

Redox halido-based reactivity on the addition of bromine to linear NHCgold halides

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Keywords: Halogen Addition; Gold chemistry; Halogen bonding; Inverted Ligand Field.

Supporting Information

^1H NMR spectra for complexes 3 – 9 in CD_3CN

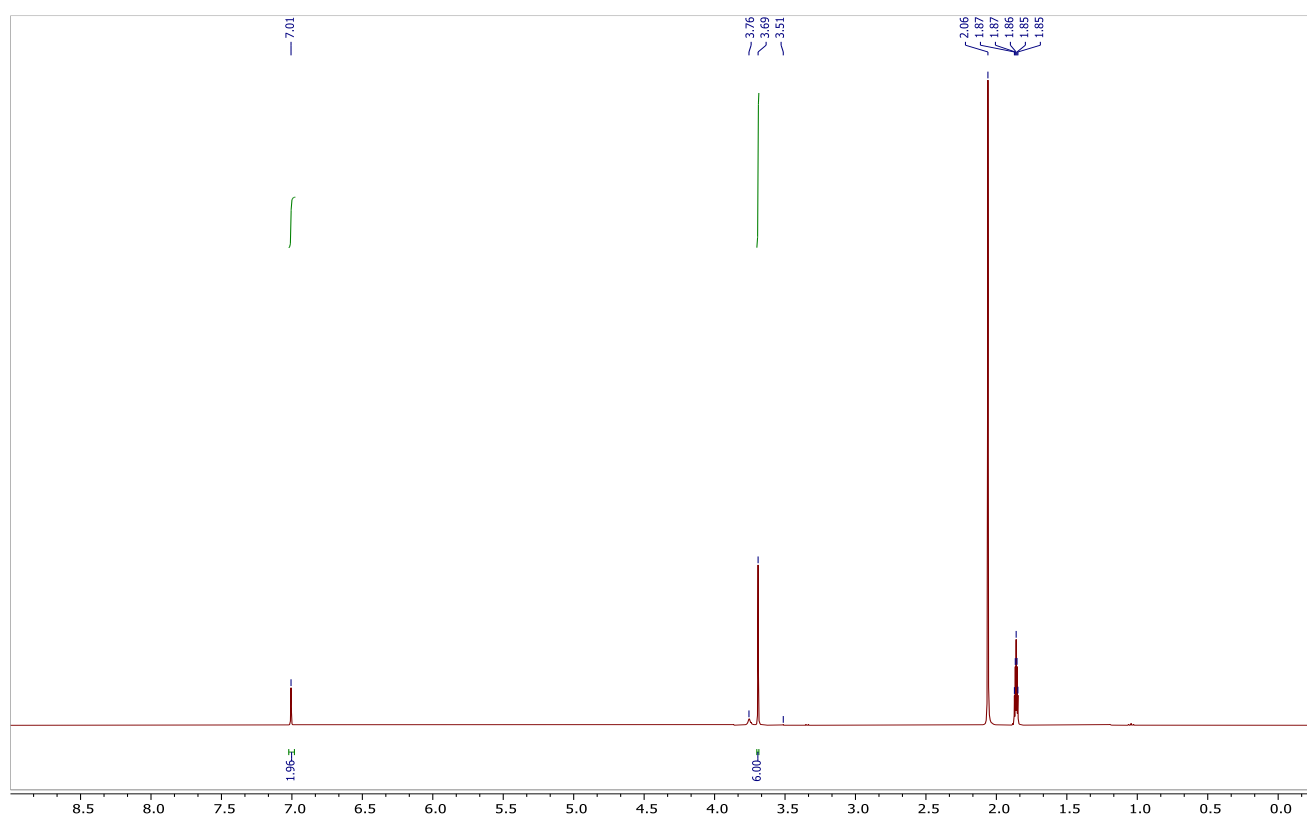


Figure 1S: ^1H NMR of complex 3

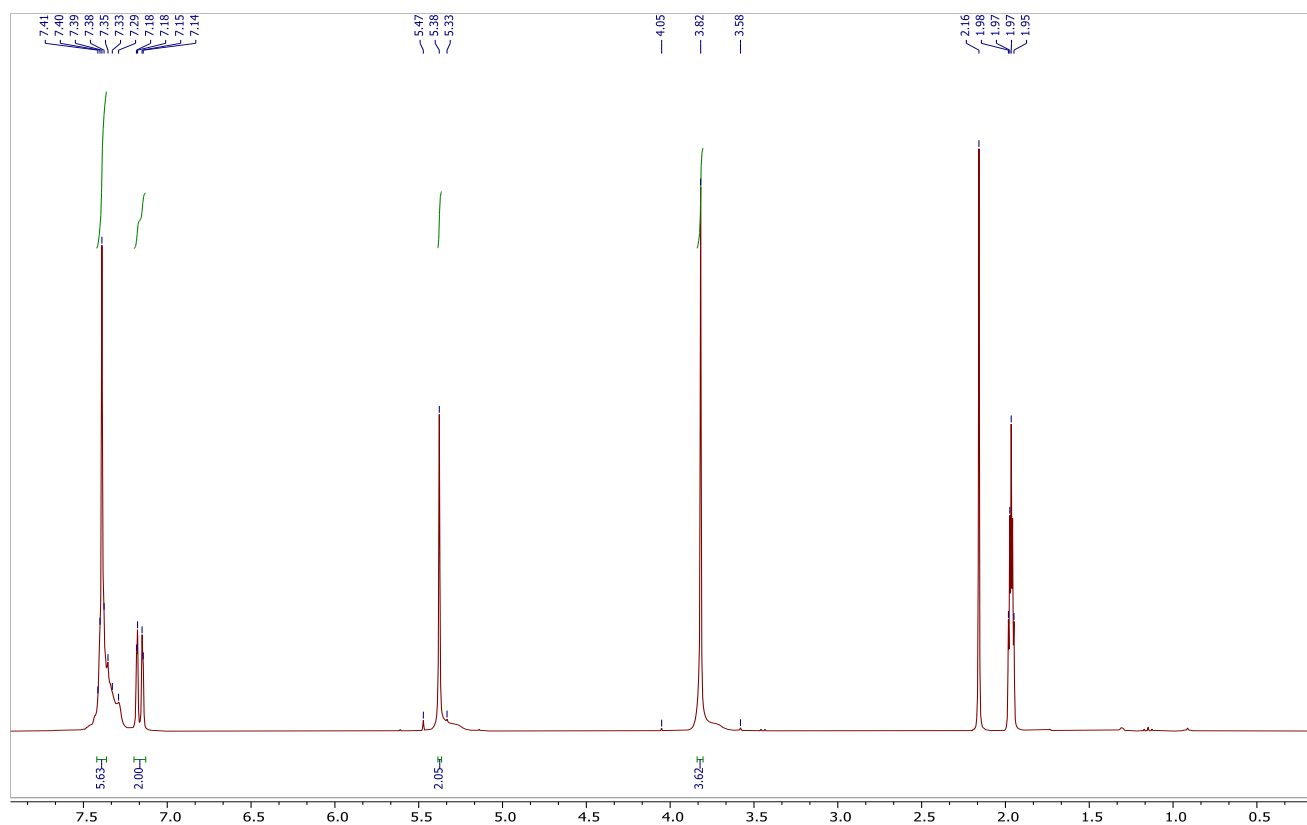


Figure 2S: ^1H -NMR of complex **4**

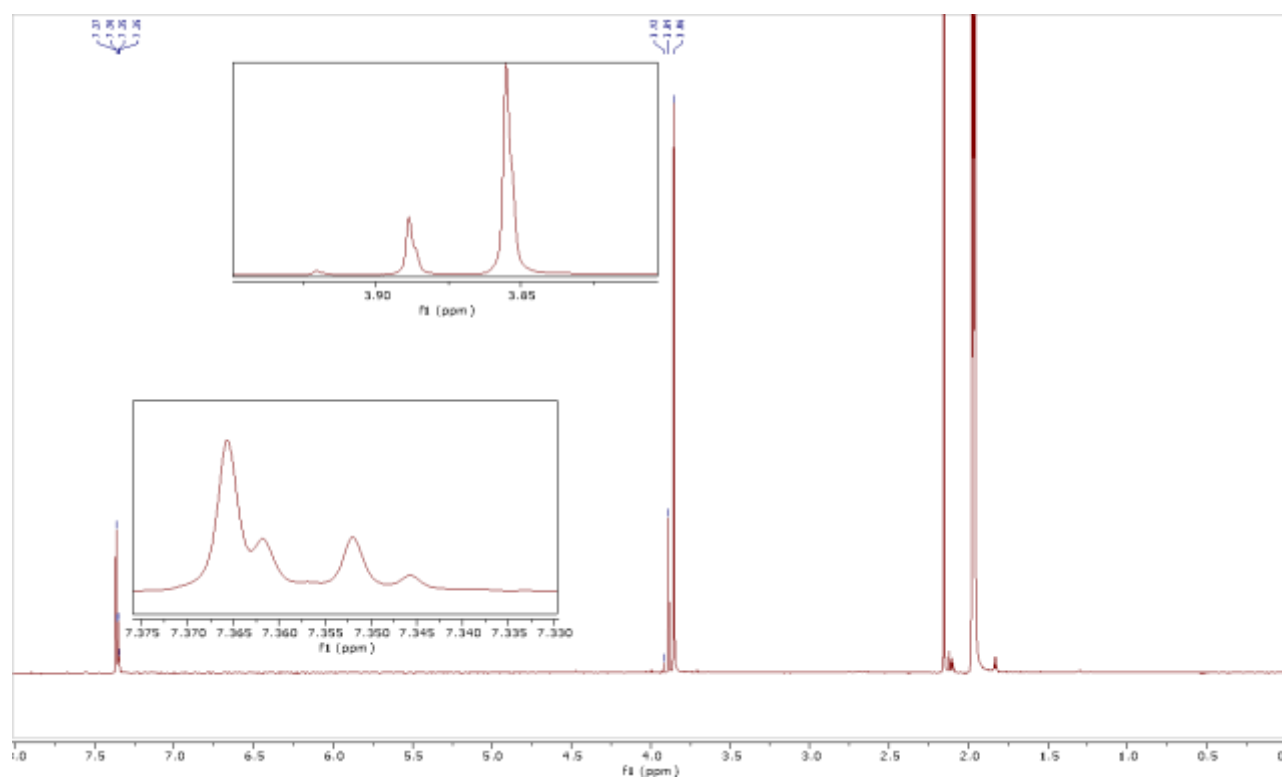


Figure 3S: ^1H NMR Spectrum of **5_{cis}** and **5_{trans}** (Pathway A)

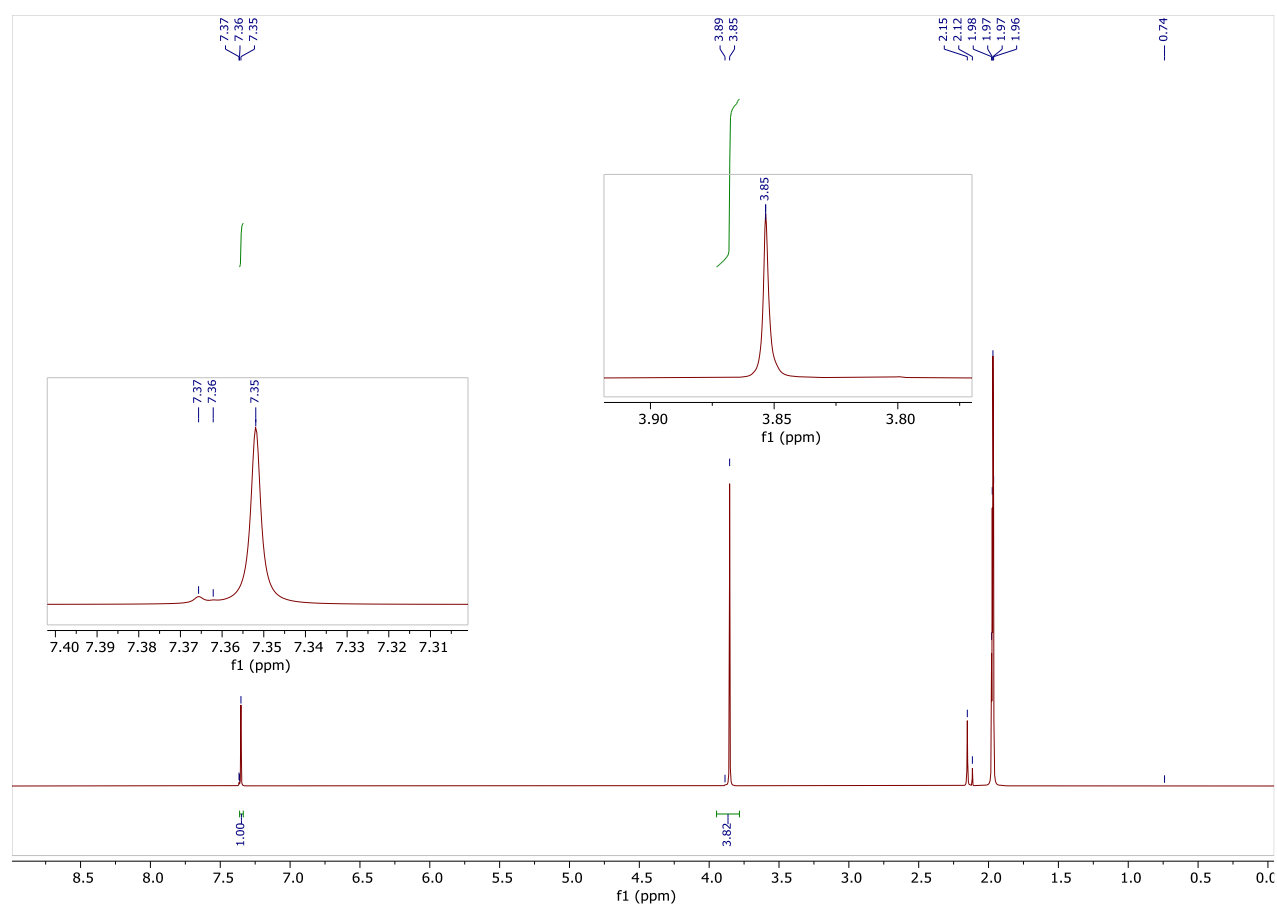


Figure 4S: ^1H NMR Spectrum of **6** and **5_{trans}** (Pathway B)

