E-Selective Hydrothiolation of Terminal Arylallenes with Arylthiols Catalyzed by Ni (PMe$_3$)$_4$

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A catalytic system of regioselective synthesis of allyl sulfides via hydrothiolation of terminal arylallenes with arylthiols has been developed using nickel(0) complex Ni (PMe$_3$)$_4$ as a catalyst. In most cases the excellent to moderate yields were obtained under mild conditions. A catalytic mechanism was suggested and partially-experimentally verified. To the best of our knowledge, this is the first example of regioselective addition of thiophenols to terminal arylallenes catalyzed by nickel(0) complex. It was noteworthy that this catalytic system was only applicable to thiophenol compounds with terminal arylallenes.

KEYWORDS

allyl sulfide, hydrothiolation, nickel complex, terminal arylallene, thiophenol

1 | INTRODUCTION

Allyl and vinyl sulfides are synthesized through different reactions and become attractive chemical reagents and intermediates which have been widely utilized in various synthetic reactions.[1–16] Traditionally, phenyl vinyl sulfides were obtained by reaction of hydrothiolation of alkynes. The non-catalytic system via free radical addition mechanism of thiophenol to alkyne gave a mixture of anti-Markovnikov isomers.[17,18] The efficient regioselective additions of thiols to alkynes catalyzed by nickel complexes were reported by Ananikov and Beletsakaya.[19,20] Ranu reported an efficient hydrothiolation of alkynes in

water without any catalysts or additives, imparting good control on regioselectivity.[21] Wilkinson's complex RhCl (PPh$_3$)$_3$ could also catalyze the regio- and stereoselective addition of thiols to alkynes leading to the anti-Markovnikov products.[22,23]

In comparison with vinyl sulfides, the reports on the synthesis of phenyl allyl sulfides through selective addition of thiols to allenes are rare. It has been reported that thiols add to allenes to give a mixture of different vinyl sulfides and allyl sulfides by a free radical mechanism.[24–27] These results make the radical reactions synthetically less useful. The Ogawa group has developed a palladium-catalyzed regioselective addition of benzenethiol to allenes but in this case the terminal vinylic sulfides were the sole products.[28,29] The regiospecific intermolecular hydrothiolation of allenes could also be catalyzed by
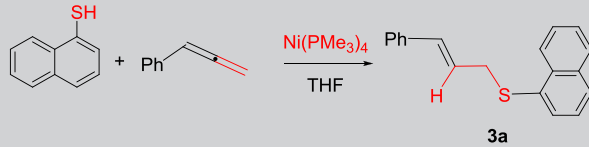
Au.[29b] In 2011, an effective method for the catalytic asymmetric addition of aryl thiols to the γ-position of allenoates catalyzed by a chiral phosphepine was developed by Fu.[30] This can be regarded as a successful example of synthesis of allyl sulfides. Recently, Breit reported the first rhodium-catalyzed enantioselective atom-economic hydrothiolation of terminal allenes with free thiols towards branched allylic thioethers and their corresponding sulfones in high yields.[31,32] However, as far as we know, until now there was no report on nickel-catalyzed regioselective addition of thiols to allenes. Herein we report the first Ni-catalyzed regioselective atom-economic addition of thiophenols to terminal allenes towards corresponding phenyl allyl sulfides in the E-form of configuration.

