Supporting information for

Al and Zn phenoxy-amidine complexes for lactide ROP catalysis

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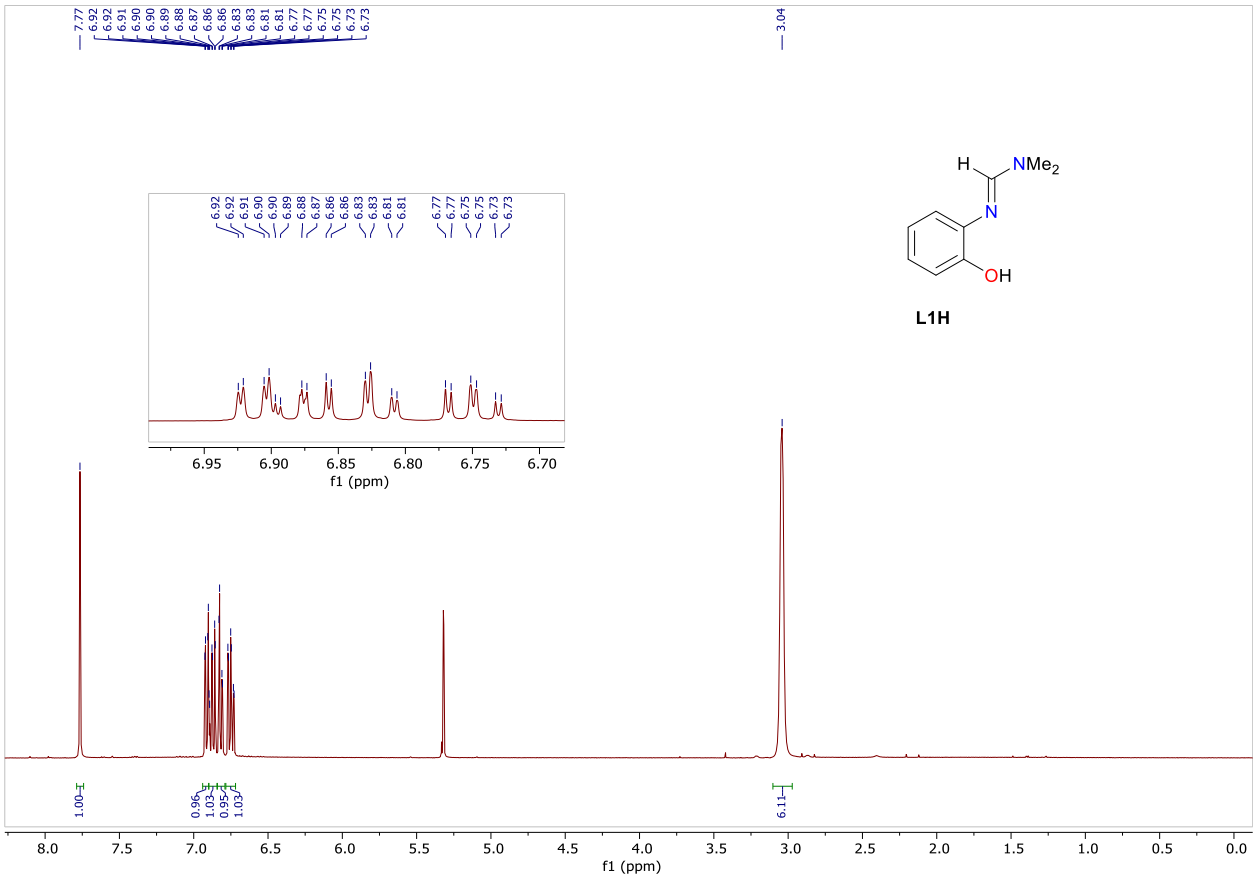


*Figure S1 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethylformamidine **L1H.***

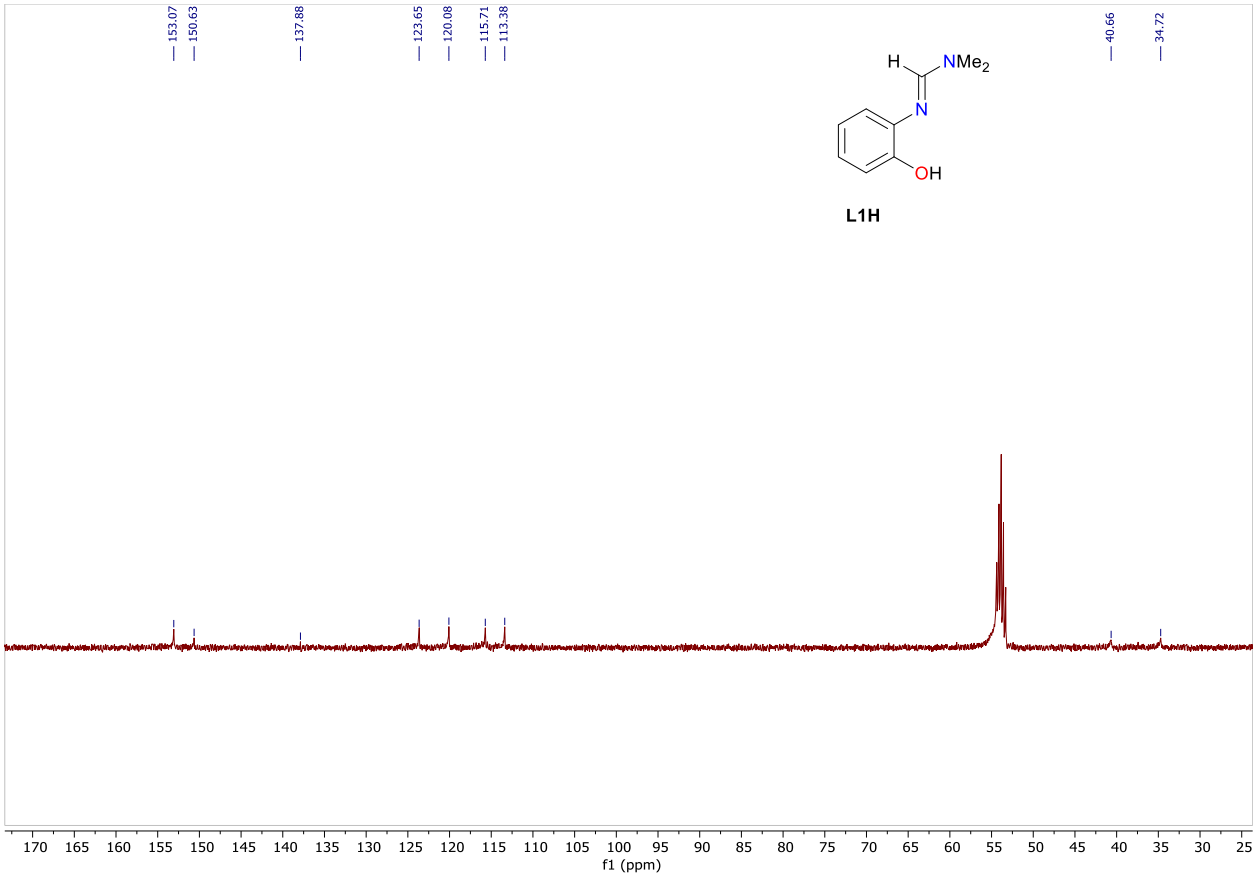


*Figure S2 $\{^{1}H\}^{13}C$ NMR (101 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethylformamidine **L1H**.*

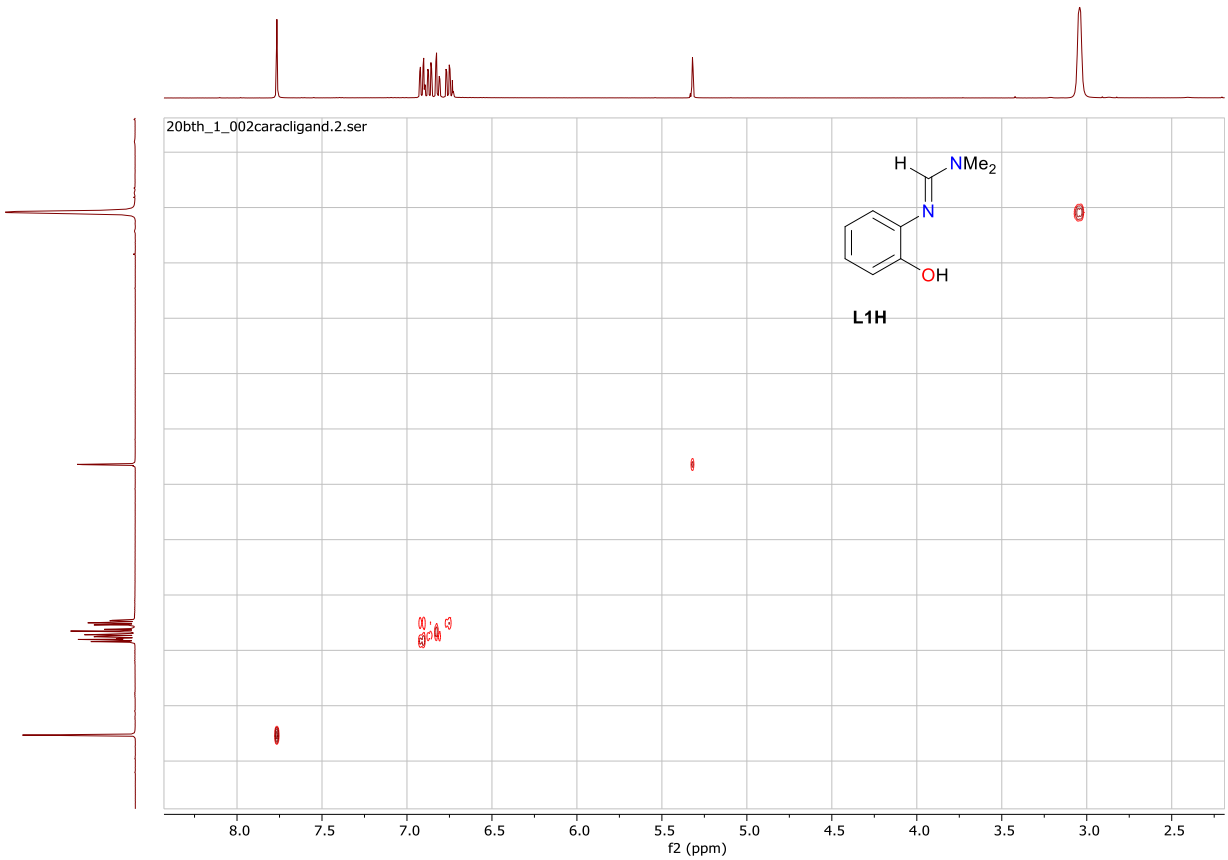


*Figure S3 ^{1}H ^{1}H COSY (400 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethylformamidine **L1H**.*