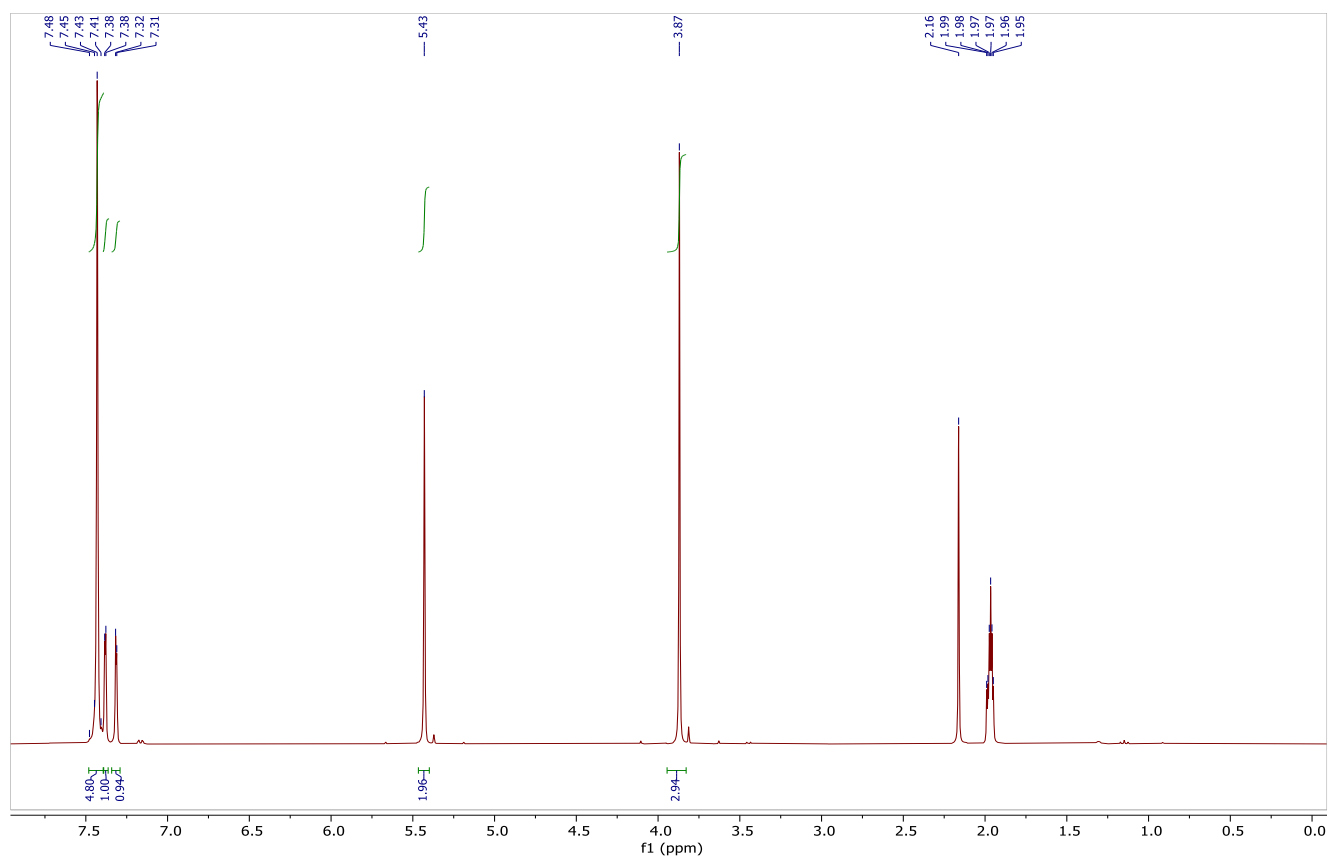


Figure 5S: ¹H NMR of complex 7

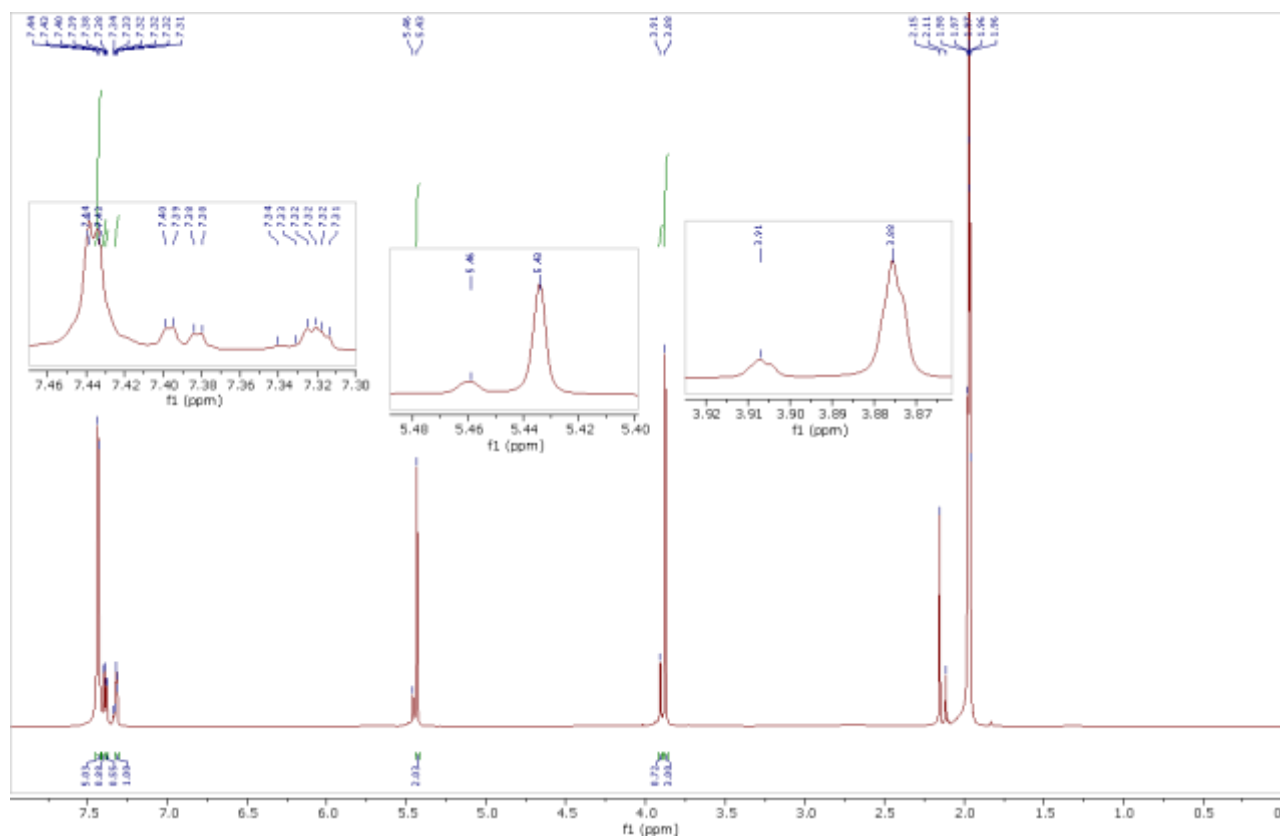


Figure 6S: ¹H NMR Spectrum of mixture of **8_{trans}** and **7** (Pathway C, room temperature)

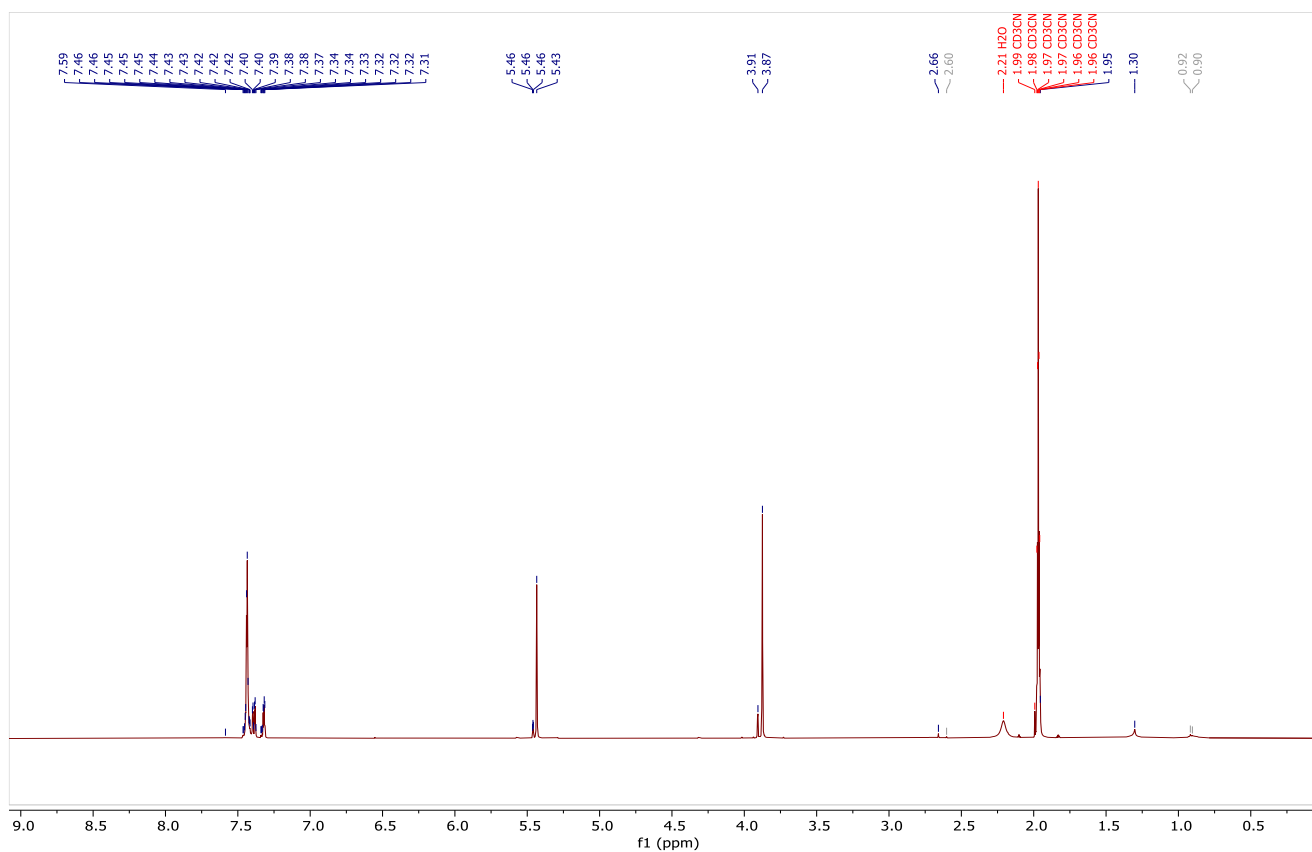


Figure 7S: ^1H NMR Spectrum of mixture of **8_{trans}** and **7** (Pathway C, 75°C)

