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$FeCl_3·6H_2O$, a Catalyst for the Diastereoselective Synthesis of *cis*-Isoxazolidines from *N*-Protected *δ*-Hydroxylamino Allylic Acetates

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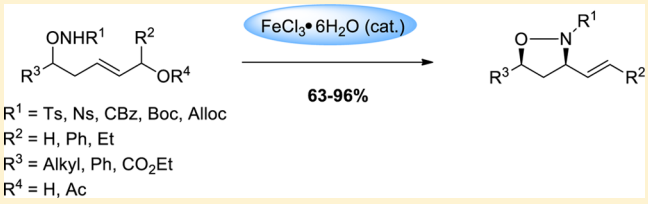
Supporting Information

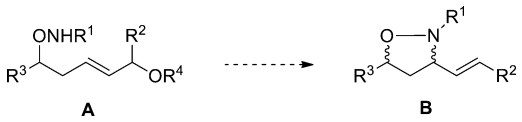
ABSTRACT: An ecofriendly and diastereoselective synthesis of *cis*-3,5-disubstituted isoxazolidines through the $FeCl_3·6H_2O$-catalyzed cyclization of *δ*-hydroxylamino allylic acetates is described. The synthetic potential of these products is highlighted by the preparation of several functionalized 1,3-amino alcohol precursors.



INTRODUCTION

Nitrogen- and oxygen-containing heterocyclic frameworks are ubiquitous subunits in biologically active products, and among them, isoxazolidines represent an interesting class of heterocycles bearing both an oxygen and a nitrogen atom embedded in a five-membered ring. Isoxazolidines can be encountered in natural products such as dactylicapnosine and pyrinodemin A,[1] and they can be precursors of various 1,3-amino alcohols when the N−O bond is reductively cleaved.[2] Although convenient methods for the construction of substituted isoxazolidines exist, the development of highly stereoselective and ecofriendly reactions to access these heterocycles remains a challenge.[3−5] Among the existing methods to synthesize isoxazolidines, metal-catalyzed cyclizations of *δ*-hydroxylamino alkenes and *δ*-hydroxylamino allenes using palladium,[6] copper,[7] silver,[8] or gold complexes[9] are attractive methods.[10,11] Recently, we have reported a highly diastereoselective synthesis of *cis*-2,6-disubstituted piperidines through the cyclization of *N*-protected *ζ*-amino allylic acetates under thermodynamic conditions.[12] Herein, we report that $FeCl_3·6H_2O$ is able to catalyze the cyclization of *δ*-hydroxylamino allylic alcohol derivatives of type **A** to produce substituted isoxazolidines **B** with good diastereoselectivities (Scheme 1).

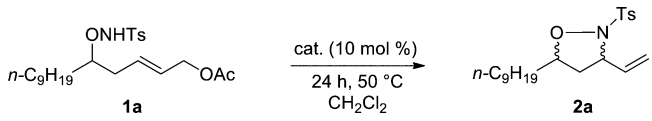
Scheme 1. Objective of the Study



RESULTS AND DISCUSSION

Synthesis of Isoxazolidines. In order to maximize the conditions allowing the cyclization of **A** to **B**, substrate **1a** was treated with various Brønsted and Lewis acids (Table 1). When *N*-tosyl *δ*-hydroxylamino allylic acetate **1a** was treated with 10 mol % of HCl, HBr/AcOH, CF_3CO_2H, or $H_2SO_4·SiO_2$ in CH_2Cl_2 for 24 h at 50 °C, no reaction occurred and **1a** was recovered (Table 1, entries 1−4). In the presence of PTSA·H_2O or TfOH, the conversion of **1a** was incomplete even after 24 h (Table 1, entries 5 and 6). When Lewis acids such as $ZnBr_2$, $Cu(OTf)_2$, $Zn(OTf)_2$, $La(OTf)_3$, or $InCl_3$ were used, isoxazolidine **2a** was formed, however, with incomplete conversion of **1a** (Table 1, entries 7−11), whereas the use of AgOTf led to almost full conversion of **1a** providing **2a** as a 90/10 *cis*/*trans* diastereomeric mixture (Table 1, entry 12).[13] The best results were obtained by using $TiCl_4$, $Bi(OTf)_3$, and $FeCl_3·6H_2O$[14] as **2a** was isolated in excellent yields with a 90/10 *cis*/*trans* ratio (Table 1, entries 13−15).[15,16] As $FeCl_3·$

Table 1. Evaluation of Various Brønsted and Lewis Acids



entry	catalyst	yield, % (conversion, %)[a]	*cis*/*trans* ratio[a]
1	HCl aq (2N)	0	–
2	HBr/AcOH	0	–
3	TFA	0	–
4	$H_2SO_4·SiO_2$	0	–
5	PTSA·H_2O	(21)	nd
6	TfOH	(59)	85/15
7	$ZnBr_2$	(50)	nd
8	$Cu(OTf)_2$	(80)	nd
9	$Zn(OTf)_2$	(77)	nd
10	$La(OTf)_3$	(67)	nd
11	$InCl_3$	(33)	nd
12	AgOTf	(96)	90/10
13	$TiCl_4$	(95)	90/10
14	$Bi(OTf)_3$	93 (100)	90/10
15	**$FeCl_3·6H_2O$**	**94 (100)**	**90/10**

[a]Ratio determined by ^1H NMR on the crude reaction mixture.

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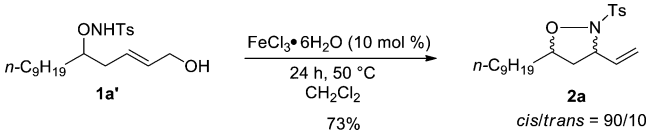
$6H_2O$ is cheap, easy to handle, and environmentally benign, it was selected to determine the scope and limitations of the δ-hydroxylamino allylic acetate cyclization.

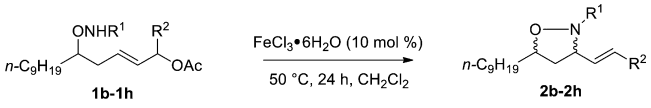
To study the influence of the nature of the leaving group on the cyclization, *N*-tosyl δ-hydroxylamino allylic alcohol **1a′** was prepared and treated with 10 mol % of $FeCl_3{\cdot}6H_2O$ (Scheme 2). Cyclization of this δ-hydroxylamino allylic alcohol proceeded with a lower yield of 73% compared to the cyclization of the corresponding δ-hydroxylamino allylic acetate (94%) (Table 1, entry 15). As a consequence, we decided to use allylic acetates for further studies.

Scheme 2. Influence of the Leaving Group



The influence of the *N*-protecting groups in **1** (R^1 group) and of the allylic substituent (R^2 group) on the cyclization was examined, and the results are summarized in Table 2. The replacement of the *N*-tosyl group by a *N*-nosyl group resulted in similar results as **2b** was isolated in 95% yield and with a 89/11 *cis*/*trans* ratio (Table 2, entry 1). The presence of a *N*-carbamate group in **1c** (*N*-Cbz) and **1d** (*N*-Alloc) provided the expected isoxazolidines **2c** and **2d** in 63% and 95% yield respectively, with a 85/15 *cis*/*trans* ratio (Table 2, entries 2 and 3). However, when a *N*-Boc or a *N*-Ac group was present in **1** such as in **1e** and **1f**, no conversion of these latter was observed (Table 2, entries 4 and 5). In addition, with **1g** and **1h** bearing an allylic phenyl substituent (R^2 = Ph), the corresponding isoxazolidines were isolated in good yield and diastereoselectivity (78% and 86% yields, respectively, with a 80/20 *cis*/*trans* ratio) (Table 2, entries 6 and 7). Noteworthy, contrary to **1f**, **1h** possessing a *N*-Boc protecting group and a phenyl R^2 substituent cyclized when treated with $FeCl_3{\cdot}6H_2O$ (Table 2, entry 7).

Table 2. Influence of the *N*-Protecting Group and of the Allylic Substituent on the Cyclization

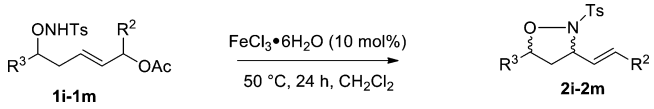


entry	R^1	R^2	1	2 (yield, %)	*cis*/*trans* ratio[a]
1	Ns	H	**1b**	**2b** (95)	89/11
2	Cbz	H	**1c**	**2c** (63)	85/15
3	Alloc	H	**1d**	**2d** (95)	85/15
4	Ac	H	**1e**	0	
5	Boc	H	**1f**	0	
6	Ts	Ph	**1g**	**2g** (78)	80/20
7	Boc	Ph	**1h**	**2h** (86)	60/40

[a]Determined by ^{1}H NMR.

The reaction conditions were applied to an array of *N*-tosyl δ-hydroxylamino allylic acetates **1i−o** to form the corresponding isoxazolidines **2i−o**; the results are reported in Table 3 and in Scheme 3. In the absence of any R^3 substituent (R^3 = H) and with an R^2 ethyl substituent (**1i**, R^2 = Et), isoxazolidine **2i** was isolated with excellent yield of 96% (Table 3, entry 1). Different R^3 alkyl groups (R^3 = Cy, Me) were introduced, and the corresponding isoxazolidines **2j,k** were isolated in good yields. When **1j** (R^2 = H, R^3 = Cy) was treated with $FeCl_3{\cdot}6H_2O$, the corresponding isoxazolidine **2j** was obtained with good yield and diastereoselectivity (Table 3, entry 2). In the absence of any allylic substitutent (R^2 = H), a good *cis*/*trans* ratio was observed even when a R^3 methyl group was present (Table 3, entry 3). When R^3 was a phenyl group, and in the absence of any allylic substituent (R^2 = H), an excellent yield of 95% in isoxazolidine **2l** was obtained and the *cis*/*trans* ratio was 86/14 (Table 3, entry 4). In the presence of an ester substituent as in **1m** (R^3 = CO_2Et), no conversion of the starting material was observed (Table 3, entry 5).[17]

Table 3. Synthesis of 3,5-Disubstituted Isoxazolidines

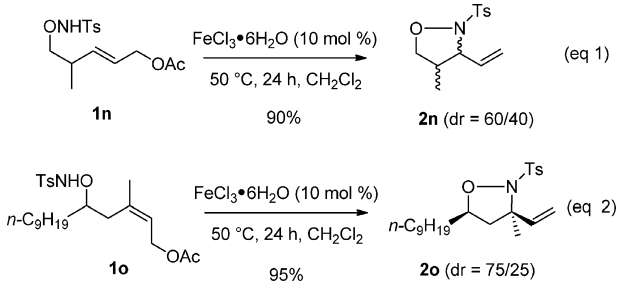


entry	R^2	R^3	1	2[a] (yield, %)	*cis*/*trans* ratio[b]
1	Et	H	**1i**	**2i** (96)	
2	H	Cy	**1j**	**2j** (83)	86/14
3	H	Me	**1k**	**2k** (83)	83/17
4	H	Ph	**1l**	**2l** (92)	86/14
5	H	CO_2Et	**1m**	**2m** (0)	

[a]Only the (*E*)-isomer was observed by ^{1}H NMR. [b]Determined by ^{1}H NMR.

In addition, allylic acetate **1n** bearing a methyl group at the γ position was synthesized and treated with 10 mol % of $FeCl_3{\cdot}6H_2O$ (Scheme 3, eq 1). The expected isoxazolidine **2n** was isolated with a good yield of 90% but with low diastereoselectivity (dr = 60/40). Interestingly, the presence of a trisubstituted double bond as in **1o** was tolerated as the corresponding isoxazolidine **2o** possessing a quaternary center was formed in 95% yield with a diastereomeric ratio of 75/25 (Scheme 3, eq 2).

Scheme 3. Synthesis of 3,4-Disubstituted and 3,3,5-Trisubstituted Isoxazolidines



It is worth noting that a six-membered ring was formed through the $FeCl_3{\cdot}6H_2O$-catalyzed cyclization of *N*-tosyl ε-hydroxylamino allylic acetate **1p** (Scheme 4). The reaction proceeded in good yield (85%) but with poor diastereoselectivity (dr = 53/47).

Mechanistic studies. Recently, we have reported that the $FeCl_3{\cdot}6H_2O$-catalyzed cyclization of *N*-protected ζ-amino allylic acetates could proceed via an allylic carbocation intermediate.[12] Furthermore, a $FeCl_3{\cdot}6H_2O$-induced reopening of the 2,6-disubstituted piperidines was observed, thus leading to the more stable *cis*-isomers under thermodynamic control. In

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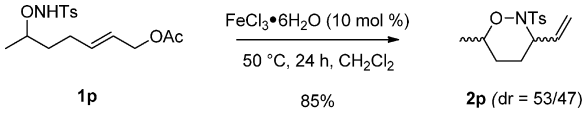
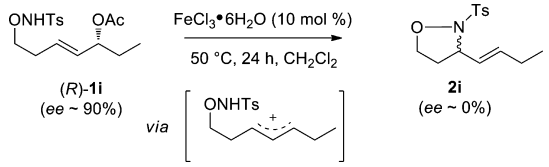
Scheme 4. Synthesis of a Six-Membered Ring



order to check if a similar mechanism was operating for the formation of isoxazolidines, the enantioenriched acetate (*R*)-**1i** (ee = 86%) was prepared and treated with 10 mol % of $FeCl_3 \cdot 6H_2O$. After 24 h at 50 °C, the corresponding isoxazolidine **2i** was obtained as a racemate, thus confirming the hypothesis of a carbocation intermediate (Scheme 5).

Scheme 5. Evidence for a Carbocation Intermediate

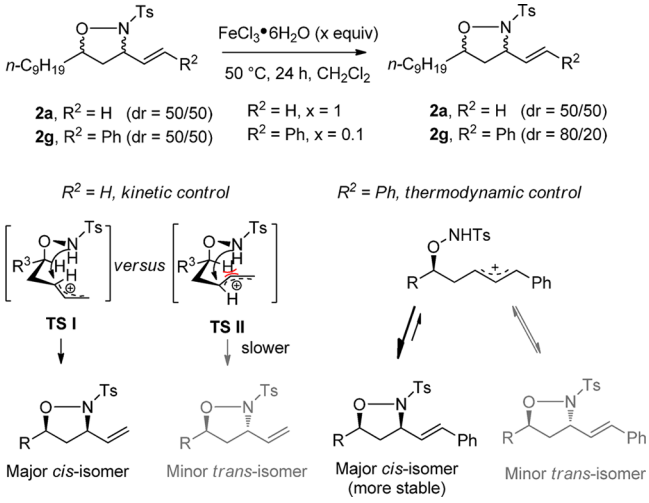


The ability of $FeCl_3 \cdot 6H_2O$ to induce the epimerization of isoxazolidines was then studied, and two compounds were examined. In the absence of any allylic substituent (R^2 = H), when the 1:1 mixture of *cis*/*trans*-isoxazolidines **2a** was treated with 1 equiv of $FeCl_3 \cdot 6H_2O$, after 24 h at 50 °C, no evolution of the diastereomeric ratio was observed. In contrast, for **2g** (R^2 = Ph), an epimerization was observed upon treatment with only 0.1 equiv of $FeCl_3 \cdot 6H_2O$, and the diastereomeric ratio was increased from 50/50 to 80/20 in favor of the more stable *cis*-isomer (Scheme 6). Thus, depending on the R^2 substituent, the reaction is under either kinetic or thermodynamic control. When R^2 = H, no epimerization of the obtained isoxazolidines occurs, the reaction proceeds under kinetic control and the diastereoselectivity observed (Table 1, entry 15) could be explained by the minimization of steric interactions in the transition state (TS **I** versus TS **II**). When R^2 = Ph, $FeCl_3 \cdot 6H_2O$ is able to epimerize the obtained isoxazolidines leading, under thermodynamic control, to the more stable *cis*-isomers as the major products (Scheme 6).

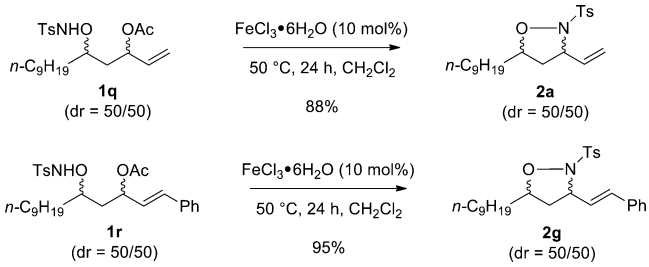
Surprisingly, when *N*-tosyl *β*-hydroxylamino allylic acetates **1q** (dr = 50/50) and **1r** (dr = 50/50) were reacted with 0.1 equiv of $FeCl_3 \cdot 6H_2O$, the corresponding isoxazolidines were isolated in 88% yield and 95% yield, respectively, but without any diastereoselectivity (Scheme 7). These results are in contrast with the reactivity of *N*-tosyl *δ*-hydroxylamino allylic acetates suggesting that in the case of *β*-hydroxylamino allylic acetates an S_N2-type mechanism may occur instead of a carbocationic pathway.

Synthetic Valorization of Isoxazolidines. Isoxazolidines bearing an insaturation are valuable compounds as they can be considered as highly functionalizable 1,3-amino alcohol precursors. In order to illustrate the great synthetic potential of the obtained isoxazolidines, isoxazolidine **2a** was used as a model substrate and involved in several transformations (Scheme 8). At first, the N–O bond was reductively cleaved upon treatment of **2a** with Zn in a $AcOH/H_2O$ mixture to give the corresponding amino alcohol **3** in quantitative yield.[2] The double bond was oxidatively cleaved (OsO_4, NMO then $NaIO_4$), and aldehyde **4** was isolated in 89% yield. An oxidation of the double bond in the presence of $RuCl_3 \cdot xH_2O$ and $NaIO_4$ furnished the carboxylic acid **5** (quant). Hydroboration using

Scheme 6. Evaluation of the $FeCl_3$-induced Epimerization of 3,5-Disubstituted Isoxazolidines and Hypothetic Mechanistic Pathways Depending on the Nature of the R^2 Group

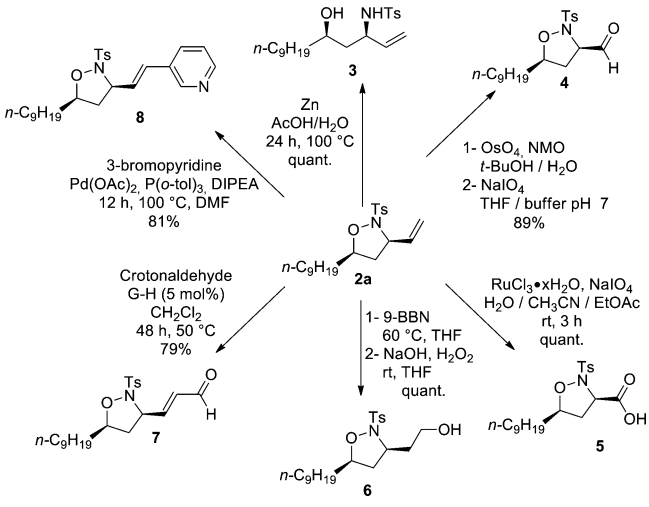


Scheme 7. Cyclization of *β*-Hydroxylamino Allylic Acetates Derivatives



9-BBN followed by oxidative treatment (NaOH, H_2O_2) led to alcohol **6** in quantitative yield. A cross-metathesis with crotonaldehyde in the presence of the second-generation Grubbs–Hoveyda catalyst (G–H) was performed, and **7** was isolated in 79% yield. Finally, a palladium-catalyzed Heck reaction with 3-bromopyridine delivered alkene **8** in 81% yield.

Scheme 8. Synthesis of Amino Alcohol and Functionalized Isoxazolidines



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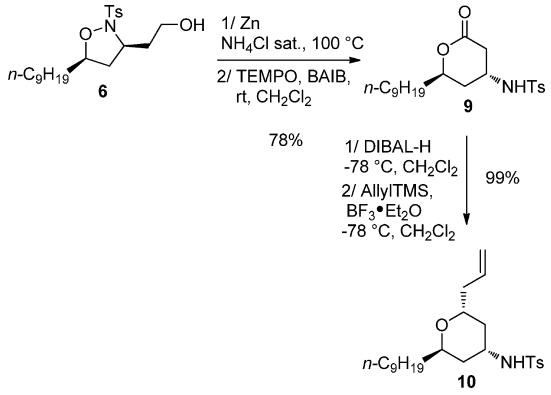
In addition, isoxazolidine **6** was efficiently transformed into lactone **9** upon reductive cleavage and subsequent oxidation of the primary alcohol (TEMPO, BAIB). Reduction of this lactone followed by addition of allyltrimethylsilane in presence of $BF_3{\cdot}OEt_2$ led to the corresponding sulfonylamidotetrahydropyran **10** in quantitative yield (Scheme 9).

