

Fluoroalkylation of aromatics: An intramolecular radical cyclization of 4-chloro-1,1,2,2,3,3,4,4-octafluorobutylbenzenes

Hai-Ping Cao, Ji-Chang Xiao, Qing-Yun Chen*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Received 12 April 2006; received in revised form 11 May 2006; accepted 15 May 2006
Available online 22 May 2006

Abstract

In the presence of sodium dithionite and DMSO, the intramolecular radical cyclization of 4-chloro-1,1,2,2,3,3,4,4-octafluorobutylbenzenes is achieved to give the corresponding cyclic compounds in moderate to good yields.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Intramolecular cyclization; Fluoroalkylation; Sulfinatodehalogenation; Free radicals

1. Introduction

Radical cyclization has become a powerful method for the construction of five- or six-membered rings via C–C bond forming process and it actually serves as one of the most reliable tools in organic synthesis during the past 40 years [1]. A systematic study of the cyclization of fluoroalkyl radicals by Dolbier and co-workers demonstrates that per- or partially fluorinated radicals are much more reactive than their hydrocarbon counterparts, which is largely attributed to the high electrophilicity of the fluorinated radicals [2]. Most of these studies focus on the intramolecular fluoroalkyl radical additions to double bonds. Nevertheless, intramolecular fluoroalkyl radical substitution on the aromatic ring has received limited attention.

On the other hand, sulfinatodehalogenation method discovered by Huang et al. [3] and modified by us [4] has become a convenient, widely used radical initiation system for perfluoroalkyl halides. For instance, initiated by sodium dithionite in DMSO, per- or polyfluoroalkyl halides (R_FX , $X = Cl, Br, I$) could be used as fluoroalkylation agents not only for the addition reaction to alkenes and alkynes, but also for substitutions on aromatic compounds [3]. Recently, we found that β -(perfluoroalkyl)tetraarylporphyrin radicals, generated from the reaction

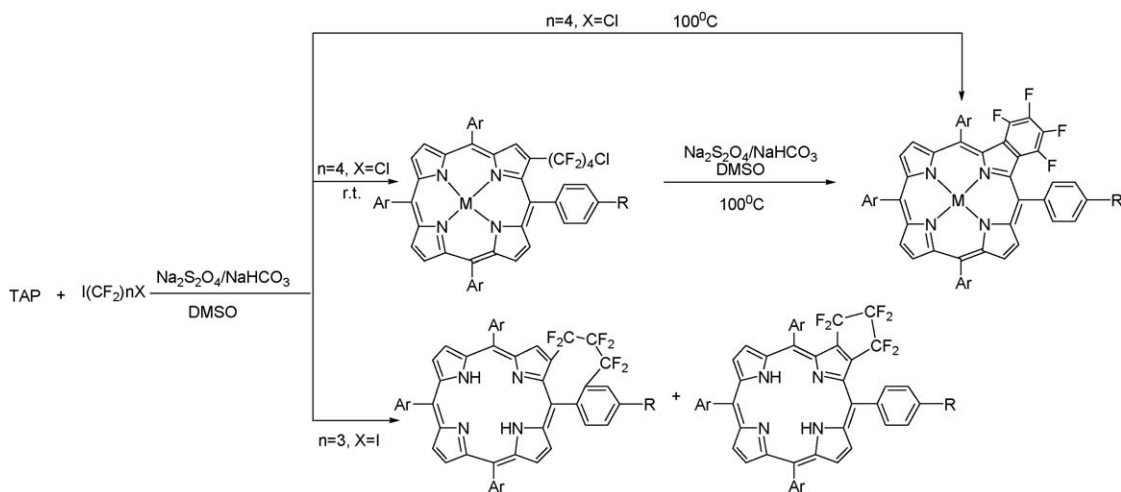
of $I(CF_2)_nX$ ($n = 2-5$; $X = Cl, I$) with tetraarylporphyrins (TAP) under sulfinatodehalogenation conditions, underwent an unexpected intramolecular cyclization at the *ortho* position of a neighboring phenyl ring as well as an adjacent pyrrolic unit (Scheme 1) [5]. Five-, six- or seven-membered fused porphyrins could be also formed, depending on the chain length of the fluoroalkyl group. These results prompted us to examine the intramolecular cyclization of ordinary perfluoroalkylbenzenes.