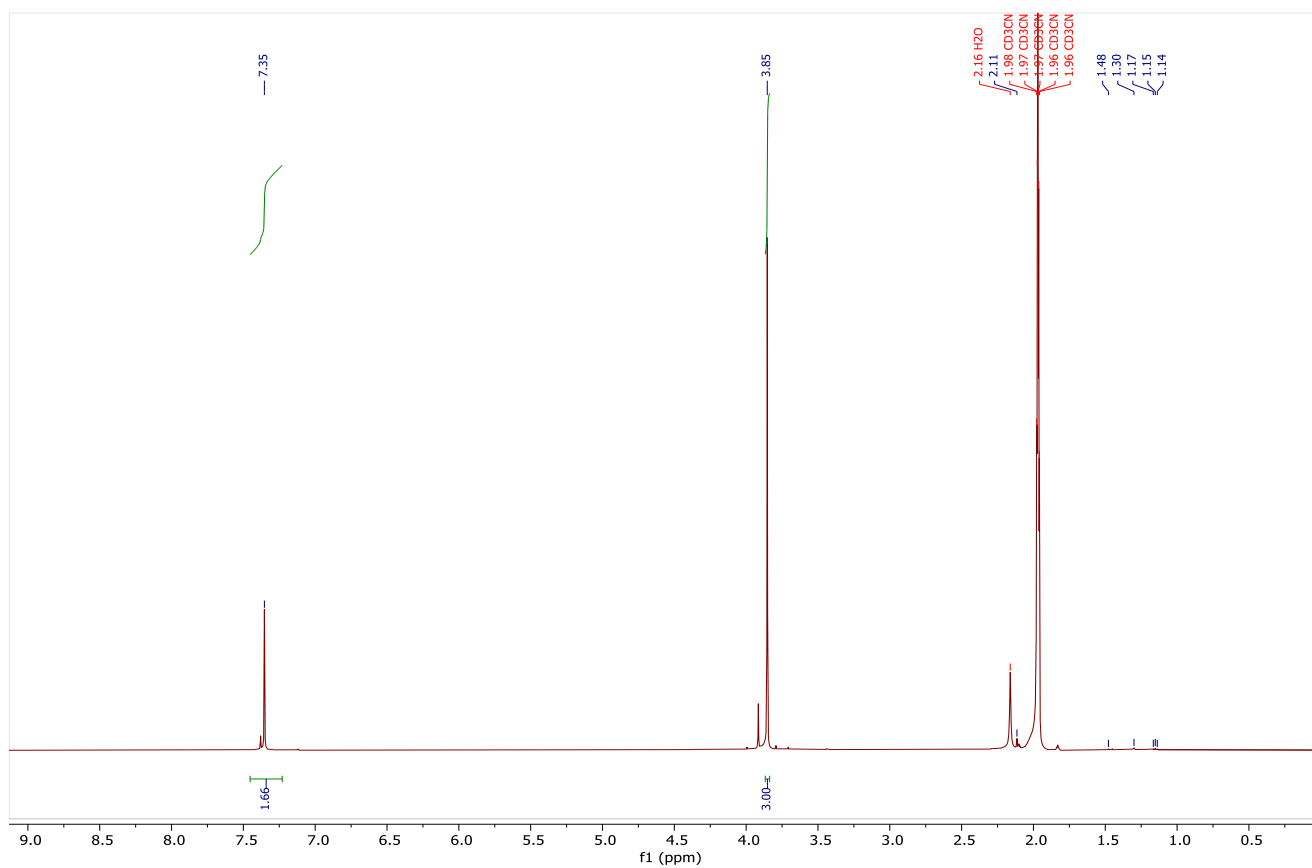


Figure 8S: ^1H NMR Spectrum of complex **6** (Pathway D)

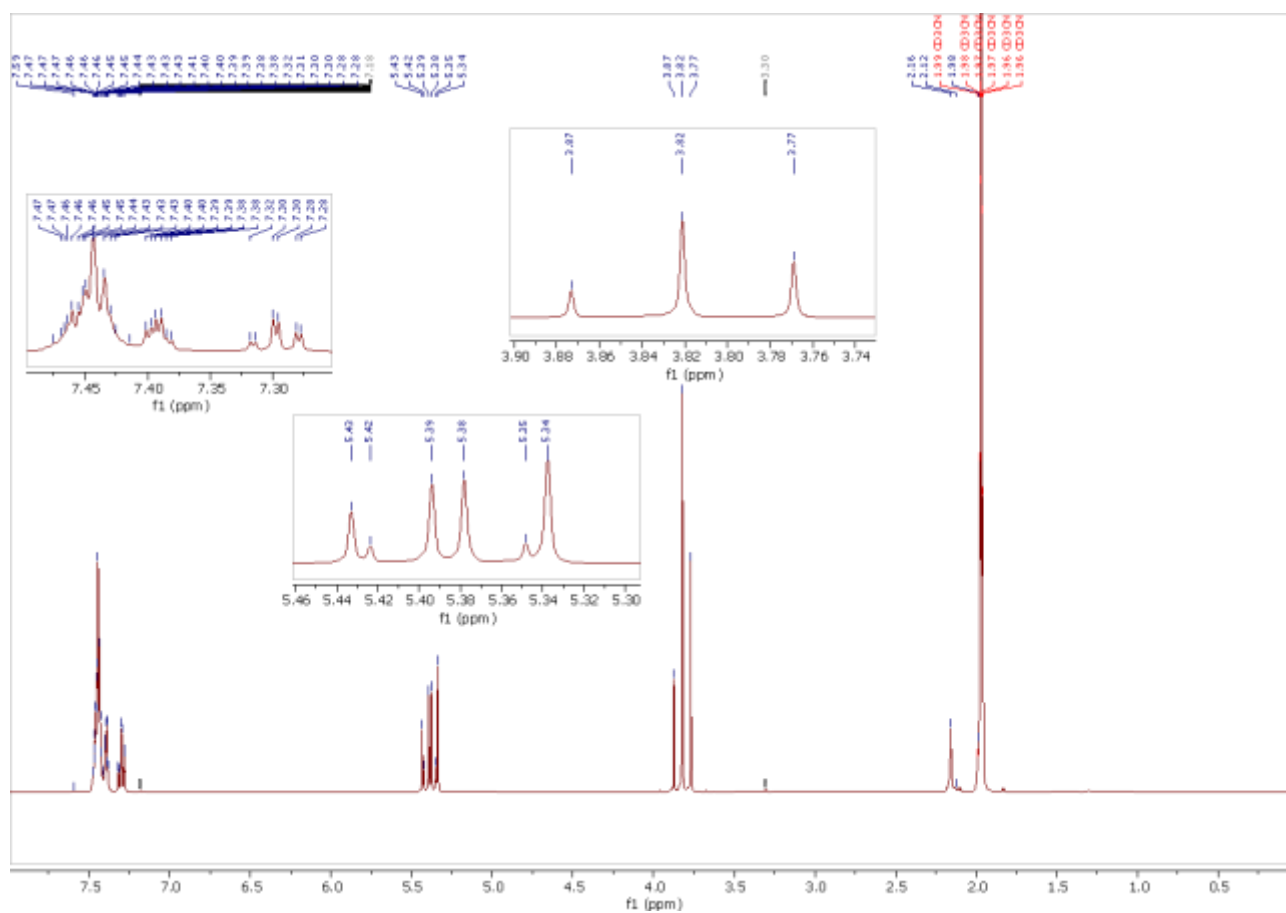


Figure 9S: ^1H NMR spectrum of **9_{cis}**.

IR Spectra of complexes 3 – 9

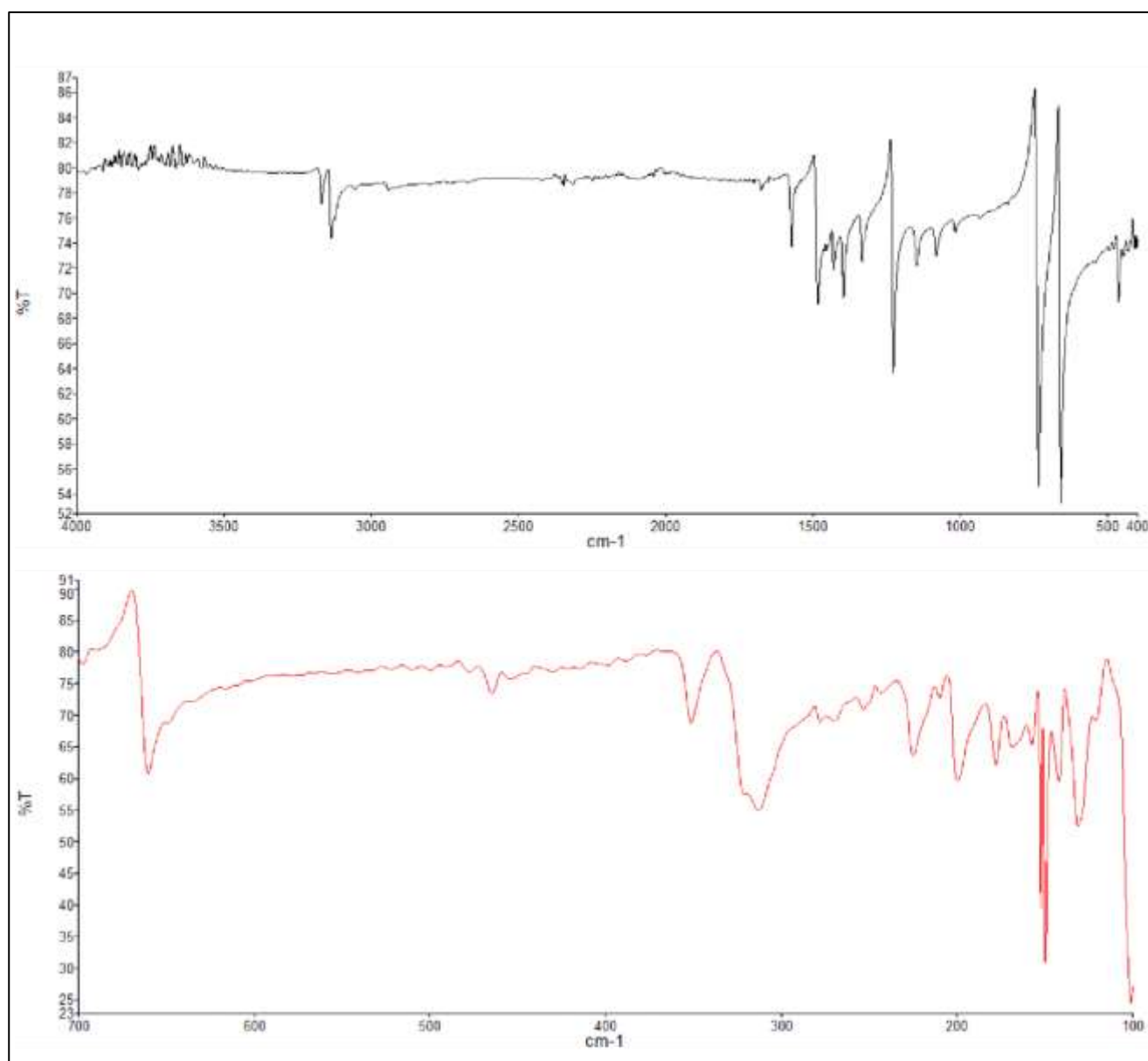


Figure 10S: Spectra of **1** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

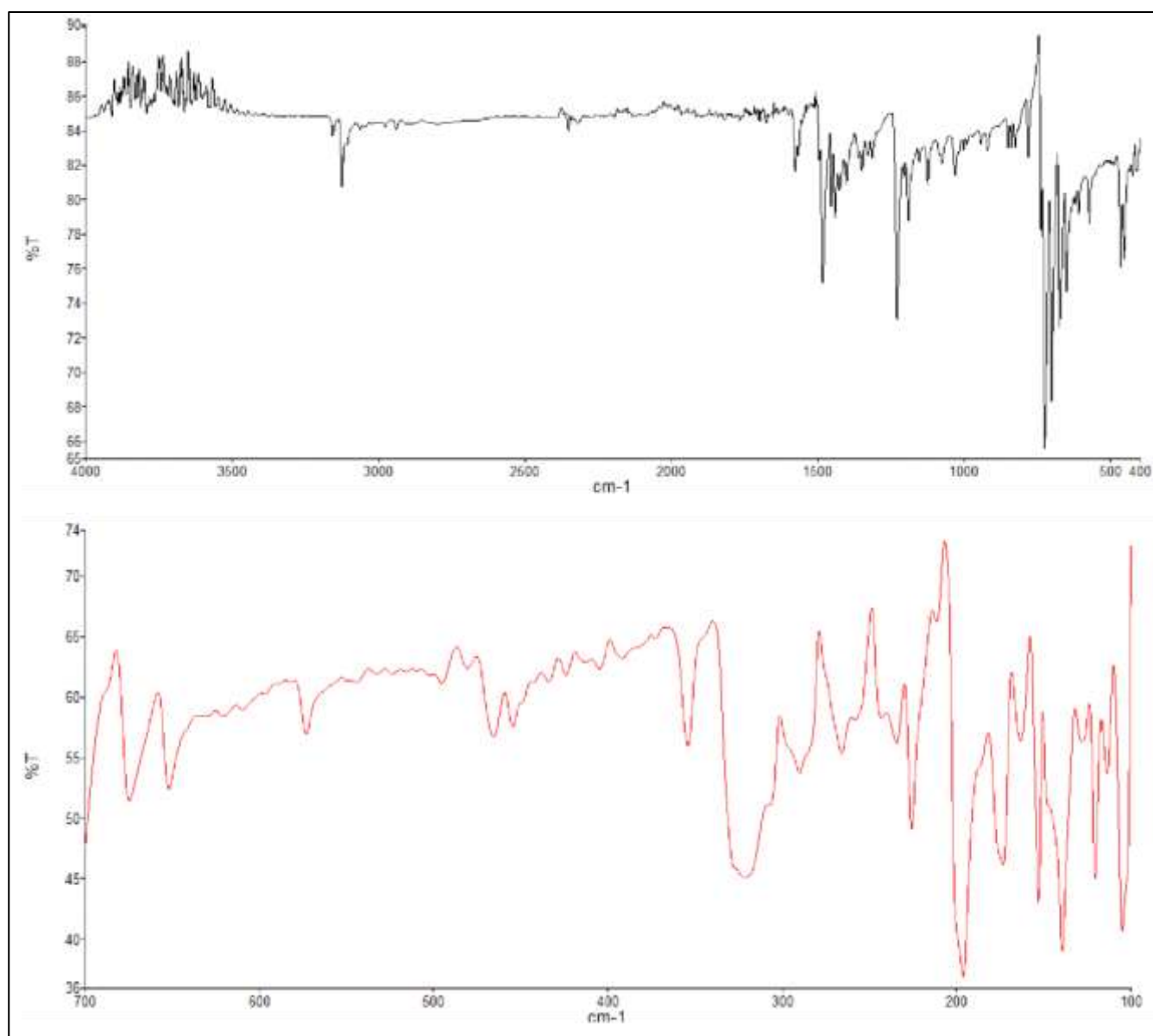


Figure 11S: Spectra of **2** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

