Efficient Method for Cleavage of Aziridines with Aromatic Amines

Govindasamy Sekar and Vinod K. Singh*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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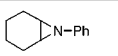
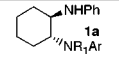
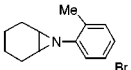
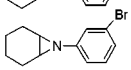
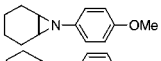
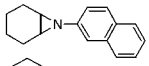
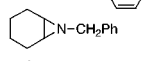
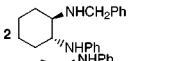
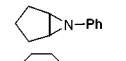
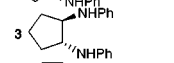
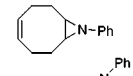
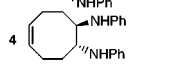
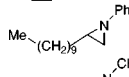
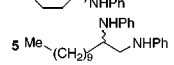
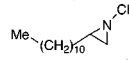
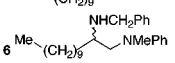
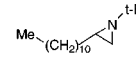
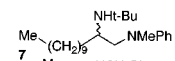
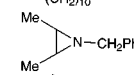
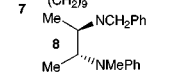
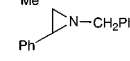
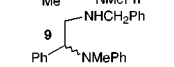
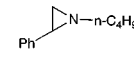
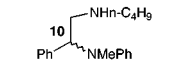
Ring opening of activated aziridines with several nucleophiles by means of Lewis acids has been studied.[1−4] If the nucleophiles are amines, the products become diamines, which synthetically are an important class of compounds. Recently, the ring opening reaction of mainly activated aziridines by amines has been reported in the presence of ytterbium triflate and other lanthanide triflates as catalysts.[5] Most of the amines used in the reaction were aliphatic, and there was only one entry where aniline was used as nucleophile. The reaction required higher concentration of the catalyst (20 mol %) and longer reaction time (1−3 d). While working on epoxide cleavage reactions with amines,[6] we discovered that aziridines were efficiently cleaved with less reactive aromatic amines and 5 mol % of $Sn(OTf)_2$ or $Cu(OTf)_2$ in a short time. The unusual feature of the reaction was that aliphatic amines did not open aziridines with these catalysts, in sharp contrast to the behavior of $Yb(OTf)_3$ and $La(OTf)_3$.[5] This prompted us to look at the reaction, and we report our results in this paper.

A variety of aziridines were synthesized from the corresponding amino alcohols in one step, using MsCl (1.1 equiv) and Et_3N (2.5 equiv) in pyridine (as solvent) at room temperature. At the outset, the opening reaction was done using *N*-phenylcyclohexeneimine and aniline, with 5 mol % of $Sn(OTf)_2$ in ether at room temperature for 10 min, and product **1a** was obtained in 91% yield (Table 1, entry 1). The reaction was studied in several solvents, such as CH_2Cl_2 (90% yield), MeCN (88% yield), and THF (80% yield), and it was found that both ether and CH_2Cl_2 were equally good solvents for the above reaction. Use of $Cu(OTf)_2$ as a catalyst facilitated the reaction equally well, but the reaction time was a little longer (1 h). The opening of *N*-phenylcyclohexeneimine was tried with a variety of aromatic amines, using both the catalysts (entries 1−12). In all the cases, a very clean reaction was observed and the trans stereochemistry of diamines was deduced from the relevant coupling constants. The aziridine opening reaction tolerated a varying degree of steric hindrance on aromatic amines such as α-naphthylamine (entry 9), diphenylamine (entry 10), and *o*,*o*′-diisopropylaniline (entry 11).

Table 1. Sn(II) and Cu(II) Triflate Catalyzed Aziridine Opening with Aromatic Amines in Ether at Room Temperature

