Convenient Access to Primary Amines by Employing the Barbier-Type Reaction of *N*-(Trimethylsilyl)imines Derived from Aromatic and Aliphatic Aldehydes

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A new versatile preparation of primary amines via benzylation of aromatic and aliphatic aldimines is described. Sonochemical and traditional methods for generation of the reactive intermediates are compared and contrasted. Competitive reactions were analyzed via free energy relationships to support the proposed alkylative mechanism.

In this paper we describe a simple method for the synthesis of primary amines, which avoids catalysts, difficult reaction conditions, or multistep procedures, using a variant of the Barbier procedure to effect the addition of a benzyl group to imines. While the addition of organolithium, organocopper, and Grignard reagents to the imine carbon is a useful method for the preparation of amines,[1−5] the low electrophilicity of the imine carbon has frequently hindered these reactions. The reactivity of imines has been improved by N-acylation or N-alkylation[6] to form reactive iminium salts[3] or by complexation with Lewis acids.[5]

Only a few examples of the addition of benzyl organometallics to imines are known; typical of these is Grignard addition to *N*-(trimethylsilyl)imines.[7] The methods described in these examples, some of which require inconvenient, long reaction times or low temperatures, proceed in fair to good yield. The preparation of the necessary benzyl organometallics is particularly troublesome since Wurtz coupling reactions are facile. Benzyl organometallics have been prepared by metalation of toluene with 1:1 mixture of *n*-BuLi/MO^{t}Bu (M = K, Rb) at ambient temperature[8] or treatment of toluene with *n*-BuLi and TMEDA.[9] The reductive cleavage of dibenzyl ether by lithium suspended in THF is also known.[10]

The Barbier synthesis[11] is a one-step alternative to the Grignard reaction[12] for the preparation of alcohols by the reaction of halides with carbonyl compounds such as aldehydes, ketones, and esters in the presence of a metal. Highly reactive, sterically strained tertiary alcohols[13] have been prepared by the Barbier reaction. Although magnesium[13] has been employed as the reductant metal, the use of lithium has been found not only to increase the yield of the Barbier reaction but also to suppress side reactions. Sonication was successfully applied to lithium-Barbier reactions[14] in 1980 with the superiority of the method strikingly evident. Although organic halides in which the halogen atom is bound to a single asymmetric carbon atom react with metals with complete loss of stereochemical integrity, the formation of enantiomeric alcohols under ultrasonic Barbier conditions has been reported.[15] While a variety of organohalides have been employed, the use of benzylic halides has remained problematic.

Results

N-(Trimethylsilyl)benzaldimine was initially employed in our search for the optimal Barbier reaction conditions for the formation of an amine from in situ generated imines. It was prepared from benzaldehyde via an addition−elimination reaction with lithium hexamethyldisilazide (LiHMDS).[8,16] *N*-(Trimethylsilyl)benzaldimine was allowed to react without isolation or purification with benzyl bromide in the presence of lithium wire in refluxing ether under sonication.[17] 1,2-Diphenylethanamine was isolated in moderate to good yields following aqueous workup. Solvents were screened in model studies to determine the most suitable medium for the sonication reaction. Initially, to optimize cavity forma-

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Table 1. Solvent Optimization

entry	solvent	Li, equiv	benzylbromide, equiv	yield,[a] %
1	diethyl ether	4	2	35
2	THF	4	2	18
3	pentane	4	2	0.0
4	DMPU	4	2	0.5
5	dioxane	4	2	0.0
6	di-*n*-butyl ether	4	2	0.7
7	DME	4	2	0.1
8	ether/DMF 1:1	4	2	0.0

[a] Yields are determined by mass balance and gas chromatographic analysis.

Table 2. Effect of the Temperature

entry	solvent	*T*, °C	yield %[a]
1	ether	0	0.0
2	THF	0	0.0
3	ether	0−5	35
4	THF	0−5	14
5	ether	reflux	61
6	THF	reflux	52
7	ether/THF 1:2	reflux	50
8	ether	60[b]	73

[a] See footnote Table 1. [b] Reaction was run in a sealed tube with the bath temperature at 60 °C.

