Supplementary Material (ESI) for Dalton Transactions
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Heterotopic Silver-NHC complexes:

From coordination polymers to supramolecular assemblies.

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General Procedures. All solvents were distilled under nitrogen in the presence of the following dessicants: sodium benzophenone ketyl for diethyl ether (Et_2O), tetrahydrofurane (THF), pentane and hexane; CaH_2 for dichloromethane (CH_2Cl_2), isopropanol and methanol; and sodium for toluene. NMR spectra (^1H and ^{13}C) were measured on a Bruker AV 400 MHz. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. UV/VIS spectroscopy experiments were performed on a HP 8453 UV/Visible System. Gel-permeation chromatography (GPC) was performed on a Shimadzu LC-20AD system with PLgel two 5µm MIXED-C column (Polymer Laboratories) with a Shimadzu RID-10A refractive index detector. Elemental analyses were carried out by Mikroanalytisch Laboratorium Dornis und Kolbe, Mülheim an der Ruhr (Germany). All reagents were purchased from commercial suppliers and used without further purification. 1-mesitylimidazole was synthesized according to published

procedure [Arduengo, A.; Harlow, R.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363].

Synthesis of compounds 1, 2, 4, 5A and 5B.

***N*-mesityl-*N'*-(3-pyridylmethyl)imidazolium chloride (1)**

3-(Chloromethyl)pyridine hydrobromide (1.76 g, 10.75 mmol) was neutralised using a saturated aqueous solution of sodium carbonate. The liberated 3-chloromethylpyridine was extracted into diethyl ether (3 × 50 cm^3) at 0 ºC, dried with magnesium sulfate and filtered. The filtrate was concentrated until a volume of 75 ml approximately. 1-mesitylimidazole (1g, 5.37 mmol) in THF (50 cm^3) at 0 ºC was added, the ether removed under reduced pressure and the solution was warmed to room temperature and then refluxed for seven days. After cooling, the solid precipated was filtered, washed with diethyl ether and dried under vacuum. White solid. Yield: 1.095g, 65%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.07 (s, 6H, 2 CH_3), 2.35 (s, 3H, CH_3), 6.25 (s, 2H, CH_2), 7.01 (s, 2H, 2 H arom), 7.14 (s, 1H, =CH), 7.54 (dd, J_{HH} = 8, 5 Hz, 1H, py), 8.05 (m, 1H, =CH), 8.66 (dd, J_{HH} = 5, 2 Hz, 1H, py), 8.70 (dt, J_{HH} = 8, 2 Hz, 1H, py), 9.16 (d, J_{HH} = 2 Hz, 1H, py), 10.95 (s, 1H, NCHN). ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 17.4 (2 Me), 20.9 (Me), 50.4 (CH_2), 122.9 (=CH), 123.3 (=CH), 124.1 (CH arom), 129.7 (2 CH arom), 130.0 (C_q arom), 130.5 (C_q arom), 133.9 (2 C_q arom), 137.2 (CH arom), 138.3 (NCN), 141.1 (C_q arom), 149.8 (CH arom), 150.4 (CH arom). HRMS (FAB): m/z, 278.1653, $[M]^+$ (exact mass calculated for $C_{18}H_{20}N_3$: 278.1657).

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[*N*-mesityl-*N'*-(3-pyridylmethyl)imidazol-2-ylidene] silver chloride (2).

