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<td>Minami, Yasunori</td>
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Studies on the Palladium- and Platinum-Mediated Cleavage of Carbon-Sulfur Bond of Thioesters and Their Addition to Alkynes

Yasunori Minami

Osaka University
2010
Studies on the Palladium- and Platinum-Mediated Cleavage of Carbon-Sulfur Bond of Thioesters and Their Addition to Alkynes

(Yasunori Minami

Osaka University

2010)
Preface

The studies described in this thesis has been carried out (2004-2010) under the supervision of Professor Nobuaki Kambe at the Department of Applied Chemistry, Graduate School of Engineering, Osaka University.

The objective of thesis is concerned with the studies on transformation of thioesters and iminosulfides with alkynes via cleavage of carbon-sulfur bond in the presence of transition-metal catalysts and the mechanistic insight into the reaction of thioesters with low-valent transition-metal complexes.

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March, 2010

Yasunori Minami
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General Introduction

Homogeneous transition metal-catalyzed reaction is one of the most important subjects in synthetic chemistry for the facile and accurate construction of a wide range of organic frameworks. It is well-known that carbon-halogen bonds are readily cleaved by the transition metal complexes, which normally act as promoters for a range of synthetic transformations (Scheme 1).

**Scheme 1. Oxidative Addition of Carbon-Halogen Bond to Transition-Metal Complex**

\[
\text{C} - \text{X} \quad \text{X} = \text{Halogen (Cl, Br, I)} \quad \text{"Oxidative Addition"} \quad \text{C} - \text{M} - \text{X} \quad \text{many catalytic reactions}
\]

Recently, catalytic reactions inspired by using other heteroatom functionalities in place of halogens are examined by many research groups (Scheme 2). On the basis of environmentally-

**Scheme 2. Oxidative Addition of Carbon-Heteroatom Bond to Transition-Metal Complex**

\[
\text{C} - \text{E} + \text{M} \rightarrow \text{C} - \text{M} - \text{E}
\]

friendly molecular transformation, an important example would be the addition reactions of carbon-heteroatom bonds to carbon-carbon unsaturated bonds that proceeds through perfect atom-economical transformation in principle to form new carbon-carbon and carbon-heteroatom bonds in a single operation. A wide range of substrates such as carbon-sulfur, \(^1\text{C(O)-SR}^2\), \(^2\)-nitrogen, \(^3\)-silicon, \(^4\)-tin and \(^6\)-boron bonds were employed for this purpose.

The author aimed at the development of new catalytic insertions of alkynes into carbon-sulfur bond employing thioesters (R\(^1\)C(O)-SR\(^2\)). Thioesters are readily accessible molecules, stable under air and useful building blocks. In organometallic chemistry, the reactivity of thioesters toward transition metal complexes (oxidative addition of carbonyl-sulfur bonds of thioesters to
transition metal complexes) lies in between esters and acid chlorides (Eq. 1). For an example,

\[
R^1 \text{H} \quad \text{m-H} \quad m = \text{SiR}_3, \quad \text{SnR}_3 \quad m = \text{SiR}_3, \quad \text{SnR}_3
\]

\[
R^1 \text{R}^3 \quad \text{m-R}^3 \quad m = \text{ZnX}, \quad \text{BX}_2
\]

\[
\text{X} = \text{Cl} > \text{SR} > \text{OR}
\]

the oxidative addition of thioester to group 10 zero-valent metal complex takes place smoothly to afford acylmetal complex under room temperature. On the other hand, oxidative addition of esters hardly proceeds. Actually, thioesters have been extensively employed as substrates in transition-metal catalyzed reactions (Scheme 3); decarbonylation, reduction to aldehydes, cross-coupling and addition to carbon-carbon unsaturated bonds. Our group also has developed a series of Pt catalyzed regio- and stereoselective decarbonylative addition of thioester (\(R^1 = \text{Ar, hetAr, vinyl}\)) to alkyne (Eq. 2). Moreover, stoichiometric reactions of thioesters with transition metal complexes were studied. Rh and Fe complexes arising from the oxidative addition of thioesters were reported by Shaver and Rauchfuss (Fig. 1). In these cases, directing groups (nitrogen and phosphorus) promoted the oxidative additions to Rh and Fe complexes. Our group have also discovered that the decarbonylation from acylplatinum complexes was promoted by the coordination of a lone pair of heteroatom to platinum in the reaction of thioesters with zero-valent platinum complexes (Scheme 4). This effect was also observed in the catalytic decarbonylation of thioesters. From these points of view, The author thought that thioesters may have the great potential as substrates for catalytic and stoichiometric reactions.
Moreover, The author also focused on iminosulfides (R^1C(NR^2)-SR^3) as analogues of thioesters. Iminosulfides are promising building blocks to introduce iminocarbon groups into other organic chemicals. However, in the field of transition-metal catalyzed reactions, the transformation using iminosulfides remains much less explored. To the best of my knowledge, only one reaction employing iminosulfides has been reported by Takemoto (Eq. 3). The author expected that the catalytic reaction using iminosulfides should proceed taking into account the results from the study on the reaction using thioesters.

This thesis describes studies on the catalytic reaction of thioesters and iminosulfides with alkynes as well as those mechanistic aspects of the oxidative addition of thioesters to low-valent transition metal complexes.

In chapter 1, Pd and Pt catalyzed CO-retained addition of thioesters to alkynes was examined (Eq. 4).
In chapter 2, Pd catalyzed addition of iminosulfides to alkynes was summarized (Eq. 5).

\[
\begin{align*}
R^1R^2N \text{SR}^3 + R\equiv R' & \xrightarrow{\text{cat. Pd}} R^1R^2N \text{SR}^3 \text{R}
\end{align*}
\]  

In chapter 3, one-pot cyclization of \(\alpha,\beta\)-unsaturated thioesters with propargyl alcohols in the presence of Pd/Cu catalyst and bases was disclosed (Eq. 6).

\[
\begin{align*}
R^1R^2S\text{Ar} + \equiv \text{OH} & \xrightarrow{\text{cat. Pd/Cu bases}} \text{R}
\end{align*}
\]

Finally, the mechanism of oxidative addition of \(\alpha,\beta\)-unsaturated thioesters to Pt(0) complexes is described in chapter 4 (Eq. 7).

\[
\begin{align*}
R^1R^2\text{SAr} & \xrightarrow{\text{Pt}(0)} R^1R^2\text{PtSAr} \rightarrow R^1R^2\text{PtSAr} \rightarrow R^1R^2\text{PtSAr}
\end{align*}
\]

References


Chapter 1
Transition-Metal Catalyzed Regioselective Acylthiolation of Alkynes
Using Thioesters

1-1. Introduction

Pt(PPh₃)₄-catalyzed intermolecular regio- and stereoselective decarbonylative arylthiolation of alkynes HC=CR (1) by R¹C(O)SR² (2, R¹ = Aryl) (Scheme 1, left)¹ to produce vinylsulfides (3) has already been reported by our group. However, straightforward intermolecular addition of C(O)-S bond of 2 to 1 producing enones has not yet been realized (Scheme 1, right).² The author expected that catalytic addition of C(O)-S bond to alkyne should proceed by the modulation of transition-metals, ligands and substituents in thioesters. Disclosed herein are the intermolecular regioselective aroylthiolation (R¹ = Aryl) and trifluoroacetylthiolation (R¹ = CF₃) of 1 to afford enone derivatives (4 and 5). The compounds containing polyfluorocarbon substituents have attracted much attention lately due to medical, material and agrichemical application.³

Scheme 1. Decarbonylative vs. CO-Retained Carbothiolation of Alkynes (1) Using Thioesters (2).

1-2. Pd/dppe-Catalyzed Aroylthiolation of Alkynes Using Ar¹C(O)SAr²

To test the idea, the attempted reaction of 1-octyne (1a; R = n-C₆H₁₃, 1.2 mmol) with Ar¹C(O)SAr² (2a; Ar¹ = p-tolyl, Ar² = p-MeO-C₆H₄, 1.0 mmol) in the presence of Pd(PPh₃)₄ (0.05 mmol) under toluene reflux gave an aroylthiolation product, (Ar¹C(O))(H)C=C(n-C₆H₁₃)(SAr²) (4a) in 10% yield (cis:trans = 39:61) together with 50% of an Ar¹SAr² (6a)⁴ and 20% of a hydrothiolation product H₂C=C(n-C₆H₁₃)(SA₁2) (7a)⁵ (run 1, Table 1). Next, the effects of various ligands were examined with Pd(dba)₂ as a palladium(0) source. No reaction occurred without an additional ligand (run 2, Table 1). The reactions using other monodentate ligands such as P(p-tolyl)₃, P(o-tolyl)₃, P(2-furyl)₃, PCy₃, P(n-Bu)₃ and PMe₂Ph also were not satisfactory: 6a and 7a were generated as major products (runs 3-8,
Table 1. The Effects of Ligands under the Pd-Catalyzed Reaction of 1a with 2a

<table>
<thead>
<tr>
<th>run</th>
<th>ligand</th>
<th>solvent</th>
<th>time (h)</th>
<th>3a (%)</th>
<th>4a (%) (cis:trans)</th>
<th>6a (%)</th>
<th>7a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh₃</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>10 (39:61)</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>P(p-tolyl)</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>9 (35:65)</td>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>P(o-tolyl)</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>P(2-furyl)</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>n.d.</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>PCy₃</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>1 (1:99)</td>
<td>22</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>P(n-Bu)₃</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>6 (50:50)</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>PMe₂Ph</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>8 (50:50)</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>dppe</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>6 (67:33)</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>dppe</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>53 (33:67)</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>11</td>
<td>dppe</td>
<td>benzene</td>
<td>20</td>
<td>n.d.</td>
<td>78 (39:61)</td>
<td>n.d.</td>
<td>16</td>
</tr>
<tr>
<td>13</td>
<td>dppp</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>16 (39:61)</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>dppb</td>
<td>toluene</td>
<td>12</td>
<td>n.d.</td>
<td>15 (39:61)</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>Pt(PPh₃)₄</td>
<td>toluene</td>
<td>13</td>
<td>75°</td>
<td>8 (&gt;99:1)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, the solution of 1a (1.0 mmol), 2a (1.2 mmol), Pd(dba)₂ (0.05 mmol), and ligand (0.12 mmol for Entries 3-8, 0.06 mmol for Entries 9-16) was stirred under toluene (0.5 mL) reflux. Yields were determined by ¹H NMR spectroscopy. b Pd(PPh₃)₄ (0.05 mmol) as a catalyst. c The formation of Ar¹C(O)C≡CR was detected in 10% yield. d Isolated yield. e Pt(PPh₃)₄ (0.05 mmol) as a catalyst. dba = dibenzylideneacetone, tolyl = methylphenyl, Cy = cyclohexyl, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)-propane, dppb = 1,4-bis(diphenylphosphino)butane.

Table 1). On the other hand, the reaction with dppe afforded 4a in 53% (cis:trans = 33/67) yield with 12% of 6a and 14% of 7a (run 10, Table 1). Gratifyingly, when the reaction was carried out under benzene reflux, the formation of 6a was suppressed and 4a was obtained in 78% yield (cis:trans = 39:61) with 10% of Ar¹C(O)C≡CR after 20 h (run 11, Table 1). When conducted for a short period of time (1 h), the reaction selectively provided cis-4a (14%), which indicated that cis-addition kinetically took place (run 12, Table 1). The employment of other bidentate ligands such as dppe, dppp and dppb significantly decreased the yield of 4a (runs 9,13,14, Table 1). It must be noted that 3a, the product of Pt(PPh₃)₄-catalyzed decarbonylative arylthiolation (run 15, Table 1), was not detected under these Pd-catalyses (runs 1-14, Table 1). No formation of 4a was confirmed with Pt[CH₂=CHSiMe₂]O], Ni(cod)₂ (cod = cyclooctadiene) or RhCl(cod)₂ in the presence of dppe.

Prompted by these results, the effects of bidentate ligand on the decarbonylation of 2a were
tested (Eq. 1). While 6a was produced in 12% and 36% yield with dppp and dppb ligands, respectively, decarbonylation hardly took place with dppe as a ligand (4%). On the other hand, the reaction between p-MeC₆H₄I and NaSC₆H₄-p-OMe catalyzed by Pd(dba)₂ (5 mol%)/dppe (6 mol%) produced 6a in 83% yield (Eq. 2). These facts indicated that dppe suppresses the decarbonylation from thiocarbonyl complex.⁸

The results of the Pd/dppe-catalyzed aroylthiolation of alkyne (1) by Ar¹C(O)SAr² (2) are summarized in Table 2. The reaction with 2a (Ar² = p-MeOC₆H₄) afforded a better yield of desired 4 (78% of 4a, run 1, Table 2) compared to the reactions with 2b (Ar² = Ph, 53% of 4b, run 2, Table 2) and 2c (Ar² = p-FC₆H₄, 46% of 4c, run 3, Table 2). In sharp contrast to the

### Table 2. Pd/dppe-Catalyzed Aroylthiolation of 1 Using 2a

<table>
<thead>
<tr>
<th>run</th>
<th>1</th>
<th>2</th>
<th>Ar¹</th>
<th>Ar²</th>
<th>4 (%) (cis:trans)</th>
</tr>
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<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>p-tolyl</td>
<td>p-MeOC₆H₄</td>
<td>4a 78 (39:61)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2b</td>
<td>p-tolyl</td>
<td>Ph</td>
<td>4b 53 (28:72)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>2c</td>
<td>p-tolyl</td>
<td>p-FC₆H₄</td>
<td>4c 46 (28:72)</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>2d</td>
<td>p-tolyl</td>
<td>p-NO₂C₆H₄</td>
<td>4d n.d.</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>2e</td>
<td>Ph</td>
<td>Ph</td>
<td>4e 66 (26:74)</td>
</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>2f</td>
<td>p-FC₆H₄</td>
<td>p-tolyl</td>
<td>4f 57 (26:74)</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>2g</td>
<td>3-pyridyl</td>
<td>p-tolyl</td>
<td>4g 74 (28:72)</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>2h</td>
<td>2-furyl</td>
<td>p-tolyl</td>
<td>4h 55 (25:75)</td>
</tr>
<tr>
<td>9</td>
<td>1a</td>
<td>2i</td>
<td>p-tolyl</td>
<td>CH₂Ph</td>
<td>4i 10° (26:74)</td>
</tr>
<tr>
<td>10</td>
<td>1a</td>
<td>2j</td>
<td>t-Bu</td>
<td>p-MeOC₆H₄</td>
<td>4j n.d.</td>
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<td>11</td>
<td>1b</td>
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<td>(CH₂)₂Cl</td>
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<td>4k 70 (33:67)</td>
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<tr>
<td>12</td>
<td>1c</td>
<td>2a</td>
<td>(CH₂)CN</td>
<td>p-tolyl</td>
<td>4l 50 (28:72)</td>
</tr>
<tr>
<td>13</td>
<td>1d</td>
<td>2a</td>
<td>(CH₂)₂CO₂Me</td>
<td>p-tolyl</td>
<td>4m 80 (25:75)</td>
</tr>
<tr>
<td>14</td>
<td>1e</td>
<td>2a</td>
<td>CH₂(c-C₆H₅)</td>
<td>p-tolyl</td>
<td>4n 66 (27:73)</td>
</tr>
<tr>
<td>15</td>
<td>1f</td>
<td>2a</td>
<td>(CH₂)₂CHMe₂</td>
<td>p-tolyl</td>
<td>4o 65 (47:53)</td>
</tr>
<tr>
<td>16</td>
<td>1g</td>
<td>2a</td>
<td>Ph</td>
<td>CH₂Ph</td>
<td>4p 40 (75:25)</td>
</tr>
<tr>
<td>17</td>
<td>1a</td>
<td>2k</td>
<td>PhC(O)SePh</td>
<td>p-MeOC₆H₄</td>
<td>4q 3° (99:1)</td>
</tr>
</tbody>
</table>

a 1 (1.2 mmol), 2 (1.0 mmol), Pd(dba)₂ (0.05 mol) and dppe (0.06 mol) under benzene (0.5 mL) reflux for 20 h. b Isolated yield. c NMR yield.
Pt-catalyzed decarbonylative arylation, no reaction took place when a thioester with Ar\(^2\) = p-NO\(_2\)C\(_6\)H\(_4\) (2d) was employed (run 4, Table 2). Phenyl and p-FC\(_6\)H\(_4\) groups at Ar\(^1\) somewhat lowered the reactivity (runs 5 and 6, Table 2). Thioesters 2g (Ar\(^1\) = 3-pyridyl) and 2h (Ar\(^1\) = 2-furyl) reacted with 1a to furnish the corresponding adducts 4g and 4h in 74% and 55% yields, respectively (runs 7 and 8, Table 2). On the other hand, a thioester with a benzyl group on sulfur (2i) gave a low yield of 4i (10%, run 9, Table 2), and the reaction with t-BuC(0)SC\(_6\)H\(_4\)-p-OMe (2j) did not produce 4j (run 10, Table 2). Terminal alkynes having chlorine (1b), a cyano group (1c), a methoxy carbonyl group (1d), a cyclopentyl group (1e), (CH\(_2\))\(_2\)CHMe\(_2\) (1f) and a phenyl group (1g) all underwent an arylation by 2a to afford 4k-p in moderate to good yields (runs 11-16, Table 2). The reactions of 1a with a selenoester (2k; PhC(0)SePh) took place to provide arylselenation product 4q, albeit in a very low yield (3%, run 17, Table 2).

1-3. Pt-Catalyzed Trifluoroacetylthiolation of Alkynes Using CF\(_3\)C(O)SR

Next, the reactions with CX\(_3\)-substituted thioesters (8; CX\(_3\)C(O)SR) were examined. The treatment of 1-octyne (1a, 0.75 mmol) with CF\(_3\)C(0)SC\(_6\)H\(_4\)-p-Me (8a; X = F, 0.5 mmol) in the presence of Pd/dppe under benzene and xylene reflux both gave trifluoroacetylthiolation product 5a in low yields: (CH\(_3\))(p-MeC\(_6\)H\(_4\)S)C=C(H)(n-C\(_5\)H\(_{11}\)) (10a) derived from 7a was

<table>
<thead>
<tr>
<th>run</th>
<th>8</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>time (h)</th>
<th>5 (%) (cis:trans)</th>
<th>9 (%)</th>
<th>10a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8a (X = F)</td>
<td>Pd(db)(_2)/dppe(^b)</td>
<td>benzene</td>
<td>20</td>
<td>8 (36:64)</td>
<td>n.d.</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>8a (X = F)</td>
<td>Pd(db)(_2)/dppe(^b)</td>
<td>xylene</td>
<td>10</td>
<td>8 (25:75)</td>
<td>n.d.</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>8a (X = F)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>10</td>
<td>28 (18:82)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
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<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>10</td>
<td>8 (18:82)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>8a (X = F)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>0.5</td>
<td>39 (21:79)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
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<td>8a (X = F)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>0.5</td>
<td>72 (21:79)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>8a (X = F)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>0.5</td>
<td>72 (21:79)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>8a (X = F)</td>
<td>Ni(cod)(_2)/PPh(_3)(^d)</td>
<td>xylene</td>
<td>10</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>8b (X = H)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>10</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>10</td>
<td>8c (X = Cl)</td>
<td>Pt(PPh(_3))(_4)</td>
<td>xylene</td>
<td>10</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise noted, the solution of 1a (0.75 mmol), 8 (0.5 mmol), catalyst (0.025 mol) and solvent (0.5 mL) was stirred under reflux for 10 h. Yields were determined by \(^1\)H NMR spectroscopy. \(^b\) Pd(db)\(_2\) (0.025 mmol) and dppe (0.03 mmol). \(^c\) Isolated yield. \(^d\) Ni(cod)\(_2\) (0.025 mmol) and PPh\(_3\) (0.1 mmol). \(^e\) 7a was obtained in 8% yield. cod = 1,5-cyclooctadiene.
generated as a major product (runs 1 and 2, Table 3). Intriguingly, the reaction using Pt(PPh3)4 as a catalyst under xylene reflux conditions remarkably improved the yield of 5a (78%, cis:trans = 18:82),9'10 compared to benzene or toluene reflux conditions (runs 3-5, Table 3). Intercepting the reaction at the early stage (cis:trans = 59:41 after 30 min) also indicates the involvement of cis-addition (run 6, Table 3). Inferior catalyses were shown by Pd(PPh3)4 (run 7, Table 3) and Ni(cod)2/4PPh3 (run 8, Table 3). On the other hand, the reaction employing CH3C(0)SC6H4-p-Me (8b; X = H) and CCl3C(0)SC6H4-p-Me (8c; X = Cl) in the presence of Pt(PPh3)4 hardly produced the corresponding 5b and 5c (runs 9 and 10, Table 3). Of noted, contrary to the case of Pt-catalyzed decarbonylative carbothiolation, the products 9 of decarbonylative trifluoromethylthiolation were not detected in all cases even with the same Pt(0) catalyst.

The results of Pt-catalyzed trifluoroacetylthiolation of alkyne (1) by CF3C(0)SR’ are shown in Table 4. Some substituents in aryl-S groups (8d; R’ = p-MeOC6H4, 8e; R’ = Ph, 8f; R’ = p-ClC6H4) hardly interfered with the addition reactions (runs 2-4, Table 4). Unlike the case of the reaction with 2, thioesters possessing an sp3-carbon substituent such as benzyl (8g) and n-decyl groups (8h) on sulfur also reacted with 1a to produce 5g and 5h in 51% and 41% yields, respectively (runs 5 and 6, Table 4). Addition of 8e to alkynes 1b-1e proceeded to afford the product 5i-1 in good yields (runs 7-10, Table 4).

**Table 4. Pt-Catalyzed Trifluoroacetylthiolation of 1 Using 8**

<table>
<thead>
<tr>
<th>run</th>
<th>1</th>
<th>7</th>
<th>8</th>
<th>5 (%)</th>
<th>(cis:trans)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>8a</td>
<td>p-tolyl</td>
<td>5a</td>
<td>78 (18:82)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>8d</td>
<td>p-MeOC6H4</td>
<td>5d</td>
<td>64 (11:89)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>8e</td>
<td>Ph</td>
<td>5e</td>
<td>82 (24:76)</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>8f</td>
<td>p-ClC6H4</td>
<td>5f</td>
<td>69 (34:66)</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>8g</td>
<td>CH2Ph</td>
<td>5g</td>
<td>51 (30:70)</td>
</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>8h</td>
<td>n-C10H21</td>
<td>5h</td>
<td>41 (18:82)</td>
</tr>
<tr>
<td>7c</td>
<td>1b</td>
<td>8e</td>
<td>5i</td>
<td>83 (29:71)</td>
<td></td>
</tr>
<tr>
<td>8c</td>
<td>1c</td>
<td>8e</td>
<td>5j</td>
<td>79 (29:71)</td>
<td></td>
</tr>
<tr>
<td>9c</td>
<td>1d</td>
<td>8e</td>
<td>5k</td>
<td>87 (26:74)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1e</td>
<td>8e</td>
<td>5l</td>
<td>70 (36:64)</td>
<td></td>
</tr>
</tbody>
</table>

*Unless otherwise noted, 1 (0.75 mmol), 8 (0.5 mmol), Pt(PPh3)4 (0.025 mmol), and xylene (0.5 mL) under reflux for 10 h. Isolated yield.*

1-4. Reaction Mechanisms

A plausible reaction mechanism of the present regioselective CO-retained addition of thioesters (2, 8; R1C(0)SR2 (R1 = Aryl or CF3)) to alkynes (1; HC=CR) was depicted in
Scheme 2. The oxidative addition of 2 or 8 to M(0)Ln (MLn = Pd(dppe) or Pt(PPh3)_4) complex triggers the reaction to afford MLn[C(O)R^1](SR^2) (11). Subsequent regio- and stereoselective insertion of alkyne 1 into the S-M bond of 11 generates MLn[C(O)R^1][(cis)-CH=C(SR^2)(R)] (12), which can react with another 1 to produce 7 and Ar^1C(O)C≡CR as by-products. Finally, the C-C bond-forming reductive elimination of cis-4, 5 from 12 with regeneration of M(0)Ln completes the catalytic cycle. cis-to-trans isomerisation of the product can be explained as follows: the oxidative addition of a vinyl-C-S bond of cis-isomer to a M(0)Ln complex to produce MLn[(cis)-C(R)=C(H){C(O)R^1}](SR^2) (cis-13), cis-to-trans isomerization of 13, and the reductive elimination of trans-4, 5 from trans-13.

Scheme 2. A Plausible Mechanism for the Transition Metal-Catalyzed Acylthiolation of Alkynes (1) Using Thioesters (2 and 8).

1-5. Conclusions
The present study substantiated that the decarbonylative arylthiolation of alkynes by thioesters is converted into CO-retained, atom-economical, regioselective carbothiolation. The author found that two simple factors; changing the catalysts from Pt(PPh3)_4 to Pd(dbta)_2/dppe or by employing CF3C(O) as a carbon functionality of thioesters even under Pt(PPh3)_4-catalyzed conditions, are keys to achieve the acylthiolation.

1-6. Experimental Section
General Comments: ^1H and ^13C NMR spectra in CDCl_3 and toluene-d_8 solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometer. The chemical shifts in the ^1H NMR spectra were recorded relative to Me_4Si as an internal standard, and the chemical shifts in the ^13C NMR spectra were recorded relative to CHCl_3 (δ 77.0). The IR spectra were measured by a Perkin-Elmer Model 1600 spectrometer. Mass spectra (EI), high-resolution mass spectra (HRMS) and elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Melting points were measured by a
MPA100 Optimelt Automated Melting Point System. Preparative TLC was carried out using Wakogel B-5F silica gel. All reactions were carried out under a N2 atmosphere. Unless otherwise noted, commercially available reagents were used without purification. All solvents were distilled before use. Thioesters 2a-j, 8b were prepared by the reactions of the corresponding acid chlorides with thiols in the presence of pyridine in THF solution, and selenoester 2k was prepared by the reaction of the benzoyl chloride with PhSeMgBr in THF solution. Thioesters 8a, c-h were synthesized according to the literature (J. Am. Chem. Soc. 2000, 122, 11260.).

The Spectrum Data or Registry Number (RN) of Thio- and Selenoesters (2 and 8):

**p-CH₃C₆H₄C(O)SC₆H₄-p-CH₃ (2a):** RN: 53271-44-6. **p-CH₃C₆H₄C(O)SC₆H₄-p-F (2c):** white solid; mp 98-100 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3 H), 7.10 (dd, J = 8.6, 2.9 Hz, 2 H), 7.23 (d, J = 8.3 Hz, 2 H), 7.44 (dd, J = 8.6, 5.1 Hz, 2 H), 7.89 (d, J = 8.3 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 116.3 (d, J_C-F = 22 Hz), 122.7 (d, J = 3.7 Hz), 128.4 (d, J = 189 Hz), 133.7, 137.0 (d, J = 8.7 Hz), 144.6, 162.2, 164.7, 189.4; IR (NaCl) 3066, 3044, 2926, 1695, 1667, 1604, 1590, 1574, 1491, 1434, 1409, 1390, 1318, 1293, 1228, 1218, 1206, 1179, 1157, 1124, 1116, 1096, 1013, 903, 850, 826, 811, 789, 718, 646, 624, 544, 499, 497, 430 cm⁻¹; mass spectrum (EI) m/z 246 (M⁺, 1.1); HRMS calcd for C₁₄H₁₁F₂O₃S: 246.0515. Found: 246.0507.

**F₃CC(O)SC₆H₄-p-CH₃ (3a):** RN: 52064-00-3. **3-C₄H₉NC(O)-SC₆H₄-p-CH₃ (2g):** RN: 52064-00-3. 2-C₆H₅OC(O)SC₆H₄-p-CH₃ (2h): RN: 17357-39-0. **C₆H₅C(O)SeC₆H₅ (2k):** RN: 38447-68-6. **F₃CC(O)SC₆H₄-p-OCH₃ (8d):** pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 3.85 (s, 3 H), 7.00 (d, J = 6.8 Hz, 2 H), 7.36 (d, J = 6.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 55.4, 115.5, 115.9 (c, J_C-F = 290 Hz), 132.3, 136.1, 161.7, 184.2 (c, J_C-F = 39.4 Hz); IR (NaCl) 2945, 2842, 1890, 1794, 1716, 1594, 1575, 1496, 1464, 1442, 1296, 1277, 1257, 1206, 1163, 1031, 937, 828, 742, 604 cm⁻¹; mass spectrum (EI) m/z 236 (M⁺, 59); HRMS calcd for C₉H₇F₃O₂S: 236.0119. Found: 236.0097.

**F₃CC(O)S-n-C₁₀H₂₁ (8h):** colorless oil; ¹H NMR (400 MHz,
\[
\text{CDCl}_3 \delta 0.88 (t, J = 6.1 \text{ Hz}, 3 \text{ H}), 1.26-1.39 (m, 14 \text{ H}), 1.65 (tt, J = 7.6, 7.3 \text{ Hz}, 2 \text{ H}), 3.05 (t, J = 7.3 \text{ Hz}, 2 \text{ H}); \ ^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 14.0, 22.7, 28.6, 28.7, 29.0, 29.3, 29.4, 29.5, 31.9, 115.6 (c, J_{C-F} = 289 \text{ Hz}), 184.5 (c, J_{C-F} = 39.4 \text{ Hz}); \text{IR (NaCl)} 2927, 2856, 2362, 1709, 1468, 1283, 1205, 1165, 956, 744 \text{ cm}^{-1}; \text{mass spectrum (EI) m/z 270 (M^+, 0.28); HRMS calcd for C}_{12}\text{H}_{21}\text{F}_3\text{OS: 270.1265. Found: 270.1258.}
\]

Reaction of p-CH_3C_6H_4C(0)SC_6H_4-p-OCH_3 (2a) with 1-Octyne (1a) in the Presence of Pd(dba)_2/dppe (run 11 of Table 1, run 1 of Table 2): General Procedure of Palladium-Catalyzed Aroylthiolation of Alkynes Using Thioesters: Into a two-necked 3 mL reaction glass were added Pd(dba)_2 (28.8 mg, 0.05 mmol), dppe (23.9 mg, 0.06 mmol), 1a (132 mg, 1.2 mmol), 2a (258 mg, 1.0 mmol) and benzene (0.5 mL) under a N\textsubscript{2} atmosphere. After the solution was refluxed for 20 h, the resultant mixture was filtered through Celite, the solvent was evaporated, and the resultant crude product was dried in vacuo. cis-4a and trans-4a were obtained in 30% (112 mg) and 48% (175 mg) yields by preparative TLC using hexane and ethyl acetate (40/1) as an eluent.

\[
\text{trans-p-CH}_3\text{C}_6\text{H}_4\text{C(0)C(H)=C(n-C}_6\text{H}_13\text{)SC}_6\text{H}_4-p-\text{OCH}_3 (trans-4a): yellow oil; \ ^{1}H NMR (400 MHz, \text{CDCl}_3) \delta 0.89 (t, J = 7.1 \text{ Hz}, 3 \text{ H}), 1.30-1.34 (m, 4 \text{ H}), 1.40-1.46 (m, 2 \text{ H}), 1.68-1.75 (m, 2 \text{ H}), 2.34 (s, 3 \text{ H}), 2.89 (t, J = 7.8 \text{ Hz}, 2 \text{ H}), 3.87 (s, 3 \text{ H}), 6.25 (s, 1 \text{ H}), 6.98 (d, J = 8.9 \text{ Hz}, 2 \text{ H}), 7.14 (d, J = 8.1 \text{ Hz}, 2 \text{ H}), 7.47 (d, J = 8.9 \text{ Hz}, 2 \text{ H}), 7.55 (d, J = 8.1 \text{ Hz}, 2 \text{ H}); \text{N.O.E. experiment: Irradiation of the vinyl singlet at } \delta 6.25 \text{ resulted in a 17.0% enhancement of the signal at } \delta 7.55 (\text{aryl doublet}); \ ^{13}\text{C NMR (100 MHz, \text{CDCl}_3) } \delta 14.1, 21.4, 22.6, 29.3, 29.9, 31.6, 34.1, 55.4 114.5, 115.3, 120.6, 128.0, 129.0, 137.1, 137.2, 142.5, 160.9, 168.1, 187.1; \text{IR (NaCl)} 2955, 2927, 2856, 1645, 1606, 1592, 1568, 1556, 1493, 1462, 1440, 1361, 1290, 1250, 1210, 1181, 1051, 1032, 830, 818, 732 \text{ cm}^{-1}; \text{mass spectrum (EI) m/e 368 (M^+, 15); Anal. Calcd for C}_{23}\text{H}_{28}\text{O}_2\text{S: C, 74.96; H, 7.66. Found: C, 74.74; H, 7.47.}}
\]

\[
\text{cis-p-CH}_3\text{C}_6\text{H}_4\text{C(0)C(H)=C(n-C}_6\text{H}_13\text{)SC}_6\text{H}_4-p-\text{OCH}_3 (cis-4a): yellow solid; mp 42.0-44.0 \text{ °C; } \ ^{1}H NMR (400 MHz, \text{CDCl}_3) \delta 0.82 (t, J = 7.1 \text{ Hz}, 3 \text{ H}), 1.08-1.10 (m, 4 \text{ H}), 1.14-1.25 (m, 2 \text{ H}), 1.38-1.44 (m, 2 \text{ H}), 2.23 (t, J = 7.6 \text{ Hz}, 2 \text{ H}), 2.40 (s, 3 \text{ H}), 3.83 (s, 3 \text{ H}), 6.90 (d, J = 8.3 \text{ Hz}, 2 \text{ H}), 7.01 (s, 1 \text{ H}), 7.25 (d, J = 8.3 \text{ Hz}, 2 \text{ H}), 7.48 (d, J = 8.3 \text{ Hz}, 2 \text{ H}); \text{N.O.E. experiment: Irradiation of the vinyl singlet at } \delta 7.01 \text{ resulted in a 8.9 % enhancement of the signal at } \delta 2.23 (\text{allyl triplet}) \text{ and 17.5 % enhancement of the signal at } \delta 7.88 (\text{aryl doublet}); \ ^{13}\text{C NMR (100 MHz, \text{CDCl}_3) } \delta 13.9, 21.5, 22.4, 28.6, 29.9, 31.3, 37.0, 55.3, 114.5, 115.3, 122.1, 128.1, 129.1, 136.3, 137.2, 142.6, 160.6, 166.4, 188.2; \text{IR (KBr) 2928, 2857, 1632, 1607, 1592, 1570, 1534, 1493, 1463, 1298, 1246, 1180, 1096, 1084, 911, 863, 831, 806, 733 \text{ cm}^{-1}; \text{mass spectrum (EI) m/e 368 (M^+, 25); HRMS calcd for C}_{23}\text{H}_{28}\text{O}_2\text{S: 368.1810. Found: 368.1817.}}
\]

14
Other aroylthiolation products 4b, 4c, 4e-i and 4k-4q were synthesized by similar procedures.

**trans-p-CH₃C₆H₄C(O)C(H)=C(n-C₆H₁₃)SC₆H₅ (trans-4b):** yellow solid; 71.9-73.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.0 Hz, 3 H), 1.32-1.34 (m, 4 H), 1.40-1.46 (m, 2 H), 1.68-1.74 (m, 2 H), 2.34 (s, 3 H), 2.91 (t, J = 7.8 Hz, 2 H), 6.28 (s, 1 H), 7.13 (d, J = 8.4 Hz, 2 H), 7.45-7.47 (m, 3 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.56-7.58 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 21.5, 22.6, 29.3, 29.8, 31.6, 34.2, 115.2, 128.0, 129.0, 129.7, 129.8, 130.2, 135.6, 137.0, 142.6, 166.9, 187.1; IR (KBr) 2944, 2916, 2855, 1646, 1604, 1578, 1468, 1436, 1352, 1255, 1230, 1211, 1180, 1055, 821, 756, 734, 708, 692 cm⁻¹; mass spectrum (EI) m/e 338 (M⁺, 16); HRMS calcd for C₂₂H₂₆O₅S: 338.1704. Found: 338.1711.

**cis-p-CH₃C₆H₄C(O)C(H)=C(n-C₆H₁₃)SC₆H₅ (cis-4b):** yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, J = 7.2 Hz, 3 H), 1.05-1.20 (m, 6 H), 1.38-1.43 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.41 (s, 3 H), 7.03 (s, 1 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.36-7.42 (m, 3 H), 7.57-7.59 (m, 2 H), 7.89 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 121.6, 22.4, 28.6, 29.9, 31.2, 37.2, 115.8, 128.1, 129.0, 129.2, 129.3, 131.5, 135.8, 136.2, 142.7, 165.1, 188.3; IR (NaCl) 2955, 2927, 2857, 1634, 1607, 1569, 1538, 1475, 1439, 1236, 1208, 1181, 1084, 1018, 863, 806, 788, 752, 704, 693 cm⁻¹; mass spectrum (EI) m/e 338 (M⁺, 17); HRMS calcd for C₂₂H₂₆O₅S: 338.1704. Found: 338.1710.

**trans-p-CH₃C₆H₄C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-F (trans-4c):** yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.42-1.45 (m, 2 H), 1.67-1.73 (m, 2 H), 2.35 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 6.22 (s, 1 H), 7.15-7.20 (m, 4 H), 7.52-7.58 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 21.5, 22.6, 29.3, 29.8, 31.6, 34.1, 115.1, 117.1 (d, J_C-F = 22.0 Hz), 125.5 (d, J_C-F = 2.4 Hz), 128.0, 129.1, 136.9, 137.8 (d, J_C-F = 8.3 Hz), 142.8, 163.7 (d, J_C-F = 250 Hz), 166.8, 187.2; IR (NaCl) 2956, 2928, 2856, 1652, 1607, 1590, 1568, 1558, 1490, 1466, 1362, 1233, 1181, 1156, 1051, 1015, 835, 817, 731 cm⁻¹; mass spectrum (EI) m/e 356 (M⁺, 8.1); HRMS calcd for C₂₂H₂₅F₅S: 356.1610. Found: 356.1606.