2. Results and discussion

1-Chloro-4-iodo-octafluorobutane **2** was chosen as the fluoroalkylation reagent in the hope of forming a fused six-membered ring. Because C–Cl bond and C–I bond in **2** could be both activated using sulfinatodehalogenation system at different temperature [5a], we attempted to perform the fluoroalkylation of aromatics and subsequent intramolecular radical cyclization in one pot. A mixture of 1,4-diaminobenzene **1a** and 1-chloro-4-iodo-octafluorobutane **2** was stirred in DMSO at room temperature in the presence of $Na_2S_2O_4$ till the complete conversion of **1a** (monitored by TLC) (Scheme 2). Then, heating the reaction mixture at 100 °C did give the cyclization product **4a**. Unfortunately, the yield was not satisfactory, only 20%. Therefore, we separated the fluoroalkylated benzene intermediate **3a** first, which then underwent six-membered ring cyclization in the presence of $Na_2S_2O_4$, leading indeed to the formation of **4a** in 85% yield. Owing to the lower yield of the

* Corresponding author. Fax: +86 21 64166128.

E-mail address: chenqy@mail.sioc.ac.cn (Q.-Y. Chen).



Scheme 1. Cyclization of porphyrin.

one pot procedure, we carried the reactions in two steps. Firstly, we synthesized **3**.

Fluoroalkylation of 1-methyl-indole **1b** gave a mixture of 2- and 3-fluoroalkylated product (Table 1, entry 2), which could not be completely separated by normal column chromatography because of their very similar polarities. As for the fluoroalkylation of pyrrole, 2-fluoroalkylated pyrrole **3c** was not isolated either. Because **3c** easily hydrolyzes and readily polymerizes under the reaction condition (Table 1, entry 3) [6]. When **1d–f** were used as substrates, the fluoroalkylation proceeded smoothly and **3d–f** were obtained in good yields (Table 1, entries 4–6).

In the case of biphenyl, its direct fluoroalkylation using sulfinatodehalogenation method might give various isomers. To avoid complications, we synthesized **3g–l** from the copper-catalyzed cross-coupling reactions of these *p*-iodo-biphenyl **1g–l** and 1-chloro-4-iodo-octafluorobutane **2** (Table 2) [7].

With the fluoroalkylated aromatics **3** in hand, we then studied their intramolecular radical cyclizations. The results are shown in Table 3. In the case of **3b**, a mixture of 2- and 3-fluoroalkylated indole, the cyclization formed a sole product **4b** (Table 3, entry 2). As for 2-fluoroalkylated pyrrole **3c**, the one

pot procedure led to rather low yield of **4c** (Table 3, entry 3), which might be the result of the lability of **3c** [6]. In the case of **3d–e**, the cyclized products were formed. To our surprise, only hydrogenated product **4d** and defluorinated **4e** and **4f** were obtained (Table 3, entries 4–6). The intramolecular cyclization of **3g–l** proceeded smoothly under sulfinatodehalogenation conditions. The cyclic products **4g–l** were obtained in high yields as sole products with complete conversion of **3g–l**. In the case of compound **3l** (Table 3, entry 12), only hydrogenated product **4l** was formed.

The structure of the products **4a–l** were all confirmed by ^1H and ^{19}F NMR, IR, MS and elemental analyses.

Based on the previous reports [5], it is reasonable to suggest that this cyclization reaction may be also involved in a single electron-transfer mechanism in both steps. The aryl tetrafluorobutyl radical generated from **3** underwent an intramolecular attack at the *ortho* position of the fluoroalkyl group to afford the cyclic product **4**, as is usual for free radical aromatic substitution [8]. However, hydrogenation and defluorination of perfluoroalkyl halides sometimes happened in this initiation system, yet their formation mechanisms are not fully understood [5a,9]. Besides we also prepared fluoroalkylated

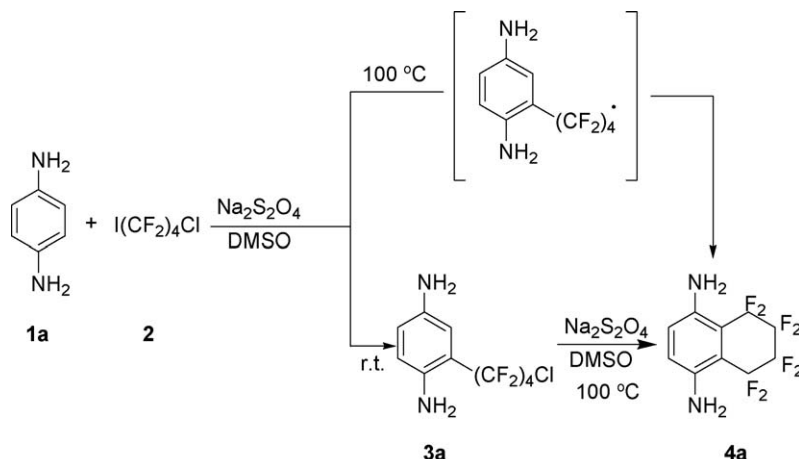
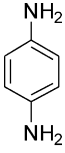
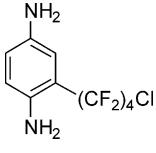
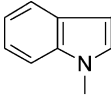
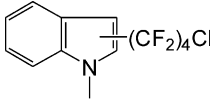

