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Fenton-Inspired C−H Functionalization: Peroxide-Directed C−H Thioetherification

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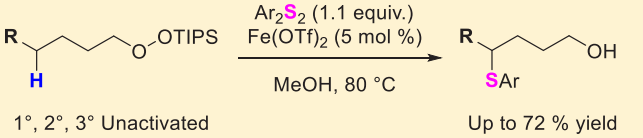
Supporting Information

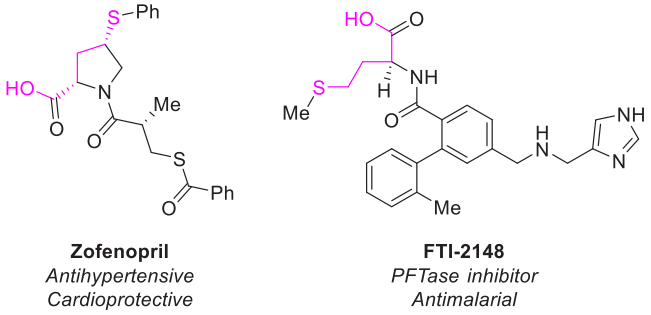
ABSTRACT: Substoichiometric iron mediates the thioetherification of unactivated aliphatic C−H bonds directed by resident silylperoxides. Upon exposure to a catalytic amount of iron(II) triflate, TIPS-protected peroxides bearing primary, secondary, and tertiary C−H sites undergo chemoselective thioetherification of remote C−H bonds with diaryl disulfides. The reaction demonstrates a broad substrate scope and functional group tolerance without the use of any noble metal additives. Mechanistic experiments suggest that the reaction proceeds through 1,5-H atom abstraction by a hydroxyl radical generated with iron.



- TIPS group biases selectivity of O–O cleavage
- Fenton-inspired system enables selective C–H functionalization

INTRODUCTION

Thioethers are versatile synthetic intermediates, as they are readily oxidized to either the sulfoxide or the sulfone.[1] Sulfoxides are well-known for enabling *syn* eliminations,[2] Mislow−Evans rearrangements,[3,4] Pummerer reactions,[5,6] and sulfoxide−metal exchanges[7,8] while also acting as a useful ligand class for transition metal catalysis.[9] The higher-oxidation state sulfones also provide ample opportunities in organic synthesis, most notably as alkene precursors in the Julia−Lythgoe olefination,[1,10] Kocienski-modified Julia olefination,[11,12] and Ramberg−Bäcklund rearrangement.[13,14] A recent report has also highlighted the utility of sulfones as radical cross-coupling partners.[15] The preparation of alkyl thioethers generally proceeds through nucleophilic displacement of a (pseudo)halide with a thiol or the trapping of an alkyl radical or organometallic nucleophile with a disulfide.[16] In addition to the synthetic versatility of thioethers, thioethers themselves are found in a variety of bioactive molecules such as Zofenopril, an FDA-approved angiotensin converting enzyme (ACE) inhibitor with antihypertensive and cardioprotective properties (Figure 1).[17] Čeković has reported that phenylsulfenyl ethers promote the selective thiophenylation of unactivated C−H bonds under photolytic conditions.[18] With this limited precedent, a robust, catalytic method for the selective thioetherification of C(sp^3)−H bonds remains desirable. While directed C−H functionalization has developed quickly over the past 20 years,[19] strict steric and electronic requirements imposed by the transition metal-mediated C−H activation step have limited extension of this strategy to C(sp^3)−H bonds. Here, we offer a directed, radical C−H thioetherification reaction that can overcome such limitations and enable facile C−H oxidations.



Zofenopril
Antihypertensive
Cardioprotective

FTI-2148
PFTase inhibitor
Antimalarial

Figure 1. Bioactive molecules bearing a 1,4-oxy-thio motif.

The Fenton reaction (Figure 2a) represents the most widely implemented C−H oxidation in history.[20−23] Inspired by this precedent, we sought to investigate an intramolecular variant of Fenton's initial discovery. We hypothesized that by harnessing the facile 1,5-H-atom abstraction observed in other heteroatom-based radical systems, we could employ easily obtained peroxides in the presence of iron to generate the requisite H-atom abstractor.

RESULTS AND DISCUSSION

To test the hypothesis, a series of peroxides were prepared from the oxidation of the primary alcohol (see the Supporting Information for full details). We have previously demonstrated that $Fe(OTf)_2$ is an effective catalyst for the generation of N-centered radicals (Figure 2b).[24] Interestingly, exposure of symmetrical peroxide **1** to $Fe(OTf)_2$ in the presence of excess disulfide trap provided the desired product in 50% NMR yield (Scheme 1). Encouraged by this preliminary result, we sought to improve the reaction with the goal of developing a general method for selective C−H thioetherification.

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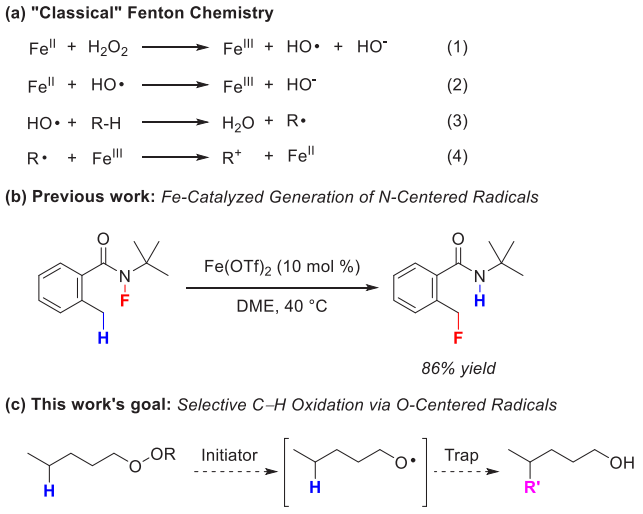
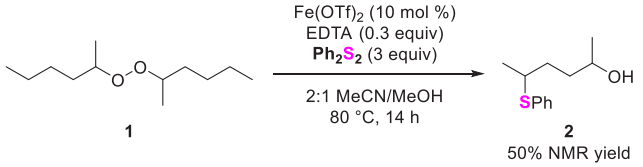


Figure 2. Directed radical chemistry as a route to C(sp^3)–H thioetherification.

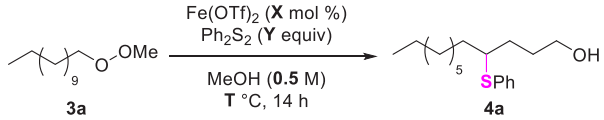
Scheme 1. Thioetherification of an Unactivated C–H Bond



The use of an unsymmetric peroxide improves the atom economy of the transformation but also introduces a challenge of selectivity for the desired alkoxy radical during O–O bond cleavage. We selected dodecyl-methyl peroxide **3a** as a model substrate for optimization of the reaction parameters (Table 1). Although the room-temperature reaction did not proceed at a low concentration, we found that at 0.5 M, the reaction with 5 mol % $Fe(OTf)_2$ and 1.5 equiv of disulfide provided **4a** in 41% yield (entries 1 and 2, Table 1). Although higher reaction temperatures, catalyst loadings, or disulfide loadings did not substantially improve the reaction (entries 3, 4, and 6–8, Table 1), we were pleased to find that the disulfide loading could be decreased to 1.1 equiv with no loss of yield (entry 5, Table 1). As with the iron-catalyzed peroxide reductions that Bao has reported,[25,26] all other precatalysts that wee evaluated were inferior to $Fe(OTf)_2$ (see the Supporting Information). At this stage, we noticed that a number of reactions with $Fe(OTf)_2$ provided yields between 40% and 45% with a nearly 1:1 **4a**:1-dodecanol ratio. Both of these outcomes suggested that all steps of the putative catalytic cycle (O–O cleavage, HAT, radical quench, and catalyst turnover) were proceeding efficiently, but the O–O cleavage simply lacked selectivity. Therefore, we reasoned that replacing the methyl with a variety of substituents would be the most likely way to improve the reaction beyond its current state.

A series of sacrificial substituents with varying electronic and steric properties were evaluated in the C–H thioetherification reaction (Table 2). The hydroperoxide provided a very similar 39% yield (entry 2, Table 2), perhaps due to the similar pK_a values of a primary alcohol and water.[27] Surprisingly, acyl peroxides performed poorly in the reaction (entry 3, Table 2).[28] Considering the mechanism of the Fenton reaction, the acyl peroxide should exhibit high selectivity for the alkoxy radical and carboxylate with negligible formation of the opposite pair. The 6% yield from trifluoroacetyl peroxide **3c**, however, was the highest of all acyl peroxides examined (see the Supporting Information). Although most silyl groups were comparable to the methyl- and hydroperoxides (entries 4–9, Table 2), triisopropylsilyl (TIPS)-protected peroxide **3j** stood out because of its incomplete conversion and 2:1 **4a**:1-dodecanol ratio (entry 10, Table 2), the first sign of selective O–O bond cleavage. Further experiments revealed that the reaction proceeded most efficiently at higher temperatures and lower concentrations, with an optimal 71% yield and 3.5:1 selectivity at 80 °C and 0.1 M (entry 11, Table 2). Further experiments revealed that the reaction proceeded to full conversion within 5 h. Slight modifications to the reaction conditions, such as addition of $Fe(OTf)_2$ as a solution in methanol (**3** is insoluble in methanol), an increased disulfide loading, or an increased catalyst loading, had a minimal impact on the reaction. The TIPS group remained superior after an extensive screening of other silyl groups (see the Supporting Information for additional details).

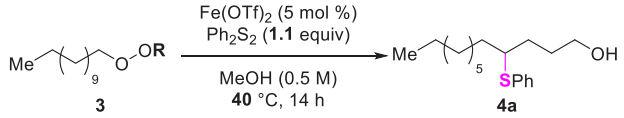
Table 1. Optimization of Pertinent Reaction Parameters



entry	Ph_2S_2 (equiv)	temp (°C)	% Fe	product (%)[a]	1-dodecanol (%)
1[b]	1.5	rt	5	0	10
2	1.5	rt	5	41	43
3	1.5	rt	20	23	52
4	1.5	40	5	41	45
5	1.1	40	5	41	43
6	1.5	80	5	45	35
7	1.5	80	20	35	42
8	4.0	rt	5	43	42

[a]NMR yield using BHT as the internal standard. Full conversion unless otherwise noted. [b]Reaction run at a 0.05 M concentration and 24% conversion.

Table 2. Investigation of Nonsymmetrical Peroxides



entry	R group		yield (%)[a]	RSM (%)	1-dodecanol (%)
1	Me	**3a**	41	0	43
2	H	**3b**	39	0	37
3	$C(O)CF_3$	**3c**	6	21	28
4	$Si(OEt)_3$	**3d**	43	0	nd
5	$SiMe_3$	**3e**	34	4	36
6	$SiEt_3$	**3f**	37	0	36
7	$Si(C_2H_3)Me_2$	**3g**	50	0	37
8	$SiMePh_2$	**3h**	44	0	30
9	$SiMe_2tBu$	**3i**	44	0	27
10	$SiiPr_3$	**3j**	23	55	11
11[b]	$SiiPr_3$		71	0	20

[a]NMR yield using BHT as an internal standard. [b]At 80 °C and 0.1 M.

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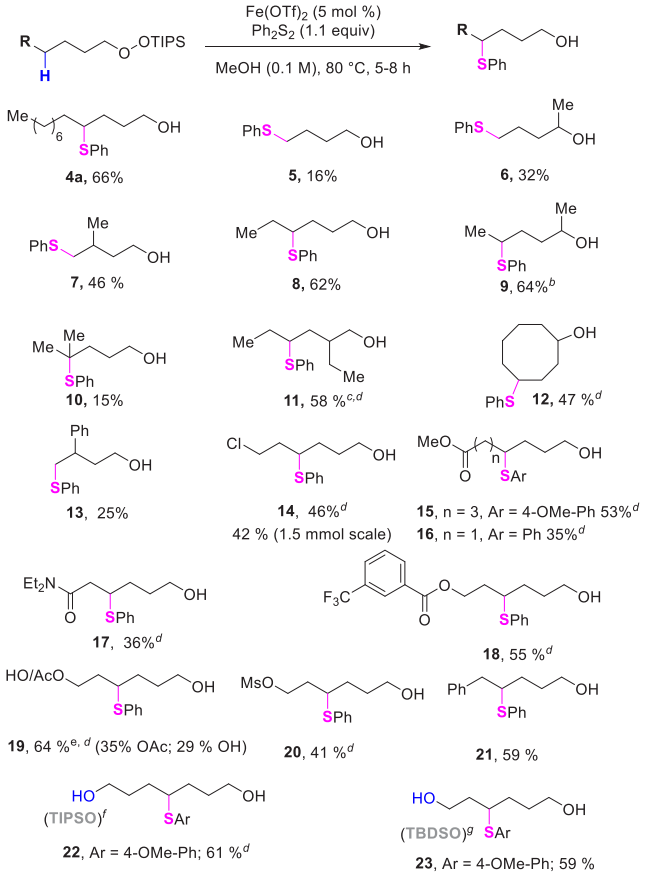
With optimized conditions for the directed C(sp^3)–H thioetherification, we evaluated the performance of the reaction across a number of substrates. Pleasingly, the reaction is effective for the functionalization of primary, secondary, and tertiary C–H sites (Table 3), with the highest yields obtained

Table 3. Substrate Scope for Thioetherification[a]

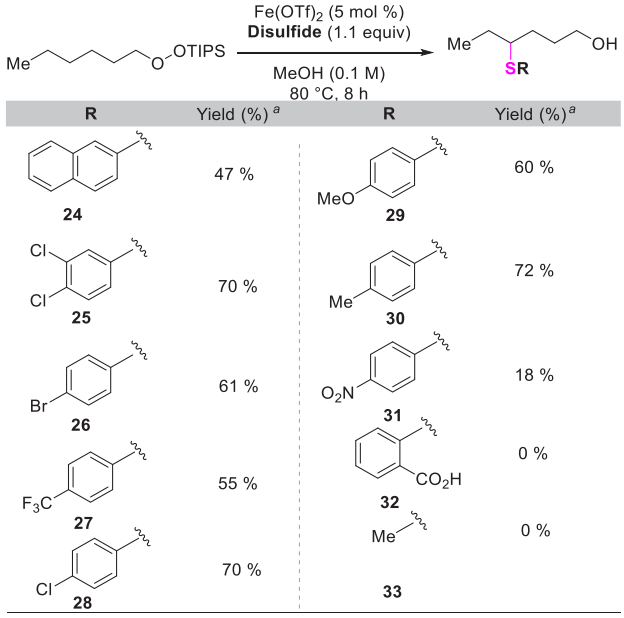


[a]Isolated yield. [b]Reaction run for 10 h. [c]Isolated as a mixture with another regioisomer with a 1:0.08 ratio. [d]Reaction run for 8 h. [e]Total thioarylation yield, as deacylation occurred in the reaction. [f]TIPS deportection of alcohol observed during the reaction. [g]TBDS deprotection of alcohol observed during the reaction, reaction run for 12 h.

for secondary systems (Table 3, **4a**, **8**, **9**, and **11**–**23**). Interestingly, the 2-hexyl peroxide provided a 5:1 mixture of [1,5] and [1,6] products, but **8** was isolated as a single isomer. The improved yield of primary thioether **6** in comparison to **5** is likely the result of a Thorpe–Ingold effect imposed by the methyl group. As expected, a secondary C–H undergoes preferential (1:0.8) thioarylation over primary C–H bonds (Table 3, **11**). Moreover, alcohols bearing chloro, ester, amide, and sulfonic ester functional groups (**14**–**20**) function well under the reaction conditions. Usefully, silyl-protected alcohols undergo desilylation during the reaction to produce thioarylated diols (**22** and **23**).

Next, we examined the scope of various disulfide traps (Table 4). Although naphthyl disulfide **4b** proved to be less effective (perhaps due to its poor solubility in methanol), we found that both electron-poor and electron-rich aryl disulfides **24**–**31** performed similarly to Ph_2S_2. In contrast, 4-nitrodisulfide **31** provided very low yields, and no product was

Table 4. Disulfide Scope for Thioetherification

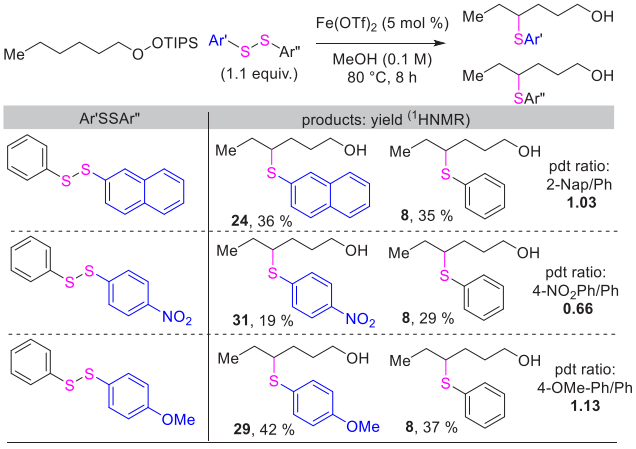


[a]Isolated yield. Full conversion in all cases.

observed with 2-carboxyphenyl disulfide **32**. Attempts to extend the methodology to dialkyl disulfides proved difficult as alkyl disulfides trap alkyl radicals more slowly than aryl disulfides.[29,30] For example, dimethyl disulfide **33** and dioctyl disulfide fail to produce any product.

To examine the electronic preference during C–S bond formation, we tested the reaction with electronically differentiated disulfides (Table 5). Little difference was observed in

Table 5. Thioetherification with an Unsymmetrical Disulfide



a competition between phenyl and naphthyl (product ratio of 1.03). Upon comparison of electron-poor (4-nitrophenyl) or electron-rich (4-methoxyphenyl) to phenyl disulfides, however, the reaction clearly favored the product that incorporated the more electron-rich sulfur system.

The presumption of a Fenton mechanism guided the conceptual development of this thioetherification reaction. To test this mechanistic hypothesis, experiments were conducted to uncover evidence of the presence of radical

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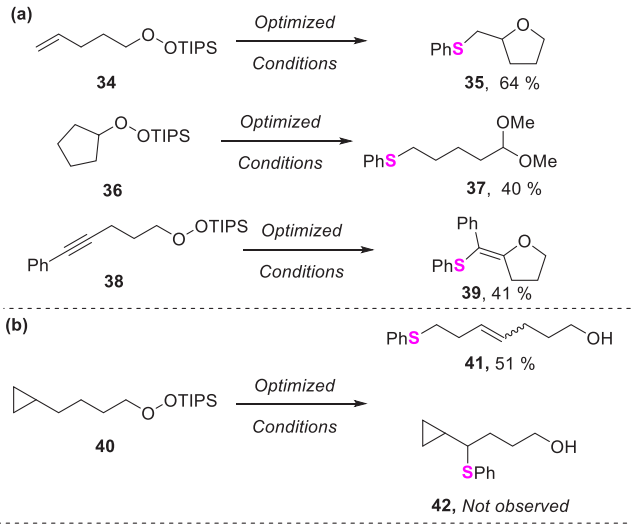
intermediates. Providing support for an oxy-radical intermediate, 1-pentenyl peroxide **34** undergoes 5-*exo-trig* cyclization and subsequent trapping to form the substituted tetrahydrofuran **35**. Additionally, cyclopentyl peroxide **36** provides α-cleavage product **37** in 40% isolated yield as the dimethyl acetal (Scheme 2a). Interestingly, substrate **38** could undergo

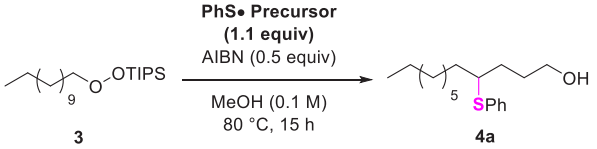
Scheme 2. Radical-Clock Experiments



5-*exo-dig* cyclization to form tetrasubstituted enol **39** in a remarkable 41% yield. Furthermore, cyclopropylmethyl substrate **40** undergoes complete ring opening to afford primary sulfide **41** in 51% isolated yield (Scheme 2b). The sum of these results suggests that the reaction occurs via a radical intermediate with a lifetime of approximately 10^{-3}–10^{-4} s.[31]

If the iron catalyst acted as an initiator and the reaction proceeded thereafter through a radical chain propagation, then PhS$^{\bullet}$ should be capable of initiating the reaction. When PhSH and AIBN were used to generate PhS$^{\bullet}$, the peroxide underwent full conversion with no sign of thioetherification (entry 1, Table 6). In contrast, with Ph_2S_2 (2.1 or 1.1 equiv) and AIBN,

Table 6. Disulfide Scope for Thioetherification



entry	precursor	yield (%)[a]	RSM (%)	1-dodecanol (%)	1-dodecanal (%)
1	PhSH	0	0	75	8
2[b]	Ph_2S_2	9	69	7	7
3	Ph_2S_2	26	36	17	12
4[c]	Ph_2S_2	54	0	21	15

[a]NMR yield using BHT as the internal standard. [b]With 2.1 equiv of Ph_2S_2. [c]No AIBN.

we observed low yields of the product (entries 2 and 3, Table 6). Additional experimentation revealed that the reaction did not require an exogenous initiator as the reaction with 1.1 equiv of Ph_2S_2 and no AIBN provided a 54% yield (entry 4, Table 6). Interestingly, the thermal, iron-free reactions produced 7–15% 1-dodecanal as a side product while the iron-catalyzed variants produced, at best, trace quantities of 1-dodecanal.