**cis-p-CH₃C₆H₄C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-F (cis-4c):** yellow solid; mp 57-60 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.83 (t, J = 7.2 Hz, 3 H), 1.09-1.10 (m, 4 H), 1.17-1.22 (m, 2 H), 1.38-1.44 (m, 2 H), 2.22 (t, J = 7.8 Hz, 2 H), 2.42 (s, 3 H), 7.04 (s, 1 H), 7.07-7.11 (m, 2 H), 7.27 (d, J = 7.6 Hz, 2 H), 7.54-7.58 (m, 2 H), 7.89 (d, J = 7.6 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 21.6, 22.4, 28.6, 29.8, 31.3, 37.1, 115.9, 116.2 (d, J_C-F = 22.0 Hz), 126.9 (d, J_C-F = 3.7 Hz), 128.1, 129.2, 136.0, 137.7
trans-C₆H₅C(O)C(H)=C(n-C₆H₁₃)SC₆H₅ (trans-4e): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.06-1.20 (m, 6 H), 1.41-1.46 (m, 2 H), 2.26 (t, J = 7.8 Hz, 2 H), 7.05 (s, 1 H), 7.39-7.60 (m, 8 H), 7.99 (d, J = 8.1 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.3, 28.6, 29.9, 31.2, 37.3, 115.7, 128.0, 128.5, 129.0, 129.3, 131.3, 132.0, 135.7, 138.7, 165.9, 188.6; IR (NaCl) 3058, 2955, 2929, 2857, 1634, 1598, 1578, 1548, 1538, 1532, 1476, 1446, 1440, 1355, 1303, 1233, 1178, 1105, 1070, 1025, 1001, 859, 828, 774, 752, 704, 676 cm⁻¹; mass spectrum (EI) m/e 324 (M⁺, 17); Anal. Calcd for C₂₁H₂₄O₅: C, 77.73; H, 7.46. Found: C, 77.59; H, 7.29.

cis-C₆H₅C(O)C(H)=C(n-C₆H₁₃)SC₆H₅ (cis-4e): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, J = 7.2 Hz, 3 H), 1.05-1.21 (m, 6 H), 1.38-1.46 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.39 (s, 3 H), 6.99 (s, 1 H), 7.11-7.16 (m, 2 H), 7.20 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.99-8.03 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 21.3, 22.4, 28.6, 30.0, 31.2, 37.2, 115.0, 115.5 (d, J_C-F = 21.5 Hz), 126.3, 130.3 (d, J_C-F = 9.2 Hz), 130.6, 135.5, 135.9 (d, J_C-F = 3.2 Hz), 140.3, 165.0 (d, J_C-F = 252 Hz), 168.7, 185.8; IR (NaCl): 2956, 2927, 2857, 1651, 1598, 1557, 1505, 1493, 1456, 1433, 1408, 1363, 1229, 1155, 1050, 1018, 829, 812 cm⁻¹; mass spectrum (EI) m/e 356 (M⁺, 10); Anal. Calcd for C₂₂H₂₅FOS: C, 74.12; H, 7.07. Found: C, 74.13; H, 7.12.

cis-p-F₆H₅C(O)C(H)=C(n-C₆H₁₃)SC₆H₅-p-CH₃ (cis-4f): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, J = 7.2 Hz, 3 H), 1.05-1.21 (m, 6 H), 1.38-1.46 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.39 (s, 3 H), 6.99 (s, 1 H), 7.11-7.16 (m, 2 H), 7.20 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.99-8.03 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 21.3, 22.4, 28.6, 30.0, 31.2, 37.2, 115.0, 115.5 (d, J_C-F = 21.5 Hz), 126.3, 130.3 (d, J_C-F = 9.2 Hz), 130.6, 135.5, 135.9 (d, J_C-F = 3.2 Hz), 140.3, 165.0 (d, J_C-F = 252 Hz), 168.7, 185.8; IR (NaCl): 2956, 2927, 2857, 1651, 1598, 1557, 1505, 1493, 1456, 1433, 1408, 1363, 1229, 1155, 1050, 1018, 829, 812 cm⁻¹; mass spectrum (EI) m/e 356 (M⁺, 10); Anal. Calcd for C₂₂H₂₅FOS: C, 74.12; H, 7.07. Found: C, 74.13; H, 7.12.
trans-(3-C₆H₄N)C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-CH₃ (trans-4g):
yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, J = 6.6 Hz, 3 H),
1.34-1.47 (m, 6 H), 1.73 (dt, 2 H), 2.42 (s, 3 H), 2.94 (t, J = 7.8 Hz,
2 H), 6.23 (s, 1 H), 7.28-7.33 (m, 3 H), 7.44 (d, J = 7.8 Hz, 2 H),
8.01 (d, J = 7.8 Hz, 1 H), 8.64 (d, J = 3.9 Hz, 1 H), 8.74 (s, 1 H); ¹³C
NMR (100 MHz, CDCl₃) δ 14.0, 21.4, 22.6, 29.3, 29.9, 31.5, 34.6, 113.2, 123.4, 125.9, 129.8,
130.7, 135.4, 135.5, 140.6, 149.1, 152.2, 171.2, 185.1; IR (NaCl) 3033, 2955, 2927, 2856,
1651, 1584, 1556, 1493, 1456, 1416, 1366, 1237, 1106, 1060, 1040, 1018, 849, 811, 732, 702,
662 cm⁻¹; mass spectrum (EI) m/e 339 (M⁺, 20); Anal. Calcd for C₂₁H₁₂₅NOS: C, 74.29; H,
7.42; N, 4.13. Found: C, 74.07; H, 7.41; N, 4.16.

cis-(3-C₆H₄N)C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-CH₃ (cis-4g):
yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, J = 8.9 Hz, 3 H),
1.05-1.21 (m, 6 H), 1.43 (dt, 2 H), 2.26 (t, J = 7.8 Hz, 2 H), 2.39
(s, 3 H), 7.01 (s, 1 H), 7.21 (d, J = 7.8 Hz, 2 H), 7.40-7.47 (m, 3 H),
8.28 (d, J = 8.1 Hz, 1 H), 8.74 (d, J = 3.2 Hz, 1 H), 9.18 (s, 1 H); ¹³C
NMR (100 MHz, CDCl₃) δ 13.9, 21.2, 22.3, 28.5, 29.9, 31.1, 37.2, 114.6, 123.5, 127.1,
129.8, 134.0, 135.4, 135.5, 139.8, 149.2, 152.3, 169.2, 186.6; IR (NaCl) 3020, 2955, 2927,
2857, 1634, 1585, 1569, 1530, 1493, 1456, 1416, 1249, 1088, 1019, 862, 812, 756, 704, 666,
620 cm⁻¹; mass spectrum (EI) m/e 339 (M⁺, 20), 123 (100); Anal. Calcd for C₂₁H₁₂₅NOS: C,
74.29; H, 7.42; N, 4.13. Found: C, 74.01; H, 7.14; N, 4.13.

trans-(2-C₄H₉O)C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-CH₃ (trans-4h):
yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.0 Hz, 2 H),
1.30-1.34 (m, 4 H), 1.42-1.46 (m, 2 H), 1.66-1.72 (m, 2 H), 2.43 (s, 3 H),
2.93 (t, J = 7.7, 2 H), 6.18 (s, 1 H), 6.40-6.41 (m, 1 H), 6.77 (d, J =
3.7 Hz, 1 H), 7.28 (d, J = 7.7 Hz, 2 H), 7.42-7.44 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ
14.0, 21.3, 22.5, 29.2, 29.8, 31.5, 34.2, 111.9, 113.4, 115.6, 126.6, 130.5, 135.6, 139.6,
145.6, 154.3, 169.0, 175.6; IR (NaCl) 2955, 2927, 2856, 1643, 1572, 1492, 1467, 1432, 1394, 1353,
1262, 1165, 1156, 1088, 1056, 1017, 913, 884, 811, 756, 732, 694 cm⁻¹; mass spectrum (EI)
m/e 328 (M⁺, 30); Anal. Calcd for C₂₀H₂₄O₂S: C, 73.13; H, 7.36. Found: C, 72.89; H, 7.08.
cis-(2-C₄H₉O)C(O)C(H)=C(n-C₆H₁₃)SC₆H₄-p-CH₃ (cis-4h):
yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, J = 7.2 Hz, 3 H),
1.06-1.08 (m, 4 H), 1.15-1.19 (m, 2 H), 1.39-1.43 (m, 2 H), 2.22 (t,
$J = 7.8, 2\ H), 2.38 (s, 3\ H), 6.52-6.56 (m, 1\ H), 6.92 (s, 1\ H), 7.18-7.20 (m, 3\ H), 7.44 (d, $J = 8.1\ Hz, 2\ H), 7.55-7.56 (m, 1\ H); NOE experiment: Irradiation of the vinyl singlet at $\delta 6.92$ resulted in a 6.9 % enhancement of the signal at $\delta 2.22; ^{13}\ C\ NMR (100\ MHz, CDCl_3) \delta 14.0, 21.3, 22.3, 28.5, 29.8, 31.2, 37.1, 112.3, 114.9, 115.6, 127.5, 129.8, 135.7, 139.6, 145.2, 154.1, 166.6, 177.3; IR (NaCl) 2955, 2928, 2858, 1633, 1574, 1538, 1493, 1470, 1258, 1157, 1101, 1010, 884, 813, 756 cm$^{-1}$; mass spectrum (EI) m/e 328 (M+, 29); Anal. Calcd for C$_{20}$H$_{24}$O$_2$S: C, 73.13; H, 7.36. Found: C, 72.90; H, 6.97.

The structure of 4i was tentatively assigned by $^1\ H\ NMR\ spectrum\ (vide\ infra).$

$trans-p-$CH$_3$C$_6$H$_4$C(O)C(H)=C(n-C$_6$H$_{13})$SCH$_2$C$_6$H$_5\ (trans-4i)$; $^1\ H\ NMR (400\ MHz, CDCl_3) \delta 6.24 (s, 1\ H, vinyl\ proton).

cis-p-$CH$_3$C$_6$H$_4$C(O)C(H)=C(n-C$_6$H$_{13})$SCH$_2$C$_6$H$_5\ (cis-4i)$; $^1\ H\ NMR (400\ MHz, CDCl_3) \delta 7.01 (s, 1\ H, vinyl\ proton).

$trans-p-$CH$_3$C$_6$H$_4$C(O)C(H)=C((CH$_2$)$_4$O)SC$_6$H$_4$-p-OCH$_3\ (trans-4k)$; yellow oil; $^1\ H\ NMR (400\ MHz, CDCl_3) \delta 1.85-1.95 (m, 4\ H), 2.35 (s, 3\ H), 2.92 (t, J = 7.3\ Hz, 2\ H), 3.59 (t, J = 6.5\ Hz, 2\ H), 3.85 (s, 3\ H), 6.29 (s, 1\ H), 6.99 (d, J = 8.6\ Hz, 2\ H), 7.15 (d, J = 8.2\ Hz, 2\ H), 7.48 (d, J = 8.6\ Hz, 2\ H), 7.54 (d, J = 8.2\ Hz, 2\ H); $^{13}\ C\ NMR (100\ MHz, CDCl_3) \delta 21.5, 27.1, 32.3, 33.0, 44.8, 55.4, 114.9, 115.3, 120.3, 128.0, 129.0, 136.9, 137.2, 142.7, 161.0, 166.9, 187.1; IR (NaCl) 2956, 2866, 2838, 1645, 1606, 1592, 1574, 1568, 1557, 1494, 1462, 1441, 1360, 1291, 1250, 1181, 1050, 1031, 830, 819, 734 cm$^{-1}$; mass spectrum (EI) m/e 374 (M+, 24); Anal. Calcd for C$_{21}$H$_{23}$ClO$_2$S: C, 67.27; H, 6.18. Found: C, 67.08; H, 5.96.

cis-p-$CH$_3$C$_6$H$_4$C(O)C(H)=C((CH$_2$)$_4$C$_1$)SC$_6$H$_4$-p-OCH$_3\ (cis-4k)$; yellow oil; $^1\ H\ NMR (400\ MHz, CDCl_3) \delta 1.58-1.61 (m, 4\ H), 2.27 (t, J = 6.8\ Hz, 2\ H), 2.41 (s, 3\ H), 3.38 (t, J = 5.7\ Hz, 2\ H), 3.84 (s, 3\ H), 6.92 (d, J = 8.6\ Hz, 2\ H), 7.02 (s, 1\ H), 7.26 (d, J = 8.1\ Hz, 2\ H), 7.49 (d, J = 8.6\ Hz, 2\ H), 7.89 (d, J = 8.1\ Hz, 2\ H); $^{13}\ C\ NMR (100\ MHz, CDCl_3) \delta 21.6, 27.0, 31.7, 36.2, 44.4, 55.4, 114.7, 115.7, 121.9, 128.1, 129.2, 136.1, 137.2, 142.8, 160.7, 165.1, 188.2; IR (NaCl) 3002, 2956, 2866, 1632, 1607, 1591, 1570, 1538, 1493, 1461, 1441, 1288, 1246, 1208, 1180, 1174, 1104, 1074, 1030, 831, 806, 754, 734 cm$^{-1}$; mass spectrum (EI) m/e 374 (M+, 23); Anal. Calcd for C$_{21}$H$_{23}$ClO$_2$S: C, 67.27; H, 6.18. Found: C, 67.26; H, 6.06.

$trans-p-$CH$_3$C$_6$H$_4$C(O)C(H)=C((CH$_2$)$_3$CN)SC$_6$H$_4$-p-OCH$_3\ (trans-4l)$; yellow solid; mp 87.4-88.6 °C; $^1\ H\ NMR (400\ MHz, CDCl_3) \delta 2.08-2.15 (m, 2\ H), 2.35 (s, 3\ H), 2.52 (t, J = 7.4\ Hz, 2
H), 2.98 (t, J = 7.6 Hz, 2 H), 3.85 (s, 3 H), 6.34 (s), 7.01 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.8, 21.5, 25.5, 32.7, 55.4, 115.5, 115.7, 119.5, 119.7, 128.0, 129.1, 136.6, 137.1, 143.0, 161.2, 164.8, 187.1; IR (KBr) 1646, 1606, 1590, 1568, 1495, 1457, 1434, 1358, 1300, 1287, 1249, 1184, 1058, 1018, 835, 816, 797, 737, 705 cm$^{-1}$; mass spectrum (EI) m/e 351 (M+, 29); Anal. Caled for C$_{21}$H$_{21}$NO$_2$S: C, 71.76; H, 6.02; N, 3.99. Found: C, 71.72; H, 6.09; N, 4.00.

trans-p-CH$_3$C$_6$H$_4$C(O)C(H)=C((CH$_2$)$_3$CO$_2$CH$_3$)SC$_6$H$_4$-p-OC

H$_3$ (trans-4m): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.07 (dt, 2 H), 2.33 (s, 3 H), 2.48 (t, J = 7.7 Hz, 3 H), 2.94 (t, J = 7.7 Hz, 2 H), 3.67 (s, 3 H), 3.84 (s, 3 H), 6.29 (s, 1 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 8.2 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.2 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.4, 24.8, 32.9, 33.4, 51.4, 55.3, 115.1, 115.3, 120.2, 127.9, 129.0, 136.8, 137.1, 142.6, 161.0, 166.3, 173.6, 186.9; IR (NaCl) 2950, 1737, 1646, 1606, 1592, 1568, 1494, 1455, 1437, 1364, 1291, 1250, 1181, 1049, 1030, 831, 819, 733 cm$^{-1}$; mass spectrum (EI) m/e 384 (M$,^+$, 17); Anal. Caled for C$_{22}$H$_{24}$O$_4$S: C, 68.72; H, 6.29. Found: C, 68.68; H, 6.14.

cis-p-CH$_3$C$_6$H$_4$C(O)C(H)=C((CH$_2$)$_3$CO$_2$CH$_3$)SC$_6$H$_4$-p-OCH$_3$

cis-4m: orange solid; mp 85.0-87.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.75 (dt, 2 H), 2.16 (t, J = 7.3 Hz, 2 H), 2.30 (t, J = 7.3 Hz, 2 H), 2.41 (s, 3 H), 3.61 (s, 3 H), 3.84 (s, 3 H), 6.92 (d, J = 7.6 Hz, 2 H), 7.02 (s, 1 H), 7.26 (d, J = 8.2 Hz, 2 H), 7.48 (d, J = 7.6 Hz, 2 H), 7.89 (d, J = 8.2 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.6, 24.8, 32.9, 36.0, 51.5, 55.4, 114.7, 116.0, 121.9, 128.1, 129.2, 136.1, 137.1, 142.8, 160.7, 164.4, 173.3, 188.2; IR (KBr) 1732, 1627, 1606, 1588, 1568, 1531, 1494, 1484, 1448, 1285, 1240, 1180, 1153, 1072, 1017, 845, 834, 809 cm$^{-1}$; mass spectrum (EI) m/e 384 (M$,^+$, 21); HRMS calcd for C$_{22}$H$_{24}$O$_4$S: 384.1395. Found: 384.1393.

trans-p-CH$_3$C$_6$H$_4$C(O)C(H)=C(CH$_2$(c=O)$_5$H$_9$)SC$_6$H$_4$-p-OCH$_3$

cis-4n: yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.29-1.34 (m, 2 H), 1.52-1.56 (m, 2 H), 1.62-1.68 (m, 2 H), 1.83-1.87 (m, 2 H), 2.29-2.35 (m, 1 H), 2.33 (s, 3 H), 3.00 (d, J = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.24 (s, 1 H), 6.98 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.4, 24.8, 32.4, 39.0, 40.5, 55.4, 115.1, 115.3, 120.8, 128.0, 129.0, 137.1, 137.2, 142.5, 160.9, 167.3, 187.3; IR (NaCl) 2951, 2866, 1647, 1606, 1592, 1560, 1493, 1462, 1440, 1407, 1360, 1290, 1250, 1210, 1181, 1104, 1050, 1032, 830, 819, 733 cm$^{-1}$; mass spectrum (EI) m/e 366 (M$,^+$, 25); Anal. Caled for C$_{23}$H$_{26}$O$_2$S: C, 75.37; H, 7.15. Found: C, 75.23; H, 7.28.
cis-p-CH₃C₆H₄C(O)C(H)=C(CH₂-c-CH₃)SC₆H₄-p-OCH₃ (cis 4n): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.97-1.03 (m, 2 H), 1.43-1.64 (m, 6 H), 1.93-1.97 (m, 1 H), 2.24 (d, J = 6.8 Hz, 2 H), 2.41 (s, 3 H), 3.84 (s, 3 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.01 (s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 24.8, 32.2, 39.6, 42.9, 55.3, 114.5, 115.9, 122.3, 128.1, 129.1, 136.4, 137.2, 142.6, 160.5, 165.3, 188.2; IR (NaCl) 2951, 2866, 1632, 1607, 1592, 1571, 1537, 1494, 1462, 1453, 1441, 1288, 1246, 1207, 1180, 1101, 1082, 1031, 1018, 862, 830, 809, 799, 788, 755, 734 cm⁻¹; mass spectrum (EI) m/e 366 (M⁺, 23); HRMS calcd for C₂₃H₂₆O₂S: 366.1654. Found: 366.1658.

cis-p-CH₃C₆H₄C(O)C(H)=COCH₂CH(CH₃)₂SC₆H₄-p-OCH₃ (cis-4o): yellow solid; mp 94.0-95.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.68 (d, J = 6.4 Hz, 6 H), 1.31-1.34 (m, 3 H), 2.25 (t, J = 7.7 Hz, 2 H), 2.41 (s, 3 H), 3.83 (s, 3 H), 6.91 (d, J = 8.8 Hz, 2 H), 7.02 (s, 1 H), 7.25 (d, J = 7.9 Hz, 2 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.89 (d, J = 7.9 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 22.1, 27.8, 35.2, 39.3, 55.4, 114.5, 115.3, 120.6, 128.0, 129.0, 137.1, 137.2, 142.5, 160.1, 168.4, 187.1; IR (NaCl) 3005, 2956, 2868, 1646, 1607, 1592, 1560, 1493, 1464, 1442, 1366, 1296, 1250, 1208, 1181, 1052, 1031, 1018, 830, 818, 759, 734 cm⁻¹; mass spectrum (EI) m/e 354 (M⁺, 26); Anal. Calcd for C₂₂H₂₆O₂S: C, 74.54; H, 7.39. Found: C, 74.38; H, 7.19.

trans-p-CH₃C₆H₄C(O)C(H)=C((CH₃)₂CH(CH₃)₂)SC₆H₄-p-OCH₃ (trans-4o): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.96 (d, J = 6.3 Hz, 6 H), 1.58-1.73 (m, 3 H), 2.35 (s, 3 H), 2.90 (t, J = 6.8 Hz, 2 H), 3.86 (s, 3 H), 6.25 (s, 1 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 7.9 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.55 (d, J = 7.9 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 22.4, 28.4, 32.2, 38.8, 55.4, 114.5, 115.3, 120.6, 128.0. 129.0, 137.1, 137.2, 142.5, 160.1, 168.4, 187.1; IR (NaCl) 3005, 2956, 2868, 1646, 1607, 1592, 1560, 1493, 1464, 1442, 1366, 1296, 1250, 1208, 1181, 1052, 1031, 1018, 830, 818, 759, 734 cm⁻¹; mass spectrum (EI) m/e 354 (Mt, 24); HRMS calcd for C₂₂H₂₆O₂S: 354.1654. Found: 354.1651.

p-CH₃C₆H₄C(O)C(H)=C(CH₅)SC₆H₄-p-OCH₃ (4p, a mixture of stereoisomer): yellow solid; ¹H NMR (400 MHz, CDCl₃) cisisomer; δ 2.41 (s, 3 H), 3.68 (s, 3 H), 6.57 (d, J = 8.8 Hz, 2 H), 7.09-7.16 (m, 9 H), 7.25 (s, 1 H), 7.93 (d, J = 8.0 Hz, 2 H); trans isomer; 2.33 (s, 3 H), 3.86 (s, 3 H), 6.28 (s, 1 H), 6.99 (d, J = 8.5 Hz, 2 H), other peaks overlap with those of cis isomer; ¹³C NMR (100 MHz, CDCl₃) cis
isomer; δ 21.6, 55.2, 113.9, 119.1, 123.4, 127.7, 128.2, 128.3, 128.9, 129.3, 136.0, 136.1, 138.9, 143.1, 159.5, 163.1, 188.3; trans isomer; δ 21.5, 55.4, 115.4, 117.4, 121.1, 128.1, 128.4, 128.5, 128.8, 129.0, 135.9, 137.1, 137.2, 142.9, 161.0, 161.1, 188.4; IR (KBr): 2929, 1626, 1605, 1591, 1570, 1560, 1492, 1460, 1443, 1406, 1333, 1302, 1291, 1245, 1174, 1106, 1030, 1017, 955, 830, 815, 770, 737, 703, 676 cm⁻¹; mass spectrum (EI) m/e 360 (M⁺, 38); (EI) m/e 360 (M⁺, 38); Anal. Calcd for C_{23}H_{20}O_{2}S: C, 76.64; H, 5.59. Found: C, 76.48; H, 5.48.

The structure of cis-4q was tentatively determined by ¹H NMR spectrum (vide infra).

cis-C₆H₅C(O)C(H)=C(n-C₆H₁₃)SeC₆H₅ (cis-4q): ¹H NMR (400 MHz, CDCl₃) δ 6.93 (s, 1 H, vinyl proton).

Reaction of p-CH₃C₆H₄(C(O)SC₆H₄-p-OCH₃ (2a) with 1-Octyne (1a) in the Presence of Pt(PPh₃)₄ (run 18 of Table 1): Into a two-necked 3 mL reaction glass were added Pt(PPh₃)₄ (62.5 mg, 0.05 mmol), 2a (254 mg, 0.983 mmol), 1a (135 mg, 1.23 mmol) and toluene (0.5 mL) under a N₂ atmosphere. After the solution was refluxed for 13 h, the resultant mixture was filtered through Celite, the solvent was evaporated, and the resultant crude product was dried in vacuo. cis-3a and trans-4a were obtained in 75% (255 mg) and 8% (30 mg) yield by preparative TLC using hexane and ethyl acetate (40/1) as an eluent.

cis-p-CH₃C₆H₄C(H)=C(n-C₆H₁₃)SC₆H₄-p-OCH₃ (cis-3a): pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.85 (t, J = 7.0 Hz, 3 H), 1.19-1.27 (m, 6 H), 1.49-1.53 (m, 2 H), 2.16 (t, J = 7.4 Hz, 2 H), 2.34 (s, 3 H), 3.78 (s, 3 H), 6.61 (s, 1 H), 6.82 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.8 Hz, 2 H), 7.45 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 21.2, 22.5, 28.5, 28.8, 31.6, 37.6, 55.3, 114.4, 124.2, 128.6, 129.1, 129.2, 134.1, 134.2, 136.6, 136.9, 159.2; IR (NaCl) 2954, 2928, 2856, 1592, 1571, 1509, 1493, 1463, 1440, 1286, 1246, 1180, 1172, 1034, 827, 806 cm⁻¹; mass spectrum (EI) m/e 340 (M⁺, 100). HRMS calcd for C₂₂H₂₈O₅S: 340.1861. Found: 340.1871.

**Cis-to-trans Isomerization of cis-4a (Eq. S1):** Into a two-necked reaction glass were added Pd(dba)$_2$ (1.5 mg, 0.0026 mmol), dppe (1.2 mg, 0.0030 mmol), cis-4a (17 mg, 0.044 mmol), 1a
(8.9 mg, 0.081 mmol) and benzene (0.5 mL) under a N₂ atmosphere. After the solution was refluxed for 15 h, the reaction mixture was filtered through Celite, and the filtrate was evaporated and dried *in vacuo*. The products were analyzed by \(^1\)H NMR spectroscopy.

*Cis-to-trans* isomerization of cis-4a occurred in the presence of catalytic amount of Pd(dba)₂ and dppe and 1.6 equiv amount of 1a. These results indicated that 1a is the crucial factor for the generation of active dppe ligated Palladium (0) complex.

**Treatment of 2a in the Presence of Pd/dppe (Eq. 1):** Into a two-necked reaction glass were added Pd(dba)₂ (28.3 mg, 0.05 mmol), dppe (24.5 mg, 0.06 mmol), 2a (262 mg, 1.01 mmol) and toluene (0.5 mL) under a N₂ atmosphere. After the solution was refluxed for 12 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. The products were analyzed by \(^1\)H NMR spectroscopy.


Decarbonylation of 2a using dppp and dppb ligands was similarly examined.

**Reaction of I-C₆H₄-p-OCH₃ with NaSC₆H₄-p-OCH₃ in the Presence of Pd/dppe (Eq. 2):** Into a two-necked reaction glass were added Pd(dba)₂ (14.4 mg, 0.025 mmol), dppe (12.0 mg, 0.030 mmol), p-MeC₆H₄I (109 mg, 0.500 mmol), NaSC₆H₄OMe-p (82 mg, 0.506 mmol) and toluene (0.5 mL) under a N₂ atmosphere. After the solution was refluxed for 12 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. The products were analyzed by \(^1\)H NMR spectroscopy.

**Reaction of F₃CC(O)SC₆H₄-p-CH₃ (8a) with 1-Octyne (1a) in the Presence of Pt(PPh₃)₄ (run 3 of Table 3, run 1 of Table 4):** General Procedure of Platinum-Catalyzed Trifluoroacetylation of Alkynes Using Thioesters: Into a two-necked 3 mL reaction glass were added Pt(PPh₃)₄ (31.1 mg, 0.025 mmol), 8a (108 mg, 0.492 mmol), 1a (82.0 mg, 0.74 mmol) and xylene (0.5 mL) under a N₂ atmosphere. After the solution was refluxed for 10 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. cis-5a and trans-5a were obtained in 14% (23.2 mg) and 64% (106 mg) yields by preparative TLC using hexane as an eluent.

trans-F₃CC(O)C(H)≡C-(n-C₆H₁₃)SC₆H₄-p-CH₃ (trans-5a): pale yellow oil; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 0.91 (t, \(J = 7.1\) Hz, 3 H), 1.32-1.48 (m, 6 H), 1.66 (tt, 2 H), 2.42 (s, 3 H), 2.89 (t, \(J = 7.6\) Hz, 2 H), 5.74 (s, 1 H), 7.29 (d, \(J = 8.1\) Hz, 2 H), 7.37 (d, \(J = 8.1\) Hz, 2 H); N.O.E. experiment: Irradiation of the singlet of vinylic proton at \(\delta\) 5.75 resulted in 2.7% enhancement of the signal at \(\delta\) 7.37 (aryl doublet) and the triplet of allylic proton at \(\delta\) 2.89 resulted in 0.58% enhancement of the signal at \(\delta\) 7.37 (aryl doublet); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 14.6, 22.0, 23.1, 29.8, 30.2, 32.0, 36.0, 108.5, 113.9 (q, \(J_{C,F} = 291\) Hz), 125.2, 131.5,
135.6, 141.8, 176.2 (q, $J_{CF} = 33.5$ Hz), 180.9; IR (NaCl) 2957, 2929, 2838, 1700, 1597, 1560, 1493, 1458, 1436, 1291, 1202, 1143, 1077, 1018, 842, 811, 725, 686 cm$^{-1}$; mass spectrum (EI) m/z 330 (M$^+$, 42); HRMS calcd for $C_{17}H_{21}F_3OS$ 330.1265, found 330.1270; Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 62.09; H, 6.69.

**cis-F$_3CC(O)C(H)=C(n-C_6H_{13})SC_6H_4-p-CH_3** (**cis-5a**): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.81 (t, $J = 6.8$ Hz, 3 H), 1.05-1.12 (m, 6 H), 1.35-1.40 (m, 2 H), 2.25 (t, $J = 7.8$ Hz, 2 H), 2.40 (s, 1 H), 6.51 (s, 1 H), 7.23 (d, $J = 7.8$ Hz, 2 H), 7.41 (d, $J = 7.8$ Hz, 2 H); N.O.E. experiment: Irradiation of the triplet of allylic proton at $\delta$ 2.25 resulted in 3.8% enhancement of the signal at $\delta$ 7.41 (aryl doublet) and 8.4% enhancement of the signal at $\delta$ 6.51 (vinyllic singlet); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 21.3, 22.3, 28.5, 29.9, 31.1, 37.5, 110.2, 116.4 (q, $J_{CF} = 290$ Hz), 125.7, 130.2, 135.4, 140.6, 177.3 (q, $J_{CF} = 34.4$ Hz), 178.0; IR (NaCl) 2931, 2860, 2359, 1681, 1674, 1598, 1563, 1548, 1538, 1532, 1520, 1506, 1494, 1463, 1456, 1362, 1300, 1199, 1146, 1105, 1018, 864, 813, 729, 686 cm$^{-1}$; mass spectrum (EI) m/z 330 (M$^+$, 41); Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 62.02; H, 6.66.

Other trifluoroacetylthiolation products 5d-1 were synthesized by similar procedures.

**trans-F$_3CC(O)C(H)=C(n-C_6H_{13})SC_6H_4-p-OCH_3** (**trans-5d**): pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91 (t, $J = 6.6$ Hz, 3 H), 1.33-1.46 (m, 6 H), 2.88 (t, $J = 7.6$ Hz, 2 H), 5.73 (s, 1 H), 7.00 (d, $J = 8.8$ Hz, 2 H), 7.40 (d, $J = 8.8$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.5, 29.3, 29.6, 31.4, 35.3, 55.4, 107.8, 115.6, 116.3 (q, $J_{CF} = 291$ Hz), 118.7, 136.7, 161.5, 175.4 (q, $J_{CF} = 33.5$ Hz), 180.9; IR (NaCl) 2958, 2930, 2858, 1697, 1593, 1560, 1553, 1496, 1465, 1441, 1292, 1254, 1202, 1174, 1143, 1106, 1077, 1031, 860, 831, 800, 726, 686 cm$^{-1}$; mass spectrum (EI) m/z 346 (M$^+$, 58); Anal. Calcd for $C_{17}H_{21}F_3O_2S$: C, 58.94; H, 6.11. Found: C, 58.88; H, 6.09.

**cis-F$_3CC(O)C(H)=C(n-C_6H_{13})SC_6H_4-p-OCH_3** (**cis-5d**): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.82 (t, $J = 7.1$ Hz, 3 H), 1.08-1.19 (m, 6 H), 1.39 (b, 2 H), 3.85 (s, 3 H), 6.51 (s, 1 H), 6.95 (d, $J = 8.6$ Hz, 2 H), 7.44 (d, $J = 8.6$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 22.3, 28.5, 29.9, 31.1, 37.5, 55.4, 110.1, 114.9, 116.4 (q, $J_{CF} = 289$ Hz), 119.8, 137.0, 161.2, 177.2 (q, $J_{CF} = 33.9$ Hz), 178.7; IR (NaCl) 2958, 2931, 2859, 1682, 1593, 1572, 1538, 1495, 1464, 1442, 1408, 1364, 1308, 1291, 1199, 1174, 1144, 1105, 1031, 864, 832, 729 cm$^{-1}$; mass spectrum (EI) m/z 346 (M$^+$, 69); Anal. Calcd for $C_{17}H_{21}F_3O_2S$: C, 58.94; H, 6.11. Found: C, 59.05; H, 6.02.

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trans-F$_3$CC(O)C(H)=C(n-C$_6$H$_{13}$)SC$_6$H$_5$ (trans-5e): pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91 (t, $J$ = 6.6 Hz, 3 H), 1.33-1.49 (m, 6 H), 1.66 (tt, 2 H), 2.90 (t, $J$ = 7.8 Hz, 2 H), 5.72 (s, 1 H), 7.50 (b, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.5, 29.2, 29.6, 31.4, 35.4, 108.1, 116.2 (q, $J_{C-F}$ = 291 Hz), 128.1, 130.1, 130.8, 135.2, 175.5 (q, $J_{C-F}$ = 33.4 Hz), 179.7; IR (NaCl) 2958, 2930, 2859, 1699, 1560, 1477, 1442, 1291, 1203, 1077, 1024, 837, 750, 706, 685 cm$^{-1}$; mass spectrum (EI) m/z 316 (M$^+$, 26); Anal. Calcd for C$_{16}$H$_{19}$F$_3$OS: C, 60.74; H, 6.05. Found: C, 60.53; H, 6.05.

cis-F$_3$CC(O)C(H)=C(n-C$_6$H$_{13}$)SC$_6$H$_5$ (cis-5e): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.80 (t, $J$ = 6.7 Hz, 3 H), 1.05-1.17 (m, 6 H), 1.39 (m, 2 H), 2.25 (t, $J$ = 7.6 Hz, 2 H), 6.53 (s, 1 H), 7.43-7.56 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 22.3, 28.6, 29.9, 31.1, 37.7, 110.5, 116.5 (q, $J_{C-F}$ = 292 Hz), 129.3, 129.5, 130.2, 135.6, 177.2, 177.4 (q, $J_{C-F}$ = 34.4 Hz); IR (NaCl) 2958, 2931, 2860, 1682, 1537, 1477, 1468, 1441, 1364, 1300, 1261, 1200, 1145, 1106, 1024, 862, 818, 752, 730, 706, 692 cm$^{-1}$; mass spectrum (EI) m/z 316 (M$^+$, 30); HRMS calcd for C$_{16}$H$_{19}$F$_3$OS: 316.1112.

trans-F$_3$CC(O)C(H)=C(n-C$_6$H$_{13}$)SC$_6$H$_4$-p-Cl (trans-5f): pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91 (t, $J$ = 6.6 Hz, 3 H), 1.31-1.48 (m, 6 H), 1.68 (m, 2 H), 2.88 (t, $J$ = 7.8 Hz, 2 H), 5.72 (s, 1 H), 7.44 (d, $J$ = 8.6 Hz, 2 H), 7.49 (d, $J$ = 8.3 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 29.2, 29.6, 31.4, 35.3, 108.3, 116.2 (q, $J_{C-F}$ = 291 Hz), 126.6, 130.5, 136.5, 137.4, 175.6 (q, $J_{C-F}$ = 33.5 Hz), 178.8; IR (NaCl) 2958, 2930, 2859, 1698, 1682, 1574, 1568, 1556, 1477, 1454, 1436, 1392, 1292, 1204, 1146, 1096, 1076, 1014, 859, 839, 825, 749, 726, 684 cm$^{-1}$; mass spectrum (EI) m/z 350 (M$^+$, 41); Anal. Calcd for C$_{16}$H$_{18}$C$_1$F$_3$OS: C, 54.78; H, 5.17. Found: C, 54.68; H, 5.13.

cis-F$_3$CC(O)C(H)=C(n-C$_6$H$_{13}$)SC$_6$H$_4$-p-Cl (cis-5f): pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.83 (t, $J$ = 7.3 Hz, 3 H), 1.07-1.43 (m, 8 H), 2.24 (t, $J$ = 7.6 Hz, 2 H), 6.54 (s, 1 H), 7.42 (d, $J$ = 8.3 Hz, 2 H), 7.49 (d, $J$ = 8.3 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.9, 22.3, 28.5, 29.7, 31.1, 37.6, 110.8, 116.3 (q, $J_{C-F}$ = 289 Hz), 127.7, 129.7, 136.8, 136.8, 176.1, 177.5 (q, $J_{C-F}$ = 34.4 Hz); IR (NaCl) 2958, 2931, 2859, 1682, 1574, 1538, 1476, 1389, 1364, 1296, 1201, 1176, 1146, 1107, 1093, 1014, 865, 824, 748, 728, 684 cm$^{-1}$; mass spectrum (EI) m/z 350 (M$^+$, 39); HRMS calcd for C$_{16}$H$_{19}$ClF$_3$OS: 350.0719. Found: 350.0714.

trans-F$_3$CC(O)C(H)=C(n-C$_6$H$_{13}$)SCH$_2$C$_6$H$_5$ (trans-5g): pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J$ = 6.8 Hz, 3 H), 1.29-1.41 (m, 6 H), 1.57 (tt, 2 H), 2.83 (t, $J$ = 7.8 Hz, 2 H), 4.09 (s, 2 H), 6.17 (s, 1 H), 7.30-7.37 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.5, 29.2, 29.7, 31.4, 36.2, 37.3, 106.9, 116.5 (q, $J_{C-F}$ = 291 Hz), 128.1, 128.9, 129.0, 133.6, 174.9
trans-F₃CC(O)C(H)=C(n-C₆H₁₃)S-(n-C₁₀H₂₁) (trans-5h): pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (b, 6 H), 1.27-1.42 (m, 20 H), 1.57 (tt, 2 H), 1.70 (tt, 2 H), 2.82-2.85 (m, 4 H), 6.01 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 14.1, 22.5, 22.7, 27.0, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 29.8, 31.4, 31.9, 32.2, 36.6, 106.2, 116.6 (q, J_{C-F} = 292 Hz), 174.7 (q, J_{C-F} = 33.0 Hz), 179.3; IR (NaCl) 2957, 2927, 2856, 1698, 1556, 1467, 1434, 1293, 1201, 1143, 1079, 860, 824, 724, 693 cm⁻¹; mass spectrum (EI) m/z 380 (M⁺, 8.5); Anal. Calcd for C₂₀H₃₅F₃OS: C, 63.12; H, 9.27. Found: C, 63.18; H, 9.23.

cis-F₃CC(O)C(H)=C((CH₂)₄Cl)SC₆H₅ (cis-5i): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.53-1.57 (m, 4 H), 2.29 (t, J = 7.2 Hz, 2 H), 3.34 (t, J = 6.0 Hz, 2 H), 6.54 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 27.0, 31.5, 36.8, 44.0, 110.7, 116.3 (q, J_{C-F} = 289 Hz), 129.0, 129.6, 130.4, 135.5, 175.8, 177.4 (q, J_{C-F} = 33.8 Hz); IR (NaCl) 3025, 2957, 2868, 1698, 1556, 1477, 1442, 1292, 1203, 1143, 1077, 1024, 838, 750, 706, 686 cm⁻¹; mass spectrum (EI) m/z 322 (M⁺, 54); HRMS calcd for C₁₇H₂₁F₃OS: 322.0406. Found: 322.0399.

trans-F₃CC(O)C(H)=C((CH₂)₂CN)SC₆H₅ (trans-5j): pale yellow solid; mp 64-66 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.05 (m, 2 H), 2.53 (t, J = 6.8 Hz, 2 H), 3.01 (t, J = 6.8 Hz, 2 H), 5.80 (s, 1 H), 7.53 (b, 5 H); ¹³C NMR (100 MHz, CDCl₃) δ 17.0, 25.2, 34.0, 109.3, 116.1 (q, J_{C-F} = 294 Hz), 118.9, 127.5, 130.4, 131.2, 135.2, 176.0 (q, J_{C-F} = 34.4 Hz), 176.2; IR (NaCl) 3064, 2954, 2244, 1687, 1548, 1478, 1453, 1439, 1294, 1274, 1188, 1145, 1078, 1025, 999, 868, 854, 840, 766, 749, 708, 685, 574, 452 cm⁻¹; mass spectrum (EI) m/z 299 (M⁺, 47); Anal. Calcd for C₁₄H₁₂F₃NOS: C, 56.18; H, 4.04; N, 4.68. Found: C, 56.18; H, 3.98; N, 4.73.

