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New Methodology for the Conversion of Epoxides to Alkenes

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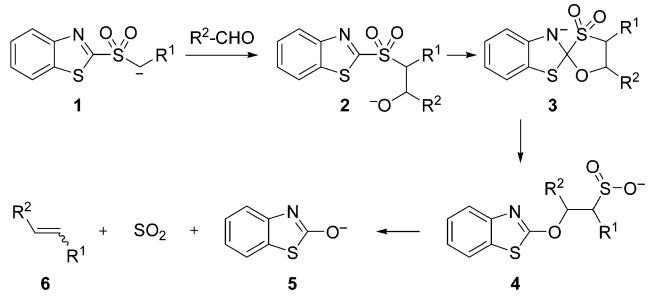
Epoxides have been transformed in good yields to alkenes by a process involving (i) ring-opening of the epoxide with 2-mercaptobenzothiazole, (ii) oxidation of the derived β-hydroxy thioethers to the corresponding sulfones, and (iii) thermal or base-promoted fragmentation of these sulfones to alkenes. The stereochemistry of the starting epoxide is transferred faithfully to the alkene product, because of the S_N2 epoxide ring-opening reactions and the antiperiplanar SO_2 elimination reaction of the β-alkoxysulfinate intermediates. This methodology may form the basis of a new protecting group strategy for alkenes.

Introduction

Protecting group strategies for alkenes are notably lacking from the arsenal of techniques available to synthetic organic chemists. Neither of the two standard monographs on protecting groups make any reference to alkene protection,[1,2] yet alkenes are of course very common functional groups, and a reliable protecting group strategy for this functionality may find wide applications in synthesis. Of the few available reversible modifications of alkenes that might be used to protect the C=C bond, most suffer the disadvantages of harsh reagents or reaction conditions, or both.

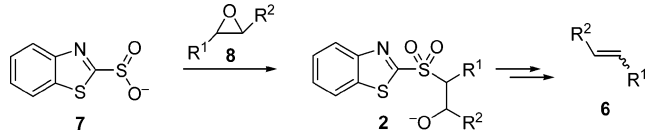
Examples of reversible chemical modifications of alkenes that have been suggested as protecting group strategies include the hydroxylation of alkenes to glycols, which may then be reconverted to alkenes via desulfonation-decarboxylation of cyclic thionocarbonate derivatives;[3] alkene bromination followed by debromination with zinc;[4] the formation of episulfides, which can be desulfurized with phosphanes, phosphites,[5,6] or thiocyanate;[7–9] and the epoxidation of alkenes, followed by regeneration of the alkene using a range of reducing agents such as Li,[10] SmI_2,[11,12] $Me_2PhSiLi$,[13] dimethyl diazomalonate/Rh_2OAc_4,[14] and $ZrCl_4$/NaI.[15]

In searching for a mild and convenient method for the deoxygenation of epoxides,[16] we considered the proposed mechanism of the modified Julia olefination,[17,18] in which a metallated benzothiazole sulfone **1** reacts with a carbonyl compound to give an intermediate alkoxide **2** that undergoes a Smiles-type rearrangement via **3**, leading to fragmentation with loss of SO_2 from **4** to give alkene **6** and the benzothiazol-2-olate heterocycle **5** (Scheme 1).



Scheme 1. The modified Julia (Julia–Kocienski) olefination reaction.

We reasoned that the alkoxide intermediate **2** might be accessed directly by the reaction of an epoxide **8** with benzothiazole-2-sulfinate **7**. This would then lead to the formation of the alkene **6** (Scheme 2). Consideration of the expected *anti* elimination of SO_2 from intermediate **4** suggested that *cis* epoxides would lead to *Z*-alkenes and that *trans* epoxides would lead to *E*-alkenes. Herein, we report our studies of the stereospecific formation of alkenes from mono-, di-, and trisubstituted epoxides.



Scheme 2. Proposed reaction of benzothiazole-2-sulfinate with epoxides to form alkenes.

Results and Discussion

At the outset of the studies, we required the sulfinate salt **7**. The synthesis of this compound from readily available 2-mercaptobenzothiazole **9** has been reported by Okai and co-workers,[19] but it was characterized only by an infrared

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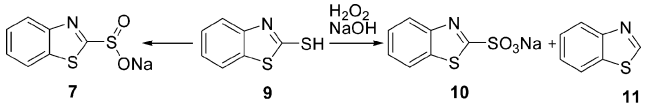
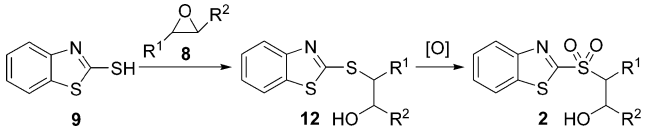
spectrum. In our hands, attempted preparation of **7** by the method of Okai and co-workers gave only a mixture of the sulfonic acid **10** and benzothiazole **11** (Scheme 3). In no trials were we able to identify the desired sulfinic acid **7** in the NMR spectra of the crude reaction product.



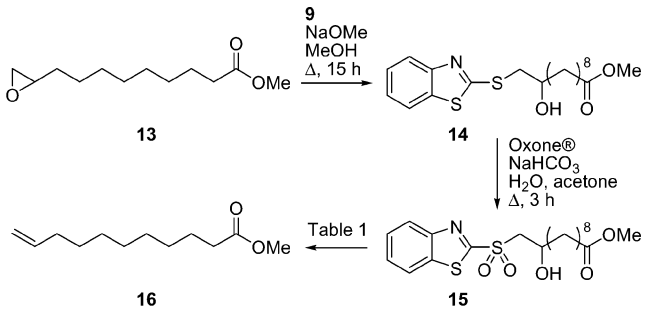
Scheme 3. Attempted synthesis of sulfinate salt **7** from 2-mercaptobenzothiazole **9**.

In light of our inability to obtain the sulfinate salt **7**, we modified our strategy and decided to react our epoxides **8** with the thiolate derived from 2-mercaptobenzothiazole **9**, followed by oxidation of the resulting thioether **12** to the corresponding sulfone, thus obtaining **2** in two steps rather than one (Scheme 4).



Scheme 4. Alternative preparation of sulfone **2** by oxidation of thioether **12**.

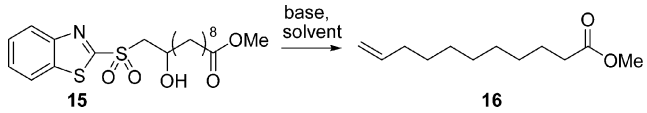
As a test substrate, we used the epoxide **13** derived from methyl undec-10-enoate to screen a range of reaction conditions for its ring-opening with 2-mercaptobenzothiazole **9** and subsequent oxidation-elimination reactions. The best conditions found for the ring-opening of the epoxide **13** with **9** were a catalytic amount of sodium methoxide in refluxing methanol solution, giving the thioether **14** in 74% yield. When one molar equivalent of sodium methoxide was employed, side-products arising from solvolysis of the epoxide were isolated, as was the episulfide corresponding to **13**. Oxidation of the thioether **14** to the sulfone **15** was achieved with either *m*CPBA in dichloromethane or, better, buffered Oxone® in refluxing aqueous acetone (76% yield) (Scheme 5).



Scheme 5. Preparation of alkene **16** from epoxide **13** via thioether **14** and sulfone **15**.

With the sulfone **15** in hand, we next investigated its reaction in a range of solvents, bases, and temperatures. Product yields were determined initially by GC–MS. For those reaction conditions in which the expected product was identified, the reactions were repeated on a preparative scale and isolated yields were determined (Table 1).

Table 1. Reaction conditions and yields for the formation of alkene **16** from sulfone **15**.



Entry	Base[a]	Solvent[b]	Temp.	Time [h]	% Yield (GC-MS)	% Yield (isolated)
1	NaOMe	MeOH	r.t.	7.5	78	71
2	K_2CO_3	MeOH	r.t.	7.5	86	75
3	DBU	MeOH	r.t.	7.5	93	86
4	DBU	THF	r.t.	17	92	89
5	DBU	CH_2Cl_2	r.t.	4	80	80
6	Et_3N[c]	MeOH	r.t.	72	80	80
7	Et_3N	THF	reflux	25	–	–
8	Et_3N	CH_2Cl_2	reflux	23	–	–
9	pyridine	MeOH	reflux	21	–	–
10	pyridine	THF	reflux	21	–	–
11	pyridine	CH_2Cl_2	reflux	21	–	–
12	TFA	CH_2Cl_2	reflux	90	–	–
13	–	toluene	reflux	22	82	82

[a] Two molar equivalents of base were used. [b] MeOH and THF were dried with molecular sieves (3 Å). [c] Four molar equivalents were used.

Several conclusions can be drawn from the results presented in Table 1. The weak base pyridine was ineffective in promoting the fragmentation of **15** (Entries 9–11). Triethylamine was also unable to promote the fragmentation in THF or dichloromethane, but worked well in methanol, albeit slowly at room temperature (Entry 6). The stronger bases DBU, potassium carbonate, and sodium methoxide were all capable of promoting the formation of the alkene **16** from the sulfone **15** in good yields at room temperature (Entries 1–5). As a control, the reaction was attempted in the presence of acid (Entry 12) but this proved ineffective. Interestingly, performing the reaction in refluxing toluene in the absence of base also led to the formation of the desired alkene in good yield (Entry 13).

