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Photochemical Reactions of Sulfide-Containing Alkyl Phenylglyoxylates

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Abstract: Ethylthioalkyl phenylglyoxylates (**2**) underwent regioselective photocyclization to produce up to 13-membered ring thiacyclols (**3**) in good yields. Cyclization occurred between the excited carbonyl group and the carbon a to the sulfur on the remote side. The more methylenes placed between the carbonyl group and the sulfide, the lower the yield of **3** while intermolecular hydrogen abstraction induced reductive dimerization and intramolecular Norrish Type II photolysis become competitive. The remote cyclization can be rationalized by a photoinduced electron transfer from the sulfur atom to the excited carbonyl group followed by proton transfer and subsequent cyclization of the resulting biradical. Rate constants for electron transfer increase as the chain connecting the electron donor and acceptor becomes longer and more flexible.
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INTRODUCTION

The synthesis of macrocycles has attracted attention[2] because of the important chemical and biological applications of both natural and synthesized analogs[3] and their functioning as a connection between classic and supramolecular chemistry.[4] Photochemical processes offer valuable methodology because of additional energy affiliated with the electronically excited state.[5]

We have been interested in the photochemical reactions of alkyl phenylglyoxylates,[6] and recently found an efficient, photoinduced electron transfer promoted cyclization in 2'-alkylthioethyl phenylglyoxylates (e. g. **2a**) leading to a seven-membered thiacyclol in high yield.[7] We have, therefore, carried out a complete study of the photochemical behavior of a series sulfide-containing alkyl phenylglyoxylates (**2**). We proposed that cyclizations analogous to those found in **2a** will furnish medium- to large-size ring systems as the chain length between the excited carbonyl group and the sulfide is increased.[6b]

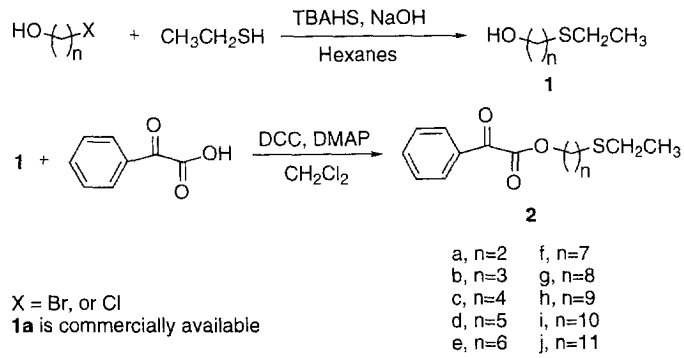
Another motive for the present work is that sulfide-containing compounds of similar chromophores, namely, phenylketones[8] and phthalimides,[9] provide substantial mechanistic information and synthetic opportunities. Our present work examines the competition between the various alternatives available to the excited state.

RESULTS

Photoreactions

Sulfur containing phenyl glyoxylates (**2**) were synthesized by DCC esterification of benzoylformic acid with the corresponding sulfide-containing alcohols (**1**). These were derived from commercially available halogenated alcohols and ethanethiol (Scheme 1).

Scheme 1



Benzene solutions of **2,** when irradiated, produce the regioselective cyclization product **3**, intermolecular dimerization product **4**, carbonyl product **5** and benzaldehyde **6**, (Scheme 2 and Table 1). Compound **3** is the expected thiacyclol and derives, we suggest,[7] from an electron transfer process. Products **4**, **5**, **6** result from inter- and intra-molecular hydrogen abstraction reactions.[6b]

Scheme 2

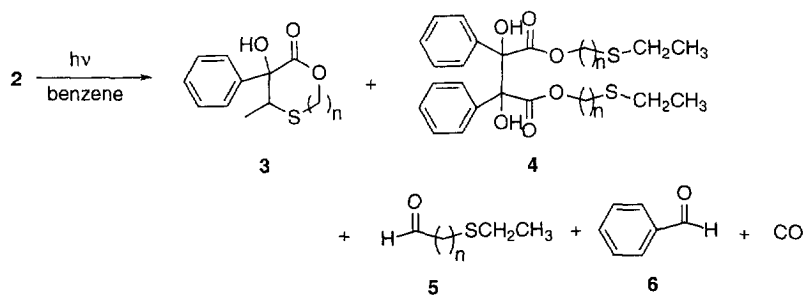


Table 1. Photoreaction products and yields.

Substrate 2	n	Products and Yields(%)[a]			
		3 (isomer ratio)	4	5	6
2a	2	100 (1.2 : 1)	b	b	b
2b	3	96 (3.6 : 1)	b	b	b
2c	4	89 (2.9 : 1)	trace	b	b
2d	5	71 (3.5 : 1)	19	trace	b
2e	6	53 (2.5 : 1)	30	trace	b
2f	7	43 (single isomer)	25	5	b
2g	8	32 (single isomer)	14	10	b
2h	9	30 (single isomer)[c]	15	15	b
2i	10	25 (single isomer)[c]	35	15	trace
2j	11	b	41	16	5

[a] Isolated unless notice otherwise.
[b] Not observed.
[c] From GC analysis.

Thiacyclol **3** is the major product in cases where n is varied from 2 to 8. Compounds **3h** and **3i** are observed when the reaction mixture is analyzed by GC/MS. Products **3** and **4** have similar R_f values on TLC in different eluents, so when **4** becomes the major product, **3** is not separated cleanly. Thiacyclol products are absent when n = 11. Under those circumstances only the normal inter- and intramolecular hydrogen abstraction derived products are observed.

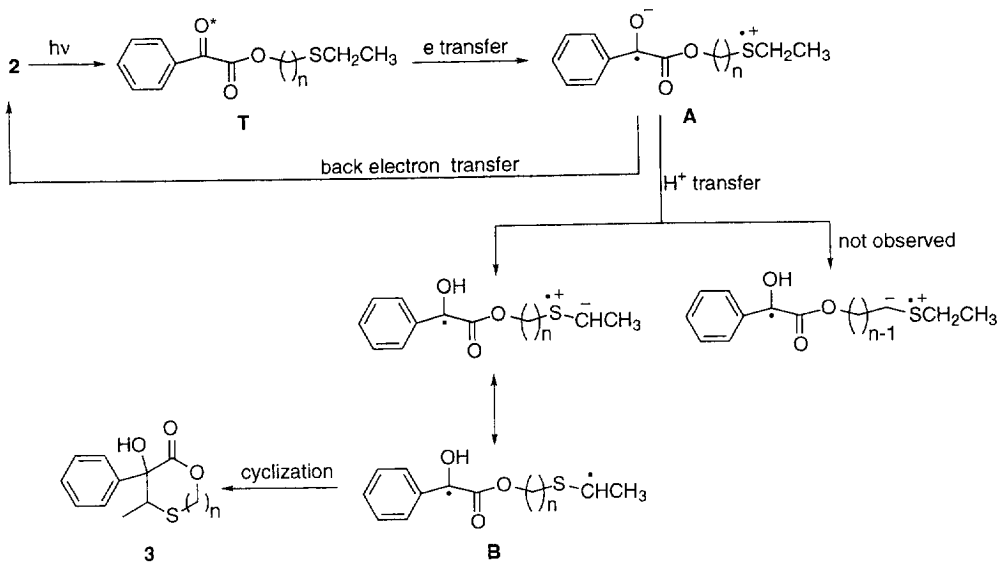
Our intention was to avoid formation of dimer **4** since its formation has been well documented,[6b] and it is not stable decomposing to starting alkyl phenylglyoxylate and the corresponding alkyl mandelate when heated.[6b,10] As shown in an earlier study, this can be accomplished by using a 'lower' concentration of starting material.[6b] At concentrations of **2** below 0.05M, dimer formation is not competitive. This is likely due to the fact that sulfur **2** activates α-hydrogens encouraging hydrogen abstraction, and the easily abstracted hydrogens are more available in **2** than in normal non-sulfide-containing alkyl phenylglyoxylates. Though some dimer formation does occur, preparative irradiations of **2** were carried out at concentrations of 0.04-0.05M. **4** was characterized by NMR (^{1}HNMR, ^{13}CNMR (APT)), and the results consistent with the product resulting from irradiation of the corresponding starting ester **2** in isopropanol.[11]

