Electronic Supplementary Information

Heteroleptic nickel(II)-diNHC complexes and unusual 'reverse' carbene-transfer to silver(I)

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Table S1. Selected Crystal Data for **2**·0.5CH_2Cl_2, **4**·0.5CH_2Cl_2·0.5C_7H_8, **5**·CH_2Cl_2 and **6**

	2·0.5CH_2Cl_2	**4**·0.5CH_2Cl_2·0.5C_7H_8	**5**·CH_2Cl_2	**6**
Formula	$C_{19.5}H_{21}ClN_{10}Ni$	$C_{23}H_{25}ClI_2N_4Ni$	$C_{23.5}H_{22}Cl_2F_{5.5}N_4NiO_{3.5}$	C_{23} H_{26} Ag_2 N_4 O_4
Formula weight	489.62	705.43	650.56	638.22
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.16 × 0.10 × 0.06	0.36 × 0.10 × 0.06	0.30 × 0.10 v 0.04	0.30 × 0.10 × 0.04
Temperature (K)	293(2)	100(2)	293(2)	100(2)
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbcn*
a (Å)	8.1139(9)	8.6988(13)	8.649(6)	16.9338(16)
b (Å)	11.2775(13)	12.4353(19)	10.986(8)	8.5206(8)
c (Å)	12.7151(14)	13.505(2)	15.733(12)	16.0788(15)
α (°)	93.185(3)	105.180(2)	81.770(16)	90
β (°)	104.866(3)	102.756(2)	85.099(18)	90
γ (°)	107.323(2)	108.548(2)	70.204(14)	90
V ($Å^3$)	1062.5(2)	1260.7(3)	1390.9(18)	2319.9(4)
Z	2	2	2	4
Density (calcd. g cm^{-3})	1.530	1.858	1.553	1.827
μ (mm^{-1})	1.069	3.342	0.961	1.726
θ range (°)	1.67 to 27.50	1.85 to 27.50	1.31 to 25.00	2.41 to 27.50
Unique data	8800	16785	27261	15192
Max., min. transmission	0.5629 and 0.4795	0.8247 and 0.3792	0.9626 and 0.7613	0.9342 and 0.6255
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0617, wR_2 = 0.1434	R_1 = 0.0592, wR_2 = 0.1577	R_1 = 0.0672, wR_2 = 0.1511	R_1 = 0.0272, wR_2 = 0.0624
R indices (all data)	R_1 = 0.0940, wR_2 = 0.1715	R_1 = 0.0838, wR_2 = 0.1728	R1 = 0.1031, wR_2 = 0.1717	R_1 = 0.0360, wR_2 = 0.0657
Goodness-of-fit on F^2	1.047	1.051	1.070	1.036
Peak hole (e $Å^{-3}$)	0.941 and -0.922	2.897 and -1.571	0.703 and -0.589	0.673 and -0.319

