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Transformation of *N*,*N*-diisopropylarylmethylamines into *N*-isopropylarylmethylamines with molecular iodine

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ABSTRACT

N,*N*-Diisopropylarylmethylamines were smoothly converted into the corresponding *N*-isopropylarylmethylamines by the reaction with molecular iodine in the presence of Na_2CO_3 in chloroform at 60 °C. Other related tertiary amines were also transformed into the corresponding secondary amines by the reaction with molecular iodine under the same reaction conditions.

Reaction of tertiary amines with oxidants is attractive and important in organic synthesis,[1] since degradation products through C–N bond cleavage occur. Today, it is a well-known fact that treatment of tertiary amines with oxidants, such as $Pb(OAc)_4$,[2a] $KMnO_4$,[2b–d] MnO_2,[2e] chromic acid,[2f] $Hg(OAc)_2$,[2g] $HgO{\cdot}I_2$,[2h] K_2FeO_4,[2i] and $Ru(bpy)_3Cl_2$ with $K_2S_2O_8$ under visible–right irradiation,[2j] or bromination reagents, such as bromocyanide[3a] and *N*-bromosuccinimide,[3b] gives the corresponding aldehydes or ketones. Moreover, treatment of *N*,*N*-dimethyl allylic tertiary amines with excess 30% H_2O_2, followed by the reaction with Ac_2O,[4a] and the irradiation of *N*,*N*-dimethyl allylic tertiary amines in the presence of molecular iodine with a flood lamp under air[4b] gave the corresponding α,β-unsaturated aldehydes. Treatment of *N*,*N*-dimethylarylmethylamines with aq H_2O_2 in the presence of 10 mol % of tetrabutylammonium iodide (TBAI) in *N*,*N*-dimethylacetamide for 24 h at 100 °C also gave the corresponding aromatic aldehydes.[5a] Similarly, treatment of *N*,*N*-diisopropylarylmethylamines with (diacetoxyiodo)benzene (DIB) in the presence of $NaHCO_3$ in $CHCl_3$ at 60 °C also gave the corresponding aromatic aldehydes.[5b] On the other hand, to the best of our knowledge, study for the direct transformation of tertiary amines into secondary amines is little studied. Today, organic transformations with less toxic reagents under mild conditions are strongly required. Molecular iodine is one of the least toxic oxidative reagents. Here, as part of our study of molecular iodine for organic synthesis,[6] we would like to report novel oxidative conversion of *N*,*N*-diisopropylarylmethylamines into the corresponding *N*-isopropylarylmethylamines with molecular iodine in the presence of Na_2CO_3.

At first, *N*,*N*-diisopropyl-*p*-bromobenzylamine was treated with molecular iodine (1.5 equiv or 1.2 equiv) in the absence or presence of Na_2CO_3, K_2CO_3, Cs_2CO_3, $NaHCO_3$ (2.0 equiv), as shown in Table 1 (entries 1–6), and it was found that the treatment of *N*,*N*-diisopropyl-*p*-bromobenzylamine with molecular iodine (1.5 equiv) in the presence of Na_2CO_3 (2.0 equiv) at 60 °C for 24 h (until the starting amine was consumed based on by TLC monitoring) gave *N*-isopropyl-*p*-bromobenzylamine in 89% yield (entry 2).[7] DIH (1,3-diiodo-5,5-dimethylhydantoin, 0.7 equiv) and NIS (*N*-iodosuccinimide, 1.5 equiv) also provide *N*-isopropyl-*p*-bromobenzylamine; however, their reactivities were lower than that of molecular iodine. On the other hand, methanesulfonic acid (MsOH) and aq. HI (55–58%), that is, Brønsted acids, did not work at all as a removal reagent of *N*-isopropyl group from *N*,*N*-diisopropyl-*p*-bromobenzylamine (entries 9 and 10). When the reaction was carried out using 10 mmol of *N*,*N*-diisopropyl-*p*-bromobenzylamine under the same conditions at 60 °C, *N*-isopropyl-*p*-bromobenzylamine was obtained in 74% yield, as shown in Table 1 (entry 2). Based on those results, various *N*,*N*-diisopropylarylmethylamines bearing a benzyl group, a *p*-chlorobenzyl group, a *m*-chlorobenzyl group, an *o*-chlorobenzyl group, a *p*-nitrobenzyl group, a *p*-ethoxycarbonylbenzyl group, a *p*-methylbenzyl group, and a *p*-methoxybenzyl group were treated with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h to provide the corresponding *N*-isopropylarylmethylamines in good to moderate yields, as shown in Table 2. Then, to check the co-products of the present reaction,

