Electronic Supplementary Material (ESI) for ChemComm.

Cytotoxic Heteroleptic Heptacoordinate Salan Zirconium (IV)-*bis*-Chelates – Synthesis, Aqueous Stability and X-ray Structure Analysis

Fabian Schneider[‡], Tiankun Zhao[‡], and Thomas Huhn*
Fachbereich Chemie and Konstanz Research School Chemical Biology, Universität Konstanz, Germany.
Tel : (+49)7531 - 88 2283; Fax: (+49) 7531-884424.
E-mail: thomas.huhn@uni-konstanz.de

[‡]equal contribution

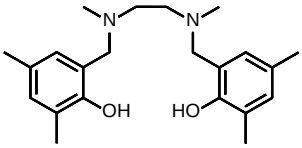
Supporting Information

(A) General Methods

All reagents, metal catalysts and solvents were obtained from commercial sources. For the ligand synthesis all solvents were used as received, all reactions with metal-precursors were run with dry solvents[1] and under strict exclusion of atmospheric moisture and oxygen by using standard Schlenk technique and nitrogen as inert gas. NMR spectra were measured on a Bruker Avance 400 and Bruker Avance DRX 600 spectrometers. Trace impurities of protonated deuterated solvent were used as reference. Following reference values were used: $CDCl_3$: δ = 7.26 ppm (^{1}H-NMR), δ = 77.16 ppm (^{13}C-NMR); d_6-DMSO: δ = 2.50 ppm (^{1}H-NMR), δ = 39.51 ppm (^{13}C-NMR). d_8-THF: δ = 1.73, 3.58 ppm (^{1}H-NMR), δ = 25.37, 67.57 ppm (^{13}C-NMR). The data was processed using the software MestReNova (v. 10.0). Following abbreviations were used for NMR data: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet. Structure assignments were done based on 2D-NMR (COSY, HMBC, HSQC) experiments. UV-Vis spectroscopy was carried out on a Varian Cary 50 spectrophotometer. The software Spekwin 32 was used for processing the data.[2] Thin layer chromatography was done on plates by Merck (F_{254}) using UV light at 254 nm for identification of spots on the TLC plate. Mass spectroscopy was carried out on a Bruker microTOF II spectrometer. IR spectra were measured on a Perkin ElmerSpectrum 100 ATR spectrometer using compounds in solid state. Combustion analyses of zirconium complexes were carried out by the microanalytical laboratory of the University of Konstanz. Satisfactory analysis could not be obtained for [Zr(L1)$_2$] and [Zr(L2)$_2$]. Data collection for X-ray structure-determination was performed at a STOE IPDS-II diffractometer equipped with a graphite monochromated radiation source (λ = 0.71073 Å), an image plate detection system and an Oxford Cryostream 700 with nitrogen as coolant gas. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell by a least-squares fit of the 2Θ values, data reduction, LP correction, and the space group determination were performed using the X-Area software package delivered with the diffractometer. A semiempirical absorption correction method was performed after indexing of the crystal faces. The structures were solved by direct methods (SHELXS-97)[3] and refined by standard Fourier techniques against F square with a full-matrix leastsquares algorithm using SHELXL-2013 and the WinGX (1.80.05)[4] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined with a riding model. Graphical representations were prepared with ORTEP-III.[5] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1439012, CCDC 1439014.

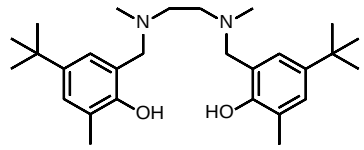
(B) Synthesis and characterization

6,6'-((ethane-1,2-diylbis(methylazanediyl))*bis*(methylene))*bis*(2,4-dimethylphenol) (L1)[6]



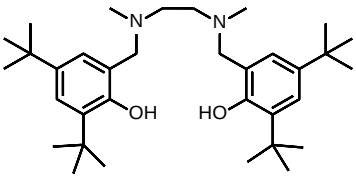
Following the literature reported method,[5] 2,4-dimethylphenol (20 g, 163.9 mmol) was dissolved in 82 mL methanol, formaldehyde 37 % aq. (123 ml) and *N*,*N*-dimethylethane-1,2-diamine (8.9 ml, 82 mmol) was added, the reaction mixture was heated to reflux for 17 h. After cooling to r.t. the colorless precipitate was filtered off and washed with methanol (50 mL) and dried in vacuo. **L1** was obtained as colorless crystals (26.90 g, 75.5 mmol, 92 %). M.p.: 126 °C; ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 6.91 (s, 2H), 6.65 (s, 2H), 3.66 (s, 4H), 2.69 (s, 4H), 2.30 (s, 6H), 2.27 (s, 6H), 2.25 (s, 6H); ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 153.4 (C_{ar}), 130.6 (C_{ar}), 127.5 (C_{ar}), 126.6 (C_{ar}), 124.6 (C_{ar}), 120.7 (C_{ar}), 61.8 (NCH_2), 54.1 (CH_2C_{ar}), 41.6 (NCH_3), 20.4 (CH_3), 15.6 (CH_3); UV-vis(THF): λ_{max} (ε) = 211 nm (98450 $M^{-1}cm^{-1}$), 280 nm (16770 $M^{-1}cm^{-1}$).

6,6'-((ethane-1,2-diylbis(methylazanediyl))*bis*(methylene))*bis*(4-(*tert*-butyl)-2-methylphenol) (L2)[7]



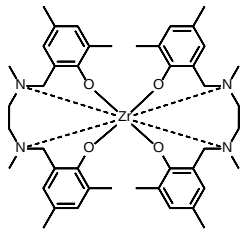
Following the same procedure as for **L1** using 2-methyl-4-*tert*-butylphenol (8.2 g, 50 mmol), *N*,*N*-dimethylethane-1,2-diamine (2.70 ml, 25 mmol), formaldehyde 37% aq. (37.5 ml) in 25 mL methanol for 20 h. **L2** was obtained as colorless crystals (5.72 g, 12.97 mmol, 52 %). M.p. 101 °C; ^{1}H-NMR (400 MHz, Chloroform-*d*): δ 7.06 (s, 2H, H_{ar}), 6.76-6.82 (m, 2H, H_{ar}), 3.68 (s, 4H, $ArCH_2N$), 2.70 (s, 4H, NCH_2), 2.29 (s, 6H, NCH_3), 2.23 (s, 6H, $ArCH_3$), 1.28 (s, 18H, *t*-Bu); ^{13}C-NMR (101 MHz, Chloroform-*d*): δ 153.5 (C_{ar}), 141.4 (C_{ar}), 127.1 (C_{ar}), 124.2 (C_{ar}), 123.0 (C_{ar}), 120.3 (C_{ar}), 62.3 ($N\underline{C}H_2C_{ar}$), 54.5 (NCH_2CH_2N), 41.9 (NCH_3), 34.0 ($\underline{C}_{ar}(CH_3)_3$), 31.8 ($C_{ar}(\underline{C}H_3)_3$), 16.1 ($C_{ar}\underline{C}H_3$).

6,6'-((ethane-1,2-diylbis(methylazanediyl))*bis*(methylene))*bis*(2,4-di-*tert*-butylphenol) (L3)[6]



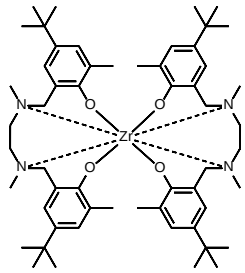
Following the same procedure as for **L1** with 2,4-di-*tert*-butylphenol (8.25 g, 40 mmol) formaldehyde 37 % aq. (15 ml) and *N*,*N*-dimethylethane-1,2-diamine (2.15 ml, 1.762 g, 20 mmol) in 20 mL methanol for 17 h. **L3** was obtained as colorless crystals (9.90 g, 18.87 mmol, 94 %). M.p.: 155 °C; ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 2H, H_{ar}), 6.82 (s, 2H, H_{ar}), 3.68 (s, 4H, $ArCH_2$), 2.66 (s, 4H, NCH_2), 2.28 (s, 6H, NCH_3), 1.42 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$); ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 154.3 (C_{ar}), 140.7 (C_{ar}), 135.8 (C_{ar}), 123.5 (C_{ar}), 123.1 (C_{ar}), 121.1 (C_{ar}), 62.9 ($N\underline{C}H_2C_{ar}$), 53.9 (NCH_2CH_2N), 41.7 (NCH_3), 35.0 ($\underline{C}_{ar}(CH_3)_3$), 34.3 ($\underline{C}_{ar}(CH_3)_3$), 31.9 ($C_{ar}\underline{C}H_3$), 29.8 ($C_{ar}\underline{C}H_3$).

[L1ZrL1]



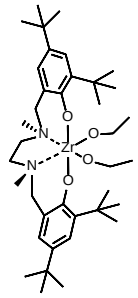
$Zr(OEt)_4$ (1.52 g, 5.61 mmol) was suspended in anhydrous THF (100 mL) under an atmosphere of nitrogen. **L1** (2.0 g, 5.61 mmol) was added to the colorless suspension and stirred at 50 °C for 18 h. ^{1}H-NMR recorded from the crude showed nearly quantitative conversion of **L1** and formation of **[L1ZrL1]**. After removal of the solvent the crude complex was directly used in the following step without further purification. An analytical pure sample was obtained by recrystallization from anhydrous hexane/THF to give **[L1ZrL1]** as colorless crystals. M.p.: 293 °C; IR absorptions (cm^{-1}, ATR): 2912, 2852, 1611, 1477, 1364, 1309, 1256, 1139, 1071, 1001, 968, 825, 738; ^{1}H-NMR (400 MHz, THF-d_8) δ 6.81 (s, 2H, H_{ar}), 6.43 (s, 2H, H_{ar}), 4.39 (d, J = 13.4 Hz, 2H, $C_{ar}CH_2$), 3.04 (d, J = 9.2 Hz, 2H, NCH_2), 2.67 (d, J = 13.4 Hz, 2H, $C_{ar}CH_2$), 2.60 (s, 6H, NCH_3), 2.39 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 1.53 (d, J = 9.2 Hz, 2H, NCH_2); ^{13}C-NMR (101 MHz, THF-d_8) δ 157.9 (C_{ar}), 132.0 (C_{ar}), 129.3 (C_{ar}), 126.4 (C_{ar}), 126.0 (C_{ar}), 125.4 (C_{ar}), 64.2 ($N\underline{C}H_2C_{ar}$), 52.5 (NCH_2), 47.2 (NCH_3), 20.6 (CH_3), 18.1 (CH_3); UV-Vis (THF): λ_{max} (ε) = 252 nm (65920 $M^{-1}cm^{-1}$), 291 nm (13750 $M^{-1}cm^{-1}$); HRMS (ESI-TOF) m/z Calcd for $C_{44}H_{61}N_4O_4Zr$ $[M+H]^+$: 799.3734. Found: 799.3740.

[L2ZrL2]



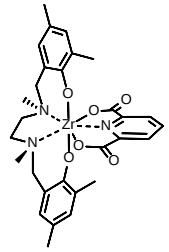
[L2ZrL2] was synthesized following the same method as for **[L1ZrL1]** using **L2** (2.47 g, 5.61 mmol) and $Zr(OEt)_4$ (1.52 g, 5.61 mmol) in THF (100 mL) and stirring at 50°C for 17 h. ^{1}H-NMR recorded from the crude showed nearly quantitative conversion of **L2** and formation of **[L2ZrL2].** After removal of the solvent the crude complex was used directly for the next step without further purification. An analytical pure sample was obtained by recrystallization from anhydrous hexane to give **[L2ZrL2]** as colorless crystals. M.p. 232 °C; IR absorptions (cm^{-1}, ATR): 2956, 2859, 1606, 1481, 1392, 1361, 1310, 1269, 1218, 1124, 1072, 1001, 872, 839, 770, 722, 683; ^{1}H-NMR (400 MHz, THF-d_8) δ 7.07 (d, J = 2.4 Hz, 2H, H_{ar}), 6.68 (d, J = 2.4 Hz, 2H, H_{ar}), 4.43 (d, J = 13.3 Hz, 2H, $C_{ar}CH_2$), 3.01 (d, J = 9.2 Hz, 2H, NCH_2), 2.73 (d, J = 13.3 Hz, 2H, $C_{ar}CH_2$), 2.62 (s, 6H, NCH_3), 2.43 (s, 6H, CH_3), 1.55 (d, J = 9.2 Hz, 2H, NCH_2), 1.22 (s, 18H, $C(CH_{3)3}$); ^{13}C-NMR (101 MHz, THF-d_8) δ 158.0 (C_{ar}), 139.6 (C_{ar}), 128.2 (C_{ar}), 126.1 (C_{ar}), 125.5 (C_{ar}), 124.9 (C_{ar}), 64.6 ($N\underline{C}H_2C_{ar}$), 52.4 (NCH_2), 47.3 (NCH_3), 34.3 ($Ar\underline{C}(CH_3)_3$), 32.1 ($ArC(\underline{C}H_3)_3$), 18.4 (CH_3); UV-Vis (THF) λ_{max} (ε) = 252 nm (72840 $M^{-1}cm^{-1}$), 287 nm (19620 $M^{-1}cm^{-1}$), 315 nm (5910 $M^{-1}cm^{-1}$); HRMS (ESI-TOF) m/z Calcd for $C_{56}H_{85}N_4O_4Zr$ $[M+H]^+$: 967.5612. Found: 967.5573.

[L3Zr(OEt)$_2$]



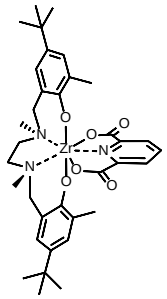
[L3Zr(OEt)$_2$] was synthesized following the same method as for **[L1ZrL1]** using $Zr(OEt)_4$ (1.52 g, 5.61 mmol), **L3** (2.94 g, 5.61 mmol) in THF (100 mL) and stirring at 50 °C for 16 h. ^{1}H-NMR recorded from the crude showed complete conversion of **L3** and the formation of **[L3Zr(OEt)$_2$]**. After removal of the solvent the crude complex was used in the following step without further purification. An analytical pure sample was obtained by recrystallization from anhydrous hexane to give **[L3Zr(OEt)$_2$]** as colorless crystals. M.p.: 212 °C; IR absorptions (cm^{-1}, ATR): 2953, 2863, 1603, 1474, 1443, 1360,1304, 1276, 1446, 1122, 1069, 1010, 914, 842, 748, 702; ^{1}H-NMR (400 MHz, THF-d_8) δ 7.24 (d, J = 2.1 Hz, 2H, H_{ar}), 6.85 (d, J = 2.1 Hz, 2H, H_{ar}), 4.43 (d, J = 13.2 Hz, 2H, $C_{ar}CH_2$), 4.21-4.06 (m, 4H, OCH_2), 3.18 (d, J = 13.2 Hz, 2H, $C_{ar}CH_2$), 3.14 (d, J = 9.5 Hz, 2H, NCH_2), 2.47 (s, 6H), 1.87 (d, J = 9.5 Hz, 2H, NCH_2), 1.50 (s, 18H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$), 1.22 (t, J = 6.9 Hz, 6H, $CH_2\underline{C}H_3$); ^{13}C-NMR (101 MHz, THF-d_8) δ 159.0 (C_{ar}), 139.0 (C_{ar}), 137.1 (C_{ar}), 125.3 (C_{ar}), 124.3 (C_{ar}), 124.3 (C_{ar}), 66.0 ($N\underline{C}H_2C_{ar}$), 52.3 (NCH_2), 47.4 (NCH_3), 35.9 ($Ar\underline{C}(CH_3)_3$), 34.7 ($Ar\underline{C}(CH_3)_3$), 32.3 ($ArC(\underline{C}H_3)_3$), 30.7 ($ArC(\underline{C}H_3)_3$), 25.4($ArC(\underline{C}H_3)_3$); UV-Vis (THF) λ_{max} (ε) = 256 nm (42200 M^{-1}cm^{-1}); HRMS (ESI-TOF) m/z Calcd for $C_{38}H_{65}N_2O_4Zr$ $[M+H]^+$: 703.3986. Found: 703.3849; Anal. Calcd for $C_{38}H_{64}N_2O_4Zr$: 64.82% (C); 9.16% (H), Found: 64.97% (C); 8.91% (H).

[L1Zr(dipic)]



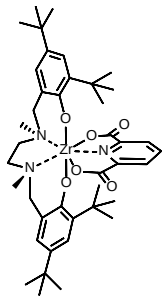
Crude **[L1ZrL1]** (3.18 g, 3.97 mmol) was dissolved in anhydrous THF (100 ml) under nitrogen protection, dipic (730.5 mg, 4.37 mmol) was added to the colorless solution. The mixture was stirred for 18 h at 50 °C while monitoring the reaction-progress by TLC. Upon completion, the obtained yellow suspension was filtered off from excess dipic. To remove co-precipitated **[L1Zr(dipic)]** the sintered glass funnel was washed with CH_2Cl_2 (3 × 30 mL). The THF mother liquor and CH_2Cl_2 were combined and evaporated. The obtained yellow solid was washed with toluene (3 × 20 mL) to remove excess **H$_2$L1**. The residue was dried in vacuo at 100 °C. **[L1Zr(dipic)]** was obtained as a yellow solid (1.23 g, 2.01 mmol, 51 %). M.p.: > 300 °C; IR absorptions (cm^{-1}, ATR): 2910, 2868, 1689, 1479, 1332, 1252, 1163, 1070, 918, 837, 740, 683, 672; ^{1}H-NMR (400 MHz, Chloroform-d) δ 8.37-8.27 (m, 3H, H_{pyr}), 6.83 (s, 2H, H_{ar}), 6.65 (s, 2H, H_{ar}), 5.08 (d, J = 13.8 Hz, 2H, $C_{ar}CH_2$), 3.27 (d, J = 9.5 Hz, 2H, NCH_2), 3.14 (d, J = 13.8 Hz, 2H, $C_{ar}CH_2$), 2.73 (s, 6H, NCH_3), 2.19 (s, 6H, $C_{ar}CH_3$), 2.02 (d, J = 9.5 Hz, 2H, NCH_2), 1.97 (s, 6H, $C_{ar}CH_3$); ^{13}C-NMR (101 MHz, Chloroform-d) δ 168.4 (C=O), 154.2 (C_{ar}), 150.5 (C_{ar}), 144.1 (C_{ar}), 131.4 (C_{ar}), 128.9 (C_{ar}), 128.0 (C_{ar}), 126.4 (C_{ar}), 126.0 (C_{ar}), 124.8 (C_{ar}), 63.7 ($\underline{C}H_2C_{ar}$), 52.4 (NCH_2), 45.7 (NCH_3), 20.7 ($C_{ar}\underline{C}H_3$), 15.8 ($C_{ar}\underline{C}H_3$); UV-Vis(THF): λ_{max} (ε) = 251 nm (34560 M^{-1}cm^{-1}), 294 nm (8870 M^{-1}cm^{-1}), 316 nm (4920 M^{-1}cm^{-1}); HRMS (ESI-TOF) m/z Calcd for $C_{29}H_{34}N_3O_6Zr$ $[M+H]^+$: 610.1489. Found: 610.1492; Anal. Calcd for $C_{29}H_{33}N_3O_6Zr$: 57.02% (C); 5.45% (H), Found: 56.89% (C); 5.46% (H).

[L2Zr(dipic)]



[L2Zr(dipic)] was synthesized following the same procedure as for **[L1Zr(dipic)]** using **[L2ZrL2]** (3.06 g, 3.15 mmol) and dipic (580.8 mg, 3.47 mmol) in anhydrous THF (100 mL) for 24 h. **[L2Zr(dipic)]** was obtained as a yellow solid (810 mg, 1.17 mmol, 37 %). M.p.: > 300 °C; IR absorptions (cm^{-1}, ATR): 2958, 2868, 1690, 1484, 1336, 1311, 1263, 1218, 1173, 1123, 1071, 844, 775, 765, 740, 682, 674; ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 8.37-8.24 (m, 3H), 7.03 (d, *J* = 2.0 Hz, 2H), 6.84 (d, *J* = 2.0 Hz, 2H), 5.12 (d, *J* = 13.9 Hz, 2H), 3.30 (d, *J* = 9.5 Hz, 2H), 3.21 (d, *J* = 13.9 Hz, 2H), 2.77 (s, 6H), 2.07 (d, *J* = 9.5 Hz, 2H), 2.00 (s, 6H), 1.24 (s, 18H); ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 168.4 (C=O), 154.1 (C_{ar}), 150.5 (C_{ar}), 144.0 (C_{ar}), 142.5 (C_{ar}), 127.7 (C_{ar}), 126.3 (C_{ar}), 125.4 (C_{ar}), 124.2 (C_{ar}), 124.1 (C_{ar}), 64.2 ($N\underline{C}H_2C_{ar}$), 52.4 (NCH_2), 45.9 (NCH_3), 34.1 ($Ar\underline{C}(CH_3)_3$), 31.7 ($ArC(\underline{C}H_3)_3$), 16.2 ($C_{ar}\underline{C}H_3$); UV-Vis(THF): λ_{max} (ε) = 250 nm (38220 $M^{-1}cm^{-1}$), 314 nm (5100 $M^{-1}cm^{-1}$); HRMS (ESI-TOF) m/z Calcd for $C_{35}H_{46}N_3O_6Zr$ $[M+H]^+$: 694.2428. Found: 694.2382; Anal. Calcd for $C_{35}H_{45}N_3O_6Zr$: 60.492% (C); 6.53% (H), Found: 60.24% (C); 6.56% (H).

