Supplementary Material

Convenient synthesis of 1,3-dithiolane-2-thiones: cyclic trithiocarbonates as conformational locks[1]

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SI-1. **X-Ray Crystallographic Data**

SI-2. **Selected ^{1}H NMR Data**

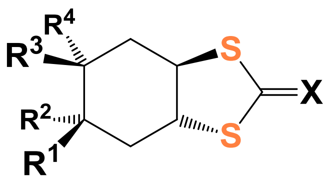
SI-1. X-Ray Crystallographic Data

Crystallographic Data for compounds **2f(*a*)**, **2f(*e*)**, **2h(*ee*)**, **3h** and **2i** were collected on Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab using monochromatic radiation (λ = 0.7749 Å) at 150(2) K. Data reduction and cell refinement for all compounds were performed with SAINT [1]. We used SADABS to obtain the absorption-corrected data [2]. Crystallographic data are given in Table S1. Selected bond distances, bond angles and torsion angles are given in Tables S2-S6. CCDC 972800 (**2f(*a*)**), 972796 (**2f(*e*)**), 972799 (**2h(*ee*)**), 972797 (**3h**) and 972798 (**2i**) 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.

[1] *SAINT Frame Integration Software*; Bruker AXS, Inc.: Madison, WI, 2008; v7.60a.

[2] *SADABS, Program for Absorption Correction of Area Detector Frames*; Bruker AXS, Inc.: Madison, WI, 2008.

Figure S1. Structural formulas for the compounds studied by X-ray crystallography.



2f(*a*)	R_1 = COOMe, $R_{2\text{-}4}$ = H, X = S
2f(*e*)	R_2 = COOMe, $R_{1,3,4}$ = H, X = S
2h(*ee*)	R_2 = R_3 = COOMe, $R_{1,4}$ = H, X = S
3h	R_2 = R_3 = COOMe, $R_{1,4}$ = H, X = O
2i	R_1 + R_3 = CONHCO, $R_{2,4}$ = H, X = S

Table S1. Crystallographic Data[a]

	2f(*a*)	**2f(*e*)**	**2h(*ee*)**	**3h**	**2i**•MeOH
formula	$C_9H_{12}O_2S_3$	$C_9H_{12}O_2S_3$	$C_{11}H_{14}O_4S_3$	$C_{11}H_{14}O_5S_2$	$C_{10}H_{13}NO_3S_3$
formula weight	248.37	248.37	306.40	290.34	291.39
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P2_1$/c	Pbcn	P-1	$P2_1$/n	$P2_1$/c
Z	8	16	2	4	4
a, Å	10.827(4)	35.215(4)	5.4533(3)	13.217(4)	14.760(3)
b, Å	18.714(7)	5.8315(8)	10.9038(6)	5.6620(15)	6.6843(13)
c, Å	10.801(4)	21.770(3)	12.1913(7)	17.219(5)	13.794(3)
α, deg	90	90	103.870(3)	90	90
β, deg	91.009(5)	90	98.299(3)	93.566(4)	110.417(2)
γ, deg	90	90	102.873(3)	90	90
V, Å^3	2188.1(13)	4470.5(10)	670.95(7)	1286.1(6)	1275.5(4)
D_c, g cm^{-3}	1.508	1.476	1.517	1.500	1.517
R_1 (wR_2) [b]	0.0399 (0.0987)	0.0664 (0.1689)	0.0277 (0.0720)	0.0549 (0.1404)	0.0495 (0.1423)
Goodness of fit	1.061	1.048	1.072	1.046	1.048
CCDC deposition No.	972800	972796	972799	972797	972798

[a] Obtained with monochromatic radiation (λ = 0.7749 Å).

[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Figure S2. Solid-state structure for the compound **2f(*a*)** with thermal ellipsoids set at the 50% probability level. There are two molecules per asymmetric unit.

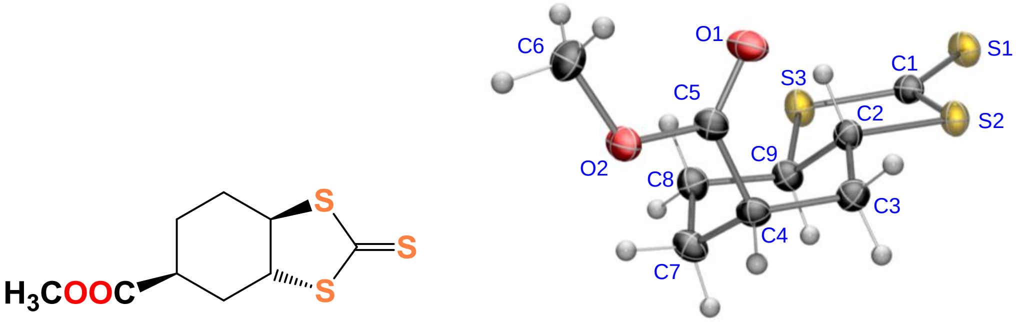


Table S2. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) for **2f(*a*)**.

