Supplementary information

Coupling Pyrazine to Dithiocarbonates for Molybdopterin Model Ligands—Indispensable Tin

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NMR spectra

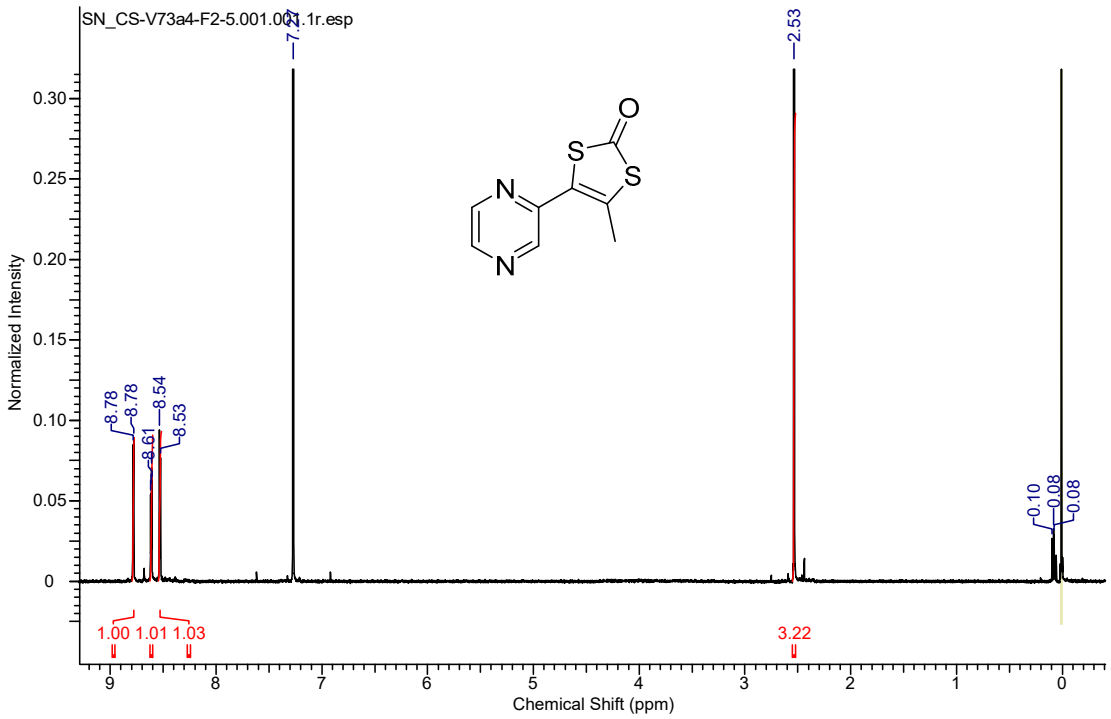

Figure S1: ^{1}H spectrum of compound **12**.