2 | RESULTS AND DISCUSSION

The studies were carried out with naphthalene-1-thiol and phenyl allene as the model substrates by using 5 mol % different nickel compounds as catalysts in THF at 40 °C (Table 1). Under the same experimental conditions, the control experiment showed that **3a** could not be detected without catalyst (Table 1, entry 1). Among the studied nickel compounds, Ni (PMe$_3$)$_4$ is the best catalyst, the substrate was completely converted to **3a** after 4 hr in a yield of 96% (Table 1, entry 2–12). When the catalyst loading was decreased to 2 mol%, the substrate was also completely converted to **3a** after 4 hr a yield of 97% (Table 1, entry 13). When the catalyst loading was decreased to 1 mol%, the isolated yield of **3a** is only 25% (Table 1, entry 14). The isolated yield of **3a** is 89% when the reaction temperature was decreased to 25 °C and reaction time raised to 8 hr (Table 1, entry 15). With the increase of the reaction temperature to 60 °C, the isolated yield of **3a** is decreased to 91% (Table 1, entry 16). When the other phosphine, such as dppp, dppe, PPh$_3$ or dppf, was added to the catalytic mixture, the isolated yield of **3a** was reduced (Table S1, entries 1–4 of the SI). However, the yield of **3a** was 20% when using 2 mol% Ni (COD)$_2$ as the catalyst (Table S1, entry 5 of the SI). The yield of **3a** was 92% when dppp was added (Table S1, entry 6 of the SI). More results were obtained with dppf as an additive for Ni (PMe$_3$)$_4$ and Ni (COD)$_2$ catalysts (Table S1, entries 4 and 9). The polarity of solvent has influence on this catalytic reaction dramatically (Table S1, entries 11–20 of the SI). The yield of **3a** in the solvent (DMSO) with large polarity was 94% (Table S1, entry 18 of the SI). The yield of **3a** in the solvent (THF) with moderate polarity was 97% (Table S1,

entry 13). The yield of the reaction in *n*-pentane is the smallest (15%) (Table S1, entry 13 of the SI).

From Table 1 we conclude that the optimized catalytic reaction conditions are: arylallene (1.0 mmol), thiophenol (1.2 mmol) and Ni (PMe$_3$)$_4$ (2 mol%) in 3 ml THF at 40 °C for 4 hr (Table 1, entry 13). Under the optimized conditions, the scope of the substrates was expanded (Table 2). The hydrothiolation addition occurred selectively at the terminal double bond of the arylallenes (Table 2). It was found that the reaction of thiophenol with phenyl allene in the presence of 2 mol % of Ni (PMe$_3$)$_4$ at 40 °C for 4 hr in THF (3 ml) led to 94% yield of phenyl allyl sulfide **1a** (Table 2, entry1). Similarly, *p*-toluenethiol underwent regioselective addition of phenyl allene to provide corresponding phenyl allyl sulfides **2a** in 68% yield (Table 2, entry 2). As for *p*-chlorophenyl allene, the addition reactions of *p*-toluenethiol, thiophenol and naphthalene-1-thiol to the terminal double bond gave rise to **4a**, **5a** and **6a** in high yields (Table 2, entries 4–6). In addition, with electron-donating methyl group at the *para*-position, the related phenyl allyl sulfide **9a** was obtained in the yield of 86% with regioselective addition of 1-naphthalene-1-thiol to *p*-methylphenyl allene (Table 2, entry 9). For thiophenol and *p*-toluenethiol, the hydrothiolations with *p*-methylphenyl allene gave the related allyl sulfides **7a** and **8a** in the moderate yields of 74% and 48% respectively (Table 2, entries 7 and 8). For *p*-fluorophenyl allene, the addition reactions with 1-naphthalene-1-thiol and thiophenol afforded the corresponding allyl sulfides **10a** and **11a** in 97% and 95% yield respectively (Table 2, entries 10 and 11). Two 2,3-addition vinyl sulfides (**12a** and **12b**) were isolated when *p*-fluorophenyl allene with *p*-toluenethiol reacted (Table 2, entry 12). The reactions of *p*-bromophenyl allene with 1-naphthalene-1-thiol gave rise to two 2,3-addition products (**13a** and **13b**) and one 1,2-addition product (**13c**) (Table 2, entry 13). The reaction of p-bromophenyl allene with thiophenol delivered also three products, two 2,3-addition products (**15a** and **15b**) and one 1,2-addition product (**15c**) (Table 2, entry 15). However, only 2,3-addition products (**14a** and **14b**) were found from the reaction of *p*-bromophenyl allene with *p*-toluenethiol (Table 2, entry 14). The reaction of 1,1-diphenyl allene with 1-naphthalene-1-thiol afforded both 1,2-addition product (**16c**) and 2,3-addition product (**16b**) without allyl sulfide (Table 2, entry 16). It is interesting that only one 2,3-addition product (**17b**, vinyl sulfide) was isolated in 96% yield (Table 2, entry 17). As in entry 16 in Table 2, two isomers of the addition products (**18b** and **18c**) were also produced in entry 18 of Table 2. The ratio of the 2,3-addition to 1,2-addition product can be derived from ^{1}H NMR spectra (see the

