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# RADICAL REACTIONS AND α-SILYLATIONS OF OPTICALLY ACTIVE 4-TRICHLOROMETHYL-β-LACTONE

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**Abstract** – Radical alkylations and α-silylations of optically active (*R*)-4-trichloromethyl-2-oxetanone are described that maintain the integrity of the β-lactone. Alternate methods for selective dechlorinations of both the β-lactone and the derived Weinreb amide are described.

This paper is dedicated to the memory of the Emeritus Professor Kenji Koga of Tokyo University.

## INTRODUCTION

Although the first β-lactone (2-oxetanone) was synthesized by Einhorn in 1883,[1] it was not until almost 100 years later that β-lactones began to emerge as valuable intermediates for organic synthesis.[2] In 1982, Wynberg and Staring, building on earlier work of Borrman and Wegler,[3] reported an efficient asymmetric, organocatalytic route to (*R*)- and (*S*)-4-trichloromethyl-2-oxetanones (**3**) employing quinine and quinidine as catalysts. The utility of these β-lactones was demonstrated in concise and efficient syntheses of both *d*- and *l*-malic acids (**5**) (Figure 1).[4] Thus, β-lactone (**3**) can serve as a malic acid surrogate and importantly it possesses orthogonal functionality and an activated ester in the form of a β-lactone.

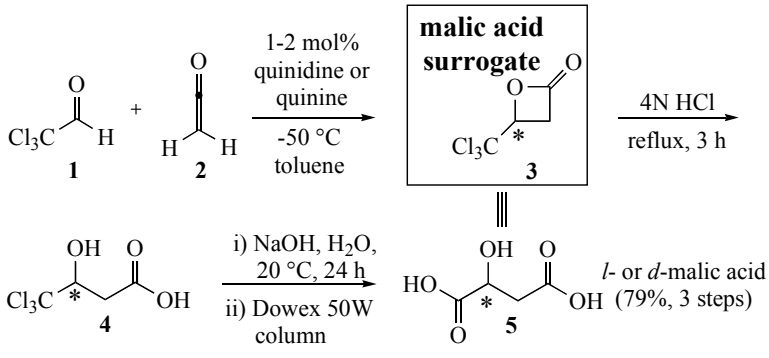



Figure 1. Wynberg's Synthesis of Optically Active β-Lactone (**3**) and Conversion to *d*- and *l*-Malic Acids.

Fujisawa and coworkers, in collaboration with Wynberg's group, described several transformations of the (*S*)-4-trichloromethyl-β-lactone (**3**), including a novel Friedel-Crafts acylation in a formal synthesis of enalapril (**9**), an angiotensin converting enzyme (ACE) inhibitor (Figure 2).[5] Fujisawa also reported a Claisen condensation with this β-lactone to give β-keto ester (**10**), an intermediate in route to the synthetically useful δ-lactone (**11**). Selective dechlorination delivered alkyl chloride (**12**), a useful optically active electrophile.[6] In a similar fashion, Song and coworkers dechlorinated β-hydroxy ester (**13**) derived from β-lactone (**3**) to deliver chlorohydrin (**14**), a useful intermediate for carnitine (**15**) synthesis. [7]