Figure S1. IR spectrum (KBr) of complex **2**

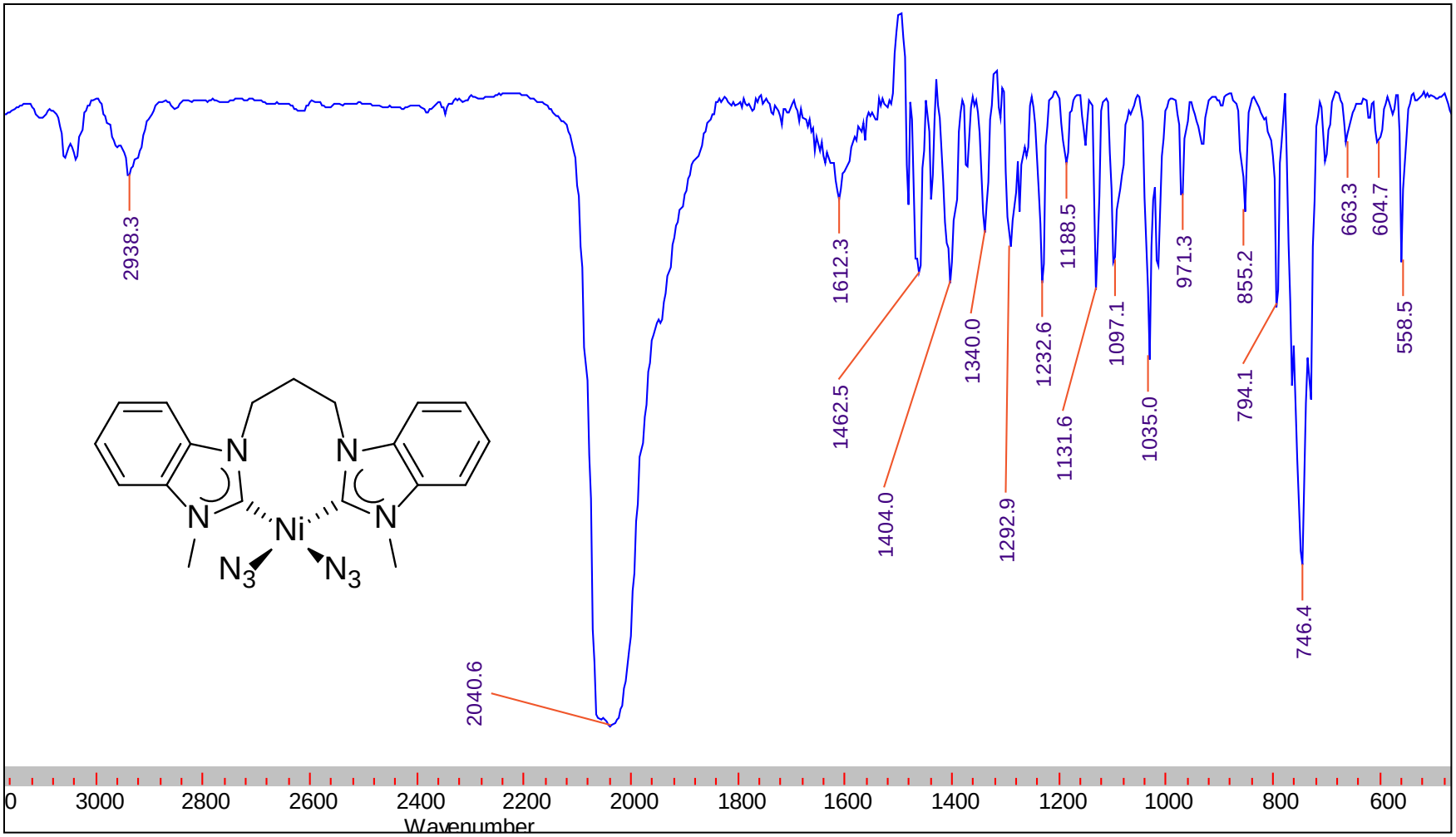