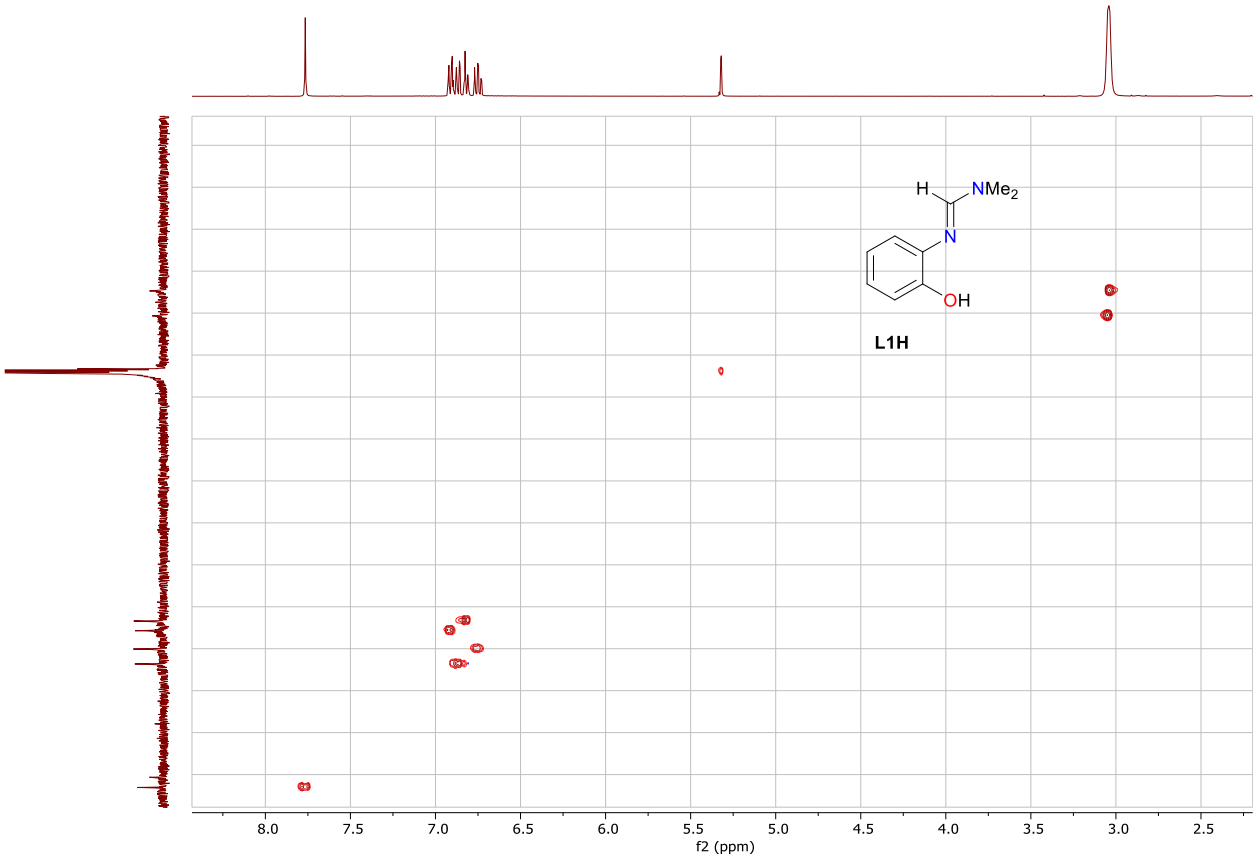


*Figure S4 ^{1}H ^{13}C HSQC (400 MHz/101 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethylformamidine **L1H**.*

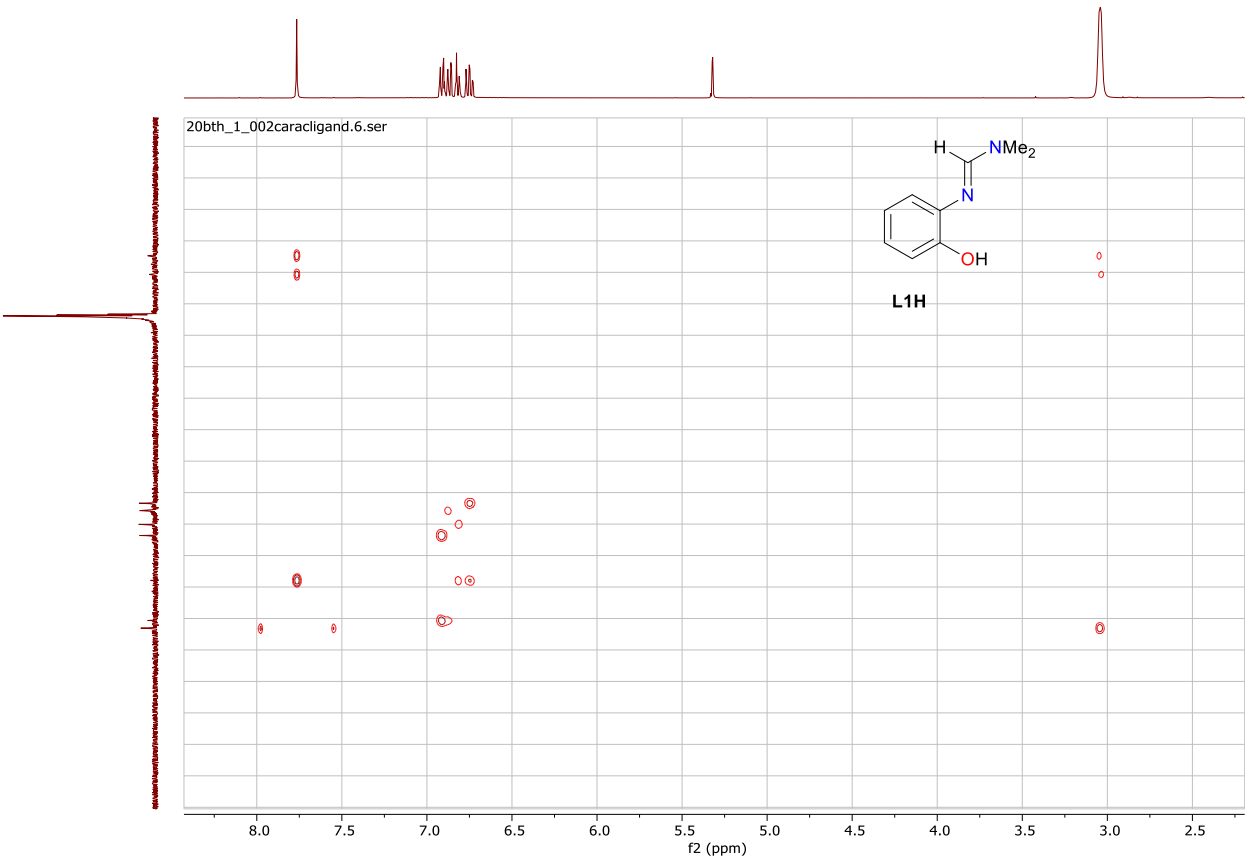


*Figure S5 ^{1}H ^{13}C HMBC (400 MHz / 141 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethylformamidine **L1H**.*

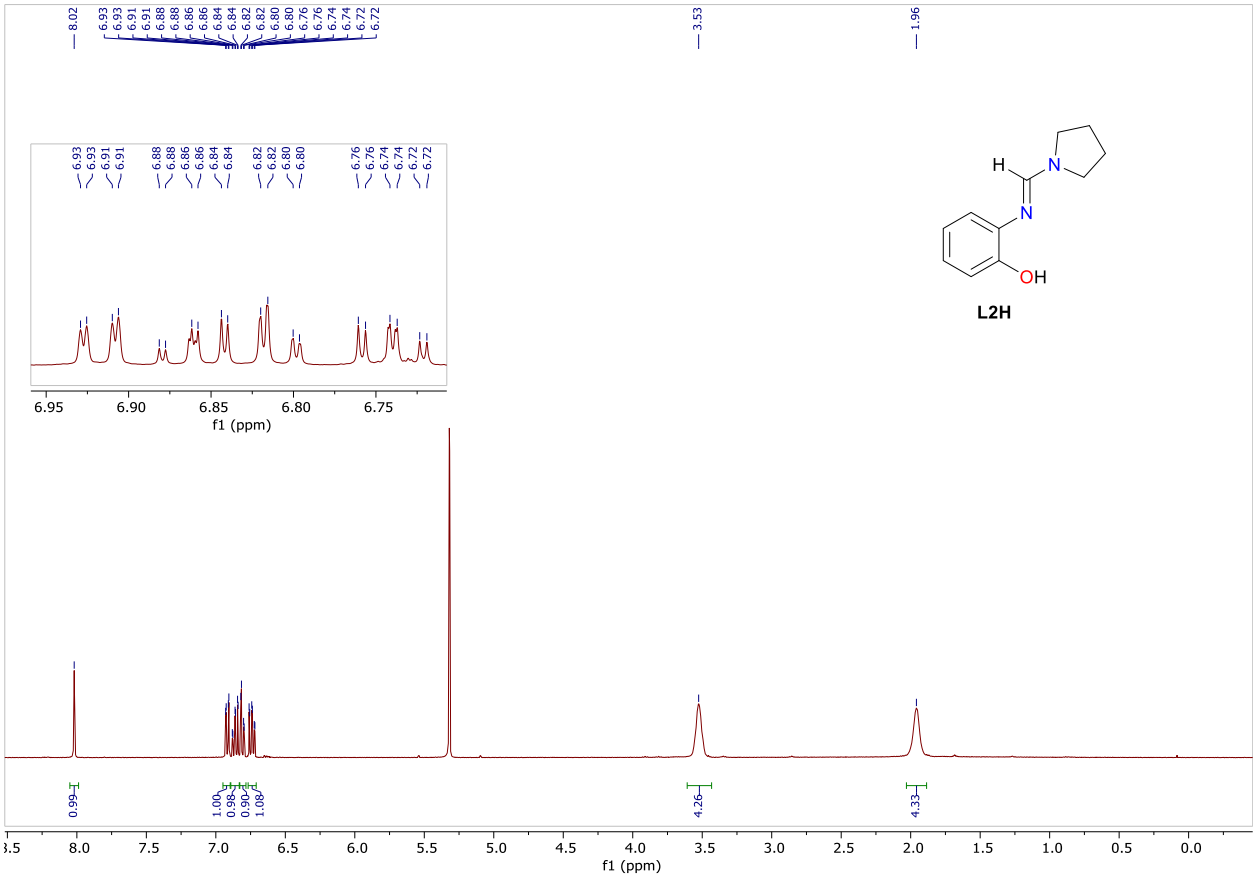


*Figure S6 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of N'(2-hydroxyphenyl)-N,N-pyrrolydinyl-formamidine **L2H**.*

