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Iron-Catalyzed Thiolation and Selenylation of Cycloalkyl Hydroperoxides via C−C Bond Cleavage

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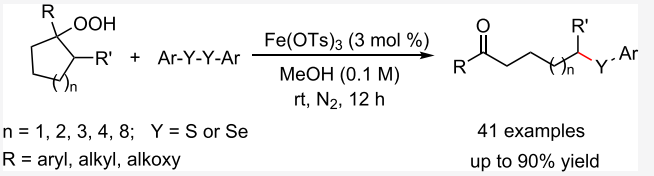
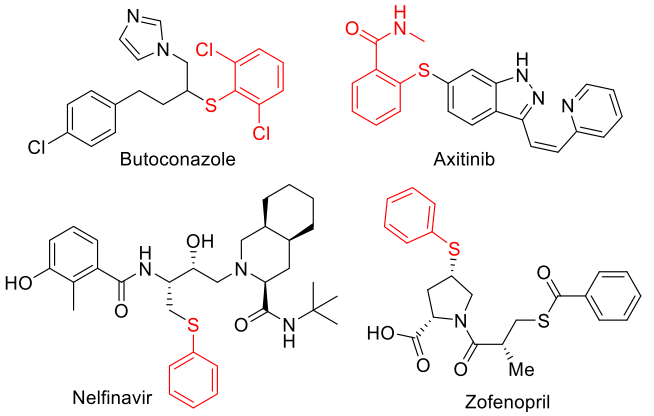
ABSTRACT: A cheap iron-catalyzed C−C bond cleavage/thiolation and selenylation of cycloalkyl hydroperoxides are presented. This redox-neutral protocol provides efficient access to diverse distal keto-functionalized thioethers and selenium compounds. Remarkably, only some amounts of disulfides are required for this transformation.



INTRODUCTION

The thioether motifs are widespread in natural products, pharmaceuticals, and functional materials (Scheme 1).[1]

Scheme 1. Pharmaceutical Molecules Containing Thioether Motifs



Moreover, thioethers are versatile synthetic intermediates for the synthesis of sulfoxide, sulfone, and other organosulfur compounds.[2] Thus, the construction of C−S bonds has received great attention from chemists, and significant progress has been made in this field.[3] Especially, the radical addition, substitution, and coupling reactions of sulfur-centered radicals have inarguably brought chemists a new platform for the construction of diverse C−S bonds.[4] In recent years, radical-mediated ring-opening C−C bond cleavage has emerged as an efficient strategy for the C−C and C-heteroatom bond formation.[5] For instance, the alkoxy radical-initiated C−C bond cleavage has become a powerful tool for the C−C, C−N, C−B, and C−Si bond formation.[6] In 2016 and 2017, Zhu et al. reported the Mn-catalyzed C−S and C−Se bond formation reaction through C−C bond cleavage of cycloalkanols, which provided an efficient approach to the thioethers and selenoether with a distal carbonyl group.[7] However, there still exists some shortages in this protocol, including the requirement of (over) stoichiometric amounts of oxidant (BI-OH) and disulfides as well as the limitation of substrate scope (limited to cyclobutanols). In fact, besides single-electron oxidation of cycloalkanols, homolysis and single-electron reduction of cycloalkyl peroxides could offer an alternative to the reactive alkoxy radical intermediates, which play a key role in the C−C bond cleavage. In this regard, our group and Maruoka's group reported a series of cheap Cu, Fe, or Ni-catalyzed C−C bond cleavage reactions of alkylsilyl peroxides under mild conditions.[8] Therein, the redox neutral reactions were developed and the unstrained substrates were well compatible. These features encouraged us to develop a simple catalytic system for the C−C bond cleavage/C−S bond formation.

Results and Discussion. Disulfides are well-known radical-trapping agents, which are widely employed for the C−S bond formation.[9] Initially, we examined the reaction of cyclopentyl silyl peroxide and diphenyl disulfide **2a** under iron catalysis. After several attempts, we found that the reaction worked well in the presence of 5 mol % $Fe(OTf)_2$ in MeOH under argon, giving the desired thioether **3a** in 85% yield. In view of step- and atom-economy, the corresponding hydroperoxide **1a** was examined instead of cyclopentyl silyl peroxide. To our delight, the reaction of **1a** and **2a** proceeded smoothly to afford **3a** in 70% yield (Table 1, entry 1). Solvent screening revealed that MeOH is the most suitable solvent (entries 2−6). Then, a series of iron salts were tested as the catalyst. Both $Fe(OTf)_3$ and $Fe(OTs)_3$ showed slightly better catalytic

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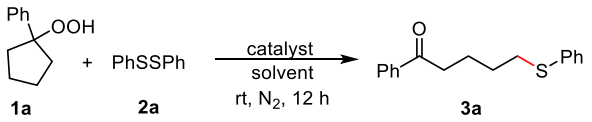
Table 1. Optimized Reaction Conditions of 1a and 2a[a]



entry	catalyst (mol %)	solvent	yield
1	$Fe(OTf)_2$ (5)	MeOH	70 (85)[b]
2	$Fe(OTf)_2$ (5)	EtOH	53
3	$Fe(OTf)_2$ (5)	NMP	63
4	$Fe(OTf)_2$ (5)	CH_3CN	51
5	$Fe(OTf)_2$ (5)	DMF	26
6	$Fe(OTf)_2$ (5)	1,4-dioxane	9
7	$Fe(OAc)_2$ (5)	MeOH	n.r.[d]
8	$FeCl_2$ (5)	MeOH	17
9	$Fe(OTf)_3$ (5)	MeOH	72
10	$Fe(OTs)_3$ (5)	MeOH	75
11	CuI (5)	MeOH	trace
12	Cu(OTf) (5)	MeOH	5
13	$Fe(OTs)_3$ (5)	MeOH	75[c]
14	$Fe(OTs)_3$ (3)	MeOH	74[c]
15		MeOH	n.r.[d]

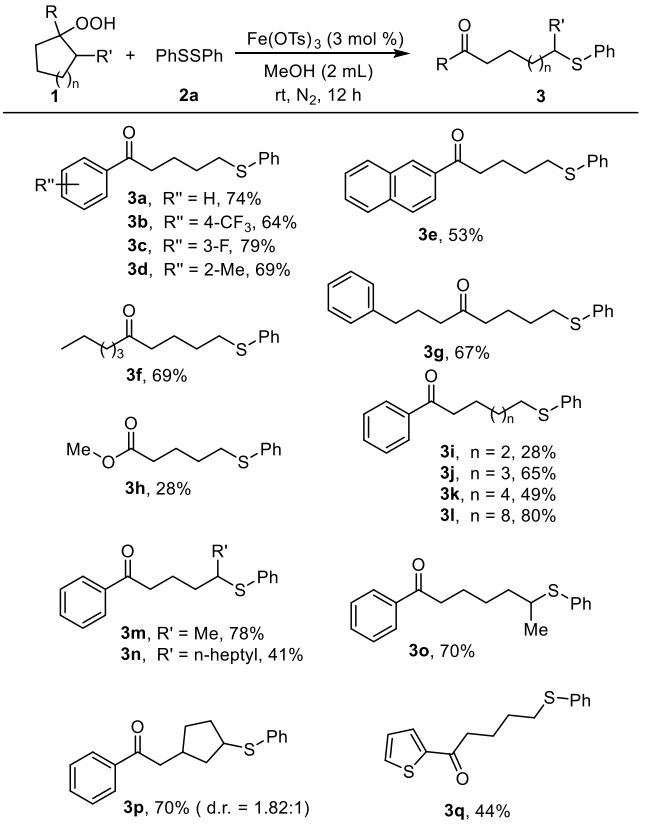
[a]Reaction conditions: catalyst (5 mol %), **1a** (0.2 mmol, 1.0 equiv), **2a** (0.22 mmol, 1.1 equiv), and solvent (2.0 mL), at room temperature, under N_2, for 12 h, isolated yield. [b]Cyclopentyl silyl peroxide was used. [c]0.16 mmol of **2a** was used. [d]No reaction.

activity than $Fe(OTf)_2$, giving **3a** in 72 and 75% yields, respectively, while $Fe(OAc)_2$ and $FeCl_2$ were less effective (entries 7−10). Switching from iron catalysts to copper catalysts such as CuI and Cu(OTf) led to poor yields of **3a** (entries 11 and 12). Therefore, the cheaper $Fe(OTs)_3$ was chosen as the catalyst. Satisfactorily, reducing the amount of diphenyl disulfide **2a** from 1.1 equiv to 0.8 equiv did not affect the yield of **3a** (entry 13), while further reduction of **2a** led to **3a** in lower yield. Finally, the catalyst loading could be reduced to 3 mol % without an obvious decrease in yield, but the catalyst is essential to this reaction (entries 14 and 15). When the reaction was carried out in the air, only a trace of **3a** was observed and **1a** was decomposed to the corresponding alcohol (not shown).

