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Rhodium-Catalyzed Isomerization and Alkyne Exchange Reactions of 1,4-Dithiins via the 1,2-Ethenedithiolato Rhodium Complex

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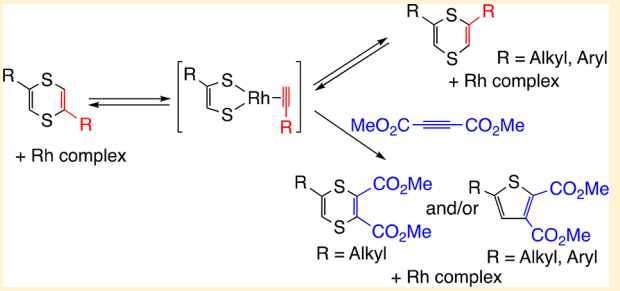
Supporting Information

ABSTRACT: Rhodium-catalyzed isomerization and alkyne exchange reactions of 1,4-dithiines occurred by cleavage of two C−S bonds. The 2,5- and 2,6-disubstituted 1,4-dithiins underwent isomerization reactions in toluene at 110 °C, providing equilibrium mixtures of isomers. At 150 °C, the reaction of 1,4-dithiins and dimethyl acetylenedicarboxylate gave unsymmetric 2,3-di(methoxycarbonyl)-1,4-dithiins and 2,3-di(methoxycarbonyl)thiophenes, the latter of which were formed by desulfurization of the 1,4-dithiins. A related reaction of the alkyne and a 1,2-dithiete gave a 2,3-di(methoxycarbonyl)thiophene. These reactions are considered to involve 1,2-ethenedithiolato rhodium intermediates.



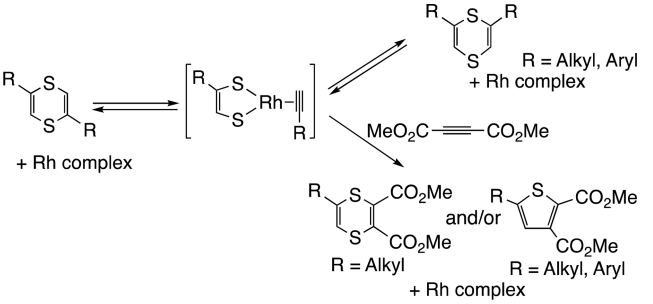
INTRODUCTION

1,4-Dithiines make up an interesting group of six-membered heterocyclic compounds containing two sulfur atoms and two C=C bonds with nonaromatic nonplanar structures.[1] The compounds, especially those not condensed with aromatic groups, exhibit notable chemical properties because of their nonaromatic nature and the presence of two reactive sulfur atoms. Theoretical and experimental studies have been conducted on the chemical reactivity of 1,4-dithiines to provide radical cations.[2] An interesting reaction is sulfur extrusion by 1,4-dithiins under heating to provide thiophenes, where two C−S bonds on a single sulfur atom were cleaved with concomitant formation of a C−C bond.[3] For example, 2,5-diphenyl-1,4-dithiin extruded a sulfur atom at 190 °C to form 2,4-diphenylthiophene.

We considered that the use of transition-metal catalysis on the reaction of 1,4-dithiins would provide a new methodology for synthesizing organosulfur compounds.[4] Described here are rhodium-catalyzed isomerization and alkyne exchange reactions of 1,4-dithiins by the cleavage of two C−S bonds (Scheme 1). The isomerization reaction between 2,5- and 2,6-disubstituted 1,4-dithiins provided equilibrium mixtures of isomers in statistical yields.[5] The alkyne exchange reactions of 2,5- and 2,6-disubstituted 1,4-dithiins with dimethyl acetylenedicarboxylate gave 5-substituted 2,3-di(methoxycarbonyl)-1,4-dithiin and/or 2,3-di(methoxycarbonyl)thiophenes. The reaction of dimethyl acetylenedicarboxylate and a 1,2-dithiete gave a 2,3-di(methoxycarbonyl)thiophene.

These rhodium-catalyzed reactions are considered to involve 1,2-ethenedithiolato rhodium intermediates. Studies of the catalytic reaction of the 1,2-ethenedithiolato rhodium complex have been limited.[6] The η^5-cyclopentadienyl (1,2-dimethoxycarbonyl-1,2-ethylenedithiolato-*S*,*S*)rhodium complex [$CpRh(S_2C_2Z_2)$, where Z = CO_2Me] was proposed to be an intermediate in the catalytic formation of 2,3,4,5-tetra(methoxycarbonyl)thiophene from dimethyl acetylenedicarboxylate and sulfur.[6a] The work presented here describes notable catalytic reactivity of 1,2-ethenedithiolato rhodium complexes.

Scheme 1. Isomerization and Exchange Reactions of 1,4-Dithiins via the 1,2-Ethenedithiolato Rhodium Intermediate



RESULTS AND DISCUSSION

The isomerization reaction of 2,5- and 2,6-disubstituted 1,4-dithiins was examined under rhodium-catalyzed conditions. When 2,6-di(*tert*-butyl)-1,4-dithiin **1a** was treated with dimethyl acetylenedicarboxylate **3** (3 equiv) in the presence of $RhH(dppe)_2$ [10 mol %; dppe = 1,2-bis(diphenylphosphino)ethane] in refluxing toluene (bp 110 °C) for 24 h, 2,5-di(*tert*-butyl)-1,4-dithiin **2a** (48%) was obtained with recovery of **1a** (51%) (Scheme 2). **1a** and **2a**

