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Selective C–H Acyloxylation of Sulfides/Disulfides Enabled by Hypervalent Iodine Reagents

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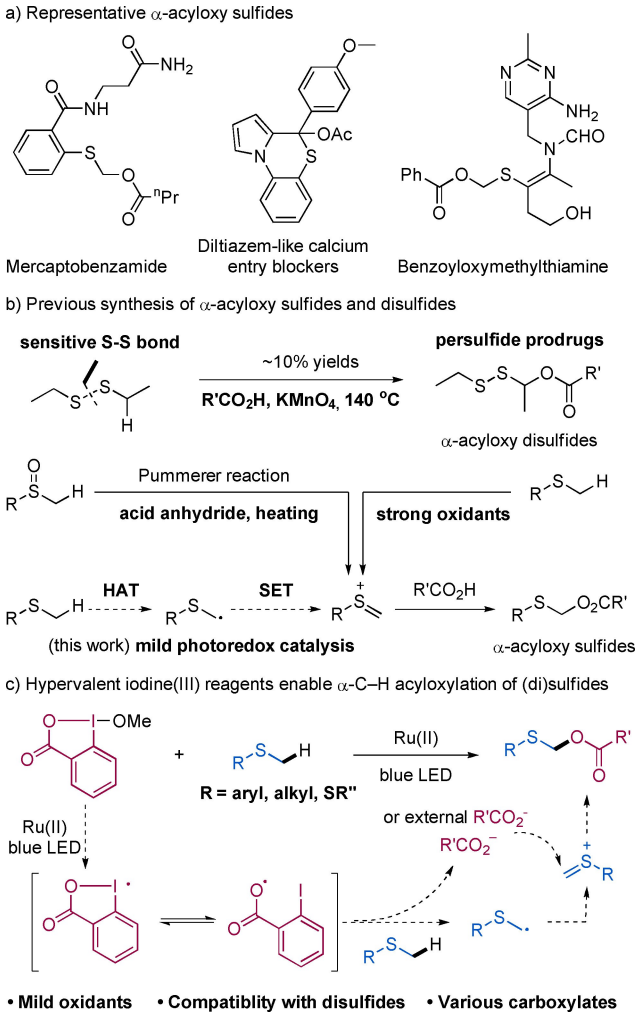
Abstract: Herein, we report the α–C–H acyloxylation of sulfides and disulfides enabled by hypervalent iodine(III) reagents *via* photoredox catalysis. The methoxylbenziodoxole derivatives serve as the hydrogen atom transfer agent, the mild oxidant, and the acyloxylation source in the reaction. External nucleophiles can also be introduced to the α–C–H of sulfides. The reaction applies to various aryl and alkyl sulfides including methionine peptide derivatives. Disulfides are applicable for the first time with excellent chemoselectivity and functional group compatibility.

Keywords: hypervalent iodine reagents; photoredox catalysis; acyloxylation; sulfides; disulfides

α-Acyloxy sulfides are privileged structural motifs in pharmaceuticals, materials, and agrochemicals. They include HIV-1 integrase inhibitor mercaptobenzamide and diltiazem-like calcium channel entry blockers (Scheme 1a).[1] In addition, α-acyloxy sulfides, e.g. benzoyloxymethylthiamines, represent protected thiol prodrugs to improve the oral administration efficiency of vitamin B_1.[2] α-Acyloxy disulfides are also widely used as persulfide prodrugs, which can be hydrolyzed by esterase under physiological conditions to release persulfides (Scheme 1b).[3] Currently, the biological roles of persulfides remain elusive, and their investigations constitute an active frontier in metabolic biology.[4] As disulfide bonds are sensitive to both oxidants and reductants,[5] current synthetic methods of



Scheme 1. C–H acyloxylation of sulfides/disulfides.

