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Visible-Light-Mediated Alkylation of Thiophenols via Electron Donor–Acceptor Complexes Formed between Two Reactants

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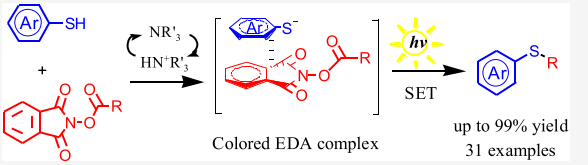
ABSTRACT: A metal-free, photocatalyst-free, photochemical system was developed for the direct alkylation of thiophenols via electron donor–acceptor (EDA) complexes (K_{EDA} = 145 M^{-1}) between two reactants, *N*-hydroxyphthalimide esters as acceptors and thiophenol anions as donors, in the presence of a tertiary amine. The EDA complexes in the reaction system have a broad range of visible-light absorption (400–650 nm) and can trigger the reaction effectively under sunlight.

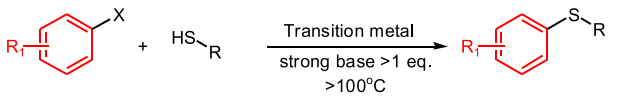


Sulfides are widely found in a variety of bioactive natural products and commercial drugs, such as Torecan, Femstat, Viracept, and Brilinta. According to an analysis of FDA-approved drugs, sulfur is the third most frequently used heteroatom after oxygen and nitrogen.[1] Among them, aryl alkyl sulfides are some of the common structural units and exhibit diverse pharmacological activities after further structural modification such as antiemetic, antifungal, antiviral, and antiplatelet properties.[2] Thus, the development of environmentally friendly and economical methods for constructing C–S bonds is of great importance in organic synthesis.

The traditional synthesis approach of sulfides is transition metal-catalyzed cross-coupling between heteroatom-substituted aromatics and mercaptans (Scheme 1a).[3] However, thiolates are prone to inactivate transition metal catalysts, so the ligands need to be specially designed and are often sensitive to air. Although these problems have been alleviated with other alternatives,[4] the harsh conditions of a high temperature and an excessively strong base (i.e., NaOtBu, LiHMDS, or Grignard reagent) still inevitably restrict the functional groups of substrates in the reaction.

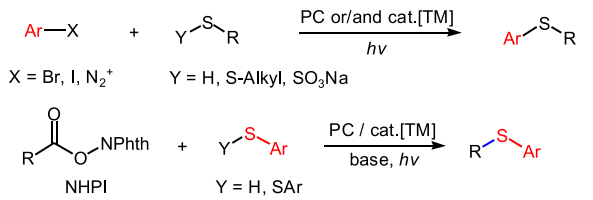
Scheme 1. Approaches for the Synthesis of Aryl Sulfides

a) Transition metal-catalyzed C-S cross-coupling reaction

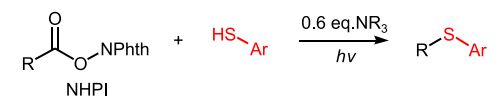


X = hal, OTf, OTs, SMe, SH, $B(OH)_2$

b) Visible-light-catalytic synthesis of aryl alkyl sulfides



c) This work



Recently, photocatalytic synthesis of sulfides has attracted more attention by a single or a dual catalytic system of transition metals or organic photocatalysts (PCs) (Scheme 1b).[5,6] The S-alkylation of thiophenols was carried out with *N*-hydroxyphthalimide (NHPI) ester as a typical alkylation precursor.[6] In the earliest work, Fu et al. developed decarboxylative alkylation of thiophenols via a complex between NHPI esters and inorganic base Cs_2CO_3.[6a]

When two colorless or nearly colorless organic molecules are put together, the appearance of strong color inspired Robert Mulliken to put forward the charge transfer theory.[7] The association of an electron-rich substrate with an electron-poor molecule can generate a new molecular aggregate, called an electron donor–acceptor (EDA) complex[8] or charge transfer complex.[9] The photochemical strategy based on the visible-light-absorbing EDA complex is a cheap and environmentally friendly organic synthesis method. The photochemistry of the EDA complex has been attracting the interest of a growing number of synthetic chemists.[10]

In this work, we developed a simple photochemical strategy for the direct alkylation of thiophenols involving visible-light-

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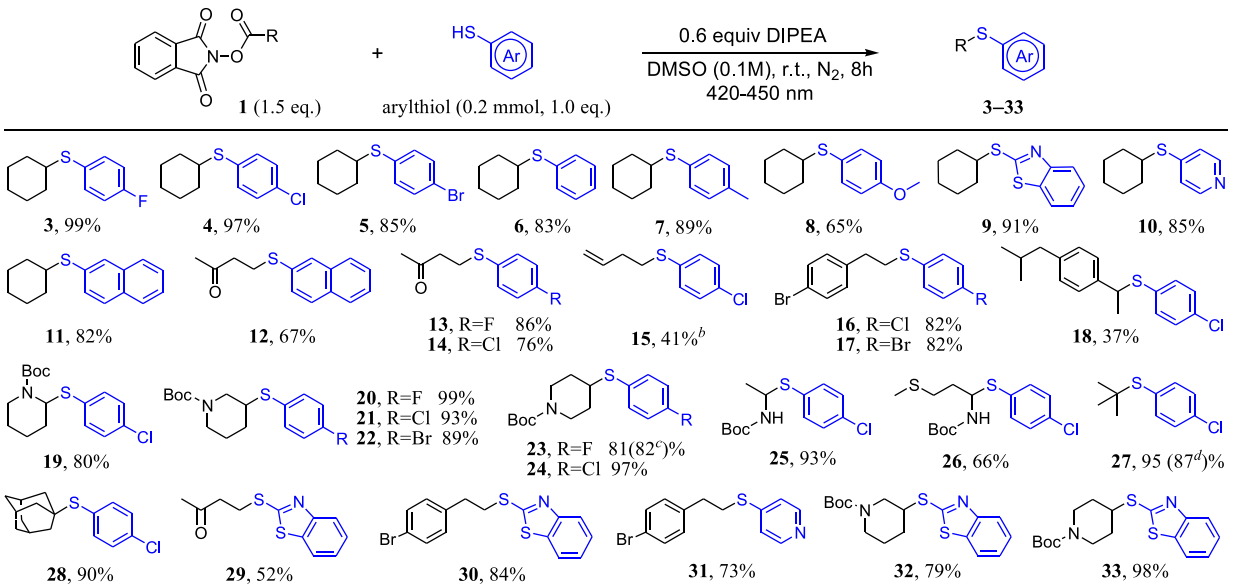
Scheme 2. Scope of the Decarboxylative Arylthiation[a]



