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Indium(III)-Catalyzed Reductive Bromination and Iodination of Carboxylic Acids to Alkyl Bromides and Iodides: Scope, Mechanism, and One-Pot Transformation to Alkyl Halides and Amine Derivatives

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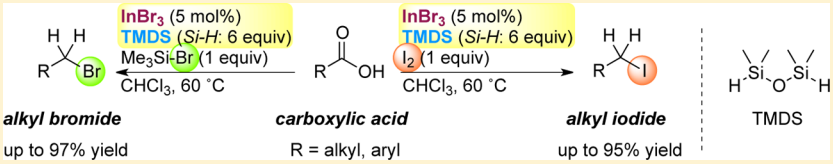
Supporting Information



ABSTRACT: Highly effective indium(III)-catalyzed reductive bromination or iodination of a variety of carboxylic acids with 1,1,3,3-tetramethyldisiloxane (TMDS) and a source of bromine or iodine is described. This functional group interconversion has high tolerance for several functional groups, such as halogens, a hydroxy group, a nitro group, an olefin part, and a sulfide moiety. This indium catalytic system is also applicable to the reductive iodination of aldehyded, acyl chlorides, and esters. Furthermore, this reducing system can be applied to the one-pot synthesis of alkyl halides and amine derivatives via the addition of nucleophiles. Insight into the reaction mechanism was gained via the time course of ^{1}H and ^{13}C NMR monitoring experiments and the corresponding stepwise reactions.

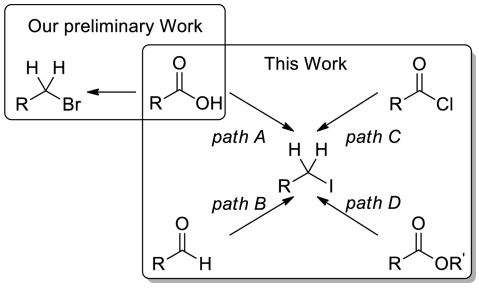
INTRODUCTION

Functional group interconversions (FGIs) with carbonyl compounds, such as aldehydes, ketones, esters, and carboxylic acids, have been occupied a central and important position of synthetic organic chemistry.[1] Among them, a reductive FGI from carboxylic acids to alkyl halides has attracted considerable attention in our field[2] because the produced alkyl halides can be easily converted to organic chemicals such as Grignard reagents and organolithium compounds or highly valuable organic compounds such as amines, ethers, and nitriles.[3] Also, because carboxylic acids generally show tolerance to the common reducing reagents, achievement of the FGI with this reducible reagent is of interest from the viewpoint of molecular conversion. A conventional method for the preparation of alkyl halides from carboxylic acids generally requires the following troublesome two steps: first, the carbonyl moiety must be reduced to a primary alcohol with a strong reducing agent, such as lithium aluminum hydride (LAH); second, the primary alcohol obtained is treated with a hydrogen halide or a phosphorus halide.[4] However, the transformation with LAH declines chemoselectivity toward other functional groups because of its high reducing ability and moisture sensitivity.

To date, the indium(III)-catalyzed reductive FGI of alcohols,[5] ketones,[6] aldehydes,[6] and acyl halides,[7] the radical reduction of organic halides,[8] and the 1,4-reduction of enones,[9] have been developed by several groups. We developed the reducing system with indium tribromide ($InBr_3$) and triethylsilane (Et_3SiH) to undertake the deoxygenation of carboxylic acids and amides, leading to the preparation of primary alcohols and secondary amines.[10,11] With this reducing reagent, the reductive FGI of several reducing reagents, such as a ketone and an acetal, and esterification of a carboxylic acid have also been achieved.[12,13] Moreover, we recently disclosed the indium-catalyzed one-pot preparation of alkyl bromides from carboxylic acids.[14]

In this paper, first, as an extension of our previous letter, we examined the direct preparation of alkyl iodides via the indium-catalyzed reduction of carboxylic acids and derivatives, such as aldehydes, acyl halides, and esters, with a siloxane and an iodine source (paths A–D in Scheme 1). Second, to show the utility of the alkyl iodides prepared by this method, we performed the consecutive transformation of in situ-prepared alkyl iodides to alkyl chlorides, alkyl fluorides, and amine derivatives using a

Scheme 1. $InBr_3$-Catalyzed Reductive Iodination of Carboxylic Acids and Their Derivatives



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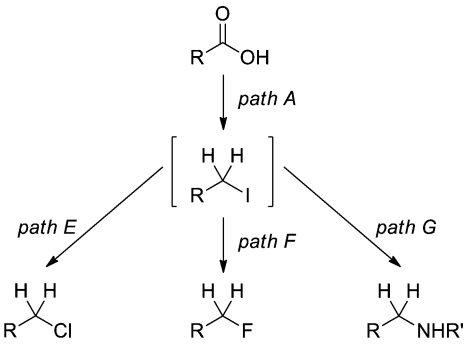
one-pot method (paths E–G in Scheme 2). Finally, we elucidated the reaction mechanism of a reductive trans-

Scheme 2. Consecutive Transformations of the in Situ-Prepared Alkyl Iodides

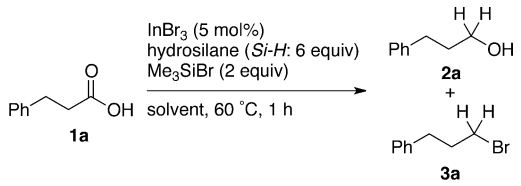


formation series from a carboxylic acid to an alkyl halide by NMR monitoring of the reaction system. Herein, we report the full details.

RESULTS AND DISCUSSION

Optimization of the Reductive Bromination of Carboxylic Acids. Table 1 shows the details of our re-

Table 1. Reaction Conditions for Reductive Bromination of Carboxylic Acid 1a[a]



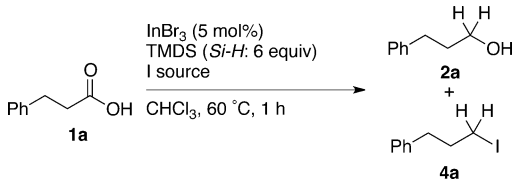
			yield (%)[b]	
entry	hydrosilane	solvent	2a	3a
1	$PhSiH_3$	$CHCl_3$	ND[d]	89
2	$PhMe_2SiH$	$CHCl_3$	ND[d]	21
3	Ph_2MeSiH	$CHCl_3$	ND[d]	19
4	Et_3SiH	$CHCl_3$	ND[d]	36
5	$(EtO)_3SiH$	$CHCl_3$	no reaction	
6	PMHS	$CHCl_3$	ND[d]	94
7	TMDS	$CHCl_3$	ND[d]	99 (96)
8	TMDS	toluene	ND[d]	99
9	TMDS	THF	no reaction	
10	TMDS	CH_3CN	no reaction	
11	TMDS	MeOH	no reaction	
12	TMDS	DMF	no reaction	
13[c]	TMDS	$CHCl_3$	ND[d]	99

