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Gallium-Catalyzed Reductive Chlorination of Carboxylic Acids with Copper(II) Chloride

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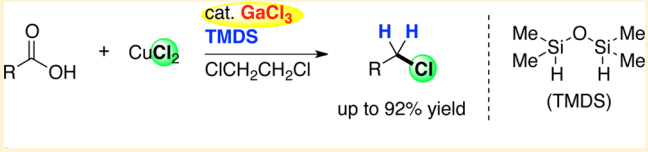
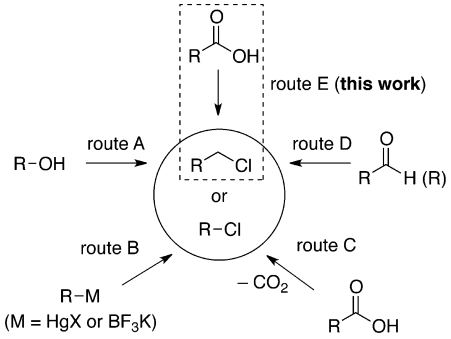
Supporting Information

ABSTRACT: Described herein is the direct chlorination of carboxylic acids using copper(II) chloride via a gallium(III)-catalyzed reduction in the presence of a hydrosiloxane. During this reductive chlorination, the counteranions of $CuCl_2$ functioned as a chloride source.



Alkyl chlorides constitute useful and versatile intermediates that can be readily transformed into other valuable compounds, such as amines, ethers, and nitriles.[1] A number of approaches toward a practical synthesis of alkyl chlorides have been attempted (Scheme 1).[1] As a representative example, the

Scheme 1. Divergent Approaches to Alkyl Chlorides



chlorination of alcohols has been reported (route A) using a number of chlorination agents: HCl,[1] $Ph_3P-CCl_4(CBrCl_3)$,[2a,b] PCl_3–DMF,[2c] $POCl_3$–DMF,[2d] $SOCl_2$,[1] HCl–$ZnCl_2$,[2e] $BiCl_3$–TMSCl,[2f] $InCl_3-Ph_2MeSiCl$,[2g] and others.[3] As unique examples using organometallic compounds, a reaction of alkylmercuric halides with sulfuryl chloride through a radical coupling that produced alkyl chlorides has been reported,[4a] and Molander et al. have reported under metal catalyst-free conditions the coupling of alkyltrifluoroborates with trichloroisocyanuric acid (route B).[4b] A Hunsdiecker-type reaction from carboxylic acids and chlorination sources along with decarboxylation has also been developed in which lead(IV) acetate and a silver(I) compound promoted a radical decarboxylative chlorination.[5,6] The reaction of a carboxylic acid ester derived from *N*-hydroxypyridine-2-thione with CCl_4 also afforded alkyl chlorides after decarboxylation (route C).[7] Thus far, a direct conversion using reducible reagents from carbonyl compounds to alkyl chlorides has not been studied extensively. Baba and co-workers, however, have developed a reductive chlorination of aldehydes and ketones using a combination of $In(OH)_3$ and Me_2SiHCl (route D).[8,9] However, as far as we could ascertain, the direct reductive conversion of carboxylic acids to alkyl chlorides without decarboxylation has not been achieved (route E). This is probably because of the lower nucleophilicity of a chloride ion, compared with that of a bromide or an iodide ion, and also because of the tolerance of a carboxylic acid for typical reducing conditions.

During research on the transformation of carboxylic acids by indium(III)-catalyzed reduction,[10] we succeeded in the one-pot chlorination of a carboxylic acid via a substitution of the alkyl iodide intermediate.[10a] However, we encountered a serious problem where the indium(III) compound, which showed a relatively mild Lewis acidity, would not undergo direct chlorination of carboxylic acids when typical chloride sources were used. After a number of examinations for a solution to this problem, we found that gallium(III) chloride exhibited the best catalytic activity for the reductive chlorination of carboxylic acids using copper(II) chloride and a hydrosiloxane.[11,12] Herein we describe a new synthetic approach to an alkyl chloride (route E).

