A novel method for introducing a polyfluoroalkyl group into aromatic compounds

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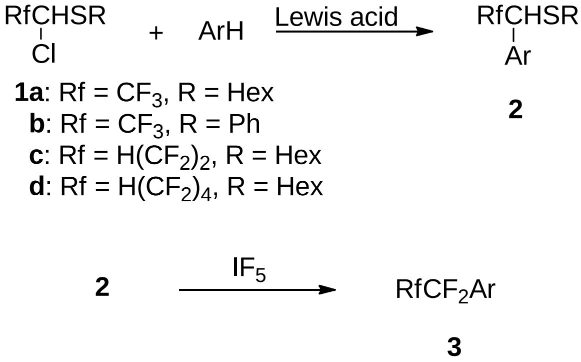
Abstract

Introduction of a polyfluoroalkyl group into aromatic compounds was achieved by Friedel-Crafts reaction using (1-chloro-1-hydroperfluoroalkyl) sulfides **1**, and the subsequent desulfurizing-difluorination of the resulting product using IF_5 / Et_3N-nHF. Perfluoroethyl, 1,1,2,2,3,3-hexafluoropropyl, and 1,1,2,2,3,3,4,4,5,5-decafluoropentyl groups were introduced to various aromatic compounds by this method. Selective perfluoroethylation of uracil at the 5-position was also performed.

1. Introduction

Introduction of a polyfluoroalkyl group into an aromatic compound has been well studied [1] because the resulting compounds exhibit remarkably different physical, chemical, and biological properties [2]. Among the many methods available for the polyfluoroalkylation of aromatic compounds, the electrophilic method has an advantage over other methods: in a nucleophilic method, an aromatic halide is required as a substrate, and in a free radical method, regioselecitivity is low. On the other hand, in an electrophilic polyfluoroalkylation, the polyfluoroalkyl group can be introduced by substitution with a hydrogen atom under mild conditions [3]. However, the electrophilic polyfluoroalkylation method requires a special reagent, which is unstable and difficult to prepare [2a, 4]. Therefore, a more convenient method for the introduction of a polyfluoroalkyl group into an aromatic compound has been desired. Previously, Uneyama et al. reported that a 1-(phenylsulfanyl)-2,2,2-trifluoroethyl group can be introduced to aromatic compounds by Friedel-Crafts reaction using (1-chloro-2,2,2-trifluoroethyl) phenyl sulfide (**1b**, R = Ph, Rf = CF_3) [5]. Various (1-chloro-1-hydroperfluoroalkyl) sulfides **1** can be prepared from commercially available 1,1-dihydroperfluoroalkanols [6], and they can be used for the reaction with aromatic compound to synthesize (1-aryl-1-hydroperfluoroalkyl) sulfides **2**. Recently, we reported a desulfurizing-difluorination reaction of benzyl sulfides having an electron-withdrawing group using IF_5, where two fluorine atoms were introduced to the benzyl position by substitution with a hydrogen atom and an alkylsulfanyl group [7]. As the perfluoroalkyl group in **2** is a strong electron-withdrawing group, the desulfurizing-difluorination reaction can be applied to **2**, and the polyfluoroalkyl group substituted aromatic compound **3** must be prepared from **2** (Scheme 1) [8].



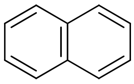
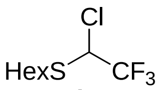
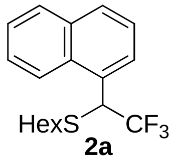
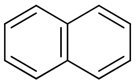
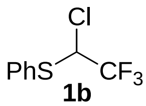
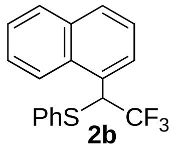
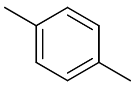
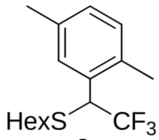
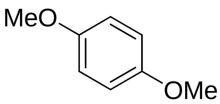
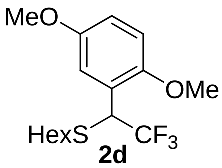
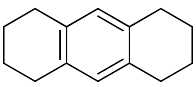
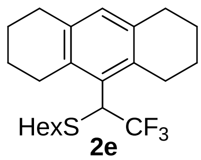
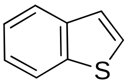
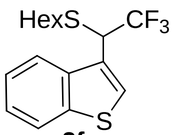
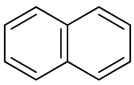
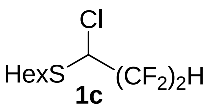
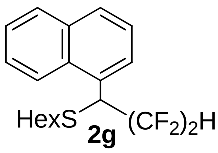
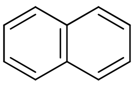
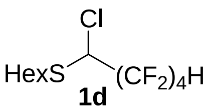
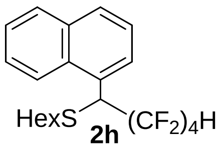
Scheme 1

2. Result and discussion

1-Chloro-2,2,2-trifluoroethyl hexyl sulfide **1a**, 1-chloro-2,2,2-trifluoroethyl phenyl sulfide **1b**, 1-chloro-2,2,3,3-tetrafluoropropyl hexyl sulfide **1c**, and 1-chloro-2,2,3,3,4,4,5,5-octafluoropentyl hexyl sulfide **1d** were prepared from the corresponding polyfluoroalcohols [6], and used for the Friedel-Crafts reaction with naphthalene in the presence of a Lewis acid ($TiCl_4$ or $SnCl_4$). The alkylation occurred selectively at 1-position and 1-(1-hexylsulfanyl-2,2,2-trifluoroethyl)naphthalene **2a**, 1-(1-phenylsulfanyl-2,2,2-trifluoroethyl)naphthalene **2b**, 1-(1-hexylsulfanyl-2,2,3,3-tetrafluoropropyl)naphthalene **2g**, and 1-(1-hexylsulfanyl-2,2,3,3,4,4,5,5-octafluoropentyl)naphthalene **2h** were obtained in good yield as shown in Table 1 [9]. Similarly, in the reaction of **1a** with *p*-xylene, *p*-dimethoxybenzene, octahydroanthracene, and benzothiophene, the corresponding 1-(hexylsulfanyl)-2,2,2-trifluoroethylated products **2c-f** were obtained in good yields (Table 1).

Table 1

Friedel-Crafts reaction of aromatic compounds with sulfide **1**[a]

Aromatic compound	Reagent	Reaction time (h)	Product	Yield (%)[b]
	 **1a**	10	 **2a**	84 (1- : 2- = 98:2)
	 **1b**	20	 **2b**	77 (1- : 2- = 96:4)
	**1a**	15	 **2c**	71
	**1a**	12	 **2d**	80
	**1a**	15	 **2e**	78
	**1a**	15	 **2f**	77[c] (3- : 2- = 77:23)
	 **1c**	15	 **2g**	82 (1- : 2- = 96:4)
	 **1d**	3	 **2h**	85[d, e] (1- : 2- = 96:4)

[a]If otherwise not mentioned, the reaction was carried out in CH_2Cl_2, using 1.5 eq of $TiCl_4$ and 2 eq of ArH.

