Synthesis A. Sokolov et al. Paper

Diastereoselective Synthesis of Cyclic sp³-Enriched *cis*-β-Alkoxysulfonyl Chlorides

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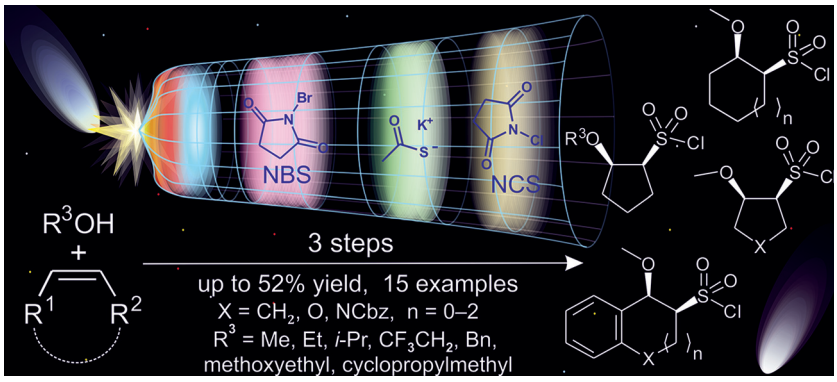

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Abstract A three-step synthesis of β-alkoxy-substituted alicyclic sulfonyl chlorides from cyclic alkenes and alcohols is reported. The scope of the method was studied for a range of the substrates with various steric and electronic properties. The title compounds were obtained on a hundred-gram scale in up to 52% overall yield scale as single *cis*-diastereomers.

Key words organosulfur compounds, alicyclic compounds, heteroaliphatic compounds, sulfonyl chlorides, building blocks

Since the nobel-prize-winning discovery of sulfonamidochrysoidine (also known as prontosil or streptocide, Figure 1) in 1932,[1] dozens of new sulfonamide-based drugs were discovered and brought to the market. The great majority of the sulfonamide drugs developed since then is derived from aromatic frameworks. Their aliphatic counterparts are less common in medicinal chemistry; they are limited mainly by simplest derivatives (e.g., methyl-, isopropyl-, cyclopropyl-substituted, etc.).[2] Despite the high potential of the aliphatic sulfonamides for design of sp³-enriched lead-like compounds, this opportunity remains largely unrealized, mainly due to the lack of well-developed approaches to their synthesis. It should be noted that this situation seems to be changing in recent years since a number of papers on the synthesis of aliphatic sulfonamides[3–6] and their synthetic precursors – sulfonyl halides[7–13] – appeared over the last decade.

One of the most intriguing applications of sulfonamides in drug design is their use for isosteric replacement of carboxamides, carboxylic acids, phosphates, and some other

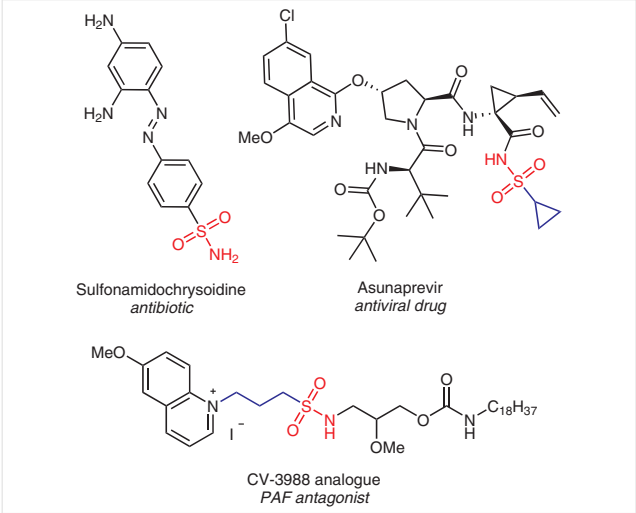
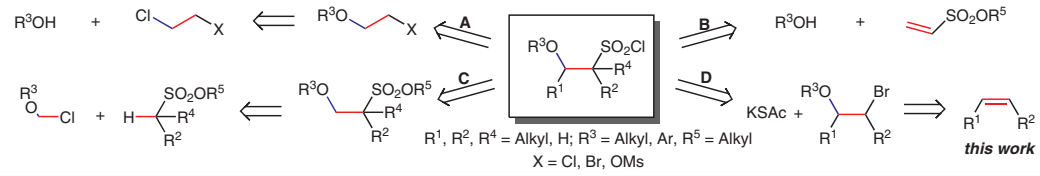


Figure 1 Some biologically active sulfonamides

related groups.[14,15] One notable example is the replacement of the carboxylic OH group by a cyclopropyl sulfonamide fragment in a HCV NS3 protease inhibitor, which has increased its potency and brought the resulting acylsulfonamide derivative, asunaprevir, to the Phase III clinical trials.[16,17] In another study, the sulfonamide functionality was used to replace the phosphate moiety in the molecule of a platelet activating factor (PAF) antagonist CV-3988;[18,19] the resulting analogue showed 50-fold increase in the potency as compared to the parent compound (Figure 1).

The aim of the current work is the development of a simple and robust method for the synthesis of β-alkoxysulfonyl chlorides. These compounds are low-molecular

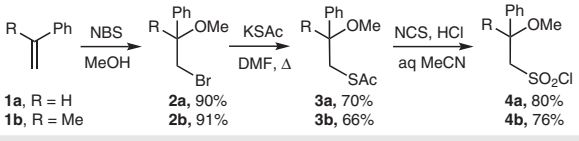


Scheme 1 Retrosynthetic disconnections of β-alkoxysulfonyl chlorides

weight, sp^3-enriched, relatively hydrophilic, conformationally restricted building blocks, which are fully compatible with the criteria of lead-oriented synthesis[20] and hence represent considerable interest for early drug discovery.

To date, only a few approaches to the preparation of β-alkoxysulfonyl chlorides were reported in the literature. One of them involves the reaction of *S*-nucleophiles and β-alkoxyalkyl halides or sulfonates, in turn prepared from 1,2-diols, β-halohydrines or 1,2-dihaloalkanes (Scheme 1, **A**).[21–25] Another approach is based on the Michael addition of alcohols to vinyl sulfonic acid derivatives (Scheme 1, **B**).[26,27] One more retrosynthetic disconnection relies on the alkylation of α-deprotonated sulfonic esters with α-chloroethers (Scheme 1, **C**).[28] All these methods have limited substrate scope (in most cases, only the parent β-alkoxyethanesufonyl chlorides were described); moreover, none of them was designed to solve the diastereoselectivity problem for α,β-disubstituted target compounds.

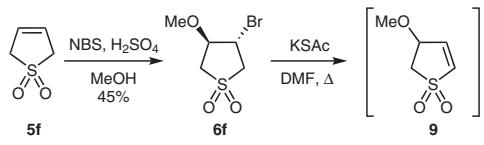
In this work, we have designed an alternative three-step reaction sequence including alkoxybromination of an appropriate alkene, nucleophilic substitution of the bromine atom by thioacetate anion, and subsequent oxidation of the thioester moiety with *N*-chlorosuccinimide (NCS) (Scheme 1, **D**). First of all, efficiency of this approach was validated for styrene (**1a**) and α-methylstyrene (**1b**). It was found that all three steps worked well for these substrates under typical conditions, and novel sulfonyl chlorides **4a** and **4b** were obtained in 50% and 45% yield, respectively (Scheme 2).



Scheme 2 Synthesis of sulfonyl chlorides **4a** and **4b**

To establish the scope of the developed method, it was applied to cyclic alkenes **5a–j** with varied steric and electronic properties (Table 1). It was found that the ring size had little impact on the outcome of the procedure, and the target compounds **8a–c** were synthesized from cycloalkenes **5a–c** in 45–50% overall yield. On the contrary, the presence of heteroatoms at the β-position to the double bond had more pronounced impact on the method efficiency. In the case of Cbz-protected pyrrolidine **5d**, the yield was slightly diminished at the third step of the reaction sequence, that is, oxidative chlorination of **7d** (67% vs 90–93% for **7a–c**), so that the product **8d** was obtained in 34% overall yield. Tetrahydrofuran derivative **5e**, which is less nucleophilic due to electron-withdrawing effect of the oxygen atom, demonstrated lowered reactivity in the methoxybromination step (55% yield of **6e**). Formation of 3,4-dibromotetrahydrofuran side product was observed by ^{1}H NMR and LC-MS of the crude reaction mixture, presumably due to NBS decomposition. Thus, the overall yield of the target product **8e** was also diminished (28%) (Table 1).