Initially, we sought an optimal chlorine source for the chlorination of *o*-tolylacetic acid (**1a**) with $InBr_3$ and 1,1,3,3-tetramethyldisiloxane (TMDS) in chloroform at 60 °C (Table 1). The use of chlorotrimethylsilane (Me_3SiCl) and hydrogen chloride gave reduced alcohol **1b** as a major product along with the undesired bromination product **1c** as a minor product, instead of the expected alkyl chloride **1a** (entries 1 and 2). These results showed that the nucleophilicity of the chloride ion was rather low, which meant that the bromide ion of $InBr_3$ functioned as a halogen source. Therefore, we attempted to use a counterion of a metal chloride. After several examinations using $AlCl_3$, $ZnCl_2$, $FeCl_3$, and CuCl (entries 3–6), we found that $CuCl_2$ was the most effective chlorine source, although solubility of the chloride compound was rather low (entry 7). Unfortunately, the reaction system shown in entry 7 produced a mixture of alkyl chloride and bromide, the formation of which made the isolation

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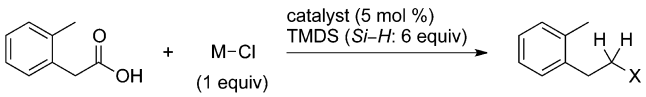
Table 1. Examination of Reaction Conditions for Chlorination[a]