[a]Reaction conditions: NHPI ester (0.3 mmol, 1.5 equiv), aryl thiol (1.0 equiv), DIPEA (0.6 equiv) in DMSO (2 mL), room temperature, N_2, 8 h, blue LEDs (420−450 nm), isolated yields. [b]DMA as the solvent. [c]On a 1 mmol scale. [d]Sunlight irradiation for 2 h.

absorbing EDA complexes between two reactants, NHPI esters and thiophenols (Scheme 1c).

To optimize the reaction condition, *tert*-butyl NHPI ester (**1a**) and 4-chlorothiophenol (**2**) were selected as the substrates of the template reaction shown in Table S1. First, among a series of organic bases being screened, including *n*-butylamine ($BuNH_2$), diethylamine [$NH(Et)_2$], piperidine, benzylamine ($BnNH_2$), morpholine, diisopropyl ethylamine (DIPEA), piperazine, and triethylamine (NEt_3), DIPEA is the most efficient (80%, entry 8), and the second most efficient is NEt_3 (74%, entry 7). We found that the effective bases are tertiary (entries 7 and 8) amines, while primary or secondary amines are ineffective (entries 1−3); only aminolysis products were observed due to a direct aminolysis between the active esters and primary or secondary amines. Furthermore, the dose of the bases, DIPEA and NEt_3, was optimized, 0.6 equiv as the largest doses for both bases (96% for DIPEA, entry 17, and 78% for NEt_3, entry 11). Next, we performed this reaction in four other solvents, 1,4-dioxane, dimethylacetamide (DMA), dimethylformamide (DMF), and acetonitrile. Among them, DMA and DMF gave excellent (94%, entry 25 in Table S1) and good (79%, entry 26 in Table S1) yields, respectively. Finally, control experiments show that both a base (entry 28) and blue light (entry 29) are necessary for the arylthiation reaction. In addition, the reaction can still work effectively (80% yield) in an air atmosphere (entry 30). This implies that the reaction is insensitive to oxygen and water.

Under the optimized reaction conditions described above, we evaluated a range of substrates for decarboxylative arylthiation of NHPI esters with thiophenols (Scheme 2). First, for the thiophenol partner, we explored the scope of readily available thiophenols with various substituents, including fluoride, chloride, bromide, methyl, and methoxyl, which react with cyclohexyl NHPI esters to give the corresponding aryl alkyl sulfides in moderate to excellent yields. Generally, thiophenols with electron-withdrawing groups (EWGs; F, Cl, and Br) afford higher yields than that with electron-donating groups (EDGs; OMe). This result could be due to thiophenols with EWGs having lower pK_a values being deprotonated more easily in the presence of a base. In addition, heteroaromatic and extended aromatic thiophenols (**9**−**12**) were effectively adapted for this protocol in >60% yields.

Next, various NHPI active esters (**1a**−**m**, shown in Chart S1) were prepared, including primary (**1b** and **1e**−**g**) and secondary (**1d** and **1h**−**j**) aliphatic carboxylic acids, α-amino acids (**1k** and **1l**), and tertiary (**1a** and **1c**) aliphatic carboxylic acids. These reaction partners are all compatible in the reaction with thiophenols to afford the desired arylthiation products. In addition, a wide range of functional groups, including carbonyl (**12**−**14**), terminal alkene (**15**), aryl bromide (**16** and **17**), and amide (**19**−**26**) groups, were tolerated under our reaction conditions, exhibiting the excellent compatibility. Only a few benzylic carboxylic acid esters have previously been reported to generate benzylation products in the absence of metal catalysts.[11,12] Ibuprofen, an anti-inflammatory agent, also resulted in the formation of the desired product **18** in 37% yield. Because of its poor solubility in DMSO, product **15** was obtained in a low yield of 41% from the NHPI ester bearing a terminal alkene in DMA, presumably due to a certain degree of solubility. To our delight, piperidine-derived esters showed good reactivity and provided a series of α-, β-, and γ-amino arylthiation products (**19**−**24**) in excellent yields. Furthermore, the NHPI esters derived from *N*-Boc-protected natural amino acids, alanine and methionine, afforded the corresponding α-amino arylthiation products **25** and **26** in 93% and 66% yields, respectively. In addition, a series of heteroaromatic sulfides (**29**−**33**) with N-heterocycles, which were generally bioactive building blocks in pharmaceutical intermediates,[13] were obtained by this method. For a 1 mmol scale, the strategy can give the desired product **22** in 82% yield. The results demonstrated the scalability of this strategy.