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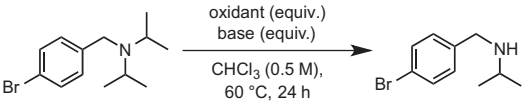
0040-4039/

Table 1
Oxidative removal of *N*-isopropyl group from *N*,*N*-diisoprolyl-*p*-bromobenzylamine with molecular iodine



Entry	Oxidant (equiv)	Base (equiv)	Yield (%)
1	I_2 (1.5)	—	40
2	I_2 (1.5)	Na_2CO_3 (2.0)	89 (74)[a]
3	I_2 (1.5)	K_2CO_3 (2.0)	70
4	I_2 (1.5)	Cs_2CO_3 (2.0)	73
5	I_2 (1.5)	$NaHCO_3$ (2.0)	75
6	I_2 (1.5)	Na_2CO_3 (2.0)	87
7	DIH (0.7)	Na_2CO_3 (2.0)	67
8	NIS (1.5)	Na_2CO_3 (2.0)	32
9	MsOH (2.0)	—	0 (90)[b]
10	aq HI (2.0)	—	0 (86)[b]

[a] Reaction was carried out on a 10 mmol starting material.
[b] Recovery of starting material.

N,*N*-dicyclohexyl-*p*-bromobenzylamine and *N*,*N*-dicyclohexybenzylamine ($R^2 = R^3 = Cy$) were treated with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h to provide *N*-cyclohexyl-*p*-bromobenzylamine and *N*-cyclohexybenzylamine in 79% and 68% yields, respectively, together with cyclohexanone in 51% and 22% yields, respectively, although the formation of 10–12% of *p*-bromobenzaldehyde and benzaldehyde was observed, respectively. Thus, the co-product of the present reaction was ketone, mainly. The same treatment of *N*,*N*-dicyclopentyl-*p*-bromobenzylamine and *N*,*N*-dicyclopentylbenzylamine ($R^2 = R^3 = Cp$) with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h also provided *N*-cyclopentyl-*p*-bromobenzylamine and *N*-cyclopentylbenzylamine in 65% and 60% yields, respectively. When *N*-isopropyl-*N*-ethyl-*p*-bromobenzylamine and *N*-isopropyl-*N*-ethylbenzylamine ($R^2 = Et$, $R^3 = i$Pr) were treated with molecular iodine under the same conditions, *N*-ethyl-*p*-bromobenzylamine and *N*-ethylbenzylamine were obtained in moderate yields, respectively, together with *N*-isopropyl-*p*-bromobenzylamine and *N*-isopropylbenzylamine also in moderate yields, respectively. On the other hand, the same treatment of *N*,*N*-diethyl-*p*-bromobenzylamine and *N*,*N*-diethylbenzylamine with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h gave *N*-ethyl-*p*-bromobenzylamine and *N*-ethylbenzylamine in 63% and 52% yields, respectively. However, the treatment of *N*,*N*-dimethyl-*p*-bromobenzylamine and *N*,*N*-dimethylbenzylamine with molecular iodine in the presence of Na_2CO_3 under the same conditions did not provide demethylated amines at all, instead, *p*-bromobenzaldehyde and benzaldehyde were obtained in moderate yields, respectively.