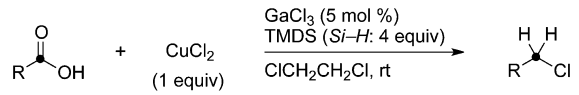


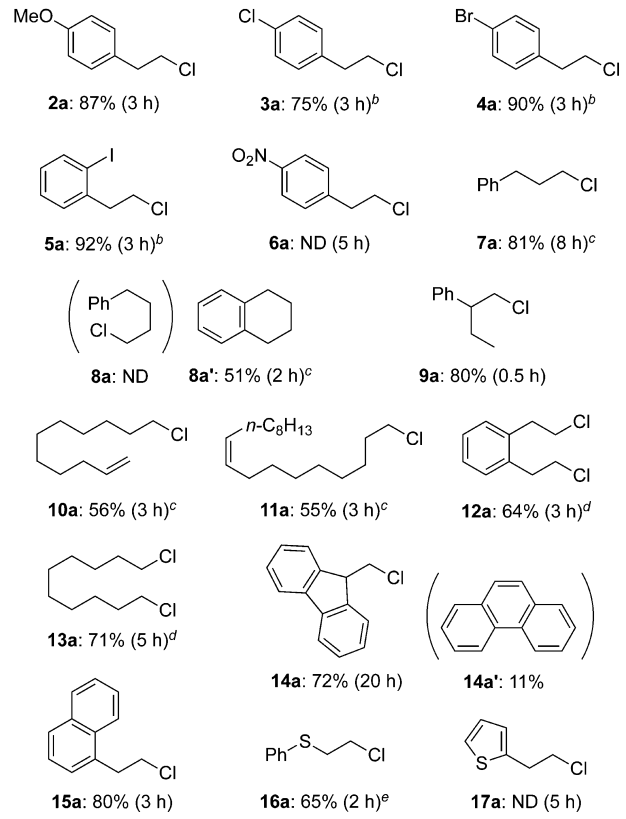
1a: X = Cl
1b: X = OH
1c: X = Br

entry	catalyst	chloride source	solvent	temp (°C)	yield[b] (%) 1a	1b	1c
1	$InBr_3$	TMSCl	$CHCl_3$	60	ND	67	8
2	$InBr_3$	HCl[c]	$CHCl_3$	60	ND	80	10
3	$InBr_3$	$AlCl_3$	$CHCl_3$	60		CM	
4	$InBr_3$	$ZnCl_2$	$CHCl_3$	60	ND	65	13
5	$InBr_3$	$FeCl_3$	$CHCl_3$	60	17	20	8
6	$InBr_3$	CuCl	$CHCl_3$	60	18	51	10
7	$InBr_3$	$CuCl_2$	$CHCl_3$	60	85	ND	9
8	$InCl_3$	$CuCl_2$	$CHCl_3$	60	ND	42	
9	$GaCl_3$	$CuCl_2$	$CHCl_3$	60	54	19	
10	$GaCl_3$	$CuCl_2$	DCE	60	76	ND	
11	$GaCl_3$	$CuCl_2$	DCE	80	ND	ND	
12	$GaCl_3$	$CuCl_2$	DCE	rt	91	ND	
13[d]	$GaCl_3$	$CuCl_2$	DCE	rt	(87)	ND	
14[d,e]	$GaCl_3$	$CuCl_2$	DCE	rt	80	ND	
15[d,f]	$GaCl_3$/AgOTf	$CuCl_2$	DCE	rt	72	ND	
16[d]		$CuCl_2$	DCE	rt		NR	
17[d,g]	$GaCl_3$	$CuCl_2$	DCE	rt		NR	

[a]Reaction conditions: *o*-tolylacetic acid (0.6 mmol), catalyst (0.03 mmol), TMDS (1.8 mmol), chloride source (0.6 mmol), solvent (0.6 mL), 3 h. [b]GC (isolated) yield. [c]4 mol/L in dioxane. [d]TMDS (*Si*−*H*: 4 equiv). [e]$CuCl_2$ (0.5 equiv). [f]$GaCl_3$ (0.03 mmol) and AgOTf (0.09 mmol) were used. [g]Without TMDS.

Scheme 2. One-Pot Synthesis of Alkyl Chlorides from Aliphatic Carboxylic Acids[a]





[a]Carboxylic acid (0.6 mmol), $GaCl_3$ (0.03 mmol), TMDS (1.2 mmol), $CuCl_2$ (0.6 mmol), $ClCH_2CH_2Cl$ (0.6 mL), rt. [b]TMDS (*Si*−*H*: 5 equiv), 40 °C. [c]TMDS (*Si*−*H*: 6 equiv), 80 °C. [d]$GaCl_3$ (10 mol %), TMDS (*Si*−*H*: 12 equiv), $CuCl_2$ (2 equiv), 60 °C. [e]TMDS (6 equiv), 60 °C.

of alkyl chloride **1a** quite troublesome. Thus, to restrain the formation of the byproduct **1c**, a counteranion of the indium catalyst was then changed. However, $InCl_3$ was ineffective for this chlorination (entry 8). We were pleased to find that $GaCl_3$ promoted the chlorination series to produce the expected alkyl chloride **1a** (entry 9) in a satisfactory yield. When the reaction was carried out in 1,2-dichloroethane (DCE), the product yield was slightly increased (entry 10). Contrary to our expectations, further increase of the reaction temperature led to the formation of a complex mixture (entry 11). In contrast, the chlorination successfully proceeded at room temperature to give the corresponding alkyl chloride **1a** in a good yield (entry 12). Also, the conditions with 2 equiv of TMDS (*Si*−*H*: 4 equiv) were determined to be the best conditions in the present chlorination (entry13). Interestingly, the use of 0.5 equiv of $CuCl_2$ gave 80% of the corresponding alkyl chloride **1a**, which showed that both counteranions of $CuCl_2$ functioned as a chloride source (entry 14). When a similar chlorination was carried out in the hope of in situ generation of the active cation species, such as $GaCl_2(OTf)$ and $GaCl(OTf)_2$, the yield was slightly decreased (entry 15).[13] Without either the gallium catalyst or the hydrosiloxane, no chlorination proceeded (entries 16 and 17).