S2-C1	1.733(2)	C4-C3-C2-S2	-176.17(13)
S2-C2	1.827(2)	C1-S2-C2-C9	37.63(14)
S3-C1	1.740(2)	C1-S2-C2-C3	160.57(14)
S3-C9	1.818(2)	C6-O2-C5-O1	5.4(3)
S1-C1	1.643(2)	C6-O2-C5-C4	-174.75(16)
O1-C5	1.202(2)	C7-C4-C5-O1	-120.7(2)
O2-C5	1.341(2)	C3-C4-C5-O1	4.8(3)
O2-C6	1.449(2)	C7-C4-C5-O2	59.4(2)
C1-S2-C2	95.80(9)	C3-C4-C5-O2	-175.01(16)
C1-S3-C9	95.84(9)	C2-S2-C1-S1	168.18(13)
C5-O2-C6	116.20(16)	C2-S2-C1-S3	-11.58(12)
C9-C2-S2	106.00(13)	C9-S3-C1-S1	167.43(13)
C3-C2-S2	113.93(13)	C9-S3-C1-S2	-12.81(12)
O1-C5-O2	123.02(18)	S2-C2-C9-C8	-174.01(13)
O1-C5-C4	126.45(18)	C3-C2-C9-S3	-174.20(13)
O2-C5 C4	110.53(16)	S2-C2-C9-S3	-49.72(14)
S1-C1-S2	122.73(12)	C7-C8-C9-S3	-179.07(13)
S1-C1-S3	122.87(12)	C1-S3-C9-C2	38.37(14)
S2-C1-S3	114.40(11)	C1-S3-C9-C8	160.23(15)
C2-C9-S3	105.95(13)		
C8-C9-S3	114.31(14)		

Figure S3. Solid-state structure for the compound **2f(*e*)** with thermal ellipsoids set at the 50% probability level. There are two molecules per asymmetric unit.

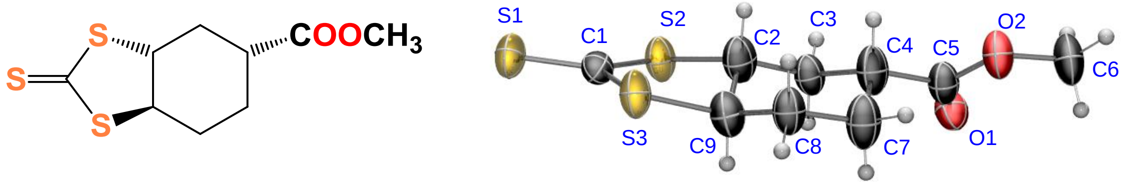


Table S3. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) for **2f(*e*)**.

O1-C5	1.201(6)	C2-S2-C1-S1	167.5(3)
O2-C5	1.322(5)	C2-S2-C1-S3	-14.0(3)
O2-C6	1.436(5)	C9-S3-C1-S1	168.9(3)
S1-C1	1.630(4)	C9-S3-C1-S2	-9.6(3)
S2-C1	1.729(4)	C1-S2-C2-C9	39.9(4)
S2-C2	1.830(5)	C1-S2-C2-C3	162.7(4)
S3-C1	1.747(4)	S2-C2-C3-C4	177.9(3)
S3-C9	1.825(5)	C6-O2-C5-O1	-0.2(7)
C5-O2-C6	116.1(4)	C6-O2-C5-C4	106.2(6)
C1-S2-C2	94.9(2)	C3-C4-C5-O1	-18.7(7)
C1-S3-C9	96.3(2)	C7-C4-C5-O2	-76.8(5)
S1-C1-S2	123.5(2)	C3-C4-C5-O2	158.2(4)
S1-C1-S3	122.7(2)	S2-C2-C9-C8	-172.3(4)
S2-C1-S3	113.8(2)	C3-C2-C9-S3	-174.0(3)
C9-C2-S2	107.4(3)	S2-C2-C9-S3	-49.8(4)
C3-C2-S2	113.2(3)	C7-C8-C9-S3	-175.1(4)
O1-C5-O2	123.5(4)	C1-S3-C9-C2	36.5(4)
O1-C5-C4	127.4(4)	C1-S3-C9-C8	157.5(4)
O2-C5-C4	109.1(4)		
C2-C9-S3	105.6(4)		
C8-C9-S3	112.9(3)		

Figure S4. Solid-state structure for the compound **2h(*ee*)** with thermal ellipsoids set at the 50% probability level.