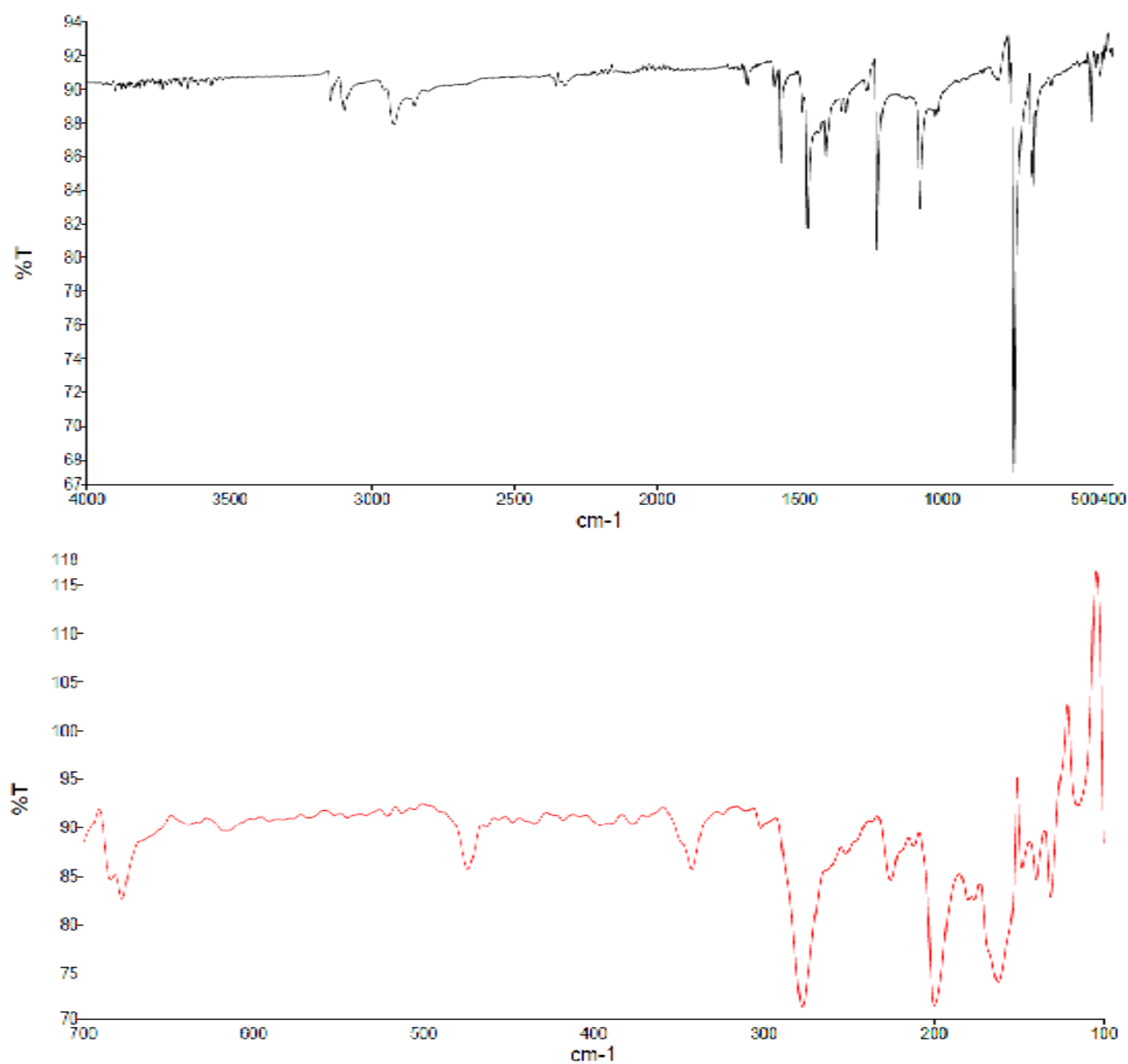


Figure 12S: Spectra of **3** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

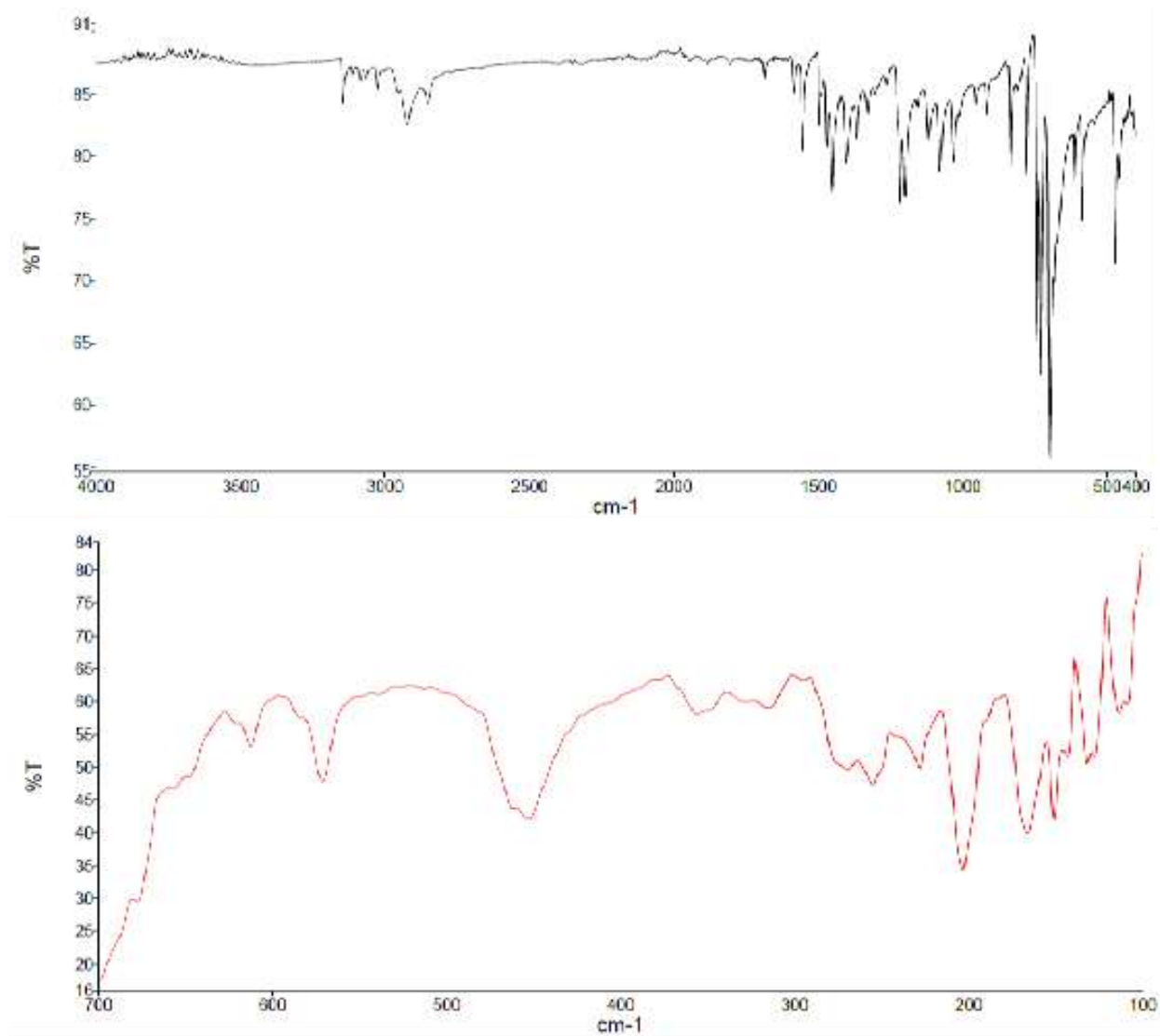


Figure 13S: Spectra of **4** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

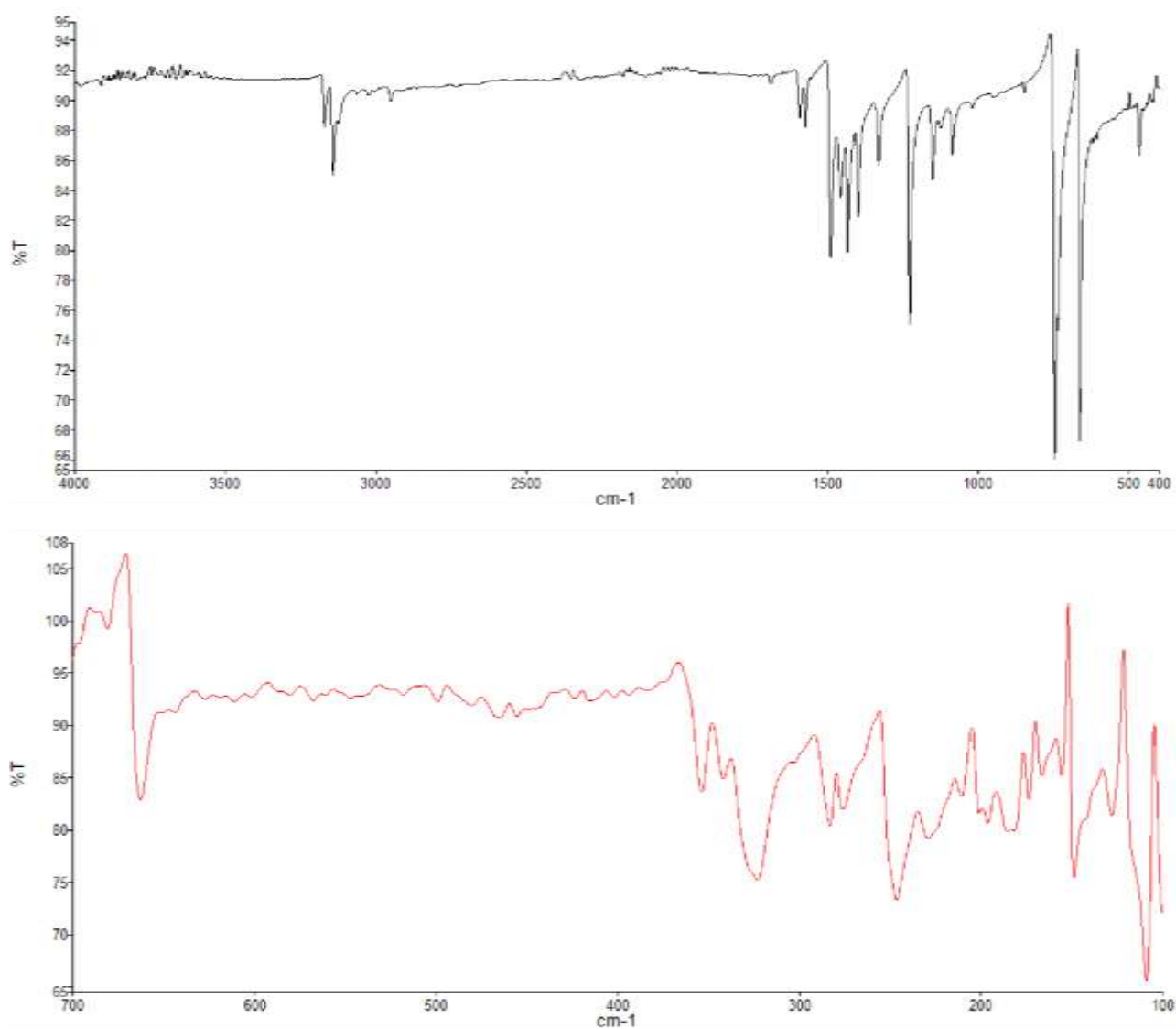


Figure 14S: IR Spectra of **5_{cis}** and **5_{trans}** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

