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N-Fluorobenzenaminium tetrafluoroborate generated *in situ* by aniline and Selectfluor as a reusable catalyst for the ring opening of epoxides with amines under microwave irradiation†

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The ring opening of epoxides with aromatic and aliphatic amines was carried out under solvent free conditions using *N*-fluorobenzenaminium tetrafluoroborate (2 mol%) generated *in situ* by the reaction of aniline and Selectfluor as a catalyst with microwave irradiation. Excellent yields of β-amino alcohols were obtained. The catalyst also results in the retention of the stereochemistry for the ring opening of enantiopure epoxide with amine. The catalyst was recovered and reused up to 4 cycles for the ring opening of cyclohexene oxide with aniline.

Introduction

Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)) is a commercially available, exceptionally stable and virtually nonhygroscopic crystalline solid which is widely used for the electrophilic fluorination of electron-rich carbon centers.[1,2] Its electrophilic and oxidative characteristics make it a useful catalyst for the cleavage of electron-rich protecting groups, such as *p*-methoxybenzylidene (PMP), tetrahydropyranyl (THP) ethers, 1,3-dithianes, the deprotection of silyl ethers and the ring opening of epoxides with ammonium thiocyanate (Scheme 1).[3–5]

The ring opening of epoxide with an amine as a nucleophile is an important route for the synthesis of β-amino alcohols.[6] β-Amino alcohols are versatile intermediates for the synthesis of a wide range of biologically active natural and synthetic products, synthetic amino acids, β-blockers in pharmaceuticals and insecticides.[7] The cleavage of epoxides with amines has been carried out in the presence of metal halides,[8] metal triflates,[9] metal alkoxides,[10] metal amides and triflamide,[11] transition metal salts,[12] hexafluoro-2-propanol under reflux (HFIP),[13] ionic liquid,[14] zirconium sulfophenyl phosphonate,[15] montmorillonite clay,[16] silica,[17] alumina/modified alumina,[18] zeolites,[19] Fe-MCM-41,[20] heterodimetallic coordination polymers,[21] poly(amidoamine) dendrimer supported on cross-linked polystyrene,[22] and *N*-formyl-L-proline,[23] in water without catalyst[24] and $Fe(Cp)_2BF_4$.[25] A few research groups have also reported the desymmetrisation of *meso* epoxides with aniline derivatives using chiral complexes and organocatalysts.[26]

Some of the existing methods still have limitations, for example, less basic amines fail to open these epoxides under ambient conditions, a high loading of expensive catalyst is required, the catalysts used may be air and moisture sensitive, non-environmentally friendly solvents are required and reactions require long times to complete. Microwave irradiation has become an increasingly popular method for accelerating synthetic transformations.[27] This technology offers a clean, effective and convenient method for heating, which often results in higher yields and shorter reaction times. Organic reactions assisted by microwave irradiation have recently attracted considerable attention.[28] So far few examples have been reported in the literature for the ring opening of epoxides with amines under microwave irradiation.[29] Herein, we report *N*-fluorobenzenaminium tetrafluoroborate

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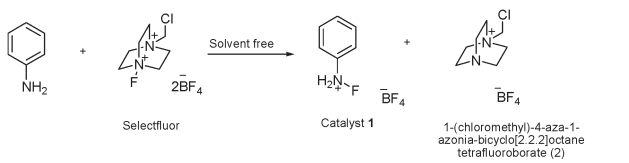
† Electronic supplementary information (ESI) available: Crystal structure analysis of (*S*)-1-(naphthalen-2-yloxy)-3-piperidin-1-yl-propan-2-ol hydrochloride (**20·HCl**): $C_{18}H_{24}NO_2Cl$, M_r = 321.83, monoclinic, space group: P_{21}, a = 8.117(5), b = 7.669(5), c = 28.305(5) Å, β = 95.859(5)°, V = 1755.6(16) Å^3, $\rho_{calcd.}$ = 1.218 g cm^{-3}, Z = 4, $F(000)$ = 688, crystal dimensions: 0.46 × 0.18 × 0.09 mm. The refinement converged at R_1 = 0.0619, wR_2 = 0.1098 for all data; final GOF: 1.003; largest peak/hole in the final difference Fourier map: 0.27/–0.16 e Å^{-3} and absolute structure parameter –0.07(6). CCDC 895046. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cy00609g