(q, J_{C-F} = 32.3 Hz), 178.1; IR (NaCl) 2957, 2930, 2858, 1698, 1552, 1455, 1435, 1295, 1203, 1142, 1079, 822, 711, 696 cm⁻¹; mass spectrum (EI) m/z 330 (M⁺, 2.2); Anal. Calcd for C₁₇H₂₁F₃OS: C, 61.80; H, 6.41. Found: C, 61.67; H, 6.42.
cis-\(\text{F}_3\text{CC(O)C(H)=C((CH_2)_3CN)SC_6H_5}\) (cis-5j): yellow oil; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.73 (tt, \(J = 7.0, 7.8\) Hz, 2 H), 2.16 (t, \(J = 7.0\) Hz, 2 H), 2.45 (t, \(J = 7.8\) Hz, 2 H), 6.56 (s, 1 H), 7.45-7.57 (m, 5 H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.7, 25.5, 36.4, 111.7, 116.5 (q, \(J_{CF} = 289\) Hz), 118.5, 128.9, 130.1, 131.0, 135.7, 173.4, 177.8 (q, \(J_{CF} = 34.8\) Hz); IR (NaCl) 3062, 2947, 2248, 1602, 1578, 1478, 1456, 1442, 1368, 1304, 1202, 1143, 1111, 1024, 1002, 865, 818, 754, 730, 706, 694 cm\(^{-1}\); mass spectrum (EI) m/z 299 (M\(^+\), 33); HRMS calcd for C\(_{14}\)H\(_{12}\)F\(_3\)NOS: 299.0592. Found: 299.0590.

trans-\(\text{F}_3\text{CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5}\) (trans-5k): pale yellow oil; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.01 (tt, 2 H), 2.48 (t, \(J = 7.6\) Hz, 2 H), 2.96 (t, \(J = 7.8\) Hz, 2 H), 3.70 (s, 3 H), 5.75 (s, 1 H), 7.50-7.54 (b, 5 H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.6, 33.3, 34.2, 51.7, 108.7, 116.1 (q, \(J_{CF} = 291\) Hz), 127.8, 130.2, 135.2, 173.3, 175.6 (q, \(J_{CF} = 33.5\) Hz), 178.0; IR (NaCl) 3063, 2953, 1738, 1698, 1565, 1556, 1477, 1441, 1368, 1293, 1255, 1204, 1142, 1076, 1024, 1000, 838, 752, 706, 689 cm\(^{-1}\); mass spectrum (EI) m/z 332 (M\(^+\), 13); Anal. Calcd for C\(_{15}\)H\(_{15}\)F\(_3\)O\(_3\)S: C, 54.21; H, 4.55. Found: C, 54.21; H, 4.49.

cis-\(\text{F}_3\text{CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5}\) (cis-5l): yellow oil; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.94 (m, 2 H), 1.47-1.57 (m, 6 H), 1.87 (m, 1 H), 2.27 (d, \(J = 7.1\) Hz, 2 H), 6.54 (s, 1 H), 7.43-7.55 (m, 5 H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.6, 32.1, 39.8, 43.4, 110.9, 116.4 (q, \(J_{CF} = 300\) Hz), 129.4, 130.1, 135.2, 135.6, 176.2, 177.2 (q, \(J_{CF} = 33.9\) Hz); IR (NaCl) 3062, 2953, 2869, 1682,
1538, 1477, 1441, 1367, 1345, 1296, 1200, 1144, 1110, 1070, 1024, 1002, 863, 819, 752, 730, 706, 693 cm⁻¹; mass spectrum (EI) m/z 314 (M⁺, 26); Anal. Calcd for C₁₆H₁₇F₃OS: C, 61.13; H, 5.45. Found: C, 61.28; H, 5.54.

Cis-to-trans Isomerization of 5a in Toluene-d₈ (Eq. S2): Into a dry Pyrex NMR tube were added 5a (cis:trans = 94:6) (0.0506 mmol), 1,4-dioxane (0.0585 mmol as an internal standard) and 0.5 mL of toluene-d₈ under N₂ atmosphere. Then the sample was heated at 100 °C for 7 h; however, isomerization was hardly confirmed by ¹H NMR spectroscopy (cis:trans = 7:93). Additional heating after the addition of Pt(PPh₃)₂(C₂H₄) (0.006 mmol) resulted in the formation of trans-5a (cis:trans = 28:72).

1-7. References and Notes


The stereochemistry of trans-4a and cis-4a was determined by N.O.E. experiment between vinyl and allyl protons.

The treatment of isolated cis-4a with 2a and a catalytic amount of Pd(dba)$_2$ (5 mol%), dppe (6 mol%) and 1.6 equivalent of 1a led to cis-to-trans isomerization (cis:trans = 39:61), while no isomerization took place without 1a under otherwise identical conditions. This result suggests that alkyne-coordinated Pd-complex induce the cis-to-trans isomerization.


The stereochemistry of trans-5a and cis-5a was determined by N.O.E. experiment between vinyl and allyl protons, and the regiochemistry of trans-5a was determined by $^1$H-$^{13}$C HMBC experiment.

See Eq. S1.


For the oxidative addition of thioesters to Pt(0) complex, see: Minami, Y.; Kato, T.; Kuniyasu, H.; Terao, J.; Kambe, N. Organometallics 2006, 25, 2949, and references therein.


Chapter 2
Pd-Catalyzed Regioselective Iminothiolation of Alkynes:
Remarkable Effects of CF₃ Group of Iminosulfides

2-1. Introduction
1-Azadienes, α,β-unsaturated imines, have been employed as versatile synthetic intermediates, which act as electrophiles in a 1,2-addition and Michael-type 1,4-addition, nucleophiles by nitrogen atom, and heterodienes in cycloaddition reaction such as hetero-Diels-Alder reaction.¹ The condensation of α,β-unsaturated ketones with primary amines is the most convenient method for the preparation of 1-azadienes (Eq. 1). On the other hand, the transition-metal catalyzed iminocarbon-vinylcarbon bond formation reaction also can be a promising alternative. Although some catalytic reactions such as Pd-catalyzed cross-coupling of imidoyl chlorides with vinyl stannanes and Pd-catalyzed Mizoroki-Heck-type reaction of imidoyl iodides with alkenes were reported,² to the best of my knowledge, catalytic introduction of imino groups by the addition reactions to alkynes is still unknown (Eq. 2).³

![Scheme 1: Condensation of α,β-unsaturated ketones with primary amines](image1.png)

![Scheme 2: Transition-metal catalyzed iminocarbon-vinylcarbon bond formation reaction](image2.png)

As a part of our studies of transition-metal catalyzed reactions of organosulfides with carbon-carbon unsaturated bonds,⁴ our group has already reported the decarbonylative carbothiolation of alkynes using thioesters to produce vinylsulfides. Moreover, the author discovered the CO-retained addition of thioesters to alkynes as noted previous chapter. This finding led me to develop a new synthetic method of β-sulfur functionalized 1-azadienes by the intermolecular addition reaction of iminosulfides (1) to alkynes (2) under similar reaction conditions of acylthiolations of alkynes.

2-2. Pd-Catalyzed Iminothiolation of Various Alkynes Using Iminosulfides
First, prompted by the success of trifluoroacetylthiolation of alkynes by CF₃C(O)SR in chapter 1, reactions using an iminosulfide [1a; CF₃C(=NPh)-S-p-tolyl] have been scrutinized
Table 1. Pd-Catalyzed Iminothiolation of Various Alkynes (2) Using 1\textsuperscript{a}

\[
\begin{array}{ccccccc}
\text{run} & \text{2} & \text{R}^1 \equiv \text{R}^2 & \text{temp (°C)} & \text{time (h)} & \text{3} & \text{(%) (cis:trans)}^b \\
1 & 2a & \text{Cl} & 80 & 1 & 3a & 89 (18:82) \\
2 & 2b & \text{Cl} & 80 & 1 & 3b & 81 (13:87) \\
3 & 2c & \text{CO}_2\text{Me} & 80 & 2 & 3c & 81 (14:86) \\
4 & 2d & \text{CO}_2\text{Me} & 80 & 2 & 3d & 87 (13:87) \\
5 & 2e & \text{H} & 80 & 3 & 3e & 76 (14:86) \\
6 & 2f & \text{H} & 80 & 1 & 3f & 89 (98:2) \\
7 & 2g & \text{CF}_3 & 80 & 1 & 3g & 95 (86:14) \\
8 & 2h & \text{CF}_3 & 160^d & 1 & 3h & 74 (98:2) \\
9 & 2i & \text{CF}_3 & 80 & 1 & 3i & 83 (>99:1) \\
10^c & 2j & \text{H} & 150^d & 3 & 3j & 14 (95:5) \\
11 & 2k & \text{H} & 100^d & 3 & 3k & n.d. \\
12 & 2l & \text{H} & 180^d & 3 & 3l & 91 (>99:1) \\
13 & 2m & \text{H} & 180^d & 3 & 3m & 51 (33:67) \\
\end{array}
\]

\textsuperscript{a}Unless otherwise noted, 1\text{a} (0.5 mmol), 2 (0.6 mmol for runs 1-5, 3.0 mmol for run 9, 1.0 mmol for runs 10-13), Pd(dba\textsubscript{2}) (0.025 mmol), PPh\textsubscript{3} (0.05 mmol) and 1,2-dichloroethane (0.5 mL) at 80 °C for 1-3 h. \textsuperscript{b}isolated yield. \textsuperscript{c}1,2-dichloroethane (0.25 mL). \textsuperscript{d}microwave irradiation.

The reaction of 1\text{a} (0.5 mmol) with 1-octyne (2\text{a}, 0.6 mmol) in the presence of Pd(dba\textsubscript{2}) (0.025 mmol) and PPh\textsubscript{3} (0.05 mmol) in 1,2-dichloroethane at 80 °C for 1 h produced desired adduct CF\textsubscript{3}C(=NPh)C(H)=C(n-C\textsubscript{6}H\textsubscript{13})(S-p-toly\textsubscript{1}) (3\text{a}) in 89% (cis:trans = 18:82) yield (run 1, Table 1). For the synthesis of 3\text{a}, the reaction of F\textsubscript{3}CC(O)C(H)=C(n-C\textsubscript{6}H\textsubscript{13})(S-p-toly\textsubscript{1}) (4\text{a}) with aniline was conceivable. However, 3\text{a} was not formed; only ketimine derivative [5\text{a}, CF\textsubscript{3}C(OH)=C(H)C(n-C\textsubscript{6}H\textsubscript{13})(=NC\textsubscript{6}H\textsubscript{5})] was yielded (Eq. 3), demonstrating the utility of the present Pd-catalyzed iminothiolation of 2 by 1. Then, the reactions using a variety of terminal alkynes (2\text{b-i}) were attempted. Functional groups such as chlorine (2\text{b}), methoxy carbonyl (2\text{c}), 2-tetrahydropyranyl (2\text{d}) and cyclohexyl (2\text{e}), were tolerant to provide the corresponding adducts 3\text{b-e} in good yields (runs 2-5, Table 1). Although excess amounts of arylalkynes (2\text{f-i},

\[
\begin{array}{cccc}
\text{F}_3\text{C} \equiv \text{S(p-toly\textsubscript{1})} & \text{PhNH}_2 \text{ (1 equiv.)} & \text{PhN} \equiv \text{S(p-toly\textsubscript{1})} & \text{F}_3\text{C} \equiv \text{O} \equiv \text{H} \\
\text{n-C}_6\text{H}_{13} & \text{ neat, 80 °C, 1 h} & \text{n-C}_6\text{H}_{13} & \text{n-C}_6\text{H}_{13} \\
\end{array}
\]

(3)
3-6 equiv.) were needed, both electron-rich and electron-poor arylalkynes reacted with 1a to form cis-3 in high yields (runs 6-9, Table 1). Because addition to internal alkynes was inefficient under similar conditions, I examined microwave irradiation (runs 10-13, Table 1). Addition to 4-octyne (2j) gave the low yield of 3j even at high temperature (run 10, Table 1). No reaction took place when diphenylacetylene (2k) was employed (run 11, Table 1). On the other hand, the reaction using ethyl phenylpropionate (2l) and 3-methoxy-1-phenylpropyne (2m), which are active for Pt-catalyzed decarbonylative arylthiolation by thioesters, proceeded regioselectively to afford 3l and 3m in 91% (cis:trans = >99:1) and 51% (cis:trans = 33:67) yields, respectively (runs 12 and 13, Table 1). The structure of cis-3l was unambiguously determined by X-ray crystallography (Fig. 1).

![Figure 1. ORTEP Diagram of cis-3l.](image)

The results of the additions of various iminosulfides (1) to 2l were summarized in Table 2. Reaction of 1b-c having electron-neutral and withdrawing substituent at the 4-position of S-aryl groups took place to give the corresponding adducts 3n and 3o, but 3o was in a moderate yield (runs 1 and 2, Table 2). Introduction of both electron-donating and withdrawing groups into 4-position of N-aryl group decreased the reactivity; poor yields of 3p and 3q were formed (runs 4 and 6, Table 2). To our delight, the yields of 3o-q were improved when increasing concentration even with shorter reaction time (runs 3, 5 and 7, Table 2). The present reaction using 1f with benzyl group at R5 also produced 3r in 91% yield (run 8, Table 2). Then, the addition of iminosulfides containing substituents at R3 were examined. In the case of 1g (R3 = Ph), the desired adduct 3s was obtained in 44% yield under 10 mol% of Pd/2P(p-tolyl)3 (run 9, Table 2). On the other hand, the reaction of phenethyl substituted iminosulfide (1h, R3 = PhCH2CH2) with 2l gave no adduct 3t (run 10, Table 2).
Table 2. Pd-Catalyzed Iminothiolation of 2l Using Various Iminosulfides (1)*

<table>
<thead>
<tr>
<th>run</th>
<th>1</th>
<th>2l</th>
<th>Ar₃</th>
<th>time (h)</th>
<th>3 (%) (cis:trans)*b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b</td>
<td>CF₃</td>
<td>Ph</td>
<td>3</td>
<td>3n 82 (&gt;99:1)</td>
</tr>
<tr>
<td>2</td>
<td>1c</td>
<td>CF₃</td>
<td>p-ClC₆H₄</td>
<td>3</td>
<td>3o 50° (&gt;99:1)</td>
</tr>
<tr>
<td>3</td>
<td>1e</td>
<td>CF₃</td>
<td>p-tolyl</td>
<td>1</td>
<td>3o 71 (&gt;99:1)</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>CF₃</td>
<td>p-MeC₆H₄</td>
<td>3</td>
<td>3p 35° (&gt;99:1)</td>
</tr>
<tr>
<td>5</td>
<td>1c</td>
<td>CF₃</td>
<td>p-tolyl</td>
<td>1</td>
<td>3p 88 (&gt;99:1)</td>
</tr>
<tr>
<td>6</td>
<td>1e</td>
<td>CF₃</td>
<td>p-tolyl</td>
<td>3</td>
<td>3q 34° (&gt;99:1)</td>
</tr>
<tr>
<td>7</td>
<td>1e</td>
<td>CF₃</td>
<td>p-tolyl</td>
<td>1</td>
<td>3q 85 (79:21)</td>
</tr>
<tr>
<td>8</td>
<td>1f</td>
<td>CF₃</td>
<td>CH₂Ph</td>
<td>2</td>
<td>3r 91 (97:3)</td>
</tr>
<tr>
<td>9</td>
<td>1g</td>
<td>Ph</td>
<td>p-tolyl</td>
<td>3</td>
<td>3s 44 (81:19)</td>
</tr>
<tr>
<td>10</td>
<td>1h</td>
<td>Ph(C₂H₅)</td>
<td>p-tolyl</td>
<td>3</td>
<td>3t n.d.</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, 1 (0.5 mmol), 2l (1.0 mmol), Pd(dba)₂ (0.025 mmol), PPh₃ (0.05 mmol) and 1,2-dichloroethane (0.5 mL for runs 1, 2, 4, 6 and 8, 0.25 mL for runs 3, 5, 7, 9 and 10) at 100 °C using microwave irradiation for 1-3 h. *Isolated yield. °NMR yield. dPd(dba)₂ (0.05 mol) and P(p-tolyl)₃ (0.1 mmol).

2-3. Oxidative Addition of R³C(=NPh)S-p-tolyl to Pt(PPh₃)₂(C₂H₄)

To get the information on the effect of CF₃ group, the oxidative addition of 1a to Pt(PPh₃)₂(C₂H₄) in C₆D₆ under room temperature was monitored by ³¹P NMR spectroscopy (Eq. 4). As a result, cis-Pt(PPh₃)₂[C(=NPh)CF₃](S-p-tolyl) (6a) was smoothly produced quantitatively for 1 h. On the other hand, the reaction using 1g was very sluggish to afford only 2% yield of 6b; even after 23 h, a mixture of 6b and 7b (dimer of 6b) was formed in 32% total yield. These facts indicated that CF₃ group accelerates the oxidative addition.

2-4. A Proposed Reaction Mechanism

A plausible reaction mechanism of the present iminothiolation of alkynes (2; R¹C≡CR²) using iminosulfides (1; R³C(=NR⁴)SR⁵) was depicted in Scheme 3. The oxidative addition of 1 to Pd(0)Lₙ complex triggers the reaction to afford PdLₙ[C(=NR⁴)R³](SR⁵) (8). Subsequent
regio- and stereoselective insertion of alkyne 2 into the S-Pd bond of 8 generates PdLₙ[C(=NR₄)R₃][cis-C(R¹)=C(SR₅)(R²)] (9). Finally, the C-C bond-forming reductive elimination of cis-3 from 9 with regeneration of Pd(0)Lₙ completes the catalytic cycle. 

Cis-to-trans isomerisation of the adduct can be explained as follows: the oxidative addition of a vinyl-C-S bond of cis-3 to a Pd(0)Lₙ complex to produce PdLₙ[cis-C(R²)=C(R¹){C(=NR₄)R₃}](SR₅) (cis-10), cis-to-trans isomerization of cis-10, and the reductive elimination of trans-3 from trans-10.

Scheme 3. A Plausible Mechanism for the Pd-Catalyzed Iminothiolation of Alkynes (2) Using Iminosulfides (1).

2-5. Synthesis of Furan Derivatives

Reagents and conditions: (a) 1a (1.0 equiv.), 2n (1.2 equiv.), Pd(dba)₂ (0.05 equiv.), PPh₃ (0.1 equiv.), DCE, 80 °C, 1 h; then, AcOH (5 equiv.), DCE, 60 °C, 11 h; (b) 1i (1.0 equiv.), 2n (1.2 equiv.), Pd(dba)₂ (0.05 equiv.), PPh₃ (0.1 equiv.), DCE, 80 °C, 1 h. Ts = p-toluenesulfonyl.
The present iminothiolation could be applied to the synthesis of furan derivatives. Furan derivatives have attracted much attention due to pharmaceuticals and flavor and fragrance compounds. Substituted furan (11a) was successfully obtained from the reaction of 1a with 3-methyl-1-butyne-3-ol (2n) and the following treatment of crude adduct (3u) with AcOH (Eq. 5). The overall yield of 11a for the two-pot sequence was 82% yield. The reaction of 1i containing tosyl group at imine moiety with 2n afforded 11b in 89% yield in one-pot without addition of AcOH (Eq. 6).

2-6. Conclusions

The present study substantiated that the iminothiolation of alkynes with iminosulfides gave rise to the formation of 1-azadiene derivatives. The author found that introduction of CF3 group to the iminocarbon moiety is a key to achieve the reaction. Furthermore, the present synthesis of 1-azadienes was applicable to the formation of furan derivatives.

2-7. Experimental Section

General Comments: 1H and 13C NMR spectra in CDCl3, benzene-d6 and toluene-d8 solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometer. The chemical shifts in the 1H NMR spectra were recorded relative to Me4Si as an internal standard and C6H6 (δ 7.15), and the chemical shifts in the 13C NMR spectra were recorded relative to CHC13 (δ 77.0) and C6H6 (δ 128.6). The IR spectra were measured by Perkin-Elmer Model 1600 spectrometer and JASCO FT/IR-4200. Mass spectra (EI), high-resolution mass spectra (HRMS) and elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Melting points were measured by a MPA100 Optimelt Automated Melting Point System. Preparative TLC was carried out using Wakogel B-5F silica gel. The X-ray crystal data of cis-3i were collected using Rigaku RAXIS-RAPID Imaging Plate diffractometer. The ORTEP diagram was shown in 50% probability ellipsoid. All reactions were carried out under a N2 atmosphere. Unless otherwise noted, commercially available reagents were used without purification. All solvents were distilled before use. Iminosulfides 1 were prepared by the reactions of the corresponding imidoyl chloride with thiols in the presence of Et3N under benzene reflux. The platinum complex Pt(PPh3)2(C2H4) was synthesized according to the literature (Inorg. Synth. 1978, 18, 120). Benzene-d6 and toluene-d8 were purified by distillation from sodium benzophenon ketyl before use.

Preparation of F3CC(=NC6H5)SC6H4-p-CH3 (1a): Into a three-necked 100 mL reaction glass equipped with reflux condenser were added p-tolythiol (6.23 g, 30.0 mmol), benzene (30 mL), F3CC(=NC6H5)Cl (3.66 g, 29.9 mmol) and triethylamine (8.0 mL, 58 mmol). After the solution was stirred under reflux for 3 h, the white precipitate was filtered and the filtrate was
evaporated and dried *in vacuo*. LA were isolated in 90% (7.94 g, 26.9 mmol) yields by recrystallization using CH₂Cl₂ and hexane.

**F₃CC(=NC₆H₅)SC₆H₄-p-CH₃ (LA):** pale yellow solid; mp 61 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.31 (s, 3 H), 6.89 (d, J = 7.8 Hz, 2 H), 7.06 (d, J = 7.8 Hz, 2 H), 7.13 (t, J = 7.3 Hz, 1 H), 7.30-7.33 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 118.5 (c, J = 279 Hz), 119.1, 122.7, 125.5, 128.9, 129.8, 135.6, 140.3, 146.9, 153.1 (c, J = 35 Hz); IR (KBr) 1627, 1594, 1485, 1451, 1280, 1214, 1186, 1178, 1160, 1148, 1120, 1107, 1074, 1019, 973, 814, 766, 696, 524, 501, 410 cm⁻¹; mass spectrum (EI) m/z 295 (M⁺, 39); HRMS calcd for C₁₅H₁₁F₃NS: 295.0643. Found: 295.0640.

Other iminosulfides (LB-I) were synthesized by similar procedures.

**F₃CC(=NC₆H₅)SC₆H₅ (LB):** pale yellow solid; mp 50 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.88 (d, J = 7.8 Hz, 2 H), 7.12 (t, J = 7.3 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 118.5 (c, J = 279 Hz), 119.1, 125.6, 126.6, 129.0, 129.1, 129.8, 135.5, 146.8, 152.4 (c, J = 35 Hz); IR (KBr) 3063, 1651, 1621, 1543, 1594, 1581, 1485, 1443, 1289, 1214, 1183, 1150, 1072, 1024, 1004, 982, 824, 770, 754, 728, 706, 695, 526, 475, 418 cm⁻¹; mass spectrum (EI) m/z 281 (M⁺, 32.8); HRMS calcd for C₁₄H₁₀F₃NS: 281.0486. Found: 281.0482.

**F₃CC(=NC₆H₅)SC₆H₄-p-Cl (1C):** yellow solid; mp 66 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.85 (d, J = 7.8 Hz, 2 H), 7.20 (d, J = 8.3 Hz, 2 H), 7.28-7.31 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 118.1 (c, J = 279 Hz), 124.6, 125.4, 128.7, 129.0, 13.2, 136.4, 146.3, 151.3 (c, J = 35.4 Hz); IR (KBr) 3034, 1630, 1594, 1572, 1477, 1450, 1392, 1280, 1215, 1185, 1148, 1094, 1026, 1015, 971, 825, 767, 746, 728, 696, 521, 501, 418, 412 cm⁻¹; mass spectrum (EI) m/z 315 (M⁺, 20.0); HRMS calcd for C₁₄H₁₀ClF₃NS: 315.0096. Found: 315.0089.

**F₃CC(=NC₆H₄-p-OCH₃)SC₆H₄-p-CH₃ (1D):** yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3 H), 3.81 (s, 3 H), 6.87 (d, J = 9.3 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 7.8 Hz, 2 H), 7.32 (d, J = 7.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 55.4, 114.1, 118.7 (c, J = 279 Hz), 121.7, 123.3, 129.9, 135.4, 139.6, 140.2, 151.1 (c, J = 35 Hz), 157.9; IR (NaCl) 2951, 2837, 1624, 1579, 1504, 1466, 1442, 1280, 1248, 1214, 1187, 1147, 1108, 1034, 1019, 975, 951, 832, 810, 765, 703 cm⁻¹; mass spectrum (EI) m/z 325 (M⁺, 35.2); HRMS calcd for C₁₆H₁₄F₃NOS: 325.0748. Found: 325.0746.
F$_3$C(-NC$_6$H$_4$-p-Cl)SC$_6$H$_4$-p-CH$_3$ (1e): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.34 (s, 3 H), 6.81 (d, $J$ = 8.3 Hz, 2 H), 7.09 (d, $J$ = 8.3 Hz, 2 H), 7.25-7.29 (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.1, 118.4 (c, $J$ = 279 Hz), 120.5, 122.3, 128.9, 129.9, 130.9, 135.5, 140.5, 145.1, 153.7 (c, $J$ = 34 Hz); IR (NaCl) 3027, 2923, 1885, 1484, 1402, 1284, 1219, 1189, 1151, 1097, 1013, 978, 953, 833, 809, 734, 732, 713, 655 cm$^{-1}$; mass spectrum (EI) m/z 329 (M$^+$, 27.7); HRMS calcd for C$_{15}$H$_{11}$ClF$_3$NS: 329.0253. Found: 329.0254.

F$_3$C(-NC$_6$H$_5$)SCH$_2$C$_6$H$_5$ (1f): pale yellow solid; mp 71 °C; $^1$H NMR (400 MHz, CDCl$_3$, -40 °C) major isomer $\delta$ 4.25 (s, 2 H), 6.90 (d, $J$ = 7.8 Hz, 2 H), 7.16 (dd, $J$ = 6.8, 8.3 Hz, 1 H), 7.22-7.33 (m, 4 H), 7.35-7.40 (m, 3 H): minor isomer $\delta$ 4.23 (s, 2 H), 6.76 (d, $J$ = 7.8 Hz, 2 H), Other peaks overlap with those of major isomer.; $^{13}$C NMR (100 MHz, CDCl$_3$, -40 °C) $\delta$ 34.6, 36.1 (c, $J$ = 3.3 Hz), 118.2, 118.4, 118.5 (c, $J$ = 278 Hz), 124.1, 125.7, 127.7, 128.2, 128.6, 128.8, 129.1, 129.4, 133.6, 135.3, 146.7, 147.9, 153.6 (c, $J$ = 34 Hz); IR (KBr) 3083, 3024, 3006, 2332, 1962, 1891, 1816, 1624, 1593, 1487, 1454, 1440, 1292, 1245, 1215, 1185, 1161, 1148, 1126, 1075, 1026, 1001, 981, 918, 908, 827, 774, 726, 700, 612, 591, 560 cm$^{-1}$; mass spectrum (EI) m/z 295 (M$^+$, 39.1); HRMS calcd for C$_{15}$H$_{12}$F$_3$NS: 295.0643. Found: 295.0645.

PhC(-NPh)SC$_6$H$_4$-p-CH$_3$ (1g): yellow solid; mp 72 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.19 (s, 3 H), 6.87 (d, $J$ = 6.8 Hz, 2 H), 6.99 (d, $J$ = 7.3 Hz, 2 H), 7.03 (d, $J$ = 7.3 Hz, 2 H), 7.13 (dd, $J$ = 6.4, 6.8 Hz, 1 H), 7.20-7.27 (m, 3 H), 7.36 (dd, $J$ = 6.3, 6.4 Hz, 2 H), 7.65 (d, $J$ = 5.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0, 120.0, 124.2, 127.9, 128.5, 128.7, 128.8, 129.0, 129.1, 129.5, 129.9, 133.4, 137.7, 150.4; IR (KBr) 3347, 3077, 3052, 3030, 2918, 1955, 1906, 1797, 1645, 1574, 1489, 1445, 1397, 1351, 1304, 1240, 1208, 1182, 1167, 1105, 1089, 1075, 1025, 1015, 998, 933, 921, 899, 847, 832, 809, 766, 690, 665, 644, 629, 609, 594, 555 cm$^{-1}$; mass spectrum (EI) m/z 303 (M$^+$, 0.2); HRMS calcd for C$_{20}$H$_{17}$NS: 303.1082. Found: 303.1090.

PhCH$_2$CH$_2$C(-NPh)SC$_6$H$_4$-p-CH$_3$ (1h): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.36 (s, 3 H), 2.62 (t, $J$ = 8.3 Hz, 2 H), 2.93 (t, $J$ = 8.3 Hz, 2 H), 6.89 (d, $J$ = 7.3 Hz, 2 H), 7.01 (d, $J$ = 6.8 Hz, 2 H), 7.10-7.24 (m, 7 H), 7.34-7.38 (m, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.3, 33.4, 39.5, 119.7, 124.1, 126.0, 126.9, 128.3, 128.5, 129.0, 130.1, 135.8, 139.8, 140.9, 150.3, 166.8; IR (NaCl) 3060, 3027, 2923, 2861, 1734, 1625, 1592, 1486, 1453, 1416, 1265, 1220, 1179, 1060, 1018, 993, 945, 901, 867, 812, 751, 696 cm$^{-1}$; mass spectrum (EI) m/z 331 (M$^+$, 0.3); HRMS calcd for C$_{22}$H$_{21}$NS: 331.1395.
Found: 331.1400.

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\text{F}_3\text{CC}(-\text{N-}\text{SO}_2\text{-C}_6\text{H}_4-p-\text{CH}_3)\text{SC}_6\text{H}_4-p-\text{CH}_3 \ (\text{II}) \ : \ \text{white solid; mp 143 °C; } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 2.41 \ (s, 3 \text{ H}), 2.47 \ (s, 3 \text{ H}), 7.24 \ (d, J = 12 \text{ Hz}, 2 \text{ H}), 7.37 \ (d, J = 12 \text{ Hz}, 2 \text{ H}), 7.50 \ (d, J = 12 \text{ Hz}, 2 \text{ H}), 7.90 \ (d, J = 12 \text{ Hz}, 2 \text{ H}); ^13\text{C NMR (100 MHz, CDCl}_3) \delta 21.5, 21.7, 117.7 \ (c, J = 283 \text{ Hz}), 121.1, 126.2, 127.7, 129.7, 130.3, 136.1, 136.2, 142.2, 145.1, 167.0 \ (c, J = 35 \text{ Hz}); IR (KBr) 3326, 3239, 3114, 1596, 1562, 1491, 1452, 1401, 1336, 1304, 1291, 1273, 1206, 1185, 1151, 1087, 1040, 1017, 982, 909, 818, 789, 722, 703, 665, 642, 603, 570 \text{ cm}^{-1}; \text{mass spectrum (EI) m/z 373 (M}, \ ^{+}, 8.3); \text{HRMS calcd for C}_{16}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}_2: 373.0418. \text{Found: 373.0420.}
\]

**Table S1.** Optimization of the reaction conditions

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<th>run</th>
<th>M</th>
<th>ligand</th>
<th>Y</th>
<th>solvent</th>
<th>temp</th>
<th>time</th>
<th>3a (%) (cis/trans)</th>
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<tr>
<td>1</td>
<td>Pd(PPh)_3</td>
<td>-</td>
<td>-</td>
<td>toluene</td>
<td>80 °C</td>
<td>25 h</td>
<td>75° (22:78)</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh)_3</td>
<td>-</td>
<td>-</td>
<td>DME</td>
<td>80 °C</td>
<td>25 h</td>
<td>71° (22:78)</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh)_3</td>
<td>-</td>
<td>-</td>
<td>1,4-dioxane</td>
<td>80 °C</td>
<td>25 h</td>
<td>56° (24:76)</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh)_3</td>
<td>-</td>
<td>-</td>
<td>MeCN</td>
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<td>25 h</td>
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<tr>
<td>5</td>
<td>Pd(PPh)_3</td>
<td>-</td>
<td>-</td>
<td>DMF</td>
<td>80 °C</td>
<td>25 h</td>
<td>69 (23:77)</td>
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<tr>
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<td>-</td>
<td>-</td>
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<td>80 °C</td>
<td>1 h</td>
<td>71 (27:73)</td>
</tr>
<tr>
<td>7</td>
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<td>-</td>
<td>-</td>
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<td>5 h</td>
<td>83 (24:76)</td>
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<tr>
<td>8</td>
<td>Pd(PPh)_3</td>
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<td>-</td>
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<td>10 h</td>
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<tr>
<td>9</td>
<td>Pd(PPh)_3</td>
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<td>r.t.</td>
<td>25 h</td>
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<td>10</td>
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<td>-</td>
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<td>r.t.</td>
<td>25 h</td>
<td>n.d.</td>
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<tr>
<td>11</td>
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<td>-</td>
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<td>n.d.</td>
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<tr>
<td>12</td>
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<td>n.d.</td>
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<tr>
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<td>1 h</td>
<td>65 (19:81)</td>
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<td>1 h</td>
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<td>1 h</td>
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<td>TFP</td>
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<td>DCE</td>
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<td>P(t-Bu)_3</td>
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<td>1 h</td>
<td>75 (20:80)</td>
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<td>DCE</td>
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<td>1 h</td>
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</tr>
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</table>

**a** Unless otherwise noted, 1a (0.5 mmol), 2a (0.6 mmol), catalyst (0.025 mmol), ligand and solvent (0.5 mL). **b** NMR yield. **c** Some byproducts were generated. **d** isolated yield. DCE = 1,2-dichloroethane. TFP = tri(2-furyl)phosphine.
Reaction of F₃CC(NC₆H₅)SC₆H₄-p-CH₃ (1a) with 1-Octyne (2a) in the Presence of Pd(dba)₂/2PPh₃ (run 1 of Table 1): General Procedure of Palladium-Catalyzed Iminothiolation of Alkynes Using Iminosulfides: Into a two-necked 3 mL reaction glass were added Pd(dba)₂ (14.4 mg, 0.025 mmol), PPh₃ (13.1 mg, 0.05 mmol), 1a (149.9 mg, 0.507 mmol), 2a (67.2 mg, 0.610 mmol) and 0.5 mL of 1,2-dichloroethane under N₂ atmosphere. After the solution was stirred at 80 °C for 1 h, the resultant mixture was filtered through Celite, and the filtrate was evaporated and dried in vacuo. 3a was isolated in 89% (183 mg, cis:trans = 18:82) yields by preparative TLC using hexane and diethyl ether (10:1) as an eluent.

**F₃csCF₃C(=NC₆H₅)C(H)=C(n-C₆H₁₃)SC₆H₄-p-CH₃ (3a):** The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 18:82); yellow oil; ^1^H NMR (400 MHz, C₆D₆)

- trans-isomer δ 0.81 (t, J = 7.1 Hz, 3 H), 0.85-0.89 (m, 2 H), 0.94-1.03 (m, 2 H), 1.68-1.75 (m, 2 H), 1.83 (t, J = 7.3 Hz, 2 H), 1.93 (s, 3 H), 5.79 (s, 1 H), 6.71 (d, J = 7.8 Hz, 2 H), 6.87 (d, J = 8.3 Hz, 2 H), 6.93-6.96 (m, 3 H), 7.09 (dd, J = 7.3, 7.8 Hz, 2 H); cis-isomer δ 1.30 (m, 2 H), 1.97 (s, 3 H), 2.13 (t, J = 7.3 Hz, 2 H), 6.54 (s, 1 H), 6.78 (d, J = 7.3 Hz, 2 H), 7.26 (d, J = 7.3 Hz, 2 H), Other peaks overlap with those of trans-isomer.; N.O.E. experiment: Irradiation of the aryl doublet at δ 6.71 resulted in a 1.7% enhancement of the signal at δ 5.79 (vinyl singlet) and a 2.4% enhancement of the signal at δ 1.83 (methylene triplet); ^1^C NMR (100 MHz, C₆D₆) trans-isomer δ 14.8, 21.5, 23.3, 28.8, 28.9, 32.3, 36.3, 118.3, 121.3 (c, J = 268 Hz), 121.6, 126.3, 129.1, 129.5, 130.6, 134.0, 139.0, 155.8 (c, J = 34 Hz); cis-isomer δ 14.7, 21.6, 23.2, 29.5, 31.0, 32.1, 38.5, 113.6, 119.3, 124.7, 129.4, 130.8, 136.1, 139.9, Other peaks cannot be detected.; IR (NaCl) 3382, 3024, 2930, 2854, 1677, 1600, 1578, 1534, 1493, 1449, 1398, 1382, 1312, 1282, 1244, 1226, 1187, 1141, 1111, 1063, 1040, 1018, 989, 912, 891, 877, 812, 761, 735, 694, 583 cm⁻¹; mass spectrum (EI) m/e 405 (M⁺, 23); HRMS calcd for C₂₃H₂₆F₃NS: 405.1738. Found: 405.1733.

Other iminothiolation products (3b-i) using terminal alkynes (2b-i) were synthesized by similar procedures.

**CF₃C(=NC₆H₅)C(H)=C((CH₂)₄C₁)SC₆H₄-p-CH₃ (3b):** The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 13:87); yellow oil; ^1^H NMR (400 MHz, C₆D₆)

- trans-isomer δ 0.97-1.04 (m, 2 H), 1.09-1.17 (m, 2 H), 1.68 (t, J = 7.3 Hz, 2 H), 1.92 (s, 3 H), 2.88 (t, J = 6.4 Hz, 2 H), 5.67 (s, 1 H), 6.70 (d, J = 7.8 Hz, 2 H), 6.88-6.94 (m, 5 H), 7.07 (dd, J = 7.8, 7.8 Hz, 2 H); cis-isomer δ 1.26 (t, J = 6.8 Hz, 2 H), 6.45 (s, 1 H), 6.74-6.82 (m 4 H), 6.97-7.01 (m, 3 H), 7.23 (d, J = 7.3 Hz, 2 H), other peaks overlap with those of trans-isomer; ^1^C NMR (100 MHz, C₆D₆) trans-isomer δ 20.9, 25.1, 31.0, 34.6, 44.4, 118.5, 120.6 (c, J = 278 Hz), 120.9, 125.8, 129.0, 130.1, 133.4, 138.5, 147.9, 148.4, 155.1 (c, J = 35 Hz); cis-isomer δ 21.0, 27.5, 31.8, 36.9, 44.2, 118.7, 135.4, 148.7, Other peaks cannot be detected.; IR (NaCl) 3393,
CF₃C(=NC₆H₅)C(H)=C((CH₂)₃CO₂CH₃)SC₆H₄-p-CH₃ (3e): The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 14:86); yellow oil; ᵃ¹H NMR (400 MHz, CDCl₃) trans-isomer δ 1.59 (tt, J = 6.8, 7.8 Hz, 2 H), 1.99 (t, J = 7.8 Hz, 2 H), 2.30 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 3.61 (s, 3 H), 6.02 (s, 1 H), 6.87 (d, J = 7.8 Hz, 2 H), 6.98 (d, J = 7.8 Hz, 2 H), 7.02 (d, J = 7.8 Hz, 2 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 2 H); cis-isomer δ 1.74 (tt, J = 6.8, 7.3 Hz, 2 H), 2.14 (tt, J = 7.3 Hz, 2 H), 2.37 (s, 3 H), 6.43 (s, 1 H), 7.40 (d, J = 8.3 Hz, 2 H), other peaks overlap with those of trans-isomer; ᵃ¹³C NMR (100 MHz, CDCl₃) trans-isomer δ 21.1, 23.0, 32.2, 34.5, 51.5, 118.1, 120.5, 122.5 (c, J = 287 Hz), 125.7, 127.5, 128.8, 129.9, 133.1, 138.5, 147.6, 155.1 (c, J = 35 Hz), 173.5: cis-isomer δ 21.3, 24.9, 32.9, 36.6, 51.6, 118.3, 128.5, 135.2, 139.5, 148.0, 173.3, Other peaks cannot be detected.; IR (NaCl) 3023, 2952, 2868, 1737, 1665, 1596, 1546, 1493, 1485, 1449, 1398, 1399, 1369, 1317, 1225, 1188, 1138, 1109, 1091, 1018, 910, 812, 759, 729, 694, 580 cm⁻¹; mass spectrum (EI) m/e 421 (M⁺, 1.7); HRMS calcd for C₂₂H₂₂F₃NO₂S: 421.1323. Found: 421.1318.

