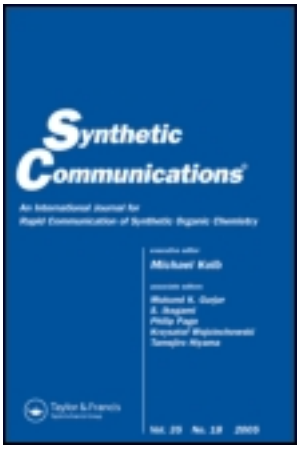

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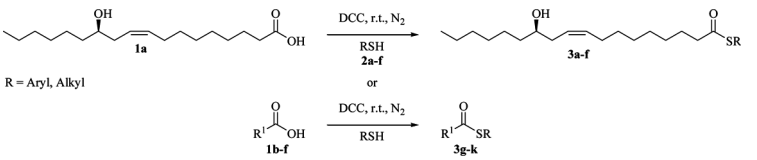
GRAPHICAL ABSTRACT



Abstract *The synthesis of several ricinoleic acid thiol esters starting from* cis-(R)*-12-hydroxyoctadec-9-enoic acid and thiols in the presence of N,N′-dicyclohexylcarbodiimide (DCC) is described. The method is efficient for aromatic and aliphatic thiols, selectively affording the respective fat acid thiol esters in good yields under mild, neutral, and solvent-free conditions. The protocol is general and was extended to other carboxylic acids, furnishing the desired products in satisfactory yields. The (*R,Z*)-12-hydroxy-octadec-9-enylic acid benzylthiol ester **3a** was successfully reduced to (*R,Z*)-12-hydroxyoctadec-9-enal **4**.*

Keywords Green chemistry; ricinoleic acid; solvent-free reaction; thiol esters

INTRODUCTION

Ricinoleic acid, (*R,Z*)-12-hydroxyoctadec-9-enoic acid, is an important commodity in the chemical and pharmaceutical industry in view of its high functionality.[1] This renewable raw material is easily available from castor bean oil and is used in processes for preparation of several compounds of interest for fine chemistry. Ricinoleic acid presents some peculiar chemical properties, making it an attractive, enantiomerically pure building block for the development of new, simple, and efficient strategies for the synthesis of complex molecules.[1g,h] Thiol esters play important roles in acyl group transfer in biological systems,[2] such as coenzyme A

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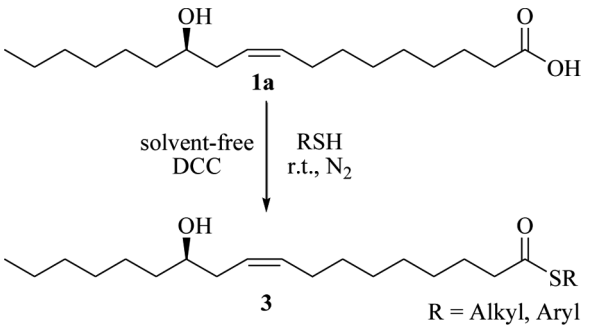


Scheme 1. General scheme of the reaction.

and *S*-acetyl dihydrolipoic acid,[2a–c] and in the biosynthesis of polyketides and nonribosomal polypeptides.[2d] More recently, it was demonstrated that 2-pyridine thiol esters have good antitumor activity.[3]

The use of thiol esters in organic synthesis goes beyond the acylating capability and includes their conversion to ketones,[4a,b] β-lactones,[4c–e] aldehydes,[4f,g] and vinyl sulfides[4h] and their use in the reductive alkylation of amines.[4i] Besides, *S*-thioester enolization has been extensively studied and can be carried out in a highly stereoselective fashion under a variety of conditions.[4j–m] Because of their biological activities, as well as their synthetic versatility, a number of methods for the preparation of thiol esters have been described. Most of them involve the condensation of a thiol with carbonyl compounds, such as acyl halides,[3,5a–e] anydrides,[5f] aldehydes,[5g] and carboxylic acids in the presence of a coupling reagent, base, and an organic solvent.[5h–k] Despite the vast range of described methods for thiol esters, several of them require vigorous reaction conditions (high temperature, long reaction time); the use of toxic, expensive, and air- and moisture-sensitive metal catalysts and volatile organic solvents; and the necessity, in some cases, of preparing the acylating starting material. Some of these drawbacks were partially circumvented with the use of acyl phosphate in aqueous media[6a] and by means of the thiocarbonylation of iodoarenes in the presence of ionic liquids.[6b]

In the past few years, our group has studied the use of renewable feedstocks in organic synthesis, following green and sustainable chemistry principles.[7] As a continuation of our studies, we report herein the preparation of thiol esters directly from ricinoleic acid and thiols under mild, neutral, and solvent-free conditions (Scheme 1).