Figure S2. IR spectrum (KBr) of complex **3**

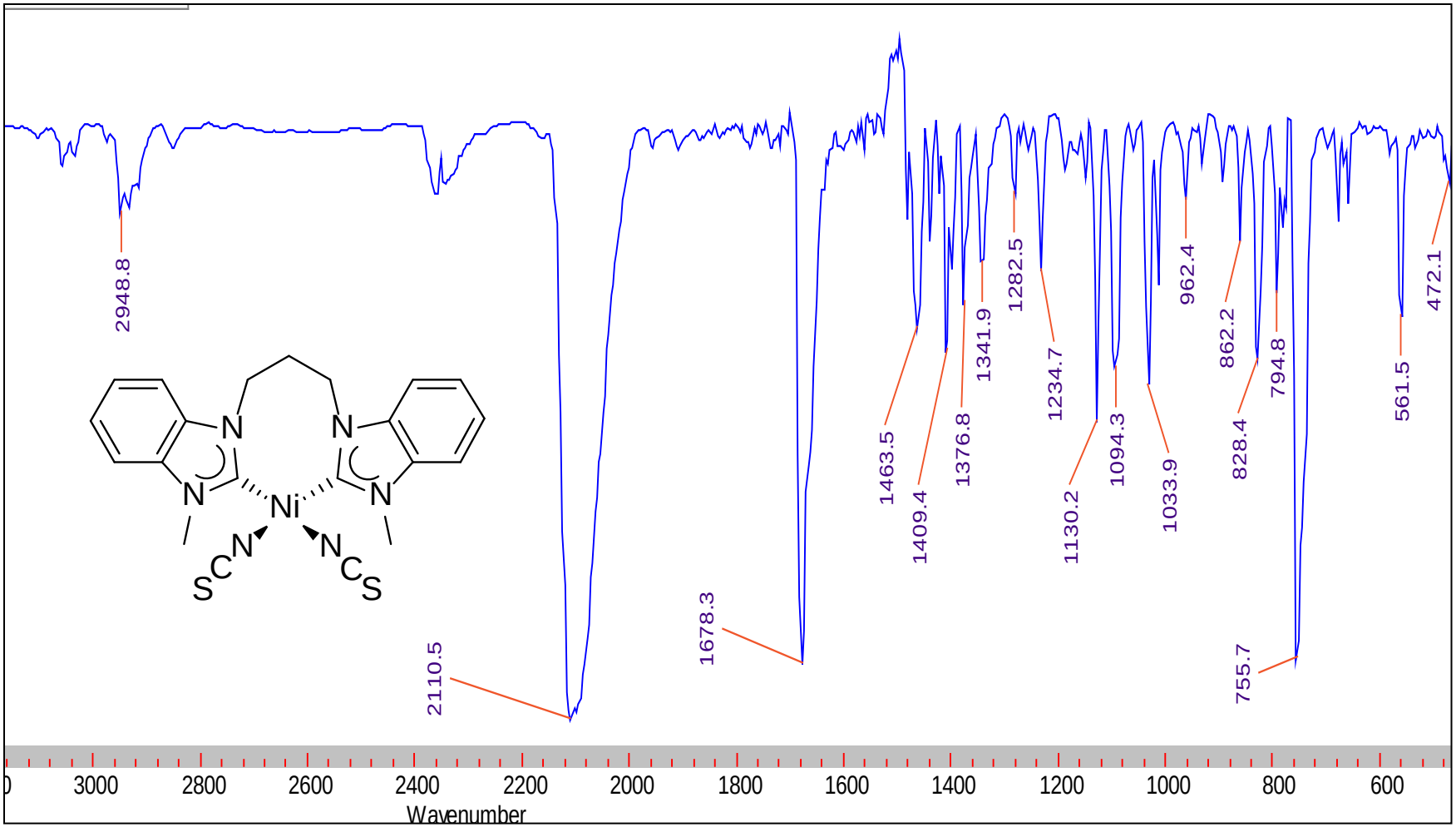


Figure S3. IR spectrum (KBr) of complex **5**