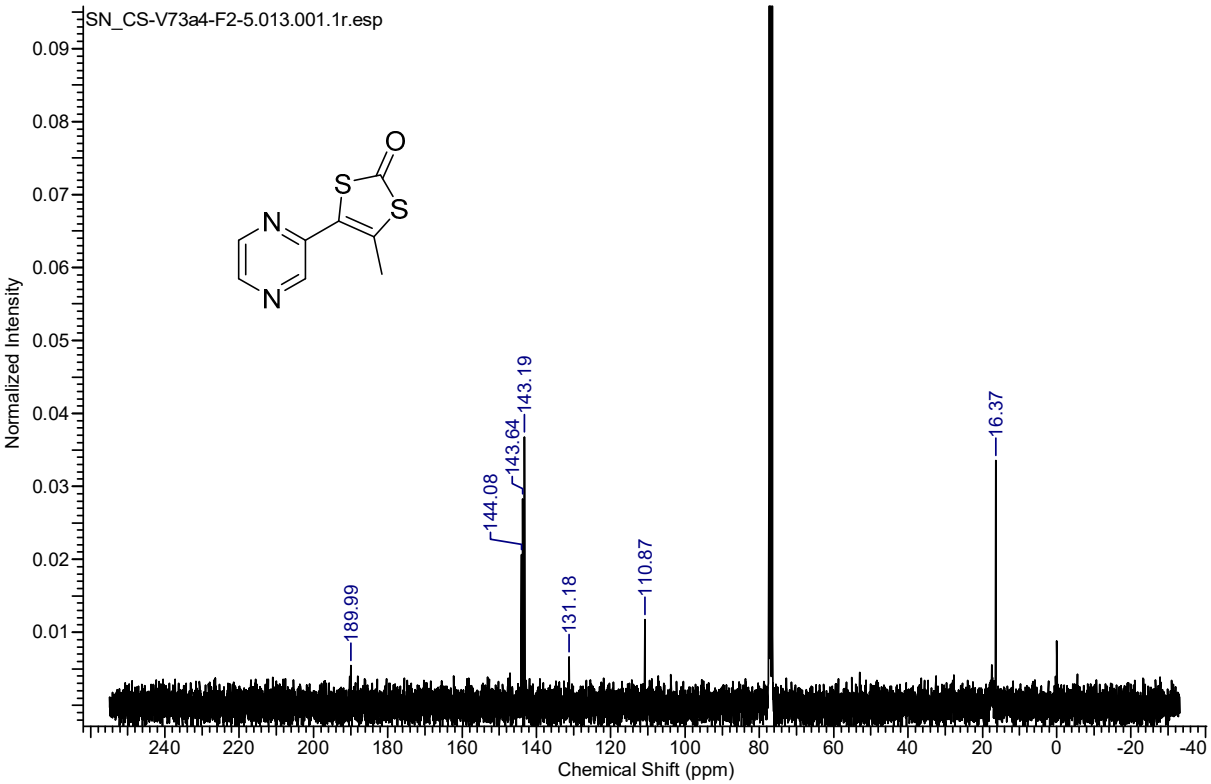

Figure S2: ^{13}C spectrum of compound **12**.

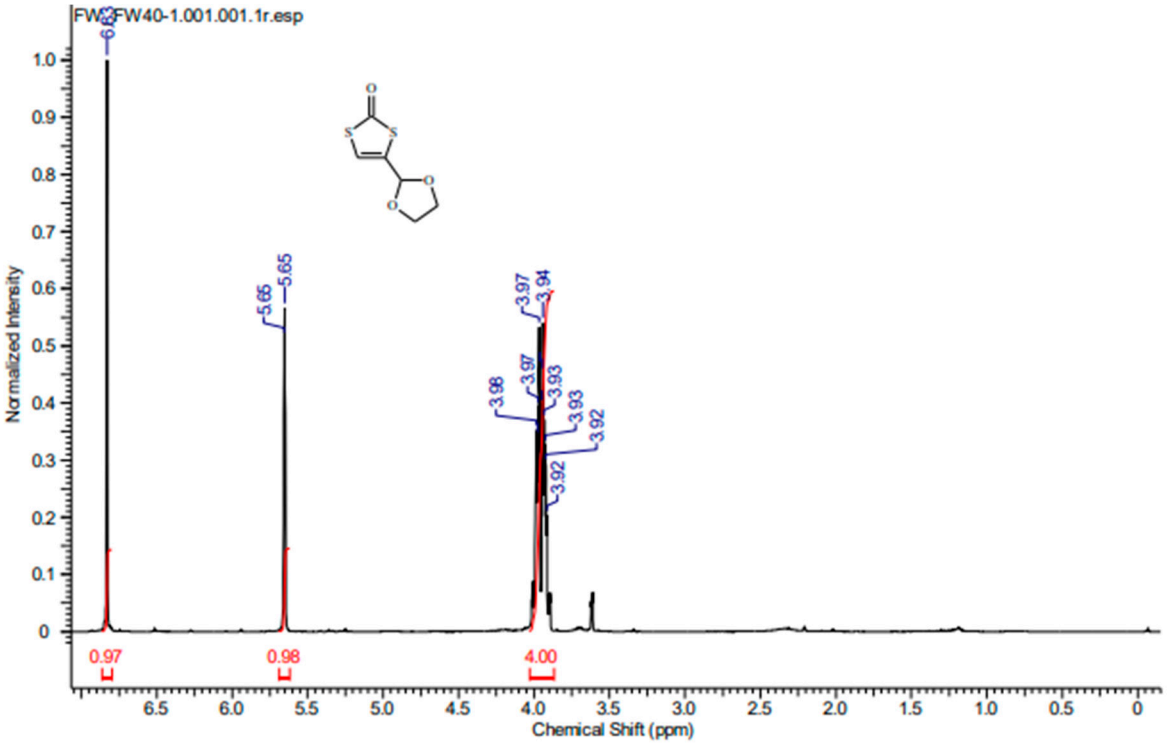

Figure S1: ^{1}H spectrum of compound **14**.

