

Electronic Supplemental Information

for

A spectroscopic, structural, and computational study of Ag-oxo interactions in $\text{UO}_2^{2+}/\text{Ag}$ complexes

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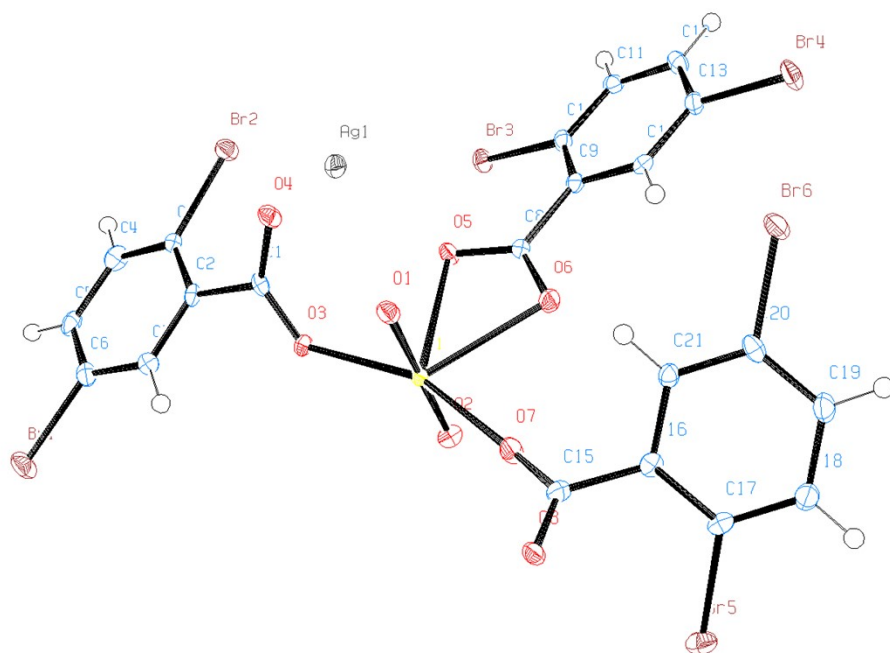


Figure S1. ORTEP illustration of 1. Ellipsoids are shown at 50% probability level.

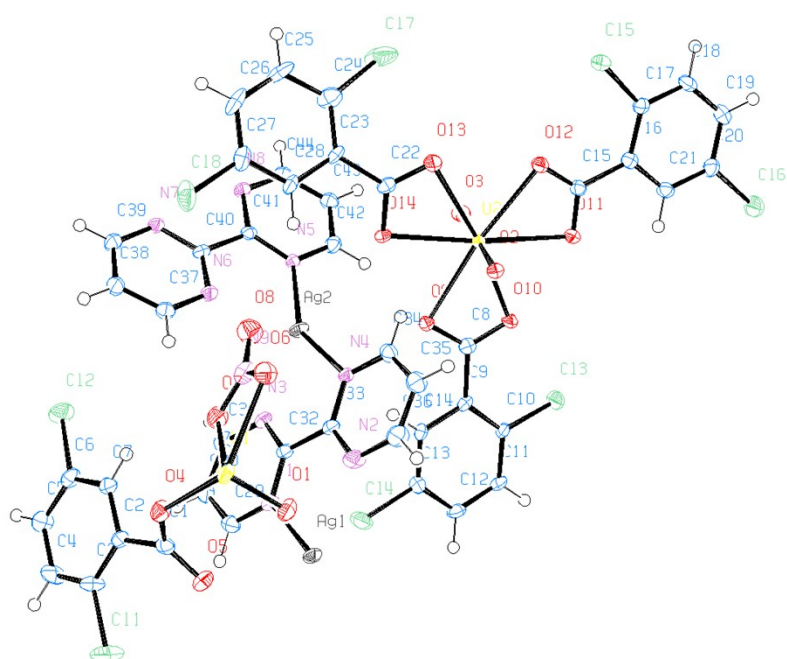


Figure S2. ORTEP illustration of compound **2**. Ellipsoids are shown at 50% probability level.

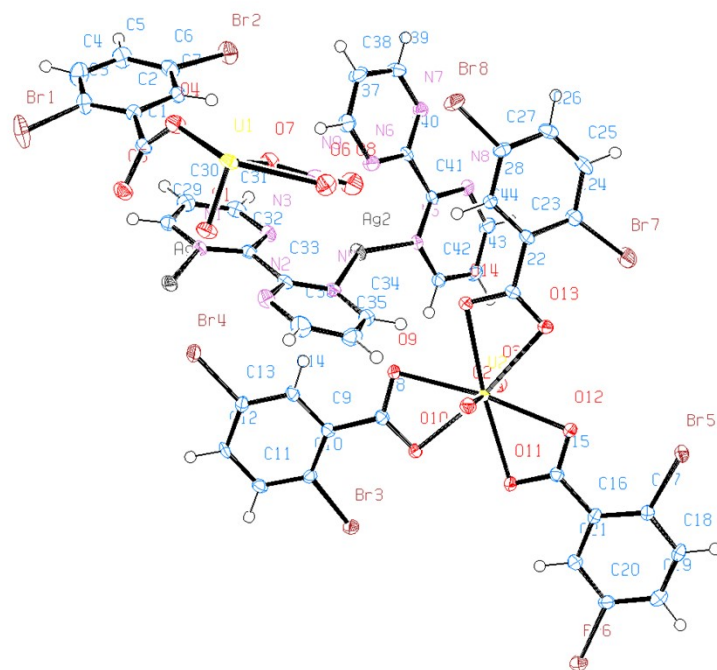


Figure S3. ORTEP illustration of compound **3**. Ellipsoids are shown at 50% probability level.

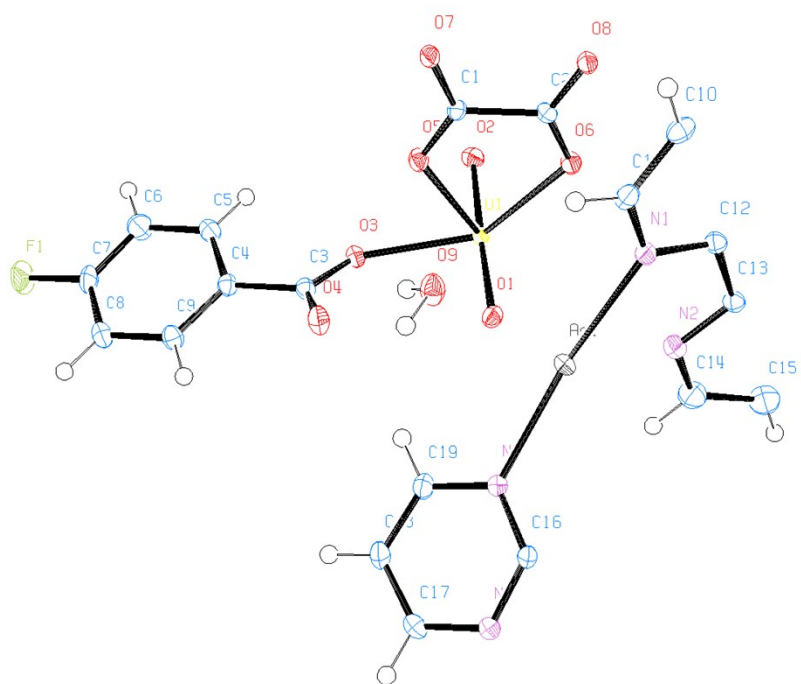


Figure S4. ORTEP illustration of compound **4**. Ellipsoids are shown at 50% probability level.