Entry	Aziridines	Diamines	Isolated Yield (Time) $Sn(OTf)_2$	Isolated Yield (Time) $Cu(OTf)_2$
1.		 **1a** R_1=H Ar=Ph	91 % (10 min)	84 % (1 h)
2.	"	**1b** R_1=Me; Ar=Ph	82 % (10 min)	61 % (1 h)
3.	"	**1c** R_1=H; Ar=C_6H_4-*p*-NO_2	82 % (10 min)	76 % (1 h)
4.	"	**1d** R_1=H; Ar=C_6H_4-*o*-OH	88 % (10 min)	85 % (1 h)
5.	"	**1e** R_1=H; Ar=C_6H_4-*o*-Me	82 % (10 min)	80 % (1 h)
6.	"	**1f** R_1=H; Ar=C_6H_3-*m*-Br	65 % (10 min)	61 % (1 h)
7.	"	**1g** R_1=H; Ar=C_6H_4-*p*-OMe	76 % (10 min)	72 % (1 h)
8.	"	**1h** R_1=H; Ar=β-naphthyl	77 % (10 min)	72 % (1 h)
9.	"	**1i** R_1=H; Ar=α-naphthyl	86 % (10 min)	86 % (1 h)
10.	"	**1j** R_1=Ar=Ph	89 % (10 min)	87 % (1 h)
11.	"	**1k** R_1=H; Ar=*o*,*o*′-diisopropyl Ph	60 % (10 min)	54 % (1 h)
12.	"	**1l** R_1=H; Ar=2-pyridine-5-Cl	56 % (10 min)	41 % (1 h)
13.		**1e**	78 % (10 min)	74 % (1 h)
14.		**1f**	90 % (10 min)	84 % (1 h)
15.		**1g**	93 % (10 min)	85 % (1 h)
16.		**1h**	95 % (10 min)	83 % (1 h)
17.		**2** 	74 % (10 min)	54 % (1 h)
18.		**3** 	71 % (10 min)	65 % (1 h)
19.		**4** 	94 % (1 h)	86 % (2.5 h)
20.		**5** 	55 % (10 min)	-
21.		**6** 	60 % (10 h)	57 % (15 h)
22.		**7** 	65 % (24 h)	-
23.		**8** 	86 % (1 h)	85 % (2.5 h)
24.		**9** 	69 % (1 h)	60 % (2.5 h)
25.		**10** 	72 % (1 h)	69 % (2.5 h)

To show the scope of the reaction, we extended it to a variety of cyclic and acyclic aziridines. In almost all cases, a high yield of the opened product was obtained. In the case of acyclic terminal aziridines, the reaction was highly regioselective. Only one product was isolated, and it was due to the attack of aromatic amines at the less hindered terminal carbon atoms (entries 20−22).[7] In the case of 2-phenyl aziridines (entries 24 and 25), the situation was the reverse; the product formed was the one due to the attack of aromatic amines at the benzylic carbon atom (internal attack).[8] The aziridine opening

* Fax: 91-512-590007. E-mail: vinodks@iitk.ac.in.

(1) (a) For a general review of aziridine chemistry, see: Pearson, W. H.; Lian, B. W.; Bergmeier, S. C. In *Comprehensive Heterocylic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds; Pergamon: New York, 1996; Vol 1a. (b) Dauben, P.; Dubois, L.; Dau, M. E. T. H.; Dodd, R. H. *J. Org. Chem*. **1995**, *60*, 2035. (c) da Zhang, Z.; Scheffold, R. *Helv. Chim. Acta* **1993**, *76*, 2602. (d) Bodenan, J.; Chanet-Ray, J.; Vessiere, R. *Synthesis* **1992**, 288. (e) Sato, K.; Kozikowski, A. P. *Tetrahedron Lett*. **1989**, *30*, 4073. (f) Nakajima, K.; Neya, M.; Yamada, S.; Okawa, K. *Bull. Chem. Soc. Jpn*. **1982**, *55*, 3049.

(2) For Cr complex catalyzed opening of aziridine with TMS azide, see: Leung, W.-H.; Yu, M.-T.; Wu, M.-C.; Yeung, L.-L. *Tetrahedron Lett*. **1996**, *37*, 891.

(3) For opening of aziridine with TMSCN in the presence of lanthanoid tricyanide, see: (a) Matsubara, S.; Kodama, T.; Utimoto, K. *Tetrahedron Lett*. **1990**, *31*, 6379. (b) Osborn, H. M. I.; Sweeney, J. B. *Synlett* **1994**, 145.

(4) While this manuscript was being prepared, a paper appeared where acylaziridine is rearranged to oxazoline by means of orthogonal Lewis acids. For reference, see: Ferraris, D.; Drury, W. J., III; Cox, C.; Lectka, T. *J. Org. Chem*. **1998**, *63*, 4568.

