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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

(パラジウム及び白金錯体によるチオエステル類の炭素－硫黄結合の切断及びアルキンへの付加反応に関する研究)

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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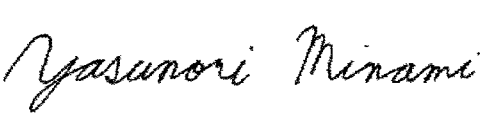
March, 2010



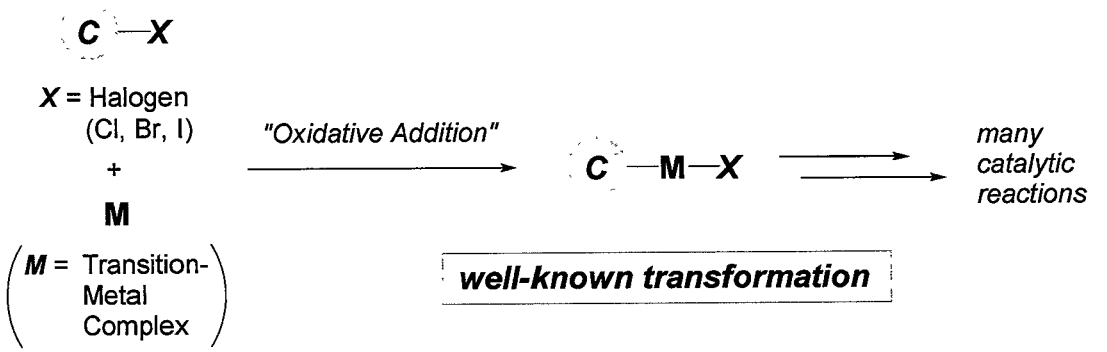
Yasunori Minami

Contents

General Introduction

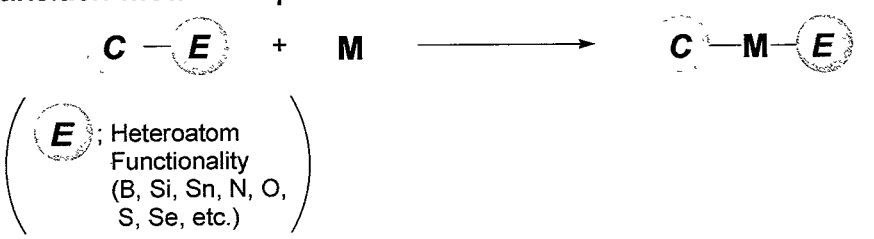
Homogeneous transition metal-catalyzed reaction is one of the most important subjects in synthetic chemistry for the facile and accurate construction of a wide range of organic frameworks. It is well-known that carbon-halogen bonds are readily cleaved by the transition metal complexes, which normally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

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



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-

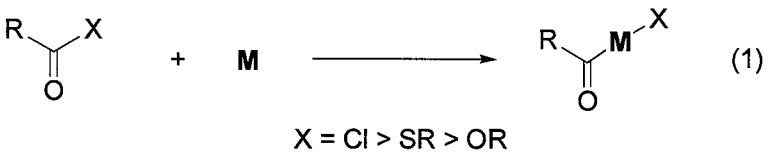
Scheme 2. Oxidative Addition of Carbon-Heteroatom Bond to Transition-Metal Complex



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,[1-2] -nitrogen,[3] -silicon,[4] -tin[5] and -boron[6] bonds were employed for this purpose.

The author aimed at the development of new catalytic insertions of alkynes into carbon-sulfur bond employing thioesters ($R^1C(O)$-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

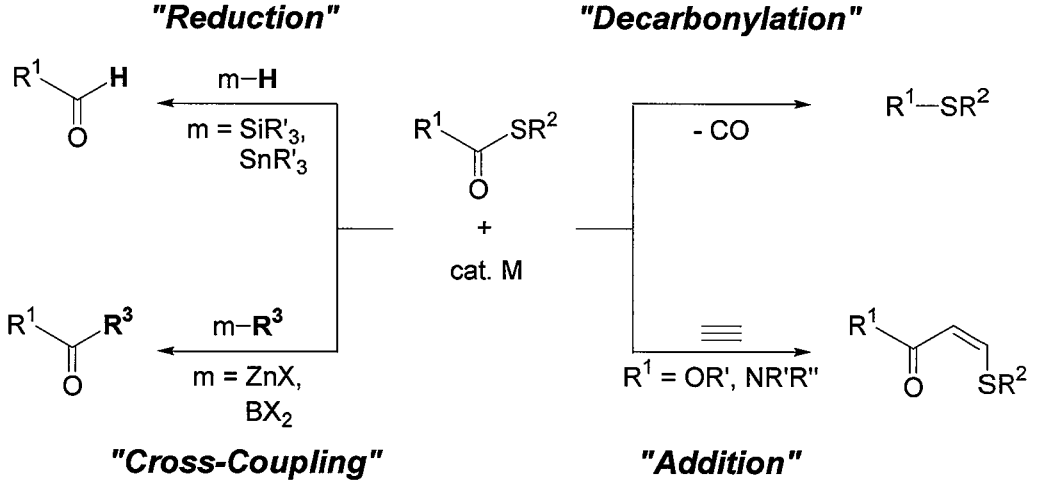
transition metal complexes) lies in between esters[7] and acid chlorides (Eq. 1).[8] For an example,

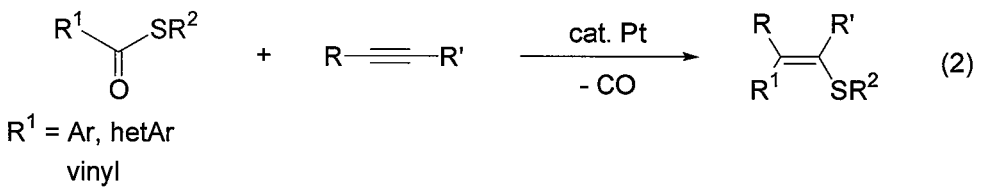


(1)

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,[9] reduction to aldehydes,[10] cross-coupling[11] and addition to carbon-carbon unsaturated bonds.[1b,2d] Our group also has developed a series of Pt catalyzed regio- and stereoselective decarbonylative addition of thioester (R^1 = Ar, hetAr, vinyl) to alkyne (Eq. 2).[2] Moreover, stoichiometric reactions of

Scheme 3. Transition-Metal Catalyzed Reaction Employing Thioester





(2)

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).[12] 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).[9d] 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.

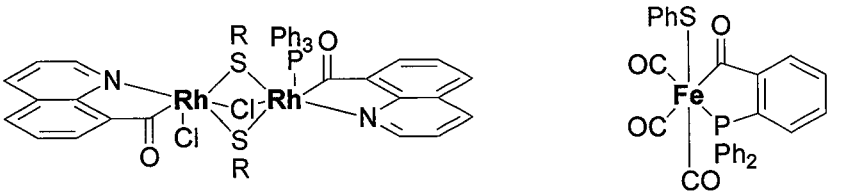
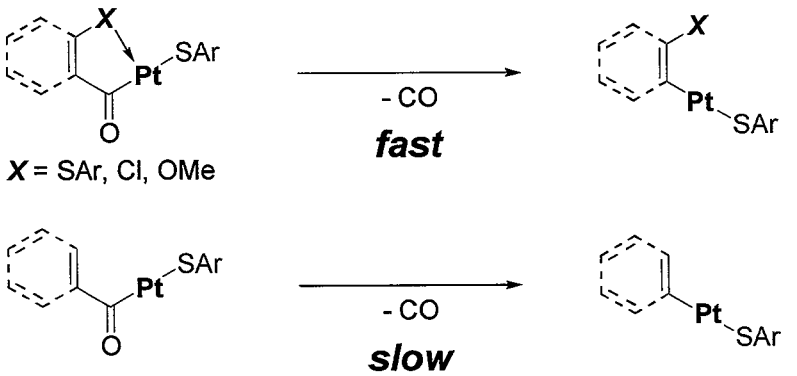
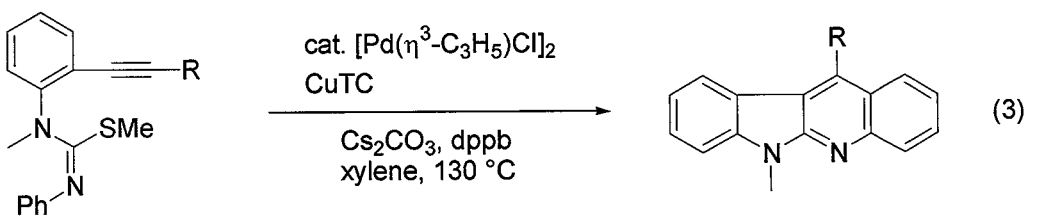


Figure 1.

Scheme 4. Transition-Metal Catalyzed Reaction Employing Thioester



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).[13] The

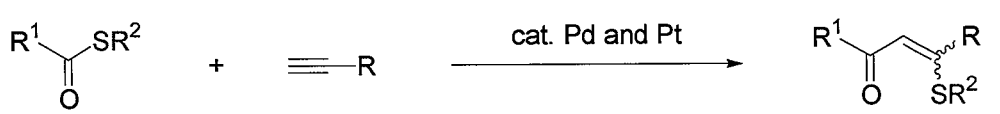


(3)

author expected that the catalytic reaction using iminosulfides should proceed taking into account the results from the study on the reaction using thioesters.

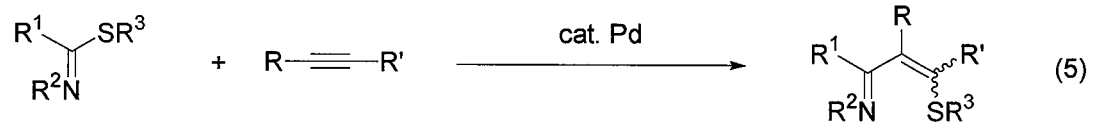
This thesis describes studies on the catalytic reaction of thioesters and iminosulfides with alkynes as well as those mechanistic aspects of the oxidative addition of thioesters to low-valent transition metal complexes.

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



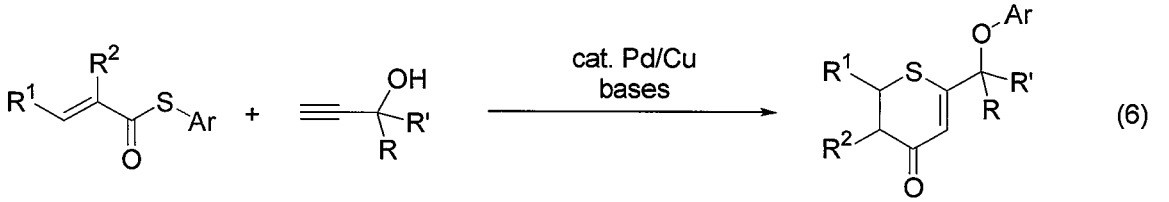
(4)

In chapter 2, Pd catalyzed addition of iminosulfides to alkynes was summarized (Eq. 5).



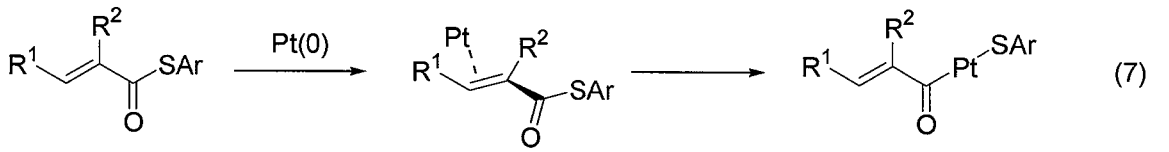
(5)

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



(6)

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



(7)

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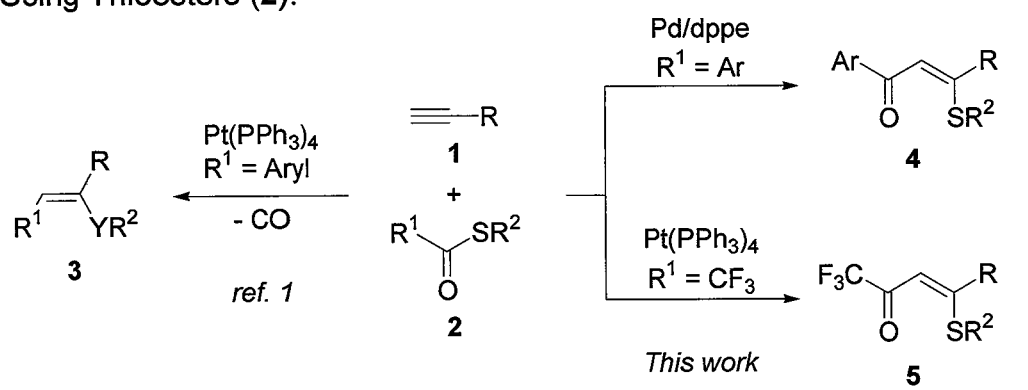
Chapter 1

Transition-Metal Catalyzed Regioselective Acylthiolation of Alkynes Using Thioesters

1-1. Introduction

$Pt(PPh_3)_4$-catalyzed intermolecular regio- and stereoselective decarbonylative arylthiolation of alkynes HC≡CR (**1**) by $R^1C(O)SR^2$ (**2**, R^1 = 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 (R^1 = Aryl) and trifluoroacetylthiolation (R^1 = CF_3) 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]

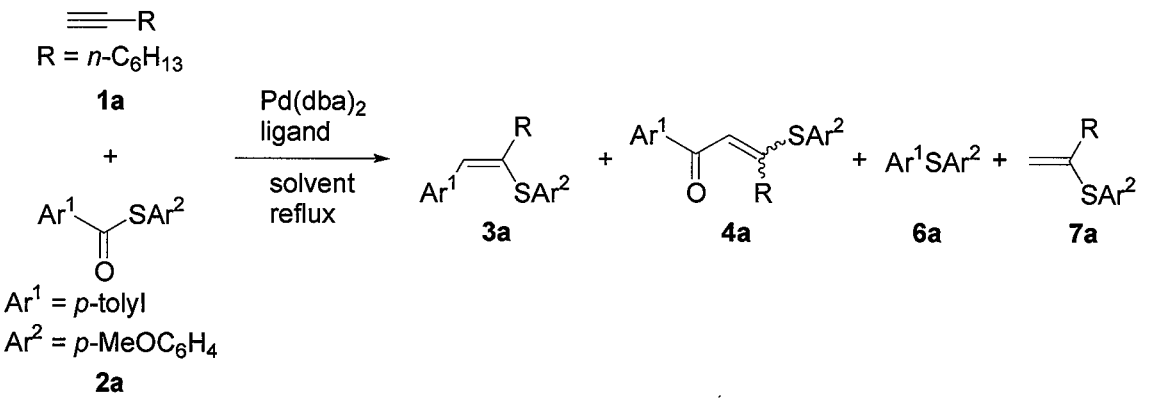
Scheme 1. Decarbonylative vs. CO-Retained Carbothiolation of Alkynes (**1**) Using Thioesters (**2**).



1-2. Pd/dppe-Catalyzed Aroylthiolation of Alkynes Using $Ar^1C(O)SAr^2$

To test the idea, the attempted reaction of 1-octyne (**1a**; R = n-C_6H_{13}, 1.2 mmol) with $Ar^1C(O)SAr^2$ (**2a**; Ar^1 = p-tolyl, Ar^2 = p-$MeOC_6H_4$, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 mmol) under toluene reflux gave an aroylthiolation product, $(Ar^1C(O))(H)C{=}C(n\text{-}C_6H_{13})(SAr^2)$ (**4a**) in 10% yield (*cis*:*trans* = 39:61) together with 50% of an Ar^1SAr^2 (**6a**)[4] and 20% of a hydrothiolation product $H_2C{=}C(n\text{-}C_6H_{13})(SAr^2)$ (**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)$_3$, PCy_3, P(n-Bu)$_3$ and PMe_2Ph 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**[a]

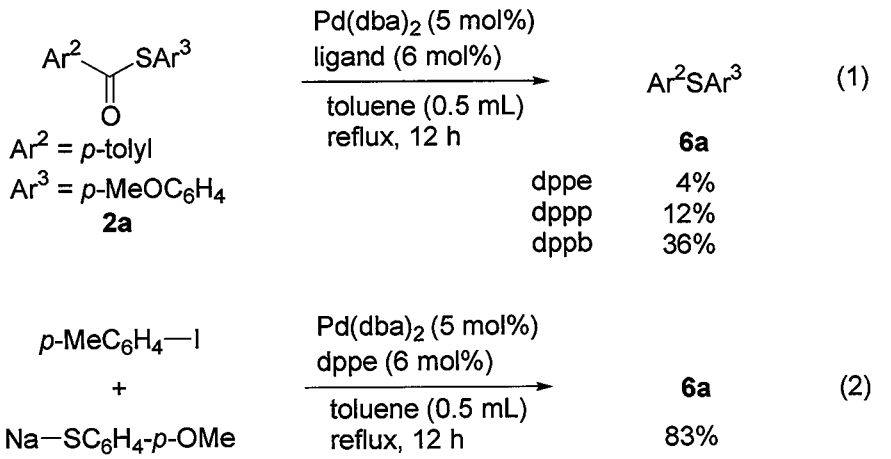


run	ligand	solvent	time (h)	**3a** (%)	**4a** (%) (*cis*:*trans*)	**6a** (%)	**7a** (%)
1	PPh_3[b]	toluene	12	n.d.	10 (39:61)	50	20
2	none	toluene	12	n.d.	n.d.	n.d.	n.d.
3	P(*p*-tolyl)$_3$	toluene	12	n.d.	9 (35:65)	34	22
4	P(*o*-tolyl)$_3$	toluene	12	n.d.	n.d.	2	n.d.
5	P(2-furyl)$_3$	toluene	12	n.d.	n.d.	8	5
6	PCy_3	toluene	12	n.d.	1 (1:>99)	22	38
7	P(*n*-Bu)$_3$	toluene	12	n.d.	6 (50:50)	30	22
8	PMe_2Ph	toluene	12	n.d.	8 (50:50)	16	16
9	dppm	toluene	12	n.d.	6 (67:33)	17	6
10	dppe	toluene	12	n.d.	53 (33:67)	12	14
11[c]	dppe	benzene	20	n.d.	78[d] (39:61)	n.d.	16
12	dppe	benzene	1	n.d.	14 (>99:1)	n.d.	n.d.
13	dppp	toluene	12	n.d.	16(39:61)	30	25
14	dppb	toluene	12	n.d.	15 (39:61)	36	35
15[e]	$Pt(PPh_3)_4$	toluene	13	75[f]	8 (>99:1)	n.d.	n.d.

[a] 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] $Pd(PPh_3)_4$ (0.05 mmol) as a catalyst. [c] The formation of $Ar^1C(O)C{\equiv}CR$ was detected in 10% yield. [d] Isolated yield. [e] $Pt(PPh_3)_4$ (0.05 mmol) as a catalyst. dba = dibenzylideneacetone, tolyl = methylphenyl, Cy = cyclohexyl, dppm = 1,1-bis(diphenylphosphino)methane, 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 $Ar^1C(O)C{\equiv}CR$ 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).[6,7] The employment of other bidentate ligands such as dppm, dppp and dppb significantly decreased the yield of **4a** (runs 9,13,14, Table 1). It must be noted that **3a**, the product of $Pt(PPh_3)_4$-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 $Pt[(CH_2{=}CHSiMe_2)_2O]$, $Ni(cod)_2$ (cod = cyclooctadiene) or $RhCl(cod)_2$ in the presence of dppe.

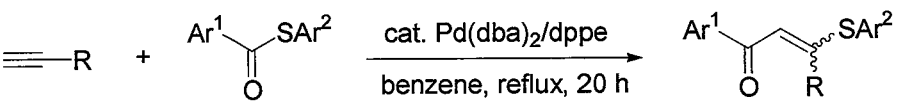
Prompted by these results, the effects of bidentate ligand on the decarbonylation of **2a** were



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*-MeC_6H_4I and $NaSC_6H_4$-*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 $Ar^1C(O)SAr^2$ (**2**) are summarized in Table 2. The reaction with **2a** (Ar^2 = *p*-$MeOC_6H_4$) afforded a better yield of desired **4** (78% of **4a**, run 1, Table 2) compared to the reactions with **2b** (Ar^2 = Ph, 53% of **4b**, run 2, Table 2) and **2c** (Ar^2 = *p*-FC_6H_4, 46% of **4c**, run 3, Table 2). In sharp contrast to the

Table 2. Pd/dppe-Catalyzed Aroylthiolation of **1** Using **2**[a]



	1		**2**			**4**	
run	**1**	R	**2**	Ar^1	Ar^2	**4**	(%) (*cis*:*trans*)[b]
1	**1a**	*n*-C_6H_{13}	**2a**	*p*-tolyl	*p*-$MeOC_6H_4$	**4a**	78 (39:61)
2	**1a**		**2b**	*p*-tolyl	Ph	**4b**	53 (28:72)
3	**1a**		**2c**	*p*-tolyl	*p*-FC_6H_4	**4c**	46 (28:72)
4	**1a**		**2d**	*p*-tolyl	*p*-$NO_2C_6H_4$	**4d**	n.d.
5	**1a**		**2e**	Ph	Ph	**4e**	66 (26:74)
6	**1a**		**2f**	*p*-FC_6H_4	*p*-tolyl	**4f**	57 (26:74)
7	**1a**		**2g**	3-pyridyl	*p*-tolyl	**4g**	74 (28:72)
8	**1a**		**2h**	2-furyl	*p*-tolyl	**4h**	55 (25:75)
9	**1a**		**2i**	*p*-tolyl	CH_2Ph	**4i**	10[c] (26:74)
10	**1a**		**2j**	*t*-Bu	*p*-$MeOC_6H_4$	**4j**	n.d.
11	**1b**	$(CH_2)_4Cl$	**2a**			**4k**	70 (33:67)
12	**1c**	$(CH_2)_3CN$	**2a**			**4l**	50 (28:72)
13	**1d**	$(CH_2)_3CO_2Me$	**2a**			**4m**	80 (25:75)
14	**1e**	CH_2(*c*-C_5H_9)	**2a**			**4n**	66 (27:73)
15	**1f**	$(CH_2)_2CHMe_2$	**2a**			**4o**	65 (47:53)
16	**1g**	Ph	**2a**			**4p**	40 (75:25)
17	**1a**		**2k**		PhC(O)SePh	**4q**	3[c] (>99:1)

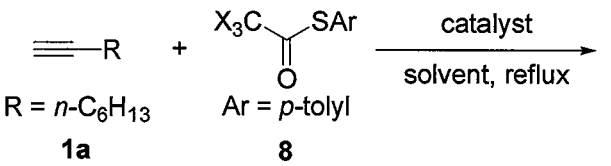
[a] **1** (1.2 mmol), **2** (1.0 mmol), $Pd(dba)_2$ (0.05 mol) and dppe (0.06 mol) under benzene (0.5 mL) reflux for 20 h. [b] Isolated yield. [c] NMR yield.

Pt-catalyzed decarbonylative arylthiolation, no reaction took place when a thioester with Ar^2 = *p*-$NO_2C_6H_4$ (**2d**) was employed (run 4, Table 2). Phenyl and *p*-FC_6H_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(O)SC_6H_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**), $(CH_2)_2CHMe_2$ (**1f**) and a phenyl group (**1g**) all underwent an aroylthiolation 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(O)SePh) took place to provide aroylselenation product **4q**, albeit in a very low yield (3%, run 17, Table 2).

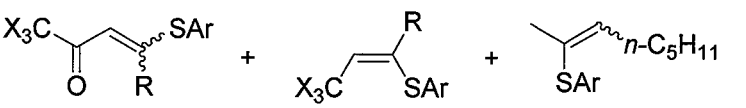
1-3. Pt-Catalyzed Trifluoroacetylthiolation of Alkynes Using $CF_3C(O)SR$

Next, the reactions with CX_3-substituted thioesters (**8**; $CX_3C(O)SR$) were examined. The treatment of 1-octyne (**1a**, 0.75 mmol) with $CF_3C(O)SC_6H_4$-*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_6H_4S)C=C(H)(*n*-C_5H_{11}) (**10a**) derived from **7a** was

Table 3. Reaction of **1a** with **8**[a]



R = *n*-C_6H_{13} (**1a**); Ar = *p*-tolyl (**8**)



5 **9** **10a**

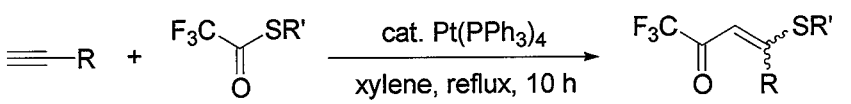
run	8	Catalyst	Solvent	time (h)	**5** (%) (*cis*:*trans*)	**9** (%)	**10a** (%)
1	**8a** (X = F)	$Pd(dba)_2$/dppe[b]	benzene	20	8 (36:64)	n.d.	16
2	**8a** (X = F)	$Pd(dba)_2$/dppe[b]	xylene	10	15 (25:75)	n.d.	31
3	**8a** (X = F)	$Pt(PPh_3)_4$	xylene	10	78[c] (18:82)	n.d.	n.d.
4	**8a** (X = F)	$Pt(PPh_3)_4$	benzene	10	8 (18:82)	n.d.	n.d.
5	**8a** (X = F)	$Pt(PPh_3)_4$	toluene	10	39 (21:79)	n.d.	n.d.
6	**8a** (X = F)	$Pt(PPh_3)_4$	xylene	0.5	15 (59:41)	n.d.	n.d.
7	**8a** (X = F)	$Pd(PPh_3)_4$	xylene	10	7 (28:72)[h]	n.d.	52
8	**8a** (X = F)	$Ni(cod)_2/PPh_3$[d]	xylene	10	n.d.	n.d.	n.d.
9	**8b** (X = H)	$Pt(PPh_3)_4$	xylene	10	n.d.	n.d.	n.d.[e]
10	**8c** (X = Cl)	$Pt(PPh_3)_4$	xylene	10	n.d.	n.d.	n.d.

[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 ^1H NMR spectroscopy. [b] $Pd(dba)_2$ (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 $Pt(PPh_3)_4$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 $Pd(PPh_3)_4$ (run 7, Table 3) and $Ni(cod)_2/4PPh_3$ (run 8, Table 3). On the other hand, the reaction employing $CH_3C(O)SC_6H_4$-*p*-Me (**8b**; X = H) and $CCl_3C(O)SC_6H_4$-*p*-Me (**8c**; X = Cl) in the presence of $Pt(PPh_3)_4$ 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 $CF_3C(O)SR'$ are shown in Table 4. Some substituents in aryl-S groups (**8d**; R' = *p*-$MeOC_6H_4$, **8e**; R' = Ph, **8f**; R' = *p*-ClC_6H_4) hardly interfered with the addition reactions (runs 2-4, Table 4). Unlike the case of the reaction with **2**, thioesters possessing an sp^3-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-l** in good yields (runs 7-10, Table 4).

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



1 **7** **8**

run	**1**	**8**	R'	**5**	(%) (*cis*:*trans*)[b]
1	**1a**	**8a**	*p*-tolyl	**5a**	78 (18:82)
2	**1a**	**8d**	*p*-$MeOC_6H_4$	**5d**	64 (11:89)
3	**1a**	**8e**	Ph	**5e**	82 (24:76)
4	**1a**	**8f**	*p*-ClC_6H_4	**5f**	69 (34:66)
5	**1a**	**8g**	CH_2Ph	**5g**	51 (30:70)
6	**1a**	**8h**	*n*-$C_{10}H_{21}$	**5h**	41 (18:82)
7[c]	**1b**	**8e**		**5i**	83 (29:71)
8[c]	**1c**	**8e**		**5j**	79 (29:71)
9[c]	**1d**	**8e**		**5k**	87 (26:74)
10	**1e**	**8e**		**5l**	70 (36:64)

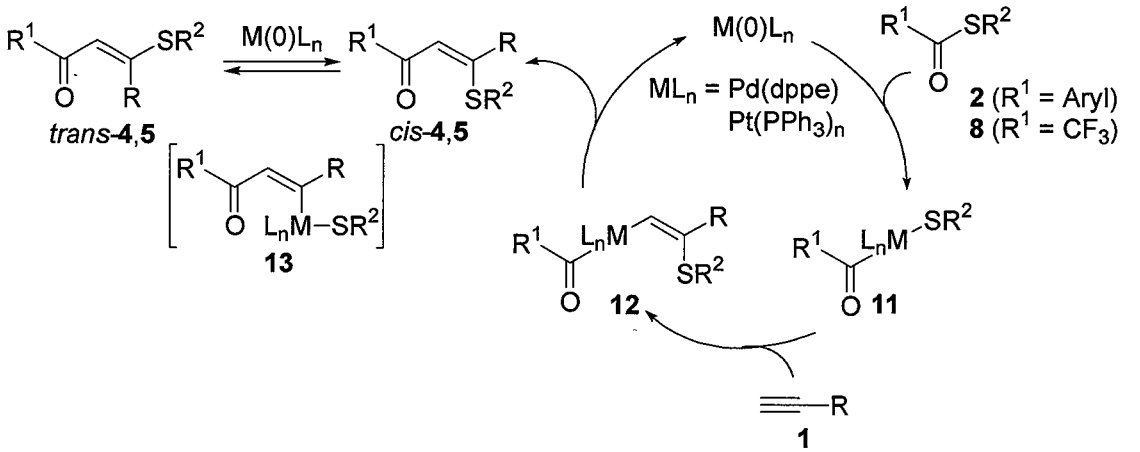
[a] Unless otherwise noted, **1** (0.75 mmol), **8** (0.5 mmol), $Pt(PPh_3)_4$ (0.025 mmol), and xylene (0.5 mL) under reflux for 10 h. [b] Isolated yield. [c] xylene (2.0 mL).

1-4. Reaction Mechanisms

A plausible reaction mechanism of the present regioselective CO-retained addition of thioesters (**2**, **8**; $R^1C(O)SR^2$ (R^1 = Aryl or CF_3)) to alkynes (**1**; HC≡CR) was depicted in

Scheme 2. The oxidative addition of **2** or **8** to $M(0)L_n$ (ML_n = Pd(dppe) or $Pt(PPh_3)_n$) complex triggers the reaction to afford $ML_n[C(O)R^1](SR^2)$ (**11**).[11] Subsequent regio- and stereoselective insertion of alkyne **1** into the S-M bond of **11** generates $ML_n[C(O)R^1][(cis)\text{-}CH{=}C(SR^2)(R)]$ (**12**),[12] which can react with another **1** to produce **7** and $Ar^1C(O)C{\equiv}CR$ as by-products. Finally, the C-C bond- forming reductive elimination of *cis*-**4**, **5** from **12** with regeneration of $M(0)L_n$ 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 $M(0)L_n$ complex to produce $ML_n[(cis)\text{-}C(R){=}C(H)\{C(O)R^1\}](SR^2)$ (*cis*-**13**),[13] *cis*-to-*trans* isomerization of **13**,[14] 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

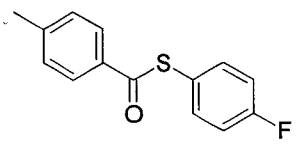
The present study substantiated that the decarbonylative arylthiolation of alkynes by thioesters is converted into CO-retained, atom-economical, regioselective carbothiolation. The author found that two simple factors; changing the catalysts from $Pt(PPh_3)_4$ to $Pd(dba)_2$/dppe or by employing $CF_3C(O)$ as a carbon functionality of thioesters even under $Pt(PPh_3)_4$-catalyzed conditions, are keys to achieve the acylthiolation.

1-6. Experimental Section

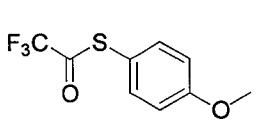
General Comments: ^1H and ^{13}C NMR spectra in $CDCl_3$ and toluene-d_8 solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometer. The chemical shifts in the ^1H NMR spectra were recorded relative to Me_4Si as an internal standard, and the chemical shifts in the ^{13}C NMR spectra were recorded 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 N_2 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.).

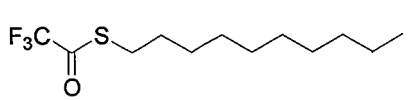
The Spectrum Data or Registry Number (RN) of Thio- and Selenoesters (2 and 8): ***p*-$CH_3C_6H_4C(O)SC_6H_4O$-*p*-CH_3 (2a):** RN: 53271-44-6. ***p*-$CH_3C_6H_4C(O)SC_6H_5$ (2b):** RN: 21122-34-2. ***p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-NO_2 (2d):** RN: 77750-05-1. **$C_6H_5C(O)SC_6H_5$ (2e):** RN: 884-09-3. ***p*-$FC_6H_4C(O)SC_6H_4$-*p*-CH_3 (2f):** RN: 90172-74-0. **3-$C_6H_4NC(O)$-SC_6H_4-*p*-CH_3 (2g):** RN: 52064-00-3. **2-$C_5H_3OC(O)SC_6H_4$-*p*-CH_3 (2h):** RN: 17357-39-0. ***p*-$CH_3C_6H_4C(O)SCH_2C_6H_5$ (2i):** RN: 17577-21-8. ***t*-$C_4H_9C(O)SC_6H_4$-*p*-OCH_3 (2j):** RN: 132381-65-8. **$C_6H_5C(O)SeC_6H_5$ (2k):** RN: 38447-68-6. **$F_3CC(O)SC_6H_4$-*p*-CH_3 (8a):** RN: 75072-07-0. **$H_3CC(O)SC_6H_4$-*p*-CH_3 (8b):** RN: 10436-83-6. **$Cl_3CC(O)SC_6H_4$-*p*-CH_3 (8c):** RN: 56956-67-3. **$F_3CC(O)SC_6H_5$ (8e):** RN: 2378-04-3. **$F_3CC(O)SC_6H_4$-*p*-Cl (8f):** RN: 181820-16-6. **$F_3CC(O)SCH_2C_6H_5$ (8g):** RN: 714-05-6.



***p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-F (2c):** white solid; mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 116.3 (d, J = 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 $C_{14}H_{11}FOS$: 246.0515. Found: 246.0507.



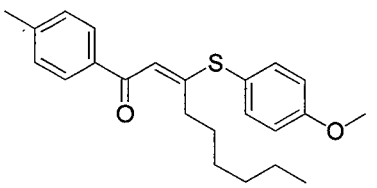
$F_3CC(O)SC_6H_4$-*p*-OCH_3 (8d): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3 H), 7.00 (d, J = 6.8 Hz, 2 H), 7.36 (d, J = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 115.5, 115.9 (c, $J_{C\text{-}F}$ = 290 Hz), 132.3, 136.1, 161.7, 184.2 (c, $J_{C\text{-}F}$ = 39.4 Hz); IR (NaCl) 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 $C_9H_7F_3O_2S$: 236.0119. Found: 236.0097.