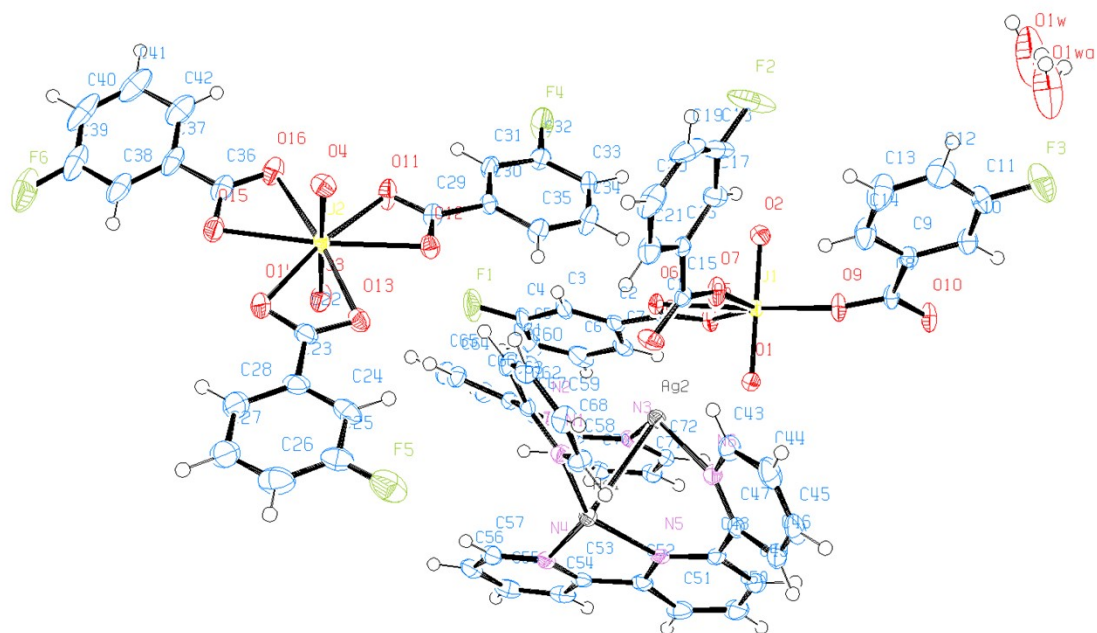


Figure S5. ORTEP illustration of compound **5**. Ellipsoids are shown at 50% probability level.

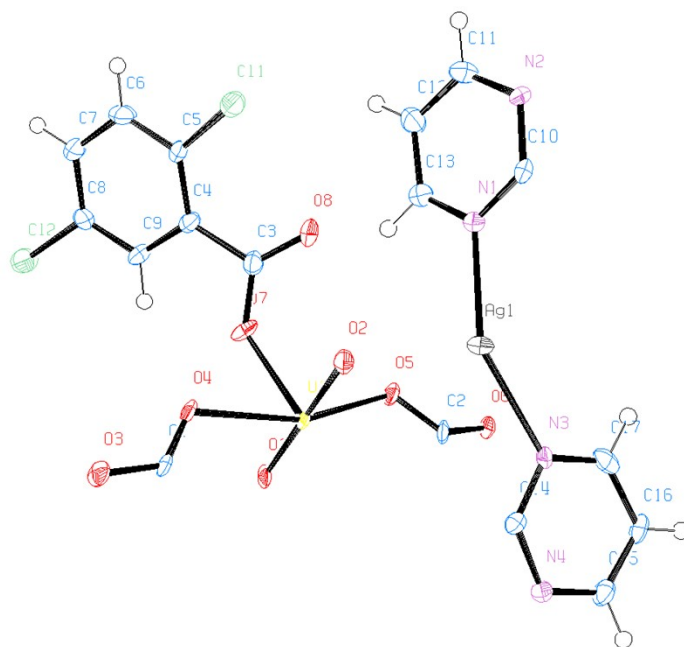


Figure S6. ORTEP illustration of compound 6. Ellipsoids are shown at 50% probability level.

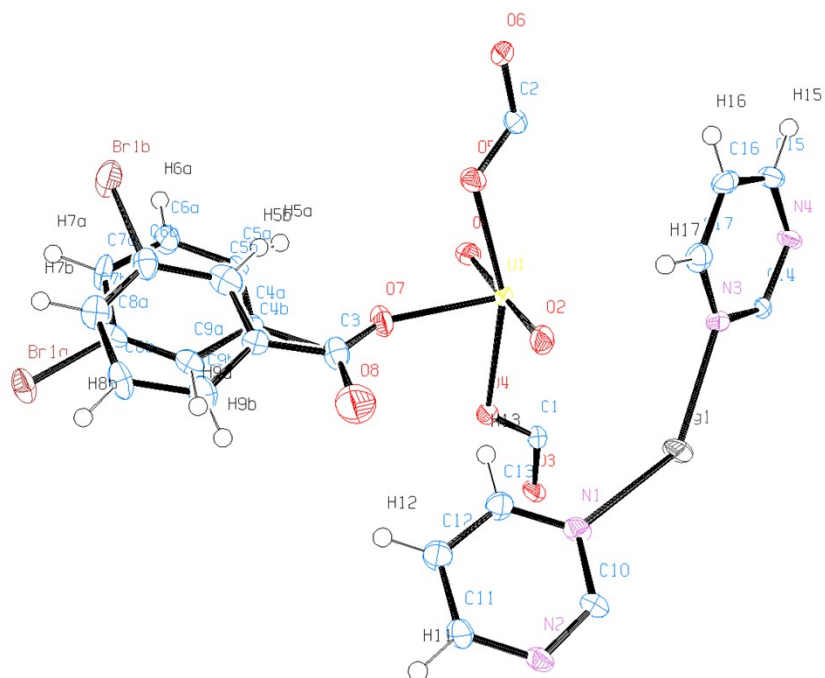


Figure S7. ORTEP illustration of compound 7. Ellipsoids are shown at 50% probability level.

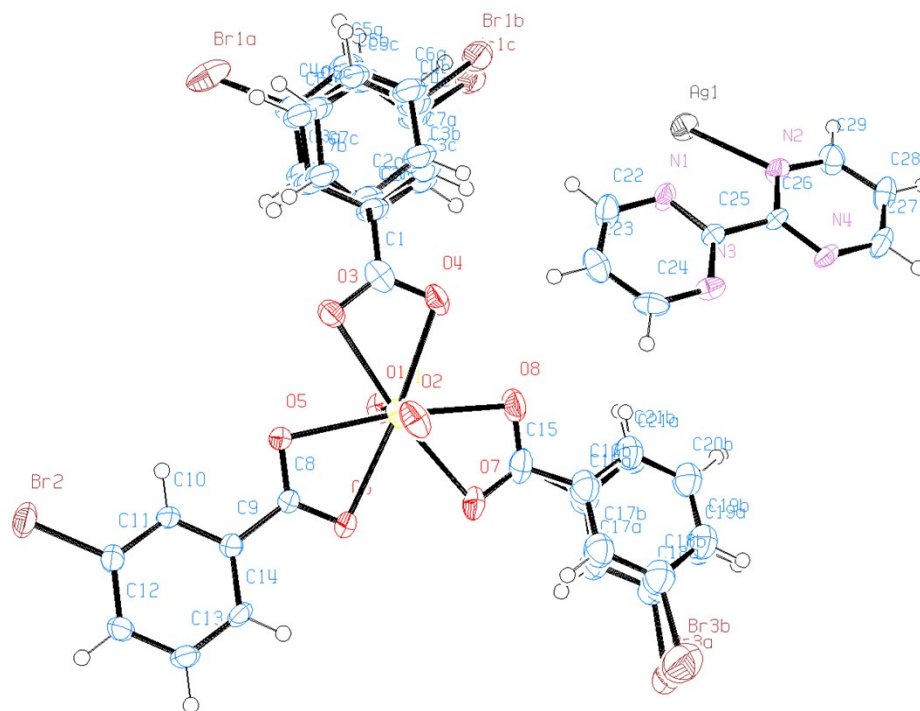


Figure S8. ORTEP illustration of compound **8**. Ellipsoids are shown at 50% probability level.