(5) (a) Meguro, M.; Asao, N.; Yamamoto, Y. *Tetrahedron Lett*. **1994**, *35*, 7395. (b). Meguro, M.; Yamamoto, Y. *Heterocycles* **1996**, *43*, 2473.

(6) .Sekar, G.; Singh, V. K. *J. Org. Chem*. **1999**, *64*, 287.

(7) This was ascertained by comparing the δ value of *N*-Me in products obtained from the opening of similar epoxide with *N*-methyl aniline. For details, see ref 6.

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reaction was also smooth in a disubstituted acyclic substrate (entry 23).

The worthy feature of the reaction is that highly deactivated amines such as *p*-nitroaniline also opened the aziridines in high yield. It is remarkable that unactivated aziridines could be opened with aromatic amines under very mild conditions. This kind of result is quite unprecedented in the literature for aziridine chemistry.

The unusual feature of this reaction is that only aromatic amines opened the aziridines. Aliphatic amines, such as diethylamine, *n*-butylamine, benzylamine, and pyrrolidine, failed to react with aziridine at room temperature for 1 d in the presence of a catalytic amount of copper or tin triflate. Although we do not have any proof for the mechanism, we feel that it is ionic in nature. It was assumed that a loose complex of an aromatic amine and the catalyst coordinated with the N of an aziridine and initiated the opening reaction. Aliphatic amines by virtue of their higher basicity made stronger complexes to the copper and tin triflate which failed to activate the aziridine. This was deduced from an observation that aniline failed to open *N*-phenylcyclohexeneimine in the presence of benzylamine and copper or tin triflate under the above conditions. Irrespective of the mechanism, the cleavage of aziridine with aromatic amines in the presence of tin or copper triflate is unique and unprecedented. A variety of chiral nonracemic ligands can be complexed with copper or tin triflate for asymmetric version of the reaction which is in progress in our laboratory.

Experimental Section[9]

General Procedure for Aziridine Opening with Aromatic Amines. A solution of an aziridine (1 mmol) and an aromatic amine (1.2 mmol) in anhydrous ether or CH_2Cl_2 (5 mL) was treated with 5 mol % of $Cu(OTf)_2$ or $Sn(OTf)_2$ for the appropriate period of time (see Table 1) at room temperature. The solvent was removed on a rotary evaporator, and the crude product was purified over silica gel by column chromatography to provide pure trans diamine in high yield.

***trans*-*N*,*N*′-Diphenyl-1,2-cyclohexanediamine (1a).** Colorless gel; R_f 0.4 (2% EtOAc in petroleum ether); IR (neat) 3390 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.23 (m, 2H), 1.42 (m, 2H), 1.8 (m, 2H), 2.39 (m, 2H), 3.24 (m, 2H), 3.92 (bs, 2H, N*H*), 6.62 (d, J = 7 Hz, 4H), 6.75 (t, J = 7 Hz, 2H), 7.21 (dd, J = 7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6, 32.5, 57.2, 113.47, 117.54, 129.3, 147.7; LCMS (APCI, *m*/*z*) 267 ($M^+ + 1$). Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.20; H, 8.27; N,10.53. Found: C, 81.02; H, 8.38; N, 10.60.

***trans*-*N*-Phenyl-(*N*′-methyl-*N*′-phenyl)-1,2-cyclohexanediamine (1b).** Viscous liquid; R_f 0.5 (2% EtOAc in petroleum ether); IR (neat) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.2−1.6 (bm, 4H), 1.82 (m, 3H), 2.42 (m, 1H), 2.66 (s, 3H), 3.31 (ddd, J = 10.2, 10.2, 3.6 Hz, 1H), 3.64 (m, 1H), 4.0 (bs, N*H*, 1H), 6.58 (m, 2H), 6.7 (m, 1H), 6.78 (m, 1H), 6.84 (m, 2H), 7.15 (m, 2H), 7.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6, 25.7, 27.8, 30.7, 33.5, 55.2, 62.9, 113.2, 114.0, 117.2, 117.3, 129.18, 129.24, 147.8, 150.8; LCMS (APCI, *m*/*z*) 281 ($M^+ + 1$). Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.42; H, 8.57; N, 10.00. Found: C, 81.28; H, 8.68; N, 10.14.