Table 3. Time Dependence of the Reaction

entry	*t*, min	yield, %[a]
1	15	18
2	30	63
3	45	69
4	60	40

[a] See footnote Table 1.

tion,[17b] temperatures between 0 and 5 °C were employed with ethereal solvents (entries 1 and 2) in Table 1. Subsequently, nonpolar pentane (entry 3) and highly polar 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone (DMPU) (entry 4) as well as ethereal solvents with varied boiling points and viscosities were employed neat (entries 5−7) and as mixtures (entry 8). As can be seen from the table, diethyl ether was superior to tetrahydrofuran, while none of the other solvents was satisfactory.

At elevated temperatures, the reaction proceeded better with diethyl ether than with tetrahydrofuran in all cases (Table 2). A mixture of these two solvents gave results consistent with those found with the major component alone. At 60 °C the yield of the reaction in experiments with diethyl ether as solvent in a sealed tube increased, but because of the associated inconvenience, all further reactions were conducted under reflux at atmospheric pressure obviating the difficulty in maintaining a stable temperature in a sonication bath. The side reaction normally observed, Wurtz coupling, was minimized at higher temperatures.

Since the reaction times of sonochemically promoted reactions can have a profound effect on yield, a survey of reaction times was undertaken to determine the length of time for the reaction (Table 3). Reaction times greater than 30 min resulted in only a modest increase in the yield of the process (entry 3), and at 60 min the yield decreased considerably (entry 4).

Quantities of benzyl halide and lithium in excess of that required stoichiometrically are necessary for the best yield in the process. Two equivalents of benzyl bromide are sufficient to compensate for the side reaction of Wurtz coupling. However, eight equivalents of lithium were

Scheme 1

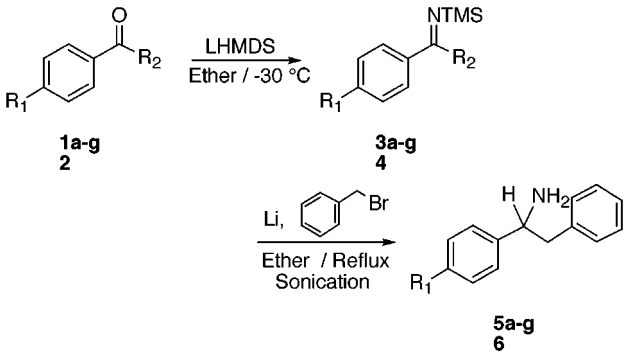


Table 4. Influence of Substituents at the Para Position on Amine Formation

entry	imine	R_1	R_2	amine	yield, %[a]
1	**3a**	$N(CH_3)_2$	H	**5a**	92
2	**3b**	OCH_3	H	**5b**	69
3	**3c**	CH_3	H	**5c**	31
4	**3d**	H	H	**5d**	63
5	**3d**	H	H	**5d**	41[b]
6	**3d**	H	H	**5d**	48[c]
7	**3d**	H	H	**5d**	55[d]
8	**3d**	H	H	**5d**	60[e]
9	**4**	H	CH_3	**6**	8
10	**3e**	F	H	**5e**	30
11	**3f**	Cl	H	**5f**	21
12	**3g**	CF_3	H	**5g**	4

[a] Isolated yields. [b] The reaction was done without sonication. [c] Slow addition of the benzyl bromide−imine mixture to a solution of lithium naphthalide in ether with no sonication. [d] Slow addition in THF with no sonication. [e] Slow addition of the reagent in refluxing ether under sonication.

necessary to maximize amine formation. The reaction is apparently relatively unaffected by concentration.

N-(Trimethylsilyl)imines with carefully selected para substituents (Scheme 1) were prepared in situ from the appropriate aromatic aldehydes and lithium hexamethyldisilazide.[7,16] In the imine-forming step, at no time was it possible to detect the aldehyde by infrared spectroscopy after as few as 15 min. It can therefore be concluded that differences in the rate of imine formation cannot account for the observed differences of amine formation.

N-(Trimethylsilyl)imines were reacted with benzyl bromide in the presence of lithium wire under the optimized conditions. The resultant primary amines were isolated in moderate to good yields following aqueous workup (Table 4). It can be seen that imines bearing electron-donating groups in the para position gave much higher yields than those having electron-withdrawing groups. While it was anticipated that the reaction would involve nucleophilic attack of a benzyllithium reagent, these results suggest that the reaction proceeds via a different mechanism.

