Intramolecular Diels–Alder reactions of 2*H*-thiopyran dienes

Dale E. Ward, Thomas E. Nixey, Yuanzhu Gai, Matthew J. Hrapchak, and M. Saeed Abaee

Abstract: A systematic survey of IMDA reactions of 4-[tris(2-methylethyl)silyl]oxy-2*H*-thiopyran derivatives with potential dienophiles tethered at the C-2, C-3, C-5, and C-6 positions is presented. Cycloaddition was not observed with a C_3 or C_4 tether and an unactivated terminal olefin as dienophile. IMDA adducts could be obtained when dienophiles activated by a carbomethoxy group were employed. Compounds having the activated dienophile attached via a C_3 tether to C-2 of the 2*H*-thiopyran gave adducts with high stereoselectivity. Substrates having the dienophile attached to C-3 with a C_3 or C_4 tether cyclized readily. With an (*E*)-enoate as the dienophile, the stereoselectivity was poor (*endo*:*exo* = 1.1–2.5:1) and essentially independent of reaction conditions (i.e., thermal vs. Lewis acid mediated). With the (*Z*)-enoate, a 7:1 mixture of *endo*:*exo* IMDA adducts was obtained under thermal conditions; with Lewis acid catalysis, isomerization of the dienophile was competitive with cycloaddition. Type II IMDA adducts were not observed with C-5 tethered substrates. Compounds having the dienophile attached to C-6 via a C_3 or a five-atom tether also failed to give IMDA adducts. No evidence for isomerization of the 2*H*-thiopyran dienes by [1,5] sigmatropic rearrangement was observed. The *endo* adducts from IMDA reactions of the C-3 tethered substrates can be desulfurized to obtain synthetically useful *trans*-fused hydrindans and decalins with angular methyl groups.

Key words: intramolecular Diels–Alder, 2*H*-thiopyran, *cis*-substituted 1,3-diene surrogate, *trans*-octahydro-3a-methyl-1*H*-indene derivatives, *trans*-decahydro-4a-methylnapthalene derivatives.

Résumé : On présente une étude des réactions DAIM des dérivés du 4-[tris(2-méthyléthyl)silyl]oxy-2*H*-thiopyrane avec des diénophiles potentiels attachés en positions C-2, C-3, C-5 et C-6. On n'observe pas de cycloaddition avec des laisses de 3 ou 4 atomes de carbone et une oléfine terminale désactivée comme diénophile. Les adduits DAIM peuvent être obtenus lorsque l'on utilise des diénophiles activés par un groupe carbométhoxy. Les composés ayant le diénophile attaché par une laisse de 3 carbones attachée au carbone en position 2 du 2*H*-thiopyrane donne des adduits avec une très grande stéréosélectivité. Les substrats ayant un diénophile attaché en C-3 avec une laisse de 3 ou 4 atomes de carbone se cyclisent rapidement. Si on utilise un (*E*)-énoate comme diénophile on obtient une faible stéréosélectivité (*endo* : *exo* = 1,1–2,5 : 1) qui est indépendante des conditions de réaction (c.-à-d., thermique versus une catalyse par acide de Lewis). Avec un (*Z*)-énoate on obtient un mélange d'adduits DAIM *endo* : *exo* dans la proportion de 7 : 1 par voie thermique tandis que la catalyse par un acide de Lewis conduit à une compétition entre l'isomérisation du diénophile et la cycloaddition. On n'a pas observé d'adduits DAIM de type II avec les substrats liés en C-5. Les composés ayant un diénophile attaché en C-6 via une liesse de 3 ou de 5 atomes de carbone ne donnent pas non plus d'adduits DAIM. On n'a pas pu mettre en évidence l'isomérisation des dienes 2*H*-thiopyranes par réarrangement sigmatropique [1,5]. Les adduits *endo* obtenus à partir des réactions DAIM des substrats liés en C-3 peuvent être désulfurisés pour obtenir des hydrindanes condensés en position *trans* et des décalines avec des groupes méthyles angulaires très utiles en synthèse.

Mots clés : Diels–Alder intramoléculaire, 2*H*-thiopyrane, substitut pour les dienes substitués en position *cis*, dérivés *trans*-octahydro-3a-méthyl-1*H*-indène, dérivés *trans*-décahydro-4a-méthylnaphtalène.

[Traduit par la rédaction]

Introduction

Despite its long history (1), the Diels–Alder reaction continues to be of fundamental importance to the theory and practice of organic chemistry (2). The increase in molecular complexity resulting from the simultaneous formation of two σ-bonds and up to four stereogenic centers coupled with the attributes of wide generality, atom economy, and predictable regio- and stereoselectivity contribute to the unrivaled synthetic utility of this reaction. One of the few limitations of the Diels–Alder reaction is the poor reactivity associated with *cis*-substituted dienes (3). As a consequence, certain stereochemical arrays are not readily generated by a Diels–Alder cycloaddition (see Scheme 1).

In an effort to address this problem, we have been investigating a strategy involving the use of 2*H*-thiopyrans as functional equivalents to *cis*-dienes (4–8). Previous work has established that the Diels–Alder adducts from reactions of 2*H*-thiopyrans with dienophiles are, after desulfurization, synthetically equivalent to adducts derived (in principle) from unreactive *cis*-dienes (Scheme 1). We have developed methods for the preparation of a wide variety of substituted 2*H*-thiopyrans

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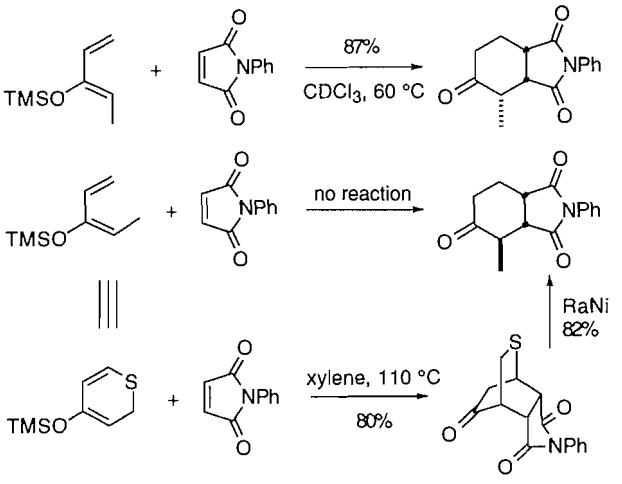
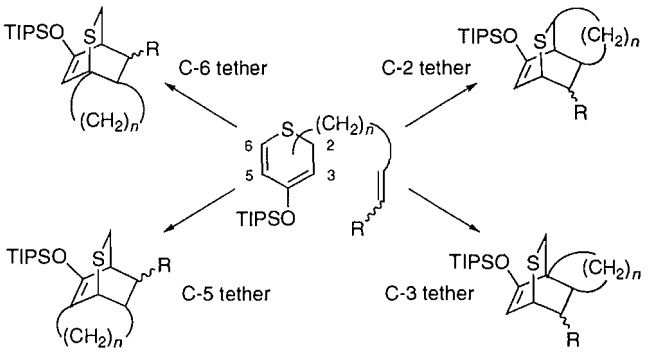
Scheme 1.



(4–9) and have systematically investigated their Diels–Alder reactivity under a variety of conditions (4–8). The reactions of 2*H*-thiopyrans bearing suitable activating substituent(s) with reactive dienophiles (e.g., maleic anhydride, maleimide) give predominantly *endo* adducts in good yield (4, 5). The reactions are slower using less reactive dienophiles (e.g., acrylate, crotonate) and modest yields are obtained because thermal decomposition of the diene competes effectively with cycloaddition (5). Lewis acid mediated reaction at lower temperatures is often satisfactory in these cases (6, 7).

The intramolecular Diels–Alder (IMDA) reaction has emerged as a powerful synthetic method for the stereoselective construction of polycyclic ring systems in a single step (10). The attenuated reactivity of *cis*-substituted dienes also limits the scope of the IMDA reaction, although not as severely as the intermolecular counterpart (10).[2] Relatively few examples of IMDA reactions involving conformationally mobile (i.e., capable of s-*cis* and s-*trans* conformers) *cis*-dienes (12) or 1,1-disubstituted-1,3-dienes (13) have been reported. Many of these examples involve particular structural elements that favor an s-*cis* conformation of the diene despite the *cis* substitution. Because (*Z*)-dienes often undergo IMDA cyclization with a much higher degree of stereoselectivity than the corresponding (*E*) isomers (10), the incorporation of a (*Z*)-diene moiety to serve as a stereochemical control element in an IMDA reaction can be an attractive tactic (10). However, this approach is limited by the reduced reactivity of (*Z*)-dienes, which can preclude IMDA reaction[3] in favor of competitive pathway(s) including the loss of stereochemical integrity by [1,5] sigmatropic rearrangement and (or) diene isomerization.[4] Preliminary results on the feasibility of using 2*H*-thiopyrans as surrogates for *cis*-dienes in IMDA reactions to address this limitation were reported (8). In this paper we present a full account of our investigations of IMDA reactions of 2*H*-thiopyrans.[5]

Fig. 1. Possible IMDA adducts from 4-(triisopropylsilyl)oxy-2*H*-thiopyran dienes with dienophiles attached at various positions.



Results and discussion

Our previous work on intermolecular Diels–Alder reactions of 2*H*-thiopyrans had established the 4-(triisopropylsilyl)oxy derivative as a moderately reactive but somewhat unstable diene (4–8). A systematic study of the reactivity of this diene in IMDA reactions was undertaken. A series of substrates with various dienophiles attached to each of the four possible positions of 4-(triisopropylsilyl)oxy-2*H*-thiopyran by a 3- or 4-atom tether were required (Fig. 1). Because our goal was to evaluate IMDA reactivity, we adopted a simple synthetic strategy to produce all of the isomeric compounds from common intermediates.

Unactivated terminal alkene dienophiles were chosen for the first series of substrates. The desired compounds were prepared from the known β-ketoester **1** (15) according to Scheme 2.[6] Alkylation (16) of **1** with 5-bromopentene (17) or 6-bromohexene (17) gave **2a** and **2b**, respectively, in modest yields along with products of *O*-alkylation and ring fragmentation (18). The decarboxylation of compounds such as **2** can be difficult (16*b*), and only a modest yield of **3** was obtained from **2** even using the recommended conditions (16*b*). Dehydrogenation of **3** by reaction with *N*-chlorosuccinimide (NCS) according to the known procedure (19) proceeded with poor regioselectivity, as expected (20), to give inseparable 1.2:1 mixtures of **4** and **5**, respectively. The mixtures of **4a/5a** and **4b/5b** were individually converted into 1.2:1 mixtures of **6a/7a** and **6b/7b** by treatment with triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) and Et_3N (5). Alternatively, CuI mediated conjugate addition (21; see also ref. 16*b*) of the Grignard reagent derived from 5-bromopentene or 6-bromo-

[2] An often cited report (12*o*) claims similar IMDA reactivity for the methyl esters of (2*E*,7*E*)- and (2*E*,7*Z*)-2,7,9-decatrienoic acid. Interpretation of these results in light of those of Roush (11) leads to the conclusion that the 7*E* isomer is considerably more reactive than the 7*Z* isomer.

[3] For examples, see refs. 12*a*, 12*b*, and 13*c*.

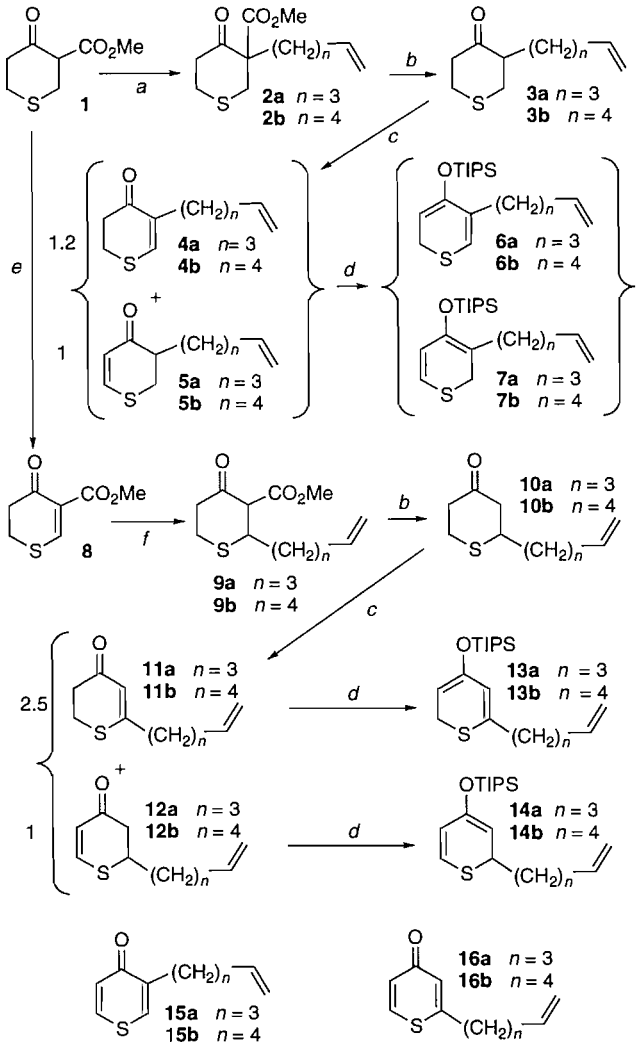
[4] For examples, see refs. 12*j*, 12*m*, and 12*n*.

[5] For a recent example involving IMDA reaction of 3*H*-benzofuro[3,2-*c*]thiopyran diene, see ref. 14.

[6] Reactions in Schemes 2–4 were not optimized. Considerable literature precedent suggests that many of these transformations would proceed in high yield if conditions were optimized for the particular substrate. Because our objective was to assess IMDA reactivity, the synthetic scheme was chosen to achieve diversity (as opposed to selectivity) and synthetic reactions were typically performed only once or twice using the published procedures "as is."

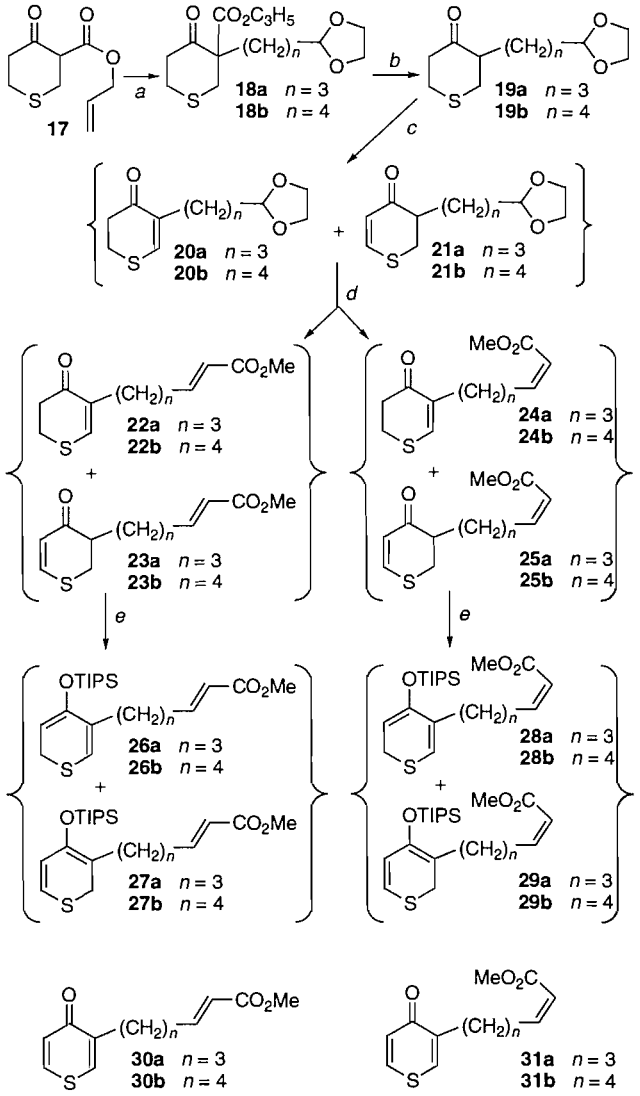
Scheme 2.

a: NaH, NaI, RX, acetone, reflux; *b*: LiI, 20% $DMF_{(aq)}$, reflux; *c*: NCS, pyridine, CH_2Cl_2; *d*: TIPSOTf, Et_3N; *e*: MnO_2, CH_2Cl_2; *f*: RMgBr, CuI, DMS.



Scheme 3.

a: NaH, NaI, RX, acetone, reflux; *b*: $(Ph_3P)_4Pd(0)$, morpholine, THF; *c*: NCS, pyridine, CH_2Cl_2; *d*: (i) $HClO_4$, acetone, (ii) $Ph_3P{=}CHCO_2Me$, MeOH; *e*: TIPSOTf, Et_3N.

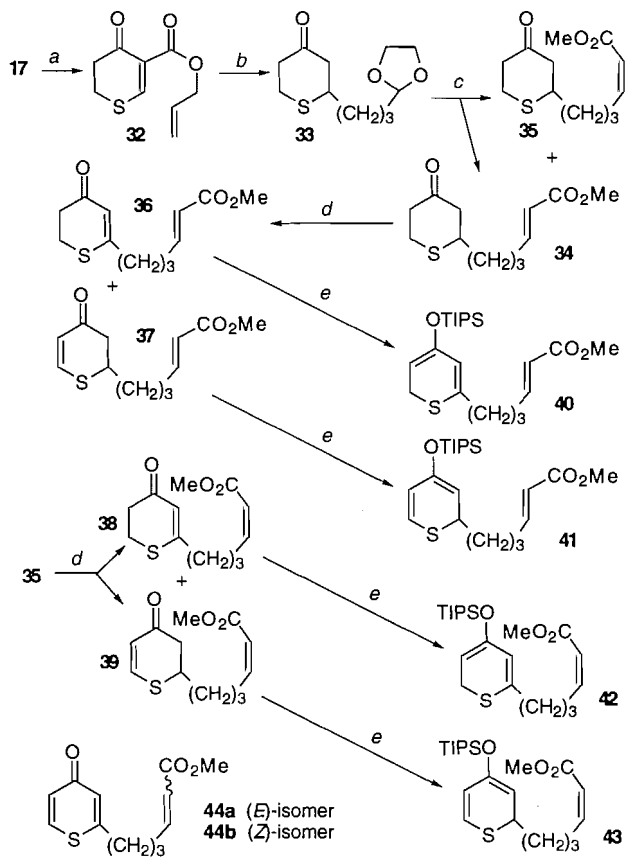


hexene to **8** (21) followed by decarboxylation of the resulting **9** produced **10**. Treatment of **10** with NCS gave separable mixtures of **11** and **12** with the former predominating by a ratio of ca. 2.5:1. The 6- and 2-substituted 2*H*-thiopyrans **13** and **14** were readily derived from **11** and **12**, respectively, by reaction with TIPSOTf. Individual solutions of the IMDA substrates **6a/7a**, **6b/7b**, **13a**, **13b**, **14a**, and **14b** in degassed C_6D_6 or $C_6D_5CD_3$ containing 2,6-di-*tert*-butyl-4-methylphenol (BHT) were heated in sealed NMR tubes at temperatures up to 200°C for several days, resulting in complete decomposition of the substrates. The reactions were monitored by ^1H NMR and, in no case, was the presence of an IMDA adduct indicated. Only products arising from desilylation (i.e., **4**, **5**, **11**, **12**) and oxidation (i.e., **15**, **16**) were detected (4, 5).

