NHPI-catalyzed Synthesis of β-phenethyl Sulfide Derivatives

Honghe JI[1,2], Yanni WU[1,2], Shaopin ZHANG[1], Chunsheng LI[1]*

1. School of Environmental and Chemical Engineering, Zhaoqing University, Zhaoqing 526061, China; 2. New Energy and New Materials Research Center, Zhaoqing 526061, China

Abstract A green and efficient protocol has been developed for the synthesis of a series of β-phenethyl sulfide derivatives via the radical reaction of styrenes with thiophenols, employing N-hydroxyphthalimide (NHPI) as a radical initiator. Systematic optimization of reaction parameters, including solvent, reaction temperature, and duration, led to the identification of optimal conditions that afforded the desired products in yields of up to 98%. Studies on substrate scope with a diverse set of styrenes and thiophenols revealed that this transformation proceeds under mild conditions with broad substrate generality and excellent functional group compatibility. Owing to these advantageous features, the present method shows potential for application in the synthesis of herbicides, acaricides, fungicides, and insecticides, while the resulting β-phenethyl sulfides serve as valuable intermediates in pesticide synthesis.

Key words β-phenethyl sulfide, Styrene, Radical initiator

0 Introduction

Sulfides, recognized as biologically active compounds, are frequently present within the structural frameworks of natural products, pharmaceuticals, and pesticides[1-3]. Owing to the distinctive physicochemical characteristics of the S atom, sulfide-containing molecules exhibit superior lipid solubility and membrane permeability, rendering them critically important in the synthesis of herbicides, insecticides, and various other pesticides[4]. Sulfides are a central focus in the research and development of novel agrochemicals and represent a fundamental component of the pesticide industry. Regarding the mechanism of drug action, sulfides exhibit mild toxicity and favorable compatibility. Upon entering the bodies of pests and pathogens, they are metabolized by cytochrome P450 enzymes to form sulfoxide and sulfone derivatives. These metabolites display significantly increased polarity, which enhances their binding affinity to biological targets. Furthermore, at the molecular level, sulfides disrupt protein thiol homeostasis in pests and pathogens and inhibit their energy transfer processes. Thus, sulfides demonstrate notable advantages compared to conventional pesticides, such as those containing C-O and C-N bonds[5].

Common sulfide pesticides are compounds characterized by the presence of aryl-S-aryl or alkyl-S-aryl moieties within their molecular structures, examples of which include tetrasul, temephos, pyrithiobac-sodium, and sulfiflumin[6-8]. The Williamson ether synthesis is a classical method for the preparation of asymmetric ethers, holding a significant place in the development of organic synthesis[9]. However, this reaction typically requires a strongly alkaline environment to facilitate the SN2 nucleophilic substitution. Such conditions often promote elimination reactions, leading to the formation of complex and heterogeneous product mixtures. The dialkylation of inorganic sulfides is the earliest industrial method for synthesizing sulfides[10-11]. However, this reaction exhibits certain limitations, as it is only suitable for the synthesis of symmetrical sulfides and often results in complex product mixtures that are difficult to separate. To date, with ongoing advancements in catalytic systems, alternative synthetic methods distinct from traditional approaches have been developed. In 2016, Akiya's research group developed an anti-Markovnikov hydrothiolation of alkenes and thiophenol catalyzed by Au, achieving high yields and excellent selectivity[12]. In 2019, Dong's research group reported a hydrothiolation of 1,3-dienes catalyzed by Rh complexes[13]. This reaction selectively produces allyl sulfides through coordination of ligands at the Rh center. In 2019, Qing's research group developed a visible light-catalyzed redox reaction[14], employing trifluoromethanesulfonic anhydride as the sulfur source and water as the hydrogen source, thereby achieving the trifluoromethylthiolation of alkenes and alkynes. In 2025, Kang's research group introduced a greener and milder reaction pathway[15]. Mediated by hydrogen sulfides, alkenes underwent selective thiolation via Markovnikov addition, notably without the need for metal catalysts or additional additives.