Scheme 9. Formation of Tetrahydropyran 10



CONCLUSION

In summary, we have developed an ecofriendly and diastereoselective method for the synthesis of *cis*-3,5-disubstituted isoxazolidines. The mild conditions are compatible with various *N*-protecting groups, and a wide range of di- and trisubstituted isoxazolidines has been prepared. These compounds can allow the access to functionalized 1,3-amino alcohols as illustrated by the synthesis of various precursors. According to the nature of the allylic substituent, kinetic or thermodynamic control could be invoked to account for the diastereoselectivities observed.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out in dry solvents under argon atmosphere unless otherwise noted. THF and CH_2Cl_2 were dried using a solvent purification system. All commercially obtained chemicals were used as received without further purification. TLC was performed on silica gel plates visualized either with a UV lamp (254 nm) or using a staining solution (*p*-anisaldehyde, $KMnO_4$, or ninhydrin solutions). Purification was performed on silica gel (230−400 mesh). NMR spectra were recorded on a 400 MHz (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. The carbon NMR spectra are recorded proton decoupled ($^{13}C\{^1H\}$). Proton chemical shifts are reported relative to residual solvent peak ($CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm, DMSO-d_6 at 2.50 ppm). Carbon chemical shifts are reported relative to residual solvent peaks ($CDCl_3$ at 77.3 ppm, C_6D_6 at 128.1 ppm, DMSO-d_6 at 39.5 ppm). Infrared (IR) spectra (IRFT): wave numbers are indicated in cm^{-1}. Mass spectra with electronic impact (MS-EI) were recorded on a GC/MS (70 eV). High-resolution mass spectra (HRMS) were performed using electrospray ionization (ESI) with Orbitrap mass analysis.

General Procedure A for the Allylation of Aldehydes and Subsequent Mitsunobu Reaction with *N*-Hydroxyphthalimide. To a solution of aldehyde (1 equiv) in THF (0.2M) at −78 °C was added allylmagnesium chloride (2 M/THF, 1.5 equiv). After 2−4 h at −78 °C, the reaction medium was warmed to room temperature and a saturated aqueous solution of NH_4Cl was added. The two phases were separated, the aqueous layer was extracted twice with Et_2O, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was filtered through silica gel to obtain the desired alcohol. To a solution of the previously synthesized alcohol (1 equiv) in THF (0.1 M) were added PPh_3 (1.3 equiv) and *N*-hydroxyphthalimide (1.3 equiv). The resulting mixture was cooled to 0 °C before DIAD (1.3 equiv) was added dropwise. After 30 min at 0 °C, the reaction medium was allowed to reach room temperature. After 4−10 h, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the desired product.

General Procedure B for the Cross-Metathesis. To a solution of alkene (1 equiv) in CH_2Cl_2 (0.1 M) were added allylic acetate (2 equiv if the partner is symmetric, otherwise 3 equiv) and Hoveyda−Grubbs II catalyst (2.5 mol %) in a sealed tube. The reaction medium was warmed to 50 °C for 12 h before another portion of Hoveyda−Grubbs catalyst (2.5 mol %) was added. After 12 h at 50 °C, the solvent was evaporated under reduced pressure. Flash chromatography on silica gel yielded the expected olefin.

General Procedure C for the Ing−Manske Phthalimide Cleavage. To a solution of phthalimide derivative (1 equiv) in THF (0.2 M) was added hydrazine hydrate (67% in water, 5 equiv). After 1−3 h, water and EtOAc were added. The aqueous layer was extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the hydroxylamine ether.

General Procedure D for the *N*-Tosylation of Hydroxylamine Ethers. To a solution of hydroxylamine ether (1 equiv) in CH_2Cl_2 (0.1 M) were added at −78 °C pyridine (2 equiv), DMAP (0.1 equiv), and TsCl (1.1 equiv). After 4 h at −78 °C, the reaction medium was allowed to reach room temperature. After 5−10 h at rt, the reaction medium was quenched by addition of a saturated aqueous solution of $CuSO_4$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. A flash chromatography on silica gel afforded the corresponding *N*-tosylhydroxylamine ether.

General Procedure E for the $FeCl_3{\cdot}6H_2O$-Catalyzed Cyclization of *N*-Protected *δ*-Hydroxylamino Allylic Acetates 1a−r into Isoxazolidines 2a−r. To a solution of *N*-protected hydroxylamine ether (1 equiv) in CH_2Cl_2 (0.1 M) was added $FeCl_3{\cdot}6H_2O$ (0.1 equiv) in a sealed vial. The reaction medium was warmed to 50 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered on a pad of basic alumina and eluted with CH_2Cl_2. The obtained products do not require further purification, unless specified.

[(*E*)-5-(*p*-Tolylsulfonylamino)oxytetradec-2-enyl] Acetate (1a). General procedure A was applied to decanal (1.8 g, 12 mmol). Purification by flash chromatography silica gel (PE/Et_2O 98/2 to 90/10) yielded 2-(1-allyldecoxy)isoindoline-1,3-dione as a yellow liquid (3.67 g, 10.7 mmol, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86−7.79 (m, 2H), 7.77−7.71 (m, 2H), 5.91 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.13 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.08 (ddt, *J* = 10.2, 2.1, 1.2 Hz, 1H), 4.31 (quint, *J* = 5.9 Hz, 1H), 2.47 (ddt, *J* = 7.0, 5.9, 1.3 Hz, 2H), 1.76−1.60 (m, 2H), 1.55−1.47 (m, 2H), 1.37−1.19 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ* 164.3, 134.4, 133.5, 129.1, 123.4, 117.6, 87.3, 37.2, 32.3, 31.9, 29.6, 29.5, 29.5, 29.3, 25.0, 22.7, 14.1; IR (neat, *ν*/cm^{-1}) 2924, 2854, 1790, 1731, 1467, 1372, 1188, 1121, 1082, 1015; MS (EI, *m*/*z*) 302 (1, $[M - CH_2CH{=}CH_2]^+$), 180 (10, $[M - PhtNOH]^+$), 164 (41), 163 (19, $[PhtNOH]^{+\cdot}$), 125 (12), 111 (26), 104 (25), 97 (55), 96 (23), 25 (15), 90 (14), 83 (69), 82 (25), 81 (27), 76 (21), 71 (15); HRMS (ESI) calcd for $C_{21}H_{29}NO_3$ $[M + Na]^+$ 366.2040, found 366.2040. General procedure B was applied to 2-(1-allyldecoxy)isoindoline-1,3-dione (3 g, 8.7 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) yielded [(*E*)-5-(1,3-dioxoisoindoline-2-yl)oxytetradec-2-enyl] as a yellow oil (2.65 g, 6.4 mmol, 74%, *E*/*Z* = 82/18): ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85−7.80 (m, 2H), 7.79−7.71 (m, 2H), 5.95−5.86 (m, 1H), 5.73−5.63 (m, 1H), 4.50 (d_{app}, *J* = 6.2 Hz, 2H), 4.29 ($quint_{app}$, *J* = 5.9 Hz, 1H), 2.56−2.45 (m, 2H), 2.04 (s, 3H), 1.77−1.61 (m, 2H), 1.54−1.45 (m, 2H), 1.38−1.23 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ* 170.8, 164.2, 134.4, 130.5, 129.0, 127.0, 123.4, 87.1, 64.8, 35.7, 32.4, 31.9, 29.6, 29.5, 29.5, 29.3, 25.0, 22.7, 21.0, 14.1; IR (neat, *ν*/cm^{-1}) 2926, 2855, 1790, 1735, 1467, 1374, 1235, 1188, 1083, 1025; MS (EI, *m*/*z*)

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253 (13, [M − PhtNOH]$^+$), 163 (14, [PhtNOH]$^{+\cdot}$), 123 (25), 111 (18), 109 (52), 104 (35), 97 (31), 95 (91), 90 (21), 83 (48), 81 (100), 80 (29), 79 (42), 77 (20), 76 (37), 71 (15), 70 (16), 69 (64), 67 (90), 57 (40), 55 (92); HRMS (ESI) calcd for $C_{24}H_{33}NO_5$ [M + Na]$^+$ 438.2251, found 438.2256. General procedure C was applied to [(*E*)-5-(1,3-dioxoisoindoline-2-yl)oxytetradec-2-enyl] (1.7 g, 4.1 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 80/20 to 65/35) yielded [(*E*)-5-aminooxytetradec-2-enyl] acetate as a colorless oil (1.07 g, 3.75 mmol, 91%, *E*/*Z* = 83/17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84−5.73 (m, 1H), 5.70−5.60 (m, 1H), 4.53 (dd, *J* = 6.3, 0.9 Hz, 2H), 3.61 (quint$_{app}$, *J* = 5.94 Hz, 1H), 2.45−2.26 (m, 2H), 2.06 (s, 3H), 1.60−1.17 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 132.3, 126.2, 83.3, 65.1, 35.6, 32.4, 31.9, 29.7, 29.6, 29.6, 29.3, 25.4, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 2925, 2854, 1741, 1594, 1463, 1378, 1232, 1025; MS (EI, *m*/*z*) 227 (1), 226 (5, [M − OAc]$^+$), 172 (4), 155 (12), 123 (3), 109 (8), 97 (7), 96 (9), 95 (22), 85 (5), 84 (3), 83 (18), 82 (6), 81 (28), 80 (4), 79 (7), 72 (5), 71 (15), 70 (8), 69 (23), 68 (6), 67 (23), 57 (25), 56 (10), 54 (100); HRMS (ESI) calcd for $C_{16}H_{31}NO_3$ [M + Na]$^+$ 308.2196, found 308.2197. General procedure D was applied to [(*E*)-5-aminooxytetradec-2-enyl] acetate (864 mg, 3 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) yielded **1a** as a pale yellow oil (1.2 g, 2.7 mmol, 91%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.90−7.83 (m, 2H), 6.86−6.81 (m, 2H), 6.63 (brs, 1H), 5.66−5.56 (m, 1H), 5.53−5.41 (m, 1H), 4.40 (dd, *J* = 6.2, 0.8 Hz, 2H), 4.21−4.09 (m, 1H), 2.26−2.09 (m, 2H), 1.88 (s, 3H), 1.69 (s, 3H), 1.53−1.12 (m, 16H), 0.93 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 170.2, 144.2, 135.4, 131.3, 129.6, 129.0, 127.3, 85.7, 64.9, 36.0, 32.8, 32.4, 31.0, 30.1, 30.0, 29.8, 25.7, 23.1, 21.2, 20.6, 14.4; IR (neat, ν/cm^{-1}) 3216, 2925, 2854, 1739, 1598, 1458, 1379, 1339, 1231, 1167, 1092, 1022; MS (EI, *m*/*z*) 171 (18, [$TsNH_2$]$^{+\cdot}$), 155 (17), 108 (15), 107 (34), 96 (14), 91 (100), 89 (14), 81 (17), 77 (13), 65 (52), 63 (23), 53 (17), 51 (15); HRMS (ESI) calcd for $C_{23}H_{37}NO_5S$ [M + Na]$^+$ 462.2285, found 462.2289.

***N*-[1-[(*E*)-4-Hydroxybut-2-enyl]decoxy]-4-methylbenzenesulfonamide (1a′).** To a solution of **1a** (90 mg, 0.2 mmol, 1 equiv) in MeOH (2 mL) was added NaOH (0.8 mL, 1 M/water, 5 equiv). The reaction medium was stirred at room temperature for 4 h before the reaction was quenched with water and diluted with EtOAc. The phases were separated, and the aqueous phase was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 70/30) to obtain **1a′** as a yellow oil (50 mg, 0.13 mmol, 63%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.98 (d$_{app}$, *J* = 7.8 Hz, 2H), 7.94 (s, 1H), 6.91 (d$_{app}$, *J* = 8.0 Hz, 2H), 5.78−5.45 (m, 2H), 4.22−4.18 (m, 1H), 4.04−3.98 (m, 2H), 2.66 (brs, 1H), 2.47−2.33 (m, 1H), 2.29−2.15 (m, 1H), 1.93 (s, 3H), 1.73−1.29 (m, 16H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 144.3, 135.0, 132.1, 129.7, 129.0, 128.1, 85.8, 63.4, 35.9, 32.8, 32.3, 30.0, 30.0, 30.0, 29.8, 25.8, 23.1, 21.4, 14.4; IR (neat, ν/cm^{-1}) 3514, 3220, 2925, 2854, 1598, 1465, 1337, 1186, 1167, 1092; MS (EI, *m*/*z*) 171 (15), 155 (17), 108 (18), 107 (40), 91 (100), 89 (18), 80 (5), 77 (5), 65 (51), 63 (23), 51 (12); HRMS (ESI) calcd for $C_{21}H_{35}NO_4S$ [M + Na]$^+$ 420.2179, found 420.2178.

(*E*)-5-[(2-Nitrophenyl)sulfonylamino)oxytetradec-2-enyl] Acetate (1b). To a solution of [(*E*)-5-aminooxytetradec-2-enyl] acetate (150 mg, 0.53 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added at 0 °C NsCl (111 mg, 0.95 equiv), Et_3N (0.15 mL, 2 equiv), and DMAP (6.5 mg, 0.1 equiv). The reaction medium was stirred for 60 h before the reaction was quenched with brine. The phases were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EtOAc 90/10) to obtain **1b** as a yellow oil (170 mg, 0.4 mmol, 72%, *E*/*Z* > 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23−8.17 (m, 1H), 7.85−7.75 (m, 2H), 7.85−7.75 (m, 2H), 5.80−5.69 (m, 1H), 5.68−5.58 (m, 1H), 4.53 (d$_{app}$, *J* = 6.0 Hz, 2H), 4.18 (quint$_{app}$, *J* = 5.8 Hz, 1H), 2.50−2.33 (m, 2H), 2.07 (s, 3H), 1.57−1.41 (m, 2H), 1.39−1.21 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 148.5, 134.7, 133.7, 132.7, 131.0, 130.6, 126.9, 125.6, 86.0, 64.8, 35.4, 32.1, 31.9, 29.6, 29.5, 29.5, 29.3, 25.2, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 3273, 2925, 2855, 1736, 1593, 1542, 1441, 1396, 1361, 1304, 1231, 1178, 1125, 1022; MS (EI, *m*/*z*) 253 (1, [M − ONHNs]$^+$), 252 (7), 203 (4), 144 (12), 143 (100), 142 (6), 129 (7), 128 (26), 117 (5), 115 (9), 105 (14), 104 (15), 91 (13), 90 (8), 77 (14), 76 (11), 51 (4); HRMS (ESI) calcd for $C_{22}H_{34}N_2O_7S$ [M + Na]$^+$ 493.1979, found 493.1978.

[(*E*)-5-(Benzyloxycarbonylaminooxy)tetradec-2-enyl] Acetate (1c). To a solution of [(*E*)-5-aminooxytetradec-2-enyl] acetate (50 mg, 0.175 mmol, 1 equiv) in a 1/1 mixture of CH_2Cl_2/water (1 mL) at −20 °C were added CbzCl (33 mg, 1.1 equiv) and Na_2CO_3 (20 mg, 1.05 equiv). After 20 h at rt, the reaction medium was quenched with water and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified on silica gel (PE/Et_2O 70/30) to obtain **1c** as a colorless oil (70 mg, 0.17 mmol, 96%, *E*/*Z* = 80/20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (m, 5H), 7.23 (brs, 1H), 5.88−5.72 (m, 1H), 5.63 (dt, *J* = 15.3, 6.2 Hz, 1H), 5.17 (s, 2H), 4.49 (d$_{app}$, *J* = 6.1 Hz, 2H), 3.81 (quint$_{app}$, *J* = 5.7 Hz, 1H), 2.37 (t$_{app}$, *J* = 6.6 Hz, 2H), 2.05 (s, 3H), 1.59−1.37 (m, 2H), 1.37−1.20 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 157.7, 135.6, 131.6, 128.6, 128.4, 128.3, 126.6, 85.2, 67.5, 65.0, 35.5, 32.2, 31.9, 29.7, 29.6, 29.5, 29.3, 25.3, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 3288, 2924, 2854, 1738, 1456, 1377, 1338, 1230, 1105, 1026; HRMS (ESI) calcd for $C_{24}H_{37}NO_5$ [M + Na]$^+$ 442.2564, found 442.2569.

(*E*)-5-((((Allyloxy)carbonyl)amino)oxy)tetradec-2-en-1-yl Acetate (1d). To a solution of (*E*)-5-aminooxytetradec-2-enyl] acetate (250 mg, 0.88 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at −78 °C were added AllocCl (106 μL, 1.1 equiv), pyridine (139 μL, 2 equiv), and DMAP (11 mg, 0.1 equiv). After 2 h at −78 °C and 48 h at room temperature, the reaction medium was quenched by addition of aq $CuSO_4$ and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 90/10) to obtain **1d** as a colorless oil (302 mg, 0.81 mmol, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 5.92 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.86−5.75 (m, 1H), 5.65 (dt, *J* = 13.8, 6.3 Hz, 1H), 5.34 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.25 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.63 (d, *J* = 5.8 Hz, 2H), 4.52 (d, *J* = 6.3 Hz, 2H), 3.91−3.74 (m, 1H), 2.36 (t$_{app}$, *J* = 6.4 Hz, 2H), 2.06 (s, 1H), 1.58−1.21 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 157.6, 132.0, 131.6, 126.6, 118.6, 85.2, 66.4, 65.0, 35.5, 32.2, 31.9, 29.7, 29.6, 29.6, 29.3, 25.3, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 3296, 2925, 2855, 1739, 1650, 1459, 1378, 1325, 1230, 1107, 1026; MS (EI, *m*/*z*) 253 (1), 224 (3), 155 (12), 123 (15), 109 (25), 97 (19), 96 (19), 95 (55), 83 (29), 82 (14), 81 (60), 71 (20), 69 (42), 67 (47), 57 (54), 55 (67), 54 (100); HRMS (ESI) calcd for $C_{20}H_{35}NO_5$ [M + Na]$^+$ 392.2407, found 392.2411.

(*E*)-5-(Acetamidooxy)tetradec-2-en-1-yl Acetate (1e). To a solution of (*E*)-5-aminooxytetradec-2-enyl] acetate (250 mg, 0.88 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at −78 °C were added AcCl (69 μL, 1.1 equiv) and pyridine (139 μL, 2 equiv). After 24 h at rt, the reaction medium was quenched by addition of aq $CuSO_4$ and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 70/30 to 50/50) to obtain **1e** as a colorless oil (250 mg, 0.77 mmol, 87%, *E*/*Z* = 81/19): ^{1}H NMR (400 MHz, DMSO) δ 10.66 (s, 1H), 5.80−5.75 (m, 1H), 5.67−5.53 (m, 1H), 4.46 (d, *J* = 6.2 Hz, 2H), 3.75−3.64 (m, 1H), 2.28−2.23 (m, 2H), 2.00 (s, 3H), 1.71 (s, 3H), 1.53−1.16 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO) δ 170.0, 166.4, 131.1, 126.4, 83.1, 64.2, 34.7, 31.5, 31.3, 29.0, 28.9, 28.9, 28.7, 24.5, 22.1, 20.6, 19.6, 13.9; IR (neat, ν/cm^{-1}) 3196, 2924, 2854, 1741, 1664, 1520, 1459, 1367, 1228, 1082, 1024; MS (EI, *m*/*z*) 208 (2), 155 (49),

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124 (5), 109 (6), 97 (10), 96 (95), 95 (41), 85 (38), 81 (96), 71 (70), 69 (19), 67 (17), 57 (70), 55 (41), 54 (100); HRMS (ESI) calcd for $C_{18}H_{33}NO_4$ $[M + Na]^+$ 350.2302, found 350.2300.