Mechanism

A mechanism involving photoinduced electron transfer from the sulfide moiety to the excited carbonyl group is proposed for the formation of **3**. This is based on similar analyses as outlined in the case of **2a** (Scheme 3).[7]

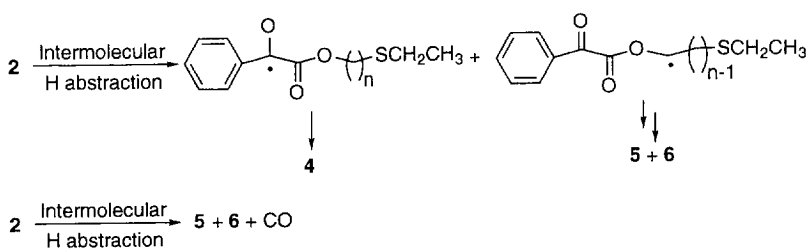
Keto ester **2** produces its triplet state (**T**) upon irradiation, and electron transfer between the donor and acceptor occurs in **T** producing the ketyl radical anion (**A**). This is deactivated to ground state **2** by back electron transfer or is converted to biradical (**B**) by a proton transfer process.

Scheme 3



The formation of **4** is accounted for by an intermolecular hydrogen abstraction and coupling of the resulting mandelate radical. Part of the observed **5** and **6** also come from this intermolecular process. The rest of these products, and carbon monoxide, are derived from the unimolecular Norrish Type II photolysis detailed in earlier work (Scheme 4).[6b]

Scheme 4



Intermolecular hydrogen abstraction in the case of **2** is more competitive with the Norrish Type II photolysis, and this differs when compared with other simple alkyl phenylglyoxylates. This is attributed to the relatively higher concentration of **2** used in the preparative photolysis and more importantly, to the more abstractable hydrogens α to sulfur.

Kinetic Studies

Nanosecond laser flash photolysis of **2a-2d** in benzene revealed two transient absorptions with maximums at approximately 470nm and 550nm respectively. As a typical example, the transient absorption spectra and decay traces for **2d** are shown in Figure 1. The absorption with a maximum at approximately 470nm is attributed to the triplet state of **2d** in agreement with earlier flash photolysis results of alkyl phenylglyoxylates.[6b,7,12] The absorption with a maximum at 550nm is broad extending downward to 470nm. When monitored at 550nm (insert 2, Figure 1) this transient has a lifetime of 2.5 μs for compounds **2a-2d** and is attributed to the ketyl radical anion (**A**). The transient monitored at 470nm decays biexponentially (insert 1, Figure 1). The first decay is attributed to the triplet state of **2** and lifetimes for several examples are collected in Table 2. The second decay, with a lifetime equal to that of the decay at 550nm, is attributed to the ketyl radical anion (**A**). As mentioned previously, this is because **A** also absorbs at 470nm and has a longer lifetime than the corresponding triplet state. Benzene solutions of **2j** give only one transient absorption maximum at 440nm after the laser flash. This transient, attributed to its triplet excited state, decays rapidly with a rate constant at the limits of detection of the nanosecond apparatus employed in this study.

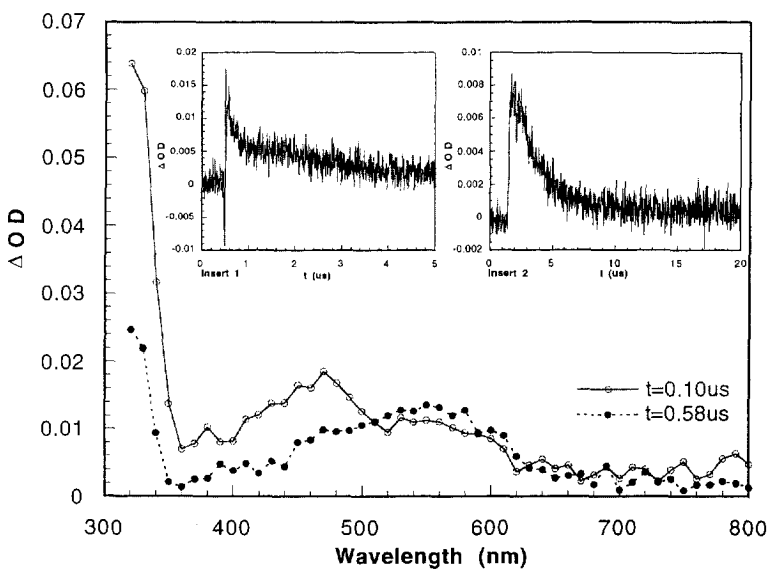


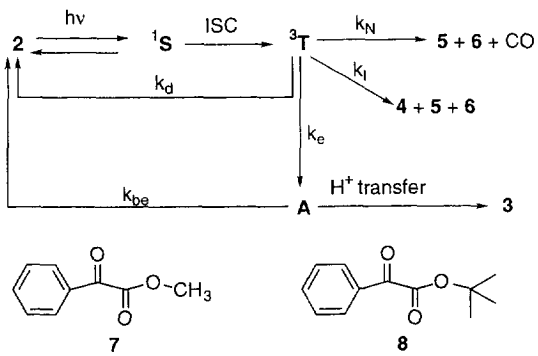
Figure 1. Transient absorption spectra after laser flash photolysis of a benzene solution (0.019M) of **2d**. Insert 1 is the decay trace monitored at 470nm. Insert 2 is the decay trace monitored at 550nm.

Table 2, Kinetic data obtained by laser falsh photolysis.