Having established the optimized reaction conditions, we set out to explore the scope of this reaction. As shown in Scheme 2, a variety of alkyl hydroperoxides **1** reacted successfully with **2a** to afford the target thioethers **3** in moderate to good yields. Both 1-aryl- and 1-alkyl-substituted cyclopentyl hydroperoxides were engaged efficiently in this C−C bond cleavage/C−S bond formation process to give the distal keto-functionalized thioethers **3a**−**3g** in good yields. 1-Alkoxyl substrate was also compatible, delivering the ester-functionalized thioether **3h** in 28% yield. Notably, this protocol was also reliable for less strained substrates with six-, seven-, eight-, and even twelve-membered rings, furnishing the corresponding desired products **3i**−**3l** in reasonable yields. 1,2-Disubstituted substrates could undergo the C−C bond cleavage regioselectively to provide the secondary alkylaryl sulfides **3m**−**3o** in 41−78% yields. Hydroperoxide **1p** derived from norcamphor was also an amenable substrate, producing **3p** in 70% yield. The thiophene substituted-cyclopentyl hydroperoxide delivered the product **3q** in a moderate yield.

Next, a wide range of disulfides were evaluated with **1a** under the optimal conditions (Scheme 3). Diverse symmetrical diaryl disulfides reacted with **1a** smoothly to afford the target

Scheme 2. Scope of Alkyl Hydroperoxides[a]



[a]Reaction conditions: $Fe(OTs)_3$ (3 mol %), **1** (0.2 mmol, 1.0 equiv), **2a** (0.16 mmol, 0.8 equiv), and MeOH (2.0 mL), at room temperature, under N_2, for 12 h, isolated yield.

thioethers **4a**−**4r** in moderate to good yields. Diaryl disulfides with electron-donating groups or electron-withdrawing groups on the aromatic ring both were efficient substrates. Synthetically useful functional groups including OMe (**4c**), OH (**4d**), NH_2 (**4e**), and Br (**4h**, **4i**, and **4m**) were well tolerated, which provide opportunities for further synthetic transformations. Notably, heteroaryl disulfides such as di(2-thienyl) disulfide, bis(2-methyl-3-furyl) disulfide, 2,2′-dipyridyl disulfide, and 4,4′-dipyridyl disulfide were compatible with the reactions, providing the corresponding products **4o**−**4r** in moderate to good yields. Unfortunately, by using dialkyl disulfides, such as dibenzyl disulfide and di-*tert*-butyl disulfide as substrates, only a trace amount of the expected products was observed, along with some amount of valerophenone obtained as major byproducts, which were formed through the C−C bond cleavage/H-atom transfer process (not shown). When the unsymmetrical disulfide, 1-(*tert*-butyl)-2-(4-methoxyphenyl)-disulfane **2t**, was subjected to the reaction system, only 11% of thioether **4c** was obtained and no dialkyl thioether **4s** was detected.

To extend the application of this protocol, diselenides were also examined for the C−C bond cleavage/C−Se bond formation reaction (Scheme 4). The reaction of hydroperoxide **1a** and diphenyl diselenides **5a** still worked to afford the keto-functionalized selenium compound **6a** in 51% yield. Unfortunately, increasing the amount of diselenide **5a** to 1.5 equiv could not improve the yield of product **6a**. Other cycloalkyl hydroperoxides were also applicable for the C−Se bond

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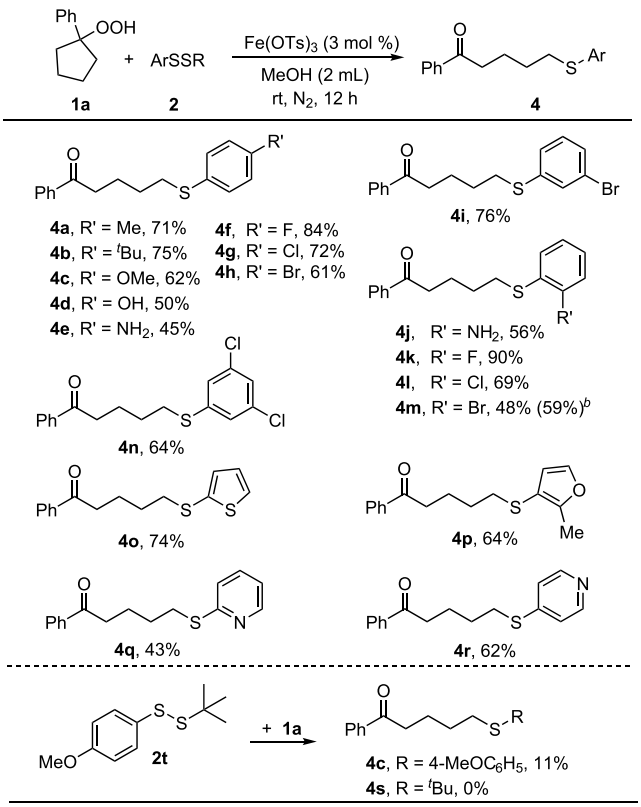
Scheme 3. Scope of Disulfides[a]

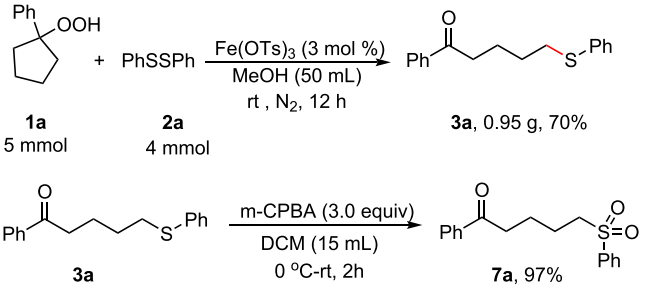


[a]Reaction conditions: $Fe(OTs)_3$ (3 mol %), **1a** (0.2 mmol, 1.0 equiv), **2** (0.16 mmol, 0.8 equiv), and MeOH (2.0 mL), at room temperature, under N_2, for 12 h, isolated yield. [b]Cyclopentyl silyl peroxide was used.

formation, producing **6b**−**6f** in moderate yields. It is worth mentioning that some amount of benzeneseleninic acid was isolated as the byproduct in most of these reactions; this is due to the further oxidation of selenoether with peroxide.

To illustrate the utilization of this simple protocol, the scale-up reaction of **1a** (5 mmol) with **2a** (4 mmol) was conducted. As shown in Scheme 5, the desired keto-functionalized thioether **3a** was still obtained in 70% yield. In addition, product **3a** could be oxidized by *m*-CPBA to afford sulfone **7a** in 97% isolated yield.

Scheme 5. Large Scale Reaction and Oxidation of Compound 3a

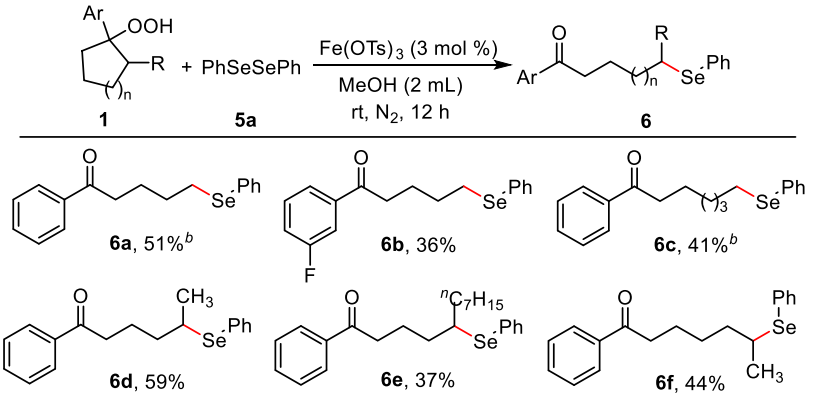


Finally, several control experiments were performed to verify the mechanism of this reaction (Scheme 6). When 2.0 equiv of TEMPO, a well-known radical-trapping agent, was added into the reaction of **1a** and **2a**, no desired product **3a** was observed. Meanwhile, the alkyl-TEMPO adduct **8a** was isolated in 79% yield. These results suggest that a radical intermediate might be involved in this reaction (eq 1). Additionally, the presence of BHT led to a decreased yield of **3a**, which also supports a radical pathway for this transformation (eq 2). Interestingly, when the ratio of **1a** and **2a** was adjusted to 3:1, 61% yield of **3a** was still isolated, which indicated that disulfide could serve as a double "S" source in this transformation (eq 3). Notably, when unsymmetrical diaryl disulfide **2u** was treated with **1a**, both thioethers **4c** and **4f** were obtained. At the same time, a certain amount of symmetrical diaryl disulfides **2d** and **2g** was also isolated (eq 4).

Base on the abovementioned results and literature,[9] a plausible mechanism is proposed in Scheme 7. Single-electron reduction of alkyl hydroperoxide **1a** by Fe(II) generates the alkoxy radical **I** and hydroxide anion. The alkoxy radical subsequently triggers *β*-carbon scission to afford the C-centered radical **II**. Then, the radical **II** is captured by disulfide **2a** to give product **3a** and sulfur-centered radical **III**, which can undergo single-electron oxidation by Fe(III) to furnish the sulfide ion **IV**. Then, the hydroxide anion bonds with **IV** to form sulfenic acid **V**. Sulfenic acid is an unstable species that could convert into disulfide **2a**.[10] In addition, a radical chain propagation process cannot be ruled out at present.

In conclusion, we have developed an efficient iron-catalyzed thiolation and selenylation of cycloalkyl hydroperoxides via C−

Scheme 4. Scope of Selenylation[a]



[a]Reaction conditions: $Fe(OTs)_3$ (3 mol %), **1** (0.2 mmol, 1.0 equiv), **5a** (0.16 mmol, 0.8 equiv), and MeOH (2.0 mL), at room temperature, under N_2, for 12 h, isolated yield. [b]$Fe(OTf)_2$ was used as the catalyst.

