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Gold(I)-Catalyzed Addition of Thiols and Thioacids to 3,3-Disubstituted Cyclopropenes

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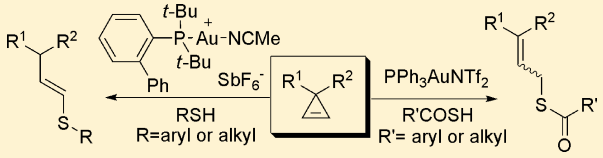
Supporting Information

ABSTRACT: Gold(I)-catalyzed reactions of thiols, thiophenols, and thioacids with 3,3-disubstituted cyclopropenes occur in a regioselective and chemoselective manner to produce either vinyl thioethers or primary allylic thioesters in good yields. A survey of commonly used gold(I) catalysts shows Echavarren's cationic gold(I) catalyst to be most tolerant of deactivation by sulfur. A novel digold with bridging thiolate complex is characterized by X-ray crystallography, shedding light on a possible deactivation pathway.



Thioethers are of academic and industrial importance because the thioether linkage is present in many pharmaceuticals, natural products and synthetic intermediates.[1] Despite the importance of sulfur-containing molecules, the formation of C−S bonds is not investigated as much as C−C, C−O and C−N bonds. For example, reports using thiols as nucleophiles with late transition metals are nowhere near as numerous as with other nucleophiles, because sulfur is known to deactivate/poison late transition metal catalysts.[2] In the burgeoning field of homogeneous gold-catalysis, for example, successful reports of thiols as nucleophiles are relatively scarce.[3−6]

One of the research efforts within our group is to explore the diverse chemistry of gold-catalyzed reactions with cyclopropenes.[7−9] While alcohols are excellent intermolecular nucleophiles (Scheme 1),[7a,c] we found that reactions with *N*-nucleophiles do not proceed to completion (max. 42% conv), presumably due to catalyst deactivation by the *N*-nucleophile (Scheme 1). We were thus very keen to see how *S*-nucleophiles, known strong coordinators to gold,[10] would compare. Despite the initial presumption that *S*-nucleophiles would fare worse than *N*-nucleophiles, we are pleased to report that the reactions are in fact mild and facile, providing **4** or **5** in good yields, regioselectivity and chemoselectivity (Scheme 1).

Following initial optimization studies (see the Supporting Information), we proceeded to investigate a selection of different thioacid and thiol nucleophiles (Table 1). While thiobenzoic and thioacetic acids produce **14a** and **14b** regioselectively as the major products (entries 1−2), the more nucleophilic thiophenol and benzyl thiol fail to react when PPh_3AuNTf_2 **12**[11] is used as a catalyst, presumably due to catalyst deactivation by these thiols (entries 3−4). Echavarren's catalyst **17**,[12] on the other hand, appears far more tolerant of thiols; catalytic activity is observed in the presence of a wide range of thiols (entries 5−12). However, when **17** is used as a catalyst with *thioacids* as nucleophiles, the product distribution changes, and the vinyl thioesters **16** begin to be observed as side products (entries 5−6). In fact, when thiophenol and thiols (both primary and tertiary) are employed as nucleophiles with catalyst **17**, it is the vinyl thioethers **16c−e** that are formed exclusively and in good yields (entries 7−9). It is interesting to note that reactions with aliphatic thiols are slower than with thioacids or thiophenol (1−20 h vs <30 min), even though aliphatic thiols are more nucleophilic, suggesting that some degree of catalyst deactivation by sulfur is taking place.

To our delight, even thiols bearing pendant nucleophilic groups react very selectively at the *S*-position (entries 10−12). Furfuryl mercaptan, for example, reacts selectively at the thiol end to produce solely **16f** (entry 10), a result that was initially very surprising, as furans are known to react with cyclopropenes in a facile manner (<2 min with 0.01 mol % of **17**).[7e] Similarly, 2-mercaptoethanol and 3-mercaptopropionic acid both react selectively at the *S*-position (entries 11−12). These results clearly indicate that thiols reduce the activity of gold(I) to an extent that other usually reactive nucleophiles such as furans and alcohols are now no longer reactive under these conditions, allowing the thiol end of the nucleophile to react *chemoselectively*.

For comparison, the in situ formed *N*-heterocyclic carbene (NHC) catalysts[13] (IPr)$AuSbF_6$ and (IPr)AuOTf as well as PPh_3AuSbF_6 were investigated (entries 13−17). With thioacetic acid, (IPr)$AuSbF_6$ and PPh_3AuSbF_6 appear to be comparable to PPh_3AuNTf_2 as a catalyst, although small amounts of **16b** are now formed (entries 13 and 15 vs. entry 2). Changing the counterion ((IPr)AuOTf, entry 14) seems to have a larger effect on the product distribution, forming predominantly **14b** but with an inseparable side product present. Since using thiophenol as a nucleophile completely deactivates catalyst **12** (entry 3) but not catalyst **17** (entry 7), we were keen to investigate how other catalysts compared. While **16c** is successfully produced using (IPr)$AuSbF_6$ and PPh_3AuSbF_6, ∼60% of a cyclopropane side-product **11**[14] is also observed

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Scheme 1. Comparison with *O*- and *N*-Nucleophiles

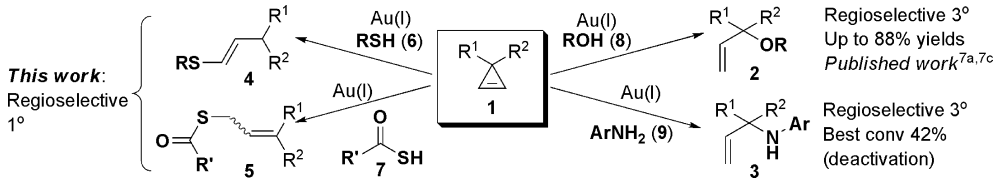
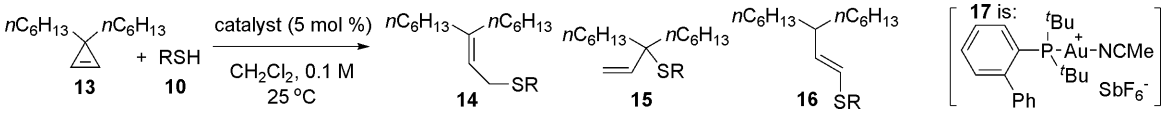
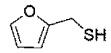
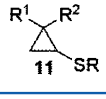


