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Equilibrium shift in the rhodium-catalyzed acyl transfer reactions

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ABSTRACT

Rhodium/phosphine complexes catalyze equilibrium acyl transfer reactions between acid fluorides, aryl esters, acylphosphine sulfides, and thioesters. The use of appropriate co-substrates to accept heteroatom groups shifted the equilibrium to desired products. Acylphosphine sulfides and aryl esters were converted to acid fluorides using benzoylpentafluorobenzene as the fluoride donor, and the fluorination reaction of thioesters employed (4-tolylthio)pentafluorobenzene. Acid fluorides were converted into acylphosphine sulfides and thioesters using diphosphine disulfides and disulfides/triphenylphosphine, respectively. Aryl esters were obtained from acid fluorides and phenols in the presence of triphenylsilane. Aryl esters, acylphosphine sulfides, and thioesters were also interconverted in the presence of rhodium complexes. These rhodium-catalyzed acyl transfer reactions proceeded under neutral conditions without using acid or base. The involvement of acyl rhodium intermediates in these reactions was suggested by the carbothiolation reaction of thioesters and alkynes.

1. Introduction

Acyl transfer reactions, which exchange acyl groups between heteroatoms, such as oxygen, nitrogen, and halogens, are important in chemistry and biology.[1] Ester formation from alcohols and carboxylic acids catalyzed by acid, for example, has been particularly well examined. Transesterification is another acyl transfer reaction for obtaining esters, and ester alkoxy groups are exchanged with alcohols under acid or base catalysis. Because the reactions are equilibria, techniques are required to obtain products in high yields. A shift of equilibrium is often achieved using excess alcohol, and alternatively azeotropic removal of water is also effective. To avoid relatively complex procedures to shift the equilibrium, reactive acylating reagents, such as acyl halides or acid anhydrides may be treated with alcohols in the presence of bases. The base traps acids formed and/or activates acylating reagents. Acyl transfer reactions have been conducted in the presence of acid or base catalysts with various devices to shift equilibrium.

The development of novel catalysts for the acyl transfer reaction is interesting, particularly when catalysts other than acid or base are used. Such reactions can proceed under mild conditions, and can exhibit different reactivity and selectivity from method using acid or base. For example, acyl transfer reactions involving sulfur, phosphorous, and fluoride atoms are of interest.

Catalyzed equilibrium reactions have an advantage of facile reaction control by catalysts and low activation energies. In addition, various products can be obtained by simply shifting the equilibria. For example, in an equilibrium reaction between $\mathbf{S_1}/\mathbf{S_2}$ and $\mathbf{P_1}/\mathbf{P_2}$, any $\mathbf{S_1}$, $\mathbf{S_2}$, $\mathbf{P_1}$, or $\mathbf{P_2}$ can be the product, depending on the conditions (Fig. 1(a)). The efficiency in such reactions is affected by the relative thermodynamic stabilities of substrates $\mathbf{S_1}/\mathbf{S_2}$ and products $\mathbf{P_1}/\mathbf{P_2}$. If their stabilities are comparable, an equilibrium state provides a mixture of four compounds, and techniques to shift the equilibrium are required to obtain the desired products in high yields. Le Chatelier's principle may be applied to control equilibrium, and pressure, temperature, or concentration may be varied for this purpose. This method, however, has relatively limited applicability from a synthetic point of view. The use of an excessive substrate can also shift equilibrium, but that is not always convenient. We considered it attractive to control the relative thermodynamic stability using co-substrates and co-products. When an appropriate co-substrate $\mathbf{S_3}$ was used in the $\mathbf{S_1}/\mathbf{S_2}$ and $\mathbf{P_1}/\mathbf{P_2}$ reaction in place of $\mathbf{S_2}$, the equilibrium could be shifted to $\mathbf{P_1}$ with the formation of $\mathbf{P_3}$ provided that the relative thermodynamic stability of the $\mathbf{P_1}/\mathbf{P_3}$ system was higher than that of the $\mathbf{S_1}/\mathbf{S_3}$ system (Fig. 1(b)). An advantage of this method is that various combinations of $\mathbf{S_3}$ and $\mathbf{P_3}$ can be used to optimize the reaction giving $\mathbf{P_1}$. It was considered interesting to apply this methodology to catalyze acyl transfer reactions.

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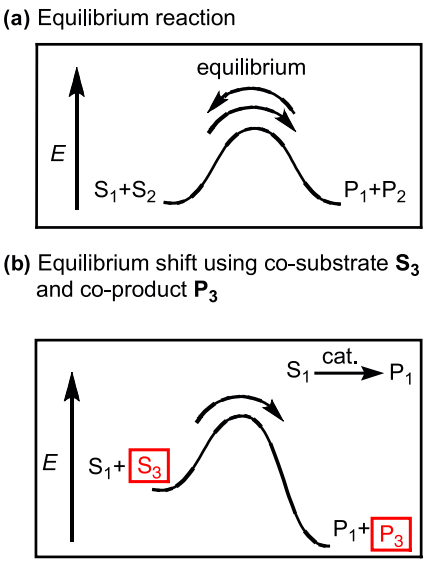
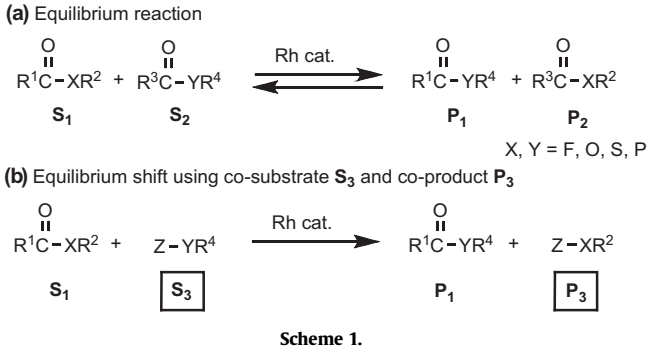


Fig. 1. Equilibrium control by co-substrate and co-product.

During our studies on the transition-metal-catalyzed synthesis of organoheteroatom compounds, we developed several acyl transfer reactions: Rhodium-catalyzed alkylthio exchange reaction of thioesters with disulfide;[2] synthesis of acylphosphine sulfides from acid fluorides and diphosphine disulfides;[3] and conversion of thioesters to acylphosphine sulfides by treatment with diphosphine disulfides.[4] We also found that the rhodium-catalyzed reaction of acid fluorides and thioesters was at equilibrium,[5] and that the equilibrium could be shifted in the presence of co-substrates: thioesters were synthesized from acid fluorides in the presence of triphenylphosphine; acid fluorides were synthesized from thioesters in the presence of hexafluorobenzene. The equilibrium was shifted by the conversion of the co-substrates to the thermodynamically stable co-products. The conversion of triphenylphosphine to triphenylphosphine difluoride promoted the formation of thioesters, and that of hexafluorobenzene to aryl sulfides promoted the formation of acid fluorides. Described in this study is an extension of this methodology to acyl transfer reactions between thioesters, acylphosphine sulfides, aryl esters, and acid fluorides, and each equilibrium (Scheme 1(a)) may be shifted to a desired product by employing an appropriate heteroatom acceptor as a co-substrate (Scheme 1(b)). Equilibrium shift in this paper means the predominant formation of product **P$_1$** based on equilibrium in Scheme 1(a). Acyl transfers catalyzed by transition metal complexes were not known prior to this study, in which all the reactions were catalyzed by rhodium/phosphine complexes. It is also noteworthy that these acyl transfer reactions proceed without using acid or base.

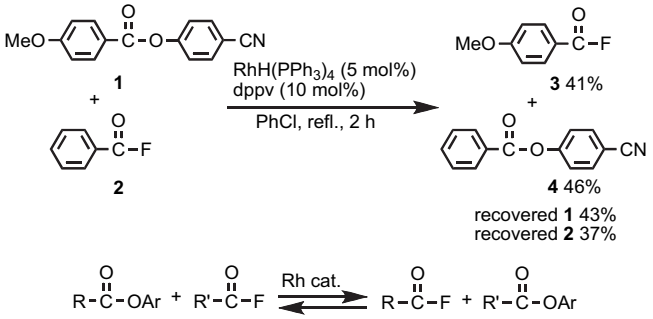


Scheme 1.

2. Results and discussion

2.1. Interconversion of aryl esters and acid fluorides

The acyl transfer reaction between esters and acid fluorides was catalyzed by a rhodium catalyst. When an equimolar mixture of 4-cyanophenyl 4-methoxybenzoate **1** and benzoyl fluoride **2** was treated with RhH(PPh$_3$)$_4$ (5 mol %) and *cis*-bis(diphenylphosphino) ethene (dppv, 10 mol %) in refluxing chlorobenzene for 3 h, a mixture of 4-methoxybenzoyl fluoride **3** (41%) and 4-cyanophenyl benzoate 4 (46%) was obtained with the recovery of **1** (43%) and **2** (37%, ^{1}H NMR yield) (Scheme 2). No reaction occurred in the absence of the rhodium complex.

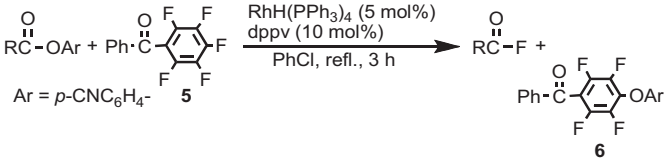


Scheme 2.

The results indicated that the acid fluoride and the aryl ester were at equilibrium. It was expected that acid fluorides could be obtained effectively from aryl esters by developing a technique to shift the equilibrium. Benzoylpentafluorobenzene **5** was an efficient co-substrate for this purpose with the formation of 1-benzoyl-4-(4-cyanophenoxy)-2,3,5,6-tetrafluorobenzene **6** as the co-product.

When **1** and **5** (1 equiv) were reacted in refluxing chlorobenzene for 3 h in the presence of RhH(PPh$_3$)$_4$ (5 mol %) and dppv (10 mol %), **3** and **6** were obtained in 92% and 96% yields, respectively (Table 1, entry 1). No reaction occurred in the absence of the rhodium complex or dppv. The reaction could be applied to several 4-cyanophenyl esters derived from aromatic and aliphatic acids in high yields (entries 2–8). 4-Tolyl 4-methoxybenzoate, however, gave a trace amount of **3**. The substantial effect of the *p*-substituent

Table 1
Synthesis of acid fluorides from aryl esters

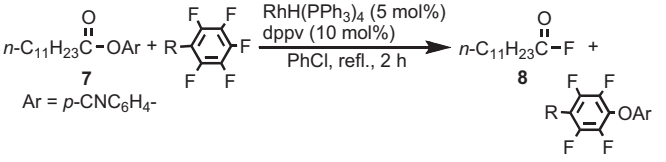


Entry	R	Yield of acid fluoride/%
1	4-MeOC$_6$H$_4$ (**1**)	92
2	3,5-(MeO)$_2$C$_6$H$_3$	93
3	4-ClC$_6$H$_4$	73
4	*n*-C$_{11}$H$_{23}$	94
5	(*n*-Pr)$_2$CH	90
6	4-(*t*-Butyl)cyclohexyl	88
7	1-Adamantyl	92
8	1-Methylcyclohexyl	88

at the phenoxy moiety may be related to the efficiency of the CO–O bond cleavage. Acid fluorides were generally synthesized from carboxylic acids by treatment with reactive fluorinating reagents, such as DAST or cyanuric fluoride.[6,7] This transition-metal-catalyzed synthesis of acid fluorides from aryl esters uses a stable fluorinating reagent.

The ability to transfer fluoride to 4-cyanophenyl dodecanoate **7** was examined using pentafluorobenzenes with different substituents (Table 2). When (diphenylamino)pentafluorobenzene or (butylthio)pentafluorobenzene was reacted, dodecanoyl acid fluoride **8** was obtained in low yields (entries 1 and 2). Inefficiency of hexafluorobenzene was unexpected (entry 4), which might be because of catalyst deactivation. In the case of (4-tolylthio)pentafluorobenzene, the yield increased to 62%, which was accompanied by 1-(4-cyanophenoxy)-4-(4-tolylthio)-2,3,5,6-tetrafluorobenzene in 62% yield (entry 3). Acetylpentafluorobenzene, benzoylpentafluorobenzene **5**, and cyanopentafluorobenzene gave **8** in 66%, 89%, and 95% yields, respectively (entries 5–7). The results indicated a higher fluoride transfer ability of pentafluorobenzene derivatives with an electron-withdrawing group. In these reactions, the co-products derived from the pentafluorobenzenes were 4-cyanophenoxy derivatives. Thus, the rhodium-catalyzed conversion of aryl esters to acid fluorides was conducted using **5** as a co-substrate giving **6** as a co-product. It is also worth noting that this reaction can be regarded as a method to synthesize polyfluorinated diaryl ethers by the substitution of aromatic fluorides. This is an advantage of the equilibrium shift method, in that various compounds may be obtained from a single reaction.

