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Stereoselective allylation of chiral monoperoxyacetals

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Abstract—Neighboring iodo-, alkoxy-, acetoxy- and silyl groups impart useful levels of diastereoselection in the Lewis acid-mediated allylation of monoperoxyacetals. Although monoperoxyacetals are found to be considerably less reactive than corresponding nonperoxidic acetals, similar stereochemical trends are observed in the two series.

1. Introduction

Although the number of reported peroxide natural products continues to increase, methodology for peroxide synthesis remains limited.[1,2] For example, there exist only a handful of approaches to homoallyl peroxides and 3-peroxyalkanoates, common subunits in peroxide natural products; some typical examples are illustrated in Figure 1. We have reported new methodology for introduction of these substructures based upon Lewis acid-mediated reactions of monoperoxyacetals with electron-rich alkenes.[3,4] We sought to extend this methodology to asymmetric synthesis and we now report the stereoselective allylation of monoperoxyacetals based upon stereoinduction from neighboring chiral centers.

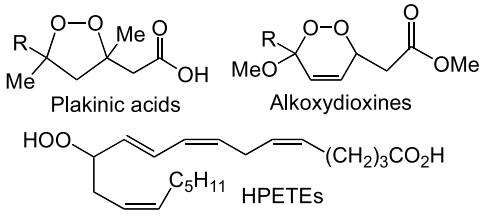

Figure 1. Naturally occurring homoallyl peroxides and 3-peroxyalkanoates.

The Lewis acid-mediated reactions of peroxyacetals appear to involve ionization to intermediate peroxycarbenium ions,[3] a mechanism which limits the stereochemical influence of the departing alkoxide, the Lewis acid, or the acetal center. We therefore chose to investigate induction from a resident stereocenter in the peroxyacetal backbone. This approach, while unexplored in peroxide chemistry, has precedent in the chemistry of simple acetals. For example, Cram–Felkin–Anh (CFA) stereoinduction has been demonstrated in reactions of acetals.[5] However, effective CFA directing groups are rarely practical in terms of the conditions required for synthetic modification or removal. We were intrigued by reports of diastereoselective displacements of nonperoxidic acetals based upon induction from neighboring heteroatoms.[6,7] We now report on the Lewis acid-mediated displacement of halo-, alkoxy, acyloxy, and silyl-substituted monoperoxyacetals. (Fig. 2).

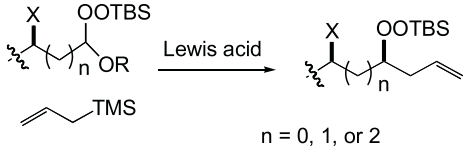

Figure 2. Overview.

2. Results and discussion

Our studies focused on induction from 2-, 3-, and 4-substituted monoperoxyacetals (Fig. 2).

2.1. Preparation of substrates

Preparation of 2-halo- and 2-mercurioperoxyacetals is illustrated in Table 1. Enol ethers **1** and **2** were prepared as isomeric mixtures and reacted with *t*-butyl hydroperoxide in the presence of NIS, NBS, or mercuric acetate to furnish 2-halo or 2-mercurioperoxyacetals as mixtures of diastereomers.[8] The diastereomeric 2-mercurioperoxyacetals were easily separated. The isomeric 2-haloperoxyacetals were inseparable but mixtures enriched in one diastereomer

Keywords: Peroxide; Monoperoxyacetal; Allylation; Lewis acid; Stereoinduction; Neighbouring group.
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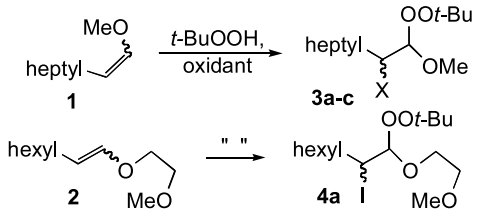
Table 1. Synthesis of 2-halo/mercurioperoxyacetals

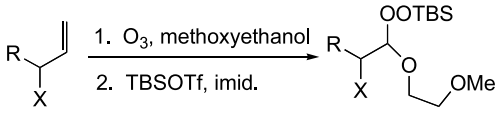


Substrate	Oxidant	Product	X	Yield (%)
1	NIS	**3a**	I	60
1	NBS	**3b**	Br	45
1	$Hg(OAc)_2$	**3c**	HgCl	80
2	NIS	**4a**	I	47

were available based upon peroxyhalogenation of samples of enol ether enriched in the *E*-isomer. The halo- and chloromercurioperoxyacetals were quite stable, except for iodoacetal **3a**, which decomposed upon prolonged storage.

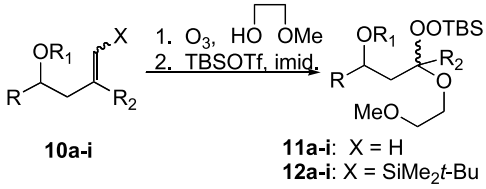
The preparation of 2-silyl peroxyacetals, an unknown class of compounds, was initially modeled for an achiral substrate (Table 2). Ozonolysis of allyltriphenylsilane in 2-methoxyethanol cleanly furnished a 2-triphenylsilyl hydroperoxyacetal, which underwent *O*-silylation to furnish peroxyacetal **5**.[9] Ozonolysis of chiral trialkylsilane **6** furnished an 85:15 mixture of diastereomeric 2-silyl hydroperoxyacetals, a result demonstrating significant influence of the trialkylsilyl group on the intermediate carbonyl oxide. Curiously, ozonolysis of the analogous

Table 2. Synthesis of 2-silyl monoperoxyacetals



Substrate	R	X	Product
$AllySiPh_3$	H	$SiPh_3$	**5** (45%)
6	Hexyl	$SiMe_2tBu$	**8** (54%)
7	Hexyl	$SiPh_3$	—

Table 3. Synthesis of 3-oxygenated peroxyacetals

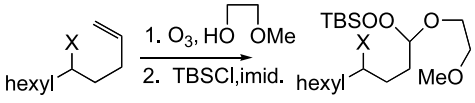


	R	R_1	R_2	X	**11a–i** (%)	**12a–i** (%)
10a	Heptyl	TBS	H	OMe	73	85
10b	Heptyl	Me	H	H	45	87
10c	Heptyl	Bn	H	H	45	88
10d	Heptyl	Ac	H	H	60	77
10e	Heptyl	Bz	H	H	40	75
10f	Heptyl	Piv	H	H	50	60
10g	Heptyl	MOM	H	H	55	82
10h	Ph	Ac	H	H	50	55
10i	Hexyl	Ac	Me	H	62	75

triphenylsilane (**7**) led only to decomposition. Attempts to prepare 2-mercapto monoperoxyacetals by a similar approach involving ozonolysis of allyl sulfides (not shown) were uniformly unsuccessful.

A series of 3-oxygenated peroxyacetals **12a–i** were prepared through ozonolysis of unsaturated ethers and esters, followed by silylation of the derived hydroperoxyacetals (Table 3). In each case, the new peroxyacetals were formed as 1:1 mixtures of epimers. Two 4-substituted peroxyacetals were prepared by a similar procedure (Table 4).

Table 4. Synthesis of 4-substituted monoperoxyacetals

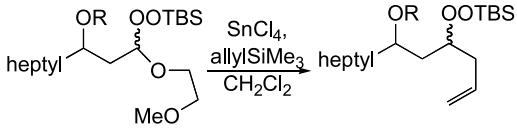


Substrate	X	Product	Yield
13a	OMe	**14a**	40
13b	I	**14b**	34

2.2. Lewis acid-mediated reactions

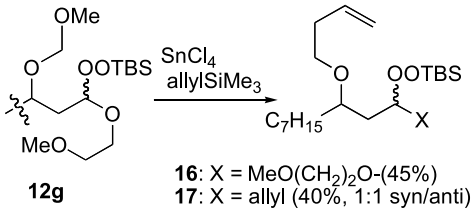
Allylations were initially investigated for 3-substituted peroxyacetals (Table 5). Optimal conditions were found to involve addition of stoichiometric $SnCl_4$ to a 0 °C solution of the peroxyacetal and allylsilane.[3] Reactions were generally complete within one to 2 h. The products were isolated and purified by standard methods, with diastereoselectivity determined by NMR integration; control experiments demonstrated no difference in diastereomer ratios before or after purification. Ether **12b** and the pivaloate ester **12f** reacted with moderate *syn* selectivity (vide infra); diastereoselection was reduced in the case of the acetate (**12d**) or benzoate (**12e**) and nonexistent for the silyloxy peroxyacetal (**12a**). A benzylic monoperoxyacetal (**12h**) and the sole monoperoxyketal (**12i**) underwent predominant decomposition under the reaction conditions (not shown).

Table 5. Allylation of 3-oxygenated peroxyacetals



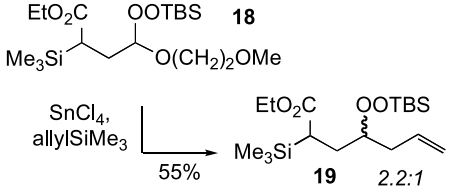
S. mat.	R	Product	Yield (%)	*syn*/*anti*
12a	$SiMe_2t$-Bu	**15a**	65	50:50
12b	Me	**15b**	60	75:25
12c	Bn	**15c**	50	60:40
12d	Ac	**15d**	60	60:40
12e	Bz	**15e**	55	62:38
12f	Piv	**15f**	55	73:27

Monoperoxyacetal **12g**, a substrate intended to explore 1,5-stereoinduction via ethereal oxygen, instead revealed the tremendous difference in reactivity between peroxidic and nonperoxidic acetals; both major products resulted from initial allylation of the MOM group (Eq. 1). To our knowledge, this is the first direct comparison of the reactivity of an acetal and a monoperoxyacetal under ionizing conditions.



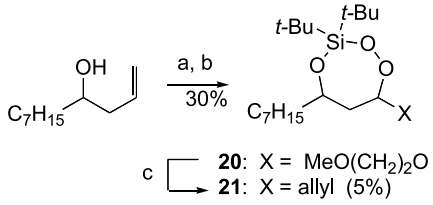
(1)

Peroxyacetal **18** was investigated as a substrate in which interaction of the ester carbonyl with the developing peroxycarbenium ion would provide a transient cyclic framework for stereoinduction from the 3-trimethylsilyl group. Diastereoselection in formation of the homoallyl peroxide was similar to that obtained for the 3-alkoxy and 3-acyloxy substrates shown above (Eq. 2).



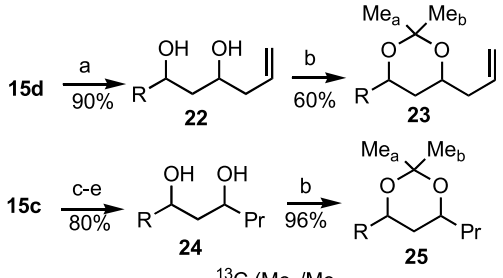
(2)

We also investigated 1,3-stereoinduction through a temporary scaffold (Scheme 1). Ozonolysis of a homoallylic alcohol followed by bissilylation of the derived hydroperoxyalcohol achieved the first synthesis of a 3-sila-1,2,4-trioxepane (**20**). Unfortunately, this substrate was nearly unreactive, furnishing <5% yield of allylated silatrioxepane under typical reaction conditions; attempted reaction at higher temperatures resulted in decomposition.



Scheme 1. Allylation of alkoxysilatrioxepane. (a) O_3, 2-methoxyethanol; (b) t-$Bu_2Si(OTf)_2$, DMF, imidazole; (c) allyltrimethylsilane, $SnCl_4$, 0 °C.

Stereochemical correlation. The major diastereomers for the 3-alkoxy- and 3-acyloxyhomoallyl peroxides **15c** and **15d** were assigned as *syn* based upon the ^{13}C chemical shifts of the derived 1,3-dioxanes **23** and **25** (Scheme 2).[10]

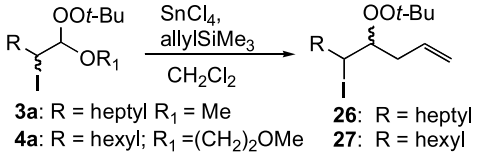


Acetonide	R	^{13}C (Me_a/Me_b, major diast.)	stereochem.
23	heptyl	30.3, 19.8	syn
25	heptyl	30.4, 19.8	syn

Scheme 2. Stereochemical correlation. (a) $LiAlH_4$; (b) 2,2-dimethoxypropane, CSA; (c) THF/HOAc/H_2O; (d) PPh_3; (e) Pd/H_2.

1,2-Stereoinduction. The observed diastereoselectivity for allylation of 2-iodoperoxyacetal **3a** varied somewhat depending upon the composition of the starting material but consistently afforded one major diastereomer (Table 6). The major product was assigned as *anti* based upon spectral correlations with reports for 2-iodoethers[5] and 2-iodoperoxides.[11] Intriguingly, iodoacetal **3a** underwent allylation at −78 °C, whereas most other peroxyacetals, including the closely related **4a**, undergo reaction only at temperatures near 0 °C. In addition, significant decomposition of **3a** was observed under the reaction conditions. The 2-bromoperoxyacetal **3b** was unreactive while the 2-chloromercurioperoxyacetal underwent rapid decomposition in the presence of either $SnCl_4$ or TMSOTf (not shown).

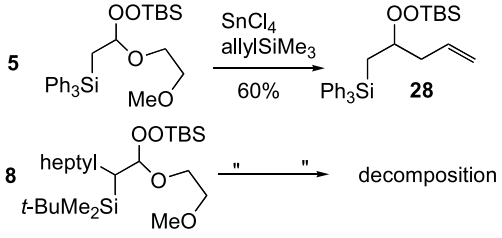
Table 6. Allylation of 2-iodoperoxyacetals



S. mat.	dr	T (°C)	Product (yield)	*syn/anti*
3a	40:60	−78	**26** (30%)	1:1.4
3a	75:25	−78	**26** (28%)	1:9
4a	76:24	0	**27** (23%)	1:3
4a	71:29[a]	0	**27** (20%)	1:5

[a] Conducted in 25% CH_3NO_2/CH_2Cl_2.

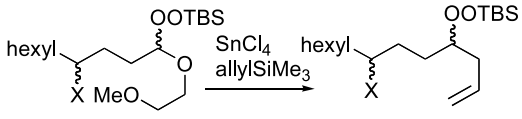
Investigation of 1,2 stereoinduction from a silyl group was thwarted by the decomposition of silyl peroxyacetal **8** under the reaction conditions (Scheme 3). This failure was curious, given the successful allylation of the achiral model (**5**).



Scheme 3. Allylation of 2-silyl monoperoxyacetals.

1,4-Stereoinduction. Allylation of the 4-methoxyl peroxyacetal **14a** proceeded in good yield and with moderate stereoselection; the 4-iodoperoxyacetal (**14b**) underwent allylation in lower yield and with reduced diastereoselection (Table 7).