CF₃C(=NC₆H₅)C(H)=C((CH₂)₃O(2-C₆H₅O))SC₆H₄-p-CH₃ (3d): The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 13:87); yellow oil; ᵃ¹H NMR (400 MHz, C₆D₆) trans-isomer δ 1.22-1.37 (m, 3 H), 1.46-1.53 (m, 2 H), 1.63-1.71 (m, 1 H), 1.90 (s, 3 H), 2.16 (t, J = 6.4 Hz, 2 H), 3.17-3.23 (m, 1 H), 3.30-3.35 (m, 1 H), 3.63-3.69 (m, 2 H), 4.40 (t, J = 3.4 Hz, 2 H), 6.02 (s, 1 H), 6.66 (d, J = 7.8 Hz, 2 H), 6.78 (d, J = 7.8 Hz, 2 H), 6.92-6.96 (m, 1 H), 6.99 (d, J = 7.3 Hz, 2 H), 7.05-7.13 (m, 2 H); cis-isomer δ 1.93 (s, 3 H), 2.49 (m, 2 H), 3.74-3.76 (m, 1 H), 6.71 (s, 1 H), 7.25 (d, J = 7.3 Hz, 2 H), other peaks overlap with those of trans-isomer; ᵃ¹³C NMR (100 MHz, C₆D₆) trans-isomer δ 19.6, 21.0, 25.9, 30.9, 36.3, 61.7, 65.1, 98.7, 119.3, 120.9 (c, J = 277 Hz), 121.5, 126.0, 128.5, 129.0, 130.2, 133.5, 138.5, 145.6, 148.3, 154.9 (c, J = 34 Hz): cis-isomer δ 19.5, 21.1, 38.1, 61.7, 66.2, 146.7, 118.8, 124.4, 128.9, 129.0, 129.3, 130.2, 135.6, 148.8. Other peaks cannot be detected.; IR (NaCl) 3058, 3022, 2944, 2871, 2280, 1734, 1662, 1595, 1547, 1492, 1485, 1452, 1398, 1385, 1352, 1322, 1286, 1225, 1186, 1136, 1077, 1033, 998, 968, 906, 871, 812, 777, 759, 728, 692, 631, 583, 557 cm⁻¹; mass spectrum (EI) m/e 449 (M⁺, 0.5); HRMS calcd for C₂₂H₂₆F₃NO₂S: 449.1636. Found: 449.1639.
**trans-CF₃C(=NC₆H₅)C(H)=C(c-C₆H₅)SC₆H₄-p-CH₃ (trans-3e):**

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.69-0.91 (m, 4 H), 1.42 (d, J = 13 Hz, 2 H), 1.66 (d, J = 12 Hz, 2 H), 1.78-1.85 (m, 1 H), 1.94 (s, 3 H), 5.88 (s, 1 H), 6.69 (d, J = 7.8 Hz, 2 H), 6.85 (d, J = 7.8 Hz, 2 H), 6.93 (t, J = 7.3 Hz, 1 H), 6.96 (d, J = 7.8 Hz, 2 H), 7.05-7.09 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.4, 26.6, 27.0, 33.5, 43.6, 117.3, 121.3 (c, J = 277 Hz), 122.0, 126.4, 129.3, 129.7, 130.6, 133.4, 138.6, 148.8, 153.7, 156.4 (c, J = 34 Hz); IR (NaCl) 3058, 3022, 2928, 2853, 1661, 1595, 1542, 1492, 1449, 1399, 1380, 1311, 1280, 1224, 1188, 1136, 1101, 1072, 1041, 986, 910, 879, 811, 761, 727, 694, 634, 587 cm⁻¹; mass spectrum (EI) m/e 403 (M⁺, 13); Anal. Calcd for C₂₃H₂₄F₃NS: C, 68.46; H, 6.00; N, 3.47. Found: C, 68.28; H, 5.88; N, 3.41.

**cis-CF₃C(=NC₆H₅)C(H)=C(C₆H₅)SC₆H₄-p-CH₃ (cis-3f):**

Yellow solid; mp 114 °C; ¹H NMR (400 MHz, CDCl₃) main isomer δ 2.13 (s, 3 H), 6.26 (s, 1 H), 6.54 (d, J = 8.0 Hz, 2 H), 6.76 (d, J = 7.8 Hz, 2 H), 7.05 (d, J = 7.8 Hz, 2 H), 7.14-7.19 (m, 4 H), 7.27-7.34 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) main isomer δ 20.9, 119.4, 119.7 (c, J = 277 Hz), 120.7, 125.9, 128.1, 128.2, 128.8, 129.1, 129.3, 131.2, 133.7, 137.0, 137.2, 147.5, 147.6, 155.1 (c, J = 35 Hz), 173.5; N.O.E. experiment: Irradiation of the vinyl singlet at δ 6.26 resulted in a 7.0% enhancement of the signal at δ 6.54 (aryl doublet); IR (KBr) 3080, 3060, 3023, 3000, 2945, 2921, 2868, 1656, 1585, 1566, 1484, 1446, 1401, 1326, 1284, 1268, 1227, 1189, 1169, 1140, 1092, 1057, 1018, 1000, 957, 916, 904, 852, 839, 818, 764, 752, 692, 583, 563, 552 cm⁻¹; mass spectrum (EI) m/e 396 (M⁺, 74); Anal. Calcd for C₂₃H₁₈F₃NS: C, 69.50; H, 4.56; N, 3.52. Found: C, 69.32; H, 4.48; N, 3.62.

**cis-CF₃C(=NC₆H₅)C(H)=C(C₆H₄-p-CH₃)SC₆H₄-p-CH₃ (cis-3g):**

Yellow solid; mp 100 °C; ¹H NMR (400 MHz, CDCl₃) main isomer δ 2.15 (s, 3 H), 2.22 (s, 3 H), 6.24 (s, 1 H), 6.55 (d, J = 7.8 Hz, 2 H), 6.78 (d, J = 7.3 Hz, 2 H), 6.95 (d, J = 7.8 Hz, 2 H), 7.04 (d, J = 7.8 Hz, 2 H), 7.14-7.21 (m, 3 H), 7.31 (t, J = 7.3 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) main isomer δ 21.9, 22.0, 119.9, 120.7 (c, J = 277 Hz), 121.7, 126.8, 129.1, 129.7, 129.8, 130.0, 130.2, 131.9, 135.2, 137.7, 140.2, 148.2, 148.6, 156.2 (c, J = 34 Hz); IR (KBr) 3023, 2924, 2324, 1903, 1658, 1584, 1505, 1484, 1448, 1401, 1300, 1232, 1308, 1285, 1264, 1227, 1188, 1169, 1141, 1092, 1059, 1018, 957, 939, 903, 855, 813, 784, 755, 714, 689, 649, 634, 596, 572 cm⁻¹; mass spectrum (EI) m/e 411 (M⁺, 48.6); Anal. Calcd for C₂₄H₂₀F₃NS: C, 70.05; H, 4.90; N, 3.40. Found: C, 69.83; H, 4.68; N, 3.47.
cis-CF$_3$C(=NC$_6$H$_5$)C(H)=C(C$_6$H$_4$-p-CF$_3$)SC$_6$H$_4$-p-CH$_3$ (cis-3h): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) main isomer $\delta$ 2.15 (s, 3 H), 6.30 (s, 1 H), 6.53 (d, $J$ = 7.8 Hz, 2 H), 6.78 (d, $J$ = 7.8 Hz, 2 H), 7.05 (d, $J$ = 7.3 Hz, 2 H), 7.20 (t, $J$ = 7.3 Hz, 2 H), 7.35-7.39 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$) main isomer $\delta$ 21.1, 119.8 (c, $J$ = 277 Hz), 120.9, 121.3, 123.8 (c, $J$ = 239 Hz), 131.0, 137.8, 141.1, 146.4, 147.6, 154.8 (c, $J$ = 35 Hz); IR (NaCl) 3059, 3026, 2979, 2925, 2869, 1794, 1660, 1615, 1593, 1493, 1485, 1450, 1408, 1325, 1297, 1268, 1226, 1169, 1131, 1090, 1066, 1017, 961, 908, 843, 809, 771, 757, 741, 693, 638, 609, 584, 555 cm$^{-1}$; mass spectrum (EI) m/e 465 (M$^+$, 31.6); Anal. Calcd for C$_{24}$H$_{17}$F$_6$NS: C, 61.93; H, 3.68; N, 3.01. Found: C, 61.68; H, 3.56; N, 2.99.

cis-CF$_3$C(=NC$_6$H$_5$)C(CO$_2$C$_2$H$_5$)=C(C$_6$H$_5$)SC$_6$H$_4$-p-CH$_3$ (cis-3l): yellow solid; mp 78 °C; $^1$H NMR (400 MHz, CDCl$_3$) main isomer $\delta$ 2.18 (s, 3 H), 6.36 (s, 1 H), 6.61 (d, $J$ = 8.3 Hz, 2 H), 6.83 (d, $J$ = 8.3 Hz, 2 H), 6.97 (d, $J$ = 5.4 Hz, 1 H), 7.01 (d, $J$ = 8.3 Hz, 2 H), 7.06 (dd, $J$ = 2.9, 4.9 Hz, 1 H), 7.15 (dd, $J$ = 7.3, 7.8 Hz, 1 H), 7.21 (d, $J$ = 2.9 Hz, 1 H), 7.30 (dd, $J$ = 7.3, 7.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) main isomer $\delta$ 21.0, 118.6, 119.7 (c, $J$ = 277 Hz), 121.0, 125.7, 125.8, 125.9, 126.8, 128.8, 129.3, 129.4, 130.5, 136.9, 138.8, 141.0, 147.6, 154.7 (c, $J$ = 35 Hz); IR (KBr) 3110, 3060, 3023, 3006, 2921, 1661, 1587, 1493, 1483, 1448, 1410, 1317, 1273, 1227, 1191, 1166, 1138, 1091, 1054, 1017, 994, 909, 888, 870, 833, 816, 778, 768, 746, 726, 688, 649, 573 cm$^{-1}$; mass spectrum (CI) m/e 404 (M$^+$, 100); Anal. Calcd for C$_{21}$H$_{16}$F$_3$NS$_2$: C, 62.51; H, 4.00; N, 3.47. Found: C, 62.22; H, 3.82; N, 3.50.

Reaction of F$_3$CC(=NC$_6$H$_5$)SC$_6$H$_4$-p-CH$_3$ (1a) with Ethyl Phenylpropiolate (2l) in the Presence of Pd(dba)$_2$/2PPh$_3$ under the Microwave Irradiation (run 12 of Table 1): General Procedure of Palladium-Catalyzed Iminothiolation of Alkynes Using Iminosulfides under the Microwave Irradiation: Into a 2 mL vial bottle were added Pd(dba)$_2$ (15.0 mg, 0.026 mmol), PPh$_3$ (13.1, 0.05 mmol), 1a (154.4 mg, 0.523 mmol), 2l (179 mg, 1.0 mmol) and 0.5 mL of 1,2-dichloroethane in the dry box (Glove box). The vial bottle was taken outside the dry box. After the solution was stirred at 100 °C for 3 h under microwave irradiation, the resultant mixture was filtered through Celite, and the filtrate was evaporated and dried in vacuo. Cis-3l was isolated in 91% (223 mg, 0.476 mmol) yields by preparative TLC using hexane and diethyl ether (10:1) as an eluent.
(m, 3 H), 7.40 (dd, J = 7.3, 7.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.1, 20.5, 60.8, 118.8, 119.1 (c, J = 278 Hz), 119.8, 125.4, 125.8, 127.0, 128.0, 128.2, 128.3, 128.8, 133.4, 134.9, 138.2, 146.8, 154.5 (c, J = 35 Hz), 159.7, 163.0; IR (KBr) 3375, 3065, 3031, 3014, 2980, 2957, 2937, 2924, 2898, 2870, 1696, 1656, 1591, 1578, 1555, 1486, 1473, 1446, 1389, 1363, 1318, 1274, 1186, 1078, 1020, 984, 937, 915, 874, 839, 812, 798, 761, 744, 717, 696, 681, 641, 625, 599, 556 cm$^{-1}$; mass spectrum (EI) m/e 469 (M$^+$, 5.4); Anal. Calcd for C$_{26}$H$_{22}$F$_3$NO$_2$S: C, 66.51; H, 4.72; N, 2.98. Found: C, 66.23; H, 4.64; N, 3.03.

Other iminothiolation products (3j, m-s) using internal alkynes (2j, 1, m) were synthesized by similar procedures.

**CF$_3$C(=NC$_6$H$_5$)C(n-C$_3$H$_7$)=C(n-C$_3$H$_7$)SC$_6$H$_4$-p-CH$_3$ (3j):** The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 95:5); pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) cis-isomer δ 0.76 (t, J = 7.3 Hz, 3 H), 0.86 (t, J = 7.3 Hz, 3 H), 1.27-1.46 (m, 4 H), 1.59 (m, 1 H), 1.96-1.99 (m, 1 H), 2.06-2.23 (m, 2 H), 2.34 (s, 3 H), 6.93 (d, J = 7.8 Hz, 2 H), 7.11-7.17 (m, 3 H), 7.21 (d, J = 8.3 Hz, 2 H), 7.33 (dd, J = 7.8, 8.3 Hz, 2 H); trans-isomer δ 0.73 (t, J = 7.3 Hz, 3 H), 0.91 (t, J = 7.3 Hz, 3 H), 1.00-1.02 (m, 4 H), 2.30 (s, 3 H), 6.73 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 7.8 Hz, 2 H), 7.38 (dd, J = 7.8, 8 Hz, 2 H). Other peaks overlap with those of cis-isomer.; $^{13}$C NMR (100 MHz, CDCl$_3$) cis-isomer δ 13.4, 14.0, 21.1, 21.2, 21.2, 32.1, 33.9, 119.4, 122.2 (c, J = 296 Hz), 125.5, 128.7, 129.3, 129.8, 131.7, 133.6, 137.7, 141.2, 147.6, 161.2 (c, J = 33 Hz); IR (NaCl) 3060, 3022, 2962, 2932, 2873, 2372, 2323, 1644, 1597, 1492, 1465, 1400, 1380, 1312, 1281, 1248, 1222, 1187, 1142, 1117, 1091, 1063, 1017, 962, 914, 809, 782, 760, 731, 693, 648, 589 cm$^{-1}$; mass spectrum (EI) m/e 405 (M$^+$, 10); HRMS calcd for C$_{23}$H$_{26}$F$_3$NS:405.1738. Found: 405.1741.

**trans-CF$_3$C(=NC$_6$H$_5$)C(CH$_2$OCH$_3$)=C(C$_6$H$_5$)SC$_6$H$_4$-p-CH$_3$ (trans-3m):** yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.13 (s, 3 H), 3.22 (s, 3 H), 3.76 (dd, J = 12.2, 67.4 Hz, 2 H), 6.62 (d, J = 7.8 Hz, 2 H), 6.75 (d, J = 7.8 Hz, 2 H), 6.99-7.01 (m, 2 H), 7.09 (s, 3 H), 7.22-7.28 (m, 3 H), 7.37 (dd, J = 7.3, 7.8 Hz, 2 H); N.O.E. experiment: Irradiation of the signal at δ 3.83 (methylene doublet) resulted in a 4.0% enhancement of the signal at δ 6.75 (aryl doublet); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.0, 58.6, 71.4, 119.3 (c, J = 218 Hz), 120.5, 125.9, 127.6, 127.8, 128.3, 128.5, 128.6, 129.0, 129.2, 133.0, 135.6, 137.7, 143.8, 147.5, 157.4 (c, J = 35 Hz); IR (NaCl) 3060, 3022, 2989, 2925, 2824, 1651, 1593, 1490, 1445, 1370, 1318, 1285, 1241, 1223, 1185, 1142, 1107, 1017, 989, 909, 809, 770, 749, 714, 696, 640, 579 cm$^{-1}$; mass spectrum (EI) m/e 441 (M$^+$, 8.5); Anal. Calcd for C$_{23}$H$_{26}$F$_3$NS: C, 68.01; H, 5.02; N, 3.17. Found: C, 67.72; H, 4.88; N, 3.21.
cis-CF₃C(=NC₆H₅)C(CO₂C₂H₅)=C(C₆H₅)SC₆H₅ (cis-3n): pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.98 (t, J = 6.8 Hz, 3 H), 3.99 (c, J = 6.8 Hz, 2 H), 6.50 (d, J = 7.3 Hz, 2 H), 6.84 (d, J = 7.8 Hz, 2 H), 6.90 (dd, J = 7.3, 7.8 Hz, 2 H), 6.98-7.05 (m, 4 H), 7.26-7.30 (m, 3 H), 7.41 (dd, J = 4.4, 7.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 61.4, 119.6 (c, J = 278 Hz), 119.8, 120.3, 126.3, 127.5, 128.4, 128.6, 128.7, 128.8, 129.6, 133.9, 135.3, 147.3, 154.9 (c, J = 35 Hz), 159.5, 163.4; IR (NaCl) 3060, 3025, 2984, 2939, 2939, 2904, 1952, 1880, 1731, 1698, 1593, 1579, 1560, 1486, 1443, 1391, 1367, 1320, 1277, 1247, 1224, 1187, 1145, 1074, 1023, 1001, 983, 931, 910, 875, 836, 746, 719, 694, 629, 600, 558 cm⁻¹; mass spectrum (EI) m/e 455 (M⁺, 3.6); Anal. Calcd for C₂₅H₂₀F₃NO₂S: C, 65.92; H, 4.43; N, 3.08. Found: C, 65.77; H, 4.21; N, 3.21.

cis-CF₃C(=NC₆H₄-p-CI)C(CO₂C₂H₅)=C(C₆H₅)SC₆H₄-p-CI (cis-3o): pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.96 (t, J = 6.8 Hz, 3 H), 3.99 (c, J = 6.8 Hz, 2 H), 6.34 (d, J = 8.3 Hz, 1 H), 6.50 (d, J = 7.8 Hz, 1 H), 6.84-8.68 (m, 2 H), 6.89 (d, J = 7.8 Hz, 2 H), 6.96-7.09 (m, 3 H), 7.26-7.29 (m, 3 H), 7.38-7.42 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ These peaks were observed as two stereoisomer of PhN=C(CF₃)R (R = C(CO₂C₂H₅)=C(C₆H₅)SC₆H₄-p-CI). δ 13.3, 13.6, 61.4, 61.5, 119.6 (c, J = 278 Hz), 119.6 (c, J = 278 Hz), 119.9, 120.3, 120.4, 120.7, 126.3, 126.4, 127.5, 127.6, 127.8, 128.3, 128.4, 128.6, 128.6, 128.6, 128.6, 128.7, 128.8, 128.8, 129.2, 129.6, 133.9, 134.7, 134.8, 135.2, 135.3147.2, 147.3, 154.6 119.6 (c, J = 35 Hz), 158.1, 159.5, 163.5; IR (NaCl) 3061, 3025, 2982, 2938, 2903, 2253, 1952, 1897, 1731, 1699, 1593, 1579, 1559, 1486, 1476, 1444, 1391, 1368, 1320, 1278, 1247, 1224, 1187, 1146, 1093, 1075, 1023, 984, 910, 875, 822, 746, 695, 648, 630, 600, 559 cm⁻¹; mass spectrum (EI) m/e 489 (M⁺, 4.9); HRMS calcd for C₂₅H₁₉ClF₃NO₂S: 489.0772. Found: 489.0777.

cis-CF₃C(=NC₆H₄-p-OCH₃)C(CO₂C₂H₅)=C(C₆H₅)SC₆H₄-p-CH₃ (cis-3p): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (t, J = 6.8 Hz, 3 H), 2.12 (s, 3 H), 3.85 (s, 3 H), 3.89 (c, J = 6.8 Hz, 2 H), 6.33 (d, J = 7.8 Hz, 2 H), 6.72 (d, J = 7.8 Hz, 2 H), 6.91 (d, J = 5.8 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 7.05-7.07 (m, 3 H), 7.29 (d, J = 8.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ These peaks were observed as two stereoisomer of PhN=C(CF₃)R (R = C(CO₂C₂H₅)=C(C₆H₅)SC₆H₄-p-CH₃). δ 13.3, 13.6, 61.3, 61.4, 114.0, 121.3 (c, J = 282 Hz), 121.2, 123.9, 126.1, 127.5, 128.5, 128.7, 129.2, 134.0, 135.6, 138.6, 140.3, 153.4 (c, J = 35 Hz), 158.6, 159.5, 163.6; IR (NaCl) 3059, 2982, 2837, 2254, 1728, 1698, 1648, 1600, 1578, 1561, 1504, 1493, 1465, 1444, 1392, 1367, 1320, 1292, 1250, 1226, 1184, 1166, 1143, 1075, 1030, 984, 910, 876, 845, 829, 809, 735, 696, 682, 648 cm⁻¹; mass spectrum (EI) m/e 499 (M⁺, 26.3); Anal. Calcd for C₂₇H₂₄F₃NO₃S: C, 64.92; H, 4.84; N, 2.80. Found: C, 64.79; H, 4.63; N, 2.88.
The title compound was obtained as a mixture of inseparable stereoisomers (cis:trans = 71:29); yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)); cis-isomer \(\delta\) 0.96 (t, \(J = 7.3\) Hz, 3 H), 2.13 (s, 3 H), 3.98 (c, \(J = 7.3\) Hz, 2 H), 6.40 (d, \(J = 7.8\) Hz, 2 H), 6.75-6.78 (m, 2 H), 6.85-6.90 (m, 3 H), 7.04-7.22 (m, 2 H), 7.24-7.26 (m, 2 H); trans-isomer \(\delta\) 1.38 (t, \(J = 7.3\) Hz, 3 H), 2.13 (s, 3 H), 3.98 (d, \(J = 7.3\) Hz, 2 H), 6.33 (d, \(J = 7.3\) Hz, 2 H), 6.47 (d, \(J = 8.3\) Hz, 2 H), 6.98-7.00 (m, 2 H), Other peaks overlap with those of cis-isomer.; \(^13\)C NMR (100 MHz, CDCl\(_3\)); cis-isomer \(\delta\) 13.5, 21.0, 61.4, 119.1, 119.4 (c, \(J = 279\) Hz), 121.7, 125.7, 127.6, 128.4, 128.6, 128.8, 129.3, 131.9, 133.6, 135.2, 138.7, 145.7, 155.5 (c, \(J = 35\) Hz), 160.0, 163.4: trans-isomer \(\delta\) 14.0, 21.0, 61.6, 115.6, 119.0 (c, \(J = 279\) Hz), 122.7, 126.6, 127.3, 128.5, 128.9, 129.1, 131.8, 134.4, 135.1, 138.9, 144.6, 155.6 (c, \(J = 35\) Hz), 163.8, 165.5; IR (NaCl) 3060, 3026, 2982, 2926, 2871, 1900, 1731, 1700, 1657, 1599, 1556, 1484, 1445, 1401, 1367, 1318, 1278, 1245, 1185, 1169, 1143, 1095, 1020, 984, 909, 874, 846, 809, 782, 748, 732, 697 cm\(^{-1}\); mass spectrum (EI) m/e 503 (M\(^+\), 9.1); Anal. Calcd for C\(_{26}\)H\(_{21}\)Cl\(_3\)NO\(_2\)S: C, 61.96; H, 4.20; N, 2.78. Found: C, 61.86; H, 3.99; N, 2.72.

cis-C\(_2\)CF\(_3\)=NC\(_6\)H\(_5\)=C(CO\(_2\)C\(_2\)H\(_5\))=C(C\(_6\)H\(_5\))SC\(_6\)H\(_4\)-p-CH\(_3\) (cis-3q): pale yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)); cis-isomer \(\delta\) 0.99 (t, \(J = 6.8\) Hz, 3 H), 3.19 (dd, \(J = 13, 77\) Hz, 2 H), 3.96 (c, \(J = 6.8\) Hz, 2 H), 6.90 (br, 2 H), 6.96 (br, 2 H), 7.12 (d, \(J = 8.3\) Hz, 2 H), 7.20-7.25 (m, 4 H), 7.32-7.39 (m, 5 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)); cis-isomer \(\delta\) 13.6, 37.3, 61.1, 119.2, 119.4 (c, \(J = 279\) Hz), 119.7, 126.1, 127.5, 127.7, 128.4, 128.5, 128.8, 128.9, 129.2, 135.1, 135.7, 147.4, 155.4 (c, \(J = 35\) Hz), 162.8; IR (NaCl) 3656, 3369, 3065, 3033, 3006, 2987, 2929, 2922, 2896, 2843, 2372, 2334, 1957, 1903, 1885, 1840, 1817, 1762, 1691, 1652, 1625, 1593, 1578, 1566, 1486, 1466, 1453, 1388, 1368, 1324, 1293, 1280, 1241, 1219, 1183, 1137, 1118, 1094, 1070, 1017, 976, 932, 919, 908, 871, 849, 833, 815, 758, 750, 720, 698, 681, 630, 600, 560 cm\(^{-1}\); mass spectrum (Cl) m/e 470 (M\(^+\), 100); Anal. Calcd for C\(_{26}\)H\(_{22}\)F\(_3\)NO\(_2\)S: C, 66.51; H, 4.72; N, 2.98. Found: C, 66.40; H, 4.67; N, 3.00.

cis-C\(_6\)H\(_5\)=NC\(_6\)H\(_5\)=C(CO\(_2\)C\(_2\)H\(_5\))=C(C\(_6\)H\(_5\))SC\(_6\)H\(_4\)-p-CH\(_3\) (cis-3s): pale yellow solid; mp 122 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)); cis-isomer \(\delta\) 0.77 (t, \(J = 7.8\) Hz, 3 H), 2.10 (s, 3 H), 3.81 (c, \(J = 7.8\) Hz, 2 H), 6.48 (d, \(J = 7.8\) Hz, 2 H), 6.70 (d, \(J = 7.8\) Hz, 2 H), 6.89 (d, \(J = 7.2\) Hz, 2 H), 7.03-7.05 (m, 3 H), 7.16 (t, \(J = 7.3\) Hz, 1 H), 7.23 (d, \(J = 7.3\) Hz, 2 H), 7.37 (t, \(J = 7.8\) Hz, 2 H); IR (KBr) 3359, 3359, 3080, 3057, 3021, 2980, 2923, 2903, 2871, 2323, 1966, 1906, 1689, 1614, 1592, 1576, 1553, 1489.
1445, 1393, 1367, 1315, 1289, 1262, 1204, 1182, 1173, 1107, 1072, 1027, 1017, 1000, 967, 931, 906, 832, 810, 768, 751, 696, 671, 591; mass spectrum (EI) m/e 477 (M+, 6.3); Anal. Calcd for C31H27NO2S: C, 77.96; H, 5.70; N, 2.93. Found: C, 77.67; H, 5.82; N, 2.88.

**Reaction of F3CC(O)C(H)=C(n-C6H13)(S-p-toly) (4a) with aniline (Eq. 3):** Into a two-necked 3 mL reaction glass were added 4a (82.0 mg, 0.248 mmol) and aniline (22.5 mg, 0.242 mmol) under N2 atmosphere. After the solution was stirred at 60 °C for 1 h, the resultant mixture was evaporated and dried in vacuo. 5a was isolated in 81% (60.1 mg, 20.1 mmol) yields by preparative TLC using hexane and diethyl ether (10:1) as an eluent.

**F3C CF3C(OH)=C(H)C(n-C6H13)(=NC6H5) (5a):** yellow oil; 1H NMR (400 MHz, C6D6) δ 0.83 (t, J = 6.8 Hz, 3 H), 1.16-1.25 (m, 6 H), 1.51 (tt, J = 7.3, 7.8 Hz, 2 H), 2.36 (t, J = 7.8 Hz, 2 H), 5.57 (s, 1 H), 7.17 (d, J = 7.8 Hz, 2 H), 7.34 (t, J = 7.3 Hz, 1 H), 7.43 (dd, J = 7.3, 7.8 Hz, 2 H); 13C NMR (100 MHz, C6D6) δ 13.9, 22.3, 28.0, 28.8, 31.2, 32.2, 89.4, 117.6 (c, J = 286 Hz), 125.7, 127.7, 129.5, 136.8, 172.8, 176.6 (c, J = 33 Hz); IR (NaCl) 3038, 2958, 2931, 2860, 1613, 1595, 1577, 1523, 1449, 1454, 1380, 1303, 1243, 1189, 1122, 1076, 1027, 1004, 872, 784, 753, 730, 696, 664, 581 cm⁻¹; mass spectrum (EI) m/e 299 (M⁺, 23); Anal. Calcd for C16H20F3NO: C, 64.20; H, 6.73; N, 4.68. Found: C, 64.40; H, 6.66; N, 4.73.

**The Preparation of cis-Pt[P(C6H5)3]2[NC6H5]CF3][SC6H4-p-CH3] (cis-6a):** Into a dry two-necked reaction vessel equipped with a stirring bar were added Pt(PPh3)2(C2H4) (371 mg, 0.496 mmol), 1a (154 mg, 0.526 mmol) and C6H6 (12.5 mL). After the reaction mixture was stirred at 25 °C for 1 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. Then the solid was washed by hexane (10 mL x 3) and dried to give cis-6a (413 mg, 82%).

**cis-6a:** white solid; mp 190 °C; 1H NMR (400 MHz, C6D6) δ 1.90 (s, 3 H), 6.68 (d, J = 7.8 Hz, 2 H), 6.74-6.94 (m, 20 H), 7.23-7.36 (m, 10 H), 7.51 (br, 5 H), 7.64 (d, J = 7.8 Hz, 2 H); 31P NMR (160 Hz, C6D6) δ 18.0 (c, Jp-P = 18 Hz, Jp-P = 1807 Hz, Jp-P = 24 Hz), 18.1 (d, Jp-P = 18 Hz, Jp-P = 3135 Hz); IR (KBr) 3054, 2358, 2309, 1586, 1484, 1436, 1248, 1142, 1122, 1095, 927, 765, 743, 694 cm⁻¹; Anal. Calcd for C51H42F3NP2PtS: C, 60.35; H, 4.17; N, 1.38. Found: C, 60.60; H, 4.18; N, 1.34.

**The Reaction of 1 with Pt(PPh3)2(C2H4) (Eq. 4):** Into a dry Pyrex NMR tube were added Pt(PPh3)2(C2H4) (0.020 mmol), 1 (0.022 mmol), S=P(C6H4OMe-p)3 (0.01 mmol as an internal standard) and benzene-d6 (0.5 mL) under N2 atmosphere. The reaction was monitored by 31P and 1H NMR spectrum at 25 °C.
cis-6a: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 18.0 (c, $J_{P-P} = 18$ Hz, $J_{P-T}$ = 1807 Hz, $J_{P-P}$ = 24 Hz), 18.1 (d, $J_{P-P} = 18$ Hz, $J_{P-T}$ = 3135 Hz). trans-6a: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 13.2 (s, $J_{P-P} = 2944$ Hz).

cis-6b: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 18.0 (d, $J_{P-P} = 19$ Hz, the value of $J_{P-T}$ was not able to read because of low intensity), 20.1 (d, $J_{P-P} = 19$ Hz, the value of $J_{P-T}$ was not able to read because of low intensity). trans-6b: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 14.6 (s, $J_{P-P} = 3133$ Hz).

**7b (syn/anti mixture):** $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 15.9 (s, value of $J_{P-T}$ was not able to read because of low intensity.), 17.1 (s, value of $J_{P-P}$ was not able to read because of low intensity.).

**Synthesis of Furan Derivatives (Eq. 5):** Into a two-necked 3 mL reaction glass were added Pd(dba)$_2$ (0.025 mmol), PPh$_3$ (0.05 mmol), 1a (0.5 mmol), 3-methyl-1-buthyne-3-ol (2n) (0.6 mmol) and 0.5 mL of 1,2-dichloroethane under N$_2$ atmosphere. After the solution was stirred at 80 °C for 1 h, the resultant mixture was filtered through Celite, and the filtrate was evaporated and dried in vacuo. The crude adduct (3u) was replaced into a two-necked 3 mL reaction glass and a solution of AcOH (2.5 mmol) in 0.7 mL of 1,2-dichloroethane was added. After the solution was stirred at 60 °C for 11 h, the resultant mixture was filtered through Celite, and the filtrate was evaporated and dried in vacuo. 11a were isolated in 82% yields by preparative TLC using hexane and diethyl ether (10/1) as an eluent.

**cis-CF$_3$C(=NC$_6$H$_5$)C=CH(C$_3$H$_2$OH)SC$_6$H$_4$-p-CH$_3$ (3u):** pale yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.23 (s, 6 H), 2.01 (s, 1 H), 2.28 (s, 3 H), 6.73 (s, 1 H), 6.95 (d, $J = 8.3$ Hz, 2 H), 6.99-7.01 (m, 4 H), 7.19 (t, $J = 7.3$ Hz, 1 H), 7.33 (t, $J = 7.8$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0, 29.5, 75.5, 119.3 (c, $J = 278$ Hz), 120.9, 121.3, 126.1, 128.6, 129.9, 130.3, 130.6, 137.6, 147.1, 153.2, 154.9 (c, $J = 34.6$ Hz); mass spectrum (EI) m/e 379 (M$^+$, 0.7); HRMS calcld for C$_{20}$H$_{20}$F$_3$NOS: 379.1218. Found: 379.1212.

**11a: white solid; mp 94 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (s, 3 H), 1.40 (s, 3 H), 2.40 (s, 3 H), 4.04 (s, 1 H), 4.80 (s, 1 H), 6.83 (d, $J = 8.3$ Hz, 2 H), 7.07 (t, $J = 7.3$ Hz, 1 H), 7.22-7.26 (m, 4 H), 7.39 (d, $J = 7.8$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.3, 27.1, 27.2, 90.0, 99.1 (c, $J = 30.5$ Hz), 111.7, 123.0 (c, $J = 284$ Hz), 123.7, 124.7, 126.4, 128.3, 130.5, 134.8, 139.9, 141.8, 155.1; IR (KBr) 3347, 3094, 3064, 3036, 3023, 2988, 2975, 2929, 2899, 2866, 1902, 1697, 1625, 1595, 1496, 1462, 1398, 1385, 1366, 1321, 1297, 1279, 1251, 1238, 1192, 1160, 1132, 1093, 1065, 1022, 1003, 981, 941, 907, 885, 838, 806, 768, 728, 692, 607, 592 cm$^{-1}$; mass spectrum (EI) m/e 379 (M$^+$, 1.5); Anal. Calcd for C$_{20}$H$_{20}$F$_3$NOS: C, 63.31; H, 5.31; N, 3.69. Found: C, 63.19; H, 5.27; N, 3.68.
130.6, 134.7, 138.2, 140.1, 143.7, 156.8; IR (KBr) 3250, 3094, 3054, 3006, 2979, 2967, 2023, 2886, 1613, 1597, 1494, 1444, 1364, 1334, 1289, 1194, 1157, 1136, 1104, 1085, 1028, 1016, 988, 944, 903, 877, 843, 808, 648, 576, 553 cm⁻¹; mass spectrum (EI) m/e 457 (Mt, 18.1); Anal. Calcd for C₂₁H₁₂₂F₃NO₃S₂: C, 55.13; H, 4.85; N, 3.06. Found: C, 55.19; H, 4.96; N, 3.10.

llb (Eq. 6): yellow solid; mp 110 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.08 (s, 3 H), 1.40 (s, 3 H), 2.42 (s, 6 H), 4.65 (s, 1 H), 5.57 (s, 1 H), 7.22-7.25 (m, 4 H), 7.43 (d, J = 7.8 Hz, 2 H), 7.60 (d, J = 7.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.3, 21.5, 26.4, 27.7, 92.1, 94.8 (c, J = 34 Hz), 106.3, 121.8 (c, J = 285 Hz), 125.5, 127.5, 129.4, 130.6, 134.7, 138.2, 140.1, 143.7, 156.8; IR (KBr) 3250, 3094, 3054, 3006, 2979, 2967, 2023, 1444, 1364, 1334, 1289, 1194, 1157, 1136, 1104, 1085, 1028, 1016, 988, 944, 903, 877, 843, 808, 648, 576, 553 cm⁻¹; mass spectrum (EI) m/e 457 (Mt, 18.1); Anal. Calcd for C₂₁H₁₂₂F₃NO₃S₂: C, 55.13; H, 4.85; N, 3.06. Found: C, 55.19; H, 4.96; N, 3.10.

**Cis-to-trans Isomerization of 3f in Toluene-d₈ (Eq. S1) (Ref. 7):** Into a dry Pyrex NMR tube were added 3f (cis:trans = 99:1) (0.02 mmol), additive and 0.5 mL of toluene-d₈ under N₂ atmosphere. After the sample was heated at 100 °C for 1 h, the cis to trans ratio was analyzed by ¹H NMR spectrum.

### 2-8. References and Notes


(3) The reaction of alkynes, nitriles with iodine by using a stoichiometric amount of zirconium complex to produce 2[(2)-β-iodoalkenyl]imines was reported; Coperet, C.; Sugihara, T.; Wu, G.; Shimoyama, T.; Negishi, E. J. Am. Chem. Soc. 1995, 117, 3422.


(5) The regio- and stereochemistry of 3a, 3f and 3m was determined by N.O.E. experiment.

(6) Heating the solution of 3f *(cis:trans = 99:1)* with the catalytic amount of Pd(dba)$_2$ and PPh$_3$ at 80 °C for 1 h resulted in the isomerization of 3f *(cis:trans = 79:21)*, while no isomerization took place without Pd(dba)$_2$ under otherwise identical conditions.

(7) When the reaction of 1a and 21 was performed at 100 °C in a sealed vessel without a microwave, 31 was obtained in a *cis to trans* ratio of 93:7 with the same yield, indicating that following isomerization of the adducts was partly suppressed by the microwave irradiation.

(8) The high reactivity and regioselectivity may conceivably be attributed to oxygen atom at propargyl moiety in alkynes. See reference 4a.

(9) Crystal data for 31: Space group Pbca (#61) with \(a = 15.2284(7) \text{ Å}, b = 17.6487(8) \text{ Å}, c = 17.8733(9) \text{ Å}, b = 96.385(2)^\circ\), \(Z = 8, \rho = 1.298 \text{ g/cm}^3, R = 0.0661, \text{ and } Rw = 0.189\).


(12) We have reported that an anion stabilizing group on β-carbon of C-S bond of vinylsulfide promotes the oxidative addition to Pt(0) complex. See: (a) Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375. (b) See reference 4b.


