Thioamide and Thioester Cyclopentane Synthesis via Trimethyltin Radical Catalyzed Alkenylation of Substituted (Thiocarbonyl)cyclopropanes

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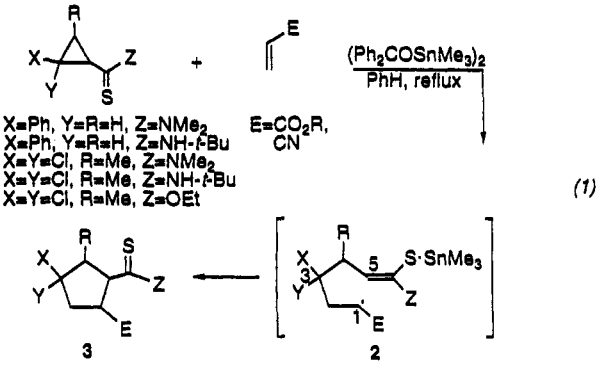
Thioamide cyclopropanes bearing phenyl substituents and thioamide- or thioester cyclopropanes bearing *gem*-dichloro and methyl substituents were subjected to trimethyltin radical catalyzed alkenylation to furnish the corresponding substituted (thiocarbonyl)cyclopentanes. The stereochemical outcome of these transformations can be rationalized by considering the effects of substituents upon cyclization of the intermediate functionalized 5-hexenyl radicals.

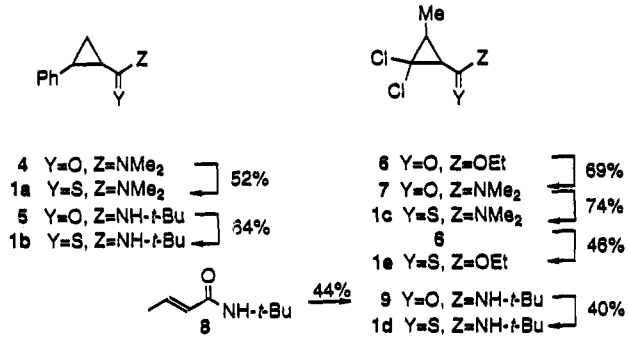
Ongoing studies in our laboratory directed toward substituted vinylcyclopentane synthesis via [3 atom + 2 atom] phenylthio radical catalyzed addition of vinylcyclopropanes to activated alkenes have provided insight into many of the regio- and stereochemical features inherent in this transformation.[1] In favorable cases, an analysis of steric interactions in various diastereomeric *chairlike* 5-hexenyl radical cyclization transition states can be used to assess relative transition-state energy and, hence, predict the product cyclopentane's relative stereochemistry. Indeed, we have already reported highly diastereoselective vinyl- and thiocarbonyl-initiated *intramolecular* [3 atom + 2 atom] radical cyclizations in the context of natural product synthesis.[1d,f] In this report, we extend our intermolecular cyclization studies to include substituted cyclopropanes featuring thiocarbonyl[2] (rather than vinyl) initiators that form thiocarbonyl-functionalized cyclopentanes upon trimethyltin radical catalyzed alkenylation (eq 1).[3] We sought to probe whether the steric



(1)

and electronic differences between the substituted (thiocarbonyl)cyclopropanes examined in this study and the *vinyl*cyclopropanes reported earlier would afford differing stereochemical profiles upon cyclopentane formation. In particular, the prospects for obtaining enhanced diastereoselectivity upon cyclization of substituted 5-hexenyl radical **2**, relative to the analogous vinyl-derived case, seemed promising based upon the additional "handle" on transannular steric interactions provided by the group Z.[4]

Scheme 1



The syntheses of all new cyclopropanes are presented in Scheme 1. Dimethylamide **7** was prepared via amidation of ethyl ester **6**,[5] and *tert*-butylamide **9** was obtained through dichlorocarbene addition to **8**.[6] Thioamide substrates **1a–d** were prepared by thionation of the corresponding amides **4**,[7] **5**,[8] **7**, and **9** with Lawesson's reagent,[9] while thionation of ethyl ester **6** with 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulfide[10] afforded thioester **1e**. Electron-deficient alkene (2.6–5 equiv) additions to the (thiocarbonyl)cyclopropanes **1a–e** were carried out under light-free conditions in an Ar atmosphere and were mediated by 0.3–0.8 equiv of bis(trimethylstannyl) benzopinacolate[11] in refluxing benzene. Product cyclopentane stereochemistry is not coupled to the configuration of the

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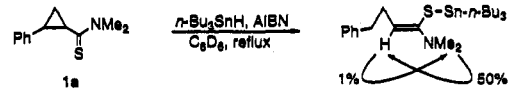
(1) (a) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (b) Feldman, K. S.; Fisher, T. E. *Tetrahedron* **1989**, *45*, 2964. (c) Feldman, K. S.; Ruckle, R. E., Jr.; Romanelli, A. L. *Tetrahedron Lett.* **1989**, *30*, 5845. (d) Feldman, K. S.; Burns, C. J. *J. Org. Chem.* **1991**, *56*, 4601. (e) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Jean, G. *J. Org. Chem.* **1992**, *57*, 100. (f) Feldman, K. S.; Berven, H. M.; Romanelli, A. L.; Parvez, M. *J. Org. Chem.* **1993**, *58*, 6851. (g) Feldman, K. S.; Berven, H. M.; Weinreb, P. H. *J. Am. Chem. Soc.*, in press.

(2) Crich, D.; Quintero, L. *Chem. Rev.* **1989**, *89*, 1413 and references cited therein.

(3) For consistency and ease of comparison, all radical species and cyclopentane products in the text are numbered as per the 5-hexenyl radical system. In the Experimental Section, the correct IUPAC numbering scheme is used.

(4) Double-bond geometry in **2** was established by DNOE measurements on the tri-*n*-butyltin hydride mediated ring opening product of **1a**:



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(7) Smejkal, J.; Farkas, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 404.

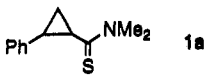
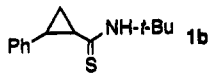
(8) Teotino, U. M.; Bella, D. D.; Gandini, A.; Benelli. G. *J. Med. Chem.* **1967**, *10*, 1091.

(9) Scheibye, S.; Pedersen, B. S.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

(10) Yokoyama, M.; Hasegawa, Y.; Hatanaka, H.; Kawazoe, Y.; Imamoto, T. *Synthesis* **1984**, 827.