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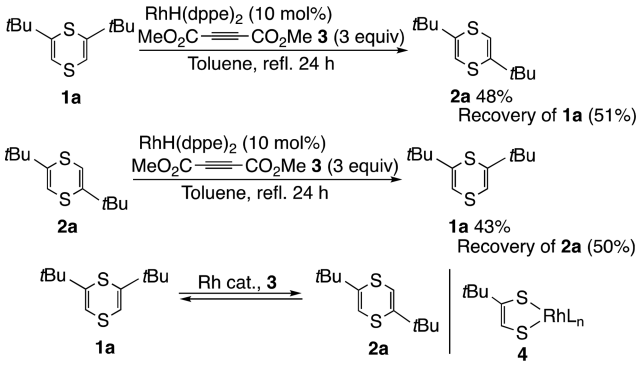
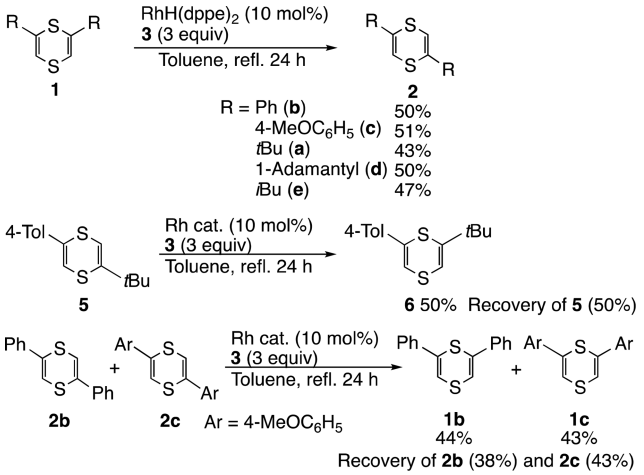
Scheme 2. Isomerization of 2,5- and 2,6-Di(*tert*-butyl)-1,4-dithiins



were readily separated by silica gel chromatography. No reaction occurred in the absence of $RhH(dppe)_2$ or **3**. The yield of **2a** was 19% at 6 h. When the molar ratio of **3** to **1a** was reduced from 3 equiv to 2, 1, and 0.5 equiv, the yield of **2a** decreased from 48% to 40%, 38%, and 15%, respectively. Although a stoichiometric amount of **3** was required for higher chemical yields, **3** was recovered quantitatively. The reverse reaction of **2a** under the same reaction conditions gave **1a** in 43% yield with recovery of **2a** (50%) (Scheme 2), which indicated the equiliblium nature of the reaction. The isomerization reaction occurred under rhodium-catalyzed conditions without desulfurization to form thiophenes. The results suggest the formation of 1,2-ethenedithiolato rhodium intermediate **4**.

Several 2,6-diaryl-1,4-dithiins (**1b** and **1c**) were isomerized to the corresponding 2,5-dialkyl-1,4-dithiins (**2b** and **2c**, respectively) in refluxing toluene (Scheme 3). 2,6-Diaryl-1,4-

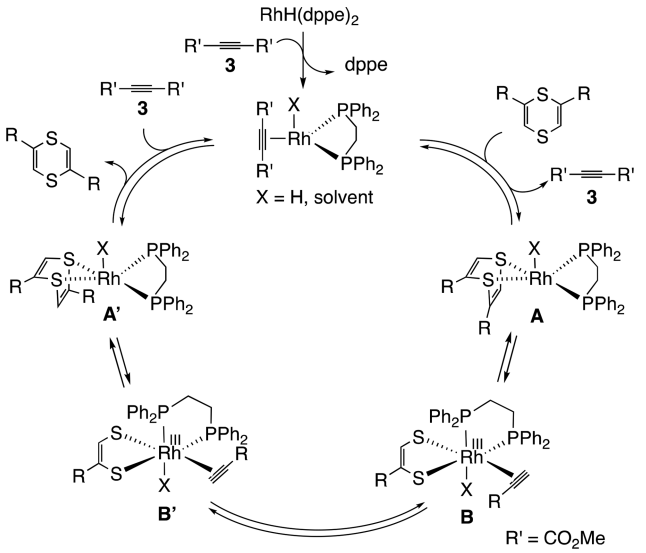
Scheme 3. Isomerization of Various 1,4-Dithiins



dithiins (**1d** and **1e**) also underwent the isomerization giving 2,5-dialkyl-1,4-dithiins (**2d** and **2e**, respectively). These 2,6-disubstituted 1,4-dithiins **1** and 2,5-disubstituted 1,4-dithiins **2** were readily separated by silica gel chromatography. The structure of the isomerized 1,4-dithiins was determined by comparison with the synthesized authentic compounds.[7] The substituent on 1,4-dithiins did not significantly affect the reaction. Unsymmetric 2-(*tert*-butyl)-5-(4-tolyl)-1,4-dithiin (**5**) isomerized to 2-(*tert*-butyl)-6-(4-tolyl)-1,4-dithiin (**6**) with a 50% yield. A crossover reaction of **2b** and **2c** provided a mixture of **1b** and **1c** with 44% and 43% yields along with recovered **2b** and **2c**. The crossover product 2-(4-methoxyphenyl)-6-phenyl-1,4-dithiin was not detected. Then, the isomerization is an intramolecular process. This reaction is a convenient method for obtaining substituted 1,4-dithiins.

A possible mechanism of the isomerization reaction is as follows (Scheme 4). The phosphine ligand in $RhH(dppe)_2$ is

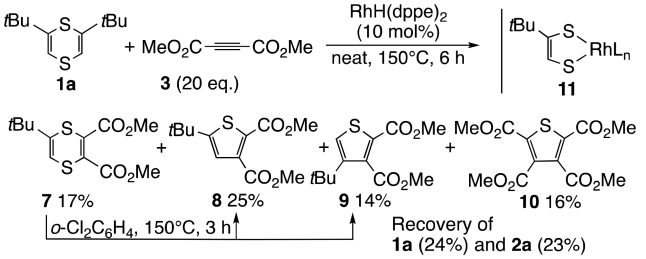
Scheme 4. Possible Mechanism of Isomerization of 1,4-Dithiins



exchanged with **3**. A 1,4-dithiin coordinates through two sulfur atoms to form intermediate **A** with release of alkyne **3**. Then, oxidative addition provides 1,2-ethenedithiolato rhodium intermediate **B**,[6] and the coordinated alkyne isomerizes from **B** to **B′**. Subsequently, reductive elimination provides an isomeric 1,4-dithiin via formation of **A′**, and the coordination of **3** regenerates the rhodium(I) catalyst.