Intrigued by this result, we examined the thermal profile of the background reaction in greater detail. When run to 18 h, thermal decomposition of the O–O bond begins between 50 and 60 °C. At temperatures above 80 °C, the maximum yield is 59%. Importantly, we found that at 80 °C, thermal decomposition only begins to set in at the 5 h mark, and the half-life of the peroxide is approximately 10 h (see the Supporting Information for full details), thereby providing strong evidence of an iron-mediated mechanism.

In conclusion, we developed a mild silylperoxide-directed C–H thioetherification reaction catalyzed by a simple iron salt, $Fe(OTf)_2$. The reaction proceeds in good yield with broad functional group tolerance under simple reaction conditions. Importantly, the use of a TIPS protecting group biases the scission of the O–O bond and enables a selective alkoxy-radical formation. The reaction proceeds through short-lived radical intermediates that provide high selectivity for 1,5-HAT.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATIONS

General Methods. Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. THF and DME were purified according to the Grubbs procedure.[32] Thin layer chromatography (TLC) was carried out on Merck 60 F_{254} precoated, glass silica plates that were visualized with ultraviolet light or stained with $KMnO_4$. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature using a Varian I400 or VXR400 (^{1}H NMR at 400 MHz and $^{13}C\{^1H\}$ NMR at 100 MHz), Varian I500 (^{1}H NMR at 500 MHz and $^{13}C\{^1H\}$ NMR at 125 MHz), and Varian I600 (^{1}H NMR at 600 MHz and $^{13}C\{^1H\}$ NMR at 150 MHz) instruments. ^{19}F NMR spectra were recorded at room temperature using a Varian I400 or VXR400 instrument (^{19}F NMR at 376 MHz). Chemical shifts are reported in parts per million with reference to solvent signals [^{1}H NMR, $CDCl_3$ (7.26 ppm) and acetone-d_6 (2.05 ppm); ^{13}C NMR, $CDCl_3$ (77.2 ppm)]. ^{19}F NMR was externally referenced to a trifluoroacetic acid standard (−77.55 ppm). Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra (IR) were recorded on a Bruker Tensor II FTIR spectrometer analyzed as a thin film and recorded in wavenumbers (cm^{-1}). High-resolution mass spectrometry (HRMS) analysis was performed using either an Agilent 7890*B*/7250 GC-QTOF system for electron-impact ionization (EI) and reported as *m*/*z* (relative intensity) for the molecular ion [M]/suitable fragment ion or a Waters/Micromass LCT Classic system (ESI-TOF) for electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) and reported molecular ion [M + H] or [M + Na] or a suitable fragment ion.

General Procedure A. Synthesis of Alkyl Mesylates. To a round-bottom flask with a stir bar were added alcohol (1 equiv), DCM (0.4 M), and methanesulfonyl chloride (1.1 equiv). At room temperature, triethylamine (1.2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for 3–15 h, the reaction quenched with 1 M aqueous HCl, and the mixture diluted with water and DCM and transferred to a separatory funnel. The organic layer was removed, and the aqueous layer was then extracted three times with DCM. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and then brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. In general, the crude alkyl mesylate was pure as determined by ^{1}H NMR and did not require further purification. The spectra of 1-butyl, 1-pentyl, 1-hexyl, 2-hexyl, 1-dodecyl, 4-pentenyl, and cyclopentyl mesylates matched the reported spectra.

General Procedure B. Synthesis of Dialkyl Peroxides.[33] To a round-bottom flask with a stir bar were added alkyl mesylate (2

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equiv), methanol (1.0 M), and 35% aqueous H_2O_2 (1 equiv). The stirred solution was cooled in an ice bath, and 50% (w/w) aqueous KOH (2 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 14−24 h. After this time, the reaction mixture was diluted with water and hexanes. The organic layer was removed, and the aqueous layer was extracted three times with hexanes. The combined organic layers were washed once with 1 M aqueous NaOH to remove residual hydrogen peroxide, washed three times with water until the washings were neutral, followed by brine, and then dried ($MgSO_4$), filtered, and concentrated by rotary evaporation (keeping the water bath below 40 °C) to afford a clear, colorless oil. The peroxides were purified by silica flash chromatography to clear, colorless oils. Typical R_f values are 0.65−0.75 in 25% EtOAc/hexanes.

General Procedure C. Synthesis of Hydroperoxides from Alkyl Mesylate.[34] To a round-bottom flask with a stir bar were added alkyl mesylate (1 equiv), methanol/water (9:1, 0.8 M), and 35% aqueous H_2O_2 (6 equiv). The stirred solution was cooled in an ice bath, and 50% (w/w) aqueous KOH (1.5 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 14−24 h. Then, the reaction mixture was diluted with water and diethyl ether. The organic layer was removed, and the aqueous layer was extracted three times with ether. The combined organic layers were washed three times with water and twice with brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation (keeping the water bath below 40 °C) to afford a clear, colorless oil. The hydroperoxides were purified by silica flash chromatography to clear, colorless oils. Hydroperoxides stain brightly with $KMnO_4$, and typical R_f values are 0.3−0.4 in 15% EtOAc/hexanes.

General Procedure D. Synthesis of Hydroperoxides from Alkyl Iodide.[35] The hydroperoxides were prepared by adding silver trifluoroacetates (1.2 equiv) in small portions to an ice-cooled solution in the ether of the appropriate alkyl halide and hydrogen peroxide in a ≤1-fold excess. The reactions were run for 1−3 h. The silver halide was filtered off, and the trifluoroacetic acid formed; the excess of hydrogen peroxide was removed by treatment with aqueous sodium bicarbonate, and the solvent was removed to leave the crude hydroperoxide. The hydroperoxides were purified by silica flash chromatography to clear, colorless oils. Hydroperoxides stain brightly with $KMnO_4$, and typical R_f values are 0.3−0.4 in 15% EtOAc/hexanes.

General Procedure E. Silylation of Hydroperoxides.[36] To a flame-dried round-bottom flask with a stir bar were added hydroperoxide (1.0 equiv) and pentane (0.5 M). The flask was cooled in an ice bath, and the silyl chloride or triflate (1.0 equiv) was added dropwise, followed by the dropwise addition of distilled 2,6-lutidine (1.0 equiv). The reaction mixture was slowly warmed to room temperature and stirred for 3−24 h. After the specified time, the reaction mixture was diluted with diethyl ether and washed with water, followed by brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated to provide a clear, colorless oil. If necessary, the alkyl silyl peroxide was purified by silica flash chromatography.

General Procedure F. Silyl Hydroperoxide Alkylation. To a reaction vial with a stir bar were added triisopropyl hydroperoxide (1 equiv) and pentane (0.5 M). The solution was cooled in an ice bath. Ag_2O (3 equiv) was added, followed by the dropwise addition of alkyl iodide (3 equiv). The reaction vessel was covered with foil and left in the ice bath to warm to room temperature slowly. After 14 h, the reaction mixture was diluted with diethyl ether, filtered, and concentrated by rotary evaporation. The alkyl silyl peroxide product was purified by silica flash chromatography. The alkyl iodide closely elutes in many cases but can often be removed under high vacuum.

General Procedure G. C−H Thioetherification Reaction. To a flame-dried 40 mL reaction vial with a septum-lined cap and a stir bar were added TIPS peroxide (1.0 equiv), disulfide (1.1 equiv), and $Fe(OTf)_2$ (0.05 equiv). The flask was evacuated and backfilled three times with N_2. Degassed MeOH (0.1 M) was added via syringe, and then the reaction mixture was heated to 80 °C on a preheated oil bath. After 5 h, the reaction mixture was cooled, diluted with ethyl acetate (5 mL), filtered through a silica plug, washing with ∼10 mL of EtOAc, and concentrated. Screening efforts were usually run on a 0.05−0.2 mmol scale. Products were isolated by flash chromatography or analyzed by crude NMR using BHT as the internal standard.

Preparation and Characterization of the Starting Material.

*1-Hydroperoxydodecane (**3b**).* 1-Dodecyl mesylate (2.652 g, 10.0 mmol) was subjected to general procedure C, using diethyl ether (1.25 M) and 12:1 MeOH/H_2O (0.3 M) as the solvents, for 42 h. Silica flash chromatography provided **3b** (1.522 g, 75% yield) as a clear, colorless oil that matched the reported spectra:[37] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.02 (t, J = 6.6 Hz, 2H), 1.62 (p, J = 7.1 Hz, 2H), 1.42−1.18 (m, 18H), 0.88 (t, J = 6.7 Hz, 3H); TLC R_f = 0.40 (20% EtOAc/hexanes).

*(Dodecylperoxy)triisopropylsilane (**3j**).* 1-Dodecyl hydroperoxide **3b** (1.089 g, 5.0 mmol, 1 equiv) was subjected to general procedure E using triisopropylsilyl triflate (1.40 mL, 5.0 mmol, 1 equiv) for 23 h. The reaction mixture was diluted with 10 mL of hexanes, filtered through a silica plug, washing with an additional 5 mL of hexanes, and concentrated to provide **3j** (1.375 g, 76% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (t, J = 6.6 Hz, 2H), 1.58 (p, J = 6.7 Hz, 2H), 1.39−1.14 (m, 21H), 1.10 (d, J = 6.8 Hz, 18H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.9, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 27.9, 26.3, 22.9, 18.1, 14.3, 11.7; LRMS (GCMS) mass fragmentation 315.3 (100), 273.1 (8), 131.2 (13), 103.1 (13), 77.1 (13), 43.2 (6); IR (neat) 2922, 2865, 1737, 1463, 1377, 997, 882, 677 cm^{-1}; TLC R_f = 0.74 (15% EtOAc/hexanes).

(Butylperoxy)triisopropylsilane. TIPSOOH (295 mg, 1.5 mmol, 1 equiv) was subjected to general procedure F for 15 h using iodobutane (0.51 mL, 4.5 mmol, 3 equiv). Silica flash chromatography provided (butylperoxy)triisopropylsilane (197.1 mg, 53% yield) as a clear, colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.00 (t, J = 6.6 Hz, 2H), 1.58 (p, J = 6.9 Hz, 2H), 1.38 (sext, J = 7.3 Hz, 2H), 1.20 (sext, J = 7.3 Hz, 2H), 1.10 (d, J = 7.4 Hz, 18H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 76.7, 30.1, 19.6, 18.1, 14.1, 11.7; HRMS (APCI) calcd for $C_{13}H_{31}O_2Si$ [M + H]$^+$ 247.2093, found 247.2086; IR (neat) 2943, 2866, 1463, 1382, 1064, 881, 676 cm^{-1}; TLC R_f = 0.63 (5% EtOAc/hexanes).

Triisopropyl(pentan-2-ylperoxy)silane. TIPSOOH (380 mg, 2.0 mmol, 1 equiv) was subjected to general procedure F for 16 h using 2-iodopentane (0.60 mL, 4.6 mmol, 2.3 equiv). Silica flash chromatography provided triisopropyl(pentan-2-ylperoxy)silane (247 mg, 47% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.04 (sextet, J = 6.0 Hz, 1H), 1.67−1.53 (m, 1H), 1.45−1.28 (m, 3H), 1.25−1.14 (m, 6H), 1.09 (d, J = 7.3 Hz, 18H), 0.94−0.88 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 81.1, 36.8, 18.9, 18.7, 18.2, 14.4, 11.8; LRMS (GCMS) mass fragmentation 201.3 (3), 173.3 (6), 147.2 (20), 105.2 (43), 103.1 (30), 77.2 (100), 76.1 (35), 61.1 (17), 43.3 (14); IR (neat) 2960, 2866, 1738, 1463, 1370, 997, 881, 676 cm^{-1}; TLC R_f = 0.71 (10% EtOAc/hexanes).

(Isopentylperoxy)triisopropylsilane. 1-Iodo-3-methylbutane (1.98 g, 10 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided 1-hydroperoxy-3-methylbutane (392 mg, 38% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 4.06 (t, J = 6.8 Hz, 2H), 1.69 (dp, J = 13.3, 6.7 Hz, 1H), 1.52 (q, J = 6.9 Hz, 2H), 0.92 (d, J = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 75.95, 36.46, 25.39, 22.84; TLC R_f = 0.5 (20% EtOAc/hexanes). 1-Hydroperoxy-3-methylbutane (330 mg, 3.17 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided (isopentylperoxy)triisopropylsilane (640 mg, 78% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, J = 6.8 Hz, 2H), 1.69 (dq, J = 13.4, 6.7 Hz, 1H), 1.55−1.40 (m, 2H), 1.29−1.13 (m, 3H), 1.15−0.99 (m, 18H), 0.90 (d, J = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 75.5, 36.7, 25.5, 22.8, 18.1, 11.7; LRMS (GCMS) mass fragmentation 201.3 (1), 175.2 (1), 168.2 (1), 147.2 (1), 129.2 (8), 119.2 (27), 77.2 (100), 76.1 (35), 69.2 (35), 61.1 (20), 43.3 (10); IR (neat) 2945, 2867, 1464, 1367, 1014, 997, 881, 819, 743 cm^{-1}; TLC R_f = 0.5 (5% EtOAc/hexanes).

1-Hydroperoxyhexane. 1-Hexyl mesylate (1.465 g, 8.0 mmol) was subjected to general procedure C for 20 h. Silica flash chromatography provided 1-hydroperoxyhexane (623 mg, 66% yield) as a clear,

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colorless oil that matched the reported spectra:[38] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91−7.84 (br s, 1H), 4.02 (t, J = 6.7 Hz, 2H), 1.61 (p, J = 7.0 Hz, 2H), 1.45−1.20 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H); TLC R_f = 0.31 (15% EtOAc/hexanes).

(Hexylperoxy)triisopropylsilane. 1-Hydroperoxyhexane (258 mg, 2.2 mmol, 1 equiv) was subjected to general procedure E using triisopropylsilyl triflate (0.59 mL, 2.2 mmol, 1 equiv) for 14 h. The reaction mixture was diluted with 3 mL of pentane, filtered through a silica plug, washing with an additional 5 mL of pentane, and concentrated to provide (hexylperoxy)triisopropylsilane (366 mg, 60% yield) as a clear, colorless oil that did not require further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (t, J = 6.6 Hz, 2H), 1.59 (p, J = 6.9 Hz, 2H), 1.41−1.25 (m, 6H), 1.21 (hept, J = 7.9, 7.1 Hz, 3H), 1.10 (d, J = 7.4 Hz, 18H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.9, 31.8, 27.9, 26.0, 22.7, 18.1, 14.1, 11.7; HRMS (EI) calcd for $C_{12}H_{27}O_2Si$ [M − C_3H_7]$^+$ 231.1775, found 231.1769; IR (neat) 2942, 2866, 1741, 1463, 1381, 882, 676 cm^{-1}.

2-Hydroperoxyhexane. 2-Hexyl mesylate (3.62 g, 20 mmol, 1 equiv) was subjected to general procedure C at a concentration of 0.3 M (12:1 MeOH/H_2O) for 19 h. Silica flash chromatography provided 2-hydroperoxyhexane (879 mg, 37% yield) as a clear, colorless oil:[39] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69−7.54 (m, 1H), 4.06 (h, J = 6.1 Hz, 1H), 1.71−1.55 (m, 1H), 1.49−1.26 (m, 5H), 1.22 (d, J = 6.2 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 81.9, 33.8, 27.7, 22.9, 18.3, 14.1; IR (neat) 3374, 2933, 2862, 1737, 1461, 1375, 1114 cm^{-1}; TLC R_f = 0.31 (15% EtOAc/hexanes).

(Hexan-2-ylperoxy)triisopropylsilane. 2-Hexyl hydroperoxide (473 mg, 4.0 mmol, 1 equiv) was subjected to general procedure E using triisopropylsilyl triflate (1.07 mL, 4.0 mmol, 1 equiv) and anhydrous ammonia as the base (sparge for 10 min and then a balloon atmosphere) for 16 h. Silica flash chromatography provided (hexan-2-ylperoxy)triisopropylsilane (796 mg, 72% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (sext, J = 6.0 Hz, 1H), 1.70−1.56 (m, 1H), 1.47−1.25 (m, 5H), 1.24−1.15 (m, 6H), 1.09 (d, J = 7.3 Hz, 18H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 81.3, 34.3, 27.8, 23.0, 18.6, 18.2, 14.2, 11.8; HRMS (EI) calcd for $C_{12}H_{27}O_2Si$ [M − C_3H_7]$^+$ 231.1775, found 231.1769; IR (neat) 2942, 2866, 1738, 1463, 1371, 881, 791 cm^{-1}; TLC R_f = 0.75 (10% EtOAc/hexanes).

Triisopropyl[(4-methylpentyl)peroxy]silane. TIPSOOH (344 mg, 1.8 mmol, 1 equiv) was subjected to general procedure F using 1-iodo-4-methylpentane (0.80 mL, 5.4 mmol, 3 equiv). Silica flash chromatography provided triisopropyl[(4-methylpentyl)peroxy]silane (205.5 mg, 41% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 6.7 Hz, 2H), 1.68−1.46 (m, 3H), 1.29−1.14 (m, 5H), 1.10 (d, J = 7.0 Hz, 18H), 0.88 (d, J = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 77.2, 35.3, 28.0, 25.8, 22.6, 18.1, 11.7; HRMS (EI) calcd for $C_{12}H_{27}O_2Si$ [M − C_3H_7]$^+$ 231.1775, found 231.1769; IR (neat) 2945, 2867, 1463, 1367, 1250, 1015, 882, 676 cm^{-1}; TLC R_f = 0.60 (5% EtOAc/hexanes).

2-Ethylhexyl Methanesulfonate. 2-Ethylhexan-1-ol (4.69 mL, 30.0 mmol) was subjected to general procedure A for 14 h. After the workup procedure, the crude material was isolated with high purity. We moved to the next step without any further purification (5.933 g, 95% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27−4.01 (m, 2H), 3.00 (s, 3H), 1.65 (p, J = 6.0 Hz, 1H), 1.48−1.20 (m, 8H), 1.02−0.82 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 72.2, 39.2, 37.1, 29.9, 28.8, 23.3, 22.9, 14.0, 10.8; HRMS (ESI) calcd for $C_9H_{20}O_3NaS$ [M + Na]$^+$ 231.1025, found 231.1026; IR (neat) 2959, 2931, 2861, 1463, 1350, 1172, 939, 845, 816, 748, 527 cm^{-1}; TLC R_f = 0.69 (30% EtOAc/hexanes).

