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镍催化硫酯转移反应合成芳基硫酯

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摘要 利用简单易得的硫酯作为硫源, 并且没有使用有毒的一氧化碳气体和硫醇, 实现了硫酯与芳基碘的镍催化官能团交换反应. 这种转移反应涉及与 Ni(0)的两个氧化加成: 芳族酯的 C—S 键和卤代芳烃的 C—I 键, 两个生成的中间体经过官能团交换反应得到新的硫酯. 此外, 该方法条件温和, 操作简单, 为硫酯的合成提供了一条实用的途径.
关键词 镍催化; 硫酯; 氧化加成

Ni-Catalyzed Aryl Thioester Synthesis via Thioester Transfer Reaction

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Abstract A nickel-catalyzed thioester transfer reaction using thioesters and aryl iodides was realized, utilizing simple and readily available thioesters as the sulfur source without smelly thiols and toxic carbon monoxide gas. The thioester transfer reaction involves two oxidative additions with Ni(0): C—S bond of the aromatic ester and C—I bond of haloarenes, and the two resulting intermediates undergoe a functional group exchange reaction to afford the new thioester. Furthermore, this approach features mild conditions and operational simplicity, providing a practical route for thioester synthesis.
Keywords Ni-catalysis; thioester; oxidative addition

1 Introduction

Thioester is one of the most important chemical motifs widely applied in biochemistry, pharmacological chemistry fields as well as advanced materials.[1] In addition, they are also used as convenient protecting groups for thiols in the synthetic chemistry.[2] Due to its versatility and importance, chemists have been focusing on expanding the synthetic methodology for thioesters. The most direct method is the reaction of activated carboxylic acids and thiols,[3] however, this transformation suffers from the odor and toxicity of thiols and is limited by the harsh reaction conditions in some cases. Since Alper and co-workers[4] reported the first palladium-catalyzed carbonylation to construct the corresponding thioesters, some elegant methodologies were realized by other groups successively.[5] Very recently, Wu/Li[6] and Lee/Kim[7] independently demonstrated the synthesis of thioesters using thioether or thioester as sulfur source via palladium-catalyzed carbonylation of aryl halides. However, the cumbersome reaction apparatus and toxicity associated with the use of CO mean that this gas operation should be avoided, which lead to the development of safety CO surrogates to avoid the handling of CO gas.[8]

Meanwhile, functional group transfer reactions have caused more attention as a conceptually novel synthetic tool.[9] As a pioneering work, Morandi and Arndtsen[10] reported respectively the aryl exchange reaction between aroyl chlorides and aryl iodides via Pd/Xantphos catalysis in 2018, which used oxidative addition and reductive elimination of C—Cl as a reversible chemical process. In 2020, Yamaguchi *et al*.[11] demonstrated a Ni-catalyzed aryl exchange reaction between aryl halides and aromatic esters to access new ester. In 2022, in the process of writing this paper, Xie *et al*.[12] reported the synthesis of thioesters using nickel catalysis.

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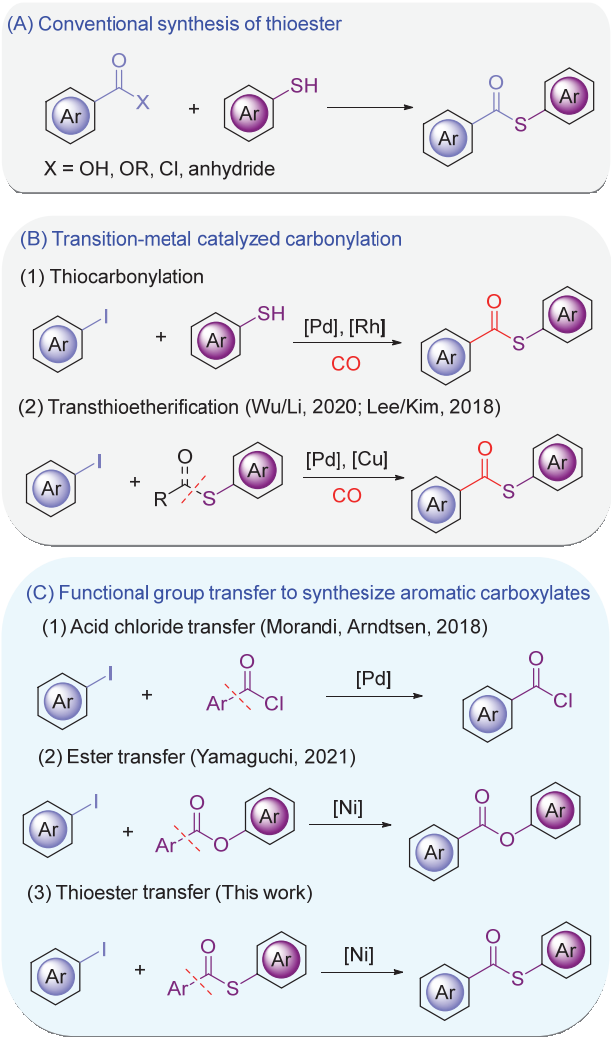