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α-acyloxy disulfides usually resulted in low yields and mixed products.[3a]

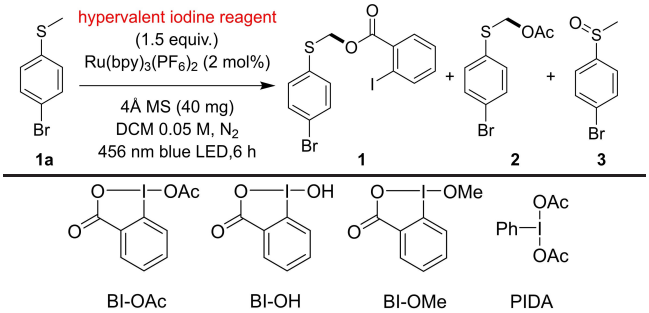
The classic Pummerer reaction is the primary method to synthesize α-acyloxy sulfides from sulfoxides with the critical sulfonium intermediate.[6] However, the sulfonium formation requires acid anhydride and heating treatment. Various methods have been implemented recently to generate sulfonium intermediates directly from sulfides. However, strong oxidative conditions are required, and these methods are unsuitable for α-acyloxy disulfide synthesis.[7]

The direct functionalization of α–C–H bonds in (di)sulfides by hydrogen atom transfer without strong oxidants is desirable.[8] However, the bond dissociation energy of α-C–H bonds (BDE = 93 kcal/mol) in (di)sulfides is similar to α-C–H bonds of ethers and amines (BDE = 92 kcal/mol),[9] which poses significant challenges for the selective functionalization of (di)sulfides.[10] To this end, the rapid oxidation of α-thioalkyl radical by mild oxidants may enable the selective sulfonium intermediate formation and α–C–H acyloxylation of (di)sulfides.[11]

We previously discovered that cyclic hypervalent iodine reagents were mild oxidative quenchers in photoredox catalysis to generate BI radicals, such as acetoxylbenziodoxole BI–OAc, hydroxylbenziodoxole BI–OH and methoxylbenziodoxole BI–OMe (Scheme 1c).[12] With structural resonance, the *ortho*-iodo substitution has a stabilizing effect on the aryl carboxyl radical for a selective hydrogen atom transfer capacity.[13] We hypothesize that benziodoxole derivatives may enable the triple roles in the reaction for hydrogen atom transfer in the α-thioalkyl radical generation, the single-electron transfer in the sulfonium formation, and the acyloxylation agent. Herein, we report a selective α-C–H acyloxylation of sulfides and disulfides to synthesize α-acyloxy (di)sulfides under mild reaction conditions by hypervalent iodine reagents, and the external nucleophiles can be introduced as well.[14]

We started the initial investigation with (4-bromophenyl)thioanisole **1a** and hypervalent iodine reagent acetoxylbenziodoxole BI–OAc under photoredox conditions with the addition of molecular sieves.[15] Using $Ru(bpy)_3(PF_6)_2$ ($E(M^+/M) = +1.26$ V vs SCE in MeCN) as the photocatalyst, the α-benzoyloxy sulfides **1** was obtained in 77% yield, and 10% yield of α-acetyloxy sulfide **2** was also obtained (Table 1, entry 1). The noncyclic phenyliodine(III) diacetate (PIDA) gave sulfoxide **3** as the main oxidation adduct in 79% yield, together with 21% yield of α-acetyloxy sulfide **2** (entry 2). Hydroxylbenziodoxole BI–OH only afforded 5% yield in low conversion of **1a** due to its poor solubility (entry 3). Gratifyingly, methoxylbenziodoxole BI–OMe afforded the optimal 93% yield of α-benzoyloxy sulfides **1** as the single product (91% isolated yield, entry 4). The use of *fac*-

Table 1. Reaction Optimization.



Entry	Conditions	**2** Yield (%)[b]	**3** Yield (%)[b]	**1** Yield (%)[b]
1	BI–OAc	10	13	77
2	PIDA	21	79	/
3	BI–OH	/	10	5
4	BI–OMe	/	<5	93(91)
5	entry 4, *fac*-Ir(ppy)$_3$		<5	45
6	entry 4, 4CzIPN		<5	13
7	entry 4, Ph–Acr–MesBF$_4$		<5	20
8	entry 4, no *hv*		<5	<5
9	entry 4, no $Ru(bpy)_3(PF_6)_2$		<5	<5
10	entry 4, no 4 Å MS		10	84

[a] Reaction conditions: sulfide **1a** (0.10 mmol, 1.0 equiv.), hypervalent iodine reagents (0.15 mmol, 1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) in 2.0 mL DCM under nitrogen with 20 W 456 nm blue LED irradiation at 25 °C for 6 h, unless otherwise noted.
[b] Yields were determined by ^{1}H NMR analysis, and isolated yields were in parentheses.