3-Sulfolene (**5f**) was even less reactive in the first step under the standard conditions (NBS, MeOH, r.t.); increasing the reaction temperature led to the formation of 3,4-dibromosulfolane as the main product according to ^{1}H NMR and LC-MS. To overcome this problem, a modified protocol was used involving the use of a catalytic amount of sulfuric acid at 0 °C to activate the bromination agent.[29] In this case, the product **6f** was obtained in 45% yield. Unfortunately, the second step (i.e., reaction of **6f** with potassium thioacetate) appeared to be unfruitful; the elimination product **9** was formed instead of **7f** according to ^{1}H NMR and LC-MS of the crude reaction mixture (Scheme 3). This result might be explained by increased acidity of the CH_2 groups in the molecule of **6f**, as well as conjugation of the double bond with the sulfone moiety in the product **9**.

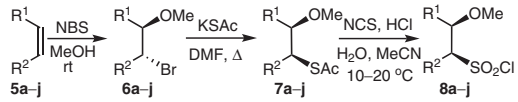


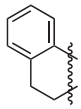
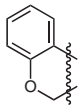
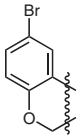
Scheme 3 Attempted preparation of **7f**

Further extension of the substrate scope included fused benzo derivatives **5g–j**, which were either commercially available (i.e., **5g**) or prepared using a slightly modified literature method[30] (i.e., **5h–j**). In particular, ketones **10h–j** were reduced with sodium borohydride to give alcohols **11h–j** (65–84% yield), which were subjected to the thermal dehydratation catalyzed with *p*-toluenesulfonic acid leading to the target substrates **5h–j** (58–91% yield) (Scheme 4).

The general method for the preparation of β-alkoxysulfonyl chlorides described in this work gave satisfactory results with indene (**5g**) and 1,2-dihydronaphthalene (**5h**); the corresponding products **8g** and **8h** were prepared in

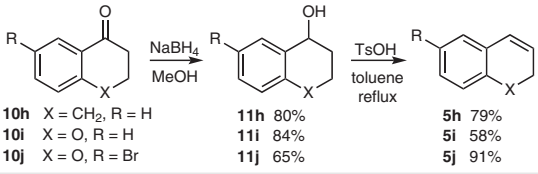
Table 1 Synthesis of Sulfonyl Chlorides **8a–j**[a]



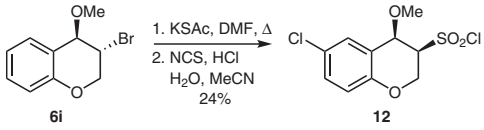
R^1/R^2	5	6 Yield (%)	7 Yield (%); conditions	8 Yield (%)
	**5a**	**6a** (75)	**7a** (71); 50 °C, 2 d	**8a** (92)
	**5b**	**6b** (72)	**7b** (70); 50 °C, 2 d	**8b** (90)
	**5c**	**6c** (67)	**7c** (81); 40 °C, 1 d	**8c** (93)
	**5d**	**6d** (73)	**7d** (70); 70 °C, 1 d	**8d** (67)
	**5e**	**6e** (55)	**7e** (79); 40 °C, 2 d	**8e** (65)
	**5f**	**6f** (45)	**7f** (0)	–
	**5g**	**6g** (73)	**7g** (64); 70 °C, 2 d	**8g** (88)
	**5h**	**6h** (88)	**7h** (59); 80 °C, 1 d	**8h** (74)
	**5i**	**6i** (71)	**7i**;[b] 110 °C, 3 d	**8i** (0)
	**5j**	**6j** (82)	**7j**;[b] 110 °C, 2 d	**8j** (47)[c]

[a] Relative configurations are shown.
[b] The product was used in the next step without purification.
[c] Yield for the two steps.

41% and 38% overall yield, respectively. In the case of 2*H*-chromene (**5i**), the second step of the standard reaction sequence (i.e., heating of bromide **6i** with potassium thioacetate in DMF) was accompanied by partial deacetylation of the thioester **7i**. Therefore, the crude product after this step was subjected directly to the oxidative chlorination; unexpectedly, sulfonyl chloride **12** was isolated in 24% yield (for two steps) instead of the target product **8i** (Scheme 5). This result might be explained by electron-donating effect of the tetrahydropyran ring in the molecule of **7i**, which increased susceptibility of the benzene ring towards electrophilic attack.



Scheme 4 Synthesis of alkenes **5h–j**



Scheme 5 Synthesis of sulfonyl chloride **12**

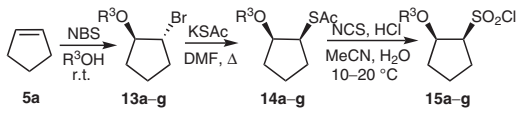
To overcome the above-mentioned effect, 6-bromo derivative **5j** was introduced into the corresponding reaction sequence. As in the case of **7i**, formation of **7j** was also accompanied by partial S-deacetylation; therefore, the crude product after the second step was used in the next step without purification. Its oxidative chlorination proceeded smoothly and gave the expected sulfonyl chloride **8j** in 47% yield (for two steps). The overall yield of **8j** (39%) is comparable to that of **8g** and **8h** (41% and 38%, respectively).

Finally, we have studied the scope of alkoxy substituents compatible with the developed synthetic approach. It was found that the yield of the alkoxybromination step decreased in the following series: methoxy (**6a**, 75%); ethoxy (**13a**, 69%); isopropoxy (**13b**, 43%); *tert*-butoxy (**13c**, traces) (Table 2). This result is consistent with the decrease of alcohol nucleophilicity in the above-mentioned series due to increasing steric hindrance. In the case of other primary alcohols, the effect of the substituent on the yield of the products **13d–g** (60–74%) was not significant. Other steps in the reaction sequence also were not susceptible to the variation of the alkoxy substituent.

Since all the three steps in the reaction sequence studied in this work should be diastereoselective, the target compounds **8a–j** and **15a–g** were expected to be obtained as single *cis*-diastereomers. Indeed, the relative *cis*-configuration was confirmed by NOE experiments with the products **8a**, **8b**, and **8d** (Figure 2).

In conclusion, β-alkoxy-substituted alicyclic sulfonyl chlorides can be obtained starting from cyclic alkenes in three steps, including alkoxybromination, nucleophilic substitution with thioacetate, and oxidative chlorination with NCS. The developed protocol allows preparation of the tar-

Table 2 Synthesis of Sulfonyl Chlorides **15a–g**[a]



R^3	**13** Yield (%)	**14** Yield (%); conditions	**15** Yield (%)
Et	**13a** (69)	**14a** (70); 50 °C, 2 d	**15a** (88)
i-Pr	**13b** (43)	**14b** (66); 50 °C, 2 d	**15b** (88)
t-Bu	**13c** (traces)	–	–
CF_3CH_2	**13d** (74)	**14d** (77); 40 °C, 1 d	**15d** (93)
Bn	**13e** (62)	**14e** (66); 50 °C, 2 d	**15e** (71)
methoxyethyl	**13f** (65)	**14f** (70); 60 °C, 2 d	**15f** (86)
cyclopropylmethyl	**13g** (60)	**14g** (61); 60 °C, 2 d	**15g** (77)

[a] Relative configurations are shown.

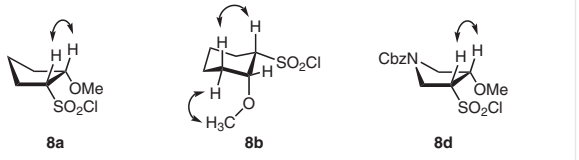


Figure 2 Significant NOE correlations observed for **8a**, **8b**, and **8d**

get compounds as pure *cis*-diastereomers in up to 52% overall yield and on a 100 g scale. The scope of the method includes cycloalkanes with different ring size, as well as heteroaliphatic compounds and benzo-fused derivatives. The limitations of the approach are related to: (i) steric hindrance in the starting alcohol used for the alkoxybromination step (e.g., from the *tert*-butyl substituent); (ii) the presence of strong electron-withdrawing groups (e.g., SO_2) at the β-position of the starting cyclic alkene; and (iii) side reactions at the benzene ring observed for electron-rich benzo-fused substrates. In all other cases, the target compounds of this study were prepared with high efficiency and can be now considered as readily available for early drug discovery programs.

