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Regioselective Ring Opening of Epoxides with Amines Using Silica-bonded S-sulfonic Acid under Solvent-free Conditions

Mahmood Tajbakhsh,* Rahman Hosseinzadeh, Parizad Rezaee, and Heshmatollah Alinezhad

Faculty of Chemistry, Mazandaran University, Babolsar, Iran, tajbaksh@umz.ac.ir Fax: +98 11253 42302

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Abstract. Silica-bonded S-sulfonic acid (SBSSA) was used as a recyclable and reusable catalyst for the synthesis of *β*-amino alcohols. Several amines were reacted with epoxides to afford regioselective *β*-amino alcohols in high yield under solvent-free conditions at room temperature.
Key words: Silica-bonded S-sulfonic acid, *β*-amino Alcohols, Epoxides, Amines.

Resumen. El ácido S-sulfónico soportado en sílica gel (ASSSG) se utilizó como un catalizador reciclable y reutilizable para la síntesis de *β*-aminoalcoholes. Se hicieron reaccionar diversas aminas con epóxidos para dar de manera regioselectiva *β*-aminoalcoholes en rendimientos altos, a temperatura ambiente y en condiciones libres de disolventes.
Palabra clave: Ácido S-sulfónico soportado en sílica gel, *β*-aminoalcoholes, epóxidos, aminas.

Introduction

Epoxides are small molecules with vast synthetic applications. They are able to react with various nucleophiles and their potential to undergo regioselective ring opening reactions adds to their importance as highly useful precursors for the synthesis of organic compounds. Among them, the reaction of epoxides with amines is particularly interesting, because it leads to the formation of *β*-amino alcohols which are the key intermediates to many organic compounds, including biologically active natural and synthetic products, and chiral auxiliaries for asymmetric synthesis [1-3].

The classical synthetic approach towards β-amino alcohols involves aminolysis of epoxides in protic solvents [4]. 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 for the sterically crowded amines/epoxides and poor regioselectivity of the epoxide ring opening. To overcome these problems, several activators and promoters have been tried and reported in the literature, including metal salts [5-7], metal amides [8,9], metal alkoxides [10,11], metal triflates [12-14], alumina [15], microwave assisted montmorillonite clay [16], ionic liquids [17], heteropoly-acids [18], amberlist-15 [19], thiourea [20], trifluoroethanol [21], silica [22], zeolites [23], organobismuth triflate complex [24], sulphated zirconia and SZ/MCM-41 [25]. However, these methods suffer from one or more disadvantages such as long reaction times [26], elevated temperatures [4, 27], high pressure [22a, 28], moderate yields [18], use of air and moisture sensitive catalysts, requirement of stoichiometric amounts of catalyst, and problems in the recovery of the catalysts [26].

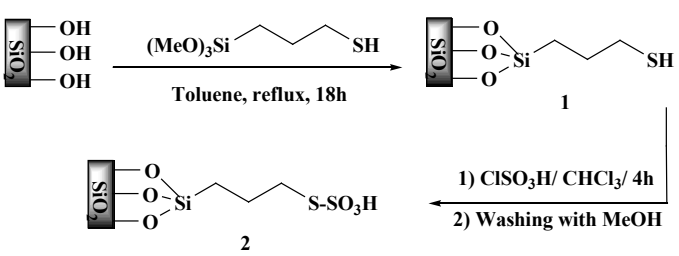
Therefore, the development of a highly efficient and a non-hazardous catalyst, which is easy to handle, is highly imperative for the synthesis of amino alcohols. Some of these problems can be overcome by employing heterogeneous catalysts, which have several intrinsic advantages like the ease of product separation, recyclability of the catalyst, and the minimization of waste production [22b-c]. In this regard, we focused our attention to solid acids which have emerged as a special class of environmentally friendly catalysts because of their ease of preparation and industrial applications.

SBSSA is a stable solid catalyst which is prepared easily from silica, 3-mercaptopropyltrimethoxysilane and chlorosulfonic acid [29] (Scheme 1). SBSSA has been used as an efficient catalyst in many organic transformations [30]. In this report, we have shown that SBSSA is a highly efficient, mild, reusable and ecofriendly for the ring opening of epoxides under solvent-free conditions at room temperature.