[(*E*)-5-(*tert*-Butoxycarbonylamino)oxytetradec-2-enyl] Acetate (1f). To a solution of [(*E*)-5-aminooxytetradec-2-enyl] acetate (150 mg, 0.53 mmol, 1 equiv) in 1,4-dioxane (5 mL) was added at 0 °C Boc_2O (186 mg, 1.6 equiv). After 12 h at rt, the reaction was diluted with water and EtOAc. The phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 70/30) to obtain **1f** as a pale yellow oil (171 mg, 0.45 mmol, 84%, *E*/*Z* = 80/20): ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (brs, 1H), 5.89−5.75 (m, 1H), 5.71−5.59 (m, 1H), 4.52 (dd, *J* = 6.4, 0.9 Hz, 2H), 3.77 ($quint_{app}$, *J* = 5.7 Hz, 1H), 2.44−2.30 (m, 2H), 2.06 (s, 3H), 1.49 (s, 9H), 1.70−1.40 (m, 2H), 1.39−1.18 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 157.1, 131.8, 126.4, 84.9, 81.6, 65.0, 35.5, 32.1, 31.9, 29.7, 29.6, 29.5, 29.3, 28.2, 25.3, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 3304, 2925, 2855, 1741, 1457, 1367, 1234, 1165, 1103, 1022; HRMS (ESI) calcd for $C_{21}H_{39}NO_5$ $[M + Na]^+$ 408.2720, found 408.2720.

Acetic Acid (*E*)-5-Aminooxy-1-phenyltetradec-2-enyl Ester (1g). General procedure B was applied to 2-(1-allyldecoxy)isoindoline-1,3-dione (343 mg, 1 mmol). Purification on silica gel (PE/Et_2O 90/10 to 80/20) yielded acetic acid (*E*)-5-(1,3-dioxo-1,3-dihydroisoindol-2-yloxy)-1-phenyltetradec-2-enyl ester as a dark pink oil (230 mg, 0.47 mmol, 47%, 50/50 mixture of diastereoisomers α and β): ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.78 (m, 2H), 7.77−7.70 (m, 2H), 7.38−7.26 (m, 5H), 6.21 (brd, *J* = 6.1 Hz, 1H), 5.91−5.69 (m, 2H), 4.27 ($sext_{app}$, *J* = 6.0 Hz, 1H), 2.51−2.44 (m, 2H), 2.08 (s, 1.5H), 2.08 (s, 1.5H), 1.77−1.11 (m, 16H), 0.90−0.85 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.0, 164.2, 139.5, 134.4, 131.4, 129.0, 129.0, 128.5, 128.5, 128.0, 126.9, 123.5, 87.2, 87.1, 75.8, 35.7, 35.6, 32.3, 32.0, 29.5, 29.5, 29.5, 29.3, 24.9, 22.7, 21.3, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1790, 1731, 1494, 1467, 1370, 1232, 1188, 1122, 1082, 1016; MS (EI, *m*/*z*) 268 (25), 169 (11), 156 (22), 155 (77), 154 (16), 142 (14), 141 (38), 130 (45), 129 (22), 128 (26), 115 (24), 92 (11), 91 (100), 79 (15); HRMS (ESI) calcd for $C_{30}H_{37}NO_5$ $[M + Na]^+$ 514.2564, found 514.2561. General procedure C was applied to acetic acid (*E*)-5-(1,3-dioxo-1,3-dihydroisoindol-2-yloxy)-1-phenyltetradec-2-enyl ester (225 mg, 0.47 mmol). Purification on silica gel (PE/Et_2O 80/20 to 50/50) yielded acetic acid (*E*)-5-aminooxy-1-phenyltetradec-2-enyl ester as a colorless oil (130 mg, 0.36 mmol, 77%, 50/50 mixture of diastereoisomers): ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.24 (m, 5H), 6.23 (brd, *J* = 6.3 Hz, 1H), 5.82−5.66 (m, 2H), 5.19 (brs, 2H), 3.60−3.51 (m, 1H), 2.33−2.29 (m, 2H), 2.10 (s, 1.5H), 2.09 (s, 1.5H), 1.54−1.43 (m, 2H), 1.35−1.19 (m, 14H), 0.92−0.84 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1, 139.7, 130.8, 130.5, 128.6, 128.0, 126.9, 83.3, 76.3, 35.8, 32.6, 32.0, 29.8, 29.7, 29.6, 29.4, 25.5, 22.8, 21.4, 14.2; IR (neat, ν/cm^{-1}) 2924, 2854, 1736, 1587, 1494, 1456, 1370, 1232, 1072, 1018; MS (EI, *m*/*z*) 130 (85), 71 (18), 70 (50), 68 (21), 67 (24), 57 (96), 56 (18), 55 (100); HRMS (ESI) calcd for $C_{20}H_{33}NO_2$ $[M + Na - Ac]^+$ 342.2791, found 342.2793. General procedure D was applied to acetic acid (*E*)-5-aminooxy-1-phenyltetradec-2-enyl ester (125 mg, 0.35 mmol). Purification on silica gel (PE/Et_2O 80/20 to 50/50) yielded **1g** as a pale yellow oil (147 mg, 0.29 mmol, 82%, 50/50 mixture of diastereoisomers): ^1H NMR (400 MHz, C_6D_6) δ 7.90−7.82 (m, 2H), 7.66 (d, *J* = 10.8 Hz, 2H), 7.20−7.14 (m, 2H), 7.10−7.04 (m, 1H), 6.86−6.79 (m, 2H), 6.42 (d, *J* = 6.8 Hz, 0.5H), 6.39 (d, *J* = 6.8 Hz, 0.5H), 5.86−5.74 (m, 2H), 4.18−4.09 (m, 1H), 2.29−2.10 (m, 2H), 1.88 (s, 1.5H), 1.87 (s, 1.5H), 1.73 (s, 1.5H), 1.69 (s, 1.5H), 1.37−1.21 (m, 16H), 0.95−0.90 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 169.8, 144.2, 140.2, 131.7, 130.3, 129.9, 129.7, 129.7, 129.0, 128.9, 128.4, 128.3, 127.5, 127.4, 85.9, 76.7, 76.3, 36.5, 33.1, 32.9, 32.4, 30.1, 30.1, 29.9, 25.7, 23.2, 21.3, 20.9, 14.5; IR (neat, ν/cm^{-1}) 3216, 2924, 2854, 1736, 1598, 1494, 1456, 1372, 1340, 1306, 1234, 1167, 1092, 1019; HRMS (ESI) calcd for $C_{29}H_{41}NO_5S$ $[M + Na]^+$: 538.2598, found 538.2597.

(*E*)-5-(((*tert*-Butoxycarbonyl)amino)oxy)-1-phenyltetradec-2-en-1-yl acetate (1h). General procedure C was applied to 2-(1-allyldecoxy)isoindoline-1,3-dione (4 g, 11.7 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 95/5 to 90/10) yielded *O*-(tridec-1-en-4-yl)hydroxylamine as a pale yellow oil (2.25 g, 10.5 mmol, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.21 (s, 2H), 5.14−5.00 (m, 2H), 3.62−3.52 (pent, *J* = 5.8 Hz, 1H), 2.39−2.18 (m, 2H), 1.56−1.18 (m, 16H), 0.87 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.2, 116.6, 83.3, 37.3, 32.3, 31.9, 29.8, 29.6, 29.6, 29.3, 25.5, 22.7, 14.1; IR (neat, ν/cm^{-1}) 3317, 3077, 2923, 2854, 1641, 1586, 1466, 1350, 1183, 1128; HRMS (ESI) calcd for $C_{13}H_{27}NO$ $[M + H]^+$ 214.2165, found 214.2166. To a solution of *O*-(tridec-1-en-4-yl)hydroxylamine (200 mg, 0.94 mmol, 1 equiv) in 1,4-dioxane (10 mL) was added at 0 °C Boc_2O (327 mg, 1.6 equiv). The reaction medium was stirred for 12 h at room temperature before the reaction was quenched with water and diluted with EtOAc. The phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 98/2 to 95/5) to obtain the expected hydroxylamine as a colorless oil (282 mg, 96%). The previously synthesized hydroxylamine (270 mg, 0.86 mmol) was subjected to procedure B (using 4 equiv of phenylallyl acetate as the partner). Purification by flash chromatography on silica gel (PE/Et_2O 90/10) yielded **1h** as a brown oil (250 mg, 0.54 mmol, 63%, 55/45 mixture of diastereoisomers): ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 5H), 6.32−6.28 (m, 1H), 6.23 (d, *J* = 6.0 Hz, 0.5H), 5.92−5.89 (m, 1H), 5.73−5.70 (m, 0.5H), 3.93−3.85 (m, 1H), 2.40−2.32 (m, 1H), 2.10−2.07 (m, 4H), 1.59−1.46 (m, 11H), 1.32−0.99 (m, 14H), 0.88 (t, *J* = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 163.5, 131.1, 130.7, 128.6, 128.3, 127.2, 126.9, 83.7, 81.0, 75.0, 31.9, 29.9, 29.8, 29.7, 29.5, 29.5, 29.3, 28.1, 25.0, 22.7, 21.3, 14.1; IR (neat, ν/cm^{-1}) 2926, 2855, 1741, 1495, 1456, 1393, 1369, 1337, 1272, 1230, 1150, 1113, 1020; HRMS (ESI) calcd for $C_{27}H_{43}NO_5$ $[M + Na]^+$ 484.3033, found 484.3036.

(*E*)-7-((4-Methylphenylsulfonamido)oxy)hept-4-en-3-yl Acetate (1i). To a solution of penten-3-ol (500 mg, 7 mmol, 1 equiv) in THF (70 mL) were added PPh_3 (2.4 g, 1.3 equiv) and *N*-hydroxyphthalimide (1.5 g, 1.3 equiv). The resulting mixture was cooled to 0 °C before DIAD (1.8 mL, 1.3 equiv) was added dropwise. After 30 min at 0 °C, the reaction medium was allowed to warm to rt. After 2 h, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (PE/Et_2O 80/20) to afford 2-(but-3-en-1-yloxy)isoindoline-1,3-dione as a colorless oil (1.56 g, 7 mmol, quant): ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (m, 2H), 7.78−7.71 (m, 2H), 5.89 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.21 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.12 (ddd, *J* = 10.3, 2.6, 1.3 Hz, 1H), 4.26 (t, *J* = 6.9 Hz, 2H), 2.57 (qt, *J* = 6.7, 1.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.6, 134.5, 133.1, 128.9, 123.5, 117.6, 77.3, 32.5; IR (neat, ν/cm^{-1}) 2954, 1788, 1727, 1642, 1611, 1467, 1391, 1372, 1290, 1245, 1186, 1127, 1082, 1018; MS (EI, *m*/*z*) 217 (0.1, $[M]^{+\cdot}$), 187 (2), 164 (3), 163 (29, $[PhtNOH]^{+\cdot}$) 148 (3), 147 (3), 146 (5), 133 (8), 130 (3), 105 (9), 104 (19), 90 (14), 77 (6), 76 (23), 75 (4), 55 (100, $[M - PhtNO]^+$); HRMS (ESI) calcd for $C_{12}H_{11}NO_3$ $[M + Na]^+$ 240.0631, found 240.0632. To a solution of 2-(but-3-en-1-yloxy)isoindoline-1,3-dione (50 mg, 0.23 mmol, 1 equiv) in CH_2Cl_2 (2 mL) were added ethyl crotonate (53 μL, 2 equiv) and Hoveyda−Grubbs II catalyst (3.6 mg, 2.5 mol %). After 24 h at rt, the solvent was evaporated under reduced pressure and flash chromatography on silica gel of the residue (PE/Et_2O 70/30 to 50/50) yielded (*E*)-2-((5-oxohept-3-en-1-yl)oxy)isoindoline-1,3-dione as a brown oil (45 mg, 0.16 mmol, 71%, *E*/*Z* > 95/5): ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (ddd, *J* = 7.1, 5.4, 3.1 Hz, 2H), 7.82−7.73 (m, 2H), 6.95 (dt, *J* = 16.0, 6.7 Hz, 1H), 6.33 (dt, *J* = 16.0, 1.5 Hz, 1H), 4.37 (t, *J* = 6.4 Hz, 2H), 2.74 (qd, *J* = 6.5, 1.5 Hz, 2H), 2.63 (q, *J* = 7.3 Hz, 2H), 1.13 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.9, 163.5, 140.9, 134.6, 132.1, 128.8, 123.6, 76.2, 33.4, 31.2, 8.0; IR (neat, ν/cm^{-1}) 2976, 1788, 1725, 1672, 1631, 1467, 1373, 1290, 1186, 1128, 1082, 1017; HRMS (ESI) calcd for $C_{15}H_{15}NO_4$ $[M + Na]^+$ 296.0893,

found 296.0895. To a solution of (*E*)-2-((5-oxohept-3-en-1-yl)oxy)-isoindoline-1,3-dione (245 mg, 0.89 mmol, 1 equiv) in a 1/1 mixture of MeOH and CH_2Cl_2 (10 mL) was added at 0 °C $CeCl_3{\cdot}7H_2O$ (400 mg, 1.2 equiv). After the mixture was stirred for 5 min at 0 °C, $NaBH_4$ (44 mg, 1.5 equiv) was added portionwise. The mixture was stirred for 2 h at 0 °C before being quenched carefully with aq NH_4Cl. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 50/50) afforded (*E*)-2-((5-hydroxyhept-3-en-1-yl)oxy)-isoindoline-1,3-dione as a colorless oil (170 mg, 0.62 mmol, 70%, *E*/*Z* > 95/5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.80 (m, 2H), 7.74−7.72 (m, 2H), 5.77−5.59 (m, 2H), 4.29−4.17 (m, 2H), 3.99 (q, *J* = 6.5 Hz, 1H), 2.53 (q, *J* = 6.5 Hz, 2H), 1.55−1.51 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.6, 136.0, 134.5, 128.9, 126.1, 123.6, 77.5, 74.2, 31.1, 30.0, 9.7; IR (neat, ν/cm^{-1}) 3503, 2962, 2930, 1790, 1731, 1467, 1374, 1292, 1187, 1130, 1082, 1017; MS (EI, *m*/*z*) 283 (8), 257 (6, [M − H_2O]$^+$), 213 (30), 183 (46), 145 (94), 135 (73), 113 (40, [M − PhtNO]$^+$), 111 (20), 91 (38), 89 (100), 85 (85), 73 (79); HRMS (ESI) calcd for $C_{15}H_{17}NO_4$ [M + Na]$^+$ 298.1050, found 298.1053. To a solution of (*E*)-2-((5-hydroxyhept-3-en-1-yl)oxy)isoindoline-1,3-dione (160 mg, 0.58 mmol, 1 equiv) in CH_2Cl_2 (10 mL) were added at 0 °C Ac_2O (0.11 mL, 2 equiv), pyridine (0.18 mL, 4 equiv), and DMAP (7 mg, 0.1 equiv). The reaction medium was stirred for 4 h at rt before the reaction was quenched with an aqueous solution of $CuSO_4$. The phases were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 80/20 to 50/50) to obtain (*E*)-7-((1,3-dioxoisoindolin-2-yl)oxy)hept-4-en-3-yl acetate as a colorless oil (160 mg, 0.5 mmol, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (m, 2H), 7.77−7.72 (m, 2H), 5.75 (dtd, *J* = 15.4, 6.6, 0.8 Hz, 1H), 5.58 (ddt, *J* = 15.6, 6.9, 1.1 Hz, 1H), 5.14 (q, *J* = 6.6 Hz, 1H), 4.23 (t, *J* = 6.9 Hz, 2H), 2.55 (q, *J* = 6.7 Hz, 2H), 2.04 (s, 3H), 1.71−1.53 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 163.6, 134.5, 131.3, 128.9, 127.9, 123.5, 77.2, 75.6, 31.0, 27.3, 21.3, 9.4; IR (neat, ν/cm^{-1}) 2969, 1789, 1726, 1467, 1371, 1237, 1186, 1127, 1082, 1017; MS (EI, *m*/*z*) 274 (3, [M − Ac]$^+$), 164 (11), 111 (12), 104 (23), 95 (100), 94 (99), 90 (19), 83 (31), 79 (90), 77 (16), 76 (30), 67 (45), 57 (39), 55 (33); HRMS (ESI) calcd for $C_{17}H_{19}NO_5$ [M + Na]$^+$ 340.1155, found 340.1153. General procedure C was applied to (*E*)-7-((1,3-dioxoisoindolin-2-yl)oxy)hept-4-en-3-yl acetate (145 mg, 0.46 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 50/50) yielded (*E*)-7-(aminooxy)hept-4-en-3-yl acetate as a colorless oil (76 mg, 0.4 mmol, 88%, *E*/*Z* = 93/7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dtd, *J* = 15.4, 6.8, 0.8 Hz, 1H), 5.47 (ddt, *J* = 15.5, 7.1, 1.4 Hz, 1H), 5.35−4.75 (m, 2H), 5.12 (q, *J* = 6.7 Hz, 1H), 3.72 (t, *J* = 6.7 Hz, 2H), 2.34 (qd, *J* = 6.5, 1.2 Hz, 2H), 2.04 (s, 3H), 1.61 (qdd, *J* = 13.8, 7.4, 6.6 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 130.3, 130.0, 76.0, 61.67, 31.5, 27.4, 21.4, 9.5; IR (neat, ν/cm^{-1}) 3320, 2969, 2936, 2879, 1727, 1673, 1591, 1458, 1371, 1238, 1074, 1018; MS (EI, *m*/*z*) 129 (12), 112 (30), 101 (33), 83 (100), 82 (79), 81 (59), 79 (51), 67 (93), 57 (48), 55 (53), 53 (34); HRMS (ESI) calcd for $C_9H_{17}NO_3$ [M + Na]$^+$ 210.1101, found 210.1100. General procedure D was applied to (*E*)-7-(aminooxy)hept-4-en-3-yl acetate (165 mg, 0.88 mmol). Purification by flash chromatography on silica gel (PE/EtOAc 90/10 to 80/20) yielded **1i** as a colorless oil (281 mg, 0.82 mmol, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.77 (m, 2H), 7.34 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.02 (d, *J* = 3.7 Hz, 1H), 5.69−5.58 (m, 1H), 5.45 (ddt, *J* = 15.5, 7.0, 1.4 Hz, 1H), 5.08 (q, *J* = 6.7 Hz, 1H), 4.03 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 2.34 (qd, *J* = 6.7, 1.0 Hz, 2H), 2.03 (s, 3H), 1.62−1.57 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 144.9, 133.7, 130.8, 129.7, 129.2, 128.6, 76.3, 75.9, 31.3, 27.4, 21.7, 21.4, 9.5; IR (neat, ν/cm^{-1}) 3213, 2967, 2938, 2880, 1730, 1712, 1598, 1403, 1372, 1339, 1307, 1291, 1240, 1165, 1120, 1092, 1074, 1019; MS (EI, *m*/*z*) 281 (6, [M − AcOH]$^+$), 155 (11, [M − ONHTs]$^+$), 126 (100), 91 (74), 84 (11), 82 (15), 81 (19), 72 (11), 67 (11), 65 (31), 56 (11), 55 (33), 54 (27); HRMS (ESI) calcd for $C_{16}H_{23}NO_5S$ [M + Na]$^+$ 364.1223, found 364.1190.

