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Graphite oxide catalyzed synthesis of β-amino alcohols by ring-opening of epoxides

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Abstract: Graphite oxide as a heterogeneous and recyclable solid acid catalyzed a simple and efficient method for the synthesis of β-amino alcohols by ring opening of epoxides with amines. This method is effective with various aromatic and aliphatic amines under solvent-free conditions. The corresponding β-amino alcohols are obtained in high yields (56%–95%) and short reaction times (15–30 min) with high regio- and chemoselectivity under metal-free conditions.

Key words: Ring opening, epoxides, amines, β-amino alcohols, graphite oxide, metal-free conditions

1. Introduction

The ring opening of epoxides with amines is an important and elegant route for the synthesis of β-amino alcohols, which are versatile intermediates for the synthesis of a wide range of natural and synthetic pharmacological products.[1,2] Therefore, a large number of methods have been developed for this chemical transformation.[3–5] The conventional synthesis of β-amino alcohols consists of heating epoxides with an excess of amines at elevated temperatures.[6] There are some limitations to this classical approach such as the requirement of elevated reaction temperatures in the case of less reactive amines, lower reactivity of the sterically hindered amines/epoxides, and poor regioselectivity of the epoxide ring opening. Thus, several promoters/activators such as Lewis acids ($Er(OTf)_3$,[7] $Yb(OTf)_3$,[8] $LiClO_4$,[9] Al_2O_3,[10] $Zn(BF_4)_2$[11]), heterogeneous catalysts (mesoporous activated carbon,[12] magnetic nano Fe_3O_4,[13] nanoporous aluminosilicates,[14] sulfated tungstate[15]), and metal halides ($ZrCl_4$[16] $SbCl_3$[17]) have been employed for the ring opening of epoxides with amines. The ring-opening reaction of epoxides with amines under solvent-free conditions has also been investigated in several reports.[11,18,19] Nevertheless, many of these methodologies suffer from one or more disadvantages such as elevated temperatures, long reaction times, high pressure, moderate yields, requirement of stoichiometric amounts of catalyst, use of air and moisture sensitive catalysts, and hazardous organic solvents. The various catalysts and experimental conditions used are summarized in Table 1.[13,14,20–27] Therefore, further efforts are required for aminolysis of epoxides with amines.

Graphite oxide (GO), an available and inexpensive material,[28] and graphene oxide and its functionalized derivatives have been utilized as heterogeneous catalysts for several organic transformations.[29–37] The surface of GO comprises several oxygen-containing groups such as epoxy, hydroxyl, and carbonyl, which provide an

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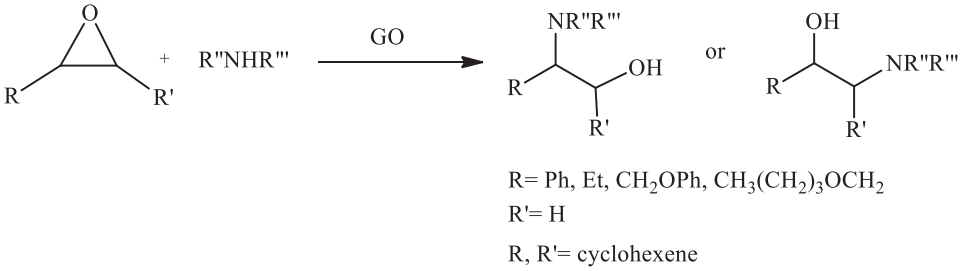
acidic character to the material. Recently, we have applied GO as a solid acid catalyst for the alcoholysis of epoxides,[38] conversion of oxiranes into thiiranes,[39] and esterification of organic acids with alcohols.[40] In continuation of our investigation on the use of GO as a heterogeneous solid acid catalyst, we report herein a simple and efficient method for the ring opening of epoxides by various amines under solvent-free conditions (Scheme 1). To the best of our knowledge, the ring-opening reaction of epoxide with amines catalyzed by GO has not been reported before.

Table 1. Various catalysts and conditions for aminolysis of epoxides with amines.

