$Fe(Cp)_2BF_4$: An Efficient Lewis Acid Catalyst for the Aminolysis of Epoxides

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Abstract: Ferrocenium tetrafluoroborate [$Fe(Cp)_2BF_4$] is an efficient Lewis acid catalyst for the aminolysis of aromatic, aliphatic, and cyclic epoxides using aniline and substituted anilines as the nucleophile to provide regioselective β-amino alcohols in 61–97% yields under solvent-free conditions at room temperature. The ring opening of cyclohexene oxide with aliphatic amines gave 2-aminocyclohexanols in 33–98% yields at 60 °C under solvent-free conditions.

Key words: epoxides, ring opening, amino alcohols, Lewis acid, $Fe(Cp)_2BF_4$

β-Amino alcohols are useful synthetic intermediates in the synthesis of a wide range of biologically active natural and synthetic products, chiral auxiliaries, unnatural β-amino acids, β-blockers in pharmaceuticals, and insecticides.[1] Ring opening of epoxides using excess amine as the nucleophile at elevated temperatures is an important and widely used route for the preparation of β-amino alcohols.[2] However, this process is not suitable particularly when dealing with thermally sensitive epoxides due to occurrence of side reactions.[3] Lewis acids, many of which suffer from deactivation of the catalyst due to complex formation with the amine, have also been used for this process. The cleavage of epoxides with amines has been developed in presence of metal halides,[4] metal triflates,[5] metal alkoxides,[6] metal amides and triflamide,[7] transition-metal salts,[8] hexafluoropropan-2-ol under reflux,[9] ionic liquid,[10] zirconium sulfophenyl phosphonate,[11] montmorillonite clay under microwave[12a] and solvent-free conditions,[12b] in water without a catalyst,[13] silica,[14] alumina/modified alumina,[15] zeolites,[16] Fe-MCM-41,[17] SBA-15-*pr*-SO_3H and Ti-MCM-41,[18] heterodimetallic coordination polymers,[19] poly(amidoamine) dendrimer supported on cross-linked polystyrene,[20] and *N*-formyl-L-proline.[21] There are still limitations with some of the existing methods; for example less basic amines fail to open these epoxides under ambient conditions or the use of high catalyst loading using expensive catalysts.

Herein, we report our investigation into the ring opening of epoxides with different amines using ferrocenium tetrafluoroborate (Figure 1) as a Lewis acid catalyst under solvent-free conditions at room temperature. In our earlier reports we used ferrocenium hexafluorophosphate as a catalyst for the cyanosilylation of carbonyl compounds and Strecker reaction of ketones and aldehydes under solvent-free conditions at room temperature.[22] Recently, enantioselective ring opening of *meso*-epoxides with aniline using Bolm's ligand and iron(II) perchlorate hexahydrate was reported by Plancq and Ollevier.[23] The better solubility of these organometallics in organic solvents and reagents may improve reactivity.

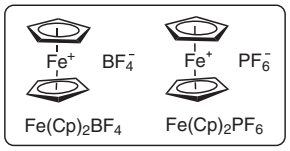

Figure 1 Structure of catalysts

The ring opening of cyclohexene oxide (**1**) with aniline under solvent-free conditions at room temperature in the presence of a catalytic amount (5 mol%) of various iron(III) salts was examined as a model reaction (Table 1). Reaction of **1** with iron(III) chloride monohydrate or iron(III) sulfate monohydrate for 23 hours gave the desired product, *trans*-2-anilinocyclohexanol (**4a**), in 16% and 78% yields, respectively (entries 1 and 2); using ferrocenium tetrafluoroborate or hexafluorophosphate as the catalyst for five hours at room temperature gave **4a** in 90% and 73% yields, respectively (entries 3 and 4). Ferrocenium tetrafluoroborate (2 mol%) also gave **4a** in a good 84% yield (entry 5). We examined the used of these two catalysts, ferrocenium tetrafluoroborate and hexafluorophosphate, in the ring opening of cyclohexene oxide (**1**) with various substituted anilines **3b**–**e**. Using 2-methoxyaniline (**3b**) as a nucleophile with ferrocenium tetrafluoroborate or hexafluorophosphate as the catalyst for five hours gave the ring-opened product **4b** in excellent yields (96% and 84%) (entries 7 and 8). The results shown in Table 1 indicate that ferrocenium tetrafluoroborate is a more active catalyst than ferrocenium hexafluorophosphate. A poor yield of product **4c** was obtained with both catalysts due to the lower solubility of solid 4-methoxyaniline in the epoxide and the reaction requires dichloromethane as a solvent to make the reaction mixture homogenous (entries 9 and 10). Using ferrocenium tetrafluoroborate as the catalyst and 2-methyl- and 4-methylaniline as nucleophiles gave ring-opened products **4d**,**e** in 73% and 91% yields, respectively, (entries 11 and 13).

