Supporting Information

New Chiral Zinc Complexes: Synthesis, Structure, and Induction of Axial Chirality

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Table of Contents

(A) General Considerations SI-2

(B) General Procedures for the Synthesis of Chiral Zinc(II) Complexes SI-3

(C) Synthesis of Mononuclear Chiral Zinc(II) Complexes SI-4

(D) Synthesis of Dinuclear Chiral Zinc(II) Complexes SI-13

(E) Single Crystal X-Ray Structure Determinations SI-18

(F) NMR Spectra of New Compounds SI-25

(A) General Considerations

All syntheses were carried out using chemicals as purchased from commercial sources unless otherwise stated. All manipulations and reactions were run under inert atmosphere using anhydrous solvents, in either a glovebox or with standard Schlenk-type techniques. Glassware was dried under vacuum and heated with a hot air gun before use. All solvents were dried by using a Solvent Purification System (SPS). THF-d_8 was dried over 4Å molecular sieves, and degassed by three freeze-thaw cycles under high vacuum. Silica gel 60 (230–400 mesh) was used for column chromatography. NMR spectra were recorded on 400 MHz and 500 MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts are quoted in ppm relative to residual solvent peaks. High resolution mass spectra (HRMS) were recorded using an ESI ionization method in positive mode.

Details on the X-Ray structure determination can be found in section E (page 20). Regarding PXRD, approximately 20 mg of non-manipulated samples were prepared in standard sample holders using two foils of polyacetate. Powder diffraction patterns were acquired on a D8 Advance Series 2Theta/Theta powder diffraction system using $Cu_{K\alpha}$-radiation in transmission geometry. The system is equipped with a VÅNTEC-1 single photon counting PSD, a Germanium monochromator, a ninety positions auto changer sample stage, fixed divergence slits and a radial soller. Programs used: Data collection with DIFFRAC plus XRD Commander V.2.5.1, and evaluation and area integration with EVA V.14.0.0.0 (Bruker-AXS 1996-2007). The standard samples were measured in the range from 4º to 40º in 2θ in a 20 minute measurement period.

2,2'-Biphenol derivatives **1** and **2**, and enantiomerically pure N,N'-substituted (1*R*,2*R*)-1,2-cyclohexanediamines **3a**–**c**, as well as their (1*S*,2*S*)-configured enantiomers, were all prepared by following the corresponding experimental procedures previously described by our group.[1]

Zinc bis[bis(trimethylsilyl)amide] ($Zn[N(TMS)_2]_2$) was prepared according to the cited literature procedure.[2] Physical and spectroscopic data of this compound were identical to the reported data.

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[1] Etxebarria, J.; Degenbeck, H.; Felten, A. S.; Serres, S.; Nieto, N.; Vidal-Ferran, A. *J. Org. Chem.* **2009**, *74*, 8794.

[2] Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107.

(B) General Procedures for the Synthesis of Chiral Zinc(II) Complexes

1. Method A: Diethylzinc (Et_2Zn) as the zinc(II) source

The required 2,2'-biphenol derivative **1** or **2** was dissolved in THF (approx. 2.5 mL/0.10 mmol) in a suitable round-bottom flask. Subsequently, 1 equivalent of a ca. 1 M solution of Et_2Zn in toluene[3] was syringed over the previous solution and the mixture was stirred for 45 min at room temperature. Occasionally, a white precipitate, presumably consisting of aggregates of the corresponding zinc(II) biphenolate, was formed. Finally, a solution of the required enantiopure 1,2-cyclohexanediamine **3** in THF (1 equiv., approx. 0.6 mL/0.1 mmol) was added and the reaction mixture was stirred for 5 min during which the former precipitate dissolved. The crude products were obtained by taking up the residue with either Et_2O or with anhydrous *n*-hexane where indicated, and filtering through a D3 Schlenk frit. The thus isolated products could be further purified by crystallization through slow diffusion of *n*-hexane into solutions in either CH_2Cl_2 or THF.

2. Method B: Zinc bis[bis(trimethylsilyl)amide] ($Zn[(NTMS)_2]_2$) as the zinc(II) source

The required 2,2'-biphenol derivative **1** or **2** was dissolved in THF (approx. 1.5 mL/0.10 mmol) in a suitable round-bottom flask. Subsequently, 1 equivalent of $Zn[N(TMS)_2]_2$, dissolved in THF (approx. 0.6 mL/0.10 mmol), was syringed over the previous solution and the mixture was stirred for 45 min at room temperature. Occasionally, a white precipitate, presumably consisting of the corresponding zinc(II) biphenolate, was formed. Finally, a solution of the required enantiopure 1,2-cyclohexanediamine **3** in THF (1 equiv., approx. 0.6 mL/0.10 mmol) was added and the reaction mixture was stirred for 5 min during which the former precipitate dissolved. The solvent was removed under vacuum for which the solution was moderately heated to 35 ºC in a water bath. The crude products were obtained by taking up the residue with either Et_2O or with *n*-hexane where indicated, and filtering through a D3 Schlenk frit. The thus isolated products could be further purified by crystallization through slow diffusion of *n*-hexane into solutions in either CH_2Cl_2 or THF.

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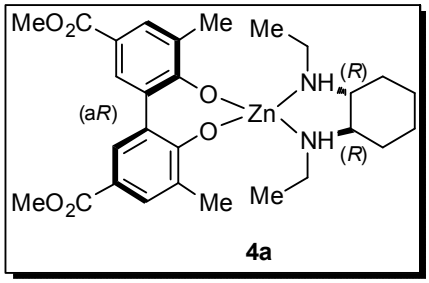
[3] The solution was titrated by ^1H NMR analysis with 1,5-cyclooctadiene (cod) as the internal standard and using a sealed capillary filled with C_6D_6 for deuterium shimming and locking.

(C) Synthesis of Mononuclear Chiral Zinc(II) Complexes

1. Synthesis of mononuclear zinc(II) complex 4a

The synthesis of complex **4a** was carried out by following method A, using 3,3'-methyl-substituted 2,2'-biphenol **1** (86 mg, 0.26 mmol), a 1.03 M solution of Et_2Zn in toluene (0.25 mL, 0.26 mmol), and (1*R*,2*R*)-*N*,*N*'-diethyl-1,2-cyclohexanediamine **3a** (44 mg, 0.26 mmol). The product was obtained as a white powder (120 mg, 82% yield) and could be crystallized by slow diffusion of *n*-hexane into CH_2Cl_2. The synthesis of complex **4a** was also successfully accomplished by following method B, using 2,2'-biphenol **1** (108 mg, 0.33 mmol), $Zn[N(TMS)_2]_2$ (0.13 mL, 0.33 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-diamine **3a** (56 mg, 0.33 mmol). The product was obtained as a white powder (150 mg, 81% yield) and could be crystallized by slow diffusion of *n*-hexane into CH_2Cl_2. Single crystal structures and spectroscopic and physical data of compound **4a** prepared according to methods A and B were in perfect agreement.



4a

Mononuclear zinc(II) complex **4a**: IR absorption (neat) ν 3200 (N–H), 1705 (C=O), 1678 (C=O) cm^{-1}; ^1H NMR (400 MHz, THF-d_8, 298 K) δ 0.69–0.83 (m, 6H, $2CH_2$*Me*), 0.90–1.02 (m, 2H, CH_2), 1.14–1.24 (m, 2H, CH_2), 1.70–1.77 (m, 2H, CH_2), 2.21 (s, 6H, 2*Me*), 2.23–2.44 (m, 6H, CH_2, 2C*H*NH, CH_2NH), 2.75–2.92 (m, 2H, CH_2NH), 3.71 (s, 6H, 2O*Me*), 3.98 (bs, 2H, 2N*H*), 7.57 (d, J = 1.3 Hz, 2H, $2H_{arom}$), 7.68 (s, 2H, $2H_{arom}$); $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8, 298 K) δ 14.4 (CH_2*Me*), 18.3 (*Me*), 25.8 (*C*H_2), 30.3 (*C*H_2), 42.4 (*C*H_2NH), 50.9 (O*Me*), 62.7 (*C*HNH), 117.2 ($C_{q\ arom}$), 127.7 ($C_{q\ arom}$), 131.1 (*C*H_{arom}), 132.9 ($C_{q\ arom}$), 134.2 (*C*H_{arom}), 167.7 ($C_{q\ arom}$–O), 170.1 (*C*=O); UV-vis (THF, 298 K) λ_{max} (ε) 287 (45800), 246 (26300) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^+): *m/z* $[M + H]^+$ calcd for $C_{28}H_{39}N_2O_6Zn$ 563.2094, found 563.2101; MS ($MALDI^+$): *m/z* M^+ found for $C_{28}H_{38}N_2O_6Zn$ 562.2; Elemental analysis: % calcd for $C_{28}H_{38}N_2O_6Zn\cdot\frac{1}{2}CH_2Cl_2$ 56.44 C, 6.48 H, 4.62 N, found 56.32 C, 6.45 H, 4.53 N.

IR spectra were recorded from neat samples of **4a** that were prepared according to methods A (Et_2Zn) and B ($Zn[N(TMS)_2]_2$). IR turned out to be a convenient spectroscopic technique to prove the equality of both methods.

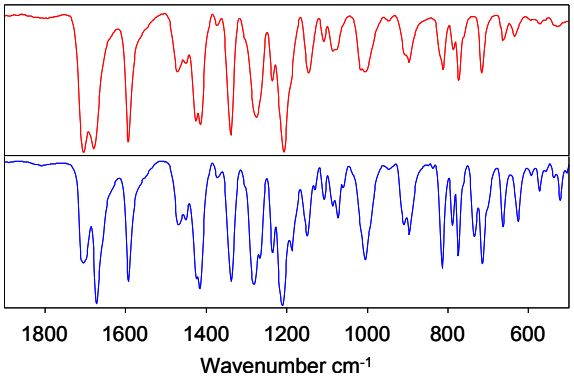


Figure 1. Comparison of the fingerprint plus carbonyl vibration region of the IR spectra of **4a** prepared by method A (red) and method B (blue).

The solution behavior of complex **4a** was also studied by NMR analysis. Figure 2 shows the ^{1}H NMR spectrum of recrystallized complex **4a** recorded at room temperature in anhydrous THF-d_8. Using other standard NMR solvents such as $CDCl_3$ or CD_2Cl_2 did not result in interpretable spectra due to significant line broadening. Assignation of the signals was aided by 2D NMR studies and comparison with spectra of complex **4b**.

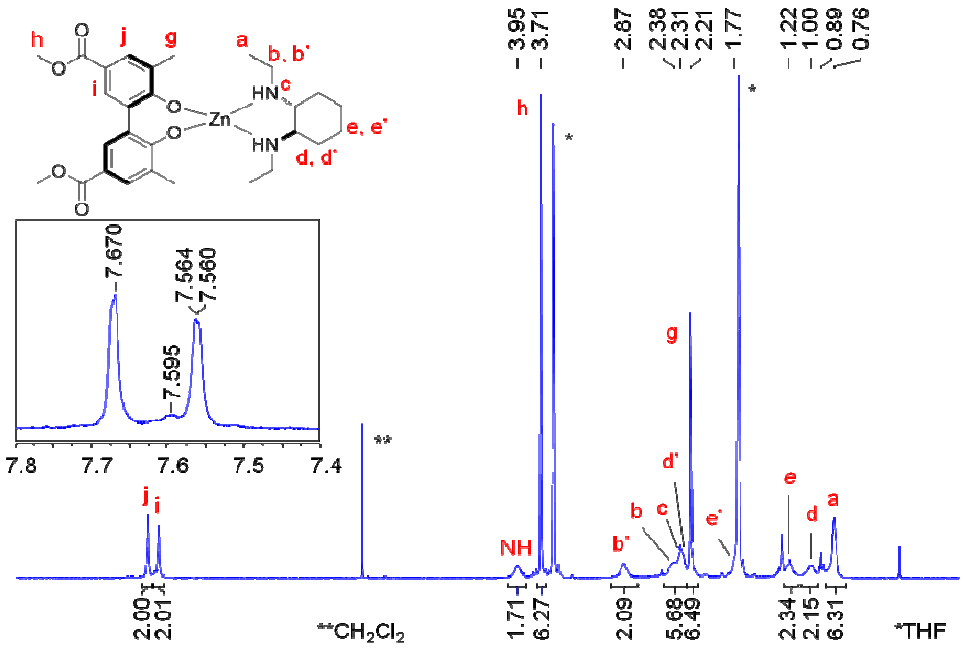


Figure 2. ^{1}H NMR (400 MHz, THF-d_8, 298 K) spectrum of complex **4a**.