Entry	Catalyst and conditions	Time	Yield (%)
1	Organobismuth triflate complex $[O(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2\ CF_3]^-$ (5 mol%), H_2O, rt.[20]	2.5–8 h	60–93
2	Mesoporous aluminosilicate (120 mg/mmol), CH_2Cl_2, rt.[21]	6–24 h	58–79
3	Nanoporous aluminosilicate materials (120 mg/mmol epoxide), CH_2Cl_2, rt.[14]	2–24 h	10–80
4	Schiff bases supported on poly(vinyl chloride) (5 mol%), 1,4-dioxane, 50 °C.[22]	6–8 h	80–93
5	Magnetic nano Fe_3O_4 (10 mol%), rt to 80 °C.[13]	6–24 h	32–99
6	Fe(III) substituted Wells–Dawson type polyoxometalate, α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}.3H_2O$ (3 mol%), CH_3CN, rt.[23]	40–350 min	60–98
7	$Y(NO_3)_3.6H_2O$ (1 mol%), rt.[24]	1–7 h	72–92
8	Zirconium sulfophenyl phosphonate (50 mg/mmol epoxide), 40 °C under N_2.[25]	2–48 h	36–94
9	Metallocene (Cp_2MCl_2, M = Ti, Zr, V) (10 mol%), rt.[26]	1.5–70 h	32–99
10	$Sn(OTf)_2$ (10 mol%), CH_3CN or CH_2Cl_2, rt to 80 °C.[27]	6–105 h	11–99



Scheme 1. Aminolysis of epoxides catalyzed by GO.

2. Results and discussion

Initially, we screened the ring-opening reaction of styrene oxide (1 mmol) with aniline (1 mmol) at room temperature in the absence of GO. The resulting mixture was stirred for the time indicated in Table 2 prior to GC/MS analysis. Only traces of the corresponding β-amino alcohol were obtained; the starting materials were recovered even after 24 h stirring at room temperature (entry 1, Table 2). In the next step, we investigated the ring-opening reaction of styrene oxide (1 mmol) with aniline (1 mmol) in the presence of 10 mg of GO. The reaction proceeded smoothly to produce 2-phenyl-2-(phenylamino)ethanol in 86% after 15 min. The result indicates that the aminolysis is regioselective. It should be noted that increasing the reaction time had low or no impact on the reaction yield; indeed, 2-phenyl-2-(phenylamino)ethanol was obtained in 87% and 90% yield after 2 and 3 h, respectively (entry 2, Table 2). We further evaluated the catalytic activity of GO in different solvents. When the aminolysis reaction of styrene oxide with aniline was performed in neat dichloromethane, acetonitrile,

or water at room temperature for 2 or 4 h in the presence of 10 mg of GO, the ring opening took place but the yields were low (entries 3–5, Table 2). The comparison of entries 2 and 3–5 clearly indicates that the tested solvents do not improve the reaction yield and solvent-free conditions are better. The obtained results under our experimental conditions showed that the reaction is faster under solvent-free conditions. It is thought that the diffusion path between molecules is small under solvent-free conditions due to the high concentrations of reactants and thus the reaction is rapid.[41,42] Finally, we examined the effect of GO concentration for aminolysis of styrene oxide with aniline (entries 6 and 7, Table 2). Notably larger amounts of GO catalyst did not improve the reaction yield. A comparison of entries 2, 6, and 7 suggests that 10 mg of GO is sufficient for this reaction.

Table 2. Different conditions for the ring opening of styrene oxide with aniline at room temperature.

Entry	GO	Solvent	Time	Yield[a] (%)
1	-	-	24 h	2
2	10 mg	-	15 min, 2 h, 3 h	86, 87, 90
3	10 mg	CH_2Cl_2	2 h, 4 h	2, 14
4	10 mg	CH_3CN	2 h, 4 h	27, 57
5	10 mg	H_2O	2 h, 4 h	10, 15
6	5 mg	-	15 min	71
7	15 mg	-	15 min	89

[a]GC/MS yield.