0022-3263/94/1959-1129$04.50/0

Table 1. Alkene Addition to Phenylcyclopropanethioamides

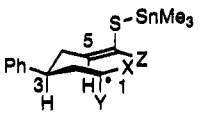
entry	phenylcyclopropanethioamide	alkene	% yield, (overall syn:anti)	cyclopentanethioamide products (E = CO_2Me or CO_2-*t*-Bu) syn, cis (a)	syn, trans (b)	anti, cis (c)	anti, trans (d)
a	 **1a**		78 (2.1:1.0)	1.3	1.0	1.1	**10a/10b/10c**
b	**1a**		58 (3.2:1.0)	1.9	1.3	1.0	**11a/11b/11c**
c	 **1b**		28 (>10:1)	1.0	1.6		**12a/12b**

starting cyclopropane substrates, as this information is lost upon trimethyltin radical ring opening of the cyclopropane. The purity of starting thioamides **1a–d**, thioester **1e**, and product cyclopentanes **10a–18a** was established primarily by inspection of ^1H NMR spectra (≥95%). The structures and stereochemistry of all (thiocarbonyl)-cyclopentane products were determined by analysis of ^1H decoupling and DNOE data (supplementary material). Resubmission experiments with cyclopentane(thiocarbonyl) products **11c** (Table 1, entry b) and **15b** (Table 2, entry c) showed that product stereochemistry was not subject to equilibration under the stated reaction conditions.

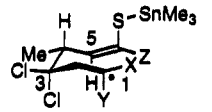
Tin radical-mediated addition of alkenes to phenylcyclopropanethioamides **1a** and **1b** afforded product cyclopentanes possessing both C(3)/C(5) syn/anti (Table 1, cyclopentanes **a** and **b** vs **c** and **d**) and C(1)/C(5) cis/trans (**a** vs **b**) stereochemical relationships. As shown in Table 1, no cyclization resulted in formation of the anti/trans cyclopentane diastereomer **d**. The overall C(3)/C(5) syn/anti selectivity for this series was increased by imposing greater steric demand on either the thioamide (Table 1, entry a vs c) or the alkene (entry a vs b) addends. However, this increase in C(3)/C(5) stereoselectivity (complete syn selectivity, entry c) is accompanied by a decrease in product yield. Within the syn product diastereomers, formation of the cis C(1)/C(5) cyclopentanes **10a** and **11a** (entries a and b, respectively) is favored upon increasing the ester's steric bulk. Increasing the steric demand of the thioamide appendage (entry c vs a) reverses this selectivity and results in a slight preference for the C(1)/C(5) trans product, **12b**. However, with the exception of the low-yielding completely syn-selective example shown in entry c, none of the putative steric interactions which contribute to product stereochemistry appear to be dominant.

The analogous cyclizations of *gem*-dichloromethylcyclopropanethioamides **1c** and **1d** and thioester **1e** with alkenes yield cyclopentane products bearing three stereocenters. In this series, complete selectivity for the C(4)/C(5) trans product diastereomers (Table 2, cyclopentanes **a** and **b**) is seen. Increasing the steric bulk of the alkene appendage correlates with an increase in product C(1)/C(5) cis selectivity (entry a vs b). Alternatively, increasing the size of the thioamide appendage (entry a vs c) results in a decrease in both selectivity and yield (both *N*-*tert*-butylcyclopropanethioamides **1b** and **1d** proved to be significantly less reactive than the other three-atom addends examined in this study). Cyclizations with cyclopropane thioester **1e** were the most diastereoselective in this series. Decreasing the alkene substituent size (Table 2, entries d–f) results in an increasing preference for formation of the C(1)/C(5) cis cyclopentanes **16a–18a** without an accompanying reduction in yield. Styrene and *n*-butyl vinyl ether proved to be ineffective two-atom addends with **1e**, emphasizing the requirement for electron-deficient alkenes with these (thiocarbonyl)cyclopropanes. Cyclization of **1e** with acrolein (not shown) provided only trace amounts of cyclopentane products (ca. 2:1 diastereomer ratio).

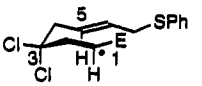
The gross chemical (but not electronic) similarity of these thiocarbonyl/stannyl radical examples to the established vinyl/thio radical system suggests that the cyclization of intermediate radical **2** proceeds through only chairlike 5-hexenyl radical conformations. For phenylcyclopropanethioamides **1a** and **1b**, this assumption leads to the conclusion that formation of the major syn/cis and syn/trans product diastereomers (Table 1, **a** and **b**) results from transition states resembling conformations **19a** and **19b**, respectively. The stereochemistry about the forming C(1)/C(5) bond should be largely controlled by transannular steric congestion between the C(1) pseudoequatorial substituent X and the thioamide appendage Z. Unfortunately, the only system where dominant transannular X/Z steric interactions appeared to significantly disfavor **19a** was accompanied by a low yield of the product formed from the alternative conformer **19b**.



Z=NMe_2 or NH-*t*-Bu
19a X=CO_2R, Y=H
19b X=H, Y=CO_2R



Z=NMe_2, NH-*t*-Bu, or OEt
20a X=CO_2R, CN, Y=H
20b X=H, Y=CO_2R, CN

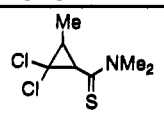
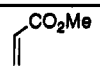
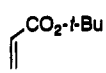
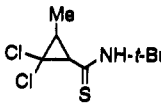
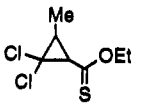
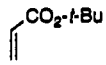


~8:1 C(1)/C(5) cis/trans
21

The issue of C(3)/C(5) syn/anti cyclopentane stereo-

(11) (a) Hillgärtner, H.; Neumann, W. P.; Schroeder, B. *Liebigs Ann. Chem.* **1975**, 586. (b) Hart, D. J.; Seely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 1631.