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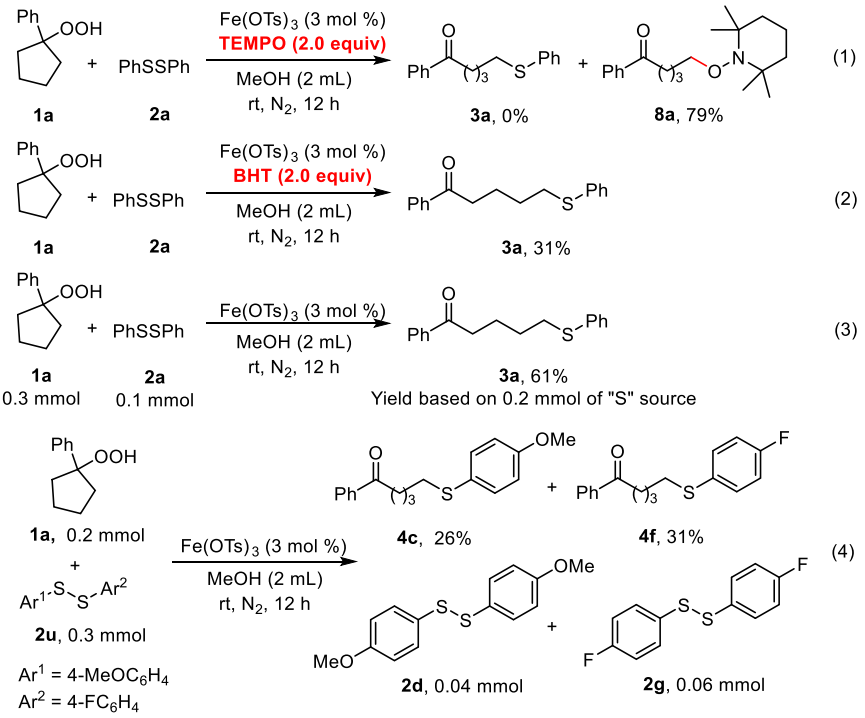
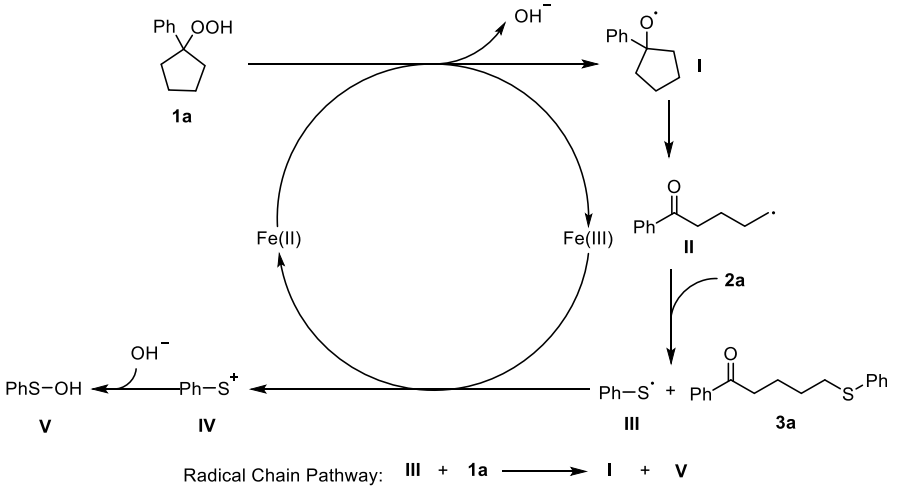
Scheme 6. Mechanism Studies



Scheme 7. Plausible Mechanism



C bond cleavage. A variety of distal keto-functionalized thioethers and selenium compounds could be synthesized with moderate to good yields. Remarkably, no external oxidant and only some amounts of disulfides were required for this transformation. Based on the control experiments, a probably radical pathway was proposed.

EXPERIMENTAL SECTION

General Methods. All commercially available reagents and solvents were used without further purification. All catalytic reactions were conducted in oven-dried Schlenk tubes. The reactions were monitored by TLC and visualized using UV light. Column chromatography was carried out on 200−300 mesh silica gel. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Advance III-400 in $CDCl_3$ at room temperature. The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm relative to either the $CDCl_3$ peak (^{13}C) (δ = 77.16 ppm) or tetramethylsilane (^{1}H) (δ = 0 ppm) as an internal standard. Data of ^{1}H NMR are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, td = triple doublets etc.), integration, coupling constant (Hz), and assignment. High-resolution mass spectrometry (HRMS) was obtained on WATERS I-Class VION IMS Q-Tof. The melting points were measured using open glass capillaries in an SGW X-4A apparatus. IR spectra were recorded on a Bruker Tensor 27 spectrometer, and only major peaks are reported (cm^{-1}).

Starting Materials. All of the cycloalkyl hydroperoxides were prepared from the corresponding cycloalkyl alcohols according to the literature on a 3 mmol scale.[8] All symmetrical and unsymmetrical disulfides were purchased from commercial resources or synthesized according to the literature.[11]

Characterization of Unknown Starting Materials 1. *(1-Hydroperoxycyclopentyl)benzene (**1a**).* Colorless oil (380 mg, 71%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56−7.01 (m, 6H), 2.20−2.19 (m, 2H), 1.86−1.81 (m, 4H), 1.67−1.66 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz,

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$CDCl_3$): δ = 141.7, 127.3, 126.5, 125.5, 94.4, 34.6, 22.7. Spectral data matched literature values.[8]

*1-(1-Hydroperoxycyclopentyl)-4-(trifluoromethyl)benzene (**1b**).* Colorless oil (501 mg, 68%). R_f 0.3 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64−7.56 (m, 4H), 7.43 (s, 1H), 2.34−2.28 (m, 2H), 2.00−1.89 (m, 4H), 1.84−1.79 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 147.1, 129.7 (q, J = 32.2 Hz), 126.7, 125.3 (q, J = 3.7 Hz), 124.1 (q, J = 270.3 Hz), 95.1, 36.0, 23.9. IR (neat): υ_{max} (cm^{-1}) 3431, 2897, 1651, 1399, 776. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{13}F_3O_2Na$, 269.0760; found, 269.0760.

*1-Fluoro-3-(1-hydroperoxycyclopentyl)benzene (**1c**).* Colorless oil (400 mg, 68%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (s, 1H), 7.32 (t, J = 6.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.19−7.16 (m, 1H), 7.03−6.95 (m, 1H), 2.36−2.22 (m, 2H), 1.98−1.85 (m, 4H), 1.83−1.73 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.0 (d, J = 244.2 Hz), 145.7 (d, J = 6.6 Hz), 129.9 (d, J = 8.1 Hz), 121.9 (d, J = 2.8 Hz), 114.4 (d, J = 21.0 Hz), 113.6 (d J = 21.8 Hz), 95.1 (d, J = 1.7 Hz), 35.9, 23.8. IR (neat): υ_{max} (cm^{-1}) 3257, 2751, 1701, 1394, 796. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{13}FO_2Na$, 219.0792; found, 219.0793.

*1-(1-Hydroperoxycyclopentyl)-2-methylbenzene (**1d**).* White solid (420 mg, 73%). m.p. 31−32 °C, R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 1H), 7.23−7.14 (m, 3H), 7.06 (s, 1H), 2.53 (s, 3H), 2.47−2.38 (m, 2H), 2.11−2.00 (m, 2H), 1.87−1.84 (m, 2H), 1.73−1.69 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.6, 137.5, 132.4, 128.2, 127.9, 125.4, 96.4, 35.4, 23.9, 21.5. IR (neat): υ_{max} (cm^{-1}) 3257, 2692, 1683, 1298, 767. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}O_2Na$, 215.1043; found, 215.1041.

*2-(1-Hydroperoxycyclopentyl)naphthalene (**1e**).* White solid (445 mg, 65%). m.p. 55−57 °C, R_f 0.30 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1H), 7.90−7.82 (m, 3H), 7.61 (dd, J = 8.4, 1.6 Hz, 1H), 7.55−7.45 (m, 2H), 7.37 (s, 1H), 2.48−2.35 (m, 2H), 2.12−2.07 (m, 2H), 2.01−1.93 (m, 2H), 1.87−1.82 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.1, 133.1, 132.8, 128.3, 128.2, 127.6, 126.3, 126.1, 125.3, 124.8, 95.7, 35.8, 24.0. IR (neat): υ_{max}(cm^{-1}) 3389, 2733, 1701, 1414, 750, 732. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}O_2Na$, 251.1043; found, 251.1045.

*1-Hydroperoxy-1-pentylcyclopentane (**1f**).* Colorless oil (305 mg, 59%). R_f 0.20 (petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1H), 1.84−1.80 (m, 2H), 1.72−1.65 (m, 4H), 1.58−1.54 (m, 2H), 1.51−1.44 (m, 2H), 1.39−1.25 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 94.9, 36.3, 34.9, 32.4, 24.6, 24.2, 22.7, 14.1. HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{10}H_{20}O_2K$, 211.1095; found, 211.1092.