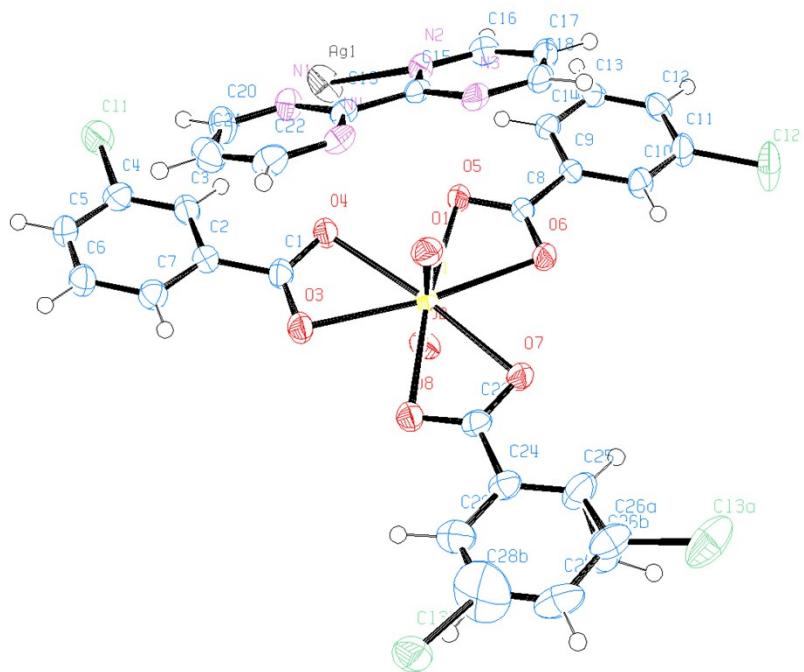


Figure S9. ORTEP illustration of compound **9**. Ellipsoids are shown at 50% probability level.

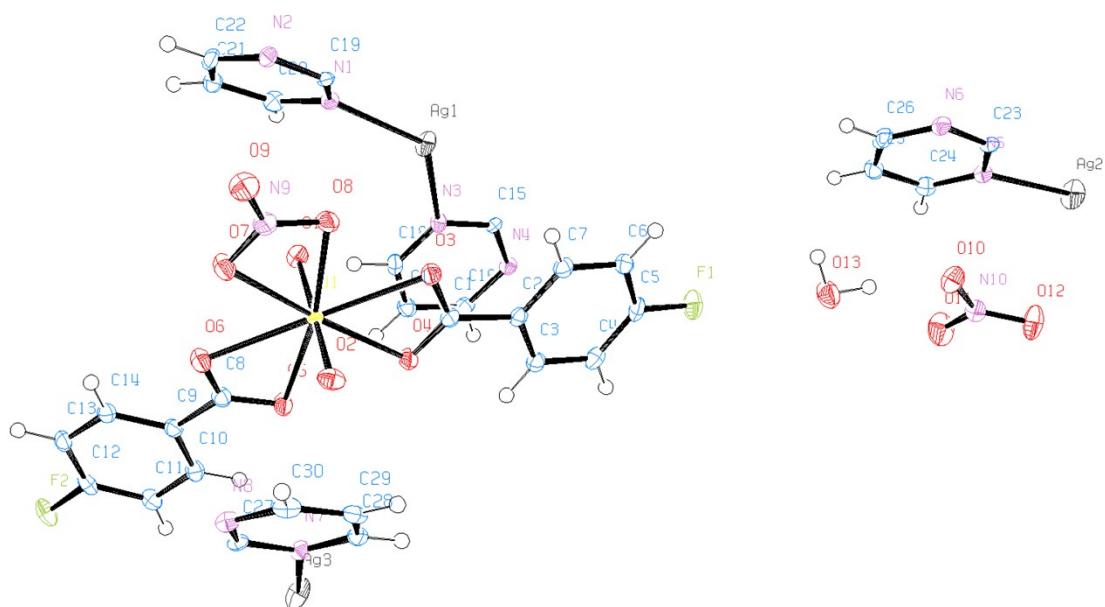


Figure S10. ORTEP illustration of compound **10**. Ellipsoids are shown at 50% probability level.

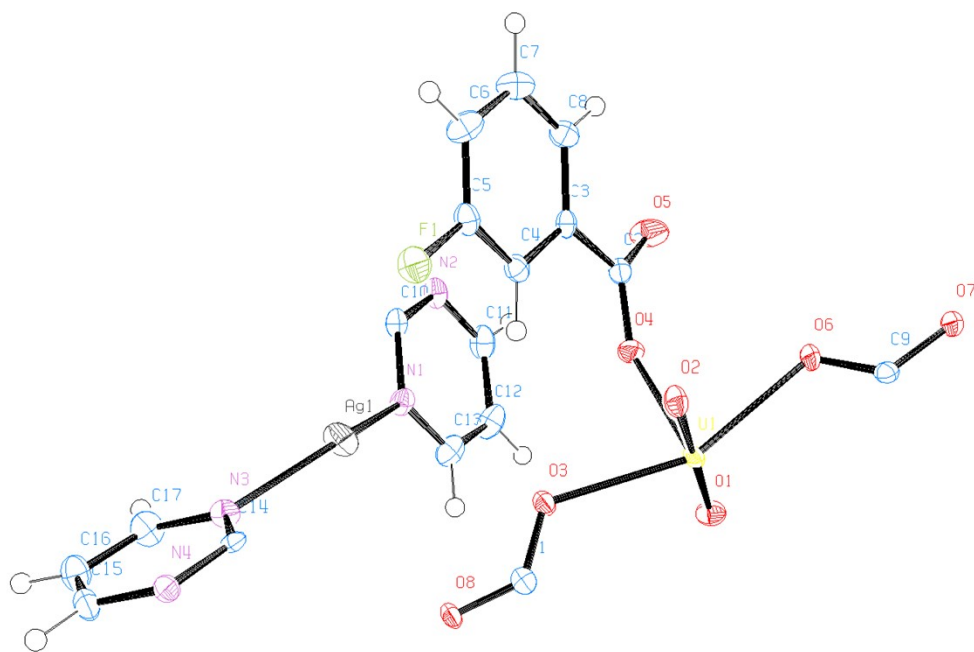


Figure S11. ORTEP illustration of compound 11. Ellipsoids are shown at 50% probability level.

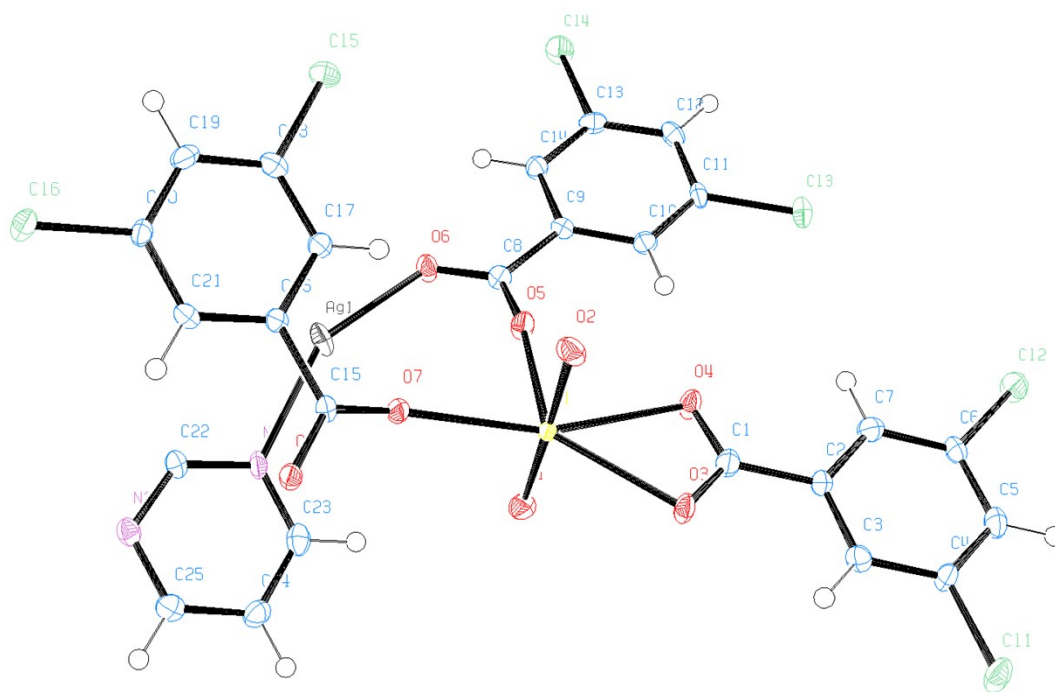


Figure S12. ORTEP illustration of compound 12. Ellipsoids are shown at 50% probability level.

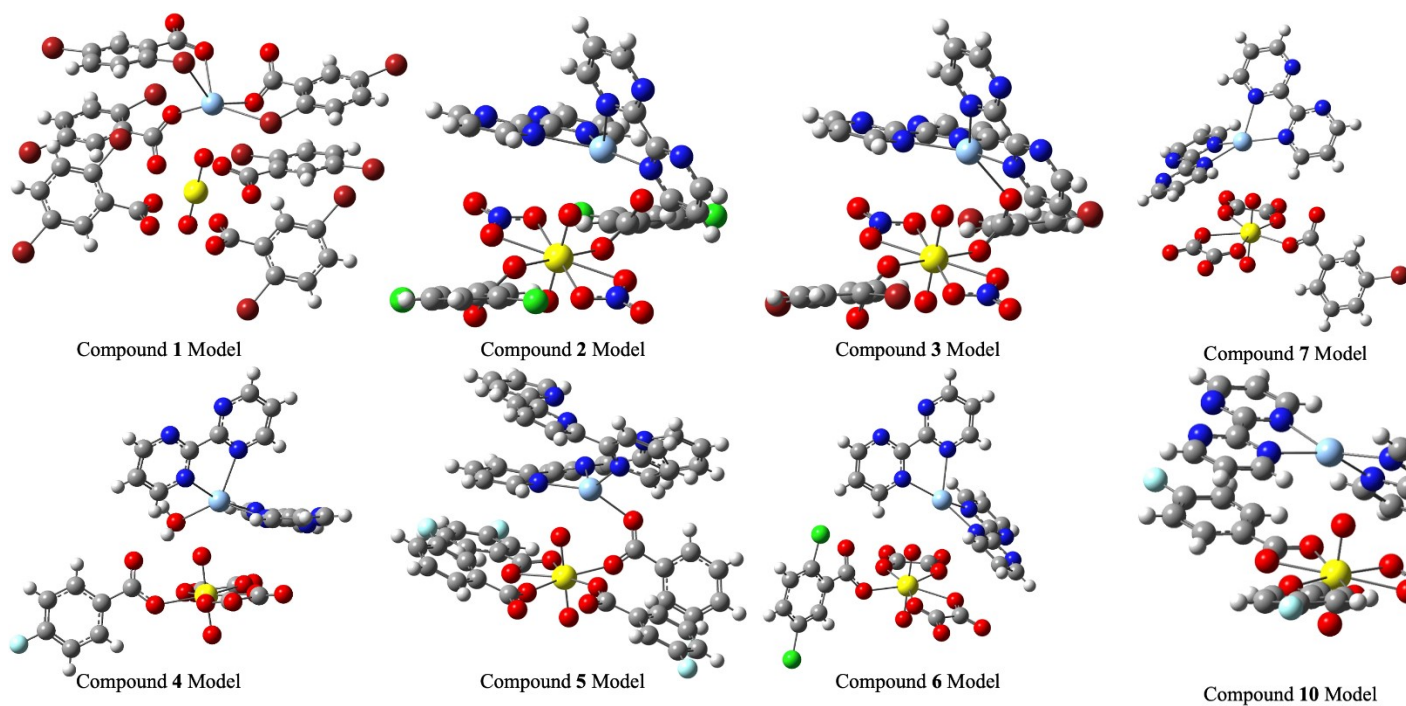


Figure S13. DFT ground state models for 1-12.

```
%nproc=16
%mem=2000MW
%chk=Cmpd1.chk
# b3lyp/genecp nosymm int=grid=ultrafine scf=(xqc,maxcycle=2000) pop=full formcheck
```

Cmpd1

-3 1

U	47.29926638	19.57654123	22.42850287
O	46.72726638	17.93854123	22.82750287
O	47.83926638	21.20454123	22.02650287
Ag	44.38526638	17.13654123	22.82550287
Br	46.42526638	19.00554123	15.06450287
Br	41.76526638	20.09454123	19.52650287
Br	42.72226638	22.45354123	23.28150287
Br	44.19026638	20.84154123	29.45050287
Br	52.70926638	20.52454123	25.66550287
Br	47.31226638	18.97754123	28.99950287
O	46.00826638	19.58554123	20.46350287
O	44.08926638	18.49054123	20.86350287
O	45.04326638	20.47754123	23.04450287
O	46.54426638	20.34654123	24.63850287
O	49.12526638	19.28954123	23.80150287
O	51.12026638	18.36754123	24.13650287
C	44.87926638	19.12854123	20.13050287
C	44.46326638	19.38654123	18.69250287
C	43.18926638	19.80954123	18.29050287
C	42.90126638	20.06954123	16.97050287
H	42.04826638	20.41154123	16.72950287
C	43.86726638	19.83054123	15.98450287
H	43.67026638	19.97654123	15.06650287
C	45.10226638	19.38054123	16.37050287
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C	45.36926638	20.63654123	24.26050287
C	44.39226638	21.14554123	25.29750287
C	43.23726638	21.87654123	25.02550287
C	42.39026638	22.29954123	26.03850287
H	41.62726638	22.82454123	25.83050287
C	42.65726638	21.95654123	27.35250287
H	42.06126638	22.21054123	28.04650287
C	43.81126638	21.23554123	27.64350287
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H	49.96526638	20.04554123	29.64750287

C	48.88726638	19.41254123	28.02750287
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Br	44.33026638	14.58454123	21.81050287
O	42.96226638	18.54754123	24.22850287
O	42.00926638	16.56054123	22.04750287
O	48.86626638	18.67054123	20.95550287
Br	47.27726638	16.51354123	19.42650287
Br	52.67426638	18.06054123	16.09250287
O	50.86126638	17.74854123	21.29050287
C	49.87026638	18.02754123	20.57050287
C	49.90826638	17.60454123	19.13950287
C	48.81926638	17.05354123	18.46950287
C	48.85326638	16.79654123	17.10950287
H	48.10426638	16.40554123	16.67550287
C	49.99426638	17.11754123	16.38650287
H	50.02126638	16.99254123	15.44450287
C	51.09926638	17.62554123	17.06450287
C	51.08726638	17.85954123	18.42250287
H	51.86126638	18.18754123	18.86450287
Br	40.62726638	18.03354123	30.02750287
Br	42.86226638	16.19654123	15.64150287
O	41.04326638	17.45354123	24.62850287
O	40.50826638	16.69154123	20.45350287
C	42.17326638	17.90954123	24.96150287
C	42.58826638	17.65154123	26.39950287
C	43.86326638	17.22954123	26.80150287
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H	45.00326638	16.62654123	28.36250287
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H	43.38226638	17.06154123	30.02550287
C	41.95026638	17.65754123	28.72150287
C	41.62026638	17.83654123	27.38450287
H	40.73626638	18.08454123	27.14150287
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C	43.81526638	15.16154123	20.06650287
C	44.66126638	14.73854123	19.05350287
H	45.42526638	14.21354123	19.26150287
C	44.39426638	15.08154123	17.73950287
H	44.99026638	14.82754123	17.04550287
C	43.24026638	15.80354123	17.44850287
C	42.37626638	16.19954123	18.46250287
H	41.58526638	16.68154123	18.24850287

C H O 0
6-311g(d,p)

Ag Br 0
Def2tzvp

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1833.7573000 0.000771
351.6863200 0.002969
S 1 1.00
104.3142600 1.0
S 3 1.00
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35.5150860 -0.245313
20.8912270 0.723847
S 1 1.00
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S 1 1.00
2.8518510 1.0
S 1 1.00
1.5316160 1.0
S 1 1.00
0.6162030 1.0
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S 1 1.00
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0.0234430 1.0
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224.6347900 0.003414
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P 1 1.00
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0.0305350 1.0
D 6 1.00
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156.3569500 0.000322