[(*E*)-5-Cyclohexyl-5-(*p*-tolylsulfonylamino)oxy-pent-2-enyl] Acetate (1j). General procedure A was applied to cyclohexanecarboxaldehyde (800 mg, 7.14 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 96/4) yielded 2-(1-cyclohexylbut-3-enoxy)-isoindoline-1,3-dione as a yellow oil (1.3 g, 3.1 mmol, 43% for the two steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.99 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.11 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.04 (dq, *J* = 10.2 Hz, 1.6 Hz, 1H), 4.13 (q, *J* = 6.4 Hz, 1H), 2.51−2.37 (m, 2H), 1.99−1.91 (m, 1H), 1.90−1.83 (m, 1H), 1.83−1.76 (m, 2H), 1.73−1.63 (m, 2H), 1.30−1.14 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 134.4, 134.4, 129.1, 123.4, 117.0, 91.0, 39.8, 34.1, 28.2, 28.0, 26.5, 26.2, 26.2; IR (neat, ν/cm^{-1}) 2925, 2853, 1790, 1729, 1641, 1467, 1449, 1372, 1187, 1122, 1081, 1025; MS (EI, *m*/*z*) 164 (9), 137 (14), 136 (26), 104 (29), 96 (8), 95 (100), 94 (9), 93 (8), 90 (16), 83 (16), 82 (10), 81 (85), 79 (17), 77 (13), 76 (30), 69 (20), 67 (50), 55 (79); HRMS (ESI) calcd for $C_{18}H_{21}NO_3$ [M + Na]$^+$ 322.1414, found 322.1416. General procedure B was applied to 2-(1-cyclohexylbut-3-enoxy)-isoindoline-1,3-dione (220 mg, 0.74 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10) yielded [(*E*)-5-cyclohexyl-5-(1,3-dioxoisoindolin-2-yl)oxy-pent-2-enyl] acetate as an oil (192 mg, 0.52 mmol, 70%, *E*/*Z* = 75/25): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.01−5.89 (m, 1H), 5.72−5.61 (m, 1H), 4.48 (dd, *J* = 6.3 Hz, 0.9 Hz, 2H), 4.12 (q_{app}, *J* = 5.2 Hz, 1H), 2.56−2.37 (m, 2H), 2.03 (s, 3H), 1.99−1.91 (m, 1H), 1.90−1.84 (m, 1H), 1.83−1.74 (m, 2H), 1.74−1.63 (m, 2H), 1.32−1.11 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 164.2, 134.4, 131.4, 129.0, 126.4, 123.4, 90.9, 64.8, 40.0, 32.6, 28.4, 27.8, 26.4, 26.2, 26.1, 20.9; IR (neat, ν/cm^{-1}) 2927, 2853, 1790, 1732, 1467, 1450, 1373, 1232, 1188, 1124, 1082, 1017; MS (EI, *m*/*z*) 209 (4), 149 (44), 148 (12), 107 (16), 105 (13), 104 (30), 95 (52), 93 (22), 91 (18), 90 (15), 83 (19), 81 (39), 79 (28), 77 (17), 76 (31), 67 (100), 55 (62), 54 (16), 53 (20); HRMS (ESI) calcd for $C_{21}H_{25}NO_5$ [M + Na]$^+$ 394.1625, found 394.1628. General procedure C was applied to [(*E*)-5-cyclohexyl-5-(1,3-dioxoisoindolin-2-yl)oxy-pent-2-enyl] acetate (190 mg, 0.52 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 70/30) yielded [(*E*)-5-aminooxy-5-cyclohexylpent-2-enyl] acetate as a colorless oil (76 mg, 0.32 mmol, 61%, *E*/*Z* = 80/20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88−5.70 (m, 1H), 5.69−5.59 (m, 1H), 4.53 (d_{app}, *J* = 6.4 Hz, 2H), 3.36 (q_{app}, *J* = 5.7 Hz, 1H), 2.39−2.20 (m, 2H), 2.05 (s, 3H), 1.81−1.48 (m, 6H), 1.29−0.93 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 133.2, 125.7, 87.9, 65.2, 39.8, 32.8, 28.9, 28.6, 26.6, 26.3, 26.2, 21.0; IR (neat, ν/cm^{-1}) 3319, 2924, 2852, 1736, 1590, 1449, 1365, 1229, 1148, 1024; MS (EI, *m*/*z*) 149 (4), 111 (16), 95 (27), 83 (55), 81 (23), 79 (19), 68 (11), 67 (47), 56 (10), 55 (100), 54 (93); HRMS (ESI) calcd for $C_{13}H_{23}NO_3$ [M + H]$^+$ 242.1751, found 242.1753. General procedure D was applied to [(*E*)-5-aminooxy-5-cyclohexylpent-2-enyl] acetate (60 mg, 0.25 mmol). Purification by flash chromatography on silica gel (benzene/Et_2O 90/10) yielded **1j** as an oil (147 mg, 0.18 mmol, 71%, *E*/*Z* = 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 1H), 5.85 −5.73 (m, 1H), 5.71−5.52 (m, 1H), 4.52 (dd, *J* = 6.4, 1.1 Hz, 2H), 3.89 (q_{app}, *J* = 5.6 Hz, 1H), 2.44 (s, 3H), 2.43−2.36 (m, 1H), 2.31−2.20 (m, 1H), 2.06 (s, 3H), 1.80−1.53 (m, 6H), 1.32−0.81 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 144.7, 134.0, 132.0, 129.6, 128.6, 126.3, 89.8, 65.0, 39.4, 32.5, 28.7, 28.2, 26.4, 26.3, 26.1, 21.6, 21.0; IR (neat, ν/cm^{-1}) 3213, 2925, 2852, 2360, 1737, 1598, 1494, 1449, 1338, 1233, 1185, 1166, 1092, 1021; MS (EI, *m*/*z*) 335 (8), 226 (11), 181 (11), 180 (83), 155 (21), 96 (27), 95 (31), 93 (15), 92 (13), 91 (100), 83 (25), 82 (11), 81 (42), 79 (22), 77 (10), 69 (12), 68 (22), 67 (54), 65 (34), 55 (62); HRMS (ESI) calcd for $C_{20}H_{29}NO_5S$ [M + Na]$^+$ 418.1659, found 418.1656.

[(*E*)-5-(*p*-Tolylsulfonylamino)oxyhex-2-enyl] Acetate (1k). To a solution of pent-4-en-2-ol (1.05 g, 17.5 mmol, 1 equiv) in THF (100 mL) were added PPh_3 (8.3 g, 1.8 equiv) and *N*-hydroxyphthalimide (5.1 g, 1.8 equiv). The mixture was cooled to 0 °C, and DIAD (5.2 mL, 1.5 equiv) was added dropwise. After 3 h, the reaction medium

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was concentrated, and the residue was purified by flash chromatography on silica gel (PE/Et_2O 90/10) to afford 2-(1-methylbut-3-enoxy)isoindoline-1,3-dione as a white solid (3.95 g, 17 mmol, 97%): mp 54 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.79 (m, 2H, H_{Ar}), 7.78−7.71 (m, 2H, H_{Ar}), 5.88 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H, H_4), 5.16 (dq, J = 17.1, 1.8 Hz, 1H, H_5), 5.10 (dq, J = 10.4, 1.6 Hz, 1H, $H_{5'}$), 4.44 ($sext_{app}$, J = 6.4 Hz, 1H, H_2), 2.62−2.35 (m, 2H, H_3), 1.35 (d, J = 6.0 Hz, 3H, H_1); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2, 134.4, 133.3, 128.9, 123.5, 117.9, 83.4, 39.3, 18.3; IR (neat, ν/cm^{-1}) 2983, 2925, 1783, 1737, 1639, 1610, 1465, 1416, 1380, 1362, 1287, 1245, 1184, 1156, 1137, 1121, 1082, 1053, 1012; MS (EI, m/z) 190 (2, $[M - CH_2CH{=}CH_2]^+$), 164 (16), 163 (14, $[PhtNOH]^{+\cdot}$), 133 (9), 105 (13), 104 (42), 90 (30), 77 (12), 76 (64), 75 (11), 69 (100), 68 (95), 67 (32), 53 (14); HRMS (ESI) calcd for $C_{13}H_{13}NO_3$ $[M + Na]^+$ 254.0788, found 254.0789. General procedure B was applied to 2-(1-methylbut-3-enoxy)isoindoline-1,3-dione (300 mg, 1.3 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 70/30) yielded [(*E*)-5-(1,3-dioxoisoindolin-2-yl)oxyhex-2-enyl] acetate as an orange oil (250 mg, 0.82 mmol, 63%, E/Z = 83/17): ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.80 (m, 2H), 7.78−7.70 (m, 2H), 5.89−5.75 (m, 1H), 5.73−5.55 (m, 1H), 4.51 (dd, J = 6.2, 1.0 Hz, 2H), 4.11 ($sext_{app}$, J = 5.9 Hz, 1H), 2.67−2.37 (m, 2H), 2.05 (s, 3H), 1.34 (d, J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 164.2, 134.5, 130.2, 129.0, 127.3, 123.5, 83.3, 64.8, 37.7, 21.0, 18.4; IR (neat, ν/cm^{-1}) 2935, 1789, 1727, 1611, 1467, 1365, 1229, 1187, 1121, 1082, 1063, 1016; MS (EI, m/z) 244 (1, $[M - OAc]^+$), 141 (48, $[M - PhtNO]^+$), 130 (7), 104 (17), 99 (14), 90 (20), 82 (7), 81 (100), 79 (15), 76 (22), 55(7), 54 (7), 53 (10); HRMS (ESI) calcd for $C_{16}H_{17}NO_5$ $[M + Na]^+$ 326.0999, found 326.1003. General procedure C was applied to [(*E*)-5-(1,3-dioxoisoindolin-2-yl)oxyhex-2-enyl] acetate (400 mg, 1.3 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 50/50) provided [(*E*)-5-aminooxyhex-2-enyl] acetate as a yellow oil (1.07 g, 0.81 mmol, 62%, E/Z = 83/17): ^1H NMR (400 MHz, $CDCl_3$) δ 5.81−5.70 (m, 1H), 5.70−5.59 (m, 1H), 4.52 (dd, J = 6.4, 0.8 Hz, 2H), 3.70 ($sext_{app}$, J = 6.1 Hz, 1H), 2.45−2.15 (m, 2H), 2.05 (s, 3H), 1.14 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 132.1, 126.2, 79.2, 65.1, 37.8, 21.1, 18.4; IR (neat, ν/cm^{-1}) 3222, 2970, 2929, 1735, 1592, 1446, 1367, 1229, 1126, 1067, 1025; HRMS (ESI) calcd for $C_8H_{15}NO_3$ $[M + Na]^+$: 196.0944, found 196.0940. General procedure D was applied to [(*E*)-5-aminooxyhex-2-enyl] acetate (30 mg, 0.17 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 60/40) yielded **1k** as a colorless oil (43 mg, 0.13 mmol, 78%, E/Z > 90/10): ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d_{app}, J = 8.0 Hz, 2H), 7.33 (d_{app}, J = 8.0 Hz, 2H), 6.91 (s, 1H), 5.77−5.56 (m, 2H), 4.52 (d_{app}, J = 6.0 Hz, 2H), 3.70 ($sext_{app}$, J = 6.2 Hz, 1H), 2.44 (s, 3H), 2.40−2.20 (m, 2H), 2.06 (s, 3H), 1.18 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 144.8, 133.8, 131.0, 129.6, 128.5, 126.8, 81.7, 64.9, 37.7, 21.6, 20.9, 18.4; IR (neat): 3213, 2976, 2933, 1736, 1716, 1598, 1446, 1379, 1341, 1307, 1232, 1165, 1120, 1091, 1067, 1023; MS (EI, m/z) 171 (19, $[TsNH_2]^{+\cdot}$), 155 (16, $[Ts]^+$), 108 (15), 107 (31), 91 (100), 89 (15), 77 (13), 65 (53), 64 (11), 63 (21), 51 (14); HRMS (ESI) calcd for $C_{15}H_{21}NO_5S$ $[M + Na]^+$ 350.1033, found 350.1024.

[(*E*)-5-Phenyl-5-(*p*-tolylsulfonamino)oxypent-2-enyl] Acetate (1l). General procedure A was applied to benzaldehyde (1.6 g, 15 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10) yielded 2-(1-phenylbut-3-enoxy)isoindoline-1,3-dione as a white solid (4.2 g, 14.3 mmol, 95%): mp 80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75−7.70 (m, 2H), 7.70−7.65 (m, 2H), 7.49−7.45 (m, 2H), 7.36−7.28 (m, 3H), 5.79 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.39 (t, J = 7.1 Hz, 1H), 5.15 (dq, J = 17.1, 1.5 Hz, 1H), 5.07 (ddt, J = 10.2, 1.8, 1.2 Hz, 1H), 2.95 (dtt, J = 14.3, 7.1, 1.3 Hz, 1H), 2.77−2.68 (dtt, J = 14.3, 7.1, 1.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.7, 137.5, 134.3, 133.0, 129.1, 128.8, 128.3, 128.2, 123.4, 118.1, 88.3, 39.2; IR (neat, ν/cm^{-1}) 3064, 1788, 1727, 1641, 1610, 1494, 1466, 1455, 1366, 1335, 1290, 1247, 1187, 1155, 1116, 1082, 1016; MS (EI, m/z) 252 (2, $[M - CH_2CH{=}CH_2]^+$), 132 (13), 131 (100, $[M - PhtNO]^+$), 130 (42), 129 (26), 128 (10), 116 (14), 115 (17), 105 (12), 104 (21), 91 (60), 90 (11), 77 (28), 76 (28); HRMS (ESI) calcd for $C_{18}H_{15}NO_3$ $[M + Na]^+$ 316.0944, found 316.0944. General procedure B was applied to 2-(1-phenylbut-3-enoxy)isoindoline-1,3-dione (300 mg, 1.02 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 70/30) yielded [(*E*)-5-(1,3-dioxoisoindolin-2-yl)oxy-5-phenyl-pent-2-enyl] acetate as a brown oil (270 mg, 0.74 mmol, 73%, E/Z > 90/10): ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.70 (m, 2H), 7.69−7.65 (m, 2H), 7.49−7.43 (m, 2H), 7.37−7.27 (m, 3H), 5.80−5.62 (m, 2H), 5.38 (t, J = 7.0 Hz, 1H), 4.49−4.46 (m, 2H), 3.03−2.92 (m, 1H), 2.80−2.68 (m, 1H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7, 163.6, 137.3, 134.3, 129.9, 129.2, 128.8, 128.3, 128.1, 127.4, 123.4, 88.1, 64.7, 37.8, 20.9; IR (neat, ν/cm^{-1}) 2930, 1789, 1728, 1610, 1496, 1467, 1456, 1364, 1289, 1187, 1125, 1082, 1016; MS (EI, m/z) 252 (7), 203 (4, $[M - PhtNO]^+$), 143 (100), 129 (7), 128 (25), 115 (9), 105 (12), 104 (13), 91 (13), 90 (8), 77 (12), 76 (9); HRMS (ESI) calcd for $C_{21}H_{19}NO_5$ $[M + Na]^+$ 388.1155, found 388.1155. General procedure C was applied to (*E*)-5-(1,3-dioxoisoindolin-2-yl)oxy-5-phenylpent-2-enyl] acetate (250 mg, 0.68 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 60/40) yielded [(*E*)-5-aminooxy-5-phenylpent-2-enyl] acetate as a colorless oil (117 mg, 0.5 mmol, 73%, E/Z > 95/5): ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.27 (m, 5H), 5.73 (dt, J = 15.1, 6.9 Hz, 1H), 5.65−5.56 (m, 1H), 4.81 (brs, 2H), 4.55 (dd, J = 7.7, 5.8 Hz, 1H), 4.52−4.46 (m, 2H), 2.71−2.54 (m, 1H), 2.47−2.36 (m, 1H), 2.05 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 140.9, 131.5, 128.6, 128.0, 126.7, 126.5, 86.4, 64.9, 39.0, 21.0; IR (neat, ν/cm^{-1}) 3321, 3030, 2935, 1734, 1586, 1494, 1454, 1364, 1228, 1073, 1024; MS (EI, m/z) 202 (0.4, $[M - NH_2OH]^{+\cdot}$), 144 (9), 143 (72), 129 (9), 128 (32), 122 (24), 1225 (13), 107 (37), 106 (18), 105 (100), 91 (17), 79 (45), 78 (12), 77 (68), 54 (95); HRMS (ESI) calcd for $C_{13}H_{17}NO_3$ $[M + Na]^+$ 258.1101, found 258.1102. General procedure was D applied to [(*E*)-5-aminooxy-5-phenylpent-2-enyl] acetate (113 mg, 0.25 mmol) (additional 0.1 equiv of DMAP after 12 h). Purification by flash chromatography on silica gel (PE/Et_2O 70/30) yielded **1l** as a colorless oil (150 mg, 0.21 mmol, 83%, E/Z > 95/5): ^1H NMR (400 MHz, $CDCl_3$) δ 7.81−7.77 (m, 2H), 7.37−7.22 (m, 7H), 6.79 (brs, 1H), 5.78−5.68 (m, 1H), 5.66−5.58 (m, 1H), 5.02 (dd, J = 8.1, 5.8 Hz, 1H), 4.52 (d_{app}, J = 6.2 Hz, 2H), 2.68−2.58 (m, 1H), 2.50−2.41 (m, 1H), 2.45 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 144.8, 139.4, 133.7, 130.7, 129.6, 128.6, 128.5, 128.3, 127.0, 126.9, 87.8, 64.7, 38.1, 21.7, 21.0; IR (neat, ν/cm^{-1}) 3210, 2925, 2854, 1736, 1598, 1495, 1455, 1343, 1307, 1233, 1186, 1166, 1091, 1024; MS (EI, m/z) 174 (19), 155 (34), 144 (41), 143 (39), 129 (76), 128 (25), 105 (18), 104 (36), 91 (100), 77 (29), 70 (15), 66 (32), 65 (38), 51 (18); HRMS (ESI) calcd for $C_{20}H_{23}NO_5S$ $[M + Na]^+$ 412.1189, found 412.1189.

(*E*)-Ethyl 6-Acetoxy-2-((4-methylphenylsulfonamido)oxy)-hex-4-enoate (1m). To a solution of ethyl glyoxylate (2,86 mL, 15 mmol, 50% in toluene, 1 equiv) in water (100 mL) at rt were added allyl bromide (1.43 mL, 1.1 equiv) and indium powder (1.74 g, 1 equiv). After 24 h at rt, the reaction medium was quenched with 1 N HCl aqueous solution, and EtOAc was added. A white precipitate was formed, and the mixture was stirred for 1.5 h. The two phases were separated, the aqueous layer was extracted twice with EtOAc, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to deliver 2-hydroxypent-4-enoic acid ethyl ester as a crude yellow oil (1.61 g). To a solution of the previously obtained alcohol (1.6 g, 11.1 mmol, 1 equiv) in THF (60 mL) were added PPh_3 (3.78 g, 1.3 equiv) and *N*-hydroxyphthalimide (2.35 g, 1.3 equiv). The resulting mixture was cooled to 0 °C before DIAD (2.8 mL, 1.3 equiv) was added dropwise. After 30 min at 0 °C, the reaction medium was warmed to room temperature. After 3 h, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (PE/Et_2O 70/30) to afford ethyl 2-((1,3-dioxoisoindolin-2-yl)oxy)pent-4-enoate as a yellow oil (1.8 g, 6.15 mmol, 41% over two steps): ^1H NMR (400 MHz, $CDCl_3$) δ 7.88−7.79 (m, 2H), 7.79−7.72 (m, 2H), 5.94 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.24 (dq, J = 17.1, 1.5 Hz, 1H), 5.18 (dd, J = 10.2, 1.1 Hz, 1H), 4.79 (t, J = 6.6 Hz, 1H), 4.32−4.18 (m, 2H), 2.87−2.69 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.7, 163.1, 134.6, 131.2, 128.8, 123.6, 119.0, 84.5, 61.7, 35.1, 14.0; IR (neat, ν/cm^{-1}) 2983, 1793, 1731, 1643, 1647, 1371, 1292, 1186, 1127, 1081,

1017; MS (EI, *m*/*z*) 216 (2), 163 (11), 133 (12), 132 (13), 130 (29), 127 (100), 105 (29), 104 (65), 103 (11), 99 (73), 90 (55), 85 (25), 81 (20), 77 (22), 76 (88), 75 (14), 71 (19), 69 (19), 64 (11), 63 (13), 55 (37); HRMS (ESI) calcd for $C_{15}H_{15}NO_5$ [M + Na]$^+$ 312.0842, found 312.0842. General procedure B was applied to ethyl 2-((1,3-dioxoisoindolin-2-yl)oxy)pent-4-enoate (300 mg, 1.04 mmol). Purification on silica gel (PE/Et_2O 60/40) yielded (*E*)-ethyl 6-acetoxy-2-((1,3-dioxoisoindolin-2-yl)oxy)hex-4-enoate as an orange oil (260 mg, 0.72 mmol, 69%, *E*/*Z* = 70/30): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (m, 2H), 7.78−7.73 (m, 2H), 5.97−5.84 (m, 1H), 5.83−5.71 (m, 1H), 4.81−4.75 (m, 1H), 4.66 (d, *J* = 6.2 Hz, 0.6H), 4.54 (d, *J* = 5.9 Hz, 1.4H), 4.29−4.19 (m, 2H), 2.92−2.71 (m, 2H), 2.06 (s, 3H), 1.31−1.23 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 168.6, 163.1, 134.6, 128.8, 128.5, 127.9, 127.5, 127.1, 123.7, 84.3, 64.5, 61.9, 61.8, 60.1, 33.7, 29.1, 20.9, 14.0, 14.0; IR (neat, ν/cm^{-1}) 2982, 1793, 1730, 1611, 1467, 1445, 1367, 1228, 1186, 1123, 1081, 1019; MS (EI, *m*/*z*) 302 (1), 199 (12), 148 (31), 147 (10), 139 (91), 130 (19), 111 (100), 105 (18), 104 (38), 99 (11), 93 (16), 90 (30), 83 (44), 81 (57), 77 (11), 76 (45), 67 (59), 55 (30); HRMS (ESI) calcd for $C_{18}H_{19}NO_7$ [M + Na]$^+$ 384.1054, found 384.1058. General procedure C was applied to (*E*)-ethyl 6-acetoxy-2-((1,3-dioxoisoindolin-2-yl)oxy)hex-4-enoate (200 mg, 0.55 mmol). Purification on silica gel (PE/Et_2O 50/50) yielded (*E*)-ethyl 6-acetoxy-2-(aminooxy)hex-4-enoate as a colorless oil (95 mg, 0.41 mmol, 75%, *E*/*Z* = 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80−5.61 (m, 4H), 4.51 (dd, *J* = 6.0, 0.9 Hz, 2H), 4.28−4.17 (m, 3H), 2.58−2.41 (m, 2H), 2.05 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 170.7, 129.8, 127.3, 82.3, 64.7, 60.9, 34.1, 21.0, 14.3; IR (neat, ν/cm^{-1}) 3330, 2925, 1733, 1586, 1446, 1368, 1228, 1190, 1128, 1025; HRMS (ESI) calcd for $C_{10}H_{17}NO_5$ [M + Na]$^+$ 254.0999, found 254.1002. General procedure D was applied to (*E*)-ethyl 6-acetoxy-2-(aminooxy)hex-4-enoate (30 mg, 0.13 mmol). Purification by chromatography on silica gel (PE/Et_2O 60/40) yielded **1m** as a waxy oil (45 mg, 0.12 mmol, 89%, *E*/*Z* > 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.63 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.76−5.61 (m, 2H), 4.63 (dd, *J* = 8.3, 4.5 Hz, 1H), 4.53 (d, *J* = 5.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.59−5.51 (m, 1H), 2.43 (s, 3H), 2.46−2.36 (m, 1H), 2.06 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 170.5, 145.0, 133.4, 129.6, 128.9, 128.6, 127.7, 83.5, 64.4, 61.4, 33.8, 21.6, 20.9, 14.1; IR (neat, ν/cm^{-1}) 3205, 2982, 1735, 1598, 1446, 1372, 1344, 1228, 1198, 1166, 1090, 1022; HRMS (ESI) calcd for $C_{17}H_{23}NO_7S$ [M + Na]$^+$ 408.1087, found 408.1086.