In an effort to enhance the IMDA reactivity, substrates with methyl 2-alkenoates as activated dienophiles were investigated. The preparation of compounds with the dienophile tethered at C-3 and C-5 of the 2*H*-thiopyran is outlined in Scheme 3.[6] Because of the low yields previously obtained in the decarboxylation of **2** and **9**, we began with the known allyl β-ketoester **17** (22). The Pd(0) catalyzed decarboxylation of alkylated derivatives of **17** is reported to be much more efficient than LiI–DMF decarboxylation of the analogous methyl esters (22). Alkylation of **17** with 2-(3-bromopropyl)-1,3-dioxolane (23) or 2-(4-bromobutyl)-1,3-dioxolane (24) gave **18a** and **18b**, respectively, in good yields. In each case, decarboxylation of **18** proceeded smoothly to give **19**, which reacted with NCS and pyridine to produce an inseparable mixture of enones **20** and **21** with a slight excess of the former. The individual mixtures of **20a/21a** and **20b/21b** were treated with aqueous acid to provide the corresponding aldehydes, which were immediately olefinated under conditions to maximize the proportion of (*Z*)-enoate formed (25). In both cases, a separable 1.7:1 mixture of (*E*)-enoates and (*Z*)-enoates was obtained. Neither the (*E*)-enoates (**22** and **23**) nor the (*Z*)-enoates (**24** and **25**) could be separated from each other and

Scheme 4.

a: MnO_2, CH_2Cl_2; *b*: (i) RMgBr, CuI, DMS, (ii) $(Ph_3P)_4Pd(0)$, morpholine, THF; *c*: (i) $HClO_4$, acetone, (ii) $Ph_3P{=}CHCO_2Me$, MeOH; *d*: NCS, pyridine, CH_2Cl_2; *e*: TIPSOTf, Et_3N.

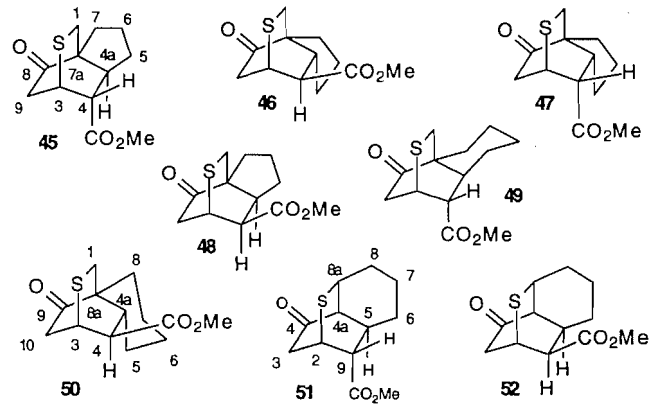


were isolated in the same ratio as that of the precursors **20** and **21** (i.e., **22**:**23** and **24**:**25** = ca. 1.25:1). The individual mixtures of **22a/23a**, **22b/23b**, **24a/25a**, and **24b/25b** were converted in the usual way into the corresponding mixtures of 2*H*-thiopyran isomers **26a/27a**, **26b/27b**, **28a/29a**, and **28b/29b**, respectively.

The preparation of 2*H*-thiopyrans with an activated dienophile attached at C-2 and C-6 is outlined in Scheme 4.[6] Conjugate addition of the Grignard reagent prepared from 2-(3-bromopropyl)-1,3-dioxolane to **32** (22) gave **33** in good yield. Hydrolysis and Wittig reaction of **33**, as described above, gave a separable 1.8:1 mixture of **34** and **35**, respectively. Oxidation of **34** with NCS gave **36** and **37** (2:1); a similar oxidation of **35** provided **38** and **39** (1.5:1). The IMDA substrates **40**–**43** were prepared by reaction of TIPSOTf with **36**–**39**, respectively.

The trienes **26**–**29** and **40**–**43** were produced in near quantitative yield as judged by ^1H NMR immediately after work-up; however, they were used immediately without further purification because of instability. In general, these IMDA substrates were highly prone to oxidation and were readily converted to the corresponding 4*H*-thiopyran-4-ones (i.e., **30**, **31**, **44**) upon heating in solution (or even on standing, especially neat). In the presence of BHT (4, 5), degassed solutions of the trienes at elevated temperatures were relatively stable towards oxidation for several days. The results of attempted IMDA reactions of **26**–**29** and **40**–**43** are presented in Table 1.

A C_6D_6 solution of a 1.2:1 mixture of **26a/27a** containing BHT (0.15 equiv.) was heated at 140°C. After 96 h, the ^1H NMR spectrum of the reaction mixture indicated the absence of **27a** and the presence of two products along with **26a** and a small amount of **30a**. Product isolation was facilitated by treatment of the crude reaction mixture with $HF_{(aq)}$ to hydrolyze the silyl enol ethers. The two IMDA adducts **45** and **46** were obtained in 55% and 43% yields, respectively (based on **23a**). In light of these results, analysis of the ^1H NMR spectrum of the mixture of **26a/27a** obtained by treatment of **22a/23a** with TIPSOTf (1.2 equiv.) in the presence of Et_3N revealed the presence of a small amount (<10%) of the same two products observed above and indicated that TIPSOTf alone could promote the IMDA reaction.[7] Reaction of the mixture of **22a/23a** with TIPSOTf (2 equiv.) for 2 h followed by HF work-up gave **45** (44%) and **46** (42%) in good yield (based on **23a**) in addition to recovered **22a** (81% based on **22a**). Similar results were obtained in a Lewis acid catalyzed reaction. Addition of $EtAlCl_2$ (0.4 equiv.) to a C_6D_6 solution of a 1.2:1 mixture of **26a/27a** resulted in consumption of **26a** within 3 min (^1H NMR) and **45** (38%) and **46** (34%) were isolated in 38% and 34% yields, respectively, after HF work-up and chromatography. Heating a 1.2:1 mixture of **28a/29a** as above (140°C, 96 h) gave the IMDA adducts **47** (70%) and **48** (10%). However, reactions promoted by TIPSOTF or $EtAlCl_2$ gave product mixtures and yields similar to those obtained from **26a/27a**, indicating that isomerization of the dienophile occurs faster than IMDA reaction under these conditions.[8]



Because of the short tether length and enforced unfavorable regiochemistry, type II IMDA adducts from **26a** (and **28a**) were not expected (27). However, Diels–Alder adducts could, in principle, be derived from **26a** by initial rearrangement to **27a** by a [1,5] sigmatropic H migration (or other mechanism).[9] To test this possibility, isomerically pure **26a** was prepared from **22a** recovered from the TIPSOTf mediated IMDA reaction of the **26a/27a** mixture. No IMDA adducts were detected after heating a C_6D_6 solution of **26a** containing BHT (0.15 equiv.) at 140°C for 4 days. Further heating up to 180°C only resulted in extensive decomposition. Similarly, treatment of **26a** with $EtAlCl_2$ failed to produce any IMDA adduct.

[7] For examples of silyl triflate mediated Diels–Alder reactions see ref. 26.

[8] **47** was shown to be stable to the $EtAlCl_2$ reaction conditions.

[9] For an example of isomerization of 2*H*-thiopyrans under similar conditions, see ref. 5.

Table 1. Attempted IMDA reactions of 4-(triisopropylsilyl)oxy-2*H*-thiopyran dienes.

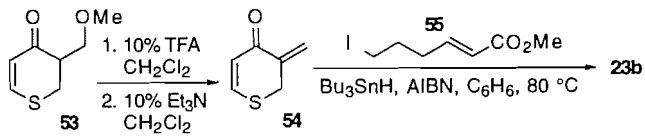
Entry	Substrate(s)	Conditions[a]	IMDA adduct(s) (% yield)[b]
1.	**6a/7a** or **6b/7b**	Thermal (150–200°C)	None
	13a or **13b**		None
	14a or **14b**		None
2.	**26a/27a** (1.2:1)	Thermal (140°C, 96 h)	**45** (55), **46** (43)
		TIPSOTf (2 h)	**45** (44), **46** (42)
		$EtAlCl_2$ (3 min)	**45** (38), **46** (34)
3.	**26b/27b** (1.3:1)	Thermal (140–180°C)	None[c]
		TIPSOTf (24 h)	None
		$EtAlCl_2$ (30 min)	**49** (40), **50** (15)
4.	**27b**	Thermal (170°C, 60 h)	**49** (37), **50** (14)
		$EtAlCl_2$ (30 min)	**49** (48), **50** (19)
5.	**28a/29a** (1.2:1)	Thermal (140°C, 96 h)	**47** (70), **48** (10)
		TIPSOTf (24 h)	**45** (44), **46** (43)
		$EtAlCl_2$ (3 min)	**45** (34), **46** (27), **47** (30), **48** (trace)[d]
6.	**28b/29b** (1.3:1)	Thermal (140–180°C)	None
		TIPSOTf (24 h)	None
		$EtAlCl_2$ (30 min)	**49** (ca. 25%)[e]
7.	**40**	Thermal (140–180°C)	None
		TIPSOTf (24 h)	None
		$EtAlCl_2$ (30 min)	None
8.	**41**	Thermal (175°C, 17 h)	**51** (86)
		TIPSOTf (13 h)	**51** (17)
		$EtAlCl_2$ (7 h)	**51** (34)
9.	**42**	Thermal (140–180°C)	None
		TIPSOTf (24 h)	None
		$EtAlCl_2$ (30 min)	None
10.	**43**	Thermal (180–210°C, 17 h)	**51** (30), **52** (33)
11.	**62a** or **62b**	Thermal (80–180°C)	None
		$EtAlCl_2$ (30 min)	None
12.	**63a** or **63b**	Thermal (80–180°C)	None
		$EtAlCl_2$ (30 min)	None

[a]See experimental section.
[b]Isolated yield based on the appropriate starting enone.
[c]This result likely due to inefficient deoxygenation (see text).
[d]Detected by ^1H NMR but not isolated.
[e]This compound was not pure; other isomers, if present, were not isolated.

Disappointingly, the expected IMDA adducts were not detected after heating C_6D_6 solutions of 1.3:1 mixtures of **26b/27b** or **28b/29b** at 140–180°C over several days. Only the oxidation products **30b** and **31b** were isolated after the usual HF work-up. Alternatively, $EtAlCl_2$ mediated reaction of a similar mixture of **26b/27b** gave **49** and **50** in 40% and 15% yields, respectively (based on **23b**). Similar treatment of **28b/29b** also produced **49** (ca. 25%) but any isomeric adducts, if present, could not be isolated. No IMDA adducts were detected or isolated after individual treatment of **22b/23b** or **24b/25b** with excess TIPSOTf in the presence of Et_3N even after prolonged reaction times (24 h). To clarify the IMDA reactivity of **27b**, a selective synthesis of **23b** was undertaken using our newly developed protocol (9). Thus, tin hydride mediated addition of **55** (28) to **54** gave **23b** directly in 45% yield (Scheme 5). Heating a degassed C_6D_6 solution of **27b** (prepared from **23b**) in a preheated oil bath at 170°C for 60 h resulted in the completed disappearance of **27b** and the adducts **49** and **50** were isolated in 37% and 14% yield, respectively, after HF work-up. The previous failure of a mixture of **26b/27b** to produce the same adducts under similar conditions is attributed to inefficient deoxygenation of the reaction solution, resulting in an increased rate of oxidation of the trienes at the expense of IMDA reaction. Treatment of **27b** with $EtAlCl_2$ gave **49** (48%) and **50** (19%) in a similar ratio and yield as previously obtained from a mixture of **26b/27b**.

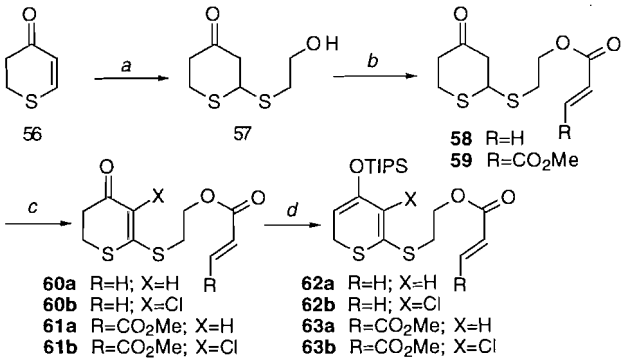
Attempted IMDA reaction of **40** under thermal (140–180°C, several days), $EtAlCl_2$, or TIPSOTf mediated conditions led only to decomposition. Similar results were obtained with **42**. Alternatively, **41** gave **51** as the only product after heating at 175°C for 17 h. The same product was obtained from **41** under Lewis acid mediated conditions. Thermal reaction of **43** is slow at 175°C and heating up to 210°C gave **52** (33%) along with **51** (30%). The formation of **51** in this reaction is due to competitive isomerization of **43** to **41** under the reaction conditions.

Scheme 5.



Scheme 6.

a: 2-Mercaptoethanol, NaH, THF; *b*: acryloyl choride or methyl fumaryl chloride, pyridine, CH_2Cl_2; *c*: NCS, CCl_4; *d*: TIPSOTf, Et_3N.



The failure of **40** and **42** to produce adducts (cf. **27**, **29**) is presumably the result of the unfavorable regiochemistry enforced by the short tether, thereby increasing the activation energy for IMDA reaction and precluding cycloaddition in favor of other pathways. To examine the possibility of effecting IMDA reaction of a C-6 tethered substrate that would allow favorable regiochemistry, compounds **62** and **63** were prepared according to Scheme 6. Addition of 2-mercaptoethanol to **56** (19) produced **57**, which was acylated with acryloyl chloride or methyl fumaryl chloride to give the unstable[10] **58** and **59**, respectively. Individual treatment of **58** and **59** with NCS produced a mixture[11] of **60a,b** and **61a,b**, respectively, which were converted into the corresponding 2*H*-thiopyrans by reaction with TIPSOTf. Adducts from IMDA reaction of **62a** and **63a** would be synthetically equivalent (via desulfurization) to adducts from an analogous intermolecular Diels–Alder reaction. Thus 2-mercaptoethanol represents a potential temporary tether of the diene to the dienophile.[12] Unfortunately, all attempts to effect IMDA reaction of **62** and **63** under thermal (in C_6D_6 or $(CD_3)_2SO$)[13] or $EtAlCl_2$ mediated conditions failed to produce any adducts. Presumably the 5-atom tether, the preference for an s-*trans* ester conformation (30),

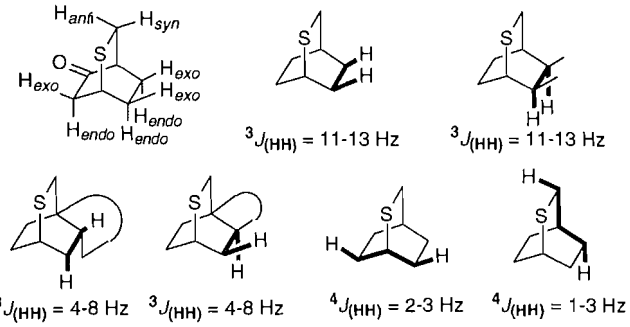
[10] These compounds were very prone to elimination to give **56** and other by-products.

[11] Chlorination under these conditions is precedented (20).

[12] For a review of the use of silicon-based temporary tethers in IMDA reactions, see ref. 29.

[13] For a review of solvent effects in IMDA reactions see ref. 30.

Fig. 2. Typical $^3J_{(HH)}$ and $^4J_{(HH)}$ coupling constants for 2*H*-thiopyran Diels–Alder adducts.



and the instability of **62** and **63** combine to favor other pathways in competition with IMDA reaction.

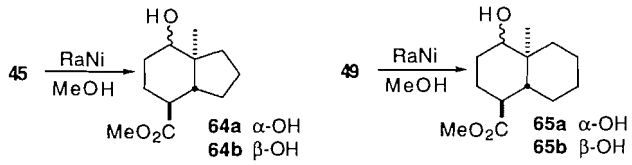
The IMDA adducts[14] **45–52** were identified on the basis of their spectroscopic properties (IR, MS, ^1H and ^{13}C NMR). In all cases, the spectral data were fully consistent with the proposed structure. In general, spectral features (especially ^1H and ^{13}C NMR) for **45–52** were similar to those from adducts obtained by intermolecular Diels–Alder reactions of 4-(triisopropylsilyl)oxy-2*H*-thiopyran with acrylate and crotonate dienophiles (7). Stereochemical assignments were based on the previously established trends (5, 7) in the $^3J_{HH}$ and $^4J_{HH}$ coupling constants outlined in Fig. 2.

Desulfurization of the IMDA adducts can potentially provide synthetically useful compounds. For example, *trans*-fused angularly methylated hydrindans (**64**) and decalins (**65**) are available by reactions of the *endo* adducts **45** and **49**, respectively, with Raney nickel (see Scheme 7). The synthetic utility of such a process will be dependent on the degree to which the diastereoselectivity (i.e., *endo* vs. *exo*) of the IMDA reaction can be controlled. Interestingly, the *endo* selectivities in the reactions of **27a** (ca. 1.1:1) and **27b** (ca. 2.5:1) are essentially independent of the reaction conditions (i.e., thermal vs. Lewis acid mediated) and are lower than **29a** (7:1).[15] As expected, only a single isomer results from cycloaddition of **41** and **43**.

[14] In principle, the same products could result from sequential Michael reactions (31). We favor a IMDA mechanism at present, because in no case have we detected or isolated the putative products from the "initial" Michael reaction. For a discussion see ref. 7.

[15] For comparison, the uncatalyzed intermolecular Diels–Alder reaction between 4-(triisopropylsilyl)oxy-2*H*-thiopyran and methyl acrylate is slightly *endo* selective (ca. 1.7:1); no adduct was obtained with methyl crotonate (7). Under Lewis acid mediated conditions (7), the reaction is *exo* selective with both methyl acrylate (1–1.6:1) and a crotonate derivative (2.5:1). In comparison to IMDA reactions of related acyclic dienes, thermal IMDA reactions of the methyl esters of (2*Z*,7*E*)- and (2*E*,7*E*)-2,7,9,-decatrienoic acids (i.e., C_3 tether) are unselective and the *endo* stereoselectivity for cycloaddition of the (2*E*,7*E*) isomer (but not the (2*Z*,7*E*) isomer) increases dramatically with Lewis acid catalysis (32*a*). Similarly, the uncatalyzed IMDA reactions (2*Z*,8*E*)- and (2*Z*,8*E*)-2,8,10-undecatrienoates (i.e., C_4 tether) are also unselective but the *endo* stereoselectivity for both isomers increases to ca. 9:1 under $EtAlCl_2$ mediated conditions (32*b*).

Scheme 7.



In conclusion, we have systematically investigated the IMDA reactions of derivatives of 4–(triisopropylsilyl)oxy-2*H*-thiopyran with potential dienophiles tethered at the C-2, C-3, C-5, and C-6 positions. Cycloaddition was only observed when dienophiles activated by a carbomethoxy group were employed. Compounds having the dienophile attached to C-2 with a C_3 tether gave adducts with high stereoselectivity. Substrates having the dienophile attached to C-3 via a C_3 or C_4 tether cyclized smoothly. With an (*E*)-enoate as the dienophile, the stereoselectivity was poor (*endo*:*exo* = 1.1–2.5:1) and essentially independent of reaction conditions (i.e., thermal vs. Lewis acid mediated). With the (*Z*)-enoate, a 7:1 mixture of *endo*:*exo* IMDA adducts was obtained under thermal conditions; with Lewis acid catalysis, isomerization of the dienophile was competitive with cycloaddition. Type II IMDA adducts were not observed with C-5 tethered substrates. Compounds having the dienophile attached to C-6 via a C_3 or a 5-atom tether also failed to give IMDA adducts. No evidence for isomerization of the 2*H*-thiopyran derivatives by [1,5] sigmatropic rearrangement was observed. The *endo* adducts obtained from the C-3 tethered substrates can be desulfurized to obtain synthetically useful *trans*-fused angularly methylated hydrindans and decalins.

Experimental

General methods

All solvents were distilled prior to use. Pyridine and Et_3N were distilled from CaH_2 and stored over KOH pellets. Anhydrous solvents were distilled under argon as follows: DMSO and DMF from CaH_2 under reduced pressure (10–15 Torr; 1 Torr = 133.3 Pa) and stored over 3Å molecular sieves; ether and tetrahydrofuran (THF) from benzophenone potassium ketyl; benzene, toluene, and CH_2Cl_2 from P_2O_5 and stored over 3Å molecular sieves; MeOH from $Mg(OMe)_2$. Benzene solutions were degassed by bubbling argon through the solvent (solution) followed by three freeze–thaw cycles under high vacuum (0.01 Torr). Unless otherwise noted, reactions were carried out under an atmosphere of argon and reaction temperatures refer to the bath. Concentration refers to removal of volatiles at water aspirator pressure on a rotary evaporator.