***trans*-*N*-Phenyl-*N*′-(*p*-nitrophenyl)-1,2-cyclohexanediamine (1c).** Yellow solid; mp 145 °C; R_f 0.8 (1:3, EtOAc in petroleum ether); IR (KBr) 3350 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22−1.6 (bm, 4H), 1.80 (m, 2H), 2.30 (m, 2H), 3.28 (m, 2H), 3.56 (bs, N*H*, 1H), 4.63 (bs, 1H, N*H*), 6.48 (m, 2H), 6.58 (m, 2H), 6.7 (m, 1H), 7.15 (m, 2H), 8.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.4, 24.6, 32.2, 32.6, 56.9, 57.4, 111.5, 113.4, 118.0, 126.4, 129.5, 138.0, 147.1, 152.9; LCMS (APCI, *m*/*z*) 312 ($M^+ + 1$). Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.45; H, 6.75; N, 13.50. Found: C, 69.38; H, 6.82; N, 13.42.

***trans*-*N*-Phenyl-*N*′-(2-hydroxyphenyl)-1,2-cyclohexanediamine (1d).** Semisolid; R_f 0.66 (1:5, EtOAc in petroleum ether); IR (KBr) 3510, 3360, 3280 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (m, 4H), 1.68 (m, 2H), 2.21 (m, 2H), 2.93 (m,1H), 3.20 (dt, J = 9.9, 3.9 Hz, 1H), 4.40 (bs, 2H, N*H*), 6.80 (m, 6H), 7.20 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9, 25.0, 32.5, 32.7, 58.5, 60.6, 114.7 118.8, 120.5, 121.7, 129.6, 135.4, 147.0, 147.5; LCMS (APCI, *m*/*z*) 283 ($M^+ + 1$). Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.60; H, 7.80; N, 9.93. Found: C, 76.62; H, 7.90; N, 9.84.

***trans*-*N*-Phenyl-*N*′-(*o*-methylphenyl)-1,2-cyclohexanediamine (1e).** Mp 70−71 °C; R_f 0.42 (2% EtOAc in petroleum ether); IR (KBr) 3390 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (m, 2H), 1.50 (m, 2H), 1.82 (m, 2H), 2.05 (s, 3H), 2.41 (m, 2H), 3.28 (ddd, J = 9.6, 9.6, 3.6 Hz, 1H), 3.37 (ddd, J = 9.9, 9.9, 3.9 Hz, 1H), 3.93 (bs, 2H, N*H*), 6.71 (m, 5H), 7.1 (d, J = 7.5 Hz, 1H), 7.23 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.5, 24.6, 24.7, 32.6, 32.7, 57.3, 57.7, 110.2, 113.7, 117.1, 117.7, 122.9, 127.0, 129.3, 130.3, 145.6, 147.5; LCMS (APCI, *m*/*z*) 281 ($M^+ + 1$). Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.43; H, 8.57; N, 10.00. Found: C, 81.46; H, 8.70; N, 9.88.

***trans*-*N*-Phenyl-*N*′-(*m*-bromophenyl)-1,2-cyclohexanediamine (1f).** Semisolid; R_f 0.39 (2% EtOAc in petroleum ether); IR (KBr) 3390 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (m, 2H), 1.45 (m, 2H), 1.81 (m, 2H), 2.38 (m, 2H), 3.19 (m, 2H), 3.82 (bs, 2H, N*H*), 6.52 (m, 1H), 6.65 (d, J = 8.5 Hz, 2H), 6.75 (m, 2H), 6.84 (m, 1H), 7.02 (m, 1H), 7.21 (m, 2H); ^{13}C NMR (CDCl3, 75 MHz) δ 24.5, 24.6, 32.3, 32.5, 57.0, 57.2, 112.2, 113.5, 115.7, 117.7, 120.1, 123.3, 129.3, 130.5, 147.5, 149.0; LCMS (APCI, *m*/*z*) 345 and 347 (1:1; $M^+ + 1$). Anal. Calcd for $C_{18}H_{21}N_2Br$: C, 62.60; H, 6.09; N, 8.12. Found: C, 62.58; H, 6.08; N, 8.06.