Having established that a number of bases and solvents were suitable for fragmenting the sulfone **15** to the alkene **16** at room temperature, we then proceeded to examine the scope of this reaction by extending it to epoxides derived from di- and tri-substituted alkenes. The 1,1-disubstituted alkene **17** and the *Z*-alkenes **18** and **19** were selected, as well as the trisubstituted alkene **20** and the diene **21** (Figure 1).

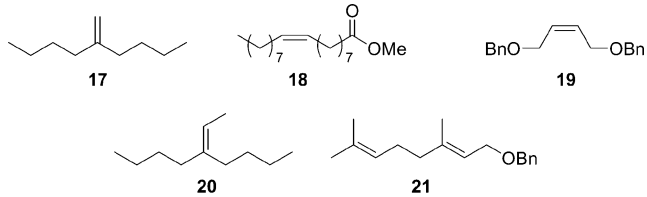


Figure 1. Di- and trisubstituted alkenes **17**–**21**.

While the conversion of alkenes **17**–**21** to their corresponding epoxides **22**–**26** (Figure 2) could generally be accomplished either with *m*CPBA in dichloromethane or Oxone® in aqueous acetone, the latter method gave some unexpected results in the case of alkenes **17** and **19**.

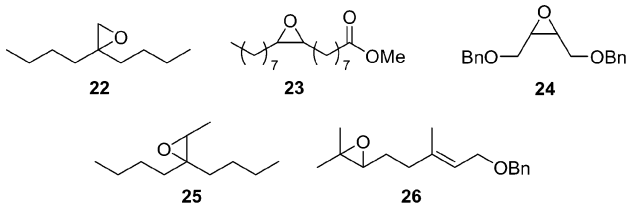
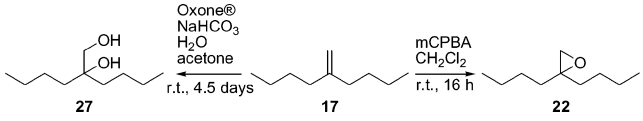


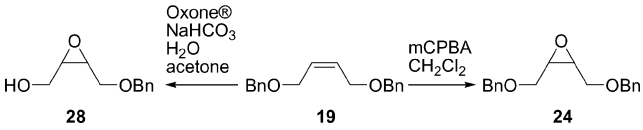
Figure 2. Di- and trisubstituted epoxides **22**–**26**.

Attempted epoxidation of alkene **17** using buffered Oxone® in aqueous acetone for several days did not give the expected epoxide **22**, but rather the corresponding glycol **27** in 93% yield. When the reaction was repeated with a reaction time of only 3 h, the desired epoxide **22** was obtained in 97% yield. Epoxidation of **17** with *m*CPBA in dichloromethane also proceeded uneventfully, to give **22** in 72% yield (Scheme 6).



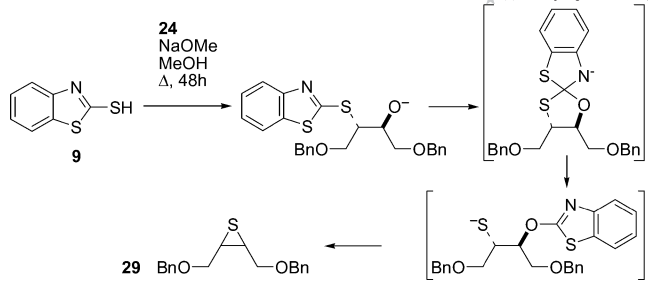
Scheme 6. Preparation of glycol **27** and epoxide **22** from alkene **17**.

Another unexpected reaction was observed when epoxidation of the dibenzyl ether **19** was attempted using buffered Oxone® in aqueous acetone. Instead of the expected epoxide **24** forming, the product was the epoxide **28**, in which one of the benzyl protecting groups had been removed.[20,21] Again *m*CPBA in dichloromethane proved effective for the epoxidation of **19**, giving **24** in 88% yield (Scheme 7).



Scheme 7. Epoxidation of alkene **19** to give **24**, and Oxone®-mediated debenzylation to give **28**.

Ring-opening of di- and tri-substituted epoxides **22**–**26** with 2-mercaptobenzothiazole proved to be more difficult than was the case for **13**. The use of sodium methoxide in methanol generally proved to be ineffective in promoting the ring opening of these epoxides. In most cases no reaction occurred, but for epoxide **24**, the product isolated was the episulfide **29**, in 44% yield, which presumably formed via the intermediates shown in Scheme 8.[22]



Scheme 8. Proposed mechanism for formation of episulfide **29** from epoxide **24** and 2-mercaptobenzothiazole **9**.

We eventually found that the use of hot, neat triethylamine as a base was effective for promoting the ring-opening of epoxides **22**–**26** with **9** in good yields (Table 2). In some cases, the addition of boron trifluoride improved the reaction yields (Table 2, Entries 1 & 3). As expected, nucleophilic attack of **9** occurred at the least hindered end of the epoxides **22**, **25**, and **26**, and no regioselectivity was observed for the ring-opening of epoxide **23**, which gave the β-hydroxy thioether isomers **31** and **32** in equal amounts.

Table 2. Reaction conditions and yields for the formation of β-hydroxy thioethers by ring-opening of epoxides.

Entry	Epoxide	Product	Reaction conditions	Time [h]	% Yield
1	**22**	**30**	Et_3N, $BF_3{\cdot}OEt_2$, Δ	18	84
2	**23**	**31** & **32**	Et_3N, Δ	3.5	86
3	**24**	**33**	Et_3N, $BF_3{\cdot}OEt_2$, Δ	6	87
4	**25**	**34**	Et_3N, Δ	48	58
5	**26**	**35**	Et_3N, Δ	18	87

Oxidation of the thioethers **30**–**35** (Figure 3) to the corresponding sulfones **36**–**41** was achieved in good yields using Oxone® in cold, buffered aqueous acetone (Table 3). For thioether **35**, the alkene group was also oxidized under these conditions to the sulfone-epoxide **41** (Figure 4). Use of the conditions previously employed to oxidize thioether **14** to sulfone **15** (refluxing solvent) or the use of *m*CPBA in dichloromethane led only to the isolation of the alkenes derived from fragmentations of the intermediate sulfones **36**–**41**, suggesting that these sulfones were much more thermally labile than **15**. This was confirmed for sulfones **37**–**41**, which proved to be unstable to storage at room temperature or towards chromatography on silica gel. Nevertheless these compounds were all obtained in good yields and in sufficient purities for subsequent steps.

With the sulfones **36**–**41** in hand we were able to confirm their facile conversion to the alkenes **17**–**20** and **43**, in good yields, by treatment with DBU at room temperature in either methanol or dichloromethane solution (Table 4). Alkenes **18** and **19** could also be obtained in equivalent yields, by heating them in toluene solution (Entries 3 and 5). In the case of alkene **17** (Entry 1), the volatility of this compound precluded an accurate determination of the yield of this reaction, and so **17** was converted in situ to its corre-

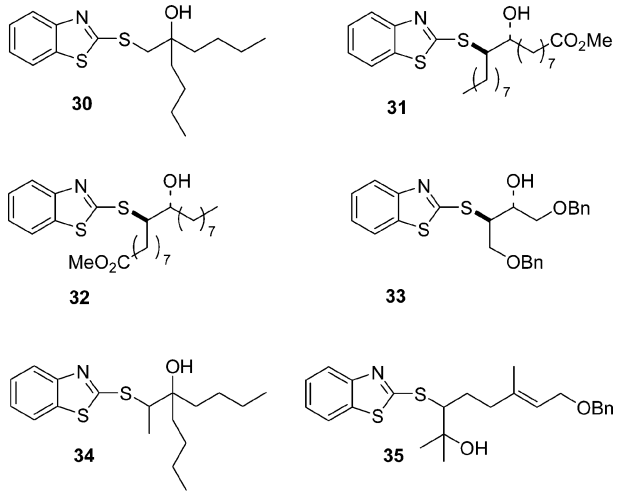
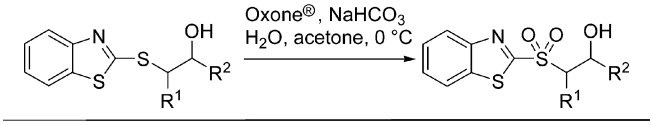


Figure 3. β-Hydroxy thioethers **30**–**35**.

Table 3. Reaction conditions and yields for the formation of sulfones from thioethers.



Entry	Thioether	Sulfone	Time [h]	% Yield
1	**30**	**36**	20	73
2	**31** & **32**	**37** & **38**	24	80
3	**33**	**39**	10	81
4	**34**	**40**	48	91
5	**35**	**41**	72	96

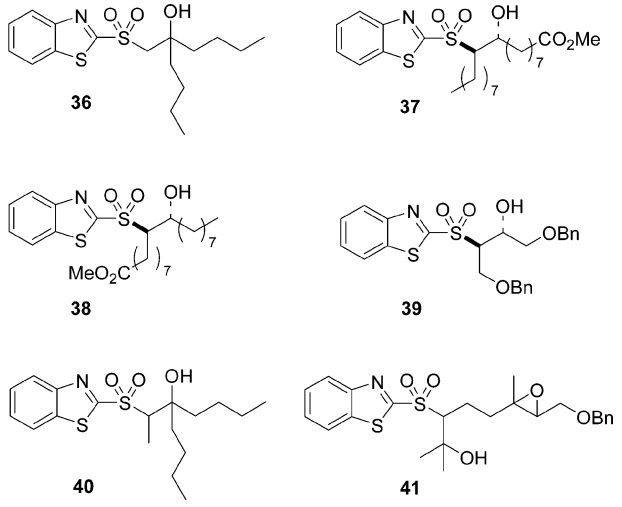
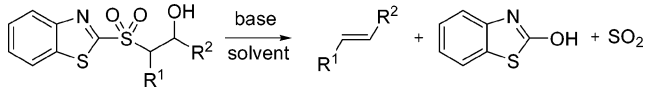


Figure 4. β-Hydroxy sulfones **36**–**41**.