In our solvent-free approach, easily available dicyclohexylcarbodiimide (DCC) was used as coupling reagent in the absence of base, allowing the direct use of carboxylic acids in the thio-esterification step.[8,9]

RESULTS AND DISCUSSION

Our initial efforts were focused on the preparation of the benzylthiol ester **3a**, derived from ricinoleic acid **1a** and benzylthiol **2a**. We examined the temperature, use of solvent, base, and inert atmosphere. To the best of our knowledge, the methods described for the preparation of thiol esters starting from carboxylic acids use basic

conditions and are conducted in the presence of an organic solvent.[4,5,8] The reaction progress was followed by thin-layer chromatography (TLC), and we observed that when a solution of benzylthiol **2a** (1.2 mmol) and ricinoleic acid **1a** (1.0 mmol) in tetrahydrofuran (THF) (5 mL) was stirred in the presence of diisopropylethylamine (DIPEA) (1.0 mmol) and N,N′-dicyolohexylcarbodiimide (DCC) (1.0 mmol) under N_2, the respective thiol ester **3a** was obtained in 68% yield after 6 h at room temperature.

Aiming to reduce the reaction time and to improve the yield, we tested several other bases [KF/Al_2O_3, 50%; Et_3N, diazabicyclo[2.2.2]octane (DABCO), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)], as well as other different solvents, such as benzene and dichloromethane. However, the product was not obtained in yields superior to 60–70%, even under mild heating (60 °C) or longer reaction time (24 h).

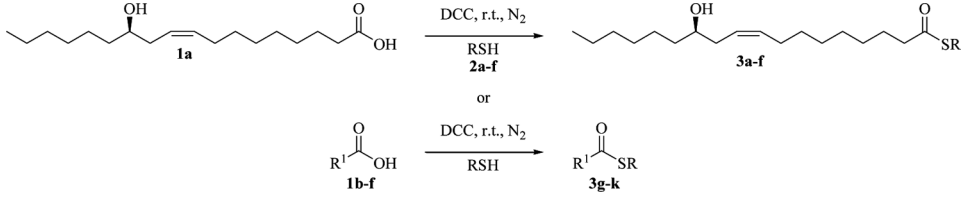
Surprisingly, the best result was obtained when the reaction was performed under solvent- and base-free conditions. Thus, when carboxylic acid **1a** and benzylthiol **2a** where simply mixed in the presence of DCC under an N_2 atmosphere at room temperature, the desired thiol ester **3a** was obtained in 76% yield after 3 h (Table 1, entry 1).

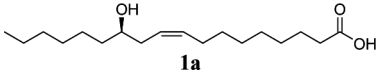
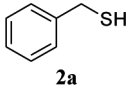
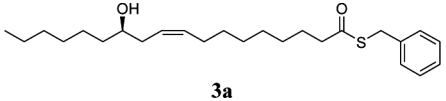
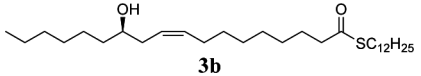
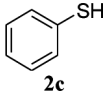
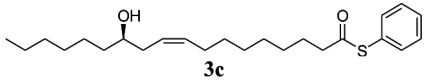
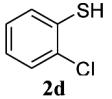
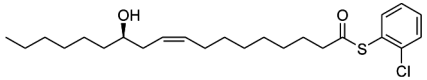
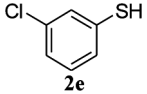
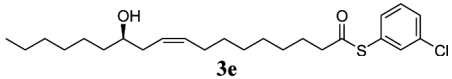
To demonstrate the efficiency of our protocol, ricinoleic acid **1a** was treated with other thiols **2a**–**f**; the results are summarized in Table 1. We observed that the reaction worked well for a variety of thiols. For example, the aliphatic dodecanethiol **2b** gives the respective thiol ester **3b** in yield comparable to aromatic thiols after the same reaction time (Table 1 entry 2). The aromatic benzenethiol **2c** reacted with ricinoleic acid **1a** to afford, after 4 h, the benzenethiol ester **3c** in 65% yield (Table 1, entry 3). The reaction also works well with aromatic substituted thiols. Thus, when chloro-substituted benzenethiols were used, the respective thiol esters were obtained in slightly superior yield after 4–5 h at room temperature (Table 1, entries 4–6). For all the tested examples, the products were obtained with the original configuration of the double bond at C-9 in the molecule. This solvent-free protocol was extended to other carboxylic acids and aliphatic and aromatic thiols (Table 1 entries 7–11). For all the tested examples, the desired thiol esters **3g–j** were obtained selectively and in satisfactory yields, except for the solid benzoic acid **1f**, which gives **3k** in only 10% yield (Table 1, entry 11).

Because our interest in the synthetic use of oils extracted from plants cultivated in southern Brazil and their constituents as renewable raw materials for use in organic synthesis, we tried to perform the direct synthesis of thiol ester from the castor bean oil (*Ricinus communis*). The major component of the castor oil was found to be ricinoleic acid (85–90%).[1a] Unfortunately, all attempts of directly converting the oil to the respective thiol esters using basic conditions failed. To circumvent this lack of reactivity, castor oil (1.02 g; ~ 3.0 mmol of ricinoleic acid) was submitted to prior alkaline hydrolysis (ethanolic KOH).[10] DCC (3.0 mmol) and benzylthiol **2a** (3.0 mmol) were directly added to the crude potassium ricinoleate generated, and the mixture was stirred at room temperature for 3 h, affording (*R,Z*)-*S*-benzyl 12-hydroxyoctadec-9-enethioate **3a** in 65% yield.

Aiming to explore the reactivity of the fat thiol esters obtained, we decide to study their conversion to the respective fat aldehyde **4** by reduction with triethylsilane in the presence of catalytic Pd on carbon.[4f,g] Thus, when a solution of (*R,Z*)-*S*-benzyl 12-hydroxyoctadec-9-enethioate **3a** in acetone (10 mL) reacted with

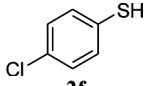
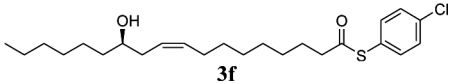
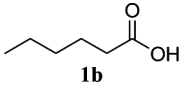
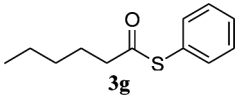
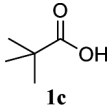
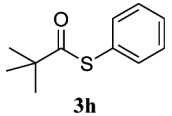
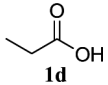
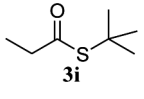
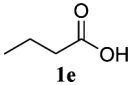
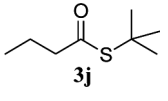
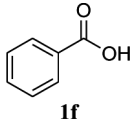
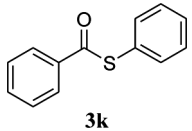
Table 1. Synthesis of thiol esters **3a–k** starting from carboxylic acids **1a–f** and thiols **2a–f**



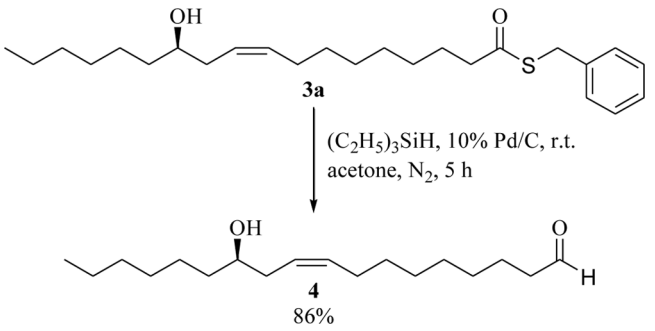
Entry	Carboxylic acid	Thiol	Product	Time (h)	Yield (%)[a]
1	 **1a**	 **2a**	 **3a**	3	76
2	**1a**	$C_{12}H_{25}SH$ **2b**	 **3b**	3	71
3	**1a**	 **2c**	 **3c**	4	65
4	**1a**	 **2d**	 **3d**	5	71
5	**1a**	 **2e**	 **3e**	4	73