[a]The reactions were carried out with **1a** (0.6 mmol), $InBr_3$ (5 mol %), hydrosilane (*Si–H*: 6 equiv), and Me_3SiBr (2 equiv) in $CHCl_3$ at 60 °C for 1 h. [b]NMR yields (an isolated yield is shown in parentheses). [c]Me_3SiBr (1 equiv) was used. [d]ND: not detected.

examination of the optimal conditions for hydrosilanes and solvents in the direct bromination of carboxylic acids. First, when 3-phenylpropanoic acid (**1a**) was treated with 5 mol % $InBr_3$, 6 equiv (*Si–H*) of $PhSiH_3$, and 2 equiv of Me_3SiBr in $CHCl_3$ at 60 °C, the corresponding alkyl bromide **3a** was obtained in 89% yield (Table 1, entry 1). The reactions with phenyldimethylsilane ($PhMe_2SiH$), methyldiphenylsilane (Ph_2MeSiH), and Et_3SiH resulted in significant decreases in the yield of **3a** (entries 2–4). When the reaction was conducted with triethoxysilane [$(EtO)_3SiH$], the corresponding bromide **3a** was not obtained at all (entry 5). In contrast, ethereal hydrosilanes such as polymethylhydrosilane (PMHS) and 1,1,3,3-tetramethyldisiloxane (TMDS) were very effective, and the corresponding bromide **3a** was obtained in excellent yield (entries 6 and 7). The screening of hydrosilanes for the bromination of **1a** identified TMDS as the optimal hydrosilane source. The solvent effect was remarkable for this reaction. The use of chloroform and toluene resulted in satisfactory bromination of the carboxylic acid (entries 7 and 8). However, the reaction did not proceed at all in tetrahydrofuran (THF), acetonitrile (CH_3CN), methanol (MeOH), or dimethylformamide (DMF) (entries 9–12). The bromination proceeded in quantitative yield even when 1 equiv of Me_3SiBr was used (entry 13). Consequently, the results of our examinations showed that the optimal conditions for the bromination of carboxylic acid **1a** are $InBr_3$ (5 mol %), TMDS (*Si–H*: 6 equiv), and Me_3SiBr (1 equiv) in $CHCl_3$ at 60 °C. The detailed scope of the direct bromination of a variety of carboxylic acids under these conditions is described in the previous work.[14]

Optimization of the Reductive Iodination of Carboxylic Acids. To apply this procedure to a reductive iodination, several iodine sources were examined. When iodotrimethysilane (Me_3SiI), which was prepared in situ from iodine and hexamethyldisilane,[15] was used, the corresponding iodide **4a** was obtained in quantitative yield (Table 2, entry 1). However,

Table 2. Reaction Conditions for Reductive Iodination of Carboxylic Acid 1a[a]



		yield (%)[b]	
entry	iodide source (equiv)	2a	4a
1	Me_3SiI (1)	ND[c]	99
2	I_2 (1)	ND[c]	98
3	I_2 (0.5)	ND[c]	86
4	CuI (1)	88	8
5	KI (1)	no reaction	

[a]The reaction was carried out with **1a** (0.6 mmol), $InBr_3$ (5 mol %), TMDS (*Si–H*: 6 equiv), and the indicated amount of the iodide source in $CHCl_3$ at 60 °C for 1 h. [b]NMR yields. [c]ND: not detected.

when 1 equiv of molecular iodine was used, an excellent yield of the corresponding iodide **4a** was obtained (entry 2). This result emphatically showed that the iodosilane was generated in situ and that the species behaved as an iodide anion source in the iodination series.[16] When 0.5 equiv of I_2 was used, a good yield of the corresponding iodide was obtained (entry 3). In short, these results showed that the in situ iodide cation was efficiently reduced to an iodo anion in the reaction. Other iodine sources, such as copper(I) iodide and potassium iodide, were ineffective for this reductive iodination (entries 4 and 5). From the viewpoints of experimental handling and cost, molecular iodine was a more useful iodine source than Me_3SiI and thus was the best iodine source used in this reaction.

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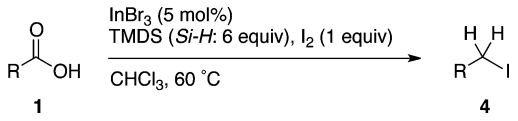
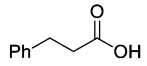
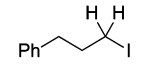
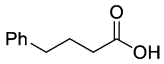
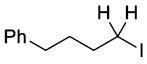
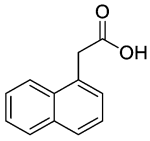
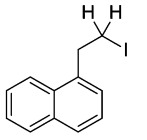
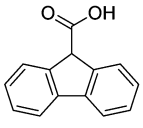
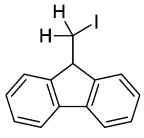
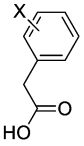
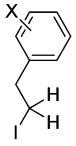
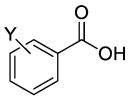
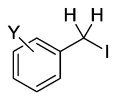
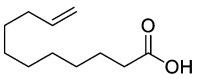
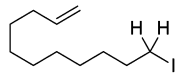
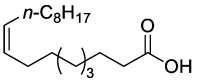
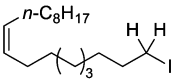
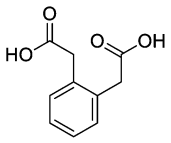
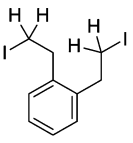
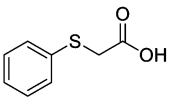
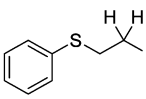
Table 3. Preparation of a Variety of Alkyl Iodides[a]



entry	carboxylic acid	product	time (h)	yield (%)[b]
1	 **1a**	 **4a**	1	91
2	 **1b**	 **4b**	0.5	0[c]
3	 **1c**	 **4c**	1	88
4	 **1d**	 **4d**	<0.1	81
5	X=*o*-Me **1e**	X=*o*-Me **4e**	1	91
6	X=*p*-Cl **1f**	X=*p*-Cl **4f**	1	94
7	 X=*p*-Br **1g**	 X=*p*-Br **4g**	1	95
8	X=*o*-I **1h**	X=*o*-I **4h**	1	91
9	X=*p*-OH **1i**	X=*p*-OH **4i**	1	89
10[d]	X=*p*-NO_2 **1j**	X=*p*-NO_2 **4j**	12	50
11	Y= *p*-OMe **1k**	Y= *p*-OMe **4k**	5	NR
12	 Y= *p*-Cl **1l**	 Y= *p*-Cl **4l**	1	93
13	Y= *p*-CF_3 **1m**	Y= *p*-CF_3 **4m**	1	87
14	 **1n**	 **4n**	1	CM[e]
15	 **1o**	 **4o**	1	CM[e]
16[f]	 **1p**	 **4p**	1	88
17	 **1q**	 **4q**	0.3	92

[a]The reaction was carried out with carboxylic acid **1** (0.6 mmol), $InBr_3$ (5 mol %), TMDS (*Si*–*H*: 6 equiv), and I_2 (1 equiv) in $CHCl_3$ at 60 °C, unless otherwise noted. [b]Isolated yields. [c]1,2,3,4-Tetrahydronaphthalene (**4b′**) was obtained in a 90% yield. [d]$InBr_3$ (10 mol %) and Me_3SiI (1 equiv) were used in 1,2-dichloroethane at 80 °C. [e]CM: A complex mixture. [f]TMDS (*Si*–*H*: 12 equiv) and I_2 (2 equiv) were employed.