Table 1. Screen of Thiol Nucleophiles and Gold Catalysts



entry	RSH	catalyst	time (min)	yield (%)	products	ratio **14**:**15**:**16**[a]
1	PhCOSH	PPh_3AuNTf_2 (**12**)	10	80	**14a**:**15a**	9:1:0
2	MeCOSH	**12**	30	76	**14b**:**15b**	9:1:0
3	PhSH	**12**	30	0[b]	-	N/A
4	BnSH	**12**	30	0[b]	-	N/A
5	PhCOSH	**17**	30	87	**14a**:**16a**	3:0:1
6	MeCOSH	**17**	30	85	**14b**:**16b**	2:0:1
7	PhSH	**17**	30	72	All **16c**[c]	All **16c**[c]
8	BnSH	**17**	180	81	All **16d**[d]	All **16d**[d]
9	*t*BuSH	**17**	1200	84	All **16e**[d]	All **16e**[d]
10		**17**	60	86	All **16f**[d]	All **16f**[d]
11	**HO**$(CH_2)_2$SH	**17**	180	82	All **16g**[d]	All **16g**[d]
12	**HO$_2$C**$(CH_2)_2$SH	**17**	120	73	All **16h**[d]	All **16h**[d]
13[e]	MeCOSH	(IPr)AuCl/$AgSbF_6$	30	71	**14b**:**15b**:**16b**	9:1.2:1
14	MeCOSH	(IPr)AuCl/AgOTf	30	ND[f]	**14b**:**16b**	99:0:1
15	MeCOSH	$PPh_3AuCl/AgSbF_6$	30	77	**14b**:**15b**:**16b**	58:5:1
16	PhSH	(IPr)AuCl/$AgSbF_6$	30	89[g]	All **16c**[g]	All **16c**[g]
17	PhSH	$PPh_3AuCl/AgSbF_6$	30	75[g]	All **16c**[g]	All **16c**[g]
18	PhSH	PPh_3AuCl/AgOTs	30	N/A[b]	-	-

[a]Determined by ^{1}H NMR analysis. [b]Unreacted starting material, **11**, and other minor unidentified products observed in crude NMR. [c]16:1 *E*:*Z*. [d]>20:1 *E*:*Z*. [e](IPr) = 1,3-*bis*(2,6-diisopropylphenyl)imidazol-2-ylidine. [f]Unidentified inseparable side-product present. [g]**11** present in ~60%.



(entries 16 and 17). Changing the counterion to a more coordinating tosylate, however, changes the outcome of the reaction, producing no desired product **16c** at all (entry 18). Thus, we conclude that among the catalysts investigated in this study, it is the identity of the *counterion* rather than the ligand that causes the complete deactivation of the gold catalyst in the presence of thiophenol, with slightly more coordinating anions (NTf_2^- and OTs^-) faring worse than the very weakly coordinating SbF_6^-. From these results, **12** was chosen as the optimal catalyst when *thioacids* are used as nucleophiles to form **14** selectively, while **17** was chosen as the optimal catalyst for *thiophenol* and *alkyl thiols* to form **16** selectively.

Next, we proceeded to explore the cyclopropene substrate scope. Thiobenzoic acid adds to a range of 3,3-disubstituted cyclopropenes to produce allylic thioesters **14a**, **14i**−**n** in good yields and generally good selectivity for the primary **14** (vs. tertiary **15**) allylic thioesters (entries 1−7, Table 2).[15] As expected, the *E*:*Z* ratio, where applicable, is good when the substituents R^1 and R^2 are sterically different (e.g., entry 6), but poor when they are sterically similar (entries 1, 3−4). Another trend to note is that small amounts of **16** begin to be observed when both substituents are bulky (entries 5 and 7). Cyclopropenes **24** and **25**, with ester as one of the substituents, do not react under these conditions (entries 8−9, rt or 70 °C), not even to form the previously reported gold-catalyzed intramolecular rearrangement to butenolide.[7a,g,9b] These results suggest that the gold catalyst in the presence of thiol is not active enough to catalyze the ring-opening of less reactive[7e] cyclopropenes **24** and **25**.

Next, a similar screen was carried out with thiophenol as a nucleophile to produce **16** (entries 10−17, Table 2). Pleasingly, the reaction with thiophenol proceeds very cleanly and in good yields with cyclopropenes **13**, **18**−**19**, **22**−**23** to produce **16** with excellent *E*-selectivity (entries 10−14). Interestingly, benzyl substituents do not seem to be tolerated under these conditions when thiophenol is used as a nucleophile (entries 15−16); a complex mixture of products is observed. We suspect that this is a result of further reaction/decomposition of the expected vinyl thioether products **16**, which so happen to be unstable when a combination of a benzyl substituent and an arylthioether are present. Indeed, when cyclopropene **20** is subjected to a different thiol (furfuryl mercaptan), the reaction now proceeds to yield **16s** (^{1}H NMR analysis of the crude mixture, entry 17), but product **16s** decomposes upon

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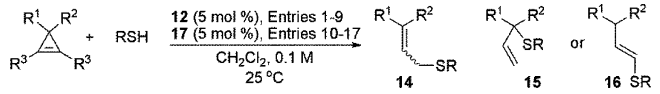
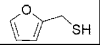
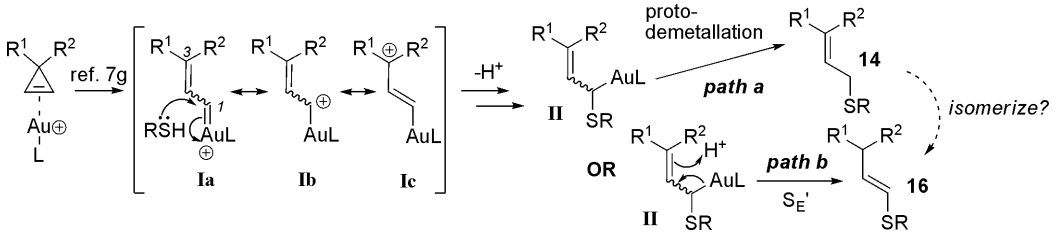
Table 2. Cyclopropene Scope with Thiobenzoic Acid or Thiophenol As Nucleophile