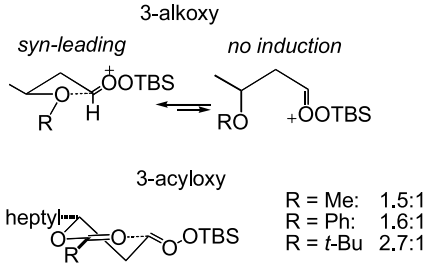
Table 7. Allylation of 4-substituted monoperoxyacetals



Substrate	X	Product	Yield (%)	dr
14a	OMe	**29a**	78	71:29
14b	I	**29b**	30	60:40

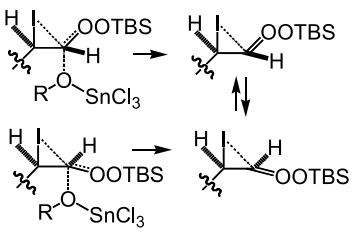
2.3. Discussion

Our results demonstrate the influence of neighboring heteroatoms on the reactivity of peroxyacetals and the stereoselectivity of peroxyacetal displacement. The degree of influence is dependent upon the nature and location of the group. Peroxyacetals bearing 3-alkoxy and 3-acyloxy substituents are as reactive as unsubstituted monoperoxyacetals,[2] suggesting only limited influence of β-oxygenation on the barriers to substrate ionization. However, the *syn* selectivity observed for reactions of 3-methoxy and 3-pivaloyloxy peroxyacetals, and the complete lack of selectivity for the 3-trialkylsiloxy substrate, indicates the importance of interactions with the intermediate peroxycarbenium ion; in the case of the 3-acyloxy groups, the diastereoselection varies with the bulk of the side chain. The outcome with the trialkylsiloxy group is similar to results observed with 3-silyloxyaldehydes (Eq. 3).[12] Our results provide a mechanistic underpinning for results reported for reactions of 3-alkoxy acetals.[5] Moderate stereochemical induction is also observed for the 4-methoxyperoxyacetal, although the selectivity is lower than that reported for reactions of 4-alkoxyacetals.[7]



(3)

The enhanced reactivity of 2-iodo and 2-triphenylsilyl peroxyacetals suggests a significant influence on substrate ionization. Allylation of the 2-iodoperoxyacetals proceeds with higher diastereoselectivity than for any of the other substrates studied. This, combined with the consistent preference for formation of the anti diastereomer, suggests a strong interaction with a peroxycarbenium ion or similar species. At the same time, the variation in product diastereoselection depending upon the composition of the starting material suggests the possibility of reaction through both intimate versus separated ion pairs (Eq. 4). While the chiral 2-trialkylsilyl peroxyacetals underwent decomposition under reaction conditions, it is interesting to note that the 2-trialkylsilyl group exerted a very strong influence on the stereochemistry of trapping of a neighboring carbonyl oxide.



(4)

3. Conclusion

Easily installed and synthetically tractable neighboring groups are shown to impart useful levels of stereoinduction to the allylation of monoperoxyacetals. The results, while paralleling previous findings for reactions of nonperoxidic acetals, are influenced by the unique reactivity patterns of the peroxyacetals. Application of these results to the synthesis of peroxide natural products is under investigation.

4. Experimental

4.1. General

Standard experimental procedures have been described elsewhere.[13] All new compounds were determined to be >95% pure based upon ^{1}H or ^{13}C NMR. Unless otherwise noted NMR spectra were recorded at 500 (^{1}H) or 125 (^{13}C) MHz in $CDCl_3$. FT-IR spectra were recorded as CH_2Cl_2 or $CDCl_3$ solutions; selected absorbances are reported in cm^{-1}. Most hydroperoxides and peroxides failed to generate identifiable molecular or fragmentation ions (HRFAB or HREI).

4.1.1. (*E*)- and (*Z*)-1-Methoxy-1-nonene (1). The title compounds were prepared as a mixture from octanal.[14]

4.1.2. (*E*)- and (*Z*)-1-(2-Methoxyethoxy)-oct-1-ene (2). The title compounds were prepared using a variation of a reported procedure.[15] Into a solution of 1-octanal (2.0 g, 16 mmol) in 2-methoxyethanol (50 mL) was added *p*-TsOH·H_2O (cat., 100 mg). The reaction was stirred for 15 min and then quenched with sat. NH_4Cl solution. (100 mL) The Et_2O extracts (2×50 mL) were dried over Na_2SO_4 and concentrated. Flash chromatography (20% EA/Hex) furnished 1,1-bis-(2-ethoxymethoxy)-octane (3.7 g, 90%). R_f=0.48 (20% EA/hex); ^{1}H δ 4.53 (t, 1H, J=6.0 Hz), 3.65 (m, 2H), 3.56 (m, 2H), 3.47 (t, 4H, J=4.7 Hz), 3.30 (s, 6H), 1.59–1.55 (2H), 1.30–1.20 (10H), 0.80 (t, 3H, J=6.6 Hz); ^{13}C δ 103.2, 71.9, 63.9, 58.7, 32.9, 31.6, 29.2, 29.0, 24.5, 22.4, 13.8; IR 1129; HRFAB calcd for $C_{14}H_{30}O_4Li$ $(M+Li)^+$: 269.2304; found: 269.2317, 4.9 ppm.

A solution of the bis-methoxyethoxy acetal (2.9 g, 11 mmol) and diisopropylethylamine (50 mL) was heated to 115–120 °C in an oil bath whereupon trimethylsilyl trifluoromethanesulfonate (2.7 g, 12 mmol, 2.2 mL) was rapidly added. After 2 min, the oil bath was removed and the reaction was quenched with 10% NaOH (50 mL) and hexanes (100 mL). The organic layer was washed with 10% NaOH (2×25 mL) and water (50 mL), dried over Na_2SO_4 and concentrated. The DIPEA was removed under vacuum and the crude product was purified by flash chromatography to furnish 1-2-(methoxyethoxy)-oct-1-ene (**2**) as a colorless liquid consisting of a 1:4.2 mixture of *E* and *Z* isomers (1.4 g, 70%): R_f=0.44 (2% EA/hex); ^{1}H δ 6.25 (d, 0.2H, J=12.6 Hz), 5.94 (d, 0.8H, J=6.3 Hz), 4.78 (dt, 0.2H, J=12.6, 7.2 Hz), 4.34 (dd, 0.8H, J=6.9, 7.2 Hz), 3.84 (t, 1.6H, J=4.7 Hz), 3.78 (t, 0.4H, J=4.7 Hz), 3.59 (t, 0.4H, J=4.7 Hz), 3.56 (t, 1.6H, J=4.7 Hz), 3.39 (s, 0.8H), 3.387 (s,

2.2H), 2.09–2.05 (1.6H), 1.91–1.87 (0.4H), 1.31–1.27 (8H), 0.87 (t, 3H, J=6.9 Hz); ^{13}C δ 146.0, 144.7, 107.8, 104.7, 71.7, 71.24, 71.21, 68.2, 59.09/59.04, 31.74/31.70, 30.6, 29.7, 28.9, 28.6, 27.6, 23.9, 22.6, 14.0; IR 1660, 1101; HRFAB calcd for $C_{11}H_{22}O_2Li$ $(M+Li)^+$: 193.1780; found: 193.1774 (3.1 ppm).

4.1.3. (*syn*)- and (*anti*)-1-*tert*-Butylperoxy-2-iodo-1-methoxynonane (3a). A solution of 70% aqueous *tert*-BuOOH (10 mL) was extracted with CH_2Cl_2 (10 mL). The organic layer was successively dried over Na_2SO_4 and $MgSO_4$ and 4 mL of the resulting solution was added into solution of enol ether **1** (1.0 equiv, 3.6 mmol, 570 mg) in CH_2Cl_2 (10 mL). The mixture was cooled to −78 °C and *N*-iodosuccinimide (1.5 equiv, 5.5 mmol, 1.23 g) was added. The reaction flask was briefly removed from cooling bath whenever the mixture solidified. After 15 min the reaction was quenched with DI water and extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was redissolved into 2% EA/hex (50 mL) and stirred over a pinch of charcoal until the reddish violet color was lost (ca. 15 min). The solution was filtered through a plug of cotton and concentrated under reduced pressure. Flash chromatography furnished 0.82 g (60%) of **3a** as a mixture of diastereomers which could not be completely separated. R_f=0.6 (2% EA/hex); ^{1}H δ 4.78 (d, 0.7H, 4.4), 4.57 (d, 0.3H, 5.0), 4.09–4.04 (m, 1H), 3.575 (s, 1.8H), 3.57 (s, 1.2H), 1.78–1.73 (2H), 1.55–1.47 (2H), 1.32–1.19 (17H, including obscured singlets from *tert*-Bu), 0.85 (t, 3H, J=6.9 Hz); ^{13}C δ 108.3/107.8, 80.9/80.7, 58.0/57.9, 34.8, 33.9, 33.2, 32.6, 31.7, 29.4, 29.37, 29.3, 29.0, 28.7, 28.6, 26.5, 22.5, 13.96; IR 2977–2851, 1358, 1249, 1199, 1110; HRFAB calcd for $C_{13}H_{26}IO_2$ $(M-OMe)^+$: 341.0978; found: 341.1177 (58.3 ppm).

4.1.4. *syn*- and *anti*-2-Bromo-1-*tert*-butylperoxy-1-methoxy-nonane (3b). Into a −20 °C solution of enol ether (522 mg, 3.3 mmol) and *tert*-BuOOH in CH_2Cl_2 (5 mL) was added NBS (2.0 equiv, 1.2 g). After 15 min, the reaction mixture was quenched with DI water, and extracted with recycled EA/Hex (3×30 mL). The organic layers were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (hexanes or *n*-pentane) furnished 490 mg (45%) of a mixture of diastereomeric bromo peroxy acetals: R_f=0.7 (*n*-pentane); ^{1}H δ 4.88 (d, 0.5H, J=4.7 Hz), 4.79 (d, 0.5H, J=5.4 Hz), 4.04–3.98 (m, 1H), 3.59 (s, 1.7H), 3.58 (s, 1.3H), 1.99–1.89 (2H), 1.8–1.71 (2H), 1.41–1.21 (17H), 0.87 (t, 3H, J=6.9 Hz); ^{13}C δ 108.0/107.7, 81.0, 58.02/57.94, 53.6/52.8, 33.2, 32.7, 31.8, 31.7, 29.0, 28.9, 28.8, 27.25, 27.24, 26.6, 26.5, 22.5, 14.0; IR 2924–2858, 1238, 1192, 1102; HRMS: no identifiable ions were observed.

4.1.5. *syn*- and *anti*-1-*tert*-Butylperoxy-2-chloromercurio-1-methoxynonane (3c). To a solution of $Hg(OAc)_2$ (1.1 equiv, 3.70 mmol, 1.18 g) and *tert*-BuOOH in CH_2Cl_2 (5 mL) in an ice bath was added, dropwise, enol ether **1** (1.0 equiv, 3.4 mmol, 525 mg) as a solution in CH_2Cl_2 (10 mL). After the addition was complete, the reaction was allowed to warm to room temperature and stirred until the salt had dissolved (5 min). Solvent was removed under reduced pressure and the residue was diluted with hexanes (50 mL). The solution was washed with satd NaCl (3×100 mL) and dried over Na_2SO_4 The precipitate obtained upon concentration was suspended in hexanes (50 mL) and filtered through a plug of cotton. Removal of solvent in vacuo followed by purification through flash silica (5% EA/hex) furnished colorless oil (1.3 g, 80%) as a mixture of diastereomers, which were easily separated by HPLC (4.6×25 mm Si, 5% EA/hex, 10 mL/min, 13.6 min, 17.0 min). *First eluting diastereomer*: R_f=0.33 (5% EA/hex); ^{1}H δ 4.96 (d, 1H, J=2.5 Hz), 3.55 (s, 3H), 2.68–2.64 (m, 1H), 1.80–1.58 (2H), 1.48–1.28 (8H), 1.26–1.25 (11H), 0.87 (t, 3H, J=6.6 Hz). ^{13}C 109.2, 80.9, 57.3, 32.5, 31.7, 31.0, 29.3, 29.0, 26.6, 24.7, 22.5, 14.0. *Second eluting diastereomer*: R_f=0.33 (5% EA/hex); ^{1}H 4.98 (d, 1H, J=3.8 Hz), 3.49 (s, 3H), 2.6–2.56 (m, 1H), 1.83–1.57 (2H), 1.47–1.29 (6H), 1.27–1.23 (13H), 0.86 (t, 3H, J=6.9 Hz); ^{13}C δ 108.8, 80.9, 56.79, 56.77, 54.6, 32.3, 31.7, 30.5, 29.3, 29.0, 26.6, 22.5, 13.93, 13.91; IR (cm^{-1}): 2924–2854, 1464, 1366, 1181, 1105; HRMS (FAB/EI) observed only high molecular weight ion aggregates.

4.1.6. *syn*- and *anti*-1-*tert*-Butylperoxy-2-iodo-1-(2-methoxyethoxy)-octane (4a). Into a −25 °C solution of enol ether **2** (845 mg, 4.5 mmol) in CH_2Cl_2 (10 mL) was added *tert*-BuOOH (5 mL of a 5.0–6.0 M solution in nonane), followed by *N*-iodosuccinimide (1.5 g, 6.8 mmol, 1.5 equiv). The reaction was stirred for 5 min and then quenched with DI water. The Et_2O extracts (2×50 mL) were dried over Na_2SO_4 and concentrated. Workup and purification as for iodoacetal **3a** furnished 0.85 g (47%) of **4a** as a 4:1 mixture of diastereomers which could not be cleanly separated. R_f=0.38 (2% EA/hex); ^{1}H δ 4.92 (d, 0.8H, J=5.0 Hz), 4.77 (d, 0.2H, J=5.0 Hz), 4.10–4.03 (2H), 3.86–3.81 (1H), 3.61–3.54 (2H), 3.38 (s, 3H), 1.84–1.74 (2H), 1.58–1.32 (8H), 1.27 (s, 6.3H), 1.268 (s, 2.7H), 0.87 (t, 3H, J=6.9 Hz); ^{13}C δ 107.4, 107.0, 81.0, 71.95/71.91, 69.79/69.76, 59.0, 34.3, 32.8, 31.60/31.57, 29.3, 28.41, 28.36, 26.6, 22.5, 14.0; IR 1242, 1195, 1125; HRFAB calcd for $C_{15}H_{31}IO_4Li$ $(M+Li)^+$: 409.1427; found: 409.1432 (1.1 ppm).

