Ring Contraction of 3,6-Dihydro-2*H*-thiopyrans to Thiolanes by an Iodo-Oxyacylation Reaction

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Reaction of functionalized 3,6-dihydro-2*H*-thiopyrans with *N*-iodosuccinimide in the presence of carboxylic acids results in the stereospecific formation of poly-functionalised thiolanes in good yield. The formation of these thiolanes is believed to proceed through either a nucleophilic or an electrophilic pathway leading to 4,5-*cis*-substituted derivatives. The use of unsymmetrical 2,2-substituted 3,6-dihydro-2*H*-thiopyrans gave mixtures of isomers that could be separated in several cases. From a 3-substituted thiopyran a 2,2,3,4,5-pentasubstituted thiolane was obtained. Attempts to use alcohols as external nucleophiles were unsuccessful with NIS, NBS, and *N*-bromoacetamide. Iodo-azidination with in situ generated IN_3 was also unsuccessful.

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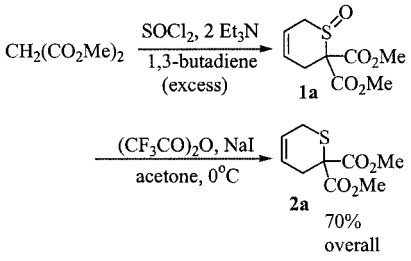
Introduction

A commonly used synthesis of 3,6-dihydro-2*H*-thiopyrans is the [4+2]-cycloaddition reaction of thiocarbonyl compounds with 1,3-dienes.[1] The required thiones are stable in a limited number of cases, but mostly they are prepared in situ in the presence of the trapping 1,3-dienes. In the past two decades the scope of these syntheses of dihydrothiopyrans has been substantially extended.[2] An attractive alternative for the synthesis of these sulfur heterocycles involves the [4+2]-cycloaddition reaction of sulfines (thione *S*-oxides) with 1,3-dienes.[3] The thus formed dihydrothiopyran *S*-oxides can readily be deoxygenated to give dihydrothiopyrans.[4] In fact, sulfines serve as synthetic equivalents of thiocarbonyl compounds.[3a] Various methods are available for the preparation of a large variety of substituted sulfines, such as oxidation of thiocarbonyl compounds with percarboxylic acids, alkylidenation of sulfur dioxide with α-silyl carbanions and dehydrohalogenation of suitably substituted sulfinyl chlorides.[3a,3c,5] The reaction of silyl enol ethers[3a,3c,5] or doubly activated methylene compounds[3a,3h,6] with thionyl chloride in the presence of a tertiary amine base is particularly attractive for the preparation of α-oxo sulfines, because of its simplicity and versatility.[3a]

For example, the reaction of dimethyl malonate with thionyl chloride in the presence of triethylamine and 1,3-butadiene as the trapping diene conveniently leads to cycloadduct **1a** in good yield[3a,5a,6] (Scheme 1). Subsequent removal of the sulfoxide oxygen by treatment with sodium iodide and trifluoroacetic anhydride in acetone[4] then produces the 3,6-dihydrothiopyran **2a** in an overall yield of 70 % (Scheme 1).



Scheme 1. Synthesis of 3,6-dihydrothiopyran **2a**

The chemical behaviour of 3,6-dihydrothiopyrans has received scant attention in the literature. Base-induced ring contractions of 2,2-disubstituted dihydrothiopyrans have been observed and explained by a ring-opening/ring-closure mechanism.[7] Electrophilic alkylation at the 2-position has been achieved for ethyl 4,5-dimethyl-3,6-dihydro-2*H*-thiopyran-2-carboxylates by treatment with LDA followed by an alkylating agent.[7a−7c] The selective *cis*-dihydroxylation of the olefinic bond has been accomplished using osmium tetroxide and more recently by an osmium trichloride system,[2,8] although success is highly dependent on the substitution pattern of the sulfur heterocycle.[9] Selective hydrogenation of the olefinic bond has also been accomplished.[5a] Selective epoxidation of this bond failed due to concurrent oxidation of sulfur.[10] Sigmatropic rearrangements of sulfonium ylids derived from 3,6-dihydro-2*H*-thiopyrans give rise to ring-contraction reactions to form either three- or five-membered rings.[7c,7k,9,11,12]

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We considered an alternative, two-step method for the dihydroxylation, viz. the so-called cohalogenation involving initial halogenation of the olefinic bond to a halonium (or π complex) followed by reaction with a carboxylate anion as a nucleophile and finally base-mediated hydrolysis to give 1,2-diols.[13] Mechanistically, this cohalogenation process is related to the halolactonization reaction. So far, this approach to the dihydroxylation of dihydro-2*H*-thiopyrans has not been investigated. The more common iodolactonization has been studied by Sutherland et al.[14] for dihydrothiopyrans bearing a CH_2CO_2H substituent at the allylic 3-position. In one case a deviant reaction was observed: treatment of these substrates with $KI_3/NaHCO_3$ in water gave a ring contraction product identified as a thiolane derivative in 67 % yield. The formation of this unwanted product was explained by invoking initial complexation of the sulfur atom with iodine.[14] In the present study the cohalogenation of dihydrothiopyran **2a** (Scheme 1) was investigated with *N*-iodosuccinimide in the presence of a carboxylic acid. Although the initial aim was to accomplish a selective oxyacylation reaction of the olefinic bond, it will be shown that actually a ring contraction to thiolanes took place exclusively.

Results and Discussion

Treatment of a solution of substrate **2a** in chloroform with *N*-iodosuccinimide as the source of electrophilic halogen in the presence of an excess of diphenylacetic acid gave a single crystalline product in 84 % yield. Comparison of the ^{1}H- and ^{13}C NMR spectroscopic data of this product with those of known thiane derivatives[3h,3i] clearly revealed that no six-membered sulfur heterocycle had been obtained, although the molecular composition was the same as expected for an iodo-oxygenation of the olefinic bond. X-ray diffraction analysis[15,16] was used to elucidate the structure of the newly formed product, which was shown to be iodothiolane **3a** (Figure 1).

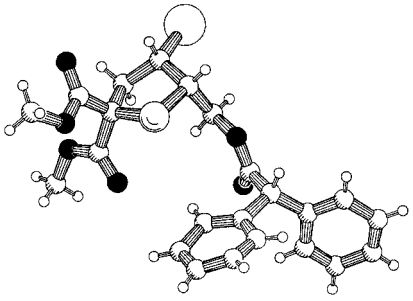
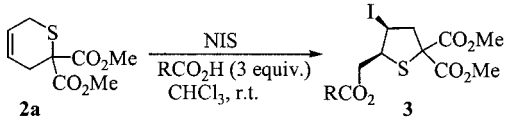


Figure 1. X-ray crystal structure of **3a**

The iodine substituent at C-4 is positioned *cis* with respect to the substituent at C-5. Thus, a ring contraction to thiolane had taken place. Once the correct structure of the product was known the signals in the ^{1}H and the ^{13}C NMR spectra could be assigned using DEPT- and H,C-correlation methods.

The reaction time for the ring contraction using diphenylacetic acid is rather long (16 h). The influence of the carboxylic acid on the reaction rate was tested by studying a series of acids as shown in Table 1. In all cases ring-contracted thiolanes were obtained as the sole product. In most cases the yields are excellent. The reaction time does indeed depend on the nature of the acid: the stronger the acid the faster the reaction. Benzoic acid failed to react even after seven days, but 2-methoxybenzoic acid gave the expected product after four days in 56 % yield. The scope of this novel ring contraction is quite substantial with respect to the carboxylic acids. In all cases the ^{1}H NMR spectra reveal that the C-4−C-5 *cis* product is obtained exclusively. The stereogenic centre in mandelic acid led to the formation of two diastereomeric products (ratio 2:3). The products **3** are stable compounds that can be stored at ambient temperature. In most cases the initially obtained oily products crystallized on standing at −20 °C, although sometimes only after several months.

Table 1. Ring contraction of **2a** upon reaction with NIS and carboxylic acids



2a **3**

3	R	Time (h)	Yield (%)
a	Ph_2CH-	16	84
b	Me	5	90
c	Cl_3C	2	97
d	$HC\equiv C-$	1.5	94
e	H	1.5	98
f	$MeOCH_2-$	3	92
g	$2\text{-}MeOC_6H_4$	96	56[a]
h	mandelic acid	2	92[b]
i	[c]	24	35[a]
j	Ph	7 days	0

[a] Incomplete conversion. [b] 2:3 mixture of diastereomers. [c] OH instead of RCO_2, reagent H_2O/THF.

The formation of the ring-contracted products can be rationalized by assuming an initial reaction of the electrophilic iodosuccinimide with the olefinic bond to give an iodonium ion **4**. By an intramolecular reaction of sulfur this ion **4** is transformed into bicyclic thiiranium ion **5**. This reaction must take place in a stereocontrolled manner because of the steric restrictions imposed by the six-membered sulfur heterocycle. In a subsequent step the carboxylate anion, formed by the reaction of the carboxylic acid with the succinimide anion released during the iodination with NIS, will attack from the least substituted carbon atom (route a in Scheme 2) to give the final product **3**. This sequence leads to the observed *cis*-relationship of the iodine substituent and the group at C-5 (Scheme 2). The alternative ring opening of species **5** following the sterically more

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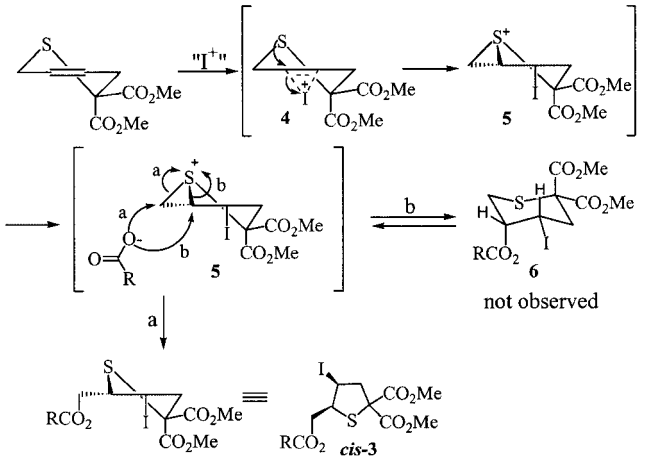
encumbered route b, would lead to the six-membered product **6**. This compound was not observed experimentally.