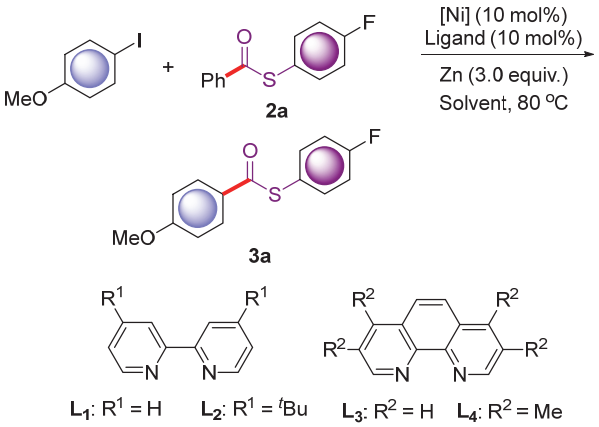
Scheme 1 Conventional synthesis of thioester, carbonylation to thioester and aromatic carboxylates synthesis via functional group transfer

However, the challenge of these methods is how to develop an appropriate catalytic system to control the cleavage and formation of two distinct chemical bonds, as well as the reservation of CO during the transformation. Considering the previous two examples, we assumed that the reductive elimination of C—I bond is more difficult than C—X bonds (C—Cl and C—O). Because the C—S bond reductive elimination is relatively facile in metal catalysis,[13] we proposed that the aryl exchange process might be reasonable and possible to realize the thioester transfer. Herein, we report a new aryl thioester synthesis via a Ni-catalyzed aryl exchange between aryl iodides and thioesters.

2 Results and discussion

Our initial investigation began with *p*-iodoanisole (**1a**) and *S*-(*p*-fluorophenyl) benzothioate (**2a**) in the presence of $NiBr_2(PPh_3)_2$ and 2,2'-bipyridine at 80 ℃ (Table 1). However, when dioxane and MeCN were utilized as solvents, there was no reaction detected and the starting materials were recovered fully. To our delight, we did isolate the desired thioester transfer product **3a** in 44% yield when *N*-methyl pyrrolidone (NMP) was used as solvent. Furthermore, dimethyl sulfoxide (DMSO), *N*,*N*′-dimethylformamide (DMF) and mixed solvents were also screened, and the results showed that NMP/DMSO (V∶V=1∶1) was effective to this transformation, delivering the corresponding products in 77% yield (Entries 4～6). In the examination of the nickel source, it was found that $NiBr_2(PPh_3)_2$ gave dominant results than $NiBr_2$•DME, $NiCl_2$•DME, $NiCl_2(PPh_3)_2$ and $NiCl_2$(dppp) (Entries 7～9). Subsequently, we also found that phenanthroline or other substituted bipyridines realized the reaction with low efficiency (Entries 10～12). However, no reaction was occurred when phosphine ligand dppe was applied as ligand, indicating that phosphine ligand is ineffective to this transformation (Table 1, Entry 13). In this study, Zn powder could play as a reductant for the generation of active Ni(0) species from Ni(II). A similar role could be expected for Mn powder, however, the yield of the target product decreased to 34% (Table 1, Entry 14). When 1.0 or 2.0 equiv. of Zn was used, however, the starting material could not be consumed and the yield was relatively low, indicating that the reductive

Table 1 Optimization of reaction condition



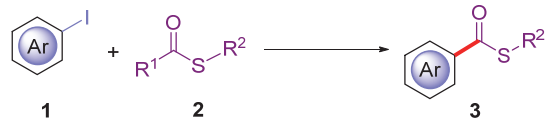
Entry	Ni catalyst	Ligand	Solvent	Yield[a]/%
1	$NiBr_2(PPh_3)_2$	**L1**	Dioxane	NR
2	$NiBr_2(PPh_3)_2$	**L1**	MeCN	NR
3	$NiBr_2(PPh_3)_2$	**L1**	NMP	44
4	$NiBr_2(PPh_3)_2$	**L1**	DMSO	56
5	$NiBr_2(PPh_3)_2$	**L1**	DMF	25
6	**$NiBr_2(PPh_3)_2$**	**L1**	**NMP/DMSO (V∶V=1∶1)**	**77**
7	$NiBr_2$•DME	**L1**	NMP/DMSO (V∶V=1∶1)	61
8	$NiBr_2(PPh_3)_2$	**L1**	NMP/DMSO (V∶V=1∶1)	68
9	$NiCl_2$•DME	**L1**	NMP/DMSO (V∶V=1∶1)	69
10	$NiBr_2(PPh_3)_2$	**L2**	NMP/DMSO (V∶V=1∶1)	26
11	$NiBr_2(PPh_3)_2$	**L3**	NMP/DMSO (V∶V=1∶1)	59
12	$NiBr_2(PPh_3)_2$	**L4**	NMP/DMSO (V∶V=1∶1)	66
13	$NiBr_2(PPh_3)_2$	DPPE	NMP/DMSO (V∶V=1∶1)	NR
14	$NiBr_2(PPh_3)_2$	**L1**	NMP/DMSO (V∶V=1∶1)	34[b]