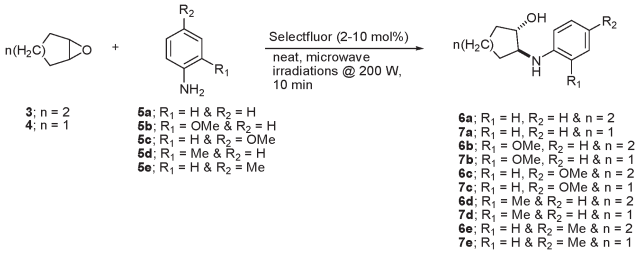
Scheme 1 *In situ* generation of catalyst *N*-fluorobenzenaminium tetrafluoroborate (**1**).

as a new catalyst *in situ* generated by the reaction of aniline and Selectfluor for the ring opening of a variety of epoxides with aliphatic and aromatic amines under solvent free conditions with microwave irradiation.

Results and discussion

We conducted the ring opening of cyclohexene oxide **3** with aniline and Selectfluor (10 mol%) with microwave irradiation at 80 °C and 200 W for 10 min giving a 94% yield of the product **6a** (Table 1, entry 1). We were interested to find out the mechanism for this reaction as well as the actual catalyst for this reaction. Aniline is a nucleophile and Selectfluor is an electrophilic reagent thus a fluorine atom could transfer to the N-atom of aniline to form *N*-fluorobenzenaminium tetrafluoroborate (**1**). The formation of *N*-fluorobenzenaminium tetrafluoroborate (**1**) was confirmed by ^{19}F-NMR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The electrophilic fluorination of amines by Selectfluor has also been reported in the literature.[30] The first experiment was carried out by mixing a 1 : 1 molar ratio of Selectfluor and aniline and recording the ^{19}F-NMR spectra . The peak for the N–F bond in Selectfluor at +47.8 ppm disappeared and a new peak at −129.6 ppm developed due to the formation of the $PhNH_2F$ cation and a peak at −150.6 was present due to the formation of the BF_4 anion (Fig. 1). The byproduct of this reaction, 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**), was confirmed by the presence in the ^{1}H NMR spectrum of peaks at 3.23 (t, J = 8.0 Hz), 3.50 (t, J = 8.0 Hz) and 5.03 (s) ppm, the spectrum was identical to that of the separately synthesized pure compound **2** (see ESI†). The ^{1}H NMR spectra of *in situ* generated catalyst **1** and isolated *N*-fluorobenzenaminium tetrafluoroborate (**1**) (see ESI†) are also identical (Fig. 2). In the ^{13}C NMR spectrum of *in situ* generated catalyst **1**, downfield shifting of 3 peaks (CH) and 1 peak upfield (quartinary carbon) were observed compared to the peaks present in the spectrum of aniline which shows that electrophilic fluorination took place on the N-atom of aniline and that the *in situ* generated catalyst **1** is *N*-fluorobenzenaminium tetrafluoroborate (**1**) (Fig. 3). Furthermore, we also confirmed that the actual catalyst is **1** by HRMS, that the peak at 112.0561 $[M]^+$

Table 1 Ring-opening of cyclic epoxides with different anilines using *in situ* generated *N*-fluorobenzenaminium tetrafluoroborate (**1**) and its derivatives by aniline/substituted anilines and Selectfluor with microwave irradiation[a]



Entry	Epoxides	Catalyst loading (mol%)	Amine	Products	Temp. (°C)	Yield[b] (%)
1	**3**	10	**5a**	**6a**	80	94
2	**3**	5	**5a**	**6a**	80	93
3	**3**	5	**5a**	**6a**	70	95
4	**3**	5	**5a**	**6a**	50	80
5	**3**	2	**5a**	**6a**	70	98
6[c]	**3**	—	**3a**	**6a**	70	—
7[d]	**3**	2	**5a**	**6a**	70	94
8[e]	**3**	2	**5a**	**6a**	70	—
9[f]	**3**	2	**5a**	**6a**	70	90
10	**3**	2	**5b**	**6b**	70	72
11	**3**	2	**5c**	**6c**	70	67
12	**3**	2	**5d**	**6d**	70	86
13	**3**	2	**5e**	**6e**	70	93
14	**4**	2	**5a**	**7a**	60	90
15	**4**	2	**5b**	**7b**	60	77
16	**4**	2	**5c**	**7c**	60	84
17	**4**	2	**5d**	**7d**	60	90
18	**4**	2	**5e**	**7e**	60	96

[a] Selectfluor (2–10 mol%) and aniline/substituted aniline (2–10 mol%), epoxides (2 mmol) and aniline/substituted aniline (2.0 mmol) were irradiated under microwave irradiation @ 200 W at specified temperature for 10 min. [b] Isolated yield after purification by column chromatography. [c] The reaction conducted in absence of Selectfluor under microwave irradiation. [d] The reaction conducted with isolated *N*-fluorobenzenaminium tetrafluoroborate (**1**) under microwave irradiation. [e] The reaction conducted with isolated 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**) under microwave irradiation. [f] The reaction conducted on conventional oil bath heating for 1.5 h.

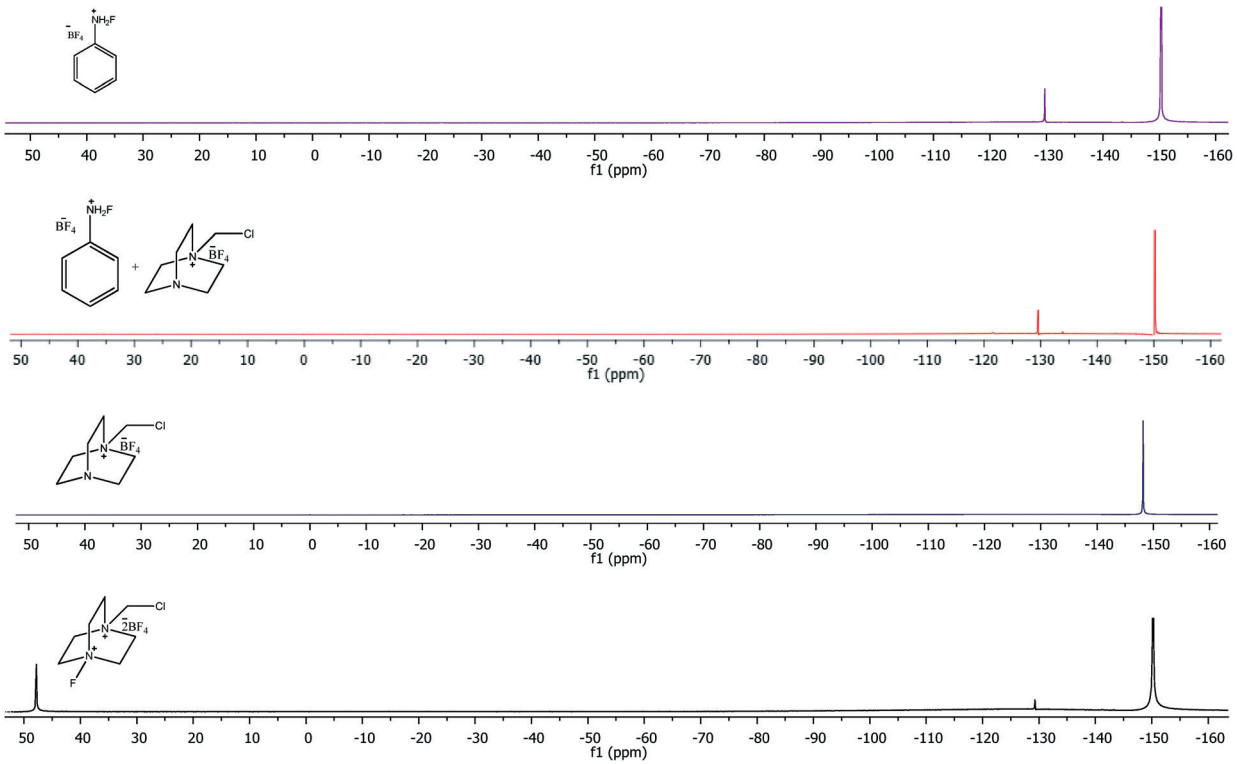


Fig. 1 ^{19}F-NMR data, recorded in D_2O solvent, for the isolated catalyst **1**, *in situ* generated catalyst **1**, 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**) and Selectfluor.

is due to *N*-fluorobenzenaminium cation and that the peak at 161.0847 is due to the byproduct of 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane cation (**2**) and these are also identical to the peaks in the spectra of their pure isolated compounds (see ESI,† Fig. S3–S5).