Substrate	Atom numbers of cyclic transition state required for Electron Transfer	Absorption maximum of triplet (nm)	Triplet lifetime (μs)	k_{et} (s^{-1})
2a	7	440	0.60	1.5×10^6
2b	8	450	0.54	1.8×10^6
2c	9	470	0.52	1.8×10^6
2d	10	470	0.25	3.9×10^6
2j	16	440	0.03	3.2×10^7

The photochemical processes proposed for **2** are outlined in Scheme 5. Upon irradiation, **2** is activated to its singlet state (**S**), which either undergoes rapid intersystem crossing (ISC) to its triplet state (**T**) or decays thermally to the ground state **2**. Depending on the structure of **2**, the triplet state (**T**) can deactivate by several routes. Firstly, it can undergo non-productive decay back to the ground state with total rate constants, k_d. Secondly, it may be quenched via an electron transfer process with a rate constant of k_e by the intramolecularly situated sulfide group and producing the ketyl radical anion **A**. Back electron transfer (rate constant, k_{be}) in **A** competes with the proton transfer process leading to product **3**. Thirdly, triplet **2** may undergo Norrish Type II photolysis (rate constant, k_N) and intermolecular hydrogen abstraction reaction (k_I). The rate constant for the non-productive decays (k_d) of **2** can be derived by the method of Dalton and Turro[13] from the lifetime (12.7 μs) of the non-reactive *tert*-butyl phenylglyoxylate (**8**) (7.88×10^4 s^{-1}).[6b] Rate constants k_N and k_I for the alkyl phenylglyoxylate are measured for the typical, **7**, to be 6.35×10^5 s^{-1} and 2.0×10^6 $M^{-1}s^{-1}$ respectively.[6b] Based on the triplet lifetime (τ) measured for compound **2**, k_e can be calculated, since $k_d + k_e + k_N + k_I [M] = 1/\tau$, $k_e = 1/\tau - k_d - k_N - k_I [M]$, with [M] being the initial concentration of **2**. (Of course, $k_N = 0$ for **2a**-**2d**, $k_I = 0$ for **2a**-**2c**). The calculated results are collected in Table 2.

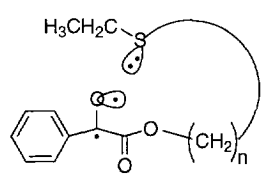
Scheme 5



It has been demonstrated that charge transfer rate constants between sulfide and triplet carbonyl groups in keto sulfides are controlled by conformation,[8] i. e.: the charge transfer rate constant is dependent on the equilibrium constant for the formation of the requisite cyclic orientation[14] between the donor orbital and the acceptor orbital. When a favorable five- and six-membered ring cyclic transition state is involved, the charge transfer rate constant in ketosulfides is 5.5 x 10^9 s^{-1} and 2.9 x 10^9 s^{-1} respectively.[8] The atom numbers of the cyclic transition state required for electron transfer in **2** are tabulated in Table 2. Cyclic transition states of rings larger than 8 are involved. This explains the relatively lower k_e observed for **2**.

The fact that k_e for **2** increases as n increases (Table 2) deserves further comment. It was our prediction that as n increases in **2**, the distance between the carbonyl group and the sulfide will increase and k_e will decrease. As shown in Table 2, for **2a**-**2d**, k_e increases as the number of methylene groups between the electron donor and acceptor increases. Yet, the values remain below the typical rate constant for the bimolecular quenching of triplet ketones by sulfides.[15] The value of k_e for **2j** is further increased and is in the region of the bimolecular quenching rate constants of ketone triplet states by sulfides since several more methylenes are placed between the carbonyl group and the sulfide. This variation in electron transfer rate constants are explained by the chain motions possible in **2**. As shown in Scheme 6, when n increases, the chain connecting the donor and acceptor becomes longer and more flexible thus better allowing the interaction between the donor and acceptor orbitals.[16]

Scheme 6



It is interesting to note that an increase in k_e does not lead to an increase in the yield of the product derived from the electron transfer process (**3**). On the contrary, as k_e increases from **2a** to **2j**, the yield of **3a** to **3j** decreases to the point that **3j** is not observed. Products from slower processes (Norrish Type II and intermolecular hydrogen abstraction) appear and become dominant. A back electron transfer process in the ketyl radical anion (**A**) explains this observation. When n increases, k_e increases; since the factors favoring electron transfer in **T** also benefit the back electron transfer in **A**, k_{be} also increases. When k_{be} increases to the extent that the product-deriving deprotonation in **A** can not compete, no thiacyclols **3** will be produced. This explanation is further confirmed by the quantum yield measurements for the disappearance of **2** (*vide infra*).

Quantum Yields

The quantum yield for starting material disappearance measured in benzene decreases as the length of the chain connecting the carbonyl group and the sulfide in **2** increases, Table 3. As the alkyl chain is lengthened, the rate of electron transfer in the triplet state (**T**) increases and the lifetime of **T** shortens. The back electron transfer rate in the ketyl radical anion (**A**) also increases efficiently returning **A** to the ground state **2**. The product-producing deprotonation becomes less efficient. As more photons dissipate through electron transfer processes, the quantum yield for the disappearance of **2** decreases.

Table 3. Quantum yields for the disappearance of **2** in benzene.

Substrate **2**	**2b**	**2d**	**2f**	**2h**	**2j**
Φ	0.32	0.16	0.10	0.08	0.06

DISCUSSION

Regioselective Deprotionation

The only thiacyclol derived from electron transfer induced cyclization is product **3**, where deprotionation and subsequent cyclization occur exclusively on the carbon α to the sulfur on the side remote from the excited carbonyl group. Deprotionation from the other α carbon is absent (Scheme 4). indicating that the α hydrogen on the remote side is kinetically more acidic. Such regioselectivity in cyclization has been observed to a lesser degree in the remote cyclization of sulfide-containing phthalimides,[9b] where in most of the cases studied, cyclization from the remote site is more than 10 times as efficient as that from the closer site.

Conclusion

Regioselective remote cyclization in alkyl phenylglyoxylates produces thiacyclol in good yields. The efficiency of such cyclizations varies with the length of the chain connecting the carbonyl group and the sulfide. Other photochemical processes compete with the photocyclization when the latter becomes less efficient.

EXPERIMENTAL SECTION

Materials

Benzene (Aldrich) was dried over sodium benzophenone ketyl under argon. Other chemicals were obtained from commercial sources and used as received. NMR spectra were taken either on a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer using chloroform-*d* as solvent. Chemical shifts are in ppm with TMS as the internal standard. GC measurements were carried out on a Hewlett-Packard(HP) 5890 Gas Chromatograph with a 30m x 0.253 mm ID x 0.25 μm film thickness DB-1 column (J & B Scientific) and a flame ionization detector. GC/MS were taken on Hewlett-Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30m x 0.25 mm ID x 0.25 μm film thickness DB-5 ms column (J & B Scientific), interfaced to a HP 2623A data processor. Infrared spectra were taken with a Galaxy™ series 6020 FTIR Spectrometer. Thin layer chromatography was performed with Whatman® silica gel coating TLC plates. Silica gel (60Å, 60-200 mesh) used in column chromatography was from J. T. Baker Chemical Company. High resolution mass spectra were obtained from the University of Illinois at Urbana-Champaign.