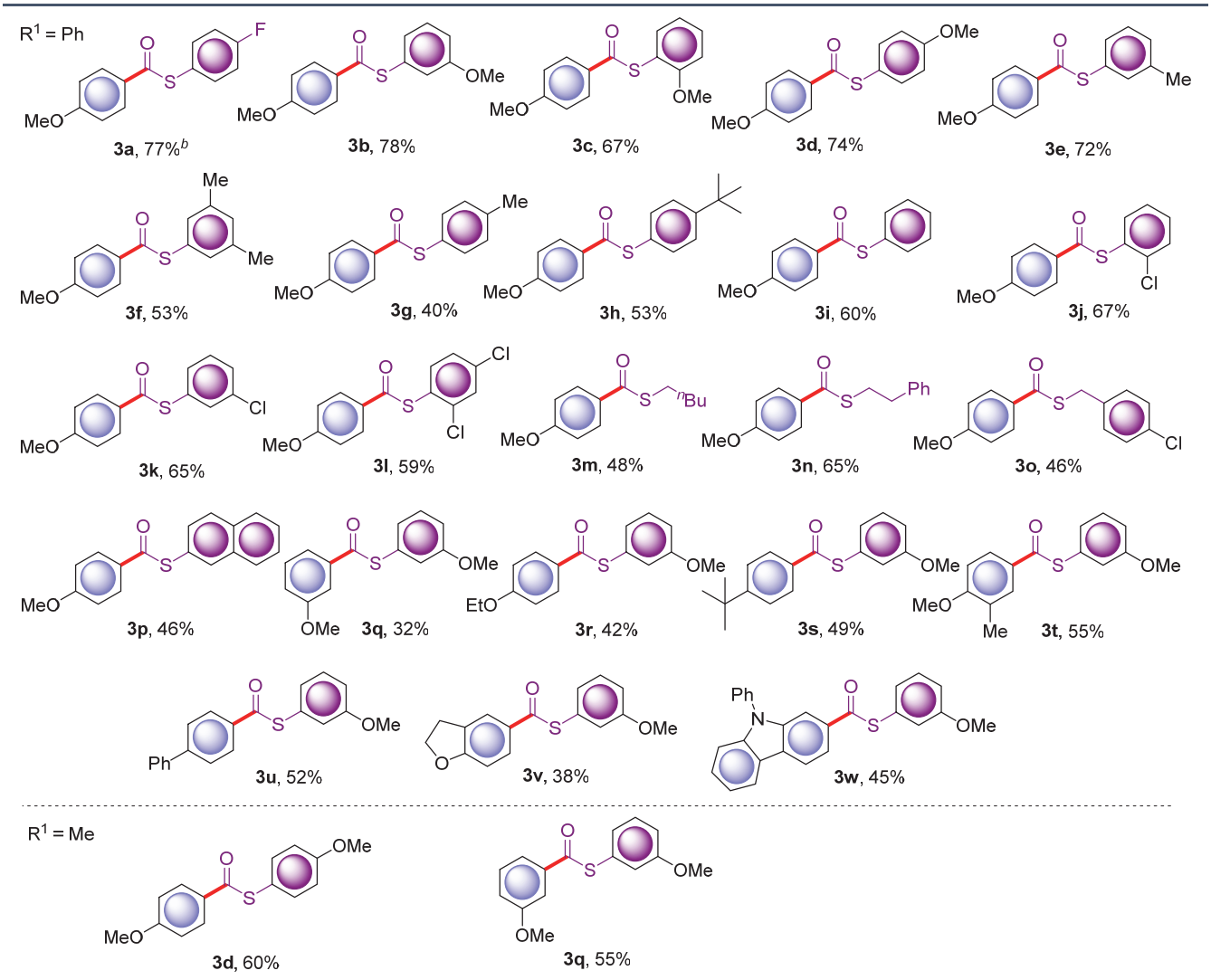
[a] Isolated yield. [b] Mn powder instead of Zn powder.

efficiency of Zn is low in the formation of catalytic Ni(0). In addition, the reaction showed no differences when Na_2CO_3 was added or not, proving that base is unnecessary. Furthermore, the ratio between NMP and DMSO was also screened, unfortunately, no better results were obtained. On the basis of the above studies, we identified the optimized conditions as $NiBr_2(PPh_3)_2$ (10 mol%), **L**$_1$ (10 mol%), zinc powder (3.0 equiv.), NMP/DMSO (V∶V=1∶1) as solvent at 80 ℃ under a N_2 atmosphere for 2 h.

With the optimized conditions in hand, the substrate universality of this reaction was investigated (Table 2). First, *p*-anisyl bromide instead of iodide was examined under the optimized conditions, however, it was revealed that the reaction of *p*-anisyl bromide resulted in very low yield (25%). Then the reaction of *p*-iodoanisolewith different thioesters (**3a**～**3p**) was screened. *S*-Aryl thioesters bearing strong electron-donating groups methoxyl at the *o*-, *m*-, *p*-position, could provide the corresponding *S*-aryl benzothioate in good yields (**3b**～**3d**). Substrates with alkylated *S*-aryl (*m*- or *p*-methyl, 3,5-dimethyl and *p*-*t*-butyl) or *S*-phenyl could also work efficiently to give the desired molecules (**3e**～**3i**). Several *S*-aryl benzothioates with halogen substituents including *p*-fluoro, *o*-chloro, *m*-chloro and *o*,*p*-dichloro, reacted with *p*-iodoanisole to afford *S*-aryl benzothioates in moderate to good yields (**3a**, **3j**～**3l**). Furthermore, *S*-alkyl thioesters such as ^{n}BuS, PhC_2H_4S, *p*-ClC_6H_4S, worked smoothly to deliver the corresponding products (**3m**～**3o**). *S*-Naphthalenyl thioester was also

Table 2 Scope with respect to aryl iodides and thioesters[a]





[a] Reaction conditions: **1** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol), $NiBr_2(PPh_3)_2$ (0.02 mmol, 10 mol%), 2,2'-bipyridine (0.02 mmol, 10 mol%), zinc powder (0.6 mmol), N_2 atmosphere, 80 ℃, 2 h; [b] Isolated yields.