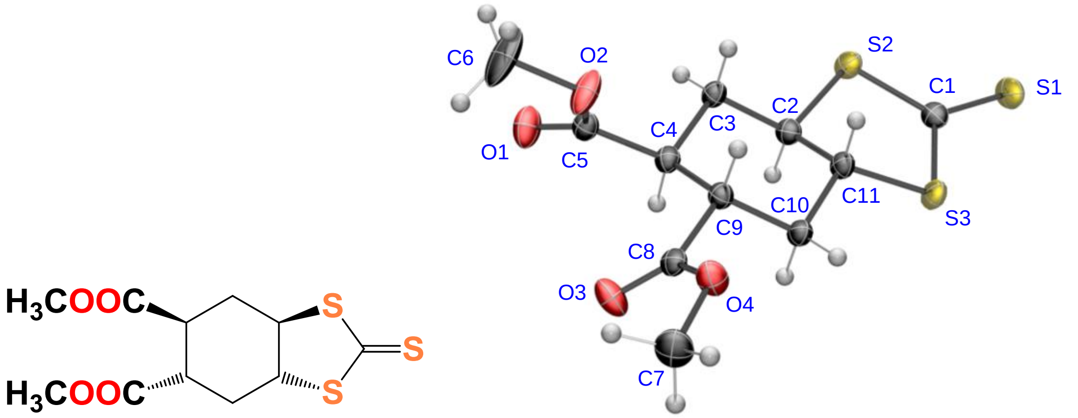


Table S4. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) for **2h(*ee*)**.

S1-C1	1.6362(15)	C2-C11-S3	106.90(10)
S2-C1	1.7388(16)	C2-S2-C1-S1	171.75(10)
S2-C2	1.8216(14)	C2-S2-C1-S3	-8.48(9)
S3-C1	1.7410(15)	C11-S3-C1-S1	164.69(10)
S3-C11	1.8201(15)	C11-S3-C1-S2	-15.08(9)
O1-C5	1.1979(19)	C1-S2-C2-C11	34.58(11)
O2-C5	1.3297(18)	C1-S2-C2-C3	156.16(11)
O2-C6	1.451(2)	S2-C2-C3-C4	-177.89(9)
O3-C8	1.2011(18)	C6-O2-C5-O1	1.9(2)
O4-C8	1.3261(18)	C6-O2-C5-C4	-179.73(16)
O4-C7	1.4463(18)	C9-C4-C5-O1	-148.77(15)
C1-S2-C2	96.84(7)	C3-C4-C5-O1	86.58(18)
C1-S3-C11	95.52(7)	C9-C4-C5-O2	32.83(17)
C5-O2-C6	115.36(13)	C3-C4-C5-O2	-91.82(15)
C8-O4-C7	116.96(12)	C7-O4-C8-O3	1.9(2)
S1-C1-S2	123.35(9)	C7-O4-C8-C9	-177.96(13)
S1-C1-S3	122.47(9)	O3-C8-C9-C4	18.7(2)
S2-C1-S3	114.18(8)	O4-C8-C9-C4	-161.45(12)

C11-C2-S2	106.01(10)	O3-C8-C9-C10	-104.34(17)
C3-C2-S2	114.04(10)	O4-C8-C9-C10	75.53(14)
O1-C5-O2	123.36(14)	C9-C10-C11-S3	178.46(9)
O1-C5-C4	124.04(14)	S2-C2-C11-C10	-174.25(10)
O2-C5-C4	112.57(12)	C3-C2-C11-S3	-171.98(9)
O3-C8-O4	124.61(13)	S2-C2-C11-S3	-48.05(11)
O3-C8-C9	125.07(13)	C1-S3-C11-C10	162.89(11)
O4-C8-C9	110.33(12)	C1-S3-C11-C2	38.84(10)
C10-C11-S3	114.88(10)		

Figure S5. Solid-state structure for the compound **3h** with thermal ellipsoids set at the 50% probability level.

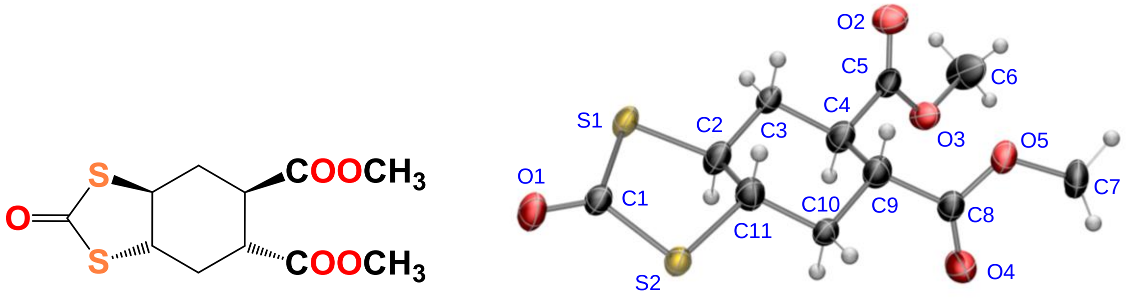


Table S5. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) for **3h**.