Unsymmetric 1,4-dithiins were formed by a rhodium-catalyzed alkyne exchange reaction, which was conducted under forced conditions using excess dimethyl acetylenedicarboxylate **3** without a solvent. When 2,6-di(*tert*-butyl)-1,4-dithiin **1a** was reacted with **3** (20 equiv) in the presence of $RhH(dppe)_2$ (10 mol %) at 150 °C for 6 h, 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)-1,4-dithiin **7** (17%), 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)thiophene **8** (25%), 4-(*tert*-butyl)-2,3-di(methoxycarbonyl)thiophene **9** (14%), and 2,3,4,5-tetra(methoxycarbonyl)thiophene **10** (16%) were obtained with recovery of **1a** (24%) and **2a** (23%) (Scheme 5). The total yield of alkyne exchange products **7**–**9**, which contained the

Scheme 5. Alkyne Exchange of 2,6-Di(*tert*-butyl)-1,4-dithiins



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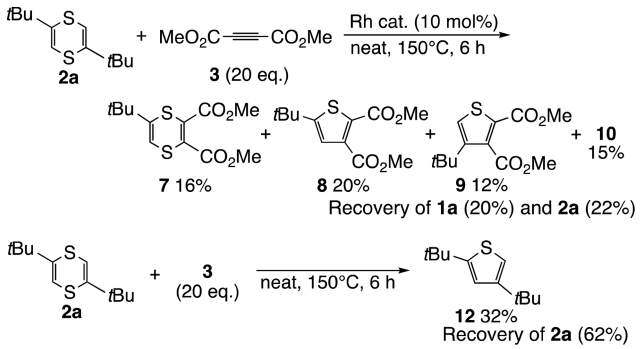
1,2-dicarboxylate moiety, reached 56%. An independent experiment confirmed thermal extrusion of a sulfur atom from **7** at 150 °C for 3 h without a catalyst.[3b] Reaction of **8** and **9** with sulfur did not provide **7** in the presence of $RhH(dppe)_2$, which indicated that the formation of **7** is irreversible. From these results, compounds **7**–**9** are thought to be the alkyne exchange products, which are derived from the cleavage of two C–S bonds in 1,4-dithiin **1a** followed by addition of **3**. It was then considered that the alkyne exchange reaction occurred via 1,2-ethenedithiolato rhodium intermediate **11**. The formation of **10** was due to the trapping of the eliminated sulfur atom derived from 1,4-dithiin **7** by two molecules of **3** (also see Scheme 7).

The reaction of 2,6-di(*tert*-butyl)-1,4-dithiin **2a** and **3** gave **7** (16%), **8** (20%), **9** (12%), and **10** (15%), which were accompanied by the recovery of **1a** (20%) and **2a** (22%) (Scheme 6). The total yield of alkyne exchange products **7**–**9**

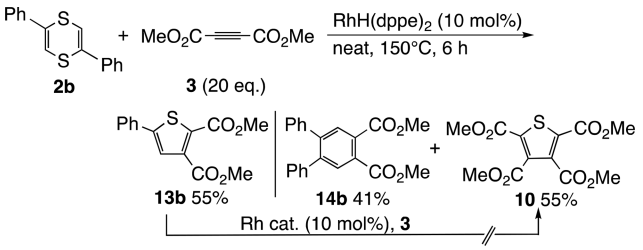
Scheme 6. Alkyne Exchange of 2,5-Di(*tert*-butyl)-1,4-dithiin



reached 48%. The formation of **7** from **1a** and **2a** in comparable yields is consistent with the involvement of 1,2-ethenedithiolato rhodium intermediate **11** (Schemes 5 and 6). Because no desulfurization products derived from **1a** and **2a** were observed, the desulfurization of **7** to thiophenes **8** and **9** appears to be faster than the desulfurization of **1a** and **2a** to 2,4-di(*tert*-butyl)thiophene **12**. In accordance with this, heating of a mixture of **2a** and **3** at 150 °C for 6 h in the absence of $RhH(dppe)_2$ gave desulfurization product **12** in only 32% yield. When the alkyne exchange reaction of **2a** was conducted with 4-tolylacetylene, 1,2-diphenylacetylene, 2-propynoic acid methyl ester, or 1-decyne instead of **3**, no reaction other than desulfurization occurred.

1,4-Dithiins with two aryl groups also underwent an alkyne exchange reaction, which showed a stronger tendency to form thiophenes. The rhodium-catalyzed reaction of 2,5-diphenyl-1,4-dithiin **2b** and **3** at 150 °C gave 2,3-di(methoxycarbonyl)-5-phenylthiophene **13b** (55%), which was accompanied by 1,2-di(4-methoxyphenyl)-4,5-diphenylbenzene **14b** (41%) and 2,3,4,5-tetra(methoxycarbonyl)thiophene **10** (55%) (Scheme 7). The structure of **13b** was determined by X-ray crystal structure analysis (Figure 1). Unsymmetric thiophene **13b** was formed by alkyne exchange of **2b** and **3** followed by desulfurization, and no corresponding dithiin was obtained. **14b** was formed by the rhodium-catalyzed trimerization reaction of **3** and phenylacetylene, which was extruded from **2b**. Because **10** was not formed by the reaction of **13b** and **3**, the formation of **10** was due to trapping of the eliminated sulfur atom derived from the 1,4-dithiins by two molecules of **3**. The formation of **10** likely proceeds via the dithiorhodium

