Supporting Information

Novel Practical Stereoselective Synthesis of a Bicyclic Hydantoinothiolactone as the Key Intermediate for Production of (+)-Biotin

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^{1}H and ^{13}C NMR Spectra of Compound **2**

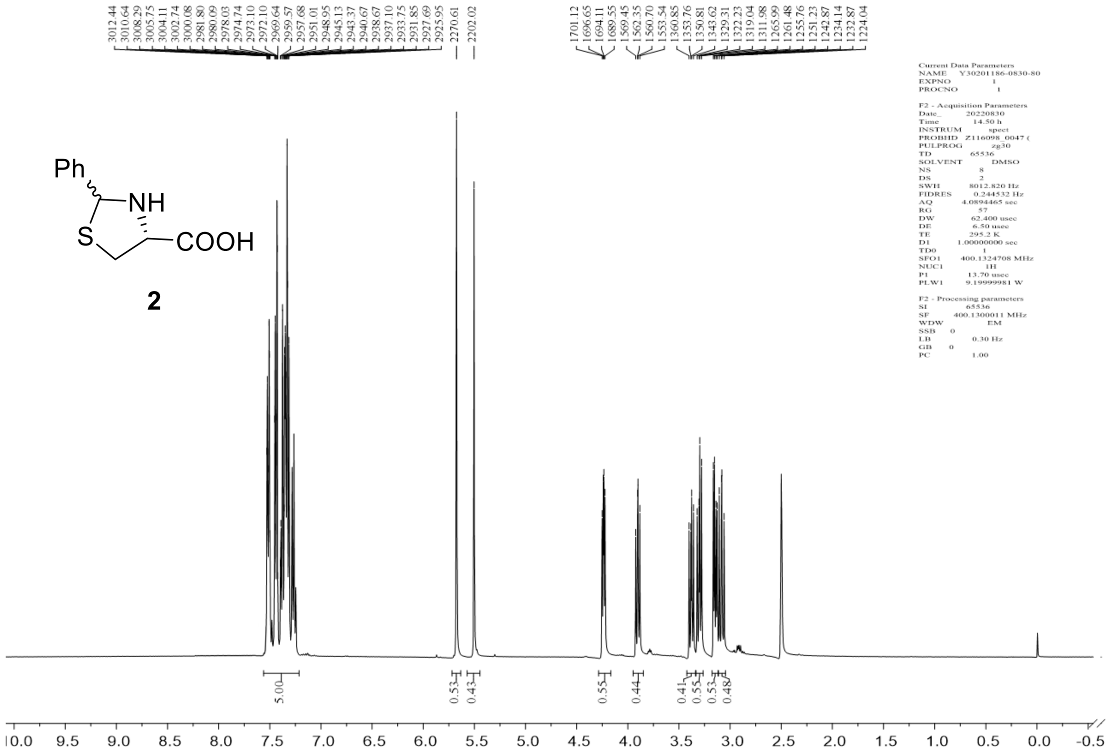


Figure S1. ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **2**

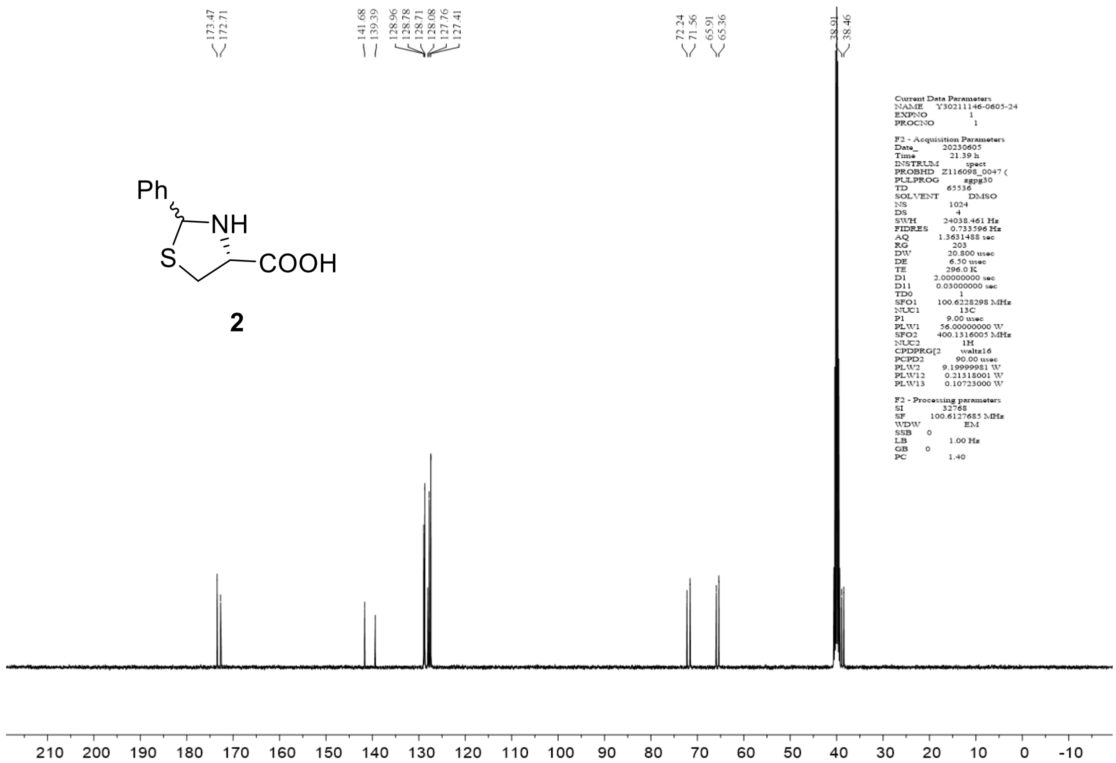


Figure S2. ^{13}C NMR (DMSO-d_6, 101 MHz) spectrum of compound **2**

[1]H and [13]C NMR Spectra of Compound **3**

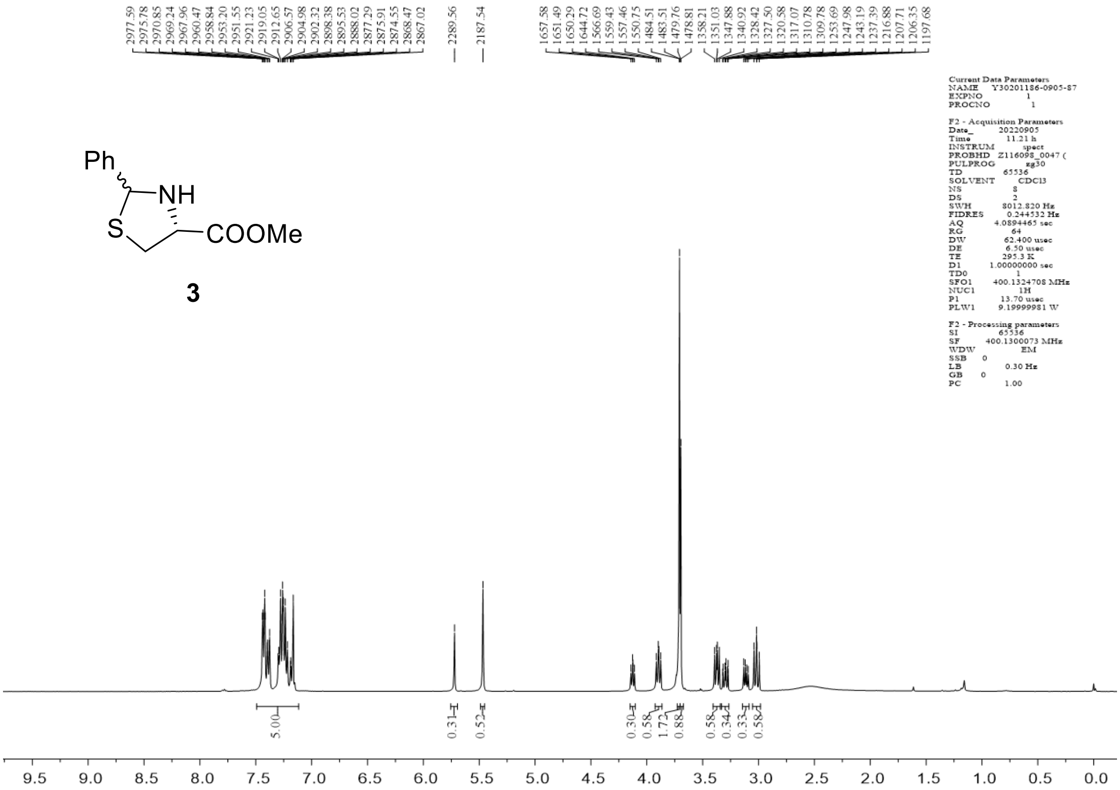


Figure S3. [1]H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3**

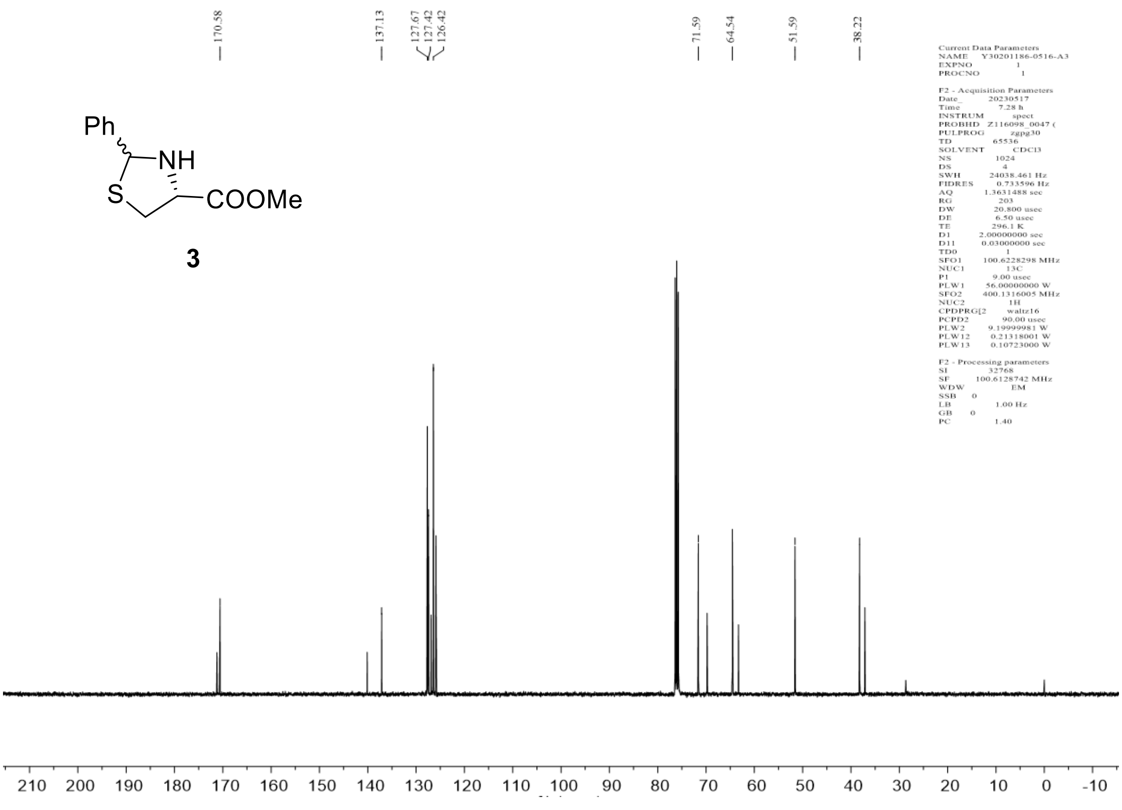
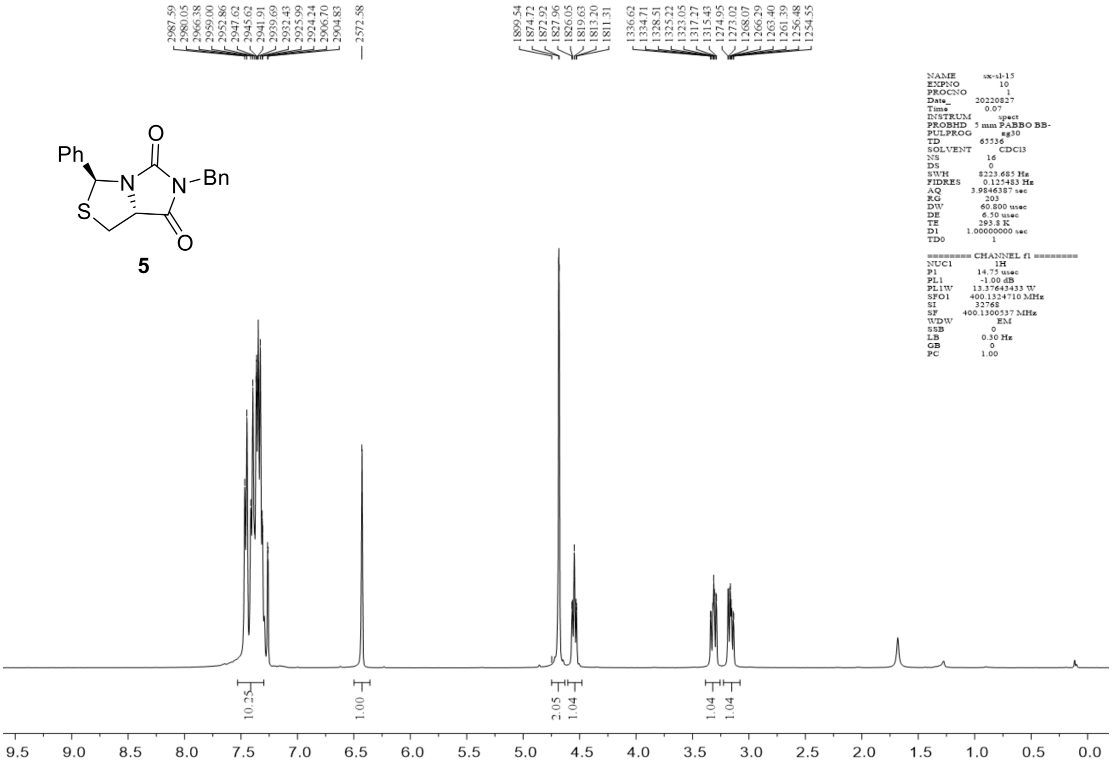


Figure S4. [13]C NMR ($CDCl_3$, 101 MHz) spectrum of compound **3**

[1]H and [13]C NMR Spectra of Compound **5**



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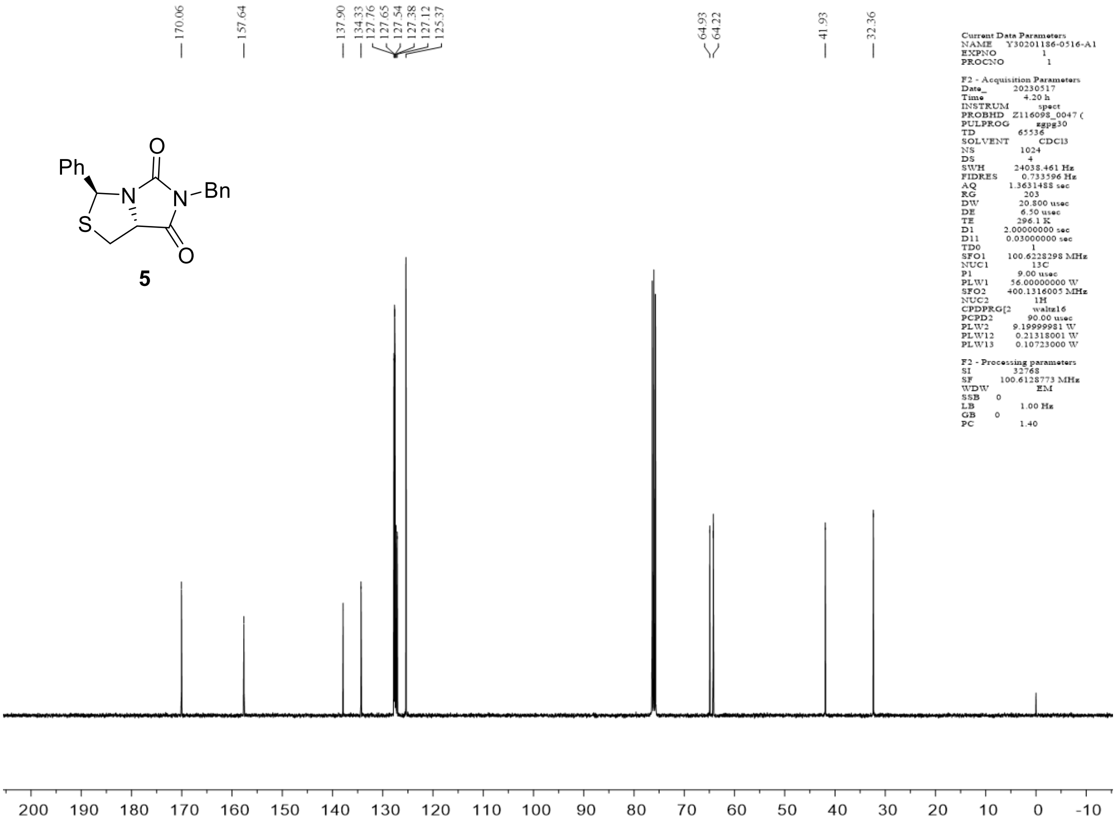
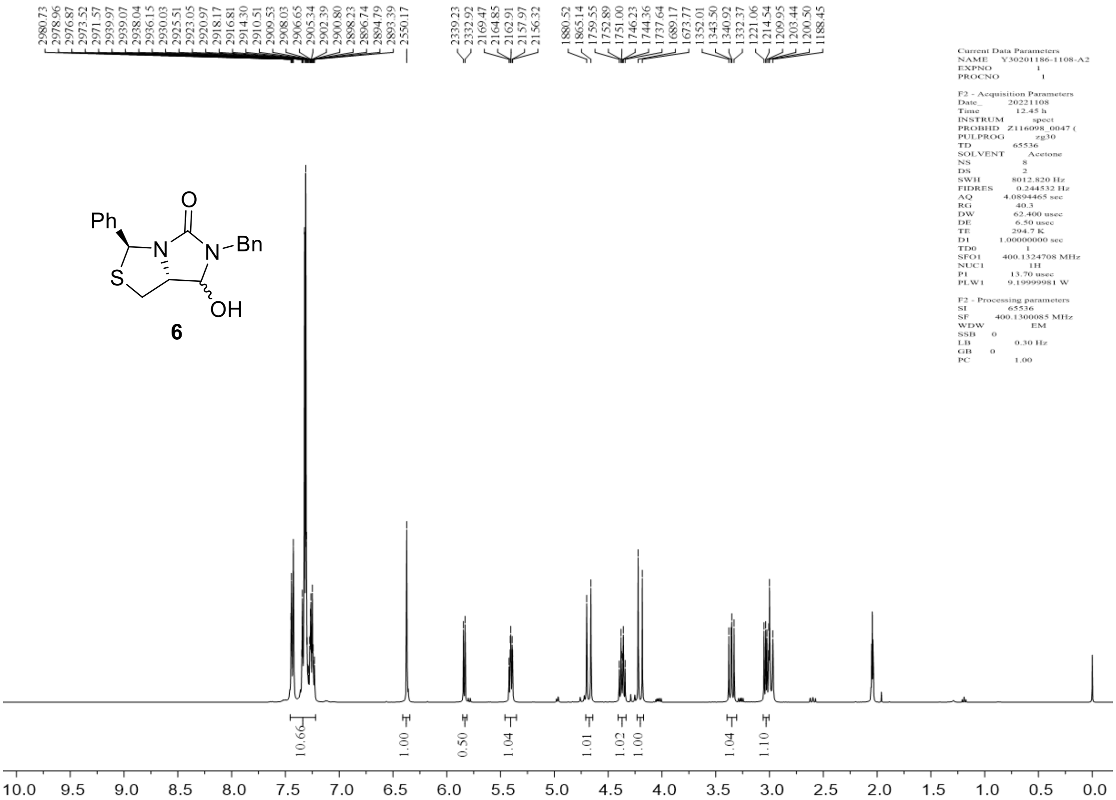