(*E*)-4-Methyl-5-((4-methylphenylsulfonamido)oxy)pent-2-en-1-yl Acetate (1n). To a solution of 2-methylbut-3-en-1-ol (1.45 g, 17 mmol, 1 equiv) in THF (80 mL) were added PPh_3 (5.8 g, 1.3 equiv) and *N*-hydroxyphthalimide (3.6 g, 1.3 equiv). The mixture was cooled to 0 °C, and DIAD (4.4 mL, 1.3 equiv) was added dropwise. After 2 h, the reaction medium was concentrated, and the residue was purified by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) to afford 2-((2-methylbut-3-en-1-yl)oxy)isoindoline-1,3-dione as a yellow oil (3.5 g, 15,1 mmol, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.82 (m, 2H), 7.77−7.73 (m, 2H), 5.86 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1H), 5.18 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.09 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.15 (dd, *J* = 8.7, 6.5 Hz, 1H), 4.02 (dd, *J* = 8.7, 7.1 Hz, 1H), 2.80−2.66 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.5, 139.3, 134.5, 129.0, 123.5, 115.3, 82.3, 36.6, 16.3; IR (neat, ν/cm^{-1}) 3506, 3081, 2968, 2882, 1789, 1728, 1641, 1610, 1467, 1417, 1391, 1374, 1290, 1245, 1187, 1159, 1126, 1082, 1017; MS (EI, *m*/*z*) 186 (0.3), 164 (13), 163 (14, [PhtNOH]$^{+\cdot}$), 104 (17), 90 (13), 76 (22), 69 (100, [M − PhtNO]$^+$), 68 (66), 67 (19); HRMS (ESI) calcd for $C_{13}H_{13}NO_3$ [M + Na]$^+$ 254.0787, found 254.0791. General procedure B was applied to 2-((2-methylbut-3-en-1-yl)oxy)isoindoline-1,3-dione (500 mg, 2.17 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) yielded (*E*)-5-((1,3-dioxoisoindolin-2-yl)oxy)-4-methylpent-2-en-1-yl acetate as a brown oil (418 mg, 1.4 mmol, 64%, *E*/*Z* > 95/5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.81 (m, 2H), 7.76−7.72 (m, 2H), 5.85−5.78 (dd, *J* = 15.7, 6.5 Hz, 1H), 5.75−5.70 (m, 1H), 4.53 (d_{app}, *J* = 5.8 Hz, 2H), 4.13 (dd, *J* = 8.8, 6.6 Hz, 1H), 4.02 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.75 ($sept_{app}$, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 163.5, 136.0, 134.5, 128.9, 124.8, 123.5, 82.1, 64.9, 35.5, 21.0, 16.4; IR (neat, ν/cm^{-1}) 2966, 1789, 1726, 1467, 1365, 1229, 1187, 1128, 1082, 1017; MS (EI, *m*/*z*) 202 (3), 141 (24), 104 (20), 99 (9), 90 (21), 81 (100), 79 (14), 76 (28), 67 (16), 55 (11), 53 (14), 50 (13); HRMS (ESI) calcd for $C_{16}H_{17}NO_5$ [M + Na]$^+$ 326.0999, found 326.1002. General procedure C was applied to (*E*)-5-((1,3-dioxoisoindolin-2-yl)oxy)-4-methylpent-2-en-1-yl acetate (385 mg, 1.3 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 80/20 to 60/40) provided (*E*)-5-(aminooxy)-4-methylpent-2-en-1-yl acetate as a yellow oil (145 mg, 0.84 mmol, 65%, *E*/*Z* > 95/5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75−5.67 (m, 1H), 5.61 (dtd, *J* = 15.5, 6.0, 0.9 Hz, 1H), 5.38 (brs, 2H), 4.52 (d, *J* = 6.2 Hz, 2H), 3.56 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.52 (dd, *J* = 8.4, 5.0 Hz, 1H), 2.57 (sept, 6.9 Hz, 1H), 2.06 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 138.2, 123.8, 80.3, 65.2, 35.5, 21.0, 16.5; IR (neat, ν/cm^{-1}) 3319, 2961, 1734, 1591, 1456, 1380, 1365, 1229, 1023; HRMS (ESI) calcd for $C_8H_{15}NO_3$ [M + Na]$^+$ 196.0944, found 196.0944. General procedure D was applied to (*E*)-5-(aminooxy)-4-methylpent-2-en-1-yl acetate (110 mg, 0.6 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 80/20 to 60/40) yielded acetate **1n** as a pale yellow oil (150 mg, 0.43 mmol, 72%, *E*/*Z* > 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.78 (m, 2H), 7.34 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.01−6.95 (m, 1H), 5.66 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.62−5.54 (m, 1H), 4.51 (d, *J* = 5.5 Hz, 2H), 3.89 (d, *J* = 6.8 Hz, 2H), 2.57 (sept, *J* = 6.7 Hz, 1H), 2.45 (s, 3H), 2.06 (s, 3H), 0.99 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 144.9, 137.2, 133.7, 129.7, 128.6, 124.4, 81.3, 65.0, 35.4, 21.7, 21.0, 16.5; IR (neat): 3212, 2963, 1736, 1598, 1455, 1381, 1364, 1338, 1306, 1234, 1186, 1165, 1092, 1026; HRMS (ESI) calcd for $C_{15}H_{21}NO_5S$ [M + Na]$^+$ 350.1033, found 350.1035

(*Z*)-3-Methyl-5-((4-methylphenylsulfonamido)oxy)tetradec-2-en-1-yl Acetate (1o). To a solution of decanal (3.6 mL, 19.2 mmol, 1 equiv) in THF (130 mL) at −78 °C was added 2-methallylmagnesium chloride (50 mL, 0.5 M/THF, 1.3 equiv). After 4 h at −78 °C, the reaction medium was warmed to rt and a saturated aqueous solution of NH_4Cl was added. The two phases were separated, the aqueous layer was extracted twice with Et_2O, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was filtered on silica gel (PE/Et_2O 90/10) to provide the corresponding alcohol. To a solution of this alcohol (1 equiv) in CH_2Cl_2 (120 mL) were added DIPEA (7 mL, 3.5 equiv) and acryloyl chloride (2.8 mL, 3 equiv) at 0 °C. After 1 h at 0 °C, the reaction medium was allowed to reach rt. After 1 h, a saturated aqueous solution of $NaHCO_3$ was added. The two phases were separated, the aqueous layer was extracted twice with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (PE/Et_2O 97/3 to 95/5 to 90/10) to obtain 2-methyltridec-1-en-4-yl acrylate as a colorless oil (3 g, 11.3 mmol, 59% over two steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (dd, *J* = 17.3, 1.6 Hz, 1H), 6.09 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.79 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.11 ($pent_{app}$, *J* = 6.2 Hz, 1H), 4.77 (dq, *J* = 2.9, 1.4 Hz, 1H), 4.71 (dt, *J* = 3.0, 0.9 Hz, 1H), 2.33 (ddd, *J* = 13.9, 7.6, 0.7 Hz, 1H), 2.23 (ddd, *J* = 14.0, 5.4, 0.5 Hz, 1H), 1.77−1.73 (t, *J* = 0.9 Hz, 3H), 1.61−1.53 (m, 2H), 1.37−1.19 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 141.8, 130.2, 128.9, 113.3, 72.5, 42.9, 34.1, 31.9, 29.5, 29.5, 29.5, 29.3, 25.3, 22.7, 22.5, 14.1; IR (neat, ν/cm^{-1}) 3076, 2956, 2926, 2855, 1725, 1638, 1458, 1405, 1378, 1296, 1270, 1193, 1047; MS (EI, *m*/*z*) 195 (0.3, [M − OCOCH=CH_2]$^+$), 138 (5), 110 (4), 96 (6), 95 (10), 83 (8), 82 (16), 81 (10), 69 (5), 68 (8), 67 (9), 57 (5), 56 (5), 55 (100); HRMS (ESI) calcd for $C_{17}H_{30}O_2$ [M + Na]$^+$ 289.2138, found 289.2139. To a solution of 2-methyltridec-1-en-4-yl acrylate (2.9 g, 11 mmol, 1 equiv) in CH_2Cl_2 (70 mL) was added Hoveyda−Grubbs catalyst (93 mg, 1 mol %). The reaction medium was warmed to 50 °C for 24 h before another portion of Hoveyda−Grubbs catalyst (2 mol %) was added. After 48 h at rt, the solvent was evaporated under reduced pressure. A flash chromatography on silica gel (PE/EtOAc 95/5 to 90/10) yielded 4-methyl-6-nonyl-5,6-dihydro-2*H*-pyran-2-one as a brown oil (1.8 g, 7.6 mmol, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82−5.78 (m, 1H),

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4.36 (dddd, J = 11.6, 7.5, 5.2, 4.0 Hz, 1H), 2.31 (ddq, J = 17.8, 11.7, 1.1 Hz, 1H), 2.18 (dd, J = 17.8, 4.0 Hz, 1H), 1.97 (t, J = 1.1 Hz, 3H), 1.78 (dddd, J = 13.5, 10.1, 7.4, 4.9 Hz, 1H), 1.62 (ddt, J = 13.5, 10.4, 5.2 Hz, 1H), 1.56−1.34 (m, 2H), 1.34−1.20 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.5, 157.1, 116.5, 77.3, 34.8, 34.7, 31.9, 29.5, 29.5, 29.4, 29.3, 24.9, 23.0, 22.7, 14.1; IR (neat, ν/cm^{-1}) 2923, 2854, 1718, 1648, 1466, 1435, 1390, 1286, 1248, 1156, 1133, 1049, 1016; MS (EI, m/z) 238 (1, $[M]^+$), 125 (2), 112 (7), 111 (100), 100 (3), 95 (4), 83 (15), 82 (29), 69 (4), 67 (5), 55 (20); HRMS (ESI) calcd for $C_{15}H_{26}O_2$ $[M + Na]^+$: 261.1825, found 261.1828. To a solution of 4-methyl-6-nonyl-5,6-dihydro-2*H*-pyran-2-one (570 mg, 2.4 mmol, 1 equiv) in CH_2Cl_2 (50 mL) was added at rt DIBAL-H (14.4 mL, 1 M/hexanes, 6 equiv) dropwise. After 4 h, the reaction was quenched by addition of a saturated aqueous solution of Rochelle's salt, and EtOAc was added. The phases were separated after stirring for 10 h, and the aqueous phase was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EtOAc 50/50) to deliver (*Z*)-3-methyltetradec-2-ene-1,5-diol as a colorless oil (545 mg, 2.26 mmol, 94%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.74 (t, J = 7.6 Hz, 1H), 4.15 (dd, J = 11.7, 8.1 Hz, 1H), 3.94 (dd, J = 11.6, 7.2 Hz, 1H), 3.74−3.64 (m, 1H), 2.46 (dd, J = 13.4, 9.8 Hz, 1H), 2.45−2.35 (brs, 2H) 2.09−1.97 (m, 1H), 1.78 (s, 3H), 1.57−1.19 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.7, 126.7, 68.7, 57.9, 39.8, 38.0, 31.9, 29.6, 29.6, 29.6, 29.3, 25.8, 23.8, 22.7, 14.1; IR (neat, ν/cm^{-1}) 3318, 2923, 2853, 1666, 1458, 1458, 1378, 1161, 1126, 1050; HRMS (ESI) calcd for $C_{15}H_{30}O_2$ $[M + Na]^+$ 265.2138, found 265.2141. To a solution of (*Z*)-3-methyltetradec-2-ene-1,5-diol (210 mg, 0.87 mmol, 1 equiv) in CH_2Cl_2 (4 mL) were added at 0 °C pyridine (82 mg, 1.2 equiv) and DMAP (10 mg, 0.1 equiv). Ac_2O (82 μL, 1.05 equiv) was then added dropwise at 0 °C. The reaction medium was stirred for 2 h at 0 °C before the reaction was quenched with an aqueous solution of $CuSO_4$. The phases were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) to obtain (*Z*)-5-hydroxy-3-methyltetradec-2-en-1-yl acetate as a colorless oil (175 mg, 0.62 mmol, 71%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.51 (t, J = 7.2 Hz, 1H), 4.64 (dd, J = 12.3, 7.8 Hz, 1H), 4.55 (dd, J = 12.3, 6.9 Hz, 1H), 3.76−3.67 (m, 1H), 2.40 (dd, J = 13.6, 9.4 Hz, 1H), 2.10 (dd, J = 13.6, 3.5 Hz, 1H), 2.04 (s, 3H), 1.80 (s, 3H), 1.53−1.42 (m, 3H), 1.32−1.00 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 139.7, 122.0, 69.4, 61.2, 40.3, 37.7, 31.9, 29.7, 29.6, 29.6, 29.3, 25.8, 23.9, 22.7, 21.1, 14.1; IR (neat, ν/cm^{-1}) 3460, 2924, 2854, 1739, 1456, 1378, 1366, 1232, 1127, 1021; MS (EI, m/z) 155 (2), 99 (14), 98 (12), 97 (46), 95 (12), 84 (10), 83 (12), 81 (14), 71 (39), 69 (61), 68 (100), 67 (32), 57 (16), 56 (12), 55 (25), 53 (11); HRMS (ESI) calcd for $C_{17}H_{32}O_3$ $[M + Na]^+$ 307.2244, found 307.2240. To a solution of (*Z*)-5-hydroxy-3-methyltetradec-2-en-1-yl acetate (400 mg, 1.4 mmol, 1 equiv) in THF (15 mL) were added PPh_3 (553 mg, 1.3 equiv) and *N*-hydroxyphthalimide (344 mg, 1.3 equiv). The resulting mixture was cooled to 0 °C before DIAD (0.42 mL, 1.3 equiv) was added dropwise. After 30 min at 0 °C, the reaction medium was allowed to warm to rt. After 48 h, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (PE/EtOAc 90/10 to 80/20) to yield (*Z*)-5-((1,3-dioxoisoindolin-2-yl)oxy)-3-methyltetradec-2-en-1-yl acetate as a yellow oil (495 mg, 1.15 mmol, 82%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 5.6, 3.0 Hz, 2H), 7.73 (dd, J = 5.6, 3.0 Hz, 2H), 5.46 (t, J = 6.8 Hz, 1H), 4.60 (dd, J = 12.3, 6.8 Hz, 1H), 4.53 (dd, J = 12.3, 6.8 Hz, 1H), 4.35 (pent, J = 6.5 Hz, 1H), 2.57 (dd, J = 14.1, 6.7 Hz, 1H), 2.44 (dd, J = 14.1, 6.7 Hz, 1H), 2.02 (s, 3H), 1.82 (d, J = 1.1 Hz, 3H), 1.70−1.59 (m, 2H), 1.54−1.45 (m, 2H), 1.36−1.15 (m, 12H), 0.85 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0, 164.3, 138.2, 134.5, 129.0, 123.5, 122.0, 86.3, 60.9, 35.8, 32.9, 31.9, 29.7, 29.6, 29.5, 29.3, 25.1, 23.9, 22.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 2925, 2855, 1790, 1733, 1467, 1376, 1236, 1188, 1123, 1082, 1023; MS (EI, m/z) 252 (2), 132 (12), 131 (100), 130 (38), 129 (19), 128 (6), 116 (11), 115 (10), 105 (8), 104 (10), 91 (46), 77 (15), 76 (12), 51 (7); HRMS (ESI) calcd for $C_{25}H_{35}NO_5$ $[M + Na]^+$ 452.2407, found 452.2407. General procedure C was applied to (*Z*)-5-((1,3-dioxoisoindolin-2-yl)oxy)-3-methyltetradec-2-en-1-yl acetate (445 mg, 1 mmol). Purification by flash chromatography on silica gel (PE/EtOAc 90/10 to 80/20) delivered (*Z*)-5-(aminooxy)-3-methyltetradec-2-en-1-yl acetate as a pale yellow oil (307 mg, 0.99 mmol, 99%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 (t_{app}, J = 7.2 Hz, 1H), 5.22 (brs, 2H), 4.61 (d, J = 7.1 Hz, 2H), 3.67−3.62 (m, 1H), 2.51 (dd, J = 13.7, 7.5 Hz, 1H), 2.11 (dd, J = 13.7, 5.6 Hz, 1H), 2.05 (s, 3H), 1.81 (dd, J = 1.9, 0.8 Hz, 3H), 1.65−1.45 (m, 2H), 1.43−1.21 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.1, 140.1, 120.9, 82.4, 61.3, 36.0, 33.1, 31.9, 29.8, 29.6, 29.6, 29.3, 25.7, 24.2, 22.7, 21.1, 14.1; IR (neat, ν/cm^{-1}) 3322, 2924, 2854, 1737, 1668, 1589, 1457, 1378, 1365, 1230, 1130, 1022; HRMS (ESI) calcd for $C_{17}H_{33}NO_3$ $[M + Na]^+$ 322.2353, found 322.2353. General procedure D was applied to (*Z*)-5-(aminooxy)-3-methyltetradec-2-en-1-yl acetate (300 mg, 1 mmol). Purification by flash chromatography on silica gel (PE/EtOAc 90/10 to 80/20) yielded acetate **1o** as a pale yellow oil (398 g, 0.88 mmol, 88%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, 2H), 7.35−7.30 (m, 2H), 7.21 (s, 1H), 5.38 (t, J = 7.0 Hz, 1H), 4.52 (dd, J = 13.0, 6.9 Hz, 1H), 4.45 (dd, J = 12.7, 6.9 Hz, 1H), 4.19−4.13 (m, 1H), 2.48 (dd, J = 14.0, 8.4 Hz, 1H), 2.44 (s, 3H), 2.07 (dd, J = 14.0, 4.8 Hz, 1H), 2.00 (s, 3H), 1.81 (d_{app}, J = 1.1 Hz, 3H), 1.58−1.36 (m, 2H), 1.36−1.22 (m, 14H), 0.89 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 144.6, 138.9, 134.0, 129.6, 128.6, 121.6, 84.7, 61.3, 36.6, 33.3, 31.9, 29.6, 29.6, 29.6, 29.3, 25.4, 23.8, 22.7, 21.7, 21.0, 14.1; IR (neat, ν/cm^{-1}) 3216, 2924, 2854, 1737, 1717, 1598, 1494, 1456, 1379, 1364, 1339, 1307, 1232, 1186, 1166, 1092, 1020; MS (EI, m/z) 222 (3), 155 (7), 123 (7), 110 (12), 109 (9), 95 (40), 85 (9), 71 (20), 69 (14), 68 (100), 67 (25), 57 (20), 55 (16); HRMS (ESI) calcd for $C_{24}H_{39}NO_5S$ $[M + Na]^+$ 476.2441, found 476.2441.