The solvents were purified according to the standard procedures.[31] All starting materials were purchased from commercial sources. Melting points were measured on MPA100 OptiMelt automated melting point system. Analytical TLC was performed using Polychrom SI F254 plates. Column chromatography was performed using silica gel Merck 60 (230–400 mesh) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 170 Avance 500 spectrometer (at 499.9 MHz for ^{1}H and 124.9 MHz for ^{13}C) and Varian Unity Plus 400 spectrometer (at 400.4 MHz for ^{1}H and 100.7 MHz for ^{13}C). Chemical shifts are reported in ppm downfield from TMS as an internal standard. Elemental analyses were performed at the Laboratory of Organic Analysis, Department of Chemistry, National Taras Shevchenko University of Kyiv. Mass spectra were recorded on an Agilent 1100 LCMSD SL instrument [chemical ionization (APCI), electrospray ionization (ESI)] and Agilent 5890 Series II 5972 GCMS instrument (electron impact ionization (EI)).

β-Methoxybromides 2a, 2b, 6a–e, and 6g–j; General Procedure

To a solution of alkene **5** (1 mol) in anhyd MeOH (1 L) was added NBS (187 g, 1.05 mol) portionwise while maintaining the temperature below 30 °C. After the addition of all the NBS, the reaction mixture was stirred at r.t. overnight. The resulting mixture was evaporated under reduced pressure; H_2O (1 L) was added, and the mixture was extracted with CH_2Cl_2 (3 × 300 mL). The combined organic phases were washed with H_2O (2 × 300 mL), 10% aq $NaHSO_3$ (2 × 300 mL), H_2O (2 × 300 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

(2-Bromo-1-methoxyethyl)benzene (2a)

Yield: 279 g (90%) from 150 g of **1a**; yellowish liquid.

For spectral and physical data, see refs.[32,33]

(1-Bromo-2-methoxypropan-2-yl)benzene (2b)

Yield: 529 g (91%) from 300 g of **1b**; yellowish liquid.

For spectral and physical data, see refs.[32,33]

trans-1-Bromo-2-methoxycyclopentane (6a)[34,35]

The product was purified by vacuum distillation; bp 80 °C/6 mmHg; yield: 380.5 g (75%) from 193 g of **5a**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24 (dt, *J* = 6.1, 2.8 Hz, 1 H), 3.96 (dt, *J* = 6.1, 2.8 Hz, 1 H), 3.35 (s, 3 H), 2.35–2.20 (m, 1 H), 2.21–2.07 (m, 1 H), 2.06–1.94 (m, 1 H), 1.92–1.70 (m, 2 H), 1.74–1.56 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 89.8, 57.3, 53.9, 34.9, 29.9, 21.9.

MS (EI): *m*/*z* = 178/180 $[M]^+$.

Anal. Calcd for $C_6H_{11}BrO$: C, 40.25; H, 6.19; Br, 44.62. Found: C, 40.14; H, 5.79; Br, 44.28.

trans-1-Bromo-2-methoxycyclohexane(6b)[32]

The product was purified by vacuum distillation; bp 96 °C/6 mmHg; yield: 254 g (72%) from 150 g of **5b**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01–3.91 (m, 1 H), 3.42 (s, 3 H), 3.27–3.17 (m, 1 H), 2.35–2.24 (m, 1 H), 2.22–2.11 (m, 1 H), 1.91–1.57 (m, 3 H), 1.40–1.21 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 83.2, 57.2, 55.4, 35.6, 30.1, 25.5, 23.3.

MS (EI): *m*/*z* = 192/194 $[M]^+$, 113 $[M - Br]^+$, 81 $[M - Br - MeOH]^+$.

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.79; Br, 41.38. Found: C, 43.34; H, 6.49; Br, 41.58.

trans-1-Bromo-2-methoxycycloheptane (6c)

The product was purified by vacuum distillation; bp 37 °C/0.1 mmHg; yield: 29 g (67%) from 20 g of **5c**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (td, *J* = 7.7, 3.6 Hz, 1 H), 3.53 (td, *J* = 7.7, 2.8 Hz, 1 H), 3.39 (s, 3 H), 2.24–2.12 (m, 1 H), 2.10–1.97 (m, 1 H), 1.93–1.81 (m, 1 H), 1.79–1.66 (m, 3 H), 1.60–1.38 (m, 4 H).

MS (EI): *m*/*z* = 206 $[M]^+$, 127 $[M - Br]^+$, 95 $[M - Br - MeOH]^+$.

Anal. Calcd for $C_8H_{15}BrO$: C, 46.39; H, 7.30; Br, 38.58. Found: C, 46.30; H, 7.46; Br, 38.95.

For additional spectral and physical data, see ref.[32]

Benzyl *trans*-3-Bromo-4-methoxypyrrolidine-1-carboxylate (6d)

The product was purified by column chromatography (gradient hexane to *t*-BuOMe); yield: 275 g (73%) from 244 g of **5d**; yellowish oil. The compound was obtained as a ca. 1:1 mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5 H), 5.19–5.13 (m, 2 H), 4.33–4.28 (m, 1 H), 4.06–3.97 (m, 2 H), 3.95–3.81 (m, 2 H), 3.63–3.51 (m, 1 H), 3.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.0, 136.7, 128.6, 128.2, 128.0, 86.0 and 85.1, 67.2, 57.41 and 57.40, 53.4 and 53.2, 49.4 and 49.3, 47.6 and 46.8.

MS (EI): *m*/*z* = 313/315 $[M]^+$, 234 $[M - Br]^+$.

Anal. Calcd for $C_{13}H_{16}BrNO_3$: C, 49.70; H, 5.13; N, 4.46; Br, 25.43. Found: C, 49.43; H, 5.02; N, 4.73; Br, 25.38.

***trans*-3-Bromo-4-methoxytetrahydrofuran (6e)**

The product was purified by column chromatography (hexane–EtOAc 5:1, R_f = 0.3); yield: 287 g (55%) from 202 g of **5e**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31–4.22 (m, 2 H), 4.19 (dd, *J* = 9.9, 4.8 Hz, 1 H), 4.15–4.09 (m, 1 H), 4.06–3.97 (m, 1 H), 3.80 (dd, *J* = 9.9, 1.8 Hz, 1 H), 3.39 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 88.2, 74.6, 71.7, 57.5, 48.6.

MS (EI): *m*/*z* = 182 $[M]^+$, 71 $[M - Br - MeO]^+$.

Anal. Calcd for $C_5H_9BrO_2$: C, 33.17; H, 5.01; Br, 44.14. Found: C, 32.77; H, 5.37; Br, 44.48.

***trans*-2-Bromo-1-methoxy-2,3-dihydro-1*H*-indene (6g)**

The product was purified by vacuum distillation; bp 82 °C/0.1 mmHg; yield: 143 g (73%) from 100 g of **5g**; colorless liquid.

For spectral and physical data, see ref.[36]

***trans*-2-Bromo-1-methoxy-1,2,3,4-tetrahydronaphthalene (6h)**

Yield: 163 g (88%) from 100 g of **5h**; yellowish liquid.

For spectral and physical data, see ref.[36]

***trans*-3-Bromo-4-methoxychroman (6i)**

The product was purified by vacuum distillation; bp 92 °C/0.1 mmHg; yield: 144 g (71%) from 110 g of **5i**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.22 (m, 2 H), 7.02–6.89 (m, 2 H), 4.56–4.47 (m, 1 H), 4.47–4.36 (m, 2 H), 4.36–4.27 (m, 1 H), 3.52 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.4, 131.1, 130.4, 121.1, 118.7, 117.1, 77.5, 65.7, 57.1, 43.8.

MS (EI): *m*/*z* = 242/244 $[M]^+$, 163 $[M - Br]^+$, 131 $[M - HBr - MeO]^+$.

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56; Br, 32.87. Found: C, 49.38; H, 4.49; Br, 32.57.

***trans*-3,6-Dibromo-4-methoxychroman (6j)**

Yield: 12.5 g (82%) from 10 g of **6j**; light yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 2 H), 6.82 (d, *J* = 8.6 Hz, 1 H), 4.49 (d, *J* = 12.2 Hz, 1 H), 4.39–4.33 (m, 1 H), 4.33–4.24 (m, 2 H), 3.53 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.4, 133.5, 133.3, 120.7, 119.0, 112.9, 77.0, 65.7, 57.3, 42.9.

MS (EI): *m*/*z* = 320/322/324 $[M]^+$, 241/243 $[M - Br]^+$, 161 $[M - Br - HBr]^+$.

Anal. Calcd for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.13; Br, 49.63. Found: C, 37.18; H, 2.80; Br, 49.28.