*(3-(1-Hydroperoxycyclopentyl)propyl)benzene (**1g**).* Colorless oil (363 mg, 55%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.2 Hz, 2H), 7.14−7.09 (m, 4H), 2.58−2.55 (m, 2H), 1.82−1.71 (m, 2H), 1.67−1.59 (m, 6H), 1.52−1.45 (m, 2H), 1.42−1.34 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.5, 128.4, 128.3, 125.8, 94.7, 36.2, 35.7, 34.9, 26.2, 24.5. IR (neat): υ_{max} (cm^{-1}) 3410, 2902, 1703, 1284, 749. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{20}O_2Na$, 243.1356; found, 243.1351.

*1-Hydroperoxy-1-methoxycyclopentane (**1h**).* Colorless oil (257 mg, 65%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (br, 1H), 3.32 (s, 3H), 2.01−1.90 (m, 2H), 1.81−1.71 (m, 2H), 1.71−1.64 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 117.6, 50.5, 33.4, 23.8. IR (neat): υ_{max} (cm^{-1}) 3420, 2957, 1711, 1172, 751. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_6H_{13}O_3$, 133.0859; found, 133.0858.

*(1-Hydroperoxycyclohexyl)benzene (**1i**).* Colorless oil (351 mg, 61%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, J = 7.2, 0.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.13 (s, 1H), 2.18−2.15 (m, 2H), 1.86−1.72 (m, 5H), 1.62−1.59 (m, 2H), 1.38−1.26 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 144.8, 128.6, 127.5, 125.7, 84.5, 34.1, 25.6, 22.0. IR (neat): υ_{max} (cm^{-1}) 3189, 2821, 1678, 754. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}O_2Na$, 215.1043; found, 215.1046.

*1-Hydroperoxy-1-phenylcycloheptane (**1j**).* Colorless oil (340 mg, 55%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 8.0, 1.2 Hz, 2H), 7.36 (t, J = 8.4 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.23 (s, 1H), 2.18−1.99 (m, 4H), 1.84−1.74 (m, 2H), 1.70−1.63 (m, 2H), 1.60−1.52 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 145.9, 128.6, 127.3, 125.6, 89.2, 37.7, 30.1, 22.7. IR (neat): υ_{max} (cm^{-1}) 3409, 2922, 1445, 1009, 753, 699. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}O_2Na$, 229.1199; found, 229.1204.

*1-Hydroperoxy-1-phenylcyclooctane (**1k**).* Colorless oil (343 mg, 52%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52−7.47 (m, 2 H), 7.42−7.31 (m, 2H), 7.30−7.21 (m, 1H), 7.16 (s, 1H), 2.25−2.17 (m, 1H), 2.09−1.91 (m, 3H), 1.74−1.63 (m, 5H), 1.59−1.47 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 143.5, 127.6, 126.4, 125.1, 88.1, 30.5, 27.4, 24.1, 20.8. IR (neat): υ_{max} (cm^{-1}) 3362, 2920, 1683, 1445, 756, 699. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{20}O_2Na$, 243.1356; found, 243.1355.

*1-Hydroperoxy-1-phenylcyclododecane (**1l**).* White solid (410 mg, 49%). m.p. 101−102 °C, R_f 0.30 (petroleum ether/ethyl acetate = 30:1).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (dd, J = 8.2, 1.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.24−7.18 (m, 1H), 7.07 (s, 1H), 2.03−1.88 (m, 2H), 1.63−1.57 (m, 2H), 1.30 (s, 16H), 1.11 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 144.2, 128.5, 127.3, 125.8, 88.6, 30.3, 26.3, 26.2, 22.3, 22.0, 19.4. IR (neat): υ_{max} (cm^{-1}) 3332, 2897, 1632, 1396, 765, 700, 685. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{28}O_2Na$, 299.1982; found, 299.1983.

*(1-Hydroperoxy-2-methylcyclopentyl)benzene (**1m**).* Colorless oil (375 mg, 65%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.35 (m, 4H), 7.34−7.27 (m, 1H), 7.22 (s, 1H), 2.48−2.42 (m, 1H), 2.30−2.09 (m, 3H), 1.98−1.81 (m, 2H), 1.40−1.33 (m, 1H), 0.55 (d, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.5, 128.4, 127.6, 127.2, 98.7, 41.5, 32.3, 30.0, 21.2, 18.7. IR (neat): υ_{max} (cm^{-1}) 3398, 2965, 1603, 1456, 788. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}O_2Na$, 215.1043; found, 215.1045.

*(2-Heptyl-1-hydroperoxycyclopentyl)benzene (**1n**).* Colorless oil (447 mg, 54%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44−7.35 (m, 4H), 7.34−7.28 (m, 1H), 7.21 (s, 1H), 2.50−2.41 (m, 1H), 2.23−2.17 (m, 1H), 2.11−2.01 (m, 1H), 2.00−1.78 (m, 3H), 1.47−1.39 (m, 1H), 1.28−1.19 (m, 4H), 1.17−1.01 (m, 7H), 0.84 (t, J = 7.2 Hz, 3H), 0.68−0.58 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.7, 128.5, 127.6, 127.2, 98.6, 47.1, 32.3, 31.9, 31.2, 29.7, 29.5, 29.3, 27.9, 22.7, 21.5, 14.2. IR (neat): υ_{max} (cm^{-1}) 3396, 2955, 1719, 1449, 760, 700. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{28}O_2Na$, 299.1982; found, 299.1979.

*(1-Hydroperoxy-2-methylcyclohexyl)benzene (**1o**).* Colorless oil (321 mg, 52%). R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43−7.37 (m, 4H), 7.3−7.27 (m, 1H), 6.92 (s, 1H), 2.31−2.27 (m, 1H), 2.10−2.0 (m, 3H), 1.84−1.77 (m, 1H), 1.73−1.68 (m, 1H), 1.54−1.63 (m, 2H), 1.39−1.34 (m, 1H), 0.65 (d, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 144.1, 128.7, 127.6, 126.1, 87.8, 37.1, 28.4, 25.1, 21.5, 19.7, 15.9. IR (neat): υ_{max} (cm^{-1}) 3424, 2936, 1691, 1446, 755. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}O_2Na$, 229.1199; found, 229.1205.

*(1S,2R,4R)-2-Hydroperoxy-2-phenylbicyclo[2.2.1]heptane (**1p**).* Colorless oil (422 mg, 69%) R_f 0.3 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 7.6 Hz, 2H), 7.40−7.35 (m, 2H), 7.32−7.29 (m, 1H), 6.98 (br, 1H), 2.73 (s, 1H), 2.42 (s, 1H), 2.10−2.01 (m, 2H), 1.91 (d, J = 14 Hz, 1H), 1.55−1.43 (m, 2H), 1.31 (d, J = 9.6 Hz, 1H), 1.17−1.00 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.2, 128.6, 128.2, 127.8, 94.8, 44.3, 40.0, 36.9, 36.6, 29.0, 23.8. IR (neat): υ_{max} (cm^{-1}) 3449, 2958, 1449, 1324, 758, 700. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{16}O_2Na$, 227.1043; found, 227.1046.

*2-(1-Hydroperoxycyclopentyl)thiophene (**1q**).* Colorless oil (331 mg, 65%). R_f 0.3 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR

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(400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.18 (d, J = 5.2 Hz, 1H), 6.96 (d, J = 3.6 Hz, 1H), 6.89 (t, J = 4.8 Hz, 1H), 2.31−2.20 (m, 2H), 1.99−1.88 (m, 2H), 1.85−1.76 (m, 2H), 1.73−1.68 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 146.1, 125.7, 124.1, 123.9, 92.0, 36.0, 22.8. IR (neat): υ_{max} (cm^{-1}) 3128, 2697, 1414, 750. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_9H_{12}O_2SNa$, 207.0450; found, 207.0452.

General Procedure for the Reaction of Cycloalkyl Hydroperoxides 1 with Disulfide 2. A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Fe(OTs)_3$ (3 mol %) and disulfide **2** (0.16 mmol, 0.8 equiv). Then, the tube was evacuated and backfilled with nitrogen three times. Subsequently, solution of cycloalkyl hydroperoxide **1** (0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added with a syringe under nitrogen. The tube was then sealed, and the mixture was stirred at a specified temperature for 12 h. After that, the resulting mixture was concentrated in vacuo to remove solvents. The crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:50) to give products **3** and **4** in yields listed in Schemes 2 and 3, respectively.

General Procedure for the Reaction of Cycloalkyl Hydroperoxides 1 with Diselenide 5. A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with a catalyst (3 mol %) and diselenide **5** (0.16 mmol, 0.8 equiv). Then, the tube was evacuated and backfilled with nitrogen three times. Subsequently, solution of cycloalkyl hydroperoxide **1** (0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added with a syringe under nitrogen. The tube was then sealed, and the mixture was stirred at a specified temperature for 12 h. After that, the resulting mixture was concentrated in vacuo to remove solvents. The crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:50) to give product **6** in yields listed in Scheme 4.

Large Scale Reaction of Cycloalkyl Hydroperoxide 1a with Disulfide 2a. To an oven-dried 200 mL Schlenk tube containing a magnetic stir bar were added $Fe(OTs)_3$ (3 mol %) and diphenyl disulfide **2a** (4 mmol, 0.8 equiv). Then, the tube was evacuated and backfilled with nitrogen three times. Subsequently, solution of cycloalkanol hydroperoxide **1a** (5 mmol, 1.0 equiv) in MeOH (50 mL) was added with a syringe under nitrogen. The tube was then sealed, and the mixture was stirred at room temperature for 12 h. After that, the resulting mixture was concentrated in vacuo to remove solvents. The crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:50) to give product **3a** as a white solid (0.95 g, 70%).

Oxidation of Compound 3a. The following procedure was adapted from the literature.[7] To a solution of **3a** (54.1 mg, 0.2 mmol) in DCM (15 mL), *m*-CPBA was added dropwise (85wt %, 122 mg, 0.6 mmol) at 0 °C. Then, the mixture was stirred at room temperature for 2 h. After the reaction was completed, saturated $NaHCO_3$ aqueous solution (10 mL) was slowly added. The mixture was extracted with DCM (10 mL × 3). The combined organic layers were washed with brine (20 mL) and dried and concentrated to give a crude residue, which was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1:5) to afford product **7a** (58.0 mg, 97%).

Radical Trapping Experiment. A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Fe(OTs)_3$ (3 mol %), diphenyl disulfide **2a** (0.16 mmol, 0.8 equiv), and TEMPO (0.4 mmol, 2 equiv). Then, the tube was evacuated and backfilled with nitrogen three times. Subsequently, solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added with a syringe under nitrogen. The tube was then sealed, and the mixture was stirred at room temperature for 12 h. After that, the resulting mixture was concentrated in vacuo to remove solvents. The crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:50) to give product **8a** in 79% yield, and no **3a** was observed.

Radical Inhibition Experiment. A 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Fe(OTs)_3$ (3 mol %), diphenyl disulfide **2a** (0.16 mmol, 0.8 equiv), and BHT (0.4 mmol, 2 equiv). Then, the tube was evacuated and backfilled with nitrogen three times. Subsequently, solution of cyclopentyl hydroperoxide **1a** (0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added with a syringe under nitrogen. The tube was then sealed, and the mixture was stirred at room temperature for 12 h. After that, the resulting mixture was concentrated in vacuo to remove solvents. The crude product was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:50) to give product **3a** in 31% yield.

Characterization of Products 3, 4, 6, and 7. *1-Phenyl-5-(phenylthio)pentan-1-one (**3a**).* White solid (39.7 mg, 74%); m.p. 86−87 °C, R_f 0.21 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.85 (m, 2H), 7.49−7.45 (m, 1H), 7.39−7.35 (m, 2H), 7.29−7.15 (m, 4H), 7.12−7.04 (m, 1H), 2.92−2.87 (m, 4H), 1.82−1.77 (m, 2H), 1.70−1.63 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 137.0, 136.7, 133.1, 129.2, 129.0, 128.7, 128.1, 125.9, 38.1, 33.5, 28.9, 23.4 ppm; IR (neat): υ_{max} 2929, 2857, 1684, 1579, 1275, 1179, 1095, 1021, 763, 749, 687 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}OSNa$, 293.0971; found, 293.0964.

*5-(Phenylthio)-1-(4-(trifluoromethyl)phenyl)pentan-1-one (**3b**).* White solid (43.3 mg, 64%); m.p. 106−107 °C, R_f 0.17 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.26−7.19 (m, 4H), 7.11−7.08 (m, 1H), 2.95−2.88 (m, 4H), 1.87−1.79 (m, 2H), 1.70−1.63 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 198.9, 139.6, 136.6, 134.4 (q, J = 32.8 Hz), 129.3, 129.0, 128.5, 126.4 (q, J = 271 Hz), 126.1, 125.8 (q, J = 3.7 Hz), 38.4, 33.6, 28.8, 23.2 ppm; IR (neat): υ_{max} 3057, 2950, 1685, 1409, 1329, 1228, 1123, 838, 740, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}F_3OSNa$, 361.0844; found, 361.0850.

*1-(3-Fluorophenyl)-5-(phenylthio)pentan-1-one (**3c**).* White solid (45.6 mg, 79%); m.p. 70−71 °C, R_f 0.18 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65−7.63 (m, 1H), 7.56−7.53 (m, 1H), 7.38−7.33 (m, 1H), 7.26−7.18 (m, 5H), 7.11−7.08 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 2.88 (t, J = 7.2 Hz, 2H), 1.85−1.78 (m, 2H), 1.69−1.63 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 198.6 (d, J = 2.0 Hz), 163.0 (d, J = 247.9 Hz), 139.1 (d, J = 6.1 Hz), 136.6, 130.4 (d, J = 7.6 Hz), 129.3, 129.0, 126.0, 123.9 (d, J = 3.0 Hz), 120.1 (d, J = 21.5 Hz), 114.9 (d, J = 22.2 Hz), 38.3, 33.5, 28.8, 23.3 ppm; IR (neat): υ_{max} 3067, 2949, 2866, 1685, 1586, 1480, 1440, 1244, 874, 749, 684 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}FOSNa$, 311.0876; found, 311.0871.

*5-(Phenylthio)-1-(o-tolyl)pentan-1-one (**3d**).* Colorless oil (39.2 mg, 69%); R_f 0.16 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.4 Hz, 1H), 7.30−7.15 (m, 7H), 7.09 (t, J = 7.2 Hz, 1H), 2.88 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.81−1.74 (m, 2H), 1.67−1.60 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 204.2, 138.10, 138.05, 136.7, 132.1, 131.3, 129.2, 129.0, 128.4, 126.0, 125.8, 41.1, 33.6, 28.9, 23.6, 21.4 ppm; IR (neat): υ_{max} 3059, 2927, 1682, 1480, 1263, 1217, 1091, 1025, 747, 691 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}OSNa$, 307.1127; found, 307.1130.

*1-(Naphthalen-2-yl)-5-(phenylthio)pentan-1-one (**3e**).* White solid (34 mg, 53%); m.p. 82−83 °C, R_f 0.12 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.96−7.80 (m, 4H), 7.54−7.48 (m, 2H), 7.28−7.17 (m, 4H), 7.14−7.10 (m, 1H), 3.06 (t, J = 7.2 Hz, 2H), 2.93 (t, J = 7.2 Hz, 2H), 1.90−1.86 (m, 2H), 1.74−1.70 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.0 136.7, 135.7, 134.4, 132.7, 129.8, 129.7, 129.3, 129.0, 128.60, 128.56, 127.9, 126.9, 126.0, 124.0, 38.2, 33.6, 28.9, 23.7. ppm; IR (neat): υ_{max} 3054, 2945, 2706, 1682, 1437, 1276, 750, 689 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}OSNa$, 343.1127; found, 343.1118.

*1-(Phenylthio)decan-5-one (**3f**).* Colorless oil (36.4 mg, 69%); R_f 0.40 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26−7.18 (m, 4H), 7.12−7.10 (m, 1H), 2.84 (t, J = 7.2 Hz, 2H), 2.35−2.28 (m, 4H), 1.64−1.46 (m, 6H), 1.24−1.18 (m, 4H), 0.81 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 211.1, 136.7, 129.1, 129.0, 125.9, 42.9, 42.2, 33.5, 31.5, 28.8, 23.7, 23.0, 22.6, 14.1 ppm; IR (neat): υ_{max} 3058, 2929, 2857, 1711, 1584, 1439, 1261, 1091, 1023, 799, 749, 691 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{24}OSNa$, 287.1440; found, 287.1440.

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*1-Phenyl-8-(phenylthio)octan-4-one (**3g**).* Colorless oil (42.0 mg, 67%); R_f 0.13 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32−7.25 (m, 5H), 7.21−7.15 (m, 4H), 2.90 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.40−2.36 (m, 4H), 1.93−1.85 (m, 2H), 1.71−1.60 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 210.5, 141.7, 136.7, 129.1, 129.0, 128.6, 128.5, 126.1, 125.9, 42.3, 42.0, 35.2, 33.5, 28.8, 25.3, 23.0 ppm; IR (neat): υ_{max} 3059, 2933, 2859, 1709, 1583, 1495, 1479, 1093, 1025, 740, 694 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{24}OSNa$, 335.1440; found, 335.1441.

*Methyl 5-(phenylthio)pentanoate (**3h**).* Colorless oil (12.5 mg, 28%); R_f 0.15 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26−7.19 (m, 4H), 7.10 (t, J = 7.2 Hz, 1H), 3.59 (s, 3H), 2.86 (t, J = 7.2 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 1.72−1.58 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 173.9, 136.6, 129.3, 129.0, 126.0, 51.7, 33.7, 33.4, 28.7, 24.2 ppm; spectral data match those previously reported.[9c]

*1-Phenyl-6-(phenylthio)hexan-1-one (**3i**).* Colorless oil (16.0 mg, 28%); R_f 0.28 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.50−7.46 (m, 1H), 7.41−7.37 (m, 2H), 7.26−7.18 (m, 4H), 7.10−7.07 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H), 1.73−1.60 (m, 4H), 1.49−1.42 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.3, 137.1, 136.9, 133.1, 129.1, 129.0, 128.7, 128.2, 125.9, 38.5, 33.6, 29.1, 28.6, 23.9 ppm; IR (neat): υ_{max} 3059, 2931, 1684, 1282, 749, 690, 656 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{20}OSNa$, 307.1127; found, 307.1122.

