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One-Pot in Situ Formation and Reaction of Trimethyl(trichloromethyl)silane: Application to the Synthesis of 2,2,2-Trichloromethylcarbinols

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Supporting Information

ABSTRACT: 2,2,2-Trichloromethylcarbinols are **1** are valuable synthetic intermediates with a multitude of uses. A scalable procedure for the synthesis of TMS-protected-2,2,2-trichloromethylcarbinols and 2,2,2-trichloromethylcarbinols **1** was developed that employs the in situ generation and reaction of trimethyl(trichloromethyl)silane (CCl_3-TMS). The procedure avoids the exposure of the carbonyl compounds to the strongly basic conditions typically used for this transformation and also avoids isolation of the difficult-to-handle CCl_3-TMS. This procedure was applied to diastereoselective trichloromethyl additions to 2-substituted 4-piperidinones and to reactions with a variety of structurally diverse aldehydes and ketones.

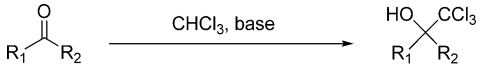
INTRODUCTION

2,2,2-Trichloromethylcarbinols **1** are useful synthetic intermediates with many applications and are most commonly prepared by the base-promoted addition of chloroform to aldehydes and ketones (Scheme 1). Bases which have been used for this reaction include amide bases,[1] amidines,[2] and hydroxide.[3] Reaction of CCl_3CO_2Na in CCl_3CO_2H-DMF also yields trichloromethyl carbinols from aldehydes.[4] 2,2,2-Trichloromethylcarbinols can also be prepared by the formation of trimethylsilyl protected 2,2,2-trichloromethylcarbinols using a variety of trichloromethyl-transferring reagents followed by deprotection. Among the reagents used for these additions are trimethyl(trichloromethyl)silane (CCl_3-TMS) with a variety of catalysts such as TASF,[5] sodium formate,[6] or thermally,[7] and trimethylsilyl trichloroacetate with catalysis by KF,[8] K_2CO_3,[9] or TBAF.[10] The combination of TMS-Cl/CCl_4/Mg/HMPT has also been employed.[11]

Of the many uses of 2,2,2-trichloromethylcarbinols, one of the most common and general reactions is the Jocic[12] and related reactions with nucleophiles to make α-substituted carboxylic acids **2** (Scheme 2). Many nucleophiles that have been used for these reactions; these include hydroxide,[12] alcohols and phenols,[3d,13] hydride,[13e] thiols and selenides,[13e,14] fluoride,[13f,15] cyanide,[13f] thiocyanate,[13f] azide,[16] amines,[16i,17] pyrroles,[18] and thiourea.[19] Trichloromethylcarbinols can also be converted to epoxides,[20] vinyl dichlorides,[21] alkynes,[22,23] vinyl dichlorides and chloroketones,[22] 2-haloalk-2(*Z*)-en-1-ols and 1-chloro-1(*Z*)-alkenes,[24] and ring-expanded ketones.[25]

As part of an ongoing project, we had a need for substantial amounts of the diastereomerically pure 2,2,2-trichloromethylcarbinol **4** (Scheme 3). This had previously been prepared in about 46% yield by adding LiHMDS to a mixture of (*S*)-2-methyl-CBZ-4-piperidinone **3** and $CHCl_3$ at less than −65 °C.[16i] The diastereomer ratio is about 2:1 at best under these conditions; $MgCl_2$ is added to this reaction to suppress competing ketone enolization, but its presence does not alter the diastereomer ratio. The addition of LiHMDS is very exothermic, and to minimize competing ketone enolization, the reaction temperature must be maintained at less than −65 °C, which is difficult on scale. In addition, gumming and balling of the poorly soluble $MgCl_2$ during the reaction and the formation of emulsions during product isolation create significant operational challenges to scale-up. It should also be noted

Scheme 1. Formation of Trichloromethylcarbinols



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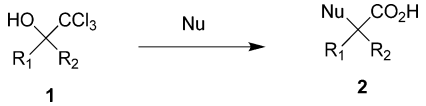
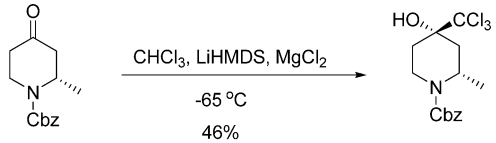
Scheme 2. Generalized Jocic Reaction



1 2

Scheme 3. Base-Promoted Reaction with (*S*)-2-Methyl-CBZ-4-piperidinone



3 4

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that little or no compound **4** is formed by reaction of **3** with $CHCl_3$ and either hydroxide or DBU.[2,3]