Figure S6. [13]C NMR ($CDCl_3$, 101 MHz) spectrum of compound **5**

[1]H and [13]C NMR Spectra of Compound **6**



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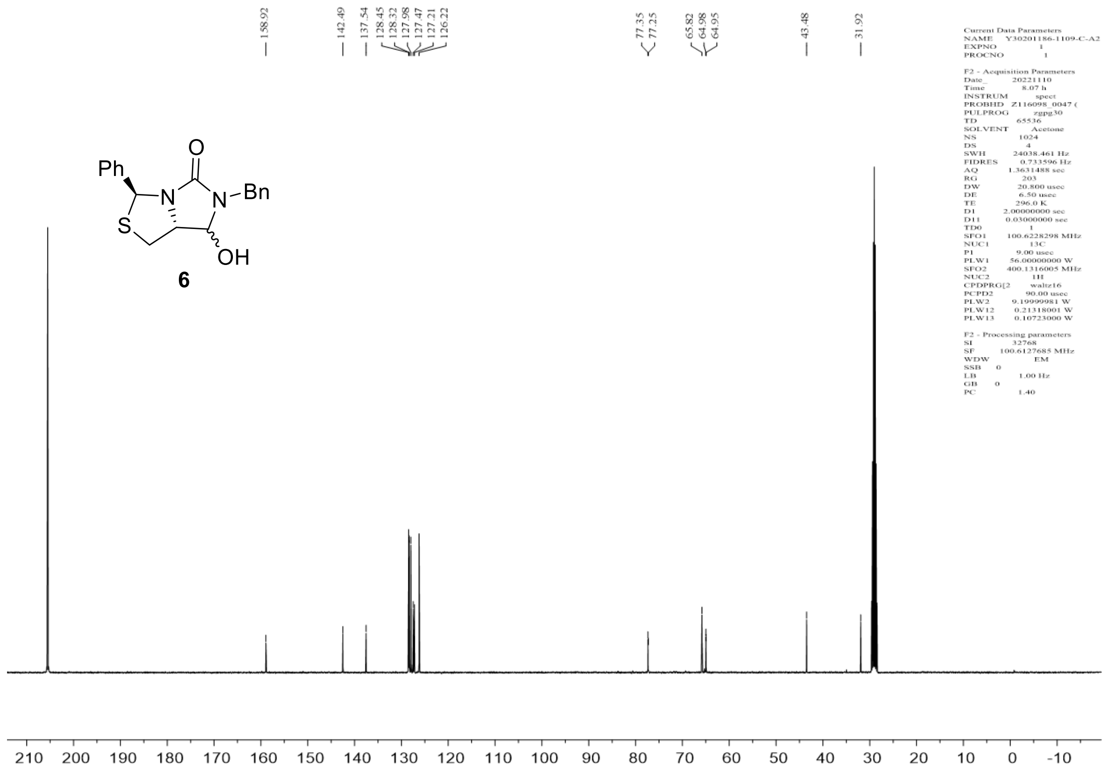


Figure S8. ^{13}C NMR (Acetone-d_6, 101 MHz) spectrum of compound **6**

[1]H and [13]C NMR Spectra of Compound **7**

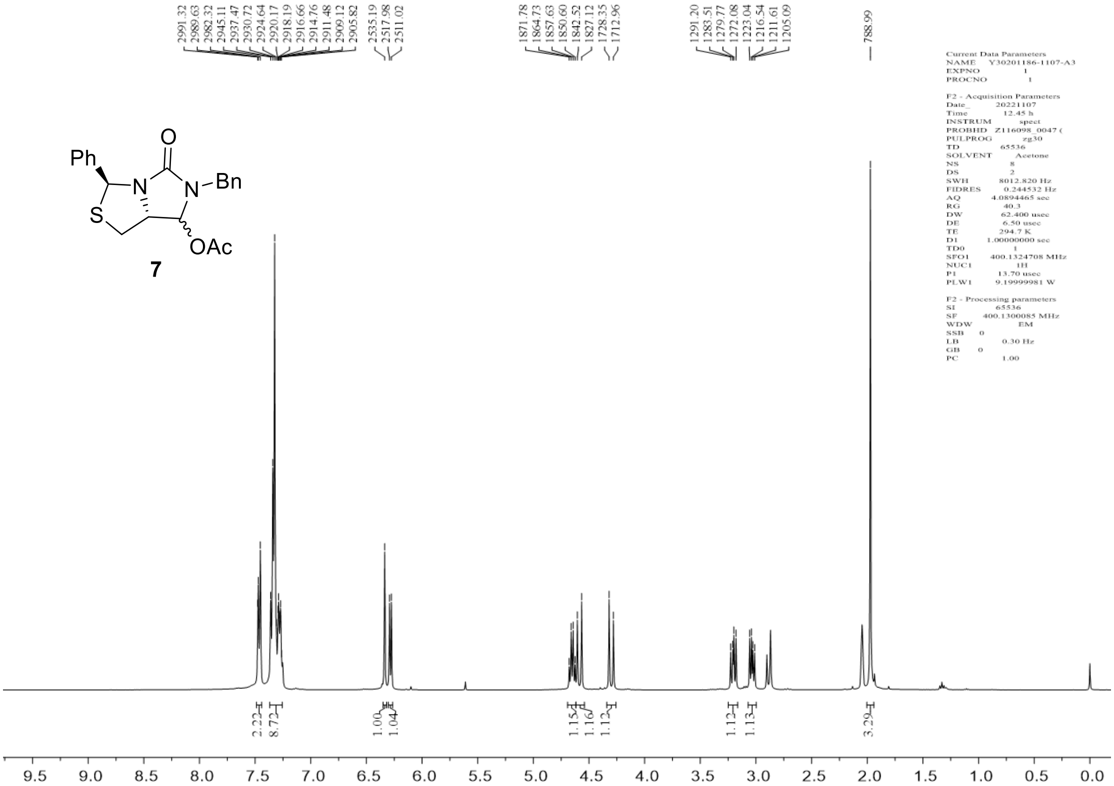
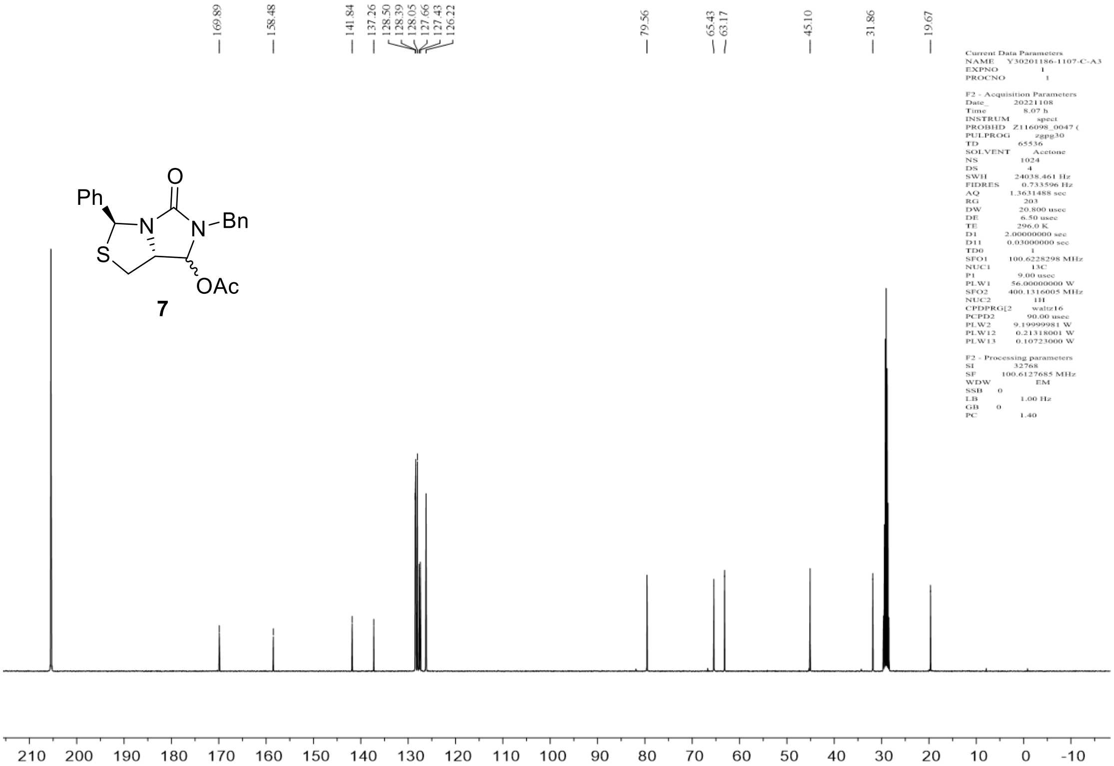


Figure S9. ^{1}H NMR (Acetone-d_6, 400 MHz) spectrum of compound **7**



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[1]H and [13]C NMR Spectra of Major diastereomer of Compound **8**

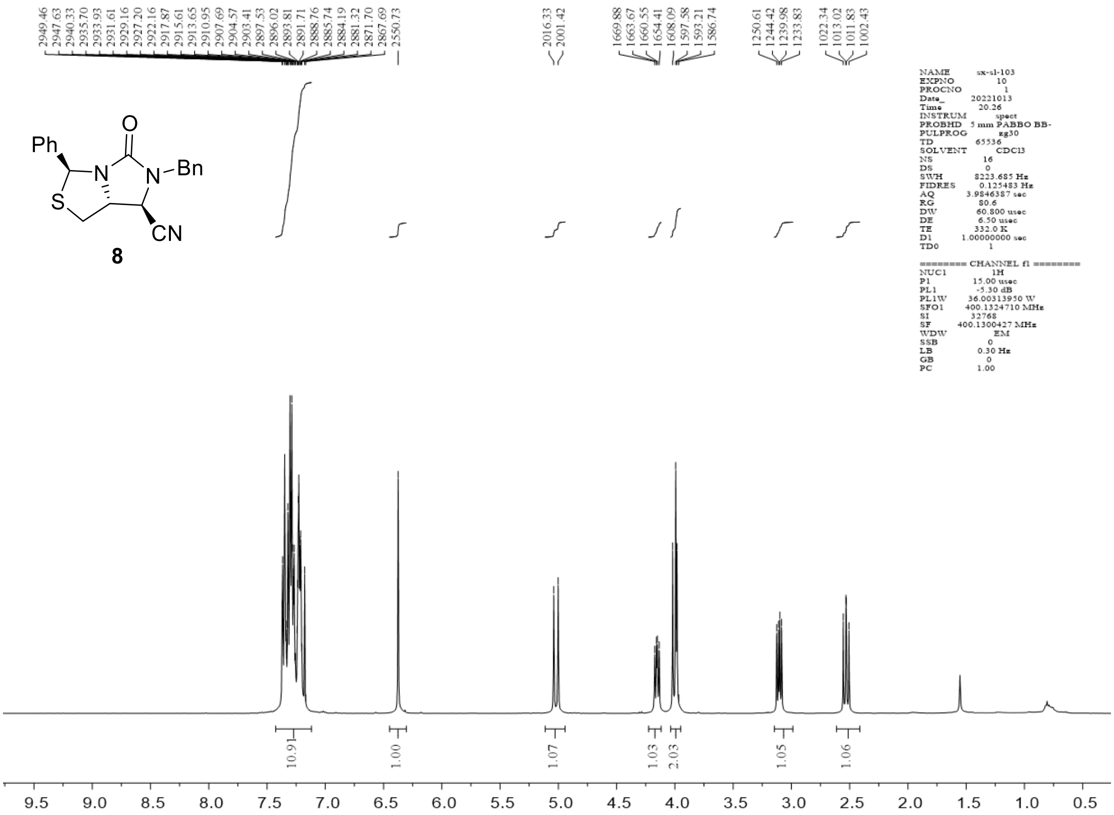
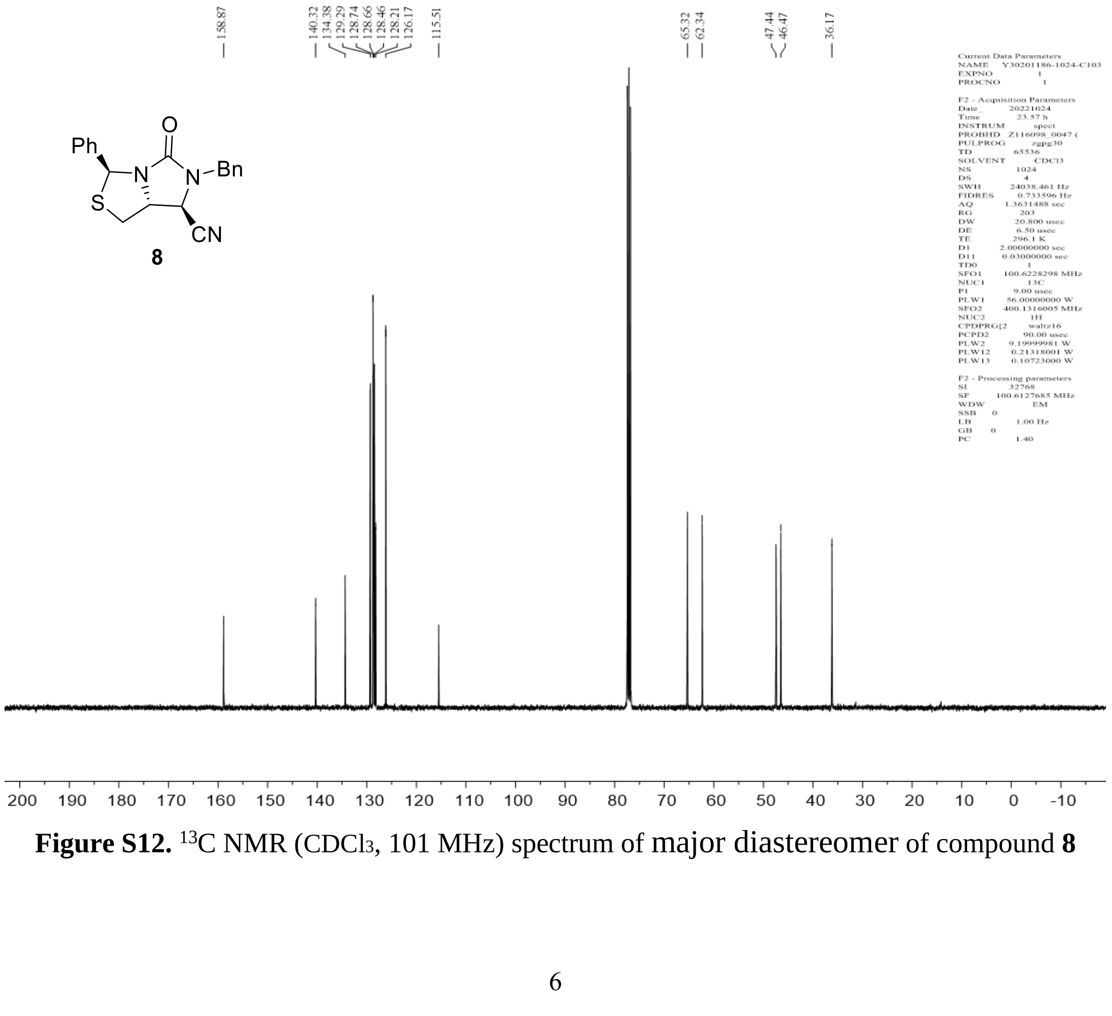


Figure S11. [1]H NMR ($CDCl_3$, 400 MHz) spectrum of major diastereomer of compound **8**



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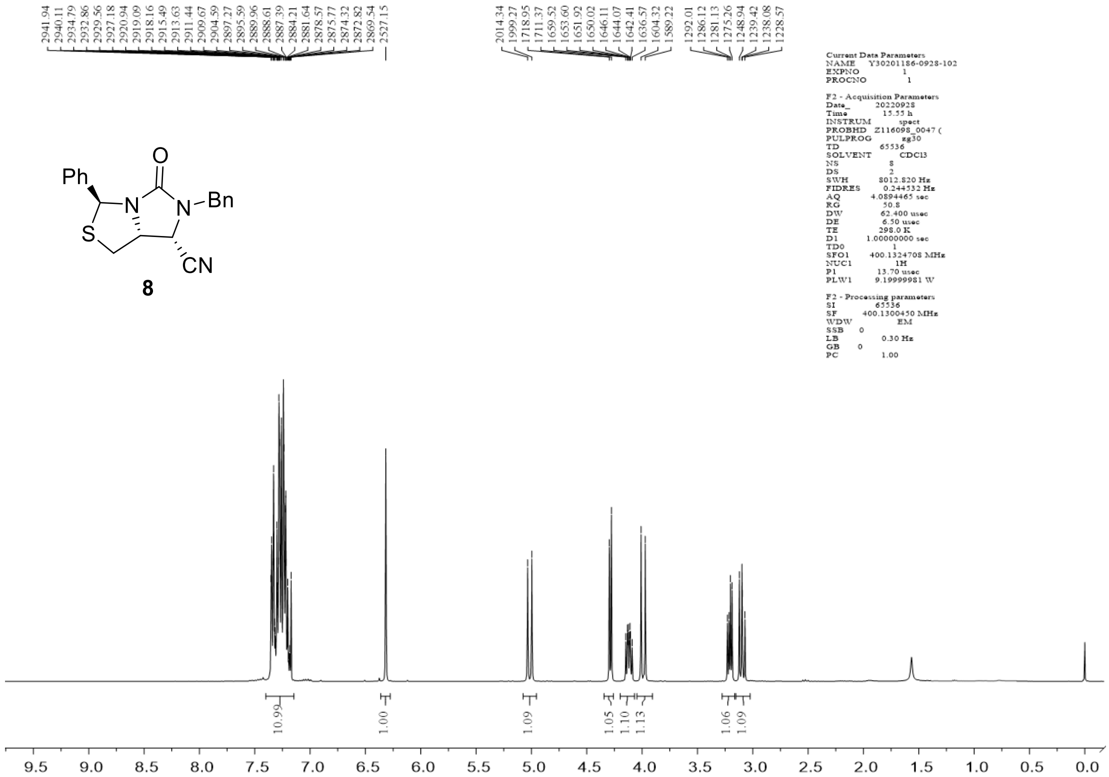

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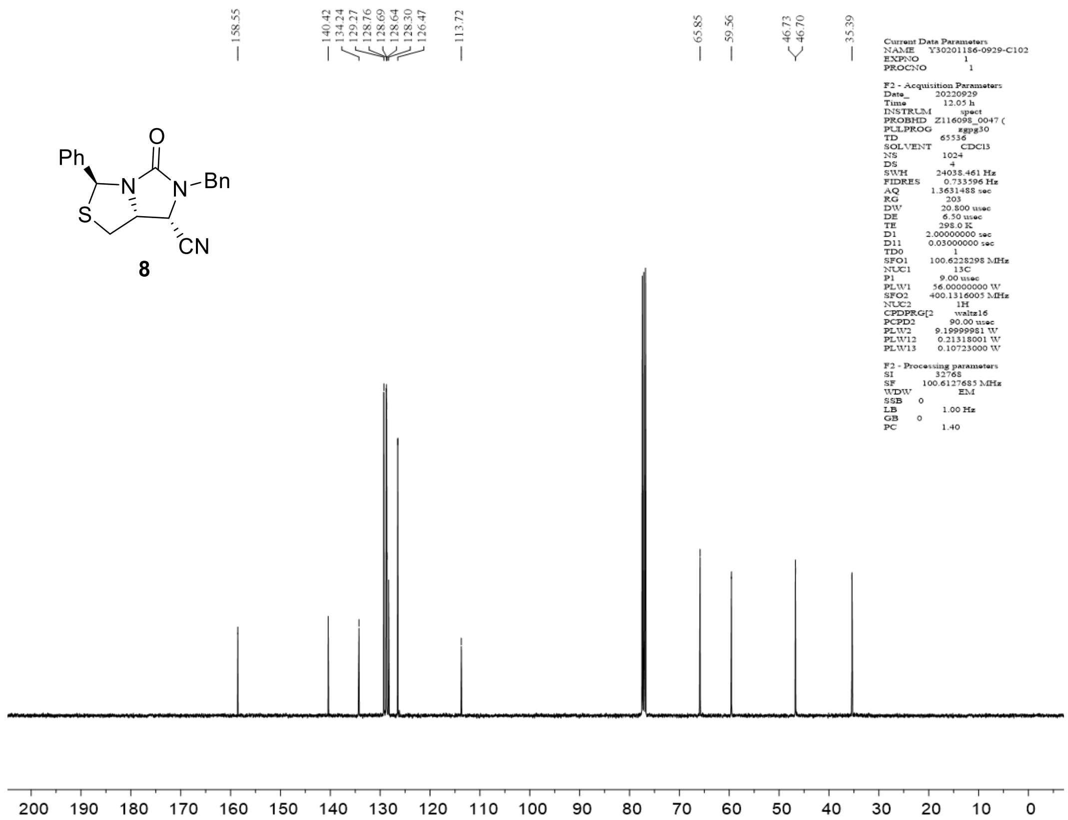

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^{1}H and ^{13}C NMR Spectra of Compound **8a**

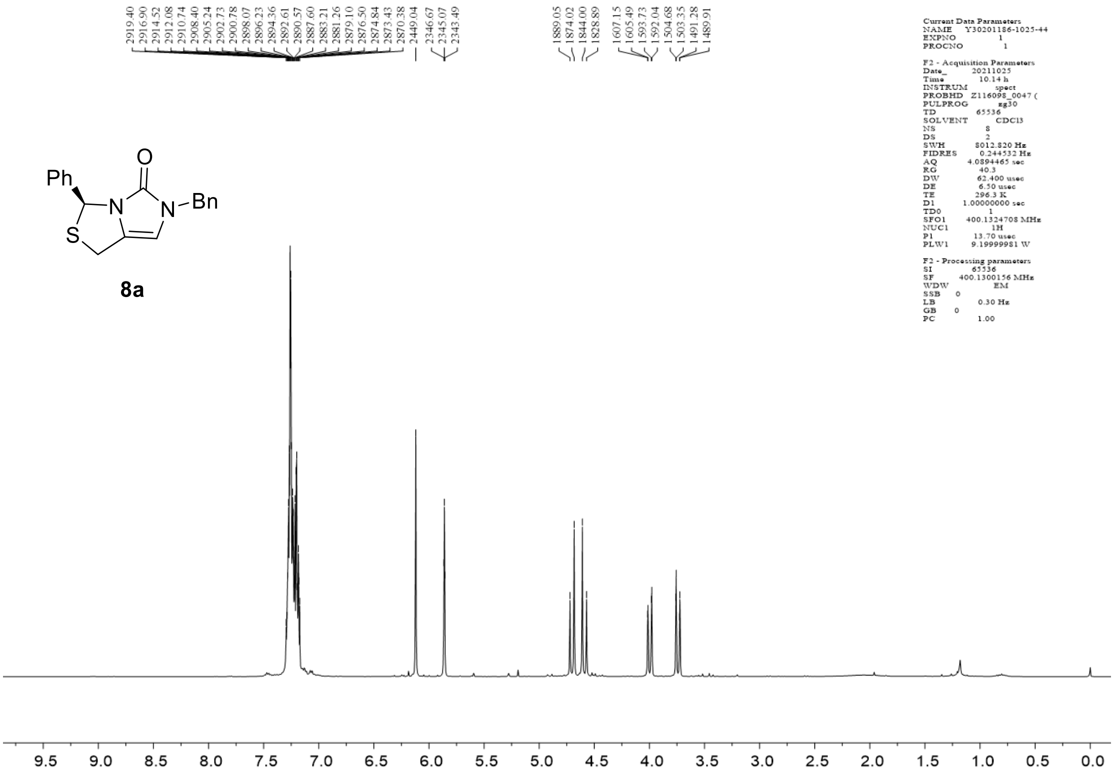


Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **8a**

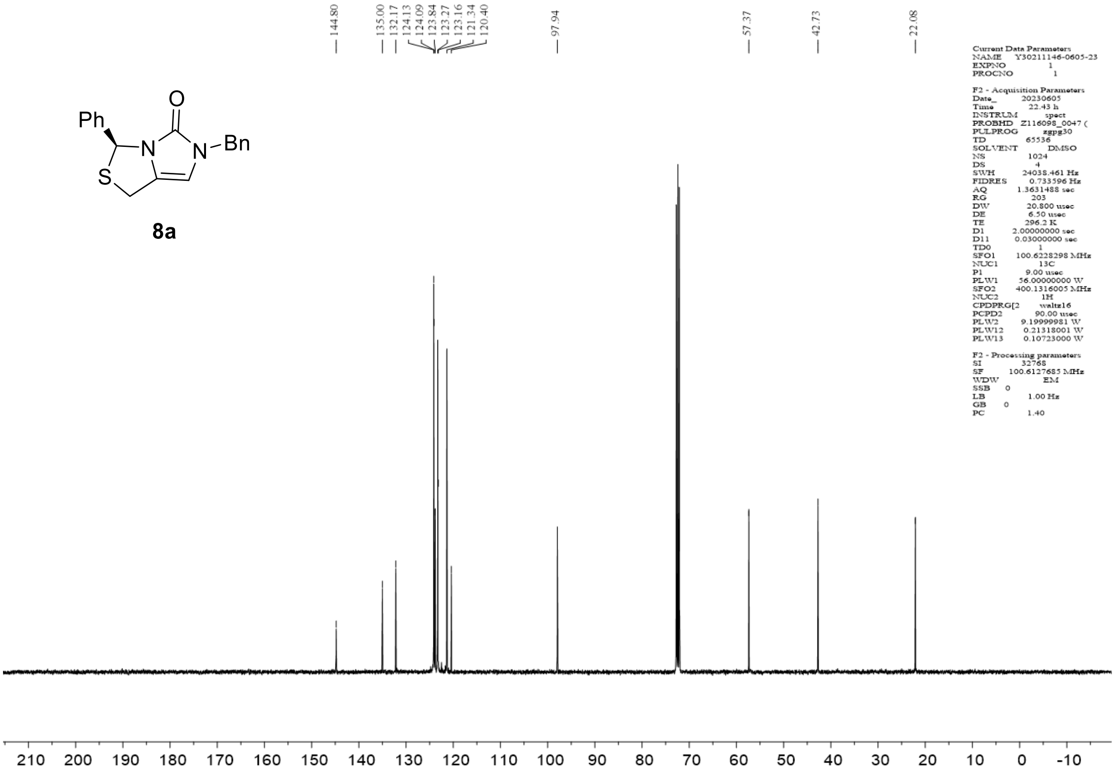
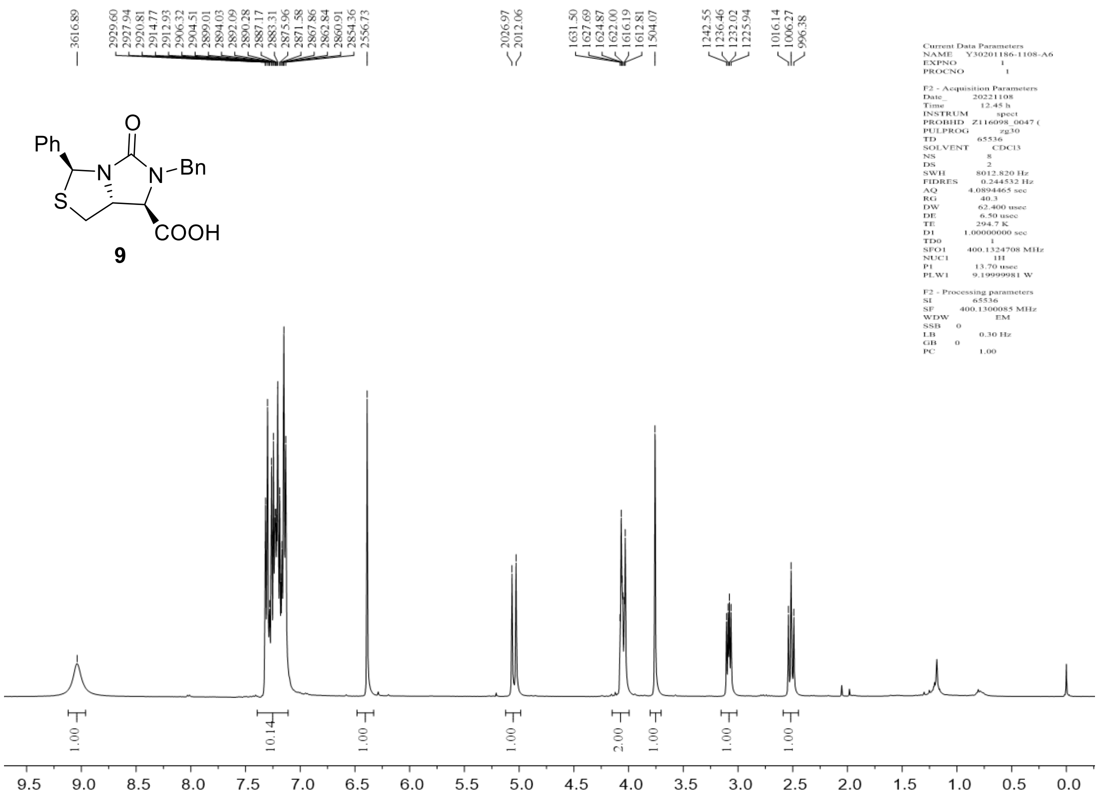


Figure S16. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound **8a**

[1]H and [13]C NMR Spectra of Compound **9**



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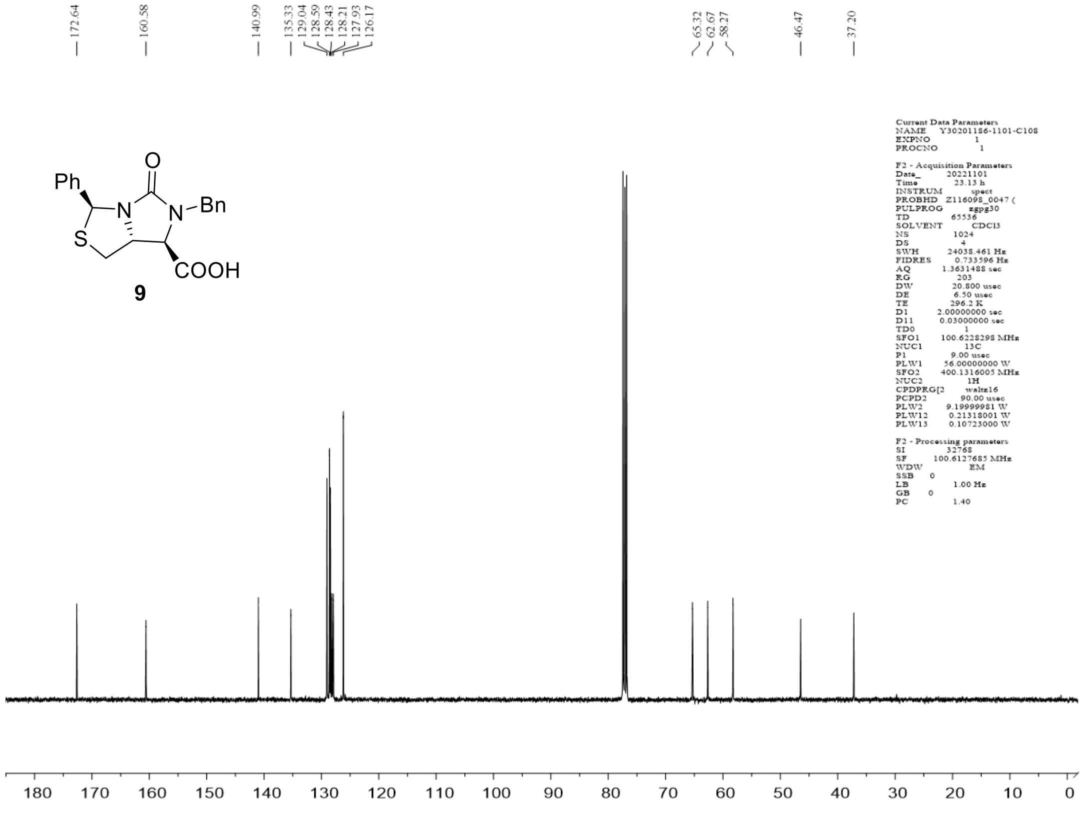

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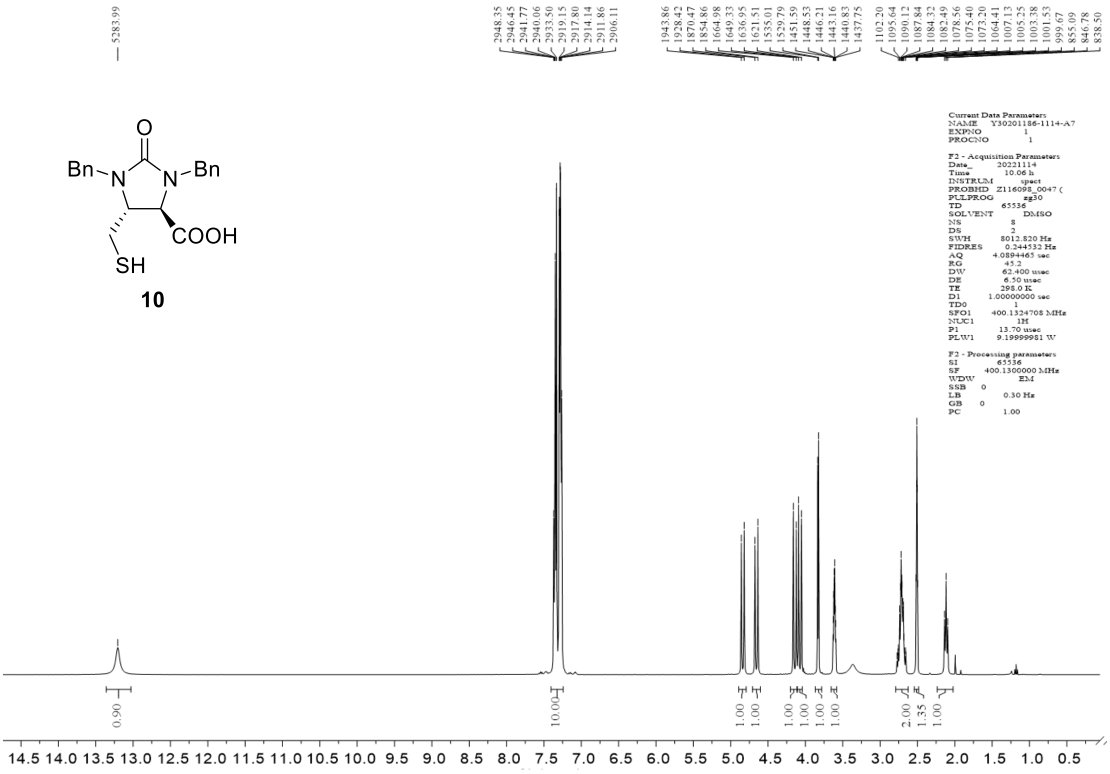

