

# **Halonium Ion Triggered Rearrangement of Unsaturated Benzo-annulated Bi- and Tricyclic Sulfonamides**

Kimberly Geoghegan, Shaun Smullen and Paul Evans\*

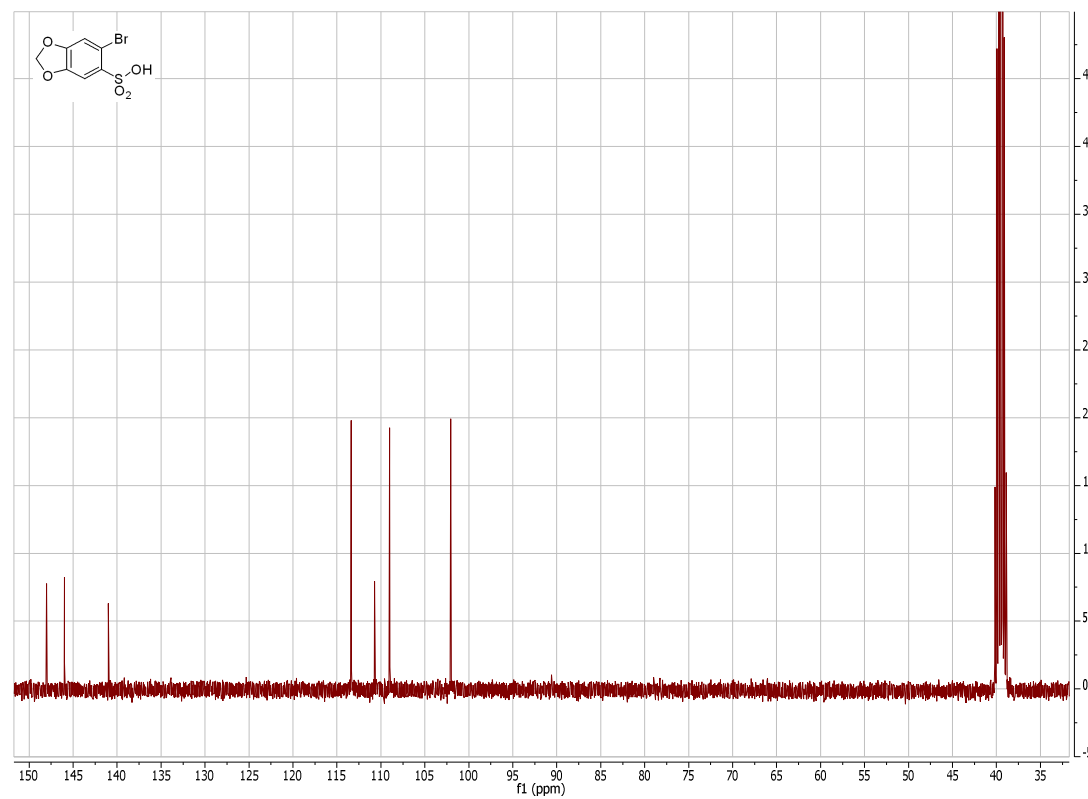
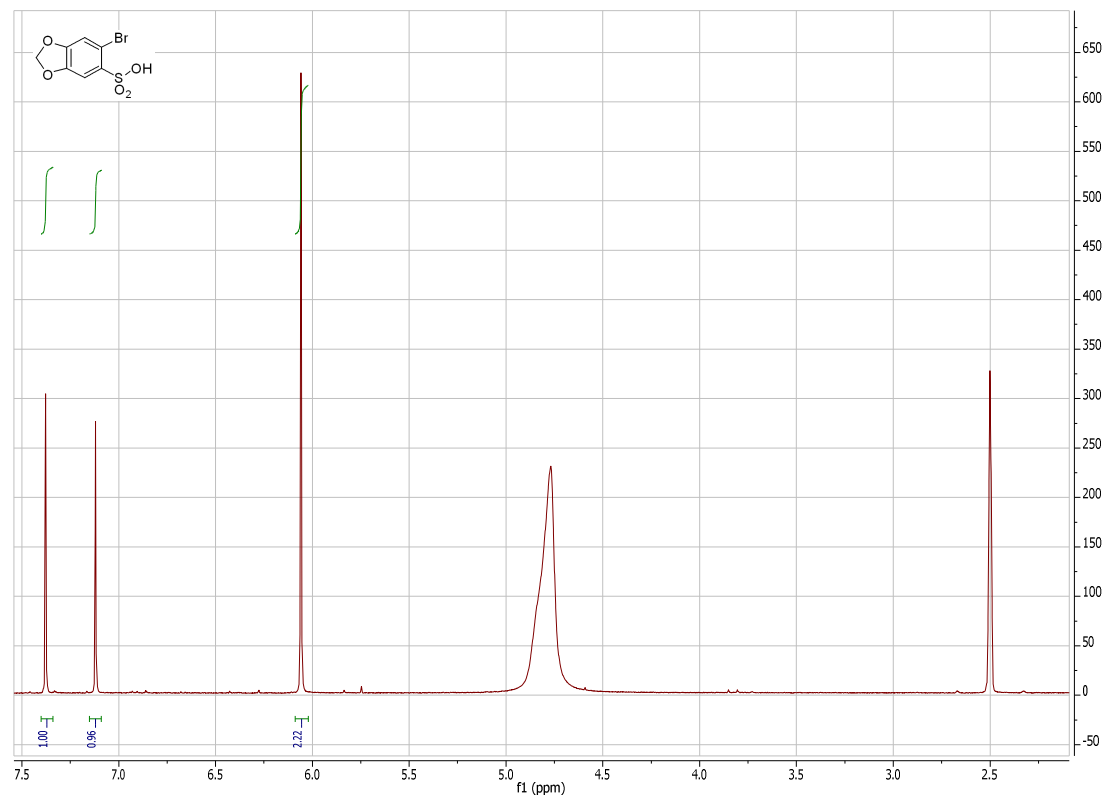
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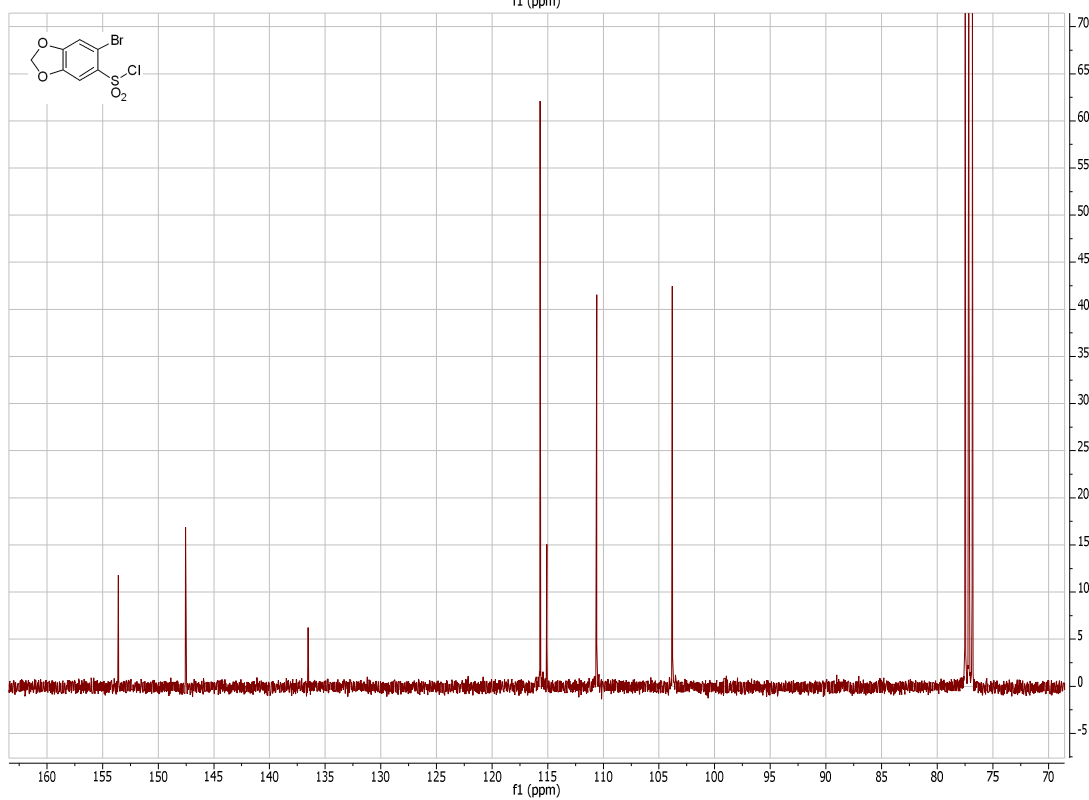
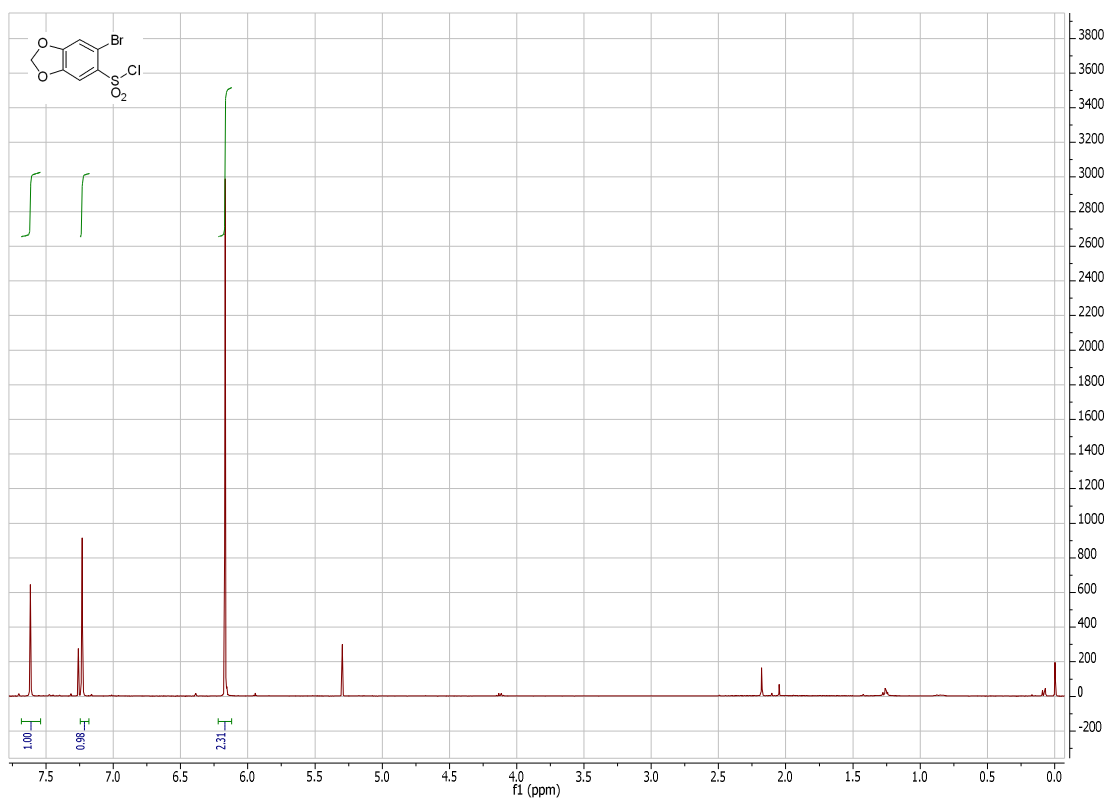
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## Proton and Carbon NMR Spectra

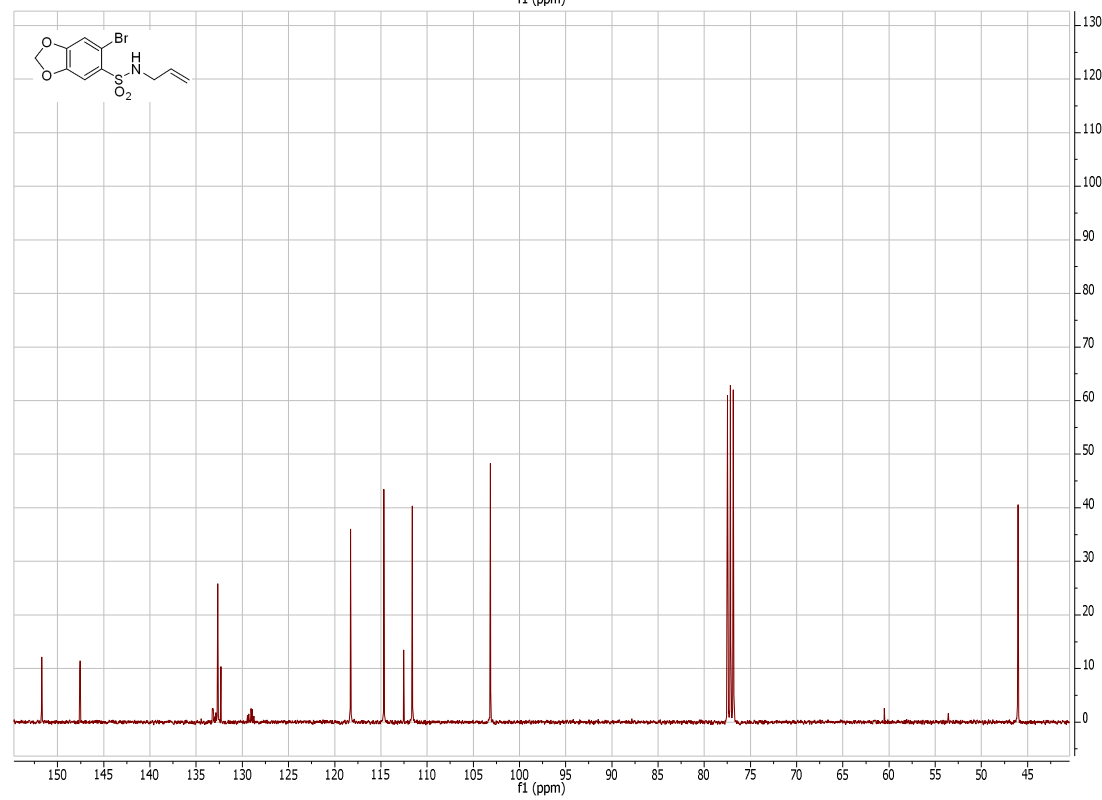
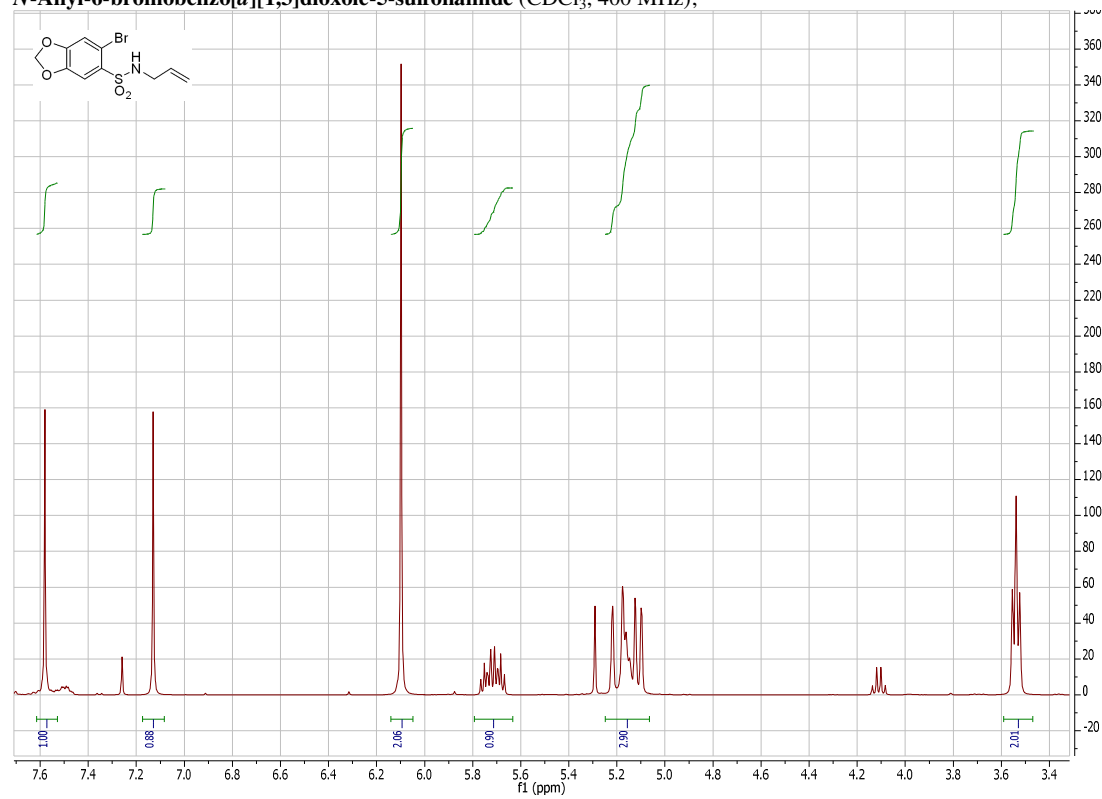
6-Bromobenzo[*d*][1,3]dioxole-5-sulfonic acid (DMSO, 400 MHz);



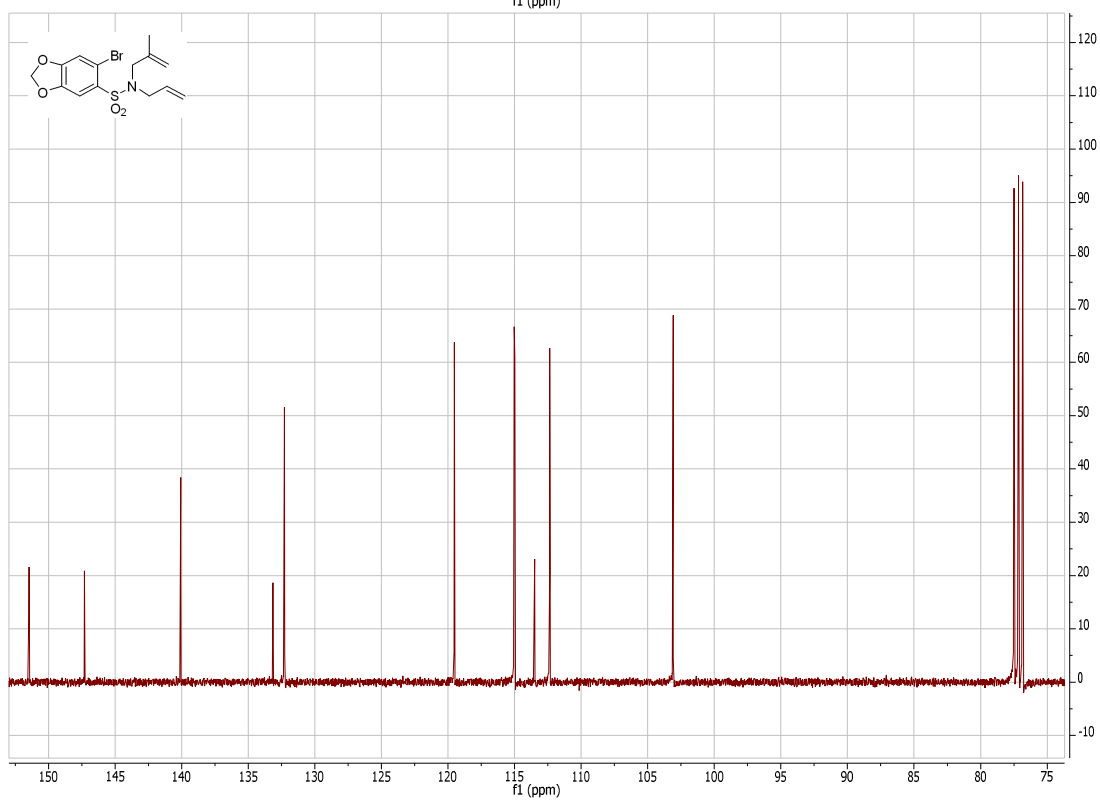
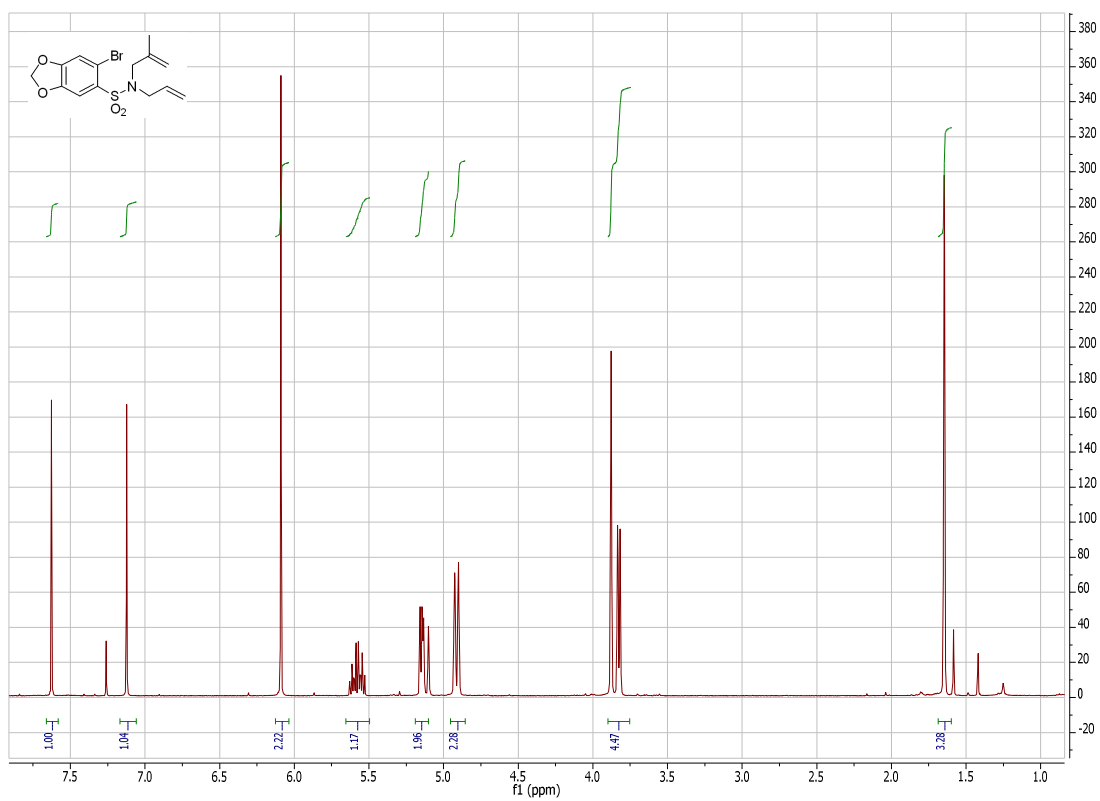
**6-Bromobenzo[d][1,3]dioxole-5-sulfonyl chloride 11b** (CDCl<sub>3</sub>, 400 MHz);