Chapter 3
One-Pot Syntheses of 2,3-Dihydrothiopyran-4-one Derivatives by
Pd/Cu-Catalyzed Reactions of α,β-Unsaturated Thioesters
with Propargyl Alcohols

3-1. Introduction

In the course of my study toward the transition-metal catalyzed reaction using thioesters, the author focused on α,β-unsaturated thioesters, which contains two reactive centers; C(O)-S and ene moieties, as substrates and examined reactions with various alkynes under a range of catalytic conditions. As a result, the author discovered the Pd/Cu-catalyzed one-pot cyclization between α,β-unsaturated thioesters 1 and propargyl alcohols 2 in the presence of bases to furnish 2,3-Dihydrothiopyran-4-one Derivatives 3 (Eq. 1). These sulfur containing six-membered heterocyclic derivatives display a wide range of biological activities.¹

\[
\begin{align*}
\text{R}_1\text{C}==\text{C}=(\text{Me})\text{C}(\text{O})\text{SC}_6\text{H}_4-p-\text{NO}_2 (1\text{a}, 0.4 \text{ mmol}) \quad + \quad \text{CH}_2==\text{C}(\text{Me})\text{C}(\text{O})\text{SC}_6\text{H}_4-p-\text{NO}_2 (1\text{a}, 0.4 \text{ mmol}) \\
\text{cat. Pd/Cu} \quad \text{bases} \quad \rightarrow \quad \text{R}_2\text{C}==\text{C}(\text{Me})\text{C}(\text{O})\text{SC}_6\text{H}_4-p-\text{NO}_2
\end{align*}
\]

3-2. The Pd/Cu-Catalyzed Reaction of α,β-Unsaturated Thioesters with Propargyl Alcohols

The reaction of CH₂=C(Me)C(O)SC₆H₄-p-NO₂ (1a, 0.4 mmol) with 2-methyl-3-butyne-2-ol (2a, 0.5 mmol) in the presence of PdCl₂ (0.004 mmol), CuI (0.04 mol) and Et₃N (0.4 mmol) in DMF (0.5 mL) at 80 °C for 6 h resulted in the formation of 3a in 34% yield along with by-products, including (ArS)₂ (10%) (run 1, Table 1). The single X-ray crystallographic analysis of 3a confirmed the structure to be a 2,3-dihydrothiopyran-4-one derivative (Fig. 1).²

It should be noted that both C-S bonds of 1a, i.e., the C(O)-S and Ar-S bonds, were cleaved and the Ar group migrated from the sulfur of 1a to the oxygen of 2a. Among the alkali salts examined (runs 2-5, Table 1), K₂CO₃ (10 mol %) resulted in the best yield (60% isolated yield) (run 3, Table 1). Alteration of the amounts of K₂CO₃ (5 mol %) (run 6, Table 1), CuI (2 mol %, 100 mol %) (runs 7 and 8, Table 1), or Et₃N (20 mol %) (run 9, Table 1) decreased the yield of 3a. Other complexes such as Pd(OAc)₂ (run 10, Table 1), PdCl₂(PhCN)₂ (run 11, Table 1), PdCl₂(PPh₃)₂ (run 12, Table 1), PdCl₂(dpff) (run 13, Table 1) and PtCl₂ (run 14, Table 1) showed inferior catalytic activity. Synthesis of 3a required both a Pd and Cu catalyst.
Table 1. Pd/Cu-Catalyzed Reaction of 1a with 2a

![Reaction Scheme](image)

<table>
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<th>run</th>
<th>M</th>
<th>CuI (X mol%)</th>
<th>Et3N (Y equiv.)</th>
<th>alkali salt</th>
<th>Yield (%)b</th>
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<td>1</td>
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<td>1</td>
<td>K2CO3</td>
<td>48</td>
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<tr>
<td>13</td>
<td>PdCl2(dpff)</td>
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<tr>
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<td>PtCl2</td>
<td>10</td>
<td>1</td>
<td>K2CO3</td>
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a Unless otherwise noted, 1a (0.4 mmol), 2a (0.5 mmol), PdCl2 (0.004 mmol), CuI (0.04 mmol), K2CO3 (0.04 mmol), Et3N (0.4 mmol), and DMF (0.5 mL) at 80 °C for 6 h. b Isolated yield. c Run 20 mol %. dppf = 1,1'-bis(diphenylphosphino)ferrocene

Figure 1. ORTEP Diagram of 3a.

The results of Pd/Cu-catalyzed reactions between various thioesters (1) and propargyl alcohols (2) under optimized conditions are summarized in Table 2. The treatment of 1a with tertiary propargyl alcohols (2b, R3 = R4 = -(CH2)4-; 2c, R3 = R4 = -(CH2)5-; 2d, R3 = Me, R4 = Ph) provided the corresponding cyclization products 3b-3d in moderate yields (runs 2-4, Table 2). Cyclization with secondary propargyl alcohol (2e, R3 = H, R4 = n-C9H19) also gave 3e in
Table 2. Pd/Cu-Catalyzed Syntheses of 2,3-Dihydrothiopyran-4-one Derivatives

![Chemical structures and reactions](image)

<table>
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<th>2</th>
<th>time (h)</th>
<th>3 (%)</th>
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</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>2f</td>
<td>6</td>
<td>3f n.d.</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>2g</td>
<td>6</td>
<td>3g n.d.</td>
</tr>
<tr>
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<td>1a</td>
<td>2h</td>
<td>6</td>
<td>3h n.d.</td>
</tr>
<tr>
<td>9</td>
<td>1b</td>
<td>2a</td>
<td>6</td>
<td>3i 60</td>
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<tr>
<td>10</td>
<td>1c</td>
<td>2a</td>
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</tr>
<tr>
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<td>1d</td>
<td>2a</td>
<td>16</td>
<td>3k 64</td>
</tr>
<tr>
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<td>1d</td>
<td>2c</td>
<td>18</td>
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<td>1e</td>
<td>2a</td>
<td>6</td>
<td>3m n.d.</td>
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<tr>
<td>14</td>
<td>1f</td>
<td>2a</td>
<td>6</td>
<td>3n n.d.</td>
</tr>
</tbody>
</table>

*Unless otherwise noted, 1 (0.4 mmol), 2 (0.5 mmol), PdCl₂ (0.004 mmol), CuI (0.04 mmol), K₂CO₃ (0.04 mmol), Et₃N (0.4 mmol), and DMF (0.5 mL) at 80 °C. b Isolated yield. c 60 °C. d 1.0 mmol.

35% yield (run 5, Table 2). However, propargyl alcohol (2f), propargyl amine (2g) and homo-propargyl alcohol (2h) gave a complicated mixture and 3 was not synthesized (runs 6-8, Table 2). In the thioesters, replacement of the Me group at R² with an i-Pr group did not interfere with cyclization (run 9, Table 2). 1c (R¹ = Ph, R² = H) was also converted into 3j in 55% yield (run 10, Table 2). The thioester with an Me group at R¹ and a second Me at R² (1d) underwent a similar transformation as a result of reaction with either 2a or 2c (runs 11 and 12, Table 2). In marked contrast, the thioester with a p-tolyl group on the sulfur (1e, X = Me) gave a complicated mixture (run 13, Table 2). No reaction took place with substrate 1f, which had a S-n-C₁₀H₂₁ group rather than SC₆H₄-p-X (run 14, Table 2). These results demonstrate that the
SC₆H₄-p-NO₂ group of thioester 1 is required for the formation of 3.

3-3. Reaction Mechanism

To elucidate the reaction pathway, the reaction of 1a with 2a in DMF-d₇ at 80 °C was monitored by ¹H NMR spectroscopy (Fig. 2). The results suggest that both alkynyl ketone 4a and vinyl sulfide 5a were converted into 3a. After 4 h, both 4a and 5a disappeared and 3a was the major product detected, in addition to unidentified by-products.

Thus, authentic 4a and 5a were prepared and the reaction mechanism was examined. 4a (0.4 mmol) reacted with p-NO₂C₆H₄SH (6a, 0.4 mmol) to give 3a in the presence of Et₃N (0.4 mmol) at 80 °C even without Pd/Cu catalysts, albeit in low yield (40%) (Eq. 2). Addition of a catalytic amount of K₂CO₃ (0.04 mmol) to the reaction mixture improved the yield of 3a (51%). However, the yields for both the catalyst-free and K₂CO₃-catalyzed reaction of 1a with 2a were

**Figure 2.** Time Course of the Pd/Cu-Catalyzed Reaction of 1a with 2a.
lower than that obtained by the Pd/Cu-catalyzed reaction due to formation of complicated byproducts (compare with run 1 of Table 2). Without Et₃N, 3a was not formed. Intramolecular cyclization of 5a (0.2 mmol) proceeded in the presence of Et₃N (0.2 mmol) at 80 °C to afford 3a in 66% yield, while no reaction took place in the absence of Et₃N (Eq. 3). These results show that Et₃N is essential for the synthesis of 5 and 3.

The reaction pathway proposed for the formation of 3 is shown in Scheme 1, with 1a and 2a as representative substrates. First, a Pd/Cu-catalyzed Sonogashira-type reaction between 1a and 2a gives 4a and 6a, and the subsequent trans-addition of 6a to the yne moiety of 4a affords

**Scheme 1. A Proposed Reaction Pathway**

1a + Pd/Cu

2a + Et₃N → 4a + ρ-NO₂C₆H₄SH → 6a → 5a → H⁺ → 3a
Intramolecular aromatic nucleophilic substitution by the oxygen anion induces migration of the \( p-\text{NO}_2\text{C}_6\text{H}_4 \) group from sulfur to oxygen. Finally, nucleophilic addition of the resultant sulfonium anion to the terminal ene moiety and the subsequent protonation yield 3a. Maintenance of low concentrations of 4a and 6a during the course of the reaction improve the yield of 3a relative to that obtained by the reaction of 4a with 6a.

**3-4. Reaction of Acid Chloride, Thiol and Propargyl Alcohol**

Toward the easy-to-use approach for the preparation of 3, I found the preparation of 3 by the reaction of acid chloride, thiol and propargyl alcohol from the one-pot operation (Eq. 4). Cu-catalyzed cross-coupling of methacryloyl chloride (7a) with 2a in the presence of K\(_2\)CO\(_3\) and Et\(_3\)N produce 4a and following reaction with 6a occurred to afford 3a in 39% yield. In this process, no Pd-catalyst was needed.

\[
\begin{align*}
7a + 2a & \xrightarrow{\text{Cul, K}_2\text{CO}_3, \text{Et}_3\text{N}} 4a \\
4a & \xrightarrow{(p-\text{NO}_2\text{C}_6\text{H}_4)\text{SH}} 3a
\end{align*}
\]

Reagents and conditions: 7a (1.0 equiv.), 2a (2.0 equiv.), Cul (0.1 equiv.), K\(_2\)CO\(_3\) (0.1 equiv.), Et\(_3\)N (0.8 M), r.t., 3 h; then, 6a (1 equiv.), DMF, 80 °C, 17 h.

**3-5. Conclusions**

This study realized the synthesis of 2,3-dihydrothiopyran-4-one derivatives by Pd/Cu-catalyzed reactions between \( \alpha,\beta \)-unsaturated thioesters and propargyl alcohols in the presence of bases. The reactions proceed through a one-pot sequence as follows: Sonogashira-type reaction; Michael-addition of thiol to yne-moiety; intramolecular aromatic nucleophilic substitution; and, cyclization.

**3-6. Experimental Section**

*General Comments:* \(^1\)H and \(^{13}\)C NMR spectra in CDCl\(_3\), and DMF-\(d_6\) solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometers. The chemical shifts in the 1H NMR
spectra were recorded relative to Me4Si as an internal standard and the chemical shifts in the
13C NMR spectra were recorded relative to CHCl3 (δ 77.0). The IR spectra were measured by
a Perkin-Elmer Model 1600 spectrometer. Mass spectra (EI), high-resolution mass spectra
(HRMS) and elemental analyses were performed in the Instrumental Analysis Center of the
Faculty of Engineering, Osaka University. Melting points were measured by a MPA100
Optimelt Automated Melting Point System. Preparative TLC was carried out using Wakogel
B-5F silica gel. The X-ray crystal data of 3a were collected using Rigaku RAXIS-RAPID
Imaging Plate diffractometer. The ORTEP diagram was shown in 50% probability ellipsoid.
All reactions were carried out under N2 atmosphere. Unless otherwise noted, commercially
available reagents were used without purification. All solvents were distilled before use.
Thioesters 1a-d, 1f were prepared from the reactions of the corresponding acid chlorides with
thiols in the presence of pyridine in THF solution. Thioester 1e was synthesized according to
the literature (Tetrahedron Lett. 2001, 42, 1567.).

The Spectrum Datas of thioesters:

H2C=C(Me)(O)SC6H4-p-NO2 (1a); yellow solid; 1H NMR (400 MHz, CDCl3) δ 2.03 (s, 3 H), 5.80 (s, 1 H), 6.25 (s, 1 H), 7.64 (d, J = 8.7 Hz, 2 H), 8.27 (d, J = 8.7 Hz, 2 H); 13C NMR (100 MHz, CDCl3) δ 18.1, 123.5, 124.7, 134.9, 136.0, 142.8, 147.8, 188.7; mass spectrum (EI) m/z 223 (M+, 1); HRMS calcd for C10H9NO3S 223.0303, found 223.0308.

H2C=C(i-Pr)(O)SC6H4-p-NO2 (1b); yellow oil; 1H NMR (400 MHz, CDCl3) δ 1.13 (d, J = 6.8 Hz, 6 H), 2.86 (sept, J = 6.8 Hz, 1 H), 5.75 (s, 1 H), 6.23 (s, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 8.26 (d, J = 8.8 Hz, 2 H); 13C NMR (100 MHz, CDCl3) δ 21.7, 30.2, 121.4, 123.7, 135.0, 136.5, 147.9, 154.2, 189.6; mass spectrum (EI) m/z 251 (M+, 0.2); HRMS calcd for C12H13NO3S 251.0616, found 251.0607.

(E)-PhC(H)=CHC(0)SC6H4-p-NO2 (1c); yellow solid; 1H NMR (400 MHz, CDCl3) δ 6.78 (d, J = 15.8 Hz, 1 H), 7.42-7.44 (m, 3 H), 7.57-7.59 (m, 2 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.72 (d, J = 15.8 Hz, 1 H), 8.27 (d, J = 8.6 Hz, 2 H); 13C NMR (100 MHz, CDCl3) δ 123.4, 123.7, 128.5, 128.9, 131.1, 133.4, 134.6, 136.2, 142.7, 147.9, 185.2; mass spectrum (Cl) m/z 286 ([M-H]+, 100); HRMS calcd for C15H12NO3S (M-H) 286.0538, found 286.0533.

(E)-Me(H)C=C(Me)(O)SC6H4-p-NO2 (1d); an pale yellow solid; mp 77 °C; 1H NMR (400 MHz, CDCl3) δ 1.91 (d, 3 H), 1.92 (s, 3 H),
6.98-7.04 (m, 1 H), 7.61 (d, 2 H, J = 8.8 Hz), 8.24 (d, 2 H, J = 8.8 Hz); 13C NMR (100 MHz, CDCl3) δ 12.4, 14.8, 123.9, 135.4, 136.7, 137.2, 138.5, 148.1, 189.3; IR (KBr) 3105, 2925, 2845, 1673, 1643, 1598, 1578, 1518, 1345, 1220, 1108, 1031, 981, 854, 742, 682, 662, 643 cm⁻¹; mass spectrum (EI) m/z 237 (M⁺, 1.6); HRMS calcd for C11H11OS 237.2760, found 237.0458.

H₂C=C(C₆H₄Me-p)C(0)SC₆H₄-p-Me (1e): an pale yellow solid; mp 92 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.37 (s, 3 H), 2.38 (s, 3 H), 5.83 (s, 1 H), 6.24 (s, 1 H), 7.17 (d, 2 H, J = 8.1 Hz), 7.23 (d, 2 H, J = 8.3 Hz), 7.32-7.35 (m, 4 H); 13C NMR (100 MHz, CDCl₃) δ 21.5, 21.6, 122.7, 124.7, 128.4, 129.2, 130.3, 133.1, 134.8, 138.9, 139.9, 148.0, 192.5; IR (KBr) 3026, 2918, 1684, 1605, 1510, 1397, 1296, 1110, 963, 925, 824, 807, 750, 731, 554, 484 cm⁻¹; mass spectrum (EI) m/z 268 (M⁺, 12); HRMS calcd for C₁₇H₁₆OS 268.0922, found 268.0924.

(E)-PhC(H)=CHC(0)S-n-C₁₀H₂₁ (1f): an pale yellow solid; mp 41 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 3 H, J = 6.4 Hz), 1.26-1.40 (m, 15 H), 1.60-1.67 (m, 2 H), 3.01 (t, 2 H, J = 7.3 Hz), 6.71 (d, 1 H, J = 15.9 Hz), 7.38-7.39 (m, 3 H), 7.53-7.54 (m, 2 H), 7.60 (d, 2 H, J = 8.1 Hz); 13C NMR (100 MHz, CDCl₃) δ 14.1, 14.2, 22.7, 28.9, 29.0, 29.2, 29.3, 29.6, 29.6, 31.9, 125.2, 128.4, 128.9, 130.4, 134.2, 140.1, 190.0; IR (KBr) 2922, 2848, 1656, 1611, 1468, 1448, 1332, 1302, 1035, 1012, 992, 890, 778, 754, 692, 578, 484, 462 cm⁻¹; mass spectrum (EI) m/z 304 (M⁺, 12); HRMS calcd for C₁₉H₂₈O₅S 304.1861, found 304.1863.

Pd/Cu-Catalyzed Reaction of CH₂=C(Me)C(0)SC₆H₄-p-NO₂ (la) with HCC=CC(Me)₂OH (2a) in the presence of Et₃N and K₂CO₃ (run 3 of Table 1); General Procedure of Cyclization of α,β-Unsaturated Thioesters with Propargyl Alcohols: Into a two-necked 3 mL reaction glass were added PdCl₂ (0.7 mg, 0.004 mmol), CuI (7.5 mg, 0.039 mmol), K₂CO₃ (6.1 mg, 0.044 mmol), la (89.5 mg, 0.401 mmol), 2a (50 µL, 0.52 mmol), Et₃N (60 µL, 0.43 mmol) and 0.5 mL of DMF under N₂ atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was separated by preparative TLC using hexane and Et₂O (10/7) as an eluent (74.5 mg, 60%).

2,3-dihydro-3-methyl-6-(dimethyl-p-nitrophenoxy-methyl)-thiophen-4-one (3a): an yellow solid; mp 111 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.25 (d, 3 H, J = 6.8 Hz), 1.72 (s, 6 H), 2.62-2.68 (m, 1 H), 3.02 (dd, 1 H, J = 13, 11 Hz), 3.19 (dd, 1 H, J = 13, 3.9 Hz), 6.28 (s, 1 H), 6.94 (d, 2 H, J = 9.3 Hz), 8.14 (d, 2 H, J = 9.3 Hz); 13C NMR (100 MHz, CDCl₃) δ 14.30, 27.61, 28.34, 33.64, 39.53, 81.80, 118.0, 119.4, 125.2, 141.7, 160.3, 166.6, 196.6; IR (KBr) 2983, 2965, 2927, 1665, 1588, 1508, 1488, 1345, 1249.
Other cyclic products 3b-3e, 3i-3l were similarly synthesized. Samples of 3d, 3e, 3j and 3k obtained after preparative TLC were a mixture of *threo* and erythro.

2,3-dihydro-3-methyl-6-(1'-p-nitrophenoxy-cyclopentyl)-thiopyran-4-one (3b): an yellow solid; mp 89 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22 (d, 3 H, $J$ = 5.2 Hz), 1.83 (m, 4 H), 2.17-2.25 (m, 4 H), 2.61-2.63 (m, 1 H), 2.98-3.18 (m, 2 H), 6.28 (s, 1 H), 6.88 (d, 2 H, $J$ = 7.1 Hz), 8.13 (d, 2 H, $J$ = 7.1 Hz); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta$ 14.1, 24.2, 24.3, 33.6, 38.59, 39.56, 91.76, 117.2, 119.0, 125.3, 141.4, 160.2, 164.9, 196.6; IR (KBr) 3294, 2968, 2934, 2871, 1657, 1607, 1586, 1508, 1488, 1342, 1331, 1312, 1236, 1196, 1166, 1112, 982, 850, 838, 752, 694, 655, 631, 586 cm$^{-1}$; mass spectrum (EI) m/z 333 (M$^+$, 12); Anal. Calcd for C$_{17}$H$_{19}$NO$_4$S: C, 61.24; H, 5.74, N, 4.20. Found: C, 61.32; H, 5.46, N, 4.09.

2,3-dihydro-3-methyl-6-(1'-p-nitrophenoxy-cyclohexyl)-thiopyran-4-one (3c): an yellow solid; mp 105 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (d, 3 H, $J$ = 6.8 Hz), 1.56-1.79 (m, 8 H), 2.33 (t, 2 H, $J$ = 13 Hz), 2.61-2.67 (m, 1 H), 3.01 (dd, 1 H, $J$ = 13, 11 Hz), 3.17 (dd, 1 H, $J$ = 13, 3.9 Hz), 6.30 (s, 1 H), 6.97 (d, 2 H, $J$ = 9.0 Hz), 8.14 (d, 2 H, $J$ = 9.0 Hz); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta$ 14.36, 21.29, 25.10, 33.60, 34.36, 35.32, 39.63, 82.73, 117.7, 119.2, 125.2, 141.5, 159.9, 167.0, 196.5; IR (KBr) 3116, 3076, 2936, 2851, 1667, 1605, 1589, 1509, 1491, 1451, 1338, 1239, 1146, 1110, 954, 850, 751, 660, 496 cm$^{-1}$; mass spectrum (EI) m/z 347 (M$^+$, 39); HRMS calcd for C$_{18}$H$_{21}$NO$_4$S 347.4297, found 347.1201. Anal. Calcd for C$_{18}$H$_{21}$NO$_4$S: C, 62.23; H, 6.09, N, 4.03. Found: C, 61.95; H, 5.91, N, 4.01.

2,3-dihydro-3-methyl-6-(methyl-phenyl-p-nitrophenoxy-methyl)-thiopyran-4-one (3d): The title compound was obtained as a mixture of inseparable diastereomers (51:49); an yellow solid; mp 111 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.22 (d, 1.5 H, $J$ = 6.8 Hz), 1.23 (d, 1.5 H, $J$ = 6.8 Hz), $^*2.02$ (s, 3 H), 2.59-2.65 (m, 1 H), 2.91-3.00 (m, 1 H), 3.02 (dd, 0.5 H, $J$ = 13, 4.2 Hz), 3.13 (dd, 0.5 H, $J$ = 13, 3.9 Hz), $^*6.33$ (s, 0.5 H), 6.44 (s, 0.5 H), $^*6.89$ (d, 2 H, $J$ = 9.3 Hz), 7.37-7.43 (m, 3 H), 7.51 (d, 2 H, $J$ = 7.6 Hz), 8.06(8.07) (d, 2 H, $J$ = 9.3 Hz); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta$ 14.21(14.25), 24.08(24.35), 33.92(33.94), 39.67(39.81), 85.04(85.14), 119.0(119.1), 120.3(120.5), 125.3,
125.9(125.9), 128.7(128.8), 128.9, 141.2(141.5), 142.3, 160.1, 167.3(167.3), 197.2; IR (KBr)
2973, 2932, 1668, 1606, 1590, 1509, 1490, 1446, 1344, 1244, 1169, 1112, 1069, 1032, 989,
921, 862, 764, 751, 698, 676, 578, 494 cm⁻¹; mass spectrum (EI) m/z 369 (M⁺, 4.0);

* Minor diastereomer

2,3-dihydro-3-methyl-6-(n-pentyl-p-nitrophenoxy-methyl)-thiopyran-4-one (3e): The title compound was obtained as a mixture of inseparable diastereomers (51:49); an yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.88-0.92 (m, 3 H), 1.19-1.22 (m, 3 H), 1.32-1.55 (m, 6 H), 1.90-2.02 (m, 2 H), 2.59-2.63 (m, 1 H), 2.97-3.07 (m, 1 H), 3.12-3.22 (m, 1 H), 4.71-4.77 (m, 1 H), 6.21 (s, 0.5 H), 6.23 (s, 0.5 H), 6.94 (d, 1 H, J= 9.3 Hz), 6.96 (d, 1 H, J= 9.3 Hz), 8.17 (d, 1 H, J= 9.3 Hz), 8.18 (d, 1 H, J= 9.3 Hz); ¹³C NMR(100 MHz, CDCl₃) δ 14.1, 14.4(14.4), 22.5, 25.1(25.2), 31.4(31.4), 33.4(33.7), 36.0(36.1), 39.8(40.2), 80.3(80.6), 115.2, 119.9(119.9), 125.7(125.7), 141.8(141.8), 161.2(161.3), 162.1, 196.0(196.1); IR (NaCl) 2995, 2930, 2860, 1666, 1609, 1591, 1514, 1494, 1456, 1344, 1252, 1174, 112, 1011, 846, 752, 689, 658 cm⁻¹; mass spectrum (EI) m/z 349 (M⁺, 87); Anal. Calcd for C₁₈H₂₃N₀₄S: C, 61.87; H, 6.63, N, 4.01. Found: C, 61.60; H, 6.46, N, 3.75. * Minor diastereomer

2,3-dihydro-3-isopropyl-6-(dimethyl-p-nitrophenoxy-methyl)-thiopyran-4-one (3i): an pale yellow solid; mp 127 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (d, 3 H, J= 6.8 Hz), 0.97 (d, 2 H, J= 6.8 Hz), 1.71 (s, 6 H), 2.22-2.26 (m, 1 H), 2.35-2.43 (m, 1 H), 3.13 (dd, 1 H, J= 8.8, 3.4 Hz), 3.25 (dd, 1 H, J= 14, 3.6 Hz), 6.24 (s, 1 H), 6.93 (d, 1 H, J= 9.3 Hz), 8.13 (d, 2 H, J= 9.3 Hz); ¹³C NMR(100 MHz, CDCl₃) δ 19.4, 20.3, 25.2, 27.7, 28.0, 28.9, 50.4, 81.8, 118.1, 119.9, 125.3, 141.9, 160.6, 166.3, 196.1; IR (KBr) 2957, 2360, 1606, 1586, 1507, 1489, 1340, 1247, 1139, 1110, 851, 752, 670 cm⁻¹; mass spectrum (EI) m/z 335 (M⁺, 25); Anal. Calcd for C₁₇H₂₁N₀₄S: C, 60.87; H, 6.31, N, 4.18. Found: C, 60.74; H, 6.12, N, 4.46.

2-phenyl-2,3-dihydro-6-(dimethyl-p-nitrophenoxy-methyl)-thiopyran-4-one (3j): an yellow solid; mp 92 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.72 (s, 6 H), 2.95 (dd, 1 H, J= 17, 3.4 Hz), 3.08 (dd, 1 H, J= 17, 13 Hz), 4.62 (dd, 1 H), 6.40 (s, 1 H), 6.91 (d, 2 H, J= 9.3 Hz), 7.34-7.37 (m, 5 H), 8.00 (d, 2 H, J= 9.3 Hz); ¹³C NMR(100 MHz, CDCl₃) δ 27.4, 28.2, 43.6, 46.3, 81.8, 118.3, 120.0, 125.3, 127.4, 128.6, 128.9, 137.3, 141.9, 160.4, 167.3, 194.7; IR (KBr) 3066, 2990, 1659, 1606, 1590, 1565, 1506, 1489, 1454, 1384, 1340, 1296, 1257, 1137, 1108, 929, 891, 856, 751, 725, 698,
2,3-dihydro-2,3-dimethyl-6-(dimethyl-p-nitrophenoxymethyl)-thiopyran-4-one (3k): The title compound was obtained as a mixture of inseparable diastereomers (55:45); an yellow solid; mp 84 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.14 (d, 1.4 H, \(J = 7.1\) Hz),* 1.25 (d, 1.6 H, \(J = 7.1\) Hz), 1.32 (d, 1.4 H, \(J = 7.1\) Hz),* 1.42 (d, 1.6 H, \(J = 7.1\) Hz), 1.71 (s, 6 H), 2.40-2.46 (m, 0.6 H), 2.67-2.70 (m, 0.4 H),* 3.22-3.28 (m, 0.6 H), 3.58-3.61 (m, 0.4 H),* 6.25 (s, 0.4 H),* 6.26 (s, 0.6 H), 6.94 (d, 0.9 H, \(J = 9.3\) Hz),* 6.94 (d, 1.1 H, \(J = 9.3\) Hz), 8.13 (d, 2 H, \(J = 9.3\) Hz); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 9.89(15.2), 13.0(18.9), 27.6(27.9), 27.8(27.9), 41.5(44.8), 42.8(46.5), 81.7(81.7), 118.0(118.8), 118.6(118.8), 125.3, 141.8, 160.1, 164.8(165.8), 197.2(198.1); IR (KBr) 3092, 2988, 2931, 1664, 1607, 1587, 1514, 1489, 1445, 1344, 1251, 1222, 1198, 1185, 1141, 1113, 947, 930, 869, 851, 752, 670, 612, 548, 495 cm\(^{-1}\); mass spectrum (EI) m/z 321 (M\(^+\), 4.0); Anal. Calcd for C\(_{16}\)H\(_{19}\)NO\(_4\)S: C, 59.79; H, 5.96, N, 4.36. Found: C, 59.51; H, 5.58, N, 4.21.* Minor diastereomer

2,3-dihydro-2,3-dimethyl-6-(1'-p-nitrophenoxycyclohexyl)-thiopyran-4-one (3l): The title compound was obtained as a mixture of inseparable diastereomers (72:28); an yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.14 (d, 2.2 H, \(J = 7.1\) Hz), 1.24 (d, 0.8 H, \(J = 7.1\) Hz),* 1.32 (d, 2.2 H, \(J = 7.1\) Hz), 1.42 (d, 0.8 H, \(J = 7.1\) Hz),* 2.32 (d, 2 H, \(J = 14\) Hz), 2.41-2.48 (m, 0.3 H),* 2.67-2.68 (m, 0.7 H),* 3.21-3.25 (m, 0.3 H),* 3.56-3.58 (m, 0.7 H), 6.27 (s, 0.7 H), 6.28 (s, 0.3 H),* 6.96 (d, 1.4 H, \(J = 9.0\) Hz), 6.97 (d, 0.6 H, \(J = 9.0\) Hz),* 8.13 (d, 2 H, \(J = 9.3\) Hz); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 9.97(15.3), 13.1(19.0), 21.2, 24.9, 34.5, 34.8, 34.9, 41.5(44.9), 42.8(46.8), 82.8(82.8), 118.0(117.9), 118.6(118.8), 125.4, 141.8, 160.3, 165.4(166.5), 197.3(198.2); IR (NaCl) 2937, 2862, 1660, 1606, 1590, 1514, 1492, 1448, 1341, 1299, 1262, 1241, 1147, 1112, 975, 958, 875, 849, 752, 693, 660 cm\(^{-1}\); mass spectrum (EI) m/z 361 (M\(^+\), 4.0); Anal. Calcd for C\(_{19}\)H\(_{23}\)NO\(_4\)S: C, 63.13; H, 6.41, N, 3.88. Found: C, 62.98; H, 6.19, N, 4.15.* Minor diastereomer

The Pd/Cu-catalyzed Reaction of 1a with 2a in DMF-\(d_7\) (Figure 2): Into a dry Pyrex NMR tube were added PdCl\(_2\) (0.004 mmol), Cul (0.04 mmol) and K\(_2\)CO\(_3\) (0.04 mmol), 1a (0.4 mmol), 2a (0.52 mmol), NEt\(_3\) (0.4 mmol), 1,4-dioxane (0.063 mmol) as an internal standard and 0.5 mL of DMF-\(d_7\) under N\(_2\) atmosphere. The reaction at 80 °C was monitored by \(^1\)H NMR spectroscopy.

Synthesis of Authentic CH\(_2=\)C(Me)C(O)C=CC(Me)\(_2\)(OH) (4a):8 Into a two-necked reaction vessel were added CH\(_2=\)C(Me)C(O)Cl (0.6 mL, 5.3 mmol) (0.6 mL, 5.3 mmol), 2a
(0.4 mL, 4.1 mmol), CuI (0.02 mmol), Et₃N (13 mL). After the solution was stirred for 44 h at 25 °C, the reaction mixture was filtrated through Celite and distilled. The compound 4a was purified by HPLC (308 mg, 49%).

4a: colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.55 (s, 6 H), 1.85 (s, 3 H), 2.91 (s, 1 H), 6.00 (s, 1 H), 6.38 (s, 1 H); ¹³C NMR(100 MHz, CDCl₃) δ 15.9, 30.6, 65.0, 78.9, 96.6, 131.3, 144.6, 180.1; mass spectrum (EI) m/z 152 (M⁺, 3.0); HRMS calcd for C₁₅H₁₇NO₄S 152.0837, found 152.0829.

Reaction of 4a with HSC₆H₄-p-NO₂ (6a) (Eq. 2): Into a two-necked reaction vessel were added K₂CO₃ (4.4 x 10⁻² mmol), 4a (0.4 mmol), 6a (0.4 mmol), Et₃N (60 µL, 0.43 mmol) and 0.5 mL of DMF under N₂ atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was filtrated through Celite and distilled under reduced pressure.

Synthesis of Authentic CH₂=C(Me)C(O)C(H)=C(C(Me)₂(OH))SC₆H₄-p-NO₂ (5a): Into a two-necked reaction vessel were added PdCl₂ (4.5 mg, 0.025 mmol), CuI (45 mg, 0.24 mmol), K₂CO₃ (38 mg, 0.28 mmol), 1a (536 mg, 2.40 mmol), 2a (300 µL, 3.1 mmol), Et₃N (340 µL, 2.4 mmol), and 0.5 mL of DMF under N₂ atmosphere. After the solution was stirred for 40 min at 80 °C, the resultant mixture was filtrated through Celite and distilled under reduced pressure. The compound 5a was isolated by preparative TLC using hexane/Et₂O/EtOH (10/7/1) as an eluent (291 mg, 39%).

5a: an yellow solid; mp 89 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.49 (s, 6 H), 1.74 (s, 3 H), 2.13 (s, 1 H), 5.86 (s, 1 H), 5.90 (s, 1 H), 7.36-7.39 (m, 3 H), 8.06 (d, 2 H, J = 8.8 Hz); ¹³C NMR(100 MHz, CDCl₃) δ 16.8, 29.2, 31.0, 75.2, 123.9, 127.6, 127.9, 132.9, 144.9, 145.6, 145.7, 148.2, 193.8; N.O.E. experiment: Irradiation of the singlet of homoallylic proton at δ 1.49 resulted in 6.4% enhancement of the signal at δ 7.39 (internal vinyl singlet) and the singlet of terminal trans-vinyl proton at δ 5.90 resulted in 2.9% enhancement of the signal at δ 7.39 (internal vinyl singlet); IR (KBr) 3452, 3098, 2977, 1652, 1595, 1575, 1514, 1340, 1182, 1109, 1090, 977, 851, 744, 686, 534, 466 cm⁻¹; mass spectrum (EI) m/z 307 (M⁺, 133); Anal. Calcd for C₁₅H₁₇NO₄S: C, 58.61; H, 5.57, N, 4.56. Found: C, 58.36; H, 5.32, N, 4.39.

Intramolecular cyclization of 5a (Eq. 3): Into a two-necked reaction vessel were added CH₂=C(Me)C(O)C(H)=C(SC₆H₄-p-NO₂)C(Me)₂(OH) (5a) (0.2 mmol), Et₃N (30 µL, 0.21 mmol) and 0.25 mL of DMF under N₂ atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was filtrated through Celite, and distilled under reduced pressure.

The Three-Component Reaction of CH₂=C(Me)C(O)Cl (7a), 2a and 6a (Eq. 4): Into a two-necked 3 mL reaction glass were added CuI (7.5 mg, 0.39 mmol), K₂CO₃ (6.1 mg, 0.044 mmol), Et₃N (0.5 mL), H₂=C(Me)C(O)Cl (7a) (0.4 mmol) and 2-Methyl-3-butyne-2-ol (2a)
(0.8 mmol) under N₂ atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was separated by preparative TLC using hexane and Et₂O (10/7) as an eluent (74.5 mg, 60%). After the solution was stirred for 3 h at room temperature, into a reaction mixture were added 0.5 mL of DMF solution including HSC₆H₄-p-NO₂ (6a) (0.4 mmol). After the solution was stirred for 17 h at 80 °C, the resultant mixture was filtrated through Celite, and evaporated under reduced pressure. 3a was isolated by preparative TLC using hexane and Et₂O (10/7) as an eluent (39%).

3-7. References and Notes


(2) Crystal data of 3a: space group monoclinic, P21/a (#14) with a = 11.1771(4) Å, b = 14.9463(5) Å, c = 11.0961(6) Å, β = 1212.578(1)°, Z = 4, ρ = 1.307 g/cm³, R = 0.074, and R_w = 0.184.

(3) The N.O.E. experiment showed that cis-isomer was exclusively produced.


(6) It has been reported that 2-aryltio-pyridine undergoes nucleophilic substitution by phenol. Inoue, S. Phosphorus Sulfur 1985, 22, 141.

(7) From 5a to 3a, β-attack of the lone pair of SAr to terminal ene moiety to afford sulfonium cation as a trigger step and following intramolecular aromatic nucleophilic substitution might be an alternative pathway (Eq. 5).
Chapter 4
Reactions of $\alpha,\beta$-Unsaturated Thioesters with Pt(0): Implication of Dual Mechanism Leading to the Formation of Acyl Platinum

4-1. Introduction

It has been well-known that two distinct reaction patterns, 1,2-addition and Michael addition, exists under the reaction of enones with nucleophiles. When the reaction mechanism of oxidative addition of allylic halide derivatives to low-valent transition-metal complexes to generate $\pi$-allyl metals is considered, it has been well-established that there are two reaction routes, syn- and anti-oxidative addition.\(^1\) The reactions of $\alpha,\beta$-unsaturated acid halides with low-valent transition-metal complexes to produce acyl metals are also familiar transformation.\(^2\) However, much attention to their reaction mechanism has not been attracted presumably due to the lack of a good reaction system to examine the details. In fact, the author attempted the reactions of H$_2$C=C(H)C(O)Cl (1a) or (E)-(Ph)(H)C=C(H)C(O)Cl (1b) with Pt(PPh$_3$)$_2$(C$_2$H$_4$) (2) in toluene-$d_8$ using a freeze-pump-thaw technique, but acyl platinums 3a or 3b were quantitatively produced even at -50 °C after 10 min in both cases (Eq. 1).\(^3\) Although the predominant formation of cis-isomer at the beginning of the reactions suggested its stereochemistry of oxidative addition, more information such as the effect of the introduction of a Ph group at $\beta$-carbon (R$^1$ = Ph) was not clearly disclosed from these experimental data.

\[
\begin{align*}
\text{R}^1 & = \text{H}, ~ \text{R}^2 = \text{H}; ~ 1\text{a} & ~ -50 ^\circ \text{C}, 10 \text{ min} & \text{3a} >99.9\% ~ (\text{cis}:\text{trans} = 57:43) \\
 & & ~ 10 ^\circ \text{C}, 10 \text{ min} & >99.9\% ~ (\text{cis}:\text{trans} = 1:99) \\
\text{R}^1 & = \text{Ph}, ~ \text{R}^2 = \text{H}; ~ 1\text{b} & ~ -50 ^\circ \text{C}, 10 \text{ min} & \text{3b} >99.9\% ~ (\text{cis}:\text{trans} = 96:4) \\
 & & ~ 10 ^\circ \text{C}, 10 \text{ min} & >99.9\% ~ (\text{cis}:\text{trans} = 1:99)
\end{align*}
\]

The author expected that the mechanistic information might be disclosed, applying the controllable reactivity of $\alpha,\beta$-unsaturated thioesters. Actually, the cleavage and formation of C-S bonds by transition-metal complexes were flexible\(^4\) and our group have already reported that such characteristics could be utilized for elucidating the mechanism of cleavage of the vinyl-X bonds by low-valent transition-metals.\(^5\) Herein the author wish to report on the effects of substituents on the reactions of $\alpha,\beta$-unsaturated thiesters (4; (R$^1$)(H)C=C(R$^2$)C(O)SAr) with
zero-valent platinum complex 2, substantiating that there are two distinct reaction routes for the formation of acyl complexes.

