Supporting information:

Preparation of (+)-2,5-dimethylthiolane 2 and (-)-2,5-dimethylsulfolane 3:

(+)-2,5-Dimethylthiolane 2: To a solution of (+)-(*2S, 5S*)-2,5-hexanediol (4.0 g, 33.6 mmol) in CH_2Cl_2 (60 mL) was added dried triethylamine (11.7 mL, 84.0 mmol). The solution was cooled to -15 ^{0}C, and methanesulfonyl chloride (5.8 mL, 75.6 mmol) was added dropwise with vigorous stirring over 90 min while the temperature was maintained between -20 and -15 ^{0}C. After the addition was complete, the mixture was allowed to warm to 0 ^{0}C and then poured into cold 1 N HCl (40 mL). The organic layer was separated, and aqueous layer extracted three times with CH_2Cl_2 (30 mL). The combined organic extracts were washed with $NaHCO_3$ (40 mL), dried with $MgSO_4$, filtered and concentrated. The resulting oil product, (*2S, 5S*)-2,5-hexanediol dimethansulfonate (9.05 g), was found to be homogeneous by TLC and ^{1}H NMR and was used without further purification(Zwaagstra, M. E.; Meetsma, A.; Feringa, B. L. *Tetrahedron: Asymmetry* **1993**, *4* , 2163).

A solution of sodium sulfide nonahydrate (12.5 g, 37.0 mmol) in ethanol (150 mL) was prepared. This solution (75mL) was then placed in a 500 mL three-necked flask equipped with two dropping funnels and a condenser. The solution was heated to reflux and the remaining solution and a solution of (*2S, 5S*)-2,5-hexanediol dimethansulfonate (9.05g) in 30 mL dimethylformamide (DMF) were simultaneously added from the two addition funnels over a period of 1.5 h. The mixture was heated and refluxed for 40 h. After cooling to room temperature, the mixture was diluted with cold water and extracted with three portions of methylene chloride. The combined organic layers were washed

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with 1 N HCl (50 mL) and five times with saturated brine (5X50 mL), dried over $MgSO_4$, and concentrated. The residue was distilled under vaccum to obtain (+)-2,5-dimethylthiolane **2** (1.76 g, 45% yield (Eliel, E. L.; Hutchins, R. O.; Mebane, R.; Willer, R. L. *J. Org. Chem.* **1976**, *41*, 1052), $[\alpha]_D^{20}$ + 139 (*c* 1.22, diethyl ether) [lit.[8] +169.6 (*c* 1.1, diethyl ether)]; GC-MS: M^+ 116; ^{1}H NMR ($CDCl_3$): δ 1.30 (d, *J*=6.7 Hz, 6H); 1.51-1.56 (m, 2H, CH_2); 2.17-2.22 (m, 2H, CH_2); 3.53-3.62 (m,2H,CH)).

(-)-2,5-Dimethylsulfolane 3: To a solution of *m*-chloroperbenzoic acid (1.04 g, 6.0 mmol) in dried methylene chloride (20 mL) was added **2** (0.31 g, 2.67 mmol) at 0 ^{0}C. After stirring for 48 h, the solid was filtered off and the organic layer washed twice with diluted $NaHCO_3$ and then with saturated brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography on silica, eluting with 1% to 5% ethyl acetate in hexane to afford **3** (0.37 g, 94% yield[8] as an oil, $[\alpha]_D^{20}$ -14.0 (*c*=1.05, diethyl ether) [lit.[8b] –13.6 (*c*=1.0, diethyl ether)]; GC-MS: M^+ 148; ^{1}H NMR($CDCl_3$): δ 1.37 (d, *J*=6.7 Hz, 6H); 1.50-1.70 (m, 2H, CH_2); 2.21-2.38 (m, 2H, CH_2); 2.91-3.05 (m, 2H, CH)).