With the optimal reaction conditions in hand, the scope and limitations for the chlorination of carboxylic acids were next investigated, and the results are shown in Scheme 2. With no reference to the type of substituent group on the benzene ring, a series of phenylacetic acids were converted to the corresponding phenethyl chloride derivatives **2a**−**5a** in good to excellent yields, but the substrate had a nitro group at the para position that led to a complex mixture. The functional groups, such as a methoxy and a halogen group, showed no reducing effect. Chlorination of 3-phenylpropanoic acid also gave a satisfactory yield of product **7a**. Unlike our previous results from the bromination of 4-phenylbutyric acid, chlorination resulted in the formation of tetralin **8a′** via intramolecular cyclization of the product **8a**. This may have been due to the fact that a stronger Lewis acid, $GaCl_3$, promoted the intramolecular Friedel−Crafts alkylation of **8a**. When 2-phenylisobutyric acid was used, which has a branched carbon adjacent to a carboxylic moiety, the desired alkyl chloride **9a** was obtained in a good yield. When 3 equiv of TMDS (*Si*−*H*: 6 equiv) was used at 80 °C, the linear fatty acids with either a terminal or an internal alkene were converted to the corresponding alkyl chlorides **10a** and **11a** in modest yields. During the chlorination series, both the alkene moiety and the *cis*-configuration of the double bond on oleic acid remained. Also, chlorination of the substrates with a dicarboxylic acid was achieved by excess amounts of TMDS and $CuCl_2$ to produce alkyl chlorides **12a** and **13a** in relatively good yields. When the reaction was conducted using the carboxylic acid with a fluorenyl moiety, alkyl chloride **14a** was obtained in a 72% yield with the

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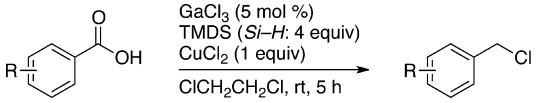
ring-expanding product, phenanthrene.[14] Chlorination of 1-naphthaleneacetic acid also yielded a good result. When a carboxylic acid containing a thioether moiety was treated under the optimal conditions, the corresponding alkyl chloride **16a** was obtained in a 65% yield. Unfortunately, the substrate with a thiophene ring did not undertake the desired chlorination. Moreover, unlike the use of **9a** and **14a**, relatively bulky carboxylic acids, such as cyclohexanecarboxylic acid and pivalic acid, produced the alcohol derivatives in 68 and 46% yields rather than the expected alkyl chlorides. We have no clear reasons for these results at this stage. To further expand the substrate scope, the chlorination was applied to several substrates, such as cinnamic acid, propiolic acid, and an aliphatic carboxylic acid having a ketone moiety. However, all examples did not include chlorination, which led to the formation of a complex mixture.

Chlorination using gallium chloride showed behavior similar to that of an aromatic carboxylic acid as well as examples of a reductive iodination/bromination of a carboxylic acid using an $InBr_3$–TMDS system.[10] In short, only benzoic acids bearing a strong electron-withdrawing group, such as a *p*-CF_3 and *p*-NO_2, managed to undertake the expected chlorination to produce alkyl chlorides **20a** and **21a** in low yields (Scheme 3). These results

Scheme 3. Chlorination of Aromatic Carboxylic Acids[a]