4-2. Reactions of H₂C=CHC(O)SAr with a Platinum (0) Complex.

First, thioesters 4a-d (H₂C=CHC(O)SC₆H₄-p-X, X = Me, H, Cl, NO₂) were prepared and the reactions with 2 were monitored by ¹H and ³¹P NMR spectroscopies at 25 °C using S=P(C₆H₄-p-OMe)₃ as an internal standard (Eq. 2).⁶ The reaction of 4a (X = Me) with 2 resulted in the quantitative formation of π-complex 5a was confirmed after 20 min both in C₆D₆ solution. Although it was not clear when the systems reached the equilibrium states due to the low yields of acyl platinum 6a and 7a (dimeric form of 6a), the formation after 3 h of 99.5% of 5a and 0.5% of 7a in C₆D₆. On the other hand, the reaction of trans-3a (0.02 mmol) with p-MeC₆H₄SNa (8, 0.06 mmol) in CD₂Cl₂ (0.5 mL) at 25 °C produced 5a (79%), trans-6a (0.6%) and 7a (13%, syn:anti = 77:23) after 17 h (Eq. 3). These results clearly showed that the equilibrium between 5a and 6a strongly leaned to the former side. The reaction employing 1b (X = H) gave the similar result of 5 and 7. The introduction of electro-withdrawing groups (Cl, NO₂) into X position slightly increased the reactivity. In the case of 4d, dimer complex 7d did not form. The fact indicates that introduction of electron withdrawing NO₂ group lowered the basicity of lone pairs on sulfur resulting in the prevention of the formation of 7.⁷
4-3. Reactions of Thioesters Having a p-MeC₆H₄S Group with a Platinum (0) Complex.

Next, when 4e (R¹ = H, R² = Me) was employed, the signal of starting 2 also completely disappeared and the formation of a mixture of the corresponding 5e, 6e and 7e were confirmed in 78%, 4.4% (cis:trans = 9:91) and 17% (syn:anti = 47:53) yields after 20 min in C₆D₆, and in 66%, 20% (cis:trans = 45:55) and 14% (syn:anti = 51:49) in CD₂Cl₂. Monitoring the reactions by ³¹P NMR spectra suggested that 6e and 7e were produced via 5e and revealed that the equilibria among 5e, 6e and 7e were attained in the periods of 3-4 h in C₆D₆ and 5-6 h in CD₂Cl₂ (runs 1 and 2, Table 1). The reactions using 4f (R¹ = Me, R² = H) also showed the formation of 5f, 6f and 7f after 20 min. It must be noted that the transformation from 5f into 6f and 7f was much faster than that from 5e into 6e and 7e; the equilibria were attained within 40 min (runs 3 and 4, Table 1). Foregoing facts demonstrate that the reaction systems of 4

Table 1. Reactions of 4 with ²

<table>
<thead>
<tr>
<th>run</th>
<th>4</th>
<th>solvent</th>
<th>time</th>
<th>⁵ : ⁶ (cis:trans)</th>
<th>time</th>
<th>⁵ : ⁶ (cis:trans) : ⁶ (syn:anti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4e</td>
<td>C₆D₆</td>
<td>3-4 h</td>
<td>51 : 49 (6:94)</td>
<td>3-4 h</td>
<td>13 (6:94) : 87 (79:21)</td>
</tr>
<tr>
<td>2</td>
<td>4e</td>
<td>C₆D₆Cl₂</td>
<td>5-6 h</td>
<td>22 : 78 (13:87)</td>
<td>5-6 h</td>
<td>22 (13:87) : 78 (83:17)</td>
</tr>
<tr>
<td>3</td>
<td>4f</td>
<td>C₆D₆</td>
<td>&lt;40 min</td>
<td>57 : 43 (1:99)</td>
<td>&lt;40 min</td>
<td>7 (1:99) : 93 (64:36)</td>
</tr>
<tr>
<td>4</td>
<td>4f</td>
<td>C₆D₆Cl₂</td>
<td>&lt;40 min</td>
<td>17 : 83 (1:99)</td>
<td>&lt;40 min</td>
<td>20 (1:99) : 80 (74:26)</td>
</tr>
<tr>
<td>5</td>
<td>4g</td>
<td>C₆D₆</td>
<td>9-10 h</td>
<td>78 : 22 (1:99)</td>
<td>3-6 h</td>
<td>7 (1:99) : 93 (74:26)</td>
</tr>
<tr>
<td>6</td>
<td>4h</td>
<td>C₆D₆</td>
<td>&lt;40 min</td>
<td>46 : 54 (1:99)</td>
<td>&lt;40 min</td>
<td>9 (1:99) : 91 (75:25)</td>
</tr>
<tr>
<td>7</td>
<td>4j</td>
<td>C₆D₆</td>
<td>52-55 h</td>
<td>81 : 19 (1:99)</td>
<td>10-15 h</td>
<td>9 (1:99) : 94 (81:19)</td>
</tr>
<tr>
<td>8</td>
<td>⁴j</td>
<td>C₆D₆</td>
<td>14-15 h</td>
<td>71 : 29 (1:99)</td>
<td>9-10 h</td>
<td>9 (1:99) : 91 (76:24)</td>
</tr>
<tr>
<td>9⁴</td>
<td>⁴j</td>
<td>C₆D₆</td>
<td>14-15 h</td>
<td>68 : 32 (1:99)</td>
<td>7-8 h</td>
<td>10 (1:99) : 90 (74:26)</td>
</tr>
<tr>
<td>10</td>
<td>⁴j</td>
<td>C₆D₆Cl₂</td>
<td>16-17 h</td>
<td>50 : 50 (21:79)</td>
<td>13-14 h</td>
<td>18 (21:79) : 82 (86:14)</td>
</tr>
<tr>
<td>11</td>
<td>⁴k</td>
<td>C₆D₆</td>
<td>&lt;40 min</td>
<td>89 : 11 (1:99)</td>
<td>&lt;40 min</td>
<td>8 (1:99) : 92 (60:40)</td>
</tr>
<tr>
<td>12⁴</td>
<td>⁴k</td>
<td>C₆D₆</td>
<td>&lt;40 min</td>
<td>91 : 9 (1:99)</td>
<td>&lt;40 min</td>
<td>7 (1:99) : 93 (63:37)</td>
</tr>
<tr>
<td>13</td>
<td>⁴k</td>
<td>C₆D₆Cl₂</td>
<td>&lt;40 min</td>
<td>70 : 30 (1:99)</td>
<td>60-80 min</td>
<td>15 (1:99) : 85 (70:30)</td>
</tr>
</tbody>
</table>

² 0.020 mmol, 4 (0.022 mmol) and solvent (0.5 mL) under N₂ atmosphere at 25 °C. 
³ Required to reach the equilibrium of 5:6. 
⁴ Ratio at equilibrium. 
⁵ Required to reach the equilibrium of 6:7. 
⁶ 4.3 equiv of ⁴j. 
⁷ 4.8 equiv of ⁴k.
possessing p-MeC₆H₄S with 2 are quite flexible and the position changes of equilibrium states caused by substituents and solvents are readily analyzable.

Furthermore, the comparison of the equilibria of 5e:6e = 51:49 (run 1, Table 1) with 5f:6f = 57:43 (run 3, Table 1) in C₆D₆ or 5e:6e = 22:78 (run 2, Table 1) with 5f:6f = 17:83 (run 4, Table 1) in CD₂Cl₂ indicates that retarded conversion of 5e into 6e and 7e is not attributable to its thermodynamics. Moreover, it took 9-10 h and even 52-55 h to reach the equilibrium states between 5 and 6 when 4g (R¹ = H, R² = n-C₆H₁₃) and 4i (R¹ = H, R² = i-Pr) were employed as starting substrates, respectively (runs 5 and 7, Table 1). It is also a noteworthy fact that 6:7 were reached the equilibrium states faster than 5:6 in theses reaction systems (3-6 h vs. 9-10 h in run 5 and 10-15 h vs. 52-55 h in run 7, Table 1). Although a larger thermodynamic driving force toward the oxidative addition from 5 to 6 was supplied by placing Ph at R² compared to Ph at R¹ (5j:6j = 71:29 of run 8 vs. 5k:6k = 89:11 of run 11 in C₆D₆ or 5j:6j = 50:50 of run 10 vs. 5k:6k = 70:30 of run 13 in CD₂Cl₂, Table 1), a much more prolonged time was again required to reach the equilibria; only < 40 min were required for 5k:6k both in C₆D₆ and CD₂Cl₂ (runs 11 and 13, Table 1), while the systems of 5j:6j came to the equilibria during the term of 14-15 h and 16-17 h, after the equilibria of 6j:7j were achieved during the period of 9-10 h and 13-14 h, respectively (runs 8 and 10, Table 1). Although there are the plural equilibrium systems such as 6:7, cis-6:trans-6 and syn-7:anti-7, all the results above indicate that introducing a bulky substituent at R² causes retardation of the process of conversion of 5 into 6. The reactions performed in the presence of excess amount of 4 toward 2 (runs 10 and 13, Table 1) in the cases of R² = Ph or R¹ = Ph showed no practical influence for both the reaction rates and the positions of equilibria, indicating that the generation of 6 from 5 is a unimolecular process.

\[
\text{PtL₂(C₂H₄)₂} \rightarrow 2 \\
\text{L = PPh₃} \\
\text{Ar = p-MeC₆H₄} \\
\text{toluene-d₈}
\]

\[
\begin{align*}
-70 ^°\text{C}, 10 \text{ min} & \quad 19\% (63:37) \\
-10 ^°\text{C}, 10 \text{ min} & \quad 92\% (96:4) \\
0 ^°\text{C}, 10 \text{ min} & \quad 74\% (>99:1) \\
25 ^°\text{C}, 10 \text{ min} & \quad 9\% (>99:1)
\end{align*}
\]

The chart of the ³¹P NMR spectrum of the reaction of 4f (R¹ = Me, R² = H) with 2 in toluene-d₈ attempted at a low reaction temperature (-70 °C after 10 min) suggested the
formation of two π-complexes at (a) δ 29.9 (d, $J_{p-P} = 44$ Hz, $J_{P-P} = 4208$ Hz) and δ 31.2 (d, $J_{p-P} = 44$ Hz, $J_{P-P} = 3373$ Hz), and (b) δ 29.4 (d, $J_{p-P} = 41$ Hz, $J_{P-P} = 3280$ Hz) and δ 30.1 (d, $J_{p-P} = 41$ Hz, $J_{P-P} = 4212$ Hz) in a ratio of 63:37 in 19% yields (Eq. 4), although the stereochemistry was not able to be determined from these spectral data. Then the ratio of the latter signal decreased at -10 °C (96:4) and completely disappeared at 0 °C. Eventually, 7f was produced as a major product at 25 °C. Only trans isomer of 6f was detected during the course of this reaction.

On the other hand, the reaction utilizing 4k ($R^1 = \text{Ph}, R^2 = \text{H}$) produced only one π-complex in 22% yield at -50 °C (Eq. 5). In this case, however, cis-6k was also detected at -30 °C (5% with cis:trans = 60:40) and trans-6k (4%) was again finally produced, indicating cis-6k was generated as a kinetic product.

The foregoing data described in Table 1 also clearly showed the following.

(1) The position of equilibria of 5:6 and 6:7 both were slightly shifted toward 6 by changing the solvent from C₆D₆ to CD₂Cl₂. (Compare 51:49 of run 3 with 22:78 of run 1 for 5e:6e and 13:87 of run 3 with 22:78 of run 2 for 6e:7e for instance in Table 1.) That is, the conversion from 5 into 6 was thermodynamically facilitated in some degree by a polar solvent and 6 has a slightly larger dipole moment than 7.

(2) The formation of cis-6 was confirmed when thioesters having the substituent at $R^2$ were employed (runs 1, 2 and 10, Table 1) and the ratios of cis-6 over trans-6 was increased by changing the solvent from C₆D₆ to CD₂Cl₂. (Compare 6:94 of run 3 with 13:87 of run 4 and 1:>99 of run 9 with 21:79 of run 11, Table 1.)

(3) The positions of equilibria between 6 and 7 were hardly influenced by the substituent at $R^1$ or $R^2$. The ratios of 6:7 were all in the narrow range from 6:94 (run 7, Table 1) to 13:87 (run 1, Table 1) in C₆D₆ and from 15:85 (run 13, Table 1) to 22:78 in CD₂Cl₂ (run 2, Table 1).
results also indicated that the basicity of the lone pair on sulfur, which can be mainly controlled by the substituent in Ar (vide infra), was the predominant factor to determine the position of equilibria between 6 and 7.\(^7\)

(4) The fact that the formation of syn-7 over anti-7 was increased by changing the solvent from $C_6D_6$ to $CD_2Cl_2$ agrees with the prediction that the dipole moment of syn-7 is slightly larger than that of anti-7.

### 4-4. Reactions of Thioesters Having $p$-$NO_2C_6H_4S$ Group with Pt(0) Complex.

It was found that more clear kinetic data from 5 to 6 was acquired by using thioesters with $p$-$NO_2C_6H_4S$ group; monitoring the reactions of 2 with 4 shown in Table 2 demonstrated that 6 was exclusively produced from 5 whose decay followed the first order kinetics. When 41 ($R_1^1 = H, R_2^1 = Me$) was employed, the half-life of 51 forming 61 was calculated to be 38 min in $C_6D_6$ (run 1, Table 2). As predicted from the results of Table 1, the introduction of Me at $R_1^1$ kinetically facilitated the reaction ($t_{1/2} = 2.1$ min, run 6, Table 2). In stark contrast, the reaction of 4p having i-Pr group at $R_2^1$, which significantly retarded the reaction in the case of ArS = $p$-MeC$_6$H$_4S$ (run 8, Table 1) took place just at a comparable reaction rate with that employing Table 2. Half-Lives from 5 to 6\(^a\)

<table>
<thead>
<tr>
<th>run</th>
<th>4</th>
<th>solvent</th>
<th>$t_{1/2}$ (min)</th>
<th>run</th>
<th>4</th>
<th>solvent</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4l</td>
<td>C$_6$D$_6$</td>
<td>38</td>
<td>10</td>
<td>4p</td>
<td>C$_6$D$_6$</td>
<td>43</td>
</tr>
<tr>
<td>2(^b)</td>
<td>4l</td>
<td>C$_6$D$_6$</td>
<td>36</td>
<td>4p</td>
<td>C$_6$D$_6$</td>
<td>43</td>
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</tr>
<tr>
<td>3</td>
<td>4l</td>
<td>CD$_2$Cl$_2$</td>
<td>14</td>
<td>4p</td>
<td>CD$_2$Cl$_2$</td>
<td>6.8</td>
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<tr>
<td>4</td>
<td>4l</td>
<td>acetone-$d_6$</td>
<td>19</td>
<td>4q</td>
<td>C$_6$D$_6$</td>
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<tr>
<td>5</td>
<td>4l</td>
<td>THF-$d_6$</td>
<td>36</td>
<td>4q</td>
<td>CD$_2$Cl$_2$</td>
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<td>3.3</td>
<td>4r</td>
<td>C$_6$D$_6$</td>
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<td>8</td>
<td>4n</td>
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<td>40</td>
<td>4r</td>
<td>CD$_2$Cl$_2$</td>
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<tr>
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<td>4o</td>
<td>C$_6$D$_6$</td>
<td>3.0</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) 2 (0.020 mmol), 4 (0.022 mmol) under N$_2$ atmosphere at 25 °C. Trans-6 was finally predominantly produced. \(^b\) 4.5 equiv of 4l. \(^c\) 5.0 equiv of 4p. \(^d\) 4.7 equiv of 4r.
Moreover, although retardation was also expected by introducing Ph at R² (vide ante), the transformation of 5q (R¹ = H, R² = Ph) to 6q was actually faster than that of 5r (R¹ = Ph, R² = H) to 6r (6.2 min, run 13 vs. 9.1 min, run 15, Table 2). The effect of solvent was also very intriguing. While the reaction rates were hardly influenced by the polarity of the solvent in the cases of substrates possessing a substituent at R¹ [2.1 min in C₆D₆ (run 6, Table 2) vs. 3.3 min in CD₂Cl₂ (run 7, Table 2) for 5m to 6m or 9.1 min in C₆D₆ (run 15, Table 2) vs. 7.8 min in CD₂Cl₂ (run 17, Table 2) for 5q to 6q], significant acceleration was detected in CD₂Cl₂ solution with the thioesters having a substituent at R². The reactions took place 2.7 times faster for 5l (38 min in C₆D₆, run 1 vs. 14 min in CD₂Cl₂, run 3, Table 2), 6.3 times faster for 5p (43 min in C₆D₆, run 10 vs. 6.8 min in CD₂Cl₂, run 12, Table 2) and 5.2 times faster for 5q (6.2 min in C₆D₆, run 13 vs. 1.2 min in CD₂Cl₂, run 14, Table 2). The reaction performed in acetone-d₆ also proceeded faster than that in C₆D₆ (19 min, run 4 vs. 38 min, run 1, Table 2), while no facilitation was observed in THE-d₈ (36 min, run 5, Table 2). Similarly to the cases of reactions shown in Table 1, the reaction rates were independent of the excess amount of 4 in the cases of thioesters with substituent at either R¹ or R² position [run 1 vs. run 2 (4.5 equiv of 4l), run 8 vs. run 9 (5.0 equiv of 4p) and run 13 vs. run 14 (4.7 equiv of 4q), Table 2].

When the reaction of 4q with 2 was performed at low reaction temperature, selective formation of 5q was confirmed at -50 °C after 10 min in 70% yield (Eq. 6). Then cis-6q was produced at -40 °C after 10 min in 3% yield and trans-6q was quantitatively provided at 25 °C.

**4-5. Proposed Dual Reaction Routes**

The experimental datas can be rationalized as follows (Scheme 1). In the case of thioesters possessing p-tolyl group on sulfur, after the formation of α-complex 5, coordinated Pt(PPh₃)₂ fragment would approach the C-S bond with the π-coordination partially retained. During the process, two PPh₃s on Pt would remain cis-coordinated, bulky substituents at R² significantly retard the reaction owing to the steric hindrance, and the cleavage of C-S bond and the
formation of C-Pt and S-Pt bonds take place through a transition state such as 8, which can possess the polarity comparable to 5.

Unlike the cases of reactions of thioesters possessing a p-MeC₆H₄S group with 2, the results from the reaction of thioesters having p-NO₂C₆H₄ group on sulfur indicated that the Pt(PPh₃)₂-fragment can also attack the β-carbon (path b, Scheme 1) as well as the direct C-S bond attack (path a). The β-attack would generate zwitterionic platinum complex 9 having anionic charge delocalized over α-carbon and carbonyl group. The formation of 9 can be facilitated to a great extent by a polar solvent and a substituent with α-anion stabilization ability such as a Ph group at R₂. The steric repulsion caused between a substituent at R₂ and Pt(PPh₃)₂-fragment would rather facilitate the β-attack by pushing out the Pt(PPh₃)₂-fragment toward a less hindered β-carbon in path b. Presumably due to the cancellation by the retardation of path a and facilitation of path b by replacing Me with i-Pr at R₂, no remarkable difference emerged in the half-lives of 5 between the reactions using 4l and 4p in C₆D₆ (run 1 vs. run 10, Table 2). On the other hand, path b would predominate in CD₂Cl₂ and the reaction utilizing 4q proceed faster than that utilizing 4l (run 3 vs. run 12, Table 2). The reaction using thioester with p-NO₂C₆H₄S and Ph group at R₂ would overwhelmingly occur via path b even in C₆D₆ solution due to the α-anion stabilization ability of Ph as well as the steric repulsion between Ph and Pt(PPh₃)₂-fragment. This is why the reaction of 4q took place faster than that of 4r even in C₆D₆ (run 13 vs. run 15, Table 2). After the generation of 9, the Pt(PPh₃)₂-fragment would migrate from β-carbon to carbonyl carbon through an η¹-η¹ type isomerization mechanism. During the process, the two PPh₃ on Pt also would retain cis configuration to give cis-6 as a kinetic product, which would isomerize into thermodynamically more stable trans-6.

**Scheme 1. A Proposed Pathway from 5 to 6**
4-6. Activation Parameters

To obtain more convincing information about the reaction mechanism, the activation parameters of the transformation of 6 from 5 were calculated by measuring the temperature dependence of reaction rates (25 °C - 40 °C) and values of $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were shown in Table 3. The following facts must be noted. First, the activation parameters of the formation of 6l from 5l in C₆D₆ significantly differed from those in CD₂Cl₂. That is, while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in C₆D₆ were 95.3±0.4 kJmol⁻¹ and 7.5±1.4 JK⁻¹mol⁻¹, those in CD₂Cl₂ were 53.5±0.1 kJmol⁻¹ and -124.4±0.2 JK⁻¹mol⁻¹. The large negative $\Delta S^\ddagger$ and relatively small positive $\Delta H^\ddagger$ in CD₂Cl₂ did not contradict the assumption that this reaction generates zwitterionic platinum complex 9, where the degree of freedom of the total reaction system was significantly diminished by a polar solvent and stiff Pt-C bond formation. On the contrary, the more positive $\Delta S^\ddagger$ and larger $\Delta H^\ddagger$ in C₆D₆ suggested the loss of bond energy and only weak bond generation at the transition state. Supposing that the π-coordination and C-S bond were weakened and emerging C-Pt and S-Pt bonds were both not strong, the transition state 8 would fulfill these criteria. Second, the negative value of $\Delta S^\ddagger$ (-49.2±0.3 JK⁻¹mol⁻¹) from 5p to 6p even in C₆D₆ also did not contradict the projection that this reaction can also proceed through path b even in C₆D₆ solution. That is, due to the significant steric hindrance caused by i-Pr located at R₂, the route of path b competitively took place. The small positive $\Delta H^\ddagger$ and large minus $\Delta S^\ddagger$ in CD₂Cl₂ also accorded with the route of path b. Third, comparing the data of formation of 6r from 5r in

### Table 3. Activation Parameters from 5l to 6l, from 5p to 6p and 5r from 6r

<table>
<thead>
<tr>
<th></th>
<th>from 5l to 6l (R¹ = H, R² = Me)</th>
<th>from 5p to 6p (R¹ = H, R² = i-Pr)</th>
<th>from 5r to 6r (R¹ = Ph, R² = H)</th>
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</thead>
<tbody>
<tr>
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<td>in C₆D₆</td>
<td>in CD₂Cl₂</td>
<td>in C₆D₆</td>
</tr>
<tr>
<td>$\Delta G^\ddagger$</td>
<td>93.0±0.1 kJmol⁻¹</td>
<td>90.5±0.1 kJmol⁻¹</td>
<td>89.8±0.1 kJmol⁻¹</td>
</tr>
<tr>
<td>$\Delta H^\ddagger$</td>
<td>95.3±0.4 kJmol⁻¹</td>
<td>53.5±0.1 kJmol⁻¹</td>
<td>68.2±0.7 kJmol⁻¹</td>
</tr>
<tr>
<td>$\Delta S^\ddagger$</td>
<td>7.5±1.4 JK⁻¹mol⁻¹</td>
<td>-49.2±0.3 JK⁻¹mol⁻¹</td>
<td>-72.5±2.4 JK⁻¹mol⁻¹</td>
</tr>
<tr>
<td>$\Delta G^\ddagger$</td>
<td>93.4±0.1 kJmol⁻¹</td>
<td>88.9±0.1 kJmol⁻¹</td>
<td>89.5±0.1 kJmol⁻¹</td>
</tr>
<tr>
<td>$\Delta H^\ddagger$</td>
<td>78.7±0.1 kJmol⁻¹</td>
<td>40.2±0.2 kJmol⁻¹</td>
<td>81.9±1.9 kJmol⁻¹</td>
</tr>
<tr>
<td>$\Delta S^\ddagger$</td>
<td>-49.2±0.3 JK⁻¹mol⁻¹</td>
<td>-163.5±0.5 JK⁻¹mol⁻¹</td>
<td>-25.5±6.4 JK⁻¹mol⁻¹</td>
</tr>
</tbody>
</table>
C₆D₆ with those in CD₂Cl₂, differences in the values of ∆Hᵢ and ∆Sᵢ as well as half-lives were much smaller than other cases. This can be nicely rationalized by assuming that reactions in both C₆D₆ and CD₂Cl₂ took place through a similar reaction route, namely, the direct C-S bond attack of a Pt(PPh₃)₂-fragment (path a) from a π-complex.

4-7. Conclusions

This study suggested that even when the substrates are α,β-unsaturated acid halide derivatives, two distinct reaction routes can similarly exist. The generality of this dual mechanism is now under investigation.

4-8. Experimental Section

General Comments: ³¹P and ¹H NMR spectra were recorded with a JEOL JMN Alice-400 spectrometer (160 MHz and 400 MHz, respectively) in C₆D₆, CD₂Cl₂ or toluene-d₈ solution. The chemical shifts of the ³¹P NMR spectra were recorded relative to 85% H₃PO₄ (aq.) as an external standard and S=P(C₆H₄OMe-p)₃ was used as an internal standard to calculate the yields of products. The chemical shifts in the ¹H NMR spectra were recorded relative to C₆H₆ (δ 7.15), CH₂Cl₂ (δ 5.32) or toluene (δ 2.09). IR spectra were recorded with a Perkin Elmer FT-IR (Model 1600) spectrometer. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Acid chlorides 1a and 1b were commercially obtained. Thioester 4a-c was prepared from the dehydrochlorination of S-aryl-3-(chloro)propanethioate using triethylamine (J. Am. Chem. Soc. 1969, 91, 913.). Thioester 4d was obtained from the reaction of CH₂=C(H)C(0)Cl with NaSC₆H₄-p-NO₂. Thioesters (4g, 4i-j) were synthesized according to the literature (Tetrahedron Lett. 2001, 42, 1567). Other thioesters (4e-f, 4h, 4k-r, S-aryl-3-(chloro)propanethioate) were prepared from the reactions of the corresponding acid chlorides with thiols in the presence of pyridine. The platinum complex Pt(PPh₃)₂(C₂H₄) (2) was synthesized according to the literature (Inorg. Synth. 1978, 18, 120.). C₆D₆, toluene-d₈ and C₆H₆ were purified by distillation from sodium benzophenon ketyl before use. CD₂Cl₂ was distilled from CaH₂. The structures of 5, trans-6 and 7 were determined by comparing their ³¹P NMR chemical shifts and coupling constants (JᵧP and JₓP) with those of the authentic samples 5a, trans-6r and 7k.

Spectrum Data of 4.

H₂C=C(H)C(O)SC₆H₄-p-CH₃ (4a): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (s, 3 H), 5.71 (dd, J = 1.6 Hz, J = 9.6 Hz, 1 H), 6.35 (d, J = 1.6 Hz, 1 H), 6.42 (d, J = 9.6 Hz, J = 17.2 Hz, 1 H), 7.21 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.4, 123.4, 126.9, 129.8, 134.1, 134.2, 139.4, 188.4; mass spectrum (EI) m/z 178 (M⁺, 40); HRMS calcd for C₁₀H₁₀OS 178.0452, found 178.0444.
H₂C=C(H)C(O)SC₆H₅ (4b): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.76-5.79 (m, 1 H), 6.36-6.49 (m, 2 H), 7.41-7.47 (m, 5 H), 7.31 (d, J= 8.0 Hz, 2 H); ¹³C NMR(100 MHz, CDCl₃) δ 127.0, 127.2, 129.0, 129.3, 134.2, 134.4, 188.1; mass spectrum (EI) m/z 164 (M⁺, 92); HRMS calcd for C₉H₇OS 164.0296, found 164.0300.

H₂C=C(He)C(O)SC₆H₄-p-Cl (4c): white solid; ¹H NMR (400 MHz, CDCl₃) δ 5.79-5.81 (m, 1 H), 6.37-6.48 (m, 2 H), 7.36-7.41 (m, 4 H), 7.31 (d, J= 8.0 Hz, 2 H); ¹³C NMR(100 MHz, CDCl₃) δ 125.4, 127.7, 129.3, 134.0, 135.6, 135.7, 187.6; mass spectrum (EI) m/z 198 (M⁺, 12); HRMS calcd for C₉H₇ClOS 197.9906, found 197.9903.

H₂C=C(H)C(O)SC₆H₄-p-NO₂ (4d): colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 5.86-5.90 (m, 1 H), 6.43-6.50 (m, 2 H), 7.65 (d, 2 H, NO₂JH-H= 8 Hz), 8.26 (d, 2 H, JH-H= 8 Hz); ¹³C NMR(100 MHz, CDCl₃) δ 123.8, 123.9, 128.7, 133.6, 134.6, 135.6, 185.8; mass spectrum (EI) m/z 209 (M⁺, 21); HRMS calcd for C₉H₇NO₃S 209.0147, found 209.0133.

H₂C=C(Me)C(0)SC₆H₄-p-CH₃ (4e): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3 H), 2.37 (s, 3 H), 5.67 (s, 1 H), 6.19 (s, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.4, 21.5, 123.5, 123.9, 129.8, 134.7, 139.4, 143.3, 191.6; mass spectrum (EI) m/z 192 (M⁺, 16); HRMS calcd for C₁₁H₁₂OS 192.0609, found 192.0611.

(E)-Me(H)C=C(H)C(O)SC₆H₄-p-CH₃ (4f): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (dd, J = 1.6 Hz, J = 7.0 Hz, 3 H), 2.36 (s, 3 H), 6.19 (dd, J = 1.6 Hz, J = 15.2 Hz, 1 H), 6.97 (dt, J = 7.2 Hz, J = 14.7 Hz, 1 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.1, 21.4, 123.8, 129.1, 129.7, 134.3, 139.2, 144.5, 187.8; mass spectrum (EI) m/z 192 (M⁺, 10); HRMS calcd for C₁₁H₁₂OS 192.0609, found 192.0613.

H₂C=C(N-C₆H₁₃)C(O)SC₆H₄-p-CH₃ (4g): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, J = 6.6 Hz, 3 H), 1.29 (br, 6 H), 1.44-1.49 (m, 2 H), 2.34 (t, J = 7.6 Hz, 2 H), 2.38 (s, 3 H), 5.64 (s, 1 H), 6.20 (s, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 21.5, 22.7, 28.3, 29.0, 31.7, 32.1, 122.4, 124.1, 129.8, 134.7, 139.4, 148.2, 191.9; mass spectrum (EI) m/z 262 (M⁺, 14); HRMS calcd for C₁₆H₂₂OS 262.1391, found 262.1393.
(E)-(n-C₆H₁₃)(H)C=C(H)C(0)SC₆H₄-p-CH₃ (4h): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, J = 6.4 Hz, 3 H), 1.28-1.49 (m, 8 H), 2.24 (m, 2 H), 2.37 (s, 3 H), 6.17 (d, J = 15.6 Hz, 1 H), 6.97 (dt, J = 7.2 Hz, J = 15.6 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 21.5, 22.7, 28.0, 28.9, 31.5, 32.4, 124.0, 127.6, 129.8, 134.3, 139.3, 146.6, 188.2.

H₂C=C(i-C₃H₇)(H)C(0)SC₆H₄-p-CH₃ (4i): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.11 (d, J = 6.8 Hz, 6 H), 2.85 (sept, J = 6.8 Hz, 1 H), 5.63 (s, 1 H), 6.18 (s, 1 H), 7.23 (d, J = 8.2 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.3, 21.5, 29.9, 119.7, 124.1, 129.6, 134.5, 139.2, 154.3, 192.2; mass spectrum (EI) m/z 220 (M⁺, 16); HRMS calcd for C₁₃H₁₆OS 220.0922, found 220.0923.

H₂C=C(C₆H₅)C(0)SC₆H₄-p-CH₃ (4j): white solid; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3 H), 5.87 (s, 1 H), 6.29 (s, 1 H), 7.22-7.45 (m, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 123.5, 124.5, 128.50, 128.55, 128.9, 130.3, 134.8, 136.0, 139.9, 148.0, 192.2; mass spectrum (EI) m/z 254 (M⁺, 13); HRMS calcd for C₁₆H₁₄OS 254.0765, found 254.0771.

(E)-(C₆H₅)(H)C=C(H)C(0)SC₆H₄-p-CH₃ (4k): white solid; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3 H), 6.78 (d, J = 16.0 Hz, 1 H), 7.24 (d, J = 7.6 Hz, 2 H), 7.36-7.40 (m, 5 H), 7.66 (d, J = 16.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 123.5, 124.5, 128.50, 128.55, 128.9, 130.3, 134.8, 136.0, 139.9, 141.1, 188.0; mass spectrum (EI) m/z 254 (M⁺, 1); HRMS calcd for C₁₆H₁₄OS 254.0765, found 254.0759.

H₂C=C(C₆H₅)C(0)SC₆H₄-p-NO₂ (4l): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 2.03 (s, 3 H), 5.80 (s, 1 H), 6.25 (s, 1 H), 7.64 (d, J = 8.7 Hz, 2 H), 8.27 (d, J = 8.7 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.1, 123.5, 124.7, 134.9, 136.0, 142.8, 147.8, 188.7; mass spectrum (EI) m/z 223 (M⁺, 1); HRMS calcd for C₁₀H₉NO₃S 223.0303, found 223.0303.

(E)-(CH₃)(H)C=C(H)C(0)SC₆H₄-p-NO₂ (4m): orange solid; ¹H NMR (400 MHz, CDCl₃) δ 1.97 (d, J = 6.8 Hz, 3 H), 6.23 (d, J = 15.2 Hz, 1 H), 7.06 (dt, J = 6.8 Hz, J = 14.8 Hz, 1 H), 7.63 (d, J = 8.2 Hz, 2 H), 8.25 (d, J = 8.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.4, 123.7, 128.8, 134.6, 143.6, 147.8, 185.1; mass spectrum (EI) m/z 223 (M⁺, 0.4); HRMS calcd for C₁₀H₉NO₃S 223.0303, found 223.0305.
H₂C=C(n-C₆H₁₃)C(O)SC₆H₄-p-NO₂ (4n): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.30-1.50 (m, 8 H), 2.36 (t, J = 7.6 Hz, 2 H), 5.76 (s, 1 H), 6.25 (s, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 8.26 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 22.7, 28.2, 28.9, 31.7, 32.0, 123.7, 123.8, 135.0, 136.4, 147.9, 189.1.

(E)-(n-C₆H₁₃)(C)=C(H)C(O)SC₆H₄-p-NO₂ (4o): colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, J = 6.4 Hz, 3 H), 1.31-1.52 (m, 8 H), 2.28 (dt, J = 20.4 Hz, J = 7.2 Hz, 2 H), 6.19 (d, J = 15.6 Hz, 1 H), 7.05 (dt, J = 6.8 Hz, J = 15.6 Hz, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 8.25 (d, J = 8.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 22.7, 28.0, 29.0, 31.7, 32.6, 123.7, 127.3, 134.6, 136.3, 147.8, 148.6, 185.3.

H₂C=C(i-Pr)C(O)SC₆H₄-p-NO₂ (4p): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.13 (d, J = 6.8 Hz, 6 H), 2.86 (sept, J = 6.8 Hz, 1 H), 5.75 (s, 1 H), 6.23 (s, 1 H), 7.63 (d, J = 8.8 Hz, 2 H), 8.26 (d, J = 8.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 30.2, 121.4, 123.7, 134.8, 135.0, 136.5, 147.9, 154.2, 189.6; mass spectrum (EI) m/z 251 (M⁺, 0.2); HRMS calcd for C₁₂H₁₃NO₃S 251.0616, found 251.0607.

H₂C=C(C₆H₅)C(O)SC₆H₄-p-NO₂ (4q): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 5.95 (s, 1 H), 6.35 (s, 1 H), 7.39-7.45 (m, 5 H), 7.65 (d, J = 9.0 Hz, 2 H), 8.26 (d, J = 9.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 123.8, 124.4, 128.2, 128.3, 128.9, 134.8, 135.0, 136.4, 147.3, 148.0, 189.0; mass spectrum (EI) m/z 285 (M⁺, 9.4); HRMS calcd for C₁₅H₁₁NO₃S 285.0460, found 285.0547.

(E)-PhC(H)=CHC(O)SC₆H₄-p-NO₂ (4r): yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 6.78 (d, J = 15.8 Hz, 1 H), 7.42-7.44 (m, 3 H), 7.57-7.59 (m, 2 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.72 (d, J = 15.8 Hz, 1 H), 8.27 (d, J = 8.6 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 123.4, 123.7, 128.5, 128.9, 131.1, 133.4, 134.6, 136.2, 142.7, 147.9, 185.2; mass spectrum (CI) m/z 286 ([M-H]⁺, 100); HRMS calcd for C₁₅H₁₂NO₃S (M-H) 286.0538, found 286.0533.

The Preparation of Authentic 5a. Into a dry two-necked reaction vessel equipped with a stirring bar were added 2 (703.0 mg, 0.94 mmol), 4a (174.9 mg, 0.98 mmol) and C₆H₆ (3 mL). After the reaction mixture was stirred at 25 °C for 30 min, hexane (ca. 50 mL) was added into
the mixture and the precipitate was collected by filtration. Then the solid was washed by hexane (10 mL x 3) and dried to give 5a (672.0 mg, 80%).

5a: mp 130 °C (a white solid); 1H NMR (400 MHz, C6D6) δ 2.01 (s, 3 H), 2.53-2.60 (m, 1 H), 3.00-3.07 (m, 1 H), 3.90-4.06 (m, 1 H), 6.84-6.97 (m, 20 H), 7.18-7.20 (m, 2 H), 7.43-7.56 (m, 12 H); 31P NMR (160 Hz, C6D6) δ 29.5 (d, Jp-p = 38 Hz, Jp-t = 4038 Hz), 31.4 (d, Jp-p = 38 Hz, Jp-t = 3567 Hz); IR (KBr) 3050, 1652, 1478, 1433, 1360, 1155, 1095, 967, 943, 808, 742, 692, 540, 517, 510 cm⁻¹; Anal. Calcd for C46H40OP2PtS: C, 61.53; H, 4.49. Found: C, 61.48; H, 4.49.

The Preparation of Authentic trans-6r. Into a dry two-necked reaction vessel equipped with a stirring bar were added 2 (747.0 mg, 1.0 mmol), 4r (301.5 mg, 1.1 mmol) and C6H6 (5 mL). After the reaction mixture was stirred at 25 °C for 1.5 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The resultant solid was washed by hexane (10 mL x 3) and methanol (10mL x 3) and then dried to give trans-6r (849.8 mg, 85%).

trans-6r: mp 142 °C (an orange solid); 1H NMR (400 MHz, C6D6) δ 6.08 (d, J = 16.0 Hz, 1 H), 6.82-7.15 (m, 27 H), 7.47 (d, J = 16.0 Hz, 1 H), 7.57 (d, J = 9.2 Hz, 2 H), 7.80-7.83 (m, 10 H); 31P NMR (160 Hz, C6D6) δ 16.0 (s, Jp-t = 3228 Hz); IR (KBr) 3056, 1580, 1566, 1493, 1482, 1435, 1319, 1094, 742, 692, 523, 514 cm⁻¹; Anal. Calcd for C51H41NO3P2PtS: C, 60.95; H, 4.11; N, 1.39. Found: C, 60.69; H, 4.03; N, 1.43.