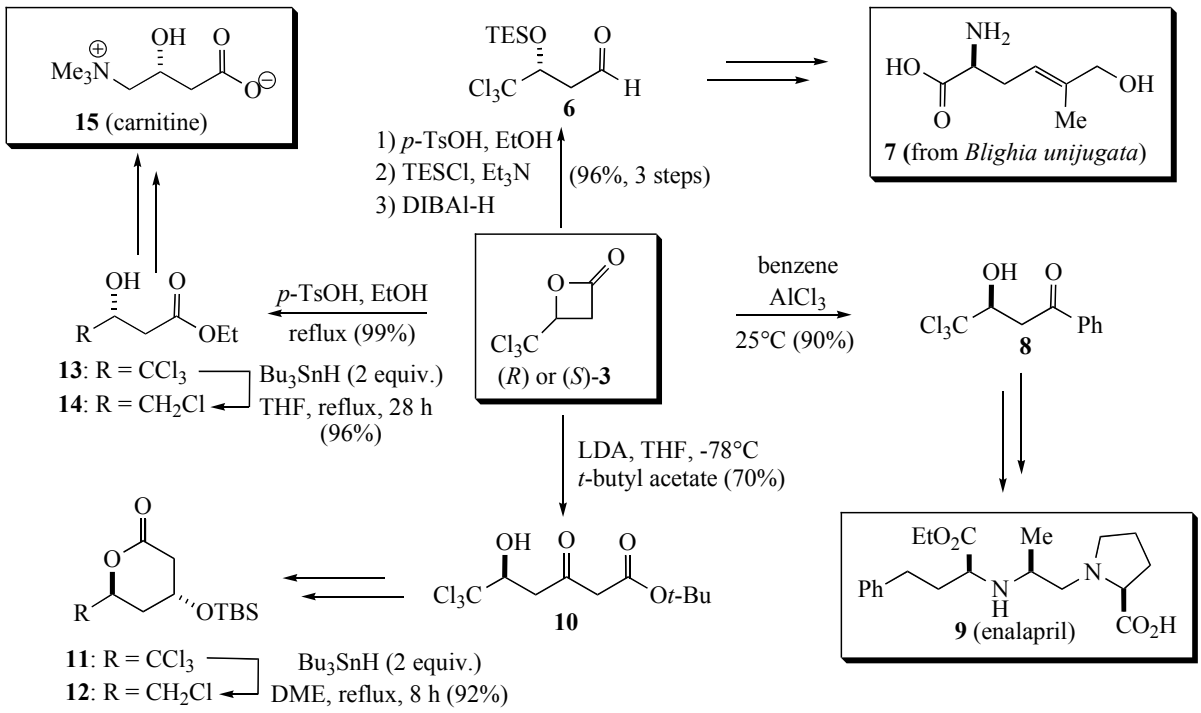
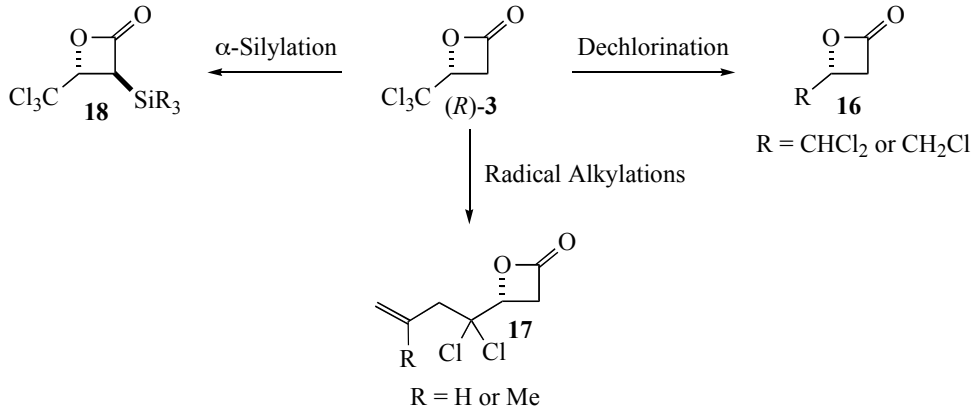



Figure 2. Utility of (*R*)- and (*S*)-4-Trichloromethyl-β-Lactones (**3**).

Our group has also developed transformations of the readily available chiron (chiral synthon) (**3**) and described its conversion into other useful chirons.[8] For example, we prepared aldehyde (**6**) containing a masked α-amino acid functionality in the form of a protected trichloromethyl carbinol, a functionality readily converted to an α-azido ester (Figure 2).[9] The chiron was used in a synthesis of the natural occurring amino acid (**7**) isolated from the seeds of the tropical plant, *Blighia unijugata.* [10]

