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

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Methods and materials

Aniline and substituted aniline, morpholine and piperidine were purchased from S.D. Fine Chemicals, India. Styrene oxide, 1-hexene oxide, 1-decene oxide, 1-octene oxide, cyclohexene oxide, cyclopentene oxide and epichlorohydrin were used as received from Aldrich, USA. Proton and carbon nuclear magnetic resonance spectra (\(^1\)H and \(^{13}\)C NMR, respectively) were recorded on 400 MHz (operating frequencies: \(^1\)H, 400.13 MHz; \(^{13}\)C, 100.61 MHz) FT spectrometers at ambient temperature. In the case of \(^1\)H and \(^{13}\)C NMR spectra, the chemical shifts (\(\delta\)) for all compounds are listed in parts per million downfield from tetramethylsilane using the NMR solvent as an internal reference. The reference values used for deuterated chloroform (CDCl\(_3\)) were 7.26 and 77.00 ppm for \(^1\)H and \(^{13}\)C NMR spectra, respectively. Infrared spectra were recorded on a Perkin Elmer Spectrum BX-2 spectrophotometer. Optical rotation values were measured on a Rudolph Autopol (IV) Research Analytical. Single crystal X-ray diffraction was recorded on Oxford diffraction X-Calibur™ S. Thin layer chromatography was carried out using Merck Kieselgel 60 F254 silica gel plates. Column chromatography separations were performed using Merck Kieselgel 60 (Art. 7734).

Crystal Structure Analysis of (S)-1-(Naphthalen-2-yloxy)-3-piperidin-1-yl-propan-2-ol hydrochloride salt (21.HCl):

C\(_{18}\)H\(_{24}\)NO\(_2\)Cl, Mr = 321.83, monoclinic, space group: \(P2_1\), \(a = 8.117(5)\), \(b = 7.669(5)\), \(c = 28.305(5)\) \(\text{Å}\), \(\beta = 95.859(5)^{\circ}\), \(V = 1755.6(16)\) \(\text{Å}^3\), \(\rho_{\text{calcld.}} = 1.218\) \(\text{g·cm}^{-3}\), \(Z = 4\), \(F(000) = 688\), 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 \(e·\text{Å}^{-3}\) and absolute structure parameter -0.07(6).Further details on the crystal structure data can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.chem.ac.uk/data_request/cif, on quoting the depository numbers CCDC. 895046

A total of 14095 reflections was collected at 273(2) K on an Oxford X calibur Ruby CCD diffractometer (MoK\(_\alpha\) radiation, \(\lambda = 0.71073\) \(\text{Å}\)). Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program.\(^1\) Direct methods were used to locate the heavy metal atoms (SHELXS-86). The remaining atoms were located from successive Fourier maps...
(SHELXL-97).\textsuperscript{2} The program PLATON was used to check the space group which falls in hexagonal system having chiral space group P 1 2 1 1 (Flack parameter -0.07(6))\textsuperscript{3}.

**General procedure for the ring opening of epoxides with amines catalysed by Selectflour**

A reaction mixture of epoxide (2 mmol), amine (2 mmol) and Selectflour (2 mol %) was irradiated under microwave for 10 minute at 70 °C temperature and 200W power. The crude product was purified over silica gel by column chromatography to provide pure β-amino alcohol.

**Synthesis of 2-(naphthalene-2-yloxy methyl) oxirane**

2-naphthol (10 mmol, 1.44 gm) was stirred with KOH (10 mmol, 0.56gm) and methanol (11.33 ml) in a 250ml round bottom flask till the reaction mixture was completely dissolved. The solvent was evaporate by rota-vapour and we obtained dry potassium salt of 2-naphthol. The reaction flask was kept in an oil bath preheated 60 to 90 °C temperature then epichlorohydrin (100mmol, 7.83mL) was added both solvent as reagent. The reaction mixture further stirred at 60 °C for 30 minutes and cooled to room temperature. The brine solution was added to the reaction mixture. Product was extracted from the aq. solution using a sufficient amount of dichloromethane. The organic layer was dried over sodium sulphate and solvent was removed under reduce pressure. The product was purified by silica gel column chromatography using 90:10 (hexane: EtOAc) afforded 92% yield as viscous liquid.

The enantioenriched 2-(naphthalene-2-yloxy methyl) oxirane was obtained using Jocobsen hydrolytic kinetic resolution (HKR) with (R, R)-Jacobsen Cobalt (III)OAc and water as a resolving reagent.\textsuperscript{4}

**Synthesis of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride\textsuperscript{16}**

![Diagram](image)

TEDA (2 g, 17.8 mmol) was dissolved in Dry DCM (5.6 mL, 89.03 mmol) and the mixture was allowed to reflux under inert atmosphere for 4 h. The dense white precipitate was formed and filtered under nitrogen atmosphere and washed with dry DCM (9 mL). The crude product was dried under vacuum to obtained 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (3.1 g., 90%).

**Chloride anion exchange of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride with tetrafluoroborate\textsuperscript{16}**

![Diagram](image)
NaBF₄ (1.68 g., 15.5 mmol) in dry acetonitrile (10 mL) was added to a stirred slurry of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (3 g., 15.5 mmol) in acetonitrile (20 mL). The mixture was stirred under inert atmosphere at room temperature for overnight. Precipitate of sodium chloride was formed. It was removed by filtration and washed with dry acetonitrile. The filtrate and washing were combined and evaporate under reduced pressure, leaving a white solid residue which was recrystallized from an ethanol/ethyl.

¹H NMR (D₂O, 400MHz): δ 4.97 (s, 2H), 3.41 (t, J = 6.59 Hz, 6H), 3.12 (t, J = 6.59 Hz, 6H) ppm. ¹⁹F NMR (D₂O, 376MHz): δ -148.14 ppm.

**Preparation of N-fluorobenzenaminium tetrafluoroborate**

\[
\begin{align*}
\text{NH}_2^+ & + \text{Cl}^- \rightarrow \text{NH}_2^+\text{BF}_4^- + 2\text{BF}_4^- \\
\text{r.t., 20 min.} & \\
\end{align*}
\]

Aniline (1 mmol, 91 µL) was taken in acetonitrile (1 mL) and Selectfluor (1 mmol, 354 mg, in acetonitrile (1.3 mL)) was slowly added and stirred for 20 min. Acetonitrile was removed under reduced pressure and the resulting white solid was dissolved in the minimum amount of acetone and a solution of 10 mL solution of H₂SO₄ (0.8 mmol, 42 µL) was added drop wise and precipitation of 1-chloromethyl-4-hydro-1,4-diazoniabicyclo [2.2.2] octane hydrogen sulphate tetrafluoroborate was removed by filtration. The filtrate was evaporated under vacuum to give N-fluorobenzenaminium tetrafluoroborate (107 mg, 96%).

¹H NMR (D₂O, 400MHz): δ 7.33-7.28 (m, 3H), 7.19-7.17 (m, 2H). ¹⁹F NMR (D₂O, 376MHz): δ -129.6, -150.6 ppm.

![Figure 1. ¹H NMR of fresh in situ generated 1 and recovered catalyst in D₂O.](image-url)
Spectroscopic data for β-aminoalcohols

*Trans*-2-anilino-1-cyclohexanol (6a)\(^5,9,11-12\):

\[ \begin{align*}
\text{H NMR (CDCl}_3, 400MHz): & \quad \delta 7.21 \text{ (m, 2H), 6.73-6.80 (m, 3H), 3.37 (ddd, } J = 10.3, 8.8, 4.4 \text{ Hz, 1H), 3.16 (ddd, } J = 11.7, 9.5, 4.4 \text{ Hz, 1H), 3.06 (brs, 2H), 2.15-2.12 \text{ (m, 2H), 1.80-1.74 (m, 2H), 1.36-1.30 (m, 3H), 1.11-1.01 (m, 1H) ppm;} \text{ 13C NMR (CDCl}_3, 100MHz) \delta 147.5, 129.0 (2C), 117.9, 114.1 (2C), 73.9, 59.7, 33.0, 31.2, 24.6, 24.0 \text{ ppm; IR (liquid in CH}_2\text{Cl}_2): 3390, 2932, 1602, 1503, 1256, 1066, 748 \text{ cm}^{-1}. 
\end{align*} \]

*Trans*-2-(o-methoxyphenylamino)cyclohexanol (6b)\(^6,9,11\):

\[ \begin{align*}
\text{H NMR (CDCl}_3, 400MHz): & \quad \delta 6.88-6.84 \text{ (m, 1H), 6.79-6.77 (m, 2H), 6.72-6.68 \text{ (m, 1H), 3.83 (3H, s), 3.41 (ddd, } J = 10.9, 9.5, 4.4 \text{ Hz, 1H), 3.14 (ddd, } J = 10.9, 8.8, 3.7 \text{ Hz, 1H), 2.10 (t, } J = 13.9 \text{ Hz, 2H), 1.69-1.78 (m, 2H), 1.28-1.36 \text{ (m, 3H), 1.11-1.02 (m, 1H) ppm;} \text{ 13C NMR (CDCl}_3, 100MHz) \delta 147.2, 137.4, 121.1, 
\end{align*} \]
117.0, 111.2, 109.5, 74.3, 59.3, 55.2, 32.9, 31.3, 24.9, 24.1 ppm; IR (liquid in CH₂Cl₂) : 3407, 2931, 1601, 1512, 1222, 1068, 1029, 735 cm⁻¹

**Trans-2-(p-methoxyphenylamino)cyclohexanol (6c)⁵⁻¹¹:**

![Structure of Trans-2-(p-methoxyphenylamino)cyclohexanol (6c)](image)

¹H NMR (CDCl₃, 400MHz) δ 6.75 (d, J = 9.5 Hz, 2H), 6.65 (d, J = 9.5 Hz, 2H), 3.72 (s, 3H), 3.29 (ddd, J = 10.9, 10.3, 4.4 Hz, 1H), 2.96 (ddd, J = 11.0, 9.5, 4.4 Hz, 1H), 2.07-2.05 (m, 2H), 1.73-1.65 (m, 2H), 1.39-1.20 (m, 3H), 1.01-0.93 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 152.6, 141.5, 116.3 (2C), 114.6 (2C), 74.0, 61.3, 55.5, 33.0, 31.3, 24.8, 24.1 ppm; IR (liquid in CH₂Cl₂) : 3369, 2931, 1512, 1239, 1065, 1038, 821 cm⁻¹.

**Trans-2-(o-tolylamino)cyclohexanol (6d)⁵⁻¹¹:**

![Structure of Trans-2-(o-tolylamino)cyclohexanol (6d)](image)

¹H NMR (CDCl₃, 400MHz) δ 7.12-7.07 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.70 (t, J = 7.3, 1H), 3.42 (ddd, J = 10.9, 10.3, 4.4 Hz, 1H), 3.20 (ddd, J = 11.9, 9.5, 4.4 Hz, 1H), 2.15 (s, 3H), 2.15-2.13 (m, 1H), 1.79-1.72 (m, 3H), 1.38-1.30 (m, 3H), 1.1-1.0 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 145.6, 130.3, 127.0, 122.9, 117.7, 111.4, 74.4, 59.7, 33.1, 31.7, 24.9, 24.2, 17.6 ppm; IR (liquid in CH₃CN) : 3405, 2931, 1605, 1511, 1378, 1258, 1066, 746 cm⁻¹.

**Trans-2-(p-tolylamino)cyclohexanol (6e)⁶⁻⁹:**

![Structure of Trans-2-(p-tolylamino)cyclohexanol (6e)](image)

¹H NMR (CDCl₃, 400MHz) δ 7.0 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.31 (ddd, J = 9.9, 8.8, 4.4 Hz, 1H), 3.14 (bri, 2H), 3.08 (ddd, J = 11.7, 9.5, 4.4 Hz, 1H), 2.26 (s, 3H), 2.13-2.05 (m, 2H), 1.77-1.69 (m, 2H), 1.35-1.27 (m, 3H), 1.05-0.97 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 145.3, 129.6 (2C), 127.5, 114.6 (2C), 74.2, 60.4, 33.0, 31.3, 24.9, 24.1, 20.2 ppm; IR (liquid in CH₂Cl₂) : 3388, 2930, 1617, 1518, 1375, 1252, 1066, 808 cm⁻¹.