[L3Zr(dipic)]



[L3Zr(dipic)] was synthesized following the same procedure as for **[L1Zr(dipic)]** using **[L3Zr(OEt)$_2$]** (3.34 g, 4.75 mmol) and dipic (872 mg, 5.22 mmol) in anhydrous THF (100 mL) for 20 h. **[L3Zr(dipic)]** was obtained as a yellow solid (2.26 g, 2.89 mmol, 61 %). M.p.: > 300 °C; IR absorptions (cm^{-1}, ATR): 2953, 2910, 2868, 1703, 1683, 1474, 1337, 1299, 1262, 1170, 1072, 920, 844, 740; ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 8.34-8.25 (m, 3H, H_{pyr}), 7.18 (d, *J* = 2.2 Hz, 2H, H_{ar}), 6.87 (d, *J* = 2.2 Hz, 2H, H_{ar}), 5.04 (d, *J* = 13.8 Hz, 2H, $C_{ar}CH_2$), 3.46 (d, *J* = 9.5 Hz, 2H, NCH_2), 3.23 (d, *J* = 13.8 Hz, 2H, $C_{ar}CH_2$), 2.82 (s, 6H, NCH_3), 2.19 (d, *J* = 9.5 Hz, 2H, NCH_2), 1.26 (s, 18H, CCH_3), 1.14 (s, 18H, CCH_3); ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 168.3 (C=O), 155.2 (C_{ar}), 150.4 (C_{ar}), 144.1 (C_{ar}), 142.0 (C_{ar}), 136.8 (C_{ar}), 126.3 (C_{ar}), 124.9 (C_{ar}), 124.7 (C_{ar}), 124.2 (C_{ar}), 64.8 ($N\underline{C}H_2C_{ar}$), 53.0 (NCH_2), 47.3 (NCH_3), 34.8 ($Ar\underline{C}(CH_3)_3$), 34.4 ($Ar\underline{C}(CH_3)_3$), 31.8 ($ArC(\underline{C}H_3)_3$), 29.7 ($ArC(\underline{C}H_3)_3$); UV-Vis (THF): λ_{max} (ε) = 255 nm (33990 $M^{-1}cm^{-1}$), 316 nm (4630 $M^{-1}cm^{-1}$); HRMS (ESI-TOF) m/z Calcd for $C_{41}H_{58}N_3O_6Zr$ $[M+H]^+$: 778.3367. Found: 778.3380; Anal. Calcd for $C_{41}H_{57}N_3O_6Zr$: 63.20% (C); 7.37% (H), Found: 63.35% (C); 7.29% (H).

(C) Crystallographic data

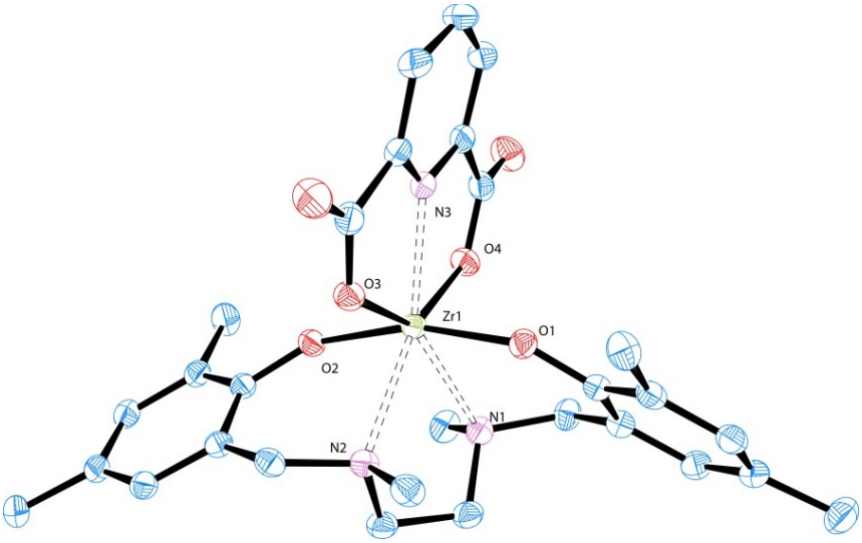


Figure S1. X-ray crystal structure of heptacoordinate **[L1Zr(dipic)]**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S1: Crystal data and structure refinement parameters

	[L1Zr(dipic)] (CCDC 1439014)
Empirical formula	$C_{29}\ H_{33}N_3O_6Zr$
Formula weight	610.80
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 21/n
Unit cell dimensions	a = 9.4729(14) Å
	b = 22.863(5) Å, β = 93.774(14)°.
	c = 12.408(2) Å.
Volume	2681.5(8) $Å^3$
Z	4
Density (calculated)	1.513 Mg/m^3
Absorption coefficient	0.459 mm^{-1}
F(000)	1264
Crystal size	0.500 × 0.387 × 0.280 mm^3
Theta range for data collection	1.781 to 26.828°.
Index ranges	-11<=h<=11, -28<=k<=28, -15<=l<=15
Reflections collected	39090
Independent reflections	5682 [$R_{(int)}$ = 0.0388]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.9353 and 0.8625
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5682 / 0 / 358
Goodness-of-fit on F^2	1.243
Final R indices [I>2sigma(I)]	R_1 = 0.0230, wR_2 = 0.0652
R indices (all data)	R_1 = 0.0285, wR_2 = 0.0665
Largest diff. peak and hole	0.348 and -0.426 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[L1Zr(dipic)]** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zr	2590(1)	-769(1)	7856(1)	18(1)
O(1)	1745(1)	-1490(1)	8443(1)	22(1)
O(2)	2884(1)	-16(1)	7098(1)	22(1)
O(3)	2668(1)	-379(1)	9440(1)	23(1)
O(4)	4014(1)	-1218(1)	6863(1)	24(1)
O(5)	3638(1)	-272(1)	11130(1)	34(1)
O(6)	6069(1)	-1679(1)	6617(1)	34(1)
N(1)	1040(1)	-1118(1)	6323(1)	23(1)
N(2)	312(1)	-279(1)	7936(1)	21(1)
N(3)	4665(1)	-993(1)	8824(1)	21(1)
C(1)	3632(2)	-471(1)	10219(1)	24(1)
C(2)	4812(2)	-857(1)	9873(1)	23(1)
C(3)	5947(2)	-1065(1)	10530(2)	30(1)
C(4)	6918(2)	-1426(1)	10061(2)	32(1)
C(5)	6773(2)	-1556(1)	8970(2)	29(1)
C(6)	5619(2)	-1327(1)	8365(1)	23(1)
C(7)	5257(2)	-1428(1)	7179(1)	25(1)
C(8)	856(2)	-1942(1)	8235(1)	21(1)
C(9)	306(2)	-2246(1)	9097(1)	23(1)
C(10)	-568(2)	-2724(1)	8863(1)	24(1)
C(11)	-915(2)	-2904(1)	7808(1)	26(1)
C(12)	-387(2)	-2581(1)	6967(1)	25(1)
C(13)	495(2)	-2101(1)	7162(1)	23(1)
C(14)	716(2)	-2065(1)	10238(1)	28(1)
C(15)	-1797(2)	-3446(1)	7584(2)	37(1)
C(16)	1101(2)	-1775(1)	6238(1)	25(1)
C(17)	-450(2)	-932(1)	6427(1)	26(1)
C(18)	-503(2)	-319(1)	6875(1)	25(1)
C(19)	498(2)	350(1)	8249(1)	22(1)
C(20)	1214(2)	727(1)	7452(1)	20(1)
C(21)	2379(2)	529(1)	6908(1)	20(1)
C(22)	3021(2)	891(1)	6173(1)	22(1)
C(23)	2528(2)	1462(1)	6034(1)	24(1)
C(24)	1417(2)	1679(1)	6598(1)	23(1)
C(25)	764(2)	1300(1)	7288(1)	22(1)
C(26)	4219(2)	658(1)	5555(2)	29(1)
C(27)	922(2)	2308(1)	6483(1)	28(1)
C(28)	1549(2)	-876(1)	5302(1)	28(1)
C(29)	-506(2)	-555(1)	8786(1)	27(1)

Table S3. Bond lengths [Å] for **[L1Zr(dipic)]**.

Zr-O(2)	1.9890(11)	N(2)-C(18)	1.485(2)	C(11)-C(12)	1.397(2)
Zr-O(1)	1.9917(11)	N(2)-C(29)	1.490(2)	C(11)-C(15)	1.511(2)
Zr-O(4)	2.1473(11)	N(2)-C(19)	1.4966(19)	C(12)-C(13)	1.392(2)
Zr-O(3)	2.1549(11)	N(3)-C(2)	1.337(2)	C(13)-C(16)	1.512(2)
Zr-N(3)	2.2931(13)	N(3)-C(6)	1.338(2)	C(17)-C(18)	1.510(2)
Zr-N(2)	2.4389(13)	C(1)-C(2)	1.509(2)	C(19)-C(20)	1.507(2)
Zr-N(1)	2.4586(13)	C(2)-C(3)	1.390(2)	C(20)-C(25)	1.389(2)
O(1)-C(8)	1.3477(18)	C(3)-C(4)	1.390(3)	C(20)-C(21)	1.405(2)
O(2)-C(21)	1.3497(18)	C(4)-C(5)	1.384(3)	C(21)-C(22)	1.401(2)
O(3)-C(1)	1.3023(19)	C(5)-C(6)	1.386(2)	C(22)-C(23)	1.393(2)
O(4)-C(7)	1.3073(19)	C(6)-C(7)	1.507(2)	C(22)-C(26)	1.507(2)
O(5)-C(1)	1.217(2)	C(8)-C(13)	1.400(2)	C(23)-C(24)	1.394(2)
O(6)-C(7)	1.216(2)	C(8)-C(9)	1.404(2)	C(24)-C(25)	1.391(2)
N(1)-C(17)	1.487(2)	C(9)-C(10)	1.391(2)	C(24)-C(27)	1.515(2)
N(1)-C(28)	1.492(2)	C(9)-C(14)	1.500(2)		
N(1)-C(16)	1.5067(19)	C(10)-C(11)	1.390(2)		

Table S4. Angles [°] for **[L1Zr(dipic)]**.

O(2)-Zr-O(1)	163.95(4)	C(28)-N(1)-Zr	109.06(9)	C(10)-C(9)-C(8)	118.33(15)
O(2)-Zr-O(4)	91.68(4)	C(16)-N(1)-Zr	110.79(9)	C(10)-C(9)-C(14)	121.83(14)
O(1)-Zr-O(4)	95.55(4)	C(18)-N(2)-C(29)	109.73(12)	C(8)-C(9)-C(14)	119.80(14)
O(2)-Zr-O(3)	94.39(4)	C(18)-N(2)-C(19)	109.52(12)	C(11)-C(10)-C(9)	122.03(15)
O(1)-Zr-O(3)	89.96(4)	C(29)-N(2)-C(19)	106.31(12)	C(10)-C(11)-C(12)	118.21(14)
O(4)-Zr-O(3)	137.40(4)	C(18)-N(2)-Zr	110.22(9)	C(10)-C(11)-C(15)	120.64(15)
O(2)-Zr-N(3)	107.45(4)	C(29)-N(2)-Zr	109.72(9)	C(12)-C(11)-C(15)	121.11(16)
O(1)-Zr-N(3)	88.53(4)	C(19)-N(2)-Zr	111.26(9)	C(13)-C(12)-C(11)	121.81(15)
O(4)-Zr-N(3)	69.19(5)	C(2)-N(3)-C(6)	121.15(13)	C(12)-C(13)-C(8)	118.42(14)
O(3)-Zr-N(3)	68.77(4)	C(2)-N(3)-Zr	119.27(10)	C(12)-C(13)-C(16)	120.69(14)
O(2)-Zr-N(2)	76.93(4)	C(6)-N(3)-Zr	118.95(10)	C(8)-C(13)-C(16)	120.83(13)
O(1)-Zr-N(2)	89.27(4)	O(5)-C(1)-O(3)	126.10(15)	N(1)-C(16)-C(13)	114.79(13)
O(4)-Zr-N(2)	146.48(4)	O(5)-C(1)-C(2)	121.60(14)	N(1)-C(17)-C(18)	110.63(12)
O(3)-Zr-N(2)	75.55(4)	O(3)-C(1)-C(2)	112.29(13)	N(2)-C(18)-C(17)	110.78(12)
N(3)-Zr-N(2)	144.24(5)	N(3)-C(2)-C(3)	121.22(15)	N(2)-C(19)-C(20)	115.46(13)
O(2)-Zr-N(1)	90.58(4)	N(3)-C(2)-C(1)	112.44(13)	C(25)-C(20)-C(21)	118.56(14)
O(1)-Zr-N(1)	77.26(4)	C(3)-C(2)-C(1)	126.33(16)	C(25)-C(20)-C(19)	119.24(14)
O(4)-Zr-N(1)	76.50(4)	C(2)-C(3)-C(4)	117.69(16)	C(21)-C(20)-C(19)	122.11(13)
O(3)-Zr-N(1)	145.36(4)	C(5)-C(4)-C(3)	120.73(15)	O(2)-C(21)-C(22)	119.67(13)
N(3)-Zr-N(1)	141.28(5)	C(6)-C(5)-C(4)	118.17(16)	O(2)-C(21)-C(20)	119.69(13)
N(2)-Zr-N(1)	72.27(4)	N(3)-C(6)-C(5)	121.00(16)	C(22)-C(21)-C(20)	120.64(14)
C(8)-O(1)-Zr	145.74(10)	N(3)-C(6)-C(7)	112.73(13)	C(23)-C(22)-C(21)	118.58(14)
C(21)-O(2)-Zr	145.25(10)	C(5)-C(6)-C(7)	126.26(15)	C(23)-C(22)-C(26)	121.69(14)
C(1)-O(3)-Zr	126.21(10)	O(6)-C(7)-O(4)	126.34(16)	C(21)-C(22)-C(26)	119.73(14)
C(7)-O(4)-Zr	126.21(10)	O(6)-C(7)-C(6)	121.37(14)	C(22)-C(23)-C(24)	121.99(14)
C(17)-N(1)-C(28)	109.24(12)	O(4)-C(7)-C(6)	112.29(13)	C(25)-C(24)-C(23)	117.94(14)
C(17)-N(1)-C(16)	109.40(12)	O(1)-C(8)-C(13)	119.40(14)	C(25)-C(24)-C(27)	120.07(14)
C(28)-N(1)-C(16)	107.05(12)	O(1)-C(8)-C(9)	119.46(14)	C(23)-C(24)-C(27)	121.99(14)
C(17)-N(1)-Zr	111.20(9)	C(13)-C(8)-C(9)	121.14(14)	C(20)-C(25)-C(24)	122.16(14)

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **[L1Zr(dipic)]**. The anisotropic displacement factor exponent takes the form: $-2\pi 2[\ h^2\ a^{*2} U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
Zr	18(1)	19(1)	19(1)	0(1)	0(1)	1(1)
O(1)	23(1)	21(1)	21(1)	-1(1)	-1(1)	-1(1)
O(2)	20(1)	20(1)	24(1)	1(1)	2(1)	1(1)
O(3)	24(1)	24(1)	22(1)	-2(1)	-2(1)	3(1)
O(4)	24(1)	24(1)	25(1)	-1(1)	2(1)	4(1)
O(5)	43(1)	35(1)	24(1)	-6(1)	-5(1)	7(1)
O(6)	33(1)	33(1)	39(1)	-1(1)	12(1)	9(1)
N(1)	24(1)	23(1)	20(1)	2(1)	0(1)	-1(1)
N(2)	20(1)	22(1)	21(1)	2(1)	2(1)	1(1)
N(3)	19(1)	18(1)	26(1)	1(1)	0(1)	-2(1)
C(1)	28(1)	21(1)	24(1)	0(1)	-2(1)	-2(1)
C(2)	22(1)	20(1)	27(1)	1(1)	-4(1)	-4(1)
C(3)	27(1)	30(1)	32(1)	1(1)	-9(1)	-3(1)
C(4)	20(1)	33(1)	40(1)	7(1)	-7(1)	0(1)
C(5)	19(1)	24(1)	44(1)	3(1)	0(1)	0(1)
C(6)	19(1)	18(1)	32(1)	1(1)	4(1)	-2(1)
C(7)	24(1)	19(1)	31(1)	2(1)	5(1)	0(1)
C(8)	18(1)	20(1)	24(1)	1(1)	0(1)	2(1)
C(9)	21(1)	22(1)	26(1)	2(1)	1(1)	5(1)
C(10)	21(1)	24(1)	29(1)	6(1)	3(1)	3(1)
C(11)	20(1)	25(1)	34(1)	4(1)	-4(1)	-1(1)
C(12)	24(1)	26(1)	24(1)	-1(1)	-4(1)	-1(1)
C(13)	21(1)	23(1)	24(1)	1(1)	0(1)	1(1)
C(14)	35(1)	26(1)	24(1)	1(1)	4(1)	2(1)
C(15)	34(1)	36(1)	38(1)	7(1)	-9(1)	-13(1)
C(16)	30(1)	24(1)	21(1)	-3(1)	0(1)	-3(1)
C(17)	22(1)	28(1)	26(1)	3(1)	-4(1)	-2(1)
C(18)	21(1)	27(1)	26(1)	4(1)	-3(1)	0(1)
C(19)	21(1)	24(1)	23(1)	0(1)	5(1)	4(1)
C(20)	20(1)	22(1)	19(1)	-1(1)	-1(1)	-1(1)
C(21)	20(1)	20(1)	18(1)	-2(1)	-2(1)	0(1)
C(22)	21(1)	23(1)	23(1)	-3(1)	1(1)	-2(1)
C(23)	25(1)	22(1)	23(1)	1(1)	0(1)	-5(1)
C(24)	24(1)	20(1)	25(1)	-3(1)	-4(1)	-1(1)
C(25)	22(1)	23(1)	21(1)	-4(1)	0(1)	1(1)
C(26)	30(1)	26(1)	34(1)	1(1)	12(1)	0(1)
C(27)	31(1)	19(1)	33(1)	-2(1)	0(1)	0(1)
C(28)	34(1)	31(1)	20(1)	3(1)	1(1)	-6(1)
C(29)	23(1)	28(1)	30(1)	5(1)	7(1)	2(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **[L1Zr(dipic)]**.

	x	y	z	U(eq)
H(3A)	6054	-966	11258	36
H(4A)	7672	-1581	10485	38
H(5A)	7431	-1789	8651	34
H(10A)	-931	-2930	9429	29
H(12A)	-632	-2691	6257	30
H(14A)	554	-1653	10317	42
H(14B)	1700	-2149	10403	42
H(14C)	157	-2277	10723	42
H(15A)	-2425	-3501	8152	55
H(15B)	-1187	-3780	7551	55
H(15C)	-2339	-3403	6908	55
H(16A)	2080	-1891	6195	30
H(16B)	590	-1893	5570	30
H(17A)	-904	-1199	6903	31
H(17B)	-962	-946	5725	31
H(18A)	-113	-48	6372	30
H(18B)	-1479	-209	6958	30
H(19A)	1045	368	8937	27
H(19B)	-427	514	8354	27
H(23A)	2954	1705	5549	28
H(25A)	1	1436	7652	26
H(26A)	3879	345	5093	44
H(26B)	4958	516	6054	44
H(26C)	4582	966	5126	44
H(27A)	1287	2477	5850	42
H(27B)	1260	2526	7109	42
H(27C)	-93	2318	6418	42
H(28A)	945	-1010	4700	42
H(28B)	2499	-1007	5219	42
H(28C)	1532	-457	5329	42
H(29A)	-695	-956	8601	40
H(29B)	-1384	-350	8837	40
H(29C)	34	-536	9468	40

Table S7. Torsion angles [°] for **[L1Zr(dipic)]**.

