Insertion of Carbon Monoxide into Allylic Carbon–Sulfur Bonds Catalyzed by Palladium and Ruthenium Complexes

Cathleen M. Crudden and Howard Alper*

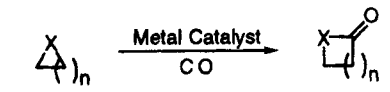
Department of Chemistry, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario, Canada K1N 6N5

Received January 27, 1995[⊗]

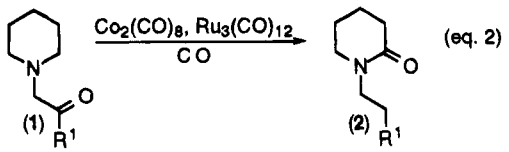
The metal complex-catalyzed insertion of carbon monoxide into the C–S bond of various allylic sulfides affords thioesters in up to 88% yield. The reaction is catalyzed by various palladium complexes, with concomitant isomerization of the olefin into conjugation with the carbonyl group. In these cases, only the trans isomer was detected by ^{1}H NMR spectroscopy. Ruthenium complexes also catalyzed the carbonylation but the initially formed β,γ-thioester was not isomerized.

Introduction

The insertion of carbon monoxide into carbon–heteroatom bonds can be effected by a variety of transition metal catalysts. In most cases, the reaction, which presumably begins by insertion of the metal into the carbon–heteroatom bond, is driven or at least aided by ring strain (eq 1). Carbonylative ring expansions have been reported for aziridines,[1a,b] azirines,[1c,d] azetidines,[1e] oxetanes,[2] thietanes,[2] and thiranes.[3a,b] Using more severe conditions, unstrained heterocycles such as pyrrolidines can be carbonylated,[4] and a novel rearrangement (**1** to **2**) reaction (eq 2) was discovered during this study which is applicable to five to eight-membered ring heterocycles having a CH_2COR group attached to the nitrogen atom.[4]

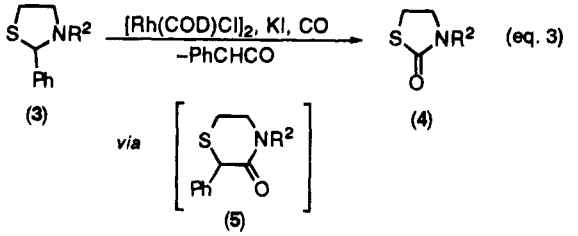


(eq. 1)

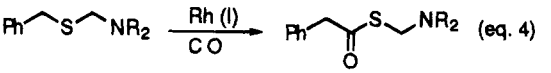


(eq. 2)

Recently, one of us reported a second example of the carbonylation of a nonstrained heterocycle.[5a] Thiazolidines **3** undergo reaction with carbon monoxide, catalyzed by $[Rh(COD)Cl]_2$, to form thiazolidinones **4** (eq 3). This process occurs via the intermediate thiazinone **5** which undergoes subsequent ketene elimination and carbonylation. It was found that even *acyclic* carbon–heteroatom bonds could be carbonylated using similar conditions (eq 4).[5b]



(eq. 3)



(eq. 4)

This is the first example of the insertion of CO into an acyclic carbon heteroatom bond that did not involve the formation of a π-allylic intermediate. The carbonylation of allylic compounds including acetates, carbonates, and phosphonates has been extensively investigated by researchers such as Murahashi, Tsuji, and Yamamoto.[6] By choosing an appropriate nucleophile, a wide variety of carbonyl-containing compounds can be prepared under mild conditions (eq 5). Alternatively, depending on the substrate, external nucleophiles need not be employed and a direct carbonylation can be carried out.[7] Recently, Murahashi and co-workers have published a full account of the first example of a direct carbonylation of an allylamine which is shown below (eq 6, X = NR_2).[8] Another technique was recently reported for the synthe-

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

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(2) Wang, M.; Calet, S.; Alper, H. *J. Org. Chem.* **1989**, *54*, 20.

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(4) Wang, M.; Alper, H. *J. Am. Chem. Soc.* **1992**, *114*, 7018.

(5) (a) Khumtaveeporn, K.; Alper, H. *J. Am. Chem. Soc.* **1994**, *116*, 5662. (b) Khumtaveeporn, K.; Alper, H. *J. Org. Chem.* **1994**, *59*, 1414.

(6) (a) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350. (b) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144. (c) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341. (d) Dent, W. T.; Long, R.; Whitfield, G. H. *J. Chem. Soc.* **1964**, 1588. (e) Ishii, Y.; Gao, C.; Xu, W.-X.; Iwasaki, M.; Hidai, M. *J. Org. Chem.* **1993**, *58*, 6818. (f) Iwasaki, M.; Kobayashi, Y.; Li, J.-P.; Matsuda, H.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922. (g) Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* **1988**, *53*, 3832. (h) Murahashi, S.-I.; Imada, Y.; Taniguchi, Y.; Higashiura, S. *J. Org. Chem.* **1993**, *58*, 1538, and references cited therein. (i) Murahashi, S.-I.; Imada, Y.; Taniguchi, Y.; Higashiura *Tetrahedron Lett.* **1988**, *29*, 4945. (j) For an excellent review on various aspects of π-allylic chemistry see: Yamamoto, A. *Adv. Organomet. Chem.* **1992**, *34*, 111. (k) Kiji, J.; Okano, T.; Ono, I.; Konishi, H. *J. Mol. Catal.* **1987**, *39*, 355.

(7) By direct carbonylation we are referring to the insertion of carbon monoxide into the C–N bond. There are many examples of the hydroformylation of allylamines: (a) Ojima, I.; Zhang, Z. *J. Organomet. Chem.* **1991**, *417*, 99. (b) Anastassiou, D.; Jackson, W. R. *J. Organomet. Chem.* **1991**, *413*, 399. (c) Alper, H.; Zhou, J.-Q. *J. Org. Chem.* **1992**, *57*, 3329.

(8) (a) Murahashi, S.-I.; Yasushi, I.; Nishimura, K. *Tetrahedron* **1994**, *50*, 453. (b) Murahashi, S.-I.; Imada, Y.; Nishimura, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1578. The carbonylation of allylamine with dicobalt octacarbonyl under photolytic conditions was reported to give low yields (17%) of the product arising from carbonylation of the C–N bond: (c) Mori, S.; Matsuyoshi, H.; Kudo, K.; Sugita, N. *Chem. Lett.* **1991**, 1397.

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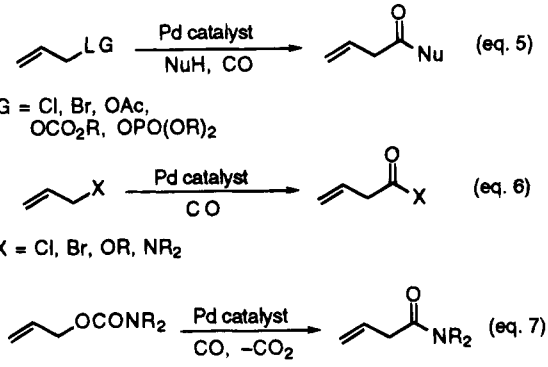
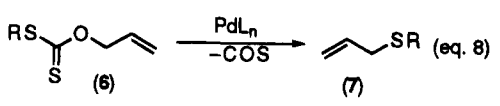
sis of allylamides in which the amine nucleophile is generated *in situ* from the allylcarbamate substrate (eq 7).[9]



There have been no reports of the direct carbonylation of allyl sulfides or of the carbonylation of π-allylic compounds in the presence of sulfur nucleophiles, presumably because sulfur is considered to be a potential catalyst poison.[10] In fact, despite possible problems with the use of sulfur nucleophiles and palladium complexes,[11] there have been several reports of the successful *alkylation* of such nucleophiles with π-allylpalladium complexes.[12] Bosnich et al.[12a] used an approach similar to that applied by Yamamoto and Tsuji by employing *O*-allyl thiocarbonates **6** as the substrates for the preparation of allyl sulfides. The key to the success of this method is that the sulfur nucleophile is generated only as quickly as it is needed (eq 8).

