Supporting Information for

Diasteroselective Multi-Component Assemblies from Dynamic Covalent Imine Condensation and Metal-Coordination Chemistry. Mechanism and Narcissistic Stereochemistry Self-Sorting

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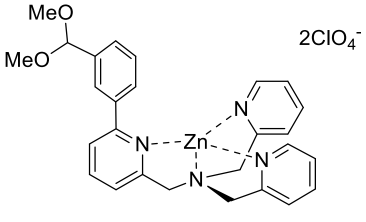
1 General Methods

Chemicals were purchased from Aldrich, Fluka or Acros and used without further purification. IR spectra were recorded with a Perkin–Elmer FTIR 1650. ^{1}H and ^{13}C NMR spectra (referenced to the solvent residual peak) were recorded at 301 K with Bruker AC-300 or 250 MHz instruments. ESI-MS experiments were carried out in positive mode with an Agilent Technologies LC/MSD Trap SL AGILENT instrument (mobile phase methanol). HRMS (ESI-TOF) analyses were performed with an Applied Biosystems ESI-TOF Mariner Biospectrometry Workstation (methanol as mobile phase with internal standards). MALDI-TOF analyses were carried out with an AB-SCIEX TOF-TOF 4800 instrument. Microanalyses were performed with a Flash 2000 Thermo Scientific Analyser. For new compounds, satisfactory determinations were obtained: C±0.3, H±0.27.

2 Synthesis and Characterization

Compounds 3, **1-aaa**, **2-aaa** were synthesized and fully characterized (^{1}H NMR, 2D NMR, MS analysis) accordingly to: F. A. Scaramuzzo, G. Licini, C. Zonta, *Chem. Eur. J.* **2013**, *19*, 16809–16813. (b) E. Badetti, K. Wurst, G. Licini, C. Zonta, *Chem. Eur. J.* **2016**, *22*, 6515–6518. The procedure for the CD analysis and X-Ray crystallization analysis are described in the above mentioned article.

2.1 Synthesis of Acetal 4



4

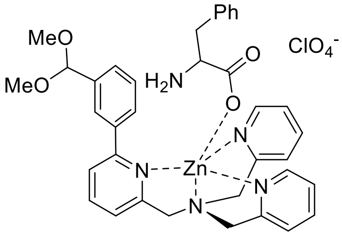
5.2 mg (0.008 mmol) of complex **3** [7a] were solubilized in 0.8 mL of deuterated methanol. The solution was let stirring at 60°C for 4 hours to yield a pale yellow solution. (pale yellow solution, yield 95%).

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.

^{1}H NMR (300 MHz, CD_3OD): δ = 8.49 (d, 2H, HAr), 8.08 (m, 3H, HAr), 7.60 (m, 10H, HAr), 5.43 (s, 1H, CH), 4.54 (d, 2H, CH_2), 4.36 (d, 4H, CH_2), the methoxy groups were not detected because of the large excess of MeOD used as reaction solvent ^{13}C NMR (50 MHz, CD_3OD): δ =155.17, 154.63, 147.65, 141.41, 140.77, 139.72, 138.96, 103.64, 59.13, 58.50, 52.89, 47.83.

HRMS (ESI-TOF) *(m/z)*: $[M+ClO_4]^+$ calcd. for $[C_{39}H_{30}N_4O_3Zn+ClO_4]^+$, 765.1094; found 765.1165. Elemental analysis: C. 54.08; H, 4.01; N, 6.85. Required [**1•Zn**]$(ClO_4)_2$. C 54.03; H, 3.49; N, 6.46.

2.2 Synthesis of Complex 5-L-Phe



5-L-Phe

1.3 mg (0.008 mmol) of L-Phe were added to the **Acetal 4** solution in deuterated methanol. The suspension was then sonicated until complete solubilisation of the amino acid. (pale yellow solution, yield 95%).

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.