TABLE 1 Exploration of hydrothiolation of phenyl allene with naphthalene 1 thiol catalyzed by nickel compounds[a]

Entry	Catalyst (mol%)	Additive (mol%)	Time (h)	Temp.(°C)	Conv.[b] (%)	Yield[c] (%)
1	0		4	40	0	0
2	Ni (acac)$_2$ (5)		4	40	10	4
3	NiBr$_2$ (5)		4	40	35	28
4	NiCl$_2$ (5)		4	40	40	30
5	Ni (OAc)$_2$ (5)		4	40	0	0
6	NiCl$_2$ (5)	dppp (20)	4	40	0	0
7	NiCl$_2$ (5)	PMe$_3$(20)	4	40	41	32
8	Ni (acac)$_2$ (5)	PPh$_3$(20)	4	40	0	0
9	Ni (acac)$_2$ (5)	PCy$_3$(20)	4	40	0	0
10	Ni (acac)$_2$ (5)	dppp (20)	4	40	39	30
11	Ni (acac)$_2$ (5)	dppe (20)	4	40	30	29
12	Ni (PMe$_3$)$_4$ (5)		4	40	99	96
13	Ni (PMe$_3$)$_4$ (2)		4	40	99	97
14	Ni (PMe$_3$)$_4$ (1)		4	40	25	25
15	Ni (PMe$_3$)$_4$ (2)		8	25	90	89
16	Ni (PMe$_3$)$_4$ (2)		4	60	92	91

a) Catalytic reaction conditions: phenyl allene (1.0 mmol), naphthalene 1 thiol (1.0 mmol), THF (3 ml).

b) Determined by GC with dodecane as an internal standard.

c) Isolated Yield.

SI). Generally, the influence of substituent group at the phenyl ring in arylallene on the yield of allyl sulfides is not significant. In comparison with thiophenol and 1-naphthalene-1-thiol, *p*-toluenethiol with an electron-donating methyl group made the breaking of the S-H bond more difficult. Therefore, the yields of products **2a**, **5a** and **8a** seem to be relatively lower. 1-Naphthalene-1-thiol was more active than thiophenol and the hydrothiolation products of 1-naphthalene-1-thiol were obtained in higher yields (comparing **1a** /**3a**; **4a**/**6a**; **7a**/**9a**). Although we have not yet concluded the rule, the formation of the addition isomers is related to the substituents of the two reactants. Among all the products, the configurations of (*E*)-1-Phenyl-3-phenylthio-1-propene (**1a**) and (*E*)-1-Phenyl-3-(p-methylphenyl)thio-1-propene (**2a**) were determined by comparing literature data.[33,34] The *E*-configuration of the products **1a, 2a, 3a, 4a, 5a, 7a, 8a, 9a, 10a, 11a, 14a, 15a** could be determined by the coupling constant $^3J_{H-H}$ (-C*H*=C*H*-). The configuration of the products **6a, 12a, 13a, 12b, 13b, 14b, 15b** could not be determined.

The molecular structure of product **7a** was determined by single crystal X-ray diffraction (Figure 1). This is a further evidence for this nickel-catalyzed regioselective hydrothiolation of terminal arylallenes with arylthiols. The bond lengths of C8-C9 (1.297(3) Å) and C7-C8 (1.508(3) Å) indicate that C8-C9 is a double bond and C7-C8 is a single bond. Compound **7a** has an (*E*)-configuration.

It was noteworthy that this catalytic system was only applicable to thiophenol compounds with aromatic terminal allenes. Under the optimized catalytic conditions, the hydrothiolation of trisubstituted or aliphatic allene with naphthalene-1-thiol and hydrothiolation of phenyl allene with thioethanol did not occur (Table 2, entries 19–21). We think that both aliphatic allenes and aliphatic thiols are not active for this catalytic system.