Table 2
Effect of pentafluorobenzenes on the acid fluorides synthesis from aryl ester **7**

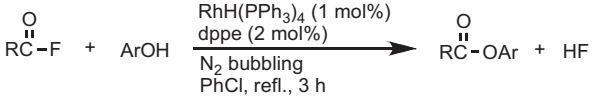


Entry	R	Yield of **8**/%
1	Ph_2N	15
2	n-C_4H_9S	31
3	4-TolS	62
4	F	8
5	MeCO	66
6	PhCO	89, 94[a]
7	CN	95
8	4-Fluoronitrobenzene	42[a]

[a] Reaction time: 3 h.

The reverse reaction, synthesis of aryl esters from acid fluorides, was examined. The reaction of benzoyl fluoride **2** and phenol (1 equiv) in the presence of $RhH(PPh_3)_4$ (1 mol %) and dppe (2 mol %) in refluxing chlorobenzene under nitrogen bubbling for 3 h gave phenyl benzoate in 92% yield (Table 3, entry 1). The rhodium complex and dppe were both essential for the reaction, and no reaction occurred in the absence of either substance. High temperatures were required, and the yield decreased to 43% in refluxing THF. Without nitrogen bubbling, the yield dropped to 31% in refluxing chlorobenzene even with the addition of 2 mol % $RhH(PPh_3)_4$ and 4 mol % dppe. The removal of hydrogen fluoride probably shifted the equilibrium to form aryl esters. The evolution of acid was indicated by pH test paper at the top of the refluxing condenser. The reaction was applied to aromatic and an aliphatic acid fluorides (entry 10). The reaction of protected tyrosine proceeded without racemization (entry 7).

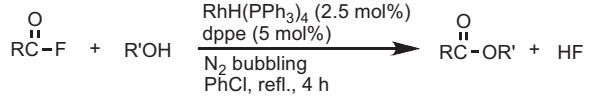
Table 3
Rhodium-catalyzed reaction of acid fluorides and phenols



Entry	R	Ar	Yield of ester/%
1	Ph	Ph	92
2	Ph	2-Tol	96
3	Ph	4-Tol	99
4	Ph	4-$MeOC_6H_4$	99
5	Ph	4-PhC_6H_4	96
6	Ph	4-$NO_2C_6H_4$	89
7	Ph	(*S*)-*p*-$C_6H_4CH_2CH(NHBoc)CO_2Me$	89, 99%ee
8	4-ClC_6H_4	4-$MeOC_6H_4$	89
9	4-$MeOC_6H_4$	4-$MeOC_6H_4$	80
10	n-C_9H_{19}	4-$MeOC_6H_4$	82

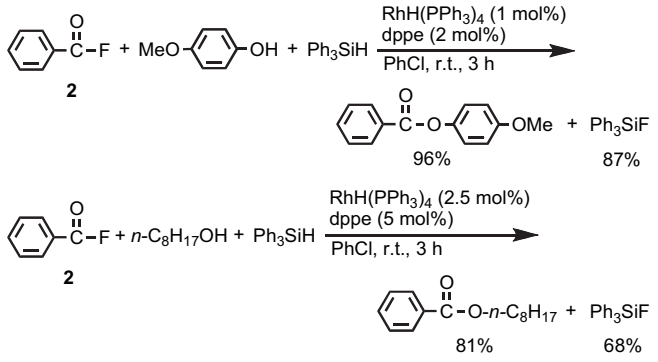
Alcohols efficiently reacted as well as phenols (Table 4). When 1-octanol was reacted with benzoyl fluoride **2** (1 equiv) in the presence of $RhH(PPh_3)_4$ (2.5 mol %) and 1,2-bis(diphenylphosphino)ethane (dppe, 5 mol %), octyl benzoate was obtained in 85% yield (entry 1). No reaction occurred in the absence of the rhodium complex and dppe. High temperature and nitrogen bubbling were again required for this reaction, and the yield of octyl benzoate decreased to 13% when the reaction was run at room temperature and to 15% without nitrogen bubbling. The synthesis of esters from acid fluorides and alcohols in the presence of a stoichiometric amount of base were reported.[6b,8] The rhodium method provides esters in high yields without using base.

Table 4
Rhodium-catalyzed reaction of acid fluorides and alcohols



Entry	R	R′	Yield of ester/%
1	Ph	n-C_8H_{17}	85
2	Ph	$PhCH_2$	87
3	n-$C_{11}H_{23}$	$PhCO_2(CH_2)_2$	62
4	1-Methylcyclohexyl	$PhCO_2(CH_2)_2$	71

The reaction shown in Tables 3 and 4 used the removal of hydrogen fluoride to shift the equilibrium between acid fluoride and aryl esters. The co-substrate method of removing hydrogen fluoride was also examined, and triphenylsilane was found to promote the aryl esterification at considerably lower temperatures. The reaction of benzoyl fluoride **2**, 4-methoxyphenol (1 equiv), and triphenylsilane in the presence of $RhH(PPh_3)_4$ (1 mol %) and dppe (2 mol %) in chlorobenzene at room temperature for 3 h gave 4-methoxyphenyl benzoate (96%) along with triphenylsilyl fluoride (87%) (Scheme 3). Using the silane, the reaction temperature could be markedly reduced from chlorobenzene reflux at 132 °C to room temperature. This equilibrium shift method employed triphenylsilane as a co-substrate giving triphenylsilyl fluoride as a co-product. This reaction is a novel esterification using acid fluorides, which are generally less reactive than acid chlorides.

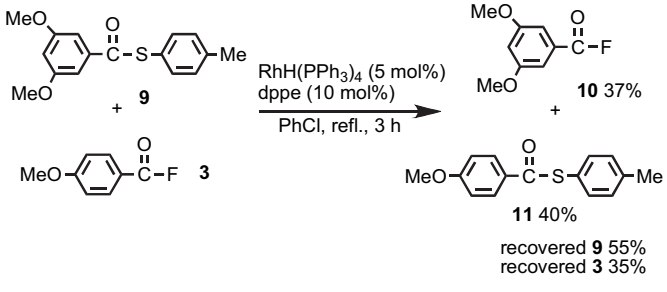


Scheme 3.

Rhodium/phosphine complexes catalyzed the equilibrium acyl transfer reaction between acid fluorides and aryl esters. In the presence of acceptors for phenoxy or fluoride, the equilibrium could be shifted to either product. The formation of acid fluorides from aryl esters was promoted by the addition of benzoylpentafluorobenzene **5** with the formation of aryl ethers; that of aryl esters from acid fluorides was promoted by the addition of triphenylsilane with the formation of triphenylsilyl fluoride or by the removal of hydrogen fluoride.

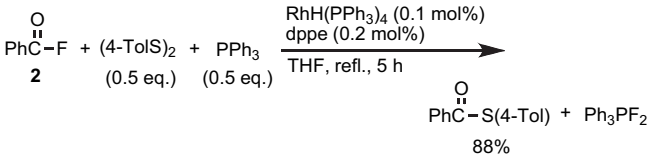
2.2. Interconversion of acid fluorides and thioesters

Our previous work described the equilibrium acyl transfer reaction between acid fluorides and thioesters (Scheme 4).[5] When *S*-(4-tolyl) 3,5-dimethoxybenzothioate **9** and 4-methoxybenzoyl fluoride **3** were treated with $RhH(PPh_3)_4$ (5 mol %) and dppe (10 mol %) in refluxing chlorobenzene for 3 h, a mixture of 3,5-dimethoxybenzoyl fluoride **10** (37%) and *S*-(4-tolyl) 4-methoxybenzothioate **11** (40%) was obtained with the recovery of **9** (55%) and **3** (35%). No reaction occurred in the absence of the rhodium complex.



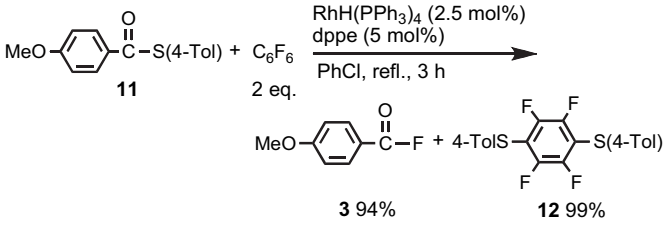
Scheme 4.

The use of triphenylphosphine as a co-substrate promoted the formation of thioesters from acid fluorides (Scheme 5).[5] For example, benzoyl fluoride **2**, di(4-tolyl) disulfide (0.5 equiv), and triphenylphosphine (0.5 equiv) were reacted in refluxing THF for 3 h in the presence of $RhH(PPh_3)_4$ (0.1 mol %) and dppe (0.2 mol %), and *S*-(4-tolyl) benzothioate was obtained in 88% yield. The formation of triphenylphosphine difluoride was confirmed by NMR. The equilibrium was shifted to thioesters by the addition of triphenylphosphine, which trapped fluoride to form triphenylphosphine difluoride.



Scheme 5.

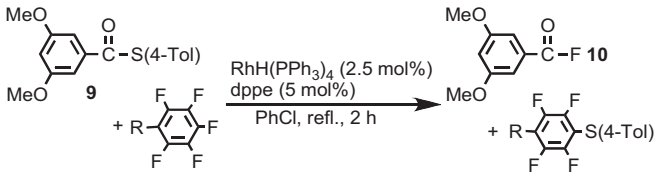
The use of hexafluorobenzene as a co-substrate promoted the formation of acid fluorides from thioesters.[5] The reaction of *S*-(4-tolyl) 4-methoxybenzothioate **11** and hexafluorobenzene (2 equiv) in the presence of $RhH(PPh_3)_4$ (2.5 mol %) and dppe (5 mol %) in refluxing chlorobenzene for 3 h gave 4-methoxybenzoyl fluoride and 1,4-di(4-tolylthio)-2,3,5,6-tetrafluorobenzene **12** in 94% and 99% yields, respectively (Scheme 6).



Scheme 6.

In this work, substituted pentafluorobenzenes were compared in the fluorination of *S*-(4-tolyl) 3,5-dimethoxybenzothioate **9** (Table 5). When (4-tolylthio)pentafluorobenzene was reacted with **9** (1 equiv) in the presence of $RhH(PPh_3)_4$ (2.5 mol %) and dppe (5 mol %), 3,5-dimethoxybenzoyl fluoride **10** was obtained in 86% yield along with 1,4-bis(4-tolylthio)-2,3,5,6-tetrafluorobenzene **12** in 92% yield (entry 3). No reaction occurred in the absence of the rhodium complex and dppe ligand. In the case of hexafluorobenzene, **10** was obtained in 79% yield along with **12** in 79% yield (based on the 4-tolylthio group) (entry 4). The yield of **10** decreased with pentafluorobenzenes possessing either electron donating groups, such as diphenylamino and butylthio groups, or electron-withdrawing groups, such as acetyl, benzoyl, and cyano groups (entries 1–2 and 5–7). In these reactions, **9** was recovered quantitatively. 4-Substituted pentafluorobenzenes were obtained as co-products derived from the 4-tolylthio group, and no other regioisomers were isolated. (4-Tolylthio)pentafluorobenzene **13**

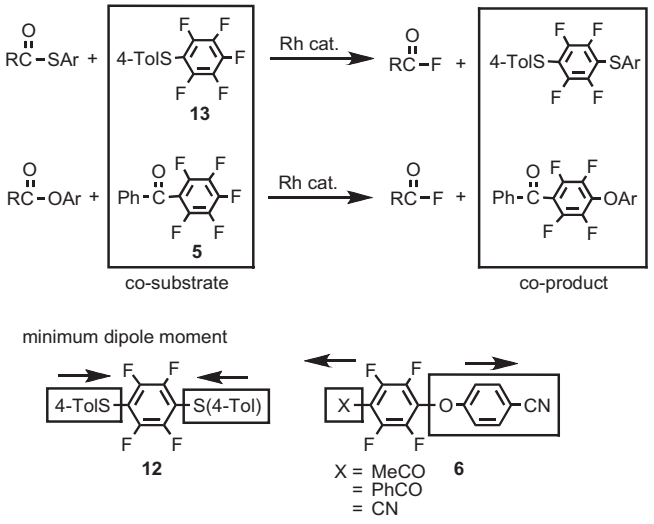
Table 5
Effect of pentafluorobenzenes on acid fluoride synthesis from thioester



Entry	R	Yield of **10**/%
1	Ph_2N	43
2	*n*-C_4H_9S	48
3	4-TolS (**13**)	86
4	F	79
5	MeCO	20
6	PhCO	49
7	CN	32

and hexafluorobenzene, which gave **12** as a co-product, showed a greater *p*-tolylthio acceptor ability.