[(2-Ethylhexyl)peroxy]triisopropylsilane. 2-Ethylhexyl methanesulfonate (5.208 g, 25.0 mmol) was subjected to general procedure C, using diethyl ether (1.25 M) and 12:1 MeOH/H_2O (0.3 M) as the solvents, for 40 h. Silica flash chromatography provided 3-(hydroperoxymethyl)heptane (1.501 g, 42% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−7.87 (m, 1H), 3.91 (d, J = 6.1 Hz, 2H), 1.61 (q, J = 5.9 Hz, 1H), 1.45−1.12 (m, 8H), 0.87 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 80.4, 38.1, 30.6, 29.1, 24.0, 23.1, 14.2, 11.1; IR (neat) 3423 (b), 2559, 2928, 1540,1462, 1379, 1172, 941, 816, 412 cm^{-1}; TLC R_f = 0.43 (30% EtOAc/hexanes). Next, 3-(hydroperoxymethyl)heptane (426 mg, 2.91 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided [(2-ethylhexyl)peroxy]-triisopropylsilane (588 mg, 67% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 3.91 (d, J = 5.9 Hz, 2H), 1.57 (td, J = 11.7, 5.7 Hz, 1H), 1.43−1.24 (m, 8H), 1.24−1.14 (m, 3H), 1.14−1.03 (m, 18H), 0.88 (t, J = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 79.8, 38.7, 30.9, 29.2, 24.3, 23.1, 18.2, 14.2, 11.7, 11.3; HRMS (EI) calcd for $C_{17}H_{38}O_2Si$ [M]$^+$ 302.2636, found 302.2632; IR (neat) 2927, 2866, 1463, 1381, 1250, 997, 881, 677 cm^{-1}; TLC R_f = 0.64 (5% EtOAc/hexanes).

(Cyclooctylperoxy)triisopropylsilane. TIPSOOH (380 mg, 2.0 mmol, 1 equiv) was subjected to general procedure F using iodocyclooctane (1.42 g, 6 mmol, 3 equiv). Silica flash chromatography provided (cyclooctylperoxy)triisopropylsilane (288 mg, 48% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, chloroform-*d*) δ 4.06 (tt, J = 8.4, 3.5 Hz, 1H), 1.92 (ddt, J = 14.0, 8.1, 2.8 Hz, 2H), 1.70 (dtd, J = 12.6, 8.0, 3.5 Hz, 2H), 1.62−1.30 (m, 10H), 1.30−1.12 (m, 3H), 1.09 (d, J = 6.7 Hz, 18H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 85.8, 30.1, 27.4, 25.9, 23.7, 18.3, 11.8; LRMS (GCMS) mass fragmentation 257.3 (3), 173.2 (3), 147.2 (33), 105.2 (66), 77.2 (100), 69.2 (20), 61.2 (20), 41.3 (13); IR (neat) 2922, 2865, 1463, 1447, 1382, 1366, 1250, 1052, 1014, 997, 881, 776, 676 cm^{-1}; TLC R_f = 0.7 (5% EtOAc/hexanes).

3-Phenylbutyl Methanesulfonate. 3-Phenylbutan-1-ol (1.5 g, 10 mmol) was subjected to general procedure A for 14 h. After the workup procedure, the crude material was isolated with high purity. We moved to the next step without any further purification (2.3 g, 98% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.2, 6.9 Hz, 2H), 7.27−7.19 (m, 3H), 4.34−3.89 (m, 2H), 3.01−2.80 (m, 4H), 2.17−1.94 (m, 2H), 1.33 (d, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.4, 128.8, 127.1, 126.7, 68.6, 37.3, 37.3, 36.3, 27.2, 22.4; HRMS (ESI) calcd for $C_{11}H_{16}O_3SNa$ [M + Na]$^+$ 251.0712, found 251.0714; IR (neat) 2962, 2935, 1494, 1348, 1170, 935, 700, 525 cm^{-1}; TLC R_f = 0.7 (30% EtOAc/hexanes).

(4-Hydroperoxybutan-2-yl)benzene. 3-Phenylbutyl methanesulfonate (1.2 g, 5.26 mmol) was subjected to general procedure C, using diethyl ether (1.25 M) and 12:1 MeOH/H_2O (0.3 M) as the solvents, for 48 h. Silica flash chromatography provided (4-hydroperoxybutan-2-yl)benzene (340 mg, 39% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.76 (m, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.24−7.16 (m, 3H), 3.97−3.86 (m, 2H), 3.14−2.74 (m, 1H), 2.01−1.86 (m, 2H), 1.29 (d, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.6, 128.6, 127.1, 126.3, 75.5, 36.7, 35.9, 22.6; HRMS (ESI) calcd for $C_{10}H_{14}O_4Na$ [M + Na + O_2]$^+$ 221.0784, found 221.0784; IR (neat) 3372 (b), 2959, 1493, 1451, 1374, 1051, 761, 698, 546 cm^{-1}; TLC R_f = 0.38 (20% EtOAc/hexanes).

Triisopropyl[(3-phenylbutyl)peroxy]silane. (4-Hydroperoxybutan-2-yl)benzene (238 mg, 2.64 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided triisopropyl[(3-phenylbutyl)peroxy]silane (611 mg, 72% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.1, 6.9 Hz, 2H), 7.22−7.14 (m, 3H), 3.91 (t, J = 6.7 Hz, 2H), 2.84 (h, J = 7.1 Hz, 1H), 1.98−1.81 (m, 2H), 1.27 (d, J = 7.0 Hz, 3H), 1.24−1.12 (m, 3H), 1.12−1.01 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.9, 128.5, 127.1, 126.2, 75.1, 36.8, 36.2, 22.6, 18.1, 11.7; HRMS (EI) calcd for $C_{16}H_{27}O_2Si$ [M − C_3H_7]$^+$ 279.1775, found 279.1776; IR (neat) 2943, 2866, 1493, 1367, 1016, 881, 759, 698, 676 cm^{-1}; TLC R_f = 0.64 (5% EtOAc/hexanes).

6-Chlorohexyl Methanesulfonate. 6-Chlorohexan-1-ol (2.732 g, 20.0 mmol) was subjected to general procedure A for 14 h. After the workup procedure, the crude material was isolated with high purity. We moved to the next step without any further purification (4.1 g, 96% yield)L ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (t, J = 6.5 Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 3.01 (s, 3H), 1.90−1.70 (m, 4H), 1.47 (dtt, J = 14.9, 9.1, 5.8 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 69.8, 44.8, 37.4, 32.3, 29.0, 26.2, 24.8; HRMS (ESI) calcd for $C_7H_{15}O_3ClNaS$ [M + Na]$^+$ 237.0323, found 237.0324; IR (neat)

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2939, 2863, 1348, 1170, 943, 915, 817, 717, 526 cm^{-1}; TLC R_f = 0.36 (30% EtOAc/hexanes).

[(6-Chlorohexyl)peroxy]triisopropylsilane. 6-Chlorohexyl methanesulfonate (3.64 g, 17.0 mmol) was subjected to general procedure C, using 12:1 MeOH/H_2O (0.3 M) as the solvents, for 18 h. Silica flash chromatography provided 1-chloro-6-hydroperoxyhexane (1.317 g, 51% yield) as a clear, colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 4.02 (t, J = 6.5 Hz, 2H), 3.53 (t, J = 6.7 Hz, 2H), 1.84−1.73 (m, 2H), 1.71−1.60 (m, 2H), 1.51−1.34 (m, 4H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 77.0, 45.1, 32.6, 27.5, 26.8, 25.3; IR (neat) 3381 (b), 2937, 2861, 1461, 1367, 1309, 109, 763, 648 cm^{-1}; TLC R_f = 0.52 (30% EtOAc/hexanes). Next, 1-chloro-6-hydroperoxyhexane (763 mg, 5 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided [(6-chlorohexyl)-peroxy]triisopropylsilane (1.278 g, 83% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 6.5 Hz, 2H), 3.51 (t, J = 6.7 Hz, 2H), 1.88−1.70 (m, 2H), 1.65−1.55 (m, 2H), 1.50−1.32 (m, 4H), 1.30−1.11 (m, 3H), 1.07 (d, J = 7.0 Hz, 18H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 75.6, 44.2, 31.6, 26.8, 26.2, 25.9, 24.6, 17.1, 10.7; LRMS (ESI) mass fragmentation 336.1 (11), 308.1 (55), 276.0 (16), 267.1 (29), 250.0 (10), 217.9 (14), 190.4 (8), 178.0 (41), 147.0 (100); IR (neat) 2942, 2865, 1463, 1366, 1015, 882, 781, 676, 661 cm^{-1}; TLC R_f = 0.66 (5% EtOAc/hexanes).

Methyl 8-Bromohexanoate. A mixture of 8-bromohexanoic acid (2.2 g, 10 mmol) and concentrated H_2SO_4 (0.3 mL) in methanol (20 mL) was refluxed for 5 h. Then, the volatile was evaporated. The mixture was poured into H_2O (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with a saturated $NaHCO_3$ solution (30 mL) and a brine solution (30 mL) and dried over anhydrous $MgSO_4$. After the solvent had evaporated, methyl 8-bromohexanoate was isolated (1.94 g, 82%) with high purity as a colorless oil that matched the reported spectra:[40] ^1H NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.38 (t, J = 6.8 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.89−1.78 (m, 2H), 1.69−1.56 (m, 2H), 1.52−1.37 (m, 2H), 1.35−1.29 (m, 4H); TLC R_f = 0.4 (20% EtOAc/hexanes).

Methyl 8-Iodomohexanoate. A mixture of methyl 8-bromohexanoate (1.91 g, 8.06 mmol) was added to a solution of NaI (3.6 g, 24.2 mmol) in acetone (15 mL), and the mixture was stirred for 2 h at 65 °C. After 2 h, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (50 mL) was added to the residue and washed with saturated aqueous $Na_2S_2O_3$ (1 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After evaporation of the solvent, methyl 8-iodohexanoate was isolated (2.15 g, 94%) with high purity as a colorless oil that matched the reported spectra:[41] ^1H NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.17 (t, J = 7.0 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.80 (p, J = 7.1 Hz, 2H), 1.68−1.55 (m, 2H), 1.43−1.35 (m, 2H), 1.31 (p, J = 3.6 Hz, 4H); TLC R_f = 0.41 (20% EtOAc/hexanes).

Methyl 8-Hydroperoxyoctanoate. Methyl 8-iodohexanoate (1.586 g, 6.19 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided methyl 8-hydroperoxyoctanoate hexanoate (810 mg, 69% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 3.99 (ddd, J = 8.4, 5.4, 1.8 Hz, 2H), 3.66 (s, 3H), 2.42−2.10 (m, 2H), 1.61 (dd, J = 9.5, 4.8 Hz, 4H), 1.36−1.25 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 175.0, 77.1, 51.8, 34.2, 29.1, 29.1, 27.6, 25.8, 24.9; TLC R_f = 0.34 (30% EtOAc/hexanes); HRMS (ESI) calcd for $C_9H_{18}O_4Na$ $[M + Ma]^+$ 213.1097, found 213.1097; IR (neat) 3400, 2933, 2857, 1736, 1715, 1437, 1363, 1252, 1203,1171, 1104, 855, 726 cm^{-1}.

Methyl 8-[(Triisopropylsilyl)peroxy]hexanoate. Methyl 8-hydroperoxyoctanoate (0.790 g, 4.157 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided methyl 8-[(triisopropylsilyl)peroxy]hexanoate (978 mg, 68% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.96 (t, J = 6.6 Hz, 2H), 3.65 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 1.59 (dt, J = 13.5, 6.9 Hz, 4H), 1.31 (d, J = 4.1 Hz, 6H), 1.25−1.11 (m, 3H), 1.08 (d, J = 7.0 Hz, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.4, 76.8, 51.6, 34.2, 29.2, 29.2, 27.9, 26.1, 25.0, 18.2, 11.7; HRMS (ESI) calcd for $C_{18}H_{38}O_4NaSi$ $[M + Na]^+$ 369.2432, found 369.2434; IR (neat) 2941, 2865, 1741, 1463, 1365, 1250, 1198, 1168, 1104, 997, 919, 882, 854, 779, 677, 663, 503 cm^{-1}; TLC R_f = 0.3 (5% EtOAc/hexanes).

Methyl 6-Bromohexanoate. A mixture of 6-bromohexanoic acid (1.95 g, 10 mmol) and concentrated H_2SO_4 (0.3 mL) in methanol (20 mL) was refluxed for 5 h, Then, the volatile was evaporated. The mixture was poured into H_2O (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with a saturated $NaHCO_3$ solution (30 mL) and a brine solution (30 mL) and dried over anhydrous $MgSO_4$. After the solvent had evaporated, methyl 6-bromohexanoate was isolated (1.585 g, 76%) with high purity as colorless oil that matched the reported spectra:[42] ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.41 (t, J = 6.8 Hz, 2H), 2.33 (t, J = 7.4 Hz, 2H), 1.97−1.83 (m, 2H), 1.73−1.60 (m, 2H), 1.53−1.41 (m, 2H); TLC R_f = 0.4 (10% EtOAc/hexanes).

Methyl 6-Iodomohexanoate. A mixture of methyl 6-bromohexanoate (1.59 g, 7.6 mmol) was added to a solution of NaI (1.245 g, 8.3 mmol) in acetone (10 mL), and the mixture was stirred for 2 h at 65 °C. After 2 h, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (50 mL) was added to the residue, and the mixture was washed with saturated aqueous $Na_2S_2O_3$ (1 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had been evaporated, methyl 6-iodohexanoate was isolated (1.710 g, 88%) with high purity as colorless oil that matched the reported spectra:[42] ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.18 (t, J = 7.0 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 2.04−1.77 (m, 2H), 1.73−1.60 (m, 2H), 1.53−1.34 (m, 2H); TLC R_f = 0.42 (10% EtOAc/hexanes).

Methyl 6-[(Triisopropylsilyl)peroxy]hexanoate. Methyl 6-iodohexanoate (1.586 g, 6.19 mmol) was subjected to general procedure F for 14 h. Silica flash chromatography provided methyl 6-[(triisopropylsilyl)peroxy]hexanoate (270 mg, 14% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.96 (t, J = 6.5 Hz, 2H), 3.64 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 1.61 (dq, J = 11.2, 7.1 Hz, 4H), 1.37 (q, J = 8.4 Hz, 2H), 1.26−1.11 (m, 3H), 1.07 (d, J = 7.1 Hz, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 76.5, 51.5, 34.1, 27.6, 25.8, 24.9, 18.1, 11.7; HRMS (EI) calcd for $C_{13}H_{27}O_4Si$ $[M - C_3H_7]^+$ 275.1673, found 275.1676; IR (neat) 2944, 2866, 1741, 1463, 1435, 1366, 1197, 1015, 882, 854, 677 cm^{-1}; TLC R_f = 0.33 (5% EtOAc/hexanes).

N,N-Diethyl-6-iodohexanamide. To a round-bottom flask with a stir bar were added 6-bromohexanoic acid (3.9 g, 20 mmol) and DCM (60 mL). DMF (0.05 equiv, 73 μL) was added at rt. Oxalyl chloride (30 mmol, 2.5 mL) was added dropwise. The reaction mixture was stirred at room temperature until bubbling stopped (1 h). Without being transferred from the reaction flask, volatile components were removed by rotary evaporation and high vacuum. The crude reaction product was dissolved in DCM (60 mL) and stirred. *N,N*-Diethylamine (20 mmol, 3.1 mL), followed by triethylamine (30 mmol, 4.2 mL), was added at room temperature, and the reaction mixture was stirred overnight. The reaction was quenched with 1 M aqueous HCl, and the mixture transferred to a separatory funnel. The crude mixture was diluted with DCM (0.1 M) and water (0.1 M). The organic layer was removed, and the aqueous layer was then extracted with DCM (3 × 0.1 M). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and then brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. Without any further purification, we isolated 6-bromo-*N,N*-diethylhexanamide as an oily liquid (4.5 g, 90%) that matched previously reported spectra:[43] ^1H NMR (400 MHz, $CDCl_3$) δ 3.47−3.33 (m, 4H), 3.29 (q, J = 7.1 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.88 (p, J = 7.0 Hz, 2H), 1.67 (p, J = 7.5 Hz, 2H), 1.57−1.37 (m, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.8, 42.0, 40.2, 33.9, 33.0, 32.8, 28.2, 24.6, 14.5, 13.3; TLC R_f = 0.17 (30% EtOAc/hexanes). Next, a mixture of 6-bromo-*N,N*-diethylhexanamide (3 g, 12 mmol) was added to a solution of NaI (2.16 g, 14.4 mmol) in acetone (20 mL), and the mixture was stirred overnight at 65 °C. Then, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (50 mL) was added to the residue

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and washed with saturated aqueous $Na_2S_2O_3$ (1 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had evaporated, *N,N*-diethyl-6-iodohexanamide was isolated (2.2 g, 62%) as a brown liquid, which matched previously reported spectra.[44] Without further purification, we proceeded to the next step: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (q, J = 7.1 Hz, 2H), 3.30 (q, J = 7.1 Hz, 2H), 3.20 (t, J = 7.0 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.85 (p, J = 7.1 Hz, 2H), 1.76−1.57 (m, 2H), 1.52−1.38 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); TLC R_f = 0.21 (30% EtOAc/hexanes).

N,N-Diethyl-6-[(triisopropylsilyl)peroxy]hexanamide. *N,N*-Diethyl-6-iodohexanamide (1.1 g, 3.7 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided *N,N*-diethyl-6-hydroperoxyhexanamide with another mixture. We proceeded to the next step with the impure *N,N*-diethyl-6-hydroperoxyhexanamide. The mixture with *N,N*-diethyl-6 hydroperoxyhexanamide was subjected to general procedure E with TIPSOTf (0.71 mL, 2.64 mmol) and lutidine (0.506 mL, 2.64 mL) for 2 h. Silica flash chromatography provided *N,N*-diethyl-6-[(triisopropylsilyl)peroxy]-hexanamide (278 mg, 21%, after two steps) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (t, J = 6.5 Hz, 2H), 3.34 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 7.1 Hz, 2H), 2.37−2.14 (m, 2H), 1.74−1.52 (m, 4H), 1.44−1.31 (m, 2H), 1.24−1.10 (m, 6H), 1.11−1.02 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 76.6, 42.0, 40.1, 33.0, 27.8, 26.1, 25.4, 18.1, 14.5, 13.2, 11.6; LRMS (GC) decomposed in GCMS; IR (neat) 3395, 2970, 2932, 2863, 1616, 1459, 1431, 1379, 1260, 1220, 1140, 1071, 1055, 605 cm^{-1}; TLC R_f = 0.32 (20% EtOAc/hexanes).