Based on the report of hydrothiolation catalyzed by Pd (PPh$_3$)$_4$,[29] a plausible mechanism for the nickel-catalyzed hydrothiolation was proposed in Scheme 1. At the beginning, Ni (PMe$_3$)$_4$ reacts with thiophenol to

TABLE 2 Hydrothiolation of arylallenes catalyzed by Ni (PMe$_3$)$_4$[a]

Entry	Allene	Thiophenol	Conv.[b]	Yield (a) [%][c]	Yield (b) [%][c]	Yield (c) [%][c]
1			96	1a (94)		
2			68	2a (61)		
3			99	3a (97)		
4			97	4a (91)		
5			93	5a (88)		
6			95	6a (90)		
7			78	7a (74)		
8			51	8a (48)		
9			91	9a (86)		
10			98	10a (97)		

(Continues)

TABLE 2 (Continued)

| Entry	Allene	Thiophenol	Conv.[b]	Yield (a) [%][c]	Yield (b) [%][c]	Yield (c) [%][c]
11			97	11a (95)		
12			85	12a (47)	12b (35)	
13[d]			96	13a (40)	13b (23)	13c (31)
14			98	14a (76)	14b (19)	
15[d]			99	15a (33)	15b (42)	15c (21)
16[d]			95		16b (50)	16c (43)
17			99		17b (96)	
18[d]			99		18b (41)	18c (57)
19			0			
20			0			

(Continues)

TABLE 2 (Continued)

Entry	Allene	Thiophenol	Conv.[b]	Yield (a) [%][c]	Yield (b) [%][c]	Yield (c) [%][c]
21	(phenylallene structure)	Et—SH	0			

[a]Catalytic reaction conditions: allene (1.0 mmol), thiophenol (1.0 mmol) and Ni (PMe₃)₄ (2 mol%) in 3 ml THF, 40 °C, 4 h.

[b]Determined by GC with *n* dodecane as an internal standard.

[c]Isolated Yields.

[d]Yields and **b/c** ratios were determined by ^{1}H NMR of mixed isomers.
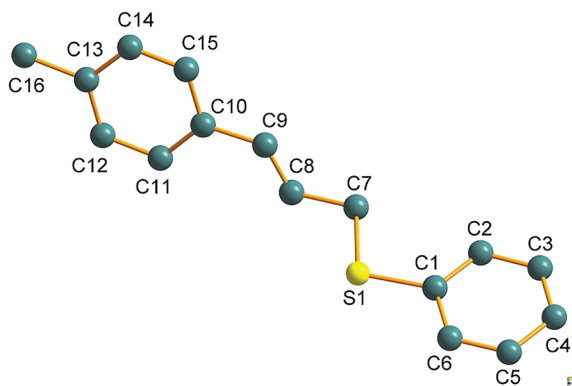

FIGURE 1 Molecular structure of compound 7a

produce hydrido nickel (II) species **A** as an active catalyst with the dissociation of two PMe₃ ligands via oxidative addition of S-H bond. π-Coordination of arylallene double bond to the nickel center affords intermediate **B**. Theoretically, there are four different coordination modes for intermediate **B** (**Ba**, **Bb**, **Bc** and **Bd**). From the four intermediate **B**s four related intermediate **C**s (**Ca**, **Cb**, **Cc** and **Cd**) as regioselective addition products in the catalytic cycle were formed through the insertion of arylallene double bond into the Ni-H bond. Reductive elimination between Ni-C and Ni-SAr₁ bond at nickel center of **C** gives rise to the final product to complete the catalytic cycle with the regeneration of the catalyst Ni (PMe₃)₄. In our results, only E-allyl sulfides (product **a**) were formed from entry 1 to 11. For entries 12 and 14 both **a** and **b** could be obtained. For entries 13 and 15 three products (**a**, **b** and **c**) were confirmed. For entries 16 and 18 **b** and **c** were verified. **b** is the sole product for entry 17. It must be point out that there was no **d** generation in any cases because the steric hindrance in intermediate **Bd** is too large. We consider that the selectivity is determined by the formation of intermediate **B**. Many factors, such as the electronic property