S2-C1	1.773(3)	C3-C2-S1	113.2(2)
S2-C11	1.803(3)	O4-C8-O5-C7	-1.1(5)
S1-C1	1.786(3)	C9-C8-O5-C7	175.5(3)
S1-C2	1.812(4)	C6-O3-C5-O2	3.3(5)
O3-C5	1.316(4)	C6-O3-C5-C4	-177.4(3)
O3-C6	1.442(4)	C11-S2-C1-O1	-168.1(3)
C8-O4	1.198(4)	C11-S2-C1-S1	12.9(2)
C8-O5	1.322(4)	C2-S1-C1-O1	-167.8(3)
O5-C7	1.454(4)	C2-S1-C1-S2	11.2(2)
O1-C1	1.201(4)	C9-C10-C11-S2	-178.6(2)
C5-O2	1.198(4)	C1-S2-C11-C2	-38.9(3)
C1-S2-C11	94.53(16)	C1-S2-C11-C10	-161.9(3)
C1-S1-C2	94.75(16)	S2-C11-C2-C3	175.3(2)
C5-O3-C6	116.3(3)	C10-C11-C2-S1	175.8(2)
O4-C8-O5	123.7(3)	S2-C11-C2-S1	51.3(3)
O4-C8-C9	126.9(3)	C4-C3-C2-S1	178.1(2)
O5-C8-C9	109.3(3)	C1-S1-C2-C11	-37.4(3)
C8-O5-C7	115.3(3)	C1-S1-C2-C3	-160.1(3)
O2-C5-O3	124.1(3)	O2-C5-C4-C9	-87.9(5)
O2-C5-C4	127.3(3)	O3-C5-C4-C9	92.9(4)

O3-C5-C4	108.6(3)	O2-C5-C4-C3	34.9(5)
O1-C1-S2	123.1(3)	O3-C5-C4-C3	-144.3(3)
O1-C1-S1	123.2(3)	O4-C8-C9-C4	-92.6(4)
S2-C1-S1	113.64(18)	O5-C8-C9-C4	90.9(4)
C2-C11-S2	107.9(2)	O4-C8-C9-C10	29.5(5)
C10-C11-S2	113.2(2)	O5-C8-C9-C10	-146.9(3)
C11-C2-S1	106.9(3)		

Figure S6. Solid-state structure for the compound **2i**•MeOH with thermal ellipsoids set at the 50% probability level.

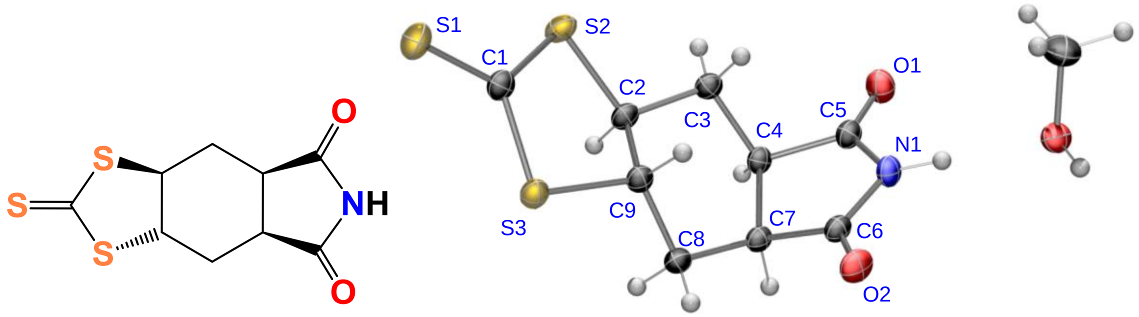


Table S6. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) for **2i**•MeOH.

S1-C1	1.6458(15)	C2-S2-C1-S1	-174.80(9)
S2-C1	1.7231(15)	C2-S2-C1-S3	6.26(9)
S2-C2	1.8187(14)	C9-S3-C1-S1	-163.15(9)
S3-C1	1.7351(14)	C9-S3-C1-S2	15.80(9)
S3-C9	1.8242(15)	C1-S2-C2-C3	-150.83(10)
N1-C5	1.3771(18)	C1-S2-C2-C9	-31.44(10)
N1-C6	1.3850(19)	S2-C2-C3-C4	178.59(8)
O1-C5	1.2215(18)	C6-N1-C5-O1	-178.12(14)
O2-C6	1.2132(17)	C6-N1-C5-C4	6.19(16)
C1-S2-C2	97.44(7)	C7-C4-C5-O1	166.01(15)
C1-S3-C9	95.89(7)	C3-C4-C5-O1	-73.63(17)
C5-N1-C6	112.70(12)	C7-C4-C5-N1	-18.45(14)
S1-C1-S2	122.98(8)	C3-C4-C5-N1	101.91(12)
S1-C1-S3	122.28(8)	C5-N1-C6-O2	-172.06(14)
S2-C1-S3	114.73(8)	C5-N1-C6-C7	9.34(16)
C3-C2-S2	111.45(9)	O2-C6-C7-C8	31.68(19)
C9-C2-S2	107.03(9)	N1-C6-C7-C8	-149.77(11)
O1-C5-N1	124.37(13)	O2-C6-C7-C4	161.24(14)
O1-C5-C4	126.99(13)	N1-C6-C7-C4	-20.21(13)