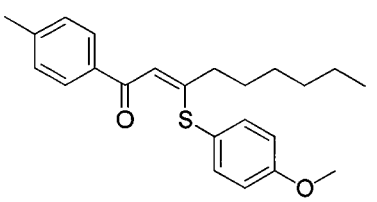
$F_3CC(O)S$-*n*-$C_{10}H_{21}$ (8h): colorless oil; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 0.88 (t, J = 6.1 Hz, 3 H), 1.26-1.39 (m, 14 H), 1.65 (tt, J = 7.6, 7.3 Hz, 2 H), 3.05 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 Hz), 184.5 (c, J_{C-F} = 39.4 Hz); IR (NaCl) 2927, 2856, 2362, 1709, 1468, 1283, 1205, 1165, 956, 744 cm^{-1}; mass spectrum (EI) m/z 270 (M^+, 0.28); HRMS calcd for $C_{12}H_{21}F_3OS$: 270.1265. Found: 270.1258.

Reaction of *p*-$CH_3C_6H_4C(O)SC_6H_4$-*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_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.

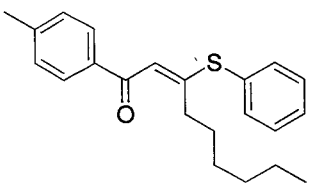


***trans*-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$OCH_3$ (*trnas*-4a):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.40-1.46 (m, 2 H), 1.68-1.75 (m, 2 H), 2.34 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 3.87 (s, 3 H), 6.25 (s, 1 H), 6.98 (d, J = 8.9 Hz, 2 H), 7.14 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.9 Hz, 2 H), 7.55 (d, J = 8.1 Hz, 2 H); N.O.E. experiment: Irradiation of the vinyl singlet at δ 6.25 resulted in a 17.0% enhancement of the signal at δ 7.55 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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; IR (NaCl) 2955, 2927, 2856, 1645, 1606, 1592, 1568, 1556, 1493, 1462, 1440, 1361, 1290, 1250, 1210, 1181, 1051, 1032, 830, 818, 732 cm^{-1}; mass spectrum (EI) m/e 368 (M^+, 15); Anal. Calcd for $C_{23}H_{28}O_2S$: C, 74.96; H, 7.66. Found: C, 74.74; H, 7.47.

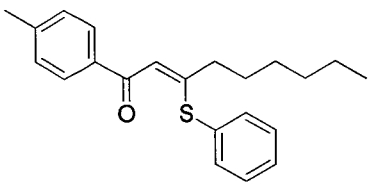


***cis*-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$OCH_3$ (*cis*-4a):** yellow solid; mp 42.0-44.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.1 Hz, 3 H), 1.08-1.10 (m, 4 H), 1.14-1.25 (m, 2 H), 1.38-1.44 (m, 2 H), 2.23 (t, J = 7.6 Hz, 2 H), 2.40 (s, 3 H), 3.83 (s, 3 H), 6.90 (d, J = 8.3 Hz, 2 H), 7.01 (s, 1 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.48 (d, J = 8.3 Hz, 2 H), 7.88 (d, J = 8.3 Hz, 2 H); N.O.E. experiment: Irradiation of the vinyl singlet at δ 7.01 resulted in a 8.9 % enhancement of the signal at δ 2.23 (allyl triplet) and 17.5 % enhancement of the signal at δ 7.88 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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; IR (KBr) 2928, 2857, 1632, 1607, 1592, 1570, 1534, 1493, 1463, 1298, 1246, 1180, 1096, 1084, 911, 863, 831, 806, 733 cm^{-1}; mass spectrum (EI) m/e 368 (M^+, 25); HRMS calcd for $C_{23}H_{28}O_2S$: 368.1810. Found: 368.1817.

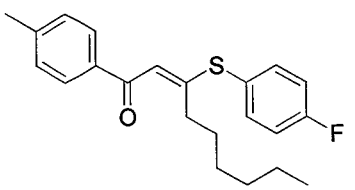
Other aroylthiolation products **4b**, **4c**, **4e-i** and **4k-4q** were synthesized by similar procedures.



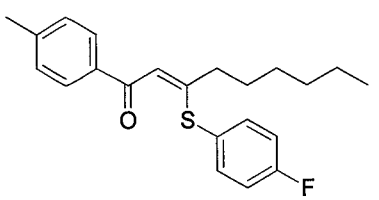
***trans-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*trans*-4b):** yellow solid; 71.9-73.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3 H), 1.32-1.34 (m, 4 H), 1.40-1.46 (m, 2 H), 1.68-1.74 (m, 2 H), 2.34 (s, 3 H), 2.91 (t, J = 7.8 Hz, 2 H), 6.28 (s, 1 H), 7.13 (d, J = 8.4 Hz, 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 709, 692 cm^{-1}; mass spectrum (EI) m/e 338 (M^+, 16); HRMS calcd for $C_{22}H_{26}OS$: 338.1704. Found: 338.1711.



***cis-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*cis*-4b):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 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, 3H), 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 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 $C_{22}H_{26}OS$: 338.1704. Found: 338.1700.

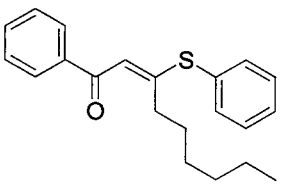


***trans-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}F$ (*trans*- 4c):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.42-1.45 (m, 2 H), 1.67-1.73 (m, 2 H), 2.35 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 6.22 (s, 1 H), 7.15-7.20 (m, 4 H), 7.52-7.58 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.5, 22.6, 29.3, 29.8, 31.6, 34.1, 115.1, 117.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 125.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.0, 129.1, 136.9, 137.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 142.8, 163.7 (d, $J_{C\text{-}F}$ = 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, 731cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 8.1); HRMS calcd for $C_{22}H_{25}FOS$: 356.1610. Found: 356.1606.

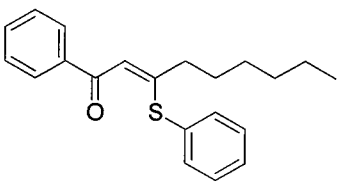


***cis-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}F$ (*cis*-4c):** yellow solid; mp 57-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3 H), 1.09-1.10 (m, 4 H), 1.17-1.22 (m, 2 H), 1.38-1.44 (m, 2 H), 2.22 (t, J = 7.8 Hz, 2 H), 2.42 (s, 3 H), 7.04 (s, 1 H), 7.07-7.11 (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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 22.4, 28.6, 29.8, 31.3, 37.1, 115.9, 116.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 126.9 (d, $J_{C\text{-}F}$ = 3.7 Hz), 128.1, 129.2, 136.0, 137.7

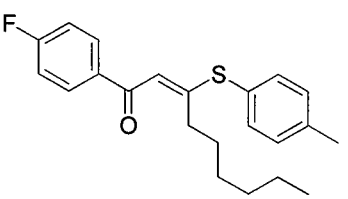
(d, $J_{C\text{-}F}$ = 8.3 Hz), 142.8, 163.5 (d, $J_{C\text{-}F}$ = 249 Hz), 164.7, 188.4; IR (KBr) 2952, 2925, 2856, 1628, 1606, 1534, 1484, 1236, 1224, 1183, 1082, 842, 808 cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 9.3); HRMS calcd for $C_{22}H_{25}FOS$: 356.1610. Found: 356.1617.



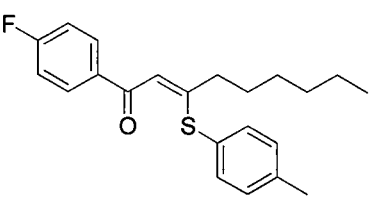
***trans*-$C_6H_5C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*trans*-4e):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.31-1.35 (m, 4 H), 1.41-1.47 (m, 2 H), 1.69-1.77 (m, 2 H), 2.92 (t, J = 7.8 Hz, 2 H), 6.29 (s, 1 H), 7.31-7.35 (m, 2 H), 7.41-7.43 (m, 1 H), 7.45-7.49 (m, 3 H), 7.56-7.59 (m, 2 H), 7.61-7.63 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.3, 29.9, 31.6, 34.3, 114.9, 127.9, 128.3, 129.8, 129.9, 130.1, 132.0, 135.7, 139.6, 167.8, 187.3; IR (NaCl) 3060, 2955, 2927, 2856, 1651, 1597, 1557, 1466, 1440, 1362, 1229, 1179, 1047, 1024, 778, 751, 692, 643 cm^{-1}; mass spectrum (EI) m/e 324 (M^+, 25); Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46. Found: C, 77.59; H, 7.29.



***cis*-$C_6H_5C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*cis*-4e):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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); HRMS calcd for $C_{21}H_{24}OS$: 324.1548. Found. Found: 324.1540.

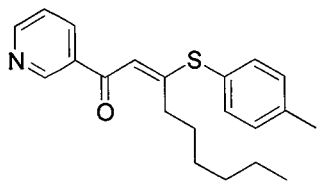


***trans*-*p*-$FC_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*trans*-4f):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3 H), 1.32-1.46 (m, 6 H), 1.68-1.75 (m, 2 H), 2.42 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 6.23 (s, 1 H), 6.98-7.02 (m, 2 H), 7.28 (d, J = 7.8 Hz, 2 H), 7.44 (d, J = 7.8 Hz, 2 H), 7.63-7.66 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.4, 22.6, 29.3, 29.9, 31.6, 34.2, 114.2, 115.3 (d, $J_{C\text{-}F}$ = 21.5 Hz), 126.3, 130.3 (d, $J_{C\text{-}F}$ = 9.2 Hz), 130.6, 135.5, 135.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 140.3, 165.0 (d, $J_{C\text{-}F}$ = 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 $C_{22}H_{25}FOS$: C, 74.12; H, 7.07. Found: C, 74.13; H, 7.12.

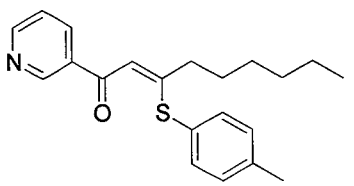


***cis*-*p*-$FC_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*cis*-4f):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3 H), 1.05-1.21 (m, 6 H), 1.38-1.46 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.39 (s, 3 H), 6.99 (s, 1 H), 7.11-7.16 (m, 2 H), 7.20 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.99-8.03 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.3, 22.4, 28.6, 30.0, 31.2, 37.2, 115.0, 115.5 (d, $J_{C\text{-}F}$ = 21.5

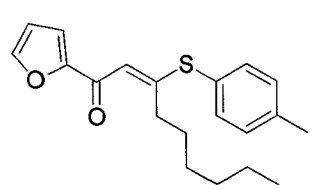
Hz), 127.6, 129.8, 130.4 (d, J_{C-F} = 8.7 Hz), 135.1 (d, J_{C-F} = 2.7 Hz), 135.6, 139.7, 165.1 (d, J_{C-F} = 252 Hz), 167.2, 187.0; IR (NaCl) 2956, 2928, 2858, 1634, 1600, 1538, 1532, 1505, 1494, 1463, 1230, 1155, 1084, 1018, 867, 852, 812, 733 cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 12); Anal. Calcd for $C_{22}H_{25}FOS$: C, 74.12; H, 7.07. Found: C, 74.02; H, 7.23.



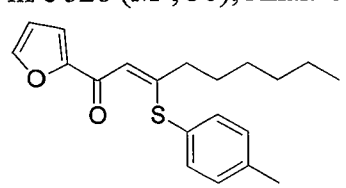
***trans*-(3-C_5H_4N)C(O)C(H)=C(*n*-C_6H_{13})SC_6H_4-*p*-CH_3 (*trans*-4g):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.6 Hz, 3 H), 1.34-1.47 (m, 6 H), 1.73 (dt, 2 H), 2.42 (s, 3 H), 2.94 (t, J = 7.8 Hz, 2 H), 6.23 (s, 1 H), 7.28-7.33 (m, 3 H), 7.44 (d, J = 7.8 Hz, 2 H), 8.01 (d, J = 7.8 Hz, 1 H), 8.64 (d, J = 3.9 Hz, 1 H), 8.74 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{21}H_{25}NOS$: C, 74.29; H, 7.42; N, 4.13. Found: C, 74.07; H, 7.41; N, 4.16.



***cis*-(3-C_5H_4N)C(O)C(H)=C(*n*-C_6H_{13})SC_6H_4-*p*-CH_3 (*cis*-4g):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{21}H_{25}NOS$: C, 74.29; H, 7.42; N, 4.13. Found: C, 74.01; H, 7.14; N, 4.13.



***trans*-(2-C_4H_3O)C(O)C(H)=C(*n*-C_6H_{13})SC_6H_4-*p*-CH_3 (*trans*-4h):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.3, 22.5, 29.2, 29.8, 31.5, 34.2, 111.9, 113.4, 115.6, 126.4, 130.5, 135.5, 140.3, 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 $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36. Found: C, 72.89; H, 7.08.



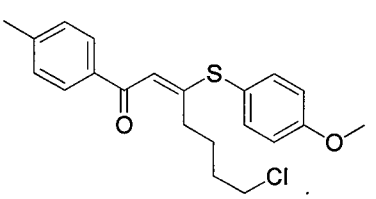
***cis*-(2-C_4H_3O)C(O)C(H)=C(*n*-C_6H_{13})SC_6H_4-*p*-CH_3 (*cis*-4h):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3 H), 1.06-1.08 (m, 4 H), 1.15-1.19 (m, 2 H), 1.39-1.43 (m, 2 H), 2.22 (t,

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 δ 6.92 resulted in a 6.9 % enhancement of the signal at δ 2.22; ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36. Found: C, 72.90; H, 6.97.

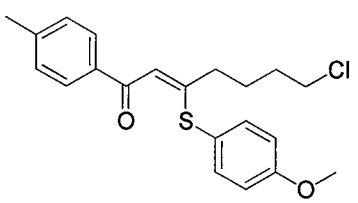
The structure of 4i was tentatively assigned by ^{1}H NMR spectrum (*vide infra*).

***trans-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*trans*-4i):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 1 H, vinyl proton).

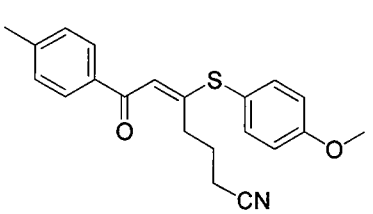
***cis-p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*cis*-4i):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1 H, vinyl proton).



***trans-p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_4Cl)SC_6H_4$-*p*-$OCH_3$ (*trans*-4k):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{21}H_{23}ClO_2S$: C, 67.27; H, 6.18. Found: C, 67.08; H, 5.96.

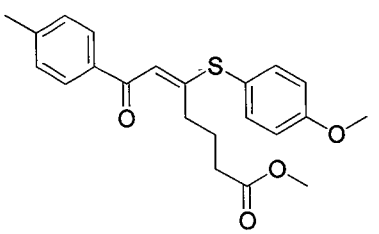


***cis-p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_4Cl)SC_6H_4$-*p*-$OCH_3$ (*cis*-4k):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.61 (m, 4 H), 2.27 (t, J = 6.8 Hz, 2 H), 2.41 (s, 3 H), 3.38 (t, J = 5.7 Hz, 2 H), 3.84 (s, 3 H), 6.92 (d, J = 8. 6 Hz, 2 H), 7.02 (s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.49 (d, J = 8.6 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 $C_{21}H_{23}ClO_2S$: C, 67.27; H, 6.18. Found: C, 67.26; H, 6.06.

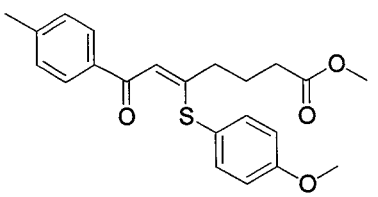


***trans-p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CN)SC_6H_4$-*p*-$OCH_3$ (*trans*-4l):** yellow solid; mp 87.4-88.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08-2.15 (m, 2 H), 2.35 (s, 3 H), 2.52 (t, J = 7.4 Hz, 2

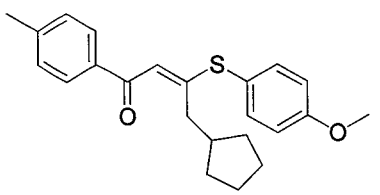
H), 2.98 (t, J = 7.6 Hz, 2 H), 3.85 (s, 3 H), 6.34 (s), 7.01 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 21.5, 25.5, 32.7, 55.4, 115.5, 115.7, 119.5, 119.7, 128.0, 129.1, 136.6, 137.1, 143.0, 161.2, 164.8, 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. Calcd for $C_{21}H_{21}NO_2S$: C, 71.76; H, 6.02; N, 3.99. Found: C, 71.72; H, 6.09; N, 4.00.



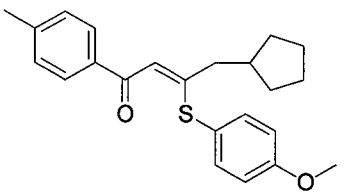
***trans*-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_4$-*p*-OCH$_3$ (*trans*-4m):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (dt, 2 H), 2.33 (s, 3 H), 2.48 (t, J = 7.7 Hz, 3 H), 2.94 (t, J = 7.7 Hz, 2 H), 3.67 (s, 3 H), 3.84 (s, 3 H), 6.29 (s, 1 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 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. Calcd for $C_{22}H_{24}O_4S$: C, 68.72; H, 6.29. Found: C, 68.68; H, 6.14.



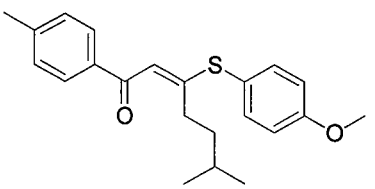
***cis*-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_4$-*p*-$OCH_3$ (*cis*-4m):** orange solid; mp 85.0-87.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (dt, 2 H), 2.16 (t, J = 7.3 Hz, 2 H), 2.30 (t, J = 7.3 Hz, 2 H), 2.41 (s, 3 H), 3.61 (s, 3 H), 3.84 (s, 3 H), 6.92 (d, J = 7.6 Hz, 2 H), 7.02 (s, 1 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 $C_{22}H_{24}O_4S$: 384.1395. Found: 384.1393.



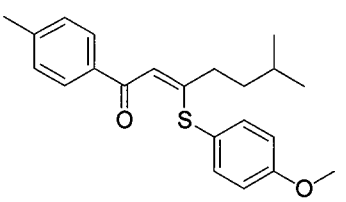
***trans*-*p*-$CH_3C_6H_4C(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_4$-*p*-$OCH_3$ (*trans*-4n):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29-1.34 (m, 2 H), 1.52-1.56 (m, 2 H), 1.62-1.68 (m, 2 H), 1.83-1.87 (m, 2 H), 2.29-2.35 (m, 1 H), 2.33 (s, 3 H), 3.00 (d, J = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.24 (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. Calcd for $C_{23}H_{26}O_2S$: C, 75.37; H, 7.15. Found: C, 75.23; H, 7.28.



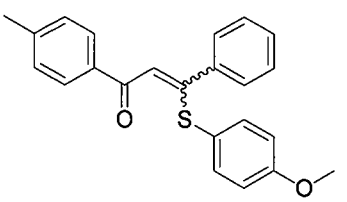
***cis-p*-$CH_3C_6H_4C(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_4$-*p*-$OCH_3$ (*cis* 4n):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97-1.03 (m, 2 H), 1.43-1.64 (m, 6 H), 1.93-1.97 (m, 1 H), 2.24 (d, J = 6.8 Hz, 2 H), 2.41 (s, 3 H), 3.84 (s, 3 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.01 (s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{23}H_{26}O_2S$: 366.1654. Found: 366.1658.



***trans-p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_2CH(CH_3)_2)SC_6H_4$-*p*-O CH_3 (*trans*-4o):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 161.0, 168.4, 187.1; IR (NaCl) 3005, 2956, 2868, 1646, 1607, 1592, 1560, 1493, 1464, 1442, 1366, 1290, 1250, 1208, 1181, 1052, 1031, 1018, 830, 818, 759, 734 cm^{-1}; mass spectrum (EI) m/e 354 (M^+, 24); HRMS calcd for $C_{22}H_{26}O_2S$: 354.1654. Found: 354.1651.



***cis-p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_2CH(CH_3)_2)SC_6H_4$-*p*-$OCH_3$ (*cis*-4o):** yellow solid; mp 94.0-95.0 °C; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.1, 27.8, 35.2, 39.3, 55.4, 114.5, 115.3, 122.1, 128.1, 129.1, 136.3, 137.3, 142.6, 160.6, 166.8, 188.3; IR (KBr) 2957, 2868, 1632, 1606, 1590, 1570, 1534, 1492, 1464, 1442, 1296, 1239, 1181, 1171, 1098, 1086, 1027, 1016, 867, 830, 799, 789 cm^{-1}; mass spectrum (EI) m/e 354 (M^+, 26); Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.54; H, 7.39. Found: C, 74.38; H, 7.19.

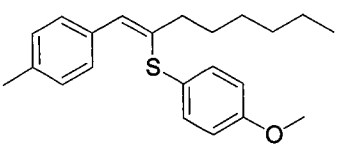


***p*-$CH_3C_6H_4C(O)C(H)=C(C_6H_5)SC_6H_4$-*p*-$OCH_3$ (4p, a mixture of stereoisomer):** yellow solid; ^1H NMR (400 MHz, $CDCl_3$) *cis*isomer; δ 2.41 (s, 3 H), 3.68 (s, 3 H), 6.57 (d, J = 8.8 Hz, 2 H), 7.09-7.16 (m, 9 H), 7.25 (s, 1 H), 7.93 (d, J = 8.0 Hz, 2 H); *trans* isomer; 2.33 (s, 3 H), 3.86 (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; ^{13}C NMR (100 MHz, $CDCl_3$) *cis*

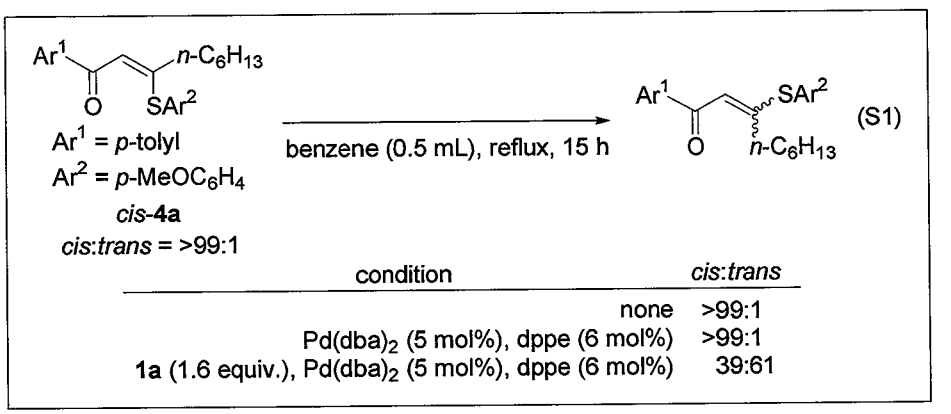
isomer; δ 21.6, 55.2, 113.9, 119.1, 123.4, 127.7, 128.2, 128.3, 128.9, 129.3, 136.0, 136.1, 138.9, 143.1, 159.5, 163.1, 188.3.; *trans* isomer; δ 21.5, 55.4, 115.4, 117.4, 121.1, 128.1, 128.4, 128.5, 128.8, 129.0, 135.9, 137.1, 137.2, 142.9, 161.0, 161.1, 188.4; IR (KBr): 2929, 1626, 1605, 1591, 1570, 1560, 1526, 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 $C_{23}H_{20}O_2S$: C, 76.64; H, 5.59. Found: C, 76.48; H, 5.48.

The structure of *cis*-4q was tentatively determined by ^{1}H NMR spectrum (*vide infra*). ***cis*-$C_6H_5C(O)C(H)=C(n\text{-}C_6H_{13})SeC_6H_5$ (*cis*-4q):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1 H, vinyl proton).

Reaction of *p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-OCH_3 (2a) with 1-Octyne (1a) in the Presence of $Pt(PPh_3)_4$ (run 18 of Table 1): Into a two-necked 3 mL reaction glass were added $Pt(PPh_3)_4$ (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 N_2 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*-$CH_3C_6H_4C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$OCH_3$ (*cis*-3a):** pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{28}OS$: 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 N_2 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.

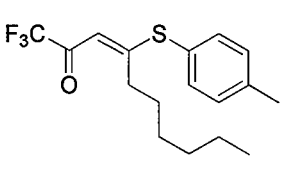
Cis-to-*trans* isomerization of *cis*-**4a** occurred in the presence of catalytic amount of $Pd(dba)_2$ and dppe and 1.6 equiv amount of **1a**. These results indicated that **1a** is the crucial factor for the generation of active dppe ligated Palladium (0) complex.

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 N_2 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.
***p*-$CH_3C_6H_4SC_6H_4$-*p*-OCH_3 (6a): RN: 6013-47-4.**

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

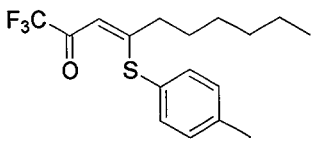
Reaction of I-C_6H_4-*p*-OCH_3 with $NaSC_6H_4$-*p*-OCH_3 in the Presence of Pd/dppe (Eq. 2): Into a two-necked reaction glass were added $Pd(dba)_2$ (14.4 mg, 0.025 mmol), dppe (12.0 mg, 0.030 mmol), *p*-MeC_6H_4I (109 mg, 0.500 mmol), $NaSC_6H_4OMe$-*p* (82 mg, 0.506 mmol) and toluene (0.5 mL) under a N_2 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 $F_3CC(O)SC_6H_4$-*p*-CH_3 (8a) with 1-Octyne (1a) in the Presence of $Pt(PPh_3)_4$ (run 3 of Table 3, run 1 of Table 4): General Procedure of Platinum-Catalyzed Trifluoroacetylthiolation of Alkynes Using Thioesters: Into a two-necked 3 mL reaction glass were added $Pt(PPh_3)_4$ (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 N_2 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.



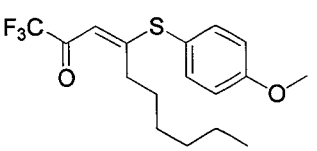
***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (*trans*-5a):** pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 3 H), 1.32-1.48 (m, 6 H), 1.66 (tt, 2 H), 2.42 (s, 3 H), 2.89 (t, J = 7.6 Hz, 2 H), 5.74 (s, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H); N.O.E. experiment: Irradiation of the singlet of vinylic proton at δ 5.75 resulted in 2.7% enhancement of the signal at δ 7.37 (aryl doublet) and the triplet of allylic proton at δ 2.89 resulted in 0.58% enhancement of the signal at δ 7.37 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 22.0, 23.1, 29.8, 30.2, 32.0, 36.0, 108.5, 113.9 (q, $J_{C\text{-}F}$ = 291 Hz), 125.2, 131.5,

135.6, 141.8, 176.2 (q, $J_{C\text{-}F}$ = 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.

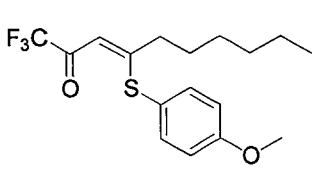


***cis*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*cis*-5a):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 6.8 Hz, 3 H), 1.05-1.12 (m, 6 H), 1.35-1.40 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.40 (s, 1 H), 6.51 (s, 1 H), 7.23 (d, J = 7.8 Hz, 2 H), 7.41 (d, J = 7.8 Hz, 2 H); N.O.E. experiment: Irradiation of the triplet of allylic proton at δ 2.25 resulted in 3.8% enhancement of the signal at δ 7.41 (aryl doublet) and 8.4% enhancement of the signal at δ 6.51 (vinylic singlet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.3, 22.3, 28.5, 29.9, 31.1, 37.5, 110.2, 116.4 (q, $J_{C\text{-}F}$ = 290 Hz), 125.7, 130.2, 135.4, 140.6, 177.3 (q, $J_{C\text{-}F}$ = 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.

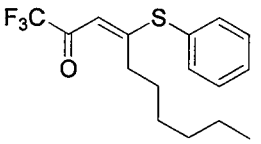
Other trifluoroacetylthiolation products **5d-l** were synthesized by similar procedures.



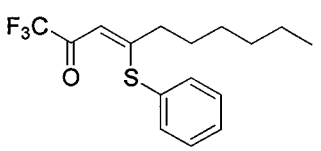
***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}OCH_3$ (*trans*-5d):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 6.6 Hz, 3 H), 1.33-1.46 (m, 6 H), 1.64 (tt, 2 H), 2.88 (t, J = 7.6 Hz, 2 H), 5.73 (s, 1 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.40 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.3, 29.6, 31.4, 35.3, 55.4, 107.8, 115.6, 116.3 (q, $J_{C\text{-}F}$ = 291 Hz), 118.7, 136.7, 161.5, 175.4 (q, $J_{C\text{-}F}$ = 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.



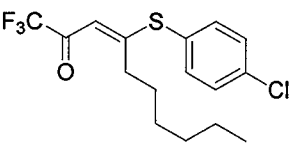
***cis*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}OCH_3$ (*cis*-5d):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.1 Hz, 3 H), 1.08-1.19 (m, 6 H), 1.39 (b, 2 H), 2.24 (t, J = 7.8 Hz, 2 H), 3.85 (s, 3 H), 6.51 (s, 1 H), 6.95 (d, J = 8.6 Hz, 2 H), 7.44 (d, J = 78.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.5, 29.9, 31.1, 37.5, 55.4, 110.1, 114.9, 116.4 (q, $J_{C\text{-}F}$ = 289 Hz), 119.8, 137.0, 161.2, 177.2 (q, $J_{C\text{-}F}$ = 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.



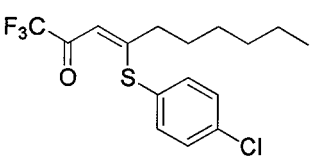
***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*trans*-5e):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 6.6 Hz, 3 H), 1.33-1.49 (m, 6 H), 1.66 (tt, 2 H), 2.90 (t, J = 7.8 Hz, 2 H), 5.72 (s, 1 H), 7.50 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.2, 29.6, 31.4, 35.4, 108.1, 116.2 (q, $J_{C\text{-}F}$ = 291 Hz), 128.1, 130.1, 130,8, 135.2, 175.5 (q, $J_{C\text{-}F}$ = 33.4 Hz), 179.7; IR (NaCl) 2958, 2930, 2859, 1699, 1560, 1477, 1442, 1291, 1203, 1143, 1077, 1024, 837, 750, 706, 685 cm^{-1}; mass spectrum (EI) m/z 316 (M^+, 26); Anal. Calcd for $C_{16}H_{19}F_3O_2S$: C, 60.74; H, 6.05. Found: C, 60.53; H, 6.05.



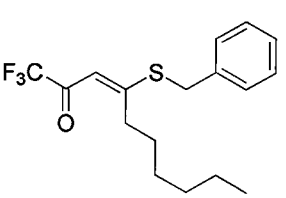
***cis*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*cis*-5e):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 6.7 Hz, 3 H), 1.05-1.17 (m, 6 H), 1.39 (m, 2 H), 2.25 (t, J = 7.6 Hz, 2 H), 6.53 (s, 1 H), 7.43-7.56 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.6, 29.9, 31.1, 37.7, 110.5, 116.5 (q, $J_{C\text{-}F}$ = 292 Hz), 129.3, 129.5, 130,2, 135.6, 177.2, 177.4 (q, $J_{C\text{-}F}$ = 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 $C_{16}H_{19}F_3OS$: 316.1109. Found: 316.1112.



***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}Cl$ (*trans*-5f):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 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), 5.73 (s, 1 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.48 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 29.6, 31.4, 35.3, 108.3, 116.2 (q, $J_{C\text{-}F}$ = 291 Hz), 126.6, 130.5, 136.5, 137.4, 175.6 (q, $J_{C\text{-}F}$ = 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 $C_{16}H_{18}ClF_3OS$: C, 54.78; H, 5.17. Found: C, 54.68; H, 5.13.

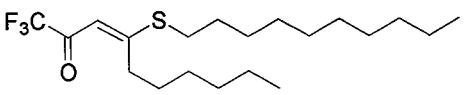


***cis*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}Cl$ (*cis*-5f):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.3 Hz, 3 H), 1.07-1.43 (m, 8 H), 2.24 (t, J = 7.6 Hz, 2 H), 6.54 (s, 1 H), 7.42 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.5, 29.7, 31.1, 37.6, 110.8, 116.3 (q, $J_{C\text{-}F}$ = 289 Hz), 127.7, 129.7, 136.8, 136.8, 176.1, 177.5 (q, $J_{C\text{-}F}$ = 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 $C_{16}H_{18}ClF_3OS$: 350.0719. Found: 350.0714.

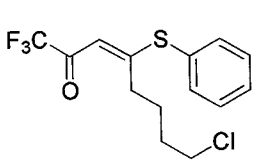


***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*trans*-5g):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.29-1.41 (m, 6 H), 1.57 (tt, 2 H), 2.83 (t, J = 7.8 Hz, 2 H), 4.09 (s, 2 H), 6.17 (s, 1 H), 7.30-7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.2, 29.7, 31.4, 36.2, 37.3, 106.9, 116.5 (q, $J_{C\text{-}F}$ = 291 Hz), 128.1, 128.9, 129.0, 133.6, 174.9

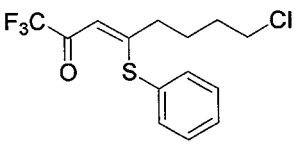
(q, $J_{C\text{-}F}$ = 32.3 Hz), 178.1; IR (NaCl) 2957, 2930, 2858, 1698, 1552, 1496, 1455, 1435, 1295, 1203, 1142, 1079, 822, 711, 696 cm^{-1}; mass spectrum (EI) m/z 330 (M^+, 2.2); Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 61.67; H, 6.42.



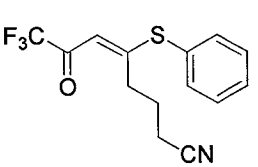
***trans*-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})S\text{-}n\text{-}C_{10}H_{21}$ (*trans*-5h):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (b, 6 H), 1.27-1.42 (m, 20 H), 1.57 (tt, 2 H), 1.70 (tt, 2 H), 2.82-2.85 (m, 4 H), 6.01 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 22.5, 22.7, 27.0, 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, $J_{C\text{-}F}$ = 292 Hz), 174.7 (q, $J_{C\text{-}F}$ = 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 $C_{20}H_{35}F_3OS$: C, 63.12; H, 9.27. Found: C, 63.18; H, 9.23.