Zr-O(3)-C(1)-O(5)	-176.22(12)	O(1)-C(8)-C(13)-C(12)	177.86(13)
Zr-O(3)-C(1)-C(2)	4.66(18)	C(9)-C(8)-C(13)-C(12)	-2.2(2)
C(6)-N(3)-C(2)-C(3)	-1.2(2)	O(1)-C(8)-C(13)-C(16)	0.5(2)
Zr-N(3)-C(2)-C(3)	169.63(11)	C(9)-C(8)-C(13)-C(16)	-179.50(14)
C(6)-N(3)-C(2)-C(1)	179.20(13)	C(17)-N(1)-C(16)-C(13)	-56.43(17)
Zr-N(3)-C(2)-C(1)	-10.01(16)	C(28)-N(1)-C(16)-C(13)	-174.68(13)
O(5)-C(1)-C(2)-N(3)	-175.26(14)	Zr-N(1)-C(16)-C(13)	66.52(14)
O(3)-C(1)-C(2)-N(3)	3.90(19)	C(12)-C(13)-C(16)-N(1)	135.79(14)
O(5)-C(1)-C(2)-C(3)	5.1(3)	C(8)-C(13)-C(16)-N(1)	-46.95(19)
O(3)-C(1)-C(2)-C(3)	-175.72(15)	C(28)-N(1)-C(17)-C(18)	-81.72(16)
N(3)-C(2)-C(3)-C(4)	-0.7(2)	C(16)-N(1)-C(17)-C(18)	161.40(13)
C(1)-C(2)-C(3)-C(4)	178.89(15)	Zr-N(1)-C(17)-C(18)	38.71(15)
C(2)-C(3)-C(4)-C(5)	2.0(2)	C(29)-N(2)-C(18)-C(17)	-75.44(16)
C(3)-C(4)-C(5)-C(6)	-1.4(2)	C(19)-N(2)-C(18)-C(17)	168.22(13)
C(2)-N(3)-C(6)-C(5)	1.7(2)	Zr-N(2)-C(18)-C(17)	45.50(14)
Zr-N(3)-C(6)-C(5)	-169.08(11)	N(1)-C(17)-C(18)-N(2)	-57.39(17)
C(2)-N(3)-C(6)-C(7)	-179.89(13)	C(18)-N(2)-C(19)-C(20)	-57.26(16)
Zr-N(3)-C(6)-C(7)	9.29(16)	C(29)-N(2)-C(19)-C(20)	-175.75(12)
C(4)-C(5)-C(6)-N(3)	-0.4(2)	Zr-N(2)-C(19)-C(20)	64.84(14)
C(4)-C(5)-C(6)-C(7)	-178.57(15)	N(2)-C(19)-C(20)-C(25)	142.97(14)
Zr-O(4)-C(7)-O(6)	-179.52(12)	N(2)-C(19)-C(20)-C(21)	-40.6(2)
Zr-O(4)-C(7)-C(6)	0.59(17)	Zr-O(2)-C(21)-C(22)	-174.69(12)
N(3)-C(6)-C(7)-O(6)	173.65(14)	Zr-O(2)-C(21)-C(20)	5.3(2)
C(5)-C(6)-C(7)-O(6)	-8.1(2)	C(25)-C(20)-C(21)-O(2)	176.48(13)
N(3)-C(6)-C(7)-O(4)	-6.45(18)	C(19)-C(20)-C(21)-O(2)	0.0(2)
C(5)-C(6)-C(7)-O(4)	171.82(14)	C(25)-C(20)-C(21)-C(22)	-3.5(2)
Zr-O(1)-C(8)-C(13)	20.4(2)	C(19)-C(20)-C(21)-C(22)	-179.94(14)
Zr-O(1)-C(8)-C(9)	-159.58(12)	O(2)-C(21)-C(22)-C(23)	-176.68(13)
O(1)-C(8)-C(9)-C(10)	-177.63(13)	C(20)-C(21)-C(22)-C(23)	3.3(2)
C(13)-C(8)-C(9)-C(10)	2.4(2)	O(2)-C(21)-C(22)-C(26)	3.3(2)
O(1)-C(8)-C(9)-C(14)	-0.1(2)	C(20)-C(21)-C(22)-C(26)	-176.74(14)
C(13)-C(8)-C(9)-C(14)	179.90(14)	C(21)-C(22)-C(23)-C(24)	-0.4(2)
C(8)-C(9)-C(10)-C(11)	-0.5(2)	C(26)-C(22)-C(23)-C(24)	179.67(15)
C(14)-C(9)-C(10)-C(11)	-177.98(14)	C(22)-C(23)-C(24)-C(25)	-2.3(2)
C(9)-C(10)-C(11)-C(12)	-1.5(2)	C(22)-C(23)-C(24)-C(27)	177.29(14)
C(9)-C(10)-C(11)-C(15)	176.41(15)	C(21)-C(20)-C(25)-C(24)	0.8(2)
C(10)-C(11)-C(12)-C(13)	1.7(2)	C(19)-C(20)-C(25)-C(24)	177.31(14)
C(15)-C(11)-C(12)-C(13)	-176.15(15)	C(23)-C(24)-C(25)-C(20)	2.1(2)
C(11)-C(12)-C(13)-C(8)	0.1(2)	C(27)-C(24)-C(25)-C(20)	-177.50(14)
C(11)-C(12)-C(13)-C(16)	177.40(14)		

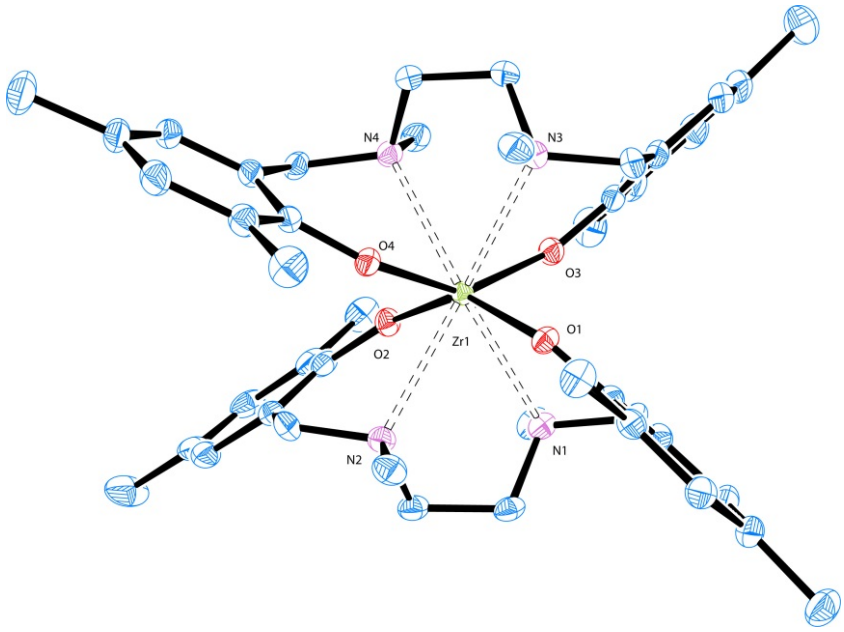


Figure S2. X-ray crystal structure of heptacoordinate **[(L1)$_2$Zr]**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and additional molecule of disordered dichloromethane are omitted for clarity.

Table S8: Crystal data and structure refinement parameters

	[(L1)$_2$Zr] (CCDC 1439012)
Empirical formula	C_{45} H_{62} Cl_2 N_4 O_4 Zr
Formula weight	885.10
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.9667(6) Å.
	b = 18.0916(8) Å, β = 95.342(4)°.
	c = 18.8976(9) Å.
Volume	4413.9(4) Å^3
Z	4
Density (calculated)	1.332 Mg/m^3
Absorption coefficient	0.416 mm^{-1}
F(000)	1864
Crystal size	0.400 x 0.300 x 0.200 mm^3
Theta range for data collection	1.561 to 26.834°.
Index ranges	-16<=h<=16, -22<=k<=22, -23<=l<=23
Reflections collected	52900
Independent reflections	9388 [$R_{(int)}$ = 0.1086]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.9487 and 0.6603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9388 / 0 / 517
Goodness-of-fit on F2	1.056
Final R indices [I>2sigma(I)]	R_1 = 0.0468, wR_2 = 0.1235
R indices (all data)	R_1 = 0.0581, wR_2 = 0.1306
Largest diff. peak and hole	1.084 and -1.501 e.Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[L1ZrL1]**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9659(2)	10909(1)	7941(2)	17(1)
C(2)	9779(2)	11392(2)	8527(2)	19(1)
C(3)	10471(2)	11979(2)	8516(2)	22(1)
C(4)	11033(2)	12124(2)	7939(2)	23(1)
C(5)	10889(2)	11646(2)	7362(2)	21(1)
C(6)	10227(2)	11042(2)	7357(2)	19(1)
C(7)	10181(2)	10496(2)	6752(2)	21(1)
C(8)	9170(2)	11274(2)	9159(2)	24(1)
C(9)	11797(3)	12750(2)	7951(2)	31(1)
C(10)	10486(2)	9266(2)	6365(2)	25(1)
C(11)	11272(2)	9659(2)	7504(2)	21(1)
C(12)	11266(2)	8961(2)	7936(2)	22(1)
C(13)	10494(2)	9408(2)	8964(2)	24(1)
C(14)	10227(2)	8154(2)	8597(2)	23(1)
C(15)	10256(2)	7578(2)	8027(2)	22(1)
C(16)	10846(2)	6943(2)	8167(2)	27(1)
C(17)	10953(2)	6411(2)	7649(2)	31(1)
C(18)	10467(2)	6542(2)	6976(2)	29(1)
C(19)	9854(2)	7164(2)	6812(2)	25(1)
C(20)	9733(2)	7689(2)	7346(2)	21(1)
C(21)	11588(3)	5727(2)	7811(3)	48(1)
C(22)	9319(3)	7264(2)	6079(2)	32(1)
C(23)	7568(2)	9972(2)	6065(2)	22(1)
C(24)	7467(3)	9795(2)	5337(2)	28(1)
C(25)	6769(3)	10194(2)	4886(2)	35(1)
C(26)	6168(3)	10762(2)	5121(2)	35(1)
C(27)	6280(2)	10930(2)	5843(2)	30(1)
C(28)	6968(2)	10541(2)	6318(2)	23(1)
C(29)	8090(3)	9180(2)	5051(2)	37(1)
C(30)	5380(3)	11157(2)	4617(2)	50(1)
C(31)	7016(2)	10706(2)	7099(2)	24(1)
C(32)	6798(2)	10276(2)	8278(2)	24(1)
C(33)	6008(2)	9603(2)	7268(2)	22(1)
C(34)	6077(2)	8814(2)	7526(2)	21(1)
C(35)	6867(2)	8241(2)	6556(2)	23(1)
C(36)	7184(2)	7751(2)	7726(2)	20(1)
C(37)	7219(2)	7847(2)	8520(2)	20(1)
C(38)	6756(2)	7313(2)	8911(2)	23(1)
C(39)	6739(2)	7364(2)	9642(2)	27(1)
C(40)	7160(2)	7996(2)	9972(2)	26(1)
C(41)	7628(2)	8552(2)	9600(2)	23(1)
C(42)	7687(2)	8464(2)	8868(2)	19(1)
C(43)	6267(3)	6756(2)	10054(2)	37(1)
C(44)	8047(3)	9233(2)	9982(2)	29(1)

C(45)	14433(4)	8342(3)	9000(3)	71(2)
N(1)	10333(2)	9718(1)	6998(1)	18(1)
N(2)	10339(2)	8922(1)	8331(1)	19(1)
N(3)	6934(2)	10029(1)	7544(1)	19(1)
N(4)	7021(2)	8450(1)	7315(1)	18(1)
O(1)	9045(1)	10314(1)	7953(1)	17(1)
O(2)	9153(2)	8291(1)	7205(1)	19(1)
O(3)	8221(2)	9584(1)	6519(1)	20(1)
O(4)	8184(1)	8972(1)	8506(1)	18(1)
Zr(1)	8645(1)	9288(1)	7548(1)	14(1)
Cl(1)	13379(1)	7839(1)	9250(1)	69(1)
Cl(2)	14192(1)	9257(1)	8836(1)	107(1)

Table S10. Bond lengths [Å] for **[L1ZrL1]**.

C(1)-O(1)	1.340(3)	C(17)-C(21)	1.503(4)	C(36)-C(37)	1.507(4)
C(1)-C(6)	1.404(4)	C(18)-C(19)	1.395(4)	C(37)-C(38)	1.386(4)
C(1)-C(2)	1.407(4)	C(19)-C(20)	1.405(4)	C(37)-C(42)	1.406(4)
C(2)-C(3)	1.392(4)	C(19)-C(22)	1.502(5)	C(38)-C(39)	1.387(4)
C(2)-C(8)	1.508(4)	C(20)-O(2)	1.336(3)	C(39)-C(40)	1.391(5)
C(3)-C(4)	1.391(4)	C(23)-O(3)	1.346(3)	C(39)-C(43)	1.509(4)
C(4)-C(5)	1.391(4)	C(23)-C(28)	1.401(4)	C(40)-C(41)	1.397(4)
C(4)-C(9)	1.502(4)	C(23)-C(24)	1.408(4)	C(41)-C(42)	1.401(4)
C(5)-C(6)	1.389(4)	C(24)-C(25)	1.387(5)	C(41)-C(44)	1.504(4)
C(6)-C(7)	1.508(4)	C(24)-C(29)	1.503(5)	C(42)-O(4)	1.345(3)
C(7)-N(1)	1.490(4)	C(25)-C(26)	1.386(5)	C(45)-Cl(2)	1.709(6)
C(10)-N(1)	1.478(3)	C(26)-C(27)	1.392(5)	C(45)-Cl(1)	1.742(5)
C(11)-N(1)	1.480(4)	C(26)-C(30)	1.511(5)	N(1)-Zr(1)	2.627(2)
C(11)-C(12)	1.505(4)	C(27)-C(28)	1.395(4)	N(2)-Zr(1)	2.617(2)
C(12)-N(2)	1.475(4)	C(28)-C(31)	1.503(4)	N(3)-Zr(1)	2.592(2)
C(13)-N(2)	1.482(4)	C(31)-N(3)	1.495(3)	N(4)-Zr(1)	2.599(2)
C(14)-N(2)	1.491(4)	C(32)-N(3)	1.483(4)	O(1)-Zr(1)	2.0542(18)
C(14)-C(15)	1.502(4)	C(33)-N(3)	1.481(4)	O(2)-Zr(1)	2.0470(19)
C(15)-C(16)	1.392(4)	C(33)-C(34)	1.509(4)	O(3)-Zr(1)	2.0424(19)
C(15)-C(20)	1.412(4)	C(34)-N(4)	1.477(4)	O(4)-Zr(1)	2.0400(19)
C(16)-C(17)	1.389(5)	C(35)-N(4)	1.478(4)		
C(17)-C(18)	1.385(5)	C(36)-N(4)	1.488(3)		

Table S11. Angles [°] for **[L1ZrL1]**.

O(1)-C(1)-C(6)	120.5(2)	C(27)-C(26)-C(30)	121.1(4)	C(31)-N(3)-Zr(1)	108.64(16)
O(1)-C(1)-C(2)	120.6(2)	C(26)-C(27)-C(28)	121.5(3)	C(34)-N(4)-C(35)	109.6(2)
C(6)-C(1)-C(2)	118.9(2)	C(27)-C(28)-C(23)	119.6(3)	C(34)-N(4)-C(36)	108.6(2)
C(3)-C(2)-C(1)	119.2(3)	C(27)-C(28)-C(31)	119.8(3)	C(35)-N(4)-C(36)	106.7(2)
C(3)-C(2)-C(8)	120.4(3)	C(23)-C(28)-C(31)	120.5(3)	C(34)-N(4)-Zr(1)	111.93(16)
C(1)-C(2)-C(8)	120.5(3)	N(3)-C(31)-C(28)	113.0(2)	C(35)-N(4)-Zr(1)	110.42(16)
C(4)-C(3)-C(2)	122.8(3)	N(3)-C(33)-C(34)	110.9(2)	C(36)-N(4)-Zr(1)	109.51(16)
C(3)-C(4)-C(5)	117.0(3)	N(4)-C(34)-C(33)	111.1(2)	C(1)-O(1)-Zr(1)	148.10(17)
C(3)-C(4)-C(9)	121.5(3)	N(4)-C(36)-C(37)	114.3(2)	C(20)-O(2)-Zr(1)	147.93(18)
C(5)-C(4)-C(9)	121.4(3)	C(38)-C(37)-C(42)	119.5(3)	C(23)-O(3)-Zr(1)	147.23(19)
C(6)-C(5)-C(4)	122.2(3)	C(38)-C(37)-C(36)	118.5(3)	C(42)-O(4)-Zr(1)	146.80(18)
C(5)-C(6)-C(1)	120.0(3)	C(42)-C(37)-C(36)	121.9(2)	O(4)-Zr(1)-O(3)	147.48(8)
C(5)-C(6)-C(7)	120.1(3)	C(37)-C(38)-C(39)	122.3(3)	O(4)-Zr(1)-O(2)	99.40(8)
C(1)-C(6)-C(7)	119.8(2)	C(38)-C(39)-C(40)	117.4(3)	O(3)-Zr(1)-O(2)	89.71(8)
N(1)-C(7)-C(6)	112.8(2)	C(38)-C(39)-C(43)	120.8(3)	O(4)-Zr(1)-O(1)	90.44(7)
N(1)-C(11)-C(12)	111.5(2)	C(40)-C(39)-C(43)	121.9(3)	O(3)-Zr(1)-O(1)	98.88(8)
N(2)-C(12)-C(11)	111.1(2)	C(39)-C(40)-C(41)	122.4(3)	O(2)-Zr(1)-O(1)	146.76(8)
N(2)-C(14)-C(15)	113.3(2)	C(40)-C(41)-C(42)	118.8(3)	O(4)-Zr(1)-N(3)	79.99(7)
C(16)-C(15)-C(20)	120.0(3)	C(40)-C(41)-C(44)	120.1(3)	O(3)-Zr(1)-N(3)	73.00(8)
C(16)-C(15)-C(14)	119.1(3)	C(42)-C(41)-C(44)	121.0(3)	O(2)-Zr(1)-N(3)	139.09(8)
C(20)-C(15)-C(14)	120.9(2)	O(4)-C(42)-C(41)	119.9(3)	O(1)-Zr(1)-N(3)	73.76(7)
C(17)-C(16)-C(15)	121.8(3)	O(4)-C(42)-C(37)	120.7(2)	O(4)-Zr(1)-N(4)	71.77(7)
C(18)-C(17)-C(16)	117.5(3)	C(41)-C(42)-C(37)	119.4(3)	O(3)-Zr(1)-N(4)	81.33(7)
C(18)-C(17)-C(21)	121.4(3)	Cl(2)-C(45)-Cl(1)	114.8(3)	O(2)-Zr(1)-N(4)	73.23(8)
C(16)-C(17)-C(21)	121.1(3)	C(10)-N(1)-C(11)	108.6(2)	O(1)-Zr(1)-N(4)	139.67(7)
C(17)-C(18)-C(19)	122.9(3)	C(10)-N(1)-C(7)	107.2(2)	N(3)-Zr(1)-N(4)	67.75(7)
C(18)-C(19)-C(20)	119.0(3)	C(11)-N(1)-C(7)	110.3(2)	O(4)-Zr(1)-N(2)	74.18(7)
C(18)-C(19)-C(22)	120.5(3)	C(10)-N(1)-Zr(1)	109.66(16)	O(3)-Zr(1)-N(2)	137.88(8)
C(20)-C(19)-C(22)	120.5(3)	C(11)-N(1)-Zr(1)	112.88(16)	O(2)-Zr(1)-N(2)	71.22(8)
O(2)-C(20)-C(19)	120.4(3)	C(7)-N(1)-Zr(1)	108.17(16)	O(1)-Zr(1)-N(2)	81.29(7)
O(2)-C(20)-C(15)	120.7(3)	C(12)-N(2)-C(13)	109.0(2)	N(3)-Zr(1)-N(2)	143.70(7)
C(19)-C(20)-C(15)	118.8(3)	C(12)-N(2)-C(14)	109.0(2)	N(4)-Zr(1)-N(2)	124.93(7)
O(3)-C(23)-C(28)	120.2(3)	C(13)-N(2)-C(14)	106.9(2)	O(4)-Zr(1)-N(1)	139.29(7)
O(3)-C(23)-C(24)	120.0(3)	C(12)-N(2)-Zr(1)	112.51(17)	O(3)-Zr(1)-N(1)	72.88(8)
C(28)-C(23)-C(24)	119.8(3)	C(13)-N(2)-Zr(1)	110.45(16)	O(2)-Zr(1)-N(1)	80.26(7)
C(25)-C(24)-C(23)	118.5(3)	C(14)-N(2)-Zr(1)	108.87(16)	O(1)-Zr(1)-N(1)	71.91(7)
C(25)-C(24)-C(29)	120.5(3)	C(33)-N(3)-C(32)	108.9(2)	N(3)-Zr(1)-N(1)	126.19(7)
C(23)-C(24)-C(29)	121.1(3)	C(33)-N(3)-C(31)	109.0(2)	N(4)-Zr(1)-N(1)	142.87(7)
C(26)-C(25)-C(24)	123.0(3)	C(32)-N(3)-C(31)	107.5(2)	N(2)-Zr(1)-N(1)	67.18(7)
C(25)-C(26)-C(27)	117.7(3)	C(33)-N(3)-Zr(1)	113.40(17)		
C(25)-C(26)-C(30)	121.1(4)	C(32)-N(3)-Zr(1)	109.20(16)		