Results and Discussion

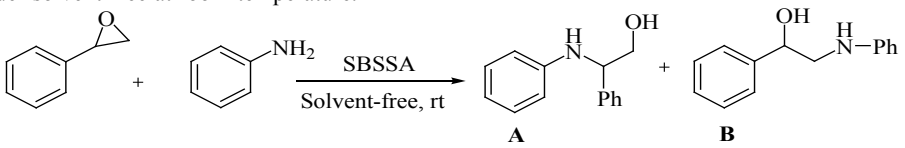
To study the effect of catalyst loading on the ring opening of epoxides with amines, the reaction of styrene oxide with aniline was chosen as a model reaction (Table 1). We examined the model reaction in the presence and absence of the catalyst under solvent-free conditions (Table 1). The results in Table 1 showed that a low yield (40%) of the product was formed after 7 h without catalyst (Table 1, entry 1), whereas, in the presence of 0.1 g SBSSA a high yield of 2-phenylamino-2-phenylethanol was obtained only after 1 h (Table 1, entry 5).

To show the efficiency of the SBSSA in this reaction, several catalysts with SO_3H group such as silica-bonded *N*-propyl sulfamic acid, p-TSA, *β*-CD-SO_3H, sulfamic acid, silica sulfuric acid, and cellulose sulfuric acid, were screened under



Scheme 1.

Table 1. Ring opening of styrene oxide with aniline in the presence of SBSSA[a] and different catalysts under solvent-free at room temperature.



A **B**

Entry	Catalyst	Catalyst loading (g)	Time (h)	Yield (%)[b]	Ratio (A:B)[c]
1		None	7	40	
2	SBSSA	0.02 (0.68 mol%)	3.	70	
3		0.05 (1.7 mol%)	2.5	85	
4		0.08 (2.7 mol%)	1.5	85	
5		0.1 (3.4 mol%)	1	98	100:0
6		0.15 (5.1 mol%)	1.5	80	
7	SBNPSA[d]	0.1 (3.4 mol%)	2	75	100:0
8	p-TSA[e]	0.017 (10 mol%)	3	45	100:0
9	βCD- SO_3H	0.07 (3.7 mol%)	3	45	100:0
10	Sulfamic acid	0.02 (20 mol%)	5	65	94:6
11	Silica sulfuric acid	0.05 (1.5 mol%)	3	70	95:5
12	Cellulose sulfuric acid	0.08 (4.4 mol%)	3	80	93:7

[a] Reaction conditions: epoxide (1mmol), aniline (1 mmol), solvent-free, room temperature.
[b] Isolated yield.
[c] Ratios determined by ^{1}HNMR
[d] Silica-bonded *N*-propyl sulfamic acid.
[e] *p*-Toluene sulfonic acid.

similar reaction conditions (Table 1, entries 7-12). Although all the catalysts showed excellent regioselectivity, the results clearly show that SBSSA is the most efficient catalyst in term of yield and reaction rate.

We have also examined the model reaction in various solvents in the presence of 0.1 g (0.034 mmol/g) of SBSSA (Table 2). The reaction in solvents gave similar regioselectivity, but required longer reaction time with lower yield of the product than solvent-free conditions (Table 2, entries 1-5).

The generality of this protocol was studied using different amines and epoxides under optimal reaction conditions (Table 3). The results clearly show both steric and electronic effects on the regioselectivity of the reaction. The reaction of styrene epoxide with aromatic amines afforded high ratio of regioisomer A, by nucleophilic attack at the benzylic carbon (Table 3, entries 1-9), which could be due to the localized positive charge on the more highly substituted benzylic carbon [31]. Aliphatic amines gave regioisomer B, with the preferential S_N2 attack [32] at the terminal carbon of the epoxides (Table 3, entries 10-12). This reversal regioselectivity was also observed when aliphatic epoxides such as phenyl glycidyl ether and epoxy propyl methacrylate were employed in this reaction (Table 3, entries 13-21). Steric factor seems to be responsible for the observed regioselectivity.