Although numerous methods for synthesizing sulfides have been documented, the development of more efficient and environmentally sustainable green synthesis techniques remains highly significant. In recent years, the emphasis on green chemistry and environmental protection has been a persistent focus within the field of synthesis. N-hydroxyphthalimide (NHPI), recognized as a free radical initiator, is cost-effective, exhibits low toxicity, and is environmentally benign, making it widely applicable in the free radical addition reactions of alkenes[16-18]. Based on the existing research foundation[19-20], we designed and synthesized a series of β-phenethyl sulfide derivatives by employing NHPI as a free radical initiator to activate thiophenol substrates, thereby facilitating their addition to aryl alkenes under mild conditions.

Received: July 20, 2026 Accepted: September 25, 2026

Supported by University-level Research Fund Project of Zhaoqing University (QN202348).

Honghe JI, master's degree, assistant lecturer, research fields: green organic synthesis and functional materials. * Corresponding author. Chunsheng LI, doctoral degree, lecturer, research fields: green organic chemical synthesis and functional materials.

1 Experiments

1.1 General steps in hydrothiolation In a 25 mL Schlenk tube, 0.6 mmol of thiophenol (1a), 0.3 mmol of styrene (2a), 0.3 mmol of NHPI, and 5 mL of acetone as the solvent were combined. The mixture was reacted at 60 ℃ for 6 – 8 h, with reaction progress monitored by TLC. Upon completion, the reaction mixture was collected and concentrated using a rotary evaporator to remove acetone. Subsequently, 10 mL of ethyl acetate was added to dissolve the residue, followed by the addition of 10 mL of saturated brine. The mixture was then extracted with 10 mL of ethyl acetate; this extraction was repeated three times. The combined organic layers were evaporated and concentrated. The final product was purified by column chromatography on 300-mesh silica gel, employing a gradient elution with ethyl acetate and petroleum ether at volume ratios ranging from 1∶100 to 1∶40.

1.2 Structural characterization

Phenethyl(*p*-tolyl) sulfane (3a), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.29 – 7.19 (m, 4 H), 7.19 – 7.11 (m, 3 H), 7.08 – 7.05 (m, 2 H), 3.13 – 3.02 (m, 2 H), 2.89 – 2.78 (m, 2 H), 2.27 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 140.6, 136.4, 132.8, 130.3, 129.9, 128.7, 128.6, 126.7, 36.1, 35.9, 21.3.

(4-Methoxyphenethyl)(phenyl) sulfane (3b), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.30 (d, J = 8.7 Hz, 2 H), 7.26 – 7.18 (m, 2 H), 7.17 – 7.04 (m, 3 H), 6.80 (d, J = 8.7 Hz, 2 H), 3.74 (s, 3 H), 3.04 – 2.96 (m, 2 H), 2.84 – 2.76 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 159.2, 140.7, 133.4, 128.6, 128.7, 126.6, 126.5, 114.8, 55.6, 37.4, 36.1.

(4-(*tert*-Butyl)phenyl)(phenethyl) sulfane (3c), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.42 – 7.32 (m, 6 H), 7.28 (t, J = 8.7 Hz, 3 H), 3.25 – 3.17 (m, 2 H), 3.04 – 2.94 (m, 2 H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 149.4, 140.4, 132.9, 129.5, 128.6, 126.6, 126.0, 35.9, 35.6, 34.6, 31.4.

(4-Fluorphenyl)(phenethyl) sulfane (3d), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.39 – 7.35 (m, 2 H), 7.33 – 7.28 (m, 2 H), 7.26 – 7.17 (m, 3 H), 7.04 – 6.99 (m, 2 H), 3.13 (dd, J = 9.0, 6.7 Hz, 2 H), 2.90 (dd, J = 9.0, 6.7 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 163.2, 160.9, 140.2, 132.6, 132.5, 131.4, 131.2, 128.8, 128.7, 116.4, 116.1, 36.6, 36.0.

(4-Chlorophenyl)(phenethyl) sulfane (3e), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.33 – 7.18 (m, 9 H), 3.16 (dd, J = 8.9, 6.8 Hz, 2 H), 2.93 (dd, J = 8.9, 6.7 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 140.1, 135.3, 132.1, 130.8, 129.3, 128.8, 128.6, 126.8, 35.6, 35.4.