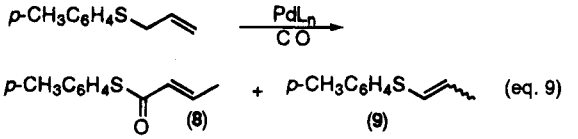


Although there are no examples of the synthesis of allyl thioesters from the carbonylation of allyl sulfides or related compounds, there are, however, many examples of the insertion of metal complexes into cyclic and acyclic C–S bonds.[13,14] Therefore, it was felt that appropriate conditions could be found to affect the carbonylation of allyl sulfides. We are pleased to report the first examples of the direct carbonylation of an allylic sulfide. Furthermore, the ruthenium-catalyzed carbonylation described herein is one of only a few reported examples of an allylic carbonylation catalyzed by a ruthenium complex.[15]

Results and Discussion

We chose allyl 4-methylphenyl sulfide as a model substrate and investigated its reaction with stoichiometric and catalytic quantities of a variety of metal complexes. The first system examined was 10% palladium acetate and 1, 3-bis(diphenylphosphino)propane (DPPP) in a 1:2 ratio, which is similar to the system reported by Murahashi et al. for the carbonylation of allylamines.[8] However, after reaction at 140 °C for 24 h in the presence of carbon monoxide (68 atm), no carbonylation was observed. Although $Pd(OAc)_2$/DPPP did not catalyze the carbonylation, tetrakis(triphenylphosphine)palladium was an effective catalyst, with allyl 4-methylphenyl sulfide being converted to the corresponding thioester by insertion of CO into the *S*-allyl bond. The carbonylation was accompanied by isomerization of the expected β,γ-thioester to the α,β-thioester **8** as shown in eq 9 and Table 1. The coupling constants for the olefinic protons in the ^{1}H NMR spectrum clearly showed that the product was >95% *trans*.

Analysis of the crude reaction mixture by ^{1}H NMR indicated that along with thioester **8**, vinyl sulfide **9** was also produced, which resulted from isomerization of the olefin unit in allyl 4-methylphenyl sulfide.[16] Optimization of the carbonylation reaction is shown in Table 1.



(9) (a) Miyazawa, M.; Yamamoto, K. *Chem. Lett.* **1994**, 491. (b) Miyazawa, M.; Wang, S.-Z.; Takeda, H.; Yamamoto, K. *Synlett* **1992**, 323.

(10) Hutton, A. T. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds., Pergamon Press: Oxford, U.K., 1984; Vol. 5, p 1151. Although sulfur is considered to be a potentially serious catalyst poison, there are many examples where sulfur-containing compounds are useful ligands: Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015, see also reference 5.

(11) See references 12 a,b. In reference 12b, it is noted that simple thiol nucleophiles were effective for the allylation reaction, but the reproducibility was poor and scaleup was found to be problematic.

(12) Most successful systems involve the generation of the sulfide nucleophiles *in situ* as with *O*-allyl thiocarbonates: (a) Auburn, P. R.; Whelan, J.; Bosnich, B. *J. Chem. Soc., Chem. Commun.* **1986**, 146. Silylated thiols can also be employed: (b) Trost, B. M.; Scanlan, T. S. *Tetrahedron Lett.* **1986**, 4141. When the π-allylpalladium complex is generated from an allylcarbonate, the liberated base can be used to deprotonate the thiol nucleophile so that large amounts of thioalkoxide or thioaryloxide salts (i.e. RSNa or ArSNa) are not necessary: (c) Goux, C.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **1992**, *52*, 8099. It has also been found that excess sodium thiophenoxide can be used successfully in allylations catalyzed by $[Pd(PPh_3)_4]$ giving high yields of the corresponding allyl sulfides: (d) Kang, S.-K.; Park, D.-C.; Jeon, J.-H.; Rho, H.-S.; Yu, C.-M. *Tetrahedron Lett.* **1994**, *35*, 2357.

(13) (a) The decarbonylation of 2-butenoic *S*-phenyl esters using catalytic $[Pd(PPh_3)_4]$ or with stoichiometric amounts of Wilkinson's complex has been reported: Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1987**, *50*, 6321. Nickel and palladium complexes are known to catalyze the cross-coupling reaction of Grignards and allyl sulfides: (b) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, 43. (c) Okamura, H.; Takei, H. *Tetrahedron Lett.* **1979**, 3425. Rhodium hydrides were shown to promote the stoichiometric reductive cleavage of allyl aryl sulfides yielding the corresponding alkenes: (d) Osakada, K.; Matsumoto, L.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 857. A similar reduction of allylic sulfides using catalytic amounts of $[Pd(PPh_3)_4]$ and stoichiometric amounts of alkalai metal borohydrides was also reported: (e) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4382. Palladium complexes were shown to oxidatively add into the C–S bond of allyl sulfides and allyl selenides producing π-allylic palladium complexes: (f) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559. (g) Osakada, K.; Ozawa, Y.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *399*, 341. Nickel catalyzed coupling reactions of dithioacetals and Grignard reactions are also reported to involve insertion into the C–S bond: (h) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc. Chem. Commun.* **1987**, 1515. (i) Yu, C. C.; Ng, D. K. P.; Chen, B.-L.; Luh, T.-Y. *Organometallics* **1994**, *13*, 1487.

(14) Transition metal-catalyzed desulfurization reactions have been studied extensively due to their industrial significance: (a) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694. (b) Alper, H.; Paik, H.-N. *J. Org. Chem.* **1977**, *42*, 3522. (c) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *26*, 1935. (d) *Ibid. Tetrahedron Lett.* **1985**, *26*, 1935. (e) Eisch, J. J.; Hallenbeck, L. E.; Kyoung, I. H. *J. Am. Chem. Soc.* **1986**, *108*, 7763. (f) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (g) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235. (h) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Chem. Soc. Chem. Commun.* **1987**, 981. (i) Chan, M.-C.; Cheng, K.-M.; Ho, K. M.; Ng, C. T.; Yam, T. M.; Wang, B. S.L.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 4466.

(15) (a) Mitsudo, T.-K.; Suzuki, N.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 7759. (b) Murahashi, S.-I.; Imada, Y. *Chem. Lett.* **1985**, 1477.

Table 1. Carbonylation of Allyl 4-Methylphenyl Sulfide with Palladium Catalysts[a]

entry	catalyst system	Pd (%)	time (h)	conversion (%)	yield (**8**) (%)	vinyl sulfide **9** (%)
1	$Pd(PPh_3)_4$	20	44	75	53	19
2	$Pd(PPh_3)_4$[b]	20	44	84	46	30
3	$Pd(PPh_3)_4$	20	72	91	62	26
4	$Pd(PPh_3)_4$[c]	10	100	100	64	11
5	$Pd(PPh_3)_4$	10	72	96	61	6
6	$Pd(OAc)_2$/DPPP (1:1)	10	45	87	73	0
7	$Pd(OAc)_2$/DPPP (1:2)	10	45	NR	–	0
8	$Pd(OAc)_2/PPh_3$ (1:2)	10	45	56	44	0
9	$Pd(OAc)_2$	10	45	NR	–	0

[a] Reaction conditions unless otherwise noted: 0.33–1.24 mmol substrate, 3–4 mL toluene, 10% palladium complex, 68 atm CO, 140 °C. Yields and conversions determined by ^1H NMR vs added internal standard (Ph_2CH_2) and are ±5%. [b] THF as solvent. [c] 100 °C.

The first reactions with $[Pd(PPh_3)_4]$ were performed at 140 °C under 68 atm of carbon monoxide for 48 h. Toluene was found to be more effective than THF for this reaction giving a slightly higher yield and less isomerization of the starting material (19% compared with 30%, entries 1 and 2). If the reaction was run for 72 h instead of 44 h, 62% of the desired thioester could be obtained, but 26% of the isomerized product was also observed. Decreasing the temperature and running the reaction for 100 h gave less isomerization (11%) while the yield of the carbonylated product remained the same (Table 1, entry 4). The best conditions found employed 10% catalyst at 140 °C for 72 h. Under these conditions, only 6% of the starting material was isomerized, and the yield of the desired product was virtually the same as in the other systems (compare entries 3 and 5 in Table 1).