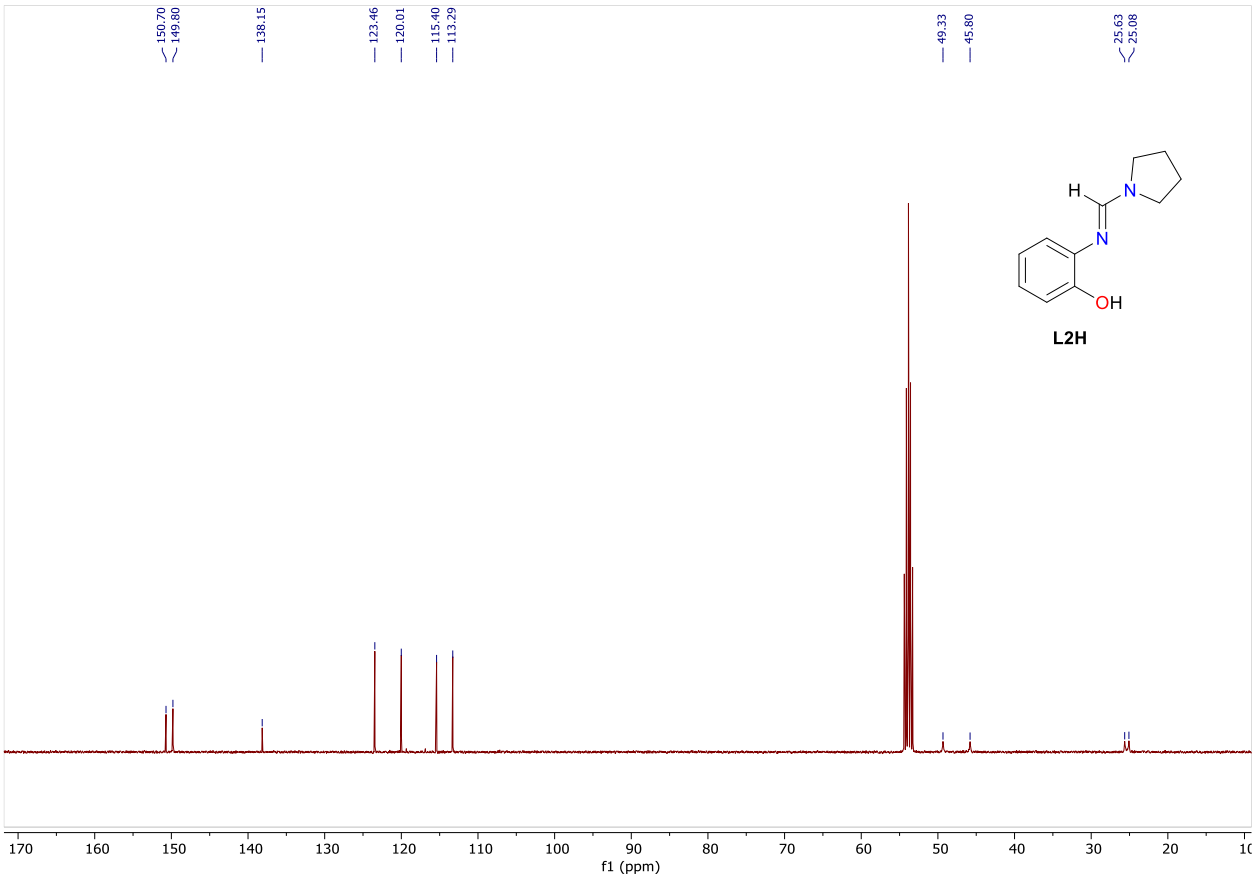


*Figure S7 {^{1}H}^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) of N'(2-hydroxyphenyl)-N,N-pyrrolydinyl-formamidine **L2H**.*

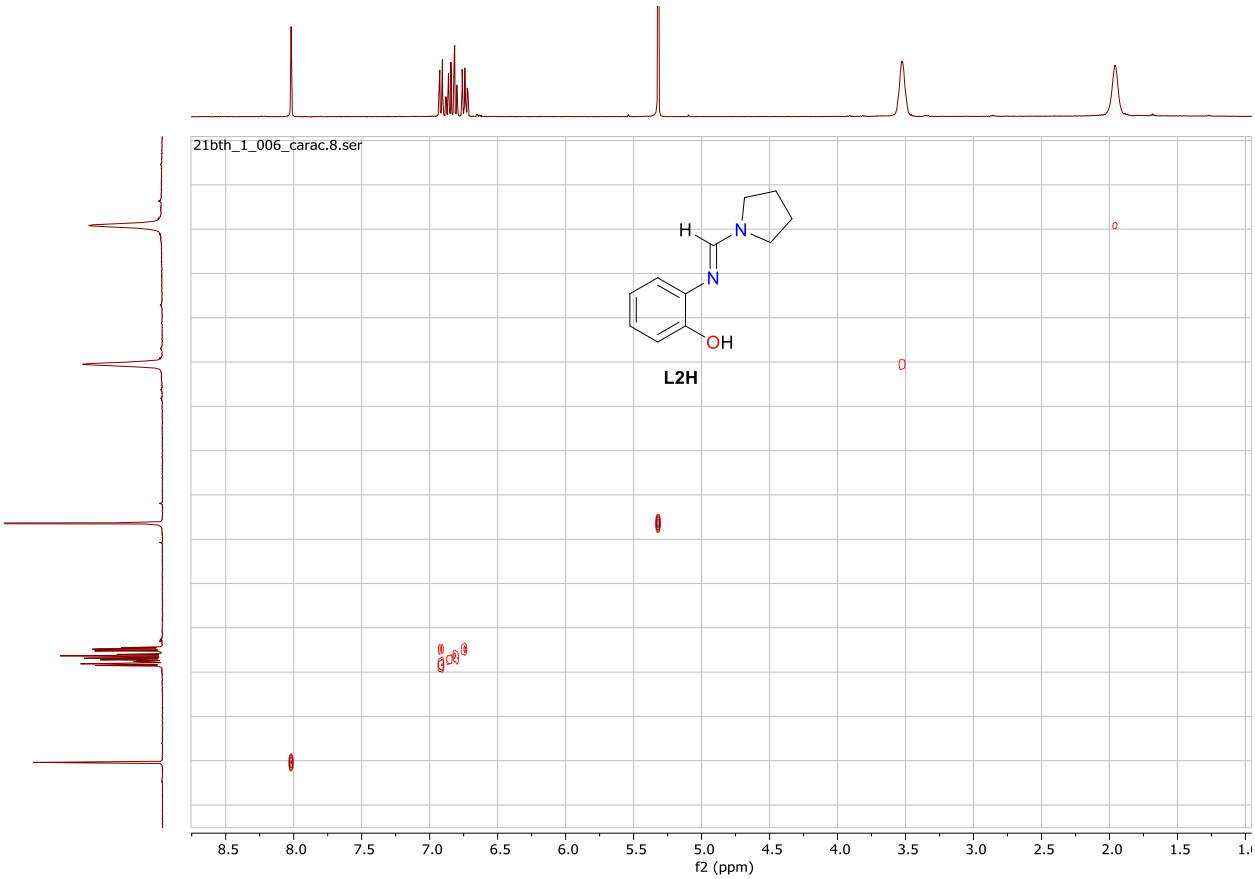


*Figure S8 ^{1}H ^{1}H COSY (400 MHz, CD_2Cl_2, 298 K) of N'(2-hydroxyphenyl)-N,N-pyrrolydinyl-formamidine **L2H**.*

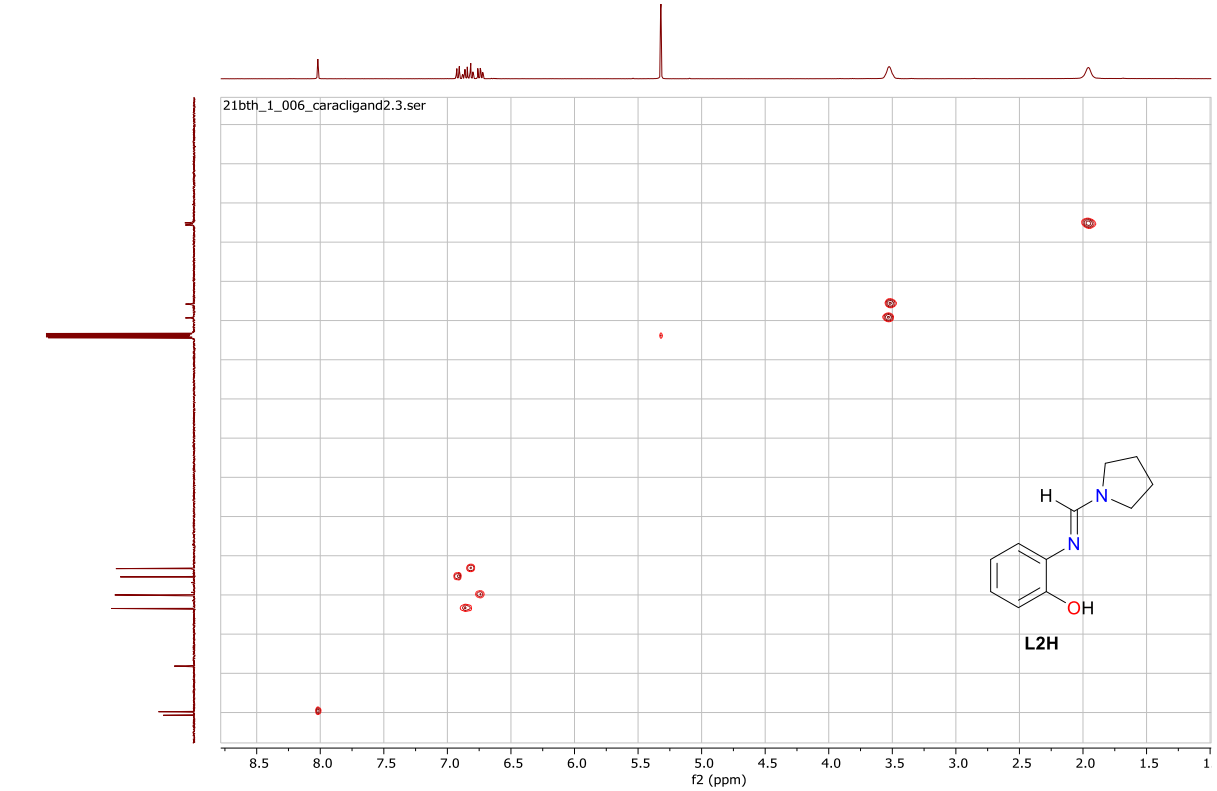


*Figure S9 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of N'(2-hydroxyphenyl)-N,N-pyrrolydinyl-formamidine **L2H**.*

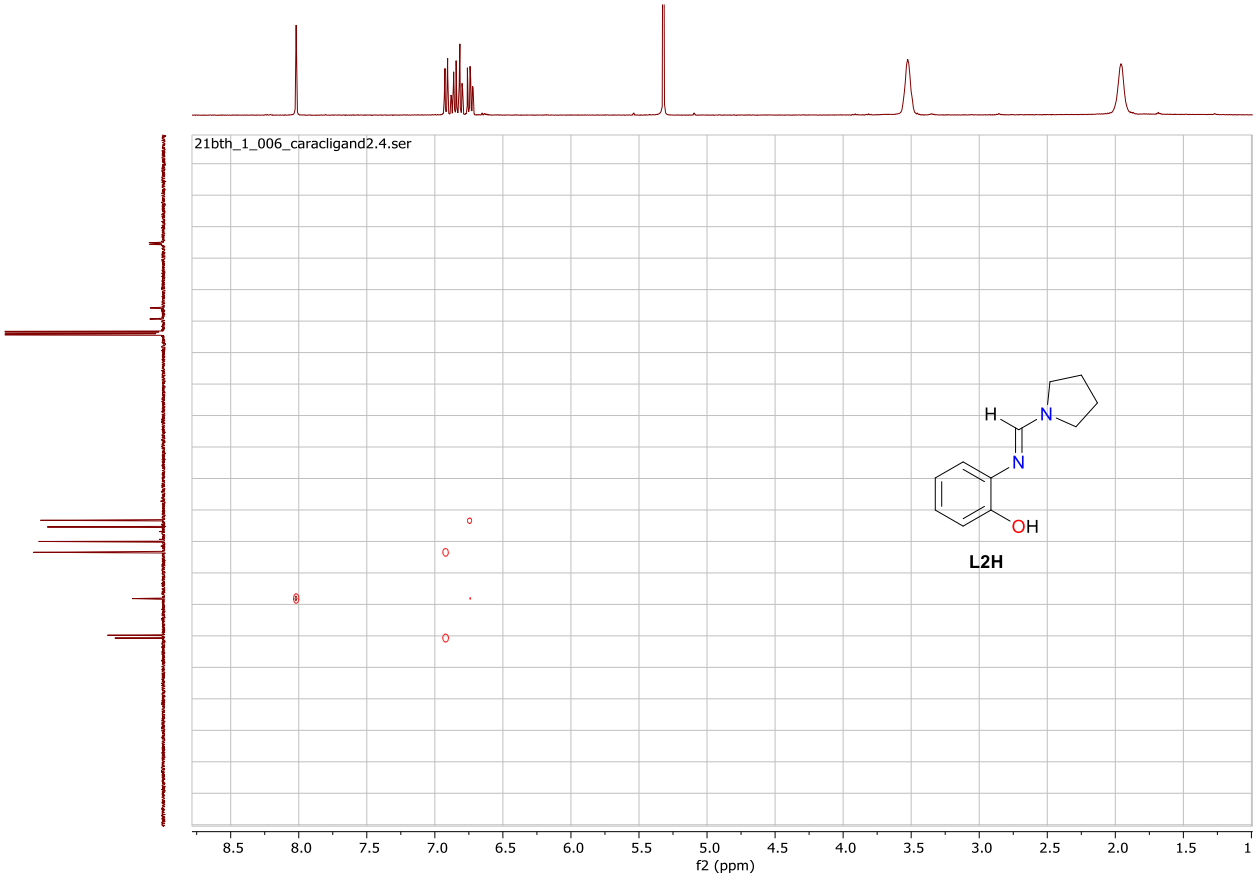


*Figure S10 ^{1}H ^{13}C HMBC (400 MHz / 141 MHz, CD_2Cl_2, 298 K) of N'(2-hydroxyphenyl)-N,N-pyrrolydinyl-formamidine **L2H**.*