(4-Bromophenyl)(phenethyl) sulfane (3f), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.42 (d, J = 8.6 Hz, 2 H), 7.34 – 7.29 (m, 2 H), 7.27 – 7.18 (m, 5 H), 3.16 (dd, J = 9.0, 6.9 Hz, 2H), 2.93 (dd, J = 9.0, 6.9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.1, 135.8, 132.2, 130.8, 128.8, 128.6, 126.9, 119.9, 35.7, 35.3.

(2-Fluorophenyl)(phenethyl) sulfane (3g), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.46 – 7.38 (m, 1 H), 7.33 (t, J = 7.2 Hz, 2 H), 7.29 – 7.18 (m, 4 H), 7.16 – 7.05 (m, 2 H), 3.24 – 3.13 (m, 2 H), 3.00 – 2.88 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 160.3, 140.1, 132.2, 132.2, 128.7, 128.5, 124.5, 122.9, 115.9, 115.6, 35.8, 34.9.

(3-Bromophenyl)(phenethyl) sulfane (3h), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.49 (s, 1 H), 7.35 (t, J = 7.3 Hz, 3 H), 7.26 (dd, J = 16.7, 7.5 Hz, 4 H), 7.17 (t, J = 7.9 Hz, 1 H), 3.24 – 3.16 (m, 2 H), 3.01 – 2.92 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 139.9, 139.0, 131.2, 130.3, 128.9, 128.6, 128.6, 127.3, 126.7, 122.9, 35.4, 34.9.

(2,6-Dimethylphenyl)(phenethyl) sulfane (3i), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.31 (d, J = 7.0 Hz, 2 H), 7.26 – 7.07 (m, 6 H), 3.00 – 2.89 (m, 2 H), 2.90 – 2.80 (m, 2 H), 2.56 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 143.2, 140.6, 133.4, 128.5, 128.4, 128.3, 128.2, 126.4, 36.6, 36.4, 22.2.

(4-Methylphenethyl)(*p*-tolyl) sulfane (4a), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.40 – 7.37 (d, J = 8.0 Hz, 2 H), 7.23 – 7.16 (m, 6 H), 3.23 – 3.19 (t, J = 7.4 Hz, 2 H), 2.99 – 2.95 (t, J = 7.4 Hz, 2 H), 2.43 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 137.6, 136.4, 136.1, 132.9, 130.2, 130.0, 129.4, 128.7, 36.1, 35.6, 21.3.

(4-Methoxyphenethyl)(*p*-tolyl) sulfane (4b), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.29 – 7.26 (d, J = 8.1 Hz, 2 H), 7.12 – 7.08 (m, 4 H), 6.84 – 6.81 (d, J = 8.5 Hz, 2 H), 3.77 (s, 3 H), 3.11 – 3.06 (t, J = 7.3 Hz, 2 H), 2.87 – 2.82 (t, J = 8.3 Hz, 2 H), 2.32 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 158.1, 136.0, 132.6, 132.2, 129.9, 129.6, 129.3, 113.8, 55.0, 36.0, 34.7, 20.9.

[4-(*tert*-Butyl)phenethyl](*p*-tolyl) sulfane (4c), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.38 – 7.23 (m, 4 H), 7.18 – 7.13 (m, 4 H), 3.16 (t, J = 7.9 Hz, 2 H), 2.90 (t, J = 7.9 Hz, 2 H), 2.37 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 149.3, 137.4, 136.0, 132.8, 129.9, 129.9, 128.3, 125.4, 35.7, 35.4, 34.4, 31.5, 21.2.

(4-Chlorophenethyl)(*p*-tolyl) sulfane (4d), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.28 – 7.22 (m, 4 H), 7.12 – 7.07 (m, 4 H), 3.10 – 3.05 (t, J = 7.4 Hz, 2 H), 2.87 – 2.82 (t, J = 8.2 Hz, 2 H), 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 138.6, 136.2, 132.1, 131.9, 130.2, 129.8, 129.6, 128.5, 35.6, 34.9, 21.0.

(4-Bromophenethyl)(*p*-tolyl) sulfane (4e), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.42 (d, J = 8.4 Hz, 2 H), 7.30 – 7.27 (d, J = 8.4 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 2 H), 7.08 – 7.05 (d, J = 8.0 Hz, 2 H), 3.11 (t, J = 7.4 Hz, 2 H), 2.88 – 2.84 (t, J = 7.4 Hz, 2 H), 2.35 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 139.4, 136.6, 132.4, 131.7, 130.6, 130.4, 130.0, 120.4, 35.9, 35.3, 21.2.