(*E*)-6-((4-Methylphenylsulfonamido)oxy)hept-2-en-1-yl Acetate (1p). To a solution of hex-5-en-2-ol (3.1 g, 31 mmol, 1 equiv) in THF (150 mL) were added PPh_3 (10.5 g, 1.3 equiv) and *N*-hydroxyphthalimide (6.5 g, 1.3 equiv). The mixture was cooled to 0 °C, and DIAD (8 mL, 1.3 equiv) was added dropwise. After 12 h, at rt, the reaction medium was concentrated, and the residue was purified by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) to afford 2-(hex-5-en-2-yloxy)isoindoline-1,3-dione as a yellow oil (7.6 g, 30.6 mmol, 99%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 2H), 7.78−7.72 (m, 2H), 5.86 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.09 (ddd, J = 17.0, 3.5, 1.6 Hz, 1H), 4.99 (ddt, J = 10.2, 1.9, 1.2 Hz, 1H), 4.44−4.34 (sext, J = 6.3 Hz, 1H), 2.38−2.21 (m, 2H), 2.00−1.90 (m, 1H), 1.75−1.64 (m, 1H), 1.35 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.4, 137.8, 134.4, 129.0, 123.5, 115.1, 83.9, 34.1, 29.5, 18.8; IR (neat, ν/cm^{-1}) 3507, 3077, 2978, 2932, 1789, 1723, 1641, 1611, 1467, 1449, 1416, 1375, 1289, 1246, 1187, 1121, 1082, 1066, 1015; MS (EI, m/z) 190 (1, $[M - CH_2CH_2CH{=}CH_2]^+$), 164 (21), 163 (22, $[PhtNOH]^{+\cdot}$), 104 (23), 83 (47, $[M - PhtNO]^+$), 82 (75), 76 (25), 67 (56), 55 (100); HRMS (ESI) calcd for $C_{14}H_{15}NO_3$ $[M + Na]^+$ 268.0944, found 268.0946. General procedure B was applied to 2-(hex-5-en-2-yloxy)isoindoline-1,3-dione (500 mg, 2.0 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) yielded (*E*)-6-((1,3-dioxoisoindolin-2-yl)oxy)hept-2-en-1-yl acetate as a brown oil (515 mg, 1.6 mmol, 81%, *E*/*Z* = 87/13): ^1H NMR (400 MHz, $CDCl_3$) δ 7.88−7.80 (m, 2H), 7.79−7.71 (m, 2H), 5.90−5.76 (m, 1H), 5.72−5.59 (m, 1H), 4.52 (dd, J = 6.3, 0.7 Hz, 2H), 4.42−4.32 (sext, J = 6.2 Hz, 1H), 2.42−2.25 (m, 2H), 2.07 (s, J = 2.2 Hz, 3H), 1.91 (dt, J = 15.0, 6.3 Hz, 1H), 1.70 (ddd, J = 14.6, 9.1, 6.2 Hz, 1H), 1.35 (d, J = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 164.4, 135.1, 134.5, 129.0, 124.6, 123.5, 83.7, 65.1, 34.1, 28.0, 21.1, 18.9; IR (neat, ν/cm^{-1}) 2935, 1789, 1727, 1467, 1364, 1228, 1187, 1122, 1082, 1016; MS (EI, m/z) 205 (0.3), 155 (8), 113 (9), 105 (8), 104 (25), 96 (8), 95 (100), 94 (66), 90 (16), 79 (24), 77 (10), 76 (30), 67 (38), 55 (20), 53 (13); HRMS (ESI) calcd for $C_{17}H_{19}NO_5$ $[M + Na]^+$ 340.1155, found 340.1156. General procedure C was applied to (*E*)-6-((1,3-dioxoisoindolin-2-yl)oxy)hept-2-en-1-yl acetate (490 mg, 1.5 mmol). Purification by flash chromatography on

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silica gel (PE/Et_2O 60/40 to 50/50) yielded (*E*)-6-(aminooxy)hept-2-en-1-yl acetate as an orange oil (180 mg, 0.93 mmol, 62%, *E*/*Z* = 88/12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83−5.73 (m, 1H), 5.63−5.53 (m, 1H), 5.21 (brs, 2H), 4.50 (dd, *J* = 6.5, 1.0 Hz, 2H), 3.69−3.59 (sext, *J* = 6.2 Hz, 1H), 2.19−2.07 (m, 2H), 2.05 (s, *J* = 3.1 Hz, 3H), 1.67 (ddt, *J* = 13.3, 8.9, 6.7 Hz, 1H), 1.51−1.41 (m, 1H), 1.15 (d, *J* = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 136.0, 124.0, 79.3, 65.2, 34.0, 28.3, 21.0, 18.6; IR (neat, ν/cm^{-1}) 3436, 2968, 2929, 1737, 1673, 1446, 1368, 1227, 1127, 1080, 1024; MS (EI, *m*/*z*) 113 (3), 112 (43), 97 (32), 83 (36), 79 (50), 70 (87), 68 (69), 67 (100), 58 (31), 57 (56), 56 (71); HRMS (ESI) calcd for $C_9H_{17}NO_3$ [M + H]$^+$ 188.1281, found 188.1279. General procedure D was applied to (*E*)-6-(aminooxy)hept-2-en-1-yl acetate (170 mg, 0.9 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 80/20 to 70/30 to 50/50) yielded **1p** as a pale yellow oil (273 mg, 0.8 mmol, 88%, *E*/*Z* > 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.76 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 5.2 Hz, 1H), 5.80−5.71 (m, 1H), 5.61−5.52 (m, 1H), 4.50 (dd, *J* = 6.4, 0.9 Hz, 2H), 4.17−4.06 (sext, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 2.17−2.07 (m, 2H), 2.07−2.05 (s, 3H), 1.66 (ddt, *J* = 13.7, 8.5, 6.8 Hz, 1H), 1.56−1.46 (m, 1H), 1.19 (d, *J* = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 144.8, 135.5, 133.9, 129.7, 128.5, 124.3, 82.2, 65.1, 33.9, 28.0, 21.7, 21.0, 18.6; IR (neat, ν/cm^{-1}) 3215, 2931, 1736, 1598, 1494, 1446, 1378, 1340, 1307, 1231, 1186, 1166, 1091, 1022; HRMS (ESI) calcd for $C_{16}H_{23}NO_5S$ [M + Na]$^+$ 364.1189, found 364.1192.

5-((4-Methylphenylsulfonamido)oxy)tetradec-1-en-3-yl Acetate (1q). To a solution of (1-allyldecyloxy)-*tert*-butyldimethylsilane (2.8 g, 9 mmol, 1 equiv) in a 1/1 mixture of *t*-BuOH/H_2O (120 mL) at rt were added OsO_4 (2.5 mL, 2.5 wt % in *t*-BuOH, 0.02 equiv) and NMO (1.6 g, 1.5 equiv). The mixture was stirred at rt for 24 h before being quenched with aq $Na_2S_2O_3$. After the mixture turned dark brown, EtOAc was added, the phases were separated and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with aq $Na_2S_2O_3$ and brine, dried over Na_2SO_4 and evaporated under reduced pressure to yield a diol. To a solution of previously synthesized crude diol (1 equiv) in a 1/1 mixture of THF/buffer pH 7 (100 mL) was added at rt sodium periodate (5.8 g, 3 equiv). After 14 h at rt, the mixture was filtered off through a pad of Celite (EtOAc). The phases were separated and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure to yield 3-(*tert*-butyldimethylsilanyloxy)dodecanal as a colorless oil (2.4 g, 85%) which was used in the next step without further purification. To a solution of the previously synthesized aldehyde (1.1 g, 3.5 mmol, 1 equiv) in THF (20 mL) at −78 °C was added vinylmagnesium bromide (5.3 mL, 2 M/THF, 1.5 equiv). After 4 h at −78 °C, the reaction medium was warmed to 0 °C, and Ac_2O (0.6 mL, 1.5 equiv) was added. After 48 h at rt, aq NH_4Cl was added. The two phases were separated, the aqueous layer was extracted twice with Et_2O, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (PE/Et_2O 100/0 to 99/1) to provide 5-((*tert*-butyldimethylsilyl)oxy)tetradec-1-en-3-yl acetate as a colorless oil (1.1 g, 7.4 mmol, 82%, 60/40 mixture of diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85−5.72 (m, 1H), 5.34 (q, *J* = 6.3 Hz, 0.6H), 5.30−5.11 (m, 2.4H), 3.78−3.65 (m, 1H), 2.07−2.02 (m, 3H), 1.90−1.60 (m, 2H), 1.53−1.37 (m, 2H), 1.37−1.19 (m, 14H), 0.89 (m, 13H), 0.08−−0.02 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 170.1, 137.1, 136.7, 116.7, 116.0, 72.3, 72.2, 69.1, 68.5, 41.8, 41.7, 37.7, 37.8, 31.9, 29.8, 29.7, 29.6, 29.6, 29.3, 25.9, 25.0, 24.6, 22.7, 21.3, 18.1, 18.0, 14.1, −4.2, −4.3, −4.5, −4.8; IR (neat, ν/cm^{-1}) 2955, 2927, 2855, 1743, 1648, 1463, 1370, 1234, 1066, 1019; MS (EI, *m*/*z*) 275 (0.1), 197 (3), 118 (9), 117 (100), 97 (3), 95 (7), 83 (4), 81 (8), 75 (33), 73 (21), 67 (11), 57 (6), 55 (5); HRMS (ESI) calcd for $C_{22}H_{44}O_3Si$ [M + Na]$^+$ 407.2952, found 407.2963. To a solution of 5-((*tert*-butyldimethylsilyl)oxy)tetradec-1-en-3-yl acetate (1 g, 2.6 mmol, 1 equiv) in THF (30 mL) at 0 °C was added TBAF (3.9 mL, 1 M/THF, 1.5 equiv). After being stirred for 12 h at rt, the mixture was carefully quenched with aq $NaHCO_3$ and diluted with EtOAc. The phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Filtration on silica gel (PE/Et_2O 60/40 to 40/60) afforded the corresponding alcohol as a yellow oil (550 mg, 78%). To a solution of this alcohol (550 mg, 2 mmol, 1 equiv) in THF (30 mL) were added PPh_3 (682 mg, 1.3 equiv) and *N*-hydroxyphthalimide (425 mg, 1.3 equiv). The resulting mixture was cooled to 0 °C before DIAD (0.5 mL, 1.3 equiv) was added dropwise. After 30 min at 0 °C, the reaction medium was allowed to reach room temperature. After 4 h at rt, the solvent was removed under reduced pressure, and the residue was filtered on a pad of silica gel (PE/Et_2O 75/25) to afford a crude oil (740 mg, 89%). This crude oil (730 mg, 4.1 mmol) was subjected to procedure C. Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 50/50) yielded 5-(aminooxy)tetradec-1-en-3-yl acetate as a colorless oil (300 mg, 1.56 mmol, 60%, 50/50 mixture of diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85−5.78 (m, 1H), 5.49−5.43 (m, 0.5H), 5.39 (q, *J* = 6.4 Hz, 0.5H), 5.27 (m, 1H), 5.22−5.12 (m, 1H), 3.66−3.57 (m, 1H), 2.08 (s, 1.5H), 2.06 (s, 1.5H), 2.10−1.97 (m, 1H), 1.84−1.71 (m, 1H), 1.71−1.39 (m, 2H), 1.37−1.20 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 136.8, 136.3, 117.1, 116.2, 80.5, 80.4, 72.6, 71.7, 37.7, 37.2, 33.1, 32.7, 31.9, 29.8, 29.7, 29.6, 29.6, 29.3, 25.2, 25.1, 22.7, 21.3, 21.3, 14.1; IR (neat, ν/cm^{-1}) 3322, 2924, 2855, 1734, 1586, 1466, 1423, 1374, 1241, 1022; HRMS (ESI) calcd for $C_{16}H_{31}NO_3$ [M + Na]$^+$ 308.2196, found 308.2195. General procedure D was applied to 5-(aminooxy)tetradec-1-en-3-yl acetate (60 mg, 0.21 mmol). Purification by flash chromatography on silica gel (PE/Et_2O 80/20) yielded **1q** as a colorless oil (67 mg, 0.15 mmol, 73%, 50/50 mixture of diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.3, 2.7 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 0.5H), 6.84 (s, 0.5H), 5.88−5.72 (m, 1H), 5.43−5.32 (m, 1H), 5.36−5.13 (m, 2H), 4.12−4.05 (m, 0.5H), 4.04−3.96 (m, 0.5H), 2.44 (s, 3H), 2.09 (s, 1.5H), 2.05−2.02 (s, 1.5H), 2.15−1.91 (m, 1H), 1.84−1.73 (m, 1H), 1.73−1.45 (m, 2H), 1.36−1.19 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 144.8, 144.8, 136.6, 135.9, 133.9, 133.8, 129.8, 129.8, 128.6, 128.6, 117.5, 116.5, 83.2, 82.8, 71.9, 71.1, 37.4, 37.1, 32.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 25.0, 24.9, 22.7, 21.7, 21.2, 14.1; IR (neat, ν/cm^{-1}) 3216, 2925, 2855, 1736, 1598, 1494, 1466, 1409, 1372, 1341, 1307, 1238, 1186, 1168, 1120, 1092, 1020; HRMS (ESI) calcd for $C_{23}H_{37}NO_5S$ [M + Na]$^+$ 462.2285, found 462.2281.

(*E*)-5-((4-Methylphenylsulfonamido)oxy)-1-phenyltetradec-1-en-3-yl Acetate (1r). To a solution of acetic acid (*E*)-5-(1,3-dioxo-1,3-dihydro-isoindol-2-yloxy)-1-phenyltetradec-2-enyl ester (250 mg, 0.5 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added SiO_2 (1 g, 400 wt %) in a sealed vial. The mixture was heated in a microwave at 80 °C for 30 min.[18] After filtration and elution with CH_2Cl_2, purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) afforded the desired compound as a pale yellow oil (224 mg, 90%, dr ∼50/50). The hydroxylamine ether derivative was prepared from the previously synthesized acetate (100 mg, 0.2 mmol) by applying procedure C. Filtration on silica gel (PE/Et_2O 50/50) provided the corresponding hydroxylamine ether (55 mg, 76%, dr ∼50/50). The previously synthesized hydroxylamine ether (42 mg, 0.12 mmol) was subjected to procedure D. Purification by flash chromatography on silica gel (PE/Et_2O 90/10 to 80/20) yielded **1r** as a colorless oil (45 mg, 0.37 mmol, 73%, 50/50 mixture of diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.41−7.24 (m, 7H), 7.01 (s, 0.5H), 6.99 (s, 0.5H), 6.69 (d, *J* = 15.9 Hz, 0.5H), 6.57 (d, *J* = 16.1 Hz, 0.5H), 6.16 (dd, *J* = 15.9, 7.3 Hz, 0.5H), 6.12 (dd, *J* = 16.1, 7.1 Hz, 0.5H), 5.62−5.48 (m, 1H), 4.11 (m, 0.5H), 4.03 (m, 0.5H), 2.43 (s, 3H), 2.10 (s, 1.5H), 2.05 (s, 1.5H), 2.00−1.75 (m, 2H), 1.72−1.44 (m, 2H), 1.25 (m, 14H), 0.92−0.86 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 144.8, 144.7, 136.2, 133.9, 133.9, 133.2, 132.3, 129.8, 129.8, 128.6, 128.6, 128.6, 128.0, 128.0, 127.7, 126.9, 126.7, 126.6, 83.4, 82.9, 72.0, 71.1, 37.8, 37.5, 32.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 25.0, 24.9, 22.7, 21.7, 21.3, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1739, 1644, 1598, 1495, 1454, 1337, 1306, 1233, 1185, 1164, 1122, 1091, 1033, 1010; HRMS (ESI) calcd for $C_{29}H_{41}NO_5S$ [M + Na]$^+$ 538.2598, found 538.2599.

(3*R,5*R**)-5-Nonyl-2-tosyl-3-vinylisoxazolidine (2a).** Prepared from **1a** (770 mg, 1.75 mmol) following the general procedure E. Filtration on a pad of basic alumina afforded **2a** as a yellow oil (627 mg, 1.65 mmol, 94%, *cis*/*trans* = 90/10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 5.89 (ddd, J = 17.1, 10.4, 6.8 Hz, 1H), 5.34 (d, J = 17.1 Hz, 1H), 5.18 (d, J = 10.4 Hz, 1H), 4.64 (q_{app}, J = 7.5 Hz, 1H), 4.06 ($sext_{app}$, J = 5.7 Hz, 1H), 2.50 (ddd, J = 12.6, 8.2, 5.6 Hz, 1H), 2.45 (s, 3H), 1.75 (ddd, J = 12.6, 9.9, 8.3 Hz, 1H), 1.69−1.14 (m, 16H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 136.9, 133.1, 129.6, 129.2, 116.8, 81.7, 62.1, 41.3, 32.6, 31.9, 29.7, 29.5, 29.4, 29.3, 26.1, 22.6, 21.7, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1744, 1645, 1598, 1494, 1458, 1361, 1334, 1305, 1237, 1162, 1091; MS (EI, m/z) 379 (5, $[M]^{+\cdot}$), 225 (16, $[M - Ts]^{+\cdot}$), 224 (100), 155 (12), 96 (27), 95 (14), 91 (59), 83 (11), 81 (21), 70 (12), 69 (22), 67 (28), 65 (18), 57 (18), 56 (14), 55 (34); HRMS (ESI) calcd for $C_{21}H_{33}NO_3S$ $[M + Na]^+$ 402.2073, found 402.2081.

