Synthesis of (*E*)-α,β-Unsaturated Esters and (*Z*)-Vinyl Halides with Total or High Diastereoselectivity by Using Samarium Metal

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A highly diastereoselective β-elimination of 2-halo-3-hydroxy esters **1** or *O*-acetylated 1,1-dihaloalkan-2-ols **4** is achieved with samarium in the presence of diiodomethane, yielding α,β-unsaturated esters **2** or vinyl halides **5**, respectively. The β-elimination reaction was promoted by samarium diiodide, which was generated in situ. The starting halohydrins **1** or **4** are easily prepared by reaction of the corresponding lithium enolates of α-halo esters or dihalomethyllithium with aldehydes at –78 °C. The influence of the reaction conditions and the structure of the starting compounds on the diastereoselectivity of the β-elimination reactions is discussed. A comparative study of the β-elimination reaction with preformed SmI_2 and metallic samarium is also performed. These elimination reactions can be explained by the proposed mechanism.

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Introduction

Few reagents have received as much attention in organic synthesis as samarium diiodide. This compound has been applied to a multitude of organic transformations, proceeding generally with high selectivity.[1] The main limitations of SmI_2 are its cost and its high sensitivity to air oxidation and moisture, because of which the reagent requires careful manipulation and storage. For these reasons, the use of the cheaper and more stable metallic samarium would be desirable. Generally, SmI_2 is prepared in THF from powdered metallic samarium and diiodomethane, 1,2-diiodoethane, or iodine.[2] An alternative strategy to the use of SmI_2 would be to generate SmI_2 in situ (for example from diiodomethane), in the presence of the starting organic compound. Moreover, this methodology would be simpler, easier and the reaction time would be shorter than that using preformed SmI_2 (i.e. by the generation of SmI_2 + subsequent reaction of SmI_2).

Previously, by using samarium diiodide prepared in situ from samarium metal and catalytic amounts of iodine, the following reactions have been described: the reduction of nitro compounds,[3] imines,[4] or azides,[5] the reductive coupling of imines,[6] the 1,4-reduction of α,β-unsaturated esters or amides,[7] the alkylation of imines,[8] the deacylation of alcohols or lactams,[9] and the Barbier reaction of carbonyl compounds.[10] However, synthetic applications in organic synthesis of SmI_2 prepared in situ from Sm and diiodomethane remain unreported.

Recently, we have reported the first general methodology of β-elimination reactions promoted by SmI_2. There, we described the synthesis of (*Z*)-vinyl halides with high stereoselectivity from *O*-acetylated 1,1-dihaloalkan-2-ols[11] and the preparation of α,β-unsaturated esters[12] with total selectivity by treatment of the easily available 2-halo-3-hydroxy esters with samarium diiodide.

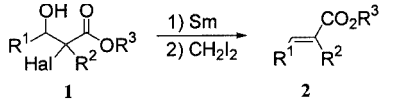
In this paper we describe a totally or highly diastereoselective synthesis of these same compounds, (*Z*)-vinyl halides (from *O*-acetylated 1,1-dihaloalkan-2-ols) and (*E*)-α,β-unsaturated esters (from 2-halo-3-hydroxy esters), by using a mixture of metallic samarium and diiodomethane. A comparative study of the β-elimination reaction by using preformed SmI_2 and metallic Sm is also accomplished.

To the best of our knowledge, this synthesis is the first example of generation of SmI_2 from diiodomethane in situ.

Results and Discussion

Synthesis of α,β-Unsaturated Esters

When diiodomethane (2.5 equiv.) is added to a suspension of samarium metal (2.5 equiv.) and 2-halo-3-hydroxy esters **1** in THF at room temperature, the corresponding



1 **2**

Scheme 1. Synthesis of (*E*)-α,β-unsaturated esters **2**

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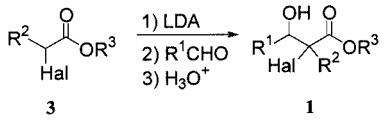
Table 1. Synthesis of α,β-unsaturated esters **2** from **1** using Sm metal

Entry	1	R^1	R^2	R^3	Hal	*de*[a]	Yield[b] (%)
1	**1a**	C_7H_{15}	H	Me	Cl	> 98	87 (70)
2	**1b**	C_7H_{15}	Me	Et	Cl	> 98	94 (75)
3	**1c**	cyclohexyl	Me	Et	Cl	> 98	93 (90)
4	**1d**	*p*-Cl−C_6H_4	H	*t*Bu	Cl	> 98	45 (72)
5	**1e**	Ph	Bu	Et	Br	> 98	90 (86)
6	**1f**	*p*-MeO−C_6H_4	Me	Et	Cl	> 98	95 (91)
7	**1g**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$	Ph	*i*Pr	Cl	> 98	97 (84)
8	**1h**	PhCH(Me)	C_6H_{13}	Et	Br	> 98	95 (87)
9	**1i**	(*E*)-MeCH=CH	C_6H_{13}	Et	Br	> 98	93 (90)

[a] Diastereoisomeric excess (*de*) determined by GC-MS and ^1H and ^{13}C NMR analysis of the crude products **2**. [b] Isolated yield, after column chromatography, based on **1**; yields of the products when using preformed SmI_2 are shown in parentheses.

α,β-unsaturated esters **2** were formed with total diastereoselectivity and in high yield (Scheme 1 and Table 1).

The 2-halo-3-hydroxy esters **1** used as starting compounds were easily prepared by reaction of the corresponding lithium enolates of α-haloesters (generated by treatment of α-halo esters **3** with LDA at −78 °C) with aldehydes at −78 °C (Scheme 2).



3 **1**

Scheme 2. Preparation of the starting compounds **1**

The reaction time was shorter (2 h) than when using preformed SmI_2 (3 h to generate SmI_2 + 30 min of reaction of SmI_2).

The diastereoisomeric excess (*de*) was determined from the crude reaction products by ^1H NMR spectroscopy (200 or 300 MHz) and GC-MS; only a single stereoisomer was found (just as when using preformed SmI_2). The (*E*) stereochemistry of the C−C double bond of the α,β-unsaturated esters **2** was assigned by comparison of their spectroscopic data with those reported previously.[12] It is noteworthy that, although the elimination reaction was carried out with a mixture of diastereoisomers (roughly 1:1) of **1**, the corresponding α,β-unsaturated esters **2** were obtained with total diastereoselectivity.

Table 1 summarizes our results. In general, the yield of the obtained α,β-unsaturated esters **2** with Sm/CH_2I_2 is higher than when using preformed SmI_2. This β-elimination reaction is general and R^1, R^2, and R^3 can be varied widely. Thus, R^1 can be aliphatic (linear, branched, or cyclic), unsaturated, or aromatic groups. The substitution at the C-2 position could also be changed using different α-halo esters **3** (again aliphatic and aromatic groups are allowed). The stereoselectivity was unaffected by the presence of bulky groups R^3 on the carboxyl ester (Table 1, Entries 4 and 7). Finally, both 2-chloro- and 2-bromo-3-hydroxy esters can be used as starting material (Table 1, Entries 5, 8, and 9).

Figure 1 shows a plausible reaction mechanism. In the first step samarium and diiodomethane would produce samarium diiodide. The metallation of **1** by SmI_2 and removal of the halogen generates an enolate intermediate. Because Sm^{III} is a strong Lewis acid and very oxophilic, it could then form a chelate with the oxygen atom of the alcohol group − which increases the ability of the hydroxy group to act as a leaving group − producing a six-membered ring.[13] We surmise that the chair-like transition-state model **A** might be involved, with the bulkier group R^1 in the equatorial orientation (to avoid 1,3-diaxial interactions). As depicted in **B** (C-2−C-3 Newman projection of **A**), R^1 and R^2 show a *cis* relationship and, consequently, elimination from **A** affords (*E*)-α,β-unsaturated esters. This proposed transition state model could also explain the total diastereoselective synthesis of **2** starting from a mixture of diastereoisomers of **1**.

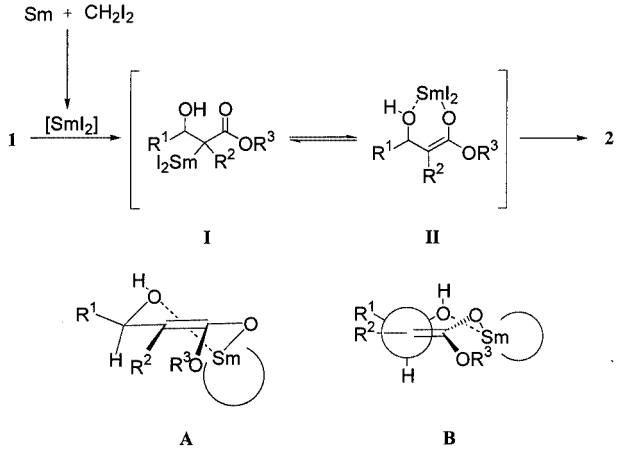
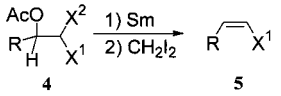


Figure 1. Proposed mechanism of the β-elimination reaction

In conclusion, this described methodology to obtain α,β-unsaturated esters from 2-halo-3-hydroxy esters with total diastereoselectivity by using in situ generated SmI_2 is better than the previously reported method using preformed SmI_2; higher yields are obtained, shorter reaction times can be used, the manipulation of Sm is easier than SmI_2 and this methodology is simpler.

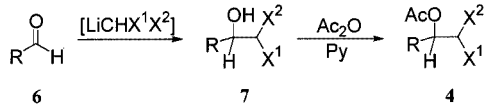
Synthesis of (*Z*)-Vinyl Halides

When diiodomethane (2.5 equiv.) is added to a suspension of a diastereoisomeric mixture of *O*-acetylated 1,1-diiodo alcohols and samarium metal (2.5 equiv.) in THF at room temperature, (*Z*)-vinyl iodides (X^1 = I) **5** were obtained with high diastereoselectivity and in high yield (Scheme 3 and Table 2).



Scheme 3. Synthesis of (*Z*)-vinyl halides **5**

The starting products **4** were prepared by reaction of dihalomethyllithium[14] with the corresponding aldehyde at −78 °C. Acetylation of the isolated alcohol **7** with Ac_2O in the presence of pyridine and DMAP, afforded the *O*-acetylated 1,1-dihalo alcohols **4** (Scheme 4).



Scheme 4. Preparation of the starting compounds **4**

The diastereoisomeric excess (*de*) was also determined from the crude reaction products by ^{1}H NMR spectroscopy (200 or 300 MHz) and GC-MS. The stereochemistry at the C−C double bond of vinyl halides **5** was assigned by comparison of their spectroscopic data with those reported previously.[11]

The yields and *de* of the (*Z*)-vinyl iodides obtained (from *O*-acetylated 1,1-diiodoalkan-2-ols) by using Sm/CH_2I_2 or preformed SmI_2 are summarized in Table 2. In the case of aliphatic vinyl iodides (Table 2, Entries 1−10), no significant differences (except for compounds **5e** and **5f**) were observed in the diastereoisomeric excesses, although higher yields (except for Entries 9 and 12) were obtained with samarium metal. No general diastereoselectivity/temperature trend was observed when using Sm/CH_2I_2; on increasing the temperature, a lower *de* of **5c** and **5d** was obtained, although in the case of compounds **5a** and **5b** a higher *de* was obtained at reflux in THF than at room temperature.[15] Surprisingly, in the case of aromatic vinyl iodides (Table 2, Entries 11−16), (*E*)-vinyl iodides were obtained as the predominant diastereoisomer. In this case, at room temperature, the use of samarium metal gave vinyl iodides with diastereoisomeric excesses and yields that were higher then when preformed SmI_2 was used. Upon increasing the temperature, the (*Z*)/(*E*) ratio increased when using both preformed SmI_2 and in situ SmI_2 (Table 2, Entries 11−12 and 14−16). At higher temperature, the (*Z*) selectivity was higher when using preformed SmI_2 (Table 2, Entry 12).

Vinyl bromides or chlorides can also be obtained starting from *O*-acetyl-1,1-dibromo- or -1,1-dichloroalkan-2-ols (Table 3, Entries 1 and 2). In the latter case, heating to reflux and a longer reaction time (6 h) were necessary due to the decrease of the reactivity of the halogen. When this reaction was performed at room temperature only a very low yield was obtained and different amounts of starting product were recovered even when the reaction time was increased (24 h).

Table 2. Synthesis of vinyl iodides **5** from **4** (X^1 = X^2 = I) using Sm metal

Entry	**4**	R[a]	Preformed SmI_2		In situ SmI_2	
			de[b]	Yield (%)[c]	*de*[b]	Yield (%)[c]
1	**4a**	C_7H_{15}	84	86	82	94
2	**4a**	C_7H_{15}[d]	88	80	90	98
3	**4b**	cyclohexyl	—[e]	–	69	64
4	**4b**	cyclohexyl[d]	88	64	84	71
5	**4c**	MeCH(Ph)	—[e]	–	83	80
6	**4c**	MeCH(Ph)[d]	88	83	72	88
7	**4d**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$	—[e]	–	91	85
8	**4d**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$[d]	88	70	84	95
9	**4e**	(*S*)-MeCH(OBn)[d]	74	75	46	63
10	**4f**	(*E*)-MeCH=CH	42	—[f]	94	—[f]
11	**4g**	Ph	0	90	29[g]	97
12	**4g**	Ph[d]	44	92	12	41
13	**4h**	*p*-MeO−C_6H_4	12[g]	87	48[g]	98
14	**4i**	2-furyl	26[g]	65	51[g]	74
15	**4i**	2-furyl	58[g] [h]	75	—[e]	–
16	**4i**	2-furyl	0[i]	62	—[e]	–

[a] Unless otherwise noted, reactions were carried out at room temperature with a reaction time of 120 min. [b] Determined by GC-MS and ^{1}H and ^{13}C NMR analysis of the crude products **5**. [c] Isolated yield after column chromatography based on compound **4**. [d] Reactions were carried out at 50 °C with preformed SmI_2 and at reflux with a reaction time of 45 min using SmI_2 generated in situ. [e] No reaction was carried out under these reaction conditions. [f] This compound decomposed on purification. [g] The (*E*) diastereoisomer was obtained instead of the (*Z*) diastereoisomer. [h] The reaction was carried out at −35 °C. [i] The reaction was carried out at 50 °C.

Table 3. Synthesis of vinyl halides **5** from **4** by using Sm metal

Entry	4	R[a]	X^1	X^2	*de*[b]	Yield (%)[c]
1	**4j**	C_7H_{15}	Br	Br	70 (82)	98 (61)
2	**4k**	C_7H_{15}[d]	Cl	Cl	66 (82)	63 (54)
3	**4l**	C_7H_{15}	Cl	I	65 (82)	99 (90)
4	**4m**	cyclohexyl	Cl	Br	74 (82)	86 (83)
5	**4n**	MeCH(Ph)	Cl	I	70 (80)	99 (95)
6	**4o**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$	Cl	Br	63 (82)	98 (93)
7	**4o**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$[e]	Cl	Br	70 (82)	95 (93)

[a] Unless otherwise noted, reactions were carried out at room temperature with a reaction time of 120 min. [b] Determined by GC-MS and ^1H and ^{13}C NMR analysis of the crude products **5**; *de* of the products formed from the reaction with preformed SmI_2 are shown in parentheses and these reactions were carried out at 50 °C. [c] Isolated yield, after column chromatography, based on compound **4**; yields of the products formed from the reaction with preformed SmI_2 are shown in parentheses. [d] The reaction was carried out at reflux with a total reaction time of 6 h. [e] The reaction was carried out at reflux with a reaction time of 45 min.

When the β-elimination was carried out starting from dihaloalkanols bearing two different halogen atoms, the products were obtained as 1:1 mixtures of diastereoisomers. However, their treatment with in situ generated SmI_2 afforded (*Z*)-vinyl halides with high or moderate diastereoselectivity. In this case, the reaction is totally chemoselective, only products resulting from the metallation of the more reactive halogen (I > Br > Cl) were found. Upon increasing the temperature (Table 3, Entries 6−7) no important difference of *de* was observed when using metallic Sm.

The synthesis of vinyl bromides or chlorides using metallic Sm proceeds with a lower *de* (8−17%) and a higher yield than when preformed SmI_2 is used.

Figure 2 shows a plausible mechanism assuming a chelation-controlled model. After formation of SmI_2 from Sm and diiodomethane, the metallation of the halogen generates intermediate **III**. Chelation of the Sm^{III} center with the carbonyl oxygen atom of the acetoxy group, produces a six-membered ring.[13] We propose a chair-like structure for **III** with an equatorial R group (in order to avoid 1,3-diaxial interactions) and an axial halogen atom (no 1,3-diaxial interactions and dipoles are present as $C-X^1$ and Sm−I are opposite each other). An elimination process as depicted in **IV** affords (*Z*)-vinyl iodides.

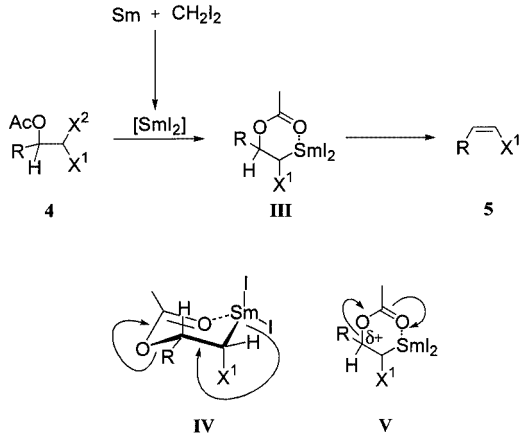


Figure 2. Mechanistic proposal for the synthesis of (*Z*)-vinyl halides **5**

Reactions of SmI_2 with optically active halides that result in racemization have been reported previously.[16] The isolation of **5** with high *de* from a mixture of diastereoisomers of **4** could be explained by assuming that the diastereoisomer with the more appropriate conformation for coordination of the samarium center to the carbonyl oxygen atom reacts directly, while the other diastereoisomer must epimerize before elimination can occur.

The lower (*Z*) selectivity observed in the synthesis of aromatic vinyl iodides can be explained by assuming a nonconcerted elimination reaction; the stabilization of the positive charge by resonance would induce prior cleavage of the C−O bond (**V** in Figure 2). In this case the most stable (*E*) diastereoisomer could be isolated by using Sm/CH_2I_2 at room temperature.

The synthesis of aliphatic vinyl iodides using SmI_2 generated in situ (instead of preformed SmI_2) is more suitable since the yields are higher, the *de* being (generally) similar or higher. When aromatic vinyl iodides were prepared, the (*E*) diastereoisomer could be obtained by using metallic samarium at room temperature. In the synthesis of vinyl bromides or chlorides a higher yield and a slight decrease in the *de* were obtained. In all cases, the total reaction time was shorter (120 min) than when a preformed samarium diiodide solution was used (210 min), and the methodology and the manipulation of Sm were simpler.

Conclusion

Herein we have presented an efficient method to obtain (*E*)-α,β-unsaturated esters and (*Z*)-vinyl halides by using samarium metal. This new methodology is simpler and easier than by using preformed SmI_2 because the generation of samarium diiodide in situ does not require a careful manipulation and storage that would be necessary if using a samarium diiodide solution. The total reaction time is shorter (45−120 min) than when using preformed SmI_2 (210 min). The yields of the products are also higher with similar or better diastereoisomeric excesses. When aromatic vinyl iodides were prepared, the (*E*) diastereoisomer could be isol-

ated by using samarium metal at room temperature. Only in the preparation of vinyl bromides or chlorides lower *de* values were obtained.

Experimental Section

General: Reactions requiring an inert gas were conducted under dry nitrogen, and the glassware was oven-dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased from Aldrich or Merck and were used without further purification. Silica gel for flash chromatography was purchased from Merck (230−400 mesh), and compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC200, AC300 or DPX300 spectrometers. All NMR spectra were registered at room temperature. ^{1}H NMR spectra were recorded at 200 or 300 MHz. ^{13}C NMR spectra and DEPT experiments were determined at 50 or 75 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants (*J*) are reported in Hz. The diastereoisomeric excesses were obtained using ^{1}H NMR analysis and GC-MS of crude products. GC-MS (HP-5973) and HRMS (Finnigan-MAT 95) were measured at 70 eV. Infrared spectra were measured with a Perkin−Elmer 1720-X FTIR. Only selected IR absorptions (in cm^{-1}) and the molecular ions and/or base peaks in the mass spectrum are given. Elemental analyses were determined with a Perkin−Elmer 2400 instrument and the optical rotation was measured with a Perkin−Elmer 241 polarimeter. The preparation and characterization of the following compounds are described in ref.[17]: methyl 2-chloro-3-hydroxydecanoate (**1a**), ethyl 2-chloro-3-hydroxy-2-methyldecanoate (**1b**), ethyl 2-chloro-3-cyclohexyl-3-hydroxy-2-methylpropanoate (**1c**), ethyl 2-bromo-2-butyl-3-hydroxy-3-phenylpropanoate (**1e**), ethyl 2-chloro-3-hydroxy-3-(4-methoxyphenyl)-2-methylpropanoate (**1f**), isopropyl 2-chloro-3-hydroxy-5,9-dimethyl-2-phenyldec-8-enoate (**1g**), ethyl 2-bromo-2-hexyl-3-hydroxy-4-phenylpentanoate (**1h**).

Synthesis of 2-Halo-3-hydroxy Esters 1: Lithium diisopropylamide [prepared from MeLi (6.4 mL of a 1.5 M solution in diethyl ether, 10 mmol) and diisopropylamine (1.4 mL, 10 mmol) in THF 50 mL at 0 °C] was added dropwise to a stirred solution of the corresponding 2-halo ester **3** (9 mmol) in dry THF (4 mL) at −85 °C. After stirring for 10 min, a solution of the corresponding aldehyde (6.75 mmol) in dry THF (4.5 mL) was added dropwise at −78 °C. After stirring for 1 h, the reaction mixture was quenched with an aqueous saturated solution of NH_4Cl (5 mL). The usual workup provided crude 2-halo-3-hydroxy esters **1**, which were purified by column flash chromatography on silica gel (hexane/ethyl acetate, 10:1) to give pure compounds **1**.

***tert*-Butyl 2-Chloro-3-(4-chlorophenyl)-3-hydroxypropanoate (1d):** Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 9 H), 1.49 (s, 9 H), 3.69 (d, *J* = 3.85 Hz, 1 H), 3.87 (d, *J* = 5.38 Hz, 1 H), 4.23 (d, *J* = 7.69 Hz, 1 H), 4.29 (d, *J* = 6.67 Hz, 1 H), 7.45−7.47 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3 (CH_3), 27.5 (CH_3), 63.1 (CH), 73.8 (CH), 74.3 (CH), 83.4 (C), 128.2 (CH), 128.3 (CH), 134.1 (C), 135.0 (C), 136.7 (C), 137.4 (C), 166.7 (C), 167.6 (C) ppm. IR (neat): ṽ = 3444, 1718 cm^{-1}. R_f (hexane/EtOAc, 20:1) = 0.3, 0.1 (two diastereoisomers).

Ethyl (*E*)-2-Bromo-2-hexyl-3-hydroxyhex-4-enoate (1i): Yield: 62%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.61−0.85 (m, 6 H), 0.91−1.35 (m, 20 H), 1.31−1.71 (m, 6 H), 1.84−2.10 (m, 6 H), 2.95−3.26 (m, 2 H), 3.87−4.25 (m, 6 H), 5.29−5.71 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.4 (CH_3), 17.2 (CH_3), 17.3 (CH_3), 21.9 (CH_2), 25.0 (CH_2), 25.2 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 30.9 (CH_2), 37.6 (CH_2), 37.8 (CH_2), 61.6 (CH_2), 61.7 (CH_2), 74.6 (C), 74.9 (C), 76.4 (CH), 76.5 (CH), 128.2 (CH), 128.4 (CH), 129.4 (CH), 130.3 (CH), 168.9 (C), 169.4 (C) ppm. IR (neat): ṽ = 3435, 1731 cm^{-1}. R_f (hexane/EtOAc 10:1) = 0.3.

Synthesis of (*E*)-α,β-Unsaturated Esters 2: A solution of the corresponding 2-halo-3-hydroxy ester **1** (0.4 mmol) in THF (2 mL) at room temperature was added to a suspension of samarium powder (1.1 mmol) in THF (12 mL). The mixture was cooled to 0 °C and diiodomethane (1 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 h. The excess of Sm^{II} was transformed into Sm^{III} by bubbling a stream of air through the reaction mixture before hydrolysis. The reaction mixture was then quenched with aqueous HCl (1 M, 5 mL). Standard workup and filtration through a pad of Celite provided pure α,β-unsaturated esters **2**. Yields are reported in the text.

Methyl (*E*)-Dec-2-enoate (2a): The spectroscopic data are in agreement with those reported previously.[18]

Ethyl (*E*)-2-Methyldec-2-enoate (2b):[19] ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2 (CH_3), 14.0 (CH_3), 14.2 (CH_3), 22.5 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 60.3 (CH_2), 127.5 (C), 142.4 (CH), 168.3 (C) ppm. IR (neat): ṽ = 2978, 2586, 1712, 1650, 1387 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

Ethyl (*E*)-3-Cyclohexyl-2-methylpropenoate (2c): The spectroscopic data are in agreement with those reported previously.[20]

***tert*-Butyl (*E*)-3-(4-Chlorophenyl)propenoate (2d):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 9 H), 6.34 (d, *J* = 16.31 Hz, 1 H), 7.31 (d, *J* = 8.72 Hz, 2 H), 7.42 (d, *J* = 8.72 Hz, 2 H), 7.53 (d, *J* = 16.31 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.0 (CH_3), 80.6 (C), 120.6 (CH), 129.0 (CH), 133.0 (C), 135.7 (C), 142.0 (CH), 165.9 (C) ppm. MS (70 eV): *m*/*z* (%) = 240 (2) $[M + 2]^+$, 238 (6) $[M]^+$, 182 (100), 165 (61), 137 (19). IR (neat): ṽ = 3005, 1707, 1636 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.4.

Ethyl (*E*)-2-Butyl-3-phenylpropenoate (2e):[21] MS (70 eV): *m*/*z* (%) = 232 (58) $[M]^+$, 203 (25), 187 (32), 159 (13), 91 (77). HRMS calcd. for $C_{15}H_{20}O_2$ 232.3181; found 232.1463. IR (neat): ṽ = 3025, 1708, 1652 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

Ethyl (*E*)-3-(4-Methoxyphenyl)-2-methylpropenoate (2f):[21] MS (70 eV): *m*/*z* (%) = 220 (100) $[M]^+$, 191 (32), 175 (85), 147 (83), 131 (72), 91 (75), 77 (59). IR (neat): ṽ = 2975, 1702, 1605 cm^{-1}. R_f (hexane/EtOAc, 5:1) = 0.4.

Isopropyl (*E*)-5,9-Dimethyl-2-phenyldec-2,8-dienoate (2g): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.53 Hz, 3 H), 0.95−2.16 (m, 7 H), 1.25 (d, *J* = 6.11 Hz, 6 H), 1.57 (s, 3 H), 1.68 (s, 3 H), 5.04−5.13 (m, 2 H), 7.03−7.39 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5 (CH_3), 19.5 (CH_3), 21.6 (CH_3), 25.3 (CH_2), 25.5 (CH_3), 32.6 (CH), 36.4 (CH_2), 36.6 (CH_2), 67.9 (CH), 124.3 (CH), 127.0 (CH), 127.6 (CH), 129.6 (CH), 131.1 (C), 134.7 (C), 135.5 (C), 143.5 (CH), 166.6 (C) ppm. IR (neat): ṽ = 3015, 1705, 1655, 1480 cm^{-1}. $C_{21}H_{30}O_2$ (314.5): calcd. C 80.21, H 9.62; found C 79.89, H 9.66. R_f (hexane/EtOAc, 5:1) = 0.5.

Ethyl (*E*)-2-Hexyl-4-phenylpent-2-enoate (2h): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87−0.89 (m, 3 H), 1.24−1.43 (m, 14 H), 2.35−2.40 (m, 2 H), 3.75−3.85 (m, 1 H), 4.19 (q, *J* = 7.12 Hz, 2 H), 6.84 (d, *J* = 10.02 Hz, 1 H), 7.15−7.38 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.1 (CH_3), 21.5 (CH_3), 22.4 (CH_2), 26.8

(CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.5 (CH_2), 38.3 (CH), 60.3 (CH_2), 126.3 (CH), 126.8 (CH), 128.5 (CH), 131.2 (C), 144.5 (C), 145.5 (CH), 167.9 (C) ppm. MS (70 eV): *m*/*z* (%) = 288 (17) $[M]^+$, 273 (2), 243 (16), 215 (89). IR (neat): $\tilde{\nu}$ = 2958, 1710, 1642 cm^{-1}. $C_{19}H_{28}O_2$ (288.4): calcd. C 79.12, H 9.78; found C 78.87, H 9.81. R_f (hexane/EtOAc, 10:1) = 0.4.

Ethyl (2*E*,4*E*)-2-Hexylhex-2,4-dienoate (2i): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83−1.32 (m, 14 H), 1.86 (dd, *J* = 6.65, 1.54 Hz, 3 H), 2.32−2.49 (m, 2 H), 4.18 (q, *J* = 7.18 Hz, 2 H), 5.98−6.15 (m, 1 H), 6.27−6.41 (m, 1 H), 7.13 (d, *J* = 11.02 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.2 (CH_3), 18.7 (CH_3), 22.5 (CH_2), 26.7 (CH_2), 29.0 (CH_2), 29.5 (CH_2), 31.5 (CH_2), 60.2 (CH_2), 127.1 (CH), 129.9 (C), 138.5 (CH), 138.3 (CH), 168.3 (C) ppm. MS (70 eV): *m*/*z* (%) = 224 (42) $[M]^+$, 209 (29), 195 (7), 179 (28), 151 (18), 139 (23). $C_{14}H_{24}O_2$ (224.3): calcd. C 74.95, H 10.78; found C 74.89, H 10.80. IR (neat): $\tilde{\nu}$ = 2359, 2342, 1718 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

Synthesis of *O*-Acetylated 1,1-Dihaloalkan-2-ols 4: Lithium diisopropylamide [prepared from BuLi (12.5 mL, 1.6 M solution in hexanes, 20 mmol), and diisopropylamine (2.82 mL, 20 mmol) in THF (20 mL) at 0 °C] was added dropwise at −78 °C to a solution of the corresponding aldehyde (10 mmol) and dihalomethane (20 mmol) in THF (20 mL). After stirring for 2 h, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (10 mL). Standard workup provided crude 1,1-dihaloalkan-2-ols. The *O*-acetylation reaction was carried out by treatment of the corresponding 1,1-dihaloalkan-2-ol (1 mmol) with pyridine (10 mL), acetic anhydride (10 mL), and a catalytic amounts of DMAP (5 mg). The reaction mixture was stirred for 12 h at room temperature, then the reaction was quenched with ice-cold water (30 mL). Usual workup provided crude *O*-acetylated 1,1-dihaloalkan-2-ols, which were purified by column flash chromatography on silica gel (hexane/ethyl acetate, 10:1) to provide pure compounds **4**.

1,1-Diiodonon-2-yl Acetate (4a): Yield: 86%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88−0.90 (m, 3 H), 1.12−1.52 (m, 12 H), 2.16 (s, 3 H), 4.45−4.47 (m, 1 H), 5.30 (d, *J* = 3.53 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −21.4 (CH_3), 13.9 (CH_3), 20.7 (CH_3), 22.2 (CH_2), 24.7 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 31.3 (CH_2), 33.4 (CH_2), 76.5 (CH), 169.3 (C) ppm. MS (70 eV): *m*/*z* (%) = 378 (24), 311 (33), 269 (20), 167 (21), 123 (65), 81 (68), 43 (100). IR (neat): $\tilde{\nu}$ = 2051, 2928, 2856, 1745, 1464, 1371, 1222, 1078, 1020, 974 cm^{-1}. $C_{11}H_{20}I_2O_2$ (438.1): calcd. C 30.16, H 4.60; found C 30.15, H 4.66. R_f (hexane/EtOAc, 10:1) = 0.5.

1-Cyclohexyl-2,2-diiodoethyl Acetate (4b): Yield: 82%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85−1.15 (m, 5 H), 1.72 (m, 6 H), 2.05 (s, 3 H), 4.37−4.39 (m, 1 H), 5.24 (d, *J* = 3.52 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −23.6 (CH), 20.6 (CH_3), 25.1 (CH_2), 25.4 (CH_2), 27.2 (CH_2), 28.4 (CH_2), 42.2 (CH), 79.8 (CH), 169.2 (C) ppm. MS (70 eV): *m*/*z* (%) = 422 (< 1) $[M]^+$, 362 (23), 295 (18), 253 (26), 235 (49), 125 (60), 107 (56), 55 (80), 43 (100). IR (neat): $\tilde{\nu}$ = 2925, 2852, 1745, 1369, 1224, 1184, 1076, 1016, 974 cm^{-1}. $C_{10}H_{16}I_2O_2$ (422.0): calcd. C 28.46, H 3.82; found C 28.51, H 3.79. R_f (hexane/EtOAc, 20:1) = 0.4.

1,1-Diiodo-3-phenylbut-2-yl Acetate (4c): Yield: 72%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.98 Hz, 3 H), 2.26 (s, 3 H), 2.92−2.95 (m, 1 H), 4.81 (d, *J* = 2.18 Hz, 1 H), 4.94 (dd, *J* = 10.03, 2.18 Hz, 1 H), 7.18−7.39 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −23.3 (CH), 18.1 (CH_3), 20.9 (CH_3), 45.2 (CH), 80.5 (CH), 127.2 (CH), 127.3 (CH), 128.9 (CH), 141.0 (C), 169.9 (C) ppm. MS (70 eV): *m*/*z* (%) = 443 (5) $[M]^+$, 383 (21), 316 (12), 257 (44), 130 (34), 105 (100), 77 (19), 43 (79). IR (neat): $\tilde{\nu}$ = 3074, 3011, 2978, 2945, 1745, 1499, 1478, 1220, 1074, 975 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

1,1-Diiodo-4,8-dimethylnon-7-en-2-yl Acetate (4d): Yield: 93%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87−1.02 (m, 3 H), 1.04−1.88 (m, 13 H), 2.14 (s, 3 H), 4.49−4.55 (m, 1 H), 5.07−5.09 (m, 1 H), 5.30−5.32 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −21.2 (CH), −20.8 (CH), 17.2 (CH_3), 18.9 (CH_3), 19.4 (CH_3), 20.4 (CH_3), 24.4 (CH_2), 24.7 (CH_2), 25.2 (CH), 27.9 (CH), 28.3 (CH), 35.4 (CH_2), 36.6 (CH_2), 39.9 (CH_2), 40.0 (CH_2), 74.2 (CH), 74.5 (CH), 123.7 (CH), 130.7 (C), 169.1 (C), 169.2 (C) ppm. MS (70 eV): *m*/*z* (%) = 464 (4) $[M]^+$, 422 (25), 404 (20), 340 (26), 337 (12), 43 (100). IR (neat): $\tilde{\nu}$ = 2964, 1741, 1455, 1369, 1226, 1021 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

(3*S*)-3-Benzyloxy-1,1-diiodobut-2-yl Acetate (4e): Yield: 58%. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.17 Hz, 3 H), 1.24 (d, *J* = 6.16 Hz, 3 H), 2.20 (s, 3 H), 2.27 (s, 3 H), 3.61−3.63 (m, 1 H), 4.25 (qd, *J* = 6.16, 3.52 Hz, 1 H), 4.44 and 4.66 (AB syst., *J* = 11.45 Hz, 2 H), 4.47 and 4.64 (AB syst., *J* = 10.86 Hz, 2 H), 4.77 (dd, *J* = 7.92, 2.64 Hz, 1 H), 5.12 (dd, *J* = 8.51, 3.52 Hz, 1 H), 5.26 (d, *J* = 8.51 Hz, 1 H), 5.61, (d, *J* = 2.65 Hz, 1 H), 7.28−7.40 (m, 10 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = −28.6 (CH), −25.8 (CH), 15.0 (CH_3), 16.2 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 67.9 (CH_2), 71.3 (CH_2), 71.4 (CH), 73.0 (CH), 78.8 (CH), 79.1 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 137.4 (C), 137.6 (C), 169.7 (C), 169.9 (C) ppm. MS (70 eV): *m*/*z* (%) = 287 (2), 181 (29), 135 (80), 107 (45), 91 (100), 43 (72). IR (neat): $\tilde{\nu}$ = 2953, 2854, 1736, 1462 cm^{-1}. R_f (hexane/EtOAc, 20:1) = 0.3.

(*E*)-1,1-Diiodopent-3-en-2-yl Acetate (4f): Yield: 71%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.76 (dd, *J* = 4.79, 1.75 Hz, 3 H), 2.05 (s, 3 H), 5.00 (dd, *J* = 6.97, 3.92 Hz, 1 H), 5.14 (d, *J* = 3.93 Hz, 1 H), 5.46 (ddq, *J* = 8.28, 6.98, 1.74 Hz, 1 H), 5.89−6.00 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −21.3 (CH), 17.8 (CH), 20.8 (CH_3), 77.3 (CH), 126.3 (CH), 133.6 (CH), 168.8 (C) ppm. MS (70 eV): *m*/*z* (%) = 380 (< 1) $[M]^+$, 320 (12), 267 (21), 41 (100). IR (neat): $\tilde{\nu}$ = 2985, 2881, 1743, 1625, 1412, 1219, 945 cm^{-1}. R_f (hexane/EtOAc, 20:1) = 0.3.

2,2-Diiodo-1-phenylethyl Acetate (4g): Yield: 72%. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 5.31 (d, *J* = 5.73 Hz, 1 H), 5.94 (d, *J* = 5.72 Hz, 1 H), 7.24−7.45 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −22.1 (CH), 20.7 (CH_3), 78.8 (CH), 126.8 (CH), 128.1 (CH), 128.7 (CH), 136.3 (C), 168.6 (C) ppm. MS (70 eV): *m*/*z* (%) = 416 (2) $[M]^+$, 289 (80), 162 (51), 91 (38), 77 (44), 43 (100). IR (neat): $\tilde{\nu}$ = 3098, 3014, 2987, 2945, 1745, 1495, 1378, 1240, 1109, 985 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

2,2-Diiodo-1-(4-methoxyphenyl)ethyl Acetate (4h): Yield: 82%. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.15 (s, 3 H), 3.74 (s, 3 H), 5.27 (d, *J* = 6.00 Hz, 1 H), 5.85 (d, *J* = 6.00 Hz, 1 H), 6.86 (d, *J* = 8.72 Hz, 2 H), 7.31 (d, *J* = 8.72 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −20.4 (CH), 20.6 (CH_3), 54.8 (CH_3), 78.5 (CH), 113.4 (CH), 128.0 (CH), 128.2 (CH), 159.4 (C), 168.4 (C) ppm. MS (70 eV): *m*/*z* (%) = 446 (10) $[M]^+$, 277 (63), 259 (72), 149 (82), 137 (100), 121 (81), 43 (78). IR (neat): $\tilde{\nu}$ = 3052, 2958, 1747 cm^{-1}. R_f (hexane/EtOAc, 5:1) = 0.4.

1-(Furan-2-yl)-2,2-diiodoethyl Acetate (4i): Yield: 85%. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 5.31 (d, *J* = 7.04 Hz, 1 H), 5.89 (d, *J* = 7.04 Hz, 1 H), 6.26−6.28 (m, 1 H), 6.41−6.43 (m, 1 H), 7.33−7.35 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = −27.4 (CH), 20.4 (CH_3), 72.6 (CH), 110.1 (CH), 110.2 (CH), 142.3 (CH), 147.8 (C), 168.1 (C) ppm. MS (70 eV): *m*/*z* (%) = 406 (9) $[M]^+$, 237 (100), 219 (83), 139 (48), 97 (55), 43 (95). IR (neat): $\tilde{\nu}$ =

1745, 1369, 1222, 1213, 1149, 1078, 1016, 746 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.4.

1,1-Dibromonon-2-yl Acetate (4j): Yield: 62%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.74−0.76 (m, 3 H), 0.91−1.45 (m, 12 H), 2.00 (s, 3 H), 4.93−4.95 (m, 1 H), 5.68 (d, *J* = 3.48 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 20.3 (CH_3), 22.2 (CH_2), 24.8 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 30.6 (CH_2), 31.4 (CH_2), 45.9 (CH), 75.8 (CH), 169.4 (C) ppm. MS (70 eV): *m*/*z* (%) = 171 (24) $[M]^+$, 123 (23), 111 (74), 43 (100). IR (neat): ṽ = 2957, 2935, 2922, 1745, 1464, 1371, 1221, 1159, 1078, 1022, 717, 696 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.7.

1,1-Dichlorononon-2-yl Acetate (4k): Yield: 76%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85−0.87 (m, 3 H), 1.11−1.51 (m, 12 H), 2.11 (s, 3 H), 5.12−5.14 (m, 1 H), 5.78 (d, *J* = 3.52 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH3), 20.4 (CH_3), 22.3 (CH_2), 24.8 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 30.0 (CH_2), 31.5 (CH_2), 72.3 (CH), 75.8 (CH), 169.8 (C) ppm. MS (70 eV): *m*/*z* (%) = 111 (12), 55 (10), 43 (100). IR (neat): ṽ = 2957, 2926, 2858, 1751, 1465, 1438, 1373, 1226, 1082, 1026, 779 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.6.

1-Chloro-1-iodonon-2-yl acetate (4l): Yield: 86%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83−0.85 (m, 6 H), 1.09−1.51 (m, 24 H), 2.08 (s, 3 H), 2.09 (s, 3 H), 4.69−4.72 (m, 1 H), 4.83−4.86 (m, 1 H), 5.81−5.83 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 20.7 (CH_3), 22.5 (CH_2), 24.9 (CH_2), 25.0 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 31.3 (CH), 31.6 (CH_2), 76.6 (CH), 77.0 (CH), 169.8 (C) ppm. MS (70 eV): *m*/*z* (%) = 346 (< 1) $[M]^+$, 219 (31), 123 (19), 81 (20), 43 (100). IR (neat): ṽ = 2955, 2928, 2856, 1749, 1458, 1371, 1224, 1024 cm^{-1}. $C_{11}H_{20}ClIO_2$ (346.6): calcd. C 38.11, H 5.82; found C 38.08, H 6.01. R_f (hexane/EtOAc, 10:1) = 0.5.

2-Bromo-2-chloro-1-cyclohexylethyl Acetate (4m): Yield: 82%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80−1.23 (m, 10 H), 1.38−1.72 (m, 12 H), 2.02 (s, 3 H), 2.03 (s, 3 H), 4.88 (dd, *J* = 7.36, 4.16 Hz, 1 H), 5.02 (dd, *J* = 7.36, 3.81 Hz, 1 H), 5.77 (d, *J* = 4.16 Hz, 1 H), 5.83 (d, *J* = 3.81 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2 (CH), 25.1 (CH_2), 25.2 (CH_2), 25.5 (CH_2), 27.0 (CH_2), 27.3 (CH_2), 28.5 (CH_2), 39.2 (CH), 39.6 (CH), 58.8 (CH), 59.7 (CH), 78.6 (CH), 79.0 (CH), 169.4 (C) ppm. MS (70 eV): *m*/*z* (%) = 155 (14), 95 (100), 43 (51). IR (neat): ṽ = 2933, 2856, 1745, 1448, 1371, 1226, 1186, 1087, 1064, 1045, 1018, 758, 717 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

1-Chloro-1-iodo-3-phenylbut-2-yl Acetate (4n): Yield: 75%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.30 (dd, *J* = 7.08, 3.01 Hz, 6 H), 2.26 (s, 3 H), 2.29 (s, 3 H), 2.97−2.99 (m, 1 H), 2.25−2.27 (m, 1 H), 4.75 (dd, *J* = 9.76, 2.18 Hz, 1 H), 5.34 (d, *J* = 2.18 Hz, 1 H), 5.49 (d, *J* = 2.23 Hz, 1 H), 5.62 (dd, *J* = 10.03, 1.96 Hz, 1 H), 7.12−7.38 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH), 18.0 (CH), 20.4 (CH_3), 20.5 (CH_3), 28.2 (CH), 32.9 (CH), 41.8 (CH), 44.3 (CH), 79.2 (CH), 80.9 (CH), 127.1 (CH), 128.0 (CH), 128.7 (CH), 128.8 (CH), 140.6 (C), 140.8 (C), 169.5 (C), 169.6 (C) ppm. MS (70 eV): *m*/*z* (%) = 226 (9), 225 (24), 167 (22), 165 (62), 106 (31), 105 (100), 43 (74). IR (neat): ṽ = 3029, 2975, 2934, 1750, 1494, 1453, 1371, 1218, 1077, 1050, 1019, 764, 701 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

1-Bromo-1-chloro-4,8-dimethylnon-7-en-2-yl Acetate (4o): Yield: 87%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90−2.90 (m, 16 H), 2.10 (br. s, 3 H), 5.00−5.26 (m, 2 H), 5.81 (br. d, *J* = 3.27 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3 (CH_3), 18.8 (CH_3), 18.9 (CH_3), 19.8 (CH_3), 20.3 (CH_3), 24.7 (CH_2), 25.0 (CH_2), 25.4 (CH_3), 28.2 (CH), 28.5 (CH), 35.5 (CH_2), 35.6 (CH_2), 36.2 (CH_2), 36.4 (CH_2), 36.6 (CH_2), 36.8 (CH_2), 37.1 (CH_2), 60.3 (CH), 60.4 (CH), 60.5 (CH), 60.6 (CH), 73.8 (CH), 74.0 (CH), 74.2 (CH), 124.0 (CH), 130.9 (C), 131.0 (C), 169.4 (C), 169.5 (C), 169.6 (C) ppm. MS (70 eV): *m*/*z* (%) = 327 (22), 325 (20), 285 (38), 283 (34), 267 (42), 265 (34), 249 (33), 247 (30), 203 (29), 201 (31), 183 (31), 43 (100). IR (neat): ṽ = 2961, 2926, 1750, 1373, 1224 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.5.

Synthesis of (*Z*)-Vinyl Halides 5: A solution of the corresponding *O*-acetylated dihaloalkan-2-ol (0.4 mmol) in THF (2 mL) was added at room temperature to a suspension of samarium powder (1.1 mmol) in THF (12 mL). The mixture was cooled to 0 °C and diiodomethane (1 mmol) was added dropwise. The reaction was performed according to the conditions indicated in Tables 3 and 4. The reaction was then quenched with aqueous HCl (1 M, 5 mL). Usual workup and purification by short-column chromatography (silica gel, hexane as eluent) provided the pure (*Z*)-vinyl halides **5**. Yields are reported in the text.

(*Z*)-1-Iodonon-1-ene (5a):[22] ^1H NMR (300 MHz, $CDCl_3$): δ = 0.72−0.95 (m, 3 H), 1.10−1.45 (m, 10 H), 2.10−2.21 (m, 2 H), 6.11−6.27 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 27.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 34.6 (CH_2), 82.0 (CH), 141.4 (CH) ppm. MS (70 eV): *m*/*z* (%) = 252 (60) $[M]^+$, 167 (23), 154 (14), 83 (58), 69 (100), 55 (61), 41 (52). IR (neat): ṽ = 2924, 1458, 909 cm^{-1}. R_f (hexane) = 0.8.

(*Z*)-2-Cyclohexyl-1-iodoethene (5b): The spectroscopic data are identical to those reported previously.[23a]

(*Z*)-1-Iodo-3-phenylbut-1-ene (5c): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.98 Hz, 3 H), 3.82−3.90 (m, 1 H), 6.24−6.33 (m, 2 H), 7.21−7.40 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9 (CH_3), 44.5 (CH), 80.9 (CH), 126.4 (CH), 126.9 (CH), 128.4 (CH), 143.7 (C), 145.4 (CH) ppm. MS (70 eV): *m*/*z* (%) = 258 (< 1) $[M]^+$, 131 (100), 116 (20), 105 (10), 91 (17). IR (neat): ṽ = 2980, 1602, 1492, 1450, 915 cm^{-1}. $C_{10}H_{11}I$ (258.1): calcd. C 46.54, H 4.30; found C 46.56, H 4.35. R_f (hexane) = 0.6.

(*Z*)-1-Iodo-4,8-dimethylnona-1,7-diene (5d): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.54 Hz, 3 H), 1.15−1.45 (m, 2 H), 1.53−1.75 (m, 7 H), 1.89−2.30 (m, 4 H), 5.07-5-14 (m, 1 H), 6.17−6.27 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH_3), 19.5 (CH_3), 25.5 (CH_2), 25.7 (CH_3), 32.0 (CH), 36.6 (CH_2), 41.6 (CH_2), 83.0 (CH), 124.5 (CH), 131.3 (C), 140.1 (CH) ppm. MS (70 eV): *m*/*z* (%) = 278 (< 1) $[M]^+$, 194 (13), 167 (17), 109 (31), 95 (72), 81 (40), 69 (100), 41 (74). IR (neat): ṽ = 2964, 2920, 1632, 1465, 1450, 1370, 738 cm^{-1}. $C_{11}H_{19}I$ (278.2): calcd. C 47.49, H 6.88; found C 47.47, H 6.92. R_f (hexane) = 0.7.

(3*S*,*Z*)-3-Benzyloxy-1-iodobut-1-ene (5e): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 6.27 Hz, 3 H), 4.31−4.33 (m, 1 H), 4.52 (AB syst., *J* = 11.72 Hz, 2 H), 6.26−6.28 (m, 1 H), 6.44 (d, *J* = 7.63 Hz, 1 H), 7.39−7.41 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9 (CH_3), 70.5 (CH_2), 77.2 (CH), 82.8 (CH), 127.5 (CH), 127.8 (CH), 128.3 (CH), 138.2 (C), 142.9 (CH) ppm. MS (70 eV): *m*/*z* (%) = 288 (29) $[M]^+$, 197 (22), 181 (21), 161 (70), 107 (30), 105 (71), 91 (100). IR (neat): ṽ = 3063, 3030, 2974, 1606, 1454, 1271, 1064 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.7. $[\alpha]_D^{18}$ = +64.3 (*c* = 1.30, $CHCl_3$).

(*Z*)-1-Iodopenta-1,3-diene (5f):[24] ^1H NMR (300 MHz, $CDCl_3$): δ = 1.81 (d, *J* = 6.54 Hz, 3 H), 5.91−6.13 (m, 2 H), 6.14−6.31 (m, 1 H), 6.67 (dd, *J* = 9.59, 7.84 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 (CH_3), 79.0 (CH), 131.7 (CH), 134.9 (CH), 138.3 (CH). R_f (hexane) = 0.6.

1-Iodo-2-phenylethene (5g). (*E*) Isomer:[22] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 15.25 Hz, 1 H), 7.23−7.73 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.6 (CH), 125.8 (CH), 128.0 (CH), 128.2 (CH), 137.5 (C), 144.8 (CH). **(*Z*) Isomer:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 8.72 Hz, 1 H), 7.23−7.73 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 79.3 (CH), 125.8 (CH), 128.0 (CH), 128.6 (CH), 136.5 (C), 138.4 (CH) ppm. MS (70 eV): *m*/*z* (%) = 230 (100) $[M]^+$, 103 (64), 77 (35). IR (neat): $\tilde{\nu}$ = 3059, 1595, 1568, 1495, 947, 727 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.7.

(*E*)-1-Iodo-2-(4-methoxyphenyl)ethene (5h): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.64 (d, *J* = 14.82 Hz, 1 H), 7.25 (d, *J* = 8.72 Hz, 2 H), 7.36 (d, *J* = 14.82 Hz, 1 H), 7.65 (d, *J* = 8.72 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.1 (CH_3), 73.5 (CH), 113.9 (CH), 127.2 (CH), 137.7 (C), 144.2 (CH), 159.5 (C) ppm. MS (70 eV): *m*/*z* (%) = 260 (100) $[M]^+$, 133.2 (41). IR (neat): $\tilde{\nu}$ = 3055, 2964, 1604, 1508, 1458, 1253, 841 cm^{-1}. R_f (hexane/EtOAc, 10:1) = 0.6.

(*E*)-2-(2-Iodovinyl)furan (5i): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 14.82 Hz, 1 H), 7.20 (d, *J* = 14.82 Hz, 1 H), 7.36−7.39 (m, 2 H), 7.48 (d, *J* = 1.75 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 74.3 (CH), 108.3 (CH), 111.1 (CH), 132.6 (CH), 142.7 (CH), 152.9 (C) ppm. MS (70 eV): *m*/*z* (%) = 220 (100) $[M]^+$, 65 (55), 39 (22). IR (neat): $\tilde{\nu}$ = 2957, 1481, 1307, 1253, 1222, 1151, 1014, 736 cm^{-1}. R_f (hexane) = 0.5.

(*Z*)-1-Bromonon-1-ene (5j):[25] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79−0.91 (m, 3 H), 1.21−1.40 (m, 10 H), 2.16−2.23 (m, 2 H), 6.07−6.16 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 28.0 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 107.4 (CH), 135.0 (CH) ppm. MS (70 eV): *m*/*z* (%) = 206 (62) $[M + 2]^+$, 204 (64) $[M]^+$, 164 (10), 162 (11), 150 (20), 148 (18), 125 (25), 83 (43), 69 (100), 55 (64), 41 (57). IR (neat): $\tilde{\nu}$ = 2965, 2923, 1622, 1458, 939 cm^{-1}. R_f (hexane) = 0.9.

(*Z*)-1-Chlorononon-1-ene (5k):[25] ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87−0.94 (m, 3 H), 1.18−1.45 (m, 10 H), 2.11−2.29 (m, 2 H), 5.75−5.77 (m, 1 H), 6.01 (dt, *J* = 8.51, 1.46 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 26.9 (CH_2), 28.3 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 31.7 (CH_2), 117.7 (CH), 131.8 (CH) ppm. MS (70 eV): *m*/*z* (%) = 160 (37) $[M]^+$, 95 (32), 82 (73), 69 (62), 55 (80), 41 (100). IR (neat): $\tilde{\nu}$ = 2967, 1629, 1486, 1465, 910 cm^{-1}. R_f (hexane/EtOAc, 20:1) = 0.3.

(*Z*)-1-Chloro-2-cyclohexylethene (5m): The spectroscopic data are identical to those reported previously.[26]

(*Z*)-1-Chloro-3-phenylbut-1-ene (5n): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.98 Hz, 3 H), 4.14−4.16 (m, 1 H), 5.93 (dd, *J* = 9.15, 6.97 Hz, 1 H), 6.08 (d, *J* = 6.97 Hz, 1 H), 7.20−7.39 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5 (CH_3), 37.1 (CH), 116.8 (CH), 126.2 (CH), 126.7 (CH), 128.4 (CH), 136.3 (CH), 144.4 (C) ppm. MS (70 eV): *m*/*z* (%) = 166 (12) $[M]^+$, 131 (100), 115 (52), 91 (24), 77 (13), 51 (17). IR (neat): $\tilde{\nu}$ = 3030, 2968, 2930, 2874, 1747, 1626, 1452, 1226 cm^{-1}. $C_{10}H_{11}Cl$ (166.6): calcd. C 72.07, H 6.65; found C 72.04, H 6.71. R_f (hexane) = 0.5.

(*Z*)-1-Chloro-4,8-dimethylnona-1,7-diene (5o): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.54 Hz, 3 H), 1.09−1.45 (m, 2 H), 1.49−1.70 (m, 7 H), 1.82−2.32 (m, 4 H), 5.11−5.15 (m, 1 H), 5.78−5.80 (m, 1 H), 6.05−6.07 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5 (CH_3), 19.4 (CH_3), 25.5 (CH_2), 25.6 (CH_3), 32.2 (CH), 33.9 (CH_2), 36.5 (CH_2), 118.5 (CH), 124.6 (CH), 130.4 (CH), 131.2 (C) ppm. MS (70 eV): *m*/*z* (%) = 186 (< 1) $[M]^+$, 109 (25), 81 (20), 59 (100). IR (neat): $\tilde{\nu}$ = 2960, 2926, 1629, 1460, 1450, 1377, 746 cm^{-1}. $C_{11}H_{19}Cl$ (186.7): calcd. C 70.76, H 10.26; found C 70.74, H 10.32. R_f (hexane) = 0.5.

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