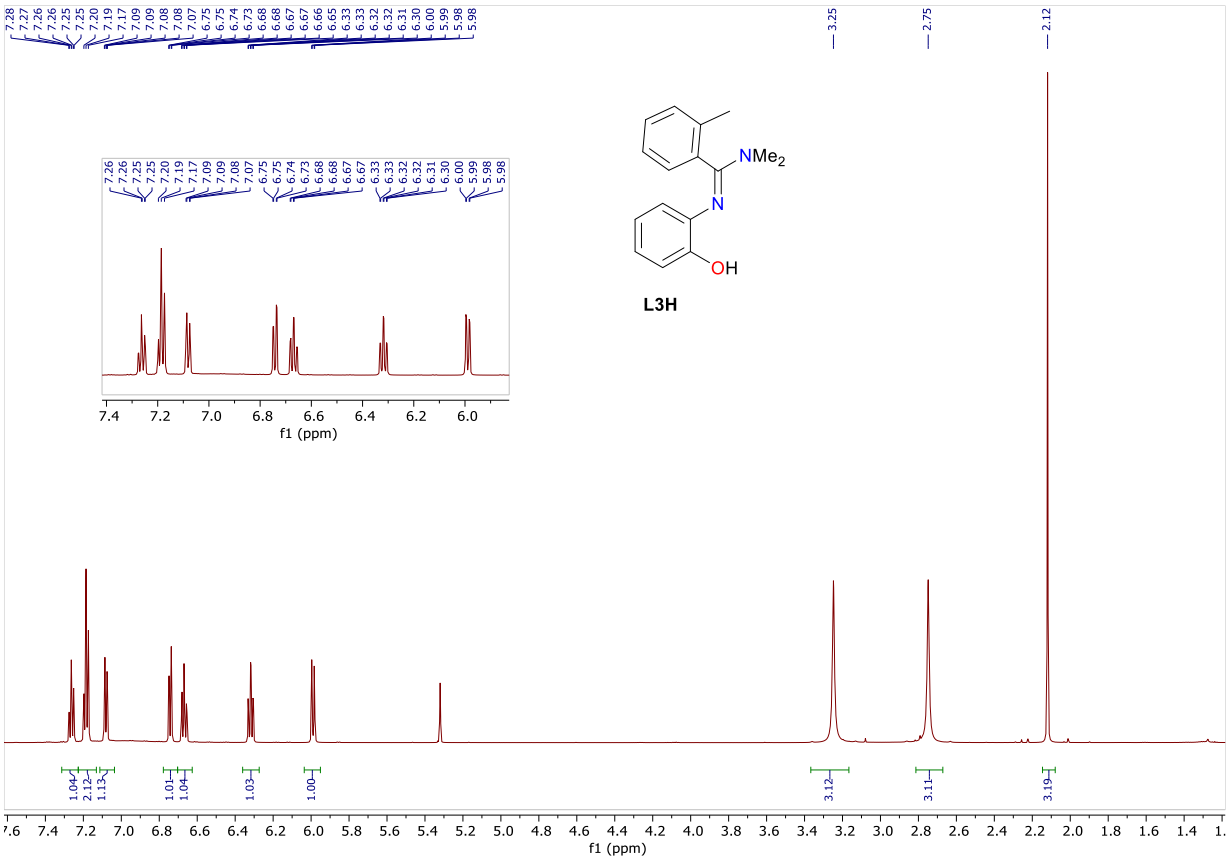


*Figure S11 ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethyl-2-methylbenzamidine **L3H**.*

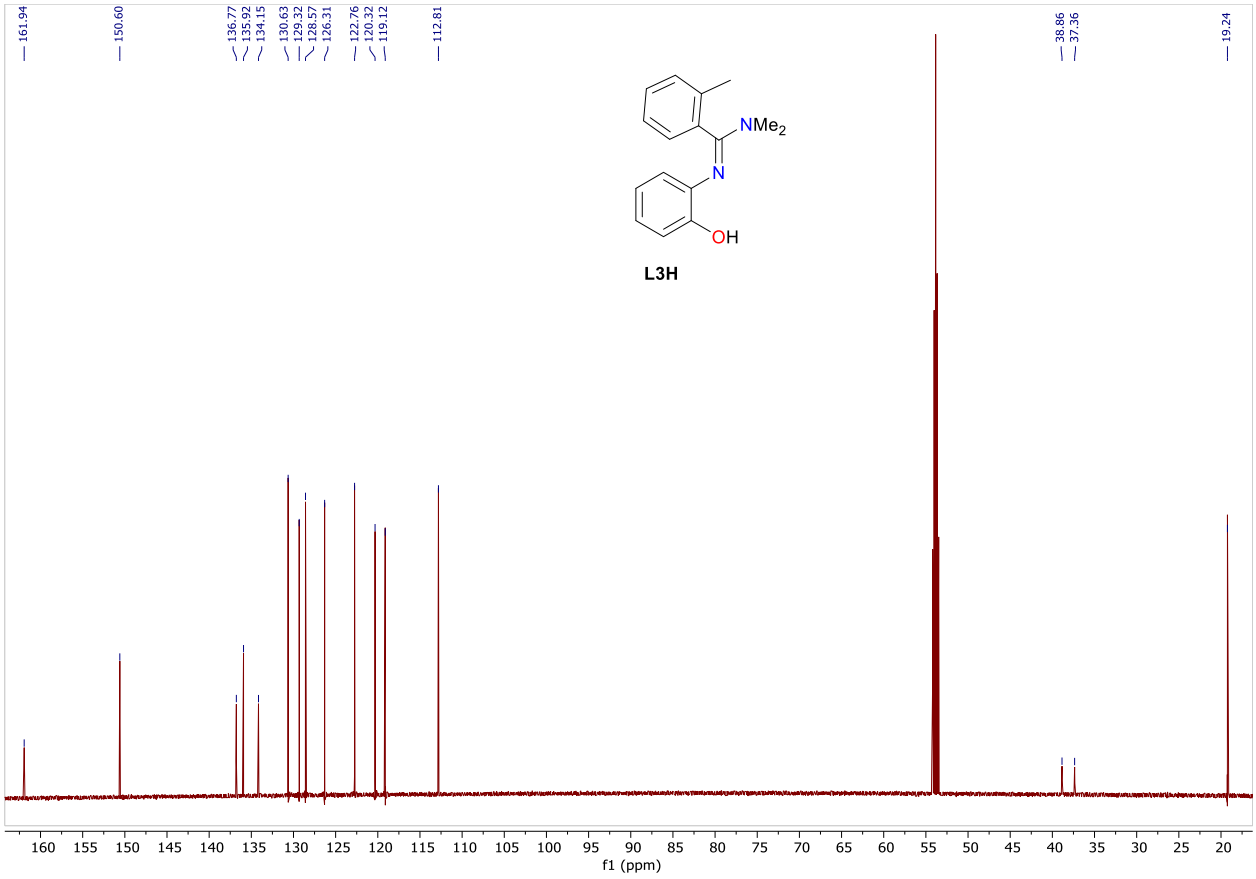


*Figure S12 $\{^{1}H\}^{13}C$ NMR (151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethyl-2-methylbenzamidine **L3H**.*

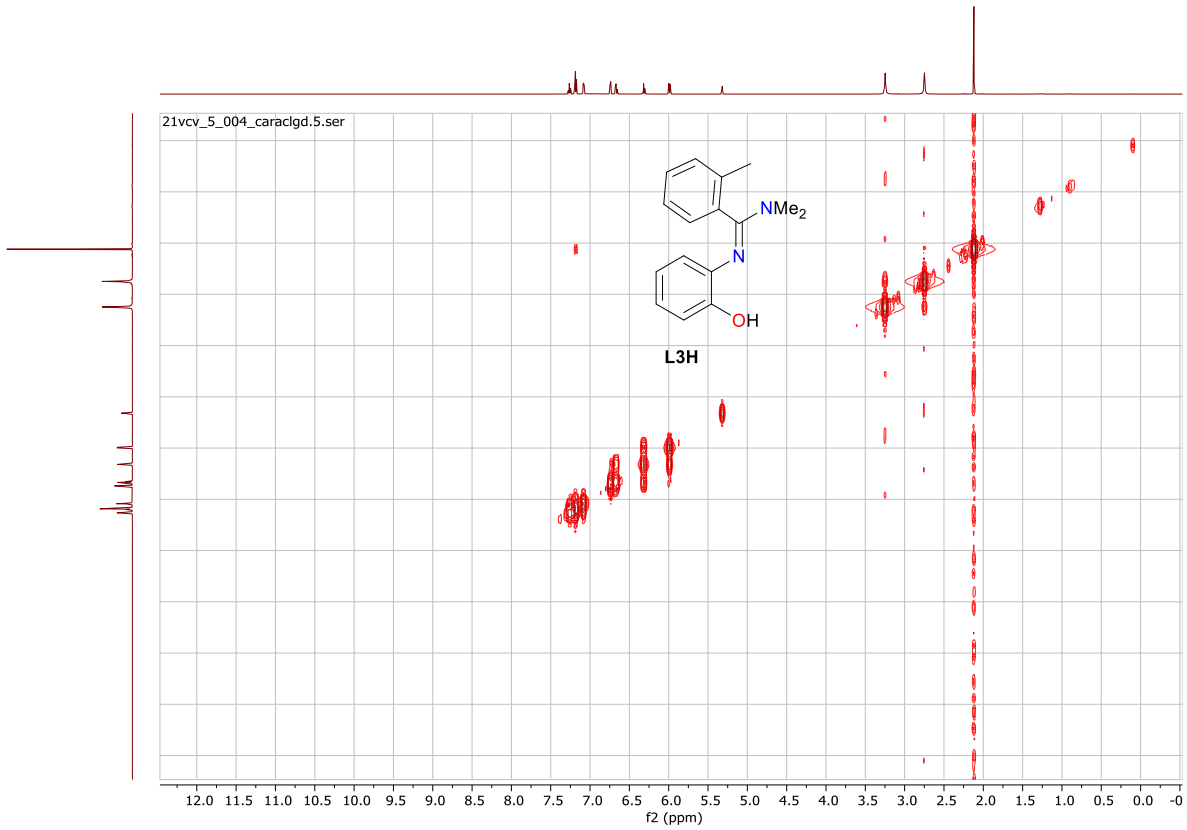


*Figure S13 ^{1}H ^{1}H COSY (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethyl-2-methylbenzamidine **L3H**.*