Different substituted pentafluorobenzenes were used for the formation of acid fluorides from aryl esters and thioesters (Scheme 7). The formation of acid fluorides from thioesters was promoted by the conversion of (4-tolylthio)pentafluorobenzene **13** or hexafluorobenzene to aryl sulfides; the formation of acid fluorides from aryl esters was promoted by the conversion of benzoylpentafluorobenzene **5** to aryl ethers; both reactions provided aryl ethers and sulfides in the *p*-orientation. Previously, we observed that the rhodium-catalyzed arylthiolation reactions of polyfluorobenzenes tended to form 1,4-difluoro derivatives (*p*-difluoride rule).[9] The results obtained in these studies may be explained by the minimization of the dipole moment in the product: in the formation of acid fluorides from thioesters, two 4-tolylthio groups at the 1,4-position in the co-product minimized the dipole moment in the product. In the reactions using hexafluorobenzene, (4-tolylthio)pentafluorobenzene **13** was not detected, which indicated a very rapid second 4-tolylthiolation reaction compared with the first reaction. Because similar 4-tolylthiolation was involved, **13** and hexafluorobenzene showed a similar reactivity. In the formation of acid fluorides from aryl esters, the 4-cyanophenoxy moiety probably balanced well with the benzoyl moiety in **6**. The rhodium complex probably recognized the bias in the π-electron distribution on the aromatic nucleus and reacted with a fluorine atom in the direction to minimize the bias.

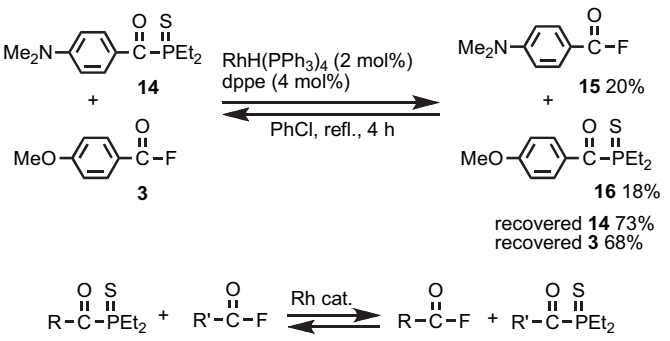


Scheme 7.

$RhH(PPh_3)_4$-dppe catalyzed the equilibrium acyl transfer reaction between acid fluorides and thioesters, and the use of a co-substrate shifted the equilibrium to either product. The reaction of acid fluorides and disulfides in the presence of triphenylphosphine gave thioesters accompanied by triphenylphosphine difluoride. The same complex catalyzed the reaction of aryl thioesters and (4-tolylthio)pentafluorobenzene **13** giving acid fluorides accompanied by 1,4-di(*p*-tolylthio)-2,3,5,6-tetrafluorobenzenes **12**.

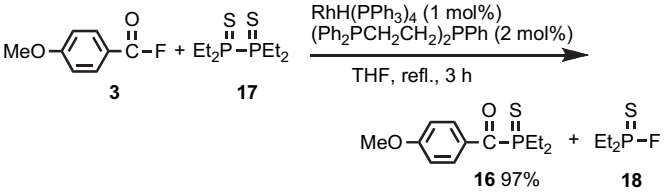
2.3. Interconversion of acylphosphine sulfides and acid fluorides

The equilibrium in rhodium-catalyzed interconversions between acid fluorides and acylphosphine sulfides was examined. When equimolar amounts of diethyl(4-dimethylaminobenzoyl) phosphine sulfide **14** and 4-methoxybenzoyl fluoride **3** were treated with $RhH(PPh_3)_4$ (2 mol %) and dppe (4 mol %) in refluxing chlorobenzene for 4 h, 4-(dimethylamino)benzoyl fluoride **15** (20%) and diethyl(4-methoxybenzoyl)phosphine sulfide **16** (18%) were obtained with recovery of **14** (73%) and **3** (68%) (Scheme 8).



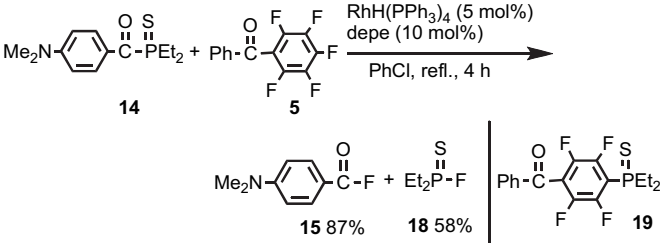
Scheme 8.

We previously reported the synthesis of acylphosphine sulfides from acid fluorides and diphosphine sulfide with concomitant formation of fluorophosphine sulfide.[3] For example, when 4-methoxybenzoyl fluoride **3** and tetraethyldiphosphine disulfide **17** (1 equiv) were treated with $RhH(PPh_3)_4$ (1 mol %) and bis(2-diphenylphosphinoethyl)phenylphosphine (2 mol %) in refluxing THF for 4 h, diethyl(4-methoxybenzoyl)phosphine sulfide **16** was obtained in 97% yield (Scheme 9). The formation of fluorodiethylphosphine sulfide **18** was confirmed by NMR analysis. The equilibrium between acid fluorides and acylphosphine sulfides was shifted to the latter using **17** as a co-substrate with the formation of **18** as a co-product.



Scheme 9.

The reverse reaction, synthesis of acid fluorides from acylphosphine sulfides, was examined using another co-substrate. When **14** and benzoylhexafluorobenzene **5** (2 equiv) were reacted in the presence of $RhH(PPh_3)_4$ (5 mol %) and 1,2-bis(diethylphosphino)ethane (depe, 10 mol %) in refluxing chlorobenzene for 4 h, acid fluoride **15** was obtained in 87% yield along with **18** in 58% yield (Scheme 10). No reaction occurred in the absence of the rhodium complex. In this reaction, the expected co-product, (4-benzoylphenyl)diethylphosphine sulfide **19** was not obtained, and **18** was formed instead. The mechanism of this reaction is now under investigation.



Scheme 10.

We have shown that acid fluorides undergo equilibrium acyl transfer reactions with aryl esters, thioesters, and acylphosphine sulfides under rhodium-catalyzed conditions. In addition, acid fluorides were converted efficiently into acylphosphine sulfides, thioesters, and aryl esters by using appropriate co-substrates (Fig. 2). The formation of acylphosphine sulfides was promoted by the conversion of tetraethylphosphine disulfide **17** as a co-substrate to diethylphosphine fluoride **18** as a co-product; the formation of thioesters was promoted by the conversion of triphenylphosphine as a co-substrate to triphenylphosphine difluoride as a co-product; and the formation of aryl esters was promoted by the conversion of triphenylsilane as a co-substrate to triphenylsilyl fluoride as a co-product or by the removal of hydrogen fluoride. Acid fluorides can be versatile reagents for the acyl transfer reaction between heteroatoms.

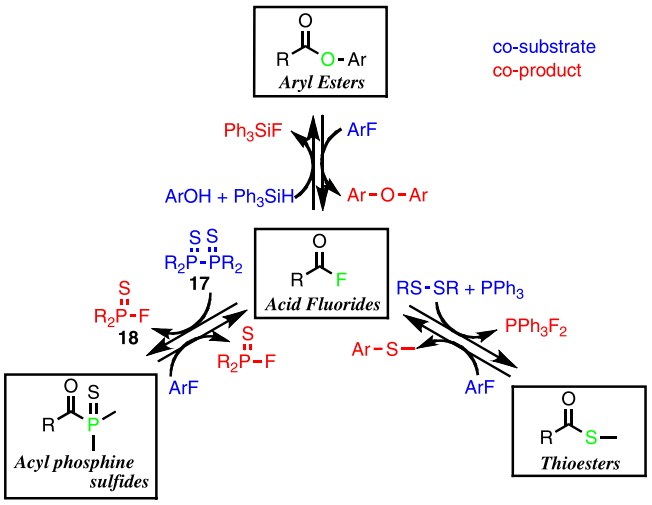
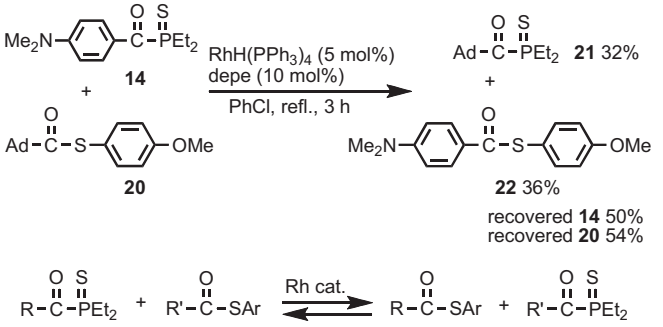


Fig. 2. Equilibrium control between acid fluorides and acylphosphine sulfides, thioesters, or aryl esters using appropriate heteroatom acceptors.

The reverse reactions to form acid fluorides from acylphosphine sulfides, aryl esters, and thioesters were conducted using appropriately substituted pentafluorobenzenes as co-substrates (Fig. 2). The formation of acid fluorides from acylphosphine sulfides was promoted by the conversion of 4-benzoylpentafluorobenzene as a co-substrate to diethylphosphine fluoride as a co-product; the formation of acid fluorides from aryl esters was promoted by the conversion of benzoylpentafluorobenzene as a co-substrate to aryl ethers as a co-product; and the formation of acid fluorides from thioesters was promoted by the conversion of (4-tolylthio)pentafluorobenzene as a co-substrate to aryl sulfides as a co-product. Thus, the equilibrium was shifted between acid fluorides and acylphosphine sulfides, thioesters, or aryl esters by using appropriate heteroatom acceptors.

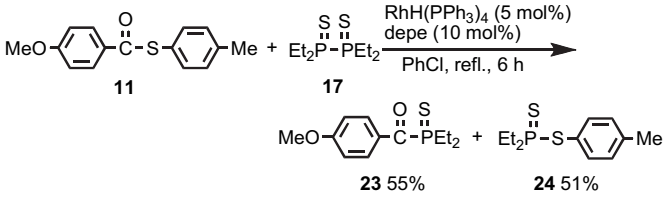
2.4. Interconversion of acylphosphine sulfides and thioesters

At this stage, it was of interest to learn whether the rhodium-catalyzed method could be used for the interconversion between aryl esters, acylphosphine sulfides, and thioesters. It was confirmed that the equilibrium between acylphosphine sulfides and thioesters was catalyzed by the rhodium complex. When diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** and *S*-(4-methoxy) adamantanoate **20** were treated with $RhH(PPh_3)_4$ (5 mol %) and depe (10 mol %) in refluxing chlorobenzene for 3 h, *S*-(4-methoxy) 4-dimethylaminobenzoate **22** (36%) and diethyl(1-adamantanecarbonyl)phosphine sulfide **21** (32%) were obtained with recovery of **14** (50%) and **20** (54%) (Scheme 11).



Scheme 11.

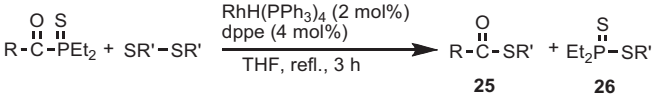
We previously reported the synthesis of acylphosphine sulfides from thioesters.[4] For example, when *S*-(4-tolyl) 4-methoxybenzothioate **11** and tetraethyldiphosphine disulfide **17** (1 equiv) were reacted in refluxing chlorobenzene in the presence of $RhH(PPh_3)_4$ (5 mol %) and depe (10 mol %), (4-methoxybenzoyl) diethylphosphine sulfide **23** was obtained in 55% yield along with 4-tolyl diethyldithiophosphinate **24** in 51% yield (Scheme 12). No reaction occurred in the absence of the rhodium complex. The equilibrium was shifted to acylphosphine sulfide using **17** as a co-substrate with the formation of **24** as a co-product.