The reaction also proceeds without sonication, however, in lower yield, and with longer reaction times (entry 5). Prolongation of the reaction time is accompanied by consumption of the benzyl bromide, as well as by decomposition of the imine at the elevated temperature employed. In light of the fact that the benzyl halide is not used efficiently in this reaction, slow addition of a mixture of imine and benzyl bromide to refluxing ether under sonication improved the yield of amine to 60% (entry 8). As mentioned previously benzyllithium is difficult to prepare by direct reaction of a benzyl halide with lithium metal because of the marked tendency for

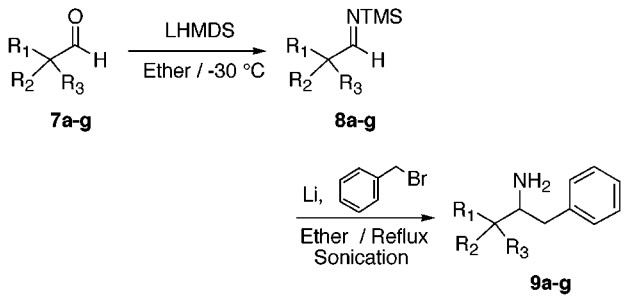
Table 5. Aliphatic Imines in the Barbier-Type Reaction

imine	R_1	R_2	R_3	amine	yield, %[a]
8a	H	H	H	**9a**	23
8b	CH_3	H	H	**9b**	52
8c	CH_3	CH_3	H	**9c**	88
8d	CH_3	CH_3	CH_3	**9d**	61
8e	C_2H_5	C_2H_5	H	**9e**	44
8f	$(CH_2)_4$	CH_2	H	**9f**	51
8g	C_3H_7	CH_3	H	**9g**	52

[a] Isolated yields.

Wurtz coupling. This difficulty has been overcome by forming a lithium−electron acceptor complex either in ether or THF before addition of the reactant mixture. To employ this strategy, lithium was added to a solution of naphthalene[12b,18] in ether and THF. When the benzyl bromide−imine mixture was added slowly to an excess of this complex, Wurtz coupling was minimized. With an addition time of 30 min, the result of the reaction under these conditions is comparable to those obtained on sonication. The yield was 48% in ether (entry 6) and 55% in THF (entry 7). Reaction with acetophenone (entry 9) failed (Table 4). Failure of acetophenone to react may be a consequence of the presence of acidic α-protons which interfere with imine formation as lithium hexamethyldisilazide is a potent base. Attempts to avoid the use of *N*-(trimethylsilyl)imines by employing a preformed imine from the reaction of benzaldehyde and benzylamine resulted in only an 8% yield of amine product.

Aliphatic aldehydes, both with and without acidic α-protons, were also employed in the reaction.



Competitive enolization of the aldehyde during the preparation of silylimine and/or competitive deprotonation of the product imine to the corresponding azaenolate may be suppressed by effecting the imine formation at −30 °C.[16]

With enolizable aldehydes bearing increasingly less acidic protons (entries **8a** thru **8c**, Table 5), the yield of amine product follows the predicted ease of imine formation. In the case of aldehydes with especially reactive hydrogens, even imine formation at −30 °C and Barbier reaction at 35 °C cannot compete with the deprotonation process. The absence of an α-proton does not necessarily result in an improvement in yield (entry **8d**) as the yield in this case is slightly decreased relative to entry **8c**.

Scheme 2

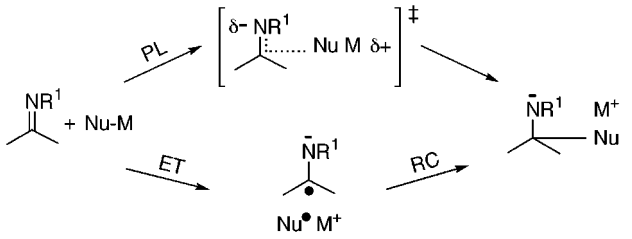


Table 6. Competitive Reactions of Aromatic Imines for the Hammett Plot

entry	R1	σ[a]	σ^+ [a]	$\log(K/K_0)$[b,c]	$\log(K/K_0)$[b,d]
1	$N(CH_3)_2$	−0.63	−1.70	+1.49	0.4
2	OCH_3	−0.27	−0.78	−0.15	*e*
3	CH_3	−0.017	−0.31	−0.36	*e*
4	H	0.0	0.0	0.0	0.0
5	F	+0.06	−0.17	−0.03	−0.05
6	Cl	+0.23	+0.11	−0.81	*e*
7	CF_3	+0.54	+0.54	−1.25	−0.95

[a] The σ values were taken from ref 25. [b] The values were calculated from the competition reactions. [c] The reactions were carried out at the boiling point of ether. [d] The temperature was kept between 0 and 5 °C. [e] These reactions were not performed.