***trans*-*N*-Phenyl-*N*′-(*p*-methoxyphenyl)-1,2-cyclohexanediamine (1g).** Colorless gel; R_f 0.3 (2% EtOAc in petroleum ether); IR (neat) 3365 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (m, 2H), 1.42 (m, 2H), 1.78 (m, 2H), 2.34 (m, 2H), 3.11 (ddd, J = 9.6, 9.6, 3.3 Hz, 1H), 3.20 (ddd, J = 9.6, 9.6, 3.3 Hz, 1H), 3.70 (bs, 2H, N*H*), 3.76 (s, 3H), 6.63 (m, 4H), 6.71 (m, 1H), 6.79 (m, 2H), 7.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6, 32.6, 55.8, 57.4, 58.4, 113.6, 115.0, 115.3, 117.6, 129.3, 141.8, 147.8, 152.4; LCMS (APCI, *m*/*z*) 297 ($M^+ + 1$). Anal. Calcd for $C_{19}H_{24}N_2O$: C, 77.03; H, 8.12; N, 9.46. Found: C, 76.78; H, 8.12; N, 9.40.

***trans*-*N*-Phenyl-*N*′-(β-naphthyl)-1,2-cyclohexanediamine (1h).** Semisolid; R_f 0.42 (2% EtOAc in petroleum ether); IR (KBr) 3380 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.3 (m, 2H), 1.5 (m, 2H), 1.82 (m, 2H), 2.42 (m, 2H), 3.32 (m, 2H), 3.98 (bs, 2H, N*H*), 6.62 (m, 2H), 6.78 (m, 1H), 6.82 (m, 2H), 7.20 (m, 3H), 7.40 (m, 1H), 7.64 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.57, 24.60, 32.2, 32.5, 57.15, 57.22, 104.8, 113.5, 117.6, 118.5, 122.0, 125.8, 126.4, 127.5, 127.6, 129.0, 129.3, 135.1, 145.3, 147.6; LCMS (APCI, *m*/*z*) 317 ($M^+ + 1$). Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.54; H, 7.59; N, 8.86. Found: C, 83.38; H, 7.58; N, 8.96.

***trans*-*N*-Phenyl-*N*′-(α-naphthyl)-1,2-cyclohexanediamine (1i).** Semisolid; R_f 0.45 (2% EtOAc in petroleum ether); IR (KBr) 3390 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.90−1.90 (m, 6H), 2.33 (m, 2H), 3.33 (m, 2H), 3.80 (bs, 2H, N*H*), 6.5 (m, 4H), 7.2 (m, 8H). Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.54; H, 7.59; N, 8.86. Found: C, 83.32; H, 7.55.

***trans*-*N*-Phenyl-*N*,*N*′-(diphenyl)-1,2-cyclohexanediamine (1j).** Mp 106−107 °C; R_f 0.6 (2% EtOAc in petroleum ether); IR (KBr) 3405 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.95−1.9 (m, 6H), 2.25 (m, 2H), 3.0 (m, 1H), 3.9 (m, 1H), 4.15 (bs, 1H, N*H*), 6.8−7.7 (m, 15H).

***trans*-*N*-Phenyl-[*N*′-(2,5-diisopropylphenyl)-1,2-cyclohexanediamine (1k).** Viscous liquid; R_f 0.45 (2% EtOAc in petroleum ether); IR (neat) 3360, 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.15 (d, J = 5.5 Hz, 6H), 1.25 (d, J = 5.5 Hz, 6H), 1.3−2.4 (m, 8H), 2.93−3.2 (m, 4H), 3.27 (q, J = 7 Hz, 2H), 6.75 (m, 2H), 7.0−7.4 (m, 6H). Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.29; H, 9.71; N, 8.00. Found: C, 82.00; H, 9.58; N, 8.38.

2-*N*-(*trans*-2′-Aminophenyl Cyclohexyl)-5-Chloro Pyridine (1l). Mp 89−90 °C; R_f 0.62 (1:10, EtOAc in petroleum ether); IR (KBr) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25

(8) This was ascertained by comparing the δ value of *N*-Me in products obtained from the opening of styrene oxide with *N*-methyl aniline. For reference, see: Chini, M.; Crotti, P.; Macchia, F. *J. Org. Chem.* **1991**, *56*, 5939.