Cartesian coordinates for the two conformations of (2R,5R)-2,5-dimethylthiolane 2 and (2R,5R)-2,5-dimethylsulfolane 3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
thiolane **2a**					
1	16	0	-0.000031	-1.188501	-0.000086
2	6	0	1.303577	0.071466	-0.419409
3	6	0	-1.303513	0.071495	0.419417
4	6	0	0.754812	1.398753	0.113626
5	6	0	-0.754786	1.398752	-0.113717
6	6	0	2.667172	-0.317659	0.135568
7	6	0	-2.667197	-0.317629	-0.135355
8	1	0	1.357108	0.114177	-1.507611
9	1	0	-1.356907	0.114258	1.507627
10	1	0	1.244881	2.242052	-0.377836

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11	1	0	0.970036	1.474558	1.182591
12	1	0	-1.244843	2.242083	0.377704
13	1	0	-0.970025	1.474485	-1.182683
14	1	0	3.000575	-1.277787	-0.257754
15	1	0	2.637060	-0.391091	1.222618
16	1	0	3.413868	0.430507	-0.141459
17	1	0	-3.000530	-1.277763	0.258011
18	1	0	-2.637251	-0.391049	-1.222410
19	1	0	-3.413854	0.430528	0.141797

thiolane **2b**

1	16	0	0.000015	-1.296166	0.000046
2	6	0	-1.254168	-0.042589	0.561286
3	6	0	1.254146	-0.042473	-0.561340
4	6	0	-0.493808	1.290822	0.585388
5	6	0	0.493747	1.290903	-0.585220
6	6	0	-2.491972	-0.034820	-0.332839
7	6	0	2.492027	-0.034834	0.332651
8	1	0	-1.543801	-0.329482	1.570910
9	1	0	1.543615	-0.329334	-1.571017
10	1	0	0.049166	1.384516	1.526860
11	1	0	-1.188418	2.131081	0.527848
12	1	0	-0.049225	1.384760	-1.526676
13	1	0	1.188346	2.131167	-0.527552
14	1	0	-3.239928	0.656430	0.064601
15	1	0	-2.943317	-1.024740	-0.385760
16	1	0	-2.247619	0.270317	-1.350112
17	1	0	2.943349	-1.024770	0.385441
18	1	0	2.247784	0.270230	1.349973
19	1	0	3.239974	0.656424	-0.064801

sulfolane **3a**

1	16	0	0.000009	-0.778802	0.000026
2	6	0	1.296544	0.452156	-0.474641
3	6	0	-1.296590	0.452132	0.474607
4	6	0	0.764774	1.776221	0.080035
5	6	0	-0.764801	1.776227	-0.079986
6	6	0	2.677131	0.032481	0.001257
7	6	0	-2.677131	0.032452	-0.001421
8	1	0	1.241568	0.453487	-1.563240
9	1	0	-1.241706	0.453428	1.563209
10	1	0	1.222474	2.619063	-0.437927
11	1	0	1.029402	1.863080	1.136504
12	1	0	-1.222502	2.619041	0.438023
13	1	0	-1.029422	1.863153	-1.136451
14	1	0	2.978191	-0.916888	-0.438964
15	1	0	2.698097	-0.076800	1.083909
16	1	0	3.410292	0.786806	-0.288618
17	1	0	-2.978214	-0.916938	0.438741
18	1	0	-2.698007	-0.076794	-1.084078
19	1	0	-3.410327	0.786756	0.288418
20	8	0	0.417836	-1.507844	1.189713
21	8	0	-0.417779	-1.507977	-1.189594

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sulfolane **3b**					
1	16	0	0.000000	0.000000	0.869561
2	6	0	-0.604614	1.253526	-0.358914
3	6	0	0.604614	-1.253526	-0.358914
4	6	0	0.000000	0.771010	-1.684514
5	6	0	0.000000	-0.771010	-1.684514
6	6	0	-2.124323	1.360067	-0.349456
7	6	0	2.124323	-1.360067	-0.349456
8	1	0	-0.149356	2.181442	-0.020568
9	1	0	0.149356	-2.181442	-0.020568
10	1	0	1.021257	1.140040	-1.783237
11	1	0	-0.566387	1.164218	-2.528648
12	1	0	-1.021257	-1.140040	-1.783237
13	1	0	0.566387	-1.164218	-2.528648
14	1	0	-2.497552	1.587622	0.646433
15	1	0	-2.433038	2.158797	-1.025726
16	1	0	-2.597564	0.434265	-0.672713
17	1	0	2.497552	-1.587622	0.646433
18	1	0	2.433038	-2.158797	-1.025726
19	1	0	2.597564	-0.434265	-0.672713
20	8	0	-1.126161	-0.566960	1.598161
21	8	0	1.126161	0.566960	1.598161