Totally, oxidative removal of *N*-^{i}Pr group ($R^2 = R^3 = Pr^i$) in $ArCH_2NR^2R^3$ with molecular iodine and K_2CO_3 proceeds more smoothly than *N*-cyclohexyl group ($R^2 = R^3 = Cy$), *N*-cyclopentyl group ($R^2 = R^3 = Cp$), and *N*-ethyl group ($R^2 = R^3 = Et$). However, there is not much difference in reactivity among $ArCH_2NPr^i_2$, $ArCH_2NCy_2$, $ArCH_2NCp_2$, and $ArCH_2NEt_2$.

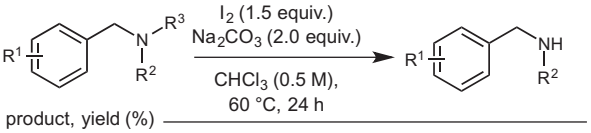
Then *N*,*N*-diisopropyl-α-methylbenzylamine was treated with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h to give *N*-isopropyl-α-methylbenzylamine in 77% yield, as shown in Scheme 1 (Eq. 1). In addition, the same treatment of *N*,*N*-diisopropyl-2-phenylethylamine and *N*,*N*-diisopropyl-3-phenylpropylamine with molecular iodine in the presence of Na_2CO_3 at 60 °C for 24 h generated *N*-isopropyl-2-phenylethylamine and *N*-isopropyl-3-phenylpropylamine in 70% and 65% yields, respectively.

On the other hand, when *N*,*N*-diisopropyl-*p*-bromobenzylamine was treated with (diacetoxyiodo)benzene (DIB)[5b] and 1-acetoxy-5-bromo-1,2-benziodoxole-3(1*H*)-one (ABBX),[8] which are trivalent iodines I(III) that have stronger oxidizing ability than molecular iodine, in the presence of K_2CO_3 in chloroform at room temperature for 12 h, *p*-bromobenzaldehyde instead of *N*-isopropyl-*p*-bromobenzylamine was obtained in 65% and 82% yields, respectively, as mentioned in the literature.[5b,9] Moreover, *N*-isopropyl-*p*-bromobenzylamine was treated with DIB (3.0 equiv), and ABBX (3.0 equiv) in the presence of K_2CO_3 in chloroform at room temperature for 12 h, *N*-isopropyl-*p*-bromobenzylamine was recovered in 63% and 60% yields, respectively, without formation of aromatic aldehydes. Thus, the oxidation products of *N*,*N*-diisopropylarylmethylamines by molecular iodine is not the same as that by trivalent iodine DIB or ABBX.

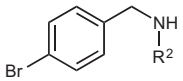
Additionally, *N*-isopropyl-*N*,*N*-di(*p*-bromobenzyl)amine and *N*-ethyl-*N*,*N*-di(*p*-bromobenzyl)amine were treated with molecular iodine (1.5 equiv and 3.0 equiv) in the presence of Na_2CO_3 (2.0 equiv) in chloroform at 60 °C for 24 h to give di(*p*-bromobenzyl)amine in 64% and 47% yields, respectively, together with *p*-bromobenzaldehyde in 3% and 7% yields, respectively.

A plausible reaction mechanism for the oxidative removal of the isopropyl group from *N*,*N*-diisopropylarylmethylamines by molec-

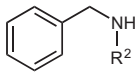
Table 2
Oxidative removal of *N*-alkyl group from *N*,*N*-dialkylarylmethylamines with molecular iodine



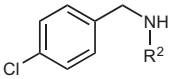
product, yield (%)



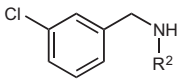
R^2, R^3=iPr, 89%
R^2, R^3=Cy, 79%[a](10%)[e](51%)[f]
R^2, R^3=Cp, 65%[a](7%)[e]
R^2=Et, R^3=iPr, 35%[a](45%)[g]
R^2, R^3=Et, 63%[a,b,d]
R^2, R^3=Me, 0%(53%)[e]



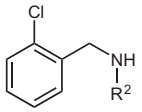
R^2, R^3=iPr, 86%[c]
R^2, R^3=Cy, 68%[a](12%)[e](22%)[f]
R^2, R^3=Cp, 60%[a](6%)[e]
R^2=Et, R^3=iPr, 41%[a](34%)[g]
R^2, R^3=Et, 52%[a,d]
R^2, R^3=Me, 0%(49%)[e]