Ir(ppy)$_3$ as the photocatalyst ($E(M^+/M) = +0.77$ V vs SCE in MeCN) gave decreased 45% yield of **1**, while 4CzIPN ($E(M^+/M) = +1.49$ V vs SCE in MeCN) or Ph–Acr–Mes$^+$ ($E^*_{red} = +2.09$ V vs SCE in MeCN) with higher oxidation capacity afforded **1** in merely 13–20% yields (entries 5–7).[16] These results suggested that the reaction did not require strong oxidation conditions. The light irradiation and photocatalysts were critical for the reaction (entries 8–9). In the absence of 4 Å MS, α-acyloxy sulfides **1** was slightly reduced to 84% yield (entry 10).

We next evaluated sulfide scopes for the α-acyloxy sulfides synthesis (Table 2). The aryl(methyl) sulfides with *para*- electron-deficient or electron-donating substitutions reacted smoothly to obtain **4**–**10** in 51–91% yields. The *ortho*-, and *meta*-substitutions on the methyl(aryl) sulfides were well tolerated to give α-acyloxy sulfides **11**–**12** in 74–81% yields. Significantly, sulfide **14a** with aldehyde substitution was also compatible to obtain **14** in 47% yield without the aldehyde consumption.[13b] The phenyl(alkyl) sulfides **16a**–**18a** afforded the sole α-acyloxylation adducts **16**–**18** in 53–82% yields, in which the free alcohol group was tolerated, and HAT at other C–H sites was not observed. The cyclopropyl groups were compatible

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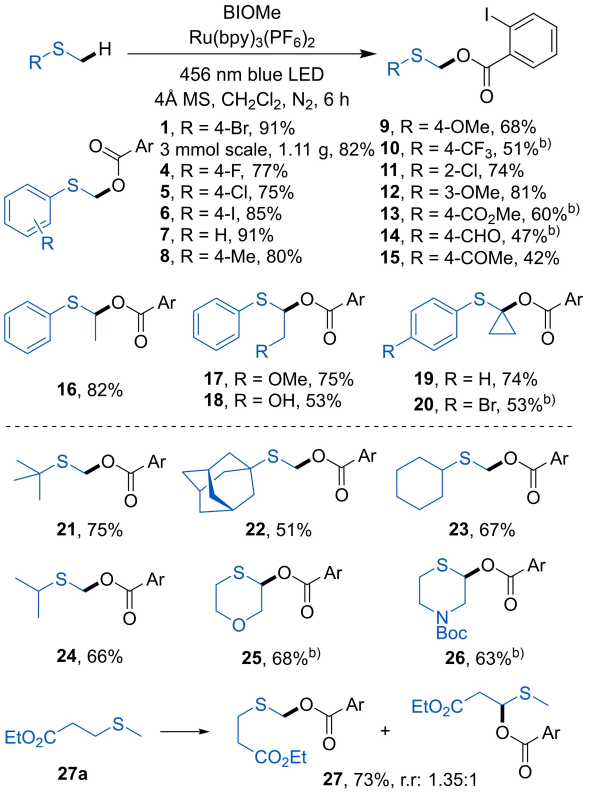
Table 2. Substrate scopes of sulfides.



[a] Reaction conditions: sulfide (0.10 mmol, 1.0 equiv.), BI–OMe (0.15 mmol, 1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) in 2.0 mL DCM under nitrogen with 20 W 456 nm blue LED irradiation at 25 °C for 6 h, unless otherwise noted. Isolated yields were reported.

[b] BI–OMe (0.2 mmol, 2.0 equiv.). r.r., regiomeric ratio. Ar = 2-I–C_6H_4.

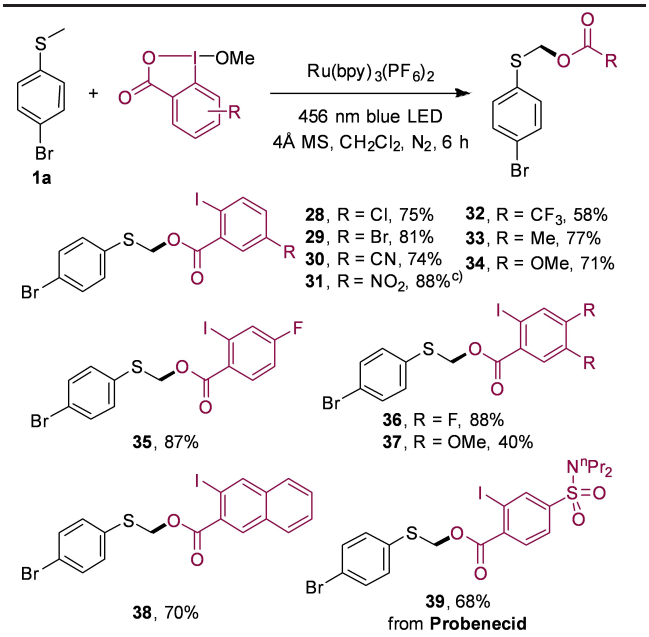
with affording **19**–**20** in 53–74% yields. The α-C–H acyloxylation of sulfides easily scaled up to 3 mmol to obtain 1.11 g of **1** in 82% yield.