To explore the mechanism, we measured UV/vis absorption spectra of reaction components at the same ratio as in the

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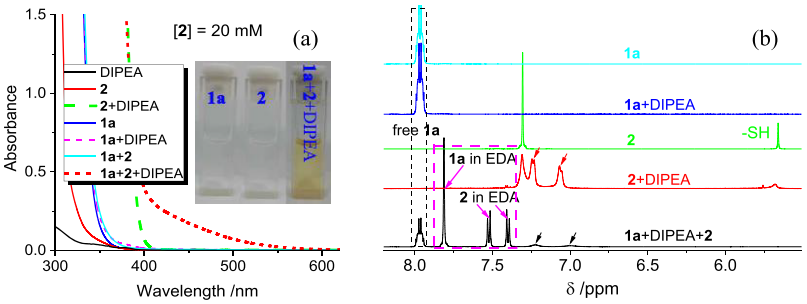


Figure 1. (a) UV/vis absorption spectra of **1a** (1.5 equiv), 4-chlorothiophenol **2** (20 mM, 1.0 equiv), and DIPEA (0.6 equiv) in DMSO. (b) Partial ^{1}H NMR spectra (500 MHz, DMSO-d_6) of **2** (50 mM, 1.0 equiv) and **1a** (1.5 equiv) with or without DIPEA (0.6 equiv).

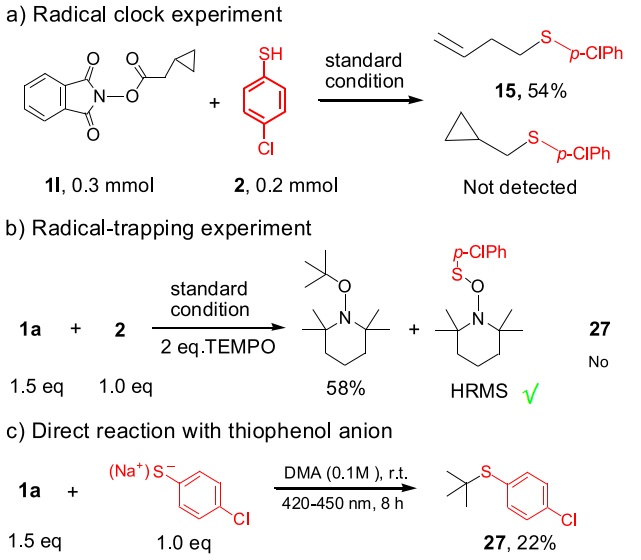
reaction (Figure 1a for a low concentration of **2** and Figure S2 for high concentrations of **2**). At all three concentrations, there is almost no absorption beyond 400 nm for either individual or two components of the reaction. An obvious red-shift was observed in the solution of **2** with DIPEA, possibly resulting from the formation of the deprotonated thiophenol anion (Figure 1a).

Upon addition of **1a** to a solution of **2** with DIPEA, we observed a remarkable red-shift of the absorption onset tailed into the visible-light region (Figure 1a). The red-shift could be due to the formation of an electron donor−acceptor (EDA) complex between the electron-rich thiophenol anion and the electron-poor NHPI ester. A larger red-shift (400−650 nm) in the absorption spectrum of the reaction system was observed (Figure S2ab), accompanied by a change from colorless to reddish brown (insets of Figure 1a and Figure S2c).

^{1}H NMR spectra provide further support for the formation of the EDA complex. Consistent with the results presented above, the intensity of the partial ^{1}H NMR proton signal of -SH significantly decreased and the aromatic hydrogen peaks of **2** shift to high field after the addition of 0.6 equiv of DIPEA (Figure 1b). When **1a**, **2**, and the base DIPEA are present, the aromatic proton signal for **1a** shifts to the high field and that of **2** to the low field in the ^{1}H NMR spectrum (Figure 1b), which is consistent with the NHPI ester being the electron acceptor and thiophenol anion being the electron donor. The association constant (K_{EDA}) of the EDA complex was estimated to be 145 M^{-1} (details provided in the Supporting Information). The value is much higher than the reported values (0.9 ± 0.1,[14a] 22,[14b] and 8.4 M^{-1}[14c]), implying there is a strong charge transfer interaction between the NHPI ester and the thiophenol anion. A thiophenol anion can also associate with a benzene halide to form an EDA complex.[15]

To confirm a radical pathway in this reaction, a radical clock experiment and a radical-trapping experiment were performed and the results are shown in Scheme 3. The radical clock experiment with cyclopropyl methyl NHPI ester showed that a ring-opened product **15** was obtained in 54% yield but no expected cyclopropyl sulfide was detected (Scheme 3a). This indicates the formation of alkyl radical in the reaction process. For the radical-trapping experiment with TEMPO, a radical-trapping agent, the expected reaction was inhibited completely, and the captured compound *tert*-butyl radical was obtained in 58% yield (Scheme 3b). Meanwhile, radical-trapping adducts of both 4-chlorothiophenol radical and *tert*-butyl radical by TEMPO were observed by HPLC-FTMS of the reaction solution (Figure S3). These results further confirm the

Scheme 3. Control Experiments for the Mechanistic Study



involvement of sulfur radical and alkyl radical in the arylthiation process.

To further explore the role of DIPEA, sodium 4-chlorobenzenethiolate was employed to replace 4-chlorothiophenol and DIPEA (Scheme 3c). Interestingly, the reaction can also work, and product **27** was obtained in 22% yield. Compared with the optimization condition (96% in Table S1, entry 17), the low yield could be due to the low solubility of 4-chlorobenzenethiolate salt in DMA. Thus, the role of DIPEA in the alkylation is to promote the deprotonation of thiophenols as a base. The quantum yield of the decarboxylative arylthiation was measured to be 0.053 (details in the Supporting Information), suggesting a closed catalytic cycle rather than a radical chain process.