^{1}H NMR (300 MHz, CD_3OD): δ = 8.51 (d, 1H, HAr), 8.31 (d, 1H, HAr), 8.08 (m, 3H, HAr), 7.58 (m, 10H, HAr), 7.30 (m, 7H, HAr) 5.30 (s, 1H, CH), 4.41 (m, 6H, CH_2), 3.46 (t, 1H, $CH_{L\text{-}Phe}$), 3.07 (dd, 1H, $CH_{2L\text{-}Phe}$), 2.90 (dd, 1H, $CH_{2L\text{-}Phe}$), as in the previous case the methoxy groups were not detected because of the deuterated solvent used.

^{13}C NMR (75.4 MHz, CD_3OD): δ =174.05, 157.72, 156.31, 150.41, 150.18, 142.70, 140.79, 140.47, 137.21, 130.59, 129.57, 128.65, 128.10, 127.09, 126.67, 126.18, 124.60, 105.32, 58.35, 57.98, 55.86, 37.68.

HRMS (ESI-TOF) *(m/z)*: $[M+ClO_4]^+$ calcd. for $[C_{39}H_{30}N_4O_3Zn+ClO_4]^+$, 765.1094; found 765.1165. Elemental analysis: C. 54.08; H, 4.01; N, 6.85. Required [**1•Zn**]$(ClO_4)_2$. C 54.03; H, 3.49; N, 6.46.

3 Demonstration of linear CD response to *e.e* independently by the formation of homo or ethero assemblies

Considering 1 mol of scalemic mixture of x mol L and (1-x) mol D

e.e. = $(x-(1-x))/(x+1+x) = ((x-(1-x))$

$$\left.\begin{array}{l} L + L \longrightarrow LL \\ D + D \longrightarrow DD \end{array}\right\} \text{Homochiral}$$

$$L + D \longrightarrow LD \qquad \text{Heterochiral}$$

Defining h = LD the amount of heterochiral formed from a mass balance

$LL = x/2 – h/2$

$DD = (1-x)/2 - h/2$

$LD = h$

The observed CD is given by

$CD = LL\ \theta_{LL} + DD\ \theta_{DD} = (x/2 – h/2)\ \theta_{LL} + ((1-x)/2 – h/2)\ \theta_{DD}$

Knowing that $\theta_{LL} = - \theta_{DD}$

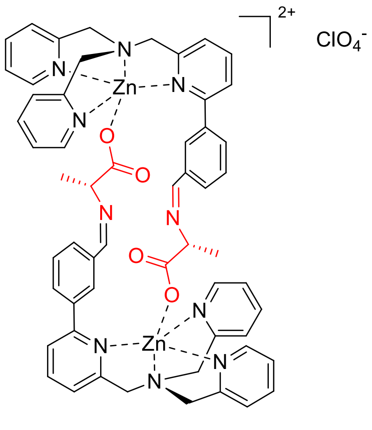
$CD = ((x/2 – h/2)) – ((1-x)/2 – h/2))\ \theta_{LL} = = ((x-(1-x))/2\ \theta_{LL}$ which is directly proportional to *e.e.*

An example of this behaviour is reported in the table below which shows the linearity in the CD signals obtained using different ratio of L and D compound in case of preferential homo or hetero assemblies formation using the model previously described

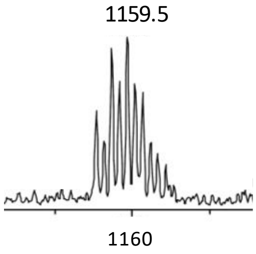
Starting mixture			**Preferential Homochiral formation**				**Preferential Heterochiral formation**			
L	D	*e.e.*	LL	DD	LD	Signal	LL	DD	LD	Signal
100	0	100	50	0	0	50	50	0	0	50
90	10	80	45	5	0	40	40	0	10	40
80	20	60	40	10	0	30	30	0	20	30
70	30	40	35	15	0	20	20	0	30	20
60	40	20	30	20	0	10	10	0	40	10