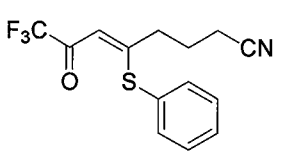
***trans*-$F_3CC(O)C(H)=C((CH_2)_4Cl)SC_6H_5$ (*trans*-5i):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.79-1.86 (tt, 2 H), 1.90-1.97 (tt, 2 H), 2.93 (t, J = 7.8 Hz, 2 H), 3.59 (t, J = 6.4 Hz, 2 H), 5.76 (s, 1 H), 7.5-7.54 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 32.1, 34.4, 44.4, 108.5, 116.1 (q, $J_{C\text{-}F}$ = 291 Hz), 127.8, 130.2, 130.9, 135.2, 175.6 (q, $J_{C\text{-}F}$ = 33.9 Hz), 178.5; IR (NaCl) 3063, 2957, 2868, 1698, 1556, 1477, 1442, 1292, 1203, 1143, 1077, 1024, 838, 750, 706, 686, cm^{-1}; mass spectrum (EI) m/z 322 (M^+, 45); Anal. Calcd for $C_{14}H_{14}ClF_3OS$: C, 52.10; H, 4.37. Found: C, 52.37; H, 4.41.



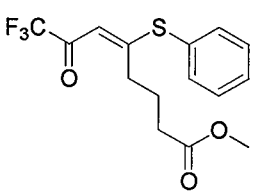
***cis*-$F_3CC(O)C(H)=C((CH_2)_4Cl)SC_6H_5$ (*cis*-5i):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53-1.57 (m, 4 H), 2.29 (t, J = 7.2 Hz, 2 H), 3.34 (t, J = 6.0 Hz, 2 H), 6.54 (s, 1 H), 7.45-7.57 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 31.5, 36.8, 44.0, 110.7, 116.3 (q, $J_{C\text{-}F}$ = 289 Hz), 129.0, 129.6, 130.4, 135.5, 175.8, 177.4 (q, $J_{C\text{-}F}$ = 33.8 Hz); IR (NaCl) 3025, 2957, 2869, 1682, 1577, 1534, 1493, 1458, 1446, 1364, 1302, 1200, 1146, 1110, 1092, 1018, 863, 813, 729, 687, 654 cm^{-1}; mass spectrum (EI) m/z 322 (M^+, 54); HRMS calcd for $C_{17}H_{21}F_3OS$: 322.0406. Found: 322.0399.



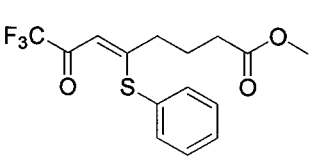
***trans*-$F_3CC(O)C(H)=C((CH_2)_3CN)SC_6H_5$ (*trans*-5j):** pale yellow solid; mp 64-66 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (m, 2 H), 2.53 (t, J = 6.8 Hz, 2 H), 3.01 (t, J = 6.8 Hz, 2 H), 5.80 (s, 1 H), 7.53 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 25.2, 34.0, 109.3, 116.1 (q, $J_{C\text{-}F}$ = 294 Hz), 118.9, 127.5, 130.4, 131.2, 135.2, 176.0 (q, $J_{C\text{-}F}$ = 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 $C_{14}H_{12}F_3NOS$: C, 56.18; H, 4.04; N, 4.68. Found: C, 56.18; H, 3.98; N, 4.73.



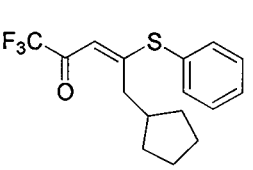
***cis*-$F_3CC(O)C(H)=C((CH_2)_3CN)SC_6H_5$ (*cis*-5j):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73 (tt, J = 7.0, 7.8 Hz, 2 H), 2.16 (t, J = 7.0 Hz, 2 H), 2.45 (t, J = 7.8 Hz, 2 H), 6.56 (s, 1 H), 7.45-7.57 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 25.5, 36.4, 111.7, 116.5 (q, J_{C-F} = 289 Hz), 118.5, 128.9, 130.1, 131.0, 135.7, 173.4, 177.8 (q, J_{C-F} = 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 $C_{14}H_{12}F_3NOS$: 299.0592. Found: 299.0590.



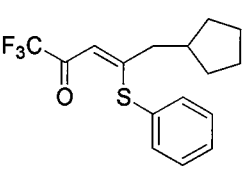
***trans*-$F_3CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5$ (*trans*-5k):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (tt, 2 H), 2.48 (t, J = 7.6 Hz, 2 H), 2.96 (t, J = 7.8 Hz, 2 H), 3.70 (s, 3 H), 5.75 (s, 1 H), 7.50-7.54 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 33.3, 34.2, 51.7, 108.7, 116.1 (q, J_{C-F} = 291 Hz), 127.8, 130.2, 130.9, 135.2, 173.3, 175.6 (q, J_{C-F} = 33.5 Hz), 178.0; IR (NaCl) 3063, 2953, 1738, 1732, 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 $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.21; H, 4.49.



***cis*-$F_3CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5$ (*cis*-5k):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (tt, 2 H), 2.11 (t, J = 7.2 Hz, 2 H), 2.32 (t, J = 7.8 Hz, 2 H), 3.60 (s, 3 H), 6.55 (s, 1 H), 7.42-7.56 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 32.6, 36.5, 51.5, 110.8, 116.3 (q, J_{C-F} = 289 Hz), 128.9, 129.5, 130.3, 135.4, 172.7, 175.3, 177.3 (q, J_{C-F} = 34.4 Hz); IR (NaCl) 3062, 2953, 1738, 1682, 1538, 1478, 1440, 1366, 1300, 1254, 1201, 1146, 1111, 1091, 1024, 1001, 887, 856, 838, 820, 754, 730, 706, 693 cm^{-1}; mass spectrum (EI) m/z 332 (M^+, 16); Anal. Calcd for $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.01; H, 4.55.

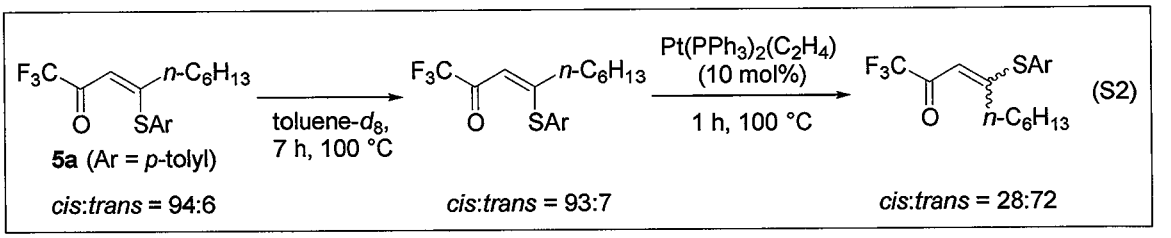


***trans*-$F_3CC(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_5$ (*trans*-5l):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (m 2 H), 1.55-1.69 (m, 4 H), 1.87 (m, 2 H), 2.21 (m, 1 H), 3.00 (d, J = 7.3 Hz, 2 H), 5.71 (s, 1 H), 7.51 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 32. 5, 40.5, 40.5, 108.5, 116.3 (q, J_{C-F} = 294 Hz), 128.4, 130.2, 130.8, 135.2, 175.7 (q, J_{C-F} = 33.6 Hz), 179.2; IR (NaCl) 3063, 2953, 2869, 1808, 1556, 1476, 1441, 1296, 1201, 1142, 1077, 1024, 846, 837, 749, 707, 690 cm^{-1}; mass spectrum (EI) m/z 314 (M^+, 22); Anal. Calcd for $C_{16}H_{17}F_3OS$: C, 61.13; H, 5.45. Found: C, 60.94; H, 5.38.



***cis*-$F_3CC(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_5$ (*cis*-5l):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 24.6, 32.1, 39.8, 43.4, 110.9, 116.4 (q, J_{C-F} = 300 Hz), 129.4, 130.1, 135.2, 135.6, 176.2, 177.2 (q, J_{C-F} = 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 $C_{16}H_{17}F_3OS$: C, 61.13; H, 5.45. Found: C, 61.28; H, 5.54.



***Cis*-to-*trans* Isomerization of 5a in Toluene-d_8 (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-d_8 under N_2 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 $Pt(PPh_3)_2(C_2H_4)$ (0.006 mmol) resulted in the formation of *trans*-**5a** (*cis*:*trans* = 28:72).

1-7. References and Notes

(1) (a) Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 5108. (b) Yamashita, F.; Kuniyasu, H.; Terao, J.; Kambe, N. *Org. Lett.* **2008**, *10*, 101.

(2) For related transition-metal-catalyzed CO-retentive additions, see: (a) Hua, R.; Takeda, H.; Onozawa, S.; Abe Y.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 2899. (b) Toyofuku, M.; Murase, E.; Fujiwara, S.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *Org. Lett.* **2008**, *10*, 3957. (c) Kashiwabara, T.: Kataoka, K.; Hua, R.; Shimada, S.; Tanaka, M. *Org. Lett.* **2005**, *7*, 2241. (d) Hua, R.; Onozawa, S.; Tanaka, M. *Chem. Eur. J.* **2005**, *11*, 3621. (e) Kashiwabara, T.; Fuse, K.; Hua, R.; Tanaka, M. *Org. Lett.* **2008**, *10*, 5469. (f) Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 2899.

(3) For a recent review, see: Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 214, and references therein.

(4) For a catalytic decarbonylation of thioesters, see: (a) Goto, T.; Onaka, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 709. (b) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1987**, *28*, 6321. (c) Wenkert, E.; Chianelli, D. *J. Chem. Soc. Chem. Commun.* **1991**, 627. (d) Kato, T.; Kuniyasu, H.; Kajiura, T.; Minami, Y.; Ohtaka, A.; Kinomoto, M.; Terao, J.; Kurosawa, H.; Kambe, N. *Chem. Commun.* **2006**, 868.

(5) For Pd- and Pt-catalyzed hydrothiolations of alkynes, see: (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902. (b) Bäckvall, J.-E.; Ericcson, A. *J. Org. Chem.* **1994**, *59*, 5850. (c) Ogawa, A.; Ikeda, T.: Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108.

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

(7) 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-coodinated Pd-complex induce the *cis*-to-*trans* isomerization. See Eq. S1.

(8) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.

(9) 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.

(10) See Eq. S2.

(11) 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.

(12) For stoichiometric insertions of alkynes into the S-M bond, see: (a) Sugoh, K.; Kuniyasu, H.; Kurosawa, H. *Chem. Lett.* **2002**, *31*, 106. (b) Kuniyasu, H.; Yamishita, F.; Terao, J.; Kambe, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 5929. (c) Kuniyasu, H.; Takekawa, K.; Yamashita, F.; Miyafuji, K.; Asano, S.; Takai, Y.; Ohtaka, A.; Tanaka, A.; Sugoh, K.; Kurosawa, H.; Kambe, N. *Organometallics* **2008**, *27*, 4788.

(13) 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) Toyofuku, M.; Fujiwara, S.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2008**, *130*, 10504.

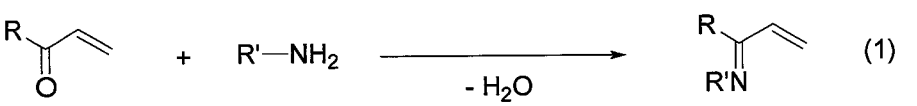
(14) For isomerizations of the alkenyl transition metal complexes, see: (a) Brady, K. A.; Nile, T. A.; *J. Organomet. Chem.* **1981**, *206*, 299. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (c) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408.

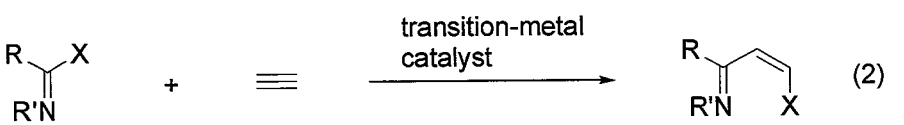
Chapter 2

Pd-Catalyzed Regioselevtive Iminothiolation of Alkynes: Remarkable Effects of CF_3 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]



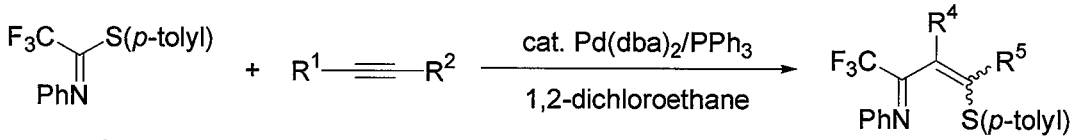


As a part of our studies of transition-metal catalyzed reactions of organosulfides with carbon-carbon unsaturated bonds,[4] our group has already reported the decarbonylative carbothiolation of alkynes using thioesters to produce vinylsulfides. Moreover, the author discovered the CO-retained addition 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 $CF_3C(O)SR$ in chapter 1, reactions using an iminosulfide [**1a**; $CF_3C(=NPh)$-S-*p*-tolyl] have been scrutinized

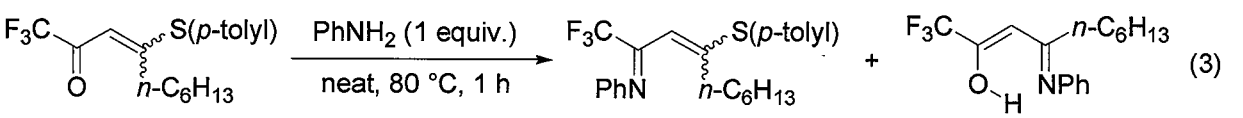
Table 1. Pd-Catalyzed Iminothiolation of Various Alkynes (**2**) Using **1a**[a]



1a **2** **3**

run	**2**	R^1—≡—R^2	temp (°C)	time (h)	**3**	(%) (*cis*:*trans*)[b]
1	**2a**		80	1	**3a**	89 (18:82)
2	**2b**	Cl	80	1	**3b**	81 (13:87)
3	**2c**	CO_2Me	80	2	**3c**	81 (14:86)
4	**2d**		80	2	**3d**	87 (13:87)
5	**2e**		80	3	**3e**	76 (14:86)
6	**2f**		80	1	**3f**	89 (98:2)
7	**2g**		80	1	**3g**	95 (86:14)
8	**2h**	CF_3	80	1	**3h**	74 (98:2)
9	**2i**	S	80	1	**3i**	83 (>99:1)
10[c]	**2j**		160[d]	1	**3j**	14 (95:5)
11	**2k**		150[d]	3	**3k**	n.d.
12	**2l**	EtOC(O)—	100[d]	3	**3l**	91 (>99:1)
13	**2m**	—O	180[d]	3	**3m**	51 (33:67)

[a] Unless otherwise noted, **1a** (0.5 mmol), **2** (0.6 mmol for runs 1-5, 3.0 mmol for runs 6-8, 1.5 mmol for run 9, 1.0 mmol for runs 10-13), $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.05 mmol) and 1,2-dichloroethane (0.5 mL) at 80 °C for 1-3 h. [b] isolated yield. [c] 1,2-dichloroethane (0.25 mL). [d] microwave irradiation.



4a **3a** n.d. **5a** 81% (3)

(Table 1). The reaction of **1a** (0.5 mmol) with 1-octyne (**2a**, 0.6 mmol) in the presence of $Pd(dba)_2$ (0.025 mmol) and PPh_3 (0.05 mmol) in 1,2-dichloroethane at 80 °C for 1 h produced desired adduct $CF_3C(=NPh)C(H)=C(n\text{-}C_6H_{13})(S\text{-}p\text{-tolyl})$ (**3a**) in 89% (*cis*:*trans* = 18:82) yield (run 1, Table 1).[5] For the synthesis of **3a**, the reaction of $F_3CC(O)C(H)=C(n\text{-}C_6H_{13})(S\text{-}p\text{-tolyl})$ (**4a**) with aniline was conceivable. However, **3a** was not formed; only ketimine derivative [**5a**, $CF_3C(OH)=C(H)C(n\text{-}C_6H_{13})(=NC_6H_5)$] 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 (**2b-i**) were attempted. Functional groups such as chlorine (**2b**), methoxy carbonyl (**2c**), 2-tetrahydropyranyl (**2d**) and cyclohexyl (**2e**), were tolerant to provide the corresponding adducts **3b-e** in good yields (runs 2-5, Table 1). Although excess amounts of arylalkynes (**2f-i**,

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).[5,6] 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 phenylpropiolate (**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).[7,8] The structure of *cis*-**3l** was unambiguously determined by X-ray crystallography (Fig. 1).[9]

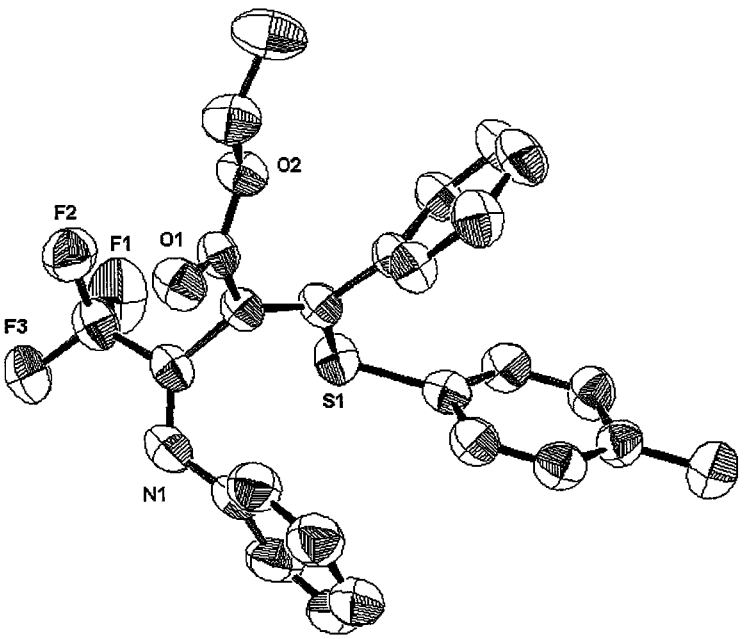
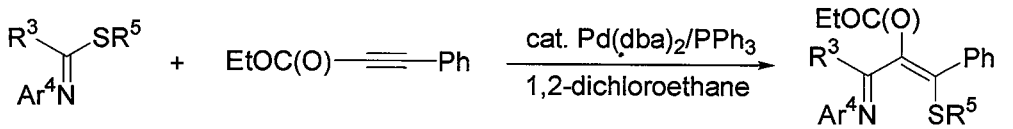


Figure 1. ORTEP Diagram of *cis*-**3l**.

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 elecrto-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 increaseing concentration even with shorter reaction time (runs 3,5 and 7, Table 2). The present reaction using **1f** with benzyl group at R^5 also produced **3r** in 91% yield (run 8, Table 2). Then, the addition of iminosulfides containing substituents at R^3 were examined. In the case of **1g** (R^3 = 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**, R^3 = $PhCH_2CH_2$) with **2l** gave no adduct **3t** (run 10, Table 2).

Table 2. Pd-Catalyzed Iminothiolation of **2l** Using Various Iminosulfides (**1**)[a]



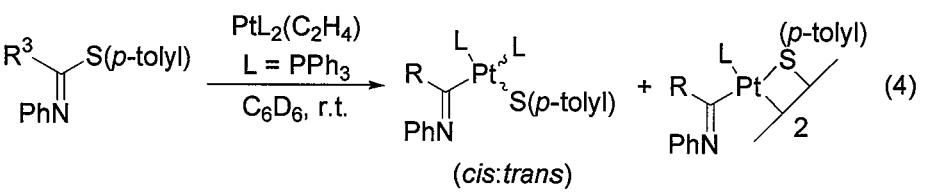
1 **2l** **3**

run	**1**	R^1	R^2	Ar^3	time (h)	**3**	(%) (*cis*:*trans*)[b]
1	**1b**	CF_3	Ph	Ph	3	**3n**	82 (>99:1)
2	**1c**	CF_3	*p*-ClC_6H_4	Ph	3	**3o**	50[c] (>99:1)
3	**1c**				1	**3o**	71 (>99:1)
4	**1d**	CF_3	*p*-tolyl	*p*-$MeOC_6H$	3	**3p**	35[c] (>99:1)
5	**1d**				1	**3p**	88 (>99:1)
6	**1e**	CF	*p*-tolyl	*p*-ClC_6H_4	3	**3q**	34[c] (>99:1)
7	**1e**				1	**3q**	85 (79:21)
8	**1f**	CF_3	CH_2Ph	Ph	2	**3r**	91 (97:3)
9[d]	**1g**	Ph	*p*-tolyl	Ph	3	**3s**	44 (81:19)
10[d]	**1h**	$Ph(CH_2)_2$	*p*-tolyl	Ph	3	**3t**	n.d.

[a] Unless otherwise noted, **1** (0.5 mmol), **2l** (1.0 mmol), $Pd(dba)_2$ (0.025 mmol), PPh_3 (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. [b] isolated yield. [c] NMR yield. [d] $Pd(dba)_2$ (0.05 mol) and P(*p*-tolyl)$_3$ (0.1 mmol).

2-3. Oxidative Addition of $R^3C(=NPh)S$-*p*-tolyl to $Pt(PPh_3)_2(C_2H_4)$

To get the imformaiton on the effect of CF_3 group, the oxidative addition of **1a** to $Pt(PPh_3)_2(C_2H_4)$ in C_6D_6 under room temperature was monitored by ^{31}P NMR spectroscopy (Eq. 4). As a result, *cis*-$Pt(PPh_3)_2[C(=NPh)CF_3](S$-*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 CF_3 group accelerates the oxidative addiition.



(4)

(*cis*:*trans*)

1a ($R^3 = CF_3$), 1 h **6a**; 99% (>99:1) **7a**; n.d.

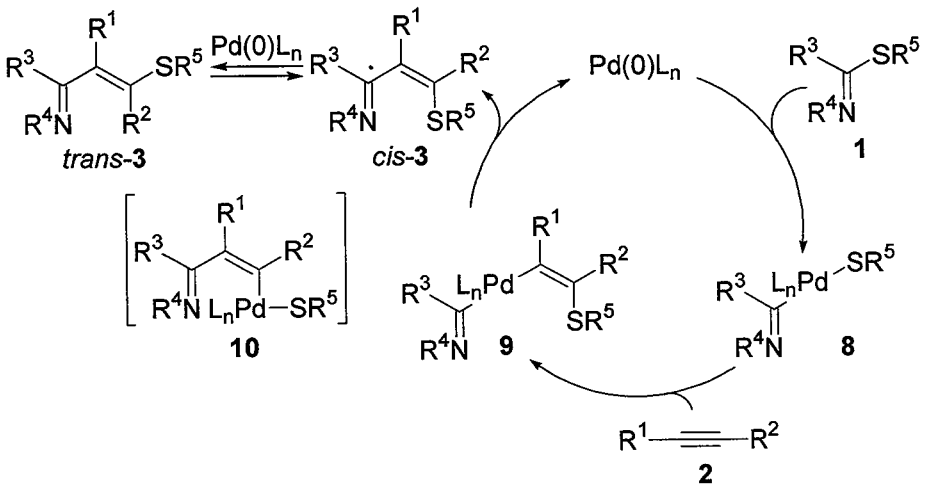
1g (R^3 = Ph), 1 h **6b**; 2% (>99:1) **7b**; n.d.
23 h 20% (65:35) 12%

2-4. A Proposed Reaction Mechanism

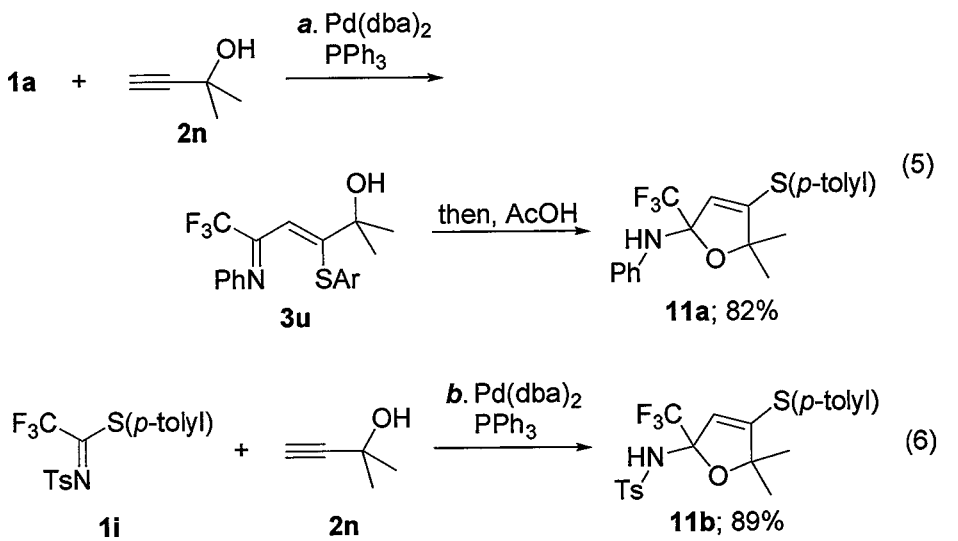
A plausible reaction mechanism of the present iminothiolation of alkynes (**2**; $R^1C{\equiv}CR^2$) using iminosulfides (**1**; $R^3C(=NR^4)SR^5$) was depicted in Scheme 3. The oxidative addition of **1** to $Pd(0)L_n$ complex triggers the reaction to afford $PdL_n[C(=NR^4)R^3](SR^5)$ (**8**).[10] Subsequent

regio- and stereoselective insertion of alkyne **2** into the S-Pd bond of **8** generates $PdL_n[C(=NR^4)R^3][cis\text{-}C(R^1)=C(SR^5)(R^2)]$ (**9**).[11] Finally, the C-C bond-forming reductive elimination of *cis*-**3** from **9** with regeneration of $Pd(0)L_n$ 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 $Pd(0)L_n$ complex to produce $PdL_n[cis\text{-}C(R^2)=C(R^1)\{C(=NR^4)R^3\}](SR^5)$ (*cis*-**10**),[12] *cis*-to-*trans* isomerization of *cis*-**10**,[13] and the reductive elimination of *trans*-**3** from *trans*-**10**.

Scheme 3. A Plausible Mechanism for the Pd-Catalyzed Imino-thiolation 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.), PPh_3 (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.), PPh_3 (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.[14] Substituted furan (**11a**) was successfully obtained from the reaction of **1a** with 3-methyl-1-butyn-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

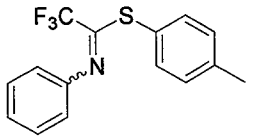
The present study substantiated that the iminothiolation of alkynes with iminosulfides gave rise to the formation of 1-azadiene derivatives. The author found that introduction of CF_3 group to the iminocarbon moiety is a key to achieve the reaction. Furthermore, the present synthesis of 1-azadienes was applicable to the formation of furan derivatives.

2-7. Experimental Section

General Comments: ^1H and ^{13}C NMR spectra in $CDCl_3$, benzene-d_6 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 C_6H_6 (δ 7.15), and the chemical shifts in the ^{13}C NMR spectra were recorded relative to $CHCl_3$ (δ 77.0) and C_6H_6 (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*-**3l** 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 N_2 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 Et_3N under benzene reflux. The platinum complex $Pt(PPh_3)_2(C_2H_4)$ was synthesized according to the literature (*Inorg. Synth.* **1978**, *18*, 120). Benzene-d_6 and toluene-d_8 were purified by distillation from sodium benzophenon ketyl before use.

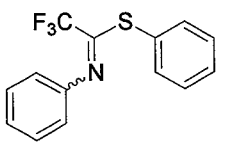
Preparation of $F_3CC(=NC_6H_5)SC_6H_4$-*p*-CH_3 (1a): Into a three-neaked 100 mL reaction glass equipped with reflux condenser were added *p*-tolylthiol (6.23 g, 30.0 mmol), benzene (30 mL), $F_3CC(=NC_6H_5)Cl$ (3.66 g, 29.9 mmol)[15] and triethylamine (8.0 mL, 58 mmol). After the solution was stirred under reflux for 3 h, the white precipitate was filtered and the filtrate was

evaporated and dried *in vacuo*. **1a** were isolated in 90% (7.94 g, 26.9 mmol) yields by recrystallization using CH_2Cl_2 and hexane.

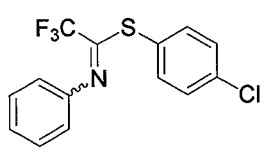


$F_3CC(=NC_6H_5)SC_6H_4$-*p*-CH_3 (1a): pale yellow solid; mp 61 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 6.89 (d, J = 7.8 Hz, 2 H), 7.06 (d, J = 7.8 Hz, 2 H), 7.13 (t, J = 7.3 Hz, 1 H), 7.30-7.33 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 118.5 (c, J = 278 Hz), 119.1, 122.7, 125.5, 128.9, 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 $C_{15}H_{12}F_3NS$: 295.0643. Found: 295.0640.

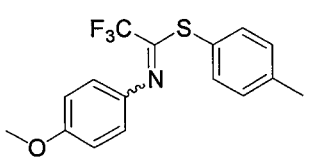
Other iminosulfides (**1b-i**) were synthesized by similar procedures.



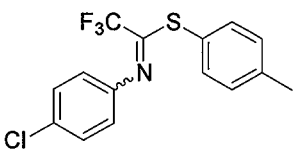
$F_3CC(=NC_6H_5)SC_6H_5$ (1b): pale yellow solid; mp 50 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 7.8 Hz, 2 H), 7.12 (t, J = 7.3 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5 (c, J = 279 Hz), 119.1, 125.6, 126.6, 129.0, 129.1, 129.8, 135.5, 146.8, 152.4 (c, J = 35 Hz); 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 $C_{14}H_{10}F_3NS$: 281.0486. Found: 281.0482.



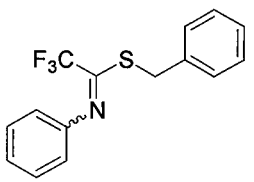
$F_3CC(=NC_6H_5)SC_6H_4$-*p*-Cl (1c): yellow solid; mp 66 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, J = 7.8 Hz, 2 H), 7.13 (t, J = 8.3 Hz, 1 H), 7.20 (d, J = 8.3 Hz, 2 H), 7.28-7.31 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.1 (c, J = 279 Hz), 124.6, 125.4, 128.7, 129.0, 13.2, 136.4, 146.3, 151.3 (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 $C_{14}H_9ClF_3NS$: 315.0096. Found: 315.0089.



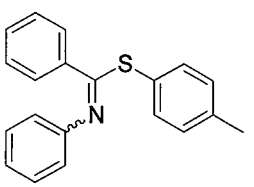
$F_3CC(=NC_6H_4$-*p*-$OCH_3)SC_6H_4$-*p*-CH_3 (1d): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 3.81 (s, 3 H), 6.87 (d, J = 9.3 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 7.8 Hz, 2 H), 7.32 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 55.4, 114.1, 118.7 (c, J = 279 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 $C_{16}H_{14}F_3NOS$: 325.0748. Found: 325.0746.



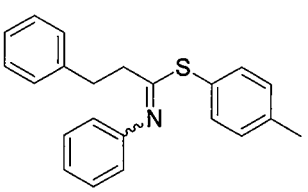
$F_3CC(=NC_6H_4$-*p*-Cl)SC_6H_4-*p*-CH_3 (1e): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 6.81 (d, J = 8.3 Hz, 2 H), 7.09 (d, J = 8.3 Hz, 2 H), 7.25-7.29 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 118.4 (c, J = 279 Hz), 120.5, 122.3, 128.9, 129.9, 130.9, 135.5, 140.5, 145.1, 153.7 (c, J = 34 Hz); IR (NaCl) 3027, 2923, 1885, 1628, 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 $C_{15}H_{11}ClF_3NS$: 329.0253. Found: 329.0254.



$F_3CC(=NC_6H_5)SCH_2C_6H_5$ (1f): pale yellow solid; mp 71 °C; ^{1}H NMR (400 MHz, $CDCl_3$, - 40 °C) major isomer δ 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 δ 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) δ 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 $C_{15}H_{12}F_3NS$: 295.0643. Found: 295.0645.

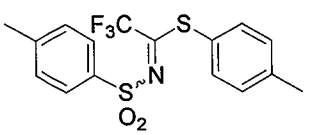


PhC(=NPh)SC_6H_4-*p*-CH_3 (1g): yellow solid; mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3 H), 6.87 (d, J = 6.8 Hz, 2 H), 6.99 (d, J = 7.3 Hz, 2 H), 7.03 (d, J = 7.3 Hz, 2 H), 7.13 (dd, J = 6.4, 6.8 Hz, 1 H), 7.20-7.27 (m, 3 H), 7.36 (dd, J = 6.3, 6.4 Hz, 2 H), 7.65 (d, J = 5.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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.



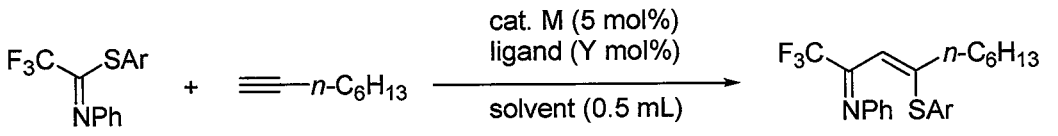
$PhCH_2CH_2C(=NPh)SC_6H_4$-*p*-CH_3 (1h): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3 H), 2.62 (t, J = 8.3 Hz, 2 H), 2.93 (t, J = 8.3 Hz, 2 H), 6.89 (d, J = 7.3 Hz, 2 H), 7.01 (d, J = 6.8 Hz, 2 H), 7.10-7.24 (m, 7 H), 7.34-7.38 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 33.4, 39.5, 119.7, 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.



$F_3CC(=N\text{-}SO_2\text{-}C_6H_4\text{-}p\text{-}CH_3)SC_6H_4\text{-}p\text{-}CH_3$ (1i): white solid; mp 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3 H), 2.47 (s, 3 H), 7.24 (d, J = 12 Hz, 2 H), 7.37 (d, J = 12 Hz, 2 H), 7.50 (d, J = 12 Hz, 2 H), 7.90 (d, J = 12 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.7, 117.7 (c, J = 283 Hz), 121.1, 126.2, 127.7, 129.7, 130.3, 136.1, 136.2, 142.2, 145.1, 167.0 (c, J = 35 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 cm^{-1}; mass spectrum (EI) m/z 373 (M^+, 8.3); HRMS calcd for $C_{16}H_{14}F_3NO_2S_2$: 373.0418. Found: 373.0420.

Table S1. Optimization of the reaction conditions[a]

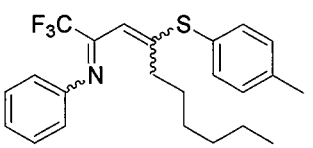


1a **2a** **3a**

run	M	ligand	Y	solvent	temp	time	**3a** (%) (*cis*/*trans*)[b]
1	$Pd(PPh_3)_4$	-	-	toluene	80 °C	25 h	75[c] (22:78)
2	$Pd(PPh_3)_4$	-	-	DME	80 °C	25 h	71[c] (22:78)
3	$Pd(PPh_3)_4$	-	-	1,4-dioxane	80 °C	25 h	56[c] (24:76)
4	$Pd(PPh_3)_4$	-	-	MeCN	80 °C	25 h	82[c] (28:72)
5	$Pd(PPh_3)_4$	-	-	DMF	80 °C	25 h	69 (23:77)
6	$Pd(PPh_3)_4$	-	-	DCE	80 °C	25 h	86 (21:79)
7	$Pd(PPh_3)_4$	-	-	DCE	80 °C	1 h	71 (27:73)
8	$Pd(PPh_3)_4$	-	-	DCE	80 °C	5 h	83 (24:76)
9	$Pd(PPh_3)_4$	-	-	DCE	80 °C	10 h	74 (22:78)
10	$Pd(PPh_3)_4$	-	-	DCE	r.t.	25 h	25 (13:87)
11	-	-	-	DCE	80 °C	25 h	n.d.
12	$Pd(dba)_2$	-	-	DCE	80 °C	1 h	n.d.
13	$Pd(dba)_2$	PPh_3	20	DCE	80 °C	1 h	84 (22:78)
14	**$Pd(dba)_2$**	**PPh_3**	**10**	**DCE**	**80 °C**	**1 h**	**93 (20:80) (89 (18:82))[d]**
15	$Pd(dba)_2$	P(*o*-tolyl)$_3$	20	DCE	80 °C	1 h	9 (14:86)
16	$Pd(dba)_2$	P(*o*-$MeOC_6H_4$)$_3$	20	DCE	80 °C	1 h	12 (15:85)
17	$Pd(dba)_2$	P(*p*-tolyl)$_3$	20	DCE	80 °C	1 h	70 (22:78)
18	$Pd(dba)_2$	P(*p*-$MeOC_6H_4$)$_3$	20	DCE	80 °C	1 h	65 (19:81)
19	$Pd(dba)_2$	P(*p*-ClC_6H_4)$_3$	20	DCE	80 °C	1 h	77 (25:75)
20	$Pd(dba)_2$	P(*p*-$CF_3OC_6H_4$)$_3$	20	DCE	80 °C	1 h	64 (20:80)
21	$Pd(dba)_2$	TFP	20	DCE	80 °C	1 h	75 (29:71)
22	$Pd(dba)_2$	PCy_3	20	DCE	80 °C	1 h	57 (25:75)
23	$Pd(dba)_2$	P(*t*-Bu)$_3$	20	DCE	80 °C	1 h	75 (20:80)
24	$Pd(dba)_2$	dppe	20	DCE	80 °C	1 h	37 (19:81)

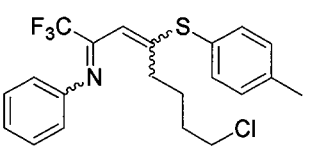
[a] Unless otherwise noted, **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (0.025 mmol), ligand and solvent (0.5 mL). [b] NMR yield. [c] Some byproducts were generated. [d] isolated yield. DCE = 1,2-dichloroethane. TFP = tri(2-furyl)phosphine.

Reaction of $F_3CC(NC_6H_5)SC_6H_4$-*p*-CH_3 (1a) with 1-Octyne (2a) in the Presence of $Pd(dba)_2/2PPh_3$ (run 1 of Table 1): General Procedure of Palladium-Catalyzed Iminothiolation of Alkynes Using Iminosulfides: Into a two-neaked 3 mL reaction glass were added $Pd(dba)_2$ (14.4 mg, 0.025 mmol), PPh_3 (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 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*. **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.



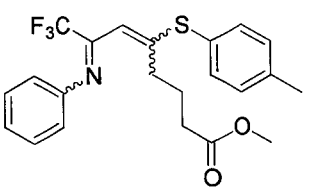
$CF_3C(=NC_6H_5)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (3a): The title compound was obtained as a mixture of inseparable stereoisomers (*cis*:*trans* = 18:82); yellow oil; ^{1}H NMR (400 MHz, C_6D_6) *trans*-isomer δ 0.81 (t, *J* = 7.1 Hz, 3 H), 0.85-0.89 (m, 2 H), 0.94-1.03 (m, 2 H), 1.68-1.75 (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); ^{13}C NMR (100 MHz, C_6D_6) *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 $C_{23}H_{26}F_3NS$: 405.1738. Found: 405.1733.

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

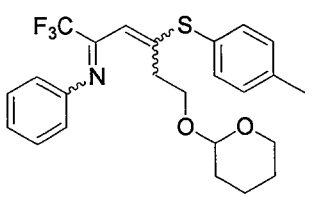


$CF_3C(=NC_6H_5)C(H)=C((CH_2)_4Cl)SC_6H_4$-*p*-$CH_3$ (3b): The title compound was obtained as a mixture of inseparable stereoisomers (*cis*:*trans* = 13:87); yellow oil; ^{1}H NMR (400 MHz, C_6D_6) *trans* -isomer δ 0.97-1.04 (m, 2 H), 1.09-1.17 (m, 2 H), 1.68 (t, *J* = 7.3 Hz, 2 H), 1.92 (s, 3 H), 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; ^{13}C NMR (100 MHz, C_6D_6) *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,

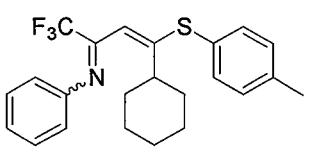
3023, 2956, 2869, 1681, 1638, 1600, 1556, 1493, 143, 1398, 1379, 1282, 1248, 1226, 1185, 1134, 1018, 1000, 907, 811, 749, 729, 695, 655, 569 cm^{-1}; mass spectrum (EI) m/e 411 (M^+, 19); HRMS calcd for $C_{21}H_{21}ClF_3NS$: 411.1035. Found: 411.1021.



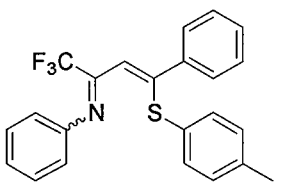
$CF_3C(=NC_6H_5)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_4$-*p*-$CH_3$ (3c): The title compound was obtained as a mixture of inseparable stereoisomers (*cis*:*trans* = 14:86); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) *trans*-isomer δ 1.59 (tt, J = 6.8, 7.8 Hz, 2 H), 1.99 (t, J = 7.8 Hz, 2 H), 2.00 (t, J = 6.8 Hz, 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; ^{13}C NMR (100 MHz, $CDCl_3$) *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, 1438, 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 $C_{22}H_{22}F_3NO_2S$: 421.1323. Found: 421.1318.



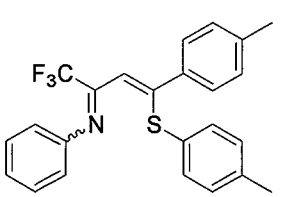
$CF_3C(=NC_6H_5)C(H)=C((CH_2)_2O(2\text{-}C_5H_9O))SC_6H_4$-*p*-$CH_3$ (3d): The title compound was obtained as a mixture of inseparable stereoisomers (*cis*:*trans* = 13:87); yellow oil; ^1H NMR (400 MHz, C_6D_6) *trans*-isomer δ 1.22-1.37 (m, 3 H), 1.46-1.53 (m, 2 H), 1.63-1.71 (m, 1 H), 1.90 (s, 3 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; ^{13}C NMR (100 MHz, C_6D_6) *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 $C_{24}H_{26}F_3NO_2S$: 449.1636. Found: 449.1639.



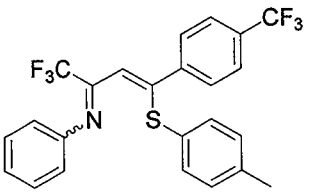
***trans*-$CF_3C(=NC_6H_5)C(H)=C(c\text{-}C_6H_{11})SC_6H_4\text{-}p\text{-}CH_3$ (*trans*-3e):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.69-0.91 (m, 4 H), 1.31 (d, J = 13 Hz, 2 H), 1.42 (d, J = 13 Hz, 2 H), 1.66 (d, J = 12 Hz, 2 H), 1.78-1.85 (m, 1 H), 1.94 (s, 3 H), 5.88 (s, 1 H), 6.69 (d, J = 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 1057, 1041, 1018, 986, 910, 879, 811, 761, 727, 694, 634, 587 cm^{-1}; mass spectrum (EI) m/e 403 (M^+, 13); Anal. Calcd for $C_{23}H_{24}F_3NS$: C, 68.46; H, 6.00; N, 3.47. Found: C, 68.28; H, 5.88; N, 3.41.



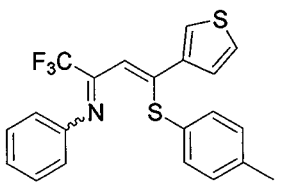
***cis*-$CF_3C(=NC_6H_5)C(H)=C(C_6H_5)SC_6H_4\text{-}p\text{-}CH_3$ (*cis*-3f):** yellow solid; mp 114 °C; ^1H NMR (400 MHz, $CDCl_3$) main isomer δ 2.13 (s, 3 H), 6.26 (s, 1 H), 6.54 (d, J = 8.0 Hz, 2 H), 6.76 (d, J = 7.8 Hz, 2 H), 7.05 (d, J = 7.8 Hz, 2 H), 7.14-7.19 (m, 4 H), 7.27-7.34 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{23}H_{18}F_3NS$: C, 69.50; H, 4.56; N, 3.52. Found: C, 69.32; H, 4.48; N, 3.62.



***cis*-$CF_3C(=NC_6H_5)C(H)=C(C_6H_4\text{-}p\text{-}CH_3)SC_6H_4\text{-}p\text{-}CH_3$ (*cis*-3g):** yellow solid; mp 100 °C; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 1380, 1322, 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 $C_{24}H_{20}F_3NS$: C, 70.05; H, 4.90; N, 3.40. Found: C, 69.83; H, 4.68; N, 3.47.

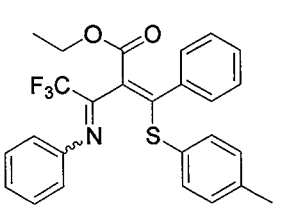


***cis*-$CF_3C(=NC_6H_5)C(H)=C(C_6H_4$-*p*-$CF_3)SC_6H_4$-*p*-$CH_3$ (*cis*-3h):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) main isomer δ 2.15 (s, 3 H), 6.30 (s, 1 H), 6.53 (d, J = 7.8 Hz, 2 H), 6.78 (d, J = 7.8 Hz, 2 H), 7.05 (d, J = 7.3 Hz, 2 H), 7.20 (t, J = 7.3 Hz, 2 H), 7.35-7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) main isomer δ 21.1, 119.8 (c, J = 277 Hz), 120.9, 121.3, 123.8 (c, J = 239 Hz), 125.3 (c, J = 4.1 Hz), 126.3, 128.1, 128.7, 129.1, 129.7, 130.0 (d, J = 32 Hz), 131.0, 137.8, 141.1, 146.4, 147.6, 154.8 (c, J = 35 Hz); IR (NaCl) 3059, 302, 2979, 2925, 2869, 1901, 1794, 1660, 1615, 1593, 1543, 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 $C_{24}H_{17}F_6NS$: C, 61.93; H, 3.68; N, 3.01. Found: C, 61.68; H, 3.56; N, 2.99.



***cis*-$CF_3C(=NC_6H_5)C(H)=C(3$-$C_4H_3S)SC_6H_4$-*p*-CH_3 (*cis*-3i):** yellow solid; mp 78 °C; ^1H NMR (400 MHz, $CDCl_3$) main isomer δ 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 δ 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, 1079, 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 $C_{21}H_{16}F_3NS_2$: C, 62.51; H, 4.00; N, 3.47. Found: C, 62.22; H, 3.82; N, 3.50.

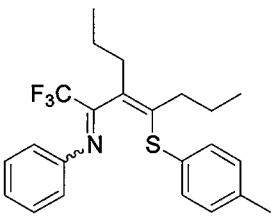
Reaction of $F_3CC(NC_6H_5)SC_6H_4$-p-CH_3 (1a) with Ethyl Phenylpropiolate (2l) in the Presence of $Pd(dba)_2$/2PPh_3 under the Microwave Irradiation (run 12 of Table 1): General Procedure of Palladium-Catalyzed Iminothiolation of Alkynes Using Iminosulfides under the Microwave Irradiation: Into a 2 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.



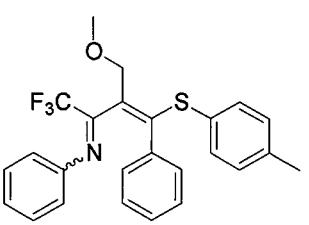
***cis*-$CF_3C(=NC_6H_5)C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-$CH_3$ (*cis*-3l):** pale yellow solid; mp 92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3 H), 3.98 (c, J = 7.3 Hz, 2 H), 6.39 (d, J = 7.8 Hz, 2 H), 6.70 (d, J = 7.8 Hz, 2 H), 6.83 (d, J = 7.8 Hz, 2 H), 6.99-7.07 (m, 3 H), 7.26-7.28

(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, 3004, 2980, 2957, 2937, 2924, 2898, 2870, 1696, 1656, 1591, 1578, 1555, 1486, 1473, 1446, 1389, 1363, 1318, 1274, 1222, 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 $C_{26}H_{22}F_3NO_2S$: C, 66.51; H, 4.72; N, 2.98. Found: C, 66.23; H, 4.64; N, 3.03.

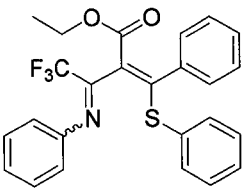
Other iminothiolation products (**3j, m-s**) using internal alkynes (**2j, l, m**) were synthesized by similar procedures.



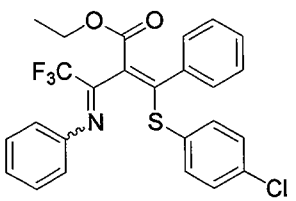
$CF_3C(=NC_6H_5)C(n\text{-}C_3H_7)=C(n\text{-}C_3H_7)SC_6H_4\text{-}p\text{-}CH_3$ (3j): The title compound was obtained as a mixture of inseparable stereoisomers (*cis*:*trans* = 95:5); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *cis*-isomer δ 0.76 (t, J = 7.3 Hz, 3 H), 0.86 (t, J = 7.3 Hz, 3 H), 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, 8.3 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 $C_{23}H_{26}F_3NS$:405.1738. Found: 405.1741.



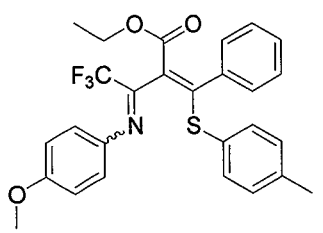
***trans*-$CF_3C(=NC_6H_5)C(CH_2OCH_3)=C(C_6H_5)SC_6H_4\text{-}p\text{-}CH_3$ (*trans*-3m):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3 H), 3.22 (s, 3 H), 3.76 (dd, J = 12.2, 67.4 Hz, 2 H), 6.62 (d, J = 7.8 Hz, 2 H), 6.75 (d, J = 7.8 Hz, 2 H), 6.99-7.01 (m, 2 H), 7.09 (s, 3 H), 7.22-7.28 (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 $C_{25}H_{22}F_3NOS$: C, 68.01; H, 5.02; N, 3.17. Found: C, 67.72; H, 4.88; N, 3.21.



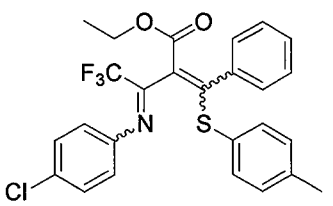
***cis*-$CF_3C(=NC_6H_5)C(CO_2C_2H_5)=C(C_6H_5)SC_6H_5$ (*cis*-3n):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 6.8 Hz, 3 H), 3.99 (c, J = 6.8 Hz, 2 H), 6.50 (d, J = 7.3 Hz, 2 H), 6.84 (d, J = 7.8 Hz, 2 H), 6.90 (dd, J = 7.3, 7.8 Hz, 2 H), 6.98-7.05 (m, 4 H), 7.26-7.30 (m, 3 H), 7.41 (dd, J = 4.4, 7.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 61.4, 119.6 (c, J = 278 Hz), 119.8, 120.3, 126.3, 127.5, 128.4, 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, 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 $C_{25}H_{20}F_3NO_2S$: C, 65.92; H, 4.43; N, 3.08. Found: C, 65.77; H, 4.21; N, 3.21.



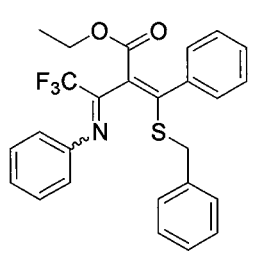
***cis*-$CF_3C(=NC_6H_5)C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-Cl (*cis*-3o):** pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 6.8 Hz, 3 H), 3.99 (c, J = 6.8 Hz, 2 H), 6.34 (d, J = 8.3 Hz, 1 H), 6.50 (d, J = 7.8 Hz, 1 H), 6.84-6.86 (m, 2 H), 6.89 (d, J = 7.8 Hz, 2 H), 6.96-7.09 (m, 3 H), 7.26-7.29 (m, 3 H), 7.38-7.42 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) These peaks were observed as two stereoisomer of $PhN=C(CF_3)R$ (R = $C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-Cl). 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, 128.4, 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 $C_{25}H_{19}ClF_3NO_2S$: 489.0772. Found: 489.0777.



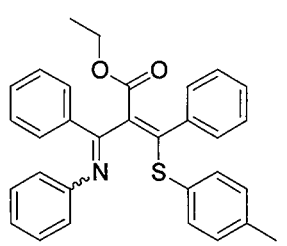
***cis*-$CF_3C(=NC_6H_4$-*p*-$OCH_3)C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-$CH_3$ (*cis*-3p):** yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 6.8 Hz, 3 H), 2.12 (s, 3 H), 3.85 (s, 3 H), 3.89 (c, J = 6.8 Hz, 2 H), 6.33 (d, J = 7.8 Hz, 2 H), 6.72 (d, J = 7.8 Hz, 2 H), 6.91 (d, J = 5.8 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 7.05-7.07 (m, 3 H), 7.29 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 21.0, 55.6, 61.3, 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 $C_{27}H_{24}F_3NO_3S$: C, 64.92; H, 4.84; N, 2.80. Found: C, 64.79; H, 4.63; N, 2.88.



$CF_3C(=NC_6H_4$-*p*-Cl)$C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-$CH_3$ (3q): 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 δ 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), 7.38 (d, *J* = 8.3 Hz, 2 H): *trans*-isomer δ 1.38 (t, *J* = 7.3 Hz, 3 H), 2.13 (s, 3 H), 3.98 (dc, *J* = 7.3, 29 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 δ 13.5, 21.0, 61.4, 119.1, 119.4 (c, *J* = 278 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 δ 14.0, 21.0, 61.6, 115.6, 119.0 (c, *J* = 279 Hz), 122.7, 126.6, 127.3, 128.3, 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 $C_{26}H_{21}ClF_3NO_2S$: C, 61.96; H, 4.20; N, 2.78. Found: C, 61.86; H, 3.99; N, 2.72.



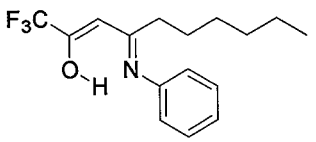
***cis*-$CF_3C(=NC_6H_5)C(CO_2C_2H_5)=C(C_6H_5)SCH_2C_6H_5$ (*cis*-3r):** pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 6.8 Hz, 3 H), 3.19 (dd, *J* = 13, 77 Hz, 2 H), 3.96 (c, *J* = 6.8 Hz, 2 H), 6.90 (br, 2 H), 6.96 (br, 2 H), 7.12 (d, *J* = 8.3 Hz, 2 H), 7.20-7.25 (m, 4 H), 7.32-7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 37.3, 61.1, 119.2, 119.4 (c, *J* = 278 Hz), 119.7, 126.1, 127.5, 127.7, 128.4, 128.4, 128.5, 128.8, 129.2, 135.1, 135.7, 147.4, 155.4 (c, *J* = 35 Hz), 162.8; IR (NaCl) 3656, 3369, 3065, 3033, 3006, 2987, 2939, 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 (CI) m/e 470 (M^+, 100); Anal. Calcd for $C_{26}H_{22}F_3NO_2S$: C, 66.51; H, 4.72; N, 2.98. Found: C, 66.40; H, 4.67; N, 3.00.



***cis*-$C_6H_5C(=NC_6H_5)C(CO_2C_2H_5)=C(C_6H_5)SC_6H_4$-*p*-$CH_3$ (*cis*-3s):** pale yellow solid; mp 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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), 7.48-7.49 (m, 3 H), 8.04-8.06 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.7, 61.4, 120.9, 124.9, 126.4, 127.4, 128.1, 128.7, 128.9, 129.1, 129.3, 129.4, 129.7, 131.5, 134.5, 137.0, 138.8, 151.7, 156.3, 164.4, 165.3; IR (KBr) 3359, 3080, 3057, 3021, 2980, 2923, 2903, 2871, 2323, 1966, 1906, 1689, 1614, 1592, 1576, 1553, 1489,

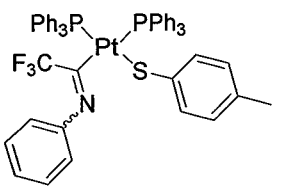
1445, 1393, 1367, 1315, 1289, 1262, 1204, 1182, 1173, 1107, 1072, 1027, 1017, 1000, 967, 931, 906, 832, 810, 768, 751, 741, 696, 671, 591 cm^{-1}; mass spectrum (EI) m/e 477 (M^+, 6.3); Anal. Calcd for $C_{31}H_{27}NO_2S$: C, 77.96; H, 5.70; N, 2.93. Found: C, 77.67; H, 5.82, N; 2.88.

Reaction of $F_3CC(O)C(H)=C(n\text{-}C_6H_{13})(S\text{-}p\text{-tolyl})$ (4a) with aniline (Eq. 3): Into a two-neaked 3 mL reaction glass were added **4a** (82.0 mg, 0.248 mmol) and aniline (22.5 mg, 0.242 mmol) under N_2 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.



$CF_3C(OH)=C(H)C(n\text{-}C_6H_{13})(=NC_6H_5)$ (5a): yellow oil; ^1H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (100 MHz, C_6D_6) 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, 1494, 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 $C_{16}H_{20}F_3NO$: C, 64.20; H, 6.73; N, 4.68. Found: C, 64.40; H, 6.66; N, 4.73.

The Preparation of *cis*-$Pt[P(C_6H_5)_3]_2[C(=NC_6H_5)CF_3](SC_6H_4\text{-}p\text{-}CH_3)$ (*cis*-6a): Into a dry two-necked reaction vessel equipped with a stirring bar were added $Pt(PPh_3)_2(C_2H_4)$ (371 mg, 0.496 mmol), **1a** (154 mg, 0.526 mmol) and C_6H_6 (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 × 3) and dried to give *cis*-**6a** (413 mg, 82%).



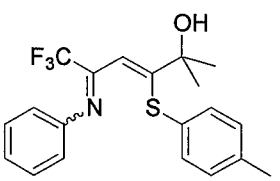
cis-**6a**: white solid; mp 190 °C; ^1H NMR (400 MHz, C_6D_6) δ 1.90 (s, 3 H), 6.68 (d, J = 7.8 Hz, 2 H), 6.74-6.94 (m, 20 H), 7.23-7.36 (m, 10 H), 7.51 (br, 5 H), 7.64 (d, J = 7.8 Hz, 2 H); ^{31}P NMR (160 Hz, C_6D_6) δ 18.0 (c, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 1807 Hz, $J_{P\text{-}F}$ = 24 Hz), 18.1 (d, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 3135 Hz); IR (KBr) 3054, 2358, 2309, 1586, 1484, 1436, 1248, 1142, 1122, 1095, 927, 765, 743, 694 cm^{-1}; Anal. Calcd for $C_{51}H_{42}F_3NP_2PtS$: C, 60.35; H, 4.17; N, 1.38. Found: C, 60.60; H, 4.18; N, 1.34.

The Reaction of 1 with $Pt(PPh_3)_2(C_2H_4)$ (Eq. 4): Into a dry Pyrex NMR tube were added $Pt(PPh_3)_2(C_2H_4)$ (0.020 mmol), **1** (0.022 mmol), $S=P(C_6H_4OMe\text{-}p)_3$ (0.01 mmol as an internal standard) and benzene-d_6 (0.5 mL) under N_2 atmosphere. The reaction was monitored by ^{31}P and ^1H NMR spectrum at 25 °C.

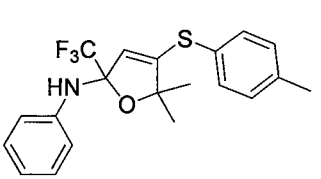
***cis*-6a:** ^{31}P NMR (160 MHz, C_6D_6) δ 18.0 (c, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 1807 Hz, $J_{Pt\text{-}F}$ = 24 Hz), 18.1 (d, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 3135 Hz). ***trans*-6a:** ^{31}P NMR (160 MHz, C_6D_6) δ 13.2 (s, $J_{Pt\text{-}P}$ = 2944 Hz).

***cis*-6b:** ^{31}P NMR (160 MHz, C_6D_6) δ 18.0 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 20.1 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6b:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, $J_{Pt\text{-}P}$ = 3133 Hz). **7b (*syn*/*anti* mixture);** ^{31}P NMR (160 MHz, C_6D_6) δ 15.9 (s, value of $J_{Pt\text{-}P}$ was not able to read because of low intensity.), 17.1 (s, value of $J_{Pt\text{-}P}$ was not able to read because of low intensity.).

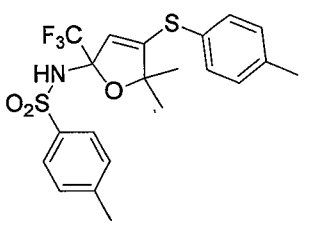
Synthesis of Furan Derivatives (Eq. 5): Into a two-neaked 3 mL reaction glass were added $Pd(dba)_2$ (0.025 mmol), PPh_3 (0.05 mmol), **1a** (0.5 mmol), 3-methyl-1-buthyne-3-ol (**2n**) (0.6 mmol) and 0.5 mL of 1,2-dichloroethane under N_2 atmosphere. After the solution was stirred at 80 °C for 1 h, 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-neaked 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.



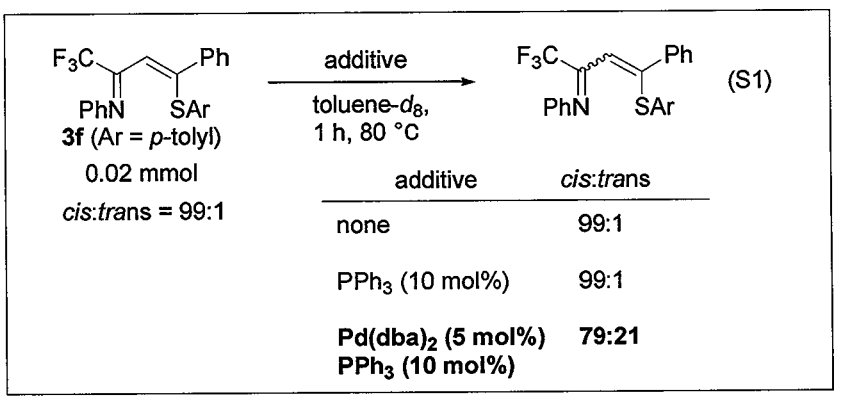
***cis*-$CF_3C(=NC_6H_5)C(H)=C[C(CH_3)_2OH]SC_6H_4$-*p*-$CH_3$ (3u):** pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 6 H), 2.01 (s, 1 H), 2.28 (s, 3 H), 6.73 (s, 1 H), 6.95 (d, J = 8.3 Hz, 2 H), 6.99-7.01 (m, 4 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.33 (t, J = 7.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 calcd for $C_{20}H_{20}F_3NOS$: 379.1218. Found: 379.1212.



11a: white solid; mp 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{20}H_{20}F_3NOS$: C, 63.31; H, 5.31; N, 3.69. Found: C, 63.19; H, 5.27; N, 3.68.



11b (Eq. 6): yellow solid; mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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, 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 (M^+, 18.1); Anal. Calcd for $C_{21}H_{22}F_3NO_3S_2$: 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-d_8 (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-d_8 under N_2 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

(1) For a recent review, see: Groenendaal, B.; Ruijter, E.; Orru, R. V. A.; *Chem. Commun.* **2008**, 5474.

(2) (a) Kobayashi, T.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1985**, *26*, 3463. (b) Kosugi, M.; Koshiba, M.; Atoh, A.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 677. (c) Kosugi, M.; Ogata, T.; Tamura, H.; Sano, H.; Migita, T. *Chem. Lett.* **1986**, 1197. (d) Uneyama, K.; Watanabe, H. *Tetrahedron Lett.* **1991**, *32*, 1459.

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

(4) For recent examples, see: (a) Yamashita, F.; Kuniyasu, H.; Terao, J.; Kambe, N. *Org. Lett.* **2008**, *10*, 101. (b) Toyofuku, M.; Fujiwara, S.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2008**, *130*, 10504. (c) Toyofuku, M.; Murase, E.; Fujiwara, S.; Shin-ike, T.;

Kuniyasu, H.; Kambe, N. *Org. Lett.* **2008**, *10*, 3957. (d) Toyofuku, M.; Murase, E.; Nagai, H.; Fujiwara, S.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *Eur. J. Org. Chem.* **2009**, 3141.

(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 **2l** was performed at 100 °C in a sealed vessel without a microwave, **3l** 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 **3l**: Space group Pbca (#61) with a = 15.2284(7) Å, b = 17.6487(8) Å, c = 17.8733(9) Å, b = 96.385(2)°, Z = 8, ρ = 1.298 g/cm^3, R = 0.0661, and Rw = 0.189.

(10) (a) Bowman, W. R.; Lyon, J. E.; Pritchard, G. J. *Synlett* **2008**, *14*, 2169. (b) Takeda, H.; Ishida, T.; Takemoto, Y. *Chem. Lett.* **2009**, 772.

(11) For a stoichiometric insertion of alkynes into the S-M bond, see: (a) Sugoh, K.; Kuniyasu, H.; Kurosawa, H. *Chem. Lett.* **2002**, *31*, 106. (b) Kuniyasu, H.; Yamishita, F.; Terao, J.; Kambe, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 5929. (c) Kuniyasu, H.; Takekawa, K.; Yamashita, F.; Miyafuji, K.; Asano, S.; Takai, Y.; Ohtaka, A.; Tanaka, A.; Sugoh, K.; Kurosawa, H.; Kambe, N. *Organometallics* **2008**, *27*, 4788.

(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.

(13) For an isomerization of vinylmetal complexes studies, see: (a) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (c) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408.

(14) *The Chemistry of Heterocycles: Structure, Reactions, Syntheses, and Applications*, (Eds.: T. Eicher, S. Hauptmann), Wiley-VCH, Weinheim, **2003**; and references therein.

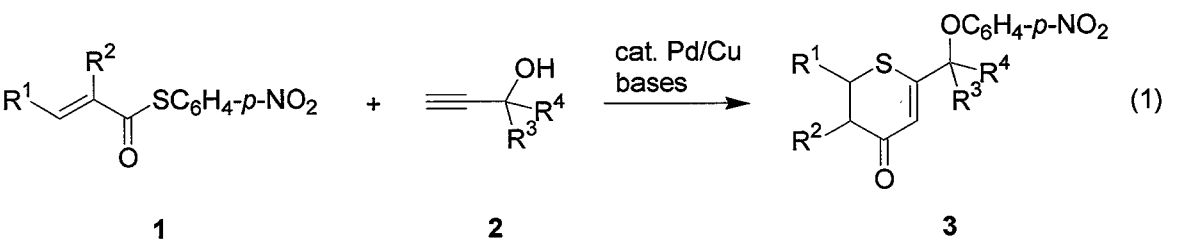
(15) Tamura, K.; Mizukami, H.; Maeda, K.; Watanabe, H.; Uneyama, K. *J. Org. Chem.* **1993**, *58*, 32

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]

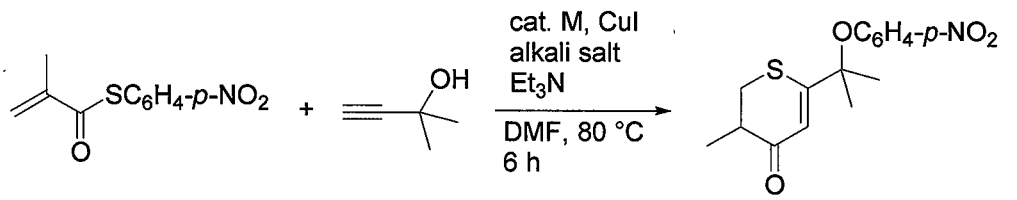


1 **2** **3**

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

The reaction of CH_2=C(Me)C(O)SC_6H_4-*p*-NO_2 (**1a**, 0.4 mmol) with 2-methyl-3-butyn-2-ol (**2a**, 0.5 mmol) in the presence of $PdCl_2$ (0.004 mmol), CuI (0.04 mol) and Et_3N (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), K_2CO_3 (10 mol %) resulted in the best yield (60% isolated yield) (run 3, Table 1). Alteration of the amounts of K_2CO_3 (5 mol %) (run 6, Table 1), CuI (2 mol %, 100 mol %) (runs 7 and 8, Table 1), or Et_3N (20 mol %) (run 9, Table 1) decreased the yield of **3a**. Other complexes such as $Pd(OAc)_2$ (run 10, Table 1), $PdCl_2(PhCN)_2$ (run 11, Table 1), $PdCl_2(PPh_3)_2$ (run 12, Table 1), $PdCl_2$(dppf) (run 13, Table 1) and $PtCl_2$ (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**[a]



1a **2a** **3a**

run	M	CuI (X mol%)	Et_3N (Y equiv.)	alkali salt	Yield (%)[b]
1	$PdCl_2$	10	1	none	34
2	$PdCl_2$	10	1	Na_2CO_3	40
3	$PdCl_2$	10	1	K_2CO_3	68 (60)[c]
4	$PdCl_2$	10	1	Cs_2CO_3	60
5	$PdCl_2$	10	1	KOAc[d]	23
6	$PdCl_2$	10	1	K_2CO_3[e]	49
7	$PdCl_2$	20	1	K_2CO_3	19
8	$PdCl_2$	100	1	K_2CO_3	16
9	$PdCl_2$	10	0.2	K_2CO_3	28
10	$Pd(OAc)_2$	10	1	K_2CO_3	45
11	$PdCl_2(PhCN)_2$	10	1	K_2CO_3	61
12	$PdCl_2(PPh_3)_2$	10	1	K_2CO_3	48
13	$PdCl_2$(dppf)	10	1	K_2CO_3	25
14	$PtCl_2$	10	1	K_2CO_3	14

[a] Unless otherwise noted, **1a** (0.4 mmol), **2a** (0.5 mmol), $PdCl_2$ (0.004 mmol), CuI (0.04 mmol), K_2CO_3 (0.04 mmol), Et_3N (0.4 mmol), and DMF (0.5 mL) at 80 °C for 6 h. [b] NMR yield. [c] Isolated yield. [d] 20 mol %. [e] 5 mol %. dppf = 1,1'-bis(diphenylphosphino)ferrocene

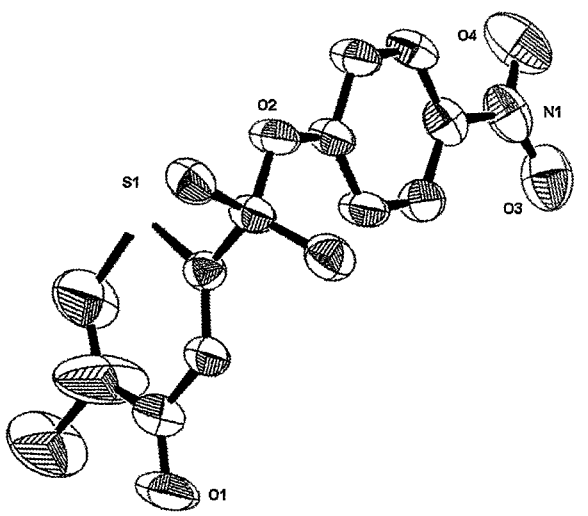
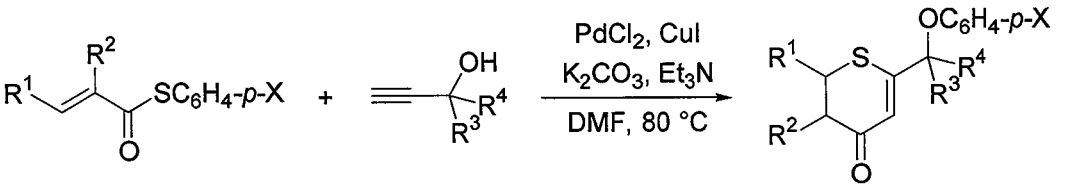


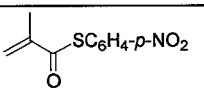
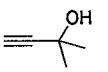
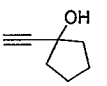
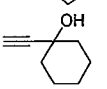
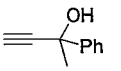
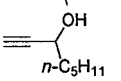
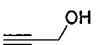
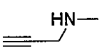
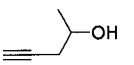
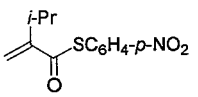
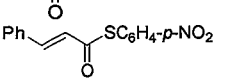
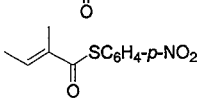
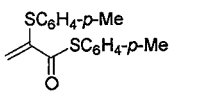
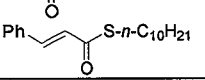
Figure 1. ORTEP Diagram of **3a**.

