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SHORT COMMUNICATION

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# Electrophilic [N—F]$^+$ catalysed asymmetric allylation of (*E*)-*N*,1-diphenylmethanimine

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**Abstract**

New efficient catalysts based on electrophilic *N*-fluoro quaternary ammonium salts are reported for catalytic allylation of (*E*)-*N*,1-diphenylmethanimine. The chiral version of the catalyst based on cinchonidine (F-CD-$BF_4$) shows high catalytic activity with approximately 94% ee and TOF (>800 $h^{-1}$). The F-CD-$BF_4$ is prepared from cinchonidine and Selectfluor by one-step transfer fluorination.

**KEYWORDS**

asymmetric allylation, cinchonidine, circular dichroism, time-dependent NMR, transfer fluorination

## 1 | INTRODUCTION

Stereoselective allylation of imines and aldehydes is the common building block for chiral organic compounds in agrochemicals and pharmaceutical.[1] For instance, chiral homoallylic amines are the synthetic intermediate of naturally occurring compounds and chiral drugs such as (−)-quinolizidine 207I,[2] (−)-histrionicotoxin 259A,[3] NNZ 2591,[4] and ORG 34167[5] (Figure 1). Recently, development of mild synthetic methods has been the focus area to prepare optically active homoallylic amines (Table S1).[6-12] Usually, allylation of imines is promoted and activated by Lewis or Bronsted acid,[13] metal triflates,[14] and chiral metal complexes.[15-22] However, chiral transfer agent requires inert and dry conditions.[14] Although first asymmetric allylation has been reported in 1993 by Mikami using air- and moisture-sensitive BINOL/Ti (IV) complex,[20] surprisingly, limited attention has been paid towards asymmetric allylation of C=O and C=N groups under ambient conditions.[18,19]

Herein, we present a series of nonhydroscopic [N—F]$^+$ reagents such as Selectfluor (**1a,** (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoro-borate)), 1-fluoro-2,4,6-trimethylpyridium tetrafluoroborate (**1b**), 1-fluoropyridium tetrafluoroborate (**1c**), and 1-fluoropyridium trifluoromethanesulfonate (**1d**) for allylation of imine under mild conditions. The asymmetric version of reaction is also explored with new chiral *N*-fluoro quaternary ammonium salt of cinchonidine (**1e**; F-CD-$BF_4$, Figure 2). As per limited reports, F-CD-$BF_4$ and Selectfluor have been reagent of choice for electrophilic fluorination.[23-26] The only example pertains to Selectfluor-mediated allystannation of aldehydes and imines was studied by Wong in 2002.[27] Although cinchona alkaloids have been used as a chiral source in indium-catalysed asymmetric allylation of aldehydes with moderate enantioselectivity,[28] there is no report available on F-CD-$BF_4$-catalysed asymmetric allylation of imine. In the present study, allylation of (*E*)-*N*,1-diphenylmethanimine is investigated as a representative example using catalytic amount of **1a-1e** and allyltributylstannane. Allyltributyltin is used as an allylic reagent due to several advantages such as easy availability, air and moisture stability, and compatibility with a variety of functional groups.[29]

## 2 | MATERIALS AND METHODS

Reactions were carried out in inert atmosphere and monitored by thin-layer chromatography (TLC). Products were purified by column chromatography and packed with silica gel of 230-400 mesh. Scanning electron microscopy (SEM, EVO18 Zeiss) was used for morphological

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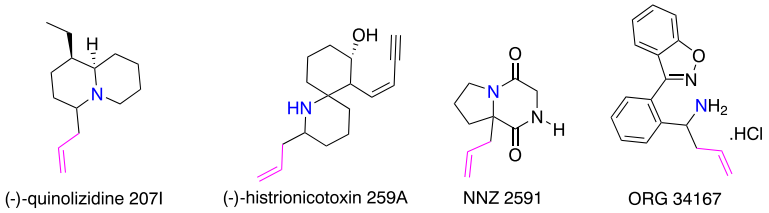