Under the above optimized reaction conditions, aminolysis of a wide range of epoxides (1 mmol) such as styrene oxide, 2-ethyloxirane, 2-(phenoxymethyl)oxirane, 2-(butoxymethyl)oxirane, and 7-oxabicyclo[4.1.0]heptane with aromatic amines (1 mmol) such as aniline; 4-methoxy, hydroxy, chloro, nitro, methyl, and 2,5-dimethylaniline; diphenyl, benzyl, and dibenzylamine; aliphatic amines such as n-propylamine; and cyclic amines such as morpholine was investigated for the synthesis of the corresponding β-amino alcohols in the presence of GO (10 mg). As indicated in Table 3, aminolysis of styrene oxide with aromatic amines such as aniline, 4-methoxy, hydroxyl, nitro, and diphenylamine in the presence of 10 mg of GO gave the corresponding β-amino alcohols in 77%–93% yield after 15 min at room temperature (entries 1–5). The results showed that the aminolysis of styrene oxide proceeds nicely with aromatic amines with electron-releasing or withdrawing groups even though the presence of withdrawing groups on the aromatic ring tends to decrease the reaction yield and prolong the reaction time (entry 4, Table 3). In contrast to aromatic amines, aliphatic amines such as n-propylamine require higher temperature (60 °C) (entry 6, Table 3).

Next, we performed the ring opening of 2-ethyloxirane with aromatic and cyclic aliphatic amines such as aniline and morpholine; 2-(phenylamino)butan-1-ol and 2-morpholinobutan-1-ol were isolated in 83% and 90% yield, respectively, after 15 min (entries 7 and 8, Table 3). It should be noted that aminolysis of styrene oxide and 2-ethyloxirane is regioselective and the corresponding β-amino alcohols resulted from nucleophilic attack at the more hindered carbon atom of the epoxide ring.

Furthermore, aminolysis of 2-(phenoxymethyl)oxirane with aniline, 4-methoxy, 2,5-dimethylaniline, benzylamine, and morpholine afforded the corresponding β-amino alcohols in 88%, 94%, 90%, 87%, and 84% yield, respectively (entries 9–13, Table 3). The reaction is regioselective with preferential nucleophilic attack at the less hindered carbon atom of the epoxide ring; steric effects dominate over electronic effects. Similarly, the ring-opening reaction of 2-(butoxymethyl)oxirane with aniline, 4-chloroaniline, and dibenzyl amine gave 1-butoxy-3-(phenylamino)propan-2-ol, 1-butoxy-3-((4-chlorophenyl)amino)propan-2-ol, and 1-butoxy-3-(dibenzylamino)propan-2-ol in 81%, 56%, and 70%, respectively, after 15 min at room temperature (entries

Table 3. Aminolysis of epoxides with amines catalyzed by GO.[a]

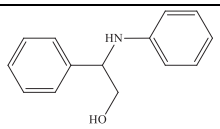
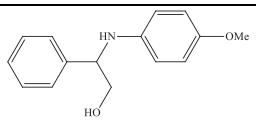
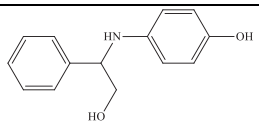
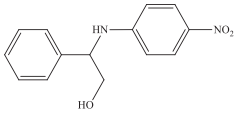
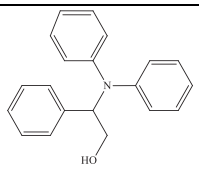
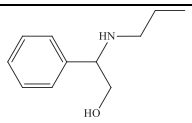
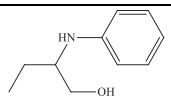
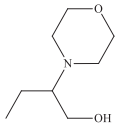
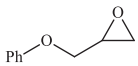
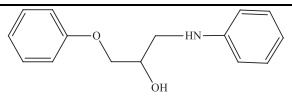
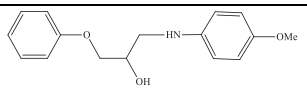
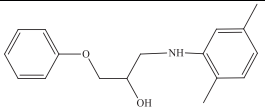
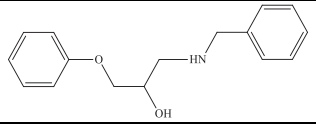
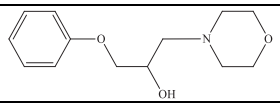
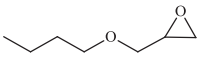
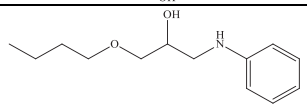
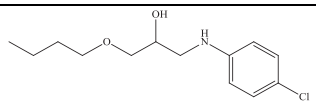
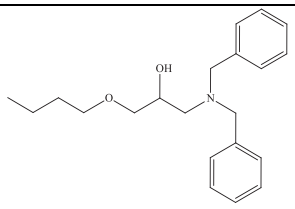
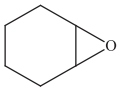
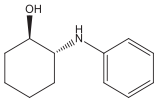
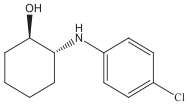
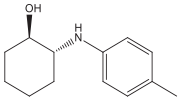
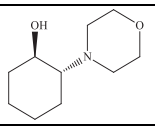
Entry	Epoxide	Amine	Product	Time (min)	Yield[b] (%)
1		aniline		15	86[43]
2		4-methoxyaniline		15	93[43]
3		4-hydroxyaniline		15	91[44]
4		4-nitroaniline		30	77[43]
5		diphenylamine		15	81[45]
6		*n*-propylamine		20[c]	91[46]
7		aniline		15	83[47]
8		morpholine		15	90[47]
9		aniline		15	88[43]
10		4-methoxyaniline		15	94[43]
11		2,5-dimethylaniline		15	90
12		benzylamine		15	87[47]

Table 3. Continued.

Entry	Epoxide	Amine	Product	Time (min)	Yield (%)
13		morpholine		15	84[48]
14		aniline		15	81[49]
15		4-chloroaniline		120[d]	56
16		dibenzylamine		15	70
17		aniline		15	80[44]
18		4-chloroaniline		15	73[50]
19		4-methylaniline		15	80[51]
20		morpholine		15	95[48]

[a] Conditions: a mixture of epoxide (1 mmol), amine (1 mmol), and GO (10 mg) was reacted at room temperature for the time indicated in Table 3.

[b] Refer to GC/MS yield.

[c] The reaction was performed at 60 °C.

[d] The reaction was performed at 80 °C.

14–16, Table 3). However, aminolysis yield of 2-(butoxymethyl)oxirane with 4-chloroaniline is moderate even at higher temperature (80 °C) and longer reaction time (120 min) (entries 15, Table 3).

Finally, we investigated the preparation of amino alcohols from a cyclic epoxide, 7-oxabicyclo[4.1.0]heptane, and aromatic amines such as aniline, 4-chloro, and 4-methylaniline and a cyclic amine such as morpholine; the corresponding amino alcohols were obtained in 80%, 73%, 80%, and 95%, respectively, after 15 min (entries 17–20, Table 3).

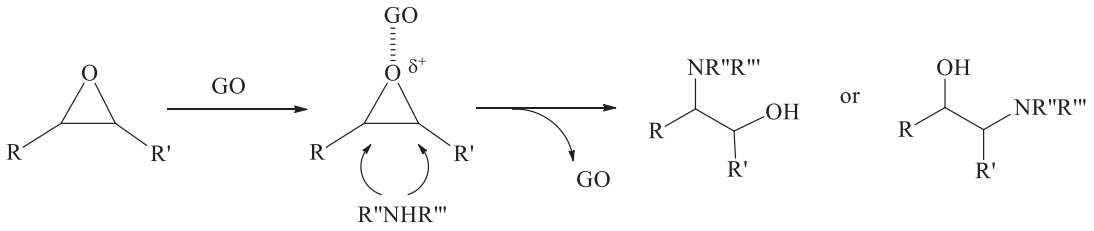
From the results in Table 3, GO allowed the synthesis of β-amino alcohols from epoxides in relatively short reaction times as compared to the methods described in the literature.[7–27] For example, when magnetic nano Fe_3O_4 (10 mol%) was used as a catalyst for aminolysis of styrene oxide with aniline, the corresponding β-amino alcohol was obtained in 83% yield after 20 h[13] compared to 86% using GO after only 15 min (entry 1, Table 3). 2-((4-Nitrophenyl)amino)-2-phenylethanol was synthesized through aminolysis of styrene oxide with 4-nitroaniline in 38%, 68%, and 58% yield, respectively, after 48, 1.5, and 48 h using metallocene (Cp_2MCl_2, M = Ti, Zr, V, 10 mol%) as catalysts;[26] the yields were lower than 77% for the same chemical transformation using GO as catalyst after only 15 min (entry 4, Table 3). In another report, Curini and co-workers[25] prepared 1-butoxy-3-(phenylamino)propan-2-ol in 94% yield by the aminolysis of 2-(butoxymethyl)oxirane with aniline using zirconium sulfophenyl phosphonate as a catalyst at 40 °C under nitrogen after 19 h. The yield was slightly higher than 81% obtained using GO, although the reaction proceeded much faster using GO (15 min) (entry 14, Table 3).