We also studied the reaction of cyclopentene oxide (**2**) with various substituted anilines using ferrocenium tetrafluoroborate (5 mol%) as the catalyst under solvent-free conditions. We obtained an excellent yield of the products

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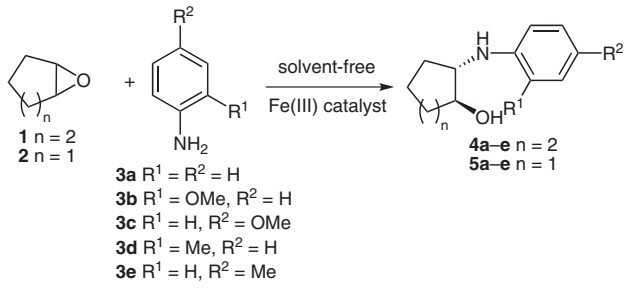
Table 1 Ring Opening of Cyclic Epoxides with Different Anilines Catalyzed by Iron(III) Salts under Solvent-Free Conditions[a]



3a $R^1 = R^2 = H$
3b $R^1 = OMe$, $R^2 = H$
3c $R^1 = H$, $R^2 = OMe$
3d $R^1 = Me$, $R^2 = H$
3e $R^1 = H$, $R^2 = Me$

Entry	Catalyst	Epoxide	Amine **3a–f**	Product	Yield[b] (%)
1	$FeCl_3 \cdot H_2O$	**1**	**3a**	**4a**	16[c]
2	$Fe_2(SO_4)_3 \cdot H_2O$	**1**	**3a**	**4a**	78[c]
3	$Fe(Cp)_2BF_4$	**1**	**3a**	**4a**	90
4	$Fe(Cp)_2PF_6$	**1**	**3a**	**4a**	73
5	$Fe(Cp)_2BF_4$	**1**	**3a**	**4a**	84[d]
6	$Fe(Cp)_2PF_6$	**1**	**3a**	**4a**	58[d]
7	$Fe(Cp)_2BF_4$	**1**	**3b**	**4b**	96
8	$Fe(Cp)_2PF_6$	**1**	**3b**	**4b**	84
9	$Fe(Cp)_2BF_4$	**1**	**3c**	**4c**	61[e]
10	$Fe(Cp)_2PF_6$	**1**	**3c**	**4c**	58[e]
11	$Fe(Cp)_2BF_4$	**1**	**3d**	**4d**	73
12	$Fe(Cp)_2PF_6$	**1**	**3d**	**4d**	64
13	$Fe(Cp)_2BF_4$	**1**	**3e**	**4e**	91
14	$Fe(Cp)_2PF_6$	**1**	**3e**	**4e**	73
15	$Fe(Cp)_2BF_4$	**2**	**3a**	**5a**	95
16	$Fe(Cp)_2BF_4$	**2**	**3b**	**5b**	90
17	$Fe(Cp)_2BF_4$	**2**	**3c**	**5c**	97
18	$Fe(Cp)_2BF_4$	**2**	**3d**	**5d**	92
19	$Fe(Cp)_2BF_4$	**2**	**3e**	**5e**	90

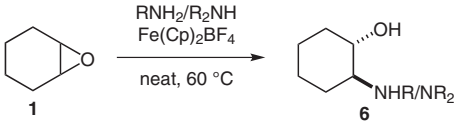
[a] Procedure: epoxide (2 mmol) was cooled to 0–5 °C, then catalyst (5 mol%) and amine (2.1 mmol) were added and the mixture was stirred at 25 °C for 5 h.
[b] Yield was measured after purification by column chromatography.
[c] The reaction was stirred for 23 h.
[d] The reaction was carried using 2 mol% of catalyst.
[e] Reaction carried out in CH_2Cl_2 (0.5 mL).