Scheme 12.

Then the reverse reaction, synthesis of thioesters from acylphosphine sulfides, was examined. The reaction of diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** and diphenyl disulfide (1 equiv) in the presence of $RhH(PPh_3)_4$ (2 mol %) and dppe (4 mol %) in refluxing THF gave *S*-phenyl 4-(dimethylamino) benzothioate in 99% yield along with phenyl diethyldithiophosphinate in 91% yield (Table 6, entry 1). No reaction occurred in the absence of the rhodium complex and dppe ligand. The reaction could be applied to aromatic and aliphatic acylphosphine sulfides. The equilibrium between acylphosphine sulfides and thioesters was shifted to thioester by converting disulfides as co-substrates to thiophosphinates as co-products.

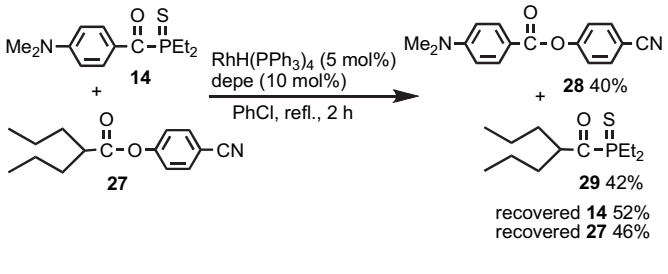
Table 6
Rhodium-catalyzed reaction of acylphosphine sulfides and disulfides



Entry	R	R′	Yield of **25**/%	Yield of **26**/%
1	4-$Me_2NC_6H_4$	Ph	99	91
2	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	93	88
3	4-$Me_2NC_6H_4$	4-Tol	97	90
4	4-$Me_2NC_6H_4$	4-ClC_6H_4	83	78
5	4-$Me_2NC_6H_4$	*n*-C_8H_{17}	99	99
6	*n*-$C_{11}H_{23}$	Ph	90	82

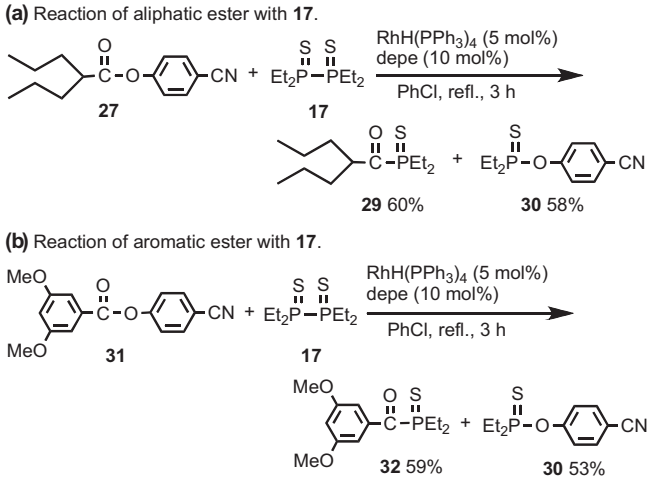
2.5. Interconversion of acylphosphine sulfide and aryl esters

The equilibrium between acylphosphine sulfides and aryl esters was examined. When **14** and 4-cyanophenyl 2-propylpentanoate **27** were reacted in refluxing chlorobenzene for 2 h in the presence of $RhH(PPh_3)_4$ (5 mol %) and depe (10 mol %), 4-cyanophenyl 4-(dimethylamino)benzoate **28** (40%) and diethyl(*2*-propylpentanoyl)phosphine sulfide **29** (42%) were obtained with recovery of **14** (52%) and **27** (46%) (Scheme 13). No reaction occurred in the absence of the rhodium complex.



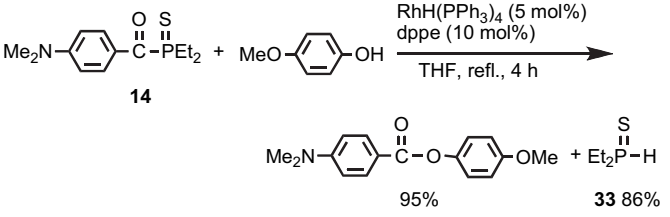
Scheme 13.

Using tetraethyldiphosphine disulfide **17** as a co-substrate, aryl esters were efficiently converted to acylphosphine sulfides. In the presence of $RhH(PPh_3)_4$ (5 mol %) and depe (10 mol %), **27** and **17** (1 equiv) were reacted in refluxing chlorobenzene for 3 h, and diethyl(2-propylpentanoyl)phosphine sulfide **29** was obtained in 60% yield along with 4-cyanophenyl diethylphosphinothioate **30** in 58% yield (Scheme 14(a)). No reaction occurred in the absence of the rhodium complex. The reaction was applied to *O*-(4-cyanophenyl) 3,5-dimethoxybenzoate **31**, and diethyl(3,5-dimethoxybenzoyl)phosphine sulfide **32** was obtained in 59% yield (Scheme 14(b)). The equilibrium was shifted to acylphosphine sulfides using **17** as a co-substrate with the formation of phosphinothioate **30** as a co-product. The results may be consistent with the P—O bond being stronger than the P—P bond. Acylphosphine sulfides can now be synthesized from aryl esters as well as acid fluorides.[3] A few syntheses of acylphosphine sulfides appear in the literature, all of which use the sulfuration reaction of acylphosphines.[10] The rhodium-catalyzed method shown in this study is versatile for the synthesis of acylphosphine sulfides.



Scheme 14.

The reverse reaction, synthesis of aryl esters from acylphosphine sulfides, was examined. In the presence of the $RhH(PPh_3)_4$ (5 mol %) and dppe (10 mol %), **14** was converted to 4-cyanophenyl 4-dimethylaminobenzoate (95%) by reaction with 4-methoxyphenol in refluxing THF for 4 h (Scheme 15). The use of the rhodium complex was essential for this reaction.

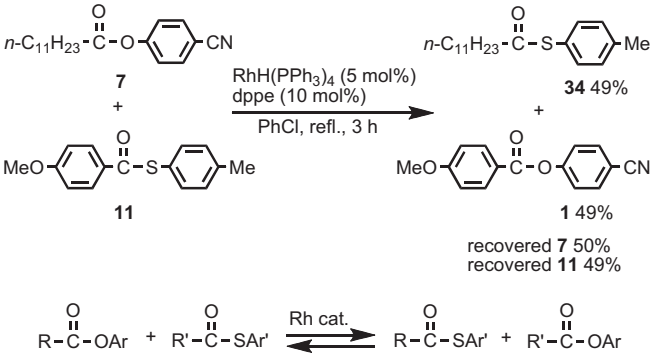


Scheme 15.

The rhodium catalyst equilibrated the acyl transfer reaction between acylphosphine sulfides and aryl esters, and the use of co-substrates shifted the reaction toward the production of either product. The use of diphosphine disulfide promoted the formation of acylphosphine sulfides, and the use of phenol promoted that of aryl esters.

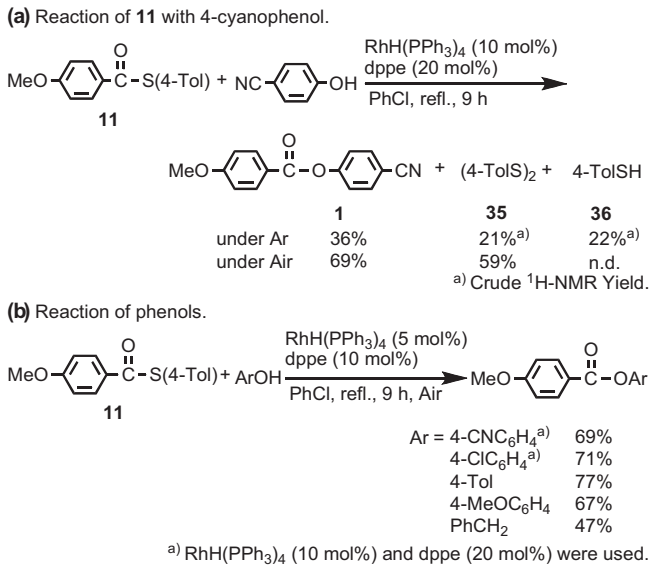
2.6. Interconversion of aryl esters and thioesters

The rhodium-catalyzed equilibrium between aryl esters and thioesters was examined. When 4-cyanophenyl dodecanoate **7** and *S*-(4-tolyl) 4-methoxybenzoate **11** were reacted in refluxing chlorobenzene in the presence of $RhH(PPh_3)_4$ (5 mol %) and depe (10 mol %), *S*-(4-tolyl) dodecanthioate **34** (49%) and 4-cyanophenyl 4-methoxybenzoate **1** (49%) were obtained with recovery of **7** (50%) and **11** (49%) (Scheme 16).



Scheme 16.

The transesterification of thioesters and alcohols has been studied in macrolactonation using acid or base promoters.[11] We describe herein the rhodium-catalyzed conversion of thioesters to aryl esters without using acid or base. *S*-(4-Tolyl) 4-methoxybenzoate **11** and 4-cyanophenol (1 equiv) were reacted in the presence of $RhH(PPh_3)_4$ (10 mol %) and dppe (20 mol %) under an air atmosphere, and 4-cyanophenyl 4-methoxybenzoate **1** was obtained in 69% yields along with di(4-tolyl) disulfide **35** in 59% yield (Scheme 17(a)). 4-Toluenethiol **36** was not detected in this reaction. Thiol **36** could be oxidized to **35** under rhodium catalysis conditions,[12] which might have shifted the equilibrium to aryl esters by removing **36** from the system. In accordance with this, when the reaction was conducted under an argon atmosphere, yield of **1** decreased to 36% and thiol **36** and disulfide **35** were obtained in 21% and 22% yields (^1H NMR), respectively. No reaction occurred in the absence of the rhodium complex. In the case of 4-chlorophenol, 4-chlorophenyl 4-methoxybenzoate was obtained in 71% yield

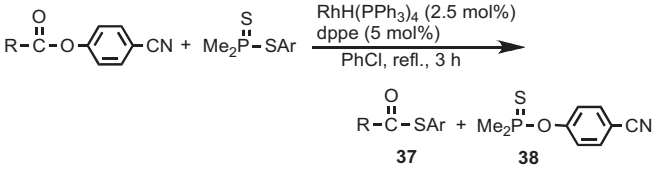


Scheme 17.

(Scheme 17(b)). 4-Cresol and 4-methoxyphenol also reacted in the presence of $RhH(PPh_3)_4$ (5 mol %) and dppe (10 mol %). Aryl esters were formed efficiently from thioesters and phenols.

The reverse reaction, synthesis of thioesters from aryl esters, was examined. When 4-cyanophenyl 3,5-dimethoxybenzoate was reacted with phenyl dimethyldithiophosphinate (1 equiv) in the presence of $RhH(PPh_3)_4$ (2.5 mol %) and dppe (5 mol %) in refluxing cholorobenzene for 3 h, *S*-phenyl 3,5-dimethoxybenzoate was obtained in 89% yield along with *O*-(4-cyanophenyl) dimethylphosphinothioate **38** in 86% yield (Table 7, entry 1). The equilibrium between aryl esters and thioesters was shifted to thioesters using dithiophosphinate as a co-substrate with the formation of phosphinothioate as a co-product. The observation may be consistent with the energy of the P–O bond being higher than that of the P–S bond.

Table 7
Rhodium-catalyzed reaction of aryl esters and dithiophosphinate



Entry	R	Ar	Yield of **37**/%	Yield of **38**/%
1	3,5-$(MeO)_2C_6H_4$	Ph	89	86
2	3,5-$(MeO)_2C_6H_4$	4-Tol	87	83
3	4-$MeOC_6H_4$	4-Tol	83	82
4	$(n\text{-}C_3H_7)_2CH$	4-Tol	84	83

A rhodium complex catalyzed the equilibrium acyl transfer reaction between aryl esters and thioesters. In the presence of phenol and dithiophosphinate as co-substrates, the equilibrium could be shifted to aryl esters and thioesters, respectively.