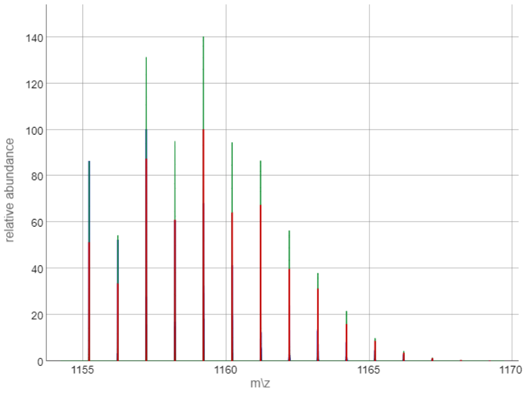
4 Comparison between theoretical and experimental MS peak in of 1-aaa and 2-aaa assembly in self-sorting experiment

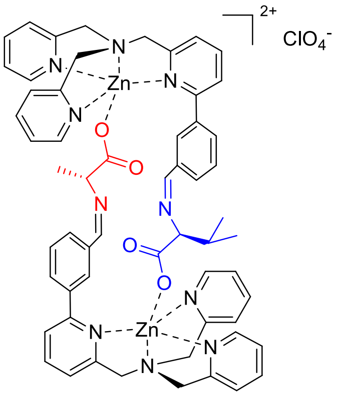
The experimental and simulated mono charged cluster peaks related to each species involved in the self-sorting experiment are reported below. The number of counter anions (perchlorate) are reported in the Chemdraw structures.