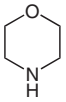
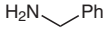
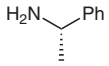
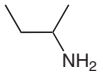
5a–e (90–97%) with substituted anilines **3a–e** in five hours (entries 15–19).

The ring opening of cyclohexene oxide (**1**) with aliphatic amines was also investigated using ferrocenium tetrafluoroborate (5 mol%) as the catalyst at 60 °C under solvent-free conditions (Table 2). Ring opening of cyclohexene oxide (**1**) with piperidine at room temperature for 24 hours gave *trans*-2-piperidinocyclohexanol in 77% yield, increasing the reaction temperature to 60 °C for six hours afforded the product in 96% yield (entries 1 and 2). When the same reaction was carried out in the absence of a catalyst at 60 °C for six hours the product was obtained in 14% yield (entry 3).

We examined the use of various aliphatic amines, such as isopropylamine, morpholine, benzylamine, (*S*)-α-methylbenzylamine, isobutylamine, ethylamine, and pyrrolidine, for the ring opening of cyclohexene oxide (**1**) (Table 2). The ring opening of cyclohexene oxide (**1**) with secondary amines is faster than ring opening with primary amines (entries 1–10). Ring opening of cyclohexene oxide (**1**) with (*S*)-α-methylbenzylamine afforded *trans*-2-[(*S*)-1-phenylethylamino)cyclohexanol in 95% yield with 58:42 diastereomeric ratio (entry 7).

Table 2 Ring Opening of Cyclohexene Oxide with Aliphatic Amines Catalyzed by Ferrocenium Tetrafluoroborate under Solvent-Free Conditions[a]



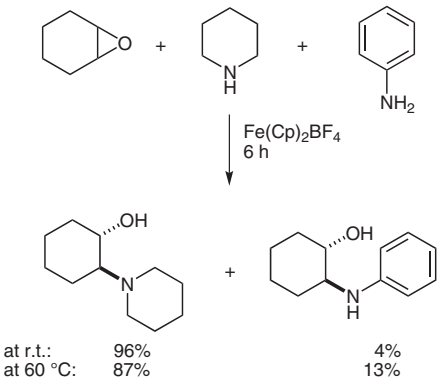
Entry	Amine	Time (h)	Yield[b] (%)
1		6	96
2		24	77[c]
3		6	14[d]
4		9	92
5		6	95
6		21	98
7		20	95[e]
8		6	33
9		6	77
10		19	85

[a] Procedure: cyclohexene oxide (**1**, 2 mmol) was cooled to 0–5 °C then $Fe(Cp)_2BF_4$ (5 mol%) and amine (2.2 mmol) were added and the mixture was stirred at 60 °C for the specified time.
[b] Isolated yield was measured after purification by column chromatography.
[c] Reaction carried out at r.t.
[d] Reaction carried out in the absence of catalyst at 60 °C
[e] Diastereomeric ratio (58:42) of product was determined by gas chromatography.

We conducted a competitive experiment for the ring-opening of cyclohexene oxide (**1**) with aliphatic and aro-

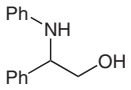
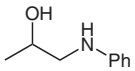
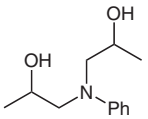
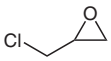
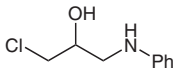
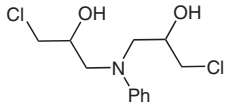
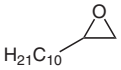
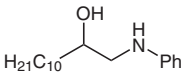
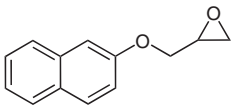
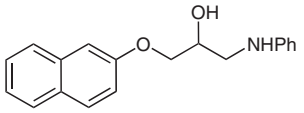
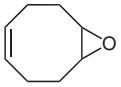
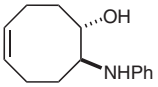
matic amines, piperidine and aniline, using ferrocenium tetrafluoroborate (5 mol%) as the catalyst at room temperature and also at 60 °C for six hours (Scheme 1). The major product was that from the ring opening of cyclohexene oxide (**1**) with piperidine and the minor product was that from the opening of **1** with aniline, *trans*-2-anilinocyclohexanol (**4a**), in a ratio of 96:4 at room temperature and 87:13 at 60 °C (product ratio was determined by gas chromatography).