*1-Phenyl-7-(phenylthio)heptan-1-one (**3j**).* White solid (38.8 mg, 65%); m.p. 87−88 °C, R_f 0.31 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89−7.86 (m, 2H), 7.51−7.45 (m, 1H), 7.42−7.36 (m, 2H), 7.25−7.18 (m, 4H), 7.10−7.07 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 2.85 (t, J = 7.2 Hz, 2H), 1.70−1.56 (m, 4H), 1.45−1.32 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.5, 137.1, 137.0, 133.1, 128.99, 128.96, 128.7, 128.2, 125.8, 38.6, 33.6, 29.1, 29.0, 28.8, 24.3 ppm; IR (neat): υ_{max} 3054, 2931, 1685, 752, 729, 687 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{19}H_{22}OSNa$, 321.1284; found, 321.1278.

*1-Phenyl-8-(phenylthio)octan-1-one (**3k**).* Colorless oil (33 mg, 49%); R_f 0.21 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90−7.87 (m, 2H), 7.48−7.40 (m, 1H), 7.38−7.37 (m, 2H), 7.26−7.18 (m, 4H), 7.10−7.08 (m, 1H), 2.88 (t, J = 7.2 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 1.68−1.53 (m, 4H), 1.39−1.28 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.6, 137.13, 137.05, 133.0, 129.0, 128.9, 128.7, 128.2, 125.8, 38.7, 33.6, 29.3, 29.19, 29.15, 28.8, 24.4. ppm; IR (neat): υ_{max} 3058, 2928, 1684, 1409, 1261, 1091, 1023, 745, 690, 657 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{24}OSNa$, 335.1440; found, 335.1442.

*1-Phenyl-12-(phenylthio)dodecan-1-one (**3l**).* White solid (59.0 mg, 80%); m.p. 38−39 °C, R_f 0.27 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89−7.87 (m, 2H), 7.49−7.45 (m, 1H), 7.39−7.36 (m, 2H), 7.25−7.17 (m, 4H), 7.09−7.06 (m, 1H), 2.88 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 1.70−1.63 (m, 2H), 1.58−1.54 (m, 2H), 1.33−1.19 (m, 14H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.7, 137.14, 137.12, 133.0, 128.9, 128.8, 128.7, 128.2, 125.7, 38.7, 33.6, 29.63, 29.58, 29.5, 29.3, 29.2, 29.0, 24.5. ppm; IR (neat): υ_{max} 3056, 2918, 2849, 1680, 1466, 753, 688, 659 cm^{-1} HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{24}H_{33}OS$, 369.2247; found, 369.2250.

*1-Phenyl-5-(phenylthio)hexan-1-one (**3m**).* Colorless oil (44.4 mg, 78%); R_f 0.16 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.85 (m, 2H), 7.48−7.46 (m, 1H), 7.40−7.31 (m, 4H), 7.23−7.14 (m, 3H), 3.18−3.17 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 1.87−1.81 (m, 2H), 1.61−1.55 (m, 2H), 1.23 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.0, 137.0, 135.2, 133.1, 132.2, 128.9, 128.7, 128.1, 126.9, 43.3, 38.4, 36.3, 21.9, 21.2 ppm; IR (neat): υ_{max} 3058, 2957, 2925, 1684, 1408, 1222, 1024, 749, 691 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{20}OSNa$, 307.1127; found, 307.1129.

*1-Phenyl-5-(phenylthio)dodecan-1-one (**3n**).* Colorless oil (30.3 mg, 41%); R_f 0.23 (petroleum ether/ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.85 (m, 2H), 7.50−7.46 (m, 1H), 7.40−7.30 (m, 4H), 7.21−7.11 (m, 3H), 3.05−3.00 (m, 1H), 2.90−2.86 (m, 2H), 1.87−1.83 (m, 2H), 1.59−1.53 (m, 4H), 1.39−1.38 (m, 2H), 1.23−1.19 (m, 8H), 0.80 (t, J = 7.2Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.1, 137.1, 135.7, 133.1, 132.1, 128.9, 128.7, 128.2, 126.7, 49.2, 38.5, 34.6, 34.2, 32.0, 29.6, 29.3, 26.9, 22.8, 21.6, 14.3 ppm; IR (neat): υ_{max} S3059, 2925, 2853, 1685, 1582, 1449, 1221, 1090, 1023, 799, 748, 690 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{24}H_{32}OSNa$, 391.2066; found, 391.2065.

*1-Phenyl-6-(phenylthio)heptan-1-one (**3o**).* Colorless oil (41.8 mg, 70%); R_f 0.20 (petroleum ether/ethyl acetate = 80:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.50−7.46 (m, 1H), 7.40−7.36 (m, 2H), 7.32−7.30 (m, 2H), 7.22−7.12 (m, 3H), 3.18−3.13 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 1.68−1.48 (m, 6H), 1.20 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.3, 137.1, 135.3, 133.1, 132.1, 128.9, 128.7, 128.1, 126.8, 43.3, 38.5, 36.5, 26.8, 24.1, 21.3 ppm; IR (neat): υ_{max} 3058, 2928, 2859, 1683, 1581, 1447, 1260, 1091, 1023, 799, 748, 690 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{19}H_{22}OSNa$, 321.1284; found, 321.1286.

*1-Phenyl-2-(3-(phenylthio)cyclopentyl)ethan-1-one (**3p**).* Colorless oil (41.6 mg, 70% d.r. = 1.82:1); R_f 0.14 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.85 (m, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.28−7.26 (m, 2H), 7.21−7.17 (m, 2H), 7.10 (t, J = 7.2 Hz, 1H), 3.65−3.62 (m, 1H), 3.01 (d, J = 6.8 Hz, 0.71H), 2.94 (d, J = 7.2 Hz, 1.29H), 2.72−2.60 (m, 0.63H), 2.51−2.36 (m, 0.73H), 2.17−1.87 (m, 2.74H), 1.71−1.58 (m, 1.30H), 1.47−1.36 (m, 0.41H), 1.28−1.17 (m, 1.45H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 198.6, 198.5, 135.97, 135.93, 135.9, 135.8, 131.98, 131.97, 129.0, 128.9, 127.8, 127.7, 127.6, 127.02, 127.00, 124.98, 124.97, 44.1, 43.7, 43.3, 39.4, 38.9, 34.3, 33.4, 32.1, 32.0, 31.1, 30.4 ppm; IR (neat): υ_{max} 3057, 2950, 2860, 1682, 1582, 1479, 1445, 1211, 1092, 1024, 798, 749, 690 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{19}H_{20}OSNa$, 319.1127; found, 319.1133.

*5-(Phenylthio)-1-(thiophen-2-yl)pentan-1-one (**3q**).* Colorless oil (24.3 mg, 44%) R_f 0.18 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, J = 4.0, 1.2 Hz, 1H), 7.55 (dd, J = 4.8, 1.2 Hz, 1H), 7.26−7.19 (m, 4H), 7.12−7.04 (m, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 1.86−1.78 (m, 2H), 1.70−1.63 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 191.8, 143.2, 135.5, 132.5, 130.7, 128.1, 127.9, 127.1, 124.8, 37.7, 32.4, 27.7, 22.7 ppm; IR (neat): υ_{max} 3065, 2935, 1686, 1448, 1191, 801, 750, 692 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{15}H_{16}OS_2Na$, 299.0535; found, 299.0534.

*1-Phenyl-5-(p-tolylthio)pentan-1-one (**4a**).* White solid (40.3 mg, 71%); m.p. 63−64 °C, R_f 0.22 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.84 (m, 2H), 7.49−7.45 (m, 1H), 7.39−7.35 (m, 2H), 7.18−7.16 (m, 2H), 7.02−7.00 (m, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 2.23 (s, 3H), 1.81−1.75 (m, 2H), 1.66−1.60 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.0, 137.0, 136.2, 133.1, 132.8, 130.1, 129.8, 128.7, 128.1, 38.1, 34.3, 29.0, 23.4, 21.1 ppm; IR (neat): υ_{max} 3055, 2914, 1683, 1491, 1280, 1241, 798, 688 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{20}OSNa$, 307.1127; found, 307.1122.

*5-((4-(tert-Butyl)phenyl)thio)-1-phenylpentan-1-one (**4b**).* White solid (48.9 mg, 75%); m.p. 68−69 °C, R_f 0.32 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95−7.93 (m, 2H), 7.58−7.54 (m, 1H), 7.48−7.44 (m, 2H), 7.32−7.26 (m, 4H), 2.99 (t, J = 7.2 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H), 1.92−1.85 (m, 2H), 1.77−1.70 (m, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.0, 149.3, 137.1, 133.1, 133.0, 129.5, 128.7, 128.2, 126.1, 38.2, 34.6, 34.0, 31.4, 29.0, 23.5 ppm; IR (neat): υ_{max} 3049, 2954, 1683, 1447, 1276, 750, 689, 657, 541 cm^{-1} HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{26}OSNa$, 349.1597; found, 349.1593.

*5-((4-Methoxyphenyl)thio)-1-phenylpentan-1-one (**4c**).* White solid (37.2 mg, 62%); m.p. 72−73 °C, R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.85 (m, 2H), 7.49−7.46 (m, 1H), 7.39−7.35 (m, 2H), 7.26 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H), 2.88 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H), 1.82−1.74 (m, 2H), 1.60−1.55 (m, 2H).