On the basis of the mechanistic studies mentioned above, we propose a visible-light-mediated S-alkylation reaction via an EDA complex, which forms between two reactants (Scheme 4). First, thiophenol (ArSH) deprotonates in the presence of a tertiary amine (NR'_3), generating a thiophenol anion (ArS^-) and an amine cation ($HN^+R'_3$). The electron-rich ArS^- can interact with the electron-poor NHPI ester to form the EDA complex, which can absorb visible light (400−650 nm). Under visible-light irradiation, a single-electron transfer (SET) process occurs from ArS^- to the NHPI ester in the EDA complex, generating thiophenol radical ($ArS^•$) and the ester radical anion. The latter cleaves to give alkyl radical ($R^•$), CO_2, and phthalimide anion, which is protonated by the amine

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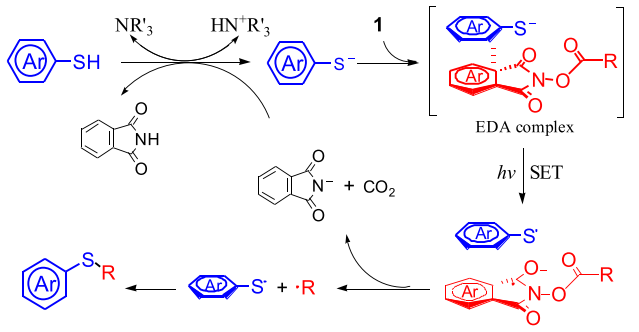
Scheme 4. Mechanism for the Photochemical Alkylation of Thiophenols



cation ($HN^+R'_3$) to regenerate NR'_3 because the pK_a of the phthalimide anion is higher (13.4 in DMSO) than that of a tertiary amine such as 9 for NEt_3.[16] Finally, the coupling of two radicals, $ArS^•$ and $R^•$, produces the desired sulfide, ArSR.

In addition, the reaction was carried out under solar light. Sulfide **27** can be obtained in a high yield of 87% under sunlight irradiation for 2 h (Table S2; the irradiation time was not optimized). This result shows the feasibility of utilizing solar energy to produce aryl alkyl sulfides.

In summary, we have developed a metal-free, photocatalyst-free, visible-light-mediated decarboxylative alkylation of thiophenols with NHPI esters in the presence of an organic base. The approach not only can avoid the use of transition metals and excessive base but also can utilize green energy, solar light. Therefore, the alkylation of thiophenols is an economical and green method for the synthesis of aryl sulfides.

EXPERIMENTAL SECTION

Materials and General Methods. All aryl thiols and solvents were obtained from commercial suppliers and used without further purification unless otherwise stated. Anhydrous DMSO was purchased from Energy Chemical and added to molecular sieves during use and stored at room temperature. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) or on a Bruker Ascend 500 MHz spectrometer (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR). The chemical shifts (δ) for ^1H and ^{13}C are reported in parts per million and are referenced to Me_4Si (TMS) and the residual undeuterated solvent resonances (TMS at 0.00 ppm; $CHCl_3$ at 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; DMSO at 2.50 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR). All UV/vis absorption spectra were recorded in 1 cm path length quartz cuvettes on a Shimadzu UV-2450 UV/vis spectrophotometer. High-resolution mass spectra (HRMS) were recorded using a Q-Exactive plus hybrid quadrupole-orbitrap mass spectrometer (Q-Orbitrap MS) (Thermo Scientific, San Jose, CA) with an electrospray ionization (ESI) source or atmospheric-pressure chemical ionization (APCI) source. A blue LED (an inner diameter of 9.5 cm, 420−450 nm, 45 W), purchased from Xuzhou Aijia Electronic Technology Company Ltd., was employed as a visible-light source without the use of filters. The emission spectrum of the lamp is shown in Figure S1.

Synthesis and Characterization of Related Compounds. *General Procedure for the Synthesis of N-Hydroxyphthalimide (NHPI) Esters.* *N*-Hydroxyphthalimide (NHPI) esters were prepared according to previously reported procedures.[17] In short, carboxylic acid (10 mmol, 1.0 equiv), *N*-hydroxyphthalimide (11 mmol, 1.1 equiv), dimethylaminopyridine (DMAP) (1.0 mmol, 0.1 equiv), and dichloromethane (100 mL, 0.1 M) were placed in a 250 mL round-bottom flask equipped with a stirring bar. After that, *N*,*N*′-diisopropylcarbodiimide (DIC) (11 mmol, 1.1 equiv) was added dropwise via syringe and the mixture was stirred at room temperature until the acid was consumed (monitored by TLC). After the reaction had reached completion, the mixture was filtered over Celite and rinsed with additional CH_2Cl_2. Then the precipitate was filtered off, and the solution was concentrated under vacuum. The corresponding NHPI esters were further purified by column chromatography on silica gel.

General Procedure for the Photomediated Arylthiation Reaction. NHPI esters (1.5 equiv) and aryl thiol (1.0 equiv) (if solid) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then, DMSO (0.1 M), DIPEA (0.6 equiv), and aryl thiol (1.0 equiv) (if liquid) were added via a gastight syringe under a nitrogen atmosphere. Afterward, the tube was sealed, and the reaction mixture was stirred under irradiation with a blue LED (420−450 nm, approximately 3.0 cm from the bulb) at room temperature for 8 h. The reaction mixture was washed with water and extracted with ethyl acetate (3 × 10 mL) to remove DMSO. The organic layers were combined and concentrated under vacuum. The desired product was purified by flash column chromatography on silica gel.

Sunlight-Driven Reaction. The reaction mixture was set up on the roof of the laboratory according to the general procedure described above. Four parallel samples were prepared for the irradiation of sunlight. 4-Chlorothiophenol **2** (0.1 mmol), NHPI esters **1a** (0.15 mmol), DIPEA (0.06 mmol), and anhydrous DMSO (1 mL) were added to the Schlenk tube and exposed to natural-light irradiation on the roof of the laboratory at the University of Science and Technology of China from 10:00 a.m. to 14:00 p.m. on May 1, 2021, on a partially cloudy day with outdoor temperatures of 22−26 °C. The reaction of one sample was terminated every 1 h for the yield analysis.