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **[L1ZrL1]**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^*2U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	14(1)	21(1)	1(1)	-1(1)	1(1)
C(2)	19(1)	18(1)	21(1)	0(1)	2(1)	3(1)
C(3)	22(1)	17(1)	26(2)	-4(1)	0(1)	1(1)
C(4)	22(1)	16(1)	32(2)	1(1)	1(1)	-1(1)
C(5)	22(1)	17(1)	27(1)	3(1)	6(1)	0(1)
C(6)	20(1)	17(1)	20(1)	1(1)	2(1)	2(1)
C(7)	24(1)	18(1)	21(1)	0(1)	8(1)	-4(1)
C(8)	29(2)	23(1)	22(1)	-4(1)	6(1)	-2(1)
C(9)	30(2)	21(1)	41(2)	-4(1)	6(1)	-7(1)
C(10)	28(2)	25(2)	24(1)	-7(1)	11(1)	-4(1)
C(11)	14(1)	19(1)	29(2)	-5(1)	5(1)	-2(1)
C(12)	15(1)	21(1)	29(2)	-3(1)	3(1)	0(1)
C(13)	24(1)	27(2)	21(1)	-2(1)	-3(1)	1(1)
C(14)	21(1)	22(1)	26(1)	6(1)	-1(1)	5(1)
C(15)	16(1)	18(1)	33(2)	4(1)	3(1)	-1(1)
C(16)	19(1)	19(1)	43(2)	4(1)	1(1)	1(1)
C(17)	16(1)	18(1)	58(2)	-1(1)	2(1)	-1(1)
C(18)	22(2)	18(1)	50(2)	-11(1)	12(1)	-4(1)
C(19)	21(1)	18(1)	36(2)	-5(1)	10(1)	-5(1)
C(20)	17(1)	15(1)	32(2)	0(1)	9(1)	-2(1)
C(21)	30(2)	23(2)	88(3)	-10(2)	-9(2)	7(1)
C(22)	38(2)	26(2)	34(2)	-10(1)	10(1)	-4(1)
C(23)	21(1)	21(1)	23(1)	7(1)	-2(1)	-5(1)
C(24)	32(2)	29(2)	22(2)	7(1)	-1(1)	-9(1)
C(25)	39(2)	40(2)	24(2)	12(1)	-7(1)	-13(2)
C(26)	31(2)	37(2)	35(2)	21(2)	-7(1)	-6(1)
C(27)	24(2)	26(2)	40(2)	14(1)	-2(1)	-1(1)
C(28)	22(1)	18(1)	29(2)	7(1)	-4(1)	-5(1)
C(29)	50(2)	41(2)	18(2)	0(1)	3(1)	-3(2)
C(30)	43(2)	57(3)	47(2)	30(2)	-10(2)	2(2)
C(31)	22(1)	17(1)	31(2)	5(1)	0(1)	2(1)
C(32)	21(1)	27(2)	26(2)	-3(1)	6(1)	6(1)
C(33)	16(1)	23(1)	27(2)	3(1)	-1(1)	0(1)
C(34)	16(1)	21(1)	26(1)	4(1)	1(1)	-1(1)
C(35)	24(1)	24(1)	21(1)	-2(1)	-2(1)	-5(1)
C(36)	21(1)	16(1)	25(1)	1(1)	4(1)	-3(1)
C(37)	18(1)	19(1)	23(1)	4(1)	4(1)	3(1)
C(38)	21(1)	19(1)	29(2)	5(1)	5(1)	2(1)
C(39)	26(2)	25(2)	32(2)	12(1)	11(1)	5(1)
C(40)	26(2)	31(2)	22(1)	7(1)	7(1)	5(1)
C(41)	23(1)	26(1)	20(1)	3(1)	4(1)	3(1)
C(42)	16(1)	19(1)	21(1)	5(1)	3(1)	2(1)
C(43)	43(2)	29(2)	41(2)	14(2)	16(2)	1(2)
C(44)	35(2)	35(2)	18(1)	-2(1)	5(1)	-1(1)

C(45)	50(3)	94(4)	69(3)	26(3)	7(2)	-5(3)
N(1)	18(1)	17(1)	20(1)	-4(1)	5(1)	-1(1)
N(2)	16(1)	19(1)	21(1)	-1(1)	1(1)	1(1)
N(3)	19(1)	17(1)	22(1)	2(1)	2(1)	1(1)
N(4)	18(1)	18(1)	19(1)	0(1)	1(1)	-2(1)
O(1)	17(1)	16(1)	19(1)	-2(1)	4(1)	-2(1)
O(2)	22(1)	15(1)	21(1)	-1(1)	2(1)	1(1)
O(3)	21(1)	20(1)	18(1)	2(1)	0(1)	-2(1)
O(4)	19(1)	18(1)	18(1)	2(1)	3(1)	-2(1)
Zr(1)	14(1)	13(1)	14(1)	0(1)	2(1)	0(1)
Cl(1)	69(1)	83(1)	56(1)	8(1)	8(1)	1(1)
Cl(2)	63(1)	78(1)	185(2)	18(1)	34(1)	4(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **[L1ZrL1]**.

	x	y	z	U(eq)
H(3A)	10564	12294	8919	26
H(5A)	11254	11735	6958	26
H(7A)	9499	10539	6472	25
H(7B)	10722	10623	6436	25
H(8A)	9143	10745	9266	29
H(8B)	8465	11463	9051	29
H(8C)	9507	11538	9571	29
H(9A)	11928	12938	8437	37
H(9B)	11513	13147	7638	37
H(9C)	12447	12572	7786	37
H(10A)	11077	9458	6134	30
H(10B)	9861	9287	6031	30
H(10C)	10621	8752	6510	30
H(11A)	11309	10091	7826	25
H(11B)	11894	9666	7237	25
H(12A)	11280	8528	7617	26
H(12B)	11896	8944	8275	26
H(13C)	9876	9392	9225	29
H(13B)	10612	9917	8812	29
H(13A)	11096	9237	9272	29
H(14A)	9561	8113	8812	28
H(14B)	10791	8054	8975	28
H(16A)	11186	6872	8629	33
H(18A)	10555	6193	6611	35
H(21A)	11219	5397	8112	57
H(21B)	12257	5864	8059	57
H(21C)	11700	5473	7366	57
H(22A)	8607	7080	6067	38
H(22B)	9692	6988	5736	38
H(22C)	9308	7790	5955	38
H(25A)	6699	10074	4395	42
H(27A)	5878	11317	6017	36
H(29A)	8155	8773	5394	44
H(29B)	8781	9364	4972	44
H(29C)	7740	9003	4601	44
H(30C)	5252	11651	4802	60
H(30B)	4731	10875	4572	60
H(30A)	5644	11201	4150	60
H(31A)	7678	10959	7247	28
H(31B)	6445	11049	7186	28
H(32A)	6217	10623	8268	29
H(32B)	7432	10521	8481	29
H(32C)	6655	9847	8570	29
H(33A)	5948	9610	6741	27
H(33B)	5379	9837	7427	27

H(34B)	6084	8806	8050	25
H(34A)	5460	8537	7324	25
H(35C)	7500	8012	6414	28
H(35B)	6705	8683	6268	28
H(35A)	6292	7888	6485	28
H(36A)	7843	7525	7610	25
H(36B)	6618	7404	7570	25
H(38A)	6440	6899	8670	27
H(40A)	7129	8052	10470	31
H(43A)	6621	6289	9976	44
H(43B)	5530	6708	9892	44
H(43C)	6345	6877	10562	44
H(44A)	8787	9167	10123	35
H(44B)	7679	9313	10406	35
H(44C)	7946	9661	9666	35
H(45B)	15006	8300	9383	85
H(45A)	14670	8114	8568	85

Table S14. Torsion angles [°] for **[L1ZrL1]**.

O(1)-C(1)-C(2)-C(3)	176.1(2)	C(26)-C(27)-C(28)-C(23)	0.4(4)
C(6)-C(1)-C(2)-C(3)	-1.2(4)	C(26)-C(27)-C(28)-C(31)	-176.1(3)
O(1)-C(1)-C(2)-C(8)	-3.7(4)	O(3)-C(23)-C(28)-C(27)	-178.8(3)
C(6)-C(1)-C(2)-C(8)	179.0(3)	C(24)-C(23)-C(28)-C(27)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	1.9(4)	O(3)-C(23)-C(28)-C(31)	-2.3(4)
C(8)-C(2)-C(3)-C(4)	-178.4(3)	C(24)-C(23)-C(28)-C(31)	176.1(3)
C(2)-C(3)-C(4)-C(5)	-0.8(4)	C(27)-C(28)-C(31)-N(3)	129.2(3)
C(2)-C(3)-C(4)-C(9)	-178.3(3)	C(23)-C(28)-C(31)-N(3)	-47.2(4)
C(3)-C(4)-C(5)-C(6)	-0.9(4)	N(3)-C(33)-C(34)-N(4)	-57.6(3)
C(9)-C(4)-C(5)-C(6)	176.5(3)	N(4)-C(36)-C(37)-C(38)	141.4(3)
C(4)-C(5)-C(6)-C(1)	1.6(4)	N(4)-C(36)-C(37)-C(42)	-37.4(4)
C(4)-C(5)-C(6)-C(7)	-173.7(3)	C(42)-C(37)-C(38)-C(39)	-0.2(4)
O(1)-C(1)-C(6)-C(5)	-177.7(2)	C(36)-C(37)-C(38)-C(39)	-179.0(3)
C(2)-C(1)-C(6)-C(5)	-0.5(4)	C(37)-C(38)-C(39)-C(40)	3.3(4)
O(1)-C(1)-C(6)-C(7)	-2.5(4)	C(37)-C(38)-C(39)-C(43)	-177.4(3)
C(2)-C(1)-C(6)-C(7)	174.7(2)	C(38)-C(39)-C(40)-C(41)	-2.7(5)
C(5)-C(6)-C(7)-N(1)	127.3(3)	C(43)-C(39)-C(40)-C(41)	178.0(3)
C(1)-C(6)-C(7)-N(1)	-47.9(3)	C(39)-C(40)-C(41)-C(42)	-0.9(5)
N(1)-C(11)-C(12)-N(2)	-57.9(3)	C(39)-C(40)-C(41)-C(44)	178.4(3)
N(2)-C(14)-C(15)-C(16)	135.5(3)	C(40)-C(41)-C(42)-O(4)	-176.3(3)
N(2)-C(14)-C(15)-C(20)	-41.7(4)	C(44)-C(41)-C(42)-O(4)	4.3(4)
C(20)-C(15)-C(16)-C(17)	0.9(4)	C(40)-C(41)-C(42)-C(37)	4.1(4)
C(14)-C(15)-C(16)-C(17)	-176.3(3)	C(44)-C(41)-C(42)-C(37)	-175.3(3)
C(15)-C(16)-C(17)-C(18)	1.5(5)	C(38)-C(37)-C(42)-O(4)	176.8(2)
C(15)-C(16)-C(17)-C(21)	-179.6(3)	C(36)-C(37)-C(42)-O(4)	-4.4(4)
C(16)-C(17)-C(18)-C(19)	-2.5(5)	C(38)-C(37)-C(42)-C(41)	-3.6(4)
C(21)-C(17)-C(18)-C(19)	178.6(3)	C(36)-C(37)-C(42)-C(41)	175.2(3)
C(17)-C(18)-C(19)-C(20)	1.0(4)	C(12)-C(11)-N(1)-C(10)	-81.3(3)
C(17)-C(18)-C(19)-C(22)	-178.1(3)	C(12)-C(11)-N(1)-C(7)	161.6(2)
C(18)-C(19)-C(20)-O(2)	179.8(3)	C(12)-C(11)-N(1)-Zr(1)	40.5(3)
C(22)-C(19)-C(20)-O(2)	-1.1(4)	C(6)-C(7)-N(1)-C(10)	-168.6(2)
C(18)-C(19)-C(20)-C(15)	1.5(4)	C(6)-C(7)-N(1)-C(11)	-50.6(3)
C(22)-C(19)-C(20)-C(15)	-179.4(3)	C(6)-C(7)-N(1)-Zr(1)	73.3(2)
C(16)-C(15)-C(20)-O(2)	179.2(3)	C(11)-C(12)-N(2)-C(13)	-78.0(3)
C(14)-C(15)-C(20)-O(2)	-3.7(4)	C(11)-C(12)-N(2)-C(14)	165.7(2)
C(16)-C(15)-C(20)-C(19)	-2.4(4)	C(11)-C(12)-N(2)-Zr(1)	44.8(3)
C(14)-C(15)-C(20)-C(19)	174.7(3)	C(15)-C(14)-N(2)-C(12)	-52.0(3)
O(3)-C(23)-C(24)-C(25)	178.5(3)	C(15)-C(14)-N(2)-C(13)	-169.6(2)
C(28)-C(23)-C(24)-C(25)	0.0(4)	C(15)-C(14)-N(2)-Zr(1)	71.1(2)
O(3)-C(23)-C(24)-C(29)	-0.8(4)	C(34)-C(33)-N(3)-C(32)	-81.9(3)
C(28)-C(23)-C(24)-C(29)	-179.2(3)	C(34)-C(33)-N(3)-C(31)	161.1(2)
C(23)-C(24)-C(25)-C(26)	0.2(5)	C(34)-C(33)-N(3)-Zr(1)	39.9(3)
C(29)-C(24)-C(25)-C(26)	179.5(3)	C(28)-C(31)-N(3)-C(33)	-52.0(3)
C(24)-C(25)-C(26)-C(27)	-0.2(5)	C(28)-C(31)-N(3)-C(32)	-169.9(2)
C(24)-C(25)-C(26)-C(30)	-177.0(3)	C(28)-C(31)-N(3)-Zr(1)	72.1(2)
C(25)-C(26)-C(27)-C(28)	-0.1(5)	C(33)-C(34)-N(4)-C(35)	-77.5(3)
C(30)-C(26)-C(27)-C(28)	176.7(3)	C(33)-C(34)-N(4)-C(36)	166.3(2)

C(33)-C(34)-N(4)-Zr(1)	45.3(3)	C(19)-C(20)-O(2)-Zr(1)	-173.5(2)
C(37)-C(36)-N(4)-C(34)	-54.5(3)	C(15)-C(20)-O(2)-Zr(1)	4.9(5)
C(37)-C(36)-N(4)-C(35)	-172.5(2)	C(28)-C(23)-O(3)-Zr(1)	17.3(5)
C(37)-C(36)-N(4)-Zr(1)	68.0(2)	C(24)-C(23)-O(3)-Zr(1)	-161.2(2)
C(6)-C(1)-O(1)-Zr(1)	17.3(5)	C(41)-C(42)-O(4)-Zr(1)	179.0(2)
C(2)-C(1)-O(1)-Zr(1)	-159.9(2)	C(37)-C(42)-O(4)-Zr(1)	-1.4(5)

(D) Bio evaluation

Materials and methods

Cytotoxicity was measured on HeLa S3 and Hep G2 cells using the AlamarBlue assay.[8] Alamarblue was purchased from Thermo Scientific. Cells were cultivated at 37 ^{o}C in humidified 5 % CO_2 atmosphere using Dulbecco's DMEM-media (Invitrogen) containing 10 % foetal calf serum (Biochrome AG), 1 % penicillin and 1 % streptomycin (both GIBCO). Cells were split every three days. Both cell lines were tested on mycoplasma infections using a mycoplasma detection kit (Roche Applied Science).

AlamarBlue Assay

The cells were seeded in 96-well plates (4.000 HeLa S3 cells/well or 8.000 Hep G2 cells/well) and allowed to attach for 24 h. The cells were then incubated with different concentrations of the reagent to be tested. Compounds to be tested were dissolved in a suitable amount of DMSO and different concentrations were prepared by serial dilution with DMSO. One part of each DMSO solution is then added to 99 parts of medium. Cells were then incubated for 48 h with 100 µl of above medium containing 1 % DMSO and a certain concentration of compound. The medium was then replaced by 100 µL medium containing 10 % AlamarBlue (BioSource Europe) and the cells were incubated for 90 min. The fluorescence at 590 nm was measured after excitation at 530 nm using a Synergy HT Microplate Reader (BioTek). Raw readout data from the assay was corrected for background fluorescens by an "onplate" blind containing only medium, 1 % DMSO and Alamarblue but no cells (0-value). The background corrected absolute read-outs were then expressed as relative values with regard to an "on-plate" 100 % standard containing untreated cells in medium with 1 % DMSO. All data was then fitted to a sigmoidal dose-response model with variable slope (4 parameter logistic nonlinear regression model) using Sigma plot 10.0.[9] Upper and lower boundaries as well as the slope were allowed to refine freely. All experiments were repeated at least three times on three different days with each experiment done in four replicates on the same plate. Replicates are treated with equal statistical weight; Error-bars representing SEM. IC_{50} values are given as means from independent experiments, error values of IC_{50} are based on standard deviation of independent experiments.

Cell viability plots

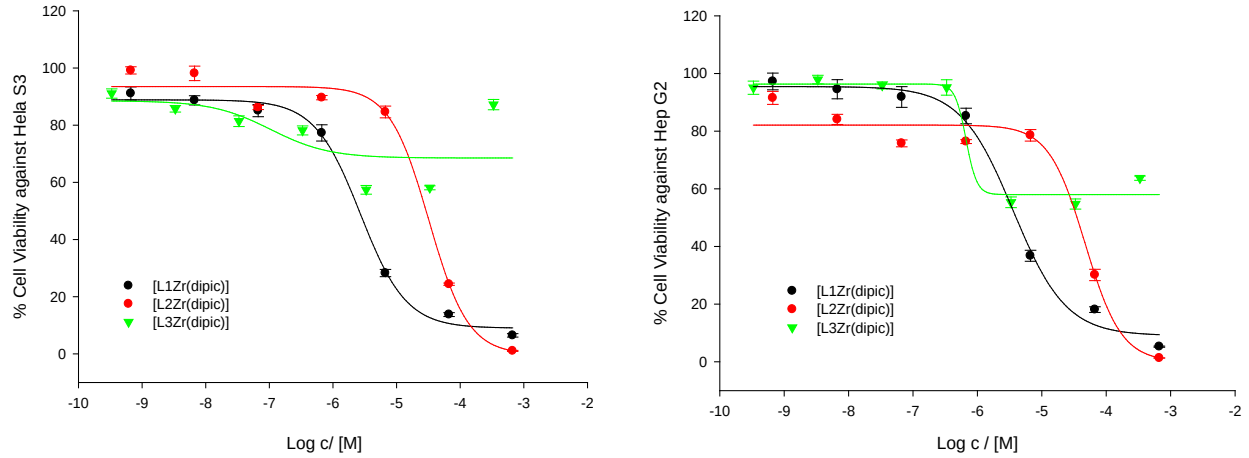


Figure S3. Loss of cell viability (HeLa S3 and Hep G2) as a function of treatment with varying concentrations of cisplatin or complexes **[L1Zr(dipic)]** ●, **[L2Zr(dipic)]** ● and **[L3Zr(dipic)]** ● after 48 h of incubation.

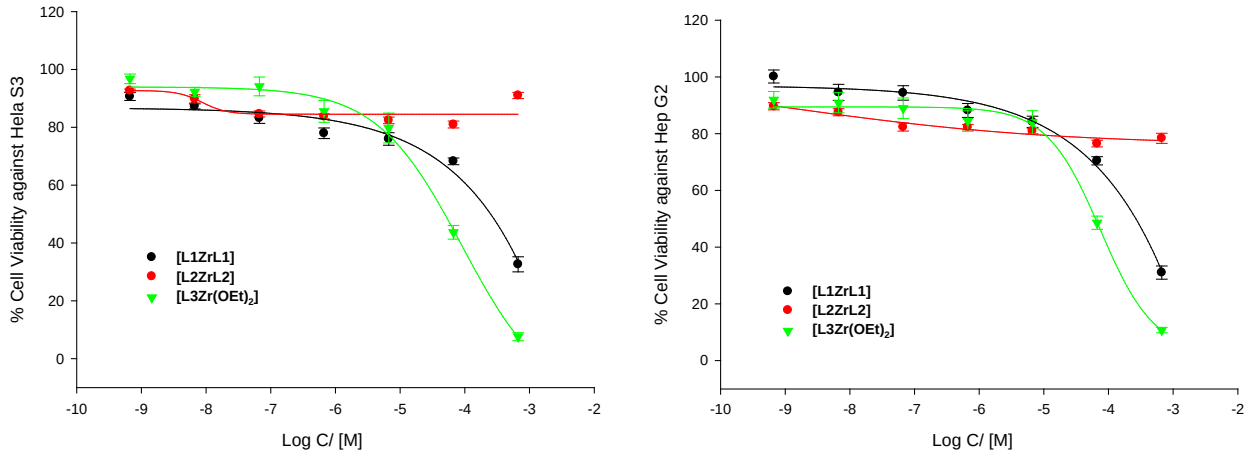


Figure S4. Loss of cell viability of Hep G2 cells (left) and Hela S3 cell (right) as a function of treatment with varying concentrations of **[L1ZrL1]** (●), **[L2ZrL2]** (●) and **[L3Zr(OEt)$_2$]** (●) after 48 h of incubation.