entry	R^1	R^2	R^3	RSH	time (min)	yield (%)	product[a]	E:Z[a] for **14/16**
1	**18** Me	$^nC_9H_{21}$	H	PhCOSH	10	67	6:1 **14i**:**15i**	1.25:1
2	**13** $^nC_6H_{13}$	$^nC_6H_{13}$	H	PhCOSH	10	80	9:1 **14a**:**15a**	N/A
3	**19** Me	CH_2CH_2Ph	H	PhCOSH	10	63	6:1 **14j**:**15j**	1:1
4	**20** Me	Bn	H	PhCOSH	10	62	14:1 **14k**:**15k**	1.7:1
5	**21** ^{i}Pr	Bn	H	PhCOSH	10	73	13:2:1 **14l**:**15l**:**16l**	1:3
6	**22** Me	Ad	H	PhCOSH	10	78	10:1 **14m**:**15m**	E only
7	**23** Cy	Cy	H	PhCOSH	10	94	7:1 **14n**:**16n**	N/A
8[c]	**24** Ph	CO_2Me	H	PhCOSH	18 h[b]	-	-[d]	N/A
9	**25** H	CO_2Et	Ph	PhCOSH	18 h[b]	-	-	N/A
10	**18** Me	$^nC_9H_{21}$	H	PhSH	30	84	**16o** only	17:1
11	**13** $^nC_6H_{13}$	$^nC_6H_{13}$	H	PhSH	30	72	**16c** only	16:1
12	**19** Me	CH_2CH_2Ph	H	PhSH	10	90	**16p** only	19:1
13	**22** Me	Ad	H	PhSH	30	76	**16q** only	17:1
14	**23** Cy	Cy	H	PhSH	30	56	**16r** only	20:1
15	**20** Me	Bn	H	PhSH	30	-	-[e]	N/A
16	**21** ^{i}Pr	Bn	H	PhSH	30	-	-[e]	N/A
17	**20** Me	Bn	H		60	27[e]	**16s**[f] only	>20:1

[a]Determined by ^{1}H NMR analysis. [b]$ClCH_2CH_2Cl$ used as solvent, 70 °C. [c]No reaction at rt. [d]**24** + Complex mixture. [e]Complex mixture. [f]Product decomposes upon purification.

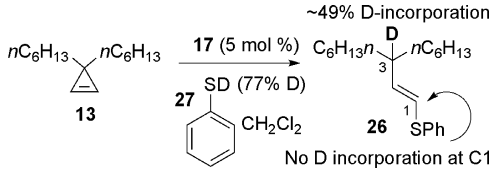
Scheme 2. Plausible Mechanistic Pathways to 14 and 16



standing/purification, resulting in a low 27% yield. This result suggests that a benzyl substituent on the cyclopropene is not an inherent problem in the gold-catalyzed reaction, but the vinyl thioethers **16** formed from it are unstable, thereby forming a complex mixture of decomposition products.

The proposed mechanism (Scheme 2) shows that **14** can be obtained from thioacid/thiol attack at the C-1 position on intermediate **I**,[7g,9f,g] followed by protodemetalation. The vinyl thioether/ester **16** can be produced either via isomerization of **14** (path a), or S_E' directly[16] from **II** (path b). A deuterium-labeling study with deuterated thiophenol **27** resulted in D-incorporation at the C-3 position only (Scheme 3), implying

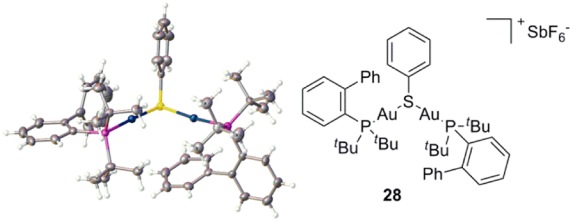
Scheme 3. Deuterium Studies



that *path b* operates. Furthermore, when **14a** is resubjected to the reaction conditions, no isomerization to **16a** is observed, further implying that **16** must be formed through path b.

Finally, in order to shed light on the interaction between the Au(I) catalyst and thiols, which causes the observed dampening of catalyst activity, a 20:1 as well as a 1:1 mixture of thiophenol:**17** were investigated by NMR. Both show almost instantaneous conversion to a new complex [^{31}P NMR (CD_2Cl_2) 57.3 ppm for **17**, 62.9 ppm for new complex],[14] and recrystallization produces novel complex **28** (confirmed by X-ray crystallography, Scheme 4). Isolated complex **28** provides

Scheme 4. Novel Digold−Thiolate Complex 28



only 6% conversion to **16c** when used as a catalyst, implying that such species are not efficient precatalysts for the reaction,[17] but may be a possible mode of deactivation in gold(I)-catalyzed reactions with thiols.

In conclusion, we have shown that various thiol *S*-nucleophiles react in a mild and facile manner to produce either **14** or **16** in good yields and selectivities. Echavarren's catalyst **17** appears more tolerant of deactivation by thiols compared to other gold(I) catalysts screened, and analysis of **17** in the presence of thiophenol led to the characterization of a novel digold−thiolate species **28**, which sheds light on a

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possible mode of deactivation by thiols. Pleasingly, the dampening of catalyst activity in the presence of thiols allows for very *chemoselective* thiol additions in the presence of other nucleophilic functional groups. We hope that our successful results presented here and in particular our investigations into the activity of various commonly used gold(I) catalysts will open the door for more future work on gold-catalyzed C−S bond formations.

EXPERIMENTAL SECTION

The gold(I)-catalyzed reactions were carried out without the need for dry solvents or inert atmosphere, except for the deuterium labeling study (Scheme 3). 3,3-Disubstituted cyclopropene substrates **18**−**25** were synthesized following previously reported procedures.[7a,b,f,18]

The following three-step procedure describes the synthesis of **13** via **29** and **30**.

1,1-Dibromo-2,2-dihexylcyclopropane 29. A solution of bromoform (2.4 mL, 26.5 mmol) in CH_2Cl_2 (0.6 mL) was added dropwise over 30 min to a stirring mixture of aqueous sodium hydroxide (5.8 mL, 10 M), alkyltrimethylammonium bromide (0.54 g), 7-methylenetridecane (2.59 g, 13.2 mmol) and CH_2Cl_2 (2.5 mL). The mixture was allowed to stir vigorously at 35 °C overnight. The reaction mixture was then diluted with water (30 mL), CH_2Cl_2 (40 mL) was added, and the layers were partitioned. The aqueous layer was washed twice with CH_2Cl_2 (40 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (hexane), and the remaining bromoform was evaporated under high vacuum (21 h, 35 °C) to yield the title compound (4.33 g, 11.7 mmol, 89%) as a colorless oil: ν_{max}/cm^{-1} 2954 m 2925 s 2857 m (C−H), 1457 m (alkyl C−H bend); ^1H NMR (300 MHz, $CDCl_3$) δ 1.73−1.19 (m, 22H), 0.95−0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.3 (C), 35.1 (CH_2), 34.4 (CH_2), 33.3 (C), 31.9 (CH_2), 29.5 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{15}H_{29}Br_2$ $[M + H]^+$ 367.0631, found 367.0627.