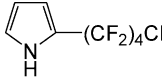
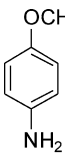
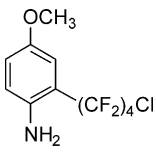
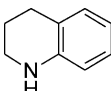
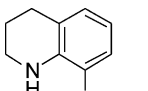
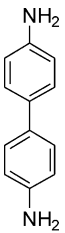
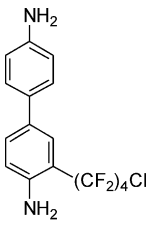
Scheme 2. Fluoroalkylation of **1a** and cyclization of **3a**.

Table 1

Synthesis of fluoroalkylated aromatic compound **3** by $\text{Na}_2\text{S}_2\text{O}_4$ $\text{Ar}-\text{H}_{1\text{a}-\text{f}} + \text{ClC}_4\text{F}_8\text{I} \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O}]{\text{Na}_2\text{S}_2\text{O}_4/\text{NaHCO}_3} \text{Ar}-\text{C}_4\text{F}_8\text{Cl}_{3\text{a}-\text{f}}$

Entry	Compound 1	<i>T</i> (°C)	<i>t</i> (h)	Product 3	Yield (%)
1	 1a	20	3	 3a	47
2	 1b	20	2	 3b	^a
3	 1c	10	0.5	 3c	^a
4	 1d	20	2	 3d	40
5	 1e	20	3	 3e	66
6	 1f	20	2	 3f	50

^a Not isolated.

Table 2

Synthesis of fluoroalkylated aromatic compound **3** induced by copper powder $\text{Ar}-\text{I} + \text{ClC}_4\text{F}_8\text{I} \xrightarrow[\text{DMSO}]{\text{Cu}} \text{Ar}-\text{C}_4\text{F}_8\text{Cl}$

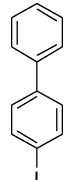
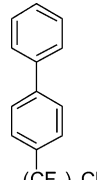
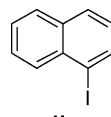
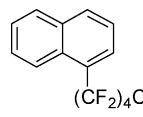
Entry	Compound 1	<i>T</i> (°C)	<i>t</i> (h)	Product 3	Yield (%)
1	 1g	100	12	 3g	56
2	 1h	100	12	 3h	57

Table 2 (Continued)

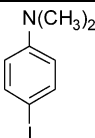
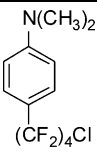
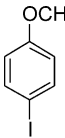
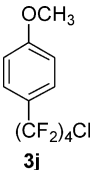
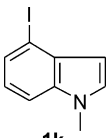
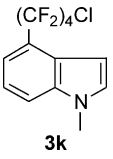
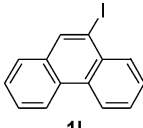
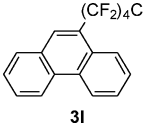
Entry	Compound 1	T (°C)	t (h)	Product 3	Yield (%)
3	 1i	100	10	 3i	69
4	 1j	100	10	 3j	80
5	 1k	80	11	 3k	50
6	 1l	80	11	 3l	53

Table 3

Cyclization of fluoroalkylated aromatic compound 3 by $\text{Na}_2\text{S}_2\text{O}_4$ $\text{Ar}-\text{C}_4\text{F}_8\text{Cl}$ $\xrightarrow[\text{DMSO}]{\text{Na}_2\text{S}_2\text{O}_4}$ Product 4