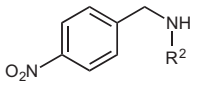
R^2, R^3=iPr, 84%[a]



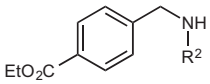
R^2, R^3=iPr, 82%[a]



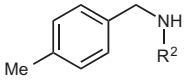
R^2, R^3=iPr, 87%



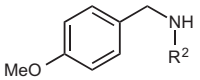
R^2, R^3=iPr, 88%



R^2, R^3=iPr, 79%[c]

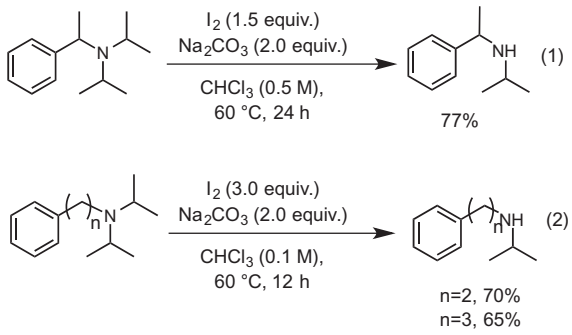


R^2, R^3=iPr, 71%[c](7%)[e]

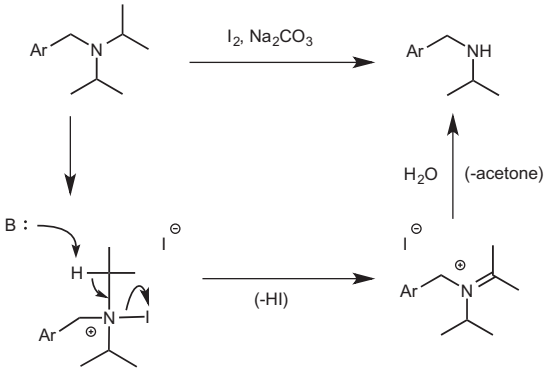


R^2, R^3=iPr, 61%[a](7%)[e]

[a] Reaction was carried out in $CHCl_3$ (0.1 M). [b] Reaction was carried out for 12 h. [c] I_2 (1.2 equiv) was used. [d] I_2 (3.0 equiv) was used. [e] Yield of aromatic aldehyde. [f] Yield of cyclohexanone. [g] Yield of *N*-isopropylarylmethylamine.



Scheme 1. Oxidative removal of *N*-isopropyl group from *N*,*N*-diisopropylalkylamines with molecular iodine.



Scheme 2. Plausible reaction mechanism.

ular iodine is shown in Scheme 2. *N*,*N*-Diisopropylarylmethylamine reacts with molecular iodine to form *N*-iodo-ammonium salt, and this is followed by HI-elimination to form iminium salt. Once iminium salt is formed, hydrolysis occurs to form *N*-isopropylarylmethylamine, together with acetone. Practically, when *N*,*N*-dicyclohexyl-*p*-bromobenzylamine was used, cyclohexanone was obtained in 51% yield. However, the reason why the benzylic proton of the *N*-iodo-ammonium salt is not eliminated is not clear. Probably, there is a steric hindrance in the HI-elimination of *N*-iodo-ammonium salt formed from the reaction of *N*,*N*-diisopropylarylmethylamines and molecular iodine, by base.

In conclusion, treatment of *N*,*N*-diisopropylarylmethylamines with molecular iodine in the presence of Na_2CO_3 gave *N*-isopropylarylmethylamines in good to moderate yields. On the other hand, treatment of those amines with DIB or ABBX, trivalent iodine I(III), gave the corresponding aromatic aldehydes. Thus, molecular iodine can be used for the direct conversion of *N*,*N*-diisopropyl tertiary amines into *N*-isopropyl secondary amines under mild, less toxic, and transition-metal-free conditions.

Acknowledgments

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Supplementary data

Supplementary data (^{1}H NMR and ^{13}C NMR spectra for all secondary *N*-isopropyl and *N*-ethylamines) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.10.044.