Furthermore, the range of application of this methodology for ring opening of various epoxides was examined using with aniline and ferrocenium tetrafluoroborate (5 mol%) as the catalyst at room temperature (Table 3). The ring opening of styrene oxide with aniline gave 2-anilino-2-phenylethanol (**7**) in 82% yield by attack of the nucleophile at benzylic carbon of styrene oxide. The product was confirmed by ^{1}H NMR and comparison with the reported literature.[4k] Ring opening of propylene oxide with aniline gave the desired product **8a** and its regioisomeric product (85:15) in 74% yield, but the dialkylated aniline **8b** was also formed in 19% yield as a byproduct due to the reaction of **8a** and propylene oxide (entry 2). Performing this reaction and monitoring it by gas chromatography gave

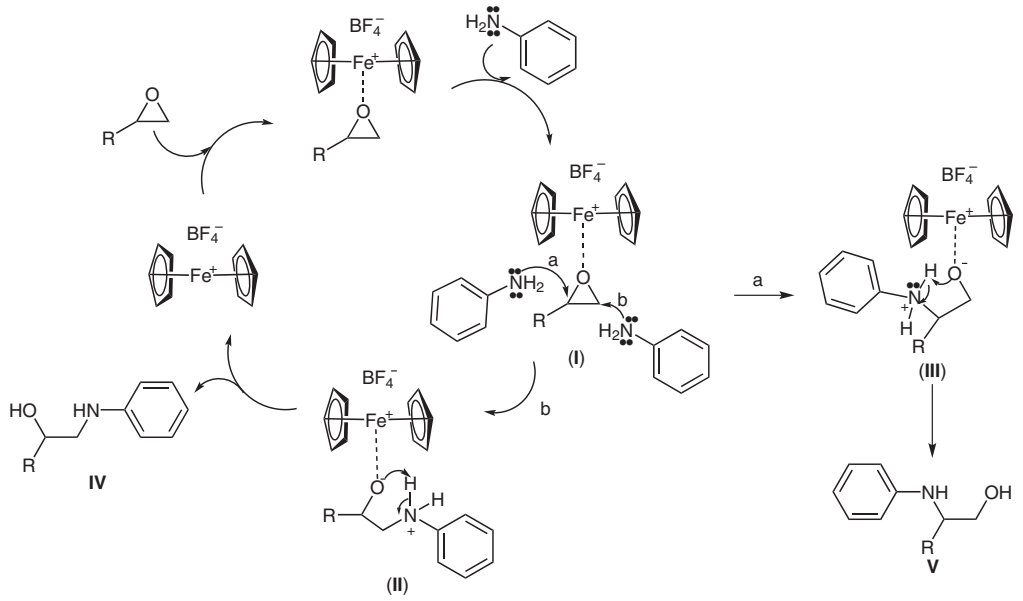


Scheme 1 Competitive ring opening of cyclohexene oxide with piperidine and aniline

Table 3 Ring Opening of a Variety of Epoxides with Aniline Catalyzed by Ferrocenium Tetrafluoroborate under Solvent-Free Conditions[a]

Entry	Epoxide	Time (h)	Product(s)	Yield[b] (%)
1		1	 **7**	82
2		7	 **8a**	**8a**, 74[c]; **8b**, 19
3		5	 **8b**	**8a**, 78[c,d]
4		6	 **9a**	**9a**, 68; **9b**, 23
			 **9b**	
5		6	 **10**	80[e]
6		5	 **11**	92
7		4	 **12**	97

[a] Conditions: epoxide (2 mmol) was cooled to 0–5 °C then $Fe(Cp)_2BF_4$ (5 mol%) and amine (2.1 mmol) were added and the mixture was stirred at 25 °C for the specified time.
[b] Isolated yield was measured after purification using column chromatography.
[c] The regioisomeric product of **8a** was obtained in 85:15 (by ^{1}H NMR).
[d] The reaction was monitored by GC and the conversion of product **8a** was 78% without formation of any byproduct.
[e] The regioisomeric product of **10** was obtained in 86:14 (by ^{1}H NMR).