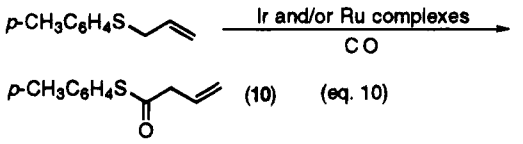
Although the yields at this point seemed to be limited to approximately 60%, the use of $Pd(OAc)_2$ with *1 equiv* of DPPP (per Pd) improved the yield to 73% and completely suppressed the isomerization of the starting material (entry 6). As previously stated, there was no reaction when palladium acetate and 2 equiv of DPPP were employed (entry 7). Other phosphines such as PPh_3 and PCy_3 were not as effective, and palladium acetate alone did not catalyze the reaction. The cationic palladium complex, $[Pd(PhCN)_2(DPPP)]^{2+}(BF_4^-)_2$, also did not catalyze the carbonylation reaction.

Other metal systems which are known to insert into C–S bonds were also examined. $Ni(PPh_3)_2(CO)_2$ and $NiCl_2(DPPE)_2$, which have been reported to catalyze the cross coupling of allyl sulfides and Grignard reagents,[13b,c] did not promote the carbonylation even using stoichiometric amounts of the transition metal complex. Molybdenum carbonyl is an effective catalyst for the alkylation of π-allyl complexes[17] and also for the desulfurization of organic sulfides, but it did not catalyze the carbonylation of allyl 4-methylphenyl sulfide. We also examined metal systems known to be useful for the carbonylation of cyclic sulfides or *N,S*-systems. However $[Rh(COD)Cl]_2$, which was used in the carbonylation of cyclic and acyclic 1,3-*N,S* systems,[5] was unreactive with allyl 4-methylphenyl sulfide, either in the presence or absence of an iodide promoter. Finally, it was found that a mixture of dicobalt octacarbonyl and ruthenium carbonyl which were previously used in the carbonylation of thietanes[3a] gave a low yield (7%) of the *unconjugated* allyl thioester **10** by NMR analysis of the crude reaction mixture. Although the

Table 2. Carbonylation of Allyl 4-Methylphenyl Sulfide with Ruthenium and Iridium Complexes[a]

entry	catalyst	cocatalyst	time (h)	conversion (%)	yield (**10**) (%)
1	$Ru_3(CO)_{12}$	$Co_2(CO)_8$	45	59	7
2	$Ru_3(CO)_{12}$	$Ir(CO)_3Cl$	60	51	NR
3	$Ru_3(CO)_{12}$	$IrCl(CO)(PPh_3)_2$	45	35	NR
4	$Ru_3(CO)_{12}$	$Ir_4(CO)_{12}$	45	30	18
5	$Ru_3(CO)_{12}$[b]	$Ir_4(CO)_{12}$	65	55	34
6	$RuCl_2(PPh_3)_3$	$Ir_4(CO)_{12}$[c]	45	2	NR
7	$RuCl_2(PPh_3)_3$	$Ir(CO)_3Cl$	69	36	27
8	$RuCl_2(PPh_3)_3$	$[Ir(COD)Cl]_2$	42	12	7
9	$RuCl_2(PPh_3)_3$	none	72	10	NR
10	$Ir_4(CO)_{12}$	none	45	7	NR
11	$Ru_3(CO)_{12}$	none	45	47	34
12	$Ru_3(CO)_{12}$	none	72	65	50

[a] Reaction conditions unless otherwise noted: ca. 1 mmol substrate, 4 mL toluene, 0.1 mmol ruthenium complex, 0.1 mmol of co-catalyst if required, 68 atm CO, 140 °C. Yields and convserions were determined by ^1H NMR vs added internal standard (Ph_2CH_2) and are ±5%. [b] 100 °C. [c] 120 °C.



(10) (eq. 10)

yield was low, the selectivity of the carbonylation was good with only the β,γ-isomer detected in the ^1H NMR of the crude reaction mixture. We therefore examined a variety of ruthenium complexes alone or in combination with iridium catalysts. Selected results are shown in Table 2.

Although a low yield was observed when $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ were employed, ruthenium carbonyl failed to catalyze the carbonylation when mixed with $Ir(CO)_3Cl$ or $IrCl(CO)(PPh_3)_2$ (see entries 2 and 3 of Table 2). In the presence of iridium carbonyl, however, 55% conversion and 34% yield of **10** was obtained after 65 h (entry 5). A different effect was observed in the $RuCl_2(PPh_3)_3$ catalyzed reactions. Of the iridium complexes examined, $Ir(CO)_3Cl$ was the best giving 36% conversion and 27% yield after 69 h, and no reaction was observed in the presence of $Ir_4(CO)_{12}$ (see entries 6–8).

These results seemed to indicate a cooperative effect since $RuCl_2(PPh_3)_3$ itself did not catalyze the reaction (entry 9). Furthermore, $Ru_3(CO)_{12}$ was inactive in the presence of all iridium complexes except $Ir_4(CO)_{12}$, which itself did not catalyze the carbonylation (compare entries 5 and 10). However, subsequent experiments demonstrated that $Ru_3(CO)_{12}$ was most effective if used alone (65% conversion and 50% yield after 72h, entry 12). It is possible that the formation of mixed metal clusters in some of the examples described in Table 2 destroyed or at least hindered the ability of $Ru_3(CO)_{12}$ to catalyze the carbonylation reaction. Thus entry 12 became our standard reaction conditions for the carbonylation of allyl sulfides leading to β,γ-unsaturated thioesters. The scope of this reaction and the palladium-catalyzed carbonylation to the α,β-unsaturated

(16) The isomerization of the starting material could occur by an addition–elimination mechanism which was shown to be operative in the reductive cleavage of allyl aryl sulfides with rhodium hydrides, see reference 13d. The base catalyzed isomerization of allyl aryl sulfides is also known: Tarbell, D. S.; McCall, M. A. *J. Am. Chem. Soc.* **1952**, *74*, 48.

(17) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469.

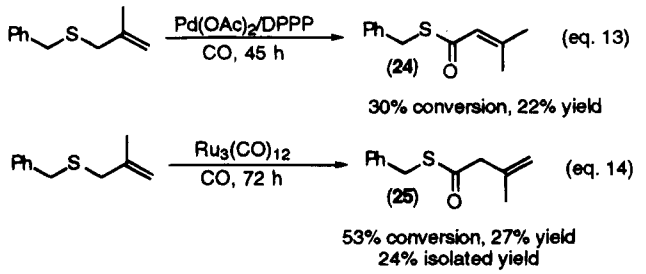
thioesters was examined using a variety of aryl sulfides (Table 3).

From Table 3 it can be seen that the yields and conversions are consistently lower with the ruthenium system. In the palladium-catalyzed carbonylation reactions, the yields of the thioesters were virtually the same for all the aryl substrates examined thus far except for *p*-fluorophenyl allyl sulfide. In this case, a considerably lower yield of the carbonylated product **15** was obtained (39%, entry 8). For the ruthenium-catalyzed carbonylation reactions, the yields were also virtually insensitive to the electronic nature of the aromatic group. 4-Methylphenyl sulfide gave the best yield of 50% (entry 4), but this is not dramatically different from the lowest yield (33% for phenyl allyl sulfide, entry 2).