This reaction was not limited to aryl sulfides that the *tert*-butyl(methyl)sulfide **21 a** and adamantyl(methyl)sulfide **22 a** afforded α-acyloxy sulfides **21**–**22** in 51–75% yields. When both primary and tertiary alkyl groups were presented in the molecule, the exclusive primary α-acyloxylation products **23**–**24** were obtained in 66–67% yields due to steric effects. The reaction was compatible with 1,4-oxathiane and thiomorpholine moieties that **25**–**26** were obtained in 63–68% yields, while the α- C–H of oxygen and nitrogen atoms remained intact. When asymmetric primary and secondary alkyl groups were presented in the sulfide molecules, a total 73% yield of **27** in 1.35:1 regiometric ratio at methyl and ethyl positions were observed, which suggested the similar reactivity of α-C–H of sulfides.

We next explored if the acyloxylation was extendable to other nucleophiles. Various aryl carboxylates successfully incorporated into α-acyloxy sulfides from the substituted BI–OMe derivatives, which could be easily prepared from *o*-iodobenzoic acid derivatives (Table 3).[12b,17] The electron-rich methoxy or electron-withdrawing halides, nitriles, and trifluoromethyl groups at the *meta*-position were all tolerated on the substituted BI–OMe derivatives, afforded **28**–**35** in 58–88% yields. Notably, the 5-nitro-2-iodobenzoic acid gave **31** in 88% yield with a prolonged 12 h reaction time.[18] The multiple substituted *o*-iodobenzoic acids were also compatible with affording **36**–**38** in 40–88% yields. Sulfonamides were tolerated to give α-acyloxy sulfide **39** in 68% yield, which were probenecid derivatives and recently shown as Transient Receptor Potential Vanilloid 2 (TRPV2) channel agonists.[19] The reaction also worked with external nucleophiles and α-acyloxy sulfides **40**–**43** were obtained in 44–57% yields, with competing side products **37** from diOMe–BI–OMe **37 b** in 17%-29% yields (Table 4).

We next carried out mechanistic investigations (Scheme 2). The (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO) addition to the reaction completely inhibited the conversion of **1 a**, and the TEMPO-

Table 3. Substrate scopes of BI–OMe derivatives.



[a] Reaction conditions: sulfide **1 a** (0.10 mmol, 1.0 equiv.), substituted BI–OMe (0.15 mmol, 1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) in 2.0 mL DCM under nitrogen with 20 W 456 nm blue LED irradiation at 25 °C for 6 h, unless otherwise noted.

[b] Isolated yields were reported.

[c] 12 h.

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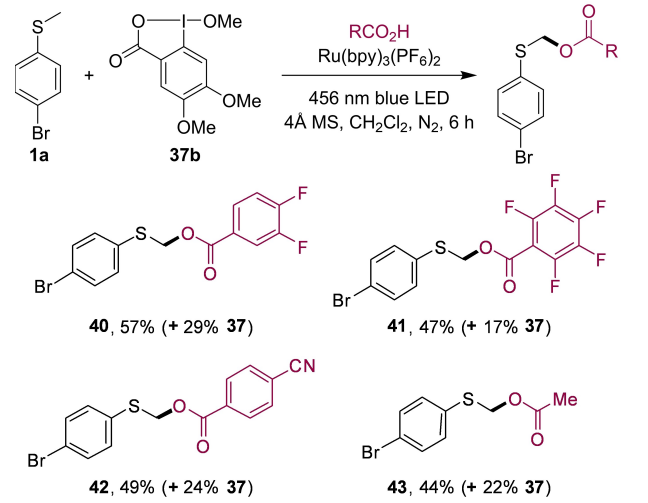
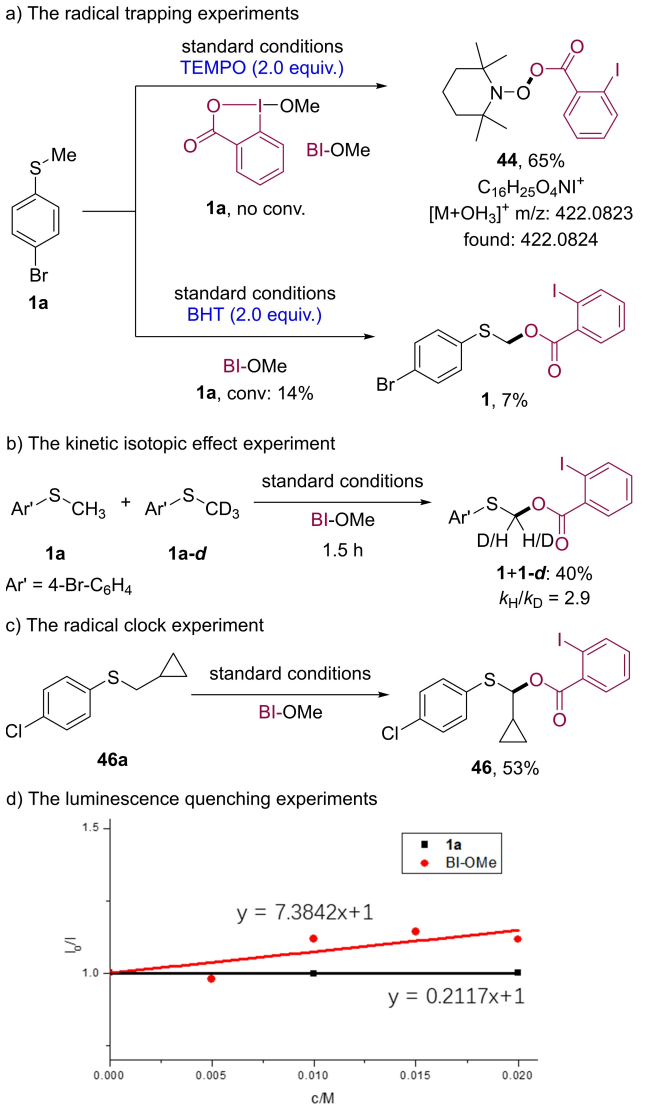
Table 4. Substrate scopes of external nucleophiles.



[a] Reaction conditions: sulfide **1a** (0.10 mmol, 1.0 equiv.), diOMe–BI–OMe **37b** (0.15 mmol, 1.5 equiv.) and external aryl carboxylic acids (0.2 mmol, 2.0 equiv.) or acetic acid (1.0 mmol, 10.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) in 2.0 mL DCM under nitrogen with 20 W 456 nm blue LED irradiation at 25 °C for 6 h, unless otherwise noted. Isolated yields were reported. The yields of side product **37** were determined by the integration of ^{1}H NMR.

addition adduct **44** was obtained in 65% yield, which was also confirmed by HRMS characterization (Scheme 2a).[20] The addition of dibutyl-hydroxytoluene (BHT) decreased the conversion of **1a** to 14% with the α-acyloxy sulfide **1** formation in 7% yield. The competitive kinetic isotope effect (KIE) experiments with **1a** and **1a**–***d*** indicated the KIE (k_H/k_D) value as 2.9, which indicated the rate-determining C–H cleavage from the primary isotope effect (Scheme 2b).[21] We also found the reaction could be initiated by benzoyl peroxide (BPO) as the aryl carboxyl radical precursor, and the α-C–H acyloxylation product **45** could be obtained in 34% yield in standard reaction conditions, suggesting the role of aryl carboxyl radicals in the reaction (Scheme S3).