Scheme 7. Alkyne Exchange of 2,5-Diphenyl-1,4-dithiins



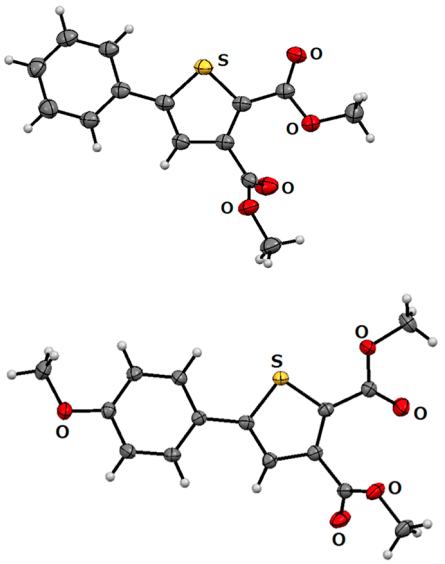
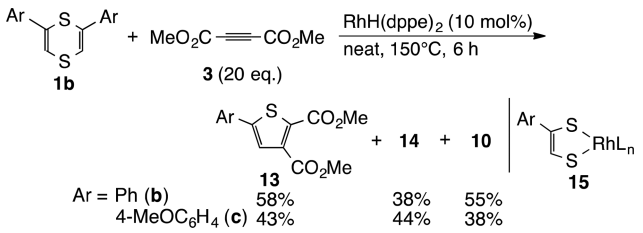


Figure 1. ORTEP views of **13b** and **13c** with thermal ellipsoids drawn at the 50% probability level.

intermediate, which is formed by trapping the sulfur atom eliminated from **2b**.[4]

2,6-Diphenyl-1,4-dithiin **1b** also gave **13b** (58%), which was accompanied by **14b** (38%) and **10** (50%) (Scheme 8).

Scheme 8. Alkyne Exchange of 2,6-Diphenyl-1,4-dithiins



Isomeric dithiins **1b** and **2b** provided the same alkyne-exchanged thiophene **13b** (Schemes 7 and 8), which is again consistent with the formation of 1,2-ethenedithiolato rhodium intermediate **15**. The reaction of 2,5-di(4-methoxyphenyl)-1,4-dithiin **1c** and **3** gave 2-(4-methoxyphenyl)-4,5-di(methoxycarbonyl)thiophene **13c** (43%), which was accompanied by **14c** (44%) and **10** (38%) (Scheme 8). The structure of **13c** was determined by X-ray crystal structure analysis (Figure 1).

The alkyne exchange reaction was summarized as follows. (i) The isomerization and alkyne exchange occurred via a similar mechanism. (ii) Desulfurization could occur at a higher temperature. (iii) These reactions could be explained by the intermediacy of the 1,2-dithiolato complex.

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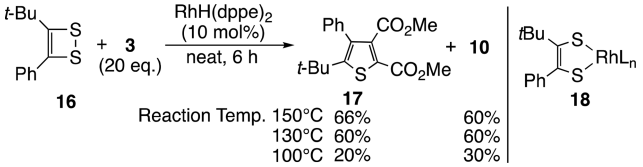
To further examine the formation of the 1,2-ethenedithiolato rhodium intermediate, the rhodium-catalyzed reaction of 1,2-dithiete **16** and alkyne **3** was conducted (Scheme 9).

Scheme 9. Reaction of 1,2-Dithiete 16 with 3



Recently, we have reported the synthesis of 1,3,2-dithiaphospholes from 1,2-dithietes, which was considered to involve a 1,2-ethenedithiolato rhodium intermediate.[8] When 3-(*tert*-butyl)-4-phenyl-1,2-dithiete **16**[9] was reacted with excess **3** (20 equiv) in the presence of $RhH(dppe)_2$ (10 mol %) at 130 °C for 6 h, 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)-4-phenylthiophene **17** (60%) was obtained, which was accompanied by **10** (60%) (Scheme 9). The structure of **17** was determined by X-ray crystal structure analysis (Figure 2). No isomeric 4-(*tert*-butyl)-2,3-di(methoxycarbonyl)-5-phenylthiophene was obtained. 6-(*tert*-Butyl)-2,3-di(methoxycarbonyl)-5-phenyl-1,4-dithiin was not detected. $RhH(dppe)_2$ and **3** were essential for the formation of thiophenes **17** and **10**, and no reaction occurred in their absence. When the reaction temperature was decreased to 100 °C, the yields of **17** and **10** decreased to 20% and 30%, respectively. It is considered that 1,2-ethenedithiolato rhodium intermediate **18** was formed.

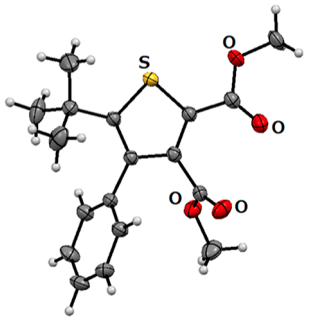


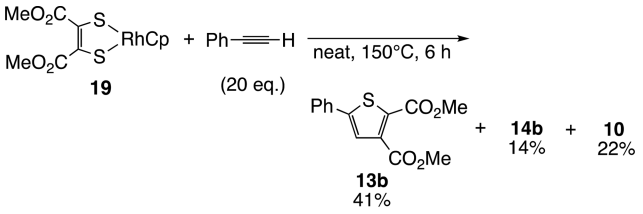
Figure 2. ORTEP view of **17** with thermal ellipsoids drawn at the 50% probability level.