Table 2. Alkene Addition to *gem*-Dichloromethylcyclopropanethioamides and Thioesters

entry	*gem*-dichloromethylcyclopropanethiocarbonyl	alkene	% yield	cyclopentanethioamide and thioester products (E = CO_2Me, CO_2-*t*-Bu, or CN) *cis (a)*	*trans (b)*	
a	 1c		71	1.2	1.0	**13a/13b**
b	1c		66	1.7	1.0	**14a/14b**
c	 1d		31	1.0	1.0	**15a/15b**
d	 1e		74	2.2	1.0	**16a/16b**
e	1e		70	3.1	1.0	**17a/17b**
f	1e		82	3.7	1.0	**18a/18b**

selectivity is absent in cyclizations involving *gem*-dichloromethyl substrates **1c–e**. However, this system introduces a C(4) methyl appendage which provides a third stereocenter. The evidence to date supports reaction through cyclization transition states resembling **20a** and **20b**, in which the methyl appendage acts as an equatorial conformational anchor. Analogous to the phenyl series, the stereochemistry obtained upon closure of the C(1)/C(5) bond may in principle correlate with the differing steric interactions between the C(1) substituents and the thiocarbonyl-derived Z moiety. In fact, the data (Table 2) support an interpretation in which competitive steric interactions between axial Cl/Y and transannular X/Z determine C(1)/C(5) stereochemistry upon cyclization. As Z diminishes in size, the former interaction becomes dominant, and the C(1)/C(5) cis product prevails.

It is plausible that subtle electronic factors also contribute to the unexpected erosion in stereoselectivity in this thiocarbonyl case compared to the similarly substituted vinylcyclopropane case.[1e,g] Thus, we suggest that, although the cyclizations reported here are likely to proceed through chairlike 5-hexenyl radical conformations, these constructs may feature C(1)/C(5) distances which vary from the ideal intramolecular alkene–radical C(1)/C(5) distance of 2.34 Å calculated for electronically unperturbed substrates.[12] The 5-hexenyl radical system **2** involves the addition of an electrophilic radical (α to an ester or nitrile) to an *electron-rich* double bond (an enamine or enol ether derivative) which is likely to be more exothermic than the comparable cyclization of an unsubstituted 5-hexenyl radical. This circumstance suggests that cyclization occurs earlier on the reaction coordinate (more "reactant like") where steric considerations may be less important. Therefore, the approaching substituted C(1) radical in **19a** or **20a** does not experience the full magnitude of steric repulsion presented by the thiocarbonyl appendage at the time of cyclization, in contrast to the less electronically "activated" vinylcyclopropane-derived system **21** which delivers higher stereoselectivity upon cyclization.

In summary, we have demonstrated that both phenyl-substituted thioamide cyclopropanes **1a** and **1b** and *gem*-dichloromethyl substituted (thiocarbonyl)cyclopropanes **1c–e** undergo [3 atom + 2 atom] addition with electron-deficient alkenes to afford substituted (thiocarbonyl)-cyclopentanes in good yield and with moderate stereoselectivity. This selectivity appears to be a function of not only steric considerations (analogous to previous vinylcyclopentane systems) but also may be modulated by an electronic effect not seen in the simpler hydrocarbon substrate. It is noteworthy that cyclopentanes derived from **1c–e** (Table 2) exhibit complete C(4)/C(5) trans selectivity. Entries d–f exploit this system's inherent C(1)/C(5) cis selectivity by systematically decreasing the steric demand of both the thiocarbonyl and alkene appendages, resulting in serviceable control over three contiguous stereocenters, entry f.

Experimental Section

Low-resolution mass spectra (MS) were obtained at 50–70 eV by electron impact. High-pressure liquid chromatography (HPLC) was performed on a ZORBAX-SIL column (25 cm × 20 mm, DuPont) or an ULTRASPHERE column (25 cm × 10 mm, Beckman). Liquid (flash)[13] chromatography was carried out with 32–63-μm silica gel and the indicated solvent. Benzene (PhH) and tetrahydrofuran (THF) were purified by distillation from sodium/benzophenone ketyl under nitrogen. Solvents for flash column chromatography (diethyl ether, hexane, ethyl acetate) were distilled from calcium hydride prior to use. Moisture- and oxygen-sensitive reactions were carried out in predried glassware under an inert atmosphere (Ar). Melting points are uncorrected.

(12) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959.

(13) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

N,N-Dimethyl-2,2-dichloro-3-methylcyclopropanamide (7). Prepared by the method of Weinreb.[14] To a solution of ethyl 2,2-dichloro-3-methylcyclopropanecarboxylate (6) (0.63 g, 3.20 mmol, 1 equiv) in 20 mL of benzene was added 10.0 mL (6.70 mmol, 2.1 equiv) of a 0.67 M solution of the dimethylamine hydrochloride/trimethylaluminum-derived amidation reagent. The solution was heated at 45 °C for 16 h. The reaction was then quenched by careful addition of 1 M HCl, diluted with ether, and washed with brine. The organic extract was dried over Na_2SO_4 and concentrated in vacuo, and the residue was distilled under aspirator pressure to give 0.43 g (69% yield) of pure dimethylamide (7) (bp = 140 °C/11 Torr) as a clear liquid: IR (thin film) 1654 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.20 (s, 3 H), 3.02 (s, 3 H), 2.24 (dq, J = 7.9, 6.3 Hz, 1 H), 2.06 (d, J = 7.9 Hz, 1 H), 1.35 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.4, 62.9, 40.0, 37.0, 35.4, 28.8, 13.8; MS m/z (relative intensity) 195 (M^+, 10), 160 (18), 72 (100).

***N-tert*-Butyl-2,2-dichloro-3-methylcyclopropanamide (9).** Prepared by the method of Dehmlow.[15] To a solution of *N-tert*-butylcrotonamide (8) (3.07 g, 21.7 mmol, 1 equiv) in 100 mL of chloroform was added 75 mL of a 50% aqueous NaOH solution and tetramethylammonium chloride (0.20 g, 1.8 mmol, 0.08 equiv). The biphasic solution was vigorously stirred without heating for 3 h, with care to avoid uncontrolled reflux. The reaction was then quenched by pouring over ice, diluted with methylene chloride, and washed with water. The organic extract was dried over Na_2SO_4 and concentrated in vacuo, and the residue was purified by initial flash column chromatography, eluting with hexane–Et_2O (3:1), and then subsequent recrystallization from hexane to give 2.16 g (44% yield) of pure *tert*-butylamide (9) (mp = 144–145 °C), as a white solid: IR (CCl_4) 3348 (NH), 1688 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.61 (s, 1 H), 2.18 (dq, J = 7.7, 6.3 Hz, 1 H), 1.81 (d, J = 7.8 Hz, 1 H), 1.38 (s, 9 H), 1.32 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.0, 63.1, 52.1, 41.3, 28.8, 28.6, 13.6; MS m/z (relative intensity) 223 (M^+, 45), 167 (86), 123 (100).