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**, $R^3 = R^4 = -(CH_2)_4-$; **2c**, $R^3 = R^4 = -(CH_2)_5-$; **2d**, R^3 = Me, R^4 = Ph) provided the corresponding cyclization products **3b-3d** in moderate yields (runs 2-4, Table 2). Cyclization with secondary propargyl alcohol (**2e**, R^3 = H, $R^4 = n\text{-}C_5H_{11}$) also gave **3e** in

Table 2. Pd/Cu-Catalyzed Syntheses of 2,3-Dihydrothiopyran-4-one Derivatives[a]



1 **2** **3**

run	1		2		time (h)	3	(%)[b]
1	**1a**		**2a**		6	**3a**	60
2	**1a**		**2b**		6	**3b**	48
3	**1a**		**2c**		16	**3c**	37
4	**1a**		**2d**		9	**3d**	37
5	**1a**		**2e**		6	**3e**	35
6	**1a**		**2f**		6	**3f**	n.d.
7	**1a**		**2g**		6	**3g**	n.d.
8	**1a**		**2h**		6	**3h**	n.d.
9	**1b**		**2a**		6	**3i**	60
10	**1c**		**2a**		19	**3j**	55
11	**1d**		**2a**		16	**3k**	64
12	**1d**		**2c**		18	**3l**	62
13	**1e**		**2a**		6	**3m**	n.d.
14	**1f**		**2a**		6	**3n**	n.d.

[a] Unless otherwise noted, **1** (0.4 mmol), **2** (0.5 mmol), $PdCl_2$ (0.004 mmol), CuI (0.04 mmol), K_2CO_3 (0.04 mmol), Et_3N (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 R^2 with an *i*-Pr group did not interfere with cyclization (run 9, Table 2). **1c** (R^1 = Ph, R^2 = H) was also converted into **3j** in 55% yield (run 10, Table 2). The thioester with an Me group at R^1 and a second Me at R^2 (**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*-$C_{10}H_{21}$ group rather than SC_6H_4-*p*-X (run 14, Table 2). These results demonstrate that the

SC_6H_4-*p*-NO_2 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-d_7 at 80 °C was monitored by ^{1}H 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.

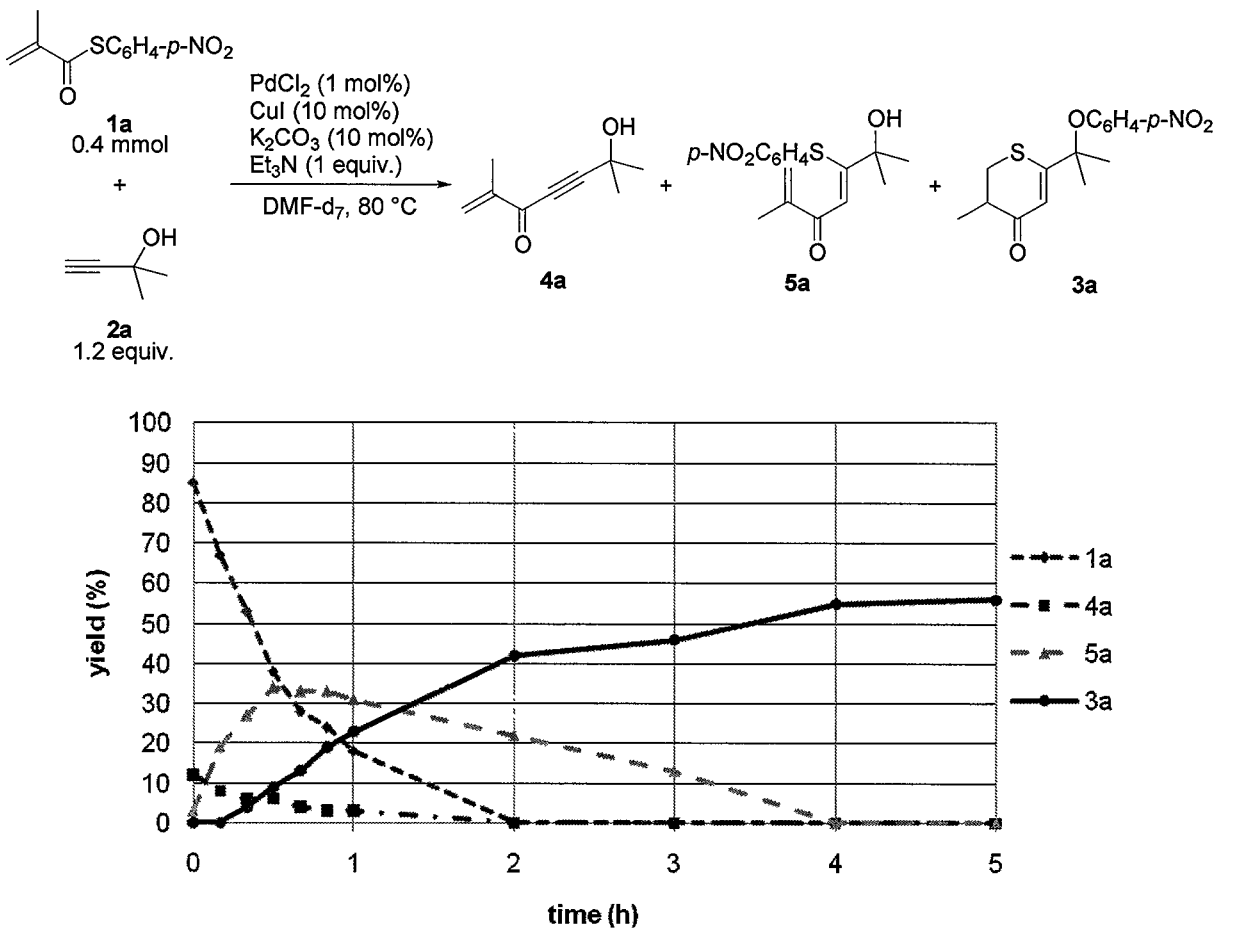
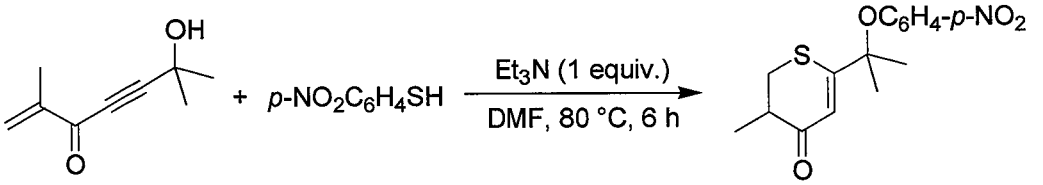


Figure 2. Time Course of the Pd/Cu-Catalyzed Reaction of **1a** with **2a**.

Thus, authentic **4a** and **5a**[3] were prepared and the reaction mechanism was examined. **4a** (0.4 mmol) reacted with *p*-$NO_2C_6H_4SH$ (**6a**, 0.4 mmol) to give **3a** in the presence of Et_3N (0.4 mmol) at 80 °C even without Pd/Cu catalysts, albeit in low yield (40%) (Eq. 2). Addition of a catalytic amount of K_2CO_3 (0.04 mmol) to the reaction mixture improved the yield of **3a** (51%). However, the yields for both the catalyst-free and K_2CO_3-catalyzed reaction of **1a** with **2a** were



(2)

4a 0.4 mmol

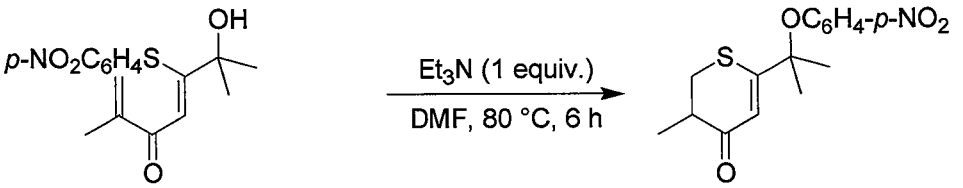
6a 1 equiv.

3a

40%

K_2CO_3 (10 mol%) 51%

without Et_3N n.d.



(3)

5a 0.2 mmol

3a

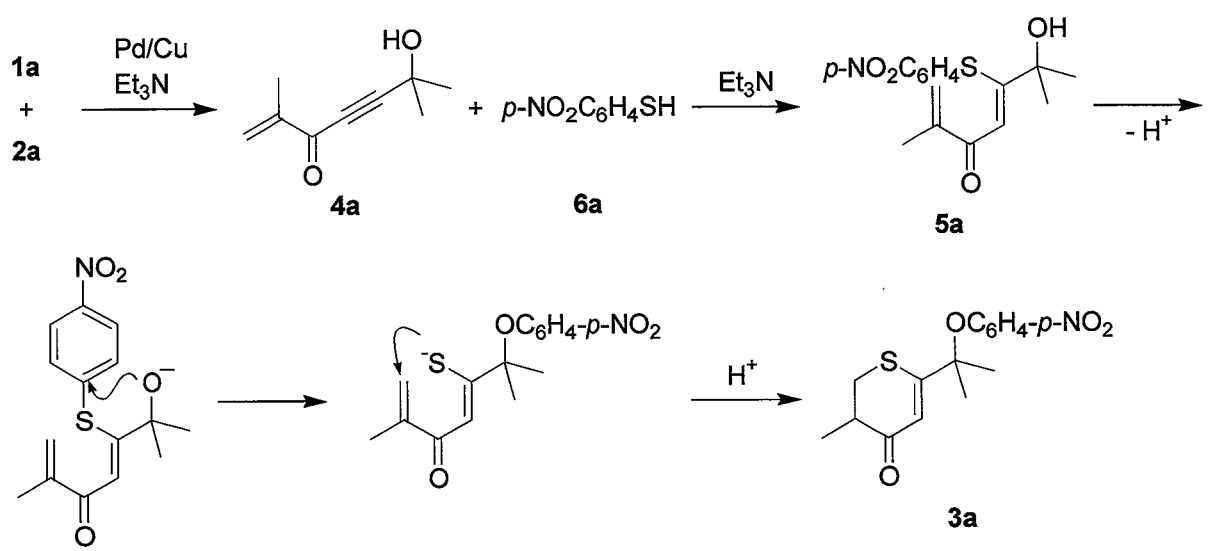
66%

without Et_3N n.d.

lower than that obtained by the Pd/Cu-catalyzed reaction due to formation of complicated byproducts (compare with run 1 of Table 2). Without Et_3N, **3a** was not formed. Intramolecular cyclization of **5a** (0.2 mmol) proceeded in the presence of Et_3N (0.2 mmol) at 80 °C to afford **3a** in 66% yield, while no reaction took place in the absence of Et_3N (Eq. 3). These results show that Et_3N 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

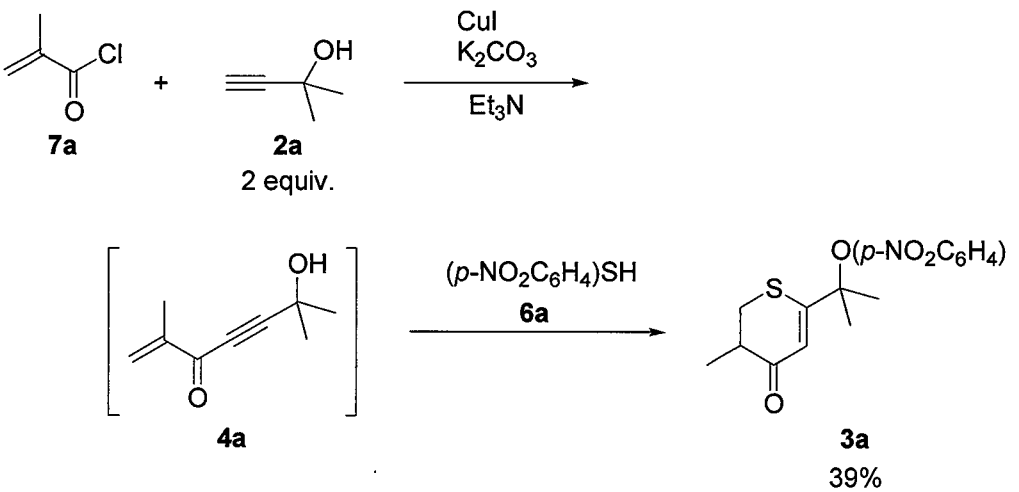
Scheme 1. A Proposed Reaction Pathway



5a.[4,5] Intramolecular aromatic nucleophilic substitution by the oxygen anion induces migration of the *p*-$NO_2C_6H_4$ group from sulfur to oxygen.[6] Finally, nucleophilic addition of the resultant sulfonium anion to the terminal ene moiety and the subsequent protonation yield **3a**.[7] 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_2CO_3 and Et_3N produce **4a**[8] and following reaction with **6a** occurred to afford **3a** in 39% yield. In this process, no Pd-catalyst was needed.



(4)

Reagents and conditions: **7a** (1.0 equiv.), **2a** (2.0 equiv.), CuI (0.1 equiv.), K_2CO_3 (0.1 equiv.), Et_3N (0.8 M), r.t., 3 h; then, **6a** (1 equiv.), DMF, 80 °C, 17 h.

3-5. Conclusions

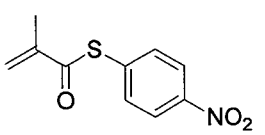
This study realized the synthesis of 2,3-dihydrothiopyran-4-one derivatives by Pd/Cu-catalyzed reactions between α,β-unsaturated thioesters and propargyl alcohols in the presence of bases. The reactions proceed through a one-pot sequence as follows: Sonogashira-type reaction; Michael-addition of thiol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

3-6. Experimental Section

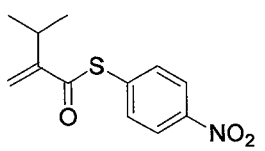
General Comments: ^1H and ^{13}C NMR spectra in $CDCl_3$, and DMF-d_8 solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometers. The chemical shifts in the 1H NMR

spectra were recorded relative to Me4Si as an internal standard and the chemical shifts in the ^{13}C 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. 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 N_2 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.).

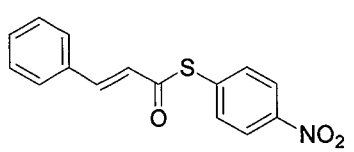
The Spectrum Datas of thioesters:



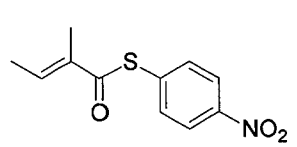
H_2C=C(Me)C(O)SC_6H_4-*p*-NO_2 (1a); yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3 H), 5.80 (s, 1 H), 6.25 (s, 1 H), 7.64 (d, *J*= 8.7 Hz, 2 H), 8.27 (d, *J*= 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 123.5, 124.7, 134.9, 136.0, 142.8, 147.8, 188.7; mass spectrum (EI) m/z 223 (M^+, 1); HRMS calcd for $C_{10}H_9NO_3S$ 223.0303, found 223.0308.



H_2C=C(*i*-Pr)C(O)SC_6H_4-*p*-NO_2 (1b); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{12}H_{13}NO_3S$ 251.0616, found 251.0607.

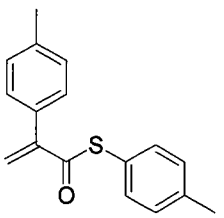


(*E*)-PhC(H)=CHC(O)SC_6H_4-*p*-NO_2 (1c); yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J*= 15.8 Hz, 1 H), 7.42-7.44 (m, 3 H), 7.57-7.59 (m, 2 H), 7.68 (d, *J*= 8.6 Hz, 2 H), 7.72 (d, *J*= 15.8 Hz, 1 H), 8.27 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.4, 123.7, 128.5, 128.9, 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 $C_{15}H_{12}NO_3S$ (M-H) 286.0538, found 286.0533.

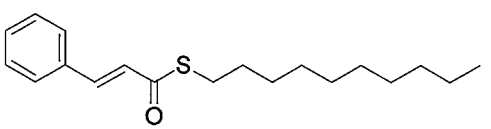


(*E*)-Me(H)C=C(Me)C(O)SC_6H_4-*p*-NO_2 (1d): an pale yellow solid; mp 77 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (d, 3 H), 1.92 (s, 3 H),

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); ^{13}C NMR(100 MHz, $CDCl_3$) 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 $C_{11}H_{11}OS$ 237.2760, found 237.0458.

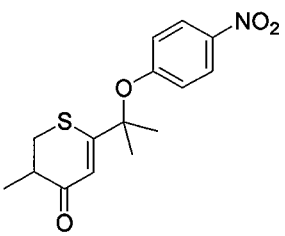


H_2C=C(C_6H_4Me-*p*)C(O)SC_6H_4-*p*-Me (1e): an pale yellow solid; mp 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3 H), 2.38 (s, 3 H), 5.83 (s, 1 H), 6.24 (s, 1 H), 7.17 (d, 2 H, J= 8.1 Hz), 7.23 (d, 2 H, J= 8.3 Hz), 7.32-7.35 (m, 4 H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 21.5, 21.6, 122.7, 124.7, 128.4, 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 $C_{17}H_{16}OS$ 268.0922, found 268.0924.



(*E*)-PhC(H)=CHC(O)S-*n*-$C_{10}H_{21}$ (1f): an pale yellow solid; mp 41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR(100 MHz, $CDCl_3$) 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 $C_{19}H_{28}OS$ 304.1861, found 304.1863.

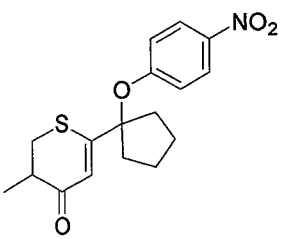
Pd/Cu-Catalyzed Reaction of CH_2=C(Me)C(O)SC_6H_4-*p*-NO_2 (1a) with HC≡CC(Me)$_2$OH (2a) in the presence of Et_3N and K_2CO_3 (run 3 of Table 1); General Procedure of Cyclization of α,β-Unsaturated Thioesters with Propargyl Alcohols: Into a two-neaked 3 mL reaction glass were added $PdCl_2$ (0.7 mg, 0.004 mmol), CuI (7.5 mg, 0.039 mmol), K_2CO_3 (6.1 mg, 0.044 mmol), **1a** (89.5 mg, 0.401 mmol), **2a** (50 μL, 0.52 mmol), Et_3N (60 μL, 0.43 mmol) and 0.5 mL of DMF under N_2 atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was separated by preparative TLC using hexane and Et_2O (10/7) as an eluent (74.5 mg, 60%).



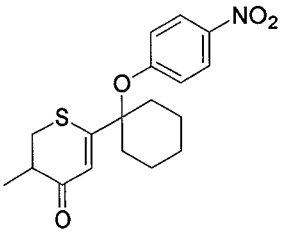
2,3-dihydro-3-methyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3a): an yellow solid; mp 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 3 H, J= 6.8 Hz), 1.72 (s, 6 H), 2.62-2.68 (m, 1 H), 3.02 (dd, 1 H, J= 13, 11 Hz), 3.19 (dd, 1 H, J= 13, 3.9 Hz), 6.28 (s, 1 H), 6.94 (d, 2 H, J= 9.3 Hz), 8.14 (d, 2 H, J= 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) 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,

1186, 1143, 949, 924, 867, 852, 752, 672 cm^{-1}; mass spectrum (EI) m/z 307 (M^+, 21); Anal. Calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.57, N, 4.56, S, 10.43. Found: C, 58.32; H, 5.29, N, 4.53, S, 10.44.

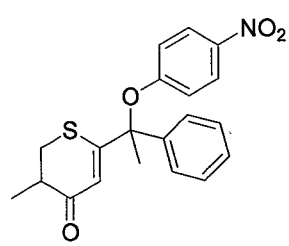
Other cyclic products **3b-3e**, **3i-3l** were similarly synthesized. Samples of **3d**, **3e**, **3j** and **3k** obtained after preparative TLC were a mixture of *threo* and *erythro*.



2,3-dihydro-3-methyl-6-(1'-*p*-nitrophenoxy-cyclopentyl)-thiopyra n-4-one (3b): an yellow solid; mp 89 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1567, 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 $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74, N, 4.20. Found: C, 61.32; H, 5.46, N, 4.09.

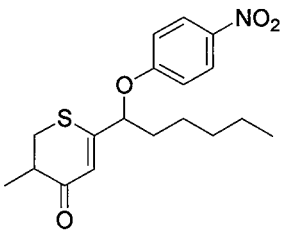


2,3-dihydro-3-methyl-6-(1'-*p*-nitrophenoxy-cyclohexyl)-thiopyra n-4-one (3c): an yellow solid; mp 105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 3 H, J= 6.8 Hz), 1.56-1.79 (m, 8 H), 2.33 (t, 2 H, J = 13 Hz), 2.61-2.67 (m, 1 H), 3.01 (dd, 1 H, J= 13, 11 Hz), 3.17 (dd, 1 H, J= 13, 3.9 Hz), 6.30 (s, 1 H), 6.97 (d, 2 H, J= 9.0 Hz), 8.14 (d, 2 H, J= 9.0 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 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 $C_{18}H_{21}NO_4S$ 347.4297, found 347.1201. Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09, N, 4.03. Found: C, 61.95; H, 5.91, N, 4.01.

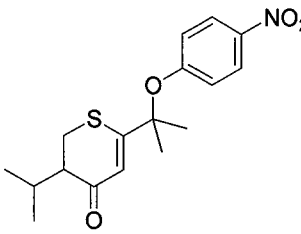


2,3-dihydro-3-methyl-6-(methyl-phenyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3d): The title compound was obtained as a mixture of inseparable diastereomers (51:49); an yellow solid; mp 111 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, 1.5 H, J= 6.8 Hz), 1.23 (d, 1.5 H, J= 6.8 Hz),* 2.02 (s, 3 H), 2.59-2.65 (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, $CDCl_3$) δ 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,

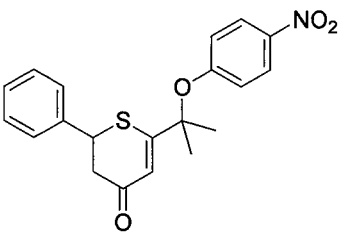
125.9(125.9), 128.7(128.8), 128.9, 141.2(141.5), 142.3, 160.1, 167.3(167.3), 197.2; IR (KBr) 2973, 2932, 1668, 1606, 1590, 1509, 1490, 1446, 1344, 1244, 1169, 1112, 1069, 1032, 989, 921, 862, 850, 764, 751, 698, 676, 578, 494 cm^{-1}; mass spectrum (EI) m/z 369 (M^+, 4.0); Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18, N, 3.79. Found: C, 64.74; H, 5.04, N, 3.65. * 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, $CDCl_3$) 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); ^{13}C NMR(100 MHz, $CDCl_3$) 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 $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63, N, 4.01. Found: C, 61.60; H, 6.46, N, 3.75. * Minor diastereomer

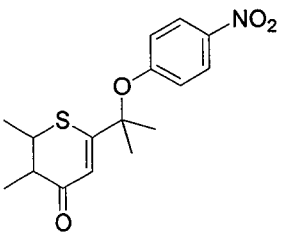


2,3-dihydro-3-isopropyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3i): an pale yellow solid; mp 127 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, 3 H, J= 6.8 Hz), 0.97 (d, 2 H, J= 6.8 Hz), 1.71 (s, 6 H), 2.22-2.26 (m, 1 H), 2.35-2.43 (m, 1 H), 3.13 (dd, 1 H, J= 8.8, 3.4 Hz), 3.25 (dd, 1 H, J= 14, 3.6 Hz), 6.24 (s, 1 H), 6.93 (d, 2 H, J= 9.3 Hz), 8.13 (d, 2 H, J= 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) 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, 1660, 1586, 1507, 1489, 1340, 1247, 1139, 1110, 851, 752, 670 cm^{-1}; mass spectrum (EI) m/z 335 (M^+, 25); Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31, N, 4.18. Found: C, 60.74; H, 6.12, N, 4.46.

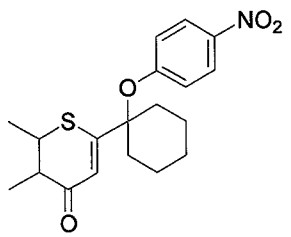


2-phenyl-2,3-dihydro-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3j): an yellow solid; mp 92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 6 H), 2.95 (dd, 1 H, J= 17, 3.4 Hz), 3.08 (dd, 1 H, J= 17, 13 Hz), 4.62 (dd, 1 H), 6.40 (s, 1 H), 6.91 (d, 2 H, J= 9.3 Hz), 7.34-7.37 (m, 5 H), 8.00 (d, 2 H, J= 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) 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,

670, 495 cm^{-1}; mass spectrum (EI) m/z 369 (M^+, 21); Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18, N, 3.79. Found: C, 65.09; H, 5.34, N, 3.73.



2,3-dihydro-2,3-dimethyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thio pyran-4-one (3k): The title compound was obtained as a mixture of inseparable diastereomers (55:45); an yellow solid; mp 84 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 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); ^{13}C NMR(100 MHz, $CDCl_3$) δ 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(118.0), 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^+, 14); Anal. Calcd for $C_{16}H_{19}NO_4S$: C, 59.79; H, 5.96, N, 4.36. Found: C, 59.51; H, 5.58, N, 4.21. * Minor diastereomer

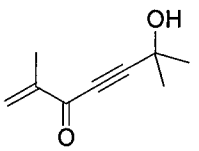


2,3-dihydro-2,3-dimethyl-6-(1'-*p*-nitrophenoxy-cyclohexyl)-thiopyr an-4-one (3l): The title compound was obtained as a mixture of inseparable diastereomers (72:28); an yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, 2.2 H, J= 7.1 Hz), 1.24 (d, 0.8 H, J= 7.1 Hz),* 1.32 (d, 2.2 H, J= 7.1 Hz), 1.42 (d, 0.8 H, J= 7.1 Hz),* 1.56-1.80 (m, 8 H), 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); ^{13}C NMR(100 MHz, $CDCl_3$) δ 9.97(15.3), 13.1(19.0), 21.2, 24.9, 34.5, 34,8, 34.9, 41.5(44.9), 42.8(46.6), 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 $C_{19}H_{23}NO_4S$: 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), CuI (0.04 mmol) and K_2CO_3 (0.04mmol), **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 ^1H 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**

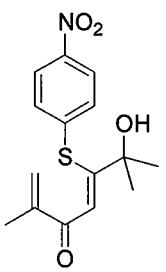
(0.4 mL, 4.1 mmol), CuI (0.02 mmol), Et_3N (13 mL). After the solution was stirred for 44 h at 25 °C, the reaction mixture was filtrated through Celite and distilled. The compound **4a** was purified by HPLC (308 mg, 49%).



4a: colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR(100 MHz, $CDCl_3$) 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 $C_{15}H_{17}NO_4S$ 152.0837, found 152.0829.

Reaction of 4a with HSC_6H_4-*p*-NO_2 (6a) (Eq. 2): Into a two-neaked reaction vessel were added K_2CO_3 (4.4 x 10^{-2} mmol), **4a** (0.4 mmol), **6a** (0.4 mmol), Et_3N (60 μL, 0.43 mmol) and 0.5 mL of DMF under N_2 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 CH_2=C(Me)C(O)C(H)=C(C(Me)$_2$(OH))SC_6H_4-*p*-NO_2 (5a): Into a two-necked reaction vessel were added $PdCl_2$ (4.5 mg, 0.025 mmol), CuI (45 mg, 0.24 mmol), K_2CO_3 (38 mg, 0.28 mmol), **1a** (536 mg, 2.40 mmol), **2a** (300 μL, 3.1 mmol), Et_3N (340 μL, 2.4 mmol), and 0.5 mL of DMF under N_2 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/Et_2O/EtOH (10/7/1) as an eluent (291 mg, 39%).



5a: an yellow solid; mp 89 °C; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR(100 MHz, $CDCl_3$) 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 $C_{15}H_{17}NO_4S$: 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-neaked reaction vessel were added CH_2=C(Me)C(O)-CH=C(SC_6H_4-*p*-NO_2)C(Me)$_2$(OH) (**5a**) (0.2 mmol), Et_3N (30 μL, 0.21 mmol) and 0.25 mL of DMF under N_2 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 CH_2=C(Me)C(O)Cl (7a), 2a and 6a (Eq. 4): Into a two-neaked 3 mL reaction glass were added CuI (7.5 mg, 0.39 mmol), K_2CO_3 (6.1 mg, 0.044 mmol), Et_3N (0.5 mL), H_2=C(Me)C(O)Cl (**7a**) (0.4 mmol) and 2-Methyl-3-butyne-2-ol (**2a**)

(0.8 mmol) under N_2 atmosphere. After the solution was stirred for 6 h at 80 °C, the reaction mixture was separated by preparative TLC using hexane and Et_2O (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 HSC_6H_4-*p*-NO_2 (**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 Et_2O (10/7) as an eluent (39%).

3-7. References and Notes

(1) (a) Ingall, A. H. In *Comprehensive Heterocyclic Chemistry II*; Boulton, A. S., McKkillop, A., Eds.; Pergamon Press: Oxford, 1996; Vol. 5, p 501. (b) Schneller, S. W. *Adv. Heterocycl. Chem.* **1975**, *18*, 59. (c) Katrizky, A. R.; Bonlton, A. J. *Adv. Heterocycl. Chem.* **1975**, *18*, 76. (d) Al-Nakib, T.; Bezjak, V.; Meegan, M.; Chandy, R. *Eur. J. Med. Chem.* **1990**, *25*, 455. (e) Al-Nakib, T.; Bezjak, V.; Rashid, S.; Fullam, B.; Meegan, M. *Eur. J. Med. Chem.* **1991**, *26*, 221. (f) van Vliet, L. A.; Rodenhuis, N.; Dijkstra, D.; Wikstrom, H.; Pugsley, T. A.; Serpa, K. A.; Meltzer, L. T.; Heffner, T. G.; Wise, L. D.; Lajiness, M. E.; Huff, R. M.; Svensson, K.; Sundell, S.; Lundmark, M. *J. Med. Chem.* **2000**, 43, 2871.

(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/cm^3, R = 0.074, and R_w = 0.184.

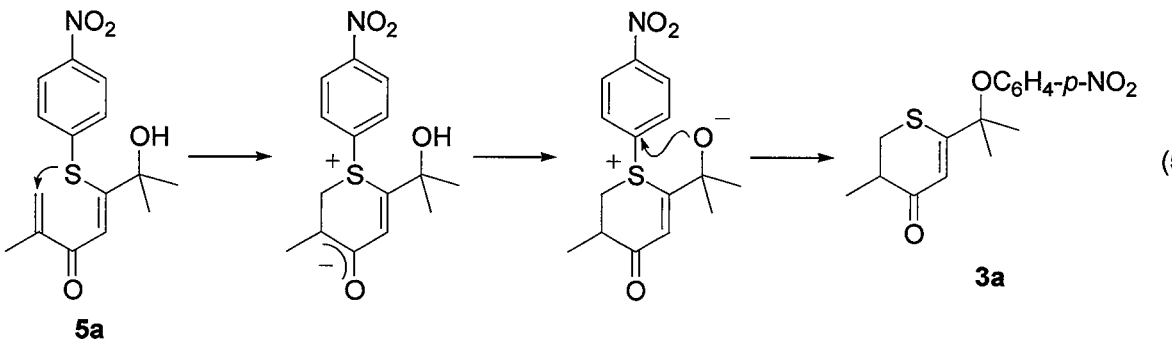
(3) The N.O.E. experiment showed that *cis*-isomer was exclusively produced.