Steric hindrance might be invoked in rationalizing the decrease in yield in the reactions of **8e** through **8g** as well.

Discussion

The Barbier reaction is generally accepted[19] to proceed either via an organometallic compound (polar (PL) route) or via a radical intermediate occurring on the surface of the metal. The latter pathway involves two steps, an electron transfer (ET) step followed by a radical coupling (RC) step (Scheme 2). Whether a reaction involves organometallic compounds (PL route) or radical intermediates (the ET−RC route) is dependent upon the nature of the nucleophile as well as the structure of the carbonyl compounds, with the determination of the dominant pathway quite difficult in some cases. In the case of the reactions of benzaldehyde derivatives under Barbier conditions, the proposed mechanism of the process is mainly considered to involve polar addition (PL addition), with no evidence for the ET mechanism.[20]

From Scheme 2 it is clear that any of three steps are potentially rate limiting.[21] The PL mechanism, the ET−RC mechanism with rate-determining ET, and the ET−RC mechanism with rate-determining RC can be distinguished.

In an effort to develop a better understanding of the process involved in the reaction of aldimines, two sets of competitive experiments at different temperatures were conducted with *N*-(trimethylsilyl)imines derived from benzaldehyde and a substituted benzaldehyde. The product ratios in these cases were used to generate the data shown in Table 6 and to establish the free energy relationship shown in Figure 1.

In those cases involving the ET−RC mechanism with ET and rate-determining step, the process would be predicted to have a very small ρ value. Since the reaction

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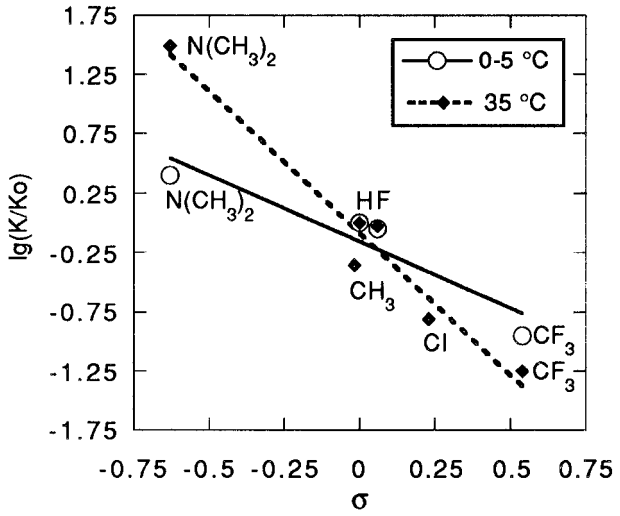

Figure 1. Substituent effects for the Barbier-type reaction of aromatic imines with benzyl bromide in the presence of lithium.

has a significant Hammett ρ value, the radical mechanism with rate-determining ET can likely be excluded. From Figure 1, it is clear that the reaction of the imine occurs with a large negative ρ value at 35 °C ($\rho = -2.39$, corr coef = 0.97 excluding the CH_3O group). With the observation that electron-releasing groups enhance the reactivity while electron-withdrawing groups retard the reactivity, polar addition of a benzyl anion is also unlikely.

The negative slope of the plot in Figure 1 is indicative of two possibilities. First, the reaction is being studied at temperatures beneath the isokinetic temperature. It is known that ρ values will approach zero when the temperature of the measurement is close to the isokinetic temperature and will change sign below that temperature.[23] From competitive reactions studied between 0 and 5 °C (Table 6), the value of ρ was determined to be −1.11. Since the value of ρ approached zero at this lower temperature, it was a clear indication that measurements at both 35 and 0−5 °C are above the isokinetic temperature. The correlation coefficient of 0.94 associated with the data obtained at lower temperature is worse than that for the data obtained under reflux as a consequence of the difficulty of controlling the temperature of the sonication bath. Second, the results suggest that the reaction process involves attack of an electrophile in a rate-determining step on the substituted imine. The negative slope associated with the plot suggests that the imine reactant acts as a nucleophile since electron-releasing groups are accelerating the reaction. A rapid electron transfer to the imine carbon from the surface of the metal to form a radical anion which then reacts as a nucleophile with benzyl bromide fits the observed data better than the assumption that the benzyl bromide is converted to an organometallic species.