2-Bromo-1,1-dihexylcyclopropane 30. A solution of ethylmagnesium bromide (1.0 M in THF, 13 mL, 13 mmol) was added over 1.5 h to a stirring solution of 1,1-dibromo-2,2-dihexylcyclopropane (4.00 g, 10.9 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.09 mmol) and THF (35 mL). The solution was allowed to stir for an additional 3 h at room temperature. The reaction was quenched by slow addition of water (35 mL), and then 20% aqueous sulfuric acid (80 mL) was added, and the resulting mixture was stirred for 30 min. Diethyl ether (70 mL) was added, and the layers were partitioned. The aqueous layer was washed a further two times with diethyl ether (70 mL). The combined organic layers were washed with saturated sodium bicarbonate (90 mL) and brine (90 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash column chromatography (pentane) to yield the title compound (2.34 g, 8.09 mmol, 74%) as a colorless oil: ν_{max}/cm^{-1} 2956 m 2925 s 2857 m (C−H), 1458 m (alkyl C−H bend); ^1H NMR (300 MHz, $CDCl_3$) δ 2.82 (dd, J = 7.6, 4.3 Hz, 1H), 1.58−1.14 (m, 20H), 0.97−0.81 (m, 7H,), 0.60 (dd, J = 6.0, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5 (CH_2), 33.3 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 30.3 (CH), 29.7 (CH_2), 29.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 25.0 (C), 22.8 (CH_2), 22.8 (CH_2), 22.2 (CH_2), 14.3 (CH_3), 14.2 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{15}H_{30}Br$ $[M + H]^+$ 289.1525, found 289.1518.

3,3-Dihexylcycloprop-1-ene 13.[19] Potassium *tert*-butoxide (1.44 g, 12.8 mmol) was dissolved in DMSO (20 mL). 2-Bromo-1,1-dihexylcyclopropane **30** (2.30 g, 7.95 mmol) was added dropwise over 15 min. The reaction mixture was allowed to stir overnight at 55 °C and then quenched by addition of water (100 mL). Pentane (100 mL) was added and the layers partitioned. The aqueous layer was washed four times with pentane (50 mL). The combined organic layers were washed three times with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (pentane) to yield **13** (1.37 g, 6.57 mmol, 88%) as a colorless oil: ν_{max}/cm^{-1} 2958 m 2921 s 2853 m (C−H), 1629 w (C═C) 1457 m (alkyl C−H bend); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 2H), 1.47−0.97 (m, 20H), 0.87 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.1 (CH), 38.8 (CH_2), 32.2 (CH_2), 29.6 (CH_2), 27.2 (CH_2), 24.8 (C), 22.9 (CH_2), 14.3 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{15}H_{29}$ $[M + H]^+$ 209.2264, found 209.2258.

Representative Procedure for Gold-Catalyzed Aniline Additions to 3,3-Disubstituted Cyclopropenes to Form *tert*-Allylic Amines 3. *4-Methoxy-N-(2-methyl-1-phenylbut-3-en-2-yl)-aniline (**3**, R^1 = Me, R^2 = Bn, Ar = p-OMeC$_6$H$_4$).* To a stirred solution of cyclopropene **20** (17.3 mg, 0.12 mmol) and anisidine (12.3 mg, 0.10 mmol) in CH_2Cl_2 (1 mL, 0.1 M), catalyst **17** was added in one portion (3.8 mg, 0.0051 mmol, 5 mol %). The resultant yellow solution was stirred for 18 h, after which point it had become dark yellow/brown. The mixture was then evaporated to dryness (^1H NMR analysis shows 42% conv), and the residue was purified by flash column chromatography (petrol ether:EtOAc, 9:1) to give the title compound as a yellow film (9 mg, 0.034 mmol, 34%): ν_{max}/cm^{-1} 3391 w (N−H) 2929 w (C−H), 1602 w (C═C), 1508 s (Ar C═C), 1234 m (C−O−C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.18 (m, 3H), 7.16−7.08 (m, 2H), 6.76−6.64 (m, 4H), 6.06 (dd, J = 17.5, 10.8 Hz, 1H), 5.20−5.10 (m, 2H), 3.73 (s, 3H), 3.40 (br s, 1H), 3.12 (d, J = 13.1 Hz, 1H), 2.81 (d, J = 13.1 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (C), 145.8 (CH), 140.2 (C), 137.1 (C), 130.9 (CH), 127.9 (CH), 126.5 (CH), 118.3 (CH), 114.3 (CH), 113.7 (CH_2), 57.8 (C), 55.7 (CH_3), 45.6 (CH_2), 25.3 (CH_3). HRMS (APCI-Orbitrap) m/z calcd for $C_{18}H_{22}ON$ $[M]^+$ 268.1696, found 268.1691.

Representative Procedure for Gold-Catalyzed Thioacid Additions to 3,3-Disubstituted Cyclopropenes to Form Allylic Thioester 14. *S-3-Hexylnon-2-enyl Benzothioate **14a**.* A solution of thiobenzoic acid (7.5 μL, 8.7 mg, 0.064 mmol) and PPh_3AuNTf_2 (2:1 toluene complex, 2.3 mg, 0.0031 mmol) in CH_2Cl_2 (0.31 mL) was added to a solution of 3,3-dihexylcycloprop-1-ene **13** (13 mg, 0.062 mmol) in CH_2Cl_2 (0.31 mL) at 25 °C and stirred for 10 min. The solution was then concentrated under reduced pressure and filtered through a plug of silica (hexane:Et_2O, 10:1). The crude mixture was then purified using flash column chromatography (hexane:Et_2O, 50:1) to yield a 9:1 ratio of **14a**:**15a** (17.2 mg, 0.0496 mmol, 80%) as a clear colorless oil: ν_{max}/cm^{-1} 2955 w (C−H), 2925 m (C−H), 2855 w (C−H), 1662 s (C═O); 1597 w, 1581 w, 1448 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06−7.40 (m, 5H), 5.31 (t, J = 7.7 Hz, 1H), 3.78 (d, J = 7.7 Hz, 2H), 2.19−2.09 (t, J = 7.5 Hz, 2H), 2.09−1.98 (t, J = 7.4 H, 2H), 1.50 - 1.23 (m, 16H), 0.99 - 0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3 (C), 145.4 (C), 137.2 (C), 133.2 (CH_2), 128.6 (CH), 127.2 (CH), 118.0 (CH), 36.9 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 30.3 (CH_2), 29.7 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 27.9 (CH_2), 27.2 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 14.1 (2 x CH_3); HRMS (ESI-Orbitrap) m/z calcd for $C_{22}H_{35}OS$ $[M + H]^+$ 347.2406, found 347.2403.