To evaluate the reusability of GO after the ring opening of styrene oxide with aniline, ethyl acetate was added and the mixture was filtered through a sintered funnel to recover the catalyst. The recovered catalyst was dried in an oven at 80 °C for 30 min. The ring opening of styrene oxide with aniline in the presence of 10 mg of the recovered GO was performed for seven consecutive cycles for 15 min at room temperature. The recycled GO was efficient for aminolysis of styrene oxide to the corresponding 2-amino alcohol even after seven consecutive times without loss of activity; the yield was about 82% (Table 4).

Table 4. Reusability of GO catalyst for the ring opening of styrene oxide with aniline.

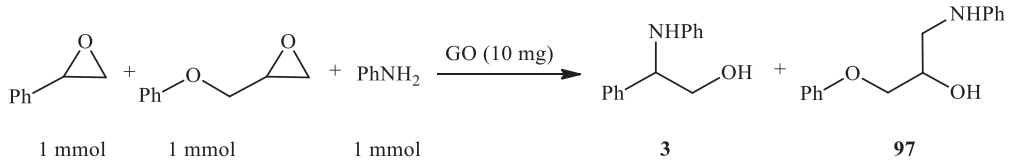
Run	1st	2nd	3rd	4th	5th	6th	7th
Yield (%)	86	89	83	83	80	81	82

The graphite oxide surface comprises various oxygen-containing groups such as hydroxyl and carbonyl groups, which confer an acidic character to the material.[52] This property has recently been exploited for the conversion of oxiranes into thiiranes,[39] esterification of organic acids,[40] and preparation of 1,4-dihydropyridines.[53] The possible mechanism of the reaction involved activation of the epoxide ring by GO (Scheme 2). Hydroxyl and carboxylic groups of GO can activate the epoxide ring through interaction with the oxygen atom of epoxide to increase the susceptibility of the epoxide ring to nucleophilic attack by the nitrogen atom of amine. As shown in Table 3, the nucleophilic attack was remarkably regioselective. For styrene oxide, the nucleophilic attack occurred at the more highly substituted carbon atom of the epoxide ring. The nucleophilic attack on the sterically more hindered position of the epoxide suggests that the reaction is controlled by electronic effects (SN_1 mechanism). Indeed, electronic effects dominate over steric effects; the intermediate carbocation is stabilized through resonance with the phenyl ring, leading to a nucleophilic attack at a more hindered position. The similar nucleophilic attack of amine at more hindered position was observed for ring opening of 2-ethyloxirane. The results obtained for other epoxides (2-(phenoxymethyl)oxirane and 2-(butoxymethyl)oxirane) indicated that the nucleophilic attack occurs at the less hindered carbon atom of the epoxide ring (SN_2 mechanism). The SN_2 mechanism is preferred in these cases due to the electron-withdrawing effect of the oxygen atom on the epoxide ring.

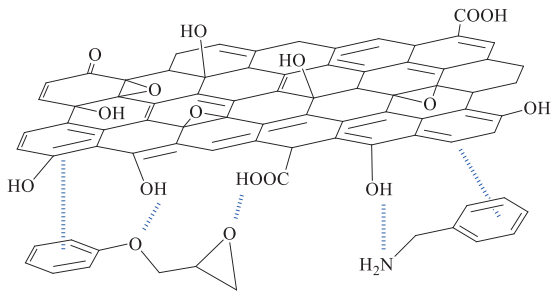


Scheme 2. A plausible mechanism for aminolysis of epoxide catalyzed by GO.

Next, we evaluated the efficiency of this methodology for selective aminolysis of epoxide rings during intermolecular competitive reactions. To demonstrate the selectivity of aminolysis, aniline (1 mmol) was added to a mixture of styrene epoxide (1 mmol) and 2-(phenoxymethyl)oxirane (1 mmol) in the presence of 10 mg of GO. The formation of the corresponding products in 3:97 ratio, respectively, after 15 min clearly indicates the high selectivity of this process (Scheme 3). The selective aminolysis of 2-(phenoxymethyl)oxirane can be explained by the chelating ability of the oxygen atoms of the phenoxy group and the epoxide oxygen atom of 2-(phenoxymethyl)oxirane with GO, which increases the susceptibility of the epoxide ring to nucleophilic attack by aniline (Scheme 4).

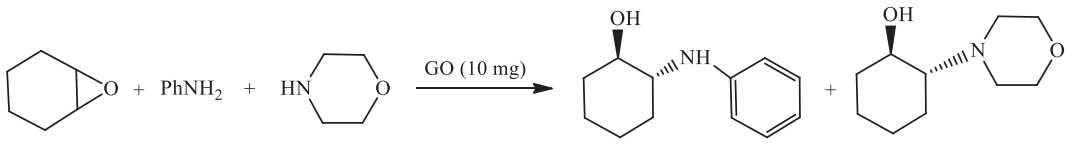


Scheme 3. Selectivity of aminolysis of epoxide during intermolecular competition catalyzed by GO.



Scheme 4. The possible chelating ability of 2-(phenoxymethyl)oxirane with GO.

To demonstrate the chemoselectivity of this method, cyclohexene oxide (1 mmol) was added to a mixture of aniline (1 mmol) and morpholine (1 mmol) in the presence of 10 mg of GO. After 15 min reaction, only the product of morpholine with cyclohexene oxide was formed, indicating the very high chemoselectivity of this process (Scheme 5).



Scheme 5. Chemoselective aminolysis of cyclohexene oxide with aromatic and aliphatic amines catalyzed by GO.

3. Conclusion

In summary, GO was used as a solid acid catalyst for the aminolysis of a wide range of epoxides with various amines. The aminolysis of epoxides in the presence of GO provided the corresponding β-amino alcohol derivatives in good to high yields. Moreover, the catalyst was reused several times without any loss of activity. This protocol offers simplicity of operation and short reaction times under metal-free conditions with high regio- and chemo-selectivity.

4. Experimental

^{1}H NMR spectra were recorded on a Bruker 500 MHz in $CDCl_3$ using tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on a Bruker 125 MHz in $CDCl_3$. Mass spectra were obtained on a FISONS GC 8000/TRIO 1000 under 70 eV. Infrared (IR) spectra were recorded from KBr disks with a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer.

4.1. General procedure for aminolysis of epoxides

To a solution of epoxide (1 mmol) and amine (1 mmol) was added 10 mg of graphite oxide (GO) at room temperature and the mixture was stirred for the time indicated in Table 3 prior to GC/MS analysis. The resulting mixture was filtered and washed with ethyl acetate for catalyst separation, and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. Purification was achieved by column chromatography using ethyl acetate/n-hexane as eluent. Spectroscopic data for unknown products:

1-(2,5-Dimethylphenylamino)-3-phenoxypropan-2-ol (entry 11, Table 3): Colorless oil, TLC R_f = 0.30 (ethyl acetate/n-hexane, 1:5); ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 2.22 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.81 (dd, J = 2.9 Hz, J = 4.9 Hz, 1H, $\underline{CH_2}NH$), 2.96 (dd, J = 4.1 Hz, J = 4.8 Hz, 1H, $\underline{CH_2}NH$), 3.52 (m, 1H, $\underline{CH}OH$), 4.02 (dd, J = 5.6 Hz, J = 11.0 Hz, 3H, $\underline{CH_2}CH\underline{OH}$), 6.65 (s, 1H, Ar), 6.99 (m, 5H, Ar), 7.35 (m, 2H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 14.56, 17.38, 45.16, 50.60, 69.12, 115.08, 116.99, 120.70, 120.88, 121.67, 129.95, 130.84, 137.12, 143.26, 158.93; MS (EI) (70 eV), m/z (%): 271 (12) $[M]^+$, 254 (9) $[M\text{-}OH]^+$, 177 (7) $[M\text{-}H\text{-}OPh]^+$, 166 (3) [M-2,5-dimethylphenyl]$^+$, 163 (12) $[M\text{-}H\text{-}CH_2OPh]^+$, 134 (37), 118 (65), 107 (7), 105 (25), 90 (35), 89 (37), 77 (95), 50 (60), 40 (100); IR (KBr): ν = 3436, 3061, 3004, 2924, 1624, 1495, 1242, 1039, 753 cm^{-1}.