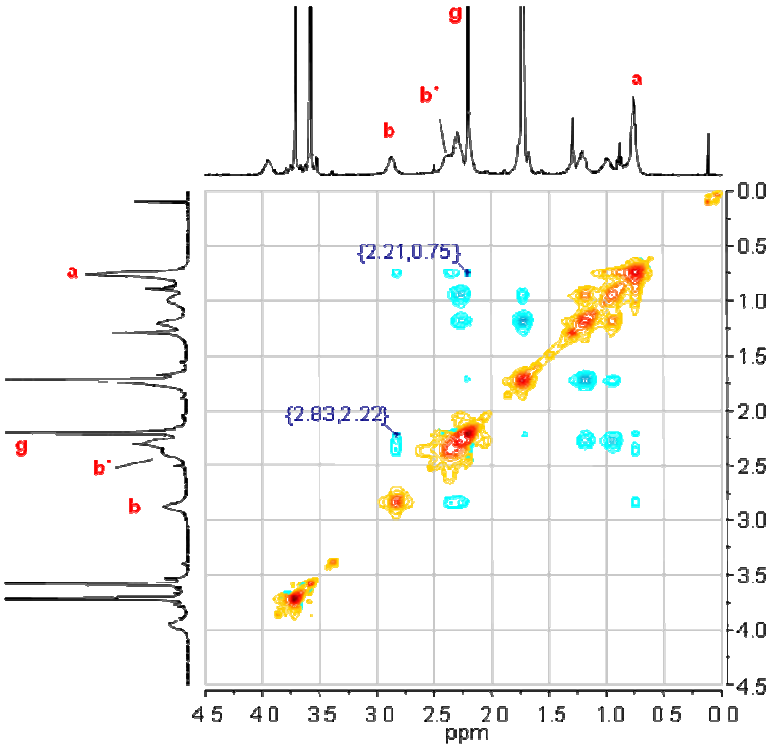
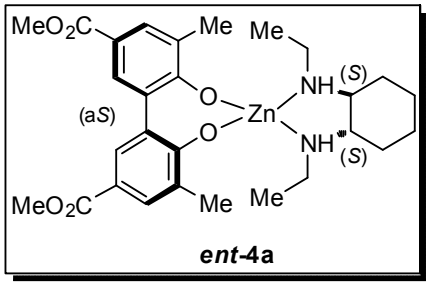


Figure 3. Detail of the ROESY spectrum (500 MHz, THF-d_8, 298 K) of complex **4a**.

2. Synthesis of mononuclear zinc(II) complex *ent*-4a



The synthesis of complex ***ent*-4a** was analogous to that of its enantiomer **4a** by following method B, using 3,3'-methyl-substituted 2,2'-biphenol **1** (120 mg, 0.36 mmol), $Zn[N(TMS)_2]_2$ (0.14 mL, 0.36 mmol, 1.0 mL ≡ 2.6 mmol), and (1*S*,2*S*)-*N*,*N*'-diethyl-1,2-cyclohexanediamine ***ent*-3a** (62 mg, 0.36 mmol). The product was obtained as a white powder (173 mg, 85% yield) and could be crystallized by slow diffusion of *n*-hexane into CH_2Cl_2. Spectroscopic and physical data of compound ***ent*-4a** were in agreement with those of its enantiomer **4a**.

Figure 4 shows the circular dichroism (CD) and UV-vis curves of complexes **4a** and its enantiomer ***ent*-4a** prepared from both (1*R*,2*R*)- and (1*S*,2*S*)-*N*,*N*'-diethyl-1,2-cyclohexanediamine (**3a** and ***ent*-3a**, respectively). Enantiopure 1,2-diamine derivatives (**3a** and ***ent*-3a**) were proven to be CD silent in the applied wavelength range and

consequently the observed Cotton effects were exclusively attributable to the biaryl chromophore.

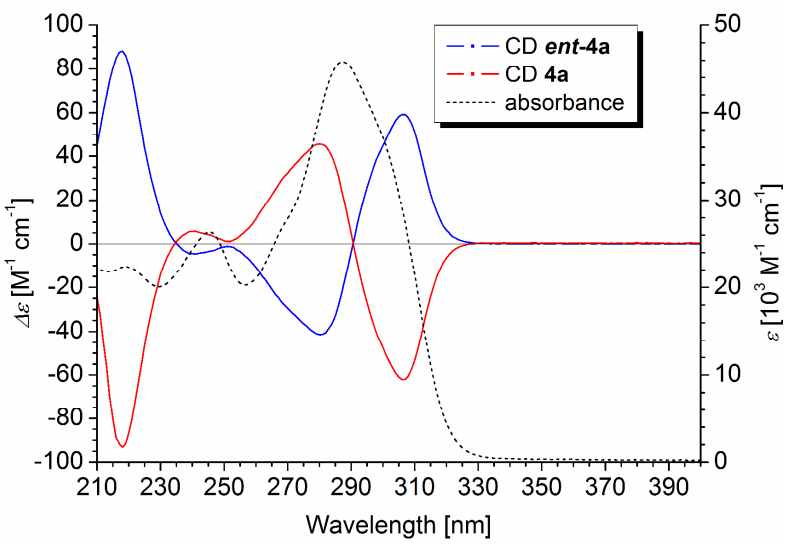


Figure 4. UV-vis absorption (dashed black line, identical for **4a** and ***ent*-4a**, right axis) and CD spectra (left axis) of **4a** and ***ent*-4a** (anhydrous THF, 298 K).

Table 1. CD and UV-vis properties of enantiomeric complexes 4a and *ent*-4a.

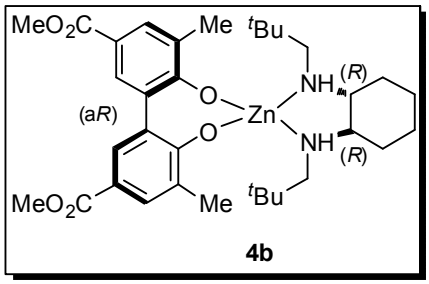
CD data	1st CE[a] Δε[b] (λ)[c]	2nd CE[a] Δε[b] (λ)[c]	3rd CE[a] Δε[b] (λ)[c]
4a	–62.1 (307)	45.5 (280)	–93.3 (218)
***ent*-4a**	59.2 (306)	–41.4 (280)	88.2 (218)
UV data	λ[c] (ε)[b]	λ[c](ε)[b]	λ[c](ε)[b]
	287 (45800)	246 (26300)	219 (22400)

[a]CE = Cotton effect. [b]$M^{-1}\cdot cm^{-1}$. [c]nm.

3. Synthesis of mononuclear zinc(II) complex 4b

The synthesis of complex **4b** was carried out by following method A, using 3,3'-methyl-substituted 2,2'-biphenol **1** (73 mg, 0.22 mmol), a 1.03 M solution of Et_2Zn in toluene (0.21 mL, 0.22 mmol), and (1*R*,2*R*)-*N*,*N*'-di-*tert*-butylmethyl-1,2-cyclohexanediamine **3b** (56 mg, 0.22 mmol). The product was obtained as a white powder (131 mg, 92% yield). The synthesis of complex **4b** was also successfully

accomplished by following method B, using 3,3'-methyl-substituted 2,2'-biphenol **1** (73 mg, 0.22 mmol), $Zn[N(TMS)_2]_2$ (0.085 mL, 0.22 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-*N*,*N*'-di-*tert*-butylmethyl-1,2-cyclohexanediamine **3b** (56 mg, 0.22 mmol). The product was obtained as a white powder (120 mg, 84% yield) and could be crystallized by slow diffusion of *n*-hexane into CH_2Cl_2.



Mononuclear zinc(II) complex **4b**: IR absorption (neat) ν 3253 (N–H), 1702 (C=O), 1680 (C=O) cm^{-1}; ^1H NMR (500 MHz, THF-d_8, 253 K) δ 0.69 (s, 18H, 2^tBu), 1.09–1.22 (m, 2H, CH_2), 1.22–1.34 (m, 2H, CH_2), 1.84 (d, J = 7.2 Hz, 2H, CH_2), 2.21 (s, 6H, 2*Me*), 2.33–2.46 (m, 4H, CH_2, 2C*H*NH), 2.56 (d, J = 11.0 Hz, 2H, CH_2NH), 2.83 (dd, J = 11.0 and 8.8 Hz, 2H, CH_2NH), 3.10 (dd, J = 11.0 and 8.8 Hz, 2H, 2N*H*), 3.70 (s, 6H, 2O*Me*), 7.47 (d, J = 1.8 Hz, 2H, 2H_{arom}), 7.67 (d, J = 1.8 Hz, 2H, 2H_{arom}); ^{13}C NMR (DEPTQ135, 125 MHz, THF-d_8, 298 K) δ 18.6 (*Me*), 25.8 (*C*H_2), 27.2 (*C*H_3(^{t}Bu)), 30.2 (*C*H_2), 31.4 (*C*(^{t}Bu)), 50.6 (O*Me*), 59.2 (*C*H_2NH), 62.9 (*C*HNH), 116.7 ($C_{q\ arom}$), 126.8 ($C_{q\ arom}$), 130.9 (*C*H_{arom}), 132.9 ($C_{q\ arom}$), 134.7 (*C*H_{arom}), 167.5 ($C_{q\ arom}$–O), 170.5 (*C*=O); UV-vis (THF, 298 K) λ_{max} (ε) 287 (40600), 245 (24100) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^+): *m/z* $[M + Na]^+$ calcd for $C_{34}H_{50}N_2NaO_6Zn$ 669.2853, found 669.2603; MS ($MALDI^+$): *m/z* M^+ found for $C_{34}H_{50}N_2O_6Zn$ 646.2.

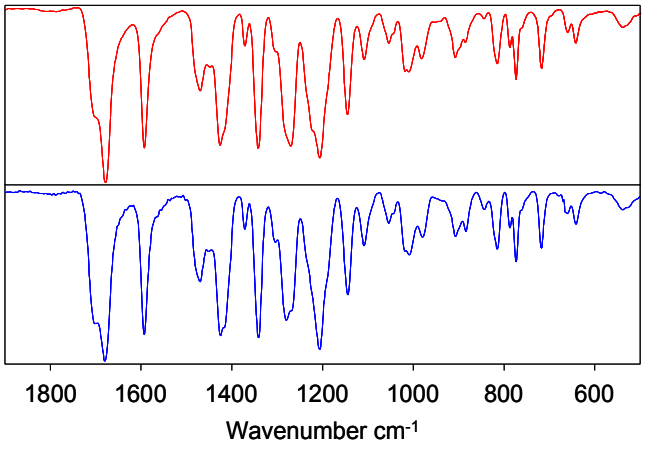


Figure 5. Comparison of the fingerprint plus carbonyl stretching vibration region of the IR spectra of **4b** prepared by method A (red) and method B (blue).

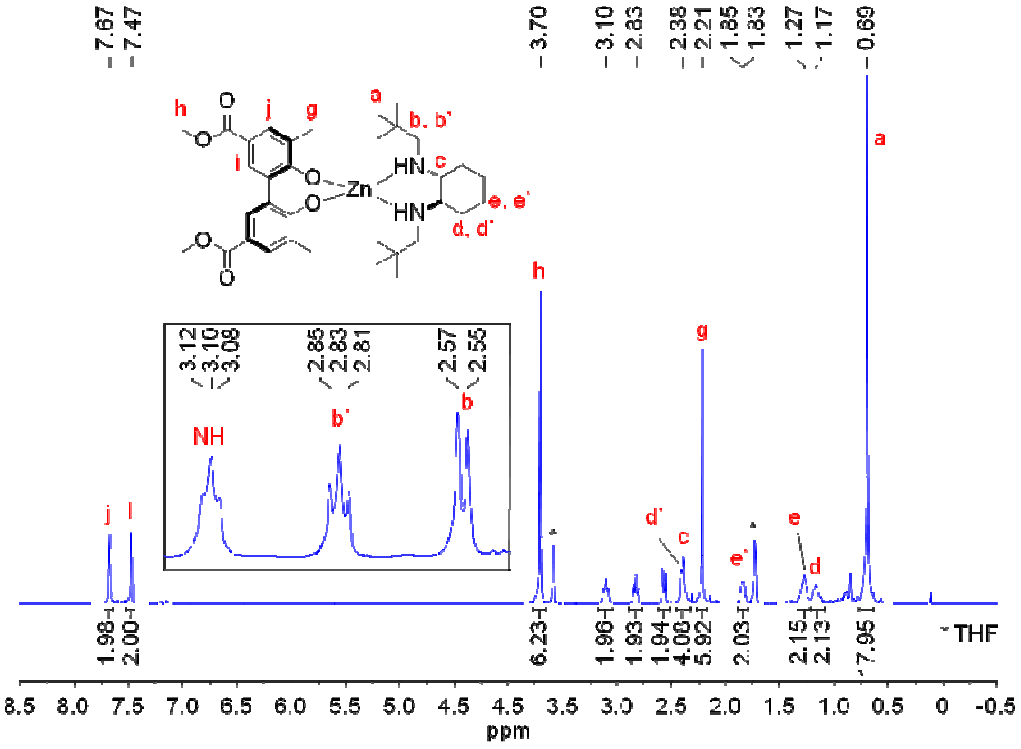


Figure 6. ^{1}H NMR (500 MHz, THF-d_8, 253 K) spectrum of complex **4b**.