The Preparation of Authentic 7k. Into a dry two-necked reaction vessel equipped with a stirring bar were added 2 (897.0 mg, 1.2 mmol), 4k (321.2 mg, 1.3 mmol) and C6H6 (5 mL). After the reaction mixture was stirred at 25 °C for 2 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The resultant solid was washed by hexane (10 mL x 3) and methanol (10 mL x 3) and then dried to give 7k (394.9 mg, 46%, syn:anti = 61:39).

7k (the following data were collected from a mixture of stereoisomers): mp 186 °C (an yellow solid); 1H NMR (160 MHz, C6D6) (syn isomer): δ 1.65 (s, 3 H), 2.11 (s, 3 H), 6.13 (d, J = 16.0 Hz, 1 H), 6.50 (d, J = 7.6 Hz, 2 H), 6.58 (d, J = 8.0 Hz, 2 H), 7.51 (d, J = 8.0 Hz, 2 H), 7.58 (d, J = 7.6 Hz, 2 H); (anti isomer): δ 1.88 (s, 6 H), 6.14 (d, J = 16.0 Hz, 1 H) (Other peaks overlapped in the region of δ 6.83-7.15 and δ 7.69-7.85 was not able to be read distinctively.); 31P NMR (160 Hz, C6D6) (syn isomer): δ 15.0 (s, Jp-t = 4164 Hz); (anti isomer): δ 16.8 (s, Jp-t = 4028 Hz); IR (KBr) 3055, 1626, 1582, 1486, 1434, 1096, 758, 693, 535, 511, 498 cm⁻¹; Anal. Calcd for C68H58O2P2Pt2S2: C, 57.38; H, 4.11. Found: C, 57.66; H, 4.03.

The Reaction of 1a with 2 (Eq. 1). Into a dry Pyrex NMR tube were added 2 (15.5 mg, 0.021 mmol), 1a (4.0 mg, 0.044 mmol) and S=P(C6H4OMe-p)3 (1.7 mg, 0.0044 mmol). Then ca. 0.5 mL of toluene-d8 was transferred by the freeze-pump-thaw method. The 31P NMR spectrum
taken after 10 min at -50 °C showed the quantitative formation of acylplatinum complex 3a (cis:trans = 57:43), which completely isomerized to trans isomer at 10 °C after 10 min. No formation of π-complex Pt[(Cl)C(O)C(H)=CH2](PPh3)2 was observed during course of the reaction.

cis-3a: 31P NMR (160 MHz, toluene-d8) δ 15.9 (d, Jp_p = 17 Hz, Jpt_p = 4662 Hz), 18.2 (d, Jp_p = 17 Hz, Jpt_p = 1378 Hz). trans-3a: 31P NMR (160 MHz, toluene-d8) δ 22.2 (s, Jp_p = 3312 Hz).

The Reaction of 1b with 2 (Eq. 1). The reaction of 1b with 2 was carried out in a similar manner to the reaction of 1b with 2. The 31P NMR spectrum taken after 10 min at -50 °C showed the quantitative formation of 3b (cis:trans = 96:4), which completely isomerized to trans isomer at 10 °C after 10 min. No formation of π-complex Pt[(Cl)C(0)C(H)=C(Ph)(H)-(E)](PPh3)2 was observed during course of the reaction.

cis-3b: 31P NMR (160 MHz, toluene-d8) δ 15.4 (d, Jp_p = 16 Hz, Jpt_p = 4715 Hz), 17.4 (d, Jp_p = 16 Hz, Jpt_p = 1349 Hz). trans-3b: 31P NMR (160 MHz, toluene-d8) δ 21.0 (s, Jp_p = 3378 Hz).

The Reaction of α,β-Unsaturated Thioester 4 with 2. General Procedure: Into a dry Pyrex NMR tube were added 2 (0.020 mmol), 4 (0.022 mmol), S=P(C6H4OMe-p)3 (0.01 mmol) and solvent (0.5 mL) under N2 atmosphere. The reaction was roughly monitored by 31P and 1H NMR spectrum at 25 °C to determine the time required for reaching the equilibrium state among 5, 6 and 7. Then the reaction was again continuously monitored by using automatic measuring system until the equilibrium of the system was well-achieved.

The Reaction of H2C=CHC(0)SC6H4Me-p (4a) with 2 in C6D6 (Eq. 2): The reaction was continuously monitored by 31P and 1H NMR spectrum using automatic measurement program system. The 31P NMR spectrum showed the formation of 5a and syn-7a. The reaction time, the yields of 5a and syn-7a at the time are shown in Table S1.

<table>
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<th>time</th>
<th>5a (%)</th>
<th>6a (%)</th>
<th>7a (%)</th>
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<td>20min</td>
<td>&gt;99</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>&gt;99</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>3 h</td>
<td>99.7</td>
<td>n.d.</td>
<td>0.3</td>
</tr>
<tr>
<td>6 h</td>
<td>99.5</td>
<td>n.d.</td>
<td>0.5</td>
</tr>
</tbody>
</table>

5a: 31P NMR (160 MHz, C6D6) δ 29.5 (d, Jp_p = 38 Hz, Jpt_p = 4038 Hz), 31.4 (d, Jp_p = 38 Hz, Jpt_p = 3567 Hz). syn-7a: 31P NMR (160 MHz, C6D6) δ 15.0 (s, Jp_p = 4171 Hz).

The Reaction of 4a with 2 in CD2Cl2 (Eq. 2): Automatic NMR measurement program system has been used to continuously monitor the reaction. The 31P NMR spectrum showed the formation of 5a, trans-6a and syn-7a. The reaction time, the yields of 5a, trans-6a and syn-7a, and at the time are shown in Table S2.

<table>
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<th>time</th>
<th>5a (%)</th>
<th>trans-6a (%)</th>
<th>syn-7a (%)</th>
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<tbody>
<tr>
<td>20min</td>
<td>98.7</td>
<td>0.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>98.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>140 min</td>
<td>98.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>6 h</td>
<td>98.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>
5a: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 28.9\) (d, \(J_{P,P} = 37 \text{ Hz}, J_{P,P} = 4060 \text{ Hz}\)), 30.7 (d, \(J_{P,P} = 37 \text{ Hz}, J_{P,P} = 3541 \text{ Hz}\)). \textit{trans}-6a: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 17.6\) (s, \(J_{P,P} = 3272 \text{ Hz}\)). \textit{syn}-7a: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 15.0\) (s, \(J_{P,P} = 4110 \text{ Hz}\)).

The Reaction of H\(_2\)C=CHC(0)SPh (4b) with 2 in C\(_6\)D\(_6\) (Eq. 2): The reaction was continuously monitored by \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectrum using automatic measurement program system. The \(^{31}\text{P}\) NMR spectrum showed the formation of 5b and \textit{syn}-7b. The reaction time, the yields of 5b and \textit{syn}-7b at the time are shown in Table S3.

Table S3
<table>
<thead>
<tr>
<th>time</th>
<th>5b (%)</th>
<th>6b (%)</th>
<th>7b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>&gt;99</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>99.1</td>
<td>n.d.</td>
<td>0.9</td>
</tr>
<tr>
<td>3 h</td>
<td>97.7</td>
<td>n.d.</td>
<td>2.3</td>
</tr>
<tr>
<td>5 h</td>
<td>97.6</td>
<td>n.d.</td>
<td>2.4</td>
</tr>
</tbody>
</table>

5b: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 29.5\) (d, \(J_{P,P} = 38 \text{ Hz}, J_{P,P} = 4049 \text{ Hz}\)), 31.3 (d, \(J_{P,P} = 38 \text{ Hz}, J_{P,P} = 3557 \text{ Hz}\)). \textit{syn}-7b: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 15.1\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity).

The Reaction of H\(_2\)C=CHC(0)SPh (4b) with 2 in CD\(_2\)Cl\(_2\) (Eq. 2): The reaction was continuously monitored by \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectrum using automatic measurement program system. The \(^{31}\text{P}\) NMR spectrum showed the formation of 5b, 6b and 7b. The reaction time, the yields of 5b, 6b and 7b at the time are shown in Table S4.

Table S4
<table>
<thead>
<tr>
<th>time</th>
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<th>6b (%)</th>
<th>7b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>&gt;99</td>
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<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>98.2</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>3 h</td>
<td>97.0</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td>6 h</td>
<td>95.1</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>22 h</td>
<td>93.6</td>
<td>0.9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

5b: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 29.0\) (d, \(J_{P,P} = 37 \text{ Hz}, J_{P,P} = 4076 \text{ Hz}\)), 30.7 (d, \(J_{P,P} = 37 \text{ Hz}, J_{P,P} = 3540 \text{ Hz}\)). 6b: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 17.0\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity). \textit{syn}-7b: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 15.1\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity). \textit{anti}-7b: \(^{31}\text{P}\) NMR (160 MHz, CD\(_2\)Cl\(_2\)) \(\delta 17.0\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity).

The Reaction of H\(_2\)C=CHC(0)SC\(_6\)H\(_4\)-p-Cl (4c) with 2 in C\(_6\)D\(_6\) (Eq. 2): The reaction was continuously monitored by \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectrum using automatic measurement program system. The \(^{31}\text{P}\) NMR spectrum showed the formation of 5c, 6c and 7c. The reaction time, the yields of 5c, 6c and 7c at the time are shown in Table S5.

Table S5
<table>
<thead>
<tr>
<th>time</th>
<th>5c (%)</th>
<th>6c (%)</th>
<th>7c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>&gt;99</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>98.2</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>3 h</td>
<td>92.2</td>
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<td>6.3</td>
</tr>
<tr>
<td>6 h</td>
<td>90.4</td>
<td>1.7</td>
<td>7.9</td>
</tr>
</tbody>
</table>

5c: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 29.3\) (d, \(J_{P,P} = 38 \text{ Hz}, J_{P,P} = 4072 \text{ Hz}\)), 31.2 (d, \(J_{P,P} = 38 \text{ Hz}, J_{P,P} = 3558 \text{ Hz}\)). 6c: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 16.3\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity). \textit{syn}-7c: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 14.8\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity). \textit{anti}-7c: \(^{31}\text{P}\) NMR (160 MHz, C\(_6\)D\(_6\)) \(\delta 16.5\) (s, the value of \(J_{P,P}\) was not able to read because of low intensity).
The Reaction of H₂C=CHC(0)SC₆H₄-p-Cl (4c) with 2 in CD₂Cl₂ (Eq. 2): The reaction was continuously monitored by ³¹P and ¹H NMR spectrum using automatic measurement program system. The ³¹P NMR spectrum showed the formation of 5c, 6c, 7c, and 8c. The reaction time, the yields of 5c, 6c, 7c, and 8c at the time are shown in Table S6.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5c (%)</th>
<th>6c (%)</th>
<th>7c (%)</th>
<th>8c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>99.5</td>
<td>0.5</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>98.1</td>
<td>1.6</td>
<td>0.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>6 h</td>
<td>87.7</td>
<td>4.0</td>
<td>8.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>19 h</td>
<td>86.3</td>
<td>5.4</td>
<td>8.3</td>
<td>1.5</td>
</tr>
<tr>
<td>22 h</td>
<td>84.1</td>
<td>5.3</td>
<td>9.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

5c: ³¹P NMR (160 MHz, CD₂Cl₂) δ 28.8 (d, Jₚ₋ₚ = 35 Hz, Jₚ₋ₚ = 4082 Hz), 30.6 (d, Jₚ₋ₚ = 35 Hz, Jₚ₋ₚ = 3530 Hz). 6c: ³¹P NMR (160 MHz, CD₂Cl₂) δ 17.0 (s, Jₚ₋ₚ = 3260 Hz). syn-7c: ³¹P NMR (160 MHz, CD₂Cl₂) δ 14.9 (s, the value of Jₚ₋ₚ was not able to read because of low intensity). anti-7c: ³¹P NMR (160 MHz, CD₂Cl₂) δ 16.5 (s, the value of Jₚ₋ₚ was not able to read because of low intensity). 10c: ³¹P NMR (160 MHz, CD₂Cl₂) δ 23.9 (s, Jₚ₋ₚ = 3260 Hz).

The Reaction of H₂C=CHC(0)SC₆H₄-p-NO₂ (4d) with 2 in C₆D₆ (Eq. 2): The ³¹P NMR spectrum showed the formation of 5d, 6d and 10d. The reaction time (the average of acquisition time), and the yields of 5r, 6r and 10r at the time are shown in Table S7 and the half-live was calculated to be 10.2 h.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5d (%)</th>
<th>6d (%)</th>
<th>7d (%)</th>
<th>8d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 min</td>
<td>&gt;99</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>4 min</td>
<td>99</td>
<td>1</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>20 min</td>
<td>97</td>
<td>3</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>40 min</td>
<td>95</td>
<td>5</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>93</td>
<td>7</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>2 h</td>
<td>87</td>
<td>13</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>3 h</td>
<td>81</td>
<td>18</td>
<td>n.d.</td>
<td>1</td>
</tr>
<tr>
<td>4 h</td>
<td>76</td>
<td>23</td>
<td>n.d.</td>
<td>1</td>
</tr>
<tr>
<td>5 h</td>
<td>71</td>
<td>28</td>
<td>n.d.</td>
<td>2</td>
</tr>
<tr>
<td>10 h</td>
<td>50</td>
<td>45</td>
<td>n.d.</td>
<td>5</td>
</tr>
<tr>
<td>19 h</td>
<td>35</td>
<td>56</td>
<td>n.d.</td>
<td>9</td>
</tr>
</tbody>
</table>

5d: ³¹P NMR (160 MHz, C₆D₆) δ 29.1 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ = 4103 Hz), 31.0 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ = 3542 Hz). 6d: ³¹P NMR (160 MHz, C₆D₆) δ 16.0 (s, Jₚ₋ₚ = 3236 Hz). 10d: ³¹P NMR (160 MHz, C₆D₆) δ 23.7 (s, Jₚ₋ₚ = 2990 Hz).

The Reaction of H₂C=CHC(0)SC₆H₄-p-NO₂ (4d) with 2 in CD₂Cl₂ (Eq. 2): The ³¹P NMR spectrum showed the formation of 5d, 6d and 10d. The reaction time (the average of acquisition time), and the yields of 5d, 6d and 10d at the time are shown in Figure S8 and the half-live was calculated to be 5.4 h.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5d (%)</th>
<th>6d (%)</th>
<th>7d (%)</th>
<th>8d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>91</td>
<td>9 (1:99)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>40 min</td>
<td>86</td>
<td>14 (1:99)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1 h</td>
<td>82</td>
<td>18 (1:99)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>2 h</td>
<td>73</td>
<td>26 (1:99)</td>
<td>n.d.</td>
<td>0.4</td>
</tr>
<tr>
<td>3 h</td>
<td>65</td>
<td>34 (1:99)</td>
<td>n.d.</td>
<td>1</td>
</tr>
<tr>
<td>4 h</td>
<td>57</td>
<td>42 (1:99)</td>
<td>n.d.</td>
<td>1</td>
</tr>
<tr>
<td>5 h</td>
<td>50</td>
<td>48 (1:99)</td>
<td>n.d.</td>
<td>2</td>
</tr>
<tr>
<td>6 h</td>
<td>42</td>
<td>55 (1:99)</td>
<td>n.d.</td>
<td>3</td>
</tr>
<tr>
<td>7.5 h</td>
<td>34</td>
<td>61 (1:99)</td>
<td>n.d.</td>
<td>3</td>
</tr>
<tr>
<td>9 h</td>
<td>31</td>
<td>66 (1:99)</td>
<td>n.d.</td>
<td>4</td>
</tr>
<tr>
<td>10 h</td>
<td>27</td>
<td>68 (1:99)</td>
<td>n.d.</td>
<td>5</td>
</tr>
</tbody>
</table>

5d: ³¹P NMR (160 MHz, CD₂Cl₂) δ 28.6 (d, Jₚ₋ₚ = 35 Hz, Jₚ₋ₚ = 4118 Hz), 30.3 (d, Jₚ₋ₚ = 35 Hz, Jₚ₋ₚ = 3513 Hz). 6d: ³¹P NMR (160 MHz, CD₂Cl₂) δ 15.9 (s, Jₚ₋ₚ = 3225 Hz). 10d: ³¹P NMR (160 MHz, CD₂Cl₂) δ 23.5 (s, Jₚ₋ₚ = 3024 Hz).

The Reaction of Trans-3a with 8 (Eq. 3). Into a dry Pyrex NMR tube were added trans-3a.
(16.2 mg, 0.020 mmol), 8 (8.8 mg, 0.060 mmol), S=P(C₆H₄OMe-p)₃ (3.6 mg, 0.0094 mmol) and CD₂Cl₂ (0.5 mL) under N₂ atmosphere. Then the reaction was monitored by ³¹P and ¹H NMR spectrum at 25 °C. After 17 h, the ³¹P NMR spectrum showed the formation of 5a (79%), trans-6a (0.6%) and 7a (13%, syn:anti = 77:23).

anti-7a: ³¹P NMR (160 MHz, CD₂Cl₂) δ 17.0 (s, Jₚₚ = 4013 Hz).

The Reaction of H₂C=C(Me)C(0)SC₆H₄-p-Me (4e) with 2 in C₆D₆ (run 1, Table 1):

Automatic NMR measurement program system has been used to continuously monitor the reaction for 7 h. The ³¹P NMR spectrum showed the formation of 5e, 6e and 7e. Selective information about the reaction time, the yields of 5e, 6e and 7e, and the ratios of 5e:6e and 6e:7e at the time are shown in Table S9. Although the ratio of 5e:6e after 3 h (58:42) was different from that after 4 h (51:49), those after 4 h and 7 h were virtually the same. This is why it was concluded that equilibrium between 5e:6e was attained in a range of time of 3-4 h (51:49). The changes of yields between 5e and 6e from the early stage of this reaction indicated 6e was produced from 5e. The equilibrium between 6e:7e was also attained in a range of time of 3-4 h (13:87).

5e: ³¹P NMR (160 MHz, C₆D₆) δ 28.0 (d, Jₚₚ = 41 Hz, Jₚₜₚ = 3827 Hz), 31.0 (d, Jₚₚ = 41 Hz, Jₚₜₚ = 3724 Hz). cis-6e: ³¹P NMR (160 MHz, C₆D₆) δ 16.7 (d, Jₚₚ = 19 Hz, the value of Jₚₜₚ was not able to read because of low intensity), 18.4 (d, Jₚₚ = 19 Hz, the value of Jₚₜₚ was not able to read because of low intensity). trans-6e: ³¹P NMR (160 MHz, C₆D₆) δ 16.4 (s, Jₚₚ = 3291 Hz). syn-7e: ³¹P NMR (160 MHz, C₆D₆) δ 14.6 (s, Jₚₜₚ = 4188 Hz). anti-7e: ³¹P NMR (160 MHz, C₆D₆) δ 16.2 (s, Jₚₜₚ = 4124 Hz).

The Reaction of 4e with 2 in CD₂Cl₂ (run 2, Table 1):

Automatic NMR measurement program system has been used to continuously monitor the reaction for 8 h. The ³¹P NMR spectrum showed the formation of 5e, 6e and 7e. Selective information about the reaction time, the yields of 5e, 6e and 7e, and the ratios of 5e:6e and 6e:7e at the time are shown in Table S10. Although the ratio of 5e:6e after 5 h (25:75) was different from that after 6 h (22:78), those after 6 h and 8 h

<table>
<thead>
<tr>
<th>Table S9</th>
<th>time</th>
<th>5e (%)</th>
<th>6e (%)</th>
<th>7e (%)</th>
<th>5e:6e</th>
<th>6e:7e</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>(cis:trans)</td>
<td>(syn:anti)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min</td>
<td>78</td>
<td>4.4 (9:91)</td>
<td>17 (47:53)</td>
<td>95:5</td>
<td>21:79</td>
<td></td>
</tr>
<tr>
<td>40 min</td>
<td>64</td>
<td>7.3 (4:96)</td>
<td>28 (68:32)</td>
<td>90:10</td>
<td>21:79</td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td>48</td>
<td>10 (10:90)</td>
<td>42 (76:24)</td>
<td>83:17</td>
<td>19:81</td>
<td></td>
</tr>
<tr>
<td>2 h</td>
<td>24</td>
<td>12 (5:95)</td>
<td>64 (80:20)</td>
<td>67:33</td>
<td>15:85</td>
<td></td>
</tr>
<tr>
<td>3 h</td>
<td>16</td>
<td>12 (6:94)</td>
<td>70 (79:21)</td>
<td>58:42</td>
<td>16:84</td>
<td></td>
</tr>
<tr>
<td>4 h</td>
<td>12</td>
<td>12 (4:96)</td>
<td>76 (80:20)</td>
<td>51:49</td>
<td>13:87</td>
<td></td>
</tr>
<tr>
<td>5 h</td>
<td>12</td>
<td>12 (4:96)</td>
<td>76 (80:20)</td>
<td>51:49</td>
<td>13:87</td>
<td></td>
</tr>
<tr>
<td>6 h</td>
<td>11</td>
<td>12 (5:95)</td>
<td>77 (81:19)</td>
<td>49:51</td>
<td>13:87</td>
<td></td>
</tr>
<tr>
<td>7 h</td>
<td>12</td>
<td>12 (7:93)</td>
<td>76 (80:20)</td>
<td>50:50</td>
<td>13:87</td>
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<table>
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<th>6e (%)</th>
<th>7e (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(cis:trans)</td>
<td>(syn:anti)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>20 min</td>
<td>66</td>
<td>20 (45:55)</td>
<td>17 (51:49)</td>
<td>77:23</td>
<td>59:41</td>
<td></td>
</tr>
<tr>
<td>40 min</td>
<td>45</td>
<td>24 (24:76)</td>
<td>28 (69:31)</td>
<td>65:35</td>
<td>44:56</td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td>33</td>
<td>26 (19:81)</td>
<td>42 (73:27)</td>
<td>56:44</td>
<td>39:61</td>
<td></td>
</tr>
<tr>
<td>2 h</td>
<td>15</td>
<td>25 (17:83)</td>
<td>64 (79:21)</td>
<td>38:62</td>
<td>30:70</td>
<td></td>
</tr>
<tr>
<td>3 h</td>
<td>10</td>
<td>24 (15:86)</td>
<td>70 (81:19)</td>
<td>29:71</td>
<td>27:73</td>
<td></td>
</tr>
<tr>
<td>4 h</td>
<td>9</td>
<td>22 (12:88)</td>
<td>76 (82:18)</td>
<td>29:71</td>
<td>24:76</td>
<td></td>
</tr>
<tr>
<td>5 h</td>
<td>7</td>
<td>21 (14:86)</td>
<td>76 (82:18)</td>
<td>25:75</td>
<td>23:77</td>
<td></td>
</tr>
<tr>
<td>6 h</td>
<td>12</td>
<td>21 (13:87)</td>
<td>77 (83:17)</td>
<td>22:78</td>
<td>22:78</td>
<td></td>
</tr>
<tr>
<td>7 h</td>
<td>6</td>
<td>20 (15:85)</td>
<td>76 (82:18)</td>
<td>23:77</td>
<td>22:78</td>
<td></td>
</tr>
<tr>
<td>8 h</td>
<td>6</td>
<td>20 (14:86)</td>
<td>74 (82:18)</td>
<td>23:77</td>
<td>21:79</td>
<td></td>
</tr>
</tbody>
</table>
were virtually the same. This is why it was concluded that equilibrium between 5e:6e was attained in a range of time of 5-6 h (22:78). The changes of yields between 5e and 6e from the early stage of this reaction indicated 6e was produced from 5e. The equilibrium between 6e:7e was also attained in a range of time of 5-6 h (22:78).

5e: 31P NMR (160 MHz, CD2Cl2) δ 27.5 (d, Jp-P = 40 Hz, Jp-P = 3836 Hz), 30.5 (d, Jp-P = 40 Hz, Jp-P = 3705 Hz). cis-6e: 31P NMR (160 MHz, CD2Cl2) δ 15.7 (d, Jp-P = 19 Hz, the value of Jp-P was not able to read because of low intensity), 17.5 (d, Jp-P = 19 Hz, the value of Jp-P was not able to read because of low intensity). trans-6e: 31P NMR (160 MHz, CD2Cl2) δ 17.1 (s, Jp-P = 3205 Hz). syn-7e: 31P NMR (160 MHz, CD2Cl2) δ 14.5 (s, Jp-P = 4138 Hz). anti-7e: 31P NMR (160 MHz, CD2Cl2) δ 16.1 (s, Jp-P = 4019 Hz).

The Reaction of (E)-MeC(H)=CH-C(O)SC6H4-p-Me (4f) with 2 in C6D6 (run 3, Table 1): The 31P NMR spectrum showed the formation of 5f, trans-6f and 7f. The reaction time, the yields of 5f, trans-6f and 7f, and the ratios of 5f:trans-6f and trans-6f:7f at the time are shown in Table S11. Although the ratio of 5f:trans-6f after 20 min (61:39) was different from that after 40 min (57:43), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between 5f:trans-6f was attained within 40 min (57:43). The equilibrium between trans-6f:7f was also attained within 40 min (7:93).

5f: 31P NMR (160 MHz, C6D6) δ 29.6 (d, Jp-P = 44 Hz, Jp-P = 4210 Hz), 30.7 (d, Jp-P = 44 Hz, Jp-P = 3376 Hz). trans-6f: 31P NMR (160 MHz, C6D6) δ 17.1 (s, Jp-P = 3310 Hz). syn-7f: 31P NMR (160 MHz, C6D6) δ 15.3 (s, Jp-P = 4208 Hz). anti-7f: 31P NMR (160 MHz, C6D6) δ 17.1 (s, Jp-P = 4083 Hz).

The Reaction of 4f with 2 in CD2Cl2 (run 4, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 1 h. The 31P NMR spectrum showed the formation of 5f, trans-6f and 7f. The reaction time, the yields of 5f, trans-6f and 7f, and the ratios of 5f:trans-6f and trans-6f:7f at the time are shown in Table S12. Although the ratio of 5f:trans-6f after 20 min (21:79) was different from that after 40 min (17:83), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between 5f:trans-6f was attained within 40 min (17:83). The equilibrium between trans-6f:7f was also attained within 40 min (20:80).

5f: 31P NMR (160 MHz, CD2Cl2) δ 29.0 (d, Jp-P = 43 Hz, the value of Jp-P was not able to read because of low intensity), 30.1 (d, Jp-P = 43 Hz, the value of Jp-P was not able to read...
because of low intensity). **trans-6f**: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 17.8 (s, $J_{P,P} = 3313$ Hz). **syn-7f**: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 15.4 (s, $J_{P,P} = 4158$ Hz). **anti-7f**: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 17.4 (s, $J_{P,P} = 4027$ Hz).

### The Reaction of H$_2$C=C(n- C$_6$H$_{13}$)C(O)SC$_6$H$_4$-p-Me (4g) with 2 in C$_6$D$_6$ (run 5, Table 1):

Automatic measurement program system has been used to continuously monitor the reaction for 13 h. The $^{31}$P NMR spectrum showed the formation of $5g$, **trans-6g** and **7g**. Selective information about the reaction time, the yields of $5g$, **trans-6g** and **7g**, and the ratios of $5g$:**trans-6g** and **trans-6g**:**7g** at the time are shown in Table S13. Although the ratio of $5g$:**trans-6g** after 9 h (81:19) was different from that after 10 h (78:22), those after 10 h and 13 h were virtually the same. This is why it was concluded that equilibrium between $5g$:**trans-6g** was attained in a range of time of 9-10 h (78:22). These data also demonstrated that **6g** was produced from $5g$. On the other hand, equilibrium between **trans-6g**:**7g** was attained in a range of time of 3-6 h (7:93).

**5g**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 27.5 (d, $J_{P,P} = 40$ Hz, $J_{P,T} = 3863$ Hz), 30.5 (d, $J_{P,P} = 40$ Hz, $J_{P,T} = 3669$ Hz). **trans-6g**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.2 (s, $J_{P,T} = 3312$ Hz). **syn-7g**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 14.6 (s, $J_{P,T} = 4177$ Hz). **anti-7g**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.3 (s, $J_{P,T} = 4124$ Hz).

### The Reaction of (E)-n-HexC(H)=CHC(O)SC$_6$H$_4$-p-Me (4h) with 2 in C$_6$D$_6$ (run 6, Table 1):

The $^{31}$P NMR spectrum showed the formation of $5h$, **trans-6h** and **7h**. The reaction time, the yields of $5h$, **trans-6h** and **7h**, and the ratios of $5h$:**trans-6h** and **trans-6h**:**7h** at the time are shown in Table S14. Although the ratio of $5h$:**trans-6h** after 20 min (52:48) was different from that after 40 min (46:54), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between $5h$:**trans-6h** was attained within 40 min (46:54). The equilibrium between **trans-6h**:**7h** was also attained within 40 min (9:91).

**5h**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 29.8 (d, $J_{P,P} = 44$ Hz, $J_{P,T} = 3863$ Hz), 30.7 (d, $J_{P,P} = 44$ Hz, $J_{P,T} = 3669$ Hz). **trans-6h**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 17.1 (s, $J_{P,T} = 3318$ Hz). **syn-7h**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 15.2 (s, $J_{P,T} = 4212$ Hz). **anti-7h**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 17.3 (s, $J_{P,T} = 4105$ Hz).
The Reaction of $\text{H}_2\text{C} = \text{C}(i\text{-Pr})\text{C}(\text{O})\text{-SC}_6\text{H}_4p\text{-Me}$ (4i) with 2 in $\text{C}_6\text{D}_6$
(run 7, Table 1): Automatic measurement program system has been used to continuously monitor the reaction for 71 h. The $^{31}\text{P}$ NMR spectrum showed the formation of 5i, trans-6i and 7i. Selective information about the reaction time, the yields of 5i, trans-6i and 7i, and the ratios of 5i:trans-6i and trans-6i:7i at the time are shown in Table S15. Although the ratio of 5i:trans-6i after 52 h (82:18) was different from that after 55 h (81:19), those after 55 h and 71 h were virtually the same. This is why it was concluded that equilibrium between 5i:trans-6i was attained in a range of time of 10-15 h (6:94).

5i: $^{31}\text{P}$ NMR (160 MHz, $\text{C}_6\text{D}_6$) $\delta$ 26.8 (d, $J_{\text{P-P}} = 37$ Hz, $J_{\text{P-L}} = 3867$ Hz), 30.2 (d, $J_{\text{P-P}} = 37$ Hz, $J_{\text{P-L}} = 3867$ Hz). trans-6i: $^{31}\text{P}$ NMR (160 MHz, $\text{C}_6\text{D}_6$) $\delta$ 15.8 (s, $J_{\text{P-L}} = 3299$ Hz). syn-7i: $^{31}\text{P}$ NMR (160 MHz, $\text{C}_6\text{D}_6$) $\delta$ 16.3 (s, $J_{\text{P-L}} = 4208$ Hz). anti-7i: $^{31}\text{P}$ NMR (160 MHz, $\text{C}_6\text{D}_6$) $\delta$ 16.3 (s, $J_{\text{P-L}} = 4114$ Hz).

The Reaction of $\text{H}_2\text{C} = \text{C}(\text{Ph})\text{C}(\text{O})\text{-SC}_6\text{H}_4p\text{-Me}$ (4j) with 2 in $\text{C}_6\text{D}_6$
(run 8, Table 1): Automatic measurement program system has been used to continuously monitor the reaction for 20 h. The $^{31}\text{P}$ NMR spectrum showed the formation of 5j, trans-6j and 7j. Selective information about the reaction time, the yields of 5j, trans-6j and 7j, and the ratios of 5j:trans-6j and trans-6j:7j at the time are shown in Table S16. Although the ratio of 5j:trans-6j after 14 h (72:28) was different from that after 15 h (71:29), those after 15 h and 20 h were virtually the same. This is why it was concluded that equilibrium between 5j:trans-6j was attained in a range of time of 14-15 h (71:29). The changes of yields between 5j and 6j from the early stage of this reaction indicated 6j was produced from 5j. On the other hand, the equilibrium between trans-6j:7j was attained in a range of time of 9-10 h (9:91).
**5j**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 26.6 (d, $J_{P,P}$ = 40 Hz, $J_{P,P}$ = 4013 Hz), 30.1 (d, $J_{P,P}$ = 40 Hz, $J_{P,P}$ = 3696 Hz). **trans-6j**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 16.1 (s, $J_{P,P}$ = 3259 Hz). **syn-7j**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 14.6 (s, $J_{P,P}$ = 4141 Hz). **anti-7j**: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 16.4 (s, $J_{P,P}$ = 4081 Hz).

The Reaction of 4j with 2 Using 4.3
Equivalent of 4j in C$_6$D$_6$ (run 9, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 20 h. The $^{31}$P NMR spectrum showed the formation of 5j, trans-6j and 7j. Selective information about the reaction time, the yields of 5j, 6j and 7j, and the ratios of 5j:trans-6j and trans-6j:7j at the time are shown in Table S17. The equilibrium between 5j and trans-6j was attained in a range of time of 13-14 h (18:82). On the other hand, the equilibrium between trans-6j and 7j was attained in a range of time of 7-8 h (9:81). The changes of yields between 5j and 6j from the early stage of this reaction indicated 6j was produced from 5j. On the other hand, the equilibrium between 5j:6j was attained in a range of time of 14-15 h (68:32). On the other hand, the equilibrium between 5j and trans-6j was attained in a range of time of 16-17 h (53:47). The changes of yields between 5j and 6j from the early stage of this reaction indicated 6j was produced from 5j. On the other hand, the equilibrium between 5j:6j was attained in a range of time of 13-14 h (18:82).

The Reaction of 4j with 2 in CD$_2$Cl$_2$
(run 10, Table 1): Automatic measurement program system has been used to continuously monitor the reaction for 20 h. The $^{31}$P NMR spectrum showed the formation of 5j, 6j and 7j. Selective information about the reaction time, the yields of 5j, 6j and 7j, and the ratios of 5j:6j and 6j:7j at the time are shown in Table S18. Although the ratio of 5j:6j after 16 h (53:47) was different from that after 17 h (50:50), those after 17 h and 20 h were virtually the same. This is why it was concluded that equilibrium between 5j:6j was attained in a range of time of 16-17 h (50:50). The changes of yields between 5j and 6j from the early stage of this reaction indicated 6j was produced from 5j. On the other hand, the equilibrium between 5j:6j was attained in a range of time of 13-14 h (18:82).

**5j**: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) δ 25.9 (d, $J_{P,P}$ = 38 Hz, $J_{P,P}$ = 4037 Hz), 29.5 (d, $J_{P,P}$ = 38 Hz, $J_{P,P}$ = 4081 Hz).
Hz, $J_{Pr-P} = 3516$ Hz). cis-6j: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 15.2 (d, $J_{Pr-P} = 20$ Hz, the value of $J_{Pr-P}$ was not able to read because of low intensity), 17.2 (d, $J_{Pr-P} = 20$ Hz, the value of $J_{Pr-P}$ was not able to read because of low intensity). trans-6j: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 16.4 (s, $J_{Pr-P} = 3241$ Hz). syn-7j: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 14.3 (s, $J_{Pr-P} = 4079$ Hz). anti-7j: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 16.1 (s, $J_{Pr-P} = 3964$ Hz).

The Reaction of (E)-PhC(H)=CH-C(O)SC$_6$H$_4$-p-Me (4k) with 2 in C$_6$D$_6$ (run 11, Table 1): The $^{31}$P NMR spectrum showed the formation of 5k, trans-6k and 7k. Selective information about the reaction time, the yields of 5k, trans-6k and 7k, and the ratios of 5k:trans-6k and trans-6k:7k at the time are shown in Table S19. Although the ratio of 5k:trans-6k after 20 min (91:9) was different from that after 40 min (89:11), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between 5k:trans-6k was attained within 40 min (89:11). The equilibrium between trans-6k:7k was also attained within 40 min (8:92).

5k: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 27.1 (d, $J_{Pr-P} = 38$ Hz, $J_{Pt-P} = 4134$ Hz), 27.8 (d, $J_{Pr-P} = 38$ Hz, $J_{Pt-P} = 3591$ Hz). trans-6k: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.8 (s, $J_{Pt-P} = 3281$ Hz). syn-7k: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 15.0 (s, $J_{Pt-P} = 4171$ Hz). anti-7k: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.8 (s, $J_{Pt-P} = 4022$ Hz).

The Reaction of 4k with 2 Using 4.8 Equivalent of 4k in C$_6$D$_6$ (run 12, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 1 h. The $^{31}$P NMR spectrum showed the formation of 5k, trans-6k and 7k. Selective information about the reaction time, the yields of 5k, trans-6k and 7k, and the ratios of 5k:trans-6k and trans-6k:7k at the time are shown in Table S20. The equilibria between 5k and trans-6k, and trans-6k and 7k were attained within 40 min (91:9 and 7:93). When this result was compared with that of Table S20, it was obvious that the time required for reaching the equilibrium was not affected by the excess amount of 4k.

The Reaction of 4k with 2 in CD$_2$Cl$_2$ (run 13, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 3 h. The $^{31}$P NMR spectrum showed the formation of 5k, trans-6k and 7k. Selective information about the reaction time, the yields of 5k, trans-6k and 7k, and the ratios of 5k:trans-6k and trans-6k:7k at the time are shown in Table S21. The ratio of 5k:trans-6k after 40 min (70:30) and 3 h (69:31) were virtually the same. This is why it was concluded that equilibrium between 5k...
and trans-6k was attained within 40 min (70:30). On the other hand, the equilibrium between trans-6k and 7k was attained in a range of time of 60-80 min (15:85).

5k: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 26.6 (d, $J_{P-P} = 37$ Hz, $J_{P-W,} = 4168$ Hz), 27.1 (d, $J_{P-P} = 37$ Hz, $J_{P-W} = 3572$ Hz). trans-6k: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 17.6 (s, $J_{P-P} = 3280$ Hz). syn-7k: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 15.3 (s, $J_{P-P} = 4133$ Hz). anti-7k: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 17.4 (s, $J_{P-P} = 3977$ Hz).

The Reaction of 4f with 2 in toluene-$d_8$ at Low Temperature (Eq. 4): Into a dry Pyrex NMR tube were added 2 (15.8 mg, 0.021 mmol), 4f (13.2 mg, 0.069 mmol) and S=P(C$_6$H$_4$OMe-p)$_3$ (1.3 mg, 0.0034 mmol). Then ca. 0.5 mL of toluene-$d_8$ was transferred by the freeze-pump-thaw method. The $^3$P NMR spectrum showed the formation of 5f, trans-6f and 7c. These results clearly showed that 6f was formed from 5f.

5f: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 30.2 (d, $J_{P-P} = 44$ Hz, $J_{P-W} = 4204$ Hz), 31.5 (d, $J_{P-P} = 44$ Hz, $J_{P-W} = 3377$ Hz). trans-6f: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 17.9 (d, $J_{P-P} = 21$ Hz, the value of $J_{P-W}$ was not able to read because of low intensity), 19.1 (d, $J_{P-P} = 21$ Hz, the value of $J_{P-W}$ was not able to read because of low intensity). syn-7f: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 15.9 (s, $J_{P-P} = 4213$ Hz). anti-7f: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 17.8 (s, $J_{P-P} = 4050$ Hz).