(E) Plots of all ^{1}H and ^{13}C-NMR spectra

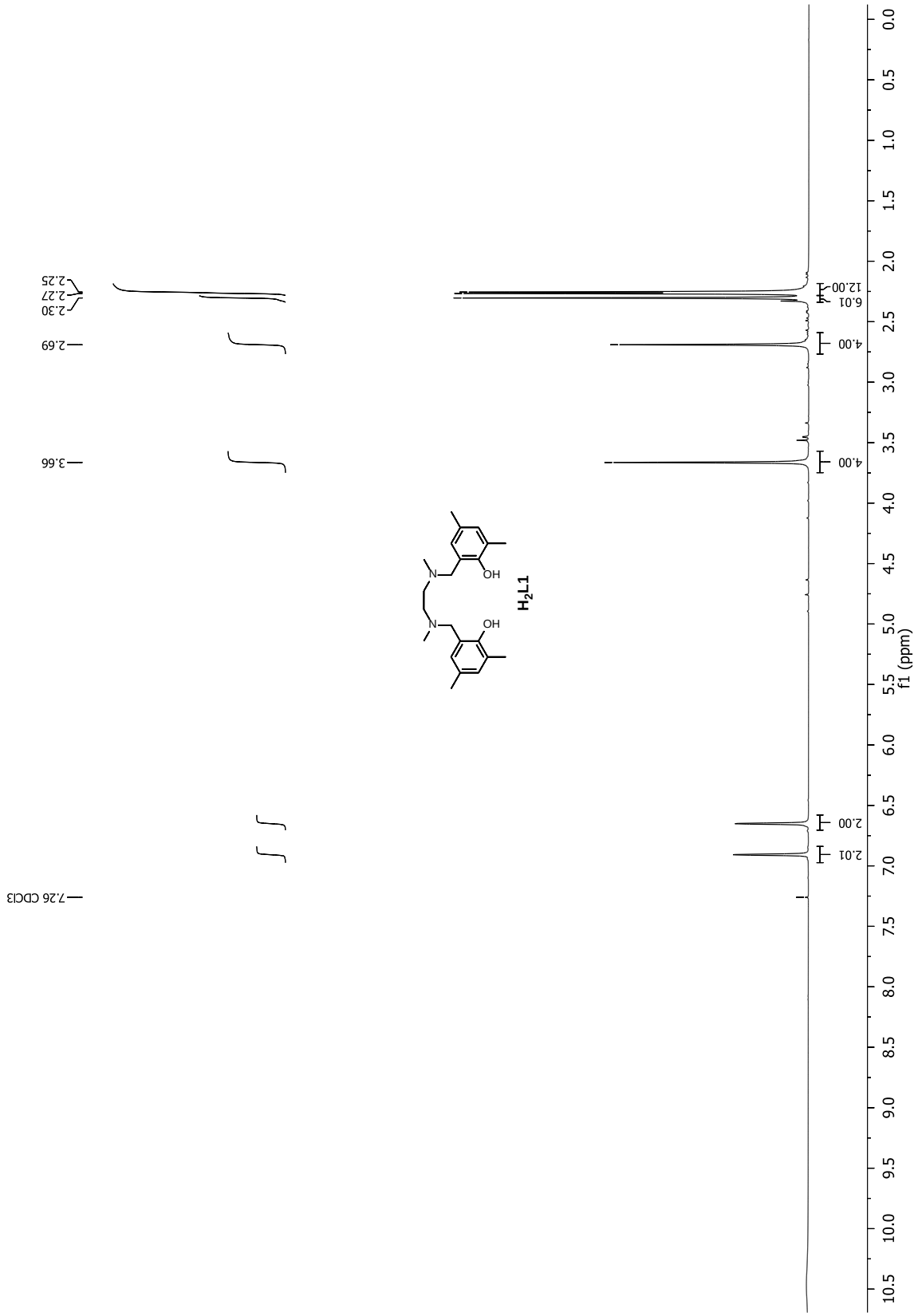


Fig. S5. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of H_2L1.

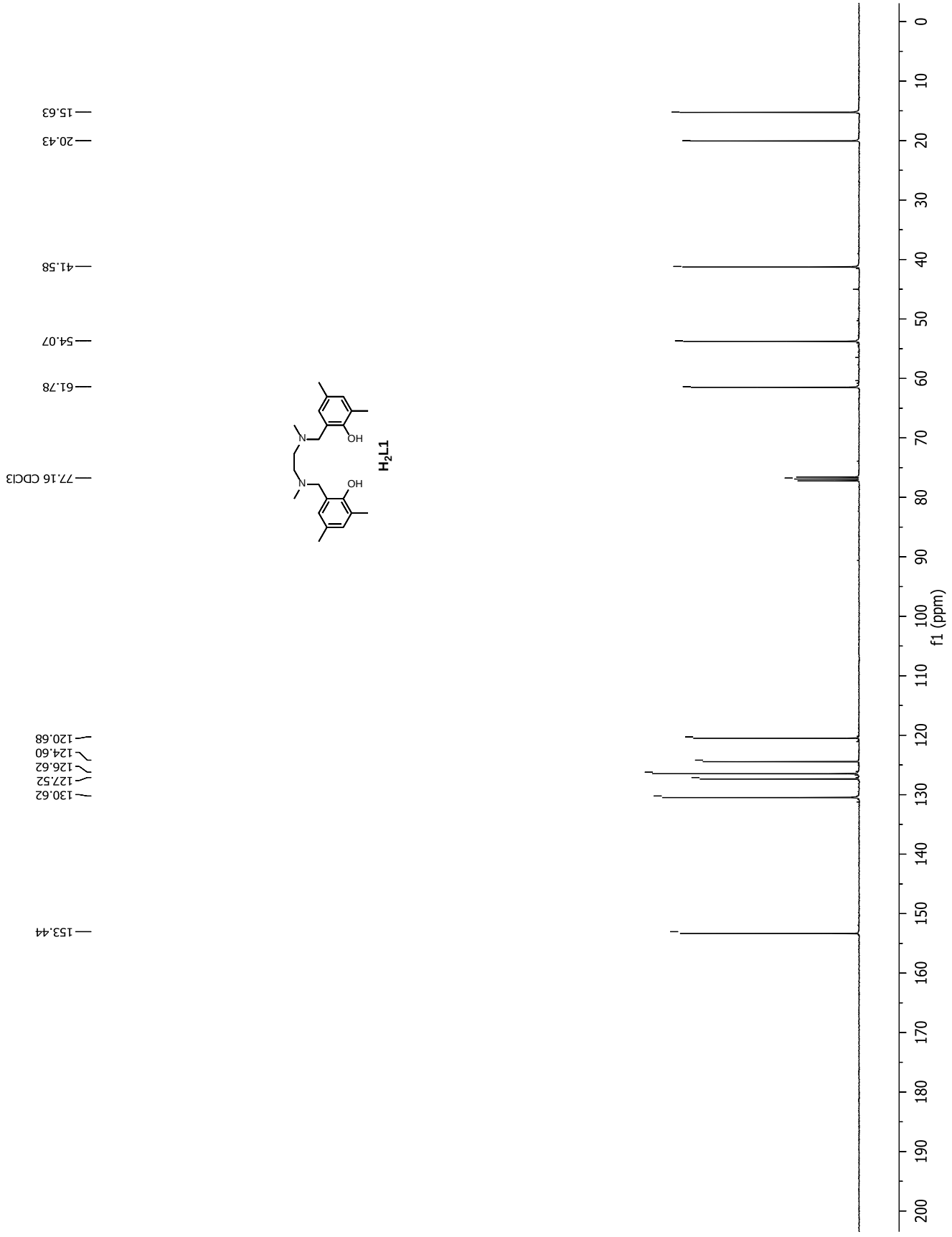


Fig. S6. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of H_2L1].

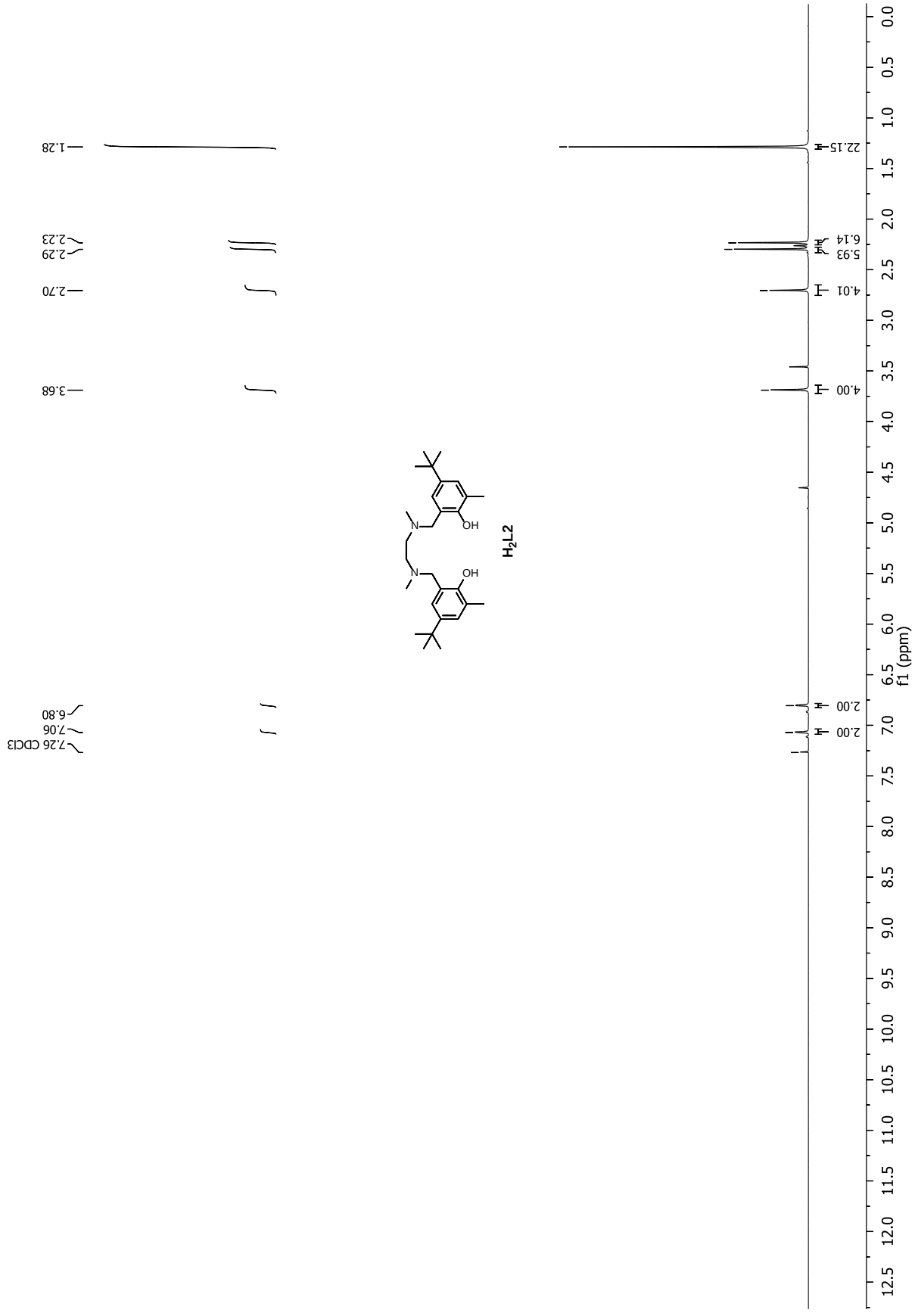


Fig. S7. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of H_2L2.

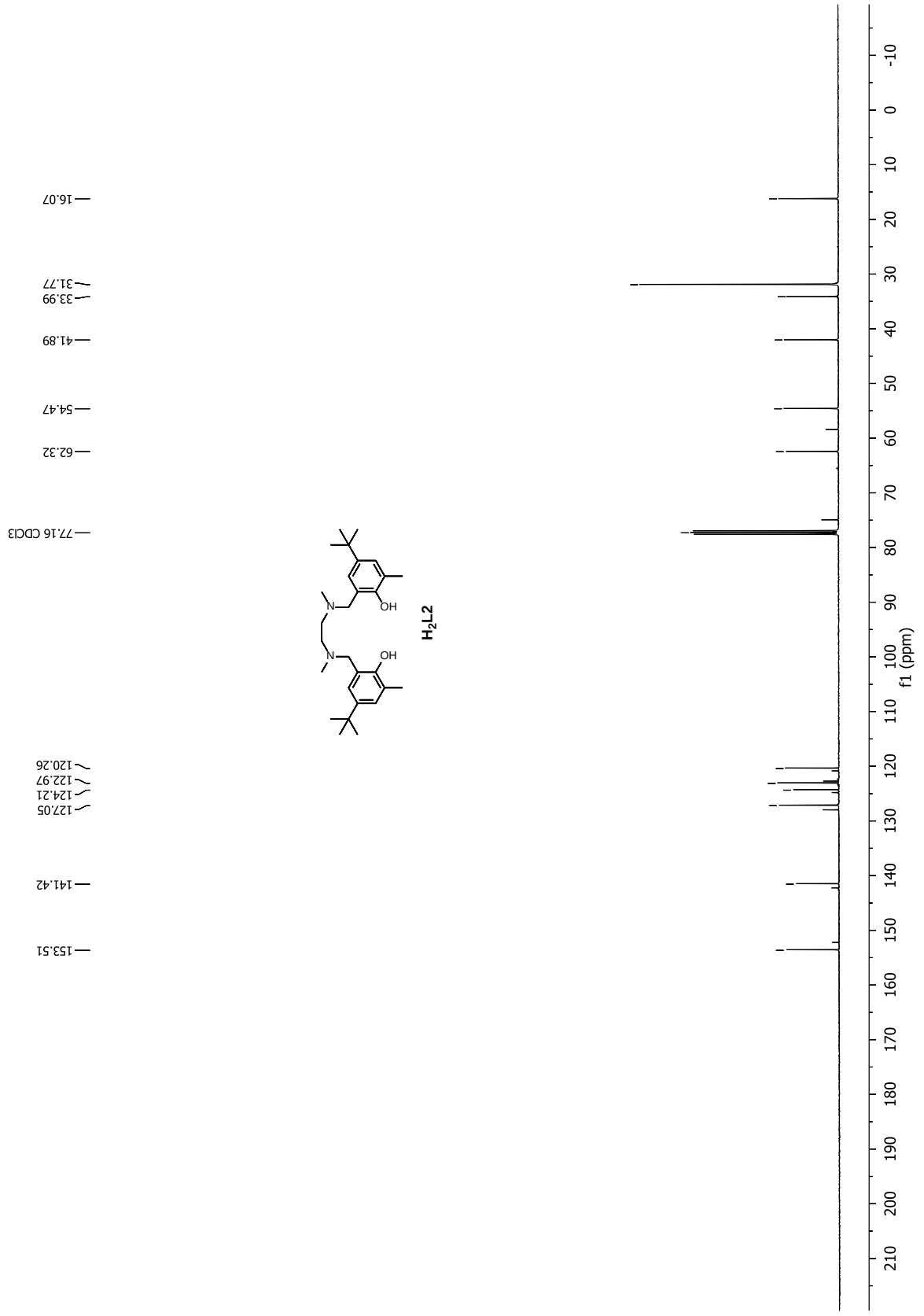


Fig. S8. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of H_2L2].

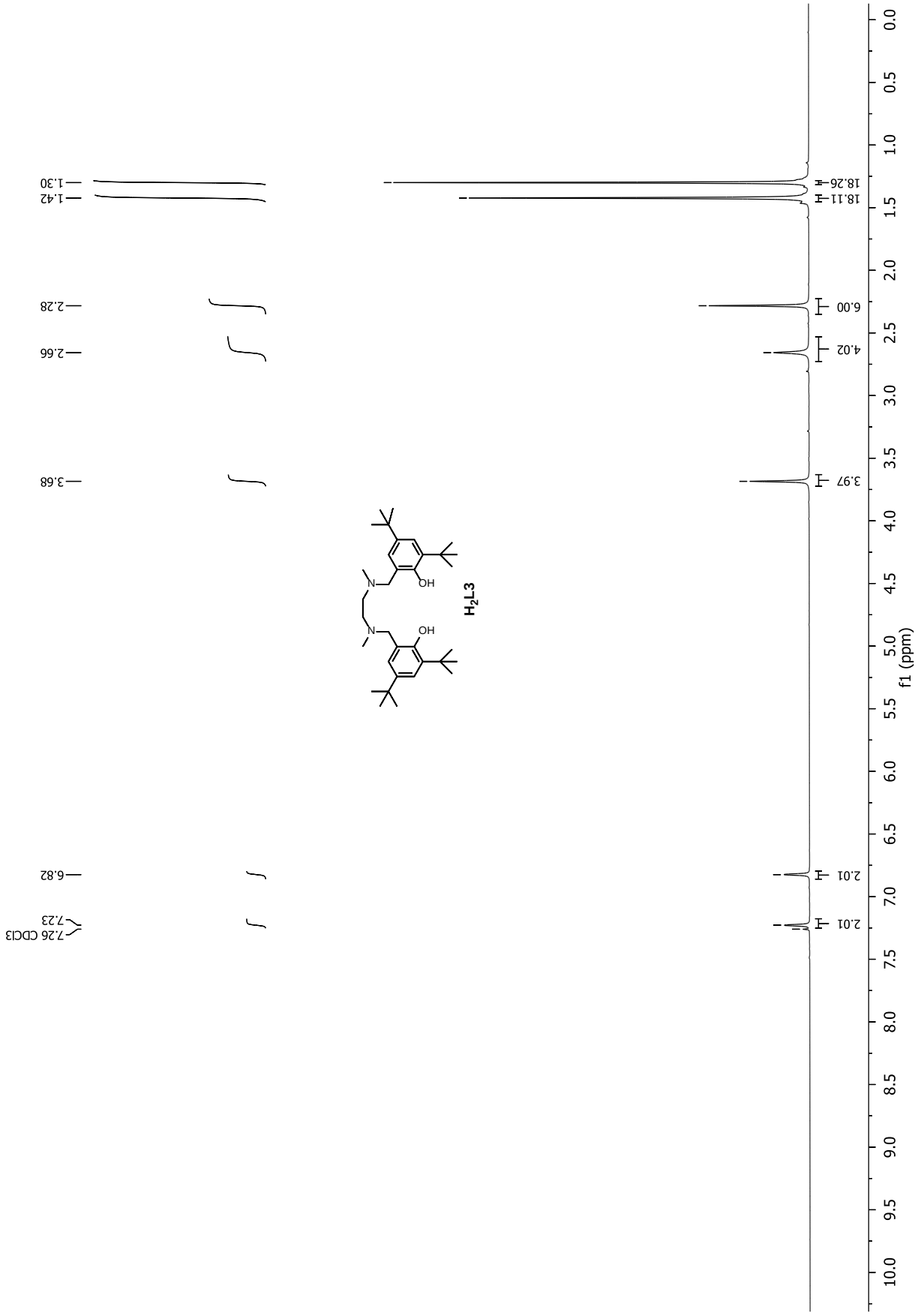


Fig. S9. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of H_2L3.

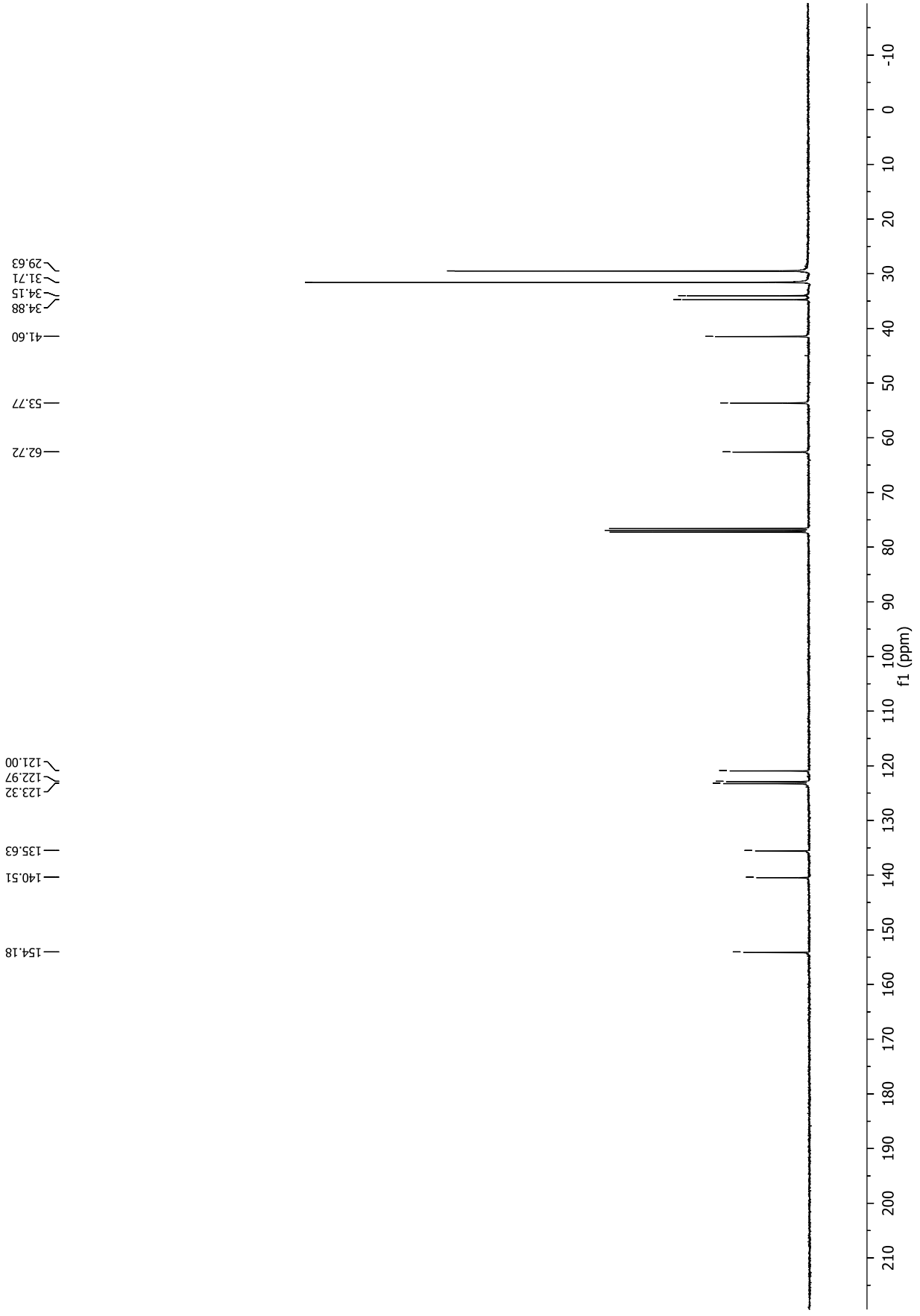


Fig. S10. ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of H_2L3.