(3*R,5*R**)-2-(2-Nitrophenylsulfonyl)-5-nonyl-3-vinylisoxazolidine (2b).** Prepared from **1b** (50 mg, 0.11 mmol) following the general procedure E. Filtration on a pad of basic alumina and purification by flash chromatography on silica gel (PE/Et_2O 90/10) afforded **2b** as a pale yellow oil (43 mg, 0.1 mmol, 95%, *cis*/*trans* = 89/11): ^{1}H NMR (400 MHz, C_6D_6) δ 7.96 (dt, J = 7.9, 1.5 Hz, 1H), 6.70 (dt, J = 7.9, 1.5 Hz, 1H), 6.65−6.60 (m, 1H), 6.58−6.51 (m, 1H), 5.80 (ddd, J = 17.1, 10.3, 6.5 Hz, 1H), 5.30 (ddt, J = 17.1, 2.2, 1.2 Hz, 1H), 5.04 (ddt, J = 10.2, 2.1, 1.1 Hz, 1H), 4.86 (q_{app}, J = 7.2 Hz, 1H), 4.41−4.33 (m, 1H), 2.04 (ddd, J = 12.0, 8.1, 6.0 Hz, 1H), 1.49−1.03 (m, 17H), 0.91 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 149.0, 136.2, 134.8, 132.3, 131.4, 129.4, 124.2, 117.4, 83.0, 61.3, 41.0, 32.7, 31.9, 29.5, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1; IR (neat, ν/cm^{-1}) 3098, 2925, 2855, 1645, 1590, 1546, 1466, 1440, 1371, 1349, 1298, 1171, 1127, 1060; HRMS (ESI) calcd for $C_{20}H_{30}N_2O_5S$ $[M + Na]^+$ 433.1768, found 433.1770

(3*R,5*R**)-5-Nonyl-3-vinylisoxazolidine-2-carboxylic Acid Benzyl Ester (2c).** Prepared from **1c** (50 mg, 0.12 mmol) following the general procedure E. Filtration on a pad of basic alumina and purification on silica gel (PE/Et_2O 90/10) afforded **2c** as an oil (27 mg, 0.08 mmol, 63%, *cis*/*trans* = 86/14): ^{1}H NMR (400 MHz, C_6D_6) δ 7.28−7.25 (m, 2H), 7.12−7.01 (m, 3H), 5.78 (ddd, J = 16.8, 10.2, 6.4 Hz, 1H), 5.27 (dt, J = 17.0, 1.4 Hz, 1H), 5.14 (m, 1H), 5.09 (m, 1H), 4.96 (dt, J = 10.3, 1.3 Hz, 1H), 4.70 (q_{app}, J = 6.6 Hz, 1H), 3.60 (ddd, J = 11.2, 8.9, 5.7 Hz, 1H), 1.94 (ddd, J = 12.0, 8.7, 5.9 Hz, 1H), 1.63−1.11 (m, 17H), 0.92 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 158.8, 138.5, 136.9, 128.6, 128.3, 128.2, 115.0, 82.0, 67.7, 62.5, 41.4, 32.7, 32.3, 29.9, 29.9, 29.8, 29.7, 26.4, 23.1, 14.4; IR (neat, ν/cm^{-1}) 2926, 2855, 1736, 1710, 1645, 1498, 1456, 1395, 1304, 1089, 1029; MS (EI, m/z) 304 (12), 222 (6), 221 (17), 220 (100), 146 (16), 130 (7), 90 (6), 89 (10), 76 (8), 75 (20), 74 (5), 73 (49), 67 (32), 59 (14); HRMS (ESI) calcd for $C_{22}H_{33}NO_3$ $[M - Na^+]$ 382.2353, found 382.2358.

(3*R,5*R**)-Allyl 5-Nonyl-3-vinylisoxazolidine-2-carboxylate (2d).** Prepared from **1d** (25 mg, 0.06 mmol, 1 equiv) following the general procedure E. Filtration on a pad of basic alumina (CH_2Cl_2) and purification on silica gel (PE/Et_2O 90/10) afforded **2d** as a yellow oil (17 mg, 0.055 mmol, 92%, *cis*/*trans* = 85/15): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddt, J = 17.2, 10.5, 5.6 Hz, 1H), 5.84 (ddd, J = 16.9, 10.2, 6.7 Hz, 1H), 5.33 (dq, J = 17.2, 1.6 Hz, 1H), 5.28 (dt, J = 17.0, 1.2 Hz, 1H), 5.23 (dq, J = 10.5, 1.3 Hz, 1H), 5.13 (dt, J = 10.2, 1.2 Hz, 1H), 4.71−4.64 (m, 3H), 3.91 (dq, J = 9.9, 6.2 Hz, 1H), 2.58 (ddd, J = 12.1, 8.6, 5.8 Hz, 1H), 1.82−1.51 (m, 3H), 1.47−1.18 (m, 14H), 0.87 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 137.6, 132.2, 118.1, 115.6, 82.0, 66.7, 62.1, 41.1, 32.3, 31.9, 29.5, 29.5, 29.5, 29.3, 25.9, 22.7, 14.1; IR (neat, ν/cm^{-1}) 2925, 2855, 1721, 1710, 1648, 1457, 1377, 1312, 1267, 1081; MS (EI, m/z) 309 (4, $[M]^{+\cdot}$), 224 (61, $[M - Alloc]^+$), 140 (10), 112 (79), 111 (11), 110 (37), 98 (12), 97 (17), 96 (100), 95 (33), 94 (11), 83 (26), 82 (25), 81 (45), 72 (26), 71 (17), 70 (21); HRMS (ESI) calcd for $C_{18}H_{31}NO_3$ $[M + Na]^+$ 332.2196, found 332.2194.

(3*R,5*R**)-5-Octyl-2-(*p*-tolylsulfonyl)-3-[(*E*)-styryl]-isoxazolidine (2g).** Prepared from **1g** (60 mg, 0.12 mmol) following the general procedure E. Filtration on a pad of silica afforded **2g** as a yellow oil (43 mg, 0.09 mmol, 78%, *cis*/*trans* = 80/20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.85 (m, 2H), 7.42−7.28 (m, 6H), 7.28−7.20 (m, 1H), 6.71 (d, J = 15.8 Hz, 0.2H), 6.64 (d, J = 15.8 Hz, 0.8H), 6.22 (dd, J = 15.9, 7.4 Hz, 0.8H), 6.20−6.12 (m, 0.2H), 4.85 (q_{app}, J = 7.9 Hz, 1H), 4.22 (t_{app}, J = 8.1 Hz, 0.2H), 4.14 ($sext_{app}$, J = 5.7 Hz, 0.8H), 2.58 (ddd, J = 12.0, 7.8, 5.4 Hz, 0.8H), 2.46 (d, J = 2.9 Hz, 0.6H), 2.45 (s, 2.4H), 2.14 (ddd, J = 11.9, 5.8, 1.7 Hz, 0.2H), 1.84 (ddd, J = 11.9, 9.9, 8.1 Hz, 1H), 1.57−1.43 (m, 2H), 1.38−1.15 (m, 14H), 0.89 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 136.3, 133.2, 132.0, 129.7, 129.3, 128.6, 128.3, 127.9, 126.6, 82.0, 62.0, 41.9, 32.7, 31.9, 29.7, 29.5, 29.5, 29.3, 26.2, 22.7, 21.7, 14.1; IR (neat, ν/cm^{-1}) 2854, 1718, 1598, 1494, 1451, 1363, 1334, 1163, 1092, 1019; MS (EI, m/z) 251 (20), 209 (32), 207 (14), 195 (35), 193 (14), 181 (43), 147 (35), 135 (52), 121 (13), 105 (11), 101 (22), 96 (14), 95 (100), 91 (23), 83 (37), 75 (11), 73 (59), 69 (17), 67 (15), 57 (25); HRMS (ESI) calcd for $C_{27}H_{37}NO_3S$ $[M + Na]^+$ 478.2386, found 478.2386.

(3*R*,5*R*)-*tert*-Butyl 5-Nonyl-3-((*E*)-styryl)isoxazolidine-2-carboxylate (2h). Prepared from **1h** (190 mg, 0.41 mmol) following the general procedure E. Filtration on a pad of basic alumina and purification by flash chromatography on silica gel (PE/Et_2O 95/5 to 90/10) afforded the title compound **2h** as a yellow oil (142 mg, 0.35 mmol, 86%, *cis*/*trans* = 60/40): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.20 (m, 5H), 6.59 (d, J = 15.6 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.17 (dd, J = 15.7, 7.2 Hz, 1H), 6.15 (dd, J = 15.7, 7.2 Hz, 1H), 4.82−4.73 (m, 1H), 4.26 (m, 0.4H), 3.91 (dq, J = 10.0, 6.0 Hz, 0.6H), 2.62 (ddd, J = 12.1, 8.5, 5.7 Hz, 0.6H), 2.25−2.19 (m, 0.4H), 1.77 (ddd, J = 12.2, 9.9, 6.9 Hz, 1H), 1.66−1.45 (m, 2H), 1.49 (s, 9H), 1.45−1.17 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 156.9, 136.6, 136.6, 130.9, 130.6, 129.6, 128.8, 128.5, 127.6, 127.6, 126.5, 81.6, 81.5, 81.4, 80.3, 62.0, 60.3, 41.8, 40.6, 33.6, 32.4, 31.9, 29.6, 29.5, 29.5, 29.5, 29.3, 28.3, 28.3, 26.2, 26.1, 22.6, 14.1; IR (neat, ν/cm^{-1}) 2925, 2854, 1762, 1703, 1495, 1456, 1367, 1330, 1252, 1164, 1082; MS (EI, m/z) 335 (6), 226 (10), 181 (13), 180 (98), 155 (23), 96 (31), 95 (35), 91 (100), 83 (28), 81 (49), 79 (25), 69 (14), 68 (27), 65 (35), 55 (70); HRMS (ESI) calcd for $C_{25}H_{39}NO_3$ $[M + Na]^+$ 424.2822, found 424.2825.

(*E*)-3-(But-1-en-1-yl)-2-tosylisoxazolidine (2i). Prepared from **1i** (85 mg, 0.25 mmol) following the general procedure E. Filtration on a pad of basic alumina afforded **2i** as a yellow oil (68 mg, 0.24 mmol, 96%): SFC separation, column OD-H, 5 mL/min, 10% MeOH, 100 bar, 220 nm (t_1 = 2.23 min, t_2 = 2.60 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.84 (m, 2H), 7.42−7.26 (m, 2H), 5.81 (dtd, J = 15.3, 6.3, 1.1 Hz, 1H), 5.44 (ddt, J = 15.3, 7.0, 1.6 Hz, 1H), 4.69 (q, J = 6.9 Hz, 1H), 4.04−3.94 (m, 2H), 2.44 (s, 3H), 2.42−2.33 (m, 1H), 2.13−2.02 (m, 3H), 0.99 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 135.3, 133.2, 129.7, 129.2, 127.1, 69.8, 60.9, 35.7, 25.1, 21.7, 13.2; IR (neat, ν/cm^{-1}) 2963, 2926, 1731, 1597, 1493, 1454, 1356, 1329, 1305, 1246, 1214, 1185, 1162, 1090; MS (EI, m/z) 155 (16, $[Ts]^+$), 127 (8), 126 (100, $[M - Ts]^+$), 92 (12), 91 (89), 82 (18), 81 (30), 79 (10), 71 (10), 67 (16), 65 (37), 56 (15), 55 (33), 54 (27), 53 (15); HRMS (ESI) calcd for $C_{14}H_{19}NO_3S$ $[M + Na]^+$ 304.0978, found 304.0975.

(3*R,5*S**)-5-Cyclohexyl-2-tosyl-3-vinylisoxazolidine (2j).** Prepared from **1j** (50 mg, 0.13 mmol) following the general procedure E. Filtration on a pad of basic alumina and purification by flash chromatography on silica gel (PE/Et_2O 90/10) afforded **2j** as a pale yellow oil (35 mg, 0.11 mmol, 83%, *cis*/*trans* = 86/14): ^{1}H NMR (400 MHz, C_6D_6) δ 8.00 (d_{app}, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 5.84 (ddd, J = 17.0, 10.2, 6.8 Hz, 1H), 5.32 (dt, J = 17.0, 1.2 Hz, 1H), 5.03 (dt, J = 10.2, 1.2 Hz, 1H), 4.83 (td, J = 7.9, 6.8 Hz, 1H), 4.10 (ddd, J = 10.0, 7.7, 5.6 Hz, 1H), 1.99 (ddd, J = 11.9, 8.1, 5.6 Hz, 1H), 1.80 (s, 3H), 1.81−0.57 (m, 12H, H_{Cy} + H_2·); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 144.1, 138.0, 135.0, 129.6, 129.5, 116.2, 85.9, 61.7, 41.0, 39.3, 30.0, 29.1, 26.5, 26.0, 25.8, 21.1; IR (neat, ν/cm^{-1}) 2924, 2853, 1728, 1598, 1450, 1357, 1333, 1290, 1185, 1166, 1119, 1091, 1020; HRMS (ESI) calcd for $C_{18}H_{25}NO_3S$ $[M + Na]^+$ 358.1447, found 358.1446.

(3*R,5*S**)-5-Methyl-2-tosyl-3-vinylisoxazolidine (2k).** Prepared from **1k** (30 mg, 0.09 mmol) following the general procedure

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E. Filtration on a pad of basic alumina afforded **2k** as an oil (20 mg, 0.07 mmol, 83%, *cis*/*trans* = 83/17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.84 (m, 2H), 7.37−7.31 (m, 2H), 5.90 (ddd, J = 17.0, 10.2, 6.7 Hz, 1H), 5.34 (ddd, J = 17.1, 1.5, 0.8 Hz, 1H), 5.18 (ddd, J = 10.2, 1.4, 0.8 Hz, 1H), 4.67 (dt, J = 7.9, 6.8 Hz, 1H), 4.24 (dp, J = 9.8, 6.0 Hz, 1H), 2.53 (ddd, J = 12.1, 7.8, 5.5 Hz, 1H), 2.44 (s, 3H), 1.75 (ddd, J = 12.1, 9.6, 7.9 Hz, 1H), 1.21 (d, J = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.8, 136.9, 133.1, 129.6, 129.1, 116.8, 77.8, 62.3, 42.8, 21.6, 17.9; IR (neat, ν/cm^{-1}) 2979, 2931, 1737, 1597, 1448, 1388, 1356, 1330, 1305, 1243, 1185, 1162, 1090, 1067, 1020; MS (EI, m/z) 268 (1, $[M + H]^+$), 267 (5, $[M]^{+\cdot}$), 155 (5, $[Ts]^+$), 113 (7), 112 (100, $[M - Ts]^+$), 111 (5), 94 (5), 92 (6), 91 (45), 79 (5), 68 (16), 67 (30), 65 (22); HRMS (ESI) calcd for $C_{13}H_{17}NO_3S$ $[M + Na]^+$ 290.0821, found 290.0825.

(3*R,5*S**)-5-Phenyl-2-tosyl-3-vinylisoxazolidine (2l).** Prepared from **1l** (50 mg, 0.13 mmol) following the general procedure E. Filtration on a pad of basic alumina and purification by flash chromatography on silica gel (PE/Et_2O 90/10) afforded **2l** as a pale orange oil (40 mg, 0.12 mmol, 92%, *cis*/*trans* = 86/14): ^{1}H NMR (400 MHz, C_6D_6) δ 7.97 (d_{app}, J = 8.2 Hz, 2H), 7.19−6.94 (m, 5H), 6.65 (d_{app}, J = 8.0 Hz, 2H), 5.86 (ddd, J = 17.0, 10.2, 6.5 Hz, 1H), 5.45 (dd, J = 9.8, 6.1 Hz, 1H), 5.37−5.30 (m, 1H), 5.06−5.01 (m, 1H), 4.98 (q_{app}, J = 6.5 Hz, 1H), 2.38−2.29 (m, 1H), 1.87−1.79 (m, 1H), 1.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 144.3, 137.7, 137.6, 134.8, 129.6, 129.5, 128.7, 128.7, 127.2, 116.6, 83.5, 62.1, 43.9, 21.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1733, 1645, 1597, 1546, 1494, 1456, 1359, 1332, 1292, 1185, 1162, 1091, 1019; MS (EI, m/z) 329 (4, $[M]^{+\cdot}$), 174 (20, $[M - Ts]^+$), 155 (38, $[Ts]^+$), 144 (48), 143 (46), 129 (83), 115 (11), 105 (17), 104 (37), 92 (13), 91 (100), 78 (11), 77 (21, $[Ph]^+$), 70 (14), 66 (31), 65 (33), 51 (13); HRMS (ESI) calcd for $C_{18}H_{19}NO_3S$ $[M + Na]^+$ 352.0978, found 352.0976.

Ethyl 2-Tosyl-3-vinylisoxazolidine-5-carboxylate (2m). To a solution of **1m** (95 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added $Bi(OTf)_3$ (16 mg, 0.1 equiv). The mixture was stirred at 50 °C for 24 h before being evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 80/20 to 60/40) yielded **2m** as a colorless oil (62 mg, 0.19 mmol, 77%, 55/45 mixture of diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.91 (m, 1.1H), 7.87−7.82 (m, 0.9H), 7.37−7.32 (m, 2H), 5.92−5.76 (m, 1H), 5.43−5.30 (m, 1H), 5.27−5.17 (m, 1H), 4.96−4.85 (m, 1.45H), 4.70−4.64 (t, J = 8.2 Hz, 0.55H), 4.26 (q, J = 7.2 Hz, 1.1H), 4.19 (qd, J = 7.1, 2.1 Hz, 0.9H), 2.87−2.70 (m, 1H), 2.50−2.45 (m, 0.55H), 2.44 (s, 3H), 2.34 (ddd, J = 12.6, 6.3, 4.1 Hz, 0.45H), 1.34 (t, J = 7.2 Hz, 1.65H), 1.25 (t, J = 7.1 Hz, 1.35H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1, 169.0, 145.3, 145.3, 135.6, 134.6, 132.6, 132.4, 129.8, 129.5, 129.3, 117.4, 117.3, 78.9, 78.8, 61.8, 61.7, 61.2, 60.8, 38.9, 37.4, 21.8, 21.7, 14.2, 14.1; IR (neat, ν/cm^{-1}) 2984, 1736, 1644, 1597, 1494, 1449, 1403, 1363, 1334, 1293, 1209, 1187, 1161, 1091, 1033; MS (EI, m/z) 325 (2), 170 (22), 155 (26), 152 (21), 124 (23), 96 (34), 92 (13), 91 (100), 81 (11), 68 (14), 65 (31), 53 (11); HRMS (ESI) calcd for $C_{15}H_{19}NO_5S$ $[M + Na]^+$ 348.0876, found 348.0870.

4-Methyl-2-tosyl-3-vinylisoxazolidine (2n). Prepared from **1n** (60 mg, 0.2 mmol) following the general procedure E. Filtration on a pad of basic alumina afforded **2n** as an orange oil (43 mg, 0.18 mmol, 89%, 60/40 mixture of diastereoisomers): ^{1}H NMR (400 MHz, C_6D_6) δ 8.02−7.95 (m, 2H), 6.74−6.67 (m, 2H), 5.79 (ddd, J = 17.1, 10.1, 7.5 Hz, 0.6H), 5.59 (ddd, J = 17.1, 10.3, 7.3 Hz, 0.4H), 5.34−5.25 (m, 1H), 5.09−5.03 (m, 1H), 4.76 (t, J = 7.4 Hz, 0.4H), 4.13 (m, 1H), 3.64−3.49 (m, 1.2H), 3.17 (ddd, J = 7.2, 5.7, 0.5 Hz, 0.4H), 2.43 (ddd, J = 14.3, 7.1, 5.7 Hz, 0.4H), 2.02−1.90 (m, 0.6H), 1.80 (s, 3H), 0.59 (d, J = 6.6 Hz, 1.8H), 0.55 (d, J = 7.0 Hz, 1.2H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 144.2, 144.2, 136.5, 134.9, 134.7, 133.3, 129.6, 129.5, 129.5, 129.5, 118.1, 117.6, 75.9, 75.4, 68.6, 64.6, 44.3, 40.8, 21.1, 13.1, 12.3; IR (neat, ν/cm^{-1}) 2955, 2922, 2852, 1737, 1646, 1597, 1493, 1460, 1403, 1358, 1332, 1305, 1293, 1261, 1212, 1167, 1090; HRMS (ESI) calcd for $C_{13}H_{17}NO_3S$ $[M + Na]^+$ 290.0821, found 290.0823.

(3*R,5*R**)-3-Methyl-5-nonyl-2-tosyl-3-vinylisoxazolidine (2o).** Prepared from **1o** (50 mg, 0.11 mmol) following the general procedure E. Filtration on a pad of basic alumina afforded **2o** as a yellow oil (40 mg, 0.1 mmol, 95%, *cis*/*trans* = 75/25): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.79 (m, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.17−6.02 (m, 1H), 5.34−5.25 (m, 1H), 5.16 (m, 1H), 4.50−4.40 (m, 0.75H), 4.35−4.25 (m, 0.25H), 2.48 (dd, J = 12.1, 7.1 Hz, 0.25H), 2.43 (s, 3H), 2.35 (dd, J = 11.9, 7.1 Hz, 0.75H), 2.19−2.12 (dd, J = 11.9, 9.8 Hz, 0.75H), 2.04 (dd, J = 12.1, 8.7 Hz, 0.25H), 1.72 (s, 2.25H), 1.67 (s, 0.75H), 1.65−1.59 (m, 1H), 1.55−1.48 (m, 1H), 1.36−1.18 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 141.2, 135.6, 129.3, 129.1, 113.5, 81.7, 71.0, 47.5, 33.8, 31.9, 29.5, 29.5, 29.4, 29.3, 26.4, 24.0, 22.7, 21.6, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1737, 1599, 1495, 1458, 1403, 1331, 1304, 1234, 1184, 1160, 1090; HRMS (ESI) calcd for $C_{22}H_{35}NO_3S$ $[M + Na]^+$ 416.2230, found 416.2229.