*S-3-Hexylnon-2-enyl Ethanethioate **14b**.* Clear colorless oil (13.8 mg, 76%, 9:1 **14b**:**15b**): ν_{max}/cm^{-1} 2956 w (C−H), 2926 m (C−H), 2856 w (C−H), 1683 s (C−H); ^1H NMR (300 MHz, $CDCl_3$) δ 5.20 (t, J = 8.0 Hz, 1H), 3.57 (d, J = 8.0 Hz, 2H), 2.39−2.29 (s, 3H), 2.06 (t, J = 7.4 Hz, 2H), 2.00 (t, J = 7.4 Hz, 2H), 1.45−1.18 (m, 16H), 1.00−0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3 (C), 145.1 (C), 118.1 (CH), 36.9 (CH_2), 31.92 (CH_2), 31.88 (CH_2), 30.6 (CH_3), 30.3 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 28.0 (CH_2), 27.3 (CH_2), 22.7 (CH_2), (plus an overlapping peak), 14.3 (2 x CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{17}H_{33}OS$ $[M + H]^+$ 285.2247, found 285.2249.

*(E/Z)-S-3-Methyldodec-2-enyl Benzothioate **14i**.* Clear colorless oil (17.2 mg, 67%, 6:1 ratio **14i**:**15i** and approximately 1.25:1 *E*:*Z* ratio of **14i**): ν_{max}/cm^{-1} 2923 s (C−H), 2853 m (C−H), 1661 s (C═O), 1597 w, 1582 w, 1448 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 - 7.38 (m, 5H),, 5.39−5.30 (m, 1H), 3.76 (d, J = 8.1 Hz, 2H), 2.22−2.09 (m, (E) 2H), 2.09−1.98 (m, (Z) 2H′), 1.76 (s, 3H) 1.52−1.16 (m, 14H), 0.98−0.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2 (2xC), 141.3 (C), 141.0 (C), 137.2 (C), 137.1 (C), 133.2

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(2xCH), 128.6 (2x CH), 127.2 (2xCH), 118.6 (CH), 118.0 (CH), 40.1 (CH_2), 39.6 (CH_2), 31.9 ($2xCH_2$), 31.9 ($2xCH_2$), 29.6 ($2xCH_2$), 29.4 (CH_2), 29.2 ($2xCH_2$), 28.1 (CH_2), 27.7 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 23.5 (CH_3), 22.7 ($2xCH_2$), 16.2 (CH_3), 14.1 ($2xCH_3$); HRMS (ESI-Orbitrap) m/z calcd for $C_{20}H_{31}OS$ $[M + H]^+$ 319.2090, found 319.2094.

(E/Z)-S-3-Methyl-5-phenylpent-2-enyl Benzothioate ***14j***. Clear colorless oil (16.9 mg, 63%, *mixture*: 6:1 ratio **14j**:**15j** and ∼1:1 *E*:*Z* ratio of **14j**): ν_{max}/cm^{-1} 2923 s (C−H), 2853 m (C−H), 1661 s (C═O), 1597 vw, 1581 w, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.08−7.39 (m, 5H + 5H′ (*E* and *Z*)), 7.39−7.05 (m, 5H + 5H′), 5.41−5.33 (m, 1H + 1H′), 3.76 (d, J = 8.1 Hz, (*Z*) 2H), 3.70−3.53 (d, J = 8.4 Hz, (*E*) 2H′), 2.88−2.66 (m, 2H + 2H′), 2.56 - 2.22 (m, 2H + 2H′), 1.93−1.69 (m, 3H + 3H′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2 (C), 192.1 (C), 141.9 (C), 141.8 (C), 139.9 (C), 139.7 (C), 137.1 (C), 137.1 (C), 132.2 (2xCH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (2xCH), 128.3 (CH), 126.2 (2xCH), 124.9 (CH), 124.8 (CH), 119.9 (CH), 119.0 (CH), 40.4 (CH_2), 33.3 ($2xCH_2$), 33.1 (CH_2), 27.2 (CH_2), 26.9 (CH_2), 22.5 (CH_3), 16.5 (CH_3); HRMS (ESI-Orbitrap) m/z calcd for $C_{19}H_{21}OS$ $[M + H]^+$ 297.1308, found 297.1313.

(E/Z)-S-3-Methyl-4-phenylbut-2-enyl Benzothioate ***14k***. Clear colorless oil (15.3 mg, 62%, 14:1 ratio **14k**:**15k** and 1.7:1 *E*:*Z* ratio of **14k**): ν_{max}/cm^{-1} 3061 vw (C−H), 3026 w (C−H), 2914 w (C−H), 1657 s (C═O), 1598 w, 1580 w, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.08−7.40 (m, 5H + 5H′), 7.40−7.11 (m, 5H + 5H′), 5.59−5.43 (m, 1H + 1H′), 3.90 (d, J = 8.1 Hz, (*Z*) 2H), 3.81 (d, J = 7.7 Hz, (*E*) 2H′), 3.54 (s, (*Z*) 2H), 3.36 (s, (*E*) 2H′), 1.79−1.66 (6H, m, 3H + 3H′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1 (C), 192.1 (C), 139.7 (C), 139.5 (C), 139.2 (C), 139.0 (C), 137.1 (C), 137.1 (C), 133.3 (CH), 133.3 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.3 (CH), 127.2 (CH), 126.2 (CH), 126.1 (CH), 120.5 (CH) (plus overlapping peaks), 46.0 (CH_2), 37.9 (CH_2), 27.3 (CH_2), 27.3 (CH_2), 23.4 (CH_3), 16.1 (CH_3); HRMS (ESI-Orbitrap) m/z calcd for $C_{18}H_{19}OS$ $[M + H]^+$ 283.1151, found 283.1155.