**FIGURE 1** Natural products and chiral drugs

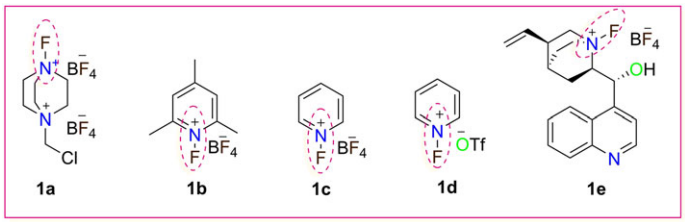



**FIGURE 2** $[N—F]^+$ catalysts

analysis of F-CD-$BF_4$ and Selectfluor. UV-visible spectra were recorded by UV-visible spectrophotometer (Varian Cary 4000). Fourier-transform infrared spectra (FTIR) were performed on a Vertex 70v spectrometer (Bruker). $^1$H NMR (500 MHz), $^{19}$F NMR (470 MHz), and $^{13}$C NMR (125 MHz) spectra were recorded on Bruker. Enantiomers were separated by HPLC (waters 2489, Daicel Chiral Cell CHIRALPAK ID 0.46 cm/25 cm) using *n*-hexane/isopropanol solvent system. The specific rotation was measured from polarimeter (Rudolph, APII/2W). The CD spectra were obtained from circular dichroism (JASCO, J-815 CD-Spectrometer) in $N_2$ atmosphere in the wavelength range of 200 to 400 nm with a quartz cuvette cell.

Imine (**SI**), (*E*)-*N*,1-diphenylmethanimine was synthesized by previously reported method (see Scheme S1).[30,31] Catalysts **1a-1d** were purchased commercially while F-CD-$BF_4$ **1e** was synthesized according to Bank's fluorine-transfer procedure, in which cinchonidine and Selectfluor **1a** were mixed in equimolar amount in dry acetonitrile under optimized reaction conditions (Figure 3A) and characterized by $^{19}$F and $^1$H NMR.[32] Chiral-fluorinated cinchonidine **1e** and other fluorinated catalysts were tested for allylation of imine **SI** (Figure 3B).

## 2.1 | F-CD-$BF_4$ (1e)

$^1$H NMR (500 MHz, $CD_3CN$): δ 8.98 (d, 4.53 Hz, 1H), 8.17 (d, J = 8.54 Hz, 1H), 8.00 (d, J = 8.54 Hz, 1H), 7.78-7.73 (m, 2H), 6.43 (d, J = 3.31 Hz, 1H), 5.73 (m, 1H), 5.12 (dd, 1H), 5.00 (s, 1H), 4.10-3.86 (m, 5H), 3.20-3.41 (m, 1H), 1.23-1.97 (m, 5H). $^{13}$C NMR (125 MHz, $CD_3CN$): δ 149.4, 149.3, 148.0, 137.5, 129.6, 129.4.0, 127.1, 125.2, 120.7, 118.3, 117.6, 80.9, 66.3, 62.3, 59.2, 34.3, 27.9, 21.6, 19.2. $^{19}$F NMR (470 MHz, $CD_3CN$): δ = 40.7 ppm ($—N—F^+$), −151.09 ppm ($BF_4^-$).

## 2.2 | (*E*)-*N*,1-diphenylmethanimine (SI)

$^1$H NMR (500 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.58-7.76 (m, 5H), 7.07-7.47 (m, 5H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 160.0, 152.0, 136.4, 131.0, 130.0, 129.2, 128.2, 127.2, 122.3.