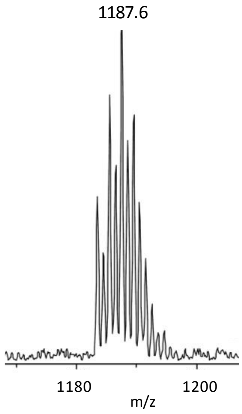
1-D-Ala-D-Ala

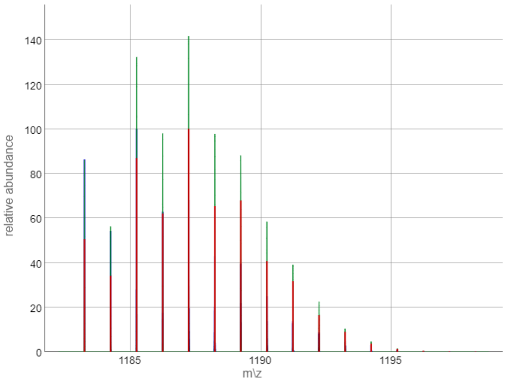


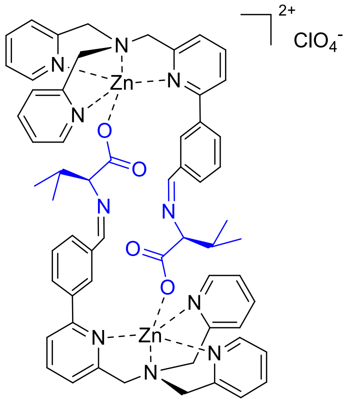




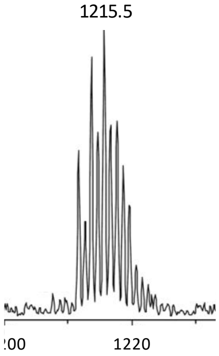
1-L-Val-D-Ala
1-D-Ala-L-Val

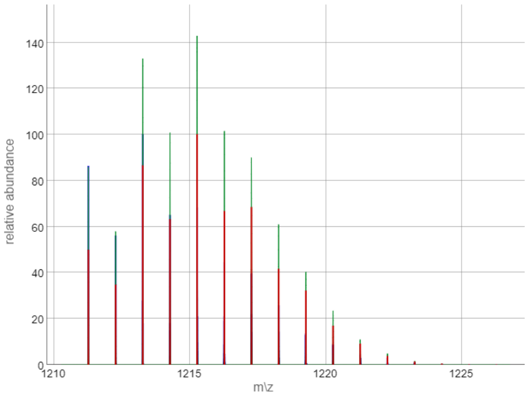