In order to show the advantages and drawbacks of our method, we have compared the model reaction with those reported in the literature in Table 4. As indicated in Table 4, the present method gives higher regioselectivity of 2-phenylamino-2-phenylethanol in shorter reaction time.

The reusability and the catalytic activity of SBSSA were investigated in this system. After completion of the reaction, CH_2Cl_2 was added and filtered to remove the catalyst. The recovered catalyst was dried and reused directly for four subsequent runs. As shown in Table 5, the yield of 2-phenylamino-2-phenylethanol decreased slightly after four runs.

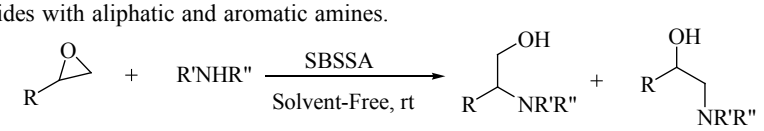
In conclusion, a mild, efficient, recyclable and reusable catalyst for the ring opening of epoxides with amines is described. The mild reaction conditions, short reaction times, excellent regio- and chemoselectivity, applicability to both aro-

Table 2. Ring opening of styrene oxide with aniline in different solvents in the presence of SBSSA (0.1g).

Entry	Solvent[a]	Time (h)	Yield (%)[b]	Ratio (A:B)[c]
1	H_2O	3	85	100:0
2	CH_2Cl_2	3	80	100:0
3	CH_3CN	3	80	95:5
4	Toluene	6	70	94:6
5	Solvent-free	1	98	100:0

[a] The reaction was carried out in 2 mL of solvent at room temperature.
[b] Isolated yield.
[c] Ratios determined by ^{1}HNMR.

Table 3. Ring opening of epoxides with aliphatic and aromatic amines.



A **B**

Entry	R	R′	R″	Product[a]	Time (h)	Yield (%)[b]	Ratio (A:B)[c]	Ref.
1	Ph	Ph	H	A	1	98	100:0	33
2	Ph	4-CH_3 C_6H_4	H	A	1	95	92:8	33
3	Ph	4-MeO C_6H_4	H	A	2	91	90:10	33
4	Ph	4-EtO C_6H_4	H	A	3	90	92:8	34
5	Ph	4-Cl C_6H_4	H	A	3	81	100:0	33
6	Ph	4-Br C_6H_4	H	A	3	81	100:0	33
7	Ph	2-CN C_6H_4	H	A	4	75	89:11	—
8	Ph	4-O_2N C_6H_4	H	A	24	50	93:7	33
9	Ph	Ph	CH_3	A	4.5	90	94:6	33
10	Ph	Cyclohexyl	H	B	5	80	6:94	35
11	Ph	Piperidyl	—	B	4	85	0:100	35
12	Ph	Morpholyl	—	B	4	82	0:100	35
13	$PhOCH_2$	Ph	H	B	2.5	95	14:86	33
14	$PhOCH_2$	4-CH_3 C_6H_4	H	B	2.5	93	10:90	33
15	$PhOCH_2$	4-MeO C_6H_4	H	B	2	85	12:88	33
16	$PhOCH_2$	4-Cl C_6H_4	H	B	4	80	14:86	33
17	$PhOCH_2$	4-Br C_6H_4	H	B	4	80	19:81	33
18	CH_2=C(CH_3)$COOCH_2$	Ph	H	B	2.5	90	10:90	33
19	CH_2=C(CH_3)$COOCH_2$	4-CH_3 C_6H_4	H	B	2.5	90	6:94	33
20	CH_2=C(CH_3)$COOCH_2$	4-Cl C_6H_4	H	B	5	80	0:100	33
21	CH_2=C(CH_3)$COOCH_2$	4-Br C_6H_4	H	B	5	80	20:80	33

[a] Only the major regioisomer is shown and the products were identified by comparing the spectral data with those reported in the literature [33-35].
[b] Isolated yield.
[c] Ratios determined by ^{1}HNMR analysis.

matic and aliphatic amines and reusability of the catalyst are main advantages of this method. The solvent-free conditions employed also make it environmentally friendly and potentially useful for industrial applications.