Quantum yields

A benzene solution (0.1M) of valerophenone as actinometer ($\Phi_{acetophenone}$ =0.33)[17] was always irradiated in parallel to the sample solution on a "merry-go-around." The disappearance of **2** was monitored by NMR since product **4** decomposes on GC. The signals from the aromatic hydrogens of the reaction mixture were used as

the internal standard since such hydrogens were conserved in the reaction process. The disappearance of **2** was monitored by its distinctive down field (≈ 8.00ppm) aromatic hydrogen signals. The appearance of acetophenone in the actinometer was conveniently monitored by GC. The GC was calibrated against using chlorobenzene as an internal standard. The quantum yields reported are the averages of three measurements.

Time resolved laser flash photolysis

Nanosecond laser flash photolysis were carried out on a setup described by Ford and Rodgers[18] using the third harmonic of a Q-switched Nd:YAG laser (Continuum, YG660) as the excitation source. The sample solution in a quartz curette was purged with argon for five minutes before and continuously purged during the experiment. Samples were excited with 355nm pulses (pulse width *ca.* 7ns).

General procedure for the synthesis of compound 1[19]

To a solution (30mmol) of ethanethiol in hexanes placed on an ice bath was added 85mg tetrabutyl ammonium hydrogen sulfate (TBAHS) and a 50% aqueous NaOH solution (from 2.6g NaOH and 2.6g H_2O). The mixture was stirred vigorously for 30 mins. Equal molar amounts (30mmol) of the halogenated alcohol was then added dropwise and the mixture was stirred for another 6 hours. The resulting mixture was subsequently poured into water and extracted three times with dichloromethane. The combined organic layers were washed with water until the washings were neutral. Evaporation of solvent in vacuo left compound **1** in 80-85% yield.

3-Ethylthio-1-propanol (**1b**). Clear oil, ^{1}HNMR (400 MHz) δ 1.27 (t, J = 7.6 Hz, 3H), 1.84 (quintet, J = 7.6 Hz, 2H), 2.56 (q, J = 7.6 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 3.73 (b, 2H). ^{13}CNMR (50 MHz) δ 14.55, 25.74, 28.14, 31.77, 61.51. MS 47 (36), 61 (63), 75 (40), 120 (100). HRMS *m/z* calculated for $C_5H_{12}SO$: 120.0609, measured: 120.0609.

4-Ethylthio-1-butanol (**1c**). Clear oil, ^{1}HNMR (400 MHz) δ 1.26 (t, J = 7.6 Hz, 3H), 1.64-1.69 (m, 4H), 2.54 (q, J = 7.6 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 3.65 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.63, 25.74, 31.25, 31.69, 62.05. MS 40 (100), 44 (47), 75 (62), 87 (16), 134 (30). HRMS *m/z* calculated for $C_6H_{14}SO$: 134.0765, measured: 134.0765.

5-Ethylthio-1-pentanol (**1d**). Clear oil, ^{1}HNMR (200 MHz) δ 1.26 (t, J = 7.6 Hz, 3H), 1.45-1.62 (m, 6H), 2.48-2.59 (m, 4H), 3.64 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.68, 24.94, 25.79, 29.25, 31.42, 62.50. MS 47 (18), 68 (33), 75 (100), 101 (23), 148 (33). HRMS *m/z* calculated for $C_7H_{16}SO$: 148.0922, measured: 148.0923.

6-Ethylthio-1-hexanol (**1e**). Clear oil, ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.6 Hz, 3H), 1.41-1.64 (m, 8H), 2.48-2.59 (m, 4H), 3.54 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.66, 25.25, 25.76, 28.54, 29.40, 31.40, 32.34, 62.52. MS 55 (33), 75 (100), 101 (3.9), 162 (48). HRMS *m/z* calculated for $C_8H_{18}SO$: 162.1078, measured: 162.1079.

7-Ethylthio-1-heptanol (**1f**). Clear oil, ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.6 Hz, 3H), 1.35-1.59 (m, 10H), 2.22 (s, 1H), 2.48-2.59 (m, 4H), 3.62 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.64, 25.48, 25.74, 28.71, 28.87, 29.38, 31.43, 32.39, 62.57. MS 55 (54), 75 (100), 96 (37), 129 (80), 176 (44). HRMS *m/z* calculated for $C_9H_{20}SO$: 176.1235, measured: 176.1235.

8-Ethylthio-1-octanol (**1g**). Clear oil, ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.6 Hz, 3H), 1.35-1.33 (m, 8H), 1.52-1.58 (m, 4H), 2.13 (s, 1H), 2.48-2.59 (m, 4H), 3.62 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ

14.66, 25.56, 28.72, 29.07, 29.16, 29.45, 31.49, 32.56, 62.68. MS 41 (44), 55 (55), 75 (100), 110 (22), 143 (86), 190 (39). HRMS *m/z* calculated for $C_{10}H_{22}SO$: 190.1391, measured: 190.1391.

9-Ethylthio-1-nonanol (**1h**). Clear oil, ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.6 Hz, 3H), 1.27-1.39 (m, 10H), 1.52-1.58 (m, 4H), 2.21 (s, 1H), 2.48-2.59 (m, 4H), 3.61 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.64, 25.59, 25.74, 28.78, 29.03, 29.23, 29.34, 29.47, 31.49, 32.58, 62.62. MS 41 (48), 55 (62), 75 (100), 81 (44), 95 (25), 157 (87), 204 (36). HRMS *m/z* calculated for $C_{11}H_{24}SO$: 204.1548, measured: 204.1548.

10-Ethylthio-1-decanol (**1i**). Clear oil, ^{1}HNMR (200 MHz) δ 1.26 (t, J = 7.6 Hz, 3H), 1.29-1.36 (m, 12H), 1.54-1.58 (m, 4H), 2.48-2.59 (m, 4H), 3.63 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.78, 25.67, 25.85, 25.87, 29.32, 29.47, 29.56, 31.58, 32.56, 32.69, 62.65. MS 41 (59), 55 (81), 75 (100), 87 (53), 171 (91), 218 (34). HRMS *m/z* calculated for $C_{12}H_{26}SO$: 218.1704, measured: 218.1704.

11-Ethylthio-1-undecanol (**1j**). Clear oil, ^{1}HNMR (200 MHz) δ 1.26 (t, J = 7.6 Hz, 3H), 1.28-1.36 (m, 14H), 1.54-1.62 (m, 4H), 2.48-2.59 (m, 4H), 3.63 (t, J = 7.6 Hz, 2H). ^{13}CNMR (50 MHz) δ 14.75, 25.67, 25.85, 28.89, 29.18, 29.36, 29.43, 29.51, 29.58, 31.60, 32.71, 62.93. MS 41 (54), 55 (78), 75 (98), 87 (53), 87 (37), 101 (17), 185 (100), 232 (26). HRMS *m/z* calculated for $C_{13}H_{28}SO$: 232.1861, measured: 232.1861.

General procedure for the synthesis of compound 2

To the appropriate alcohol **1** in a round bottom flask, benzoylformic acid, and 4-N, N'-dimethylaminopyridine (molar ratio: 1.0:1.1:0.1) were added. Dry dichloromethane was added to make an approximately 0.2M solution. The solution was then placed over ice and cooled to 0°C. An equal molar amount of 1,3-dicyclohexylcarbodiimide (DCC) in dry dichloromethane was added dropwise to the stirring solution. Generally, a white precipitate formed instantly. The mixture was then allowed to warm up room temperature and stirred overnight. The precipitate was filtered and the solvent evaporated in vacuo. Purification by flash column chromatography with the indicated eluents produces **2** in a yield better than 85%.