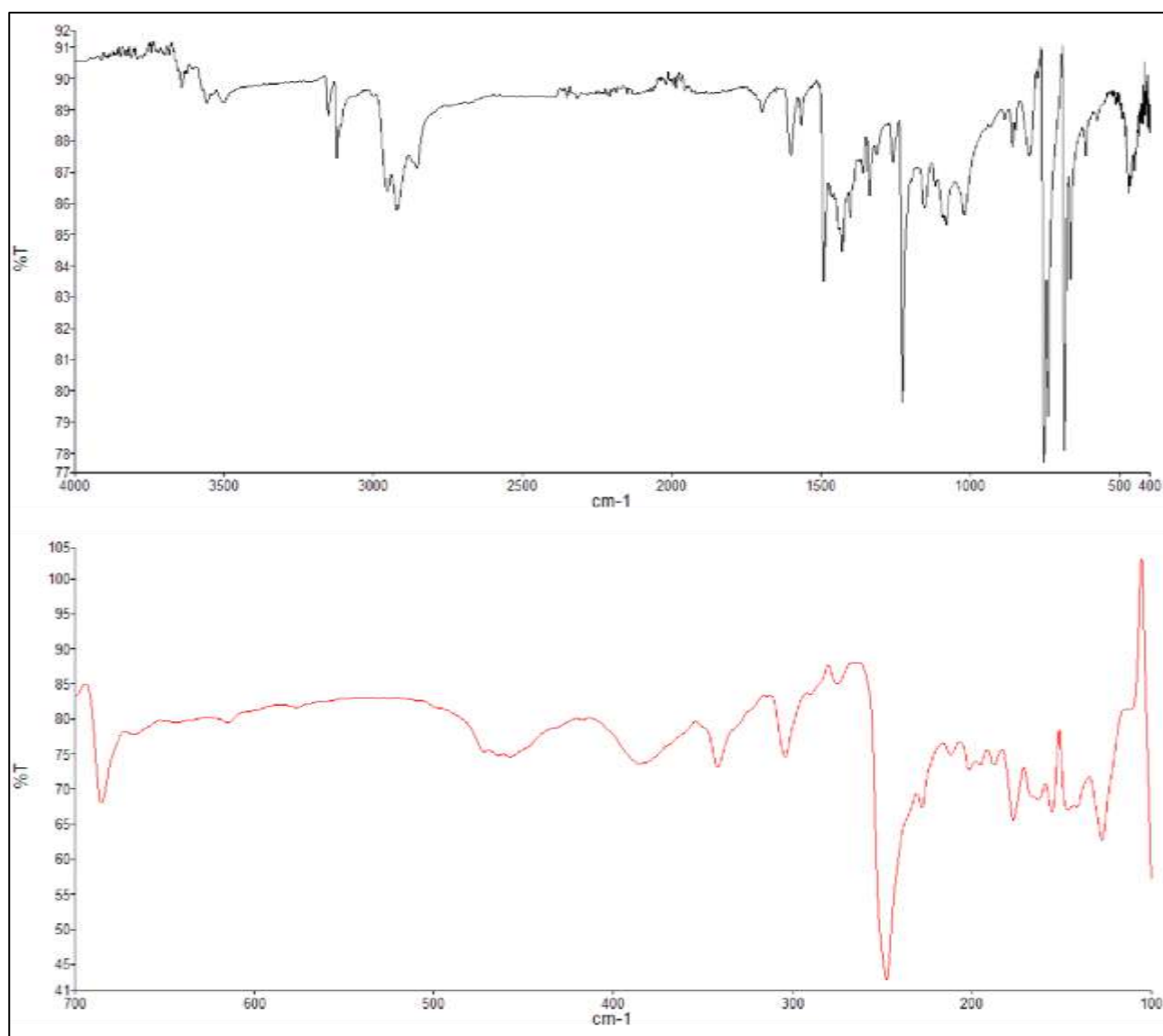


Figure 15S: Spectra of **6** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

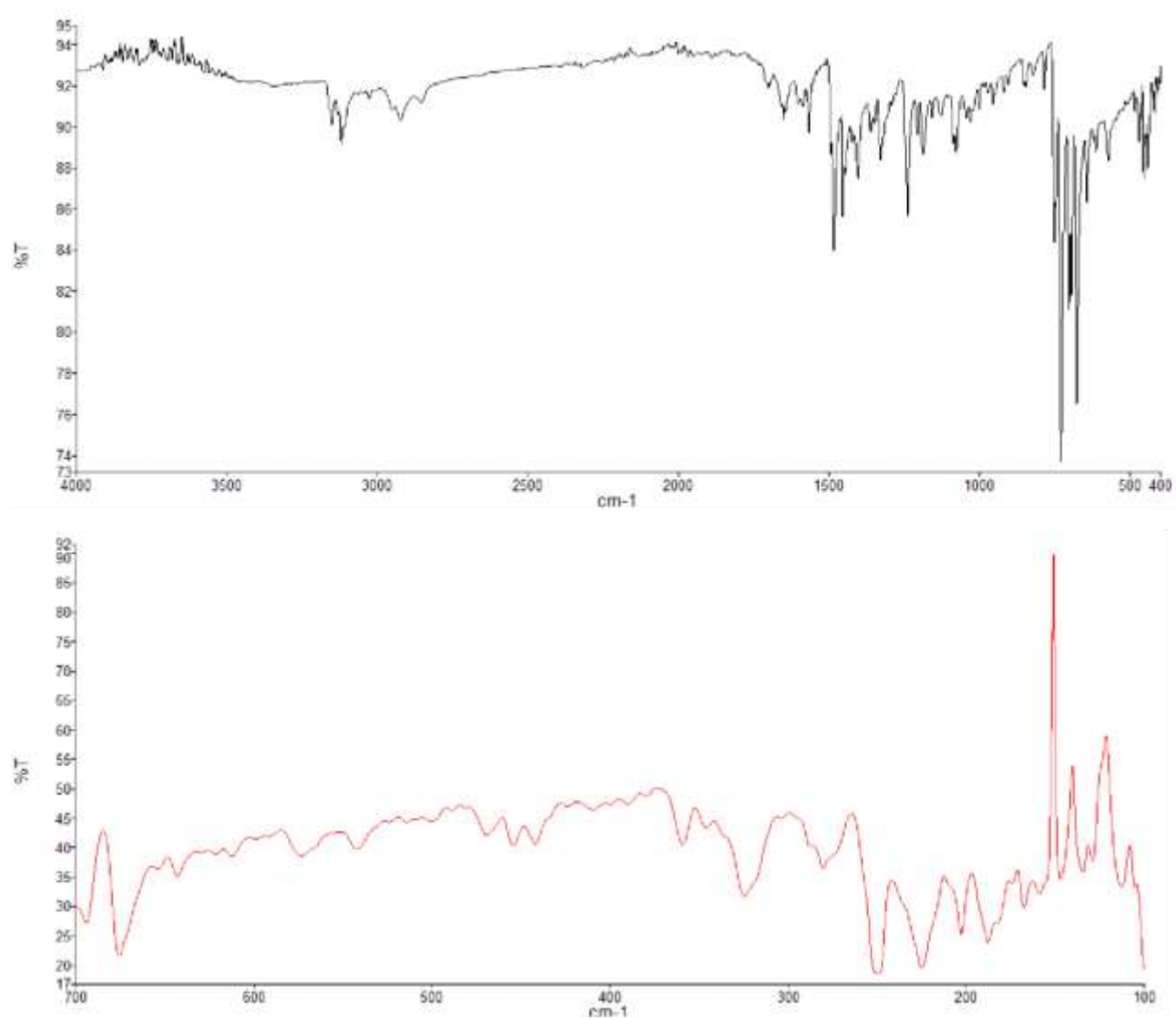


Figure 16S: Spectra of 7 recorded in the Medium (top) and Far (bottom) IR range of frequencies.

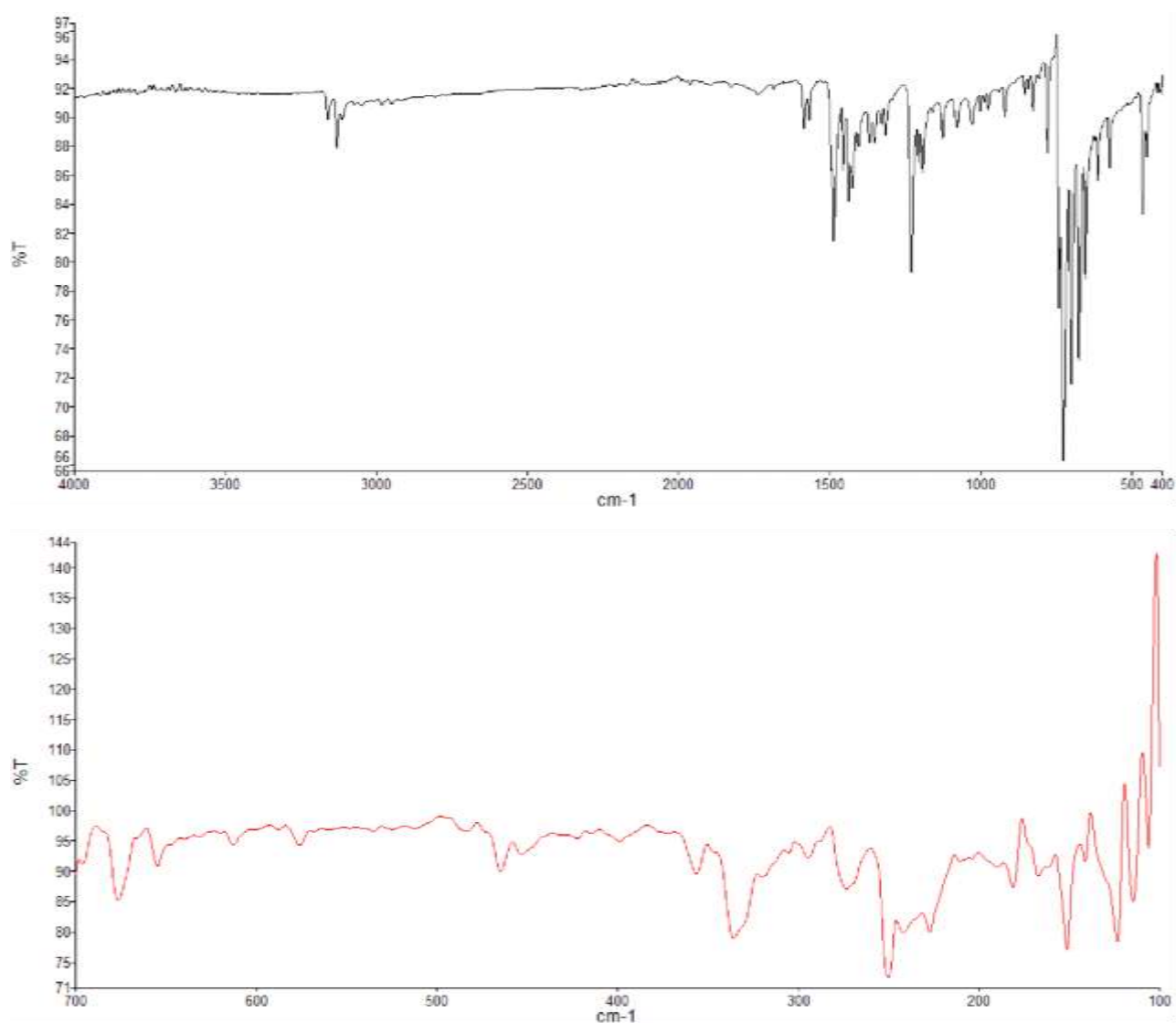


Figure 17S: Spectra of **8_{trans}** and **7** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