*Cyclohexyl (4-Fluorophenyl) Sulfide (**3**).*[18] NHPI ester **1d** (82.0 mg, 0.3 mmol) and 4-fluorothiophenol (25.6 mg, 0.2 mmol) in DMSO (2 mL) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) to afford compound **3** (41.6 mg, 99%) as a colorless oil. The eluent was petroleum ether. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.38 (m, 2H), 7.00−6.97 (m, 2H), 2.98 (m, 1H), 1.95−1.93 (m, 2H), 1.77−1.65 (m, 2H), 1.62−1.60 (m, 1H), 1.36−1.19 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.5, 161.0, 135.0, 129.8, 115.9, 115.7, 47.6, 33.3, 26.0, 25.7. ^{19}F NMR (375 MHz, $CDCl_3$): δ −114.9.

*(4-Chlorophenyl)(cyclohexyl) Sulfide (**4**).*[18] NHPI ester **1d** (82.0 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in DMSO (2 mL) were irradiated with DIPEA (15.5 mg, 0.12 mmol) to obtain compound **4** as a colorless oil in 97% (44.0 mg) yield. The eluent was petroleum ether. ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.31 (m, 2H), 7.26−7.24 (m, 2H), 3.08−3.03 (m, 1H), 1.97−1.95 (m, 2H), 1.78−1.76 (m, 2H), 1.63−1.61 (m, 1H), 1.38−1.22 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 133.6, 133.2, 132.6, 128.9, 46.8, 33.2, 26.0, 25.7.

*(4-Bromophenyl)(cyclohexyl) Sulfide (**5**).*[19] This compound was prepared by NHPI ester **1d** (82.0 mg, 0.3 mmol) and 4-bromothiophenol (37.8 mg, 0.2 mmol) with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) under irradiation to afford a 85% (45.9 mg) yield as a colorless oil. The eluent was petroleum ether. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.38 (m, 2H), 7.26−7.23 (m, 2H), 3.10−3.04 (m, 1H), 1.97−1.95 (m, 2H), 1.77−1.76 (m, 2H), 1.63−1.60 (m, 1H), 1.39−1.23 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 134.4, 133.4, 131.8, 120.6, 46.7, 33.2, 26.0, 25.7.

*Cyclohexyl (Phenyl) Sulfide (**6**).*[18] This compound was prepared by NHPI ester **1d** (82.0 mg, 0.3 mmol) and thiophenol (22.0 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) under irradiation in 83% (31.9 mg) yield as a colorless oil. The eluent was petroleum ether. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40−7.38 (m, 2H), 7.29−7.25 (m, 2H), 7.22−7.19 (m, 1H), 3.12−3.07 (m, 1H), 1.99−1.97 (m, 2H), 1.79−1.76 (m, 2H), 1.63−1.60 (m, 1H), 1.41−1.23 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 135.2, 131.9, 128.7, 126.6, 46.6, 33.3, 26.1, 25.8.

*Cyclohexyl (p-Tolyl) Sulfide (**7**).*[18] NHPI ester **1d** (82.0 mg, 0.3 mmol) and 4-methylthiophenol (24.8 mg, 0.2 mmol) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) to provide compound **7** (36.7 mg, 89%) as a colorless oil. The eluent

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was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 3.03−2.99 (m, 1H), 2.32 (s, 3H), 1.97−1.94 (m, 2H), 1.75−1.59 (m, 2H), 1.59 (m, 1H), 1.37−1.21 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.9, 132.8, 131.2, 129.5, 47.1, 33.4, 26.1, 25.8, 21.1.

*Cyclohexyl (4-Methoxyphenyl) Sulfide (**8**).*[19] NHPI ester **1d** (82.0 mg, 0.3 mmol), 4-methoxythiophenol (28.0 mg, 0.2 mmol), and DIPEA (15.5 mg, 0.12 mmol) were irradiated in DMSO (2 mL) to provide compound **8** (28.9 mg, 65%) as a yellow oil. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.37 (m, 2H), 6.86−6.83 (m, 2H), 3.80 (s, 3H), 2.92−2.88 (m, 1H), 1.94−1.92 (m, 2H), 1.76−1.74 (m, 2H), 1.61−1.59 (m, 1H), 1.34−1.19 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.3, 135.7, 124.9, 114.3, 55.3, 47.9, 33.4, 26.2, 25.8.

*2-(Cyclohexylthio) Benzo[d]thiazole (**9**).*[20] This compound was prepared by NHPI ester **1d** (82.0 mg, 0.3 mmol) and 2-mercaptobenzothiazole (33.4 mg, 0.2 mmol) with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) under irradiation in 45.4 mg (91%) yield as a yellow solid. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.40 (td, J = 7.8, 1.1 Hz, 1H), 7.28 (td, J = 7.8, 1.1 Hz, 1H), 3.92−3.88 (m, 1H), 2.21−2.18 (m, 2H), 1.82−1.78 (m, 2H), 1.66−1.55 (m, 3H), 1.51−1.43 (m, 2H), 1.37−1.25 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.5, 153.4, 135.3, 125.9, 124.2, 121.6, 120.9, 47.3, 33.3, 25.8, 25.6.

*2-(Cyclohexylthio) Pyridine (**10**).*[19] NHPI ester **1d** (82.0 mg, 0.3 mmol) and 4-mercaptopyridine (22.2 mg, 0.2 mmol) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) to obtain compound **10** (32.9 mg, 85%) as a yellow solid. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, J = 5.8 Hz, 2H), 7.13 (d, J = 5.8 Hz, 2H), 3.38−3.33 (m, 1H), 2.08−2.05 (m, 2H), 1.81 (m, 2H), 1.66 (m, 1H), 1.48−1.31 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 149.2, 148.7, 121.8, 43.4, 32.9, 25.9, 25.6.