3'-Ethylthio n-propyl phenylglyoxylate (**2b**). (Hexanes: Ethyl acetate=10:1), yellowish oil. ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 2.03-2.10 (m, 2H), 2.54 (q, J = 7.2 Hz, 2H), 2.65 (t, J = 7.2 Hz, 2H), 4.50 (t, J = 7.2 Hz, 2H), 7.49-7.53 (m, 2H), 7.64-7.68 (m, 1H), 7.99-8.01 (m, 2H). ^{13}CNMR (50 MHz) δ 14.57, 25.79, 27.59, 28.28, 64.60, 128.81, 129.87, 132.27, 143.86, 183.67, 186.11. MS 51 (9.4), 77 (31), 105 (100), 147 (2.0), 231 (0.5), 252 (0.3). HRMS *m/z* calculated for $C_{13}H_{16}SO_3$: 252.0820, measured: 252.0821.

4'-Ethylthio n-butyl phenylglyoxylate (**2c**). (Hexanes: Ethyl acetate=15:1), yellowish oil. ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.69-1.77 (m, 2H), 1.88-1.95 (m, 2H), 2.53 (q, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 4.42 (t, J = 7.2 Hz, 2H), 7.50-7.54 (m, 2H), 7.65-7.69 (m, 1H), 7.99-8.02 (m, 2H). ^{13}CNMR (50 MHz) δ 14.72, 25.77, 25.86, 27.57, 31.02, 65.75, 128.88, 129.97, 132.39, 134.90, 163.84, 186.27. MS 55 (9.8), 77 (33), 105 (100), 115 (29), 133 (7.1), 196 (5.2), 224 (1.8), 266 (0.2). HRMS *m/z* calculated for $C_{14}H_{18}SO_3$: 266.0977, measured: 266.0974.

5'-Ethylthio n-pentyl phenylglyoxylate (**2d**). (Hexanes: Ethyl acetate=15:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.53-1.70 (m, 4H), 1.77-1.85 (m, 2H), 2.48-2.59 (m, 4H), 4.40 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.69 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.71, 25.01, 25.85, 28.03, 29.03, 31.29, 66.01, 128.83, 129.92, 132.36, 134.85, 163.84, 186.31. MS 51 (8.2), 77 (29),

105 (100), 129 (13), 147 (10), 196 (3.2), 280 (0.5). HRMS *m/z* calculated for $C_{15}H_{20}SO_3$: 280.1133, measured: 280.1135.

6'-Ethylthio n-hexyl phenylglyoxylate (**2e**). (Hexanes: Ethyl acetate=15:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.42-1.79 (m, 8H), 2.47-2.58 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.67 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.75, 25.41, 25.87, 28.32, 29.34, 31.42, 66.15, 128.84, 129.94, 132.39, 134.85, 163.89, 186.37. MS 55 (9.8), 77 (26), 105 (100), 161 (8.4), 189 (0.5), 294 (3.3). HRMS *m/z* calculated for $C_{16}H_{22}SO_3$: 294.1290, measured: 294.1291.

7'-Ethylthio n-heptyl phenylglyoxylate (**2f**). (Hexanes: Ethyl acetate=12:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.34-1.58 (m, 8H), 1.75-1.79 (m, 2H), 2.47-2.58 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.55 (m, 2H), 7.63-7.66 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.00, 22.55, 25.59, 28.29, 28.60, 29.36, 31.45, 31.49, 66.15, 128.77, 129.88, 132.36, 134.78, 163.86, 186.31. MS 55 (12), 77 (23), 105 (100), 129 (5.0), 175 (7.7), 308 (3.8). HRMS *m/z* calculated for $C_{17}H_{24}SO_3$: 308.1446, measured: 308.1446.

8'-Ethylthio n-octyl phenylglyoxylate (**2g**). (Hexanes: Ethyl acetate=12:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.26-1.36 (m, 8H), 1.53-1.60 (m, 2H), 1.70-1.78 (m, 2H), 2.48-2.59 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.67 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.75, 25.65, 25.83, 28.34, 28.71, 28.96, 29.49, 31.53, 66.25, 128.81, 129.92, 132.37, 134.81, 163.89, 186.38. MS 55 (8.6), 77 (21), 105 (100), 143 (4.6), 189 (7.1), 322 (4.7). HRMS *m/z* calculated for $C_{18}H_{26}SO_3$: 322.1603, measured: 322.1603.

9'-Ethylthio n-nonyl phenylglyoxylate (**2h**). (Hexanes: Ethyl acetate=12:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.26-1.40 (m, 8H), 1.52-1.59 (m, 2H), 1.71-1.78 (m, 2H), 2.48-2.59 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.67 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.73, 25.67, 25.83, 28.36, 28.80, 29.01, 29.25, 29.52, 31.54, 66.28, 128.81, 129.92, 132.37, 134.81, 163.89, 186.40. MS 55 (9.7), 77 (20), 105 (100), 157 (3.4), 203 (7.4), 336 (4.5). HRMS *m/z* calculated for $C_{19}H_{28}SO_3$: 336.1759, measured: 336.1760.

10'-Ethylthio n-decyl phenylglyoxylate (**2i**). (Hexanes: Ethyl acetate=10:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.25-1.39 (m, 14H), 1.73-1.78 (m, 2H), 2.48-2.59 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.67 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.07, 25.72, 25.87, 28.40, 28.87, 29.07, 29.34, 29.60, 31.54, 66.32, 128.84, 129.95, 132.45, 134.83, 163.95, 186.42. MS 55 (11), 77 (18), 105 (100), 217 (7.8), 350 (3.8). HRMS *m/z* calculated for $C_{20}H_{30}SO_3$: 350.1916, measured: 350.1914.

11'-Ethylthio n-undecyl phenylglyoxylate (**2j**). (Hexanes: Ethyl acetate=10:1), yellowish oil. ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 1.25-1.36 (m, 14H), 1.53-1.58 (m, 2H), 1.74-1.78 (m, 2H), 2.48-2.59 (m, 4H), 4.39 (t, J = 7.2 Hz, 2H), 7.48-7.56 (m, 2H), 7.63-7.68 (m, 1H), 7.98-8.03 (m, 2H). ^{13}CNMR (50 MHz) δ 14.78, 25.72, 25.88, 28.41, 28.91, 29.11, 29.20, 29.41, 29.62, 31.63, 66.36, 128.84, 129.97, 132.45, 134.83, 163.95, 186.44. MS 55 (12), 77 (17), 105 (100), 185 (2.7), 231 (8.2), 364 (3.4). HRMS *m/z* calculated for $C_{21}H_{32}SO_3$: 364.2072, measured: 364.2073.