General Procedure A. Thionation of Cyclopropylcarbonyl Substrates. A deoxygenated mixture of cyclopropylamide or cyclopropyl ester (1 equiv) and thionating agent (Lawesson's reagent or 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulfide, 0.5–1 equiv, see below) in either THF (amide) or toluene (ester) was heated at reflux for the indicated time. The crude product was filtered through silica gel, washed with hexane, and concentrated in vacuo, and the pure cyclopropyl(thiocarbonyl) substrates were isolated by subsequent flash column chromatography and/or distillation of the residue.

N,N-Dimethyl-2-phenylcyclopropanethioamide (1a). Following general procedure A, a mixture of *N,N*-dimethyl-2-phenylcyclopropaneamide (4) (1.55 g, 8.20 mmol, 1 equiv) and Lawesson's reagent (1.65 g, 4.08 mmol, 0.5 equiv) in 70 mL of THF were heated at reflux for 30 min. Flash column chromatography, eluting with Et_2O, of the crude product followed by distillation of the residue gave 0.88 g (52% yield) of pure thioamide 1a (bp = 152 °C/0.03 Torr), as a yellow solid: IR ($CHCl_3$) 1600 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.10 (m, 5 H), 3.54 (s, 3 H), 3.37 (s, 3 H), 2.66 (ddd, J = 9.0, 6.4, 4.3 Hz, 1 H), 2.23 (ddd, J = 8.0, 5.4, 4.3 Hz, 1 H), 2.06 (ddd, J = 9.3, 5.2, 4.2 Hz, 1 H), 1.49 (ddd, J = 8.0, 6.5, 4.3 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.0, 140.7, 128.5, 126.3, 126.1, 45.0, 41.4, 32.2, 30.1, 20.6; MS m/z (relative intensity) 205 (M^+, 100), 190 (8); HRMS calcd for $C_{12}H_{15}NS$ 205.0925, found 205.0939.

***N-tert*-Butyl-2-phenylcyclopropanethioamide (1b).** Following general procedure A, a mixture of *N-tert*-butyl-2-phenylcyclopropaneamide (5) (1.64 g, 7.55 mmol, 1 equiv) and Lawesson's reagent (1.59 g, 3.93 mmol, 0.5 equiv) in 30 mL of THF were heated at reflux for 22 h. Flash column chromatography, eluting with hexane–Et_2O (3:1), of the crude product gave 1.13 g (64% yield) of pure thioamide (1b) (mp = 110–112 °C) as a yellow solid: IR ($CHCl_3$) 1600 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.05 (m, 5 H), 2.67 (ddd, J = 9.1, 6.6, 4.2 Hz, 1 H), 2.00–1.82 (m, 2 H), 1.57 (s, 9 H), 1.45–1.29 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.7, 140.9, 128.4, 126.3, 126.1, 56.0, 38.2, 29.3, 28.0, 19.7; MS m/z (relative intensity) 233 (M^+, 100), 176 (49), 160 (22); HRMS calcd for $C_{14}H_{19}NS$ 233.1238, found 233.1251.

N,N-Dimethyl-2,2-dichloro-3-methylcyclopropanethioamide (1c). Following general procedure A, a mixture of *N,N*-dimethyl-2,2-dichloro-3-methylcyclopropaneamide (7) (0.41 g, 2.10 mmol, 1 equiv) and Lawesson's reagent (0.43 g, 1.06 mmol, 0.5 equiv) in 22 mL of THF were heated at reflux for 1 h. Flash column chromatography, eluting with hexane–Et_2O (1:1), of the crude product gave 0.33 g (74% yield) of pure thioamide (1c) (mp = 65–66 °C), as a yellow solid: IR (CCl_4) 1507 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.53 (s, 3 H), 3.49 (s, 3 H), 2.48 (dq, J = 8.1, 6.3 Hz, 1 H), 2.14 (d, J = 8.0 Hz, 1 H), 1.40 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.4, 63.1, 46.9, 44.3, 42.0, 33.8, 14.1; MS m/z (relative intensity) 211 (M^+, 100), 176 (89); HRMS calcd for $C_7H_{11}Cl_2NS$ 210.9989, found 211.0005.

***N-tert*-Butyl-2,2-dichloro-3-methylcyclopropanethioamide (1d).** Following general procedure A, a mixture of *N-tert*-butyl-2,2-dichloro-3-methylcyclopropaneamide (9) (2.18 g, 9.77 mmol, 1 equiv) and Lawesson's reagent (4.88 g, 12.06 mmol, 1.2 equiv) in 100 mL of THF were heated to reflux for 23 h. Flash column chromatography, eluting with hexane–Et_2O (3:1), of the crude product gave 0.93 g (40% yield) of pure thioamide (1d) (mp = 72–76 °C), as a yellow solid: IR ($CHCl_3$) 3360 (NH) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.11 (s, 1 H), 2.34 (dq, J = 8.0, 6.1 Hz, 1 H), 2.22 (d, J = 8.0 Hz, 1 H), 1.58 (s, 9 H), 1.36 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.2, 62.9, 56.4, 49.4, 32.0, 27.7, 14.0; MS m/z (relative intensity) 239 (M^+, 6), 84 (80), 49 (100); HRMS calcd for $C_9H_{15}Cl_2NS$ 239.0302, found 239.0310.

Ethyl 2,2-Dichloro-3-methylcyclopropanethiocarboxylate (1e). Following general procedure A, a mixture of ethyl 2,2-dichloro-3-methylcyclopropanecarboxylate (6) (4.00 g, 20.3 mmol, 1 equiv) and 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (8.30 g, 20.3 mmol, 1 equiv) in 60 mL of toluene were heated to reflux for 20 h. Aspirator pressure distillation of the crude product, subsequent washing of the distillate with 0.2 M NaOH, and redistillation of the residue gave 2.00 g (46% yield) of pure thioester (1e) (bp = 120 °C/12 Torr) as a yellow liquid: IR (thin film) 1454 (C=S) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.55 (dq, J = 7.2, 1.2 Hz, 2 H), 2.63 (d, J = 8.2 Hz, 1 H), 2.48 (dq, J = 8.2, 6.2 Hz, 1 H), 1.42 (t, J = 7.1 Hz, 3 H), 1.36 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 212.0, 69.0, 64.3, 49.6, 33.0, 13.9, 13.6; MS m/z (relative intensity) 212 (M^+, 38), 177 (53), 45 (100).

General Procedure B. Cyclopentane Synthesis. A solution of bis(trimethylstannyl) benzopinacolate (0.4–0.8 equiv, see below) in 2–4 mL of deoxygenated benzene was added dropwise via motor-driven syringe over 2 h to a stirring deoxygenated solution of (thiocarbonyl)cyclopropane substrate (1 equiv) and substituted alkene (2.6–5 equiv, see below) in 2–4 mL of refluxing benzene (~0.25 M based on (thiocarbonyl)-cyclopropane). After the indicated time, the reaction solution was quenched with saturated KF in ethanol, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Cyclopentane diastereomers were isolated by flash column chromatography of the crude product residue on silica gel. In some cases, additional chromatography and/or HPLC was necessary to give isomerically pure cyclopentanes.

Reaction of N,N-Dimethyl-2-phenylcyclopropanethioamide (1a) with Methyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (68 mg, 0.1 mmol, 0.4 equiv) was added to a refluxing benzene solution of *N,N*-dimethyl-2-phenylcyclopropanethioamide (1a) (104 mg, 0.5 mmol, 1 equiv) and methyl acrylate (220 mg, 2.5 mmol, 5 equiv) and allowed to react for 24 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (1:1), gave 114 mg (78% yield) of the cyclopentanes **10a/10b/10c** as a 1.3:1.0:1.1 ratio of isomers by ^1H NMR integration. The isomers were separated by HPLC (ZORBAX-SIL column), eluting with hexane–EtOAc (95:5).

***N,N*-Dimethyl-*c*-2-carbomethoxy-*c*-4-phenylcyclopentane-*r*-thioamide (10a):** IR ($CHCl_3$) 1715 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5 H), 4.05 (ddd, J = 10.0, 7.5, 5.5 Hz, 1 H), 3.92 (ddd, J = 10.9, 7.4, 6.8 Hz, 1 H), 3.69 (s, 3 H), 3.54 (s, 3 H), 3.46 (s, 3 H), 3.26 (m, 1 H), 2.44–2.26 (m, 3 H), 2.12 (dt, J = 12.0, 11.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.2, 176.1,

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143.4, 128.4, 127.1, 126.4, 52.0, 51.3, 50.8, 45.3, 45.2, 42.7, 41.6, 37.9; MS *m/z* (relative intensity) 291 (M^+, 100), 258 (27), 232 (53); HRMS calcd for $C_{16}H_{21}NO_2S$ 291.1293, found 291.1287.

***N,N*-Dimethyl-*t*-2-carbomethoxy-*c*-4-phenylcyclopentane-*r*-thioamide (10b)**: IR ($CHCl_3$) 1705 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.16 (m, 5 H), 4.16 (ddd, J = 11.7, 8.5, 7.1 Hz, 1 H), 3.94 (ddd J = 9.9, 8.6, 6.1 Hz, 1 H), 3.69 (s, 3 H), 3.56 (m, 1 H), 3.53 (s, 3 H), 3.42 (s, 3 H), 2.59 (pentet, J = 6.4 Hz, 1 H), 2.32–2.08 (m, 2 H), 1.98 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 175.4, 143.9, 128.5, 126.9, 126.3, 52.6, 52.0, 49.5, 45.3, 44.4, 41.6, 41.3, 38.8; MS *m/z* (relative intensity) 291 (M^+, 100), 232 (27), 174 (72); HRMS calcd for $C_{16}H_{21}NO_2S$ 291.1293, found 291.1281.

***N,N*-Dimethyl-*c*-2-carbomethoxy-*t*-4-phenylcyclopentane-*r*-thioamide (10c)**: IR ($CHCl_3$) 1720 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.15 (m, 5 H), 3.82 (dt, J = 9.8, 7.2 Hz, 1 H), 3.62 (s, 3 H), 3.48 (s, 3 H), 3.45 (s, 3 H), 3.21 (dt, J = 9.7, 7.6 Hz, 1 H), 3.11 (tt, J = 11.8, 6.9 Hz, 1 H), 2.67 (m, 2 H), 2.30 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 173.2, 143.4, 128.4, 127.4, 126.3, 51.9, 49.8, 48.5, 44.9, 42.5, 41.6, 36.4; MS *m/z* (relative intensity) 291 (M^+, 100), 258 (23), 232 (39); HRMS calcd for $C_{16}H_{21}NO_2S$ 291.1293, found 291.1305.

Reaction of *N,N*-Dimethyl-2-phenylcyclopropanethioamide (1a) with *tert*-Butyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (72 mg, 0.1 mmol, 0.4 equiv) was added to a refluxing benzene solution of *N,N*-dimethyl-2-phenylcyclopropanethioamide (**1a**) (102 mg, 0.5 mmol, 1 equiv) and *tert*-butyl acrylate (324 mg, 2.5 mmol, 5 equiv) and allowed to react for 28 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (2:1), gave 96 mg (58% yield) of the cyclopentanes **11a/11b/11c** as a 1.9:1.3:1.0 ratio of isomers by ^1H NMR integration. Isomer **11c** was isolated during this procedure, while isomers **11a** and **11b** were separated by HPLC (Ultrasphere column), eluting with hexane–EtOAc (8:2).

***N,N*-Dimethyl-*c*-2-carbo-*tert*-butoxy-*c*-4-phenylcyclopentane-*r*-thioamide (11a)**: IR ($CHCl_3$) 1705 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.10 (m, 5 H), 3.97–3.80 (m, 2 H), 3.53 (s, 3 H), 3.46 (s, 3 H), 3.22 (m, 1 H), 2.42–2.26 (m, 3 H), 2.12 (tdd, J = 12.2, 7.8, 2.6 Hz, 1 H), 1.44 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.9, 174.9, 143.6, 128.4, 127.1, 126.3, 80.4, 52.5, 50.5, 45.2, 45.1, 42.8, 41.6, 38.2, 28.1; MS *m/z* (relative intensity) 333 (M^+, 100), 277 (92), 260 (57); HRMS calcd for $C_{18}H_{27}NO_2S$ 333.1762, found 333.1771.

***N,N*-Dimethyl-*t*-2-carbo-*tert*-butoxy-*c*-4-phenylcyclopentane-*r*-thioamide (11b)**: IR ($CHCl_3$) 1710 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.10 (m, 5 H), 4.02 (ddd, J = 11.2, 8.2, 7.1 Hz, 1 H), 3.90 (ddd, J = 9.7, 8.2, 5.8 Hz, 1 H), 3.55 (m, 1 H), 3.53 (s, 3 H), 3.42 (s, 3 H), 2.58 (m, 1 H), 2.32–2.02 (m, 2 H), 1.92 (q, J = 11.6 Hz, 1 H), 1.43 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.5, 174.1, 144.1, 128.4, 127.0, 126.2, 80.4, 53.8, 49.1, 45.2, 44.4, 41.6, 41.4, 39.2, 28.1; MS *m/z* (relative intensity) 333 (M^+, 59), 277 (87), 160 (100); HRMS calcd for $C_{19}H_{27}NO_2S$ 333.1762, found 333.1765.

***N,N*-Dimethyl-*c*-2-carbo-*tert*-butoxy-*t*-4-phenylcyclopentane-*r*-thioamide (11c)**: IR ($CHCl_3$) 1710 (C=O) cm^{-1}; ^1H NMR (200 MHz $CDCl_3$) δ 7.45–7.10 (m, 5 H), 3.76 (td, J = 9.8, 7.2 Hz, 1 H), 3.50 (s, 3 H), 3.44 (s, 3 H), 3.12 (td, J = 9.9, 7.6 Hz, 1 H), 3.05 (m, 1 H), 2.81–2.50 (m, 2 H), 2.29 (m, 2 H), 1.42 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 171.8, 143.6, 128.3, 127.4, 126.2, 80.6, 49.6, 49.0, 44.8, 44.7, 42.9, 41.8, 37.0, 28.2; MS *m/z* (relative intensity) 333 (M^+, 74), 277 (55), 116 (100); HRMS calcd for $C_{19}H_{27}NO_2S$ 333.1762, found 333.1779.

Reaction of *N*-*tert*-Butyl-2-phenylcyclopropanethioamide (1b) with Methyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (61 mg, 0.09 mmol, 0.4 equiv) was added to a refluxing benzene solution of *N*-*tert*-butyl phenylcyclopropanethioamide (**1b**) (102 mg, 0.44 mmol, 1 equiv) and methyl acrylate (191 mg, 2.2 mmol, 5 equiv) and allowed to react for 24 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (4:1), gave 39 mg (28% yield) of the fully separated cyclopentanes **12a/12b** as a 1.0:1.6 ratio of isomers by ^1H NMR integration.

***N*-*tert*-Butyl-*c*-2-carbomethoxy-*c*-4-phenylcyclopentane-*r*-thioamide (12a)**: IR ($CHCl_3$) 3365 (NH), 1715 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1 H), 7.40–7.15 (m, 5 H), 3.72 (s, 3 H), 3.54–3.28 (m, 3 H), 2.78 (dddd, J = 13.5, 8.7, 4.9, 1.2 Hz, 1 H), 2.52 (m, 1 H), 1.95 (m, 2 H), 1.55 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.0, 175.7, 144.0, 128.4, 127.0, 126.2, 56.4, 55.6, 52.1, 51.9, 44.5, 40.3, 38.6, 27.7; MS *m/z* (relative intensity) 319 (M^+, 39), 230 (15), 57 (100); HRMS calcd for $C_{18}H_{25}NO_2S$ 319.1606, found 319.1585.

***N*-*tert*-Butyl-*t*-2-carbomethoxy-*c*-4-phenylcyclopentane-*r*-thioamide (12b)**: IR ($CHCl_3$) 3365 (NH), 1715 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 7.40–7.10 (m, 5 H), 3.73 (s, 3 H), 3.47 (ddd, J = 11.3, 8.2, 4.9 Hz, 1 H), 3.26 (ddd, J = 11.0, 8.3, 6.7 Hz, 1 H), 3.18 (m, 1 H), 2.42 (m, 2 H), 2.22 (m, 2 H), 1.56 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 204.6, 176.4, 143.4, 128.4, 127.0, 126.3, 58.3, 55.6, 52.1, 49.7, 44.4, 41.8, 37.5, 27.7; MS *m/z* (relative intensity) 319 (M^+, 29), 260 (7), 57 (100); HRMS calcd for $C_{18}H_{25}NO_2S$ 319.1606, found 319.1616.

Reaction of *N,N*-Dimethyl-2,2-dichloro-3-methylcyclopropanethioamide (1c) with Methyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (72 mg, 0.1 mmol, 0.4 equiv) was added to a refluxing benzene solution of *N,N*-dimethyl-2,2-dichloro-3-methylcyclopropanethioamide (**1c**) (103 mg, 0.49 mmol, 1 equiv) and methyl acrylate (210 mg, 2.4 mmol, 5 equiv) and allowed to react for 24 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (5:1 then 1:1), gave 102 mg (71% yield) of the fully separated cyclopentanes **13a/13b** as a 1.2:1.0 ratio of isomers by ^1H NMR integration.

***N,N*-Dimethyl-*c*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (13a)**: IR ($CHCl_3$) 1730 (C=O) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 3.92 (dq, J = 10.3, 6.4 Hz, 1 H), 3.44 (dd, J = 13.9, 10.2 Hz, 1 H), 3.24 (s, 3 H), 3.15 (t, J = 10.7, Hz, 1 H), 2.97 (s, 3 H), 2.90 (m, 1 H), 2.72 (dd, J = 13.8, 7.5 Hz, 1 H), 2.43 (s, 3 H), 1.19 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.0, 171.0, 94.6, 57.3, 53.4, 52.3, 48.9, 45.2, 44.5, 41.9, 12.4; MS *m/z* (relative intensity) 297 (M^+, 13), 262 (83), 88 (100); HRMS calcd for $C_{11}H_{17}Cl_2NO_2S$ 297.0357, found 297.0357.

***N,N*-Dimethyl-*t*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (13b)**: IR ($CHCl_3$) 1730 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (dd, J = 10.8, 7.2 Hz, 1 H), 3.80 (ddd, J = 11.8, 7.2, 2.9 Hz, 1 H), 3.71 (s, 3 H), 3.57 (s, 3 H), 3.56 (s, 3 H), 3.22 (dd, J = 14.6, 2.9 Hz, 1 H), 3.06 (dd, J = 14.6, 11.6 Hz, 1 H), 3.05 (dq, J = 10.8, 6.6 Hz, 1 H), 1.16 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 204.7, 173.9, 94.5, 59.6, 53.5, 52.3, 49.9, 48.8, 45.8, 42.1, 11.4; MS *m/z* (relative intensity) 297 (M^+, 15), 262 (100), 226 (89); HRMS calcd for $C_{11}H_{17}Cl_2NO_2S$ 297.0357, found 297.0351.