These rhodium-catalyzed reactions provided moderate yields of unsymmetric 5-alkyl/aryl-2,3-di(methoxycarbonyl)-thiophenes **8**, **9**, **13b**, **13c**, and **17**, which have rarely been synthesized.[10]

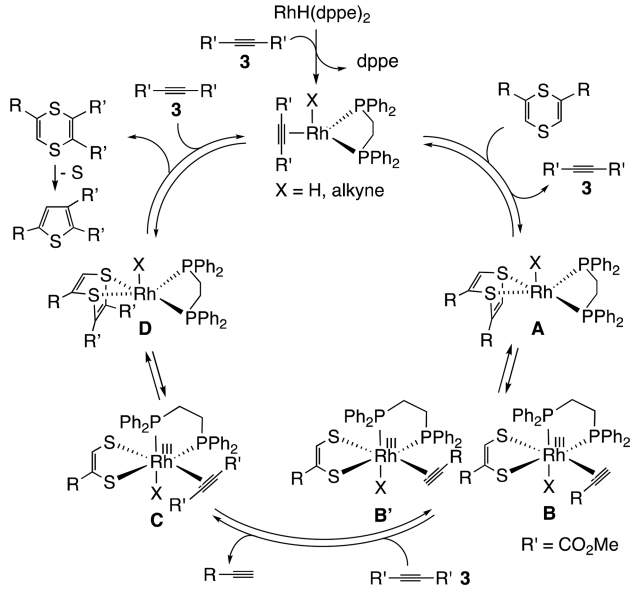
The reactivity of the 1,2-ethenedithiolato rhodium intermediate was also examined using **19** [$CpRh(S_2C_2Z_2)$, where Z = CO_2Me].[6a] The reaction of **19** in refluxing phenylacetylene (bp 143 °C) gave unsymmetric thiophene **13b** (41%), which was accompanied by **14b** (14%) and **10** (22%) (Scheme 10). Thiophene **13b** was obtained by the stoichiometric reaction of 1,2-ethenedithiolato rhodium **19** and an alkyne.

The formation of 1,2-ethenedithiolato rhodium intermediates by the cleavage of two C−S bonds in 1,4-dithiins is supported by the following observations. (i) Isomerization between 2,5- and 2,6-disubstituted 1,4-dithiins occurs. (ii) Alkyne-exchanged 1,4-dithiin and/or thiophenes are obtained by the reaction of 1,4-dithiins and **3**. (iii) Liberated alkynes derived from 1,4-dithiins are captured by trimerization to form benzene derivatives. (iv) The reaction of a 1,2-dithiete and **3** gives a thiophene. (v) The stoichiometric reaction of a 1,2-ethenedithiolato rhodium complex and an alkyne gives a thiophene. A possible mechanism of the alkyne exchange reaction of a 1,4-dithiin follows (Scheme 11). The phosphine ligand in $RhH(dppe)_2$ is exchanged with **3**, and a 1,4-dithiin coordinates through two sulfur atoms to form intermediate **A** with release of alkyne **3**. Then, oxidative addition provides an isomeric mixture of 1,2-ethenedithiolato rhodium intermediates **B** and **B′**. The alkyne exchange in **B** and **B′** with **3** forms another 1,2-ethenedithiolato rhodium intermediate **C**. Subsequently, reductive elimination provides a 1,4-dithiin via formation of **D**, and the coordination of **3** regenerates the rhodium(I) catalyst.

Scheme 10. Synthesis of 13b Using the 1,2-Ethenedithiolato Rhodium Complex



Scheme 11. Possible Mechanism of the Alkyne Exchange Reaction of 1,4-Dithiins



CONCLUSIONS

In summary, rhodium-catalyzed isomerization and alkyne exchange reactions involving the cleavage of two C−S bonds of 1,4-dithiins are developed. The reactions are novel synthetic methods for substituted 1,4-dithiins and 2,3-di(methylcarbonyl)thiophenes. These reactions involve formation of 1,2-ethenedithiolato rhodium intermediates from 1,4-dithiins, which can be used for the synthesis of various organosulfur compounds.

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EXPERIMENTAL SECTION

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury instrument (400 MHz), and tetramethylsilane was used as a standard. Infrared (IR) spectra were recorded on a JASCO FT/IR-410 spectrophotomer. Melting points were determined with a Yanagimoto micro melting point apparatus without correction. High- and low-resolution mass spectra were recorded on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. X-ray diffraction data were recorded on a Rigaku R-AXIIS RAPID instrument. Kanto Chemical. Co. Inc. silica gel 60 (63−210 μm) was employed for flash column chromatography. Starting materials **1a**−**1c**, **2a**−**2e**, and **5** were synthesized by literature methods.[5,7] **1d** and **1e** were synthesized by the rhodium-catalyzed isomerization of **2d** and **2e** presented here.

Typical Procedures for Isomerization of 1a to 2a. In a two-neck flask were placed RhH(dppe)$_2$ [45.0 mg, 10 mol %; dppe = 1,2-bis(diphenylphosphino)ethane], dimethyl acetylenedicarboxylate (1.5 mmol, 184.2 μL), and 2,6-di(1,1-dimethylethyl)-1,4-dithiin **1a** (0.5 mmol, 114.0 mg) in toluene (0.5 mL) under an argon atomosphere, and the mixture was heated at reflux for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2,5-di(1,1-dimethylethyl)-1,4-dithiin **2a** [54.9 mg, 48%, R_f = 0.43 (hexane)] and **1a** [59.6 mg, 51%, R_f = 0.38 (hexane)]. **2a**:[5] colorless solid; mp 81.0−82.5 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (18H, s), 6.08 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 37.9, 115.2, 154.0; IR (KBr) 2964, 1458, 1361 cm^{-1}; MS (EI) m/z 228 (M$^+$, 100%), 157 (M$^+$ − 71, 57%); HRMS calcd for $C_{12}H_{20}S_2$ 228.1006, found 228.0981. **1a**:[5] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (18H, s), 6.20 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 38.5, 116.7, 151.9; IR (neat) 2964, 2868, 1459, 1239 cm^{-1}; MS (EI) m/z 228 (M$^+$, 100%), 157 (M$^+$ − 71, 94%); HRMS calcd for $C_{12}H_{20}S_2$ 228.1006, found 228.1014.