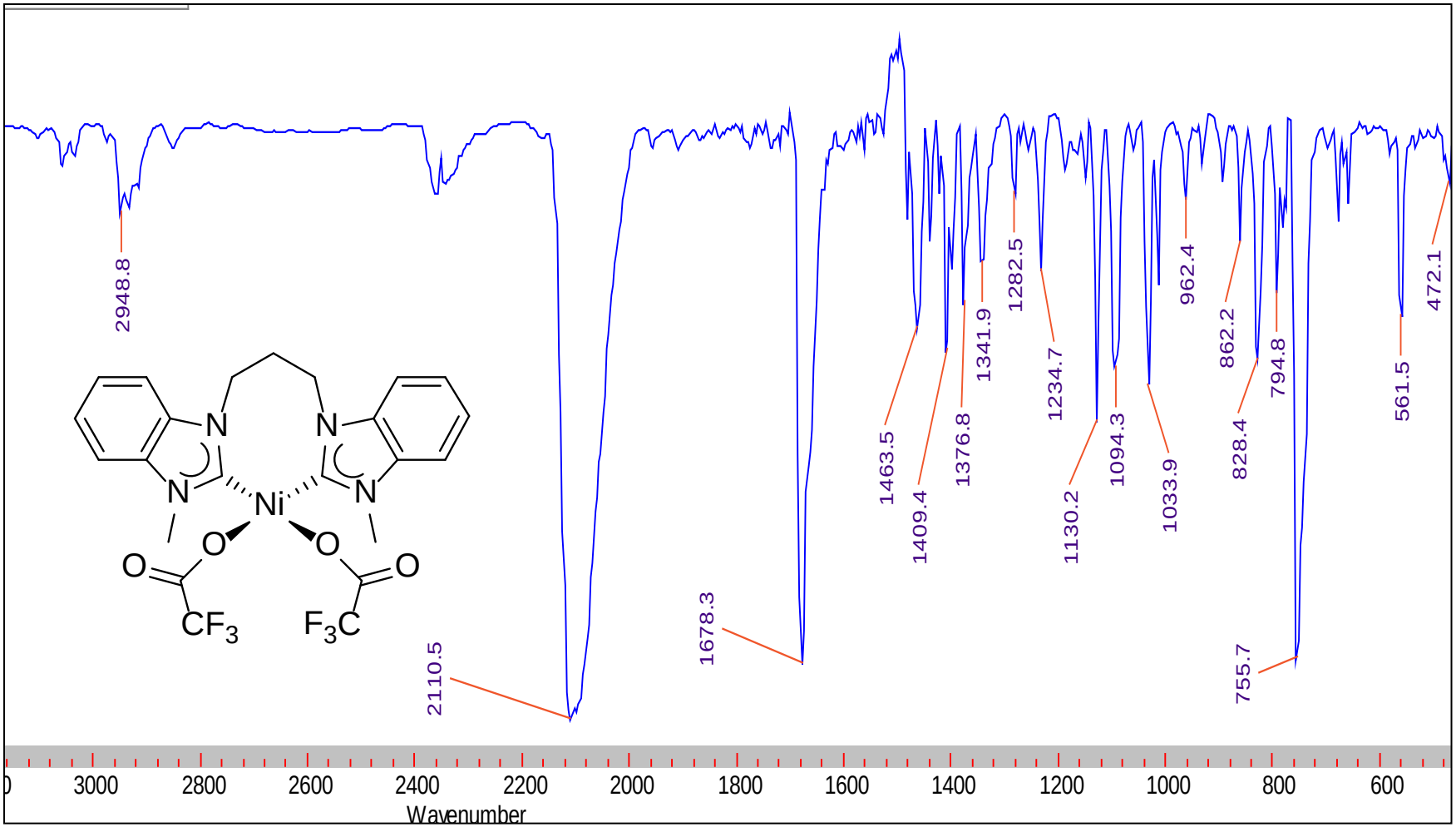
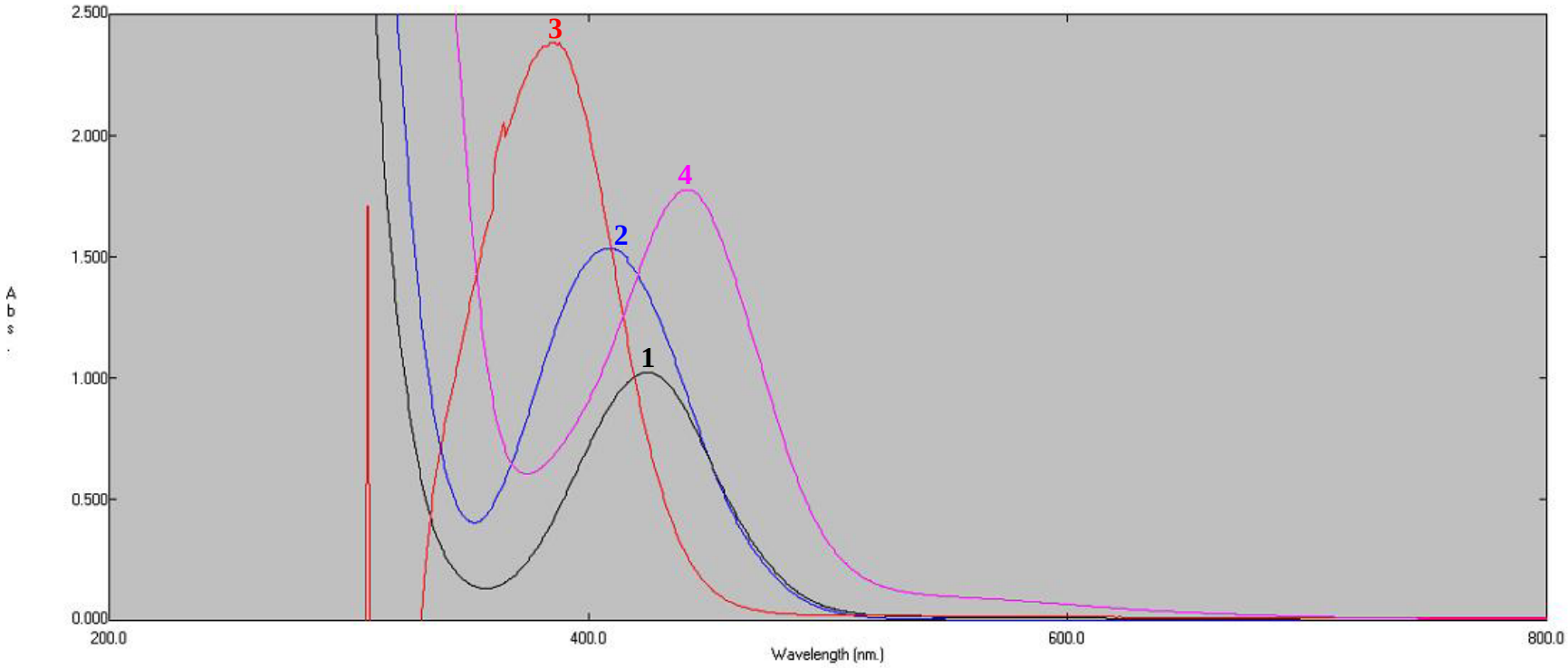