Reaction of *N,N*-Dimethyl-2,2-dichloro-3-methylcyclopropanethioamide (1c) with *tert*-Butyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (62 mg, 0.09 mmol, 0.4 equiv) was added to a refluxing benzene solution of *N,N*-dimethyl-2,2-dichloro-3-methylcyclopropanethioamide (**1c**) (100 mg, 0.47 mmol, 1 equiv) and *tert*-butyl acrylate (158 mg, 1.23 mmol, 2.6 equiv) and allowed to react for 30 h. The refluxing solution was then charged with an additional portion of bis(trimethylstannyl) benzopinacolate (62 mg, 0.09 mmol, 0.4 equiv) and heated for an additional 18 h. Purification of the crude reaction mixture by flash chromatography, eluting with hexane–Et_2O (8:2), gave 105 mg (66% yield) of the separated cyclopentanes **14a/14b** as a 1.7:1.0 ratio of isomers by ^1H NMR integration.

***N,N*-Dimethyl-*c*-5-carbo-*tert*-butoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (14a)**: IR ($CHCl_3$) 1710 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.59 (dq, J = 10.0, 6.4 Hz, 1 H), 3.51 (s, 3 H), 3.42 (s, 3 H), 3.40 (t, J = 10.4, Hz, 1 H), 3.25 (td, J = 10.7, 6.7 Hz, 1 H), 3.15 (dd, J = 12.9, 10.6 Hz, 1 H), 2.81 (dd, J = 13.1, 6.6 Hz, 1 H), 1.40 (s, 9 H), 1.16 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.0, 169.5, 94.7, 81.6, 57.9, 53.3, 49.3, 45.1, 44.9, 42.1, 28.1, 12.6; MS *m/z* (relative intensity) 339 (M^+, 1), 248 (13), 88 (100); HRMS calcd for $C_{14}H_{23}Cl_2NO_2S$ 339.0826, found 339.0828.

***N,N*-Dimethyl-t-5-carbo-*tert*-butoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (14b)**: IR ($CHCl_3$) 1715 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.92 (dd, J = 10.8,

6.7 Hz, 1 H), 3.66 (ddd, J = 11.5, 6.7, 2.6 Hz, 1 H), 3.57 (s, 6 H), 3.19 (dd, J = 14.4, 2.6 Hz, 1 H), 3.04 (dq, J = 10.8, 6.5 Hz, 1 H), 3.00 (dd, J = 14.3, 11.6 Hz, 1 H), 1.44 (s, 9 H), 1.16 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.4, 172.6, 94.9, 81.5, 59.8, 53.5, 50.4, 50.1, 45.8, 42.2, 28.0, 11.5; MS m/z (relative intensity) 339 (M^+, 9), 268 (28), 248 (100); HRMS calcd for $C_{14}H_{23}Cl_2NO_2S$ 339.0826, found 339.0831.

Reaction of *N-tert*-Butyl-2,2-dichloro-3-methylcyclopropanethioamide (1d) with Methyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (81 mg, 0.12 mmol, 0.5 equiv) was added to a refluxing benzene solution of *N-tert*-butyl 2,2-dichloro-3-methylcyclopropanethioamide (**1d**) (118 mg, 0.49 mmol, 1 equiv) and methyl acrylate (210 mg, 2.44 mmol, 5 equiv) and allowed to react for 24 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (3:1), gave 49 mg (31% yield) of the separated cyclopentanes **15a/15b** as a 1.0:1.0 ratio of isomers by ^{1}H NMR integration.

***N-tert*-Butyl-*c*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (15a):** IR ($CHCl_3$) 3380 (NH), 1730 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 1 H), 3.62 (s, 3 H), 3.38–3.25 (m, 2 H), 3.15 (dd, J = 13.7, 11.3 Hz, 1 H), 2.86 (t, J = 10.5 Hz, 1 H), 2.83 (dd, J = 13.7, 7.2 Hz, 1 H), 1.56 (s, 9 H), 1.17 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.1, 171.3, 94.2, 62.4, 56.9, 56.1, 52.1, 49.3, 44.8, 27.6, 12.2; MS m/z (relative intensity) 325 (M^+, 10), 290 (68), 57 (100); HRMS calcd for $C_{13}H_{21}Cl_2NO_2S$ 325.0670, found 325.0658.

***N-tert*-Butyl-*t*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thioamide (15b):** IR ($CHCl_3$) 3370 (NH), 1720 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (s, 1 H), 3.74 (s, 3 H), 3.36 (ddd, J = 12.0, 7.1, 2.6 Hz, 1 H), 3.21 (dd, J = 14.6, 2.6 Hz, 1 H), 3.06 (dq, J = 11.2, 6.1 Hz, 1 H), 2.96 (dd, J = 11.3, 7.0 Hz, 1 H), 2.91 (dd, J = 14.6, 12.1 Hz, 1 H), 1.56 (s, 9 H), 1.17 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.0, 174.4, 94.5, 61.6, 56.0, 55.9, 52.6, 49.3, 46.5, 27.7, 11.6; MS m/z (relative intensity) 325 (M^+, 11), 290 (45), 57 (100); HRMS calcd for $C_{13}H_{21}Cl_2NO_2S$ 325.0670, found 325.0642.

Reaction of Ethyl 2,2-Dichloro-3-methylcyclopropanethiocarboxylate (1e) with *tert*-Butyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (66 mg, 0.1 mmol, 0.4 equiv) was added to a refluxing benzene solution of ethyl 2,2-dichloro-3-methylcyclopropanethiocarboxlate (**1e**) (104 mg, 0.49 mmol, 1 equiv) and *tert*-butyl acrylate (315 mg, 2.5 mmol, 5 equiv) and allowed to react for 20 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–EtOAc (97:3), gave 123 mg (74% yield) of the cyclopentanes **16a/16b** as a 2.2:1.0 ratio of isomers by ^{1}H NMR integration. These isomers were separated by additional flash column chromatography, eluting with hexane–Et_2O (9:1).

Ethyl *c*-5-carbo-*tert*-butoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thiocarboxylate (16a): IR (CCl_4) 1746 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.48 (m, 2 H), 3.41–3.31 (m, 2 H), 3.04–2.78 (m, 3 H), 1.41 (t, J = 7.1 Hz, 3 H), 1.38 (s, 9 H), 1.25 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 220.0, 170.1, 94.0, 81.5, 68.6, 60.5, 56.2, 49.8, 45.6, 28.0, 13.4, 12.8; MS m/z (relative intensity) 340 (M^+, 0.1), 213 (49), 57 (100); HRMS calcd for $C_{14}H_{22}Cl_2O_3S$ 340.0667, found 340.0683.

Ethyl *t*-5-carbo-*tert*-butoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thiocarboxylate (16b): IR (CCl_4) 1726 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.57 (m, 2 H), 3.54 (ddd, J = 11.4, 7.7, 3.1 Hz, 1 H), 3.37 (dd, J = 11.0, 7.7 Hz, 1 H), 3.24 (dd, J = 14.6, 3.0 Hz, 1 H), 2.87 (dd, J = 14.6, 11.4 Hz, 1 H), 2.63 (dq, J = 11.1, 6.5 Hz, 1 H), 1.44 (s, 9 H), 1.43 (t, J = 7.1 Hz, 3 H), 1.23 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 223.2, 171.5, 94.4, 81.4, 68.9, 61.3, 57.9, 49.4, 47.9, 27.9, 13.6, 12.1; MS m/z (relative intensity) 340 (M^+, 0.5), 230 (85), 202 (100); HRMS calcd for $C_{14}H_{22}Cl_2O_3S$ 340.0667, found 340.0661.

Reaction of Ethyl 2,2-Dichloro-3-methylcyclopropanethiocarboxylate (1e) with Methyl Acrylate. Following general procedure B, a 2-mL benzene solution of bis(trimethylstannyl) benzopinacolate (65 mg, 0.09 mmol, 0.4 equiv) was added to a refluxing benzene solution of ethyl 2,2-dichloro-3-methylcyclopropanethiocarboxylate (**1e**) (104 mg, 0.49 mmol, 1 equiv) and methyl acrylate (210 mg, 2.4 mmol, 5 equiv) and allowed to react for 4 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–Et_2O (75:25), gave 102 mg (70% yield) of the cyclopentanes **17a/17b** as a 3.1:1.0 ratio of isomers by ^{1}H NMR integration. These isomers were separated by additional flash column chromatography, eluting with hexane–Et_2O (95:5).

Ethyl *c*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thiocarboxylate (17a): IR (CCl_4) 1732 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.46 (q, J = 7.2 Hz, 2 H), 3.60 (s, 3 H), 3.55–3.34 (m, 2 H), 3.12–2.82 (m, 3 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.25 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 219.7, 171.5, 93.8, 68.8, 60.5, 55.8, 51.9, 49.5, 44.8, 13.4, 12.6; MS m/z (relative intensity) 298 (M^+, 1), 227 (67), 173 (100); HRMS calcd for $C_{11}H_{16}Cl_2O_3S$ 298.0197, found 298.0196.

Ethyl *t*-5-carbomethoxy-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thiocarboxylate (17b): IR (CCl_4) 1739 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.58 (m, 2 H), 3.71 (s, 3 H), 3.68 (ddd, J = 11.3, 7.6, 3.2 Hz, 1 H), 3.43 (dd, J = 11.1, 7.7 Hz, 1 H), 3.26 (dd, J = 14.6, 3.2 Hz, 1 H), 2.93 (dd, J = 14.6, 11.6 Hz, 1 H), 2.63 (dq, J = 11.1, 6.5 Hz, 1 H), 1.43 (t, 7.1 Hz, 3 H), 1.25 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 222.7, 173.0, 94.1, 69.1, 60.8, 57.8, 52.4, 49.4, 46.8, 13.6, 12.2; MS m/z (relative intensity) 298 (M^+, 1), 230 (58), 216 (100); HRMS calcd for $C_{11}H_{16}Cl_2O_3S$ 298.0197, found 298.0189.

Reaction of Ethyl 2,2-Dichloro-3-methylcyclopropanethiocarboxylate (1e) with Acrylonitrile. Following general procedure B, a 4-mL benzene solution of bis(trimethylstannyl) benzopinacolate (111 mg, 0.16 mmol, 0.3 equiv) was added to a refluxing benzene solution of ethyl 2,2-dichloro-3-methylcyclopropanethiocarboxylate (**1e**) (208 mg, 0.98 mmol, 1 equiv) and acrylonitrile (250 mg, 4.7 mmol, 4.8 equiv) and allowed to react for 4 h. Purification of the crude reaction mixture by flash column chromatography, eluting with hexane–EtOAc (9:1), gave 213 mg (82% yield) of the cyclopentanes **18a/18b** as a 3.7:1.0 ratio of isomers by ^{1}H NMR integration. Additional flash column chromatography of this mixture, eluting with the same solvent system, afforded the major diastereomer **18a** and a component corresponding to **18b** that decomposed over time.

Ethyl *c*-5-cyano-3,3-dichloro-*t*-2-methylcyclopentane-*r*-thiocarboxylate (18a): IR (CCl_4) 2247 (CN) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.62 (q, J = 7.1 Hz, 2 H), 3.54 (td, J = 10.6, 7.5 Hz, 1 H), 3.29 (t, J = 10.4 Hz, 1 H), 3.18 (dq, J = 11.5, 6.0 Hz, 1 H), 3.11 (dd, J = 13.7, 7.5 Hz, 1 H), 2.82 (dd, J = 13.6, 10.8 Hz, 1 H), 1.47 (t, J = 7.1 Hz, 3 H), 1.26 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 215.8, 117.9, 92.2, 69.6, 59.0, 54.6, 50.5, 29.5, 13.6, 12.4; MS m/z (relative intensity) 265 (M^+, 2), 230 (12), 114 (100); HRMS calcd for $C_{10}H_{13}Cl_2NOS$ 265.0095, found 265.0095.

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Supplementary Material Available: DNOE measurements for **10a–c** and **14a,b** and ^{1}H and ^{13}C NMR spectra for **1a–e, 7, 9, 10a–c, 11a–c, 12a,b, 13a,b, 14a,b, 15a,b, 16a,b, 17a,b,** and **18a** (54 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.