*2,6-Diphenyl-1,4-dithiin (**1b**).* Orange solid [recovery of **1b**, 64.3 mg, 48%, R_f = 0.70 (4/1 hexane/ethyl acetate)]; mp 63.0−64.5 °C (hexane) (lit.[7a] 62.0−63.0 °C); ^{1}H NMR (400 MHz, acetone-d_6) δ 6.83 (2H, s), 7.35−7.43 (6H, m), 7.72 (4H, dd, J = 6.8, 1.6 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 119.9, 127.6, 129.5, 129.6, 137.8, 138.8; IR (KBr) 3027, 1533, 1488 cm^{-1}; MS (EI) m/z 268 (M$^+$, 100%), 121 (M$^+$ − 147, 33%); HRMS calcd for $C_{16}H_{12}S_2$ 268.0380, found 268.0394.

*2,5-Diphenyl-1,4-dithiin (**2b**).* Yellow solid [67.1 mg, 50%, R_f = 0.72 (4/1 hexane/ethyl acetate)]; mp 117.5−119.0 °C (hexane) [lit.[11] 116.5−118.0 °C (methanol)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (2H, s), 7.32−7.38 (6H, m), 7.60 (4H, dd, J = 8.4, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.3, 127.1, 128.6, 128.7, 136.5, 140.6; IR (KBr) 3027, 1542, 1481, 1441 cm^{-1}; MS (EI) m/z 268 (M$^+$, 100%), 121 (M$^+$ − 147, 38%); HRMS calcd for $C_{16}H_{12}S_2$ 268.0380, found 268.0367.

*2,6-Di(4-methoxyphenyl)-1,4-dithiin (**1c**).*[12] Yellow solid [recovery of **1c**, 77.1 mg, 47%, R_f = 0.50 (4/1 hexane/ethyl acetate)]; mp 124.0−125.5 °C (hexane) (lit.[12] 125.5−127.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (6H, s), 6.42 (2H, s), 6.89 (4H, d, J = 8.8 Hz), 7.58 (4H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.9, 116.3, 128.3, 129.7, 139.4, 159.9; IR (KBr) 2927, 1604, 1505, 1253, 1175, 1032 cm^{-1}; MS (EI) m/z 328 (M$^+$, 100%), 313 (M$^+$ − 15, 37%); HRMS calcd for $C_{18}H_{16}O_2S_2$ 328.0592, found 328.0600.

*2,5-Di(4-methoxyphenyl)-1,4-dithiin (**2c**).* Yellow solid [83.5 mg, 51%, R_f = 0.52 (4/1 hexane/ethyl acetate)]; mp 172.5−173.5 °C (hexane) [lit.[3c] 167.0−169.0 °C (methylene choloride/petroleum ether)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (6H, s), 6.45 (2H, s), 6.88 (4H, d, J = 8.8 Hz), 7.55 (4H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 113.9, 115.2, 128.5, 129.2, 141.1, 160.0; IR (KBr) 2958, 1601, 1502, 1252, 1175, 1028, 785 cm^{-1}; MS (EI) m/z 328 (M$^+$, 100%), 313 (M$^+$ − 15, 28%); HRMS calcd for $C_{18}H_{16}O_2S_2$ 328.0592, found 328.0587.

*2,6-Di(1-adamantyl)-1,4-dithiin (**1d**).* Colorless solid [recovery of **1d**, 89.8 mg, 47%, R_f = 0.20 (hexane)]; mp 213.0−214.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.74 (12H, m), 1.83 (12H, d, J = 2.8 Hz), 2.02−2.06 (12H, m), 6.15 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 36.6, 40.2, 41.9, 117.2, 152.1; IR (KBr) 2901, 2845, 1552, 1446 cm^{-1}; MS (EI) m/z 384 (M$^+$, 100%), 135 (M$^+$ − 249, 87%); HRMS calcd for $C_{24}H_{32}S_2$ 384.1945, found 384.1940.

*2,5-Di(1-adamantyl)-1,4-dithiin (**2d**).* Colorless solid [96.6 mg, 50%, R_f = 0.22 (hexane)]; mp 164.5−166.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64−1.73 (12H, m), 1.81 (12H, d, J = 2.8 Hz), 2.01−2.04 (12H, m), 6.00 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 36.6, 39.7, 41.8, 115.1, 154.7; IR (KBr) 2901, 2846, 1548, 1446 cm^{-1}; MS (EI) m/z 384 (M$^+$, 97%), 135 (M$^+$ − 249, 100%); HRMS calcd for $C_{24}H_{32}S_2$ 384.1945, found 384.1937.

*2,6-Di(2-methylpropyl)-1,4-dithiin (**1e**).* Yellow oil [recovery of **1e**, 57.5 mg, 50%, R_f = 0.50 (hexane)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (12H, d, J = 6.4 Hz), 1.91 (2H, septet, J = 6.8 Hz), 2.22 (4H, d, J = 6.8, 0.4 Hz), 5.91 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 27.4, 45.5, 116.2, 139.7; IR (neat) 2954, 2925, 2868, 1464, 1385 cm^{-1}; MS (EI) m/z 228 (M$^+$, 100%), 185 (M$^+$ − 43, 29%); HRMS calcd for $C_{12}H_{20}S_2$ 228.1006, found 228.1005.