at the Ni canter or at the C=C bond, the electronic property and steric hindrance of Ar₁, Ar₂ and Ar₃, ... have effects on the formation of **B**. A concrete rule has not been drawn out because of the limited substrates. In short, the selectivity of the system is very complicated. Regrettably, isolation of intermediates **A**, **B** and **C** was not successful. According to this mechanism, we believe that the aliphatic thiol does not react because its S-H bond is less susceptible to oxidative addition and it has no aromatic *p*-π conjugation. The allenes bearing a Cl or a F atom at the *para*-position (entries 4–6 and 9–11, Table 2) gave products **a** as the sole products, whereas the allenes bearing a Br atom at the *para*-position (entries 13–15, Table 2) showed lower selectivity. We believe that the electron-withdrawing ability of Br atom is less than that of F and Cl atom, which leads to a decrease in the polarity of the allene double bonds of the intermediate **B** in the reaction mechanism, resulting in a decrease in selectivity.

In order to verify the feasibility of this nickel-catalyzed reaction mechanism, the following experiments were performed (Scheme 2 and **Equations (1)–(2)**). In the first experiment, Ni (PMe₃)₄ reacted with stoichiometric thiophenol (Scheme 2). From this reaction *trans*-Ni (PMe₃)₂(SPh)₂ as S-H bond activation product was obtained and its molecular structure was confirmed by ^{1}H NMR and ^{31}P NMR.