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D 1 1.00
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F 5 1.00
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35.1011810 0.002308
14.5641380 0.009253
4.6518850 0.136949
2.2559730 0.339801
F 1 1.00
1.0102740 1.0
F 1 1.00
0.4116800 1.0
F 1 1.00
0.1441200 1.0
G 4 1.00
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35.1011810 0.001831
14.5641380 0.019940
4.6518850 0.110758
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2.2559730 1.0
G 1 1.00
1.0102740 1.0

Ag Br 0
Def2tzvp
U 0
ECP60MWB 5 60
H-Komponente
1
2 1.00000000 0.00000000
S-H
1
2 16.41403869 536.51662778
P-H
1
2 9.06055606 169.54492465
D-H
1
2 8.83183198 142.61559837

F-H

1

2 7.01851629 60.39307602

G-H

1

2 12.80408844 -60.1299895

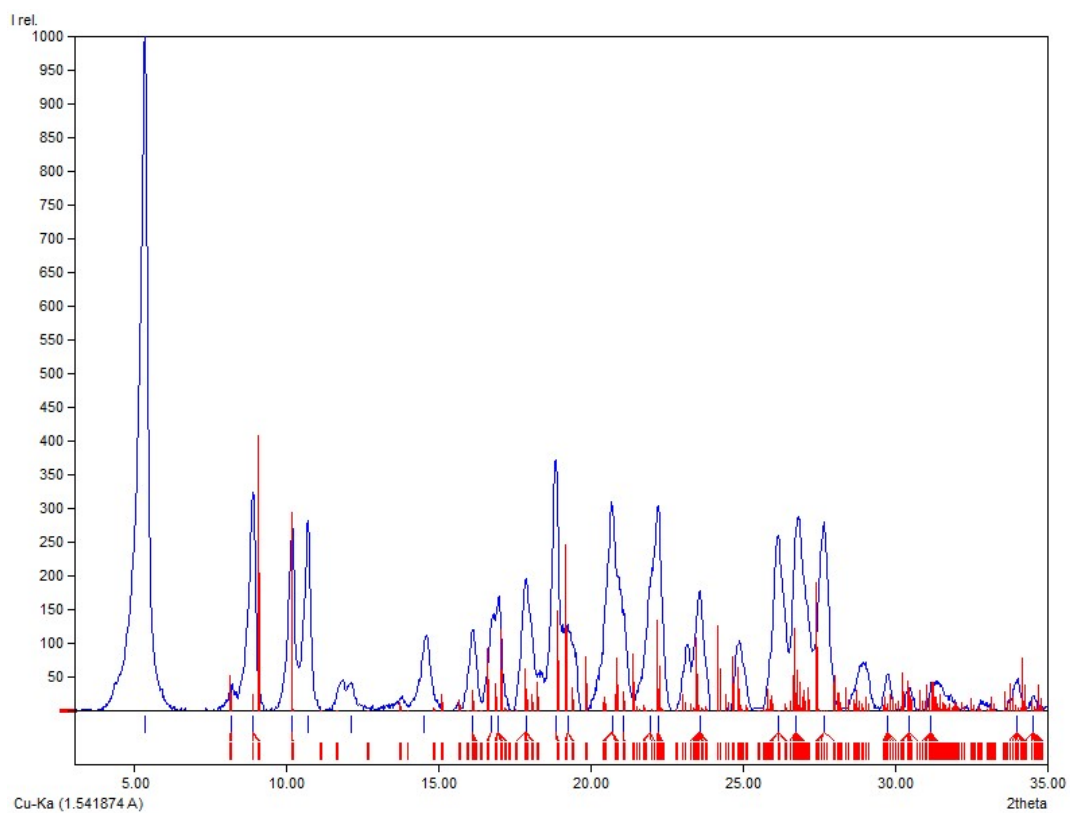


Figure S14. Powder pattern (blue) of **1** with overlaid calculated pattern from CIF (red). Peaks at 5.35°, 10.71°, 12.13° and 14.53° do not correspond to any of the known reactants or impurities and were not identified.

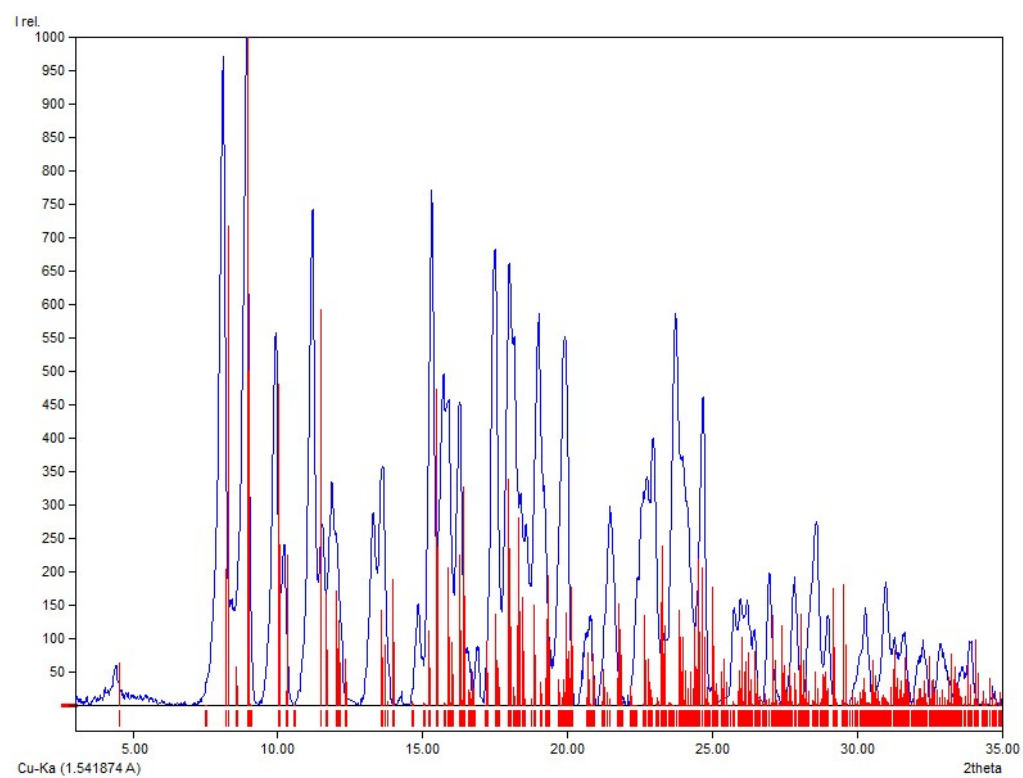


Figure S15. Powder pattern (blue) of **2** with overlaid calculated pattern from CIF (red).

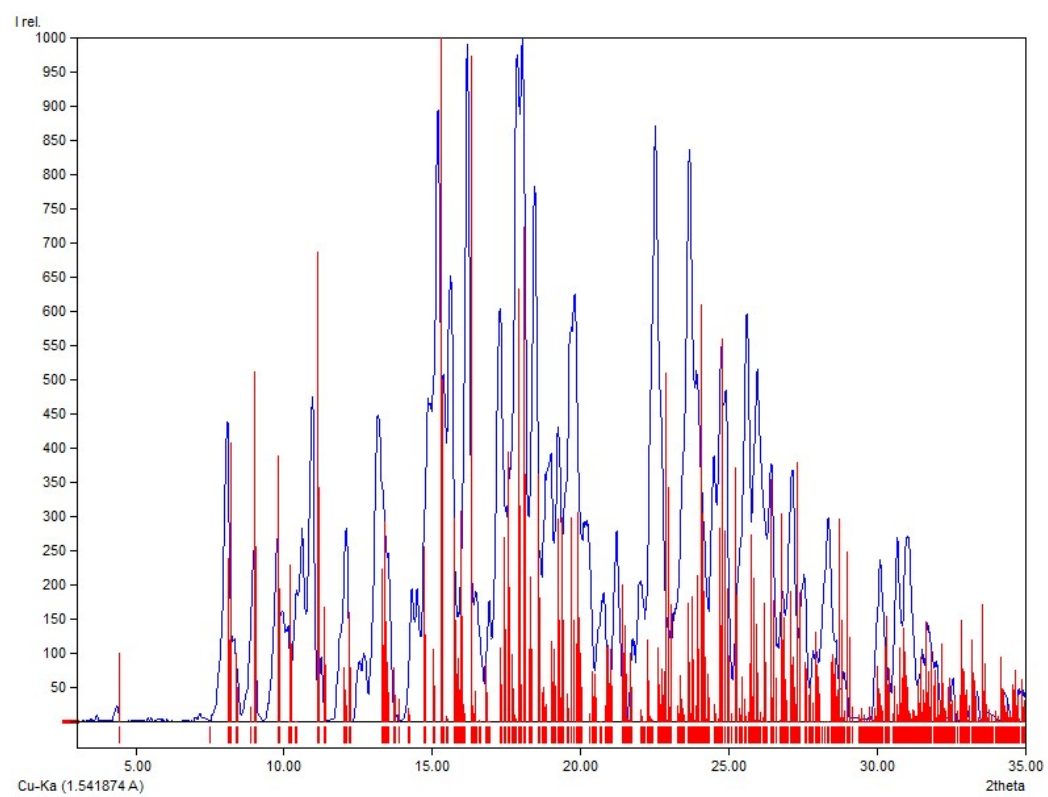


Figure S16. Powder pattern (blue) of **3** with overlaid calculated pattern from CIF (red).

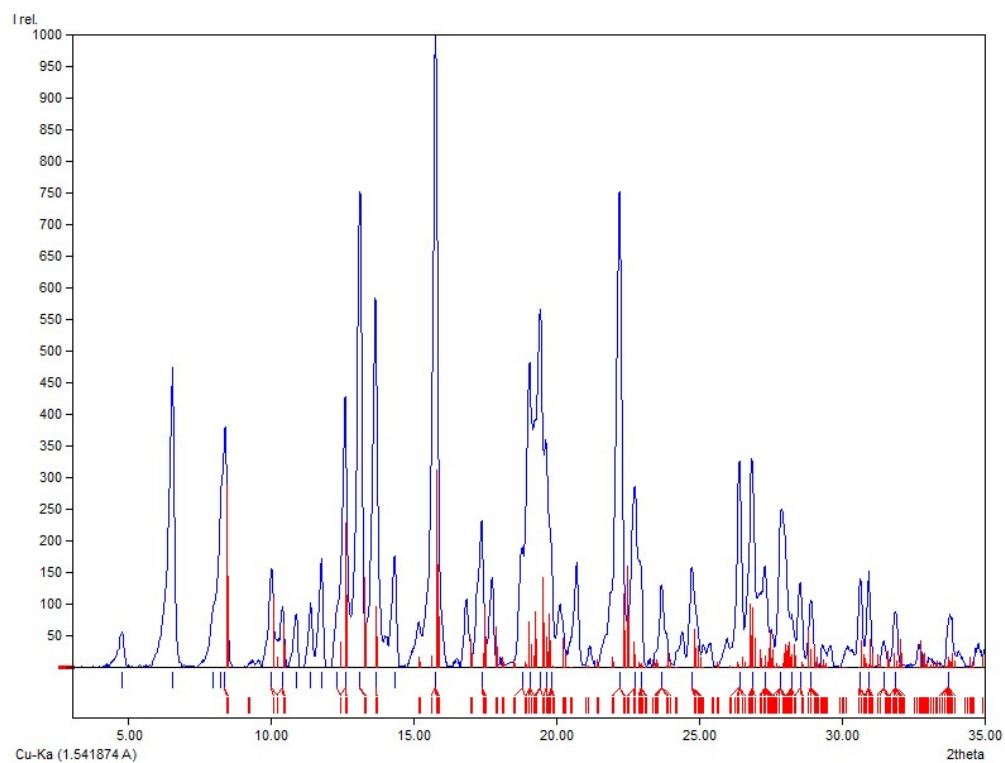


Figure S17. Powder pattern (blue) of **4** with overlaid calculated pattern from CIF (red). Peaks at 4.79°, 6.57°, 10.89°, 11.40°, 11.78°, and 14.34° do not correspond to any of the known reactants or impurities and were not identified.

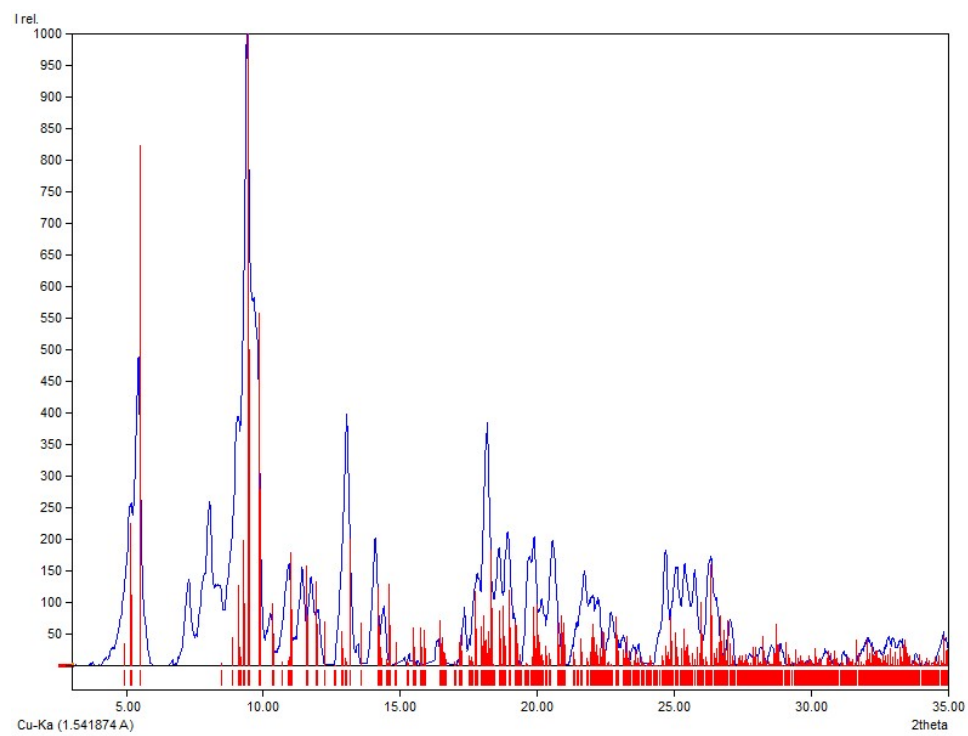


Figure S18. Powder pattern (blue) of **5** with overlaid calculated pattern from CIF (red). Peaks at 7.24° , and 8.05° do not correspond to any of the known reactants or impurities and were not identified.

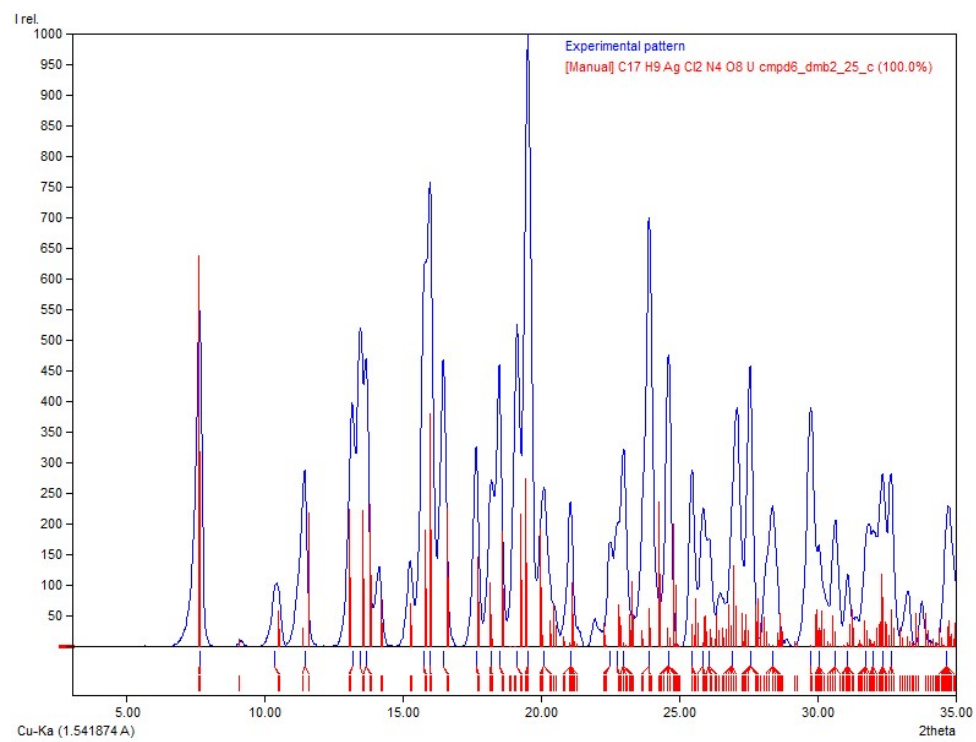


Figure S19. Powder pattern (blue) of **6** with overlaid calculated pattern from CIF (red).