*2,5-Di(2-methylpropyl)-1,4-dithiin (**2e**).* Yellow oil [53.7 mg, 47%, R_f = 0.53 (hexane)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (12H, d, J = 6.8 Hz), 1.90 (2H, septet, J = 6.8 Hz), 2.21 (4H, dd, J = 6.8, 0.4 Hz), 5.93 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 27.3, 46.0, 116.4, 138.9; IR (neat) 2954, 2925, 2868, 1566, 1464 cm^{-1}; MS (EI) m/z 228 (M$^+$, 100%), 185 (M$^+$ − 43, 33%); HRMS calcd for $C_{12}H_{20}S_2$ 228.1006, found 228.1000.

*2-(1,1-Dimethylethyl)-5-(4-tolyl)-1,4-dithiin (**5**).* Orange solid [recovery of **5**, 62.4 mg, 48%, R_f = 0.32 (20/1 hexane/toluene)]; mp 47.0−48.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (9H, s), 2.34 (3H, s), 6.20 (1H, d, J = 0.4 Hz), 6.45 (1H, d, J = 0.4 Hz), 7.14 (2H, d, J = 8.4, 0.8 Hz), 7.48 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 29.7, 38.1, 114.8, 117.0, 126.9, 129.2, 133.9, 138.5, 142.3, 152.9; IR (KBr) 3025, 2964, 1541, 1503, 1456 cm^{-1}; MS (EI) m/z 262 (M$^+$, 100%), 247 (M$^+$ − 15, 49%); HRMS calcd for $C_{16}H_{12}S_2$ 262.0850, found 262.0838.

*2-(1,1-Dimethylethyl)-6-(4-tolyl)-1,4-dithiin (**6**).* Yellow oil [65.8 mg, 50%, R_f = 0.29 (20/1 hexane/toluene)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (9h, s), 2.35 (3H, s), 6.20 (1H, s), 6.55 (1H, s), 7.14 (2H, d, J = 8.0 Hz), 7.49 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 29.8, 38.6, 115.9, 119.1, 126.9, 129.2, 134.6, 138.4, 140.4, 151.5; IR (neat) 3024, 2965, 1547, 1505, 1460 cm^{-1}; MS (EI) m/z 262 (M$^+$, 84%), 206 (M$^+$ − 56, 100%); HRMS calcd for $C_{15}H_{18}S_2$ 262.0850, found 262.0866.

Typical Procedures for Alkyne Exchange Reaction of 1a with 3. In a two-neck flask were placed RhH(dppe)$_2$ [45.0 mg, 10 mol %; dppe = 1,2-bis(diphenylphosphino)ethane], 2,6-di(1,1-dimethylethyl)-1,4-dithiin **1a** (0.5 mmol, 114.0 mg), and dimethyl acetylenedicarboxylate **3** (10.0 mmol, 1.23 μL) under an argon atomosphere, and the mixture was heated at 150 °C for 6 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)-1,4-dithiin **7** [24.0 mg, 17%, R_f = 0.37 (4/1 hexane/ethyl acetate)], 5-(*tert*-butyl)-2,3-di-(methoxycarbonyl)thiophene **8** [32.3 mg, 25%, R_f = 0.37 (4/1 hexane/ethyl acetate)], 4-(*tert*-butyl)-2,3-di(methoxycarbonyl)-thiophene **9** [17.7 mg, 14%, R_f = 0.33 (4/1 hexane/ethyl acetate)], and 2,3,4,5-tetra(methoxycarbonyl)thiophene **10** [24.9 mg, 16%, R_f = 0.15 (4/1 hexane/ethyl acetate)] with recovery of **1a** (27.4 mg, 24%) and **2a** (26.2 mg, 23%). Then, **7** and **8** were separated by recycling gel permeation chromatography. **7**:[13] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (9H, s), 3.85 (3H, s), 3.89 (3H, s), 6.09 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.1, 35.0, 52.5, 52.6, 123.4, 129.8, 136.9, 161.6, 163.2, 165.0; IR (neat) 2925, 1731, 1464, 1261, 1075 cm^{-1}; MS (EI) m/z 288 (M$^+$, 100%), 57 (M$^+$ − 231, 71%); HRMS calcd for $C_{12}H_{16}O_4S_2$ 288.0490, found 288.0487. **8**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (9H, s), 3.85 (3H, s), 3.94 (3H, s), 7.23 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 34.5, 52.4, 52.9, 126.0, 131.3, 138.9, 150.8, 161.6, 168.2; IR (neat) 2924, 2854, 1741, 1457, 1242, 1022 cm^{-1}; MS (EI) m/z 256 (M$^+$, 16%), 209 (M$^+$ − 47, 100%); HRMS calcd for $C_{12}H_{16}O_4S$ 256.0769, found 256.0761. **9**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (9H, s), 3.86

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(3H, s), 3.90 (3H, s), 7.02 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 35.0, 52.5, 52.6, 123.4, 129.8, 136.9, 161.6, 163.2, 165.0; IR (neat) 2957, 1723, 1452, 1246, 1092, 802 cm^{-1}; MS (EI) m/z 256 (M^+, 18%), 241 ($M^+ - 15$, 100%); HRMS calcd for $C_{12}H_{16}O_4S$ 256.0769, found 256.0781. **10**:[14] colorless solid; mp 126.5−127.5 °C (hexane) (lit.[14] 129.3−131.1 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.921 (6H, s), 3.923 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 53.3, 136.0, 137.0, 160.2, 162.8; IR (KBr) 2960, 1733, 1437, 1230 cm^{-1}; MS (EI) m/z 316 (M^+, 16%), 285 ($M^+ - 31$, 100%); HRMS calcd for $C_{12}H_{12}O_8S$ 316.0253, found 316.0259.