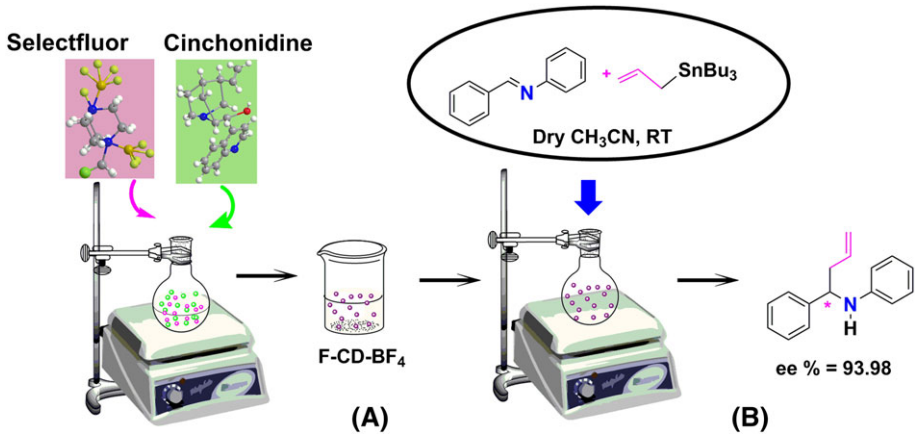



**FIGURE 3** A, Synthesis of fluorinated cinchonidine, F-CD-$BF_4$, and, B, asymmetric allylation of (*E*)-*N*,1-diphenylmethanimine (**SI**)

### 2.2.1 | *N*-(1-phenylbut-3-en-1-yl)aniline (P1)

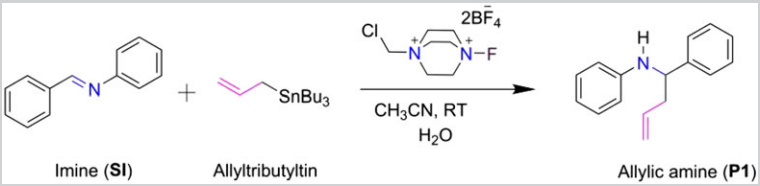
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H), 7.08 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.82 (m, 1H), 5.13 (m, 1H), 4.88 (m, 1H), 3.94 (dd, J = 8.0, 5.2 Hz, 1H), 2.63-2.36 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 147.6, 140.6, 134.3, 129.5, 128.5, 126.9, 126.7, 120.8, 116.4, 113.5, 63.4, 44.4 (Figures S8 and S9). $[\alpha]_D^{20°C}$ = +15 (C = 1.0 in $CHCl_3$)

## 3 | RESULTS AND DISCUSSION

The fluorine transfer was monitored by time-dependent $^{19}$F NMR study in 10-second interval at room temperature (293 K). It has been observed that the fluorine transfer started quickly and slowed down to complete in 12 hours. The chemical shift of $^{19}$F NMR moved to 40.7 ppm from 48.0 ppm. The peak at 40.7 ppm indicates the formation of $[N—F]^+$ bond in cinchonidine (Figure S1). The counterion $[BF_4]^-$ also shows a slight shift due to change the electronic environment (see Figure S2). Furthermore, it is noteworthy that quinuclidine ring of cinchonidine is analogous to Selectfluor, which could assist in one-step transfer-fluorination to form F-CD-$BF_4$ (**1e**).[23,33] The conversion of dicationic Selectfluor to two monocations of ammonium salts is also a driving force for fluorine transfer,[34] as no transfluorination were observed with other monocataionic $[N—F]^+$ reagents (**1b**-**1c**). The fluorine transfer is also established by EDX mapping (Figures S3 and S4). In FTIR, stretching and vibration frequencies related to $[N—F]^+$ are observed at 924, 769.7, 715, and 1477 $cm^{-1}$.[35] Other bands are slightly similar to cinchonidine (Figure S5). In situ UV-vis spectra were recorded in acetonitrile (Figure S6), where cinchonidine bands were observed at 205, 225, and 278 nm.[36] The bands at 205 and 278 nm related to π → π* and n → π* transitions, respectively. Upon addition of Selectfluor, band intensity of n → π* transition lowered, indicating the involvement of the fluorine atom in bonding with the N atom of the cinchonidine.