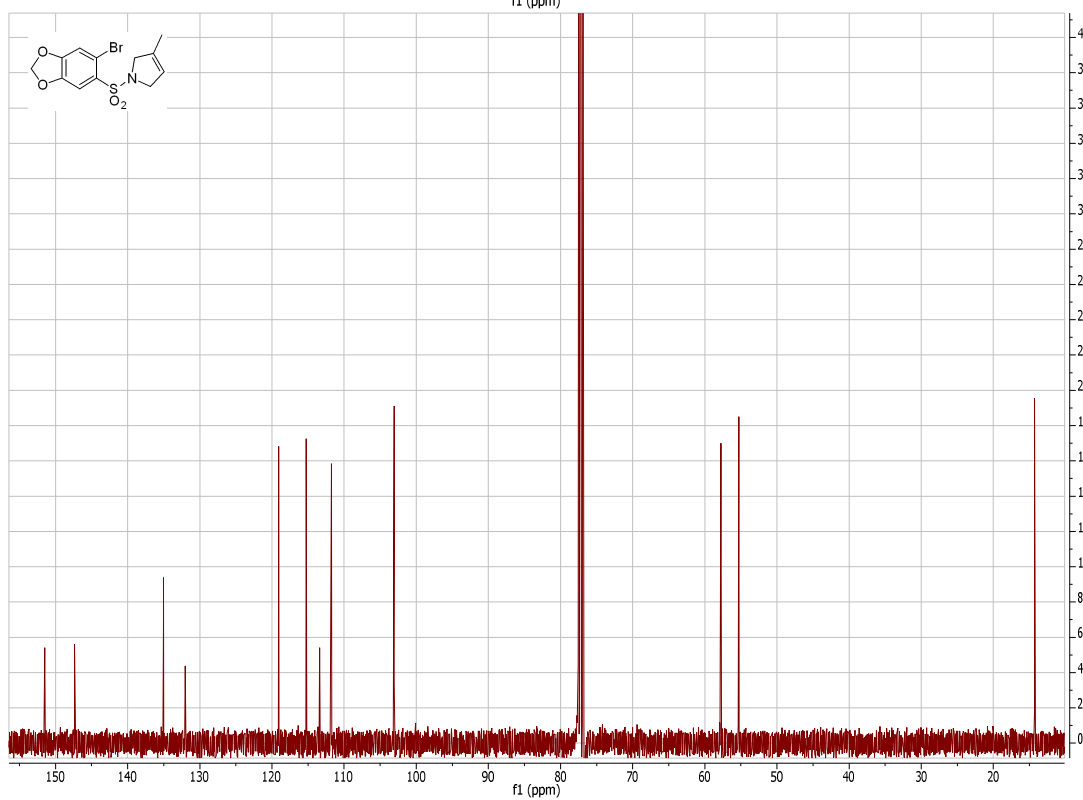
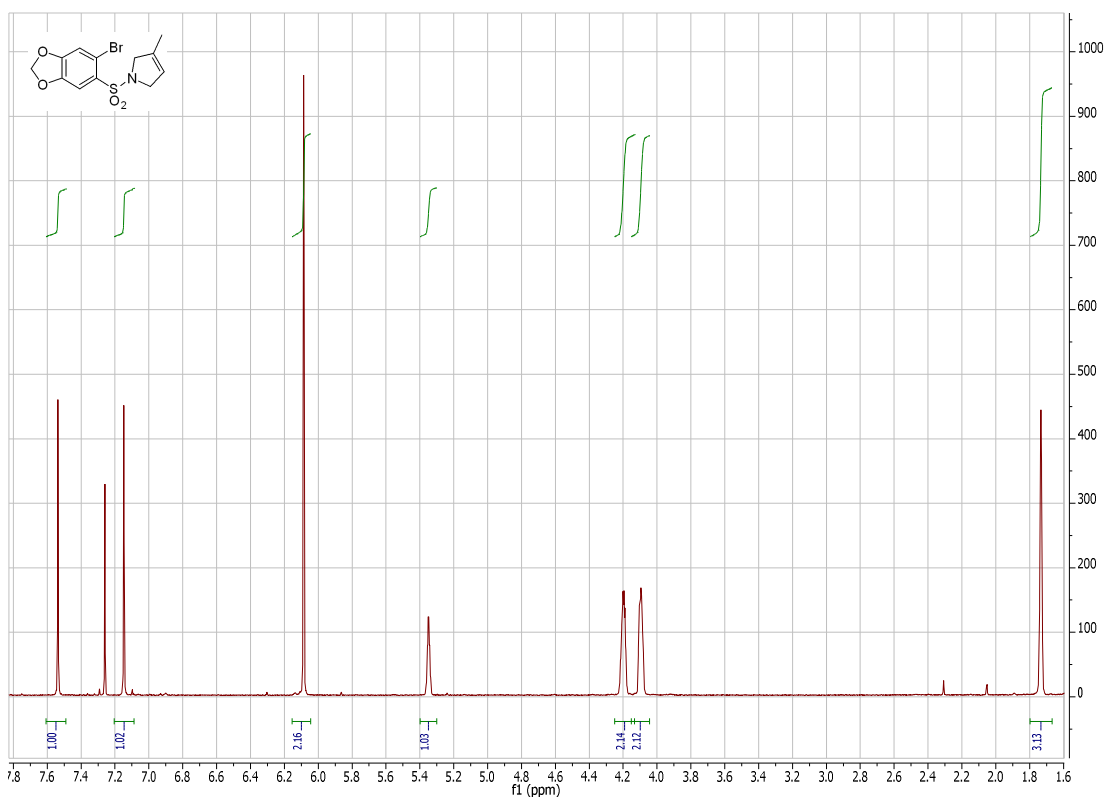
***N*-Allyl-6-bromobenzo[*d*][1,3]dioxole-5-sulfonamide (CDCl<sub>3</sub>, 400 MHz);**



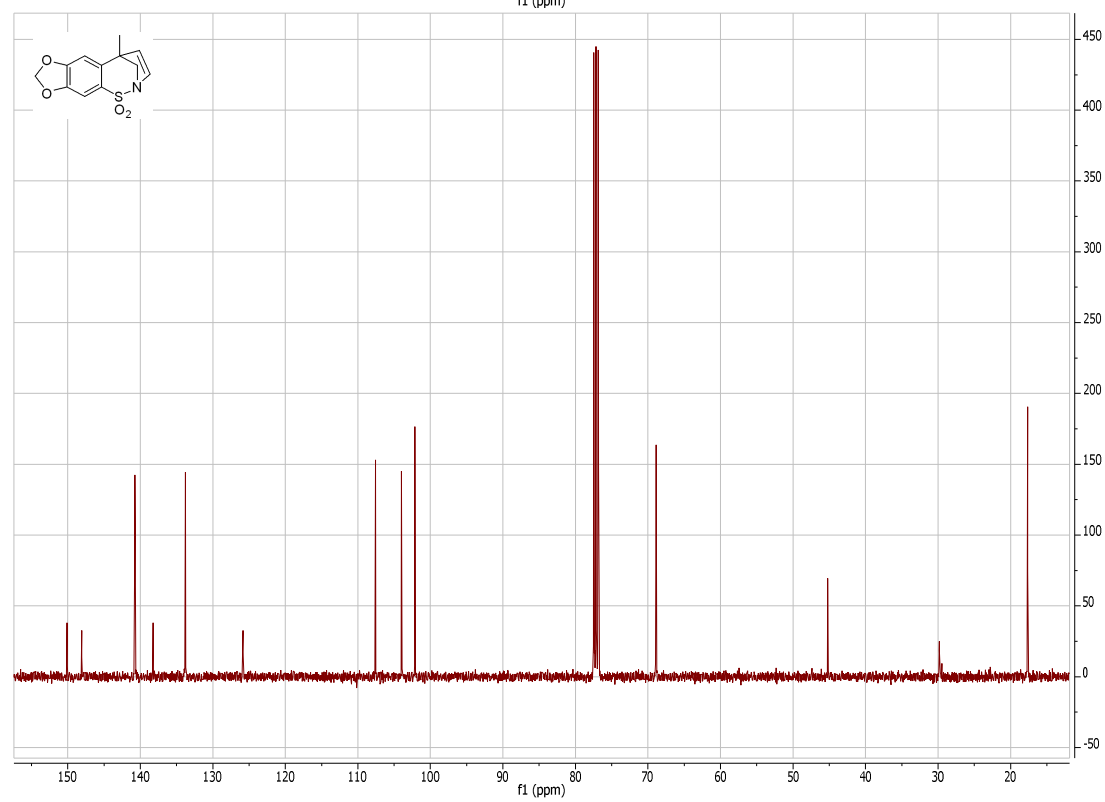
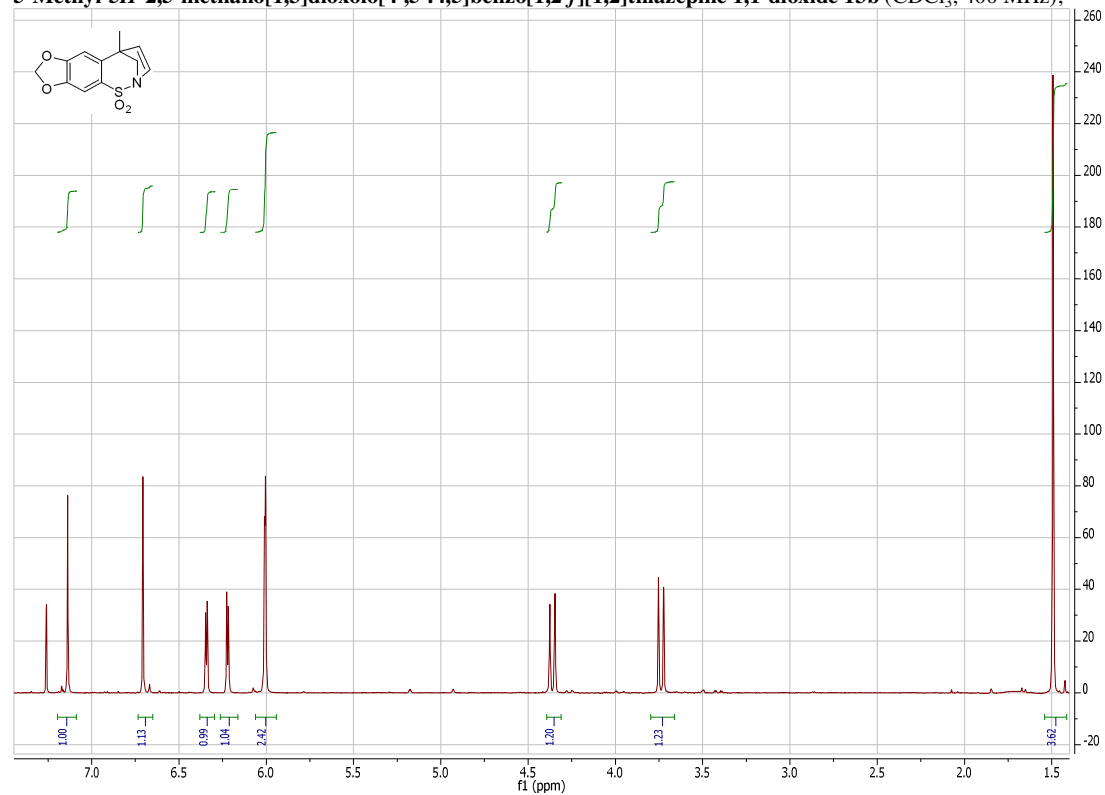
***N*-Allyl-6-bromo-*N*-(2-methylallyl)benzo[*d*][1,3]dioxole-5-sulfonamide (CDCl<sub>3</sub>, 400 MHz);**



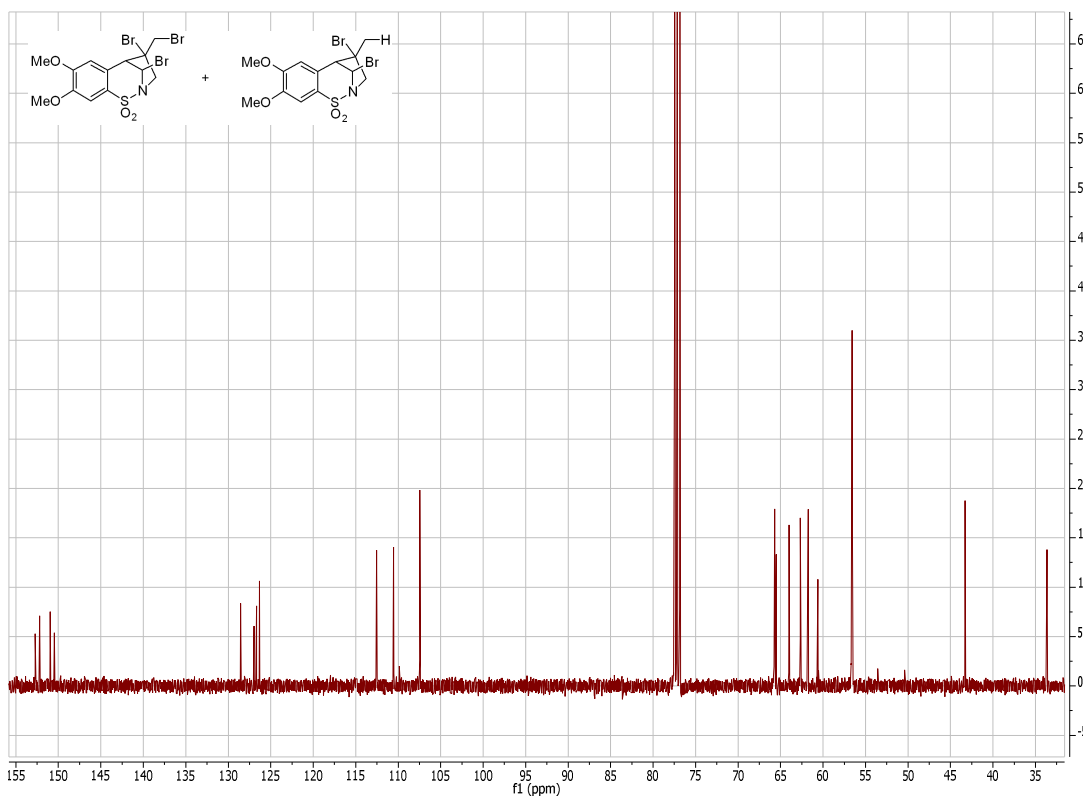
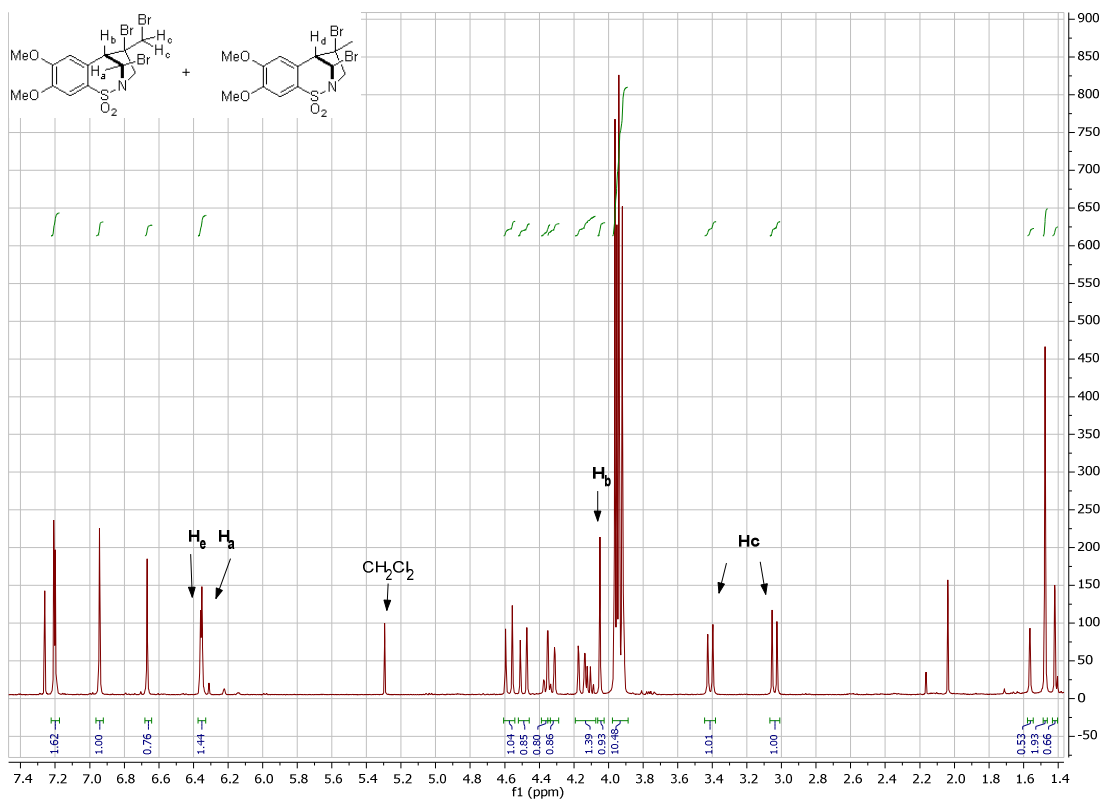
**1-((6-Bromobenzo[d][1,3]dioxol-5-yl)sulfonyl)-3-methyl-2,5-dihydro-1H-pyrrole 12b** (CDCl<sub>3</sub>, 400 MHz);



5-Methyl-5*H*-2,5-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 13b (CDCl<sub>3</sub>, 400 MHz);

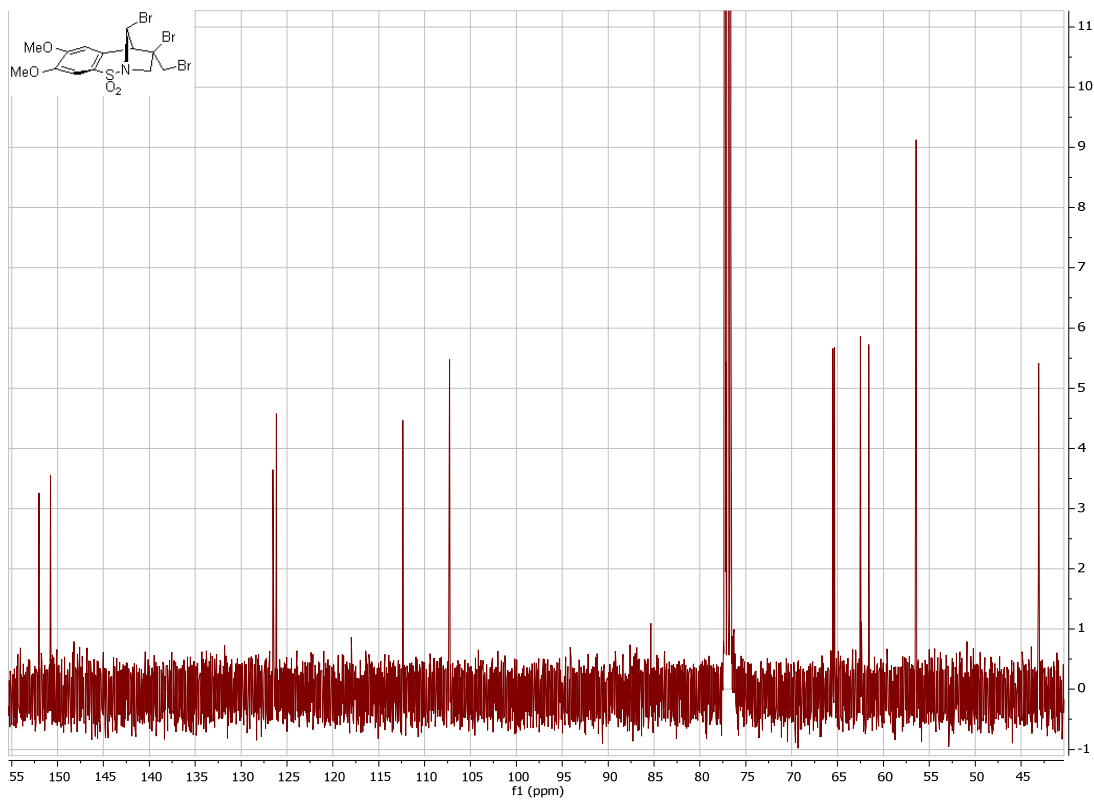
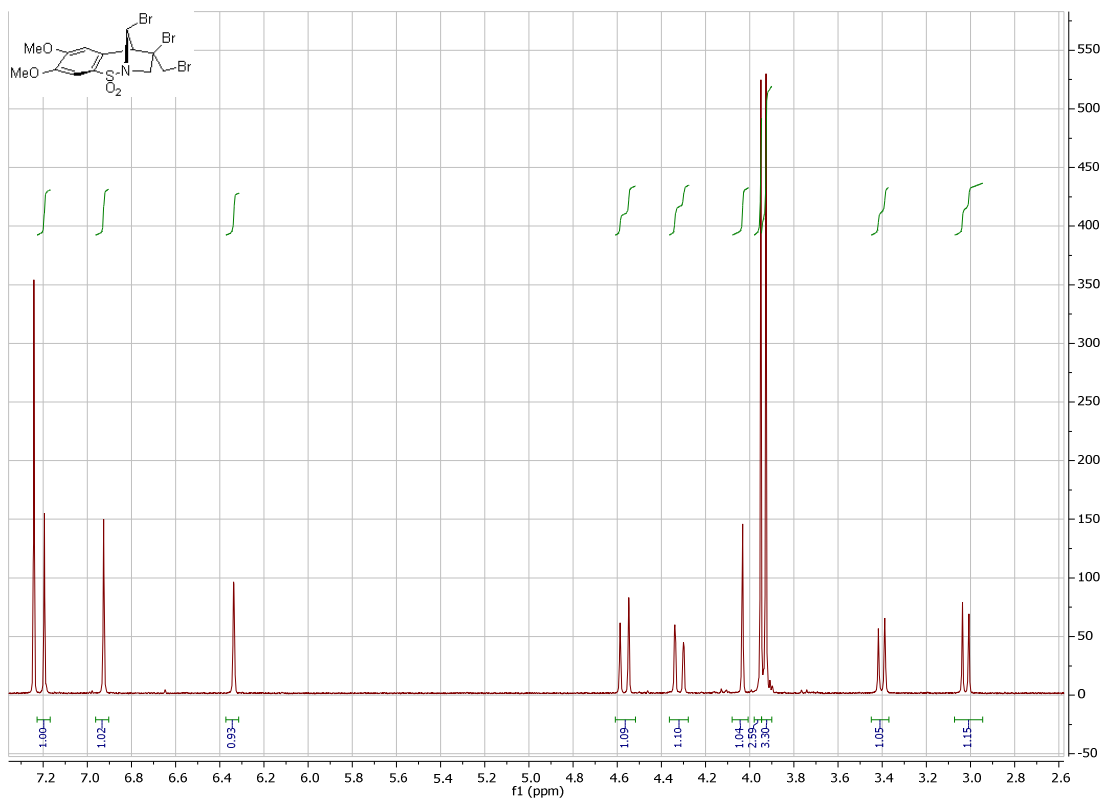