Desulfurization of 7 to 8 and 9. In a two-neck flask was placed 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)-1,4-dithiin **7** (20.2 mg, 0.07 mmol) in 1,2-dichlorobenzene (0.5 mL) under an argon atomosphere, and the mixture was heated at 150 °C for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 5-(*tert*-butyl)-2,3-di(methoxycarbonyl)thiophene **8** (9.7 mg, 54%) and 4-(*tert*-butyl)-2,3-di(methoxycarbonyl)thiophene **9** (6.5 mg, 36%).

*2,4-Di(tert-butyl)thiophene (**12**).* Colorless oil [0.5 mmol scale, 31.0 mg, 32%, R_f = 0.45 (hexane)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (9H, s), 1.37 (9H, s), 6.72 (1H, d, J = 1.6 Hz), 6.77 (1H, d, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 32.5, 33.5, 34.5, 114.3, 120.6, 152.4, 157.0; IR (neat) 2964, 1462, 1364, 1249 cm^{-1}; MS (EI) m/z 196 (M^+, 20%), 181 ($M^+ - 15$, 100%); HRMS calcd for $C_{12}H_2S$ 196.1286, found 196.1299.

*5-Phenyl-2,3-thiophenedicarboxylic Acid 2,3-Dimethyl Ester (**13b**).* Colorless solid [76.2 mg, 55%, R_f = 0.33 (4/1 hexane/ethyl acetate)]; mp 92.0−93.0 °C (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s), 3.94 (3H, s), 7.38−7.45 (3H, m), 7.46 (1H, s), 7.61 (2H, dd, J = 6.8, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.67, 52.69, 124.30, 126.2, 129.2, 131.6, 132.4, 138.0, 147.4, 149.1, 161.4, 164.5; IR (KBr) 2951, 1728, 1442, 1249 cm^{-1}; MS (EI) m/z 276 (M^+, 90%), 245 ($M^+ - 31$, 100%); HRMS calcd for $C_{14}H_{12}O_4S$ 276.0456, found 276.0458.

*1,2-Diphenyl-4,5-di(methoxycarbonyl)benzene (**14b**).*[15] Colorless solid [35.4 mg, 41% based on phenyl aetylene, R_f = 0.35 (4/1 hexane/ethyl acetate)]; mp 107.0−108.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (6H, s), 7.12−7.15 (4H, m), 7.23−7.25 (6H, m), 7.79 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 127.4, 128.1, 129.6, 130.7, 131.2, 139.5, 143.4, 167.9; IR (KBr) 2922, 1455, 805, 751 cm^{-1}; MS (EI) m/z 346 (M^+, 100%), 315 ($M^+ - 31$, 74%); HRMS calcd for $C_{22}H_{18}O_4$ 346.1205, found 346.1205.

*5-(4-Methoxyphenyl)-2,3-thiophenedicarboxylic Acid 2,3-Dimethyl Ester (**13c**).* Yellow solid [88.3 mg, 58%, R_f = 0.26 (4/1 hexane/ethyl acetate)]; mp 109.5−111.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s), 3.90 (3H, s), 3.94 (3H, s), 6.94 (2H, d, J = 9.2 Hz), 7.34 (1H, s), 7.54 (2H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 52.7, 55.4, 114.6, 123.2, 125.2, 127.6, 130.3, 138.2, 149.3, 160.5, 161.4, 164.7; IR (KBr) 2955, 2839, 1713, 1438, 1257, 1088, 1029 cm^{-1}; MS (EI) m/z 306 (M^+, 100%), 275 ($M^+ - 31$, 54%); HRMS calcd for $C_{15}H_{14}O_5S$ 306.0562, found 306.0562.

*1,2-Di(4-methoxyphenyl)-4,5-di(methoxycarbonyl)benzene (**14c**).* Colorless solid [38.7 mg, 38% based on 4-methoxyphenyl acetylene, R_f = 0.33 (4/1 hexane/ethyl acetate)]; mp 120.5−122.0 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (6H, s), 3.93 (6H, s), 6.79 (4H, d, J = 8.4 Hz), 7.07 (4H, d, J = 8.4 Hz), 7.74 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 55.2, 113.6, 130.3, 130.7, 131.2, 132.0, 142.9, 158.9, 168.0; IR (KBr) 2953, 2840, 1726, 1608, 1517, 1249, 1134, 835 cm^{-1}; MS (EI) m/z 406 (M^+, 100%), 375 ($M^+ - 31$, 20%); HRMS calcd for $C_{24}H_{22}O_6$ 406.1416, found 406.1406.

*5-tert-Butyl-4-phenyl-2,3-thiophenedicarboxylic Acid 2,3-Dimethyl Ester (**17**).* Colorless solid [0.25 mmol scale, 50.0 mg, 60%, R_f = 0.30 (4/1 hexane/ethyl acetate)]; mp 81.0−83.0 °C (hexane); ^{1}H NMR (400 MHz, acetone-d_6) δ 1.24 (9H, s), 3.49 (3H, s), 3.83 (3H, s), 7.24−7.26 (2H, m), 7.37−7.40 (3H, m); ^{13}C NMR (100 MHz, acetone-d_6) δ 32.3, 36.8, 52.3, 52.6, 124.6, 128.5, 128.9, 131.4, 136.2, 138.2, 143.2, 159.2, 161.7, 165.7; IR (KBr) 2954, 1741, 1718, 1442, 1289 cm^{-1}; MS (EI) m/z 332 (M^+, 29%), 285 ($M^+ - 47$, 100%); HRMS calcd for $C_{18}H_{20}O_4S$ 332.1082, found 332.1088.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00498.

NMR spectra and crystallographic details (PDF)

Accession Codes

CCDC 1527675, 1559628, and 1560074 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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