Scheme 2 Proposed catalytic cycle for the ring opening of epoxide with aniline (a) R = alkyl, product **IV** is the major regioisomer and **V** is the minor regioisomer; if R = Ph, **V** is the exclusive product

exclusively **8a** in 78% after five hours with no byproduct. Ring opening of epichlorohydrin with aniline gave the desired product **9a** in 68% isolated yield and byproduct **9b** in 23% yield (entry 4). We also used aliphatic epoxides 1,2-epoxydodecane with aniline as the nucleophile, in this case the major product **10** was obtained by attack of aniline at the terminal carbon of the aliphatic epoxide and a minor regioisomeric product was also formed; the regioisomeric ratio was 86:14 and the total yield was 80%. The ring opening of β-naphthylglycidyl ether for five hours gave the desired product **11** in 92% yield (entry 7). 1,2-Epoxycyclooct-5-ene also afforded *trans*-β-amino alcohol **12** in 97% yield in four hours.

We proposed the mechanism for the ring opening of an epoxide with an amine, according to the major regioisomer formed during the reaction. The ferrocenium tetrafluoroborate acts as a Lewis acid and weak interaction is possible with the oxygen of the epoxide. Nucleophile amine can attack on both carbons of the epoxide, but the formation of the major regioisomer depends on the nature of epoxide and amine (Scheme 2). In the ring opening of aliphatic epoxides with aniline attack occurs on the terminal carbon (path b, intermediate **II**) of the epoxide and give the major product **IV** and its regioisomeric minor product **V** was also obtained due to attack of aniline at the secondary carbon of the epoxide. The ring opening of styrene oxide with aniline gave the product **V** by attack of the nucleophile aniline at the benzylic carbon (path a, intermediate **III**) of the epoxide.

In conclusion, we have demonstrated a new catalyst ferrocenium tetrafluoroborate for the ring opening of cyclic epoxides with aliphatic and aromatic amines giving β-amino alcohols in good and excellent yields in 5–20 hours under solvent-free conditions. The catalyst was also used for the ring opening of aliphatic and aromatic epoxides with aniline to afford the corresponding β-amino alcohols in 68–97% yield (1–7 h).

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz (operating frequencies: ^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz) Jeol FT-NMR spectrometers at r.t. using the NMR solvent as an internal reference [$CDCl_3$: δ = 7.26 (^{1}H) and 77.00 (^{13}C)]. HRMS analysis was carried out using Bruker QSTAR XL Pro system microTOF-Q-II. IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer. Optical rotation values were measured on a Rudolph digital polarimeter. TLC was carried out using Merck Kieselgel 60 F254 silica gel plates. Column chromatography separations were performed using Merck Kieselgel 60 (Art. 7734). All new and known compounds were characterized by ^{1}H and ^{13}C NMR and IR. The ^{1}H and ^{13}C NMR data of known compounds **4a**,[4m] **4b**,[11] **4c**,[4m] **4d**,[4g] **4e**,[4f] **5a**,[4m] **5b**,[4k] **5c**,[4m] **5d**,[4g] **5e**,[4f] compounds from Table 2 (entries 1,[4m] 4,[4m] 5,[4m] 6,[4i] 7[24] and 10[5g]), **7**,[4k] **8a**,[8c] **9a**,[8c] **11**[4k] and **12**[5e] are similar to those reported in the literature.

β-Amino Alcohols; General Procedure

Catalyst $Fe(Cp)_2BF_4$ (5 mol%) was added to the cooled epoxide (2 mmol) at 0–5 °C and then amine (2.1 mmol) was added. The resulting mixture was stirred at 25 °C for the specified time (TLC monitoring). When the reaction was complete, the crude product was purified by column chromatography. For entry 9 in Table 1, CH_2Cl_2 (0.5 mL) was used as solvent.

3,3′-(Phenylazanediyl)bis(propan-2-ol) (8b)

Brown liquid; yield: 81 mg (19%).