6-Hydroperoxyhexyl 3-(Trifluoromethyl)benzoate. To a flame-dried round-bottom flax equipped with a stir bar was added 6-bromohexan-1-ol (2.6 mL, 20 mmol); 50 mL of dry DCM was then added via syringe. Then, 3-(trifluoromethyl)benzoyl chloride (3.01 mL, 20 mmol) was added dropwise. Then, triethylamine (3.1 mL, 22 mmol) was added to the mixture dropwise (15 min) with constant stirring. The total reaction mixture was stirred at room temperature overnight. After the reaction had reached completion, 10 mL of water was added to it. The DCM layer was separated with a separatory funnel. The DCM layer was washed with saturated $NaHCO_3$ (20 mL) and a saturated NaCl solution. Then, the final organic portion was passed through anhydrous $MgSO_4$ and dried in rotavap. With the concentrated organic portion as 6-bromohexyl 3-(trifluoromethyl)-benzoate (6.4 g, 91%, ∼90% pure), we proceeded to the next step without any further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 4.36 (t, J = 6.6 Hz, 2H), 3.42 (t, J = 6.7 Hz, 2H), 1.98−1.75 (m, 4H), 1.62−1.42 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 132.9, 131.3, 131.1 (q, J = 32.0 Hz), 129.5 (q, J = 4.0 Hz), 129.1, 126.5 (q, J = 4.0 Hz), 123.8 (q, J = 272.5 Hz), 65.6, 33.8, 32.7, 28.6, 27.9, 25.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.84; LRMS (GCMS) mass fragmentation 235.0 (3), 233.0 (3), 191.1 (40), 173.1 (100), 162.1 (40), 164.1 (40), 145.1 (75), 125.1 (10), 95.1 (10), 83.2 (45), 69.2 (10), 55.2 (25), 41.2 (10); IR (neat) 2937, 2860, 1721, 1617, 1440, 1333, 1300, 1248, 1166, 1123, 1086, 1071, 921, 820, 756, 693, 649, 561 cm^{-1}; TLC R_f = 0.5 (20% EtOAc/hexanes). In the next step, a mixture of 6-bromohexyl 3-(trifluoromethyl)benzoate (5.36 g, 15.2 mmol) was added to a solution of NaI (2.5 g, 16.7 mmol) in acetone (45 mL) and the mixture was stirred overnight at 65 °C. Then, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (50 mL) was added to the residue and washed with saturated aqueous $Na_2S_2O_3$ (1 × 50 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had evaporated, 6-iodohexyl 3-(trifluoromethyl)benzoate was isolated (4.2 g, 68%, ∼90% pure) as a brown liquid. Without any further purification, we proceeded to the next step: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 4.35 (t, J = 6.6 Hz, 2H), 3.18 (t, J = 6.9 Hz, 2H), 1.82 (dt, J = 19.1, 6.8 Hz, 4H), 1.47 (p, J = 3.5 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 132.8, 131.3, 131.0 (q, J = 32.3 Hz), 129.3 (q, J = 4.0 Hz), 129.1, 126.5 (q, J = 3.9 Hz), 123.7 (q, J = 273.5 Hz), 65.5, 33.3, 30.2, 28.6, 25.1, 6.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.83; LRMS (GCMS) mass fragmentation 273.1 (34), 210.1 (10), 191.1 (37), 173.1 (100), 145.1 (75), 125.1 (10), 83.2 (63), 55.2 (30), 41.1 (10); IR (neat) 2934, 2858, 1721, 1617, 1441, 1333, 1247, 1166, 1123, 1086, 1071, 920, 819, 756, 693, 650, 602 cm^{-1}; TLC R_f = 0.52 (20% EtOAc/hexanes). Finally, 6-iodohexyl 3-(trifluoromethyl)benzoate (2 g, 5 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided 6-hydroperoxyhexyl 3-(trifluoromethyl)benzoate (550 mg, 36% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 4.36 (t, J = 6.6 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.80 (p, J = 6.7 Hz, 2H), 1.68 (p, J = 6.7 Hz, 2H), 1.51−1.41 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*) δ 165.6, 132.9, 131.4, 131.2 (q, J = 32.8 Hz), 129.6 (q, J = 3.7 Hz), 129.2, 126.6 (q, J = 3.9 Hz), 123.8 (q, J = 173.9 Hz), 77.02, 65.70, 28.71, 27.63, 25.97, 25.74; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.85; HRMS (ESI) calcd for $C_{14}H_{17}F_3O_4Na$ [M + Na]$^+$ 329.0971, found 329.0974; IR (neat) 3414, 2939, 2863, 1721, 1617, 1334, 1248, 1166, 1123, 1087, 1071, 979, 920, 821, 757, 693, 650 cm^{-1}; TLC R_f = 0.35 (20% EtOAc/hexanes).

6-[(Triisopropylsilyl)peroxy]hexyl 3-(Trifluoromethyl)benzoate. 6-Hydroperoxyhexyl 3-(trifluoromethyl)benzoate (496 mg, 1.62 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 6-[(triisopropylsilyl)peroxy]hexyl 3-(trifluoromethyl)benzoate (480 mg, 65% isolated as pure) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) 8.29 (d, J = 2.2 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 4.35 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 1.80 (p, J = 6.8 Hz, 2H), 1.64 (p, J = 6.7 Hz, 2H), 1.49−1.40 (m, 4H), 1.29−1.13 (m, 3H), 1.14−0.93 (m, 18H); ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*) δ 165.4, 132.9, 131.5, 131.2 (q, J = 34.0 Hz), 129.5 (q, J = 3.7 Hz), 129.2, 126.6 (q, J = 3.9 Hz), 123.9 (q, J = 272.2 Hz), 76.64, 65.71, 28.77, 27.88, 26.05, 26.02, 18.13, 11.72; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.87; HRMS (ESI) calcd for $C_{23}H_{37}F_3O_4SiNa$ [M + Na]$^+$ 485.2305, found 485.2307; IR (neat) 2943, 2867, 1726, 1464, 1335, 1250, 1169, 1132, 1086, 1072, 920, 883, 757, 694 cm^{-1}; TLC R_f = 0.38 (5% EtOAc/hexanes).

6-Hydroperoxyhexyl Acetate. 6-Iodohexyl acetate (1.37 g, 5.10 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided 6-hydroperoxyhexyl acetate (267 mg, 30% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 4.05 (t, J = 6.7 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.04 (s, 3H), 1.70−1.58 (m, 4H), 1.46−1.32 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.6, 77.0, 64.6, 28.6, 27.5, 25.8, 25.6, 21.1; LRMS (GCMS) mass fragmentation 115.1 (13), 98.1 (12), 80.1 (10), 69 (20), 61.1 (50), 55.1 (40), 43.1 (100); IR (neat) 3401, 2939, 2862, 1737, 1718, 1389, 1367, 1240, 1036 cm^{-1}; TLC R_f = 0.2 (20% EtOAc/hexanes).

6-[(Triisopropylsilyl)peroxy]hexyl Acetate. 6-Hydroperoxyhexyl acetate (260 mg, 1.47 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 6-[(triisopropylsilyl)-peroxy]hexyl acetate (330 mg, 68% isolated as pure) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, J = 6.7 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 2.01 (s, 3H), 1.63−1.55 (m, 4H), 1.35 (p, J = 3.6 Hz, 4H), 1.24−1.11 (m, 3H), 1.10−1.03 (m, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 76.7, 64.6, 28.6, 27.8, 26.0, 21.1, 18.1, 11.7; HRMS (EI) calcd for $C_{14}H_{29}O_4Si$ [M − C_3H_7]$^+$ 289.1830, found 289.1827; IR (neat) 2942, 2866, 1741, 1463, 1365, 1233, 1037, 919, 882, 781, 677, 606, 462 cm^{-1}; TLC R_f = 0.41 (10% EtOAc/hexanes).

6-Iodohexyl Methanesulfonate. 6-Iodohexan-1-ol (1.71 g, 7.5 mmol) was subjected to general procedure A for 14 h. After the workup procedure, the crude material was isolated with high purity. We moved to the next step without any further purification (1.94 g, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (t, J = 6.5 Hz, 2H), 3.18 (t, J = 6.9 Hz, 2H), 2.99 (d, J = 1.1 Hz, 3H), 1.90−1.67 (m, 4H), 1.52−1.36 (m, 4H); HRMS (ESI) calcd for $C_7H_{15}IO_3SNa$ [M + Na]$^+$ 328.9679, found 328.9679; IR (neat) 2935, 2858, 1347, 1331, 1206,

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1169, 971, 938, 908, 827, 718, 526, 459 cm^{-1}; TLC R_f = 0.4 (30% EtOAc/hexanes).

6-Hydroperoxyhexyl Methanesulfonate. 6-Iodohexyl 4-methylbenzenesulfonate (0.915 g, 3 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided 6-hydroperoxyhexyl methanesulfonate (265 mg, 42% yield) as a clear, colorless oil: ^1H NMR (400 MHz, CD_3OD) δ 4.87 (s, 1H), 4.38 (t, J = 6.4 Hz, 2H), 4.07 (t, J = 6.4 Hz, 2H), 3.20 (s, 3H), 1.94−1.86 (m, 2H), 1.78 (p, J = 6.7 Hz, 2H), 1.67−1.45 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 76.0, 70.4, 35.7, 28.7, 27.2, 25.1, 24.9; HRMS (ESI) calcd for $C_7H_{16}O_5SNa$ $[M + Na]^+$ 235.0611, found 235.0609; IR (neat) 3428, 2940, 2864, 1344, 1168, 973, 952, 926, 820, 528 cm^{-1}; TLC R_f = 0.5 (50% EtOAc/hexanes).

6-[(Triisopropylsilyl)peroxy]hexyl Methanesulfonate. 6-Hydroperoxyhexyl methanesulfonate (248 mg, 1.17 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 6-[(triisopropylsilyl)peroxy]hexyl methanesulfonate (295 mg, 68%) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.4 Hz, 2H), 2.96 (s, 3H), 1.80−1.67 (m, 2H), 1.63−1.53 (m, 2H), 1.45−1.33 (m, 4H), 1.25−1.10 (m, 3H), 1.10−0.98 (m, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 76.5, 70.1, 37.4, 29.1, 27.7, 25.7, 25.4, 18.1, 11.6; HRMS (ESI) calcd for $C_{16}H_{36}O_5SSiNa$ $[M + Na]^+$ 391.1945, found 391.1949; IR (neat) 2942, 2866, 1464, 1354, 1174, 972, 955, 924, 882, 855, 815, 781, 678, 664, 528 cm^{-1}; TLC R_f = 0.63 (30% EtOAc/hexanes).

(5-Iodopentyl)benzene. A mixture of (5-bromopentyl)benzene (909 mg, 4 mmol) was added to a solution of NaI (2 g, 12 mmol) in acetone (10 mL), and the mixture was stirred overnight at 65 °C. Then, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (30 mL) was added to the residue and washed with saturated aqueous $Na_2S_2O_3$ (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had evaporated, (5-iodopentyl)benzene was isolated (1.01 g, 93%) as a brown liquid. Without any further purification, we proceeded to the next step:[45] ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.6, 6.6 Hz, 2H), 7.24−7.13 (m, 3H), 3.19 (t, J = 7.0 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.87 (p, J = 7.2 Hz, 2H), 1.75−1.61 (m, 2H), 1.51−1.35 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.5, 128.6, 128.5, 126.0, 35.9, 33.7, 30.6, 30.4, 7.2; TLC R_f = 0.5 (5% EtOAc/hexanes).

(5-Hydroperoxypentyl)benzene. (5-Iodopentyl)benzene (1 g, 3.6 mmol) was subjected to general procedure D for 1.5 h. Silica flash chromatography provided (5-hydroperoxypentyl)benzene (279 mg, 43% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.33−7.25 (m, 2H), 7.22−7.15 (m, 3H), 4.02 (t, J = 6.6 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.78−1.54 (m, 4H), 1.52−1.35 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.6, 128.6, 128.5, 125.9, 77.2, 36.0, 31.4, 27.6, 27.3, 25.7; TLC R_f = 0.33 (20% EtOAc/hexanes); LRMS (GCMS, mass fragmentation) 162.1 (100), 144 (83), 133.1 (31), 129.1 (54), 120.0 (42), 118.1 (37), 117.1 (25), 105.1 (12), 92.1 (37), 91.0 (4); IR (neat) 3376, 3025, 2933, 2856, 1602, 1495, 1452, 1367, 1030, 745, 697, 493 cm^{-1}.

Triisopropyl[(5-phenylpentyl)peroxy]silane. (5-Hydroperoxypentyl)benzene (0.180 g, 1.5 mmol) was subjected to general procedure E for 3 h. Silica flash chromatography provided triisopropyl[(5-phenylpentyl)peroxy]silane (201 mg, 40% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 2H), 7.24−7.17 (m, 3H), 4.03 (t, J = 6.6 Hz, 2H), 2.65 (t, J = 7.7 Hz, 2H), 1.80−1.59 (m, 4H), 1.44 (dddd, J = 14.8, 9.3, 6.6, 3.4 Hz, 2H), 1.32−1.18 (m, 3H), 1.14 (d, J = 6.9 Hz, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.7, 128.6, 128.4, 125.8, 76.8, 36.0, 31.5, 27.9, 26.0, 18.3, 18.2, 18.2, 11.7; HRMS (EI) calcd for $C_{17}H_{29}O_2Si$ $[M - C_3H_7]^+$ 293.1931, found 293.1933; IR (neat) 2940, 2865, 1495, 1462, 1382, 1366, 1250, 1050, 1014, 997, 919, 882, 849, 783, 744, 696, 676, 569, 462 cm^{-1}; TLC R_f = 0.6 (5% EtOAc/hexanes).

7-[(Triisopropylsilyl)oxy]heptan-1-ol. To a round-bottom flask equipped with a stir bar was added sodium hydride (60% dispersion in mineral oil, 1.2 g, 30 mmol). The sodium hydride was washed three times with hexanes and dried under an argon atmosphere. Thirty milliliters of THF was then added, and the resulting heterogeneous solution was cooled to 0 °C. 1,7-Heptanediol (4.2 mL, 30 mmol) in 15 mL of THF was added via syringe. The reaction mixture was warmed to room temperature for 30 min and then cooled to 0 °C. Triisopropylsilyl chloride (6.4 mL, 30 mmol) in 15 mL of THF was added via syringe, and the reaction mixture was allowed to stir for 40 min at 0 °C and then overnight at rt. The reaction was quenched by the addition of water, and the mixture was extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The desired product was isolated by silica flash chromatography (2.93 g, 34% yield) as a colorless oil that matched previously reported spectra:[46] ^1H NMR (400 MHz, $CDCl_3$) δ 3.76−3.53 (m, 4H), 1.56 (m, 5H), 1.36 (m, 6H), 1.13−0.99 (m, 21H); HRMS (ESI) calcd for $C_{16}H_{37}O_2Si$ $[M - H]^+$ 289.2557, found 289.2559; IR (neat) 3327, 2933, 2891, 2864, 1462, 1382, 1366, 1247, 1101, 1059, 1012, 994, 918, 881, 840, 791, 716, 677, 657 cm^{-1}; TLC R_f = 0.47 (20% EtOAc/hexanes).

[(7-Iodoheptyl)oxy]triisopropylsilane. A flame-dried flask equipped with a stir bar was charged with PPh_3 (4.7 g, 7.2 mmol), imidazole (1.2 g, 7.2 mmol), and I_2 (4.5 g, 7.2 mmol) under N_2. Anhydrous DCM (0.2 M) was added; the flask was cooled in an ice bath, and the mixture was stirred for 10 min. Alcohol (1.728 g, 6 mmol), diluted in a 5:1 ratio in DCM, was added dropwise at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 12 h. The reaction mixture was concentrated under reduced pressure, diluted with 25% EtOAc in hexanes, and filtered through a plug of silica. The filtrate was concentrated under reduced pressure, and silica flash chromatography provided [(7-iodoheptyl)oxy]triisopropylsilane (1.48 g, 62% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, J = 6.5 Hz, 2H), 3.18 (t, J = 7.0 Hz, 2H), 1.82 (p, J = 7.1 Hz, 2H), 1.53 (p, J = 6.7 Hz, 2H), 1.44−1.27 (m, 6H), 1.05 (d, J = 4.3 Hz, 21H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 63.5, 33.7, 33.0, 30.6, 28.5, 25.8, 18.2, 12.1, 7.3; HRMS (ESI) calcd for $C_{16}H_{36}OISi$ $[M + H]^+$ 399.1575, found 399.1576; IR (neat) 2931, 2891, 2863, 1461, 1382, 1245, 1103, 994, 918, 881, 789, 717, 678, 654 cm^{-1}; TLC R_f = 0.49 (5% EtOAc/hexanes).

[(7-Hydroperoxyheptyl)oxy]triisopropylsilane. [(7-Iodoheptyl)-oxy]triisopropylsilane (1.3 g, 3.2 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided [(7-hydroperoxyheptyl)oxy]triisopropylsilane (340 mg, 35% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 4.02 (t, J = 6.6 Hz, 2H), 3.67 (t, J = 6.6 Hz, 2H), 1.67−1.59 (m, 2H), 1.54 (p, J = 6.6 Hz, 2H), 1.44−1.30 (m, 6H), 1.15−0.99 (m, 21H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 77.3, 63.6, 33.0, 29.0, 27.6, 26.1, 25.9, 18.2, 12.2; HRMS (ESI) calcd for $C_{16}H_{37}O_3Si$ $[M + H]^+$ 305.2506, found 305.2508; IR (neat) 3357, 2938, 2864, 1462, 1382, 1366, 1248, 1101, 1067, 1013, 995, 918, 881, 792, 717, 679, 657, 460 cm^{-1}; TLC R_f = 0.11 (5% EtOAc/hexanes).

3,3,14,14-Tetraisopropyl-2,15-dimethyl-4,5,13-trioxa-3,14-disilahexadecane. [(7-Iodoheptyl)oxy]triisopropylsilane (330 mg, 1.08 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 3,3,14,14-tetraisopropyl-2,15-dimethyl-4,5,13-trioxa-3,14-disilahexadecane (355 mg, 72% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, J = 6.6 Hz, 2H), 3.66 (t, J = 6.6 Hz, 2H), 1.56 (ddd, J = 22.2, 10.4, 4.3 Hz, 4H), 1.39−1.28 (m, 6H), 1.28−1.14 (m, 3H), 1.15−1.02 (m, 39H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 76.9, 63.6, 33.1, 29.5, 27.9, 26.3, 25.9, 18.2, 18.1, 12.2, 11.7; HRMS (EI) calcd for $C_{25}H_{57}O_3Si_2$ $[M]^+$ 459.3684, found 459.3686; IR (neat) 2940, 2865, 1462, 1382, 1366, 1248, 1101, 1069, 1013, 996, 919, 881, 783, 677, 459 cm^{-1}; TLC R_f = 0.7 (5% EtOAc/hexanes).

5-[(Triisopropylsilyl)oxy]pentan-1-ol. To a round-bottom flask equipped with a stir bar was added sodium hydride (60% dispersion in mineral oil, 1 g, 25 mmol). The sodium hydride was washed three times with hexanes and dried under an argon atmosphere. Thirty millilitersof THF was then added, and the resulting heterogeneous solution was cooled to 0 °C. 1,5-Pentanediol (2.6 mL, 25 mmol) in 15 mL of THF was added via syringe. The reaction mixture was warmed to room temperature for 30 min and then cooled to 0 °C.

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Triisopropylsilyl chloride (5.3 mL, 50 mmol) in 15 mL of THF was added via syringe, and the reaction mixture was allowed to stir for 40 min at 0 °C and then overnight at rt. The reaction was quenched by the addition of water, and the mixture was extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The desired product was isolated by silica flash chromatography (2.73 g, 42% pure isolated) as a colorless oil that matched the reported spectra:[47] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, J = 6.3 Hz, 2H), 3.63 (t, J = 7.1 Hz, 2H), 1.64−1.51 (m, 4H), 1.46−1.37 (m, 2H), 1.03 (m, 21H); IR (neat) 3330, 2939, 2864, 1462, 1382, 1248, 1102, 1069, 994, 918, 881, 790, 718, 678, 656 cm^{-1}; TLC R_f = 0.45 (20% EtOAc/hexanes).

5-[(Triisopropylsilyl)oxy]pentyl Methanesulfonate. 5-[(Triisopropylsilyl)oxy]pentan-1-ol (2.33 g, 8.87 mmol) was subjected to general procedure A for 14 h. After the workup procedure, the crude material was isolated with high purity. We moved to the next step without any further purification (2.86 g, 95% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (t, J = 6.6 Hz, 2H), 3.69 (t, J = 6.1 Hz, 2H), 3.00 (s, 3H), 1.79 (p, J = 6.8 Hz, 2H), 1.63−1.45 (m, 4H), 1.18−0.90 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 70.0, 62.9, 37.3, 32.2, 28.9, 27.1, 21.9, 18.0, 11.9; HRMS (ESI) calcd for $C_{15}H_{35}O_4SSi$ [M + H]$^+$ 339.2020, found 339.2020; IR (neat) 2941, 2864, 1463, 1351, 1172, 1110, 949, 881, 828, 719, 677, 657, 527, 459 cm^{-1}; TLC R_f = 0.17 (10% EtOAc/hexanes).