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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.0, 159.0, 137.0, 133.3, 133.1, 128.7, 128.1, 126.6, 114.6, 55.4, 38.1, 35.7, 29.0, 23.4 ppm; IR (neat): υ_{max} 3059, 3003, 1683, 1493, 1280, 1241, 808, 730, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}O_2SNa$, 323.1076; found, 323.1073.

5-((4-Hydroxyphenyl)thio)-1-phenylpentan-1-one (**4d**). White solid (28.6 mg, 50%); m.p. 94−95 °C, R_f 0.20 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89−7.86 (m, 2H), 7.51−7.47 (m, 1H), 7.41−7.37 (m, 2H), 7.22−7.19 (m, 2H), 6.72−6.70 (m, 2H), 5.50 (s, 1H), 2.90 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 1.82−1.75 (m, 2H), 1.63−1.55 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.7, 155.2, 136.9, 133.6, 133.3, 128.8, 128.2, 126.5, 116.2, 38.2, 35.8, 29.0, 23.4 ppm; IR (neat): υ_{max} 3426, 3059, 2950, 1667, 1496, 1263, 817, 730, 683, 640, 505 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}O_2SNa$, 309.0920; found, 309.0917.

5-((4-Aminophenyl)thio)-1-phenylpentan-1-one (**4e**). White solid (25.7 mg, 45%); m.p. 72−73 °C, R_f 0.21 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 3.64 (s, 2H), 2.88 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 1.81−1.73 (m, 2H), 1.61−1.56 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.1, 146.0, 137.0, 134.1, 133.1, 128.7, 128.2, 123.4, 115.7, 38.2, 36.3, 29.1, 23.4 ppm; IR (neat): υ_{max} 3457, 3221, 3063, 2931, 2859, 1678, 596, 1494, 1448, 1276, 1219, 972, 821, 750, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NOSNa$, 308.1080; found, 308.1082.

5-((4-Fluorophenyl)thio)-1-phenylpentan-1-one (**4f**). White solid (48.4 mg, 84%); m.p. 91−92 °C, R_f 0.25 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95−7.93 (m, 2H), 7.56−7.53 (m, 1H), 7.47−7.43 (m, 2H), 7.35−7.31 (m, 2H), 7.00−6.96 (m, 2H), 2.98 (t, J = 7.2 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 1.89−1.83 (m, 2H), 1.72−1.67 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 161.8 (d, J = 246.1 Hz), 137.0, 133.1, 132.4 (d, J = 8.0 Hz), 131.4 (d, J = 3.3 Hz), 127.7, 128.1, 116.1 (d, J = 21.9 Hz), 38.0, 35.0, 28.9, 23.3 ppm; IR (neat): υ_{max} 3057, 2949, 1680, 1490, 1280, 819, 748, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}FOSNa$, 311.0876; found, 311.0869.

5-((4-Chlorophenyl)thio)-1-phenylpentan-1-one (**4g**). White solid (43.7 mg, 72%); m.p. 107−108 °C, R_f 0.25 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.86 (m, 2H), 7.50−7.47 (m, 1H), 7.40−7.36 (m, 2H), 7.19−7.17 (m, 4H), 2.91 (t, J = 7.2 Hz, 2H), 2.86 (t, J = 7.2 Hz, 2H), 1.84−1.76 (m, 2H), 1.68−1.60 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 137.0, 135.2, 133.2, 131.9, 130.6, 129.1, 128.7, 128.1, 38.0, 33.9, 28.7, 23.4 ppm; IR (neat): υ_{max} 3060, 2948, 2863, 1680, 1477, 1277, 1098, 750, 688 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}ClOSNa$, 327.0581; found, 327.0585.

5-((4-Bromophenyl)thio)-1-phenylpentan-1-one (**4h**). White solid (42.6 mg, 61%); m.p. 117−118 °C, R_f 0.26 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.51−7.47 (m, 1H), 7.41−7.37 (m, 2H), 7.32−7.30 (m, 2H), 7.12−7.10 (m, 2H), 2.92 (t, J = 7.2 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H), 1.85−1.77 (m, 2H), 1.68−1.61 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 137.0, 136.0, 133.2, 132.0, 130.7, 128.7, 128.1, 119.8, 38.0, 33.7, 28.7, 23.4 ppm; IR (neat): υ_{max} 3058, 2936, 1680, 1276, 750, 689 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}BrOSNa$, 371.0076; found, 371.0066.

5-((3-Bromophenyl)thio)-1-phenylpentan-1-one (**4i**). White solid (53.1 mg, 76%); m.p. 58−59 °C, R_f 0.24 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.85 (m, 2H), 7.48−7.46 (m, 1H), 7.40−7.35 (m, 3H), 7.21−7.12 (m, 2H), 7.04 (t, J = 8.0 Hz, 1H), 2.93−2.87 (m, 4H), 1.83−1.79 (m, 2H), 1.69−1.64 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.8, 139.4, 137.0, 133.2, 131.1, 130.3, 128.8, 128.7, 128.1, 127.2, 122.9, 38.0, 33.3, 28.6, 23.4 ppm; IR (neat): υ_{max} 3060, 2934, 1679, 1595, 1459, 1280, 1218, 750, 689 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}BrOSNa$, 371.0076; found, 371.0071.

5-((2-Aminophenyl)thio)-1-phenylpentan-1-one (**4j**). Dark oil (31.9 mg, 56%); R_f 0.50 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 6.8 Hz, 1H), 7.39−7.29 (m, 3H), 7.04 (t, J = 7.6 Hz, 1H), 6.71−6.51 (m, 2H), 4.65 (s, 2H), 2.87 (t, J = 7.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 1.79−1.73 (m, 2H), 1.61−1.55 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.1, 148.0, 137.0, 135.9, 133.1, 129.7, 128.7, 128.1, 118.8, 118.2, 115.2, 38.1, 34.7, 29.3, 23.3 ppm; IR (neat): υ_{max} 3454, 3355, 3060, 2930, 1680, 1604, 1478, 1261, 1022, 799, 750, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NOSNa$, 308.1080; found, 308.1084.

5-((2-Fluorophenyl)thio)-1-phenylpentan-1-one (**4k**). White solid (51.9 mg, 90%); m.p. 42−43 °C, R_f 0.24 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.8 Hz, 2H), 7.49−7.45 (m, 1H), 7.38−7.37 (m, 2H), 7.30−7.26 (m, 1H), 7.12−7.10 (m, 1H), 7.01−6.93 (m, 2H), 2.91−2.85 (m, 4H), 1.82−1.79 (m, 2H), 1.64−1.61 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 161.5 (d, J = 244.7 Hz), 136.9, 133.1, 132.0 (d, J = 2.1 Hz), 128.7, 128.3 (d, J = 7.8 Hz), 128.1, 124.5 (d, J = 3.8 Hz), 123.3 (d, J = 17.7 Hz), 115.7 (d, J = 22.4 Hz), 38.0, 33.1, 28.9, 23.3 ppm; IR (neat): υ_{max} 3084, 2936, 1677, 1468, 1449, 1281, 1214, 1071, 750, 727, 687 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}FOSNa$, 311.0876; found, 311.0881.

5-((2-Chlorophenyl)thio)-1-phenylpentan-1-one (**4l**). White solid (48.9 mg, 69%); m.p. 55−56 °C, R_f 0.33 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.48−7.46 (m, 1H), 7.40−7.36 (m, 2H), 7.29−7.26 (m, 1H), 7.20−7.12 (m, 2H), 7.04−7.02 (m, 1H), 2.93 (t, J = 7.2 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 1.87−1.83 (m, 2H), 1.73−1.69 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.8, 137.0, 136.2, 133.5, 133.2, 129.8, 128.7, 128.3, 128.1, 127.2, 126.4, 38.0, 32.4, 28.4, 23.6 ppm; IR (neat): υ_{max} 3059, 2931, 1681, 1450, 1033, 745, 689 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}ClOSNa$, 327.0581; found, 327.0574.

5-((2-Bromophenyl)thio)-1-phenylpentan-1-one (**4m**). White solid (33.5 mg, 48%); m.p. 51−52 °C, R_f 0.30 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89−7.86 (m, 2H), 7.48−7.44 (m, 2H), 7.40−7.36 (m, 2H), 7.19−7.15 (m, 2H), 6.96−6.92 (m, 1H), 2.96−2.89 (m, 4H), 1.88−1.82 (m, 2H), 1.76−1.70 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.9, 138.3, 137.0, 133.2, 133.1, 128.7, 128.1, 127.9, 127.8, 126.5, 123.5, 38.1, 32.8, 28.2, 23.6 ppm; IR (neat): υ_{max} 3058, 2930, 1681, 1447, 1218, 1040, 745, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}BrOSNa$, 371.0076; found, 371.0072.

5-((3,5-Dichlorophenyl)thio)-1-phenylpentan-1-one (**4n**). White solid (43.6 mg, 64%); m.p. 62−63 °C, R_f 0.27 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.0 Hz, 2H), 7.50−7.47 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.05 (s, 3H), 2.95−2.88 (m, 4H), 1.85−1.70 (m, 2H), 1.71−1.66 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 198.5, 139.7, 135.8, 134.1, 132.1, 127.6, 127.0, 124.8, 124.5, 36.8, 31.8, 27.2, 22.2 ppm; IR (neat): υ_{max} 3073, 2937, 1677, 1533, 1419, 1294, 1097, 830, 798, 754, 729, 689 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}Cl_2OSNa$, 361.0191; found, 361.0196.