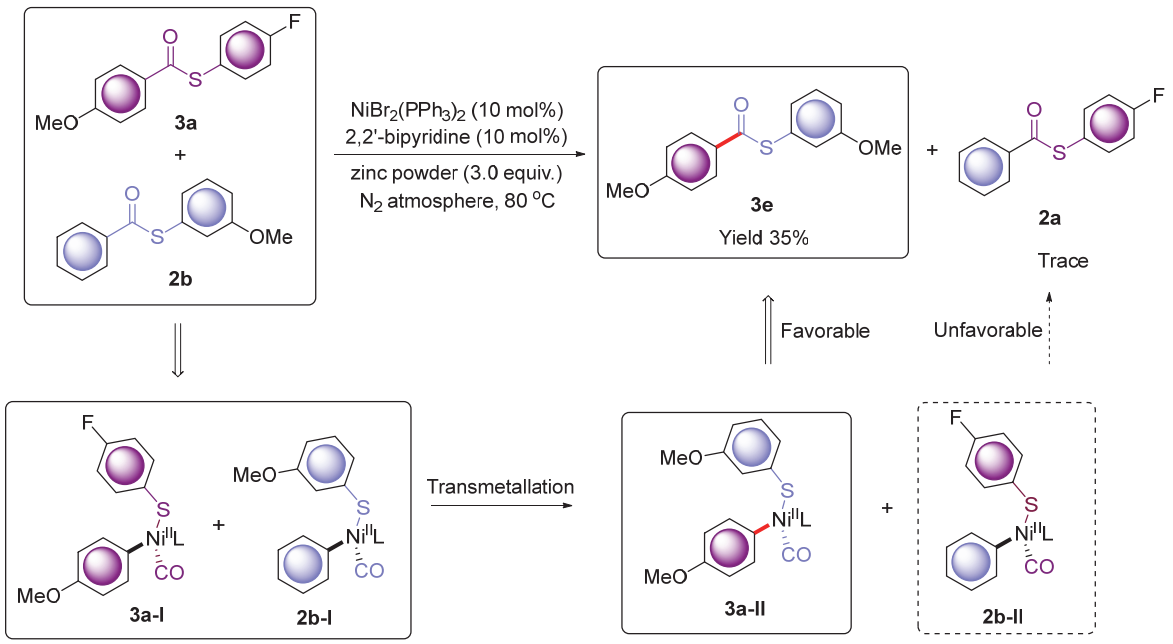
compatible with the standard conditions with moderate yield (**3p**). The reaction of *p*-iodoanisole with *S*-phenyl thioester bearing electron-withdrawing substituents such as nitro group did not yield any target product, and *p*-iodoanisole with multialkane substituted thioesters such as *o*-*tert*-butyl could not yield the target product due to steric hindrance. Subsequently, various substituted aryl iodides were examined. Notably, substituents at *meta*- or *para*-position of aryl iodides showed good compatibility to this system (*m*-OMe, *p*-OEt, *p*-^{t}Bu, *p*-Me and *m*-Me-*p*-OMe) (**3q**～**3u**), however, at this stage, *o*-substituted aryl iodides showed poor reactivity, affording the corresponding thioesters in less than 10% yield. In addition, fused heterocyclic aryl iodides also underwent the present reaction, albeit affording lower yields of thioesters **3v** and **3w**. Finally, *S*-aryl thioacetates were also subjected to the standard conditions, which delivered the thioester transfer products **3d** and **3q** in 60% and 55% yields, respectively. On the basis of the control experiments, we found that the aryl iodide with electron-withdrawing group reacted with thioester to deliver thioether as main product instead of the target thioester. The reaction of electronrich group substituted aryl iodobenzene with thioester could also produce trace of thioether byproducts detected via gas chromatography mass spectrometry (GCMS). On the other hand, steric hindrance has a significant effect on the yield of the reaction. *Ortho* substituted aryl iodide produced the target product in quite low yield and the system was messy. Aryl bromides yielded products in low yields, whereas aryl chlorides did not deliver the target product. All the results indicated the electron-donating groups on ArI is necessary for this transformation while the reason was not quite clear for now.

Furthermore, the transformation of **3a** with **2b** was investigated using GCMS. Besides the desired molecule **3e**, trace amount of byproduct **2a** was found. This result proved that the functional group exchanging reaction occurred between thioesters **3a** and **2b** (Scheme 2).

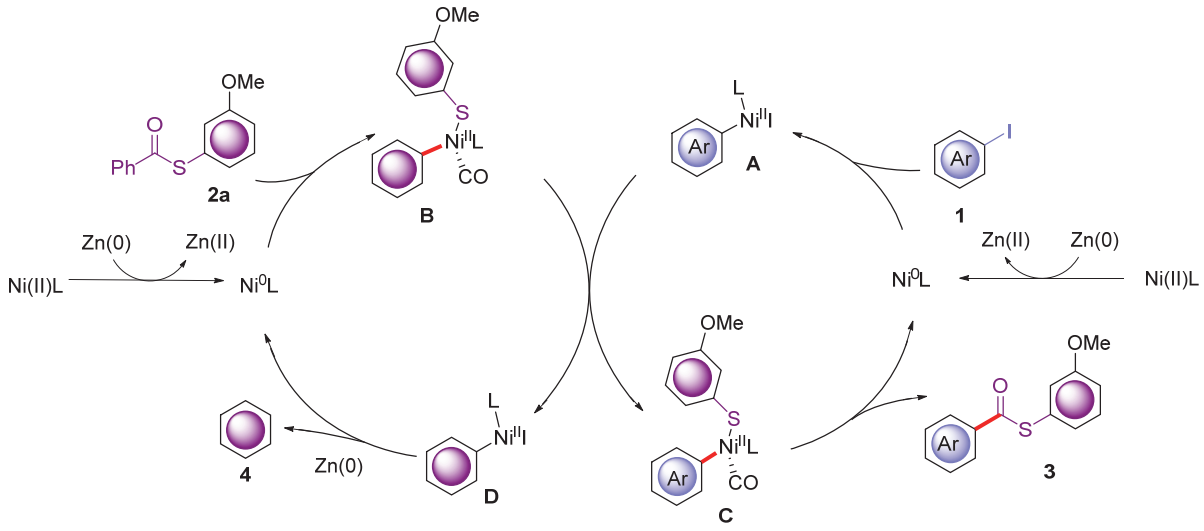
A plausible mechanism of this reaction is demonstrated in Scheme 3. In cycle I, the Ni(II) catalyst is reduced to Ni(0) in the presence of Zn dust, which then cleaves the C—I bond of aryl iodide via oxidative addition. Meanwhile, the similar reduction and oxidative addition to C(O)—S bond of nickel catalyst could generate the intermediate **B** as shown in cycle II. Subsequently, an exchange reaction between the two complexes delivers intermediates **C** and **D**, respectively. Finally, the intermediate **C** undergoes carbonylation and reductive elimination of C—S bond to generate thioester group transfer products **3** and release Ni(0) species for the next catalytic cycle. Reductive elimination from **D** would give the byproduct benzene **4** and Ni(0) species. Although the reaction may proceed through functional group exchange, solid evidence is still required to verify this mechanistic hypothesis.

3 Conclusions

A nickel-catalyzed thioester transfer reaction of thioesters with aryl iodides using thioesters as the sulfur source was developed, avoiding the use of smelly thiols and toxic carbon monoxide gas. This strategy shows simple operation and mild conditions, which provides a novel route for the synthesis of thioesters. The tentative investigation to the mechanism shows two oxidative additions with Ni(0): C—S bond of the aromatic ester and C—I bond of haloarenes, and the two resulting intermediates undergoes a functional group exchange reaction to afford the new thioester. Further research is underway in our laboratory, focusing on the elucidation of the functional group exchange reaction mechanism.



Scheme 2 Functional group transfer between two thioesters



Scheme 5 Proposed mechanism

4 Experimental section

4.1 General information

DMSO and NMP were dried from CaH_2 and purified by distillation before being used. Purifications of products were carried out by column chromatography on silica gel (200～300 mesh) using a mixture of petroleum ether (60～90 ℃) and ethyl acetate as eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Electrospray mass spectra were obtained using Bruker micrOTOF-Q II 10410 Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

4.2 Synthesis of hioesters

Bottom reaction tube equipped with a stir bar was charged with thiol (1 mmol, 1.0 equiv.), benzoyl chloride (1 mmol, 1.0 equiv.), and ZnO (0.5 mmol, 0.5 equiv.) under air (neat reaction). The sealed reaction vessel was stirred at room temperature for 30 min. The reaction was diluted with EtOAc, dried over anhydrous Na_2SO_4 and filtrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, V∶V=100∶1～50∶1) to yield the desired product **2**.[14]

4.3 Typical procedure for reductive aryl thiocarbonylation

To a 25 mL of Schlenk tube were added aryl iodide **1** (0.4 mmol, 2.0 equiv.), aryl thioester **2** (0.2 mmol, 1.0 equiv.), $NiBr_2(PPh_3)_2$ (0.02 mmol, 10 mol%), 2,2'-bipyridine (0.02 mmol, 10 mol%) and zinc (0.6 mmol, 3.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, NMP (1 mL) and DMSO (1 mL) were then added. The Schlenk tube was screw capped and put into a pre-heated oil bath (80 ℃). After stirring for 2 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (40 mL). After washed with water (15 mL×2) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 ℃. The residue was purified with column chromatography (petroleum ether/ethyl acetate, V∶V=50∶1) on silica gel to give pure product **3**. Among them, **3a**[15], **3b**[15], **3d**[15], **3g**[22], **3h**[16], **3i**[15], **3k**[15], **3m**[18], **3n**[20], **3p**[21] and **3d**[15] are known compounds.