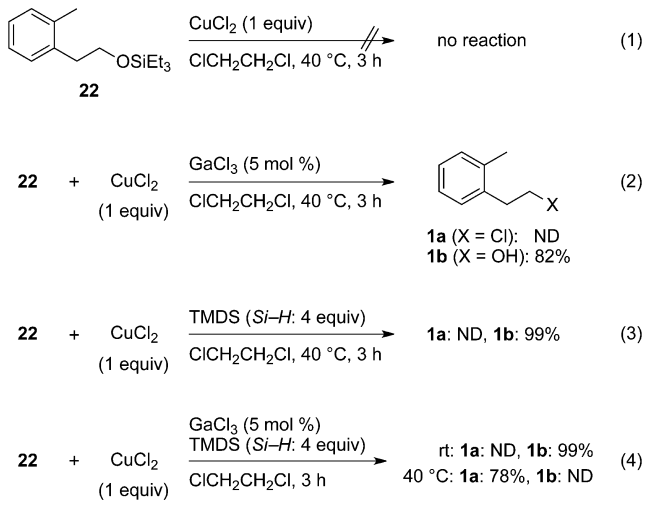
18a (R = *o*-MeO):NR **20a** (R = *p*-CF_3): 33%
19a (R = *p*-Cl): ND **21a** (R = *p*-NO_2): 23%

[a]Isolated yield.

indicated that the electronic effect of an electron-donating substituent decreased the electrophilicity of the carbonyl group on the aromatic carboxylic acid, which led to the deactivation of the initial hydrosilylation by the hydrosiloxane.

When a mixture of 3-phenylpropionic acid (δ = 179.3 ppm) and a stoichiometric amount of $GaCl_3$ in a $CDCl_3$ solution was measured with ^{13}C NMR, a remarkably lower magnetic field (δ = 187.1 ppm) was observed. This result shows that there was an interaction with $GaCl_3$ and the carboxylic moiety. We then examined several control experiments, and the results are listed in Scheme 4.[15] Based on the results obtained by an indium-catalyzed bromination/iodination of carboxylic acids, we anticipated that the reaction intermediate of the chlorination series would be a silyl ether. Initially, when the silyl ether **22**, which was prepared from *o*-tolylethanol and triethylsilane,[16] was treated either with $CuCl_2$ alone or with the $GaCl_3$–$CuCl_2$ system in the absence of the hydrosiloxane, both reactions would not undergo the desired chlorination (eqs 1 and 2). Also, without $GaCl_3$, silyl ether **22** was quantitatively converted to the desilylated alcohol **1b** (eq 3). These results indicated that a combination of $GaCl_3$ with TMDS was indispensable for the promotion of a substitution of the silyl ether with the chloride ion. Strangely, when the silyl ether was used under our optimal conditions at room temperature, the desired chlorination would not occur at all. Under slight heating conditions (40 °C), a smooth conversion to alkyl chloride **1a** was observed (eq 4). During the preparatory step, and after the final addition of TMDS, quite an exothermic phenomenon with an emission of hydrogen gas was observed, the heat of which led to the

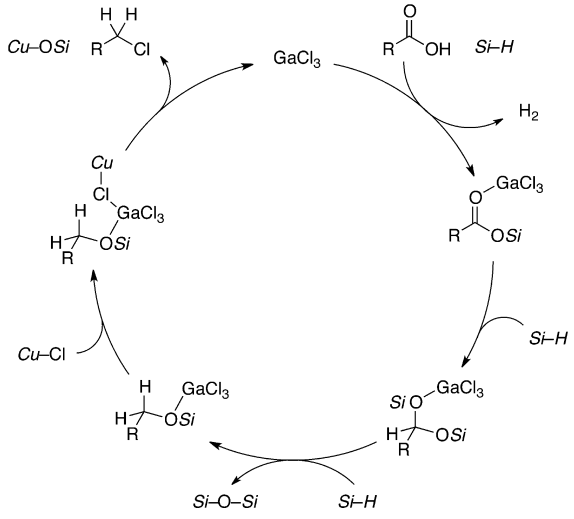
Scheme 4. Control Experiments for the Reductive Chlorination[a]



[a]NMR yield.

promotion of a substitution by the chloride ion. In this context, when the reaction with *o*-tolylacetic acid was conducted with our optimal conditions (rt, 3 h) in a large-scale reaction (3 mmol), the remarkable decrease of chlorinated product **1a** (56%) and the formation of reduced alcohol **1b** (12%) was observed. On the basis of these results, a plausible mechanism for this chlorination is shown in Scheme 5. We assumed that a route from a carboxylic