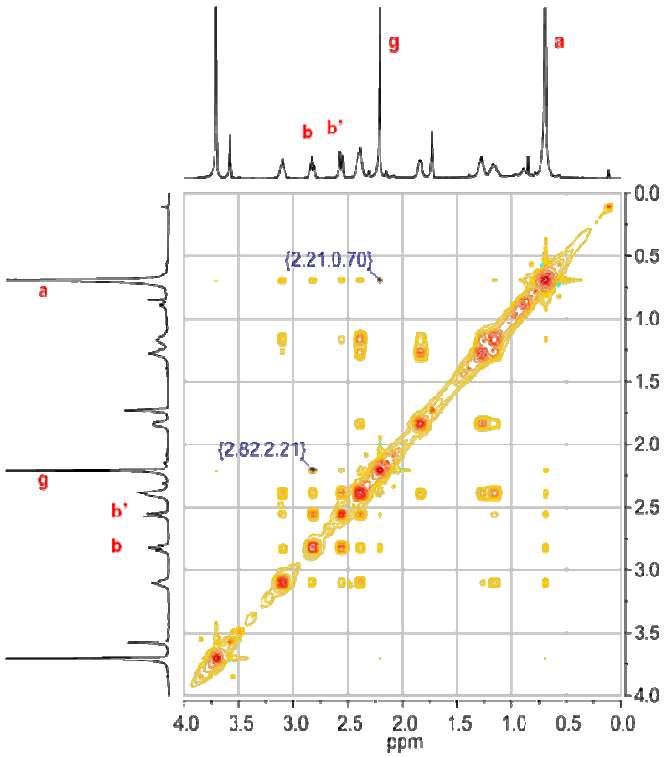


Figure 7. Detail of the NOESY spectrum (500 MHz, THF-d_8, 253 K) of complex **4b**.

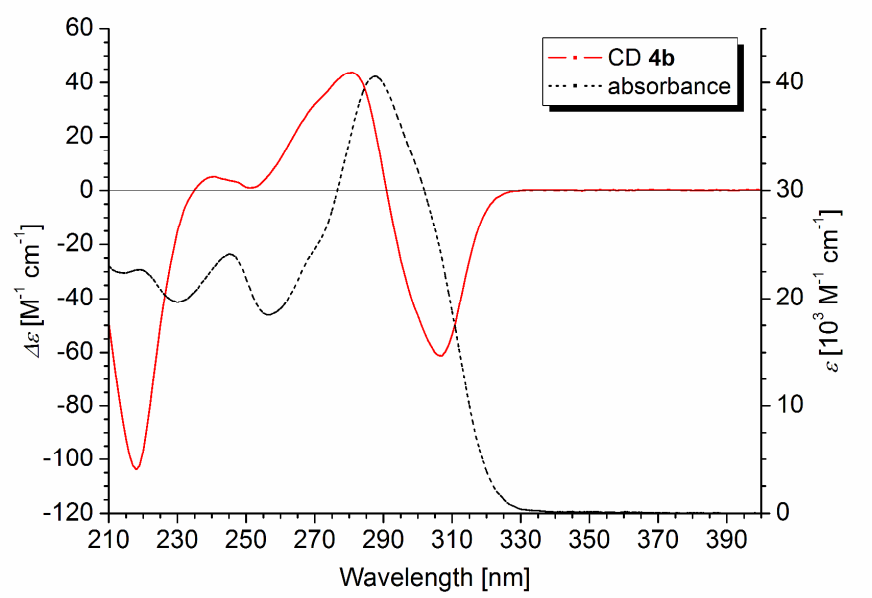


Figure 8. UV-vis absorption (dashed black line, right axis) and CD spectrum (left axis) of **4b** (anhydrous THF, 298 K).

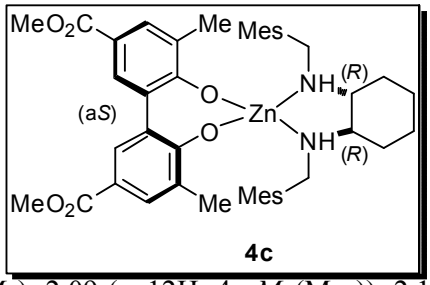
Table 2. CD and UV-vis properties of complex 4b.

CD data	1st CE[a]	2nd CE[a]	3rd CE[a]
	$\Delta\varepsilon^b$ $(\lambda)^c$	$\Delta\varepsilon^b$ $(\lambda)^c$	$\Delta\varepsilon^b$ $(\lambda)^c$
	−61.3 (307)	43.9 (281)	−103 (218)
UV data	λ^c $(\varepsilon)^b$	$\lambda^c(\varepsilon)^b$	$\lambda^c(\varepsilon)^b$
	288 (40600)	245 (24100)	219 (22700)

[a]CE = Cotton effect. [b]$M^{-1}\cdot cm^{-1}$. [c]nm.

4. Synthesis of mononuclear zinc(II) complex 4c

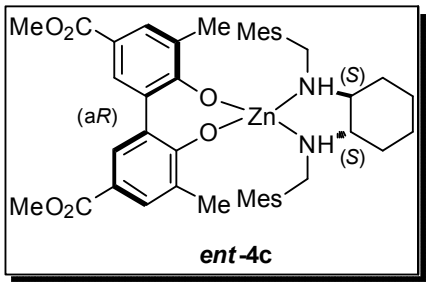
The synthesis of complex **4c** was carried out by following method B, using 3,3'-methyl-substituted 2,2'-biphenol **1** (100 mg, 0.30 mmol), $Zn[N(TMS)_2]_2$ (0.12 mL, 0.30 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-*N*,*N*'-dimesitylmethyl-1,2-cyclohexanediamine **3c** (115 mg, 0.30 mmol). The product was obtained as a white powder (150 mg, 65% yield). The same result (64% yield) was obtained by using method A.



4c

Mononuclear zinc(II) complex **4c**: IR absorption (neat) ν 3585 (N–H), 1707 (C=O) cm^{-1}; ^1H NMR (400 MHz, THF-d_8, 298 K) δ 1.12–1.22 (m, 2H, CH_2), 1.29–1.37 (m, 2H, CH_2), 1.78–1.83 (m, 2H, CH_2), 1.90 (s, 6H, 2*Me*), 2.09 (s, 12H, 4*o*-*Me*(Mes)), 2.17 (s, 6H, 2*p*-*Me*(Mes)), 2.34–2.40 (m, 2H, CH_2), 2.52–2.63 (m, 2H, 2N*H*), 2.77–2.88 (m, 2H, 2C*H*NH), 3.73 (s, 6H, 2O*Me*), 3.95 (dd, *J* = 13.2 and 8.2 Hz, 2H, CH_2NH), 4.04 (dd, *J* = 13.2 and 5.2 Hz, 2H, CH_2NH), 6.64 (s, 4H, 4H_{arom}(Mes)), 7.47 (d, *J* = 2.1 Hz, 2H, 2H_{arom}), 7.62 (d, *J* = 2.1 Hz, 2H, 2H_{arom}); $^{13}C\{^1H\}$ NMR (DEPTQ135, 125 MHz, THF-d_8, 298 K) δ 18.3 (*Me*), 19.6 (*o*-*Me*(Mes)), 20.8 (*p*-*Me*(Mes)), 25.7 (*C*H_2), 32.2 (*C*H_2), 46.2 (*C*H_2NH), 50.7 (O*Me*), 63.9 (*C*HNH), 116.9 ($C_{q\ arom}$), 127.4 ($C_{q\ arom}$), 130.2 (*C*H_{arom}(Mes)), 130.8 ($C_{q\ arom}$(Mes)), 130.9 (*C*H_{arom}), 132.5 ($C_{q\ arom}$), 134.0 (*C*H_{arom}), 137.5 ($C_{q\ arom}$(Mes)), 138.2 ($C_{q\ arom}$(Mes)), 167.6 ($C_{q\ arom}$–O), 170.0 (*C*=O); UV-vis (THF, 298 K) λ_{max} (ε) 287 (35300), 246 (23300), 218 (40300) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^+): *m/z* $[M + H]^+$ calcd for $C_{44}H_{55}N_2O_6Zn$ 771.3346, found 771.3185; MS ($MALDI^+$): *m/z* $[M + H]^+$ found for $C_{44}H_{55}N_2O_6Zn$ 771.4.

5. Synthesis of mononuclear zinc(II) complex *ent*-4c



***ent*-4c**

The synthesis of complex ***ent*-4c** was analogous to that of its enantiomer **4c** by following method A, using 3,3'-methyl-substituted 2,2'-biphenol **1** (100 mg, 0.30 mmol), a 1.03 M solution of Et_2Zn in toluene (0.29 mL, 0.30 mmol), and (1*S*,2*S*)-*N*,*N*'-dimesitylmethyl-1,2-cyclohexanediamine ***ent*-3c** (115 mg, 0.30 mmol). The product was obtained as a white powder (152 mg, 65% yield). Spectroscopic and physical data of compound ***ent*-4c** were in agreement with those of its enantiomer **4c**.

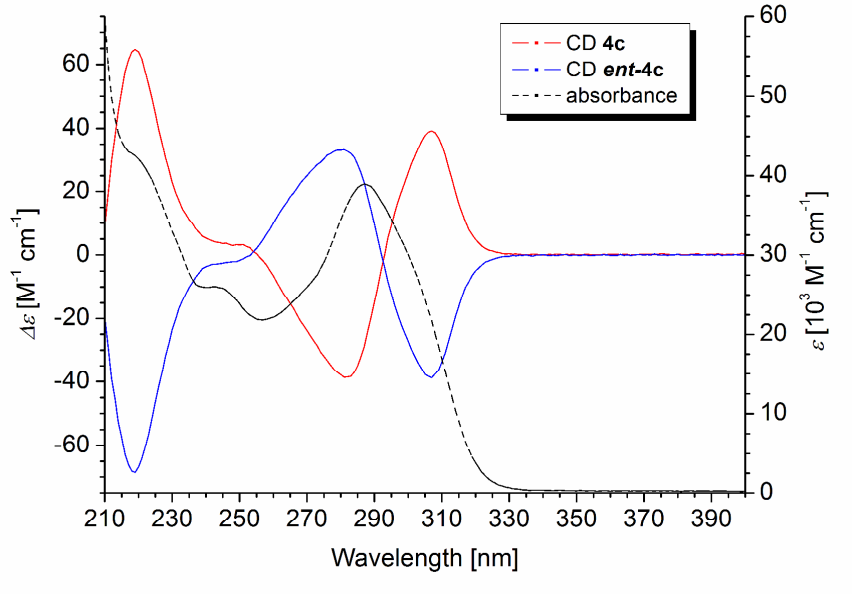


Figure 9. UV-vis absorption (dashed black curve, identical for **4c** and ***ent*-4c**, right axis) and CD spectra (left axis) of **4c** and ***ent*-4c** measured in anhydrous THF at 298 K.

Table 3. CD and UV-vis properties of enantiomeric complexes 4c and *ent*-4c.

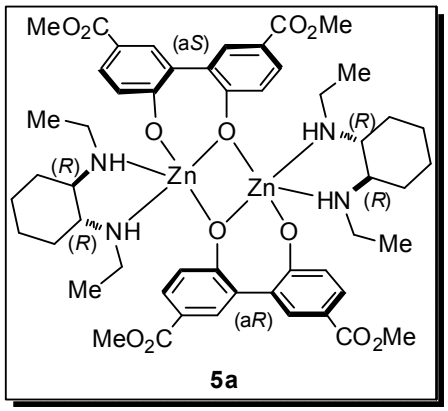
CD data	1st CE[a] Δε[b] (λ)[c]	2nd CE[a] Δε[b] (λ)[c]	3rd CE[a] Δε[b] (λ)[c]
4c	39.2 (307)	–38.6 (282)	64.7 (219)
***ent*-4c**	–38.8 (306)	33.2 (281)	–68.6 (219)
UV data	λ[c] (ε)[b]	λ[c](ε)[b]	λ[c](ε)[b]
	287 (39000)	243 (26100)	217 (43100)

[a]CE = Cotton effect. [b]$M^{-1}\cdot cm^{-1}$. [c]nm.

(D) Synthesis of Dinuclear Chiral Zinc(II) Complexes

1. Synthesis of dinuclear zinc(II) complex 5a and *ent*-5a

The synthesis of complex **5a** was carried out by following method B, using 3,3'-unsubstituted 2,2'-biphenol **2** (88 mg, 0.29 mmol), $Zn[N(TMS)_2]_2$ (0.11 mL, 0.29 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-*N*,*N*'-diethyl-1,2-cyclohexanediamine **3a** (50 mg, 0.29 mmol). The product was obtained as a white powder (117 mg, 75% yield) and could be crystallized by slow diffusion of *n*-hexane into CH_2Cl_2. The complex **5a** was also prepared by following method A resulting in higher yield (85% yield). The enantiomeric complex of **5a** (***ent*-5a**) was also prepared by following methods A (69% yield) and B (74% yield) starting from (1*S*,2*S*)-*N*,*N*'-diethyl-1,2-cyclohexanediamine (***ent*-3a**). Spectroscopic and physical data of compound ***ent*-5a** were in agreement with those of its enantiomer **5a**.