Preparative TLC was carried out on glass plates (20 × 20 cm) precoated (0.25 mm) with silica gel 60 F_{254}. Materials were detected by visualization under an ultraviolet lamp (254 nm) and (or) by treating a 1 cm vertical strip removed from the plate with a solution of phosphomolybdic acid (5%) containing a trace of ceric sulfate in aqueous sulfuric acid (5% v/v), followed by charring on a hot plate. Flash column chromatography (FCC) was performed according to Still et al. (33) with Merck Silica Gel 60 (40–63 μm). Medium pressure chromatography (MPC) was performed with minor modifications of the procedure reported by Taber (34). All mixed solvent eluents are reported as v/v solutions.

Spectral data

High-resolution (HRMS) spectra (exact mass measurement) were obtained on a double focussing VG 70E instument. Low-resolution mass spectra (LRMS) were recorded on a VG-70E or a single sectored, magnetic scanning MS-12. EI ionization was accomplished at 70 eV and CI at 50 eV with ammonia or isobutane as the reagent gas; only partial data are reported. IR spectra were recorded on a Fourier transform interferometer using a diffuse reflectance cell; only diagnostic peaks are reported. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ solution at 300 MHz for ^1H and 75 MHz for ^{13}C. For ^1H NMR, residual $CHCl_3$ in $CDCl_3$ was employed as the internal standard (7.26 δ); for ^{13}C NMR, $CDCl_3$ was employed (77.0 δ). The ^1H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), ap (apparent); the list of coupling constants (*J*) corresponds to the order of the multiplicity assignment. ^1H NMR spectra were normally obtained with a digital resolution of 0.244 Hz/pt (sweep width = 4000 Hz, FID = 32 K data points) and coupling constants are reported to the nearest 0.5 Hz. The ^1H NMR assignments were made on the basis of chemical shift and multiplicity and were confirmed, where necessary, by homonuclear decoupling and (or) NOE experiments. The multiplicity of ^{13}C NMR signals refers to the number of attached H's (i.e., s = C, d = CH, t = CH_2, q = CH_3) and was determined by *J*-modulation (35). The ^{13}C assignments were made on the basis of chemical shift, multiplicity, and consistency within a series of similar structures. Assignments for ^{13}C signal of the same multiplicity and similar chemical shift (i.e., $\Delta\delta < 1$ ppm) are tentative. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer.

Materials

Compounds **1** (15), **8** (21), **17** (22), **32** (22), **55** (28), **56** (19), 5-bromopentene (17), 6-bromohexene (17), 2-(3-bromopropyl)-1,3-dioxolane (23), 2-(4-bromobutyl)-1,3-dioxolane (24), 4-[(trimethylsilyl)oxy]-2*H*-thiopyran (5), and methyl fumaryl chloride (36) were prepared as reported. All other reagents were commercially available and, unless otherwise noted, were used as received.

*General procedure for alkylation of **1** and **17** (16)*

NaH (1.2 equiv.) was added to a solution of NaI (1.0 equiv.) and the β-ketoester **1** or **17** in acetone (5 mL/mmol of β-ketoester). After stirring for 5 min at room temperature (rt), the alkyl halide (3 equiv.) was added and the reaction mixture was heated under reflux for 24 h. The resulting mixture was diluted with H_2O, extracted with CH_2Cl_2 (×3), and the combined organic layers were dried over Na_2SO_4, concentrated, and fractionated by FCC to give the products **2** or **18**.

*General procedure for decarboxylation of **2** and **9** (16b)*

LiI (3 equiv.) was added to a solution of the β-ketoester in 20% (v/v) aqueous DMF (6 mL/mmol of β-ketoester) and the reaction mixture was heated under reflux until the starting material was consumed (3–5 days). The cooled (rt) reaction

mixture was diluted with CH_2Cl_2 and washed with water. The aqueous layer was extracted with CH_2Cl_2 (×2) and the combined organic layers were dried over Na_2SO_4, concentrated, and fractionated to give the products.

General procedure for decarboxylation of ***18*** *and the product from conjugate addition to* ***32*** *(22)*

A solution of tetrakis(triphenylphosphine)palladium(0) (0.05 equiv.), morpholine (10 equiv.), and the allyl β-ketoester in THF (8 mL/mmol of β-ketoester) was stirred at rt for 24 h. The reaction mixture was concentrated and fractionated to give the products.

General procedure for dehydrogenation of ***3, 10, 19, 34,*** *and* ***35*** *(19, 20)*

NCS (1.00 equiv.) was added to a stirred solution of the substrate and pyridine (1.05 equiv.) in CH_2Cl_2 (20 mL/mmol of substrate). After stirring for 10–30 min, the reaction mixture was washed with water, dried over Na_2SO_4, concentrated, and fractionated by FCC to give the products.

General procedure for conjugate addition to ***8*** *and* ***32*** *(21)*

A solution of the alkyl bromide (2.0 equiv.) in THF (1 mL/mmol of bromide) was added to a stirred suspension of Mg turnings (2.2 equiv.) in THF (2 mL/mmol of bromide) and the resulting mixture was heated under reflux for 90 min (on occasion I_2 crystals were added to initiate the reaction) and then was allowed to cool to rt.

Dimethyl sulfide (1.3 mL/mmol of CuI) was added dropwise over 5 min to a suspension of CuI (2.1 equiv.) in THF (0.65 mL/mmol of CuI) at −23°C. The resulting mixture was cooled to −78°C, and the Grignard reagent prepared above was added dropwise over 5 min. After 1.5 h, a solution of **8** or **32** in dimethyl sulfide (2 mL/mmol of ketoester) was added dropwise over a 10 min period. The reaction mixture was stirred at −78°C for 1.5 h and then was diluted with ether, warmed to 0°C, washed with $NH_4Cl_{(aq)}$ and with H_2O, dried over Na_2SO_4, concentrated, and fractionated to give the products.

General procedure for Wittig homologation of ***21*** *and* ***33***

A solution of the acetal and $HClO_4$ (0.3 M, 3 equiv.) in acetone (50 mL/mmol of acetal) was stirred at rt for 48 h. Half-saturated $NaHCO_{3(aq)}$ (ca. 1 mL) was added and most of the acetone was evaporated at reduced pressure. The resulting mixture was diluted with H_2O, extracted with CH_2Cl_2 (×2), and the combined organic layers were dried over Na_2SO_4 and concentrated to give a crude aldehyde(s) (^{1}H NMR). Methyl (triphenylphosphoranylidene)acetate (1.2 equiv.) was added to the solution of crude aldehyde(s) in MeOH (20 mL/mmol of acetal). After stirring for 3.5 h, the reaction mixture was concentrated and fractionated to give the *E* and *Z* enoates (ca. 1.5–2:1).

General procedure for preparation of 4-[tris(2-methylethyl)silyl]oxy-2H-thiopyrans

TIPSOTf (1.2 equiv.) was added to a solution of the enone and Et_3N (2.4 equiv.) in CH_2Cl_2 (ca. 10 mL/mmol of enone). The reaction was monitored by TLC and, when the enone was completely consumed (typically 10–20 min), the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, concentrated, and placed under high vacuum (ca. 0.1 Torr) for 2 h. The crude products were characterized by ^{1}H NMR, which, in each case, indicated essentially complete conversion of the enone to the silyloxy diene(s). The dienes were unstable (especially neat) and were used directly without further purification.

General procedure for Diels–Alder reactions

Thermal reaction: A solution of the crude silyloxy diene(s) (0.1–0.2 mmol) and BHT (0.15 equiv.) in C_6D_6 or $C_6D_5CD_3$ (1 mL) was degassed by several freeze–thaw cycles and sealed under vacuum in an NMR tube. The mixture was heated in an oil bath and the progress of the reaction was monitored by ^{1}H NMR. When the diene was consumed, the reaction mixture was concentrated and the residue was dissolved in CH_3CN (2 mL) and HF (48–51% aqueous solution; 70 μL) was added. After stirring for 5 min, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, concentrated, and fractionated to give the products.

Lewis acid catalyzed reaction: $EtAlCl_2$ (1 M solution in hexanes, 0.4–1 equiv.) was added to a solution of the silyloxy diene(s) (0.1–0.2 mmol) in C_6D_6 or CH_2Cl_2 (1–2 mL) at rt. After a suitable reaction time, the mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, and concentrated. The residue was dissolved in CH_3CN (2 mL) and HF (48–51% aqueous solution; 70 μL) was added. After stirring for 5 min, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, concentrated, and fractionated to give the products.

TIPSOTf catalyzed reaction: In this case the general procedure for the preparation of the silyloxy dienes was followed except 1.5–2.0 equiv. of TIPSOTf was used. After stirring for several hours, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, and concentrated. The residue was dissolved in CH_3CN (2 mL) and HF (48–51% aqueous solution; 70 μL) was added. After stirring for 5 min, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_{3(aq)}$, dried over Na_2SO_4, concentrated, and fractionated to give the products.

IMDA reaction of ***26a/27a***

IMDA adducts were obtained after PTLC (0.8% MeOH in CH_2Cl_2). Thermal reaction of a 1.2:1 mixture of **26a** and **27a** (prepared from a 1.2:1 mixture of **22a** and **23a**; 37.8 mg, 0.157 mmol) at 140°C for 96 h gave **45** (9.3 mg, 55%) and **46** (7.4 mg, 43%). Lewis acid catalyzed reaction of a similar mixture of **26a** and **27a** (prepared from a 1.2:1 mixture of **22a** and **23a**; 55 mg, 0.23 mmol) for 10 min gave **45** (9.4 mg, 38%) and **46** (8.5 mg, 34%). TIPSOTf catalyzed reaction (2 h) of a 1.2:1 mixture of **22a** and **23a** (24 mg, 0.1 mmol) gave **45** (4.8 mg, 44%) and **46** (4.5 mg, 42%). In each case a fraction containing a mixture of **22a** and **30a** (^{1}H NMR), which could be further purified, was obtained.

IMDA reaction of ***28a/29a***

IMDA adducts were obtained after PTLC (50% ether in hexane). Thermal reaction of a 1.2:1 mixture of **28a** and **29a** (pre-

pared from a 1.2:1 mixture of **24a** and **25a**; 18 mg, 0.075 mmol) at 140°C for 96 h gave **47** (5.7 mg, 70%) and **48** (0.8 mg, 10%). Lewis acid catalyzed reaction of a similar mixture of **28a** and **29a** (prepared from a 1.2:1 mixture of **24a** and **25a**; 22 mg, 0.092 mmol) for 10 min gave **45** (3.4 mg, 34%), **47** (3.0 mg, 30%), and **46** (2.7 mg, 27%). TIPSOTf catalyzed reaction (24 h) of a 1.2:1 mixture of **24a** and **25a** (14.6 mg, 0.061 mmol) gave **45** (2.9 mg, 44%) and **46** (2.8 mg, 43%). In each case a fraction containing a mixture of **22a** (**24a** in the thermal reaction) and **30a** (**31b** in the thermal reaction) (^{1}H NMR) was obtained but not further purified.

*IMDA reaction of **27b***

IMDA adducts were obtained after FCC (20–75% EtOAc in hexane). Thermal reaction **27b** (prepared from **23b**; 58 mg, 0.23 mmol) at 170°C for 60 h gave **49** (23 mg, 40%) and **50** (8 mg, 14%) along with **23b** (11 mg, 19%) and **30b** (11 mg, 19%). Lewis acid catalyzed reaction of **27b** (prepared from **23b**; 13 mg, 0.041 mmol) for 30 min gave **49** (5 mg, 48%) and **50** (2 mg, 19%) along with **23b** (2 mg, 19%) and **30b** (0.8 mg, 8%). A similar reaction of a 1.3:1 mixture of **26b** and **27b** (prepared from a 1.3:1 mixture of **22b** and **23b**; 46 mg, 0.181 mmol) for 30 min gave **49** (8 mg, 40%) and **50** (3 mg, 15%). No adducts were obtained in TIPSOTf catalyzed reactions.

*IMDA reaction of **28b** and **29b***

No adducts were obtained from attempted thermal or TIPSOTf catalyzed reactions of a 1.3:1 mixture of **28b** and **29b**. A $EtAlCl_2$ mediated reaction of a 1.3:1 mixture of **28b** and **29b** (prepared from a 1.3:1 mixture of **24b** and **25b**; 23 mg, 0.089 mmol) for 30 min gave **49** (3 mg, slightly impure; ca. 25%) after fractionation (PTLC; 50% ether in hexane). Other isomers, if present, could not be isolated. Fractionation (PTLC; 50% ether in hexane) of an attempted thermal reaction of a 1.3:1 mixture of **28b** and **29b** yielded a 1:1 mixture of **30b** and **31b**.

*IMDA reaction of **41***

IMDA adducts were obtained after PTLC (50% ether in hexane). Thermal reaction of **41** (prepared from **37**; 11 mg, 0.046 mmol) at 175°C for 17 h gave **51** (9.5 mg, 86%). Lewis acid catalyzed reaction of **41** (prepared from **37**; 11.8 mg, 0.049 mmol) for 30 min gave **51** (8.1 mg, 68%). TIPSOTf catalyzed reaction (13 h) of **37** (11.8 mg, 0.049 mmol) gave **51** (2 mg, 17%).

*IMDA reaction of **43***

IMDA adducts were obtained after PTLC (1% MeOH in CH_2Cl_2). Thermal reaction of **43** (prepared from **39**; 21.6 mg, 0.090 mmol) at 180°C for 9 h and 210°C for 11 h gave **52** (7.2 mg, 33%) and **51** (6.5 mg, 30%). Due to the previously established propensity for isomerization of the enoates, Lewis acid mediated IMDA reactions were not attempted.

*Methyl tetrahydro-4-oxo-3-(4-pentenyl)-4*H*-thiopyran-3-carboxylate (**2a**)*: 192 mg (48%) from **1** (261 mg, 1.50 mmol) after FCC (25% ether in hexane): IR ν_{max}: 3075, 1729, 1712, 1201 cm^{-1}; ^{1}H NMR δ: 5.75 (1H, dddd, J = 6.5, 6.5, 10.5, 17 Hz, HC-4′), 5.00 (1H, br d, J = 17 Hz, HC-5′), 4.95 (1H, br d, J = 10.5 Hz, HC-5′), 3.77 (3H, s, H_3CO), 3.27 (1H, dd, J = 3, 13.5 Hz, HC-2), 3.00–2.75 (4H, m, HC-5, HC-6), 2.71 (1H, d, J = 13.5 Hz, HC-2), 2.04 (2H, ap dt, J = 6.5, 6.5 Hz, HC-3′), 1.92 (1H, ap dt, J = 4.5, 13.5 Hz, HC-1′), 1.64 (1H, ap dt, J = 4.5, 13.5 Hz, HC-1′), 1.42 (1H, ap dtt, J = 12, 4.5, 7 Hz, HC-2′), 1.21 (1H, ap dtt, J = 12, 4.5, 7 Hz, HC-2′); ^{13}C NMR δ: 205.3 (s, C-4), 171.5 (s, O=CO), 138.0 (d, C-4′), 115.0 (t, C-5′), 63.0 (s, C-3), 52.4 (q, CH_3O), 43.2 (t, C-5), 38.6 (t, C-1′), 33.9 (t, C-2), 33.9 (t, C-3′), 30.8 (t, C-6), 23.8 (t, C-2′); LRMS (CI, NH_3), *m/z* (relative intensity): 260 ([M+18]$^+$, 100), 243 ([M+1]$^+$, 85), 192 (12), 173 (16).

*Methyl 3-(5-hexenyl)-tetrahydro-4-oxo-4*H*-thiopyran-3-carboxylate (**2b**)*: 185 mg (42%) from **1** (300 mg, 1.72 mmol) after FCC (25% ether in hexane): IR ν_{max}: 3074, 1730, 1712, 1201 cm^{-1}; ^{1}H NMR δ: 5.77 (1H, ap ddt, J = 10.5, 17, 6.5 Hz, HC-5′), 4.95 (2H, m, HC-6′), 3.77 (3H, s, H_3CO), 3.28 (1H, dd, J = 2.5, 14 Hz, HC-2), 3.00–2.75 (4H, m, HC-5, HC-6), 2.71 (1H, d, J = 14 Hz, HC-2), 2.08–1.98 (2H, m, HC-4′), 1.98–1.86 (1H, m, HC-1′), 1.70–1.60 (1H, m, HC-1′), 1.45–1.10 (4H, m, HC-2′, HC-3′); ^{13}C NMR δ: 205.4 (s, C-4), 171.5 (s, O=CO), 138.6 (d, C-5′), 114.6 (t, C-6′), 63.0 (s, C-3), 52.4 (q, CH_3O), 43.2 (t, C-5), 38.6 (t, C-1′), 34.2 (t, C-2), 33.4 (t, C-4′), 30.8 (t, C-6), 29.1 (t, C-3′), 24.0 (t, C-2′); LRMS (CI, NH_3), *m/z* (relative intensity): 274 ([M+18]$^+$, 100), 257 ([M+1]$^+$, 84), 173 (24).

*Tetrahydro-3-(4-pentenyl)-4*H*-thiopyran-4-one (**3a**)*: 41 mg (29%) from **2a** (189 mg, 0.78 mmol) after FCC (35% ether in hexane): IR ν_{max}: 3074, 1715, 1424, 914 cm^{-1}; ^{1}H NMR δ: 5.76 (1H, ddt, J = 10, 17, 6.5 Hz, HC-4′), 5.03–4.90 (2H, m, HC-5′), 2.98–2.88 (3H, m, HC-2, H_2C-6), 2.74–2.60 (4H, m, HC-2, HC-3, H_2C-5), 2.04 (2H, ap dt, J = 6.5, 7 Hz, H_2C-3′), 1.90–1.82 (1H, m, HC-1′), 1.42–1.30 (3H, m, HC-1′, H_2C-2′); ^{13}C NMR δ: 210.4 (s, C-4), 138.3 (d, C-4′), 114.8 (t, C-5′), 52.9 (d, C-3), 43.8 (t, C-5), 35.9 (t, C-1′), 33.6 (t, C-3′), 31.0 (t, C-2), 28.9 (t, C-6), 26.2 (t, C-2′); LRMS (CI, NH_3), *m/z* (relative intensity): 202 ([M+18]$^+$, 100), 185 ([M+1]$^+$, 48), 116 (75).

*3-(5-Hexenyl)tetrahydro-4*H*-thiopyran-4-one (**3b**)*: 57 mg (48%) from **2b** (154 mg, 0.60 mmol) after FCC (35% ether in hexane): IR ν_{max}: 3016, 1707, 1464, 965 cm^{-1}; ^{1}H NMR δ: 5.75 (1H, ddt, J = 10, 17, 6.5 Hz, HC-5′), 5.04–4.89 (2H, m, H_2C-6′), 2.98–2.88 (3H, m, H_2C-6, HC-2), 2.76–2.58 (4H, m, HC-2, HC-3, H_2C-5), 2.04 (2H, dt, J = 6.5, 7 Hz, H_2C-4′), 1.93–1.82 (1H, m, HC-1′), 1.44–1.24 (5H, m, HC-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ: 210.4 (s, C-4), 138.7 (d, C-5′), 114.5 (t, C-6′), 52.9 (d, C-3), 43.8 (t, C-5), 35.9 (t, C-1′), 33.5 (t, C-4′), 31.0 (t, C-2), 29.2 (t, C-6), 28.8 (t, C-3′), 26.4 (t, C-2′); LRMS (EI), *m/z* (relative intensity): 198 ([M]$^+$, 49), 180 (11), 116 (100), 95 (22), 88 (28).