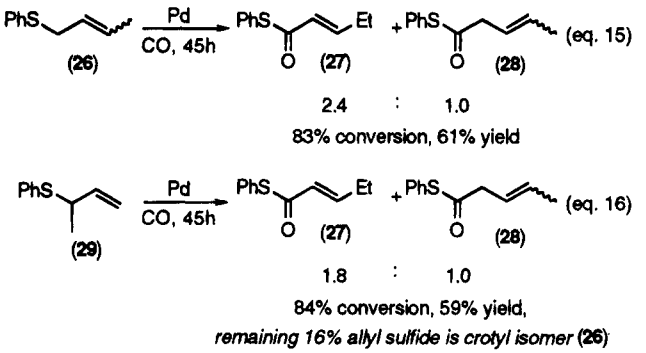
The alkyl allyl sulfides examined in this study are shown in Table 4. As in the aryl series, the palladium acetate/DPPP system catalyzed the carbonylation of the allyl sulfides to form the α,β-thioesters specifically. The yields in these systems were good, with 100% conversion being obtained in 45 h for both the *sec*-butyl and *n*-hexyl substrates. The NMR yields of the desired products were 88 and 86% for the *n*-hexyl and *sec*-butyl cases (see entries 1 and 4 of Table 4), respectively. Since 100% conversion was observed under these conditions, the reactions were repeated and stopped after 25 h. Although the reactions were not complete, ca. 50% of the desired products were isolated (entries 2 and 5). These results and others are compiled in Table 4.

When allyl *n*-dodecyl sulfide was treated with CO under the standard reaction conditions for 65 h, compound **20** was obtained in 66% NMR yield (59% isolated). Allyl benzyl sulfide afforded only a moderate amount of the desired thioester **22** (43% yield, 59% conversion, entry 8) after 44 h. The ruthenium system gave much lower yields with the alkyl sulfides (14–24%) which further illustrates the difference between the ruthenium and palladium systems. Allyl benzyl sulfide was an exception to this trend since it gave 50% of the desired thioester by NMR (40% isolated) (entry 9).

Another alkyl substrate that was examined in the reaction was benzyl (2-methyl-2-propenyl) sulfide which affords low yields of the carbonylated products, **24** and **25**, in both the ruthenium and palladium catalyzed reactions, as shown in eqs 13 and 14. Comparison of these yields with the results obtained in the simple allyl benzyl sulfide system (entries 8 and 9) shows that substitution in the 2-position of the allylic moiety decreases the yields of both the α,β- and β,γ-unsaturated thioesters. Thus the reaction of benzyl (2-methyl-2-propenyl) sulfide gave 22% yield of the desired α,β-thioester while simple allyl benzyl sulfide afforded 43% of the same compound under identical conditions. The ruthenium reaction was also sensitive to steric effects giving only 22% of the β,γ-thioester vs 50% for the carbonylation of allyl benzyl sulfide.



In order to confirm the π-allylic nature of the reaction, 2-butenyl (**26**) and 3-(1-butenyl) phenyl sulfide (**29**) were subjected to the conditions developed for allyl 4-methylphenyl sulfide. As expected, both substrates yielded the same product, resulting from carbonylation at the least hindered site[18] when they were treated with $Pd(OAc)_2$, DPPP, and CO according to the general procedure. The crude spectra of the two experiments were virtually identical. The exact conversions and yields are given in eqs 15 and 16 and are the same within experimental error.



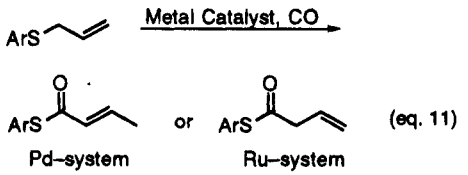
Unlike the other substrates examined thus far, the isomerization of the initially formed β,γ-isomer **28** was incomplete after 48 h. However, the most interesting aspect of these experiments is that the starting material remaining from the 3-(1-butenyl) (**29**) reaction was the crotyl isomer **26**! This suggests that formation of the π-allylpalladium complex **30** is complete and that the remaining starting material arises from reductive elimination of the sulfide and the π-allylic ligands on palladium prior to carbonylation. This is shown in Scheme 1. However, it should be noted that these observations, while consistent with oxidative addition occurring via a π-allyl complex, do not prove that the *carbonylation* proceeds through a π-allyl intermediate.

Conclusions

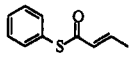
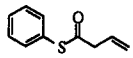
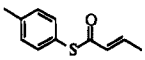
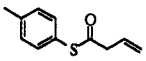
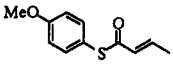
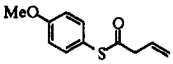
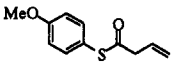
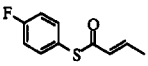
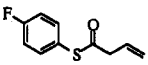
We have found that a variety of allyl aryl and allyl alkyl sulfides can be carbonylated to the corresponding thioesters in variable yields depending on the nature of the substrate. The carbonylation reaction is catalyzed by both palladium and ruthenium systems, and these two metals give complementary results. With the palladium system, the initially formed β,γ-unsaturated thioester underwent complete isomerization yielding the α,β-unsaturated thioester (>95% *trans*). The ruthenium system, on the other hand, afforded the β,γ-unsaturated thioester without concomitant isomerization.

(18) This is generally considered to be proof of a stepwise reaction involving a π-allylic intermediate (see reference 6j for a discussion of this strategy). Others have also cited this reaction outcome as evidence of a π-allylic intermediate: Tsuji, Y.; Mukai, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *369*, C57. See also references 6c, 8a, 8b and 15. It was recently shown by Brookhart et al. that the extent of carbonylation at the less hindered M–allyl bond (in η^3-allyl iron anions) is dependent on the ancillary ligands, with carbon monoxide favoring carbonylation at the less hindered position: Chang, S.; Yoon, J.; Brookhart, M. *J. Am. Chem. Soc.* **1994**, *116*, 1869. This finding does not affect the conclusion from the crotyl/methallyl experiments described in this paper or in others.

Table 3. Palladium and Ruthenium Catalyzed Carbonylation of Substituted Allyl Aryl Sulfides[a]



(eq. 11)

Entry	Ar	Catalyst System	Product[b]	Comp. No.	Conv. (%)	Yield (%)
1	C_6H_5	$Pd(OAc)_2$/DPPP		(11)	92	69
2	C_6H_5	$Ru_3(CO)_{12}$		(12)	55	33 (30)[c]
3	*p*-MeC_6H_4	$Pd(OAc)_2$/DPPP		(8)	87	73
4	*p*-MeC_6H_4	$Ru_3(CO)_{12}$		(10)	65	50
5	*p*-$MeOC_6H_4$	$Pd(OAc)_2$/DPPP		(13)	n.d.[d]	(62)
6	*p*-$MeOC_6H_4$	$Ru_3(CO)_{12}$		(14)	n.d.[d]	(37)
7	*p*-$MeOC_6H_4$[e]	$Ru_3(CO)_{12}$		(14)	n.d.[d]	(39)
8	*p*-FC_6H_4	$Pd(OAc)_2$/DPPP		(15)	74	39
9	*p*-FC_6H_4	$Ru_3(CO)_{12}$		(16)	60	35 (32)

[a]Reaction conditions unless otherwise noted: 1.99-0.94 mmol substrate, 4-8 mL toluene, 10% metal complex, 10% mmol of phosphine if required, 68 atm CO, 140 °C. Yields and conversions are determined by ^1H NMR vs. added internal standard (Ph_2CH_2) and are ±5%. [b]α, β-thioesters are all >95% trans. [c] Isolated yields given in parentheses. [d]n.d. = not determined due to interference of the OCH_3 signal with the internal standard. [e]This reaction was run at 120 °C.

The reactions were usually very clean, with only the product and unreacted starting material detected in the crude NMR of the reaction mixture. In those reactions catalyzed by $[Pd(PPh_3)_4]$, some isomerization of the starting allyl sulfide to the vinyl sulfide was observed. It was subsequently found that palladium acetate/DPPP was a more effective system than $[Pd(PPh_3)_4]$, and under these conditions, none of the vinyl sulfide was observed. None of the isomerization product **8** was found in any of the ruthenium catalyzed reactions, except in the presence of 5 equiv of NaOAc.

The palladium and ruthenium catalyzed carbonylation reactions described herein represent the first example (to our knowledge) of the insertion of carbon monoxide into the carbon–sulfur bond of allyl sulfides.