1-Butoxy-3-((4-chlorophenyl)amino)propan-2-ol (entry 15, Table 3): Pale yellow oil, TLC R_f = 0.37) dichloromethane); ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 0.83 (t, J= 7.4 Hz, 3H, CH_3), 1.15 (m, 2H, $\underline{CH_2}CH_3$), 1.36 (m, 2H, $\underline{CH_2}CH_2CH_3$), 2.87 (dd, J = 6.5 Hz, J = 11.0 Hz, 1H, $\underline{CH_2}NH$), 3.05 (dd, J = 4.9 Hz, J = 11.2 Hz, 1H, $\underline{CH_2}NH$), 3.31 (m, 2H, $O\underline{CH_2}CH_2$), 3.32 (m, 2H, $\underline{CH_2}CHOH$), 3.68 (m, 1H, $\underline{CH}OH$), 3.98 (m, 1H, $CH_2\underline{NH}$), 5.82 (s, 1H, $CH\underline{OH}$), 6.7 (m, 4H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 14.78, 19.71, 31.84, 47.33, 68.82, 71.16, 73.82, 114.18, 119.56, 129.33, 148.75; MS (EI) (70 eV), m/z (%): 257 (12) $[M]^+$, 240 (3) $[M\text{-}OH]^+$, 222 (2) $[M\text{-}Cl]^+$, 184 (2) $[M\text{-}OBu]^+$, 167 (5) $[M\text{-}OH\text{-}OBu]^+$, 140 (100), 126 (5), 117 (5), 111 (57), 87 (10), 75 (20), 57 (40), 43 (8); IR (KBr): ν = 3390, 2963, 1622, 1495, 1261, 1091, 800, 637 cm^{-1}.

1-Butoxy-3-(dibenzylamino)propan-2-ol (entry 16, Table 3): Colorless oil, TLC R_f = 0.42 (ethyl acetate/n-hexane, 1:5); ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 0.97 (t, J = 7.4 Hz, 3H, CH_3), 1.43 (m, 2H, $CH_3\underline{CH_2}$), 1.62 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2O$), 2.64 (dd, J = 6.5 Hz, J = 2.7 Hz, 1H, $\underline{CH_2}N$), 2.82 (dd, J= 4.2 Hz, J =

2.7 Hz, 1H, $\underline{CH_2}N$), 3.21 (m, 1H, $\underline{CH}OH$), 3.41 (m, 2H, $CH_3CH_2CH_2\underline{CH_2}O$), 3.72 (m, 3H, $O\underline{CH_2}CH\underline{OH}$), 3.8 (s, 4H, $N\underline{CH_2}Ar$), 7.36 (m, 10H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 14.42, 16.68, 32.19, 44.71, 51.39, 53.41, 77.25, 77.26, 77.77, 127.45, 128.66, 128.83, 140.34; MS (EI) (70 eV), m/z (%): 328 (37) $[MH]^+$, 327 (10) $[M]^+$, 326 (30) $[M\text{-}H]^+$, 310 (5) $[M\text{-}OH]^+$, 254 (3) $[M\text{-}OBu]^+$, 248 (20) $[M\text{-}H_2\text{-}Ph]^+$, 236 (3) $[M\text{-}CH_2Ph]^+$, 210 (100), 194 (3), 174 (3), 134 (10), 118 (7), 106 (10); IR (KBr): ν = 3459, 3062, 2931, 2870, 1645, 1495, 1251, 1115, 1028, 746 cm^{-1}.

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