Substrate Scope of the Reductive Iodination of Carboxylic Acids. With the optimal conditions, the scope of the direct iodination of various carboxylic acids was investigated (Table 3).[17] The iodination of aliphatic carboxylic acids **1a**, **1c**, and **1d** was complete within 1 h and afforded the corresponding iodides **4a**, **4c**, and **4d** in high yields (entries 1, 3 and 4). However, when 4-phenylbutanoic acid (**1b**) was used, the intramolecular cyclization product 1,2,3,4-tetrahydronaphthalene (**4b′**) was obtained as the major product rather than the desired alkyl iodide **4b** (entry 2). It was suggested that although the iodination of carboxylic acid **1b** was rapidly completed, $InBr_3$, which remained intact in the reaction mixture, further accelerated the annulation of the intermediate, alkyl iodide **4b**. The reducing system did not affect functional groups on the benzene ring, such as a methyl group, halogens, and a hydroxy group (entries 5–10). Carboxylic acid **1j** containing a nitro group was transformed into the corresponding iodide **4j** in moderate yield with $InBr_3$ (10 mol %), TMDS (*Si*–*H*: 12 equiv), and Me_3SiI (1 equiv) in 1,2-dichloroethane at 80 °C. Interestingly, this result was in clear contrast with the results of the previous bromination. The use of an iodine source with a nucleophilicity that was stronger than that of bromotrimethylsilane succeeded in halogenation of the carboxylic acid. Application of the procedure to aromatic carboxylic acids was then examined. The iodination of *p*-methoxybenzoic acid (**1k**) did not occur, probably because of a decrease in the electrophilicity of the carbonyl carbon (entry 11). When reactions were performed with benzoic acids **1l** and **1m**, which had either a chlorine or a trifluoromethyl group the expected iodides **4l** and **4m**, respectively, were obtained in high yields (entries 12 and 13). Carboxylic acids with terminal or internal alkenes were consumed within a short time but did not give the corresponding iodides **4n** and **4o** (entries 14 and 15). Unlike the bromination of **1n** and **1o**, an olefin moiety was also reduced, but the desired products were not detected. The iodination of dicarboxylic acid **1p** was undertaken using $InBr_3$ (10 mol %), TMDS (*Si*–*H*: 12 equiv), and I_2 (1 equiv) and gave the corresponding iodide **4p** in 88% yield (entry 16). This iodination was applicable to the carboxylic acid with a thioether

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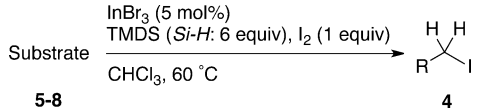
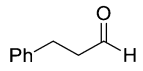
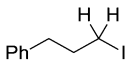
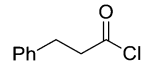
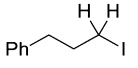
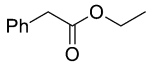
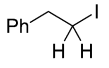
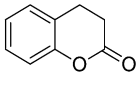
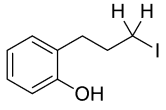
moiety, **1q**, which produced the corresponding sulfide **4q** in 92% yield (entry 17).

Reductive Iodination of Carbonyl Compounds and Carboxylic Acid Derivatives. As an application, iodinations of an aldehyde and carboxylic acid derivatives, such as an acyl chloride and an ester, were conducted (Table 4). When both aldehyde **5** and acyl chloride **6** were subjected to the optimal conditions, the corresponding iodide **4a** was obtained in good yields (entries 1 and 2). Similarly, when the iodination was performed with alkyl ester **7**, both deoxygenation of the carbonyl moiety and substitution of the ethoxy group occurred smoothly, producing 2-phenyl-1-iodoethane (**4r**) in 92% yield (entry 3). When this iodination was also examined with a cyclic ester, 3,4-dihydrocoumarin (**8**), the ring-opening product **4s** was obtained in a practical yield (entry 4). These results proved that cleavage of the C−O single bond on the ester proceeded selectively.

Table 4. Reductive Transformations of Carboxylic Acid Derivatives to Alkyl Iodides[a]

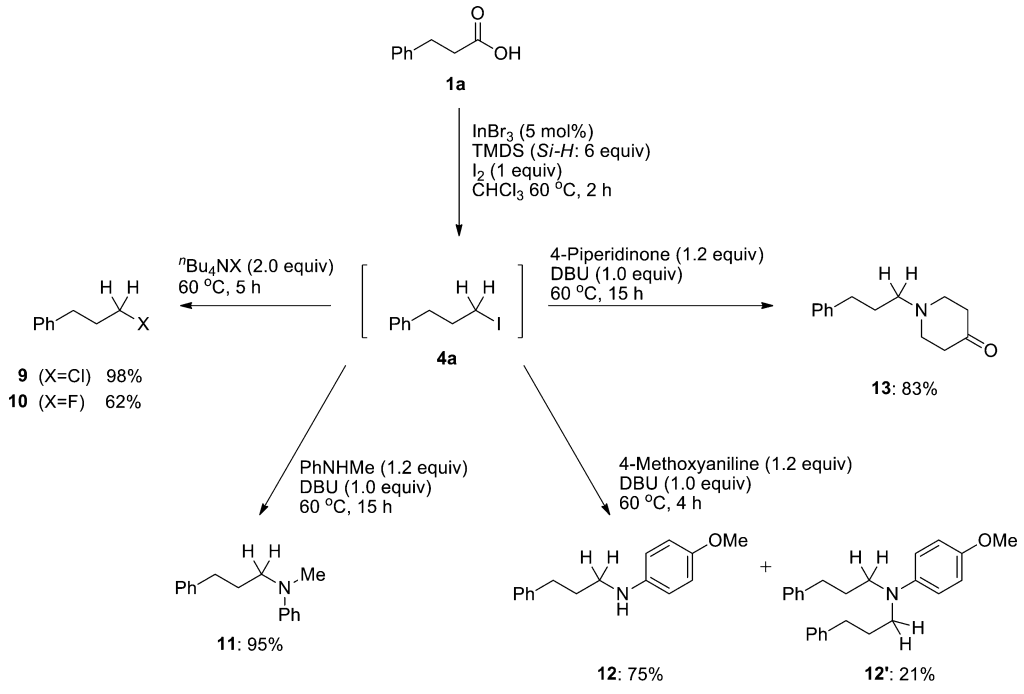


entry	substrate		product		time (h)	yield (%)[b]
1		**5**		**4a**	1	(85)[c]
2		**6**		**4a**	1	(99)[c]
3		**7**		**4r**	1	92
4		**8**		**4s**	2	70

[a]The reaction was carried out with the substrate (0.6 mmol), $InBr_3$ (5 mol %), TMDS (*Si*−*H*: 6 equiv), and I_2 (1 equiv) in $CHCl_3$ at 60 °C. [b]Isolated yields (GC yields are shown in parentheses).

