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A General and Diastereoselective Route to Five-Membered Carbocycles and Heterocycles from Acyclic Vinyl Sulfone-Modified Carbohydrates

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Pentosyl and hexosyl acyclic vinyl sulfones having a suitably positioned leaving group reacted with externally delivered carbon, nitrogen, oxygen, and sulfur nucleophiles to afford a series of five-membered carbocycles and heterocycles in a diastereoselective fashion. This diversity-oriented synthetic method generates a wide range of chirally pure cyclic compounds from easily accessible starting materials and reagents.

Introduction

The importance of five-membered heterocycles[1] and carbocycles[2] in natural products and pharmaceuticals led to outstanding developments in the area of synthetic strategies for achieving these structures. Tetrahydrofurans, for example, are among the most significant classes of heterocycles in natural products, and consequently a wide range of methods for synthesis has been developed.[1a–1c,1h,1l,1n,1s–1v,3] The N-containing five-membered core is a structural motif of particular interest in synthetic and medicinal chemistry, as it is present in a large number of natural products and biologically active compounds.[1d,1j–1t,1v,1w,4] The importance of natural products and pharmaceuticals containing the cyclopentyl moiety has also led to the development of numerous synthetic methods to construct such rings with various functional groups attached to the ring structure.[2,5] Some of these strategies have also been utilized, albeit less frequently, for the synthesis of tetrahydrothiophene derivatives.[1t,6] A selection of the targeted structures by other groups reported in the literature are depicted in Figure 1. We were also intrigued by the number of five-membered carbocycles or heterocycles as intermediates or final products having sulfone groups attached to the ring known so far (Figure 2).

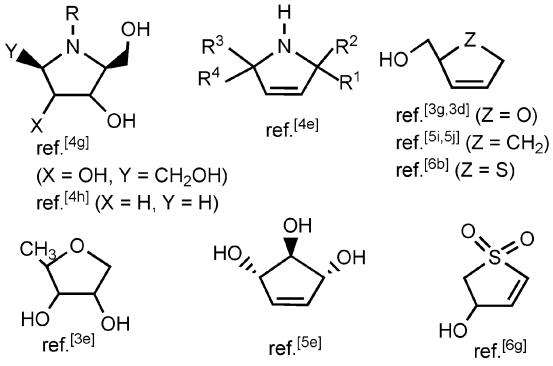

Figure 1. Five-membered carbocycle or heterocycle structures reported by other groups.

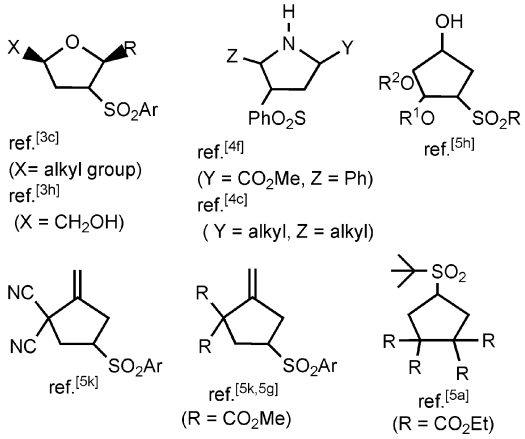

Figure 2. Five-membered carbocycles or heterocycles with sulfone groups on the ring.

Results and Discussion

Several attempts have been made in the past to develop general strategies for the synthesis of five-membered carbocycles and heterocycles from carbohydrates. For example, reactions like free radical cyclizations,[2a,2b] transition-metal-mediated deoxygenative ring contractions,[2b,2f] and olefin metathesis[2g] have been applied in the recent past for the conversion of carbohydrates to carbocycles. On the

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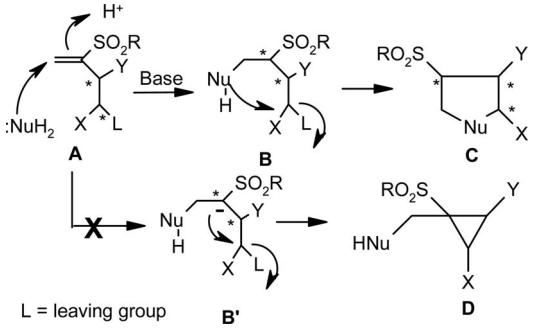
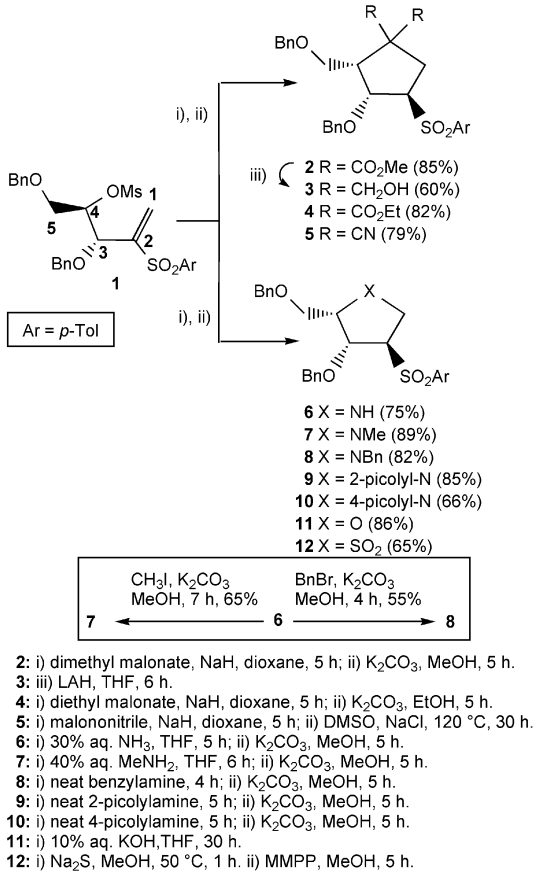
other hand, carbohydrates were also found to be useful starting materials for the synthesis of heterocycles.[1e–1g,1i] However, to the best of our knowledge, virtually no method involving carbohydrates had the potential to be used as a general strategy for the synthesis of carbocycles as well as heterocycles containing O-, N-, and S-.

In continuation of our research on the designing of strategies for the synthesis of carbocycles[7a,7b] and heterocycles[7c] starting from vinyl sulfone-modified carbohydrates,[8] we envisioned that by properly designing acyclic vinyl sulfone-modified carbohydrates,[8b] it would be possible to synthesize analogs of carbocycles and heterocycles depicted in Figure 1 and Figure 2. Since carbon and other heteroatomic nucleophiles react efficiently at the electrophilic β-position of vinylic sulfones,[8] we opined that the vinyl sulfone group of the acyclic carbohydrate-modified vinyl sulfones with a properly positioned leaving group as in **A** (Scheme 1) would be in a position to react with externally delivered nucleophiles preferentially; intermediate **B** would then intramolecularly attack the carbon atom bearing the mesylate group in S_N2 fashion, causing ring formation with complete stereocontrol to afford compound **C**. It should be noted that the selection of nucleophiles with two abstractable protons would rule out the possibility of formation of cyclopropanes **D** via intermediates **B′** as reported earlier,[7a,7b] because in all cases the hydrogen atom attached to the intramolecular nucleophile such as -CH, -NH, -OH, or -SH (as in **B**) would be more easily abstracted than the proton attached to the sulfone-bearing carbon atom. Since the vinyl sulfone group is implanted on carbohydrate moieties, the chiral environment of the parent carbohydrate molecule would be transferred to the cyclic compounds.



Scheme 1. General strategy for the synthesis of five-membered carbocycles and heterocycles.

Following this strategy, carbon nucleophiles generated from active methylene groups of dimethyl malonate, diethyl malonate, and malononitrile were treated with the pentosyl acyclic vinyl sulfone **1**[7a] (Scheme 2), which yielded a mixture of compounds in each case. The mixture obtained from dimethyl malonate was treated with K_2CO_3/MeOH to obtain a single diastereomer **2** (Scheme 2). Compound **2** was converted into the corresponding alcohol **3** by LAH in THF. Similarly, mixtures produced by diethyl malonate and malononitrile were separately treated with K_2CO_3/EtOH and DMSO/NaCl to generate single diastereomers **4** and **5**, respectively. The THF solution of **1** was separately treated with 30% aq. ammonia and 40% aq. methylamine solutions to generate a mixture of products in each case; these mixtures were also treated with K_2CO_3/MeOH to afford single isomers **6** and **7**, respectively. On the other hand, **1** was treated with neat benzylamine, 2-picolylamine, and 4-picolylamine to generate mixtures; separate treatment of these mixtures with K_2CO_3/MeOH generated single diastereomers **8**, **9**, and **10**, respectively. Pentosyl vinyl sulfone **1** also reacted with the oxygen nucleophile generated from aq. KOH to afford a single isomer **11**. Reaction of Na_2S with **1** afforded a tetrahydrothiophene derivative, which was oxidized with magnesium bis(monoperoxyphthalate) hexahydrate (MMPP) to form **12** in good overall yield (Scheme 2).

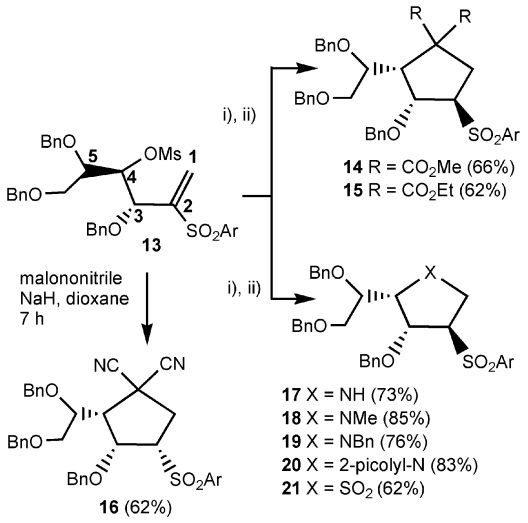


Scheme 2. Synthesis of five-membered carbocycles and heterocycles from pentosyl acyclic vinyl sulfone.

In order to establish the general reaction patterns of acyclic vinyl sulfones, hexosyl vinyl sulfone **13**[7a] was treated with carbon nucleophiles generated from dimethyl malonate and diethyl malonate, as reported earlier, to afford **14** and **15**, respectively (Scheme 3). However, malononitrile reacted with **13** to generate **16** without base treatment. Compound **13** was treated with 30% aq. ammonia solution, 40% aq. methylamine solution, neat benzylamine, and 2-picolyl-

amine in the same way described above to afford **17**, **18**, **19**, and **20**, respectively. Vinyl sulfone **13** was treated with Na_2S, and the product was oxidized to compound **21** with MMPP (Scheme 3). It should be noted that the stereochemistry at C-3 of **1** and **13** was known, and it was expected that the intramolecular backside attack would invert the configuration of C-4 centers. Since the carbon center attached to SO_2Ar in cyclized products corresponding to C-2 of **1** or **13** would be the newly generated stereocenter, it was necessary to establish the configuration of this center. The structure of compound **3** obtained from **2** was confirmed by the X-ray diffraction analysis of the former (Figure 3). The stereochemistry of compounds **4** and **5** were expected to be similar to that of **2**; a comparison of the spectroscopic data of **4** and **5** with those of **2** also confirmed this hypothesis. Compound **6** was treated with methyl iodide and benzyl bromide separately to afford *N*-methylated **7** and *N*-benzylated **8**, respectively. Since the stereochemistry of **8** was confirmed by the X-ray diffraction analysis (Figure 4), the configurations at various carbon centers of **6** and **7** were automatically established. The ^1H NMR spectral pattern of **9** was comparable to that of **8**, proving thereby the structural similarities of the two compounds. We expected compounds **10**, **11**, and **12** to have the same stereochemistry like other compounds in this series. The stereochemistry of SO_2Ar-bearing carbon of **14** was confirmed by COSY-NOESY experiments, and we presumed that compounds **14** and **15** had similar stereochemistries. Compound **17** was treated with methyl iodide and benzyl bromide separately to afford *N*-methylated **18** and *N*-benzylated **19**, respectively. The stereochemistry of **19** was also confirmed by COSY-NOESY experiments, which established the similarity in the structural patterns of **17**–**19**. The ^1H NMR spectral pattern of **20** was comparable to that of **19**, proving thereby the structural similarities of the two compounds. We expected the chiralities on the ring carbons of **21** to be the same as those of other compounds in this series.

It should be noted that, in most of the cases, after the attack of a nucleophile at the electron-deficient methylene carbon of **1** or **13**, the mixture is constituted of two diastereomers generated by the scrambling of the carbon center attached to the -SO_2Ar group. This was confirmed by the ^1H NMR spectra of any of the mixtures in which the peak of mesylate was absent. These compounds were converted to single diastereomers like **2**, **4**, **5**–**10** (Scheme 2), **14**, **15**, and **17**–**20** (Scheme 3) by treating the mixtures with K_2CO_3/MeOH. However, the K_2CO_3/MeOH system hydrolyzed the products generated by the reaction of malononitrile and **1**; therefore, the original mixture was treated with DMSO/NaCl at an elevated temperature to afford a single compound **5**. We presume that under these reaction conditions the epimeric mixture (at SO_2Ar-bearing carbon) isomerized to the more stable epimer. Another malononitrile product, **16**, obtained as a single epimer from **13** (Scheme 3), did not undergo any further transformation when treated with DMSO/NaCl. The structure of **16**, considered as an exception, was confirmed by X-ray diffraction analysis (Figure 5).



14: i) dimethyl malonate, NaH, dioxane, 6 h; ii) K_2CO_3, MeOH, 5 h.
15: i) diethyl malonate, NaH, dioxane, 6 h; ii) K_2CO_3, EtOH, 6 h.
17: i) 30% aq. NH_3, THF, 7 h; ii) K_2CO_3, MeOH, 6 h.
18: i) 40% aq. $MeNH_2$, THF, 6 h; ii) K_2CO_3, MeOH, 5 h.
19: i) neat $BnNH_2$, 3 h; ii) K_2CO_3, MeOH, 5 h,
20: i) neat 2-picolylamine, 2 h; ii) K_2CO_3, MeOH, 5 h.
21: i) Na_2S, MeOH, 50 °C, 1.5 h. ii) MMPP, MeOH, 5 h.

Scheme 3. Synthesis of five-membered carbocycles and heterocycles from hexosyl acyclic vinyl sulfone.

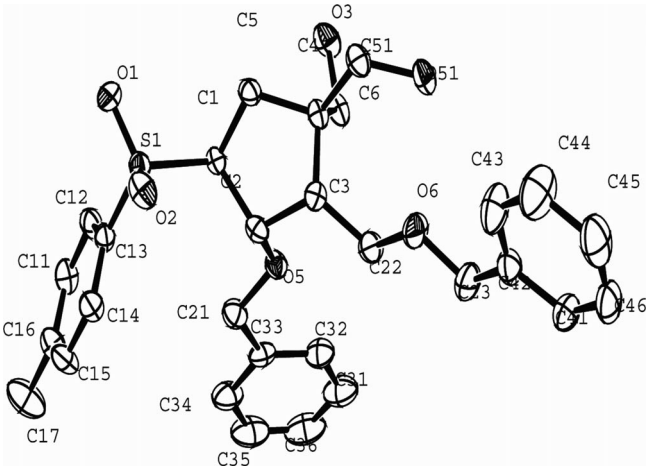


Figure 3. The crystal structure of compound **3**.

It is clear from most of the reported synthetic strategies for the preparation of five-membered carbocycles and heterocycles that the carbon or the heteroatom that is destined to become part of the ring structure is a constituent of the predesigned substrate undergoing the cyclization reaction.[1a–1g,1j,1m–1q,1t,1v,1w,2a–2c,2f,2i,9] All these strategies,[1a–1g,1j,1m–1q,1t,1v,1w,2a–2c,2f,2i,9] therefore require the te-

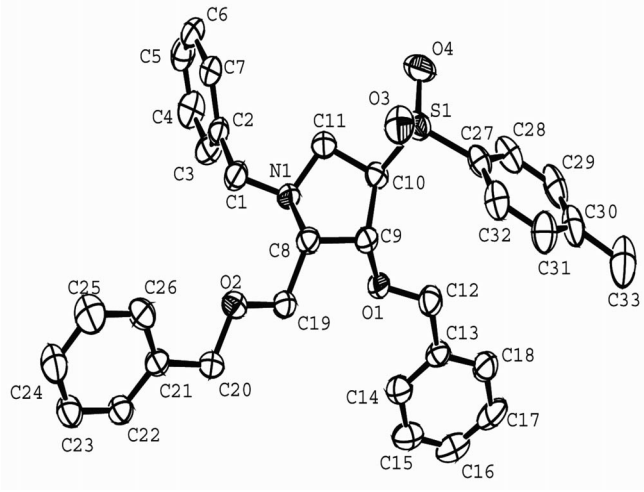


Figure 4. The crystal structure of compound **8**.

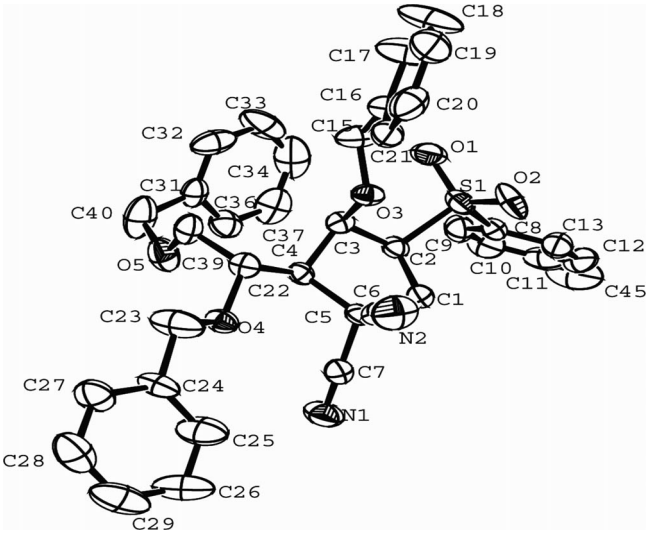
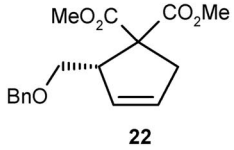
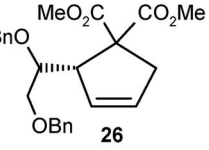
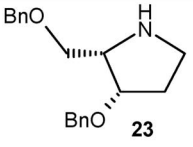
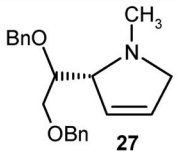
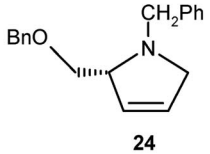
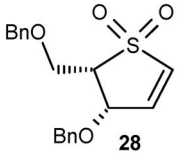
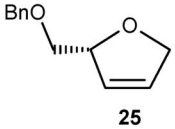
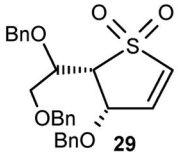


Figure 5. The crystal structure of compound **16**.

dious synthesis of separate starting materials for the preparation of carbocycles as well as each of N-, O-, or S-containing heterocycles.[1,2,9] We, on the other hand, used a diversity-oriented synthetic method by reacting easily accessible starting materials like **1** or **13** with inexpensive nucleophiles like amines, KOH, Na_2S, dialkyl malonates, and malononitrile.

All compounds, **2**–**12**, **14**–**21**, generated so far had the sulfone group attached to them. Since one of our target group of molecules was five-membered carbocycles and heterocycles without the sulfone group (Figure 1), we experimented with several desulfonylating agents known in the literature[10] for the desulfonylation of a group of selected compounds. Na(Hg) mediated reduction, the most widely used radical-based method for the desulfonylation of organic molecules,[10] was used for the desulfonylation of compound **2** to afford **22** (Table 1). In the case of compound **6**, it was necessary to block the free NH group with Boc before desulfonylation with Na(Hg); the Boc group was removed from the desulfonylated product to afford **23**. Benzyl protected amine **8** and furanose derivative **11** were desulfonylated by the same reagent to afford compounds **24** and **25**, respectively, in moderate yields. Compounds **14** and **18** were also desulfonylated to afford **26** and **27**, respectively. It is known that the desulfonylation is initiated by an electron transfer to the sulfone group; the loss of arenesulfinate anion generates a β-hydroxy or β-alkoxy carbanion, which undergoes elimination to afford an olefin.[10] This phenomena may explain the formation of olefin compounds **22**, **24**–**27**. We also observed earlier that olefin formation during desulfonylation of furanose systems was the most dominating reaction pathway.[11]

Table 1. Desulfonylation of selected compounds.

Desulfonylated products	Desulfonylated products
 **22**	 **26**
2→ 22 6% Na(Hg), Na_2HPO_4, MeOH, 5 h, 54%	**14→ 26** 6% Na(Hg), Na_2HPO_4, MeOH, 5 h, 56%
 **23**	 **27**
6→ 23 i. $(Boc)_2O$, DCM, 5 h, 85% ii. 6% Na(Hg), Na_2HPO_4, MeOH, 4 h, 52% iii. 50% TFA-DCM, 2 h, 95%	**18→ 27** 6% Na(Hg), Na_2HPO_4, MeOH, 5 h, 80%
 **24**	 **28**
8→ 24 6% Na(Hg), Na_2HPO_4, MeOH, 5 h, 77%	**12→ 28** DBU, DCM, 3 h, 82%
 **25**	 **29**
11→ 25 6% Na(Hg), Na_2HPO_4, MeOH, 5 h, 55%	**21→ 29** DBU, DCM, 4 h, 73%

However, in one case exclusive desulfonylation generated the deoxy derivative **23**. It appears that the presence of an electron-withdrawing group like "Boc" used for the protection of the ring nitrogen prevented olefin formation. We

also used the other well-known electron-transfer method with Mg metal in methanol,[10] but the products were obtained in reduced yields. The Mg-MeOH-$NiBr_2$ desulfonylating reagent, used successfully in the synthesis of 2,3-dideoxyaminopentofuranosides,[11] failed to generate any desulfonylated compounds. In an alternative approach, the exocyclic sulfonyl groups of **12** and **21** were removed by DBU treatment via an elimination process to generate a new series of vinyl sulfones **28** and **29**, respectively (Table 1).

Conclusions

We have established that suitably functionalized acyclic chiral vinyl sulfones can be used effectively for the synthesis of carbocycles, pyrrolidines, tetrahydrofurans, and tetrahydrothiophenes by externally delivering different nucleophiles in a diastereoselective fashion to substrates like **1** or **13**. It should be noted that our strategy avoids the prior synthesis of separate starting materials for the preparation of carbocycles as well as each of O-, N-, or S-containing heterocycles. Since each of our starting materials, **1** or **13**, is capable of producing a plethora of cyclic compounds by reacting with simple nucleophiles, this expedient and general strategy would certainly enrich the arsenal of synthetic chemists interested in the preparation of any of these five-membered cyclic compounds.

Experimental Section

General Methods: See Supporting Information.

Compound 2: To a well-stirred solution of compound **1** (0.20 g, 0.38 mmol) in 1,4-dioxane. (10 mL) was added the solution of dimethyl malonate (0.2 mL, 1.9 mmol) in oil-free NaH (0.027 g, 1.14 mmol). The mixture was stirred under N_2. After 4–5 h, dioxane was removed under vacuum, and the reaction mixture was poured into saturated aq. $NaHCO_3$ solution. The product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was passed through a silica gel column. A solution of the residue in MeOH (20 mL) was treated with K_2CO_3 (0.158 g, 1.14 mmol). After 5 h, MeOH was removed under reduced pressure, and the residue was poured into saturated aq. $NaHCO_3$ solution. The aqueous part was washed with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **2** (0.18 g, 85%). Colorless oil, $[\alpha]_D^{24}$ = +96.5 (*c* = 0.30, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1458, 1498, 1560, 1637, 1654, 1719, 1735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (dd, *J* = 8.0, 14.0 Hz, 1 H), 2.43 (s, 3 H), 2.91 (dd, *J* = 9.6, 14.0 Hz, 1 H), 3.05 (q, *J* = 5.6, 12.8 Hz, 1 H), 3.54 (s, 3 H), 3.68–3.72 (m, 2 H), 3.74 (s, 3 H), 3.75–3.81 (m, 1 H), 4.28 (q, *J* = 11.6, 16.8 Hz, 2 H), 4.41 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 4.53–4.55 (m, 1 H), 7.05–7.07 (m, 2 H), 7.21–7.35 (m, 10 H), 7.78 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 33.6 (CH_2), 50.4, 52.5, 53.0, 60.3, 65.6 (CH_2), 68.0, 71.5 (CH_2), 73.0 (CH_2), 78.7, 127.2, 127.4, 127.5, 128.1, 128.2, 128.6, 130.0, 135.1, 137.5, 138.3, 145.0, 169.4, 170.4 ppm. HRMS (ES^+): calcd. for $C_{31}H_{34}O_8SNa$ $[M + Na]^+$ 589.1872; found 589.1871.

Compound 3: To a well-stirred solution of **2** (0.15 g, 0.27 mmol) in dry THF (20 mL) was added LAH (0.06 g, 1.62 mmol) at 0 °C under argon, and the mixture was stirred at ambient temperature. After 6 h, saturated NH_4Cl solution was added, and the product was extracted with EtOAC (3 × 15 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **3** (0.08 g, 60%). White solid, m.p 132 °C, $[\alpha]_D^{24}$ = +3.5 (*c* = 0.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.66 (dd, *J* = 8.4, 14.0 Hz, 1 H), 1.99–2.05 (m, 1 H), 2.32–2.37 (m, 1 H), 2.44 (s, 3 H), 2.94 (br. s, 1 H), 3.45 (d, *J* = 11.2 Hz, 1 H), 3.53–3.75 (m, 6 H), 3.85 (br. s, 1 H), 4.34 (d, *J* = 12 Hz, 1 H), 4.48–4.57 (m, 4 H), 7.17–7.19 (m, 2 H), 7.26–7.36 (m, 10 H), 7.76 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 32.6 (CH_2), 51.3, 51.5, 63.5 (CH_2), 66.0 (CH_2), 68.6 (CH_2), 69.0, 71.6 (CH_2), 73.7 (CH_2), 81.0, 127.8, 127.9, 128.0, 128.1, 128.4, 128.5, 128.6, 130.0, 135.1, 136.7, 136.9, 145.0 ppm. HRMS (ES^+): calcd. for $C_{29}H_{34}O_6SNa$ $[M + Na]^+$ 533.1974; found 533.1978.

Compound 4: To a well-stirred solution of compound **1** (0.15 g, 0.283 mmol) in 1,4-dioxane (10 mL) was added the solution of diethyl malonate (0.2 mL, 1.42 mmol) in oil-free NaH (0.02 g, 0.85 mmol). The mixture was stirred under N_2. After 5 h, dioxane was removed under vacuum, and the reaction mixture was poured into saturated aq. $NaHCO_3$ solution. The product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was just passed through a silica gel column. A solution of the residue in EtOH (20 mL) was treated with K_2CO_3 (0.117 g, 0.85 mmol). After 5 h, EtOH was removed under reduced pressure, and the residue was poured into saturated aq. $NaHCO_3$ solution. The aqueous part was washed with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **4** (0.13 g, 82%). Colorless oil, $[\alpha]_D^{27}$ = +85.1 (*c* = 0.29, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 2.30 (dd, *J* = 8.0, 14.0 Hz, 1 H), 2.43 (s, 3 H), 2.92 (dd, *J* = 9.6, 13.6 Hz, 1 H), 3.01–3.05 (m, 1 H), 3.68–3.84 (m, 3 H), 4.00–4.06 (m, 2 H), 4.14–4.31 (m, 4 H), 4.41 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.53–4.56 (m, 1 H), 7.05–7.07 (m, 2 H), 7.23–7.34 (m, 10 H), 7.78 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 13.9, 21.6, 33.5 (CH_2), 50.2, 60.4, 61.6 (CH_2), 61.9 (CH_2), 65.7 (CH_2), 68.1, 71.5 (CH_2), 73.0 (CH_2), 78.8, 127.2, 127.3, 127.4, 127.5, 128.1, 128.2, 128.6, 129.9, 135.1, 137.5, 138.3, 144.9, 168.9, 169.9 ppm. HRMS (ES^+): calcd. for $C_{33}H_{38}O_8SNa$ $[M + Na]^+$ 617.2186; found 617.2185.

Compound 5: To a well-stirred solution of compound **1** (0.20 g, 0.38 mmol) in 1,4-dioxane (40 mL) was added the solution of malononitrile (0.10 mL, 1.9 mmol) in oil-free NaH (0.027 g, 1.14 mmol). Then the mixture was stirred under N_2. After 5 h, dioxane was evaporated, the reaction mixture was poured into saturated aq. $NaHCO_3$ solution, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was passed through a silica gel column. The residue was heated at 120–130 °C with a mixture of NaCl (0.12 g, 1.9 mmol) in DMSO (15 mL) and H_2O (1.5 mL). After 30 h, saturated aq. $NaHCO_3$ solution was added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **5** (0.14 g, 79%). Gummy liquid, $[\alpha]_D^{27}$ = +62.2 (*c* = 0.09, $CHCl_3$). IR ($CDCl_3$): $\tilde{\nu}$ = 1155, 1304, 1454, 1498, 1597, 2252,

2873, 3031 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 2.74 (dd, J = 8.0, 14.4 Hz, 1 H), 2.84 (dd, J = 9.2, 14.8 Hz, 1 H), 2.97–3.02 (m, 1 H), 3.79–3.83 (m, 2 H), 3.91 (t, J = 8.4 Hz, 1 H), 4.36 (d, J = 12.4 Hz, 1 H), 4.51–4.55 (m, 3 H), 4.62 (d, J = 11.6 Hz, 1 H), 7.17–7.19 (m, 2 H), 7.29–7.37 (m, 8 H), 7.41 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 36.5, 38.2 (CH_2), 53.9, 65.5 (CH_2), 68.1, 71.8 (CH_2), 73.8 (CH_2), 78.0, 113.7, 115.0, 127.5, 127.7, 127.9, 128.1, 128.4, 128.5, 128.6, 130.5, 133.9, 136.5, 137.2, 146.2 ppm. HRMS (ES^+): calcd. for $C_{29}H_{28}N_2O_4SNa$ $[M + Na]^+$ 523.1668; found 523.1667.

Compound 6: To a well-stirred solution of compound **1** (0.25 g, 0.472 mmol) in THF (30 mL) was added 30% aq. NH_3 solution (5 mL). After 5 h, THF was evaporated under reduced pressure, saturated aq. $NaHCO_3$ solution was added, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and concentrated under reduced pressure. The residue was passed through a silica gel column. A solution of the residue in MeOH (20 mL) was treated with K_2CO_3 (0.196 g, 1.42 mmol). After 5 h, MeOH was removed under reduced pressure, and the residue was poured into saturated aq. $NaHCO_3$ solution. The aqueous part was washed with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **6** (0.148 g, 75%). Gummy liquid, $[\alpha]_D^{27}$ = +22.2 (c = 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 3.25 (dd, J = 6.4, 12.4 Hz, 1 H), 3.31–3.37 (m, 2 H), 3.57–3.62 (m, 1 H), 3.65–3.70 (m, 2 H), 4.30 (d, J = 11.6 Hz, 1 H), 4.38–4.49 (m, 2 H), 4.52 (q, J = 12.0, 15.2 Hz, 2 H), 7.11–7.13 (m, 2 H), 7.26–7.37 (m, 10 H), 7.78 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 46.4 (CH_2), 63.0, 68.3 (CH_2), 70.4, 71.6 (CH_2), 73.4 (CH_2), 80.3, 127.5, 127.6, 127.7 (2 × C), 128.2, 128.3, 130.0, 135.4, 137.3, 138.0, 145.0 ppm. HRMS (ES^+): calcd. for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896; found 452.1882.

Compound 7: *Method A*: A solution of compound **1** (0.15 g, 0.283 mmol) in THF (10 mL) was treated with 40% aq. methylamine solution (5 mL) following the procedure described for **6** to afford **7** (0.117 g, 89%). Colorless oil, $[\alpha]_D^{27}$ = +61.2 (c = 0.24, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 2.45 (s, 3 H), 2.57–2.65 (m, 2 H), 3.22 (t, J = 9.2 Hz, 1 H), 3.57–3.61 (m, 1 H), 3.71–3.77 (m, 2 H), 4.33 (d, J = 12.0 Hz, 1 H), 4.41–4.47 (m, 4 H), 7.16–7.18 (m, 2 H), 7.25–7.37 (m, 10 H), 7.79 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 40.8, 55.7 (CH_2), 68.5 (CH_2), 68.6, 69.1, 71.7 (CH_2), 73.4 (CH_2), 79.5, 127.6, 127.8, 128.2, 128.4, 128.5, 130.1, 135.4, 137.5, 138.1, 145.1 ppm. HRMS (ES^+): calcd. for $C_{27}H_{32}NO_4S$ $[M + H]^+$ 466.2052; found 466.2031. *Method B*: Compound **6** (0.05 g, 0.11 mmol) was stirred at 0 °C with K_2CO_3 (0.06 g, 0.44 mmol) and MeI (0.04 mL, 0.66 mmol) in MeOH. The mixture was stirred at room temperature under N_2. After 7 h, the reaction mixture was poured into a saturated aq. solution of NH_4Cl, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure to obtain a residue. The residue was purified over silica gel to afford **7** (0.034 g, 65%).

Compound 8: *Method A*: A solution of compound **1** (0.25 g, 0.472 mmol) was treated with neat benzylamine (0.5 mL, 4.72 mmol) following the procedure described for **6** to afford **8** (0.209 g, 82%). White solid, m.p 82 °C, $[\alpha]_D^{24}$ = +2.7 (c = 0.09, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 2.60–2.64 (m, 1 H), 2.95–2.99 (m, 1 H), 3.11 (t, J = 9.2 Hz, 1 H), 3.37 (d, J = 13.6 Hz, 1 H), 3.62–3.66 (m, 1 H), 3.69–3.79 (m, 2 H), 4.13 (d, J = 13.2 Hz, 1 H), 4.36–4.48 (m, 5 H), 7.15–7.16 (m, 2 H), 7.20–7.33 (m, 15 H), 7.73 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 52.3 (CH_2), 58.1 (CH_2), 67.0, 68.6, 68.8 (CH_2), 72.0 (CH_2), 73.4 (CH_2), 79.4, 127.0, 127.5, 127.6, 127.8, 128.2, 128.4, 128.5, 128.7, 130.0, 135.4, 137.5, 138.1, 138.2, 144.9 ppm. HRMS (ES^+): calcd. for $C_{33}H_{36}NO_4S$ $[M + H]^+$ 542.2365; found 542.2358. *Method B*: Compound **6** (0.04 g, 0.089 mmol) was stirred at 0 °C with K_2CO_3 (0.05 g, 0.36 mmol) and BnBr (0.06 mL, 0.53 mmol) in MeOH. The mixture was stirred at room temperature under N_2. After 7 h, the reaction mixture was poured into a saturated aq. solution of NH_4Cl, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel to afford **8** (0.026 g, 55%).

Compound 9: A solution of compound **1** (0.10 g, 0.189 mmol) was treated with neat 2-picolylamine (0.2 mL, 1.89 mmol) following the procedure described for **6** to afford **9** (0.087 g, 85%). Colorless oil, $[\alpha]_D^{27}$ = +50.8 (c = 0.19, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.75–2.80 (m, 1 H), 3.04–3.08 (m, 1 H), 3.19 (t, J = 8.8 Hz, 1 H), 3.62–3.67 (m, 2 H), 3.74–3.79 (m, 2 H), 4.21 (d, J = 14.4 Hz, 1 H), 4.39–4.50 (m, 5 H), 7.12–7.17 (m, 3 H), 7.25–7.32 (m, 10 H), 7.37 (d, J = 7.6 Hz, 1 H), 7.58–7.62 (m, 1 H), 7.74 (d, J = 8.4 Hz, 2 H), 8.50 (d, J = 4.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 52.6 (CH_2), 59.5 (CH_2), 66.9, 68.7, 68.8 (CH_2), 72.1 (CH_2), 73.4 (CH_2), 79.3, 122.1, 122.9, 127.6, 127.7, 127.8, 128.3, 128.4, 128.6, 130.0, 135.4, 136.5, 137.6, 138.1, 145.0, 149.0, 158.6 ppm. HRMS (ES^+): calcd. for $C_{32}H_{35}N_2O_4S$ $[M + H]^+$ 543.2318; found 543.2346.

Compound 10: Compound **1** (0.20 g, 0.37 mmol) was converted to **10** (0.139 g, 66%) by following the procedure described for the preparation of **9**. White liquid, $[\alpha]_D^{24}$ = +14.4 (c = 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 2.63–2.66 (m, 2 H), 3.03–3.13 (m, 2 H), 3.46 (d, J = 14.8 Hz, 1 H), 3.59–3.63 (m, 1 H), 3.72–3.75 (m, 2 H), 4.16 (d, J = 14.8 Hz, 1 H), 4.35–4.48 (m, 4 H), 7.15–7.16 (m, 2 H), 7.24–7.37 (m, 12 H), 7.74 (d, J = 8.0 Hz, 2 H), 8.49 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 52.5 (CH_2), 57.0 (CH_2), 67.0, 68.6, 68.9 (CH_2), 72.0 (CH_2), 73.4 (CH_2), 79.1, 123.5, 127.6, 127.7, 127.8 (2 × C), 127.9, 128.3, 128.4, 130.0, 135.2, 137.3, 137.8, 145.1, 148.7, 149.0 ppm. HRMS (ES^+): calcd. for $C_{32}H_{35}N_2O_4S$ $[M + H]^+$ 543.2318; found 543.2336.

Compound 11: To a well-stirred solution of compound **1** (0.15 g, 0.283 mmol) in THF (10 mL) was added 10% aq. KOH solution. After 30 h, THF was evaporated under reduced pressure, saturated aq. $NaHCO_3$ solution was added, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **11** (0.11 g, 86%). White gum, $[\alpha]_D^{27}$ = +37.0 (c = 0.26, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 3.70 (d, J = 5.6 Hz, 2 H), 3.85 (t, J = 8.4 Hz, 1 H), 4.02–4.07 (m, 2 H), 4.21 (t, J = 9.2 Hz, 1 H), 4.43 (d, J = 12.0 Hz, 1 H), 4.45–4.52 (m, 3 H), 4.58 (d, J = 11.6 Hz, 1 H), 7.15–7.17 (m, 2 H), 7.26–7.33 (m, 8 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 66.4 (CH_2), 67.9 (CH_2), 70.1, 71.6 (CH_2), 73.4 (CH_2), 79.5, 81.8, 127.6, 127.7, 127.8, 128.3, 128.4, 130.2, 135.1, 137.0, 137.9, 145.4 ppm. HRMS (ES^+): calcd. for $C_{26}H_{28}O_5SNa$ $[M + Na]^+$ 475.1550; found 475.1555.

Compound 12: To a well-stirred solution of compound **1** (0.30 g, 0.566 mmol) in MeOH (30 mL) was added Na_2S (0.053 g, 0.679 mmol). The mixture was heated at 50 °C with stirring under N_2. After 1 h, MeOH was concentrated to dryness under reduced

pressure, and the residue was poured into saturated aq. $NaHCO_3$ solution. The aqueous part was washed with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was dissolved in dry MeOH (15 mL), and magnesium monoperoxyphthalate hexahydrate (0.98 g, 1.98 mmol) was added. After 5 h, MeOH was removed under reduced pressure, and the residue was poured into saturated aq. $NaHCO_3$ solution. The aqueous part was washed with EtOAc (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **12** (0.18 g, 65%). White liquid, $[\alpha]_D^{24}$ = +24.7 (*c* = 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 3.37–3.53 (m, 3 H), 3.83 (d, *J* = 4.4 Hz, 2 H), 4.05–4.11 (m, 1 H), 4.40–4.54 (m, 4 H), 4.77 (t, *J* = 6.4 Hz, 1 H), 7.10 (d, *J* = 3.6 Hz, 2 H), 7.26–7.35 (m, 10 H), 7.74 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 50.2 (CH_2), 62.9 (CH_2), 63.0, 64.7, 73.2 (CH_2), 73.9 (CH_2), 74.4, 127.8, 127.9, 128.0, 128.3, 128.5, 128.7, 130.3, 134.3, 136.2, 137.1, 146.0 ppm. HRMS (ES^+): calcd. for $C_{26}H_{28}O_6S_2Na$ $[M + Na]^+$ 523.1225; found 523.1217.

Compound 14: Compound **13** (0.20 g, 0.37 mmol) was converted to **14** (0.139 g, 66%) by following the procedure described for the preparation of **2**. White liquid, $[\alpha]_D^{24}$ = +52.9 (*c* = 0.33, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1086, 1147, 1257, 1654, 1725, 1736 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (dd, *J* = 9.6, 12.8 Hz, 1 H), 2.44 (s, 3 H), 2.75 (dd, *J* = 8.4, 12.8 Hz, 1 H), 3.00 (dd, *J* = 5.6, 10.4 Hz, 1 H), 3.27 (s, 3 H), 3.42 (dd, *J* = 4.4, 10.8 Hz, 1 H), 3.59 (dd, *J* = 2.8, 10.8 Hz, 1 H), 3.64–3.69 (m, 4 H), 4.04 (d, *J* = 12.0 Hz, 1 H), 4.29–4.33 (m, 1 H), 4.39–4.48 (m, 4 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.70 (d, *J* = 10.4 Hz, 1 H), 7.18 (d, *J* = 6.4 Hz, 2 H), 7.19–7.39 (m, 15 H), 7.77 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 36.1 (CH_2), 52.3, 52.4, 55.4, 60.8, 68.3, 70.1 (CH_2), 70.2 (CH_2), 72.5 (CH_2), 73.4 (CH_2), 75.8, 77.8, 127.3, 127.5, 127.6 (2 × C), 127.9, 128.0, 128.2, 128.3, 128.4, 128.6, 130.0, 134.7, 137.3, 138.1, 138.6, 145.1, 169.9, 170.7 ppm. HRMS (ES^+): calcd. for $C_{39}H_{42}O_9SNa$ $[M + Na]^+$ 709.2447; found 709.2444.

Compound 15: Compound **13** (0.20 g, 0.308 mmol) was converted to **15** (0.13 g, 62%) by following the procedure described for the preparation of **4**. Colorless oil, $[\alpha]_D^{27}$ = +30.4 (*c* = 0.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 2.22 (dd, *J* = 9.6, 12.8 Hz, 1 H), 2.43 (s, 3 H), 2.78 (dd, *J* = 8.4, 12.8 Hz, 1 H), 2.97 (dd, *J* = 5.6, 10.4 Hz, 1 H), 3.40 (dd, *J* = 4.4, 10.4 Hz, 1 H), 3.57 (dd, *J* = 2.8, 10.8 Hz, 1 H), 3.56–3.78 (m, 3 H), 4.05–4.21 (m, 3 H), 4.31–4.55 (m, 6 H), 4.68 (d, *J* = 10.4 Hz, 1 H), 7.17–7.35 (m, 17 H), 7.77 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 14.0, 21.6, 36.2 (CH_2), 54.9, 60.9, 61.4 (CH_2), 68.4, 70.1 (CH_2), 72.2 (CH_2), 73.3 (CH2), 75.9, 78.0, 127.2, 127.6, 127.8, 127.9, 128.1, 128.4, 128.6, 130.0, 134.6, 137.3, 138.1, 138.8, 145.0, 169.5, 170.2 ppm. HRMS (ES^+): calcd. for $C_{41}H_{46}O_9SNa$ $[M + Na]^+$ 737.2760; found 737.2760.

Compound 16: Compound **13** (0.20 g, 0.308 mmol) was converted to **16** (0.13 g, 62%) by following the procedure described for the preparation of **5** without DMSO treatment. White solid, m.p 135 °C, $[\alpha]_D^{27}$ = +61.0 (*c* = 0.20, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1086, 1190, 1304, 1317, 1454, 1597, 2253, 2365 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 2.57 (q, *J* = 7.6, 13.2 Hz, 1 H), 2.86 (m, 1 H), 2.97 (m, 1 H), 3.36 (t, *J* = 12.8 Hz, 1 H), 3.48–3.50 (m, 2 H), 3.96 (d, *J* = 9.6 Hz, 1 H), 4.34 (d, *J* = 12.0 Hz, 1 H), 4.45–4.53 (m, 3 H), 4.61 (q, *J* = 10.8, 21.6 Hz, 2 H), 5.08 (d, *J* = 11.6 Hz, 1 H), 7.26–7.39 (m, 17 H), 7.75 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 34.6, 38.0 (CH_2), 57.0, 66.8, (CH_2) 67.0, 72.5 (CH_2), 73.4 (CH_2), 74.1 (CH_2), 76.0, 78.4, 115.0, 117.0, 127.6 (2 × C), 127.9, 128.0 (2 × C), 128.1, 128.3, 128.4, 128.5, 130.4, 136.0, 137.1, 137.3, 137.4, 145.8 ppm. HRMS (ES^+): calcd. for $C_{37}H_{36}N_2O_5SNa$ $[M + Na]^+$ 643.2242; found 643.2242.

Compound 17: Compound **13** (0.22 g, 0.338 mmol) was converted to **17** (0.14 g, 73%) by following the procedure described for the preparation of **6**. Colorless oil, $[\alpha]_D^{27}$ = –0.86 (*c* = 0.40, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 3.15 (dd, *J* = 7.2, 11.6 Hz, 1 H), 3.24 (t, *J* = 6.0 Hz, 1 H), 3.32 (dd, *J* = 8.4, 11.2 Hz, 1 H), 3.46 (dd, *J* = 5.2, 10.0 Hz, 1 H), 3.55 (dd, *J* = 3.6, 10.0 Hz, 1 H), 3.72–3.77 (m, 1 H), 3.86 (q, *J* = 4.8, 10.8 Hz, 1 H), 4.24 (d, *J* = 11.6 Hz, 1 H), 4.36–4.39 (m, 2 H), 4.44–4.53 (m, 3 H), 4.68 (d, *J* = 11.2 Hz, 1 H), 7.19–7.36 (m, 17 H), 7.74 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 46.5 (CH_2), 63.9, 70.2, 70.3 (CH_2), 71.2 (CH_2), 73.0 (CH_2), 73.3 (CH_2), 77.9, 79.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4 (2 × C), 130.0, 135.3, 137.1, 138.1, 138.6, 145.0 ppm. HRMS (ES^+): calcd. for $C_{34}H_{38}NO_5S$ $[M + H]^+$ 572.2471; found 572.2438.

Compound 18: *Method A*: Compound **13** (0.25 g, 0.38 mmol) was converted to **18** (0.191 g, 85%) by following the procedure described for the preparation of **7**. White oil, $[\alpha]_D^{27}$ = +86.7 (*c* = 0.40, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.45 (s, 3 H), 2.59–2.64 (m, 1 H), 2.76 (t, *J* = 5.6 Hz, 1 H), 3.27 (t, *J* = 8.8 Hz, 1 H), 3.60–3.70 (m, 2 H), 3.80–3.85 (m, 1 H), 3.88–3.91 (m, 1 H), 4.28 (d, *J* = 11.6 Hz, 1 H), 4.39 (d, *J* = 12.0 Hz, 1 H), 4.43–4.48 (m, 3 H), 4.56 (d, *J* = 11.2 Hz, 1 H), 4.73 (d, *J* = 11.6 Hz, 1 H), 7.19–7.21 (m, 2 H), 7.28–7.38 (m, 15 H), 7.76 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 42.3, 55.5 (CH_2), 67.9, 69.2, 70.3 (CH_2), 71.5 (CH_2), 72.5 (CH_2), 73.2 (CH_2), 78.8, 79.4, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.2 (2 × C), 128.3, 128.4, 129.9, 135.4, 137.1, 138.3, 138.5, 144.9 ppm. HRMS (ES^+): calcd. for $C_{35}H_{40}NO_5S$ $[M + H]^+$ 586.2624; found 586.2656. *Method B*: Compound **17** (0.040 g, 0.069 mmol) was converted to **18** (0.023 g, 57%) by following the procedure described for the preparation of **7** (*Method B*).

Compound 19: *Method A*: Compound **13** (0.225 g, 0.34 mmol) was converted to **19** (0.174 g, 76%) by following the procedure described for the preparation of **8**. Semisolid, $[\alpha]_D^{24}$ = –41.6 (*c* = 0.09, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.72 (dd, *J* = 4.0, 7.2 Hz, 1 H), 3.17–3.27 (m, 2 H), 3.49 (d, *J* = 13.2 Hz, 1 H), 3.64–3.74 (m, 2 H), 3.80–3.85 (m, 1 H), 3.89–3.93 (m, 1 H), 4.0 (d, *J* = 13.2 Hz, 1 H), 4.33–4.39 (m, 4 H), 4.50–4.53 (m, 2 H), 4.69 (d, *J* = 11.2 Hz, 1 H), 7.09–7.11 (m, 2 H), 7.20–7.32 (m, 20 H), 7.37 (d, *J* = 4.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 51.9 (CH_2), 60.1 (CH_2), 67.2, 68.9, 70.7 (CH_2), 72.4 (CH_2), 73.0 (CH_2), 73.2 (CH_2), 78.6, 79.5, 127.0, 127.4, 127.6 (2 × C),127.7, 127.8 (2 × C), 127.9, 128.0 (2 × C), 128.1 (2 × C), 128.2 (2 × C), 128.3 (2 × C), 128.5 (2 × C), 128.6, 128.8, 129.8, 135.7, 137.4, 138.3, 138.7, 138.8, 144.7 ppm. HRMS (ES^+): calcd. for $C_{41}H_{44}NO_5S$ $[M + H]^+$ 662.2940; found 662.2934. *Method B*: Compound **17** (0.03 g, 0.047 mmol) was converted to **19** (0.018 g, 51%) by following the procedure described for the preparation of **8** (*Method B*).

Compound 20: Compound **13** (0.20 g, 0.308 mmol) was converted to **20** (0.168 g, 83%) by following the procedure described for the preparation of **9**. Colorless oil, $[\alpha]_D^{27}$ = –4.2 (*c* = 0.53, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.86 (dd, *J* = 7.6, 11.2 Hz, 1 H), 3.29–3.37 (m, 2 H), 3.61–3.68 (m, 2 H), 3.76 (d, *J* = 14.4 Hz, 1 H), 3.87–3.95 (m, 2 H), 4.16 (d, *J* = 14.4 Hz, 1 H), 4.36–4.43 (m, 4 H), 4.48–4.55 (m, 2 H), 4.69 (d, *J* = 11.2 Hz, 1 H), 7.10–7.15 (m, 3 H), 7.24–7.33 (m, 16 H), 7.55–7.60 (m, 1 H), 7.69

(d, J = 8.0 Hz, 2 H), 8.49 (d, J = 4.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 52.2 (CH_2), 61.3 (CH_2), 66.8, 68.7, 70.5 (CH_2), 72.3 (CH_2), 72.9 (CH_2), 73.2 (CH_2), 78.4, 79.3, 121.9, 122.8, 127.4, 127.5, 127.6 (2 × C), 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 129.8, 135.6, 136.4, 137.3, 138.2, 138.6, 144.7, 148.9, 158.9 ppm. HRMS (ES^+): calcd. for $C_{40}H_{43}N_2O_5S$ [M + H]$^+$ 663.2893; found 663.2880.

Compound 21: Compound **13** (0.15 g, 0.23 mmol) was converted to **21** (0.084 g, 62%) by following the procedure described for the preparation of **12**. White liquid, $[\alpha]_D^{24}$ = –46.7 (c = 0.09, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.32–3.41 (m, 3 H), 3.58 (dd, J = 3.6, 10.4 Hz, 1 H), 3.76–3.80 (m, 1 H), 3.86–3.87 (m, 1 H), 4.23–4.32 (m, 3 H), 4.43–4.49 (m, 2 H), 4.64–4.69 (m, 3 H), 7.13–7.15 (m, 2 H), 7.26–7.39 (m, 15 H), 7.66 (m, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 49.6 (CH_2), 62.9, 64.6, 68.5 (CH_2), 71.9 (CH_2), 73.2 (CH_2), 73.3 (CH_2), 73.9, 74.0, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 128.6, 128.7, 130.4, 133.5, 135.9, 137.6, 137.7, 146.1 ppm. HRMS (ES^+): calcd. for $C_{34}H_{36}O_7S_2Na$ [M + Na]$^+$ 643.1800; found 643.1804.

Compound 22: To a well-stirred solution of compound **2** (0.08 g, 0.141 mmol) in MeOH (15 mL) was added Na_2HPO_4 (0.12 g, 0.846 mmol). After 15–20 min Na(Hg) (0.05 g) was added and stirred at room temperature under N_2. After 5–6 h, the reaction mixture was filtered through Celite, and the solids were washed with EtOAc. The clear filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford **22** (0.023 g, 54%). White liquid, $[\alpha]_D^{27}$ = +265.7 (c = 0.08, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82 (d, J = 17.2 Hz, 1 H), 3.28–3.33 (m, 1 H), 3.44–3.46 (m, 2 H), 3.58 (s, 3 H), 3.74 (s, 3 H), 3.85 (br. s, 1 H), 4.43 (s, 2 H), 5.61–5.63 (m, 1 H), 5.70–5.72 (m, 1 H), 7.24–7.34 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.4 (CH_2), 51.4, 52.4, 53.9, 61.2, 69.3 (CH_2), 73.1 (CH_2), 127.5, 127.6, 128.3, 129.0, 130.1, 138.1, 170.8, 172.7 ppm. HRMS (ES^+): calcd. for $C_{17}H_{20}O_5Na$ [M + Na]$^+$ 327.1204; found 327.1208.

Compound 23: To a well-stirred solution of compound **6** (0.20 g, 0.44 mmol) in DCM was added Boc-anhydride (0.4 mL) and a catalytic amount of DMAP (0.03 g), and the mixture was stirred at room temperature under N_2. After 5 h, DCM was concentrated to dryness under reduced pressure. The residue was purified over silica gel to afford the Boc-protected derivative (0.207 g, 85%). The Boc-protected compound was desulfonylated (yield 52%) by following the procedure described for the preparation of **22**. After desulfonylation, the Boc-protected compound (0.08 g, 0.201 mmol) was treated with 50% TFA in DCM under N_2. After 2 h, the reaction mixture was poured into a saturated aq. $NaHCO_3$ solution, and the product was extracted with DCM (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford compound **23** (0.064 g, 95%). Colorless oil, $[\alpha]_D^{27}$ = +47.4 (c = 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91–1.96 (m, 2 H), 2.86–2.92 (m, 1 H), 3.13–3.20 (m, 1 H), 3.25 (q, J = 5.2, 12.0 Hz, 1 H), 3.64–3.68 (m, 1 H), 3.77 (dd, J = 5.6, 9.6 Hz, 1 H), 4.05–4.08 (m, 1 H), 4.41 (d, J = 12.4 Hz, 1 H), 4.53–4.59 (m, 3 H), 7.26–7.34 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.5 (CH_2), 44.0 (CH_2), 62.3, 69.2 (CH_2), 71.0 (CH_2), 73.4 (CH_2), 79.1, 127.3, 127.4, 127.5, 127.7, 128.2, 128.3, 138.3, 138.5 ppm. HRMS (ES^+): calcd. for $C_{19}H_{24}NO_2$ [M + H]$^+$ 298.1809; found 298.1797.

Compound 24: Compound **8** (0.10 g, 0.185 mmol) was converted to **24** (0.04 g, 77%) by following the procedure described for the preparation of **22**. White oil, $[\alpha]_D^{24}$ = +6.6 (c = 0.13, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.21–3.30 (m, 1 H), 3.40–3.56 (m, 2 H), 3.62–3.74 (m, 2 H), 3.85 (q, J = 9.4, 21.3 Hz, 1 H), 4.14 (d, J = 26.6 Hz, 1 H), 4.54 (s, 2 H), 5.79–5.83 (m, 2 H), 7.20–7.32 (m, 10 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 59.7 (CH_2), 60.5 (CH_2), 70.3, 73.4 (CH_2), 74.4 (CH_2), 126.8, 127.5, 127.6, 128.0, 128.2, 128.3, 128.6, 129.4, 138.5, 140.1 ppm. HRMS (ES^+): calcd. for $C_{19}H_{22}NO$ [M + H]$^+$ 280.1701; found 280.1693.

Compound 25: Compound **11** (0.12 g, 0.265 mmol) was converted to **25** (0.03 g, 55%) by following the procedure described for the preparation of **22**. White oil, $[\alpha]_D^{27}$ = +129.2 (c = 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (d, J = 4.8 Hz, 2 H), 4.55–4.75 (m, 4 H), 5.0 (br. s, 1 H), 5.80–5.81 (m, 1 H), 5.98 (d, J = 6.0 Hz, 1 H), 7.26–7.35 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.7 (CH_2), 73.3 (CH_2), 75.4 (CH_2), 85.4, 126.9, 127.5, 127.6, 128.0, 128.3, 138.2 ppm. HRMS (ES^+): calcd. for $C_{12}H_{14}O_2Na$ [M + Na]$^+$ 213.0892; found 213.0892.

Compound 26: Compound **14** (0.05 g, 0.073 mmol) was converted to **26** (0.017 g, 56%) by following the procedure described for the preparation of **22**. Colorless liquid, $[\alpha]_D^{27}$ = +52.2 (c = 0.07, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.91 (d, J = 17.2 Hz, 1 H), 3.23–3.28 (m, 1 H), 3.36 (s, 3 H), 3.48–3.53 (m, 1 H), 3.60–3.62 (m, 2 H), 3.72 (s, 3 H), 4.03 (d, J = 7.2 Hz, 1 H), 4.42 (d, J = 12.0 Hz, 1 H), 4.47 (d, J = 12.0 Hz, 1 H), 4.55 (d, J = 12.0 Hz, 1 H), 4.64 (d, J = 12.0 Hz, 1 H), 5.61 (br. s, 1 H), 5.69–5.70 (m, 1 H), 7.22–7.35 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.4 (CH_2), 52.2, 52.8, 53.4, 61.8, 70.1 (CH_2), 70.9 (CH_2), 73.2 (CH_2), 77.7, 127.1, 127.2, 127.5, 127.6, 128.1, 128.3, 129.2, 130.0, 138.2, 138.7, 171.0, 172.8 ppm. HRMS (ES^+): calcd. for $C_{25}H_{28}O_6Na$ [M + Na]$^+$ 447.1783; found 447.1784.

Compound 27: Compound **18** (0.10 g, 0.17 mmol) was converted to **27** (0.05 g, 80%) by following the procedure described for the preparation of **22**. White oil, $[\alpha]_D^{27}$ = +58.3 (c = 0.09, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.21 (d, J = 13.2 Hz, 1 H), 3.51–3.56 (m, 1 H), 3.62 (br. s, 2 H), 3.72–3.75 (m, 1 H), 3.84 (d, J = 13.6 Hz, 1 H), 4.49–4.57 (m, 2 H), 4.68–4.71 (m, 1 H), 4.77–4.80 (m, 1 H), 5.68–5.69 (m, 1 H), 5.75 (br. s, 1 H), 7.16–7.39 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.7, 62.8 (CH_2), 71.6 (CH_2), 72.5 (CH_2), 73.3 (CH_2), 73.9, 81.0, 127.3, 127.4, 127.5, 127.7, 128.2 (3 × C), 138.5, 139.0 ppm. HRMS (ES^+): calcd. for $C_{21}H_{26}NO_2$ [M + H]$^+$ 324.1953; found 324.1958.

Compound 28: To a well-stirred solution of compound **12** (0.11 g, 0.22 mmol) in DCM (20 mL) was added DBU (0.15 mL, 1.10 mmol). The solution was stirred at room temperature under N_2. After 3–4 h, the reaction mixture was poured into a saturated aq. solution of $NaHCO_3$, and the product was extracted with DCM (3 × 20 mL). The combined organic layer was dried with anhyd. Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford the **28** (.061 g, 82%). White oil, $[\alpha]_D^{24}$ = +87.0 (c = 0.43, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (q, J = 6.8, 13.2 Hz, 1 H), 3.95–4.06 (m, 2 H), 4.56–4.60 (m, 2 H), 4.65–4.69 (m, 2 H), 4.74–4.77 (m, 1 H), 6.66–6.68 (m, 1 H), 6.72 (d, J = 6.8 Hz, 1 H), 7.26–7.37 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.6, 63.8 (CH_2), 73.0 (CH_2), 73.9 (CH_2), 74.7, 127.8, 127.9, 128.0, 128.4, 128.5, 128.7, 133.8, 137.0, 137.5, 137.8 ppm. HRMS (ES^+): calcd. for $C_{19}H_{20}O_4SNa$ [M + Na]$^+$ 367.0980; found 367.0977.

Compound 29: Compound **21** (0.12 g, 0.193 mmol) was converted to **29** (0.066 g, 73%) by following the procedure described for the preparation of **28**. Glassy liquid, $[\alpha]_D^{24}$ = +101.4 (c = 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61 (dd, J = 3.2, 10.8 Hz, 1 H), 3.71–3.76 (m, 2 H), 4.29–4.48 (m, 5 H), 4.61 (d, J = 12.0 Hz, 1 H), 4.68 (d, J = 10.8 Hz, 1 H), 4.82 (d, J = 10.8 Hz, 1 H), 6.62–6.65 (m, 1 H), 6.76 (d, J = 6.8 Hz, 1 H), 7.19–7.21 (m, 2 H), 7.25–7.38

(m, 11 H), 7.46 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.5, 68.2 (CH_2), 71.7 (CH_2), 73.2 (CH_2), 73.4 (CH_2), 73.8, 75.2, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 135.2, 135.8, 136.7, 137.9 ppm. HRMS (ES^+): calcd. for $C_{27}H_{28}O_5SNa$ $[M + Na]^+$ 487.1555; found 487.1521.

CCDC-735067, -735068, -735069 (for compounds **3**, **8** and **16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): General experimental methods, ^{1}H and ^{13}C NMR spectra for the new compounds, and NOESY-COSY data for **14** and **19**.

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