N1-C5-C4	108.49(12)	C7-C8-C9-S3	177.47(9)
O2-C6-N1	124.85(13)	S2-C2-C9-C8	169.28(9)
O2-C6-C7	127.69(13)	C3-C2-C9-S3	165.46(9)
N1-C6-C7	107.45(11)	S2-C2-C9-S3	44.66(10)
C8-C9-S3	114.33(9)	C1-S3-C9-C8	-158.76(10)
C2-C9-S3	107.07(9)	C1-S3-C9-C2	-36.99(10)

SI-2. Selected ^{1}H NMR Data

^{1}H-, ^{1}H-^{1}H-dqf-COSY, and ^{1}H-^{13}C-HMQC NMR spectra of the compounds were acquired spinning at room temperature on a JEOL-ECA-600 MHz instrument. The 1D-spectra were zero-filled four times prior to Fourier transformation. The 2D-spectra were not zero-filled. All 1D-pfg-ROESY spectra were acquired non-spinning for 256 transients with a spinlock pulse of 15.4 ms at 22 dB, a mixing time of 300 ms, and a relaxation delay of 10 s. After gradient-shimming of the sample, the spinner was turned off and the shim settings were optimized manually. The TOCSY-NOESY ("STEP-NOESY") experiments [3,4] were carried out non-spinning and with Gauss-shaped 180º-pulses (30.8 ms at 56.5 dB). The TOCSY mixing time was optimized in each case to allow spin density to build up at the desired resonance for subsequent NOESY irradiation. The NOESY mixing time was 500 ms and the relaxation delay was 10 s.

(see examples of spectra below)

[3] Hu, H.; Bradley, S. A.; Krishnamurthy, K. *J. Magn. Reson.* **2004**, *171*, 201-206.

[4] Thrippleton, M. J.; Keeler, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3938-3941.

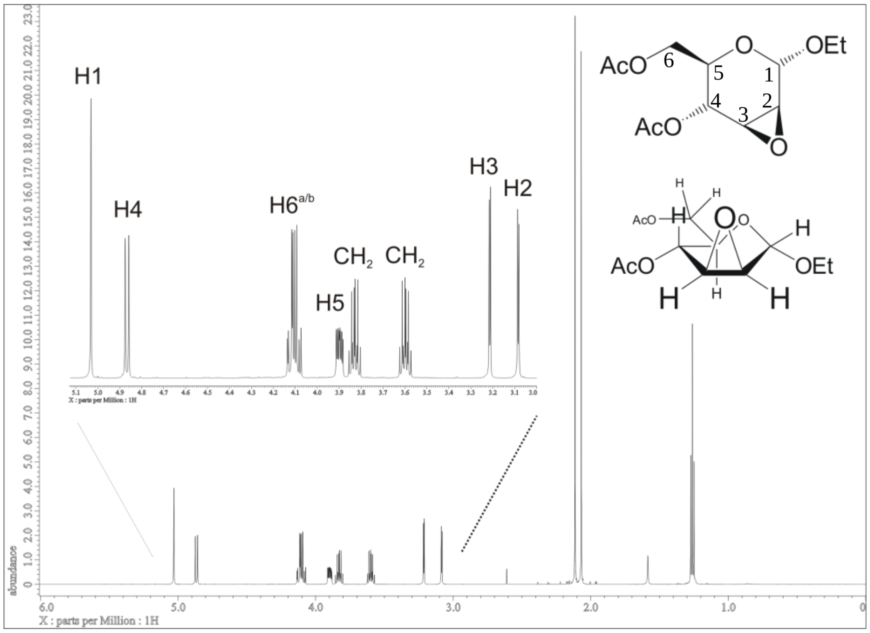


Figure S7. ^{1}H NMR spectrum for epoxide **1l** (600 MHz, in CDCl$_3$).