[35] Even though intermediate **A** could not be isolated, the similar hydrido thiophenolato iron complexes could be obtained from the reaction of Fe (PMe₃)₄ with thiophenol.[36] Therefore, it is proposed that *trans*-Ni (PMe₃)₂(SPh)₂ was formed through the dismutation of Ni(I) intermediate **D** with the production of Ni (PMe₃)₄. As another alternative, the disproportionation of intermediate **A** also gives rise to Ni (SAr)₂(PPh₃)₂ and Ni (PPh₃)₄ with the release of molecular hydrogen. The formation of H₂ was confirmed by GC. In the second experiment *trans*-Ni (PMe₃)₂(SPh)₂ as a
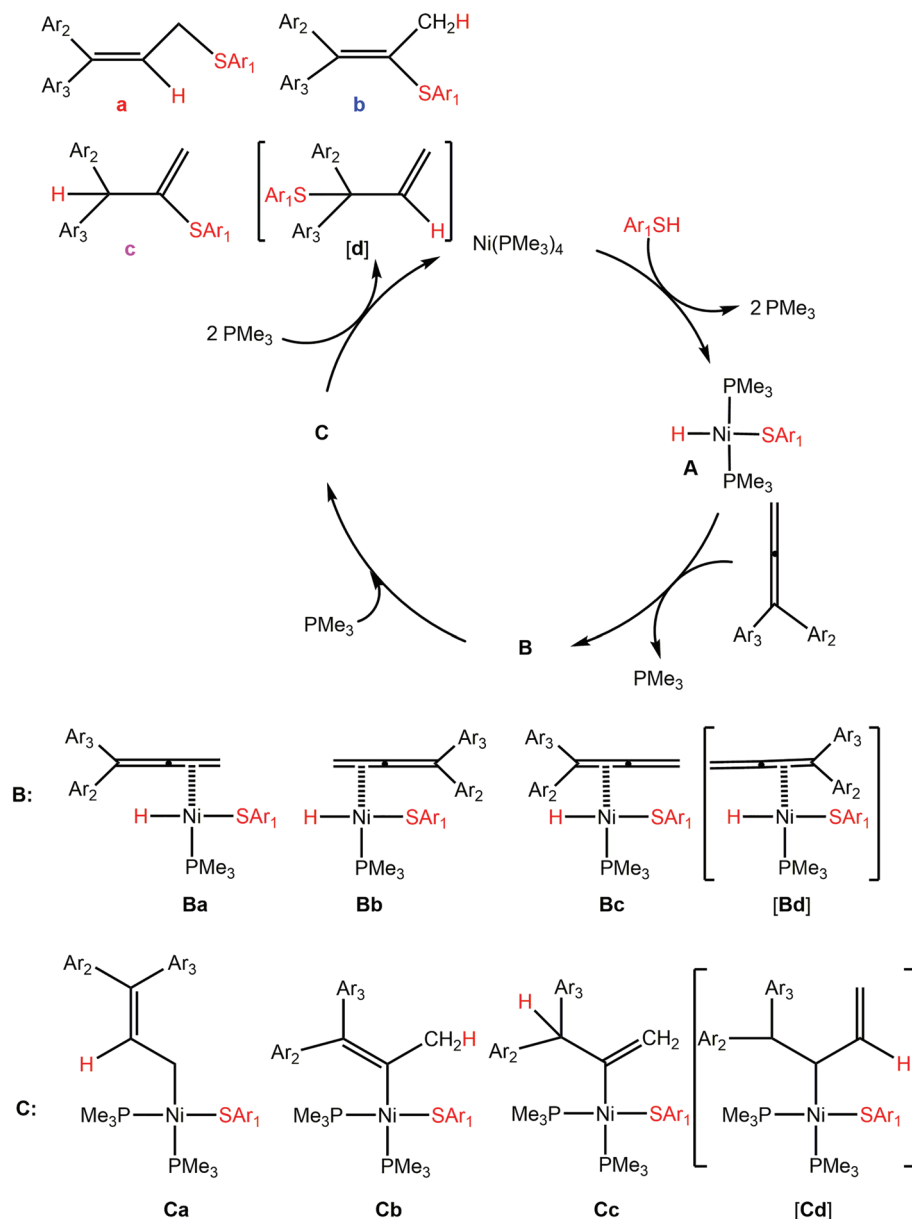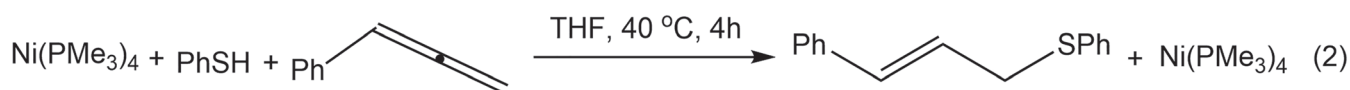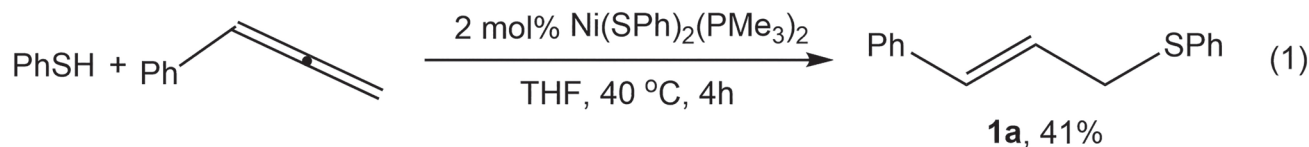
SCHEME 1 Plausible mechanism for the nickel catalyzed hydrothiolation
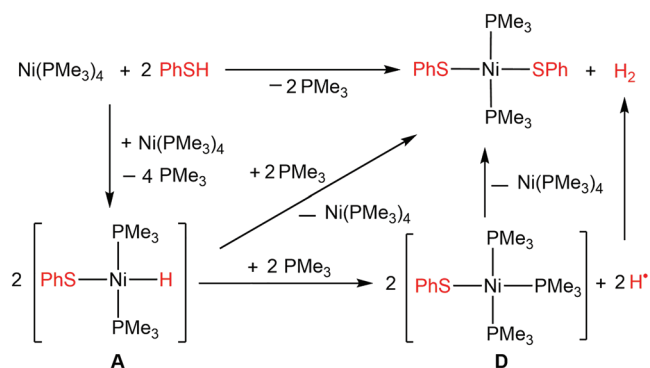
SCHEME 2 Investigation of the mechanism

catalyst (2 mol %) was used in the thiophenol addition reaction to phenyl allene, **1a** was isolated in only 41% yield at 40 °C after 4 h (**Equation (1)**). The catalytic activity of *trans*-Ni (PMe$_3$)$_2$(SPh)$_2$ is much lower than Ni (PMe$_3$)$_4$. This implies that *trans*-Ni (PMe$_3$)$_2$(SPh)$_2$ is not the real catalyst in this catalytic system. In order to further verify that *trans*-Ni (PMe$_3$)$_2$(SPh)$_2$ does not participate in the catalytic cycle, the three-component-reaction of Ni (PMe$_3$)$_4$ with thiophenol and phenyl allene was carried out (**Equation (2)**). Through this reaction **1a** was isolated and at the same time Ni (PMe$_3$)$_4$ was recovered. No *trans*-Ni (PMe$_3$)$_2$(SPh)$_2$ was detected in this reaction.