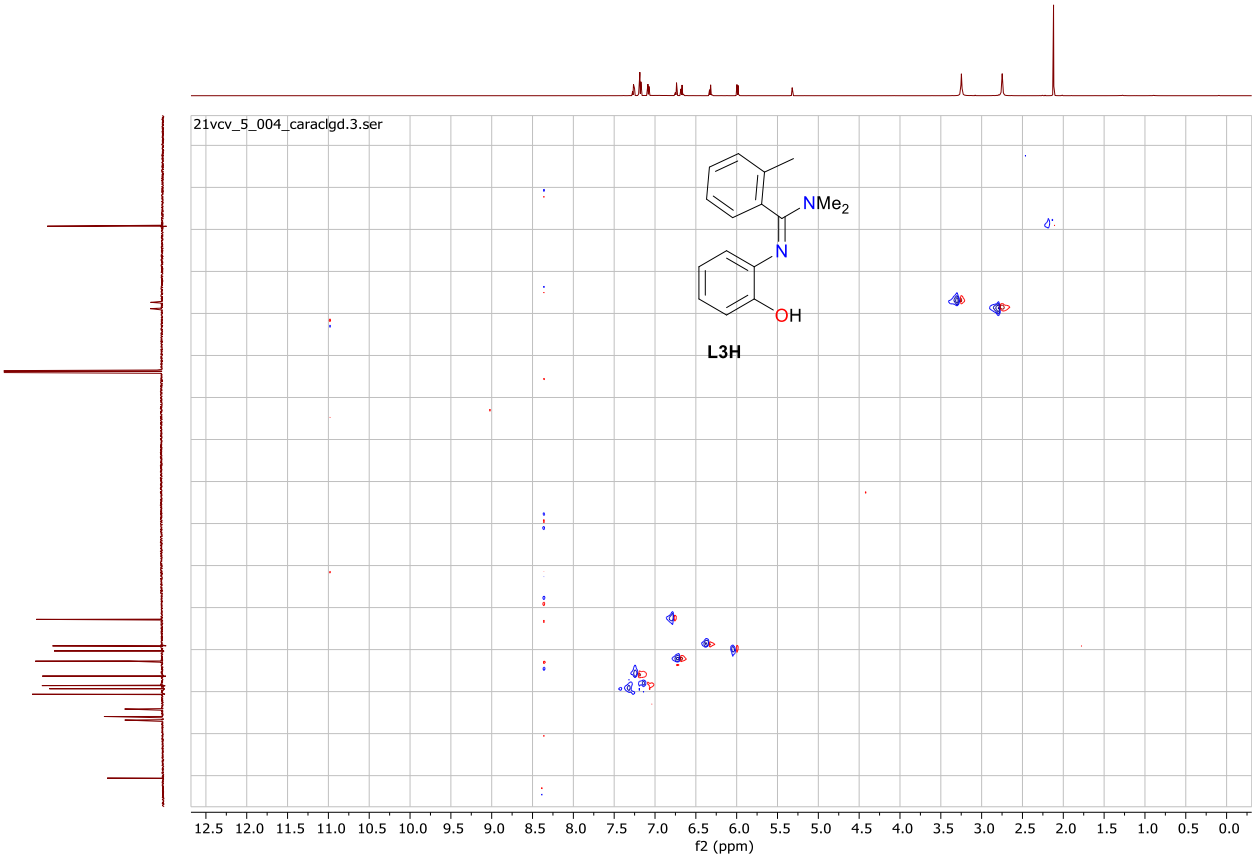


*Figure S14 ^{1}H ^{13}C HSQC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethyl-2-methylbenzamidine **L3H**.*

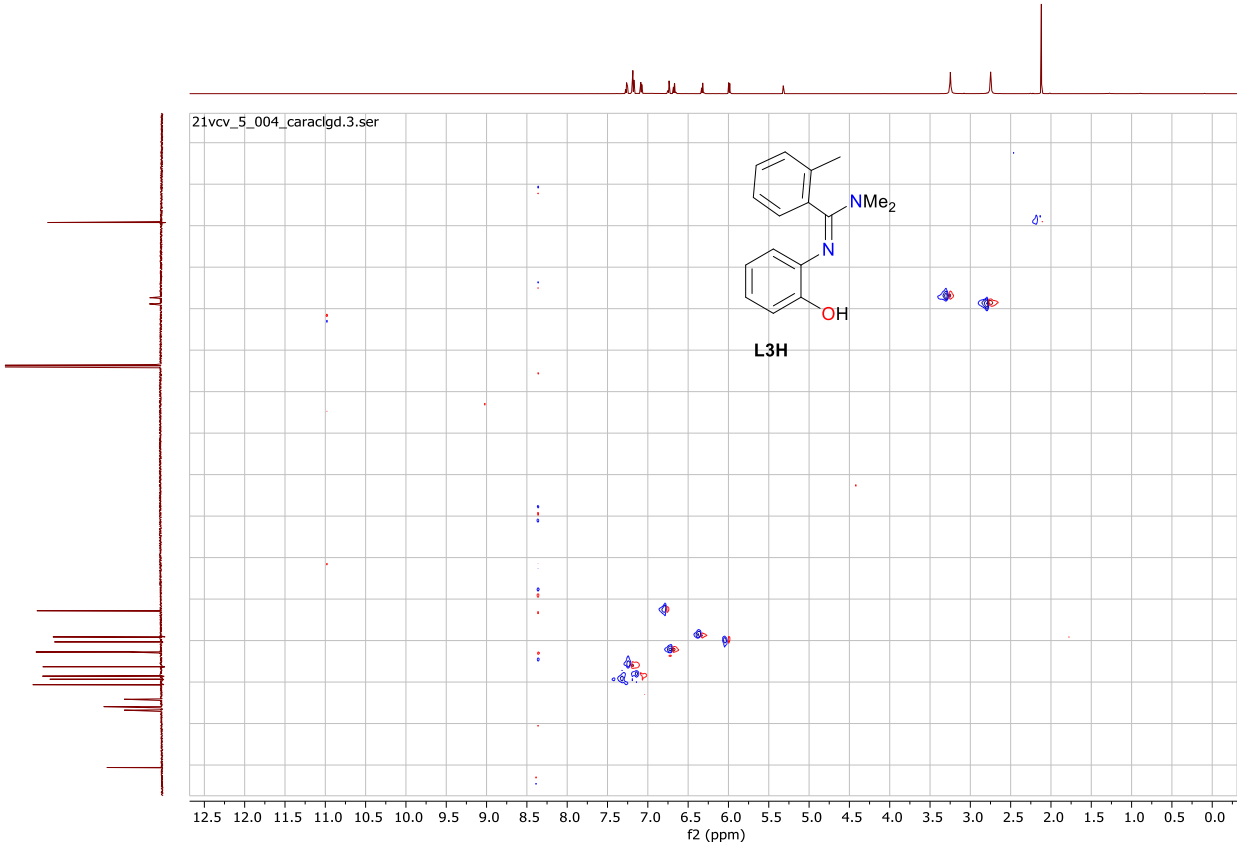


*Figure S15 ^{1}H ^{13}C HMBC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-dimethyl-2-methylbenzamidine **L3H**.*

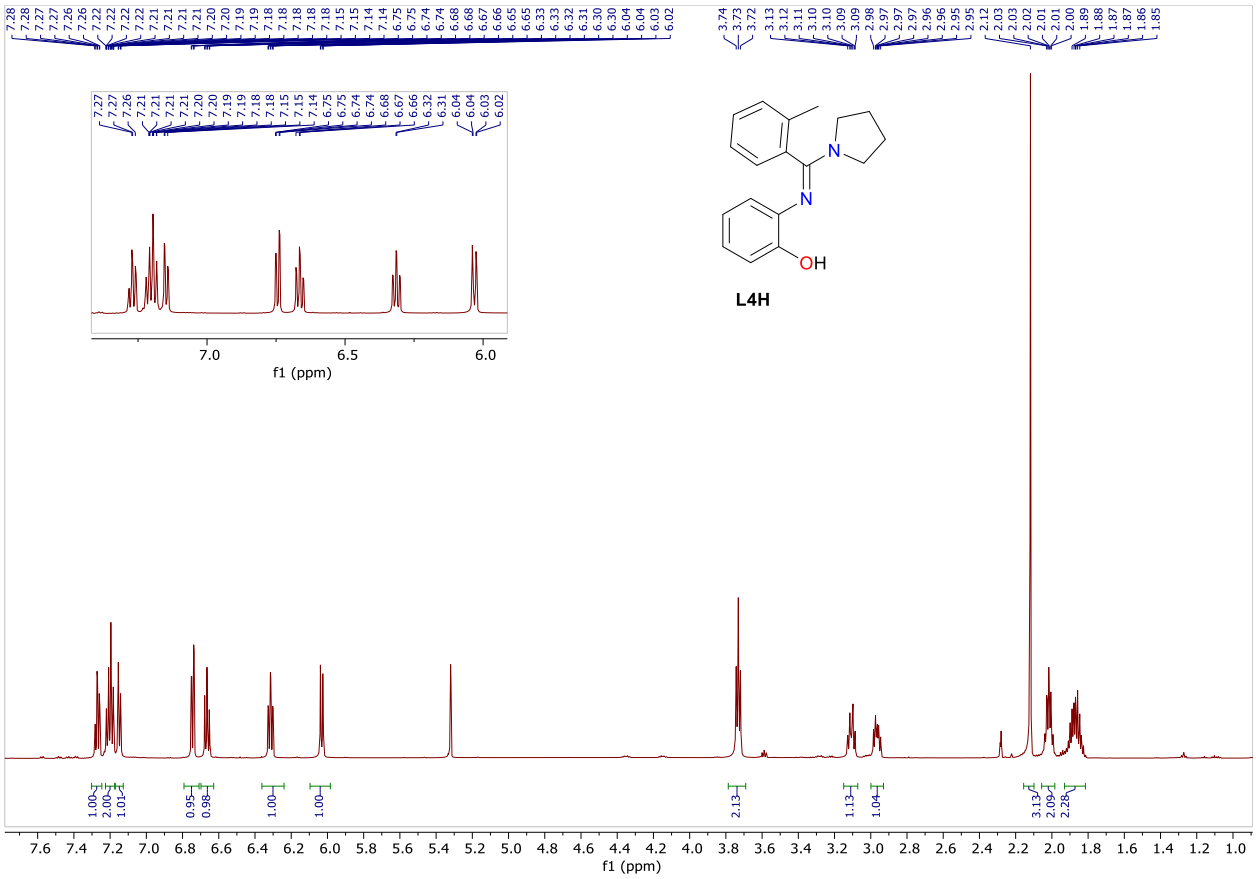


*Figure S16 ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-2-methylbenzamidine **L4H**.*