Experimental Section

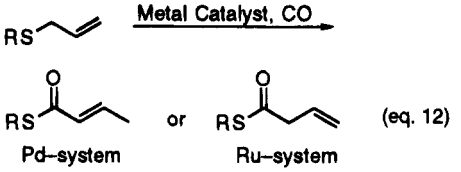
General Procedure for the Carbonylation Reactions. An autoclave, its glass liner, and a magnetic stirring bar were dried in an oven and then cooled in a dry box. The liner was charged with the catalyst (10% unless otherwise noted), and any cocatalyst or promoter (10–20% unless otherwise noted). The allyl sulfide (ca. 1 mmol) and solvent (ca. 4 mL) were then added to the liner. An additional amount of solvent (from 2–9 mL) was placed in the autoclave prior to insertion of the liner. The gauge and gauge block assembly were attached, the CO line was flushed three times with CO, and the system was also pressurized and flushed three times with CO, gradually increasing the pressure to the desired level. The system was then filled with 68 atm of CO, and the autoclave was placed in the center of an oil bath on a heater-stirrer preset to the reaction temperature. After the appropriate time, the autoclave was removed from the oil bath and allowed to cool to room temperature. The excess gas was discharged and the system disassembled. The internal standard was added and the contents of the liner transferred to a round bottom flask. The volatiles were removed *in vacuo* and the yield and conversion measured by ^1H NMR. These yields and conversions are accurate to ±5%. In some cases the products were then isolated by column chromatography and/or recycling HPLC using a gel permeation column. After isolation, NMR analyses were performed and the spectra compared with available data from the literature.

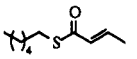
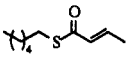
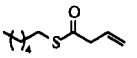
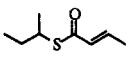
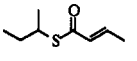
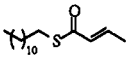
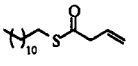
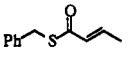
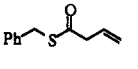
Preparation of Starting Materials. Allyl 4-Fluorophenyl Sulfide. Prepared by the method in given in ref 19 in 86% isolated yield (on a 19 mmol scale) after purification by Kugelrohr distillation. ^1H NMR (200 MHz, $CDCl_3$) δ 7.28–7.21 (m, 2H), 6.93–6.84 (m, 2H), 5.84–5.64 (m, 1H), 4.99–4.88 (m, 2H), 3.48 (dt, J = 7.0, 1.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 246 Hz), 133.5, 133.2 (d, J_{C-F} = 8.1 Hz), 130.5 (d, J_{C-F} = 3.3 Hz), 117.6, 115.8 (d, J_{C-F} = 21.8 Hz), 38.5 ppm; IR neat, υ_{max} 1636, 1590, 1489, 1225, 1157, 1013, 921, 824 cm^{-1}; MS (*m/z*) 168 (100, M^+), 127, 100, 91; HRMS calcd for C_9H_9FS, 168.0364, found 168.0398.

Allyl 4-Methoxyphenyl Sulfide. Prepared by the method given in reference 19 in 90% isolated yield (on a 16 mmol scale) after purification by Kugelrohr distillation. ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 5.81–5.64 (m, 1H), 4.93–4.83 (m, 2H), 3.69 (s, 3H), 3.33 (dt, J = 8.3, 1.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 133.98, 133.85, 125.7, 117.2, 114.3, 55.2, 39.2 ppm; IR neat, υ_{max} 1634, 1592, 1462, 1285, 1243, 1176, 1032, 919, 824 cm^{-1}; MS (*m/z*) 180 (M^+), 139 (100), 100; HRMS calcd for $C_{10}H_{12}OS$, 180.0609, found 180.0589.

Allyl Benzyl Sulfide. Prepared by the general method in ref 19 in 70% yield (on a 16.8 mmol scale) after purification

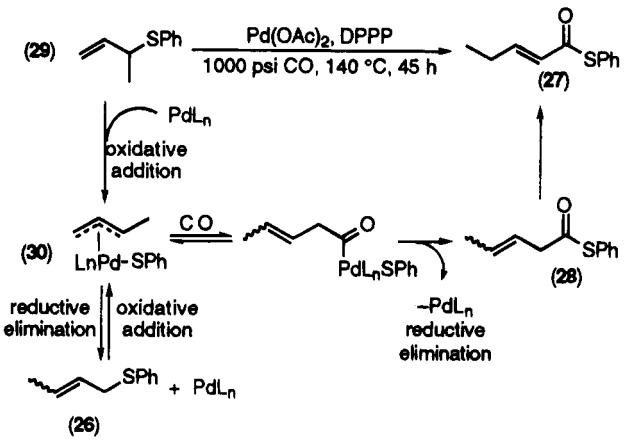
Table 4. Palladium and Ruthenium Catalyzed Carbonylation of Substituted Allyl Alkyl Sulfides[a]



Entry	R	Catalyst System	Time (h)	Product[b]	Comp. No.	Conv. (%)	Yield (%)
1	*n*-hexyl	$Pd(OAc)_2$/DPPP	48		(17)	100	88 (74)
2	*n*-hexyl	$Pd(OAc)_2$/DPPP	24		(17)	65	45 (46)[c]
3	*n*-hexyl	$Ru_3(CO)_{12}$	72		(18)	58	24
4	*s*-butyl	$Pd(OAc)_2$/DPPP	45		(19)	100	86
5	*s*-butyl	$Pd(OAc)_2$/DPPP	24		(19)	87	51 (49)
6	*n*-dodecyl	$Pd(OAc)_2$/DPPP	65		(20)	82	66 (59)
7	*n*-dodecyl	$Ru_3(CO)_{12}$	72		(21)	55	24
8	benzyl	$Pd(OAc)_2$/DPPP	44		(22)	59	43
9	benzyl	$Ru_3(CO)_{12}$	72		(23)	72	50 (40)

[a] Reaction conditions unless otherwise noted: 1.99-0.94 mmol substrate, 4-8 mL toluene, 10% metal complex, 10% mmol of phosphine if required, 68 atm CO, 140 °C. Yields and conversions are determined by ^{1}H NMR vs. added internal standard (Ph_2CH_2) and are ±5%. [b] α, β-thioesters are all >95% trans. [c] Isolated yields given in parentheses. [d] This reaction was run at 120 °C.

Scheme 1



by Kugelrohr distillation. Further purification by column chromatography was necessary to remove traces of another unidentified compound. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24–7.16 (m, 4H), 5.81–5.60 (m, 1H), 5.01–4.94 (m, 2H), 3.56 (s, 3H), 2.94 (d, J =7.0 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 134.1, 129.0, 128.6, 128.4, 127.9, 126.9, 117.3, 34.8, 34.0 ppm; IR neat, ν_{max} 1634, 1592, 1462, 1285, 1243, 1176, 1032, 919, 824 cm^{-1}; MS (*m/z*) 164 (M^+), 122, 100, 91 (100); HRMS calcd for $C_{10}H_{12}S$, 164.0660, found 164.0662.

2-Butenyl Phenyl Sulfide (26). Prepared by the method in given in ref 19 in 58% isolated yield (on a 19.5 mmol scale) as a 70/30 *E/Z* mixture after purification by Kugelrohr distillation. Spectra match those given in ref 16.

3-(1-Butenyl) Phenyl Sulfide (29). Prepared by the method given in ref 19 in 28% isolated yield (on a 19.5 mmol scale) along with 2-butenyl sulfide (35% of total sulfide, as a 70/30 *E/Z* mixture) after purification by Kugelrohr distillation. Spectra match those given in ref 19.