(E/Z)-S-3-Benzyl-4-methylpent-2-enyl Benzothioate ***14l***. Clear colorless oil (14.8 mg, 73%, 13:2:1 ratio **14l**:**15l**:**16l** and 1:3 *E*:*Z* ratio of **14l**): ν_{max}/cm^{-1} 3060 vw (C−H), 3025 vw (C−H), 2960 w (C−H), 2927 w (C−H), 2870 vw (C−H), 1660 s (C═O), 1598 w, 1580 w, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04−7.43 (m, 5H + 5H′), 7.37−7.14 (m, 5H + 5H′), 5.58 (t, J = 7.9 Hz, 1H′ (*E*)), 5.10 (t, J = 8.1 Hz, 1H (*Z*)), 3.87−3.79 (m, 2H + 2H′), 3.60 (s, 2H′(*E*)), 3.36 (s, 2H (*Z*)), 3.11−2.99 (m, 1H (*Z*)), 2.32−2.21 (m, 1H′ (*E*)), 1.07 (d, J = 6.9 Hz, 6H (*Z*)), 1.02 (d, J = 6.9 Hz, 6H′ (*E*)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1 (C), 192.0 (C), 149.4 (C), 148.3 (C), 140.1 (C), 139.7 (C), 137.3 (C), 137.1 (C), 133.3 (CH), 133.3 (CH), 131.0 (CH), 129.4 (CH), 128.2 (CH), 127.2 (CH), 126.0 (CH), 126.0 (CH), 119.8 (CH), 118.3 (CH), (plus overlapping peaks), 38.1 (CH_2), 35.3 (CH_2), 34.0 (CH), 29.3 (CH), 27.5 (CH_2), 26.6 (CH_2), 21.9 (CH_3), 21.4 (CH_3); HRMS (ESI-Orbitrap) m/z calcd for $C_{20}H_{23}OS$ $[M + H]^+$ 311.1464, found 311.1470.

(E)-S-3-(3-(Adamantan-1-yl)but-2-enyl Benzothioate ***14m***. Clear colorless oil (15.8 mg, 78%, 10:1 **14m**:**15m**): ν_{max}/cm^{-1} 2900 s (C−H), 2847 m (C−H), 1660 s (C═O); 1596 vw, 1581 vw, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06−7.40 (m, 5H), 5.34 (t, J = 7.8 Hz, 1H), 3.79 (d, J = 7.8 Hz, 2H), 2.03 (br-s, 3H), 1.79−1.60 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4 (C), 149.1 (C), 137.2 (CH), 133.2 (CH), 128.6 (CH), 127.2 (CH), 115.3 (CH), 40.7 (CH_2) 38.0 (C), 37.0 (CH_2), 36.9 (CH_2), 28.6 (CH), 27.7 (CH_2), 11.9 (CH_3); HRMS (ESI-Orbitrap) m/z calcd for $C_{21}H_{27}OS$ $[M + H]^+$ 327.1777, found 327.1781.

S-3,3-Dicyclohexylallyl Benzothioate ***14n***. Clear colorless oil (19.7 mg, 94%, 7:1 ratio of **14n**:**16n**): ν_{max}/cm^{-1} 2922 s (C−H), 2849 m (C−H), 1660 s (C═O), 1597 vw, 1581 w, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04−7.40 (m, 5H),, 5.37−5.25 (t, J = 8.1 Hz, 1H), 3.83 (d, J = 8.1 Hz, 2H), 2.01−0.98 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5 (C), 155.6 (C), 137.2 (C), 133.2 (CH), 128.7 (CH), 127.2 (CH), 115.8 (CH), 40.9 (CH), 40.52 (CH), 34.7 (CH_2), 31.0 (CH_2), 27.1 (CH_2), 27.0 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 26.1 (CH_2); HRMS (ESI-Orbitrap) m/z calcd for $C_{22}H_{31}OS$ $[M + H]^+$ 343.2090, found 343.2094.

Representative Procedure for Gold-Catalyzed Thiophenol or Thiol Additions to 3,3-Disubstituted Cyclopropenes to Form Vinyl Thioether 16. *(E)-(3-Hexylnon-1-enyl)(phenyl)sulfane* ***16c***. A solution of thiophenol (7 μL, 8.1 mg, 0.065 mmol) and catalyst **17** (2.5 mg, 0.0033 mmol) in CH_2Cl_2 (0.33 mL) was added to a solution of 3,3-dihexylcycloprop-1-ene **13** (13.6 mg, 0.065 mmol) in CH_2Cl_2 (0.32 mL) at 25 °C and stirred for 30 min. The solution was then concentrated under reduced pressure and filtered through a plug of silica (hexane:Et_2O, 10:1). The crude mixture was then purified using flash column chromatography (hexane:Et_2O, 50:1) to yield (*E*)-(3-hexylnon-1-enyl)(phenyl)sulfane **16c** (15 mg, 0.047 mmol, 72%) as a clear colorless oil: ν_{max}/cm^{-1} 2955 m (C−H), 2923 s (C−H), 2853 m (C−H), 1584 w, 1479 m, 1466 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.12 (m, 5H), 6.10 (d, J = 14.9 Hz,1H), 5.79 (dd, J = 9.2, 14.9 Hz, 1H), 2.20−2.07 (m, 1H), 1.51−1.19 (m, 20H), 1.00−0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (CH), 137.0 (C), 129.9 (CH), 128.1 (CH), 125.9 (CH), 119.9 (CH), 43.8 (CH), 35.1 (CH_2), 31.9 (CH_2), 29.4 (CH_2), 27.3 (CH_2), 22.7 (CH_2), 14.2 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{21}H_{35}S$ $[M + H]^+$ 319.2454, found 319.2455.

(E)-Benzyl(3-hexylnon-1-enyl)sulfane ***16d***. Clear colorless oil (17.3 mg, 81%): ν_{max}/cm^{-1} 2955 m (C−H), 2925 s (C−H), 2853 m (C−H), 1602 w, 1494 w, 1453 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.46−7.18 (m, 5H), 5.84 (d, J = 15.0 Hz, 1H), 5.43 (dd, J = 9.0, 15.0 Hz, 1H), 3.99−3.81 (m, 2H), 2.04−1.88 (m, 1H), 1.44−1.01 (m, 20H), 0.91 (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0 (CH), 136.9 (CH), 127.7 (CH), 127.4 (CH), 125.9 (CH), 120.0 (CH), 42.7 (CH), 36.7 (CH_2), 34.3 (CH_2), 30.8 (CH_2), 28.4 (CH_2), 26.1 (CH_2), 21.7 (CH_2), 13.1 (CH_2); HRMS (APCI-Orbitrap) m/z calcd for $C_{22}H_{37}S$ $[M + H]^+$ 333.2610, found 333.2613.