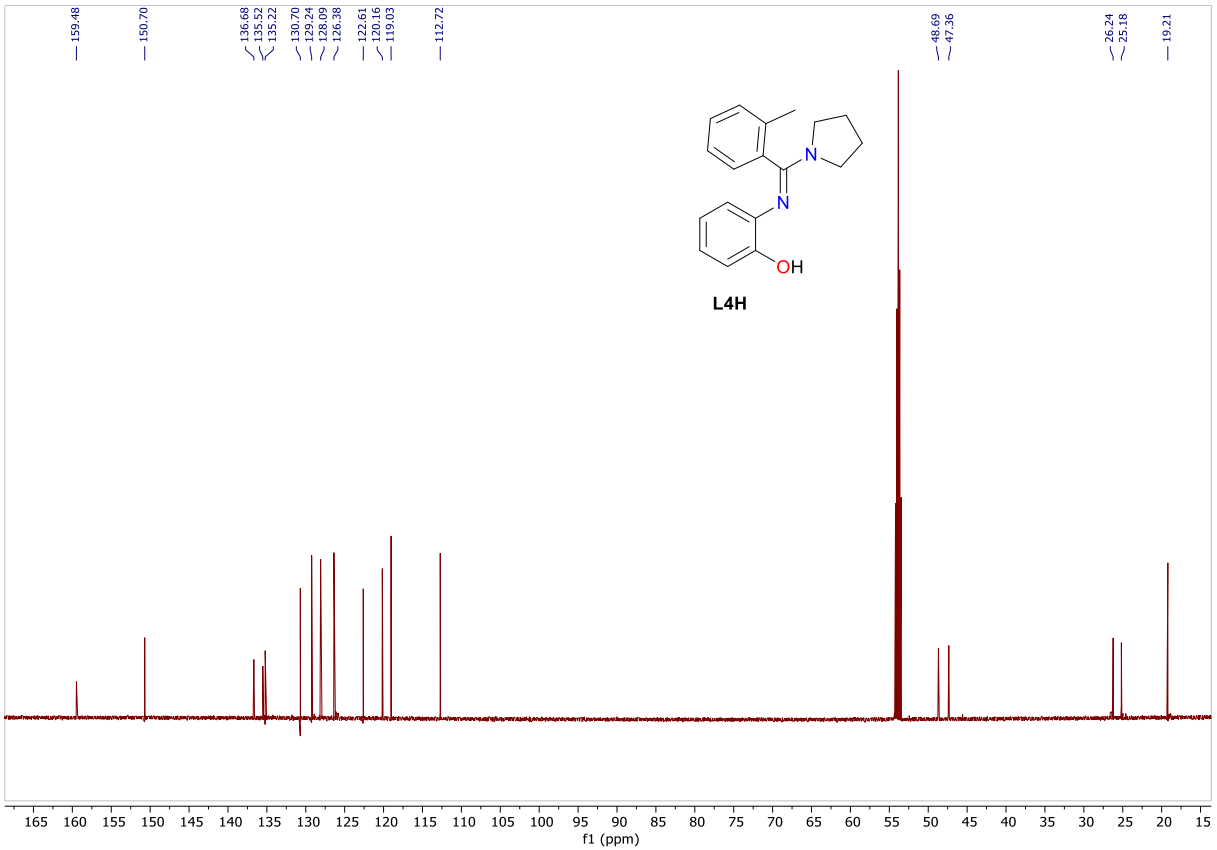


*Figure S17 {^{1}H}^{13}C NMR (151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-2-methylbenzamidine **L4H**.*

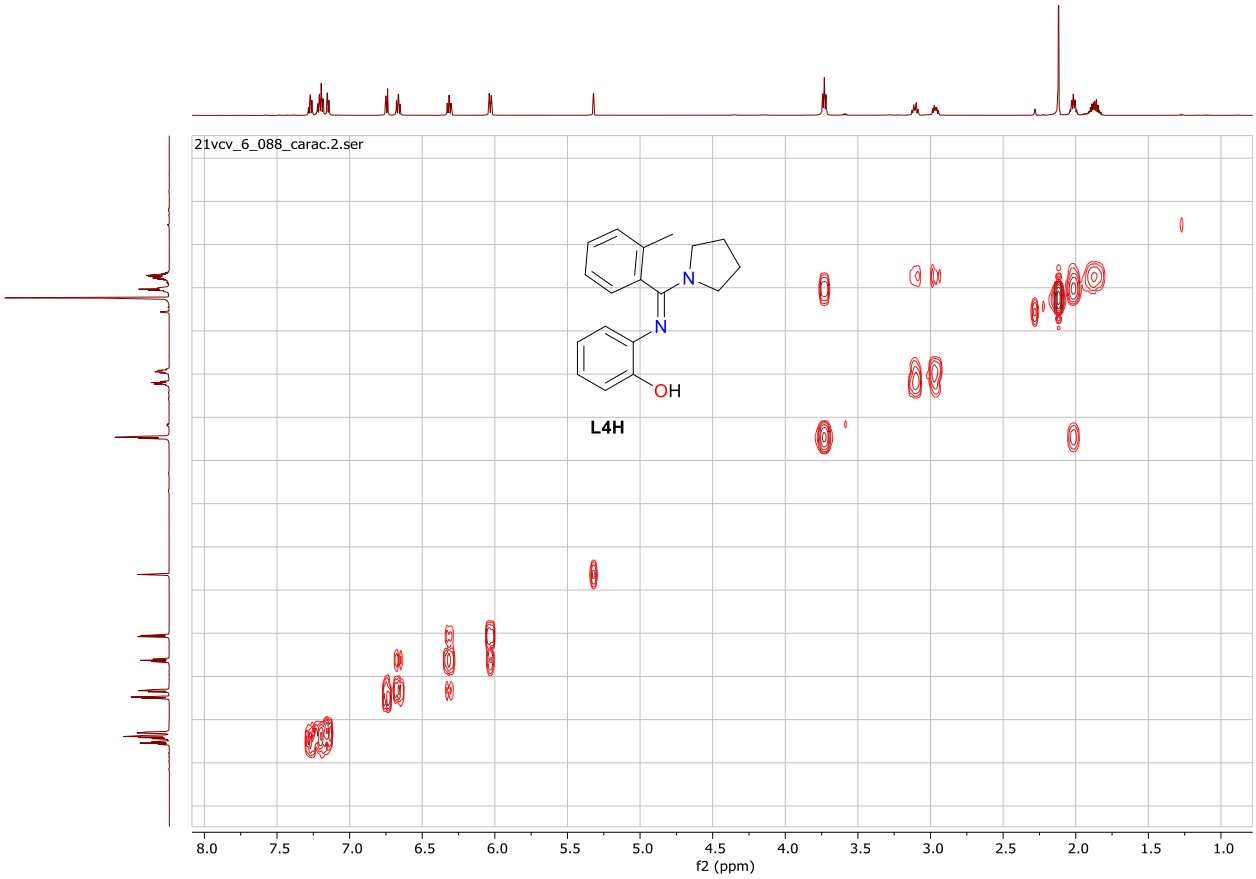


*Figure S18 ^{1}H ^{1}H COSY (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-2-methylbenzamidine **L4H**.*

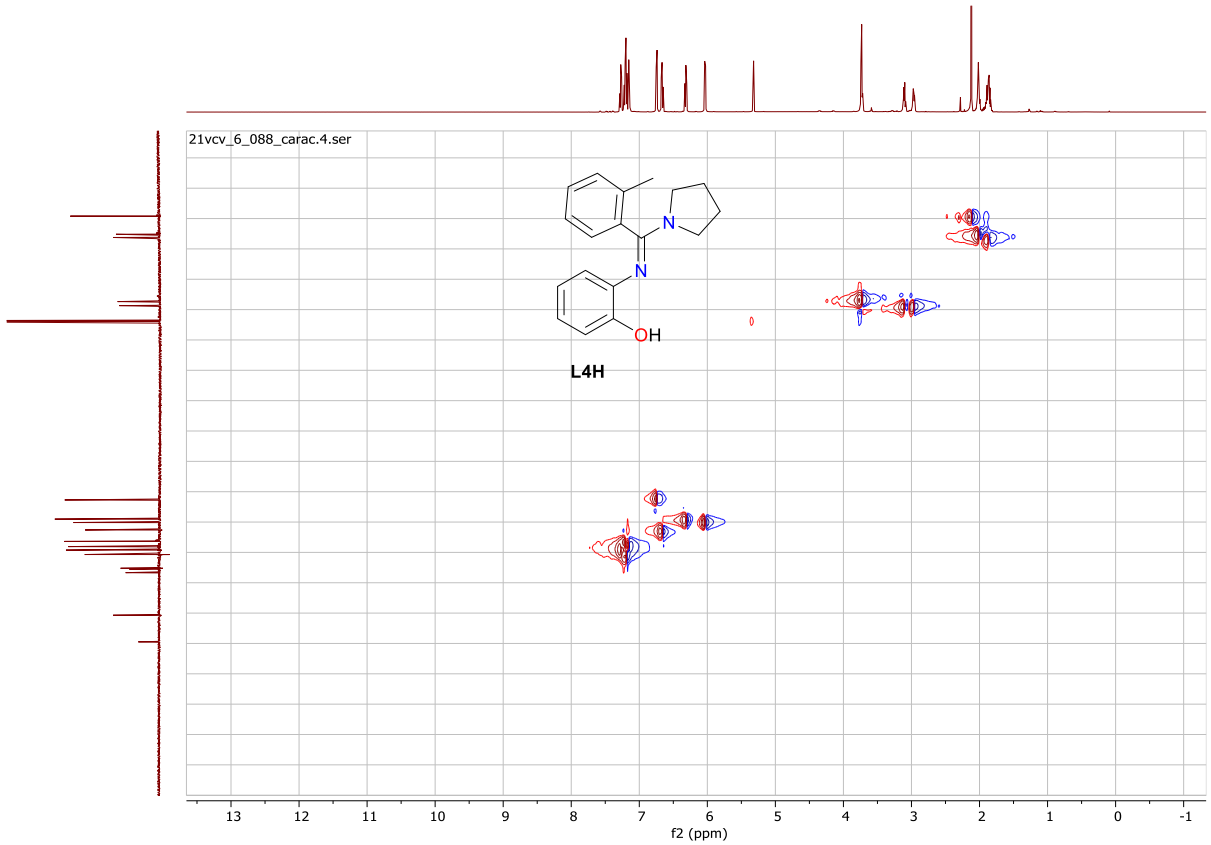


*Figure S19 ^{1}H ^{13}C HSQC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-2-methylbenzamidine **L4H**.*