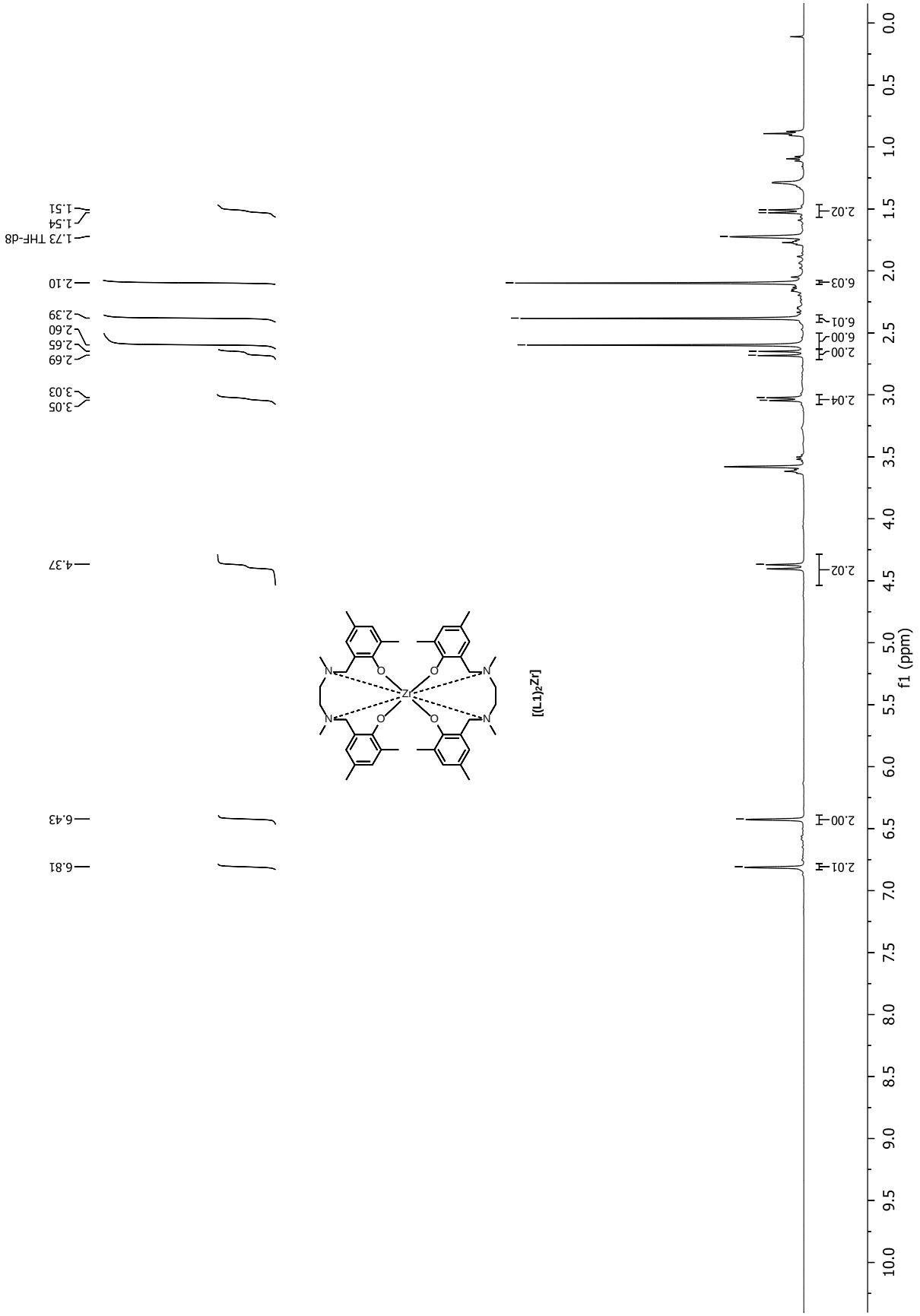


Fig. S11. ^{1}H-NMR (400 MHz, THF-d_8) spectrum of [$(L1)_2Zr$].

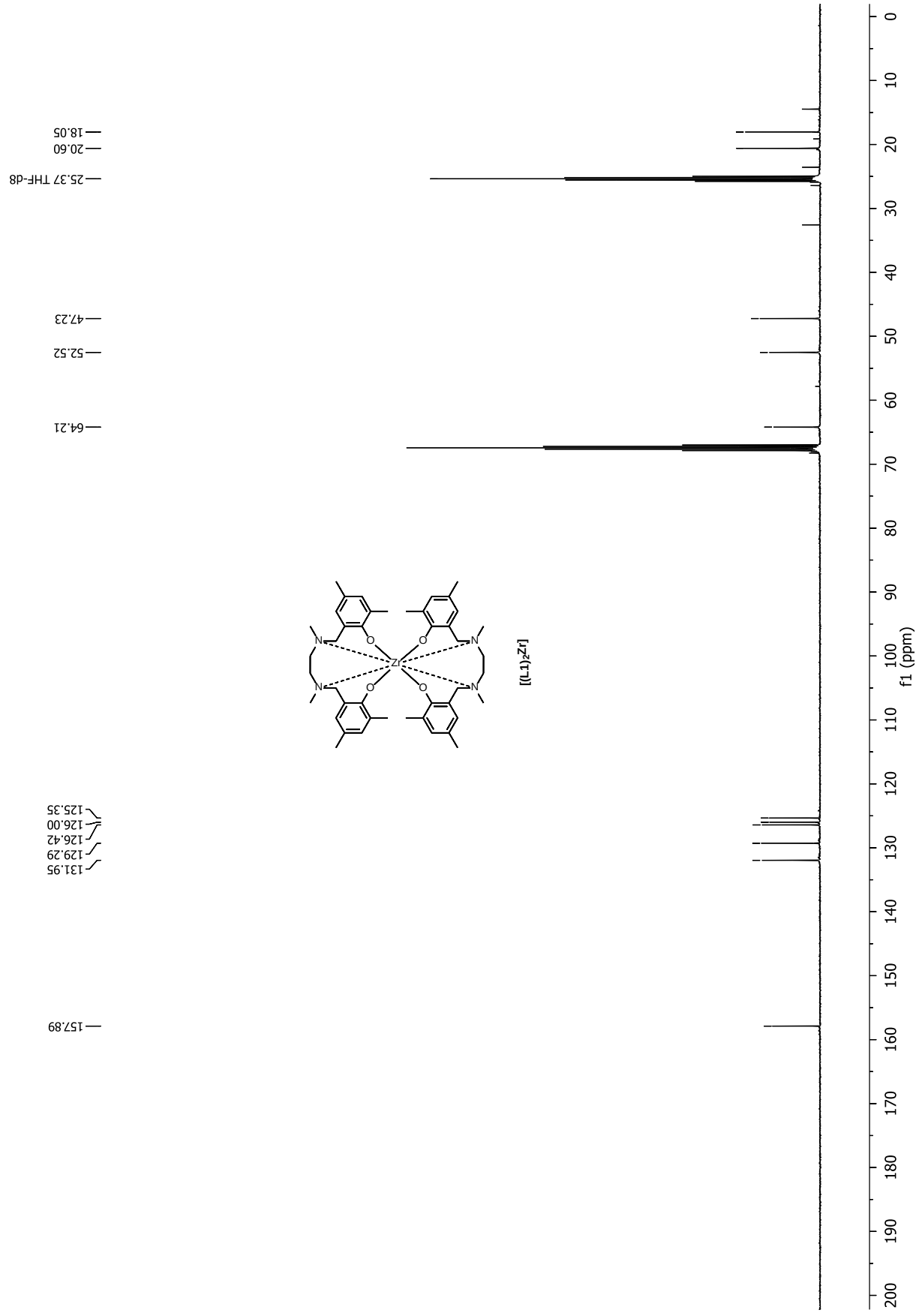


Fig. S12. ^{13}C-NMR spectrum (101 MHz, THF-d_8) of [$(L1)_2$Zr].

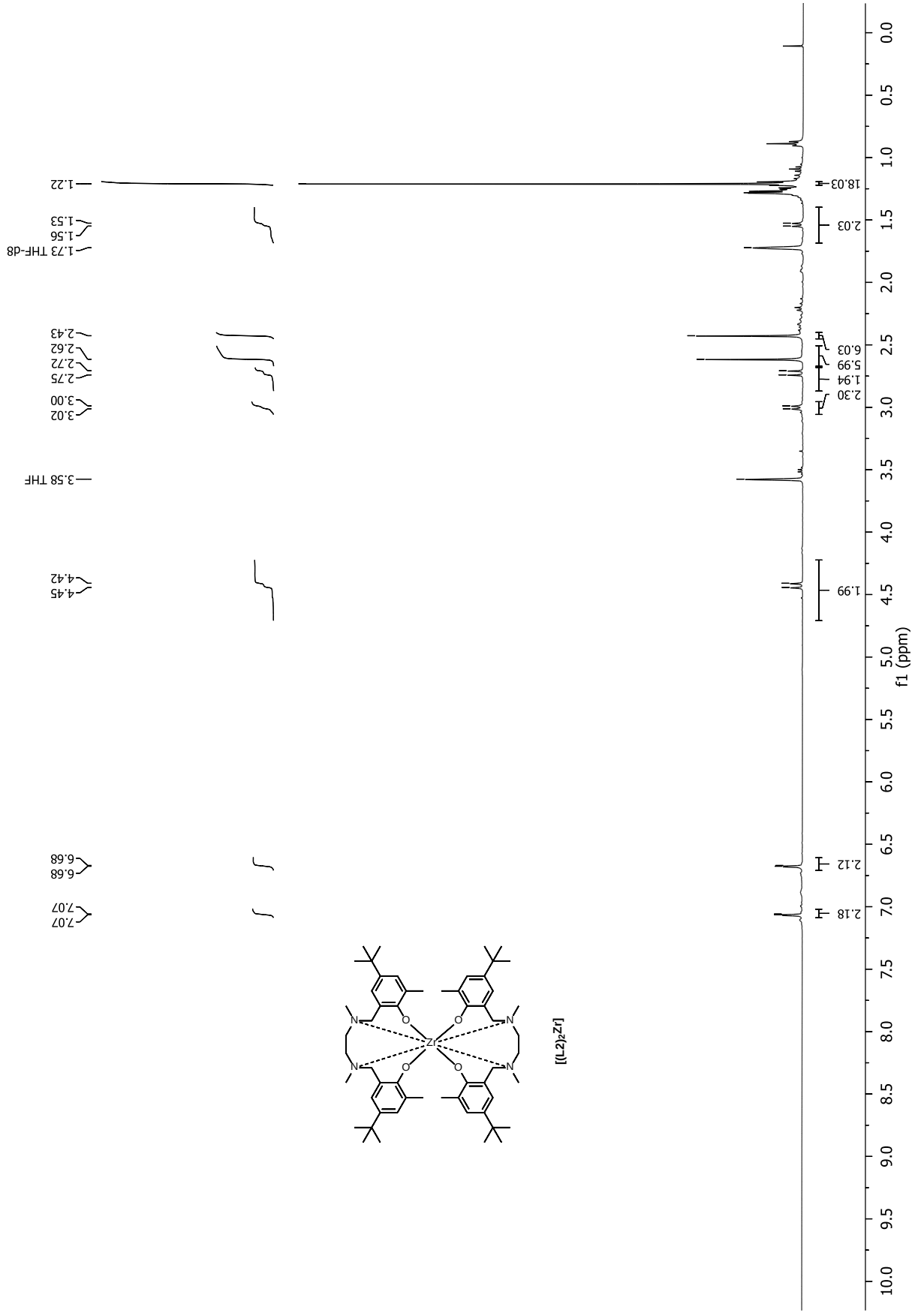


Fig. S13. ^{1}H-NMR (400 MHz, THF-d_8)spectrum of [$(L2)_2Zr$].

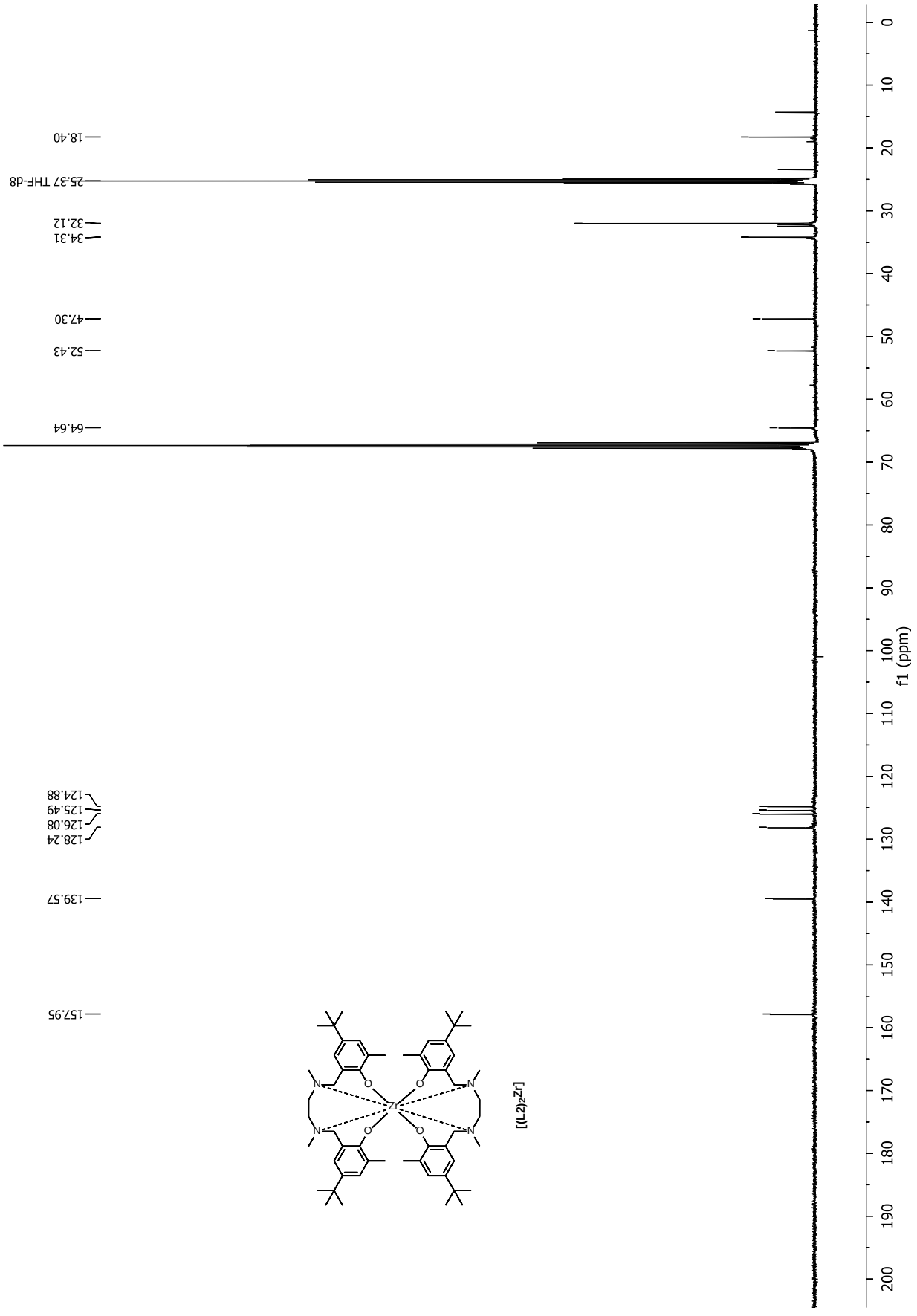


Fig. S14. ^{13}C-NMR spectrum (101 MHz, THF-d_8) of [$(L2)_2Zr$].

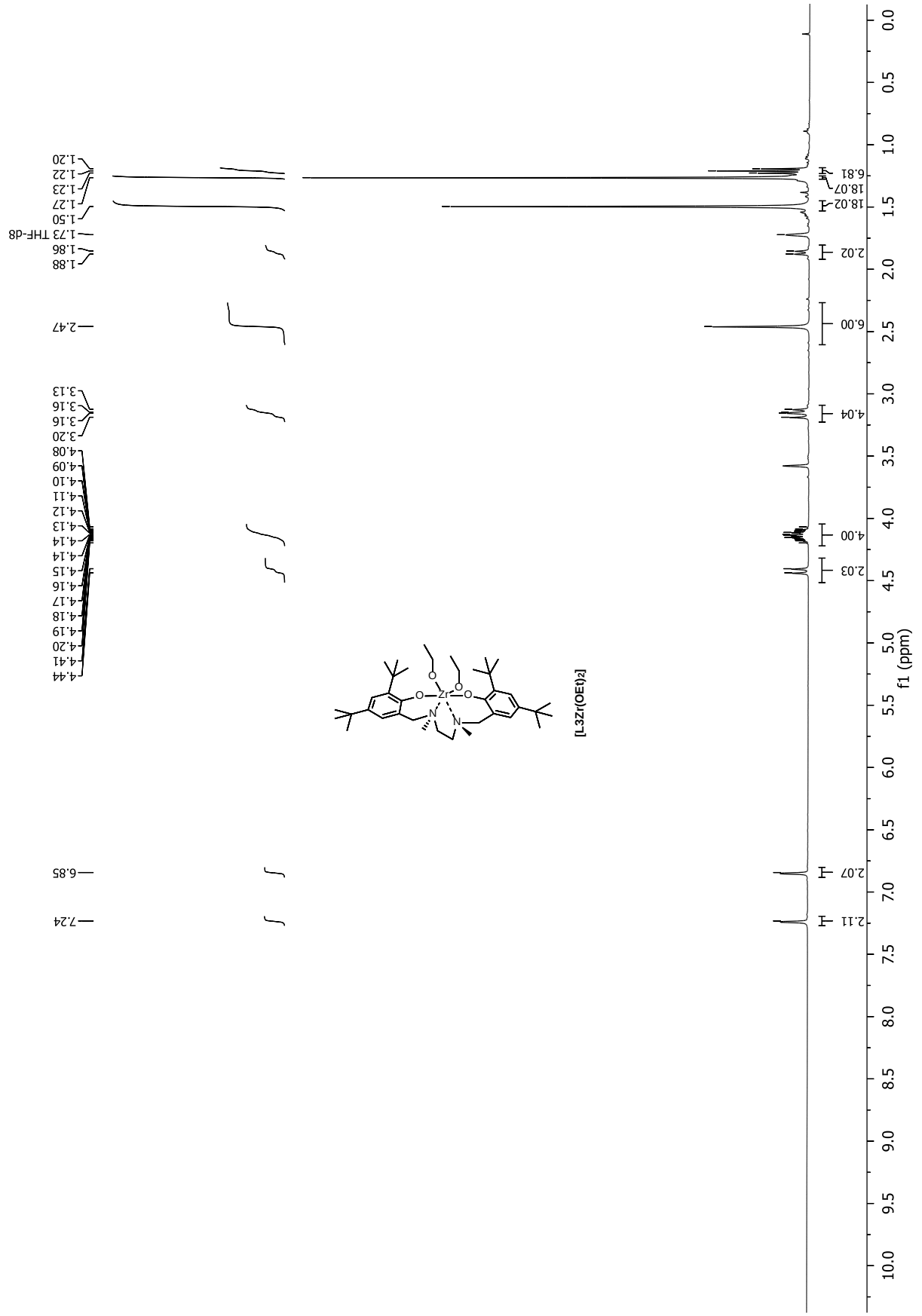


Fig. S15. ^{1}H-NMR (400 MHz, THF-d_8) spectrum of [L3Zr(OEt)$_2$].

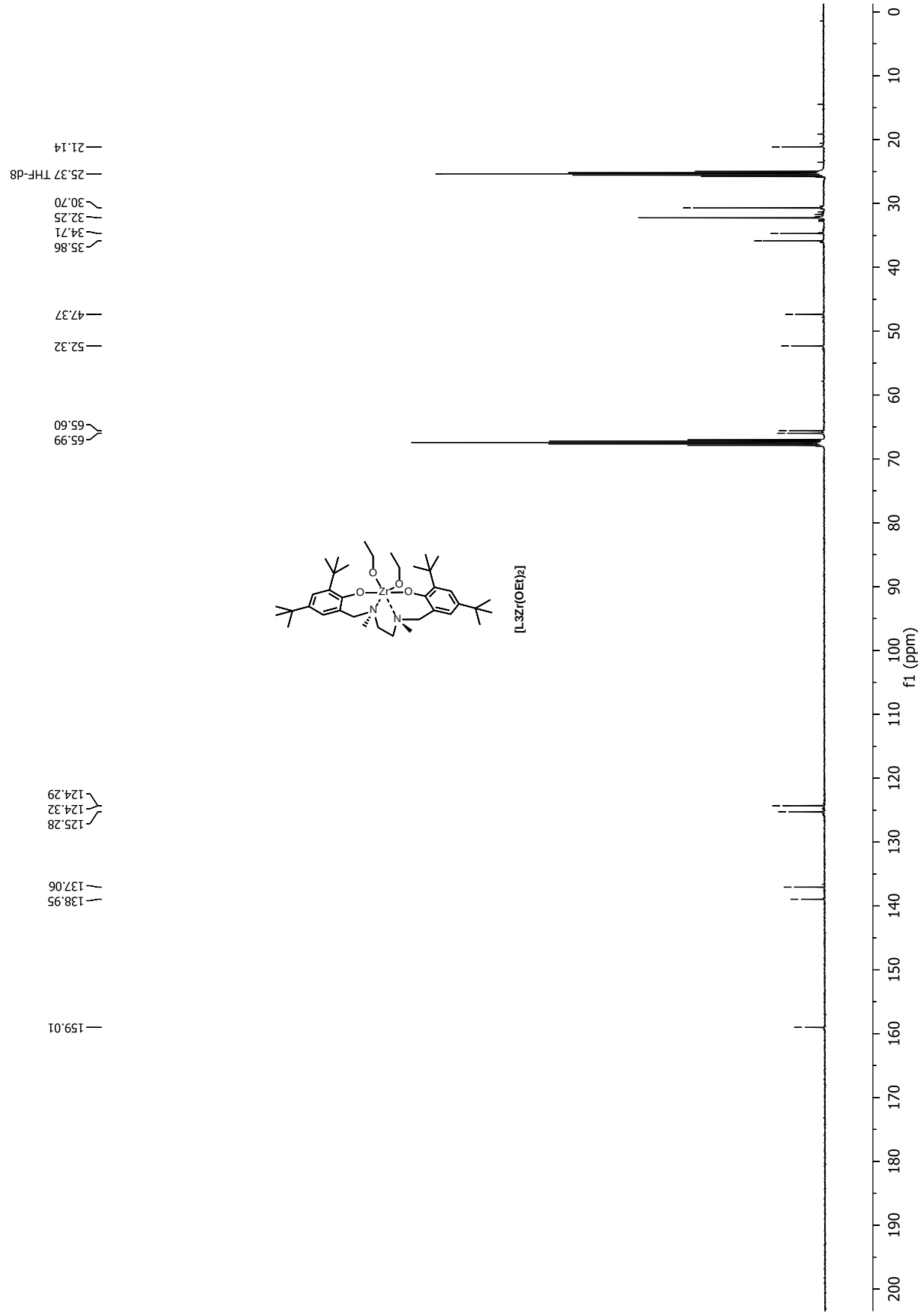


Fig. S16. ^{13}C-NMR spectrum (101 MHz, THF-d_8) of [L3Zr(OEt)$_2$].

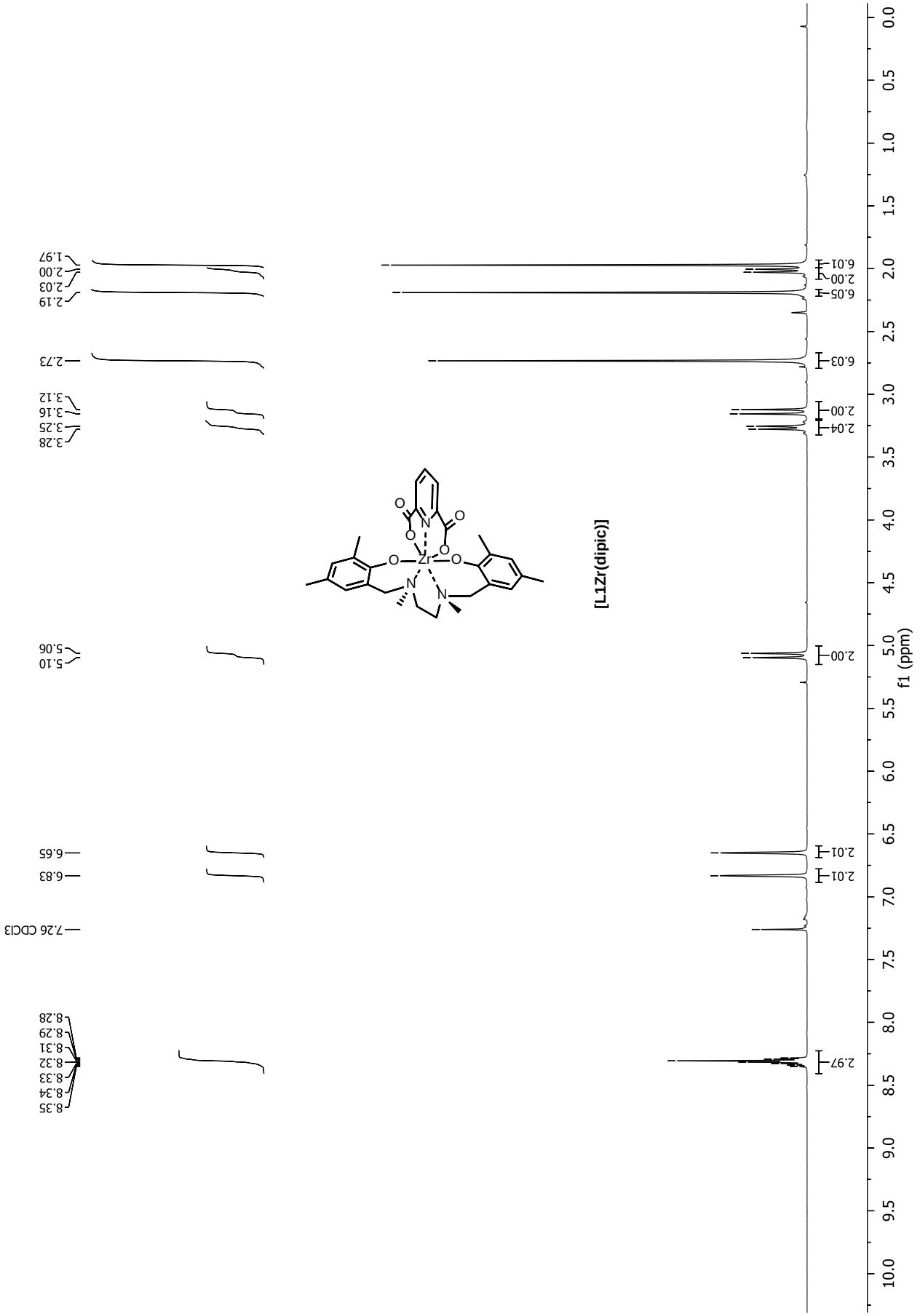


Fig. S17. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of [L1Zr(dipic)].

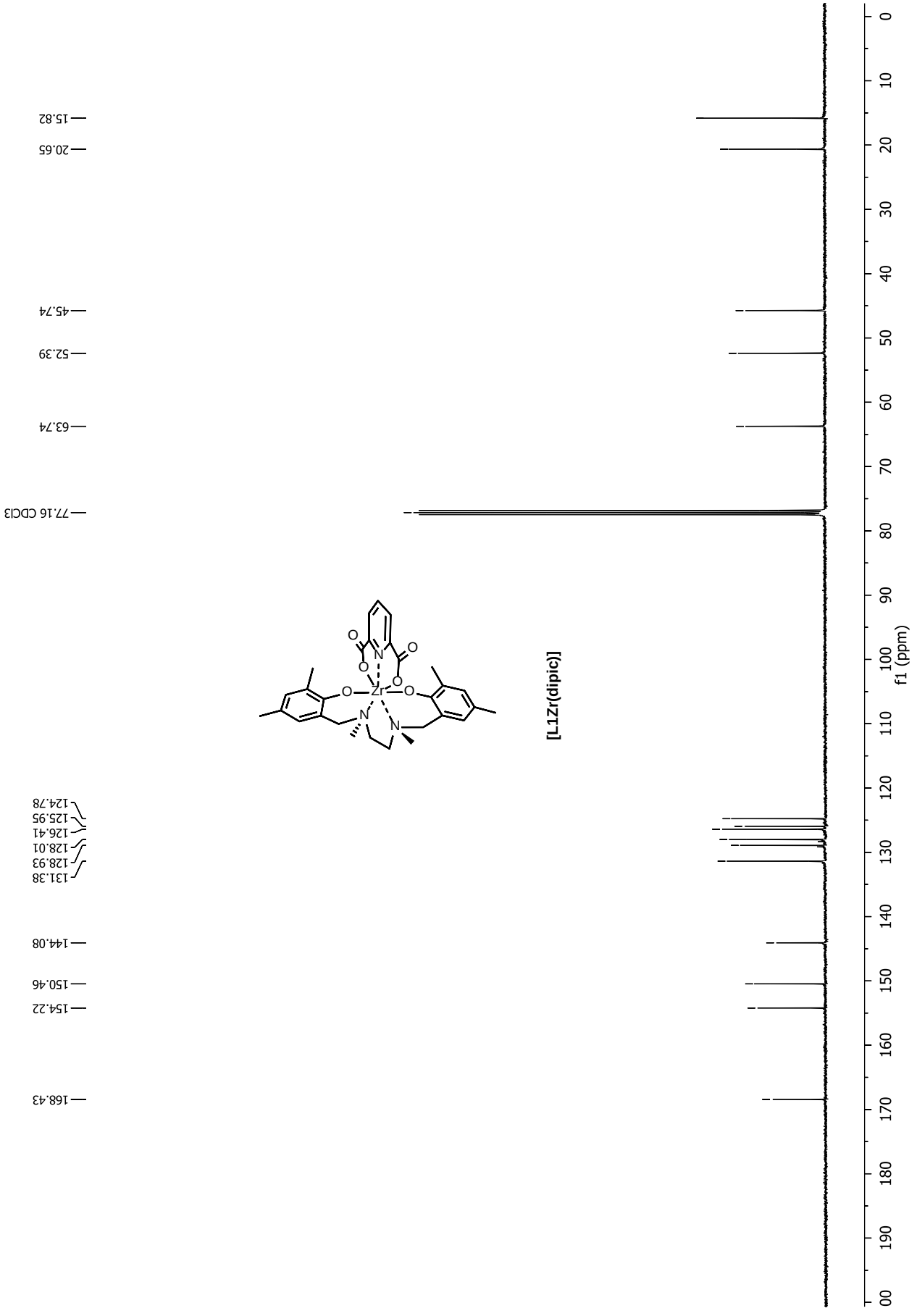


Fig. S18. ^{13}C-NMR (101 MHz, CDCl3) spectrum of [L1Zr(dipic)].

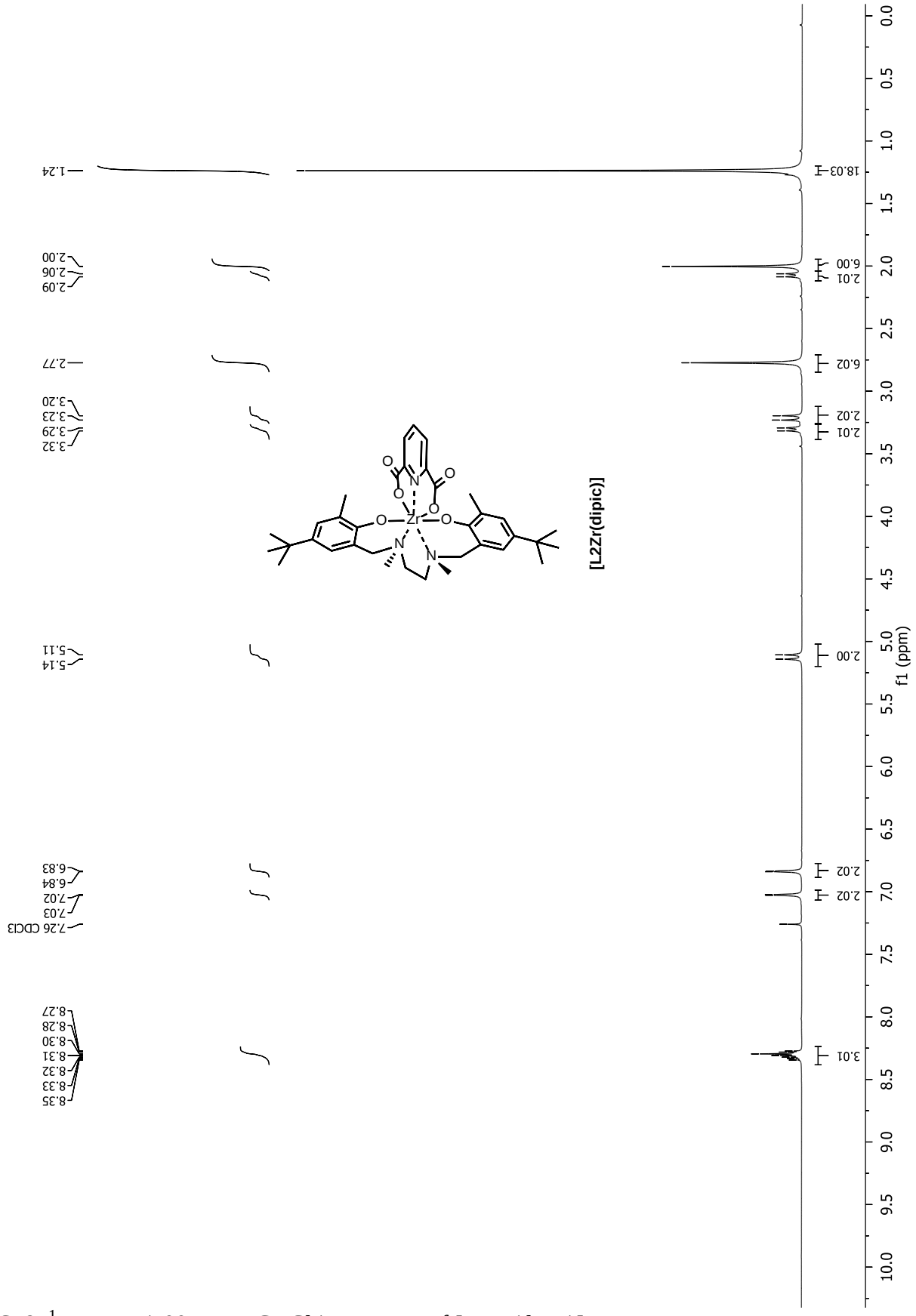


Fig. S19. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of [L2Zr(dipic)].

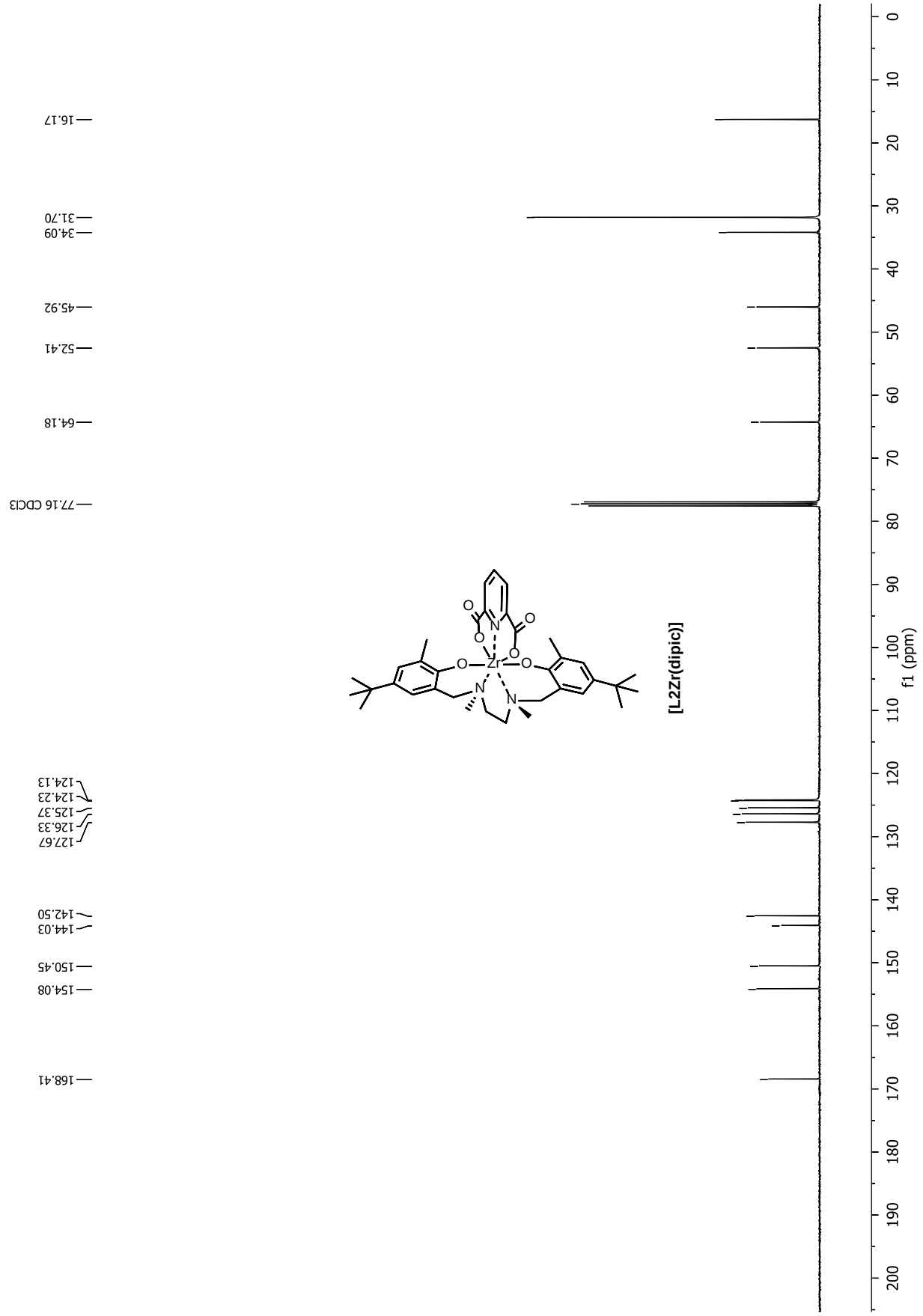


Fig. S20. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of [L2Zr(dipic)].

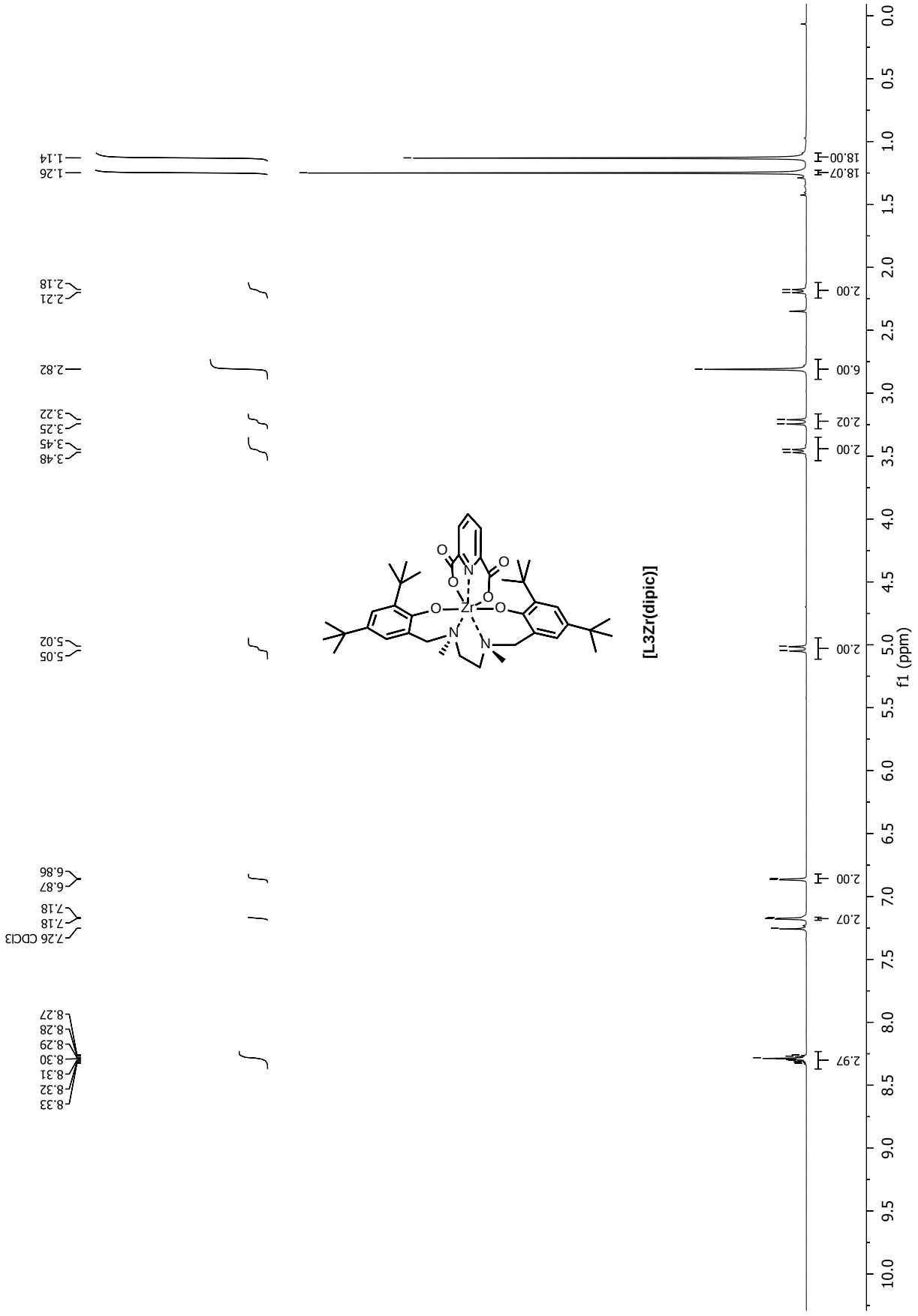


Fig. S21. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of [L3Zr(dipic)].