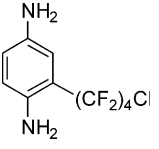
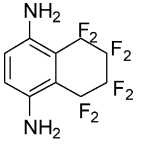
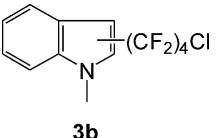
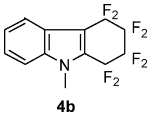
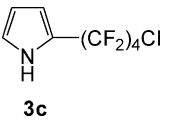
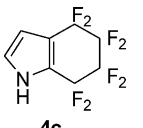
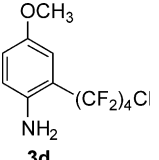
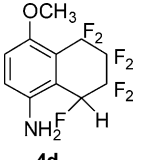
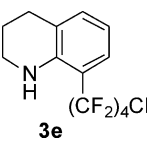
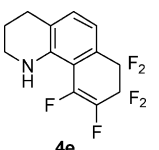
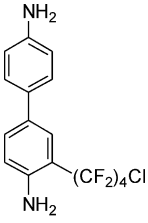
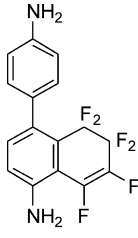
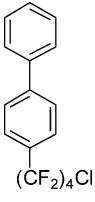
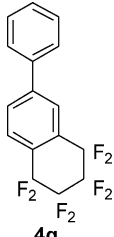
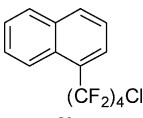
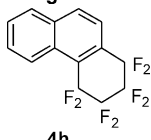
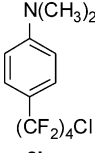
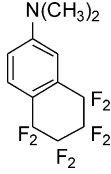
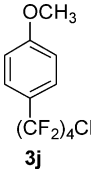
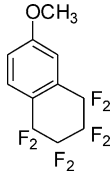
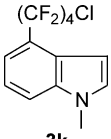
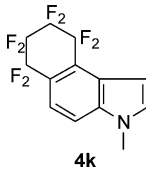
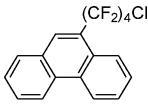
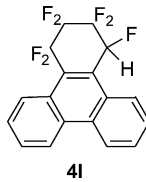
Entry	Compound 3	T (°C)	t (min)	Product 4	Yield (%)
1	 3a	100	15	 4a	85
2	 3b	100	15	 4b	40
3	 3c	100	15	 4c	10
4	 3d	100	20	 4d	40
5	 3e	100	15	 4e	52

Table 3 (Continued)

Entry	Compound 3	T (°C)	t (min)	Product 4	Yield (%)
6	 3f	100	18	 4f	83
7	 3g	100	15	 4g	76
8	 3h	100	15	 4h	62
9	 3i	100	20	 4i	50
10	 3j	100	20	 4j	65
11	 3k	100	18	 4k	72
12	 3l	100	15	 4l	68

aromatics such as $\text{Ar}(\text{CF}_2)_3\text{I}$, $\text{Ar}(\text{CF}_2)_6\text{Cl}$ by the reactions of $\text{I}(\text{CF}_2)_3\text{I}$ and $\text{I}(\text{CF}_2)_6\text{Cl}$ with aromatics, respectively and attempted to perform the subsequent intramolecular cyclization. Unfortunately, these attempts only led to the formation of hydrogenated products [$\text{Ar}(\text{CF}_2)_n\text{H}$, $n = 3, 6$] or sulfonates [$\text{Ar}(\text{CF}_2)_n\text{SO}_2\text{Na}$, $n = 3, 6$]. No desired five- or seven-membered fused compounds were obtained. This might be

largely due to the difference of intramolecular cyclization between fluorinated porphyrin radicals and aromatic ones.

3. Conclusion

In summary, we described a new intramolecular radical cyclization of chloro-octafluorobutyl benzenes under modified

sulfinatodehalogenation conditions. Further studies on other intramolecular fluoroalkyl radical substitutions are underway in our laboratory.

4. Experimental

4.1. General

^1H NMR and ^{19}F NMR spectra were recorded at 300 and 282 MHz. Chemical shifts were reported in parts per million relative to TMS as an internal standard for ^1H NMR and to CFCl_3 as an external standard (positive for up field shifts) for ^{19}F NMR. The solvent for NMR measurement was CDCl_3 (unless otherwise noted). DMSO were distilled from CaH_2 . The other chemicals used were obtained commercially.

4.2. Preparation of 4-chloro-1,1,2,2,3,3,4,4-octafluoroaromatic compounds **3a–f** from aromatics

A mixture of 4-chloro-octafluorobutyliodide (1.81 g, 5 mmol), 1,4-diamino-benzene (0.54 g, 5 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (1.31 g, 7.5 mmol), NaHCO_3 (0.63 g, 7.5 mmol) and DMSO (25 mL) was stirred at room temperature for 3 h under nitrogen. The mixture was poured into ice water (30 mL). The aqueous layer was extracted with ether (3×30 mL). The combined extracts were washed with water (3×20 mL) and dried over Na_2SO_4 . After removing ether, the residue was subjected to column chromatography on silica gel to give **3a** as a brown solid.