Allylation reaction was optimized with Selectfluor **1a** using allyltributylstannane in dry $CH_3CN$. Maximum conversion was found with 0.1 mol% of Selectfluor within 1 hour (Table 1). The typical optimized process involved 0.10 mol% (0.25 mg) Selectfluor dissolved in 5 mL of acetonitrile followed by sonication for 10 minutes. After 5 minutes, 0.13 g (0.7 mmol) of imine **SI** and 0.25 mL (0.8 mmol) of allyltributyltin were added and stirred for 1 hour. The product was extracted with dichloromethane (5 mL × 2) after quenching with water. The product was isolated with 10% ethyl acetate in *n*-hexane using silica column to get 98% semisolid racemic homoallylic amine (Figure S11 inset). No allylation product was observed in absence of Selectfluor under similar reaction condition

**TABLE 1** Optimization of allylation of imine (**SI**) with Selectfluor **1a**[a]




| Entry | 1a, mol% | Time, h | Yield, %[b] |
|---|---|---|---|
| 1 | 0.0 | 1 | 0.0 |
| 2 | 0.01 | 0.5 | 40 |
| 3 | 0.05 | 0.5 | 55 |
| 4 | 0.09 | 0.5 | 77 |
| 5 | 0.10 | 0.5 | 83 |
| 6 | 0.10 | 1.0 | 98 |
| 7 | 0.10 | 1.5 | 98 |
| 8 | 0.15 | 1.5 | 98 |

Standard reaction condition:

[a]To a solution of imine **SI** (0.7 mmol, Table S1) in dry $CH_3CN$ (5 mL), and allyltributylstannane (0.8 mmol) were added and stirred for 10 minutes at RT. Catalyst **1a** was added and stirred for the given time.

[b]The product was separate by HPLC and by NMR (see Figures S8, S9, and S11).

(Table 1, entry 1). This result encouraged us to screen other catalysts **1b**-**1d** (Table 2), under optimized conditions that showed good catalytic activity.

The catalyst **1d** with triflate counterion exhibited good activity due to its acidic nature.[37] Catalysts **1b** and **1c** with monocationic trifluoroborate counterion showed lesser activity with moderate conversion. To study asymmetric version of this reaction, F-CD-$BF_4$ **1e** was tested under similar reaction condition, which gave low conversion (80%, TOF = 800 $h^{-1}$) and excellent enantioselectivity (94%). The low conversion and high ee could be consequence of steric discrimination of cinchonidine moiety. No fluorinated side products were observed in current allylation process, although fluorination of amines has been reported with Selectfluor under different reaction conditions.[27,38]

Although the mechanism for this transformation is still under investigation, it can be stated that $[N—F]^+$ reagents may act as a Lewis acid to activate the imine for nucleophilic addition.[27] The low activity is aligning with decreasing the Lewis acidity of $[N—F]^+$ reagents. The Lewis acidity was assumed by pH of the aqueous solution of $[N—F]^+$ reagents and found maximum in case of **1a** while minimum in case of **1b** (Table 3). This may be because of the presence of extra $—N^+CH_2Cl$ that makes it more electron deficient (Lewis acidity 2.9), and other $[N—F]^+$ reagents are relatively electron rich with aromatic ring (**1b**-**1e**). The chemical shift of all reagents revealed the electron-deficient order of $[N—F]^+$ bond in $^{19}F$ NMR, and it was observed that the $[N—F]^+$ bond of **1a** catalyst is more electron deficient while **1b** is comparatively rich (Table 3) due to electron-donating methyl groups.

