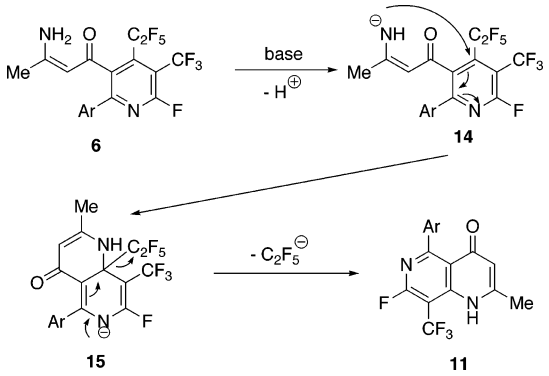


pleted within 24 h to produce the corresponding fluorine-containing 1,6-naphthyridines **11a**−**k** in good to excellent yields (Scheme 4).

A plausible reaction path for the intermolecular cyclization of the 1-azaallylic anion with fluoroalkene **8** is shown in Scheme 5. First, the carbon anion of the 1-azaallyl anion regioselectively would attack the electron-deficient carbon on the alkene to produce the corresponding intermediate **12** with elimination of a fluoride anion. Subsequently, the formed fluoride anion would promote the intramolecular cyclization to give the pyridine derivative **13**. Finally, the aromatization of the pyridine **13**, along with elimination of HF, would promote the driving force to completion, leading to the production of the corresponding final product **9**. On the other hand, in the case of the intramolecular cyclization by the tethered amino group (Scheme 6), the amide anion, which was generated by the treatment of a base such as NaOH, would attack intramolecularly at the 4-position carbon

(13) Crystal data for **11k**: $C_{12}H_{10}F_4N_2O$, $M = 274.22$, monoclinic, $a = 5.107(14)$ Å, $b = 17.390(5)$ Å, $c = 12.980(3)$ Å, $U = 1132.5(5)$ Å^3, $T = 273$ K, space group $P2(1)/c$, $Z = 4$, μ(Mo Kα) = 0.149 mm^{-1}, 6710 reflections measured, 2600 independent reflections ($R_{int} = 0.0390$), $R_1 = 0.058$, $wR_2 = 0.152$. Also see the details in the Supporting Information.

SCHEME 6



on the pyridine ring to produce a bicyclic intermediate, **15**. Successively, the similar aromatization of the formed dihydropyridine derivative **15** would occur to produce the corresponding 1,6-naphythyridin-4-one derivative **11**.

A simple and convenient method was developed for the synthesis of fluorocarbon-containing pyridine derivatives via the intermolecular cyclization of a variety of 1-azaallylic anion intermediates with the perfluoroalkene. Also developed was the facile reductive ring-opening reaction of the isoxazole ring. Moreover, it was found that the β-aminoenone group formed by the reduction undergoes a consecutive intramolecular cyclization with the perfluoroethyl group on the pyridine ring, providing a practical preparation for the perfluoroalkyl group-containing 1,6-naphthyridin-4-one derivatives. This combined procedure appeared to be an efficient and practical method to produce a new type of fluorine-containing quinolone framework. Further investigations toward the biological evaluation of fluoro-containing pyridine derivatives synthesized are currently in progress.

Experimental Section

General Procedure for the Synthesis of Perfluoro-Substituted Pyridine 9. To a THF solution (50 mL) of 3-methyl-5-[(trimethylsilyl)methyl]isoxazole (**5a**; 2.30 g, 13.6 mmol) was added *n*-BuLi (15.9 mmol, in hexane) at −70 °C, and the reaction mixture was stirred at the same temperature. After 1 h, benzonitrile (**6a**; 1.64 g, 15.9 mmol) was added to the solution via a syringe, and the solution was stirred for 1 h at −70 °C and then 2 h at room temperature. Perfluoro-2-methyl-2-pentene (**8**; 12.2 g, 40.8 mmol) was gradually added to the solution at −70 °C, and the mixture was stirred at the same temperature and then for 24 h at room temperature. To quench the reaction, a saturated aqueous solution of NH_4Cl (50 mL) was added to the mixture. The organic layer was extracted with Et_2O, and the separated organic layer was dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane−AcOEt) to give perfluoro-substituted pyridine **9a** (4.89 g, 82%): colorless needles (hexane); mp 89.4−89.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 5.84 (s, 1H), 7.30−7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 108.1, 110.9−117.8 (m), 113.5 (tqd, J_{CF} = 3.5, 35, and 260 Hz), 118.4 (qt, J_{CF} = 35 and 260 Hz), 120.8 (dd, J_{CF} = 3.5 and 10 Hz), 121.0 (qd, J_{CF} = 10 and 260 Hz), 128.3, 128.8, 130.4, 135.9, 142.9 (t, J_{CF} = 35 Hz), 159.8, 160.6 (d, J_{CF} = 240 Hz), 162.7, 164.3 (d, J_{CF} = 14 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ 56.9 (m, 4F), 36.4 (s, 3F), 15.1 (m, 2F); MS (FAB) *m*/*z* 441 (M + H, 100). Anal. Calcd for $C_{18}H_8N_2F_9O$: C, 49.10; H, 2.06; N, 6.36. Found: C, 49.10; H, 2.10; N, 6.40.