Experimental

Starting materials used in the reactions were supplied commercially from Aldrich or Merck Chemical Co. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DRX-400 AVANCE (400 and 100MHz for ^{1}H and ^{13}C respectively) in $CDCl_3$ as solvent. SBSSA [29] were prepared according to the reported procedure. Chemical shifts are on the δ scale, relative to internal Me_4Si. Mass spectra were obtained on an Agilent technologies instrument and IR spectra were determined on a Shimadzu instrument.

Catalyst Preparation. Silica gel (Merck, Silica-gel 60) was activated by refluxing in concentrated hydrochloric acid (6 M) for 24 h and then washed thoroughly with the deionized water and dried. the activated silica gel (10 g) was refluxed with 3-mercaptopropyltrimethoxysilane (5 mmol) in dry toluene for 18 h, then, the solid was filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhlet). The solid was dried in oven at 110 °C overnight to give 3-mercaptopropylsilica **1**. To a magnetically stirred mixture of 3-mercaptopropylsilica (**1**, 5 g) in $CHCl_3$ (20 mL), was added chlorosulfonic acid (1.00 g, 9 mmol) dropwise at 0 °C during 2 h. After the addition was complete, the mixture was stirred for another 2 h until all HCl was removed from the reaction vessel and then filtered, washed with methanol (30 mL) and dried at room temperature to give the Silica-bonded S-sulfonic acid **2** (SBSSA).

pH analysis of the SBSSA. The SO_3H loading of SBSSA was determined to be 0.34 mmol/g by titration an aqueous suspension of 0.1 g SBSSA with NaOH solution or by pH analysis of an aqueous suspension of 0.1 g SBSSA with NaCl solution (1 M) [29].

Table 4. Comparison of our method with other catalysts of functionalized silica in the reaction of styrene oxide with aniline.

Entry	Catalyst	Amount of catalyst	Time (h)	Temp (°C)	Ratio (A:B) (%)	Ref
1	SBA-15-pr-SO_3H	0.56 (mmol/g)-SO_3H	4	25	89.8:10.2	36
2	Ti-MCM-41	50 mg	4	35	93.8:6.2	36
3	SBA-15/Co	200 mg	12	27	98:2	37
4	Fe-MCM-41	0.05 mmol	2	25	91	38
5	Nano SiO_2-Cl	30 mg[a]	68 min	25	93:7	39
6	SBSSA	0.034 (mmol/g) -SO_3H	1	25	100:0	—

[a] In CH_2Cl_2.

Table 5. Recovery of SBSSA in the reaction of styrene epoxide with aniline.

Run	Yield (%)[a]	Recovery of SBSSA (%)
1	98	97
2	95	94
3	92	91
4	92	90

[a] Isolated yield.

General procedure for the ring opening of epoxides. To a magnetically stirred mixture of epoxide (1 mmol) and amine (1 mmol), SBSSA catalyst (100 mg, 3.4 mol%) was added and the reaction mixture was stirred at room temperature for appropriate time (Table 3). After completion of the reaction, the mixture was diluted with CH_2Cl_2 and filtered off to remove the catalyst. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to provide the crude product, which was purified by column chromatography to afford the corresponding *β*-amino alcohols. All compounds were fully characterized by IR, ^{1}H NMR and ^{13}C NMR data.

Spectral data of all products are as follows:

2-Phenyl-2-(phenylamino) ethanol (Table 3, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (broad, exchangeable with D_2O, 2H, NH and OH), 3.74 (dd, *J* = 7.2 Hz, 11.2 Hz, 1H, CH), 3.93 (dd, *J* = 4.0 Hz, 11.2 Hz, 1H, CH), 4.52 (dd, *J* = 4.0 Hz, 7.2 Hz, 1H, CH), 6.63 (d, *J* = 7.6 Hz, 2H, Ar-CH), 6.75 (t, *J* = 7.2 Hz, 1H, Ar-CH), 7.17 (t, *J* = 6.8 Hz, 2H, Ar-CH), 7.30-7.42 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.93, 67.33, 113.95, 117.94, 126.82, 127.64, 128.86, 129.24, 140.24, 147.34.