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7. *Typical experimental procedure for removal of N-isopropyl group from N,N-diisopropylarylmethylamine:* To a solution of *N*,*N*-diisopropyl-*p*-bromobenzylamine (1.0 mmol, 270.2 mg) in $CHCl_3$ (2.0 mL) was added I_2 (1.5 mmol, 380.7 mg) and Na_2CO_3 (2.0 mmol, 212.0 mg) at room temperature, and the mixture was stirred for 24 h at 60 °C. The reaction mixture was cooled to room temperature and quenched by satd aq Na_2SO_3 (10 mL), and extracted with $CHCl_3$ (20 mL × 3). Then, the organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the yield was determined by ^{1}H NMR analysis (89%). The residue was purified by short column chromatography on neutral silica gel (AcOEt/EtOH = 7:3) to afford *N*-isopropyl-*p*-bromobenzylamine.
N-Isopropyl-p-bromobenzylamine: Yield: 89%; oil; IR (neat): $\tilde{\nu}$ = 3311 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 6.1 Hz, 6H), 2.83 (sep, *J* = 6.3 Hz, 1H), 3.73 (s, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 48.1, 50.8, 120.5, 129.8, 131.4, 139.6 ppm; HRMS (ESI): calcd for $C_{10}H_{15}NBr$ $[M+H]^+$ 228.0382, found 228.0381.
N-Cyclohexyl-p-bromobenzylamine: Yield: 79%; oil; IR (neat): $\tilde{\nu}$ = 3311 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07–1.27 (m, 5H), 1.59–1.63 (m, 1H), 1.71–1.75 (m, 2H), 1.88–1.91 (m, 2H), 2.42–2.49 (m, 1H), 3.76 (s, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.0, 26.1, 33.5, 50.3, 56.1, 120.5, 129.8, 131.4, 140.0 ppm; HRMS (ESI): calcd for $C_{13}H_{19}NBr$ $[M+H]^+$ 268.0695, found 268.0695.
N-Cyclopentyl-p-bromobenzylamine: Yield: 65%; oil; IR (neat): $\tilde{\nu}$ = 3307 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31–1.38 (m, 2H), 1.47–1.58 (m, 2H), 1.65–1.75 (m, 2H), 1.80–1.88 (m, 2H), 3.09 (quin, *J* = 6.8 Hz, 1H), 3.72 (s, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.0, 33.2, 52.0, 59.1, 120.5, 129.9, 131.4, 139.8 ppm; HRMS (ESI): calcd for $C_{12}H_{17}NBr$ $[M+H]^+$ 254.0539, found 254.0538.
N-Ethyl-p-bromobenzylamine: Yield: 63%; oil; IR (neat): $\tilde{\nu}$ = 3309 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 7.3 Hz, 3H), 2.70 (q, *J* = 7.0 Hz, 2H), 3.78 (s, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 43.4, 52.9, 120.8, 129.9, 131.4, 138.7 ppm; HRMS (ESI): calcd for $C_9H_{13}NBr$ $[M+H]^+$ 214.0226, found 214.0222.
N-Isopropylbenzylamine: Yield: 86%; oil; IR (neat): $\tilde{\nu}$ = 3310 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.3 Hz, 6H), 2.83 (sep, *J* = 6.3 Hz, 1H), 3.79 (s, 2H), 7.20–7.34 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 48.1, 51.5, 126.9, 128.1, 128.4, 140.6 ppm; HRMS (ESI): calcd for $C_{10}H_{16}N$ $[M+H]^+$ 150.1277, found 150.1273.
N-Cyclohexylbenzylamine: Yield: 68%; oil; IR (neat): $\tilde{\nu}$ = 3280 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08–1.31 (m, 5H), 1.59–1.63 (m, 1H), 1.72–1.76 (m, 2H), 1.90–1.93 (m, 2H), 2.45–2.52 (m, 1H), 3.81 (s, 2H), 7.21–7.33 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.0, 26.1, 33.4, 51.0, 56.1, 126.8, 128.1, 128.4, 140.73 ppm; HRMS (ESI): calcd for $C_{13}H_{20}N$ $[M+H]^+$ 190.1590, found 190.1586.
N-Cyclopentylbenzylamine: Yield: 60%; oil; IR (neat): $\tilde{\nu}$ = 3309 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33–1.43 (m, 2H), 1.48–1.58 (m, 2H), 1.65–1.75 (m, 2H),

1.82–1.90 (m, 2H), 3.12 (quin, J = 6.7 Hz, 1H), 3.77 (s, 2H), 7.21–7.33 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 33.1, 52.7, 59.1, 126.8, 128.2, 128.3, 140.7 ppm; HRMS (ESI): calcd for $C_{12}H_{18}N$ $[M+H]^+$ 176.1434, found 176.1431.

N-Ethylbenzylamine: (Commercial) Yield: 52%; oil; IR (neat): $\tilde{\nu}$ = 3281 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, J = 7.2 Hz, 3H), 2.69 (q, J = 7.2 Hz, 2H), 3.79 (s, 2H), 7.22–7.33 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 43.6, 53.9, 126.9, 128.1, 128.4, 140.4 ppm.

N-Isopropyl-p-chlorobenzylamine: Yield: 84%; oil; IR (neat): $\tilde{\nu}$ = 3315 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.3 Hz, 6H), 2.84 (sep, J = 6.3 Hz, 1H), 3.75 (s, 2H), 7.24–7.30 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 48.1, 50.7, 128.4, 129.4, 132.5, 139.1 ppm; HRMS (ESI): calcd for $C_{10}H_{15}NCl$ $[M+H]^+$ 184.0888, found 184.0887.

N-Isopropyl-m-chlorobenzylamine: Yield: 82%; oil; IR (neat): $\tilde{\nu}$ = 3313 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.3 Hz, 6H), 2.84 (heptet, J = 6.3 Hz, 1H), 3.76 (s, 2H), 7.18–7.33 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.9, 48.1, 51.0, 123.2, 126.9, 128.1, 129.6, 134.2, 143.0 ppm; HRMS (ESI): calcd for $C_{10}H_{15}NCl$ $[M+H]^+$ 184.0888, found 184.0886.

N-Isopropyl-o-chlorobenzylamine: Yield: 87%; oil; IR (neat): $\tilde{\nu}$ = 3310 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.3 Hz, 6H), 2.83 (sep, J = 6.1 Hz, 1H), 3.87 (s, 2H), 7.16–7.25 (m, 2H), 7.34–7.40 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.9, 47.9, 49.0, 126.8, 128.2, 129.5, 130.2, 133.7, 138.0, ppm; HRMS (ESI): calcd for $C_{10}H_{15}NCl$ $[M+H]^+$ 184.0888, found 184.0885.

N-Isopropyl-p-nitrobenzylamine: Yield: 88%; oil; IR (neat): $\tilde{\nu}$ = 1173, 1341, 3330 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, J = 6.3 Hz, 6H), 2.86 (sep, J = 6.3 Hz, 1H), 3.90 (s, 2H), 7.52 (d, J = 8.2 Hz 2H), 8.17 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.7, 48.3, 50.1, 123.4, 128.6, 146.8, 148.4 ppm; HRMS (ESI): calcd for $C_{10}H_{15}O_2N_2$ $[M+H]^+$ 195.1128, found 195.1125.

N-Isopropyl-p-ethoxycarbonylbenzylamine: Yield: 79%; oil; IR (neat): $\tilde{\nu}$ = 1714, 3312 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, J = 6.1 Hz, 6H), 1.40 (t, J = 7.3 Hz, 3H) 2.85 (sep, J = 6.1 Hz, 1H), 3.84 (s, 2H), 4.37 (q, J = 7.0 Hz, 2H) 7.40 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.9, 48.2, 51.2, 60.8, 127.9, 129.0, 129.7, 146.0, 166.5 ppm; HRMS (ESI): calcd for $C_{13}H_{20}O_2N$ $[M+H]^+$ 222.1489, found 222.1484.

N-Isopropyl-p-methylbenzylamine: Yield: 71%; oil; IR (neat): $\tilde{\nu}$ = 3308 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.3 Hz, 6H), 2.33 (s, 3H) 2.85 (heptet, J = 6.3 Hz, 1H), 3.75 (s, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 22.8, 47.9, 51.2, 128.1, 129.1, 136.4, 137.4 ppm; HRMS (ESI): calcd for $C_{11}H_{18}N$ $[M+H]^+$ 164.1434, found 164.1428.

N-Isopropyl-p-methoxybenzylamine: Yield: 61%; oil; IR (neat): $\tilde{\nu}$ = 1244, 3311 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, J = 6.3 Hz, 6H), 2.86 (sep, J = 6.3 Hz, 1H), 3.73 (s, 2H), 3.79 (s, 3H), 6.86 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 48.0, 50.9, 55.2, 113.8, 129.3, 132.6, 158.5 ppm; HRMS (ESI): calcd for $C_{11}H_{18}ON$ $[M+H]^+$ 180.1383, found 180.1378.

N-Isopropyl-α-methylbenzylamine: Yield: 77%; oil; IR (neat): $\tilde{\nu}$ = 3325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–1.03 (m, 6H), 1.34 (d, J = 6.5 Hz, 3H), 2.62 (sep, J = 6.3 Hz, 1H), 3.89 (q, J = 6.5 Hz, 1H), 7.21–7.35 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 24.0, 24.8, 45.5, 55.1, 126.4, 126.8, 128.4, 145.8 ppm; HRMS (ESI): calcd for $C_{11}H_{18}N$ $[M+H]^+$ 164.1434, found 164.1434.

N-Isopropyl-2-phenylethylamine: Yield: 70%; oil; IR (neat): $\tilde{\nu}$ = 3298 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (d, J = 6.1 Hz, 6H), 2.78–2.90 (m, 5H), 7.19–7.23 (m, 3H), 7.28–7.32 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.9, 36.6, 48.5, 48.8, 126.1, 128.4, 128.7, 140.1 ppm; HRMS (ESI): calcd for $C_{11}H_{18}N$ $[M+H]^+$ 164.1434, found 164.1432.

N-Isopropyl-3-phenylpropylamine: Yield: 65%; oil; IR (neat): $\tilde{\nu}$ = 3302 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (d, J = 6.3 Hz, 6H), 1.81 (quin, J = 7.7 Hz, 2H), 2.61–2.68 (m, 4H), 2.77 (sep, J = 6.3 Hz, 1H), 7.16–7.20 (m, 3H), 7.26–7.31 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.0, 32.0, 33.8, 47.1, 48.7, 125.7, 128.3, 128.4, 142.2 ppm; HRMS (ESI): calcd for $C_{12}H_{20}N$ $[M+H]^+$ 178.1590, found 178.1589.

Bis(4-bromobenzyl)amine: (Commercial) Yield 64% and 47%; oil; IR (neat): $\tilde{\nu}$ = 3336 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 4H), 7.21 (d, J = 8.3 Hz, 4H), 7.45 (d, J = 8.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.3, 120.8, 129.8, 131.5, 139.1 ppm.

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9. *Typical experimental procedure for oxidation of N,N-diisopropyl-p-bromobenzylamine:* To a solution of *N,N*-diisopropyl-*p*-bromobenzylamine (0.5 mmol, 135.1 mg) in $CHCl_3$ (5.0 mL) was added ABBX (1.5 mmol, 577.4 mg) and K_2CO_3 (1.0 mmol, 138.2 mg) at room temperature, and the mixture was stirred for 12 h. The reaction mixture was quenched by satd aq Na_2SO_3 (10 mL), and extracted with Et_2O (20 mL × 3). Then, the organic layer was washed with brine (20 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by short column chromatography on neutral silica gel (hexane/AcOEt = 9:1) to afford *p*-bromobenzaldehyde in 82% yield (76.1 mg).