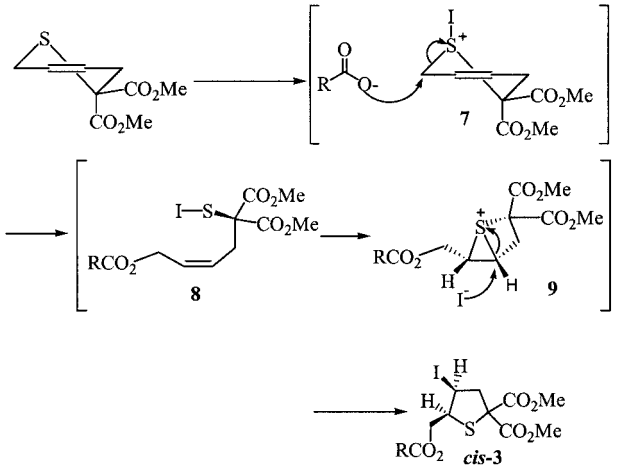
Scheme 2. Proposed mechanism for the ring-contraction reaction

This mechanism is similar to the one suggested by Hughes[17] and Altenbach[18] in their work on the ring contraction of (thio)sugars derived from tetrahydrothiopyrans. In contrast to their work, the leaving group that is expelled by sulfur (iodide in our case) remains part of the product, thus resulting in the introduction of two functionalities with simultaneous ring contraction.

An alternative explanation involves initial iodination of the sulfur atom to sulfonium species **7**, which on reaction with carboxylate anion opens up to sulfanyl iodide **8** (Scheme 3). It must then be assumed that an intramolecular reaction occurs with the olefinic bond resulting in thiiranium ion **9**. Cleavage of the three-membered ring by opening the central bond in **9** by an iodide ion then leads to product **3**. Cyclizations of alkenylsulfanyl halides are indeed believed to occur by an electrophilic addition to the double bond giving a thiiranium intermediate.[19] For substrates having short tethers, as in the present case, the formation of the bicyclic species (here **9** is a [2.1.0]-system, while **5** is a [3.1.0]-system) may be difficult owing to strain effects.[14] Furthermore, the stereoelectronic alignment for the 5-*endo-trig* closure of **8** to **9** may be sterically considerably hampered.[14] For these reasons this alternative mechanism is considered unlikely.

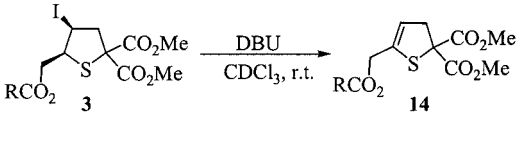
It should be noted that Sutherland et al.[14] explained the deviant formation of a ring-contracted product (a thiolane) during the iodolactonization of a dihydrothiopyran with a CH_2CO_2H substituent, by invoking a bicyclic thiiranium ion resembling structure **5** in Scheme 2, although its formation was not clearly specified.

By monitoring the reaction of **2a** with NIS and acetic acid with ^1H NMR spectroscopy we attempted to spot an intermediate in this ring-contraction process. However, we observed only the appearance of product **3b** and the disappearance of the substrate **2a**. We also attempted to use molecular iodine as the iodination agent,[14,19a] but observed no reaction even after several days. This was somewhat surprising as alkenyl sulfides undergo a cyclization reaction to thiolanes and/or thianes upon treatment with iodine or bromine.[19a]Attempts to accomplish a reaction with in situ generated IN_3 from NIS and NaN_3, ICl and NaN_3, or NIS and HN_3 did not lead to any product at all; the substrate was recovered quantitatively. When *N*-bromosuccinimide or *N*-bromoacetamide were used instead of NIS, hardly any reaction was detected. Replacement of the carboxylic acid by alcohols (such as allyl-, benzyl-, and methyl alcohol) resulted in complete failure of the reaction. Only with 80 % aqueous THF using two equivalents of NIS was the corresponding iodo alcohol **3i** obtained, albeit in a modest yield (35 %).



Scheme 3. Alternative mechanism for the ring-contraction reaction

Unfortunately, attempts to substitute the iodide functionality in **3a** with an azide failed. Treatment of **3a** with sodium- or lithium azide in DMSO, DMF or acetonitrile only led to HI-elimination to give derivative **14a**. Treatment of **3a**−**c**,**e**, and **g** with DBU in $CDCl_3$ was monitored by ^1H NMR spectroscopy and showed, as expected, quantitative conversion into derivatives **14a**−**c**,**e**, and **g**, respectively (Scheme 4).



Scheme 4. Dehydroiodination of thiolanes **3**

As mentioned in the introduction, the reaction of doubly activated methylene compounds with thionyl chloride in the presence of triethylamine and a trapping 1,3-diene is an effective way to prepare dihydrothiopyran-*S*-oxides.[3] This method was applied for methyl phenylacetate, ethyl cyanoacetate, and diethyl cyanomethanephosphonate. Subsequent deoxygenation[4] then gives the dihydrothiopyrans shown in Table 2. These unsymmetrically substituted sulfur heterocycles were subjected to the optimal ring-contraction

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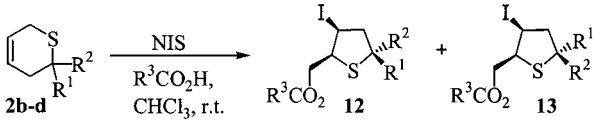
conditions with NIS as the electrophilic reagent. The expected thiolanes were obtained as a 1:1 mixture of isomers **12** and **13** (Table 2). The reaction with diphenylacetic acid as the carboxylate was slow for substrate **2b** and failed for substrates **2c** and **2d**. The more reactive acids, acetic acid, formic acid and propiolic acid gave good to excellent yields of thiolanes (Table 2). During the reaction of **2b** with NIS and acetic acid some by-products were also formed. These minor products showed a vinylic proton signal at ca. 6.3 ppm that suggested elimination of HI had taken place. However, the structure of these by-products remained obscure. In the case of products **12/13e**,**g** and **h**, separation of isomers could be achieved by chromatography.

Table 2. Ring contraction of unsymmetrically substituted 3,6-dihydrothiopyrans **2b**−**d**



2	R^1	R^2	R^3	Products **12** +**13**	Yield (%)
b	CO_2Me	Ph	Ph_2CH−	**a**	52
b	CO_2Me	Ph	Me	**b**	74
c	CO_2Et	CN	Ph_2CH−	**c**	–
c	CO_2Et	CN	H	**d**	91
c	CO_2Et	CN	HC≡C−	**e**	93
d	CN	$(EtO)_2P(O)$−	Ph_2CH−	**f**	–
d	CN	$(EtO)_2P(O)$−	H	**g**	88
d	CN	$(EtO)_2P(O)$−	HC≡C−	**h**	93

The structures of the obtained products could be deduced from the NMR spectral characteristics. The overall patterns closely resemble those of product **3b** obtained from substrate **2a**. The substituents at C-4 and C-5 have a *cis*-relationship as is apparent from the coupling constant $J(H^4,H^5)$. All other signals could be properly assigned. The structures of **12e** and **12h** were eventually established unambiguously by means of X-ray diffraction analysis (Figure 2).

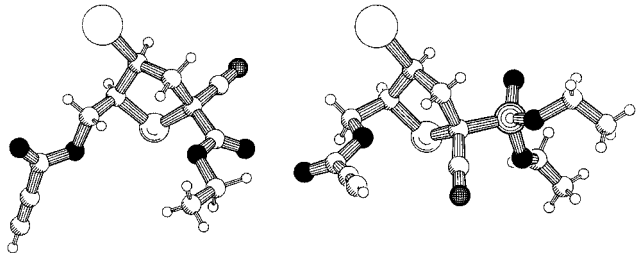
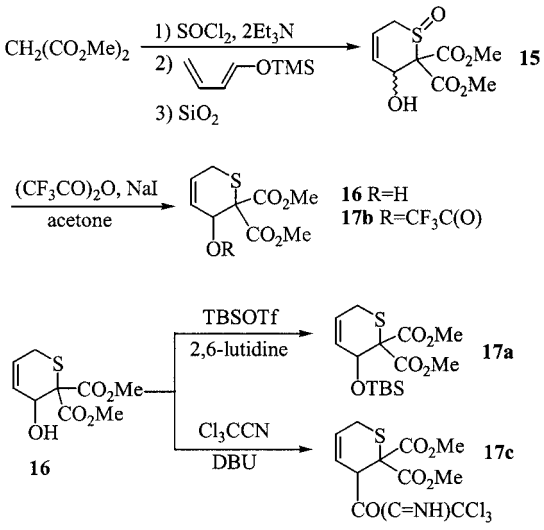


Figure 2. X-ray crystal structures of **12e** and **12h**

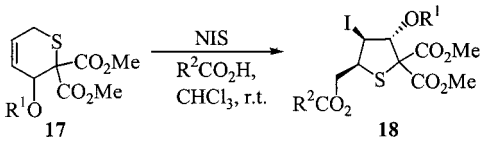
The sulfine derived from dimethyl malonate was also trapped with 1-trimethylsilyloxy-1,3-butadiene. The resulting 3-OTMS derivative (mixture of isomers) was deprotected by stirring overnight with silica gel in ethyl acetate to give **15**. Subsequent deoxygenation with trifluoroacetic anhydride and sodium iodide gave **16** together with variable amounts of trifluoroacetate **17b**. Treatment of **16** with TBSOTf in the presence of 2,6-lutidine produced **17a** in 82 % yield while reaction with trichloroacetonitrile and DBU led to **17c** in 92 % yield (Scheme 5).