[b]Isolated yield based on **1** used. In parenthese, isomer ratio.

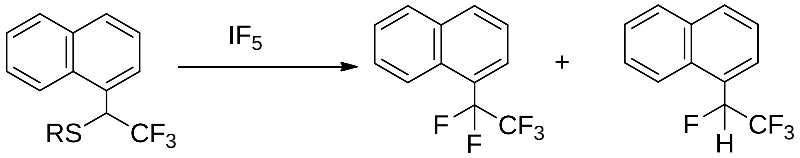
[c]1.2 eq of $SnCl_4$ was used as Lewis-acid.

[d]1.0 eq of $SnCl_4$ was used.

[e]5.0 eq of naphthalene was used.

Next, the desulfurizing-difluorination of 1-(1-hexylsulfanyl-2,2,2-trifluoroethyl)naphthalene **2a** and 1-(1-phenylsulfanyl-2,2,2-trifluoroethyl)naphthalene **2b** was investigated for the synthesis of 1-(perfluoroethyl)naphthalene **3a**. When **2a** was subjected to the reaction with IF_5, the expected **3a** was obtained in 77% yield. However, 1-(1,2,2,2-tetrafluoroethyl)naphthalene **4a** was also formed in 14% yield (Entry 1 in Table 2). When IF_5 / Et_3N-3HF was used instead of IF_5 to prevent the formation of **4a** [10], the yield of **4a** was reduced to 8% (Entry 2). Finally, **3a** was selectively obtained using IF_5 / Et_3N-2HF (Entry 3). On the other hand, in the reaction of **2b** with IF_5, the decomposition of **2b** took place under the same conditions, and neither **3a** nor **4a** was obtained in reasonable yield (Entry 4). In the reaction of **2b** with IF_5 / Et_3N-3HF, **4a** was selectively obtained in good yield without the formation of **3a** (Entries 5 and 6). Consequently, the perfluoroethyl or the 1,2,2,2-tetrafluoroethyl group can be selectively introduced to 1-position of naphthalene using **1a** or **1b**.

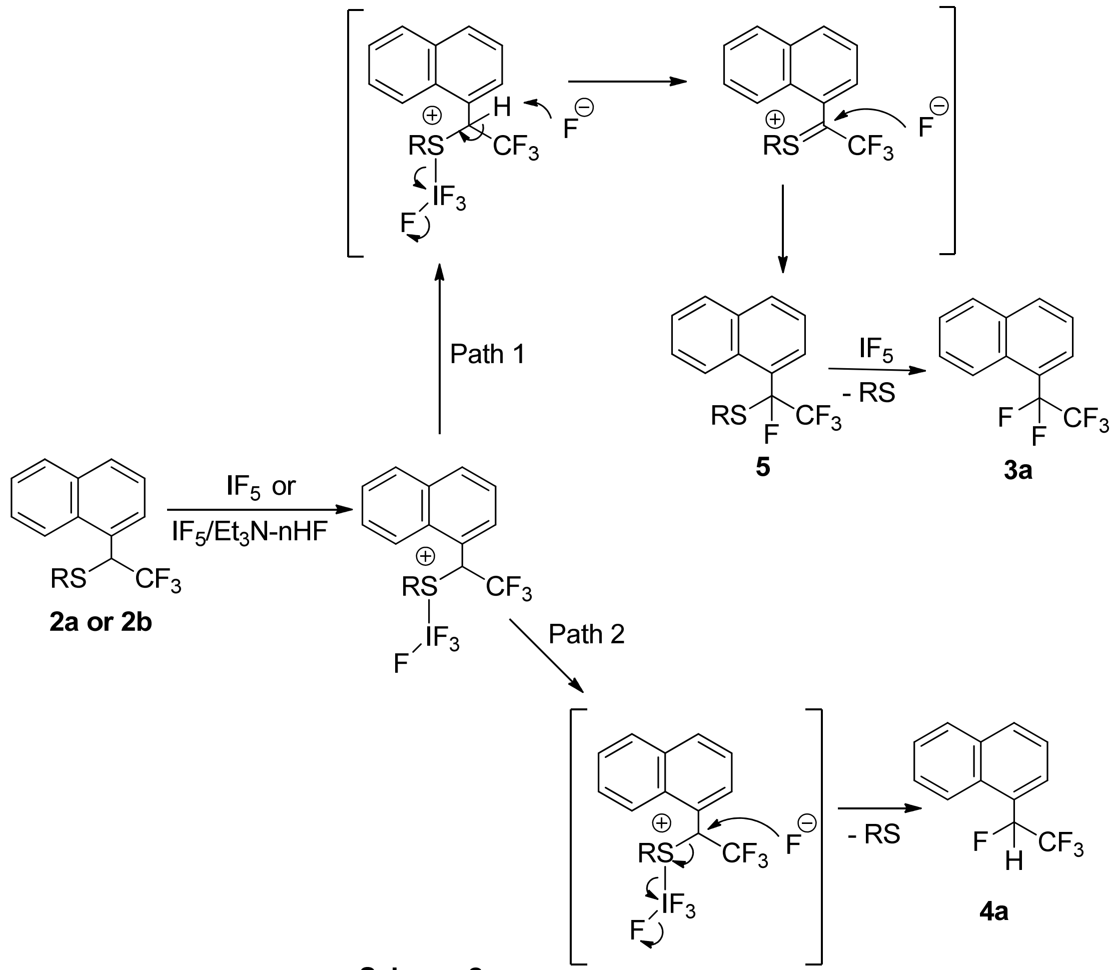
Table 2
Desulfurizing-difluorination reaction of **2a** and **2b**[a]



Entry	Substrate	Reagent	Condition	Yield (%)[b]	
				3a	**4a**
1	**2a** (R = Hex)	IF_5	0 °C, 13 h	77	14
2	**2a**	IF_5 / Et_3N-3HF	0 °C, 8 h	86	8
3	**2a**	IF_5 / Et_3N-2HF	rt, 65 h	98(80)	0
4	**2b** (R = Ph)	IF_5	0 °C, 13 h	0	3
5	**2b**	IF_5 / Et_3N-3HF[c]	0 °C, 60 h	0	68
6	**2b**	IF_5 / Et_3N-3HF[c]	rt, 18 h	0	92(80)

[a] If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 using 1.5 eq of IF_5 reagent.
[b] ^{19}F NMR yield based on **2** used. In parentheses, isolated yield.
[c] 0.75 eq of IF_5 / Et_3N-3HF was used.

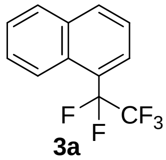
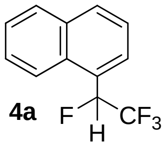
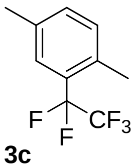
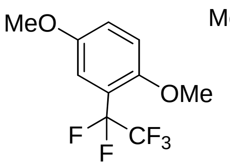
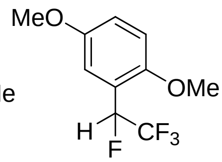
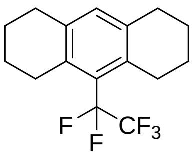
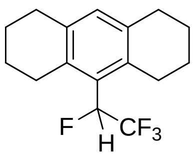
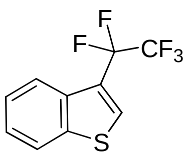
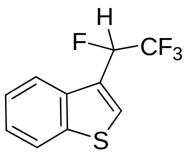
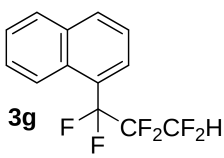
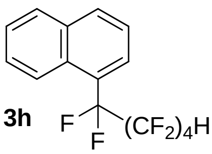
The difference in the reactivities of **2a** and **2b** can be explained from leaving ability of the alkylsulfanyl group (Scheme 2): In path 1, substitution of hydrogen with a fluoride (fluoro-Pummerer reaction) initially took place to afford tetrafluoro-sulfide **5**. In the next step, **5** was converted to **3a** by the substitution of the alkylsulfanyl group with a fluoride (desulfurizing-fluorination reaction). In path 2, the desulfurizing-fluorination reaction initially took place to afford **4a**. The reaction of **2a** mainly proceeded though path 1 and **3a** was formed as a main product. When a less reactive IF_5 / Et_3N-nHF was used as a fluorination reagent, the reaction predominantly proceeded through path 1 and **3a** was formed selectively (Entries 1-3 in Table 2). On the other hand, in the reaction of **2b**, because of the higher leaving ability of the phenylsulfanyl group, the reaction proceeded through path 2 to afford **4a** selectively (Entries 5 and 6).



Scheme 2

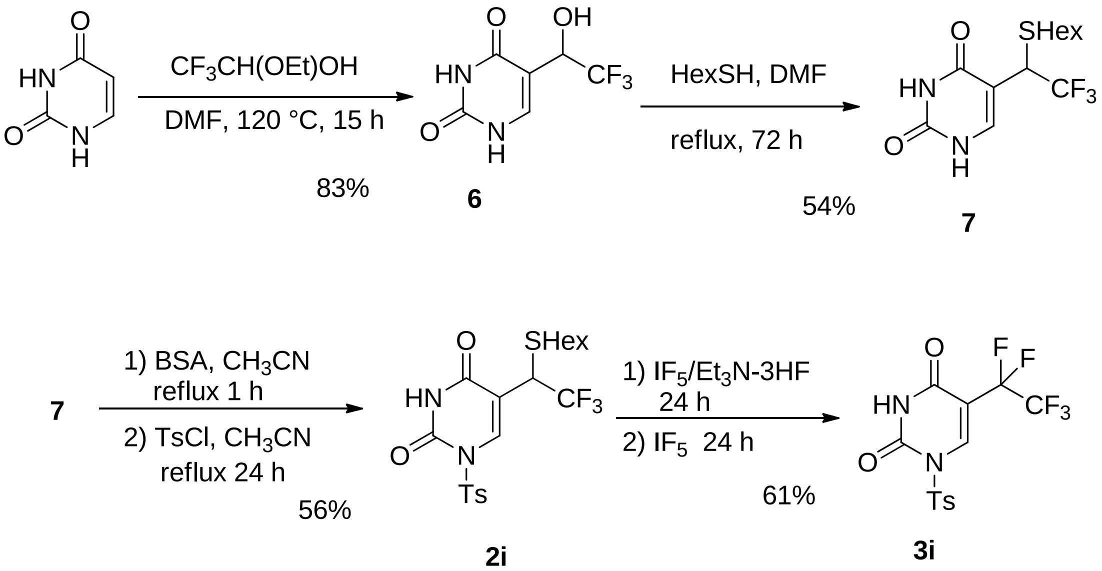
From various (1-aryl-2,2,2-trifluoroethyl) hexyl sulfides **2a and 2c-f**, the corresponding perfluoroethylated aromatic compounds **3a** and **3c-f** were obtained with good selectivity (100-90%) by desulfurizing-difluorination reaction using IF_5 / Et_3N-nHF, as shown in Table 3. Similarly, 1-(1,1,2,2,3,3-hexafluoropropyl) and 1-(1,1,2,2,3,3,4,4,5,5-decafluoropentyl)naphthalene **3g-h** were selectively formed by the reaction of the corresponding sulfides **2g-h** with IF_5 / Et_3N-HF.

Table 3
The desulfurizing-fluorination reaction of **2**[a]

Substrate	reagent	conditon	Product (ratio)	Yield (%)[b]
2a	IF_5 / Et_3N-2HF	rt, 65 h	 **3a**	80 (99)
2b	IF_5 / Et_3N-3HF	rt, 18 h	 **4a**	80 (92)[c]
2c	IF_5 / Et_3N-3HF	rt, 60 h	 **3c**	80
2d	IF_5 / Et_3N-HF	rt, 37 h	  **3d** 96 : 4 **4d**	86
2e	IF_5 / Et_3N-2HF	rt, 70 h	  **3e** 92 : 8 **4e**	75
2f	IF_5 / Et_3N-HF	rt, 50 h	  **3f** 90 : 10 **4f**	79
2g	IF_5 / Et_3N-HF	rt, 32 h	 **3g**	86
2h	IF_5 / Et_3N-HF	rt, 24 h	 **3h**	83

[a]If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 using 1.5 eq of IF_5 reagent.
[b]Isolated yield based on **2** used. In parentheses, ^{19}F NMR yield.
[c]0.75 eq of IF_5/Et_3N-3HF was used.

Fluorine-containing pyrimidine derivatives including uracils and nucleosides are potent antitumor and antiviral agents [11], and much effort has gone into the synthesis of 5-(trifluoromethyl)uracil derivatives [12]. However, there are few reports on the synthesis of their perfluoroethyl derivatives. Therefore, we used our method for the synthesis of a 5-(perfluoroethyl)uracil derivative. The Friedel-Crafts reaction of **1a** with uracil or *N*-protected uracil was unsuccessful, and the expected 5-(2,2,2-trifluoro-1-(hexylsulfanyl)ethyl)uracil **7** was not obtained. Therefore, **7** was prepared by the reaction of uracil with trifluoroacetaldehyde ethyl hemiacetal [13], and the subsequent reaction of the resulting product with hexanethiol (Scheme 3) [14]. The nitrogen atom at 1-position in **7** was protected with a tosyl group to afford 1-tosyl-5-{2,2,2-trifluoro-1-(hexylsulfanyl)ethyl}uracil **2i**. In the reaction of **2i** with IF_5, the expected 5-(perfluoroethyl)uracil **3i** was obtained in 54% yield with 3% of 5-(1,2,2,2-tetrafluoroethyl)uracil. On the other hand, when IF_5 / Et_3N-3HF was used for the reaction with **2i**, the formation of **3i**, and 5-{1,2,2,2-tetrafluoro-1-(hexylsulfanyl)ethyl}uracil (the fluoro-Pummerer rearrangement product), and the absence of 5-(tetrafluoroethyl)uracil were confirmed from ^{19}FNMR analysis of the reaction mixture after 24 h at room temperature. Under these conditions, the desulfurizing-fluorination reaction is slow and is the rate-determining step. The desulfurizing-fluorination step was accelerated by the addition of IF_5 to the reaction mixture, and **3i** was obtained in 61% yield in 48 h (Scheme 3).



Scheme 3

3. Conclusion

Perfluoroethyl, hexafluoropropyl, and decafluoropentyl groups can be introduced to various aromatic compounds by Friedel-Crafts reaction with (1-chloro-1-hydroperfluoro)alkyl sulfides **1**, and the subsequent desulfurizing-difluorination of the resulting product with IF_5 / Et_3N-nHF. As the starting sulfides **1** can be prepared from commercially available polyfluoro-alcohols, our method is useful for introducing various polyfluoro-alkyl groups into aromatic compounds. In order to demonstrate the usefulness of our method, 5-(perfluoroethyl)uracil was synthesized.

4. Experimental

4.1. General

The melting points were measured with a Yanagimoto micro melting-point apparatus.

The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H NMR (400 MHz) spectra, ^{19}F NMR (376 MHz) spectra, and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ on a JEOL JNM-A400II FT NMR and the chemical shift, δ, is referred to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F), respectively. The EI-high-resolution mass spectra were measured on a JEOL JMS-700TZ. IF_5 in a stainless-steel cylinder was supplied by Asahi Glass Co., Ltd. IF_5 was transferred through a Teflon™ tube into a Teflon™FEP bottle from the cylinder under an N_2 atmosphere. IF_5 was transferred quickly from the bottle to the reaction vessel made of Teflon ™ FEP in open air. IF_5 / $5CH_2Cl_2$ and IF_5 / Et_3N-3HF were prepared as described previously [10]. IF_5 decomposes in air emitting HF fume, and, therefore, it should be carefully handled in a bench hood with rubber-gloved hands. 2,2,3,3-Tetrafluoropropanol and 2,2,3,3,4,4,5,5-octafluoropentanol were donated from Daikin Industries, Ltd. (1-Chloro-2,2,2-trifluoroethyl) hexyl sulfide **1a**, (1-chloro-2,2,2-trifluoroethyl) phenyl sulfide **1b**, (1-chloro-2,2,3,3-tetrafluoropropyl) hexyl sulfide **1c**, and (1-chloro-2,2,3,3,4,4,5,5-octafluoropentyl) hexyl sulfide **1d** were prepared from 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, and 2,2,3,3,4,4,5,5-octafluoropentanol, respectively, according to the reported procedure [6].

*4.2. Friedel-Crafts reaction of aromatic compounds with **1***

*4.2.1. 1-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}naphthalene (**2a**)*

To a CH_2Cl_2 solution (20 mL) of naphthalene (1.28 g, 10 mmol) and **1a** (1.18 g, 5 mmol) was added $TiCl_4$ (1.44 g, 7.5 mmol) under N_2 atmosphere at 0 °C. The mixture was stirred at room temperature for 10 h and then 3 M aqueous HCl (10 mL) was added. After stirring for 30 min, the mixture was extracted with CH_2Cl_2 (30 mL X 3). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:benzene = 50:1) gave **2a** (1.37 g) in 84% yield (containing ca 2% of 2-substituted isomer). Pure **2a** is obtainable by careful column chromatography. Oil: IR (neat) 2929, 1251, 1149, 1105 cm^{-1}. ^1H NMR δ 0.84 (3H, t, J = 7.0 Hz), 1.18-1.35 (6H, m), 1.48-1.61 (2H, m), 2.64-2.76 (2H, m), 5.19 (1H, brs), 7.48-7.60 (3H, m), 7.62-8.05 (4H, m). ^{13}C NMR δ 13.9, 22.4, 28.3, 28.9, 31.2, 33.1, 46.3 (q, $^2J_{C\text{-}F}$ = 29.3 Hz), 122.2, 125.2, 125.9 (2C), 126.5 (q, $^1J_{C\text{-}F}$ = 279.4 Hz), 126.8, 129.2, 129.3, 129.5, 131.1, 133.8. ^{19}F NMR δ -67.54 (3F, s). HRMS (EI) calcd for $C_{18}H_{21}F_3S$ (M^+) 326.13161, found 326.13105.

*4.2.2. 1-{2,2,2-Trifluoro-1-(phenlsulfanyl)ethyl}naphthalene (**2b**)*

Oil: IR (neat) 3062, 1248, 1105 cm^{-1}. ^1H NMR δ 5.45 (1H, q, J = 7.8 Hz), 7.24-7.32 (3H, m), 7.41-7.65 (6H, m), 7.85-8.00 (3H, m). ^{13}C NMR δ 50.8 (q, $^2J_{C\text{-}F}$ = 29.2 Hz), 122.2, 125.2, 125.9, 126.1 (q, $^1J_{C\text{-}F}$ = 280.4 Hz), 126.8, 127.0, 128.8 (2C), 129.1 (2C), 129.2 (2C), 129.4, 130.9, 132.7, 133.8, 134.0. ^{19}F NMR δ –67.16 (3F, d, J = 6.2 Hz). HRMS (EI) calcd for $C_{18}H_{13}F_3S$ (M^+) 318.06901, found 318.06848.

*4.2.3. 2-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,4-dimethylbenzene (**2c**)*

Oil: IR (neat) 2928, 1255, 1147, 1111 cm^{-1}. ^1H NMR δ 0.87 (3H, t, J = 6.9 Hz), 1.20-1.39 (6H, m), 1.50-1.63 (2H, m), 2.32 (3H, s), 2.35 (3H, s), 2.60-2.72 (2H, m), 4.50 (1H, q, J = 8.5 Hz), 7.02-7.08 (2H, m), 7.26-7.27 (1H, m). ^{13}C NMR δ 14.0, 19.2, 21.0, 22.5, 28.3, 29.1, 31.3, 33.1, 47.2 (q, $^2J_{C\text{-}F}$ = 31.5 Hz), 126.5 (q, $^1J_{C\text{-}F}$ = 279.6 Hz), 128.8, 129.3, 130.4, 131.9, 132.9, 136.1. ^{19}F NMR δ -68.11 (3F, d, J = 7.1 Hz). HRMS (EI) calcd for $C_{16}H_{23}F_3S$ (M^+) 304.14726, found 304.14684.

*4.2.4. 2-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,4-dimethoxybenzene (**2d**)*

Oil: IR (neat) 2931, 1503, 1236 cm^{-1}. ^1H NMR δ 0.87 (3H, t, J = 7.0 Hz), 1.23-1.39 (6H, m), 1.54-1.62 (2H, m), 2.59-2.72 (2H, m), 3.77 (3H, s), 3.82 (3H, s), 4.92-4.98 (1H, q, *J* = 8.8 Hz), 6.844 (2H, brs), 7.03 (1H, s). ^{13}C NMR δ 14.0, 22.4, 28.3, 29.0, 31.3, 33.1, 43.3 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 55.7, 56.3, 111.9, 114.8, 114.9, 123.4, 126.3 (q, $^{1}J_{C\text{-}F}$ = 279.4 Hz), 150.8, 153.6. ^{19}F NMR δ -68.48 (3F, d, *J* = 8.9 Hz). HRMS (EI) calcd for $C_{16}H_{23}F_3O_2S$ (M^+) 336.13708, found 336.13645.

*4.2.5. 9-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,2,3,4,5,6,7,8-octahydroanthracene (**2e**)*

Oil: IR (neat) 2930, 1250, 1146, 1102 cm^{-1}. ^{1}H NMR δ 0.88 (3H, t, *J* = 6.7 Hz), 1.25-1.43 (6H, m), 1.54-1.89 (10H, m), 2.68-2.94 (10H, m), 4.77 (1H, q, *J* = 10.0 Hz), 6.84 (1H, s). ^{13}C NMR δ 14.0, 21.9, 22.3, 22.5 (2C), 23.9, 27.7, 27.8 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 28.4, 29.3, 29.4, 30.2, 31.3, 35.8, 47.2 (q, $^{2}J_{C\text{-}F}$ = 30.7 Hz), 127.0 (q, $^{1}J_{C\text{-}F}$ = 281.4 Hz), 130.6 (2C), 132.6, 134.9, 136.5, 136.7. ^{19}F NMR δ -65.70 (3F, d, *J* = 9.0 Hz). HRMS (EI) calcd for $C_{22}H_{32}F_3S$ (M^++1) 385.21768, found 385.21366.

*4.2.6. 3-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)benzo[b]thiophene (**2f**)*

Oil. IR (neat) 2928, 1253, 1150, 1108 cm^{-1}. ^{1}H NMR δ 0.84 (3H, t, *J* = 6.6 Hz), 1.18-1.34 (6H, m), 1.44-1.59 (2H, m), 2.53-2.60 (1H, m), 2.67-2.74 (1H, m), 4.73 (1H, q, *J* = 8.4 Hz), 7.39-7.47 (2H, m), 7.56 (1H, s), 7.87 (2H, dd, *J* = 15.1, 8.5 Hz). ^{13}C NMR δ 13.9, 22.4, 28.3, 28.9, 31.2, 32.5, 45.5 (q, $^{2}J_{C\text{-}F}$= 30.8 Hz), 121.6, 122.9, 124.4, 124.8, 126.0, 126.1 (q, $^{1}J_{C\text{-}F}$= 279.7 Hz), 127.1, 137.3, 139.9. ^{19}F NMR δ -68.27 (3F, d, *J* = 9.0 Hz). HRMS (EI) calcd for $C_{16}H_{19}F_3S_2$ (M^+) 332.08803, found 332.08739.

*4.2.7. 1-{2,2,3,3-Tetrafluoro-1-(hexylsulfanyl)propyl}naphthalene (**2g**)*

Oil: IR (neat) 2929, 1227, 1115, 1041 cm^{-1}. ^{1}H NMR δ 0.82 (3H, t, *J* = 6.7 Hz), 1.14-1.26 (6H, m), 1.45-1.54 (2H, m), 2.50-2.63 (2H, m), 5.17 (1H, t, *J* = 15.2 Hz), 5.97 (1H, tt, *J* = 54.4, 5.2 Hz), 7.51-7.61 (3H, m), 7.86-7.92 (3H, m), 8.00 (1H, d, *J* = 8.9 Hz).

^{13}C NMR δ 13.9, 22.4, 28.2, 29.0, 31.2, 32.8, 44.2 (t, $^{2}J_{C-F}$ = 22.9 Hz), 109.5 (tt, $^{1}J_{C-F}$ = 251.8 Hz, $^{2}J_{C-F}$ = 33.7 Hz), 116.9 (tt, $^{1}J_{C-F}$ = 254.1 Hz, $^{2}J_{C-F}$ = 25.3 Hz), 122.1. 125.4, 125.9, 126.9, 128.0, 129.2, 129.3, 129.9, 131.5, 133.7. ^{19}F NMR δ -119.58 to -119.64 (2F, m), -138.30 (2F, ddt, *J* = 297.3, 53.7, 7.2 Hz). HRMS (EI) calcd for $C_{19}H_{22}F_4S$ (M^+) 358.13783, found 358.13732.

*4.2.8. 1-{2,2,3,3,4,4,5,5-Octafluoro-1-(hexylsulfanyl)pentyl}naphthalene (**2h**)*

Oil: IR (neat) 2930, 1172, 1130 cm^{-1}. ^{1}H NMR δ 0.82 (3H, t, *J* = 6.8 Hz), 1.16-1.32 (6H, m), 1.46-1.57 (2H, m), 2.55-2.67 (2H, m), 5.36 (1H, dd, *J* = 17.9, 12.9 Hz), 5.97 (1H, tt, *J* = 52.1, 5.5 Hz), 7.49-7.61 (3H, m), 7.82-7.99 (4H, m). ^{13}C NMR δ 13.8, 22.4, 28.2, 29.0, 31.2, 33.4, 44.2 (t, $^{2}J_{C-F}$ = 23.2 Hz), 104.8-120.3 (4C, m), 121.7, 125.3, 125.8, 127.0, 128.0, 129.2, 129.3, 129.7, 131.1, 133.7. ^{19}F NMR δ -108.60 (1F, dt, *J* = 276.7, 13.8 Hz), -120.84 (1F, d, *J* = 274.9 Hz), -122.67 to -121.64 (2F, m), -130.49 to -130.62 (2F, m), -136.83 to -138.73 (2F, m). HRMS (EI) calcd for $C_{21}H_{22}F_8S$ (M^+) 458.13145, found 458.13161

*4.3.1. 1-(Perfluoroethyl)naphthalene (**3a**)*

IF_5 / Et_3N-2HF (0.75 mmol) was prepared in situ by the addition of Et_3N (25.3 mg, 0.25 mmol) to a mixture of IF_5 / $5CH_2Cl_2$ (0.16 g, 0.25 mmol), IF_5 / Et_3N-3HF (190 mg, 0.5 mmol), and CH_2Cl_2 (0.5 mL) at 0 °C in Teflon PFA bottle. To the resulting CH_2Cl_2 solution of IF_5 / Et_3N-2HF (0.75 mmol), a CH_2Cl_2 solution (2.5 mL) of **2a** (164 mg, 0.5 mmol) was added at 0 °C and the mixture was stirred at room temperature for 65 h. The mixture was poured into saturated aqueous $NaHCO_3$ (30 mL) and extracted with ether (30 mL X 3). The combined organic phase was washed with aqueous $Na_2S_2O_3$, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel / hexane:CH_2Cl_2 = 50:1) gave **3a** (100 mg) in 80% yield.

Oil: IR (neat) 3059, 1133 cm^{-1}. ^{1}H NMR δ 7.52-7.62 (3H, m), 7.83 (1H, d, *J* = 7.3 Hz), 7.92 (1H, d, *J* = 8.3 Hz), 8.04 (1H, *J* = 8.2 Hz), 8.24 (1H, d, *J* = 8.3 Hz). ^{13}C NMR δ 115.3 (tq, $^1J_{C-F}$ = 255.3 Hz, $^2J_{C-F}$ = 39.4 Hz), 119.7 (tq, $^2J_{C-F}$ = 39.3 Hz, $^1J_{C-F}$ = 287.0 Hz), 124.2 (t, $^2J_{C-F}$ = 21.7 Hz), 124.3, 124.7-124.8 (m), 126.4, 127.4 (t, $^3J_{C-F}$ = 9.5 Hz), 127.6 129.0, 129.9, 133.3, 134.1. ^{19}F NMR δ -83.97 (3F, s), -108.90 (2F, s) (lit. [15] -83.8 (3F, s), -108.9 (2F, s)).

*1-(1,2,2,2-Tetrafluoroethyl)naphthalene (**4a**)*

Oil: IR (neat) 3059, 1359, 1274, 1185, 1140 cm^{-1}. ^{1}H NMR δ 6.42 (1H, dq, *J* = 43.5, 5.8 Hz), 7.26-7.62 (3H, m), 7.77 (1H, d, *J* = 7.2 Hz), 7.92-7.98 (3H, m). ^{13}C NMR δ 85.8 (dq, $^1J_{C-F}$ = 185.7 Hz, $^2J_{C-F}$ = 35.0 Hz), 122.5, 122.9 (dq, $^1J_{C-F}$ = 282.3 Hz, $^2J_{C-F}$ = 29.5 Hz), 125.0, 126.0 (d, $^2J_{C-F}$ = 18.3 Hz), 126.1, 126.3 (d, $^3J_{C-F}$ = 10.5 Hz), 127.2, 129.1, 130.6 (d, $^3J_{C-F}$ = 3.8 Hz), 131.1 (d, $^4J_{C-F}$ = 1.9 Hz), 133.6. ^{19}F NMR δ -78.09 (3F, dd, *J* = 12.5, 5.4 Hz), -195.1 (1F, dq, *J* = 43.0, 12.6 Hz) (lit. [16] -77.9 (3F, dd, *J* = 13, 6 Hz), -194.9 (1F, dq, *J* = 44, 13 Hz)).

*2-(Perfluoroethyl)-1,4-dimethylbenzene (**3c**)*

Oil: IR (neat) 2931, 1207, 1187 cm^{-1}. ^{1}H NMR δ 2.36 (3H, s), 2.43 (3H, t, *J* = 3.0 Hz), 7.14-7.31 (3H, m). ^{13}C NMR δ 19.7-19.8 (m), 20.7, 115.0 (tq, $^1J_{C-F}$ = 254.2 Hz, $^2J_{C-F}$ = 38.2 Hz), 119.7 (tq, $^2J_{C-F}$ = 40.1 Hz, $^1J_{C-F}$ = 286.1), 126.6 (t, $^2J_{C-F}$ = 21.7 Hz), 128.5 (t, $^3J_{C-F}$ = 8.6 Hz), 132.4, 132.5, 134.7 (t, $^3J_{C-F}$ = 2.2 Hz), 135.8. ^{19}F NMR δ -84.86 (3F, s), -110.94 (2F, s), (lit. [17] -84.72 (3F, s), -110.78 (2F, s)).

*2-(Perfluoroethyl)-1,4-dimethoxybenzene (**3d**)*

Oil: IR (neat) 2958, 2842, 1057, 1200 cm^{-1}. ^{1}H NMR δ 3.79 (3H, s), 3.82 (3H, s), 6.94-6.97 (1H, m), 7.04-7.05 (2H, m). ^{13}C NMR δ 55.8, 56.6, 113.4 (tq, $^1J_{C-F}$ = 255.6 Hz, $^2J_{C-F}$ = 39.3 Hz), 114.1 (t, $^3J_{C-F}$ = 9.0 Hz), 114.2, 117.4(t, $^2J_{C-F}$ = 16.1 Hz), 118.5, 119.4 (qt, ${}^{1}J_{C\text{-}F}$ = 296.6, ${}^{2}J_{C\text{-}F}$ = 39.1 Hz), 152.4 (t, ${}^{3}J_{C\text{-}F}$ = 2.9 Hz), 153.2. ^{19}F NMR δ -84.4 (3F, s), -112.5 (2F, s). HRMS (EI) calcd for $C_{10}H_9F_5O_2$ (M^+) 256.05227, found 256.05179.

*2-(1,2,2,2-Tetrafluoroethyl)-1,4-dimethoxybenzene (**4d**)*

Oil: IR (neat) 2958, 2842, 1506, 1226, 1184 cm^{-1}. ^{1}H NMR δ 3.79 (3H, s), 3.82 (3H, s), 6.14 (1H, dt, *J* = 43.8, 6.1 Hz), 6.87 (1H, d, *J* = 9.0 Hz), 6.96 (1H, dd, *J* = 9.1, 3.2 Hz), 7.07 (1H, d, *J* = 2.8 Hz). ^{13}C NMR δ 55.6, 56.0, 82.9 (dq, ${}^{1}J_{C\text{-}F}$ = 182.1 Hz, ${}^{2}J_{C\text{-}F}$ = 35.6 Hz), 122.6 (dq, ${}^{2}J_{C\text{-}F}$ = 30.6 Hz, ${}^{1}J_{C\text{-}F}$ = 281.3 Hz), 112.0, 113.3 (d, J ${}^{3}J_{C\text{-}F}$ = 7.6 Hz), 116.7 (d, ${}^{4}J_{C\text{-}F}$ = 1.9 Hz), 119.5 (d, ${}^{2}J_{C\text{-}F}$ = 20.0 Hz), 151.4 (d, ${}^{3}J_{C\text{-}F}$ = 5.5 Hz), 153.7. ^{19}F NMR δ -79.31 (3F, dd, *J* = 13.4, 6.3 Hz), -198.77 (1F, dq, *J* = 43.8, 12.4 Hz). HRMS (EI) calcd for $C_{10}H_{10}F_4O_2$ (M^+) 238.06169, found 238.06115.

*9-(Perfluoroethyl)-1,2,3,4,5,6,7,8-octahydroanthracene (**3e**)*

Oil: IR (neat) 2937, 1200, 1146, 1033 cm^{-1}. ^{1}H NMR δ 1.71-1.72 (8H, m), 2.73-2.83 (8H, m), 6.98 (1H, s). ^{13}C NMR δ 21.87 (2C), 23.1 (2C, t, ${}^{3}J_{C\text{-}F}$ = 1.9 Hz), 27.3-27.5 (2C, m), 30.0 (2C), 117.0 (tq, ${}^{1}J_{C\text{-}F}$ = 256.5 Hz, ${}^{2}J_{C\text{-}F}$ = 39.1 Hz), 121.6 (qt, ${}^{1}J_{C\text{-}F}$ = 288.0 Hz, ${}^{2}J_{C\text{-}F}$ = 39.1 Hz), 124.8 (t, ${}^{2}J_{C\text{-}F}$ = 19.8 Hz), 133.9, 136.4 (2C), 137.0 (2C, t, ${}^{3}J_{C\text{-}F}$ = 2.6 Hz). ^{19}F NMR δ -83.61 (3F, t, *J* = 3.5 Hz), -99.65 (2F, s). HRMS (EI) calcd for $C_{16}H_{17}F_5$ (M^+) 304.12504, found 304.12414.

*9-(1,2,2,2-Tetrafluoroethyl)-1,2,3,4,5,6,7,8-octahydroanthracene (**4e**)*

Oil: IR (neat) 2935, 1274, 1180, 1138 cm^{-1}. ^{1}H NMR δ 1.68-1.83 (8H, m), 2.74 (8H, brs), 6.16 (1H, dt, *J* = 36.5, 7.5 Hz), 6.92 (1H, s). ^{13}C NMR δ 22.3 (2C), 23.2 (2C), 26.5-26.6 (2C), 29.8 (2C), 87.2 (dq, ${}^{1}J_{C\text{-}F}$ =187.2, ${}^{2}J_{C\text{-}F}$ = 35.3 Hz), 123.5 (dq, ${}^{2}J_{C\text{-}F}$ = 28.7 Hz, 283.4 Hz), 125.5 (2C, d, ${}^{3}J_{C\text{-}F}$= 16.5 Hz), 129.6, 132.5 (2C), 135.6. ^{19}F NMR δ -75.39 (3F, dd, *J* =13.4, 7.2 Hz), -196.47 (1F, dq, *J* = 43.9, 13.4 Hz), HRMS (EI) calcd for $C_{16}H_{18}F_4$ (M^+) 286.13446, found 286.13371.

*3-(Perfluoroethyl)benzo[b]thiophene (**3f**)*

Oil: IR (neat) 3112, 1332, 1202 cm^{-1}. ^{1}H NMR δ 7.42-7.49 (2H, m), 7.90-7.98 (3H, m). ^{13}C NMR δ 112.9 (tq, $^1J_{C-F}$ = 252.7 Hz, $^2J_{C-F}$ = 40.1 Hz), 119.2 (qt, $^1J_{C-F}$ = 286.4, $^2J_{C-F}$ = 39.1 Hz), 122.7, 123.2 (t, $^3J_{C-F}$ = 2.6 Hz), 124.1 (t, $^2J_{C-F}$ = 26.4 Hz), 125.2, 125.3, 130.8 (t, $^3J_{C-F}$ = 17.6 Hz), 135.1, 140.4. ^{19}F NMR δ -84.80 (3F, s), -110.83 (2F, s). HRMS (EI) calcd for $C_{10}H_5F_5S$ (M^+) 252.00321, found 252.00271.

*3-(1,2,2,2-Tetrafluoroethyl)benzo[b]thiophene (**4f**)*

Oil: IR (neat) 3086, 1278, 1187, 1147 cm^{-1}. ^{1}H NMR δ 6.00 (1H, dq, J = 44.0 Hz, J =6.1 Hz), 7.40-7.48 (2H, m), 7.74 (1H, d, J = 1.7 Hz), 7.85 (1H, d, J = 7.8 Hz), 7.90-7.92 (1H, m). ^{13}C NMR δ 85.0 (dq, $^1J_{C-F}$ =185.0 Hz, $^2J_{C-F}$ =36.2 Hz), 122.0, 122.3 (dq, $^2J_{C-F}$ = 29.4 Hz, $^1J_{C-F}$ = 281.3 Hz), 122.9, 124.9, 125.1, 125.2 (d, $^3J_{C-F}$ = 21.2 Hz), 128.6 (d, $^3J_{C-F}$ = 7.9 Hz), 136.6 (d, $^3J_{C-F}$ = 6.0 Hz), 140.2. ^{19}F NMR δ -78.21 (3F, dd, J = 13.4 Hz, 6.2 Hz), -192.95 (1F, dq, J = 43.8 Hz, J = 13.5 Hz). HRMS (EI) calcd for $C_{10}H_6F_4S$ (M^+) 234.01263, found 234.01224.

*1-(1,1,2,2,3,3-Hexafluoropropyl)naphthalene (**3g**)*

Oil: IR (neat) 3059, 1516, 1133 cm^{-1}. ^{1}H NMR δ 6.15 (1H, tt, J = 52.2, 5.5 Hz), 7.26-7.62 (3H, m), 7.80 (1H, d, J = 7.3 Hz), 7.91 (1H, d, J = 6.8 Hz), 8.05 (1H, J = 8.2 Hz), 8.24 (1H, d, J = 8.0 Hz). ^{13}C NMR δ 105.8 (tt, $^1J_{C-F}$ = 252.9 Hz, $^2J_{C-F}$ = 15.8 Hz), 110.7-114.1 (m), 117.8 (tt, $^1J_{C-F}$ =254.1 Hz, $^2J_{C-F}$ = 33.0 Hz), 124.2, 124.8 (t, $^2J_{C-F}$ = 21.7 Hz), 124.9-125.1 (m), 126.3, 127.5, 127.6 (t, $^3J_{C-F}$ = 9.8 Hz), 129.0, 130.2, 133.2, 134.1. ^{19}F NMR δ -106.09 (2F, t, J = 7.5 Hz), -129.34 to -129.38 (2F, m), -137.00 to -137.21 (2F, m). HRMS (EI) calcd for $C_{13}H_8F_6$ (M^+) 278.05302, found 278.05256.

*1-(1,1,2,2,3,3,4,4,5,5-Decafluoropentyl)naphthalene (**3h**)*

Oil: IR (neat) 1516, 1188, 1132 cm^{-1}. ^{1}H NMR δ 6.06 (1H, tt, *J* = 52.6, 5.3 Hz), 7.54-7.63 (3H, m), 7.83 (1H, d, *J* = 7.5 Hz), 7.93 (1H, d, *J* = 9.5 Hz), 8.06 (1H, d, *J* = 8.2 Hz), 8.23 (1H, d, *J* = 8.5 Hz). ^{13}C NMR δ 104.9-120.9 (5C, m), 124.2, 124.7(t, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 124.8-125.0 (m), 126.4, 127.6, 128.0 (t, $^{3}J_{C\text{-}F}$ =9.9 Hz), 129.0, 130.3, 133.4, 134.1. ^{19}F NMR δ -105.12 (2F, t, *J* = 6.6 Hz), -120.99 (2F, s), -123.64 (2F, s), -130.38 (2F, s), -137.66 (2F, dm, *J* = 51.9 Hz). HRMS (EI) calcd for $C_{15}H_8F_{10}$ (M^+) 378.04663, found 378.04593.

*5-(2,2,2-Trifluoro-1-hydroxyethyl)uracil (**6**)*

5-(2,2,2-Trifluoro-1-hydroxyethyl)uracil **6** was prepared by the modification of the reported procedure [13]. A mixture of uracil (3.37 g, 30 mmol) and trifluoroacetaldehyde ethyl hemiacetal (containing 10% EtOH) in DMF (18 mL) was stirred at 120 °C for 15 h. After cooling to room temperature, the mixture was poured into saturated aqueous NH_4Cl (30 mL) and extracted with AcOEt (20 mL X 3). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The remained solid was washed with acetone to give **6** (5.23 g, 83%) which was used for the next step without further purification.

*5-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)uracil (**7**)*

A mixture of crude **6** (5.23 g, 25 mmol) and hexanethiol (10 mL) in DMF (8 mL) was stirred under reflux for 48 h. After cooling to room temperature, volatile part was removed under reduced pressure. Purification by column chromatography (silica gel/hexane:acetone = 3:1) gave **7** (3.22 g) in 54% yield.

*5-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)-1-tosyluracil (**2i**)*

To a CH_3CN solution (5 mL) of **7** (467 mg, 1.5 mmol) was added *N,O*-bis(trimethylsilyl)acetamide (610 mg, 3 mmol) at room temperature under N_2

atmosphere. The mixture was stirred under reflux for 1h, and then cooled to 0 °C. To the mixture, TsCl (574 mg, 3 mmol) was added and the mixture was stirred under reflux for 24 h. After cooling to room temperature, a volatile part was removed under reduced pressure. Purification by column chromatography (silica gel / hexane:acetone = 3:1) gave **2i** (390 mg, 0.84 mmol) in 56% yield. White solid. Mp 120-121 °C. IR (KBr) 3060, 2931, 2857, 1738, 1685, 1261, 1194 cm^{-1}. ^{1}H NMR δ 0.89 (3H, t, J = 6.7 Hz), 1.28-1.42 (6H, m), 1.58-1.66 (2H, m), 2.48 (3H, s), 2.68-2.80 (2H, m), 4.56 (1H, q, J = 8.4 Hz), 7.40 (2H, d, J = 8.2 Hz), 7.96 (2H, d, J = 8.5 Hz), 8.27 (1H, s), 8.47 (1H, s). ^{13}C NMR δ 13.9, 21.8, 22.4, 28.2, 28.9, 31.2, 33.8, 41.5 (q, $^{2}J_{C\text{-}F}$ = 31.7 Hz), 110.4, 125.4 (q, $^{1}J_{C\text{-}F}$ = 279.2 Hz), 129.8 (2C), 129.9 (2C), 132.4, 137.3, 146.5, 147.2, 161.7. ^{19}F NMR δ -69.31 (3F, d, J = 8.1 Hz). HRMS (EI) calcd for $C_{19}H_{23}F_3N_2O_4S_2$ (M^+) 464.10513, found 464.10639.

*5-(Perfluoroethyl)-1-tosyluracil (**3i**)*

To IF_5 / Et_3N-3HF (250 mg, 0.65 mmol) in Teflon PFA bottle was added a CH_2Cl_2 solution (3 mL) of **2i** (198.5 mg, 0.43 mmol) at 0 °C and the mixture was stirred at room temperature for 24 h (complete consumption of **3** was confirmed from NMR analysis). To the reaction mixture, IF_5 / $5CH_2Cl_2$ (280 mg, 0.43 mmol) was added and the mixture was stirred at room temperature for another 24 h. Then, the mixture was poured into saturated aqueous $NaHCO_3$ (20 mL) and extracted with ether (30 mL X 3). The combined organic layer was washed with saturated aqueous $Na_2S_2O_3$ (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel / hexane:acetone = 3:1) gave **3i** (101 mg) in 61% yield. White solid. Mp 211-212 °C. IR (KBr) 3437, 1709, 1205, 1179 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 2.47 (3H, s), 7.51 (2H, d, J = 8.4 Hz), 8.04 (2H, d, J = 8.5 Hz), 8.54 (1H, s), 10.82 (1H, brs). ^{13}C NMR (acetone-d$_6$) δ 21.6, 104.8 (t, $^{2}J_{C-F}$ = 23.8 Hz), 112.8 (tq, $^{1}J_{C-F}$ = 255.6 Hz, $^{2}J_{C-F}$ = 41.0 Hz), 119.7 (qt, $^{1}J_{C-F}$ = 286.1, $^{2}J_{C-F}$ = 39.1 Hz), 130.6 (2C), 130.8 (2C), 133.6, 142.2 (t, $^{2}J_{C-F}$ = 10.4 Hz), 147.1, 148.1, 158.8 (t, $^{3}J_{C-F}$ = 1.8 Hz). ^{19}F NMR (acetone-d$_6$) δ -81.91 (3F, s), -111.94 (2F, s). HRMS (EI) calcd for $C_{13}H_8F_5N_2O_4S$ (M^+-1) 383.01304, found 383.01329.

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