[(5-Hydroperoxypentyl)oxy]triisopropylsilane. 5-[(Triisopropylsilyl)oxy]pentyl methanesulfonate (2.85 g, 8.46 mmol) was subjected to general procedure C, using 12:1 MeOH/H_2O (0.3 M) and Et_2O (0.8 M) as the solvents, for 44 h. Silica flash chromatography provided [(5-hydroperoxypentyl)oxy]-triisopropylsilane (1.19 g, 51% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12−7.66 (m, 1H), 4.03 (t, J = 6.6 Hz, 2H), 3.69 (t, J = 6.4 Hz, 2H), 1.74−1.63 (m, 2H), 1.62−1.54 (m, 2H), 1.50−1.40 (m, 2H), 1.14−0.91 (m, 21H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 77.3, 63.3, 32.8, 27.4, 22.4, 18.2, 12.1; IR (neat) 3333, 2938, 2864, 1462, 1382, 1248, 1102, 1069, 994, 918, 881, 791, 718, 678, 656, 454 cm^{-1}; TLC R_f = 0.1 (5% EtOAc/hexanes).

3,3,12,12-Tetraisopropyl-2,13-dimethyl-4,5,11-trioxa-3,12-disilatetradecane. [(5-Hydroperoxypentyl)oxy]triisopropylsilane (1.19 g, 4.31 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 3,3,12,12-tetraisopropyl-2,13-dimethyl-4,5,11-trioxa-3,12-disilatetradecane (780 mg, 42% isolated as pure) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, J = 6.6 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H), 1.71−1.51 (m, 4H), 1.48−1.38 (m, 2H), 1.28−1.14 (m, 3H), 1.14−1.01 (m, 39H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 76.9, 63.3, 33.0, 27.8, 22.7, 18.2, 18.1, 12.2, 11.7; HRMS (ESI) calcd for $C_{23}H_{53}O_3Si_2$ [M + H]$^+$ 433.3528, found 433.3530; IR (neat) 2941, 2865, 1462, 1382, 1248, 1102, 1068, 996, 919, 881, 783, 718, 677, 659, 458 cm^{-1}; TLC R_f = 0.7 (5% EtOAc/hexanes).

[(6-Bromohexyl)oxy](tert-butyl)diphenylsilane. To a round-bottom flask equipped with a stir bar were added 6-bromohexanol (2.6 mL, 30 mmol) and TBDCl (33 mmol, 5.2 mL) in DCM (60 mL). Then, triethylamine (4.6 mL, 45 mol) was added dropwise. The reaction mixture was stirred overnight at room temperature. Then, the reaction was quenched with a 10% $NaHCO_3$ solution (40 mL), and the solution was diluted with ethyl acetate (40 mL). The organic layer was extracted; the aqueous layer was washed with ethyl acetate (3 × 20 mL), and the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The pure desired product was isolated by silica gel column chromatography using hexane as the eluent. The isolated pure product (35%, 2.9 g) was a colorless oil that matched previously reported spectra:[48] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.59 (m, 4H), 7.50−7.34 (m, 6H), 3.66 (t, J = 6.4 Hz, 2H), 3.39 (t, J = 6.8 Hz, 2H), 1.83 (td, J = 8.6, 7.8, 5.9 Hz, 2H), 1.70−1.51 (m, 2H), 1.44−1.36 (m, 4H), 1.05 (s, 9H); TLC R_f = 0.6 (2% EtOAc/hexanes).

[(6-Iodoohexyl)oxy](tert-butyl)diphenylsilane. A mixture of [(6-bromohexyl)oxy](*tert*-butyl)diphenylsilane (900 mg, 2.15 mmol) was added to a solution of NaI (894 mg, 6 mmol) in acetone (10 mL), and the mixture was stirred overnight at 65 °C. Then, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (30 mL) was added to the residue and washed with saturated aqueous $Na_2S_2O_3$ (1 × 20 mL), H_2O (1 × 20 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had evaporated, [(6-iodoohexyl)oxy](*tert*-butyl)diphenylsilane was isolated (871 mg, 87%) as a brown liquid. Without any further purification, we proceeded to the next step:[49] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.55 (m, 4H), 7.39 (m, 6H), 3.66 (t, J = 6.4 Hz, 2H), 3.39 (q, J = 6.7 Hz, 2H), 1.83 (q, J = 7.0 Hz, 2H), 1.54 (m, 2H), 1.47−1.33 (m, 4H), 1.04 (s, 9H); TLC R_f = 0.6 (5% EtOAc/hexanes).

tert-Butyl[(6-hydroperoxyhexyl)oxy]diphenylsilane. [(6-Iodoohexyl)oxy](*tert*-butyl)diphenylsilane (800 mg, 1.7 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided *tert*-butyl[(6-hydroperoxyhexyl)oxy]diphenylsilane (505 mg, 47% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.65−7.53 (m, 4H), 7.44−7.23 (m, 6H), 3.90 (t, J = 6.6 Hz, 2H), 3.58 (t, J = 6.5 Hz, 2H), 1.58−1.42 (m, 4H), 1.27 (ddt, J = 14.5, 12.7, 5.0 Hz, 4H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.7, 134.2, 129.6, 127.7, 77.2, 64.0, 32.5, 27.7, 27.0, 25.8, 25.7, 19.4; HRMS (ESI) calcd for $C_{22}H_{33}O_3Si$ [M + H]$^+$ 373.2193, found 373.2195; IR (neat) 3363, 2931, 2857, 1472, 1427, 1389, 1187, 1108, 1093, 822, 739, 700, 688, 613, 503, 488 cm^{-1}; TLC R_f = 0.26 (10% EtOAc/hexanes).

3,3-Diisopropyl-2,14,14-trimethyl-13,13-diphenyl-4,5,12-trioxa-3,13-disilapentadecane. *tert*-Butyl[(6-hydroperoxyhexyl)oxy]-diphenylsilane (270 mg, 0.72 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided 3,3-diisopropyl-2,14,14-trimethyl-13,13-diphenyl-4,5,12-trioxa-3,13-disilapentadecane (273 mg, 72% isolated as pure) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.57 (m, 4H), 7.55−7.29 (m, 6H), 4.10−3.89 (m, 2H), 3.73−3.54 (m, 2H), 1.72−1.47 (m, 4H), 1.35 (m, 4H), 1.29−1.16 (m, 3H), 1.10 (m, 18H), 1.06 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.7, 134.3, 129.7, 127.8, 76.9, 64.1, 32.6, 28.0, 27.1, 2618, 25.9, 19.4, 18.2, 18.2, 12.2, 11.7; HRMS (ESI) calcd for $C_{31}H_{53}O_3Si_2$ [M + H]$^+$ 529.3528, found 529.3528; IR (neat) 2939, 2864, 1462, 1427, 1385, 1362, 1257, 1106, 997, 882, 822, 781, 738, 700, 684, 613, 503, 487 cm^{-1}; TLC R_f = 0.63 (10% EtOAc/hexanes).

*Triisopropyl(pent-4-en-1-ylperoxy)silane (**34**).* TIPSOOH (284 mg, 1.5 mmol, 1 equiv) was subjected to general procedure F using 5-iodo-1-pentene (0.55 mL, 4.5 mmol, 3 equiv). Silica flash chromatography provided **34** (164.9 mg, 42% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (dd, J = 17.1, 1.8 Hz, 1H), 4.97 (dd, J = 10.1, 1.8 Hz, 1H), 4.00 (t, J = 6.5 Hz, 2H), 2.12 (q, J = 7.1 Hz, 2H), 1.71 (p, J = 7.6, 6.8, 6.8 Hz, 2H), 1.29−1.14 (m, 3H), 1.10 (d, J = 7.1 Hz, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.2, 115.0, 76.1, 30.4, 27.2, 18.1, 11.7; LRMS (GCMS) mass fragmentation 171.2 (15), 169.2 (15), 141.2 (15), 129.2 (25), 105.1 (30), 103.1 (30), 77.1 (100), 76.1 (40), 61.1 (20), 41.2 (10); IR (neat) 3079, 2943, 2866, 1642, 1463, 995, 911, 882, 676 cm^{-1}; TLC R_f = 0.58 (5% EtOAc/hexanes).

Hydroperoxycyclopentane. Cylopentyl mesylate (1.96 g, 12 mmol, 1 equiv) was subjected to general procedure C at a concentration of 0.3 M (12:1 MeOH/H_2O) for 22 h. Silica flash chromatography provided hydroperoxycyclopentane (539 mg, 44% yield) as a clear, colorless oil that matched the reported spectra:[50] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (br s, 1H), 4.60 (tt, J = 5.9, 3.1 Hz, 1H), 1.89−1.61 (m, 6H), 1.63−1.48 (m, 2H); TLC R_f = 0.36 (20% EtOAc/hexanes).

*(Cyclopentylperoxy)triisopropylsilane (**36**).* Hydroperoxycyclopentane (322 mg, 3.0 mmol, 1 equiv) was subjected to general procedure E using triisopropylsilyl chloride (0.65 mL, 3.0 mmol, 1 equiv), Ag_2O (686 mg, 3.0 mmol, 1 equiv), and anhydrous ammonia as the base (sparge for 10 min and then a balloon atmosphere) for 15 h. The crude mixture was filtered through a silica plug, eluting with 10% EtOAc/hexanes to provide **36** (395 mg, 51% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (dt, J = 5.6, 2.9 Hz, 1H), 1.86−1.73 (m, 2H), 1.72−1.57 (m, 5H), 1.58−1.44 (m, 2H), 1.28−1.13 (m, 2H), 1.08 (d, J = 6.8 Hz, 18H); ^{13}C{^{1}H} NMR (100

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MHz, $CDCl_3$) δ 87.1, 31.1, 24.2, 18.2, 11.8; LRMS (GCMS) mass fragmentation 199.3 (3), 173.2 (3), 147.2 (15), 105.2 (43), 77.2 (100), 76.1 (40), 61.1 (15), 45.2 (10); IR (neat) 2943, 2866, 1463, 1346, 1071, 881, 675 cm^{-1}; TLC R_f = 0.6 (5% EtOAc/hexanes).

(5-Bromopent-1-yn-1-yl)benzene. To phenylacetylene (1.7 mL, 15 mmol) in anhydrous THF (28 mL) was added *n*-BuLi (2.2 M solution in hexanes, 22 mmol) dropwise at room temperature over 5 min before the mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature before 1,4-diiodobutane (2.0 equiv) was added as a THF solution (0.4 M). The reaction mixture was refluxed overnight, returned to room temperature, quenched with H_2O (10 mL), and extracted with Et_2O (3 × 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give a residue. Silica flash chromatography provided (5-bromopent-1-yn-1-yl)benzene (1.66 g, 50%) as a clear, colorless oil, which matched previously reported spectra:[51] ^1H NMR (400 MHz, $CDCl_3$) δ 7.46−7.33 (m, 2H), 7.32−7.14 (m, 3H), 3.57 (t, *J* = 6.5 Hz, 2H), 2.59 (td, *J* = 6.9, 4.8 Hz, 3H), 2.12 (p, *J* = 6.7 Hz, 2H).

(5- Iodopent-1-yn-1-yl)benzene. A mixture of (5-bromopent-1-yn-1-yl)benzene (1.332 g, 6 mmol) was added to a solution of NaI (3 g, 18 mmol) in acetone (20 mL), and the mixture was stirred overnight at 65 °C. Then, the reaction mixture was cooled to room temperature, the precipitate filtered, and the filtrate evaporated. Then, Et_2O (40 mL) was added to the residue and washed with saturated aqueous $Na_2S_2O_3$ (1 × 20 mL), H_2O (1 × 30 mL), and brine (1 × 50 mL). The organic solution was dried over anhydrous $MgSO_4$. After the solvent had evaporated, (5-iodopent-1-yn-1-yl)benzene was isolated (1.474 g, 91%) as a brown liquid, which matched previously reported spectra. Without any further purification, we proceeded to the next step:[52] ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 6.2, 4.5, 2.7 Hz, 2H), 7.34−7.09 (m, 3H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 6.7 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 2H).

*Triisopropyl[(5-phenylpent-4-yn-1-yl)peroxy]silane (**38**).* (5-Iodopent-1-yn-1-yl)benzene (1.458 g, 5.4 mmol) was subjected to general procedure D for 2 h. Silica flash chromatography provided (5-hydroperoxypent-1-yn-1-yl)benzene (522 mg, 55% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.45−7.37 (m, 2H), 7.27 (dt, *J* = 4.7, 2.9 Hz, 3H), 4.16 (t, *J* = 6.2 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.10−1.67 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 131.7, 128.3, 127.8, 123.7, 89.3, 81.3, 75.7, 26.9, 16.1; IR (neat) 3369, 3059, 2936, 2232, 1709, 1598, 1489, 1441, 1275, 1176, 1069, 1027, 755, 713, 690, 526 cm^{-1}; TLC R_f = 0.27 (20% EtOAc/hexanes). Next, (5-hydroperoxypent-1-yn-1-yl)benzene (475 mg, 2.7 mmol) was subjected to general procedure E for 2 h. Silica flash chromatography provided triisopropyl[(5-phenylpent-4-yn-1-yl)-peroxy]silane (609 mg, 68% isolated as pure) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (tt, *J* = 5.7, 2.3 Hz, 2H), 7.30−7.21 (m, 3H), 4.13 (t, *J* = 6.1 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.98−1.89 (m, 2H), 1.26−1.15 (m, 3H), 1.08 (d, *J* = 7.1 Hz, 18H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 131.7, 131.7, 128.4, 127.8, 89.5, 75.3, 27.4, 27.3, 18.2, 18.2, 16.5, 11.7; LRMS (GCMS) mass fragmentation 273.1 (27), 231.2 (100), 203.2 (27), 155.2 (7), 115.2 (17), 75.2 (3); IR (neat) 2943, 2865, 1598, 1490, 1463, 1366, 1069, 997, 918, 881, 753, 687 cm^{-1}; TLC R_f = 0.7 (5% EtOAc/hexanes).

(4-Iodobutyl)cyclopropane. To a 50 mL two-neck flask with a stir bar and a reflux condenser were added 5-hexen-1-ol (0.840 mL, 7.0 mmol, 1 equiv), diiodomethane (0.710 mL, 8.75 mmol, 1.25 equiv), and anhydrous DCM (1.0 M).[53] While the mixture was being stirred at room temperature, trimethylaluminum (8.0 mL, 15.4 mmol, 2.2 equiv, 2 M in hexanes) was added dropwise over ∼5 min. The reaction mixture was stirred at room temperature for 10 min and then heated to 40 °C overnight. After 14 h, the reaction mixture was cooled to room temperature and diluted with 10 mL of DCM, and the reaction carefully quenched with water (dropwise addition of 1 mL of water, ∼1 drop/10 s). After vigorous bubbling had stopped, the mixture was transferred to a separatory funnel with DCM and an additional 3 mL of water was slowly added. Once all bubbling had stopped, an additional ∼25 mL of water was added. The mixture was diluted with DCM and 1 M aqueous NaOH (∼50 mL each). The organic layer was removed and extracted with 3 × 50 mL of aqueous DCM. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to provide 4-cyclopropylbutan-1-ol as a clear yellow oil. The product was pure as determined by ^1H NMR analysis and directly subjected to Appel conditions. To a 50 mL flask with a stir bar were added triphenylphosphine (1.835 g, 7.0 mmol, 1 equiv), imidazole (488 mg, 7.0 mmol, 1 equiv), and iodine (1.769 g, 7.0 mmol, 1 equiv). The flask was placed in an ice bath, and DCM (0.5 M) was added. The resulting opaque yellow solution was stirred at 0 °C for 50 min. A solution of the crude alcohol in 2 mL of DCM was added dropwise, and the reaction mixture was slowly warmed to room temperature overnight. After 14 h, solvents were removed by rotary evaporation, providing a viscous yellow oil. This oil was filtered through a pad of silica, washing with ∼100 mL of hexanes, and then concentrated to provide (4-iodobutyl)cyclopropane (1.295 g, 82% yield over two steps) as a clear, colorless oil that did not require further purification: ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (t, *J* = 7.1 Hz, 1H), 1.86 (p, *J* = 7.2 Hz, 1H), 1.50 (ddd, *J* = 12.5, 8.2, 6.2 Hz, 1H), 1.21 (q, *J* = 7.2 Hz, 1H), 0.64 (ddt, *J* = 9.7, 7.2, 3.6 Hz, 1H), 0.50−0.34 (m, 1H), −0.00 (t, *J* = 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, chloroform-*d*) δ 33.8, 33.5, 30.7, 10.8, 7.4, 4.6; HRMS (EI) calcd for $C_7H_{13}I$ $[M]^+$ 224.0056, found 224.0053; IR (neat) 3073, 2998, 2923, 2850, 1455, 1426, 1221, 1179, 1166, 1013, 820, 720, 597, 504 cm^{-1}; TLC R_f = 0.68 (10% EtOAc/hexanes).

*[(4-Cyclopropylbutyl)peroxy]triisopropylsilane (**40**).* TIPSOOH (288 mg, 1.5 mmol, 1 equiv) was subjected to general procedure F using (4-iodobutyl)cyclopropane (1.010 g, 4.5 mmol, 3 equiv). Silica flash chromatography provided **40** (118.0 mg, 27% yield) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, *J* = 6.6 Hz, 2H), 1.64 (dt, *J* = 8.7, 6.6 Hz, 2H), 1.57−1.40 (m, 2H), 1.35−1.18 (m, 5H), 1.12 (d, *J* = 6.9 Hz, 18H), 0.81−0.59 (m, 1H), 0.49−0.35 (m, 2H), 0.07 to −0.05 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 77.0, 34.7, 27.8, 26.3, 18.2, 11.8, 10.9, 4.6; LRMS (GCMS) mass fragmentation 227.3 (1), 185.2 (10), 183.2 (10), 155.2 (20), 131.2 (20), 105.2 (42), 103.2 (30), 77.2 (100), 76.1 (38), 61.1 (20), 41.2 (10); IR (neat) 2942, 2866, 1463, 1382, 1366, 1256, 1014, 997, 881, 859, 789, 676, 663 cm^{-1}; TLC R_f = 0.69 (5% EtOAc/hexanes).

5-Hydroperoxypent-1-ene. 4-Pentenyl mesylate (1.310 g, 8 mmol, 1 equiv) was subjected to general procedure C at a concentration (of 0.3 M 12:1 MeOH/H_2O) for 20 h. Silica flash chromatography provided 5-hydroperoxypent-1-ene (380 mg, 46% yield) as a clear, colorless oil that matched the reported spectra:[54] ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.05 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.04 (t, *J* = 6.5 Hz, 2H), 2.14 (q, *J* = 7.1 Hz, 2H), 1.75 (p, *J* = 7.0 Hz, 2H); TLC R_f = 0.38 (20% EtOAc/hexanes).