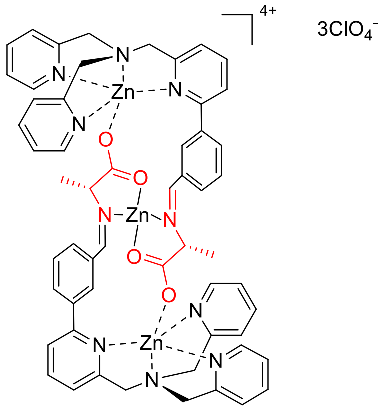




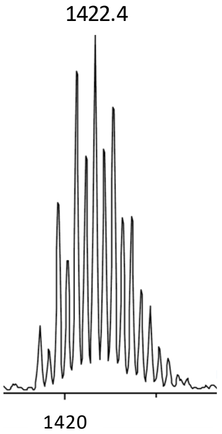
1-L-Val-LVal

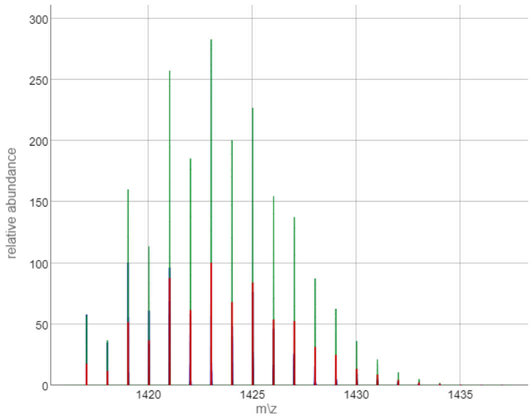


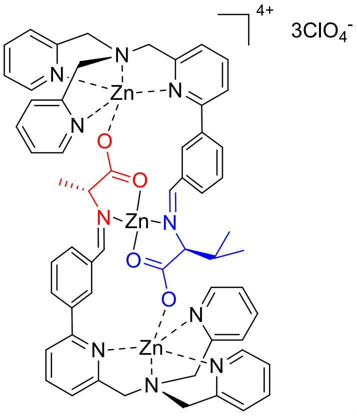




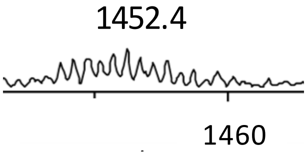
2-D-Ala-D-Ala