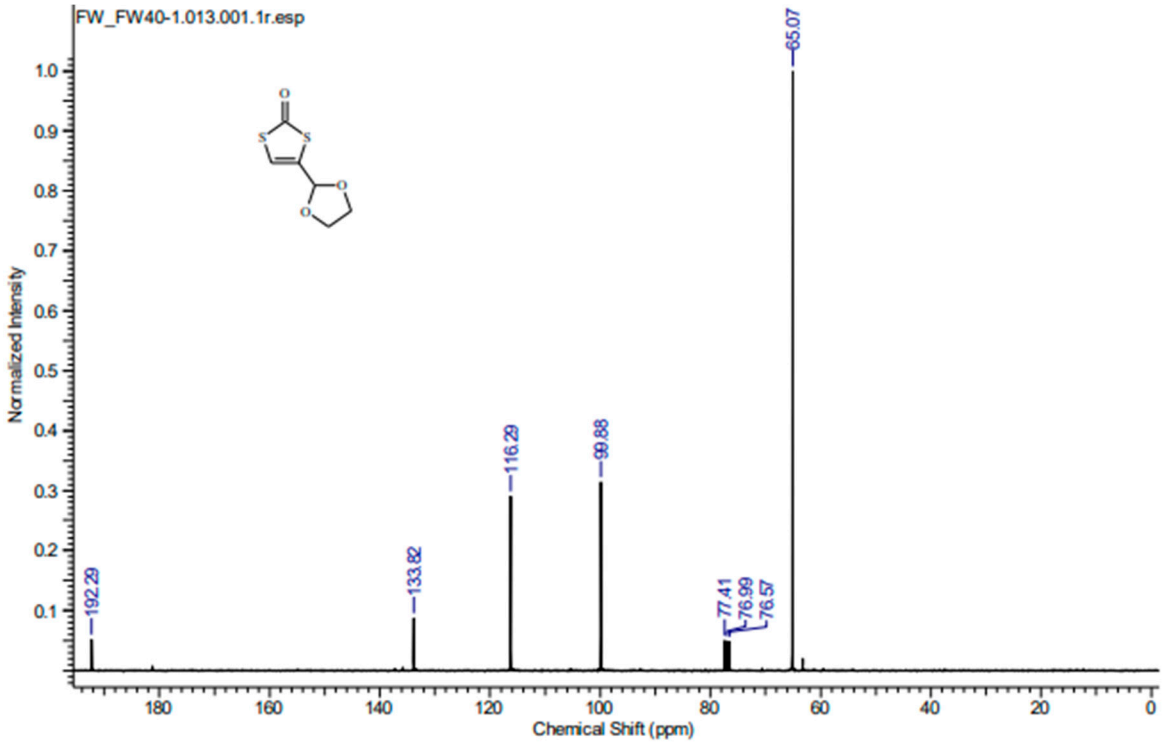

Figure S2: ^{13}C spectrum of compound **14**.

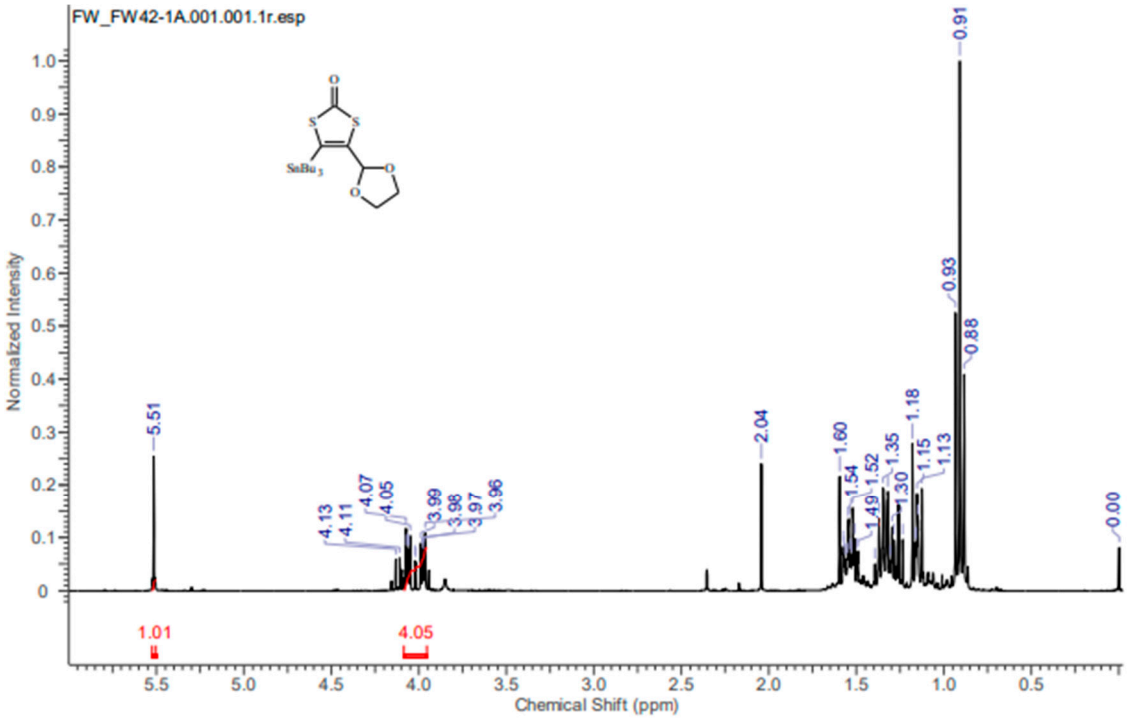

Figure S3: ^{1}H spectrum of compound **15**.

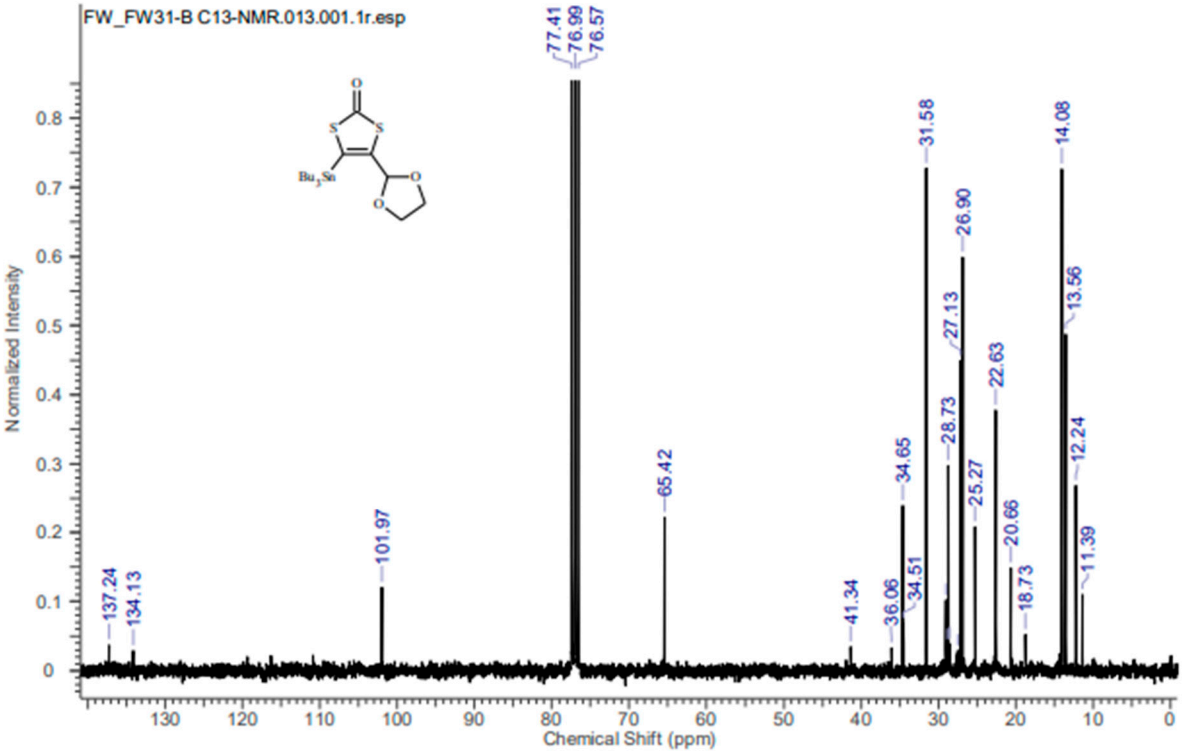

Figure S4: ^{13}C spectrum of compound **15**.

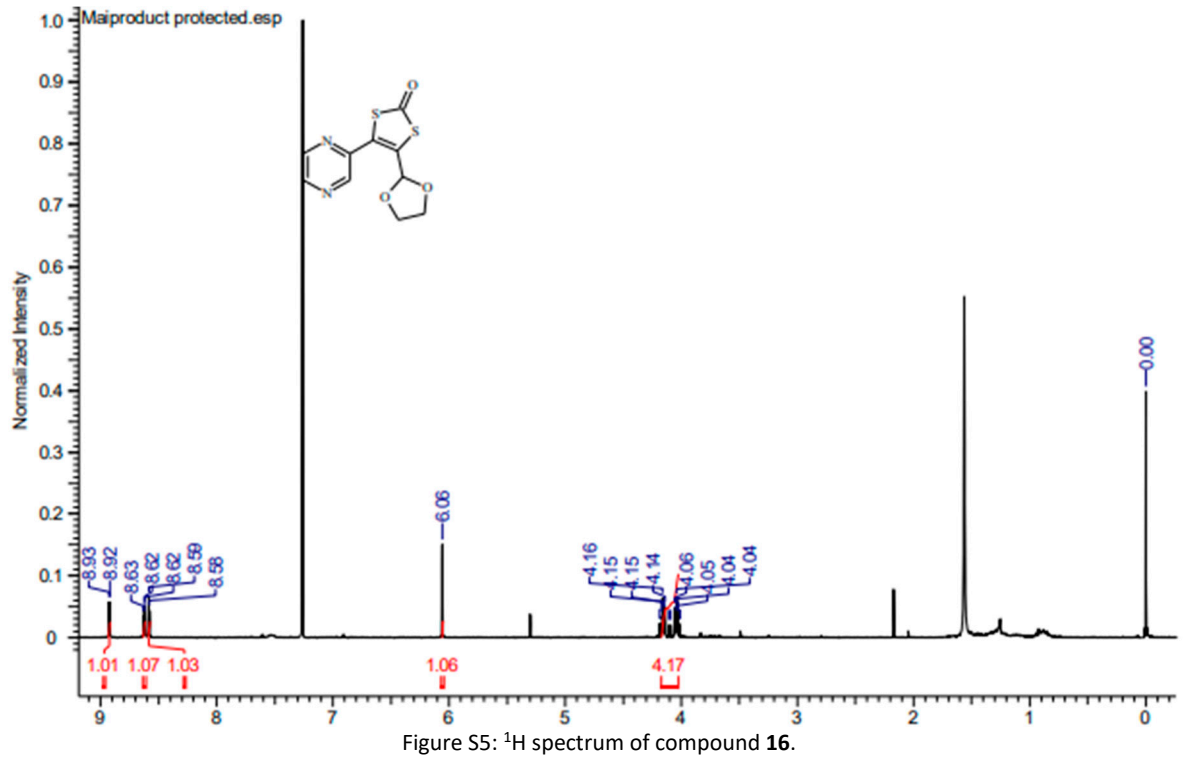

Figure S5: ^{1}H spectrum of compound **16**.

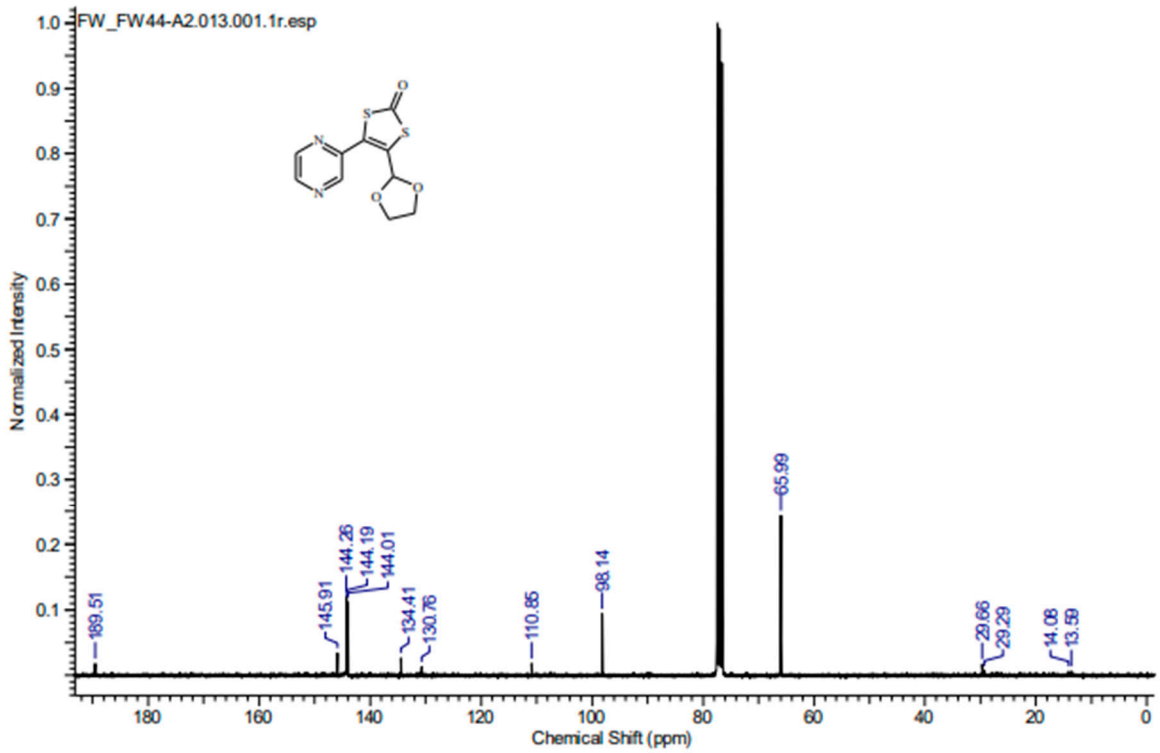

Figure S6: ^{13}C spectrum of compound **16**.

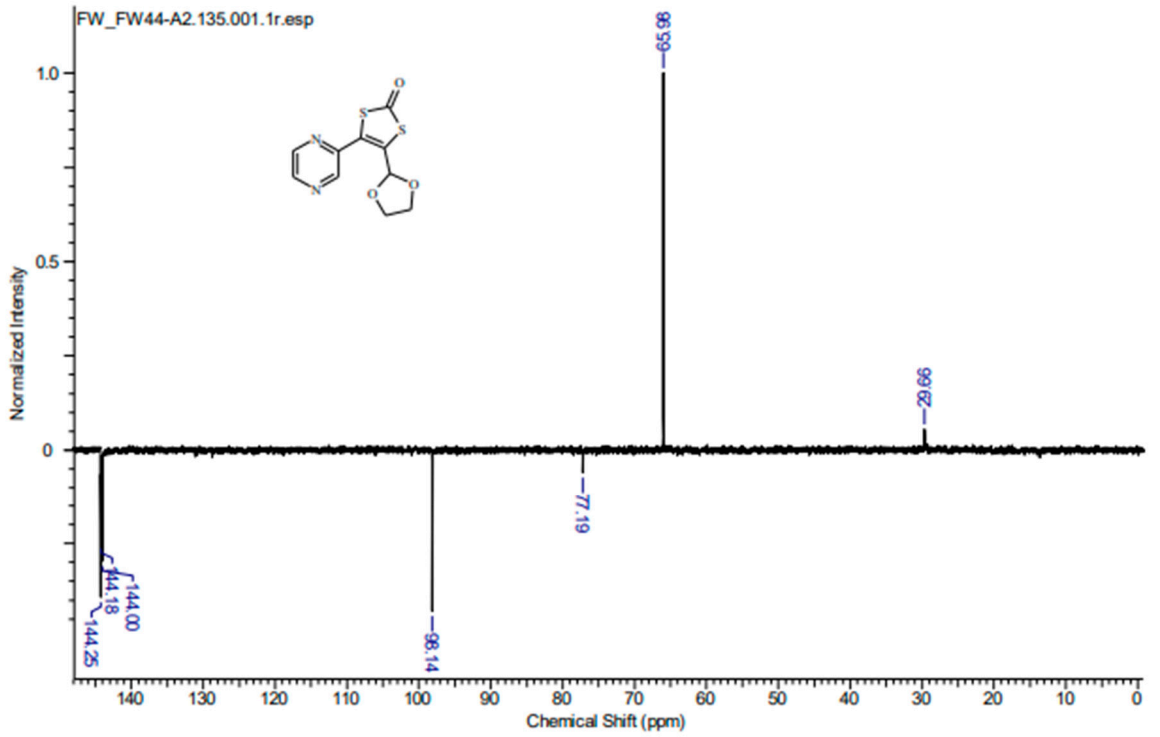

Figure S7:

X-Ray Single crystal diffraction data

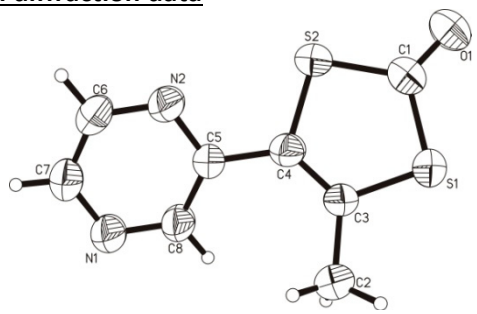

Figure S10: Molecular structure of 12

Table S1: Crystal Data and Structure Refinement for 12.

	12
empirical formula	$C_8H_6N_2OS_2$
M (g/mol)	210.27
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	3.8549(7)
b (Å)	14.330(3)
c(Å)	15.849(3)
V (Å^3)	874.1(3)
Z	4
D (calcd) (g/cm^3)	1.598
abs coeff (mm^{-1})	0.564
reflections collected/unique	7157 / 1838 [*R*(int) = 0.0812]
final *R* [I > 2σ(*I*)]	R_1 = 0.0563, wR^2 = 0.1568
R indices (all data)	R_1 = 0.1109, wR^2 = 0.1765
data / restraints / parameters	1838 / 0 / 120
goodness of fit on F^2	1.000
Largest diff. peak and hole (e/Å^3)	0.425 and -0.338

Table S2: Bond lengths [Å] and angles [°] for 12.

Bond lengths		Angles	
S(1)-C(3)	1.734(5)	C(3)-S(1)-C(1)	97.1(2)
S(1)-C(1)	1.766(5)	C(4)-S(2)-C(1)	96.7(2)
S(2)-C(4)	1.751(4)	C(7)-N(1)-C(8)	115.1(4)
S(2)-C(1)	1.757(5)	C(6)-N(2)-C(5)	116.4(4)
O(1)-C(1)	1.209(6)	O(1)-C(1)-S(2)	123.7(4)
N(1)-C(7)	1.335(6)	O(1)-C(1)-S(1)	124.1(4)
N(1)-C(8)	1.336(6)	S(2)-C(1)-S(1)	112.2(3)
N(2)-C(6)	1.319(6)	C(3)-C(2)-H(2A)	109.5
N(2)-C(5)	1.343(5)	C(3)-C(2)-H(2B)	109.5
C(2)-C(3)	1.508(6)	H(2A)-C(2)-H(2B)	109.5
C(2)-H(2A)	0.9600	C(3)-C(2)-H(2C)	109.5
C(2)-H(2B)	0.9600	H(2A)-C(2)-H(2C)	109.5
C(2)-H(2C)	0.9600	H(2B)-C(2)-H(2C)	109.5
C(3)-C(4)	1.345(6)	C(4)-C(3)-C(2)	128.1(4)
C(4)-C(5)	1.470(6)	C(4)-C(3)-S(1)	116.9(3)
C(5)-C(8)	1.377(6)	C(2)-C(3)-S(1)	114.9(3)
C(6)-C(7)	1.366(7)	C(3)-C(4)-C(5)	128.5(4)
C(6)-H(6)	0.9300	C(3)-C(4)-S(2)	117.0(3)
C(7)-H(7)	0.9300	C(5)-C(4)-S(2)	114.5(3)
C(8)-H(8)	0.9300	N(2)-C(5)-C(8)	120.2(4)
		N(2)-C(5)-C(4)	116.5(4)
		C(8)-C(5)-C(4)	123.2(4)
		N(2)-C(6)-C(7)	123.0(4)
		N(2)-C(6)-H(6)	118.5
		C(7)-C(6)-H(6)	118.5
		N(1)-C(7)-C(6)	121.8(4)
		N(1)-C(7)-H(7)	119.1
		C(6)-C(7)-H(7)	119.1
		N(1)-C(8)-C(5)	123.3(4)
		N(1)-C(8)-H(8)	118.3
		C(5)-C(8)-H(8)	118.3

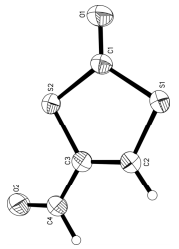

Figure S11: Molecular structure of 13

Table S3: Crystal Data and Structure Refinement for 13.

	13
empirical formula	$C_4H_2O_2S_2$
M (g/mol)	146.18
crystal system	orthorhombic
space group	*Fdd*2
a (Å)	22.215(4)
b (Å)	26.550(5)
c(Å)	3.8162(8)
V (Å^3)	2250.8(8)
Z	16
D (calcd) (g/cm^3)	1.725
abs coeff (mm^{-1})	0.836
reflections collected/unique	5648 / 1416 [*R*(int) = 0.1381]
final *R* [I > 2σ(*I*)]	R_1 = 0.0435, wR^2 = 0.0981
R indices (all data)	R_1 = 0.0627, wR^2 = 0.1268
data / restraints / parameters	1416 / 1 / 82
goodness of fit on F^2	1.099
Largest diff. peak and hole (e/Å^3)	0.417 and -0.796

Table S4: Bond lengths [Å] and angles [°] for 13.

Bond lengths		**Angles**	
C(1)-O(1)	1.197(8)	O(1)-C(1)-S(2)	124.4(6)
C(1)-S(2)	1.766(6)	O(1)-C(1)-S(1)	122.8(5)
C(1)-S(1)	1.783(7)	S(2)-C(1)-S(1)	112.8(4)
C(2)-C(3)	1.334(9)	C(3)-C(2)-S(1)	118.1(5)
C(2)-S(1)	1.714(6)	C(2)-C(3)-C(4)	122.7(6)
C(3)-C(4)	1.458(9)	C(2)-C(3)-S(2)	117.9(5)
C(3)-S(2)	1.737(6)	C(4)-C(3)-S(2)	119.4(5)
C(4)-O(2)	1.204(8)	O(2)-C(4)-C(3)	123.8(6)
		C(2)-S(1)-C(1)	95.7(3)
		C(3)-S(2)-C(1)	95.4(3)

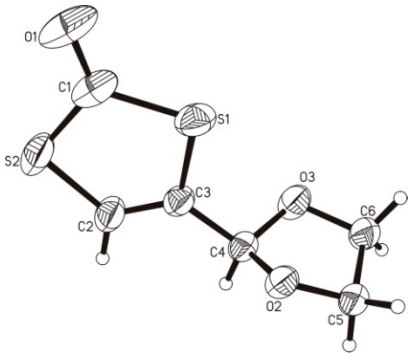

Figure S12: Molecular structure of 14

Table S5: Crystal Data and Structure Refinement for 14.

	14
empirical formula	$C_6H_6O_3S_2$
M (g/mol)	190.23
crystal system	monoclinic
space group	*Cc*
a (Å)	18.353(4)
b (Å)	4.9592(10)
c(Å)	9.3924(19)
V (Å^3)	785.3(3)
Z	4
D (calcd) (g/cm^3)	1.609
abs coeff (mm^{-1})	0.629
reflections collected/unique	4039 / 1913 [*R*(int) = 0.0328]
final *R* [I > 2σ(*I*)]	R_1 = 0.0326, wR^2 = 0.0883
R indices (all data)	R_1 = 0.0357, wR^2 = 0.0906
data / restraints / parameters	1913 / 2 / 104
goodness of fit on F^2	1.082
Largest diff. peak and hole (e/Å^3)	0.282 and -0.305

Table S6: Bond lengths [Å] and angles [°] for 14.

Bond lengths		Angles	
S(1)-C(3)	1.737(3)	C(3)-S(1)-C(1)	96.06(16)
S(1)-C(1)	1.773(4)	C(2)-S(2)-C(1)	96.22(17)
S(2)-C(2)	1.725(4)	C(4)-O(2)-C(5)	103.6(2)
S(2)-C(1)	1.773(4)	C(4)-O(3)-C(6)	107.0(2)
O(1)-C(1)	1.200(5)	O(1)-C(1)-S(1)	124.3(4)
O(2)-C(4)	1.398(3)	O(1)-C(1)-S(2)	123.6(4)
O(2)-C(5)	1.433(4)	S(1)-C(1)-S(2)	112.12(19)
O(3)-C(4)	1.411(4)	C(3)-C(2)-S(2)	118.1(3)
O(3)-C(6)	1.432(4)	C(3)-C(2)-H(2)	117(3)
C(2)-C(3)	1.327(5)	S(2)-C(2)-H(2)	124(3)
C(2)-H(2)	1.01(5)	C(2)-C(3)-C(4)	124.1(3)
C(3)-C(4)	1.487(4)	C(2)-C(3)-S(1)	117.5(3)
C(4)-H(4)	1.0000	C(4)-C(3)-S(1)	118.4(2)
C(5)-C(6)	1.507(4)	O(2)-C(4)-O(3)	105.5(2)
C(5)-H(5A)	0.9900	O(2)-C(4)-C(3)	110.8(2)
C(5)-H(5B)	0.9900	O(3)-C(4)-C(3)	110.3(2)
C(6)-H(6A)	0.9900	O(2)-C(4)-H(4)	110.1
C(6)-H(6B)	0.9900	O(3)-C(4)-H(4)	110.1
		C(3)-C(4)-H(4)	110.1
		O(2)-C(5)-C(6)	102.9(2)
		O(2)-C(5)-H(5A)	111.2
		C(6)-C(5)-H(5A)	111.2
		O(2)-C(5)-H(5B)	111.2
		C(6)-C(5)-H(5B)	111.2
		H(5A)-C(5)-H(5B)	109.1
		O(3)-C(6)-C(5)	104.5(2)
		O(3)-C(6)-H(6A)	110.9
		C(5)-C(6)-H(6A)	110.9
		O(3)-C(6)-H(6B)	110.9
		C(5)-C(6)-H(6B)	110.9
		H(6A)-C(6)-H(6B)	108.9

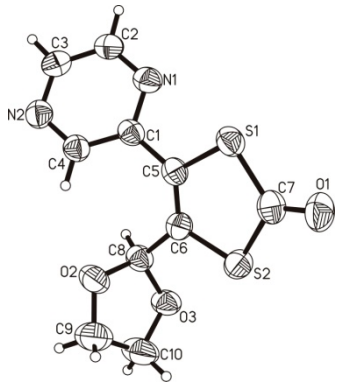

Figure S13: Molecular structure of 16

Table S7: Crystal Data and Structure Refinement for 16.

	16
empirical formula	$C_{10}H_8N_2O_3S_2$
M (g/mol)	268.30
crystal system	orthorhombic
space group	*Pbca*
a (Å)	14.614(3)
b (Å)	8.1344(16)
c(Å)	18.224(4)
V (Å^3)	2166.4(8)
Z	8
D (calcd) (g/cm^3)	1.645
abs coeff (mm^{-1})	0.488
reflections collected/unique	22164 / 2818 [*R*(int) = 0.1175]
final *R* [I > 2σ(*I*)]	R_1 = 0.0582, wR^2 = 0.1365
R indices (all data)	R_1 = 0.1022, wR^2 = 0.1652
data / restraints / parameters	2818 / 0 / 154
goodness of fit on F^2	0.845
Largest diff. peak and hole (e/Å^3)	0.397 and -0.364

Table S8: Bond lengths [Å] and angles [°] for 16.

Bond lengths		Angles	
S(1)-C(5)	1.755(3)	C(5)-S(1)-C(7)	96.28(17)
S(1)-C(7)	1.761(4)	C(6)-S(2)-C(7)	96.17(17)
S(2)-C(6)	1.735(4)	C(9)-O(2)-C(8)	108.5(3)
S(2)-C(7)	1.762(4)	C(8)-O(3)-C(10)	108.3(3)
O(1)-C(7)	1.210(4)	C(2)-N(1)-C(1)	115.8(3)
O(2)-C(8)	1.417(4)	C(3)-N(2)-C(4)	115.8(3)
O(3)-C(8)	1.412(4)	N(1)-C(1)-C(4)	121.0(3)
O(3)-C(10)	1.411(5)	N(1)-C(1)-C(5)	116.2(3)
N(1)-C(2)	1.335(5)	C(4)-C(1)-C(5)	122.9(3)
N(1)-C(1)	1.347(4)	N(1)-C(2)-C(3)	122.7(3)
N(2)-C(3)	1.334(5)	N(2)-C(3)-C(2)	121.8(3)
N(2)-C(4)	1.333(5)	N(2)-C(4)-C(1)	122.9(3)
C(1)-C(5)	1.466(5)	C(6)-C(5)-C(1)	127.8(3)
C(2)-C(3)	1.378(5)	C(6)-C(5)-S(1)	116.4(3)
C(5)-C(6)	1.339(5)	C(1)-C(5)-S(1)	115.8(2)
C(6)-C(8)	1.514(5)	C(5)-C(6)-S(2)	118.1(3)
C(9)-C(10)	1.437(6)	C(8)-C(6)-S(2)	115.3(2)
		O(1)-C(7)-S(1)	124.0(3)
		O(1)-C(7)-S(2)	123.1(3)
		S(1)-C(7)-S(2)	113.0(2)
		O(2)-C(8)-O(3)	107.7(3)
		O(2)-C(8)-C(6)	109.1(3)
		O(3)-C(8)-C(6)	110.3(3)
		O(2)-C(9)-C(10)	108.9(4)
		O(3)-C(10)-C(9)	106.5(3)