(4) For additions of thiol to eynone, see: (a) Perlmutter, P. In *Conjugate Addition Reactions in Organic Synthesis*; Baldwin, J. E., Magnus, P. D., Eds.; Pergamon Press: Oxford, UK, 1992; Vol. 9, pp 310-322. (b) Blanco, L.; Bloch, R.; Bugnet, E.; Deloisy, S. *Tetrahedron Lett.* **2000**, *41*, 7875. (c) Gardiner, J. M.; Giles, P. E.; Martin, M. L. M. *Tetrahedron Lett.* **2002**, *43*, 5415. (d) Maezaki, N.; Yagi, S.; Yoshigami, R.; Maeda, J.; Suzuki, T.; Ohsawa, S.; Tsukamoto, K.; Tanaka, T. *J. Org. Chem.* **2003**, *68*, 5550. (e) Hollowood, C. J.; Yamanoi, S.; Ley, S. V. *Org. Biomol. Chem.* **2003**, *1*, 1664. (f) Ding, F.; Jennings, M. P. *Org. Lett.* **2005**, *7*, 2321.

(5) For copper catalyzed acyl-selenation and -telluration of alkynes, see: (a) Zhao, C.-Q.; Huang, X.; Meng, J.-B. *Tetrahedron Lett.* **1998**, *39*, 1933. (b) Zhao, C.-Q.; Li, J.-L.; Meng, J.-B.; Wang, Y.-M. *J. Org. Chem.* **1998**, *63*, 4170.

(6) It has been reported that 2-arylthio-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).



(5)

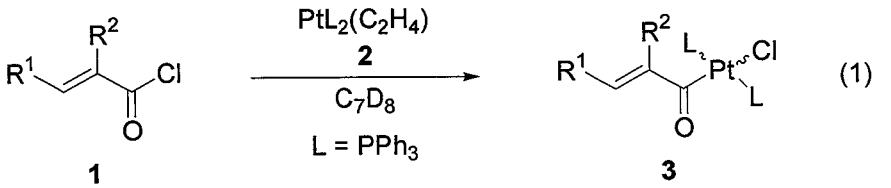
(8) Chowdhury, C.; Kundu, N. G. *Tetrahedron* **1999**, *55*, 7011.

Chapter 4

Reactions of α,β-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-additon 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 π-allyl metals is considered, it has been well-established that there are two reaction routes, *syn*- and *anti*-oxidative addition.[1] The reactions of α,β-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_2C=C(H)C(O)Cl (**1a**) or (*E*)-(Ph)(H)C=C(H)C(O)Cl (**1b**) with $Pt(PPh_3)_2(C_2H_4)$ (**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 β-carbon (R^1 = Ph) was not clearly disclosed from these experimental data.



1 **3** (1)

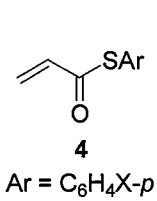
R^1 = H, R^2 = H ; **1a**	- 50 °C, 10 min	**3a** >99.9%	(*cis*:*trans* = 57:43)
	10 °C, 10 min	>99.9%	(*cis*:*trans* = 1:>99)
R^1 = Ph, R^2 = H; **1b**	- 50 °C, 10 min	**3b** >99.9%	(*cis*:*trans* = 96:4)
	10 °C, 10 min	>99.9%	(*cis*:*trans* = 1:>99)

The author expected that the mechanistic information might be disclosed, applying the controllable reactivity of α,β-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 α,β-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.

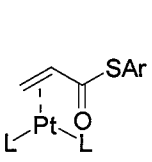
4-2. Reactions of H_2C=C(H)C(O)SAr with a Platinum (0) Complex.

First, thioesters **4a-d** (H_2C=C(H)C(O)SC_6H_4-*p*-X, X = Me, H, Cl, NO_2) were prepared and the reactions with **2** were monitored by ^1H and ^{31}P NMR spectroscopies at 25 °C using S=P(C_6H_4-*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 C_6D_6 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 C_6D_6. On the other hand, the reaction of *trans*-**3a** (0.02 mmol) with *p*-MeC_6H_4SNa (**8**, 0.06 mmol) in CD_2Cl_2 (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, NO_2) 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 NO_2 group lowered the basicity of lone pairs on sulfur resulting in the prevention of the formation of **7**.[7]

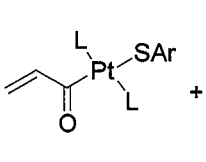


4
Ar = C_6H_4X-*p*
0.022 mmol

$PtL_2(C_2H_4)$
2
0.02 mmol
C_6D_6(0.5 mL)
25 °C
L = PPh_3



5



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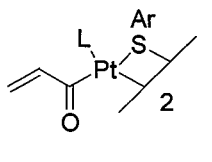
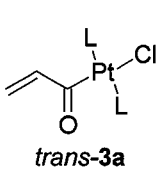


7 (*syn*:*anti* mixture)

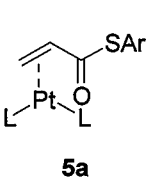
(2)

4a	X = Me	20 min	>99.9%	n.d.	n.d.
		3 h	99.5%	n.d.	0.5%
4b	X = H	20 min	>99.9%	n.d.	n.d.
		3 h	97.7%	n.d.	2.3%
4c	X = Cl	20 min	>99.9%	n.d.	n.d.
		3 h	92.2%	1.5%	6.3%
4d	X = NO_2	20 min	97%	3%	n.d.
		3 h	81%	18%	n.d.

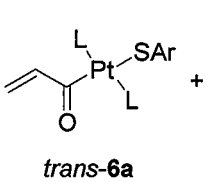


trans-**3a**

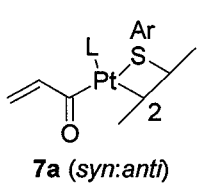
p-MeC_6H_4SNa
8
CD_2Cl_2
25 °C, 17 h
L = PPh_3



5a
79%



trans-**6a**
0.6%



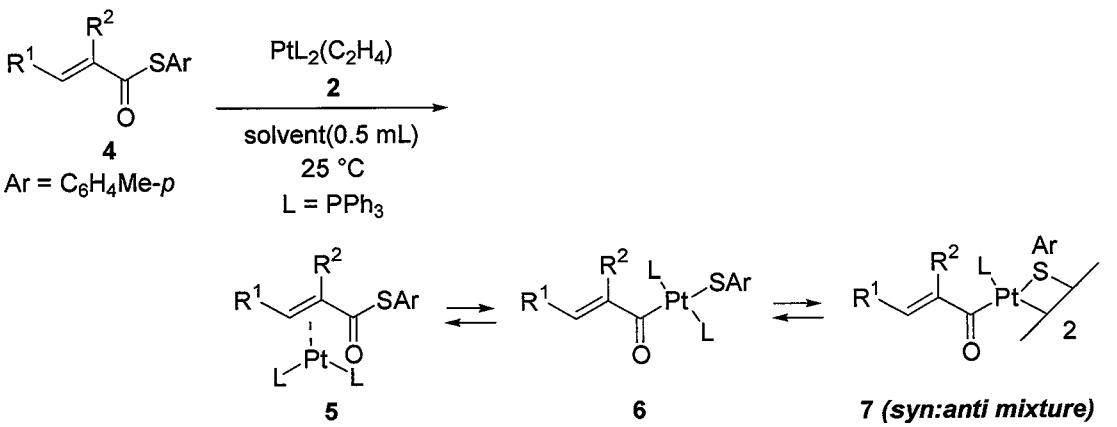
7a (*syn*:*anti*)
13% (77:23)

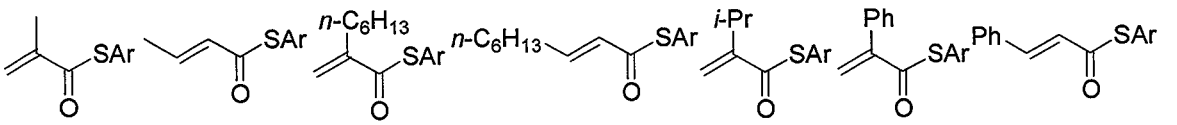
(3)

4-3. Reactions of Thioesters Having a *p*-MeC_6H_4S Group with a Platinum (0) Complex.

Next, when **4e** (R^1 = H, R^2 = 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 C_6D_6, and in 66%, 20% (*cis*:*trans* = 45:55) and 14% (*syn*:*anti* = 51:49) in CD_2Cl_2. Monitoring the reactions by ^{31}P 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 C_6D_6 and 5-6 h in CD_2Cl_2 (runs 1 and 2, Table 1).[8,9] The reactions using **4f** (R^1 = Me, R^2 = 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**[a]





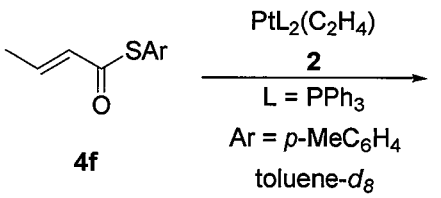
4e **4f** **4g** **4h** **4i** **4j** **4k**

run	4	solvent	time[b]	**5** : **6** (*cis*:*trans*)[c]	time[d]	**5** (*cis*:*trans*) : **6** (*syn*:*anti*)[c]
1	**4e**	C_6D_6	3-4 h	51 : 49 (6:94)	3-4 h	13 (6:94) : 87 (79:21)
2	**4e**	CD_2Cl_2	5-6 h	22 : 78 (13:87)	5-6 h	22 (13:87) : 78 (83:17)
3	**4f**	C_6D_6	< 40 min	57 : 43 (1:>99)	< 40 min	7 (1:>99) : 93 (64:36)
4	**4f**	CD_2Cl_2	< 40 min	17 : 83 (1:>99)	< 40 min	20 (1:>99) : 80 (74:26)
5	**4g**	C_6D_6	9-10 h	78 : 22 (1:>99)	3-6 h	7 (1:>99) : 93 (74:26)
6	**4h**	C_6D_6	< 40 min	46 : 54 (1:>99)	< 40 min	9 (1:>99) : 91 (75:25)
7	**4i**	C_6D_6	52-55 h	81 : 19 (1:>99)	10-15 h	6 (1:>99) : 94 (81:19)
8	**4j**	C_6D_6	14-15 h	71 : 29 (1:>99)	9-10 h	9 (1:>99) : 91 (76:24)
9[e]	**4j**	C_6D_6	14-15 h	68 : 32 (1:>99)	7-8 h	10 (1:>99) : 90 (74:26)
10	**4j**	CD_2Cl_2	16-17 h	50 : 50 (21:79)	13-14 h	18 (21:79) : 82 (86:14)
11	**4k**	C_6D_6	< 40 min	89 : 11 (1:>99)	< 40 min	8 (1:>99) : 92 (60:40)
12[f]	**4k**	C_6D_6	< 40 min	91 : 9 (1:>99)	< 40 min	7 (1:>99) : 93 (63:37)
13	**4k**	CD_2Cl_2	< 40 min	70 : 30 (1:>99)	60-80 min	15 (1:>99) : 85 (70:30)

[a] **2** (0.020 mmol), **4** (0.022 mmol) and solvent (0.5 mL) under N_2 atmosphere at 25 °C. [b] Required to reach the equilibrium of **5**:**6**. [c] Ratio at equilibrium. [d] Required to reach the equilibrium of **6**:**7**. [e] 4.3 equiv of **4j**. [f] 4.8 equiv of **4k**.

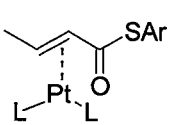
possessing *p*-MeC_6H_4S with **2** are quite flexible and the position changes of equilibrium states caused by substituents and solvents are readily analyzable.

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 C_6D_6 or **5e**:**6e** = 22:78 (run 2, Table 1) with **5f**:**6f** = 17:83 (run 4, Table 1) in CD_2Cl_2 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** (R^1 = H, R^2 = *n*-C_6H_{13}) and **4i** (R^1 = H, R^2 = *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 R^2 compared to Ph at R^1 (**5j**:**6j** = 71:29 of run 8 vs. **5k**:**6k** = 89:11 of run 11 in C_6D_6 or **5j**:**6j** = 50:50 of run 10 vs. **5k**:**6k** = 70:30 of run 13 in CD_2Cl_2, Table 1), a much more prolonged time was again required to reach the equilibria; only < 40 min were required for **5k**:**6k** both in C_6D_6 and CD_2Cl_2 (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 R^2 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 R^2 = Ph or R^1 = 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.

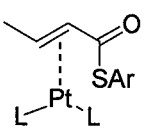


4f

$PtL_2(C_2H_4)$
2
L = PPh_3
Ar = *p*-MeC_6H_4
toluene-d_8



+



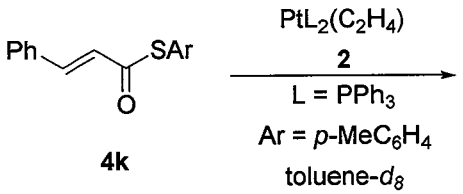
+ *trans*-**6f** + **7f** (*syn*:*anti*) (4)

s-*cis*-**5f** s-*trans*-**5f**

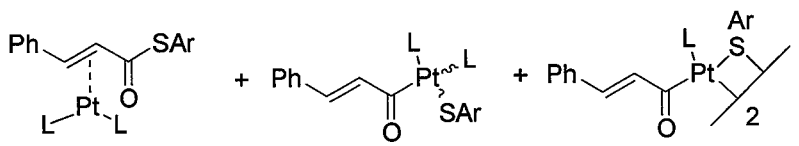
- 70 °C, 10 min	19%	(63:37)	n.d.	n.d.
- 10 °C, 10 min	92%	(96:4)	5%	3% (67:33)
0 °C, 10 min	74%	(>99:1)	11%	14% (79:21)
25 °C, 10 min	9%	(>99:1)	4%	87% (61:39)

The chart of the ^{31}P NMR spectrum of the reaction of **4f** (R^1 = Me, R^2 = H) with **2** in toluene-d_8 attempted at a low reaction temperature (-70 °C after 10 min) suggested the

formation of two π-complexes at (a) δ 29.9 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 4208 Hz) and δ 31.2 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 3373 Hz), and (b) δ 29.4 (d, $J_{P\text{-}P}$ = 41 Hz, $J_{Pt\text{-}P}$ = 3280 Hz) and δ 30.1 (d, $J_{P\text{-}P}$ = 41 Hz, $J_{Pt\text{-}P}$ = 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.[10] 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.



(5)



	5k	**6k** (*cis*:*trans*)	**7k** (*syn*:*anti*)
- 50 °C, 10 min	22%	n.d.	n.d.
- 30 °C, 10 min	63%	5% (60:40)	n.d.
10 °C, 10 min	87%	5% (1:>99)	6.6% (91:9)
25 °C, 2 h	61%	4% (1:>99)	35% (60:40)

On the other hand, the reaction utilizing **4k** (R^1 = Ph, R^2 = 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 C_6D_6 to CD_2Cl_2. (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 C_6D_6 to CD_2Cl_2. (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 C_6D_6 and from 15:85 (run 13, Table 1) to 22:78 in CD_2Cl_2 (run 2, Table 1). These

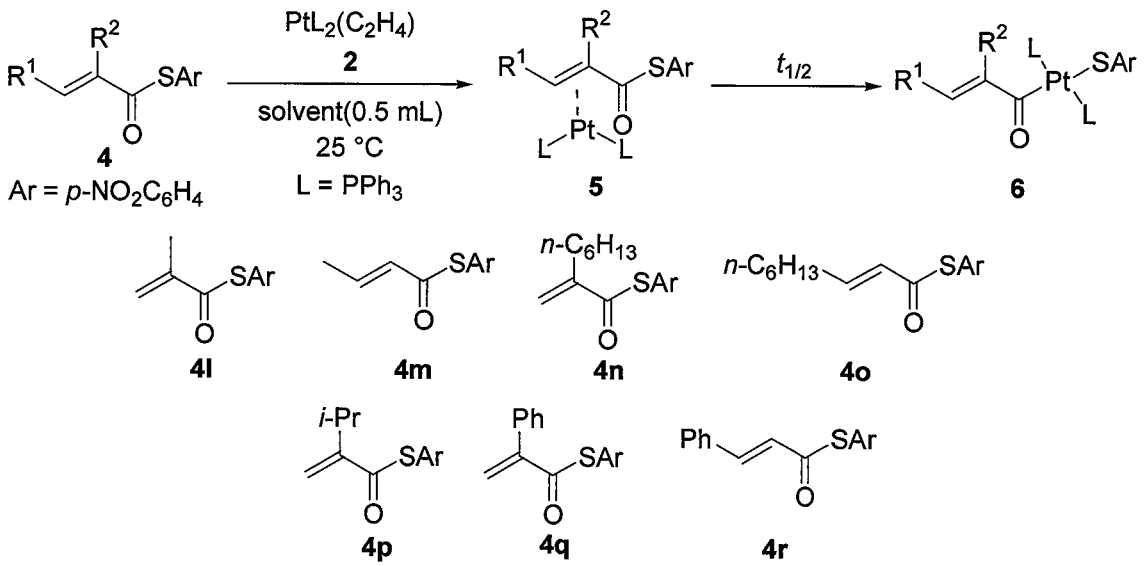
results also indicated that the basicity of the lone pair on sulfur, which can be mainly controlled by the substituent in Ar (*vide infra*), was the predominant factor to determine the position of equilibria between **6** and **7**.[7]

(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 **4l** (R^1 = H, R^2 = Me) was employed, the half-life of **5l** forming **6l** 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 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, which significantly retarded the reaction in the case of ArS = *p*-MeC_6H_4S (run 8, Table 1) took place just at a comparable reaction rate with that employing

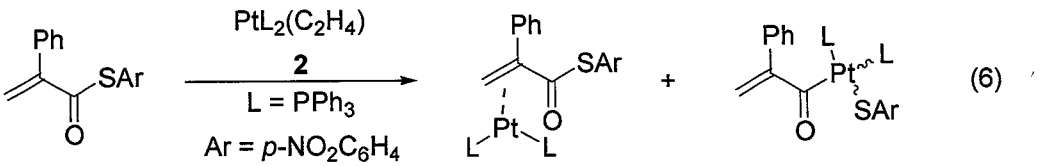
Table 2. Half-Lives from **5** to **6**[a]



run	4	solvent	$t_{1/2}$ (min)	run	4	solvent	$t_{1/2}$ (min)
1	**4l**	C_6D_6	38	10	**4p**	C_6D_6	43
2[b]	**4l**	C_6D_6	36	11[c]	**4p**	C_6D_6	43
3	**4l**	CD_2Cl_2	14	12	**4p**	CD_2Cl_2	6.8
4	**4l**	acetone-d_6	19	13	**4q**	C_6D_6	6.2
5	**4l**	THF-d_8	36	14	**4q**	CD_2Cl_2	1.2
6	**4m**	C_6D_6	2.1	15	**4r**	C_6D_6	9.1
7	**4m**	CD_2Cl_2	3.3	16[d]	**4r**	C_6D_6	9.1
8	**4n**	C_6D_6	40	17	**4r**	CD_2Cl_2	7.8
9	**4o**	C_6D_6	3.0				

[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**.

4l ($t_{1/2}$ = 43 min, run 10 vs. $t_{1/2}$ = 38 min, run 1, Table 2). Moreover, although retardation was also expected by introducing Ph at R^2 (*vide ante*), the transformation of **5q** (R^1 = H, R^2 = Ph) to **6q** was actually faster than that of **5r** (R^1 = Ph, R^2 = 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 R^1 [2.1 min in C_6D_6 (run 6, Table 2) vs. 3.3 min in CD_2Cl_2 (run 7, Table 2) for **5m** to **6m** or 9.1 min in C_6D_6 (run 15, Table 2) vs. 7.8 min in CD_2Cl_2 (run 17, Table 2) for **5q** to **6q**], significant acceleration was detected in CD_2Cl_2 solution with the thioesters having a substituent at R^2. The reactions took place 2.7 times faster for **5l** (38 min in C_6D_6, run 1 vs. 14 min in CD_2Cl_2, run 3, Table 2), 6.3 times faster for **5p** (43 min in C_6D_6, run 10 vs. 6.8 min in CD_2Cl_2, run 12, Table 2) and 5.2 times faster for **5q** (6.2 min in C_6D_6, run 13 vs. 1.2 min in CD_2Cl_2, run 14, Table 2). The reaction performed in acetone-d_6 also proceeded faster than that in C_6D_6 (19 min, run 4 vs. 38 min, run 1, Table 2), while no facilitation was observed in THF-d_8 (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 R^1 or R^2 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].



(6)

4q		**5q**	**6q** (*cis*/*trans*)	
	- 50 °C, 10 min	70%	n.d.	
	- 40 °C, 10 min	77%	3%	(>99:1)
	- 10 °C, 10 min	67%	24%	(92:8)
	25 °C, 1 h	n.d.	100%	(1:>99)

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.

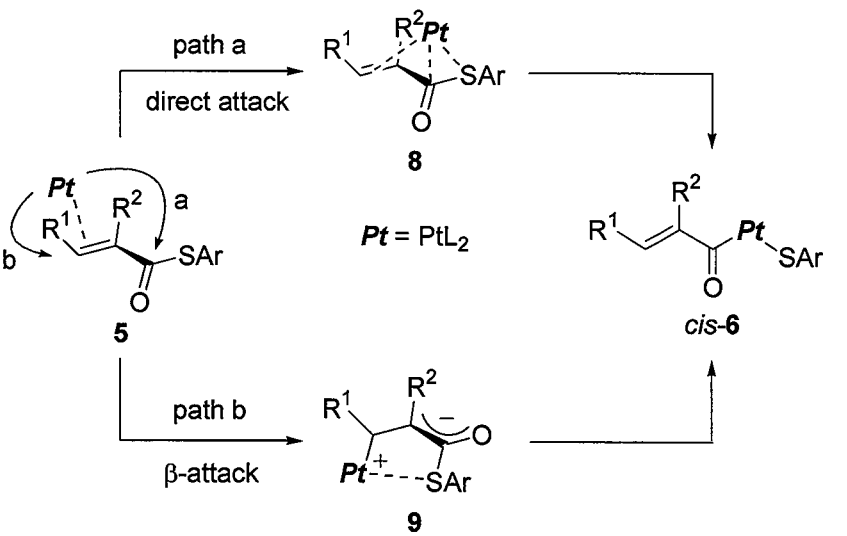
4-5. Proposed Dual Reaction Routes

The experimental datas can be rationalized as follows (Scheme 1). In the case of thioesters posessing *p*-tolyl group on sulfur, after the formation of π-complex **5**, coordinated $Pt(PPh_3)_2$ fragment would approach the C-S bond with the π-coordination partially retained.[11] During the process, two PPh_3s on Pt would remain *cis*-coordinated,[5] bulky substituents at R^2 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*-MeC_6H_4S group with **2**, the results from the reaction of thioesters having *p*-$NO_2C_6H_4$ group on sulfur indicated that the $Pt(PPh_3)_2$-fragment can also attack the β-carbon (path b, Scheme 1) as well as the direct C-S bond attack (path a).[12] 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 R^2.[13] The steric repulsion caused between a substituent at R^2 and $Pt(PPh_3)_2$-fragment would rather facilitate the β-attack by pushing out the $Pt(PPh_3)_2$-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 R^2, no remarkable difference emerged in the half-lives of **5** between the reactions using **4l** and **4p** in C_6D_6 (run 1 vs. run 10, Table 2). On the other hand, path b would predominate in CD_2Cl_2 and the reaction utilizing **4q** proceed faster than that utilizing **4l** (run 3 vs. run 12, Table 2). The reaction using thioester with *p*-$NO_2C_6H_4S$ and Ph group at R^2 would overwhelmingly occur *via* path b even in C_6D_6 solution due to the α-anion stabilization ability of Ph as well as the steric repulsion between Ph and $Pt(PPh_3)_2$-fragment. This is why the reaction of **4q** took place faster than that of **4r** even in C_6D_6 (run 13 vs. run 15, Table 2). After the generation of **9**, the $Pt(PPh_3)_2$-fragment would migrate from β-carbon to carbonyl carbon through an η^1-η^3-η^1 type isomerization mechanism. During the process, the two PPh_3 on Pt also would retain *cis* configuration to give *cis*-**6** as a kinetic product, which would isomerize into thermodynamically more stable *trans*-**6**.

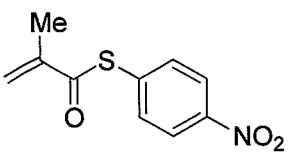
Scheme 1. A Proposed Pathway from **5** to **6**



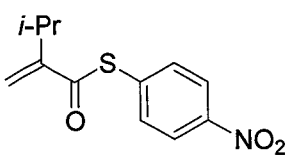
4-6. Activation Parameters

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 C_6D_6 significantly differed from those in CD_2Cl_2. That is, while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in C_6D_6 were 95.3±0.4 kJmol^{-1} and 7.5±1.4 JK^{-1}mol^{-1}, those in CD_2Cl_2 were 53.5±0.1 kJmol^{-1} and -124.4±0.2 JK^{-1}mol^{-1}. The large negative $\Delta S^{\ddagger}$ and relatively small positive $\Delta H^{\ddagger}$ in CD_2Cl_2 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 C_6D_6 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^{-1}mol^{-1}) from **5p** to **6p** even in C_6D_6 also did not contradict the projection that this reaction can also proceed through path b even in C_6D_6 solution. That is, due to the significant steric hindrance caused by *i*-Pr located at R^2, the route of path b competitively took place. The small positive $\Delta H^{\ddagger}$ and large minus $\Delta S^{\ddagger}$ in CD_2Cl_2 also accorded with the route of path b. Third, comparing the data of formation of **6r** from **5r** in

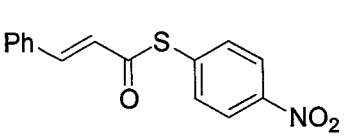
Table 3. Activation Parameters from **5l** to **6l**, from **5p** to **6p** and **5r** from **6r**



from **5l** to **6l** (R^1 = H, R^2 = Me)	
in C_6D_6	in CD_2Cl_2
$\Delta G^{\ddagger}$ = 93.0±0.1 kJmol^{-1}	$\Delta G^{\ddagger}$ = 90.5±0.1 kJmol^{-1}
$\Delta H^{\ddagger}$ = 95.3±0.4 kJmol^{-1}	$\Delta H^{\ddagger}$ = 53.5±0.1 kJmol^{-1}
$\Delta S^{\ddagger}$ = 7.5±1.4 JK^{-1}mol^{-1}	$\Delta S^{\ddagger}$ = -124.4±0.2 JK^{-1}mol^{-1}



from **5p** to **6p** (R^1 = H, R^2 = *i*-Pr)	
in C_6D_6	in CD_2Cl_2
$\Delta G^{\ddagger}$ = 93.4±0.1 kJmol^{-1}	$\Delta G^{\ddagger}$ = 88.9±0.1 kJmol^{-1}
$\Delta H^{\ddagger}$ = 78.7±0.1 kJmol^{-1}	$\Delta H^{\ddagger}$ = 40.2±0.2 kJmol^{-1}
$\Delta S^{\ddagger}$ = -49.2±0.3 JK^{-1}mol^{-1}	$\Delta S^{\ddagger}$ = -163.5±0.5 JK^{-1}mol^{-1}



from **5r** to **6r** (R^1 = Ph, R^2 = H)	
in C_6D_6	in CD_2Cl_2
$\Delta G^{\ddagger}$ = 89.8±0.1 kJmol^{-1}	$\Delta G^{\ddagger}$ = 89.5±0.1 kJmol^{-1}
$\Delta H^{\ddagger}$ = 68.2±0.7 kJmol^{-1}	$\Delta H^{\ddagger}$ = 81.9±1.9 kJmol^{-1}
$\Delta S^{\ddagger}$ = -72.5±2.4 JK^{-1}mol^{-1}	$\Delta S^{\ddagger}$ = -25.5±6.4 JK^{-1}mol^{-1}

C_6D_6 with those in CD_2Cl_2, differences in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as well as half-lives were much smaller than other cases. This can be nicely rationalized by assuming that reactions in both C_6D_6 and CD_2Cl_2 took place through a similar reaction route, namely, the direct C-S bond attack of a $Pt(PPh_3)_2$-fragment (path a) from a π-complex.

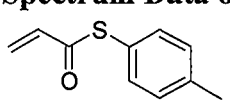
4-7. Conclusions

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.

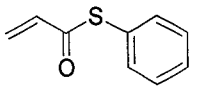
4-8. Experimental Section

General Comments: ^{31}P and ^{1}H NMR spectra were recorded with a JEOL JMN Alice-400 spectrometer (160 MHz and 400 MHz, respectively) in C_6D_6, CD_2Cl_2 or toluene-d_8 solution. The chemical shifts of the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 (aq.) as an external standard and $S{=}P(C_6H_4OMe\text{-}p)_3$ was used as an internal standard to calculate the yields of products. The chemical shifts in the ^{1}H NMR spectra were recorded relative to C_6H_6 (δ 7.15), CH_2Cl_2 (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 $CH_2{=}C(H)C(O)Cl$ with $NaSC_6H_4\text{-}p\text{-}NO_2$. 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 $Pt(PPh_3)_2(C_2H_4)$ (**2**) was synthesized according to the literature (*Inorg. Synth.* **1978**, *18*, 120.). C_6D_6, toluene-d_8 and C_6H_6 were purified by distillation from sodium benzophenon ketyl before use. CD_2Cl_2 was distilled from CaH_2. The structures of **5**, *trans*-**6** and **7** were determined by comparing their ^{31}P NMR chemical shifts and coupling constants ($J_{P\text{-}P}$ and $J_{Pt\text{-}P}$) with those of the authentic samples **5a**, *trans*-**6r** and **7k**.

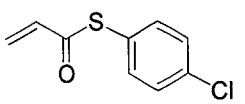
Spectrum Data of 4.



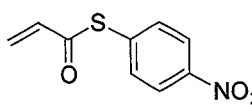
$H_2C{=}C(H)C(O)SC_6H_4\text{-}p\text{-}CH_3$ (4a): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3 H), 5.71 (dd, J= 1.6 Hz, J= 9.6 Hz, 1 H), 6.35 (dd, J= 1.6 Hz, 17.2 Hz, 1 H), 6.42 (dd, J= 9.6 Hz, J= 17.2 Hz, 1 H), 7.21 (d, J= 8.2 Hz, 2 H), 7.31 (d, J= 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{10}H_{10}OS$ 178.0452, found 178.0444.



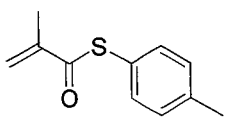
H_2C=C(H)C(O)SC_6H_5 (4b): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76-5.79 (m, 1 H), 6.36-6.49 (m, 2 H), 7.41-7.47 (m, 5 H), 7.31 (d, J= 8.0 Hz, 2 H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 127.0, 127.2, 129.0, 129.3, 134.2, 134.4, 188.1; mass spectrum (EI) m/z 164 (M^+, 92); HRMS calcd for C_9H_8OS 164.0296, found 164.0300.



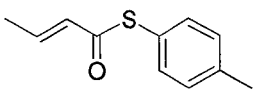
H_2C=C(He)C(O)SC_6H_4-*p*-Cl (4c): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79-5.81 (m, 1 H), 6.37-6.48 (m, 2 H), 7.36-7.41 (m, 4 H), 7.31 (d, J= 8.0 Hz, 2 H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 125.4, 127.7, 129.3, 134.0, 135.6, 135.7, 187.6; mass spectrum (EI) m/z 198 (M^+, 12); HRMS calcd for C_9H_7ClOS 197.9906, found 197.9903.



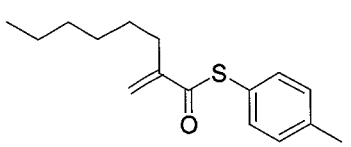
H_2C=C(H)C(O)SC_6H_4-*p*-NO_2 (4d): colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.90 (m, 1 H), 6.43-6.50 (m, 2 H), 7.65 (d, 2 H, $J_{H\text{-}H}$= 8 Hz), 8.26 (d, 2 H, $J_{H\text{-}H}$= 8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 123.8, 123.9, 128.7, 133.6, 134.6, 135.6, 185.8; mass spectrum (EI) m/z 209 (M^+, 21); HRMS calcd for $C_9H_7NO_3S$ 209.0147, found 209.0133.



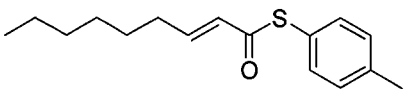
H_2C=C(Me)C(O)SC_6H_4-*p*-CH_3 (4e): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 2.37 (s, 3 H), 5.67 (s, 1 H), 6.19 (s, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.31 (d, J= 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 21.5, 123.5, 123.9, 129.8, 134.7, 139.4, 143.3, 191.6; mass spectrum (EI) m/z 192 (M^+, 16); HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0611.



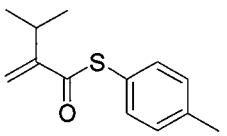
***(E)*-Me(H)C=C(H)C(O)SC_6H_4-*p*-CH_3 (4f):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (dd, J= 1.6 Hz, J= 7.0 Hz, 3 H), 2.36 (s, 3 H), 6.19 (dd, J= 1.6 Hz, J= 15.2 Hz, 1 H), 6.97 (dt, J= 7.2 Hz, J= 14.7 Hz, 1 H), 7.20 (d, J= 8.0 Hz, 2 H), 7.31 (d, J= 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 21.4, 123.8, 129.1, 129.7, 134.3, 139.2, 141.5, 187.8; mass spectrum (EI) m/z 192 (M^+, 10); HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0613.



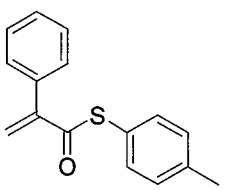
H_2C=C(*n*-C_6H_{13})C(O)SC_6H_4-*p*-CH_3 (4g): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H), 1.29 (br, 6 H), 1.44-1.49 (m, 2 H), 2.34 (t, J= 7.6 Hz, 2 H), 2.38 (s, 3 H), 5.64 (s, 1 H), 6.20 (s, 1 H), 7.22 (d, J= 8.0 Hz, 2 H), 7.31 (d, J= 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{16}H_{22}OS$ 262.1391, found 262.1393.