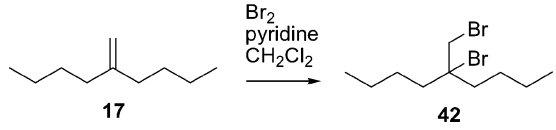
sponding dibromide **42** by treatment with elemental bromine and a catalytic amount of pyridine (Scheme 9). The dibromide **42** was then isolated in 68% yield for the two steps.

Table 4. Reaction conditions and yields for the formation of alkenes from sulfones.



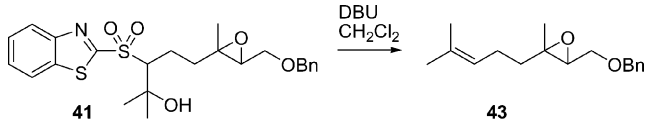
Entry	Sulfone	Alkene	Solvent	Base	Time [h]	% Yield
1	**36**	**17**	MeOH	DBU	17	68[a]
2	**37** & **38**	**18**	MeOH	DBU	1	83
3	**37** & **38**	**18**	toluene, Δ	–	3	83
4	**39**	**19**	MeOH	DBU	3	80
5	**39**	**19**	toluene, Δ	–	3	80
6	**40**	**20**	CH_2Cl_2	DBU	2	62
7	**41**	**43**	CH_2Cl_2	DBU	3	70

[a] Isolated as the dibromide.



Scheme 9. Preparation of the dibromide **42** from the volatile alkene **17**.

Fragmentation of sulfone **41** gave the monoepoxide **43** (Scheme 10). Alkenes **18** and **19** were obtained exclusively as the *Z*-isomers, confirming the stereochemical integrity of both the ring-opening reactions of the epoxides **23** and **24**, and the subsequent antiperiplanar fragmentation reaction of the β-alkoxysulfinates (cf. **4** in Scheme 1). Thus, this methodology preserves the stereochemistry of the alkenes through the epoxidation and deoxygenation steps.



Scheme 10. Preparation of the monoepoxide **43** from the sulfone **41**.

Conclusions

New methodology has been developed for the stereospecific conversion of epoxides into alkenes. Base-promoted ring-opening of mono-, di-, and trisubstituted epoxides with 2-mercaptobenzothiazole has been demonstrated, followed by oxidation of the resulting thioethers to their corresponding sulfones. These (often unstable) sulfones undergo facile fragmentation to alkenes, 2-hydroxybenzothiazole, and sulfur dioxide on treatment with base at room temperature, or in hot toluene without base. The alkene products are obtained in good yield.

Experimental Section

General Methods: ^1H and ^{13}C NMR spectra were recorded on Bruker AV500, AV400, or AV300 spectrometers in $CDCl_3$. NMR spectroscopic data for thermally unstable sulfones **36**–**41** were ac-

quired at 5 °C, and rotary evaporations of solutions of these sulfones were performed at 0 °C. MeOH and THF were dried with molecular sieves (3 Å). Low resolution mass spectrometry was performed on a Finnigan AP1–3 sprayer mass spectrometer in positive electrospray ionization mode. High resolution electrospray ionization accurate mass measurements were recorded in positive and negative mode on a Bruker MicroTOF-Q instrument with a Bruker ESI source. Accurate mass measurements were carried out with external calibration using sodium formate as reference calibrant and/or Agilent tune mix. Melting points were measured with a capillary apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminium sheets.

Methyl 9-(Oxiran-2-yl)nonanoate (13): To a suspension of methyl undec-10-enoate (**16**, 3.23 g, 16.3 mmol) and $NaHCO_3$ (8.65 g, 103 mmol) in acetone (60 mL) at 0 °C was added a solution of Oxone® (15.2 g, 24.5 mmol) in water (60 mL) cautiously and portionwise over a period of 30 min. The mixture was stirred and warm to room temperature for 11 h. The reaction mixture was extracted with Et_2O (2 × 60 mL), washed with water (60 mL), then dried ($MgSO_4$) and evaporated to give the oxirane **13**[23] (2.77 g, 79%) as a pale yellow oil. R_f = 0.54 (*n*-hexan/EtOAc = 6:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (br. s, 8 H, 4,5,6,7-H), 1.36–1.45 (m, 2 H, 8-H), 1.47–1.51 (m, 2 H, 9-H), 1.54–1.62 (m, 2 H, 3-H), 2.27 (t, J = 7.5 Hz, 2 H, 2-H), 2.43 (dd, J = 4.9, 2.7 Hz, 1 H, 11-H_a), 2.71 (t, J = 4.6 Hz, 1 H, 11-H_b), 2.85–2.88 (m, 1 H, 10-H), 3.63 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (C-3), 25.9 (C-8), 29.0 (C-4), 29.1 (C-5), 29.2 (C-6), 29.3 (C-7), 32.4 (C-9), 34.0 (C-2), 47.0 (C-11), 51.4 (C-10), 52.3 (CH_3), 174.2 (CO) ppm. LRMS: m/z = 237 [M + Na]$^+$. HRMS: calcd. for $C_{12}H_{22}NaO_3$ 237.1467 [M + Na]$^+$; found 237.1466. $C_{12}H_{22}O_3$ (214.30): calcd. C 67.26, H 10.35; found C 66.87, H 10.31.

Methyl 11-(Benzo[*d*]thiazol-2-ylthio)-10-hydroxyundecanoate (14): To a solution of sodium (12.8 mg, 0.56 mmol) in dry MeOH (10 mL) at 0 °C under argon was added 2-mercaptobenzothiazole (**9**, 936 mg, 5.60 mmol). Methyl 9-(oxiran-2-yl)nonanoate (**13**, 1.2 g, 5.60 mmol) in MeOH (5 mL) was added to the stirred mixture which was then heated under reflux overnight. Saturated aqueous NH_4Cl solution (50 mL) was added before removing the MeOH in vacuo. The remaining aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL). The combined extracts were dried ($MgSO_4$) and evaporated, then the residual oil was purified by silica flash column chromatography (*n*-hexan/EtOAc = 3:1) to afford the thioether **14** (1.55 g, 73%) as a yellow oil. R_f = 0.33 (*n*-hexan/EtOAc = 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.49 (br. s, 10 H, 4,5,6,7,8-H), 1.51–1.66 (m, 4 H, 3,9-H), 2.26 (t, J = 7.6 Hz, 2 H, 2-H), 3.30 (dd, J = 14.2, 7.2 Hz, 1 H, 11-H_a), 3.51 (dd, J = 14.2, 3.0 Hz, 1 H, 11-H_b), 3.62 (s, 3 H, CH_3), 3.95–4.03 (m, 1 H, 10-H), 7.25 (td, J = 8.1, 1.2 Hz, 1 H, arom. CH), 7.36 (td, J = 7.2, 1.2 Hz, 1 H, arom. CH), 7.69 (d, J = 7.8 Hz, 1 H, arom. CH), 7.79 (d, J = 7.4 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8 (C-3), 25.5 (C-4), 29.0 (C-5), 29.1 (C-6), 29.2 (C-7), 29.4 (C-8), 34.0 (C-2), 36.5 (C-9), 40.9 (C-11), 51.4 (CH_3), 71.2 (C-10), 120.9, 121.1, 124.6, 126.2 (arom. C), 135.0, 151.9, 168.1 (arom. C_{ipso}), 174.3 (CO) ppm. LRMS: m/z = 404 [M + Na]$^+$. HRMS: calcd. for $C_{19}H_{27}NS_2NaO_3$ 404.1334 [M + Na]$^+$; found 404.1334.

Methyl 11-(Benzo[*d*]thiazol-2-ylsulfonyl)-10-hydroxyundecanoate (15): To a solution of **14** (4.74 mg, 12.4 mmol) and $NaHCO_3$ (6.66 g, 79.4 mmol) in acetone (250 mL) and water (125 mL) was added Oxone® (24.6 g, 39.7 mmol) cautiously and portionwise. The mixture reaction was heated under reflux for 3 h. It was then extracted with Et_2O (3 × 100 mL), washed with water (2 × 80 mL), dried (Na_2SO_4) and evaporated to give the sulfone **15** as a pale yellow solid (3.91 g, 76%); m.p. 62–65 °C. R_f = 0.27 (*n*-hexan/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19–1.42 (m, 10 H, 4,5,6,7,8-H), 1.45–1.62 (m, 4 H, 3,9-H), 2.26 (t, J = 5.2 Hz, 2 H, 2-H), 3.60–3.62 (m, 5 H, 11-H, CH_3), 4.29–4.39 (m, 1 H, 10-H), 7.56–7.63 (m, 2 H, arom. CH), 7.98–8.02 (m, 1 H, arom. CH), 8.16–8.18 (m, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (C-3), 24.9 (C-4), 28.9 (C-5), 29.0 (C-6), 29.1 (C-7), 29.2 (C-8), 34.0 (C-2), 36.3 (C-9), 51.4 (CH_3), 61.4 (C-11), 66.0 (C-10), 122.4, 125.4, 127.7, 128.1 (arom. C), 136.5, 152.3, 166.3 (arom. C_{ipso}), 174.2 (CO) ppm. LRMS: m/z = 436 [M + Na]$^+$. HRMS: calcd. for $C_{19}H_{27}NS_2NaO_5$ 436.1228 [M + Na]$^+$; found 436.1238.