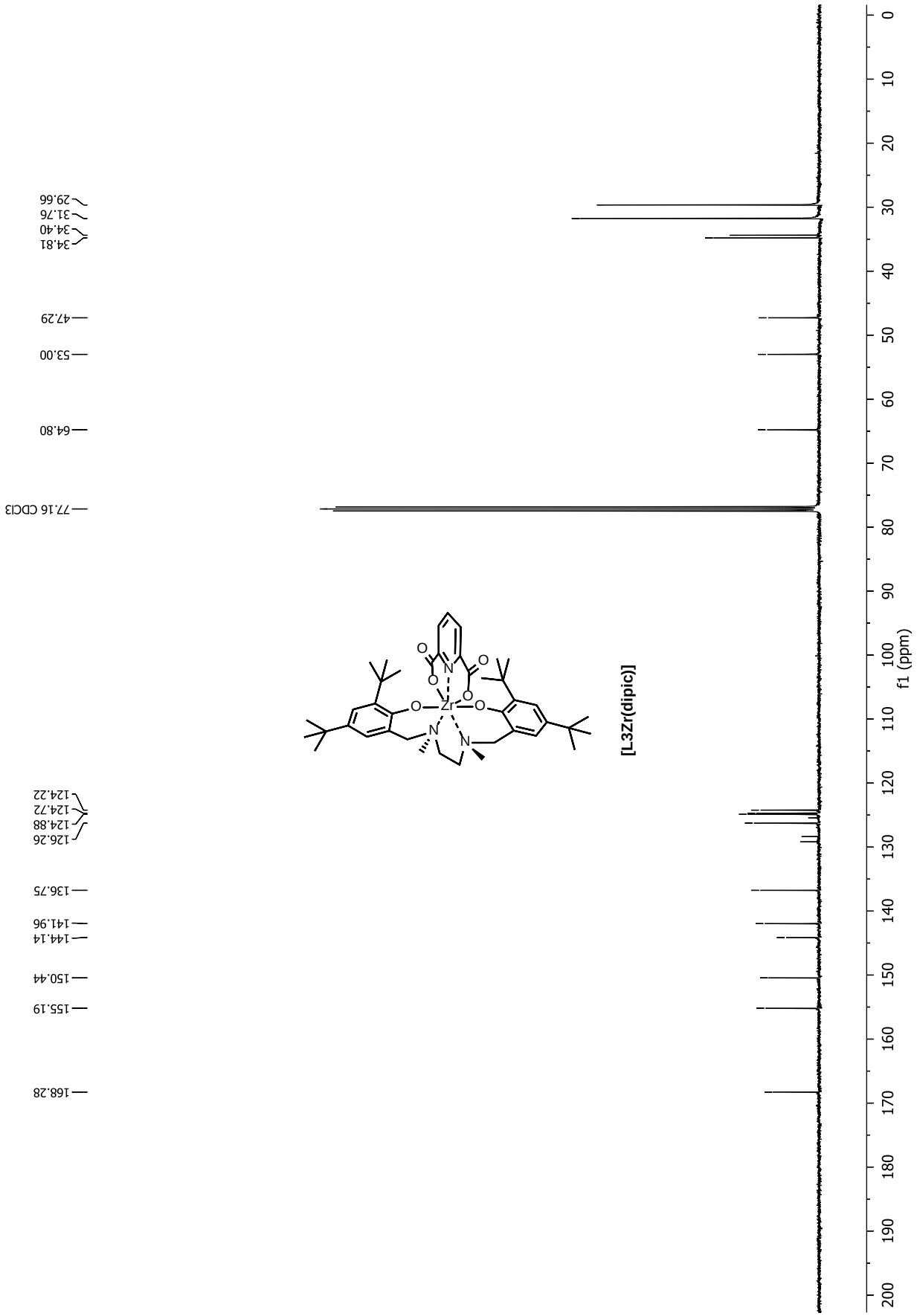


Fig. S22. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of [L3Zr(dipic)].

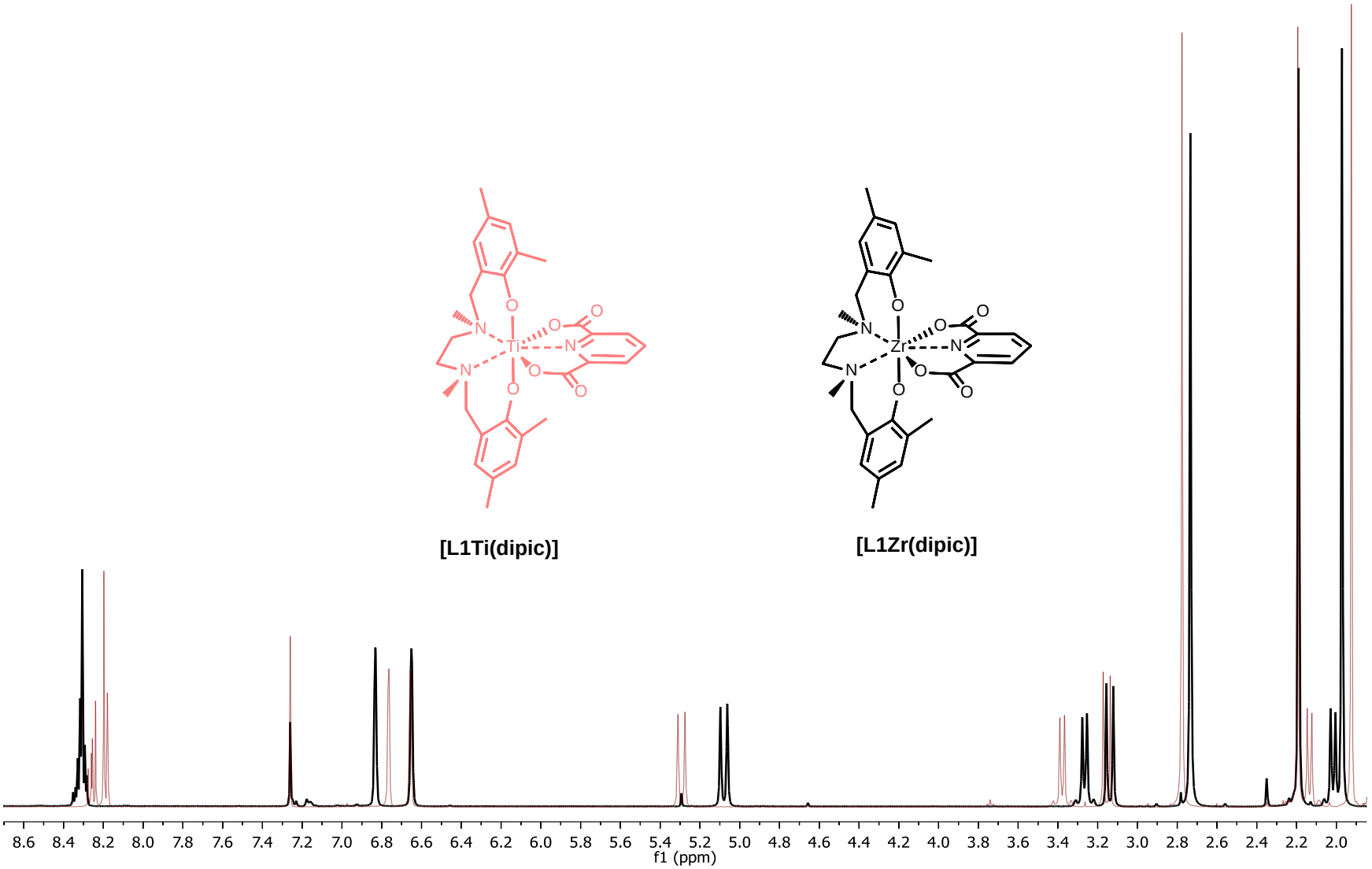


Figure S23: Overlay of 1H-NMR spectra of **[L1Ti(dipic)]** (red) and **[L1Zr(dipic)]** (black) recorded in $CDCl_3$.

Table S15. Comparison of selected bond length [Å] of **[(L1)Zr(dipic)]** and **[L1Ti(dipic)]**

[L1Zr(dipic)]		**[L1Ti(dipic)]**	
O1–Zr	1.992(1)	O1–Ti	1.844(1)
O2–Zr	1.989(1)	O2–Ti	1.850(1)
O3–Zr	2.155(1)	O3–Ti	2.046(1)
O4–Zr	2.147(1)	O4–Ti	2.043(1)
N1–Zr	2.459(1)	N1–Ti	2.350(2)
N2–Zr	2.439(1)	N2–Ti	2.384(2)
N3–Zr	2.293(1)	N3–Ti	2.185(2)

(F) Hydrolysis

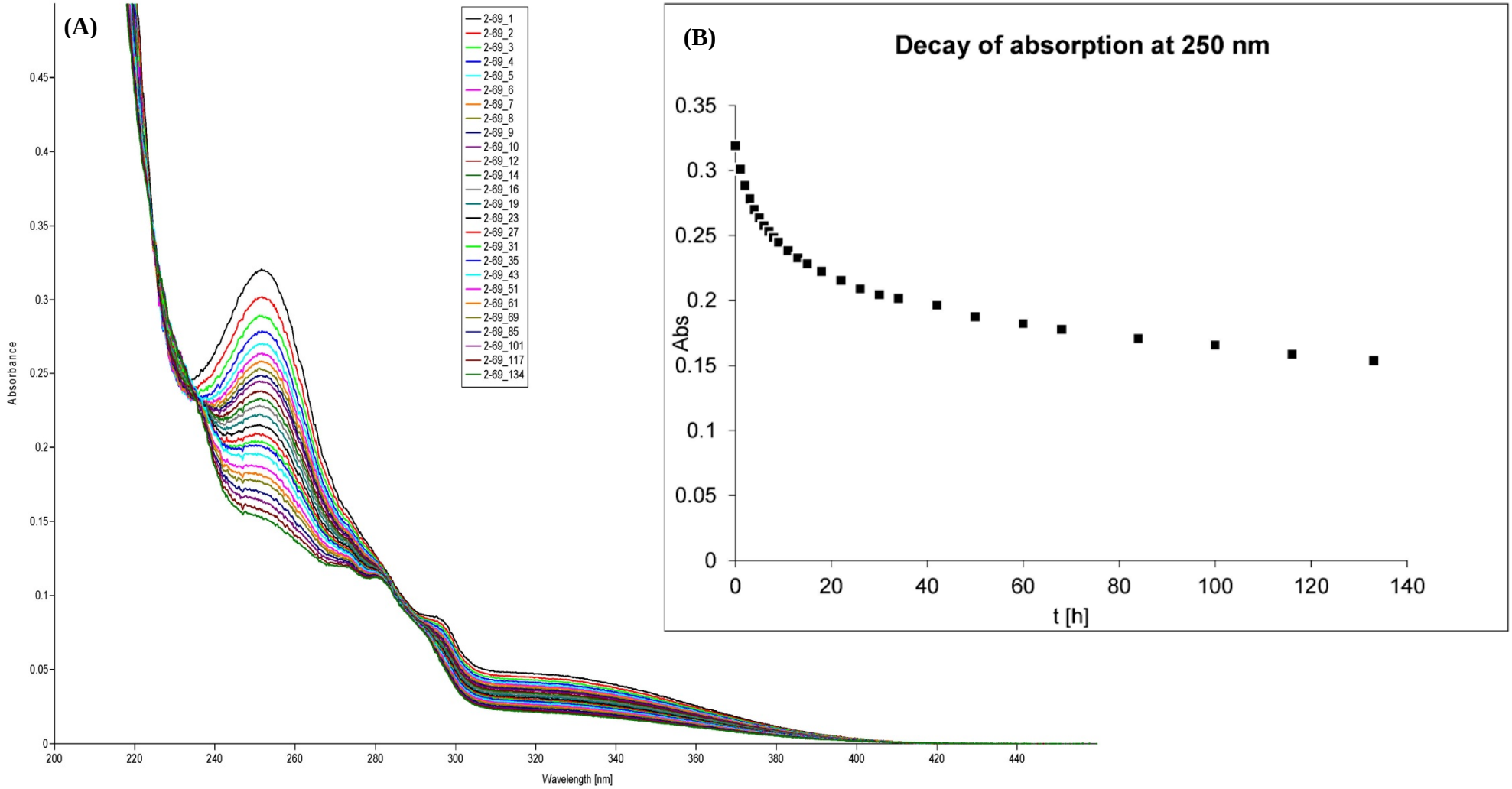


Figure S24: (**A**) Time resolved UV-vis spectra of **[L1Zr(dipic)]** (c = 5 x 10^{-5} mol/l in THF/water 1 / 100.000) show a slow decrease in overall absorption. Spectra were recorded every hour during first 10 hours, later less frequently. The postfix "_X-1" gives the number of hours after addition of water. (**B**) Inset shows the decay of absorption at λ_{max} = 250 nm over time.

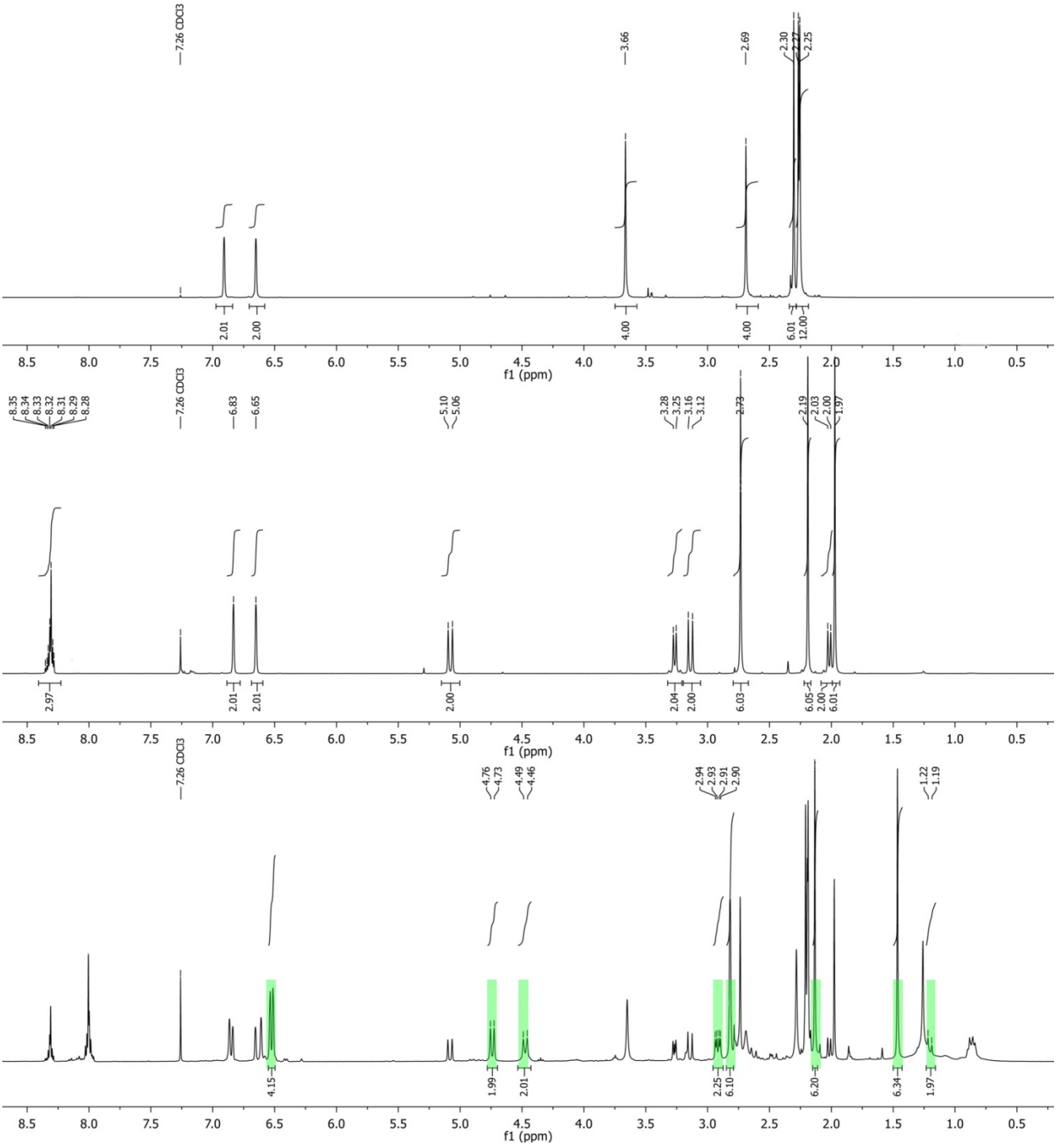


Figure S25: Bottom panel shows ^{1}H-NMR of a hydrolyzed sample of [**L1Zr(dipic)**]. Conditions: [**L1Zr(dipic)**] (30 mg) dissolved in THF (30 ml), then addition of 1.000 eq. H_2O and stirring for a total of 6 days (Solvent has been removed in vacuo prior to NMR recording). Signals marked in green represent a well-defined, newly formed complex which resulted from hydrolysis. ^{1}H-NMR spectra of **H_2L1** (top) and [**L1Zr(dipic)**] (middle) are shown for comparison and measured under identical conditions.

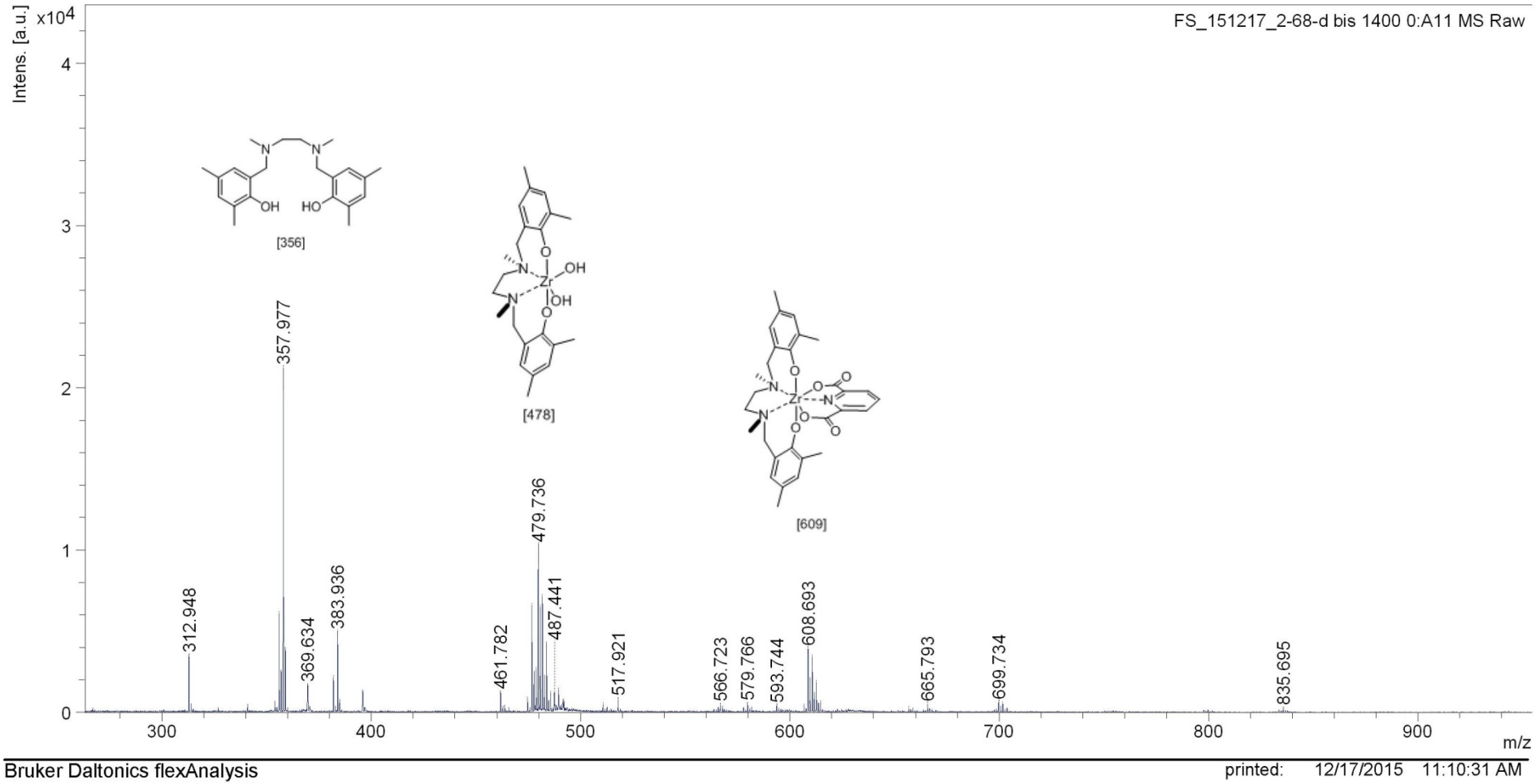


Figure S26: LDI-TOF mass spectrum of a hydrolyzed sample of [**L1Zr(dipic)**]. Conditions: [**L1Zr(dipic)**] dissolved in THF, then adding 1.000 eq. H_2O and stirring for a total of 6 days. (Solvent has been removed in vacuo prior to MS recording). Besides free ligand **H2L1** and starting material [**L1Zr(dipic)**] the bis-hydroxo zirconium salan **[L1Zr(OH)2]** was identified.

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