(E)-tert-Butyl(3-hexylnon-1-en-1-yl)sulfane ***16e***. Clear colorless oil (18.1 mg, 84%): ν_{max}/cm^{-1} 2956 m 2925 s 2854 s (C−H), 1601 w (C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 5.98 (d, J = 14.8 Hz, 1H), 5.63 (dd, J = 14.8, 9.2 Hz, 1H), 2.10−1.93 (m, 1H), 1.32 (s, 9H), 1.47−1.08 (m, 20H), 0.87 (t, J = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (CH), 119.1 (CH), 44.0 (CH), 43.7 (C), 35.4 (CH_2), 32.0 (CH_2), 30.9 (CH_3), 29.5 (CH_2), 27.4 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (APCI-Orbitrap) m/z calcd for $C_{19}H_{39}S$ $[M + H]^+$ 299.2767, found 299.2771.

(E)-2-(((3-Hexylnon-1-en-1-yl)thio)methyl)furan ***16f***. Yellow oil (20.3 mg, 86%): ν_{max}/cm^{-1} 2957 m 2922 s, 2854 m (C−H), 1594 w (C═C), 1503 m, 1458 m (Ar C═C) 1010 s (C−O−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 1.9, 0.8 Hz, 1H), 6.29 (dd, J = 3.2, 1.9 Hz, 1H), 6.18 (dd, J = 3.2, 0.8 Hz, 1H), 5.84 (d, J = 15.0 Hz, 1H), 5.45 (dd, J = 15.0, 9.2 Hz, 1H), 3.83 (s, 2H), 2.03−1.90 (m, 1H), 1.45−1.07 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6 (C), 142.2 (CH), 138.9 (CH), 120.8 (CH), 110.5 (CH), 107.6 (CH), 43.9 (CH), 35.4 (CH_2), 32.0 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 27.3 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (APCI-Orbitrap) m/z calcd for $C_{20}H_{35}OS$ $[M + H]^+$ 323.2403, found 323.2405.

(E)-2-((3-Hexylnon-1-en-1-yl)thio)ethanol ***16g***. Clear colorless oil (17.1 mg, 82%): ν_{max}/cm^{-1} 3400−3200 br. w (O−H), 2955 m, 2921 s, 2854 s (C−H), 1606 w (C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (d, J = 15.0 Hz, 1H), 5.51 (dd, J = 15.0, 9.1 Hz, 1H), 3.81−3.71 (m, 2H), 2.83 (t, J = 5.9 Hz, 2H), 2.12−1.90 (m, 2H), 1.40−1.08 (m, 20H), 0.87 (t, J = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2 (CH), 120.4 (CH), 60.7 (CH_2), 43.9 (CH), 36.5 (CH_2), 35.3 (CH_2), 32.0 (CH_2), 29.5 (CH_2), 27.4 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (APCI-Orbitrap) m/z calcd for $C_{17}H_{35}OS$ $[M + H]^+$ 287.2403, found 287.2406.

(E)-3-((3-Hexylnon-1-en-1-yl)thio)propanoic Acid ***16h***. Clear colorless oil (16.5 mg, 73%): ν_{max}/cm^{-1} 3100−2700 br. w (O−H), 2956 m 2924 s 2854 s (C−H), 1711 s (C═O), 1604 w (C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 10.78−9.74 (br s, 1H), 5.80 (d, J = 15.0 Hz, 1H), 5.46 (dd, J = 15.0, 9.1 Hz, 1H), 2.88 (t, J = 7.0 Hz, 2H), 2.69 (t, J = 7.0 Hz, 2H), 2.08−1.91 (m, 1H), 1.41−1.10 (m, 20H), 0.87 (t, J = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2 (C), 139.0 (CH),

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120.5 (CH), 43.9 (CH), 35.4 (CH_2), 34.5 (CH_2), 32.0, (CH_2) 29.5 (CH_2), 27.6 (CH_2), 27.4 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI-Orbitrap) m/z calcd for $C_{18}H_{33}O_2S$ $[M - H]^-$ 313.2207, found 313.2198.

(E)-(3-Methyldodec-1-enyl)(phenyl)sulfane **16o**. Clear colorless oil (14.9 mg, 84%): ν_{max}/cm^{-1} 2970 s (C−H), 2922 s (C−H), 1583 w, 1454 m, 1439 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.26−7.39 (m, 5H), 6.05−6.21 (d, J = 15.0 Hz, 1H), 5.84 - 6.02 (dd, J = 15.0, 7.9 Hz, 1H), 2.21−2.41 (m, 1H), 1.16−1.44 (m, 16H), 1.01−1.13 (d, J = 6.6 Hz, 3H), 0.82−0.98 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (CH), 136.8 (C), 128.9 (CH), 128.3 (CH), 125.9 (CH), 119.0 (CH), 37.6 (CH), 36.8 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 20.4 (CH_3), 14.2 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{19}H_{31}S$ $[M + H]^+$ 291.2141, found 291.2142.

The reaction was also carried out on a larger 1.11 mmol scale to give a clear colorless oil (256 mg, 78%).

(E)-(3-Methyl-5-phenylpent-1-enyl)(phenyl)sulfane **16p**. Clear colorless oil (23.2 mg, 90%): ν_{max}/cm^{-1} 2969 s (C−H), 2922 s (C−H), 1594 w, 1582 m, 1494 m, 1478 m, 1453 m, 1439 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44−7.12 (m, 10H), 6.25−6.12 (d, J = 15.0 Hz, 1H), 5.95 (dd, J = 8.1, 15.0 Hz, 1H), 2.78−2.56 (m, 2H), 2.43−2.29 (m, 1H), 1.71 (q, J = 7.6 Hz, 2H), 1.20−1.04 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4 (CH), 142.3 (C), 136.5 (C), 129.0 (CH), 128.5 (CH) 128.4 (CH) 128.4 (CH) 129.2 (CH) 125.8 (CH) 120.11 (CH), 38.5 (CH_2), 37.2 (CH), 33.7 (CH_2), 20.48 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{18}H_{21}S$ $[M + H]^+$ 269.1358, found 269.1361.

(E)-(3-(3-(Adamantan-1-yl)but-1-enyl)(phenyl)sulfane **16q**. Clear colorless oil (15.7 mg, 76%): ν_{max}/cm^{-1} 2946 m (C−H), 2925 s (C−H), 2847 m (C−H), 1582 w, 1478 m, 1438 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43−7.25 (m, 5H), 6.16−5.93 (m, 2H), 2.09−1.94 (m, 3H), 1.98−1.84 (m, 1H), 1.83−1.46 (m, 12H), 1.07−0.93 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7 (CH) 137.0 (C), 128.9 (CH), 128.2 (CH), 125.9 (CH), 120.0 (CH), 48.7 (CH), 39.9 (CH_2), 37.2 (CH_2), 34.9 (C), 28.7 (CH), 13.8 (CH_3); HRMS (APCI-Orbitrap) m/z calcd for $C_{20}H_{27}S$ $[M + H]^+$ 299.1828, found 299.1830.

(E)-(3,3-Dicyclohexylprop-1-enyl)(phenyl)sulfane **16r**. Clear colorless oil (10.8 mg, 56%): ν_{max}/cm^{-1} 2928 s (C−H), 2850 m (C−H), 1583 w, 1478 w, 1447 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39−7.26 (m, 5H), 6.08−5.95 (d, J = 15.0 Hz, 1H), 5.88 - 5.73 (dd, J = 10.4, 15.0 Hz, 1H), 1.86−0.78 (m, 23H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2 (CH) 137.0 (C), 128.9 (CH), 128.1 (CH), 125.8 (CH), 121.1 (CH), 55.7 (CH), 37.7 (CH), 32.0 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 26.7 (CH_2), 26.6 (CH_2); HRMS (APCI-Orbitrap) m/z calcd for $C_{21}H_{31}S$ $[M + H]^+$ 315.2141, found 315.2146.

(E)-2-(((3-Methyl-4-phenylbut-1-en-1-yl)thio)methyl)furan **16s**. Clear colorless oil (7.1 mg, 27%): ν_{max}/cm^{-1} 3026 w 2959 m 2923 m (C−H), 1601 m (C═C), 1497 m 1453 m (Ar C═C) 1010 s (C−O−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (dd, J = 1.9, 0.8 Hz, 1H), 7.31−7.06 (m, 5H), 6.29 (dd, J = 3.2, 1.9 Hz, 1H), 6.12 (dd, J = 3.2, 0.8 Hz, 1H), 5.86 (d, J = 15.2 Hz, 1H), 5.68 (dd, J = 15.1, 6.9 Hz, 1H), 3.79 (s, 2H), 2.71−2.40 (m, 3H), 0.98 (d, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4 (C), 142.2 (CH), 140.4 (C), 137.8 (CH), 129.4 (CH), 128.3 (CH), 126.0 (CH), 120.7 (CH), 110.6 (CH), 107.7 (CH), 43.5 (CH_2), 39.3 (CH), 29.9 (CH_2), 19.8 (CH_3). HRMS (APCI-Orbitrap) m/z calcd for $C_{16}H_{19}OS$ $[M + H]^+$ 259.1151, found 259.1151.

(E)-(3-Deutero-3-hexylnon-1-en-1-yl)(phenyl)sulfane **26**. Deuterated thiophenol **27**[20] (77% D-incorporation, 7.4 μL, 7.9 mg, 0.072 mmol) was added via syringe to a solution of catalyst **17** (2.9 mg, 0.0038 mmol) in dry CH_2Cl_2 (0.42 mL). The resulting solution was transferred immediately to a solution of cyclopropene **13** in dry CH_2Cl_2 (0.30 mL) via syringe. The reaction was stirred at 25 °C for 30 min under argon, and then the mixture was filtered through a short plug of silica using 10:1 hexane:diethyl ether to yield the product as a colorless oil (4.9 mg, 0.047 mmol, 65%), with approximately 49% D-incorporation by ^1H NMR, and MS data indicates 55% ± 10% D-incorporation: ν_{max}/cm^{-1} 2955 m 2923 s 2854 s (C−H), 2163 w (C-D), 1679 w (C═C), 1584 m 1479 m (Ar C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.27 (m, 4H), 7.23−7.14 (m, 1H), 6.07 (d, J = 14.9 Hz, 1H), 5.76 (dd, J = 14.9, 9.2 Hz, 1H, from nondeuterated), 5.76 (d, J = 14.9 Hz, 1H), 2.17−2.06 (m, 1H, from nondeuterated), 1.47−1.13 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.13 (CH nondeuterated), 143.10 (CH deuterated), 137.1 (C), 129.0 (CH), 128.3 (CH), 126.0 (CH), 120.09 (CH nondeuterated), 120.07 (CH deuterated), 43.9 (CH nondeuterated), 43.4 (t, J = 19.1 HZ, CD), 35.3 (CH_2 nondeuterated), 35.2 (CH_2 deuterated), 32.0 (CH_2), 29.5 (CH_2), 27.5 (CH_2 nondeuterated), 27.4 (CH_2 deuterated), 22.8 (CH_2), 14.3 (CH_3). HRMS (EI-ion trap) m/z calcd for $C_{21}H_{33}DS$ $[M]^+$ 319.2439, found 319.2434.

Complex **28**. Thiophenol (2.8 mg, 2.7 μL, 0.026 mmol) was added to a solution of catalyst **17** (20 mg, 0.026 mmol) in CH_2Cl_2 (0.70 mL). Single crystals were grown from slow evaporation of the CH_2Cl_2 solution: mp 184 °C (decomposes); ν_{max}/cm^{-1} 2951 m 2886 w (C−H), 1577 m 1469 m 1440 m (Aromatic C═C); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.93−7.84 (m, 2H), 7.62−7.45 (m, 6H), 7.35−7.16 (m, 11H), 7.15−7.09 (m, 4H), 1.37 (d, $J(^1H-^{31}P)$ = 15.8 Hz, 36H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 149.8 (d, $J(^{13}C-^{31}P)$ = 14.2 Hz, C), 143.3 (d, $J(^{13}C-^{31}P)$ = 6.7 Hz, C), 134.4 (CH), 133.73 (d, $J(^{13}C-^{31}P)$ = 7.6 Hz, CH), 133.72 (CH), 131.7 (CH), 129.9 (CH), 129.7 (CH), 129.3 (CH), 129.2 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.8 (C), 127.5 (CH), 125.8 (d, $J(^{13}C-^{31}P)$ = 44.3 Hz, C), 38.5 (d, $J(^{13}C-^{31}P)$ = 23.7 Hz, C), 31.3 (d, $J(^{13}C-^{31}P)$ = 6.9 Hz, CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 62.87. Crystal Data: $C_{46}H_{59}Au_2F_6P_2SSb$, M = 1335.61, monoclinic, a = 24.6918(3) Å, b = 13.08924(15) Å, c = 29.3558(4) Å, β = 90.7654(11)°, V = 9486.84(19) Å^3, T = 120.01(10), space group Cc (no. 9), Z = 8, μ(Cu Kα) = 17.388, 77919 reflections measured, 19283 unique (R_{int} = 0.0447), which were used in all calculations. The final wR_2 was 0.0820 (all data) and R_1 was 0.0313 (>2$\sigma(I)$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, initial optimization studies, X-ray data for compound **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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