***trans*-3-Bromo-4-methoxytetrahydrothiophene 1,1-Dioxide (6f)**

To a solution of 2,5-dihydrothiophene 1,1-dioxide (**5f**; 100 g, 0.846 mol) in anhyd MeOH (850 mL) was added NCS (113 g, 0.846 mol). The solution was cooled to 0 °C, and a catalytic amount of H_2SO_4 was added dropwise at the same temperature, and the reaction mixture was stirred at 0 °C for 2 h. Then it was allowed to warm up to r.t. and stirred overnight. The resulting mixture was evaporated under reduced pressure, H_2O (500 mL) was added, and the precipitate formed was filtered. The crude product was dissolved in $CHCl_3$ (1 L), washed with 10% aq $NaHSO_3$ (2 × 300 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure; yield: 87.3 g (45%); white crystals; mp 93–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.58–4.50 (m, 1 H), 4.33–4.26 (m, 1 H), 3.79 (dd, *J* = 14.2, 6.7 Hz, 1 H), 3.64 (dd, *J* = 13.8, 5.7 Hz, 1 H), 3.49–3.38 (m, 4 H), 3.23 (dd, *J* = 13.8, 3.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 82.9, 58.23, 58.18, 54.4, 42.7.

MS (APCI): *m*/*z* = 229/231 $[M]^+$.

Anal. Calcd for $C_5H_9BrO_3S$: C, 26.21; H, 3.96; S, 13.99; Br, 34.88. Found: C, 25.96; H, 3.87; S, 14.28; Br, 35.18.

β-Alkoxy Bromides 13a and 13b; General Procedure

To a solution of cyclopentene (**5a**; 50.0 g, 0.734 mol) in the corresponding anhyd alcohol (700 mL), was added NBS (103 g, 0.771 mol) portionwise while maintaining the temperature below 30 °C. After the addition of all the NBS, the reaction mixture was stirred overnight at r.t. The resulting mixture was evaporated under reduced pressure, H_2O (700 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic phases were washed with H_2O (2 × 200 mL), 10% aq $NaHSO_3$ (2 × 200 mL), H_2O (2 × 300 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

***trans*-1-Bromo-2-ethoxycyclopentane (13a)**

The product was purified by vacuum distillation; bp 38 °C/1 mmHg; yield: 97.8 g (69%) from 50 g of **5a**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27–4.19 (m, 1 H), 4.10–4.02 (m, 1 H), 3.63–3.43 (m, 2 H), 2.36–2.22 (m, 1 H), 2.21–2.07 (m, 1 H), 2.06–1.93 (m, 1 H), 1.92–1.70 (m, 2 H), 1.68–1.56 (m, 1 H), 1.18 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 88.0, 65.1, 54.7, 35.0, 30.3, 22.0, 15.6.

MS (EI): *m*/*z* = 192/194 $[M]^+$, 67 $[M - HBr - MeCH_2O]^+$.

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.79; Br, 41.38. Found: C, 43.65; H, 6.70; Br, 41.29.

***trans*-1-Bromo-2-isopropoxycyclopentane (13b)**

The product was purified by column chromatography (gradient hexane to *t*-BuOMe); yield: 65.4 g (43%) from 50 g of **5a**; colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.19–4.16 (m, 1 H), 4.14–4.10 (m, 1 H), 3.69 (sept, *J* = 6.1 Hz, 1 H), 2.34–2.25 (m, 1 H), 2.20–2.08 (m, 1 H), 2.06–1.94 (m, 1 H), 1.90–1.73 (m, 2 H), 1.63–1.55 (m, 1 H), 1.17–1.11 (m, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 85.6, 70.7, 55.7, 34.8, 30.8, 23.2, 22.4, 22.0.

MS (EI): *m*/*z* = 206/208 $[M]^+$, 127 $[M - Br]^+$, 67 $[M - HBr - Me_2CHO]^+$.

Anal. Calcd for $C_8H_{15}BrO$: C, 46.39; H, 7.30; Br, 38.58. Found: C, 46.22; H, 7.57; Br, 38.21.

β-Alkoxy Bromides 13d–g; General Procedure

The corresponding alcohol (0.440 mol) was added to a solution of cyclopentene (**5a**; 10.0 g, 0.147 mol) in anhyd $CHCl_3$ (150 mL), and NBS (20.6 g, 0.154 mol) was added portionwise while maintaining the temperature below 30 °C. After the addition of all the NBS, the reaction mixture was stirred overnight at r.t. The resulting mixture was washed with H_2O (2 × 30 mL), 10% aq $NaHSO_3$ (2 × 30 mL), H_2O (2 × 30 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure. The obtained mixture was dissolved in hexane (100 mL), the hexane layer was washed with H_2O (5 × 30 mL), dried (anhyd Na_2SO_4), and concentrated under vacuum.

trans-1-Bromo-2-(2,2,2-trifluoroethoxy)cyclopentane (13d)

The crude product was dissolved in hexane (100 mL), washed with H_2O (5 × 30 mL), dried (anhyd Na_2SO_4), and concentrated under vacuum. The product was purified by vacuum distillation; bp 41 °C/1 mmHg; yield: 26.8 g (74%) from 10.0 g of **5a**; colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.25–4.16 (m, 2 H), 3.96–3.80 (m, 2 H), 2.40–2.27 (m, 1 H), 2.25–2.14 (m, 1 H), 2.07–1.97 (m, 1 H), 1.94–1.76 (m, 2 H), 1.78–1.68 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 123.9 (q, *J* = 279.0 Hz), 90.0, 67.3 (q, *J* = 34.2 Hz), 53.3, 34.7, 29.9, 21.7.

MS (EI): *m*/*z* = 246/248 $[M]^+$, 67 $[M – HBr – CF_3CH_2O]^+$.

Anal. Calcd for $C_7H_{10}BrF_3O$: C, 34.03; H, 4.08; Br, 32.34. Found: C, 34.26; H, 4.42; Br, 32.69.

trans-{[(2-Bromocyclopentyl)oxy]methyl}benzene (13e)

Anhyd hexane (50 mL) was added to the obtained crude product. The bottom layer containing most of benzyl alcohol was separated, and the remaining hexane solution was concentrated under vacuum. The product was purified by vacuum distillation (bp 80–85 °C/0.1 mmHg) and subsequent column chromatography (gradient hexane to *t*-BuOMe as eluent); yield: 23.2 g (62%) from 10 g of **5a**.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 5 H), 4.60 (d, *J* = 11.8 Hz, 1 H), 4.55 (d, *J* = 11.8 Hz, 1 H), 4.34–4.31 (m, 1 H), 4.21–4.18 (m, 1 H), 2.40–2.31 (m, 1 H), 2.22–2.13 (m, 1 H), 2.08–1.98 (m, 1 H), 1.94–1.79 (m, 2 H), 1.78–1.68 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.3, 128.6, 127.8, 127.7, 87.7, 71.7, 54.5, 35.0, 30.2, 22.0.

MS (EI): *m*/*z* = 254 $[M]^+$, 175 $[M – Br]^+$.

Anal. Calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93; Br, 31.32. Found: C, 56.61; H, 6.25; Br, 31.36.

trans-1-Bromo-2-(2-methoxyethoxy)cyclopentane (13f)

The product was purified by vacuum distillation; bp 60 °C/1 mmHg; yield: 21.3 g (65%) from 10 g of **5a**.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28–4.23 (m, 1 H), 4.11–4.06 (m, 1 H), 3.69–3.57 (m, 2 H), 3.51 (t, *J* = 4.7 Hz, 2 H), 3.37 (s, 3 H), 2.34–2.23 (m, 1 H), 2.19–2.09 (m, 1 H), 2.02–1.94 (m, 1 H), 1.88–1.73 (m, 2 H), 1.71–1.61 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 88.7, 72.0, 69.0, 59.1, 54.3, 34.9, 30.1, 21.9.

MS (EI): *m*/*z* = 207 $[M – Me]^+$, 191 $[M – OMe]^+$, 163 $[M – MeOCH_2CH_2]^+$, 147/149 $[M – MeOCH_2CH_2O]^+$.

Anal. Calcd for $C_8H_{15}BrO_2$: C 43.07; H 6.78; Br 35.81. Found: C 43.37; H 6.88; Br 35.85.

trans-1-Bromo-2-(cyclopropylmethoxy)cyclopentane (13g)

The product was purified by vacuum distillation; bp 65 °C/1 mmHg; yield: 19.3 g (60%) from 10 g of **5a**; colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.28–4.24 (m, 1 H), 4.12–4.08 (m, 1 H), 3.37–3.29 (m, 2 H), 2.36–2.25 (m, 1 H), 2.22–2.11 (m, 1 H), 2.06–1.96 (m, 1 H), 1.90–1.74 (m, 2 H), 1.70–1.62 (m, 1 H), 1.10–0.98 (m, 1 H), 0.60–0.49 (m, 2 H), 0.27–0.16 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 87.9, 74.6, 54.7, 35.0, 30.3, 22.0, 11.0, 3.3, 3.2.

MS (EI): *m*/*z* = 220 $[M]^+$, 147/148 $[M – (CH_2)_2CHCH_2O]^+$.

Anal. Calcd for $C_9H_{15}BrO$: C, 49.33; H, 6.90; Br, 36.47. Found: C, 49.67; H, 7.04; Br, 36.24.

Ethanethioates 3a,b, 7a–e, 7g,h, 14a,b, and 14d–g; General Procedure

KSAc (143 g, 1.25 mol) was added portionwise to a solution of the corresponding alkoxy bromide (0.500 mol) in anhyd DMF (1 L), and the reaction mixture was stirred at the temperature given below for the preparation of each ethanethioate derivative until 100% conversion of the starting material was observed. The resulting mixture was cooled to r.t., poured into ice-cold H_2O (2.5 L), and extracted with EtOAc (3 × 1 L). The combined organic extracts were washed with H_2O (5 × 1 L), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

S-(2-Methoxy-2-phenylethyl) Ethanethioate (3a)

The reaction mixture was stirred overnight at 70 °C. The product was purified by vacuum distillation; bp 96 °C/0.1 mmHg; yield: 103 g (70%) from 150 g of **2a**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.23 (m, 5 H), 4.21 (dd, *J* = 8.6, 4.4 Hz, 1 H), 3.30–3.19 (m, 4 H), 3.07 (dd, *J* = 13.8, 8.6 Hz, 1 H), 2.32 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 195.6, 140.3, 128.7, 128.3, 126.7, 82.6, 57.2, 36.5, 30.7.

MS (EI): *m*/*z* = 121 $[PhCHOMe]^+$.

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.74; H, 6.75; S, 15.32.

S-(2-Methoxy-2-phenylpropyl) Ethanethioate (3b)

The reaction mixture was stirred overnight at 100 °C. The product was purified by vacuum distillation; bp 107 °C/0.1 mmHg; yield: 110 g (66%) from 170 g of **2b**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.32 (m, 4 H), 7.33–7.24 (m, 1 H), 3.41 (d, *J* = 13.5 Hz, 1 H), 3.28 (d, *J* = 13.5 Hz, 1 H), 3.10 (s, 3 H), 2.31 (s, 3 H), 1.58 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 195.3, 143.5, 128.4, 127.6, 126.3, 78.5, 50.9, 41.1, 30.6, 22.4.

MS (EI): *m*/*z* (%) = 135 $[PhC(Me)OMe]^+$.

Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.37; H, 7.09; S, 14.06.

***cis*-*S*-(2-Methoxycyclopentyl) Ethanethioate (7a)**

The reaction mixture was stirred for 2 days at 50 °C. The product was purified by vacuum distillation; bp 61 °C/0.1 mmHg; yield: 69.1 g (71%) from 100 g of **6a**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84–3.74 (m, 2 H), 3.30 (s, 3 H), 2.33 (s, 3 H), 2.17–2.00 (m, 1 H), 1.91–1.53 (m, 5 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.6, 83.2, 57.1, 47.1, 30.8, 30.7, 29.7, 21.5.

MS (EI): *m*/*z* = 174 $[M]^+$, 131 $[M - MeCO]^+$, 98 $[M - MeCOSH]^+$.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.24; H, 7.97; S, 18.61.

***cis*-*S*-(2-Methoxycyclohexyl) Ethanethioate (7b)**

The reaction mixture was stirred for 2 days at 50 °C. The product was purified by vacuum distillation; bp 73 °C/0.1 mmHg; yield: 68.3 g (70%) from 100 g of **6b**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92–3.83 (m, 1 H), 3.43–3.35 (m, 1 H), 3.31 (s, 3 H), 2.32 (s, 3 H), 1.89–1.63 (m, 3 H), 1.62–1.52 (m, 3 H), 1.51–1.28 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.0, 78.8, 56.5, 46.2, 31.0, 29.5, 28.9, 24.5, 21.2.

MS (EI): *m*/*z* = 188 $[M]^+$, 145 $[M - MeO]^+$, 112 $[M - MeCOSH]^+$, 81 $[M - MeCOSH - MeO]^+$.

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57; S, 17.03. Found: C, 57.34; H, 8.68; S, 17.42.

***cis*-*S*-(2-Methoxycycloheptyl) Ethanethioate (7c)**

The reaction mixture was stirred overnight at 40 °C. The product was purified by vacuum distillation; bp 97 °C/0.1 mmHg; yield: 15.8 g (81%) from 20.0 g of **6c**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (dt, *J* = 9.6, 3.0 Hz, 1 H), 3.49 (td, *J* = 5.6, 2.9 Hz, 1 H), 3.32 (s, 3 H), 2.32 (s, 3 H), 1.98–1.84 (m, 1 H), 1.82–1.36 (m, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.1, 82.5, 57.0, 48.6, 31.0, 30.8, 30.4, 27.0, 25.9, 21.8.

MS (EI): *m*/*z* = 202 $[M]^+$, 159 $[M - MeO]^+$, 126 $[M - MeCOSH]^+$, 95 $[M - MeCOSH - MeO]^+$.

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.37; H, 8.97; S, 15.85. Found: C, 59.69; H, 8.64; S, 15.57.

Benzyl *cis*-3-(Acetylthio)-4-methoxypyrrolidine-1-carboxylate (7d)

The reaction mixture was stirred overnight at 70 °C. The product was purified by column chromatography (gradient hexane to *t*-BuOMe as eluent); yield: 186 g (70%) from 270 g of **6d**; yellowish oil.The product was obtained as a ca. 2:3 mixture of rotamers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 5 H), 5.20–5.06 (m, 2 H), 4.10–4.01 (m, 1 H), 3.94–3.81 (m, 2 H), 3.72 (d, *J* = 11.7 Hz, 0.6 H), 3.60 (d, *J* = 11.8 Hz, 0.4 H) 3.55–3.45 (m, 1 H), 3.49–3.28 (m, 4 H), 2.38–2.32 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.3 and 195.1, 154.8 and 154.6, 136.7 and 136.6, 128.6, 128.1, 128.0, 80.5 and 79.9, 67.12 and 67.08, 57.6 and 57.4, 49.73 and 49.68, 49.5 and 49.4, 44.9 and 44.3, 30.7 and 30.6.

MS (APCI): *m*/*z* = 267 $[M - MeCO + H]^+$.

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.36. Found: C, 58.06; H, 6.41; N, 4.48; S, 10.73.

***cis*-*S*-(4-Methoxytetrahydrofuran-3-yl) Ethanethioate (7e)**

The reaction mixture was stirred for 2 days at 40 °C. The product was purified by vacuum distillation; bp 73 °C/0.1 mmHg; yield: 76.9 g (79%) obtained from 100 g of **6e**; yellowish liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.21–4.12 (m, 1 H), 4.09–4.01 (m, 1 H), 4.00–3.85 (m, 3 H), 3.70–3.61 (m, 1 H), 3.35 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 195.7, 81.0, 71.7, 71.6, 57.9, 45.5, 30.7.

MS (EI): *m*/*z* = 176 $[M]^+$, 133 $[M - MeO]^+$.

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.71; H, 6.86; S, 18.19. Found: C, 47.38; H, 7.21; S, 17.98.

***cis*-*S*-(1-Methoxy-2,3-dihydro-1*H*-inden-2-yl) Ethanethioate (7g)**

The reaction mixture was stirred for 2 days at 70 °C. The product was purified by vacuum distillation; bp 120 °C/0.1 mmHg; yield: 35.7 g (64%) from 57 g of **6g**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.3 Hz, 1 H), 7.32–7.17 (m, 3 H), 4.67 (d, *J* = 5.5 Hz, 1 H), 4.38 (td, *J* = 7.5, 5.5 Hz, 1 H), 3.36 (s, 3 H), 3.26 (dd, *J* = 15.8, 7.5 Hz, 1 H), 3.06 (dd, *J* = 15.8, 7.5 Hz, 1 H), 2.35 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.4, 142.1, 140.9, 129.1, 126.7, 125.2, 125.0, 84.0, 56.9, 47.7, 38.0, 30.8.

MS (EI): *m*/*z* = 146 $[M - MeCOSH]^+$, 115 $[M - MeCOSH - MeO]^+$.

Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42. Found: C, 64.5; H, 6.30; S, 14.37.