Scheme 5. Synthesis of thiopyrans to be used for the ring contraction to fully substituted thiolanes

Ring contraction with NIS in the presence of a carboxylic acid now produced penta-substituted thiolanes **18**. The reaction with diphenylacetic acid is sluggish and low yielding, but with propiolic acid the yield of **18b** was excellent (Table 3). The trifluoroacetyl-protected substrate **17c** failed to react, possibly due to a deactivating effect of this substituent on the olefinic bond. Also trichloroimidate **17c** failed to react. In this case no intramolecular iodoimidation occurred either, which is notable as several examples of such intramolecular iodoimidations with similar derivatives (with either carbon or oxygen in the position of the sulfur) are known.[13f]

Table 3. Synthesis of fully substituted thiolanes **18**



17	R^1	R^2	Product **18**	Yield (%)
a	TBDMS	Ph_2CH-	**a**	20
a	TBDMS	HC≡C-	**b**	95
b	$CF_3C(=O)$-	HC≡C-	**c**	–
c	$C(=NH)CCl_3$	HC≡C-	**d**	–

The products **18a** and **18b** were obtained as single isomers. It may be assumed that the substituents at C-4 and C-5 are positioned in a *cis* manner although the $J(H^4,H^5)$

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value of 7.2 Hz is a little high. 3-H and 4-H have a *trans* relationship as is apparent from the $J(H^3,H^4)$ values of 9.9 and 9.7 Hz, respectively.

In summary, ring contraction of 3,6-dihydrothiopyrans derived from doubly activated methylene compounds via a sulfine intermediate can be readily accomplished by treatment with *N*-iodosuccinimide in the presence of a range of carboxylic acids. In most cases the yields are high. This reaction proceeds in a stereocontrolled manner to give thiolanes with the substituents at C-4 and C-5 in a *cis* relationship. Mechanistically this ring contraction takes place by an initial iodination of the olefinic bond, followed by an intramolecular reaction of the ring sulfur atom to give a thiiranium ion as the key intermediate, which upon attack by the carboxylate opens up to produce the five-membered ring products.

Experimental Section

General Remarks: Melting points were determined with a Reichert Thermopan microscope and are uncorrected. ^{1}H- and ^{13}C NMR spectra were recorded with Bruker AC 300 MHz and Varian Unity Inova HR 400 MHz FT spectrometers. Mass spectra were obtained with a VG7070E Mass Spectrometer. Elemental analyses were obtained using a Carlo Erba EA 1108 element analyzer. Thin-layer chromatography was carried out on Merck silica-gel 60 F-254 plates. Spots were visualized with UV and by dipping in a staining solution (6.2 % sulfuric acid aqueous solution, containing 42 g of ammonium molybdate and 42 g of ceric ammonium sulfate per litre) followed by charring. Gravity column chromatography was carried out on Silica 60 (Baker).

Chemicals: The rearrangement reactions were performed in chloroform (p.a.). Dichloromethane and acetonitrile were distilled from P_2O_5, ethyl acetate was distilled from K_2CO_3, and heptane from CaH_2. Diisopropyl ether (p.a., Acros) was used as received. NIS and NBS were purchased from Aldrich and used as such.

Ethyl 2-Cyano-3,6-dihydro-1-oxo-2*H*-thiopyran-2-carboxylate (1c):[3h,3i,6] Under an argon atmosphere a solution of ethyl cyanoacetate (4.52 g, 40 mmol) and triethylamine (8.5 g, 84 mmol, 2.1 equiv.) in diethyl ether (100 mL) was added dropwise over 45 min to a cooled (−78 °C) solution of thionyl chloride (2.98 mL, 41 mmol) in diethyl ether (100 mL) into which an excess of 1,3-butadiene had been condensed. Once addition was complete, the reaction mixture was stirred for 30 min at −78 °C after which the temperature was allowed to rise to 0 °C. After stirring for 3 h the temperature was raised to room temperature and stirring was continued overnight under a slow stream of argon. The reaction mixture was poured into a 500-mL separating funnel containing water (150 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 75 mL), and the combined organic fractions were dried ($MgSO_4$) and filtered. Removal of the solvents in vacuo gave 8.35 g of crude product as a dark yellow to brown oil. Purification by column chromatography (silica gel, ethyl acetate/heptane = 1:1) yielded 6.91 g (81 %) of a yellow oil that crystallized upon standing. mp.: 98−101 °C. ^{1}H NMR (300 MHz): δ = 1.37 (t, *J* = 7.2 Hz, 3 H, -C*H*$_3$), 3.0 (br. s, 2 H, H_2C-C-S=O), 3.72 (br. d, 1 H, *H*HC-S=O), 3.94 (dd, *J* = 6.2, 20.2 Hz, 1 H, *H*HC-S=O), 4.40 (q, *J* = 7.2 Hz, 2 H, OCH_2-), 5.66−5.86 (m, 2 H, *H*C=C*H*) ppm. ^{13}C NMR (75 MHz): δ = 13.9 (*C*H$_3$), 32.4 (H_2*C*-C-S=O), 49.0 (H_2*C*-S=O), 63.9 (NC*C*-S=O), 64.6 (O*C*H$_2$-), 112.9 (*C*N), 118.7, 125.2 (H*C*=*C*H), 164.1 (*C*=O) ppm. Mass (EI): *m*/*z* = 213 [M$^+$].

Ethyl 2-Cyano-3,6-dihydro-2*H*-thiopyran-2-carboxylate (2c): Prepared by reduction of **1c** according to a literature procedure.[4] Obtained from the *S*-oxide (2.13 g, 10.0 mmol) as a viscous yellow oil (1.67 g, 85 %) after column chromatography (ethyl acetate/heptane = 1:4).^{1}H NMR (300 MHz): δ = 1.35 (t, *J* = 7.2 Hz, 3 H, -C*H*$_3$), 2.82 (m, 2 H, H_2C-C-S), 3.25 (dd, *J* = 4.0, 18.0 Hz, 1 H, *H*HC-S), 3.71 (br. d, 1 H, *J* = 18.0 Hz, *H*HC-S), 4.32 (q, *J* = 7.2 Hz, 2 H, OCH_2-), 5.80−6.04 (m, 2 H, *H*C=C*H*) ppm. ^{13}C NMR (75 MHz): δ = 13.7 (*C*H$_3$), 32.1 (H_2*C*-C-S), 42.5 (H_2*C*-S), 60.1(NC*C*-S), 63.7 (O*C*H$_2$-), 116.0 (*C*N), 123.3, 123.6 (H*C*=*C*H), 165.4 (*C*=O) ppm. Mass (EI): *m*/*z* = 197 [M$^+$].

Diethyl 2-Cyano-3,6-dihydro-1-oxo-2*H*-thiopyran-2-phosphonate (1d): Prepared according to procedure for **1c** from *O*,*O*-diethyl cyanomethylphosphonate (3.54 g, 20.0 mmol). Obtained as a viscous yellow oil (4.32 g, 78 %) after column chromatography (ethyl acetate/heptane = 1:1), sufficiently pure for *S*-oxide reduction. (^{1}H NMR showed the presence of a small amount of *O*,*O*-diethyl cyanomethylphosphonate). ^{1}H NMR (300 MHz): δ = 1.43 [m, 6 H, P(OCH$_2$C*H*$_3$)$_2$], 2.93 (m, 2 H, H_2CC-S=O), 3.71 (br. d, 1 H, *J* = 16.5 Hz, *H*HC-S=O), 3.98 (d of triplets, 1 H, *J* = 16.5, 4.8 Hz, *H*HC-S=O), 4.30−4.40 [m, 4 H, P(OCH_2CH$_3$)$_2$], 5.75−5.83 (m, 2 H, *H*C=C*H*) ppm. ^{13}C NMR (75 MHz): δ = 16.2 (d, *J* = **?** Hz, 2 × -*C*H$_3$), 31.0 (H_2*C*C-S=O), 48.8 (H_2*C*-S=O), 65.0, 65.4 (d, *J* = 30 Hz, O*C*H$_2$CH$_3$)$_2$, 119.2 (*C*N), 125.2, 125.4 (H*C*=*C*H) ppm. Mass (EI): *m*/*z* = 277 [M$^+$].

Diethyl 2-Cyano-3,6-dihydro-2*H*-thiopyran-2-phosphonate (2d): Prepared by reduction of **1d** according to a literature procedure.[4] Obtained from the *S*-oxide (2.77 g, 10.0 mmol) as a yellow oil (2.14 g, 82 %). ^{1}H NMR (300 MHz): δ = 1.42 [t, 6 H, *J* = Hz, P(OCH$_2$C*H*$_3$)$_2$], 2.80 (AB of multiplets, 2 H, H_2CC-S), 3.21 (d of multiplets, 1 H, *J* = 17.7 Hz, *H*HCC-S), 3.71 (d of multiplets, 1 H, *J* = 17.7 Hz, *H*HCC-S), 4.29−4.40 [m, 4 H, P(OCH_2CH$_3$)$_2$], 5.85 (m, 1 H, *H*C=CH), 6.00 (m, 1 H, HC=C*H*) ppm. ^{13}C NMR (75 MHz): δ = 16.2, 16.3 [P(OCH$_2$*C*H$_3$)$_2$], 25.0 (d, *J* = 5.3 Hz, H_2*C*C-S), 30.6 (d, *J* = 3 Hz, H_2*C*-S), 35.5+37.3 (d, $J_{P,C}$ = 135 Hz, P-*C*-S), 65.0, 65.4 [2 × d, $J_{P,C}$ = 7.5 Hz, P(O*C*H$_2$CH$_3$)$_2$], 116.4 (d, $J_{P,C}$ = 7.5 Hz, *C*N), 123.5 (H*C*=CH), 123.8 (HC=*C*H) ppm. Mass (EI): *m*/*z* = 261 [M$^+$].

Dimethyl 3,6-Dihydro-3-[trifluoroacetyloxy]-2*H*-thiopyran-2,2-dicarboxylate (17b): Obtained in varying amounts (0−35 %), together with hydroxy derivative **9a**, as a white crystalline solid by reduction of **16**.[6] (Separated from **9a** during column chromatography.) mp.: 105−106 °C. ^{1}H NMR (300 MHz): δ = 3.25 (m, 2 H, CH_2S), 3.81 (s, 6 H, 2 -CO$_2$C*H*$_3$), 5.93−6.04 [m, 2 H, C=C*H*-C*H*OC(=O)CF$_3$], 6.23−6.29 (m, 1 H, CH$_2$C*H*=CH-) ppm. ^{13}C NMR (75 MHz): δ = 24.4 (*C*H$_2$S), 53.8 (2 × -CO$_2$*C*H$_3$), 58.3 [C=CH-*C*HOC(=O)CF$_3$], 69.1 [S-*C*(CO$_2$Me)$_2$], 122.8 (HC=*C*H-CHOC=OCF$_3$), 130.3 (H*C*=CH-CHOC=OCF$_3$), 165.6 (2 *C*=O methyl ester), 166.3 [F$_3$C*C*(=O)-O-] ppm. Mass (EI): *m*/*z* = 328 [M$^+$]. Elemental analysis: calculated for $C_{11}H_{11}F_3O_6S$ (328.26): C 40.25, H 3.78 %; found C 40.21, H 3.51 %.