N-mesityl-*N'*-(3-pyridylmethyl)imidazolium chloride (**1**) (200 mg, 0.64 mmol) and Ag_2O (74 mg, 0.32 mmol) were mixed in DCM (30 mL) and heated to 40 ºC for 3 hours. After cooling down the reaction mixture was filtered through celite and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the solid product was washed with diethyl ether and dried *in vacuo*. Yellow solid. Yield: 240 mg, 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 2.06 (s, 6H, 2 CH_3), 2.40 (s, 3H, CH_3), 5.49 (s, 2H, CH_2), 7.07 (s, 2H, 2 H arom), 7.08 (d, J_{HH}= 4 Hz, 1H, =CH), 7.20 (d, J_{HH}= 4 Hz, 1H, =CH), 7.39 (dd, J_{HH}= 8, 4 Hz, 1H, H arom), 7.67 (bd, J_{HH}= 8 Hz, 1H, H arom), 8.61 (d, J_{HH}= 8, 2 Hz, 1H, H arom), 8.64 (dd, J_{HH}= 4, 2 Hz, 1H, H arom). ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 17.3 (2 Me), 20.7 (Me), 53.0 (CH_2), 121.0 (CH arom), 123.6 (CH arom), 123.8 (CH arom), 129.2 (2 CH arom), 131.4 (C_q arom), 134.7 (2 C_q arom), 135.0 (CH arom), 135.3 (C_q arom), 139.6 (C_q arom), 148.7 (CH arom), 149.9 (CH arom), 181.7 (N*C*N). HRMS (FAB): m/z cacd. for $C_{18}H_{19}N_3Ag$: 384.0630; found: 384.0638 $[M\text{-}Cl]^+$. Elemental Analysis: $C_{18}H_{19}N_3AgCl$ (420.68): calcd. C 51.4, H 4.5, N 10.0; found C 51.3, H 4.5, N 10.1.

[*N*-mesityl-*N'*-(3-pyridylmethyl)imidazol-2-ylidene] silver(I) triflate (4).

[*N*-mesityl-*N'*-(3-pyridylmethyl)imidazol-2-ylidene] silver chloride (**2**) (200 mg, 0.47 mmol) and silver (I) triflate (125 mg, 0.48 mmol) were mixed in dichloromethane (30 mL) and stirred for 30 min in the absence of light. The mixture was filtered over a short pad of celite and the solvent was removed under vacuum. The product was precipitated from a dichlromethane/Et_2O mixture and washed with Et_2O. White solid. Yield: 230 mg, 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.91 (bs, 6H, 2 CH_3), 2.39 (s, 3H, CH_3), 5.51 (bs, 2H, CH_2), 6.99 (s, 2H, 2 H arom), 7.07 (bs, 1H, =CH), 7.50 (bs, 1H, H arom), 7.56

(bs, 1H, =CH), 7.80 (bs, 1H, H arom), 8.44 (bs, 1H, H arom), 9.05 (bs, 1H, H arom). ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 17.4 (2 Me), 20.9 (Me), 52.0 (CH_2), 122.7 (CH arom), 123.5 (CH arom), 125.7 (CH arom), 129.3 (2 CH arom), 134.4 (C_q arom), 134.9 (CH arom), 135.8 (C_q arom), 138.3 (C_q arom), 138.8 (C_q arom), 139.6 (C_q arom), 151.7 (CH arom), 151.8 (CH arom), (N*C*N not observed). Elemental analysis: $C_{19}H_{19}AgF_3N_3O_3S$: calcd. C 42.71, H 3.58, N 7.86; found C 42.30, H 3.92, N 7.78.

5A: **2** and **A** were mixed in dichloromethane and stirred for few minutes. The volatiles were removed under reduced pressure. Purple solid. Quantitative yield. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.77 (s, 6H, 2 Me), 2.30 (s, 3H, Me), 3.55 (bs, 1H, H arom), 3.71 (bs, 1H, H arom), 4.34 (s, 2H, 2 =CH), 5.94 (dd, J_{HH}= 8, 5 Hz, 1H, H arom), 6.10 (d, J_{HH}= 2 Hz, 1H, =CH), 6.59 (bd, J_{HH}= 8 Hz, 1H, H arom), 6.75 (d, J_{HH}= 2 Hz, 1H, =CH), 6.93 (s, 2H, 2 H arom), 7.70-7.80 (m, 12H, 12 H arom), 8.19 (dd, 8H, 8 H arom), 8.89 (s, 8H, 8 H arom).