General procedures for irradiation of samples and isolating products

Samples were dissolved in proper solvent and sealed with a rubber septum bound by sticky parafilm. Degassing

was achieved by bubbling dry argon gas through the solution for 10-15 mins. Irradiation was carried out in a Rayonet RPR-100 photoreactor equipped with 16 350nm GE® F8T5·BLB UV lamps. After irradiation, solvent was evaporated on a rotary evaporator and the resulting solution was chromatographied under pressure using hexanes:ethyl acetate as eluting solvent.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cyclooctanelactone (**3b**). (Hexanes: ethyl acetate=5:1), Diastereoisomer with higher R_f (0.71 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.08 (d, J = 7.2 Hz, 3H), 2.05 (dt, J_1 = 9.6 Hz, J_2 = 6.4 Hz, 1H), 2.30-2.38 (m, 1H), 2.71 (dd, J_1 = 11.6 Hz, J_2 = 15.2 Hz, 1H), 2.96 (dd, J_1 = 15.2 Hz, J_2 = 6.4 Hz, 1H), 3.73 (q, J = 7.2 Hz, 1H), 3.80 (s, 1H), 3.89-3.96 (m, 1H), 4.81-4.87 (m, 1H), 7.31-7.39 (m, 3H), 7.73-7.75 (m, 2H). ^{13}CNMR (50 MHz) δ 15.88 (CH_3), 29.71 (CH_2), 31.71 (CH_2), 56.13 (CH), 64.44 (CH_2), 79.84 (C), 126.02 (CH), 127.93 (CH), 128.23 (CH), 138.00 (C), 175.59 (C=O). MS 77 (30), 105 (100), 119 (9.1), 147 (4.9), 252 (4.7). IR (film) 3521.68, 2964.11, 2942.81, 1740.31, 1107.45. HRMS *m/z* calculated for $C_{13}H_{16}SO_3$: 252.0820, measured: 252.0821. Diastereoisomer with lower R_f (0.65 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.22 (d, J = 7.2 Hz, 3H), 2.23-2.28 (m, 1H), 2.47 (dd, J_1 = 7.6 Hz, J_2 = 3.6 Hz, 1H), 2.55 (ddd, J_1 = 8 Hz, J_2 = 15.6 Hz, J_3 = 1.2 Hz, 1H), 2.85 (dd, J_1 = 15.6 Hz, J_2 = 10 Hz, 1H), 3.26 (q, J = 7.2 Hz, 1H), 3.98 (s, 1H), 4.18-4.24 (m, 1H), 4.89-4.97 (m, 1H), 7.26-7.41 (m, 3H), 7.67-7.69 (m, 2H). ^{13}CNMR (50 MHz) δ 17.26 (CH_3), 28.27 (CH_2), 31.54 (CH_2), 54.93 (CH), 65.34 (CH_2), 80.28 (C), 126.46 (CH), 127.12 (CH), 128.10 (CH), 138.03 (C), 175.88 (C=O). MS 77 (32), 105 (100), 119 (9.1), 147 (4.6), 252 (3.0). IR (film) 3534.67, 2971.29, 2926.84, 1740.33, 1254.46. HRMS *m/z* calculated for $C_{13}H_{16}SO_3$: 252.0820, measured: 252.0821.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cyclononanelactone (**3c**). (Hexanes: ethyl acetate=5:1), Diastereoisomer with higher R_f (0.71 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.15 (d, J = 7.2 Hz, 3H), 1.60-1.80 (m, 1H), 1.91- 2.02 (m, 1H), 2.35-2.61 (m, 1H), 2.80 (td, J_1 = 10.8 Hz, J_2 = 4.0 Hz, 1H), 3.25-3.32 (m, 1H), 3.42 (q, J = 7.2 Hz, 1H), 3.98 (td, J_1 = 10.8 Hz, J_2 = 2.8 Hz, 1H), 4.95 (td, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.27-7.37 (m, 3H), 7.66-7.69 (m, 2H). ^{13}CNMR (50 MHz) δ 17.04 (CH_3), 24.41 (CH_2), 27.14 (CH_2), 37.40 (CH_2), 54.53 (CH), 67.68 (CH_2), 81.91 (C), 125.73 (CH), 127.92 (CH), 128.23 (CH), 139.07 (C), 174.43 (C=O). MS 55 (12), 77 (35), 105 (100), 115 (54), 133(14), 161 (4.7), 196 (8.4), 266 (2.2). IR (film) 3519.24, 2987.43, 2932.70, 1728.75, 1450.92, 1142.21. HRMS *m/z* calculated for $C_{14}H_{18}SO_3$: 266.0977, measured: 266.0974. Diastereoisomer with lower R_f (0.72 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.13 (d, J = 7.2 Hz, 3H), 1.70-1.80 (m, 1H), 1.84-1.91 (m, 1H), 2.49 (dd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 1H), 2.70 (ddd, J_1 = 14.8 Hz, J_2 = 3.6 Hz, J_3 = 7.6 Hz, 1H), 2.89 (qd, J_1 = 7.6 Hz, J_2 = 4.0 Hz, 1H), 2.98 (ddd, J_1 = 14.8 Hz, J_2 = 9.6 Hz, J_3 = 4.0 Hz, 1H), 3.16 (q, J = 7.2 Hz, 1H), 3.95 (s, 1H), 4.17-4.28 (m, 1H), 4.87 (td, J_1 = 6.8 Hz, J_2 = 4.0 Hz, 1H), 7.29-7.41 (m, 3H), 7.65-7.67 (m, 2H). ^{13}CNMR (50 MHz) δ 17.59 (CH_3), 25.50 (CH_2), 27.36 (CH_2), 31.13 (CH_2), 50.96 (CH), 67.06 (CH_2), 82.08 (C), 126.04 (CH), 127.90 (CH), 129.01 (CH), 138.49 (C), 175.50 (C=O). MS 55 (11), 77 (36), 105 (100), 115 (58), 133 (16), 161 (7.5), 196 (8.7), 266 (3.4). IR (film) 3520.57, 2942.65, 2914.03, 1728.20, 1242.54. HRMS *m/z* calculated for $C_{14}H_{18}SO_3$: 266.0977, measured: 266.0974.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cyclodecanelactone (**3d**). (Hexanes: ethyl acetate=5:1), Diastereoisomer with higher R_f (0.77 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.13 (d, J = 7.2 Hz, 3H), 1.60-1.63 (m, 1H), 1.67-1.81 (m, 1H), 2.04-2.21 (m, 1H), 2.46 (td, J_1 = 5.6 Hz, J_2 =