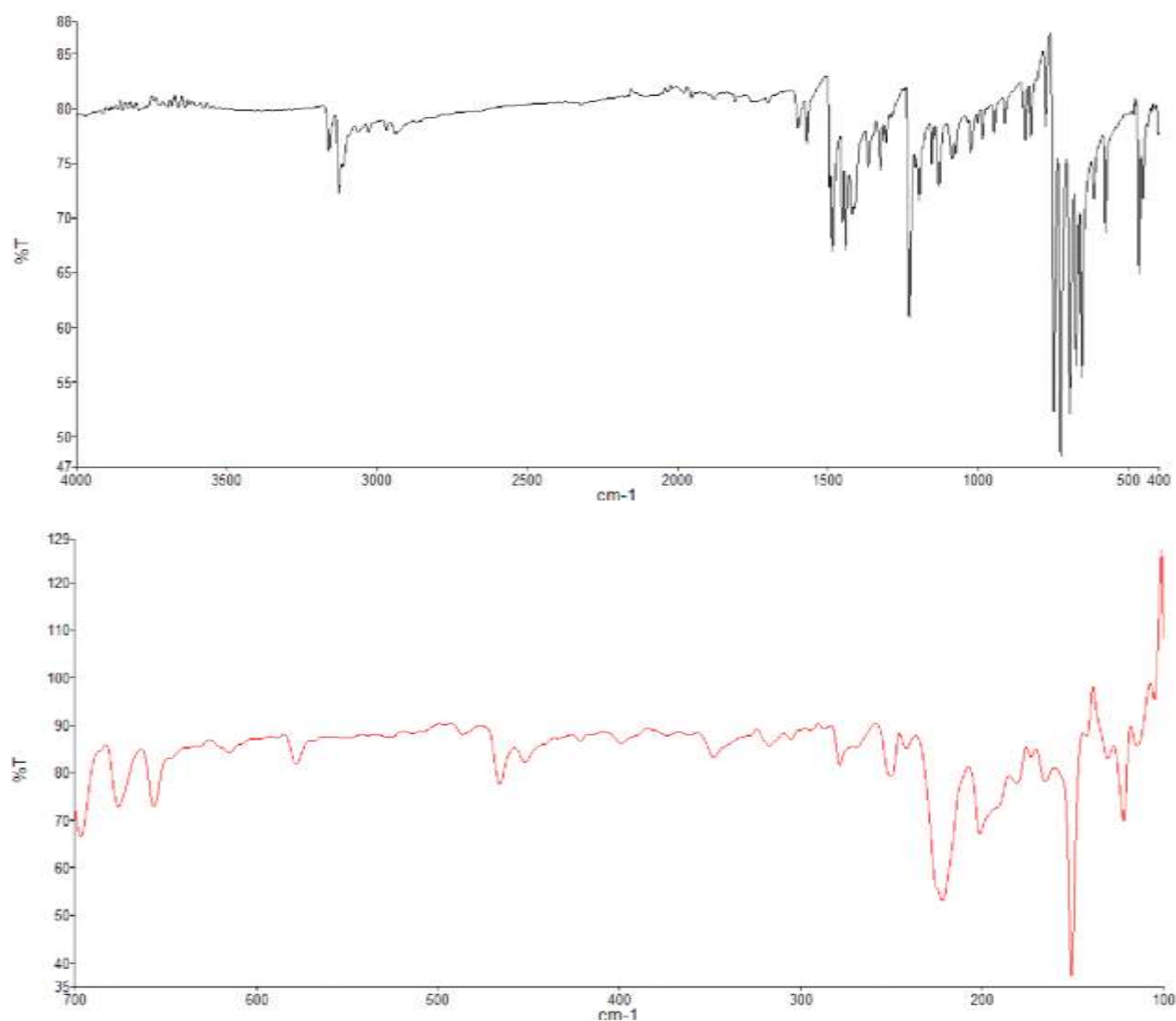


Figure 18S: Spectra of **9_{cis}** recorded in the Medium (top) and Far (bottom) IR range of frequencies.

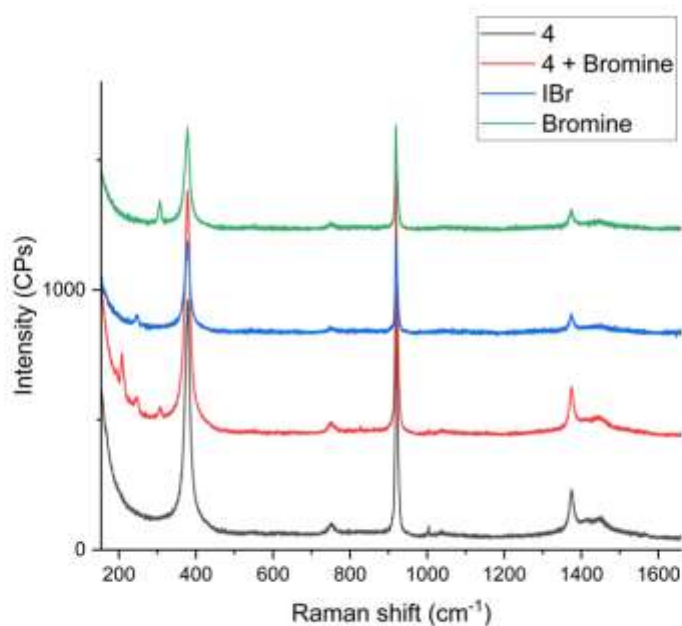


Figure 19S. Raman spectra recorded for 80 mM acetonitrile solutions of IBr, for the 80 mM acetonitrile solution of $\text{NHC}^{\text{Bz}}\text{AuI}$ (**4**), for 80 mM solution of Bromine and for the reaction of **4** with Bromine with the formation of IBr, revealed with a peak at 248 cm^{-1} .

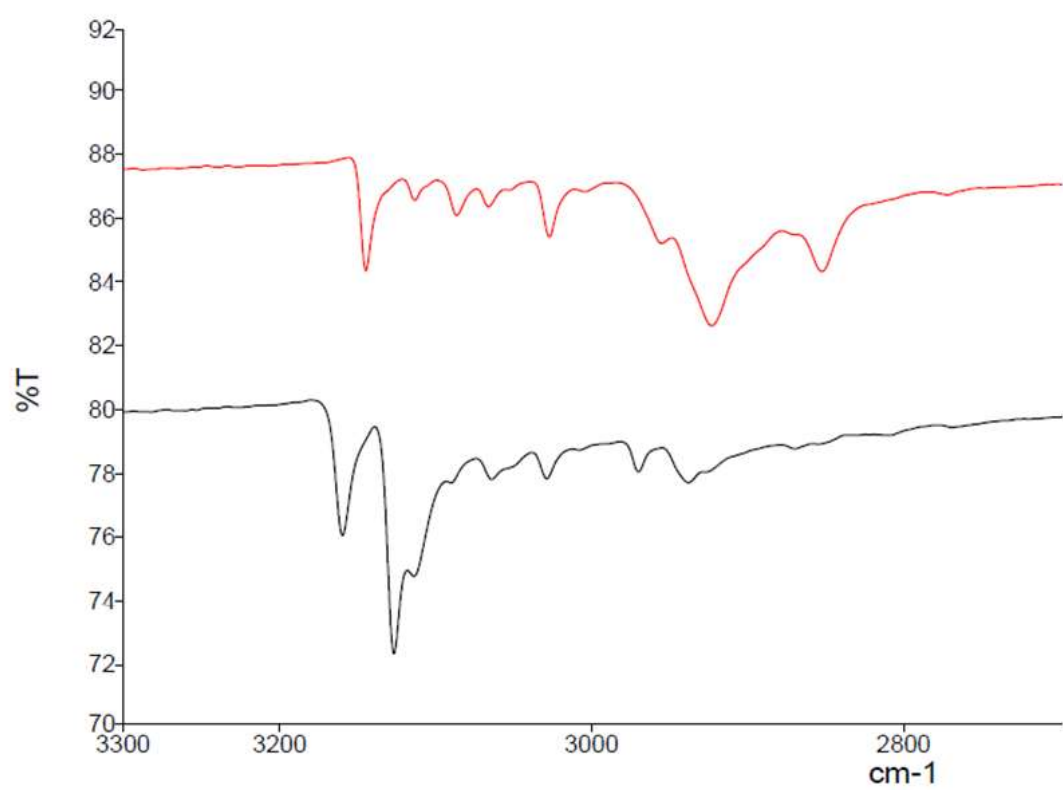


Figure 20S: IR spectra of **4** (red spectrum) and **9_{cis}** (black spectrum) in the 3300-2700 cm⁻¹ range of frequencies.

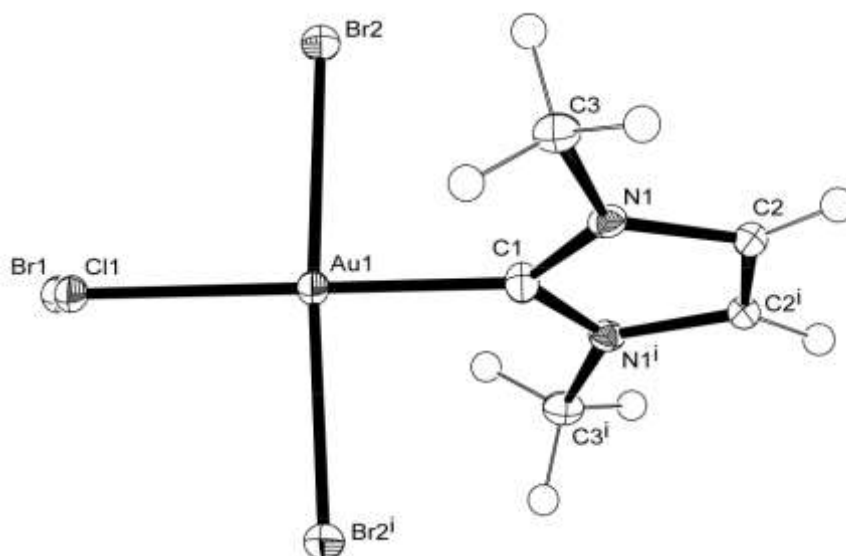


Figure 21S. Molecular structures (featuring **6** and **5_{trans}**) (ORTEP diagram) of the crystals recovered from (Scheme 1, path B 75°C) showing the atom labelling scheme. Thermal ellipsoids are shown at a 50% probability level. Symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 1/2$.

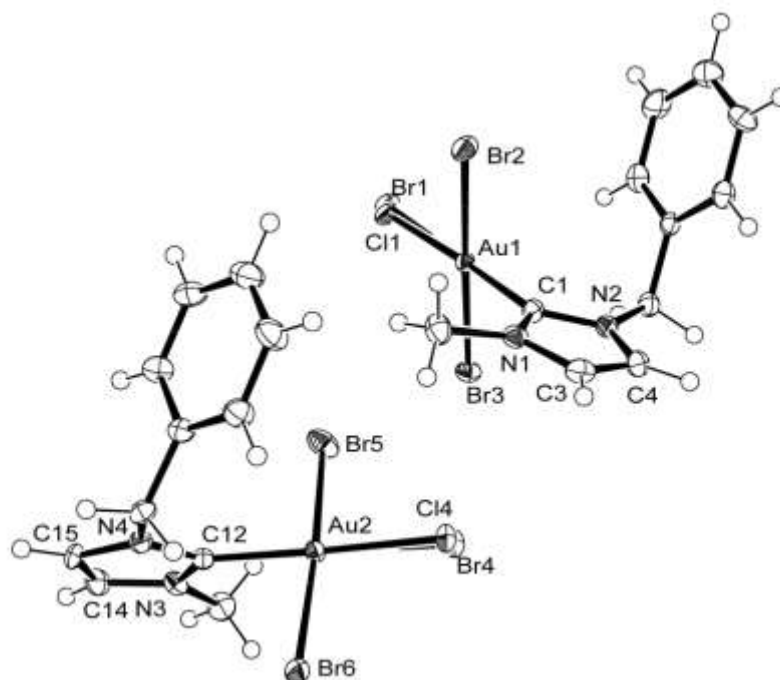


Figure 22S. Molecular structures (featuring **7** and **8_{trans}**) (ORTEP diagram) of the crystals recovered from (Scheme 1, path C 75°C) showing the atom labelling scheme. Thermal ellipsoids are shown at a 50% probability level.

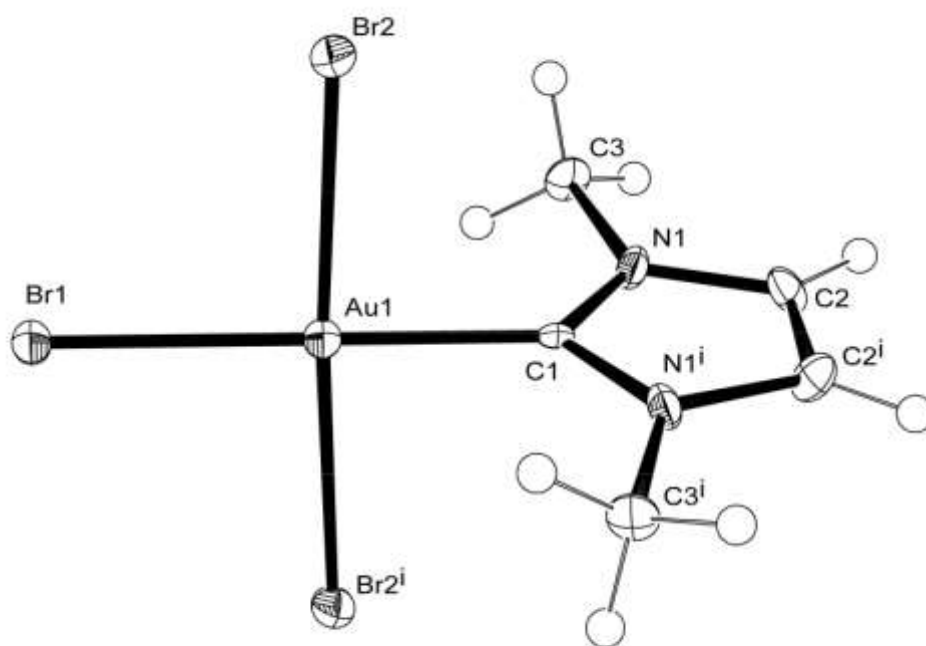


Figure 23S. Molecular structures (featuring **6**) (ORTEP diagram) of the crystals recovered from (Scheme 1, path D) showing the atom labelling scheme. Thermal ellipsoids are shown at a 50% probability level. Symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 1/2$.

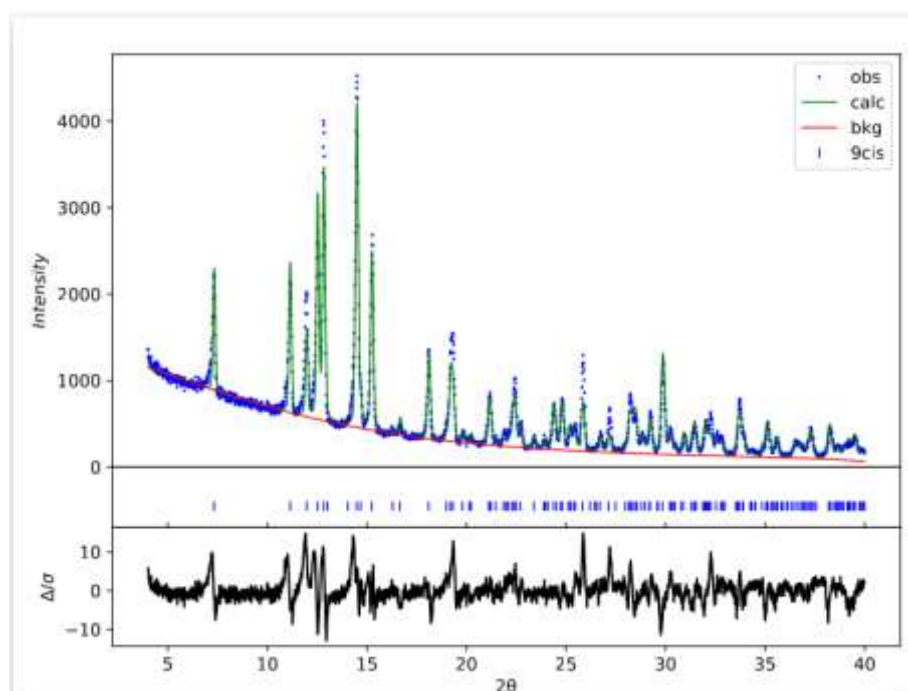


Figure 24S. Rietveld full-profile fit of the powder X-ray diffraction pattern using **9_{cis}** confirming the phase purity at room temperature of the sample. Calculated unit-cell parameters are: 8.021(3) Å, 24.104(3) Å, 9.124(6) Å, 113.008(8)°, Volume = 1623.6(2) Å³.

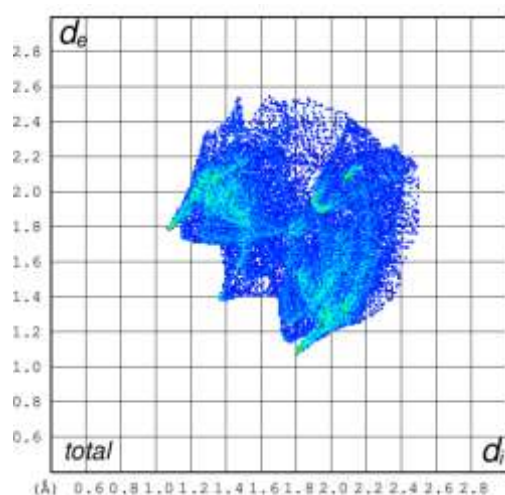
Table 1S. Averaged values of Au-X (X=Cl, Br, I) are calculated from the N-carbene gold structures found in the CSD database.

Type	Hits	Distance (Å)
Au-Cl _{trans}	66	2.317(12)
Au-Cl _{cis}	58	2.28(2)
Au-Br _{trans}	49	2.434(16)
Au-Br _{cis}	51	2.415(7)
Au-I _{trans}	4	2.630(15)
Au-I _{cis}	10	2.621(8)

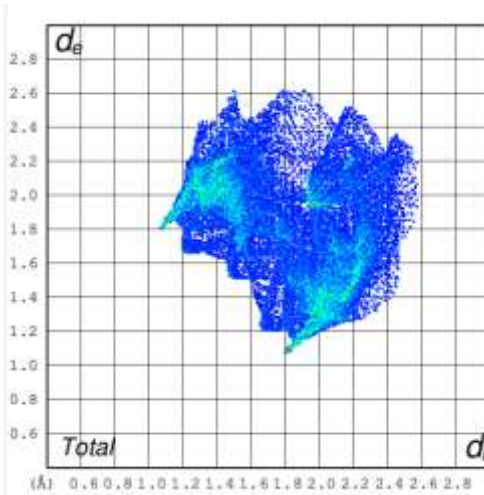
Table 2S. Comparison of percentage distribution of different interactions as obtained from fingerprint plots in the reported structures.

		H---H	H---C	H---Cl	H---Br	H---I	Others	H---R (R=H,C)	H---X (X=Cl,Br,I)
Path A 5 _{cis} /5 _{trans}	Me	16.9	8.1	11.7	51.0	-	12.3	25.9	62.7
Path B 6/5 _{trans}	Me	16.8	8.1	5.3	57.8		12.0	24.9	63.1
Path C ^a 7/8 _{trans}	Bz	26.8	17.2	6.8	40.6	-	8.6	44.0	47.4
Path C ^b 7/8 _{trans}	Bz	31.4	13.6	8.2	39.2	-	7.6	45.0	47.4
Path D6	Me	16.7	7.9		63.2		12.2	24.6	63.2
Path E 9 _{cis}	Bz	28.1	15.0	-	30.6	17.0	9.3	43.1	47.6

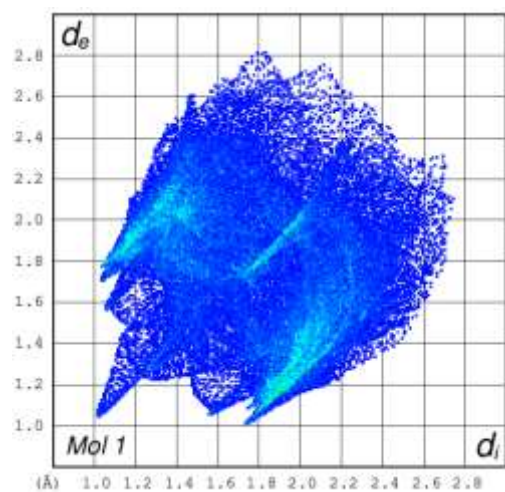
(a) values for the first unit in the unit cell; (b) values for the first unit in the unit cell. Note that only the structure obtained at room temperature is reported.



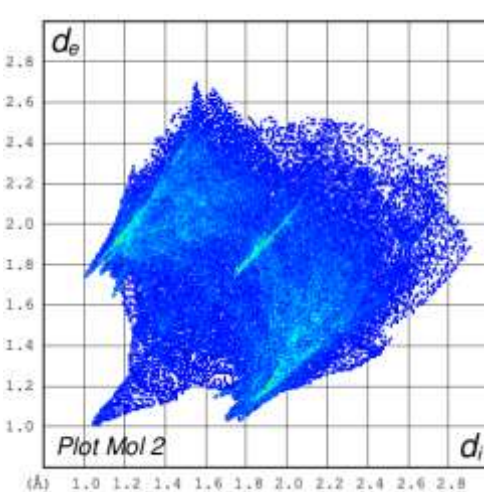
Path A 5cis/5trans



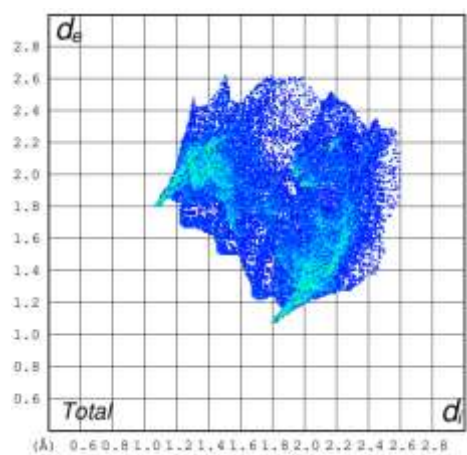
Path B 6/5trans



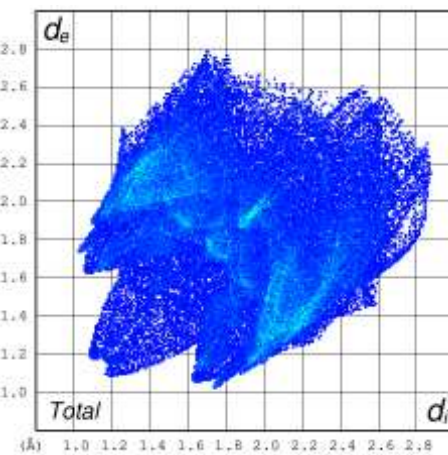
Path C 7/8trans Unit a



Path C 7/8trans Unit a



Path D6



Path E 9cis

Figure 25S. Fingerprint plots for the different structure reported. For Path C 7/8trans, only the structure obtained at room temperature is reported.

Table 3S. Crystal data and structure refinement.

	Path B: 6 + 5_{trans}	Path C (25°): 7 + 8_{trans}	Path C (75°): 7 + 8_{trans}	Path D: 6	Path E: 9_{cis}
Empirical formula	C5 H8 Au Br2.97 Cl0.03 N2	C22 H24 Au2 Br5.39 Cl0.61 N4	C22 H24 Au2 Br5.46 Cl0.54 N4	C5 H8 Au Br3 N2	C11 H12 Au Br2 I N2
Formula weight	531.50	1190.72	1193.84	532.83	655.91
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	Pbcn	P2 ₁ /n	P2 ₁ /n	Pbcn	P2 ₁ /c
Unit cell dimensions (Å, °)	a = 7.7434(5) b = 14.6668(6) c = 9.0138(5)	a = 17.0127(4) b = 8.6992(2) c = 21.0602(5)Å β = 109.9960(10)	a = 16.9944(5) b = 8.6999(3) c = 21.0549(7) β = 109.9450(10)	a = 7.7438(3) b = 14.6973(4) c = 9.0592(3)	a = 7.9034(3) b = 23.8409(7) c = 8.9795(3) β = 112.6840(10)
Volume (Å ³)	1023.71(10)	2928.95(12)	2926.24(17)	1031.05(6)	1561.07(9)
Z	4	4	4	4	4
Density (calculated) (Mg/m ³)	3.449	2.700	2.710	3.433	2.791
Absorption coefficient (mm ⁻¹)	25.915	17.434	17.540	25.838	16.502
F(000)	942	2164	2169	944	1176
Crystal size (mm ³)	0.060 x 0.040 x 0.040	0.080 x 0.080 x 0.060	0.400 x 0.250 x 0.200	0.124 x 0.082 x 0.072	0.160 x 0.120 x 0.080
Theta range for data collection (°)	2.778 to 33.362	2.058 to 33.205	1.892 to 26.372.	2.771 to 28.27	2.603 to 35.059
Index ranges	-11<=h<=11, - 22<=k<=22, - 13<=l<=13	-26<=h<=23, - 13<=k<=13, - 32<=l<=32	-21<=h<=21, - 10<=k<=10, - 26<=l<=26	-10<=h<=10, - 19<=k<=19, - 12<=l<=12	-12<=h<=12, - 38<=k<=38, - 14<=l<=14
Reflections collected	28908	125658	65188	20173	74940
Independent reflections	1986 [R(int) = 0.1000]	11214 [R(int) = 0.0974]	5977 [R(int) = 0.1006]	1279 [R(int) = 0.0625]	6895 [R(int) = 0.0834]
Completeness to theta = 25.242°	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Numerical	Semi-empirical from equivalents
Max. and min. transmission	0.7466 and 0.5323	0.7465 and 0.6028	0.7465 and 0.6478	0.3750 and 0.1523	0.7469 and 0.4109
Refinement method	Full-matrix least-	Full-matrix least-	Full-matrix least-	Full-matrix least-	Full-matrix least-

	squares on F ²	squares on F ²	squares on F ²	squares on F ²	squares on F ²
Data / restraints / parameters	1986 / 2 / 55	11214 / 4 / 317	5977 / 4 / 317	1279 / 0 / 53	6895 / 4 / 174
Goodness-of-fit on F ²	1.025	1.043	1.047	1.139	1.018
Final <i>R</i> indices [I>2σ(I)]	<i>R</i> ₁ = 0.0326, <i>wR</i> ₂ = 0.0560	<i>R</i> ₁ = 0.0371, <i>wR</i> ₂ = 0.0549	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0421	<i>R</i> ₁ = 0.0263, <i>wR</i> ₂ = 0.0663	<i>R</i> ₁ = 0.0347, <i>wR</i> ₂ = 0.0632
<i>R</i> indices (all data)	<i>R</i> ₂ = 0.0685, <i>wR</i> ₂ = 0.0667	<i>R</i> ₁ = 0.0700, <i>wR</i> ₂ = 0.0637	<i>R</i> ₁ = 0.0474, <i>wR</i> ₂ = 0.0473	<i>R</i> ₂ = 0.0372, <i>wR</i> ₂ = 0.0709	<i>R</i> ₁ = 0.0623, <i>wR</i> ₂ = 0.0707
Largest diff. peak and hole (e.Å ⁻³)	2.442 and -2.089	1.563 and -2.467	0.931 and -0.961	2.002 and -2.538	1.442 and -2.181

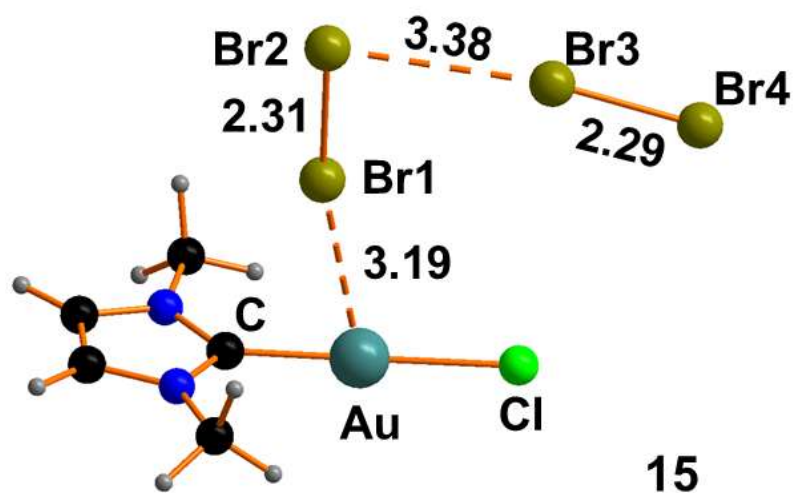


Figure 26S. Optimized structure of adduct **15** between linear complex **1** and two Br₂ molecules.