5B: **2** and **B** were mixed in dichloromethane and stirred for few minutes. The volatiles were removed under reduced pressure. Orange solid. Quantitative yield. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.32 (s, 18H, 2 CMe_3), 1.48 (s, 18H, 2 CMe_3), 1.92 (s, 6H, 2 CH_3), 2.34 (s, 3H, CH_3), 5.28 (s, 2H, CH_2), 6.78 (d, J_{HH}= 2 Hz, 1H, =CH), 6.90 (d, J_{HH}= 2 Hz, 1H, =CH), 7.00 (s, 2H, 2 H arom), 7.10 (bs, 2H, 2 H arom), 7.33 (m, 3H, 3 H arom), 7.42 (d, J_{HH}= 2 Hz, 2H, 2 H arom), 7.69 (m, 3H, 3 H arom), 8.34 (dd, J_{HH}= 5, 2 Hz, 1H, H arom), 8.46 (d, J_{HH}= 2 Hz, 1H, H arom), 8.85 (bs, 2H, 2 =CH). HRMS (FAB): m/z cacd for $C_{54}H_{65}AgN_5O_2Zn$: 986.3475; found: 986.3445 $[M\text{-}Cl]^+$.

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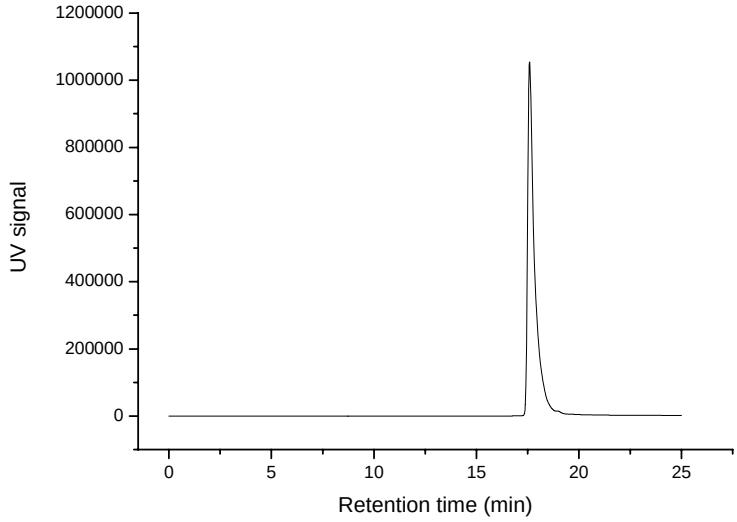
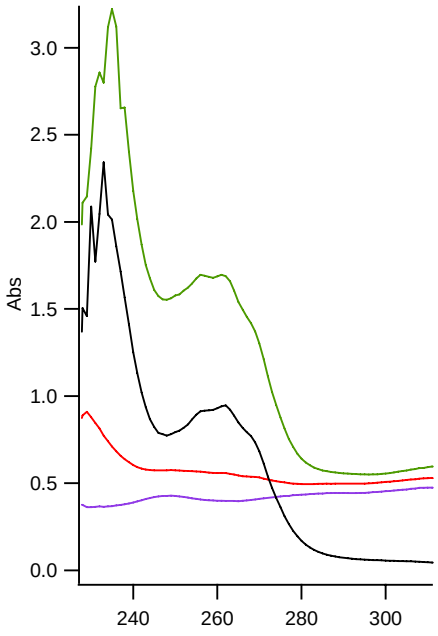
GPC analysis (Calibration against polystyrene to estimate the molecular weights)

Mw = 520 [Mw (**2**) = 420,68]



UV/Vis absortion spectra (dichloromethane) of **A** (purple); **2** (black); **5A** (red); excess of **2** over **5A** (green).



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Binding constants determinations by Uv/Vis titrations (dichloromethane, typical concentrations of host 3 x 10^{-5} M^{-1}):

5A:

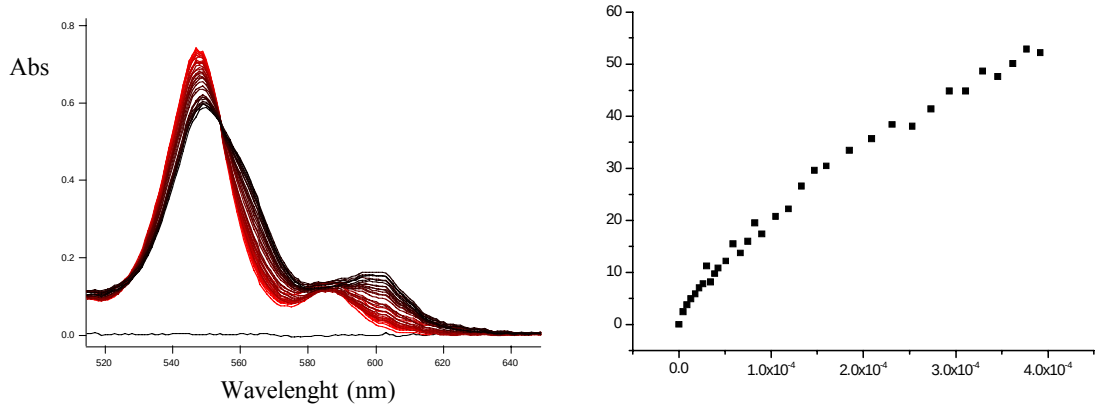

Figure: Electronic absorption spectra recorded during titration of Zn^{II}-TPP by complex **2** in dichloromethane (left). Titration curve at 565 nm (right). K_{ass} = 3.0x10^3 M^{-1}.

5B:

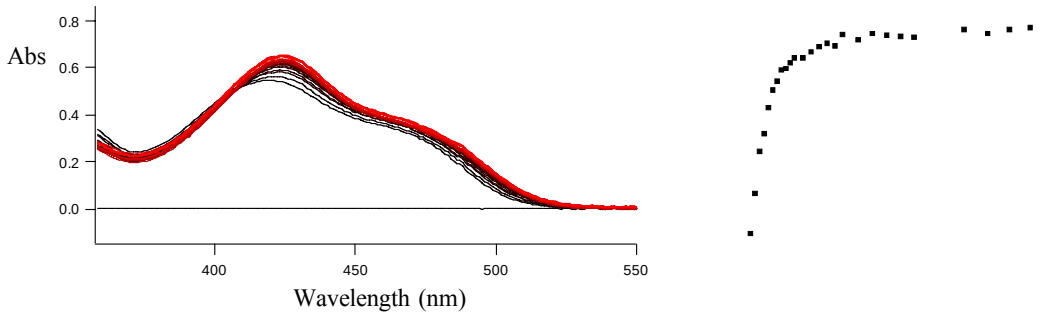

Figure: Electronic absorption spectra recorded during titration of Zn^{II}-salphen by complex **2** in dichloromethane (left). Titration curve at 565 nm (right). K_{ass} = 6.5x10^5 M^{-1}.

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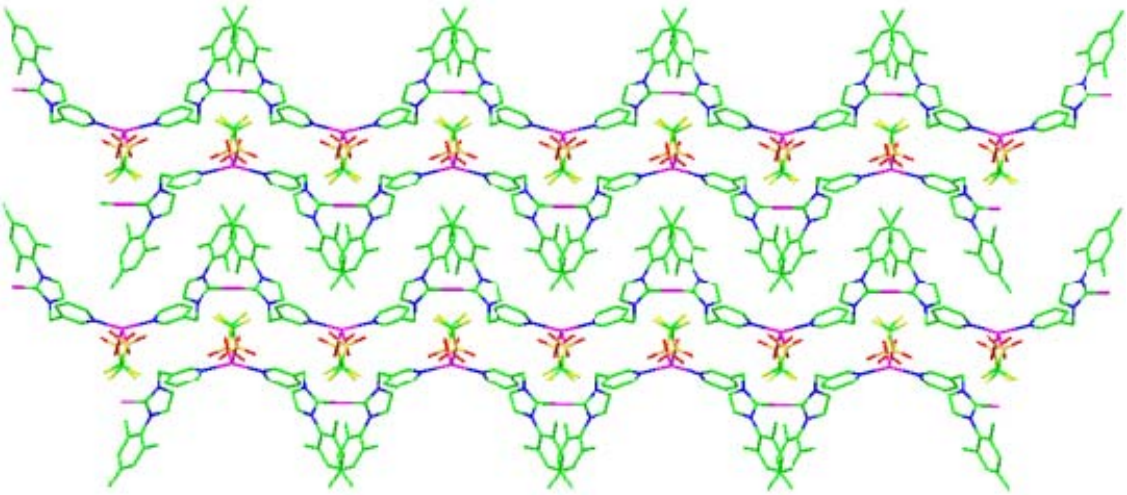
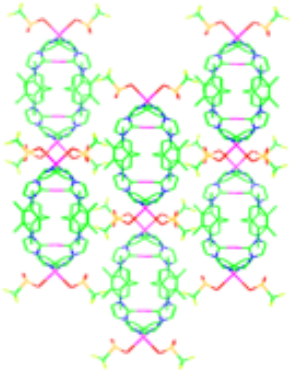
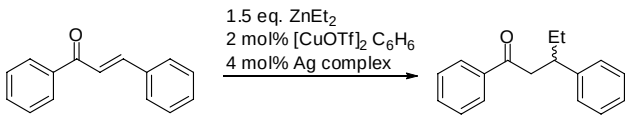
Perspective of compound 4:





Applications of silver complexes in catalysis:

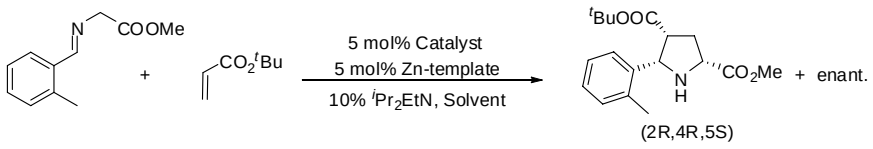
A) Copper-catalyzed Michael addition of $ZnEt_2$ to *trans*-chalcone:



Entry	Catalyst	Solvent	T	Time (h)	Yield (%)
1	**2**	Et_2O	-20ºC	22	100
2	**5B**	Et_2O	-20ºC	2	95
2	**5B**	Tolueno	-20ºC	2	90

Representative procedure: A solution of the copper salt (5.9 μmol) and the silver complex (12 μmol) in the appropiate solvent (2 mL) was stirred for 15 minutes and cooled down to -20 ºC. Then *trans*-chalcone (62 mg, 0.3 mmol) was added, stirred for 5 minutes and $ZnEt_2$ (0.45 mL 1M in hexanes, 0.45 mmol) was added dropwise. The reaction was quenched with HCl 2M (2 mL) and the product was extracted with Et_2O (3 x 2 mL). The conversion was analyzed by ^{1}H-NMR.

B) 1,3-dipolar cycloaddition to imines:



Entry	Catalyst	Solvent	T	Time (h)	Yield (%)
1	**2**	CH_2Cl_2	r.t.	48	39
2	**5A**	CH_2Cl_2	r.t.	48	38

Representative procedure: To a suspension of *N*-(4-bromobenzylidene)glycine methyl ester (0.15 mmol, 38 mg) and the catalyst ($7.5 \cdot 10^{-3}$ mmol, 5 mol %) in dichloromethane

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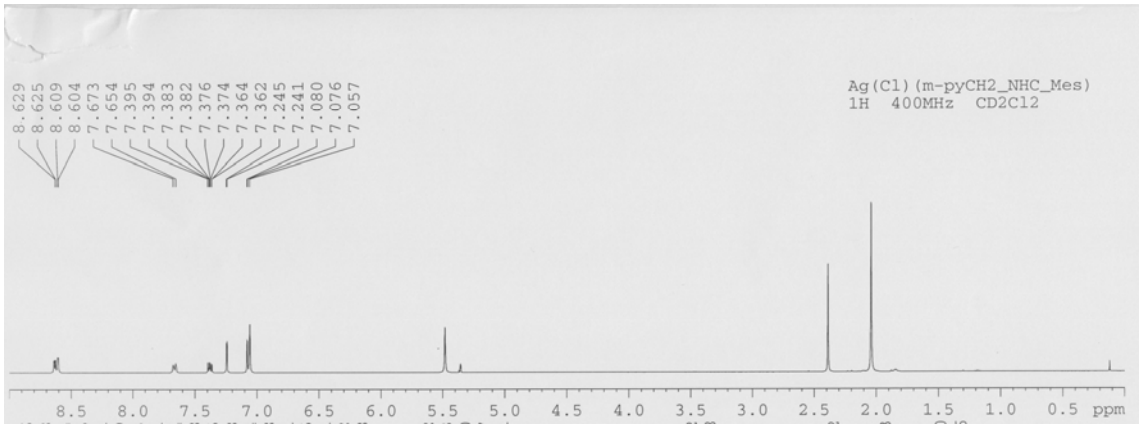
(0.25 mL) was added $^{i}Pr_2EtN$ (3 μL, 0.015 mmol, 10 mol%) and the mixture was stirred in the darkness for one hour at room temperature. Then, *tert*-butyl acrylate (27 μL, 0.18 mmol) was added and the mixture was stirred for 48 hours. Then the solvent was removed under vacuum and the residue was purified by flash chromatography (1:1 Et_2O-hexane) to obtain the product as a white solid.