S-(4-Fluorophenyl) 4-methoxybenzothioate (**3a**): White solid, 40.3 mg, 77% yield. m.p. 87～88 ℃ (lit.[16] 86～87 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.8 Hz, 2H), 7.40 (t, J=8.0 Hz, 2H), 7.07 (t, J=8.8 Hz, 2H), 6.89 (d, J=8.8 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.6, 164.1, 163.6 (d, J=248.0 Hz), 137.2 (d, J=8.4 Hz), 129.7, 129.1, 122.9 (d, J=3.3 Hz), 116.4 (d, J=21.8 Hz), 163.9, 137.3, 129.1, 116.5, 116.3, 113.9, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 111.1.

S-(3-Methoxyphenyl) 4-methoxybenzothioate (**3b**):[16] White solid, 42.7 mg, 78% yield. m.p. 73～76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=12.0 Hz, 2H), 7.36 (t, J=8.4 Hz, 1H), 7.11 (d, J=7.6 Hz, 1H), 7.06 (s, 1H), 6.97 (t, J=11.6 Hz, 3H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.5, 164.0, 159.9, 129.9, 129.7, 129.5, 128.6, 127.4, 120.2, 115.6, 113.9, 55.5, 55.4.

S-(2-Methoxyphenyl) 4-methoxybenzothioate (**3c**): White solid, 36.7 mg, 67% yield. m.p. 87～90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J=6.4 Hz, 2H), 7.37 (q, J=7.2 Hz, 2H), 6.94 (q, J=6.4 Hz, 2H), 6.94 (d, J=6.4 Hz, 1H), 6.86 (d, J=7.2 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.8, 163.8, 159.8, 137.4, 131.6, 129.8, 129.6, 121.1, 113.8, 111.6, 56.0, 55.3; HRMS (ESI) calcd for $C_{15}H_{15}O_3SNa$ $[M+Na]^+$ 275.0742, found 275.0747.

S-(4-Methoxyphenyl) 4-methoxybenzothioate (**3d**): White solid, 40.5 mg, 74% yield. m.p. 131.1～132.2 ℃ (lit.[16] 138～139 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J=6.8 Hz, 2H), 7.32 (d, J=5.6 Hz, 2H), 6.88 (t, J=8.8 Hz, 4H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.5, 164.0, 160.7, 136.7, 129.7, 118.2, 114.9, 113.9, 55.5, 55.4.

S-(3-Methylphenyl) 4-methoxybenzothioate (**3e**): White solid, 40.3 mg, 72% yield. m.p. 90～91 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.4 Hz, 2H), 7.24 (d, J=8.4 Hz, 3H), 7.16 (d, J=6.8 Hz, 1H), 6.86 (d, J=8.8 Hz, 2H), 3.78 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.8, 164.0, 139.0, 135.7, 132.2, 130.2, 129.7, 129.5, 129.0, 127.3, 113.9, 55.5, 21.3; HRMS (ESI) calcd for $C_{15}H_{15}O_2SNa$ $[M+Na]^+$ 259.0793, found 259.0791.

S-(3,5-Dimethylphenyl) 4-methoxybenzothioate (**3f**): White solid, 29.0 mg, 53% yield. m.p. 85～88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=7.2 Hz, 2H), 7.13 (s, 2H), 7.06 (s, 1H), 6.95 (d, J=7.2 Hz, 2H), 3.87 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.2, 163.9, 138.8, 132.8, 131.3, 129.7, 129.5, 126.8, 113.9, 55.5, 21.25; HRMS (ESI) calcd for $C_{16}H_{17}O_2S$ $[M+Na]^+$ 273.0949, found 273.0955.

S-(4-Methylphenyl) 4-methoxybenzothioate (**3g**): White solid, 20.6 mg, 40% yield. m.p. 63～64 ℃ (lit.[16] 65～66 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=7.2 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 7.25 (d, J=8.0 Hz, 2H), 6.94 (d, J=7.2 Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.1, 163.9, 139.6, 135.1, 130.0, 129.7, 129.4, 124.0, 113.9, 55.9, 21.4.

S-(4-(*tert*-Butyl)phenyl) 4-methoxybenzothioate (**3h**):[16] White solid, 31.8 mg, 53% yield. m.p. 78～80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=6.4 Hz, 2H), 7.45 (q, J=8.4 Hz, 4H), 6.95 (d, J=6.4 Hz, 2H), 3.88 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.0, 163.9, 152.6, 134.8, 129.7, 126.3, 124.1, 113.9, 55.5, 34.8, 31.2.

S-Phenyl 4-methoxybenzothioate (**3i**): White solid, 29.3 mg, 60% yield. m.p. 91～92 ℃ (lit.[16] 92～93 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=8.8 Hz, 2H), 7.50～7.52 (m, 2H), 7.43～7.45 (m, 3H),6.95 (d, J=6.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.6, 164.0, 135.2, 129.7, 129.4, 129.2, 127.5, 55.9.

S-(2-Chlorophenyl) 4-methoxybenzothioate (**3j**): White solid, 37.9 mg, 67% yield. m.p. 95～96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, J=9.2 Hz, 2H), 7.60 (d, J=7.6 Hz, 1H), 7.55 (d, J=8.0 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.33 (t, J=7.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 164.1, 139.2, 137.7, 131.1, 130.3, 129.9, 129.1, 127.3, 127.2, 114.0, 55.6; HRMS (ESI) calcd for $C_{14}H_{12}O_2ClSNa$ $[M+Na]^+$ 279.0241, found 279.0248.

S-(3-Chlorophenyl) 4-methoxybenzothioate (**3k**):[15] White solid, 36.1 mg, 65% yield. m.p. 96～97 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J=8.4 Hz, 2H), 7.45 (s, 1H), 7.16 (t, J=7.2 Hz, 3H), 6.89 (d, J=8.4 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 187.7, 164.2, 134.8, 134.7, 133.2, 130.1, 129.8, 129.5, 129.5, 129.1, 114.0, 55.5.

S-(2,4-Dichlorophenyl) 4-methoxybenzothioate (**3l**): White solid, 36.9 mg, 59% yield. m.p. 59～61 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=8.8 Hz, 2H), 7.46 (q, J=8.4 Hz, 1H), 6.98 (t, J=8.0 Hz, 4H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.6, 164.2, 138.3, 138.2, 129.9, 128.7, 114.0, 112.3, 112.1, 105.2, 104.9, 104.7, 55.6. HRMS (ESI) calcd for $C_{14}H_{11}Cl_2O_2SNa$ $[M+Na]^+$ 312.9857, found 312.9867.

S-Pentyl 4-methoxybenzothioate (**3m**):[18] Colorless oil, 25.0 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J=5.6 Hz, 3H), 6.82 (d, J=6.0 Hz, 3H), 3.76 (s, 3H), 2.95 (t, J=7.2 Hz, 2H), 1.58 (t, J=7.6 Hz, 2H), 1.24～1.36 (m, 4H), 0.82 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.6, 162.5, 129.1, 129.0, 128.2, 127.2, 112.6, 54.4, 30.0, 28.3, 27.8, 21.2, 12.9.

S-Phenethyl 4-methoxybenzothioate (**3n**):[20] Colorless oil, 35.3 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=5.6 Hz, 2H), 7.21～7.33 (m, 5H), 6.91 (d, J=6.8 Hz, 2H), 3.85 (s, 3H), 3.29 (t, J=8.4 Hz, 2H), 2.96 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.3, 163.7, 140.2, 130.0, 129.4, 128.7, 128.5, 126.5, 113.7, 55.5, 36.1, 30.3.

S-(4-Chlorobenzyl) 4-methoxybenzothioate (**3o**): White solid, 26.9 mg, 46% yield. m.p. 50～51 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, J=8.4 Hz, 2H), 7.28 (q, J=8.4 Hz, 4H), 6.91 (d, J=8.8 Hz, 2H), 4.24 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.5, 163.9, 136.5, 133.0, 130.3, 129.5, 129.4, 128.7, 113.8, 55.5, 32.4; HRMS (ESI) calcd for $C_{15}H_{14}O_2ClSNa$ $[M+Na]^+$ 293.0403, found 293.0411.

S-(2-Naphthalen) 4-methoxybenzothioate (**3p**):[20] White solid, 27.0 mg, 46% yield. m.p. 124～126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=5.6 Hz, 3H), 7.73～7.80 (m, 3H), 7.42～7.46 (m, 3H), 6.86 (d, J=6.4 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.8, 164.0, 135.0, 133.6, 133.4, 132.6, 131.6, 129.8, 129.4, 128.8, 129.2, 128.0, 127.8, 127.1, 126.5, 125.0, 114.0, 55.6.

S-(3-Methoxyphenyl) 3-methoxybenzothioate (**3q**):[20] White solid, 17.6 mg, 32% yield. m.p. 124～126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J=8.0 Hz, 1H), 7.50 (s, 1H), 7.38 (q, J=8.0 Hz, 2H), 7.12 (dd, J=8.4, 17.2 Hz, 2H), 7.07 (s, 1H), 6.99 (d, J=8.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.0, 159.9, 159.8, 137.9, 130.0, 129.8, 128.2, 127.3, 120.1, 120.0, 115.8, 111.7, 55.5, 55.4; HRMS (ESI) calcd for $C_{15}H_{15}O_3SNa$ $[M+Na]^+$ 275.0742, found 275.0745.

S-(3-Methoxyphenyl) 4-ethoxybenzothioate (**3r**): White solid, 24.2 mg, 42% yield. m.p. 58～60 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=8.0 Hz, 2H), 7.35 (t, J=6.4 Hz, 1H), 7.10 (d, J=7.6 Hz, 1H), 7.06 (s, 1H), 6.98 (d, J=8.4 Hz, 1H), 6.94 (d, J=8.0 Hz, 2H), 4.10 (q, J=5.6 Hz, 2H), 3.82 (s, 3H), 1.45 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.5, 163.4, 159.8, 129.9, 129.7, 129.1, 128.5, 127.4, 120.1, 115.6, 114.3, 63.8, 55.4, 14.7; HRMS (ESI) calcd for $C_{16}H_{17}O_3SNa$ $[M+Na]^+$ 289.0898, found 289.0901.

S-(3-Methoxyphenyl) 4-(*tert*-butyl)benzothioate (**3s**): White solid, 29.4 mg, 49% yield. m.p. 65～68 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J=5.6 Hz, 2H), 7.49 (d, J=5.6 Hz, 2H), 7.35 (t, J=7.6 Hz, 1H), 7.10 (d, J=7.6 Hz, 1H), 7.07 (s, 1H), 6.98 (d, J=8.4 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.6, 159.9, 157.5, 134.0, 129.9, 128.4, 127.4, 127.3, 125.7, 120.1, 115.7, 55.4, 35.2, 31.1; HRMS (ESI) calcd for $C_{18}H_{21}O_2SNa$ $[M+Na]^+$ 301.1262, found 301.1270.

S-(3-Methyl-4-methoxyphenyl) 3-methoxybenzothioate

(**3t**): White solid, 31.6 mg, 55% yield. m.p. 66～68 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J=8.4 Hz, 2H), 7.81 (s, 1H), 7.35 (t, J=8.0 Hz, 1H), 7.10 (d, J=7.6 Hz, 1H), 7.07 (s, 1H), 6.98 (d, J=8.4 Hz, 1H), 6.86 (d, J=10.8 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.7, 162.2, 159.8, 130.0, 129.9, 128.8, 128.7, 127.6, 127.4, 127.1, 120.1, 115.6, 109.4, 55,4, 16.3; HRMS (ESI) calcd for $C_{16}H_{17}O_3SNa$ $[M+Na]^+$ 289.0898, found 289.0895.

S-(3-Methyl-4-methoxyphenyl) 3-methoxybenzothioate (**3u**): White solid, 33.3 mg, 52% yield. m.p. 88～91 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=8.4 Hz, 1H), 7.59 (d, J=8.4 Hz, 1H), 7.35 (t, J=8.0 Hz, 1H), 7.25～7.30 (m, 2H), 7.03 (d, J=7.2, Hz, 1H), 6.99 (s, 1H), 3.89 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.6, 159.9, 146.4, 139.7, 135.3, 130.0, 129.0, 128.4, 128.3, 128.1, 127.4, 127.3, 120.1, 115,8, 55.4; HRMS (ESI) calcd for $C_{20}H_{17}O_2SNa$ $[M+Na]^+$ 321.0949, found 321.0953.

S-(3-Methoxyphenyl)2,3-dihydrobenzofuran-5-carbothioate (**3v**): White solid, 21.7 mg, 38% yield. m.p. 88～89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=8.4 Hz, 2H), 7.35 (s, J=4.4 Hz, 1H), 7.09 (d, J=7.6 Hz, 1H), 7.06 (s, 1H), 6.97 (d, J=8.8 Hz, 1H), 6.82 (d, J=7.6 Hz, 1H), 4.68 (t, J=8.8 Hz, 2H), 3.82 (s, 3H), 3.26 (t, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.4, 164.9, 129.9, 129.6, 129.4, 128.6, 127.9, 127.6, 127.4, 124.7, 120.2, 115.6, 109.3, 72.3, 55.4, 29.0; HRMS (ESI) calcd for $C_{16}H_{17}O_3SNa$ $[M+Na]^+$ 289.0898, found 289.0902.

S-(3-Methoxyphenyl)9-phenyl-9*H*-carbazole-2-carbothioate (**3w**): Yellow oil, 36.8 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (s, 1H), 8.20 (d, J=7.6 Hz, 1H), 8.08 (d, J=8.4 Hz, 1H), 7.61 (t, J=8.0 Hz, 2H), 7.52 (d, J=6.4 Hz, 3H), 7.44 (d, J=8.0 Hz, 1H), 7.33～7.40 (m, 4H), 7.16 (d, J=7.6 Hz, 1H), 7.13 (s, 1H), 6.99 (d, J=8.4 Hz, 1H) , 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.3, 159.9, 143.9, 141.8, 136.8, 130.1, 129.9, 128.9, 128.8, 128.2, 127.5, 127.1, 126.9, 125,7, 123.3, 123.2, 121.1, 120.9, 120.7, 120.2, 115.7, 110.3, 109.7, 55.4; HRMS (ESI) calcd for $C_{26}H_{20}NO_2SNa$ $[M+Na]^+$ 410.1215, found 410.1220.

4.4 Functional group exchange reaction between thioesters

To a 25 mL Schlenk tube were added aryl thioester **3a** (0.2 mmol, 1.0 equiv.), aryl thioester **2b** (0.2 mmol, 1.0 equiv.), $NiBr_2(PPh_3)_2$ (0.02 mmol, 10 mol%), 2,2'-bipyridine (0.02 mmol, 10 mol%) and zinc (0.6 mmol, 3.0 equiv.). The mixture was evacuated and backfilled with N_2 for three times, NMP (1 mL) and DMSO (1 mL) were then added. The Schlenk tube was capped with screw and put into a preheated oil bath (80 ℃). After stirring for 2 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (40 mL). After washed with water (15 mL×2) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 ℃. The residue was purified with column chromatography on silica gel to give pure product **3a** as white solid.

Supporting Information Copies of ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra for all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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