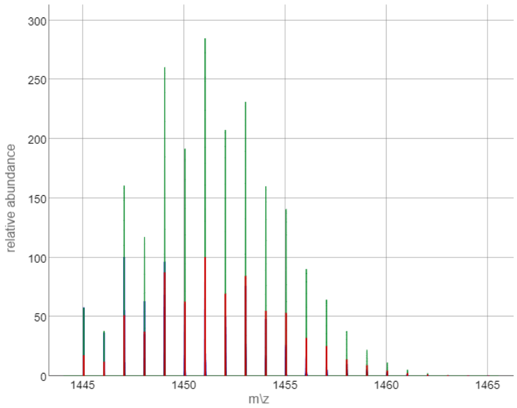


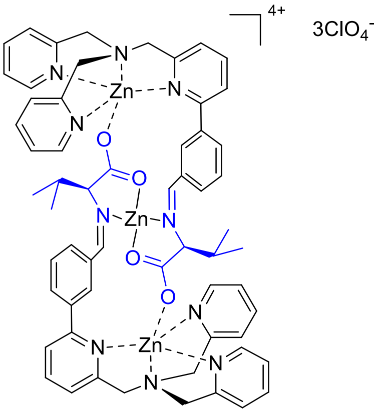




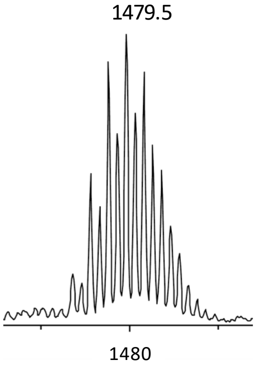
2-L-Val-D-Ala
2-D-Ala-L-Val

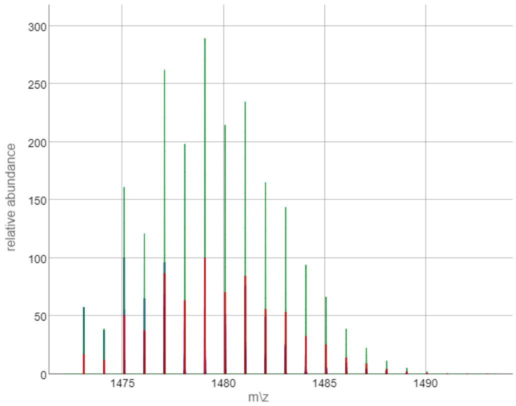






2-L-Val-LVal





5 NMR and HRMS characterization

5.1 Acetal 4

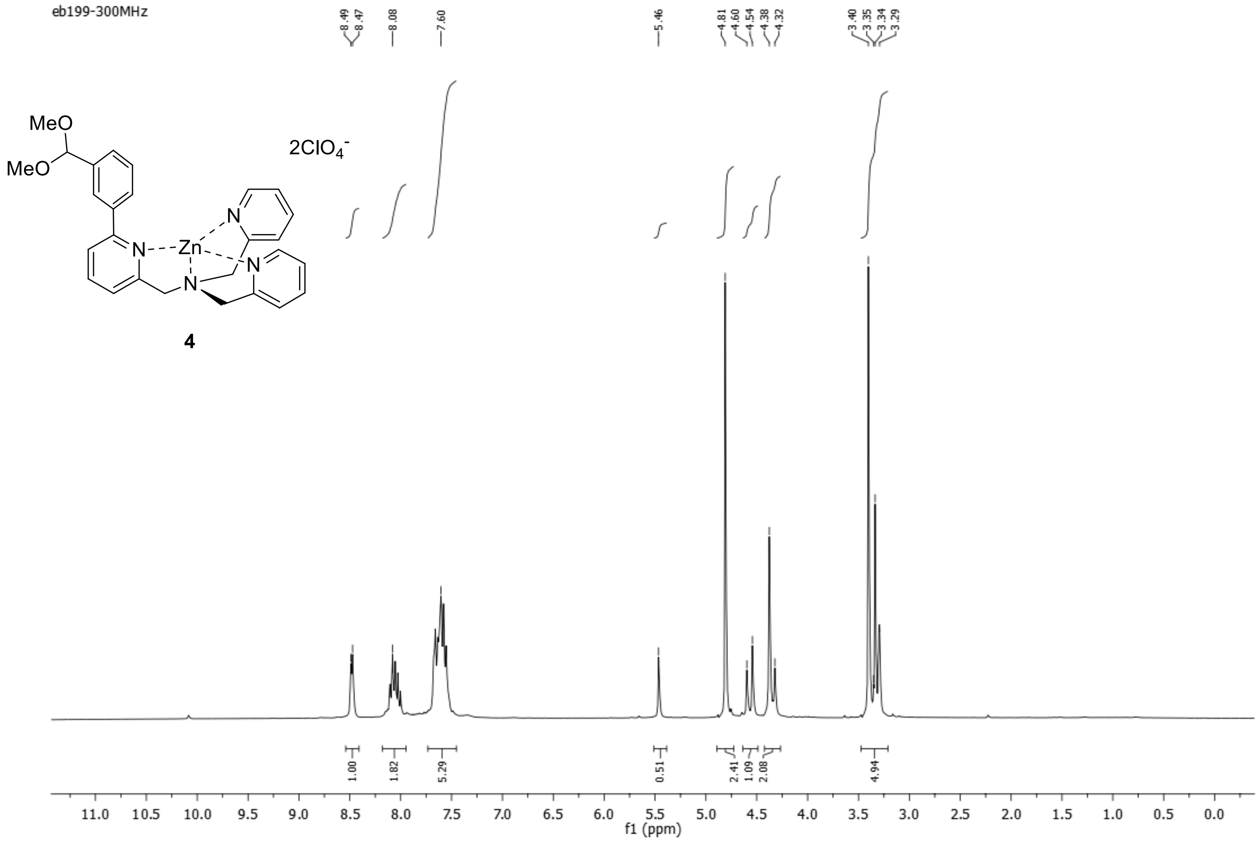


Figure S1 ^{1}H NMR spectrum (300 MHz, 301 K, CD_3OD) of acetal **4.**

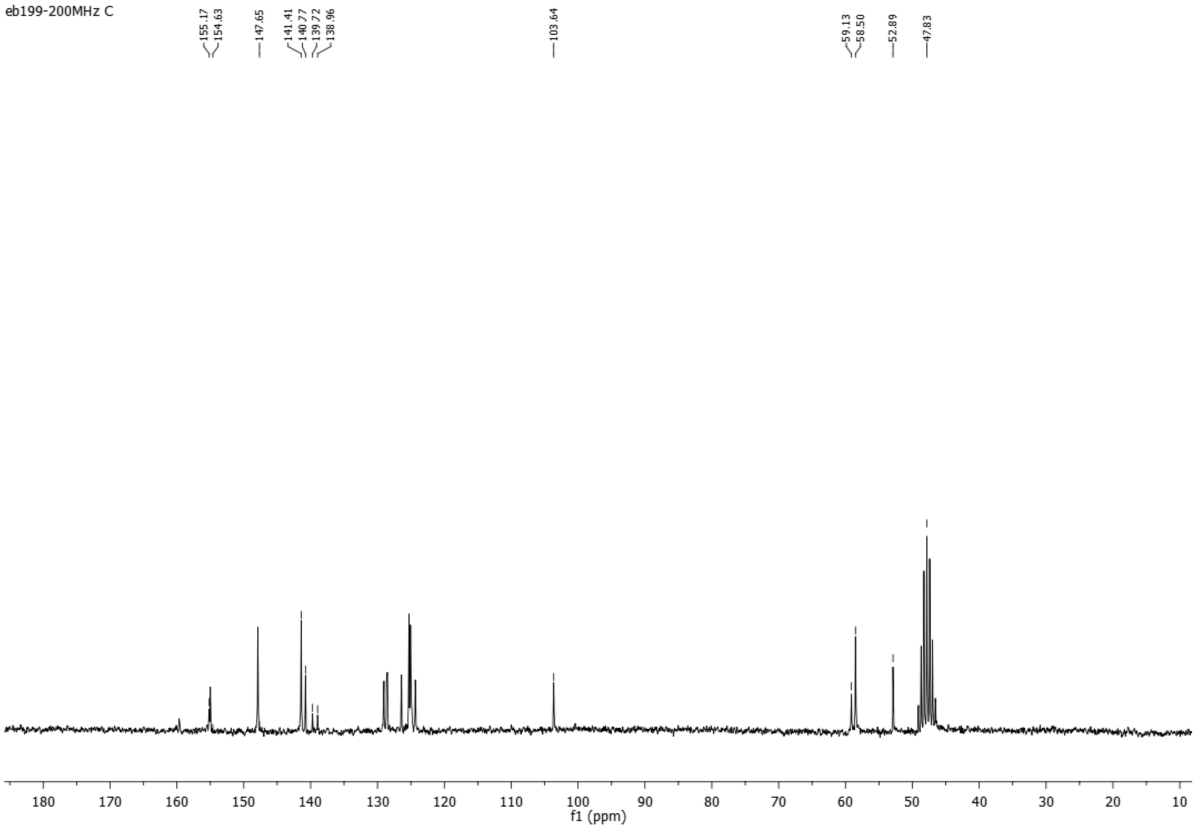


Figure S2 ^{13}C NMR spectrum (300 MHz, 301 K, CD_3OD) of acetal **4.**