**(4*R*\*,5*S*\*,10*S*\*)-4,10-Dibromo-4-(bromomethyl)-7,8-dimethoxy-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]thiazepine 1,1-dioxide 15a and (4*R*\*,5*S*\*,10*S*\*)-4,10-Dibromo-7,8-dimethoxy-4-methyl-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]thiazepine 1,1-dioxide 14a (CDCl<sub>3</sub>, 400 MHz);**

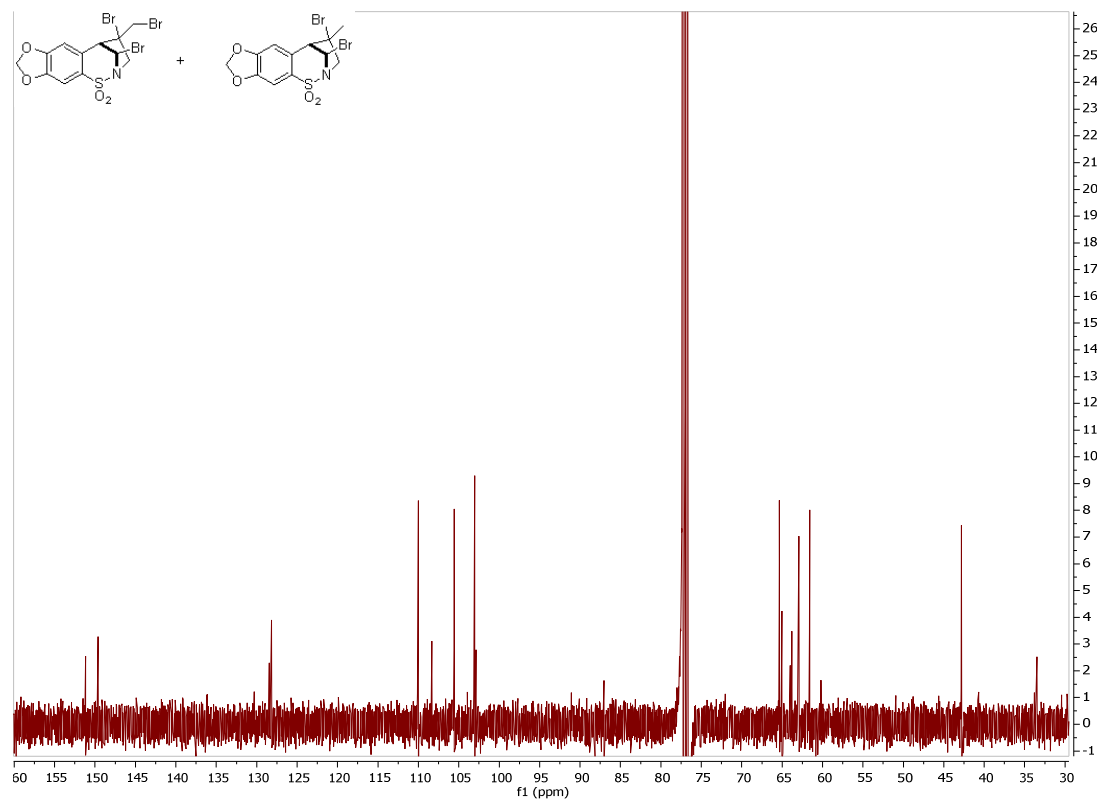
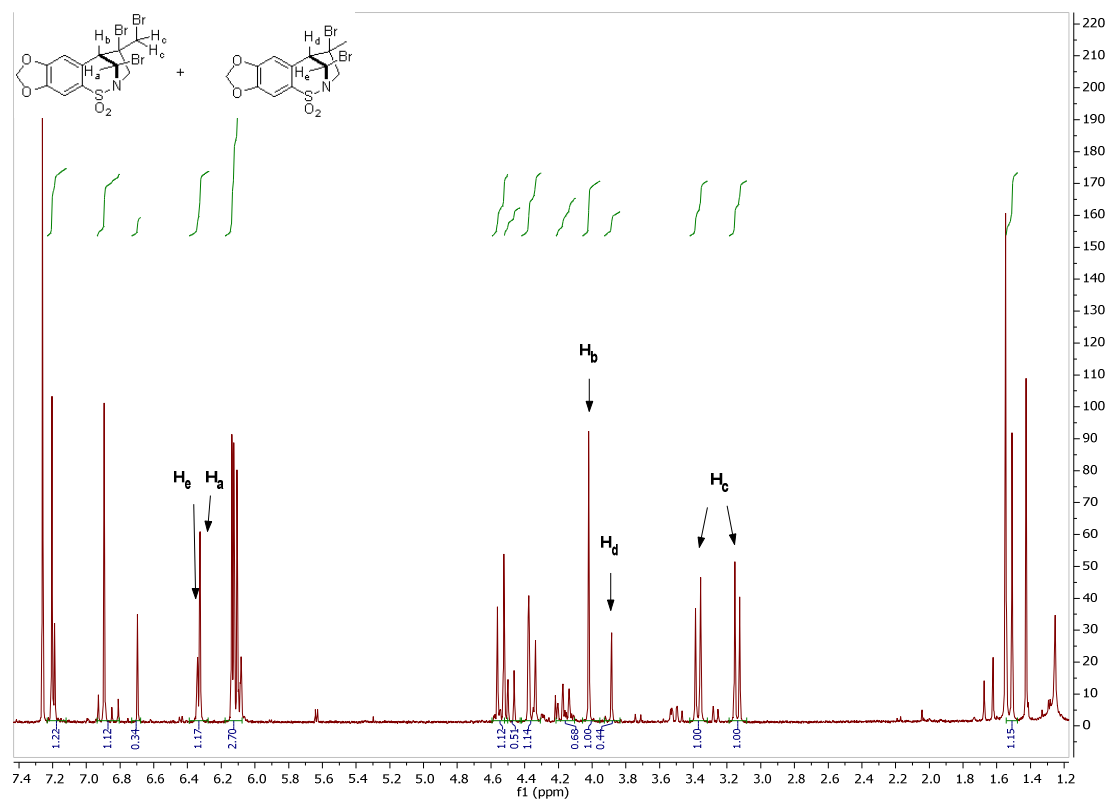




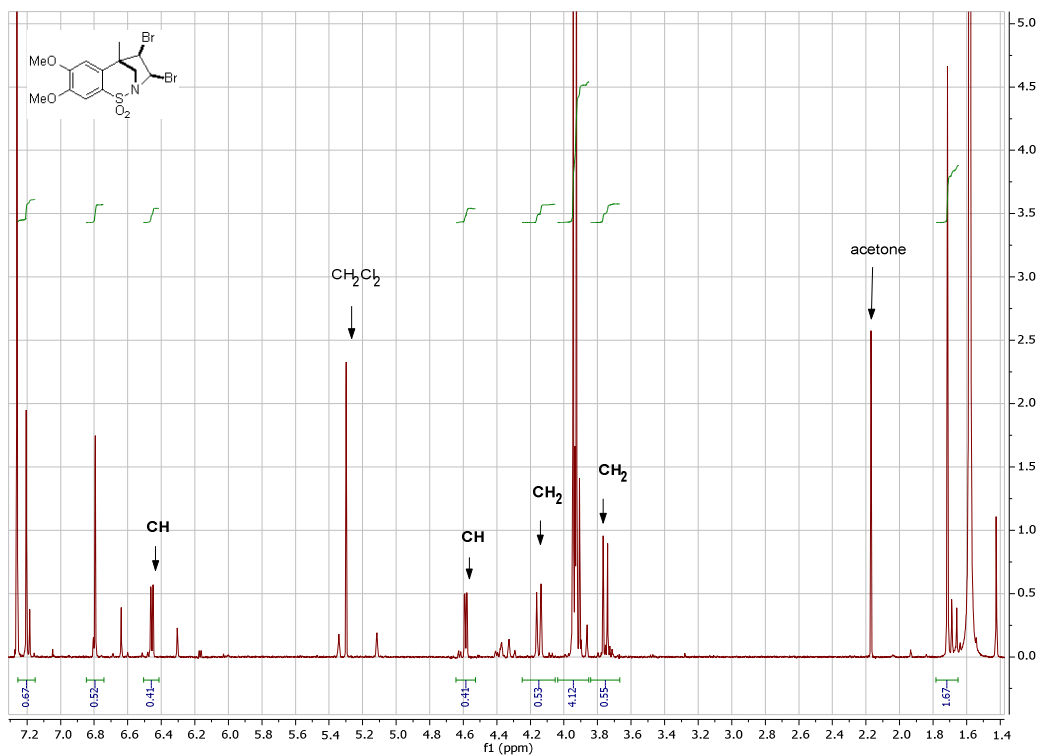
**(4*R*\*,5*S*\*,10*S*\*)-4,10-Dibromo-4-(bromomethyl)-7,8-dimethoxy-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]thiazepine 1,1-dioxide 15a** (CDCl<sub>3</sub>, 400 MHz):



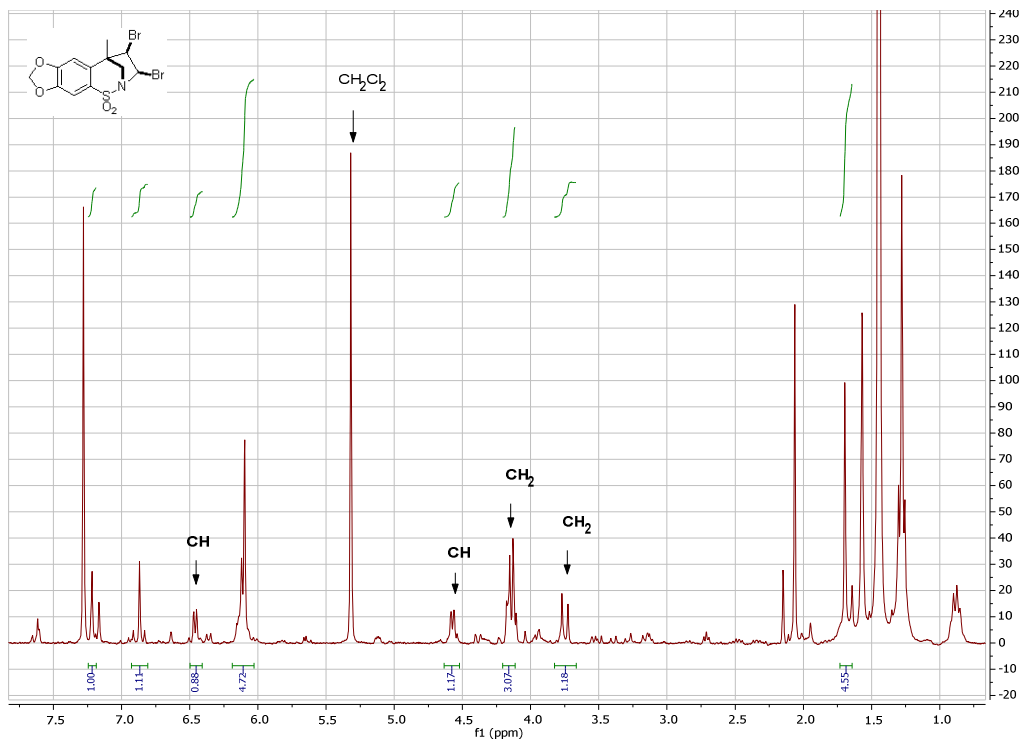
**(4*R*\*,5*S*\*,11*S*\*)-4,11-Dibromo-4-(bromomethyl)-4,5-dihydro-3*H*-2,5-methano[1,3]-dioxolo[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 15b and (4*R*\*,5*S*\*,11*S*\*)-4,11-dibromo-4-methyl-4,5-dihydro-3*H*-2,5-methano[1,3]dioxolo-[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 14b (CDCl<sub>3</sub>, 400 MHz);**



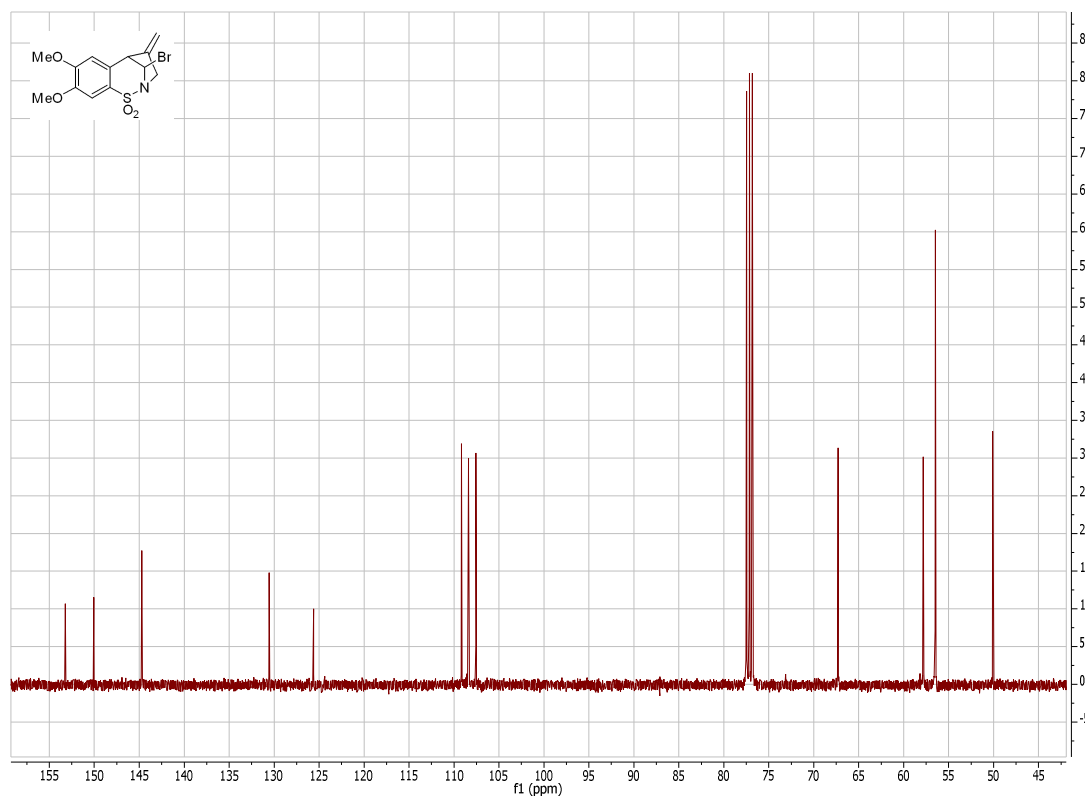
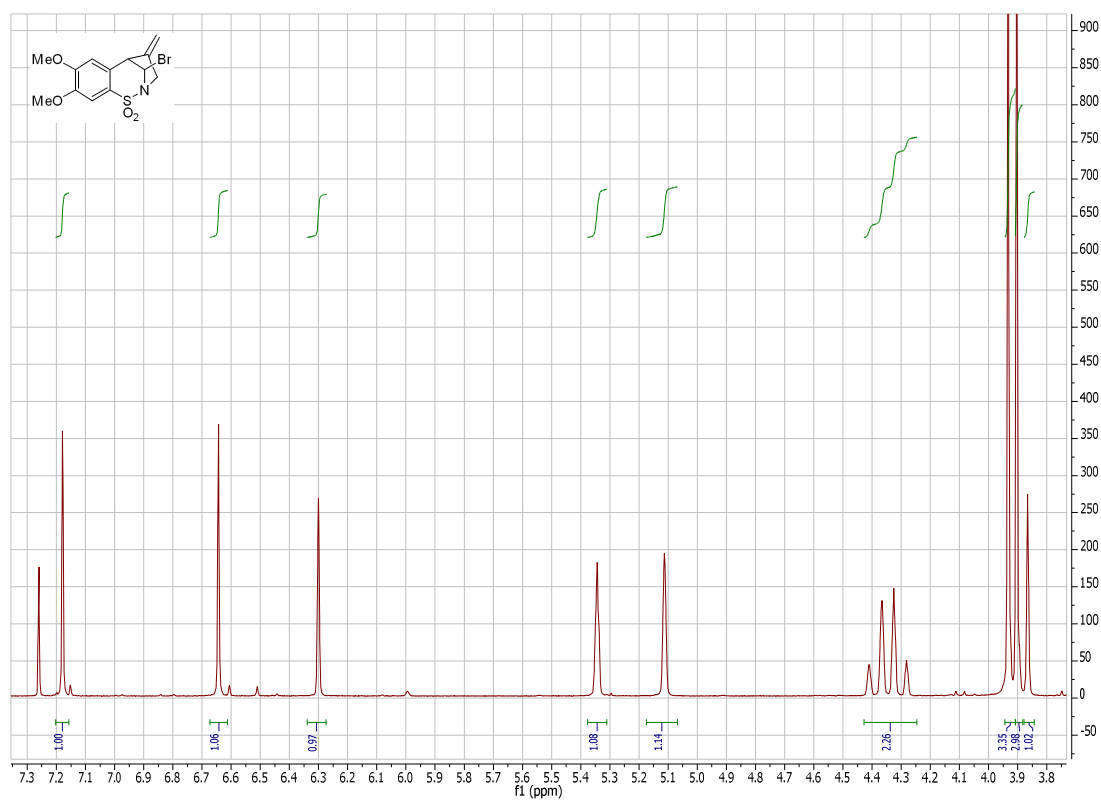
**(3*R*\*,4*R*\*,5*S*\*)-3,4-Dibromo-7,8-dimethoxy-5-methyl-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]thiazepine 1,1-dioxide 16a** (CDCl<sub>3</sub>, 400 MHz);