Dimethyl 3-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxy}-3,6-dihydro-2*H*-thiopyran-2,2-dicarboxylate (17a): Under an argon atmosphere a solution of *tert*-butyldimethylsilyl triflate (0.48 mL, 2.1 mmol) in dichloromethane (10 mL) was added dropwise to a solution of **16**[6] (464 mg, 2.0 mmol) and 2,6-lutidine (0.25 mL, 2.1 mmol) in dichloromethane (10 mL) at 0 °C. After completion of the reaction (monitored by TLC, ethyl acetate/heptane = 1:1) the reaction mixture was poured into a separating funnel with water (25 mL), the

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layers were separated and the water layer was extracted with dichloromethane (2 × 20 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. Purification by column chromatography over silica gel (ethyl acetate/heptane = 1:2) gave 567 mg (82 %) **17a** as a white crystalline solid, mp.: 72−74 °C. ^{1}H NMR (300 MHz): δ = 0.00 (s, 3 H, H_3CSiMe*t*Bu), 0.04 (s, 3 H, H_3CSiMe*t*Bu), 0.78 [s, 9 H, $(H_3C)_3$CSiMe$_2$], 3.04 (m, 2 H, CH_2S), 3.68 (s, 3 H, -CO_2CH_3), 3.71 (s, 3 H, -CO_2CH_3), 4.75 (d, *J* = 3.6 Hz, 1 H, C=CH-C*H*OTBS), 5.88−6.00 (m, 2 H, -C*H*=C*H*-) ppm. ^{13}C NMR (75 MHz): δ = −4.8 (H_3CSiMe*t*Bu), −3.5 (H_3CSiMe*t*Bu), 17.9 [Si*C*(Me)$_3$], 25.3 (*C*H$_2$S), 25.6 [SiC(*C*H$_3$)$_3$], 53.1 (2 -CO_2CH_3), 64.8 (*C*-OSi), 125.3, 129.3 (-H*C*=*C*H-), 168.0 (2 O=*C*-OMe) ppm. Mass (EI): *m*/*z* = 346 [M$^+$].

Dimethyl 3,6-Dihydro-3-{[trichloroethanimidoyl]oxy}-2*H*-thiopyran-2,2-dicarboxylate (17c): DBU (0.05 mL, 0.3 mmol, 0.3 equiv.) was added to a cooled (0 °C) solution of **16** (232 mg, 1.0 mmol) and trichloroacetonitrile (1.0 mL, 10.0 mmol) in dichloromethane (5.0 mL). After stirring for 10 min the reaction mixture was poured into a separating funnel containing water (25 mL). The layers were separated and the water layer was extracted with dichloromethane (2 × 15 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. Purification by column chromatography over silica gel (ethyl acetate/heptane = 1:1) gave 345 mg (92 %) of **17c** as a white crystalline solid. After storage at −20 °C for three months, the compound showed some signs of decomposition (TLC). mp.: 87−90 °C. ^{1}H NMR (300 MHz): δ = 3.22 (m, 2 H, CH_2S), 3.80 (s, 6 H, -CO_2CH_3), 5.97 [br. d, 1 H, *J* = 3.3 Hz, C=CH-C*H*OC(=NH)CCl_3], 6.15−6.25 (m, 2 H, -C*H*=C*H*-), 8.46 (br. s, 1 H, C=N*H*) ppm. ^{13}C NMR (75 MHz): δ = 25.4 (*C*H$_2$S), 53.5, 53.6 (2 -CO_2CH_3), 59.1 [*C*(CO_2Me)$_2$], 69.4 (*C*-O-C=N), 91.2 (*C*Cl_3), 122.9, 128.6 (-H*C*=*C*H-), 161.1 (*C*=NH), 166.1, 166.8 (O=*C*-OMe) ppm. Mass (EI): *m*/*z* = 375 [M$^+$]. HRMS: calculated for $C_{11}H_{12}Cl_3INO_5S$: 374.95018; found 374.95021.

Synthesis of 4-Iodotetrahydrothiophenes, Typical Procedure: *N*-Iodosuccinimide (270 mg, 1.2 mmol, 1.2 equiv.) was added to a solution of the dihydrothiopyran (1.0 mmol) and carboxylic acid (3.0 mmol) in chloroform (6 mL) in three portions at approximately 10-min intervals. The reaction was monitored by TLC, and once it was complete (Table 1) chloroform (15 mL) was added and the solution was poured into a separating funnel containing 10 % sodium thiosulfate (25 mL). The layers were separated and the aqueous layer was extracted with chloroform (2 × 20 mL). The combined organic fractions were washed successively with 3 % sodium hydrogencarbonate solution and water. Drying ($MgSO_4$), filtration, and removal of the solvent in vacuo yielded the crude product. Column chromatography over silica gel gave the pure products.

Using this procedure, the following derivatives were prepared:

Dimethyl (4,5-*cis*)-5-[(2,2-Diphenylacetyloxy)methyl]-4-iodotetrahydrothiophene-2,2-dicarboxylate (3a): Obtained as a white crystalline solid (465 mg, 84 %) after column chromatography (ethyl acetate/heptane = 1:3). Crystallization from diisopropyl ether gave small transparent needles suitable for X-ray diffraction analysis. Crystal data for **3a** are shown in Table 4. mp.: 109−110 °C. ^{1}H NMR (300 MHz): δ = 2.73 [dd, *J* = 13.7, 11.5 Hz, 1 H, H_{trans}HCC(CO_2Me)$_2$], 3.04 [dd, *J* = 13.7, 5.7 Hz, 1 H, H_{cis}HCC(CO_2Me)$_2$], 3.57 (m, 1 H, *H*C-S), 3.74 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, CO_2CH_3), 4.37 (dd, *J* = 11.5, 6.7 Hz, 1 H, O-CH_{trans}H-CH-S), 4.48 (dd, *J* = 11.5, 4.8 Hz, 1 H partial overlap with multiplet CH-*H*C-I), 5.05 (s, 1 H, Ph$_2$C*H*-), 7.23−7.33 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz): δ = 22.5 (d, *C*-I), 46.6 [t, H$_2$*C*-C(CO_2Me)$_2$], 51.1 (d, OCH$_2$-*C*H-S), 53.7 (2 × CO_2*C*H$_3$), 56.9 (Ph$_2$*C*H-), 64.5 [s, S-*C*(CO_2Me)$_2$], 68.7 (t, O*C*H$_2$-CH-S), 127.2, 127.3, 128.5, 2 × 128.6, 128.7 (C-arom), 138.2 (C_{ipso}), 168.7, 170.0, 171.9 (s, *C*=O) ppm. Mass (EI): *m*/*z* = 554 [M$^+$]. Elemental Analysis: calculated for $C_{23}H_{23}IO_6S$ (554.39): C 49.83, H 4.18 %; found C 49.82, H 4.09 %.

Table 4. Crystal data and structure refinement for **3a**

Crystal colour	transparent, colourless
Crystal shape	regular fragment
Crystal size	0.29 × 0.21 × 0.15 mm
Empirical formula	$C_{23}H_{23}IO_6S$
Molecular mass	554.37
Temperature	293(2) K
Radiation/wavelength	Mo-K_α (graphite-monochromated)/0.71073 Å
Crystal system, space group	monoclinic, *Pn*
Unit cell dimensions (25 reflections, 10.523 < θ < 14.466)	*a*, α = 10.7956(16) Å, 90° *b*, β = 12.1197(15) Å, 92.054(19)° *c*, γ = 17.677(3) Å, 90°
Volume	2311.4(6) Å^3
Z, Calculated density	4, 1.593 Mg/m^3
Absorption coefficient	1.512 mm^{-1}
Diffractometer/scan	Enraf−Nonius CAD4/Ω
F(000)	1112
θ-range for data collection	3.36 to 27.48°
Index ranges	0 ≤ *h* ≤ 14, −15 ≤ *k* ≤ 0, −22 ≤ *l* ≤ 22
Reflections collected/unique	5554/5554
Reflections observed	2607 ([$I_o > 2\sigma(I_o)$])
Absorption correction	Semi-empirical from Ψ-scans
Range of relat. transm. factors	1.169 and 0.814
Refinement method	Full-matrix least-squares on F^2
Computing	SHELXL-97 (Sheldrick, 1997)
Data/restraints/parameters	5554/2/563
Goodness-of-fit on F^2	1.043
SHELXL-97 weight parameters	0.112600, 0.000000
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0922, wR_2 = 0.1954
R indices (all data)	R_1 = 0.2030, wR_2 = 0.2513
Largest diff. peak and hole	1.500 and −0.781 e·Å^{-3}

Dimethyl (4,5-*cis*)-5-[(Acetyloxy)methyl]-4-iodotetrahydrothiophene-2,2-dicarboxylate (3b): Obtained as a white crystalline solid (360 mg; 90 %) after column chromatography (ethyl acetate/heptane = 1:3). Crystallization from diisopropyl ether gave long transparent needles. mp.: 120−121 °C. ^{1}H NMR (300 MHz): δ = 2.08 (s, 3 H, H_3C-CO_2-), 2.87 (dd, *J* = 11.7, 13.5 Hz, 1 H, H_{trans}HCC(-CO_2Me)$_2$], 3.16 (dd, *J* = 5.7, 13.5 Hz, 1 H, H_{cis}HCC(CO_2Me)$_2$], 3.60 (m, 1 H, *H*C-S), 3.79 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, CO_2CH_3), 4.24 (dd, *J* = 6.9, 11.7 Hz, 1 H, O-CH_{trans}H-CH-S), 4.49 (dd, *J* = 4.5, 11.7 Hz, 1 H, O-CH_{cis}H-CH-S), 4.58 (m, 1 H, I-C*H*-CH-S) ppm. ^{13}C NMR (75 MHz): δ = 20.9 (H_3C-CO_2-), 22.6 (I-*C*H-), 46.9 (t, H$_2$*C*-C(CO_2Me)$_2$], 51.3 (d, OCH$_2$-*C*H-S), 53.8 (2q, 2 CO_2*C*H$_3$), 64.5 [s, S-*C*(CO_2Me)$_2$], 68.2 (t, MeCO_2-*C*H$_2$-), 168.8, 170.0, 170.3 (*C*=O). Mass (EI): *m*/*z* = 402 [M$^+$]. Elemental analysis: calculated for $C_{11}H_{15}IO_6S$ (402.20): C 32.85, H 3.76 %; found C 32.80, H 3.71 %.

Dimethyl (4,5-*cis*)-4-Iodo-5-[(2,2,2-trichloroacetyloxy)methyl]tetrahydrothiophene-2,2-dicarboxylate (3c): Obtained as a colourless oil (488 mg, 97 %) after column chromatography (ethyl acetate/heptane = 1:3) which slowly crystallized at −20 °C. Crystallization from diisopropyl ether gave small white needles. mp.: 83−85 °C. ^{1}H NMR (300 MHz): δ = 2.89 [dd app. as triplet, 1 H, *J* = 13.5,

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13.5 Hz, H_{trans}HCC($CO_2Me)_2$], 3.16 [dd, J = 5.7, 13.5 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.79 (m, 7 H, *H*C-S and 2 CO_2CH_3), 4.58−4.71 (m, 3 H, $MeCO_2$-CH_2- and I-C*H*-) ppm. ^{13}C NMR (75 MHz): δ = 21.4 (*C*-I), 46.6 (H_2C-C($CO_2Me)_2$], 50.3 (*C*H-S), 2 × 53.7 (2 CO_2CH_3), 64.5 (S-*C*($CO_2Me)_2$], 72.4 ($Cl_3CCO_2-CH_2-$), 161.1 (Cl_3C-*C*=O), 168.1, 168.6 (*C*=O). Mass (EI): *m*/*z* = 504 [M^+]. HRMS: calculated for $C_{11}H_{12}Cl_3IO_6S$, 503.8466; found 503.8468.

Dimethyl (4,5-*cis*)-4-Iodo-5-[(propioloyloxy)methyl]tetrahydrothiophene-2,2-dicarboxylate (3d): Obtained as a colourless oil (387 mg, 94 %) after column chromatography (ethyl acetate/heptane = 1:3) which slowly crystallized at −20 °C. Crystallization from diisopropyl ether gave small white needles. mp.: 96−98 °C. ^{1}H NMR (300 MHz): δ = 2.84 [dd, J = 13.7, 11.7 Hz, 1 H, H_{trans}HCC(-$CO_2Me)_2$], 2.97 (s, 1 H, *H*C≡C-), 3.20 [dd, J = 13.7, 5.8 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.64 (m, 1 H, *H*C-S), 3.79 (br. s, 6 H, 2 × CO_2CH_3), 4.37 (dd, J = 11.5, 7.0 Hz, 1 H, O-C*H*H-CH-S), 4.56−4.64 [m, 3 H (dd, $J \approx$ 5.0, 11.5 Hz, C≡C-CO_2-CH_2-, overlapping with m, 1 H, CH-*H*C-I)] ppm. ^{13}C NMR (75 MHz): δ = 22.0 (H*C*-I), 46.7 [H_2C-C($CO_2Me)_2$], 50.9 (*C*H-S), 2 × 53.8 (2 CO_2CH_3), 64.5 [S-*C*($CO_2Me)_2$], 69.6 (HC≡C-CO_2-*C*H_2-), 74.2 (HC≡*C*-C), 75.6 (HC≡C), 151.8 (HC≡C-*C*=O), 168.6, 170.0 (*C*O_2Me) ppm. Mass (EI): *m*/*z* = 412 [M^+]. HRMS: calculated for $C_{12}H_{13}IO_6S$: 411.9478, found 411.9478.

Dimethyl (4,5-*cis*)-5-[(Formyloxy)methyl]-4-iodotetrahydrothiophene-2,2-dicarboxylate (3e): Obtained as a colourless oil (380 mg, 98 %) after column chromatography (ethyl acetate/heptane = 1:3). ^{1}H NMR (300 MHz): δ = 2.86 [dd, J = 13.7, 11.6 Hz, 1 H, H_{trans}HCC($CO_2Me)_2$], 3.18 [dd, J = 13.7, 5.7 Hz, 1 H, H_{cis}HCC(-$CO_2Me)_2$], 3.66 (m, 1 H, *H*C-S), 3.79 (br. s, 6 H, 2 × CO_2CH_3), 4.31 (dd, J = 11.5, 7.3 Hz, 1 H, O-C*H*H-CH-S), 4.57−4.66 (m, 2 H, *H*C-I, overlapping with dd, 1 H, O-C*H*H-CH-S), 8.09 [s, 1 H, H-C(O)O-] ppm. ^{13}C NMR (75 MHz): δ = 22.2 (H*C*-I), 46.5 [H_2C-C($CO_2Me)_2$], 50.9 (*C*H-S), 53.6, 53.7 (2 CO_2CH_3), 64.3 [S-*C*($CO_2Me)_2$], 67.3 (HC≡C-CO_2-*C*H_2), 160.0 (H-*C*=O), 168.5, 169.6 (-*C*O_2Me) ppm. Mass (EI): *m*/*z* = 388 [M^+]. HRMS: calculated for $C_{10}H_{13}IO_6S$: 387.9478, found 387.94770.

Dimethyl(4,5-*cis*)-4-Iodo-5-[(2-methoxyacetyloxy)methyl]tetrahydrothiophene-2,2-dicarboxylate (3f): Obtained as a colourless oil (397 mg, 92 %) after column chromatography (ethyl acetate/heptane = 1:3) which slowly crystallized at −20 °C. mp.: 88−89 °C. ^{1}H NMR (300 MHz): δ = 2.85 [dd, J = 13.6, 11.9 Hz, 1 H, H_{trans}HCC($CO_2Me)_2$], 3.16 [dd, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.45 (d, J = 2.1 Hz, 3 H, H_3C-O-), 3.65 (m, 1 H, *H*C-S), 3.78, 3.79 (2 × s, 6 H, 2 × CO_2CH_3), 4.05 (AB, 2 H, MeO-CH_2-), 4.36 (dd, J = 11.5, 6.6 Hz, 1 H, O=C-O-C*H*H-), 4.56−4.64 (m, 2 H, O=C-O-C*H*H- and I-C-*H*) ppm. ^{13}C NMR (75 MHz): δ = 22.4 (*C*-I), 46.6 [H_2C-C($CO_2Me)_2$], 50.9 (*C*H-S), 2 × 53.8 (2 -CO_2CH_3), 59.2 (H_3C-O), 64.3 [S-*C*($CO_2Me)_2$], 68.1, 69.4, 168.4, 169.5, 169.7 (*C*=O) ppm. Mass (CI): *m*/*z* = 432 [M^+]. Elemental analysis: calculated for $C_{12}H_{17}IO_7S$ (432.23): C 33.35, H 3.96 %; found C 33.14, H 3.86 %.

Dimethyl (4,5-*cis*)-4-Iodo-5-[(2-methoxybenzoyloxy)methyl]tetrahydrothiophene-2,2-dicarboxylate (3g): Obtained as a colourless oil (276 mg, 56 %) after column chromatography (ethyl acetate/heptane = 1:3). ^{1}H NMR (300 MHz): δ = 2.98 [dd, J = 13.7, 11.1 Hz, 1 H, H_{trans}HCC($CO_2Me)_2$], 3.12 [dd, J = 13.7, 5.7 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.65 (s, 3 H, 2-H_3C-O-Ph), 3.72 (m, 1 H, *H*C-S-), 3.78 (s, 3 H, -CO_2CH_3), 3.90 (s, 3 H, -CO_2CH_3), 4.43 (dd, J = 11.5, 6.8 Hz, 1 H, O=C-O-C*H*H-), 4.63−4.76 (m, 2 H, O=C-O-C*H*H- overlap with *H*C-I), 6.99 (m, 2 H, arom), 7.48 (m, 1 H, arom), 7.82 (m, 1 H, arom) ppm. ^{13}C NMR (75 MHz): δ = 23.3 (*C*-I), 46.7 [H_2C-C($CO_2Me)_2$], 51.5 (*C*H-S), 53.6, 53.7 (2 -CO_2CH_3), 55.8 (H_3CO-), 64.5 [S-*C*($CO_2Me)_2$], 68.5 (O=C-O-CH_2-), 111.9, 119.4, 120.0, 131.8, 133.8 (C-arom.), 159.2 (O-C_{ipso}), 165.4, 168.7, 170.0 (*C*=O) ppm. Mass (CI): *m*/*z* = 494 [M^+]. HRMS: calculated for $C_{18}H_{21}IO_7S$: 493.98962; found 493.98973.

Dimethyl (4,5-*cis*)-5-{[((2*R*)-2-Hydroxy-2-phenyl)ethanoyloxy]-methyl}-4-iodotetrahydrothiophene-2,2-dicarboxylate (3h, mixture of diastereomers): Obtained as colourless viscous oil, approx. 2:3 mixture of diastereomers (455 mg, 92 %). *Major isomer:* ^{1}H NMR (300 MHz): δ = 2.68 [dd, J = 12.8, 12.8 Hz, 1 H, H_{trans}HCC(-$CO_2Me)_2$], 2.97 [dd, J = 12.8, 6.0 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.62 (br. s, 1 H, O*H* overlapping with OH of minor diastereomer), 3.77 (2 × s, 6 H, -CO_2CH_3, overlapping with minor diastereomer), 4.35−4.51 (m, 3 H, O=C-O-CH_2- and *H*C-I overlapping with minor diastereomer), 5.18 [br. s, PhC*H*(OH)], 7.29−7.44 (m, 5 H, arom. overlapping) ppm. ^{13}C NMR (75 MHz): δ = 22.2 (*C*-I), 46.5 [H_2C-C($CO_2Me)_2$], 50.7 (*C*H-S), 53.6, 53.7 (2 × -CO_2CH_3), 64.5 [S-*C*($CO_2Me)_2$], 69.2 [O=C-O-CH_2-], 73.0 [Ph*C*H(OH)], 126.7, 128.5 (C-arom), 173.8 (C_{ipso}), 168.6, 169.8, (2 × 2 -*C*O_2Me), 172.9 (C=O, mandelic ester) ppm. *Minor isomer:* ^{1}H NMR (300 MHz): δ = 2.79 [dd, J = 13.5, 11.7 Hz, 1 H, H_{trans}HCC($CO_2Me)_2$], 3.12 [dd, J = 13.5, 5.7 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.54 (m, 2 H, 2 × *H*C-S-), 3.60 (br. s, 2 H, 2 × O*H*), 3.77 (br. s, 6 H, 2 × -CO_2CH_3), 4.32 (m, 3 H, O=C-O-CH_2- and *H*C-I), 5.23 [br. s, PhC*H*(OH), minor isomer], 7.29−7.44 (m, 5 H, arom) ppm. ^{13}C NMR (75 MHz): δ = 21.4 (*C*-I), 46.6 [H_2C-C($CO_2Me)_2$], 50.8 (*C*H-S), 53.7, 53.8 (2 × -CO_2CH_3), 64.3 [S-*C*($CO_2Me)_2$], 69.3 (O=C-O-CH_2-), 73.0 [Ph*C*H(OH)), 126.5, 128.4 (C-arom), 137.7 (C_{ipso}), 168.8, 169.7 (2 × -*C*O_2Me), 172.6 (C=O, mandelic ester) ppm. Mass (EI): *m*/*z* = 494 [M^+]. HRMS: calculated for $C_{17}H_{19}IO_7S$: 493.98962; found 493.98956.

Dimethyl (4,5-*cis*)-5-(Hydroxymethyl)-4-iodotetrahydrothiophene-2,2-dicarboxylate (3i): Obtained as a colourless viscous oil (125 mg, 35 %) after column chromatography (ethyl acetate/ heptane = 1:3). (Slowly turned yellow, even when stored at −20 °C.) ^{1}H NMR (300 MHz): δ = 2.45 (br. s, 1 H, O*H*), 2.76 [dd appearing as triplet, 1 H, J = 12.9, 12.9 Hz, H_{trans}HCC($CO_2Me)_2$], 3.21 [dd, J = 12.9, 6.0 Hz, 1 H, H_{cis}HCC($CO_2Me)_2$], 3.56 (m, 1 H, *H*C-S-), 3.79 (br. s, 6 H, 2 -CO_2CH_3), 3.88−4.05 (m, 2 H, O=C-O-CH_2-), 4.57 (m, 1 H, *H*C-I) ppm. ^{13}C NMR (75 MHz): δ = 23.2 (*C*-I), 47.0 [H_2C-C($CO_2Me)_2$], 53.6, 54.0 (2 -CO_2CH_3), 55.4 (*C*H-S), 64.8, [S-*C*($CO_2Me)_2$], 66.3 (O=C-O-CH_2-), 169.6, 169.7 (*C*=O) ppm. Mass (EI): *m*/*z* = 360 [M^+]. Exact mass: calculated for $C_9H_{13}IO_5S$ 359.9529; found: 359.95293.

Methyl (4,5-*cis*)-5-[(2,2-Diphenylacetyloxy)methyl]-4-iodo-2-phenyltetrahydrothiophene-2-carboxylate (12a/13a): Obtained as a colourless oil (295 mg, 52 %, ca. 9:1 mixture of isomers) after column chromatography (ethyl acetate/heptane = 1:3) which crystallized upon standing. Recrystallization from diisopropyl ether gave small transparent needles (mixture of isomers). mp.: 144−149 °C. *Major isomer:* ^{1}H NMR (300 MHz): δ = 2.21 (dd app. as triplet, 1 H, J = 13.2, 13.2 Hz, S-C-CH^{3a}H), 3.39 (dd, J = 13.2, 5.7 Hz, 1 H, S-C-CH^{3b}H), 3.68 (s, 3 H, OCH_3), 3.72 (m, 1 H, H^5C-S), 4.37 (dd, J = 11.6, 6.6 Hz, 1 H, OCH^{6a}H-CH-S), 4.50 (dd, J = 11.6, 4.2 Hz, 1 H, OCH^{6b}H-CH-S), 4.64 (m, 1 H, *H*-C-I), 4.80 (s, 1 H, Ph_2CH-), 7.18−7.40 (m, 15 H, arom.) ppm. ^{13}C NMR (75 MHz): δ = 22.1 (H-*C*-I), 50.4 (S-C-*C*H_2-), 50.7 (H-*C*-S), 53.2 (2 × O-*C*H_3), 56.9 (Ph_2CH), 65.4 (S-*C*-CO_2Me), 69.4 (O*C*H_2-CH-S), 126.3, 126.5, 127.8, 128.2, 128.5, 128.7, 128.8, 129.0 (*C*-arom), 138.0, 140.0 (C_{ipso}), 171.9, 173.5 (*C*=O). *Minor isomer:* ^{1}H NMR (300 MHz): δ = 2.65 (dd, 1 H, $J \approx$ 5−6, ≈ 13 Hz, S-C-CH^{3b}H), 3.44 (dd app. as triplet, 1 H, $J \approx$ 13 Hz, S-C-CH^{3a}H), 3.62 (s, 3 H, OCH_3), 4.20

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(m, 1 H, *H*-C-I), 5.10 (s, 1 H, Ph_2CH-) ppm, signals for other protons are overlapped by main isomer. ^{13}C NMR (75 MHz): δ = 21.9 (H-*C*-I), 50.1 (S-C-CH_2-), 51.0 (H-*C*-S), 53.3 (2 × O-CH_3), 56.9 (Ph_2CH), 65.3 (S-*C*-CO_2Me), 69.4 (OCH_2-CH-S), 126.5, 127.8, peaks overlapped by main isomer (C-arom), 138.1, 140.8 (C_{ipso}), 172.0, 173.5 (C=O) ppm. Mass (EI): *m*/*z* = 572 [M^+]. Elemental analysis: calculated for $C_{27}H_{25}IO_4S$ (572.45): C 56.65, H 4.40 %; found C 56.57, H 4.26 %.

Methyl (4,5-*cis*)-5-[(Acetyloxy)methyl]-4-iodo-2-phenyltetrahydrothiophene-2-carboxylate (12b/13b): Obtained as a colourless oil (310 mg, 74 %, ca. 3:1 mixture of isomers) after column chromatography (ethyl acetate/heptane = 1:3). *Major isomer:* ^1H NMR (300 MHz): δ = 1.87 [s, 3 H, H_3C-C(=O)O-], 2.46 (dd, *J* = 13.0, 13.0 Hz, 1 H, S-C-CH^{3a}H), 3.54 (dd, *J* = 13.0, 5.6 Hz, 1 H, S-C-CH^{3a}H), 3.71 (s, 3 H, O=C-OCH_3), 3.74 (m, 1 H, H^5C-S), 4.25 (dd, *J* = 11.6, 6.2 Hz, 1 H, OCH^{6a}H-CH-S), 4.56 (dd, *J* = 11.6, 4.2 Hz, 1 H, OCH^{6b}H-CH-S), 4.72 (m, 1 H, H-*C*-I), 7.28−7.48 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz): δ = 20.7 [H_3C-C(=O)O-], 22.7 (H-*C*-I), 50.6 (S-*C*-CH_2-), 51.2 (H-*C*-S), 53.2 (O=C-OCH_3), 65.4 (S-*C*-CO_2Me), 68.4 (OCH_2-CH-S), 126.4, 127.8, 128.5 (*C*-arom), 140.1 (C_{ipso}), 170.3, 173.5 (*C*=O) ppm. *Minor isomer:* ^1H NMR (300 MHz): δ = 2.10 [s, 3 H, H_3C-C(=O)O-], 2.74 (dd, *J* = 12.9, 5.2 Hz, 1 H, S-C-CH^{3b}H), 3.51 (dd app. as triplet, 1 H, *J* = 12.9 Hz, S-C-CH^{3a}H) ppm, other signals overlapped by main product. ^{13}C NMR (75 MHz): δ = 20.9 [H_3C-C(=O)O-], 21.9 (H-*C*-I), 50.1 (S-C-CH_2-), 51.1 (H-*C*-S), 53.3 (O=C-OCH_3), 65.2 (S-*C*-CO_2Me), 68.9 (OCH_2-CH-S), 126.6, 127.9, 128.6 (*C*-arom), 140.8 (C_{ipso}), 170.5, 172.2 (*C*=O). Mass (EI): *m*/*z* = 420 [M^+], 293 (M^+ − I). HRMS: Calculated for $C_{15}H_{17}IO_4S$: 419.98923; found 419.98918.

Ethyl (4,5-*cis*)-2-Cyano-5-[(formyloxy)methyl)]-4-iodotetrahydrothiophene-2-carboxylate (12d/13d): Obtained as a colourless oil (335 mg, 91 %, ca. 1:1 mixture of isomers) after column chromatography (ethyl acetate/heptane = 1:3) which only partly crystallized upon standing. *Fast isomer:* ^1H NMR (300 MHz): δ = 1.36 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.98 (dd, *J* = 14.0, 5.6 Hz, 1 H, S-C-CH^{3b}H), 3.19 (dd appearing as triplet, 1 H, *J* = 14.0, 14.0 Hz, S-C-CH^{3a}H), 3.91 (m, 1 H, H^5C-S), 4.30 (dd of doublets, 1 H, *J* = 11.6, 7.6, 0.8 Hz, OCH^{6a}H-CH-S) partial overlap with 4.32 (m, 2 H, OCH_2CH$_3$), 4.65 (m, 1 H, *H*-C-I), 4.71 (dd of doublets, 1 H, *J* = 11.6, 4.0, 0.8 Hz, OCH^{6b}H-CH-S), 8.07 (s, 1 H, *H*-CO_2-) ppm. ^{13}C NMR (75 MHz): δ = 13.7 (OCH_2CH_3), 18.6 (H-*C*-I), 47.9 (S-C-CH_2-), 50.4 (S-*C*-C≡N), 51.5 (H-*C*-S), 64.3 (OCH_2CH$_3$), 66.9 (O-CH_2CH-S), 118.2 (C≡N), 159.9 (H-*C*=O), 164.9 (O=*C*-OEt) ppm. *Slow isomer:* ^1H NMR (300 MHz): δ = 1.36 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.92 (dd, *J* = 13.5, 11.7 Hz, 1 H, S-C-CH^{3a}H), 3.27 (dd, *J* = 13.5, 6.0 Hz, 1 H, S-C-CH^{3b}H), 3.77 (m, 1 H, H^5C-S), 4.32 (m, 2 H, OCH_2CH$_3$), 4.47 (dd, *J* = 12.0, 5.3 Hz, 1 H, OC*H*H-CH-S), 4.68−4.75 (m, 2 H, OC*H*H-CH-S and *H*-C-I), 8.16 (s, 1 H, *H*-CO_2-) ppm. ^{13}C NMR (75 MHz): δ = 13.7 (OCH_2CH_3), 21.6 (H-*C*-I), 48.2 (S-C-CH_2-), 49.5 (S-*C*-C≡N), 52.4 (H-*C*-S), 64.1 (OCH_2CH$_3$), 66.9 (O-CH_2CH-S), 117.3 (*C*≡N), 159.9 (H-*C*=O), 166.4 (O=*C*-OEt) ppm. Mass (EI): *m*/*z* = 369 [M^+]. HRMS: calculated for $C_{10}H_{12}INO_4S$: 368.95318; found 368.95310.

Ethyl (4,5-*cis*)-2-Cyano-4-iodo-5-[(propioloyloxy)methyl]tetrahydrothiophene-2-carboxylate (12e/13e): Isomers were separated by careful column chromatography (ethyl acetate/heptane = 1:3). *Fast isomer:* Colourless oil (197 mg, 50 %) which crystallized upon standing. Recrystallization from diisopropyl ether gave small transparent needles for X-ray diffraction analysis. Crystal data for **12e** are shown in Table 5. mp.: 38−40 °C. ^1H NMR (400 MHz): δ = 1.36 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 3.00 (dd, *J* = 13.6, 5.6 Hz, 1 H, S-C-CH^{3b}H) overlapping with 3.00 (s, 1 H, *H*-C≡C-), 3.14 (dd appearing as t, 1 H, *J* = 13.6, 13.6 Hz, S-C-CH^{3a}H), 3.91 (m, 1 H, H^5C-S), 4.26−4.41 (m, 3 H, O-CH^{6a}H-CH-S overlapping with OCH_2CH$_3$), 4.62 (m, 1 H, H^4-C-I), 4.71 (dd, *J* = 11.4, 4.4 Hz, 1 H, O-CH^{6b}H-CH-S) ppm. ^{13}C NMR (75 MHz): δ = 13.8 (OCH_2CH_3), 18.0 (H-*C*-I), 47.9 (S-C-CH_2-), 50.5 (S-*C*-C≡N), 51.2 (H-*C*-S), 64.4 (OCH_2CH$_3$), 69.2 (O-CH_2CH-S), 74.0 (-*C*≡CH), 76.4 (-C≡*C*H), 118.2 (*C*≡N), 151.7 (HC≡C*C*O_2-), 164.8 (-CO_2Et) ppm. Mass (EI): *m*/*z* = 393 [M^+]. Elemental analysis: calculated for $C_{12}H_{12}INO_4S$ (393.20): C 36.66, H 3.08; N, 3.56 %, found C 36.49, H 3.11, N 3.49 %. *Slow isomer:* Obtained as a colourless oil (170 mg, 43 %). ^1H NMR (300 MHz): δ = 1.36 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 2.90 (dd, *J* = 13.3, 11.7 Hz, 1 H, S-C-CH^{3a}H), 3.02 (s, 1 H, *H*-C≡C-), 3.27 (dd, *J* = 13.3, 6.0 Hz, 1 H, S-C-CH^{3b}H), 3.75 (m, 1 H, H^5C-S), 4.24−4.37 (m, 2 H, OCH_2CH$_3$), 4.51 (dd, *J* = 9.0, 5.8 Hz, 1 H, O-CH^{6a}H-CH-S), 4.64 (dd, *J* = 9.0, 4.1 Hz, 1 H, O-CH^{6b}H-CH-S), 4.72 (m, 1 H, H^4-C-I) ppm. ^{13}C NMR (75 MHz): δ = 13.8 (OCH_2CH_3), 21.1 (H-*C*-I), 48.2 (S-C-CH_2-), 49.4 (S-*C*-C≡N), 52.0 (H-*C*-S), 64.2 (OCH_2CH$_3$), 69.2 (O-CH_2CH-S), 73.8 (−*C*≡CH), 76.4 (-C≡*C*H), 117.0 (*C*≡N), 151.7 (C≡C*C*O_2-), 166.5 (-*C*O_2Et) ppm. Mass (EI): *m*/*z* = 393[M^+].

Table 5. Crystal data and structure refinement for **12e**

Crystal colour	transparent, colourless
Crystal shape	rather regular rod
Crystal size	0.44 × 0.19 × 0.13 mm
Empirical formula	$C_{12}H_{12}INO_4S$
Molecular mass	393.19
Temperature	293(2) K
Radiation/Wavelength	Mo-K_α (graphite-monochromated)/0.71073 Å
Crystal system, space group	monoclinic, *P*21/*c*
Unit cell dimensions (25 reflections 10.359 < θ < 12.704)	*a*, α = 12.9002(19) Å, 90° *b*, β = 6.9645(7) Å, 95.485(8)° *c*, γ = 16.202(2) Å, 90°
Volume	1449.0(3) $Å^3$
Z, Calculated density	4, 1.802 Mg/m^3
Absorption coefficient	2.362 mm^{-1}
Diffractometer/scan	Enraf−Nonius CAD4/Ω-2θ
F(000)	768
θ-range for data collection	2.53 to 27.48°
Index ranges	$-16 \le h \le 16$, $0 \le k \le 9$, $-21 \le l \le 0$
Reflections collected/unique	3426/3307 [R_{int} = 0.0427]
Reflections observed	2867 ([$I_o > 2\sigma(I_o)$])
Absorption correction	Semi-empirical from Ψ-scans
Range of relat. transm. factors	1.288 and 0.813
Refinement method	Full-matrix least-squares on F^2
Computing	SHELXL-97 (Sheldrick, 1997)
Data/restraints/parameters	3307/0/205
Goodness-of-fit on F^2	1.150
SHELXL-97 weight parameters	0.102000, 0.761400
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0463, wR_2 = 0.1426
R indices (all data)	R_1 = 0.0531, wR_2 = 0.1484
Largest diff. peak and hole	1.409 and −1.754 e·$Å^{-3}$

Diethyl (4,5-*cis*)-2-Cyano-5-[(formyloxy)methyl]-4-iodotetrahydrothiophene-2-phosphonate (12g/13g): Isomers were separated by column chromatography (ethyl acetate/ heptane = 1:3). *Fast isomer:* Obtained as colourless oil (180 mg, 42 %). ^1H NMR (300 MHz): δ = 1.40 [t of doublets, 6 H, *J* = 6.9, 1.8 Hz, P(OCH_2CH_3)$_2$], 2.93 (dd of quadruplet, 1 H, *J* = Hz, S-C-C*H*H), 2.95−2.99 (m, 1 H, S-C-C*H*H), 3.91 (m, 1 H, H^5C-S), 4.20 (dd, *J* = 11.3, 8.0 Hz, 1 H,

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O-CH^{6a}H-CH-S), 4.25−4.37 [m, 4 H, P(OCH_2CH$_3$)$_2$], 4.58 (m, 1 H, H^4-C-I), 4.74 (dd of doublets, 1 H, J = 11.3, 4.0, 0.8 Hz, O-CH^{6b}H-CH-S), 8.10 (s, 1 H, H-CO$_2$-) ppm. ^{13}C NMR (75 MHz): δ = 16.2, 16.3 [P(OCH$_2$CH_3)$_2$], 17.9 (d, I-C-H, J = 11.8 Hz), 44.8 (d, S-C-P, J = 159 Hz), 46.5 (S-C-CH$_2$-), 50.6 (d, J = 2.2 Hz, H-C-S), 65.4 [d, P(OCH$_2$CH$_3$)$_2$, J = 7.0 Hz], 65.6 [d, P(OCH$_2$CH$_3$)$_2$, J = 7.0 Hz], 67.1 (O-CH$_2$CH-S), 118.2 (C≡N), 160.1 (H-CO$_2$-) ppm. Mass (EI): m/z = 433 [M$^+$], HRMS: calculated for $C_{11}H_{17}INO_5PS$: 432.96098; found 432.96104. *Slow isomer:* Obtained as a colourless oil (200 mg, 46 %) which crystallized upon standing. Recrystallization from diisopropyl ether gave small transparent needles. mp.: 46−47 °C. ^{1}H NMR (300 MHz): δ = 1.40 [t, J = 6.9 Hz, 6 H, P(OCH$_2$CH_3)$_2$], 2.91−3.20 (m, 2 H, S-C-CH_2-CHI), 3.70 (m, 1 H, H^5C-S), 4.32 [m, 4 H, P(OCH_2CH$_3$)$_2$], 4.47 (dd, J = 11.9, 5.2 Hz, 1 H, O-CHH-CH-S), 4.66−4.79 (m, 2 H, O-CHH-CH-S and I-C-H), 8.16 (H-CO$_2$-) ppm. ^{13}C NMR (75 MHz): δ = 16.3 [2 × doublet appearing as triplet, J = 6.0 Hz, P(OCH$_2$CH_3)$_2$], 22.1 (d, J = 2.5 Hz, I-C-H), 43.9 (d, J = 159 Hz, S-C-P), 47.0 (d, J = 2.5 Hz, S-C-CH$_2$-CHI), 52.1 (H-C-S), 65.2 [d, J = 7.3 Hz, P(OCH$_2$CH$_3$)$_2$], 66.1 [d, J = 7.3 Hz, P(OCH$_2$CH$_3$)$_2$], 67.0 (O-CH$_2$CH-S), 117.6 (C≡N), 159.8 (H-CO$_2$-) ppm. Mass (EI): m/z = 433 [M$^+$]. Elemental analysis: calculated for $C_{11}H_{17}INO_5PS$ (433.20): C 30.50, H 3.96, N 3.23 %; found C 30.31, H 3.86, N 3.30 %.

Diethyl (4,5-*cis*)-2-Cyano-5-[(propionyloxy)methyl]-4-iodotetrahydrothiophene-2-phosphonate (12h/13h): *Fast isomer:* Obtained as a colourless oil (220 mg, 48 %) after column chromatography (ethyl acetate/heptane = 1:2). ^{1}H NMR (300 MHz): δ = 1.40 [triplet of doublets, 6 H, J = 2.7, 8.4 Hz, P(OCH$_2$CH_3)$_2$], 2.82 (m, 1 H,S-C-CHH-CHI), 2.97 (dd of doublets, 1 H, J = 12.8, 5.3, 1.1 Hz, S-C-CHH-CHI), 3.07 (s, 1 H, H-C≡C-), 3.97 (m, 1 H, H^5C-S), 4.20−4.38 [m, 5 H, P(OCH_2CH$_3$)$_2$ overlapping with O-CHH-CH-S], 4.56 (m, 1 H, I-C-H^4), 4.66 (dd, J = 11.4, 4.3 Hz, 1 H, O-CHH-CH-S) ppm. ^{13}C NMR (75 MHz): δ = 16.2 [d, J = 2.5 Hz, P(OCH$_2$$CH_3$)], 16.3 [d, J = 2.1 Hz, P(OCH$_2$$CH_3$)], 17.1 (d, J = 11.6 Hz, I-C-H), 44.9 (d, J = 159 Hz, S-C-P), 46.5 (d, J = 2.0 Hz, S-C-CH$_2$-CHI), 50.1 (H-C-S), 65.5 [d, J = 6.5 Hz, P(OCH$_2$CH$_3$)$_2$], 69.5 (O-CH$_2$CH-S), 73.9 (−C≡CH), 76.1 (C≡CH), 118.1 (C≡N), 151.7 (C=O) ppm. Mass (EI): m/z = 457 [M$^+$]. Exact mass: calculated for $C_{13}H_{17}INO_5PS$: 457.9610, found 456.9610. *Slow isomer:* Obtained as a colourless oil (205 mg, 45 %) which crystallized upon standing. Crystallization from diisopropyl ether gave small transparent needles suitable for X-ray diffraction analysis. Crystal data for **12h** are shown in Table 6. mp.: 137−140 °C. ^{1}H NMR (300 MHz): δ = 1.42 [triplet of doublets, 6 H, J = 8.4 Hz, P(OCH$_2$CH_3)$_2$], 2.90−3.20 (m, 2 H, S-C-CH_2-CHI), 3.02 (s, 1 H, H-C≡C-), 3.69 (m, 1 H, H^5C-S), 4.25−4.41 [m, 4 H, P(OCH_2CH$_3$)$_2$], 4.51 (dd, J = 12.0, 5.7 Hz, 1 H, O-CH^{6a}H-CH-S), 4.63 (dd, J = 12.0, 4.2 Hz, 1 H, O-CH^{6b}H-CH-S), 4.77 (m, 1 H, I-C-H^4) ppm. ^{13}C NMR (75 MHz): δ = 16.3 [d, J ≈ 7 Hz, P(OCH$_2$$CH_3$)], 16.4 [d, J ≈ 7 Hz, P(OCH$_2$$CH_3$)], 21.6 (d, J = 2.6 Hz, I-C-H), 43.9 (d, J = 159 Hz, S-C-P), 47.1 (d, J = 2.5 Hz, S-C-CH$_2$-CHI), 51.8 (H-C-S), 65.2 [d, J = 7.4 Hz, P(OCH$_2$CH$_3$)], 66.3 [d, J = 7.9 Hz, P(OCH$_2$CH$_3$)], 69.3 (O-CH$_2$CH-S), 73.9 (C≡CH), 76.3 (C≡CH), 117.4 (C≡N), 151.7 (C=O) ppm. Mass (EI): m/z = 457 [M$^+$]. Elemental analysis: calculated for $C_{13}H_{17}INO_5PS$ (457.22): C 34.15, H 3.75, N 3.06; found C 34.36, H 3.69, N 3.04 %.

Dimethyl (3,4-*trans*-4,5-*cis*)-3-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]-oxy}-5-[(2,2-diphenylacetyloxy)methyl]-4-iodotetrahydrothiophene-2,2-dicarboxylate (18a): Compound (350 mg; ca. 52 %) could not be separated from an unknown impurity. ^{1}H NMR (300 MHz): δ = 0.05 (s, 3 H, H_3CSiMetBu), 0.22 (s, 3 H, H_3CSiMetBu), 0.90 [s, 9 H, (H_3C)$_3$CSiMe$_2$], 3.53 (m, 1 H, H-C-S), 3.68 (s, 3 H, CO$_2$CH_3), 3.74 (s, 3 H, CO$_2$CH_3), 4.47 (d, J = 4.5 Hz, 2 H, -O-CH_2-CH-S), 4.80 (dd, J = 7.2, 9.7 Hz, 1 H), 5.15 (s, 1 H, Ph$_2$CHC=O), 5.26 (d, J = 9.7 Hz, 1 H, H-C-OSiMe$_2$$t$Bu), 7.18−7.35 (m, aromatic) ppm. ^{13}C NMR (75 MHz): δ = −4.7 ($H_3$$C$SiMe$t$Bu), −4.2 ($H_3$$C$SiMe$t$Bu), 18.1 [($H_3$C)$_3$$C$SiMe$_2$], 26.3 [($H_3$$C$)$_3$CSiMe$_2$], 33.7 ($C$-I), 44.6 (H-$C$-S), 53.2 (2 × O=C-O$CH_3$), 63.9 [S-$C$-(CO$_2$Me)$_2$], 69.0 (O-$CH_2$CH-S), 82.4 (H$C$-OSiMe$_2$$t$Bu), aromatic C's overlap with impurity, 138.4, 139.8 (2 × C_{ipso}), 168.6 (Ph$_2$CHCO$_2$-), 171.3, 171.9 (2 × O=C-OMe) ppm. Mass: (CI): m/z = 685 [M$^+$].

Dimethyl (3,4-*trans*-4,5-*cis*)-3-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]-oxy}-5-[(propioloyloxy)methyl]-4-iodotetrahydrothiophene-2,2-dicarboxylate (18b): Obtained as a white solid (515 mg, 95 %), but attempts to obtain suitable crystals for X-ray diffraction analysis failed. mp.: 108−110 °C dec. ^{1}H NMR (400 MHz): δ = 0.08 (s, 3 H, H_3CSiMetBu), 0.32 (s, 3 H, H_3CSiMetBu), 0.90 [s, 9 H, (H_3C)$_3$CSiMe$_2$], 3.00 (s, 1 H, HC≡C-), 3.60 (m, 1 H, H-C-S), 3.77 (s, 3 H, CO$_2$CH_3), 3.80 (s, 3 H, CO$_2$CH_3), 4.42 (dd, J = 11.6, 6.0 Hz, 1 H, O=C-O-CH^{6a}H-), 4.57 (dd, 1 H, J = 11.6.3.6 Hz, O=C-O-CH^{6b}H-), 4.84 (dd, J = 7.2, 9.9 Hz, 1 H, H-C-I), 5.20 (d, J = 9.9 Hz, 1 H, H-C-OTBS) ppm. ^{13}C NMR (75 MHz): δ = −4.9 ($H_3$$C$SiMe$t$Bu), −4.2 ($H_3$$C$SiMe$t$Bu), 18.2 [($H_3$C)$_3$$C$SiMe$_2$], 26.1 [($H_3$$C$)$_3$CSiMe$_2$], 32.7 ($C$-I), 43.9 (H-$C$-S), 53.2, 53.3 (2 × O=C-OCH$_3$), 63.6 [S-C-(CO$_2$Me)$_2$], 70.2 (O-CH$_2$CH-S), 74.1 (C≡CH), 75.7 (C≡CH), 82.4 (HC-OSiMe$_2$$t$Bu), 151.8 (HC≡C-$C$=O), 168.1, 168.6 (O=$C$-OMe) ppm. Mass (CI): m/z = 543 [M$^+$ + H]. Elemental analysis: calculated for $C_{18}H_{27}IO_7SSi$ (542.46): C 39.85, H 5.02 %; found: C 39.53, H 5.12 %.

Table 6. Crystal data and structure refinement for **12h**

Crystal colour	transparent, colourless
Crystal shape	regular rod
Crystal size	0.60 × 0.16 × 0.14 mm
Empirical formula	$C_{13}H_{17}INO_5PS$
Molecular mass	457.21
Temperature	293(2) K
Radiation/Wavelength	Mo-K_α (graphite-monochromated)/0.71073Å
Crystal system, space group	monoclinic, $P21/c$
Unit cell dimensions	a, α = 8.2923(6) Å, 90°
(25 reflections	b, β = 17.8310(13) Å, 91.743(8)°
10.243 < θ < 12.761)	c, γ = 12.2414(11) Å, 90°
Volume	1809.2(2) Å^3
Z, Calculated density	4, 1.679 Mg/m^3
Absorption coefficient	1.993 mm^{-1}
Diffractometer/scan	Enraf−Nonius CAD4/Ω-2θ
F(000)	904
θ-range for data collection	2.71 to 27.41°
Index ranges	$-10 \le h \le 10$, $-23 \le k \le 0$, $-15 \le l \le 0$
Reflections collected/unique	4294/4106 [R_{int} = 0.0242]
Reflections observed	3097 ([$I_o > 2\sigma(I_o)$])
Absorption correction	Semi-empirical from Ψ-scans
Range of relat. transm. factors	1.066 and 0.972
Refinement method	Full-matrix least-squares on F^2
Computing	SHELXL-97 (Sheldrick, 1997)
Data/restraints/parameters	4106/0/229
Goodness-of-fit on F^2	1.055
SHELXL-97 weight parameters	0.058600 1.847500
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0432, wR_2 = 0.1085
R indices (all data)	R_1 = 0.0624, wR_2 = 0.1201
Largest diff. peak and hole	0.981 and −0.694 e·Å^{-3}

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