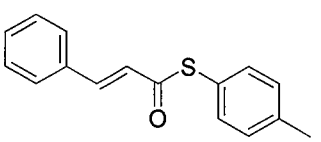
(*E*)-(*n*-C_6H_{13})(H)C=C(H)C(O)SC_6H_4-*p*-CH_3 (4h): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.4 Hz, 3 H), 1.28-1.49 (m, 8 H), 2.24 (m, 2 H), 2.37 (s, 3 H), 6.17 (d, *J*= 15.6 Hz, 1 H), 6.97 (dt, *J*= 7.2 Hz, *J*= 15.6 Hz, 1 H), 7.22 (d, *J*= 8.0 Hz, 2 H), 7.31 (d, *J*= 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



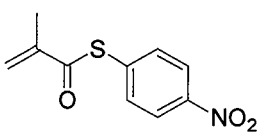
H_2C=C(*i*-C_3H_7)C(O)SC_6H_4-*p*-CH_3 (4i): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.8 Hz, 6 H), 2.85 (sept, *J* = 6.8 Hz, 1 H), 5.63 (s, 1 H), 6.18 (s, 1 H), 7.23 (d, *J*= 8.2 Hz, 2 H), 7.32 (d, *J*= 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.5, 29.9, 119.7, 124.1, 129.6, 134.5, 139.2, 154.3, 192.2; mass spectrum (EI) m/z 220 (M^+, 16); HRMS calcd for $C_{13}H_{16}OS$ 220.0922, found 220.0923.



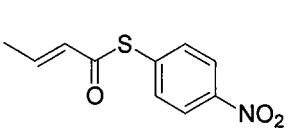
H_2C=C(C_6H_5)C(O)SC_6H_4-*p*-CH_3 (4j): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 5.87 (s, 1 H), 6.29 (s, 1 H), 7.22-7.45 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 123.5, 124.5, 128.50, 128.55, 128.9, 130.3, 134.8, 136.0, 139.9, 148.0, 192.2; mass spectrum (EI) m/z 254 (M^+, 13); HRMS calcd for $C_{16}H_{14}OS$ 254.0765, found 254.0771.



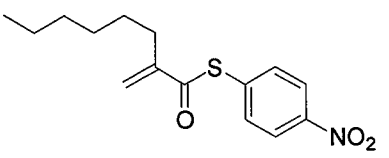
(*E*)-(C_6H_5)(H)C=C(H)C(O)SC_6H_4-*p*-CH_3 (4k): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 6.78 (d, *J*= 16.0 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.36-7.40 (m, 5 H), 7.53-7.55 (m, 2 H), 7.66 (d, *J*= 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 123.9, 124.0, 128.3, 128.8, 129.8, 130.5, 133.8, 134.3, 139.5, 141.1, 188.0; mass spectrum (EI) m/z 254 (M^+, 1); HRMS calcd for $C_{16}H_{14}OS$ 254.0765, found 254.0759.



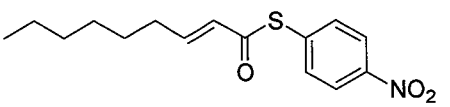
H_2C=C(CH_3)C(O)SC_6H_4-*p*-NO_2 (4l): yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3 H), 5.80 (s, 1 H), 6.25 (s, 1 H), 7.64 (d, *J*= 8.7 Hz, 2 H), 8.27 (d, *J*= 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 123.5, 124.7, 134.9, 136.0, 142.8, 147.8, 188.7; mass spectrum (EI) m/z 223 (M^+, 1); HRMS calcd for $C_{10}H_9NO_3S$ 223.0303, found 223.0308.



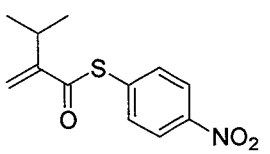
(*E*)-(CH_3)(H)C=C(H)C(O)SC_6H_4-*p*-NO_2 (4m): orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (d, *J*= 6.8 Hz, 3 H), 6.23 (d, *J*= 15.2 Hz, 1 H), 7.06 (dt, *J*= 6.8 Hz, *J*= 14.8 Hz, 1 H), 7.63 (d, *J*= 8.2 Hz, 2 H), 8.25 (d, *J*= 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 123.7, 128.8, 134.6, 136.2, 143.6, 147.8, 185.1; mass spectrum (EI) m/z 223 (M^+, 0.4); HRMS calcd for $C_{10}H_9NO_3S$ 223.0303, found 223.0305.



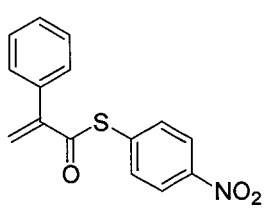
H_2C=C(*n*-C_6H_{13})C(O)SC_6H_4-*p*-NO_2 (4n): colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2Hz, 3 H), 1.30-1.50 (m, 8 H), 2.36 (t, *J*= 7.6 Hz, 2 H), 5.76 (s, 1 H), 6.25 (s, 1 H), 7.63 (d, *J*= 8.8 Hz, 2 H), 8.26 (d, *J*= 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.2, 28.9, 31.7, 32.0, 123.7, 123.8, 135.0, 136.4, 147.9, 189.1.



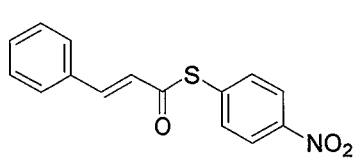
(*E*)-(*n*-C_6H_{13})(H)C=C(H)C(O)SC_6H_4-*p*-NO_2 (4o): colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.4 Hz, 3 H), 1.31-1.52 (m, 8 H), 2.28 (dt, *J*= 20.4 Hz, J = 7.2 Hz, 2 H), 6.19 (d, *J*= 15.6 Hz, 1 H), 7.05 (dt, *J*= 6.8 Hz, *J*= 15.6 Hz, 1 H), 7.63 (d, *J*= 8.8 Hz, 2 H), 8.25 (d, *J*= 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



H_2C=C(*i*-Pr)C(O)SC_6H_4-*p*-NO_2 (4p): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{12}H_{13}NO_3S$ 251.0616, found 251.0607.



H_2C=C(C_6H_5)C(O)SC_6H_4-*p*-NO_2 (4q): yellow solid; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{11}NO_3S$ 285.0460, found 285.0547.



(*E*)-PhC(H)=CHC(O)SC_6H_4-*p*-NO_2 (4r): yellow solid; ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{12}NO_3S$ (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 C_6H_6 (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 × 3) and dried to give **5a** (672.0 mg, 80%).

5a: mp 130 °C (a white solid); ^{1}H NMR (400 MHz, C_6D_6) 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); ^{31}P NMR (160 Hz, C_6D_6) δ 29.5 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 4038 Hz), 31.4 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3567 Hz); IR (KBr) 3050, 1652, 1478, 1433, 1360, 1155, 1095, 967, 943, 808, 742, 692, 540, 517, 510 cm^{-1}; Anal. Calcd for $C_{46}H_{40}OP_2PtS$: 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 C_6H_6 (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 × 3) and methanol (10mL × 3) and then dried to give *trans*-**6r** (849.8 mg, 85%).

***trans*-6r:** mp 142 °C (an orange solid); ^{1}H NMR (400 MHz, C_6D_6) 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); ^{31}P NMR (160 Hz, C_6D_6) δ 16.0 (s, $J_{Pt\text{-}P}$ = 3228 Hz); IR (KBr) 3056, 1580, 1566, 1493, 1482, 1435, 1319, 1094, 742, 692, 523, 514 cm^{-1}; Anal. Calcd for $C_{51}H_{41}NO_3P_2PtS$: 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 C_6H_6 (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 × 3) and methanol (10 mL × 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); ^{1}H NMR (160 MHz, C_6D_6) (*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.); ^{31}P NMR (160 Hz, C_6D_6) (*syn* isomer): δ 15.0 (s, $J_{Pt\text{-}P}$ = 4164 Hz); (*anti* isomer): δ 16.8 (s, $J_{Pt\text{-}P}$ = 4028 Hz); IR (KBr) 3055, 1626, 1582, 1486, 1434, 1096, 758, 693, 535, 511, 498 cm^{-1}; Anal. Calcd for $C_{68}H_{58}O_2P_2Pt_2S_2$: 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(C_6H_4OMe-*p*)$_3$ (1.7 mg, 0.0044 mmol). Then ca. 0.5 mL of toluene-d_8 was transferred by the freeze-pump-thaw method. The ^{31}P 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)=CH_2](PPh_3)$_2$ was observed during course of the reaction.

***cis*-3a:** ^{31}P NMR (160 MHz, toluene-d_8) δ 15.9 (d, $J_{P\text{-}P}$ = 17 Hz, $J_{Pt\text{-}P}$ = 4662 Hz), 18.2 (d, $J_{P\text{-}P}$ = 17 Hz, $J_{Pt\text{-}P}$ = 1378 Hz). ***trans*-3a:** ^{31}P NMR (160 MHz, toluene-d_8) δ 22.2 (s, $J_{Pt\text{-}P}$ = 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 ^{31}P 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(O)C(H)=C(Ph)(H)-(*E*)](PPh_3)$_2$ was observed during course of the reaction.

***cis*-3b:** ^{31}P NMR (160 MHz, toluene-d_8) δ 15.4 (d, $J_{P\text{-}P}$ = 16 Hz, $J_{Pt\text{-}P}$ = 4715 Hz), 17.4 (d, $J_{P\text{-}P}$ = 16 Hz, $J_{Pt\text{-}P}$ = 1349 Hz). ***trans*-3b:** ^{31}P NMR (160 MHz, toluene-d_8) δ 21.0 (s, $J_{Pt\text{-}P}$ = 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(C_6H_4OMe-*p*)$_3$ (0.01 mmol) and solvent (0.5 mL) under N_2 atmosphere. The reaction was roughly monitored by ^{31}P and ^{1}H 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 H_2C=CHC(O)SC_6H_4Me-*p* (4a) with 2 in C_6D_6 (Eq. 2): The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectrum using automatic measurement program system. The ^{31}P 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 S1

time	**5a** (%)	**6a** (%)	**7a** (%)
20min	>99	n.d.	n.d.
1 h	>99	n.d.	n.d.
3 h	99.7	n.d.	0.3
6 h	99.5	n.d.	0.5

5a: ^{31}P NMR (160 MHz, C_6D_6) δ 29.5 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 4038 Hz), 31.4 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3567 Hz). ***syn*-7a:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.0 (s, $J_{Pt\text{-}P}$ = 4171 Hz).

The Reaction of 4a with 2 in CD_2Cl_2 (Eq. 2): Automatic NMR measurement program system has been used to continuously monitor the reaction. The ^{31}P 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 S2

time	**5a** (%)	*trans*-**6a** (%)	*syn*-**7a** (%)
20min	99.7	0.3	n.d.
1 h	99.4	0.3	0.3
140 min	98.9	0.4	0.7
6 h	98.9	0.4	0.7

5a: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.9 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 4060 Hz), 30.7 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3541 Hz). ***trans*-6a:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.6 (s, $J_{Pt\text{-}P}$ = 3272 Hz). ***syn*-7a:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.0 (s, $J_{Pt\text{-}P}$ = 4110 Hz).

The Reaction of H_2C=CHC(O)SPh (4b) with 2 in C_6D_6 (Eq. 2): The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectrum using automatic measurement program system. The ^{31}P NMR spectrum showed the formation of **5b** and *syn*-**7b**. The reaction time, the yields of **5b** and *syn*-**7b** at the time are shown in Table S3.

Table S3

time	**5b** (%)	**6b** (%)	*syn*-**7b** (%)
20min	>99	n.d.	n.d.
1 h	99.1	n.d.	0.9
3 h	97.7	n.d.	2.3
5 h	97.6	n.d.	2.4

5b: ^{31}P NMR (160 MHz, C_6D_6) δ 29.5 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 4049 Hz), 31.3 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3557 Hz). ***syn*-7b:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.1 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity).

The Reaction of H_2C=CHC(O)SPh (4b) with 2 in CD_2Cl_2 (Eq. 2): The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectrum using automatic measurement program system. The ^{31}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

time	**5b** (%)	**6b** (%)	**7b** (%)
10 min	>99	n.d.	n.d.
1 h	98.2	0.7	1.1
3 h	97.0	1.0	1.9
6 h	95.1	1.1	3.8
22 h	93.6	0.9	5.6

5b: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 29.0 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 4076 Hz), 30.7 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3540 Hz). **6b:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.0 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***syn*-7b:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.1 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***anti*-7b:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.0 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity).

The Reaction of H_2C=CHC(O)SC_6H_4-*p*-Cl (4c) with 2 in C_6D_6 (Eq. 2): The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectrum using automatic measurement program system. The ^{31}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

time	**5c** (%)	**6c** (%)	**7c** (%)
20 min	>99	n.d.	n.d.
1 h	98.2	0.5	1.4
3 h	92.2	1.5	6.3
6 h	90.4	1.7	7.9

5c: ^{31}P NMR (160 MHz, C_6D_6) δ 29.3 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 4072 Hz), 31.2 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3558 Hz). **6c:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***syn*-7c:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.8 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***anti*-7c:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.5 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity).

The Reaction of H_2C=CHC(O)SC_6H_4-*p*-Cl (4c) with 2 in CD_2Cl_2 (Eq. 2): The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectrum using automatic measurement program system. The ^{31}P 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 S6

time	5c (%)	6c (%)	7c (%)	8c (%)
20 min	99.5	0.5	n.d.	n.d.
1 h	98.1	1.6	0.3	n.d.
6 h	87.7	4.0	8.3	n.d.
19 h	86.3	5.4	8.3	1.5
22 h	84.1	5.3	9.4	1.1

5c: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.8 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 4082 Hz), 30.6 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3530 Hz). **6c:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.0 (s, $J_{Pt\text{-}P}$ = 3260 Hz). ***syn*-7c:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.9 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***anti*-7c:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.5 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). **10c:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 23.9 (s, $J_{Pt\text{-}P}$ = 3260 Hz).

The Reaction of H_2C=CHC(O)SC_6H_4-*p*-NO_2 (4d) with 2 in C_6D_6 (Eq. 2): The ^{31}P 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 S7

time	5d (%)	6d (%)	7d (%)	8d (%)
3 min	>99	n.d.	n.d.	n.d.
4 min	99	1	n.d.	n.d.
20 min	97	3	n.d.	n.d.
40 min	95	5	n.d.	n.d.
1 h	93	7	n.d.	n.d.
2 h	87	13	n.d.	n.d.
3 h	81	18	n.d.	1
4 h	76	23	n.d.	1
5 h	71	28	n.d.	2
10 h	50	45	n.d.	5
19 h	35	56	n.d.	9

5d: ^{31}P NMR (160 MHz, C_6D_6) δ 29.1 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 4103 Hz), 31.0 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 3542 Hz). **6d:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.0 (s, $J_{Pt\text{-}P}$ = 3236 Hz). **10d:** ^{31}P NMR (160 MHz, C_6D_6) δ 23.7 (s, $J_{Pt\text{-}P}$ = 2990 Hz).

The Reaction of H_2C=CHC(O)SC_6H_4-*p*-NO_2 (4d) with 2 in CD_2Cl_2 (Eq. 2): The ^{31}P 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 S8

time	5d (%)	6d (%) (*cis*:*trans*)	7d (%)	8d (%)
20 min	91	9 (1:>99)	n.d.	n.d.
40 min	86	14 (1:>99)	n.d.	n.d.
1 h	82	18 (1:>99)	n.d.	n.d.
2 h	73	26 (1:>99)	n.d.	0.4
3 h	65	34 (1:>99)	n.d.	1
4 h	57	42 (1:>99)	n.d.	1
5 h	50	48 (1:99)	n.d.	2
6 h	42	55 (1:99)	n.d.	3
7.5 h	34	61 (1:99)	n.d.	3
9 h	31	65 (1:99)	n.d.	4
10 h	27	68 (1:99)	n.d.	5

5d: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.6 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 4118 Hz), 30.3 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3513 Hz). **6d:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.9 (s, $J_{Pt\text{-}P}$ = 3225 Hz). **10d:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 23.5 (s, $J_{Pt\text{-}P}$ = 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(C_6H_4OMe-*p*)$_3$ (3.6 mg, 0.0094 mmol) and CD_2Cl_2 (0.5 mL) under N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectrum at 25 °C. After 17 h, the ^{31}P NMR spectrum showed the formation of **5a** (79%), *trans*-**6a** (0.6%) and **7a** (13%, *syn*:*anti* = 77:23).

***anti*-7a:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.0 (s, J_{Pt-P} = 4013 Hz).

The Reaction of H_2C=C(Me)C(O)SC_6H_4-*p*-Me (4e) with 2 in C_6D_6 (run 1, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 7 h. The ^{31}P 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).

Table S9

time	5e (%)	6e (%) (*cis*:*trans*)	7e (%) (*syn*:*anti*)	5e:6e	6e:7e
20 min	78	4.4 (9:91)	17 (47:53)	95:5	21:79
40 min	64	7.3 (4:96)	28 (68:32)	90:10	21:79
1 h	48	10 (10:90)	42 (76:24)	83:17	19:81
2 h	24	12 (5:95)	64 (80:20)	67:33	15:85
3 h	16	12 (6:94)	70 (79:21)	58:42	16:84
4 h	12	12 (6:94)	76 (80:20)	51:49	13:87
5 h	12	12 (4:96)	76 (80:20)	51:49	13:87
6 h	11	12 (5:95)	77 (81:19)	49:51	13:87
7 h	12	12 (7:93)	76 (80:20)	50:50	13:87

5e: ^{31}P NMR (160 MHz, C_6D_6) δ 28.0 (d, J_{P-P} = 41 Hz, J_{Pt-P} = 3827 Hz), 31.0 (d, J_{P-P} = 41 Hz, J_{Pt-P} = 3724 Hz). ***cis*-6e:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.7 (d, J_{P-P} = 19 Hz, the value of J_{Pt-P} was not able to read because of low intensity), 18.4 (d, J_{P-P} = 19 Hz, the value of J_{Pt-P} was not able to read because of low intensity). ***trans*-6e:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.4 (s, J_{Pt-P} = 3291 Hz). ***syn*-7e:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, J_{Pt-P} = 4188 Hz). ***anti*-7e:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.2 (s, J_{Pt-P} = 4124 Hz).

The Reaction of 4e with 2 in CD_2Cl_2 (run 2, Table 1): Automatic NMR measurement program system has been used to continuously monitor the reaction for 8 h. The ^{31}P 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 S10

time	5e (%)	6e (%) (*cis*:*trans*)	7e (%) (*syn*:*anti*)	5e:6e	6e:7e
20 min	66	20 (45:55)	17 (51:49)	77:23	59:41
40 min	45	24 (24:76)	28 (69:31)	65:35	44:56
1 h	33	26 (19:81)	42 (73:27)	56:44	39:61
2 h	15	25 (17:83)	64 (79:21)	38:62	30:70
3 h	10	24 (15:85)	70 (81:19)	29:71	27:73
4 h	9	22 (12:88)	76 (82:18)	29:71	24:76
5 h	7	21 (14:86)	76 (82:18)	25:75	23:77
6 h	6	21 (13:87)	77 (83:17)	22:78	22:78
7 h	6	20 (15:85)	76 (82:18)	23:77	22:78
8 h	6	20 (14:86)	74 (82:18)	23:77	21:79

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: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 27.5 (d, $J_{P\text{-}P}$ = 40 Hz, $J_{Pt\text{-}P}$ = 3836 Hz), 30.5 (d, $J_{P\text{-}P}$ = 40 Hz, $J_{Pt\text{-}P}$ = 3705 Hz). ***cis*-6e:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.7 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 17.5 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6e:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.1 (s, $J_{Pt\text{-}P}$ = 3205 Hz). ***syn*-7e:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.5 (s, $J_{Pt\text{-}P}$ = 4138 Hz). ***anti*-7e:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, $J_{Pt\text{-}P}$ = 4019 Hz).

The Reaction of (*E*)-MeC(H)=CH-C(O)SC$_6$H$_4$-*p*-Me (4f) with 2 in C_6D_6 (run 3, Table 1): The ^{31}P 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).

Table S11

time	5f (%)	*trans*-6f (%)	7f (%) (*syn*:*anti*)	5f:6f	6f:7f
20 min	11	7	82 (63:37)	61:39	8:92
40 min	8	6	86 (64:36)	57:43	7:93
1 h	8	6	86 (63:37)	57:43	7:93

5f: ^{31}P NMR (160 MHz, C_6D_6) δ 29.6 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 4210 Hz), 30.7 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 3376 Hz). ***trans*-6f:** ^{31}P NMR (160 MHz, C_6D_6) δ 17.1 (s, $J_{Pt\text{-}P}$ = 3310 Hz). ***syn*-7f:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.3 (s, $J_{Pt\text{-}P}$ = 4208 Hz). ***anti*-7f:** ^{31}P NMR (160 MHz, C_6D_6) δ 17.1 (s, $J_{Pt\text{-}P}$ = 4083 Hz).

The Reaction of 4f with 2 in CD_2Cl_2 (run 4, 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 **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).

Table S12

time	5f (%)	*trans*-6f (%)	7f (%) (*syn*:*anti*)	5f:6f	6f:7f
20 min	6	22	72 (75:25)	21:79	23:77
40 min	4	19	77 (74:26)	17:83	20:80
1 h	4	18	78 (74:26)	18:82	19:81

5f: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 29.0 (d, $J_{P\text{-}P}$ = 43 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 30.1 (d, $J_{P\text{-}P}$ = 43 Hz, the value of $J_{Pt\text{-}P}$ was not able to read

because of low intensity). ***trans*-6f:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.8 (s, J_{Pt-P} = 3313 Hz). ***syn*-7f:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.4 (s, J_{Pt-P} = 4158 Hz). ***anti*-7f:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.4 (s, J_{Pt-P} = 4027 Hz).

The Reaction of H_2C=C(*n*-C_6H_{13})C(O)SC_6H_4-*p*-Me (4g) with 2 in C_6D_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).

Table S13

time	**5g** (%)	*trans*-**6g** (%)	**7g** (%) (*syn*:*anti*)	**5g**:**6g**	**6g**:**7g**
20 min	95	2	2 (>99:1)	98:2	50:50
40 min	87	2	11 (66:34)	98:2	15:85
1 h	79	2	19 (65:35)	98:2	10:90
3 h	53	4	43 (70:30)	93:7	9:91
6 h	32	5	63 (74:26)	86:14	7:93
7 h	28	5	67 (74:26)	85:15	7:93
8 h	24	5	71 (74:26)	83:17	7:93
9 h	22	5	72 (75:25)	81:19	6:94
10 h	21	6	73 (76:24)	78:22	8:92
13 h	18	5	77 (73:27)	78:22	6:94

5g: ^{31}P NMR (160 MHz, C_6D_6) δ 27.5 (d, J_{P-P} = 40 Hz, J_{Pt-P} = 3863 Hz), 30.5 (d, J_{P-P} = 40 Hz, J_{Pt-P} = 3669 Hz). ***trans*-6g:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.2 (s, J_{Pt-P} = 3312 Hz). ***syn*-7g:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, J_{Pt-P} = 4177 Hz). ***anti*-7g:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, J_{Pt-P} = 4124 Hz).

The Reaction of (*E*)-*n*-HexC(H)=CHC(O)SC_6H_4-*p*-Me (4h) with 2 in C_6D_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).

Table S14

time	**5h** (%)	*trans*-**6h** (%)	**7h** (%) (*syn*:*anti*)	**5h**:**6h**	**6h**:**7h**
20 min	9	9	82 (74:26)	52:48	10:90
40 min	7	9	84 (75:25)	46:54	9:91
1 h	7	9	84 (74:26)	44:56	9:91

5h: ^{31}P NMR (160 MHz, C_6D_6) δ 29.8 (d, J_{P-P} = 44 Hz, J_{Pt-P} = 3863 Hz), 30.7 (d, J_{P-P} = 44 Hz, J_{Pt-P} = 3669 Hz). ***trans*-6h:** ^{31}P NMR (160 MHz, C_6D_6) δ 17.1 (s, J_{Pt-P} = 3318 Hz). ***syn*-7h:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.2 (s, J_{Pt-P} = 4212 Hz). ***anti*-7h:** ^{31}P NMR (160 MHz, C_6D_6) δ 17.3 (s, J_{Pt-P} = 4105 Hz).

The Reaction of H_2C=C(*i*-Pr)C(O)-SC_6H_4-*p*-Me (4i) with 2 in C_6D_6 (run 7, Table 1): Automatic measurement program system has been used to continuously monitor the reaction for 71 h. The ^{31}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 52-55 h (81:19). These data also demonstrated that **6i** was produced from **3i**. On the other hand, the equilibrium between *trans*-**4i**:**5i** was attained in a range of time of 10-15 h (6:94).

Table S15

time	**5i** (%)	*trans*-**6i** (%)	**7i** (%) (*syn*:*anti*)	**5i**:**6i**	**6i**:**7i**
20 min	99.5	0.5	n.d.	99.5:0.5	>99:1
40 min	98.3	0.7	0.9 (>99:1)	99:1	44:56
1 h	96.6	0.7	2.7 (82:18)	99:1	21:79
6 h	79	2	19 (80:20)	98:2	10:90
10 h	65	3	32 (81:19)	96:4	9:91
15 h	53	3	44 (81:19)	95:5	6:94
21 h	43	4	53 (80:20)	91:9	7:93
25 h	37	4	59 (81:19)	90:10	6:94
30 h	32	4	64 (82:18)	89:11	6:94
35 h	30	4	66 (81:19)	88:12	6:94
40 h	27	4	69 (80:20)	87:13	5:95
47 h	25	5	70 (82:18)	83:17	7:93
52 h	23	5	72 (81:19)	82:18	6:94
55 h	22	5	73 (81:19)	81:19	6:94
66 h	21	5	74 (80:20)	81:19	6:94
71 h	21	5	74 (81:19)	81:19	6:94

5i: ^{31}P NMR (160 MHz, C_6D_6) δ 26.8 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3867 Hz), 30.2 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3732 Hz). ***trans*-6i:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.8 (s, $J_{Pt\text{-}P}$ = 3299 Hz). ***syn*-7i:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.4 (s, $J_{Pt\text{-}P}$ = 4208 Hz). ***anti*-7i:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, $J_{Pt\text{-}P}$ = 4114 Hz).

The Reaction of H_2C=C(Ph)C(O)-SC_6H_4-*p*-Me (4j) with 2 in C_6D_6 (run 8, 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**, *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 14-15h (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).

Table S16

time	**5j** (%)	*trans*-**6j** (%)	**7j** (%) (*syn*:*anti*)	**5j**:**6j**	**6j**:**7j**
20 min	98	2	n.d.	98:2	>99:1
40 min	91	4	5 (60:40)	96:4	44:56
1 h	86	5	9 (67:33)	95:5	36:64
3 h	69	6	24 (75:25)	92:8	20:80
6 h	50	8	41 (78:22)	86:14	16:84
7 h	32	8	60 (78:22)	80:20	12:88
8 h	29	8	63 (78:22)	78:22	11:89
9 h	27	8	65 (78:22)	77:23	11:89
10 h	26	7	67 (76:24)	79:21	9:91
11 h	24	7	69 (76:24)	77:23	9:91
12 h	21	7	72 (76:24)	75:25	9:91
13 h	20	7	73 (76:24)	74:26	9:91
14 h	18	7	75 (76:24)	72:28	9:91
15 h	17	7	76 (76:24)	71:29	8:92
20 h	14	6	80 (77:23)	70:30	7:93

5j: ^{31}P NMR (160 MHz, C_6D_6) δ 26.6 (d, $J_{P\text{-}P}$ = 40 Hz, $J_{Pt\text{-}P}$ = 4013 Hz), 30.1 (d, $J_{P\text{-}P}$ = 40 Hz, $J_{Pt\text{-}P}$ = 3696 Hz). ***trans*-6j:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.1 (s, $J_{Pt\text{-}P}$ = 3259 Hz). ***syn*-7j:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, $J_{Pt\text{-}P}$ = 4141 Hz). ***anti*-7j:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.4 (s, $J_{Pt\text{-}P}$ = 4081 Hz).

The Reaction of 4j with 2 Using 4.3 Equivalent of 4j in C_6D_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**, *trans*-**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 14-15 h (68:32). On the other hand, the equilibrium between *trans*-**6j** and **7j** was attained in a range of time of 7-8 h (10:90). When this result was compared with that of Table S17, it was obvious that the time required for reaching the equilibrium was not affected by the excess amount of **4j**.

Table S17

time	**5j** (%)	*trans*-**6j** (%)	**7j** (%) (*syn*:*anti*)	**5j**:**6j**	**6j**:**7j**
20 min	98	2	n.d.	98:2	>99:1
40 min	89	4	7 (73:27)	96:4	36:64
1 h	82	6	12 (71:29)	93:7	33:67
3 h	57	8	35 (77:23)	88:12	19:81
6 h	35	8	56 (77:23)	81:19	13:87
7 h	32	8	59 (78:22)	80:20	12:88
8 h	28	7	65 (74:26)	80:20	10:90
9 h	25	8	67 (77:23)	76:24	11:89
10 h	23	8	69 (76:24)	74:26	10:90
11 h	21	8	71 (77:23)	72:28	10:90
12 h	21	7	72 (76:24)	75:25	9:91
13 h	19	8	73 (78:22)	70:30	10:90
14 h	18	8	74 (76:24)	69:31	10:90
15 h	17	8	75 (78:22)	68:32	10:90
20 h	15	7	78 (76:24)	68:32	8:92

The Reaction of 4j with 2 in CD_2Cl_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).

Table S18

time	**5j** (%)	**6j** (%) (*cis*:*trans*)	**7j** (%) (*syn*:*anti*)	**5j**:**6j**	**6j**:**7j**
20 min	92	6 (17:83)	2 (60:40)	94:6	80:20
40 min	88	9 (22:78)	3 (69:31)	91:9	76:24
1 h	85	11 (19:81)	4 (68:32)	89:11	71:29
3 h	55	19 (22:78)	26 (75:25)	75:25	42:58
6 h	33	19 (17:83)	48 (82:18)	64:36	28:72
10 h	24	17 (20:80)	59 (85:15)	58:42	22:78
11 h	22	17 (20:80)	61 (85:15)	56:44	21:79
12 h	20	16 (21:79)	64 (84:14)	55:45	20:80
13 h	19	15 (20:80)	66 (86:14)	55:45	19:81
14 h	18	15 (19:81)	67 (86:14)	54:46	18:82
15 h	17	15 (19:81)	68 (86:14)	54:46	18:82
16 h	16	15 (21:79)	69 (86:14)	53:47	18:82
17 h	15	15 (21:79)	70 (86:14)	50:50	18:82
20 h	14	14 (20:80)	72 (87:13)	50:50	17:83

5j: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 25.9 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 4037 Hz), 29.5 (d, $J_{P\text{-}P}$ = 38

Hz, J_{Pt-P} = 3516 Hz). ***cis*-6j:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.2 (d, J_{P-P} = 20 Hz, the value of J_{Pt-P} was not able to read because of low intensity), 17.2 (d, J_{P-P} = 20 Hz, the value of J_{Pt-P} was not able to read because of low intensity). ***trans*-6j:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.4 (s, J_{Pt-P} = 3241 Hz). ***syn*-7j:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.3 (s, J_{Pt-P} = 4079 Hz). ***anti*-7j:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, J_{Pt-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).

Table S19

time	5k (%)	*trans*-6k (%)	7k (%) (*syn*:*anti*)	5k:6k	6k:7k
20 min	51	5	44 (59:41)	91:9	9:91
40 min	42	5	53 (60:40)	89:11	8:92
1 h	37	5	58 (64:36)	88:12	8:92

5k: ^{31}P NMR (160 MHz, C_6D_6) δ 27.1 (d, J_{P-P} = 38 Hz, J_{Pt-P} = 4134 Hz), 27.8 (d, J_{P-P} = 38 Hz, J_{Pt-P} = 3591 Hz). ***trans*-6k:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.8 (s, J_{Pt-P} = 3281 Hz). ***syn*-7k:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.0 (s, J_{Pt-P} = 4171 Hz). ***anti*-7k:** ^{31}P NMR (160 MHz, C_6D_6) δ 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**.

Table S20

time	5k (%)	*trans*-6k (%)	7k (%) (*syn*:*anti*)	5k:6k	6k:7k
20 min	46	5	48 (60:40)	90:10	9:91
40 min	39	4	56 (63:37)	91:9	7:93
1 h	36	4	56 (63:37)	90:10	7:93

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).

Table S21

time	**5k** (%)	*trans*-**6k** (%)	**7k** (%) (*syn*:*anti*)	**5k**:**6k**	**6k**:**7k**
20 min	38	16	45 (71:29)	70:30	26:74
40 min	32	14	53 (72:28)	70:30	21:79
60 min	28	13	59 (71:29)	68:32	18:82
80 min	26	11	63 (70:30)	70:30	15:85
100 min	24	11	65 (71:29)	69:31	14:86
2 h	22	11	67 (70:30)	67:33	14:86
140 min	24	11	65 (72:28)	69:31	14:86
160 min	24	11	65 (72:28)	69:31	14:86
3 h	23	10	67 (69:31)	69:31	13:87

5k: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.6 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 4168 Hz), 27.1 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3572 Hz). ***trans*-6k:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.6 (s, $J_{Pt\text{-}P}$ = 3280 Hz). ***syn*-7k:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.3 (s, $J_{Pt\text{-}P}$ = 4133 Hz). ***anti*-7k:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.4 (s, $J_{Pt\text{-}P}$ = 3977 Hz).

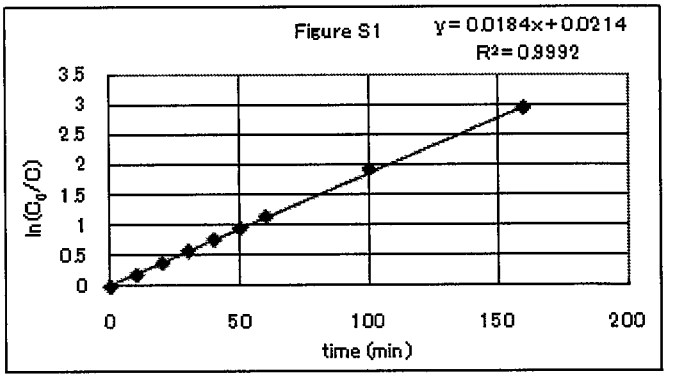
The Reaction of 4f with 2 in toluene-d_8 at Low Temperature (Eq. 4): Into a dry Pyrex NMR tube were added **2** (15.8 mg, 0.021 mmol), **4f** (13.2 mg, 0.069 mmol) and S=P(C_6H_4OMe-*p*)$_3$ (1.3 mg, 0.0034 mmol). Then ca. 0.5 mL of toluene-d_8 was transferred by the freeze-pump-thaw method. The ^{31}P NMR spectrum showed the formation of **5f**, *trans*-**6f** and **7c**. These results clearly showed that **6f** was formed from **5f**.