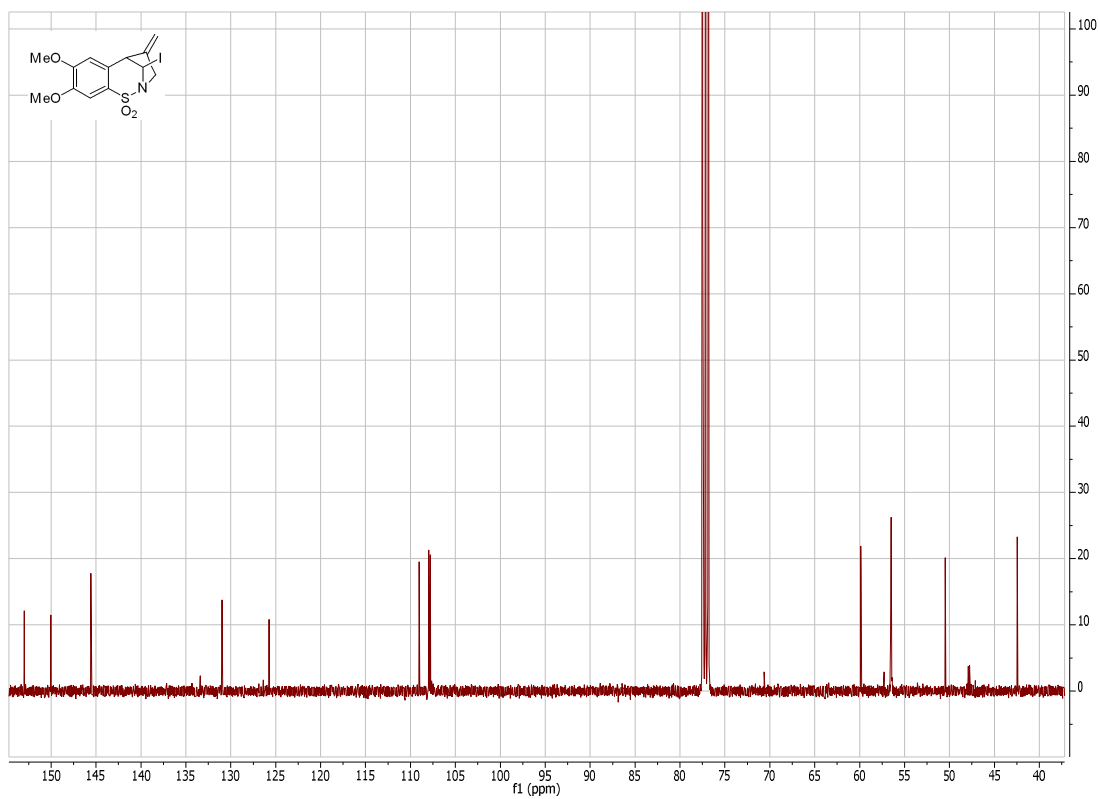
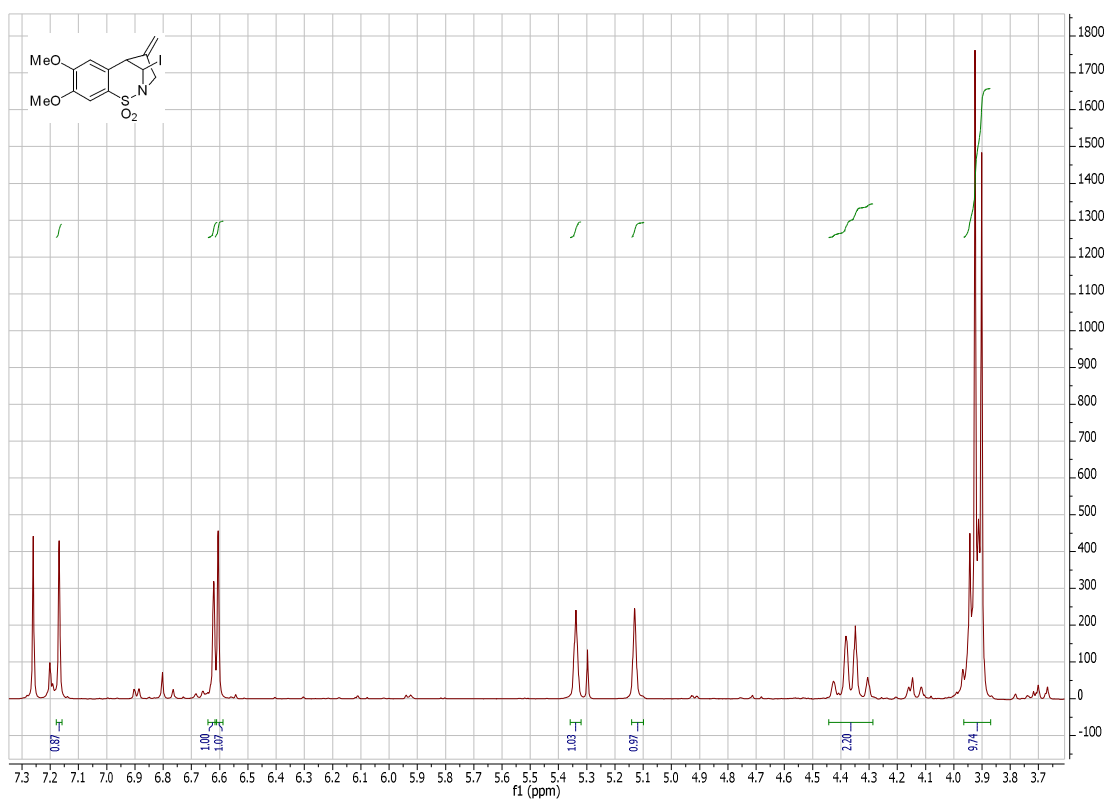
**(3*R*\*,4*R*\*,5*S*\*)-3,4-Dibromo-5-methyl-4,5-dihydro-3*H*-2,5-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 16b** (CDCl<sub>3</sub>, 400 MHz);



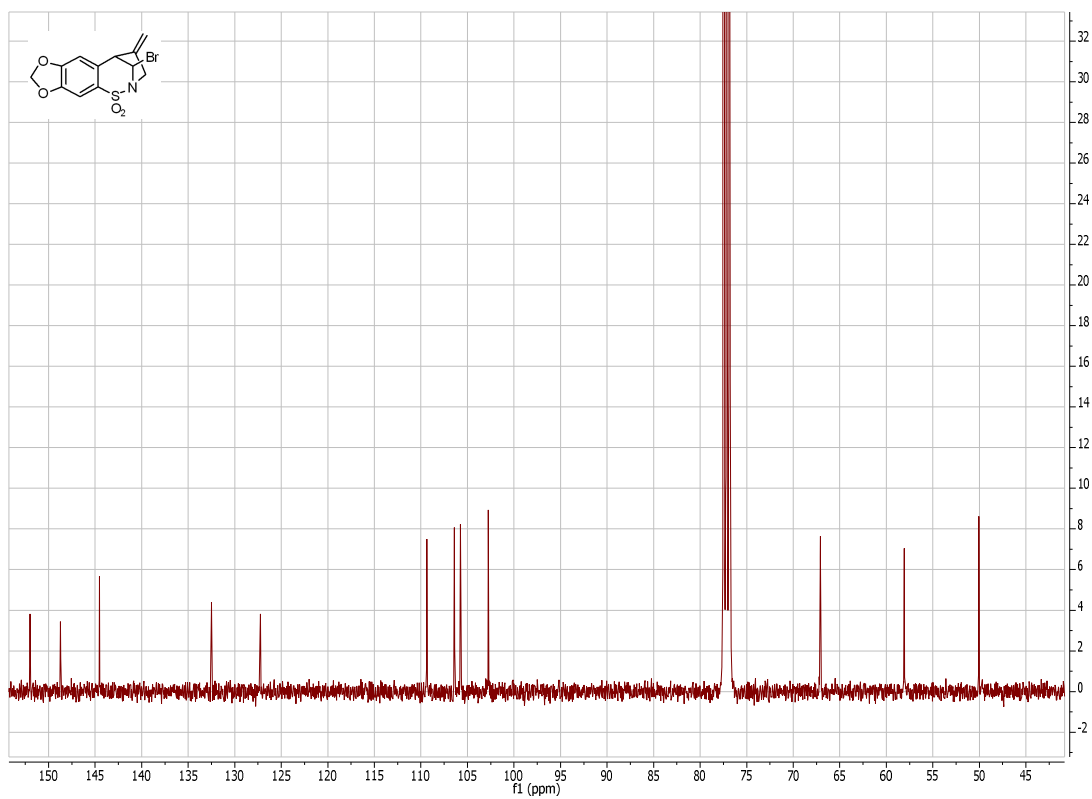
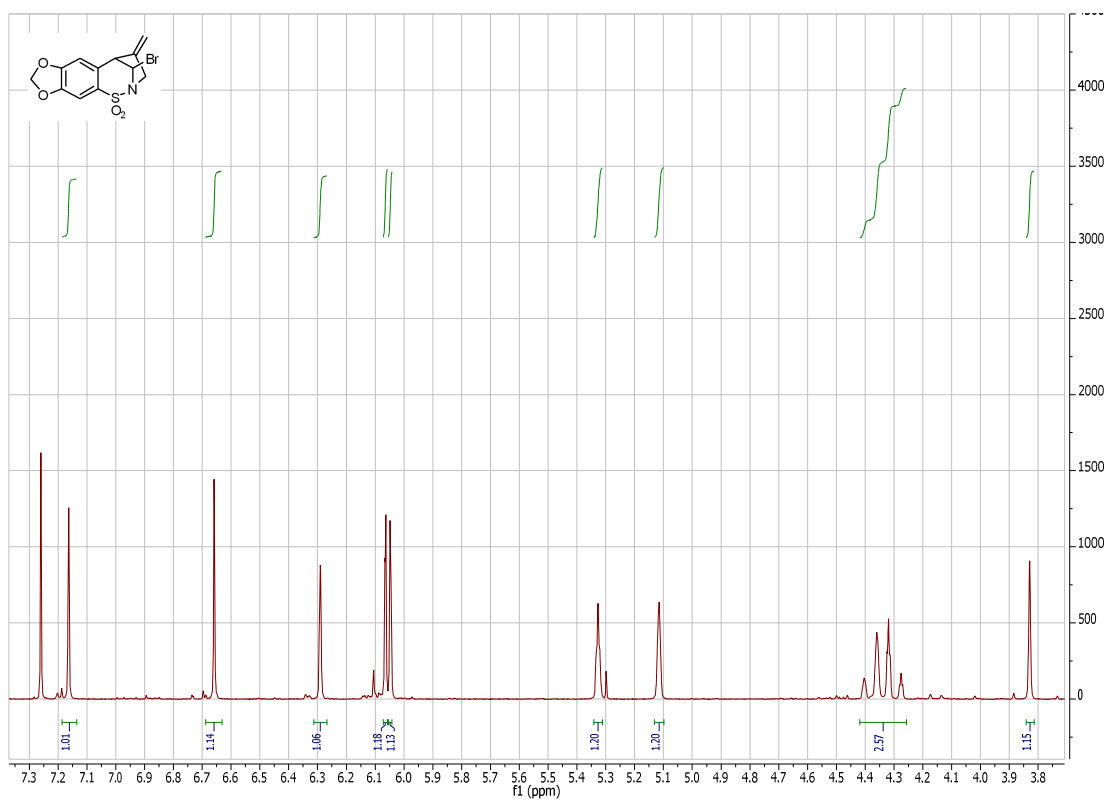
**(5*S*\*,10*S*\*)-10-Bromo-7,8-dimethoxy-4-methylene-4,5-dihydro-3*H*-2,5-methanobenzo-[*f*][1,2]thiazepine 1,1-dioxide** **17a** (CDCl<sub>3</sub>, 400 MHz);



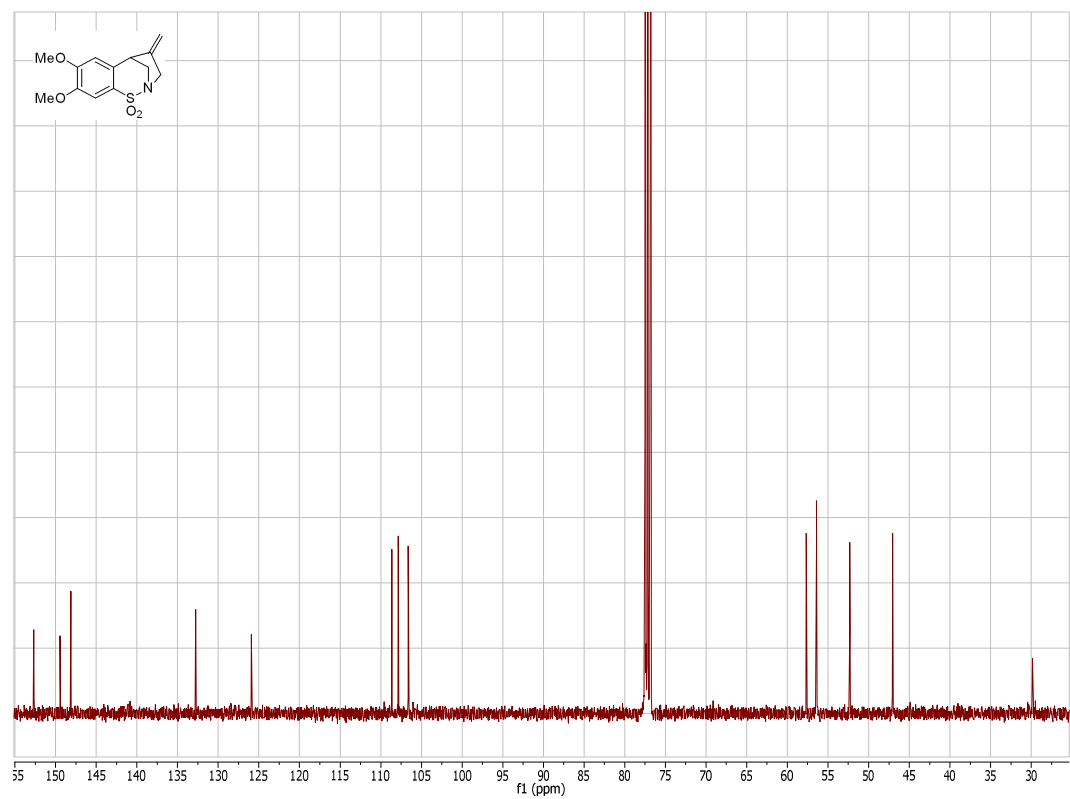
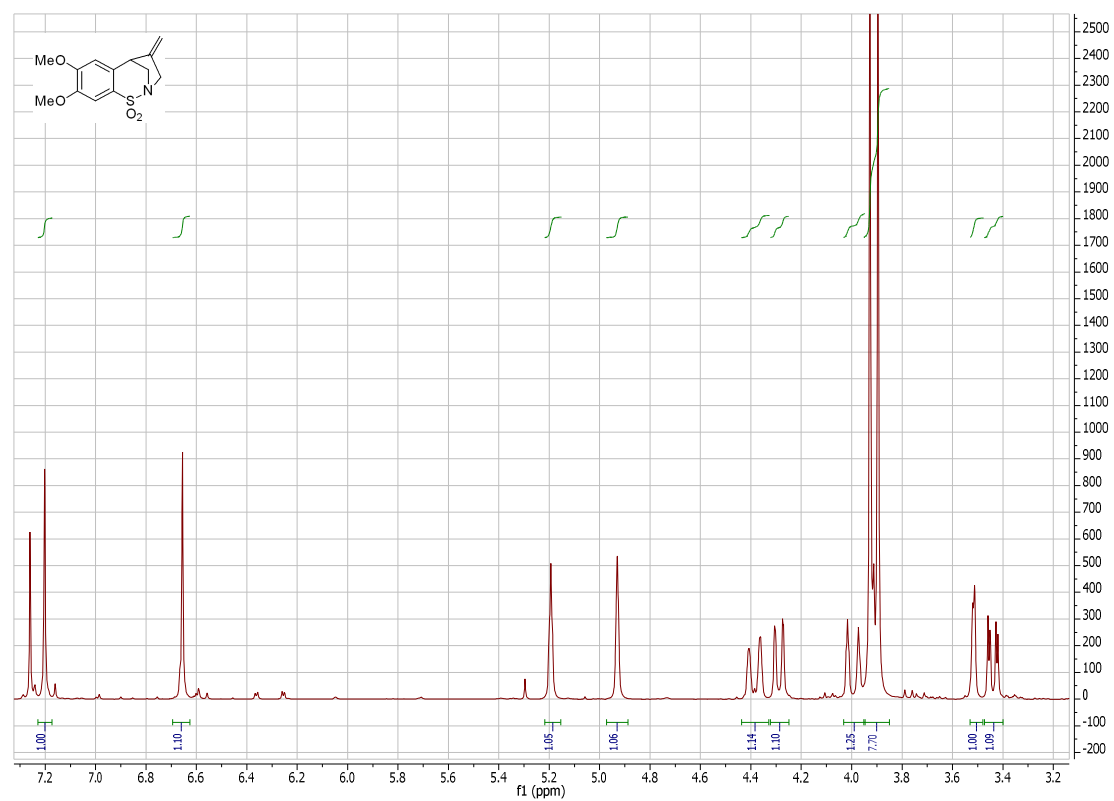
(5*S*\*,10*S*\*)-10-Iodo-7,8-dimethoxy-4-methylene-4,5-dihydro-3*H*-2,5-Methanobenzo[*f*][1,2]thiazepine 1,1-dioxide 18a  
(CDCl<sub>3</sub>, 400 MHz);



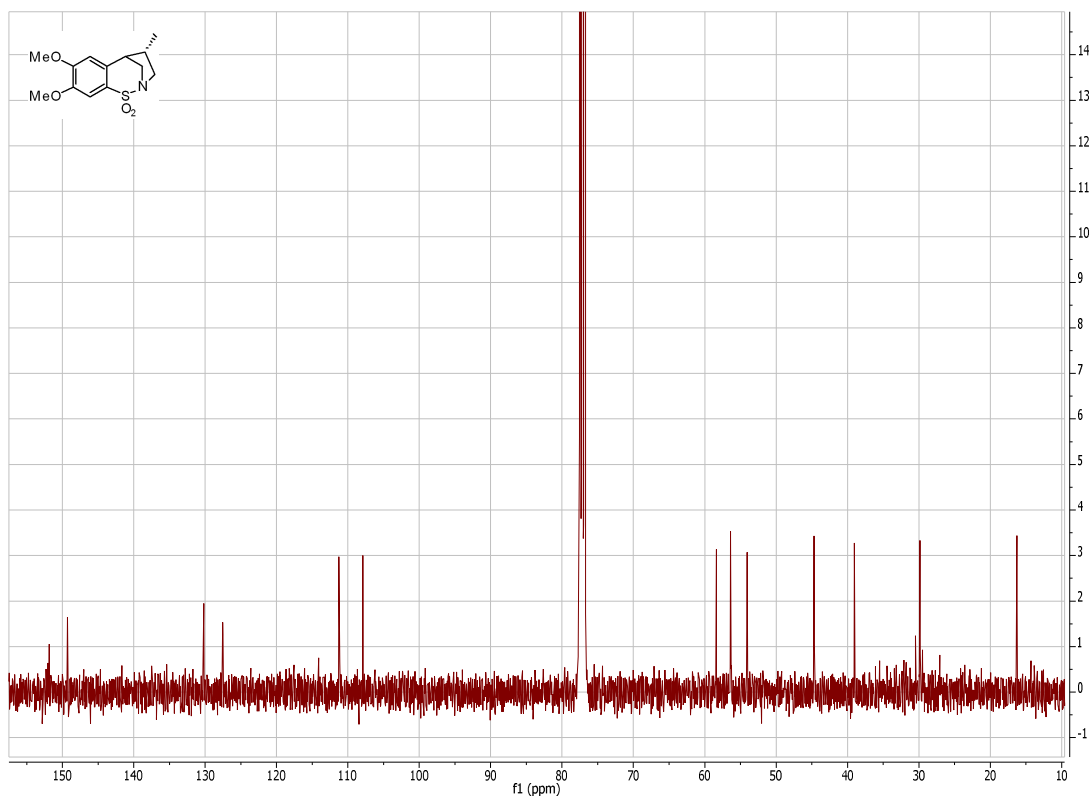
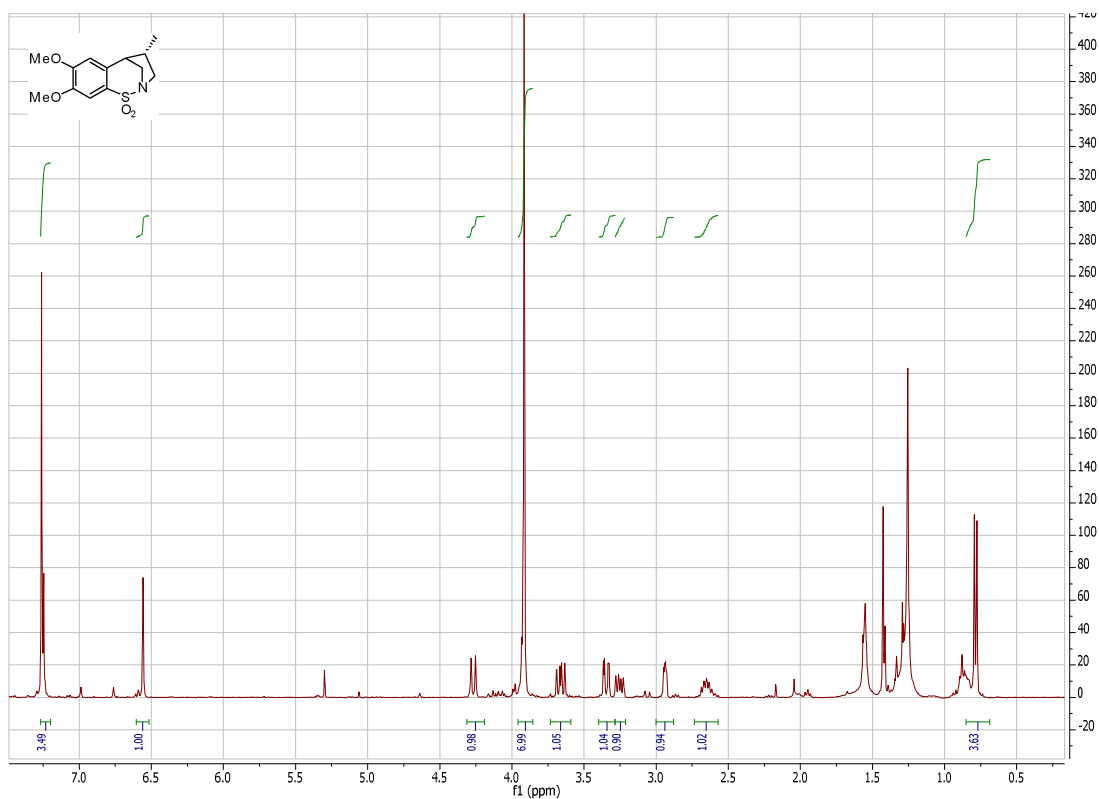
**(5*S*\*,11*S*\*)-11-Bromo-4-methylene-4,5-dihydro-3*H*-2,5-methano[1,3]-dioxolo[4',5':4,5]-benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 17b** (CDCl<sub>3</sub>, 400 MHz);



(2*R*,5*S*)-7,8-Dimethoxy-4-methylene-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]thiazepine 1,1-dioxide (CDCl<sub>3</sub>, 400 MHz);