4.1.7. 1-(2-Methoxyethoxy)-2-triphenylsilyl ethyl *tert*-butyl dimethylsilyl peroxide (5). Yield=0.65 g, 50%. 1-(2-Methoxyethoxy)-2-triphenylsilyl ethyl hydroperoxide was prepared by ozonolysis of allyltriphenylsilane in 2-methoxyethanol using the procedure described for homoallyl ethers and esters (vide infra). R_f=0.52 (50% EA/hex); ^{1}H (400 MHz) δ 10.58 (s, 1H), 7.72–7.69 (6H), 7.49–7.40 (9H), 5.19 (dd, 1H, J=4.5, 8.3 Hz), 3.62–3.48 (3H), 3.47–3.41 (1H), 3.4 (s, 3H), 2.24 (dd, 1H, J=8.3, 14.9 Hz), 2.05 (dd, 1H, J=4.5, 15.2 Hz). ^{13}C (100 MHz) δ 135.5, 134.1, 129.2, 127.5, 105.5, 72.2, 65.1, 58.5, 17.5; IR 3306 (broad), 1481, 1350, 1196, 1128; HRMS: no identifiable ions were observed.

Silylation of the hydroperoxyacetal under standard conditions (vide infra) furnished the silyl peroxyacetal **5**: Yield=429 mg, 90%. R_f=0.35 (5% EA/hex); ^{1}H (400 MHz) δ 7.66–7.64 (6H), 7.48–7.40 (9H), 5.11 (dd, 1H, J=4.3, 8.1 Hz), 4.06 (m, 1H), 3.43 (m, 1H), 3.32 (m, 1H), 3.32 (t, 2H, J=5.05 Hz) 3.296 (s, 3H), 2.13 (dd, 1H, J=8.1, 14.9 Hz), 1.92 (dd, 1H, J=4.3, 14.9 Hz), 0.98 (s, 9H), 0.19 (s, 3H), 0.13 (s, 3H). ^{13}C (100 MHz) δ 135.7,

134.6, 129.4, 127.7, 106.9, 71.6, 69.4, 58.6, 26.1, 18.0, −5.7, −5.8; IR 1473, 1326, 1188, 1124. HRFAB calcd for $C_{29}H_{40}O_4Si_2Li$ $(M+Li)^+$: 515.2625; found: 515.2620 (1.0 ppm).

4.1.8. *tert*-Butyldimethyl(1-nonen-3-yl)silane (6). The title compound was prepared by C-silylation of octanal *tert*-butylimine followed by Wittig methylenation of the derived aldehyde.[16]

4.1.9. 1-Nonen-3-yl triphenylsilane (7). The title compound was prepared by a similar procedure as for **6**; the yield for methylenation was less than 5% (812 mg). R_f=0.72 (2% EA/hex); ^{1}H (400 MHz) δ 7.58–7.55 (6H), 7.43–7.33 (9H), 5.71 (ddd, 1H, J=16.9, 10.1, 7.0 Hz), 4.96 (broad d, 1H, J=10.4, 1.5 Hz), 4.90 (broad d, 1H, J=17.2 Hz), 2.48 (td, 1H, J=10.6, 7.5 Hz), 1.75–1.70 (1H), 1.50–1.42 (2H), 1.26–1.14 (7H), 0.85 (t, 3H, J=7.3 Hz). ^{13}C (100 MHz) δ 138.9, 136.2, 134.2, 129.3, 127.7, 114.6, 32.1, 31.8, 29.0, 28.9, 22.6, 14.1; IR 1623, 1489, 1469, 1429; HRFAB calcd for $C_{27}H_{32}SiLi$ $(M+Li)^+$: 391.2433, found: 391.2442 (2.3 ppm).

4.1.10. 2-(*tert*-Butyldimethylsilyl)-1-(2-methoxyethoxy)-oct-1-yl *tert*-butyldimethylsilyl peroxide (8). Ozonolysis of allylsilane **6** as above gave 2-(*tert*-butyldimethylsilyl)-1-(2-methoxyethoxy)-octyl hydroperoxide (1.7 g, 60% yield). R_f=0.48 (10% EA/hex); ^{1}H δ 10.38 (s, 1H), 5.04 (d, 0.2H, J=5.36 Hz), 4.88 (d, 0.8H, J=6.6 Hz), 3.94–3.82 (m, 2H), 3.67–3.63 (m, 1H), 3.55–3.53 (m, 1H), 3.44 (s, 3H), 1.44–1.26 (13H), 0.89 (s, 9H), 0.07 (s, 0.5H), 0.04 (s, 0.8H), 0.017 (s, 2H), 0.01 (s, 2.7H). ^{13}C δ 111.5/111.3, 73.4/73.3, 68.2, 67.7, 59.1, 59.0, 31.8, 31.7, 30.6, 30.5, 30.1, 29.7, 29.0, 28.4, 27.8, 27.5, 27.3, 27.25, 27.17, 26.7, 22.7/22.6, 17.7, 17.5, 14.1, −5.04/-5.15, −5.4/-5.8; IR 3324 (b), 1136 cm^{-1}. HRMS: no identifiable ions were observed.

Silylation of this hydroperoxide under standard conditions furnished silyl peroxyacetal **8** in 1.1 g, 90% yield: R_f=0.63 (10% EA/hex); ^{1}H δ 5.04 (d, 0.1H, J=2.5 Hz), 5.0 (d, 0.9H, J=3.5 Hz), 4.17 (m, 0.1H), 4.13 (m, 0.9H), 3.77 (m, 1H), 3.52 (m, 2H), 3.359 (s, 2.5H), 3.554 (s, 0.5H), 1.53–1.253 (13H), 1.11 (m, 1H), 0.93 (s, 9H), 0.89–0.87 (3H), 0.88 (s, 9H), 0.17 (s, 2.8H), 0.16 (s, 3.2H), 0.05 (s, 2.9H), 0.03 (s, 3H); ^{13}C δ 111.7, 111.5, 72.4, 72.3, 70.6, 58.8, 31.9, 31.8, 30.3, 29.6, 28.9, 27.7, 27.2, 27.1, 26.2, 25.6, 22.7, 18.0, 17.4, 14.1, 14.0, −4.56, −5.47, −5.5, −5.9; IR 1132, 1104. HRFAB calcd for $C_{23}H_{52}O_4Si_2Na$ $(M+Na)^+$: 471.3304, found: 471.3313 (2.3 ppm).

4.2. Preparation of homoallyl ethers and esters (10a–10i)

Compounds **10a–i** were prepared by etherification or esterification of the corresponding homoallyl alcohol.[17]

4.2.1. 4-(*tert*-Butyldimethylsilyloxy)-1-methoxy-1-undecene (10a).[18] R_f=0.76 (5% EtOAc/Hex); ^{1}H δ 5.90 (d, 1H, 6.3), 4.39 (dd, 1H, J=7.2, 13.6 Hz), 3.65 (m, 1H), 3.55 (s, 3H), 2.23–2.19 (2H), 1.27–1.44 (12H), 0.88–0.90 (12H), 0.05 (6H); ^{13}C δ 147.0, 103.0, 72.2, 59.3, 36.8, 31.8, 31.7, 29.7, 29.3, 25.9, 25.4, 22.7, 14.1, −4.4, −4.6; IR 1667, 1251, 1108; HRMS calcd for $C_{18}H_{37}O_2Si$ $(M-H)^+$: 313.2562, found: 313.2556 (2.1 ppm).

4.2.2. 4-Methoxyundec-1-ene (10b). To a 1.0 M solution of undec-1-ene-4-ol (650 mg, 3.8 mmol) in DMF was added NaH (305 mg, 60% suspension in mineral oil, 7.6 mmol), MeI (0.3 mL, 5 mmol), 6.8 mmol), Py (0.6 mL, 6.8 mmol) at 0 °C and the reaction mixture was stirred overnight (convenience). The reaction mixture was quenched with satd NH_4Cl and extracted with recycled 20% EA/hexanes (3×25 mL), the organics were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Flash chromatography (5% EA/hexanes) of the crude product furnished 493 mg (70%) of the methyl ether. R_f=0.42 (5% EA/hex); ^{1}H δ 5.89 (ddt, 1H, J=17.6, 10.1, 6.9 Hz), 5.07 (dd, 1H, J=17.3, 1.9 Hz), 5.04 (dd, 1H, J=10.1, 1.8 Hz), 3.33 (s, 3H), 3.19–3.18 (m, 1H), 2.28–2.24 (m, 2H), 1.47–1.35 (12H), 0.87 (t, 3H, J=6.9 Hz); ^{13}C δ 135.1, 116.6, 80.6, 56.5, 37.8, 33.4, 31.8, 29.7, 29.3, 25.3, 22.6, 14.0; IR 1643, 1100; HREI: calcd for $C_{12}H_{23}O$ $(M-H)^+$: 183.1747, found: 183.1744 (2.8 ppm).

4.2.3. 4-Benzyloxy-undec-1-ene (10c). To a 1.0 M solution of undec-1-ene-4-ol (2.0 g, 12.0 mmol) in DMF was added neat NaH (0.58 g 24 mmol), BnBr (2.2 mL, 18 mmol), and a catalytic amount of Bu_4NI at 0 °C and the reaction mixture was stirred overnight (convenience). The reaction mixture was quenched with satd NH_4Cl and extracted with recycled 20% EA/hexanes (3×50 mL), the organics were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Flash chromatography (5% EA/hexanes) of the crude product furnished 2.12 g (70%) of the methyl ether (∼5 g scale, 63%). R_f=0.69 (5% EA/hex); ^{1}H δ 7.43–7.40 (5H), 5.93 (ddt, 1H, J=17.3, 10.1, 7.2 Hz), 5.23 (dd, 1H, J=17.3, 2.2 Hz), 5.17 (dd, 1H, J=10.1, 2.2 Hz), 4.60 (d, 1H, J=2.7 Hz), 4.58 (d, 1H, J=2.7 Hz), 3.50 (m, 1H), 2.39 (dd, 2H, J=2.9, 1.4 Hz), 1.65–1.30 (12H), 0.96 (t, 3H, J=6.9 Hz); ^{13}C δ 139.1, 135.1, 128.2, 127.6, 127.3, 116.6, 70.9, 38.3, 33.8, 31.8, 29.7, 29.2, 25.3, 22.6, 14.0; IR 1639, 1492, 1454, 1205, 1096; HREI: calcd for $C_{18}H_{28}O$ $(M)^+$: 260.2140, found: 260.2134 (2.3 ppm).

4.2.4. Acetic acid, 1-undecene-4-yl ester (10d). To a 1.0 M solution of undec-1-ene-4-ol (579 mg, 3.4 mmol) in CH_2Cl_2 was added Ac_2O (0.7 mL, 6.8 mmol), and pyridine (0.6 mL, 7 mmol) at 0 °C and the reaction mixture was stirred overnight (convenience). The solvent was removed under reduced pressure, and excess Ac_2O, Py were removed under high vacuum. Flash chromatography (5% EA/hexanes) furnished 581 mg (75%) of the acyl ester (∼5 g scale, 78–80%). R_f=0.54 (5% EA/hex); ^{1}H δ 5.69 (ddt, 1H, J=17.1, 10.0, 7.0 Hz), 5.02 (broad dd, 1H, J=17.0, 1.5 Hz), 4.99 (broad dd, 1H, J=10.0, 0.8 Hz), 4.86 (m, 1H), 2.24 (m, 2H), 2.0 (s, 3H), 1.40 (2H), 1.25 (broad, 10H), 0.83 (t, 3H, J=7.0 Hz); ^{13}C δ 170.5, 133.7, 117.3, 73.2, 38.5, 33.5, 31.7, 29.3, 29.1, 25.3, 22.5, 21.0, 13.9; IR 1739, 1641; HRFAB calcd for $C_{13}H_{24}OLi$ $(M+Li)^+$: 219.1936, found: 219.1186 (88 ppm).

4.2.5. Benzoic acid, undecene-4-yl ester (10e). To a 1.0 M solution of undec-1-ene-4-ol (740 mg, 4.3 mmol) in CH_2Cl_2/Py (1:3) was added benzoyl chloride (1.5 mL, 13 mmol). The reaction mixture turns pink after the addition of reagents is complete. After 1 h the reaction mixture is quenched with sat. NH_4Cl at 0 °C and extracted with 30% recycled EA/hexanes (3×50 mL). The organics were dried

over Na_2SO_4. The solvent was removed under reduced pressure and flash chromatography of the crude product (10% EA/hexanes) furnished 1.1 g (90%) of the benzoyl ester. R_f=0.68 (10% EA/hex); ^{1}H (400 MHz) δ 8.05 (broad d, 2H, J=7.6 Hz), 7.55 (dt, 1H, J=7.3, 1.3 Hz), 7.43 (broad t, 2H, J=7.3 Hz) 5.83 (ddt, 1H, J=17.2, 10.4, 7.0 Hz), 5.20–5.15 (m, 1H), 5.11 (dd, 1H, J=17.2, 1.5 Hz), 5.06 (dd, 1H, J=10.4, 1.7 Hz), 2.45 (t, 2H, J=6.6 Hz), 1.76–1.61 (2H), 1.43–1.25 (10H), 0.87 (t, 3H, J=6.8 Hz); ^{13}C (100 MHz) δ 166.2, 133.7, 132.7, 130.7, 129.5, 128.3, 117.7, 74.0, 38.7, 33.6, 31.7, 29.4, 29.1, 25.3, 22.6, 14.0; IR 1719, 1643; HRFAB calcd for $C_{18}H_{26}O_2Li$ $(M+Li)^+$: 281.2093; found: 281.2095 (0.7 ppm).

4.2.6. 4-(Methoxymethoxy)-undec-1-ene (10g). To a 1.0 M solution of undec-1-ene-4-ol (1.6 g, 9.2 mmol) in DIPEA/CH_2Cl_2 (1:1) was added chloromethyl methyl ether (1.4 mL, 18 mmol) at 0 °C and the reaction mixture was stirred overnight (convenience). The reaction mixture was quenched with satd NH_4Cl at 0 °C and the aqueous layer was extracted with recycled 20% EA/hexanes (3×25 mL). The combined organics were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Flash chromatography (5% EA/hexanes) of the crude product furnished 1.51 g (75%) of the methoxymethyl ether. R_f= 0.39 (5% EA/hex); ^{1}H δ 5.76 (ddt, 1H, J=17.0, 10.1, 6.9 Hz), 5.0 (dd, 1H, J=17.3, 1.9 Hz), 4.97 (dd, 1H, J= 10.1, 1.9 Hz), 4.5 (dd, 2H, J=12.9, 6.9 Hz), 3.54 (m, 1H), 3.31 (s, 3H), 2.23 (broad t, 2H, J=6.6 Hz), 1.45–1.23 (12H), 0.83 (t, 3H, J=6.9 Hz); ^{13}C δ 135.0, 116.7, 95.5, 76.8, 55.3, 39.0, 34.3, 31.8, 29.7, 29.3, 25.3, 22.6, 13.9; IR 1646, 1149, 1099; HREI calcd for $C_{10}H_{21}O_2$ $(M-allyl)^+$: 173.1542, found: 173.1547 (2.8 ppm).