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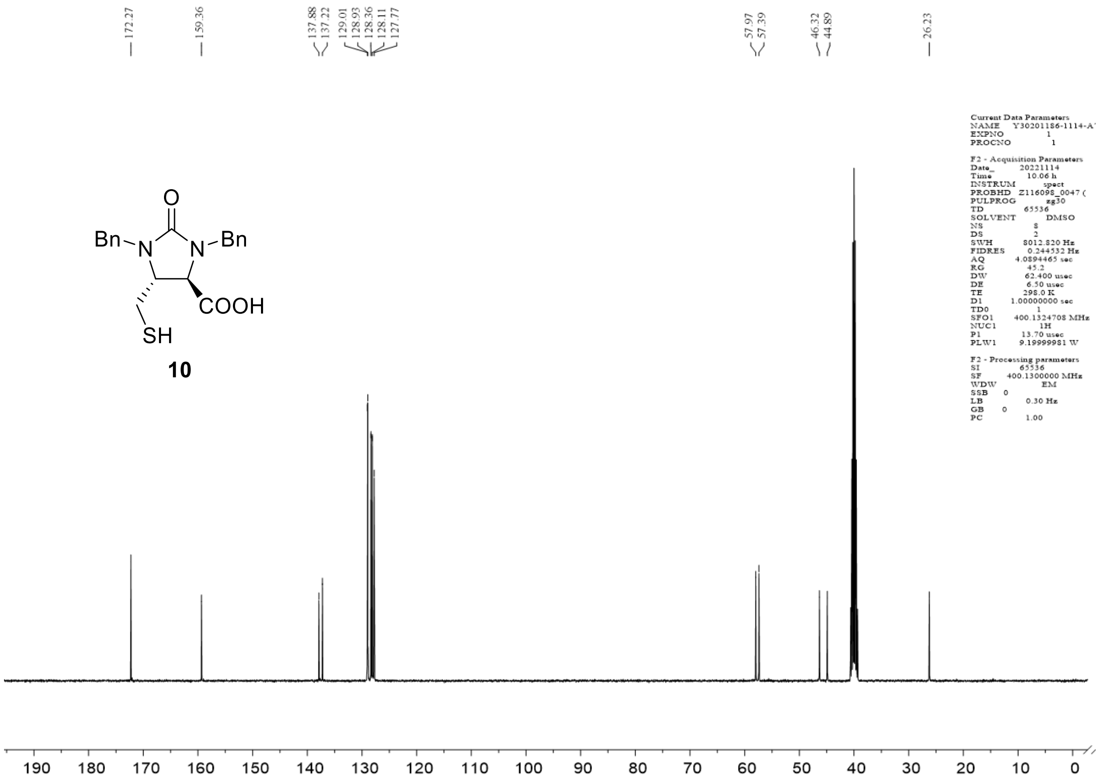


Figure S20. ^{13}C NMR (DMSO-d_6, 101 MHz) spectrum of compound **10**

[1]H and [13]C NMR Spectra of Compound ***trans*-1**

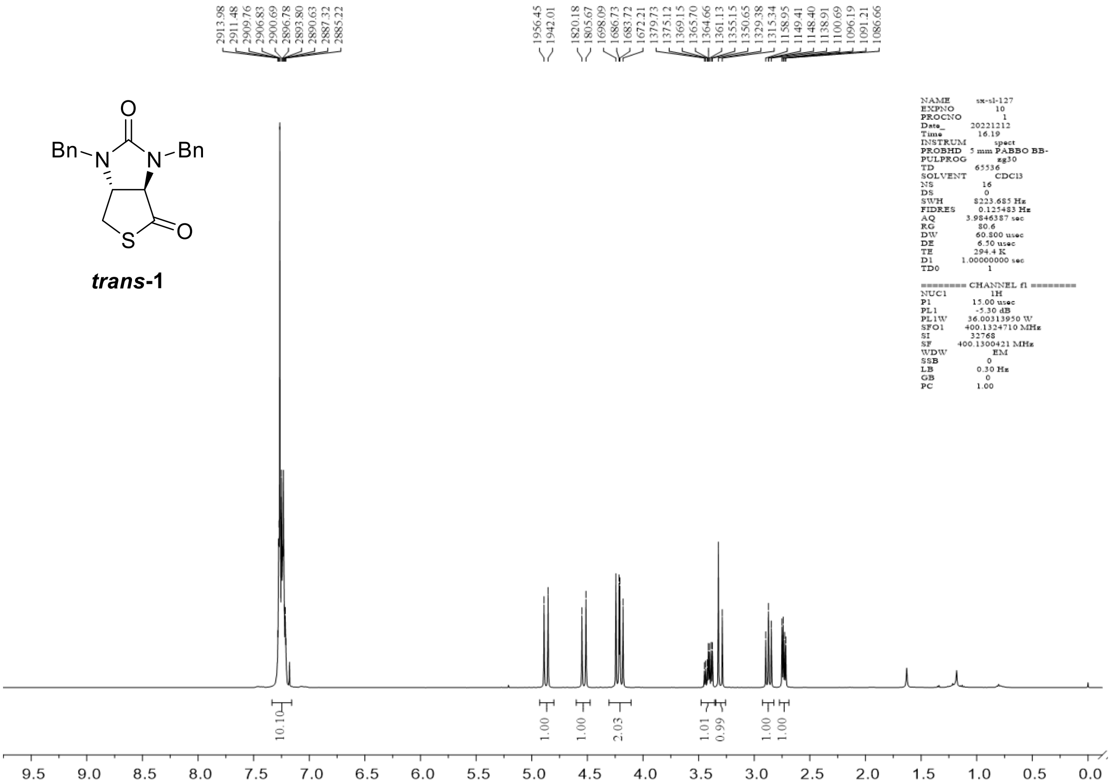


Figure S21. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound ***trans*-1**

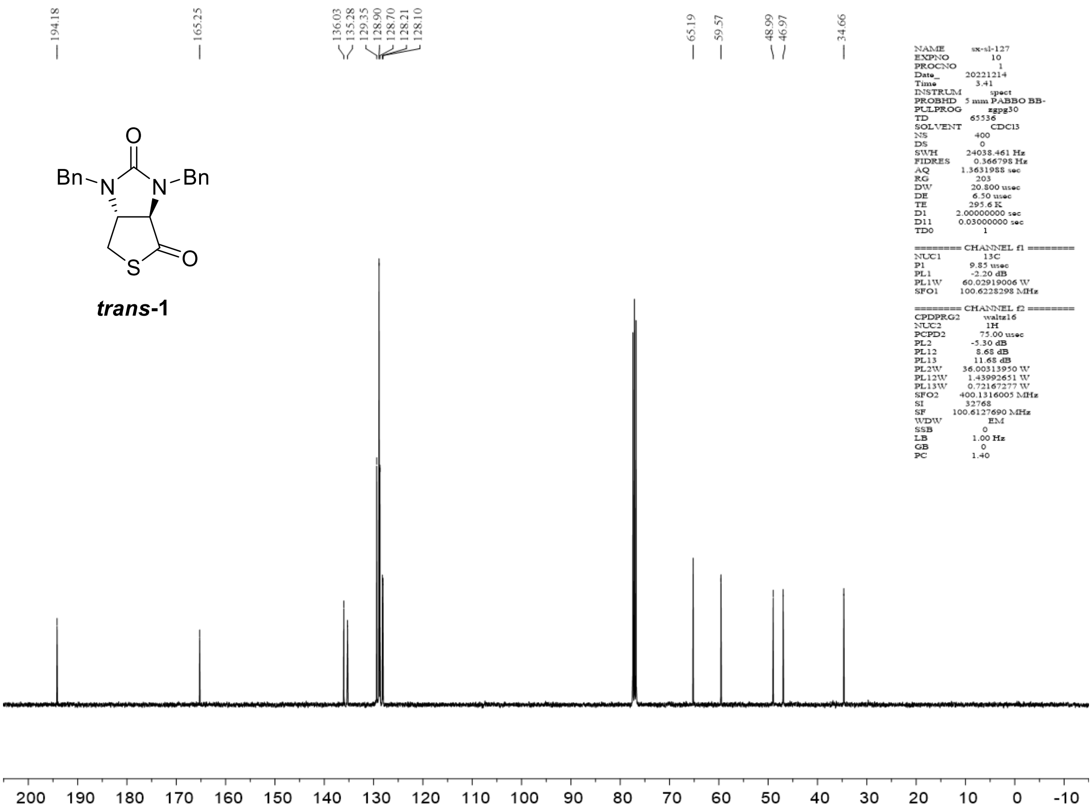


Figure S22. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of compound ***trans*-1**