5.2 Complex 5-L-Phe

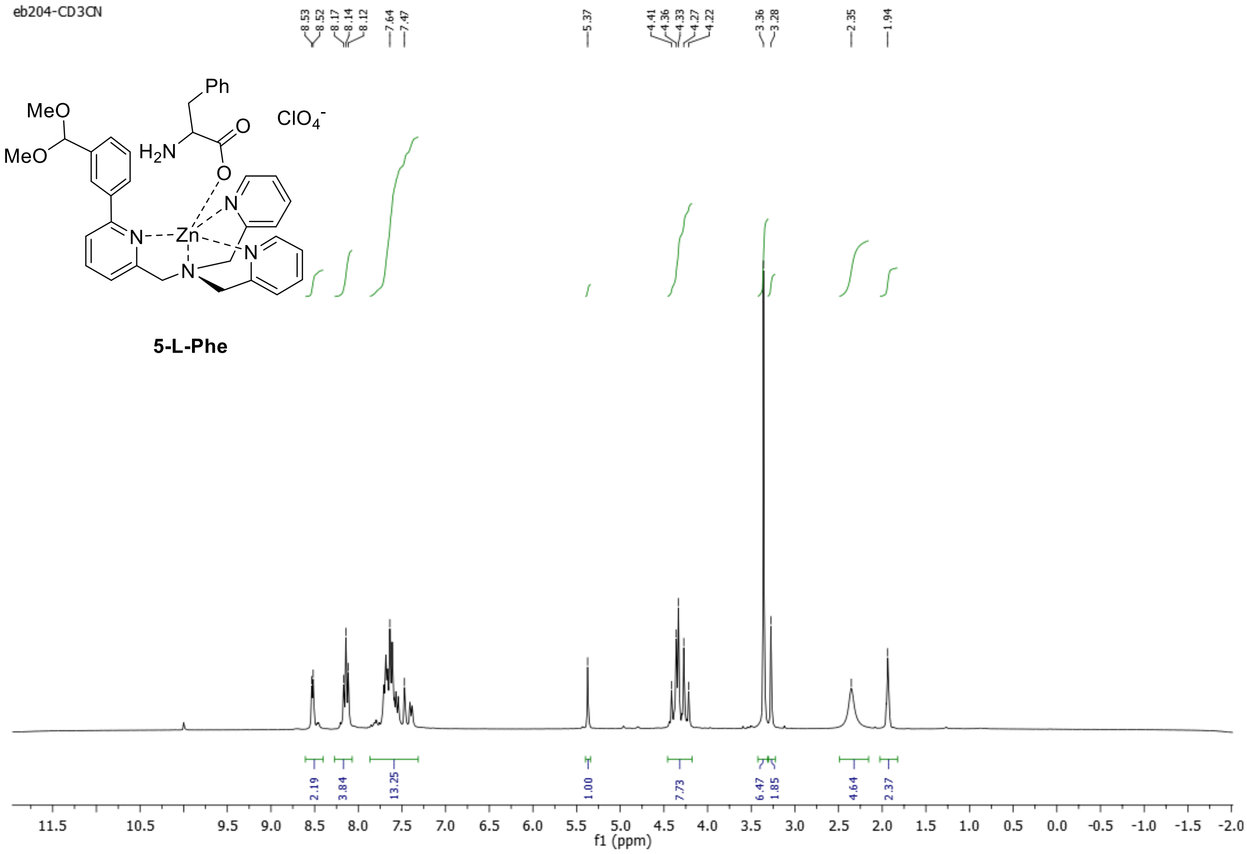


Figure S3 ^{1}H NMR spectrum (300 MHz, 301 K, CD_3OD) of complex **5-L-Phe**

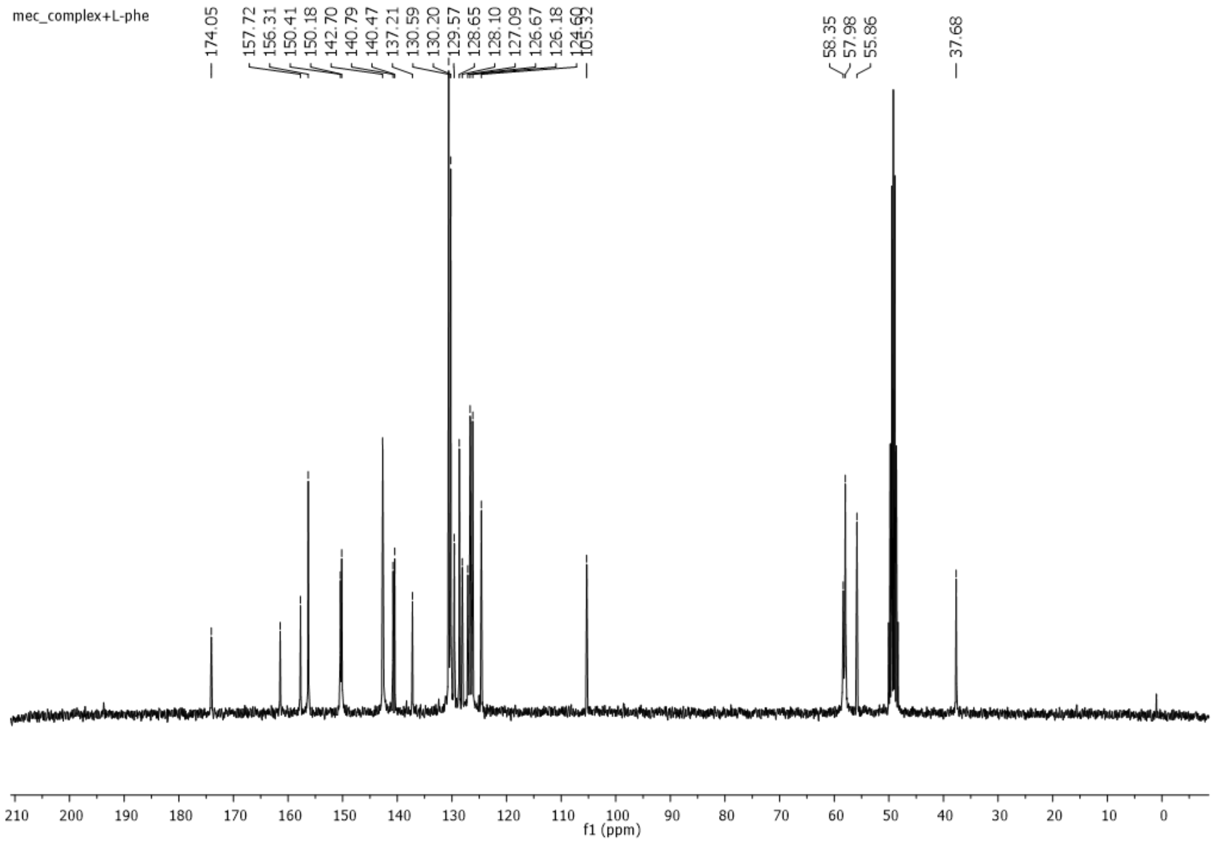


Figure S4 ^{13}C NMR spectrum (300 MHz, 301 K, CD_3OD) of complex **5-L-Phe**