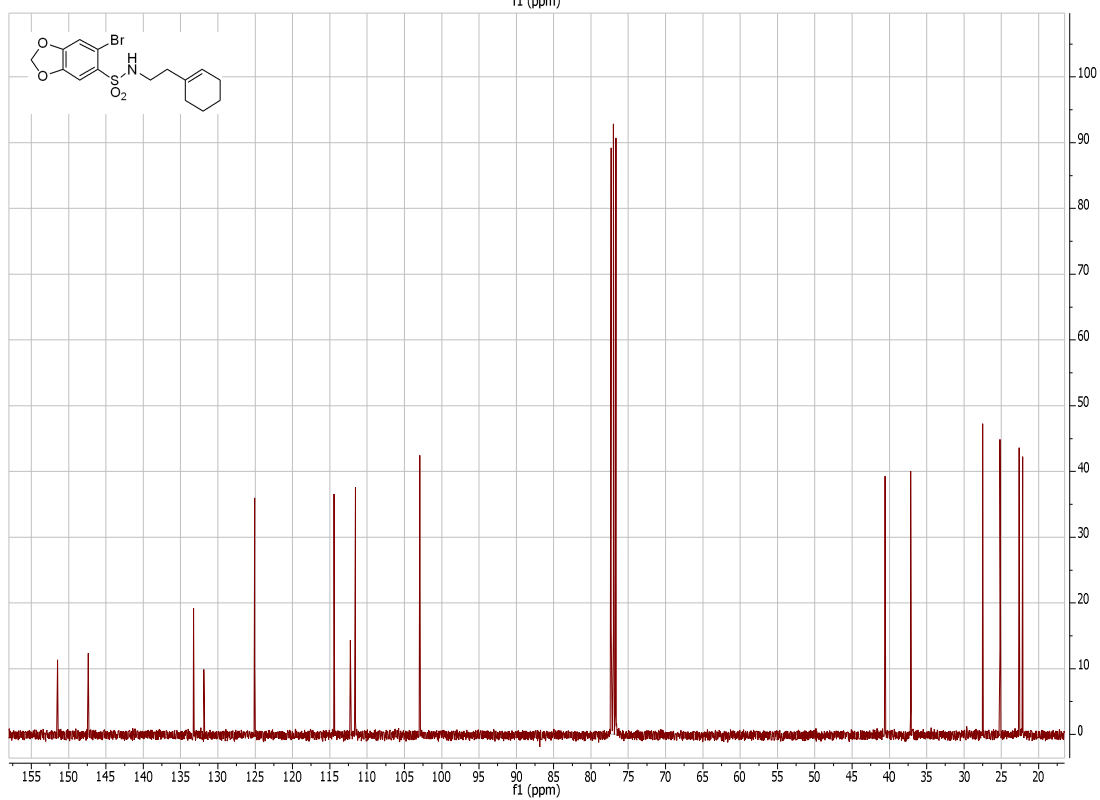
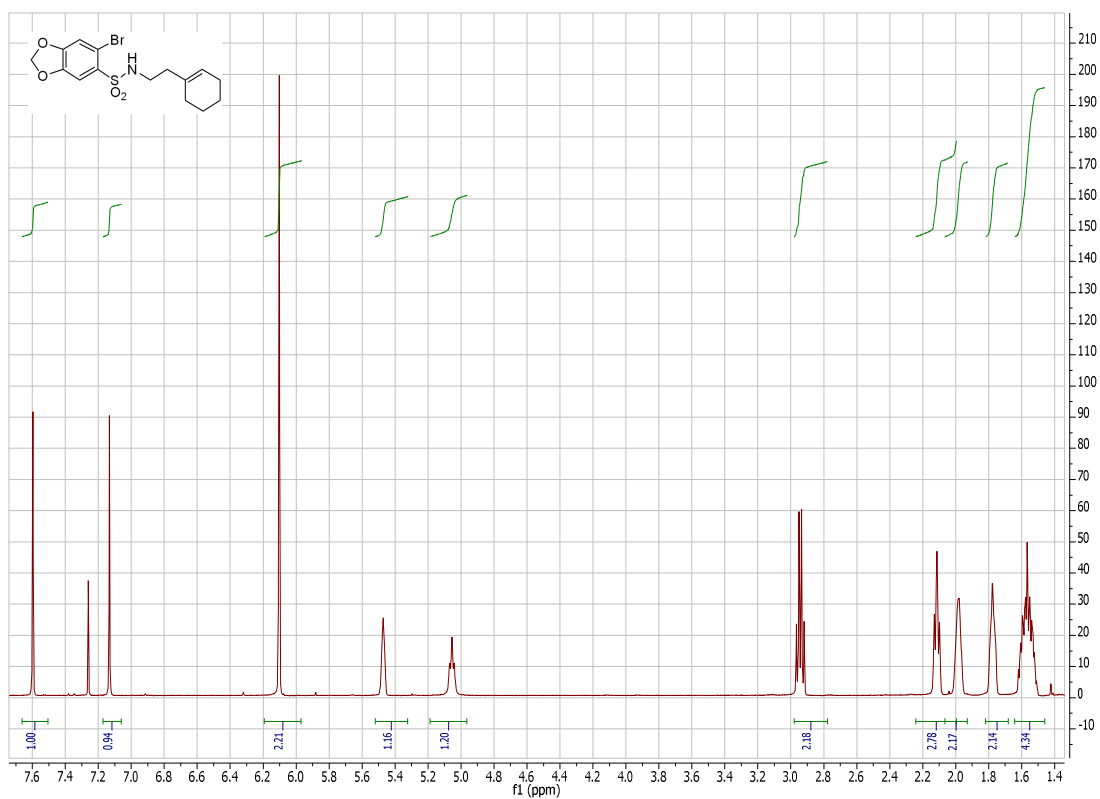


(4*S*\*,5*S*\*)-7,8-Dimethoxy-4-methyl-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]-thiazepine 1,1-dioxide 19a (CDCl<sub>3</sub>, 400 MHz);

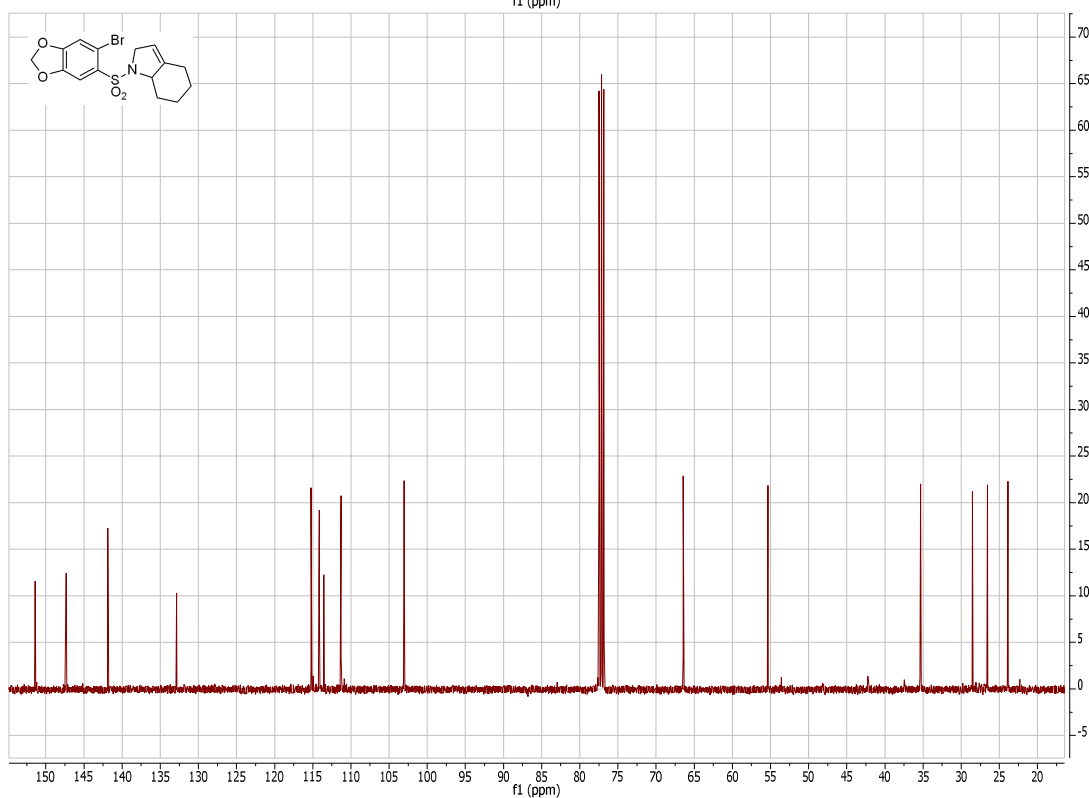
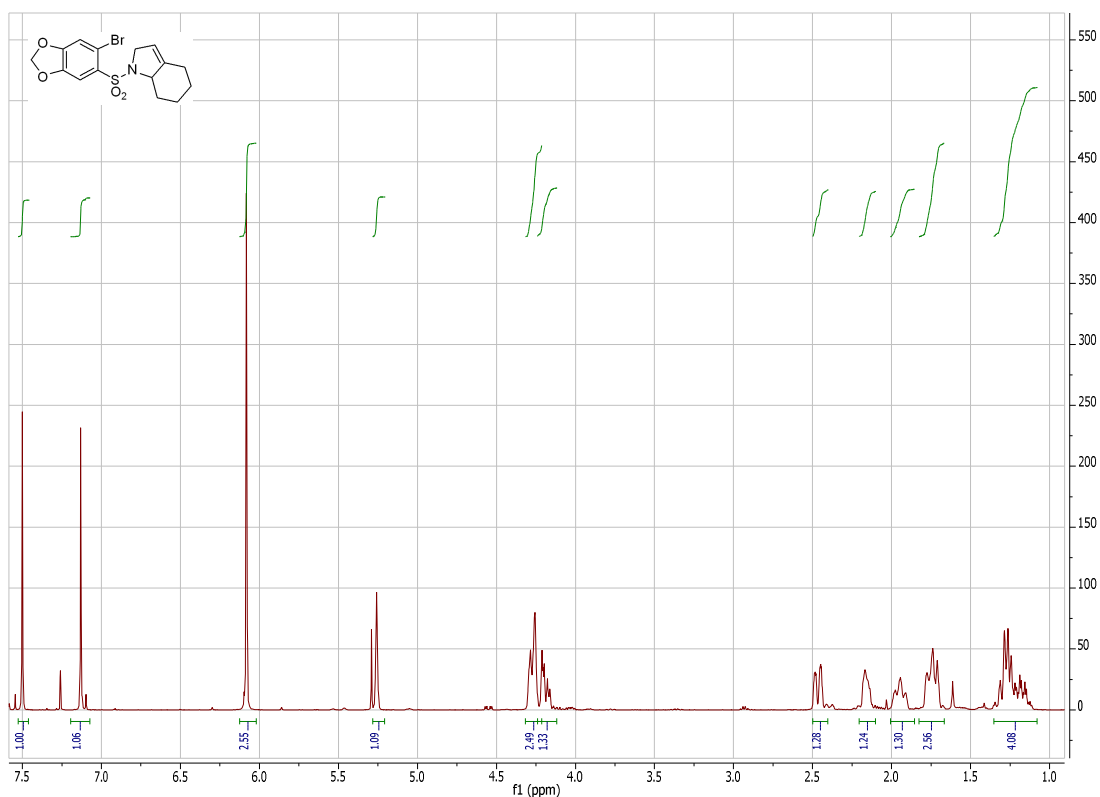




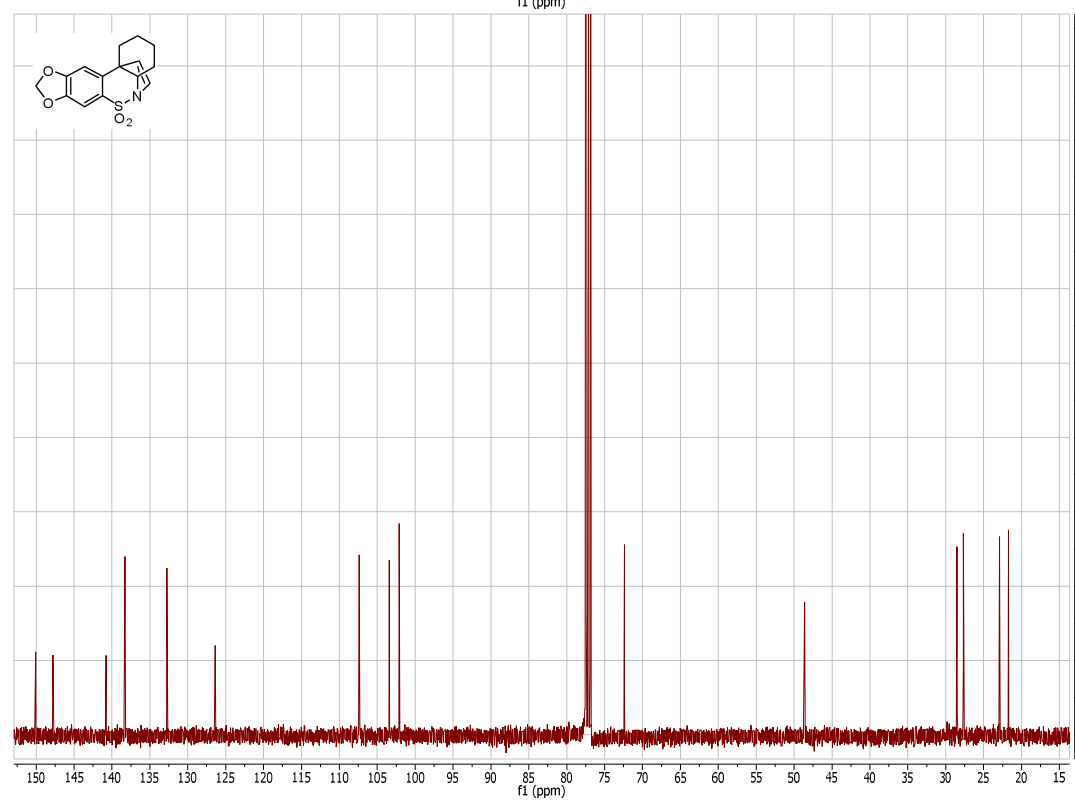
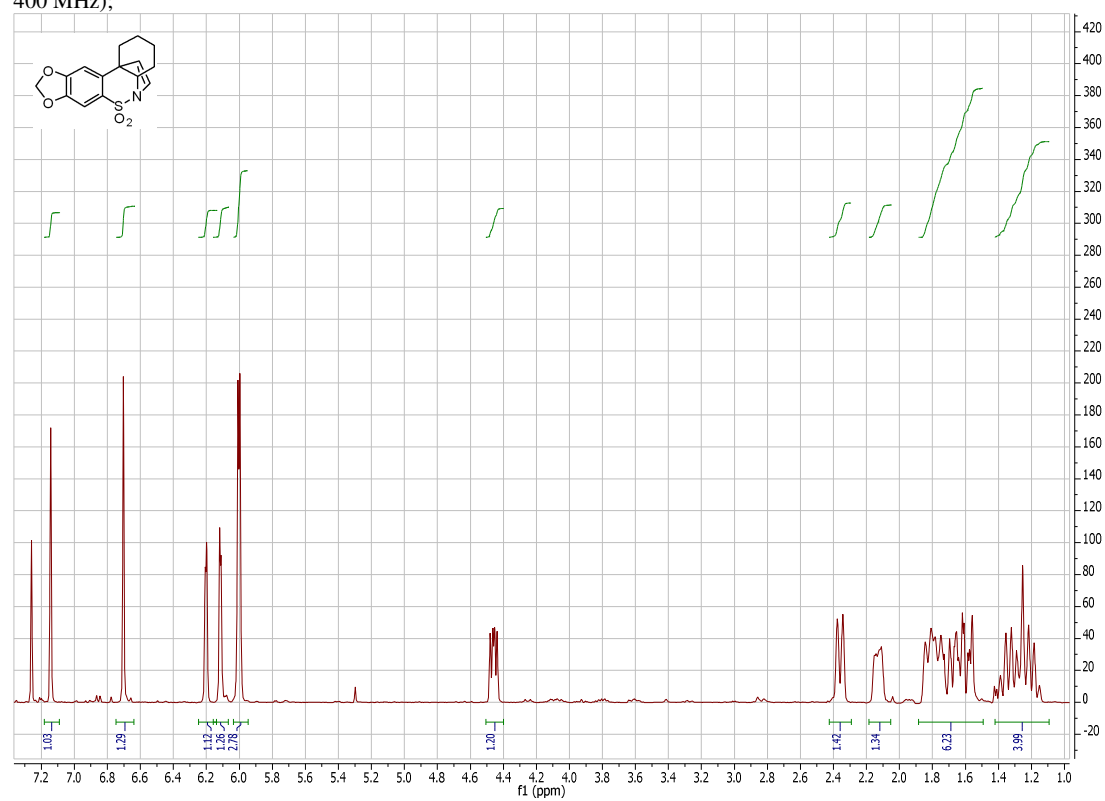
**6-Bromo-N-(2-(cyclohex-1-en-1-yl)ethyl)benzo[d][1,3]dioxole-5-sulfonamide 21b** (CDCl<sub>3</sub>, 400 MHz);



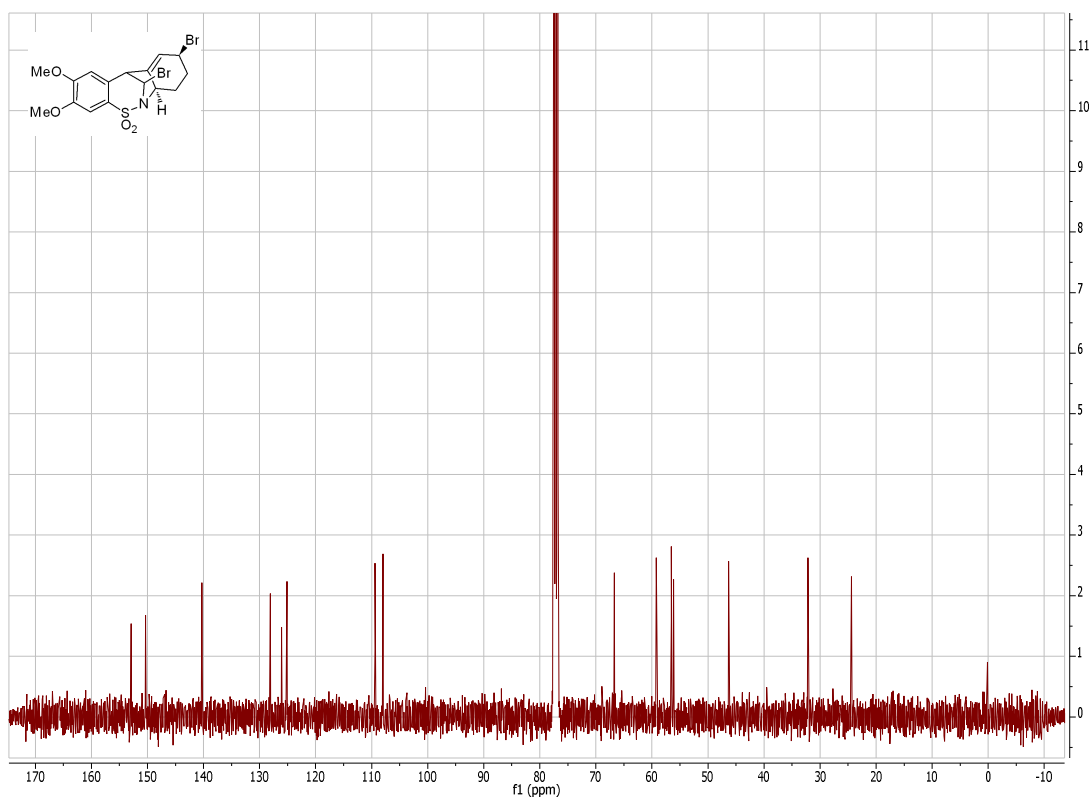
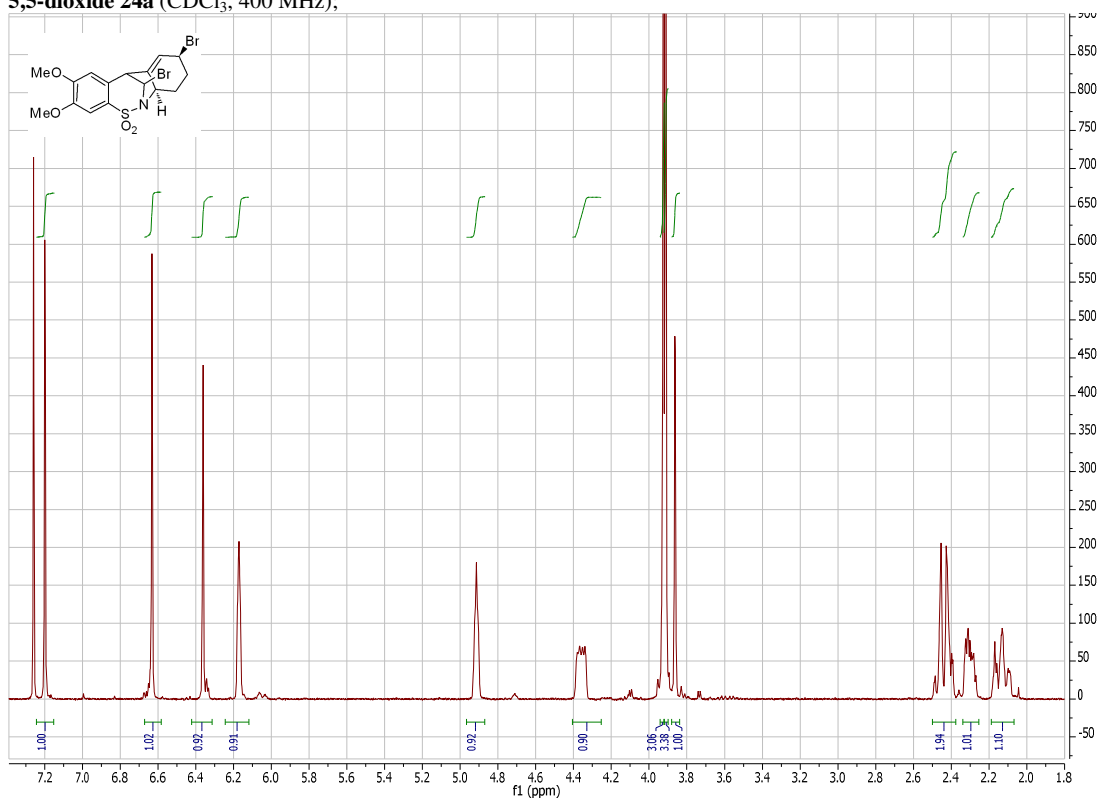
**1-((6-Bromobenzo[d][1,3]dioxol-5-yl)sulfonyl)-2,4,5,6,7,7a-hexahydro-1H-indole 22b (CDCl<sub>3</sub>, 400 MHz);**