1-Phenyl-5-(thiophen-2-ylthio)pentan-1-one (**4o**). Colorless oil (40.9 mg, 74%); R_f 0.25 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96−7.94 (m, 2H), 7.58−7.54 (m, 1H), 7.48−7.44 (m, 2H), 7.34−7.32 (m, 1H), 7.12−7.10 (m, 1H), 6.98−6.96 (m, 1H), 2.98 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 1.88−1.83 (m, 2H), 1.74−1.68 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.0, 137.0, 134.6, 133.7, 133.1, 129.3, 128.7, 128.2, 127.6, 38.8, 38.1, 29.1, 23.1 ppm; IR (neat): υ_{max} 3064, 2932, 1682, 1448, 1179, 750, 691 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}OS_2Na$, 299.0535; found, 299.0529.

5-((2-Methylfuran-3-yl)thio)-1-phenylpentan-1-one (**4p**). Colorless oil (35.1 mg, 64%); R_f 0.22 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 2.0 Hz, 1H), 6.26 (d, J = 2.0 Hz, 1H), 2.89 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.25 (s, 3H), 1.81−1.73 (m, 2H), 1.58−1.51 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.0, 154.8, 140.6, 137.0, 133.1, 128.7, 128.1, 115.1, 110.3, 38.2, 35.8, 29.3, 23.2, 12.0 ppm; IR (neat):

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υ_{max} 3060, 2920, 2857, 1682, 1956, 1512, 1447, 1269, 1088, 749, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}O_2SNa$, 297.0920; found, 297.0922.

*1-Phenyl-5-(pyridin-2-ylthio)pentan-1-one (**4q**).* Colorless oil (23.0 mg, 43%); R_f 0.22 (petroleum ether/ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 4.8 Hz, 1H), 7.96−7.94 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.47−7.44 (m, 3H), 7.16 (d, J = 8.0 Hz, 1H), 6.97−6.94 (m, 1H), 3.22 (t, J = 7.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 1.93−1.88 (m, 2H), 1.85−1.79 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.1, 159.3, 149.6, 137.1, 136.0, 133.1, 128.7, 128.2, 122.4, 119.4, 38.2, 29.8, 29.2, 23.6 ppm; IR (neat): υ_{max} 3060, 2930, 2854, 1683, 1597, 1451, 1414, 1276, 1124, 751, 691 cm^{-1} HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NOS$, 272.1104; found, 272.1106.

*1-Phenyl-5-(pyridin-4-ylthio)pentan-1-one (**4r**).* White solid (33.7 mg, 62%); m.p. 102−103 °C, R_f 0.11 (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 4.0 Hz, 2H), 7.88 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 5.2 Hz, 2H), 2.97−2.93 (m, 4H), 1.89−1.70 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.6, 149.6, 149.1, 136.9, 133.2, 128.7, 128.1, 120.8, 37.9, 30.6, 28.2, 23.4 ppm; IR (neat): υ_{max} 3067, 2935, 2870, 1679, 1574, 1406, 1281, 799, 751, 732, 690 cm^{-1} HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}OS$, 272.1104; found, 272.1105.

*1-Phenyl-5-(phenylselanyl)pentan-1-one (**6a**).* Light yellow solid (32.4 mg, 51%); R_f 0.24 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.85 (m, 2H), 7.50−7.46 (m, 1H), 7.43−7.36 (m, 4H), 7.18−7.17 (m, 3H), 2.92−2.86 (m, 4H), 1.82−1.72 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.0, 137.0, 133.1, 132.7, 130.4, 129.2, 128.7, 128.2, 126.9, 38.0, 29.9, 27.7, 24.5 ppm; spectral data match those previously reported.[12]

*1-(3-Fluorophenyl)-5-(phenylselanyl)pentan-1-one (**6b**).* Light yellow solid (24.1 mg, 36%); m.p. 52−53 °C, R_f 0.20 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.8 Hz, 1H), 7.55−7.42 (m, 1H), 7.42−7.33 (m, 3H), 7.20−7.16 (m, 4H), 2.89−2.85 (m, 4H), 1.81−1.69 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 198.6 (d, J = 2.1 Hz), 163.0 (d, J = 247.9 Hz), 139.1 (d, J = 6.0 Hz), 132.7, 130.4 (d, J = 7.2 Hz), 129.2, 126.9, 123.9 (d, J = 3.0 Hz), 120.1 (d, J = 21.6 Hz), 114.9 (d, J = 22.2 Hz), 38.2, 29.8, 27.6, 24.3 ppm; IR (neat): υ_{max} 3067, 2936, 1685, 1585, 1478, 1439, 1262, 1238, 1020, 873, 797, 761, 729, 683 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}FOSeNa$, 359.0321; found, 359.0325.

*1-Phenyl-7-(phenylselanyl)heptan-1-one (**6c**).* Light yellow solid (28.3 mg, 41%); m.p. 68−69 °C, R_f 0.28 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89−7.86 (m, 2H), 7.50−7.31 (m, 5H), 7.19−7.14 (m, 3H), 2.91−2.82 (m, 4H), 1.69−1.61 (m, 4H), 1.42−1.25 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.5, 137.1, 133.0, 132.5, 130.7, 129.1, 128.7, 128.2, 126.8, 38.6, 30.1, 29.8, 28.9, 27.9, 24.3 ppm; IR (neat): υ_{max} 3056, 2928, 2853, 1682, 1578, 1275, 1017, 907, 797, 750, 687 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}OSeNa$, 369.0728; found, 369.0730.

*1-Phenyl-5-(phenylselanyl)hexan-1-one (**6d**).* Light yellow oil (39.1 mg, 59%); R_f 0.22 (petroleum ether/ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.85 (m, 2H), 7.50−7.37 (m, 5H), 7.20−7.19 (m, 3H), 3.29−3.20 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 1.87−1.80 (m, 2H), 1.70−1.58 (m, 2H), 1.36 (d, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.1, 137.1, 135.1, 133.1, 129.3, 129.0, 128.7, 128.2, 127.5, 39.6, 38.3, 37.3, 22.7, 22.3 ppm; IR (neat): υ_{max} 3058, 2955, 2850, 1683, 1579, 1448, 1275, 1261, 1020, 797, 750, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{20}OSeNa$, 355.0572; found, 355.0576.

*1-Phenyl-6-(phenylselanyl)heptan-1-one (**6e**).* Light yellow oil (31 mg, 37%); R_f 0.39 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87−7.85 (m, 2H), 7.50−7.45 (m, 3H), 7.38 (t, J = 7.6 Hz, 2H), 7.19−7.17 (m, 3H), 3.14−3.07 (m, 1H), 2.87 (td, J = 7.2, 2.0 Hz, 2H), 1.90−1.79 (m, 2H), 1.64−1.52 (m, 4H), 1.42−1.35 (m, 2H), 1.18 (br s, 8H), 0.80 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.0, 135.9, 133.9, 131.9, 128.4, 127.8, 127.5, 127.0, 126.3, 45.5, 37.3, 34.3, 34.0, 30.8, 28.4, 28.2, 26.6, 21.6, 21.4, 13.1 ppm; IR (neat): υ_{max} 3059, 2926, 2854, 1687, 1448, 1261, 1022, 802, 750, 692 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{32}OSeNa$, 439.1511; found, 439.1511.

*1-Phenyl-5-(phenylselanyl)dodecan-1-one (**6f**).* Light yellow oil (30.1 mg, 44%); R_f 0.29 (petroleum ether/ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.86 (m, 2H), 7.50−7.37 (m, 5H), 7.19−7.17 (m, 3H), 3.27−3.19 (m, 1H), 2.89 (t, J = 7.2 Hz, 2H), 1.68−1.45 (m, 6H), 1.33 (d, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.3, 137.1, 135.1, 133.1, 129.4, 129.0, 128.7, 128.2, 127.5, 39.7, 38.5, 37.4, 27.6, 24.0, 22.3 ppm; IR (neat): υ_{max} 3057, 2929, 2857, 1684, 1579, 1448, 1260, 1095, 1021, 799, 749, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}OSeNa$, 369.0728; found, 369.0731.

*1-Phenyl-5-(phenylsulfonyl)pentan-1-one (**7a**).* White solid (58.6 mg, 97%); m.p. 114−115 °C, R_f 0.21 (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84−7.83 (m, 4H), 7.60−7.57 (m, 1H), 7.51−7.47 (m, 3H), 7.40−7.36 (m, 2H), 3.08 (t, J = 7.2 Hz, 2H), 2.91 (t, J = 6.4 Hz, 2H), 1.76−1.74 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 199.2, 139.1, 136.7, 133.8, 133.3, 129.4, 128.7, 128.12, 128.05, 56.2, 37.8, 22.7, 22.5. ppm; IR (neat): υ_{max} 3062, 2946, 1681, 1447, 1288, 1146, 1086, 750, 690 cm^{-1} HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}O_3SNa$, 325.0869; found, 325.0871.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01366.

Optimization of the reaction conditions and ^1H and ^{13}C spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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