Carbonylation Reactions with $Pd(OAc)_2$/DPPP and $Ru_3(CO)_{12}$. (*E*)-2-Butenoic Acid *S*-Phenyl Ester (11).[20] Following the general procedure, palladium acetate (45 mg, 0.199 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (82 mg, 0.199 mmol, 10%) were placed in a dry autoclave liner followed by allyl phenyl sulfide (299 mg, 1.99 mmol) and 8 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 44 h. The ^{1}H NMR yield based on added internal standard was determined to be 69% with 92% conversion. Purification by column chromatography on silica gel eluting with 5% ethyl acetate in hexanes afforded the pure product (Table 3, entry 1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.30 (m, 5H), 6.90 (dq, J = 15.4, 6.9 Hz, 1H), 6.11 (dq, J = 15.4, 1.7 Hz, 1H), 1.82 (dd, J = 6.9, 1.7 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.8, 142.1, 134.7, 129.4, 129.3, 129.1, 18.1 ppm.; IR neat, ν_{max} 1685, 1636, 1478, 1440, 1285, 1154, 1040, 961, 910, 800, 739, 689 cm^{-1}; MS (*m/z*) 178 (M^+), 109, 100, 88, 70 (100); HRMS calcd for $C_{10}H_{10}OS$, 178.0452, found 178.0430.

3-Butenoic Acid *S*-Phenyl Ester (12). Following the general procedure, ruthenium carbonyl (118 mg, 0.18 mmol, 10%) and allyl phenyl sulfide (276 mg, 1.84 mmol) were placed in a dry autoclave liner followed by 7 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 72 h. The ^{1}H NMR yield based on added internal standard was determined to be 33% with 55% conversion. Purification by column chromatography on silica gel yielded 98 mg (0.55 mmol, 30%) of the pure product (Table 3, entry 2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.3 (br s, 5H), 5.98–5.77 (m, 1H), 5.22–

(19) Cope, A. C.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59.
(20) Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756.

5.13 (m, 2H), 3.31 (dt, J = 7.1, 1.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 134.5, 130.0, 129.6, 129.4, 129.2, 120.1, 48.1 ppm; IR neat, υ_{max} 1704, 1656, 1638, 1477, 1440, 1277, 998, 746, 689 cm^{-1}; MS (m/z) 178 (M^+), 137, 110 (100), 91, 77; HRMS calcd for $C_{10}H_{10}OS$, 178.0452, found 178.0458. Anal. Calcd for $C_{10}H_{10}OS$: C, 67.42; H, 5.62. Found: C, 67.56; H, 5.31.

(*E*)-2-Butenoic Acid *S*-(4-Methylphenyl) Ester (8). Following the general procedure, palladium acetate (22 mg, 0.098 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (41 mg, 0.098 mmol, 10%) were placed in a dry autoclave liner followed by allyl 4-methylphenyl sulfide (161 mg, 0.98 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 44 h. The ^{1}H NMR yield based on added internal standard was determined to be 73% with 87% conversion. Purification by flash chromatography on silica gel with hexanes as eluant yielded 85% of the product which was slightly impure by ^{1}H NMR. Further purification by recycling HPLC gave 93 mg (0.48 mmol, 50%) of the pure product (Table 3, entry 3). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.89 (dq, J = 15.4, 6.9 Hz, 1H), 6.11 (dq, J = 15.4, 1.7 Hz, 1H), 2.28 (s, 3H), 1.82 (dd, J = 6.9, 1.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.3, 141.8, 139.6, 129.9, 129.3, 124.0, 21.3, 18.0 ppm; IR neat, υ_{max} 1681, 1637, 1493, 1284, 1039, 805 cm^{-1}; MS (m/z) 192 (M^+), 123, 91, 69 (100), 41; HRMS calcd for $C_{11}H_{12}OS$, 192.0609, found 192.0622. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.62; H, 6.09.

3-Butenoic Acid *S*-(4-Methylphenyl) Ester (10). Following the general procedure, ruthenium carbonyl (60 mg, 0.09 mmol, 10%) and allyl 4-methylphenyl sulfide (155 mg, 0.94 mmol) were placed in a dry autoclave liner followed by 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was run at 140 °C for 72 h. The ^{1}H NMR yield based on added internal standard was determined to be 50% with 65% conversion. Purification by recycling HPLC chromatography gave the pure product (Table 3, entry 4). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 5.99–5.78 (m, 1H), 5.22–5.13 (m, 2H), 3.30 (dt, J = 6.8, 1.2 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 139.7, 134.4, 130.0, 129.7, 124.0, 119.9, 48.0, 21.3 ppm; IR neat, υ_{max} 1703, 1639, 1493, 1299, 996, 807 cm^{-1}; MS (m/z) 192 (M^+), 124 (100), 91, 69, 41; HRMS calcd for $C_{11}H_{12}OS$, 192.0609, found 192.0621.

(*E*)-2-Butenoic Acid *S*-(4-Methoxyphenyl) Ester (13). Following the general procedure, palladium acetate (24 mg, 0.105 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (44 mg, 0.105 mmol, 10%) were placed in a dry autoclave liner followed by allyl 4-methoxyphenyl sulfide (190 mg, 1.05 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 45 h. ^{1}H NMR yield and conversion were not calculated due to interference of the OCH_3 signal with the Ph_2CH_2 signal. Purification by flash chromatography on silica gel with 5% ethyl acetate in hexanes as eluant afforded 136 mg (0.65 mmol, 62%) of the pure product (Table 3, entry 5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (d, J = 8.9 Hz, 2H), 6.97–6.79 (m, 3H), 6.10 (dq, J = 15.4, 1.7 Hz, 1H), 3.72 (s, 3H), 1.81 (dd, J = 6.9, 1.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8, 160.5, 141.7, 136.2, 129.2, 118.2, 114.8, 55.3, 18.0 ppm; IR neat, υ_{max} 1680, 1636, 1593, 1494, 1289, 1249, 1176, 1154, 1034, 908, 800 cm^{-1}; MS (m/z) 208 (100, M^+), 140, 125, 100; HRMS calcd for $C_{11}H_{12}O_2S$, 208.0558, found 208.0552. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.28; H, 5.96.

3-Butenoic Acid *S*-(4-Methoxyphenyl) Ester (14). Following the general procedure, ruthenium carbonyl (63 mg, 0.1 mmol, 10%) and allyl 4-methoxyphenyl sulfide (177 mg, 0.98 mmol) were placed in a dry autoclave liner followed by 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 120 °C for 72 h. The ^{1}H NMR yield based on added internal standard could not be determined because the OCH_3 signal interfered with the Ph_2CH_2 signal. Purification by silica gel chromatography using hexanes and ethyl acetate as the eluants afforded 80 mg (0.38 mmol, 39%) of the pure product (Table 3, entry 7). Another reaction performed at 140 °C using 89 mg of $Ru_3(CO)_{12}$ and 245 mg of allyl 4-methoxyphenyl sulfide gave 106 mg (0.51 mmol, 37%) of the desired product after purification by recycling HPLC (Table 3, entry 6). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.22 (d, J = 8.9 Hz), 6.83 (d, J = 8.9 Hz), 5.94–5.77 (m, 1H), 5.21–5.12 (m, 2H), 3.72 (s, 3H), 3.28 (dt, J = 7.0, 1.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 160.6, 136.0, 129.7, 119.9, 118.2, 114.8, 55.2, 47.8 ppm; IR neat, υ_{max} 1701, 1638, 1593, 1574, 1495, 1462, 1292, 1249, 1178, 1113, 1029, 997, 921, 828, 643 cm^{-1}; MS (m/z) 208 (M^+), 140 (100), 119; HRMS calcd for $C_{11}H_{12}O_2S$, 208.0558, found 208.0543. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.63; H, 6.11.

(*E*)-2-Butenoic Acid *S*-(4-Fluorophenyl) Ester (15). Following the general procedure, palladium acetate (22 mg, 0.098 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (41 mg, 0.098 mmol, 10%) were placed in a dry autoclave liner followed by allyl 4-fluorophenyl sulfide (165 mg, 0.98 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 45 h. The ^{1}H NMR yield was determined to be 39% with 74% conversion. Purification by chromatography on silica gel with 5% ethyl acetate in hexanes as eluant afforded the pure product (Table 3, entry 8). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.05–6.81 (m, 3H), 6.10 (dq, J = 15.4, 1.7 Hz, 1H), 1.83 (dd, J = 6.9, 1.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 163.5 (d, J_{C-F} = 250.0 Hz), 142.4, 136.7 (d J_{C-F} = 8.9 Hz), 129.2, 122.9, 116.4 (d J_{C-F} = 21.9 Hz), 18.1 ppm; IR neat, υ_{max} 1681, 1637, 1591, 1491, 1441, 1287, 1229, 1155, 1040, 960, 816 cm^{-1}; MS (m/z) 196 (M^+, 100), 143, 127, 100, 84; HRMS calcd for $C_{10}H_9FOS$, 196.0358, found 196.0353.

3-Butenoic Acid *S*-(4-Fluorophenyl) Ester (16). Following the general procedure, ruthenium carbonyl (59 mg, 0.09 mmol, 10%) and allyl 4-fluorophenyl sulfide (154 mg, 0.92 mmol) were placed in a dry autoclave liner followed by 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 87 h. ^{1}H NMR yield based on added internal standard was determined to be 35% with 60% conversion. Purification by silica gel chromatography gave 58 mg (0.29 mmol, 32%) of the pure product (Table 3, entry 9). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31–7.23 (m, 2H), 7.06–6.94 (m, 2H), 5.97–5.76 (m, 1H), 5.23–5.12 (m, 2H), 3.30 (dt, J = 7.0, 1.3, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 163.5 (d, J_{C-F} = 250.1 Hz), 136.6 (d, J_{C-F} = 8.0 Hz), 130.0, 129.4, 120.3, 116.5 (d, J_{C-F} = 22.2 Hz), 48.0 ppm; IR neat, υ_{max} 1704, 1639, 1591, 1490, 1399, 1228, 1158, 1118, 1092, 1003, 829, 778, 704 cm^{-1}; MS (m/z) 196 (M^+), 169, 128 (100), 119, 83; HRMS calcd for $C_{11}H_{12}FOS$, 196.0358, found 196.0351.

(*E*)-2-Butenoic Acid *S*-Hexyl Ester (17). Following the general procedure, palladium acetate (24 mg, 0.11 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (44 mg, 0.11 mmol, 10%) were placed in a dry autoclave liner followed by allyl hexyl sulfide (169 mg, 1.06 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 48 h. The ^{1}H NMR yield based on added internal standard was determined to be 88% with 100% conversion. Purification by column chromatography on silica gel with hexanes as the eluant gave 146 mg (0.78 mmol, 74%) of the pure product (Table 4, entry 1). An experiment run for 24 h using 192.7 mg (1.2 mmol) of substrate, 27 mg of $[Pd(OAc)_2]$ (0.12 mmol), and 50 mg of DPPP (0.12 mmol) in 4 mL of toluene gave 46% isolated yield (104 mg) (Table 4, entry 2). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.79 (dq, J = 15.4, 6.9 Hz, 1H), 6.02 (dq, J = 15.4, 1.7 Hz, 1H), 2.82 (t, J = 7.1 Hz, 2H), 1.77 (dd, J = 6.9, 1.7 Hz, 3H) 1.51–1.11 (m, 8H), 0.78 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 140.3, 130.2, 31.3, 29.5, 28.55, 28.48, 22.5, 17.8, 13.9 ppm; IR neat, υ_{max} 2933, 2858, 1673, 1638, 1448, 1284, 1162, 1046, 961, 911, 813 cm^{-1}; MS (m/z) 188 (M^+), 69 (100), 41, 39; HRMS calcd for $C_{10}H_{18}OS$, 186.1078, found 186.1068.

3-Butenoic Acid *S*-Hexyl Ester (18). Following the general procedure, ruthenium carbonyl (81 mg, 0.13 mmol,

10%) and allyl hexyl sulfide (199 mg, 1.25 mmol) were placed in a dry autoclave liner followed by 5 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 130 °C for 72 h. The ^{1}H NMR yield based on added internal standard was determined to be 24% with 58% conversion. Purification by recycling HPLC chromatography gave the pure product (Table 4, entry 3). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.00−5.83 (m, 1H), 5.25−5.16 (m 2H), 3.30 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 1.61−1.20 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 130.1, 119.6, 48.6, 31.2, 29.4, 28.9, 22.5, 14.0 ppm; IR neat, υ_{max} 2956, 2926, 2857, 1688, 1640, 1558, 1459, 1260, 1055, 701cm^{-1}; MS (m/z) 186 (M^+), 131, 119 (100), 85; HRMS calcd for $C_{10}H_{18}OS$, 186.1078, found 186.1080.

(*E*)-2-Butenoic Acid *S*-(*sec*-Butyl) Ester (19). Following the general procedure, palladium acetate (20 mg, 0.08 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (36 mg, 0.08 mmol, 10%) were placed in a dry autoclave liner followed by allyl *s*-butyl sulfide (114 mg, 0.88 mmol) and 3 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 45 h. The ^{1}H NMR yield based on added internal standard was determined to be 86% with 100% conversion. Purification by column chromatography on silica gel eluting with hexanes afforded the pure product (Table 4, entry 4). An experiment run for 24 h using 268 mg (2.1 mmol) of substrate, 46 mg of $[Pd(OAc)_2]$ (0.2 mmol), and 85 mg of DPPP (0.2 mmol) in 8 mL of toluene gave the product in 49% isolated yield (160 mg) (Table 4, entry 5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.77 (dq, J = 15.4, 6.9 Hz, 1H), 6.00 (dq, J = 15.4, 1.7 Hz, 1H), 3.47 (tq, app sextet, J = 6.9, 6.9 Hz, 1H), 1.75 (dd, J = 6.9, 1.7 Hz, 3H) 1.58−1.44 (m, 2H), 1.20 (d, J = 6.9 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 140.0, 130.4, 40.4, 29.5, 20.8, 17.7, 10.3 ppm; IR neat, υ_{max} 2966, 2874, 1670, 1636, 1448, 1378, 1284, 1159, 1177, 1045, 961, 911, 812 cm^{-1}; MS (m/z) 158 (M^+), 103, 69 (100), 57, 41; HRMS calcd for C_8H_{14}-OS, 158.0767, found 158.0761.

(*E*)-2-Butenoic Acid *S*-Dodecyl Ester (20). Following the general procedure, palladium acetate (26 mg, 0.12 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (48 mg, 0.12 mmol, 10%) were placed in a dry autoclave liner followed by allyl dodecyl sulfide (284 mg, 1.17 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 65 h. The ^{1}H NMR yield based on added internal standard was determined to be 66% with 82% conversion. Purification by column chromatography on silica gel eluting with hexanes gave 217 mg (0.69 mmol, 59%) of the pure product (Table 4, entry 6). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.90 (dq, J = 15.4, 6.9 Hz, 1H), 6.13 (dq, J = 15.4, 1.6 Hz, 1H), 2.92 (t, J = 7.1 Hz, 2H), 1.87 (dd, J = 6.8, 1.6 Hz, 3H) 1.70−1.20 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.1, 140.4, 130.3, 31.9, 29.61 (2), 29.59, 29.48, 29.3, 29.1, 28.9, 28.6, 22.7, 17.9, 14.1 ppm; IR neat, υ_{max} 2906, 1678, 1639, 1451, 1376, 1282, 1162, 1116, 1046, 961, 912, 812, 702 cm^{-1}; MS (m/z) 207 (M^+), 201 (100), 184, 168, 131, 119, 105, 87; HRMS calcd for $C_{16}H_{30}OS$, 270.2017, found 270.1994. Anal. Calcd for: C, 71.05; H, 11.18. Found: C, 70.76; H, 11.25.

3-Butenoic Acid *S*-Dodecyl Ester (21). Following the general procedure, ruthenium carbonyl (75 mg, 0.12 mmol, 10%) and allyl dodecyl sulfide (284 mg, 1.17 mmol) were placed in a dry autoclave liner followed by 5 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 72 h. The ^{1}H NMR yield based on added internal standard was determined to be 24% with 55% conversion. Purification by recycling HPLC chromatography afforded the pure product (Table 4, entry 7). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.00−5.83 (m, 1H), 5.25−5.16 (m 2H), 3.30 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 1.61−1.20 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 130.1, 119.6, 48.6, 31.2, 29.4, 28.9, 22.5, 14.0; IR neat, υ_{max} 2941, 2854, 1689, 1639, 1459, 1292, 1120, 1006, 918, 729 cm^{-1}; MS (m/z) 270 (M^+), 201, 168, 85, 69 (100), 57, 41; HRMS calcd for $C_{16}H_{30}OS$, 270.2017, found 270.1988.

(*E*)-2-Butenoic Acid *S*-Benzyl Ester (22). Following the general procedure, palladium acetate (21 mg, 0.094 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (39 mg, 0.094 mmol, 10%) were placed in a dry autoclave liner followed by allyl benzyl sulfide (155 mg, 0.94 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 45 h. The ^{1}H NMR yield based on added internal standard was determined to be 43% with 59% conversion. Purification by flash chromatography on silica gel with 5% ethyl acetate in hexanes as eluant afforded the pure product (Table 4, entry 8). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33−7.22 (m, 5H), 6.93 (dq, J = 15.4, 6.9, Hz, 1H), 6.14 (dq, J = 15.4, 1.7 Hz, 1H), 4.18 (s, 2H), 1.87 (dd, J = 6.9, 1.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 141.2, 137.7, 129.7, 128.8, 128.6, 127.2, 32.8, 17.9 ppm; IR neat, υ_{max} 1686, 1638, 1495, 1553, 1415, 1294, 1242, 1119, 1071, 1007, 921, 702 cm^{-1}; MS (m/z) 192 (M^+), 131, 119 (100), 100, 91; HRMS calcd for $C_{11}H_{12}$-OS 192.0609, found 192.0605.

3-Butenoic Acid *S*-Benzyl Ester (23). Following the general procedure, ruthenium carbonyl (74 mg, 0.116 mmol, 10%) and allyl benzyl sulfide (190 mg, 1.16 mmol) were placed in a dry autoclave liner followed by 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 72 h. ^{1}H NMR yield based on added internal standard was determined to be 50% with 72% conversion. Purification by gel permeation chromatography on a polystyrene packed HPLC column yielded 88 mg (0.46 mmol, 40%) of the pure product (Table 4, entry 9). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30−7.21 (m, 5H), 6.03−5.82 (m, 1H), 5.26−5.16 (m, 2H), 4.12, (s, 2H), 3.21 (dt, J = 7.0, 1.3 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 137.4, 129.7, 128.8, 128.6, 127.3, 119.9, 48.2, 33.2 ppm; IR neat, υ_{max} 1674, 1637, 1495, 1446, 1285, 1161, 1046, 961, 913, 811, 701 cm^{-1}; MS (m/z) 192, 91, 69 (100), 41; HRMS calcd for $C_{11}H_{12}OS$, 192.0609, found 192.0596. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.66; H, 6.56.

3-Methyl-2-butenoic Acid *S*-Benzyl Ester (24). Following the general procedure, palladium acetate (44 mg, 0.199 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (82 mg, 0.199 mmol, 10%) were placed in a dry autoclave liner followed by benzyl (2-methyl-2-propenyl) sulfide (352 mg, 1.98 mmol) and 8 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 44 h. ^{1}H NMR yield based on added internal standard was determined to be 22% with 30% conversion. The product was purified by recycling HPLC. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23−7.15 (m, 5H), 5.89 (apparent quintet, J = 1.3 Hz, 1H), 4.05 (s, 2H), 2.09 (d, J = 1.3 Hz, 3H), 1.78 (d, J = 1.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.3, 154.2, 138.1, 128.8, 128.5, 127.0, 122.8, 32.9, 27.2, 21.2 ppm; IR neat, υ_{max} 1674, 1629, 1444, 1379, 1204, 1092, 1012, 841, 798, 704 cm^{-1}; MS (m/z) 206 (M^+), 91, 83 (100); HRMS calcd for $C_{12}H_{14}OS$, 206.0765, found 206.0775; Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 70.04; H, 6.76.

3-Methyl-3-butenoic Acid *S*-Benzyl Ester (25). Following the general procedure, ruthenium carbonyl (115 mg, 0.18 mmol, 10%) and benzyl (2-methyl-2-propenyl) sulfide (322 mg, 1.8 mmol) were placed in a dry autoclave liner followed by 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 72 h. ^{1}H NMR yield based on added internal standard was determined to be 27% with 53% conversion. Purification by recycling HPLC chromatography gave the pure product (88 mg, 24% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21−7.16 (m, 5H), 4.87−4.80 (m, 2H), 4.03 (s, 2H), 3.17 (s, 2H), 1.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) d 196.3, 138.3, 137.4, 128.7, 128.5, 127.2, 115.9, 52.4, 33.3, 22.3 ppm; IR neat, υ_{max} 1688, 1648, 1496, 1453, 1377, 1186, 1059, 1004, 900, 701 cm^{-1}; MS (m/z) 206 (M^+), 178, 122, 91 (100), 83; HRMS calcd for $C_{12}H_{14}OS$, 206.0765, found 206.0785. Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.98 H, 7.06.

(*E*)-2-Pentenoic Acid *S*-Phenyl Ester (27) and 3-Pentenoic Acid *S*-Ester (28) from 1-(2-Butenyl) Phenyl Sulfide (26). Following the general procedure, palladium acetate (22 mg, 0.1 mmol, 10%) and 1,3-bis (diphenylphosphi-

no)propane (41 mg, 0.1 mmol, 10%) were placed in a dry autoclave liner followed by 1-(2-butenyl) phenyl sulfide (**26**) (164 mg, 1.0 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 44 h. The ^{1}H NMR yield based on added internal standard was determined to be 83% with 61% conversion. Purification by recycling HPLC on polystyrene afforded 100 mg (0.52 mmol, 52%) of the pure product as an inseparable mixture of **27** and **28**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34–7.31 (m, 10H), 6.96 (dt, J = 15.5, 6.2 Hz, 1H), 6.09 (dt, J = 15.5, 1.7 Hz, 1H), 5.67–5.41 (m, 2H), 3.36–3.28 (m, 0.2 × 2H), 3.26–3.19 (m, 0.8 × 2H), 2.26–2.10 (m, 2H), 1.68–59 (m, 3H), 1.01 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 195.6, 188.1, 148.1, 134.6, 134.5, 131.4, 129.3, 129.1, 127.9, 127.7, 126.9, 122.0, 121.0, 47.2, 41.8, 25.3, 17.9, 12.2 ppm; IR neat, υ_{max} 2969, 1683, 1632, 1477, 1440, 1276, 1152, 1054, 980, 790, 688 cm^{-1}; MS (*m/z*) 192 (M^+), 109, 83 (100); HRMS calcd for $C_{11}H_{12}OS$, 192.0609, found 192.0614. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.76; H, 6.38.

***(E)*-2-Pentenoic Acid *S*-Phenyl Ester (27) and 3-Pentenoic Acid *S*-Ester (28) from 3-(1-Butenyl) Phenyl Sulfide (29).** Following the general procedure, palladium acetate (26 mg, 0.12 mmol, 10%) and 1,3-bis(diphenylphosphino)propane (48 mg, 0.12 mmol, 10%) were placed in a dry autoclave liner followed by 3-(1-butenyl) phenyl sulfide (**29**) (190 mg, 1.15 mmol) and 4 mL of dry distilled toluene. After assembly of the autoclave and pressurizing to 68 atm of CO, the reaction was allowed to proceed at 140 °C for 44 h. The ^{1}H NMR yield based on added internal standard was determined to be 59% with 84% conversion. Purification by recycling HPLC on polystyrene gave 107 mg (0.64 mmol, 56%) of the pure product as an inseparable mixture with compound (**29**). (Spectral data are identical to those obtained in the previous reaction with 2-butenyl phenyl sulfide.)

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this research. One of us (C.C.) is appreciative to NSERC for a Postgraduate Scholarship.

Supporting Information Available: Copies of ^{1}H and ^{13}C-NMR spectra of allyl 4-fluorophenyl sulfide, allyl 4-methoxyphenyl sulfide, **10**, and **15–21** (19 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.

JO9501708