Spectra:

2: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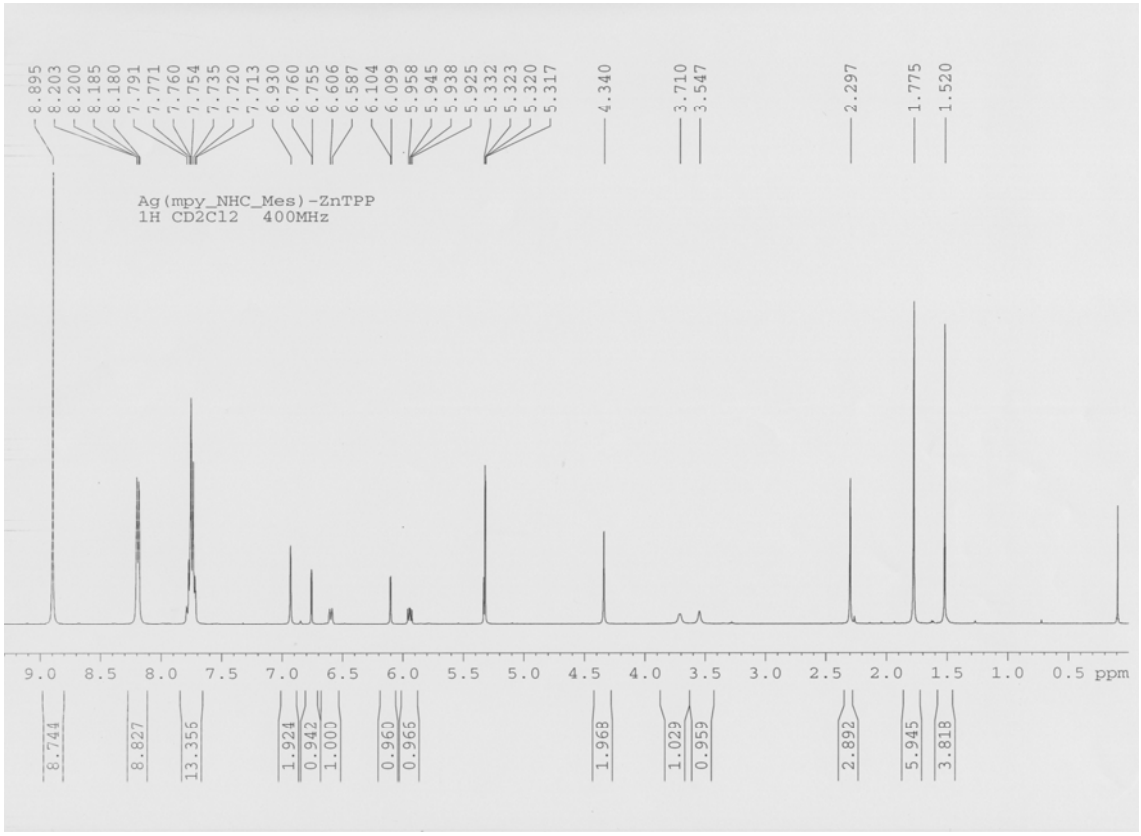
8.625
8.609
8.604
7.673
7.654
7.395
7.394
7.383
7.382
7.376
7.374
7.364
7.362
7.245
7.241
7.080
7.076
7.057
Ag(Cl)(m-pyCH2_NHC_Mes)
1H 400MHz CD2Cl2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