The cyclopropylmethyl sulfide **46a** as the radical clock afforded the α-acyloxy sulfide **46** in 53% yield without cyclopropyl ring-opening acyloxylation adducts (Scheme 2c). These results suggested that the oxidation of the α-thioalkyl radical to sulfoniums was very rapid and faster than the ring-opening of the cyclopropyl methyl radical, which may also explain the preferential reaction at the α-C–H of sulfides.[22] The luminescence quenching experiments suggested BI–OMe quenched the excited $Ru(bpy)_3^{2+}$*, while sulfide **1a** had no effect (Scheme 2d).[12b] From cyclic voltammetry measurements, the oxidation potential of sulfide **1a** (E_p = +1.47 V vs SCE in MeCN) was too



Scheme 2. Mechanistic Investigations.

high to be oxidized by either the excited $Ru(bpy)_3^{2+}$* (E = +0.77 V vs SCE in MeCN)[23] or $Ru(bpy)_3^{3+}$ (Schemes S5–S11).[24] These results suggested the single-electron transfer of the excited photocatalyst by BI–OMe rather than by sulfide **1a**.

Based on the mechanistic investigations above, we proposed that the photoredox catalysis started with visible light irradiation on $Ru(bpy)_3^{2+}$ to afford the excited-state $Ru(bpy)_3^{2+}$* (Scheme 3). The hypervalent iodine(III) reagent BI–OMe was single-electron reduced by $Ru(bpy)_3^{2+}$* to form the BI radical with the $Ru(bpy)_3^{3+}$ generation. The tautomerized form of the BI radical as *o*-iodobenzoyloxy radical **I** underwent hydrogen atom transfer with sulfides to afford the α-thioalkyl radical **II** and *o*-iodobenzoic acid.[25] α-Thioalkyl radical **II** was rapidly oxidized to sulfonium III with the $Ru(bpy)_3^{2+}$ turnover. The sulfonium **III**

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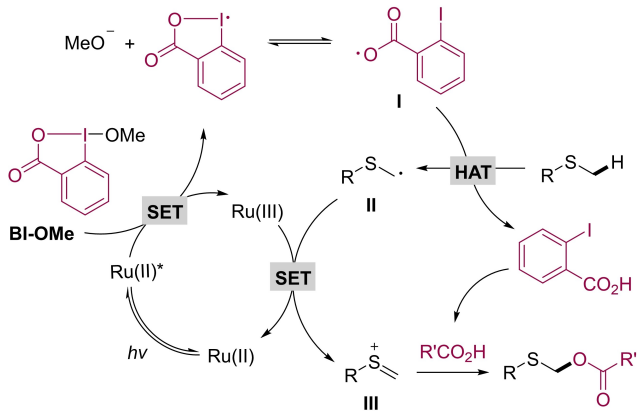


Scheme 3. Proposed Mechanism.

was then attacked by *o*-iodobenzoic acid or other nucleophiles to provide the α-acyloxy (di)sulfides.

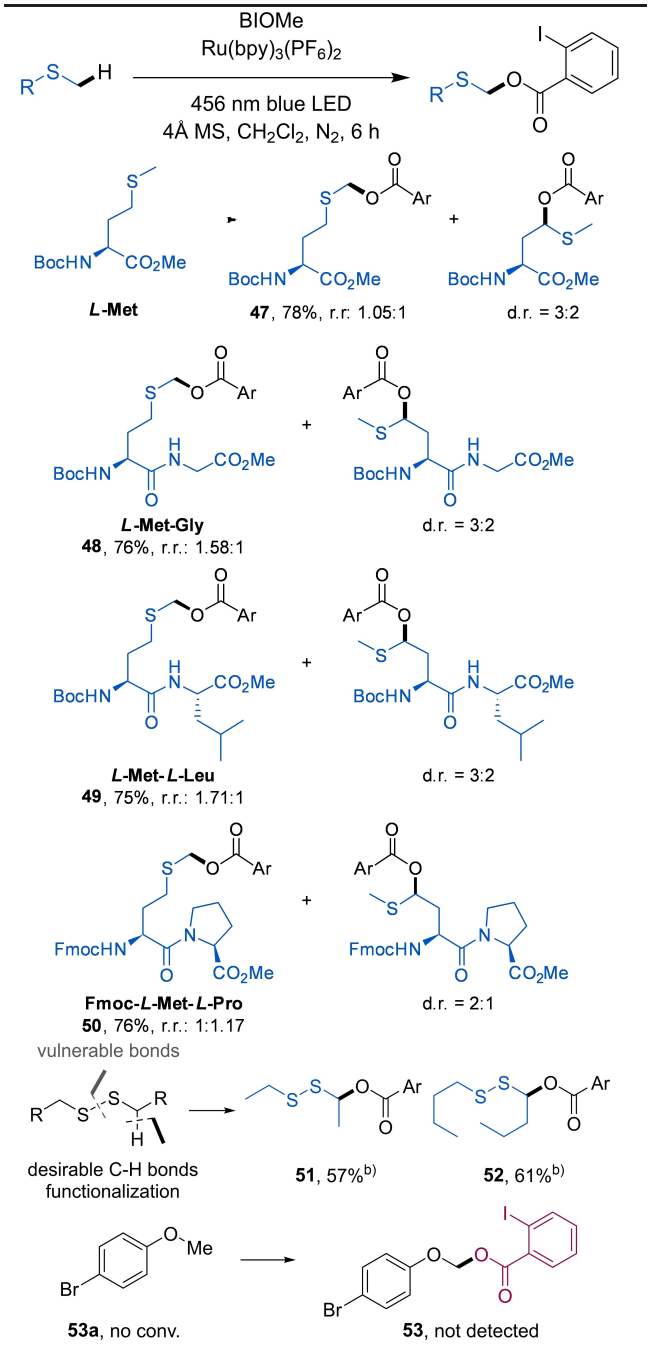
The α-C–H acyloxylation of sulfides extended to methionine derivatives to afford 78% yield of **47**, with a 1.05:1 regiometric ratio (Table 5). In addition, dipeptide methionine derivatives also showed excellent reactivity to give **48**–**50** in 75–76% yields, in which the reactive proline was not affected in the reaction.[26] Disulfides have vulnerable S–S bonds, which selective C–H functionalization is more challenging than in sulfides.[5] In our standard reaction conditions, diethyl disulfides and dibutyl disulfides **51**–**52 a** both successfully reacted to provide α-acyloxy disulfides **51**–**52** in 57–61% yields, and the sensitive disulfide bond remains intact in the reaction (Table 5).[3a] The reaction was ineffective for ether **53 a** and could not provide the α-acyloxy ether **53**, indicating excellent chemoselectivity for α-C–H functionalization of sulfides.