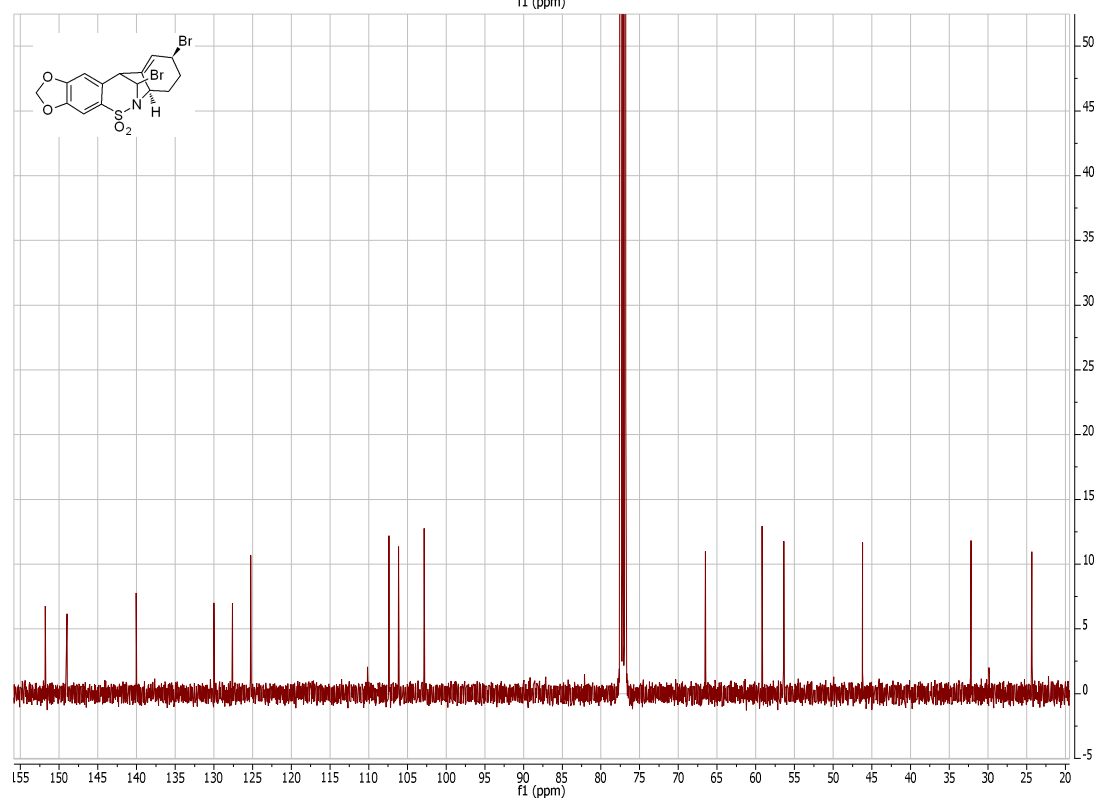
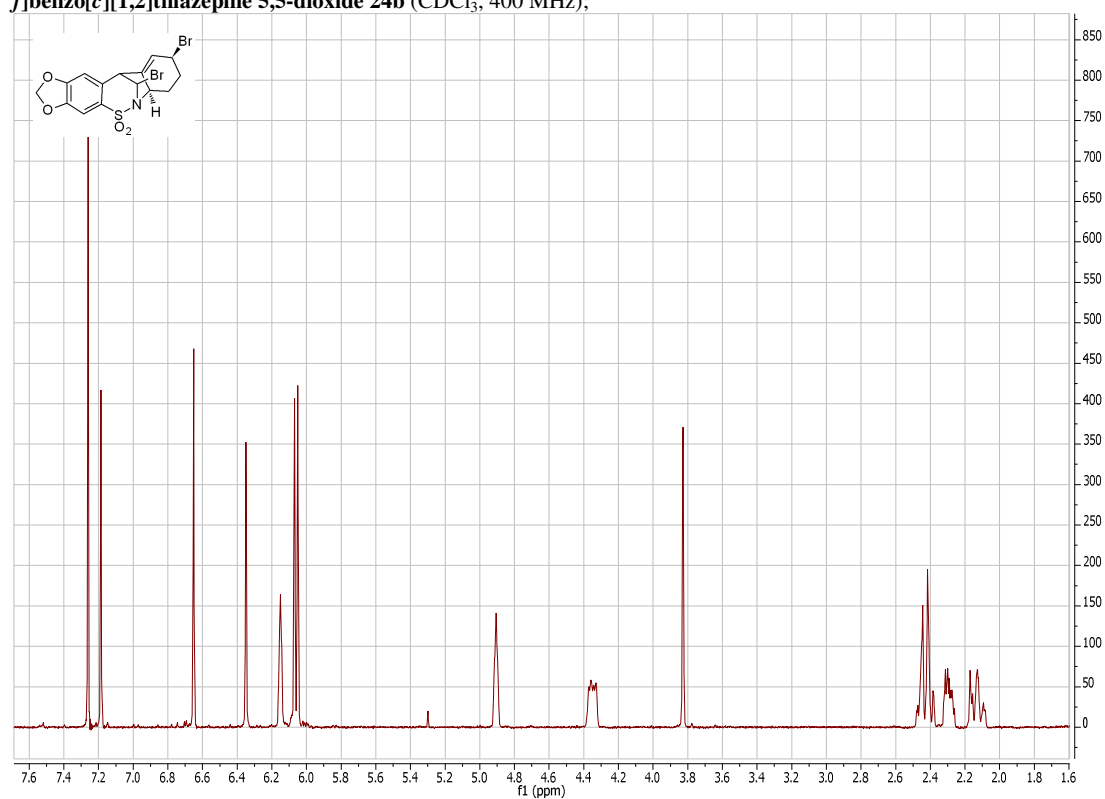
2,3,4,4a-Tetrahydro-1H-5,11b-etheno[1,3]dioxolo[4',5':4,5]benzo[1,2-e]benzo[c][1,2]-thiazine 6,6-dioxide 23b (CDCl<sub>3</sub>, 400 MHz);



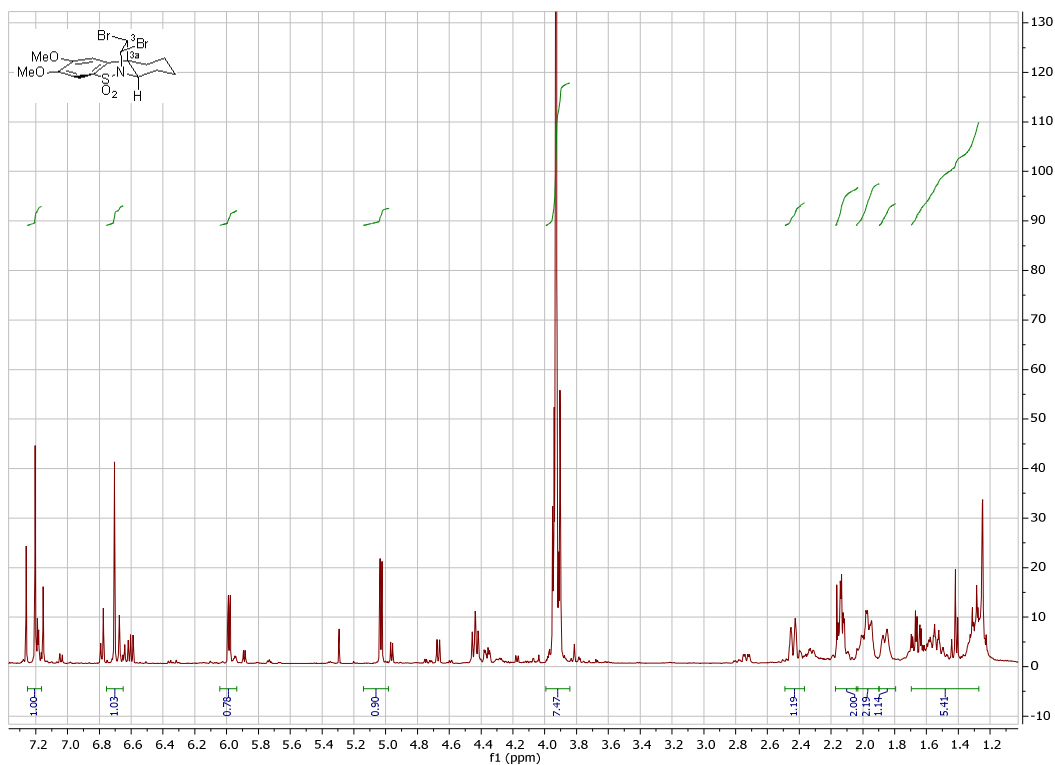
**(6a*R*\*,9*S*\*,11*S*\*,12*S*\*)-9,12-Dibromo-2,3-dimethoxy-7,8,9,11-tetrahydro-6a*H*-6,11-methanodibenzo[*c,f*][1,2]thiazepine 5,5-dioxide 24a** (CDCl<sub>3</sub>, 400 MHz);



(6a*R*\*,9*S*\*,11*S*\*,13*S*\*)-9,13-Dibromo-7,8,9,11-tetrahydro-6a*H*-6,11-methano-[1,3]-dioxolo-[4',5':4,5]benzo[1,2-*f*]benzo[*c*][1,2]thiazepine 5,5-dioxide 24b (CDCl<sub>3</sub>, 400 MHz);



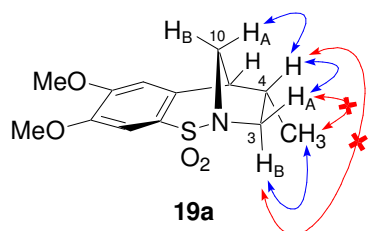
**(6a*R*\*,10a*R*\*,11*R*\*,12*S*\*)-11,12-Dibromo-2,3-dimethoxy-7,8,9,10-tetrahydro-6a*H*-6,10a-ethanodibenzo[*c,e*][1,2]thiazine 5,5-dioxide 25a** (CDCl<sub>3</sub>, 400 MHz);



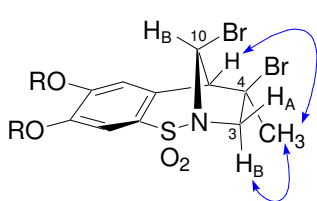
**(5a*R*\*,11b*R*\*,12*R*\*,13*S*\*)-12,13-Dibromo-2,3,4,4a-tetrahydro-1*H*-5,11b-ethano[1,3]dioxolo[4',5':4,5]benzo[1,2-*e*]benzo[*c*][1,2]thiazine 6,6-dioxide 25b** (CDCl<sub>3</sub>, 400 MHz);



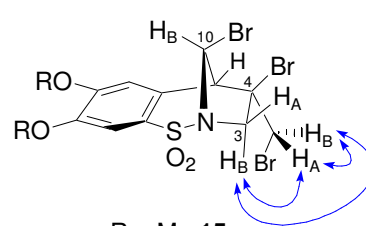
## NOESY Spectral Correlation for Compounds 19a, 14 and 15



10-H<sub>B</sub> = 4.25 ppm  
 10-H<sub>A</sub> = 3.35 ppm  
 3-H<sub>A</sub> = 3.70 ppm  
 3-H<sub>B</sub> = 3.20 ppm  
 4-H = 2.63 ppm  
 5-H = 2.92 ppm  
 CH<sub>3</sub> = 0.78 ppm

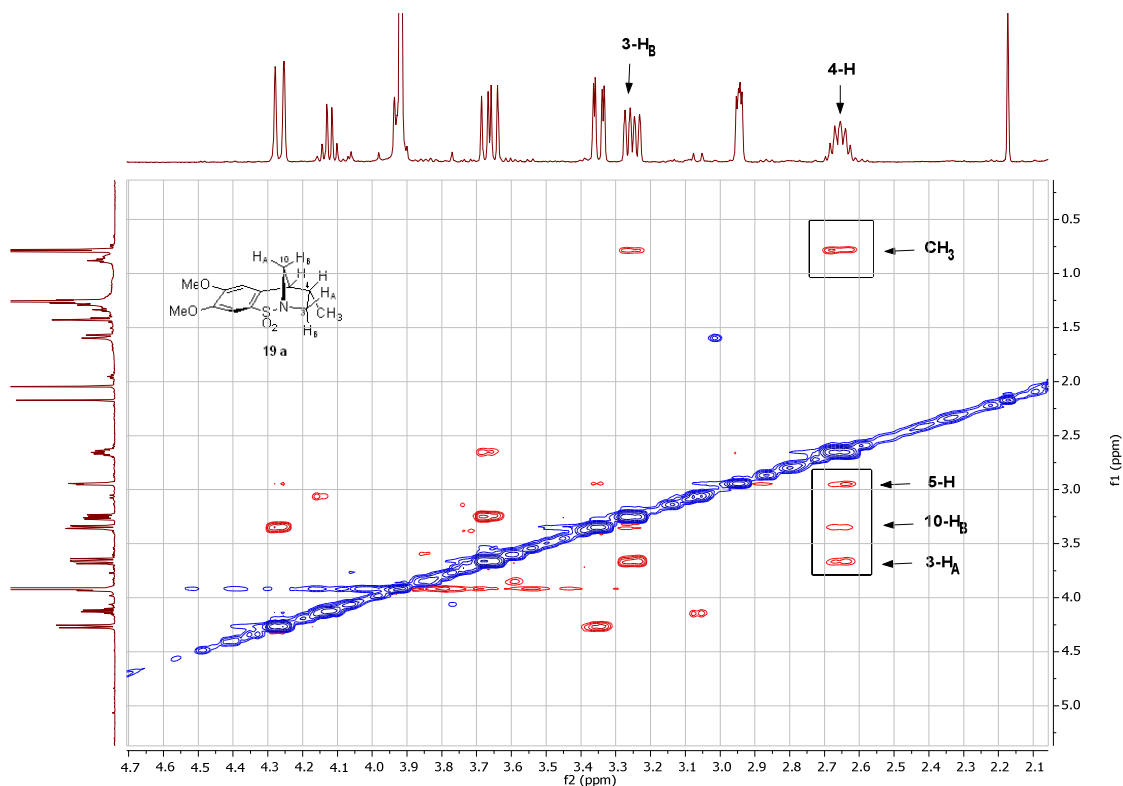


10-H<sub>B</sub> = 6.35 ppm  
 3-H<sub>A</sub> = 4.45 ppm  
 3-H<sub>B</sub> = 4.15 ppm  
 5-H = 3.90 ppm  
 CH<sub>3</sub> = 1.50 ppm

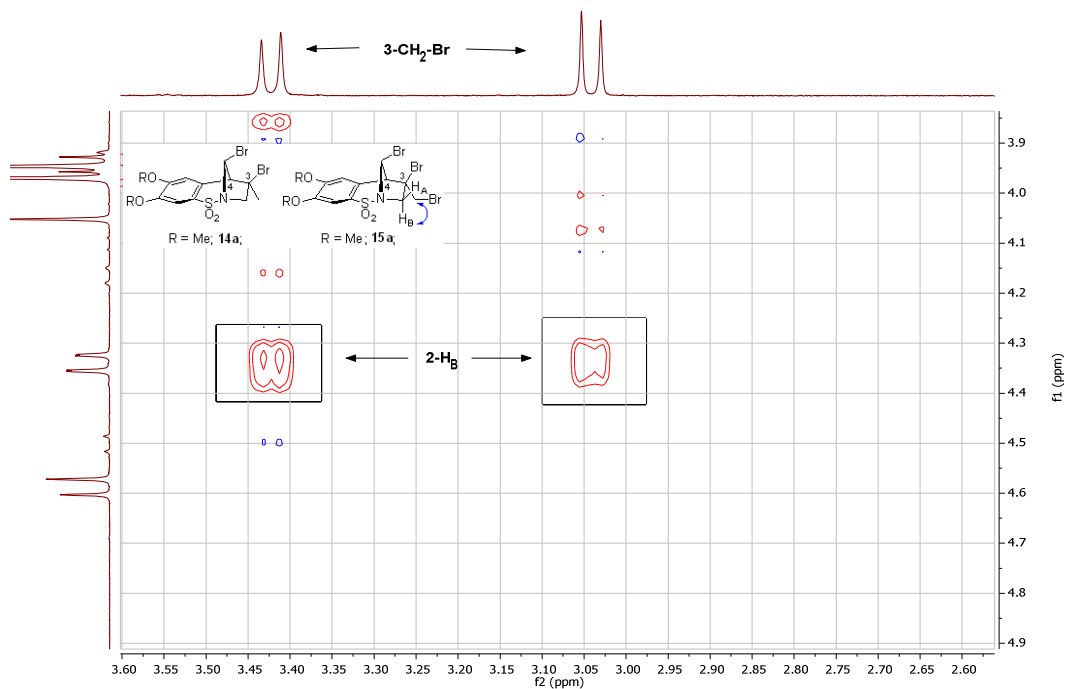


10-H<sub>B</sub> = 6.35 ppm  
 3-H<sub>A</sub> = 4.55 ppm  
 3-H<sub>B</sub> = 4.45 ppm  
 5-H = 4.00 ppm  
 CH<sub>2A/B</sub> = 3.40/3.10 ppm

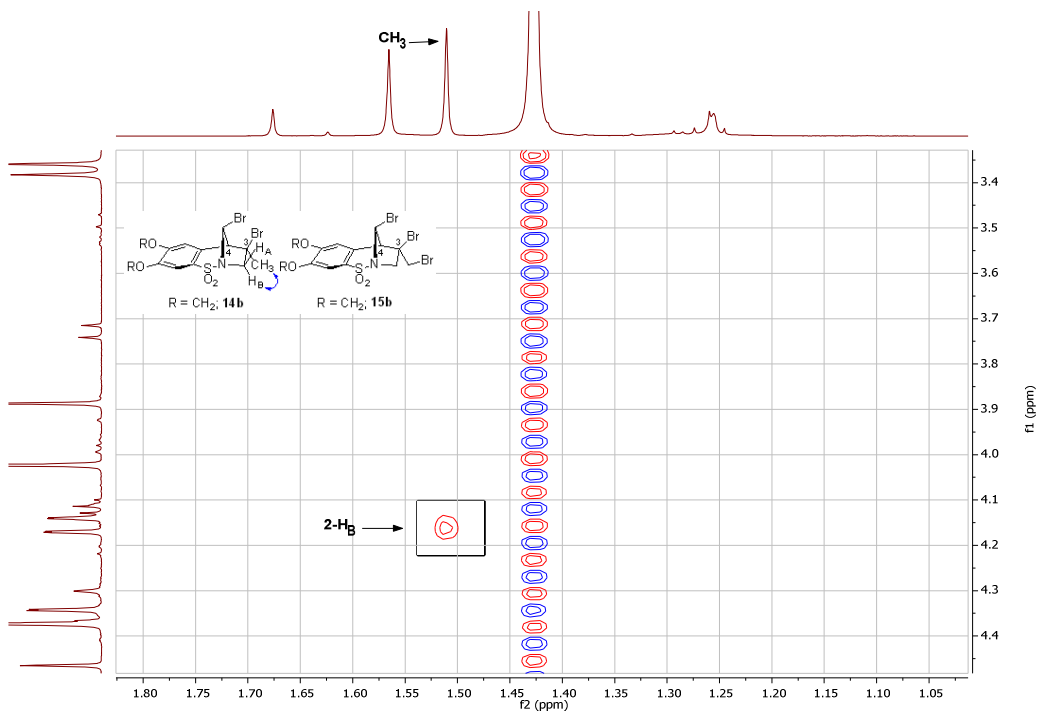
Expanded NOESY spectrum for (4*S*\*,5*S*\*)-7,8-dimethoxy-4-methyl-4,5-dihydro-3*H*-2,5-methanobenzo[*f*][1,2]-thiazepine 1,1-dioxide **19a** (CDCl<sub>3</sub>, 400 MHz; nt = 16; ni = 256; d1 = 1; mixT = 500 ms);



Expanded NOESY spectrum for the mixture of (4*R*\*,5*S*\*,10*S*\*)-4,10-dibromo-4-(bromomethyl)-7,8-dimethoxy-4,5-dihydro-3*H*-2,5-methanobenzof[1,2]thiazepine 1,1-dioxide 15a and (4*R*\*,5*S*\*,10*S*\*)-4,10-Dibromo-7,8-dimethoxy-4-methyl-4,5-dihydro-3*H*-2,5-methanobenzof[1,2]thiazepine 1,1-dioxide 14a (CDCl<sub>3</sub>, 400 MHz; nt = 64; ni = 128; d1 = 1; mixT = 500 ms);

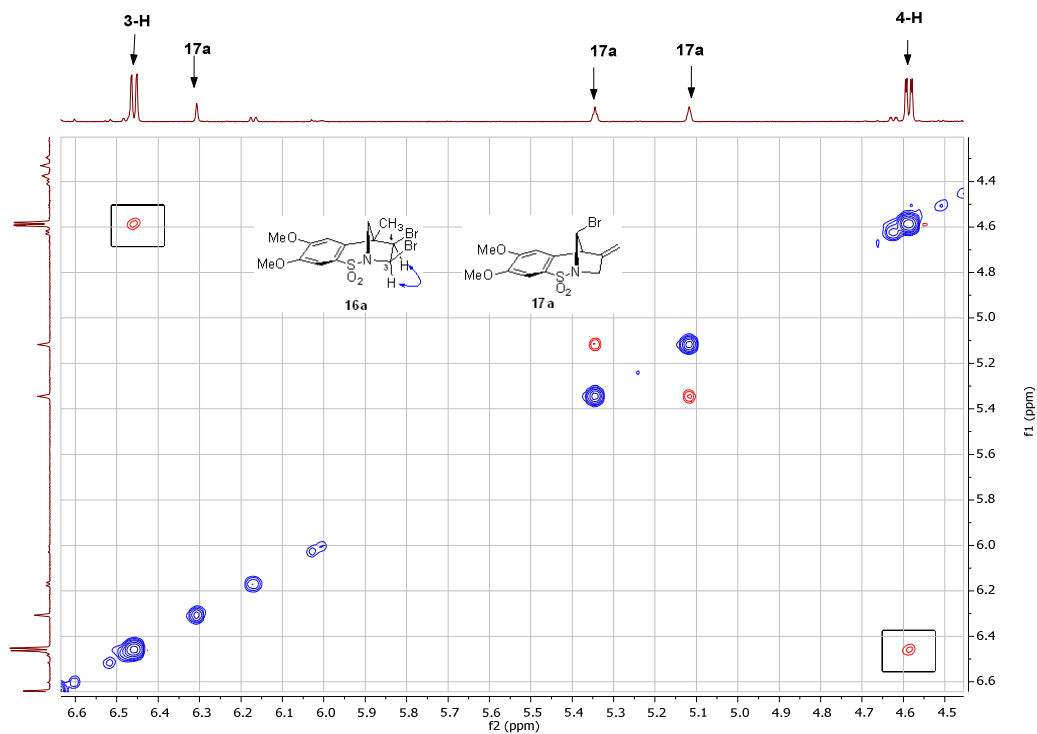


Expanded NOESY spectrum for (4*R*\*,5*S*\*,11*S*\*)-4,11-dibromo-4-(bromomethyl)-4,5-dihydro-3*H*-2,5-methano[1,3]-dioxolo[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 15b and (4*R*\*,5*S*\*,11*S*\*)-4,11-dibromo-4-methyl-4,5-dihydro-3*H*-2,5-methano[1,3]-dioxolo[4',5':4,5]benzo[1,2-*f*][1,2]thiazepine 1,1-dioxide 14b (CDCl<sub>3</sub>, 400 MHz; nt = 64; ni = 128; d1 = 1; mixT = 500 ms);

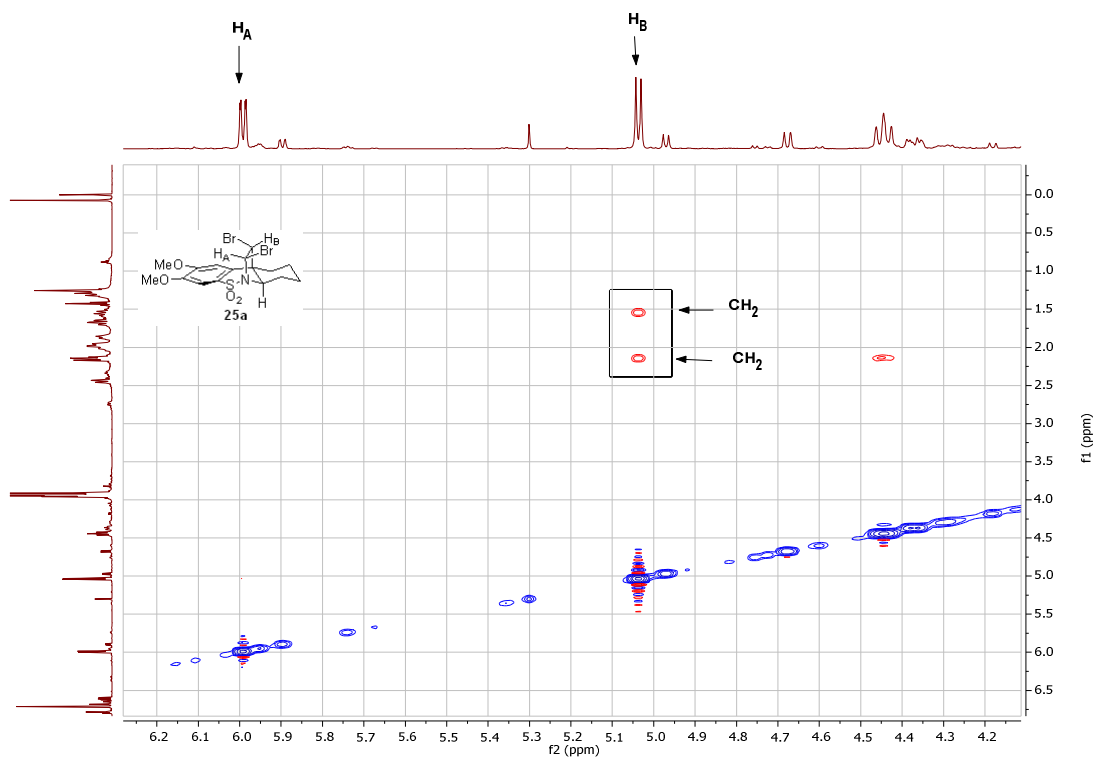




Expanded NOESY spectrum for (3*R*\*,4*R*\*,5*S*\*)-3,4-dibromo-7,8-dimethoxy-5-methyl-4,5-dihydro-3*H*-2,5-methanobenzof[1,2]thiazepine 1,1-dioxide **16a** {contaminated with **17a**} (CDCl<sub>3</sub>, 400 MHz; nt = 4; ni = 128; d1 = 1; mixT = 500 ms);



(6*aR*\*,10*aR*\*,11*R*\*,12*S*\*)-11,12-dibromo-2,3-dimethoxy-7,8,9,10-tetrahydro-6*aH*-6,10a-ethanodibenzo[*c,e*][1,2]thiazine 5,5-dioxide **25a** (CDCl<sub>3</sub>, 400 MHz; nt = 8; ni = 256; d1 = 1; mixT = 500 ms);



## X-Ray Crystallographic Data for Compound 13b

CCDC: 947375

Empirical formula	C <sub>12</sub> H <sub>11</sub> N O <sub>4</sub> S	
Formula weight	265.28	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1 (#2)	
Unit cell dimensions	a = 8.7295(3) Å	α = 96.205(2)°.
	b = 9.9483(2) Å	β = 104.131(3)°.
	c = 13.9369(4) Å	γ = 100.355(2)°.
Volume	1139.85(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.546 Mg/m <sup>3</sup>	
Absorption coefficient	2.613 mm <sup>-1</sup>	
F(000)	552	
Crystal size	0.2222 x 0.1045 x 0.0262 mm <sup>3</sup>	
Theta range for data collection	4.58 to 77.03°.	
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	
Reflections collected	32389	
Independent reflections	4641 [R(int) = 0.0453]	
Completeness to theta = 68.00°	98.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.937 and 0.688	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4641 / 0 / 327	
Goodness-of-fit on F <sup>2</sup>	1.092	
Final R indices [I > 2σ(I)]	R1 = 0.0557, wR2 = 0.1371	
R indices (all data)	R1 = 0.0585, wR2 = 0.1388	
Largest diff. peak and hole	0.664 and -0.596 e.Å <sup>-3</sup>	

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

Atom	x	y	z	U(eq)
S(1)	3692(1)	3237(1)	1688(1)	28(1)
O(1)	4878(3)	3966(2)	1271(2)	38(1)
O(2)	2032(3)	2939(2)	1115(2)	40(1)
C(1)	4228(3)	1679(2)	2014(2)	24(1)
C(2)	4272(3)	716(3)	1211(2)	26(1)
C(3)	4711(3)	-481(3)	1458(2)	25(1)
O(3)	4820(3)	-1604(2)	827(2)	33(1)
C(4)	5086(3)	-719(3)	2434(2)	26(1)
O(4)	5420(3)	-2016(2)	2464(2)	34(1)
C(12)	5485(4)	-2510(3)	1474(2)	33(1)
C(5)	5036(3)	212(3)	3221(2)	28(1)
C(6)	4591(3)	1460(3)	3012(2)	25(1)
C(7)	4484(3)	2553(3)	3850(2)	29(1)
C(11)	4335(4)	1984(3)	4809(2)	42(1)
C(8)	3088(4)	3253(3)	3417(2)	38(1)
N(1)	3813(3)	4170(2)	2781(2)	30(1)
C(9)	5908(4)	3758(3)	4011(2)	36(1)
C(10)	5508(4)	4614(3)	3394(2)	38(1)
S(2)	10338(1)	7966(1)	4027(1)	34(1)
O(5)	8957(3)	7561(3)	4392(2)	50(1)
O(6)	11774(3)	8799(2)	4717(2)	42(1)
C(13)	9823(3)	8829(3)	2977(2)	27(1)
C(14)	9292(3)	10060(3)	3166(2)	29(1)
C(15)	8911(3)	10739(3)	2364(2)	27(1)
O(7)	8337(3)	11936(2)	2328(2)	32(1)
C(16)	9011(3)	10227(3)	1423(2)	27(1)
O(8)	8462(3)	11045(2)	750(2)	32(1)

C(24)	8307(4)	12265(3)	1347(2)	31(1)
C(17)	9536(3)	9024(3)	1228(2)	28(1)
C(18)	9958(3)	8299(3)	2031(2)	26(1)
C(19)	10517(4)	6935(3)	1889(2)	29(1)
C(23)	11062(4)	6671(3)	946(2)	34(1)
C(20)	11805(4)	6880(3)	2853(2)	30(1)
N(2)	10812(3)	6532(2)	3564(2)	35(1)
C(21)	9163(4)	5782(3)	1959(3)	40(1)
C(22)	9354(4)	5597(3)	2902(3)	42(1)

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Table 2. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

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S(1)–O(1)	1.433(2)
S(1)–O(2)	1.433(2)
S(1)–N(1)	1.665(2)
S(1)–C(1)	1.771(2)
C(1)–C(6)	1.400(4)
C(1)–C(2)	1.405(4)
C(2)–C(3)	1.368(4)
C(2)–H(2)	0.9500
C(3)–C(4)	1.377(4)
C(3)–O(3)	1.377(3)
O(3)–C(12)	1.440(3)
C(4)–C(5)	1.371(4)
C(4)–O(4)	1.375(3)
O(4)–C(12)	1.431(4)
C(12)–H(12A)	0.9900
C(12)–H(12B)	0.9900
C(5)–C(6)	1.405(4)
C(5)–H(5)	0.9500
C(6)–C(7)	1.540(3)
C(7)–C(9)	1.517(4)
C(7)–C(11)	1.533(4)
C(7)–C(8)	1.540(4)
C(11)–H(11A)	0.9800
C(11)–H(11B)	0.9800
C(11)–H(11C)	0.9800
C(8)–N(1)	1.503(4)
C(8)–H(8A)	0.9900
C(8)–H(8B)	0.9900
N(1)–C(10)	1.477(4)
C(9)–C(10)	1.306(5)

C(9)–H(9)	0.9500
C(10)–H(10)	0.9500
S(2)–O(5)	1.429(2)
S(2)–O(6)	1.431(3)
S(2)–N(2)	1.663(2)
S(2)–C(13)	1.780(3)
C(13)–C(14)	1.407(3)
C(13)–C(18)	1.408(4)
C(14)–C(15)	1.370(4)
C(14)–H(14)	0.9500
C(15)–O(7)	1.374(3)
C(15)–C(16)	1.384(4)
O(7)–C(24)	1.435(3)
C(16)–O(8)	1.364(3)
C(16)–C(17)	1.379(3)
O(8)–C(24)	1.442(3)
C(24)–H(24A)	0.9900
C(24)–H(24B)	0.9900
C(17)–C(18)	1.406(4)
C(17)–H(17)	0.9500
C(18)–C(19)	1.531(3)
C(19)–C(23)	1.516(4)
C(19)–C(21)	1.522(4)
C(19)–C(20)	1.541(4)
C(23)–H(23A)	0.9800
C(23)–H(23B)	0.9800
C(23)–H(23C)	0.9800
C(20)–N(2)	1.496(3)
C(20)–H(20A)	0.9900
C(20)–H(20B)	0.9900
N(2)–C(22)	1.467(4)
C(21)–C(22)	1.321(5)

C(21)–H(21)	0.9500
C(22)–H(22)	0.9500
O(1)–S(1)–O(2)	118.10(14)
O(1)–S(1)–N(1)	107.62(13)
O(2)–S(1)–N(1)	107.27(13)
O(1)–S(1)–C(1)	109.74(12)
O(2)–S(1)–C(1)	109.00(13)
N(1)–S(1)–C(1)	104.18(12)
C(6)–C(1)–C(2)	123.6(2)
C(6)–C(1)–S(1)	120.94(19)
C(2)–C(1)–S(1)	115.5(2)
C(3)–C(2)–C(1)	115.9(2)
C(3)–C(2)–H(2)	122.1
C(1)–C(2)–H(2)	122.1
C(2)–C(3)–C(4)	121.7(2)
C(2)–C(3)–O(3)	128.1(3)
C(4)–C(3)–O(3)	110.1(2)
C(3)–O(3)–C(12)	105.4(2)
C(5)–C(4)–O(4)	127.6(2)
C(5)–C(4)–C(3)	122.8(2)
O(4)–C(4)–C(3)	109.6(2)
C(4)–O(4)–C(12)	106.0(2)
O(4)–C(12)–O(3)	107.2(2)
O(4)–C(12)–H(12A)	110.3
O(3)–C(12)–H(12A)	110.3
O(4)–C(12)–H(12B)	110.3
O(3)–C(12)–H(12B)	110.3
H(12A)–C(12)–H(12B)	108.5
C(4)–C(5)–C(6)	118.0(2)
C(4)–C(5)–H(5)	121.0
C(6)–C(5)–H(5)	121.0
C(1)–C(6)–C(5)	118.1(2)

C(1)–C(6)–C(7)	120.6(2)
C(5)–C(6)–C(7)	121.3(2)
C(9)–C(7)–C(11)	113.9(3)
C(9)–C(7)–C(6)	107.5(2)
C(11)–C(7)–C(6)	113.9(2)
C(9)–C(7)–C(8)	99.8(2)
C(11)–C(7)–C(8)	112.6(2)
C(6)–C(7)–C(8)	108.1(2)
C(7)–C(11)–H(11A)	109.5
C(7)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11B)	109.5
C(7)–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11C)	109.5
H(11B)–C(11)–H(11C)	109.5
N(1)–C(8)–C(7)	101.8(2)
N(1)–C(8)–H(8A)	111.4
C(7)–C(8)–H(8A)	111.4
N(1)–C(8)–H(8B)	111.4
C(7)–C(8)–H(8B)	111.4
H(8A)–C(8)–H(8B)	109.3
C(10)–N(1)–C(8)	101.3(2)
C(10)–N(1)–S(1)	110.97(18)
C(8)–N(1)–S(1)	109.46(18)
C(10)–C(9)–C(7)	109.1(3)
C(10)–C(9)–H(9)	125.4
C(7)–C(9)–H(9)	125.4
C(9)–C(10)–N(1)	112.2(3)
C(9)–C(10)–H(10)	123.9
N(1)–C(10)–H(10)	123.9
O(5)–S(2)–O(6)	118.01(16)
O(5)–S(2)–N(2)	107.67(14)
O(6)–S(2)–N(2)	107.54(14)



O(5)–S(2)–C(13)	110.27(14)
O(6)–S(2)–C(13)	108.09(13)
N(2)–S(2)–C(13)	104.37(13)
C(14)–C(13)–C(18)	123.2(3)
C(14)–C(13)–S(2)	115.5(2)
C(18)–C(13)–S(2)	121.3(2)
C(15)–C(14)–C(13)	115.9(2)
C(15)–C(14)–H(14)	122.1
C(13)–C(14)–H(14)	122.1
C(14)–C(15)–O(7)	128.3(2)
C(14)–C(15)–C(16)	121.9(2)
O(7)–C(15)–C(16)	109.7(2)
C(15)–O(7)–C(24)	105.2(2)
O(8)–C(16)–C(17)	127.0(2)
O(8)–C(16)–C(15)	110.1(2)
C(17)–C(16)–C(15)	122.9(3)
C(16)–O(8)–C(24)	105.1(2)
O(7)–C(24)–O(8)	107.2(2)
O(7)–C(24)–H(24A)	110.3
O(8)–C(24)–H(24A)	110.3
O(7)–C(24)–H(24B)	110.3
O(8)–C(24)–H(24B)	110.3
H(24A)–C(24)–H(24B)	108.5
C(16)–C(17)–C(18)	117.3(2)
C(16)–C(17)–H(17)	121.4
C(18)–C(17)–H(17)	121.4
C(17)–C(18)–C(13)	118.8(2)
C(17)–C(18)–C(19)	121.5(2)
C(13)–C(18)–C(19)	119.7(2)
C(23)–C(19)–C(21)	112.9(2)
C(23)–C(19)–C(18)	114.7(2)
C(21)–C(19)–C(18)	107.3(2)

C(23)–C(19)–C(20)	113.3(2)
C(21)–C(19)–C(20)	99.4(2)
C(18)–C(19)–C(20)	107.9(2)
C(19)–C(23)–H(23A)	109.5
C(19)–C(23)–H(23B)	109.5
H(23A)–C(23)–H(23B)	109.5
C(19)–C(23)–H(23C)	109.5
H(23A)–C(23)–H(23C)	109.5
H(23B)–C(23)–H(23C)	109.5
N(2)–C(20)–C(19)	102.7(2)
N(2)–C(20)–H(20A)	111.2
C(19)–C(20)–H(20A)	111.2
N(2)–C(20)–H(20B)	111.2
C(19)–C(20)–H(20B)	111.2
H(20A)–C(20)–H(20B)	109.1
C(22)–N(2)–C(20)	102.2(2)
C(22)–N(2)–S(2)	109.75(19)
C(20)–N(2)–S(2)	108.97(18)
C(22)–C(21)–C(19)	109.7(3)
C(22)–C(21)–H(21)	125.1
C(19)–C(21)–H(21)	125.1
C(21)–C(22)–N(2)	111.4(3)
C(21)–C(22)–H(22)	124.3
N(2)–C(22)–H(22)	124.3

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Symmetry transformations used to generate equivalent atoms:

Table 3. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
S(1)	39(1)	20(1)	32(1)	8(1)	13(1)	15(1)
O(1)	58(1)	26(1)	43(1)	16(1)	27(1)	17(1)
O(2)	44(1)	35(1)	42(1)	3(1)	4(1)	22(1)
C(1)	24(1)	18(1)	31(1)	6(1)	10(1)	8(1)
C(2)	33(1)	25(1)	27(1)	8(1)	12(1)	12(1)
C(3)	28(1)	18(1)	31(1)	2(1)	11(1)	8(1)
O(3)	47(1)	22(1)	36(1)	4(1)	16(1)	17(1)
C(4)	29(1)	18(1)	36(1)	9(1)	12(1)	9(1)
O(4)	48(1)	20(1)	44(1)	12(1)	19(1)	17(1)
C(12)	37(2)	20(1)	47(2)	7(1)	16(1)	14(1)
C(5)	35(2)	25(1)	29(1)	8(1)	12(1)	11(1)
C(6)	25(1)	21(1)	29(1)	4(1)	10(1)	6(1)
C(7)	31(1)	26(1)	30(1)	2(1)	10(1)	9(1)
C(11)	54(2)	40(2)	38(2)	6(1)	21(2)	13(1)
C(8)	43(2)	33(2)	41(2)	-3(1)	20(1)	10(1)
N(1)	36(1)	20(1)	36(1)	3(1)	14(1)	11(1)
C(9)	37(2)	33(2)	38(2)	-2(1)	11(1)	7(1)
C(10)	41(2)	31(2)	43(2)	1(1)	14(1)	11(1)
S(2)	44(1)	33(1)	36(1)	10(1)	23(1)	18(1)
O(5)	64(2)	50(1)	62(2)	25(1)	46(1)	27(1)
O(6)	56(1)	40(1)	35(1)	3(1)	14(1)	18(1)
C(13)	30(1)	22(1)	34(1)	5(1)	15(1)	9(1)
C(14)	34(2)	25(1)	31(1)	0(1)	15(1)	10(1)
C(15)	30(1)	17(1)	36(1)	-2(1)	14(1)	9(1)
O(7)	45(1)	21(1)	37(1)	2(1)	17(1)	16(1)
C(16)	32(1)	18(1)	33(1)	2(1)	13(1)	8(1)
O(8)	48(1)	21(1)	32(1)	2(1)	13(1)	16(1)

C(24)	40(2)	18(1)	38(2)	1(1)	15(1)	12(1)
C(17)	38(2)	20(1)	30(1)	-1(1)	13(1)	11(1)
C(18)	28(1)	19(1)	34(1)	1(1)	12(1)	7(1)
C(19)	36(2)	19(1)	36(2)	2(1)	14(1)	12(1)
C(23)	41(2)	27(1)	36(2)	0(1)	11(1)	17(1)
C(20)	36(2)	25(1)	37(2)	6(1)	18(1)	12(1)
N(2)	45(2)	29(1)	43(1)	12(1)	25(1)	16(1)
C(21)	36(2)	19(1)	64(2)	1(1)	14(2)	9(1)
C(22)	41(2)	23(1)	72(2)	11(1)	28(2)	9(1)

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Table 4. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

Atom	x	y	z	U(eq)
H(2)	4012	885	538	32
H(12A)	4846	-3471	1248	39
H(12B)	6617	-2501	1464	39
H(5)	5295	19	3888	34
H(11A)	5337	1701	5119	63
H(11B)	3428	1183	4645	63
H(11C)	4146	2703	5278	63
H(8A)	2120	2564	3009	46
H(8B)	2793	3800	3955	46
H(9)	6927	3872	4486	44
H(10)	6225	5427	3344	45
H(14)	9203	10400	3810	34
H(24A)	9212	13047	1387	37
H(24B)	7278	12532	1044	37
H(17)	9608	8699	577	34
H(23A)	11898	7461	924	51
H(23B)	10138	6548	357	51
H(23C)	11504	5832	948	51
H(20A)	12416	6157	2742	36
H(20B)	12572	7784	3103	36
H(21)	8310	5272	1409	48
H(22)	8638	4942	3123	51

Table 5. Torsion angles [°].

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O(1)–S(1)–C(1)–C(6)	116.5(2)
O(2)–S(1)–C(1)–C(6)	–112.8(2)
N(1)–S(1)–C(1)–C(6)	1.5(2)
O(1)–S(1)–C(1)–C(2)	–63.0(2)
O(2)–S(1)–C(1)–C(2)	67.8(2)
N(1)–S(1)–C(1)–C(2)	–178.0(2)
C(6)–C(1)–C(2)–C(3)	–0.5(4)
S(1)–C(1)–C(2)–C(3)	178.9(2)
C(1)–C(2)–C(3)–C(4)	0.0(4)
C(1)–C(2)–C(3)–O(3)	178.5(3)
C(2)–C(3)–O(3)–C(12)	174.4(3)
C(4)–C(3)–O(3)–C(12)	–7.0(3)
C(2)–C(3)–C(4)–C(5)	0.4(4)
O(3)–C(3)–C(4)–C(5)	–178.3(3)
C(2)–C(3)–C(4)–O(4)	177.6(2)
O(3)–C(3)–C(4)–O(4)	–1.1(3)
C(5)–C(4)–O(4)–C(12)	–174.2(3)
C(3)–C(4)–O(4)–C(12)	8.7(3)
C(4)–O(4)–C(12)–O(3)	–12.9(3)
C(3)–O(3)–C(12)–O(4)	12.2(3)
O(4)–C(4)–C(5)–C(6)	–177.0(3)
C(3)–C(4)–C(5)–C(6)	–0.4(4)
C(2)–C(1)–C(6)–C(5)	0.5(4)
S(1)–C(1)–C(6)–C(5)	–178.9(2)
C(2)–C(1)–C(6)–C(7)	–178.8(2)
S(1)–C(1)–C(6)–C(7)	1.8(3)
C(4)–C(5)–C(6)–C(1)	–0.1(4)
C(4)–C(5)–C(6)–C(7)	179.2(2)
C(1)–C(6)–C(7)–C(9)	–72.9(3)
C(5)–C(6)–C(7)–C(9)	107.8(3)

C(1)–C(6)–C(7)–C(11)	159.9(3)
C(5)–C(6)–C(7)–C(11)	–19.4(4)
C(1)–C(6)–C(7)–C(8)	34.0(3)
C(5)–C(6)–C(7)–C(8)	–145.3(3)
C(9)–C(7)–C(8)–N(1)	37.4(3)
C(11)–C(7)–C(8)–N(1)	158.6(2)
C(6)–C(7)–C(8)–N(1)	–74.7(3)
C(7)–C(8)–N(1)–C(10)	–36.5(3)
C(7)–C(8)–N(1)–S(1)	80.8(2)
O(1)–S(1)–N(1)–C(10)	–47.8(2)
O(2)–S(1)–N(1)–C(10)	–175.82(19)
C(1)–S(1)–N(1)–C(10)	68.7(2)
O(1)–S(1)–N(1)–C(8)	–158.8(2)
O(2)–S(1)–N(1)–C(8)	73.2(2)
C(1)–S(1)–N(1)–C(8)	–42.3(2)
C(11)–C(7)–C(9)–C(10)	–145.6(3)
C(6)–C(7)–C(9)–C(10)	87.2(3)
C(8)–C(7)–C(9)–C(10)	–25.4(3)
C(7)–C(9)–C(10)–N(1)	2.4(3)
C(8)–N(1)–C(10)–C(9)	22.4(3)
S(1)–N(1)–C(10)–C(9)	–93.8(3)
O(5)–S(2)–C(13)–C(14)	61.6(3)
O(6)–S(2)–C(13)–C(14)	–68.8(2)
N(2)–S(2)–C(13)–C(14)	177.0(2)
O(5)–S(2)–C(13)–C(18)	–118.7(2)
O(6)–S(2)–C(13)–C(18)	110.9(2)
N(2)–S(2)–C(13)–C(18)	–3.4(3)
C(18)–C(13)–C(14)–C(15)	–0.4(4)
S(2)–C(13)–C(14)–C(15)	179.3(2)
C(13)–C(14)–C(15)–O(7)	178.6(3)
C(13)–C(14)–C(15)–C(16)	1.3(4)
C(14)–C(15)–O(7)–C(24)	174.1(3)

C(16)–C(15)–O(7)–C(24)	–8.4(3)
C(14)–C(15)–C(16)–O(8)	175.8(3)
O(7)–C(15)–C(16)–O(8)	–1.9(3)
C(14)–C(15)–C(16)–C(17)	–1.7(4)
O(7)–C(15)–C(16)–C(17)	–179.4(3)
C(17)–C(16)–O(8)–C(24)	–171.4(3)
C(15)–C(16)–O(8)–C(24)	11.2(3)
C(15)–O(7)–C(24)–O(8)	15.1(3)
C(16)–O(8)–C(24)–O(7)	–16.2(3)
O(8)–C(16)–C(17)–C(18)	–176.2(3)
C(15)–C(16)–C(17)–C(18)	0.9(4)
C(16)–C(17)–C(18)–C(13)	0.1(4)
C(16)–C(17)–C(18)–C(19)	178.6(2)
C(14)–C(13)–C(18)–C(17)	–0.3(4)
S(2)–C(13)–C(18)–C(17)	–180.0(2)
C(14)–C(13)–C(18)–C(19)	–178.8(3)
S(2)–C(13)–C(18)–C(19)	1.5(4)
C(17)–C(18)–C(19)–C(23)	17.8(4)
C(13)–C(18)–C(19)–C(23)	–163.7(3)
C(17)–C(18)–C(19)–C(21)	–108.5(3)
C(13)–C(18)–C(19)–C(21)	70.0(3)
C(17)–C(18)–C(19)–C(20)	145.1(3)
C(13)–C(18)–C(19)–C(20)	–36.4(3)
C(23)–C(19)–C(20)–N(2)	–155.7(2)
C(21)–C(19)–C(20)–N(2)	–35.6(2)
C(18)–C(19)–C(20)–N(2)	76.2(3)
C(19)–C(20)–N(2)–C(22)	35.7(3)
C(19)–C(20)–N(2)–S(2)	–80.4(2)
O(5)–S(2)–N(2)–C(22)	48.0(2)
O(6)–S(2)–N(2)–C(22)	176.1(2)
C(13)–S(2)–N(2)–C(22)	–69.2(2)
O(5)–S(2)–N(2)–C(20)	159.2(2)



O(6)–S(2)–N(2)–C(20)	–72.7(2)
C(13)–S(2)–N(2)–C(20)	42.0(2)
C(23)–C(19)–C(21)–C(22)	143.8(3)
C(18)–C(19)–C(21)–C(22)	–88.9(3)
C(20)–C(19)–C(21)–C(22)	23.4(3)
C(19)–C(21)–C(22)–N(2)	–1.2(3)
C(20)–N(2)–C(22)–C(21)	–22.4(3)
S(2)–N(2)–C(22)–C(21)	93.2(3)

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Symmetry transformations used to generate equivalent atoms:

## X-Ray Crystallographic Data for Compound 24b

CCDC: 947372

Empirical formula	C <sub>15</sub> H <sub>13</sub> N O <sub>4</sub> S Br <sub>2</sub>
Formula weight	463.14 gmol <sup>-1</sup>
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c (#14)
Unit cell dimensions	a = 11.8097(2) Å α = 90°. b = 18.8010(3) Å β = 102.774(2)° c = 7.3495(1) Å γ = 90°.
Volume	1591.45(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.933 Mg/m <sup>3</sup>
Absorption coefficient	5.244 mm <sup>-1</sup>
F(000)	912
Crystal size	0.1910 x 0.1531 x 0.0738 mm <sup>3</sup>
Theta range for data collection	2.80 to 29.48°.
Index ranges	-15 ≤ h ≤ 16, -24 ≤ k ≤ 25, -10 ≤ l ≤ 10
Reflections collected	34858
Independent reflections	4186 [R(int) = 0.0318]
Completeness to theta = 28.00°	99.5 %
Absorption correction	Analytical
Max. and min. transmission	0.710 and 0.471
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4186 / 0 / 208
Goodness-of-fit on F <sup>2</sup>	1.056
Final R indices [I > 2σ(I)]	R1 = 0.0303, wR2 = 0.0654
R indices (all data)	R1 = 0.0342, wR2 = 0.0672
Largest diff. peak and hole	1.927 and -1.887 e.Å <sup>-3</sup>

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

$U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

Atom	x	Y	z	U(eq)
S	6766(1)	730(1)	-2856(1)	12(1)
O(1)	7475(2)	516(1)	-4117(2)	18(1)
O(2)	5676(2)	1068(1)	-3604(2)	19(1)
C(1)	6551(2)	-11(1)	-1499(3)	10(1)
C(2)	6095(2)	-629(1)	-2474(3)	12(1)
C(3)	5970(2)	-1204(1)	-1394(3)	12(1)
O(3)	5548(2)	-1861(1)	-1966(2)	16(1)
C(7)	5796(2)	-2299(1)	-320(3)	16(1)
C(4)	6261(2)	-1177(1)	545(3)	12(1)
O(4)	6031(2)	-1820(1)	1258(2)	17(1)
C(5)	6680(2)	-573(1)	1503(3)	13(1)
C(6)	6837(2)	31(1)	453(3)	10(1)
N	7548(2)	1274(1)	-1284(3)	11(1)
C(8)	6937(2)	1346(1)	270(3)	11(1)
C(9)	7368(2)	697(1)	1481(3)	11(1)
C(10)	8646(2)	747(1)	1490(3)	12(1)
C(11)	8738(2)	985(1)	-438(3)	13(1)
Br(1)	7362(1)	2232(1)	1617(1)	14(1)
C(12)	9727(2)	1515(1)	-322(4)	19(1)
C(13)	10819(2)	1146(2)	799(4)	26(1)
C(14)	10733(2)	934(1)	2755(4)	23(1)
Br(2)	11191(1)	1747(1)	4522(1)	36(1)
C(15)	9547(2)	726(1)	2943(4)	18(1)

Table 2. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

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S–O(2)	1.4314(18)
S–O(1)	1.4371(18)
S–N	1.6618(19)
S–C(1)	1.763(2)
C(1)–C(6)	1.402(3)
C(1)–C(2)	1.409(3)
C(2)–C(3)	1.368(3)
C(2)–H(2)	0.9500
C(3)–O(3)	1.363(3)
C(3)–C(4)	1.391(3)
O(3)–C(7)	1.439(3)
C(7)–O(4)	1.447(3)
C(7)–H(7A)	0.9900
C(7)–H(7B)	0.9900
C(4)–O(4)	1.367(3)
C(4)–C(5)	1.371(3)
C(5)–C(6)	1.408(3)
C(5)–H(5)	0.9500
C(6)–C(9)	1.524(3)
N–C(8)	1.487(3)
N–C(11)	1.506(3)
C(8)–C(9)	1.529(3)
C(8)–Br(1)	1.946(2)
C(8)–H(8)	1.0000
C(9)–C(10)	1.510(3)
C(9)–H(9)	1.0000
C(10)–C(15)	1.331(3)
C(10)–C(11)	1.513(3)
C(11)–C(12)	1.523(3)
C(11)–H(11)	1.0000

C(12)–C(13)	1.534(4)
C(12)–H(12A)	0.9900
C(12)–H(12B)	0.9900
C(13)–C(14)	1.517(4)
C(13)–H(13A)	0.9900
C(13)–H(13B)	0.9900
C(14)–C(15)	1.490(4)
C(14)–Br(2)	2.001(3)
C(14)–H(14)	1.0000
C(15)–H(15)	0.9500
O(2)–S–O(1)	118.59(11)
O(2)–S–N	107.97(10)
O(1)–S–N	107.86(10)
O(2)–S–C(1)	109.78(11)
O(1)–S–C(1)	108.72(10)
N–S–C(1)	102.74(10)
C(6)–C(1)–C(2)	123.0(2)
C(6)–C(1)–S	120.15(17)
C(2)–C(1)–S	116.82(16)
C(3)–C(2)–C(1)	115.8(2)
C(3)–C(2)–H(2)	122.1
C(1)–C(2)–H(2)	122.1
O(3)–C(3)–C(2)	128.0(2)
O(3)–C(3)–C(4)	109.8(2)
C(2)–C(3)–C(4)	122.1(2)
C(3)–O(3)–C(7)	105.45(17)
O(3)–C(7)–O(4)	106.54(17)
O(3)–C(7)–H(7A)	110.4
O(4)–C(7)–H(7A)	110.4
O(3)–C(7)–H(7B)	110.4
O(4)–C(7)–H(7B)	110.4
H(7A)–C(7)–H(7B)	108.6

O(4)–C(4)–C(5)	128.0(2)
O(4)–C(4)–C(3)	109.60(19)
C(5)–C(4)–C(3)	122.4(2)
C(4)–O(4)–C(7)	105.22(17)
C(4)–C(5)–C(6)	117.6(2)
C(4)–C(5)–H(5)	121.2
C(6)–C(5)–H(5)	121.2
C(1)–C(6)–C(5)	119.0(2)
C(1)–C(6)–C(9)	122.19(19)
C(5)–C(6)–C(9)	118.75(19)
C(8)–N–C(11)	106.43(16)
C(8)–N–S	107.47(14)
C(11)–N–S	112.92(14)
N–C(8)–C(9)	102.62(17)
N–C(8)–Br(1)	110.75(14)
C(9)–C(8)–Br(1)	111.81(14)
N–C(8)–H(8)	110.5
C(9)–C(8)–H(8)	110.5
Br(1)–C(8)–H(8)	110.5
C(10)–C(9)–C(6)	110.74(18)
C(10)–C(9)–C(8)	99.05(17)
C(6)–C(9)–C(8)	108.65(17)
C(10)–C(9)–H(9)	112.5
C(6)–C(9)–H(9)	112.5
C(8)–C(9)–H(9)	112.5
C(15)–C(10)–C(9)	128.5(2)
C(15)–C(10)–C(11)	123.4(2)
C(9)–C(10)–C(11)	107.01(18)
N–C(11)–C(10)	103.88(18)
N–C(11)–C(12)	114.92(19)
C(10)–C(11)–C(12)	110.7(2)
N–C(11)–H(11)	109.0

C(10)–C(11)–H(11)	109.0
C(12)–C(11)–H(11)	109.0
C(11)–C(12)–C(13)	106.2(2)
C(11)–C(12)–H(12A)	110.5
C(13)–C(12)–H(12A)	110.5
C(11)–C(12)–H(12B)	110.5
C(13)–C(12)–H(12B)	110.5
H(12A)–C(12)–H(12B)	108.7
C(14)–C(13)–C(12)	113.8(2)
C(14)–C(13)–H(13A)	108.8
C(12)–C(13)–H(13A)	108.8
C(14)–C(13)–H(13B)	108.8
C(12)–C(13)–H(13B)	108.8
H(13A)–C(13)–H(13B)	107.7
C(15)–C(14)–C(13)	114.7(2)
C(15)–C(14)–Br(2)	105.43(18)
C(13)–C(14)–Br(2)	110.42(18)
C(15)–C(14)–H(14)	108.7
C(13)–C(14)–H(14)	108.7
Br(2)–C(14)–H(14)	108.7
C(10)–C(15)–C(14)	121.3(2)
C(10)–C(15)–H(15)	119.4
C(14)–C(15)–H(15)	119.4

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Symmetry transformations used to generate equivalent atoms:

Table 3. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

Atom	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
S	18(1)	9(1)	7(1)	0(1)	1(1)	0(1)
O(1)	31(1)	14(1)	10(1)	0(1)	9(1)	0(1)
O(2)	23(1)	13(1)	15(1)	0(1)	-5(1)	2(1)
C(1)	11(1)	10(1)	10(1)	0(1)	2(1)	-1(1)
C(2)	14(1)	11(1)	11(1)	-2(1)	0(1)	0(1)
C(3)	10(1)	11(1)	14(1)	-3(1)	3(1)	-1(1)
O(3)	23(1)	9(1)	15(1)	-2(1)	1(1)	-4(1)
C(7)	19(1)	11(1)	16(1)	-1(1)	1(1)	0(1)
C(4)	13(1)	11(1)	14(1)	2(1)	5(1)	-2(1)
O(4)	26(1)	11(1)	15(1)	1(1)	7(1)	-5(1)
C(5)	16(1)	14(1)	10(1)	0(1)	4(1)	-3(1)
C(6)	9(1)	12(1)	10(1)	-1(1)	2(1)	-2(1)
N	13(1)	9(1)	10(1)	-1(1)	3(1)	-1(1)
C(8)	12(1)	11(1)	11(1)	-3(1)	3(1)	-1(1)
C(9)	14(1)	11(1)	9(1)	-1(1)	3(1)	-4(1)
C(10)	15(1)	8(1)	13(1)	0(1)	2(1)	0(1)
C(11)	12(1)	10(1)	17(1)	1(1)	4(1)	1(1)
Br(1)	16(1)	11(1)	15(1)	-5(1)	3(1)	-1(1)
C(12)	14(1)	16(1)	29(1)	2(1)	9(1)	-2(1)
C(13)	11(1)	22(1)	44(2)	-2(1)	6(1)	1(1)
C(14)	15(1)	14(1)	36(2)	-6(1)	-4(1)	2(1)
Br(2)	20(1)	26(1)	54(1)	-16(1)	-6(1)	-3(1)
C(15)	19(1)	11(1)	20(1)	-1(1)	-4(1)	0(1)



Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ).

Atom	x	y	z	U(eq)
H(2)	5888	-646	-3798	15
H(7A)	6478	-2605	-317	19
H(7B)	5123	-2607	-272	19
H(5)	6857	-561	2828	16
H(8)	6077	1321	-214	14
H(9)	7212	735	2760	13
H(11)	8888	561	-1171	15
H(12A)	9567	1956	313	23
H(12B)	9827	1639	-1587	23
H(13A)	10970	715	117	31
H(13B)	11490	1470	884	31
H(14)	11274	528	3175	28
H(15)	9432	575	4123	22

Table 5. Torsion angles [°].

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O(2)–S–C(1)–C(6)	–103.59(19)
O(1)–S–C(1)–C(6)	125.20(19)
N–S–C(1)–C(6)	11.1(2)
O(2)–S–C(1)–C(2)	76.81(19)
O(1)–S–C(1)–C(2)	–54.4(2)
N–S–C(1)–C(2)	–168.51(17)
C(6)–C(1)–C(2)–C(3)	–1.6(3)
S–C(1)–C(2)–C(3)	178.02(17)
C(1)–C(2)–C(3)–O(3)	179.5(2)
C(1)–C(2)–C(3)–C(4)	0.8(3)
C(2)–C(3)–O(3)–C(7)	169.9(2)
C(4)–C(3)–O(3)–C(7)	–11.3(2)
C(3)–O(3)–C(7)–O(4)	17.7(2)
O(3)–C(3)–C(4)–O(4)	0.1(3)
C(2)–C(3)–C(4)–O(4)	179.0(2)
O(3)–C(3)–C(4)–C(5)	–178.2(2)
C(2)–C(3)–C(4)–C(5)	0.7(4)
C(5)–C(4)–O(4)–C(7)	–170.8(2)
C(3)–C(4)–O(4)–C(7)	11.0(2)
O(3)–C(7)–O(4)–C(4)	–17.7(2)
O(4)–C(4)–C(5)–C(6)	–179.4(2)
C(3)–C(4)–C(5)–C(6)	–1.4(3)
C(2)–C(1)–C(6)–C(5)	0.9(3)
S–C(1)–C(6)–C(5)	–178.70(17)
C(2)–C(1)–C(6)–C(9)	177.8(2)
S–C(1)–C(6)–C(9)	–1.7(3)
C(4)–C(5)–C(6)–C(1)	0.6(3)
C(4)–C(5)–C(6)–C(9)	–176.5(2)
O(2)–S–N–C(8)	64.83(16)
O(1)–S–N–C(8)	–165.89(14)

C(1)–S–N–C(8)	–51.15(16)
O(2)–S–N–C(11)	–178.11(15)
O(1)–S–N–C(11)	–48.82(17)
C(1)–S–N–C(11)	65.92(17)
C(11)–N–C(8)–C(9)	–36.8(2)
S–N–C(8)–C(9)	84.46(16)
C(11)–N–C(8)–Br(1)	82.70(17)
S–N–C(8)–Br(1)	–156.07(10)
C(1)–C(6)–C(9)–C(10)	–77.9(3)
C(5)–C(6)–C(9)–C(10)	99.1(2)
C(1)–C(6)–C(9)–C(8)	29.9(3)
C(5)–C(6)–C(9)–C(8)	–153.1(2)
N–C(8)–C(9)–C(10)	45.13(19)
Br(1)–C(8)–C(9)–C(10)	–73.60(18)
N–C(8)–C(9)–C(6)	–70.5(2)
Br(1)–C(8)–C(9)–C(6)	170.80(14)
C(6)–C(9)–C(10)–C(15)	–116.0(3)
C(8)–C(9)–C(10)–C(15)	130.0(2)
C(6)–C(9)–C(10)–C(11)	75.9(2)
C(8)–C(9)–C(10)–C(11)	–38.1(2)
C(8)–N–C(11)–C(10)	12.7(2)
S–N–C(11)–C(10)	–104.98(17)
C(8)–N–C(11)–C(12)	–108.4(2)
S–N–C(11)–C(12)	133.88(18)
C(15)–C(10)–C(11)–N	–152.2(2)
C(9)–C(10)–C(11)–N	16.6(2)
C(15)–C(10)–C(11)–C(12)	–28.3(3)
C(9)–C(10)–C(11)–C(12)	140.52(19)
N–C(11)–C(12)–C(13)	172.7(2)
C(10)–C(11)–C(12)–C(13)	55.4(3)
C(11)–C(12)–C(13)–C(14)	–59.8(3)
C(12)–C(13)–C(14)–C(15)	33.1(3)

C(12)–C(13)–C(14)–Br(2)	–85.9(2)
C(9)–C(10)–C(15)–C(14)	–166.9(2)
C(11)–C(10)–C(15)–C(14)	–0.6(4)
C(13)–C(14)–C(15)–C(10)	–1.6(3)
Br(2)–C(14)–C(15)–C(10)	120.1(2)

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Symmetry transformations used to generate equivalent atoms: