Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The assembly of "S_3N"- ligands decorated with an azo-dye as potential sensors for heavy metal ions

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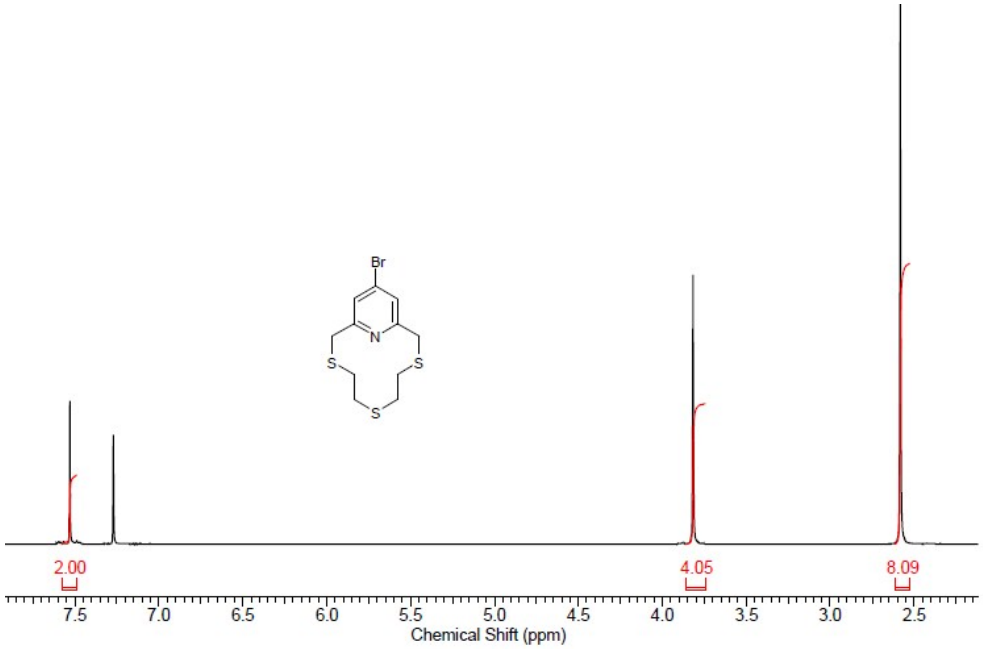
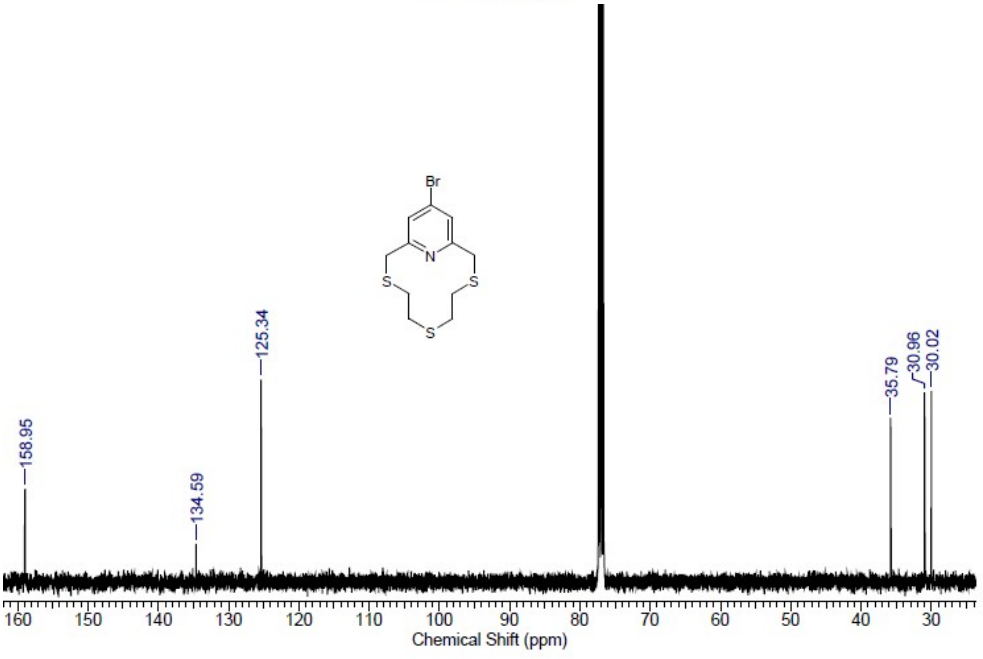
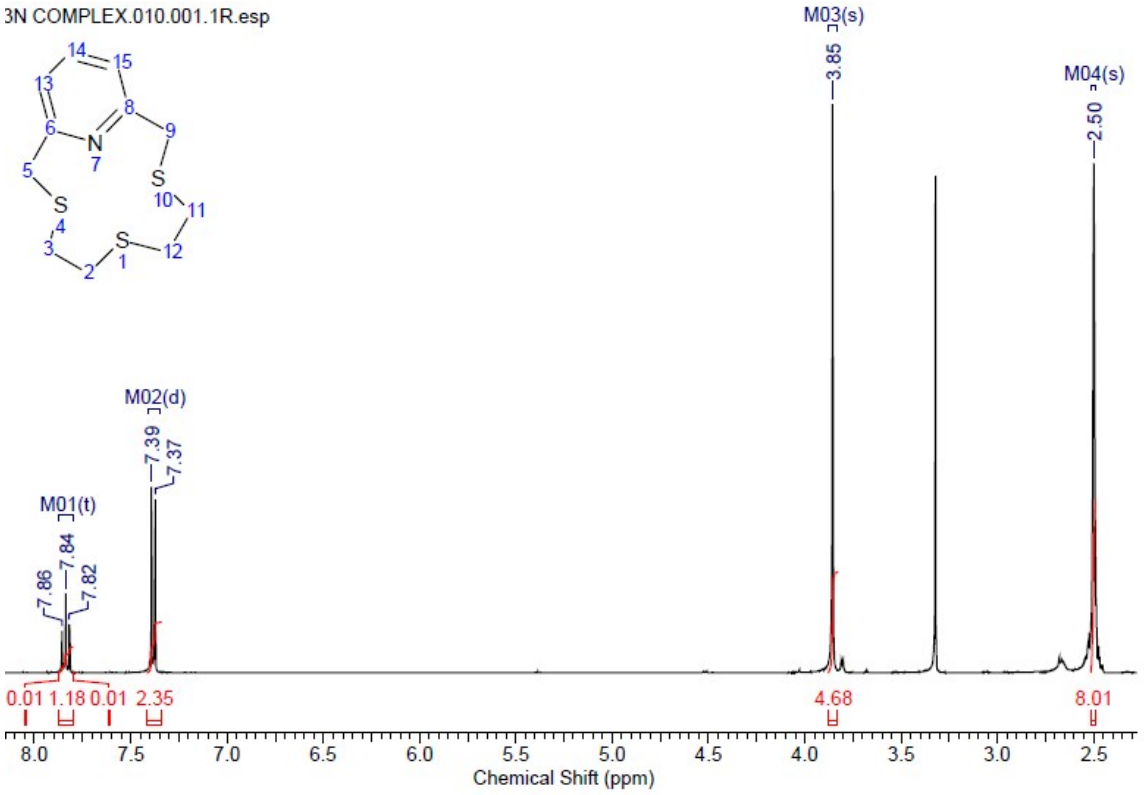
i. ^{1}H and ^{13}C NMR data

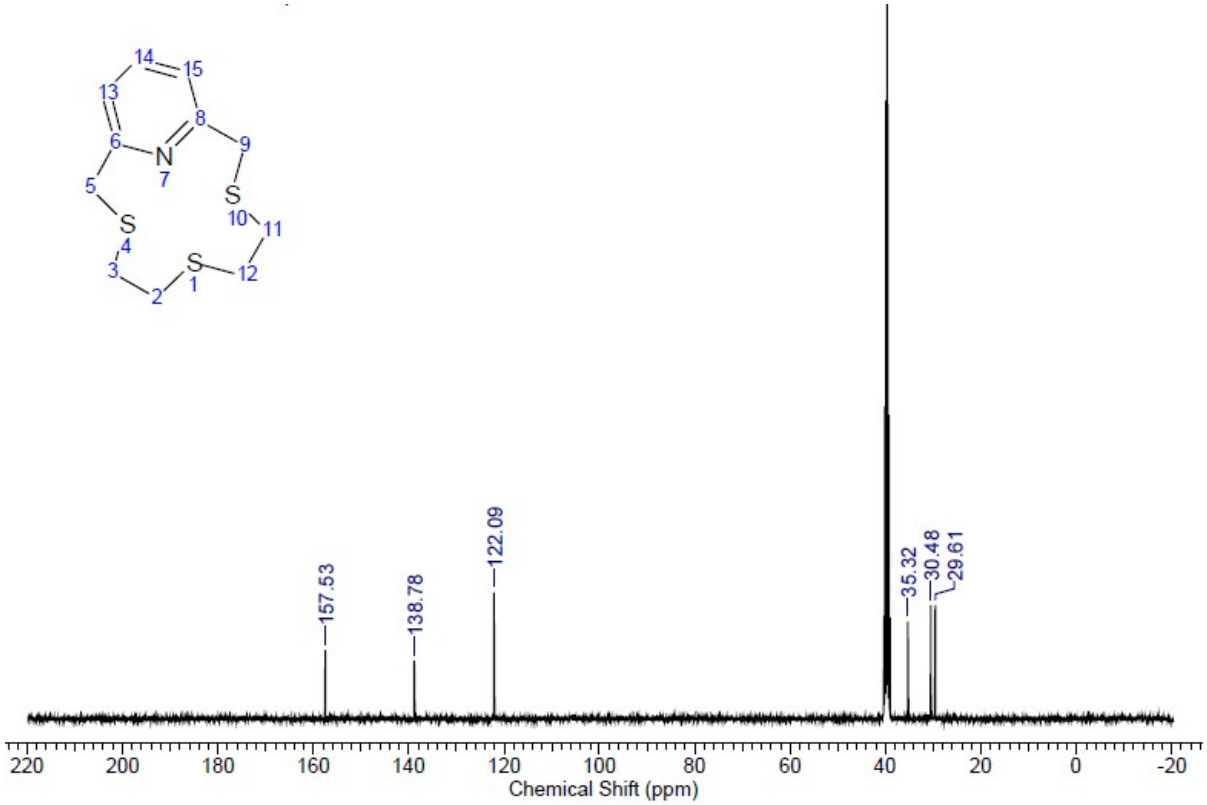
Synthesis of 3,6,9-trithia-1(2,6)-pyridinacyclodecaphane (6)



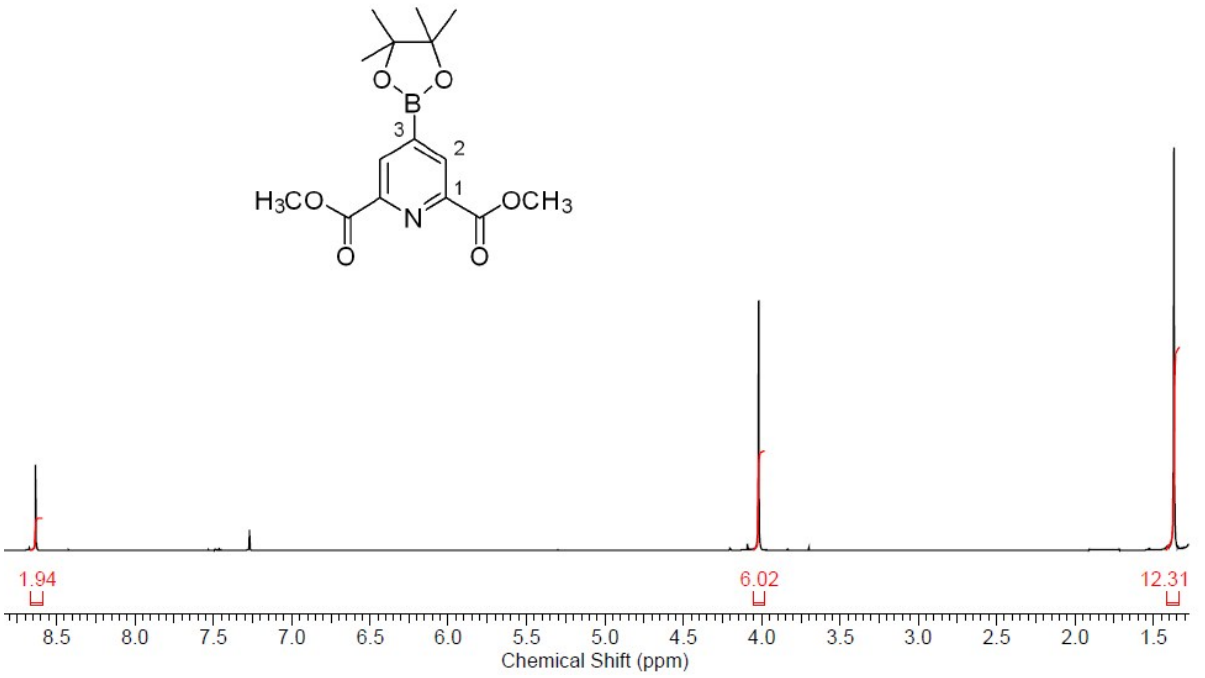


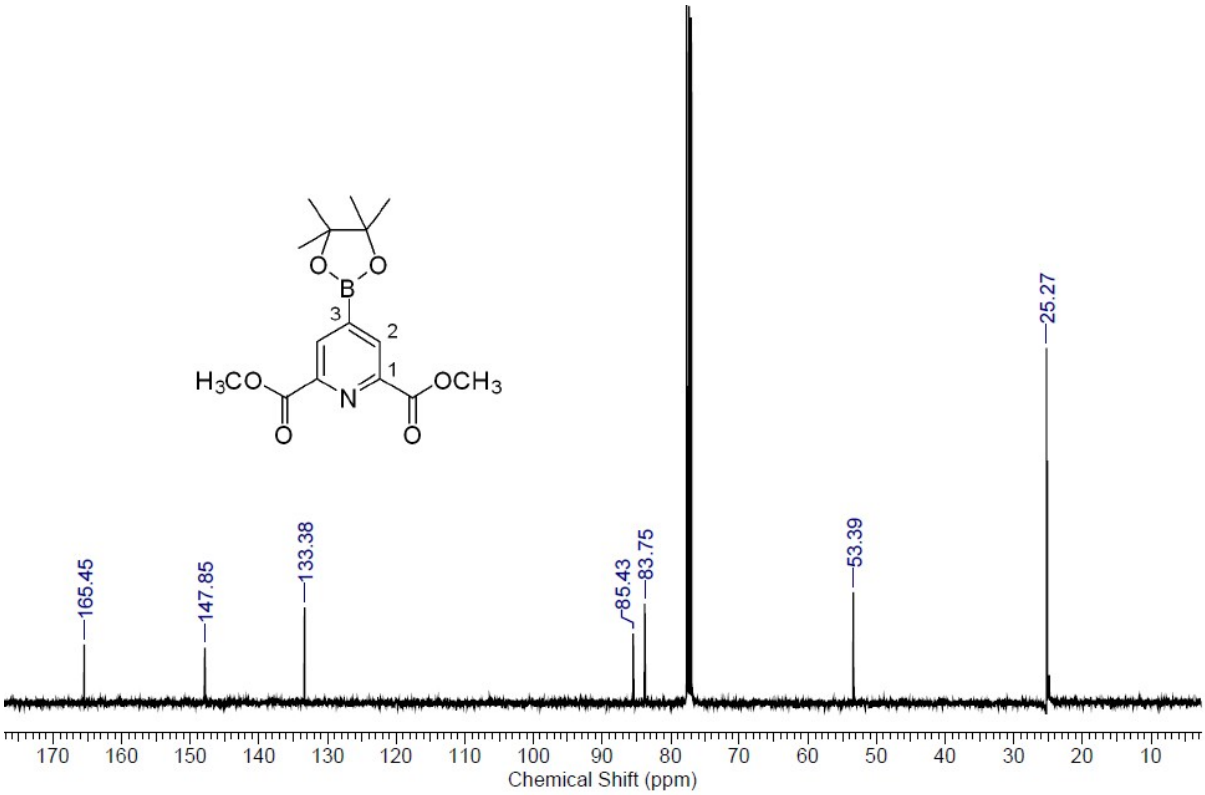
Synthesis of 3,6,9-trithia-1(2,6)-pyridinacyclodecaphane (8):



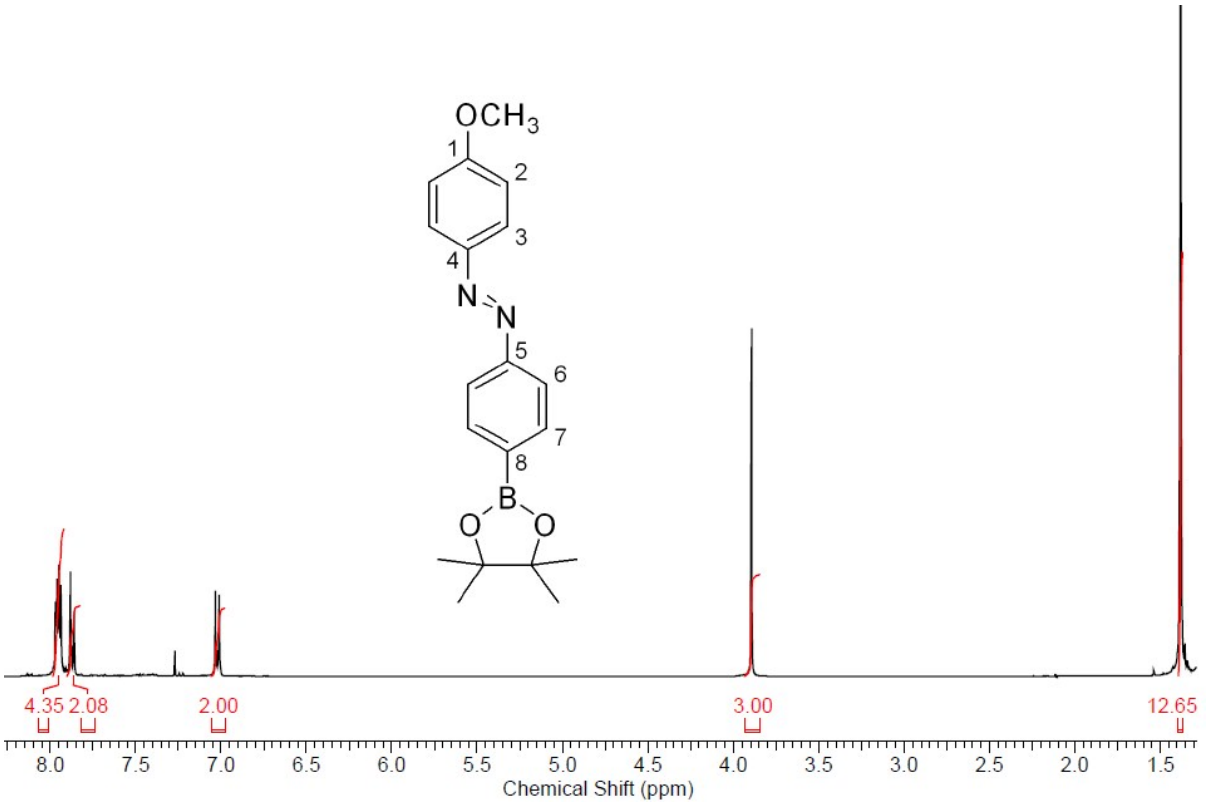


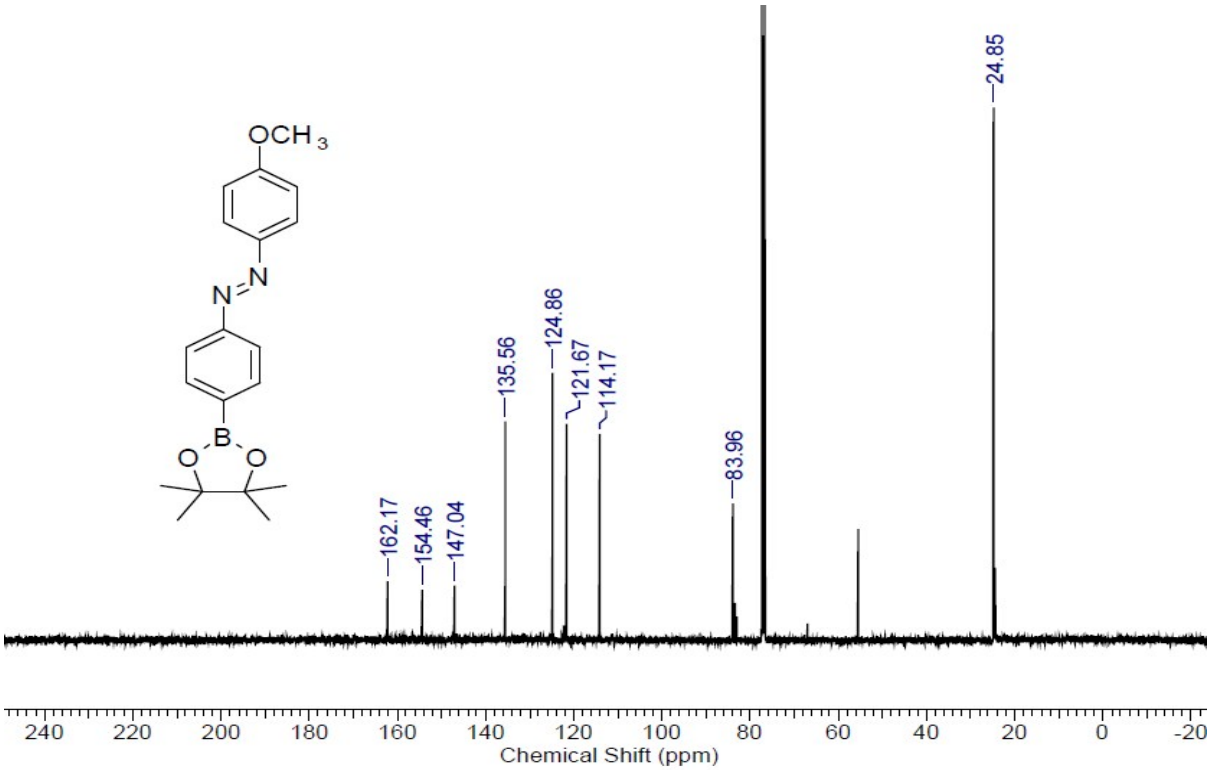
Synthesis of dimethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine-2,6-dicarboxylate (10)