Figure S4. Combined UV-Vis spectrum of complexes **1**–**4**



Measuring Mode: Abs. Scan Speed: Fast Slit Width: 2.0 Sampling Interval: 0.5

Complex	**X**	**Wavelength [nm]**	**Abs**	**ε ($M^{-1}cm^{-1}$)**
1	Br	424.5	1.02	1.02×10^5
2	N_3	409.0	1.54	1.54×10^5
3	SCN	384.0	2.38	2.38×10^5
4	I	440.0	1.78	1.78×10^5

Figure S5. Calculated (a) and experimental ESI-MS (+) isotopic splitting pattern (b) for the $[Ag_2(^{Me}CC_{prop})_2]^{2+}$ dicationic fragment.

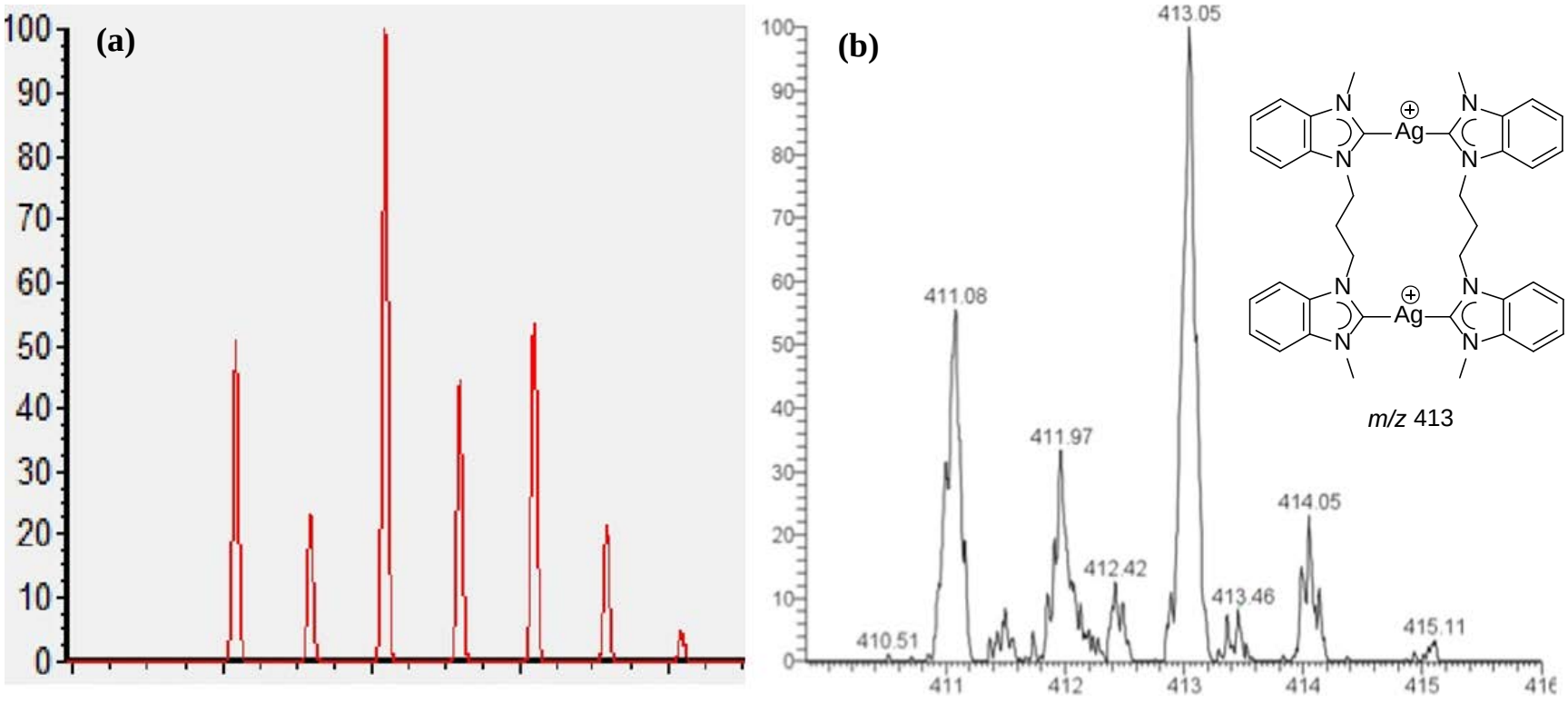
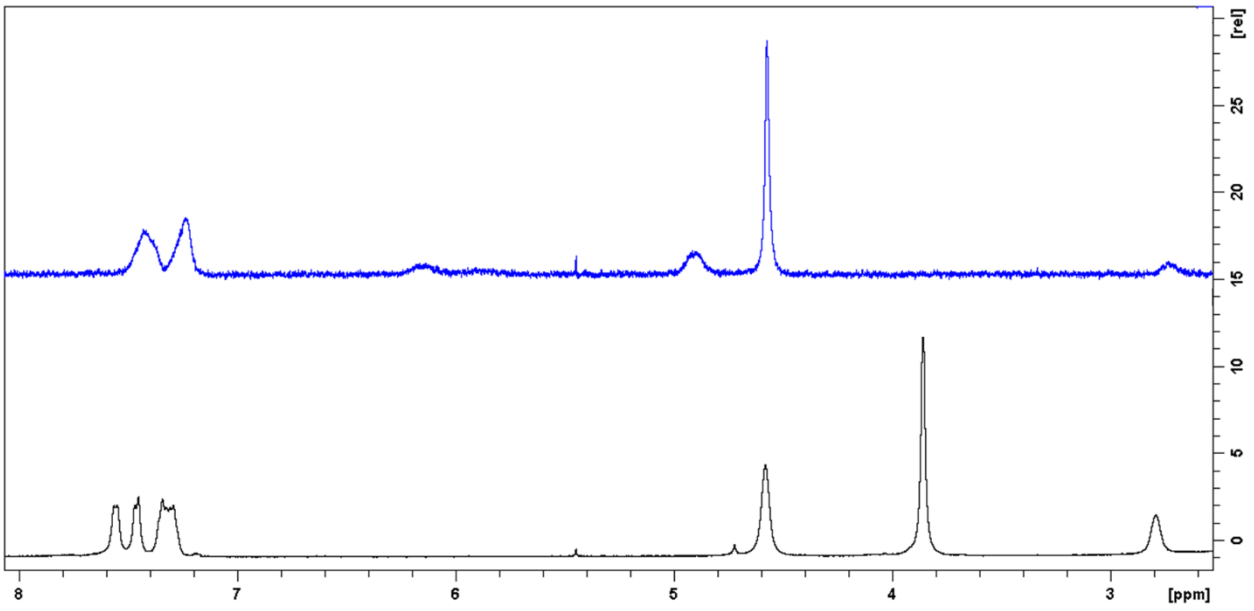