3.6 Hz, 1H), 2.49-2.54 (m, 1H), 2.82 (ddd, J_1 = 14.4 Hz, J_2 = 5.6 Hz, J_3 = 3.6 Hz, 1H), 3.52 (q, J = 7.2 Hz, 1H), 3.91-3.98 (m, 1H), 4.08 (s, 1H), 4.98 (td, J_1 = 9.0 Hz, J_2 = 7.2 Hz, 1H), 7.29-7.37 (m, 3H), 7.66-7.68 (m, 2H). ^{13}CNMR (50 MHz) δ 16.73 (CH_3), 24.19 (CH_2), 25.83 (CH_2), 26.50 (CH_2), 31.25 (CH_2), 43.32 (CH), 68.01 (CH_2), 81.57 (C), 125.79 (CH), 127.66 (CH), 128.83 (CH), 139.51 (C), 174.56 (C=O). MS 55 (7.2), 77 (29), 105 (100), 129 (15), 147(12), 196 (3.9), 280 (0.5). IR (film) 3511.52, 2932.70, 2863.24, 1724.89, 1092.05. HRMS *m/z* calculated for $C_{15}H_{20}SO_3$: 280.1133, measured: 280.1132. we were able to separate the Diastereoisomer with lower R_f (0.72 in hexanes: ethyl acetate=2:1) cleanly because of its low yield and its R_f being the same as that of **4d**. The ratio of the two diastereoisomers reported is based on the ratio of their signal upon GC analysis.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cycloundecanelactone (**3e**). (Hexanes: ethyl acetate =5:1), Diastereoisomer with higher R_f (0.79 in hexanes: ethyl acetate=2:1): colorless oil. ^{1}HNMR (400 MHz) δ 1.13 (d, J = 7.2 Hz, 3H), 1.42-1.47 (m, 1H), 1.59-1.69 (m, 2H), 1.78-1.85 (m, 1H), 1.94-2.03 (m, 1H), 2.34 (ddd, J_1 = 12.8 Hz, J_2 = 14.4 Hz, J_3 = 3.6 Hz, 1H), 2.46 (td, J_1 = 7.6 Hz, J_2 = 2.8 Hz, 1H), 2.51-2.54 (m, 1H), 2.89 (dt, J_1 = 14.4 Hz, J_2 = 3.6 Hz, 1H), 3.46 (q, J = 7.2 Hz, 1H), 3.49-3.56 (m, 1H), 3.89 (ddd, J_1 = 10.8 Hz, J_2 = 5.6 Hz, J_3 = 0.8 Hz, 1H), 4.04 (s, 1H), 4.69 (td, J_1 = 10.8 Hz, J_2 = 0.8 Hz, 1H), 7.28-7.44 (m, 3H), 7.62-7.64 (m, 2H). ^{13}CNMR (50 MHz) δ 17.42 (CH_3), 23.05 (CH_2), 23.99 (CH_2), 25.92 (CH_2), 26.44 (CH_2), 31.73 (CH_2), 46.01 (CH), 66.70 (CH_2), 81.80 (C), 125.73 (CH), 127.83 (CH), 128.28 (CH), 139.94 (C), 174.34 (C=O). MS 55 (11), 77 (26), 105 (100), 143 (6.8), 161 (8.6), 294 (3.5). IR (film) 3530.82, 2936.56, 2863.24, 1721.03, 1261.83. HRMS *m/z* calculated for $C_{16}H_{22}SO_3$: 294.1290, measured: 294.1288. we were able to separate the Diastereoisomer with lower R_f (0.78 in hexanes: ethyl acetate=2:1) cleanly because of its low yield and its R_f being the same as that of **4e**. The ratio of the two diastereoisomers reported is based on the ratio of their signal upon GC analysis.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cyclododecanelactone (**3f**). (Hexanes: ethyl acetate=5:1 to 10:1), One diastereoisomer: colorless oil. ^{1}HNMR (400 MHz) δ 1.11 (d, J = 7.2 Hz, 3H), 1.33-1.45 (m, 3H), 1.48-1.64 (m, 2H), 1.70-1.77 (m, 2H), 1.77-1.85 (m, 1H), 2.42 (td, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 2.47-2.53 (m, 2H), 2.77 (ddd, J_1 = 14.0 Hz, J_2 = 5.6 Hz, J_3 = 3.2 Hz, 1H), 3.59 (q, J = 7.2 Hz, 1H), 3.83 (dt, J_1 = 10.8 Hz, J_2 = 2.8 Hz, 1H), 4.12 (s, 1H), 4.70 (dt, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 1H), 7.28-7.37 (m, 3H), 7.65-7.72 (m, 2H). ^{13}CNMR (50 MHz) δ 16.02 (CH_3), 22.19 (CH_2), 23.26 (CH_2), 24.21 (CH_2), 25.68 (CH_2), 26.41 (CH_2), 30.62 (CH_2), 45.90 (CH), 67.05 (CH_2), 81.08 (C), 126.02 (CH), 127.68 (CH), 128.10 (CH), 139.78 (C), 174.54 (C=O). MS 55 (14), 77 (24), 105 (100), 129 (5.3), 156 (3.1), 175 (7.8), 308 (3.6). IR (film) 3507.67, 2936.56, 2859.38, 1721.03, 1254.12. HRMS *m/z* calculated for $C_{17}H_{24}SO_3$: 308.1446, measured: 308.1445.

3-Hydroxyl-4-methyl-3-phenyl-5-thia-cyclotridecanelactone (**3g**). (Hexanes: ethyl acetate =5:1), One diastereoisomer: colorless oil. ^{1}HNMR (400 MHz) δ 1.09 (d, J = 7.2 Hz, 3H), 1.55-1.67 (m, 4H), 2.43-2.54 (m, 4H), 2.56-2.68 (m, 2H), 2.84-2.89 (m, 2H), 3.31-3.42 (m, 2H), 3.49-3.54 (m, 2H), 3.60 (q, J = 7.2 Hz, 1H), 3.98 (s, 1H), 4.07 (m, 1H), 4.50 (dt, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.26-7.40 (m, 3H), 7.64-7.67 (m, 2H). ^{13}CNMR (50 MHz) δ 16.42 (CH_3), 22.99 (CH_2), 24.50 (CH_2), 25.21 (CH_2), 26.10 (CH_2), 27.78 (CH_2), 29.54 (CH_2), 31.56 (CH_2), 48.36 (CH), 66.57 (CH_2), 81.37 (C), 125.88 (CH), 127.17 (CH), 128.17 (CH), 140.02 (C), 174.54 (C=O). MS 55 (8.9), 77 (21), 105 (100), 143 (4.8), 189 (7.5), 322 (4.7). IR (film) 3507.57, 2932.70, 2859.38, 1721.03, 1088.19. HRMS *m/z* calculated for $C_{18}H_{26}SO_3$: 322.1603,

measured: 322.1603.

Di(5'-ethylthio-n-pentyl)-2,3-dihydroxy-2,3-diphenyl succinate (**4d**). ^{1}HNMR (200 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 1.53-1.80 (m, 12H), 2.48-2.59 (m, 8H), 4.38-4.42 (m, 4H), 5.04 (s, 2H), 7.11-7.38 (m, 8H), 7.56-7.64 (m, 2H). ^{13}CNMR (50 MHz) δ 14.73 (CH_3), 24.99 (CH_2), 25.85 (CH_2), 27.85 (CH_2), 28.00 (CH_2), 31.27 (CH_2), 65.20 (CH_2), 82.73 (C), 126.95 (CH), 128.84 (CH), 129.94 (CH), 135.98 (C), 172.15 (C=O). IR (film) 3511.52, 2932.70, 2883.24, 1724.89, 1092.05.