Methyl Undec-10-enoate (16): To a suspension of undec-10-enoic acid, zinc salt (10.0 g, 23.2 mmol) in MeOH (200 mL) under argon was added concd. H_2SO_4 (6 mL). The mixture was stirred and heated under reflux for 4 h. The solvent was removed under vacuum and the residue was taken up in Et_2O (200 mL). The solution was washed with saturated aqueous $NaHCO_3$ solution (3 × 200 mL), water (3 × 200 mL), and brine (150 mL), then dried ($MgSO_4$) and the solvents evaporated. The residual oil was purified by silica flash column chromatography (petroleum ether/EtOAc = 19:1) to give the methyl ester **16**[24] (8.48 g, 92%) as a colorless oil. R_f = 0.33 (petroleum ether/EtOAc = 19:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.36 (br. s, 10 H, 4,5,6,7,8-H), 1.54–1.61 (m, 2 H, 3-H), 1.96–2.04 (m, 2 H, 9-H), 2.27 (t, J = 7.4 Hz, 2 H, 2-H), 3.63 (s, 3 H, CH_3), 4.88–4.92 (m, 1 H, 11-H_a), 4.92–4.99 (m, 1 H, 11-H_b), 5.17–5.84 (m, 1 H, 10-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 (C-3), 28.8 (C-4), 29.0 (C-5), 29.1 9 (C-6), 29.16 (C-7), 29.24 (C-8), 33.7 (C-2), 34.0 (C-9), 51.3 (CH_3), 114.1 (C-11), 139.1 (C-10), 174.2 (CO) ppm. HRMS: calcd. for $C_{12}H_{22}O_2$ 198.1618 [M]$^+$; found 198.1621. $C_{12}H_{22}O_2$ (198.30): calcd. C 72.68, H 11.18; found C 72.80, H 11.38.

2-Butyl-1-hexene (17): Triphenylphosphane (10.4 g) was recrystallized from EtOH and dried in vacuo for 8 h. The recrystallized triphenylphosphane (9.34 g, 35.6 mmol) and iodomethane (5.40 g, 38.0 mmol) in benzene (35 mL) were stirred at room temperature overnight. The precipitate was filtered off and dried with P_2O_5 under high vacuum for 8 h to give the phosphonium salt in 89% yield (12.8 g). *n*BuLi (5 mL; 2.0 M solution in cyclohexane) was added dropwise to an ice-cold solution of methyltriphenylphosphonium iodide (5.68 g, 14.1 mmol) in dry THF (20 mL) under argon. 5-Nonanone (1.0 g, 7.1 mmol) in dry THF (30 mL) was added dropwise to the stirred ylide (red-orange) via syringe. The reaction mixture was stirred and warm to room temperature for 2 d. Petroleum ether (100 mL) was added to the mixture and the supernatant solution was decanted and filtered. The filtrate was washed with water (3 × 50 mL) and dried (Na_2SO_4). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether) to give the alkene **17**[25] (683 mg, 69%) as a colorless oil. R_f = 0.74 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.9 (t, J = 7.1 Hz, 6 H, 2 x CH_3), 1.26–1.44 (m, 8 H, 4 × CH_2), 2.00 (t, J = 7.2 Hz, 4 H, 2 × CH_2), 4.69 (quintet, J = 1.1 Hz, 2 H, CH_2) ppm. LRMS: m/z = 140 [M]$^+$.

Methyl Oleate (18): To a solution of oleic acid (5.06 g, 17.9 mmol) in dry MeOH (20 mL) was added concd. H_2SO_4 (5 drops). The reaction mixture was heated under reflux for 1 d. The solvent was removed in vacuo and the residue was taken up in Et_2O (2 × 50 mL), washed with saturated aqueous $NaHCO_3$ solution (2 × 50 mL), water (3 × 50 mL) and brine (2 × 50 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether/EtOAc = 19:1) to afford the methyl ester **18**[26] (4.93 g, 93%) as a pale orange oil. R_f = 0.44 (petroleum ether/EtOAc = 19:1). ^{1}H

NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.8 Hz, 3 H, CH_3), 1.25–1.29 (m, 20 H, 5× CH_2), 1.58–1.63 (m, 2 H, CH_2), 1.96–2.04 (m, 4 H, 2× CH_2), 2.29 (t, J = 7.4 Hz, 2 H, CH_2), 3.62 (s, 3 H, CH_3), 5.28–5.32 (m, 2 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 24.9, 27.1, 27.2, 29.0, 29.11, 29.14, 29.3, 29.5, 29.6, 29.7, 31.8, 34.0 (CH_2), 51.4 (CH_3), 129.7, 129.9 (CH), 174.2 (CO) ppm.

(*Z*)-1,4-Bis(benzyloxy)but-2-ene (19): To a solution of (*Z*)-butene-1,4-diol (2.76 g, 30.8 mmol) in dry THF (50 mL) was added NaH (60% dispersion in mineral oil; 3.37 g, 135 mmol) under argon. The reaction mixture was heated under reflux for 2 h and cooled to room temperature. A solution of benzyl bromide (20.7 g, 118 mmol) in dry THF (50 mL) was added dropwise to the stirred mixture. The reaction mixture was then stirred and heated under reflux for 1 h, followed by 4 d stirring at room temperature. The excess NaH was destroyed by careful addition of water (20 mL) then the THF was removed in vacuo. The residue was taken up in CH_2Cl_2 (3×40 mL), washed with saturated aqueous NH_4Cl solution (3×40 mL), water (40 mL) and brine (40 mL), and then dried ($MgSO_4$). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether/EtOAc = 9:1) to generate the dibenzyl ether **19**[27] (8.27 g, 98%) as a colorless oil. R_f = 0.64 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.06–4.07 (m, 4 H, 1,4-H), 4.49 (s, 4 H, 2× $PhCH_2$), 5.79–5.81 (m, 2 H, 2× CH), 7.26–7.32 (m, 10 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 65.7 (C-1), 72.2 (C-2), 127.6, 127.7, 128.3, 129.4, 138.1 (CH, arom. C) ppm. LRMS: m/z = 291 $[M + Na]^+$.

5-Ethylidenenonane (20): Triphenylphosphane (11.4 g) was recrystallized from EtOH and dried under vacuum overnight. The recrystallized triphenylphosphane (10.7 g, 40.7 mmol) and iodoethane (8.26 g, 52.9 mmol) in toluene (40 mL) were heated under reflux for 36 h. Petroleum ether (100 mL) was added to the reaction mixture. The precipitate was filtered off and washed with more petroleum ether. It was then dried with P_2O_5 under high vacuum for 12 h to afford the phosphonium salt in 70% yield (11.8 g). To a solution of the phosphonium salt (5.88 g, 14.1 mmol) in dry THF (30 mL) at 0 °C was added *n*BuLi (6.5 mL; 2.0 M solution in cyclohexane) slowly. The reaction mixture was stirred at 0 °C for 30 min before adding a solution of 5-nonanone (1.01 g, 7.10 mmol) in dry THF (13 mL) dropwise. The reaction mixture was stirred and warm to room temperature for 1 d. Petroleum ether (100 mL) was added, then the supernatant solution was decanted and filtered. The organic layer was washed with water (3×60 mL) and dried (Na_2SO_4). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether) to afford the alkene **20**[28] (504 mg, 42%) as a colorless oil. R_f = 0.83 (petroleum ether) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.9 (q, J = 7.1 Hz, 6 H, CH_3), 1.24–1.37 (m, 8 H, 4× CH_2), 1.57 (d, J = 6.6 Hz, 3 H, CH_3), 1.95 (t, J = 7.2 Hz, 2 H, CH_2), 2.00 (t, J = 7.3 Hz, 2 H, CH_2), 5.18 (q, J = 6.6 Hz, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1, 14.03, 14.06 (CH_3), 22.5, 22.8, 29.4, 30.45, 30.48, 36.7 (CH_2), 117.9 (CH), 140.6 (C) ppm.

Benzyl Geranyl Ether (21): To a solution of geraniol (2.7 g, 17.5 mmol) in dry THF (80 mL) was added NaH (60% dispersion in mineral oil; 1.56 g, 65.0 mmol) under argon. The reaction mixture was stirred at room temperature for 1 h and then heated under reflux for 30 min. The mixture was allowed to cool to room temperature before adding a solution of benzyl bromide (7.92 g, 62.6 mmol) in dry THF (50 mL) dropwise. A catalytic amount of tetrabutylammonium iodide was also added. The reaction mixture was stirred at room temperature for 3 d. The excess NaH was destroyed by carefully adding water (20 mL) and then the THF was removed in vacuo. Another 50 mL of water was added and the mixture was acidified with HCl (5%), extracted with CH_2Cl_2 (3×100 mL), washed with water (60 mL) and brine (60 mL), then dried ($MgSO_4$). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether/EtOAc = 17:3) to afford the benzyl ether **21**[29] (3.91 g, 92%) as a colorless oil. R_f = 0.75 (petroleum ether/EtOAc = 17:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.61 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 2.04–2.07 (m, 2 H, CH_2), 2.10–2.13 (m, 2 H, CH_2), 4.04 (d, J = 6.7 Hz, 2 H, CH_2), 4.51 (s, 2 H, CH_2), 5.11 (t, J = 6.7 Hz, 1 H, CH), 5.41 (t, J = 6.7 Hz, 1 H, CH), 7.27–7.39 (m, 5 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.4, 17.6, 25.6 (CH_3), 26.3, 39.5, 66.5, 71.9 (CH_2), 120.8, 123.9, 127.4, 127.8, 128.3 (CH, arom. C), 131.6, 138.5, 140.3 (C, arom. C_{ipso}) ppm.

2-Butyl-1,2-epoxyhexane (22): (i) To a solution of *m*CPBA (1.48 g as a 77 wt.-% solid, 6.6 mmol) in CH_2Cl_2 (30 mL) at 0 °C under argon was added 2-butyl-1-hexene (**17**, 600 mg, 4.28 mmol). The reaction mixture was stirred and warm to room temperature overnight. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 1 M NaOH (3×50 mL) and water (50 mL), and dried (Na_2SO_4). Evaporation of the solvent gave the epoxide **22**[30] as a colorless oil (480 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.0 Hz, 6 H, 2× CH_3), 1.29–1.36 (m, 8 H, 4× CH_2), 1.47–1.52 (m, 2 H, CH_2), 1.57–1.61 (m, 2 H, CH_2), 2.56 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.8, 27.0, 33.9, 52.5 (CH_2), 59.5 (C) ppm.

(ii) To a suspension of 2-butyl-1-hexene (264 mg, 1.89 mmol) and $NaHCO_3$ (950 mg, 11.3 mmol) in acetone (6 mL) at 0 °C was added a solution of Oxone® (2.92 g, 4.71 mmol) in water (6 mL) cautiously and portionwise over a period of 30 min. The reaction mixture was stirred and warm to room temperature for 3 h. The mixture was extracted with CH_2Cl_2 (3×10 mL), washed with water (15 mL), dried ($MgSO_4$) and evaporated to give **22**, identical to that described above (286 mg, 97%).

Methyl 8-(3-Octyloxiran-2-yl)octanoate (23): To a suspension of methyl oleate (**18**, 1.09 g, 3.68 mmol) and $NaHCO_3$ (2.31 g, 27.5 mmol) in acetone (40 mL) at 0 °C was added a solution of Oxone® (5.29 g, 8.54 mmol) in water (40 mL) cautiously and portionwise over a period of 30 min. The reaction mixture was stirred and warm to room temperature overnight. The mixture was extracted with CH_2Cl_2 (3×50 mL), washed with water (50 mL) and dried ($MgSO_4$). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether/EtOAc = 9:1) to afford the epoxide **23**[31] (933 mg, 89%) as a colorless yellow oil. R_f = 0.48 (petroleum ether/EtOAc = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 1.24–1.36 (m, 16 H, 8× CH_2), 1.47–1.50 (m, 6 H, 3× CH_2), 1.55–1.56 (m, 2 H, CH_2), 1.60–1.63 (m, 2 H, CH_2), 2.30 (t, J = 7.4 Hz, 2 H, 2× CH), 2.87–2.91 (m, 2 H, CH_2), 3.66 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 24.9, 26.54, 26.59, 27.7, 27.8, 29.0, 29.1, 29.2, 29.3, 29.51, 29.54, 31.8, 34.0, 51.4 (CH_3), 57.1, 57.2 (CH), 174.2 (CO) ppm.

2,3-Bis(benzyloxymethyl)oxirane (24): To a solution of *m*CPBA (5.25 g as a 77 wt.-% solid, 23.4 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added a solution of (*Z*)-1,4-bis(benzyloxy)but-2-ene (**19**, 2.01 g, 7.49 mmol) in CH_2Cl_2 (30 mL) dropwise. The reaction mixture was stirred and warm to room temperature overnight. The mixture was diluted with CH_2Cl_2 (70 mL), washed with 1 M NaOH (3×70 mL), water (70 mL) and dried ($MgSO_4$). Evaporation of the solvent gave a residue which was purified by silica flash column

chromatography (petroleum ether/EtOAc = 17:3) to afford the epoxide **24**[27] (1.87 g, 88%) as a colorless oil. R_f = 0.46 (petroleum ether/EtOAc = 17:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23–3.25 (m, 2 H, 2× CH), 3.52 (dd, J = 11.3, 6.4 Hz, 2 H, 1,1′-H_a), 3.68 (dd, J = 11.3, 3.8 Hz, 2 H, 1,1′-H_b), 4.49 (d, J = 11.9 Hz, 2 H, 2,2′-H_a), 4.59 (d, J = 11.9 Hz, 2 H, 2,2′-H_b), 7.26–7.35 (m, 10 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.4 (CH), 68.0 (C-1), 73.2 (C-2), 127.7, 127.8, 128.4 (arom. C), 137.7 (arom. C_{ipso}) ppm. LRMS: m/z = 307 [M + Na]$^+$. HRMS: calcd. for $C_{18}H_{20}NaO_3$ 307.1305 [M + Na]$^+$; found 307.1307.

2,2-Dibutyl-3-methyloxirane (25): To a solution of *m*CPBA (1.89 g as a 77 wt.-% solid, 8.4 mmol) in CH_2Cl_2 (30 mL) at 0 °C under argon was added 5-ethylidenenonane (**20**, 400 mg, 2.59 mmol) portionwise. The reaction mixture was stirred and warm to room temperature for 24 h. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 1 M NaOH (3 × 50 mL) and water (50 mL), and then dried (Na_2SO_4). Evaporation of the solvent gave a residue which was purified by silica flash column chromatography (petroleum ether/EtOAc = 17:3) to afford the epoxide **25**[32] (388 mg, 96%) as a colorless oil. R_f = 0.79 (petroleum ether/EtOAc = 17:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (q, J = 7.2 Hz, 6 H, 2× CH_3), 1.26 (d, J = 5.4 Hz, 3 H, CH_3), 1.21–1.35 (m, 10 H, 5× CH_2), 1.46–1.57 (m, 2 H, CH_2), 2.82 (q, J = 5.6 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.0 (CH_3), 22.8, 23.0, 26.9, 27.3, 29.5, 34.9 (CH_2), 59.0 (C), 63.3 (CH) ppm.

(3*E*)-3-(5-Benzyloxy-3-methylpent-3-enyl)-2,2-dimethyloxirane (26): To a solution of *m*CPBA (2.27 g as a 77 wt.-% solid, 10.1 mmol) in CH_2Cl_2 (30 mL) at 0 °C under argon was added a solution of benzyl geranyl ether (**21**, 3.2 g, 13.1 mmol) in CH_2Cl_2 (20 mL) dropwise. The reaction mixture was stirred and warm to room temperature for 3.5 h. The mixture was diluted with CH_2Cl_2 (50 mL), washed with 1 M NaOH (3 × 50 mL) and water (50 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a crude product, which was purified by silica flash column chromatography (petroleum ether/EtOAc = 17:3) to afford the epoxide **26**[33] (2.69 g, 79%) as a yellow oil. R_f = 0.41 (petroleum ether/EtOAc = 17:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.63–1.69 (m, 5 H, CH_3, CH_2), 2.14–2.22 (m, 2 H, CH_2), 2.71 (t, J = 6.2 Hz, 1 H, CH), 4.03 (d, J = 6.7 Hz, 2 H, CH_2), 4.50 (s, 2 H, CH_2), 5.43–5.47 (m, 1 H, CH), 7.26–7.34 (m, 5 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.4, 18.6, 24.7 (CH_3), 27.1, 36.1 (CH_2), 58.2 (C), 63.9 (CH), 66.4, 72.0 (CH_2), 121.3 (CH), 127.4, 127.7, 128.2, 138.4, 139.3 (C, arom. C) ppm. LRMS: m/z = 283 [M + Na]$^+$.

2-Butylhexane-1,2-diol (27): To a mixture of **17** (100 mg, 0.71 mmol) and $NaHCO_3$ (363 mg, 4.32 mmol) in acetone (7 mL) at 0 °C was added a solution of Oxone® (1.10 g, 1.77 mmol) in water (7 mL) slowly and portionwise. The reaction mixture was stirred and warm to room temperature for 4.5 d. The mixture was dilute with water (15 mL), extracted with dichloromethane (3 × 10 mL), and then dried (Na_2SO_4). Evaporation of the solvent gave the diol **27**[34] as a colorless oil (106 mg, 93%). R_f = 0.17 (petroleum ether/EtOAc/CH_2Cl_2 = 14:5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.0 Hz, 6 H, 2× CH_3), 1.21–1.37 (m, 8 H, 4× CH_2), 1.40–1.51 (m, 4 H, 2× CH_2), 3.45 (s, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 23.2, 25.5, 35.5, 68.0 (CH_2), 74.8 (C) ppm.

[3-(Benzyloxymethyl)oxiranyl]methanol (28): To a solution of **19** (1.35 g, 5.03 mmol) and $NaHCO_3$ (2.58 g, 30.7 mmol) in acetone (50 mL) at 0 °C was added a solution of Oxone® (7.84 g, 12.6 mmol) in water (50 mL) slowly and portionwise. The reaction mixture was stirred and warm to room temperature for 1.5 d. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed with water (50 mL) and dried ($MgSO_4$). Evaporation of the solvent gave a crude mixture which was purified by silica flash column chromatography (petroleum ether/EtOAc = 4:1) to give the epoxy alcohol **28**[27] (243 mg, 25%). R_f = 0.11 (petroleum ether/EtOAc = 7:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (br. s, 1 H, OH), 3.16–3.21 (m, 1 H, CH), 3.24–3.29 (m, 1 H, CH), 3.64 (d, J = 2.6 Hz, 1 H, 1-H_a), 3.66 (d, J = 3.6 Hz, 1 H, 1-H_b), 3.70 (d, J = 5.4 Hz, 2 H, CH_2), 4.54 (q, J = 11.8 Hz, 2 H, 2-H), 7.27–7.34 (m, 5 H, arom. CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.7, 55.7 (CH), 60.5, 67.9, 73.4 (CH_2), 127.8, 127.9, 128.4 (arom. C), 137.3 (arom. C_{ipso}) ppm. LRMS: m/z = 217 [M + Na]$^+$.

2,3-Bis(benzyloxymethyl)thiirane (29): Sodium (414 mg, 18.0 mmol) was dissolved in dry MeOH (50 mL) under argon and 7 mL of this NaOMe solution was added to a flask equipped with 2-mercaptobenzothiazole (**9**, 294 mg, 1.76 mmol). The mixture was stirred at 0 °C for 20 min, followed by addition of a solution of 2,3-bis(benzyloxymethyl)oxirane (**24**, 0.5 g, 1.76 mmol) in dry MeOH (7 mL) slowly and dropwise. The reaction mixture was stirred and warm to room temperature for 23 h, and then heated under reflux for 48 h. The mixture was quenched with saturated aqueous NH_4Cl solution (50 mL) before the MeOH was removed in vacuo. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), washed with brine (50 mL) and water, and then dried ($MgSO_4$). Evaporation of the solvent gave a crude mixture, which was purified by silica flash column chromatography (petroleum ether/EtOAc = 7:3) to give the episulfide **29**[35] (234 mg, 44%). R_f = 0.74 (petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = .3.18–3.21 (m, 2 H, 2× CH), 3.65–3.67 (m, 4 H, 1,1′-H), 4.39 (q, J = 11.9 Hz, 4 H, 2,2′-H), 7.27–7.32 (m, 10 H, arom CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.5 (CH), 70.0, 73.1 (CH_2), 127.75, 127.77, 128.4 (arom. C), 137.8 (arom. C_{ipso}) ppm. LRMS: m/z = 323 [M + Na]$^+$. HRMS: calcd. for $C_{18}H_{20}SNaO_2$ 323.1082 [M + Na]$^+$; found 323.1076.

5-[(Benzo[*d*]thiazol-2-ylthio)methyl]nonan-5-ol (30): To a mixture of **9** (465 mg, 2.64 mmol) and Et_3N (7.0 g, 69.1 mmol) was added 1,2-epoxy-2-butylhexane (**22**, 265 mg, 1.70 mmol) then $BF_3{\cdot}OEt_2$ (20 drops). The reaction mixture was heated at 80 °C overnight. Dichloromethane (30 mL) was added and the mixture was washed with saturated aqueous NH_4Cl solution (3 × 30 mL), saturated aqueous $NaHCO_3$ solution (30 mL) and water (30 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a crude semisolid, which was purified by silica flash column chromatography (petroleum ether/EtOAc = 9:1) to afford the thioether **30** (459 mg, 84%) as colorless solids. R_f = 0.63 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.1 Hz, 6 H, 2× CH_3), 1.30–1.40 (m, 8 H, 4× CH_2), 1.61–1.65 (m, 4 H, 2× CH_2), 3.51 (s, 2 H, CH_2), 7.30 (td, J = 7.1, 1.1 Hz, 1 H, arom. CH), 7.41 (td, J = 7.2, 1.1 Hz, 1 H, arom. CH), 7.73 (d, J = 8.0 Hz, 1 H, arom. CH), 7.56 (d, J = 8.0 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 23.2, 25.9, 38.5, 44.1 (CH_2), 73.8 (C), 121.00, 121.08, 124.6, 126.3 (arom. C), 135.0, 151.8, 169.0 (arom. C_{ipso}) ppm. LRMS: m/z = 346 [M + Na]$^+$. HRMS: calcd. for $C_{17}H_{25}NS_2NaO$ 346.1270 [M + Na]$^+$; found 346.1265.

Methyl 10-(Benzo[*d*]thiazol-2-ylthio)-9-hydroxyoctadecanoate (31) and Methyl 9-(benzo[*d*]thiazol-2-ylthio)-10-hydroxyoctadecanoate (32): To a mixture of **9** (557 mg, 3.33 mmol) and Et_3N (246 mg, 2.43 mmol) was added methyl 8-(3-octyloxiran-2-yl)octanoate (**23**, 670 mg, 2.15 mmol) portionwise. The reaction mixture was heated at 90 °C for 3.5 h. The cooled reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous $NaHCO_3$ solution (3 × 50 mL), water (50 mL) and brine (50 mL), then dried

(Na_2SO_4). Evaporation of the solvent gave a crude mixture which was purified by silica flash column chromatography (petroleum ether/EtOAc = 17:3) to afford the thioethers **31** and **32** (888 mg, 86%) as a yellow semisolid. R_f = 0.50 (petroleum ether/EtOAc = 17:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.0 Hz, 6 H, 2× CH_3), 1.20–1.43 (m, 32 H, 16× CH_2), 1.44–1.65 (m, 16 H, 8× CH_2), 1.84–1.91 (m, 4 H, 2× CH_2), 2.27 (m, 4 H, 2× CH_2), 3.64 (s, 3 H, CH_3), 3.65 (s, 3 H, CH_3), 3.83–3.87 (m, 2 H, 2× CH), 4.06–4.13 (m, 2 H, 2× CH), 7.30 (td, J = 7.6, 1.1 Hz, 2 H, arom. CH), 7.41 (td, J = 7.7, 1.2 Hz, 2 H, arom. CH), 7.74 (d, J = 7.6 Hz, 2 H, arom. CH), 7.84 (d, J = 8.4 Hz, 2 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.96, 13.97 (CH_3), 22.50, 22.52, 24.73, 24.77, 25.7, 25.8, 27.2, 27.3, 28.87, 28.89, 28.92, 28.96, 29.06, 29.12, 29.17, 29.25, 29.28, 29.4, 29.5, 31.70, 31.73, 33.91, 33.94, 36.07, 36.09 (CH_2), 51.3 (CH_3), 56.4, 56.5, 73.4, 73.5 (CH), 120.8, 121.2, 124.4, 126.0 (arom. C), 135.4, 152.5, 166.41, 166.44 (arom. C_{ipso}), 174.13, 174.17 (CO) ppm. LRMS: m/z = 502 [M + Na]$^+$. HRMS: calcd. for $C_{26}H_{41}NS_2NaO_3$ 502.2420 [M + Na]$^+$; found 502.2419.

3-(Benzo[*d*]thiazol-2-ylthio)-1,4-bis(benzyloxy)butan-2-ol (33): To a mixture of **9** (1.69 g, 10.1 mmol) and Et_3N (26.2 g, 259 mmol) was added 2,3-bis(benzyloxymethyl)oxirane (**24**, 1.87 g, 6.56 mmol) then $BF_3{\cdot}OEt_2$ (18 drops). The reaction mixture was heated at 90 °C for 6 h. Dichloromethane (60 mL) was added to the cooled mixture and it was washed with saturated aqueous $NaHCO_3$ solution (3 × 60 mL) and water (60 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a crude oil which was purified by silica flash column chromatography (petroleum ether/EtOAc = 3:2) to afford the thioether **33** (2.58 g, 87%) as colorless oil. R_f = 0.43 (petroleum ether/EtOAc = 3:2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.69 (d, J = 6.1 Hz, 2 H, CH_2), 3.97 (dd, J = 5.6, 3.0 Hz, 2 H, CH_2), 4.38–4.43 (m, 2 H, 2× CH), 4.49–4.61 (m, 4 H, CH_2), 7.23–7.32 (m, 11 H, arom. CH), 7.41 (td, J = 7.7, 1.3 Hz, 1H. arom. CH), 7.74 (d, J = 8.1 Hz, 1 H, arom. CH), 7.82 (d, J = 8.0 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.0, 70.5, 70.8, 72.0, 73.35, 73.39 (CH, CH_2), 120.8, 121.3, 124.3, 126.0, 127.5, 127.6, 127.7, 128.2, 128.3 (arom. C), 135.4, 137.5, 137.8, 152.6, 166.1 (arom. C_{ipso}) ppm. LRMS: m/z = 474 [M + Na]$^+$. HRMS: calcd. for $C_{25}H_{25}NS_2NaO_3$ 474.1168 [M + Na]$^+$; found 474.1180.

5-[1-(Benzo[*d*]thiazol-2-ylthio)ethyl]nonan-5-ol (34): To a mixture of **9** (312 mg, 1.87 mmol) and Et_3N (172 mg, 1.70 mmol) was slowly added 2,2-dibutyl-3-methyloxirane (**25**, 265 mg, 1.56 mmol). The reaction mixture was heated to 80 °C for 2 d. Dichloromethane (30 mL) was added to the cooled mixture and it was washed with saturated aqueous $NaHCO_3$ solution (3 × 20 mL), water (20 mL) and brine (20 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a crude liquid which was purified by silica flash column chromatography (petroleum ether/EtOAc = 9:1) to afford the thioether **34** (302 mg, 58%) as a colorless oil. R_f = 0.43 (petroleum ether/EtOAc = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90–0.94 (m, 6 H, 2× CH_3), 1.30–1.48 (m, 10 H, 5× CH_2), 1.53 (d, J = 7.1 Hz, 3 H, CH_3), 1.65–1.71 (m, 2 H, CH_2), 1.72–1.79 (m, 1 H, OH), 4.02 (q, J = 7.2 Hz, 1 H, CH), 7.29 (td, J = 7.3, 1.3 Hz, 1 H, arom. CH), 7.40 (td, J = 7.2, 1.2 Hz, 1 H, arom. CH), 7.73 (dt, J = 8.2, 0.7 Hz, 1 H, arom. CH), 7.86 (dt, J = 7.9, 0.8 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 16.8 (CH_3), 23.2, 23.4, 25.6, 25.7, 36.0, 37.6 (CH_2), 54.0 (CH), 75.8 (C), 120.9, 121.3, 124.4, 126.1 (arom. C), 135.4, 152.6, 167.5 (arom. C_{ipso}) ppm. LRMS: m/z = 360 [M + Na]$^+$. HRMS: calcd. for $C_{18}H_{27}NS_2NaO$ 360.1426 [M + Na]$^+$; found 360.1422.

(*E*)-3-(Benzo[*d*]thiazol-2-ylthio)-8-benzyloxy-2,6-dimethyloct-6-en-2-ol (35): To a mixture of **9** (700 mg, 3.05 mmol) was added Et_3N (286 mg, 2.83 mmol). The mixture was heated at 80 °C for 1 h then 1-benzyloxy-6,7-epoxy-3,7-dimethyl-2-octene (**26**, 700 mg, 2.69 mmol) was added. The reaction mixture was stirred at 80 °C for 20 h. Dichloromethane (50 mL) was added to the mixture and it was washed with saturated aqueous $NaHCO_3$ solution (3 × 30 mL), water (30 mL) and brine (30 mL), then dried (Na_2SO_4). Evaporation of the solvent gave a crude liquid which was purified by silica flash column chromatography (petroleum ether/EtOAc = 4:1) to afford the thioether **35** (997 mg, 87%) as a yellow wax. R_f = 0.38 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.66–1.75 (m, 1 H, 1-H_a), 2.04–2.08 (m, 1 H, 1-H_b), 2.22–2.28 (m, 2-H_a), 2.38–2.43 (m, 1 H, 2-H_b), 3.72 (dd, J = 11.6, 2.1 Hz, 1 H, CH), 3.93–4.01 (m, 2 H, CH_2), 4.43 (s, 2 H, CH_2), 5.40 (td, J = 6.7, 1.1 Hz, 1 H, CH), 7.25–7.43 (m, 6 H, arom. CH), 7.39 (td, J = 8.2, 1.2 Hz, 1 H, arom. CH), 7.71 (d, J = 8.1 Hz, 1 H, arom. CH), 7.82 (d, J = 8.1 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.3, 26.0 (CH_3), 28.2 (CH_2), 29.2 (CH_3), 37.7 (CH_2), 61.9 (CH), 66.4, 72.0 (CH_2), 72.9 (C), 120.9, 121.1, 122.2, 124.6, 126.2, 127.5, 127.7, 128.3 (CH, arom. C), 135.1, 138.3, 138.7, 152.1, 168.3 (arom. C_{ipso}) ppm. LRMS: m/z = 450 [M + Na]$^+$. HRMS: calcd. for $C_{24}H_{29}NS_2NaO_2$ 450.1532 [M + Na]$^+$; found 450.1539.

5-[(Benzo[*d*]thiazol-2-ylsulfonyl)methyl]nonan-5-ol (36): To a solution of 2-(benzo[*d*]thiazole-2-ylthio)methyl)nonan-5-ol (**30**, 78 mg, 0.24 mmol) and $NaHCO_3$ (205 mg, 2.44 mmol) in acetone (10 mL) at 0 °C was added a mixture of Oxone® (751 mg, 1.21 mmol) in water (5 mL) cautiously and portionwise. The reaction mixture was stirred at 0 °C for 20 h. The mixture was diluted with cold water (10 mL), extracted with cold Et_2O (5 × 20 mL) and dried (Na_2SO_4). Removal of the solvent gave the unstable sulfone **36** as a colorless solid (81.1 mg, 95%). R_f = 0.43 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.0 Hz, 6 H, 2× CH_3), 1.24–1.30 (m, 8 H, 4× CH_2), 1.69–1.72 (m, 4 H, 2× CH_2), 3.77 (s, 2 H, CH_2), 7.58–7.66 (m, 2 H, arom. CH), 8.01–8.03 (m, 1 H, arom. CH), 8.20–8.22 (m, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.9, 25.6, 38.9, 62.0 (CH_2), 74.3 (C), 122.3, 125.4, 127.7, 128.1 (arom. C), 136.6, 152.4, 167.2 (arom. C_{ipso}) ppm. LRMS: m/z = 378 [M + Na]$^+$. HRMS: calcd. for $C_{17}H_{25}NS_2NaO_3$ 378.1168 [M + Na]$^+$; found 378.1176.

Methyl 10-(Benzo[*d*]thiazol-2-ylsulfonyl)-9-hydroxyoctadecanoate (37) and Methyl 9-(Benzo[*d*]thiazol-2-ylsulfonyl)-10-hydroxyoctadecanoate (38): To a solution of methyl 4-(benzo[*d*]thiazole-2-ylthio)-4-hydroxyhexanoate (**31**) and methyl 3-(benzo[*d*]thiazole-2-ylthio)-3-hydroxyhexanoate (**32**) (870 mg, 1.81 mmol) and $NaHCO_3$ (1.84 g, 219 mmol) in acetone (30 mL) at 0 °C was added a mixture of Oxone® (7.33 g, 11.8 mmol) in water (15 mL) cautiously and portionwise. The reaction mixture was stirred at 0 °C for 1 d. The mixture was diluted with cold water (100 mL), extracted with cold Et_2O (5 × 70 mL) and dried (Na_2SO_4). Evaporation of the solvent gave a mixture of the sulfones **37** and **38** as unstable colorless solids (774 mg, 84%). R_f = 0.22 (petroleum ether/EtOAc = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.86 (m, 6 H, 2× CH_3), 1.18–1.25 (m, 36 H, 18× CH_2), 1.49–1.70 (m, 12 H, 6× CH_2), 1.89–1.96 (m, 4 H, 2× CH_2), 2.27 (m, 4 H, 2× CH_2), 3.651 (s, 3 H, CH_3), 3.65 (s, 3 H, CH_3), 3.69–3.74 (m, 2 H, 2× CH), 4.15–4.19 (m, 2 H, 2× CH), 7.57–7.65 (m, 4 H, arom. CH), 8.00–8.02 (m, 2 H, arom. CH), 8.19–8.20 (m, 2 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.5, 22.6, 24.72, 24.76, 25.5, 25.60, 25.65, 26.9, 27.0, 28.7, 28.8, 28.9, 29.05, 29.09, 29.1, 29.24, 29.29, 29.4, 31.71, 31.78, 33.93, 33.97, 34.2 (CH_2), 51.5 (CH_3), 69.2, 69.3, 69.8, 69.9 (CH), 122.2, 125.3, 127.6, 127.9 (arom. C), 136.5, 152.3, 167.3 (arom. C_{ipso}), 174.33, 174.38 (CO) ppm. LRMS: m/z = 534 [M +

Na]$^+$. HRMS: calcd. for $C_{26}H_{41}NS_2NaO_5$ 534.2318 [M + Na]$^+$; found 534.2305.

3-(Benzo[*d*]thiazole-2-ylsulfonyl)-1,4-bis(benzyloxy)butan-2-ol (39): To a solution of 3-(benzo[*d*]thiazole-2-ylthio)-1,4-bis(benzyloxy) butan-2-ol (**33**, 111 mg, 0.25 mmol) and $NaHCO_3$ (159 mg, 1.89 mmol) in acetone (6 mL) at 0 °C was added a mixture of Oxone® (471 mg, 0.76 mmol) in water (3 mL) cautiously and portionwise. The reaction mixture was stirred at 0 °C for 10 h. The mixture was diluted with cold water (50 mL), extracted with cold Et_2O (5× 50 mL) and dried (Na_2SO_4). Removal of the solvent gave the sulfone **38** as an unstable yellow oil (101 mg, 84%). R_f = 0.26 (petroleum ether/EtOAc = 7:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.35 (br. s, 1 H, OH), 3.61 (dd, J = 10.2, 4.8 Hz, 1 H, 1-H$_a$), 3.72 (dd, J = 10.2, 3.3 Hz, 1 H, 1-H$_b$), 3.80 (dd, J = 11.8, 5.8 Hz, 1 H, 1′-H$_a$), 4.13–4.16 (m, 2 H, 1′-H$_b$, CH), 4.23 (d, J = 11.7 Hz, 1 H, 2-H$_a$), 4.37 (d, J = 11.9 Hz, 1 H, 2-H$_b$), 4.40 (d, J = 12.0 Hz, 1 H, 2′-H$_a$), 4.55 (d, J = 11.8 Hz, 1 H, 2′-H$_b$,), 4.65–4.67 (m, 1 H, CH), 6.99 (d, J = 6.9 Hz, 2 H, arom. CH), 7.12–7.19 (m, 3 H, arom. CH), 7.26–7.33 (m, 5 H, arom. CH), 7.54 (t, J = 7.3 Hz, 1 H, arom. CH), 7.60 (t, J = 7.4 Hz, 1 H, arom. CH), 7.91 (d, J = 8.0 Hz, 1 H, arom. CH), 8.16 (d, J = 8.1 Hz, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 64.9 (CH_2), 67.6, 67.7 (CH), 70.5, 73.2, 73.4 (CH_2), 122.2, 125.2, 127.3, 127.6, 127.7, 127.93, 127.98, 128.13, 128.4 (arom. C), 136.5, 136.7, 137.2, 152.2, 167.3 (arom. C_{ipso}) ppm. LRMS: m/z = 506 [M + Na]$^+$. HRMS: calcd. for $C_{25}H_{25}NS_2NaO_5$ 506.1066 [M + Na]$^+$; found 506.1058.

5-(1-(Benzo[*d*]thiazol-2-ylsulfonyl)ethyl)nonan-5-ol (40): To a solution of 5-(1-(benzo[*d*]thiazol-2-ylthio)ethyl)nonan-5-ol **34** (190 mg, 0.56 mmol) and $NaHCO_3$ (450 mg, 5.36 mmol) in acetone (14 mL) at 0 °C was added a mixture of Oxone® (1.75 g, 2.82 mmol) in water (7 mL) cautiously and portionwise. The reaction mixture was stirred at 0 °C for 2 d. The mixture was diluted with ice-cold water (30 mL), extracted with ice-cold CH_2Cl_2 (5× 30 mL) and dried (Na_2SO_4). Evaporation of the solvent gave the sulfone **40** as an unstable colorless solid (200 mg, 96%). R_f = 0.54 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.3 Hz, 3 H, CH_3), 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.14–1.37 (m, 8 H, 4× CH_2), 1.41 (d, J = 7.2 Hz, 3 H, CH_3), 1.47–1.53 (m, 2 H, CH_2), 1.74–1.81 (m, 2 H, CH_2), 4.00 (q, J = 7.2 Hz, 1 H, CH), 7.58–7.66 (m, 2 H, arom. CH), 8.00–8.02 (m, 1 H, arom. CH), 8.22–8.24 (m, 1 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.7, 14.0, 14.1 (CH_3), 23.0, 23.1, 24.8, 25.0, 36.7 (CH_2), 36.9 (CH), 53.4 (C), 66.3 (CH), 122.2, 125.5, 127.7, 128.1 (arom. C), 136.7, 152.5, 166.1 (arom. C_{ipso}) ppm. LRMS: m/z = 392 [M + Na]$^+$. HRMS: calcd. for $C_{18}H_{27}NS_2NaO_3$ 392.1325 [M + Na]$^+$; found 392.1313.

(*E*)-3-(Benzo[*d*]thiazol-2-ylsulfonyl)-5-(3-(benzyloxymethyl)-2-methyloxiran-2yl)-2-methylpentan-2-ol (41): To a suspension of (*E*)-3-(benzo[*d*]thiazol-2-ylthio)-8-(benzyloxy)-2,6-dimethyloct-6-en-2-ol (**35**, 1.4 g, 3.28 mmol) and $NaHCO_3$ (3.47 g, 41.3 mmol) in acetone (30 mL) at 0 °C was added a solution of Oxone® (13.5 g, 21.8 mmol) in water (15 mL) cautiously and portionwise. The reaction mixture was stirred at 0 °C for 3 d. The mixture was diluted with ice-cold water (50 mL), extracted with ice-cold CH_2Cl_2 (5× 50 mL) and dried (Na_2SO_4). Evaporation of the solvent gave the sulfone **41** as an unstable colorless solid (1.51 g, 97%). R_f = 0.21 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.66–1.75 (m, 2 H, CH_2), 1.79–1.85 (m, 2 H, CH_2), 1.92–2.02 (m, 2 H, CH_2), 2.18–2.21 (m, 2 H, CH_2), 2.85 (dd, J = 6.1, 4.5 Hz, 1 H, CH), 2.98 (t, J = 5.6 Hz, 1 H, CH′), 3.45 (dd, J = 11.1, 6.1 Hz, 1 H, 1-H$_a$), 3.55 (t, J = 5.5 Hz, 2 H, 1′-H), 3.61 (dd, J = 11.1, 4.4 Hz, 1 H, 1-H$_b$), 3.79–3.81 (m, 2 H, 2× CH), 4.46 (dd, J = 11.7, 7.4 Hz, 2 H, 2-H$_a$, 2′-H$_a$), 4.57 (dd, J = 11.7, 4.7 Hz, 2 H, 2-H$_b$, 2′-H$_b$), 7.29–7.34 (m, 10 H, arom. CH), 7.58–7.63 (m, 4 H, arom. CH), 7.98–8.01 (m, 2 H, arom. CH), 8.19 (d, J = 8.1 Hz, 2 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.1, 16.6 (CH_3), 21.8, 22.1 (CH_2), 26.7, 27.5, 28.3, 29.2 (CH_3), 37.1, 37.9 (CH_3), 60.1, 61.4 (CH), 68.41, 68.49 (CH_2), 72.2 (CH) 72.8, 72.9, 73.32, 73.37 (CH_2), 122.36, 122.37, 125.3, 127.7, 127.95, 127.97, 128.14, 128.17, 128.40, 128.45 (arom. C), 136.51, 136.58, 137.2, 137.5, 152.2, 152.3, 167.1, 167.2 (arom. C_{ipso}) ppm. LRMS: m/z = 498 [M + Na]$^+$. HRMS: calcd. for $C_{24}H_{29}NS_2NaO_5$ 498.1379 [M + Na]$^+$; found 498.1364.

5-Bromo-5-(bromomethyl)nonane (42): (i) To a solution of 2-(benzo[*d*]thiazole-2-ylsulfonyl)methyl)nonan-5-ol (**36**, 120 mg, 0.34 mmol) in dry CH_2Cl_2 (15 mL) was added DBU (104 mg, 0.68 mmol). The reaction mixture was stirred at room temperature for 5 h under argon. The reaction mixture was treated with catalytic amount of pyridine (0.02 mL) and bromine (53.5 mg, 0.33 mmol), and then stirred at room temperature overnight. Carbon tetrachloride (10 mL) was added to the reaction mixture. Removal of the solvent gave a crude residue, which was purified by flash chromatography (petroleum ether) to give the dibromide **42** as a colorless oil (69 mg, 68%). R_f = 0.73 (petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.2 Hz, 6 H, 2× CH_3), 1.32–1.43 (m, 4 H, 2× CH_2), 1.44–1.54 (m, 4 H, 2× CH_2), 1.82–1.95 (m, 4 H, 2× CH_2), 3.82 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.5, 27.0, 39.4, 40.9 (CH_2), 73.9 (C) ppm. HRMS: calcd. for $C_{10}H_{20}Br$ 219.0143, 221.0143 [M]; found 219.0745, 221.0723. $C_{10}H_{20}Br_2$: calcd. C 40.03, H 6.72; found C 40.37, H 6.65.

(ii) To a solution of **17** (196 mg, 1.39 mmol) in hexane (2 mL) under argon was added pyridine (0.08 mL) and excess bromine slowly. The reaction was stirred at room temperature for 4 h. Removal of the solvent gave a crude residue which was purified by flash chromatography (petroleum ether) to give the dibromide **42** (232 mg, 56%), identical to that described above.

3-(Benzyloxymethyl)-2-methyl-2-(4-methylpent-3-enyl)oxirane (43): To a solution of (*E*)-3-(benzo[*d*]thiazol-2-ylsulfonyl)-5-(3-benzyloxymethyl-2-methyloxiran-2-yl)-2-methylpentan-2-ol (**41**, 180 mg, 0.38 mmol) in dry CH_2Cl_2 (10 mL) was added DBU (121 mg, 0.78 mmol). The reaction mixture was stirred at room temperature for 3 h under argon. Evaporation of the solvent gave a crude mixture, which was purified by silica flash column chromatography (petroleum ether/EtOAc = 4:1) to give the epoxy alkene **43**[36] (71.8 mg, 73%) as a colorless oil. R_f = 0.57 (petroleum ether/EtOAc = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (s, 3 H, CH_3), 1.45–1.51 (m, 1 H, 2-H$_a$), 1.60 (s, 3 H, CH_3), 1.62–1.65 (m, 1 H, 2-H$_b$), 1.67 (s, 3 H, CH_3), 2.05–2.10 (m, 2 H, CH_2), 3.01 (dd, J = 6.0, 4.5 Hz, 1 H, CH), 3.55 (dd, J = 11.2, 6.1 Hz, 1 H, 3-H$_a$), 3.68 (dd, J = 11.2, 4.5 Hz, 1 H, 3-H$_b$), 4.53 (d, J = 11.9 Hz, 1 H, 4-H$_a$), 4.63 (d, J = 11.8 Hz, 1 H, 4-H$_b$), 5.07–5.10 (m, 1 H, CH), 7.28–7.35 (m, 5 H, arom. CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7, 23.6, 25.6, 38.3 (CH_3, CH_2), 61.2, 68.8, 73.1 (C, CH, CH_2), 123.4, 127.7, 128.4, 132.0, 137.9 (C, CH, arom. C) ppm.

General Procedure for Desulfonation of 36–41: (i) To a solution of sulfone (1 equiv.) in DCM or MeOH, was added DBU (2 equiv.) slowly. The mixture was stirred under argon The solvent was removed under reduced pressure and the crude residue was purified by chromatography to afford the alkenes **17**–**20** and **43**.

(ii) A solution of the sulfone **36**–**41** in toluene was heated at reflux until TLC analysis indicated complete consumption of starting material. The toluene was removed under reduced pressure and the

crude residue was purified by flash chromatography to afford the alkenes **17**–**20** and **43**.

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