IR (CH_2Cl_2): 3318, 2967, 1598, 1504, 1375, 1083, 747, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.19 (m, 2 H), 6.78–6.76 (m, 2 H), 6.54 (d, *J* = 8.05 Hz, 1 H), 4.16–4.08 (m, 2 H), 3.64 (dd, *J* = 15.38, 2.20 Hz, 1 H), 3.36 (dd, *J* = 14.64, 2.93 Hz, 1 H), 3.15 (dd, *J* = 15.38, 9.52 Hz, 1 H), 3.00 (dd, *J* = 15.38, 9.52 Hz, 1 H), 2.01 (br s, OH, 1 H), 1.17 (t, *J* = 5.86 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.14, 147.91, 129.18, 129.3, 117.41, 116.63, 114.01, 112.10, 66.02, 64.94, 62.45, 59.97, 20.15, 20.14.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{20}NO_2$: 210.1494; found: 210.1492.

3,3′-(Phenylazanediyl)bis(1-chloropropan-2-ol) (9b)
Brown liquid; yield: 127 mg (23%).

IR (CH_2Cl_2): 3338, 2955, 1599, 1505, 1362, 1103, 994, 750, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.16 (m, 2 H), 6.76–6.60 (m, 3 H), 4.15–4.13 (m, 1 H), 4.07–4.05 (m, 1 H), 3.82 (dd, *J* = 14.28, 2.20 Hz, 2 H), 3.55–3.47 (m, 4 H), 3.39 (dd, *J* = 15.38, 8.79 Hz, 1 H), 3.08 (dd, *J* = 15.38, 8.79 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.47, 147.87, 132.93, 131.00, 118.15, 117.99, 114.46, 112.82, 69.32, 68.52, 58.72, 55.51, 47.15, 47.15.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}Cl_2NO_2$: 278.0715; found: 278.0671.

1-(Phenylamino)dodecan-2-ol (10)
Purple solid; yield: 480 mg (80%).

IR (CH_2Cl_2): 3393, 2925, 603, 1505, 1258, 1072, 748 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) (major): δ = 7.23 (t, *J* = 7.59 Hz, 2 H), 6.77–6.66 (m, 3 H), 3.82–3.75 (m, 1 H), 3.25 (dd, *J* =13.18, 2.93 Hz, 1 H), 2.99 (dd, *J* = 12.47, 8.79 Hz, 1 H), 1.53 (m, 2 H), 1.34–1.25 (m, 18 H), 0.96–0.95 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.19, 129.37, 117.67, 113.17, 70.16, 50.16, 35.03, 31.99, 29.52 (4 C), 29.26, 25.58, 22.59, 14.02.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{32}NO$: 278.2484; found: 278.2447.

***trans*-2-(*sec*-Butylamino)cyclohexanol (Table 2, Entry 8)**
Colorless liquid; yield: 113 mg (33%).

IR (CH_2Cl_2): 3394, 2932, 2859, 1450, 1085, 847 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.34 (br s, 1 H), 3.03–3.01 (m, 1 H), 2.62–2.58 (m, 2 H), 2.16–2.13 (m, 1 H), 1.98–1.95 (m, 2 H), 1.62–1.58 (m, 2 H), 1.30–1.04 (m, 6 H), 0.97 (d, *J* = 6.59 Hz, 1.25 H), 0.91 (d, *J* = 6.59 Hz, 1.75 H), 0.85–0.77 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.60, 60.36, 50.88, 32.96, 31.33, 30.78, 25.19, 24.20, 20.01, 10.36 (Major).73.82, 61.05, 51.27, 33.06, 30.90, 28.84, 25.19, 24.23, 21.27, 9.55 (minor).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{22}NO$: 172.1701; found: 172.1722.

***trans*-2-(Ethylamino)cyclohexanol (Table 2, Entry 9)**
Brown liquid; yield: 110 mg (77%).

IR (CH_2Cl_2): 3390, 2932, 1450, 1084, 839 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.33–3.30 (m, 1 H), 2.87 (dt, *J* = 13.91, 10.98, 7.32 Hz, 1 H), 2.66–2.58 (m, 1 H), 2.44–2.39 (m, 1 H), 1.96–1.83 (m, 3 H), 1.63 (m, 2 H), 1.20–1.10 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.66, 62.76, 40.18, 33.81, 28.23, 24.36, 24.03, 13.30.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_8H_{18}NO$: 144.1388; found: 144.1392.

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