6-Methyl-2-toxyl-3-vinyl-1,2-oxazinane (2p). Prepared from **1p** (100 mg, 0.29 mmol) following the general procedure E. Filtration on a pad of basic alumina afforded **2p** as a colorless oil (60 mg, 0.25 mmol, 85%, 53/47 mixture of two diastereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.73 (m, 2H), 7.32−7.25 (m, 2H), 6.05 (ddd, J = 17.2, 10.3, 8.8 Hz, 0.47H), 5.92 (ddd, J = 17.5, 10.6, 7.3 Hz, 0.53H), 5.20 (dt, J = 17.5, 1.3 Hz, 0.53H), 5.08 (dd, J = 10.3, 1.4 Hz, 0.47H), 5.06 (dt, J = 10.5, 1.3 Hz, 0.53H), 4.98 (ddd, J = 17.2, 1.3, 0.7 Hz, 0.47H), 4.56 (dddd, J = 6.4, 5.2, 2.3, 1.2 Hz, 0.53H), 4.17−4.04 (m, 1H), 3.20 (td, J = 9.4, 3.3 Hz, 0.47H), 2.44 (s, 1.59H), 2.42 (s, 1.41H), 2.17−2.09 (m, 0.53H), 1.83−1.65 (m, 1.9H), 1.55−1.48 (m, 1.1H), 1.32−1.18 (m, 0.47H), 1.20−1.10 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 144.0, 136.9, 134.4, 134.0, 131.8, 129.5, 129.1, 129.1, 129.1, 117.5, 115.1, 78.2, 77.5, 64.4, 57.1, 31.8, 30.8, 29.5, 27.6, 21.7, 21.6, 19.9, 19.4; IR (neat, ν/cm^{-1}) 2926, 2855, 1740, 1641, 1598, 1494, 1446, 1359, 1306, 1291, 1230, 1185, 1167, 1091, 1043, 1020; MS (EI, m/z) 281 (11, $[M]^{+\cdot}$), 157 (9), 155 (14, $[Ts]^+$), 126 (100, $[M - Ts]^+$), 95 (13), 93 (10), 91 (72), 81 (16), 67 (27), 65 (31), 55 (24), 54 (38); HRMS (ESI) calcd for $C_{14}H_{19}NO_3S$ $[M + Na]^+$ 304.0978, found 304.0979.

***N*-((3*R**,5*R**)-5-Hydroxytetradec-1-en-3-yl)-4-methylbenzenesulfonamide (3).** To a solution of **2a** (40 mg, 0.1 mmol, *cis*/*trans* = 9/1) in satd aq solution of NH_4Cl (1 mL) was added zinc (130 mg, 20 equiv). The mixture was stirred in a sealed vial at 100 °C. After 24 h at 100 °C, the reaction was cooled to rt and then evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 80/20 to 50/50) afforded **3** as a colorless oil (40 mg, 0.1 mmol, quant, *cis*/*trans* = 9/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.60 (d, J = 6.1 Hz, 1H), 5.65−5.54 (m, 1H), 5.03 (dd, J = 17.1, 1.0 Hz, 1H), 4.96 (dd, J = 10.3, 0.9 Hz, 1H), 3.85 (m, 1H), 3.60−3.52 (m, 1H), 2.41 (s, 3H), 1.92 (brs, 1H), 1.67−1.52 (m, 2H), 1.43−1.14 (m, 16H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.3, 138.2, 137.6, 129.5, 127.4, 116.0, 70.5, 56.0, 42.2, 38.2, 31.9, 29.6, 29.5, 29.5, 29.3, 25.3, 22.7, 21.5, 14.1; IR (neat, ν/cm^{-1}) 3502, 3263, 2924, 2854, 1645, 1599, 1495, 1434, 1378, 1323, 1305, 1288, 1185, 1155, 1093; MS (EI, m/z) 210 (65), 155 (65), 92 (20), 91 (100), 81 (16), 71 (13), 70 (48), 65 (29), 57 (23), 56 (29), 55 (25); HRMS (ESI) calcd for $C_{21}H_{35}NO_3S$ $[M + Na]^+$ 404.2230, found 404.2232.

(3*R,5*R**)-5-Nonyl-2-tosylisoxazolidine-3-carboxaldehyde (4).** To a solution of **2a** (200 mg, 0.50 mmol, 1 equiv, *cis*/*trans* = 9/1) in a 1/1 mixture of *t*-BuOH/H_2O (7 mL) at rt were added OsO_4 (0.14 mL, 2.5 wt % in *t*-BuOH, 0.02 equiv) and NMO (88 mg, 1.5 equiv). After 24 h at rt, the reaction medium was quenched by addition of aq $Na_2S_2O_3$. After the mixture turned dark brown, EtOAc was added, the phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with aq $Na_2S_2O_3$ and brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/Et_2O 80/20 to Et_2O) provided the expected diol as a yellow oil (157 mg, 95%, 67/23 diastereomeric mixture). To a solution of the previously obtained diol (30 mg, 0.07 mmol, 1 equiv) in a 1/1 mixture of THF/buffer pH 7 (1 mL) at rt was added sodium periodate (45 mg, 3 equiv). After 14 h at rt, the reaction mixture on a pad of Celite (EtOAc). The phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give **4** as a yellow oil (25 mg, 0.47 mmol, 94%, *cis*/*trans* = 9/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ

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9.66 (d, J = 1.1 Hz, 1H), 7.91−7.86 (m, 2H), 7.40−7.37 (m, 2H), 4.66 (ddd, J = 9.1, 5.7, 1.1 Hz, 1H), 4.30−4.25 (m, 1H), 2.55−2.49 (ddd, J = 12.4, 9.1, 6.9 Hz 1H), 2.47 (s, 3H), 2.20−2.13 (ddd, J = 12.4, 8.3, 5.7 Hz, 1H), 1.54−1.36 (m, 2H), 1.33−1.18 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.7, 145.6, 132.3, 129.9, 129.3, 82.5, 65.9, 34.7, 32.9, 31.9, 29.5, 29.4, 29.4, 29.3, 26.0, 22.7, 21.8, 14.1; IR (neat, ν/cm^{-1}) 3487, 2924, 2854, 1738, 1597, 1494, 1456, 1358, 1335, 1305, 1292, 1185, 1163, 1091, 1019; MS (EI, m/z) 225 (1), 196 (17), 155 (13), 137 (12), 122 (11), 112 (13), 110 (12), 108 (13), 98 (28), 95 (46), 83 (32), 82 (25), 81 (53), 72 (15), 71 (35), 70 (47), 69 (66), 68 (25), 67 (40), 55 (100); HRMS (ESI) calcd for $C_{20}H_{31}NO_4S$ [M + Na]$^+$ 404.1866, found 404.1866.

(3*R,5*R**)-5-Nonyl-2-tosylisoxazolidine-3-carboxylic Acid (5).** To a solution of **2a** (200 mg, 0.53 mmol, 1 equiv, *cis*/*trans* = 9/1) in a 2/1/1 mixture of water/MeCN/EtOAc (20 mL) were added sodium periodate (2 g, 17 equiv) and $RuCl_3.xH_2O$ (12 mg, 0.12 equiv), and the solution turned brown then orange. The mixture was stirred for 3 h, and *i*-PrOH (5 mL) was added. The mixture turned brown with a precipitate and was filtered on a pad of Celite (EtOAc). The two phases were separated and the aqueous phase was extracted with EtOAc twice. The combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 50/50 + 1% AcOH) afforded **5** as a colorless oil (201 mg, 0.5 mmol, 95%, *cis*/*trans* = 9/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.88 (dd, J = 8.8, 6.8 Hz, 1H), 4.28−4.23 (m, 1H), 2.71 (ddd, J = 12.6, 9.2, 6.5 Hz, 1H), 2.46 (s, 3H), 2.22 (ddd, J = 12.6, 9.1, 6.8 Hz, 1H), 1.66−1.43 (m, 2H), 1.36−1.18 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.8, 132.1, 130.0, 129.3, 82.8, 77.2, 38.0, 32.6, 31.9, 29.5, 29.4, 29.3, 29.3, 26.0, 22.7, 21.8, 14.1; IR (neat, ν/cm^{-1}) 3250, 2925, 2855, 1733, 1597, 1457, 1402, 1362, 1338, 1306, 1293, 1186, 1165, 1092, 1039; HRMS (ESI) calcd for $C_{20}H_{31}NO_5S$ [M + Na]$^+$ 420.1815, found 420.1816.

2-((3*S,5*R**)-5-Nonyl-2-tosylisoxazolidin-3-yl)ethanol (6).** To a solution of **2a** (210 mg, 0.55 mmol, 1 equiv, *cis*/*trans* = 9/1) in THF (5 mL) was added 9-BBN (3 mL, 0.5 M/THF, 3 equiv), and the mixture was refluxed for 10 h. The reaction medium was cooled to 0 °C, NaOH (5 mL, 3 M/H_2O) and H_2O_2 (0.6 mL, 35% v/v in H_2O) were added successively, and the mixture was stirred for 24 h at rt. Water was added, the phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/Et_2O 60/40 to 40/60) yielded **6** as a yellow oil (222 mg, 0.55 mmol, quant., *cis*/*trans* = 9/1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.51−4.41 (m, 1H), 4.25−4.02 (m, 1H), 3.95−3.85 (m, 1H), 3.80−3.70 (m, 1H), 2.54 (ddd, J = 12.0, 8.2, 6.0 Hz, 1H), 2.45 (s, 3H), 1.92 (ddd, J = 14.2, 9.3, 4.4 Hz, 1H), 1.80−1.69 (m, 1H), 1.70−1.37 (m, 5H), 1.39−1.17 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 133.2, 129.8, 129.1, 82.0, 59.8, 56.9, 41.3, 39.0, 32.9, 31.9, 29.5, 29.4, 29.4, 29.3, 26.2, 22.7, 21.7, 14.1; IR (neat, ν/cm^{-1}) 3404, 2925, 2855, 1598, 1465, 1355, 1333, 1160, 1092, 1052; HRMS (ESI) calcd for $C_{21}H_{35}NO_4S$ [M + Na]$^+$ 420.2179, found 420.2172.

(*E*)-3-((3*R,5*R**)-Nonyl-2-tosylisoxazolidin-3-yl)acrylaldehyde (7).** To a solution of **2a** (54 mg, 0.14 mmol, 1 equiv, *cis*/*trans* = 9/1) in CH_2Cl_2 (2.5 mL) were added crotonaldehyde (98 mg, 10 equiv) and Grubbs−Hoveyda II catalyst (2 mg, 2.5 mol %). After 12 h at rt, an additional amount of Grubbs−Hoveyda II catalyst (2.5 mol %). After 12 h, evaporation and purification by flash chromatography on silica gel (PE/Et_2O 80/20 to Et_2O) afforded **7** as a brown oil (45 mg, 0.11 mmol, 79%, *cis*/*trans* = 9/1): ^1H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, J = 7.7 Hz, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.80 (dd, J = 15.6, 5.9 Hz, 1H), 6.34 (ddd, J = 15.6, 7.7, 1.2 Hz, 1H), 5.02−4.80 (m, 1H), 4.26−4.15 (m, 1H), 2.67 (ddd, J = 12.0, 8.2, 5.5 Hz, 1H), 2.46 (s, 3H), 1.82 (ddd, J = 12.0, 9.7, 8.0 Hz, 1H), 1.63−1.41 (m, 4H), 1.39−1.19 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.0, 153.5, 145.4, 132.6, 132.4, 129.8, 129.2, 82.1, 59.9, 40.8, 32.5, 31.9, 29.5, 29.4, 29.4, 29.3, 26.1, 22.7, 21.7, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1692, 1597, 1457, 1359, 1335, 1305, 1185, 1163, 1121, 1090, 1017; HRMS (ESI) calcd for $C_{22}H_{33}NO_4S$ [M + Na]$^+$ 430.2023, found 430.2025.

(3*R,5*R**)-5-Nonyl-3-((*E*)-2-(pyridin-3-yl)vinyl)-2-tosylisoxazolidine (8).** To a solution of **2a** (50 mg, 0.14 mmol, 1 equiv, *cis*/*trans* = 9/1) in DMF (2 mL) were added $Pd(OAc)_2$ (1.6 mg, 5 mol %), P(*o*-Tol)$_3$ (4 mg, 10 mol %), DIPEA (361 mg, 20 equiv), and 2-bromopyridine (15 μL, 1.1 equiv) in a sealed vial under Ar. After 24 h at 100 °C, the reaction was cooled to rt and quenched by addition of aq NH_4Cl. Et_2O was added, the phases were separated, and the aqueous layer was extracted twice with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/Et_2O 95/5 to 90/10) yielded **8** as a yellow oil (52 mg, 0.11 mmol, 81%, *cis*/*trans* = 90/10, *E*/*Z* > 95/5): ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (brs, 1H), 8.49 (brs, 1H), 7.88 (d_{app}, J = 8.3 Hz, 2H), 7.72 (d, J = 7.9 Hz, 1H), 7.36 (d_{app}, J = 8.0 Hz, 2H), 7.33−7.27 (m, 1H), 6.66 (d, J = 15.8 Hz, 1H), 6.30 (dd, J = 15.9, 7.1 Hz, 1H), 4.86 (q, J = 7.2 Hz, 1H), 4.14 (ddt, J = 10.5, 7.1, 5.4 Hz, 1H), 2.60 (ddd, J = 12.2, 7.9, 5.3 Hz, 1H), 2.45 (s, 3H), 1.84 (ddd, J = 12.0, 10.0, 8.2 Hz, 1H), 1.63−1.42 (m, 2H), 1.37−1.19 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.6, 148.2, 145.1, 133.4, 133.0, 130.8, 129.7, 129.6, 129.3, 128.3, 123.5, 82.0, 61.7, 41.8, 32.6, 31.9, 29.5, 29.5, 29.4, 29.3, 26.2, 22.7, 21.7, 14.1; IR (neat, ν/cm^{-1}) 2924, 2854, 1596, 1569, 1456, 1417, 1358, 1333, 1305, 1184, 1162, 1091, 1023 ; HRMS (ESI) calcd for $C_{26}H_{36}N_2O_3S$ [M + H]$^+$ 457.2519, found 457.2523.

4-Methyl-*N*-((2*R,4*R**)-2-nonyl-6-oxotetrahydro-2*H*-pyran-4-yl)benzenesulfonamide (9).** To a solution of **6** (100 mg, 0.25 mmol, 1 equiv, *cis*/*trans* = 9/1) in satd aq NH_4Cl solution (2.5 mL) was added zinc (329 mg, 20 equiv). The mixture was stirred at 100 °C for 24 h. EtOAc was added, the phases were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Filtration through a pad of silica gel (PE/EtOAc 50/50) afforded the expected diol as a yellow oil (86 mg, 86%). To a solution of the previously synthesized diol (30 mg, 0.07 mmol, 1 equiv) in CH_2Cl_2 (1 mL) at 0 °C were added TEMPO (2.3 mg, 0.2 equiv) and BAIB (73 mg, 3 equiv). After 3 h at rt, the reaction medium was evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 80/20) afforded **9** as a white solid (27 mg, 0.23 mmol, 91%): mp =114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.12 (d, J = 6.0 Hz, 1H), 4.52−4.41 (m, 1H), 3.78−3.70 (m, 1H), 2.62 (dd, J = 17.5, 6.0 Hz, 1H), 2.44 (s, 3H), 2.39 (ddd, J = 17.5, 5.2, 1.0 Hz, 1H), 2.01 (dt, J = 14.6, 3.5 Hz, 1H), 1.77−1.62 (m, 2H), 1.55−1.35 (m, 2H), 1.28 (m, 13H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.3, 144.1, 136.9, 130.0, 127.1, 76.5, 45.6, 36.4, 35.4, 34.0, 31.9, 29.5, 29.5, 29.3, 29.3, 24.9, 22.7, 21.6, 14.1; IR (neat, ν/cm^{-1}) 3267, 2915, 2849, 1710, 1495, 1463, 1397, 1346, 1319, 1305, 1266, 1241, 1165, 1081, 1067, 1038, 1019; HRMS (ESI) calcd for $C_{21}H_{33}NO_4S$ [M + Na]$^+$ 418.2023, found 418.2022.

***N*-((2*R**,4*R**,6*R**)-2-Allyl-6-nonyltetrahydro-2*H*-pyran-4-yl)-4-methylbenzenesulfonamide (10).** To a stirred solution of **9** (18 mg, 0.04 mmol, 1 equiv, *cis*/*trans* = 9/1) in CH_2Cl_2 (1.5 mL) at −78 °C was added DIBAL-H (68 μL, 1 M/toluene, 1.5 equiv). After 2 h at −78 °C, the reaction was quenched by addition of a satd aq solution of Rochelle's salt. The mixture was stirred for 1 h, and the phases were separated. The aqueous layer was extracted with CH_2Cl_2, and the organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to deliver a lactol that was used in the next step without further purification. To the previously synthesized lactol in CH_2Cl_2 (1 mL) were added allyltrimethylsilane (22 μL, 3 equiv) and $BF_3{\cdot}OEt_2$ (14 μL, 2.5 equiv) at −78 °C. After 4 h at −78 °C and 8 h at rt, an aqueous solution of $NaHCO_3$ was added, the phases were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc 80/20 to 50/50) afforded **10** as an oil (19 mg, 0.04 mmol, 99%, dr >95/5): ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d_{app}, J = 8.6 Hz, 2H), 7.30 (dd, J

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= 8.6, 0.6 Hz, 2H), 5.72 (ddt, J = 17.5, 10.5, 7.0 Hz, 1H), 5.09−4.96 (m, 2H), 4.51 (d, J = 8.0 Hz, 1H), 3.86 (m, 1H), 3.58−3.42 (m, 2H), 2.43 (s, 3H), 2.25−2.14 (m, 1H), 2.12−1.98 (m, 1H), 1.77 (dm, J = 12.5 Hz, 1H), 1.71−1.60 (m, 1H), 1.58−1.50 (m, 1H), 1.50−1.40 (m, 2H), 1.34−1.14 (m, 14H), 1.05 (ddd, J = 12.5, 11.4, 11.4 Hz, 1H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.4, 138.4, 134.4, 129.8, 126.9, 117.0, 72.7, 67.9, 47.0, 40.5, 39.2, 36.1, 31.9, 30.5, 29.6, 29.6, 29.4, 29.3, 25.9, 22.7, 21.5, 14.1; IR (neat, ν/cm^{-1}) 3270, 2924, 2854, 1624, 1599, 1496, 1441, 1378, 1325, 1289, 1184, 1158, 1093; MS (EI, m/z) 380 (16), 336 (33), 294 (20), 226 (13), 224 (15), 210 (12), 209 (65), 198 (11), 172 (13), 155 (57), 123 (33), 109 (11), 96 (15), 95 (28), 91 (100), 83 (14), 31 (32), 79 (24), 69 (22), 67 (28), 65 (13), 57 (15); HRMS (ESI) calcd for $C_{24}H_{39}NO_3S$ $[M + Na]^+$ 444.2543, found 444.2544.

■ ASSOCIATED CONTENT

Supporting Information

^1H and $^{13}C\{^1H\}$ NMR spectra of precursors **1a−r**, isoxazolidines **2a−d,g−2p**, as well as compounds **3−10** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) The same results were obtained using anhydrous $FeCl_3$, but $FeCl_3{\cdot}6H_2O$ was preferred as it is easier to handle.

(15) When the reaction was run at room temperature using 10 mol % of $FeCl_3{\cdot}6H_2O$, after 24 h, low conversion (5%) of the starting material was obtained. When the reaction was heated at 90 °C for 24 h, the formation of a complex mixture of products was observed.

(16) Reduction of the catalytic loading of $FeCl_3{\cdot}6H_2O$ to 5 mol % resulted in a longer reaction time as complete conversion was reached after 48 h.

(17) When $Bi(OTf)_3$ (10 mol %) was used instead of $FeCl_3{\cdot}6H_2O$, after 48 h at 50 °C, **1m** was converted to the corresponding isoxazolidine **2m** in 77% yield but with low diastereoselectivity (55/45).

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