Computational Details

Cartesian coordinates and free energies of all the optimized structures at M062X-DFT level of theory.

Compound **3**

Cartesian Coordinates

Au	-0.0537	-0.0000	-0.0000
I	-2.7623	-0.0000	0.0000
C	1.9616	-0.0000	0.0000
N	2.7765	1.0688	0.0000
C	4.0953	-0.6759	-0.0001
C	4.0953	0.6760	0.0000
H	4.9043	-1.3838	-0.0001
H	4.9042	1.3839	0.0001
N	2.7765	-1.0687	-0.0000
C	2.3173	-2.4509	0.0001
H	1.7190	-2.6385	0.8886
H	1.7183	-2.6384	-0.8880
H	3.1857	-3.1029	-0.0003
C	2.3171	2.4509	0.0001
H	1.7189	2.6386	-0.8885
H	1.7181	2.6383	0.8881
H	3.1855	3.1029	0.0005

Free Energy : -451.828772 hartrees

Compound **Br₂**

Cartesian Coordinates

Br	0.000000	0.000000	0.105748
Br	0.000000	0.000000	2.394252

Free Energy : -5148.400116 hartrees

Adduct **10**

Cartesian Coordinates

Au	-1.6360	1.1314	-0.0099
I	0.4607	2.8371	-0.0388
C	-3.1860	-0.1671	0.0155
N	-3.8049	-0.6705	1.0984
C	-4.7631	-1.6194	-0.6236
C	-4.7783	-1.5683	0.7268
H	-5.3636	-2.1792	-1.3178

H	-5.3944	-2.0748	1.4479
N	-3.7805	-0.7517	-1.0400
C	-3.4085	-0.5527	-2.4332
H	-2.8504	0.3753	-2.5156
H	-2.7918	-1.3829	-2.7735
H	-4.3100	-0.4933	-3.0378
C	-3.4576	-0.3671	2.4793
H	-2.7517	-1.1055	2.8558
H	-3.0091	0.6214	2.5195
H	-4.3616	-0.3834	3.0821
Br	-0.3655	-1.7969	-0.0062
Br	1.0815	-3.5965	-0.0161
Br	3.3519	-1.0585	0.0137
Br	4.6841	0.8084	0.0423

Free Energy : -10748.618180 hartrees

Intermediate **11⁺**

Cartesian Coordinates

Au	0.2008	-0.7099	0.0114
I	-2.4175	-0.4001	-0.0325
C	0.3045	1.2327	0.0016
N	0.4250	1.9857	-1.0834
C	0.4643	3.3094	0.6712
C	0.5256	3.2998	-0.6799
H	0.5060	4.1181	1.3780
H	0.6334	4.0980	-1.3918
N	0.3277	2.0011	1.0822
C	0.2233	1.5412	2.4651
H	-0.7297	1.0352	2.6039
H	1.0464	0.8649	2.6835
H	0.2783	2.4110	3.1109
C	0.4532	1.5073	-2.4642
H	1.3011	0.8386	-2.5949
H	-0.4772	0.9879	-2.6844
H	0.5571	2.3705	-3.1127
Br	2.6302	-0.9340	0.0250

Free Energy : -3025.804240 hartrees

Compound **Br₃⁻**

Cartesian Coordinates

Br	0.000000	0.000000	2.562414
Br	0.000000	0.000000	0.000000
Br	0.000000	0.000000	-2.562414

Free Energy : -7722.799949 hartrees

Compound 12

Cartesian Coordinates

Au	-0.2778	-0.2402	0.0096
I	-0.3745	2.4332	-0.0567
C	1.7066	-0.0411	0.0038
N	2.4899	-0.0837	-1.0728
C	3.8063	0.1716	0.6613
C	3.8057	0.0460	-0.6843
H	4.6121	0.2930	1.3622
H	4.6110	0.0348	-1.3961
N	2.4911	0.1141	1.0699
C	2.0252	0.2098	2.4488
H	1.3689	1.0721	2.5497
H	1.4901	-0.6994	2.7154
H	2.8913	0.3284	3.0917
C	2.0163	-0.2507	-2.4418
H	1.4800	-1.1938	-2.5255
H	1.3581	0.5762	-2.7010
H	2.8775	-0.2553	-3.1021
Br	0.1066	-2.6916	0.0588
Br	-2.7901	-0.4844	0.0083

Free Energy : -5600.245430 hartrees

Adduct 13

Cartesian Coordinates

Au	1.2622	0.4105	-0.0098
I	-0.4824	-1.6240	-0.0835
C	2.6872	-0.9890	0.0357
N	3.2161	-1.5421	1.1267
C	4.2412	-2.4269	-0.5981
C	4.1887	-2.4436	0.7524
H	4.8558	-2.9732	-1.2902
H	4.7490	-3.0068	1.4764
N	3.3006	-1.5148	-1.0240
C	3.0091	-1.1773	-2.4127
H	1.9875	-1.4676	-2.6508
H	3.1359	-0.1068	-2.5583
H	3.7030	-1.7185	-3.0477
C	2.8233	-1.2341	2.4976
H	2.9948	-0.1779	2.6944
H	1.7705	-1.4726	2.6348

H	3.4268	-1.8367	3.1685
Br	3.0874	2.0799	0.0686
Br	-0.5396	2.1694	-0.0709
Br	-3.6978	-0.4409	0.0048
Br	-5.9382	0.1181	0.0662

Free Energy : -10748.637553 hartrees

Intermediate **14⁺**

Cartesian Coordinates

Au	0.0506	-0.7355	-0.0079
C	-0.0746	1.2039	0.0043
N	-0.3888	1.9387	1.0623
C	-0.0819	3.2920	-0.6424
C	-0.3991	3.2602	0.6719
H	0.0192	4.1135	-1.3282
H	-0.6313	4.0483	1.3649
N	0.1204	1.9898	-1.0459
C	0.5007	1.5619	-2.3919
H	1.4465	1.0273	-2.3412
H	-0.2763	0.9220	-2.8026
H	0.6090	2.4509	-3.0037
C	-0.6775	1.4406	2.4065
H	-1.5300	0.7667	2.3619
H	0.1962	0.9228	2.7947
H	-0.9111	2.2940	3.0338
Br	-2.3686	-0.8568	-0.1944
Br	2.4643	-0.5858	0.1984

Free Energy : -5588.623052 hartrees

Compound **IBr₂⁻**

Cartesian Coordinates

I	0.000000	0.000000	2.300573
Br	0.000000	0.000000	-0.418285
Br	0.000000	0.000000	-3.065440

Free Energy : -5159.988100 hartrees

Compound **6**

Cartesian Coordinates

Au	-0.3019	-0.0000	-0.0000
C	1.6928	-0.0011	-0.0000

C	3.7956	-0.1504	0.6597
H	4.6039	-0.3072	1.3508
H	4.6047	0.3052	-1.3490
N	2.4771	-0.2398	1.0500
N	2.4778	0.2375	-1.0496
C	3.7960	0.1486	-0.6584
C	2.0086	0.5500	-2.3957
H	1.4217	-0.2819	-2.7789
H	1.4008	1.4518	-2.3638
H	2.8751	0.7109	-3.0288
C	2.0069	-0.5512	2.3960
H	1.4273	0.2846	2.7815
H	1.3917	-1.4479	2.3627
H	2.8727	-0.7210	3.0277
Br	-2.8273	0.0015	0.0002
Br	-0.1739	2.4578	0.1797
Br	-0.1769	-2.4579	-0.1802

Free Energy : -8163.064084 hartrees

Compound IBr

Cartesian Coordinates

Br	0.000000	0.000000	-0.052422
I	0.000000	0.000000	2.452422

Free Energy : -2585.587659 hartrees

Compound 5_{cis}

Cartesian Coordinates

Au	0.3084	-0.2137	0.0291
C	-1.6833	-0.1635	0.0211
C	-3.7837	-0.3159	-0.6405
H	-4.5912	-0.4931	-1.3275
H	-4.5938	0.2423	1.3423
N	-2.4653	-0.4403	-1.0205
N	-2.4673	0.1317	1.0557
C	-3.7849	0.0438	0.6629
C	-1.9963	0.4879	2.3902
H	-1.4477	-0.3485	2.8177
H	-1.3512	1.3613	2.3221
H	-2.8601	0.7153	3.0064
C	-1.9919	-0.8164	-2.3490
H	-1.4150	0.0018	-2.7747
H	-1.3737	-1.7082	-2.2710
H	-2.8561	-1.0207	-2.9726

Br	0.2443	2.2180	-0.2787
Cl	0.1418	-2.5267	0.3205
Br	2.8325	-0.2801	0.0318

Free Energy : -6049.060077 hartrees

Compound **5_{trans}**

Cartesian Coordinates

Au	0.5421	-0.0000	-0.0000
C	-1.4432	0.0000	-0.0000
C	-3.5459	-0.1476	0.6596
H	-4.3543	-0.3021	1.3509
H	-4.3544	0.3023	-1.3506
N	-2.2277	-0.2356	1.0506
N	-2.2278	0.2357	-1.0506
C	-3.5460	0.1477	-0.6594
C	-1.7588	0.5438	-2.3978
H	-1.1447	1.4414	-2.3678
H	-1.1785	-0.2925	-2.7815
H	-2.6253	0.7103	-3.0293
C	-1.7586	-0.5438	2.3979
H	-1.1451	-1.4417	2.3678
H	-1.1778	0.2922	2.7813
H	-2.6252	-0.7098	3.0294
Cl	2.9311	0.0000	0.0000
Br	0.4207	-2.4568	-0.1779
Br	0.4208	2.4568	0.1779

Free Energy : -6049.061908 hartrees

Adduct **15**

Cartesian Coordinates

Au	-0.8634	0.5620	0.1584
C	-1.8422	-1.1177	-0.2157
C	-3.4538	-2.5832	-0.5671
H	-4.4660	-2.9317	-0.6627
H	-2.0463	-4.2583	-0.9028
N	-3.1631	-1.2679	-0.2762
N	-1.2812	-2.3004	-0.4604
C	-2.2729	-3.2309	-0.6833
C	0.1549	-2.5593	-0.4909
H	0.6124	-1.9819	-1.2923
H	0.5926	-2.2784	0.4655
H	0.3046	-3.6194	-0.6679
C	-4.1382	-0.2028	-0.0665

H	-4.0468	0.1788	0.9482
H	-3.9580	0.5952	-0.7838
H	-5.1301	-0.6164	-0.2164
Cl	0.3965	2.5616	0.5975
Br	-0.7539	-0.1678	2.5098
Br	-1.1004	1.0816	-2.2403
Br	2.7201	0.5071	0.0478
Br	4.2780	-1.1321	-0.3820

Free Energy : -11197.453003 hartrees

Adduct **16**

Cartesian Coordinates

Au	1.0001	-0.3613	-0.2327
C	1.8850	1.4189	-0.0477
C	3.3581	3.0586	-0.1882
H	4.2926	3.5261	-0.4401
H	2.0253	4.5263	0.7962
N	3.1090	1.7332	-0.4699
N	1.3477	2.5105	0.4947
C	2.2520	3.5468	0.4158
C	-0.0070	2.6143	1.0267
H	-0.7204	2.6263	0.2051
H	-0.2078	1.7673	1.6783
H	-0.0787	3.5358	1.5955
C	4.0392	0.8144	-1.1189
H	4.2806	0.0030	-0.4359
H	3.5862	0.4176	-2.0247
H	4.9391	1.3660	-1.3711
Br	2.3243	-1.0854	1.6916
Cl	-0.1904	0.5242	-2.0511
Br	-0.1159	-2.6122	-0.4744
Br	-2.8951	0.4512	-0.4526
Br	-4.8634	0.4875	0.7368

Free Energy : -11197.450884 hartrees