Preliminary results indicated that the product of Wurtz coupling is also formed, implying that a second process competes with the proposed alkylative mechanism. We have shown that formation of the Wurtz coupling product can be suppressed by raising the reaction temperature. The proposed mechanism for the reaction of imines accommodates that observation that polar addition to an imine is often more difficult than that to an aldehyde since the imine is less reactive toward the addition of an anion. One the other hand, the imine can be reduced in a one-electron-transfer step to an intermediate radical anion. Although the reduction potentials of benzaldehyde and the corresponding imines are very close, shifts in the reduction potential can be expected in the case of the Schiff bases. Reduction of the carbon−nitrogen double bond in these cases is facilitated by electron-withdrawing substituents[24] on either portion of the imine bond. Following electron transfer to the carbon−nitrogen double bond, the radical anion may also be stabilized by the trimethylsilyl group. The reactivity of the resultant anion is most significantly moderated by the substituents on the aromatic ring. Obviously it is the effect of the substituents on the reactivity of the anion that is reflected in the linear free energy relationship, rather than the effect of the substituents on the redox potential of the imine.

Conclusion

In situ prepared (trimethylsilyl)imines have been found to react with benzyl bromide in the presence of lithium metal upon sonication to give primary amines in fair to good yield. The optimum solvent for the reaction was diethyl ether with the best yields occurring when the reaction was conducted at 60 °C. Competitive experiments suggest that the rate-limiting step involves attack of a nucleophilic species (formed by reduction of the imine reactant) on benzyl bromide. The reaction was extended to encompass imines prepared from aliphatic aldehydes.

Experimental Section

^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 300, 75, and 282 MHz, respectively. ^{19}F NMR chemical shifts were referenced to $CFCl_3$. Diethyl ether was distilled from sodium in the presence of sodium benzophenone ketyl. Hexamethyldisilazane was dried with calcium hydride. Aldehydes were distilled before use. The imines were prepared immediately before utilization in the Barbier reaction. All reactions were carried out under an argon atmosphere. Lithium wire (sodium content 1%) was purchased from Aldrich. The sonication was carried out in a Branson 2200 type ultrasonic cleaning bath.

General Method for Aliphatic Imine Formation. To a solution of lithium hexamethyldisilazide (4.3 mmol) in 8 mL of diethyl ether at −30 °C was added the appropriate aliphatic aldehyde (3.9 mmol) dropwise in 3 mL of diethyl ether. The reaction mixture was stirred at this temperature for 30 min.

General Method for Aromatic Imine Formation. These compounds were prepared under the same conditions as the aliphatic compounds except that the temperature was 0 °C.

General Method for the Barbier-Type Reaction. Dry ethyl ether (20 mL) and lithium (16 mmol) cut into small pieces were placed in a reaction flask equipped with a condenser. The flask was immersed into an ultrasonic cleaning bath containing warm water. Sonication was started after the reflux in the flask had begun. While under reflux, a mixture of imine (2 mmol) and benzyl bromide (4 mmol) was added via syringe. The reaction mixture was transferred into 20 mL of a saturated NH_4Cl solution and extracted with EtOAc. The combined organic phase was extracted with a 10% HCl solution, and the aqueous phase was washed with EtOAc. The pH of the aqueous phase was adjusted to 12, and the solution was extracted with EtOAc. The organic layer was then washed with water and brine and dried over $MgSO_4$.

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General Method for the Relative Reactivity. A pair of aldehydes (the parent and substituted, 1.95 mmol each) in 3 mL of dry ether were added to a solution of LiHMDS (4.3 mmol) in 5 mL of dry ethyl ether, and the solution was stirred for 30 min. The Barbier-type reaction was performed in the same manner as before. After aqueous workup of the reaction, the ratio of the two amines was determined by GC from the crude product.

1-(4-(*N′*,*N′*-Dimethylamino)phenyl)-2-phenylethan-1-amine (5a): IR (neat) 3363, 3300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4−6.7 (br, 9H), 4.15 (dd, J = 8.7, 4.8 Hz, 1H), 3.05 (dd, J = 13.2, 5.1 Hz, 1H), 2.98 (s, 6H), 2.87 (dd, J = 13.1, 8.9 Hz, 1H), 1.83 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 149.6, 139.3, 133.2, 129.1, 128.1, 126.9, 126.0, 112.4, 56.7, 46.2, 40.5. Anal. Calcd for $C_{16}H_{20}N$: C, 79.95; H, 8.38. Found: C, 79.88; H, 8.34.

1-(4-Methoxyphenyl)-2-phenylethan-1-amine[25] (5b): IR (neat) 3373, 3316 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3−7.1 (br, 9H), 4.16 (dd, J = 7.9, 6.0 Hz, 1H), 3.78 (s, 3H), 3.01 (dd, J = 13.3, 5.7 Hz, 1H), 2.90 (dd, J = 13.2, 8.2 Hz, 1H), 2.67 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 158.5, 138.6, 136.4, 129.2, 128.2, 127.5, 126.2, 113.6, 56.9, 55.1, 45.9. Anal. Calcd for $C_{15}H_{17}N$: C, 79.26; H, 7.54. Found: C, 79.09; H, 7.50.

1-(4-Methylphenyl)-2-phenylethan-1-amine[26] (5c): IR (neat) 3356, 3287 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2−7.0 (br, 9H), 4.08 (dd, J = 7.0, 7.0 Hz, 1H), 3.62 (br, 2H), 2.94 (dd, J = 13.2, 6.2 Hz, 1H), 2.87 (dd, J = 13.3, 7.9 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 140.0, 138.2, 136.9, 129.2, 129.0, 128.2, 126.5, 126.3, 57.2, 45.0, 21.0.

2-Phenylethan-1-amine[25] (5d): IR (neat) 3375, 3300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (m, 10H), 4.22 (dd, J = 8.8, 4.9 Hz, 1H), 3.03 (dd, J = 13.3, 4.9 Hz, 2H), 2.85 (dd, J = 13.3, 8.9 Hz, 1H), 1.66 (b, 2H); ^{13}C NMR ($CDCl_3$) δ 145.5, 138.9, 129.2, 128.3, 127.0, 126.35, 126.31, 57.4, 46.0.

1-(4-Fluorophenyl)-2-phenylethan-1-amine (5e): IR (neat) 3373, 3298 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15 (m, 9H), 4.21 (br, 1H), 2.98 (dd, J = 13.0, 4.9 Hz, 1H), 2.84 (dd, J = 13.2, 8.5 Hz, 1H), 1.91 (b, 2H); ^{13}C NMR ($CDCl_3$) δ 161.8 (d, J^1_{C-F} = 245 Hz), 140.8, 138.5 (d, J^4_{C-F} = 2.7 Hz), 129.2, 128.3, 127.9 (d, J^3_{C-F} = 8 Hz), 126.3, 115.0 (d, J^2_{C-F} = 21.6 Hz), 56.8, 46.3; ^{19}F NMR ($CDCl_3$) δ −63.07. Anal. Calcd for $C_{14}H_{14}N$: C, 78.11; H, 6.56. Found: C, 78.35; H, 6.72.

1-(4-Chlorophenyl)-2-phenylethan-1-amine[26] (5f): IR (neat) 3370, 3297 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4−7.1 (br, 9H), 4.19 (m, 1H), 3.03 (dd, J = 13.5, 5.0 Hz, 1H), 2.82 (dd, J = 13.2, 8.5 Hz, 1H), 1.58 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 143.9, 138.4, 132.4, 129.2, 128.3, 127.7, 126,3, 56.8, 46.3.

1-(4-(α′,α′,α′-Trifluoromethyl)phenyl)-2-phenylethan-1-amine (5g): IR (neat) 3364, 3283 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (m, 4H), 7.30−7.15 (br, 5H), 4.28 (dd, J = 5.2, 8.4 Hz, 1H), 3.00 (dd, J = 5.0, 13.5 Hz, 1H), 2.85 (dd, J = 8.7, 13.2 Hz, 1H), 1.85 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 149.4, 138.3, 161.8 (q, J^2_{C-F} = 270 Hz), 129.3, 128.5, 126.8, 126.6, 125.3 (q J^1_{C-F} = 270 Hz), 57.2, 46.3; ^{19}F NMR ($CDCl_3$) δ −62.9.

1-Phenylpropan-2-amine[27] (9a): IR (neat) 3355, 3296 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.14 (m, 5H), 3.07 (m, 1H), 2.62 (dd, J = 5.6, 13.4 Hz, 1H), 2.43 (dd, J = 8.2, 13.2 Hz, 1H), 1.75 (b, 2H), 1.03 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.4, 129.0, 128.1, 125.9, 48.3, 46.4, 23.3.

1-Phenylbutan-2-amine[28] (9b): IR (neat) 3352, 3264 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 5H), 4.30 (br, 2H), 3.05 (m, 1H), 2.83 (dd, J = 13.4, 6.2 Hz, 1H), 2.73 (dd, J = 13.2, 7.8 Hz, 1H), 1.53 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.0, 129.1, 128.3, 126.2, 54.2, 41.6, 27.8, 10.1.

3-Methyl-1-phenylbutan-2-amine[29] (9c): IR (neat) 3375, 3307 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (m, 5H), 2.78 (dd, J = 10.0, 4.1 Hz, 1H), 2.41 (dd, J = 14.1, 10.0 Hz, 1H), 2.28 (br, 2H), 1.64 (m, 1H), 0.94 (dd, J = 6.2, 6.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 139.7, 129.1, 128.3, 126.0, 58.1, 40.6, 32.4, 19.2, 17.3.

3′,3-Dimethyl-1-phenylbutan-2-amine (9d): IR (neat) 3385, 3325 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 5H), 2.98 (dd, J = 13.2, 2.1 Hz, 1H), 2.69 (dd, J = 11.0, 2.3 Hz, 1H), 2.22 (dd, J = 13.2, 11.0 Hz, 1H), 1.21 (br, 2H), 1.01 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 140.7, 128.9, 128.2, 125.8, 61.8, 38.4, 34.0, 26.1. Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80. Found: C, 81.40; H, 11.00.

3-Ethyl-1-phenylpentan-2-amine (9e): IR (neat) 3374, 3310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 5H), 3.19 (dd, J = 7.9, 4.3 Hz, 1H), 2.85 (dd, J = 13.5, 5.0 Hz, 1H), 2.59 (dd, J = 12.8, 9.3 Hz, 1H), 1.49 (m, 2H), 1.36 (m, 2H), 1.24 (br, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.4, 129.1, 128.4, 126.1, 54.2, 45.4, 39.9, 22.3, 21.5, 12.0, 11.9. Anal. Calcd for $C_{13}H_{21}N$: C, 81.61; H, 11.06. Found: C, 81.46; H, 10.93.

2-Cyclohexyl-1-phenylethan-2-amine (9f): IR (neat) 3374, 3305 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.15 (br, 5H), 2.87 (dd, J = 13, 3.9 Hz, 1H), 2.81 (dd, J = 4.0, 3.4 Hz, 2H), 2.43 (dd, J = 12.0, 9.6 Hz, 1H), 1.91 (br, 2H), 1.9−1.5 (br, 5H), 1.4−0.9 (br, 6H); ^{13}C NMR ($CDCl_3$) δ 140.0, 129.2, 128.4, 126.1, 57.6, 43.1, 40.9, 29.7, 28.1, 26.5, 26.4, 26.3. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41. Found: C, 82.49; H, 10.21.

(*l*,*u*)-3-Methyl-1-phenylhexan-2-amine (9g): IR (neat) 3375, 3307 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (m, 5H), 3.0−2.7 (br, 2H), 2.41 (m, 1H), 1.6−1.3 (br, 3H), 1.3−1.1 (br, 4H), 0.93 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 1140.1, 140.0, 129.0, 128.9, 128.2, 125.8, 57.2, 56.4, 41.6, 40.2, 37.9, 37.2, 35.9, 34.5, 20.4, 20.3, 15.4, 14.2, 14.1, 13.7. Anal. Calcd for $C_{13}H_{21}N_1$: C, 81.61; H, 11.06. Found: C, 81.39; H, 11.03.

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