**Trans-2-(phenylamino)cyclopentanol (7a)⁵⁻⁹:**
$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.17 (t, $J = 7.3$ Hz, 2H), 6.71 (t, $J = 7.3$ Hz, 1H), 6.65 (d, $J = 8.1$ Hz, 2H), 4.02 (dd, $J = 10.3$, 4.4 Hz, 1H), 3.58 (dd, $J = 6.6$, 4.4 Hz, 1H), 2.75 (brs, 2H), 2.29-2.21 (m, 1H), 1.98-1.91 (m, 1H), 1.82-1.68 (m, 2H), 1.66-1.57 (m, 1H), 1.42-1.33 (m, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 147.6, 129.2 (2C), 117.4 (2C), 113.3, 78.0, 61.9, 32.6, 31.0, 20.8 ppm; IR (liquid in CH$_2$Cl$_2$) : 3396, 2917, 1602, 1503, 1277, 1044, 749 cm$^{-1}$

**Trans-2-(o-methoxyphenylamino)cyclopentanol (7b)$^6$:**

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 6.86-6.66 (m, 4H), 4.08 (dd, $J = 9.5$, 4.4 Hz, 1H), 3.83 (s, 3H), 3.59 (dd, $J = 6.6$, 4.4 Hz, 1H), 2.29-2.24 (m, 1H), 2.00-1.94 (m, 1H), 1.81-1.74 (m, 2H), 1.65-1.60 (m, 1H), 1.46-1.41 (m, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 146.7, 137.5, 120.9, 116.5, 109.3, 109.3, 78.1, 61.7, 55.3, 32.8, 31.1, 21.0 ppm; IR (liquid in CH$_2$Cl$_2$): 3412, 2959, 1602, 1513, 1222, 1028, 738 cm$^{-1}$

**Trans-2-(p-methoxyphenylamino)cyclopentanol (7c)$^5$:**

$^1$H NMR (CDCl$_3$) $\delta$ 6.75 (d, $J = 9.5$, 2H), 6.64-6.61 (d, $J = 9.5$, 2H), 4.01 (dd, $J = 10.9$, 5.1 Hz, 1H), 3.73 (s, 3H), 3.51 (dd, $J = 7.3$, 5.1 Hz, 1H), 2.75 (brs, 2H), 2.25-2.19 (m, 1H), 1.98-1.93 (m, 1H), 1.80-1.69 (m, 2H), 1.63-1.58 (m, 1H), 1.38-1.33 (m, 1H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 152.2, 141.7, 116.4(2C), 114.7(2C), 78.1, 62.9, 55.7, 32.7, 31.0, 20.8 ppm; IR (liquid in CH$_2$Cl$_2$): 3378, 2955, 1512, 1238, 1099, 1037, 821 cm$^{-1}$

**Trans-2-(o-tolylamino)cyclopentanol (7d)$^{5,7,8}$:**

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.23 (t, $J = 8.1$ Hz, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 6.84 (d, $J = 8.1$ Hz, 1H), 6.78 (t, $J = 7.3$ Hz, 1H), 4.17 (dd, $J = 10.3$, 4.4 Hz, 1H), 3.74 (dd, $J = 6.5$, 3.7 Hz, 1H), 2.42-2.36 (m, 1H), 2.22 (s, 3H), 2.09-2.05 (m, 1H), 1.94-1.86 (m, 2H), 1.74-1.72 (m, 1H), 1.55-1.49 (m, 1H) ppm; $^{13}$C NMR
(CDCl₃, 100 MHz) δ 145.5, 130.0, 127.0, 121.9, 117.0, 110.6, 78.0, 61.8, 32.7, 31.3, 21.0, 17.4 ppm; IR (liquid in CH₃CN): 3406, 2960, 1605, 1511, 1378, 1264, 1052, 748 cm⁻¹

**Trans-2-(p-tolylamino)cyclopentanol (7e)⁶:**

![2-(p-tolylamino)cyclopentanol](image)

¹H NMR (CDCl₃, 400MHz) δ 7.01 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.1 Hz, 2H), 4.02 (dd, J = 10.3, 5.1 Hz, 1H), 3.56 (dd, J = 6.6, 4.4 Hz, 1H), 3.34 (brs, 2H), 2.26 (s, 3H), 2.25-2.22 (m, 1H), 1.97-1.93 (m, 1H), 1.80-1.71 (m, 2H), 1.62-1.61 (m, 1H), 1.41-1.37 (m, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 144.9, 129.6 (2C), 126.9, 113.8 (2C), 76.6, 62.4, 32.4, 30.7, 20.7, 20.2 ppm; IR (liquid in CH₂Cl₂) : 3369, 2960, 1618, 1519, 1302, 1261, 1041, 808 cm⁻¹

**1-phenyl-2-(phenylamino)ethanol (19)⁹,¹¹:**

![1-phenyl-2-(phenylamino)ethanol](image)