(*Continued*)

Table 1. Continued

Entry	Carboxylic acid	Thiol	Product	Time (h)	Yield (%)[a]
6	**1a**	 **2f**	 **3f**	5	72
7	 **1b**	**2c**	 **3g**	2	78
8	 **1c**	**2c**	 **3h**	3	82
9	 **1d**	 **2g**	 **3i**	2	72
10	 **1e**	**2g**	 **3j**	2	76
11	 **1f**	**2c**	 **3k**	5	10

[a]Yields of pure products isolated by column chromatography.



Scheme 2. Synthesis of (*R,Z*)-12-hydroxyoctadec-9-enal.

$(C_2H_5)_3SiH$ (3 equiv) in the presence of 10% Pd on carbon (5 mol %), the respective aldehyde **4** was selectively obtained in 86% yield after stirring for 5 h at room temperature (Scheme 2). Similarly to the methods described in the literature for aromatic thiol esters, (*R,Z*)-*S*-phenyl 12-hydroxyoctadec-9-enethioate **3c** was inert against the reduction with$(C_2H_5)_3SiH$, even after stirring for several hours.

In conclusion, an improved, solvent- and base-free protocol to prepare thiol esters directly from carboxylic acids, without the tedious and harmful preparation of acyl chlorides, was developed. The minimization of the use of volatile organic solvents and harmful reagents are important advantages of this improved procedure. Besides, the obtained thiol esters can be explored as enantiomerically pure building blocks in the synthesis of more, complex bioactive candidate molecules.

EXPERIMENTAL

General Remarks

The ^1H and ^{13}C NMR sectra of $CDCl_3$ solutions were recorded with a 200-MHz or 400-MHz spectrometer (Bruker DPX), as noted. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Low-resolution mass spectra (LRMS, EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer. High-resolution mass spectra (HRESI-MS) were performed in the positive mode (UltrOTOF-Q system, version 1.10, Bruker Daltonics, MA, USA). Merck's silica gel (230–400 mesh) was used for flash chromatography.

Thiol Esters 3

General procedure. A mixture of carboxylic acid **1** (1.0 mmol) and DCC (1.0 mmol, 0.206 g) was stirred at room temperature for 15 min. Then, thiol **2** (1.2 mmol) was added, and the resulting mixture was stirred under a nitrogen atmosphere. The reaction progress was followed by thin-layer chromatography (TLC), and after 2–5 h (see Table 1) the crude product was purified on column chromatography of silica gel using ethyl acetate–hexanes (3:7) as eluent. Spectral data of **3a**–**k** are listed.

(*R,Z*)-*S*-Benzyl 12-hydroxyoctadec-9-enethioate (3a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24–7.26 (m, 5H), 5.54 (dt, $J = 10.2$ and 7.2 Hz, 1H), 5.36 (dt, $J = 10.2$ and 6.6 Hz, 1H), 4.11 (s, 2H), 3.58 (quint, $J = 6.8$ Hz, 1H), 2.55 (t, $J = 7.4$ Hz, 2H), 2.20 (t, $J = 6.6$ Hz, 2H), 1.28–2.12 (m, 22H), 1.78 (br s, 1H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.8, 137.7, 134.4, 128.8, 128.5, 127.1, 125.9, 70.9, 43.8, 40.7, 36.7, 33.1, 32.5, 31.8, 29.3, 29.2, 29.0, 28.8, 25.6, 25.5, 22.5, 14.0; IR (KBr) ν (C=O) 1686 cm^{-1}; MS m/z (rel. int.) 557 ($M^+ - 1$, 14.6), 295 (15.2), 91 (100.0). HRMS (ESI): m/z calcd. for $C_{25}H_{40}O_2S$ $[M + Na]^+$: 427.2647; found: 427.2646.

(*R,Z*)-*S*-Dodecyl 12-hydroxyoctadec-9-enethioate (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (dtt, $J = 10.8$, 7.6 and 1.2 Hz, 1H), 5.40 (dtt, $J = 10.8$, 6.4 and 1.2 Hz, 1H), 3.61 (quint, $J = 6.8$ Hz, 1H), 2.86 (t, $J = 7.2$ Hz, 2H), 2.53 (t, $J = 7.6$ Hz, 2H), 2.21 (t, $J = 6.0$ Hz, 2H), 1.25–2.01 (m, 43H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 134.4, 125.9, 70.9, 44.1, 40.7, 36.7, 32.6, 31.9, 31.8, 29.7, 29.57, 29.5, 29.4, 29.3 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 25.6, 22.7, 22.6, 14.1, 14.0; IR (KBr) ν (C=O) 1695 cm^{-1}; MS m/z (rel. int.) 328 ($M^+ - C_{11}H_{24}$, 22.4), 282 (25.8), 166 (38.5), 55 (100.0). HRMS (ESI): m/z calcd. for $C_{30}H_{58}O_2S$ $[M + Na]^+$: 505.4055; found: 505.4043.

(*R,Z*)-*S*-Phenyl 12-hydroxyoctadec-9-enethioate (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.41 (m, 5H), 5.54 (dtt, $J = 10.8$, 6.8 and 1.0 Hz, 1H), 5.41 (dtt, $J = 10.8$, 6.4 and 1.0 Hz, 1H), 3.60 (quint, $J = 6.8$ Hz, 1H), 2.64 (t, $J = 7.6$ Hz, 2H), 2.20 (t, $J = 6.4$ Hz, 2H), 2.02–2.07 (m, 2H), 1.66–1.74 (m, 2H), 1.28–1.47 (m, 19H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.4, 134.3, 129.2, 129.0, 127.9, 125.9, 125.2, 70.9, 43.6, 40.6, 36.7, 35.3, 32.5, 31.8, 29.3, 29.2, 29.0, 28.8, 25.6, 25.5, 22.5, 14.0; IR (KBr) ν (C=O) 1711 cm^{-1}; MS m/z (rel. int.) 281 ($M^+ - C_6H_5S$, 9.3), 263 (49.3), 109 (53.8), 55 (100.0). HRMS (ESI): m/z calcd. for $C_{24}H_{38}O_2S$ $[M + Na]^+$: 413.2490; found: 413.2505.

(*R,Z*)-*S*-2-Chlorophenyl 12-hydroxyoctadec-9-enethioate (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.50 (m, 4H), 5.54 (dt, $J = 10.2$ and 7.0 Hz, 1H), 5.41 (dt, $J = 10.2$ and 6.8 Hz, 1H), 3.57–3.62 (m, 1H), 2.67 (t, $J = 7.2$ Hz, 2H), 2.21 (t, $J = 6.4$ Hz, 2H), 2.01–2.06 (m, 2H), 1.14–1.76 (m, 21H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.4, 138.6, 136.9, 133.0, 130.9, 130.1, 127.3, 127.1, 125.2, 71.3, 43.6, 36.7, 35.2, 32.5, 31.7, 29.4, 29.2, 29.0, 28.9, 28.7, 25.6, 25.4, 22.5, 14.0; IR (KBr) ν (C=O) 1714 cm^{-1}; MS m/z (rel. int.) 281 ($M^+ - 2\text{-}ClC_6H_4S$, 1.8), 167 (42.2), 109 (18.5), 55 (100.0). HRMS (ESI): m/z calcd. for $C_{24}H_{37}ClO_2S$ $[M + Na]^+$: 447.2100; found: 447.2105.

(*R,Z*)-*S*-3-Chlorophenyl 12-hydroxyoctadec-9-enethioate (3e). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26–7.44 (m, 4H), 5.53 (dt, $J = 10.2$ and 7.0 Hz, 1H), 5.37 (dt, $J = 10.2$ and 6.8 Hz, 1H), 3.58–3.62 (m, 1H), 2.65 (t, $J = 7.2$ Hz, 2H), 2.21 (t, $J = 6.4$ Hz, 2H), 2.01–2.04 (m, 2H), 1.28–1.74 (m, 21H), 0.85 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 134.6, 134.4, 134.0, 132.5, 130.0, 129.4, 125.9, 70.9, 43.7, 40.6, 36.7, 32.5, 31.8, 29.3, 29.0, 28.8, 25.6, 25.4, 22.5, 14.0; IR (KBr) ν (C=O) 1713 cm^{-1}; MS m/z (rel. int.) 281 ($M^+ - 3\text{-}ClC_6H_4S$, 1.5), 167 (43.5), 109 (19.2), 55 (100.0). HRMS (ESI): m/z calcd. for $C_{24}H_{37}ClO_2S$ $[M + Na]^+$: 447.2100; found: 447.2104.

(*R,Z*)-*S*-4-Chlorophenyl 12-hydroxyoctadec-9-enethioate (3f). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38 (dt, $J = 8.8$ and 2.0 Hz, 2H), 7.34 (dt, $J = 8.8$ and 2.0 Hz, 2H), 5.54 (dt, $J = 10.2$ and 6.8 Hz, 1H), 5.43 (dt, $J = 10.2$ and 6.8 Hz, 1H), 3.58–3.63 (m, 1H), 2.66 (t, $J = 7.2$ Hz, 2H), 2.22 (t, $J = 6.4$ Hz, 2H), 2.01–2.08 (m, 2H), 1.28-1.74 (m, 21H), 0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 135.6, 134.4, 129.4, 126.4, 126.0, 125.3, 70.9, 43.7, 40.7, 36.8, 36.7, 35.3, 32.6, 31.8, 29.3, 29.0, 28.9, 28.8, 25.5, 22.6, 14.1; IR (KBr) ν (C=O) 1711 cm^{-1}; MS m/z (rel. int.) 281 ($M^+ - 4$-ClC_6H_4S, 10.0), 263 (46.1), 144 (79.8), 109 (100.0). 55 (95.0). HRMS (ESI): m/z calcd. for $C_{24}H_{37}ClO_2S$ $[M + Na]^+$: 447.2100; found: 447.2090.

S-Phenyl hexanethioate (3g)[11]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33–7.40 (m, 5H), 2.63 (t, $J = 7.2$ Hz, 2H), 1.67 (qui, $J = 7.2$ Hz, 2H), 1.31–1.35 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); IR (KBr) ν (C=O) 1708 cm^{-1}; MS m/z (rel. int.) 208 (M^+, 2.2), 137 (9.1), 131 (3.2), 110 (23.2), 85 (34.0), 57 (94.7), 43 (100.0).

S-Phenyl 2,2-dimethylpropanethiolate (3h)[12]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (br s, 5H), 1.32 (s, 9H); IR (KBr) ν (C=O) 1710 cm^{-1}.

***S-tert*-Butyl propanethioate (3i)[13].** IR (KBr) ν (C=O) 1708 cm^{-1}; MS m/z (rel. int.) 145 ($M^+ - 1$, 1.0), 129 (5.6), 126 (100.0), 117 (75), 111 (95), 91 (3.6), 57 (43.3).

***S-tert*-Butyl butanethioate (3j)[14].** IR (KBr) ν (C=O) 1709 cm^{-1}; MS m/z (rel. int.) 159 ($M^+ - 1$, 1.0), 154 (25.1), 149 (65.0), 131 (54.6), 126 (100.0).

S-Phenyl benzothioate (3k)[6b]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.12–8.16 (m, 2H), 7.61–7.68 (m, 2H), 7.52–7.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.3, 129.4, 130.3, 130.6, 131.0, 135.5, 136.9, 138.5, 191.1; IR (KBr) ν (C=O) 1707 cm^{-1}; MS m/z (rel. int.) 122 (74.0), 105 (100.0), 77 (2.7).

General Procedure for the Synthesis of (*R,Z*)-12-Hydroxyoctadec-9-enal (4)[15]

$(C_2H_5)_3SiH$ (0.348 g, 3 mmol) was added to a stirred mixture of thiol ester **3a** (0.389 g, 1 mmol) and 10% Pd on carbon (5 mol%) in acetone (10 mL) at room temperature a under nitrogen atmosphere. The stirring was continued at rt until the reduction was completed (5 h, TLC). The catalyst was filtered off through celite and washed with acetone (3 × 5 mL). Evaporation and separation on a silica-gel column gave a colorless oil, characterized as the aldehyde **4**. IR (KBr) ν (C=O) 1711 cm^{-1}; MS m/z (rel. int.) 246 ($M^+ - 2H_2O$, 1.0), 217 (93.0), 189 (100.0), 161 (61.0).

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