*2,3-Dihydro-5-(4-pentenyl)-4*H*-thiopyran-4-one (**4a**) and 2,3-dihydro-3-(4-pentenyl)-4*H*-thiopyran-4-one (**5a**)*: 9.7 mg (46%; as a 1.2:1 mixture of **4a** and **5a**, respectively) from **3a** (21 mg, 0.12 mmol) after PTLC (50% ether in hexane): ^{1}H NMR δ for **4a**: 7.15 (1H, s, HC-6), 5.79 (1H, ddt, J = 10, 17, 6.5 Hz, HC-4′), 5.07–4.92 (2H, m, H_2C-5′), 3.19–3.13 (1H, m, HC-2), 2.77–2.71 (1H, m, HC-3), 2.29 (1H, ap t, J = 7.5 Hz, HC-1′), 2.14–2.00 (2H, m, HC-3′), 1.64–1.37 (2H, m, HC-2′); δ for **5a**: 7.35 (1H, d, J = 10 Hz, HC-6), 6.11 (1H, d, J = 10 Hz, HC-5), 5.79 (1H, ddt, J = 10, 17, 6.5 Hz, HC-4′), 5.07–4.92

(2H, m, H_2C-5′), 3.31 (1H, dd, J = 4, 13.5 Hz, HC-2), 3.05 (1H, dd, J = 9, 13.5 Hz, HC-2), 2.53 (1H, dddd, J = 4, 5.5, 8, 9 Hz, HC-3), 2.14–2.00 (2H, m, H_2C-3′), 1.86 (1H, dddd, J = 5.5, 5.5, 10.5, 13.5 Hz, HC-1′), 1.64–1.37 (3H, m, HC-1′, H_2C-2′); ^{13}C NMR δ for **4a**: 193.6 (s, C-4), 140.3 (d, C-6), 138.5 (d, C-4′), 134.8 (s, C-5), 114.7 (t, C-5′), 38.4 (t, C-3), 33.6 (t, C-3′), 30.8 (t, C-1′), 28.2 (t, C-2′), 27.3 (t, C-2); δ for **5a**: 196.2 (s, C-4), 145.1 (d, C-6), 138.2 (d, C-4′), 123.2 (d, C-3), 114.9 (t, C-5′), 45.1 (d, C-3), 33.3 (t, C-3′), 31.8 (t, C-1′), 27.6 (t, C-2), 26.3 (t, C-2′).

*5-(5-Hexenyl)-2,3-dihydro-4*H*-thiopyran-4-one (**4b**) and 3-(5′-hexenyl)-2,3-dihydro-4*H*-thiopyran-4-one (**5b**)*: 15.2 mg (71%; as a 1.2:1 mixture of **4b** and **5b**, respectively) from **3b** (22 mg, 0.11 mmol) after PTLC (50% ether in hexane): ^{1}H NMR δ for **4b**: 7.14 (1H, br s, HC-6), 5.79 (1H, ddt, J = 10, 17, 6.5 Hz, HC-5′), 5.04–4.90 (2H, m, H_2C-6′), 3.19–3.13 (2H, m, H_2C-2), 2.77–2.71 (2H, m, H_2C-3), 2.32–2.34 (2H, m, H_2C-1′), 2.11–2.00 (2H, m, H_2C-4′), 1.64–1.30 (4H, m, H_2C-2′, H_2C-3′); δ for **5b**: 7.35 (1H, d, J = 10 Hz, HC-6), 6.11 (1H, d, J = 10 Hz, HC-5), 5.79 (1H, ddt, J = 10, 17, 6.5 Hz, HC-5′), 5.04–4.90 (2H, m, HC-6′), 3.31 (1H, dd, J = 4, 13.5 Hz, HC-2), 3.04 (1H, dd, J = 8.5, 13.5 Hz, HC-2), 2.52 (1H, dddd, J = 4, 5.5, 8.5, 9 Hz, HC-3), 2.11–2.00 (2H, m, H_2C-4′), 1.90–1.80 (1H, m, HC-1′), 1.64–1.30 (5H, m, HC-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ for **4b**: 193.6 (s, C-4), 140.0 (d, C-6), 138.9 (d, C-5′), 135.0 (s, C-5), 114.4 (t, C-6′), 38.4 (t, C-3), 33.6 (t, C-4′), 31.1 (t, C-1′), 28.6 (t, C-3′), 28.5 (t, C-2′), 27.3 (t, C-2); δ for **5b**: 196.3 (s, C-4), 145.1 (d, C-6), 138.7 (d, C-5′), 123.1 (d, C-5), 114.6 (t, C-6′), 45.2 (d, C-3), 33.6 (t, C-4′), 31.7 (d, C-1′), 28.8 (t, C-3′), 27.9 (t, C-2), 26.4 (t, C-2′).

*4-[[Tris(1-methylethyl)silyl]oxy]-5-(4-pentenyl)-2*H*-thiopyran (**6a**) and 4-[[tris(1-methylethyl)silyl]oxy]-3-(4-pentenyl)-2*H*-thiopyran (**7a**)*

Obtained as a 1.2:1 mixture of **6a** and **7a** from a 1.2:1 mixture of **4a** and **5a**: ^{1}H NMR ($C_6D_5CD_3$) δ for **6a** (partial data): 5.87 (1H, s, HC-6), 5.78–5.68 (1H, m, HC-4′), 5.05–4.91 (2H, m, HC-5′), 4.62 (1H, t, J = 5.5 Hz, HC-3), 2.99 (2H, d, J = 5.5 Hz, HC-2); δ for **7a** (partial data): 5.95 (1H, d, J = 10 Hz, HC-6), 5.87 (1H, d, J = 10 Hz, HC-5), 5.78–5.68 (1H, m, HC-4′), 5.05–4.91 (2H, m, HC-5′), 3.01 (2H, s, HC-2).

*5-(5′-Hexenyl)-4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran (**6b**) and 3-(5′-hexenyl)-4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran (**7b**)*

Obtained as a 1.2:1 mixture of **6b** and **7b** from a 1.2:1 mixture of **4b** and **5b**: ^{1}H NMR ($C_6D_5CD_3$) δ for **6b** (partial data): 5.86 (1H, s, HC-6), 5.75–5.65 (1H, m, HC-5′), 5.01–4.87 (2H, m, HC-6′), 4.61 (1H, t, J = 5.5 Hz, HC-3), 2.99 (2H, d, J = 5.5 Hz, HC-2); δ for **7b** (partial data): 5.92 (1H, d, J = 10 Hz, HC-6), 5.84 (1H, d, J = 10 Hz, HC-5), 5.75–5.65 (1H, m, HC-5′), 5.01–4.87 (2H, m, HC-6′), 3.04 (2H, s, HC-2).

*Methyl tetrahydro-4-oxo-2-(4-pentenyl)-4*H*-thiopyran-3-carboxylate (**9a**)*: 310 mg (88%) from **8** (250 mg, 1.45 mmol) after FCC (20% EtOAc in hexane): IR ν_{max}: 3075, 1746, 1714, 1649, 1609 cm^{-1}; ^{1}H NMR (a 1:2 mixture of keto:enol tautomers) δ: 12.69 (0.7H, s, HO[enol]), 5.88–5.68 (1H, m, HC-4′), 5.04–4.91 (2H, m, HC-5′), 3.88 (2H, s, H_3CO[enol]), 3.88 (1H, s, H_3CO[keto]), 3.48–3.41 (1.3H, m, HC-2, HC-3[keto]), 3.02–2.80 (1.7H, m, H_2C-6[enol], HC-6[keto]), 2.70–2.43 (2.3H, m, H_2C-5, HC-6[keto]), 2.17–1.95 (2H, m, H_2C-3′), 1.77–1.39 (4H, m, H_2C-1′, H_2C-2′); ^{13}C NMR δ for keto form: 203.7 (s, C-4), 168.8 (s, OC=O), 137.7 (d, C-4′), 114.8 (t, C-5′), 64.5 (d, C-3), 52.1 (q, CH_3O), 45.7 (d, C-2), 42.4 (t, C-5), 32.8 (t, C-1′ or C-3′), 32.7 (t, C-3′ or C-1′), 26.6 (t, C-6), 25.7 (t, C-2′); δ for enol form: 172.5 (s, C-4), 171.6 (s, OC=O), 138.4 (d, C-4′), 114.3 (t, C-5′), 102.6 (s, C-3), 51.5 (q, CH_3O), 36.1 (d, C-2), 35.0 (t, C-5), 32.8 (t, C-3′), 30.5 (t, C-1′), 27.1 (t, C-2′), 19.8 (t, C-6); LRMS (EI), *m/z* (relative intensity): 242 ([M]$^+$, 21), 173 (73), 141 (77), 83 (100).

*Methyl 2-(5-hexenyl)tetrahydro-4-oxo-4*H*-thiopyran-3-carboxylate (**9b**)*: 190 mg (85%) from **8** (150 mg, 0.871 mmol) after FCC (20% EtOAc in hexane): IR ν_{max}: 3074, 1746, 1714, 1649, 1609 cm^{-1}; ^{1}H NMR (a 1:2 mixture of keto:enol tautomers) δ: 12.64 (0.7H, s, HO[enol]), 5.85–5.67 (1H, m, HC-5′), 5.01–4.88 (2H, m, H_2C-6′), 3.74 (2H, s, H_3CO[enol]), 3.74 (1H, s, H_3CO[keto]), 3.45–3.36 (1.3H, m, HC-2, HC-3[keto]), 3.00–2.77 (1.7H, m, H_2C-6[enol], HC-6[keto]), 2.67–2.41 (2.3H, m, H_2C-5, HC-6[keto]), 2.08–1.97 (2H, m, H_2C-4′), 1.74–1.28 (6H, m, H_2C-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ for keto form: 203.9 (s, C-4), 169.0 (s, OC=O), 138.5 (d, C-5′), 114.6 (t, C-6′), 64.8 (d, C-3), 52.3 (q, CH_3O), 46.0 (d, C-2), 42.7 (t, C-5), 33.4 (t, C-1′), 33.4 (t, C-4′), 28.3 (t, C-3′), 26.9 (t, C-6), 26.1 (t, C-2′); δ for enol form: 172.7 (s, C-4), 171.9 (s, OC=O), 138.9 (d, C-5′), 114.3 (t, C-6′), 102.9 (s, C-3), 51.7 (q, CH_3O), 36.4 (d, C-2), 35.6 (t, C-5), 33.7 (t, C-4′), 30.8 (t, C-1′), 28.2 (t, C-3′), 27.6 (t, C-2′), 20.0 (t, C-6); LRMS (EI), *m/z* (relative intensity): 256 ([M]$^+$, 12), 197 (24), 173 (62), 141 (62), 84 (100).

*Tetrahydro-2-(4-pentenyl)-4*H*-thiopyran-4-one (**10a**)*: 45 mg (33%) from **9a** (180 mg, 0.743 mmol) after by FCC (30% ether in hexane): IR ν_{max}: 3075, 1712, 1643 cm^{-1}; ^{1}H NMR δ: 5.77 (1H, dddd, J = 6.5, 6.5, 10.5, 17 Hz, HC-4′), 5.00 (1H, br d, J = 17 Hz, HC-5′), 4.96 (1H, br d, J = 10.5 Hz, HC-5′), 3.07 (1H, dddd, J = 3.5, 6.5, 6.5, 10.5 Hz, HC-2), 3.00–2.82 (2H, m, H_2C-6), 2.73 (1H, ddd, J = 1, 3.5, 14 Hz, HC-3), 2.68–2.55 (2H, m, H_2C-5), 2.43 (1H, dd, J = 10.5, 14 Hz, HC-3), 2.10–2.00 (2H, m, H_2C-3′), 1.65–1.45 (4H, m, H_2C-1′, H_2C-2′); ^{13}C NMR δ: 208.7 (s, C-4), 138.1 (d, C-4′), 115.0 (t, C-5′), 50.7 (t, C-3), 44.7 (d, C-2), 43.4 (t, C-5), 35.0 (t, C-1′), 33.3 (t, C-3′), 28.1 (t, C-6), 26.0 (t, C-2′); LRMS (EI), *m/z* (relative intensity): 184 ([M]$^+$, 40), 141 (39), 128 (52), 115 (100).

*2-(5-Hexenyl)tetrahydro-4*H*-thiopyran-4-one (**10b**)*: 87 mg (74%) from **9b** (142 mg, 0.554 mmol) after fractionation by FCC (30% ether in hexane): IR ν_{max}: 3075, 1713, 1640 cm^{-1}; ^{1}H NMR δ: 5.77 (1H, dddd, J = 6.5, 6.5, 10.5, 17.5 Hz, HC-5′), 4.99 (1H, br d, J = 17.5 Hz, HC-6′), 4.94 (1H, br d, J = 10.5 Hz, HC-6′), 3.06 (1H, dddd, J = 3.5, 6.5, 6.5, 10.5 Hz, HC-2), 3.00–2.82 (2H, m, H_2C-6), 2.73 (1H, ddd, J = 1, 3.5, 14 Hz, HC-3), 2.68–2.55 (2H, m, H_2C-5), 2.43 (1H, dd, J = 10.5, 14 Hz, HC-3), 2.10–2.00 (2H, m, H_2C-4′), 1.65–1.35 (6H, m, H_2C-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ: 208.7 (s, C-4), 138.6 (d, C-5′), 114.6 (t, C-6′), 50.7 (t, C-3), 44.7 (d, C-2), 43.4 (t, C-5), 35.5 (t, C-1′), 33.5 (t, C-4′), 28.5 (t, C-3′), 28.1 (t, C-6), 26.3 (t, C-2′); LRMS (CI, NH_3), *m/z* (relative intensity): 216 ([M + 18]$^+$, 100), 198 (36), 141 (19), 115 (24), 83 (28).

*2,3-Dihydro-6-(4-pentenyl)-4H-thiopyran-4-one (**11a**) and 2,3-dihydro-2-(4-pentenyl)-4H-thiopyran-4-one (**12a**)*

11a (13 mg, 40%) and **12a** (6 mg, 18%) were obtained from **10a** (33 mg, 0.18 mmol) after FCC (50% ether in hexane).

For **11a**: IR ν_{max}: 3075, 1655, 1571 cm^{-1}; ^1H NMR δ: 6.08 (1H, s, HC-5), 5.78 (1H, ap ddt, J = 10.5, 17, 7 Hz, HC-4′), 5.08–5.98 (2H, m, H_2C-5′), 3.19–3.14 (2H, m, H_2C-2), 2.67–2.62 (2H, m, H_2C-3), 2.39 (2H, ap t, J = 7 Hz, H_2C-1′), 2.10 (2H, ap dt, J = 7, 7 Hz, H_2C-3′), 1.70 (2H, ap tt, J = 7, 7 Hz, H_2C-2′); ^{13}C NMR δ: 144.3 (s, C-4), 164.6 (s, C-6), 137.5 (d, C-4′), 121.9 (d, C-5), 115.5 (t, C-5′), 37.6 (t, C-1′), 36.8 (t, C-3), 32.8 (t, C-3′), 27.8 (t, C-2 or C-2′), 27.4 (t, C-2 or C-2′); LRMS (EI), *m/z* (relative intensity): 182 ([M]$^+$, 73), 128 (100), 126 (45), 100 (100), 85 (64).

For **12a**: IR ν_{max}: 3075, 1661, 1548 cm^{-1}; ^1H NMR δ: 7.42 (1H, d, J = 10 Hz, HC-6), 6.16 (1H, d, J = 10 Hz, HC-5), 5.76 (1H, dddd, J = 7, 7, 10.5, 17 Hz, HC-4′), 5.05–4.95 (2H, m, H_2C-5′), 3.53–3.45 (1H, m, HC-2), 2.78 (1H, dd, J = 3.5, 16 Hz, HC-3), 2.58 (1H, dd, J = 11.5, 16 Hz, HC-3), 2.07 (2H, ap dt, J = 7, 7 Hz, H_2C-3′), 1.78–1.68 (2H, m, H_2C-1′), 1.58–1.47 (2H, m, H_2C-2′); ^{13}C NMR δ: 194.6 (s, C-4), 145.6 (d, C-6), 137.7 (d, C-4′), 123.4 (d, C-5), 115.3 (t, C-5′), 44.5 (t, C-3), 43.0 (d, C-2), 33.3 (t, C-1′ or C-3′), 33.2 (t, C-1′ or C-3′), 25.8 (t, C-2′); LRMS (EI), *m/z* (relative intensity): 182 ([M]$^+$, 22), 154 (82), 126 (35), 113 (78), 86 (100).

*6-(5-Hexenyl)-2,3-dihydro-4H-thiopyran-4-one (**11b**) and 2-(5′-hexenyl)-2,3-dihydro-4H-thiopyran-4-one (**12b**)*

11b (45 mg, 60%) and **12b** (15 mg, 20%) were obtained from **10b** (76 mg, 0.38 mmol) after FCC (60% ether in hexane).

For **11b**: IR ν_{max}: 3074, 1653, 1571 cm^{-1}; ^1H NMR δ: 6.08 (1H, s, HC-5), 5.78 (1H, ap ddt, J = 10.5, 17, 7 Hz, HC-5′), 5.06–4.96 (2H, m, H_2C-6′), 3.18–3.13 (2H, m, H_2C-2), 2.67–2.62 (2H, m, H_2C-3), 2.38 (2H, ap t, J = 7 Hz, H_2C-1′), 2.07 (2H, ap dt, J = 7, 7 Hz, H_2C-4′), 1.66–1.55 (2H, m, H_2C-2′), 1.48–1.38 (2H, m, H_2C-3′); ^{13}C NMR δ: 194.4 (s, C-4), 164.9 (s, C-6), 138.3 (d, C-5′), 121.7 (d, C-5), 114.9 (t, C-6′), 38.2 (t, C-1′), 36.8 (t, C-3), 33.3 (t, C-4′), 28.1 (t , C-2′), 28.1 (t, C-3′), 27.4 (t, C-2); LRMS (EI), *m/z* (relative intensity): 196 ([M]$^+$, 24), 167 (22), 141 (46), 128 (100), 100 (99).

For **12b**: IR ν_{max}: 3075, 1663, 1548 cm^{-1}; ^1H NMR δ: 7.42 (1H, d, J = 10 Hz, HC-6), 6.16 (1H, d, J = 10 Hz, HC-5), 5.78 (1H, dddd, J = 7, 7, 10.5, 17 Hz, HC-5′), 5.05–4.95 (2H, m, H_2C-6′), 3.53–3.45 (1H, m, HC-2), 2.78 (1H, dd, J = 3.5, 16 Hz, HC-3), 2.58 (1H, dd, J = 11.5, 16 Hz, HC-3), 2.12–2.01 (2H, m, H_2C-4′), 1.71 (2H, m, H_2C-1′), 1.51–1.35 (4H, m, H_2C-2′, H_2C-3′); ^{13}C NMR δ: 194.7 (s, C-4), 145.7 (d, C-6), 138.4 (d, C-5′), 123.4 (d, C-5), 114.8 (t, C-6′), 44.5 (t, C-3), 43.1 (d, C-2), 33.8 (t, C-1′), 33.4 (t, C-4′), 28.4 (t, C-3′), 26.0 (t, C-2′); LRMS (EI), *m/z* (relative intensity): 196 ([M]$^+$, 11), 168 (9), 139 (10), 113 (52), 86 (100).

*4-[[Tris(1-methylethyl)silyl]oxy]-6-(4′-pentenyl)-2H-thiopy-ran (**13a**)*: ^1H NMR ($C_6D_5CD_3$) (partial data) δ: 5.86 (1H, d, J = 1 Hz, HC-5), 5.64 (1H, ddt, J = 10.5, 17, 7 Hz, HC-4′), 4.98–4.88 (2H, m, HC-5′), 4.52 (1H, dt, J = 1, 6.5 Hz, HC-3), 3.11 (2H, d, J = 5.5 Hz, HC-2).

*6-(5′-Hexenyl)-4-[[tris(1-methylethyl)silyl]oxy]-2H-thi-opyran (**13b**)*: ^1H NMR ($C_6D_5CD_3$) (partial data) δ: 5.87 (1H, d, J = 1 Hz, HC-5), 5.68 (1H, ddt, J = 10.5, 17, 7 Hz, HC-5′), 4.98–4.88 (2H, m, HC-6′), 4.53 (1H, dt, J = 1, 5.5 Hz, HC-3), 3.12 (2H, d, J = 5.5 Hz, HC-2).

*4-[[Tris(1-methylethyl)silyl]oxy]-2-(4′-pentenyl)-2H-thiopy-ran (**14a**)*: ^1H NMR ($C_6D_5CD_3$) (partial data) δ: 5.97 (1H, d, J = 10 Hz, HC-6), 5.87 (1H, dd, J = 1, 10 Hz, HC-5), 5.63 (1H, ddt, J = 10.5, 17, 7 Hz, HC-4′), 4.97–4.87 (2H, m, HC-5′), 4.77 (1H, dd, J = 1, 6.5 Hz, HC-3), 3.17 (1H, br ddd, J = 6.5, 6.5, 6.5 Hz, HC-2).