RESULTS AND DISCUSSION

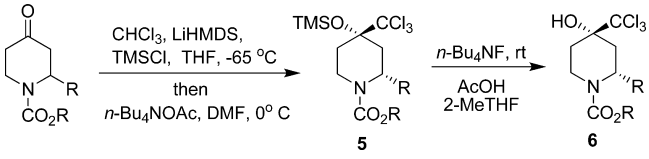
Use of a bulkier trichloromethyl-transferring reagent should provide better diastereoselectivity, and we found that trimethyl(trichloromethyl)silane (CCl_3-TMS) with catalysis by sodium formate using the procedure of Kister and Mioskowski[6] gives the desired diastereomer with about 9:1 selectivity. The primary limitation to scale-up of this procedure is the need for isolated CCl_3-TMS, which is not commercially available and is difficult to handle on scale due to its volatility and propensity for sublimation. A number of methods have been reported for the preparation of CCl_3-TMS. The simplest procedure is by amine-promoted decarboxylation of trimethylsilyl trichloroacetate,[26] but we found that scale-up of this procedure was complicated by erratic reaction rates and stalled reactions. Crude solutions containing CCl_3-TMS from this reaction work, but these have a low DSC thermal onset (87 °C, 399 J/g), which precludes scale-up. The other reported methods for the synthesis of CCl_3-TMS all have critical features that limit their practicality for large-scale synthesis: photochemical chlorination of trichloromethylsilane,[27] $CHCl_3$/TMS-Cl/*n*-BuLi/-110 °C,[28] TMS-Cl/CCl_4/Mg/HMPT,[29] and $CHCl_3$/TMS-Cl/P-$(NEt_2)_3$.[30]

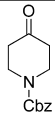
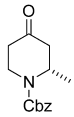
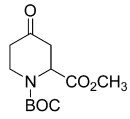
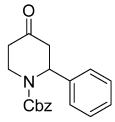
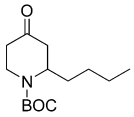
We found that CCl_3-TMS is rapidly and cleanly formed by the direct treatment of $CHCl_3$ and TMS-Cl with LiHMDS in THF at less than −60 °C. The characteristic ^{1}H NMR resonance of CCl_3-TMS at δ 0.37 is observable in these solutions. Formation of CCl_3-TMS is further demonstrated by its isolation as a crystalline solid. Temperature control is important, and the reagent does not form properly above about −60 °C. In contrast to the reaction of ketone **3** with $CHCl_3$ and LiHMDS, the addition of LiHMDS to the mixture of $CHCl_3$ and TMS-Cl is not particularly exothermic, and the required temperatures that are easily within the range of conventional mechanical chillers. The unprocessed solutions containing CCl_3-TMS yield TMS protected 2,2,2-trichloromethyl carbinols upon reaction with aldehydes and ketones. In the absence of any additive, the reaction is slow; for example, ketone **3** undergoes about 20% conversion after 18 h. Addition of tetra *n*-butylammonium acetate markedly accelerates the reaction. Other potential catalysts such as sodium formate, cesium acetate, or betaine are ineffective due to poor solubility.

Reaction of ketone **3** with the in situ generated CCl_3-TMS gives the same product diastereomer ratio as with the isolated CCl_3-TMS, which is about 9:1 at 0 °C. The reaction becomes sluggish at lower temperatures, and the diastereomer ratio does not substantially improve. The slow non-tetra *n*-butylammonium acetate-promoted background reaction is somewhat less selective and gives a diastereomer ratio of about 4:1. The intermediate TMS ether formed is remarkably stable. Acid-promoted desilylation was slow with partial loss of the CBZ group with HCl in methanol; accordingly, the silyl group was removed with TBAF. Control reactions showed that some reversion of the 2,2,2-trichloromethylcarbinol **4** to the ketone **3** occurs with TBAF alone, and AcOH was added to prevent this. The isolated yield of **4** was 78% by crystallization on a 1 kg scale with less than 0.1% of the undesired diastereomer.

The in situ generated CCl_3-TMS undergoes reaction with a number of 4-piperidinones to give the expected products in good to excellent yield (Table 1). CBZ 4-piperidinone (entry 1) gave the TMS-protected trichloromethylcarbinol **5a** in high

Table 1. Additions to 4-Piperidones



Entry	Ketone		Yield (%)		Yield (%)	dr
1		**5a**	97	**6a**	94	NA
2		**3**	a	**4**	78[b]	9:1
3		**5b**	a	**6b**	53[c]	5:1
4		**5c**	a	**6c**	80[c]	2:1
5		**5d**	a	**6d**	65	>20:1

[a]not isolated. [b]isolated yield of major diastereomer. [c]total yield of diastereomers.

yield. The other entries gave varying amounts of recovered starting ketone after the desilylation, presumably due to competing silyl enol ether formation during the trichloromethyl addition. In these cases, all of the ketone was consumed in the reaction with CCl_3-TMS, but ketone was recovered after the desilylation; as noted above, control reactions showed the product trichloromethylcarbinols are stable to TBAF/AcOH. The diastereoselectivity in the additions to the 2-substituted 4-piperidones in entries 3, 4, and 5 is good to excellent. Assignments of the relative configurations of the major diastereomers for **6b**, **6c**, and **6d** are based on analogy with the reaction of ketone **3** to yield **4**. Product diastereomer ratios were determined by ^{1}H NMR integrations of the crude products, and the yields given in Table 2 are for the purified diastereomer mixtures. Partial separation of the **6b** and **6c** diastereomers was possible by either chromatography or crystallization.