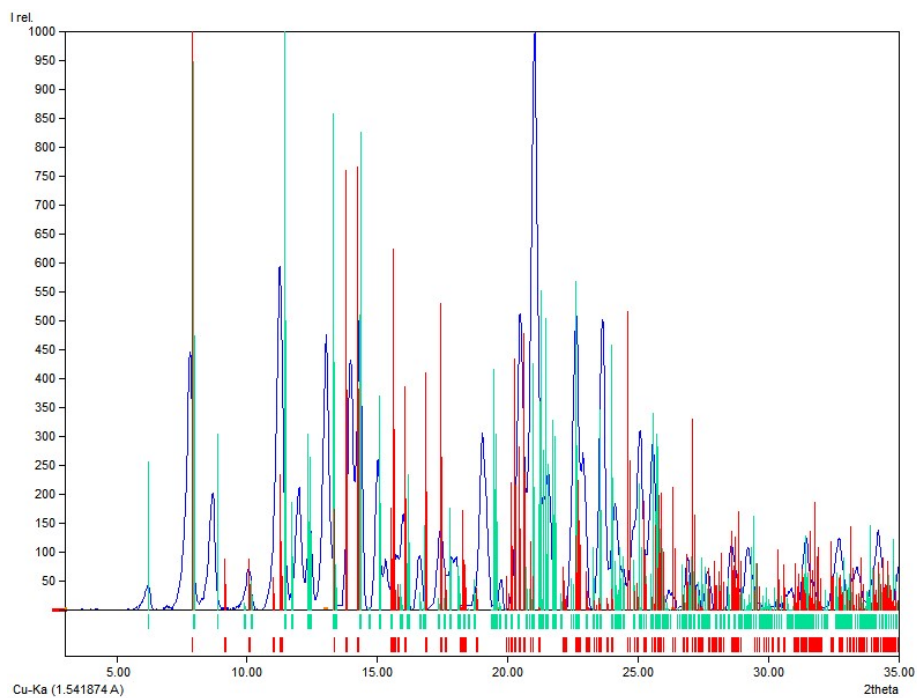


Figure S20. Powder pattern (blue) of **7** and **8** with overlaid calculated pattern from CIFs (**7** in red and **8** in green).

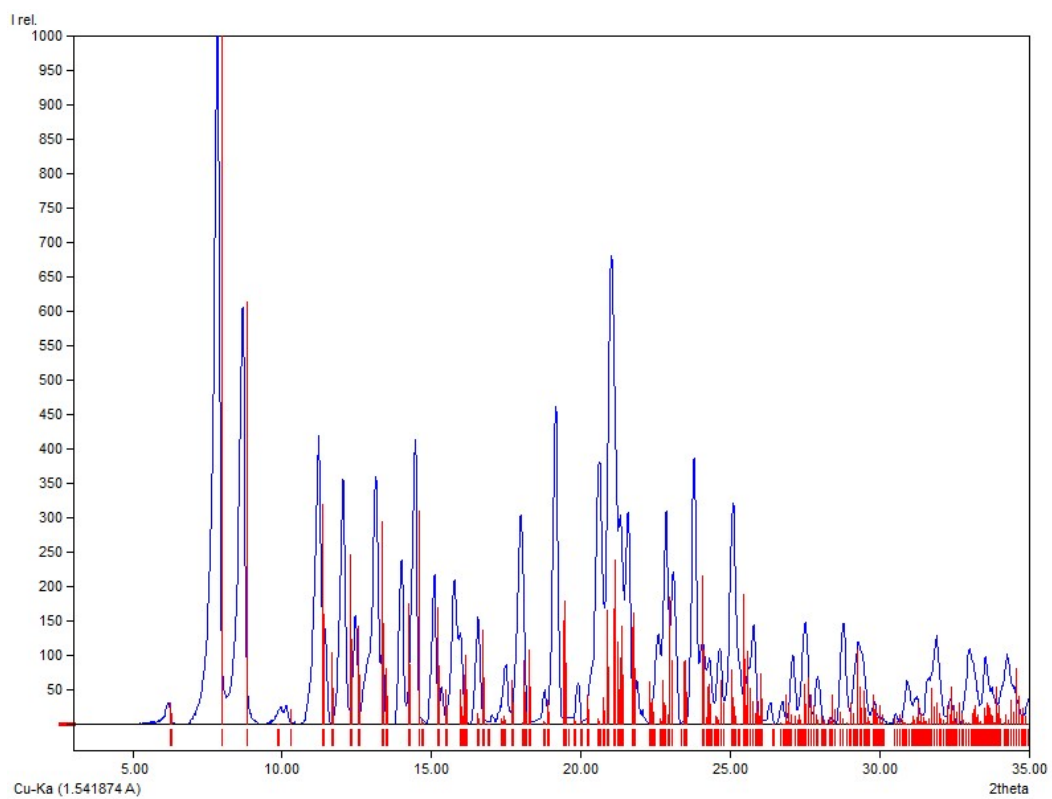


Figure S21. Powder pattern (blue) of **9** with overlaid calculated pattern from CIF (red).

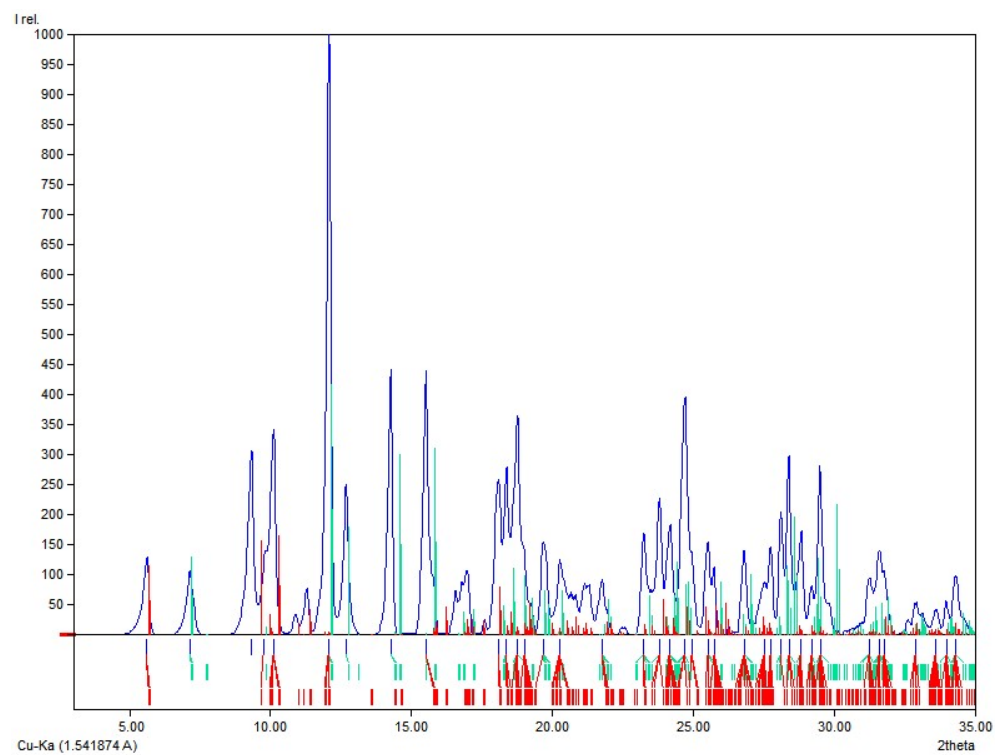


Figure S22. Powder pattern (blue) of **12** with overlaid calculated pattern from CIF (red). An additional Ag^+ /bypm phase ($[\text{Ag}(\text{C}_8\text{H}_6\text{N}_4)] \text{NO}_3 \cdot \text{H}_2\text{O}$) was identified from the CSD (Refcode: YABDIQ) and the CIF (green) overlaid.¹

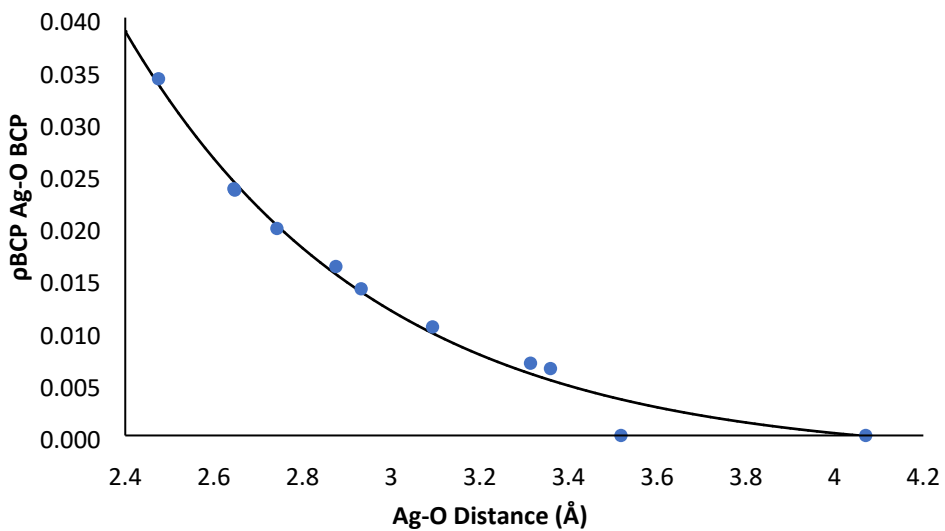


Figure S23. ρ_{BCP} of Ag-oxo interaction vs. Ag-O distance as calculated by QTAIM for **1-12**. Line fit equation: $y = 2.87281 \cdot \exp(-x/0.56433) - 0.00218$.

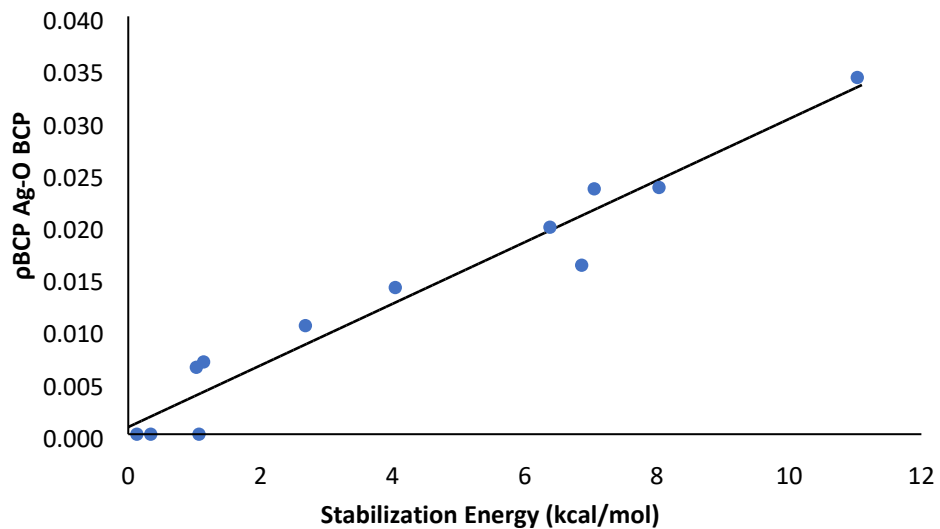


Figure S24. ρ_{BCP} of Ag-oxo interaction vs. stabilization energies (kcal/mol) as calculated by SOPT and QTAIM for **1-12**. Line fit equation: $y = 0.00295x + 6.8443 \cdot 10^{-4}$

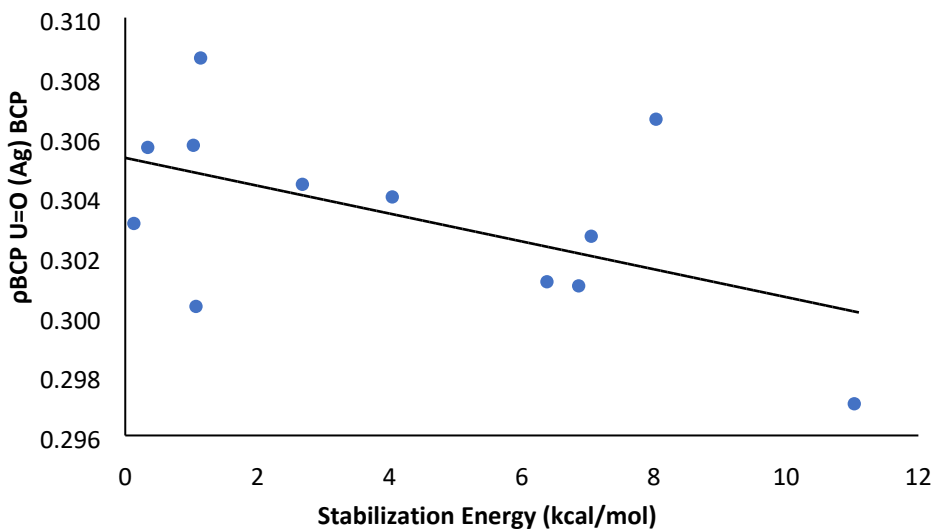


Figure S25. ρ_{BCP} for the U=O bond canted towards the Ag⁺ vs stabilization energy values from SOPT and QTAIM of **1-12**. Line fit equation: $y = -4.6659 \cdot 10^{-4} \cdot x + 0.3053$.

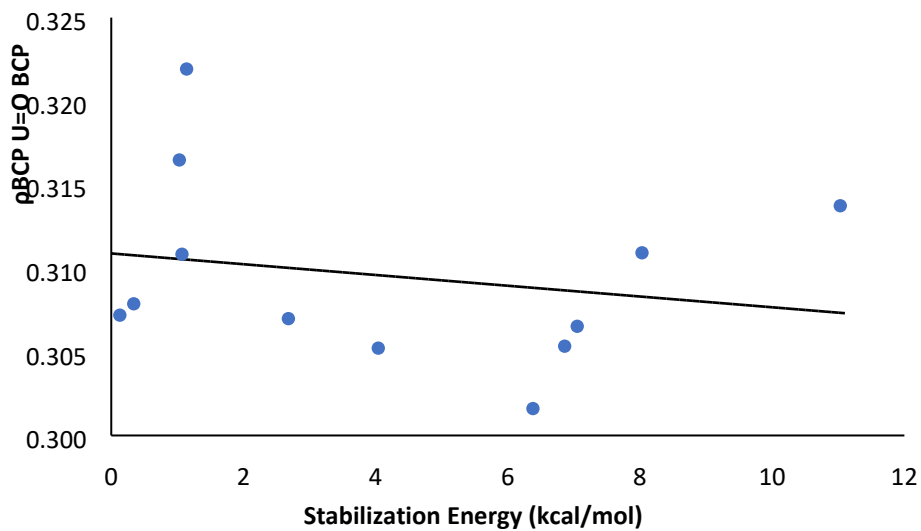


Figure S26. ρ_{BCP} for the U=O bond canted away from Ag^+ vs stabilization energy values from SOPT and QTAIM of **1-12**. Line fit equation: $y = -3.22096 \cdot 10^{-4} \cdot x + 0.31089$.