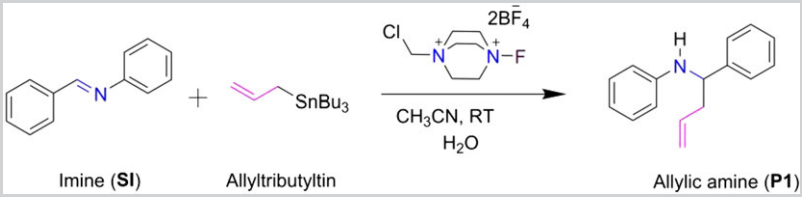
**TABLE 3** Measured pH value of aqueous $[N—F]^+$ catalysts

| Entry | $[N—F]^+$ Catalysts | pH | $^{19}F$ Chemical Shift, ppm |
|---|---|---|---|
| 1 | **1a** | 2.9 | 48.0 |
| 2 | **1b** | 4.1 | 15.9 |
| 3 | **1c** | 3.1 | 46.1 |
| 4 | **1d** | 3.0 | 46.2 |
| 5 | **1e** | 3.9 | 40.7 |

To understand the mechanistic aspect, proton NMR studies were carried out between (*E*)-*N*,1-diphenylmethanimine and catalysts **1e** that shows downfield shift of imine proton, suggesting C—H activation towards nucleophilic addition (Figure S10), although no conclusive interactions were observed between allyltributyltin and $[N—F]^+$. However, It can be assumed that tributyltin cation could be an effective Lewis acid, generated in conjunction with allylfluoride during the reaction of allyltributyltin and $[N—F]^+$ reagents.[39]

Optical purity of P1 was determined by HPLC and polarimeter. Chiral product was separated by a normal-phase Daicel CHIRALPAK ID (0.46 cm/25 cm) chiral column under isocratic and isothermal (at 30°C) conditions using respective mixture of *n*-hexane/isopropanol (90/10) as the mobile phase with 1.0-mL/min flow rate. Specific rotation measurement revealed that R enantiomer is first eluted (Table 2). To evaluate the optical activity of samples, circular dichroism (CD) spectra were recorded at 20°C with 50 nm $min^{-1}$ sweep rates between 400 and 200 nm (Figure S7). The smoothed CD spectra of cinchona alkaloids show the cotton effect in the range of 208 to 330 nm including two positive cotton and two

**TABLE 2** Allylation of (*E*)-*N*,1-diphenylmethanimine (**SI**) with $[N—F]^+$ catalysts (**1a**-**e**)[a]




| Catalysts | Yield, %[b] | ee, %[c] | $[\alpha]_D^{20°C}$ [d] |
|---|---|---|---|
| **1a** | 98 | 0.0 | 0.0 |
| **1b** | 88 | 0.0 | 0.0 |
| **1c** | 89 | 0.0 | 0.0 |
| **1d** | 92 | 0.0 | 0.0 |
| **1e** | 80 | 93.9 | +15 |

[a]Reaction condition is similar to Table 1. Catalysts/reaction time/imine/allyltributylstannane:0.1 mol%/1 hour/0.7 mmol/0.8 mmol

[b]The products were separated by column chromatography.

[c]Determined by chiral column under isocratic and isothermal conditions using respective mixture of *n*-hexane/isopropanol as the mobile phase.

[d]The optical activity was measured by polarimeter (C 1.00; Chloroform).

negative cotton shifts at the range 330 to 278, 259 to 228, 278 to 259, and 228 to 208 nm, respectively.[40] For cinchonine, opposite cotton shifts were observed (Figure S7A). The cotton shifts of F-CD-$BF_4$ were opposite of cinchonidine and similar to cinchonine, indicating configurational changes during fluorination (Figure S7B). The optical activity of F-CD-$BF_4$ was transferred into the product of allylation as indicated by CD spectra (Figure S7C) with wavelength shifts due to counterion change.

## 4 | CONCLUSION

In summary, a series of highly active electrophilic $[N—F]^+$ catalytic reagents have been investigated for allylation of (*E*)-*N*,1-diphenylmethanimine using allyltributyltin under ambient and non-inert conditions. High chemical yield (approximately 98%) of homoallylic amines has been attained. For chiral catalyst (F-CD-$BF_4$), high enantioselectivity of approximately 94% was achieved. Investigation towards detailed mechanism and scope of substrate will be involved in future work.

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## SUPPORTING INFORMATION

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