Rhodium catalysts equilibrated acyl transfer reactions between acid fluorides, acylphosphine sulfides, thioesters, and aryl esters, and the use of appropriate heteroatom acceptors as co-substrates shifted the equilibrium to desired products (Fig. 3). Aryl esters were synthesized from acylphosphine sulfides, thioesters, and acid fluorides by reaction with phenols (reactions **B**, **F**, and **D**), in which the formation of diethylphosphine sulfide, disulfides, and triphenylsilyl fluoride, or removal of hydrogen fluoride, respectively, shifted the equilibrium to aryl ethers. Aryl esters were converted to these compounds using oxygen acceptors as co-substrates. Acylphosphine sulfides were formed using the conversion of tetraethylphosphine disulfide to *O*-aryl diethylphosphinothioates (reaction **A**); thioesters, by the conversion of *S*-aryl diethylphosphinothioate to *O*-aryl diethylphosphinothioates (reaction **E**); and acid fluorides, by the conversion of benzoylpentafluorobenzene to aryl ethers (reaction **C**). The synthesis of acid fluorides from acylphosphine sulfides or thioesters was conducted using substituted pentafluorobenzenes as co-substrates. Acid fluorides were formed from acylphosphine sulfides using the conversion of 4-benzoylpentafluorobenzene to diethylphosphine fluoride (reaction **H**); acid fluorides were formed from thioesters using the conversion of 4-tolylpentafluorobenzene to aryl sulfides (reaction **J**). The reverse conversions of acid fluorides into acylphosphine sulfides and thioesters were conducted in the presence of fluoride acceptors as co-substrates. Acylphosphine sulfides were formed using the conversion of tetraethyldiphosphine disulfide to diethylphosphine fluoride (reaction **G**); thioesters were formed using the conversion of triphenylphosphine to triphenylphosphine difluoride (reaction **I**). The equilibrium reaction between acylphosphine sulfides and thioesters was shifted using disulfides for the formation of thioesters (reaction **K**), and tetraethyldiphosphine disulfides for the formation of acylphosphine sulfides (reaction **L**). These are novel rhodium-catalyzed acyl transfer reactions via equilibrium shifts using appropriate co-substrates.

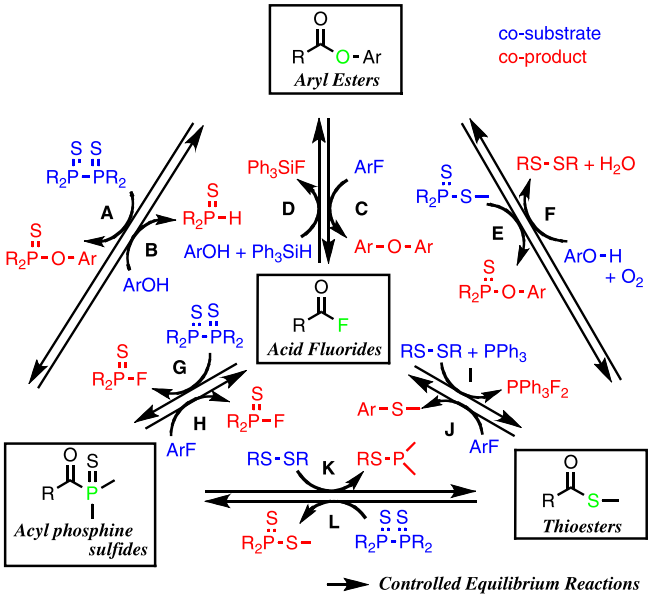


Fig. 3. Equilibrium control of rhodium-catalyzed acyl transfer reactions.

2.7. Mechanistic considerations

A possible mechanism of these acyl transfer reactions is as follows (Fig. 4). Oxidative addition of an acyl compound to a low valent rhodium complex provides a C(O)–Rh–XR intermediate, which undergoes an exchange reaction with another acyl compound C′(O)–YR′ forming a new C(O)–Rh–YR′ complex. Then, the

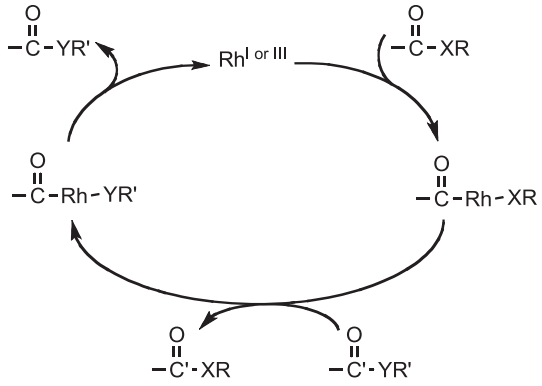
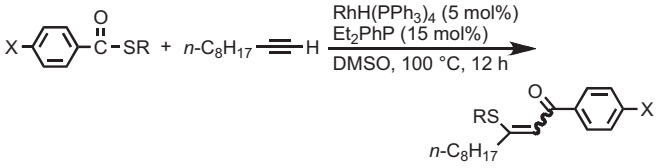


Fig. 4. Possible mechanism of acyl transfer reaction.

product is liberated by reductive elimination with the regeneration of the rhodium catalyst.

The carbothiolation reaction[13] of thioesters and 1-alkynes proceeded under rhodium catalysis, which is consistent with the formation of RCO–Rh–XR′ complex under the stated conditions. When an equimolar mixture of *S*-butyl 4-cyanobenzothioate and 1-decyne in DMSO was heated at 100 °C for 12 h in the presence of $RhH(PPh_3)_4$ (10 mol %) and Et_2PhP (30 mol %), (*E*)-3-butylthio-1-(4-cyanophenyl)-2-undecen-1-one **39** was obtained in 57% yield (*E*/*Z*=77/23) as a mixture of stereoisomers (Table 8, entry 2). No reaction occurred in the absence of the rhodium complex and Et_2PhP ligand. The solvent was not limited to DMSO, and using THF solvent **39** was obtained in 20% yield (*E*/*Z*=60/40) in the presence of $RhH(PPh_3)_4$ (5 mol %) and Et_2PhP (10 mol %) (entry 3). When the *p*-substituent was changed to chloride or hydrogen, the yield of the carbothiolated products decreased (entries 4 and 5). The reaction of *S*-alkyl thioesters also gave products in moderate yields. An aliphatic thioester and *S*-aryl ester gave the product in low yields. It is likely that the rhodium complex oxidatively added to the CO–S bond of thioesters to form CO–Rh–S species, which underwent carbothiolation with an alkyne. A metal-catalyzed carbothiolation reaction of aryl thioesters and 1-alkynes was reported by Kambe.[14] Alkyl thioesters, however, were less reactive, and trifluoroacetyl thioesters were used instead. The rhodium-catalyzed method exhibited different reactivity. In many of the acyl transfer reactions described, the oxidative addition of the rhodium complex to the –CO–X compounds probably occurred.

Table 8
Carbothiolation reaction of thioesters and a 1-alkyne



Entry	R	X	Yield/%
1	n-C_4H_9	CN (**39**)	49 (*E*/*Z*=73/27)
2	n-C_4H_9	CN (**39**)	57 (*E*/*Z*=77/23)[a]
3	n-C_4H_9	CN (**39**)	20 (*E*/*Z*=60/40)[b]
4	n-C_4H_9	Cl	37 (*E*/*Z*=82/18)[a]
5	n-C_4H_9	H	28 (*E*/*Z*=79/21)[a]
6	Me	CN	55 (*E*/*Z*=69/31)[a]
7	$PhCH_2$	CN	58 (*E*/*Z*=72/28)[a]
8	4-Tol	CN	3 (*Z* major)
9[c]	n-C_8H_{17}		16 (*E* only)

[a] $RhH(PPh_3)_4$ (10 mol %) and Et_2PhP (30 mol %) were used.
[b] THF refl.
[c] *S*-Octyl octanoate was used.

3. Conclusion

In summary, the rhodium-catalyzed method can be used for acyl transfer equilibrium between acid fluorides, acylphosphine sulfides, thioesters, and aryl esters. Appropriate co-substrates changed the relative thermodynamic stabilities of substrates and products, and efficiently provided desired products. This method using the combination of a transition metal catalyst and heteroatom acceptors can be generally used to shift equilibria.

4. Experimental section

4.1. General

^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on a Varian Mercury (400 MHz) or a JEOL JNM-ECA 600 (600 MHz). Tetramethylsilane (δ 0.00) was used as internal standard for ^1H NMR. ^{13}C NMR was referenced to the residual solvent ($CDCl_3$, δ 77.0). Trifluoroacetic acid (δ −79.0) and triphenylphosphine (δ −6.0) were used as external standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotometer. Melting points were determined with a Yanaco micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. KANTO CHEMICAL Co., Inc. silica gel 60 (40–50 μm) was employed for flash column chromatography.

4.2. Equilibrium reaction of aryl ester and acid fluoride (Scheme 2)

In a two-necked flask equipped with a reflux condenser were placed 4-cyanophenyl 4-methoxybenzoate **1** (0.25 mmol, 63.3 mg), benzoyl fluoride **2** (0.25 mmol, 27 μL), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and *cis*-1,2-bis(diphenylphosphino)ethene (10 mol %, 9.9 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-methoxybenzoyl fluoride **3** (15.7 mg, 41%) and 4-cyanophenyl benzoate **4** (25.7 mg, 46%) as well as recovered **1** (27.3 mg, 43%) and **2** (37% by ^1H NMR yield). Compound **3**: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 3.90 (3H, s), 6.99 (2H, dd, J=8.8, 1.2 Hz), 8.00 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 114.4, 116.8 (d, J=61.4 Hz), 133.8 (d, J=3.8 Hz), 157.3 (d, J=337.2 Hz), 165.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ 13.0. IR (neat) ν 1799, 1607, 1513, 1254, 1171, 1021, 1001 cm^{-1}. MS (EI) m/z 154 (M^+, 100%), 126 (M^+–CO, 30%). HRMS calcd for $C_8H_7O_2F$: 154.0430. Found: 154.0412. Compound **4**: colorless solid. Mp 91.5–92.5 °C (hexane). Lit.[15] 91.0–91.5 °C (benzene). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, d, J=8.8 Hz), 7.54 (2H, t, J=7.6 Hz), 7.68 (1H, t, J=7.6 Hz), 7.75 (2H, d, J=8.8 Hz), 8.20 (2H, d, J=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.8, 118.2, 122.9, 128.6, 128.7, 130.2, 133.7, 134.1, 154.2, 164.3. IR (KBr) ν 3049, 2229, 1735, 1502, 1269, 1217, 1065 cm^{-1}. MS (EI) m/z 223 (M^+, 22%), 105 (M^+–C_7H_4NO, 100%). HRMS calcd for $C_{14}H_9O_2N$: 223.0633. Found: 223.0632.

4.3. Typical procedures for the synthesis of acid fluoride, synthesis of *p*-methoxybenzoyl fluoride 3 (Table 1)

In a two-necked flask equipped with a reflux condenser were placed **1** (0.25 mmol, 63.3 mg), benzoylpentafluorobenzene **5** (0.25 mmol, 68 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and *cis*-1,2-bis(diphenylphosphino)ethene (10 mol %, 9.9 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column

chromatography on silica gel giving 4-methoxybenzoyl fluoride **3** (35.3 mg, 92%) and 1-benzoyl-4-(4-cyanophenoxy)-2,3,5,6-tetrafluorobenzene **6** (88.8 mg, 96%). Compound **6**: colorless solid. Mp 100.5–101.5 °C (hexane/diethyl ether=2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (2H, d, J=8.8 Hz), 7.56 (2H, t, J=8.0 Hz), 7.70 (2H, d, J=8.8 Hz), 7.71 (1H, t, J=8.0 Hz), 7.90 (2H, d, J=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.9, 115.8 (t, J=20.8 Hz), 116.3, 118.1, 129.1, 129.7, 133.7 (t, J=12.7 Hz), 134.4, 135.1, 135.8, 141.2 (dm, J=253.0 Hz), 144.0 (dddd, J=252.0, 12.7, 8.2, 4.5 Hz), 159.4, 185.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ −151.7 (2F, dd, J=21.4, 8.3 Hz), −139.4 (2F, dd, J=21.4, 8.3 Hz). IR (KBr) ν 3076, 2229, 1682, 1493, 1236 cm^{-1}. MS (EI) m/z 371 (M^+, 100%), 105 ($M^+-C_{13}H_4F_4NO$, 65%). HRMS calcd for $C_{20}H_9O_2F_4N$: 371.0569. Found: 371.0565.

4.4. Synthesis of acid fluoride from *p*-cyanophenyl dodecanoate 7 and benzoylpentafluorobenzene 5 (Table 2)

In a two-necked flask equipped with a reflux condenser were placed **7** (0.25 mmol, 75.3 mg), **5** (0.25 mmol, 68.0 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and *cis*-1,2-bis(diphenylphosphino) ethene (10 mol %, 9.9 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving dodecanoyl fluoride **8** (44.8 mg, 89%) and **6** (78.0 mg, 84%). Compound **8**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J=7.6 Hz), 1.26–1.38 (16H, m), 1.68 (2H, quint, J=7.2 Hz), 2.50 (2H, t, J=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.9 (d, J=1.5 Hz), 28.7, 29.1, 29.2, 29.3, 29.5, 29.6, 31.9, 32.1 (d, J=48.5 Hz), 163.6 (d, J=358.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ 42.4. IR (neat) ν 2926, 2856, 1844, 1088 cm^{-1}. MS (EI) m/z 202 (M^+, 0.5%), 100 ($M^+-C_7H_{16}$, 100%). HRMS calcd for $C_{12}H_{23}FO$: 202.3088. Found: 202.1733.

4.5. Typical procedures for the synthesis of esters, synthesis of phenyl benzoate (Tables 3 and 4)

In a two-necked flask equipped with a reflux condenser were placed **2** (0.5 mmol, 54 μL), phenol (0.5 mmol, 47.0 mg), $RhH(PPh_3)_4$ (1 mol %, 5.8 mg), and 1,2-bis(diphenylphosphino)ethane (2 mol %, 4.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux with nitrogen bubbling for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving phenyl benzoate (45.4 mg, 92%) as colorless solid. Mp 69.5–70.0 °C (ethanol). Lit.[15] 69–70 °C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (2H, d, J=8.0 Hz), 7.27 (1H, t, J=8.0 Hz), 7.43 (2H, t, J=8.0 Hz), 7.51 (2H, t, J=8.0 Hz), 7.64 (1H, t, J=8.0 Hz), 8.21 (2H, d, J=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.7, 125.9, 128.5, 129.5, 129.6, 130.1, 133.6, 150.9, 165.2. IR (KBr) ν 3058, 1731, 1266, 1199, 1064 cm^{-1}. MS (EI) m/z 198 (M^+, 20%), 105 ($M^+-C_6H_5O$, 100%). HRMS calcd for $C_{13}H_{10}O_2$: 198.0681. Found: 198.0677.

4.6. The synthesis of esters from benzoyl fluoride 2 and 4-methoxyphenol using triphenylsilane (Scheme 3)

In a two-necked flask equipped with a reflux condenser were placed **2** (0.5 mmol, 54 μL), 4-methoxyphenol (0.5 mmol, 62 mg), triphenylsilane (0.5 mmol, 130 mg), $RhH(PPh_3)_4$ (1 mol %, 5.8 mg), and 1,2-bis(diphenylphosphino)ethane (2 mol %, 4.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-methoxyphenyl benzoate (109.1 mg, 96%) and triphenylsilyl fluoride (121.1 mg, 87%). 4-*Methoxyphenyl benzoate* colorless solid. Mp 89.0–90.0 °C (petroleum ether). Lit.[15] 87–88 °C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (3H, s), 6.94 (2H, tt, J=1.2, 9.2 Hz), 7.13 (2H, dd, J=1.2, 9.2 Hz), 7.51 (2H, tt, J=1.6, 8.0 Hz), 7.63 (1H, tt, J=1.6, 7.2 Hz), 8.20 (2H, dt, J=8.8, 5.2 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 114.5, 122.4, 128.5, 129.6, 130.1, 133.5, 144.4, 157.3, 165.5. IR (KBr) ν 2935, 1729, 1594, 1508, 1454, 1195, 1029, 869, 754, 713 cm^{-1}. MS (EI) m/z 228 (M^+, 43%), 105 ($M^+-C_7H_7O_2$, 100%). HRMS calcd for $C_{14}H_{12}O_3$: 228.0396. Found: 228.0768. *Triphenylsilyl fluoride* colorless solid. Mp 64.0–65.0 °C (hexane). Lit.[16] 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (6H, t, J=7.6 Hz), 7.48 (3H, t, J=7.6 Hz), 7.65 (6H, dd, J=7.6, 1.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.1, 130.8, 132.5 (d, J=16.7 Hz), 135.0 (d, J=2.3 Hz). IR (KBr) ν 3051, 3025, 1429, 1124, 841 cm^{-1}. MS (EI) m/z 278 (M^+, 100%), 201 ($M^+-C_6H_5$, 41%). HRMS calcd for $C_{18}H_{15}SiF$: 278.0948. Found: 278.0927.

4.7. Equilibrium reaction of thioester and acid fluoride (Scheme 4)

In a two-necked flask equipped with a reflux condenser were placed *S*-(4-tolyl) 3,5-dimethoxybenzothioate **9** (0.25 mmol, 72 mg), 4-methoxybenzoyl fluoride **3** (0.25 mmol, 38.5 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and 1,2-bis(diphenylphosphino) ethane (10 mol %, 10.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 3,5-dimethoxybenzoyl fluoride **10** (17.2 mg, 37%) and *S*-(4-tolyl) 4-methoxybenzothioate **11** (25.8 mg, 40%) as well as recovered **9** (39.7 mg, 55%) and **3** (13.6 mg, 35%). Compound **10**: colorless solid. Mp 57.5–58.0 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (6H, *s*), 6.76 (1H, t, J=2.4 Hz), 7.17 (2H, d, J=2.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 108.0, 108.8 (d, J=3.8 Hz), 126.5 (d, J=60.6 Hz), 157.2 (d, J=341.8 Hz), 161.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ 15.6. IR (neat) ν 3099, 3066, 2947, 2844, 1805, 1606, 1593, 1468, 1429, 1356, 1306, 1209, 1200, 1186, 1161, 1065, 1022, 930, 876, 750, 688 cm^{-1}. MS (EI) m/z 184 (M^+, 100%), 154 (M^+-CH_2O, 13%). HRMS calcd for $C_9H_9O_3F$: 184.0536. Found: 184.0540. Compound **11**: colorless crystals. Mp 64.5–65.5 °C (hexane/diethyl ether=5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (3H, s), δ 3.89 (3H, *s*), 6.96 (2H, d, J=8.8 Hz), 7.26 (2H, d, J=8.4 Hz), 7.39 (2H, d, J=8.4 Hz), 8.01 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 55.5, 113.8, 124.0, 129.4, 129.6, 130.0, 135.1, 139.6, 163.9, 189.0. IR (KBr) ν 1664, 1599, 1506, 1257, 1210, 1169 cm^{-1}. MS (EI) m/z 258 (M^+, 2%), 135 ($M^+-MeC_6H_4S$, 100%). HRMS calcd for $C_{15}H_{14}O_2S$: 258.0715. Found: 258.0699.

4.8. Synthesis of *S*-(4-tolyl) benzothioate (Scheme 5)

In a two-necked flask equipped with a reflux condenser were placed benzoyl fluoride **2** (620 mg, 5.0 mmol), bis(4-tolyl) disulfide (615 mg, 2.5 mmol), $RhH(PPh_3)_4$ (5.8 mg, 0.1 mol %), 1,2-bis(diphenylphosphino)ethane (4.0 mg, 0.2 mol %), and triphenylphosphine (655 mg, 50 mol %) in tetrahydrofuran (2 mL) under an argon atmosphere, and the solution was stirred under reflux for 5 h. The solvent was removed under reduced pressure, and $RhH(PPh_3)_4$ was removed by short flash column chromatography on silica gel. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving *S*-(4-tolyl) benzothioate (1.006 g, 88%). Colorless solid. Mp 76–78 °C (hexane). Lit.[17] 73–73.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (3H, s), 7.27 (2H, d, J=7.2 Hz), 7.40 (2H, d, J=6.8 Hz), 7.48 (2H, t, J=7.2 Hz), 7.60 (1H, t, J=8.0 Hz), 8.03 (2H, d, J=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 123.7, 127.5, 128.7, 130.1, 133.6, 135.0, 136.7, 139.8, 190.6. IR (KBr) ν 1669, 1205, 899 cm^{-1}. MS (EI) m/z 228 (M^+, 12%), 105 ($M^+-C_7H_7S$, 100%). HRMS calcd for $C_{14}H_{12}OS$: 228.0609. Found: 228.0589.

4.9. Synthesis of 4-methoxybenzoyl fluoride using hexafluorobenzene (Scheme 6)

In a two-necked flask equipped with a reflux condenser were placed *S*-(4-tolyl) 4-methoxybenzothioate **11** (0.25 mmol, 64.5 mg), hexafluorobenzene (0.5 mmol, 57.7 μL), $RhH(PPh_3)_4$ (2.5 mol %, 7.2 mg), and 1,2-bis(diphenylphosphino)ethane (5 mol %, 5.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-methoxybenzoyl fluoride **3** (36.3 mg, 94%) and 2,3,5,6-tetrafluoro-1,4-bis(4-tolylthio)benzene **12** (97.3 mg, 99%). Compound **12**: mp 123–124 °C (ethyl acetate). Lit.[18] 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (6H, s), 7.11 (4H, d, J=8.4 Hz), 7.32 (4H, d, J=8.0 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.1, 115.7 (m), 128.9, 130.1, 131.8, 138.5, 146.8 (m). ^{19}F NMR (565 MHz, $CDCl_3$) δ 136.02. IR (KBr) ν 2920, 1491, 1462, 1397, 1243, 957, 810, 640, 620, 512, 488 cm^{-1}. MS (EI) m/z 394 (M^+, 29%), 271 ($M^+-C_7H_7S$, 14%). HRMS calcd for $C_{20}H_{14}F_4S_2$: 394.0473. Found: 394.0487.

4.10. Synthesis of 3,5-dimethoxybenzoyl fluoride 10 using substituted pentafluorobenzene, reaction of 4-tolylthiopentafluorobenzene (Table 5)

In a two-necked flask equipped with a reflux condenser were placed *S*-(4-tolyl) 3,5-dimethoxybenzothioate **9** (0.25 mmol, 72 mg), (4-tolylthio)pentafluorobenzene **13** (0.25 mmol, 72.5 mg), $RhH(PPh_3)_4$ (2.5 mol %, 7.2 mg), and 1,2-bis(diphenylphosphino) ethane (5 mol %, 5.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 3,5-dimethoxybenzoyl fluoride **10** (39.5 mg, 86%) and 1,4-bis(4-tolylthio)-2,3,5,6-tetrafluoro benzene **12** (94.3 mg, 96%) as colorless solid.

4.11. Equilibrium reaction of acylphosphine sulfide and acid fluoride (Scheme 8)

In a two-necked flask equipped with a reflux condenser were placed diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** (0.5 mmol, 134.5 mg), 4-methoxybenzoyl fluoride **3** (0.5 mmol, 77 mg), $RhH(PPh_3)_4$ (2 mol %, 11.5 mg), and 1,2-bis(diphenylphosphino)ethane (4 mol %, 8.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-dimethylaminobenzoyl fluoride **15** (16.6 mg, 20%) and diethyl(4-methoxybenzoyl)phosphine sulfide **16** (23 mg, 18%) as well as recovered **14** (97.8 mg, 73%) and **3** (52.4 mg, 68%). Compound **15**: colorless solid. Mp 126.5–127.0 °C (hexane/AcOEt=2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (6H, s), 6.66 (2H, d, J=8.0 Hz), 7.87 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 110.3, 110.9 (d, J=1.5 Hz), 133.4 (d, J=3.7 Hz), 154.5, 158.2 (d, J=332.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ 9.2. IR (neat) ν 2921, 2832,2683, 1778, 1612, 1540,1488,1447, 1381, 1321, 1273, 1235, 1185, 1069, 1015, 982, 943, 821, 779, 754, 693, 585, 518, 499 cm^{-1}. MS (EI) m/z 167 (M^+, 96), 166 (M^+-H, 100). HRMS calcd for $C_9H_{10}OFN$: 167.0746. Found: 167.0732. Compound **16**: pale yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (6H, dt, J=18.8, 8.0 Hz), 1.99–2.32 (4H, m), 3.90 (3H, s), 6.96 (2H, d, J=8.0 Hz), 8.59 (2H, d, J=8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.4 (d, J=4.5 Hz), 23.7 (d, J=48.5 Hz), 55.5, 113.9, 129.0 (d, J=46.9 Hz), 132.7, 164.7, 198.5 (d, J=50.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.4. IR (neat) ν 3071, 3005, 2972, 2936, 2909, 2877, 2840, 1638, 1596, 1573, 1508, 1457, 1422, 1312, 1267, 1234, 1170, 1028, 920, 841, 769, 749, 581 cm^{-1}. MS (EI) m/z 256 (M^+, 6%), 135 ($M^+-MeOC_6H_4CO$, 100%). HRMS calcd for $C_{12}H_{17}O_2PS$: 256.0687. Found: 256.0705.

4.12. The reaction of 4-methoxybenzoyl fluorides 3 and tetraethyldiphosphine disulfide 17 (Scheme 9)

In a two-necked flask equipped with a reflux condenser were placed 4-methoxybenzoyl fluoride **3** (77.1 mg, 0.5 mmol), tetraethyldiphosphine disulfide **17** (121.2 mg, 0.5 mmol), $RhH(PPh_3)_4$ (5.8 mg, 1.0 mol %), and bis(2-diphenylphosphinoethyl)phenylphosphine (5.3 mg, 2.0 mol %) in tetrahydrofuran (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 4 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel within 10–15 min giving the diethyl(4-methoxybenzoyl)phosphine sulfide **16** (124.6 mg, 97%). *Diethylfluorophosphine sulfide* **18**[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (6H, dt, J=20.8, 7.6 Hz), 2.01–2.19 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.3 (d, J=4.6 Hz), 27.1 (dd, J=67.4, 15.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ −96.3 (d, J=1017.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.4 (d, J=1012.7 Hz). IR (neat) ν 2979, 2943, 2912, 2883, 1801, 1606, 1458, 1404, 1255, 1171, 1038, 1018, 820, 783 cm^{-1}. MS (EI) m/z 140 (M^+, 100%), 112 ($M^+-C_2H_4$, 97%). HRMS calcd for $C_4H_{10}FPS$: 140.0225. Found: 140.0211.

4.13. The reaction of diethyl{4-(dimethylamino)benzoyl} phosphine sulfide 14 and benzoylpentafluorobenzene 5 (Scheme 10)

In a two-necked flask equipped with a reflux condenser were placed **14** (0.25 mmol, 67.3 mg), **5** (0.5 mmol, 136 mg), $RhH(PPh_3)_4$ (5.0 mol %, 14.4 mg), and 1,2-bis(diethylphosphino)ethane (10.0 mol %, 5.2 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-(dimethylamino)benzoyl fluoride **15** (36.3 mg, 87%) and diethylfluorophosphine sulfide **18** (20.3 mg, 58%).

4.14. Equilibrium reaction of acylphosphine sulfide and thioester (Scheme 11)

In a two-necked flask equipped with a reflux condenser were placed diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** (0.25 mmol, 67.3 mg), *S*-(4-methoxyphenyl) adamantanthioate **20** (0.25 mmol, 75.5 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and 1,2-bis(diethylphosphino)ethane (10 mol %, 4.9 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 1-(adamantanecarbonyl)diethylphosphine sulfide **21** (22.6 mg, 32%) and *S*-(4-methoxyphenyl) 4-dimethylaminobenzothioate **22** (25.6 mg, 36%) as well as recovered **14** (33.5 mg, 50%) and **20** (40.7 mg, 54%). Compound **21**: colorless solid. Mp 83.0–83.5 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (6H, dt, J=19.6, 7.6 Hz), 1.75 (6H, t, J=2.8 Hz), 1.76–1.89 (2H, m), 2.05–2.18 (5H, m), 2.21 (6H, d, J=3.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.4 (d, J=3.8 Hz), 24.6 (d, J=47.8 Hz), 27.7, 36.2, 36.8, 52.5 (d, J=37.9 Hz), 216.8 (d, J=25.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.7. IR (KBr) ν 3326, 2971, 2919, 2885, 2852, 1674, 1454, 1148, 1046, 990, 925, 763, 743, 718, 674, 574 cm^{-1}. MS (EI) m/z 284 (M^+, 6%), 135 ($M^+-C_5H_{10}OPS$, 100). HRMS calcd for $C_{15}H_{25}OPS$: 284.1364. Found: 284.1358. Compound **22**: colorless solid. Mp 207.0–208.0 °C (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (6H, s), 3.84 (3H, s), 6.66 (2H, d, J=9.2 Hz), 6.96 (2H, d, J=8.8 Hz), 7.41 (2H, d, J=9.2 Hz), 7.93 (2H, d, J=9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 55.3, 110.7, 114.7,

118.9, 124.0, 129.6, 136.8, 153.8, 160.4, 188.5. IR (KBr) ν 2905, 1605, 1591, 1242, 1172, 820 cm^{-1}. MS (EI) m/z 287 (M^+, 4%), 148 ($M^+-SC_7H_7O$, 100%). HRMS calcd for $C_{16}H_{17}O_2NS$: 287.0980. Found: 287.0990.

4.15. Reaction of *S*-(4-tolyl) 4-methoxybenzothioate 11 and tetraethyldiphosphine disulfide 17 (Scheme 12)

In a two-necked flask equipped with a reflux condenser were placed $RhH(PPh_3)_4$ (5.0 mol %, 14.4 mg), *S*-(4-tolyl) 4-methoxybenzothioate **11** (0.25 mmol, 64.5 mg), and tetraethyldiphosphine disulfide **17** (0.25 mmol, 60.5 mg) under an argon atmosphere. Dry chlorobenzene (0.5 mL) and 1,2-bis(diethylphosphino)ethane (10.0 mol %, 4.9 mg) were added, and the solution was heated at reflux for 6 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving the diethyl(4-methoxybenzoyl)phosphine sulfide **23** (35.1 mg, 55%) as yellow solids and 4-tolyl diethyldithiophosphinate **24** (31.1 mg, 51%) as colorless oil. Compound **23**: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (6H, dt, J=20.0, 7.2 Hz), 2.00–2.32 (4H, m), 2.43 (3H, s), 7.29 (2H, d, J=8.8 Hz), 8.44 (2H, d, J=8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.4 (d, J=4.5 Hz), 21.9, 23.7 (d, J=48.5 Hz), 129.4, 130.1, 133.4 (d, J=46.2 Hz), 146.0, 200.5 (d, J=49.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.5. IR (neat) ν 3060, 3032, 2974, 2936, 2878, 1784, 1704, 1645, 1602, 1572, 1456, 1408, 1379, 1223, 1209, 1178, 1119, 1032, 920, 825, 769, 726, 708, 635, 581 cm^{-1}. MS (EI) m/z 240 (M^+, 16), 136 (MeC_6H_4CO-O, 13), 119 (MeC_6H_4CO, 100), 91 (MeC_6H_4, 16). HRMS calcd for $C_{12}H_{17}OPS$: 240.0738. Found: 240.0740. Compound **24**: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (6H, dt, J=21.2, 7.6 Hz), 1.92–2.07 (4H, m), 2.36 (3H, d, J=2.0 Hz), 7.19 (2H, d, J=8.0 Hz), 7.41 (2H, dd, J=8.0, 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8 (d, J=5.2 Hz), 21.2, 27.5 (d, J=49.9 Hz), 123.5 (d, J=6.7 Hz), 130.1 (d, J=2.2 Hz), 136.0 (d, J=3.7 Hz), 140.0 (d, J=3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.7. IR (neat) ν 2971, 2933, 1491, 1452, 1018, 810, 769 cm^{-1}. MS (EI) m/z 244 (M^+, 100%), 121 ($M^+-C_7H_7S$, 80%). HRMS calcd for $C_{11}H_{17}PS_2$: 244.0509. Found: 244.0502.

4.16. The reaction of acylphosphine sulfides and disulfides (Table 6), synthesis of *S*-phenyl 4-(dimethylamino) benzothioate

In a two-necked flask equipped with a reflux condenser were placed diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** (0.25 mmol, 67.3 mg), diphenyl disulfide (0.25 mmol, 54.5 mg), $RhH(PPh_3)_4$ (2.0 mol %, 5.8 mg), and 1,2-bis(diphenylphosphino) ethane (4.0 mol %, 4.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving *S*-phenyl 4-(dimethylamino)benzothiate (63.4 mg, 99%) and phenyl diethyldithiophosphinate (52.1 mg, 91%). *S-Phenyl 4-(dimethylamino)benzothioate* colorless solid. Mp 196.5–197.5 °C (ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$) δ 3.07 (6H, s), 6.66 (2H, d, J=9.2 Hz), 7.38–7.46 (3H, m), 7.48–7.54 (2H, m), 7.93 (2H, d, J=9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 110.7, 124.0, 128.3, 129.0, 129.0, 129.6, 135.3, 153.9, 187.7. IR (KBr) ν 2908, 1653, 1600, 1377, 1181, 897, 820 cm^{-1}. MS (EI) m/z 257 (M^+, 5%), 148 (M^+-SPh, 100%). HRMS calcd for $C_{15}H_{15}ONS$: 257.0874. Found: 257.0872. *Phenyl diethyldithiophosphinate* colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (6H, dt, J=21.6, 7.6 Hz), 1.92–2.11 (4H, m), 7.36–7.54 (3H, m), 7.52–7.56 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9 (d, J=5.2 Hz), 27.8 (d, J=50.6 Hz), 127.2 (d, J=6.7 Hz), 129.3 (d, J=2.2 Hz), 129.7 (d, J=3.0 Hz), 136.2 (d, J=3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.5. IR (neat) ν 2972, 2933, 1472, 1023, 772, 749 cm^{-1}. MS (EI) m/z 230 (M^+, 100%), 121 (M^+-SPh, 95%). HRMS calcd for $C_{10}H_{15}PS_2$: 230.0353. Found: 230.0356.

4.17. Equilibrium reaction of acylphosphine sulfide and aryl ester (Scheme 13)

In a two-necked flask equipped with a reflux condenser were placed diethyl{4-(dimethylamino)benzoyl}phosphine sulfide **14** (0.25 mmol, 67.3 mg), 4-cyanophenyl 2-propylpentanoate **27** (0.25 mmol, 61.3 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and 1,2-bis(diphenylphosphino)ethane (10 mol %, 10.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-cyanophenyl 4-(dimethylamino)benzoate **28** (26.6 mg, 40%) and diethyl(2-propylpentanoyl) phosphine sulfide **29** (26.0 mg, 42%) as well as recovered **14** (34.8 mg, 52%) and **27** (28.1 mg, 46%). Compound **28**: colorless solid. Mp 156.0–157.0 °C (ethyl acetate). Lit.[15] 152–153 °C (benzene). ^1H NMR (400 MHz, $CDCl_3$) δ 3.08 (6H, s), 6.68 (2H, d, J=8.8 Hz), 7.32 (2H, d, J=8.8 Hz), 7.69 (2H, d, J=8.8 Hz), 8.01 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 109.0, 110.8, 114.6, 118.5, 123.1, 133.5, 154.0, 154.8, 164.3. IR (neat) ν 2914, 2823, 1718, 1599, 1163, 1049 cm^{-1}. MS (EI) m/z 266 (M^+, 13%), 148 ($M^+-C_7H_4NO$, 100%). HRMS calcd for $C_{16}H_{24}O_2N_2$: 266.1055. Found: 266.1048. Compound **29**: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (6H, t, J=7.2 Hz), 1.15 (6H, dt, J=19.6, 7.6 Hz), 1.21–1.46 (6H, m), 1.65–1.76 (2H, m), 1.80–2.10 (4H, m), 3.82 (1H, tt, J=6.8, 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.3 (d, J=4.4 Hz), 14.1, 20.4, 22.8 (d, J=46.8 Hz), 32.3, 48.5 (d, J=38.7 Hz), 219.0 (d, J=34.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.7. IR (neat) ν 3348, 2959, 2934, 2873, 1685, 1458, 1407, 1379, 1234, 1101, 1047, 1018, 1001, 775, 747, 730, 587 cm^{-1}. MS (EI) m/z 248 (M^+, 100%), 127 (M^+-Pr_2CHCO, 52%). HRMS calcd for $C_{12}H_{25}OPS$: 248.1364. Found: 248.1364.

4.18. Reaction of aryl esters and tetraethyldiphosphine disulfide 17 (Scheme 17), synthesis of diethyl(2-propylpentanoyl)phosphine sulfide 29

In a two-necked flask equipped with a reflux condenser were placed 4-cyanophenyl 2-propylpentanoate **27** (0.25 mmol, 61.3 mg), tetraethyldiphosphine disulfide **17** (0.25 mmol, 60.5 mg), $RhH(PPh_3)_4$ (5.0 mol %, 14.4 mg), and 1,2-bis(diethylphosphino)ethane (10.0 mol %, 4.9 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving diethyl(2-propylpentanoyl) phosphine sulfide **29** (37 mg, 60%) and 4-cyanophenyl diethylphosphinothioate **30** (34.5 mg, 58%). Compound **30**: colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (6H, dt, J=20.8, 7.6 Hz), 2.12–2.22 (4H, m), 7.29 (2H, d, J=8.8 Hz), 7.63 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.7 (d, J=5.2 Hz), 27.4 (d, J=69.2 Hz), 108.6, 118.3, 122.6 (d, J=4.5 Hz), 133.7, 154.3 (d, J=9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 111.3. IR (neat) ν 2977, 2881, 2227, 1601, 1500, 1225, 893, 789 cm^{-1}. MS (EI) m/z 239 (M^+, 100%), 121 ($M^+-C_7H_4NO$, 82%). HRMS calcd for $C_{11}H_{14}ONPS$: 239.0534. Found: 239.0521.

4.19. Reaction of diethyl{4-(dimethylamino)benzoyl} phosphine sulfide 14 and 4-methoxyphenol (Scheme 15)

In a two-necked flask equipped with a reflux condenser were placed **14** (0.25 mmol, 67.3 mg), 4-methoxyphenol (0.25 mmol, 31 mg), $RhH(PPh_3)_4$ (5.0 mol %, 14.4 mg), and 1,2-bis(diphenylphosphino)ethane (10.0 mol %, 10.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-methoxyphenyl 4-dimethylaminobenzoate (64.4 mg, 95%) and diethylphosphine sulfide **33** (26.2 mg, 86%). 4-

Methoxyphenyl 4-*dimethylaminobenzoate* colorless solid. Mp 169.5–171.0 °C (ethyl acetate/hexane=2/1). Lit.[15] 173–173.5 °C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (6H, s), 3.81 (3H, s), 6.69 (2H, d, J=9.2 Hz), 6.92 (2H, d, J=8.8 Hz), 7.11 (2H, d, J=9.2 Hz), 8.05 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 55.6, 110.7, 114.3, 116.0, 122.6, 131.9, 144.8, 153.6, 156.9, 165.8. IR (KBr) ν 2906, 1712, 1188, 1066 cm^{-1}. MS (EI) m/z 271 (M^+, 16%), 148 ($M^+-C_7H_7O_2$, 100%). HRMS calcd for $C_{16}H_{17}O_3N$: 271.1208. Found: 271.1205. Compound **33**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (6H, dt, J=21.2, 7.6 Hz), 1.88–2.06 (4H, m), 6.49 (1H, dm, J=433.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9 (d, J=4.6 Hz), 22.8 (d, J=52.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9. IR (neat) ν 2935, 2877, 1456, 1045, 901 cm^{-1}. MS (EI) m/z 122 (M^+, 100%), 94 (M^+-28, 60%). HRMS calcd for $C_4H_{11}PS$: 122.0319. Found: 122.0306.

4.20. Equilibrium reaction of thioester and aryl ester (Scheme 16)

In a two-necked flask equipped with a reflux condenser were placed 4-cyanophenyl dodecanoate **7** (0.25 mmol, 75.3 mg), *S*-(4-tolyl) 4-methoxybenzothioate **11** (0.25 mmol, 64.5 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and 1,2-bis(diphenylphosphino) ethane (10 mol %, 10.0 mg) in chlorobenzene (1 mL) under an argon atmosphere, and the solution was stirred under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving *S*-(4-tolyl) dodecanethioate **34** (37.4 mg, 49%) and 4-cyanophenyl 4-methoxybenzoate **1** (30.9 mg, 49%) as well as recovered **7** (37.6 mg, 50%) and **11** (31.4 mg, 49%). Compound **34**:[20] colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J=6.4 Hz), 1.26–1.33 (16H, m), 1.70 (2H, quint, J=7.2 Hz), 2.37 (3H, s), 2.63 (2H, t, J=7.2 Hz), 7.22 (2H, d, J=8.0 Hz), 7.29 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.3, 22.7, 25.6, 29.0, 29.2, 29.3, 29.4, 29.6, 31.9, 43.6, 77.2, 124.4, 130.0, 134.4, 139.5, 198.1. IR (neat) ν 2925, 2854, 1710 cm^{-1}. MS (EI) m/z 306 (M^+, 21%), 183 ($M^+-MeC_6H_4S$, 98%), 124 (MeC_6H_4SH, 100%). HRMS calcd for $C_{19}H_{30}OS$: 306.2017. Found: 306.2010. Compound **1**: colorless solid. Mp 114–115 °C (hexane/ethylacetate=5/1). Lit.[15] 109–110 °C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s), 7.00 (2H, dd, J=6.8, 2.0 Hz), 7.36 (2H, dd, J=6.8, 2.0 Hz), 7.74 (2H, dd, J=6.8, 2.4 Hz), 8.14 (2H, dd, J=6.8, 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 109.5, 114.0, 118.4, 120.8, 123.0, 132.5, 133.7, 154.4, 164.0, 164.3 cm^{-1}. IR (KBr) ν 3106, 2942, 2848, 2229, 1731, 1610, 1583, 1515, 1213, 1168. MS (EI) m/z 253 (M^+, 2%), 135 ($M^+-MeOPh$, 100%). HRMS calcd for $C_{15}H_{11}NO_3$: 253.0739. Found: 253.0719.

4.21. Reaction of thioesters and phenols (Scheme 17), synthesis of 4-cyanophenyl 4-methoxybenzoate 1

In a two-necked flask equipped with a reflux condenser were placed *S*-(4-tolyl) methoxybenzothioate **11** (0.25 mmol, 64.5 mg), 4-cyanophenol (0.25 mmol, 29.8 mg), $RhH(PPh_3)_4$ (10 mol %, 28.8 mg), and 1,2-bis(diphenylphosphino)ethane (20 mol %, 20.0 mg) in chlorobenzene (1 mL) under an air at reflux for 9 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-cyanophenyl 4-methoxybenzoate **1** (43.5 mg, 69%), and bis(4-tolyl) disulfide (18.5 mg, 59%), as well as recovered **11** (15.3 mg, 24%) and 4-cyanophenol (5.9 mg, 20%).

4.22. Reaction of aryl esters and dithiophosphinate (Table 7), synthesis of *S*-phenyl 3,5-dimethoxybenzoate

In a two-necked flask equipped with a reflux condenser were placed 4-cyanophenyl 3,5-dimethoxybenzoate (0.25 mmol, 70.8 mg), phenyl dimethyldithiophosphinate (0.25 mmol, 50.5 mg), $RhH(PPh_3)_4$ (5 mol %, 14.4 mg), and 1,2-bis(diphenylphosphino) ethane (10 mol %, 10.0 mg) in chlorobenzene (1 mL) under an air at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving *S*-phenyl 3,5-dimethoxybenzothioate (61.1 mg, 89%) and *O*-(4-cyanophenyl) dimethylphosphinothioate **38** (45.5 mg, 86%). *S*-Phenyl 3,5-dimethoxybenzothioate colorless solid. Mp 73.5–75.0 °C (hexane/ethyl acetate=4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (6H, s), 6.68 (1H, t, J=2.4 Hz), 7.16 (2H, d, J=2.4 Hz), 7.43–7.46 (3H, m), 7.49–7.52 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 105.1, 105.9, 127.3, 129.2, 129.5, 135.0, 138.4, 160.8, 190.0. IR (KBr) ν 2939, 2837, 1680, 1593, 1159 cm^{-1}. MS (EI) m/z 274 (M^+, 15%), 165 ($M^+-C_6H_5S$, 100%). HRMS calcd for $C_{15}H_{14}O_3S$: 274.0663. Found: 274.0650. Compound **38**: colorless solid. Mp 73.5–74.5 °C (hexane/diethyl ether=3/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (6H, d, J=13.2 Hz), 7.31 (2H, dd, J=8.8, 1.2 Hz), 7.65 (2H, d, J=8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1 (d, J=72.8 Hz), 108.9 (d, J=1.5 Hz), 118.2, 122.6 (d, J=4.5 Hz), 133.8, 153.9 (d, J=9.1 Hz). IR (KBr) ν 3101, 3066, 2983, 2235, 1602, 1500, 1211, 742 cm^{-1}. MS (EI) m/z 211 (M^+, 100%), 93 (M^+-118 (C_7H_4NO), 61%). HRMS calcd for $C_9H_{10}OSNP$: 211.0221. Found: 211.0202.

4.23. Typical procedures for carbothiolation reaction of thioesters (Table 8)

In a two-necked flask equipped with a reflux condenser were placed $RhH(PPh_3)_4$ (5 mol %, 17.3 mg), diethylphenylphosphine (15 mol %, 7.8 μL), *S*-butyl 4-cyanobenzothioate (0.30 mmol, 65.7 mg), and 1-decyne (0.30 mmol, 41.5 mg) in dimethyl sulfoxide (0.75 mL) under an argon atmosphere, and the solution was heated at 100 °C for 12 h. The mixture was purified by flash column chromatography on silica gel giving (*E*)-3-*n*-butylthio-1-(4-cyanophenyl)-2-undecen-1-one (*E*)-**39** (38.3 mg, 36%) and (*Z*)-3-*n*-butylthio-1-(4-cyanophenyl)-2-undecen-1-one (*Z*)-**39** (14.2 mg, 13%). Compound (*E*)-**39**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J=7.0 Hz), 0.98 (3H, t, J=7.4 Hz), 1.22–1.37 (8H, m), 1.42 (2H, tt, J=7.2, 7.2 Hz), 1.51 (2H, tq, J=7.5, 7.5 Hz), 1.64 (2H, tt, J=7.7, 7.7 Hz), 1.72 (2H, tt, J=7.4, 7.4 Hz), 2.87 (4H, t, J=7.2 Hz), 6.49 (1H, s), 7.75 (2H, d, J=8.0 Hz), 7.96 (2H, d, J=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.1, 22.2, 22.6, 29.2, 29.3, 29.4, 29.7, 30.1, 31.6, 31.8, 35.6, 111.5, 115.0, 118.2, 128.3, 132.3, 143.7, 171.0, 184.9. IR (neat) ν 2956, 2927, 2855, 1652, 1549, 1223, 1053, 819 cm^{-1}. MS (EI) m/z 357 (M^+, 12%), 300 ($M^+-C_4H_9$, 100%). HRMS calcd for $C_{22}H_{31}NOS$: 357.2126. Found: 315.2117. Compound (*Z*)-**39**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J=7.0 Hz), 0.95 (3H, t, J=7.4 Hz), 1.24–1.36 (8H, m), 1.41 (2H, tt, J=7.3, 7.3 Hz), 1.49 (2H, tq, J=7.4, 7.4 Hz), 1.65 (2H, tt, J=7.9, 7.9 Hz), 1.67 (2H, tt, J=7.5, 7.5 Hz), 2.61 (2H, t, J=8.0 Hz), 2.90 (2H, t, J=7.4 Hz), 6.92 (1H, s), 7.73 (2H, d, J=8.0 Hz), 8.00 (2H, dt, J=1.8, 8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 14.1, 22.1, 22.6, 29.16, 29.23, 29.3, 30.26, 30.33, 30.9, 31.8, 37.3, 115.0, 115.1, 118.3, 128.3, 132.3, 142.4, 170.1, 186.3. IR (neat) ν 2927, 2855, 1633, 1526, 1238 cm^{-1}. MS (EI) m/z 357 (M^+, 15%), 300 ($M^+-C_4H_9$, 100%). HRMS calcd for $C_{22}H_{31}NOS$: 357.2126. Found: 315.2116.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.07.031. These data include MOL files and InChIKeys of the most important compounds described in this article.

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