Additions of CCl_3-TMS to a diverse array of aldehydes and ketones are summarized in Table 2 and generally proceed in high yield. The two low-yielding entries (4 and 6) in the trichloromethyl addition are both with readily enolized substrates. Benzyloxyacetaldehyde (entry 4) gave substantial amounts of recovered starting material after the desilylation, and the reaction with 2-indanone (entry 6) gave tars in addition to the intended product. Entry 7 proceeded with high diastereoselectivity to give the product **8h** as a single stereoisomer, identified by comparison with reported data,[25] where as expected the trichloromethyl addition occurred *trans* to the phenyl group. Under conventional conditions ($CHCl_3$−

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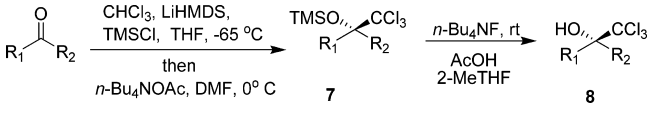
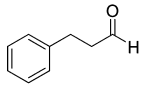
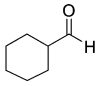
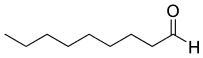
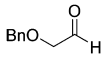
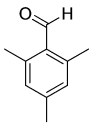
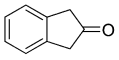
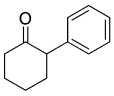
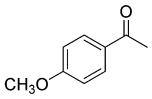
Table 2. Additions to Aldehydes and Ketones



Entry	Aldehyde/Ketone	Yield (%)		Yield (%)
1		**7a** 85	**8a**	91
2		**7b** 98	**8b**	94
3		**7c** 96	**8c**	95
4		**7d** 36	**8d**	86
5		**7e** 98	**8e**	78
6		**7f** 42	**8f**	97
7		**7g** 96	**8g**	95[a]
8		**7h** 95	**8h**	83

[a] single diastereomer (>20:1).

LiHMDS, −78 °C), 5:1 selectivity was observed for this reaction.[25] The desilylation reactions in Table 2 were generally uneventful and gave the desilylated products in high yield. Exceptions were entry 5, where some unidentified nonpolar byproduct were formed in the desilylation (only a trace of mesitylaldehyde was formed), and entry 8, which showed significant loss of the trichloromethyl group during the desilylation (about 10% 4-methoxyacetophenone was recovered), even with the addition of AcOH.[31]

■ CONCLUSIONS

In conclusion, we have demonstrated the one-pot in situ formation and reaction of trimethyl(trichloromethyl)silane with a wide variety of aldehydes and ketones to yield trichloromethylcarbinols and their trimethylsilyl ethers. This expands the utility of this reagent, which is difficult to isolate, and provides a procedure which can be run on a large scale.

■ EXPERIMENTAL SECTION

Trimethyl(trichloromethyl)silane. Chloroform (5.0 mL, 62.3 mmol) and chlorotrimethylsilane (5.2 mL, 40.9 mmol) were dissolved in 25 mL of THF and cooled to −65 °C internal. LiHMDS solution (1 M in THF, 40 mL, 40 mmol) was added over about 20 min, keeping the internal temp between −60 and −70 °C (mostly about −62 °C). The mixture was stirred at −65 °C for 20 min and then allowed to warm to rt. The mixture was concentrated by rotary evaporation (40 °C bath) to a slurry, and then 20 mL of water and 50 mL of pentane were added. The aqueous phase was separated and extracted with 50 mL of pentane. The combined pentane solutions were washed with 20 mL of water, dried briefly over Na_2SO_4, and evaporated (40 °C bath) to yield a colorless syrup that formed white solids on standing. Filtration gave 3.5 g (44% yield) of a white solid. The solids were mostly pure trimethyl(trichloromethyl)silane containing a small amount of hexamethyldisilazane by ^{1}H NMR. The solids were sublimed to yield 2.0 g of trimethyl(trichloromethyl)silane as a colorless waxy solid: mp 131−133 °C (lit. mp 130−132 °C);[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.87, 95.41. LRMS-ACPI *m/z* 73, 93, 95, 113, 115, 117.

(2*S*,4*S*)-Benzyl 4-hydroxy-2-methyl-4-(trichloromethyl)-piperidine-1-carboxylate (4).[16i] Chloroform (810 mL, 10.1 mol) and chlorotrimethylsilane (990 mL, 7.8 mol) were dissolved in 3.75 L of THF and cooled to about −65 °C internal. LiHMDS solution (1 M in THF, 7.4 L, 7.4 mols) was added over about 20 min, keeping the internal temp between −60 and −70 °C. The mixture was stirred between −60 and −70 °C for 20 min and then allowed to warm to about −20 °C. A solution of (*S*)-benzyl 2-methyl-4-oxopiperidine-1-carboxylate (**3**) (1.00 kg, 4.04 mols) dissolved in 3.16 L of DMF was added over about 30 min, and then a solution of tetra *n*-butylammonium acetate (110 g, 0.37 mol) dissolved in 810 mL of DMF was added. The mixture was allowed to stir at less than 0 °C until complete and then warmed to rt, and 2.8 L of water and 2.8 L of MTBE were added. The organic phase was washed with 2.8 L of water, 2.8 L of 1 M HCl, and 2 × 2.8 L of water. The organic solution was distilled under vacuum to a low volume, 2-MeTHF (12.2 L) was added, and the mixture was distilled under vacuum to a volume of about 4 L. AcOH (240 mL, 4 mol) was added. Tetra *n*-butylammonium fluoride solution (1 M in THF, 4.04 L, 4.04 mol) was added, and the mixture was stirred for 30 min. A solution of 650 g of K_2CO_3 in 4 L of water was added, and the mixture was stirred for 30 min. The phases were separated, and the organic phase was washed with water (3 × 4 L). The organic solution was distilled under vacuum to a volume of about 4 L. Dichloromethane (8 L) was added, and the solution was filtered through 1 kg of Florisil. The filtrate was distilled under vacuum to a volume of about 4 L, then 5 L of MTBE was added, and the distillation was continued under atmospheric pressure, adding MTBE to maintain the volume at about 7 L, until the head temp was greater than 54 °C. The slurry was cooled to 0 °C for 12 h and then filtered. Yield: 1164 g (78.9%) of **4** as a white solid: mp 146.8−147.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.42 (m, 5H), 5.16 (s, 2H), 4.55−4.75 (m, 1H), 4.08−4.28 (m, 1H), 3.21−3.38 (m, 1H), 2.40 (s, 1H), 2.30−2.38 (m, 1H), 1.87−2.24 (m, 3H), 1.36−1.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 154.7, 136.6, 128.5, 128.0, 127.9, 127.8, 109.1, 81.1, 67.2, 45.7, 45.5, 34.8, 34.5, 34.3, 31.4, 31.1, 18.5, 17.9.

Procedure A. General Procedure for the One-Step in Situ Generation and Reaction of Trimethyl(trichloromethyl)silane To Form Trimethylsilyl-Protected 2,2,2-Trichloromethylcarbinols 5 and 7. Chloroform (4.5 mL, 56.2 mmol) and chlorotrimethylsilane (4.9 mL, 38.6 mmol) were dissolved in 20 mL of THF and cooled to about −65 °C internal. LiHMDS solution (1 M in THF, 36 mL, 36 mmol) was added over about 20 min, keeping the internal temp between −60 and −70 °C. The mixture was stirred between −60 and −70 °C for 30 min and then allowed to warm to about −20 °C. The carbonyl compound (21.4 mmol) dissolved in 10 mL of DMF was added over 10 min, and then a solution of tetra *n*-butylammonium acetate (0.56 g, 1.9 mmol) in 5 mL of DMF was added. The mixture was allowed to stir at less than 0 °C until complete and then warmed to rt, and 15 mL of water and 15 mL of MTBE were added. The organic phase was washed with 15 mL of water, 15 mL of 1 M HCl, and 2 × 15 mL of water, and then dried over Na_2SO_4. The organic solution was filtered through a short plug of silica or Florisil and concentrated to yield the trimethylsilyl protected intermediate.

Procedure B. General Procedure for the Trimethylsilyl Deprotection To Yield 2,2,2-Trichloromethylcarbinols 6 and 8. The trimethylsilyl protected intermediate was dissolved in 2-

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MeTHF (10 mL/g), and AcOH (1.2 mL, 21.5 mmol) was added. Tetra *n*-butylammonium fluoride solution (1 M in THF, 21 mL, 21 mmol) was added, and the mixture was stirred for 10 min. One molar aqueous K_2CO_3 solution (24 mL) was added, and the mixture was stirred for 30 min. The phases were separated, and the organic phase was washed with water (3 × 25 mL). The organic solution was dried over anhydrous Na_2SO_4 and evaporated to yield the product, which was purified by chromatography or crystallized.

Benzyl 4-(Trichloromethyl)-4-(trimethylsilyloxy)piperidine-1-carboxylate (5a). Following Procedure A, 5.0 g (21.4 mmol) of CBZ-4-piperidinone yielded 8.92 g (98%) of **5a** after filtration through a short plug of silica with 2:1 heptane/EtOAc as an oil that crystallized on standing: mp 71.4−74.7 °C; FT-IR (SB-DC) cm^{-1} 1700, 838; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.44 (m, 5H), 5.16 (s, 2H), 4.13−4.36 (m, 2H), 2.90−3.08 (m, 2H), 1.92−2.20 (m, 4H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 136.5, 128.4, 127.9, 84.6, 67.2, 40.0, 31.8, 31.6, 2.4; HRMS (GC-ESI) calcd for $C_{17}H_{25}Cl_3NO_3Si$ [(M + H)$^+$] m/z 424.0669, found 424.0664.

Benzyl 4-Hydroxy-4-(trichloromethyl)piperidine-1-carboxylate (6a). Following Procedure B, 8.53 g of **5a** yielded 7.12 g (97%) of **6a** as an oil that crystallized on standing: mp 146.4−148.6 °C; FT-IR (SB-DC) cm^{-1} 3368, 1670, 820; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.50 (m, 5H), 5.15 (s, 2H), 4.12−4.34 (m, 2H), 3.06−3.24 (m, 2H), 3.03 (s, 1H), 2.05−2.11 (m, 2H), 1.89−2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.5, 128.5, 127.8, 108.8, 80.3, 77.2, 67.3, 39.8, 31.1; HRMS (GC-ESI) calcd for $C_{14}H_{17}Cl_3NO_3$ [(M + H)$^+$] m/z 352.0274, found 352.0272.

1-*tert*-Butyl 2-Methyl 4-hydroxy-4-(trichloromethyl)-piperidine-1,2-dicarboxylate (6b). Following Procedure A, without isolation of **6a** and Procedure B, 2.79 g (10.84 mmol) of methyl 1-BOC-4-oxopiperidine-2-carboxylate was chromatographed on silica (2:1 heptane/EtOAc) to yield the product as a colorless oil that partially solidified on standing. 1.15 g of the major diastereomer was obtained as a solid and 1.28 g of a mixture of diastereomers was isolated as an oil. Total yield 2.43 g (59%). 0.53 g of the starting ketone was recovered. Major diastereomer: mp 166.7−168.0 °C; FT-IR (SB-DC) cm^{-1} 3380, 1747, 167, 818; ^1H NMR (400 MHz, $CDCl_3$) δ 4.81−4.85 and 5.0−5.05 (2 multiplets, total 1H), 3.96−4.04 and 4.07−4.14 (2 multiplets, total 1H), 3.73 and 3.75 (2 singlets, total 3H), 3.15−3.38 (m, 1H), 2.71−2.87 (m, 1H), 2.29−2.40 (m, 1H), 1.94−2.16 (m, 2H), 1.43 and 1.48 (2 singlets, total 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 172.2, 155.2, 154.9, 108.0, 80.67, 80.65, 80.1, 80.0, 52.49, 52.45, 52.41, 51.3, 37.7, 36.8, 32.2, 32.0, 30.2, 30.0, 28.3; HRMS (GC-ESI) calcd for $C_8H_{13}Cl_3NO_3$ [(M-BOC+H)$^+$] m/z 275.9961, found 275.9961.

Benzyl 4-Hydroxy-2-phenyl-4-(trichloromethyl)piperidine-1-carboxylate (6c). Following Procedure A, without isolation of 5c, and Procedure B, 4.0 g (12.9 mmol) of 1-CBZ-4-oxo-2-phenylpiperidine yielded after chromatography on a silica eluting with 85:15 heptane/EtOAc, 2.82 g of the major diastereomer as an oil that solidified on standing and 1.63 g of the minor diastereomer as a solid. Total yield 4.45 g (80.2%). Major diastereomer: mp 130.1−131.9 °C; FT-IR (SB-DC) cm^{-1} 3380, 1662, 814; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.53 (m, 10H), 5.82−5.66 (m, 2H), 5.29−5.12 (m, 2H), 4.43−4.26 (m, 1H), 3.50−3.33 (m, 1H), 2.89−2.76 (m, 1H), 2.72−2.62 (m, 1H), 2.29−2.12 (m, 1H), 2.08−1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.5, 128.6, 126.5, 125.0, 108.7, 80.4, 67.5, 67.3, 52.0, 51.6, 36.7, 33.9, 33.2, 30.9, 30.6; HRMS (GC-ESI) calcd for $C_{20}H_{21}Cl_3NO_3$ [(M + H)$^+$] m/z 428.0587, found 428.0583. Minor diastereomer: mp 156.6−157.6 °C; FT-IR (SB-DC) cm^{-1} 3380, 1667; ^1H NMR (400 MHz, $CDCl_3$) δ 7.0−7.4 (m, 10H), 5.14−5.18 (m, 1H), 5.1 (d, J = 12.5 Hz, 1H), 5.02 (d, J = 12.5 Hz, 1H), 4.40−4.07 (m, 1H), 3.36−3.47 (m, 1H), 3.04 (s, 1H), 2.39−2.54 (m, 3H), 2.02−2.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 143.0, 136.4, 128.7, 128.3, 127.5, 125.5, 108.5, 81.1, 67.2, 53.1, 39.5, 37.1, 34.0; HRMS (GC-ESI) calcd for $C_{20}H_{21}Cl_3NO_3$ [(M + H)$^+$] m/z 428.0587, found 428.0584.

***tert*-Butyl 2-Butyl-4-hydroxy-4-(trichloromethyl)piperidine-1-carboxylate (6d).** Following Procedure A without isolation of **5d** and then Procedure B, 0.6 g (2.53 mmol) of 1-CBZ-4-oxo-2-butylpiperidine yielded 0.58 g (65.8%) of **6d** as a single diastereomer as an oil after chromatography on silica (8:1 heptane/EtOAc): FT-IR (SB-DC) cm^{-1} 3379, 1661, 814; ^1H NMR (400 MHz, $CDCl_3$) δ 4.24−4.44 (m, 1H), 4.19−3.93 (m, 1H), 3.23−3.03 (m, 1H), 2.93−2.76 (m, 1H), 2.29−2.18 (m, 1H), 2.17−1.84 (m, 4H), 1.69−1.49 (m, 1H), 1.44 (s, 9H), 1.37−1.15 (m, 4H), 0.94−0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.4, 109.3, 81.2, 81.2, 79.7, 79.6, 50.0, 49.0, 35.1, 33.9, 33.0, 32.4, 31.6, 31.5, 31.2, 29.1, 28.3, 22.5, 22.3, 14.0; HRMS (GC-ESI) calcd for $C_{10}H_{19}Cl_3NO$ [(M − BOC + H)$^+$] m/z 274.0532, found 274.0523.

Trimethyl(1,1,1-trichloro-4-phenylbutan-2-yloxy)silane (7a).[6] Following Procedure A, 0.94 g (7 mmol) of hydrocinnamaldehyde yielded 1.95 g (85.5%) of **7a** as a colorless oil after chromatography on silica eluting with 98:2 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 863, 837; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (m, 5H), 4.17 (dd, J = 9.3, 1.9 Hz, 1H), 2.98 (ddd, J = 14.0, 10.6, 5.0 Hz, 1H), 2.69 (ddd, J = 13.7, 10.3, 6.5 Hz, 1H), 2.53−2.42 (m, 1H), 2.13−2.00 (m, 1H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 128.5, 128.3, 126.2, 103.8, 83.7, 34.6, 32.4, 0.8; LRMS-EI calcd for $C_{13}H_{20}Cl_3OSi$ [(M + H)$^+$] m/z 325, found 325.

1,1,1-Trichloro-4-phenylbutan-2-ol (8a).[23] Following Procedure B, 0.326 g (1.0 mmol) of **7a** yielded 0.225 g (91%) of **8a** as a colorless oil after chromatography on silica eluting with 93:7 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 3400, 807; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.35 (m, 2H), 7.21−7.27 (m, 3H), 4.00 (ddd, J = 10.0, 5.5, 2.0 Hz, 1H), 3.02 (ddd, J = 13.7, 9.0, 4.7 Hz, 1H), 2.75−2.83 (m, 1H), 2.76 (dd, J = 5.5, 1.8 Hz, 1H), 2.36−2.44 (m, 1H), 1.95−2.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 128.6, 128.5, 126.3, 104.1, 82.0, 32.9, 31.9; LRMS-CI calcd for $C_{10}H_{11}Cl_3O$ [M$^+$] m/z 252, found 252.

Trimethyl(2,2,2-trichloro-1-cyclohexylethoxy)silane (7b).[9] Following Procedure A, 0.79 g cyclohexanecarboxaldehyde (7.1 mmol) yielded 2.1 g (98%) of **7b** as a colorless oil after chromatography on silica eluting with 98:2 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 835; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (d, J = 2.2 Hz, 1H), 2.02−2.13 (m, 2H), 1.72−1.80 (m, 2H), 1.64−1.70 (m, 2H), 1.08−1.40 (m, 5H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.0, 87.9, 40.7, 33.5, 27.2, 26.8, 26.3, 26.1, 0.6; LRMS-CI calcd for $C_{11}H_{22}Cl_3OSi$ [(M + H)$^+$] m/z 303, found 303.

2,2,2-Trichloro-1-cyclohexylethanol (8b).[2] Following Procedure B, 0.304 g (1.0 mmol) of **7b** yielded 0.217 g (94%) of **8b** as a colorless oil after chromatography on silica eluting with 92:8 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 3500, 806; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (dd, J = 6.6, 2.7 Hz, 1H), 2.70 (d, J = 6.6 Hz, 1H), 2.02−2.13 (m, 2H), 1.73−1.83 (m, 3H), 1.65−1.72 (m, 1H), 1.14−1.50 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.2, 86.4, 39.9, 32.3, 26.7, 26.6, 26.1, 25.9; LRMS-CI calcd for $C_8H_{14}Cl_3O$ [(M + H)$^+$] m/z 231, found 231.

Trimethyl(1,1,1-trichlorodecan-2-yloxy)silane (7c). Following Procedure A, 1.01 g (7.1 mmol) of nonaldehyde yielded 2.29 g (96%) of **7c** as a colorless oil after chromatography on silica eluting with 98:2 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 881, 839; ^1H NMR (400 MHz, $CDCl_3$) δ 4.04 (dd, J = 9.4, 2.0 Hz, 1H), 2.00−2.08 (m, 1H), 1.63−1.73 (m, 1H), 1.50−1.59 (m, 1H), 1.25−1.36 (m, 11H), 0.90 (t, J = 6.6 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.1, 84.3, 32.3, 31.9, 29.44, 29.37, 29.2, 29.0, 26.3, 22.7, 14.11, 14.08, 0.7; LRMS-CI calcd for $C_{13}H_{28}Cl_3OSi$ [(M + H)$^+$] m/z 333, found 333; HRMS (GC-ESI) calcd for $C_{13}H_{27}Cl_2SiO$ [(M + H − HCl)$^+$] m/z 297.1208, found 297.1202.

1,1,1-Trichlorodecan-2-ol (8c).[23] Following Procedure B, 0.325 g (1.0 mmol) of **7c** yielded 0.24 g (94%) of **8c** as a colorless oil after chromatography on silica eluting with 95:5 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 3400, 812; ^1H NMR (400 MHz, $CDCl_3$) δ 4.01 (ddd, J = 9.8, 5.9, 2.0 Hz, 1H), 2.69 (dd, J = 5.5, 1.6 Hz, 1H), 2.00−2.10 (m, 1H), 1.60−1.71 (m, 2H), 1.24−1.51 (m, 11H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.4, 83.0, 31.8, 31.5, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1; LRMS-CI calcd for $C_{10}H_{20}Cl_3O$ [(M + H)$^+$] m/z 261, found 261.

(3-(Benzyloxy)-1,1,1-trichloropropan-2-yloxy)-trimethylsilane (7d). Following Procedure A, 2.02 g (6.9 mmol) of

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2-(benzyloxy)acetaldehyde yielded 0.85 g (36%) of **7d** as a colorless oil after chromatography on silica eluting with 92:8 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 836, 836; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.41 (m, 5H), 4.61 (dd, J = 15.4, 11.9 Hz, 2H) 4.35 (dd, J = 7.2, 2.0 Hz, 1H), 4.12 (dd, J = 9.8, 2.0 Hz, 1H), 3.63 (dd, J = 10.0, 7.2 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 128.4, 127.7, 127.6, 100.8, 83.0, 73.6, 72.1, 0.4; LRMS-CI calcd for $C_{13}H_{20}C_{l3}O_2Si$ $[(M + H)^+]$ m/z 341, found 341; HRMS (GC-ESI) calcd for $C_{13}H_{19}C_{l3}O_2Si$ $[M^+]$ m/z 340.0220, found 340.0219.

3-(Benzyloxy)-1,1,1-trichloropropan-2-ol (8d). Following Procedure B, 0.35 g (1.02 mmol) of **7d** yielded 0.24 g (86%) of **8d** as a white solid after chromatography on silica eluting with 1:1 heptane/EtOAc: mp 105.4−106.3 °C; FT-IR (SB-DC) cm^{-1} 3389, 807; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.41 (m, 5H), 4.65 (dd, J = 16.0, 12.1 Hz, 2H), 4.36 (m, 1H), 4.04 (dd, J = 10.2, 3.1 Hz, 1H), 3.77 (dd, J = 10.2, 6.6 Hz, 1H), 3.51 (d, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 128.6, 128.1, 127.8, 100.5, 80.9, 73.7, 69.6; LRMS-CI calcd for $C_{10}H_{11}Cl_3O_2$ $[M^+]$ m/z 268, found 268; HRMS (GC-ESI) calcd for $C_{10}H_{11}Cl_3O_2$ $[M^+]$ m/z 267.9825, found 267.9824.

Trimethyl(2,2,2-trichloro-1-mesitylethoxy)silane (7e). Following Procedure A, 3.22 g (21.7 mmol) of mesitylaldehyde yielded 7.2 g (97%) of **7e** as a white solid after passing through a short plug of silica eluting with 8:1 heptane/EtOAc: mp 73.6−75.6 °C; FT-IR (SB-DC) cm^{-1} 3483, 853, 815; ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.84 (s, 1H), 5.72 (s, 1H), 2.70 (s, 3H), 2.50 (s, 3H), 2.27 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.0, 137.9, 132.2, 130.1, 129.2, 104.2, 83.7, 22.6, 22.4, 20.8, −0.2; HRMS (GC-ESI) calcd for $C_{14}H_{20}Cl_3OSi$ $[(M - H)^+]$ m/z 337.0349, found 337.0351.

2,2,2-Trichloro-1-mesitylethanol (8e).[2] Following Procedure B, 6.4 g (18.8 mmol) of **7e** yielded 3.97 g (78%) of **8e** as a colorless oil after chromatography on silica eluting with 95:5 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 881, 833; ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.91 (s, 1H), 5.83 (d, J = 4.6 Hz, 1H), 3.41 (d, J = 4.6 Hz, 1H), 2.77 (s, 3H), 2.53 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 138.4, 132.2, 129.4, 128.1, 104.7, 83.5, 22.8, 20.8, −0.2; HRMS (GC-ESI) calcd for $C_{11}H_{13}Cl_2O$ $[(M + H - HCl)^+]$ m/z 231.0343, found 231.0340.

Trimethyl(2-(trichloromethyl)-2,3-dihydro-1*H*-inden-2-yloxy)silane (7f). Following Procedure A, 2.83 g (21.4 mmol) of 2-indanone yielded 2.90 g (42%) of **7f** as a white solid after chromatography on silica eluting with 8:1 heptane/EtOAc: mp 38.1−39.8 °C; FT-IR (SB-DC) cm^{-1} 869, 838; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.27 (m, 4H), 3.85 (d, J = 17.1 Hz, 1H), 3.17 (d, J = 17.1, 1H), −0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 127.1, 124.8, 106.6, 94.2, 44.1, −1.6; HRMS (GC-ESI) calcd for $C_{10}H_{10}Cl_3O$ $[(M - TMS + H)^+]$ m/z 250.9797, found 250.9790.

2-(Trichloromethyl)-2,3-dihydro-1*H*-inden-2-ol (8f). Following Procedure B, 2.05 g (6.3 mmol) of **7f** yielded 1.55 g (78%) of **8f** as a colorless solid after clarification through a plug of Florisil eluting with 95:5 heptane/EtOAc: mp 97.5−99.5 °C; FT-IR (SB-DC) cm^{-1} 3543, 832; ^1H NMR (400 MHz, DMSO) δ 7.20−7.26 (m, 4H), 6.51 (s, 1H), 3.62 (d, J = 16.8 Hz, 1H), 3.14 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 140.1, 127.0, 125.0, 107.7, 90.8, 43.7; HRMS (GC-ESI) calcd for $C_{10}H_{10}Cl_3O$ $[(M + H)^+]$ m/z 250.9797, found 250.9792.

***erythro*-Trimethyl-2-phenyl-1-(trichloromethyl)-cyclohexyloxy)silane (7g).** Following Procedure A, 1.21 g (7 mmol) of 2-phenylcyclohexanone yielded 2.45 g (96%) of **7g** as a colorless oil after chromatography on silica eluting with 98:2 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 836; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (br s, 2H), 7.16−7.27 (m, 3H), 3.25 (dd, J = 12.5, 3.3 Hz, 1H), 2.45 (m, 1H), 1.92−2.03 (m, 2H), 1.80−1.91 (m, 2H), 1.64−1.78 (m, 2H), 1.36−1.48 (m, 1H), 0.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 129.6, 127.6, 126.3, 108.9, 88.2, 50.4, 33.10, 33.07, 26.0, 23.0, 2.5; HRMS (GC-ESI) calcd for $C_{16}H_{23}Cl_3OSi$ $[M^+]$ m/z 364.0584, found 364.0582.

***erythro*-2-Phenyl-1-(trichloromethyl)cyclohexanol (8g).**[25] Following Procedure B, 0.366 g (1.0 mmol) of **7g** yielded 0.28 g (95%) of **8g** as a white solid after chromatography eluting with 90:10 heptane/EtOAc: mp 57.3−59.2 °C; FT-IR (SB-DC) cm^{-1} 3400, 798; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.20 (m, 5H), 3.39 (dd, 1H, J = 12.7, 3.7 Hz). 2.49−2.41 (m, 1H), 2.17−2.05 (m, 1H), 2.03−1.93 (m, 1H), 1.89−1.79 (m, 3H), 1.76−1.69 (m, 1H), 1.47−1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.4, 126.9, 109.2, 83.6, 48.3, 33.8, 32.49, 25.9, 22.4; LRMS-EI calcd for $C_{13}H_{16}Cl_3O$ $[(M + H)^+]$ m/z 293, found 293.

Trimethyl(1,1,1-trichloro-2-(4-methoxyphenyl)propan-2-yloxy)silane (7h). Following Procedure A, 3.25 g (21.6 mmol) of 4-methoxyacetophenone yielded 7.04 g (95%) of **7h** as an oil after chromatography a short plug of silica eluting with 8:1 heptane/EtOAc: FT-IR (SB-DC) cm^{-1} 881, 833; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H), 2.09 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.46, 132.32, 130.39, 112.28, 108.51, 85.41, 55.14, 24.74, 1.94; HRMS (GC-ESI) calcd for $C_{13}H_{20}Cl_3O_2Si$ $[(M + H)^+]$ m/z 341.0298, found 341.0296.

1,1,1-Trichloro-2-(4-methoxyphenyl)propan-2-ol (8h). Following Procedure B, 6.8 g (19.9 mmol) of **7h** yielded 4.45 g (83%) of **8h** after chromatography eluting with 95:5 heptane/EtOAc as a colorless oil that solidified on standing: mp 71.8−73.5 °C; FT-IR (SB-DC) cm^{-1} 3472, 832, 792; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.9 Hz, 2H), 6.9 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 2.94 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 130.4, 129.7, 112.6, 108.4, 83.1, 55.2, 25.8; HRMS (GC-ESI) calcd for $C_{10}H_{12}Cl_3O_2$ $[(M + H)^+]$ m/z 268.9903, found 268.9901.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra (^1H and ^{13}C) for all products. 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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