(4-Nitrophenethyl)(*p*-tolyl) sulfane (4f), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.23 – 8.13 (m, 2 H), 7.42 –

7.25 (m, 4 H), 7.17 (d, J=8.0 Hz, 2 H), 3.25–3.14 (m, 2 H), 3.04 (dd, J=8.5, 6.5 Hz, 2 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 148.0, 146.7, 137.0, 131.6, 130.8, 129.9, 129.6, 123.8, 35.5, 35.5, 21.2.

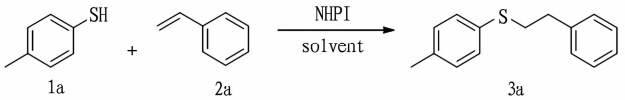
***p*-Tolyl(2,4,6-trimethylphenethyl)sulfane(4g)**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.43 (d, J=8.0 Hz, 2 H), 7.22 (d, J=8.0 Hz, 2 H), 6.92 (d, J=8.0 Hz, 2 H), 3.03 (t, J=7.3 Hz, 2 H), 2.97 (t, J=7.3 Hz, 2 H), 2.43 (s, 3 H), 2.31 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 136.6, 136.4, 136.0, 134.3, 132.7, 130.9, 129.9, 129.3, 33.6, 30.1, 21.3, 21.0, 19.9.

2 Results and analysis

2.1 Screening and optimization of conditions In this study, p-toluenethiol (1a) and styrene (2a) served as the model substrates for the optimization of reaction conditions. Various catalysts, solvents, reaction temperatures, and durations were systematically evaluated, leading to the identification of the optimal conditions (Entry 8). The details of the optimization process are presented in Fig. 1. Based on previous research foundations[19-20], we initially screened solvents suitable for this reaction (Entries 1-6). The reaction was conducted at 40 ℃ using 0.2 mmol of p-toluenethiol (1a, 1 eq) and 0.2 mmol of styrene (2a, 1 eq) as substrates. In the presence of a catalytic amount (20%) of NHPI, the solubility of the reaction mixture in DCM and dioxane was found to be poor, resulting in a turbid solution. When DMF was employed as the solvent, only trace amounts of product were observed. Conversely, when MeCN, THF, and acetone were used as solvents (Entries 4-6), GC-MS analysis revealed the formation of sulfohydride products (3a) as well as disulfide products arising from the self-polymerization of thiophenol. Given the inevitability of thiophenol self-polymerization under the specified conditions, we hypothesized that increasing the amounts of NHPI and thiophenol would enhance the proportion of sulfohydride products. When the NHPI dosage was increased to 1.0 eq and thiophenol to 1.5 eq, the reaction yield improved to 73% (Entry 7). Further increasing the thiophenol dosage to 2.0 eq resulted in a yield of 92% (Entry 8). However, raising the temperature to 80 ℃ promoted the self-polymerization of thiophenol, leading to disulfide formation. Eventually, the conditions described in Entry 8 were selected as optimal for the reaction.

2.2 Substrate scope

2.2.1 Substrate scope of thiophenol derivatives. Following the identification of optimal reaction conditions, we proceeded to investigate the substrate scope applicable to the reaction. Specifically, substrates (1a) bearing various substituent groups on the benzene ring of thiophenol were examined, as illustrated in Fig. 2. Overall, all substrates afforded good to excellent yields. The electronic effects imparted by different substituents on the benzene ring of thiophenol exhibited minimal influence on the reaction outcome. In the presence of electron-donating groups such as methyl, methoxy, and tert-butyl, the corresponding product yields (3a, 3b, 3c) were 89%, 86%, and 82%, respectively. When the para-orienting substituents on the benzene ring of thiophenol were electron-withdrawing groups, such as halogen atoms (–F, –Cl, –Br), the yields were 91%, 92%, and 94% (3d, 3e, 3f), respectively, indicating that the electron-withdrawing effect did not significantly influence the reaction. This suggests that the reaction exhibits low sensitivity to electronic effects. In contrast, the steric hindrance imposed by substituents on the benzene ring markedly affected the reaction outcome. When substituents were located at the ortho and meta positions, the yields decreased to varying extents (3g, 3h, 3i). For example, the presence of F at the ortho position reduced the yield to 76%, while the introduction of two methyl groups at the ortho position further decreased the yield to 64%. These observations may be attributed to the steric hindrance from bulky groups on the benzene ring of thiophenol, which likely impedes the activation of NHPI and the thiol (–SH) group of thiophenol.