3a: brown solid. IR (KBr): 3239, 1490, 1309, 1219, 1195, 1171, 1011, 913 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 6.72$ (m, 2H), 6.60 (dd, $J = 0.6, 8.4$ Hz, 1H), 3.57 (br, 4H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.25$ (t, $J = 14.4$ Hz, 2F), 109.07 (t, $J = 14.5$ Hz, 2F), 120.26 (m, 2F), 121.57 (m, 2F). MS (EI, 70 eV): m/z (%) = 344 (18), 342 (58) $[M]^+$. Anal. Calcd. for $\text{C}_{10}\text{H}_7\text{F}_8\text{ClN}_2$: C, 35.06; H, 2.06; N, 8.18. Found: C, 35.41; H, 2.07; N, 8.17.

3d: brown oil. IR (film): 1509, 1188, 1134, 1045, 747 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 6.94$ (m, 1H), 6.87 (d, $J = 2.9$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 1H), 3.87 (br, 5H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.34$ (m, 2F), 109.18 (m, 2F), 120.30 (m, 2F), 122.58 (m, 2F). MS (EI, 70 eV): m/z (%) = 357 (9) $[M]^+$, 69 (66). Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{F}_8\text{ClNO}$: C, 36.94; H, 2.25; N, 3.92. Found: C, 37.02; H, 2.31; N, 3.69.

3e: yellow oil. IR (film): 3059, 1606, 1513, 1189, 1138, 1081 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.12$ (d, $J = 8.4$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.58 (t, $J = 7.5$ Hz, 1H), 4.75 (s, 1H), 3.34 (t, $J = 5.6$ Hz, 2H), 2.79 (t, $J = 6.5$ Hz, 2H), 1.90 (m, 2H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.20$ (t, $J = 13.0$ Hz, 2F), 107.9 (t, $J = 13.7$ Hz, 2F), 120.23 (m, 2F), 121.52 (t, $J = 10.9$ Hz, 2F). MS (EI, 70 eV): m/z (%) = 369 (36), 367 (98) $[M]^+$. Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{F}_8\text{ClN}$: C, 42.47; H, 2.74; N, 3.81. Found: C, 42.86; H, 2.93; N, 3.80.

3f: brown solid. IR (KBr): 1633, 1501, 1187, 1127, 761 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.46$ (d, $J = 7.2$ Hz, 2H), 7.32 (m, 2H), 6.72 (m, 3H), 4.19 (br, 2H), 3.62 (br, 2H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.20$ (m, 2F),

108.87 (m, 2F), 120.13 (m, 2F), 121.44 (m, 2F). MS (ESI): $m/z = 419$ $[M + \text{H}]^+$. Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{F}_8\text{ClN}_2$: C, 45.90; H, 2.65; N, 6.69. Found: C, 46.01; H, 3.03; N, 6.62.

4.3. Preparation of 4-chloro-1,1,2,2,3,3,4,4-octafluoroaromatic compounds **3g–l** [8] from iodoaromatics

A mixture of 4-chloro-octafluorobutyliodide (1.81 g, 5 mmol), 4-iodoanisole (1.17 g, 5 mmol) and copper (1.0 g, 15.6 mmol) in DMSO (10 mL) was stirred at 100 °C for 12 h under nitrogen. The mixture was filtered. The solid was washed twice with ether. The filtrate was hydrolyzed with dilute HCl acid (2N, 20 mL), then was extracted with ether (3×20 mL). The combined extracts were washed with water, dried over anhydride Na_2SO_4 . After removing ether, the residue was subjected to column chromatography on silica gel to give **3j** as a white solid.

3g: white solid. IR (KBr): 1792, 1133, 772, 740, 701 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.66$ (m, 6H), 7.45 (m, 3H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 69.24$ (t, $J = 13.7$ Hz, 2F), 111.98 (t, $J = 14.4$ Hz, 2F), 120.81 (t, $J = 14.2$ Hz, 2F), 122.48 (t, $J = 14.2$ Hz, 2F). MS (EI, 70 eV): m/z (%) = 388 (29) $[M]^+$, 203 (100). Anal. Calcd. for $\text{C}_{16}\text{H}_9\text{F}_8\text{Cl}$: C, 49.44; H 2.33. Found: C, 49.35; H, 2.71.

3h: colorless oil. IR (film): 1195, 1137, 1083, 776, 767 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 8.26$ (d, $J = 8.1$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.93 (d, $J = 9.6$ Hz, 1H), 7.85 (d, $J = 7.2$ Hz, 1H), 7.59 (m, 3H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.0$ (m, 2F), 104.7 (m, 2F), 119.8 (m, 4F). MS (EI, 70 eV): m/z (%) = 364 (4), 362 (13) $[M]^+$. Anal. Calcd. for $\text{C}_{14}\text{H}_7\text{F}_8\text{Cl}$: C, 46.37; H, 1.95. Found: C, 46.02; H, 2.08.

3i: yellow oil. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.40$ (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 9.0$ Hz, 2H), 2.99 (s, 6H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 67.8$ (t, $J = 13.8$ Hz, 2F), 109.2 (t, $J = 13.1$ Hz, 2F), 119.5 (m, 2F), 121.2 (m, 2F).

3j: colorless oil. IR (film): 1617, 1520, 1311, 1263, 1183, 1137 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.55$ (d, $J = 9.0$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 2H), 3.86 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.4$ (t, $J = 13.3$ Hz, 2F), 110.2 (t, $J = 14.9$ Hz, 2F), 119.9 (m, 2F), 121.7 (m, 2F). MS (EI, 70 eV): m/z (%) = 342 (4) $[M]^+$, 157 (100). Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{F}_8\text{OCl}$: C, 38.56; H, 2.06. Found: C, 38.51; H, 2.06.

3k: colorless oil. IR (film): 1516, 1296, 1195, 1135, 752, 705 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 7.55$ (d, $J = 8.1$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.19 (d, $J = 3.3$ Hz, 1H), 6.77 (d, $J = 0.9$ Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.06$ (m, 2F), 108.89 (m, 2F), 119.87 (m, 2F), 121.01 (m, 2F). MS (EI, 70 eV): m/z (%) = 365 (26) $[M]^+$, 180 (100). Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{F}_8\text{ClN}$: C, 42.70; H, 2.21; N, 3.83. Found: C, 42.95; H, 2.45; N, 3.94.

3l: colorless oil. IR (film): 1191, 1134, 990, 767, 700 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 8.79$ (dd, $J = 2.1, 6.9$ Hz, 1H), 8.71 (d, $J = 8.1$ Hz, 1H), 8.36 (d, $J = 7.5$ Hz, 1H), 8.20 (s, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.74 (m, 4H). ^{19}F NMR (282 MHz, CDCl_3): $\delta = 68.31$ (t, $J = 12.8$ Hz, 2F), 104.94 (t, $J = 14.4$ Hz, 2F), 119.63 (t, $J = 12.5$ Hz, 2F), 120.12 (m, 2F). MS (EI,

70 eV): m/z (%) = 412 (46) $[M]^+$, 227 (100). Anal. Calcd. for $C_{18}H_9F_8Cl$: C, 52.38, H, 2.20. Found: C, 52.49; H, 2.12.

4.4. Typical procedure for the cyclization reaction of 3

Under a nitrogen atmosphere, **3a** (1.71 g, 5 mmol), $Na_2S_2O_4$ (4.35 g, 25 mmol), $NaHCO_3$ (2.1 g, 25 mmol) and DMSO (25 mL) was added to a 50 mL three-necked round bottomed flask equipped with a magnetic stir bar and a condenser. The mixture was then heated to 100 °C for 20 min with stirring. The conversion of **3a** was 100%, determined by ^{19}F NMR. After cooling, the mixture was poured into ice water (30 mL). The aqueous layer was extracted with ether (3 × 30 mL). The combined extracts were washed with water (3 × 20 mL) and dried over Na_2SO_4 . After removing ether, the residue was subjected to column chromatography on silica gel to give **4a** as a brown solid.

4a: brown solid. IR (KBr): 3226, 1516, 1208, 1124, 753, 676 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 6.73 (s, 2H), 4.00 (br, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 108.05 (m, 4F), 135.35 (m, 4F). MS (EI, 70 eV): m/z (%) = 306 (100) $[M]^+$, 286 (33). Anal. Calcd. for $C_{10}H_6F_8N_2$: C, 39.23; H, 1.98; N, 9.15. Found: C, 39.63; H, 2.11; N, 9.26.

4b: white solid. IR (KBr): 1491, 1248, 1180, 1161, 1077, 1004, 945, 752 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.1 Hz, 1H), 7.47 (m, 2H), 7.34 (m, 1H), 3.96 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 103.44 (m, 2F), 105.44 (m, 2F), 132.04 (m, 2F), 133.00 (m, 2F). MS (EI, 70 eV): m/z (%) = 330 (13), 329 (100) $[M]^+$. Anal. Calcd. for $C_{13}H_7F_8N$: C, 47.43; H, 2.14; N, 4.25. Found: C, 47.45; H, 2.19; N, 4.04.

4c: brown oil. IR (film): 3474, 1310, 1272, 1174, 987, 968 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 9.10 (br, 1H), 7.12 (t, J = 2.0 Hz, 1H), 6.58 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 102.73 (m, 2F), 103.92 (m, 2F), 132.67 (m, 4F). MS (EI, 70 eV): m/z (%) = 265 (60) $[M]^+$, 246 (32). HRMS-EI: m/z $[M]^+$ calcd. for $C_8H_3F_8N$: 265.01377. Found: 265.01474.

4d: brown solid. IR (KBr): 3381, 1496, 1289, 1222, 986 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.06 (dd, J = 2.4, 9.0 Hz, 1H), 6.92 (d, J = 9.0 Hz, 1H), 5.77 (ddd, J = 4.5, 8.4, 48.9 Hz, 1H), 3.87 (s, 5H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 103.77 (ddd, J = 7.9, 16.5, 287.1 Hz, 1F), 113.77 (ddd, J = 12.1, 22.6, 289.3 Hz, 1F), 122.99 (m, 1F), 129.10 (m, 1F), 133.77 (m, 1F), 143.94 (m, 1F), 186.28 (m, 1F). MS (EI, 70 eV): m/z (%) = 303 (100) $[M]^+$, 288 (87). Anal. Calcd. for $C_{11}H_8F_8NO$: C, 43.58; H, 2.66; N, 4.62. Found: C, 44.06; H, 2.81; N, 4.29.

4e: brown solid. IR (KBr): 3510, 1517, 1327, 1272, 1255, 1077, 1066, 1002 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (d, J = 7.5 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 5.30 (d, J = 14.7 Hz, 1H), 3.38 (m, 2H), 2.79 (t, J = 6.0 Hz, 2H), 1.91 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 119.13 (d, J = 7.1 Hz, 2F), 127.65 (m, 2F), 140.00 (m, 1F), 169.14 (m, 1F). MS (EI, 70 eV): m/z (%) = 293 (99) $[M]^+$, 292 (100). Anal. Calcd. for $C_{13}H_9F_6N$: C, 53.25; H, 3.09; N, 4.78. Found: C, 52.97; H, 3.24; N, 4.37.

4f: brown solid. IR (KBr): 3382, 1627, 1485, 1228, 979, 877 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.06 (m, 3H), 6.70 (m, 3H), 4.49 (br, 2H), 3.64 (br, 2H). ^{19}F NMR (282 MHz,

$CDCl_3$): δ = 111.50 (m, 2F), 125.57 (m, 2F), 139.24 (m, 1F), 167.68 (m, 1F). MS (EI, 70 eV): m/z (%) = 344 (100) $[M]^+$, 345 (22). HRMS-EI: m/z $[M]^+$ calcd. for $C_{16}H_{10}F_6N_2$: 344.07482. Found: 344.07462.

4g: white solid. IR (KBr): 1618, 1308, 1239, 1168, 1030, 1008, 972, 913, 776 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.95 (q, J = 8.4 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.50 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 103.18 (m, 2F), 103.54 (m, 2F), 134.86 (m, 4F). MS (EI, 70 eV): m/z (%) = 353 (17), 352 (100) $[M]^+$. Anal. Calcd. for $C_{16}H_8F_8$: C, 54.56; H, 2.29. Found: C, 54.86; H, 2.22.

4h: white solid. IR (KBr): 1281, 1181, 1114, 993, 829, 766 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 8.14 (m, 4H), 7.68 (t, J = 7.8 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 103.2 (m, 4F), 127.4 (m, 4F). MS (EI, 70 eV): m/z (%) = 326 (100) $[M]^+$, 257 (41). Anal. Calcd. for $C_{14}H_6F_8$: C, 51.55; H, 1.85. Found: C, 51.87; H, 1.96.

4i: colorless oil. IR (film): 1619, 1261, 1193, 1169, 1014, 944 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 9.2 Hz, 1H), 6.95 (m, 2H), 3.09 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 100.4 (m, 2F), 104.0 (t, J = 7.4 Hz, 2F), 134.3 (m, 2F), 134.5 (m, 2F). MS (ESI): m/z = 320 $[M + H]^+$. HRMS-ESI: m/z $[M + H]^+$ calcd. for $C_{12}H_{10}F_8N$: 320.06855. Found: 320.06800.

4j: colorless oil. IR (film): 1619, 1297, 1226, 1190, 980, 923 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 9.6 Hz, 1H), 7.28 (m, 2H), 3.94 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 101.5 (m, 2F), 103.6 (m, 2F), 134.5 (m, 4F). MS (EI, 70 eV): m/z (%) = 306 (100) $[M]^+$, 287 (30). Anal. Calcd. for $C_{11}H_6F_8O$: C, 43.16; H, 1.98. Found: C, 42.85; H, 1.94.