Application to the One-Pot Synthesis of Alkyl Chlorides, Alkyl Fluorides, and Amine Derivatives. To show the utility of this iodination, we then attempted a one-pot conversion to alkyl chlorides, alkyl fluorides, and amine derivatives via in situ-generated alkyl iodides.[18] As shown in Scheme 3, the iodination of 3-phenylpropanoic acid (**1a**) was initially carried out with our standard conditions consisting of $InBr_3$ (5 mol %), TMDS (*Si*−*H*: 6 equiv), and I_2 (1 equiv), and subsequent treatment with tetrabutylammonium chloride (2.0 equiv) produced 1-chloro-3-phenylpropane (**9**) in nearly quantitative yield. Similarly, when carboxylic acid **1a** was subjected to the iodination series and then treated with tetrabutylammonium fluoride (TBAF), the corresponding alkyl fluoride **10** was obtained in a 62% yield. These results demonstrated that this catalytic system could transform carboxylic acids into alkyl fluorides, chlorides, bromides, and iodides by the combination of $InBr_3$, a hydrosilane, and an appropriate halogen source. To the intermediate **4a** was added an aniline derivative, *N*-methylaniline (1.2 equiv), and treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1 equiv) afforded the corresponding tertiary amine **11** in 95% yield. The reaction with a primary amine, 4-methoxyaniline, also produced the corresponding secondary amine **12** in 75% yield along with a 21% yield of a byproduct, tertiary amine **12′**. When 4-piperidinone was used as a nucleophile, the

Scheme 3. One-Pot Conversion of Carboxylic Acids to Alkyl Chlorides, Alkyl Fluorides, and Amine Derivatives



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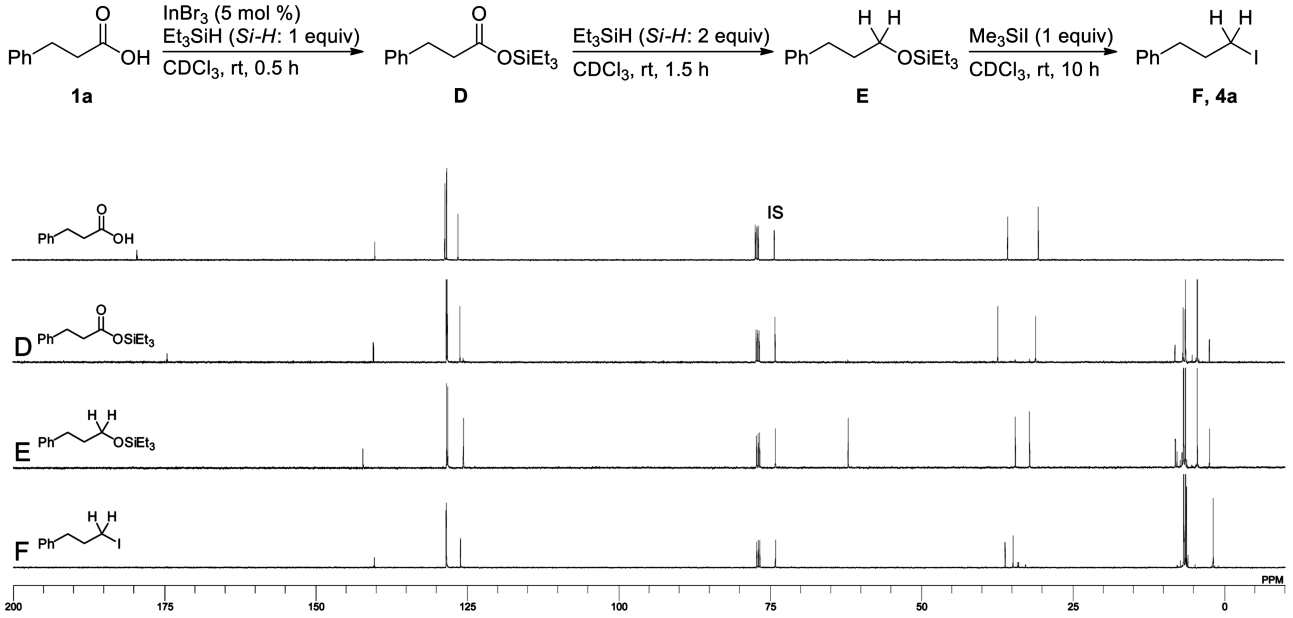

Figure 1. Monitoring of $InBr_3$-catalyzed reductive iodination of carboxylic acid **1a** by ^{13}C NMR.

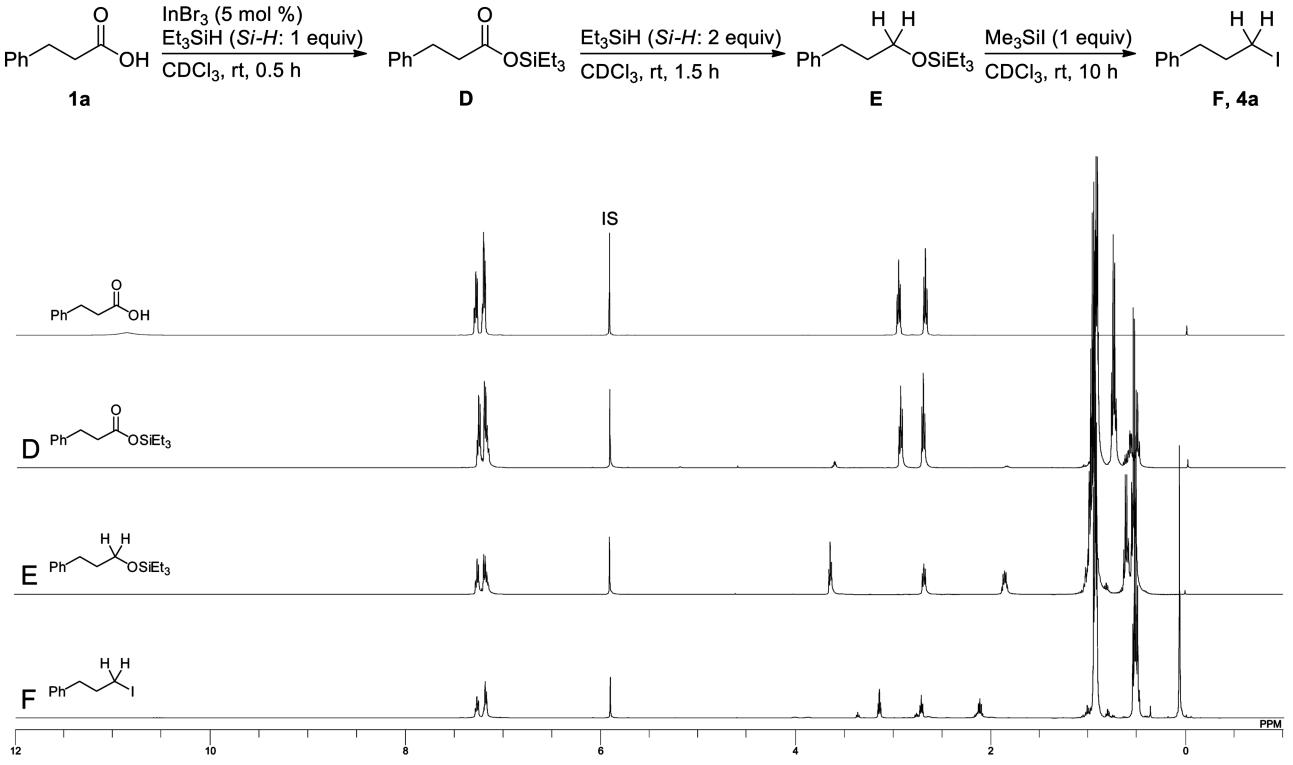

Figure 2. Monitoring of $InBr_3$-catalyzed reductive iodination of carboxylic acid **1a** by ^{1}H NMR.

corresponding 1-(3-phenylpropyl)-4-piperidinone (**13**) was obtained in 83% yield. In this context, Elpern et al.[19] reported a synthetic route for the compound **13**, as a strong analgesics precursor. However, their synthetic method for compound **13** required multistep operations, and the total yield of the desired compound was rather low. Our method, via the reductive iodination of a carboxylic acid, required only a one-pot, two-step synthesis, which amounted to a more convenient and practical synthetic process.

Control Experiments for Mechanistic Studies. The mechanism of the bromination of a carboxylic acid was investigated in our previous work.[14] Thus, to further clarify the reaction mechanism of the $InBr_3$-catalyzed reductive iodination of a carboxylic acid series, both ^{1}H NMR and ^{13}C NMR monitoring of the iodination of 3-phenylpropanoic acid (**1a**) were conducted with triethylsilane instead of TMDS. Each intermediate of the iodination series could be easily isolated, and the NMR results are presented in Figures 1 and 2. In addition, the results from the synthesis of 1-iodo-3-phenylpropane (**4a**) that was separately synthesized from **1a** by the stepwise reaction shown in Scheme 4 agreed with the results of NMR monitoring of the series of control experiments. First, in

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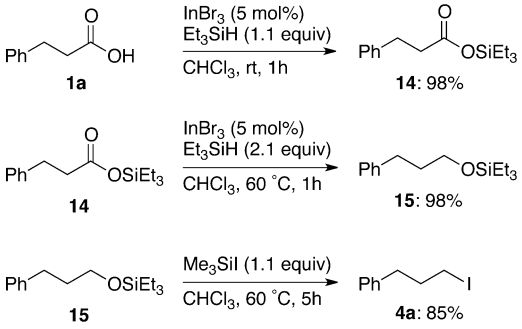
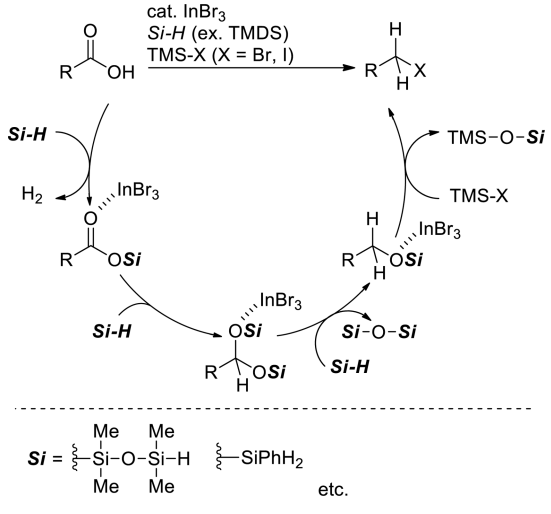
Scheme 4. Stepwise Conversion of Carboxylic Acid 1a to Alkyl Iodide 4a via $InBr_3$-Catalyzed Reductive Iodination



the ^{13}C NMR monitoring, when the reaction was carried out with **1a** and 1 equiv of Et_3SiH in the presence of $InBr_3$ (5 mol %), the carbonyl peak of **1a** (179.4 ppm) disappeared as the reaction proceeded, and a new peak appeared at 174.5 ppm, which was assigned to the corresponding silyl ester (**D** in Figure 1). In the ^1H NMR monitoring, the proton peak of the corresponding carboxylic acid (10.87 ppm) disappeared (**D** in Figure 2). The spectrum of the intermediate **D** agreed with that of the isolated 3-phenylpropanoic acid silyl ester **14** prepared from 3-phenylpropanoic acid (**1a**) with $InBr_3$ and Et_3SiH. Further addition of 2 equiv of Et_3SiH to the resultant NMR tube resulted in the disappearance of the peak of the silyl ester **D** and the formation of a new peak at 62.1 ppm, which was derived from the corresponding C−O bond of silyl ether **E** (**E** in Figure 1). The ^1H NMR spectrum of the silyl ether corresponded to that of silyl ether **15** (**E** in Figure 2). In the final step, the addition of 1 equiv of Me_3SiI to the resultant NMR tube showed a quantitative transformation to 1-iodo-3-phenylpropane (**4a**) (**F** in Figures 1 and 2).

On the basis of the NMR monitoring experiments and the several control experiments involving the corresponding intermediates, the plausible mechanistic aspects of the reductive halogenation series are shown in Scheme 5. Initially, the reaction of the carboxylic acid and the hydrosilane generates a silyl ester with the liberation of H_2 gas. Then, 2 equiv of the hydrosilane is added to form a silyl ether intermediate through the formation of a silyl acetal. In final step, the formed silyl ether is substituted with an appropriate halogen source (Me_3SiBr or Me_3SiI), leading to the preparation of the alkyl halide.

Scheme 5. Plausible Reaction Pathway for Reductive Halogenation of Carboxylic Acids



CONCLUSION

We have found that a combination of $InBr_3$, TMDS, and an appropriate halogen source, such as TMSBr, I_2, or TMSI, achieves direct bromination or iodination of a variety of carboxylic acids and their derivatives, such as an acyl chloride, an aldehyde, and an ester. This indium catalyst system is tolerant of a variety of reducible substrates involving common electron-withdrawing groups, such as halogens, a hydroxy group, a thioether, and an olefin. Furthermore, we have demonstrated the one-pot synthesis of alkyl halide and amine derivatives via the addition of nucleophiles into this reaction system. Insight into the reaction mechanism was gained via the time course of NMR monitoring experiments and the corresponding stepwise reactions.

EXPERIMENTAL SECTION

CAUTION: During examinations of the reaction conditions for bromination, when we added bromine (Br_2) to a chloroform solution containing $InBr_3$, $PhSiH_3$, and a reducible substrate under atmosphere, we encountered a small explosion with combustion.[14,20]

General. ^1H NMR spectra were measured at 500 or 300 MHz using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were measured at 125 or 75 MHz using the respective residual solvent resonances. High-resolution mass spectra (FAB or ESI) were measured using *p*-nitrobenzyl alcohol (FAB) as a matrix. Infrared (IR) spectra were recorded under neat conditions. Thin-layer chromatography (TLC) was undertaken using silica gel 60 F_{254}. Column chromatography was performed using silica gel 60 F_{254}. Manipulations were carried out under a nitrogen atmosphere unless otherwise noted. Chloroform was distilled from P_2O_5, and the distillate was redistilled from K_2CO_3 and then finally kept dry on molecular sieves (4 Å). Indium tribromide, bromine sources, hydrosilanes, carboxylic acids **1a**−**q**, aldehyde **5**, acyl chloride **6**, and esters **7** and **8** were commercially available and were used without further purification. With the exception of the compounds **4g**, **4s**, **11**, **12**, **12′**, **13**, **14**, and **15**, the compounds prepared with this method were identified in comparison with spectroscopic data reported in the corresponding literature.

Typical Procedure for the Reductive Bromination of a Carboxylic Acid. In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**) (0.600 mmol, 90.1 mg), 1,1,3,3-tetramethyldisiloxane (1.80 mmol, 318 μL), and trimethylbromosilane (0.600 mmol, 78.0 μL) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at room temperature for 5 min. The resultant solution was further stirred under the conditions shown in Table 1. After the reaction, the mixture was cooled to room temperature and quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 99:1) to afford the corresponding alkyl bromide **3a** in 96% yield (114.7 mg).

Typical Procedure for the Reductive Iodination of a Carboxylic Acid. In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**) (0.600 mmol, 90.1 mg), 1,1,3,3-tetramethyldisiloxane (1.80 mmol, 318 μL), and iodine (0.600 mmol, 152 mg) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at room temperature for 5 min. The resultant solution was further stirred

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under the conditions shown in Tables 2 and 3. After the reaction, the mixture was cooled to room temperature and quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 99:1) to afford the corresponding alkyl iodide **4a** in 91% yield (134.4 mg).

One-Pot Synthesis of Alkyl Halides via Reductive Iodination of Carboxylic Acid. In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**) (0.600 mmol, 90.1 mg), 1,1,3,3-tetramethyldisiloxane (1.80 mmol, 318 μL), and iodine (0.600 mmol, 152 mg) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at room temperature for 5 min. The resultant solution was further stirred at 60 °C for 2 h. The reaction mixture was cooled to room temperature, and then either tetrabutylammonium chloride or tetrabutylammonium fluoride (1.200 mmol) was added. The resultant solution was stirred at 60 °C for 5 h. After the reaction, the mixture was cooled to room temperature and quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 80:20) to afford the corresponding alkyl halide.

One-Pot Synthesis of Amine Derivatives via Reductive Iodination of a Carboxylic Acid. In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**) (0.600 mmol, 90.1 mg), 1,1,3,3-tetramethyldisiloxane (1.80 mmol, 318 μL), and iodine (0.600 mmol, 152 mg) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at room temperature for 5 min. The resultant solution was further stirred at 60 °C for 2 h. The reaction mixture was cooled to room temperature, and then an amine (0.720 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.600 mmol, 91.3 mg) were added. The resultant solution was stirred at 60 °C. After the reaction, the mixture was cooled to room temperature and quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 80:20) to afford the corresponding amine.

^{1}H and ^{13}C NMR Monitoring of the Reductive Iodination of 3-Phenylpropanoic Acid. In a glovebox, $InBr_3$ (0.010 mmol, 3.5 mg) was placed in a screw-capped NMR tube. The tube was sealed with a septum cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**, 0.200 mmol, 29.4 mg), 1,1,2,2-tetrachloroethane (0.130 mmol, 21.3 mg) as an internal standard, and dried $CDCl_3$ (400 μL) were successively added. The NMR spectra were measured at room temperature using the following procedure: (1) addition of 1 equiv (*Si*–*H* for **1a**) of triethylsilane (0.200 mmol, 31.9 μL) (the second-row spectra **D** shown in Figures 1 and 2); (2) addition of 2 equiv (*Si*–*H* for **1a**) of triethylsilane (0.400 mmol, 63.7 μL) (the third row spectra **E** shown in Figures 1 and 2); and (3) addition of trimethyliodosilane (0.200 mmol, 28.0 μL) (the bottom spectra **F** shown in Figures 1 and 2).

Stepwise Reductive Iodination Reaction. In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid (**1a**) (0.600 mmol, 90.1 mg) and triethylsilane (0.660 mmol, 105 μL) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at room temperature for 1 h. After the reaction, the mixture was quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 97:3) to afford 3-phenylpropanoic acid triethylsilyl ester (**14**) (155.5 mg, 98% yield). In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under a N_2 atmosphere and removed from the glovebox. Then 3-phenylpropanoic acid triethylsilyl ester (**14**) (0.600 mmol, 159 mg) and triethylsilane (1.26 mmol, 201 μL) were added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at 60 °C for 1 h. After the reaction, the mixture was quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 99:1) to afford 3-phenylpropyl triethylsilyl ether (**15**) (147.3 mg, 98% yield). In a glovebox, $InBr_3$ (0.0300 mmol, 10.6 mg) was placed in a screw vial. The vial was sealed with a PTFE-sealed screw cap under N_2 atmosphere and removed from the glovebox. Then 3-phenylpropyl triethylsilyl ether (**15**) (0.600 mmol, 150 mg) and trimethyliodosilane (0.660 mmol, 91.1 μL) were successively added to a distilled chloroform (600 μL) solution containing $InBr_3$. The solution was stirred at 60 °C for 5 h. After the reaction, the mixture was quenched with H_2O (2 mL). The organic layer was washed with dichloromethane, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 99:1) to afford 1-iodo-3-phenylpropane (**4a**) (125.5 mg, 85% yield)

*3-Phenylpropyl Bromide (**3a**).*[21] 96% yield (114.7 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (quint, 2H, *J* = 7.5 Hz), 2.76 (t, 2H, *J* = 7.5 Hz), 3.38 (t, 2H, *J* = 7.5 Hz), 7.18–7.21 (m, 3H), 7.27–7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.0, 33.9, 34.1, 126.1, 128.4, 128.5, 140.5; MS (EI-Quadrupole) *m*/*z* 199 (M^+, 2%), 201 (M^+ + 2, 2%), 91 (M^+ − 108, 100%).

*3-Phenylpropyl Iodide (**4a**).*[22] 91% yield (134.4 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (quint, 2H, *J* = 7.0 Hz), 2.73 (t, 2H, *J* = 7.0 Hz), 3.17 (t, 2H, *J* = 7.0 Hz), 7.19–7.23 (m, 3H), 7.27–7.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.3, 34.9, 36.2, 126.2, 128.4, 128.5, 140.4; MS (EI-Quadrupole) *m*/*z* 246 (M^+, 42%), 91 (M^+ − 155, 100%).

*1,2,3,4-Tetrahydronaphthalene (**4b′**).*[23] 90% yield (71.4 mg); a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48–1.81 (m, 4H), 2.74–2.76 (m, 4H), 7.03–7.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2, 29.4, 125.4, 129.1, 137.1; MS (EI-Quadrupole) *m*/*z* 132 (M^+, 75%), 104 (M^+ − 18, 100%).

*1-(2-Iodoethyl)naphthalene (**4c**).*[24] 88% yield (149.0 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46 (t, 2H, *J* = 8.0 Hz), 3.65 (t, 2H, *J* = 8.0 Hz), 7.36 (d, 1H, *J* = 8.0 Hz), 7.40–7.44 (m, 1H), 7.48–7.51 (m, 1H), 7.52–7.56 (m, 1H), 7.79 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 8.0 Hz), 7.97 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.4, 37.9, 123.1, 125.5, 125.8, 126.3, 126.6, 127.7, 128.9, 131.3, 134.0, 136.8; MS (EI-Quadrupole) *m*/*z* 282 (M^+, 55%), 57 (M^+ − 225, 100%).

*9-(Iodomethyl)fluorene (**4d**).*[25] 81% yield (148.8 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (d, 2H, *J* = 5.0 Hz), 4.18 (t, 2H, *J* = 5.0 Hz), 7.33–7.37 (m, 2H), 7.41–7.45 (m, 2H), 7.64 (d, 2H, *J* = 7.5 Hz), 7.76 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.5, 48.1, 120.0, 124.2, 127.2, 128.0, 141.0, 145.5; MS (EI-Quadrupole) *m*/*z* 178 (M^+ − 127, 100%).

*o-Methylphenethyl Iodide (**4e**).*[26] 91% yield (134.4 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.20 (t, 2H, *J* = 8.0 Hz), 3.30 (t, 2H, *J* = 8.0 Hz), 7.14–7.17 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.9, 19.2, 38.0, 126.2, 127.0, 128.9, 130.5, 135.7, 139.0; MS (EI-Quadrupole) *m*/*z* 246 (M^+, 10%), 119 (M^+ − 127, 100%).

*p-Chlorophenethyl Iodide (**4f**).*[27] 94% yield (150.3 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.15 (t, 2H, *J* = 7.5 Hz), 3.32 (t, 2H, *J* = 7.5 Hz), 7.13 (d, 2H, *J* = 8.5 Hz), 7.29 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.2, 39.4, 128.8, 129.7, 132.7, 138.9; MS (EI-Quadrupole) *m*/*z* 266 (M^+, 13%), 268 (M^+ + 2, 4%), 139 (M^+ − 127, 100%).

*p-Bromophenethyl Iodide (**4g**).* 95% yield (177.2 mg); a colorless oil; IR (neat) ν/cm^{-1} 2959, 1067, 800; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (t, 2H, *J* = 7.5 Hz), 3.31 (t, 2H, *J* = 7.5 Hz), 7.06 (d, 2H, *J* = 8.0 Hz), 7.43 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.9,

39.5, 120.7, 130.0, 131.7, 139.4; HRMS (FAB-Magnetic Sector) calcd for C_8H_8BrI 309.8854, found 309.8845.

*o-Iodophenethyl Iodide (**4h**).*[28] 91% yield (195.4 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.26−3.30 (m, 2H), 3.31−3.35 (m, 2H), 6.94−6.98 (m, 1H), 7.23−7.26 (m, 1H), 7.29−7.33 (m, 1H), 7.81−7.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.3, 45.0, 99.9, 128.5, 128.7, 129.8, 139.8, 143.3; MS (EI-Quadrupole) m/z 358 (M^+, 18%), 221 (M^+ − 137, 100%).

*o-Hydroxyphenethyl Iodide (**4i**).*[29] 89% yield (132.5 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (t, 2H, J = 8.0 Hz), 3.31 (t, 2H, J = 8.0 Hz), 4.93 (s, 1H), 6.76−6.80 (m, 2H), 7.04−7.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.4, 39.5, 115.4, 129.5, 133.0, 154.4; MS (EI-Quadrupole) m/z 248 (M^+, 36%), 121 (M^+ − 127, 100%).

*p-Nitrophenethyl Iodide (**4j**).*[30] 50% yield (83.1 mg); a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (t, 2H, J = 7.0 Hz), 3.39 (t, 2H, J = 7.0 Hz), 7.37 (d, 2H, J = 8.5 Hz), 8.20 (d, 2H, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.6, 39.4, 123.9, 129.3, 147.0, 147.6; MS (EI-Quadrupole) m/z 277 (M^+, 100%).

*p-Chlorobenzyl Iodide (**4l**).*[31] 93% yield (140.9 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (s, 2H), 7.24−7.27 (m, 2H), 7.29−7.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.2, 129.0, 130.0, 133.6, 137.8; MS (EI-Quadrupole) m/z 252 (M^+, 25%), 254 (M^+ + 2, 5%). 121 (M^+ − 127, 100%).

*p-(Trifluoromethyl)benzyl Iodide (**4m**).*[32] 87% yield (149.3 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (s, 2H), 7.48 (d, 2H, J = 8.0 Hz), 7.55 (d, 2H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.15, 123.9 (q, J_{C-F} = 272.5 Hz), 125.8 (q, J_{C-F} = 3.9 Hz), 129.0, 130.0 (q, J_{C-F} = 32.7 Hz), 143.3 (d, J_{C-F} = 1.0 Hz); MS (EI-Quadrupole) m/z 286 (M^+, 10%), 159 (M^+ − 127, 100%).

*1,2-Bis(2-iodoethyl)benzene (**4p**).*[33] 88% yield (203.8 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.20 (t, 4H, J = 8.0 Hz), 3.31 (t, 4H, J = 8.0 Hz), 7.17−7.19 (dd, 2H, J = 3.0 Hz, 3.0 Hz), 7.23−7.26 (dd, 2H, J = 3.0 Hz, 3.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.2, 37.0, 127.4, 129.5, 138.5; MS (EI-Quadrupole) m/z 386 (M^+, 10%), 259 (M^+ − 127, 100%).

*Phenylthioethyl Iodide (**4q**).*[34] 92% yield (145.8 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24−3.29 (m, 2H), 3.30−3.35 (m, 2H), 7.23−7.27 (m, 1H), 7.30−7.34 (m, 2H), 7.36−7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 2.5, 37.0, 127.1, 129.2, 130.6, 134.0; MS (EI-Quadrupole) m/z 264 (M^+, 25%), 137 (M^+ − 127, 100%).

*2-Phenylethyl Iodide (**4r**).*[35] 92% yield (128.1 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (t, 2H, J = 8.0 Hz), 3.35 (t, 2H, J = 8.0 Hz), 7.19 (d, 2H, J = 7.5 Hz), 7.25−7.28 (m, 1H), 7.30−7.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.6, 40.3, 126.8, 128.3, 128.6, 140.6; MS (EI-Quadrupole) m/z 232 (M^+, 10%), 105 (M^+ − 127, 100%).

*o-Hydroxyphenylpropyl Iodide (**4s**).* 70% yield (110.1 mg); a colorless oil; IR (neat) ν/cm^{-1} 3518, 2930, 1452, 1212, 753; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (quint, 2H, J = 7.0 Hz), 2.74 (t, 2H, J = 7.0 Hz), 3.21 (t, 2H, J = 7.0 Hz), 4.76 (brs, 1H), 6.74 (d, 1H, J = 7.5 Hz), 6.88 (t, 1H, J = 7.5 Hz), 7.10 (t, 1H, J = 7.5 Hz), 7.14 (d, 1H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.8, 30.7, 33.3, 115.3, 120.9, 127.5, 130.6, 153.5; HRMS (FAB-Magnetic Sector) calcd for $C_9H_{11}IO$ 385.9028, found 385.9028.

*3-Phenylpropyl Chloride (**9**).*[36] 91% yield (84.4 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (quint, 2H, J = 7.0 Hz), 2.78 (t, 2H, J = 7.0 Hz), 3.52 (t, 2H, J = 7.0 Hz), 7.18−7.22 (m, 3H), 7.29−7.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.7, 34.0, 44.2, 126.1, 128.4, 128.5, 140.7; MS (EI-Quadrupole) m/z 154 (M^+, 100%), 156 (M^+ + 2, 75%).

*3-Phenylpropyl Fluoride (**10**).*[37] 62% yield (51.4 mg); a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93−2.04 (m, 2H), 2.73 (t, 2H, J = 7.5 Hz), 4.43 (dt, 2H, J = 47.0, 6.0 Hz), 7.17−7.20 (m, 3H), 7.26−7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.3 (d, J_{C-F} = 5.3 Hz), 32.0 (d, J_{C-F} = 19.6 Hz), 83.0 (d, J_{C-F} = 165.0 Hz), 126.0, 128.4, 128.5, 141.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −220.5 (m, 1F); MS (EI-Quadrupole) m/z 138 (M^+, 70%), 91 (M^+ − 47, 100%).

*N-Methyl-N-phenyl-3-phenylpropylamine (**11**).* 95% yield (128.4 mg); a colorless oil; IR (neat) ν/cm^{-1} 2941, 1363; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90 (quint, 2H, J = 7.5 Hz), 2.64 (t, 2H, J = 7.5 Hz), 2.90 (s, 3H), 3.33 (t, 2H, J = 7.5 Hz), 6.64−6.69 (m, 3H), 7.16−7.22 (m, 5H), 7.25−7.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 33.3, 38.2, 52.2, 112.2, 116.0, 125.8, 128.3, 128.4, 129.1, 141.8, 149.3; HRMS (FAB-Magnetic Sector) calcd for $C_{16}H_{19}N$ 225.1517, found 225.1543.

*N-(4-Methoxyphenyl)-3-phenylpropylamine (**12**).* 75% yield (108.6 mg); an orange oil; IR (neat) ν/cm^{-1} 3412, 2964, 2892, 2840, 1268; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (quint, 2H, J = 7.5 Hz), 2.72 (t, 2H, J = 7.5 Hz), 3.10 (t, 2H, J = 7.5 Hz), 3.73 (s, 3H), 6.54 (d, 2H, J = 9.0 Hz), 6.76 (d, 2H, J = 9.0 Hz), 7.18−7.24 (m, 3H), 7.28 (t, 2H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 33.4, 44.4, 55.8, 114.1, 114.9, 125.9, 128.3, 128.4, 141.7, 142.6, 152.0; HRMS (FAB-Magnetic Sector) calcd for $C_{16}H_{19}NO$ 241.1467, found 241.1460.

*N-(4-Methoxyphenyl)bis(3-phenylpropyl)amine (**12′**).* 21% yield (45.3 mg); a yellow oil; IR (neat) ν/cm^{-1} 3412, 2964, 2892, 2840, 1268; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.84 (quint, 4H, J = 7.5 Hz), 2.61 (t, 4H, J = 7.5 Hz), 3.19 (t, 4H, J = 7.5 Hz), 3.74 (s, 3H), 6.60 (d, 2H, J = 8.5 Hz), 6.78 (d, 2H, J = 8.5 Hz), 7.14−7.19 (m, 6H), 7.23−7.28 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 33.4, 51.6, 55.8, 114.8, 115.4, 125.8, 128.3, 128.4, 141.9, 143.2, 151.6; HRMS (FAB-Magnetic Sector) calcd for $C_{25}H_{29}NO$ 359.2249, found 359.2239.

*N-(3-Phenylpropyl)-4-piperidone (**13**).* 83% yield (108.2 mg); a yellow oil; IR (neat) ν/cm^{-1} 2948, 1715, 1352; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (quint, 2H, J = 7.5 Hz), 2.43−2.49 (m, 6H), 2.68 (t, 2H, J = 7.5 Hz), 2.73 (t, 4H, J = 6.5 Hz), 7.19 (t, 3H, J = 7.5 Hz), 7.28 (t, 2H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 33.5, 41.2, 53.0, 56.6, 125.8, 128.2, 128.3, 141.9, 209.2; HRMS (FAB-Magnetic Sector) calcd for $C_{14}H_{20}NO$ 218.1545, found 218.1559.

*3-Phenylpropyl Triethylsilyl Ester (**14**).* 98% yield (155.5 mg); a colorless oil; IR (neat) ν/cm^{-1} 1239, 1100; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.59 (q, 6H, J = 8.0 Hz), 0.96 (t, 9H, J = 8.0 Hz), 2.66 (t, 2H, J = 7.5 Hz), 2.94 (t, 2H, J = 7.5 Hz), 7.18−7.21 (m, 3H), 7.26−7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.6, 6.5, 30.6, 35.6, 126.3, 128.2, 128.5, 140.2, 178.4; HRMS (ESI-TOF) calcd for $C_{15}H_{24}O_2Si$ (M^+ + Na) 287.1443, found 287.1421.

*3-Phenylpropyl Triethylsilyl Ether (**15**).* 98% yield (147.3 mg); a colorless oil; IR (neat) ν/cm^{-1} 1710, 1252, 1076; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60 (q, 6H, J = 8.0 Hz), 0.97 (t, 9H, J = 8.0 Hz), 1.85 (quint, 2H, J = 7.5 Hz), 2.68 (t, 2H, J = 7.5 Hz), 3.64 (t, 2H, J = 7.5 Hz), 7.15−7.20 (m, 3H), 7.22−7.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.5, 6.8, 32.1, 34.5, 62.1, 125.6, 128.3, 128.4, 142.2; HRMS (ESI-TOF) calcd for $C_{15}H_{26}OSi$ (M^+ + Na) 273.1651, found 273.1651.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for the compounds prepared with this method. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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