***cis*-*S*-(1-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl) Ethanethioate (7h)**

The reaction mixture was stirred overnight at 80 °C. The product was purified by vacuum distillation; bp 125 °C/0.1 mmHg; yield: 11.6 g (59%) from 20 g of **6h**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–6.81 (m, 4 H), 4.23 (d, *J* = 3.3 Hz, 1 H), 4.10–4.00 (m, 1 H), 3.37 (s, 3 H), 3.07–2.73 (m, 2 H), 2.49–2.10 (m, 4 H), 2.02–1.93 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 195.9, 135.7, 134.8, 129.2, 129.1, 128.3, 125.5, 79.0, 57.2, 44.3, 30.8, 28.0, 24.9.

MS (EI): *m*/*z* = 193 $[M - MeCO]^+$, 160 $[M - MeCOSH]^+$, 128 $[M - MeCOSH - MeOH]^+$.

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 65.95; H, 6.96; S, 13.66.

***cis*-*S*-(2-Ethoxycyclopentyl) Ethanethioate (14a)**

The reaction mixture was stirred for 2 days at 50 °C. The product was purified by vacuum distillation; bp 70 °C/0.1 mmHg; yield: 61.4 g (70%) from 90.0 g of **13a**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78–3.73 (m, 1 H), 3.72–3.65 (m, 1 H), 3.46–3.24 (m, 2 H), 2.21 (s, 3 H), 2.04–1.92 (m, 1 H), 1.76–1.47 (m, 5 H), 1.05 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.3, 81.1, 64.8, 47.2, 30.7, 30.5, 30.4, 21.3, 15.2.

MS (EI): *m*/*z* = 188 $[M]^+$, 145 $[M - MeCO]^+$, 112 $[M - MeCOSH]^+$.

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57; S, 17.03. Found: C, 57.65; H, 8.67; S, 16.66.

***cis*-*S*-(2-Isopropoxycyclopentyl) Ethanethioate (14b)**

The reaction mixture was stirred for 2 days at 50 °C. The product was purified by vacuum distillation; bp 79 °C/0.1 mmHg; yield: 48.4 g (66%) from 75.0 g of **13b**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91–3.83 (m, 1 H), 3.74–3.61 (m, 1 H), 3.51 (sept, *J* = 6.1 Hz, 1 H), 2.24 (s, 3 H), 2.06–1.93 (m, 1 H), 1.83–1.59 (m, 4 H), 1.58–1.44 (m, 1 H), 1.08–1.00 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.7, 78.9, 70.6, 47.5, 31.8, 30.8, 30.6, 22.7, 22.2, 21.5.

MS (EI): *m*/*z* = 202 $[M]^+$, 159 $[M - MeCO]^+$, 126 $[M - MeCOSH]^+$, 67 $[M - MeCOSH - Me_2CHO]^+$.

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.37; H, 8.97; S, 15.85. Found: C, 58.97; H, 8.69; S, 15.70.

***cis*-*S*-[2-(2,2,2-Trifluoroethoxy)cyclopentyl] Ethanethioate (14d)**

The reaction mixture was stirred overnight at 40 °C; yield: 3.78 g (77%) from 5 g of **13d**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07–3.99 (m, 1 H), 3.91–3.71 (m, 3 H), 2.34 (s, 3 H), 2.14–2.02 (m, 1 H), 1.97–1.48 (m, 5 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.5, 123.9 (q, *J* = 279.4 Hz), 84.0, 67.4 (q, *J* = 34.1 Hz), 47.0, 30.7, 30.6, 30.0, 21.4.

MS (EI): *m*/*z* = 199 $[M - MeCO]^+$, 166 $[M - MeCOSH]^+$.

Anal. Calcd for $C_9H_{13}F_3O_2S$: C, 44.62; H, 5.41; S, 13.23. Found: C, 44.56; H, 5.24; S, 13.54.

***cis*-*S*-[2-(Benzyloxy)cyclopentyl] Ethanethioate (14e)**

The reaction mixture was stirred for 2 days at 50 °C. The product was purified by vacuum distillation; bp 135 °C/0.1 mmHg; yield: 6.48 g (66%) from 10.0 g of **13e**; yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 5 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.40 (d, *J* = 12.0 Hz, 1 H), 4.01–3.97 (m, 1 H), 3.85–3.80 (m, 1 H), 2.26 (s, 3 H), 2.16–2.06 (m, 1 H), 1.92–1.73 (m, 4 H), 1.71–1.59 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.6, 138.6, 128.4, 127.52, 127.50, 81.0, 71.2, 47.4, 30.9, 30.8, 30.4, 21.5.

MS (EI): *m*/*z* = 250 $[M]^+$, 207 $[M - MeCHO]^+$, 174 $[M - MeCOSH]^+$, 67 $[M - MeCOSH - PhCH_2OH]^+$.

Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; S, 12.81. Found: C, 67.55; H, 7.47; S, 13.11.

***cis*-*S*-[2-(2-Methoxyethoxy)cyclopentyl] Ethanethioate (14f)**

The reaction mixture was stirred for 2 days at 60 °C. The product was purified by vacuum distillation; bp 96 °C/0.1 mmHg; yield: 13.7 g (70%) from 20.0 g of **13f**; yellowish liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.95–3.88 (m, 1 H), 3.79 (td, *J* = 8.1, 4.9 Hz, 1 H), 3.64–3.46 (m, 4 H), 3.37 (s, 3 H), 2.31 (s, 3 H), 2.13–2.02 (m, 1 H), 1.89–1.78 (m, 3 H), 1.78–1.70 (m, 1 H), 1.67–1.56 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.6, 82.1, 72.0, 69.1, 59.2, 47.3, 30.8, 30.7, 30.5, 21.4.

MS (EI): *m*/*z* = 175 $[M - MeCO]^+$, 142 $[M - MeCOSH]^+$.

Anal. Calcd for $C_{10}H_{18}O_3S$: C, 55.02; H, 8.31; S, 14.69. Found: C, 54.65; H, 7.97; S, 14.38.

***cis*-*S*-[2-(Cyclopropylmethoxy)cyclopentyl] Ethanethioate (14g)**

The reaction mixture was stirred for 2 days at 60 °C. The product was purified by vacuum distillation; bp 99 °C/0.1 mmHg; yield: 8.94 g (61%) from 15.0 g of **13g**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93–3.84 (m, 1 H), 3.84–3.73 (m, 1 H), 3.33–3.16 (m, 2 H), 2.33 (s, 3 H), 2.12–2.00 (m, 1 H), 1.85–1.66 (m, 4 H), 1.63–1.54 (m, 1 H), 1.05–0.94 (m, 1 H), 0.53–0.42 (m, 2 H), 0.24–0.13 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8, 81.1, 74.3, 47.5, 31.0, 30.8, 30.7, 21.5, 10.8, 3.1, 3.0.

MS (EI): *m*/*z* = 171 $[M - MeCO]^+$, 138 $[M - MeCOSH]^+$.

Anal. Calcd for $C_{11}H_{18}O_2S$: C, 61.65; H, 8.47; S, 14.96. Found: C, 61.46; H, 8.31; S, 14.71.

Sulfonyl Chlorides 8a–e, 8g, 8h, 15a, 15b, and 15d–g; General Procedure

To a mixture of NCS (267 g, 2 mol), concd HCl (28 mL), H_2O (100 mL), and MeCN (1 L) was added a solution of the corresponding ethanethioates **3**, **7**, or **14** (0.500 mol) in MeCN (600 mL) dropwise at 10 °C. When the addition was finished and no more exothermic reaction was observed, the solution was stirred at 10–20 °C for an additional 40 min. The reaction mixture was poured into H_2O (2 L) and extracted with *t*-BuOMe (3 × 1 L). The combined organic phases were washed with brine (5 × 1 L), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

2-Methoxy-2-phenylethanesulfonyl Chloride (4a)

Yield: 107 g (80%) from 120 g of **3a**; yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.33 (m, 5 H), 4.91 (dd, *J* = 9.5, 2.9 Hz, 1 H), 4.19 (dd, *J* = 14.3, 9.5 Hz, 1 H), 3.87 (dd, *J* = 14.3, 2.9 Hz, 1 H), 3.32 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.3, 129.4, 126.7, 78.5, 72.3, 57.3.

MS (APCI): *m*/*z* = 215 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.06; H, 4.72; S, 13.66; Cl, 15.11. Found: C, 45.75; H, 4.39; S, 13.52; Cl, 15.40.

2-Methoxy-2-phenylpropane-1-sulfonyl Chloride (4b)

Yield: 85.1 g (76%) from 101 g of **3b**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.30 (m, 5 H), 4.26 (d, *J* = 14.0 Hz, 1 H), 4.04 (d, *J* = 14.0 Hz, 1 H), 3.16 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.0, 129.1, 128.7, 126.3, 78.5, 77.8, 51.0, 21.5.