1a 2a 3a

Entry[a]	Cat.	1a	Solvent	Temperature	Time	Yield[b]
1	0.2 eq.	1.0 eq.	DCM	40 ℃	6 h	/
2	0.2 eq.	1.0 eq.	Dioxane	40 ℃	6 h	/
3	0.2 eq.	1.0 eq.	DMF	40 ℃	6 h	trace
4	0.2 eq.	1.0 eq.	MeCN	40 ℃	6 h	29%
5	0.2 eq.	1.0 eq.	THF	40 ℃	6 h	32%
6	0.2 eq.	1.0 eq.	Acetone	40 ℃	6 h	37%
7	1.0 eq.	1.5 eq.	Acetone	40 ℃	8 h	73%
8	1.0 eq.	2.0 eq.	Acetone	60 ℃	8 h	92%
9	1.0 eq.	2.0 eq.	Acetone	80 ℃	8 h	61%

NOTE [a]Unless otherwise specified, the reaction was performed with 2a (0.2 mmol) in the presence of NHPI and an anhydrous solvent (3.0 mL). [b]Yield of crude product GC-MS using *n*-undecane as an internal standard.

Fig. 1 Optimization of reaction conditions

2.2.2 Substrate scope of styrenes. Substrates (2a) bearing various substituents on the styrene moiety were investigated, as illustrated in Fig. 3. Overall, all substrates achieved good to excellent yields. Both electronic effects and steric hindrance exerted minimal influence on the sulfur hydrogenation reaction, indicating a high tolerance of the reaction toward different styrene derivatives. Substrates with electron-donating substituents on the benzene ring of styrene exhibited higher yields, reaching 92%, 94%, and 83% (4a, 4b, and 4c), respectively. In contrast, electron-withdrawing groups on the benzene ring had a relatively minor effect on the reaction yield, which attained 95%, 96%, and 98% (4d, 4e, and 4f), respectively. Similarly, substitution at the ortho and

para positions of styrene with methyl groups did not result in a decrease in reaction yield.