2-Phenyl-2-(p-tolylamino) ethanol (Table 3, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 3.05 (broad, exchangeable with D_2O, 2H, NH and OH), 3.73 (dd, *J* = 7.2 Hz, 10.8 Hz, 1H, CH), 3.94 (dd, *J* = 4.4 Hz, 11.2 Hz, 1H, CH), 4.50 (dd, *J* = 4.4 Hz, 7.2 Hz, 1H, CH), 6.55 (d, *J* = 8.0 Hz, 2H, Ar-CH), 6.97 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.29-7.41 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.43, 60.24, 67.35, 114.14, 126.79, 127.19, 127.58, 128.82, 129.72, 140.35, 144.96.

2-(4-Methoxyphenylamino)-2-phenylethanol (Table 3, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19 (broad, exchangeable with D_2O, 2H, NH and OH), 3.68-3.74 (m, 4H, CH and OCH_3), 3.91 (dd, *J* = 4.0 Hz, 11.2 Hz, 1H, CH), 4.43 (dd, *J* = 4.0 Hz, 7.6 Hz, 1H, CH), 6.56 (d, *J* = 9.2 Hz, 2H, Ar-CH), 6.73 (d, *J* = 8.8 Hz, 2H, Ar-CH), 7.29-7.42 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.74, 60.92, 67.31, 114.80, 115.37, 126.81, 127.57, 128.79, 140.45, 141.87, 152.37.

2-(4-Ethoxyphenylamino)-2-phenylethanol (Table 3, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, *J* = 7.2 Hz, 3H, CH_3), 3.35 (broad, exchangeable with D_2O, 2H, NH and OH), 3.67 (dd, *J* = 7.6 Hz, 11.4 Hz, 1H, CH), 3.88 (dd, *J* = 4.4 Hz, 11.4 Hz, 1H, CH), 3.99 (q, *J* = 6.8 Hz, 2H, OCH_2), 4.40 (dd, *J* = 4.4 Hz, 8.0 Hz, 1H, CH), 6.55 (d, *J* = 10.0 Hz, 2H, Ar-CH), 6.72 (d, *J* = 8.8 Hz, 2H, Ar-CH), 7.27-7.41 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.02, 60.94, 94.10, 67.28, 115.71, 115.83, 116.70, 126.84, 127.50, 128.60, 140.62, 151.94.

2-(4-Chlorophenylamino)-2-phenylethanol (Table 3, entry 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.27 (broad, exchangeable with D_2O, 2H, NH and OH), 3.75 (dd, *J* = 8.0 Hz, 12.0 Hz, 1H, CH), 3.94 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H, CH), 4.46 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H, CH), 6.50 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.06 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.29-7.38 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.95, 67.26, 114.97, 122.45, 126.72, 127.79, 128.92, 129.00, 139.62, 145.78.

2-(4-Bromophenylamino)-2-phenylethanol (Table 3, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (broad, exchangeable with D_2O, 2H, NH and OH), 3.76 (dd, *J* = 6.8 Hz, 12.0 Hz, 1H, CH), 3.95 (dd, *J* = 4.0 Hz, 11.2 Hz, 1H, CH), 4.26 (dd, *J* = 4.0 Hz, 6.8 Hz, 1H, CH), 6.484 (d, *J* = 8.8 Hz, 2H, Ar-CH), 7.19 (d, *J* = 8.08 Hz, 2H, Ar-CH), 7.28-7.37 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.80, 67.27, 109.49, 115.42, 126.69, 127.80, 128.93, 131.86, 139.56, 146.22.