4.2.7. Acetic acid, 1-phenyl-3-buten-1-yl ester (10h). To a 1.0 M solution of benzaldehyde (10.6 g, 100 mmol), in THF was added a 2.0 M solution of allylmagnesium chloride (76 mL, 150 mmol) in THF at 0 °C. The color of the reaction mixture changed from reddish brown to dark green as the reaction progressed. After 24 h the reaction mixture was quenched with sat. NH_4Cl at 0 °C and extracted with recycled 20% EA/hexanes (3×150 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was distilled under reduced pressure to furnish 6.9 g (46%) of 1-phenyl-3-butenol. A portion of the alcohol (4.5 g, 30.3 mmol) was acylated using a procedure similar to compound **10d** to furnish the acetate ester in 4.15 g (72%) yield. R_f=0.5 (4% EA/hex); ^{1}H δ 7.48–7.25 (5H), 5.80 (t, 1H, J=6.3 Hz), 5.69 (ddt, 1H, J=17.3, 10.4, 6.9 Hz), 5.05 (dd, 1H, J=17.9, 1.9 Hz), 5.03 (dd, 1H, J=10.1, 1.6 Hz), 2.67–2.52 (m, 2H), 2.03 (s, 3H); ^{13}C δ 170.0, 140.0, 133.2, 128.3, 127.8, 126.4, 117.8, 75.0, 40.6, 21.0; IR 1748, 1637, 1492, 1458, 1424; HRFAB calcd for $C_{12}H_{14}O_2Li$ $(M+Li)^+$: 197.1154, found: 197.115 (0.9 ppm).

4.2.8. Acetic acid, 2-methyl-1-undecene-4-yl ester (10i). To a 1.0 M solution of heptanal (5 g, 43.8 mmol) in THF was added a solution of methallyl magnesium bromide (1.1 equiv) in THF at 0 °C. After 24 h stirring the reaction mixture was quenched with satd NH_4Cl and the aqueous layer was extracted with recycled 20% EA/hexanes. The organics were washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. Distillation of the crude product furnished 2-methyl-1-decene-4-ol in (5.6 g, 75%) yield. Acylation of the alcohol by a similar procedure as employed for the preparation of compound **10d** furnished the desired acetate ester in 62% yield. R_f=0.74 (5% EA/hex); ^{1}H δ 5.02 (m, 1H), 4.74 (d, 1H, J=6.3 Hz), 4.67 (d, 1H, J=6.3 Hz), 2.27–2.14 (2H), 1.98 (s, 3H), 1.72 (s, 3H), 1.49 (2H), 1.24 (broad, 8H), 0.85 (t, 3H, J=6.9 Hz); ^{13}C δ 170.5, 141.8, 113.0, 72.1, 42.9, 34.0, 31.7, 29.0, 25.3, 22.5, 22.4, 21.0, 13.9; IR 1735, 1643; HR-EI calcd for $C_{11}H_{19}$ $(M-AcOH)^+$: 152.1643; found: 152.1571 (47 ppm).

4.3. Ozonolysis of homoallyl ethers/esters (illustrated for 11d)

Into a −78 °C solution of alkene **10d** (4.70 g, 20.6 mmol) in 2-methoxyethanol (100 mL, excess) tinted slightly pink with a trace of Sudan Red B was bubbled a gaseous solution of O_3/O_2. After the reddish color had faded to light yellow and TLC analysis displayed little or no starting material, ozonolysis was stopped and residual ozone was removed by sparging with O_2 or N_2. The reaction mixture was allowed to warm to room temperature and was diluted with DI water (100 mL). The organic extracts (recycled EA/hex, 3× 100 mL), were dried over Na_2SO_4 and the solution was concentrated in vacuo. Residual methoxyethanol was removed under high vacuum, and the residue was purified by flash chromatography (20% EA/hex) to furnish 3.7 g (59%) of hydroperoxy acetal **11d**. Compounds **11a–i** were prepared by a similar procedure. Unless otherwise noted, the hydroperoxyacetals were formed as approximately 1:1 mixtures of diastereomers.

4.3.1. 3-*tert*-Butyldimethylsilyloxy-1-hydroperoxy-1-(2-methoxyethoxy)decane (11a). Yield=1.8 g, 73%. R_f= 0.39 (10% EA/hex); ^{1}H δ 10.30 (s, 0.5H), 10.25 (s, 0.5H), 4.97–4.92 (1H), 3.85–3.78 (3H), 3.66–3.60 (1H), 3.56–3.52 (1H), 3.43 (s, J=1.6 Hz), 3.42 (s, 1.4H), 1.97–1.89 (2H), 1.83–1.79 (2H), 1.46–1.41 (2H), 1.29–1.24 (8H), 0.87 (s, 5H), 0.86 (s, 4H), 0.86–0.87 (3H), 0.05 (s, 1.4H), 0.04 (s, 1.4H), 0.38 (s, 3.2H); ^{13}C δ 105.1, 105.0, 72.9, 72.8, 69.0, 68.9, 65.4, 65.3, 58.6, 38.7, 38.4, 37.62, 37.59, 31.8, 31.7, 29.72, 29.68, 29.2, 25.9, 25.8, 24.7, 22.6, 18.01, 18.0, 14.0, −4.3, −4.4, −4.6, −4.7; IR 3428, 2857–2848, 1255, 1102–1124; HRMS: no identifiable ions were observed.

4.3.2. (1-Hydroperoxy)-3-methoxy-1-(2-methoxyethoxy)-decane (11b). Yield=204 mg, 45%. R_f=0.6 (40% EA/hex); ^{1}H δ 10.31 (s, 0.6H), 10.27 (s, 0.3H), 4.97–4.93 (m, 1H), 3.87–3.77 (m, 1H), 3.64–3.59 (2H), 3.56–3.49 (2H), 3.41 (s, 1.2H), 3.40 (s, 1.8H), 3.30 (s, 1.2H), 3.29 (s, 1.8H), 1.96–1.23 (m, 14H), 0.83 (t, 3H, J=6.3 Hz); ^{13}C δ 105.1, 104.8, 77.5, 77.4, 72.7, 72.5, 65.7, 65.5, 58.9, 58.8, 56.7, 56.4, 35.9, 35.8, 33.3, 33.0, 31.7, 29.6, 29.1, 24.7, 22.5, 14.0; IR 3331, 1198, 1104; HRMS: no identifiable ions were observed.

4.3.3. 3-Benzyloxy-1-hydroperoxy-1-(2-methoxyethoxy)-decane (11c). Yield=300 mg, 50%. R_f=0.45 (20% EA/hex); ^{1}H δ 10.27 (s, 0.8H), 9.73 (t, 0.2H, J=1.9 Hz), 7.35–7.24 (5H), 5.05–5.02 (m, 0.4H), 4.99 (broad t, 0.6H, J= 6.0 Hz), 4.60–4.50 (2H), 3.86–3.78 (m, 0.7H), 3.72–3.68

(m, 0.3H), 3.65–3.57 (m, 2H), 3.56–3.45 (m, 2H), 3.43 (s, 1.2H), 3.42 (s, 1.8H), 2.40 (m, 0.4H), 2.05–1.79 (m, 1.6H), 1.65–1.27 (12H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C δ 138.7, 128.3, 128.24/128.22, 127.77, 127.73, 127.66, 127.51, 127.48, 127.43, 127.41, 127.38, 105.2, 105.0, 75.9, 75.7, 72.8, 72.7, 72.6, 71.3, 70.9, 69.9, 65.9, 58.8, 43.7, 36.3, 34.9, 33.9, 31.7, 29.64/29.62, 29.4, 29.1, 25.8, 24.9, 24.8, 22.5, 21.8, 14.0; IR 3331, 1495, 1451, 1198, 1096; HRMS: no identifiable ions were observed.

4.3.4. Acetic acid, 1-hydroperoxy-1-(2-methoxyethoxy) decane-3-yl ester (11d). Yield=2.9 g, 60%. R_f=0.39 (20% EA/hex); ^{1}H δ 10.33 (s, 0.8H), 10.23 (s, 0.2H), 4.94 (m, 1H), 4.79 (m, 1H), 3.94–3.83 (m, 2H), 3.72–3.59 (m, 2H), 3.50 (s, 1.8H), 3.49 (s, 1.2H), 2.09 (s, 1.8H), 2.08 (s, 1.2H), 1.99–1.94 (m, 2H), 1.62–1.60 (m, 2H), 1.31 (broad s, 10H), 0.92 (t, 3H, J=6.6 Hz); ^{13}C δ 170.5/170.4, 104.8/104.5, 72.5/72.4, 71.7/71.6, 66.5, 65.4, 58.7, 36.3, 35.9, 34.4, 34.1, 31.5, 31.0, 29.1, 28.9, 28.3, 24.9, 24.86, 22.4, 20.93, 20.9, 13.8; IR 3300 (b), 1734, 1124, 1100; HRMS: no identifiable ions were observed.

4.3.5. Benzoic acid, 1-hydroperoxy-1-(2-methoxyethoxy) decane-3-yl ester (11e). Yield=510 mg, 40%. R_f=0.47 (20% EA/hex); ^{1}H δ 10.46 (s, 0.6H), 10.30 (s, 0.4H), 8.0 (broad d, 2H, J=7.9 Hz), 7.53–7.51 (1H), 7.41 (broad t, 2H, J=7.6 Hz), 5.31–5.25 (m, 1H), 4.96 (t, 0.5H, J=6.0 Hz), 4.93 (t, 0.5H, J=6.0 Hz), 3.8–3.7 (2H), 3.66–3.62 (2H), 3.40 (s, 1.8,H), 3.38 (s, 1.2H), 2.16–2.02 (2H), 1.76–1.61 (4H), 1.39–1.22 (8H), 0.83 (broad t, 3H, J=6.3 Hz); ^{13}C δ 166.0, 132.8, 132.7, 130.5, 130.3, 129.5, 129.4, 128.25, 128.2, 104.8, 104.5, 72.6, 72.5, 71.6, 66.5, 65.3, 58.83, 58.76, 36.4, 36.1, 34.6, 34.3, 31.6, 29.3, 29.0, 25.01, 24.99, 22.5, 13.9; IR 3315 (b), 1719, 1581, 1450, 1192, 1102, 1071; HRMS: no identifiable ions were observed.

4.3.6. 2,2-Dimethylpropionic acid, 1-hydroperoxy-1-(2-methoxyethoxy) decane-3-yl ester (11f). The title compound was prepared by esterification of undecen-4-ol followed by ozonolysis of the crude pivaloate ester in 325 mg, 50% yield. R_f=0.26 (20% EA/hex); ^{1}H δ 10.38 (0.4H), 10.25 (0.6H), 5.04–4.92 (1H), 4.88 (t, 0.6H, J=6.0 Hz), 4.83 (t, 0.4H, J=5.7 Hz), 3.86–3.78 (2H), 3.67–3.51 (2H), 3.425 (s, 1.8H), 3.429 (s, 1.2H), 1.93–1.85 (2H), 1.67–1.55 (4H), 1.179 (s, 3.6H), 1.173 (s, 5.4H), 1.17–1.50 (8H), 0.85 (t, 3H, J=6.9 Hz); ^{13}C δ 178.0/177.9, 105.1, 104.7, 72.8, 72.7, 70.7, 70.6, 70.3, 70.2, 66.6, 65.2, 63.5, 58.9, 58.87, 58.83, 39.2, 38.8, 38.76, 36.5, 36.1, 34.5, 34.2, 33.9, 31.7, 29.3, 29.2, 29.1, 27.16, 27.13, 27.0, 24.97, 24.94, 22.5, 13.1; IR 1725, 1159, 1130, 1101; HRMS: no identifiable ions were observed.

4.3.7. 1-(2-Ethoxymethoxy)-3-(methoxymethoxy)decyl hydroperoxide (11g). Yield=0.8 g, 55%. R_f=0.39 (20% EA/hex); ^{1}H δ 10.27 (s, 1H), 4.90 (s, 0.1H), 4.77 (t, 1H, J=6 Hz), 4.52 (s, 1.9H), 3.77–3.75 (1H), 3.57–3.47 (2H), 3.43 (t, 2H, J=6.3 Hz), 3.37 (s, 3H), 3.30 (s, J=0.3 Hz), 3.27 (s, 2.7H), 1.68–1.28 (17H); ^{13}C δ 107.2, 99.0, 96.3, 77.2, 72.6, 72.3, 67.0, 67.5, 65.3, 58.7, 54.8, 31.1, 29.4, 28.3, 25.5 25.8, 24.4, 24.2, 12.0; IR 3316, 1196, 1102, 1044; HRMS: no identifiable ions were observed.

4.3.8. Acetic acid, 1-hydroperoxy-1-(2-methoxyethoxy)-3-phenyl propane-3-yl ester (11h). Yield=2.8 g, 50%. R_f=0.44 (40% EA/hex); ^{1}H δ 10.53 (s, 1H), 7.53–7.40 (5H), 6.07–5.99 (1H), 4.97–4.95 (0.7H), 4.88 (t, 0.3H, J=6.0 Hz), 3.96–3.92 (2H), 3.79–3.70 (2H), 3.56 (s, 1H), 3.55 (s, 2H), 2.16 (s, 3H), 1.85–1.43 (2H); ^{13}C δ 169.9, 140.0, 128.4, 128.0, 126.42, 126.38, 104.37, 104.0, 72.65, 72.63, 72.57, 72.54, 72.4, 66.2, 58.8, 38.3, 37.9, 21.0; IR 3330 (b), 1740, 1490, 1600, 1124; HRMS: no identifiable ions were observed.

4.3.9. Acetic acid, 2-hydroperoxy-2-methoxyethoxy-decane-4-yl ester (11i). Yield=493 mg, 62%. R_f=0.64 (40% EA/hex); ^{1}H δ 10.14 (s, 0.6H), 10.10 (s, 0.4H), 5.0 (m, 1H), 3.50–3.41 (4H), 3.329 (s, 1.3H), 3.326 (s, 1.7H), 1.98 (s, 1H), 1.90 (s, 2H), 1.88–1.87 (1H), 1.45–1.14 (m, 3H), 1.24 (s, 1.8H), 1.22 (s, 1.2H), 1.18–1.15 (8H), 0.76 (t, 3H, J=7.0 Hz); ^{13}C δ 170.4, 170.2, 105.7, 105.5, 72.6, 70.5, 70.3, 59.8, 59.7, 58.6, 39.64, 39.59, 35.1, 35.0, 31.4, 28.8, 24.7, 22.3, 21.03, 21.0, 19.6, 19.4, 13.8; IR 3308, 1734, 1125; HRMS: no identifiable ions were observed.

4.4. Silylation of hydroperoxyacetals (illustrated for 12d)

Into a 0 °C solution of hydroperoxyacetal **11d** (3.70 g, 12.0 mmol) in DMF (15 mL) under N_2, was added imidazole (1.5 equiv, 1.22 g, 18 mmol) followed by TBSOTf (18 mmol, 4.2 mL, dropwise). The reaction was stirred for 25–30 min and then quenched with DI water (50 mL). The combined organic extracts (recycled EA/hexane, 3×100 mL) were dried over Na_2SO_4, and the solvent removed in vacuo. The crude product was purified by flash chromatography (10% EA/hex) to furnish 4.5 g (88%) of the silyl peroxyacetal **12d**. Compounds **12a–i** were prepared by similar procedures.

4.4.1. 1-(*tert*-Butyldimethylsilyldioxy)-3-(*tert*-butyldimethylsilyloxy)-1-(2-methoxyethoxy)-decane (12a). Yield=427 mg, 85%. R_f=0.65 (10% EA/hex); ^{1}H δ 4.99–4.94 (1H), 4.10–4.05 (0.5H), 4.02–3.98 (0.5H), 3.83–3.71 (2H), 3.59–3.49 (2H), 3.36 (s, 1.6H), 3.356 (s, 1.4H), 1.89–1.68 (2H), 1.43 (broad peak, 2H), 1.25 (broad peak, 12H), 0.92 (s, 9H), 0.87 (s, 9H), 0.88–0.85 (3H), 0.15 (s, 6H), 0.05 (s, 1.6H), 0.04 (4.4H); ^{13}C δ 106.5, 105.9, 72.1, 72.0, 69.2, 69.0, 68.9, 68.7, 58.9, 58.87, 39.8, 39.5, 37.6, 37.5, 31.79, 31.78, 29.7, 29.2, 26.12, 26.1, 25.8, 24.9, 24.7, 22.6, 18.1, 18.01, 18.0, 14.0, −4.3, −4.4, −4.6, −4.6, −5.7; IR 2959–2851, 1101, 1252, 1203; HRMS: no identifiable ions were observed.

4.4.2. 1-(*tert*-Butyldimethylsilyldioxy)-3-methoxy-1-(2-methoxyethoxy) decane (12b). Yield=135 mg, 87%. R_f=0.68 (20% EA/hex); ^{1}H δ 5.02 (m, 1H), 4.10–4.03 (m, 1H), 3.83–3.75 (m, 2H), 3.61–3.51 (2H), 3.38 (s, 1.7H), 3.37 (s, 1.3H), 3.32 (s, 3H), 1.87–1.66 (m, 2H), 1.50–1.25 (12H), 0.92 (s, 3.8H), 0.91 (s, 5.2H), 0.85 (t, 3H, J=6.6 Hz), 0.26 (s, 3.4H), 0.16 (s, 2.6H); ^{13}C δ 106.4/106.1, 77.4, 72.1, 72.0, 69.4, 69.0, 58.82, 58.78, 56.3, 37.0, 33.7, 33.6, 31.8, 29.75, 29.68, 29.2, 26.1, 25.7, 25.6, 24.9, 22.6, 18.1, 14.0, −3.0, −5.7; IR 2962–2851, 1249, 1199, 1095; HRFAB calcd for $C_{20}H_{44}O_5SiLi$ $(M+Li)^+$: 399.3118; found: 399.3125 (1.6 ppm).

4.4.3. 1-(*tert*-Butyldimethylsilyldioxy)-3-benzyloxy-1-(2-methoxyethoxy)-decane (12c). Yield=2.8 g, 88%. R_f=0.71 (20% EA/hex); ^{1}H δ 7.37–7.27 (5H), 5.14–5.07 (1H), 4.50–4.49 (2H), 4.10–3.96 (1H), 3.65–3.46 (2H), 3.39–3.34 (2H), 3.36 (s, 3H), 1.95–1.78 (2H), 1.63–1.50 (2H), 1.48–1.3 (10H), 0.97 (s, 4.6H), 0.969 (s, 4.4H), 0.92 (t, 3H, J=6.6 Hz), 0.19 (s, 2.7H), 0.18 (s, 3.3H); ^{13}C δ 139.0, 138.97, 128.2, 128.1, 127.6, 127.58, 127.5, 127.46, 127.43, 127.3, 127.26, 106.3, 106.0, 75.8, 75.7, 72.8, 72.0, 70.9, 70.8, 69.4, 38.9, 58.73, 58.69, 37.35, 37.26, 34.1, 34.0, 31.7, 29.7, 29.6, 29.1, 26.1, 25.7, 25.0, 24.9, 22.5, 18.05, 18.03, 13.9, −4.1, −4.2, −5.73, −5.7; IR 2962–2855, 1494, 1462, 1249, 1106; HRFAB calcd for $C_{26}H_{48}O_5SiNa$ $(M+Na)^+$: 491.3171; found: 491.3151 (3.6 ppm).

4.4.4. Acetic acid, 1-(*tert*-butyldimethylsilyldioxy)-1-(2-methoxyethoxy)-decane-3-yl ester (12d). Yield=4.5 g, 88%. R_f=0.42 (10% EA/hex); ^{1}H δ 5.0 (m, 1H), 3.99–3.96 (m, 1H), 3.74–3.68 (2H), 3.54–3.47 (2H), 3.46 (s, 1.2H), 3.45 (s, 1.8H), 2.0 (s, 1.8H), 1.99 (s, 1.2H), 1.95–1.76 (4H), 1.60–1.40 (broad peak, 2H), 1.15–1.30 (8H), 0.9 (s, 6.7H), 0.89 (s, 2.3H), 0.83 (t, 3H, J=6 Hz), 0.125 (s, 4H), 0.11 (s, 1.9H). ^{13}C δ 170.24/170.21, 105.9/105.5, 72.0/71.97, 71.1/71.0, 69.76/68.74, 58.78/58.71, 37.0, 36.8, 34.5, 34.2, 31.6, 29.3, 29.0, 26.04, 26.02, 25.7, 25.6, 25.0, 22.5, 21.1, 21.0, 18.0, 13.9, −5.8; IR 2928–2850, 1734, 1233, 1130, 1101; HRMS: no identifiable ions were observed.

4.4.5. Benzoic acid, 1-(*tert*-butyldimethylsilyldioxy)-1-(2-methoxyethoxy)-decane-3-yl ester (12e). Yield=291 mg, 75%. R_f=0.5 (10% EA/hex); ^{1}H δ 8.03 (broad d, 2H, J=8.2 Hz), 7.55–7.51 (m, 1H), 7.43–7.40 (m, 2H), 5.31–5.21 (m, 0.4H), 5.03–4.96 (m, 0.6H), 4.06 (broad t, 1H, J=5.0 Hz), 3.76–3.70 (m, 2H), 3.52–3.42 (m, 2H), 3.30 (s, 1H), 3.29 (s, 2H), 2.02–1.98 (m, 2H), 1.75–1.64 (m, 2H), 1.40–1.20 (m, 10H), 0.91 (s, 9H), 0.84 (broad t, 3H, J=6 Hz), 0.16 (s, 3.9H), 0.13 (s, 2.1H); ^{13}C δ 165.8, 165.78, 132.7, 132.6, 130.6, 130.5, 129.5, 128.23, 128.19, 105.9, 105.4, 72.0, 71.9, 71.8, 71.7, 69.9, 68.7, 58.8, 58.7, 37.1, 36.8, 34.6, 34.3, 31.7, 29.36, 29.32, 29.0, 26.0, 24.99, 24.97, 22.5, 18.04, 18.02, 14.0, −5.8; IR 2859–2849, 1710, 1601, 1580, 1462, 1441, 1275, 1175, 1106, 1023; HRFAB calcd for $C_{26}H_{46}O_6SiLi$ $(M+Li)^+$: 489.3224; found: 489.3243 (3.9 ppm).

4.4.6. 2,2-Dimethylpropionic acid, 1-(*tert*-butyldimethylsilyldioxy)-1-(2-methoxyethoxy)-decane-3-yl ester (12f). Yield=212 mg, 60%. R_f=0.72 (20% EA/hex); ^{1}H δ 5.03–4.81 (m, 1H), 4.07–3.96 (1H), 3.75–3.68 (2H), 3.56–3.48 (2H), 3.35 (s, 1.2H), 3.33 (1.8H), 1.56–1.48 (2H), 1.28–1.20 (12H), 1.17 (s, 3.7H), 1.16 (s, 5.3H), 0.91 (s, 9H), 0.84 (broad t, 3H), 0.14 (s, 3.4H), 0.13 (s, 2.6H); ^{13}C δ 177.57, 177.55, 106.0, 105.4, 72.0, 71.9, 70.7, 70.68, 70.0, 68.6, 58.84, 58.80, 45.2, 38.73, 38.7, 37.1, 36.8, 34.5, 34.1, 31.7, 29.3, 29.1, 27.2, 27.1, 26.08, 26.06, 25.7, 25.6, 25.5, 24.8, 22.5, 18.07, 18.05, 14.0; IR 2953–2855, 1729, 1246, 1158, 1109; HRFAB calcd for $C_{24}H_{50}O_6SiLi$ $(M+Li)^+$: 469.3537; found: 469.3541 (0.8 ppm).

4.4.7. 1-(*tert*-Butyldimethylsilyldioxy)-3-methoxymethoxy-1-(2-methoxyethoxy)decane (12g). Yield=293 mg, 82%. R_f=0.6 (20% EA/hex); ^{1}H δ 4.97 (s, 0.1H), 4.80 (t, 0.9H, J=5.7 Hz), 4.53 (s, 1.9H), 4.15 (t, 0.1H, J=4.73 Hz), 3.99 (m, 1H), 3.78–3.70 (2H), 3.52–3.42 (2H), 3.30 (s, 3H), 3.27 (s, 3H), 1.59–1.49 (6H), 1.40–1.30 (8H), 0.86 (s, 9H), 0.83 (broad t, 3H, J=6.6 Hz), 0.10 (s, 6H); ^{13}C δ 108.2, 99.7, 96.2, 72.0, 71.7, 69.1, 68.7, 67.4, 58.8, 58.7, 54.8, 32.1, 30.1, 29.4, 26.0, 25.8, 24.4, 17.9, −5.8, −6.0; IR 1111, 1045; HRMS: no identifiable ions were observed.

4.4.8. Acetic acid, 1-(*tert*-butyldimethylsilyldioxy)-3-phenyl-1-(2-methoxyethoxy)-decane-3-yl ester (12h). Yield=2.0 g, 55%. R_f=0.5 (20% EA/hex); ^{1}H δ 7.49–7.17 (5H), 5.91–5.85 (1H), 4.96–4.94 (0.8H), 4.81 (t, 0.2H, J=6.0 Hz), 4.07–3.70 (2H), 3.71–3.49 (2H), 3.38 (s, 1.2H), 3.36 (s, 1.8H), 2.36–2.33 (m, 2H), 2.03 (s, 1.8H), 2.02 (s, 1.2H), 0.94 (5.6H), 0.93 (3.4H), 0.18 (s, 3.4H), 0.17 (s, 2.6H); ^{13}C δ 169.66, 169.62, 140.3, 140.1, 128.39, 128.36, 127.9, 127.8, 126.4, 126.3, 105.3, 105.1, 72.7, 72.66, 72.0, 71.8, 69.5, 68.8, 58.8, 58.7, 39.1, 38.8, 26.03, 26.0, 25.6, 21.0, 20.96, 18.0, 17.8, −3.7, −5.8; IR 2930–2848, 1741, 1464, 1366, 1230, 1116; HRFAB calcd for $C_{20}H_{34}O_6SiNa$ $(M+Na)^+$: 421.2025, found: 421.2036 (2.6 ppm).

4.4.9. Acetic acid, 2-(*tert*-butyldimethylsilyldioxy)-2-(2-methoxyethoxy)-nonane-4-yl ester (12i). Yield=584 mg, 75%. R_f=0.65 (20% EA/hex); ^{1}H δ 5.03 (m, 1H), 3.59 (broad t, 2H, J=5.0 Hz), 3.47 (broad t, 2H, J=5 Hz), 3.30 (s, 3H), 1.95 (s, 3H), 2.08–2.04 (1.2H), 1.78–1.74 (0.8H), 1.53–1.49 (3H), 1.29 (s, Me, 1.4H), 1.27 (s, Me, 1.6H), 1.21 (broad peak, 7H), 0.88 (s, 9H), 0.81 (t, 3H, J=6.3 Hz), 0.10 (s, 1.5H), 0.08 (s, 4.5H); ^{13}C δ 170.2, 170.1, 105.6, 105.4, 71.9, 71.8, 71.1, 70.6, 60.9, 60.4, 58.8, 40.4, 40.3, 35.5, 35.2, 31.6, 29.1, 29.0, 26.05, 26.03, 24.95, 24.87, 22.4, 21.2, 21.1, 20.4, 19.8, 18.15, 18.11, 13.9, −5.8; IR 2928–2855, 1739, 1247, 1130; HRFAB calcd for $C_{21}H_{44}O_6SiNa$ $(M+Na)^+$: 443.2807; found: 443.2822 (3.3 ppm).

4.4.10. Undecene-5-ol.[19] The title compound was prepared by a reported procedure.

4.4.11. 5-Methoxyundecene (13a). The title compound was prepared using a reported procedure[7]. Yield=1.3 g, 75%. R_f=0.2 (2% EA/hex); ^{1}H δ 5.82 (ddt, 1H, J=17.0, 10.4, 6.6 Hz), 5.01 (broad dd, 1H, J=17.0, 1.9 Hz), 4.98 (dd, 1H, J=10.1, 1.9 Hz), 3.31 (s, 3H), 3.14 (m 1H), 2.19–2.01 (2H), 1.69–1.21 (12H), 0.88 (t, 3H, J=6.9 Hz); ^{13}C δ 138.8, 114.3, 80.3, 56.4, 33.5, 32.85, 29.6, 29.5, 25.2, 22.6, 14.0; IR 1633, 1103, 1158; HREI calcd for $C_{12}H_{25}O$ $(M+H)^+$: 185.1905; found: 185.1896 (4.8 ppm).

4.4.12. 5-Iodoundecene (13b). Into a 0 °C solution of undec-1-ene-5-ol (3.6 g, 21.1 mmol) in CH_2Cl_2 (50 mL) were successively added PPh_3 (6.1 g, 23.2 g), I_2 (7.5 g, 29.5 mmol) and imidazole (2.0 g, 29.5 mmol). The reaction was stirred overnight (convenience), diluted with CH_2Cl_2 (50 mL) and then quenched with DI water and washed with aqueous sodium thiosulphate solution (3×100 mL). The organic layer was dried over Na_2SO_4 and concentrated to give a white solid which was washed with hexanes (3×100 mL). The hexanes were removed under reduced pressure to give a colorless liquid which was purified by flash chromatography (10% EA/hex) to furnish the iodide (5.2 g, 88%): R_f=0.88 (10% EA/hex); ^{1}H (400 MHz) δ 5.77

(ddt, 1H, $J=17.2$, 10.4, 6.8 Hz), 5.07 (broad dd, 1H, $J=$ 17.2, 1.5 Hz), 5.0 (broad dd, 1H, $J=10.4$, 1.8 Hz), 4.1 (m, 1H), 2.34–2.12 (2H), 2.0–1.65 (4H), 1.56–1.28 (8H), 0.88 (t, 3H, $J=6.8$ Hz); ^{13}C (100 MHz) δ 137.0, 115.6, 40.6, 39.6, 39.4, 33.6, 31.6, 29.4, 28.5, 22.6, 14.0; IR 1636, 1300, 1225, 1151; HREI calcd for $C_{11}H_{21}I$ $(M)^+$: 280.0688; found: 280.0685 (1.0 ppm).

4.4.13. [1-*tert*-Butyldimethylsilyldioxy]-4-methoxy-1-(2-methoxyethoxy) decane (14a). Ozonolysis of 5-methoxyundecene in 2-methoxyethanol furnished 4-methoxy-1-(2-methoxyethoxy)-dec-1-yl-hydroperoxide in 307 mg, 50% yield: $R_f=0.33$ (20% EA/hex); ^{1}H δ 10.32 (s, 0.6H), 10.30 (0.4H), 4.81 (t, 1H, $J=6.0$ Hz), 3.83–3.76 (2H), 3.62–3.58 (1H), 3.55–3.51 (1H), 3.41 (s, 3.0H), 3.274 (s, 1.5H), 3.271 (s, 1.5H), 3.15–3.09 (m, 1H), 1.79–1.24 (14H), 0.84 (t, 3H, $J=6.3$ Hz); ^{13}C δ 107.4, 80.4, 72.7, 65.3, 65.1, 58.8, 56.2, 56.1, 33.3, 31.7, 29.45, 29.38, 28.4, 28.2, 27.06, 25.15, 25.13, 22.5, 13.9; IR 3332, 1174, 1086; HRMS: no identifiable ions were observed.

Silylation of the hydroperoxyacetal under standard conditions furnished silyl peroxyacetal **14a** in 268 mg, 87% yield: $R_f=0.68$ (20% EA/hex); ^{1}H δ 4.81 (broad t, 1H, $J=$ 5.7 Hz), 4.0–3.96 (m, 1H), 3.74–3.69 (m, 1H), 3.51–3.43 (m, 2H), 3.29 (s, 3H), 3.22 (s, 3H), 3.06 (m, 1H), 1.70–1.20 (14H), 0.87 (s, 9H), 0.8 (t, 3H, $J=6.0$ Hz), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C δ 108.41, 108.36, 80.4, 80.2, 72.1, 69.1, 69.0, 58.7, 56.1, 33.3, 33.2, 31.7, 29.3, 28.2, 28.1, 28.0, 27.9, 26.0, 25.0, 22.4, 17.9, 13.8, −5.8; IR 2955–2819, 1198, 1247, 1106; HRFAB calcd for $C_{20}H_{44}O_5SiLi$: (M+Li): 399.3118; found: 399.3132 (3.6 ppm).

4.4.14. [1-*tert*-Butyldimethylsilyldioxy]-4-iodo-1-(2-methoxyethoxy)-decane (14b). Ozonolysis of iodoundecene in 2-methoxyethanol furnished 4-iodo-1-(2-methoxyethoxy)-dec-1-yl-hydroperoxide in 1.7 g, 45% yield: $R_f=0.42$ (20% EA/hex); ^{1}H δ 10.36 (s, 0.5H), 10.33 (s, 0.5H), 4.83 (t, 0.8H, $J=6.31$ Hz), 4.21 (t, 0.2H, $J=$ 4.73 Hz), 4.12–4.06 (m, 1H), 3.86–3.78 (2H), 3.65–3.53 (2H), 3.434 (s, $J=1.6$ Hz), 3.431 (s, 1.4H), 1.87–1.63 (6H), 1.49–1.26 (8H), 0.86 (t, 3H, $J=6.9$ Hz); ^{13}C δ 106.4, 106.3, 72.8, 70.4, 65.5, 65.23, 63.5, 58.9, 40.71, 40.68, 40.5, 38.9, 38.7, 38.0, 35.8, 35.6, 35.4, 34.2, 31.6, 31.3, 29.35, 29.32, 28.4, 22.5, 13.9; IR 3370 (b), 1371, 1192, 1084; HRMS: no identifiable ions were observed.

Silylation of the hydroperoxyacetal furnished **14b** in 1.3 g, 79% yield. $R_f=0.36$ (2% EA/hex); ^{1}H δ 4.89–4.86 (1H), 4.10–4.01 (2H), 3.77 (m, 1H), 3.57–3.49 (2H), 3.36 (s, 1.5H), 3.356 (s, $J=1.5$ Hz), 1.92–1.62 (6H), 1.52–1.26 (8H), 0.92 (s, 9H), 0.86 (t, 3H, $J=6.9$ Hz), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C δ 107.6, 107.5, 72.2, 69.4, 69.3, 58.9, 58.89, 40.65, 40.6, 38.99, 38.9, 35.64, 35.56, 32.5, 32.3, 31.6, 29.4, 28.4, 26.1, 25.7, 25.6, 22.5, 18.1, 14.0, −3.0, −5.7; IR 2949–2849 (several bands), 1356, 1202, 1102; HRFAB calcd for $C_{19}H_{41}IO_4SiLi$ $(M+Li)^+$: 495.1229; found: 495.1995 (3.2 ppm).

4.5. Allylation of peroxyacetals (illustrated for 15d)

Into a 0 °C solution of silyl peroxy acetal **12d** (171 mg, 0.35 mmol) and allylsilane (2.0 equiv, 0.7 mmol, 0.1 mL) in CH_2Cl_2 (4 mL) under N_2, was added a solution of $SnCl_4$ in CH_2Cl_2, (nominally 1.0 M solution, 0.4 mL, dropwise). The reaction mixture was allowed to stir for 1hr, and then quenched with DI water. The organic extracts (50% recycled EA/hex, 3×15 mL) were dried over Na_2SO_4, and solvent was removed under reduced pressure. Flash chromatography (5% EA/hex) furnished 95 mg (60%) of the allylated peroxide (**15d**). Compounds **15a–f**, **16**, **17**, **19** and **21** were prepared similarly.

4.5.1. 4-(*tert*-Butyldimethylsilyldioxy)-6-(*tert*-butyldimethylsilyloxy)-1-tridecene (15a). Yield=63 mg, 65%. $R_f=0.82$ (5% EA/hex); ^{1}H δ 5.82 (m, 1H), 5.08 (dd, 1H, $J=$ 17.0, 1.9 Hz), 5.04 (dd, 1H, $J=9.1$, 1.9 Hz), 4.10–4.01 (m, 1H), 3.85–3.76 (m, 1H), 2.55–2.25 (2H), 1.80–1.27 (broad, 17H), 0.94 (s, 5.4H), 0.93 (s, 3.6H), 0.88 (s, 9H), 0.15 (s, 6H), 0.06 (s, 2.8H), 0.05 (s, 3.2H); ^{13}C δ 135.0/134.7, 116.9, 116.7, 81.94, 81.87, 69.8, 69.6, 39.7, 38.2, 37.8, 37.4, 37.0, 31.9, 29.8, 29.3, 26.2, 26.0, 25.96, 25.2, 24.9, 22.6, 18.2, 18.1, 14.0, 12.2, −4.2, −4.37, −4.41, −5.58, −5.61; IR 2962–2851, 1641, 1249; HRMS: no identifiable ions were observed.

4.5.2. 4-(*tert*-Butyldimethylsilyldioxy)-6-methoxy-1-tridecene (15b). Yield=61 mg, 60%. $R_f=0.64$ (5% EA/hex); ^{1}H δ 5.82 (ddt, 1H, $J=17.3$, 10.1, 6.9 Hz), 5.07 (broad dd, 1H, $J=15.1$, 1.9 Hz), 5.04 (broad dd, 1H, $J=10.4$, 1.6 Hz), 4.16–4.11 (m, 1H), 4.06–4.01 (m, 1H), 3.33 (s, 0.9H), 3.29 (s, 2.1H), 2.53–2.28 (m, 2H), 1.88 (m, 0.3H), 1.68–1.58 (m, 1.7H), 1.54–1.27 (12H), 0.94 (s, 9H), 0.88 (t, 3H, $J=6.9$ Hz), 0.16 (s, 1.4H), 0.15 (s, 4.5H); ^{13}C δ 134.8/134.6, 117.04/117.01, 81.9, 78.0, 56.0, 37.7, 37.2, 35.8, 35.7, 33.8, 31.8, 29.8, 29.3, 26.2, 25.2, 25.0, 22.6, 18.2, 14.0, 14.02, −5.6; IR 2948–2854, 1635, 1246, 1130; HRMS: no identifiable ions were observed.

4.5.3. 6-Benzyloxy-4-(*tert*-butyldimethylsilyldioxy)-1-tridecene (15c). Yield=60 mg, 50%. $R_f=0.55$ (5% EA/hex); ^{1}H δ 7.35–7.27 (5H), 5.85–5.77 (ddt, 1H, $J=17.0$, 10.1, 6.9 Hz), 5.19 (dd, 1H, $J=17.0$, 1.3 Hz), 5.15 (dd, 1H, $J=$ 10.4, 1.3 Hz), 4.50 (s, 1.2H), 4.49 (s, $J=0.8$ Hz), 4.11–4.06 (m, 0.4H), 3.71–3.66 (m, 0.6H), 3.57–3.53 (m, 0.4H), 3.47 (m, 0.6H), 2.52–2.17 (2H), 1.75–1.28 (14H), 0.94 (s, 3.7H), 0.89 (s, 5.3H), 0.90–0.88 (3H, along with *tert*-Bu) 0.05 (s, 3.6H), 0.049 (s, 2.4H); ^{13}C δ 139.0, 138.7, 135.4, 134.7, 134.6, 128.3, 128.7, 127.7, 127.6, 127.5, 127.43, 127.37, 117.1, 116.9, 116.5, 81.9, 76.5, 76.0, 72.9, 72.0, 71.2, 70.4, 41.9, 37.7, 37.5, 37.2, 36.7, 36.2, 34.4, 34.0, 31.8, 29.8, 29.7, 29.3, 26.3, 26.2, 25.9, 25.3, 25.2, 25.1, 22.6, 18.2, 18.1, 14.0, −1.0, −4.4, −4.5, −5.6; IR 2951–2848, 1638, 1502, 1469, 1247, 1209, 1095; HRMS: no identifiable ions were observed.

4.5.4. Acetic acid, 4-(*tert*-butyldimethylsilyldioxy)-1-tridecen-6-yl ester (15d). Yield=95 mg, 65%. $R_f=0.62$ (5% EA/hex); ^{1}H δ 5.78 (ddt, 1H, $J=17.0$, 9.0, 7.0 Hz), 5.18–4.99 (3H), 3.99–3.94 (m, 1H), 2.008 (s, 1.2H), 2.006 (s, 1.8H), 2.50–2.26 (m, 2H), 1.92–1.63 (m, 2H), 1.21 (broad, 12H), 0.92 (s, 3.2H). 0.91 (s, 5.8H), 0.83 (t, 3H, $J=6.9$ Hz), 0.13 (s, 3.4H), 0.12 (s, 2.6H); ^{13}C δ 170.46/170.42, 134.3/134.1, 117.4/117.2, 81.6/81.5, 71.9/71.5, 37.4, 36.7, 36.6, 36.0, 34.7, 34.3, 31.7, 34.3, 31.7, 29.4, 29.3, 29.1, 26.15,

26.13, 25.9, 25.8, 25.7, 25.2, 25.0, 22.6, 21.2, 18.1, 14.0, −5.72/-5.74; IR 2954–2853, 1736, 1640, 1232; HRFAB calcd for $C_{21}H_{42}O_4SiLi$ $(M+Li)^+$: 393.3012; found: 393.3009 (0.9 ppm).

4.5.5. Benzoic acid, 4-(*tert*-butyldimethylsilyldioxy)-1-tridecen-6-yl ester (15e). Yield=57 mg, 55%. R_f=0.43 (5% EA/hex); ^1H δ 8.04 (broad dd, 2H, J=5.4, 2.2 Hz), 7.56–7.53 (1H), 7.45–7.42 (2H), 5.8 (ddt, 1H, J=17.3, 10.7, 6.9 Hz), 5.29–5.22 (1H), 5.08 (broad dd, J=17.0, 1.9 Hz), 5.05 (broad dd, 1H, J=10.1, 1.9 Hz), 4.10–4.04 (1H), 2.55–2.42 (2H), 1.97–1.81 (2H), 1.76–1.60 (2H), 1.40–1.24 (10H), 0.92 (s, 3.5H), 0.916 (s, 5.4H), 0.86 (t, 3H, J=6.9 Hz), 0.13 (s, 4.3H), 0.10 (s, 1.7H); ^{13}C δ 166.05/166.01, 134.3, 134.1, 132.74/132.66, 130.8, 130.6, 129.56/129.51, 128.3, 117.5, 117.3, 81.58/81.55, 72.7, 72.1, 37.4, 36.7, 36.67, 36.0, 34.8, 34.4, 31.7, 29.5, 29.2, 26.1, 26.13, 25.2, 25.1, 22.6, 18.1, 14.0, −5.7; IR 2924–2859, 1719, 1638, 1458, 1500; HRMS: no identifiable ions were observed.

4.5.6. 2,2-Dimethylpropionic acid, 4-(*tert*-butyldimethylsilyldioxy)-1-tridecen-6-yl ester (15f). Yield=35 mg, 55%. R_f=0.69 (5% EA/hex); ^1H δ 5.76 (ddt, 1H, J=17.0, 10.4, 7.0 Hz), 5.07 (dd, 1H, J=11.3, 1.6 Hz), 5.05 (dd, 1H, J=6.6, 1.9 Hz), 4.99–4.93 (m, 1H), 4.91–4.86 (0.2H), 3.99–3.93 (0.8H), 2.51–2.26 (m, 2H), 1.82–1.65 (2H), 1.59–1.50 (2H), 1.31–1.22 (10H), 1.19 (s, 2.3H), 1.18 (s, 6.7H), 0.93 (s, 2.3H), 0.926 (s, J=6.7 Hz), 0.87 (t, 3H, J=6.9 Hz), 0.15 (s, 4.5H), 0.14 (s, 1.5H); ^{13}C δ 177.9, 177.8, 134.4, 134.2, 117.3, 117.2, 81.6, 81.58, 72.8, 71.6, 70.9, 45.2, 38.8, 38.7, 37.5, 36.8, 36.6, 36.1, 34.7, 34.3, 33.6, 31.7, 30.8, 29.43, 29.38, 29.2, 27.2, 26.2, 25.2, 25.1, 24.9, 22.6, 18.1, 14.0, −5.67, −5.68; IR 2928–2855, 1734, 1642, 1286; HRMS: no identifiable ions were observed.

4.5.7. Acetic acid, 3-(*tert*-butyldimethylsilyldioxy)-1-phenyl-hex-5-enyl ester (15h). Yield=11 mg, 10%. R_f=0.33 (5% EA/hex); ^1H δ 7.40–7.30 (5H), 5.90 (ddt, 1H, J=17.3, 10.7, 6.9 Hz), 5.20 (broad dd, 1H, J=17.0, 1.9 Hz), 5.12 (broad dd, 1H, J=9.1, 1.9 Hz), 5.19–5.09 (1H), 4.05–3.90 (t, 0.5H, J=6.6 Hz), 3.91 (t, 0.5H, J=6.0 Hz), 2.05 (s, 1.5H), 2.04 (s, 1.5H), 1.64–1.56 (2H), 1.38–1.25 (2H), 0.944 (s, 4.6H), 0.936 (s, 4.4H), 0.152–0.148 (s, 6H); ^{13}C δ 171.1, 169.9, 141.1, 134.7, 134.2, 128.6, 128.5, 128.2, 127.8, 127.0, 126.5, 117.9, 117.4, 116.9, 84.6, 82.2, 81.0, 80.4, 73.2, 72.7, 64.5, 47.7, 39.3, 37.5, 37.3, 36.9, 31.7, 28.6, 26.2, 25.1, 21.1, 20.9, 18.2, −1.09, −5.6, −5.7; IR 2957–2859, 1741, 1638, 1496, 1475, 1238; HRMS: no identifiable ions were observed.

4.5.8. 3-But-3-enyloxy-1-(2-methoxyethoxy)-1-(*tert*-butyldimethylsilyldioxy)-decane (16). Yield=63 mg, 45%. R_f=0.34 (10% EA/hex); ^1H δ 5.81 (ddt, 1H, J=17.0, 10.1, 0.9 Hz), 5.07 (broad dd, 1H, J=17.3, 1.6 Hz), 5.01 (broad dd, 1H, J=10.1, 0.9 Hz), 4.86 (t, 0.5H, J=6.0 Hz), 4.07–4.03 (m, 0.5H), 3.80–3.76 (m, 1H), 3.58–3.50 (m, 2H), 3.40 (t, 2H, J=6.9 Hz), 3.39 (2H, t, J=6.6 Hz), 3.36 (s, 3H), 2.31 (broad q, 2H, J=6.6 Hz), 1.66–1.53 (6H), 1.44–1.31 (8H), 0.93 (s, 9H), 0.88 (t, 3H, J=6.3 Hz), 0.16 (s, 3.1H), 0.15 (s, 2.8H); ^{13}C δ 135.4, 116.1, 108.5, 72.3, 70.8, 70.2, 69.2, 58.9, 34.2, 32.3, 29.6, 26.1, 26.0, 24.6, 18.1, −5.7; IR 2923–2855, 1632, 1642, 1106; HRMS: no identifiable ions were observed.

4.5.9. 6-But-3-enyloxy-tridec-1-en-4-yl *tert*-butyl dimethylsilyl peroxide (17). Yield=52 mg, 40%. R_f=0.7 (10% EA/hex); ^1H δ 5.86–5.75 (ddt, 2H, J=16.1, 10.4, 6.6 Hz), 5.08 (dd, 2H, J=16.7, 1.9 Hz), 5.03 (dd, 2H, J=10.4, 1.6 Hz), 3.90 (m, 1H), 3.45 (t, 1H, J=6.9 Hz), 3.40 (t, 1H, J=6.6 Hz), 3.40–3.50 (1H), 2.47–2.25 (4H), 1.57–1.22 (14H), 0.93 (s, 9H), 0.89–0.88 (3H), 0.15 (s, 3.1H), 0.14 (2.9H); ^{13}C δ 135.3, 134.7, 116.2, 84.6, 70.8, 70.1, 36.8, 34.2, 31.7, 29.7, 29.6, 26.2, 25.9, 25.3, 18.1, −5.6; IR 2928–2855, 1632, 1642, 1111; HRMS: no identifiable ions were observed.

4.5.10. Ethyl-4-*tert*-butyldimethylsilyldioxy-4-(2-methoxyethoxy)-2-trimethylsilylbutyrate (18). 4-Hydroperoxy-4-(2-methoxyethoxy)-2-trimethylsilyl-butyric acid ethyl ester was prepared by ozonolysis of 2-trimethylsilyl-pent-4-enoic acid ethyl ester in 2.9 g, 58% yield: R_f=0.33 (20% EA/hex); ^1H δ 10.1 (s, 0.5H), 10.0 (s, 0.5H), 4.71 (broad q, 2H, J=5.7 Hz), 4.08–3.99 (1H), 3.81–3.68 (2H), 3.60–3.44 (2H), 3.36 (s, 1.4H), 3.35 (s, 1.6H), 2.23–2.15 (m, 0.5H), 2.09–1.96 (0.5H), 1.80 (broad dd, 1H, J=7.88 Hz),1.65 (broad dd, 1H, J=6.3 Hz), 1.17 (broad dd, 3H, J=6.9, 7.2 Hz), 0.16 (s, 5H), 0.01 (s, 4H); ^{13}C δ 175.7, 175.0, 106.9, 106.3, 72.5, 72.2, 66.1, 65.8, 60.0, 59.7, 58.8, 58.7, 33.2, 32.5, 28.1, 27.9, 14.2, −2.9, −3.0; IR 3335, 1716, 1252, 1100–1130; HRMS: no identifiable ions were observed.

Silylation of the hydroperoxide under standard conditions afforded silyl peroxide **18** in 916 mg, 88% yield: R_f=0.67 (20% EA/hex); ^1H δ 4.86 (dd, 0.8H, J=3.8, 7.9 Hz), 4.82–4.80 (dd, 0.2H, J=3.8, 7.9 Hz), 4.11–4.04 (1.4H), 4.03–3.98 (0.6H), 3.76–3.71 (1.3H), 3.53–3.46 (2.7H), 3.34 (s, 0.6H), 3.33 (s, 2.4H), 2.22 (t, 0.7H, J=2.2 Hz), 2.20 (0.3H), 2.14–1.56 (2H), 1.21 (broad t, 3H, J=6.9 Hz), 0.90 (s, 6H), 0.83 (s, 3H), 0.14 (s, 2H), 0.04 (s, 4H), −0.01 (s, 9H); ^{13}C δ 174.7, 174.6, 107.7, 107.2, 72.0, 71.9, 69.7, 68.9, 59.7, 58.8, 58.7, 32.7, 32.6, 30.2, 28.9, 26.1, 25.63, 25.6, 18.06, 18.0, 14.4, 14.3, −2.76, −2.8, −3.0, −5.8. IR 2952–2859, 1714, 1464, 1252, 1160, 1100; HRFAB calcd for $C_{18}H_{40}O_6Si_2Li$ $(M+Li)^+$: 415.2523, found: 415.2527 (0.8 ppm).

4.5.11. 4-*tert*-Butyldimethylsilyldioxy-2-trimethylsilyl-6-heptenoic acid ethyl ester (19). The title compound was prepared by allylation of **18** under standard conditions: Yield=200 mg, 55%. R_f=0.48 (5% EA/hex); ^1H δ 5.8 (ddt, 1H, J=17.6, 10.4, 7.2 Hz), 5.08 (broad dd, 1H, J=17.3, 1.6 Hz), 5.04 (broad dd, 1H, J=10.1, 1.6 Hz), 4.14–4.04 (m, 2.3H), 3.93–3.83 (m, 0.7H), 2.55–1.96 (2H), 1.77–1.66 (0.5H), 1.70–1.66 (0.5H), 1.60–1.56 (2H), 1.21 (t, 2H, J=2.0 Hz), 1.99 (t, 1H, J=2.0 Hz), 0.92 (s, 2.8H), 0.91 (s, 6.2H), 0.16 (s, 0.7H), 0.14 (s, 1.2H), 0.13 (s, 2H), 0.11 (s, 2.1H), 0.06 (s, 3.4H), 0.05 (s, 5.6H); ^{13}C δ 175.07/175.04, 134.6, 134.4, 117.0, 116.8, 101.6, 84.6, 84.2, 59.7, 59.6, 37.5, 35.7, 33.8, 33.1, 31.6, 29.4, 28.3, 26.2, 25.8, 22.6, 18.2, 18.1, 14.4, 14.0, −2.6, −2.68, −2.75, −5.7; IR 2949–2855, 1714, 1638, 1252; HRMS: no identifiable ions were observed.

4.5.12. Formation of silatrioxepane: 3,3-di-*tert*-butyl-5-heptyl-7-(2-methoxyethoxy)-3-sila-[1,2,4]-trioxepane (20). 1-Hydroperoxy-1-(2-methoxyethoxy)-decan-3-ol was prepared by ozonolysis of undecen-4-ol in

2-methoxyethanol in 530 mg, 65% yield: R_f=0.37 (40% EA/hex); ^{1}H δ 10.8 (s, 0.1H), 10.46 (s, 0.9H), 5.09 (t, 0.1H, J=4.7 Hz), 5.05–4.99 (0.9H), 3.91–3.85 (0.6H), 3.84–3.76 (2H), 3.64–3.52 (2H), 3.40 (s, 1.3H), 3.40 (s, J=1.7 Hz), 3.36–3.34 (0.4H), 2.84 (broad peak, 2H), 1.91–1.23 (13H), 0.84 (broad t, 3H, J=6.3 Hz); ^{13}C δ 106.2, 106.1, 72.6, 72.5, 68.4, 68.3, 66.9, 66.3, 66.5, 58.8, 38.7, 38.5, 37.4, 31.7, 31.0, 29.5, 29.1, 25.5, 25.4, 25.3, 22.5, 13.9; IR 3364, 1198, 1143, 1095; HRMS: no identifiable ions were observed.

A solution of *tert*-BuSi(OTf)$_2$ (700 mg, 0.6 mL, 1.6 mmol, 3.0 equiv) and imidazole (180 mg, 2.6 mmol, 5 equiv) in DMF (2 mL) was stirred for few minutes, after which was added a dropwise solution of the hydroperoxyalcohol (140 mg, 0.53 mmol) in DMF (2 mL). After 15 min the reaction mixture was quenched with DI water and extracted into recycled 50% EA/hex (3×50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Flash chromatography (20% EA/Hex) furnished 85 mg (45%) of silatrioxepane (**20**): R_f=0.68 (20% EA/hex); ^{1}H δ 5.02 (t, 0.4H, J=4.1 Hz), 4.93–4.91 (m, 0.6H), 4.10–4.12 (0.4H), 4.00–3.96 (0.6H), 3.71–3.59 (2H), 3.56–3.51 (2H), 3.375 (s, 1.1H), 3.372 (s, 1.9H), 2.23–2.18 (0.8H), 1.92–1.83 (m, 1.2H), 1.57–1.26 (12H), 1.07 (s, 5.7H), 1.05 (s, 3.3H), 1.03 (s, 2.8H), 1.0 (s, 6.2H), 0.87 (broad t, 3H, J=6.0 Hz); ^{13}C δ 107.4, 104.4, 71.9, 71.5, 70.6, 67.2, 67.1, 59.0, 58.98, 40.6, 40.4, 38.6, 37.5, 31.8, 31.7, 29.5, 29.44, 29.37, 29.3, 29.1, 28.1, 28.0, 27.9, 27.7, 27.5, 27.2, 27.0, 26.9, 26.7, 25.9, 25.3, 24.9, 22.6, 21.9, 21.5, 20.5, 20.3, 14.1; IR 2933–2850, 1111; HRFAB calcd for $C_{21}H_{44}O_5SiNa$ $(M+Na)^+$: 427.2858, found: 427.2867 (2.7 ppm).

4.5.13. 3,3-Di-*tert*-butyl-5-heptyl-7-(2-propenyl)-1,2,4,3-trioxasilepane (21). The title compound was prepared by allylation of **20** under conditions similar to those described for compound **15d**: yield=4 mg, 5%. R_f=0.78 (5% EA/hex); ^{1}H δ 5.86 (ddt, 1H, J=17.3, 10.1, 6.9 Hz), 5.07 (dd, 1H, J=17.3, 1.6 Hz), 5.05 (dd, 1H, J=9.1, 1.3 Hz), 4.16 (m, 1H), 4.08 (m, 1H), 2.43–2.37 (1H), 2.24–2.18 (m, 1H), 1.78–1.67 (2H), 1.63–1.56 (1H), 1.43–1.28 (11H), 1.0 (s, 4.6H), 0.99 (s, 4.4H), 0.96 (s, 4.6H), 0.95 (s, 4.4H), 0.88 (broad t, 3.0H, J=6.9 Hz); ^{13}C δ 135.3, 116.7, 100.8, 70.0, 42.3, 38.2, 37.9, 31.8, 29.7, 29.5, 29.3, 27.6, 27.5, 27.3, 27.1, 25.6, 22.6, 21.0, 14.1, 9.4, 2.1; IR 2930–2848, 1638, 1247, 1073; HRMS: no identifiable ions were observed.

4.5.14. Reduction of peroxides: tridec-1-ene-4,6-diol (22). Into a solution of allylated peroxide **15d** (201 mg, 0.52 mmol) in THF (6 mL) was added $LiAlH_4$ (2.6 mmol, 99 mg). The reaction was stirred overnight, and then quenched with dilute HCl. The extracts (50% recycled EA/hex, 3×15 mL) were dried over Na_2SO_4, and solvent was removed in vacuo. The crude product was purified by flash chromatography (20% EA/hex) to furnish 62 mg (55%) and 35 mg (35%) of diastereomeric diols.

Minor diastereomer. R_f=0.51 (40% EA/hex); ^{1}H δ 5.81 (ddt, 1H, J=16.4, 9.5, 6.9 Hz), 5.08 (dd, 1H, J=17.0, 1.9 Hz), 5.04 (dd, 1H, J=10.4, 2.2 Hz), 3.93–3.88 (m, 1H), 3.87–3.82 (m, 1H), 2.88 (broad s, 2H), 2.29–2.19 (m, 2H), 1.64–1.60 (2H), 1.52–1.39 (4H), 1.33–1.24 (8H), 0.88 (t, 3H, J=6.6 Hz); ^{13}C δ 134.4, 118.2, 72.9, 71.9, 42.64/42.60, 38.2, 31.8, 29.6, 29.2, 25.4, 22.6, 14.0.

Major diastereomer. R_f=0.49 (40% EA/hex); ^{1}H δ 5.8 (ddt, 1H, J=16.4, 9.1, 5.4 Hz), 5.15–5.11 (2H), 4.01–3.96 (m, 1H), 3.93–3.90 (m, 1H), 2.44 (broad s, 2.0H), 2.28–2.25 (m, 2H), 1.62–1.60 (2H), 1.53–1.28 (12H), 0.88 (t, 3H, J=6.9 Hz); ^{13}C δ 134.7, 118.0, 69.3, 68.27, 42.1, 37.5, 31.8, 29.6, 29.2, 25.7, 22.6, 14.6, 14.0; IR 3347 (b), 1637; HRFAB calcd for $C_{13}H_{26}O_2Li$ $(M+Li)^+$: 221.2093, found: 221.2086 (3.2 ppm).

4.5.15. Formation of acetonides: 4-(2-propenyl)-6-heptyl-2,2-dimethyl-1,3-dioxane (23). Into a solution of diol **22** (100 mg, 0.46 mmol) in 2,2-dimethoxypropane (6 mL, excess), was added a catalytic amount of *S*-(+)-camphor sulphonic acid (5 mg). The reaction mixture was stirred for twenty minutes, after which solvent was removed in vacuo. The crude product was purified by flash chromatography (5% EA/hex) to furnish 71 mg (60%) of a mixture of diastereomeric acetonides: R_f=0.65 (10% EA/hex); ^{1}H δ 5.88 (ddt, 1H, J=17.3, 10.0, 6.9 Hz), 5.09 (broad dd, 1H, J=17.3, 1.9 Hz), 5.04 (broad dd, 1H, J=10.4, 1.8 Hz), 3.88–3.81 (m, 1H), 3.79–3.72 (m, 1H), 2.32–2.26 (1H), 2.20–2.11 (1H), 1.51–1.47 (4H), 1.38 (s, 3H), 1.339 (s, 3H), 1.30–1.27 (10H), 0.87 (t, 3H, J=6.9 Hz).

Mixture of diastereomers. DEPT 135 ^{13}C δ 134.6 (+), 134.3 (+), 116.9 (−), 116.7 (−), 100.1 (−), 98.3 (−), 69.0 (+), 68.7 (+), 66.6 (+), 66.2 (+), 40.9 (−), 40.2 (−), 38.2 (−), 36.5 (−), 36.49 (−), 36.0 (−), 31.8 (−), 30.3 (+), 29.7 (−), 29.55 (−), 29.5 (−), 29.23 (−), 29.21 (−), 25.3 (−), 24.95 (+), 24.87, 24.8 (+), 22.6 (−), 19.8 (+), 14.0 (+); IR 1638, 1165, 1116; HREI calcd for $C_{15}H_{27}O_2$ $(M-CH_3)^+$: 239.2011; found: 239.2012 (0.4 ppm).

4.5.16. Tridecane-4, 6-diol (24). Peroxide **15c** (345 mg, 0.8 mmol), and BHT (5 mg), were dissolved in THF/AcOH/H_2O (5:3:2, 10 mL). Following disappearance of starting material (2 days, TLC), triphenyl phosphine (4 mmol, 1 g) was added. After an additional 24 h, the reaction mixture was diluted with 50 mL of 40% recycled EA/hex, and washed sequentially with saturated NH_4Cl (4×20 mL) solution and brine solution (2×15 mL). The separated organic layers were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (5% EA/hex) furnished 217 mg (89%) of 4-hydroxy 6-benzyloxy tridecene as an inseparable mixture of diastereomers. R_f=0.2 (5% EA/hex); ^{1}H δ 7.35–7.27 (5H), 5.84 (ddt, 1H, J=17.3, 10.4, 7.2 Hz), 5.14 (dd, 1H, J=17.0, 1.9 Hz), 5.12 (dd, 1H, J=10.0, 2.0 Hz), 4.64 (d, 0.6H, J=11.3 Hz), 4.44 (d, 0.6H, J=11.3 Hz), 4.56 (dd, 0.5H, J=11.3, 15.3 Hz), 3.99–3.94 (0.3H), 3.86–3.81 (1H), 3.73–3.65 (1H), 3.53 (s, 0.9H), 2.78 (s, 0.1H), 2.27–2.17 (2H), 1.72–1.50 (4H), 1.37–1.24 (broad, 10H), 0.90 (t, 3H, J=6.9 Hz); ^{13}C δ 138.2, 135.0, 134.9, 128.4, 128.3, 127.8, 127.7, 127.6, 117.3, 117.1, 79.6, 71.2, 70.7, 70.6, 67.8, 42.2, 42.1, 40.5, 39.7, 33.6, 33.5, 31.7, 29.8, 29.7, 29.2, 25.4, 24.7, 22.6, 13.9; IR 3449, 1647, 1494, 1451; HREI calcd for $C_{20}H_{33}O_2$ $(M+H)^+$: 305.2481; found: 305.2483 (0.9 ppm).

A mixture of 4-hydroxy-6-benzyloxy tridecene (217 mg,

0.71 mmol) and 10% Pd/C (10 mol%, 76 mg) in MeOH (5 mL) was placed under an atmosphere of H_2 (balloon). After 3 days, the reaction mixture was filtered through a plug of cotton and the solvent was removed under reduced pressure. Flash chromatography (20% EA/Hex) furnished tridecane-4,6-diol (**24**) as a mixture of two diastereomers in a total yield of 78%. The first eluting diastereomer was a colorless oil (86 mg). The second eluting isomer was a white solid (35 mg).

Major diastereomer. R_f=0.3 (20% EA/hex); ^{1}H δ 3.81–3.80 (2H), 3.53 (broad peak, 2H), 1.58–1.26 (18H), 0.9 (t, 3H, J=6.3 Hz), 0.85 (t, 3H, J=6.3 Hz); ^{13}C δ 73.1, 72.8, 42.7, 40.32, 38.2, 31.8, 29.6, 29.2, 25.3, 22.6, 18.5, 14.0, 13.99; IR 3294, 1062.

Minor diastereomer. Mp 55–56 °C; ^{1}H δ 3.93–3.89 (2H), 2.53 (broad peak, 2H), 1.60–1.28 (18H), 0.92 (t, 3H, J=6.3 Hz), 0.87 (t, 3H, J=6.3 Hz); ^{13}C δ 69.4, 69.1, 42.3, 39.6, 37.5, 31.8, 29.6, 29.2, 25.8, 22.6, 18.9, 14.0, 12.1; HRFAB calcd for $C_{13}H_{28}O_2Li$ $(M+Li)^+$: 223.2249, found: 223.2240 (4.1 ppm).

4.5.17. 2,2-Dimethyl- 4-heptyl-6-propyl-1,3-dioxane (25). Into a solution of diol **24** (70 mg, 0.32 mmol) in 2,2 dimethoxypropane (4 mL, excess), was added (*S*)-(+)-camphor sulfonic acid (5 mg). After 30 min solvent was removed in vacuo. Flash chromatography (5% EA/hex) furnished 80 mg (96%) of acetonide. R_f=0.5 (5% EA/hex) ^{1}H δ 3.80–3.73 (2H), 1.54–1.44 (3H), 1.40 (s, 3H), 1.36 (s, 3H), 1.34–1.25 (14H), 1.07 (q, 1H, J=11.9 Hz), 0.88 (t, 3H, J=6.6 Hz), 0.86 (t, 3H, J=6.6 Hz); DEPT 135 ^{13}C δ 69.0 (+), 68.7 (+), 38.6 (−), 37.0 (−), 36.5 (−), 31.8 (−), 30.3 (−), 29.5 (−), 29.2 (−), 24.9 (−), 22.6 (−), 19.8 (+), 18.1 (−), 14.0 (+), 13.97 (+), 12.1 (−); IR 1165, 1116; HREI calcd for $C_{13}H_{28}O_2Li$ $(M+H)^+$: 257.2481, found: 257.2483 (0.9 ppm).

4.5.18. 4-*tert*-Butyldioxy-5-iodo-dodec-1-ene (26). Into a −78 °C solution of iodoperoxy acetal (0.35 mmol, 134 mg) **3a** and allylsilane (2 equiv, 0.7 mmol, 0.1 mL) in CH_2Cl_2 (5 mL) was added drop wise $SnCl_4$ (1.1 equiv, 0.4 mL, 1.0 M in CH_2Cl_2). After 30 min the reaction mixture was quenched with DI water and allowed to warm to room temperature. The combined extracts (recycled 50% EA/hex, 3×30 mL) were dried over Na_2SO_4 and concentrated. Flash chromatography (2% EA/Hex) furnished allylated peroxide in 48 mg, 35% yield. R_f=0.88 (2% EA/hex); ^{1}H δ 5.89 (ddt, 1H, J=17.0, 10.0, 6.9 Hz), 5.14 (dd, 1H, J=17.3, 1.6 Hz), 5.08 (dd, 1H, J=10.1, 1.8 Hz), 4.51 (dt, 1H, J=9.8, 4.1 Hz), 4.41 (m, 0.1H), 3.95 (m, 0.1H), 3.46 (m, 0.9H), 2.40–2.37 (2H), 1.86–1.58 (3H), 1.40–1.26 (broad 9H), 1.25 (s, 8.2H), 1.23 (s, 1.1H), 0.88 (t, 3H, J=6.6 Hz); ^{13}C δ 134.7/134.3, 117.3/117.2, 85.0, 80.4, 40.4, 36.5, 36.0, 31.8, 29.9, 29.8, 29.11/29.07, 28.8, 26.7, 26.5, 22.6; IR 2977–2844, 1643, 1358, 1252, 1196; HRFAB calcd for $C_{13}H_{26}IO_2$ $(M-allyl)^+$: 341.0978; found: 341.0207 (22 ppm).

4.5.19. 4-*tert*-Butyldioxy-5-iodo-undec-1-ene (27). The title compound was prepared by allylation of iodoperoxy acetal **4a** at 0 °C (43 mg, 23%). R_f=0.63 (2% EA/hex); ^{1}H δ 5.90 (ddt, 1H, J=17.3, 10.4, 7.2 Hz), 5.15 (broad dd, 1H, J=17.0, 1.6 Hz), 5.08 (broad dd, 1H, J=10.1, 1.6 Hz), 4.56–4.54 (m, 0.8H), 4.47–4.43 (0.2H), 4.01–3.98 (m, 0.2H), 3.49–3.46 (0.8H), 2.44–2.30 (2H), 1.75–1.59 (2H), 1.36–1.29 (8H), 1.25 (s, 7.5H), 1.23 (s, 1.5H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C δ 134.7, 134.3, 117.3, 117.2, 85.7, 85.0, 80.5, 80.4, 40.8, 38.6, 36.4, 36.0, 34.4, 34.2, 31.6, 30.3, 29.9, 29.7, 28.53, 28.49, 26.7, 26.5, 22.6, 22.2, 14.1; IR 1642, 1243, 1199; HRMS: no identifiable ions were observed.

Allylation of peroxyacetals **5** and **14a,b** was carried out under similar procedures as described earlier.

4.5.20. 1-Triphenylsilyl-4-penten-2-yl *tert*-butyldimethylsilylperoxide (28). The title compound was prepared by allylation of triphenylsilyl peroxyacetal **5**. Yield= 118 mg, 60%. R_f=0.33 (2% EA/hex); ^{1}H δ 7.75–7.64 (6H), 7.48–7.40 (9H), 5.80 (ddt, 1H, J=17.0, 10.1, 6.9 Hz), 5.05 (dd, 1H, J=10.7, 1.9 Hz), 4.88 (1H, dd, J=17.0, 1.6 Hz), 4.35 (m, 1H), 2.24 (m, 2H), 0.96 (d, 2H, J= 7.8 Hz), 0.98 (s, 9H), 0.18–0.10 (overlapping s, 6H). ^{13}C δ 135.7, 134.9, 134.5, 129.5, 127.8, 117.2, 82.2, 38.9, 26.1, 18.1, 16.9, 2.0, −5.5, −5.6; IR 1639, 1493, 1477, 1362; HRFAB calcd for $C_{29}H_{38}O_2Si_2Li$ $(M+Li)^+$: 481.2571; found: 481.2583 (2.4 ppm).

4.5.21. 7-Methoxy-tridec-1-en-4-yl *tert*-butyldimethylsilyl peroxide (29a). The title compound was prepared by allylation of peroxyacetal **14a**. Yield=87 mg, 78%. R_f= 0.73 (10% EA/hex); ^{1}H δ 5.80 (ddt, 1H, J=17.0, 10.1, 6.9 Hz), 5.06 (dd, 1H, J=17.0, 1.6 Hz), 5.04 (dd, 1H, J= 9.1, 1.9 Hz), 3.91 (m, 1H), 3.30 (s, 3H), 3.11 (m, 1H), 2.49–2.43 (1H), 2.31–2.20 (1H), 1.64–1.18 (14H), 0.93 (s, 9H), 0.88 (t, 3H, J=6.3 Hz), 0.15 (s, 3.4H), 0.14 (s, 2.6H); ^{13}C δ 134.7, 116.8, 84.9, 84.7, 80.9, 80.7, 56.3, 56.2, 37.0, 33.45/ 33.41, 31.8, 29.7, 29.5, 29.2, 28.8, 27.6, 26.2, 26.1, 25.3, 25.2, 22.6, 18.2, 14.0, −5.6; IR 2954–2810, 1650, 1193, 1093; HRMS: no identifiable ions were observed.

4.5.22. 4-*tert*-Butyldimethyl silyldioxy-7-iodo-tridec-1-ene (29b). The title compound was prepared by allylation of acetal **14b** under standard conditions. Yield=68 mg, 30%. R_f=0.8 (2% EA/hex); ^{1}H δ 5.80 (ddt, 1H, J=17.0, 10.1, 6.9 Hz), 5.08 (broad dd, 1H, J=17.0, 1.6 Hz), 5.06 (broad dd, 1H, J=10.1, 1.6 Hz), 4.15–4.07 (1H), 3.95–3.89 (1H), 2.49–2.42 (1H), 2.31–2.23 (1H), 1.95–1.63 (5H), 1.47–1.24 (9H), 0.94 (s, 9H), 0.90 (t, 3H, J=6.6 Hz), 0.16 (s, 2.4H), 0.15 (s, 3.6H); ^{13}C δ 134.43/134.40, 84.2, 83.7, 40.71, 40.68, 39.8, 39.76, 36.9, 36.7, 36.2, 32.0, 31.8, 31.7, 29.7, 29.5, 29.4, 28.5, 26.2, 22.6, 18.2, 14.0, −5.62, −5.64; IR 1642, 1247, 1151; HRMS: no identifiable ions were observed.

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