Di(6'-ethylthio-n-hexyl)-2,3-dihydroxy-2,3-diphenyl succinate. (**4e**). ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 1.53-1.79 (m, 16H), 2.46-2.56 (m, 8H), 4.17-4.29 (m, 4H), 5.02 (s, 2H), 7.21-7.41 (m, 8H), 7.66-7.68 (m, 2H). ^{13}CNMR (50 MHz) δ 14.78 (CH_3), 25.41 (CH_2), 25.78 (CH_2), 28.34 (CH_2), 29.34 (CH_2), 31.45 (CH_2), 66.70 (CH_2), 82.75 (C), 126.99 (CH), 128.03 (CH), 128.33 (CH), 136.01 (C), 172.23 (C=O). IR (film) 3492.23, 2936.56, 2863.24, 1724.89, 1454.77, 1261.83.

Di(7'-ethylthio-n-heptyl)-2,3-dihydroxy-2,3-diphenyl succinate. (**4f**). ^{1}HNMR (400 MHz) δ 1.27 (t, J = 7.2 Hz, 6H), 1.15-1.38 (m, 16H), 1.52-1.63 (m, 4H), 2.49-2.56 (m, 8H), 4.18 (t, J = 7.2 Hz, 4H), 5.04 (s, 2H), 7.21-7.41 (m, 8H), 7.61-7.65 (m, 2H). ^{13}CNMR (50 MHz) δ 14.77 (CH_3), 25.63 (CH_2), 25.88 (CH_2), 28.14 (CH_2), 28.67 (CH_2), 29.41 (CH_2), 31.54 (CH_2), 66.76 (CH_2), 82.73 (C), 126.95 (CH), 128.03 (CH), 128.28 (CH), 136.01 (C), 172.21 (C=O). IR (film) 3511.52, 2932.70, 2859.38, 1724.89, 1261.83.

Di(8'-ethylthio-n-octyl)-2,3-dihydroxy-2,3-diphenyl succinate. (**4g**). ^{1}HNMR (400 MHz) δ 1.26 (t, J = 7.2 Hz, 6H), 1.24-1.31 (m, 16H), 1.53-1.72 (m, 8H), 2.49-2.56 (m, 8H), 4.18 (t, J = 7.2 Hz, 4H), 5.03 (s, 2H), 7.20-7.44 (m, 8H), 7.64-7.68 (m, 2H). ^{13}CNMR (50 MHz) δ 14.09 (CH_3), 22.63 (CH_2), 25.68 (CH_2), 25.90 (CH_2), 28.21 (CH_2), 28.76 (CH_2), 29.01 (CH_2), 29.54 (CH_2), 31.56 (CH_2), 66.81 (CH_2), 82.75 (C), 126.95 (CH), 128.28 (CH), 128.48 (CH), 136.05 (C), 172.23 (C=O). IR (film) 3511.52, 2932.70, 2859.38, 1724.89, 1257.97.

Di(9'-ethylthio-n-nonyl)-2,3-dihydroxy-2,3-diphenyl succinate (**4h**). ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 1.24-1.40 (m, 20H), 1.51-1.62 (m, 8H), 2.50-2.56 (m, 8H), 4.18 (t, J = 7.2 Hz, 4H), 5.03 (s, 2H), 7.20-7.39 (m, 8H), 7.64-7.69 (m, 2H). ^{13}CNMR (50 MHz) δ 14.07 (CH_3), 22.63 (CH_2), 25.72 (CH_2), 25.90 (CH_2), 28.21 (CH_2), 29.01 (CH_2), 29.30 (CH_2), 31.56 (CH_2), 31.63 (CH_2), 66.83 (CH_2), 82.75 (C), 126.92 (CH), 128.06 (CH), 128.24 (CH), 136.05 (C), 172.23 (C=O). IR (film) 3511.52, 2955.85, 2859.38, 1724.89, 1261.83.

Di(10'-ethylthio-n-decyl)-2,3-dihydroxy-2,3-diphenyl succinate. (**4i**). ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 1.23-1.41 (m, 28H), 1.54-1.78 (m, 4H), 2.51-2.53 (m, 8H), 4.20 (t, J = 7.2 Hz, 4H), 5.02 (s, 2H), 7.20-7.39 (m, 8H), 7.53-7.66 (m, 2H). ^{13}CNMR (50 MHz) δ 14.75 (CH_3), 25.68 (CH_2), 25.83 (CH_2), 26.76 (CH_2), 28.18 (CH_2), 28.76 (CH_2), 29.01 (CH_2), 29.25 (CH_2), 29.56 (CH_2), 31.58 (CH_2), 32.53 (CH_2), 66.81 (CH_2), 82.73 (C), 126.88 (CH), 128.03 (CH), 129.92 (CH), 136.01 (C), 172.21 (C=O). IR (film) 3488.37, 2932.70, 2859.38, 1728.75.

Di(11'-ethylthio-n-undecyl)-2,3-dihydroxy-2,3-diphenyl succinate (**4j**). ^{1}HNMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 1.25-1.40 (m, 28H), 1.54-1.63 (m, 8H), 2.50-2.55 (m, 8H), 4.18 (t, J = 7.2 Hz, 4H), 5.02 (s, 2H), 7.20-7.41 (m, 8H), 7.54-7.67 (m, 2H). ^{13}CNMR (50 MHz) δ 14.73 (CH_3), 25.67 (CH_2), 25.79 (CH_2), 28.14 (CH_2), 28.83 (CH_2), 28.99 (CH_2), 29.14 (CH_2), 29.34 (CH_2), 29.54 (CH_2), 31.56 (CH_2), 66.77 (CH_2), 82.70 (C), 126.82 (CH), 127.99 (CH), 128.17 (CH), 135.99 (C), 172.15 (C=O). IR (film)

3511.52, 2928.84, 2855.53, 1724.89, 1257.97.

\Carbonyl product (**5**) were not fully characterized since its formation has been well documented.[20] A typical example is provided.

11-Ethylthio-undecanal (**5j**). clear oil. ^{1}HNMR (200 MHz) δ 1.26 (t, J = 7.2 Hz, 3H), 1.24-1.42 (m, 12H), 1.51-1.63 (m, 4H), 2.42 (td, J_1 = 7.4 Hz, J_2 = 3.6 Hz, 2H), 2.52 (t, J_1 = 14.4 Hz, J_2 = 5.6 Hz, J_3 = 3.6 Hz, 1H), 3.52 (q, J = 7.2 Hz, 1H), 3.91-3.98 (m, 1H), 4.08 (s, 1H), 4.98 (td, J = 7.4 Hz, 2H), 9.77 (t, J = 3.6 Hz, 1H),. ^{13}CNMR (50 MHz) δ 14.78 (CH_3), 22.03 (CH_2), 25.58 (CH_2), 26.23 (CH_2), 27.76 (CH_2), 28.27 (CH_2), 28.91 (CH_2), 29.29 (CH_2), 29.62 (CH_2), 31.63 (CH_2), 43.88 (CH_2), 179.78 (C=O). MS 55 (64), 75 (100), 173 (100), 230 (2.4). HRMS *m/z* calculated for $C_{13}H_{26}SO_3$: 230.1704, measured: 230.1703.

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