5a

Dinuclear zinc(II) complex **5a**: IR absorption (neat) ν 3232 (N–H), 1700 (C=O) cm^{-1}; ^1H NMR (500 MHz, THF-d_8, 298 K) δ 0.65–0.82 (m, 4H, 2CH_2), 0.84–1.01 (m, 12H, 4CH_2Me), 1.03–1.21 (m, 4H, 2CH_2), 1.55–1.68 (m, 4H, 2CH_2), 1.84–2.14 (m, 12H, 2CH_2, 4C*H*NH, 2CH_2NH), 2.33–2.55 (bs, 4H, 4N*H*), 2.56–2.77 (m, 4H, 2CH_2NH), 3.76 (s, 12H, 4O*Me*), 6.70–6.86 (m, 4H, 4H_{arom}), 7.78 (d, J = 7.3 Hz, 4H, 4H_{arom}), 7.84 (s, 4H, 4H_{arom}); $^{13}C\{^1H\}$ NMR Due to the poor signal to noise ratio, no ^{13}C NMR spectrum could be recorded for this compound; UV-vis (THF, 298 K) λ_{max} (ε) 283 (41200), 241 (23700) nm ($M^{-1}\cdot cm^{-1}$); UV-vis (CH_2Cl_2, 298 K) λ_{max} (ε) 284 (40000), 240 (24700) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^+): *m/z* $[M + Na]^+$ calcd for monomer $C_{26}H_{34}N_2NaO_6Zn$ 557.1601, found 557.1542, *m/z* $[M + Na]^+$ calcd for dimer $C_{52}H_{68}N_4NaO_{12}Zn_2$ 1091.3309, found 1091.3115; MS ($MALDI^+$) *m/z* M^+ found for monomer $C_{26}H_{34}N_2O_6Zn$ 534.1; Elemental analysis: % calcd for $C_{52}H_{68}N_4O_{12}Zn_2\cdot\frac{1}{3}CH_2Cl_2$ 57.13 C, 6.29 H, 5.09 N, found 57.59 C, 6.29 H, 5.19 N.

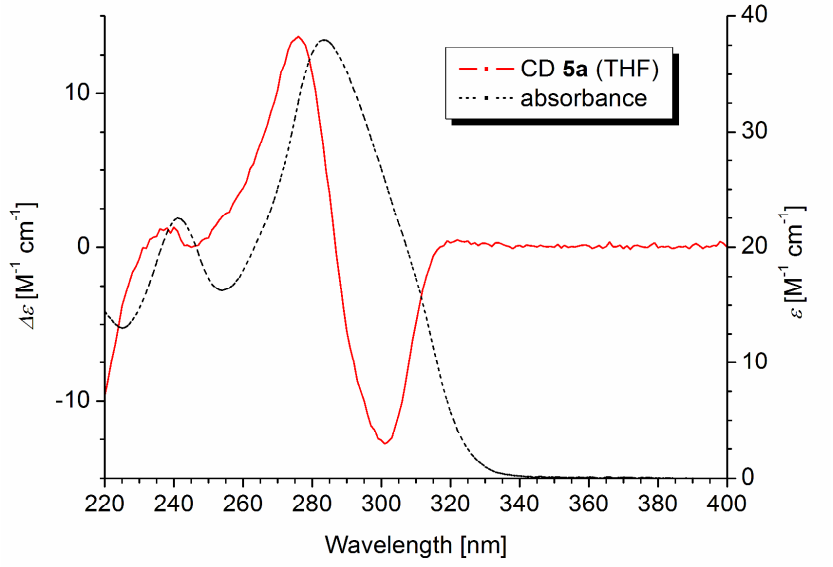
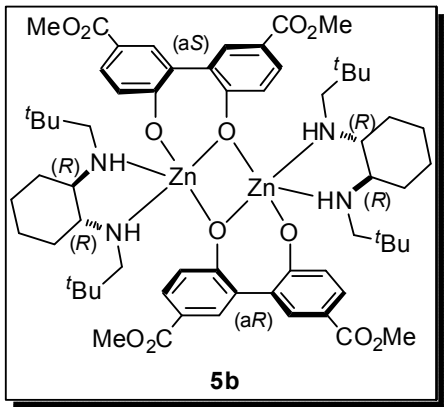


Figure 10. CD and UV spectra of complex **5a** in anhydrous THF ($1.3 \cdot 10^{-4}$ M).

2. Synthesis of dinuclear zinc(II) complex 5b

The synthesis of complex **5b** was carried out by following the method B, using 3,3'-unsubstituted 2,2'-biphenol **2** (67 mg, 0.22 mmol), $Zn[N(TMS)_2]_2$ (0.085 mL, 0.22 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-*N*,*N*'-di-*tert*-butylmethyl-1,2-cyclohexanediamine **3b** (56 mg, 0.22 mmol). The product was obtained as a white powder (80 mg, 90% yield). The complex **5b** was also prepared by following method A resulting in similar yield (81% yield).



5b

Dinuclear zinc(II) complex **5b**: IR absorption (neat) ν 3258 (N–H), 3165 (N–H), 1709 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8, 298 K) δ 0.25–2.80 (m, 64H, ^tBu, CH_2, and CH), 3.79 (s, 12H, 4OMe), 6.40–7.25 (m, 4H, $4H_{arom}$), 7.35–8.30 (m, 8H, $8H_{arom}$), 4H were missing since the N–H protons were not detected, protons were not unequivocally assigned because of the broadening of the signals; $^{13}C\{^1H\}$ NMR Due to the poor signal to noise ratio, no ^{13}C NMR spectrum could be recorded for this compound; UV-vis

(THF, 298 K) λ_{max} (ε) 278 (47900), 240 (34200) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^+): *m/z* [M + Na]$^+$ calcd for monomer $C_{32}H_{46}N_2NaO_6Zn$ 641.2540, found 641.2973, *m/z* [M + H]$^+$ calcd for monomer $C_{32}H_{47}N_2O_6Zn$ 619.2720, found 619.3359, *m/z* [M + H]$^+$ calcd for dimer $C_{64}H_{93}N_4O_{12}Zn_2$ 1237.5367, found 1237.5771; MS ($MALDI^+$) *m/z* M^+ found for monomer $C_{32}H_{46}N_2O_6Zn$ 618.3.

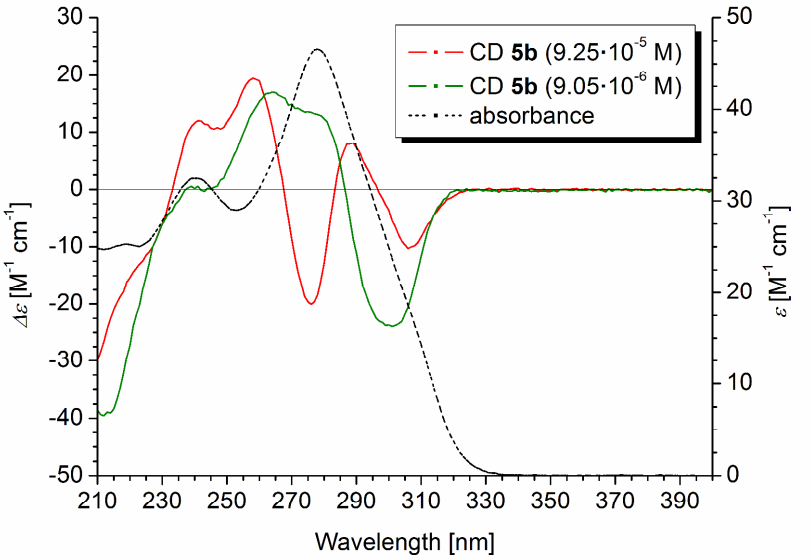
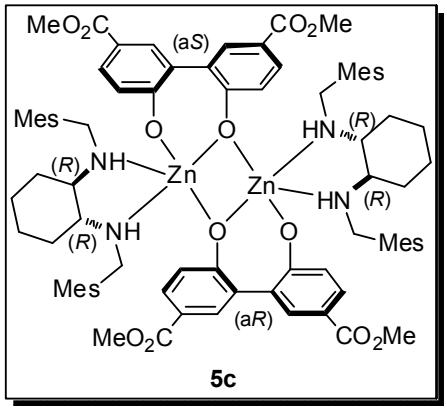


Figure 11. CD and UV spectra of complex **5b** in anhydrous THF at different concentrations.

3. Synthesis of dinuclear zinc(II) complex 5c and *ent*-5c

The synthesis of complex **5c** was carried out by following method B, using 3,3'-unsubstituted 2,2'-biphenol **2** (100 mg, 0.33 mmol), $Zn[N(TMS)_2]_2$ (0.13 mL, 0.34 mmol; 1.0 mL ≡ 2.6 mmol), and (1*R*,2*R*)-*N*,*N*'-dimesitylmethyl-1,2-cyclohexanediamine **3c** (127 mg, 0.33 mmol). The product was obtained as a white powder (214 mg, 83% yield) and could be crystallized by slow diffusion of *n*-hexane into THF. The enantiomeric complex of **5c** (***ent*-5c**) was also prepared by following methods A (84% yield) and B (80% yield) starting from (1*S*,2*S*)-*N*,*N*'-dimesitylmethyl-1,2-cyclohexanediamine (***ent*-3c**). Spectroscopic and physical data of compound ***ent*-5c** were in agreement with those of its enantiomer **5c**.



5c

Dinuclear zinc(II) complex **5c**: IR absorption (neat) ν 3335 (N–H), 1709 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8, 298 K) δ 0.60–1.61 (m, 16H, 8CH_2), 2.19 (s, 24H, 8*o*-*Me*(Mes)), 2.19–2.57 (m, 8H, 4C*H*NH and 4N*H*), 2.24 (s, 12H, 4*p*-*Me*(Mes)), 3.66–4.08 (m, 8H, 4CH_2NH), 3.84 (s, 12H, 4O*Me*), 6.58–6.94 (m, 12H, 4H_{arom} and 8H_{arom}(Mes)), 7.55–7.98 (m, 8H, 8H_{arom}); $^{13}C\{^{1}H\}$ NMR Due to the poor signal to noise ratio, no ^{13}C NMR spectrum could be recorded for this compound; UV-vis (THF, 298 K) λ_{max} (ε) 279 (43400) nm ($M^{-1}\cdot cm^{-1}$); HRMS (ESI^{+}): *m/z* $[M + H]^{+}$ calcd for monomer $C_{42}H_{51}N_2O_6Zn$ 743.3033, found 743.2747, *m/z* $[M + H]^{+}$ calcd for dimer $C_{84}H_{101}N_4O_{12}Zn_2$ 1489.5993, found 1489.5979; MS ($MALDI^{+}$) *m/z* $[M + H]^{+}$ found for monomer $C_{42}H_{51}N_2O_6Zn$ 743.3.

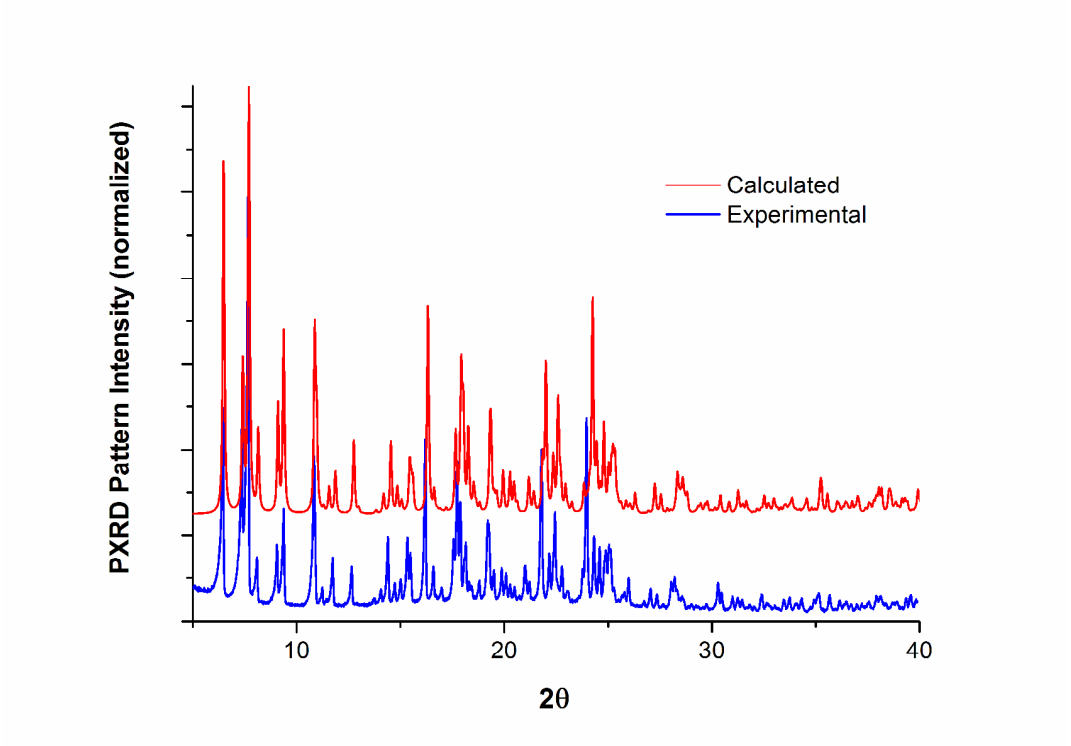


Figure 12. Calculated (red) and experimental (blue) powder diffraction pattern of complex **5c**.

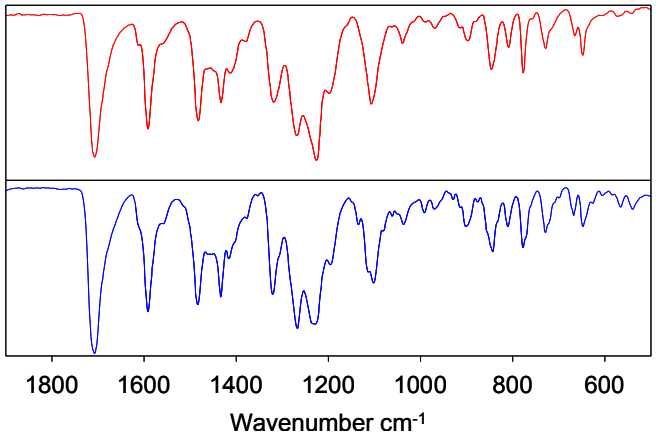


Figure 13. Comparison of the carbonyl stretching vibration and fingerprint regions of the IR spectra of **5c** prepared by method A (red) and method B (blue).

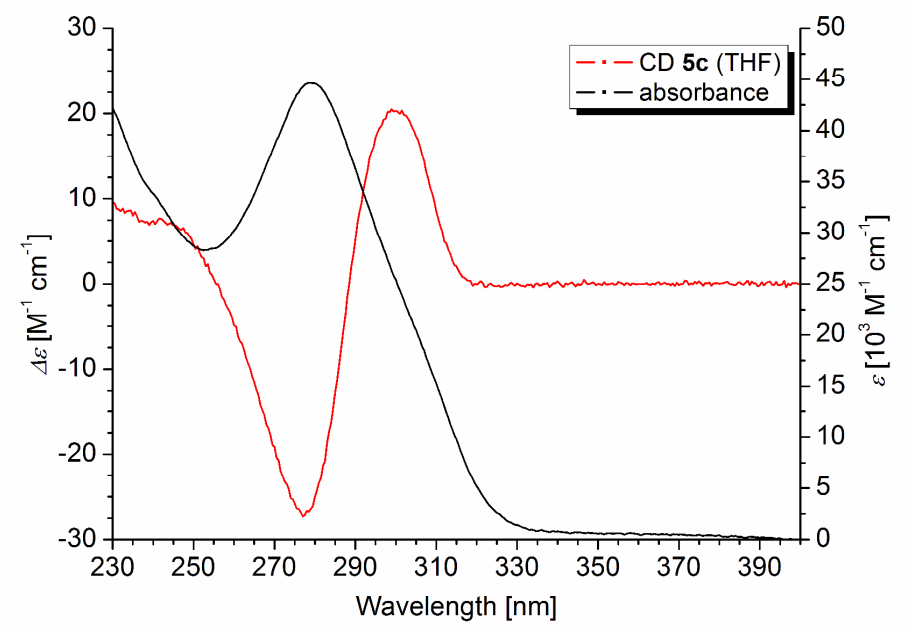


Figure 14. CD and UV spectra of complex **5c** in anhydrous THF.

(E) Single Crystal X-Ray Structure Determinations

Crystal preparation: Crystals of **4a**, ***ent*-4a**, **4b** and **5a** were obtained by slow diffusion of *n*-hexane into dichloromethane and **5c** and ***ent*-5c** were obtained by slow diffusion of *n*-hexane into THF. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determinations for samples **4a**, ***ent*-4a**, **4b**, **5a**, and **5c** were carried out using a Bruker-Nonius diffractometer equipped with an APEX II 4K CCD area detector, a FR591 rotating anode with MoK_α radiation, Montel mirrors as monochromator, a Kappa 4-axis goniometer and a Oxford Cryosystem plus low temperature device (T = –173 °C). Crystal structure determination for sample ***ent*-5c** was carried out on a APEX DUO Kappa 4-axis goniometer equipped with an APEX II 4K CCD area detector, two Microfocus E025 IμS X-ray sources ($Mo_{K\alpha}$ and $Cu_{K\alpha}$), Quazar MX multilayer optics and an Oxford Cryosystem plus low temperature device (T = –173 °C).

Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection APEX-2[4], data reduction Bruker Saint[5] V/.60A and absorption correction with SADABS[6]

Structure Solution and Refinement: Crystal structure solutions were achieved using direct methods as implemented in SHELXTL[7] and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXTL. All non hydrogen atoms were refined including anisotropic displacement parameters. The crystal data parameters are listed in Tables 4 and 5.

Compound **4a** crystallizes as a dichloromethane hemisolvate. The structure of ***ent*-4a** is identical to **4a** but with inverted stereogenic elements. The asymmetric unit of **4b** contains three independent molecules of the complex, one *n*-hexane molecule disordered in three positions (ratio 50:30:20) and two water molecules (one of the water

[4] Data collection with APEX II versions v1.0-22, v2009.1-0 and v2009.1-02. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[5] Data reduction with Bruker SAINT versions V.2.10(2003), V/.60A and V7.60A. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[6] SADABS: V.2.10(2003); V2008 and V2008/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA. Blessing, *Acta Cryst.* **1995**, *A51* 33.
[7] Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112. SHELXTL versions V6.12 and 6.14.

molecules is disordered in two positions with a ratio 70:30). Compound **5a** is a dichloromethane disolvate. This structure shows pseudo centrosymmetry and can also be refined applying a disorder model in the space group *P*-1. Since it is known that enantiomerically pure amine **3a** was used in its synthesis, its structure was refined in the chiral space group *P*1. Due to the effects of the pseudo centrosymmetry the structure was refined as a twin leading to a Flack/BASF value of 0.09(3). Compound **5c** crystallizes as a tetrahydrofurane disolvate. The structure of ***ent*-5c** is identical to **5c** but with inverted stereogenic elements.

Table 4: Crystal data for compounds **4a, *ent*-4a**, and **4b**.

Compound	**4a**	***ent*-4a**	**4b**
Formula	$C_{28}H_{38}N_2O_6Zn_1$	$C_{28}H_{38}N_2O_6Zn_1$	3 $C_{34}H_{50}N_2O_6Zn_1$
Solvent	+ 1/2 CH_2Cl_2	+ 1/2 CH_2Cl_2	+ *n*-C_6H_{14} + 2 H_2O
Formula weight (total)	606.44	606.44	688.86
Crystal size (mm^3)	0.20 x 0.10 x 0.01	0.20 x 0.10 x 0.10	0.05 x 0.05 x 0.03
Crystal color	colorless	colorless	colorless
Temp (K)	100	100	100
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$C222_1$	$C222_1$	$P2_12_12_1$
A (Å)	13.3467(5)	13.2743(7)	16.1449(13)
B (Å)	29.9015(11)	29.7684(14)	24.1265(18)
C (Å)	14.6339(6)	14.6565(7)	30.798(2)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V ($Å^3$)	5840.2(4)	5791.6(5)	11996.4(16)
Z	8	8	12
ρ (g/cm^3)	1.379	1.391	1.144
μ (mm^{-1})	0.976	0.984	0.657
θ_{max} (°)	29.62	35.93	25.53
Reflec. measured	28332	18859	83795
Unique reflections obv.	6065 [R_{int} = 0.0707]	10313 [R_{int} = 0.0251]	11517 [R_{int} = 0.1871]
Absorpt. correct.	SADABS	SADABS	SADABS
Trans. min/max	081/0.98	0.91/1.00	0.9679/0.9806
Parameters	354	362	1346
R1/wR2 [I>2σ(I)]	0.0433/0.0933	0.0389/0.0942	0.0782/0.1715
R1/wR2 [all data]	0.0685/0.1031	0.0519/0.1013	0.1668/0.2106
Goodness-of-fit (F^2)	1.013	1.033	1.030
Abs. Struct. Flack (std)	0.005(10)	–0.033(7)	0.00(4)
Peak/hole (e/$Å^3$)	0.768/–0.412	1.004/–0.423	0.752/–0.568

Table 5: Crystal data for compounds **5a, 5c**, and ***ent*-5c**.

Compound	**5a**	**5c**	***ent*-5c**
Formula	$C_{54}H_{68}N_4O_{12}Zn_2$	$C_{84}H_{100}N_4O_{14}Zn_2$	$C_{84}H_{100}N_4O_{14}Zn_2$
Solvent	+ 2 CH_2Cl_2	+ 2 $C_4H_8O_1$(THF)	+ 2 $C_4H_8O_1$(THF)
Formula weight (total)	1241.70	1632.63	1632.63
Crystal size (mm^3)	0.20 x 0.02 x 0.01	0.08 x 0.03 x 0.02	0.08 x 0.03 x 0.02
Crystal color	colorless	colorless	colorless
Temp (K)	100	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	*P*1	*P*1	*P*1
A (Å)	8.3882(11)	11.8749(4)	11.8706(7)
B (Å)	11.5834(12)	12.7931(5)	12.7734(9)
C (Å)	15.6238(17)	14.4674(6)	14.4742(10)
α (deg)	104.822(7)	106.696(2)	106.635(2)
β (deg)	95.921(7)	97.038(2)	97.083(2)
γ (deg)	93.118(8)	100.631(2)	100.6200(10)
V ($Å^3$)	1454.6(3)	2032.77(13)	2030.4(2)
Z	1	1	1
ρ (g/cm^3)	1.418	1.334	1.335
μ (mm^{-1})	1.070	0.658	0.659
θ_{max} (°)	25.47	32.74	30.69
Reflec. measured	16626	43671	24647
Unique reflections obv.	6143 [R_{int} = 0.0549]	19129 [R_{int} = 0.0504]	17008 [R_{int} = 0.0255]
Absorpt. correct.	SADABS	SADABS	SADABS
Trans. min/max	0.82/0.98	0.91/1.00	0.9492/0.9869
Parameters	668	1053	1053
R1/wR2 [I>2σ(I)]	0.0896/0.2350	0.0461/0.1011	0.0481/0.1274
R1/wR2 [all data]	0.1238/0.2631	0.0686/0.1111	0.0616/0.1577
Goodness-of-fit (F^2)	1.088	0.986	1.037
Abs. Struct. Flack (std)	0.09(3)	0.002(6)	-0.024(8)
Peak/hole (e/$Å^3$)	2.145/–1.088	0.694/–0.361	0.882/–1.226

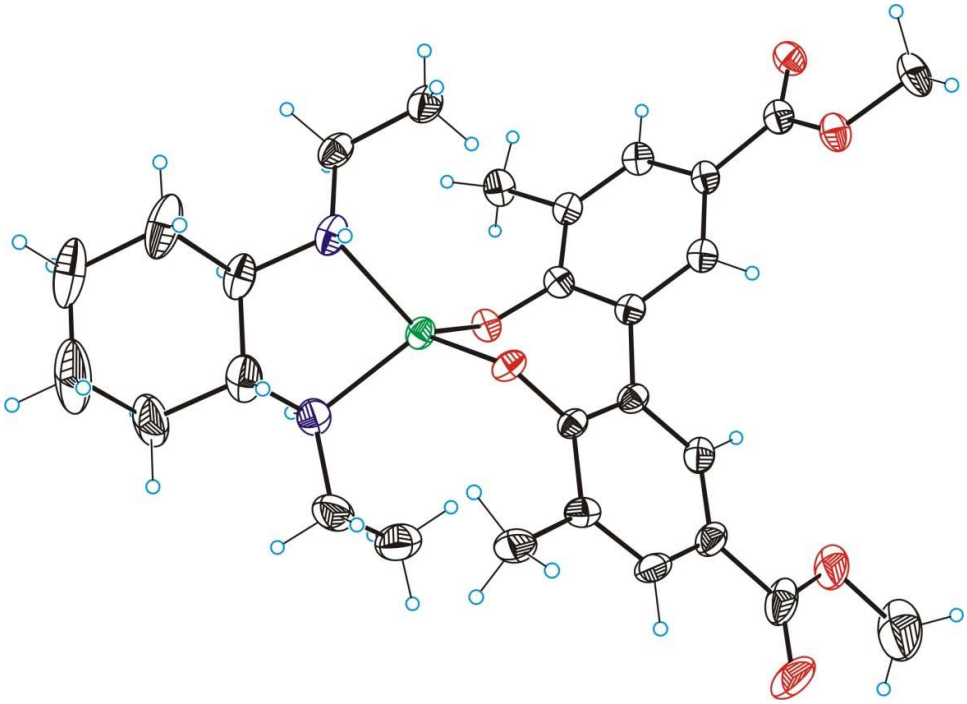


Figure 15. Ortep plot (50%) showing the molecular structure of compound **4a**.

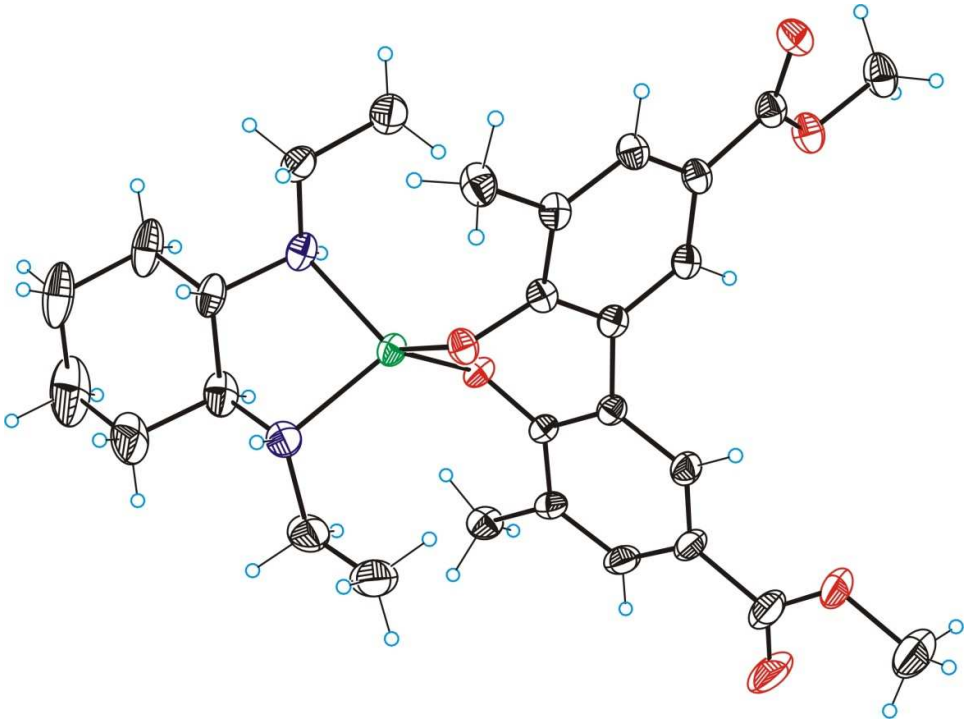


Figure 16. Ortep plot (50%) showing the molecular structure of compound ***ent*-4a**.

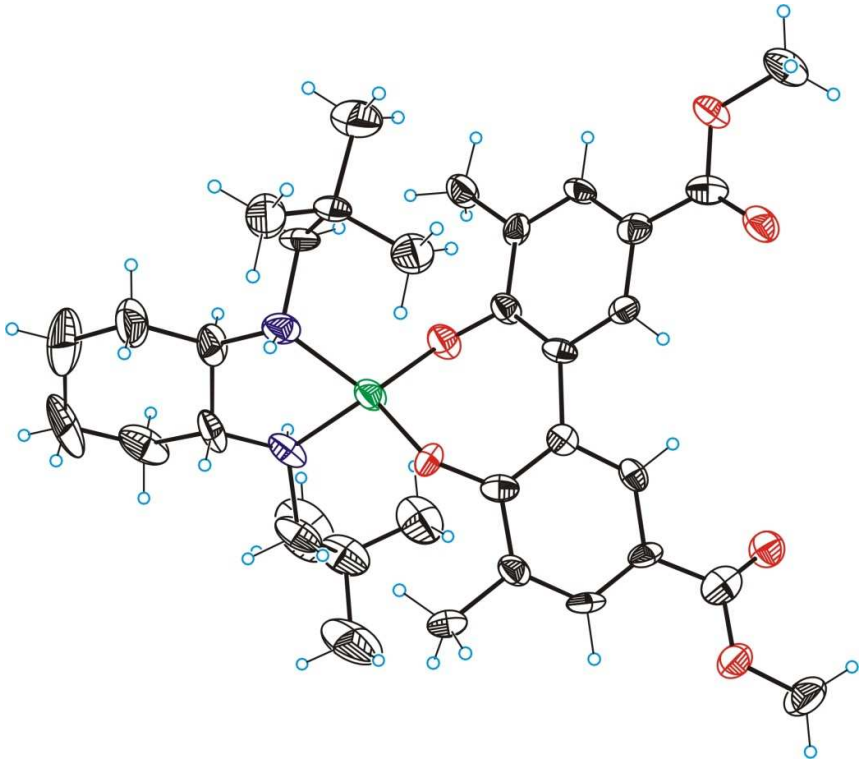


Figure 17. Ortep plot (50%) showing the molecular structure of compound **4b**.

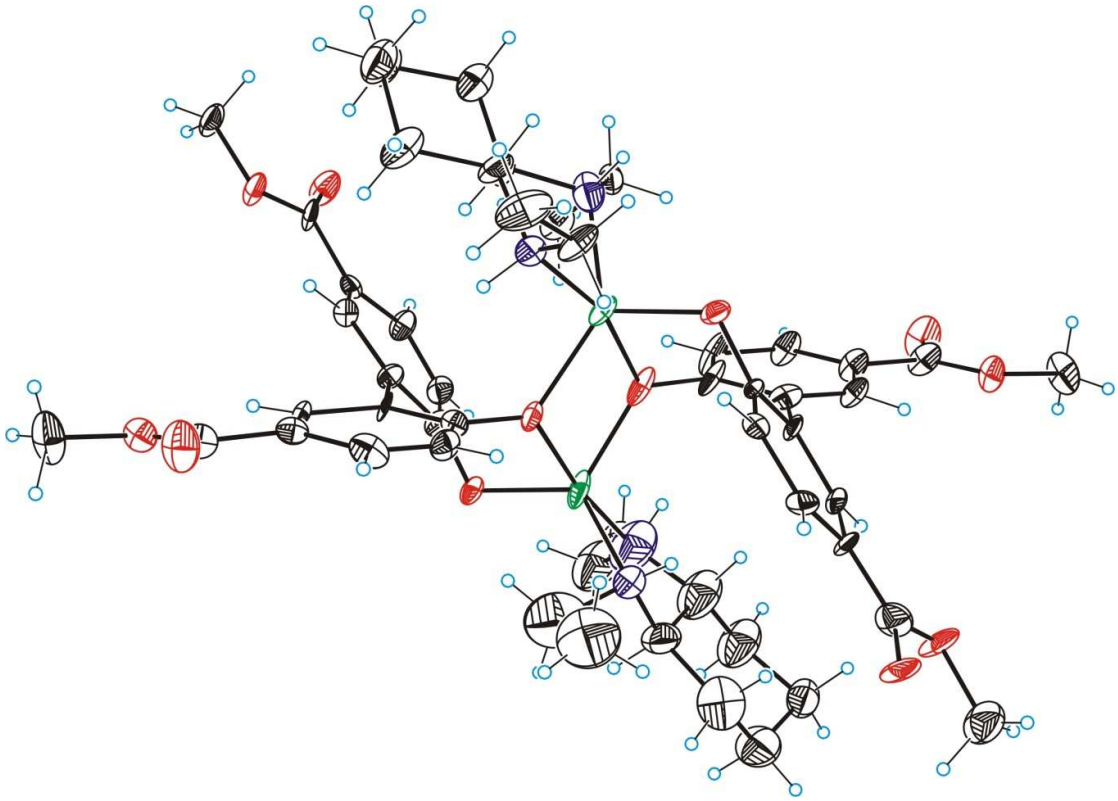


Figure 18. Ortep plot (50%) showing the molecular structure of compound **5a**.

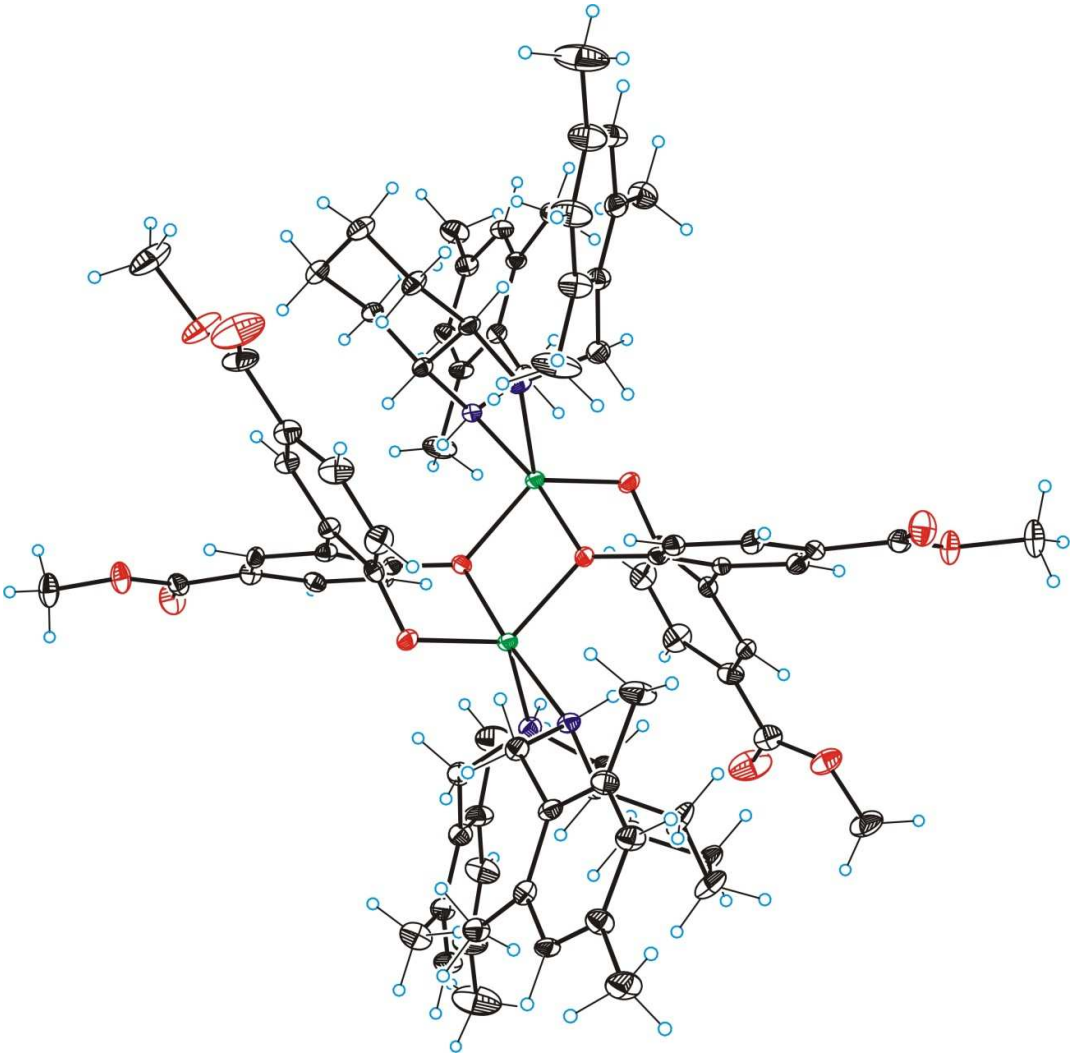


Figure 19. Ortep plot (50%) showing the molecular structure of compound **5c**.

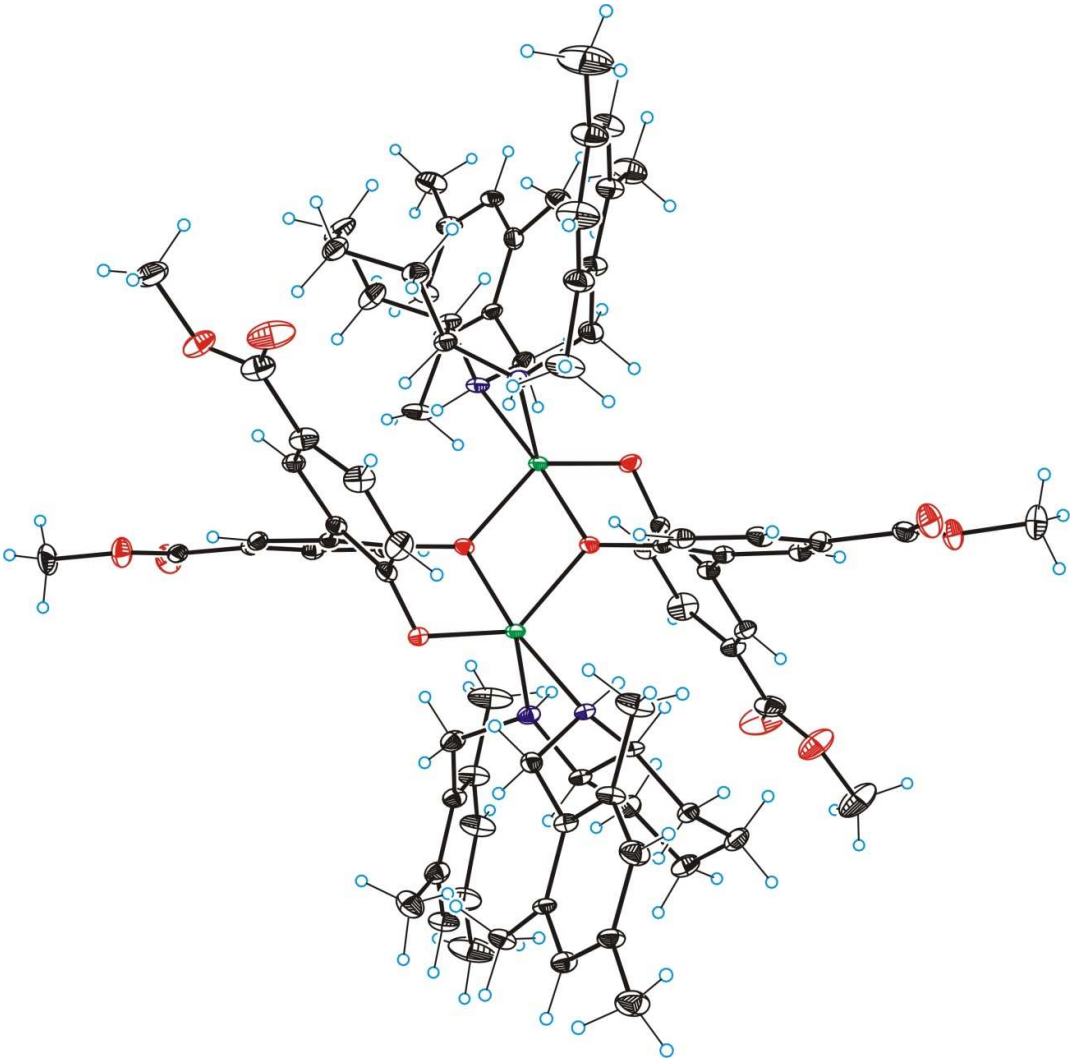
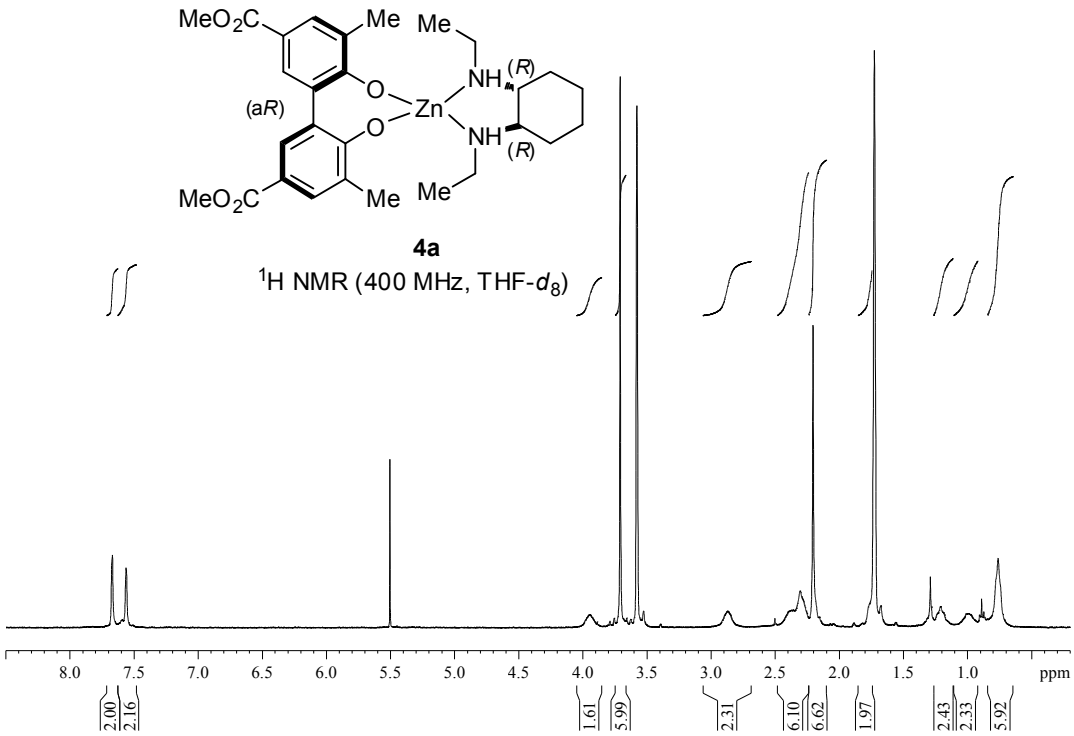


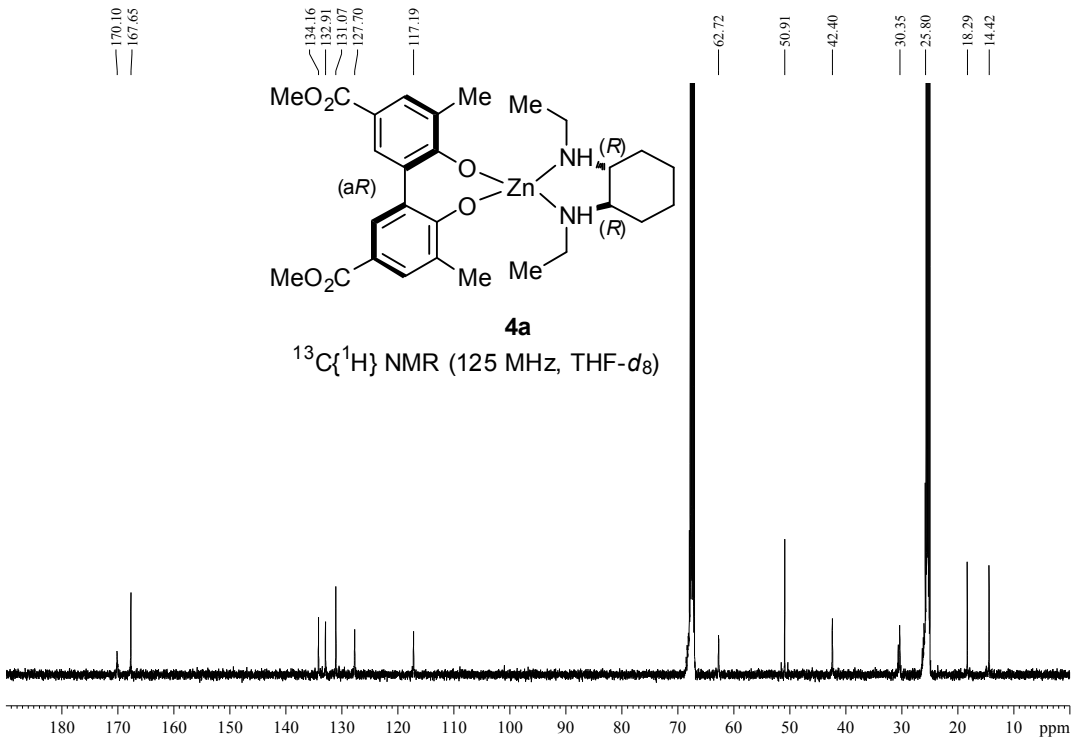
Figure 20. Ortep plot (50 %) showing the molecular structure of compound ***ent*-5c**.

(H) NMR Spectra of New Compounds



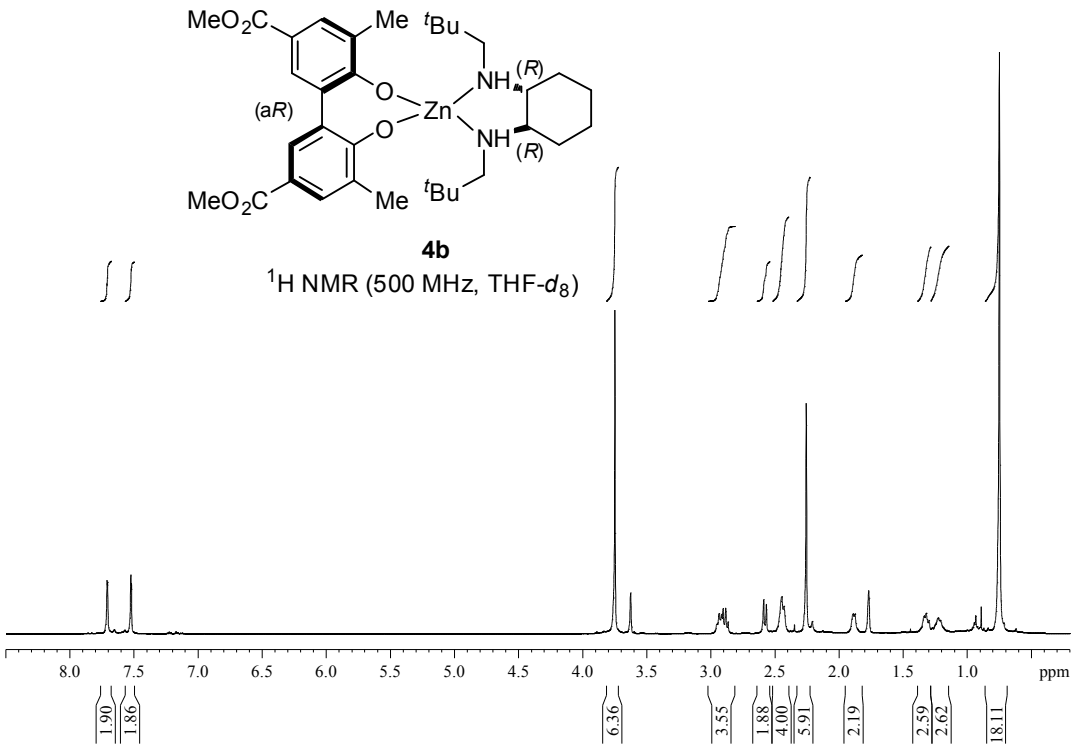
4a

^{1}H NMR (400 MHz, THF-d_8)



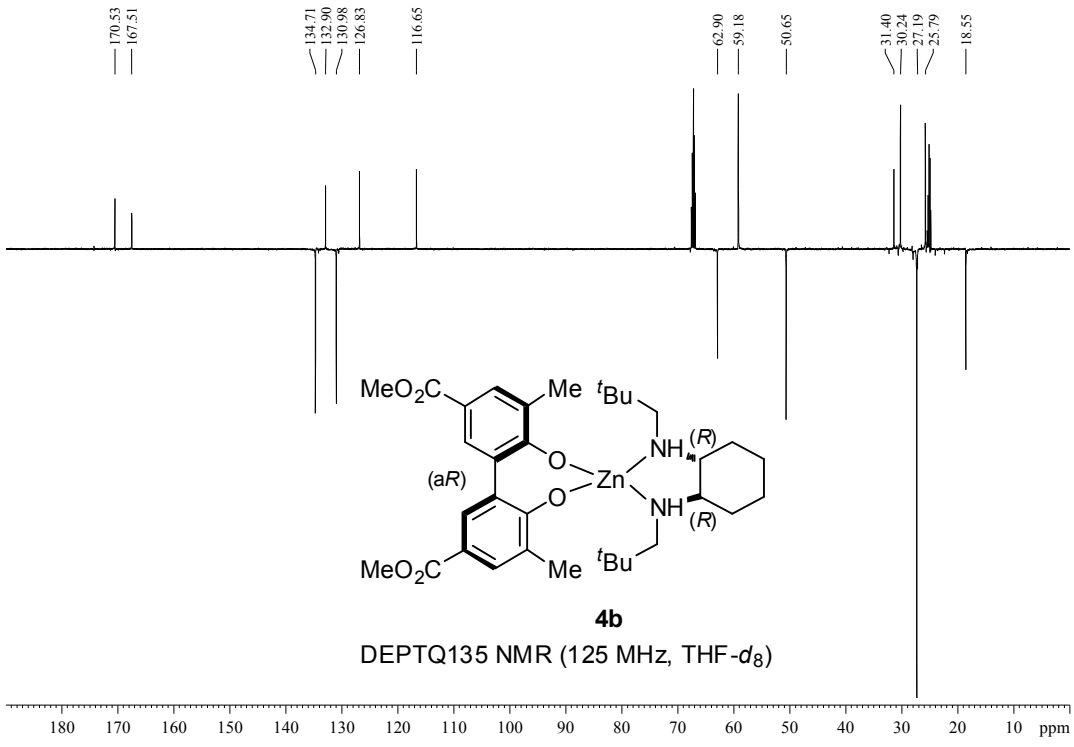
4a

^{13}C{^{1}H} NMR (125 MHz, THF-d_8)



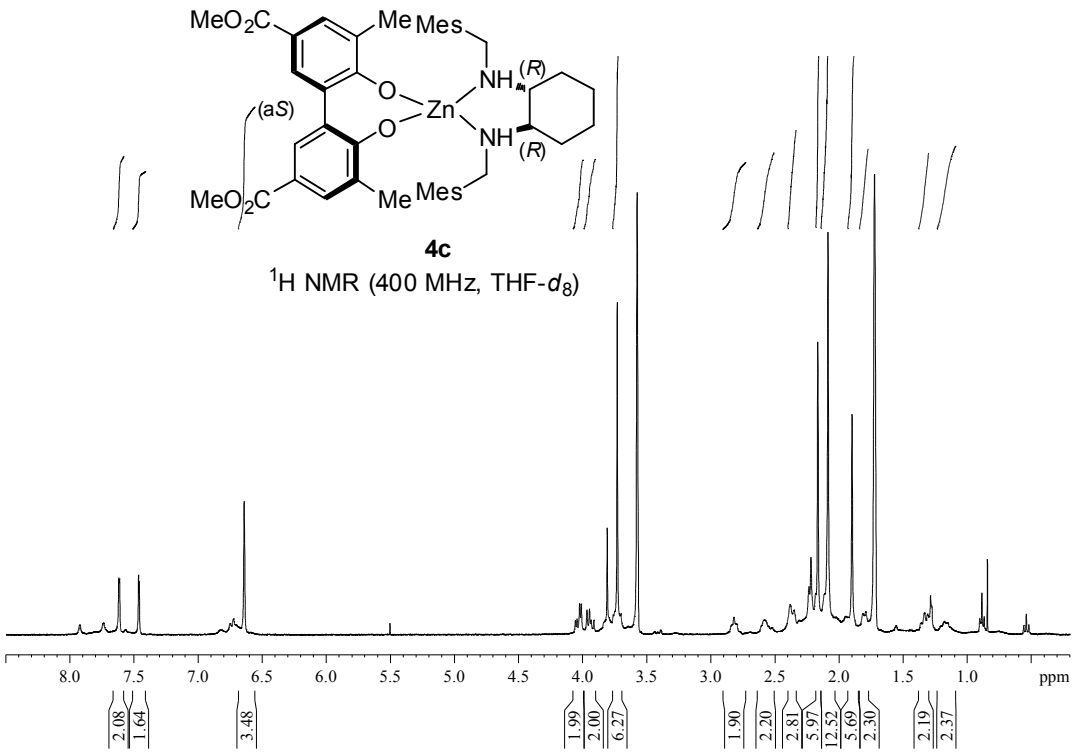
4b

^{1}H NMR (500 MHz, THF-d_8)



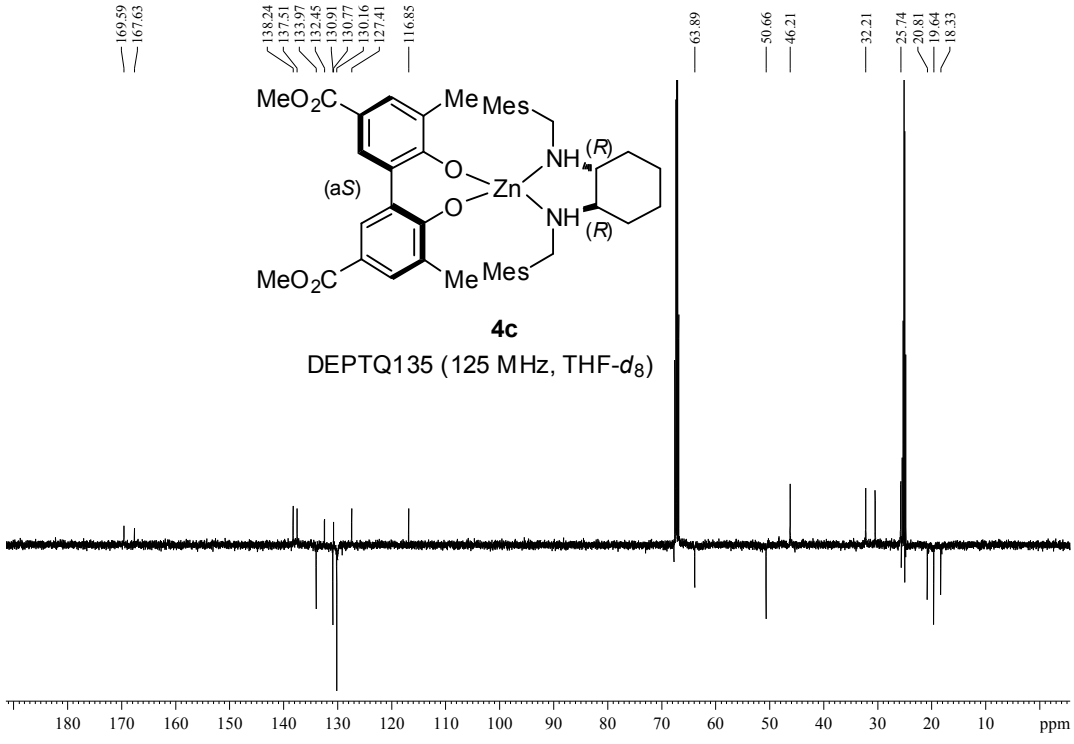
4b

DEPTQ135 NMR (125 MHz, THF-d_8)



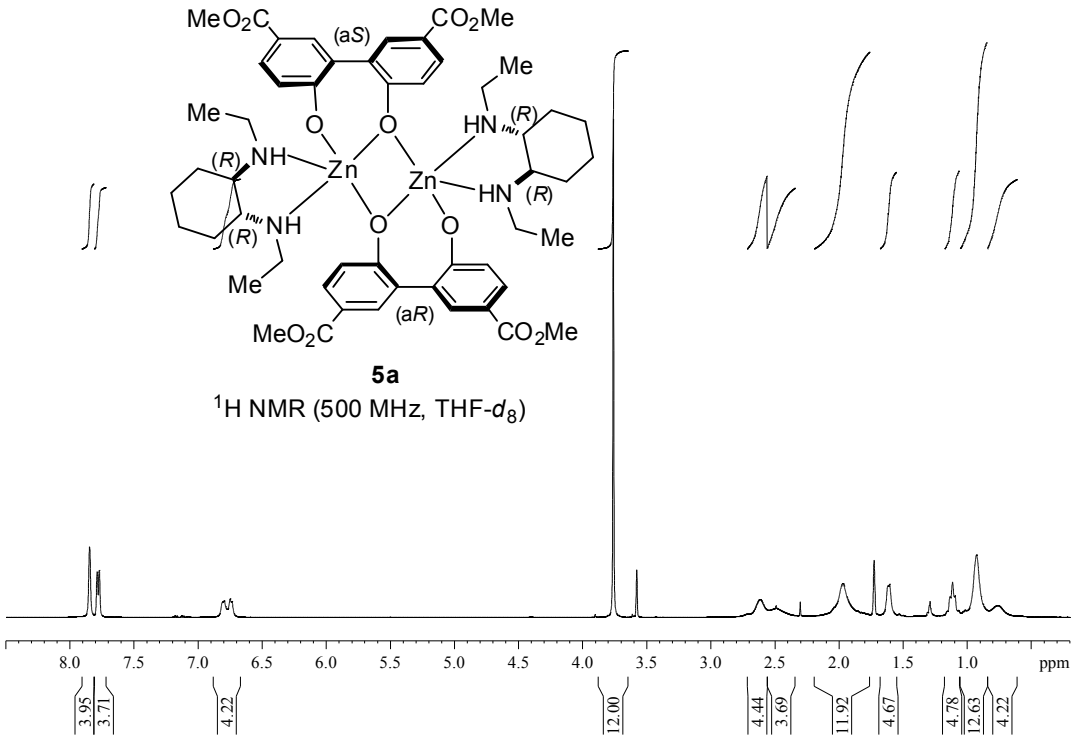
4c

^{1}H NMR (400 MHz, THF-d_8)



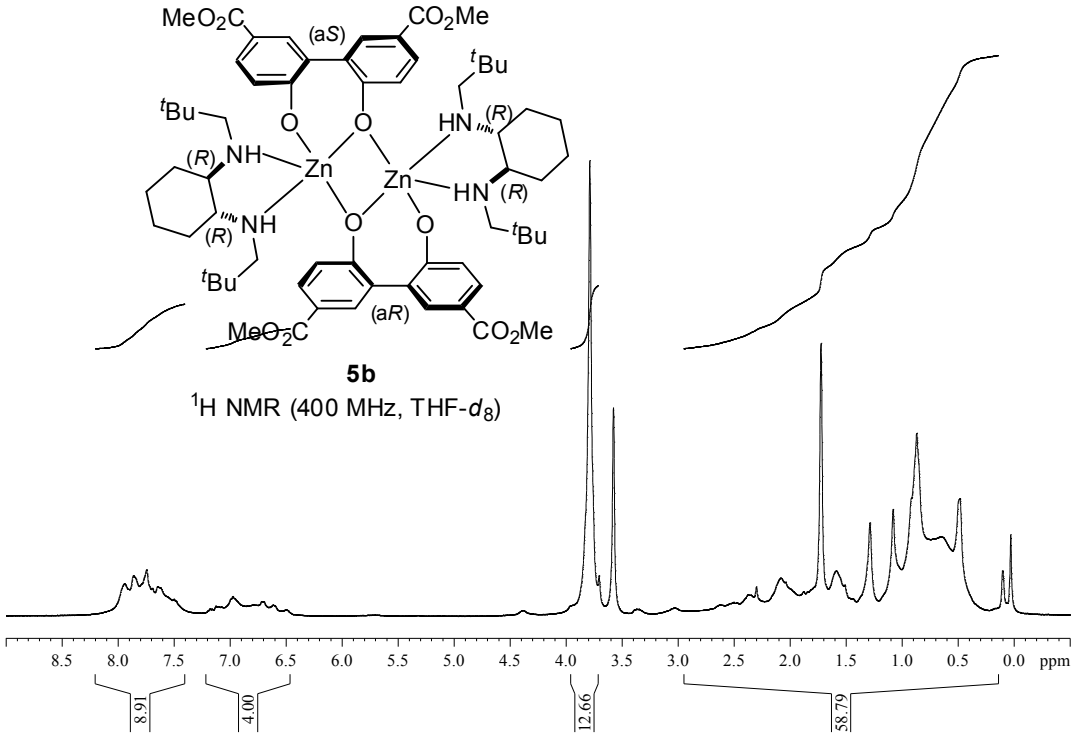
4c

DEPTQ135 (125 MHz, THF-d_8)



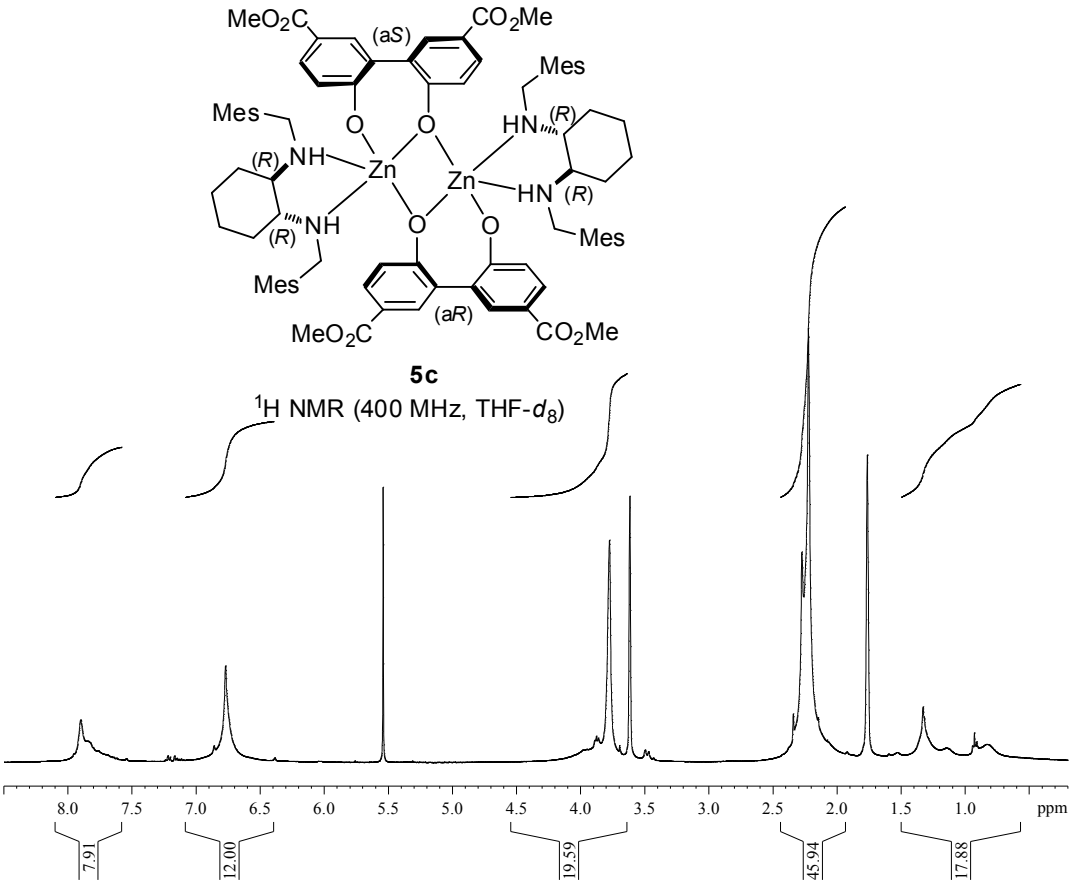
5a

^{1}H NMR (500 MHz, THF-d_8)



5b

^{1}H NMR (400 MHz, THF-d_8)


MeO2C
(aS)
CO2Me
Mes
Mes
O
O
HN (R)
(R) NH
Zn
Zn
HN (R)
(R) NH
O
O
Mes
Mes
(aR)
MeO2C
CO2Me
5c
1H NMR (400 MHz, THF-d8)
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
ppm
7.91
12.00
19.59
45.94
17.88