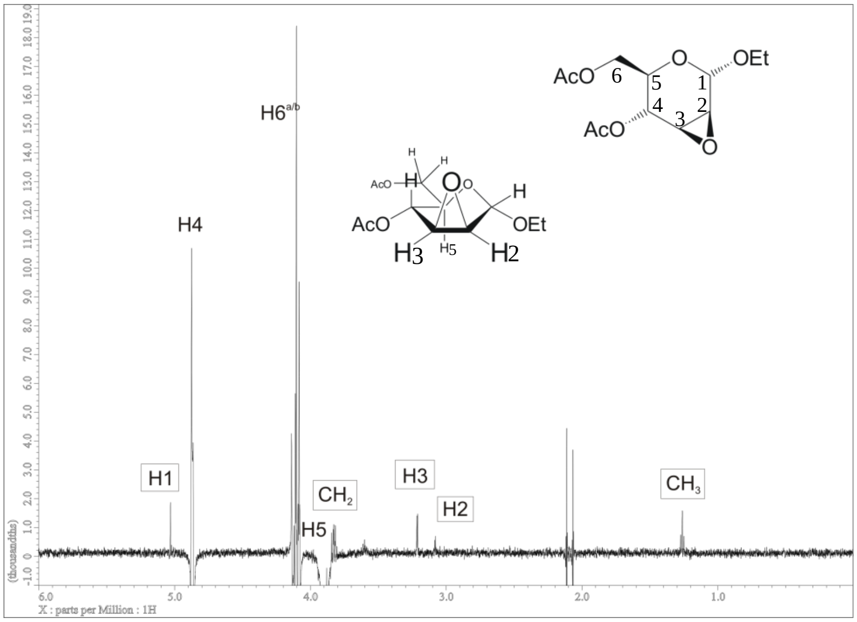


Figure S8. STEP-NOESY spectrum of epoxide **1l**. 1D-pfg-TOCSY irradiation of the resonance at 4.87ppm (H4) was followed by a short mixing time (30 ms) and subsequent 1D-pfg-NOESY irradiation of H5 at 3.90ppm. Aside from the COSY-coupled signals, the enhancement at H2 and H3 across the ring *cis* to H5 was clearly visible albeit weak. The ethyl aglycon CH$_2$-group protons were also enhanced. In addition, a small enhancement was observed at the methyl group and H1. The latter might be attributed to a weak W-coupling between H5 and H1 and hence might be a COSY-coupling.

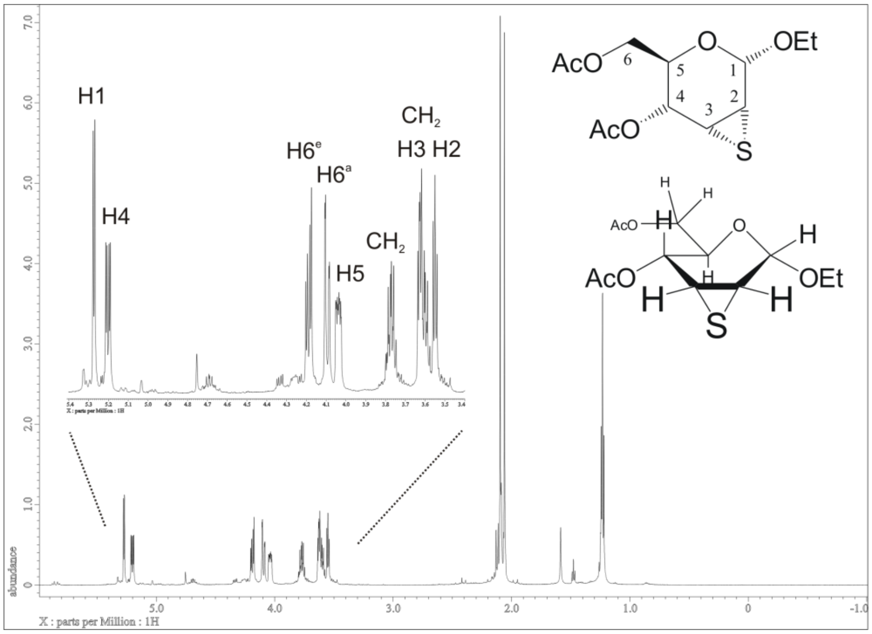


Figure S9. ^{1}H NMR spectrum for thiirane **2l** (600 MHz, in $CDCl_3$).

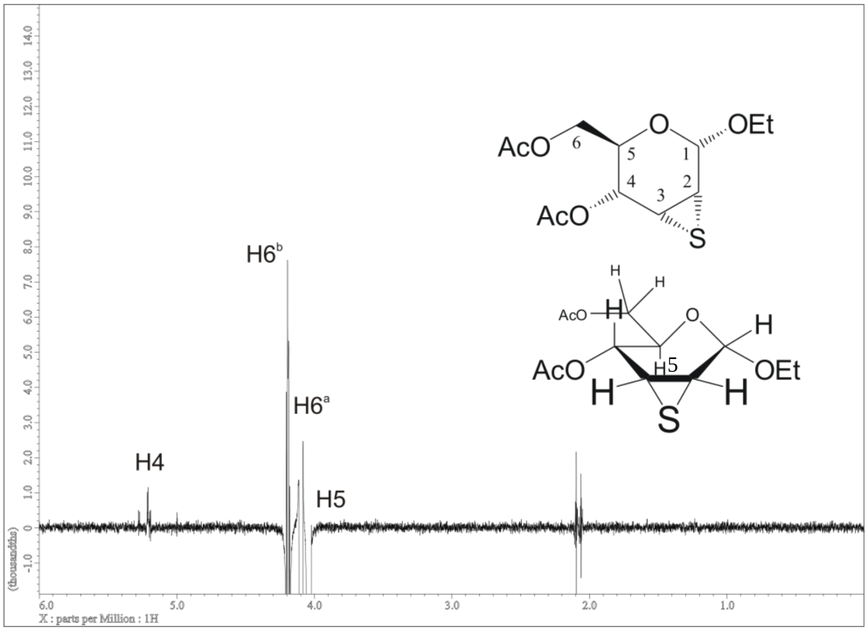
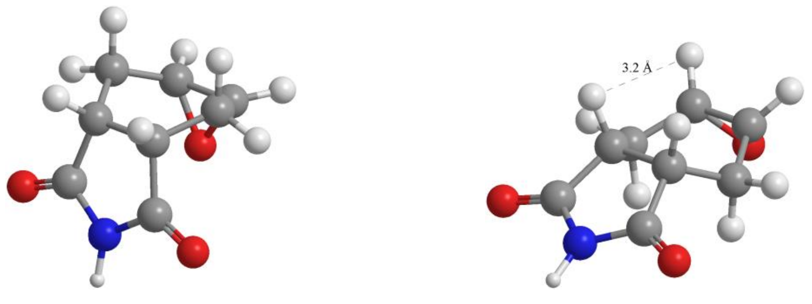


Figure S10. STEP-NOESY spectrum of thiirane **2l**. 1D-pfg-TOCSY irradiation of the resonance at 4.19ppm (H6b) was followed by a short mixing time (30 ms) and subsequent 1D-pfg-NOESY irradiation of H5 at 4.04ppm. Aside from the COSY-coupled signals at H6$^{a/b}$ and H4, no diagnostic nOe enhancements were observed. In addition, a very small enhancement was observed at H1, probably due to a weak W-coupling between H5 and H1 and hence might be a COSY-coupling.



0 kcal/mol 1.6 kcal/mol

Figure S11. Molecular modeling for the *syn*-isomer **1i** at the AM1-level (in vacuum). The diagnostic protons geminal to substituents are far away from each other in the most stable conformer of **1i** (left) and should not produce any nOe enhancement. The same is true for the *anti*-isomer (not shown). Indeed, no enhancements were observed in both cases.

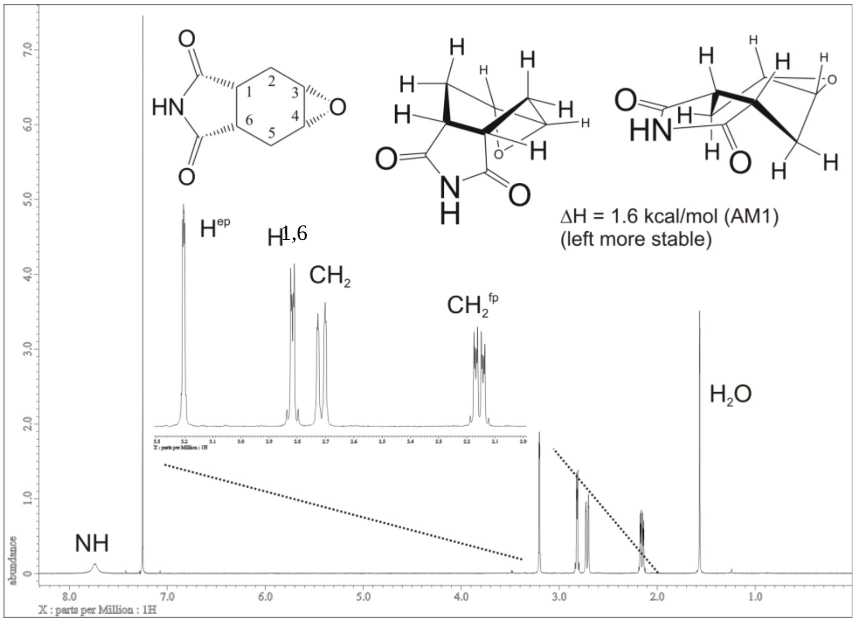


Figure S12. ^{1}H NMR spectrum of **1i** (600 MHz; in CDCl$_3$).

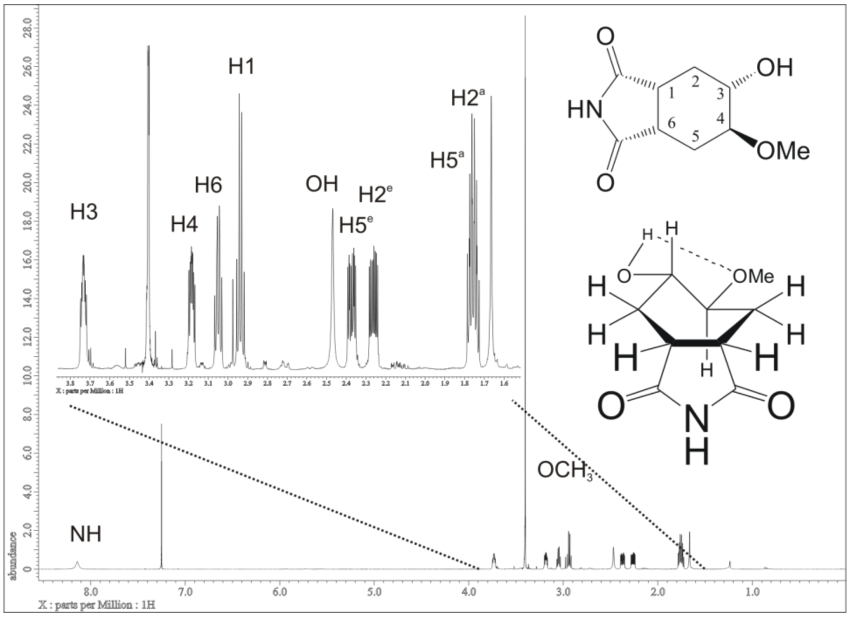


Figure S13. ^{1}H NMR spectrum for compound **4** (600 MHz, in $CDCl_3$).

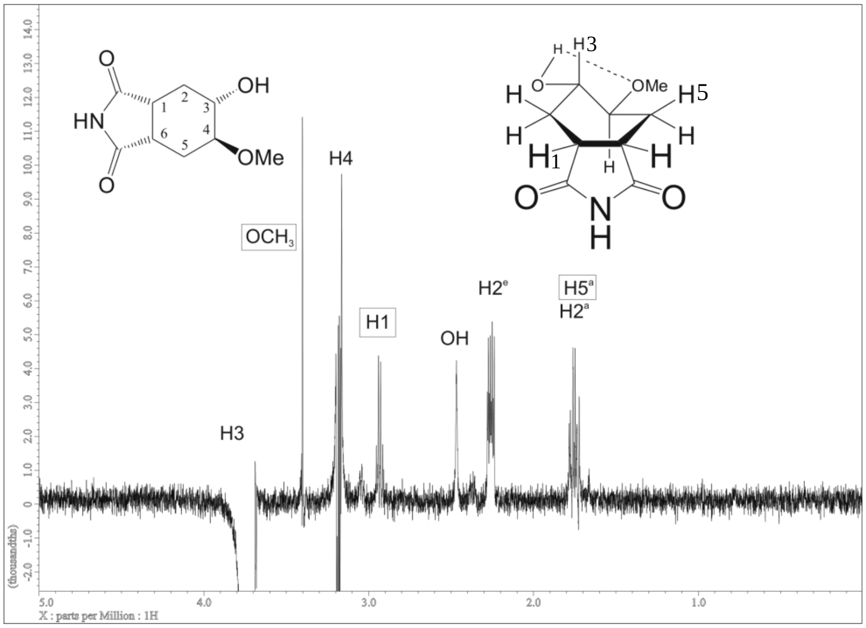


Figure S14. 1D-rOe spectrum of compound **4**. Irradiation of H3 resulted in expected COSY-coupled signals as well as characteristic enhancements at the methoxy group and H1 as well as at the *trans*-annular pseudo-axial H5.

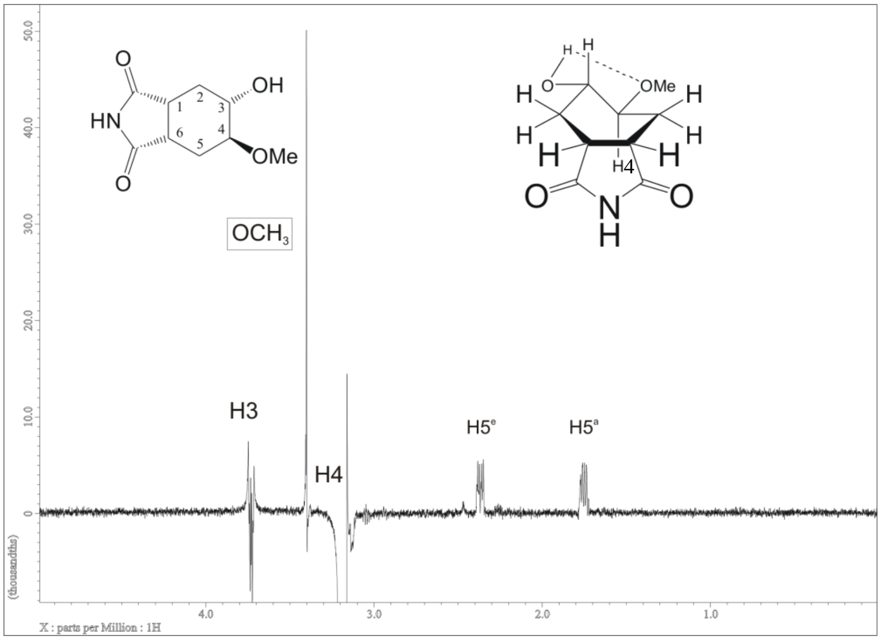


Figure S15. 1D-rOe spectrum of compound **4**. Irradiation of H4 resulted in expected COSY-coupled signals as well as only one dipolar enhancements at the methoxy group.