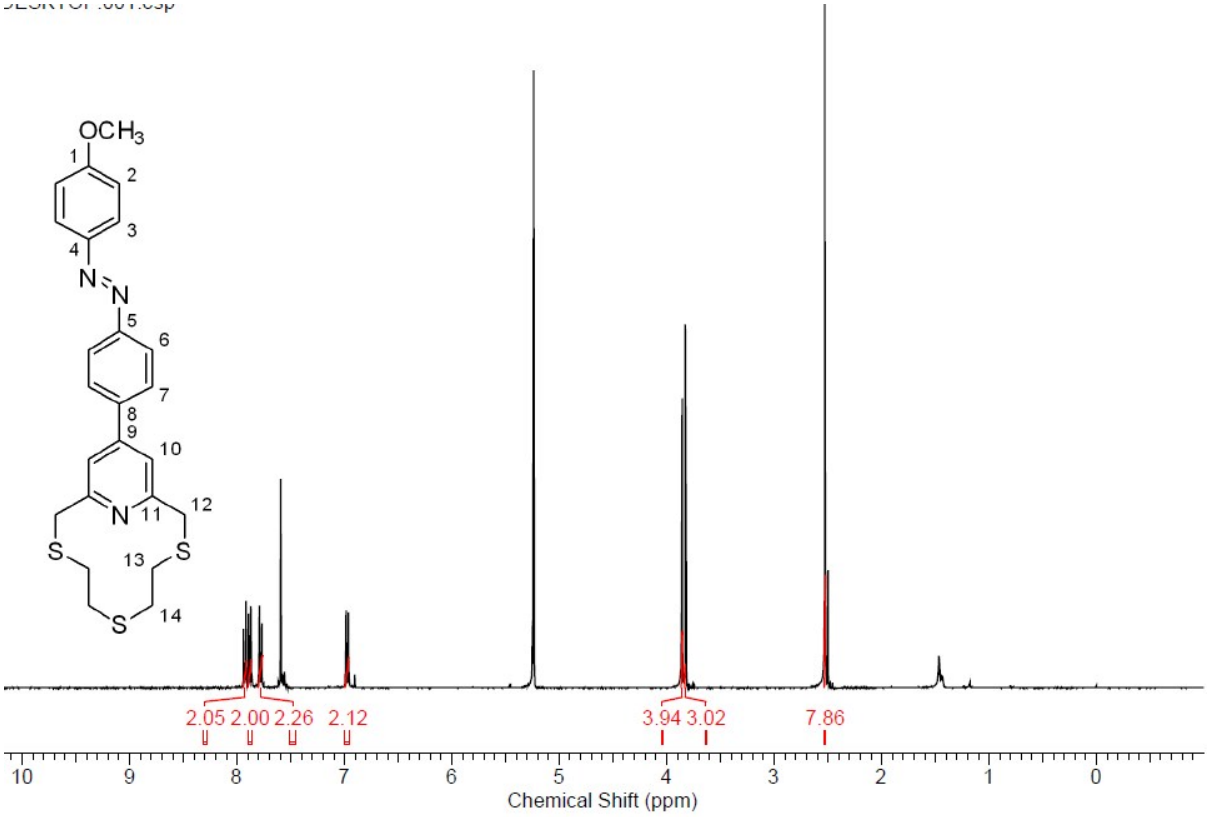


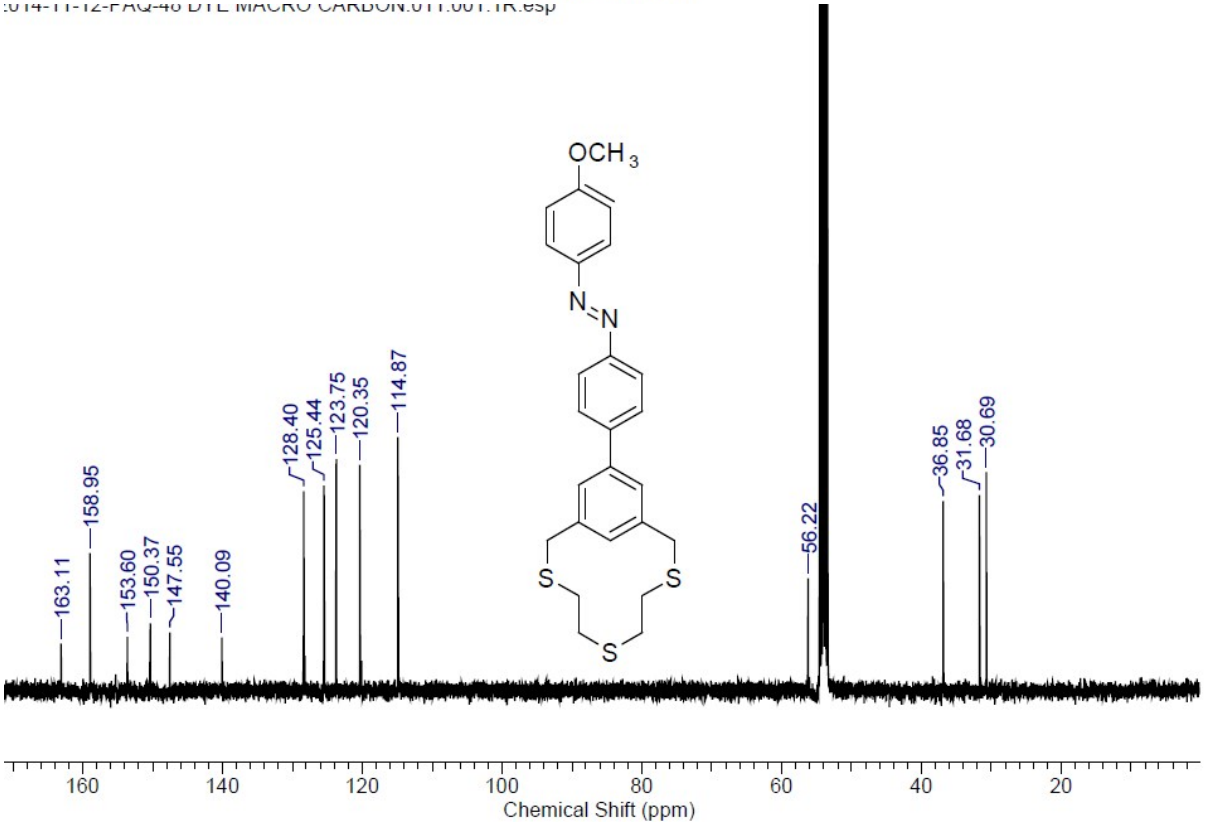
Synthesis of (E)-1-(4-methoxyphenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (12):



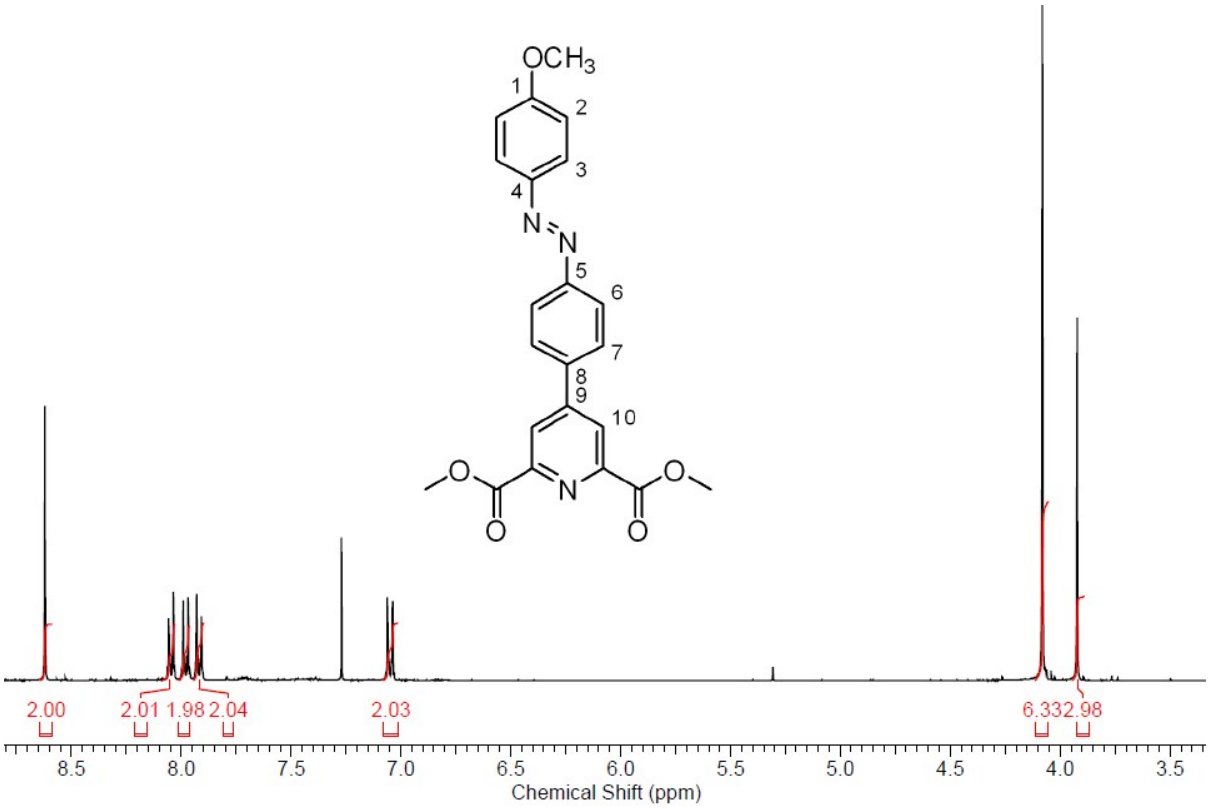


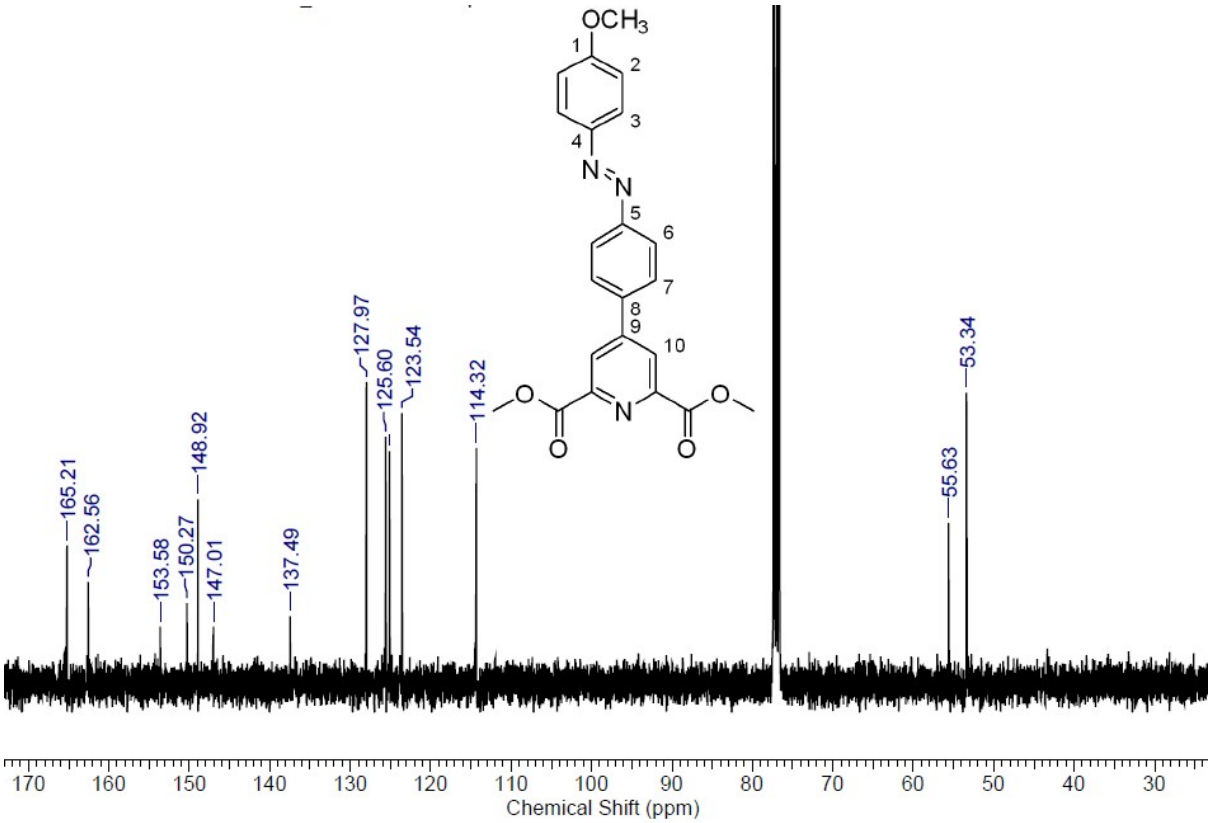
(*E*)-1^4-(4-((4-methoxyphenyl)diazenyl)phenyl)-3,6,9-trithia-1(2,6)-pyridinacyclodecaphane (13):



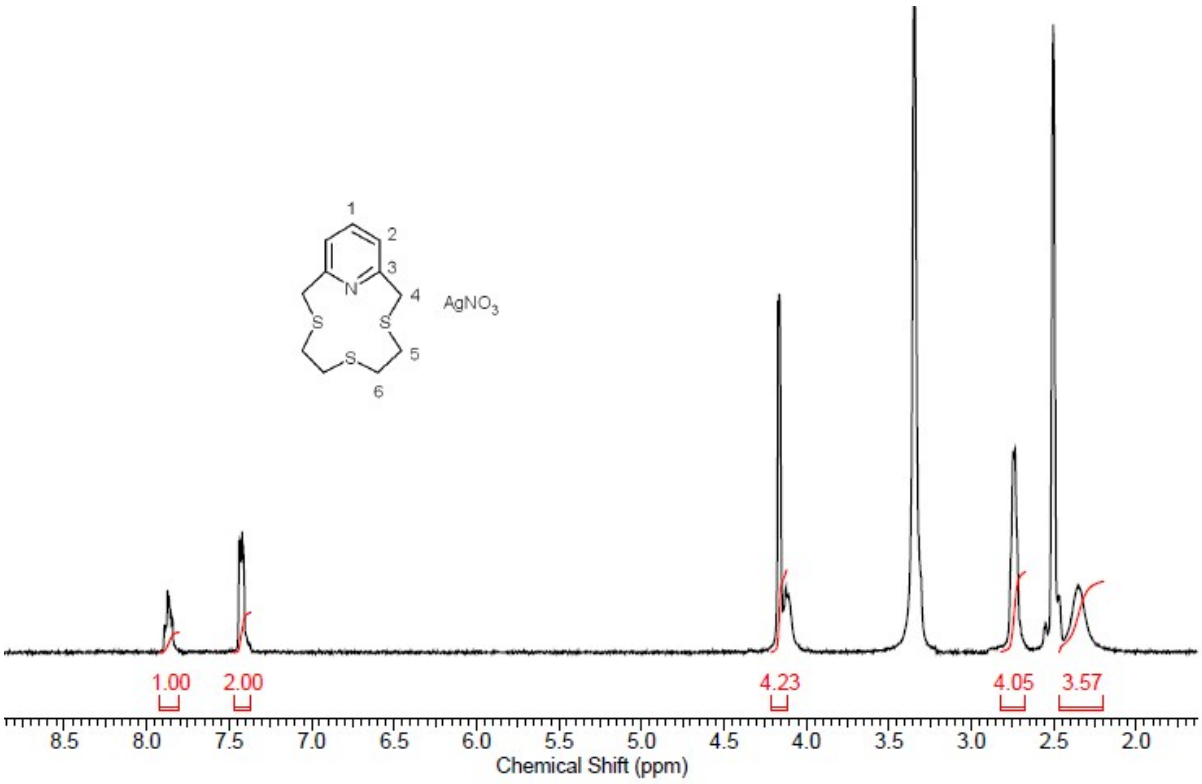


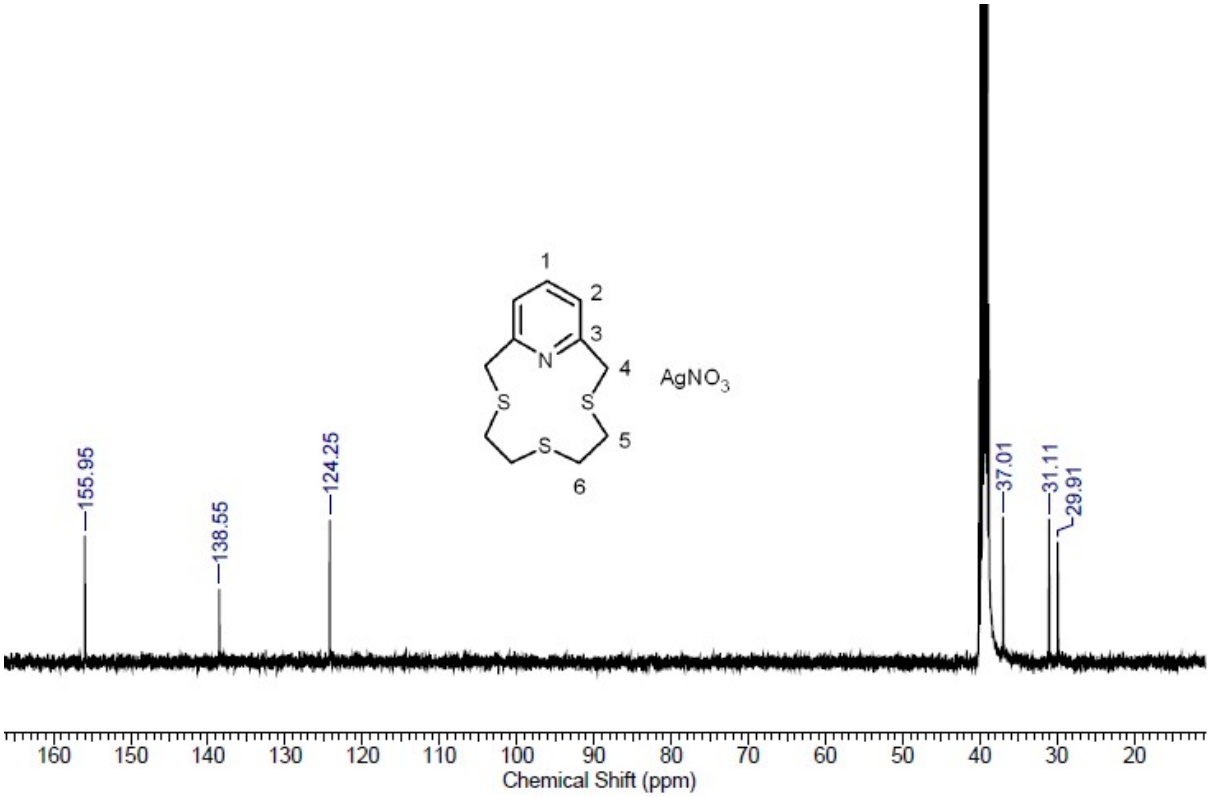
Synthesis of dimethyl (E)-4-(4-((4-methoxyphenyl)diazenyl)phenyl)pyridine-2,6-dicarboxylate (14):



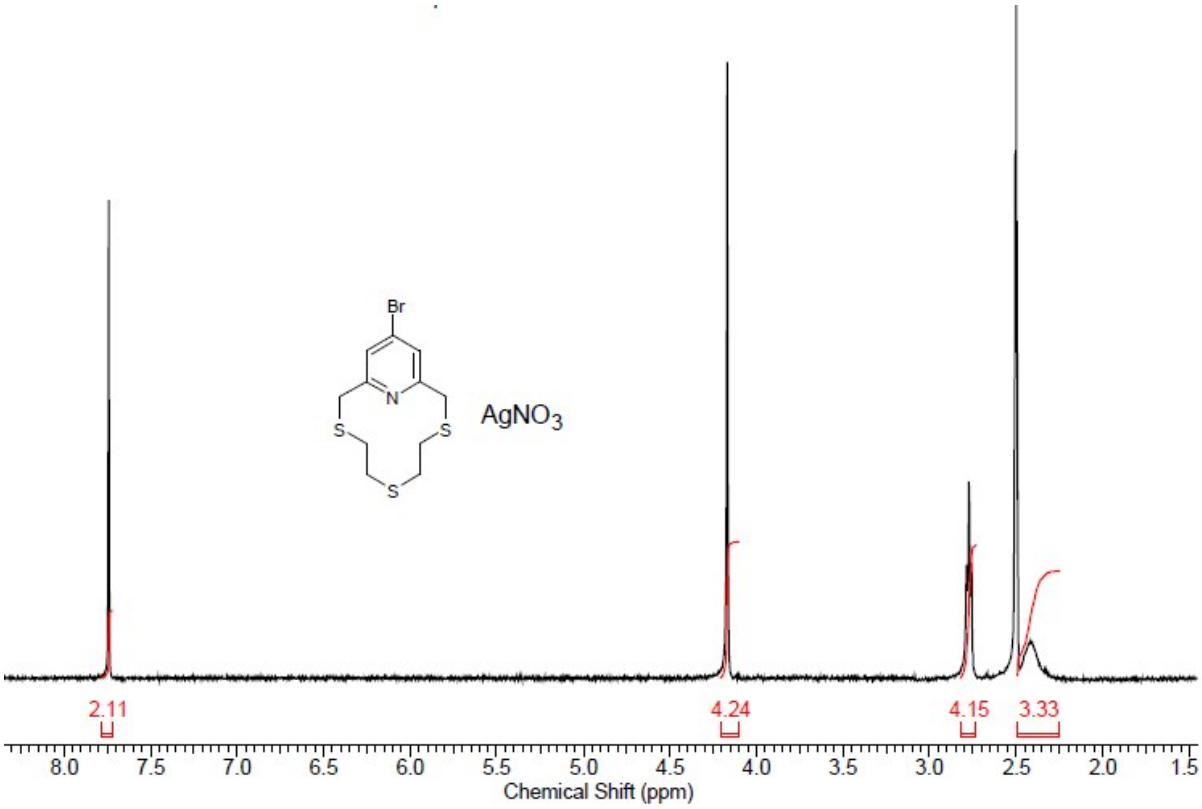


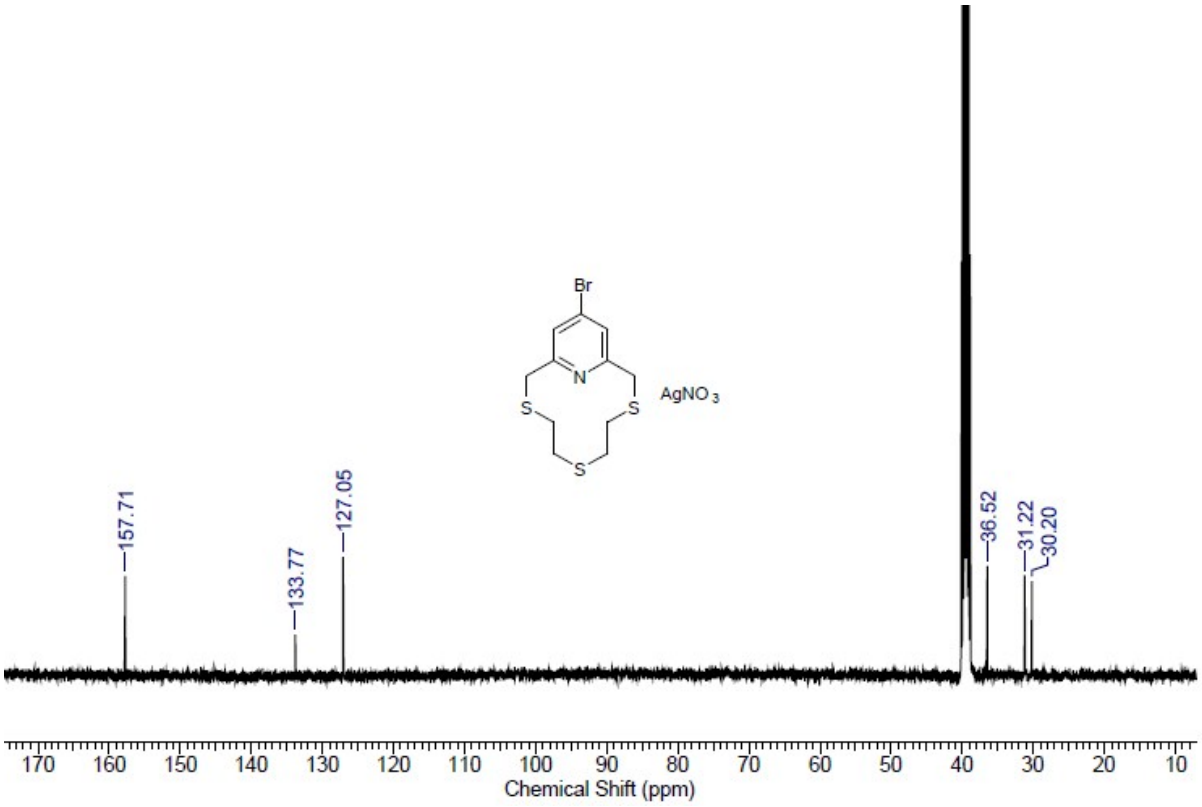
Silver complex(15):



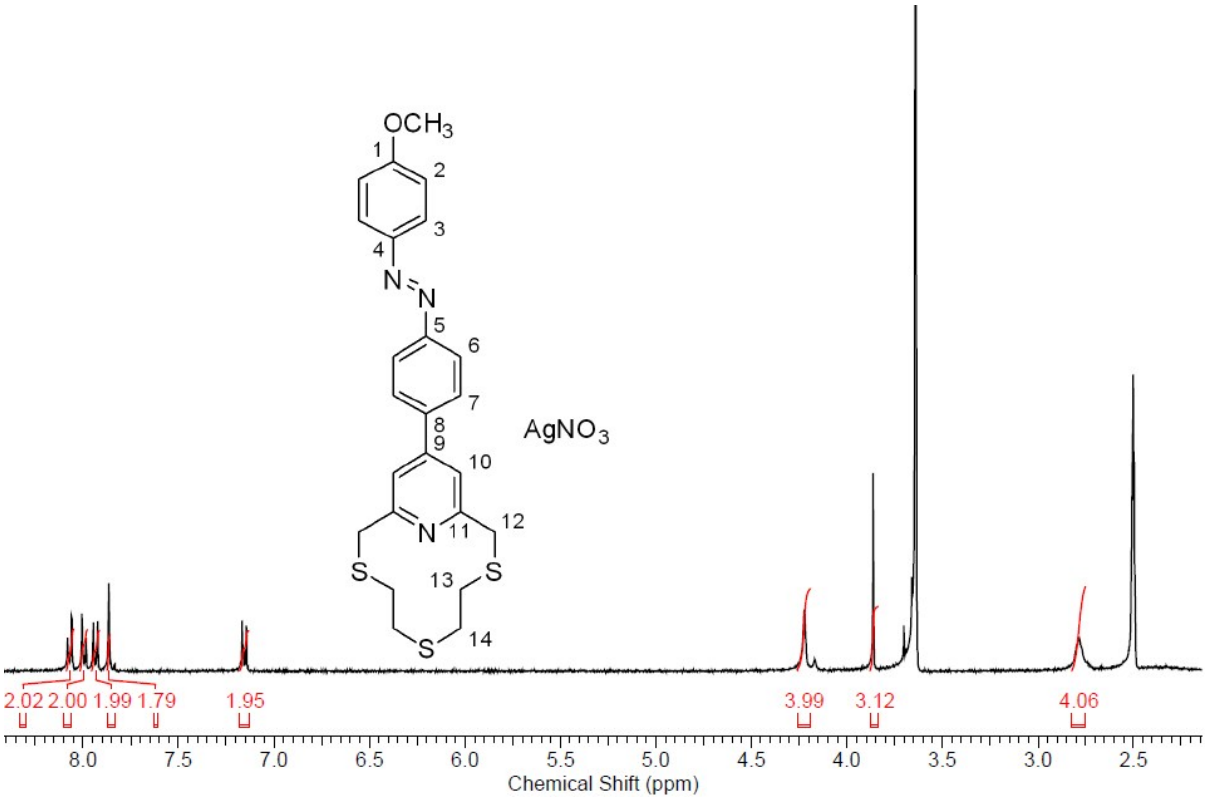


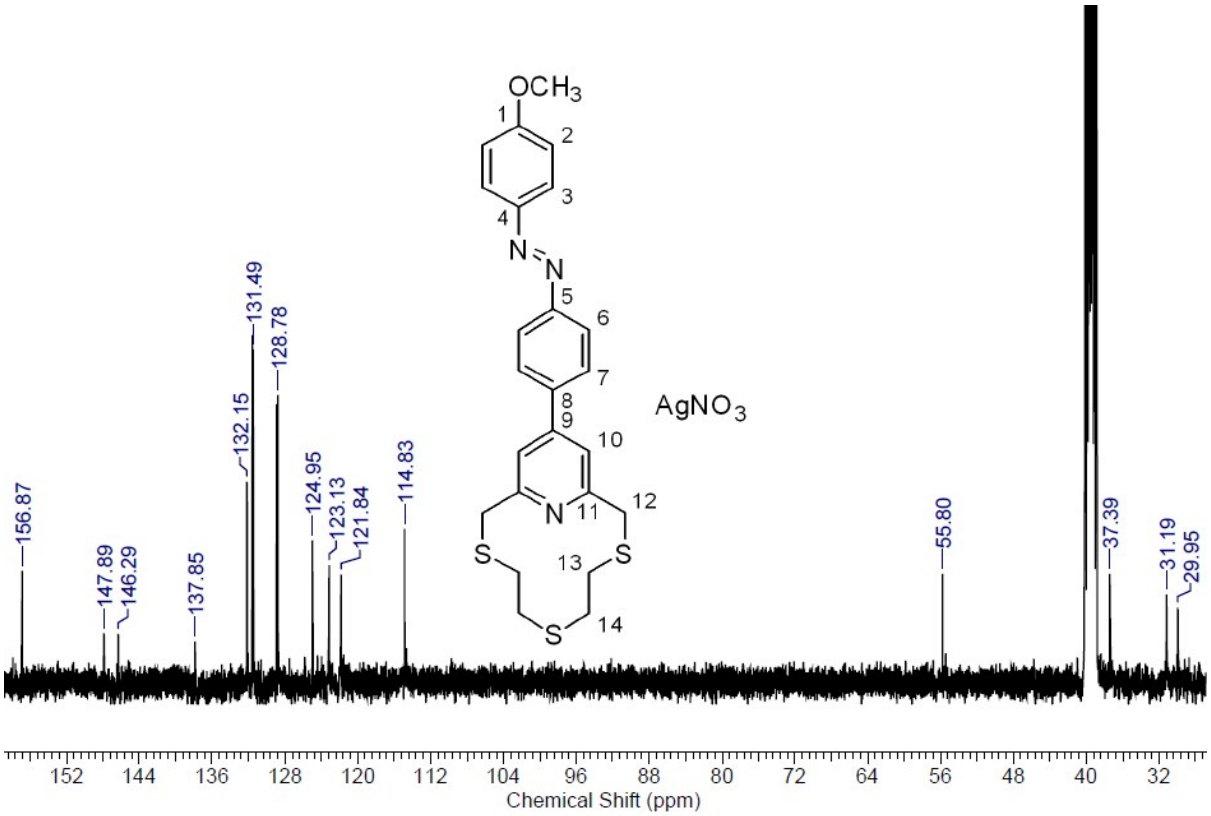
Silver complex (16):



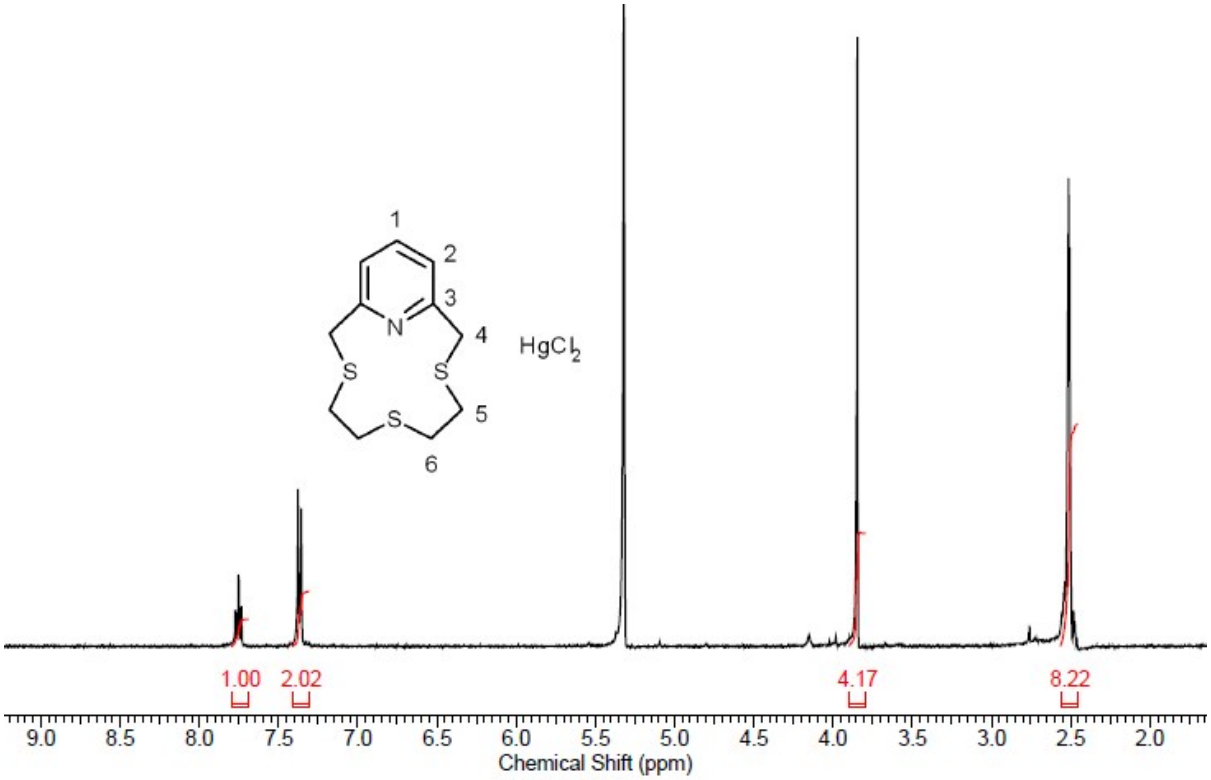


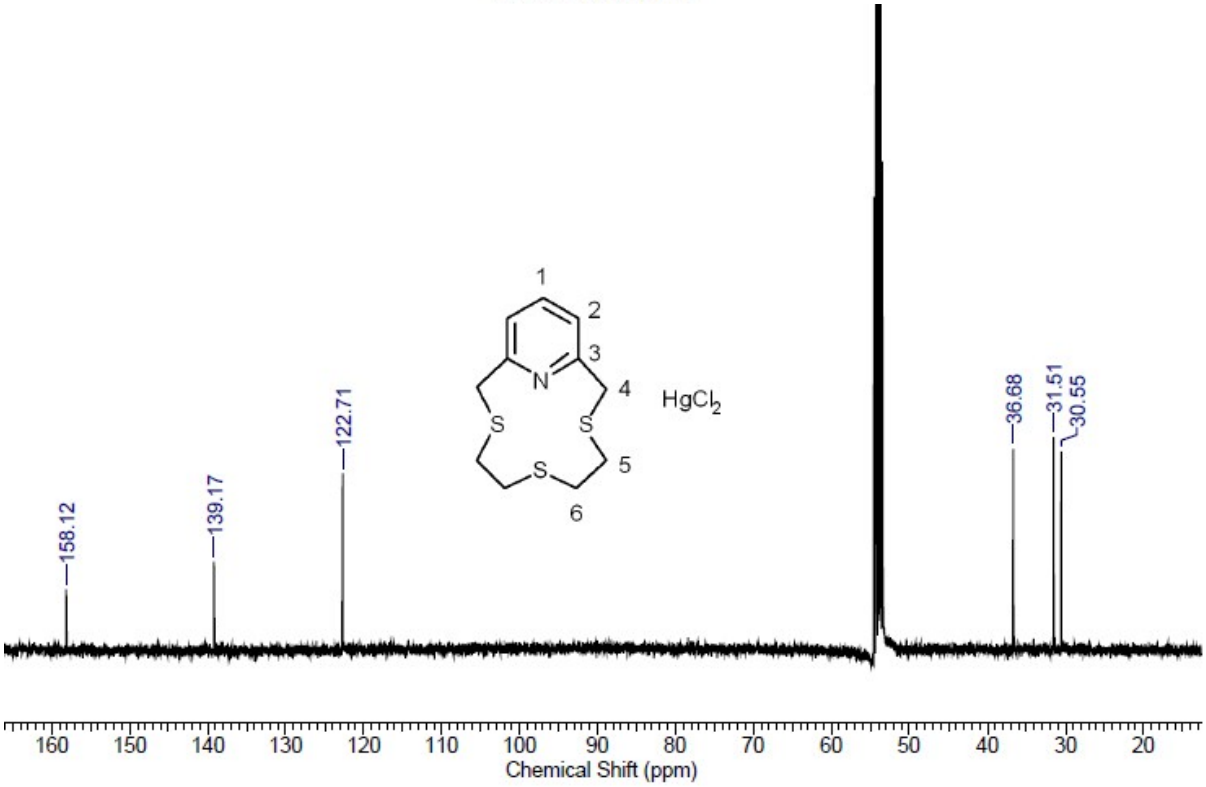
Silver complex (17):



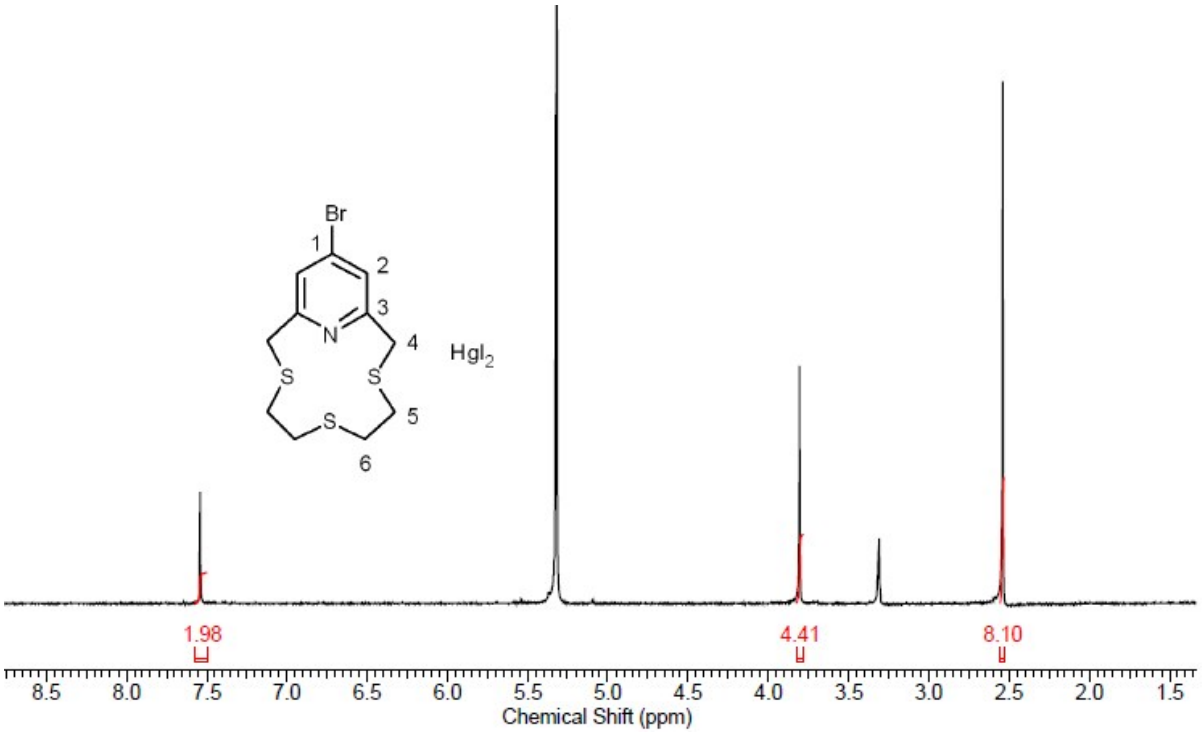


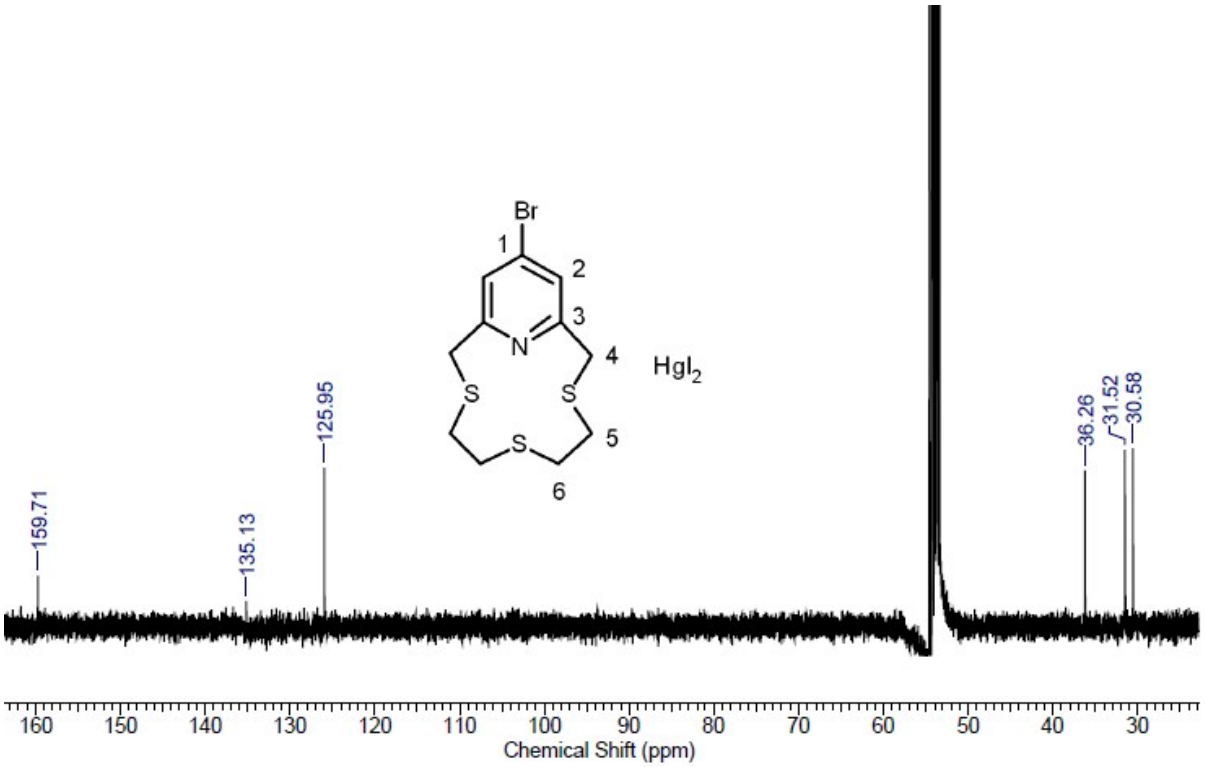
Mercury complex (21):



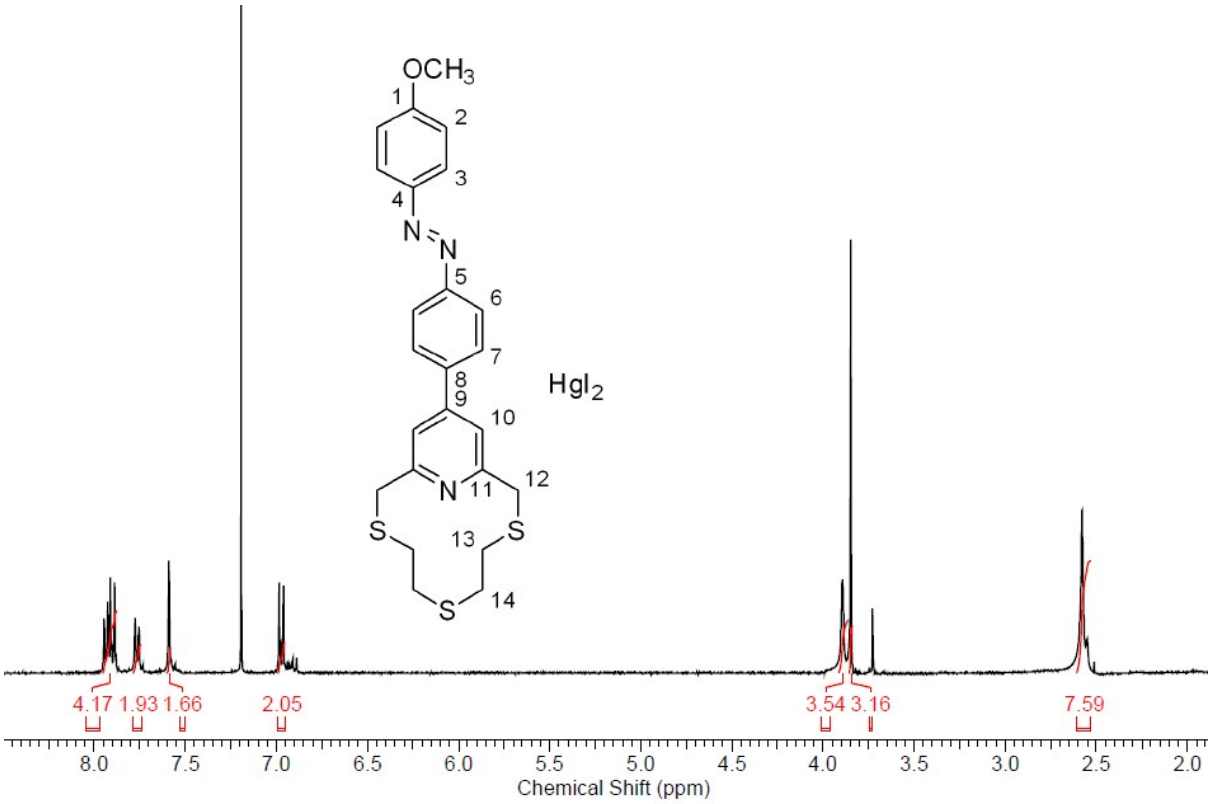


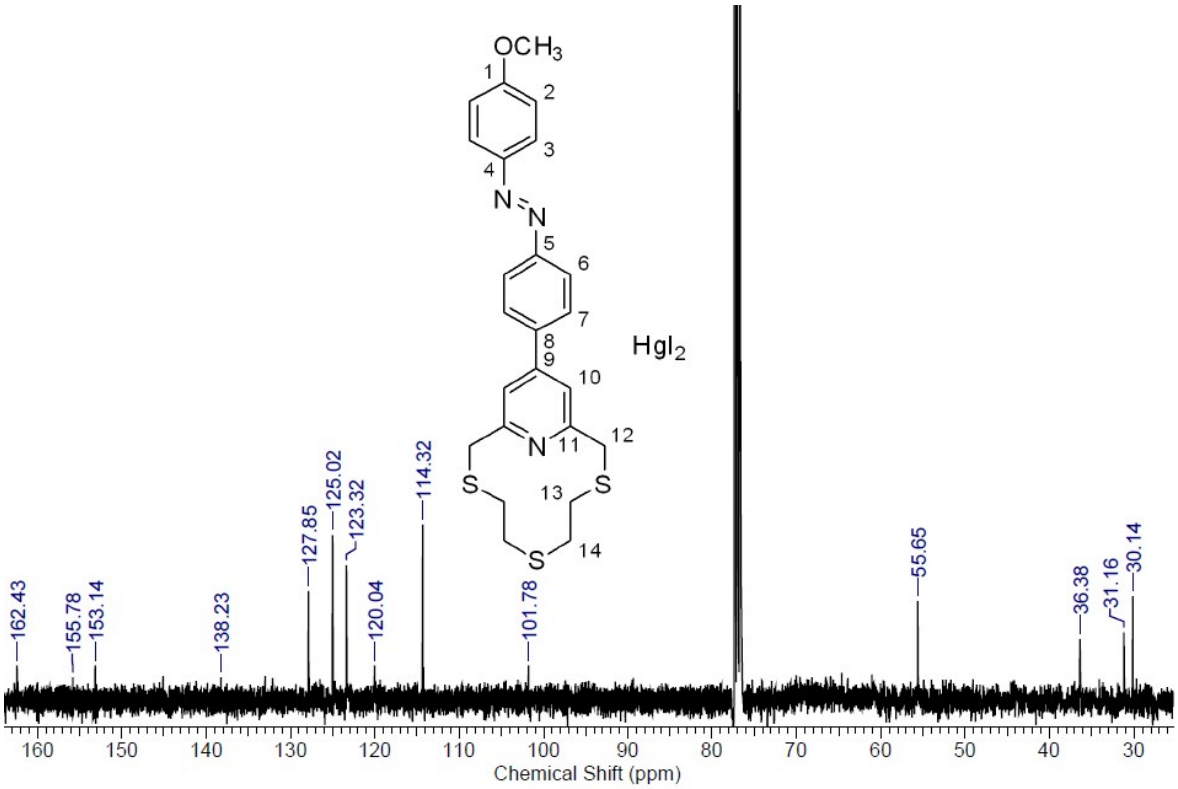
Mercury Complex (22):



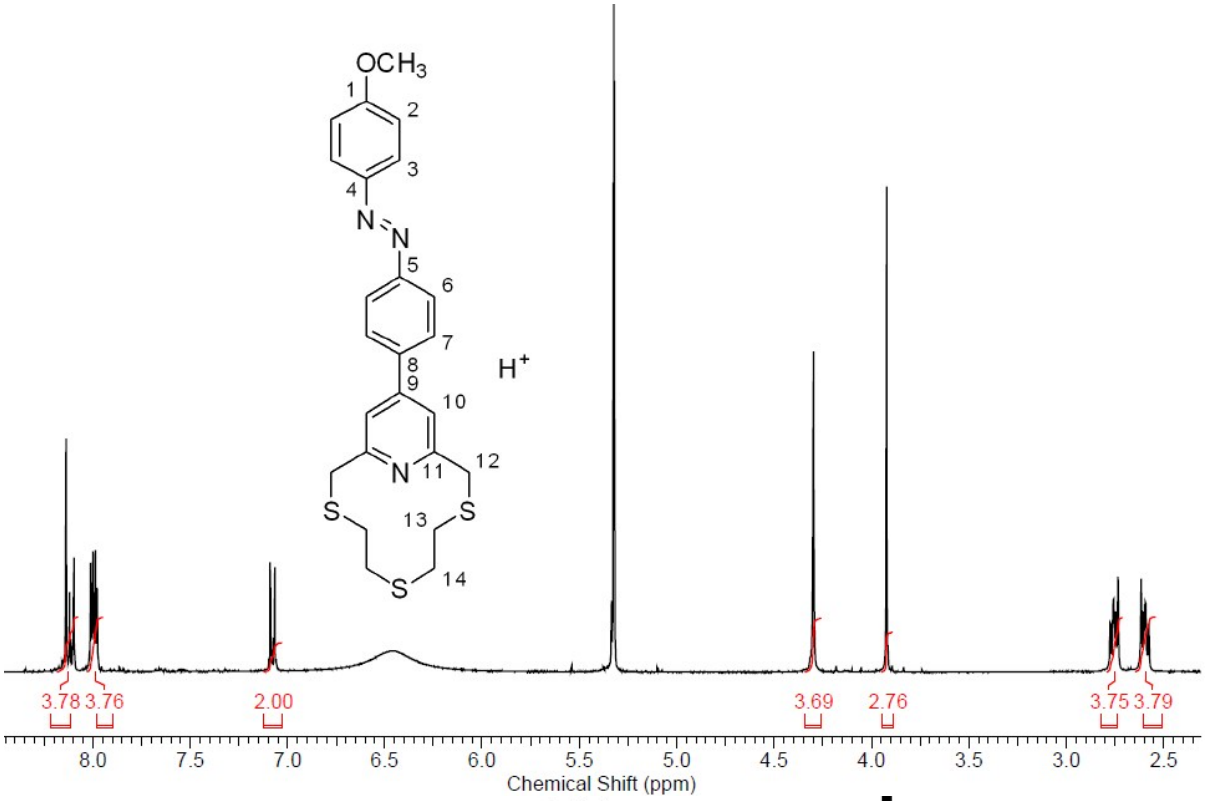


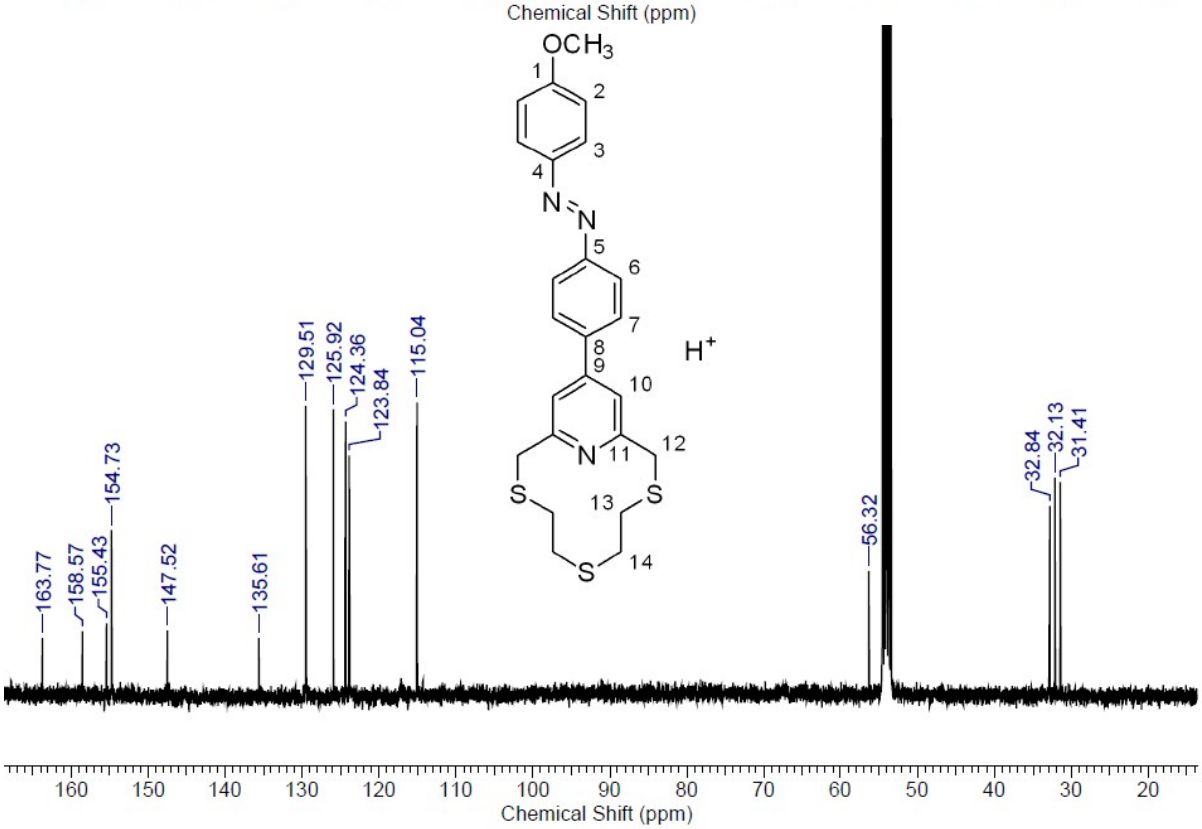
Mercury complex (23):



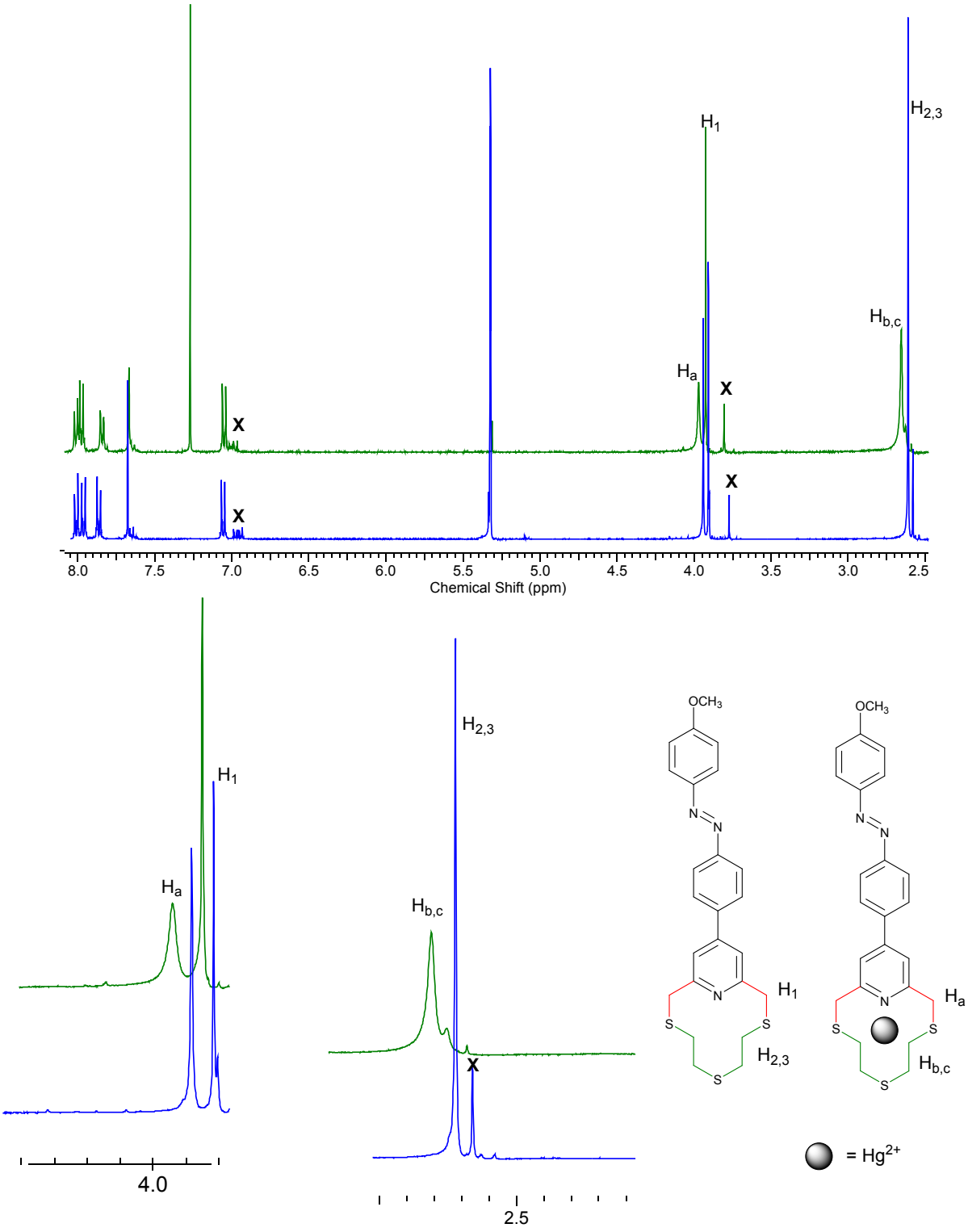


ii. TFA Blank reaction (24):





iii. **^{1}H NMR Studies: Complexation of 13 with Hg_2I_4 to afford complex 23**



(X = impurity, possibly the *Z*-isomer of the azo dye)

iv. Single crystal X-ray diffraction

a. Data Collection. **Data Collection**. Single crystal X-ray diffraction data were collected for the crystal structures **6**, **13**, **14, 19, 21** and **23** at a temperature of 100 K using Cu-Kα radiation on a X8 Bruker prospector, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data were measured using Bruker Apex2 suite of programs.

Single crystal X-ray diffraction data were collected for the crystal structure **22** at a temperature of 150 K using Mo-Kα radiation on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data were measured using CrisAlisPro suite of programs.

b. Crystal structure determinations and refinements.

X-ray data was processed and reduced using Bruker Apex2 for crystal structures **6**, **13**, **14, 19, 21** and **23**. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles using SADABS. X-ray data was processed and reduced using CrisALisPro for crystal structure **22**. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles using SCALE3 ABSPACK. The crystal structures were solved and refined against all F^2 values using the SHELX and Olex 2 suite of programs.[1] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Atomic displacement parameters were restrained using RIGU and ISOR Shelx commands.

CCDC 1445149-1445161contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

c. **Table S1.** Crystallographic information for **6**, **13**, **14** and **19**

	6	**13**	**14**	**19**
Crystal colour	White	yellow	yellow	Blue
Crystal size (mm)	0.21 × 0.2 × 0.16	0.15 × 0.1 × 0.04	0.13 × 0.12 × 0.01	0.13 × 0.09 × 0.02
Crystal system	Orthorombic	Triclinic	Triclinic	Monoclinic
Space group, *Z*	Pbcn, *8*	P-1, *2*	P-1, *2*	$P2_1/c$, *4*
a (Å)	13.0722(6)	5.5032(2)	4.5402(3)	7.7435(2)
b (Å)	7.8927(4)	13.7541(5)	10.8201(7)	19.9374(4)
c (Å)	25.4406(12)	16.2814(5)	19.7081(11)	11.9344(3)
α (°)	90	66.950(2)	80.037(4)	90
β (°)	90	85.649(2)	86.240(5)	113.918(11)
γ (°)	90	82.232(2)	87.076(4)	90
V (Å^3)	2624.8(2)	1123.22(7)	950.74(10)	1809.47(7)
Density (Mg.m^{-3})	1.702	1.383	1.416	1.989
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178
Temperature (K)	100	100	100	100
μ(Mo-Kα) (mm^{-1})	8.498	3.189	0.848	7.920
2Θ range (°)	6.948 to 144.584	7.03 to 144.516	8.304 to 136.474	8.752 to 143.988
Reflns collected	15381	20554	6897	6852
Independent reflns (R_{int})	2584 (0.071)	4168 (0.0214)	3319 (0.0376)	3416 (0.0276)
L.S. parameters, *p*	145	281	274	241
No. of restraints, *r*	0	0	0	4
*R*1 (*F*)[a] *I* > 2.0σ*(I)*	0.0378	0.0394	00447	0.0367
*wR*2(F^2),[b] all data	0.0960	0.1073	0.1285	0.0979
S(F^2),[c] all data	1.062	1.046	1.022	1.047

[a] $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

d. Table S2. Crystallographic information for **21-23.**

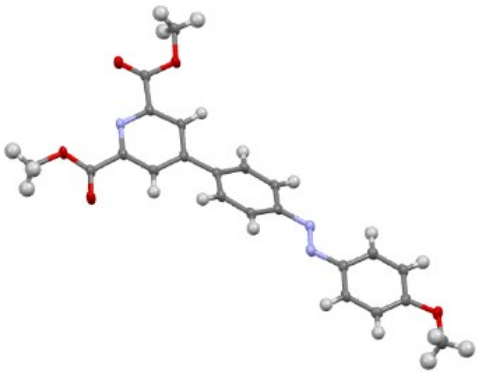
	21	**22**	**23**
Crystal colour	White	White	Yellow
Crystal size (mm)	0.16 × 0.05 × 0.02	0.14 × 0.11 × 0.04	0.13 × 0.12 × 0.02
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, *Z*	$P2_1/n$, *4*	$P2_1/c$, *4*	$P2_1/c$, *4*
a (Å)	8.86244(15)	17.1949(11)	26.2853(4)
b (Å)	15.5399(3)	8.5255(5)	8.5588(2)
c (Å)	13.2869(2)	15.9682(10)	15.9777(2)
β (°)	93.3355(14)	91.274(6)	97.033(2)
V (Å^3)	1826.80(5)	2340.3(3)	3567.47(11)
Density (Mg.m^{-3})	2.910	3.534	2.721
Wavelength (Å)	1.54178	0.71073	1.54178
Temperature (K)	100	150	100
μ(Mo-Kα) (mm^{-1})	38.240	20.351	45.621
2Θ range (°)	8.764 to 148.584	6.732 to 50.698	6.776 to 149.176
Reflns collected	9572	8124	17878
Independent reflns (R_{int})	3542 (0.0321)	4278 (0.0406)	7066 (0.0391)
L.S. parameters, *p*	190	199	362
No. of restraints, *r*	174	189	303
*R*1 (*F*)[a] *I* > 2.0σ*(I)*	0.0292	0.0378	0.0415
*wR*2(F^2),[b] all data	0.0810	0.0682	0.1072
S(F^2),[c] all data	1.127	1.003	1.049

[a] $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

[1] a) G. M. Sheldrick., ***Acta Crystallogr.*****, 2015,** ***C71*****, 3-8, b)** O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009,** *42*, 339–341

e. Selected bond lengths, bond angles and torsion angles.

Compound : 6 (UoM: s3707ma)



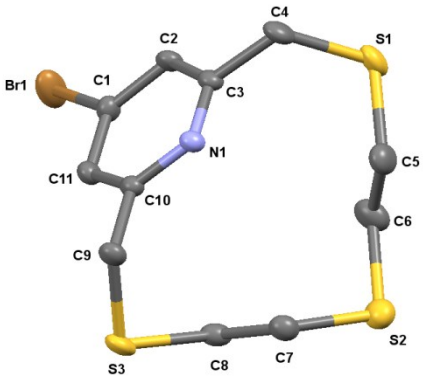
Selected torsion angles (°):

N(1)-C(3)-C(4)-S(1) = 92.9(2);
S(1)-C(5)-C(6)-S(2) = -179.40(15);
S(2)-C(7)-C(8)-S(3) = -177.67(13);
S(3)-C(9)-C(10)-N(1) = -121.4(2);
C(6)-C(5)-S(1)-C(4) = 109.2(2);
C(10)-C(9)-S(3)-C(8) = 47.7(2).

Selected bond lengths (Å):

Br(1)-C(1) = 1.891(3);
C(5)-S(1) = 1.826(3);
C(8)-S(3) = 1.816(3);
C(7)-S(2) = 1.812(3);
C(5)-S(1) = 1.826(3);
C(4)-S(1) = 1.825(3).

Compound: 14 (UoM: s3976ma)



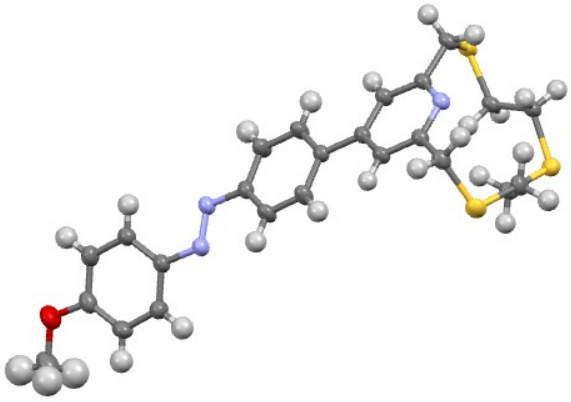
Selected torsion angles (°):

C(10)-C(11)-C(14)-C(15) = -26.1(3);
C(12)-C(11)-C(14)-C(18) =-27.5(3);
C(3)-C(4)-N(1)-N(2) =-172.71(17);
C(5)-C(4)-N(1)-N(2) = 8.1(3);
C(4)-N(1)-N(2)-C(8) = -178.64(15);
C(13)-C(8)-N(2)-N(1) =-170.59(16);
C(9)-C(8)-N(2)-N(1) = 11.4(3).

Selected bond lengths (Å):

C(11)-C(14) = 1.482(3);
C(8)-N(2) = 1.418(3);
N(1)-N(2) = 1.257(2);
C(4)-N(1) = 1.422(3);
C(1)-O(1) = 1.359(3).

Compound: 13 (UoM: s4010ma)



Selected torsion angles (°):

S(2)-C(1)-C(2)-S(1) = 175.94(10);
S(1)-C(3)-C(4)-N(1) = 118.67(17);
S(1)-C(3)-C(4)-C(9) = -59.5(2);
N(1)-C(5)-C(6)-S(3) = -98.68(18);
S(3)-C(7)-C(8)-S(2) = 178.96(11);
C(9)-C(10)-C(12)-C(17) = -8.3(3);
C(11)-C(10)-C(12)-C(17) = 172.3(2);
C(9)-C(10)-C(12)-C(13) = 170.1(2);
C(11)-C(10)-C(12)-C(13) = -9.3(3);
C(16)-C(15)-N(2)-N(3) = 162.9(2);
C(14)-C(15)-N(2)-N(3) = -18.6(3);
C(15)-N(2)-N(3)-C(18) = 178.35(16);
C(19)-C(18)-N(3)-N(2) = 165.31(19);
C(23)-C(18)-N(3)-N(2) = -14.5(3).

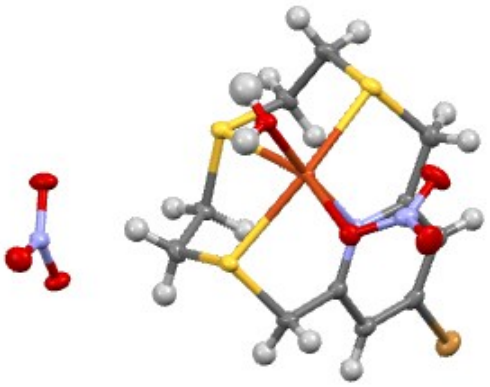
Selected bond lengths (Å):

N(2)-N(3) = 1.254(2);
C(10)-C(12) = 1.493(2);
C(15)-N(2) = 1.429(2);
C(18)-N(3) = 1.422(2);
C(21)-O(1) = 1.364(3)

Compound: 19 (UoM: s4114ma)

Selected bond angles (°):

O(1)-Cu(1)-N(1) = 172.16(11);
O(1)-Cu(1)-O(2) = 86.14(10);
N(1)-Cu(1)-O(2) = 87.62(10);
O(1)-Cu(1)-S(1) = 92.03(9);
N(1)-Cu(1)-S(1) = 86.21(8);
O(2)-Cu(1)-S(1) = 114.23(7);
O(1)-Cu(1)-S(3) = 97.74(9);
N(1)-Cu(1)-S(3) = 85.90(8);
O(2)-Cu(1)-S(3) = 80.61(6);
S(1)-Cu(1)-S(3) = 162.86(3);
O(1)-Cu(1)-S(2) = 92.35(8);
N(1)-Cu(1)-S(2) = 95.06(8);
O(2)-Cu(1)-S(2) = 161.61(6);
S(1)-Cu(1)-S(2) = 84.12(3);
S(3)-Cu(1)-S(2) = 81.45(3).

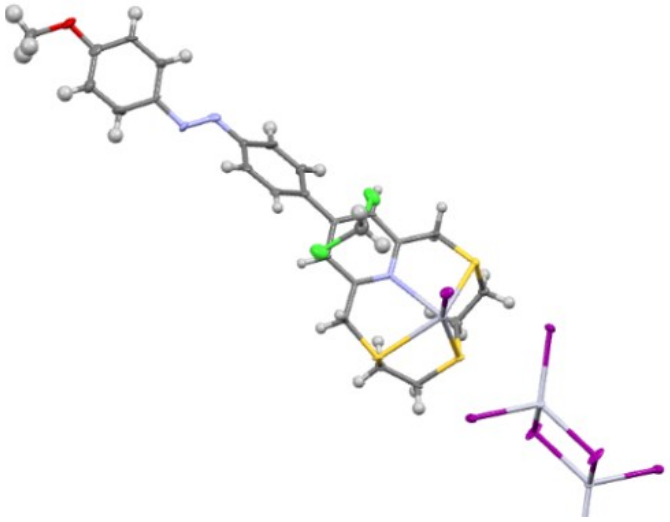


Selected bond lengths (Å):

Br(1)-C(1) = 1.878(3);
C(4)-S(1) = 1.803(4);
C(5)-S(1) = 1.832(4);
C(6)-S(2) = 1.823(3);
C(7)-S(2) = 1.815(3);
C(8)-S(3) = 1.815(4);
C(9)-S(3) = 1.807(3);
Cu(1)-N(1) = 1.978(3);
Cu(1)-O(1); 1.929(2);
Cu(1)-O(2) = 2.335(3);
Cu(1)-S(1) = 2.3736(9);
Cu(1)-S(2) = 2.7304(10);
Cu(1)-S(3) = 2.4301(8).

Compound: 23 (UoM: s4137na)

Selected bond lengths (Å):
C(21)-O(1) = 1.366(12);
C(18)-N(3) = 1.420(10);
N(2)-N(3) = 1.257(12);
C(15)-N(2) = 1.417(12);
C(1)-C(2) = 1.389(11);
Hg(1)-S(2) = 2.539(2);
Hg(1)-N(1) = 2.563(6);
Hg(1)-I(1) = 2.6562(6);
Hg(1)-S(1) = 2.739(2);
Hg(1)-S(3) = 2.760(2);
Hg(2)-I(3) = 2.7330(6);
Hg(2)-I(2) = 2.7357(6);
Hg(2)-I(4) = 2.7736(7).



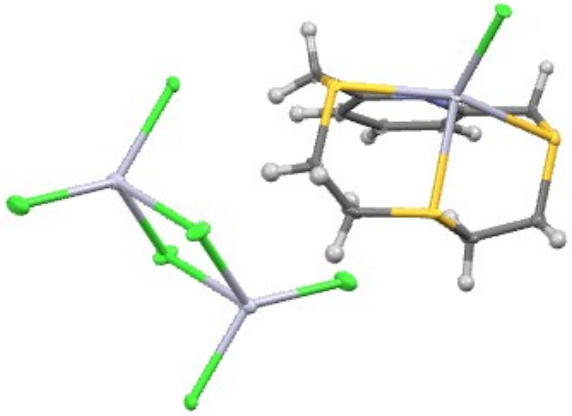
Selected bond angles (Å):
S(2)-Hg(1)-N(1) = 102.16(15);
S(2)-Hg(1)-I(1) = 154.72(5);
N(1)-Hg(1)-I(1) = 103.08(15);
S(2)-Hg(1)-S(1) = 82.13(6);
N(1)-Hg(1)-S(1) = 71.73(15);
I(1)-Hg(1)-S(1) = 104.60(5);
S(2)-Hg(1)-S(3) = 82.05(6);
N(1)-Hg(1)-S(3) = 72.20(16);
I(1)-Hg(1)-S(3) = 106.99(5);
S(1)-Hg(1)-S(3) = 136.23(6);
I(3)-Hg(2)-I(2) = 108.544(19);
I(3)-Hg(2)-I(4) = 116.84(2);
I(2)-Hg(2)-I(4) = 125.21(2);
I(3)-Hg(2)-I(4)#1 = 104.23(2);
I(2)-Hg(2)-I(4)#1 = 107.63(2);
I(4)-Hg(2)-I(4)#1 = 89.807(18);
Hg(2)-I(4)-Hg(2)#1 = 90.195(18).

Selected torsion angles (Å):
C(2)-C(1)-C(12)-C(17) = 36.4(12);
C(11)-C(1)-C(12)-C(17) = -144.1(9);
C(2)-C(1)-C(12)-C(13) - = 140.2(9);
C(11)-C(1)-C(12)-C(13) = 39.4(12);
C(14)-C(15)-N(2)-N(3) = 154.4(9);
C(16)-C(15)-N(2)-N(3) = - 27.2(13);
C(15)-N(2)-N(3)-C(18) = 177.7(8);
C(19)-C(18)-N(3)-N(2) = -12.2(13);
C(23)-C(18)-N(3)-N(2) = 168.3(9).

Compound: 21 (UoM: s4146na)

Selected bond angles (°):

Hg(2)-Cl(4)-Hg(2)#1 = 93.65(5);
Cl(1)-Hg(1)-N(1) = 125.25(12);
Cl(1)-Hg(1)-S(2) = 144.48(5);
N(1)-Hg(1)-S(2) = 89.36(12);
Cl(1)-Hg(1)-S(3) = 109.96(5);
N(1)-Hg(1)-S(3) = 76.28(13);
S(2)-Hg(1)-S(3) = 83.68(5);
Cl(1)-Hg(1)-S(1) = 99.32(5);
N(1)-Hg(1)-S(1) = 75.41(12);
S(2)-Hg(1)-S(1) = 80.37(5);
S(3)-Hg(1)-S(1) = 147.50(5);
Cl(2)-Hg(2)-Cl(3) = 131.07(6);
Cl(2)-Hg(2)-Cl(4) = 119.00(6);
Cl(3)-Hg(2)-Cl(4) = 108.19(6).

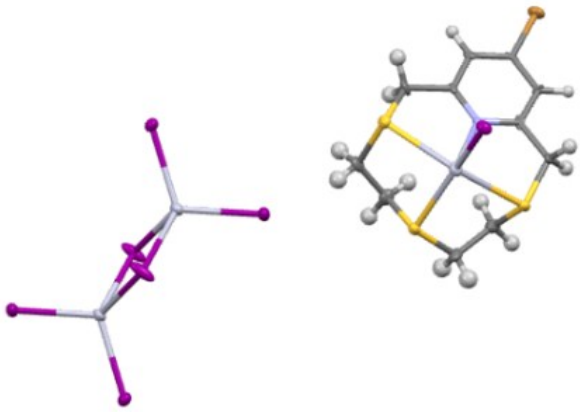


Selected bond lengths (Å):

Hg(1)-N(1) = 2.463(5);
Hg(1)-S(2) = 2.6089(15);
Hg(1)-S(3) = 2.6617(15);
Hg(1)-S(1) = 2.7276(15);
Hg(2)-Cl(4)#1 = 2.8671(17);
Cl(1)-Hg(1) = 2.4041(15);
Cl(2)-Hg(2) = 2.3730(18);
Cl(3)-Hg(2) = 2.4402(16);
Cl(4)-Hg(2) = 2.5223(16).

Compound: 22 (UoM: s4155na)

Selected bond angles (°): and Selected bond lengths (Å):



Br(1)-C(1)	1.898(10)
C(1)-C(2)	1.358(13)
C(1)-C(11)	1.393(12)
C(2)-C(3)	1.396(13)
C(2)-H(2)	0.9500
C(3)-N(1)	1.343(11)
C(3)-C(4)	1.513(13)
C(4)-S(1)	1.802(11)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.508(12)
C(5)-S(1)	1.809(9)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-S(2)	1.826(10)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.524(15)
C(7)-S(2)	1.813(10)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-S(3)	1.819(10)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.507(12)
C(9)-S(3)	1.806(10)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(1)	1.354(11)
C(10)-C(11)	1.388(13)
C(11)-H(11)	0.9500
Hg(1)-S(2)	2.550(2)
Hg(1)-N(1)	2.602(8)
Hg(1)-I(1)	2.6558(7)
Hg(1)-S(3)	2.726(2)
Hg(1)-S(1)	2.781(3)
Hg(2)-I(4)	2.7286(7)
Hg(2)-I(2)	2.7396(8)
Hg(2)-I(3)	2.7755(9)
Hg(2)-I(3)#1	3.0088(8)
I(3)-Hg(2)#1	3.0088(8)

C(2)-C(1)-C(11)	119.9(9)
C(2)-C(1)-Br(1)	121.5(7)
C(11)-C(1)-Br(1)	118.5(7)
C(1)-C(2)-C(3)	119.8(9)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
N(1)-C(3)-C(2)	121.5(9)
N(1)-C(3)-C(4)	120.9(9)
C(2)-C(3)-C(4)	117.6(8)
C(3)-C(4)-S(1)	119.0(7)
C(3)-C(4)-H(4A)	107.6
S(1)-C(4)-H(4A)	107.6
C(3)-C(4)-H(4B)	107.6
S(1)-C(4)-H(4B)	107.6
H(4A)-C(4)-H(4B)	107.0
C(6)-C(5)-S(1)	116.4(7)
C(6)-C(5)-H(5A)	108.2
S(1)-C(5)-H(5A)	108.2
C(6)-C(5)-H(5B)	108.2

S(1)-C(5)-H(5B)	108.2
H(5A)-C(5)-H(5B)	107.4
C(5)-C(6)-S(2)	110.1(7)
C(5)-C(6)-H(6A)	109.6
S(2)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6B)	109.6
S(2)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
C(8)-C(7)-S(2)	116.4(6)
C(8)-C(7)-H(7A)	108.2
S(2)-C(7)-H(7A)	108.2
C(8)-C(7)-H(7B)	108.2
S(2)-C(7)-H(7B)	108.2
H(7A)-C(7)-H(7B)	107.4
C(7)-C(8)-S(3)	111.9(7)
C(7)-C(8)-H(8A)	109.2
S(3)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8B)	109.2
S(3)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(10)-C(9)-S(3)	118.1(7)
C(10)-C(9)-H(9A)	107.8
S(3)-C(9)-H(9A)	107.8
C(10)-C(9)-H(9B)	107.8
S(3)-C(9)-H(9B)	107.8
H(9A)-C(9)-H(9B)	107.1
N(1)-C(10)-C(11)	123.1(8)
N(1)-C(10)-C(9)	120.4(9)
C(11)-C(10)-C(9)	116.5(8)
C(10)-C(11)-C(1)	117.5(9)
C(10)-C(11)-H(11)	121.3
C(1)-C(11)-H(11)	121.3
S(2)-Hg(1)-N(1)	100.69(17)
S(2)-Hg(1)-I(1)	153.21(7)
N(1)-Hg(1)-I(1)	105.95(15)
S(2)-Hg(1)-S(3)	82.75(8)
N(1)-Hg(1)-S(3)	70.85(16)
I(1)-Hg(1)-S(3)	108.47(6)
S(2)-Hg(1)-S(1)	81.03(8)
N(1)-Hg(1)-S(1)	71.07(17)
I(1)-Hg(1)-S(1)	104.88(5)
S(3)-Hg(1)-S(1)	134.67(8)
I(4)-Hg(2)-I(2)	109.19(3)
I(4)-Hg(2)-I(3)	126.58(3)
I(2)-Hg(2)-I(3)	115.97(3)
I(4)-Hg(2)-I(3)#1	104.51(3)
I(2)-Hg(2)-I(3)#1	106.55(3)
I(3)-Hg(2)-I(3)#1	88.89(2)
Hg(2)-I(3)-Hg(2)#1	91.11(2)
C(3)-N(1)-C(10)	118.2(8)
C(3)-N(1)-Hg(1)	121.3(6)
C(10)-N(1)-Hg(1)	118.0(6)
C(4)-S(1)-C(5)	103.0(5)
C(4)-S(1)-Hg(1)	104.0(3)
C(5)-S(1)-Hg(1)	98.1(3)
C(7)-S(2)-C(6)	101.4(5)
C(7)-S(2)-Hg(1)	102.8(3)
C(6)-S(2)-Hg(1)	99.2(3)
C(9)-S(3)-C(8)	101.4(5)
C(9)-S(3)-Hg(1)	99.9(3)
C(8)-S(3)-Hg(1)	94.3(3)