2-(2-Hydroxy-1-phenylethylamino) benzonitrile (Table 3, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (broad, exchangeable with D_2O, 1H, OH), 3.82-3.87 (dd, *J* = 8.0 Hz, 12.0 Hz, 1H, CH), 3.97-4.01 (dd, *J* = 8.0 Hz, 12.0 Hz, 1H, CH), 4.58-4.62 (dd, *J* = 4.0 Hz, 12.0 Hz, 1 H, CH), 5.49 (broad, exchangeable with D_2O, 1H, NH), 6.45 (d, *J* = 12.0 Hz, 1H, Ar-CH), 6.67 (t, *J* = 8.0 Hz 1H, Ar-CH), 7.20-7.43 (m, 7H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.53, 66.88, 96.44, 112.37, 117.13, 118.07, 126.62, 127.96, 129.00, 132.80, 134.16, 139.01, 149.61; MS (*m*/*z*): calc. for $C_{15}H_{14}N_2O$ 238.28 $[M]^+$, found 238.20.

2-(4-Nitrophenylamino)-2-phenylethanol (Table 3, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (dd, *J* = 6.4 Hz, 11.2 Hz, 1H, CH), 4.03 (dd, *J* = 3.6 Hz, 11.6 Hz, 1H, CH), 4.60 (dd, *J* = 5.6 Hz, 10.0 Hz, 1H, CH), 5.61 (d, *J* =5.2, exchangeable with D_2O, 2H, NH and OH), 6.49, (d, *J* = 9.2 Hz, 2H, Ar-CH), 7.30-7.40 (m, 5H, Ar-CH), 7.99 (d, *J* = 9.2 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.29, 66.87, 112.22, 126.24, 126.56, 128.14, 129.11, 138.50, 152.70.

2-(Methyl(phenyl)amino)-2-phenylethanol (Table 3, entry 9). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.62 (broad, exchangeable with D_2O, 1H, OH), 2.79 (s, 3H, CH_3), 4.16-4.18 (m 2H, 2CH), 5.15 (t, *J* = 7.6 Hz, 1H, CH), 6.91 (t, *J* = 7.2 Hz, 1H, Ar-CH), 7.01 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.23 (d, *J* = 6.8 Hz 2H, Ar-CH), 7.33-7.41 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.15, 61.83, 64.46, 114.64, 118.23, 127.28, 127.64, 128.66, 129.36, 137.79, 151.15.

2-(Cyclohexylamino)-1-phenylethanol (Table 3, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03-1.40 (m, 8H, CH_2), 1.72-1.77 (m, 2H, CH_2), 1.93 (broad, exchangeable with D_2O, 2H, NH and OH), 2.41-2.52 (m, 1H, CH), 2.70 (dd, *J* = 9.2 Hz, 12.0 Hz, 1H, CH), 3.00 (dd, *J* = 3.6 Hz, 12.2 Hz, 1H, CH), 4.70 (dd, *J* = 3.6 Hz, 9.2 Hz, 1H, CH), 7.28-7.40 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.00, 26.01, 29.71, 33.47, 33.83, 54.15, 56.53, 125.80, 127.44, 128.35, 128.63, 142.70.

1-Phenyl-2-(piperidin-1-yl)ethanol (Table 3, entry 11). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48-1.52 (m, 2H, CH_2), 1.55-1.69 (m, 5H, CH_2), 2.39-2.44 (m, 3H, CH_2), 2.51 (dd, *J* = 3.6 Hz, 12.8 Hz, 1H, CH), 2.72 (broad, exchangeable with D_2O, 1H, OH), 4.74 (dd, *J* = 3.6 Hz, 10.8 Hz, 1H, CH), 7.26-7.41 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.28, 26.14, 26.49, 54.46, 66.94, 68.66, 70.30, 125.86, 127.37, 128.98, 142.47.

2-Morpholino-1-phenylethanol (Table 3, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40-2.59 (m, 6H, CH_2), 2.73-2.76 (m, 2H, CH_2), 3.59 (dd, *J* = 5.2 Hz, 8.8 Hz, 1H, CH), 3.97 (dd, *J* = 8.4 Hz, 10.8 Hz, 1H, CH), 4.77 (dd, *J* = 3.6 Hz, 10.4 Hz, 1H, CH), 7.26-7.40 (m, 5H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.47, 66.70, 67.02, 67.20, 68.62, 125.85, 127.60, 128.40, 141.90.

1-Phenoxy-3-(phenylamino)propan-2-ol (Table 3, entry 13). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 (dd, *J* = 7.6 Hz, 13.2 Hz, 1H, CH), 3.46 (dd, *J* = 4.4 Hz, 13.2 Hz, 1H, CH), 3.52 (broad, exchangeable with D_2O, 2H, NH and OH), 4.01-4.10 (m, 2H, CH_2), 4.26-4.30 (m, 1H, CH), 6.74 (d, *J* = 7.6 Hz, 2H, Ar-CH), 6.84 (t, *J* = 7.2 Hz, 1H, Ar-CH), 6.99 (d, *J* = 8.4 Hz, 2H, Ar-CH), 7.07 (t, *J* = 8.0 Hz, 1H, Ar-CH), 7.28 (t, *J* = 9.2 Hz, 2H, Ar-CH), 7.38 (t, *J* = 9.6 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.76, 68.82, 70.11, 113.46, 114.66, 118.15, 121.39, 129.45, 129.70, 148.15, 158.51.

1-Phenoxy-3-(p-tolylamino)propan-2-ol (Table 3, entry 14). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, CH_3), 3.29 (dd, *J* = 8.0 Hz, 12.0 Hz, 1H, CH), 3.38 (broad, exchangeable with D_2O, 2H, NH and OH), 3.44 (dd, *J* = 4.0 Hz, 16.0 Hz, 1H, CH), 3.90-4.08 (m, 2H, CH_2), 4.25-4.30 (m, 1H, CH), 6.66 (d, *J* = 8.0 Hz, 2H, Ar-CH), 6.98 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.03-7.08 (m, 3H, Ar-CH), 7.36 (t, *J* = 8.0 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.47, 47.17, 68.81, 70.13, 113.65, 114.62, 121.32, 127.41, 129.63, 129.89, 145.81, 158.50.

1-(4-Methoxyphenylamino)-3-phenoxypropan-2-ol (Table 3, entry 15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.17 (broad, exchangeable with D_2O, 2H, NH and OH), 3.26 (dd, *J* = 7.2 Hz, 12.8 Hz, 1H, CH), 3.40 (dd, *J* = 4.0 Hz, 12.8 Hz, 1H, CH), 3.78 (s, 3H, OCH_3), 4.02-4.10 (m, 2H, CH_2), 4.24-4.29 (m, 1H, CH), 6.68 (d, *J* = 8.8 Hz, 2H, Ar-CH), 6.82 (d, *J* = 9.2 Hz, 2H, Ar-CH), 6.95 (d, *J* = 7.6 Hz, 2H, Ar-CH), 7.01 (t, *J* = 7.6 Hz, 1H, Ar-CH), 7.33 (t, *J* = 5.2 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.80, 55.81, 68.79, 70.11, 114.55, 114.86, 114.94, 121.30, 129.60, 142.15, 152.63, 158.44.

1-(4-Chlorophenylamino)-3-phenoxypropan-2-ol (Table 3, entry 16). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (dd, *J* = 7.2 Hz, 12.8 Hz, 1H, CH), 3.39 (dd, *J* = 4.0 Hz, 13.6 Hz, 1H, CH), 3.52 (broad, exchangeable with D_2O, 2H, NH and OH), 3.99-4.08 (m, 2H, CH_2), 4.22-4.28 (m, 1H, CH), 6.60 (d, *J* = 8.8 Hz, 2H, Ar-CH), 6.95 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.04 (t, *J* = 7.6 Hz, 1H, Ar-CH), 7.16 (d, *J* = 8.8 Hz, 2H, Ar-CH), 7.34 (t, *J* = 8.0 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.73, 68.74, 69.44, 114.58, 114.87, 121.45, 122.56, 129.25, 129.69, 146.69, 158.34.