*2-(5′-Hexenyl)-4-[[tris(1-methylethyl)silyl]oxy]-2H-thiopy-ran (**14b**)*: ^1H NMR ($C_6D_5CD_3$) (partial data) δ: 5.97 (1H, d, J = 10 Hz, HC-6), 5.87 (1H, dd, J = 1, 10 Hz, HC-5), 5.68 (1H, ddt, J = 10.5, 17, 7 Hz, HC-5′) 4.98–4.88 (2H, m, HC-6′), 4.78 (1H, dd, J = 1, 6.5 Hz, HC-3), 3.17 (1H, ddd, J = 6.5, 6.5, 6.5 Hz, HC-2).

*2-Propenyl 3-[3-(1,3-dioxolan-2-yl)propyl]tetrahydro-4-oxo-2H-thiopyran-3-carboxylate (**18a**)*: 591 mg (75%) from **17** (500 mg, 2.50 mmol) after FCC (60% ether in hexane): IR ν_{max}: 1727, 1711, 1129 cm^{-1}; ^1H NMR δ: 5.92 (1H, dddd, J = 5.5, 5.5, 10.5, 17 Hz, HC-2′), 5.35 (1H, br d, J = 17 Hz, HC-3′), 5.26 (1H, br d, J = 10.5 Hz, HC-3′), 4.83 (1H, dd, J = 4.5, 4.5 Hz, HC-2‴), 4.68 (2H, br d, J = 5.5 Hz, H_2C-1′), 3.98–3.79 (4H, m, H_2C-4‴, H_2C-5‴), 3.31 (1H, dd, J = 2.5, 13.5 Hz, HC-2), 2.99–2.74 (4H, m, H_2C-5, H_2C-6), 2.73 (1H, d, J = 13.5 Hz, HC-2), 1.97 (1H, ddd, J = 4.5, 12, 12.5 Hz, HC-1″), 1.74 (1H, ddd, J = 4.5, 12, 12.5 Hz, HC-1″), 1.70–1.62 (2H, m, H_2C-3″), 1.55–1.25 (2H, m, H_2C-2″); ^{13}C NMR δ: 205.1 (s, C-4), 170.6 (s, OC=O), 131.5 (d, C-2′), 119.1 (t, C-3′), 104.2 (d, C-2‴), 66.1 (t, C-1′), 64.9 (t ×2, C-4‴, C-5‴), 63.0 (s, C-3), 43.2 (t, C-5), 38.4 (t, C-1″), 34.2 (t, C-2 or C-3″), 34.0 (t, C-2 or C-3″), 30.8 (t, C-6), 19.1 (t, C-2″); LRMS (EI), *m/z* (relative intensity): 314 ([M]$^+$, 5), 252 (23), 199 (44), 141 (74), 114 (100).

*2-Propenyl 3-[4-(1,3-dioxolan-2-yl)butyl]tetrahydro-4-oxo-2H-thiopyran-3-carboxylate (**18b**)*: 1.35 g (79%) from **17** (1.04 g, 5.20 mmol) after FCC (35% EtOAc in hexane): IR ν_{max}: 1730, 1712, 1129 cm^{-1}; ^1H NMR δ: 5.90 (1H, ap ddt, J = 17, 10, 4.5 Hz, HC-2′), 5.35 (1H, dddd, J = 1.5, 1.5, 1.5, 17 Hz, HC-3′), 5.26 (1H, dddd, J = 1.5, 1.5, 1.5, 10 Hz, HC-3′), 4.82 (1H, dd, J = 4.5, 4.5 Hz, HC-2‴), 4.67 (2H, br d, J = 5.5 Hz, H_2C-1′), 4.00–3.78 (4H, m, H_2C-4‴, H_2C-5‴), 3.29 (1H, dd, J = 2.5, 13.5 Hz, HC-2), 3.01–2.73 (4H, m, H_2C-5, H_2C-6), 2.72 (1H, d, J = 13.5 Hz, HC-2), 1.99–1.88 (1H, m, HC-1″), 1.75–1.12 (7H, m, HC-1″, H_2C-2″, H_2C-3″, H_2C-4″); ^{13}C NMR δ: 205.3 (s, C-4), 170.7 (s, OC=O), 131.5 (d, C-2′), 119.1 (t, C-3′), 104.4 (d, C-2‴), 66.0 (t, C-1′), 64.9 (t ×2, C-4‴, C-5‴), 63.0 (s, C-3), 43.2 (t, C-5), 38.6 (t, C-1″), 34.3 (t, C-2), 33.5 (t, C-4″), 30.9 (t, C-6), 24.4 (t, C-2″ or C-3″), 24.3 (t, C-2″ or C-3″); LRMS (EI), *m/z* (relative intensity): 328 ([M]$^+$, 34), 311 (25), 268 (25), 267 (100), 244 (29), 240 (22).

*3-[3-(1,3-Dioxolan-2-yl)propyl]-tetrahydro-4H-thiopyran-4-one (**19a**)*: 453 mg (74%) from **18a** (835 mg, 2.66 mmol) after FCC (60% ether/hexane): IR ν_{max}: 1707, 1422, 1140 cm^{-1}; ^1H NMR δ: 4.84 (1H, dd, J = 4.5, 4.5 Hz, HC-2″), 3.98–3.80 (4H, m, H_2C-4″, H_2C-5″), 3.00–2.60 (7H, m, H_2C-2, HC-3, H_2C-5, H_2C-6), 1.96–1.85 (1H, m, HC-1′), 1.70–1.62 (2H, m, HC-3′), 1.45–1.35 (3H, m, HC-1′, H_2C-2′); ^{13}C NMR δ: 210.2 (s, C-4),

104.3 (d, C-2″), 64.9 (t ×2, C-4″, C-5″), 53.0 (d, C-3), 43.9 (t, C-5), 35.8 (t, C-3′), 33.8 (t, C-1′), 31.0 (t, C-2), 29.2 (t, C-6), 21.4 (t, C-2′); LRMS (CI, NH_3), *m/z* (relative intensity): 248 ($[M+18]^+$, 54), 231 ($[M+1]^+$, 27), 213 (82), 73 (100).

*3-[4-(1,3-Dioxolan-2-yl)butyl]-4*H*-thiopyran-4-one* (***19b***): 576 mg (61%) from **18b** (1.28 g, 3.90 mmol) after FCC (35% ether in hexane): IR ν_{max}: 2949, 2876, 1708, 1140, 1026 cm^{-1}; ^{1}H NMR δ: 4.83 (1H, dd, J = 4.5, 4.5 Hz, HC-2″), 4.00–3.80 (4H, m, H_2C-4″, H_2C-5″), 3.00–2.91 (3H, m, HC-2, H_2C-6), 2.75–2.62 (4H, m, HC-2, HC-3, H_2C-5), 1.95–1.84 (1H, m, HC-1′), 1.69–1.61 (2H, m, H_2C-4′), 1.49–1.27 (5H, m, HC-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ: 210.3 (s, C-4), 104.5 (d, C-2″), 64.9 (t ×2, C-4″, C-5″), 52.9 (d, C-3), 43.8 (t, C-5), 35.9 (t, C-1′), 33.7 (t, C-4′), 31.0 (t, C-2), 29.4 (t, C-6), 26.9 (t, C-2′), 24.0 (t, C-3′); LRMS (EI), *m/z* (relative intensity): 244 ($[M]^+$, 55), 182 (100), 154 (30), 126 (45), 116 (73), 99 (88).

*5-[3-(1,3-Dioxolan-2-yl)propyl]-2,3-dihydro-4*H*-thiopyran-4-one* (***20a***) *and 3-[3-(1,3-dioxolan-2-yl)propyl]-2,3-dihydro-4*H*-thiopyran-4-one* (***21a***): 132 mg (55%; as a 1.1:1 mixture of **20a** and **21a**, respectively) from **19a** (242 mg, 1.05 mmol) after FCC (40% EtOAc in hexane): ^{1}H NMR δ for **20a**: 7.16 (1H, br s, HC-6), 4.84 (1H, t, J = 4 Hz, HC-2″), 3.98–3.80 (4H, m, H_2C-4″, H_2C-5″), 3.18–3.12 (1H, m, HC-2), 2.76–2.70 (1H, m, HC-3), 2.32 (1H, t, J = 7.5 Hz, HC-1′), 1.73–1.61 (2H, m, H_2C-3′), 1.60–1.50 (2H, m, H_2C-2′); δ for **21a**: 7.35 (1H, d, J = 10 Hz, HC-6), 6.10 (1H, d, J = 10 Hz, HC-5), 4.85 (1H, t, J = 4 Hz, HC-2″), 3.98–3.80 (4H, m, H_2C-4″, H_2C-5″), 3.30 (1H, dd, J = 3.5, 13.5 Hz, HC-2), 3.04 (1H, br dd, J = 9, 13.5 Hz, HC-2), 2.52 (1H, dddd, J = 3.5, 5.5, 8, 9 Hz, HC-3), 1.88 (1H, dddd, J = 5.5, 5.5, 10, 13 Hz, HC-1′), 1.73–1.61 (2H, m, H_2C-3′), 1.60–1.50 (2H, m, H_2C-2′), 1.48–1.40 (1H, m, HC-1′); ^{13}C NMR δ for **20a**: 193.5 (s, C-4), 140.5 (d, C-6), 134.5 (s, C-5), 104.4 (d, C-2″), 64.9 (t ×2, C-4″, C-5″), 38.3 (t, C-3), 33.3 (t, C-3′), 30.9 (t, C-1′), 27.3 (t, C-2), 23.3 (t, C-2′); δ for **21a**: 74, 196.0 (s, C-4), 145.1 (d, C-6), 123.2 (d, C-5), 104.2 (d, C-2″), 64.9 (t ×2, C-4″, C-5″), 45.2 (d, C-3), 33.7 (t, C-3′), 31.6 (t, C-1′), 27.9 (t, C-2), 21.4 (t, C-2′).

*5-[4-(1,3-Dioxolan-2-yl)butyl]-2,3-dihydro-4*H*-thiopyran-4-one* (***20b***) *and 3-[4-(1,3-dioxolan-2-yl)butyl]-2,3-dihydro-4*H*-thiopyran-4-one* (***21b***): 198 mg (31%; as a 1.3:1 mixture of **20b** and **21b**, respectively) from **19b** (635 mg, 2.60 mmol) after FCC (50% EtOAc in hexane): IR ν_{max}: 2943, 1775, 1713, 1661, 1352, 1176, 1140 cm^{-1}; ^{1}H NMR δ for **20b**: 7.15 (1H, s, HC-6), 4.85 (1H, dd, J = 2.5, 5 Hz, HC-2″), 4.10–3.20 (4H, m, H_2C-4″, H_2C-5″), 3.19–3.13 (2H, m, H_2C-2), 2.77–2.71 (2H, m, H_2C-3), 2.31–2.26 (2H, m, H_2C-1′), 1.75–1.60 (2H, m, H_2C-4′), 1.60–1.40 (4H, m, H_2C-2′, H_2C-3′); δ for **21b**: 7.35 (1H, d, J = 10 Hz, HC-6), 6.10 (1H, d, J = 10 Hz, HC-5), 4.85 (1H, dd, J = 2.5, 5 Hz, HC-2″), 4.10–3.20 (4H, m, H_2C-4″, H_2C-5″), 3.32 (1H, dd, J = 4, 13 Hz, HC-2), 3.04 (1H, dd, J = 9, 13 Hz, HC-2), 2.56–2.48 (1H, m, HC-3), 1.93–1.80 (1H, m, HC-1′), 1.75–1.60 (2H, m, H_2C-4′), 1.60–1.40 (5H, m, HC-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ for **20b**: 193.5 (s, C-4), 145.1 (d, C-6), 134.8 (s, C-5), 104.5 (d, C-2″), 64.8 (t ×2, C-4″, C-5″), 38.4 (t, C-3), 33.7 (t, C-4′), 31.2 (t, C-1′), 28.9 (t, C-2′), 27.2 (t, C-2), 23.7 (t, C-3′); δ for **21b**: 196.2 (s, C-4), 140.2 (d, C-6), 123.1 (d, C-5), 104.4 (d, C-2″), 64.8 (t ×2, C-4″, C-5″), 45.1 (d, C-3), 33.7 (t, C-4′), 31.7 (t, C-1′), 28.0 (t, C-2), 26.9 (t, C-2′), 23.9 (t, C-3′); LRMS (EI), *m/z* (relative intensity): 242 ($[M]^+$, 3), 197 (3), 114 (9), 99 (28), 73 (100), 56 (19), 45 (15).

Methyl (E)*-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-5-yl)-2-hexenoate* (***22a***)*, methyl* (E)*-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-3-yl)-2-hexenoate* (***23a***)*, methyl* (Z)*-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-5-yl)-2-hexenoate* (***24a***)*, and methyl* (Z)*-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-3-yl)-2-hexenoate* (***25a***)

A 1.2:1 mixture of **22a** and **23a** (31 mg, 35%) and a 1.2:1 mixture of **24a** and **25a** (18 mg, 21%) were obtained from a 1.2:1 mixture of **20a** and **21a** (84 mg, 0.37 mmol) after PTLC (50% ether in hexane, developed ×2)

For **22a/23a**: ^{1}H NMR δ for **22a**: 7.16 (1H, br s, HC-6′), 6.94 (1H, dt, J = 15.5, 7 Hz, HC-3), 5.82 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.72 (3H, s, H_3CO), 3.19–3.13 (2H, m, HC-2′), 2.77–2.71 (2H, m, HC-3′), 2.29 (2H, ap t, J = 7.5 Hz, H_2C-6), 2.20 (2H, ap ddt, J = 1.5, 7.5, 7 Hz, H_2C-4), 1.59 (2H, ap tt, J = 7.5, 9 Hz, H_2C-5); δ for **23a**: 7.35 (1H, d, J = 10 Hz, HC-6′), 6.94 (1H, dt, J = 15.5, 7 Hz, HC-3), 6.09 (1H, d, J = 10 Hz, HC-5′), 5.82 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.72 (3H, s, H_3CO), 3.29 (1H, dd, J = 4, 13.5 Hz, HC-2′), 3.03 (1H, dd, J = 9, 13.5 Hz, HC-2′), 2.57–2.48 (1H, m, HC-3′), 2.26–2.19 (2H, m, H_2C-4), 1.89–1.81 (1H, m, HC-6), 1.62–1.50 (3H, m, H_2C-5, HC-6); ^{13}C NMR δ for **22a**: 193.4 (s, C-4′), 167.0 (s, C-1), 148.9 (d, C-3), 140.8 (d, C-6′), 134.2 (s, C-5′), 121.2 (d, C-2), 51.4 (q, CH_3O), 38.3 (t, C-3′), 31.8 (t, C-6), 30.9 (t, C-4), 27.4 (t, C-5), 27.2 (t, C-2′); δ for **23a**: 195.8 (s, C-4′), 167.0 (s, C-1), 148.5 (d, C-3), 145.2 (d, C-6′), 123.1 (d, C-5′), 121.4 (d, C-2), 51.3 (q, CH_3O), 45.0 (d, C-3′), 32.0 (t, C-4), 31.7 (t, C-6), 27.8 (t, C-2′), 25.5 (t, C-5).

For **24a/25a**: ^{1}H NMR δ for **24a**: 7.17 (1H, br s, HC-6′), 6.22 (1H, dt, J = 11.5, 7.5 Hz, HC-3), 5.78 (1H, dt, J = 11.5, 1.5 Hz, HC-2), 3.71 (3H, s, H_3CO), 3.19–3.13 (2H, m, H_2C-2′), 2.77–2.71 (2H, m, H_2C-3′), 2.69–2.61 (2H, m, H_2C-4), 2.32 (2H, ap t, J = 7.5 Hz, H_2C-6), 1.63–1.52 (2H, m, H_2C-5); δ for **25a**: 7.35 (1H, d, J = 10 Hz, HC-6′), 6.22 (1H, dt, J = 11.5, 7.5 Hz, HC-3), 6.10 (1H, d, J = 10 Hz, HC-5′), 5.78 (1H, br d, J = 11.5 Hz, HC-2), 3.71 (3H, s, H_3CO), 3.31 (1H, dd, J = 3.5, 13.5 Hz, HC-2′), 3.05 (1H, dd, J = 8.5, 13.5 Hz, HC-2′), 2.69–2.61 (2H, m, H_2C-4), 2.60–2.50 (1H, m, HC-3′), 1.87 (1H, dddd, J = 5.5, 5.5, 10, 13 Hz, HC-6), 1.64–1.48 (3H, m, H_2C-5, HC-6); ^{13}C NMR δ for **24a**: 193.5 (s, C-4′), 166.8 (s, C-1), 150.2 (d, C-3), 140.7 (d, C-6′), 134.4 (s, C-5′), 119.6 (d, C-2), 51.0 (q, CH_3O), 38.4 (t, C-3′), 31.1 (t, C-6), 28.5 (t, C-4), 28.3 (t, C-5), 27.3 (t, C-2′); δ for **25a**: 196.0 (s, C-4′), 166.8 (s, C-1), 149.7 (d, C-3), 145.2 (d, C-6′), 123.1 (d, C-5′), 119.9 (d, C-2), 51.0 (q, CH_3O), 45.0 (d, C-3′), 31.8 (t, C-6), 28.7 (t, C-4), 27.8 (t, C-2′), 26.4 (t, C-5).

Methyl (E)*-7-(3,4-dihydro-4-oxo-2*H*-thiopyran-5-yl)-2-heptenoate* (***22b***)*, methyl* (E)*-7-(3,4-dihydro-4-oxo-2*H*-thiopyran-3-yl)-2-heptenoate* (***23b***)*, methyl* (Z)*-7-(3,4-dihydro-4-oxo-2*H*-thiopyran-5-yl)-2-heptenoate* (***24b***)*, and methyl* (Z)*-7-(3,4-dihydro-4-oxo-2*H*-thiopyran-3-yl)-2-heptenoate* (***25b***)

A 1.3:1 mixture of **22b** and **23b** (64 mg, 31%) and a 1.3:1 mixture of **24b** and **25b** (36 mg, 17%) were obtained from a 1.3:1 mixture of **20b** and **21b** (198 mg, 0.818 mmol) after PTLC (50% ether in hexane).

For **22b/23b**: IR ν_{max}: 2931, 1721, 1658, 1435, 1272, 1202,

1175 cm^{-1}; ^1H NMR δ for **22b**: 7.14 (1H, s, HC-6′), 6.95 (1H, dt, J = 15.5, 7 Hz, HC-3), 5.78 (1H, br d, J = 15.5 Hz, HC-2), 3.70 (3H, s, H_3CO), 3.15–3.09 (2H, m, H_2C-2′), 2.73–2.67 (2H, m, H_2C-3′), 2.26–2.14 (4H, m, H_2C-4, H_2C-7), 1.56–1.30 (4H, m, H_2C-5, H_2C-6); δ for **23b**: 7.36 (1H, d, J = 10 Hz, HC-6′), 6.95 (1H, dt, J = 15.5, 7 Hz, HC-3), 6.07 (1H, d, J = 10 Hz, HC-5′), 5.78 (1H, br d, J = 15.5 Hz, HC-2), 3.70 (3H, s, H_3CO), 3.26 (1H, dd, J = 4, 13 Hz, HC-2′), 3.01 (1H, dd, J = 8.5, 13 Hz, HC-2′), 2.52–2.44 (1H, m, HC-3′), 2.26–2.14 (2H, m, HC-4), 1.88–2.75 (1H, m, HC-7), 1.56–1.30 (5H, m, H_2C-5′, H_2C-6, HC-7); ^{13}C NMR δ for **22b**: 193.5 (s, C-4′), 167.0 (s, C-1), 149.3 (d, C-3), 140.4 (d, C-6′), 134.6 (s, C-5′), 121.0 (d, C-2), 51.4 (q, CH_3O), 38.3 (t, C-3′), 31.7 (t, C-4), 31.0 (t, C-7), 28.5 (t, C-6), 27.7 (t, C-5), 27.2 (t, C-2′); δ for **23b**: 196.1 (s, C-4′), 167.0 (s, C-1), 149.1 (d, C-3), 145.1 (d, C-6′), 123.1 (d, C-5′), 121.1 (d, C-3), 51.4 (q, CH_3O), 45.1 (d, C-3′), 31.9 (t, C-4), 31.7 (t, C-7), 27.9 (t, C-2′ or C-5), 27.8 (t, C-2′ or C-5), 26.4 (t, C-6); LRMS (EI), *m/z* (relative intensity): 254 ($[M]^+$, 11), 194 (27), 155 (20), 139 (13), 127 (33), 114 (100).

For **24b/25b**: IR ν_{max}: 2927, 1720, 1658, 1437, 1199, 1174 cm^{-1}; ^1H NMR δ for **24b**: 7.13 (1H, br s, HC-6′), 6.18 (1H, dt, J = 12, 8 Hz, HC-3), 5.74 (1H, br d, J = 12 Hz, HC-2), 3.66 (3H, s, H_3CO), 3.16–3.10 (2H, m, H_2C-2′), 2.73–2.66 (2H, m, H_2C-3′), 2.65–2.58 (2H, m, H_2-C4), 2.31–2.20 (2H, m, H_2C-7), 1.60–1.30 (4H, m, H_2C-5, H_2C-6); δ for **25b**: 7.33 (1H, d, J = 10 Hz, HC-6′), 6.18 (1H, dt, J = 11.5, 8 Hz, HC-3), 6.07 (1H, d, J = 10 Hz, HC-5′), 5.74 (1H, br d, J = 11.5 Hz, HC-2), 3.66 (3H, s, H_3CO), 3.28 (1H, dd, J = 4, 13 Hz, HC-2′), 3.01 (1H, dd, J = 9, 13 Hz, HC-2′), 2.65–2.58 (2H, m, H_2C-4), 2.53–2.44 (1H, m, HC-3′), 1.87–1.78 (1H, m, HC-7), 1.60–1.30 (5H, m, H_2C-5, H_2C-6, HC-7); ^{13}C NMR δ for **24b**: 193.5 (s, C-4′), 166.8 (s, C-1), 150.5 (d, C-3), 145.1 (d, C-6′), 134.8 (s, C-5′), 119.5 (d, C-2), 51.0 (q, CH_3O), 38.4 (t, C-3′), 31.0 (t, C-7), 28.8, 28.7, and 28.6 (t ×3, C-4, C-5, C-6), 27.2 (t, C-2′); δ for **25b**: 196.1 (s, C-4′), 166.8 (s, C-1), 150.3 (d, C-3), 140.2 (d, C-6′), 123.1 (d, C-5′), 119.4 (d, C-2), 51.0 (q, CH_3O), 45.1 (d, C-3′), 31.7 (t, C-7), 28.7 (t, C-4 or C-5), 28.6 (t, C-4 or C-5), 27.8 (t, C-2′), 26.6 (t, C-6); LRMS (EI), *m/z* (relative intensity): 254 ($[M]^+$, 7), 194 (40), 155 (10), 127 (22), 114 (100), 113 (32).

*Methyl (*E*)-7-(3,4-dihydro-4-oxo-*2H*-thiopyran-3-yl)-2-heptenoate (**23b**)*

From **54**: A solution of Bu_3SnH (0.3 mL, 1.1 mmol) and AIBN (10 mg, 0.06 mmol) in dry deoxygenated benzene (5 mL) was added over 30 min to a solution of **54** (126 mg, 1 mmol) and **55** (382 mg, 1.5 mmol) in dry deoxygenated benzene (15 mL) heated under reflux in an oil bath preheated to 90°C. After 8 h, the reaction mixture was concentrated and fractionated by MPC (25% ethyl acetate in hexane) to give **23b** (116 mg, 45%) and **54** (23.5 mg, 19%). IR ν_{max}: 2930, 1721, 1658, 1554, 1272, 1202 cm^{-1}; ^1H NMR δ: 7.33 (1H, d, J = 10 Hz, HC-6′), 6.91 (1H, dt, J = 15.5, 7 Hz, HC-3), 6.07 (1H, d, J = 10 Hz, HC-5′), 5.78 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.68 (1H, s, H_3CO), 3.27 (1H, dd, J = 3.5, 13.5 Hz, HC-2′), 3.00 (1H, ddd, J = 0.5, 9, 13.5 Hz, HC-2′), 2.52–2.44 (1H, m, HC-3′), 2.18 (2H, ap ddt, J = 1.5, 7, 7 Hz, HC-4), 1.88–1.76 (1H, m, HC-7), 1.56–1.30 (5H, m, H_2C-5, H_2C-6, HC-7); ^{13}C NMR δ: 196.0 (s, C-4′), 167.0 (s, C-1), 149.1 (d, C-3), 145.1 (d, C-6′), 123.1 (d, C-5′), 121.1 (d, C-2), 51.4 (q, CH_3O), 45.1 (d, C3), 31.9 (t, C-4), 31.7 (t, C-7), 27.9 (t, C-2′ or C-5), 27.8 (t, C-2′ or C-5), 26.4 (t, C-6); LRMS (EI), *m/z* (relative intensity): 254 ($[M]^+$, 20), 223 (9), 195 (12), 114 (100), 86 (91).

*Methyl (*E*)-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-5-yl]-2-heptenoate (**26b**) and methyl (*E*)-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-3-yl]-2-heptenoate (**27b**)*

Obtained as a 1.3:1 mixture from a similar mixture of **22b** and **23b**: ^1H NMR δ for **26b**: 6.96 (1H, dt, J = 15.5, 7 Hz, H-3), 6.05 (1H, s, H-6′), 5.80 (1H, d, J = 15.5 Hz, H-2), 4.76 (1H, t, J = 7 Hz, H-3′), 3.70 (3H, s, H_3CO), 3.19 (2H, d, J = 7 Hz, H_2C-2′), 2.25–2.15 (4H, m, H_2C-4, H_2C-7), 1.52–1.38 (4H, m, H_2C-5, H_2C-6), 1.30–0.90 (21H, m, $(H_3C)_2CHSi$); δ for **27b**: 6.96 (1H, dt, J = 15.5, 7 Hz, H-3), 6.18 (1H, d, J = 10 Hz, H-6′), 5.94 (1H, d, J = 10 Hz, H-5′), 5.80 (1H, d, J = 15.5 Hz, H-2), 3.70 (3H, s, H_3CO), 3.25 (2H, s, H_2C-2′), 2.25–2.15 (4H, m, H_2C-4, H_2C-7), 1.52–1.38 (4H, m, H_2C-5, H_2C-6), 1.30–0.90 (21H, m, $(H_3C)_2CHSi$).

*Methyl (*E*)-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-3-yl]-2-heptenoate (**27b**)*: ^1H NMR δ: 6.97 (1H, ddd, J = 7, 7, 15.5 Hz, HC-3), 6.18 (1H, d, J = 10 Hz, HC-6′), 5.95 (1H, d, J = 10 Hz, HC-5′), 5.82 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.73 (3H, s, H_3CO), 3.28 (2H, s, H_2C-2′), 2.26–2.18 (4H, m, H_2C-7, H_2C-4), 1.50–1.38 (4H, m, H_2C-5, H_2C-6), 1.30–0.90 (21H, m, $(H_3C)_2CHSi$).

*Methyl (*Z*)-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-5-yl]-2-heptenoate (**28b**) and methyl (*Z*)-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-3-yl]-2-heptenoate (**29b**)*

Obtained as a 1.3:1 mixture from a similar mixture of **24b** and **25b**: ^1H NMR δ for **28b**: 6.21 (1H, dt, J = 15.5, 7 Hz, H-3), 6.05 (1H, s, H-6′), 5.78 (1H, d, J = 15.5 Hz, H-2), 4.76 (1H, t, J = 7 Hz, H-3′), 3.70 (3H, s, H_3CO), 3.19 (2H, d, J = 7 Hz, H_2C-2′), 2.78–2.60 (2H, m, H_2C-4), 2.23–2.13 (2H, m, H_2C-7), 1.52–1.38 (4H, m, H_2C-5, H_2C-6), 1.30–0.90 (21H, m, $(H_3C)_2CHSi$); δ for **29b**: 6.21 (1H, dt, J = 11.5, 7 Hz, H-3), 6.18 (1H, d, J = 10 Hz, H-6′), 5.94 (1H, d, J = 10 Hz, H-5′), 5.78 (1H, d, J = 11.5 Hz, H-2), 3.70 (3H, s, H_3CO), 3.25 (2H, s, H_2C-2′), 2.69 (2H, m, H_2C-4), 2.23–2.13 (2H, m, H_2C-7), 1.52–1.38 (4H, m, H_2C-5, H_2C-6), 1.30–0.90 (21H, m, $(H_3C)_2CHSi$).

*Methyl (*E*)-6-(4-oxo-4*H*-thiopyran-3-yl)-2-hexenoate (**30a**)*

A solution of a 1.2:1 mixture of **26a** and **27a** (8.3 mg, 0.021 mmol) in $C_6D_5CD_3$ (0.5 mL) was heated at 75°C for 24 h. ^1H NMR of the reaction solution showed essentially complete conversion to **30a**. The mixture was concentrated and fractionated by PTLC to give **30a** (4 mg, 75%). IR ν_{max}: 3024, 1718, 1605, 1272 cm^{-1}; ^1H NMR δ: 7.74 (1H, dd, J = 4, 10 Hz, HC-6′), 7.54 (1H, d, J = 4 Hz, HC-2′), 7.05 (1H, d, J = 10 Hz, HC-5′), 6.98 (1H, dt, J = 15.5, 7 Hz, HC-3), 5.86 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.72 (3H, s, H_3CO), 2.64–2.58 (2H, m, H_2C-6), 2.28 (2H, ap ddt, J = 1.5, 7, 7 Hz, H_2C-4), 1.80–1.70 (2H, m, H_2C-5); LRMS (CI, NH_3), *m/z* (relative intensity): 256 ($[M+18]^+$, 25), 239 ($[M+1]^+$, 100), 83 (25).

*Methyl (*E*)-7-(4-oxo-4*H*-thiopyran-3-yl)-2-heptenoate (**30b**)*

Obtained as a minor by-product (<20% yield) from thermal

reaction of a mixture of **26b** and **27b**: IR ν_{max}: 3023, 2945, 1731, 1716, 1653, 1614, 1601, 1271 cm^{-1}; ^1H NMR δ: 7.74 (1H, dd, J = 4, 10 Hz, HC-6′), 7.53 (1H, d, J = 10 Hz, HC-2′), 7.04 (1H, d, J = 10 Hz, HC-5′), 6.94 (1H, dt, J = 15.5, 7 Hz, HC-3), 5.81 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.69 (3H, s, H_3CO), 2.61–2.55 (2H, m, H_2C-7), 2.23 (2H, ap dt, J = 6.5, 6.5, 6.5 Hz, H_2C-4), 1.64–1.48 (4H, m, H_2C-5, H_2C-6); ^{13}C NMR δ: 179.3 (s, C-4′), 167.0 (s, C-1), 149.1 (d, C-3), 143.6 (s, C-3′), 136.8 (d, C-6′), 132.4 (d, C-2′), 130.4 (d, C-5′), 121.1 (d, C-2), 51.3 (q, CH_3O), 31.9 (t, C-4), 31.6 (t, C-7), 27.7 (t, C-5), 27.4 (t, C-6); LRMS (EI), *m/z* (relative intensity): 252 ($[M]^+$, 12), 221 (12), 193 (12), 154 (15), 153 (100).

*Methyl (*E*)-7-(4-oxo-4*H*-thiopyran-3-yl)-2-heptenoate (**30b**) and methyl (*Z*)-7-(4-oxo-4*H*-thiopyran-3-yl)-2-heptenoate (**31b**)*

Obtained as an ca. 1:1 mixture (<20% yield) from thermal reaction of a mixture of **28b** and **29b**: IR ν_{max}: 3043, 2929, 2858, 1720, 1656, 1608, 1271, 1200 cm^{-1}; ^1H NMR δ for **30b**: 7.73 (1H, dd, J = 6, 10.5 Hz, HC-6′), 7.54 (1H, d, J = 6 Hz, HC-2′), 7.04 (1H, d, J = 10.5 Hz, HC-5′), 6.95 (1H, dt, J = 15, 8 Hz, HC-3), 5.81 (1H, d, J = 15 Hz, HC-2), 3.72 (3H, s, H_3CO), 2.65–2.57 (2H, m, H_2C-7), 2.40–2.30 (2H, m, H_2C-4), 1.65–1.35 (4H, m, H_2C-5, H_2C-6); δ for **31b**: 7.73 (1H, dd, J = 10.5, 6 Hz, HC-6′), 7.53 (1H, d, J = 6 Hz, HC-2′), 7.04 (1H, d, J = 10.5 Hz, HC-5′), 6.22 (1H, dt, J = 11.5, 8 Hz, HC-3), 5.77 (1H, d, J = 11.5 Hz, HC-2), 3.72 (3H, s, H_3CO), 2.73–2.65 (2H, m, H_2C-4), 2.65–2.57 (2H, m, H_2C-7), 1.65–1.35 (4H, m, H_2C-5, H_2C-6).

*2-[3-(1,3-Dioxolan-2-yl)propyl]-tetrahydro-4*H*-thiopyran-4-one (**33**)*

In this case, the product obtained from addition of the cuprate derived from 2-(4-bromobutyl)-1,3-dioxolane to **32** (750 mg, 769 mmol) according to the general procedure was contaminated with 2-propyl-1,3-dioxolane. This crude product was directly subjected to decarboxylation according to the general procedure to obtain **33** (355 mg, 41%) after FCC (80% ether in hexane): IR ν_{max}: 1711, 1410, 1139 cm^{-1}; ^1H NMR δ: 4.84 (1H, dd, J = 4, 4.5 Hz, HC-2″), 4.00–3.80 (4H, m, H_2C-4″, H_2C-5″), 3.11–3.02 (1H, m, HC-2), 3.00–2.82 (2H, m, HC-6), 2.74 (1H, br dd, J = 3.5, 13.5 Hz, HC-3), 2.70–2.53 (2H, m, H_2C-5), 2.44 (1H, dd, J = 10.5, 13.5 Hz, HC-3), 1.70–1.50 (6H, m, H_2C-1′, H_2C-2′, H_2C-3′); ^{13}C NMR δ: 208.4 (s, C-4), 104.1 (d, C-2″), 64.8 (t ×2, C-4″, C-5″), 50.5 (t, C-3), 44.5 (d, C-2), 43.3 (t, C-5), 35.3 (t, C-1′), 33.3 (t, C-3′), 27.9 (t, C-6), 21.2 (t, C-2′); LRMS (EI), *m/z* (relative intensity): 230 ($[M]^+$, 11), 168 (32), 112 (21), 99 (23), 73 (100).

*Methyl (*E*)-6-(tetrahydro-4-oxo-2*H*-thiopyran-2-yl)-2-hexenoate (**34**) and methyl (*Z*)-6-(tetrahydro-4-oxo-2*H*-thiopyran-2-yl)-2-hexenoate (**35**)*

34 (48 mg, 47%) and **35** (27 mg, 26%) were obtained from **33** (125 mg, 0.534 mmol) after PTLC (50% ether in hexane, developed ×2).

For **34**: IR ν_{max}: 3031, 1715, 1656, 1272 cm^{-1}; ^1H NMR δ: 6.93 (1H, ap dt, J = 15.5, 7 Hz, HC-3), 5.84 (1H, ap dt, J = 15.5, 1.5 Hz, HC-2), 3.72 (3H, s, H_3CO), 3.11–3.01 (1H, m, HC-2′), 2.99–2.83 (2H, m, HC-6′), 2.73 (1H, dd, J = 3.5, 13.5 Hz, HC-3′), 2.72–2.55 (2H, m, HC-5′), 2.44 (1H, dd, J = 10.5, 13.5 Hz, HC-3′), 2.26–2.18 (2H, m, HC-4), 1.66–1.54 (4H, m, H_2C-5, H_2C-6); ^{13}C NMR δ: 208.4 (s, C-4′), 166.9 (s, C-1), 148.4 (d, C-3), 121.5 (d, C-2), 51.4 (q, CH_3O), 50.6 (t, C-3′), 44.5 (d, C-2′), 43.4 (t, C-5′), 34.9 (t, C-6), 31.7 (t, C-4), 28.0 (t, C-6′), 25.3 (t, C-5); LRMS (CI, NH_3), *m/z* (relative intensity): 260 ($[M+18]^+$, 100), 243 ($[M+1]^+$, 84), 211 (26).

For **35**: IR ν_{max}: 3032, 1717, 1644, 1197 cm^{-1}; ^1H NMR δ: 6.19 (1H, dt, J = 11.5, 7.5 Hz, HC-3), 5.79 (1H, dt, J = 11.5, 1.5 Hz, HC-2), 3.70 (3H, s, H_3CO), 3.15–3.05 (1H, m, HC-2′), 3.01–2.82 (2H, m, HC-6′), 2.73 (1H, br dd, J = 3.5, 13.5 Hz, HC-3′), 2.70–2.55 (4H, m, H_2C-4, H_2C-5′), 2.43 (1H, dd, J = 10.5, 13.5 Hz, HC-3′), 1.66–1.54 (4H, m, H_2C-5, H_2C-6); ^{13}C NMR δ: 208.5 (s, C-4′), 166.7 (s, C-1), 149.6 (d, C-3), 120.0 (d, C-2), 51.1 (q, CH_3O), 50.6 (t, C-3′), 44.5 (d, C-2′), 43.4 (t, C-5′), 35.0 (t, C-6), 28.4 (t, C-4), 28.1 (t, C-6′), 26.2 (t, C-5); LRMS (CI, NH_3), *m/z* (relative intensity): 260 ($[M+18]^+$, 100), 243 ($[M+1]^+$, 63), 211 (20), 199 (16).

*Methyl (*E*)-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-6-yl)-2-hexenoate (**36**) and methyl (*E*)-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-2-yl)-2-hexenoate (**37**)*

36 (22 mg, 63%) and **37** (10 mg, 29%) were obtained from **34** (35 mg, 0.14 mmol) after PTLC (50% EtOAc in hexane).

For **36**: IR ν_{max}: 3016, 1720, 1654, 1180 cm^{-1}; ^1H NMR δ: 6.92 (1H, dt, J = 15.5, 7 Hz, HC-3), 5.84 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 6.06 (1H, s, HC-5′), 3.71 (3H, s, H_3CO), 3.19–3.13 (2H, m, H_2C-2′), 2.67–2.61 (2H, m, H_2C-3′), 2.39 (2H, ap t, J = 7.5 Hz, H_2C-6), 2.24 (2H, ap ddt, J = 1.5, 7, 7.5 Hz, H_2C-4), 1.77 (2H, ap tt, J = 7.5, 7.5 Hz, H_2C-5); ^{13}C NMR δ: 194.2 (s, C-4′), 166.8 (s, C-1), 163.8 (s, C-6′), 147.8 (d, C-3), 122.1 (d, C-5′), 121.9 (d, C-2), 51.5 (q, CH_3O), 37.6 (t, C-6), 36.8 (t, C-3′), 31.2 (t, C-4), 27.4 (t, C-2′), 26.9 (t, C-5); LRMS (CI, NH_3), *m/z* (relative intensity): 241 ($[M+18]^+$, 100), 180 (12).

For **37**: IR ν_{max}: 3031, 1720, 1659, 1271 cm^{-1}; ^1H NMR δ: 7.41 (1H, d, J = 10 Hz, HC-6′), 6.92 (1H, dt, J = 15.5, 7 Hz, HC-3), 6.17 (1H, d, J = 10 Hz, HC-5′), 5.84 (1H, dt, J = 15.5, 1.5 Hz, HC-2), 3.74 (3H, s, H_3CO), 3.53–3.42 (1H, m, HC-2′), 2.78 (1H, dd, J = 3.5, 16.5 Hz, HC-3′), 2.59 (1H, dd, J = 11.5, 16.5 Hz, HC-3′), 2.24 (2H, ap ddt, J = 1.5, 7, 7.5 Hz, H_2C-4), 1.80–1.55 (4H, m, H_2C-5, H_2C-6); ^{13}C NMR δ: 194.3 (s, C-4′), 166.9 (s, C-1), 148.0 (d, C-3), 145.3 (d, C-6′), 123.5 (d, C-5′), 121.8 (d, C-2), 51.5 (q, CH_3O), 44.4 (t, C-3′), 42.8 (d, C-2′), 33.3 (t, C-6), 31.6 (t, C-4), 25.1 (t, C-5); LRMS (CI, NH_3), *m/z* (relative intensity): 258 ($[M+18]^+$, 14), 241 ($[M+1]^+$, 100), 113 (20).

*Methyl (*Z*)-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-6-yl)-2-hexenoate (**38**) and methyl (*Z*)-6-(3,4-dihydro-4-oxo-2*H*-thiopyran-2-yl)-2-hexenoate (**39**)*

38 (39 mg, 48%) and **39** (24 mg, 30%) were obtained from **35** (81 mg, 0.33 mmol) after PTLC (50% EtOAc in hexane).

For **38**: IR ν_{max}: 3032, 1718, 1649, 1198 cm^{-1}; ^1H NMR δ: 6.17 (1H, dt, J = 11.5, 7.5 Hz, HC-3), 6.04 (1H, br s, HC-5′), 5.79 (1H, dt, J = 11.5, 1.5 Hz, HC-2), 3.67 (3H, s, H_3CO), 3.18–3.12 (2H, m, HC-2′), 2.68 (2H, ap ddt, J = 1.5, 7.5, 7.5 Hz, H_2C-4), 2.64–2.58 (2H, m, H_2C-3′), 2.39 (2H, ap t, J = 7.5 Hz, H_2C-6), 1.73 (2H, ap tt, J = 7.5, 7.5 Hz, H_2C-5); ^{13}C NMR δ: 194.3 (s, C-4′), 166.6 (s, C-1), 164.2 (s, C-6′), 148.9 (d, C-3), 121.9 (d, C-5′), 120.3 (d, C-2), 51.1 (q, CH_3O), 37.8 (t, C-6), 36.8 (t, C-3′), 28.1 (t, C-4 or 5), 28.0 (t, C-4 or 5), 27.4 (t,

C-2′); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 6), 208 (18), 180 (100), 141 (69), 128 (88).

For **39**: IR ν_{max}: 3032, 1719, 1660, 1199 cm^{-1}; ^{1}H NMR δ: 7.41 (1H, d, *J* = 10 Hz, HC-6′), 6.19 (1H, ap dt, *J* = 11.5, 7.5 Hz, HC-3), 6.16 (1H, d, *J* = 10 Hz, HC-5′), 5.81 (1H, ap dt, *J* = 11.5, 1.5 Hz, HC-2), 3.70 (3H, s, OCH_3), 3.57–3.46 (1H, m, HC-2′), 2.79 (1H, dd, *J* = 3.5, 16 Hz, HC-3′), 2.69 (2H, ap ddt, *J* = 1.5, 7.5, 7.5 Hz, H_2C-4), 2.59 (1H, dd, *J* = 11.5, 16 Hz, HC-3′), 1.81–1.69 (2H, m, H_2C-6), 1.68–1.53 (2H, m, H_2C-5); ^{13}C NMR δ: 194.4 (s, C-4′), 166.7 (s, C-1), 149.1 (d, C-3), 145.5 (d, C-6′), 123.5 (d, C-5′), 120.2 (d, C-2), 51.1 (q, CH_3O), 44.4 (t, C-3′), 42.8 (d, C-2′), 33.4 (t, C-6), 28.3 (t, C-4), 25.9 (t, C-5); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 12), 139 (24), 113 (100).

Methyl (E)*-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]-2-hexenoate* (***40***): ^{1}H NMR ($C_6D_5CD_3$) (partial data) δ: 6.84 (1H, dt, *J* = 16, 6.5 Hz, HC-3), 5.80 (1H, d, *J* = 1 Hz, HC-5′), 5.72 (1H, br d, *J* = 16 Hz, HC-2), 4.52 (1H, dt, *J* = 1, 5.5 Hz, HC-3′), 3.10 (2H, d, *J* = 5.5 Hz, HC-2′).

Methyl (E)*-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-2-yl]-2-hexenoate* (***41***): ^{1}H NMR ($C_6D_5CD_3$) (partial data) δ: 6.85 (1H, dt, *J* = 16, 6.5 Hz, H-4′), 5.92 (1H, d, *J* = 10 Hz, H-6), 5.84 (1H, dd, *J* = 1, 10 Hz, H-5), 5.71 (1H, br d, *J* = 16 Hz, H-5′), 4.72 (1H, dd, *J* = 1, 6.5 Hz, H-3), 3.04 (1H, br dt, *J* = 6.5, 6.5 Hz, H-2).

Methyl (Z)*-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]-2-hexenoate* (***42***): ^{1}H NMR ($C_6D_5CD_3$) (partial data): δ 5.84 (1H, d, *J* = 1 Hz, HC-5′), 5.81–5.74 (1H, m, HC-3), 5.67 (1H, br d, *J* = 12 Hz, HC-2), 4.52 (1H, dt, *J* = 1, 5.5 Hz, HC-3′), 3.12 (2H, d, *J* = 5.5 Hz, HC-2′).

Methyl (Z)*-6-[4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-2-yl]-2-hexenoate* (***43***): ^{1}H NMR ($C_6D_5CD_3$) (partial data) δ: 5.94 (1H, d, *J* = 10 Hz, H-6′), 5.85 (1H, dd, *J* = 1, 10 Hz, H-5′), 5.81–5.74 (1H, m, H-3), 5.67 (1H, br d, *J* = 12 Hz, H-2), 4.76 (1H, dd, *J* = 1, 6.5 Hz, H-3′), 3.17 (1H, br dt, *J* = 6.5, 6.5 Hz, H-2′).

*Methyl (3*S**,4*R**,4a*S**,7a*S**)-hexahydro-8-oxo-1*H*-3,7a-ethanocyclopenta[c]thiopyran-4-carboxylate* (***45***): IR ν_{max}: 1726, 1435, 1236 cm^{-1}; ^{1}H NMR δ: 3.73 (3H, s, H_3CO), 3.38 (1H, ddd, *J* = 1, 2.5, 3.5 Hz, HC-3), 3.13 (1H, ddd, *J* = 1, 1.5, 8.5 Hz, HC-4), 3.10 (1H, d, *J* = 11.5 Hz, HC-1), 2.91 (1H, dd, *J* = 2.5, 18.5 Hz, H_{endo}C-9), 2.70 (1H, ddd, *J* = 1.5, 3.5, 18.5 Hz, H_{exo}C-9), 2.64 (1H, d, *J* = 11.5 Hz, HC-1), 2.30–2.09 (3H, m, HC-4a, HC-5, HC-7), 1.86–1.67 (3H, m, HC-5, H_2C-6), 1.42 (1H, ddd, *J* = 4, 10, 14.5 Hz, HC-7); ^{13}C NMR δ: 211.6 (s, C-8), 173.6 (s, OC═O), 54.1 (s, C-7a), 52.3 (q, CH_3O), 51.0 (d, C-4), 45.3 (t, C-9), 42.4 (d, C-4a), 36.6 (d, C-3), 28.1 (t, C-1 or 5 or 7), 28.1 (t, C-1 or 5 or 7), 27.1 (t, C-1 or 5 or 7), 21.7 (t, C-6); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 87), 212 (19), 127 (61), 113 (77), 105 (100).

*Methyl (3*S**,4*S**,4a*R**,7a*S**)-hexahydro-8-oxo-1*H*-3,7a-ethanocyclopenta[c]thiopyran-4-carboxylate* (***46***): IR ν_{max}: 1722, 1232, 1181 cm^{-1}; ^{1}H NMR δ: 3.77 (3H, s, H_3CO), 3.58 (1H, m, HC-3), 3.03 (1H, d, *J* = 11 Hz, HC-1), 2.88 (1H, dd, *J* = 2.5, 19.5 Hz, HC-9), 2.84 (1H, d, *J* = 11 Hz, HC-1), 2.68 (1H, dd, *J* = 4, 19.5 Hz, HC-9), 2.68–2.61 (2H, m, HC-4, HC-4a), 2.56 (1H, ddd, *J* = 5.5, 9, 13 Hz, HC-7), 2.18–2.08 (1H, m, HC-5), 1.81–1.62 (2H, m, H_2C-6), 1.19 (1H, ddd, *J* = 6.5, 10.5, 13 Hz, HC-7), 1.03–0.87 (1H, m, HC-5); δ in $CDCl_3$/C_6D_6: 2.49 (1H, ddd, *J* = 7, 7, 12.5 Hz, HC-4a), 2.39–2.35 (1H, m, HC-4; on irradiation of HC-3, this signal becomes a 7 Hz doublet); ^{13}C NMR δ: 211.2 (s, C-8), 172.7 (s, OC═O), 52.8 (s, C-7a), 52.4 (q, CH_3O), 51.7 (d, C-3), 48.2 (t, C-9), 45.2 (d, C-4a), 38.3 (d, C-3), 32.9 (t, C-4 or 9), 32.8 (t, C-4 or 9), 28.5 (t, C-7), 22.0 (t, C-6); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 83), 212 (21), 149 (56), 119 (70), 113 (100)

*Methyl (3*S**,4*R**,4a*R**,7a*S**)-hexahydro-8-oxo-1*H*-3,7a-ethanocyclopenta[c]thiopyran-4-carboxylate* (***47***): IR ν_{max}: 1725, 1435, 1174, 956 cm^{-1}; ^{1}H NMR δ: 3.67 (3H, s, H_3CO), 3.61 (1H, ddd, *J* = 2, 2.5, 11.5 Hz, HC-4), 3.41 (1H, dd, *J* = 3, 19.5 Hz, H_{endo}C-9), 3.32 (1H, ddd, *J* = 2.5, 2.5, 3 Hz, HC-3), 3.02 (1H, d, *J* = 11 Hz, HC-1), 2.92 (1H, d, *J* = 11 Hz, HC-1), 2.77 (1H, ddd, *J* = 2, 2.5, 19.5 Hz, H_{exo}C-9), 2.54 (1H, ddd, *J* = 4, 9.5, 13 Hz, HC-7), 2.51 (1H, ddd, *J* = 7, 11.5, 13 Hz, HC-4a), 1.90 (1H, dddd, *J* = 2.5, 7, 7.5, 13 Hz, HC-5), 1.77–1.53 (2H, m, H_2C-6), 1.14 (1H, ddd, *J* = 7, 11, 13 Hz, HC-7), 0.97 (1H, ap tt, *J* = 9.5, 13 Hz, HC-5); ^{13}C NMR δ: 211.4 (s, C-8), 172.4 (s, OC═O), 53.9 (s, C-7a), 51.5 (q, CH_3O), 47.5 (d, C-4), 44.7 (d, C-4a), 44.5 (t, C-9), 36.7 (d, C-3), 32.4 (t, C-1), 28.9 (t, C-5), 28.5 (t, C-7), 20.9 (t, C-6); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 100), 212 (46), 193 (87), 127 (88), 113 (88).

*Methyl (3*S**,4*S**,4a*S**,7a*S**)-hexahydro-8-oxo-1*H*-3,7a-ethanocyclopenta[c]thiopyran-4-carboxylate* (***48***): IR ν_{max}: 1725, 1435, 1171 cm^{-1}; ^{1}H NMR δ: 3.46 (1H, ddd, *J* = 3, 3.5, 4 Hz, HC-3), 3.36 (1H, dd, *J* = 4, 11.5 Hz, HC-4), 3.20 (1H, br d, *J* = 11.5 Hz, HC-1), 2.89 (1H, dd, *J* = 3.5, 18.5 Hz, HC-9), 2.81 (1H, br d, *J* = 18.5 Hz, HC-9), 2.58 (1H, br d, *J* = 11.5 Hz, HC-1), 2.48 (1H, dddd, *J* = 9, 10.5, 13, 13 Hz, HC-5), 2.22 (1H, ddd, *J* = 5, 11.5, 14 Hz, HC-7), 2.22–2.11 (1H, m, HC-4a), 1.99–2.89 (1H, m, HC-5), 1.82 (1H, ddddd, *J* = 1.5, 5, 9.5, 9.5, 14, Hz, HC-6), 1.63.1–53 (1H, m, HC-6), 1.27 (1H, ddd, *J* = 6, 9.5, 14 Hz, HC-7); LRMS (EI), *m/z* (relative intensity): 240 ([M]$^+$, 100), 153 (20), 113 (96), 91 (35), 81 (56).

*Methyl (3*S**,4*R**,4a*S**,8a*S**)-hexahydro-9-oxo-3*H*-3,8a-ethano-1*H*-2-benzothiopyran-4-carboxylate* (***49***): IR ν_{max}: 2930, 1724, 1446, 1237, 1197 cm^{-1}; ^{1}H NMR δ: 3.72 (3H, s, CH_3O), 3.44 (1H, d, *J* = 11.5 Hz, H_{syn}C-1), 3.32 (1H, ddd, *J* = 2, 2.5, 3.5 Hz, HC-3), 2.87 (1H, dd, *J* = 2.5, 19 Hz, H_{endo}C-10), 2.86 (1H, ddd, *J* = 2, 2, 7.5 Hz, HC-4), 2.72 (1H, ddd, *J* = 2, 3.5, 19 Hz, H_{exo}C-10), 2.47 (1H, dd, *J* = 1.5, 11.5 Hz, H_{anti}C-1), 2.06 (1H, dddd, *J* = 1.5, 4, 7.5, 12 Hz, HC-4a), 2.01–1.91 (1H, m, HC-8), 1.80–1.50 (5H, m, HC-5, H_2C-6, H_2C-7), 1.44–1.18 (2H, m, HC-5, HC-8); ^{13}C NMR δ: 212.5 (s, C-9), 173.3 (s, OC═O), 52.8 (d, C-4), 52.3 (q, CH_3O), 45.1 (s, C-3), 44.4 (t, C-10), 36.9 (d), 34.8 (d), 30.3 (t), 29.0 (t), 25.3 (t), 25.2 (t), 20.9 (t); LRMS (EI), *m/z* (relative intensity): 254 ([M+]$^+$, 85), 227 (27), 195 (26), 151 (22), 127 (100).

*Methyl (3*S**,4*S**,4a*R**,8a*S**)-hexahydro-9-oxo-3*H*-3,8a-ethano-1*H*-2-benzothiopyran-4-carboxylate* (***50***): IR ν_{max}: 2933, 1735, 1721, 1435, 1223, 1203 cm^{-1}; ^{1}H NMR δ: 3.79 (3H, s, H_3CO), 3.49 (1H, ddd, *J* = 3, 3, 3 Hz, HC-3), 2.84 (1H, dd,

J = 3, 19 Hz, HC-10), 2.77 (1H, d, J = 11 Hz, HC-1), 2.65 (1H, d, J = 11 Hz, HC-1), 2.62 (1H, br dd, J = 3, 19 Hz, HC-10) 2.61–2.55 (2H, m, HC-4, HC-4a), 2.21–2.12 (1H, m, HC-8), 1.85–1.77 (1H, m, HC-5), 1.70–1.40 (3H, m, HC-6, H_2C-7), 1.36–1.23 (1H, m, HC-6), 1.10–0.85 (2H, m, HC-5, HC-8); ^{13}C NMR δ: 212.2 (s, C-9), 172.6 (s, OC=O), 52.7 (d, C-4), 52.3 (q, CH_3O), 47.9 (t, C-10), 46.5 (s, C-8a), 39.4 (d), 37.0 (d), 34.8 (t), 34.5 (t), 31.8 (t), 25.6 (t), 22.8 (t); LRMS (CI, NH_3), *m/z* (relative intensity): 272 ($[M+18]^+$, 20), 255 ($[M+1]^+$, 100), 226 (21), 209 (33).

Methyl (2S,4aS*,5R*,8aS*,9R*)-octahydro-4-oxo-2,5-methano-2H-1-benzothiopyran-9-carboxylate (**51**)*: IR ν_{max}: 1730, 1442, 1289, 1202 cm^{-1}; ^1H NMR δ: 3.71 (3H, s, H_3CO), 3.56–3.49 (2H, m, HC-2, HC-8a), 3.14–3.10 (1H, m, HC-9), 2.71–2.56 (3H, m, H_2C-3, HC-5), 2.44 (1H, dd, J = 3.5, 3.5 Hz, HC-4a), 2.13–1.45 (6H, m, H_2C-6, H_2C-7, H_2C-8); δ in $CDCl_3/C_6D_6$: 2.85 (1H, ddd, J = 2, 3, 5 Hz, HC-9), 2.45 (1H, ddd, J = 2, 3.5, 19.5 Hz, $H_{exo}C$-3), [irradiation of HC-2 reveals $^4J_{HexoC\text{-}3,HC\text{-}9}$ = 2 Hz and $^3J_{HC\text{-}5,HC\text{-}9}$ = 5 Hz]; ^{13}C NMR δ: 212.2 (s, C-4), 173.3 (s, OC=O), 52.3 (q, CH_3O), 50.8 (d, C-4a), 49.2 (d, C-9), 43.3 (t, C-3), 35.7 (d, C-2 or 8a), 35.3 (d, C-2 or 8a), 30.7 (t, C-8), 29.1 (d, C-5), 28.5 (t, C-6), 13.9 (t, C-7); LRMS (EI), *m/z* (relative intensity): 240 ($[M]^+$, 100), 208 (19), 181 (67), 113 (62), 81 (61).

Methyl (2S,4aS*,5R*,8aS*,9S*)-octahydro-4-oxo-2,5-methano-2H-1-benzothiopyran-9-carboxylate (**52**)*: IR ν_{max}: 1730, 1712, 1436, 1177 cm^{-1}; ^1H NMR δ: 3.79 (3H, s, H_3CO), 3.52–3.48 (1H, m, HC-8a), 3.49–3.44 (1H, m, HC-2), 3.13 (1H, dd, J = 2, 12 Hz, HC-9), 2.81 (1H, dd, J = 3, 19.5 Hz, HC-3), 2.56 (1H, dd, J = 3.5, 19.5 Hz, HC-3), 2.58–2.49 (2H, m, HC-4a, HC-5), 2.28–2.18 (1H, m, HC-7), 2.04–1.86 (1H, m, HC-7), 1.76–1.67 (1H, m, HC-8), 1.66–1.53 (1H, m, HC-8), 1.48–1.38 (1H, m, HC-6), 1.32 (1H, ddd, J = 4, 4, 14 Hz, HC-6), [irradiation of HC-2 reveals $^3J_{HC\text{-}5,HC\text{-}9}$ = 12.5 Hz]; ^{13}C NMR δ: 212.8 (s, C-4), 172.0 (s, OC=O), 51.8 (q, CH_3O), 51.5 (d, C-4a), 48.8 (t, C-3), 46.7 (d, C-9), 35.3 (d, C-2), 34.1 (d, C-8a), 30.8 (t, C-8), 27.6 (d, C-5), 26.0 (t, C-6), 15.4 (t, C-7); LRMS (EI), *m/z* (relative intensity): 240 ($[M]^+$, 90), 161 (22), 127 (87), 113 (47), 80 (100).

*2,3-Dihydro-3-(methoxymethyl)-4H-thiopyran-4-one (**53**)*
A solution of anhydrous $ZnBr_2$ in ether (0.25 M, 0.16 mL, 0.040 mmol) was added to a solution of chloromethyl methyl ether (91 μL, 96 mg, 1.2 mmol) and 4-trimethylsilyloxy-2*H*-thiopyran (186 mg, 1.00 mmol) in dry CH_2Cl_2 (5 mL) at rt. After stirring for 30 min, the mixture was poured onto saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over Na_2SO_4, concentrated, and fractionated by MPC (30% EtOAc in hexane) to give **56** (10 mg, 9%) and **53** as a clear oil (110 mg, 70%): IR ν_{max}: 3029, 1657, 1555, 1204, 1118 cm^{-1}; ^1H NMR δ: 7.42 (1H, dd, J = 1.5, 10 Hz, HC-6), 6.15 (1H, d, J = 10 Hz, HC-5), 3.74 (1H, dd, J = 4.5, 9.5 Hz, HC-1′), 3.59 (1H, dd, J = 9, 9.5 Hz, HC-1′), 3.37 (3H, s, H_3CO), 3.33 (1H, ddd, J = 1.5, 4.5, 13.5 Hz, HC-2), 3.26 (1H, dd, J = 11, 13.5 Hz, HC-2), 2.87 (1H, dddd, J = 4.5, 4.5, 9, 11 Hz, HC-3); ^{13}C NMR δ: 193.8 (s, C-4), 146.3 (d, C-6), 123.7 (d, C-5), 69.6 (t, C-1′), 59.0 (q, CH_3O), 45.8 (d, C-3), 29.7 (t, C-2); LRMS (EI), *m/z* (relative intensity): 158 ($[M]^+$, 81), 126 (22), 125 (15), 113 (72), 86 (100), 58 (37).

*2,3-Dihydro-3-methlyene-4H-thiopyran-4-one (**54**)*
TFA (0.25 mL) was added to a solution of **53** (100 mg, 0.63 mmol) in CH_2Cl_2 (2 mL) at rt. After stirring for 5 days, the reaction mixture was concentrated and filtered through a short column of silica gel eluting with C_6H_6. The filtrate was concentrated and the residue dissolved in CH_2Cl_2 (2 mL). Et_3N (0.25 mL) was added and after stirring for 1–3 days, the reaction mixture was concentrated and fractionated by FCC (20% ether in hexane) to yield **54** as an oil (60 mg, 75%): IR ν_{max}: 3033, 2900, 1786, 1729, 1658, 1611, 1540, 1167 cm^{-1}; ^1H NMR δ: 7.48 (1H, br d, J = 10 Hz, HC-6), 6.25 (1H, br d, J = 10 Hz, HC-5), 6.06 (1H, br s, HC-1′), 5.51 (1H, br s, HC-1′), 3.87 (2H, br s, H_2C-2); ^{13}C NMR δ: 185.2 (s, C-4), 146.3 (d, C-6), 139.0 (s, C-3), 124.5 (d, C-5), 123.4 (t, C-1′), 34.2 (t, C-2); LRMS (CI, NH_3), *m/z* (relative intensity): 144 ($[M+18]^+$, 4), 127 ($[M+1]^+$, 100), 126 (14), 97 (4).

*2-(2-Hydroxyethylthio)-tetrahydro-4H-thiopyran-4-one (**57**)*
2-Mercaptoethanol (0.13 mL, 1.8 mmol) was added to a suspension of NaH (3 mg, 0.1 mmol) in THF (5 mL). Compound **56** (100 mg, 0.80 mmol) was added and the mixture was stirred at rt for 10 h. The reaction mixture was concentrated and the residue dissolved in CH_2Cl_2; the solution was washed with H_2O (×3), dried over Na_2SO_4, concentrated, and fractionated by FCC (35% EtOAc in hexane) to give **57** (92 mg, 55%): ^1H NMR δ: 4.27 (1H, br t, J = 4.5 Hz, HC-2), 3.64 (1H, s, HO), 3.52 (2H, ap t, J = 6 Hz, H_2C-2′), 3.04 (1H, ddd, J = 6.5, 7, 14 Hz, HC-6), 2.85 (1H, dd, J = 4.5, 14.5 Hz, HC-3), 2.72–2.55 (2H, m, HC-6, HC-1′,), 2.55–2.38 (4H, m, HC-3, H_2C-5, HC-1′); ^{13}C NMR δ: 206.4 (s, C-4), 61.1 (t, C-2′), 49.5 (d, C-2), 48.1 (t, C-3), 42.9 (t, C-5), 34.4 (t, C-1′), 26.0 (t, C-6); LRMS (EI), *m/z* (relative intensity): 192 ($[M]^+$, 10), 115 (100), 87 (41), 73 (35). HRMS *m/z* calcd. for $C_7H_{12}O_2S_2$: 192.0279; found: 192.0278. Anal. calcd. for $C_7H_{12}O_2S_2$: C 43.72, H 6.29; found: C 42.92, H 6.34.

*2-[(Tetrahydro-4-oxo-2H-thiopyran-2-yl)thio]ethyl propenoate (**58**)*
Compound **57** (75 mg, 0.39 mmol) was added to a stirred solution of acryloyl chloride (70 mg, 0.77 mmol) and pyridine (0.6 mL, 0.8 mmol) in CH_2Cl_2 (3 mL) at rt. After 5 h, the reaction mixture was washed with H_2O (5 mL), dried over Na_2SO_4, concentrated, and fractionated by FCC (25% EtOAc in hexane) to give **58** (43 mg, 45%; note: higher yields are obtained if the reaction is conducted at 0°C): ^1H NMR δ: 6.45 (1H, dd, J = 1.5, 17.5 Hz, HC-3), 6.15 (1H, dd, J = 10.5, 17.5 Hz, HC-2), 5.85 (1H, dd, J = 1.5, 10.5 Hz, HC-3), 4.55–4.20 (3H, m, H_2C-1′, HC-2″), 3.28–3.14 (2H, m), 3.13–2.95 (2H, m), 3.10–2.95 (2H, m), 2.90–2.55 (4H, m).

*2-[(Tetrahydro-4-oxo-2H-thiopyran-2-yl)thio]ethyl methyl (E)-butendioate (**59**)*
Methyl fumaryl chloride (535 mg, 4 mmol) was added dropwise to a solution of **57** (517 mg, 2.7 mmol) and pyridine (0.3 mL, 4 mmol) in CH_2Cl_2 at 0°C and the mixture was stirred at rt for 4 h. The mixture was diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4, concentrated, and fractionated by FCC (30% EtOAc in hexane) to give **59** (1.02 g, 89%): ^1H

NMR δ: 6.77 (2H, ap s, HC-2, HC-3), 4.42–4.38 (1H, m, HC-2″), 4.37–4.18 (2H, m, H_2C-1′), 3.73 (3H, s, H_3CO), 3.21 (1H, ddd, J = 5, 9, 14 Hz, HC-6″), 3.01 (1H, dd, J = 5, 14.5 Hz, HC-3″), 3.00–2.92 (1H, m, HC-2′), 2.82–2.76 (1H, m, HC-2′), 2.78–2.69 (1H, m, HC-6″), 2.70–2.55 (3H, m, J = 5.5, 14.5 Hz, HC-3″, H_2C-5″); ^{13}C NMR δ: 205.0 (s, C-4″), 164.9 (s, C-1 or C-4), 164.3 (s, C-1 or C-4), 133.6 (d, C-2 or C-3), 133.0 (d, C-2 or C-3), 63.7 (t, C-1′), 51.3 (q, CH_3O), 49.1 (d, C-2″), 48.2 (t, C-3″), 42.8 (t, C-5″), 30.3 (t, C-2′), 25.8 (t, C-6″); LRMS (CI, NH_3), *m/z* (relative intensity): 322 ([M+18]$^+$, 52), 132 (9), 115 (100), 87 (9). HRMS *m/z* calcd. for $C_{12}H_{16}O_5S_2$: 304.0439; found: 304.0430. Anal. calcd. for $C_{12}H_{16}O_5S_2$: C 47.35, H 5.30; found: C 46.84, H 5.33.

*2-[(3,4-Dihydro-4-oxo-2*H*-thiopyran-6-yl)thio]ethyl propenoate (**60a**), 2-[(5-chloro-3,4-dihydro-4-oxo-2*H*-thiopyran-6-yl)thio]ethyl propenoate (**60b**), 2-[(3,4-dihydro-4-oxo-2*H*-thiopyran-6-yl)thio]ethyl methyl (*E*)-butendioate (**61a**), and 2-[(5-chloro-3,4-dihydro-4-oxo-2*H*-thiopyran-6-yl)thio]ethyl methyl (*E*)-butendioate (**61b**)*

NCS (1.0–1.2 equiv.) was added in portions to a stirred solution of **58** (30 mg, 0.12 mmol) or **59** (255 mg, 0.84 mmol) in CCl_4 (ca. 10 mL/mmol of **58** or **59**) at 0°C. After 15–20 h, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4, concentrated, and fractionated by PTLC (30% EtOAc in hexane) to give a mixture of **60a,b** or **61a,b**. Further fractionated by PTLC (%1 MeOH in CH_2Cl_2) gave the pure components **60a** (7 mg, 24%), **60b** (8 mg, 24%), **61a** (57 mg, 22%), and **61b** (63 mg, 22%).

For **60a**: ^{1}H NMR δ: 6.45 (1H, dd, J = 1.5, 17.5 Hz, HC-3), 6.29 (1H, s, HC-5″), 6.13 (1H, dd, J = 10.5, 17.5 Hz, HC-2), 5.89 (1H, dd, J = 1.5, 10.5 Hz, HC-3), 4.38 (2H, ap t, J = 6.5 Hz, H_2-C1′), 3.26 (2H, ap t, J = 6.5 Hz, H_2C-2′), 3.27–3.15 (2H, m, H_2C-2″), 2.77–2.69 (2H, m, H_2C-3″); ^{13}C NMR δ: 191.4 (s, C-4″), 165.6 (s, C-1), 161.4 (s, C-6″), 131.6 (t, C-3), 127.8 (d, C-2), 119.8 (d, C-5″), 62.1 (t, C-1′), 37.5 (t, C-3″), 32.6 (t, C-2′), 28.6 (t, C-2″); LRMS (CI, NH_3), *m/z* (relative intensity): 245 ([M+1]$^+$, 100), 172 (8.6), 147 (11), 115 (11). HRMS *m/z* calcd. for $C_{10}H_{12}O_3S_2$: 244.0228; found: 244.0231.

For **60b**: ^{1}H NMR δ: 6.47 (1H, dd, J = 1.5, 17.5 Hz, HC-3), 6.15 (1H, dd, J = 10.5, 17.5 Hz, HC-2), 5.90 (1H, dd, J = 1.5, 10.5 Hz, HC-3), 4.43 (2H, ap t, J = 6.5 Hz, HC-1′), 3.35 (2H, ap t, J = 6.5 Hz, HC-2′), 3.31–3.25 (2H, m, HC-2″), 2.98–2.92 (2H, m, H_2C-3″); ^{13}C NMR δ: LRMS (CI, NH_3), *m/z* (relative intensity): 281 ([M+1]$^+$, 50), 279 ([M+1]$^+$, 100), 206 (15), 147 (13), 99 (15). HRMS *m/z* calcd. for $C_{10}H_{11}{}^{35}ClO_3S_2$: 277.9838; found: 277.9836.

For **61a**: ^{1}H NMR δ: 6.87 (2H, ap s, HC-2, HC-3), 6.27 (1H, s, HC-5″), 4.41 (2H, ap t, J = 6.5 Hz, HC-2′), 3.82 (3H, s, H_3CO), 3.27 (2H, ap t, J = 6.5 Hz, H_2C-1′), 3.24–3.18 (2H, m, H_2C-2″), 2.77–2.71 (2H, m, HC-3″); ^{13}C NMR δ: 191.4 (s, C-4″), 165.1 (s, C-1 or C-4), 164.4 (s, C-1 or C-4), 161.1 (s, C-6″), 134.1 (d, C-2 or C-3), 132.8 (d, C-2 or C-3), 119.9 (d, C-5″), 62.8 (t, C-1′), 52.4 (q, CH_3O), 37.5 (t, C-3″), 31.1 (t, C-2′), 28.6 (t, C-2″); LRMS (EI), *m/z* (relative intensity): 302 ([M]$^+$, 30), 172 (36), 139 (50), 113 (60), 85 (100). HRMS *m/z* calcd. for $C_{12}H_{14}O_5S_2$: 302.0283; found: 302.283. Anal. calcd. for $C_{12}H_{14}O_5S_2$: C 47.67, H 4.67; found: C 47.87, H 4.41.

For **61b**: ^{1}H NMR δ: 6.87 (2H, ap s, HC-2, HC-3), 4.45 (2H, ap t, J = 6.5 Hz, H_2C-1′), 3.80 (3H, s, H_3CO), 3.34 (2H, ap t, J = 6.5 Hz, H_2C-2′), 3.31–3.25 (2H, m, H_2C-2″), 2.96–2.90 (2H, m, H_2C-3″); ^{13}C NMR δ: 183.5 (s, C-4″), 165.1 (s, C-1 or C-4), 164.4 (s, C-1 or C-4), 156.2 (s, C-6″), 134.2 (d, C-2 or C-3), 132.8 (d, C-2 or C-3), 119.9 (s, C-5″), 63.1 (t, C-1′), 52.4 (q, CH_3O), 38.4 (t, C-3″), 31.0 (t, C-2′), 28.1 (t, C-2″); LRMS (CI, NH_3), *m/z* (relative intensity): 338 ([M]$^+$, 20), 336 ([M]$^+$, 44), 208 (42), 206 (100), 157 (97), 113 (97). HRMS *m/z* calcd. for $C_{12}H_{13}{}^{35}ClO_5S_2$: 335.9893; found: 335.9892. Anal. calcd. for $C_{12}H_{13}ClO_5S_2$: C 42.79, H 3.89; found: C 43.03, H 4.05.

*2-[4-[[Tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]thio]ethyl propenoate (**62a**)*: ^{1}H NMR δ: 6.42 (1H, dd, J = 1.5, 17.5 Hz, HC-3), 6.24 (1H, d, J = 1.5 Hz, HC-5″), 6.12 (1H, dd, J = 10.5, 17.5 Hz, HC-2), 5.84 (1H, dd, J = 1.5, 10.5 Hz, HC-3), 4.76 (1H, dt, J = 1.5, 5.5 Hz, HC-3″), 4.34 (2H, ap t, J = 7 Hz, H_2C-1′), 3.34 (2H, d, J = 5.5 Hz, H_2C-2″), 3.14 (2H, ap t, J = 7 Hz, H_2C-2′), 1.15–1.04 (21H, m, $(H_3C)_2$CHSi).

*2-[5-Chloro-4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]thio]ethyl propenoate (**62b**)*: ^{1}H NMR δ: 6.40 (1H, dd, J = 1.5, 17.5 Hz, HC-3), 6.25 (1H, d, J = 1.5 Hz, HC-5″), 6.10 (1H, dd, J = 10.5, 17.5 Hz, HC-2), 5.85 (1H, dd, J = 1.5, 10.5 Hz, HC-3), 4.95 (1H, dt, J = 1.5, 5.5 Hz, HC-3″), 4.35 (2H, ap t, J = 7 Hz, H_2C-1′), 3.30 (2H, d, J = 5.5 Hz, H_2C-2″), 3.20 (2H, ap t, J = 7 Hz, H_2C-2′), 1.15–1.04 (21H, m, $(H_3C)_2$CHSi).

*2-[[4-[[Tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]thio]ethyl methyl (*E*)-butendioate (**63a**)*: ^{1}H NMR δ: 6.86 (2H, ap s, HC-2, HC-3), 6.23 (1H, d, J = 1.5 Hz, HC-5″), 4.76 (1H, dt, J = 1.5, 5.5 Hz, HC-3″), 4.36 (2H, ap t, J = 6.5 Hz, H_2C-1′), 3.80 (3H, s, H_3CO), 3.33 (2H, d, J = 5.5 Hz, H_2C-2″), 3.13 (2H, ap t, J = 6.5 Hz, H_2C-1′), 1.15–1.04 (21H, m, $(CH_3)_2$CHSi).

*2-[[5-Chloro-4-[[tris(1-methylethyl)silyl]oxy]-2*H*-thiopyran-6-yl]thio]ethyl methyl (*E*)-butendioate (**63b**)*: ^{1}H NMR δ: 6.88 (2H, ap s, HC-2, HC-3), 4.98 (1H, dt, J = 1.5, 5.5 Hz, HC-3″), 4.38 (2H, ap t, J = 6.5 Hz, H_2C-1′), 3.80 (3H, s, H_3CO), 3.31 (2H, d, J = 5.5 Hz, H_2C-2″), 3.25 (2H, ap t, J = 6.5 Hz, H_2C-1′), 1.15–1.04 (21H, m, $(CH_3)_2$CHSi).

*Methyl (3a*S**,4*S**,7*R**,7a*R**)-octahydro-7-hydroxy-7a-methyl-1*H*-indene-4-carboxylate (**64a**) and methyl (3a*S**,4*S**,7*S**,7a*R**)-octahydro-7-hydroxy-7a-methyl-1*H*-indene-4-carboxylate (**64b**)*

Raney Ni (0.30 mL) was added to a stirred solution of **45** (5.7 mg, 0.024 mmol) in MeOH (1 mL) and the resuling suspension was heated under reflux for 1 h. The reaction mixture was filtered through Celite with the aid of MeOH. The combined filtrate and washings were concentrated and fractionated by MPC (28% ethyl acetate in hexane) to give **64a** (1.9 mg, 38%) and **64b** (3.1 mg, 62%).

For **64a**: IR ν_{max}: 3468, 2950, 2871, 1735, 1450, 1155 cm^{-1}; ^{1}H NMR δ: 3.67 (3H, s, H_3CO), 3.46 (1H, dd, J = 4.5, 11 Hz, HC-7), 2.28–2.21 (1H, m, HC-4), 1.93–1.25 (11H, m), 0.75 (3H, s, H_3CC-7a); ^{13}C NMR (125 MHz) δ: 176.3, 78.7, 51.4, 49.3, 46.1, 42.2, 37.8, 29.7, 28.5, 25.7, 19.6, 11.2; LRMS (CI, NH_3), *m/z* (relative intensity): 230 ([M+18]$^+$, 67), 227 ([M+1]$^+$, 59), 195 (82), 180 (100), 135 (88), 130 (92).

For **64b**: IR ν_{max}: 3515, 2950, 2874, 1735, 1165 cm^{-1}; ^{1}H NMR δ: 3.80–3.76 (1H, m, HC-7), 3.66 (3H, s, H_3CO), 2.34 (1H, ddd, J = 4, 10, 10 Hz, HC-4), 1.92–1.61 (9H, m), 1.40–

1.22 (2H, m), 0.77 (3H, s, H_3CC-7a); ^{13}C NMR δ: 176.1, 71.6, 51.3, 45.3, 43.4, 41.6, 32.6, 28.3, 25.4, 23.8, 19.2, 18.0; LRMS (CI, NH_3), *m/z* (relative intensity): 2230 ($[M+18]^+$, 61), 227 ($[M+1]^+$, 24), 195 (100), 135 (56), 130 (67).

Methyl (1S,R*,4aR*,8aS*)-decahydro-4-hydroxy-4a-methylnaphthalene-1-carboxylate (**65a**) and methyl (1S*,4S*,4aR*,8aS*)-decahydro-4-hydroxy-4a-methylnaphthalene-1-carboxylate, (**65b**)*

Raney Ni (0.15 mL) was added to a stirred solution of **49** (12.5 mg, 0.049 mmol) in MeOH (2 mL) and the resulting suspension heated under reflux for 1 h. The reaction mixture was filtered through Celite with the aid of MeOH. The combined filtrate and washings were concentrated and fractionated by MPC (20% ethyl acetate in hexane) to give **65a** (5.3 mg, 48%) and **65b** (5.3 mg, 48%).

For **65a**: IR ν_{max}: 3480, 2927, 2862, 1735, 1436, 1171 cm^{-1}; ^{1}H NMR δ: 3.65 (3H, s, H_3CO), 3.32 (1H, dd, J = 4.5, 11 Hz, HC-4), 2.23 (1H, dt, J = 4, 11 Hz, HC-1), 2.02–1.09 (13H, m), 0.85 (3H, s, H_3C); ^{13}C NMR δ: 176.6, 78.5, 51.4, 45.7, 44.4, 38.8, 37.1, 29.0, 28.0, 26.2, 25.2, 21.2, 10.3; LRMS (CI, NH_3), *m/z* (relative intensity): 244 ($[M+18]^+$, 100), 227 ($[M+1]^+$, 45), 209 (50), 194 (26).

For **65b**: IR ν_{max}: 3513, 2926, 2859, 1735, 1443, 1153 cm^{-1}; ^{1}H NMR δ: 3.65 (3H, s, H_3CO), 3.36 (1H, br s, HC-4), 2.30 (1H, ddd, J = 4, 4, 12 Hz, HC-1), 1.92–1.00 (13H, m), 0.87 (3H, s, H_3C); ^{13}C NMR δ: 176.4, 74.4, 51.2, 45.0, 39.1, 37.8, 34.8, 27.6, 26.3, 25.7, 23.9, 21.4, 16.7; LRMS (CI, NH_3), *m/z* (relative intensity): 244 ($[M+18]^+$, 37), 227 ($[M+1]^+$, 31), 209 (100).

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