[1]H and [13]C NMR Spectra of Compound ***cis*-1**

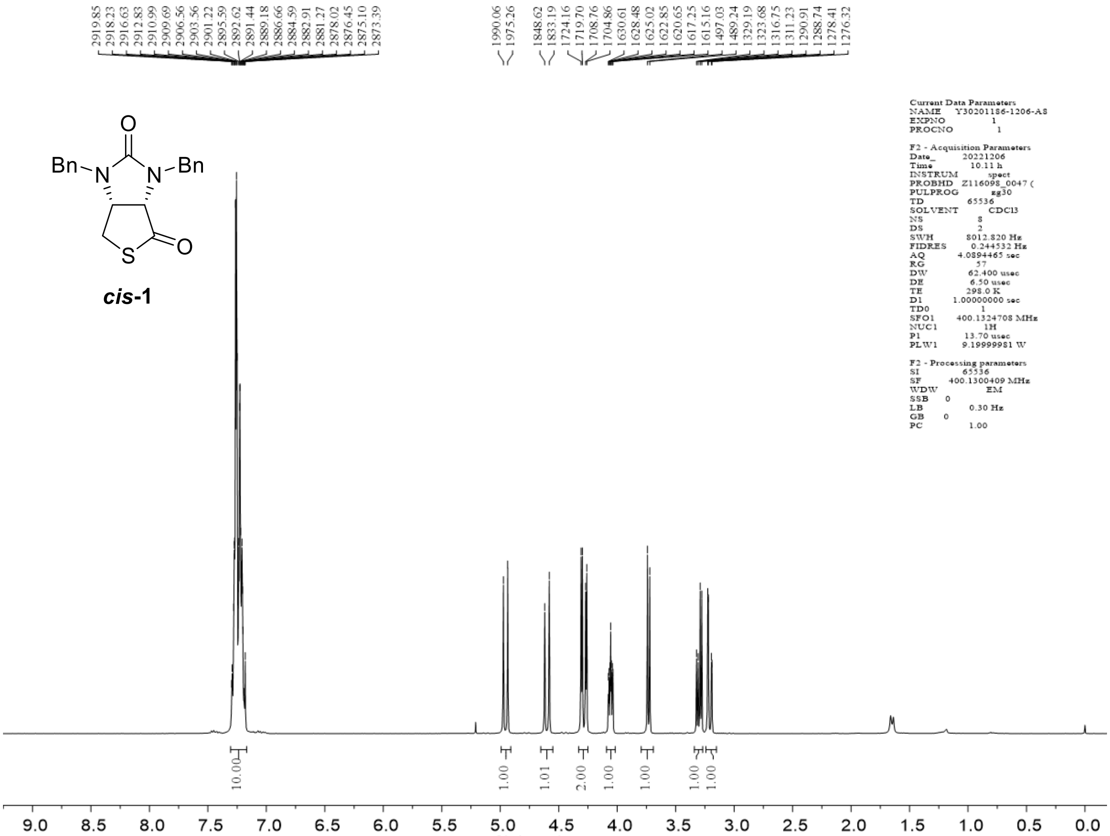


Figure S23. [1]H NMR ($CDCl_3$, 400 MHz) spectrum of compound ***cis*-1**

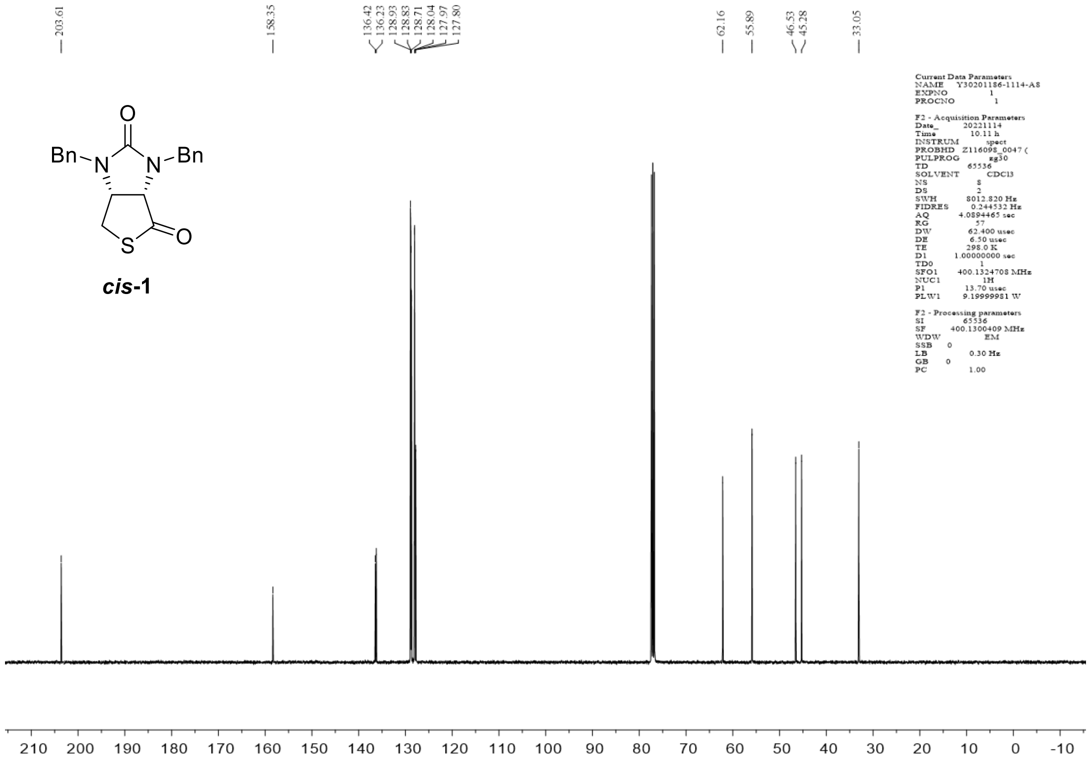


Figure S24. [13]C NMR ($CDCl_3$, 101 MHz) spectrum of compound ***cis*-1**

HR MS (ESI) Spectra of Compounds **5-10** and **1**

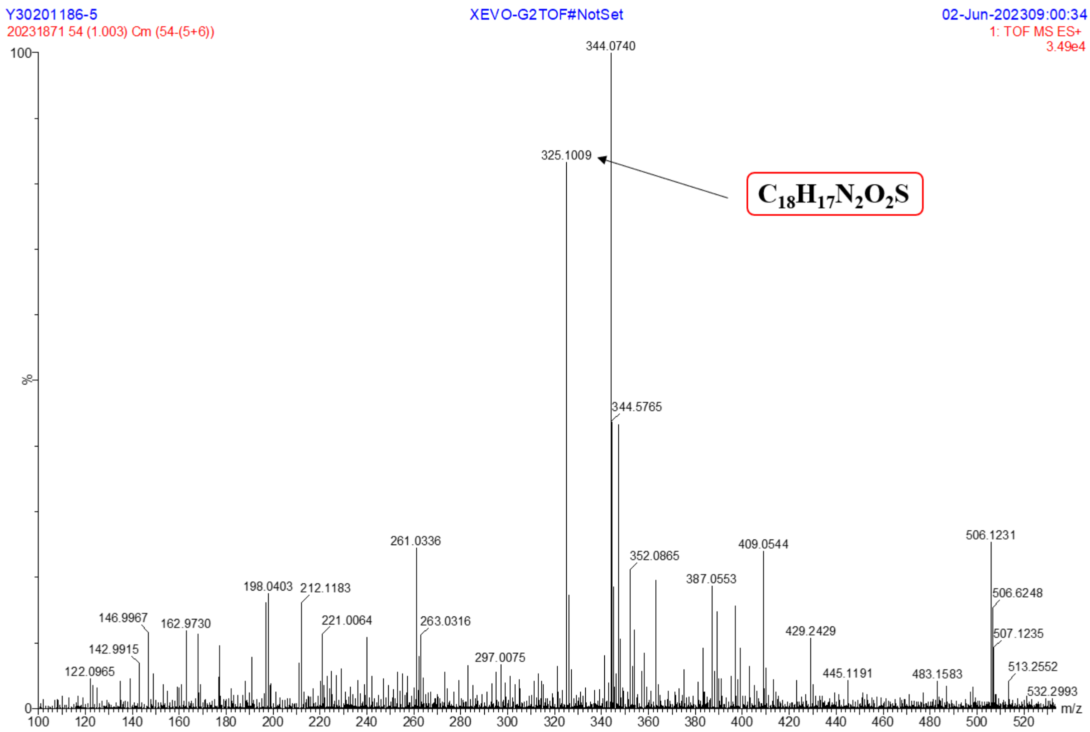


Figure S25. ESI Spectra of compound **5**

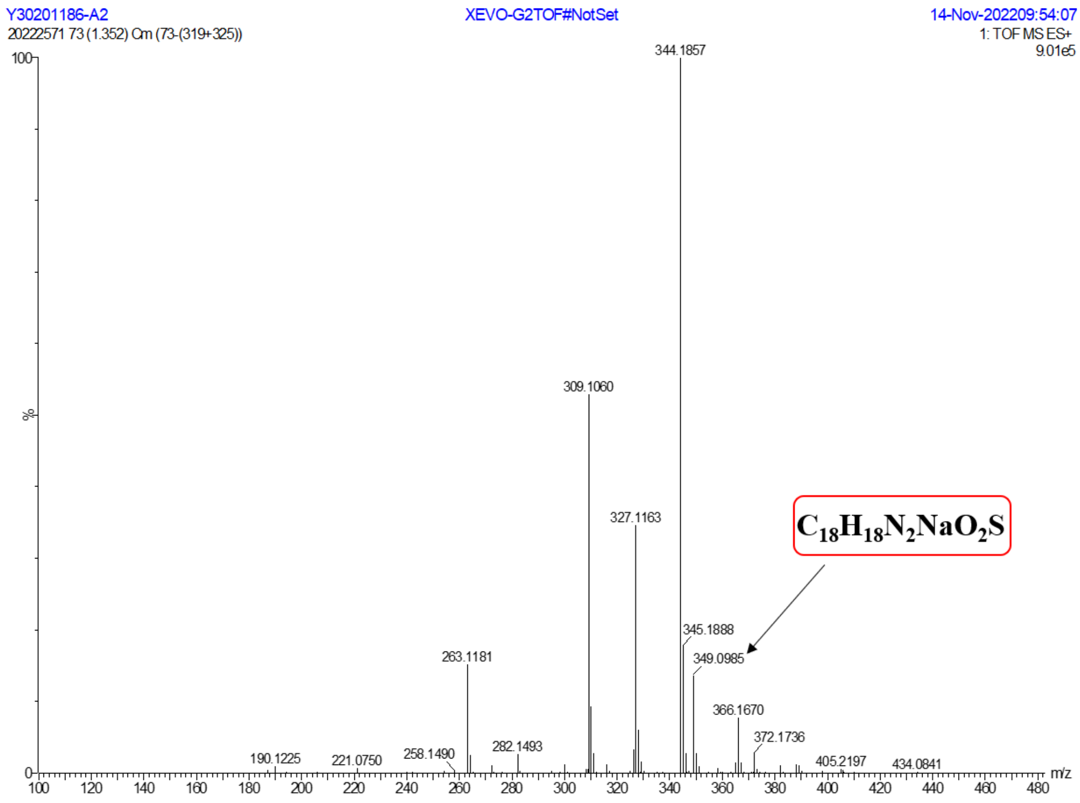


Figure S26. ESI Spectra of compound **6**

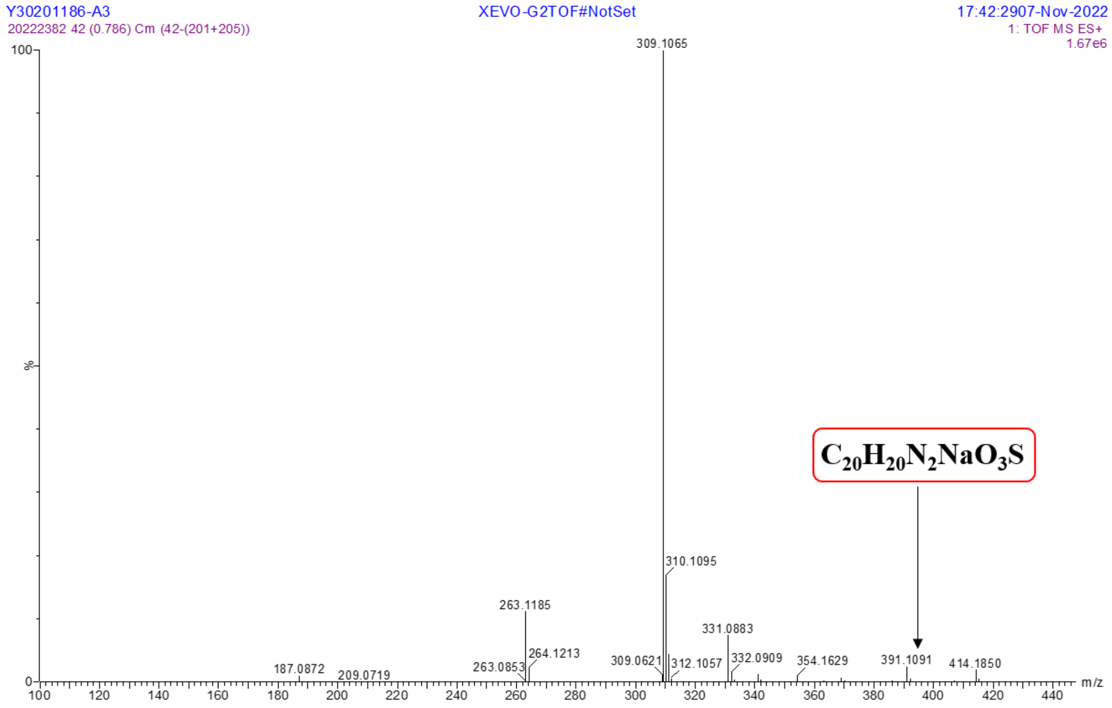


Figure S27. ESI Spectra of compound **7**

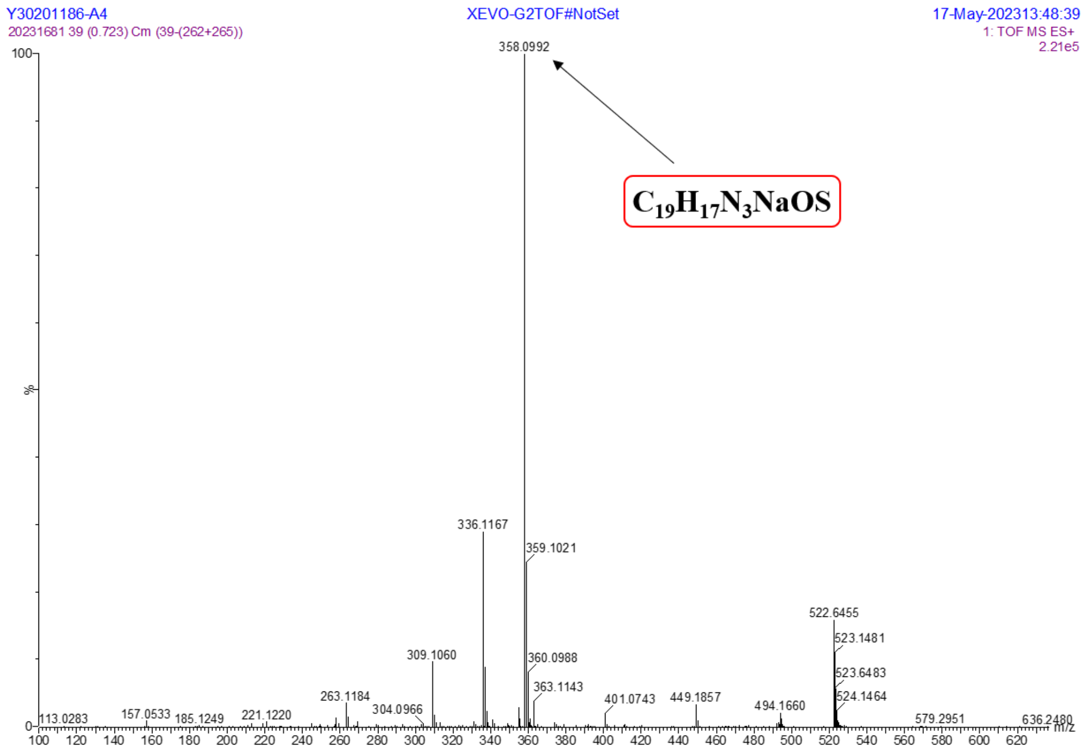


Figure S28. ESI Spectra of compound **8**

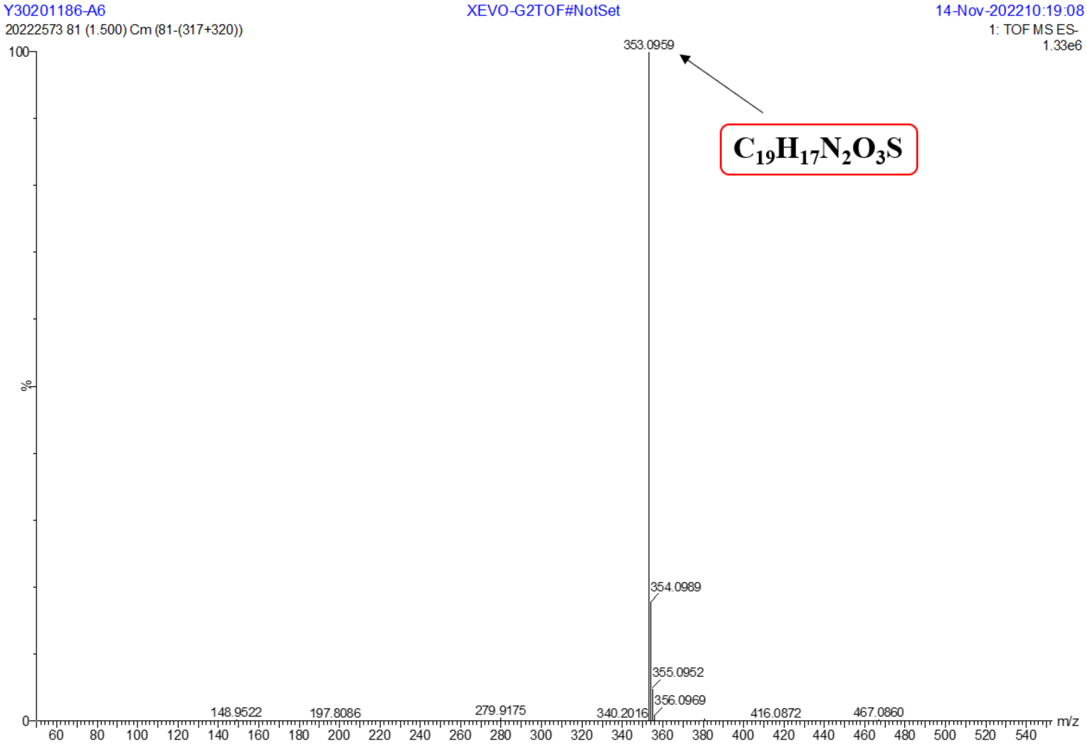


Figure S29. ESI Spectra of compound **9**

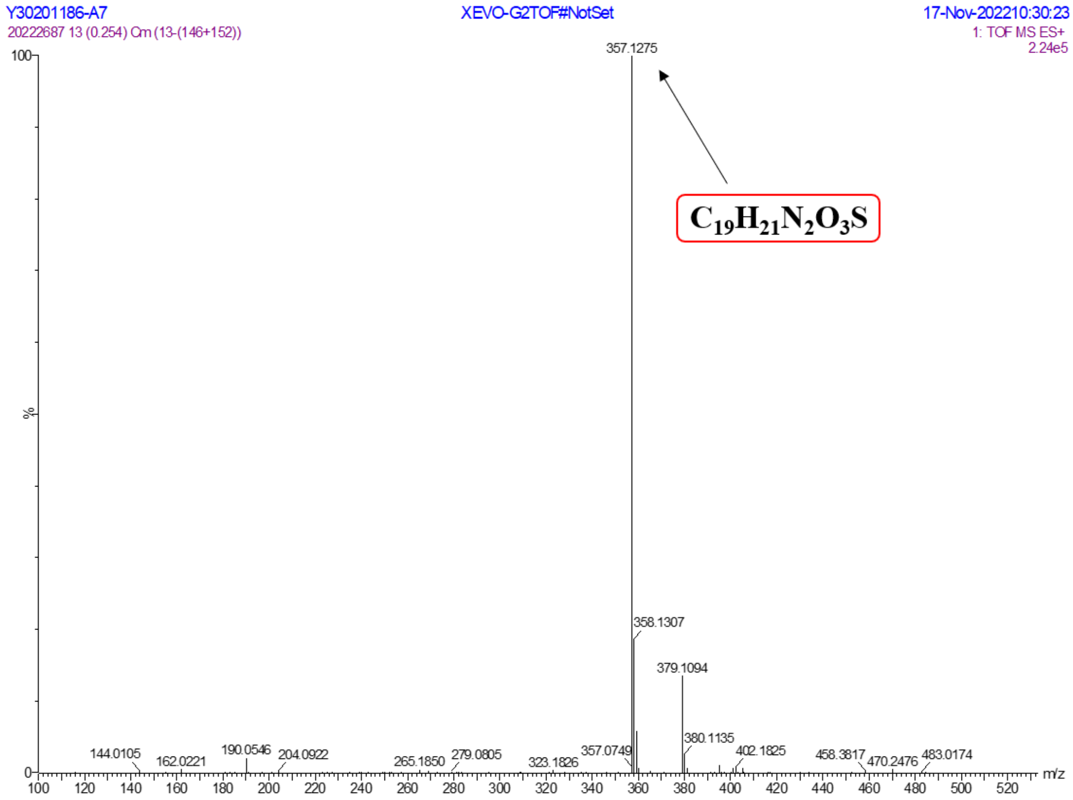


Figure S30. ESI Spectra of compound **10**

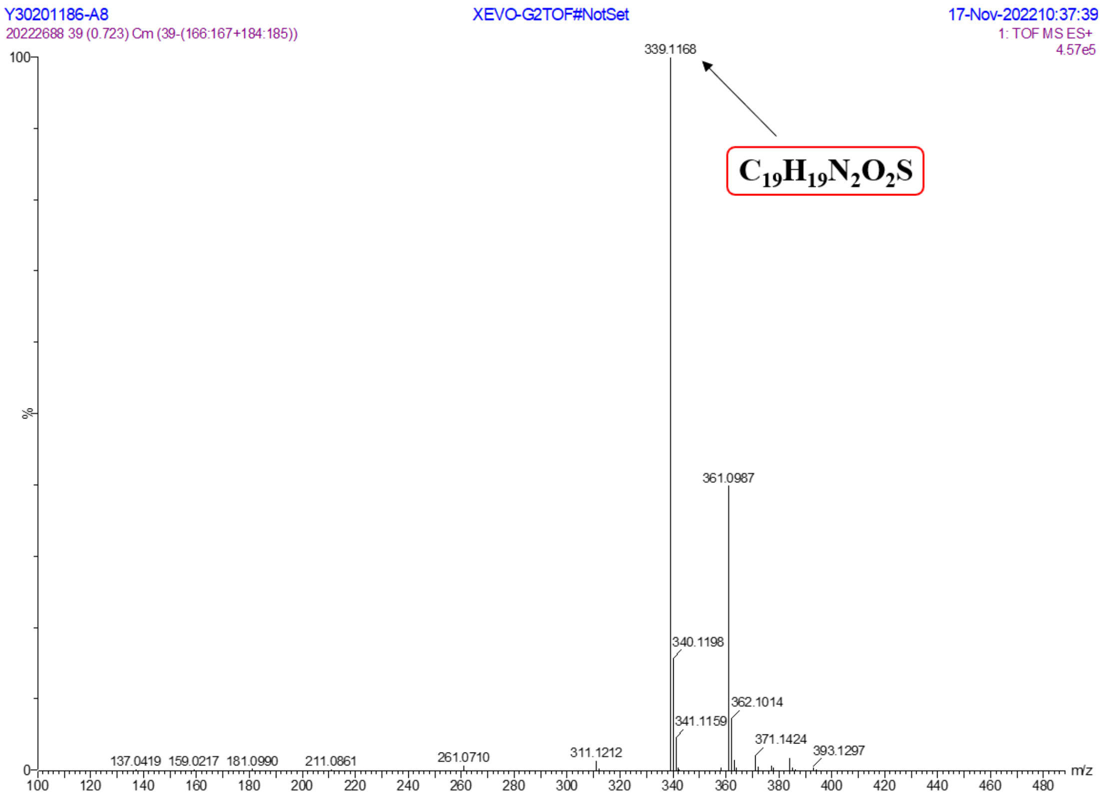
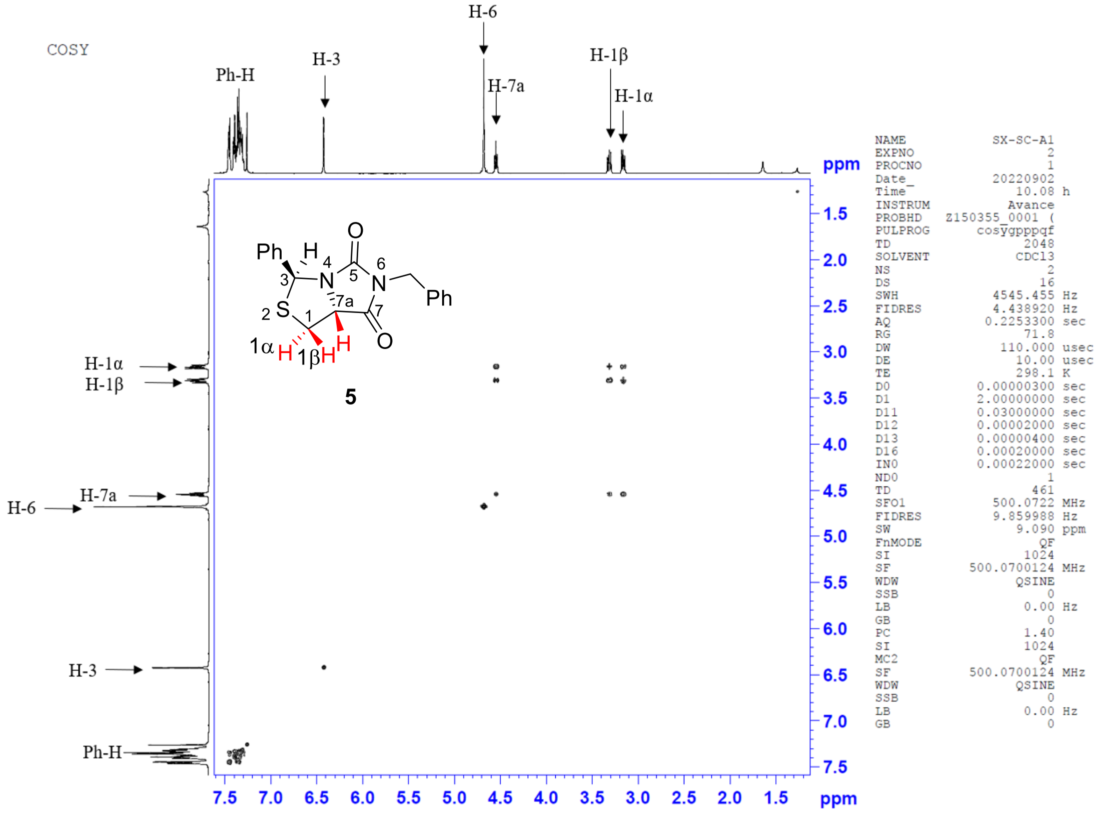


Figure S31. ESI Spectra of compound **1**

^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY Spectra of Compound **5**



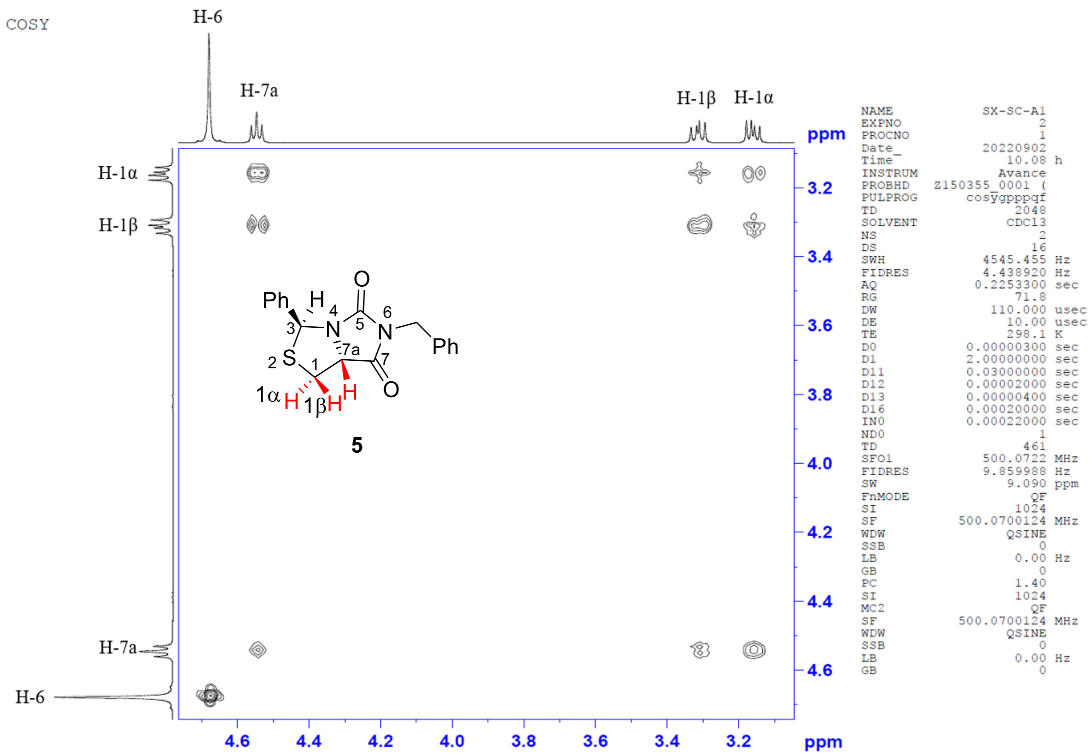
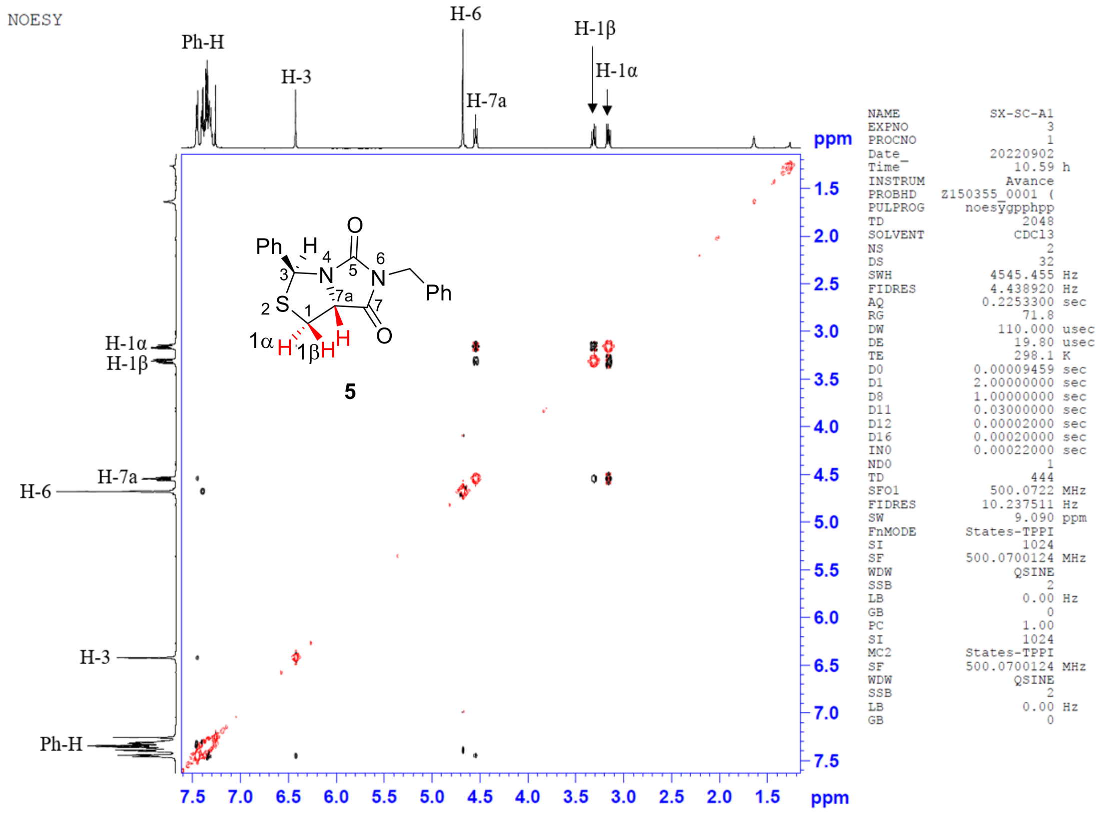


Figure S32. ^{1}H-^{1}H COSY spectrum of compound **5**



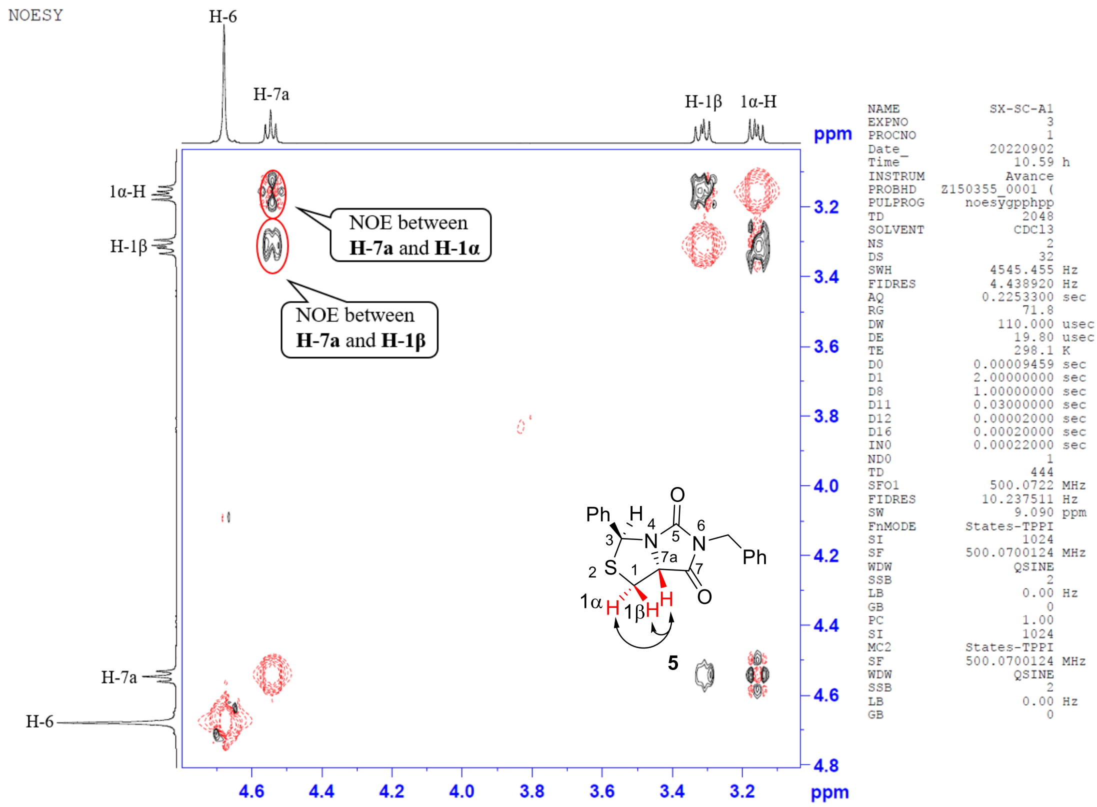
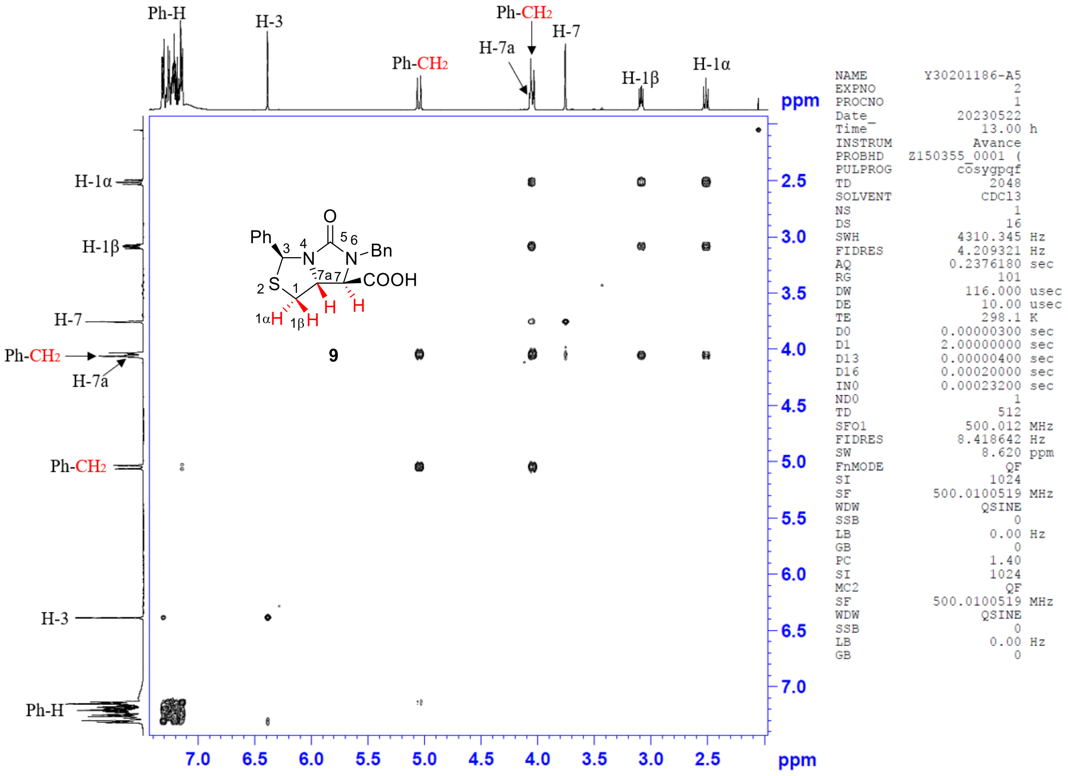


Figure S33. ^{1}H-^{1}H NOESY spectrum of compound **5**

^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY Spectra of Compound **9**

COSY



COSY

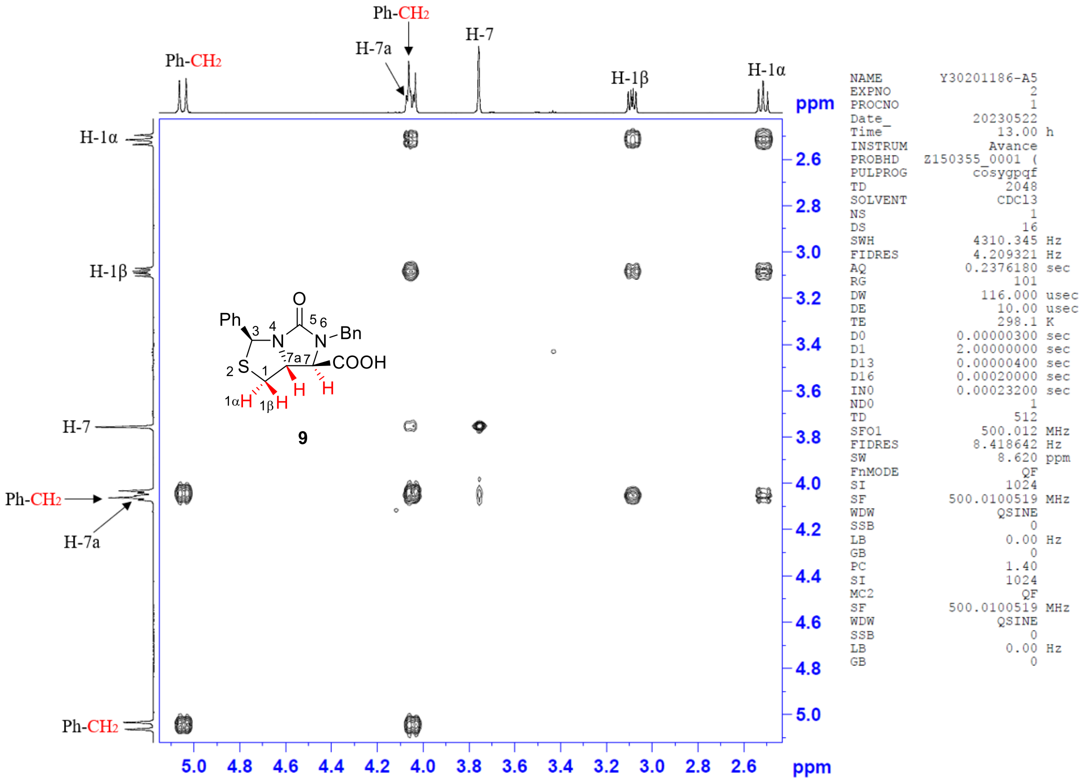
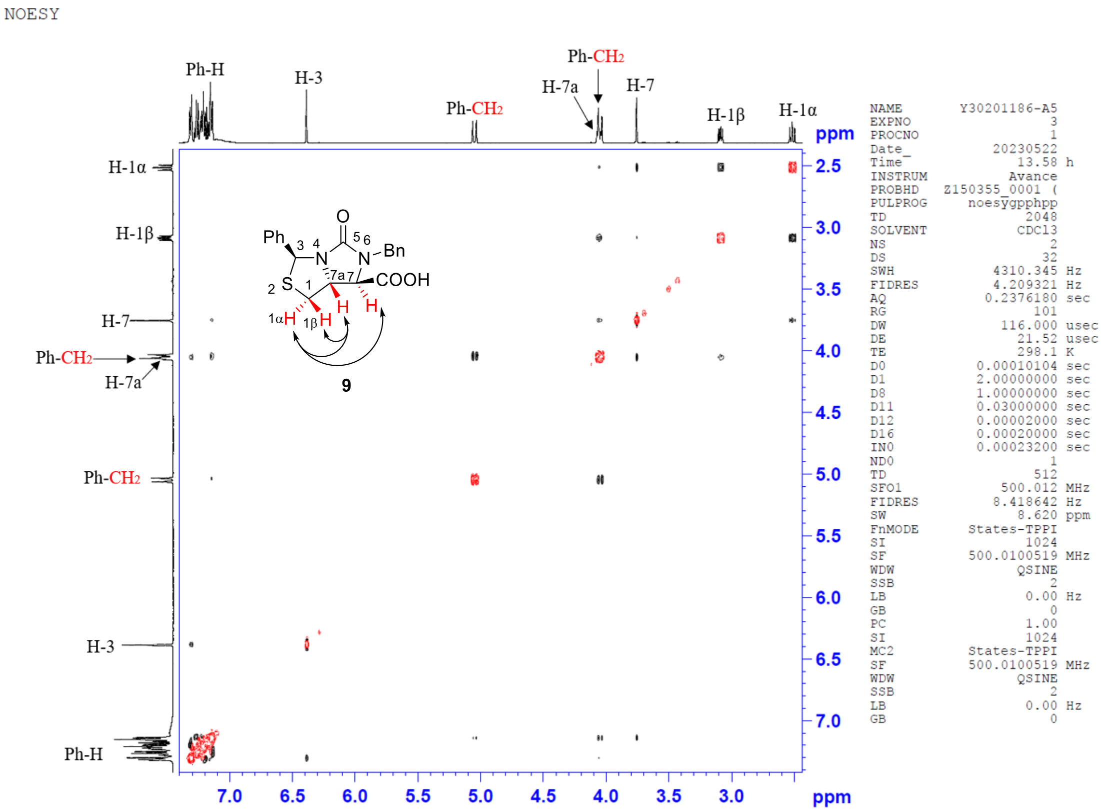


Figure S34. ^{1}H-^{1}H COSY spectrum of compound **9**



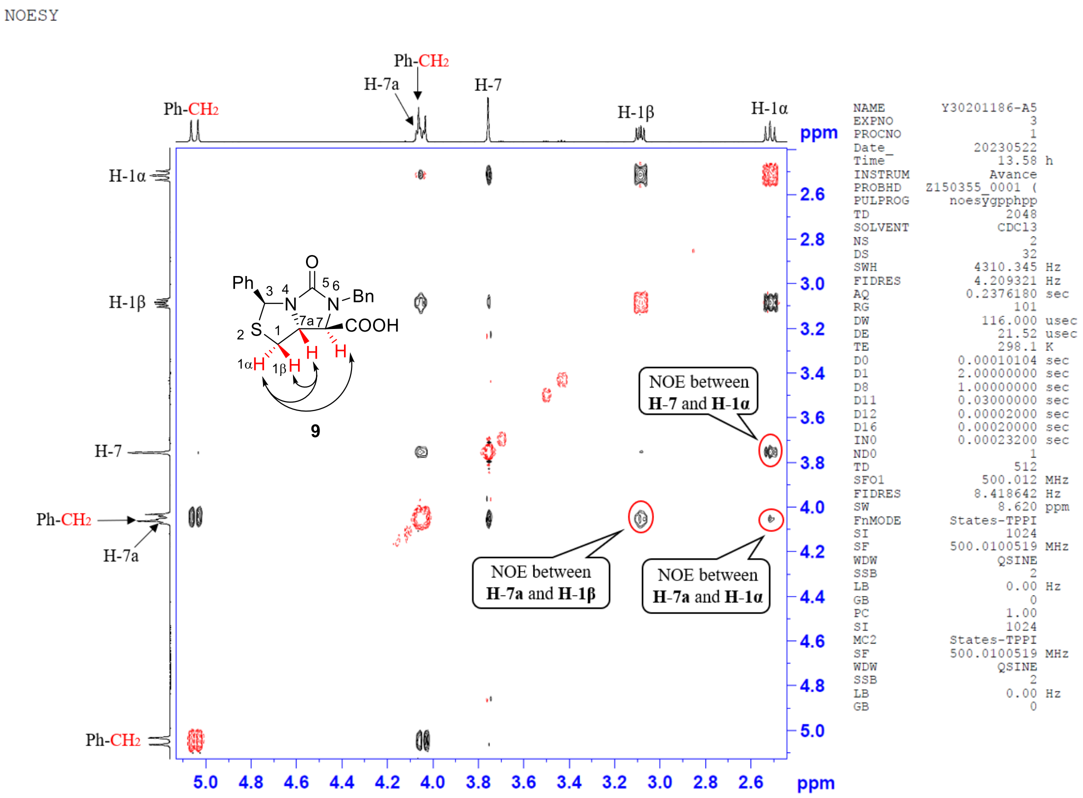
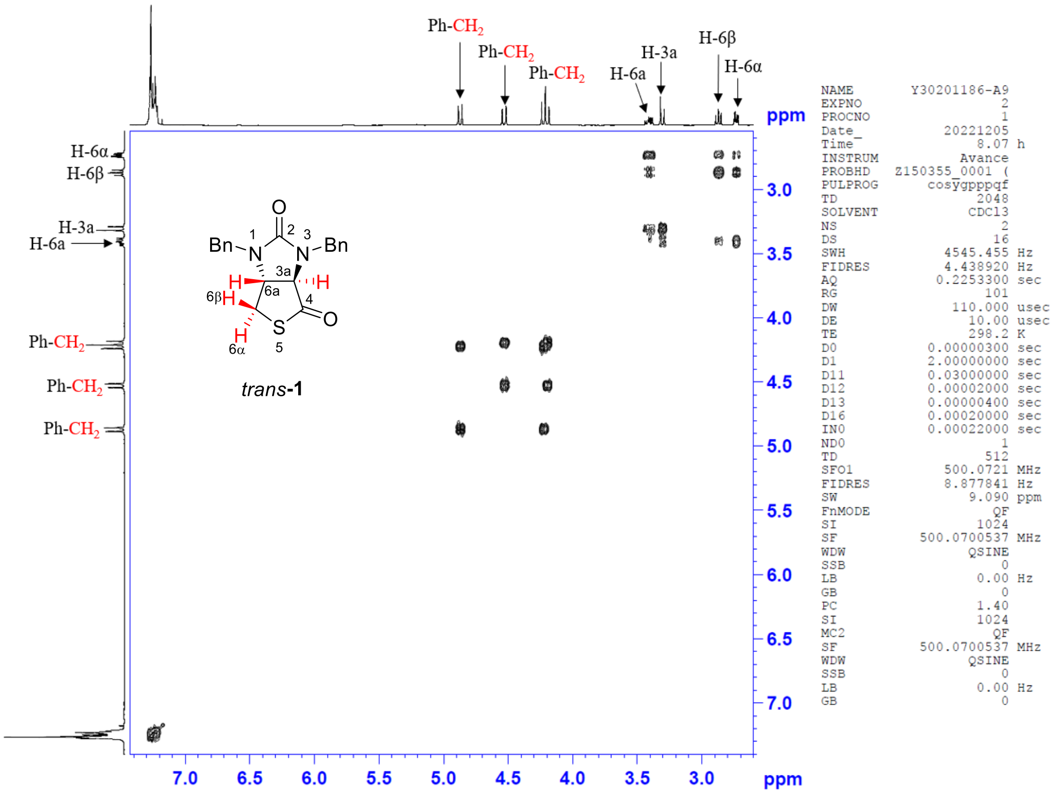


Figure S35. ^{1}H-^{1}H NOESY spectrum of compound **9**

^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY Spectra of Compound ***trans*-1**

COSY



COSY

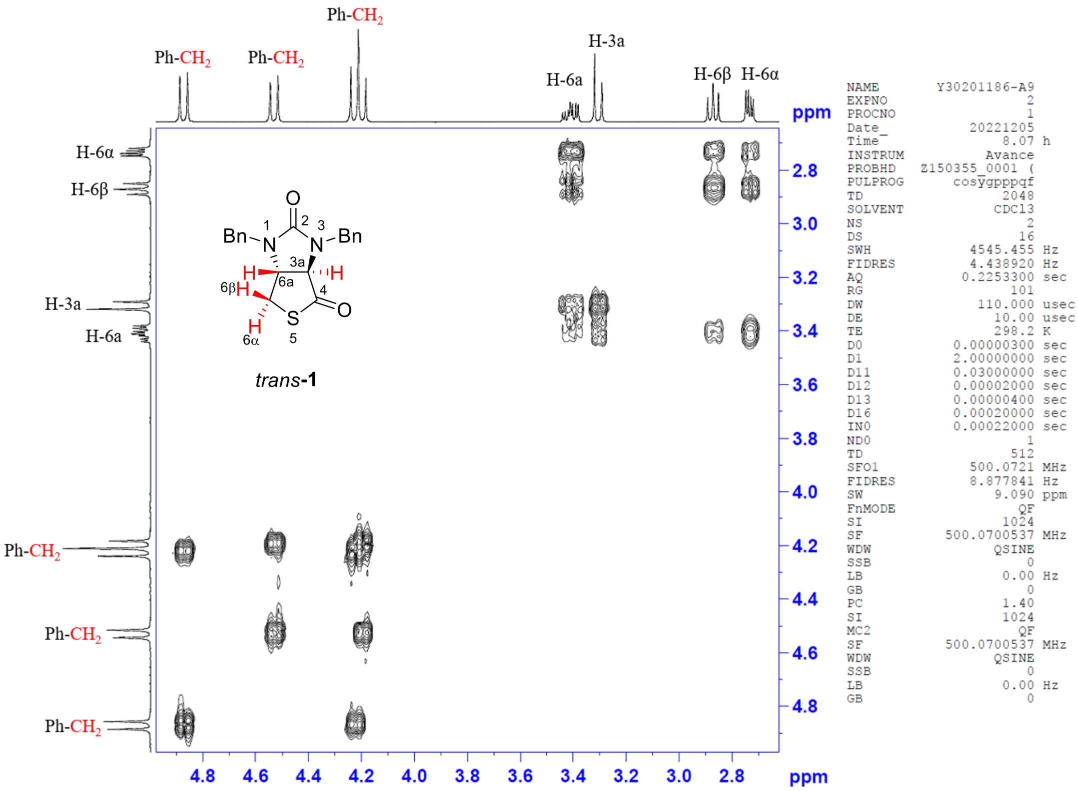
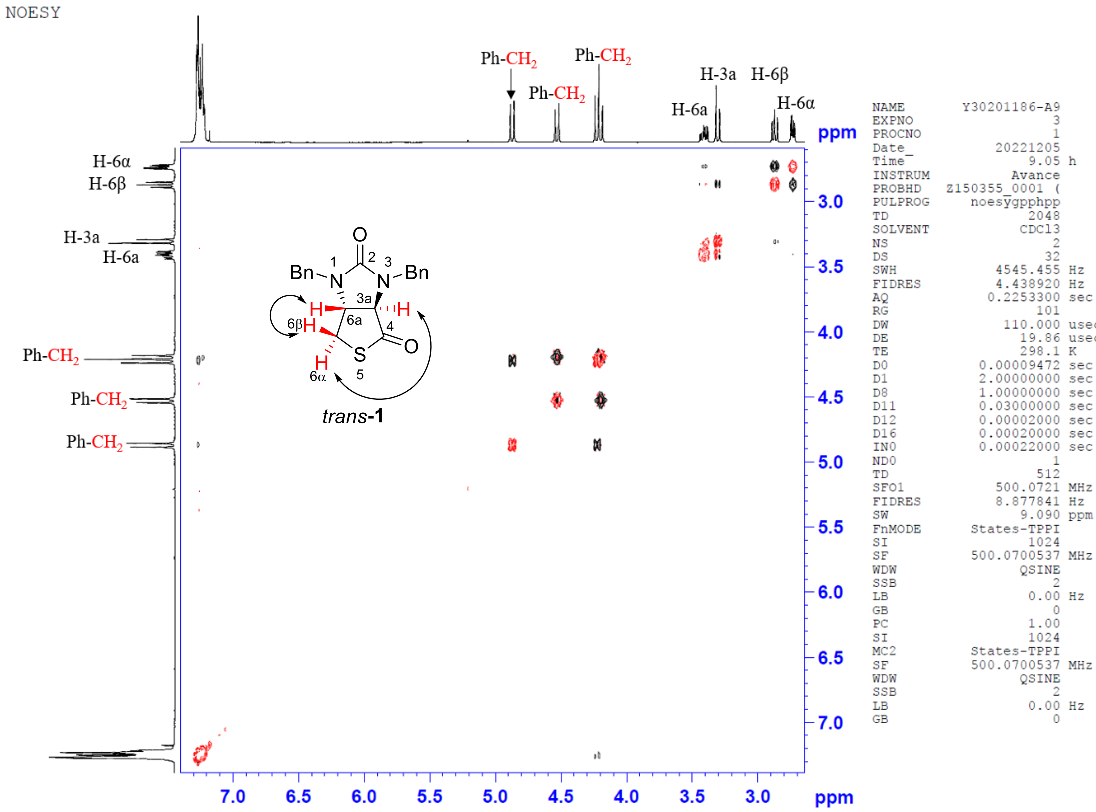


Figure S36. ^{1}H-^{1}H COSY spectrum of compound ***trans*-1**



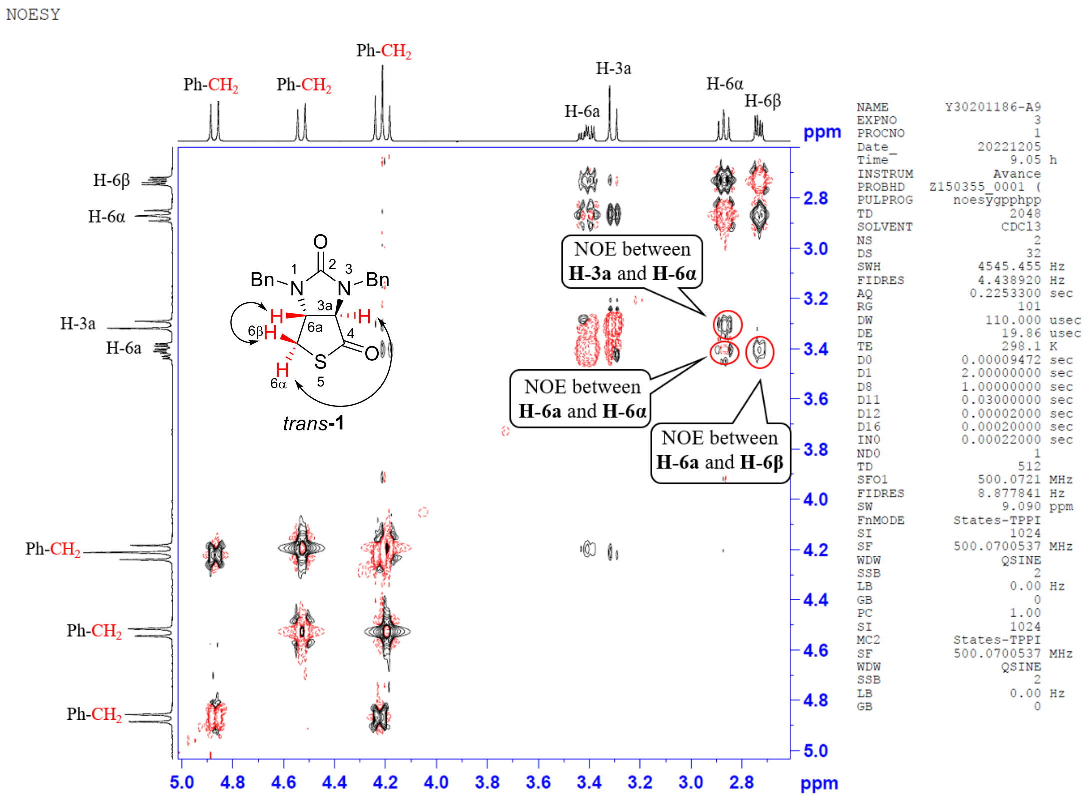
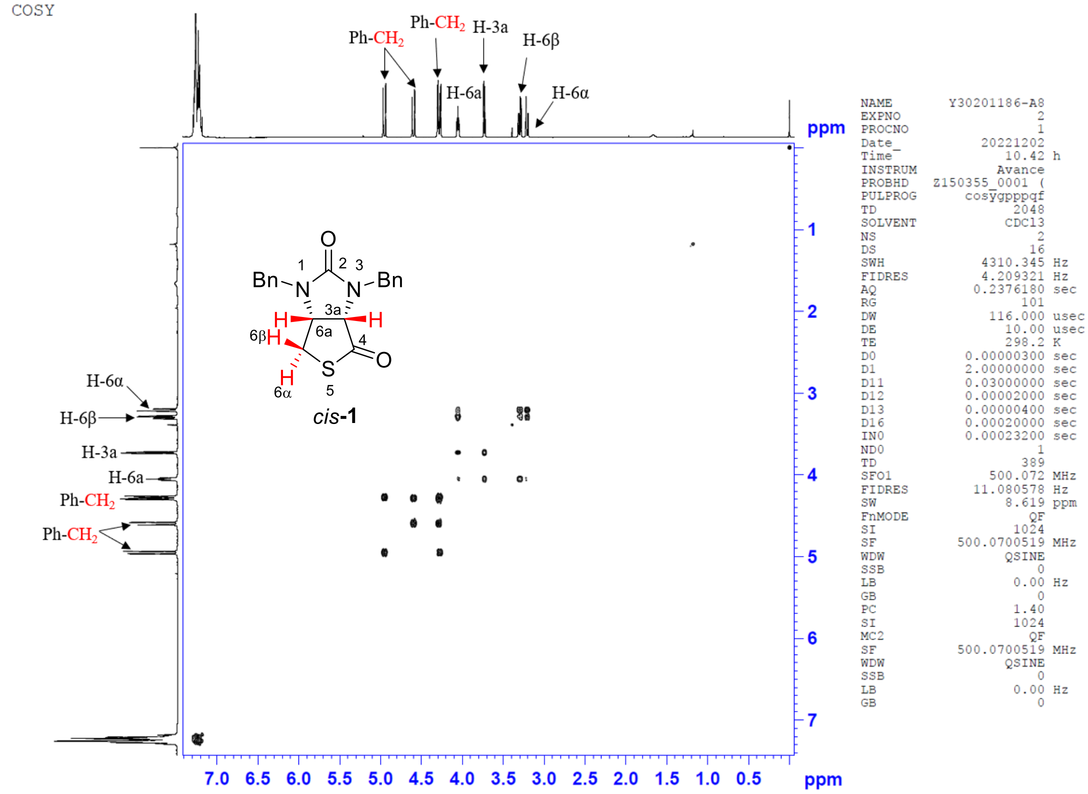


Figure S37. [1]H-[1]H NOESY spectrum of compound ***trans*-1**

^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY Spectra of Compound ***cis*-1**



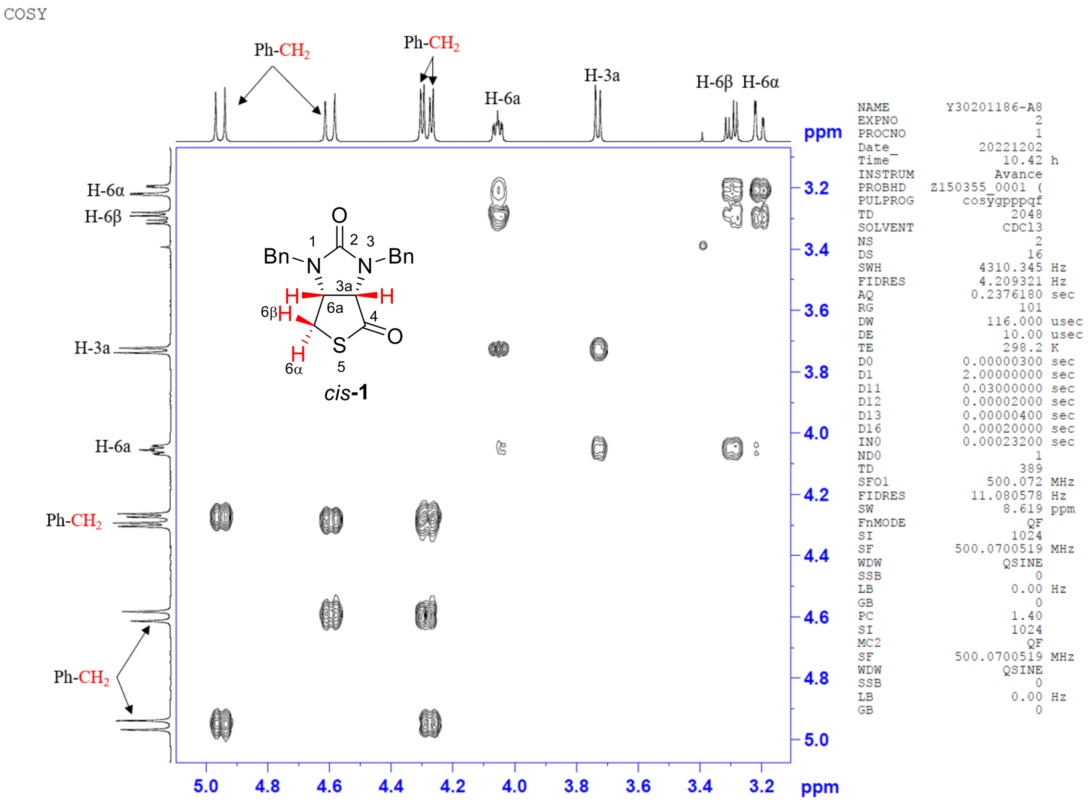


Figure S38. ^{1}H-^{1}H COSY spectrum of compound ***cis*-1**

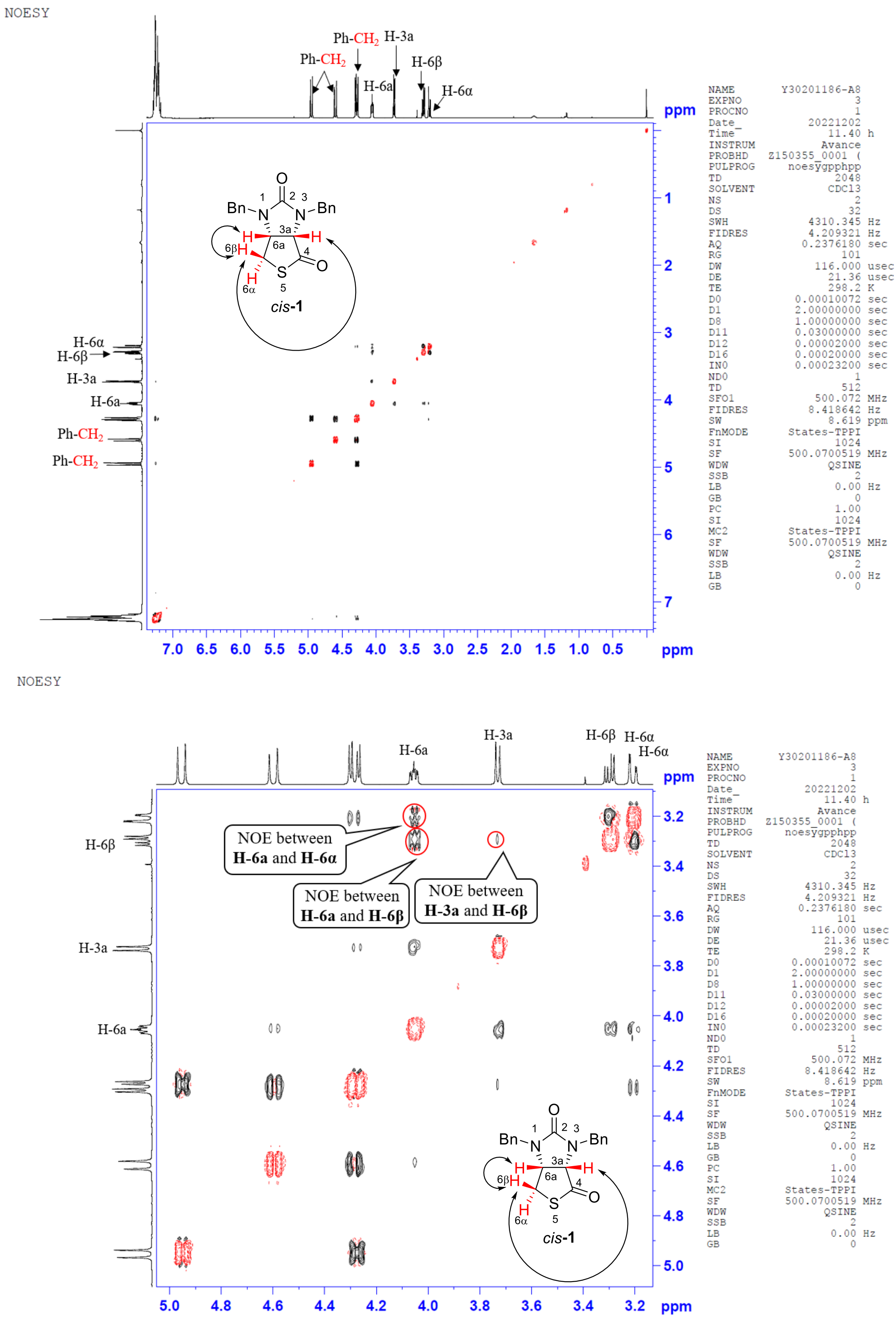
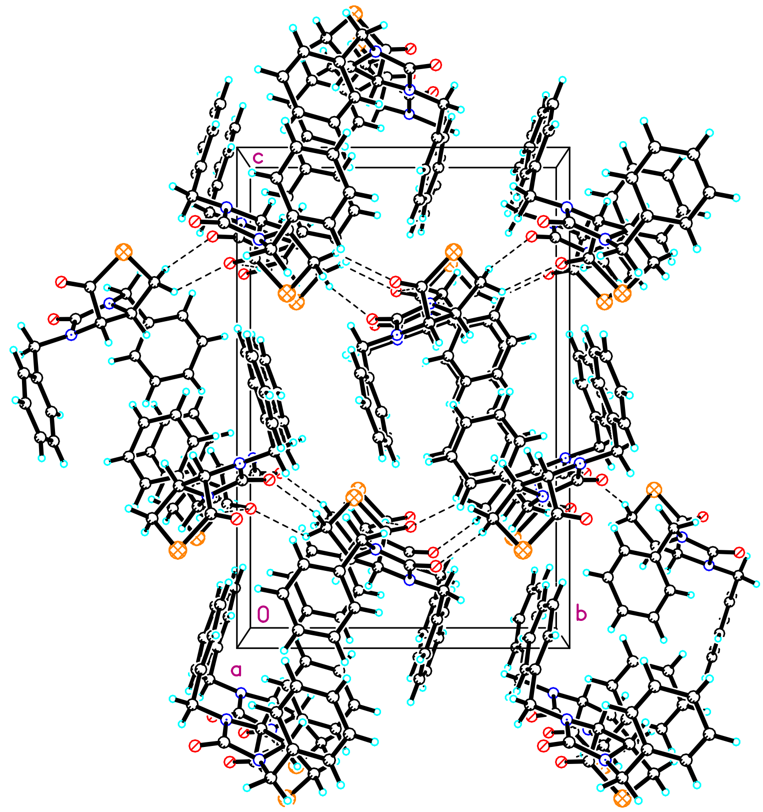