(9) (a) For general methods, see: Sekar, G.; DattaGupta, A.; Singh, V. K. *J. Org. Chem.* **1998**, *63*, 2961. (b) Silica gel coated TLC plates were used.

(m, 4H), 1.78 (m, 2H), 2.2 (m, 1H), 2.28 (m, 1H), 3.13 (m, 2H), 3.81 (m, 1H), 4.37 (m, 1H), 6.24 (m, 1H), 6.48 (m, 2H), 6.62 (m, 1H), 7.05 (m, 2H), 7.26 (m, 1H), 8.05 (m, 1H). Anal. Calcd for $C_{17}H_{20}N_3Cl$: C, 67.66; H, 6.63; N, 13.93. Found: C, 67.37; H, 6.57; N, 13.80.

***trans*-*N*-Phenyl-*N*′-benzyl-1,2-cyclohexanediamine (2).** Mp 68−70 °C; R_f 0.58 (1:3, EtOAc in petroleum ether); IR (KBr) 3295 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.1 (m, 1H), 1.23 (m, 3H), 1.7 (m, 2H), 2.10 (bs, 1H, N*H*), 2.18 (m, 2H), 2.33 (ddd, J = 9.9, 9.9, 4.2 Hz, 1H), 3.12 (ddd, J = 10.2, 10.2, 3.6 Hz, 1H), 3.37 (bs, 1H, N*H*), 3.80 (AB_q, J = 13.5 Hz, 2H), 6.64 (m, 3H), 7.13 (m, 2H), 7.25 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6, 25.0, 31.4, 32.5, 50.7, 57.5, 60.8, 114.0, 117.7, 126.9, 128.1, 128.4, 129.2, 140.6, 148.2; LCMS (APCI, *m*/*z*) 281 ($M^+ + 1$). Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.43; H, 8.57; N, 10.00. Found: C, 81.58; H, 8.49; N, 9.96.

***trans*-*N*,*N*′-Diphenyl-1,2-cyclopentanediamine (3).** Viscous liquid; R_f 0.3 (2% EtOAc in petroleum ether); IR (neat) 3365 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.5 (m, 2H), 1.8 (m, 2H), 2.21 (m, 2H), 3.6 (m, 2H), 3.78 (bs, 2H, N*H*), 6.64 (m, 4H), 6.70 (m, 2H), 7.18 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 31.2, 60.7, 113.4, 117.5, 129.3, 147,7; LCMS (APCI, *m*/*z*) 253 ($M^+ + 1$). Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.95; H, 7.94; N, 11.11. Found: C, 80.87; H, 7.89; N, 11.20.

***trans*-*N*,*N*′-Diphenyl-1,2-cyclooct-5-enediamine (4).** Mp 71−72 °C; R_f 0.34 (2% EtOAc in petroleum ether); IR (KBr) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62 (m, 2H), 2.10 (m, 2H), 2.30 (m, 2H), 2.43 (m, 2H), 3.66 (d, J = 8.7 Hz, 2H), 3.93 (bs, 2H, N*H*), 5.78 (t, J = 5.4 Hz, 2H), 6.54 (m, 4H), 6.7 (m, 2H), 7.18 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.8, 33.1, 56.2, 113.2, 117.3, 129.3, 129.7; LCMS (APCI, *m*/*z*) 293 ($M^+ + 1$). Anal. Calcd for $C_{20}H_{24}N_2$; C, 82.19; H, 8.22; N, 9.59. Found: C, 81.98; H, 8.10; N, 9.86.

***N*,*N*′-Diphenyl-1,2-dodecanediamine (5).** Viscous liquid; R_f 0.55 (2% EtOAc in petroleum ether); IR (neat) 3150−3440 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 1.00 (t, J = 4.4 Hz, 3H), 1.25 (m, 18H), 3.5 (m, 5H), 6.7 (m, 5H), 7.5 (m, 5H). Anal. Calcd for $C_{24}H_{36}N_2$: C, 81.82; H, 10.23; N, 7.95. Found: C, 81.48; H, 10.18.