Scheme 5. Plausible Mechanism for $GaCl_3$-Catalyzed Chlorination of a Carboxylic Acid



acid to a silyl ether would pass through the same steps as that described in our reductive bromination or iodination of a carboxylic acid.[10] Although an explanation for the final step that involves transformation of the silyl ether to the alkyl chloride is unclear at this point, we supposed that a substitution via the intermediate of the chlorocopper species coordinated gallium complex occurred, finally producing the alkyl chloride.[17,18]

In conclusion, we have demonstrated the direct chlorination of aliphatic and aromatic carboxylic acids through a $GaCl_3$-catalyzed reduction using $CuCl_2$ as a chloride source. In addition, we found that the gallium compound positively activated the carbonyl moiety of a carboxylic acid and disclosed that both counteranions

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of $CuCl_2$ functioned as a chloride source. This reducing system showed a tolerance toward functional groups, such as an alkyl group, a methoxy group, a halogen substituent, an alkene moiety, and a nitro group. This procedure provided a novel example of the one-pot direct chlorination of carboxylic acids with the chloride ion of a metal compound.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a N_2 atmosphere, unless otherwise noted. 1,2-Dichloroethane (DCE) and chloroform were freshly distilled from K_2CO_3 after the removal of H_2O by P_2O_5 prior to use. All metal compounds, chloride sources, and carboxylic acids were commercially available and were used without further purification. Hydrosilanes were also used without further purification. Silyl ether **22** shown in Scheme 3 was prepared by a previously established method.[16] Reactions were monitored by TLC analysis of reaction aliquots. Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254}, and the components were located by observation under UV light. Column chromatography was also performed using silica gel. ^{1}H NMR spectra were measured at 500 or 300 MHz using tetramethylsilane as an internal standard (0.00 ppm). ^{13}C NMR spectra were measured at 125 or 75 MHz using the center peak of chloroform (77.0 ppm).

General Procedure for the Gallium-Catalyzed Reductive Chlorination of a Carboxylic Acid. To a freshly distilled DCE solution (0.6 mL) in a screw-capped vial under an N_2 atmosphere were successively added a magnetic stirrer bar, $GaCl_3$ (0.030 mmol, 5.3 mg), $CuCl_2$ (0.600 mmol, 80.9 mg), a carboxylic acid (0.60 mmol), and TMDS (1.2 mmol, 2.2 × 10^2 μL). The vial was sealed with a cap that contained a PTFE septum. After the final addition of TMDS, the color of the reaction mixture was changed from yellowish brown to black with an exothermic phenomenon and an emission of hydrogen gas. If necessary, an appropriate release of the gas is required. During the stirring of the reaction mixture under the conditions noted in the text, the reaction was monitored by TLC until consumption of the silyl ether intermediate that, in practice, was observed as the desilylated alcohol. The resultant mixture was filtered using a Celite pad to remove the black solid. H_2O (6 mL) was poured into the filtrate, and the aqueous layer was extracted three times with EtOAc (6 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 99/1 = hexane/EtOAc) to give the corresponding alkyl chloride. The spectral data of the produced chlorides were determined after further purification by gel permeation chromatography.

*o-Methylphenethyl chloride (**1a**):*[19] colorless oil (80.7 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.08 (t, *J* = 8.0 Hz, 2H), 3.67 (t, *J* = 8.0 Hz, 2H), 7.16 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 36.6, 43.8, 126.2, 127.0, 129.4, 130.5, 136.2; MS (EI) *m*/*z* 154 (M^+, 100), 156 (M^+ + 2, 31).

*p-Methoxyphenethyl chloride (**2a**):*[20] colorless oil (89.1 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.00 (t, *J* = 7.0 Hz, 2H), 3.66 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.3, 45.3, 55.2, 113.9, 129.8, 130.1, 158.5; MS (EI) *m*/*z* 170 (M^+, 100), 172 (M^+ + 2, 34).

*p-Chlorophenethyl chloride (**3a**):*[20] colorless oil (78.8 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01 (t, *J* = 7.5 Hz, 2H), 3.67 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.2, 44.7, 128.6, 130.1, 132.6, 136.4; MS (EI) *m*/*z* 174 (M^+, 100), 176 (M^+ + 2, 66).

*p-Bromophenethyl chloride (**4a**):*[21] colorless oil (118.5 mg, 90%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01 (t, *J* = 7.0 Hz, 2H), 3.69 (t, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.4, 44.6, 120.8, 130.5, 131.6, 137.0; MS (EI) *m*/*z* 220 (M^+ + 2, 100), 218 (M^+, 81), 222 (M^+ + 4, 28).

*o-Iodophenethyl chloride (**5a**):*[22] colorless oil (147.1 mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (t, *J* = 7.5 Hz, 2H), 3.71 (t, *J* = 7.5 Hz, 2H), 6.93−6.97 (m, 1H), 7.26−7.32 (m, 2H), 7.83−7.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.4, 43.7, 100.3, 128.4, 128.8, 130.5, 139.7, 140.6; MS (EI) *m*/*z* 266 (M^+, 100), 268 (M^+ + 2, 33).

*3-Phenylpropyl chloride (**7a**):*[23] colorless oil (75.2 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05−2.10 (m, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 7.18−7.21 (m, 3H), 7.27−7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.7, 34.0, 44.2, 126.1, 128.5, 128.5, 140.7; MS (EI) *m*/*z* 154 (M^+, 100), 156 (M^+ + 2, 33).

*1,2,3,4-Tetrahydronaphthalene (**8a′**):*[24] colorless oil (40.5 mg, 51%); ^{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) *m*/*z* 132 (M^+, 100).

*1-Chloro-2-phenylbutane (**9a**):*[25] colorless oil (81.0 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.5 Hz, 2H), 1.64−1.73 (m, 1H), 1.81−1.89 (m, 1H), 3.04 (d, *J* = 6.5 Hz, 2H), 4.02−4.08 (m, 1H), 7.21−7.22 (m, 2H), 7.25−7.26 (m, 1H), 7.30−7.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 30.6, 44.6, 65.6, 126.7, 128.4, 129.3, 138.1; MS (EI) *m*/*z* 168 (M^+, 100), 170 (M^+ + 2, 33).

*11-Chloro-1-undecene (**10a**):*[26] colorless oil (63.4 mg, 56%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29−1.43 (m, 13H), 1.76 (quint, *J* = 7.0 Hz, 2H), 2.02−2.06 (m, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 4.92−4.94 (m, 1H), 4.97−5.01 (m, 1H), 5.77−5.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.9, 28.9, 28.9, 29.1, 29.4, 29.4, 32.6, 33.8, 45.1, 114.1, 139.1; MS (EI) *m*/*z* 188 (M^+, 100), 190 (M^+ + 2, 34).

*1-Chlorooctadecane-9-ene (**11a**):*[27] colorless oil (94.7 mg, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.26−1.30 (m, 22H), 1.76 (quint, *J* = 7.0 Hz, 2H), 2.01−2.03 (m, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 5.33−5.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 26.9, 27.2, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 32.6, 45.1, 129.7, 130.0; MS (EI) *m*/*z* 286 (M^+, 100), 288 (M^+ + 2, 33).

*1,2-Bis(2-chloroethyl)benzene (**12a**):* colorless oil (78.0 mg, 64%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (t, *J* = 7.5 Hz, 4H), 3.68 (t, *J* = 7.5 Hz, 4H), 7.20−7.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 44.3, 127.3, 129.8, 136.2; HRMS (EI-Quadrupole) calcd for $C_{10}H_{12}Cl_2$ (M^+) 202.0316, found 202.0325.

*1,10-Dichlorodecane (**13a**):*[28] colorless oil (90.0 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (m, 8H), 1.41−1.44 (m, 4H), 1.77 (quint, *J* = 7.0 Hz, 4H), 3.53 (t, *J* = 7.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 28.8, 29.3, 32.6, 45.1; MS (EI) *m*/*z* 91 ($M^+ - C_6H_{12}Cl$, 100), 93 ($M^+ - C_6H_{12}Cl$ + 2, 33).

*9-(Chloromethyl)fluorene (**14a**):*[29] colorless oil (92.7 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (d, *J* = 6.5 Hz, 2H), 4.23 (t, *J* = 6.5 Hz, 1H), 7.31−7.34 (m, 2H), 7.39−7.42 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.9, 49.3, 120.0, 124.9, 127.2, 128.0, 141.1, 144.0; MS (EI) *m*/*z* 214 (M^+, 100), 216 (M^+ + 2, 37).

*Phenanthrene (**14a′**):*[30] colorless oil (11.8 mg, 11%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.59 (m, 2H), 7.61−7.65 (m, 2H), 7.72 (s, 2H), 7.85−7.88 (m, 2H), 8.66 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.6 (2C), 126.5 (4C), 126.9 (2C), 128.5 (2C), 130.3 (2C), 132.0 (2C); MS (EI) *m*/*z* 178 (M^+, 100).

*1-(2-Chloroethyl)naphthalene (**15a**):*[31] colorless oil (91.5 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (t, *J* = 7.5 Hz, 2H), 3.83 (t, *J* = 7.5 Hz, 2H), 7.37−7.57 (m, 4H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 36.5, 44.1, 123.1, 125.5, 125.7, 126.3, 127.2, 127.8, 129.0, 131.7, 133.9, 133.9; MS (EI) *m*/*z* 190 (M^+, 100), 192 (M^+ + 2, 38).

*Phenylthioethyl chloride (**16a**):*[32] colorless oil (67.3 mg, 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21−3.24 (m, 2H), 3.60−3.63 (m, 2H), 7.23−7.26 (m, 1H), 7.30−7.33 (m, 2H), 7.39−7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.1, 42.3, 127.1, 129.2, 130.5, 134.2; MS (EI) *m*/*z* 172 (M^+, 100), 174 (M^+ + 2, 38).

*p-(Trifluoromethyl)benzyl chloride (**20a**):*[33] colorless oil (38.5 mg, 33%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.0, 123.9 (q, J_{C-F} = 271.7 Hz), 125.7 (q, J_{C-F} = 3.8 Hz), 128.8, 130.5 (q, J_{C-F} = 32.7 Hz), 141.3; MS (EI) *m*/*z* 286 (M^+, 100), 288 (M^+ + 2, 32).

*p-Nitrobenzyl chloride (**21a**):*[34] yellow oil (23.7 mg, 23%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (s, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 8.23 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.5, 123.9, 129.3, 144.3, 147.7; MS (EI) *m*/*z* 171 (M^+, 100), 173 (M^+ + 2, 31).

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*o-Methylphenethyl triethylsilyl ether (**22**):* colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.58 (q, J = 8.0 Hz, 6H), 0.94 (t, J = 8.0 Hz, 9H), 2.33 (s, 3H), 2.87 (t, J = 7.5 Hz, 2H), 3.76 (t, J = 7.5 Hz, 2H), 7.09−7.15 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.3, 6.7, 19.4, 36.9, 63.2, 125.9, 126.3, 129.7, 130.1, 136.3, 136.9; HRMS (ESI-TOF) calcd for $C_{15}H_{26}OSi$ (M^+ + Na) 273.1651, found 273.1662.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of the ^{1}H and ^{13}C NMR spectra of the chlorinated products produced by 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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