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A Convenient Preparation of Fluorinating Reagent F-TEDA Bearing Bisphenylsulfonylimide Counterion and Its Fluorination to Oxindoles

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The direct preparation of a kind of fluorinating reagent **1** [F-TEDA-N($SO_2Ph)_2$] was realized in high yield via the complexation of *N*-fluorobenzenesulfonimide (NFSI) with 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium *N*′,*N*′-bis-(benzenesulfonylimide) salt. In its fluorination to oxindoles, the fluorinating products **6** were afforded in moderate to high yields.

Keywords fluorinating reagent, fluorination, oxindoles

Introduction

Both Selectfluor and NFSI are important and commercial N-F fluorinated reagents. A lot of literatures have demonstrated their applications[1-4] in chemical, pharmaceutical, agricultural and material fields. For broadening the more extensive applications and meeting the more effective requirements, new N-F reagents were continually reported[5] and developing novel N-F reagents is still meaningful.

We envision that a kind of N-F compounds bearing both Selectfluor and NFSI fragments might display their common properties. According to this idea, a N-F compound structurally containing bisphenylsulfonylimide and triethylenediamine **1** [F-TEDA-N($SO_2Ph)_2$] is designed (Structure **A** in Figure 1), where the F atom lies between two nitrogen atoms and a N-F-N three-center-four-electron bond is formed, then naturally it displays common chemical characteristics of NFSI and Selectfluor, or F-TEDA-N($SO_2Ph)_2$ might exist in a salt form (Structure **B** in Figure 1), and if so, it will behave more like Selectfluor than NFSI.

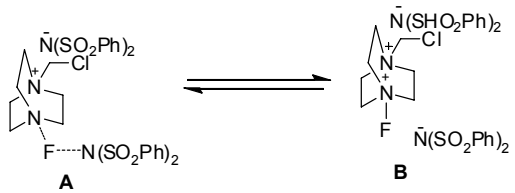

Figure 1 Designed complex structure containing the skeleton of Selectfluor and NFSI.

Results and Discussion

Herein, according to Scheme 1, the preparation route for the designed fluorinating reagent F-TEDA-N($SO_2Ph)_2$ is tried. Starting from **2**, intermediates **3**, **4** were achieved conveniently in high yields. After that, the reaction of **4** with NFSI was tried in various solvents. As shown in Table 1, no product was detected in CH_2Cl_2, DMF, EA, EtOH, *i*-PrOH, MTBE, THF and H_2O (Entries 1—8); while in MeOH, ^{19}F NMR monitoring shows that F-TEDA-N($SO_2Ph)_2$ was achieved in 11% yield after stirring for 8 d (Entry 9). Fortunately, F-TEDA-N($SO_2Ph)_2$ was afforded in 83% monitored yield in MeCN for 8 d (Entry 10).

Then the starting material ratios were screened. Monitored ^{19}F NMR exposed that starting material ratio

Scheme 1 Preparation route for **1** [F-TEDA-N($SO_2Ph)_2$] from NFSI

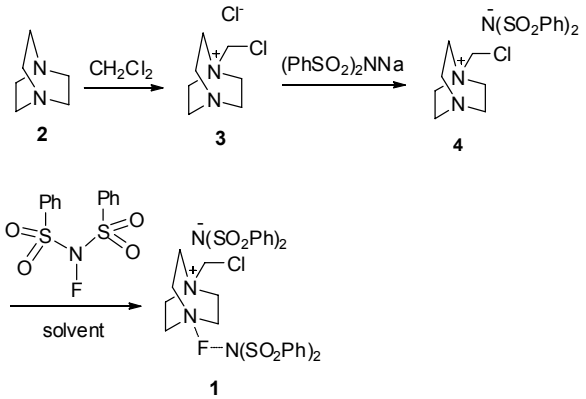

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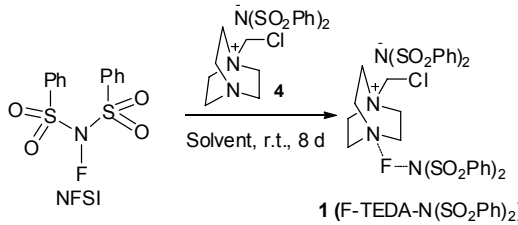
Table 1 Preparation of **1** via the reaction of **4** with NFSI in various solvents



Entry	Solvent	^{19}F NMR[a]	**1**[b]/%
1	CH_2Cl_2	−39, −111	N.d
2	DMF	−39, −111	N.d
3	EA	−39, −111	N.d
4	EtOH	+39, −39, −111	N.d
5	*i*-PrOH	−49, −92, −111	N.d
6	MTBE	−39, −111	N.d
7	THF	−39, −111,−150	N.d
8	H_2O	−39, −111	N.d
9	MeOH	+49, +39, −39, −100, −111	11
10	CH_3CN	49, −39, −111	83[c]

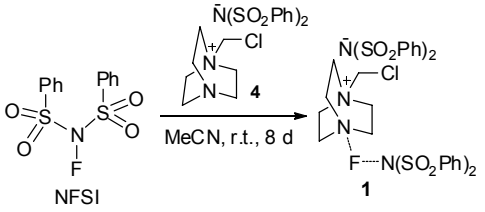
[a] NFSI (35 mg, 0.11 mmol), 5 mL of solvent and **4** (50 mg, 0.11 mmol) were added into a flask under stirring, then the reaction system was stirred at room temperature for 8 d. The mixture system was monitored by ^{19}F NMR and gave the monitored yields. [b] The monitored yield was calculated by the peak area of F-TEDA-N$(SO_2Ph)_2$ divided by the total peak area of all peaks. [c] NFSI is consumed almost completely with the peak area ratio of F-TEDA-N$(SO_2Ph)_2$: NFSI = 1 : 0.02 in the ^{19}F NMR spectra.

of **4** : NFSI changed from 1 : 1 to 10 : 1 which led to complete conversion of NFSI to F-TEDA-N$(SO_2Ph)_2$ (Entries 1−5 in Table 2). ^{1}H NMR monitoring indicated that ratio of **4** : NFSI changed from 1 : 1 to 1 : 20 resulting in 92% conversion of compound **4** to F-TEDA-N$(SO_2$-Ph$)_2$ (Entries 5, 10 in Table 2).

In the ^{19}F NMR of F-TEDA-N$(SO_2Ph)_2$ (Figure 2), chemical shift of fluorine atom was presented at δ 49, which was very close to the site of Selectfluor (δ 48) but far away from that of NFSI (δ −39). It demonstrated that compound F-TEDA-N$(SO_2Ph)_2$ will act more like Selectfluor. Solubility test showed that F-TEDA-N$(SO_2Ph)_2$ was resolved easily in H_2O, MeCN and MeOH, slightly in CH_2Cl_2, but not in EA. The melting point and DSC test indicated F-TEDA-N$(SO_2$ Ph$)_2$ will begin to melt at 137 ℃ and decompose at 139 ℃.

Furthermore, experiments were made to explore the fluorinating ability of F-TEDA-N$(SO_2Ph)_2$. 3-Phenyl-2-oxindoles (**5**) were chosen to react with F-TEDA-N$(SO_2Ph)_2$ in the presence of $(DHQD)_2$ANQ (Table 3).[6] Except that **5g** (R^5 = Me, Entry 9) and **5k** (R^2 = *p*-MeC_6H_4 and R^3 = Me Entry 13) gave the correspond ing products **6g** and **6k** in lower yields, other substrates afforded **6** in good yields. Enantioselectivities were tested, however the results were bad.

Table 2 Preparation of **1** from the reaction of **4** with NFSI in various ratios



Entry	**4** : NFSI[a]	Yield[b]/%	Yield[c]/%
1	10 : 1	0.14	100
2	5 : 1	7	98
3	2 : 1	34	91
4	1.5 : 1	47	85
5	1 : 1	67	83
6	1 : 1.5	73	58
7	1 : 2	73	43
8	1 : 5	82	13
9	1 : 10	92	7
10	1 : 20	92	5

[a] Reaction underwent at room temperature for 8 d. [b] The monitored yield was calculated by the peak area of $ClCH_2$ in F-TEDA-N$(SO_2Ph)_2$ (δ 5.42) divided by the peak area of $ClCH_2$ in **4** (δ 5.08) in ^{1}H NMR. [c] The monitored yield was calculated by the peak area of F-TEDA-N$(SO_2Ph)_2$ divided by the total peak area of all peaks in ^{19} F NMR.

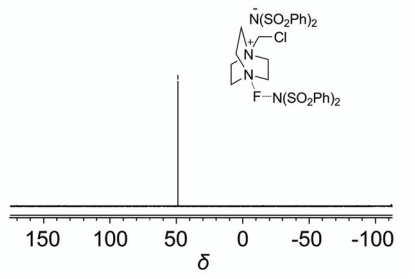
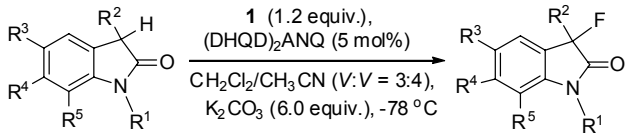


Figure 2 The ^{19}F NMR spectra of compound **1**.

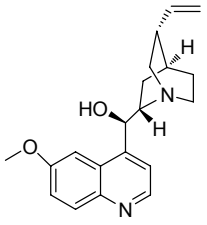
Conclusions

In conclusion, a kind of Selectfluor with two $(PhSO_2)_2N^-$ as counterions was synthesized via a convenient complexation between NFSI and 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium *N*′,*N*′-bis-(benzenesulfonimide) salt in a high yield. Preliminary experiments demonstrated that F-TEDA-N$(SO_2Ph)_2$ exhibited its properties similar to commercial Selectfluor. It is the first report of the preparation of Selectfluor bearing bisphenylsulfonylimide counterion. It is also an example of preparing a stronger fluorinating reagent from a weaker fluorinating reagent. The fluorination of oxindoles with F-TEDA-N$(SO_2Ph)_2$ afforded fluorinating products **6** in moderate to high yields similar to Selectfluor and NFSI. Further study on the application of

Table 3 Fluorination of 2-oxindines (**5**) with **1**



5 **6**



(DHQD)$_2$ANQ

Entry	**5** (R^1/R^2/R^3/R^4/R^5)	Condition[a]	Yield (*ee*)/% of **6**[b,c]
1	**5a** (BOC/C_6H_5/H/H/H)	Selectfluor, 96 h	72 (62)
2	**5a** (BOC/C_6H_5/H/H/H)	NFSI, 48 h	66 (77)
3	**5a** (BOC/C_6H_5/H/H/H)	**1**, 96 h	74 (55)
4	**5b** (BOC/*p*-MeC_6H_4/H/H/H)	**1**, 48 h	74 (6)
5	**5c** (BOC/C_6H_5/H/Cl/H)	**1**, 48 h	82 (4)
6	**5d** (BOC/*p*-FC_6H_4/F/H/H)	**1**, 48 h	79 (33)
7	**5e** (BOC/*p*-OMeC_6H_4/H/H/H)	**1**, 48 h	71 (30)
8	**5f** (BOC/C_6H_5/F/H/H)	**1**, 48 h	76 (31)
9	**5g** (BOC/C_6H_5/H/H/Me)	**1**, 48 h	66 (37)
10	**5h** (BOC/*p*-FC_6H_4/H/H/H)	**1**, 24 h	82 (23)
11	**5i** (BOC/C_6H_5/Me/H/H)	**1**, 24 h	81(23)
12	**5j** (BOC/*β*-naphthyl/H/H/H)	**1**, 24 h	80 (31)
13	**5k** (BOC/*p*-MeC_6H_4/Me/H/H)	**1**, 48 h	69 (55)

[a] Compound **5** (0.16 mmol), F-TEDA-N(SO_2Ph)$_2$ (0.18 mmol), K_2CO_3 (0.97 mmol) were resolved in CH_2Cl_2 and MeCN (*V*∶*V*=4∶3, 6 mL) at −78 ℃ till TLC indicated that the reaction was complete. [b] Separated yields. [c] The absolute configurations of **6** were determined by comparison with HPLC data in the literature.

F-TEDA-N(SO_2Ph)$_2$ is in progress.

Experimental

General information

All the starting chemicals were commercially available and used without further purification, fluorinating reagents NFSI and Selectfluor were purchased from Shanghai Science Bio-pharmaceutical Co. Ltd. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz instrument. Flash column chromatography was performed using silica gel (300−400 mesh). Melting points were uncorrected.

Preparation of 1-(chloromethyl)-1,4-diazabicyclo-[2.2.2]octan-1-ium chloride (3) from TEDA (2)

TEDA (2.5 g, 22.3 mmol) and CH_2Cl_2 (45 mL) were added into a 100 mL three-neck glass flash, then refluxed for 2 h. The mixture was filtered after being cooled and the filtered cake was washed with CH_2Cl_2 for two times. Compound **3** (3 g) was gotten in 75% yield. A white solid; ^{1}H NMR (D_2O, 400 MHz) *δ*: 5.01 (s, 2H), 3.47−3.43 (m, 6H), 3.17−3.13 (m, 6H).

Preparation of 1-(chloromethyl)-1,4-diazabicyclo-[2.2.2]octan-1-ium *N′*,*N′*-bisbenzenesulfonylimide salt (4) from 3

3 (0.5 g, 2.5 mmol) and 50 mL MeCN were added into a flask and stirred to get a clear mixture, then bisphenylsulfonylimide sodium salt (0.81 g, 2.5 mmol) and another 50 mL of MeCN were added. Small quantity of solid deposited after the reaction system was resolved. The mixture system was then filtered after stirring overnight. The filtrate was evaporated under reduced pressure at 50 ℃. After the removal of most of the solvent, the crude solid was cooled and recrystallized. Solid **4** (0.91g) was gotten in 79% yield. A white solid; ^{1}H NMR (D_2O, 400 MHz) *δ*: 7.51−7.48 (m, 4H), 7.42−7.39 (m, 2H), 7.31−7.26 (m, 4H), 5.00 (s, 2H), 3.45−3.40 (m, 6H), 3.16−3.11 (m, 6H).

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Preparation of F-TEDA-N(SO_2Ph)$_2$ from compound 4 and NFSI

NFSI (7 g, 22 mmol), **4** (1 g, 2.2 mmol) and 70 mL MeCN were added into a flask, then stirred for 8 d. The solvent was removed under reduced pressure, the residue was washed with EA, and the crude product was gotten in 93% yield and 91% HPLC purity. 5 g NFSI can be recovered after removal of EA from the EA filtrate. The crude solid was recrystalled in EA/MeCN (V∶V=20∶1) and the product was gotten in 80% yield and 96% purity. F-TEDA-N(SO_2Ph)$_2$: A white solid; m.p. 133 ℃; ^{1}H NMR (CD_3CN, 400 MHz) δ: 7.76−7.73 (m, 8H), 7.48−7.44 (m, 4H), 7.41−7.36 (m, 8H), 5.59 (m, 2H), 4.99−4.94 (m, 6H), 4.65−4.61 (m, 6H); ^{19}F NMR (CD_3CN, 397 MHz) δ: 48.6; ^{13}C NMR (D_2O, 100 MHz) δ: 140.80, 132.31, 128.83, 126.01, 68.94, 57.29 (d, $^3J_{CF}$=15 Hz), 54.66; IR (KBr) ν: 3038, 2984, 2922, 2853, 1446, 1298, 1274, 1152, 1083, 788, 720, 592, 574, 556 cm^{-1}.

Fluorination of 2-oxindoles (5) with F-TEDA-N(SO_2Ph)$_2$

Compound **5** (0.16 mmol), F-TEDA-N(SO_2Ph)$_2$ (0.18 mmol) and K_2CO_3 (0.97 mmol) were resolved in CH_2Cl_2 and MeCN (V∶V=4∶3, 6 mL) at −78 ℃ till TLC indicated that the reaction was complete. The mixture was roughly purified by direct flash column chromatography with EA as fluent phase. EA solution was added silica and the solvent was removed under reduced pressure, then the residue was finely purified by column chromatography with PE/EA (V∶V=30∶1) as fluent phase, then pure compounds **6** were gotten.

N-*tert*-Butoxycarbonyl-3-fluoro-3-(phenyl)-2-oxindole (**6a**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (d, J=8.4 Hz, 1H), 7.53−7.51 (m, 1H), 7.40−7.29 (m, 6H), 7.27 (d, J=6.0 Hz, 1H), 1.62 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −145.37 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-2-oxindole (**6b**):[6b] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.00 (d, J=8.3 Hz, 1H), 7.53−7.46 (m, 1H), 7.40−7.35 (m, 1H), 7.29−7.24 (m, 3H), 7.20−7.18 (m, 2H), 2.35 (s, 3H), 1.60 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −145.53 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(phenyl)-6-chloro-2-oxindole (**6c**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.61 (s, 9H), 7.28 (d, J=1.6 Hz, 1H), 7.29 (d, J=1.6 Hz, 1H), 7.35−7.31 (m, 2H), 7.41−7.38 (m, 3H), 8.10 (s, 1H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: –145.07 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(4-fluorophenyl)-5-fluoro-2-oxindole (**6d**):[7b] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (dd, J=9.0, 4.2 Hz, 1H), 7.37 (dd, J=8.7, 5.2 Hz, 2H), 7.30−7.19 (m, 1H), 7.16−7.07 (m, 3H), 1.63 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −111.02 (d, J=3.4 Hz, 1F), −115.70 (d, J=1.9 Hz, 1F), −144.1 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(4-methoxyphenyl)-2-oxindole (**6e**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.0 (d, J=8.0 Hz, 1H), 7.53−7.48 (m, 1H), 7.37 (d, J=7.6 Hz, 1H), 7.30−7.25 (m, 2H), 6.98−6.97 (m, 2H), 6.92 (dd, J=2.8, 2.4 Hz, 1H), 6.83 (d, J=7.6 Hz, 1H), 3.81 (s, 3H), 1.62 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: –145.99 (s, 1F).

N-*tert*-Butoxycarbonyl-3,5-fluoro-3-(phenyl)-2-oxindole (**6f**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02 (ddd, J=9.0, 4.4, 1.0 Hz, 1H), 7.45−7.30 (m, 5H), 7.25−7.16 (m, 1H), 7.12−7.04 (m, 1H), 1.61 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −115.93 (d, J=2.7 Hz, 1F), −146.47 (d, J=2.3 Hz, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(phenyl)-7-methyl-2-oxindole (**6g**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33−7.42 (m, 6H), 7.19−7.24 (m, 2H), 2.32 (s, 3H), 1.63 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: –146.11 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(4-fluorophenyl)-2-oxindole (**6h**):[7c] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (d, J=8.3 Hz, 1H), 7.56−7.49 (m, 1H), 7.40−7.33 (m, 3H), 7.29 (t, J=7.5 Hz, 1H), 7.07 (t, J=8.4 Hz, 2H), 1.62 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −111.54 (d, J=3.2 Hz, 1F), −142.95 (d, J=3.7 Hz, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-phenyl-5-methyl-2-oxindole (**6i**):[7b] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (d, J=8.4 Hz, 1H), 7.42−7.33 (m, 5H), 7.30 (d, J=8.4 Hz, 1H), 7.17 (s, 1H), 2.36 (s, 3H), 1.61 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −145.63 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(β-naphthyl)-2-oxindole (**6j**):[7a] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (d, J=8.3 Hz, 1H), 7.91−7.77 (m, 3H), 7.73 (s, 1H), 7.59−7.45 (m, 4H), 7.42 (d, J=7.6 Hz, 1H), 7.30 (t, J=7.5 Hz, 1H), 1.61 (s, 9H); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −145.22 (s, 1F).

N-*tert*-Butoxycarbonyl-3-fluoro-3-(4-ethylphenyl)-5-methyl-2-oxindole (**6k**):[7d] A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86 (d, J=8.4 Hz, 1H), 7.39 (d, J=8.4 Hz, 1H), 7.28−7.22 (m, 5H), 2.37 (s, 3H), 2.36 (s, 3H), 1.61 (s, 9H); ^{19}F NMR (CD_3CN, 376 MHz) δ: −141.90 (s, 1F).

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