The Reaction of 4k with 2 in toluene-$d_8$ at Low Temperature (Eq. 5). Into a dry Pyrex NMR tube were added 2 (15.1 mg, 0.020 mmol), 4k (5.7 mg, 0.022 mmol) and S=P(C$_6$H$_4$OMe-p)$_3$ (0.9 mg, 0.0023 mmol). Then ca. 0.5 mL of toluene-$d_8$ was transferred by the freeze-pump-thaw method. The $^3$P NMR spectrum showed the formation of 5k, 6k and 7k. These results clearly showed that 5k was kinetic product, which isomerized to cis-6k then trans-6k and 7k.

5k: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 27.2 (d, $J_{P-P} = 37$ Hz, $J_{P-W} = 4124$ Hz), 28.1 (d, $J_{P-P} = 37$ Hz, $J_{P-W} = 3597$ Hz). cis-6k: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 17.1 (d, $J_{P-P} = 21$ Hz, the value of $J_{P-W}$ was not able to read because of low intensity), 19.1 (d, $J_{P-P} = 21$ Hz, the value of $J_{P-W}$ was not able to read because of low intensity). trans-6k: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 17.6 (s, $J_{P-P} = 3277$ Hz). syn-7k: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 15.8 (s, $J_{P-P} = 4189$ Hz). anti-7k: $^3$P NMR (160 MHz, toluene-$d_8$) $\delta$ 17.5 (s, the value of $J_{P-W}$ was not able to read because of low intensity).
The Half-Life of the Reaction of Pt[H₂C=C(OMe)C(O)SC₆H₄-p-NO₂](PPh₃)₂ (5I) to trans-Pt[C(O)C(OMe)=CH₂]-(SC₆H₄-p-NO₂)(PPh₃)₂ (6I) in C₆D₆ (run 1, Table 2): The ³¹P NMR spectrum showed the formation of 5I and 6I. The reaction time (the average of acquisition time), and the yields of 5I and 6I at the time were: 20 min, 75%, 25% (cis:trans = 13:87); 30 min, 62%, 38% (cis:trans = 7:93); 40 min, 51%, 49% (cis:trans = 4:96); 50 min, 42%, 57% (cis:trans = 3:97); 60 min, 35%, 64% (cis:trans = 3:97); 70 min, 29%, 71% (cis:trans = 3:97); 80 min, 24%, 76% (cis:trans = 1:99); 120 min, 11%, 89% (trans only); 180 min, 4%, 96% (trans only); 6 h, n.d., >99% (trans only). The consumption rate of 5I obeyed the first-order kinetics (Figure S1) and the half-life was calculated to be 38 min.

5I: ³¹P NMR (160 MHz, C₆D₆) δ 27.6 (d, Jₚ-P = 38 Hz, Jₚ-P = 3863 Hz), 30.6 (d, Jₚ-P = 38 Hz, Jₚ-P = 3683 Hz). cis-6I: ³¹P NMR (160 MHz, C₆D₆) δ 14.5 (d, Jₚ-P = 18 Hz, the value of Jₚ-P was not able to read because of low intensity), 17.9 (d, Jₚ-P = 18 Hz, the value of Jₚ-P was not able to read because of low intensity). trans-6I: ³¹P NMR (160 MHz, C₆D₆) δ 15.1 (s, Jₚ-P = 3228 Hz).

The Half-Life of the Reaction of 5I to 6I Using 4.5 Equivalent of 4I in C₆D₆ (run 2, Table 2): The ³¹P NMR spectrum showed the formation of 5I and 6I. The reaction time (the average of acquisition time), and the yields of 5I and 6I at the time were: 12 min, 82%, 18% (cis:trans = 19:81); 20 min, 72%, 28% (cis:trans = 9:91); 30 min, 60%, 40% (cis:trans = 5:95); 40 min, 50%, 50% (cis:trans = 2:98); 50 min, 41%, 59% (cis:trans = 4:96); 60 min, 33%, 67% (cis:trans = 3:97); 70 min, 27%, 73% (trans only); 80 min, 22%, 78% (trans only); 120 min, 12%, 88% (trans only); 180 min, 3%, 97% (trans only); 9 h, n.d., >99% (trans only). The consumption rate of 5I obeyed the first-order kinetics (Figure S2) and the half-life was calculated to be 36 min. The present result did not contradict the idea that the transformation from 5I to 6I was a unimolecular process.
The Half-Life of the Reaction of 5l to 6l in CD₂Cl₂ (run 3, Table 2): The ³¹P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 10 min, 69%, 30% (cis:trans = 67:33); 20 min, 44%, 54% (cis:trans = 42:58); 30 min, 29%, 70% (cis:trans = 30:70); 40 min, 17%, 81% (cis:trans = 20:80); 50 min, 12%, 87% (cis:trans = 12:88); 60 min, 7%, 92% (cis:trans = 9:91); 70 min, 4%, 94% (cis:trans = 7:93); 80 min, 2%, 96% (cis:trans = 6:94); 2 h, n.d., 99% (cis:trans = 3:97). The consumption rate of 5l obeyed the first-order kinetics (Figure S3) and the half-life was calculated to be 14 min.

5l: ³¹P NMR (160 MHz, CD₂Cl₂) δ 27.2 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ₁ = 4025 Hz), 30.0 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ₁ = 3667 Hz). cis-6l: ³¹P NMR (160 MHz, CD₂Cl₂) δ 14.1 (d, Jₚ₋ₚ = 18 Hz, Jₚ₋ₚ₁ = 1336 Hz), 17.0 (d, Jₚ₋ₚ = 18 Hz, Jₚ₋ₚ₁ = 3765 Hz). trans-6l: ³¹P NMR (160 MHz, CD₂Cl₂) δ 15.1 (s, Jₚ₋ₚ = 3225 Hz).

The Half-Life of the Reaction of 5l to 6l in acetone-­­d₆ (run 4, Table 2): The ³¹P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 3.0 min, 92%, 8% (cis:trans = 88:12); 4.0 min, 89%, 11% (cis:trans = 68:32); 5.0 min, 85%, 15% (cis:trans = 60:40); 6.0 min, 81%, 19% (cis:trans = 59:41); 8.0 min, 76%, 24% (cis:trans = 49:51); 18 min, 54%, 46% (cis:trans = 27:63); 20 min, 50%, 50% (cis:trans = 28:72); 30 min, 34%, 67% (cis:trans = 16:84); 40 min, 25%, 75% (cis:trans = 11:89); 50 min, 17%, 83% (cis:trans = 7:93); 60 min, 9%, 91% (cis:trans = 4:96); 70 min, 6%, 94% (cis:trans = 4:96). The consumption rate of 5l obeyed the first-order kinetics (Figure S4) and the half-life was calculated to be 19 min.

5l: ³¹P NMR (160 MHz, acetone-d₆) δ 27.8 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ₁ = 3882 Hz), 30.8 (d, Jₚ₋ₚ = 36 Hz, Jₚ₋ₚ₁ = 3672 Hz). cis-6l: ³¹P NMR (160 MHz, acetone-d₆) δ 15.7 (d, Jₚ₋ₚ = 19 Hz, the value of Jₚ₋ₚ₁ was not able to read because of low intensity), 19.3 (d, Jₚ₋ₚ = 19 Hz, the value of Jₚ₋ₚ₁ was not able to read because of low intensity). trans-6l: ³¹P NMR (160 MHz, acetone-d₆) δ 15.8 (s, Jₚ₋ₚ = 3243 Hz).
The Half-Life of the Reaction of 5l to 6l in THF-\textit{d}_8 (run 5, Table 2): The $^{31}$P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 4.0 min, 98%, 2% (\textit{trans} only); 5.0 min, 96%, 4% (\textit{trans} only); 6.0 min, 95%, 5% (\textit{trans} only); 8.0 min, 90%, 10% (\textit{cis:trans} = 31/69); 9.0 min, 89%, 11% (\textit{cis:trans} = 30:70); 20 min, 74%, 26% (\textit{cis:trans} = 15:85); 30 min, 63%, 37% (\textit{cis:trans} = 10:90); 40 min, 52%, 48% (\textit{cis:trans} = 8:92); 50 min, 40%, 60% (\textit{cis:trans} = 5:95); 60 min, 34%, 66% (\textit{trans} only); 70 min, 28%, 72% (\textit{trans} only). The consumption rate of 5l obeyed the first-order kinetics (Figure S5) and the half-life was calculated to be 36 min. **5l:** $^{31}$P NMR (160 MHz, THF-\textit{d}_8) $\delta$ 29.0 (d, $J_{PP} = 37$ Hz, $J_{PT} = 3983$ Hz), 32.0 (d, $J_{PP} = 37$ Hz, $J_{PT} = 3678$ Hz). **cis-6l:** $^{31}$P NMR (160 MHz, THF-\textit{d}_8) $\delta$ 16.0 (d, $J_{PP} = 18$ Hz, the value of $J_{PT}$ was not able to read because of low intensity), 19.2 (d, $J_{PP} = 18$ Hz, the value of $J_{PT}$ was not able to read because of low intensity). **trans-6l:** $^{31}$P NMR (160 MHz, THF-\textit{d}_8) $\delta$ 16.5 (s, $J_{PT} = 3224$ Hz).

The Half-Life of the Reaction of Pt[(\textit{E})-MeC(=CHC(0)SC$_6$H$_4$-p-NO$_2$](PPh$_3$)$_2$ (5m) to Pt[CrC(=CH(Me)-(\textit{E})]-SC$_6$H$_4$-p-NO$_2$](PPh$_3$)$_2$ (6m) in C$_6$D$_6$ (run 6, Table 2): Into a dry Pyrex NMR tube were added 2 (15.0 mg, 0.020 mmol), 4m (4.9 mg, 0.022 mmol), S=P(C$_6$H$_4$OMe-p)$_3$ (1.0 mg, 0.0027 mmol) and C$_6$D$_6$ (0.5 mL) under N$_2$ atmosphere. Then the reaction was monitored by $^{31}$P and $^1$H NMR spectrum at 25 °C. The reaction time (the average of acquisition time), and the yields of 5m and \textit{trans}-6m at the time were 2.0 min, 8.3%, 85.7%; 2.5 min, 8.2%, 90.0%; 3.0 min, 7.8%, 92.2%; 3.5 min, 7.2%, 92.8%; 4.0 min, 5.5%, 94.5%; 4.5 min, 4.8%, 95.2%; 5.0 min, 3.6%, 96.4%; 5.5 min, 3.0%, 93.2%; 6.0 min, 2.7%, 96.8%; 6.5 min, 2.2%, 90.5%; 7.0 min, n.d., >99%. The consumption rate of 5m obeyed the first-order kinetics (Figure S6) and the half-life was calculated to be ca. 2.1 min. All reactions shown in Table 2 were carried out similarly. **5m:** $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 29.1 (d, $J_{PP} = 42$ Hz, the value of $J_{PT}$ was not able to read because of low intensity), 30.3 (d, $J_{PP} = 42$ Hz, the value of $J_{PT}$ was not able to read because of low intensity). **trans-6m:** $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.3 (s, $J_{PT} = 3268$ Hz).
The Half-Life of the Reaction of 5m to 6m in CD$_2$Cl$_2$ (run 7, Table 2): The $^3$P NMR spectrum showed the formation of 5m and trans-6m. The reaction time (the average of acquisition time), and the yields of 5m and trans-6m at the time were 2.0 min, 4.6%, 95.4%; 2.5 min, 3.6%, 96.4%; 3.0 min, 3.3%, 96.7%; 3.5 min, 2.9%, 97.1%; 4.0 min, 2.6%, 97.4%; 4.5 min, 2.5%, 97.5%; 5.0 min, 2.3%, 97.7%; 5.5 min, 2.2%, 97.8%; 6.0 min, 1.8%, 98.2%; 6.5 min, 1.6%, 98.4%; 7.0 min, n.d., >99%. The consumption rate of 5m obeyed the first-order kinetics (Figure S7) and the half-life was calculated to be ca. 3.3 min.

5m: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) δ 28.7 (d, $J_{pp} = 40$ Hz, the value of $J_{pt-p}$ was not able to read because of low intensity), 29.7 (d, $J_{pp} = 40$ Hz, the value of $J_{pt-p}$ was not able to read because of low intensity). trans-6m: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) δ 16.3 (s, $J_{pt-p} = 3258$ Hz).

The Half-Life of the Reaction of Pt[H$_2$C=C(n-Hex)C(O)SC$_6$H$_4$p-NO$_2$](PP$_3$)$_2$ (5n) to trans-Pt[C(O)C(n-Hex)=CH$_2$]-SC$_6$H$_4$p-NO$_2$)(PP$_3$)$_2$ (6n) in C$_6$D$_6$ (run 8, Table 2): The $^3$P NMR spectrum showed the formation of 5n and trans-6n. The reaction time (the average of acquisition time), and the yields of 5n and trans-6n at the time were 10 min, 89%, 11%; 20 min, 74%, 24%; 30 min, 62%, 36%; 40 min, 52%, 47%; 50 min, 44%, 54%; 60 min, 38%, 60%; 70 min, 31%, 67%; 80 min, 28%, 72%; 120 min, 14%, 84%; 180 min, 5%, 93%. The consumption rate of 5n obeyed the first-order kinetics (Figure S8) and the half-life was calculated to be 40 min.

5n: $^3$P NMR (160 MHz, C$_6$D$_6$) δ 27.2 (d, $J_{pp} = 37$ Hz, $J_{pt-p} = 3898$ Hz), 30.3 (d, $J_{pp} = 37$ Hz, $J_{pt-p} = 3692$ Hz). trans-6n: $^3$P NMR (160 MHz, C$_6$D$_6$) δ 14.9 (s, $J_{pt-p} = 3358$ Hz).

The Half-Life of the Reaction of Pt[(E)-(n-Hex)C(H)=CHC(O)SC$_6$H$_4$p-NO$_2$]-PP$_3$)$_2$ (5o) to trans-Pt[(E)(C(O)C(n-Hex)=CH(n-Hex)-(E)](SC$_6$H$_4$p-NO$_2$)(PP$_3$)$_2$ (6o) in C$_6$D$_6$ (run 9, Table 2): The $^3$P NMR spectrum showed the formation of 5o and trans-6o. The reaction time (the average of acquisition time), and the yields of 5o and trans-6o at the time were 2 min, 29%, 71%; 2.5 min, 24%, 77%; 3 min, 21%, 79%; 3.5 min,
20%, 80%; 4 min, 18%, 82%; 4.5 min, 14%, 86%; 5 min, 13%, 87%; 6 min, 10%, 90%; 7 min, 9%, 91%; 8 min, 7%, 93%; 20 min, nd, > 99%. The consumption rate of 5o obeyed the first-order kinetics (Figure S9) and the half-life was calculated to be 3.0 min.

5o: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 29.3 (d, $J_{p\_p} = 40$ Hz, the value of $J_{p\_t}$ was not able to read because of low intensity), 30.3 (d, $J_{p\_p} = 40$ Hz, the value of $J_{p\_t}$ was not able to read because of low intensity). trans-6o: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 16.29 (s, $J_{p\_p} = 3277$ Hz).

The Half-Life of the Reaction of Pt[H$_2$C=C(i-Pr)C(0)SC$_6$H$_4$-p-NO$_2$](PPh$_3$)$_2$ (5p) to Pt[C(0)C(i-Pr)=CH$_2$](SC$_6$H$_4$-p-NO$_2$)-(PPh$_3$)$_2$ (6p) in C$_6$D$_6$ (run 10, Table 2): The $^{31}$P NMR spectrum showed the formation of 5p and trans-6p. The reaction time (the average of acquisition time), and the yields of 5p and trans-6p at the time were 10 min, 90%, 10%; 20 min, 78%, 21%; 30 min, 66%, 32%; 40 min, 57%, 42%; 50 min, 48%, 49%; 60 min, 42%, 52%; 70 min, 34%, 63%; 80 min, 29%, 68%; 24 h, n.d., 98%. The consumption rate of 5p obeyed the first-order kinetics (Figure S10) and the half-life was calculated to be 43 min.

5p: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 26.5 (d, $J_{p\_p} = 35$ Hz, $J_{p\_t} = 3909$ Hz), 30.1 (d, $J_{p\_p} = 35$ Hz, $J_{p\_t} = 3697$ Hz). trans-6p: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 14.8 (s, $J_{p\_p} = 3192$ Hz).

The Half-Life of the Reaction of 5p to 6p
Using 5.0 Equivalent of 4m in C$_6$D$_6$ (run 11, Table 2): The $^{31}$P NMR spectrum showed the formation of 5p and trans-6p. The reaction time (the average of acquisition time), and the yields of 5p and trans-6p at the time were 5 min, 93%, 7%; 6 min, 92%, 8%; 8 min, 88%, 10%; 10 min, 85%, 13%; 20 min, 73%, 23%; 30 min, 62%, 34%; 40 min, 54%, 42%; 50 min, 45%, 50%; 60 min, 38%, 57%; 70 min, 32%, 63%; 80 min, 28%, 67%. The consumption rate of 5p obeyed the first-order kinetics (Figure S11) and the half-life was calculated to be 43 min, showing that the transformation from 5p to 6p was a unimolecular process.

The Half-Life of the Reaction of 5p to 6p in CD$_2$Cl$_2$ (run 12, Table 2): The $^{31}$P NMR spectrum showed the formation of 5p and 6p. The reaction time (the average of acquisition time), and the yields of 5p and 6p at the time were 4 min, 72%, 28% (cis:trans = 69:31); 5 min, 63%, 37% (cis:trans = 60:40); 6 min, 60%, 40% (cis:trans = 56:44); 7 min, 56%, 44% (cis:trans = 53:47); 8 min, 51%, 47% (cis:trans = 48:52); 10 min, 43%, 54% (cis:trans =
41:59); 20 min, 15%, 79% (cis:trans = 18:82); 30 min, 5%, 92% (cis:trans = 10:90); 40 min, n.d., 97% (cis:trans = 5:95).

The consumption rate of 5p obeyed the first-order kinetics (Figure S12) and the half-life was calculated to be 6.8 min.

5p: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) δ 26.0 (d, $J_{P-P} = 35$ Hz, $J_{P-P} = 3938$ Hz), 29.8 (d, $J_{P-P} = 35$ Hz, $J_{P-P} = 3684$ Hz). cis-6p: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) δ 14.2 (d, $J_{P-P} = 19$ Hz, $J_{P-P} = 1311$ Hz), 17.3 (d, $J_{P-P} = 19$ Hz, $J_{P-P} = 3824$ Hz).

trans-6p: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) δ 14.7 (s).

The Half-Life of the Reaction of Pt[H$_2$C=C(Ph)C(0)SC$_6$H$_4$-p-NO$_2$](PPh$_3$)$_2$ (5q) to Pt[C(0)C(Ph)=CH$_2$]-SC$_6$H$_4$-p-NO$_2$)(PPh$_3$)$_2$ (6q) in C$_6$D$_6$ (run 13, Table 2): The $^{31}$P NMR spectrum showed the formation of 5q and trans-6q. The reaction time (the average of acquisition time) and the yields of 5q and trans-6q at the time were 2 min, 25%, 75%; 4 min, 21%, 79%; 6 min, 15%, 85%; 8 min, 12%, 88%; 10 min, 9%, 91%; 12 min, 8%, 88%; 14 min, 7%, 88%; 37 min, n.d., >99%. The consumption rate of 5q obeyed the first-order kinetics (Figure S13) and the half-life was calculated to be 6.2 min.

5q: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 26.2 (d, the value of $J_{P-P}$ was not able to read because of low intensity of the signal), 29.9 (d, $J_{P-P} = 37$ Hz, the value of $J_{P-P}$ was not able to read because of low intensity of the signal). trans-6q: $^{31}$P NMR (160 MHz, C$_6$D$_6$) δ 14.8 (s).

The Half-Life of the Reaction of 5q to 6q in CD$_2$Cl$_2$ (run 14, Table 2): The $^{31}$P NMR spectrum showed the formation of 5q and 6q. The reaction time (the average of acquisition time), and the yields of 5q and 6q at the time were 2 min, 32%, 68% (cis:trans = 58:42); 4 min, 8%, 86% (cis:trans = 34:66); 5 min, 4%, 90% (cis:trans = 24:76); 6 min, 3%, 91% (cis:trans = 20:80); 7 min, 2%, 92% (cis:trans = 15:85); 20 min, n.d., 97% (cis:trans = 2:98). The consumption rate of 5q obeyed the first-order kinetics (Figure S14) and the half-life was calculated to be 1.2 min.
5q: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 25.7 (d, $J_{P,P} = 35$ Hz, the value of $J_{Pt,P}$ was not able to read because of low intensity of the signal), 29.2 (d, $J_{P,P} = 35$ Hz, the value of $J_{Pt,P}$ was not able to read because of low intensity of the signal). cis-6q: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 13.9 (d, $J_{P,P} = 19$ Hz, $J_{Pt,P} = 1328$ Hz), 17.1 (d, $J_{P,P} = 19$ Hz, $J_{Pt,P} = 3720$ Hz). trans-6q: $^{31}$P NMR (160 MHz, CD$_2$Cl$_2$) $\delta$ 14.6 (s, $J_{Pt,P} = 3186$ Hz).

The Half-Live of the Reaction of Pt[(E)-PhC(H)=CHC(0)SC$_6$H$_4$-p-NO$_2$](PPh$_3$)$_2$ (5r) to Pt[C(0)C(H)=CH(Ph)-(E)]-(SC$_6$H$_4$-p-NO$_2$)(PPh$_3$)$_2$ (6r) in C$_6$D$_6$ (run 15, Table 2): The $^{31}$P NMR spectrum showed the formation of 5r and trans-6r. The reaction time (the average of acquisition time), and the yields of 5r and trans-6r at the time were 10 min, 41%, 59%; 20 min, 21%, 74%; 30 min, 11%, 86%; 40 min, 4%, 92%; 50 min, 2%, 95%; 60 min, 1%, 95%; 3 h, n.d., 95%. The consumption rate of 5r obeyed the first-order kinetics (Figure S15) and the half-live was calculated to be 9.1 min.

5r: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 26.7 (d, $J_{P,P} = 36$ Hz, $J_{Pt,P} = 4178$ Hz), 27.4 (d, $J_{P,P} = 36$ Hz, $J_{Pt,P} = 3552$ Hz). trans-6r: $^{31}$P NMR (160 MHz, C$_6$D$_6$) $\delta$ 16.0 (s, $J_{Pt,P} = 3229$ Hz).

The Half-Live of the Reaction of 5r to 6r Using 4.7 Equivalent of 4r in C$_6$D$_6$ (run 16, Table 2): The $^{31}$P NMR spectrum showed the formation of 5r and trans-6r. The reaction time (the average of acquisition time), and the yields of 5r and trans-6r at the time were 10 min, 40%, 58%; 20 min, 23%, 75%; 30 min, 13%, 83%; 40 min, 6%, 86%; 50 min, 2%, 90%; 60 min, 1%, 94%; 70 min, n.d., 92%. The consumption rate of 5r obeyed the first-order kinetics (Figure S16) and the half-live was calculated to be 9.1 min. The present result did not contradict the idea that the transformation from 5r to 6r was a unimolecular process.

The Half-Live of the Reaction of 5r to 6r in CD$_2$Cl$_2$ (run 17, Table 2): The $^{31}$P NMR spectrum showed the formation of 5r and 6r. The reaction time (the average of acquisition time), and the yields of 5r and 6r at the time were 10 min, 31%, 69% (cis:trans = 1:99); 20
min, 12%, 88% (cis:trans = 2:98); 30 min, 6%, 94% (cis:trans = 2:98); 40 min, 2%, 98% (trans only); 50 min, n.d., >99% (trans only). The consumption rate of 5r obeyed the first-order kinetics (Figure S17) and the half-live was calculated to be 7.8 min.  
5r: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) δ 26.3 (d, $J_{P-P} = 35$ Hz, $J_{PT-P} = 4208$ Hz), 26.7 (d, $J_{P-P} = 35$ Hz, $J_{PT-P} = 3525$ Hz). cis-6r: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) δ 14.1 (d, $J_{P-P} = 19$ Hz, the value of $J_{PT-P}$ was not able to read because of low intensity), 17.8 (d, $J_{P-P} = 19$ Hz, the value of $J_{PT-P}$ was not able to read because of low intensity). trans-6r: $^3$P NMR (160 MHz, CD$_2$Cl$_2$) δ 16.1 (s, $J_{PT-P} = 3217$ Hz).

The Reaction of 4q with 2 in CD$_2$Cl$_2$ at Low Temperature (Eq. 6): Into a dry Pyrex NMR tube were added 2 (15.2 mg, 0.020 mmol), 4q (6.4 mg, 0.022 mmol) and S=P(C$_6$H$_4$OMe-p)$_3$ (1.1 mg, 0.0028 mmol). Then ca. 0.5 mL of CD$_2$Cl$_2$ was transferred by the freeze-pump-thaw method. The $^3$P NMR spectrum showed the formation of 5q and 6q. The reaction temperature and time (the average of acquisition time). These results clearly showed that 5q was kinetic product, which selectively isomerized to cis-6q then trans-6q.

The Half-Lives of the Reaction of 5l to 6l in C$_6$D$_6$ at 30 ºC: The $^3$P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 5 min, 90%, 10% (trans only); 6 min, 88%, 12% (trans only); 8 min, 81%, 19% (cis:trans = 11:89); 10 min, 77%, 23% (cis:trans = 9:91); 20 min, 55%, 45% (cis:trans = 4:96); 30 min, 39%, 61% (trans only); 40 min, 30%, 70% (trans only); 50 min, 21%, 79% (trans only). The consumption rate of 5l obeyed the first-order kinetics (Figure S18) and the half-live was calculated to be 21.5 min.

The Half-Lives of the Reaction of 5l to 6l in C$_6$D$_6$ at 35 ºC: The $^3$P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 5 min, 85%, 15% (trans only); 6 min, 78%, 22% (cis:trans = 13:87); 8 min, 70%, 30% (cis:trans = 7:93); 10 min, 62%, 38% (cis:trans = 8:92); 20 min, 33%, 67% (trans only); 30 min, 16%, 84% (trans only); 40 min, 8%, 92% (trans only). The consumption rate of 5l obeyed the first-order kinetics (Figure S19) and the half-live was calculated to be 7.96 min.
The Half-Life of the Reaction of 5l to 6l in C6D6 at 40 °C: The 31P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 10 min, 45%, 55% (trans only); 20 min, 14%, 86% (trans only); 27 min, 4%, 96% (trans only); 30 min, 3%, 97% (trans only). The consumption rate of 5l obeyed the first-order kinetics (Figure S20) and the half-life was calculated to be 4.97 min.

The Half-Life of the Reaction of 5l to 6l in CD2Cl2 at 30 °C: The 31P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 5 min, 77%, 23% (cis:trans = 65:35); 6 min, 73%, 27% (cis:trans = 63:37); 8 min, 64%, 36% (cis:trans = 53:47); 10 min, 56%, 44% (cis:trans = 45:55); 20 min, 25%, 75% (cis:trans = 23:77); 30 min, 11%, 89% (cis:trans = 13:87). The consumption rate of 5l obeyed the first-order kinetics (Figure S21) and the half-life was calculated to be 8.81 min.

The Half-Life of the Reaction of 5l to 6l in CD2Cl2 at 35 °C: The 31P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 5 min, 70%, 30% (cis:trans = 53:47); 6 min, 62%, 38% (cis:trans = 47:53); 8 min, 50%, 50% (cis:trans = 36:64); 10 min, 41%, 59% (cis:trans = 27:73); 20 min, 8%, 92% (cis:trans = 8:82); 30 min, n.d., >99% (cis:trans = 3:97). The consumption rate of 5l obeyed the first-order kinetics (Figure S22) and the half-life was calculated to be 6.57 min.

The Half-Life of the Reaction of 5l to 6l in CD2Cl2 at 40 °C: The 31P NMR spectrum showed the formation of 5l and 6l. The reaction time (the average of acquisition time), and the yields of 5l and 6l at the time were 6 min, 64%, 36% (cis:trans = 42:58); 7 min, 53%, 47% (cis:trans = 32:68); 8 min, 43%, 57% (cis:trans = 27:73); 9 min, 38%, 62% (cis:trans = 22:78); 10 min, 32%, 68% (cis:trans = 19:81); 11 min, 28%, 72% (cis:trans = 15:85); 12 min, 24%, 76%
(cis:trans = 13:87); 13 min, 22%, 78% (cis:trans = 12:88); 15 min, 18%, 82% (cis:trans = 10:90); 20 min, 12%, 88% (cis:trans = 7:93). The consumption rate of 5l obeyed the first-order kinetics (Figure S23) and the half-live was calculated to be 4.54 min.

The Half-Live of the Reaction of 5p to 6p in C6D6 at 30 °C: The 31P NMR spectrum showed the formation of 5p and trans-6p. The reaction time (the average of acquisition time), and the yields of 5p and trans-6p at the time were 4 min, 95%, 5%; 5 min, 93%, 7%; 6 min, 91%, 9%; 8 min, 89%, 11%; 10 min, 84%, 16%; 20 min, 66%, 34%; 30 min, 51%, 49%; 40 min, 39%, 61%; 50 min, 30%, 70%; 60 min, 23%, 77%. The consumption rate of 5p obeyed the first-order kinetics (Figure S24) and the half-live was calculated to be 27.4 min.

The Half-Live of the Reaction of 5p to 6p in C6D6 at 35 °C: The 31P NMR spectrum showed the formation of 5p and trans-6p. The reaction time (the average of acquisition time), and the yields of 5p and trans-6p at the time were 7 min, 88%, 12%; 8 min, 85%, 15%; 9 min, 81%, 19%; 10 min, 79%, 21%; 20 min, 51%, 49%; 30 min, 31%, 69%; 40 min, 20%, 80%; 50 min, 12%, 88%. The consumption rate of 5p obeyed the first-order kinetics (Figure S25) and the half-live was calculated to be 14.9 min.

The Half-Live of the Reaction of 5p to 6p in C6D6 at 40 °C: The 31P NMR spectrum showed the formation of 5p and trans-6p. The reaction time (the average of acquisition time), and the yields of 5p and trans-6p at the time were 3 min, 96%, 4%; 4 min, 88%, 12%; 5 min, 83%, 17%; 6 min, 77%, 23%; 8 min, 68%, 32%; 9 min, 64%, 36%; 18 min, 29%, 71%; 20 min, 25%, 75%; 30 min, 8%, 92%; 40 min, 4%, 96%. The consumption rate of 5p obeyed the first-order kinetics (Figure S26) and the half-live was calculated to be 8.96 min.
The Half-Live of the Reaction of 5p to 6p in CD$_2$Cl$_2$ at 30 °C: The $^{31}$P NMR spectrum showed the formation of 5p and 6p. The reaction time (the average of acquisition time), and the yields of 5p and 6p at the time were 2 min, 81%, 19% (cis:trans = 69:31); 3 min, 69%, 31% (cis:trans = 63:37); 4 min, 61%, 39% (cis:trans = 56:44); 5 min, 55%, 45% (cis:trans = 47:53); 6 min, 49%, 51% (cis:trans = 42:58); 7 min, 44%, 56% (cis:trans = 37:63); 8 min, 39%, 61% (cis:trans = 33:67); 20 min, 6%, 94% (cis:trans = 4:96). The consumption rate of 5p obeyed the first-order kinetics (Figure S27) and the half-live was calculated to be 5.94 min.

The Half-Live of the Reaction of 5p to 6p in CD$_2$Cl$_2$ at 35 °C: The $^{31}$P NMR spectrum showed the formation of 5p and 6p. The reaction time (the average of acquisition time), and the yields of 5p and 6p at the time were 3 min, 61%, 39% (cis:trans = 48:52); 4 min, 50%, 50% (cis:trans = 38:62); 5 min, 43%, 57% (cis:trans = 32:68); 6 min, 36%, 64% (cis:trans = 26:74); 7 min, 31%, 69% (cis:trans = 22:78); 8 min, 27%, 73% (cis:trans = 19:81); 20 min, n.d., >99% (cis:trans = 4:96). The consumption rate of 5p obeyed the first-order kinetics (Figure S28) and the half-live was calculated to be 4.33 min.

The Half-Live of the Reaction of 5p to 6p in CD$_2$Cl$_2$ at 40 °C: The $^{31}$P NMR spectrum showed the formation of 5p and 6p. The reaction time (the average of acquisition time), and the yields of 5p and 6p at the time were 3 min, 49%, 51% (cis:trans = 34:66); 3.5 min, 41%, 59% (cis:trans = 29:71); 4 min, 36%, 64% (cis:trans = 24:76); 5 min, 28%, 72% (cis:trans = 18:82); 6 min, 21%, 79% (cis:trans = 14:86); 7 min, 17%, 83% (cis:trans = 11:89); 8 min, 14%, 86% (cis:trans = 10:90); 20 min, n.d., >99% (cis:trans = 3:97). The consumption rate of 5p obeyed the first-order kinetics (Figure S29) and the half-live was calculated to be 2.83 min.

Activation Parameters (Table 3). Activation parameters of the transformation of 5l to 6l, 5p to 6p, and 5r to 6r were calculated by measuring the temperature dependence of reaction rates.
at the range from 25 °C - 40 °C in both C₆D₆ and CD₂Cl₂ according to the equation: \( k = (k_B T/h)\exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/(RT)] \).

**Activation Parameters of the Transformation of 5l to 6l in C₆D₆:** Reaction temperature and reaction rates were as follows: 298 K, 0.000307 s⁻¹; 303 K, 0.000538 s⁻¹; 308 K, 0.00112 s⁻¹; 313 K, 0.00233 s⁻¹.

**Activation Parameters of the Transformation of 5l to 6l in CD₂Cl₂:** Reaction temperature and reaction rates were as follows: 298 K, 0.000822 s⁻¹; 303 K, 0.00131 s⁻¹; 308 K, 0.00178 s⁻¹; 313 K, 0.00255 s⁻¹.

**Activation Parameters of the Transformation of 5p to 6p in C₆D₆:** Reaction temperature and reaction rates were as follows: 298 K, 0.000270 s⁻¹; 303 K, 0.000422 s⁻¹; 308 K, 0.000773 s⁻¹; 313 K, 0.00133 s⁻¹.

**Activation Parameters of the Transformation of 5p to 6p in CD₂Cl₂:** Reaction temperature and reaction rates were as follows: 298 K, 0.00171 s⁻¹; 303 K, 0.00194 s⁻¹; 308 K, 0.00267 s⁻¹; 313 K, 0.00408 s⁻¹.

**Activation Parameters of the Transformation of 5r to 6r in C₆D₆:** Reaction temperature and reaction rates were as follows: 293 K, 0.000633 s⁻¹; 298 K, 0.00127 s⁻¹; 303 K, 0.00171 s⁻¹; 308 K, 0.00267 s⁻¹.

**Activation Parameters of the Transformation of 5r to 6r in CD₂Cl₂:** Reaction temperature and reaction rates were as follows: 293 K, 0.000750 s⁻¹; 298 K, 0.00149 s⁻¹; 303 K, 0.00169 s⁻¹; 308 K, 0.00471 s⁻¹.

4-9. Reference and Note


Chem. 2006, 691, 1873.

(6) No interaction between $S=P(C_6H_4OMe-p)_3$ and other reagents has been confirmed during the course of the present study.


(8) The reactions were continuously monitored until the equilibria were fully-achieved.


(10) It has been already reported that the X-ray crystallographic structure of $Pt[(PhH_2CO)(O)C(H)C=CH_2](PPh_3)_2$ showed the $s$-$cis$ configuration as to $C=O$ and $C=C$ moieties. Chaloner, P. A.; Davies, S. E.; Hitchcock, P. B. J. Organomet. Chem. 1997, 527, 145.


(12) It has been reported that $\alpha,\beta$-unsaturated thioesters were employed as an excellent acceptors of Michael additions. Mazery, R. D.; Pullez, M.; López, F.; Harutyunyan, S. R.; Minnaard, A. J.; Feringa, B. L. J. Am. Chem. Soc. 2005, 127, 9966 and references therein.

Summary

In this study, the author succeeded in developing novel transition metal-catalyzed reaction of thioesters and iminosulfides with alkynes and discovering the mechanism under the reaction of α,β-unsaturated thioesters to platinum complexes. The results were summarized as follows.

In chapter 1, it was described that the intermolecular CO-retentive addition of thioesters to alkynes, which afford enone derivatives having sulfur functionality at β-position. The use of DPPE (1,2-bis-(diphenylphosphino)ethane) as a ligand is of critical importance to achieve Pd-catalyzed aroylthiolation. On the other hand, trifluoroacetylthiolation by CF$_3$C(O)SR was successfully catalyzed by Pt(PPh$_3$)$_4$, the same catalyst employed for decarbonylative arylthiolation by ArC(O)SR. The CF$_3$ group is requisite for the transformation; the reactions using Me- and CC$_1$)$_3$-substituted thioesters hardly furnished the desired products.

In chapter 2, a new synthetic method of β-sulfur functionalized 1-azadienes by the intermolecular addition reaction of iminosulfides to alkynes was successfully realized using Pd(dba)$_2$/PAR$_3$ as the catalytic system. The reaction was promoted by introducing CF$_3$ group bound to the iminocarbon probably due to the acceleration of the oxidative addition of iminosulfides to Pd-catalyst. Furthermore, the present iminothiolation could be applied to the synthesis of furan derivatives.

In chapter 3, it was revealed that one-pot syntheses of 2,3-dihydrothiopyran-4-one derivatives by Pd/Cu-catalyzed reactions of α,β-unsaturated thioesters with propargyl alcohols. The transformation successively takes place in a flask by a single operation and consists of four consecutive reactions: the Pd/Cu-catalyzed Sonogashira-type cross-coupling reaction of thioester with propargyl alcohol; the trans-addition of in situ generated thiol to alkyne moiety; an intramolecular aromatic nucleophilic substitution; and a cyclization reaction.

Finally, it was suggested that there would be two reaction pathways of the oxidative addition of α,β-unsaturated thioesters to zero-valent platinum complexes. One is the direct approach of Pt-fragment coordinated on the carbon-carbon double bond toward the carbon-sulfur bond, and the other is the attack of Pt-fragment at the vinylic β-carbon and details were summarized in chapter 4.

These new aspects revealed through this study show a great benefit in transition metal-mediated various catalytic and stoichiometric transformation using organosulfur compounds in synthetic chemistry.
List of Publications

(1) Transition-Metal-Catalyzed Regioselective Aroyl- and Trifluoroacetylthiolation of Alkynes Using Thioesters
Yasunori Minami, Hitoshi Kuniyasu, Kiyoshi Miyafuji, Nobuaki Kambe

(2) Pd-Catalyzed Regioselective Iminothiolation of Alkynes: Remarkable Effects of CF₃ Group of Iminosulfides
Yasunori Minami, Hitoshi Kuniyasu, Nobuaki Kambe
in preparation.

(3) One-Pot Syntheses of 2,3-Dihydrothiopyran-4-one Derivatives by Pd/Cu-Catalyzed Reactions of α,β-Unsaturated Thioesters with Propargyl Alcohols
Yasunori Minami, Hitoshi Kuniyasu, Nobuaki Kambe

(4) Reactions of α,β-Unsaturated Thioesters with Pt(0): Implication of Dual Mechanism Leading to the Formation of Acyl Platinum
Yasunori Minami, Tomohiro Kato, Hitoshi Kuniyasu, Jun Terao, Nobuaki Kambe
Organometallics 2006, 25, 2949-2959.
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