Figure S6. ^{1}H NMR spectra of complex **1** in CD_3CN before (blue line) and after the addition of 2 equiv. of AgOAc (black line).



After addition of AgOAc, only signals due to disilver complex **6** were observed. Immediate precipitation of $NiBr_2$ was also observed.

Figure S7. ^{1}H NMR spectra of complex **6** in CD_3CN before (blue line) and after the addition of 1 equiv. of $[NiBr_2(PPh_3)_2]$ (black line).

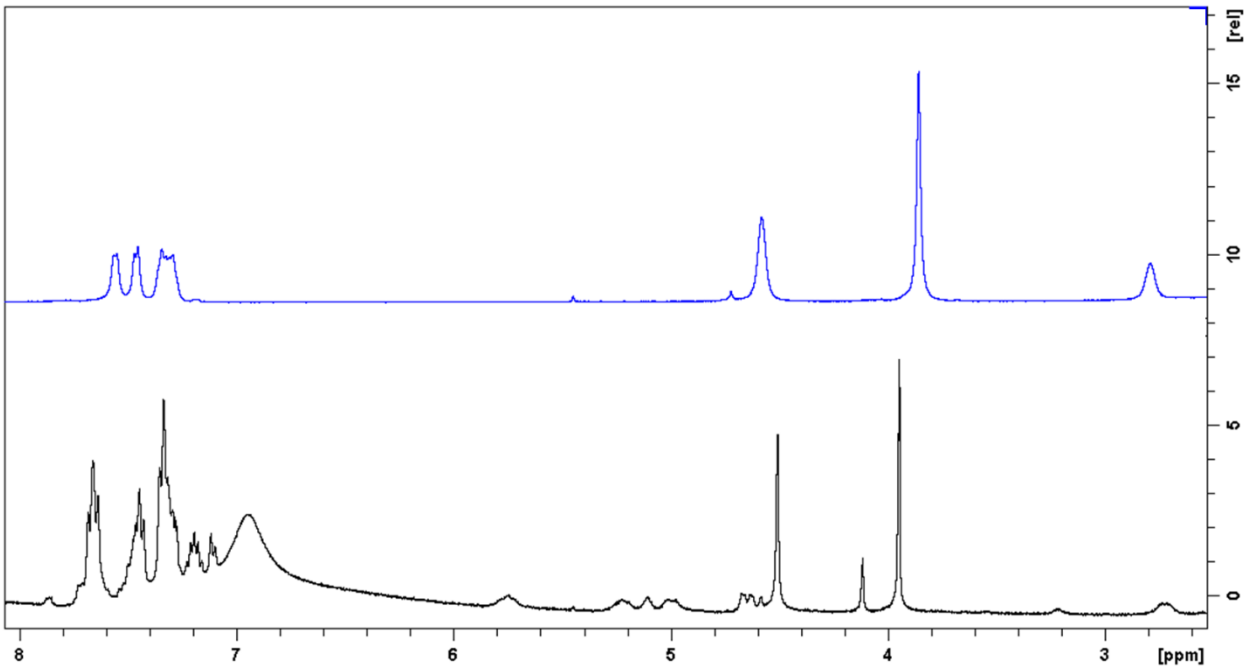
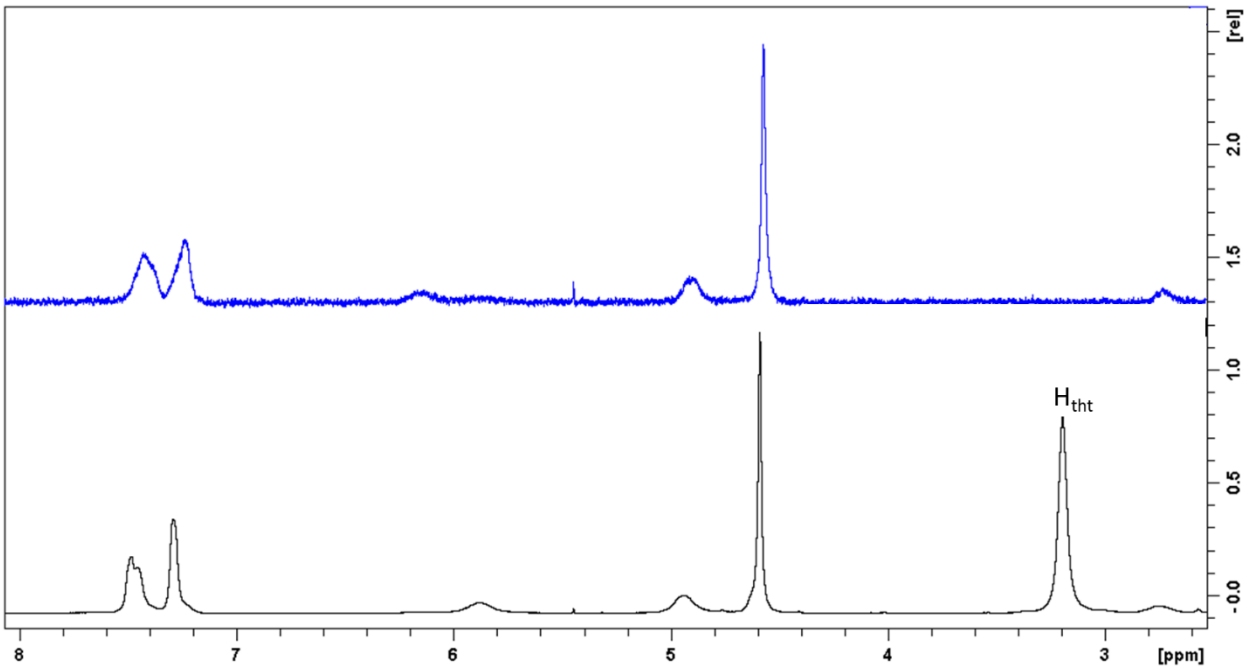


Figure S8. ^{1}H NMR spectra of **1** in CD_3CN before (blue line) and after the addition of 2 equiv. of [AuCl(tht)] and stiring for 10 h (black line).



ESI mass analysis of the mixture:

After mixing [$NiBr_2$($^{Me}CC_{prop}$)] (**1**) with [AuCl(tht)] in 1:2 mole ratio, the following fragments were observed on ESI-MS.

[Ni($^{Me}CC_{prop}$)$(MeCN)_2$]$^{2+}$: Calcd. *m/z* for $C_{23}H_{26}N_6Ni$: 222. Found *m/z* 222 (100%)

[NiCl($^{Me}CC_{prop}$)]$^{+}$: Calcd. *m/z* for $C_{19}H_{20}ClN_4Ni$: 397. Found *m/z* 397 (15%)

[NiCl($^{Me}CC_{prop}$)(MeOH)]$^{+}$: Calcd. *m/z* for $C_{20}H_{24}ClN_4NiO$: 429. Found *m/z* 429 (40%)

[NiCl($^{Me}CC_{prop}$)(MeCN)]$^{+}$: Calcd. *m/z* for $C_{21}H_{23}ClN_5Ni$: 438. Found *m/z* 438 (80%)