MS (APCI): *m*/*z* = 229 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{10}H_{13}ClO_3S$: C, 48.29; H, 5.27; S, 12.89; Cl, 14.25. Found: C, 48.36; H, 5.49; S, 13.04; Cl, 14.05.

***cis*-2-Methoxycyclopentane-1-sulfonyl Chloride (8a)**

Yield: 84.9 g (92%) from 81 g of **7a**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.25–4.12 (m, 2 H), 3.38 (s, 3 H), 2.59–2.45 (m, 1 H), 2.33–2.23 (m, 1 H), 2.14–1.96 (m, 2 H), 1.86–1.66 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 82.8, 79.5, 57.8, 30.5, 26.8, 21.2.

MS (APCI): *m*/*z* = 179 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_6H_{11}ClO_3S$: C, 36.28; H, 5.58; S, 16.14; Cl, 17.84. Found: C, 36.56; H, 5.71; S, 16.22; Cl, 17.65.

***cis*-2-Methoxycyclohexane-1-sulfonyl Chloride (8b)**

Yield: 102 g (90%) from 100 g of **7b**; yellowish liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.11–4.05 (m, 1 H), 3.73–3.64 (m, 1 H), 3.26 (s, 3 H), 2.20–2.04 (m, 3 H), 1.94–1.83 (m, 1 H), 1.58–1.37 (m, 2 H), 1.37–1.16 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 79.6, 73.9, 56.3, 27.4, 24.4, 22.5, 18.4.

MS (APCI): *m*/*z* = 193 $[M–H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_7H_{13}ClO_3S$: C, 39.53; H, 6.16; S, 15.07; Cl, 16.67. Found: C, 39.67; H, 5.93; S, 14.81; Cl, 16.51.

***cis*-2-Methoxycycloheptane-1-sulfonyl Chloride (8c)**

Yield: 14.6 g (93%) from 14 g of **7c**; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.37–4.30 (m, 1 H), 3.69–3.58 (m, 1 H), 3.37 (s, 3 H), 2.39–2.23 (m, 2 H), 2.18–2.05 (m, 1 H), 2.00–1.87 (m, 1 H), 1.79–1.64 (m, 2 H), 1.64–1.41 (m, 4 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 82.1, 76.4, 57.1, 30.2, 26.8, 25.4, 23.5, 21.1.

MS (EI): *m*/*z* = 127 $[M – SO_2Cl]^+$, 95 $[M – SO_2Cl – MeOH]^+$.

Anal. Calcd for $C_8H_{15}ClO_3S$: C, 42.38; H, 6.67; S, 14.14; Cl, 15.64. Found: C, 41.98; H, 6.35; S, 14.18; Cl, 15.48.

***cis*-Benzyl 3-(Chlorosulfonyl)-4-methoxypyrrolidine-1-carboxylate (8d)**

Yield: 62.2 g (67%) from 86 g of **7d**; brown oil. The product was obtained as a ca. 45:55 mixture of rotamers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 4 H), 5.19–5.08 (m, 2 H), 4.44–4.33 (m, 2 H), 4.29–3.98 (m, 2 H), 3.89–3.81 (m, 0.55 H), 3.78–3.70 (m, 0.45 H), 3.65–3.57 (m, 0.45 H), 3.57–3.49 (m, 0.55 H), 3.45 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.5, 136.24 and 136.16, 128.7, 128.45 and 128.41, 128.31 and 128.20, 80.1 and 79.1, 75.8 and 74.9, 67.7 and 67.6, 58.5 and 58.2, 50.1 and 49.7, 46.4 and 45.6.

MS (APCI): *m*/*z* = 314 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{13}H_{16}ClNO_5S$: C, 46.78; H, 4.83; N, 4.20; S, 9.61; Cl, 10.62. Found: C, 47.03; H, 5.09; N, 4.04; S, 9.36; Cl, 10.81.

***cis*-4-Methoxytetrahydrofuran-3-sulfonyl Chloride (8e)**

The product was purified by vacuum distillation; bp 101 °C/0.1 mmHg; yield: 37.0 g (65%) obtained from 50 g of **7e**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.59–4.45 (m, 2 H), 4.42–4.33 (m, 1 H), 4.37–4.25 (m, 1 H), 4.01 (dd, *J* = 9.8, 4.0 Hz, 1 H), 3.94 (dd, *J* = 9.8 Hz, 4.7, 1 H), 3.48 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 81.3, 76.7, 72.0, 68.3, 59.3.

MS (APCI): *m*/*z* = 181 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_5H_9ClO_4S$: C, 29.93; H, 4.52; S, 15.98; Cl, 17.67. Found: C, 29.69; H, 4.16; S, 16.29; Cl, 18.00.

***cis*-1-Methoxy-2,3-dihydro-1*H*-indene-2-sulfonyl Chloride (8g)**

Yield: 54.7 g (88%) from 56 g of **7g**; yellowish crystals; mp 63–65 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.27 (m, 4 H), 5.11 (d, *J* = 5.7 Hz, 1 H), 4.63 (td, *J* = 8.5, 5.7 Hz, 1 H), 3.91 (dd, *J* = 15.9, 8.5 Hz, 1 H), 3.52–3.41 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.3, 138.2, 130.3, 127.8, 125.5, 125.4, 83.4, 78.4, 57.6, 33.8.

MS (EI): *m*/*z* = 147 $[M – SO_2Cl]^+$, 115 $[M – SO_2Cl – MeOH]^+$.

Anal. Calcd for $C_{10}H_{11}ClO_3S$: C, 48.68; H, 4.49; S, 13.00; Cl, 14.37. Found: C, 48.81; H, 4.40; S, 13.29; Cl, 14.02.

***cis*-1-Methoxy-1,2,3,4-tetrahydronaphthalene-2-sulfonyl Chloride (8h)**

Yield: 8.16 g (74%) from 10 g of **7h**; yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.28 (m, 1 H), 7.29–7.13 (m, 3 H), 4.87 (d, *J* = 2.8 Hz, 1 H), 4.07–3.98 (m, 1 H), 3.39 (s, 3 H), 3.23 (ddd, *J* = 17.4, 7.0, 2.7 Hz, 1 H), 2.97 (ddd, *J* = 17.4, 10.9, 7.0 Hz, 1 H), 2.85–2.69 (m, 1 H), 2.56–2.45 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 135.5, 132.1, 130.1, 129.7, 129.5, 126.2, 77.9, 75.7, 56.9, 27.8, 19.5.

MS (APCI): *m*/*z* = 241 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{11}H_{13}ClO_3S$: C, 50.67; H, 5.03; S, 12.30; Cl, 13.60. Found: C, 50.82; H, 5.28; S, 12.02; Cl, 13.29.

***cis*-2-Ethoxycyclopentane-1-sulfonyl Chloride (15a)**

Yield: 32.8 g (88%) from 33 g of **14a**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.33–4.24 (m, 1 H), 4.24–4.12 (m, 1 H), 3.64–3.48 (m, 2 H), 2.62–2.46 (m, 1 H), 2.35–2.20 (m, 1 H), 2.13–1.93 (m, 2 H), 1.88–1.68 (m, 2 H), 1.18 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 81.1, 79.6, 66.2, 31.5, 27.0, 21.3, 15.1.

MS (APCI): *m*/*z* = 193 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_7H_{13}ClO_3S$: C, 39.53; H, 6.16; S, 15.07; Cl, 16.67. Found: C, 39.81; H, 5.76; S, 14.68; Cl, 17.07.

***cis*-2-Isopropoxycyclopentane-1-sulfonyl Chloride (15b)**

Yield: 44.4 g (88%) from 45 g of **14b**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.41–4.32 (m, 1 H), 4.20–4.09 (m, 1 H), 3.70 (sept, *J* = 6.3 Hz, 1 H), 2.59–2.44 (m, 1 H), 2.32–2.18 (m, 1 H), 2.12–1.98 (m, 1 H), 1.98–1.85 (m, 1 H), 1.86–1.60 (m, 2 H), 1.13 (t, *J* = 6.3 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.2, 78.8, 72.5, 32.9, 27.1, 22.6, 22.0, 21.5.

MS (APCI): *m*/*z* = 207 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_8H_{15}ClO_3S$: C, 42.38; H, 6.67; S, 14.14; Cl, 15.64. Found: C, 42.11; H, 6.44; S, 14.34; Cl, 15.84.