4k: white solid. IR (KBr): 1510, 1261, 1191, 1153, 1008, 954, 815 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.1 Hz, 1H), 7.48 (m, 2H), 7.36 (m, 1H), 3.96 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 99.57 (m, 2F), 103.61 (m, 2F), 133.92 (m, 2F), 134.47 (m, 2F). MS (EI, 70 eV): m/z (%) = 329 (83) $[M]^+$, 215 (58). Anal. Calcd. for $C_{13}H_7F_8N$: C, 47.43; H, 2.14; N, 4.25. Found: C, 47.66; H, 2.29; N, 4.20.

4l: white solid. IR (KBr): 1451, 1235, 1163, 1116, 992, 850, 763, 725 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 8.73 (d, J = 8.4 Hz, 2H), 8.56 (t, J = 4.2 Hz, 1H), 8.21 (m, 1H), 7.79 (m, 4H), 6.45 (m, 1H). ^{19}F NMR: δ = 98.06 (m, 1F), 106.02 (m, 1F), 123.20 (m, 1F), 128.42 (m, 1F), 133.51 (m, 1F), 142.25 (m, 1F), 180.03 (m, 1F). MS (EI, 70 eV): m/z (%) = 359 (20), 358 (100) $[M]^+$. Anal. Calcd. for $C_{18}H_9F_7$: C, 60.35; H, 2.53. Found: C, 60.53; H, 2.90.

Acknowledgment

We thank the National Science Foundation of China (Nos. 20272026, D20032010) for financial support of this work.

References

- [1] (a) D.P. Curran, *Synthesis* (1988) 417–439; (b) B.B. Snider, *Chem. Rev.* 96 (1996) 339–363; (c) B. Giese, in: J.E. Baldwin (Ed.), *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon Press, Oxford, 1986.

- [2] (a) X.X. Rong, H.Q. Pan, W.R. Dolbier Jr., *J. Am. Chem. Soc.* 116 (1994) 4521–4522;
(b) W.R. Dolbier Jr., *Chem. Rev.* 96 (1996) 1557–1584;
(c) W.R. Dolbier Jr., A. Li, B.E. Smart, Z.Y. Yang, *J. Org. Chem.* 63 (1998) 5687–5688;
(d) A. Li, A.B. Shtarev, B.E. Smart, Z.Y. Yang, J. Luszytk, K.U. Ingold, A. Bravo, W.R. Dolbier Jr., *J. Org. Chem.* 64 (1999) 5993–5999.
- [3] (a) W.Y. Huang, L. Lu, *Organofluorine chemistry in China*, in: W.Y. Huang (Ed.), *Sulfinatodehalogenation Reaction*, Shanghai Science and Technology Press, Shanghai, 1996, p. 203 (Chapter 8);
(b) W.Y. Huang, F.H. Wu, *Isr. J. Chem.* 39 (1999) 167.
- [4] (a) Z.Y. Long, Q.Y. Chen, *J. Org. Chem.* 64 (1999) 4775–4782;
(b) Z.Y. Long, Q.Y. Chen, *Tetrahedron Lett.* 39 (1998) 8487–8490;
(c) X.T. Huang, Z.Y. Long, Q.Y. Chen, *J. Fluorine Chem.* 111 (2001) 107–113.
- [5] (a) Z. Zeng, C. Liu, L.M. Jin, C.C. Guo, Q.Y. Chen, *Eur. J. Org. Chem.* (2005) 306–316;
(b) L. Chen, L.M. Jin, C.C. Guo, Q.Y. Chen, *Synlett* (2005) 963–970;
(c) L.M. Jin, Z. Zeng, C.C. Guo, Q.Y. Chen, *J. Org. Chem.* 68 (2003) 3912–3917.
- [6] (a) Q.L. Zhou, Y.Z. Huang, *J. Fluorine Chem.* 43 (1989) 385–392;
(b) Q.L. Zhou, Y.Z. Huang, *J. Fluorine Chem.* 39 (1988) 87–98.
- [7] (a) V.C.R. Mcloughlin, J. Thrower, *Tetrahedron* 25 (1969) 5921–5940;
(b) Z.Y. Yang, Ph.D. Thesis, The Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Shanghai, China, 1986.
- [8] T.H. Lowery, K.S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., Kluwer Academic Publishers, Boston, 1987, pp. 795–796.
- [9] (a) I. Rico, C. Wakselman, *Tetrahedron Lett.* 22 (1981) 323–326;
(b) I. Rico, D. Cantacuzene, C. Wakselman, *J. Chem. Soc., Perkin Trans. 1* (1982) 1063–1066;
(c) X.C. Guo, Q.Y. Chen, *J. Fluorine Chem.* 93 (1999) 81–86.