1-(4-Bromophenylamino)-3-phenoxypropan-2-ol (Table 3, entry 17). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (dd, *J* = 7.6 Hz, 12.8 Hz, 1H, CH), 3.40 (dd, *J* = 4.4 Hz, 12.8 Hz, 1H, CH), 3.99-4.09 (m, 2H, CH_2), 4.24-4.27 (m, 1H, CH), 6.56 (d, *J* = 8.4 Hz, 2H, Ar-CH), 6.94 (d, *J* = 8.0 Hz, 2H, Ar-CH), 7.02 (t, *J* = 7.6 Hz, 1H, Ar-CH), 7.28 (d, *J* = 8.8 Hz, 2H, Ar-CH), 7.33 (t, *J* = 7.6 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.57, 68.72, 69.94, 109.63, 114.54, 114.87, 121.47, 129.66, 132.03, 147.08, 158.30.

2-Hydroxy-3-(phenylamino)propyl methacrylate (Table 3, entry 18). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H, CH_3), 3.19 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H, CH), 3.28 (broad, exchangeable with D_2O, 2H, NH and OH), 3.34 (dd, *J* = 4.4 Hz, 12.8 Hz, 1H, CH), 4.11-4.16 (m, 1H, CH), 4.23-4.31 (m, 2H, CH_2), 5.64 (t, *J* = 1.6 Hz, 1H, CH), 6.18 (t, *J* = 1.2 Hz, 1H, CH), 6.67 (d, *J* = 7.6 Hz, 2H, Ar-CH), 6.77 (t, *J* = 7.2 Hz, 1H, Ar-CH), 7.21 (t, *J* = 7.2 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.35, 46.69, 66.81, 68.44, 113.33, 118.11, 126.44, 129.37, 135.87, 147.94, 167.64.

2-Hydroxy-3-(p-tolylamino)propyl methacrylate (Table 3, entry 19). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H, CH), 2.27 (s, 3H, CH_3), 3.16 (dd, *J* = 7.6 Hz, 16.0 Hz, 1H, CH), 3.32 (dd, *J* = 4.0 Hz, 13.2 Hz, 1H, CH), 3.43 (broad, exchangeable with D_2O, 2H, NH and OH), 4.10-4.15 (m, 1H, CH), 4.22-4.30 (m, 2H, CH_2), 5.64 (t, *J* = 1.6, 1H, CH), 6.18 (s, 1H, CH), 6.60 (d, *J* = 8.4 Hz, 2H, Ar-CH), 7.02 (d, *J* = 8.0 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.35, 20.40, 47.16, 66.84, 68.42, 113.61, 126.37, 127.43, 129.84, 135.90, 145.63, 167.61.

3-(4-Chlorophenylamino)-2-hydroxypropyl methacrylate (Table 3, entry 20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H, CH), 3.16 (dd, *J* = 7.6 Hz, 13.0 Hz, 1H, CH), 3.30 (dd, *J* = 4.4 Hz, 12.8 Hz, 1H, CH), 4.10-4.15 (m, 1H, CH), 4.23-4.31 (m, 2H, CH_2), 5.64 (t, *J* = 1.2, 1H, CH), 6.17 (s, 1H, CH), 6.58

(d, J = 8.8 Hz, 2H, Ar-CH), 7.13 (d, J = 8.8 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.33, 46.71, 66.80, 68.50, 114.36, 122.64, 126.53, 129.15, 135.78, 146.51, 167.62.

3-(4-Bromophenylamino)-2-hydroxypropyl methacrylate (Table 3, entry 21). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H, CH), 3.11 (dd, J = 7.6 Hz, 13.2 Hz, 1H, CH), 3.25 (dd, J = 7.6 Hz, 14.0 Hz, 1H, CH), 4.05-4.11 (m, 1H, CH), 4.22 (d, J = 5.2 Hz, 2H, CH_2), 5.62 (t, J = 1.2, 1H, CH), 6.15 (s, 1H, CH), 6.50 (d, J = 8.8 Hz, 2H, Ar-CH), 7.23 (d, J = 8.8 Hz, 2H, Ar-CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.33, 46.58, 66.69, 68.29, 109.46, 114.80, 126.63, 131.98, 135.77, 147.02, 167.69.

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