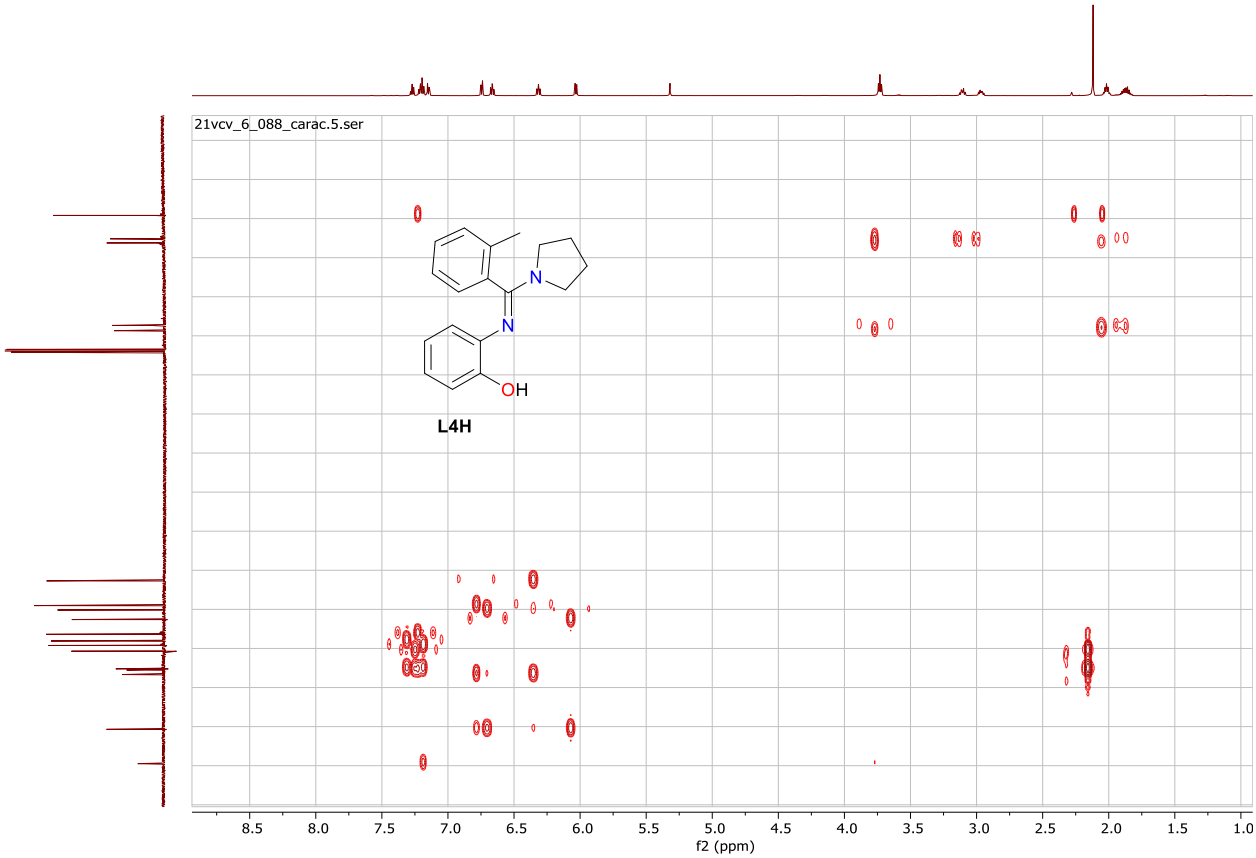


*Figure S20 ^{1}H ^{13}C HMBC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-2-methylbenzamidine **L4H**.*

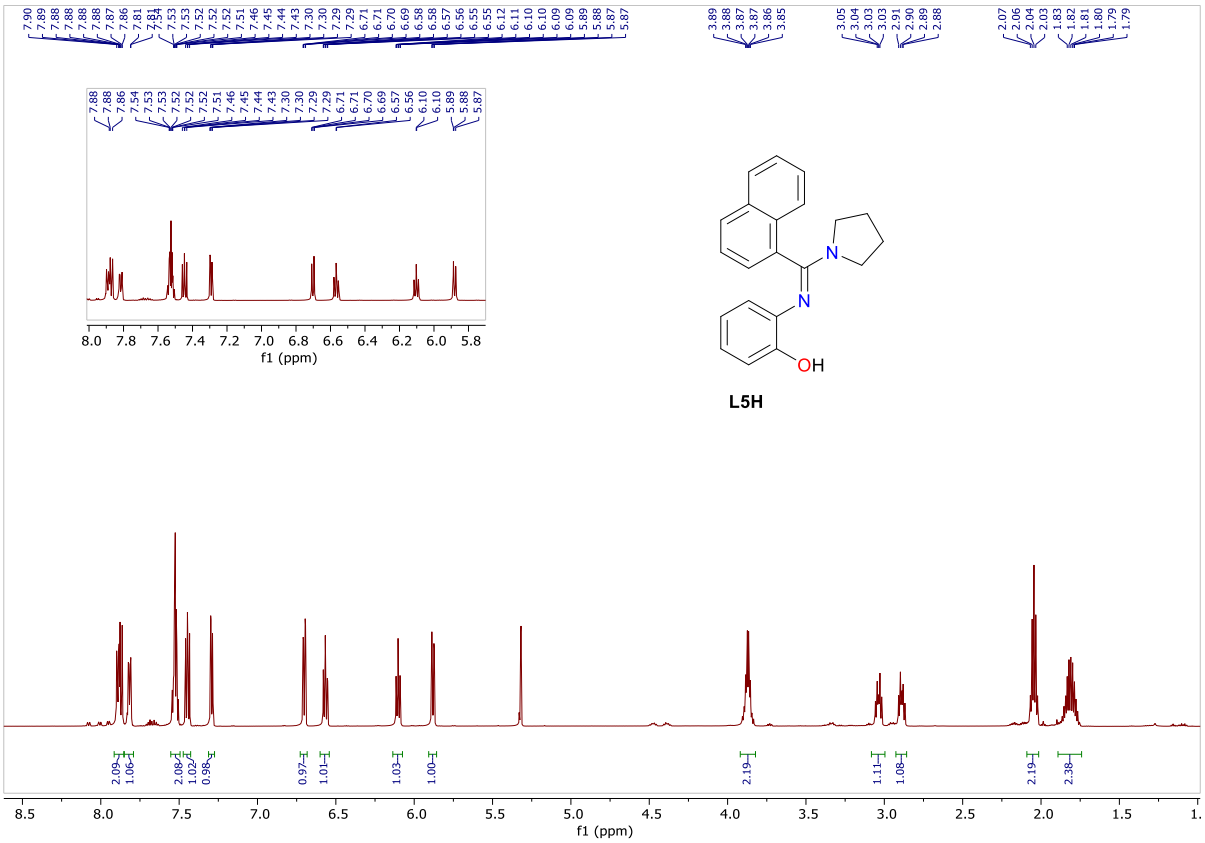


*Figure S21 ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-1-naphtylamidine **L5H**.*

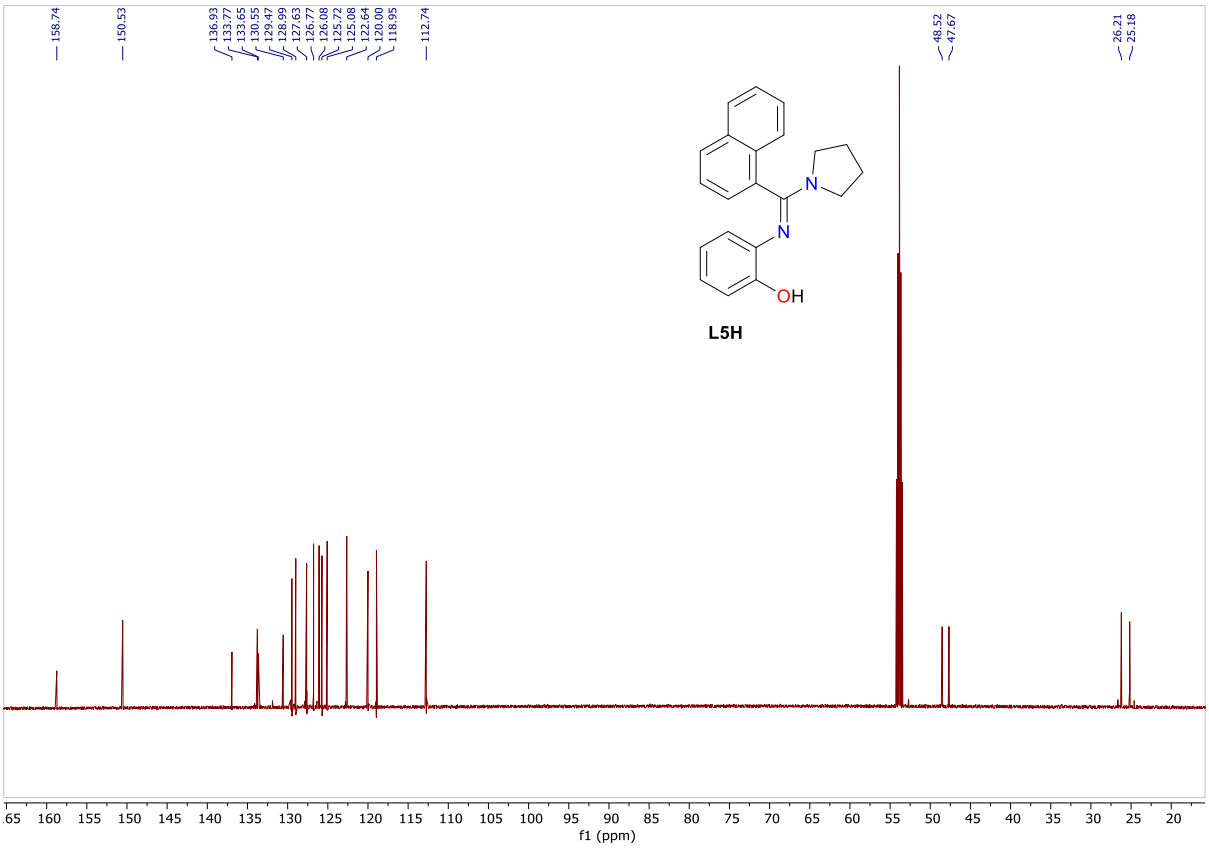


*Figure S22 $\{^{1}H\}^{13}C$ NMR (151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-1-naphtylamidine **L5H**.*

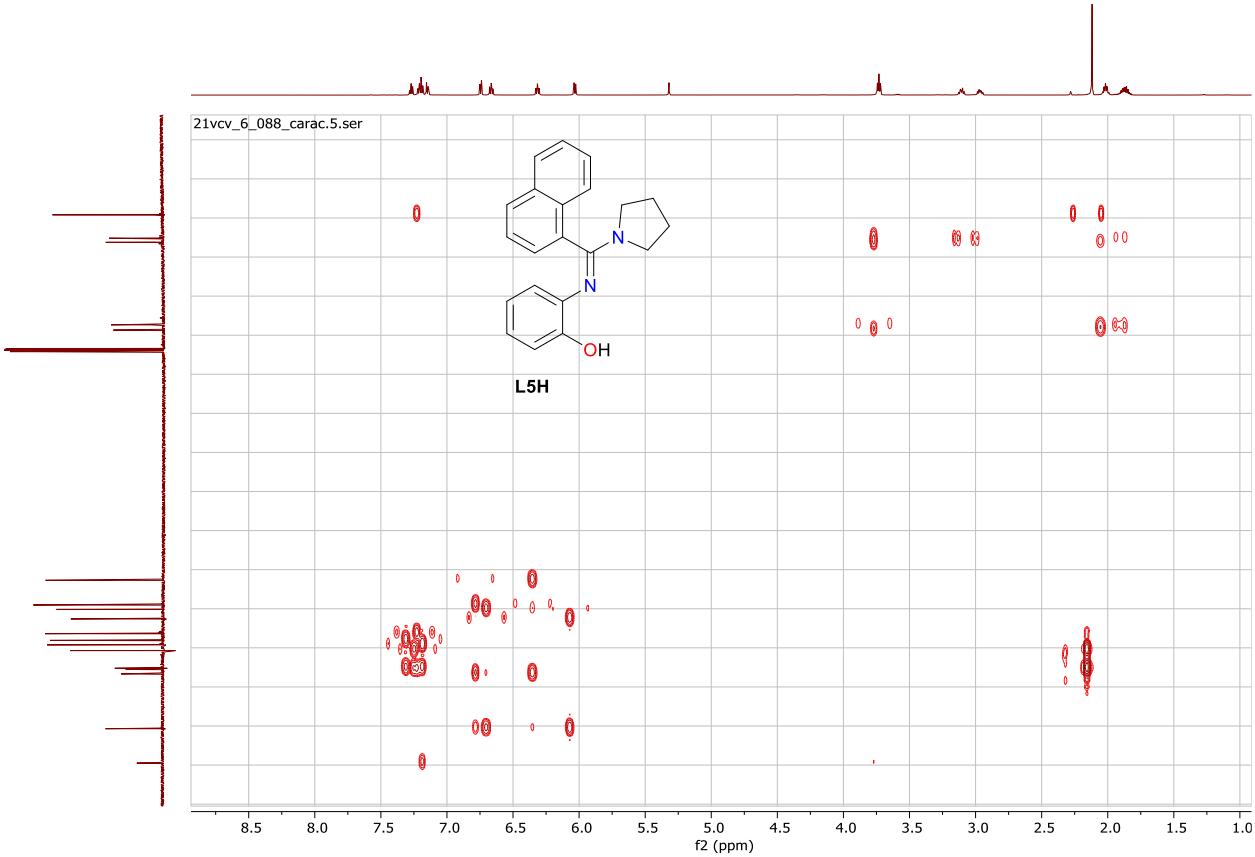


*Figure S23 ^{1}H ^{1}H COSY (600 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-1-naphtylamidine **L5H**.*