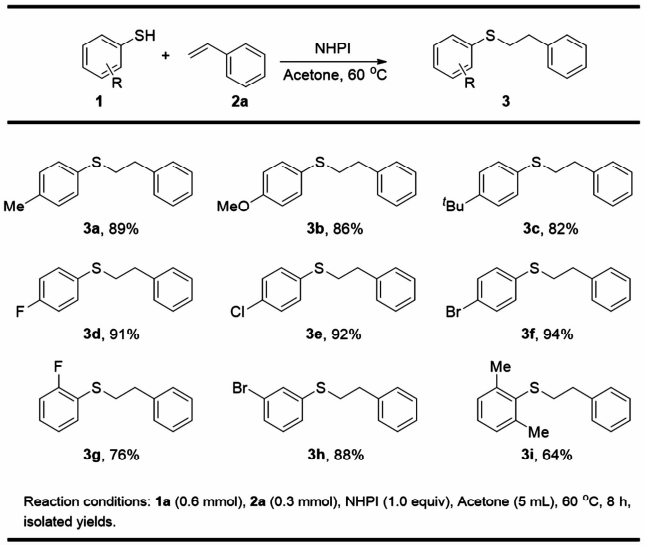


Fig. 2 Substrate scope of thiophenols

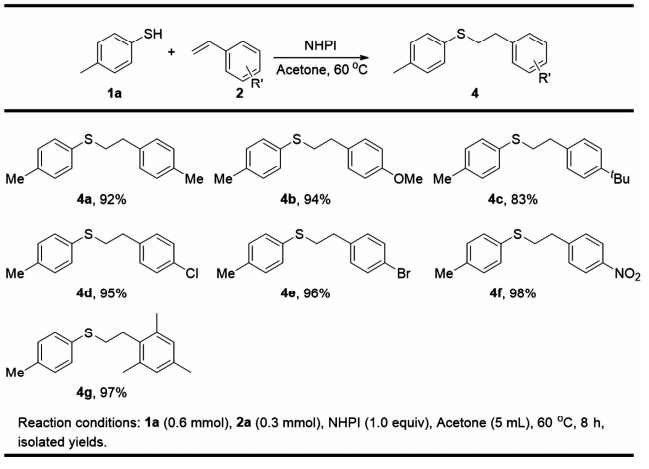


Fig. 3 Substrate scope of styrenes

3 Exploration of mechanisms

To further investigate the reaction mechanism, we performed a series of controlled experiments, as illustrated in Fig. 4. Using compounds 1a and 2a as model substrates, nitrogen purging and deoxygenation treatments were performed on the dry, anhydrous acetone solvent. The entire reaction system was maintained under a nitrogen atmosphere. After 8 h, only trace amounts of product 3a were detected by GC-MS analysis. These results suggest that the reaction is aerobic and that oxygen is essential for its progression. Subsequently, 1.0 eq of the TEMPO reagent was introduced into the reaction mixture. Upon completion, GC-MS analysis confirmed the presence of TEMPO capturing thiophenol radicals, providing evidence for the involvement of thiophenol radicals in the reaction.

Based on the above control experiments and existing literature reports[21], we propose that the mechanism of this reaction is as illustrated in Fig. 5. NHPI was activated to form PINO · radicals in the presence of oxygen. These PINO · radicals abstracted H atoms from the S-H bond in substrate 1, generating the thiophenol radical 4 and regenerating NHPI. Subsequently, styrene underwent an anti-Markovnikov addition reaction with the free radical intermediate 4, producing the sulfohydride free radical intermediate 5. Finally, a hydrogen transfer process with NHPI occurred, ultimately yielding the sulfohydride addition product of styrene.

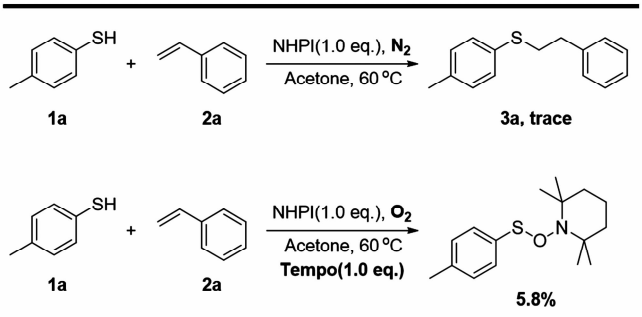


Fig. 4 Controlled experiments

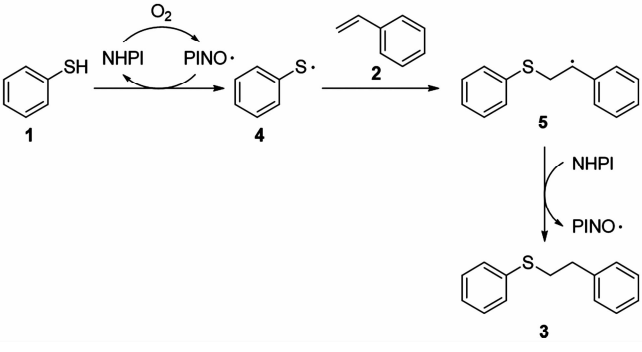


Fig. 5 Plausible reaction mechanism

4 Conclusions

In this study, an NHPI-catalyzed sulfohydride addition reaction between thiophenol and styrene was developed. The reaction proceeded under mild conditions without the requirement for metal catalysts or additives. A series of styrene sulfohydride addition products, featuring two methylene active sites, were synthesized in moderate to excellent yields. These products exhibit high functional group compatibility and broad substrate generality, offering a potential pathway for the development of next-generation innovative pesticides. Mechanistic investigations suggest that the reaction may proceed via an NHPI/PINO · catalytic cycle. Further research is ongoing to address the challenges of minimizing thiophenol self-polymerization to disulfides under mild conditions and enhancing the specificity of hydrothiolation.

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