*Cyclohexyl (Naphthalen-2-yl) Sulfide (**11**).*[3f] Compound **11** was prepared by NHPI ester **1d** (82.0 mg, 0.3 mmol) and 2-naphthalenethiol (32.0 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) to obtain 82% (39.7 mg) yield as a colorless oil. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (m, 1H), 7.79−7.73 (m, 3H), 7.48−7.41 (m, 3H), 3.22 (m, 1H), 2.04−2.00 (m, 2H), 1.80−1.76 (m, 2H), 1.64−1.60 (m, 1H), 1.45−1.22 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 133.7, 132.6, 132.1, 130.2, 129.6, 128.2, 127.7, 127.2, 126.4, 125.8, 46.5, 33.4, 26.0, 25.8.

*4-(Naphthalen-2-ylthio)butan-2-one (**12**).*[21] This compound was prepared by NHPI ester **1e** (78.4 mg, 0.3 mmol) and 2-naphthalenethiol (32.0 mg, 0.2 mmol) with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) under irradiation in 67% (30.9 mg) yield as an orange solid. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80−7.74 (m, 4H), 7.49−7.40 (m, 3H), 3.23 (t, J = 7.3 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.14 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 206.6, 133.7, 133.1, 131.9, 128.6, 127.7, 127.5, 127.3, 127.1, 126.6, 125.8, 43.0, 30.1, 27.3.

*4-[(4-Fluorophenyl)thio]butan-2-one (**13**).*[22] NHPI ester **1e** (78.4 mg, 0.3 mmol) and 4-fluorothiophenol (25.6 mg, 0.2 mmol) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) to afford compound **13** (34.1 mg, 86%) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.34 (m, 2H), 7.02−6.99 (m, 2H), 3.08 (t, J = 7.3 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.14 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 206.5, 163.0, 161.0, 132.8, 132.7, 130.5, 116.2, 116.1, 43.1, 30.1, 28.9. ^{19}F NMR (375 MHz, $CDCl_3$): δ −115.1.

*4-[(4-Chlorophenyl)thio]butan-2-one (**14**).*[23] NHPI ester **1e** (78.4 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) were irradiated with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) to obtain compound **14** (32.6 mg, 76%) as a yellow solid. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.37 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 3.10 (t, J = 7.0 Hz, 2H), 2.77 (t, J = 7.0 Hz, 2H), 2.10 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 206.9, 135.6, 130.8, 130.1, 129.5, 42.5, 30.2, 26.7.

*But-3-en-1-yl (4-Chlorophenyl) Sulfide (**15**).*[24] Compound **15** was obtained by NHPI ester **1f** (73.6 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMA (2 mL) under irradiation to afford 41% (16.3 mg) yield as a colorless liquid. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27−7.24 (m, 4H), 5.86−5.79 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.05−5.10 (m, 2H), 2.59 (t, J = 7.5 Hz, 2H), 2.59 (q, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.1, 135.0, 131.9, 130.6, 129.0, 116.4, 33.3, 33.2.

*(4-Bromophenethyl)(4-chlorophenyl) Sulfide (**16**).* Compound **16** was obtained by NHPI ester **1g** (112.3 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) in 82% (53.7 mg) yield as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.3 Hz, 2H), 7.25−7.24 (m, 4H), 7.04 (d, J = 8.3 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.84 (t, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.8, 134.6, 132.2, 131.6, 130.8, 130.3, 129.1, 120.4, 35.3, 34.9. HRMS (APCI) m/z: $[M]^+$ calcd for $C_{14}H_{12}ClBrS^+$ 325.9532, found 325.9533.

*(4-Bromophenethyl)(4-bromophenyl) Sulfide (**17**).* NHPI ester **1g** (112.3 mg, 0.3 mmol) and 4-bromothiophenol (37.8 mg, 0.2 mmol) were irradiated with DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) to provide compound **17** (61.0 mg, 82%) as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.38 (m, 4H), 7.19−7.17 (m, 2H), 7.04 (d, J = 8.3 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.85 (t, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.8, 135.3, 132.0, 131.6, 130.9, 130.3, 120.4, 120.0, 35.1, 34.9. HRMS (APCI) m/z: $[M]^+$ calcd for $C_{14}H_{12}Br_2S^+$ 369.9026, found 369.9027.

*(4-Chlorophenyl)[1-(4-isobutylphenyl)ethyl] Sulfide (**18**).* NHPI ester **1m** (105.4 mg, 0.3 mmol), 4-chlorothiophenol (28.9 mg, 0.2 mmol), and DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) were irradiated to afford compound **18** (22.6 mg, 37%) as a yellow oil. The eluent was a 50/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16−7.14 (m, 6H), 7.05−7.03 (m, 2H), 4.28 (q, J = 6.9 Hz, 1H), 2.43 (d, J = 7.1 Hz, 2H), 1.83−1.80 (m, 1H), 1.61 (d, J = 6.9 Hz, 3H), 0.88 (d, J = 6.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.8, 140.0, 134.1, 133.7, 133.4, 129.2, 128.8, 127.1, 48.1, 45.1, 30.2, 22.4, 22.1. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{18}H_{20}ClS^-$ 303.0980, found 303.0982.

*tert-Butyl 2-[(4-Chlorophenyl)thio] Piperidine-1-carboxylate (**19**).* Compound **19** was prepared from NHPI ester **1h** (112.3 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) under irradiation in 80% (52.4 mg) yield as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. The product gives two sets of NMR signals at an approximate ratio of 4/5, due to there being conformational isomers of tertiary amines. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (m, 2H), 7.27−7.20 (m, 2H), 6.03−5.74 (m, 1H), 4.05−3.84 (m, 1H), 3.29−3.23 (td, J = 13.0, 2.6 Hz, 1H), 1.95 (m, 1H), 1.90−1.81 (m, 2H), 1.72−1.67 (m, 2H), 1.46−1.44 (m, 1H), 1.30 (s, 4H), 1.19 (s, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 154.0, 153.7, 136.3, 135.4, 134.4, 133.9, 132.3, 132.1, 129.2, 129.0, 80.1, 64.3, 62.0, 39.4, 38.0, 31.1, 30.3, 28.3, 28.0, 25.4, 19.8. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{22}ClNO_2NaS^+$ 350.0952, found 350.0948.

*tert-Butyl 3-[(4-Fluorophenyl)thio] Piperidine-1-carboxylate (**20**).* NHPI active ester **1i** (112.3 mg, 0.3 mmol), 4-fluorothiophenol (25.6 mg, 0.2 mmol), and DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) were irradiated to afford **20** (61.7 mg, 99%) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.41 (m, 2H), 7.02−6.99 (m, 2H), 4.04 (br, 1H), 3.87−3.85 (m, 1H), 3.10−2.98 (m, 1H), 2.86−2.79 (m, 2H), 2.08−2.05 (m, 1H), 1.77−1.73 (m, 1H), 1.53−1.44 (m, 2H), 1.41 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 163.4, 161.4, 154.4, 134.9, 128.7, 116.1, 116.0, 79.6, 49.6, 44.8, 43.9, 30.9, 28.4, 25.1. ^{19}F NMR (375 MHz, $CDCl_3$): δ −114.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{22}FNO_2NaS^+$ 334.1247, found 334.1243.

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*tert-Butyl 3-[(4-Chlorophenyl)thio] Piperidine-1-carboxylate (**21**).* NHPI ester **1i** (112.3 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated and isolated to give **21** (61.0 mg, 93%) as a yellow oil. The eluent was a 10/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.34 (m, 2H), 7.28−7.26 (m, 2H), 4.06 (br, 1H), 3.88−3.85 (m, 1H), 3.10−3.06 (m, 1H), 2.86−2.83 (m, 2H), 2.09−2.07 (m, 1H), 1.74 (m, 1H), 1.57−1.49 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 133.2, 132.7, 131.0, 129.1, 79.7, 49.8, 49.4, 44.1, 30.8, 28.4, 25.1. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{22}ClNO_2NaS^+$ 350.0952, found 350.0949.

*tert-Butyl 3-[(4-Bromophenyl)thio] Piperidine-1-carboxylate (**22**).* NHPI ester **1i** (112.3 mg, 0.3 mmol), 4-bromothiophenol (37.8 mg, 0.2 mmol), and DIPEA (15.5 mg, 0.12 mmol) in DMSO were irradiated and isolated to afford **22** (66.3 mg, 89%) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43−7.41 (m, 2H), 7.29−7.27 (m, 2H), 4.07 (m, 1H), 3.88−3.84 (m, 1H), 3.12−3.07 (m, 1H), 2.90−2.81 (m, 2H), 2.09−2.06 (m, 1H), 1.78−1.74 (m, 1H), 1.57−1.45 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.4, 133.3, 133.1, 132.0, 121.1, 79.7, 49.6, 43.9, 30.8, 28.4, 25.1. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{22}BrNO_2NaS^+$ 394.0447, found 394.0442.

*tert-Butyl 4-[(4-Fluorophenyl)thio] Piperidine-1-carboxylate (**23**).*[25] NHPI ester **1j** (112.3 mg, 0.3 mmol) and 4-fluorothiophenol (25.6 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to afford **23** (50.4 mg, 81%), or NHPI ester **1j** (561.6 mg, 1.5 mmol) and 4-fluorothiophenol (168.2 mg, 1.0 mmol) in the presence of DIPEA (77.5 mg, 0.6 mmol) were irradiated for a prolonged time of 24 h to give **23** (255.4 mg, 82%) as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44−7.41 (m, 2H), 7.03−6.99 (m, 2H), 3.97(dt, *J* = 13.6, 3.8 Hz, 2H), 3.09 (tt, *J* = 10.3, 3.8 Hz, 1H), 2.90−2.85 (m, 2H), 1.90−1.85 (m, 2H), 1.53−1.46 (m, 2H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.6, 161.6, 154.7, 135.8, 135.7, 128.6, 128.5, 116.1, 116.0, 79.6, 45.4, 43.2, 32.1, 28.4. ^{19}F NMR (375 MHz, $CDCl_3$): δ −113.8.

*tert-Butyl 4-[(4-Chlorophenyl)thio] Piperidine-1-carboxylate (**24**).* NHPI ester **1j** (112.3 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) to afford **24** (97%, 63.6 mg) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.98−3.95 (m, 2H), 3.16 (m, 1H), 2.91 (m, 2H), 1.90 (m, 2H), 1.54−1.47 (m, 2H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.6, 134.0, 133.5, 132.3, 129.1, 79.6, 44.8, 43.1, 32.0, 28.4. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{22}ClNO_2NaS^+$ 350.0952, found 350.0950.

*tert-Butyl {1-[(4-Chlorophenyl)thio]ethyl}carbamate (**25**).* NHPI ester **1k** (100.3 mg, 0.3 mmol), 4-chlorothiophenol (28.9 mg, 0.2 mmol), and DIPEA (15.5 mg, 0.12 mmol) in DMSO (2 mL) were irradiated to give **25** (53.5 mg, 93%) as a white solid. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.41 (d, *J* = 8.3 Hz, 2H), 7.28−7.26 (d, *J* = 8.3 Hz, 2H), 5.25 (s, 1H), 4.71−4.70 (m, 1H), 1.48−1.46 (m, 3H), 1.34 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 135.2, 134.2, 131.3, 129.0, 80.1, 54.9, 28.2, 22.4. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{18}ClNO_2NaS^+$ 310.0639, found 310.0637.

*tert-Butyl {1-[(4-Chlorophenyl)thio]-3-(methylthio)propyl} Carbamate (**26**).* NHPI ester **1l** (118.3 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to give **26** (45.9 mg, 66%) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.41 (m, 2H), 7.28−7.27 (m, 2H), 5.24−5.23 (m, 1H), 4.79−4.77 (d, *J* = 9.5 Hz, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 2.06−2.02 (m, 1H), 1.99−1.93 (m, 1H), 1.48−1.46 (m, 1H), 1.35 (s, 8H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.4, 135.1, 134.3, 130.8, 129.1, 80.2, 58.6, 35.5, 30.7, 28.2, 12.6. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{22}ClNO_2NaS_2^+$ 370.0673, found 370.0676.

*tert-Butyl (4-Chlorophenyl) Sulfide (**27**).*[26] Active ester **1a** (74.2 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in DMSO (2 mL) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol), and compound **27** (38.1 mg, 95%) was obtained as a yellow oil. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.6, 135.1, 131.2, 128.6, 46.1, 30.8.

*1-Adamantyl (4-Chlorine) Phenyl Sulfide (**28**).*[27] NHPI ester **1c** (97.6 mg, 0.3 mmol) and 4-chlorothiophenol (28.9 mg, 0.2 mmol) in DMSO were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) to afford **28** (50.2 mg, 90%) as a white solid. The eluent was petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.41 (d, *J* = 8.3 Hz, 2H), 7.29−7.28 (d, *J* = 8.3 Hz, 2H), 2.01 (s, 3H), 1.79 (m, 6H), 1.66−1.58 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.82, 135.07, 129.12, 128.52, 48.17, 43.55, 36.11, 29.97.

*4-(Benzo[d]thiazol-2-ylthio)butan-2-one (**29**).* Active NHPI ester **1e** (78.4 mg, 0.3 mmol) and 2-mercaptobenzothiazole (33.4 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to give **29** (24.7 mg, 52%) as a yellow needle solid. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 (td, *J* = 7.8, 1.2 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.30 (td, *J* = 7.8, 1.2 Hz, 1H), 4.67 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 205.9, 189.1, 141.2, 127.9, 127.1, 124.9, 121.4, 112.6, 41.0, 39.9, 30.2. HRMS (ESI) *m*/*z*: [M + H]$^+$ calcd for $C_{11}H_{12}NOS_2^+$ 238.0355, found 238.0353.

*2-[(4-Bromophenethyl)thio]benzo[d]thiazole (**30**).* NHPI ester **1g** (112.3 mg, 0.3 mmol) and 2-mercaptobenzothiazole (33.4 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to afford compound **30** (58.8 mg, 84%) as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.44−7.40 (m, 3H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.55 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.3, 153.2, 138.6, 135.2, 131.7, 130.5, 126.1, 124.3, 121.5, 121.0, 120.6, 35.0, 34.5. HRMS (ESI) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}BrNS_2^+$ 349.9667, found 349.9668.

*4-[(4-Bromophenethyl)thio]pyridine (**31**).* Active ester **1g** (112.3 mg, 0.3 mmol) and 4-mercaptopyridine (22.2 mg, 0.2 mmol) in DMSO (2 mL) were irradiated in the presence of DIPEA (15.5 mg, 0.12 mmol) to give **31** (42.9 mg, 73%) as a yellow oil. The eluent was a 6/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 5.3 Hz, 2H), 7.45−7.43 (m, 2H), 7.11−7.09 (m, 4H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.2, 148.8, 138.3, 131.8, 130.3, 120.8, 120.7, 34.2, 31.9. HRMS (ESI) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{13}BrNS^+$ 293.9947, found 293.9947.

*tert-Butyl 3-(Benzo[d]thiazol-2-ylthio) Piperidine-1-carboxylate (**32**).* Active ester **1i** (112.3 mg, 0.3 mmol) and 2-mercaptobenzothiazole (33.4 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to afford **32** (55.4 mg, 79%) as a yellow oil. The eluent was a 20/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 4.13 (br, 1H), 4.01 (m, 1H), 3.68−3.64 (m, 1H), 3.44−3.35 (m, 1H), 3.23 (br, 1H), 2.20 (br, 1H), 1.80−1.76 (m, 2H), 1.64 (m, 1H), 1.46−1.42 (m, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.2, 154.6, 153.2, 135.2, 126.1, 124.4, 121.6, 121.0, 79.9, 49.5, 44.5, 30.4, 28.4, 25.8, 24.3. HRMS (ESI) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{23}N_2O_2S_2^+$ 351.1195, found 351.1193.

*tert-Butyl 4-(Benzo[d]thiazol-2-ylthio)piperidine-1-carboxylate (**33**).*[28] NHPI ester **1j** (112.3 mg, 0.3 mmol) and 2-mercaptobenzothiazole (33.4 mg, 0.2 mmol) in the presence of DIPEA (15.5 mg, 0.12 mmol) were irradiated to afford **33** (68.7 mg, 98%) as a yellow oil. The eluent was a 30/1 petroleum ether/ethyl acetate mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 4.13 (m, 1H), 3.99−3.96 (m, 2H), 3.16−3.09 (m, 2H), 2.21−2.17 (m, 2H),

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1.76−1.69 (m, 2H), 1.47 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 165.4, 154.6, 152.9, 135.1, 126.2, 124.5, 121.6, 121.0, 79.8, 44.7, 43.2, 32.1, 28.4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01433.

Condition optimization, mechanistic investigations, calculation of association constant K_{EDA}, and copies of NMR spectra of related compounds (PDF)

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Notes

The authors declare no competing financial interest.

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