$$PhSH + Ph\diagup\!\!\!\!\diagdown \xrightarrow[\text{THF, 40 °C, 4h}]{\text{2 mol\% Ni(SPh)}_2\text{(PMe}_3)_2} Ph\diagup\!\!\!\diagdown SPh \quad (1)$$

1a, 41%

$$Ni(PMe_3)_4 + PhSH + Ph\diagup\!\!\!\!\diagdown \xrightarrow{\text{THF, 40 °C, 4h}} Ph\diagup\!\!\!\diagdown SPh + Ni(PMe_3)_4 \quad (2)$$

In comparison with the early reported reactions of allenes with thiols,[24–27] Our system is regioselective and useful for the synthesis of allyl sulfides. In addition, this transformation is atom-economic. This is also an example of catalytic hydrothiolation catalyzed by base metal complex.

3 | CONCLUSIONS

In summary, a catalytic system of regioselective addition of thiophenols to terminal arylallenes has been established using nickel(0) complex Ni (PMe$_3$)$_4$. The excellent to moderate yields were obtained under mild conditions. A catalytic mechanism was suggested and partially-experimentally verified. To the best of our knowledge, this is the first example of regioselective addition of thiophenols to terminal allenes catalyzed by nickel(0) complex. It was noteworthy that this catalytic system was only applicable to the reactions of thiophenol compounds with aromatic terminal allenes.

4 | EXPERIMENTAL

4.1 | General procedures and materials

Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. ^{1}H NMR and ^{13}C{H} NMR spectra were recorded using Bruker Avance 300 MHz spectrometers. GC–MS was recorded on a TRACE-DSQ instrument and GC was recorded on a Fuli 9790 instrument. Melting points were measured in capillaries sealed under N$_2$ and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII. Ni (PMe$_3$)$_4$ was prepared according to literature procedure.[37,38] All the allenes and thiophenols were synthesized according to literature.[39,40]

4.2 | General procedure for nickel-catalyzed hydrothiolation of terminal allenes with thiols

To a 25 ml Schlenk tube containing a solution of 2 mol% Ni (PMe$_3$)$_4$ in 3 ml of THF was added an allene (1.0 mmol) and thiophenol (1.2 mmol). The reaction mixture was stirred at 40 °C for 4 hr (monitored by TLC). Then 20 ml of Et$_2$O was added to the mixture and the remaining thiophenol was removed by extraction with 25 ml of aqueous NaOH (5 M). The organic layer was dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under vacuum. The product was further purified using flash column chromatography. The ^{1}H NMR and ^{13}C NMR spectra of the products are provided in the Supporting Information.

4.3 | Reaction of Ni (PMe$_3$)$_4$ with PhSH

A sample of Ni (PMe$_3$)$_4$ (0.86 g, 2.36 mmol) in 50 ml of pentane was combined with PhSH (0.26 g, 2.36 mmol) in 30 ml of pentane at −78 °C. The reaction mixture was warmed to 25 °C and stirred for 24 hr to get a red solution. Ni (SPh)$_2$(PMe$_3$)$_2$[35] as red crystals was obtained after filtering at −20 °C. Yield: 0.27 g (0.63 mmol, 53%).

4.4 | X-ray structure determination

The single crystals of **7a** were obtained from its Et$_2$O solution by evaporation. Intensity data were collected on a STOE STADIVARI Cu diffractometer. Using Olex2,[41] the structure was solved with ShelXS[42] structure solution program using Direct Methods and refined with the ShelXL[43] refinement package using Least Squares minimization. CCDC 1515027 (**7a**) contains supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223–336-033; e-mail: deposit@ccdc.cam.ac.uk).

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