5f: ^{31}P NMR (160 MHz, toluene-d_8) δ 30.2 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 4204 Hz), 31.5 (d, $J_{P\text{-}P}$ = 44 Hz, $J_{Pt\text{-}P}$ = 3377 Hz). ***trans*-6f:** ^{31}P NMR (160 MHz, toluene-d_8) δ 17.9 (s, $J_{Pt\text{-}P}$ = 3304 Hz). ***syn*-7f:** ^{31}P NMR (160 MHz, toluene-d_8) δ 15.9 (s, $J_{Pt\text{-}P}$ = 4213 Hz). ***anti*-7f:** ^{31}P NMR (160 MHz, toluene-d_8) δ 17.8 (s, $J_{Pt\text{-}P}$ = 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_6H_4OMe-*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 ^{31}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**.

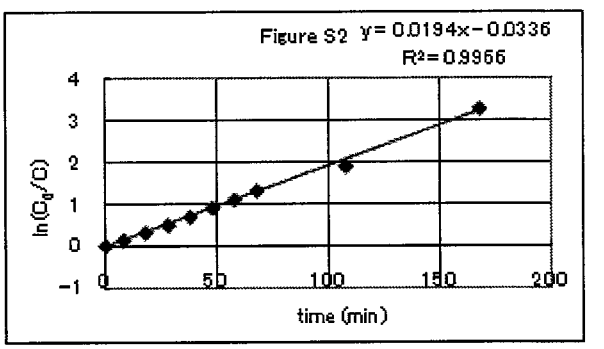
5k: ^{31}P NMR (160 MHz, toluene-d_8) δ 27.2 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 4124 Hz), 28.1 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3597 Hz). ***cis*-6k:** ^{31}P NMR (160 MHz, toluene-d_8) δ 17.1 (d, $J_{P\text{-}P}$ = 21 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 19.1 (d, $J_{P\text{-}P}$ = 21 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6k:** ^{31}P NMR (160 MHz, toluene-d_8) δ 17.6 (s, $J_{Pt\text{-}P}$ = 3277 Hz). ***syn*-7k:** ^{31}P NMR (160 MHz, toluene-d_8) δ 15.8 (s, $J_{Pt\text{-}P}$ = 4189 Hz). ***anti*-7k:** ^{31}P NMR (160 MHz, toluene-d_8) δ 17.5 (s, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity).

The Half-Live of the Reaction of Pt[H_2C=C(Me)C(O)SC_6H_4-*p*-NO_2](PPh_3)$_2$ (5l) to *trans*-Pt[C(O)C(Me)=CH_2]-(SC_6H_4-*p*-NO_2)(PPh_3)$_2$ (6l) in C_6D_6 (run 1, 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 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 **5l** obeyed the first-order kinetics (Figure S1) and the half-live was calculated to be 38 min.

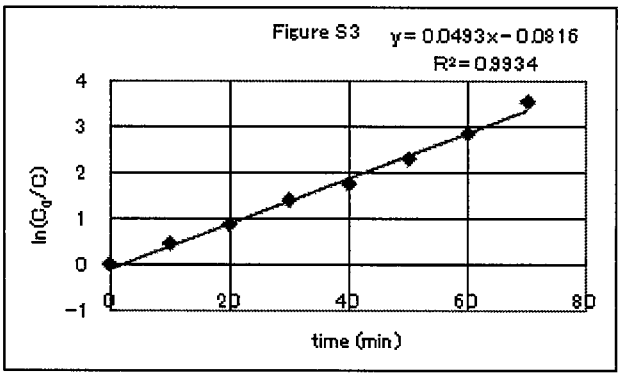


5l: ^{31}P NMR (160 MHz, C_6D_6) δ 27.6 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3863 Hz), 30.6 (d, $J_{P\text{-}P}$ = 38 Hz, $J_{Pt\text{-}P}$ = 3683 Hz). ***cis*-6l:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.5 (d, $J_{P\text{-}P}$ = 18 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 17.9 (d, $J_{P\text{-}P}$ = 18 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6l:** ^{31}P NMR (160 MHz, C_6D_6) δ 15.1 (s, $J_{Pt\text{-}P}$ = 3228 Hz).

The Half-Live of the Reaction of 5l to 6l Using 4.5 Equivalent of 4l in C_6D_6 (run 2, 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 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 **5l** obeyed the first-order kinetics (Figure S2) and the half-live was calculated to be 36 min. The present result did not contradict the idea that the transformation from **5l** to **6l** was a unimolecular process.

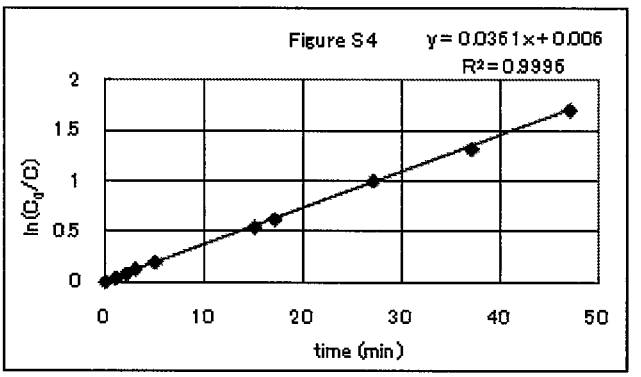


The Half-Live of the Reaction of 5l to 6l in CD_2Cl_2 (run 3, Table 2): The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 10 min, 69%, 30% (*cis*:*trans* = 67:33); 20 min, 44%, 54% (*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-live was calculated to be 14 min.



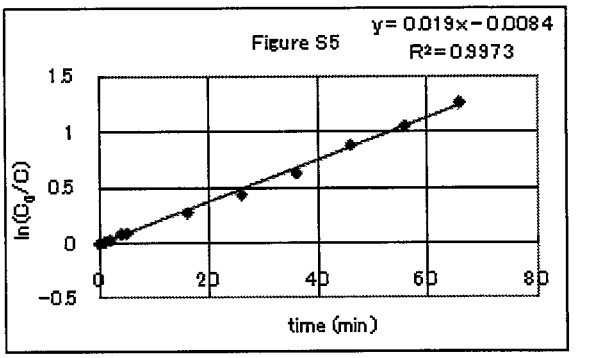
5l: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 27.2 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 4025 Hz), 30.0 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 3667 Hz). ***cis*-6l:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.1 (d, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 1336 Hz), 17.0 (d, $J_{P\text{-}P}$ = 18 Hz, $J_{Pt\text{-}P}$ = 3765 Hz). ***trans*-6l:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.1 (s, $J_{Pt\text{-}P}$ = 3225 Hz).

The Half-Live of the Reaction of 5l to 6l in acetone-d_6 (run 4, 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 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-live was calculated to be 19 min.



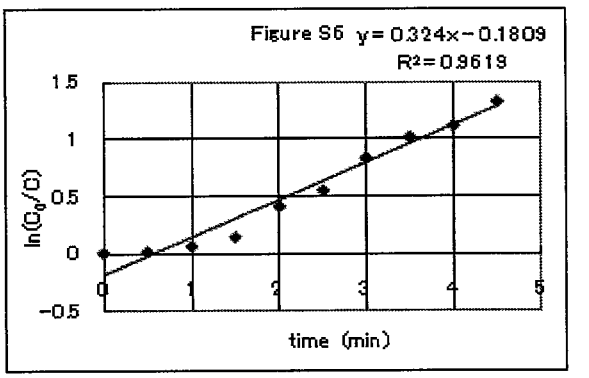
5l: ^{31}P NMR (160 MHz, acetone-d_6) δ 27.8 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 3882 Hz), 30.8 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 3672 Hz). ***cis*-6l:** ^{31}P NMR (160 MHz, acetone-d_6) δ 15.7 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 19.3 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6l:** ^{31}P NMR (160 MHz, acetone-d_6) δ 15.8 (s, $J_{Pt\text{-}P}$ = 3243 Hz).

The Half-Live of the Reaction of 5l to 6l in THF-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% (*trans* only); 5.0 min, 96%, 4% (*trans* only); 6.0 min, 95%, 5% (*trans* only); 8.0 min, 90%, 10% (*cis*:*trans* = 31/69); 9.0 min, 89%, 11% (*cis*:*trans* = 30:70); 20 min, 74%, 26% (*cis*:*trans* = 15:85); 30 min, 63%, 37% (*cis*:*trans* = 10:90); 40 min, 52%, 48% (*cis*:*trans* = 8:92); 50 min, 40%, 60% (*cis*:*trans* = 5:95); 60 min, 34%, 66% (*trans* only); 70 min, 28%, 72% (*trans* only). The consumption rate of **5l** obeyed the first-order kinetics (Figure S5) and the half-live was calculated to be 36 min.



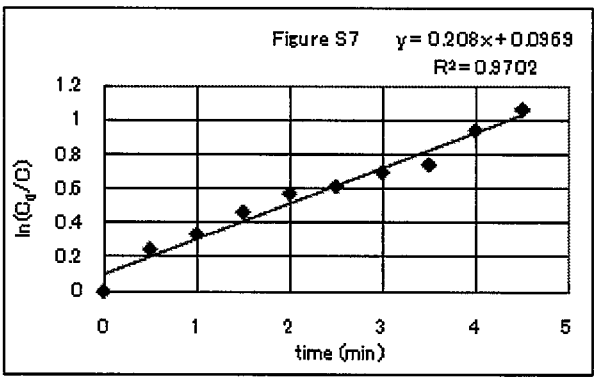
5l: ^{31}P NMR (160 MHz, THF-d_8) δ 29.0 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3983 Hz), 32.0 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3678 Hz). ***cis*-6l:** ^{31}P NMR (160 MHz, THF-d_8) δ 16.0 (d, $J_{P\text{-}P}$ = 18 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 19.2 (d, $J_{P\text{-}P}$ = 18 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6l:** ^{31}P NMR (160 MHz, THF-d_8) δ 16.5 (s, $J_{Pt\text{-}P}$ = 3224 Hz).

The Half-Live of the Reaction of Pt[(*E*)-MeC(H)=CHC(O)SC$_6$H$_4$-*p*-NO$_2$](PPh$_3$)$_2$ (5m) to Pt[C(O)C(H)=CH(Me)-(*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 *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-live was calculated to be ca. 2.1 min. All reactions shown in Table 2 were carried out similarly.



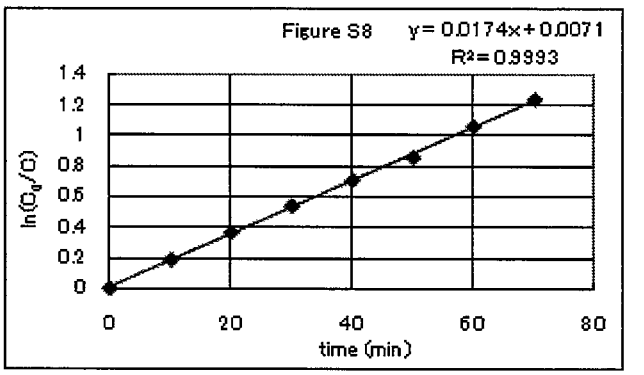
5m: ^{31}P NMR (160 MHz, C$_6$D$_6$) δ 29.1 (d, $J_{P\text{-}P}$ = 42 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 30.3 (d, $J_{P\text{-}P}$ = 42 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6m:** ^{31}P NMR (160 MHz, C$_6$D$_6$) δ 16.3 (s, $J_{Pt\text{-}P}$ = 3268 Hz).

The Half-Live of the Reaction of 5m to 6m in CD_2Cl_2 (run 7, Table 2): The ^{31}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-live was calculated to be ca. 3.3 min.



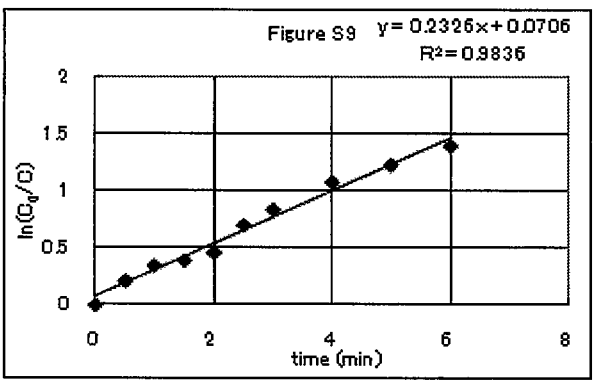
5m: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.7 (d, $J_{P\text{-}P}$ = 40 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 29.7 (d, $J_{P\text{-}P}$ = 40 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6m:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.3 (s, $J_{Pt\text{-}P}$ = 3258 Hz).

The Half-Live of the Reaction of Pt[H_2C=C(*n*-Hex)C(O)SC_6H_4-*p*-NO_2](PPh$_3$)$_2$ (5n) to *trans*-Pt[C(O)C(*n*-Hex)=CH_2]-(SC_6H_4-*p*-NO_2)(PPh$_3$)$_2$ (6n) in C_6D_6 (run 8, Table 2): The ^{31}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, 442%, 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-live was calculated to be 40 min.



5n: ^{31}P NMR (160 MHz, C_6D_6) δ 27.2 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3898 Hz), 30.3 (d, $J_{P\text{-}P}$ = 37 Hz, $J_{Pt\text{-}P}$ = 3692 Hz). ***trans*-6n:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.9 (s, $J_{Pt\text{-}P}$ = 3235 Hz).

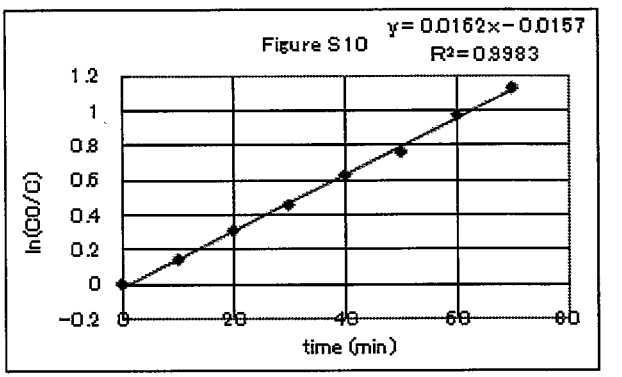
The Half-Live of the Reaction of Pt[(*E*)-(*n*-Hex)C(H)=CHC(O)SC_6H_4-*p*-NO_2]-(PPh$_3$)$_2$ (5o) to *trans*-Pt[C(O)C(H)=CH-(*n*-Hex)-(*E*)](SC$_6$H$_4$-*p*-NO_2)(PPh$_3$)$_2$ (6o) in C_6D_6 (run 9, Table 2): The ^{31}P NMR spectrum showed the formation of **5o** and *trans*-**6o**. The reaction time (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-live was calculated to be 3.0 min.

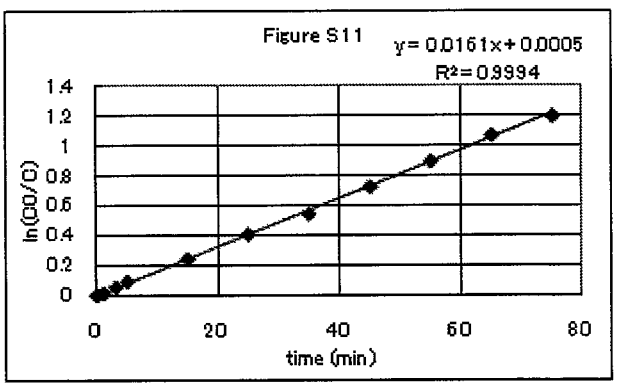
5o: ^{31}P NMR (160 MHz, C_6D_6) δ 29.3 (d, $J_{P\text{-}P}$ = 40 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 30.3 (d, $J_{P\text{-}P}$ = 40 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6o:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.29 (s, $J_{Pt\text{-}P}$ = 3277 Hz).

The Half-Live of the Reaction of Pt[H_2C=C(*i*-Pr)C(O)SC_6H_4-*p*-NO_2](PPh_3)$_2$ (5p) to Pt[C(O)C(*i*-Pr)=CH_2](SC_6H_4-*p*-NO_2)-(PPh_3)$_2$ (6p) in C_6D_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-live was calculated to be 43 min.



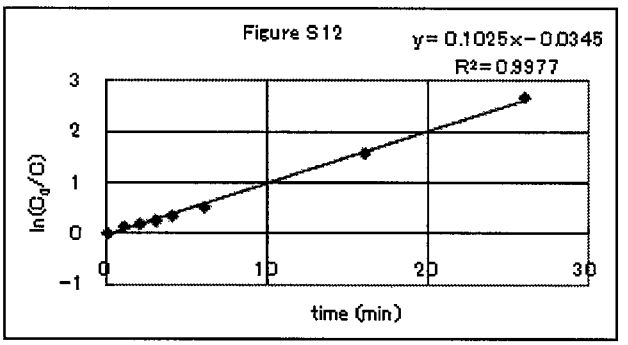
5p: ^{31}P NMR (160 MHz, C_6D_6) δ 26.5 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3909 Hz), 30.1 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3697 Hz). ***trans*-6p:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.8 (s, $J_{Pt\text{-}P}$ = 3192 Hz).

The Half-Live of the Reaction of 5p to 6p Using 5.0 Equivalent of 4m in C_6D_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-live was calculated to be 43 min, showing that the transformation from **5p** to **6p** was a unimolecular process.



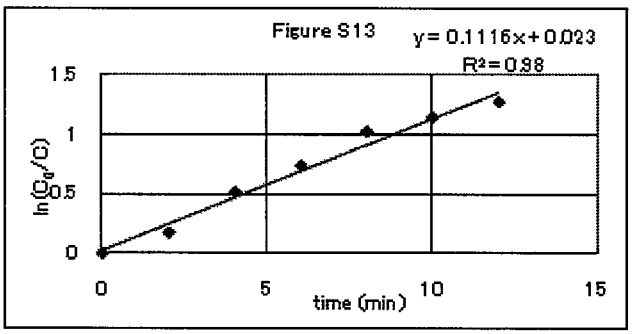
The Half-Live of the Reaction of 5p to 6p in CD_2Cl_2 (run 12, Table 2): The ^{31}P NMR spectrum showed the formation of **5p** and **6p**. The reaction time (the average of acquisition time), and the yields of **5p** and **6p** at the time were 4 min, 72%, 28% (*cis*:*trans* = 69:31); 5 min, 63%, 37% (*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-live was calculated to be 6.8 min.



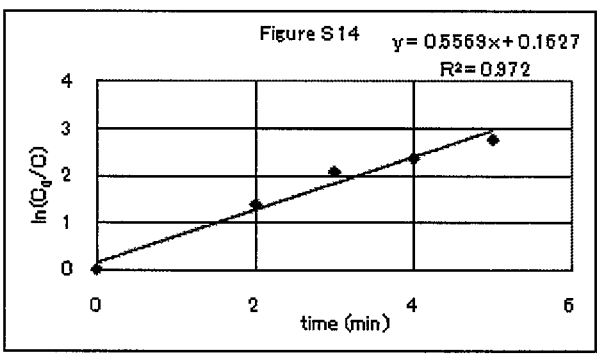
5p: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.0 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3938 Hz), 29.8 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3684 Hz). ***cis*-6p:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.2 (d, $J_{P\text{-}P}$ = 19 Hz, $J_{Pt\text{-}P}$ = 1311 Hz), 17.3 (d, $J_{P\text{-}P}$ = 19Hz, $J_{Pt\text{-}P}$ = 3824 Hz). ***trans*-6p:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.7 (s, $J_{Pt\text{-}P}$ = 3239 Hz).

The Half-Live of the Reaction of Pt[H_2C=C(Ph)C(O)SC_6H_4-*p*-NO_2](PPh_3)$_2$ (5q) to Pt[C(O)C(Ph)=CH_2]-(SC_6H_4-*p*-NO_2)(PPh_3)$_2$ (6q) in C_6D_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-live was calculated to be 6.2 min.



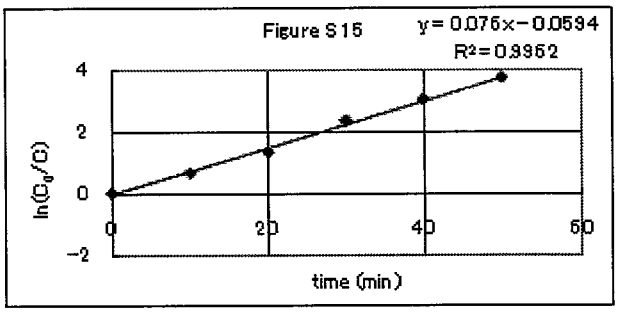
5q: ^{31}P NMR (160 MHz, C_6D_6) δ 26.2 (d, $J_{P\text{-}P}$ = 37 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity of the signal), 29.9 (d, $J_{P\text{-}P}$ = 37 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity of the signal). ***trans*-6q:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.8 (s, $J_{Pt\text{-}P}$ = 3206 Hz).

The Half-Live of the Reaction of 5q to 6q in CD_2Cl_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-live was calculated to be 1.2 min.



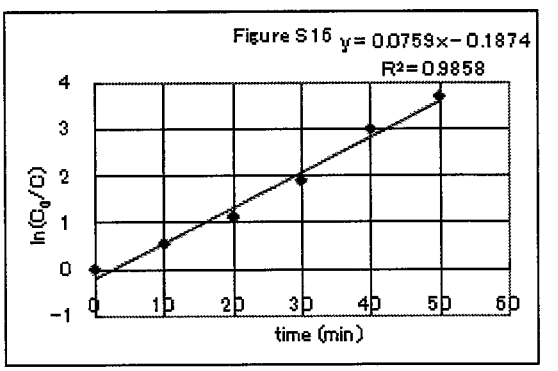
5q: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 25.7 (d, $J_{P\text{-}P}$ = 35 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity of the signal), 29.2 (d, $J_{P\text{-}P}$ = 35 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity of the signal). ***cis*-6q:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 13.9 (d, $J_{P\text{-}P}$ = 19 Hz, $J_{Pt\text{-}P}$ = 1328 Hz), 17.1 (d, $J_{P\text{-}P}$ = 19 Hz, $J_{Pt\text{-}P}$ = 3720 Hz). ***trans*-6q:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.6 (s, $J_{Pt\text{-}P}$ = 3186 Hz).

The Half-Live of the Reaction of Pt[(*E*)-PhC(H)=CHC(O)SC$_6$H$_4$-*p*-NO$_2$](PPh$_3$)$_2$ (5r) to Pt[C(O)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.

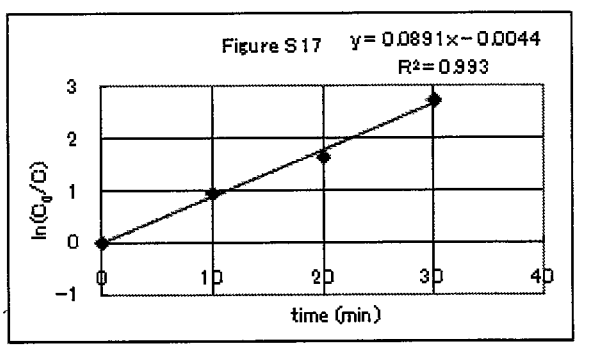


5r: ^{31}P NMR (160 MHz, C_6D_6) δ 26.7 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 4178 Hz), 27.4 (d, $J_{P\text{-}P}$ = 36 Hz, $J_{Pt\text{-}P}$ = 3552 Hz). ***trans*-6r:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.0 (s, $J_{Pt\text{-}P}$ = 3229 Hz).

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



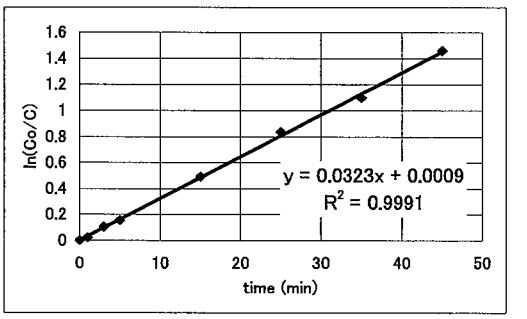
min, 12%, 88% (*cis*:*trans* = 2:98); 30 min, 6%, 94% (*cis*:*trans* = 2:98); 40 min, 2%, 98% (*trans* only); 50 min, n.d., >99% (*trans* only). The consumption rate of **5r** obeyed the first-order kinetics (Figure S17) and the half-live was calculated to be 7.8 min.

5r: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.3 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 4208 Hz), 26.7 (d, $J_{P\text{-}P}$ = 35 Hz, $J_{Pt\text{-}P}$ = 3525 Hz). ***cis*-6r:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.1 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity), 17.8 (d, $J_{P\text{-}P}$ = 19 Hz, the value of $J_{Pt\text{-}P}$ was not able to read because of low intensity). ***trans*-6r:** ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, $J_{Pt\text{-}P}$ = 3217 Hz).

The Reaction of 4q with 2 in CD_2Cl_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_6H_4OMe-*p*)$_3$ (1.1 mg, 0.0028 mmol). Then ca. 0.5 mL of CD_2Cl_2 was transferred by the freeze-pump-thaw method. The ^{31}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**.

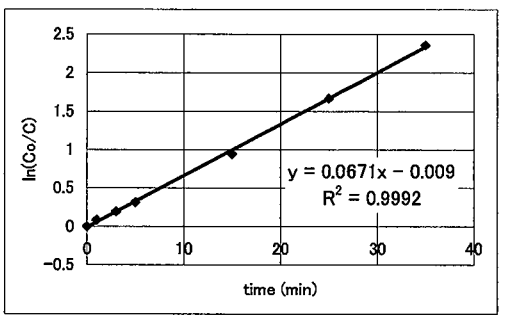
The Half-Live of the Reaction of 5l to 6l in C_6D_6 at 30 °C: The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 5 min, 90%, 10% (*trans* only); 6 min, 88%, 12% (*trans* only); 8 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.

Figure S18



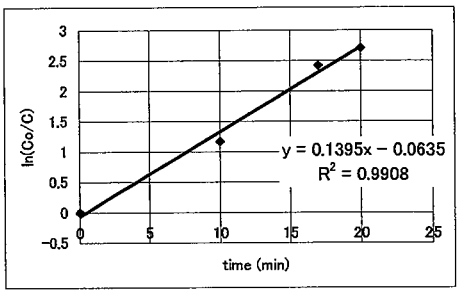
The Half-Live of the Reaction of 5l to 6l in C_6D_6 at 35 °C: The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 5 min, 85%, 15% (*trans* only); 6 min, 78%, 22% (*cis*:*trans* = 13:87); 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.

Figure S19



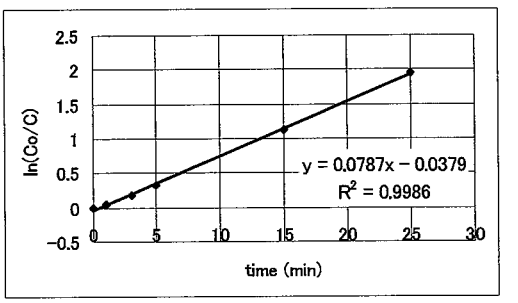
The Half-Live of the Reaction of 5l to 6l in C_6D_6 at 40 °C: The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 10 min, 45%, 55% (*trans* only); 20 min, 14%, 86% (*trans* only); 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-live was calculated to be 4.97 min.

Figure S20



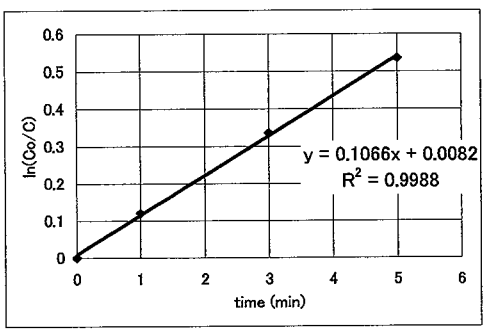
The Half-Live of the Reaction of 5l to 6l in CD_2Cl_2 at 30 °C: The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 5 min, 77%, 23% (*cis*:*trans* = 65:35); 6 min, 73%, 27% (*cis*:*trans* = 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-live was calculated to be 8.81 min.

Figure S21



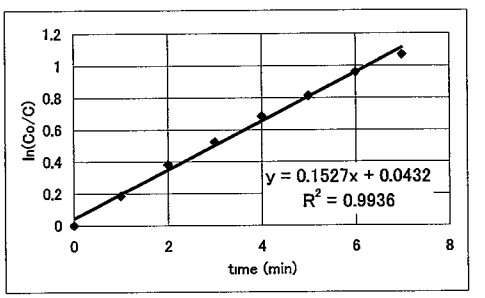
The Half-Live of the Reaction of 5l to 6l in CD_2Cl_2 at 35 °C: The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time), and the yields of **5l** and **6l** at the time were 5 min, 70%, 30% (*cis*:*trans* = 53:47); 6 min, 62%, 38% (*cis*:*trans* = 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-live was calculated to be 6.57 min.

Figure S22



The Half-Live of the Reaction of 5l to 6l in CD_2Cl_2 at 40 °C: 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 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%

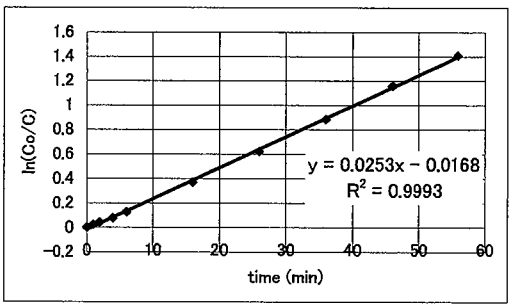
Figure S23



(*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.

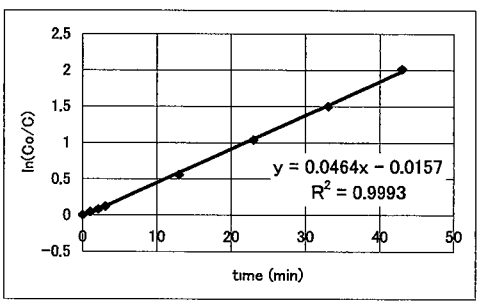
The Half-Live of the Reaction of 5p to 6p in C_6D_6 at 30 °C: The ^{31}P NMR spectrum showed the formation of **5p** and *trans*-**6p**. The reaction time (the average of acquisition time), and the yields of **5p** and *trans*-**6p** at the time were 4 min, 95%, 5%; 5 min, 93%, 7%; 6 min, 91%, 9%; 8 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.

Figure S24



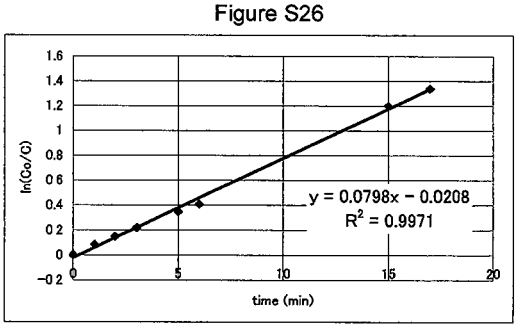
The Half-Live of the Reaction of 5p to 6p in C_6D_6 at 35 °C: The ^{31}P NMR spectrum showed the formation of **5p** and *trans*-**6p**. The reaction time (the average of acquisition time), and the yields of **5p** and *trans*-**6p** at the time were 7 min, 88%, 12%; 8 min, 85%, 15%; 9 min, 81%, 19%; 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.

Figure S25



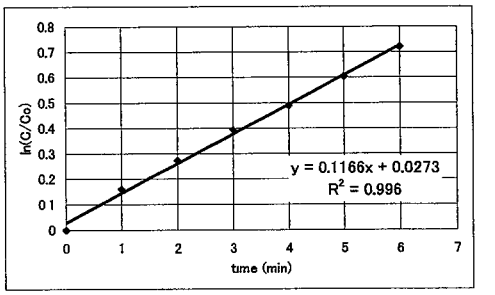
The Half-Live of the Reaction of 5p to 6p in C_6D_6 at 40 °C: The ^{31}P NMR spectrum showed the formation of **5p** and *trans*-**6p**. The reaction time (the average of acquisition time), and the yields of **5p** and *trans*-**6p** at the time were 3 min, 96%, 4%; 4 min, 88%, 12%; 5 min, 83%, 17%; 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.

Figure S26



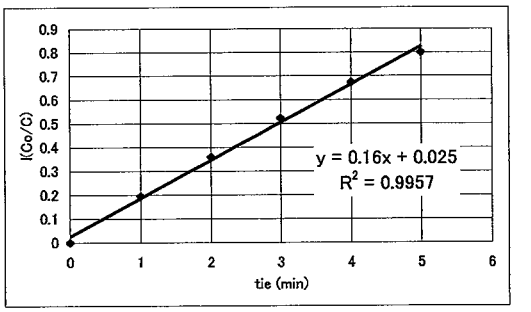
The Half-Live of the Reaction of 5p to 6p in CD_2Cl_2 at 30 °C: The ^{31}P NMR spectrum showed the formation of **5p** and **6p**. The reaction time (the average of acquisition time), and the yields of **5p** and **6p** at the time were 2 min, 81%, 19% (*cis*:*trans* = 69:31); 3 min, 69%, 31% (*cis*:*trans* = 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* = 9:91); 30 min, n.d., >99% (*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.

Figure S27



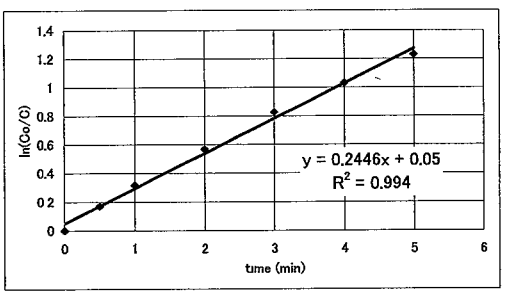
The Half-Live of the Reaction of 5p to 6p in CD_2Cl_2 at 35 °C: The ^{31}P NMR spectrum showed the formation of **5p** and **6p**. The reaction time (the average of acquisition time), and the yields of **5p** and **6p** at the time were 3 min, 61%, 39% (*cis*:*trans* = 48:52); 4 min, 50%, 50% (*cis*:*trans* = 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.

Figure S28



The Half-Live of the Reaction of 5p to 6p in CD_2Cl_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.

Figure S29



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 C_6D_6 and CD_2Cl_2 according to the equation: $k = (k_BT/h)\{\exp[-(\Delta H^{\ddagger}-T\Delta S^{\ddagger})/(RT)]\}$.

Activation Parameters of the Transformation of 5l to 6l in C_6D_6: 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 CD_2Cl_2: 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 C_6D_6: 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 CD_2Cl_2: 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 C_6D_6: 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 CD_2Cl_2: 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

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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 $CF_3C(O)SR$ 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 CCl_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
Chem. Commun. **2009**, 3080-3082.

(2) Pd-Catalyzed Regioselevtive Iminothiolation of Alkynes: Remarkable Effects of CF_3 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
Org. Lett. **2008**, *10,* 2469-2472.

(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
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