In conclusion, we report the first α-C–H acyloxylation of sulfides and disulfides to synthesize various α-acyloxy sulfides and disulfides under mild photoredox catalysis conditions. Cyclic iodine(III) reagents afforded the carboxyl radical for the hydrogen atom transfer, the mild oxidant for the single-electron transfer, and the benzoic acid as the nucleophile. External nucleophiles can also be introduced. The reaction is compatible with various functional groups and can react with methionine, dipeptide, and disulfide derivatives.

Experimental Section

General procedure for the acyloxylation of sulfides: Sulfides (0.10 mmol, 1.0 equiv.), substituted BI–OMe (1.5 equiv. or 2.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.8 mg, 0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) were placed in a 4 mL clear-colored glass vial equipped with a magnetic stir bar. After 2.0 mL degassed DCM were added, the vial was sealed and exposed to 2×20 W 456 nm blue LEDs (5 cm away from the vial) at room temperature for 6 h with stirring. The reaction mixture was concentrated and purified directly by column chromatography to afford the α-acyloxy (di)sulfides **1**, **4**–**39**, **47**–**52**.

Table 5. Synthetic Potentials.



[a] Reaction conditions: sulfide (0.10 mmol, 1.0 equiv.), BI–OMe (0.15 mmol, 1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) in 2.0 mL DCM under nitrogen with 20 W 456 nm blue LED irradiation at 25 °C for 6 h, unless otherwise noted. Isolated yields were reported.

[b] BI–OMe (0.2 mmol, 2.0 equiv.). r.r., regiomeric ratio. Ar = 2-I–C_6H_4.

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General procedure for the acyloxylation of sulfides with external nucleophiles: (4-bromophenyl)(methyl)sulfane **1a** (0.10 mmol, 1.0 equiv.), diOMe–BI–OMe **37b** (50.7 mg, 0.15 mmol, 1.5 equiv.), aryl carboxylic acid (0.2 mmol, 2.0 equiv.) or acetic acid (1.0 mmol, 10.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.8 mg, 0.002 mmol, 0.02 equiv.) and 4 Å MS (40.0 mg) were placed in a 4 mL clear-colored glass vial equipped with a magnetic stir bar. After 2.0 mL degassed DCM were added, the vial was sealed and exposed to 2×20 W 456 nm blue LEDs (5 cm away from the vial) at room temperature for 6 h with stirring. The reaction mixture was concentrated and purified directly by column chromatography to afford the α-acyloxy sulfides **40**–**43**.

Acknowledgements

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