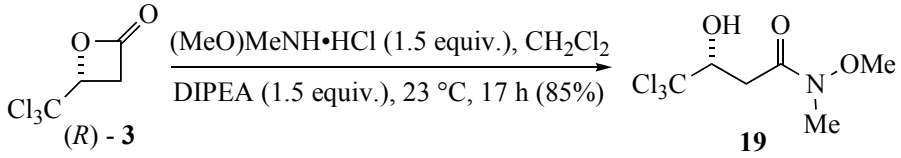
As part of our continuing efforts to demonstrate the utility of chiron (**3**), herein we describe several new transformations of this β-lactone that further demonstrates its usefulness as a malic acid surrogate (Figure 3). A unique aspect of several of the described reactions is the ability to perform them while maintaining the integrity of the β-lactone. Several of these transformations were designed to provide

access to orthogonally protected malic acid surrogates to circumvent numerous protection/deprotection steps often required to employ this useful chiral synthon.[11] Although selective dechlorination of the trichloromethyl moiety is known for systems derived from these β-lactones,[5-7] we now report direct dechlorination in the presence of the β-lactone (*i.e.* **3** → **16**). Building on these results, we also developed a radical alkylation enabling C-C bond formation at the trichloromethyl center while maintaining the integrity of the β-lactone (*i.e.* **3** → **17**). Finally, we found that α-silylation of β-lactone (**3**) is possible (*i.e.* **3** → **18**). Based on prior work,[12] this will enable α-alkylation while circumventing the problematic alkylation of α-unsubstituted β-lactones due to competing Claisen condensations.[13]




## RESULTS AND DISCUSSION

β-Lactone (**3**) was readily opened to Weinreb amide (**19**) under mild conditions in 85% yield (Scheme 1).[14] This compound is a very useful malic acid surrogate as it contains three orthogonally reactive moieties; a trichloromethyl group, a hydroxy group, and a Weinreb amide.

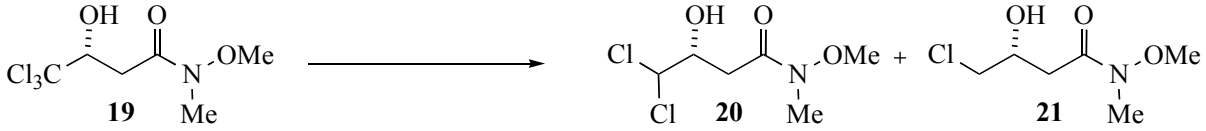



Scheme 1

Weinreb amide (**19**) was converted to the dichloride (**20**) by reductive dechlorination, without the need for additional radical initiator, by the method of Song and Fujisawa.[5-7] However, attempts to prepare the monochloride (**21**) directly from the trichloride (**19**) in this manner with 2.0 equivalents of $Bu_3SnH$ were unsuccessful delivering primarily the dichloride (**20**) in 78% yield (Table 1, Entry 1). Standard radical dehalogenation conditions were then employed with 2,2'-azobisisobutyronitrile (AIBN) as initiator.[15] In this way, the monochloride (**21**) was obtained in 77% yield (Table 1, Entry 2). This constitutes a complimentary route to chiron (**21**) prepared previously by other methods including Noyori

hydrogenation. [16] We also investigated a tin-free method for dechlorination involving trimethylsilylsilane[17] and this also delivered the monochloride in similar yield (Entry 3). It is worth noting that the dichloride can also be obtained under all conditions studied by the use of 1.0 equivalent of hydrogen atom donor. Thus, selective radical dehalogenation of Weinreb amide (**19**) provides malic acid surrogates (**20**) and (**21**) with orthogonal functionality without recourse to tin-mediated processes.

Table 1. Selective dechlorinations of Weinreb Amide (19).

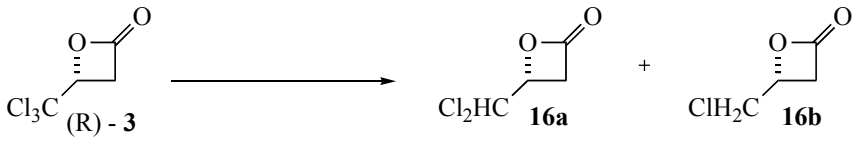



| Entry | Conditions | **20** (% yield)[a] | **21** (% yield)[a] |
|---|---|---|---|
| 1 | $Bu_3SnH$ (1.1-2.2 equiv.), THF, reflux, 24 h | 78 | <5[b] |
| 2 | $Bu_3SnH$ (2.1 equiv.), PhH, 10 mol % AIBN, 60°C, 16 h | <5[b] | 77 |
| 3 | $(TMS)_3SiH$ (2.1 equiv.), toluene, $Et_3B$, air, 23°C, 1 h | <5[b] | 78 |

[a]Refers to isolated yields. [b]The minor products were detected in the crude $^1H$ NMR spectra but were removed by chromatography.

We next studied direct radical dechlorination of β-lactone (**3**). There are a few examples of radical cleavage of halogens at the γ-carbon of β-lactones, which proceed without cleavage of the ring.[18] For example, Crich has previously described radical dehalogenations of γ-bromo-β-lactones, and described the use of a full equivalent of $Ph_2Se_2$ (*i.e.* 2.0 equiv. of PhSeH) to suppress ring cleavage processes in favor of debromination.[18e] Similar to dechlorination of amide (**19**), initiator-free conditions applied to β-lactone (**3**) delivered primarily the dichloride (**16a**) (70% yield) with only traces of the monochloride (**16b**) present in the crude $^1H$ NMR spectrum (Table 2, Entry 1). We also obtained the volatile monochloride (**16b**) when AIBN was added to the reaction, albeit in only 32% yield (Entry 2). Attempted silicon-mediated dechlorination gave the dichloride (**16a**) in 57% yield with only one equivalent of silane (Entry 3), however under these conditions with 2.2 equiv. of silane the monochloride proved difficult to separate from boron by-products. Ultimately, the use of tributyltin hydride and triethylborane cleanly provided the monochloride (**16b**) albeit in 25% yield with no dichloride detected (Entry 4). The volatility of the monochloride undoubtedly contributes to lower yields in this case but may also be a result of alternative reaction pathways leading to highly volatile by-products (*e.g.* **27b**, *vide infra*). To the best of our knowledge, these are the first direct reductive dechlorinations of β-lactones (**3**) that maintain the integrity

Table 2. Dechlorination of Trichloromethyl β-Lactone ((*R)*-**3**)

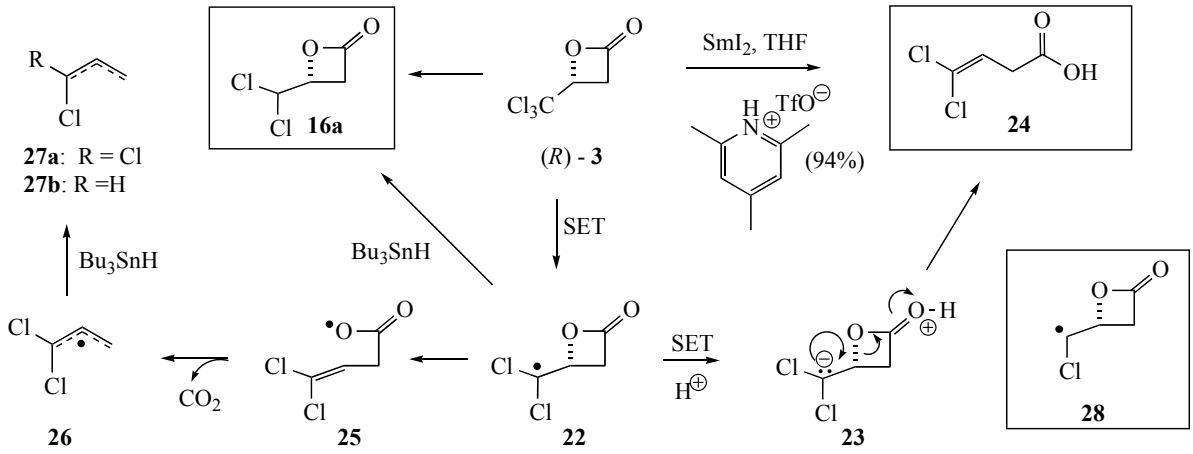



| Entry | Conditions | **16a** (% yield)[a] | **16b** (% yield)[a] |
|---|---|---|---|
| 1 | $Bu_3SnH$ (1.1-2.2 equiv.), THF, reflux, 24 h | 78 | <5[b] |
| 2 | $Bu_3SnH$ (2 equiv.), PhH, AIBN, 60 °C, 16 h | <5[b] | 32 |
| 3 | $(TMS)_3SiH$ (1.1 equiv.), toluene, $Et_3B$, air, 23 °C, 1 h | 57 | 0 |
| 4 | $Bu_3SnH$ (2 equiv.), toluene, $Et_3B$, air, 23°C, 3 h | 0 | 25 |

[a]Refers to isolated yields. [b]The minor products were detected in the crude $^1$H NMR spectra but were removed by chromatography.

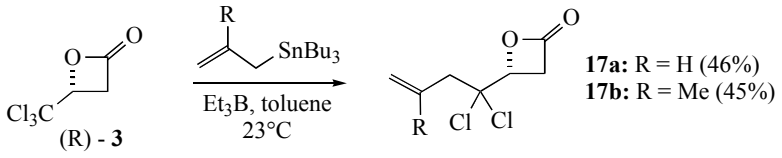
of the strained heterocycle. In contrast to examples by Crich, these transformations may be possible due to the stabilizing effect of the resident chlorine atoms on the radical center. [18e]

We also attempted to dechlorinate β-lactone (**3**) using $SmI_2$ by an ionic pathway in the presence of the non-nucleophilic proton source, collidinium triflate (Scheme 2).[19] The dichloride (**16a**) was not formed but rather the corresponding known acid (**24**)[20] derived from ring scission was obtained in 94% yield. We propose that the samarium diiodide promotes two consecutive single electron transfers (SETs) to the trichloromethyl moiety, and collidinium triflate may catalyze ring opening of the β-lactone by activation of the carbonyl group leading to carboxylic acid (**24**). Thus, these reactions demonstrate an interesting dichotomy between radical and anionic dechlorination of γ-halo-β-lactones and may reflect the relative stability of an oxy radical versus an oxy anion. Based on the work of Crich,[18e] radical (**22**) could undergo fragmentation but possibly due to the chlorine atoms is stabilized by through space electron donation and thus it may have sufficient lifetime to abstract a hydrogen atom leading to dichloride (**16a**) as described above. However, in the case of $SmI_2$, following a second SET leading to anion (**23**), rapid E1 elimination occurs promoted by acid leading to carboxylic acid (**24**). In the event that ring scission does occur *via* radical (**22**) leading to oxy radical (**25**), it would undergo rapid decarboxylation as observed by Crich[18e] and then reduction if a hydrogen atom donor is present. This pathway would ultimately deliver the volatile dichloroalkenes (**27a**,**b**) (as mixtures of regioisomers) which we have not been able to detect in reactions with $Bu_3SnH$ but may contribute to low mass recovery in some cases (see Table 2). Interestingly, the expected difference in stability of dichloro radical (**22**) versus that of monochloro radical (**28**) (inset, Scheme 2) may be reflected in the lower yields obtained in bis-dechlorinations leading to monochloro-β-lactone (**16b**) (Table 2).




Scheme 2

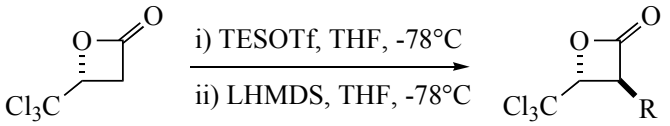
Encouraged by successful dechlorinations in the presence of the β-lactone moiety and with some understanding of the reactivity of the dichloro radical (*i.e.* **22**), we turned our attention to tin-mediated C-C formation. [21] Several attempts with allylstannes, including allyltributylstannane, allyltriphenylstannane, and tetraallyltin, gave promising results, but could not be driven to completion when 1.0 equiv. of stannane was used and this was complicated further by the inability to separate products from starting material. However, we ultimately found that treatment of β-lactone (**3**) with 2.5 equiv. of allyltributylstannane provided the monoalkylated product (**17a**) in 46% yield. Employing methallyltributylstannane under similar conditions delivered β-lactone (**17b**) in 45% yield. Although the yields are moderate, this represents a novel functionalization of β-lactone (**3**) and this method may be amenable to radical alkylations of other trichloromethyl moieties.[22]




Scheme 3

In efforts to functionalize the α-carbon of β-lactone (**3**), we studied enolization and trapping with various electrophiles. Prior attempts to alkylate α-unsubstituted β-lactones have proven to be difficult and inefficient due to both self-condensation (Claisen) and dialkylation with only a few examples being successful with highly reactive electrophiles.[13] Attempts to apply several of these reported methods to β-lactone (**3**) were unsuccesful. However, we discovered a novel α-silylation of β-lactone (**3**) when it was treated with lithium hexamethyldisilazide (LiHMDS) in the presence of silyl triflates at –78 °C.

This provided a moderate yield (31%) of α-triethylsilyl-β-lactone (**18a**) along with recovered starting material while the use of TMSOTf returned starting material possibly due to reaction of the base with this triflate. In the case of TIPSOTf, sterics may slow the reaction leading to reduced yields. We have not determined if this reaction proceeds through direct α-silylation or by *O*-silylation followed by Brook rearrangement.




(*R*)-**3** **18a:** R = $SiEt_3$ (31%, ~50% based on rec. SM)
**18b:** R = $Si(i\text{-}Pr)_3$ (20%)

Scheme 4

In conclusion, we have demonstrated several new transformations of readily available (*R*)-4-trichloromethyl-β-lactone (**3**) including radical alkylations, α-silylations, and alternative, tin-free methods for mono- and bis-dechlorinations. Importantly, several of these reactions can be conducted while maintaining the integrity of the β-lactone, thus enabling subsequent acylations or alkylations with the β-lactone moiety. Weinreb amide (**19**) was readily prepared and then selectively dechlorinated providing access to malic acid surrogates with orthogonal functional groups. Chain extensions at the γ-carbon were possible *via* radical alkylations providing access to further functionalized chloro-β-lactones. α-Silylations of β-lactone (**3**) were shown to be feasible and this enables further functionalization at the α-carbon as previously demonstrated by Pons[23] and Mead.[24] We are continuing to develop further transformations of these readily available chirons and these studies will be reported in due course.

## EXPERIMENTAL

**Trichloro Weinreb amide (19):** To a solution of β-lactone (**3**) (500 mg, 2.68 mmol) in $CH_2Cl_2$ (25 mL) was added solid *N,O*-dimethylhydroxylamine hydrochloride (392 mg, 4.02 mmol) followed by diisopropylethylamine (700 μL, 4.02 mmol) at 23 °C. This solution was stirred for 17 h and then quenched with saturated aq. $NH_4Cl$ and diluted with ether. The organics were separated and washed with water, brine, and then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (60:40, hexanes:ethyl acetate) delivered amide (**19**) (571 mg, 85%) as a white solid: $R_f$ 0.35 (50:50, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +44.6° (*c* = 1.00, $CHCl_3$); IR (thin film) 3384, 1684 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.95 (dd, *J* = 9.3, 16.5 Hz, 1H), 3.16 (dd, *J* = 2.4, 16.5 Hz, 1H), 3.24 (s, 3H), 3.75 (s, 3H), 4.48 (d, *J* = 4.2 Hz, 1H), 4.65 (ddd, *J* = 2.4, 4.2, 9.3 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ

32.3, 34.5, 61.5, 79.2, 102.9, 171.2; ESI HRMS calcd for $C_6H_{10}NO_3Cl_3$ [M + H]: 249.9805, found 249.9803.

**Dichloro Weinreb amide (20):** To a solution of Weinreb amide (**19**) (2.50 g, 9.98 mmol) in THF (20 mL) was added tributyltin hydride (3.00 mL, 11.0 mmol). This solution was refluxed for 24 h and then cooled and concentrated *in vacuo*. The residue was redissolved in acetonitrile, washed with hexanes to remove tin by-products, and concentrated *in vacuo*. Flash column chromatography (50:50, hexanes:ethyl acetate) gave amide (**20**) (1.69 g, 78%) as a white solid: $R_f$ 0.56 (30:70, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +42.4° (*c* = 1.00, $CHCl_3$); IR (thin film) 3355, 1649 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.89 (dd, *J* = 7.8, 17.1 Hz, 1H), 2.99 (dd, *J* = 3.9, 17.1 Hz, 1H), 3.23 (s, 3H), 3.74 (s, 3H), 4.09 (d, *J* = 4.8 Hz, 1H), 4.36-4.43 (m, 1H), 5.90 (d, *J* = 3.9 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 32.1, 33.5, 61.5, 72.8, 75.2, 171.9; ESI HRMS calcd for $C_6H_{11}NO_3Cl_2$ [M + Li] 222.0976, found 222.0296.

**Chloro Weinreb amide (21):** To a solution of Weinreb amide (**19**) (500 mg, 2.00 mmol) in toluene (5.0 mL) was added tris(trimethylsilyl)silane (1.35 mL, 4.20 mmol) and triethylborane (4.40 mL, 4.40 mmol) sequentially at 23°C and open to the air. This solution was stirred for 2 h and then dissolved in acetonitrile, washed with hexanes to remove silyl by-products, and concentrated *in vacuo*. Flash column chromatography (30:70, hexanes:ethyl acetate) afforded amide (**21**) (280 mg, 77%) as a pale red oil: $R_f$ 0.37 (30:70, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +46.5° (*c* = 1.00, $CHCl_3$); IR (thin film) 3423, 1643 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.73 (dd, *J* = 7.8, 17.1 Hz, 1H), 2.83 (dd, *J* = 3.9, 17.1 Hz, 1H), 3.22 (s, 3H), 3.63-3.65 (m, 2H), 3.73 (s, 3H), 3.98 (d, *J* = 4.2 Hz, 1H), 4.22-4.31 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 31.9, 35.3, 48.1, 61.4, 68.1, 172.6; ESI HRMS calcd for $C_6H_{12}NO_3Cl$ [M + H] 182.0584, found 182.0589.

**β-Lactone (16a):** To a solution of β-lactone (**3**) (3.00 g, 16.1 mmol) in THF (30 mL) was added tributyltin hydride (4.80 mL, 17.7 mmol) at 23°C. This solution was refluxed for 24 h at which time it was cooled and concentrated *in vacuo*. Two sequential flash column purifications (80:20, pentane:ether) were required to remove all tin impurities and gave β-lactone (**16a**) (1.90 g, 78%) as a clear oil: $R_f$ 0.72 (70:30, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +31.2° (*c* = 1.00, $CHCl_3$); IR (thin film) 1846 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.58 (dd, *J* = 3.9, 16.8 Hz, 1H), 3.67 (dd, *J* = 6.0, 16.8 Hz, 1H), 4.81 (ddd, *J* = 3.9, 4.8, 6.0 Hz, 1H), 5.98 (d, *J* = 4.8 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 41.1, 70.6, 71.0, 165.7, ESI HRMS calcd for $C_4H_4Cl_2O_2$ [M + Li] 160.9748, found 160.9741.

**β-Lactone (16b):** To a solution of β-lactone (**3**) (1.00 g, 5.37 mmol) in toluene (6 mL) was added tributyltin hydride (3.00 mL, 11.0 mmol) followed by 11.0 mL of triethylborane (1.0 M in hexanes, 11.0 mmol) at 23 °C and the reaction was left open to the air. After stirring for 5 h, the reaction was poured over a pad of silica gel and eluted with hexanes to remove tin by-products, eluted with ether to remove the product. Following removal of ether, the residue was purified by two sequential flash columns (80:20, pentane:ether) to obtain β-lactone (**16b**) (160 mg, 25%) as a clear oil: $R_f$ 0.35 (70:30, hexanes:ethyl

acetate); $[\alpha]_D^{23}$ +10.2° (*c* = 1.00, $CHCl_3$); IR (thin film) 1836 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.42 (dd, *J* = 4.2, 16.5 Hz, 1H), 3.62 (dd, *J* = 5.7, 16.5 Hz, 1H), 3.81 (dd, *J* = 5.7, 12.3 Hz, 1H), 3.87 (dd, *J* = 4.8, 12.3 Hz, 1H), 4.78-4.71 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 41.7, 44.5, 68.6, 166.7; ESI HRMS calcd for $C_4H_5O_2Cl$ [M + Li] 127.0138, found 127.0141.

**Carboxylic acid (24):** To a mixture of β-lactone (**3**) (100 mg, 0.54 mmol) and collidinium triflate (473 mg, 1.61 mmol) at 23 °C was added 16.0 mL of $SmI_2$ solution (0.1 M in THF, 1.61 mmol). The solution was stirred for 2 h and then the reaction was quenched with aq. saturated $Na_2S_2O_3$, diluted with ether, and the organics were washed with aq. 10% $K_2CO_3$. The combined aqueous extracts were acidified to pH 2 with 1 N HCl, extracted with ethyl acetate (3 x 25 mL), and the combined organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to deliver a pale yellow solid (80 mg, 94%). Spectral data for this compound matched that previously reported.[25]

**β-Lactone (17a):** To a solution of β-lactone (**3**) (500 mg, 2.67 mmol) in toluene (3 mL) was added neat allyltributylstannane (2.1 mL, 6.68 mmol) at 23°C followed by triethylborane (1.0M in hexanes, 6.68 mmol) and reaction was stirred open to the air for 5 h. The crude reaction mixture was directly loaded on a silica gel column and purified by two successive flash columns (gradient elution, 99:1 → 97:3, pentane:ether) to deliver β-lactone (**17a**) in 46% yield: $R_f$ 0.60 (70:30, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +12.5° (*c* = 1.00, $CHCl_3$); IR (thin film) 3090, 3015, 1851, 1643 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.00 (ddt, *J* = 0.9, 7.5, 14.7 Hz, 1H), 3.13 (ddt, *J* = 1.2, 6.6, 14.7 Hz, 1H), 3.62 (dd, *J* = 5.7, 16.8 Hz, 1H), 3.72 (dd, *J* = 3.9, 16.8 Hz, 1H), 4.73 (dd, *J* = 3.9, 5.7 Hz, 1H), 5.28-5.39 (m, 2H), 5.89-6.03 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 41.8, 48.5, 72.7, 89.8, 122.2, 129.9, 165.7; ESI HRMS calcd for $C_7H_8O_2Cl_2$ [M + Li] 201.0061, found 201.0070.

**β-lactone (17b):** To a solution of methallyltributylstannane (4.56 g, 2.95 mmol) in toluene (3 mL) was added β-lactone (**3**) (1.00 g, 5.28 mmol) at 23 °C followed by 13.2 mL of triethylborane (1.0 M in hexanes, 13.2 mmol) and the reaction was stirred open to the air for 6 h. The crude reaction mixture was directly loaded on a silica gel column and purified by two successive flash columns (gradient elution, 99:1 → 97:3, pentane:ether) to deliver β-lactone (**17a**) in 45% yield: $R_f$ 0.81 (70:30, hexanes:ethyl acetate); $[\alpha]_D^{23}$ +9.7° (*c* = 1.00, $CHCl_3$); IR (thin film) 3082, 1855, 1647 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 1.97 (m, 3H), 3.07 (s, 2H), 3.62 (dd, *J* = 5.4, 16.8 Hz, 1H), 3.73 (dd, *J* = 3.9, 16.8 Hz, 1H), 4.79 (dd, *J* = 3.9, 5.4 Hz, 1H), 5.01-5.02 (m, 1H), 5.15-5.17 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 24.2, 41.7, 51.5, 72.5, 89.8, 119.5, 138.1, 165.8; ESI HRMS calcd for $C_8H_{10}O_2Cl_2$ [M + Li] 215.0218, found 215.0223.

**β-lactone (18b):** To a solution of β-lactone (**3**) (200 mg, 1.07 mmol) in THF (10 mL) was added TESOTf (250 μL, 1.07 mmol) dropwise at -78°C followed by LiHMDS (1.00 mL, 1.07 mmol) down the side of the flask to ensure cooling. An additional 10 mL of THF was used to wash the side of the flask. The reaction was stirred for 1.5 h at -78°C, quenched with saturated aqueous $NH_4Cl$, and warmed to

23°C. The mixture was diluted with ether and washed with additional saturated aq. $NH_4Cl$, water and brine. The organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pentane:ether 95:5) delivered the β-lactone (**18b**) (100 mg, 31%, 50% based on recovered starting material) as a clear oil: $R_f$ 0.75 (hexanes:ethyl acetate 80:20); $[\alpha]_D^{23}$ +10.0° (*c* = 1.00, $CHCl_3$); IR (thin film) 1841 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 0.79-0.84 (m, 6H), 1.03-1.08 (m, 9H), 3.46 (d, *J* = 3.9 Hz, 1H), 4.78 (d, *J* = 3.9 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 2.7, 7.1, 45.3, 78.5, 98.4, 167.9; ESI HRMS calcd for $C_{10}H_{17}O_2Cl_3Si$ [M + Li] 309.0223, found 309.0229.

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