5A: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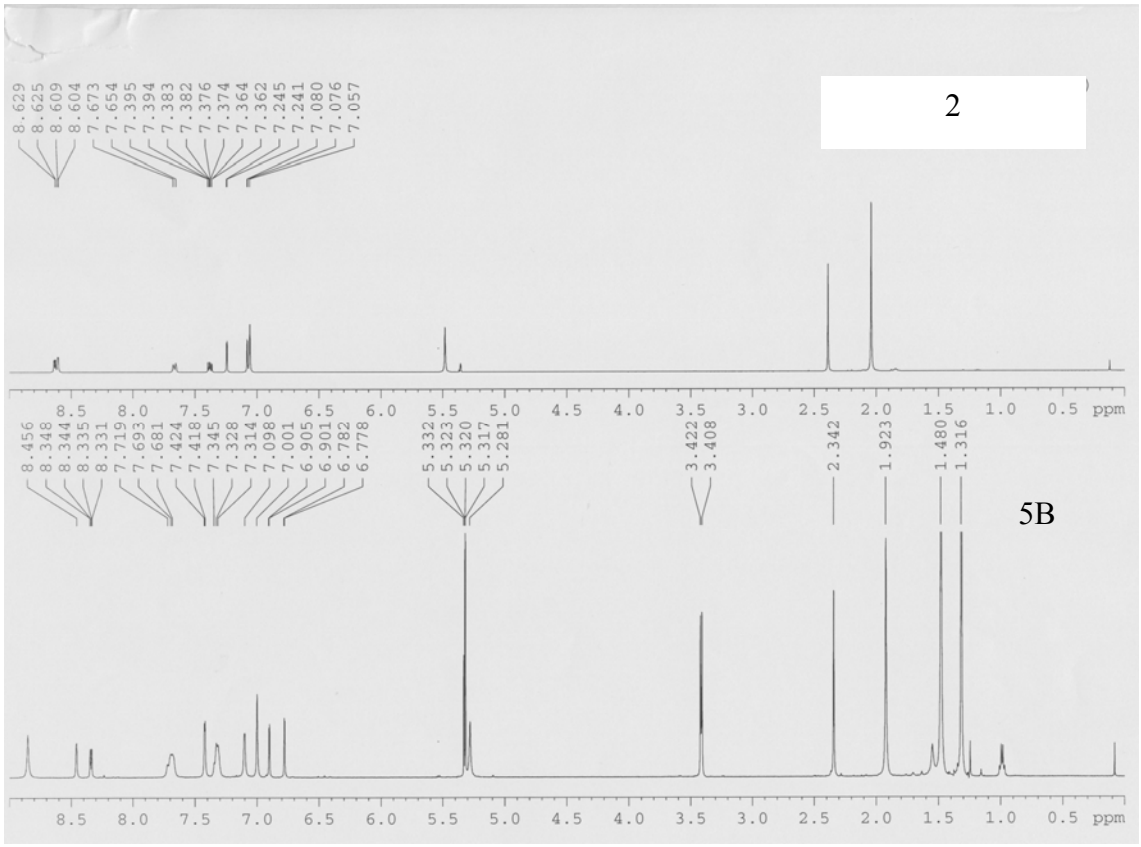
8.203
8.200
8.185
8.180
7.791
7.771
7.760
7.754
7.735
7.720
7.713
6.930
6.760
6.755
6.606
6.587
6.104
6.099
5.958
5.945
5.938
5.925
5.332
5.323
5.320
5.317
4.340
3.710
3.547
2.297
1.775
1.520
Ag(mpy_NHC_Mes)-ZnTPP
1H CD2Cl2 400MHz
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.744
8.827
13.355
1.924
0.942
1.000
0.960
0.965
1.968
1.029
0.959
2.892
5.945
3.818

5B:


2
5B
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7.418
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7.328
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6.782
6.778
5.332
5.323
5.320
5.317
5.281
3.422
3.408
2.342
1.923
1.480
1.316
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm