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SYNTHESIS OF 4*H*-3,1-BENZOXAZINES BY THE REACTION OF *o*-(*N*-ACYLAMINO)BENZYL ALCOHOLS WITH DAST

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Abstract- The treatment of *o*-(*N*-acylamino)benzyl alcohols (**1**) with **DAST** afforded the dehydrative cyclization product, 4*H*-3,1-benzoxazines (**4**) and the hydroxy replacement product, *o*-(*N*-acylamino)benzyl fluorides (**5**). The yields of benzoxazines (**4**) and fluorides (**5**) depend on the substituents at α-position and acyl groups. The treatment of α,α-diaryl-*o*-(*N*-acylamino)benzyl alcohols (**1a-c**) with **DAST** yielded benzoxazines (**4a-c**) exclusively, while that of α-monosubstituted *o*-(*N*-acylamino)benzyl alcohols (**1d-k**) with **DAST** yielded benzoxazines (**4d-k**) and fluorides (**5d-k**). In the reaction of *o*-(*N*-acylamino)benzyl alcohol (**1l**) with **DAST**, the formation of fluoride (**5l**) became predominant and that of benzoxazine (**4l**) was suppressed almost completely.

INTRODUCTION

The 1,3-thiazines[1] and 1,3-oxazines[1a,2] are a class of heterocycles that have received considerable attention due to their interesting activities and many reports on the synthesis of them have been appeared. Recently we reported the facile syntheses of the sulfur-containing six-membered heterocycles such as 1,3-thaizines[3] and 3,1-benzothiazines[4] by the reaction of 3-*N*-acylamino alcohols with Lawesson's reagent [(2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane 2,4-disulfide: **LR**). For example, treatment of *o*-(*N*-acylamino)benzyl alcohols (**1**) with **LR** yielded 4*H*-3,1-benzothiazines (**2**) together with a small amount of the corresponding thiols (**3**) (Scheme 1). Diethylaminosulfur trifluoride (SF_3NEt_2: **DAST**), an important and powerful fluorinating and hydroxy activating reagent[5] is applied to the synthesis of

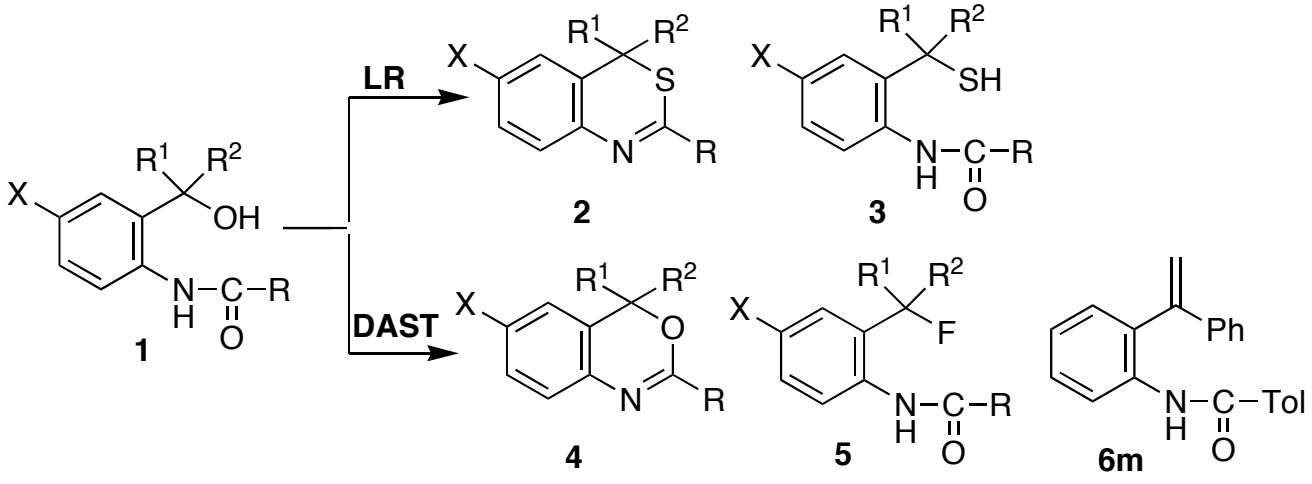
Dedicated to Professor B. M. Trost on the occasion of his 65th birthday.

oxazolines from 1,2-acetamido alcohols.[6] To extend the usage of **DAST** to other multifunctional substrates leading to the synthesis of benzoxazines, we have investigated the reaction between *o*-(*N*-acylamino)benzyl alcohols (**1**) and **DAST** and our results are described in this paper.

RESULTS AND DISCUSSION

For optimization, α-phenyl-[*o*-(*N*-toluoylamino)]benzyl alcohol (**1e**) was chosen as a substrate and its reaction with **DAST** was examined under various reaction conditions (Table 1). The treatment of **1e** (1 mmol) and **DAST** (2 mmol) in dichloromethane at -78°C for 1 h under argon gave the dehydrative cyclization product, 3,1-benzoxazine (**4e**) and the hydroxy replacement product, fluoride derivative (**5e**) in 63 and 27% yields, respectively (Scheme 1 and Table1, Entry 1). The yield of **4e** decreased with reducing the amount of **DAST** (Entries 1-3). Among the solvents examined such as dichloromethane, benzene and THF, dichloromethane was revealed to be the solvent of choice (Entries 5, 7-8). The reaction temperature effected alteration of the product ratio. At higher temperature, the yield of **4e** decreased while that of **5e** increased (Entries 1, 4-6).

Scheme 1



The reactions of various *o*-(*N*-acylamino)benzyl alcohols (**1**) with **DAST** were carried out using the reaction conditions in Entry 1. Benzoxazines (**4a-c**) were obtained exclusively in high yields when α,α-diaryl-*o*-(*N*-acylamino)benzyl alcohols (**1a-c**) were treated with **DAST** (Table 2, Entries 1-3). Similarly, the treatment of α-monosubstituted *o*-(*N*-acylamino)benzyl alcohols (**1d-k**) with **DAST** gave benzoxazines (**4d-k**) and the corresponding fluorides (**5d-k**), respectively (Entries 4-11). The benzoxazine (**4e**) could not be derived from fluoride (**5e**) since the treatment of **5e** with **DAST** did not afford **4e** under the above reaction conditions (Scheme 2). In these cases, fluorination of **1d-k** competes with the formation of benzoxazines (**4d-k**). The treatment of *o*-(*N*-toluoylamino)benzyl alcohol (**1l**) without substituent at its α-position with **DAST** yielded the corresponding fluoride (**5l**) predominantly together

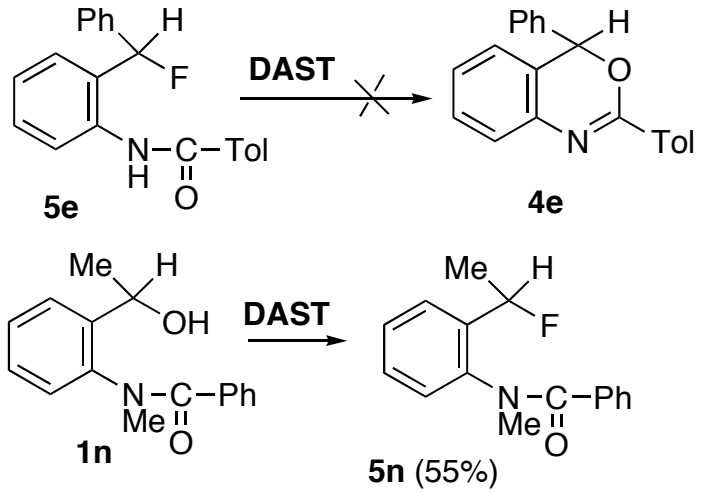
with a small amount of benzoxazine (**4l**) (Entry 12). The treatment of 1-phenyl-1-[*o*-(*N*-toluoylamino)phenyl]ethanol (**1m**) with **DAST** gave benzoxazine (**4m**), fluoride (**5m**) and the dehydration product, 1,1-diarylethylene derivative (**6m**) (Entry 13). Treatment of 1-[*o*-(*N*-methyl-*N*-benzoylamino)phenyl]ethanol (**1n**) with **DAST** gave fluoride (**5n**) as the sole product (Scheme 2).

Table 1. Yields of benzoxazine (**4e**) and fluoride (**5e**) derived from **1e** under various conditions[a]

Entry			Molar ratio	Yield (%)		
	Temp (°C)	Solvent	**DAST/1e**	**4e**	**5e**	
1	-78	CH_2Cl_2	2	63	27	
2	-78	CH_2Cl_2	1	53	24	
3	-78	CH_2Cl_2	0.5	14	3	(63)[b]
4	-38	CH_2Cl_2	2	60	39	
5	0	CH_2Cl_2	2	40	46	
6	rt	CH_2Cl_2	2	29	65	
7	0	Benzene	2	39	59	
8	0	THF	2	28	18	(49)[b]

[a]Reaction time: 1 h. [b]Recovery of **1e**.

Scheme 2

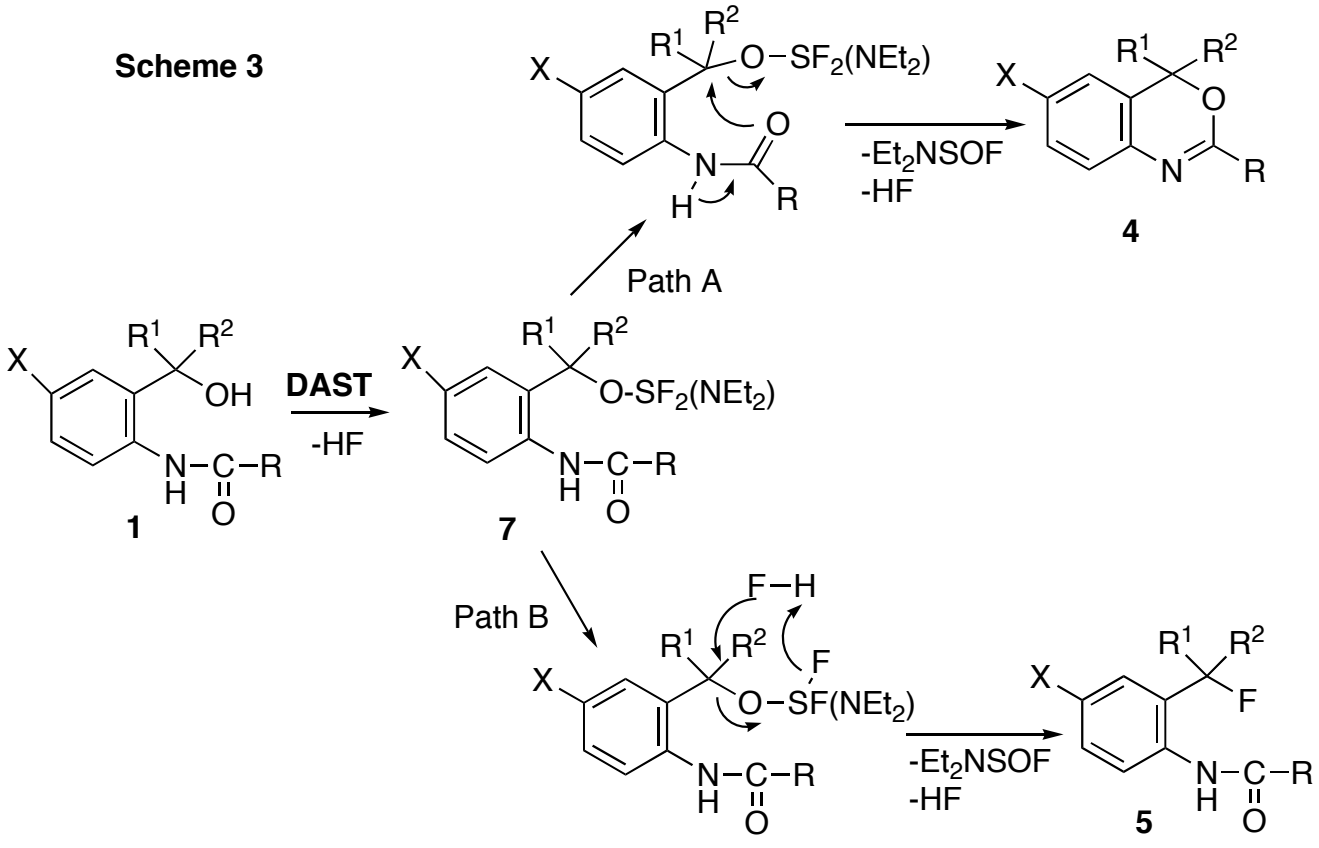


A reasonable mechanism for the formation of benzoxazines (**4**) and fluorides (**5**) is depicted in Scheme 3. Initially, *o*-(*N*-acylamino)benzyl alcohols (**1**) react with **DAST** to give the intermediate (**7**) which could either yield benzoxazines (**4**) by an intramolecular cyclization through a nucleophilic substitution with the amide carbonyl oxygen (path A) or yield fluorides (**5**) through the normal fluorinating mechanism (Path B).[7]

Table 2. Yields of products (**4-6**)

Entry		R	R^1	R^2	X	Isolated Yield (%) **4**	**5**	**6**
1	**1a**	*p*-Tol	Ph	*p*-Tol	H	96	0	
2	**1b**	*p*-Tol	Ph	Ph	H	90	0	
3	**1c**	Me	Ph	Ph	H	84	0	
4	**1d**	Ph	Ph	H	H	50	39	
5	**1e**	*p*-Tol	Ph	H	H	63	27	
6	**1f**	*p*-Tol	Ph	H	Cl	50	41	
7	**1g**	*p*-ClC_6H_4	Ph	H	H	66	26	
8	**1h**	*p*-$MeOC_6H_4$	Ph	H	H	76	3	
9	**1i**	*t*-Bu	Ph	H	H	53	40	
10	**1j**	*p*-Tol	Me	H	H	42	47	
11	**1k**	*t*-Bu	Me	H	H	47	45	
12	**1l**	*p*-Tol	H	H	H	3	60	
13	**1m**	*p*-Tol	Ph	Me	H	28	47	28

Scheme 3



EXPERIMENTAL

Flash column chromatography was carried out with silica gel Wakogel C-300. Melting points and boiling points were determined on a Yanaco micro melting-point apparatus (MP-J3) and a Shibata glass tube oven distillation apparatus (GTO-350RD), respectively, and are uncorrected. IR spectra were recorded on a JASCO FT/IR-300 spectrophotometer, in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX-270 (270 MHz) or VARIAN GEMINI 200 (200 MHz); measured in $CDCl_3$ using TMS as an internal standard. ^{19}F-NMR spectra were recorded on a JEOL LAMDA-400 (400 MHz) in $CDCl_3$ using $CFCl_3$ as an internal standard; δ values in ppm, *J* values in Hz.

Reaction of *o*-(*N*-acylamino)benzyl alcohols (1) with DAST: A typical experimental procedure. The *o*-(*N*-acylamino)benzyl alcohol (**1**) (1 mmol) dissolved in CH_2Cl_2 (10 mL) was cooled at -78°C, unless otherwise noted, under argon and **DAST** (2 eq. molar) was slowly added by means of a syringe. After completion of the reaction (~1 h, by TLC), The reaction mixture was hydrolyzed with crushed ice added with 28 % NH_4OH (30 mL). The aqueous layer was then extracted with CH_2Cl_2, the combined organic layers dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatograhed with toluene-ethyl acetate (19:1-4:1) to give products (**4-6**). The structures of 4,4-diphenyl-2-(*p*-tolyl)-4*H*-3,1-benzoxazine (**4b**) and 1-phenyl-1-[2-(*N*-*p*-toluoylamino)phenyl]ethylene (**6m**) were confirmed by direct comparison of their spectral data cited in the literature.[3]

4-Phenyl-2,4-di-(*p*-tolyl)-4*H*-3,1-benzoxazine (4a): mp 152-153°C ($CHCl_3$-hexane): ^{1}H-NMR δ 2.27 (3H, *s*), 2.32 (3H, *s*), 6.72 (1H, *dd*, *J*=1.2, 7.6), 7.03-7.42 (14H, *m*), 8.10 (2H, *d*, *J*=8.2); ^{13}C-NMR δ 20.6, 21.1, 85.5, 156.5 in addition to aromatic carbon peaks. Anal. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60. Found: C, 86.57; H, 6.17; N, 3.59.

4,4-Diphenyl-2-methyl-4*H*-3,1-benzoxazine (4c): mp 136-137.5°C ($CHCl_3$-hexane): ^{1}H-NMR δ 2.15 (3H, *s*), 6.67 (1H, *dd*, *J*=1.4, 7.6), 7.04-7.35 (13H, *m*); ^{13}C-NMR δ 21.6, 84.4, 157.5 in addition to aromatic carbon peaks. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.96; H 5.88; N, 4.62.

2,4-Diphenyl-4*H*-3,1-benzoxazine (4d): mp 112-114°C ($CHCl_3$-hexane) (lit.,[8] mp 114°C): ^{1}H-NMR δ 6.41 (1H, *s*), 6.82 (1H, *d*, *J*=7.4), 7.04-7.48 (13H, *m*), 8.12 (1H, *dd*, *J*=1.4, 8.2); ^{13}C-NMR δ 95.8, 164.8 in addition to aromatic carbon peaks.

***N*-Benzoyl-2-(α-fluorobenzyl)aniline (5d):** mp 70-71°C ($CHCl_3$-hexane); IR (KBr) 3294, 1651; ^{1}H-NMR δ 6.64 (1H, *d*, *J*=47.8), 7.19-7.61 (14H, *m*), 8.26 (1H, *d, J*=8.2); ^{13}C-NMR δ 92.7 (*d*, *J*=332), 164.8 in addition to aromatic carbon peaks. Anal. Calcd for $C_{20}H_{16}NOF$: C, 78.68; H, 5.28; N, 4.59. Found: C, 78.85; H, 4.95; N, 4.68.

4-Phenyl-2-*p*-tolyl-4*H*-3,1-benzoxazine (4e): mp 155-156°C ($CHCl_3$-hexane) (lit.,[8] mp 158°C); ^{1}H-NMR δ 2.37 (3H, *s*), 6.40 (1H, *s*), 6.82 (1H, *d*, *J*=7.4), 7.08-7.35 (10H, *m*), 8.01 (2H, *d*, *J*=8.2); ^{13}C-NMR δ 21.0,

75.8, 156.0 in addition to aromatic carbon peaks.

***N*-*p*-Toluoyl-2-(α-fluorobenzyl)aniline (5e):** mp 112-114°C ($CHCl_3$-hexane); IR (KBr) 3281, 1643; ^{1}H-NMR δ 2.39 (3H, *s*), 6.67 (1H, *d*, *J*=47.8), 7.18-7.51 (13H, *m*), 8.32 (1H, *d, J*=8.2); ^{13}C-NMR δ 21.3, 94.9 (*d*, *J*=352), 176.4 in addition to aromatic carbon peaks.

6-Chloro-4-phenyl-2-*p*-tolyl-4*H*-3,1-benzoxazine (4f): mp 181.5-183°C ($CHCl_3$-hexane); ^{1}H-NMR δ 2.37 (3H, *s*), 6.34 (1H, *s*), 6.79 (1H, *s*), 7.17-7.59 (9H, *m*), 7.99 (2H, *d*, *J*=8.4); ^{13}C-NMR δ 21.0, 77.4, 156.7 in addition to aromatic carbon peaks. Anal. Calcd for $C_{21}H_{16}NOCl$: C, 75.55; H, 4.83; N, 4.19. Found: C, 75.26; H, 5.05; N, 4.19.

***N*-*p*-Toluoyl-4-chloro-2-(α-fluorobenzyl)aniline (5f):** mp 141-143°C ($CHCl_3$-hexane); IR (KBr) 3284, 1641; ^{1}H-NMR δ 2.39 (3H, *s*), 6.63 (1H, *d*, *J*=47.9), 7.17-7.48 (11H, *m*), 8.15 (1H, br *s*), 8.24 (1H, *d, J*=8.8); ^{13}C-NMR δ 21.4, 93.9 (*d*, *J*=336), 165.0 in addition to aromatic carbon peaks. ^{19}F-NMR δ -166.2 (1F, *dd*, *J*=6.0, 41.9). Anal. Calcd for $C_{21}H_{16}NOClF$: C, 71.28; H, 4.84; N, 3.96. Found: C, 71.11; H, 5.05; N, 3.98.

2-*p*-Chlorophenyl-4-phenyl-4*H*-3,1-benzoxazine (4g): mp 117.5-118.5°C ($CHCl_3$-hexane); ^{1}H-NMR δ 6.39 (1H, *s*), 6.80 (1H, *d*, *J*=7.4), 7.07-7.50 (10H, *m*), 8.12 (2H, *dd*, *J*=1.4, 8.0); ^{13}C-NMR δ 77.9, 155.3 in addition to aromatic carbon peaks. Anal. Calcd for $C_{20}H_{14}NOCl$: C, 75.12; H, 4.14; N, 4.38. Found: C, 75.26; H, 4.05; N, 4.29.

***N*-*p*-Chlorobenzoyl-2-(α-fluorobenzyl)aniline (5g):** mp 116-117.5°C ($CHCl_3$-hexane); IR (KBr) 3276, 1643; ^{1}H-NMR δ 6.66 (1H, *d*, *J*=47.8), 7.26-7.51 (13H, *m*), 8.29 (1H, *d, J*=8.2); ^{13}C-NMR δ 95.5 (*d*, *J*=333), 164.1 in addition to aromatic carbon peaks. Anal. Calcd for $C_{13}H_{18}NOF$: C, 69.98; H, 8.13; N, 6.28. Found: C, 69.71; H, 7.83; N, 6.28.

2-*p*-Methoxyphenyl-4-phenyl-4*H*-3,1-benzoxazine (4h): mp 112-114°C ($CHCl_3$-hexane) (lit.,[8] 112-114°C): ^{1}H-NMR δ 3.79 (3H, *s*), 6.37 (1H, *s*), 6.88 (1H, *d*, *J*=8.8), 7.05-7.38 (10H, *m*), 8.07 (2H, *dd*, *J*=2.0, 7.2); ^{13}C-NMR δ 54.8, 77.7, 161.8 in addition to aromatic carbon peaks.

***N*-*p*-Methoxybenzoyl-2-(α-fluorobenzyl)aniline (5h):** mp 120-122°C ($CHCl_3$-hexane); IR (KBr) 3291, 1654; ^{1}H-NMR δ 3.82 (3H, *s*), 6.46 (1H, *d*, *J*=30.6), 6.78-8.31 (13H, *m*); ^{13}C-NMR δ 55.7, 93.9 (*d*, *J*=315), 170.7 in addition to aromatic carbon peaks.

2-*tert*-Butyl-4-phenyl-4*H*-3,1-benzoxazine (4i): mp 82.5-84°C ($CHCl_3$-hexane); ^{1}H-NMR δ 1.16 (9H, *s*), 6.22 (1H, *s*), 6.77 (1H, *d*, *J*=7.8), 7.06-7.39 (8H, *m*); ^{13}C-NMR δ 26.8, 36.7, 77.2, 167.3 in addition to aromatic carbon peaks. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.47; H, 7.11; N, 5.32.

***N*-Pivaloyl-2-(α-fluorobenzyl)aniline (5i):** mp 91-92°C ($CHCl_3$-hexane); IR (KBr) 3303, 1647; ^{1}H-NMR δ 1.04 (9H, *s*), 6.59 (1H, *d*, *J*=7.0, 48.3), 7.06-7.48 (8H, *m*), 7.81 (1H, br *s*), 8.20 (1H, *d*, *J*=8.4); ^{13}C-NMR δ 26.5, 38.9, 95.3 (*d*, *J*=329), 175.9 in addition to aromatic carbon peaks. ^{19}F-NMR δ -164.7 (1F, *dd*, *J*=7.0, 47.5). Anal. Calcd for $C_{18}H_{20}NOF$: C, 75.76; H, 7.07; N, 4.91. Found: C75.48; H, 7.13; N, 4.92

4-Methyl-2-*p*-tolyl-4*H*-3,1-benzoxazine (4j): mp 157-158°C ($CHCl_3$-hexane); ^{1}H-NMR δ 1.67 (3H, *d*, *J*=6.6), 2.42 (3H, *s*), 5.56 (1H, *q*, *J*=6.6), 7.00-7.38 (6H, *m*), 8.04 (2H, *d*, *J*=8.2); ^{13}C-NMR δ 20.6, 21.0, 72.2, 156.6 in addition to aromatic carbon peaks. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.18; N, 5.90. Found: C, 80.68; H, 6.18; N, 5.71.

***N*-*p*-Toluoyl-2-(α-fluoroethyl)aniline (5j)**: mp 115-116°C ($CHCl_3$-hexane); IR (KBr) 3236, 1642; ^{1}H-NMR δ 1.75 (3H, *dd*, *J*=6.6, 47.3), 2.43 (3H, *s*), 5.83 (1H, *dq*, *J*=6.6, 24.1), 7.14-7.45 (5H, *m*), 7.81 (2H, *d*, *J*=8.2), 8.23 (1H, *d*, *J*=8.2), 8.70 (1H, br *d*, *J*=10.2); ^{13}C-NMR δ 26.5, 38.9, 92.2 (*d*, *J*=318), 175.9 in addition to aromatic carbon peaks. ^{19}F-NMR δ -164.3 (1F, *ddq*, *J*=10.2, 24.1, 47.3). Anal. Calcd for $C_{16}H_{16}NOF$: C, 74.68; H, 6.27; N, 5.44. Found: C, 74.39; H, 6.02; N, 5.55.

2-*tert*-Butyl-4-methyl-4*H*-3,1-benzoxazine (4k): mp 91.5-93°C ($CHCl_3$-hexane); ^{1}H-NMR δ 1.25 (9H, *s*), 1.48 (3H, *d*, *J*=6.6), 5.31 (1H, *q*, *J*=6.6), 6.92 (1H, *d*, *J*=7.2), 7.07-7.33 (3H, *m*); ^{13}C-NMR δ 21.2, 26.9, 36.6, 71.6, 167.6 in addition to aromatic carbon peaks. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.37; N, 7.32. Found: C, 75.05; H, 8.27; N, 7.16.

***N*-Pivaloyl-2-(α-fluoroethyl)aniline (5k):** mp 85-86.5°C ($CHCl_3$-hexane); IR (KBr) 3447, 1654; ^{1}H-NMR δ 1.32 (9H, *s*), 1.74 (3H, *dd*, *J*=6.4, 47.5), 5.73 (*dq*, *J*=6.4, 47.5), 7.04-7.38 (4H, *m*), 8.09 (1H, *d*, *J*=8.0), 8.21 (br *d*, *J*=10.8); ^{13}C-NMR δ 20.3 (*d*, *J*=23.9), 27.6, 39.7, 92.1 (*d*, *J*=319), 176.8 in addition to aromatic carbon peaks. ^{19}F-NMR δ -164.6 (1F, *ddq, J*=10.8, 24.1, 47.5). Anal. Calcd for $C_{13}H_{18}NOF$: C, 69.93; H, 8.13; N, 6.28. Found: C, 69.71; H, 7.83; N, 6.53.

2-*p*-Tolyl-4*H*-3,1benzoxazine (4l): mp 102-104°C ($CHCl_3$-hexane) (lit.,[9] 104-105.5 °C): ^{1}H-NMR δ 2.39 (3H, *s*), 5.34 (2H, *s*), 6.98 (1H, *d*, *J*=7.4), 7.11-7.34 (5H, *m*), 8.02 (2H, *d*, *J*=8.2).

***N*-*p*-Toluoyl-2-fluoromethylaniline (5l):** mp 82.5-84°C ($CHCl_3$-hexane); IR (KBr) 3288, 1649; ^{1}H-NMR δ 2.43 (3H, *s*), 5.48 (2H, *d*, *J*=48.3), 7.13-7.48 (5H, *m*), 7.80 (2H, *d*, *J*=8.0), 8.14 (1H, *d*, *J*=7.8), 8.45 (1H, br *s*); ^{13}C-NMR δ 20.9, 83.6 (*d*, *J*=318), 164.9 in addition to aromatic carbon peaks. ^{19}F-NMR δ -5.9 (1F, *dt*, *J*=4.7, 48.3). Anal. Calcd for $C_{15}H_{14}NOF$: C, 73.84; H, 6.05; N, 5.79. Found: C, 74.05; H, 5.80; N, 5.76.

4-Methyl-4-*p*-tolyl-2-phenyl-4*H*-3,1-benzoxazine (4m): bp 210°C (3 mmHg); ^{1}H-NMR δ 2.15 (3H, *s*), 2.34 (3H, *s*), 7.08-7.39 (13H, *m*), 8.09 (2H *d*, *J*=8.2). ^{13}C-NMR δ 21.0, 27.3, 80.6, 164.8 in addition to aromatic carbon peaks. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.25; H, 6.37; N, 4.67.

***N*-*p*-Toluoyl-[(α-fluoro-α-phenyl)ethyl]aniline (5m):** mp 148-150°C; IR (KBr) 3265, 1646; ^{1}H-NMR δ 2.07 (3H, *s*), 2.348 (3H, s), 7.00-7.56 (13H, *m*), 8.09 (2H *d*, *J*=8.2). Anal. Calcd for $C_{22}H_{20}NOF$: C, 79.25; H, 6.05; N, 4.20. Found: C, 79.39; H, 6.39; N, 4.14

***N*-Benzoyl-*N*-methyl-2-(α-fluoroethyl)aniline (5n):** mp 142.5-144°C ($CHCl_3$-hexane); IR(KBr) 1639; ^{1}H-NMR δ 1.69 (3H, *dd*, *J*=6.6, 23.7), 3.79 (3H, *s*), 5.63 (*dq*, *J*=6.6, 46.2), 7.04-7.58 (9H, *m*); ^{13}C-NMR δ 19.9 (*d*, *J*=24.7), 29.6, 88.0 (*d*, *J*=334), 160.4 in addition to aromatic carbon peaks. ^{19}F-NMR δ -174.5 (1F,

dq, *J*=23.7, 46.2). Anal. Calcd for $C_18H_{17}NOF$: C, 74.39; H, 6.63; N, 5.42. Found: C, 74.49; H, 6.37; N, 5.76.

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