Hydroperoxytriisopropylsilane (TIPSOOH). To a 100 mL round-bottom flask with a stir bar were added TIPSCl (4.30 mL, 20 mmol, 1 equiv) and dry Et_2O (1.0 M). The solution was cooled in an ice bath, and urea/H_2O_2 (3.86 g, 40 mmol, 2 equiv) was added in a single portion. The reaction mixture was sparged with anhydrous ammonia for 15 min and then left under an atmosphere of NH_3, warming to room temperature overnight. The next morning, the reaction mixture was diluted with hexane and water (∼20 mL each). The organic layer was removed, and the aqueous layer extracted with hexanes (2 × 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated to provide a clear colorless oil. Silica flash chromatography provided hydroperoxytriisopropylsilane (2.021 g, 53%) as a clear, colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (br s, 1H), 1.26 (sept, *J* = 7.3 Hz, 3H), 1.11 (d, *J* = 7.3 Hz, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 18.1, 11.6; IR (neat) 3331, 2944, 2867, 1463, 1384, 998, 881, 733, 676 cm^{-1}; TLC R_f = 0.40 (15% EtOAc/hexanes) (stains brightly with $KMnO_4$); TLC silanol side product R_f = 0.34 (15% EtOAc/hexanes) (stains faintly with $KMnO_4$)

*1-(Methylperoxy)dodecane (**3a**).* To a 25 mL round-bottom flask with a stir bar were added 1-dodecyl hydroperoxide **391** (404 mg, 2.0 mmol, 1 equiv) and MeOH (0.8 M). The solution was cooled in an ice bath, and 50 wt % aqueous KOH (225 mg, 2.0 mmol, 1 equiv) and iodomethane (0.45 mL, 5.0 mmol, 2.5 equiv) were added

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successively. The reaction mixture was stirred overnight, warming to room temperature. After 15 h, the mixture was diluted with DCM (~25 mL) and water (~50 mL). The organic layer was removed, and the aqueous layer extracted with 3 × 25 mL of DCM. The combined organic layers were washed sequentially with water, potassium thiosulfate, and brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation, keeping the water bath below 40 °C. Silica flash chromatography provided **3a** (368 mg, 85% yield) as a clear, colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.97 (t, J = 6.6 Hz, 2H), 3.82 (s, 3H), 1.59 (p, J = 6.8 Hz, 2H), 1.26 (d, J = 4.4 Hz, 18H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 74.2, 62.2, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 28.0, 26.2, 22.8, 14.3; IR (neat) 2922, 2853, 1742, 1466, 1376, 1017 cm^{-1}; TLC R_f = 0.66 (20% EtOAc/hexanes).

*Dodecyl 2,2,2-Trifluoroethaneperoxoate (**3c**).*[55] To a screw-cap test tube with a stir bar was added 1-dodecyl hydroperoxide **3b** (204.5 mg, 1.0 mmol, 1 equiv). The flask was cooled in an ice bath, and trifluoroacetic anhydride (0.140 mL, 1.0 mmol, 1 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h, the reaction quenched with 3 mL of water, and the mixture diluted with 10 mL of DCM. The mixture was washed with saturated aqueous $NaHCO_3$, the organic layer removed, and the aqueous layer extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to provide **3c** (241 mg, 81% yield) as a clear, colorless oil in 90% purity (dodecanal as the contaminant). The crude product was used without further purification: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.38 (t, J = 6.6 Hz, 2H), 1.72 (p, J = 6.8 Hz, 2H), 1.41 (p, J = 7.0 Hz, 2H), 1.36−1.16 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.43; IR (neat) 2923, 2854, 1785, 1466, 1162, 779 cm^{-1}.

*(Dodecylperoxy)triethoxysilane (**3d**).* 1-Dodecyl hydroperoxide **3b** (102.4 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using chlorotriethoxysilane (0.10 mL, 0.5 mmol, 1 equiv) and triethylamine (0.14 mL, 1.0 mmol, 2 equiv) as the base for 15 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated by rotary evaporation. NMR analysis showed incomplete conversion; the crude material was dissolved in DCM (3 mL), and triethylamine (0.10 mL, 0.72 mmol, 1.5 equiv) was added. The reaction mixture was stirred for 14 h, filtered, and concentrated to provide **3d** (95.3 mg, 52% yield) in ~80% purity by ^{1}H NMR, which was used without further purification: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.03 (t, J = 6.6 Hz, 2H), 3.87 (q, J = 6.8 Hz, 6H), 1.69−1.51 (m, 4H), 1.39−1.18 (m, 25H), 0.88 (t, J = 7.0 Hz, 3H); TLC R_f = 0.50 (15% EtOAc/hexanes), hydrolyzes on silica gel.

*(Dodecylperoxy)triisopropoxysilane (**SI-3k**).* 1-Dodecyl hydroperoxide **3b** (103.4 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using chlorotriisopropoxysilane[56] (0.14 mL, 0.5 mmol, 1 equiv) and triethylamine (0.14 mL, 1.0 mmol, 2 equiv) as the base for 15 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated by rotary evaporation. NMR analysis showed incomplete conversion; the crude material was dissolved in DCM (3 mL), and triethylamine (0.10 mL, 0.72 mmol, 1.5 equiv) was added. The reaction mixture was stirred for 14 h, filtered, and concentrated to provide **SI-3k** (138.0 mg, 68% yield) in ~85% purity by ^{1}H NMR, which was used without further purification: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.24 (hept, J = 6.3 Hz, 3H), 3.99 (t, J = 6.7 Hz, 3H), 1.61 (p, J = 6.9, Hz, 2H), 1.36−1.21 (m, 17H), 1.19 (d, J = 6.1 Hz, 18H), 0.86 (t, J = 6.9 Hz, 3H).

*(Dodecylperoxy)trimethylsilane (**3e**).* 1-Dodecyl hydroperoxide **3b** (102.5 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using chlorotrimethylsilane (0.130 mL, 1.0 mmol, 2 equiv) and pyridine (0.080 mL, 1.0 mmol, 2 equiv) as the base at a concentration of 0.2 M for 40 min. The reaction mixture was diluted with pentane, filtered, and then concentrated to provide **3e** (74.3 mg, 54% yield) in >95% purity by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 6.6 Hz, 2H), 1.60 (p, J = 6.9 Hz, 2H), 1.39−1.18 (s, 19H), 0.88 (t, J = 6.7 Hz, 3H), 0.20 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 77.3, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 27.9, 26.2, 22.8, 14.3, −1.3; IR (neat) 2923, 2853, 1250, 879, 732 cm^{-1}; TLC, hydrolyzes on silica gel.

*(Dodecylperoxy)triethylsilane (**3f**).* 1-Dodecyl hydroperoxide **3b** (40.5 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using triethylsilyl triflate (0.040 mL, 0.18 mmol, 0.9 equiv). The reaction mixture was diluted with diethyl ether, filtered, and then concentrated to provide **3f** (74.3 mg, 54% yield) as a clear, colorless oil in ~85% purity by ^{1}H NMR with contaminating hydroperoxide. **3f** decomposed under all purification attempts and was used without further purification: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.97 (t, J = 6.6 Hz, 2H), 1.61 (p, J = 6.8 Hz, 2H), 1.40−1.20 (m, 18H), 1.00 (t, J = 8.0 Hz, 9H), 0.89 (t, J = 7.0 Hz, 3H), 0.70 (q, J = 8.0 Hz, 6H); TLC, hydrolyzes on silica gel.

*(Dodecylperoxy)dimethyl(vinyl)silane (**3g**).* 1-Dodecyl hydroperoxide **3b** (103.0 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using chloro(dimethyl)vinylsilane (0.070 mL, 0.5 mmol, 1 equiv) for 14 h. The reaction mixture was diluted with pentane, filtered, and then concentrated to provide **3g** (102.5 mg, 71% yield) as a clear, colorless oil in ~80% purity by ^{1}H NMR with contaminating hydroperoxide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26−6.03 (m, 2H), 5.87 (dd, J = 19.8, 4.3 Hz, 1H), 3.97 (t, J = 6.6 Hz, 2H), 1.69−1.55 (m, 2H), 1.44−1.15 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H), 0.28 (s, 6H); TLC, hydrolyzes on silica gel.

*(Dodecylperoxy)(methyl)diphenylsilane (**3h**).* 1-Dodecyl hydroperoxide **3b** (200.6 mg, 1.0 mmol, 1 equiv) was subjected to general procedure E using chloro(methyl)diphenylsilane (0.070 mL, 0.5 mmol, 1 equiv) and silver triflate (257.0 mg, 1.0 mmol, 1 equiv) for 14 h. To remove residual hydroperoxide, the crude material was diluted with pentane (3 mL) and flushed through a silica plug, washing with an additional ~10 mL of pentane, and concentrated to provide **3h** (110.0 mg, 27% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, J = 6.5, 1.6 Hz, 3H), 7.52 (dt, J = 6.7, 1.5 Hz, 1H), 7.47−7.35 (m, 5H), 7.31 (dd, J = 7.9, 6.4 Hz, 1H), 3.93 (t, J = 6.6 Hz, 2H), 1.58−1.47 (m, 2H), 1.40−1.12 (m, 18H), 0.89 (t, J = 6.7 Hz, 3H), 0.76 (s, 3H); TLC R_f = 0.73 (15% EtOAc/hexanes).

*tert-Butyl(dodecylperoxy)dimethylsilane (**3i**).* 1-Dodecyl hydroperoxide **3b** (120.0 mg, 0.6 mmol, 1 equiv) was subjected to general procedure E using *tert*-butyldimethylsilyl triflate (0.140 mL, 0.6 mmol, 1 equiv) at a concentration of 0.75 M for 14 h to provide **3i** (136.0 mg, 71% yield) as a clear, colorless oil. The crude material was >95% pure as determined by ^{1}H NMR and did not require purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (t, J = 6.6 Hz, 2H), 1.59 (p, J = 6.6 Hz, 2H), 1.40−1.17 (m, 18H), 0.94 (s, 9H), 0.88 (t, J = 6.6 Hz, 3H), 0.16 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 77.2, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 27.9, 26.4, 26.3, 22.9, 18.3, 14.3, −5.7; IR (neat) 924, 2854, 1738, 1462, 1250, 835, 733 cm^{-1}.

*tert-Butyl(dodecylperoxy)diphenylsilane (**SI-3l**).* 1-Dodecyl hydroperoxide **3b** (203.8 mg, 1.0 mmol, 1 equiv) was subjected to general procedure E using *tert*-butyl(chloro)diphenylsilane (0.26 mL, 1.0 mmol, 1 equiv) and silver triflate (248.4 mg, 0.97 mmol, 1 equiv) for 14 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated. Silica flash chromatography provided **SI-3l** (107.0 mg, 24% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (td, J = 8.7, 7.9, 1.2 Hz, 4H), 7.50−7.31 (m, 6H), 3.92 (t, J = 6.6 Hz, 2H), 1.53−1.44 (m, 2H), 1.37−1.06 (m, 27H), 0.88 (t, J = 6.7 Hz, 3H); IR (neat) 2926, 2855, 1738, 1462, 1112, 906, 730 cm^{-1}; TLC R_f = 0.73 (15% EtOAc/hexanes).

*Di-tert-butyl(dodecylperoxy)(isobutyl)silane (**SI-3m**).* 1-Dodecyl hydroperoxide **3b** (101.2 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using di-*tert*-butyl-isobutylsilyl triflate (0.14 mL, 1.0 mmol, 1 equiv) for 16 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated. Elution through a silica plug (hexanes) provided **SI-3m** (18.7 mg, 9% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, J = 6.5 Hz, 2H), 2.00 (septet, J = 6.6 Hz, 1H), 1.58 (p, J = 6.9 Hz, 2H), 1.39−1.18 (m, 18H), 1.05 (s, 18H), 0.99 (d, J = 6.5 Hz, 6H), 0.88 (t, J = 6.7 Hz, 3H), 0.68 (d, J = 6.6 Hz, 2H); TLC R_f = 0.79 (5% EtOAc/hexanes).

*(2,3-Dimethylbutan-2-yl)(dodecylperoxy)dimethylsilane (**SI-3n**).* 1-Dodecyl hydroperoxide **3b** (101.2 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using chlorodimethylhexylsilane

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(0.10 mL, 0.5 mmol, 1 equiv) for 16 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated. Elution through a silica plug (hexanes) provided **SI-3n** (24.9 mg, 14% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (t, J = 6.6 Hz, 2H), 1.70−1.49 (m, 2H), 1.38−1.18 (m, 18H), 0.94−0.83 (m, 16H), 0.21 (s, 6H); TLC R_f = 0.71 (5% EtOAc/hexanes).

*tert-Butoxy(dodecylperoxy)diphenylsilane (**SI-3o**).* 1-Dodecyl hydroperoxide **3b** (100.6 mg, 0.5 mmol, 1 equiv) was subjected to general procedure E using *tert*-butoxy(chloro)diphenylsilane[57] (148.1 mg, 0.5 mmol, 1 equiv) for 14 h. The reaction mixture was diluted with diethyl ether, filtered, and then concentrated. Silica flash chromatography provided **SI-3o** (132.5 mg, 58% yield) as a clear, colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76−7.63 (m, 4H), 7.47−7.39 (m, 2H), 7.38−7.30 (m, 4H), 3.88 (t, J = 6.6 Hz, 2H), 1.49 (p, J = 6.6 Hz, 2H), 1.36 (s, 9H), 1.34−1.10 (m, 18H), 0.89 (t, J = 6.8 Hz, 3H); TLC R_f = 0.65 (15% EtOAc/hexanes).

*(Dodecylperoxy)(isopropoxy)diisopropylsilane (**SI-3p**).* 1-Dodecyl hydroperoxide **3b** (198.9 mg, 1.0 mmol, 1 equiv) was subjected to general procedure E using chloro(isopropoxy)diisopropylsilane (216.1 mg, 1.0 mmol, 1 equiv) for 16 h. The reaction mixture was diluted with pentane, filtered, and then concentrated. Silica flash chromatography provided **SI-3p** (143.0 mg, 38% yield) as a clear, colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.27 (sept, J = 6.0 Hz, 1H), 4.02 (t, J = 6.6 Hz, 2H), 1.60 (p, J = 6.8 Hz, 2H), 1.39−1.23 (m, 18H), 1.20 (d, J = 6.1 Hz, 6H), 1.13−1.01 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); TLC R_f = 0.73 (15% EtOAc/hexanes).

1,2-Di(naphthalen-2-yl)disulfane. To a 25 mL flask with a stir bar were added 2-thionaphthol (807 mg, 5 mmol, 1 equiv) and ethyl lactate (0.67 M). The reaction mixture was stirred at 60 °C, open to air.[58] After 16 h, the reaction was quenched with water and the mixture transferred to a separatory funnel, diluting with ∼50 mL each of ethyl acetate and water. The organic layer was removed, and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water and then brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. Trituration with diethyl ether provided 1,2-di(naphthalen-2-yl)-disulfane (377 mg, 47% yield) as an off-white solid that matched the reported spectrum:[58] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.86−7.68 (m, 6H), 7.62 (dd, J = 8.7, 1.9 Hz, 2H), 7.52−7.38 (m, 4H).

1,2-Bis(3,4-dichlorophenyl)disulfane. The compound was prepared following the same procedure that was used for 1,2-di(naphthalen-2-yl)disulfane, using 3,4-dichlorothiophenol (0.64 mL, 5 mmol). Trituration with diethyl ether provided 1,2-bis(3,4-dichlorophenyl)disulfane (353 mg, 39% yield) as an off-white solid that matched the reported spectrum:[59] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H).

1,2-Bis(4-bromophenyl)disulfane. The compound was prepared following the same procedure that was used for 1,2-di(naphthalen-2-yl)disulfane, using 4-bromothiophenol (383 mg, 2 mmol). Silica flash chromatography provided 1,2-bis(4-bromophenyl)disulfane (302 mg, 80% yield) as a white solid that matched the reported spectrum:[58] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.5 Hz, 4H); TLC R_f = 0.66 (15% EtOAc/hexanes).

1,2-Bis[4-(trifluoromethyl)phenyl]disulfane. The compound was prepared following the same procedure that was used for 1,2-di(naphthalen-2-yl)disulfane, using 4-(trifluoromethyl)thiophenol (0.40 mL, 3 mmol). Trituration with diethyl ether provided 1,2-bis[4-(trifluoromethyl)phenyl]disulfane (210 mg, 39% yield) as a white solid that matched the reported spectrum:[60] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 8H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.64.

1,2-Bis(4-methoxyphenyl)disulfane. To a 100 mL round-bottom flask with a stir bar were added silica gel (6.4 g) and water (1 M). The mixture was stirred for 5 min to hydrate silica, leaving a free-flowing powder. DCM (0.1 M) and 4-methoxybenzenethiol (0.62 mL, 5 mmol, 1 equiv) were added, and then while the mixture was being stirred at room temperature, a solution of bromine (0.26 mL, 5.05 mmol, 1.01 equiv) in 5 mL of DCM was added dropwise.[61] After 20 min, the reaction mixture was filtered, washing with ∼75 mL of DCM, and concentrated to provide a clear red-orange oil. Silica flash chromatography provided 1,2-bis(4-methoxyphenyl)disulfane (618 mg, 88% yield) as a clear, viscous yellow oil that matched the reported spectrum:[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 4H), 6.84 (d, J = 8.8 Hz, 4H); TLC R_f = 0.19 (25% EtOAc/hexanes).

1,2-Bis(4-nitrophenyl)disulfane. The compound was prepared following the same procedure that was used for 1,2-di(naphthalen-2-yl)disulfane, using 4-nitrothiophenol (785 mg, 5 mmol). Trituration with diethyl ether provided 1,2-bis(4-nitrophenyl)disulfane (508 mg, 66% yield) as a light yellow solid that matched the reported spectrum:[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 4H), 7.62 (d, J = 9.0 Hz, 4H); TLC R_f = 0.50 (25% EtOAc/hexanes).

2,2′-Disulfanediyldibenzoic Acid. The compound was prepared following the same procedure that was used for 1,2-di(naphthalen-2-yl)disulfane, using 2-mercaptobenzoic acid (769 mg, 5 mmol). Trituration with diethyl ether provided 2,2′-disulfanediyldibenzoic acid (194 mg, 25% yield) as a white solid that matched the reported spectrum:[62] ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.55 (br s, 2H), 8.02 (d, J = 7.7 Hz, 2H), 7.69−7.51 (m, 4H), 7.34 (t, J = 7.4 Hz, 2H).

1-(Naphthalen-2-yl)-2-phenyldisulfane.[63] To a solution of the 1,2-di(naphthalen-2-yl)disulfane (1.0 mmol) in tetrahydrofuran (THF) (5.0 mL) at 0 °C was added slowly SO_2Cl_2 (1.1 mmol). The reaction mixture was stirred for 1 h at the same temperature. This solution was used immediately in the next step.

To a solution of the thiophenol (1.0 mmol), triethylamine (2.2 mmol), and water (10 mmol) in THF (4.0 mL) at room temperature was added the solution from the first step (1 mmol of sulfenyl chloride dissolved in THF) while the mixture was being stirred. The reaction mixture was stirred for 6 h at room temperature. The reaction mixture was diluted with DCM (20 mL), washed with a saturated aqueous $NaHCO_3$ solution and water, and then dried over anhydrous $MgSO_4$. The solvent was removed by evaporation, and 1-(naphthalen-2-yl)-2-phenyldisulfane was purified by column chromatography using hexanes as the eluent and isolated as a white solid in 35% yield (94 mg), which matched the reported spectrum:[64] ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.95 (s, 1H), 7.85−7.77 (m, 2H), 7.75 (d, J = 8.1 Hz, 1H), 7.60 (dd, J = 8.6, 1.9 Hz, 1H), 7.57−7.50 (m, 2H), 7.50−7.41 (m, 2H), 7.29 (dd, J = 8.4, 6.8 Hz, 2H), 7.25−7.17 (m, 1H).

1-(4-Methoxyphenyl)-2-phenyldisulfane. To a solution of the 1,2-bis(4-methoxyphenyl)disulfane (1.0 mmol) in tetrahydrofuran (THF) (5.0 mL) at 0 °C was added slowly SO_2Cl_2 (1.1 mmol). The reaction mixture was stirred for 1 h at the same temperature. This solution was used immediately in the next step.

To a solution of the thiophenol (1.0 mmol), triethylamine (2.2 mmol), and water (10 mmol) in THF (4.0 mL) at room temperature was added the solution from the first step (1 mmol of sulfenyl chloride dissolved in THF) while the mixture was being stirred. The reaction mixture was stirred for 6 h at room temperature. The reaction mixture was diluted with DCM (20 mL), washed with a saturated aqueous $NaHCO_3$ solution and water, and then dried over anhydrous $MgSO_4$. The solvent was removed by evaporation, and 1-(4-methoxyphenyl)-2-phenyldisulfane was purified by column chromatography using a mixture of hexanes and ethyl acetate as the eluent and isolated as an oily liquid in 75% yield (186 mg), which matched the reported spectrum:[65] ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.51 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.35−7.27 (m, 2H), 7.27−7.20 (m, 1H), 6.83 (d, J = 8.3 Hz, 2H), 3.77 (s, 2H).

1-(4-Nitrophenyl)-2-phenyldisulfane. To a solution of 1,2-bis(4-nitrophenyl)disulfane (1.0 mmol) in tetrahydrofuran (THF) (5.0 mL) at 0 °C was added slowly SO_2Cl_2 (1.1 mmol). The reaction mixture was stirred for 1 h at the same temperature. This solution was used immediately in the next step.

To a solution of the thiophenol (1.0 mmol), triethylamine (2.2 mmol), and water (10 mmol) in THF (4.0 mL) at room temperature was added the solution from the first step (1 mmol of sulfenyl chloride dissolved in THF) while the mixture was being stirred. The reaction mixture was stirred for 6 h at room temperature. The reaction mixture was diluted with DCM (20 mL), washed with a saturated aqueous $NaHCO_3$ solution and water, and then dried over

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anhydrous $MgSO_4$. The solvent was removed by evaporation, and 1-(4-nitrophenyl)-2-phenyldisulfane was purified by column chromatography using a mixture of hexanes and ethyl acetate as the eluent and isolated as an oily liquid in 55% yield (145 mg), which matched the reported spectrum:[65] ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.25−8.10 (m, 2H), 7.71−7.58 (m, 2H), 7.55−7.43 (m, 2H), 7.41−7.25 (m, 3H).

Preparation and Characterization of Thioarylated Products. *4-(Phenylthio)dodecan-1-ol (**4a**).* (Dodecylperoxy)triisopropylsilane **3j** (179.4 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **4a** (98.4 mg, 66% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.3 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 3.63 (t, J = 6.3 Hz, 2H), 3.10 (p, J = 6.4 Hz, 1H), 1.82−1.36 (m, 10H), 1.26 (s, 11H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.7, 132.0, 128.9, 126.7, 62.9, 49.1, 34.7, 32.0, 30.8, 30.0, 29.6, 29.6, 29.4, 26.9, 22.8, 14.2; HRMS (APCI) calcd for $C_{18}H_{31}OS$ $[M + H]^+$ 295.2096, found 295.2092; FTIR (neat) 3320, 3073, 2923, 2852, 1478, 1090, 738, 691 cm^{-1}; TLC R_f = 0.22 (20% EtOAc/hexanes).

*4-(Phenylthio)butan-1-ol (**5**).* (Butylperoxy)triisopropylsilane (125.7 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **5** (15.3 mg, 16% yield) as a clear, colorless oil that matched the reported spectrum:[66] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.7 Hz, 2H), 7.27 (d, J = 15.0 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 3.65 (t, J = 5.9 Hz, 2H), 2.95 (t, J = 6.7 Hz, 2H), 1.80−1.64 (m, 4H), 1.50−1.63 (s, 1H); TLC R_f = 0.11 (25% EtOAc/hexanes).

*5-(Phenylthio)pentan-2-ol (**6**).* Triisopropyl(pentan-2-ylperoxy)-silane (129.8 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **6** (32.0 mg, 32% yield) as a clear, colorless oil that matched the reported spectrum:[67] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.4 Hz, 2H), 7.29−7.22 (m, 2H), 7.15 (t, J = 7.3 Hz, 1H), 3.80 (p, J = 6.3 Hz, 1H), 2.93 (t, J = 7.2 Hz, 2H), 1.82−1.72 (m, 2H), 1.44−1.34 (m, 2H), 1.23 (s, 1H), 1.17 (d, J = 6.2 Hz, 3H); TLC R_f = 0.28 (35% EtOAc/hexanes).

*3-Methyl-4-(phenylthio)butan-1-ol (**7**).* (Isopentylperoxy)-triisopropylsilane (130 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided the pure product (45 mg, 46% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 7.5 Hz, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.21−7.11 (m, 1H), 3.76−3.65 (m, 2H), 2.89 (ddd, J = 66.8, 12.7, 6.6 Hz, 2H), 2.08−1.69 (m, 2H), 1.63−1.46 (m, 1H), 1.44 (s, 0H), 1.06 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.2, 129.1, 129.0, 125.9, 60.9, 41.3, 39.0, 30.1, 19.7; HRMS (EI) calcd for $C_{11}H_{16}OS$ $[M]^+$ 196.0916, found 196.0920; FTIR (neat) 3329, 2955, 2924, 2871, 1583, 1479, 1437, 1088, 735, 689 cm^{-1}; TLC R_f = 0.21 (20% EtOAc/hexanes).

*4-(Phenylthio)hexan-1-ol (**8**).* (Hexylperoxy)triisopropylsilane (137.7 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **7** (65.0 mg, 62% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.35 (m, 2H), 7.33−7.24 (m, 2H), 7.24−7.17 (m, 1H), 3.64 (t, J = 6.2 Hz, 2H), 3.12−3.00 (m, 1H), 1.83−1.55 (m, 6H), 1.51 (s, 1H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.6, 132.0, 128.9, 126.7, 62.9, 50.7, 30.3, 30.1, 27.5, 11.3; HRMS (APCI) calcd for $C_{12}H_{19}OS$ $[M + H]^+$ 211.1157, found 211.1151; FTIR (neat) 3345, 3073, 2961, 2872, 1478, 1057, 1024, 908, 731 cm^{-1}; TLC R_f = 0.26 (35% EtOAc/hexanes).

*5-(Phenylthio)hexan-2-ol (**9**).* (Hexan-2-ylperoxy)-triisopropylsilane (137.1 mg, 0.5 mmol) was subjected to general procedure G for 10 h. The crude reaction mixture showed a 5:1 **9**:**9-isomer** mixture. Silica flash chromatography provided **9** (67.8 mg, 64% yield, sole isomer) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 7.7, 7.0 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 3.78 (sextet, J = 5.6 Hz, 1H), 3.22 (heptet, J = 6.5 Hz, 1H), 1.68−1.48 (m, 4H), 1.28 (dd, J = 6.7, 1.5 Hz, 3H), 1.18 (dd, J = 6.2, 2.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.3, 132.1, 132.1, 128.9, 126.9, 126.8, 68.1, 68.0, 43.6, 43.4, 36.7, 36.5, 32.9, 32.7, 23.7, 23.7, 21.4, 21.3; HRMS (APCI) calcd for $C_{12}H_{19}OS$ $[M + H]^+$ 211.1157, found 211.1150; FTIR (neat) 3374, 3074, 2965, 2925, 1478, 1024, 906, 728 cm^{-1}; TLC R_f = 0.29 (25% EtOAc/hexanes).

*4-Methyl-4-(phenylthio)pentan-1-ol (**10**).* Triisopropyl[(4-methylpentyl)peroxy]silane (137.9 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **10** (15.8 mg, 15% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.48 (m, 2H), 7.38−7.29 (m, 3H), 3.65 (t, J = 6.5 Hz, 2H), 1.83−1.73 (m, 2H), 1.57−1.49 (m, 2H), 1.34 (s, 1H), 1.25 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.6, 132.3, 128.8, 128.6, 63.4, 49.1, 38.5, 29.0, 28.4; HRMS (APCI) calcd for $C_{12}H_{19}OS$ $[M + H]^+$ 211.1157, found 211.1157; FTIR (neat) 3330, 3072, 2942, 2866, 1472, 1451, 1056, 748, 693 cm^{-1}; TLC R_f = 0.16 (30% EtOAc/hexanes).

*2-Ethyl-4-(phenylthio)hexan-1-ol (**11**).* [(2-Ethylhexyl)peroxy]-triisopropylsilane (150 mg, 0.5 mmol) was subjected to general procedure G for 8 h. The crude reaction mixture showed a 1:0.07 mixture of regioisomers. Silica flash chromatography provided the desired product with 2-ethylhexan-1-ol as an inseparable mixture, and then high vacuum provided the pure product (69 mg, 58% yield, 1:1 dr) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.34 (m, 2H), 7.32−7.22 (m, 2H), 7.23−7.13 (m, 1H), 3.63−3.52 (m, 2H), 3.18−3.02 (m, 1H), 1.83−1.67 (m, 1H), 1.67−1.44 (m, 4H), 1.44−1.20 (m, 3H), 0.99 (t, J = 7.4 Hz, 3H), 0.87 (td, J = 7.5, 2.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.6, 135.5, 132.2, 132.1, 129.1, 129.0, 128.9, 126.8, 126.8, 125.9, 65.3, 64.9, 48.9, 48.7, 39.9, 39.5, 35.9, 35.5, 28.3, 28.2, 24.1, 23.6, 11.2, 11.10, 11.07, 11.06; HRMS (EI) calcd for $C_{14}H_{22}OS$ $[M]^+$ 238.1386, found 238.1386; FTIR (neat) 3331, 2960, 2926, 2873, 1583, 1460, 1437, 1378, 1090, 1036, 1025, 914, 738, 690 cm^{-1}; TLC R_f = 0.37 (20% EtOAc/hexanes).

*4-(Phenylthio)cyclooctan-1-ol (**12**).* (Cyclooctylperoxy)-triisopropylsilane (150 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided the desired product with cyclooctanol as an inseparable mixture, and then high vacuum provided the pure product (55 mg, 47% yield, 1:1 dr) as a clear, colorless oil: ^{1}H NMR: (400 MHz, chloroform-*d*) δ 7.31 (dt, J = 8.1, 1.5 Hz, 2H), 7.26−7.18 (m, 2H), 7.18−7.11 (m, 1H), 3.79 (ddq, J = 14.9, 7.5, 4.4 Hz, 1H), 3.45−3.18 (m, 1H), 2.18−1.88 (m, 1H), 1.87−1.58 (m, 7H), 1.58−1.46 (m, 2H), 1.46−1.11 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 135.8, 135.7, 132.1, 131.9, 129.0, 126.9, 126.9, 72.0, 71.6, 48.3, 48.2, 34.3, 34.1, 33.0, 32.8, 30.6, 30.5, 27.9, 27.8, 25.5, 25.2, 22.9, 22.3; HRMS (EI) calcd for $C_{14}H_{20}OS$ $[M]^+$ 236.1229, found 236.1229; FTIR (neat) 3345, 2923, 2852, 1583, 1473, 1437, 1089, 1043, 1024, 1001, 977, 737, 690 cm^{-1}; TLC R_f = 0.14 (20% EtOAc/hexanes).

*3-Phenyl-4-(phenylthio)butan-1-ol (**13**).* Triisopropyl[(3-phenylbutyl)peroxy]silane (81 mg, 0.25 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided the desired product with 3-phenylbutan-1-ol as an inseparable mixture, and then high vacuum provided the pure product (13 mg, 21% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.16 (m, 7H), 7.16−7.06 (m, 3H), 3.55−3.34 (m, 2H), 3.20−3.04 (m, 2H), 2.93 (dtd, J = 10.4, 7.2, 4.6 Hz, 1H), 2.15 (dtd, J = 14.1, 7.2, 4.6 Hz, 1H), 1.82 (ddt, J = 13.7, 10.2, 5.8 Hz, 1H), 1.07 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.2, 136.6, 129.2, 128.9, 128.7, 127.6, 126.9, 126.0, 60.9, 42.1, 40.8, 38.1; HRMS (EI) calcd for $C_{16}H_{18}OS$ $[M]^+$ 258.1073, found 258.1074; FTIR (neat) 3346, 3026, 2925, 1582, 1479, 1452, 1438, 1087, 1042, 1025, 737, 699 cm^{-1}; TLC R_f = 0.22 (20% EtOAc/hexanes).

*6-Chloro-4-(phenylthio)hexan-1-ol (**14**).* [(6-Chlorohexyl)-peroxy]triisopropylsilane (148 mg, 0.5 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product with 6-chlorohexan-1-ol as an inseparable mixture, and then high vacuum provided the pure product (56 mg, 46% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.39 (m, 2H), 7.39−7.29 (m, 2H), 7.30−7.24 (m, 1H), 3.66 (t, J = 6.2 Hz, 2H), 3.39−3.17 (m, 1H), 2.11−1.94 (m, 2H), 1.92−1.60 (m, 4H), 1.55 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.3, 132.7, 129.1, 127.4, 62.6, 46.5, 42.6, 37.7, 31.3, 29.9; HRMS (EI) calcd for $C_{12}H_{17}ClOS$ $[M]^+$ 244.0689, found 244.0683; FTIR (neat) 3319,

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2936, 2866, 1582, 1475, 1437, 1274, 1055, 1023, 937, 911, 740, 691, 658 cm^{-1}; TLC R_f = 0.24 (30% EtOAc/hexanes).

1.5 mmol Scale Reaction. To a flame-dried 100 mL Schlenk flask with a stir bar were added [(6-chlorohexyl)peroxy]triisopropylsilane (1.5 mmol, 459 mg), disulfide (1.65 mmol, 360 mg), and $Fe(OTf)_2$ (0.075 mmol, 26.5 mg). The flask was evacuated and backfilled three times with N_2. Degassed MeOH (15 mL) was added via syringe, and then the reaction mixture was heated to 80 °C on a preheated oil bath in a nitrogen atmosphere. After 12 h, the reaction mixture was cooled, diluted with ethyl acetate (15 mL), filtered through a silica plug, washing with ∼30 mL of EtOAc, and concentrated. Products were isolated by flash chromatography using a mixture of ethyl acetate and hexanes as the eluent. The product was eluted in a 23% mixture of ethyl acetate and hexanes. The isolated yield was 42% (152 mg).

*Methyl 8-Hydroxy-5-[(4-methoxyphenyl)thio]octanoate (**15**).* Methyl 8-[(triisopropylsilyl)peroxy]octanoate (173 mg, 0.5 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product (82 mg, 53% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.24 (m, 2H), 6.93−6.75 (m, 2H), 3.78 (s, 3H), 3.64 (s, 3H), 3.61 (t, J = 6.4 Hz, 2H), 2.86 (p, J = 6.4 Hz, 1H), 2.28 (t, J = 7.4 Hz, 2H), 1.91−1.63 (m, 5H), 1.63−1.42 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.1, 159.6, 135.9, 124.7, 114.6, 62.8, 55.4, 51.7, 50.0, 34.0, 33.9, 30.6, 30.0, 22.3; HRMS (ESI) calcd for $C_{16}H_{24}O_4SNa$ [M + Na]$^+$ 335.1288, found 335.1289; FTIR (neat) 3400, 2939, 2867, 1732, 1591, 1569, 1492, 1437, 1282, 1241, 1171, 1056, 1028, 827, 798, 640 cm^{-1}; TLC R_f = 0.14 (30% EtOAc).

*Methyl 6-Hydroxy-3-(phenylthio)hexanoate (**16**).* Methyl 6-[(triisopropylsilyl)peroxy]hexanoate (127 mg, 0.4 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product with methyl 6-hydroxyhexanoate as an inseparable mixture, and then high vacuum provided the pure product (35 mg, 35% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.32 (m, 2H), 7.24 (dd, J = 8.2, 6.4 Hz, 2H), 7.21−7.17 (m, 1H), 3.65−3.54 (m, 5H), 3.44 (tdd, J = 8.1, 6.6, 4.5 Hz, 1H), 2.63−2.39 (m, 2H), 1.83−1.72 (m, 1H), 1.72−1.63 (m, 2H), 1.61−1.51 (m, 1H), 1.47 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.2, 133.8, 133.1, 129.1, 127.7, 62.5, 51.9, 44.9, 40.6, 30.9, 30.0; HRMS (ESI) calcd for $C_{13}H_{18}O_3SNa$ [M + Na]$^+$ 277.0869, found 277.0871; FTIR (neat) 3375, 2946, 2865, 1732, 1583, 1475, 1436, 1354, 1231, 1152, 1055, 1023, 754, 692 cm^{-1}; TLC R_f = 0.17 (30% EtOAc/hexanes).

*N,N-Diethyl-6-hydroxy-3-(phenylthio)hexanamide (**17**).* *N,N*-Diethyl-6-[(triisopropylsilyl)peroxy]hexanamide (72 mg, 0.2 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product (21 mg, 36% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.38 (m, 2H), 7.32−7.26 (m, 2H), 7.24−7.19 (m, 1H), 4.00−3.61 (m, 3H), 3.46−3.12 (m, 4H), 2.72−2.44 (m, 2H), 1.93−1.52 (m, 4H), 1.25 (s, 1H), 1.16−1.02 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 135.1, 131.8, 129.1, 127.0, 61.8, 43.8, 42.0, 40.6, 39.5, 30.8, 29.8, 29.5, 14.4, 13.2; HRMS (ESI) calcd for $C_{16}H_{25}O_2NNaS$ [M + Na]$^+$ 318.1498, found 318.1500; FTIR (neat) 3405, 2930, 2871, 1699, 1437, 1380, 1362, 1259, 1220, 1141, 1068, 1030, 787, 745, 692, 639, 516 cm^{-1}; TLC R_f = 0.25 (60% EtOAc/hexanes).

*6-Hydroxy-3-(phenylthio)hexyl 3-(Trifluoromethyl)benzoate (**18**).* 6-[(Triisopropylsilyl)peroxy]hexyl 3-(trifluoromethyl)benzoate (115 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica gel chromatography provided the desired product (54 mg, 55% yield) as a clear, colorless oil, using dichloromethane as the eluent: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.49−7.35 (m, 2H), 7.30−7.23 (m, 2H), 7.23−7.19 (m, 1H), 4.69−4.39 (m, 2H), 3.67 (t, J = 6.0 Hz, 2H), 3.26 (tt, J = 7.9, 5.2 Hz, 1H), 2.22−1.97 (m, 2H), 1.94−1.66 (m, 4H), 1.25 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.3, 134.7, 133.0, 132.6, 131.2 (q, J = 32.7 Hz) 131.2, 129.6 (q, J = 3.8 Hz), 129.2, 129.2, 127.4, 126.6 (q, J = 3.8 Hz), 123.8 (q, J = 272.2 Hz), 63.4, 62.7, 46.5, 34.2, 31.4, 30.1; ^{19}F NMR (376 MHz, chloroform-*d*) δ −62.82; HRMS (ESI) calcd for $C_{20}H_{21}F_3O_3SNa$ [M + Na]$^+$ 421.1056, found 421.1056; FTIR (neat) 3399, 3074, 2930, 2859, 1721, 1439, 1333, 1247, 1167, 1123, 1070, 755, 691, 650 cm^{-1}; TLC R_f = 0.26 (30% EtOAc/hexanes).

*6-Hydroxy-3-(phenylthio)hexyl Acetate (**19**) and 3-(Phenylthio)-hexane-1,6-diol (**19-diol**).* 6-[(Triisopropylsilyl)peroxy]hexyl acetate (83 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product with 6-hydroxyhexyl acetate as an inseparable mixture, and then high vacuum provided the pure product (23 mg, 35% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.37 (m, 2H), 7.33−7.28 (m, 2H), 7.28−7.24 (m, 1H), 4.27 (t, J = 6.5 Hz, 2H), 3.66 (t, J = 6.2 Hz, 2H), 3.19 (tt, J = 7.7, 5.4 Hz, 1H), 2.03 (s, 3H), 2.00−1.55 (m, 7H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.2, 134.6, 132.6, 129.0, 127.3, 62.6, 62.2, 46.1, 33.9, 31.2, 30.0, 21.0; HRMS (ESI) calcd for $C_{14}H_{20}O_3SNa$ [M + Na]$^+$ 291.1025, found 291.1024; FTIR (neat) 3399, 2937, 2865, 1735, 1583, 1475, 1365, 1233, 1024, 743, 691, 605 cm^{-1}; TLC R_f = 0.14 (30% EtOAc/hexanes).

Silica flash chromatography provided 3-(phenylthio)hexane-1,6-diol with hexane-1,6-diol (<10%) as an inseparable mixture (17 mg, 29% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.45−7.40 (m, 2H), 7.29 (dd, J = 8.3, 6.7 Hz, 2H), 7.25−7.20 (m, 1H), 3.91−3.76 (m, 2H), 3.64 (t, J = 6.1 Hz, 2H), 3.39−3.24 (m, 1H), 2.08−1.47 (m, 8H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.9, 132.4, 129.1, 127.2, 62.8, 60.7, 46.2, 37.5, 31.4, 29.9; HRMS (EI) calcd for $C_{12}H_{18}O_2S$ [M]$^+$ 226.1022, found 226.1019; FTIR (neat) 3332, 2933, 2872, 1583, 1477, 1438, 1258, 1168, 1025, 745, 692, 640 cm^{-1}; TLC R_f = 0.2 (50% EtOAc/hexanes).

*6-Hydroxy-3-(phenylthio)hexyl Methanesulfonate (**20**).* 6-[(Triisopropylsilyl)peroxy]hexyl methanesulfonate (92 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the desired product with methyl 6-hydroxyhexanoate as an inseparable mixture, and then high vacuum provided the pure product (31 mg, 41% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.37 (m, 2H), 7.36−7.21 (m, 3H), 4.59−4.38 (m, 2H), 3.66 (t, J = 6.0 Hz, 2H), 3.29−3.17 (m, 1H), 2.94 (s, 3H), 2.14−2.01 (m, 1H), 2.00−1.87 (m, 1H), 1.87−1.60 (m, 4H), 1.25 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.0, 132.7, 129.2, 127.6, 67.8, 62.5, 45.5, 37.3, 34.4, 31.3, 29.9; HRMS (ESI) calcd for $C_{13}H_{20}O_4S_2Na$ [M + Na]$^+$ 327.0695, found 327.0698; FTIR (neat) 3381, 2936, 2863, 1582, 1474, 1438, 1346, 1169, 956, 913, 798, 743, 692, 526 cm^{-1}; TLC R_f = 0.18 (50% EtOAc/hexanes).

*5-Phenyl-4-(phenylthio)pentan-1-ol (**21**).* Triisopropyl[(5-phenylpentyl)peroxy]silane (139 mg, 0.41 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided the pure product (65 mg, 59% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43−7.36 (m, 2H), 7.33−7.25 (m, 4H), 7.25−7.20 (m, 2H), 7.19−7.15 (m, 2H), 3.59 (t, J = 6.2 Hz, 2H), 3.36 (tdd, J = 8.2, 5.9, 4.3 Hz, 1H), 3.00 (dd, J = 14.0, 5.9 Hz, 1H), 2.80 (dd, J = 13.9, 8.3 Hz, 1H), 1.85 (dddd, J = 12.7, 9.1, 6.6, 2.3 Hz, 1H), 1.72 (dddd, J = 15.0, 12.5, 8.2, 5.1 Hz, 2H), 1.64−1.51 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.3, 135.3, 132.2, 129.3, 129.0, 128.5, 127.0, 126.5, 62.8, 50.6, 41.7, 30.0, 29.9; HRMS (APCI) calcd for $C_{17}H_{21}OS$ [M + H]$^+$ 273.1308, found 273.1309; FTIR (neat) 3328, 3059, 3025, 2934, 2853, 1582, 1494, 1477, 1437, 1055, 1024, 739, 692 cm^{-1}; TLC R_f = 0.24 (20% EtOAc/hexanes).

*4-[(4-Methoxyphenyl)thio]heptane-1,7-diol (**22**).* 3,3,14,14-Tetraisopropyl-2,15-dimethyl-4,5,13-trioxa-3,14-disilahexadecane (115 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (41 mg, 61% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.42−7.29 (m, 2H), 6.86−6.71 (m, 2H), 3.77 (s, 3H), 3.60 (t, J = 6.4 Hz, 4H), 2.98−2.83 (m, 1H), 1.73 (ddt, J = 13.1, 9.3, 6.8 Hz, 6H), 1.65−1.49 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 159.4, 135.6, 124.6, 114.4, 62.6, 55.3, 49.9, 30.6, 29.8; HRMS (ESI) calcd for $C_{14}H_{23}O_3S$ [M + H]$^+$ 271.1362, found 271.1363; FTIR (neat) 3273, 2927, 2854, 1592, 1493, 1445, 1283, 1240, 1173, 1089, 1057, 1026, 816, 636 cm^{-1}; TLC R_f = 0.41 (60% EtOAc/hexanes).

*3-[(4-Methoxyphenyl)thio]hexane-1,6-diol (**23**).* 3,3-Diisopropyl-2,14,14-trimethyl-13,13-diphenyl-4,5,12-trioxa-3,13-disilapentadecane (132 mg, 0.25 mmol) was subjected to general procedure G for 12 h.

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Silica flash chromatography provided the pure product (38 mg, 59% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.40 (dd, J = 8.5, 1.9 Hz, 2H), 6.93−6.72 (m, 2H), 4.04−3.75 (m, 5H), 3.65 (t, J = 6.3 Hz, 2H), 3.07 (td, J = 8.3, 4.1 Hz, 1H), 1.87−1.70 (m, 4H), 1.70−1.53 (m, 3H), 1.25 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*) δ 159.7, 136.0, 124.3, 114.7, 62.8, 60.9, 55.5, 47.3, 37.3, 31.2, 30.0; HRMS (ESI) calcd for $C_{13}H_{21}O_3S$ [M + H]$^+$ 257.1206, found 257.1208; FTIR (neat) 3265, 2923, 2854, 1592, 1493, 1454, 1296, 1247, 1170, 1097, 1045, 1019, 815, 800, 642 cm^{-1}; TLC R_f = 0.37 (60% EtOAc/hexanes).

4-(Naphthalen-2-ylthio)hexan-1-ol (**24**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (30 mg, 47% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$; 400 MHz, chloroform-*d*) δ 7.85 (s, 1H), 7.77 (dd, J = 17.9, 8.3 Hz, 3H), 7.46 (h, J = 6.9, 6.0 Hz, 3H), 3.65 (t, J = 6.1 Hz, 2H), 3.20 (p, J = 6.2 Hz, 1H), 1.86−1.60 (m, 6H), 1.35 (s, 1H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 133.9, 133.3, 132.2, 130.3, 129.7, 128.4, 127.8, 127.4, 126.6, 126.0, 63.0, 50.6, 30.4, 30.2, 27.6, 11.4; HRMS (ESI) calcd for $C_{16}H_{20}O_2NaS$ [M + O + Na]$^+$ 299.1077, found 299.1077; FTIR (neat) 3331, 3052, 2928, 2870, 1624, 1586, 1499, 1453, 1377, 1132, 1061, 942, 851, 811, 742, 633, 602 cm^{-1}; TLC R_f = 0.16 (20% EtOAc/hexanes).

4-[(3,4-Dichlorophenyl)thio]hexan-1-ol (**25**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (48 mg, 70% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$; 400 MHz, chloroform-*d*) δ 7.45 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 8.4, 2.1 Hz, 1H), 3.66 (t, J = 6.1 Hz, 2H), 3.07 (p, J = 6.3 Hz, 1H), 1.83−1.51 (m, 6H), 1.31 (s, 1H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 136.4, 132.9, 132.9, 130.8, 130.6, 62.9, 51.0, 30.3, 30.0, 27.5, 11.3; HRMS (ESI) calcd for $C_{12}H_{16}O_2Cl_2NaS$ [M + O + Na]$^+$ 317.0140, found 317.0138; FTIR (neat) 3318, 2931, 2871, 1568, 1545, 1457, 1362, 1130, 1095, 1057, 1028, 810, 675, 554 cm^{-1}; TLC R_f = 0.17 (20% EtOAc/hexanes).

4-[(4-Bromophenyl)thio]hexan-1-ol (**26**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (44 mg, 61% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.44−7.39 (m, 2H), 7.30−7.23 (m, 2H), 3.75−3.57 (m, 2H), 3.11−2.99 (m, 1H), 1.81−1.58 (m, 6H), 1.32 (d, J = 4.1 Hz, 1H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.9, 133.5, 132.0, 120.8, 62.8, 51.0, 30.3, 30.0, 27.5, 11.3; HRMS (ESI) calcd for $C_{12}H_{17}BrO_2SNa$ [M + O + Na]$^+$ 329.0003, found 329.0004; FTIR (neat) 3319, 2930, 2871, 1566, 1471, 1383, 1089, 1066, 1006, 921, 809, 728, 480 cm^{-1}; TLC R_f = 0.25 (20% EtOAc/hexanes).

4-{[4-(Trifluoromethyl)phenyl]thio}hexan-1-ol (**27**). (Hexylperoxy)triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (38 mg, 55% yield) as a clear, colorless oil with a minor unknown isomer (6:1 ratio): ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.51 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 3.66 (d, J = 6.0 Hz, 2H), 3.21 (p, J = 5.9, 5.4 Hz, 1H), 1.93−1.58 (m, 6H), 1.35−1.27 (m, 1H), 1.03 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 130.0, 128.1 (q, J = 32.8 Hz), 125.8 (q, J = 3.8 Hz), 124.3 (q, J = 272.2 Hz), 62.8, 49.8, 30.4, 30.0, 27.6, 11.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.51; HRMS (ESI) calcd for $C_{13}H_{17}O_2F_3NaS$ [M + O + Na]$^+$ 317.0794, found 317.0795; FTIR (neat) 3335, 2934, 2874, 1606, 1454, 1401, 1321, 1162, 1120, 1093, 1061, 1012, 825, 701, 592, 494 cm^{-1}; TLC R_f = 0.24 (20% EtOAc/hexanes).

4-[(4-Chlorophenyl)thio]hexan-1-ol (**28**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (43 mg, 70% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.28 (m, 2H), 7.26−7.22 (m, 2H), 3.64 (t, J = 6.2 Hz, 2H), 3.08−2.97 (m, 1H), 1.89−1.51 (m, 6H), 1.43−1.21 (m, 1H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.2, 133.5, 132.9, 129.1, 62.9, 51.2, 30.3, 30.1, 27.5, 11.3; HRMS (EI) calcd for $C_{12}H_{17}ClOS$ [M]$^+$ 244.0683, found 244.0683; FTIR (neat) 3321, 2931, 2872, 1572, 1474, 1458, 1387, 1093, 1057, 1011, 921, 816, 744 cm^{-1}; TLC R_f = 0.22 (20% EtOAc/hexanes).

4-[(4-Methoxyphenyl)thio]hexan-1-ol (**29**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (36 mg, 60% yield) as a clear, colorless oil: ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.45−7.31 (m, 2H), 6.96−6.65 (m, 2H), 3.79 (s, 3H), 3.72−3.54 (m, 2H), 2.91−2.76 (m, 1H), 1.82−1.68 (m, 2H), 1.67−1.50 (m, 4H), 1.36 (s, 1H), 1.06−0.94 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 135.7, 125.2, 114.5, 62.9, 55.4, 52.0, 30.2, 30.1, 27.4, 11.3; HRMS (ESI) calcd for $C_{13}H_{20}O_3NaS$ [M + O + Na]$^+$ 279.1025, found 279.1027; FTIR (neat) 3331, 2932, 2871, 1591, 1492, 1460, 1282, 1241, 1171, 1092, 921, 826, 640, 526 cm^{-1}; TLC R_f = 0.15 (20% EtOAc/hexanes).

4-(p-Tolylthio)hexan-1-ol (**30**). (Hexylperoxy)triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (40 mg, 72% yield) as a clear, colorless oil with a minor unknown isomer (15:1 ratio): ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.36−7.28 (m, 2H), 7.09 (d, J = 7.8 Hz, 2H), 3.64 (t, J = 6.5 Hz, 2H), 2.96 (dq, J = 7.3, 6.1 Hz, 1H), 2.32 (s, 3H), 1.83−1.68 (m, 2H), 1.68−1.53 (m, 4H), 1.36 (s, 1H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.1, 133.0, 131.6, 129.7, 63.0, 51.2, 30.3, 30.1, 27.5, 21.2, 11.3; HRMS (ESI) calcd for $C_{13}H_{21}OS$ [M + H]$^+$ 225.1308, found 225.1308; FTIR (neat) 3320, 2928, 2871, 1491, 1449, 1377, 1057, 1017, 921, 807, 632 cm^{-1}; TLC R_f = 0.24 (20% EtOAc/hexanes).

4-[(4-Nitrophenyl)thio]hexan-1-ol (**31**). (Hexylperoxy)-triisopropylsilane (67 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided the pure product (11 mg, 18% yield) as a clear, colorless oil with a minor unknown isomer (6:1 ratio): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.06 (m, 2H), 7.49−7.32 (m, 2H), 3.68 (m, 2H), 3.34 (t, J = 6.2 Hz, 1H), 1.92−1.63 (m, 6H), 1.25 (s, 1H), 1.04 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.6, 145.4, 128.1, 124.1, 62.7, 49.1, 30.3, 30.0, 27.5, 11.3; HRMS (EI) calcd for $C_{12}H_{17}NO_3S$ [M]$^+$ 255.0924, found 255.0925; FTIR (neat) 3346, 2982, 2856, 1576, 1507, 1476, 1456, 1332, 1182, 1081, 851, 837, 741, 683 cm^{-1}; TLC R_f = 0.61 (50% EtOAc/hexanes).

Reaction with Unsymmetrical Disulfide: Reaction with 1-(Naphthalen-2-yl)-2-phenyldisulfane. (Hexylperoxy)-triisopropylsilane (55 mg, 0.2 mmol) and 1-(naphthalen-2-yl)-2-phenyldisulfane (60 mg, 0.22 mmol) were subjected to general procedure G. After the reaction mixture was stirred at 80 °C for 8 h, the reaction mixture was filtered through a 1 cm silica pad and washed with an additional 10 mL of ethyl acetate. The organic portion was concentrated, and to it was added 10.5 mg of 1,3,5-trimethoxybenzene as an internal standard. The yield was calculated by ^{1}H NMR analysis of the crude reaction mixture, comparing the previously isolated pure products. The yield of compound **24** was 36%. The yield of compound **8** was 35%.

Reaction with 1-(4-Nitrophenyl)-2-phenyldisulfane. (Hexylperoxy)triisopropylsilane (28 mg, 0.1 mmol) and 1-(4-nitrophenyl)-2-phenyldisulfane (29 mg, 0.21 mmol) were subjected to general procedure G. After the reaction mixture was stirred at 80 °C for 8 h, the reaction mixture was filtered through a 1 cm silica pad and washed with an additional 10 mL of ethyl acetate. The organic portion was concentrated, and to it was added 8.2 mg of 1,3,5-trimethoxybenzene as internal standard. The yield was calculated by ^{1}H NMR analysis of the crude reaction mixture, comparing the previously isolated pure products. The yield of compound **31** was 19%. The yield of compound **8** was 29%.

Reaction with 1-(4-Methoxyphenyl)-2-phenyldisulfane. (Hexylperoxy)triisopropylsilane (28 mg, 0.1 mmol) and 1-(4-methoxyphenyl)-2-phenyldisulfane (29 mg, 0.21 mmol) were subjected to general procedure G. After the reaction mixture was stirred at 80 °C for 8 h, reaction mixture was filtered through a 1 cm silica pad and washed with an additional 10 mL of ethyl acetate. The organic portion was concentrated, and to it was added 6.2 mg of 1,3,5-trimethoxybenzene as internal standard. The yield was calculated by

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^{1}H NMR analysis of the crude reaction mixture, comparing the previously isolated pure products. The yield of compound **28** was 42%. The yield of compound **8** was 37%.

*2-[(Phenylthio)methyl]tetrahydrofuran (**35**).* Triisopropyl(pent-4-en-1-ylperoxy)silane **34** (129.1 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **35** (62.4 mg, 64% yield) as a clear, colorless oil that matched the reported spectrum:[68] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 4.06 (p, J = 6.6 Hz, 1H), 3.96−3.86 (m, 1H), 3.81−3.71 (m, 1H), 3.24−3.11 (m, 1H), 2.97 (dd, J = 13.0, 6.8 Hz, 1H), 2.15−2.00 (m, 1H), 1.99−1.80 (m, 2H), 1.74−1.60 (m, 1H); TLC R_f = 0.34 (15% EtOAc/hexanes).

*(5,5-Dimethoxypentyl)(phenyl)sulfane (**37**).* (Cyclopentylperoxy)triisopropylsilane **36** (130.3 mg, 0.5 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **37** (48.1 mg, 40% yield) as a clear, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.23 (m, 4H), 7.17 (t, J = 7.2 Hz, 1H), 4.34 (t, J = 5.6 Hz, 1H), 3.31 (s, 6H), 2.92 (t, J = 7.3 Hz, 2H), 1.74−1.56 (m, 4H), 1.56−1.43 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.9, 129.1, 129.0, 125.9, 104.5, 52.9, 33.6, 32.2, 29.1, 24.0; HRMS (EI) calcd for $C_{13}H_{20}O_2S$ $[M]^+$ 240.1184, found 240.1171; FTIR (neat) 3073, 2985, 2828, 1583, 1438, 1123, 1024, 908, 734 cm^{-1}; TLC R_f = 0.43 (25% EtOAc/hexanes).

*7-(Phenylthio)hept-4-en-1-ol (**41**).* [(4-Cyclopropylbutyl)peroxy]-triisopropylsilane **40** (72 mg, 0.25 mmol) was subjected to general procedure G for 5 h. Silica flash chromatography provided **42** (28 mg, 51%) as a clear colorless liquid in a 3.5:1 isomeric ratio: ^{1}H NMR (400 MHz, chloroform-d) δ 7.30−7.16 (m, 4H), 7.09 (tt, J = 6.6, 1.5 Hz, 1H), 5.53−5.14 (m, 2H), 3.56 (dt, J = 12.8, 6.4 Hz, 2H), 2.87 (td, J = 7.3, 1.8 Hz, 2H), 2.44−2.16 (m, 2H), 2.13−1.95 (m, 2H), 1.83−1.39 (m, 2H), 1.21 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.7, 131.9, 131.2, 129.1, 129.0, 129.0, 128.6, 128.0, 126.0, 126.0, 124.2, 62.6, 33.8, 33.7, 32.6, 32.4, 32.4, 29.9, 29.0, 27.1; HRMS (EI) calcd for $C_{13}H_{18}OS$ $[M]^+$ 222.1073, found 222.1072; FTIR (neat) 3332, 2925, 2848, 1583, 1479, 1437, 1055, 1024, 967, 736, 689 cm^{-1}; TLC R_f = 0.35 (20% EtOAc/hexanes).

*2-[Phenyl(phenylthio)methylene]tetrahydrofuran (**39**).* Triisopropyl[(5-phenylpent-4-yn-1-yl)peroxy]silane **38** (83 mg, 0.25 mmol) was subjected to general procedure G for 8 h. Silica flash chromatography provided 2-[phenyl(phenylthio)methylene]-tetrahydrofuran (27 mg, 41%) as a clear colorless liquid: ^{1}H NMR (500 MHz, chloroform-d) δ 7.73−7.66 (m, 2H), 7.26−7.15 (m, 3H), 7.11 (d, J = 5.0 Hz, 3H), 7.08−7.03 (m, 1H), 7.00−6.93 (m, 1H), 4.33 (t, J = 6.9 Hz, 2H), 2.97 (t, J = 7.7 Hz, 2H), 2.05−1.80 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, chloroform-d) δ 166.6, 139.0, 138.3, 129.0, 128.4, 128.0, 126.1, 125.3, 124.7, 98.0, 73.9, 32.1, 24.3; HRMS (EI) calcd for $C_{14}H_{20}OS$ $[M]^+$ 236.1228, found 236.1228; FTIR (neat) 295 6, 2922, 2852, 1625, 1578, 1474, 1438, 1368, 1240, 1176, 1074, 1043, 1024, 799, 754, 735, 689 cm^{-1}; TLC R_f = 0.33 (5% EtOAc/hexanes).

■ ASSOCIATED CONTENT

Supporting Information

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Reaction optimization and spectroscopic data (PDF)

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Notes

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