We optimised the reaction conditions for the ring opening of cyclohexene oxide (**3**) with aniline. The catalyst loading was reduced by 5 mol% and the temperature was decreased to 70 °C, which improved the yield (Table 1, entries 2 and 3). Furthermore, the reaction temperature was decreased to 50 °C and comparative lower yield (80%) was obtained (Table 1, entry 4). The catalyst loading (2 mol%) was sufficient to catalyse the reaction and afforded a 98% yield of the product **6a** (Table 1, entry 5). We were unable to obtain product **6a**, in the absence of catalyst and the unreacted substrates were recovered (Table 1, entry 6). The isolated catalyst **1**, also gave a 94% yield of the product **6a** but 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**) did not catalyse the reaction (Table 1, entries 7 and 8).

The ring opening of epoxide **3** with aniline at 70 °C with conventional oil bath heating afforded **6a** in 90% yield after 1.5 h (Table 1, entry 9). The reaction of epoxide **3** with 2-methoxy, 2-methyl, 4-methoxy and 4-methyl aniline using Selectfluor (2 mol%) with microwave irradiation, *in situ* generated substituted *N*-fluorobenzenaminium tetrafluoroborate as a catalyst and gave corresponding products **6b–e** in 67–93% yields. Furthermore, the ring opening of cyclopentene oxide **4** with aniline, 2-methoxy, 2-methyl, 4-methoxy and 4-methyl aniline were also investigated with microwave irradiation and resulted in 77–96% yields of the products **7a–e** (Table 1, entries 14–18).

The ring opening of cyclohexene oxide (**3**) with primary amines and secondary amines were carried out with microwave irradiation at 70 °C for 10 min. The ring opening of cyclohexene oxide (**3**) with piperidine in the absence of *N*-fluorobenzenaminium tetrafluoroborate (**1**), gave 28% conversion of the product (Table 2, entry 1). The use of *N*-fluorobenzenaminium tetrafluoroborate (**1**) as a catalyst improved the conversion up to 45% (Table 2, entry 2). We also used morpholine, which gave 99% conversion of epoxide to the product (Table 2, entry 3). Primary amines like benzyl amine and (*S*)-α-methylbenzylamine gave 94–96% conversions of the corresponding products (Table 2, entries 4 and 5).

The ring opening of a variety of epoxides with aniline was carried out using *in situ* generated *N*-fluorobenzenaminium tetrafluoroborate (**1**) as a catalyst under solvent free conditions with microwave irradiation at 70 °C for 10 min. The ring opening of 1,2-epoxy-5-cyclooctene (**8**) with aniline afforded a 69% yield of the *trans*-β-amino alcohol **9**. The ring opening of terminal aliphatic epoxides (1,2-epoxyhexane **10** and 1,2-epoxydecane **12**) with aniline occurred at the terminal carbon of the epoxides, resulting in the major products **11a** and **13a**. Minor regioisomeric products **11b** and **13b** were also obtained by nucleophilic attack of aniline at the secondary carbon of the epoxides. The regioisomeric ratio was determined by ^{1}H NMR by integrating peaks at δ 3.72 and

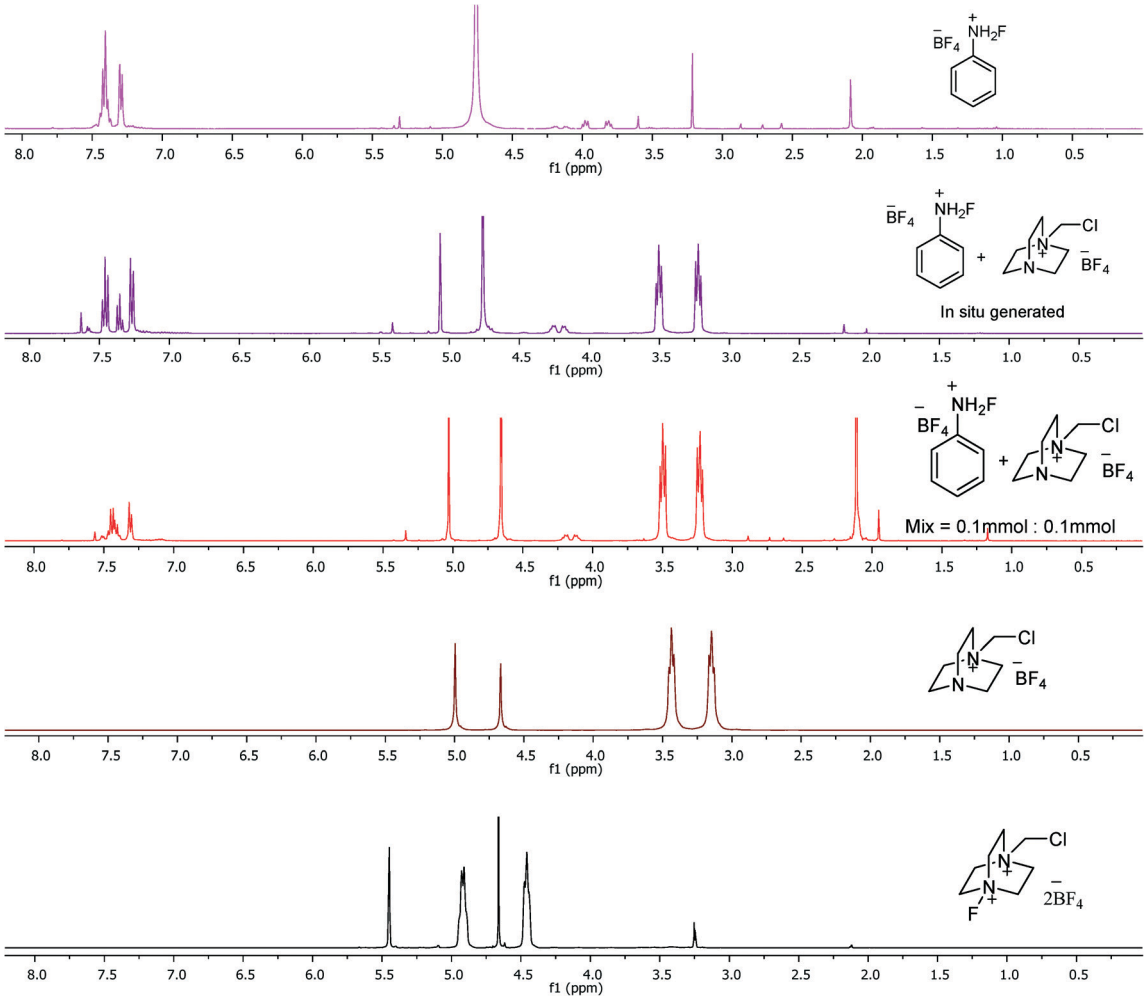


Fig. 2 ^{1}H-NMR data, recorded in D_2O solvent, for the isolated catalyst **1**, *in situ* generated catalyst **1**, 1 : 1 mixed isolated catalyst **1** and 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**), 1-(chloromethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane tetrafluoroborate (**2**) and Selectfluor.

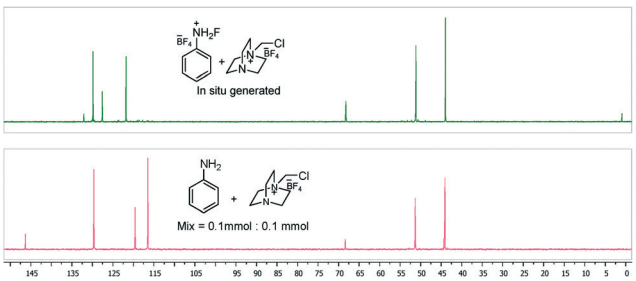


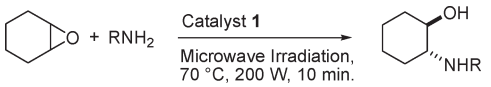
Fig. 3 ^{13}C-NMR of *in situ* generated catalyst **1** and a mixture of aniline and compound **2**.

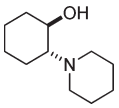
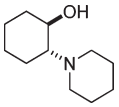
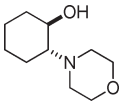
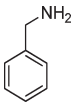
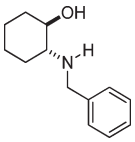
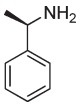
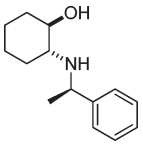
3.64 ppm corresponding to compounds **11a** and **11b**. The total yield of both of the regioisomers (**11a** and **11b**) was 88% with a ratio of 77 : 23 (Table 3, entry 2). The ring opening of epichlorohydrin with aniline resulted exclusively in β-amino alcohol **15** as a product. The ring opening of 2-((naphthalen-1-yloxy) methyl)oxirane (**16**) with aniline gave an 82% yield of product **17** (Table 3, entry 5). The ring opening of styrene oxide resulted in 2-anilino-2-phenyl ethanol (**19**) with 65% yield.

We also tested the *in situ* generation of *N*-fluorobenzenaminium tetrafluoroborate (**1**) as a catalyst for the ring opening of (*S*)-2-((naphthalen-1-yloxy)methyl)oxirane (**16**)-*S* with morpholine and piperidine, this afforded excellent yields of products **20** and **21** with retention of the stereochemistry (Scheme 2). The enantiopure epoxide **16**-(*S*) was synthesized by the resolution of racemic epoxide **16** using Jacobsen's HKR (hydrolytic kinetic resolution) with water, affording a 45% yield.[31] The naphthyloxy-β-amino alcohols **20** and **21** have been reported in the literature to have antimalarial activity.[32] The absolute configuration of compound **20** was determined by single crystal X-ray diffraction by preparing its hydrochloride salt and the absolute configuration of **20**·**HCl** salt was found to be (*S*) (see Fig. 4).

We also investigated whether the *in situ* generated *N*-fluorobenzenaminium tetrafluoroborate (**1**) could be recycled and reused for the next catalytic run. The ring opening of cyclohexene oxide with aniline was carried out at 8 mmol using *in situ* generated *N*-fluorobenzenaminium tetrafluoroborate (**1**) (2 mol%), to afford product **6a** with 98%

Table 2 Ring-opening of cyclohexene oxide with different aliphatic amines using *in situ* generated catalyst **1** as the catalyst with microwave irradiation[a]



Entry	Amine	Product	Conversion[b] (%)
1			28[c]
2			45
3			99
4			94
5			96[d]

[a] The *in situ* generated catalyst **1** (2 mol%), cyclohexene oxide (2 mmol) and amines (2.0 mmol) were microwave irradiated at 200 W and 70 °C for 10 min. [b] Conversion of epoxide to product was determined by gas chromatography.[c] The reaction was carried out in the absence of *in situ* generated catalyst **1**. [d] The diasteromeric ratio was determined by gas chromatography and was found to be 1 : 0.94.

yield. The reaction mixture was diluted with diethyl ether (1 mL) and then hexane (5 mL) was added and the resulting mixture was stirred for 2 minutes, the solvent was then decanted. The *in situ* generated catalyst **1** was separated out as a viscous oil, which was dried under vacuum and reused for the next catalytic run. The ^{1}H and ^{19}F NMR spectra of recovered catalyst **1**, were similar to those of the *in situ* generated catalyst **1** (see ESI,† Fig. S1–S2). The catalyst was reused up to 4 cycles. The yields of the products were found to be in the range of 95–86% for up to 3 cycles but in the 4th cycle we obtained a 40% yield which may be due to the physical loss of the catalyst (Table 4).

Conclusions

In conclusion, we investigated the catalysis of the ring opening of epoxides with aliphatic and aromatic amines under solvent free conditions with microwave irradiation by *N*-fluorobenzenaminium tertrafluoroborate *in situ* generated by Selectfluor and aniline. We obtained an excellent yield of β-amino alcohols by the reaction of the cyclic epoxides with aniline or substituted anilines. We have also synthesized enantiopure naphthyloxy-β-amino alcohols, which has antimalarial activity. In addition, we have demonstrated that *in situ* generated catalyst **1** could be recovered from the reaction mixture and reused up to 4 cycles with a reasonably good yield of product.

Acknowledgements

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6 (*a*) D. M. Hodgson, A. R. Gibbs and G. P. Lee, *Tetrahedron*, 1996, **52**, 14361; (*b*) S. C. Bergmeier, *Tetrahedron*, 2000, **56**, 2561.
7 (*a*) D. J. Ager, I. Prakash and D. R. Schaad, *Chem. Rev.*, 1996, **96**, 835; (*b*) E. J. Corey and F.-Y. Zhang, *Angew. Chem., Int. Ed.*, 1999, **38**, 1931; (*c*) C. W. Johannes, M. S. Visser, G. S. Weatherhead and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1998, **120**, 8340; (*d*) B. L. Chng and A. Ganesan, *Bioorg. Med. Chem. Lett.*, 1997, **7**, 1511; (*e*) D. A. Alonso, D. Guijarro, P. Pinho, O. Temme and P. G. Andersson, *J. Org. Chem.*, 1998, **63**, 2749; (*f*) P. Castejon, A. Moyano, M. A. Pericas and A. Riera, *Tetrahedron*, 1996, **52**, 7063; (*g*) G. Li, H.-T. Chang and K. B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 451.
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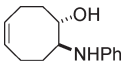
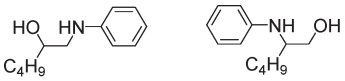
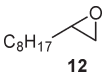
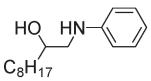
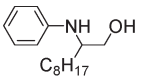
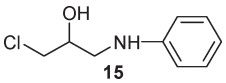
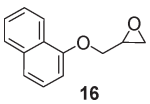
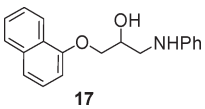
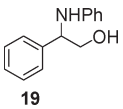
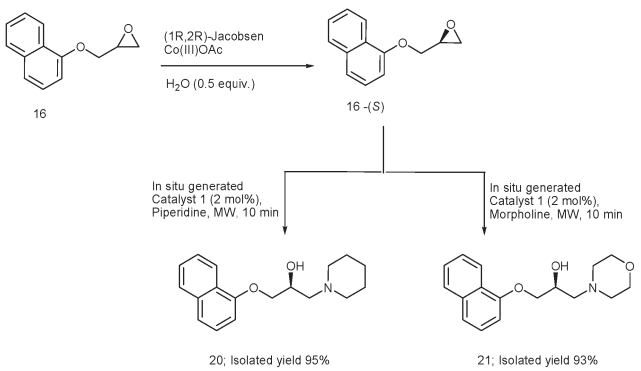
Table 3 Ring-opening of different epoxides with aniline using Selectfluor as the catalyst and microwave irradiation[a]

Entry	Epoxide	Product	Isolated yield[b] (%)
1	 **8**	 **9**	69
2	 **10**		88[c]
3	 **12**	**11a**; Major product  **11b**; Minor product 	64[d]
4	 **14**	**13a**; Major product **13b**; Minor product  **15**	84
5	 **16**	 **17**	82
6	 **18**	 **19**	65

[a] Selectfluor (2 mol%), aniline (2 mol%), epoxides (2 mmol) and aniline (2.0 mmol) were microwave irradiated at 200 W and 70 °C for 10 min. [b] Isolated yield after purification by column chromatography. [c] Regioisomeric ratio of compound **11a** and **11b** is 77 : 23. [d] Regioisomeric ratio of compound **13a** and **13b** is 79 : 21.



Scheme 2 Synthesis of enantiopure naphthyloxy-β-amino alcohols **20** and **21**.

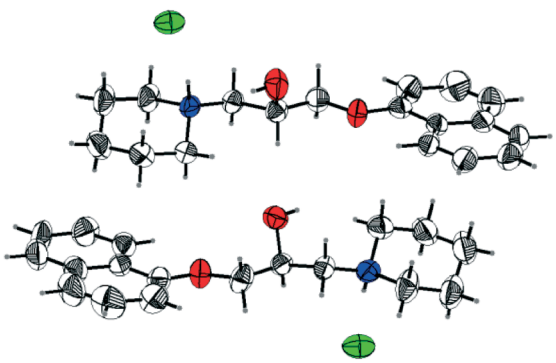


Fig. 4 Ortep diagram of compound (*S*)-naphthyloxy-β-aminoalcohol **20**·**HCl** (50% thermal ellipsoid) color code: black and white octants: C; red octants: O; blue octants: N; green octants: chlorine; grey balls.

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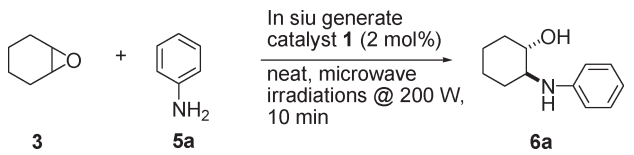
Table 4 Recycling and reusability of *in situ* generated catalyst **1** for ring opening of cyclohexene oxide with aniline with microwave irradiation[a]



Entry	Recycles	Yield[b] (%)
1	0	98
2	1	95
3	2	91
4	3	86
5	4	40

[a] The *in situ* generated catalyst **1** (2 mol%), cyclohexene oxide (8 mmol) and amines (8.0 mmol) were microwave irradiated at 200 W and 70 °C for 10 min. [b] Yield after purification by column chromatography.

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