Figure S39. ^{1}H-^{1}H NOESY spectrum of compound ***cis*-1**

X-ray crystal structure and crystallographic data of compound *cis*-**1**:



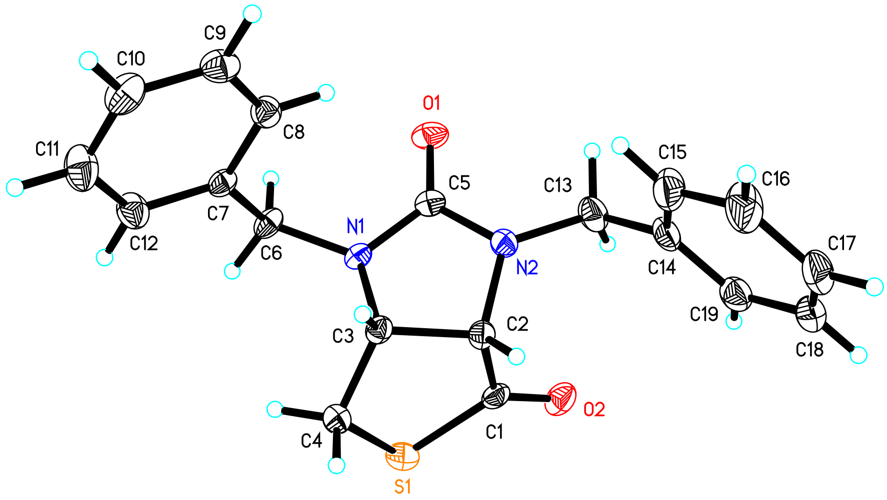


Figure S40. X-ray crystal structure of compound **1**

Table 1. Crystal data and structure refinement for mo_d8v23078_0m

Identification code	mo_d8v23078_0m
Empirical formula	C19 H18 N2 O2 S
Formula weight	338.41
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 7.8298(4) Å a= 90°.
	b = 11.9363(7) Å b= 90°.
	c = 17.9486(9) Å g = 90°.
Volume	1677.46(16) Å3
Z	4
Density (calculated)	1.340 Mg/m3
Absorption coefficient	0.206 mm-1
F(000)	712
Crystal size	0.180 x 0.150 x 0.120 mm3
Theta range for data collection	2.838 to 25.994°.
Index ranges	-9<=h<=9, -10<=k<=14, -22<=l<=21
Reflections collected	8352
Independent reflections	3278 [R(int) = 0.0416]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5072
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3278 / 0 / 218
Goodness-of-fit on F2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0810
R indices (all data)	R1 = 0.0346, wR2 = 0.0833
Absolute structure parameter	0.02(4)
Extinction coefficient	0.080(8)
Largest diff. peak and hole	0.161 and -0.210 e.Å-3

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103)
for mo_d8v23078_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	9060(1)	6530(1)	7934(1)	45(1)
O(1)	4908(2)	4027(1)	6640(1)	43(1)
O(2)	10449(2)	4769(1)	7302(1)	44(1)
N(1)	5695(2)	5838(1)	6955(1)	28(1)
N(2)	7491(2)	4805(1)	6286(1)	32(1)
C(1)	9488(3)	5549(2)	7225(1)	32(1)
C(2)	8446(3)	5789(2)	6517(1)	29(1)
C(3)	7036(2)	6614(2)	6729(1)	28(1)
C(4)	7667(3)	7368(2)	7353(1)	40(1)
C(5)	5913(3)	4804(2)	6630(1)	30(1)
C(6)	4014(3)	6229(2)	7187(1)	33(1)
C(7)	3073(2)	6884(2)	6594(1)	28(1)
C(8)	2833(3)	6433(2)	5889(1)	34(1)
C(9)	1932(3)	7018(2)	5352(1)	41(1)
C(10)	1248(3)	8048(2)	5513(1)	47(1)
C(11)	1458(4)	8504(2)	6211(2)	53(1)
C(12)	2382(3)	7925(2)	6750(1)	42(1)
C(13)	8283(3)	3755(2)	6034(2)	43(1)
C(14)	9510(3)	3947(2)	5401(1)	40(1)
C(15)	8938(4)	4331(3)	4715(1)	56(1)
C(16)	10045(4)	4499(3)	4133(2)	67(1)
C(17)	11764(4)	4270(3)	4220(2)	60(1)
C(18)	12350(4)	3879(2)	4893(2)	53(1)
C(19)	11234(3)	3723(2)	5482(2)	45(1)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v23078_0m.

S(1)-C(1)	1.762(2)
S(1)-C(4)	1.810(2)
O(1)-C(5)	1.217(2)
O(2)-C(1)	1.205(3)
N(1)-C(5)	1.376(3)
N(1)-C(6)	1.457(3)
N(1)-C(3)	1.459(3)
N(2)-C(5)	1.381(3)
N(2)-C(2)	1.453(3)
N(2)-C(13)	1.469(3)
C(1)-C(2)	1.537(3)
C(2)-C(3)	1.528(3)
C(2)-H(2)	0.9900
C(3)-C(4)	1.520(3)
C(3)-H(3)	0.9900
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(6)-C(7)	1.513(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(7)-C(12)	1.383(3)
C(7)-C(8)	1.389(3)
C(8)-C(9)	1.383(3)
C(8)-H(8)	0.9400
C(9)-C(10)	1.372(4)
C(9)-H(9)	0.9400
C(10)-C(11)	1.376(4)
C(10)-H(10)	0.9400
C(11)-C(12)	1.391(4)
C(11)-H(11)	0.9400
C(12)-H(12)	0.9400
C(13)-C(14)	1.506(4)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(14)-C(19)	1.384(4)
C(14)-C(15)	1.387(4)
C(15)-C(16)	1.373(4)
C(15)-H(15)	0.9400
C(16)-C(17)	1.383(4)
C(16)-H(16)	0.9400
C(17)-C(18)	1.373(4)
C(17)-H(17)	0.9400

C(18)-C(19)	1.385(4)
C(18)-H(18)	0.9400
C(19)-H(19)	0.9400

C(1)-S(1)-C(4)	93.79(11)
C(5)-N(1)-C(6)	121.38(18)
C(5)-N(1)-C(3)	111.22(16)
C(6)-N(1)-C(3)	121.74(16)
C(5)-N(2)-C(2)	109.45(17)
C(5)-N(2)-C(13)	120.93(18)
C(2)-N(2)-C(13)	124.05(18)
O(2)-C(1)-C(2)	124.8(2)
O(2)-C(1)-S(1)	123.31(18)
C(2)-C(1)-S(1)	111.84(15)
N(2)-C(2)-C(3)	102.74(16)
N(2)-C(2)-C(1)	111.05(17)
C(3)-C(2)-C(1)	107.37(17)
N(2)-C(2)-H(2)	111.8
C(3)-C(2)-H(2)	111.8
C(1)-C(2)-H(2)	111.8
N(1)-C(3)-C(4)	113.86(17)
N(1)-C(3)-C(2)	100.35(16)
C(4)-C(3)-C(2)	109.29(17)
N(1)-C(3)-H(3)	111.0
C(4)-C(3)-H(3)	111.0
C(2)-C(3)-H(3)	111.0
C(3)-C(4)-S(1)	107.05(15)
C(3)-C(4)-H(4A)	110.3
S(1)-C(4)-H(4A)	110.3
C(3)-C(4)-H(4B)	110.3
S(1)-C(4)-H(4B)	110.3
H(4A)-C(4)-H(4B)	108.6
O(1)-C(5)-N(1)	126.7(2)
O(1)-C(5)-N(2)	125.9(2)
N(1)-C(5)-N(2)	107.48(17)
N(1)-C(6)-C(7)	113.90(17)
N(1)-C(6)-H(6A)	108.8
C(7)-C(6)-H(6A)	108.8
N(1)-C(6)-H(6B)	108.8
C(7)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
C(12)-C(7)-C(8)	118.6(2)
C(12)-C(7)-C(6)	120.88(19)
C(8)-C(7)-C(6)	120.44(19)

C(9)-C(8)-C(7)	120.6(2)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(10)-C(9)-C(8)	120.3(2)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	120.0(2)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(10)-C(11)-C(12)	119.9(2)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(7)-C(12)-C(11)	120.6(2)
C(7)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
N(2)-C(13)-C(14)	111.80(19)
N(2)-C(13)-H(13A)	109.3
C(14)-C(13)-H(13A)	109.3
N(2)-C(13)-H(13B)	109.3
C(14)-C(13)-H(13B)	109.3
H(13A)-C(13)-H(13B)	107.9
C(19)-C(14)-C(15)	118.2(2)
C(19)-C(14)-C(13)	120.8(2)
C(15)-C(14)-C(13)	120.9(2)
C(16)-C(15)-C(14)	121.3(3)
C(16)-C(15)-H(15)	119.3
C(14)-C(15)-H(15)	119.3
C(15)-C(16)-C(17)	119.9(3)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(18)-C(17)-C(16)	119.5(3)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(17)-C(18)-C(19)	120.4(3)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
C(14)-C(19)-C(18)	120.6(3)
C(14)-C(19)-H(19)	119.7
C(18)-C(19)-H(19)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å2x 103) for mo_d8v23078_0m. The anisotropic
displacement factor exponent takes the form: -2p2[h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	41(1)	48(1)	46(1)	-11(1)	-9(1)	-3(1)
O(1)	39(1)	36(1)	54(1)	5(1)	-6(1)	-13(1)
O(2)	31(1)	41(1)	60(1)	9(1)	-1(1)	5(1)
N(1)	21(1)	31(1)	32(1)	3(1)	1(1)	-2(1)
N(2)	32(1)	26(1)	38(1)	-3(1)	2(1)	0(1)
C(1)	21(1)	32(1)	43(1)	2(1)	3(1)	-5(1)
C(2)	28(1)	25(1)	35(1)	2(1)	5(1)	-1(1)
C(3)	25(1)	26(1)	35(1)	3(1)	3(1)	-1(1)
C(4)	34(1)	31(1)	54(1)	-8(1)	2(1)	0(1)
C(5)	30(1)	30(1)	30(1)	6(1)	-4(1)	-3(1)
C(6)	23(1)	48(1)	28(1)	6(1)	3(1)	1(1)
C(7)	21(1)	37(1)	27(1)	3(1)	4(1)	-3(1)
C(8)	34(1)	37(1)	32(1)	-1(1)	2(1)	1(1)
C(9)	44(1)	52(2)	29(1)	1(1)	-5(1)	-4(1)
C(10)	43(1)	56(2)	40(1)	17(1)	-5(1)	6(1)
C(11)	63(2)	46(1)	49(1)	5(1)	2(1)	18(1)
C(12)	50(1)	44(1)	33(1)	-5(1)	0(1)	7(1)
C(13)	52(1)	29(1)	49(1)	-4(1)	4(1)	5(1)
C(14)	47(1)	32(1)	40(1)	-11(1)	-2(1)	10(1)
C(15)	50(2)	79(2)	41(1)	-14(1)	-2(1)	21(2)
C(16)	70(2)	99(3)	33(1)	-9(2)	3(1)	23(2)
C(17)	59(2)	75(2)	44(1)	-22(1)	11(1)	10(2)
C(18)	43(1)	52(2)	62(2)	-22(1)	-1(1)	10(1)
C(19)	49(1)	37(1)	49(1)	-8(1)	-6(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v23078_0m.

	x	y	z	U(eq)
H(2)	9173	6083	6110	35
H(3)	6674	7062	6292	34
H(4A)	6700	7650	7645	48
H(4B)	8291	8009	7148	48
H(6A)	4145	6703	7629	39
H(6B)	3320	5580	7329	39
H(8)	3287	5724	5775	41
H(9)	1787	6708	4875	50
H(10)	637	8443	5146	56
H(11)	977	9205	6324	63
H(12)	2539	8243	7224	51
H(13A)	7388	3234	5874	52
H(13B)	8894	3411	6452	52
H(15)	7768	4479	4648	68
H(16)	9634	4770	3675	81
H(17)	12527	4381	3822	71
H(18)	13517	3716	4953	63
H(19)	11651	3462	5942	54

Table 6. Torsion angles [°] for mo_d8v23078_0m.

C(4)-S(1)-C(1)-O(2)	177.68(19)
C(4)-S(1)-C(1)-C(2)	-4.31(16)
C(5)-N(2)-C(2)-C(3)	-25.5(2)
C(13)-N(2)-C(2)-C(3)	-179.2(2)
C(5)-N(2)-C(2)-C(1)	89.1(2)
C(13)-N(2)-C(2)-C(1)	-64.7(3)
O(2)-C(1)-C(2)-N(2)	51.7(3)
S(1)-C(1)-C(2)-N(2)	-126.26(16)
O(2)-C(1)-C(2)-C(3)	163.30(19)
S(1)-C(1)-C(2)-C(3)	-14.7(2)
C(5)-N(1)-C(3)-C(4)	-140.47(18)
C(6)-N(1)-C(3)-C(4)	65.7(2)
C(5)-N(1)-C(3)-C(2)	-23.9(2)
C(6)-N(1)-C(3)-C(2)	-177.64(17)
N(2)-C(2)-C(3)-N(1)	28.4(2)
C(1)-C(2)-C(3)-N(1)	-88.76(18)
N(2)-C(2)-C(3)-C(4)	148.38(18)
C(1)-C(2)-C(3)-C(4)	31.2(2)
N(1)-C(3)-C(4)-S(1)	77.00(19)
C(2)-C(3)-C(4)-S(1)	-34.3(2)
C(1)-S(1)-C(4)-C(3)	22.10(16)
C(6)-N(1)-C(5)-O(1)	-17.0(3)
C(3)-N(1)-C(5)-O(1)	-170.9(2)
C(6)-N(1)-C(5)-N(2)	163.02(17)
C(3)-N(1)-C(5)-N(2)	9.1(2)
C(2)-N(2)-C(5)-O(1)	-168.8(2)
C(13)-N(2)-C(5)-O(1)	-14.1(3)
C(2)-N(2)-C(5)-N(1)	11.1(2)
C(13)-N(2)-C(5)-N(1)	165.82(19)
C(5)-N(1)-C(6)-C(7)	-91.1(2)
C(3)-N(1)-C(6)-C(7)	60.1(2)
N(1)-C(6)-C(7)-C(12)	-128.7(2)
N(1)-C(6)-C(7)-C(8)	53.6(3)
C(12)-C(7)-C(8)-C(9)	0.5(3)
C(6)-C(7)-C(8)-C(9)	178.2(2)
C(7)-C(8)-C(9)-C(10)	-0.7(4)
C(8)-C(9)-C(10)-C(11)	0.0(4)
C(9)-C(10)-C(11)-C(12)	0.9(4)
C(8)-C(7)-C(12)-C(11)	0.3(3)
C(6)-C(7)-C(12)-C(11)	-177.3(2)
C(10)-C(11)-C(12)-C(7)	-1.0(4)
C(5)-N(2)-C(13)-C(14)	154.2(2)

C(2)-N(2)-C(13)-C(14)	-54.9(3)
N(2)-C(13)-C(14)-C(19)	116.4(3)
N(2)-C(13)-C(14)-C(15)	-65.0(3)
C(19)-C(14)-C(15)-C(16)	-0.8(4)
C(13)-C(14)-C(15)-C(16)	-179.5(3)
C(14)-C(15)-C(16)-C(17)	0.9(5)
C(15)-C(16)-C(17)-C(18)	-0.2(6)
C(16)-C(17)-C(18)-C(19)	-0.5(5)
C(15)-C(14)-C(19)-C(18)	0.0(4)
C(13)-C(14)-C(19)-C(18)	178.7(2)
C(17)-C(18)-C(19)-C(14)	0.7(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v23078_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(13)-H(13B)...O(2)	0.98	2.54	3.085(3)	115.2
C(13)-H(13B)...S(1)#1	0.98	2.97	3.849(3)	149.8
C(6)-H(6B)...O(2)#2	0.98	2.45	3.297(3)	144.8
C(4)-H(4B)...O(2)#3	0.98	2.52	3.282(3)	134.3
C(4)-H(4A)...O(1)#4	0.98	2.44	3.354(3)	155.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+3/2 #2 x-1,y,z #3 -x+2,y+1/2,-z+3/2

#4 -x+1,y+1/2,-z+3/2