***cis*-2-(2,2,2-Trifluoroethoxy)cyclopentane-1-sulfonyl Chloride (15d)**

Yield: 4.09 g (93%) from 4 g of **14d**; yellowish liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.52–4.45 (m, 1 H), 4.19–4.09 (m, 1 H), 4.10–3.94 (m, 1 H), 3.94–3.81 (m, 1 H), 2.63–2.50 (m, 1 H), 2.40–2.28 (m, 1 H), 2.21–2.03 (m, 2 H), 1.97–1.85 (m, 1 H), 1.87–1.74 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 123.7 (q, *J* = 279.5 Hz), 83.5, 78.8, 68.3 (q, *J* = 34.6 Hz), 32.0, 26.6, 21.3.

MS (APCI): *m*/*z* = 247 $[M – H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_7H_{10}ClF_3O_3S$: C, 31.53; H, 3.78; S, 12.02; Cl, 13.29. Found: C, 31.26; H, 3.4; S, 11.76; Cl, 13.53.

***cis*-2-(Benzyloxy)cyclopentane-1-sulfonyl Chloride (15e)**

Yield: 3.89 g (71%) from 5 g of **14e**; yellowish crystals, mp 47–49 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.15 (m, 5 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.45–4.37 (m, 1 H), 4.19 (td, *J* = 8.8, 5.3 Hz, 1 H), 2.65–2.52 (m, 1 H), 2.37–2.25 (m, 1 H), 2.15–2.01 (m, 2 H), 1.83–1.66 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.4, 128.5, 127.9, 127.8, 80.5, 79.4, 72.2, 31.2, 27.0, 21.3.

MS (APCI): *m*/*z* = 255 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{12}H_{15}ClO_3S$: C, 52.46; H, 5.50; S, 11.67; Cl, 12.90. Found: C, 52.14; H, 5.55; S, 11.71; Cl, 12.85.

cis-2-(2-Methoxyethoxy)cyclopentane-1-sulfonyl Chloride (15f)

Yield: 10.5 g (86%) from 11 g of **14f**; yellowish liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.44–4.37 (m, 1 H), 4.22–4.13 (m, 1 H), 3.74–3.66 (m, 2 H), 3.61–3.50 (m, 2 H), 3.38 (s, 3 H), 2.62–2.53 (m, 1 H), 2.35–2.24 (m, 1 H), 2.16–2.01 (m, 2 H), 1.90–1.79 (m, 1 H), 1.79–1.69 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.0, 79.5, 72.1, 70.1, 59.3, 31.5, 27.0, 21.2.

MS (APCI): *m*/*z* = 223 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_8H_{15}ClO_4S$: C, 39.59; H, 6.23; S, 13.21; Cl, 14.61. Found: C, 39.74; H, 5.96; S, 13.18; Cl, 14.99.

cis-2-(cyclopropylmethoxy)cyclopentane-1-sulfonyl Chloride (15g)

Yield: 4.71 g (77%) from 5.5 g of **14g**; yellowish liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.36–4.28 (m, 1 H), 4.14 (td, *J* = 8.7, 5.5 Hz, 1 H), 3.45–3.29 (m, 2 H), 2.62–2.47 (m, 1 H), 2.33–2.19 (m, 1 H), 2.13–1.95 (m, 2 H), 1.85–1.64 (m, 2 H), 1.10–0.95 (m, 1 H), 0.53–0.45 (m, 2 H), 0.28–0.14 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 80.8, 79.7, 75.0, 31.6, 27.0, 21.4, 10.5, 3.2, 3.0.

MS (APCI): *m*/*z* = 219 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_9H_{15}ClO_3S$: C, 45.28; H, 6.33; S, 13.43; Cl, 14.85. Found: C, 45.11; H, 6.06; S, 13.64; Cl, 15.04.

Sulfonyl Chlorides 12 and 8j; General Procedure

KSAc (28.5 g, 0.250 mol) was added portionwise to a solution of **6i** or **j** (0.100 mol) in anhyd DMF (200 mL), and the reaction mixture was stirred at 110 °C for the time given below for the preparation of **12** and **8j**. The resulting mixture was cooled to r.t., poured into ice-cold H_2O (500 mL), and extracted with EtOAc (3 × 200 mL). The combined organic extracts were washed with H_2O (5 × 200 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure. The crude product was used in the next step without further purification. To a mixture of NCS (53.4 g, 0.400 mol), concd HCl (5.7 mL), H_2O (20 mL), and MeCN (200 mL) was added a solution of the crude product from the previous step in MeCN (120 mL) dropwise at 10 °C. When the addition was finished and no more exothermic reaction was observed, the solution was stirred at 10–20 °C for 40 min. The reaction mixture was poured into H_2O (400 mL) and extracted with *t*-BuOMe (3 × 200 mL). The combined organic phases were washed with brine (5 × 200 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

cis-6-Chloro-4-methoxychroman-3-sulfonyl Chloride (12)

The reaction mixture was stirred at 110 °C for 3 d. The product was purified by column chromatography (gradient $CHCl_3$ to *t*-BuOMe as eluent); yield: 8.8 g (24%) from 30 g of **6i**; yellowish oil;

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.21 (d, *J* = 2.6 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 1 H), 4.82–4.78 (m, 1 H), 4.79–4.67 (m, 2 H), 4.28–4.21 (m, 1 H), 3.50 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.9, 131.4, 130.0, 126.0, 119.6, 119.1, 73.1, 71.9, 60.1, 57.1.

MS (APCI): *m*/*z* = 277 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{10}H_{10}Cl_2O_4S$: C, 40.42; H, 3.39; S, 10.79; Cl, 23.86. Found: C, 40.56; H, 3.32; S, 11.19; Cl, 23.88.

Cis-6-Bromo-4-methoxychroman-3-sulfonyl Chloride (8j)

The reaction mixture was stirred at 110 °C for 2 d. The product was purified by column chromatography (gradient hexane to *t*-BuOMe as eluent); yield: 4.99 g (47%) from 10 g of **6j**; yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.33 (d, *J* = 2.7 Hz, 1 H), 6.83 (d, *J* = 8.8 Hz, 1 H), 4.86 – 4.61 (m, 3 H), 4.26–4.17 (m, 1 H), 3.49 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.5, 134.3, 132.9, 120.2, 119.5, 113.1, 73.1, 71.8, 60.1, 57.1.

MS (APCI): *m*/*z* = 321/323 $[M - H]^-$ (for the corresponding sulfonic acid).

Anal. Calcd for $C_{10}H_{10}BrClO_4S$: C, 35.16; H, 2.95; S, 9.39; Cl, 10.38; Br, 23.39. Found: C, 34.93; H, 3.03; S, 9.13; Cl, 10.03; Br, 23.17.

Compounds 11h–j; General Procedure

To a solution of ketone **10** (1.00 mol) in anhyd MeOH (2 L) was added $NaBH_4$ (75.7 g, 2.00 mol) portionwise at r.t. The reaction mixture was stirred overnight and evaporated under reduced pressure. The residue was dissolved in H_2O (1.5 L) and extracted with $CHCl_3$ (3 × 500 mL). The combined organic phases were washed with H_2O (3 × 500 mL), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

1,2,3,4-Tetrahydronaphthalen-1-ol (11h)

Yield: 36.5 g (80%) from 45.0 g of **10h**; colorless oil.

For spectral and physical data, see ref.[37]

Chroman-4-ol (11i)

Yield: 128 g (84%) from 150 g of **10i**; colorless oil.

For spectral and physical data, see ref.[38]

6-Bromochroman-4-ol (11j)

Yield: 5.04 g (65%) from 7.7 g of **10j**; yellowish crystals.

For spectral and physical data, see ref.[39]

Compounds 5h–j; General Procedure

p-TsOH·H_2O (0.25 mol) was added to a solution of alcohol **11** (0.1 mol) in anhyd toluene (4 L), and the solution was refluxed until the complete conversion of the starting material. Then, the reaction mixture was cooled to r.t., washed with H_2O (2 × 1 L), 10% aq $NaHCO_3$ (3 × 1 L), and H_2O (2 × 1 L), dried (anhyd Na_2SO_4), and evaporated under reduced pressure.

1,2-Dihydronaphthalene (5h)

Yield: 25.3 g (79%) from 36.5 g of **11h**; colorless oil.

For spectral and physical data, see refs.[40,41]

2*H*-Chromene (5i)

The product was purified by vacuum distillation; bp 45 °C/0.1 mmHg; yield: 41.3 g (58%) from 81 g of **11i**; colorless liquid.

For spectral and physical data, see ref.[41]

6-Bromo-2*H*-chromene (5j)

Yield: 11.7 g (91%) from 14.0 g of **11j**; yellowish oil.

For spectral and physical data, see ref.[42]

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611277.

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