***N*-Methyl-*N*-phenyl[2-(*N*′-benzyl)amino]tridecanylamine (6).** Viscous liquid; R_f 0.3 (1:10, EtOAc in petroleum ether); IR (neat) 3340 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 5.4 Hz, 3H), 1.26 (m, 18H), 1.49 (m, 2H), 1.65 (bs, 1H, N*H*), 2.87 (s, 3H), 2.92 (m, 1H), 3.20 (dd, J = 14.4, 5.4 Hz, 1H), 3.34 (dd, J = 14.4, 8.4 Hz, 1H), 3.79 (ABq, J = 13.5 Hz, 2H), 6.71 (m, 3H), 7.23 (m, 7H); MS (EI, *m*/*z*) 394 (M^+). Anal. Calcd for $C_{27}H_{42}N_2$: C, 82.23; H, 10.66; N, 7.11. Found: C, 82.00; H, 10.58; N, 7.32.

***N*-Methyl-*N*-phenyl[2-(*N*′-*tert*-butyl)amino]tridecanylamine (7).** Viscous liquid; R_f 0.15 (1:10, EtOAc in petroleum ether); IR (neat) 3380 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, J = 6.8 Hz, 3H), 1.05 (s, 9H), 1.25 (m, 18H), 1.36 (m, 2H), 2.89 (s, 3H), 2.94 (m, 1H), 3.19 (d, J = 6.0 Hz, 2H), 6.70 (m, 3H), 7.21 (m, 2H); MS (EI, *m*/*z*) 360 (M^+). Anal. Calcd for $C_{24}H_{44}N_2$; C, 80.00; H, 12.22; N, 7.78. Found: C, 79.72; H, 12.21; N, 7.96.

***N*-Methyl-*N*-phenyl[3-benzylamino]butyl-2-amine (8).** Viscous liquid; R_f 0.32 (1:10, EtOAc in petroleum ether); IR (neat) 3300 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (d, J = 6.6 Hz, 3H), 1.14 (d, J = 6.6 Hz, 3H), 2.30 (bs, 1H, N*H*), 2.50 (s, 3H), 2.73 (m, 1H), 3.67 (m, 1H), 3.81 (ABq, J = 13.5 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.8 (d, J = 8.1 Hz, 2H), 7.26 (m, 7H); MS (EI, *m*/*z*) 268 (M^+). Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.60; H, 8.95; N, 10.45. Found: C, 80.44; H, 8.89; N, 10.58.

***N*-Benzyl-[2-(*N*′-methyl-*N*′-phenyl)amino]-2-phenylethylamine (9).** Viscous liquid; R_f 0.14 (1:20, EtOAc in petroleum ether); IR (neat) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72 (bs, 1H, N*H*), 2.67 (s, 3H), 3.22 (d, J = 7.8 Hz, 2H), 3.89 (ABq, J = 13.5 Hz, 2H), 5.21 (t, J = 7.2 Hz, 1H), 6.78 (t, J = 8.1 Hz, 1H), 6.91 (d, J = 8.1 Hz, 2H), 7.19 (m, 2H), 7.29 (m, 10H); MS (EI, *m*/*z*) 316 (M^+). Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.54; H, 7.59; N, 8.86. Found: C, 83.32; H, 7.48; N, 9.02.

***N*-*n*-Butyl-[2-(*N*′-methyl-*N*′-phenyl)amino]-2-phenylethylamine (10).** Viscous liquid; R_f 0.65 (1:5, EtOAc in petroleum ether); IR (neat) 3300 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, J = 7.2 Hz, 3H), 1.33 (m, 2H), 1.47 (m, 2H), 1.55 (bs, 1H, N*H*), 2.68 (m, 2H), 2.71 (s, 3H), 3.20 (d, J = 7.8 Hz, 2H), 5.16 (t, J = 6.6 Hz, 1H), 6.75 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 7.27 (m, 7H); MS (EI, *m*/*z*) 282 (M^+). Anal. Calcd for $C_{19}H_{26}N_2$: C, 80.85; H, 9.22; N, 9.93. Found: C, 80.58; H, 9.18; N, 10.00.

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