General Procedure for the Reductive Ring-Opening. Method A. To an EtOH solution (30 mL) of pyridine **9a** (1.01 g, 2.30 mmol) was added PtO_2 (42 mg, 0.19 mmol). The mixture was hydrogenated at room temperature under atmospheric pressure. After 12 h, the catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane−AcOEt) to give pyridine **10a** (1.00 g, 99%) as yellow crystals.

Method B. To a CH_3CN (61.4 mL) and H_2O (6.8 mL) solution of pyridine **9a** (1.50 g, 3.41 mmol) was added $Mo(CO)_6$ (0.45 g, 1.7 mmol). The mixture was heated under reflux. After 2 h, the volatile compounds were removed under reduced pressure. The residue was filtered by a Celite pad, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane−AcOEt) to give pyridine **10a** (1.29 g, 86%): colorless needles (AcOEt−hexane); mp 120.4−121.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (s, 3H), 4.71 (s, 1H), 5.18 (br s, 1H), 7.24−7.41 (m, 3H), 7.59−7.61 (m, 2H), 9.62 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 98.5, 109.8−110.7 (m), 114.5 (tqd, J_{CF} = 3.5, 35, and 260 Hz), 118.8 (qt, J_{CF} = 35 and 260 Hz), 121.4 (qd, J_{CF} = 6.5 and 260 Hz), 128.1, 129.3, 130.1, 135.2 (dd, J_{CF} = 3.5 and 6.5 Hz), 137.0, 140.3 (t, J_{CF} = 35 Hz), 158.9 (d, J_{CF} = 260 Hz), 160.2 (d, J_{CF} = 14 Hz), 163.2, 187.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −94.5 (m, 2F), −75.1 (s, 3F), −60.6 (m, 1F), −55.7 (s, 3F); MS (FAB) *m*/*z* 443 (M + H, 100). Anal. Calcd for $C_{18}H_{11}N_2F_9O$: C, 48.88; H, 2.51; N, 6.33. Found: C, 49.14; H, 2.25; N, 6.42.

General Procedure for the Synthesis of 1,6-Naphthyridin-4(1*H*)-one. A solution of pyridine **10a** (345 mg, 0.782 mmol) in THF (10 mL) was added to 3 N NaOH(aq) (0.800 mL, 2.35 mmol) at room temperature. The reaction mixture was stirred for 24 h at the same temperature. The reaction mixture was then quenched and neutralized by a 1 N HCl aqueous solution. Then $CHCl_3$ (20 mL) and brine (20 mL) were added to the reaction mixture, and the organic layer was extracted with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (AcOEt) to give 1,6-naphthyridin-4(1*H*)-one (**11a**; 249 mg, 99%): colorless solids (AcOEt−hexane); mp 174.5−175.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.10 (s, 1H), 7.37−7.48 (m, 5H), 8.42 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 95.0−95.5 (m), 114.4 116.7 (d, J_{CF} = 3.5 Hz), 123.0 (qd, J_{CF} = 6.0 and 270 Hz), 127.7, 128.7, 129.5, 138.9, 146.9 (d, J_{CF} = 3.5 Hz), 147.6, 159.2 (d, J_{CF} = 260 Hz), 166.1 (d, J_{CF} = 14 Hz), 176.6; ^{19}F NMR (470 MHz, acetone-d_6) δ −65.2 (m, 1F), −56.1 (m, 3F); MS (FAB) *m*/*z* 323 (M + H, 100). Anal. Calcd for $C_{16}H_{10}N_2F_4O$: C, 59.63; H, 3.13; N, 8.69. Found: C, 59.45; H, 3.11; N, 8.54.

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Supporting Information Available: Detailed procedures and spectroscopic data for novel compounds in Tables 1 and 2, ORTEP diagrams of **9k** and **11k**, X-ray data for **9k** and **11k**, and ^{1}H NMR of novel compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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