¹H NMR (CDCl₃, 400MHz) δ 7.37-7.25 (m, 5H), 7.12-7.08 (m, 2H), 6.69-6.55 (m, 3H), 4.47 (dd, J = 7.3, 4.4 Hz, 1H), 3.90 (dd, J = 10.9, 3.7 Hz, 1H), 3.71 (dd, J = 10.9, 7.3 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 147.1, 140.0, 128.9(2C), 128.5(2C), 127.3 (2C), 126.5 (2C), 117.6, 113.6, 66.9, 59.6 ppm; IR (liquid in CH₂Cl₂) : 3393, 2927, 1602, 1503, 1267, 1066, 751 cm⁻¹

**1-chloro-3-(phenylamino)propan-2-ol (17)⁹:**

![1-chloro-3-(phenylamino)propan-2-ol](image)

¹H NMR (CDCl₃, 400MHz) δ 7.16 (t, J = 7.7 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 8.8 Hz, 2H), 4.07-4.04 (m, 1H), 3.67-3.62 (m, 2H), 3.36 (dd, J = 13.2, 4.4 Hz, 1H), 3.21 (dd, J = 13.2, 8.1 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 147.6, 129.6 (2C), 118.6, 113.2(2C), 69.7, 47.6, 47.0 ppm; IR (liquid in CH₃CN): 3341, 2925, 1601, 1261, 1074, 750, 694 cm⁻¹

**1-(phenylamino)hexan-2-ol (11a) and 2-(phenylamino)hexan-1-ol (11b)¹²:**
The compound 11a was obtained as major regioisomer with ratio of 11a:11b (77:23), the ratio of regioisomer was determined by $^1$H NMR by integrating peaks at $\delta$ 3.72 and 3.64 ppm corresponding to compound 11a and 11b.

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.21-7.20 (m, 2H), 6.64 (t, $J$ = 7.3 Hz, 1H), 6.55 (d, $J$ = 7.3 Hz, 2H), 3.72-3.71 (m, 1H), 3.15 (dd, $J$ = 12.5, 2.9 Hz, 1H), 2.90 (dd, $J$ = 13.2, 8.8 Hz,1H), 1.43-1.25 (m, 6H), 0.86-0.82(t, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 100MHz) (Major) $\delta$ 148.2, 129.2 (2C), 117.74, 113.54 (2C), 70.20, 50.16, 34.71, 27.17, 22.66, 13.95 ppm; (Minor) $\delta$ 147.73, 129.29(2C), 117.68, 113.58(2C), 64.31, 55.19, 31.79, 28.26, 13.93 ppm; IR (liquid in CH$_2$Cl$_2$): 3393, 2930, 1603, 1504, 1257, 1061, 748 cm$^{-1}$

1-(phenylamino)decan-2-ol (13):

The compound 13a was obtained as major regioisomer with ratio of 13a:13b (79:21), the ratio of regioisomer was determined by $^1$H NMR by integrating peaks at $\delta$ 3.83 and 3.75 ppm corresponding to compound 13a and 13b.

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.21 (t, $J$ = 7.3 Hz, 2H), 6.77 (t, $J$ = 7.3 Hz, 1H) 6.67 (d, $J$ = 5.9 Hz, 2H), 3.81-3.84 (m, 1H), 3.26 (dd, $J$ = 13.2, 3.7 Hz, 1H), 2.99 (dd, $J$ = 13.2, 8.8 Hz, 1H), 1.33 (brs, 14H), 0.93-0.96 (t, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 100MHz) (Major) $\delta$ 148.24, 129.34(2C), 117.82, 113.27(2C), 70.35, 64.47, 55.36, 50.31, 35.08, 31.84, 29.65, 25.61, 22.64, 14.10 ppm; (Minor) $\delta$ 147.74, 129.24(2C), 117.59, 113.55(2C), 64.03, 55.08, 31.97, 30.79, 29.71, 29.41, 29.15, 26.07 ppm; IR (liquid in CH$_2$Cl$_2$) : 3393, 2925, 1603, 1505, 1258, 1072, 748 cm$^{-1}$

Trans-8-(phenylamino)cyclooct-4-enol (9)$^{10,11}$:

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.14-7.05 (m, 2H), 6.74-6.60 (m, 3H), 5.67-5.63 (m, 1H), 5.52-5.45 (m, 1H), 3.57 (ddd, $J$ = 11.7, 8.1, 3.7 Hz, 1H), 3.39 (ddd, $J$ = 11.7, 8.8, 3.7 Hz, 1H), 2.40-2.29 (m, 2H), 2.23-2.16 (m, 2H), 2.04-1.91 (m, 2H), 1.69-1.61(m, 1H), 1.50-1.42 (m, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 147.8,
130.4, 129.0 (2C), 127.6, 118.7, 114.7 (2C), 72.7, 58.7, 33.1, 31.8, 23.1, 22.6 ppm; IR (liquid in CH₂Cl₂): 3389, 2930, 1601, 1499, 1252, 1050, 869, 750, 698 cm⁻¹.

1-(naphthalen-2-yloxy)-3-(phenylamino)propan-2-ol (17)⁸,¹³,¹⁴:

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\[\text{CH}_3\text{CH}_2\text{OH} - \text{N} - \text{C}_6\text{H}_4\text{NH} - \text{C}_10\text{H}_8\text{O} \]
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¹H NMR (CDCl₃, 400MHz) δ 7.80-7.72 (m, 3H), 7.48-7.44 (m, 1H), 7.39-7.35 (m, 1H), 7.21-7.19 (m, 4H), 6.77 (t, \(J = 7.3\) Hz, 1H), 6.70 (d, \(J = 7.3\) Hz, 2H), 4.35-4.29 (m, 1H), 4.20-4.13 (m, 2H), 3.47 (dd, \(J = 13.2, 4.4\) Hz, 1H), 3.34 (dd, \(J = 13.2, 7.3\) Hz, 1H); ¹³C NMR (CDCl₃, 100MHz) δ 156.2, 147.9, 134.3, 129.4, 129.2(2C), 129.0, 127.5, 126.7, 126.4, 123.8, 118.4, 117.9, 113.2(2C), 106.8, 70.0, 68.6, 46.5 ppm; IR (liquid in CH₂Cl₂) 3400, 2927, 1629, 1602, 1258, 1034, 750 cm⁻¹

(S)-1-(naphthalen-2-yloxy)-3-(piperidin-1-yl)propan-2-ol (21):

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\[\text{CH}_3\text{CH}_2\text{OH} - \text{N} - \text{C}_6\text{H}_4\text{NH} - \text{C}_6\text{H}_{11} \]
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¹H NMR (CDCl₃, 400MHz) δ 7.69-7.63 (m, 3H), 7.37-7.07 (m, 4H), 4.11-4.05 (m, 1H), 4.01-3.97 (m, 2H), 3.22(brs, 1H), 2.60-2.51 (m, 2H), 2.47-2.33 (m, 4H), 1.58-1.50 (m, 4H), 1.40-1.37 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 156.7, 134.4, 129.3, 129.0, 127.6, 126.7, 126.3, 123.6, 118.9, 106.6, 70.4, 65.2, 61.2, 54.7 (2C), 25.9 (2C), 24.1 ppm; IR (liquid in CH₂Cl₂) 3401, 2931, 1629, 1600, 1258, 1218, 1037, 747 cm⁻¹

(S)-1-morpholino-3-(naphthalen-2-yloxy)propan-2-ol (22):

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\[\text{CH}_3\text{CH}_2\text{OH} - \text{N} - \text{C}_6\text{H}_4\text{NH} - \text{C}_6\text{H}_{11} \]
```

¹H NMR (CDCl₃, 400 MHz) δ 8.17-8.15 (m, 1H), 7.73-7.71 (m, 1H), 7.43-7.18 (m, 4H), 6.74(d, \(J = 7.3\) Hz, 1H), 4.29-4.23 (m, 1H), 4.15-4.12 (m, 1H), 4.07-4.03 (m, 1H), 3.75-3.66 (m, 4H), 2.73-2.65 (m, 4H), 2.56-2.54 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100MHz) δ 154.2, 134.4, 127.5, 126.4, 125.8, 125.5, 125.2, 121.8, 120.6, 104.8, 70.3, 66.6(2C), 65.6, 61.4, 53.7 (2C) ppm; IR (liquid in CH₂Cl₂): 3419, 2922, 1628, 1518, 1270, 1241, 1117, 1035, 1070, 772 cm⁻¹

2-(piperidin-1-yl)cyclohexanol :⁹
\[ \text{[Chemical structures images]} \]

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 3.34-3.28 \text{ (m, 1H), 2.65-2.59 \text{ (m, 2H), 2.27} \text{ (brs, 2H), 2.12-2.04} \text{ (m, 2H), 1.75-1.70} \text{ (m, 2H), 1.66-1.64 \text{ (m, 1H), 1.60-1.44} \text{ (m, 4H), 1.40-1.34} \text{ (m, 2H), 1.24-1.04} \text{ (m, 6H) ppm.} \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 70.94, 68.49, 49.73 \text{ (2C), 33.20, 26.66} \text{ (2C), 25.58, 24.79, 24.06, 22.09} \text{ ppm.} \]

2-morpholinocyclohexanol:

\[ \text{[Chemical structures images]} \]

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 4.59 \text{ (brs, 1H), 3.71-3.67 \text{ (m, 4H), 3.38-3.32 \text{ (m, 1H), 2.72-2.69} \text{ (m, 2H), 2.44-2.43 \text{ (m, 2H), 2.19-2.18} \text{ (m, 1H), 2.09-2.06} \text{ (m, 1H), 1.80-1.73} \text{ (m, 2H), 1.67-1.65} \text{ (m, 1H), 1.16-1.11} \text{ (m, 4H) ppm. \]} \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 70.46, 68.34, 67.37 \text{ (2C), 48.65} \text{ (2C), 33.11, 25.36, 23.94, 22.19} \text{ ppm.} \]

2-(benzylamino)cyclohexanol:

\[ \text{[Chemical structures images]} \]

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.33-7.22 \text{ (m, 5H), 3.93} \text{ (d,} J = 13.18 \text{ Hz, 1H), 3.67} \text{ (d,} J = 13.18 \text{ Hz, 1H), 3.22-3.18 \text{ (m, 2H), 2.34-2.28} \text{ (m, 1H), 2.13-2.09} \text{ (m, 1H), 1.95-1.93} \text{ (m, 1H), 1.70-1.67} \text{ (m, 2H), 1.25-1.16} \text{ (m, 3H) ppm. \]} \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 139.48, 128.32 \text{ (2C), 128.12} \text{ (2C), 127, 73.1,} 62.8, 50.45, 33.43, 29.85, \text{ 24.75, 24.18} \text{ ppm.} \]

2-((1-phenylethyl)amino)cyclohexanol:

\[ \text{[Chemical structures images]} \]

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.29-7.16 \text{ (m, 5H), 3.89-3.84} \text{ (q,} J = 6.59 \text{ Hz, 1H), 3.07-3.02} \text{ (m, 1H), 2.30-2.24} \text{ (m, 1H), 2.0-1.95} \text{ (m, 1H), 1.87-1.83} \text{ (m, 1H), 1.63-1.56} \text{ (m, 2H), 1.28} \text{ (d,} 3H), 1.22-1.08 \text{ (m, 4H) ppm. \]} \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 146.68, 128.44 \text{ (2C), 127.02, 126.38} \text{ (2C), 74.02, 61.51, 55.21, 32.94, 31.25, 25.35, 24.20, 23.42} \text{ ppm.} \]

References

Figure 3. HRMS of N-Fluorobenzenaminium tetrafluoroborate

Figure 3. HRMS of in situ generated N-Fluorobenzenaminium tetrafluoroborate
Figure 4. HRMS of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride with tetrafluoroborate
Figure 5. HRMS of Selectfluor
Table 1: entry (without catalyst)
GC chromatogram for the table 2

**Conditions for GC:** GC parameters for capillary columns (30 m × 0.25 mm): injector 250 °C; detector 250 °C; oven 100 °C for 3 min then 5 °C min⁻¹ until 180 °C for 15 min; column pressure 118.3 kPa, column flow 1.36 mL min⁻¹; linear velocity 35 cm s⁻¹; total flow 45.1 mL min⁻¹.

Trans-2-(piperidin-1-yl)cyclohexanol

![Chemical structure of Trans-2-(piperidin-1-yl)cyclohexanol](image)

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Trans-2-morpholinocyclohexanol

![Molecular structure of Trans-2-morpholinocyclohexanol]

**Chromatogram**

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Trans-2-(benzylamino)cyclohexanol :

\[
\begin{align*}
\text{OH} & \quad \text{N} \\
\end{align*}
\]

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Trans-2-((S)-1-phenylethylamino)cyclohexanol:

\[
\text{OH} \\
\text{N} \begin{array}{c}
\ddot{\text{H}} \\
\ddot{\text{H}} \\
\text{phenylethylamino}
\end{array} \text{cyclohexanol}
\]

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Conc.
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Peak
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