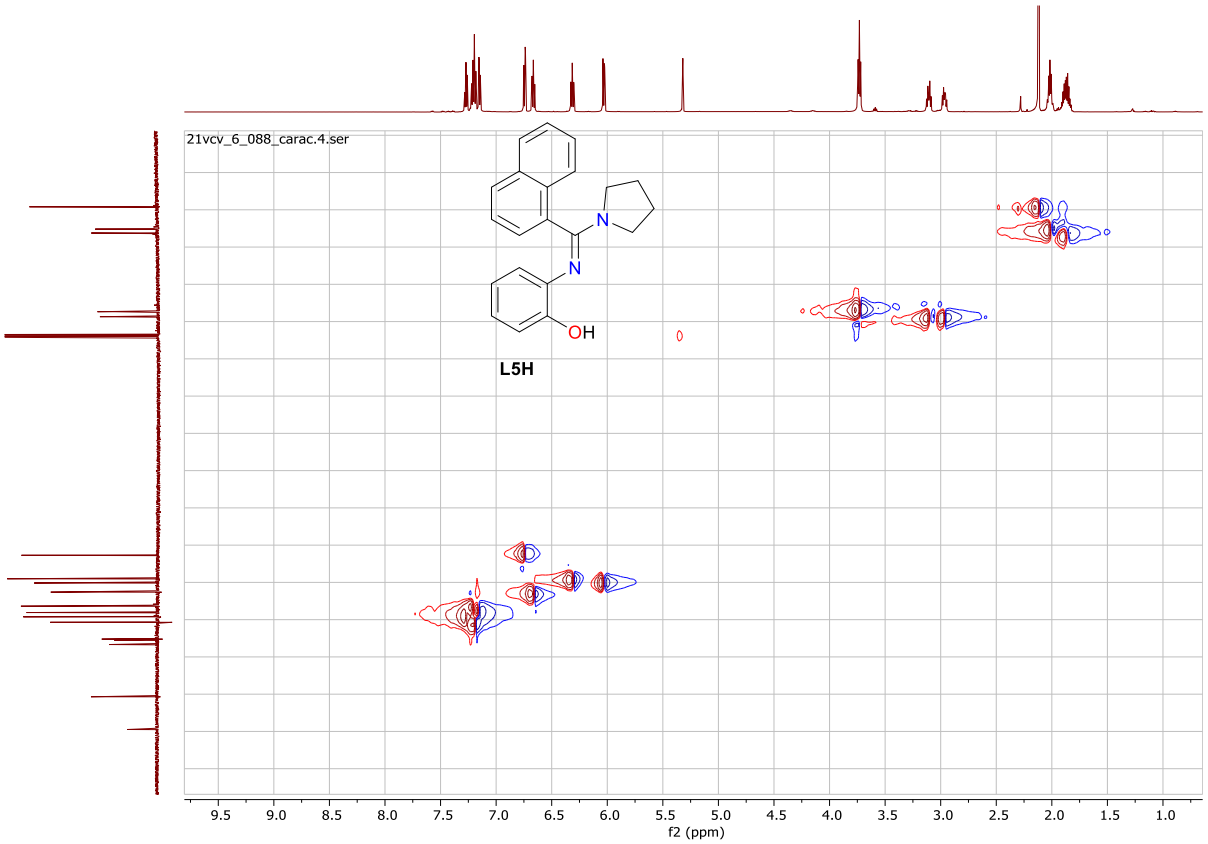


*Figure S24 ^{1}H ^{13}C HSQC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-1-naphtylamidine **L5H**.*

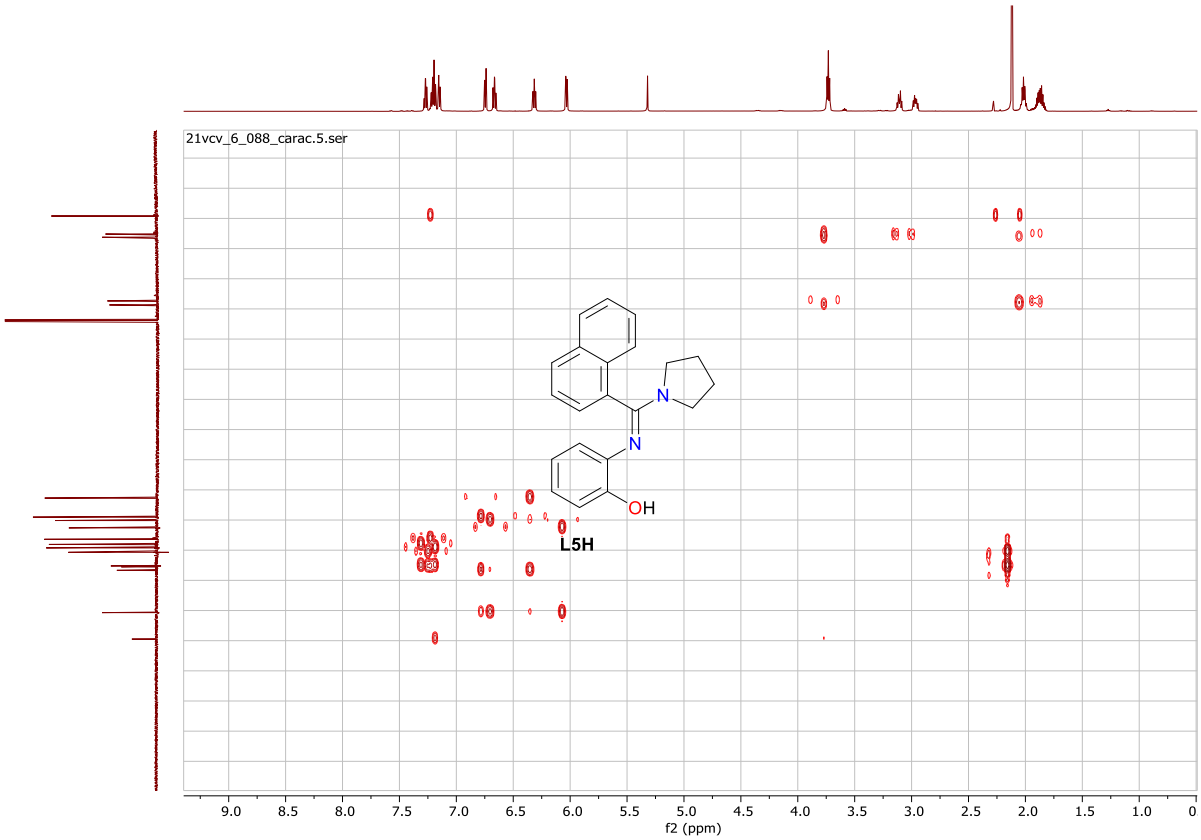


*Figure S25 ^{1}H ^{13}C HMBC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of N'-(2-hydroxyphenyl)-N,N-pyrrolidinyl-1-naphtylamidine **L5H**.*

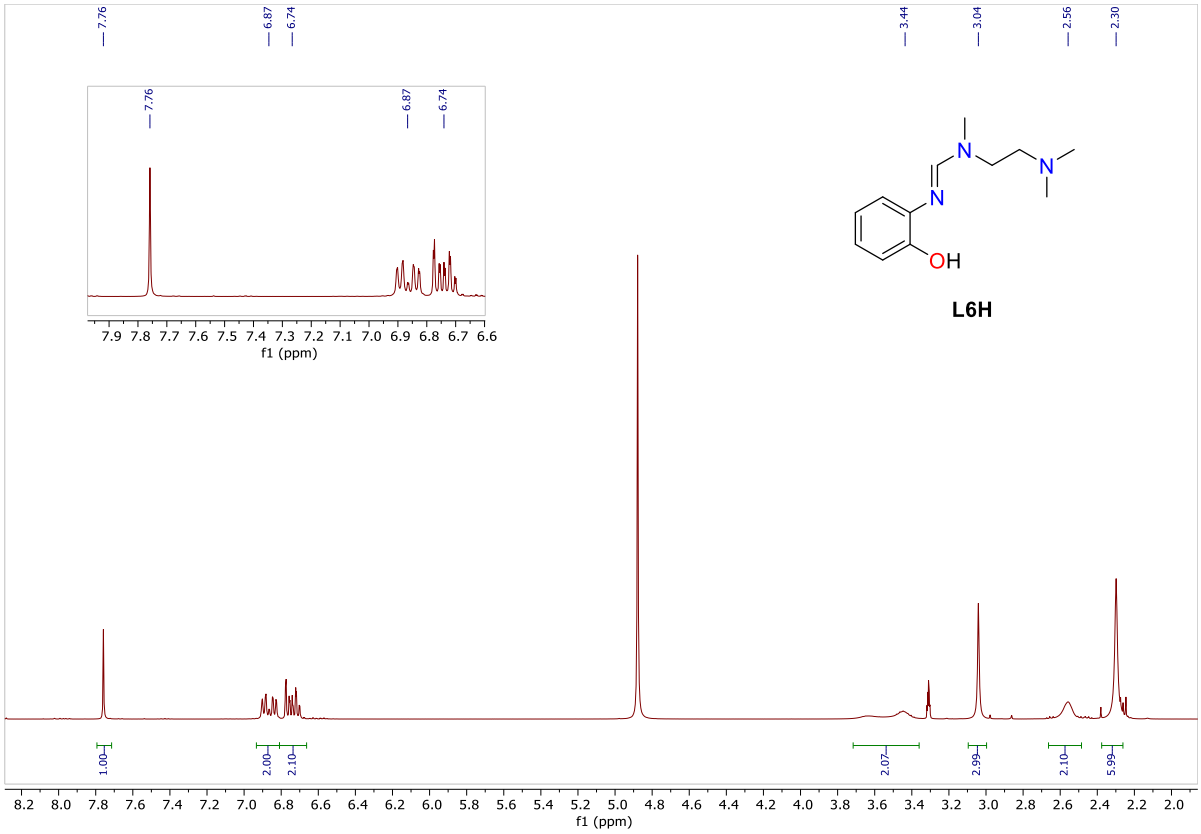


*Figure S26 ^{1}H NMR (400 MHz, MeOD, 298 K) of N'-(2-hydroxyphenyl)-N-methyl-N-(dimethylaminoethyl)formamidine **L6H**.*

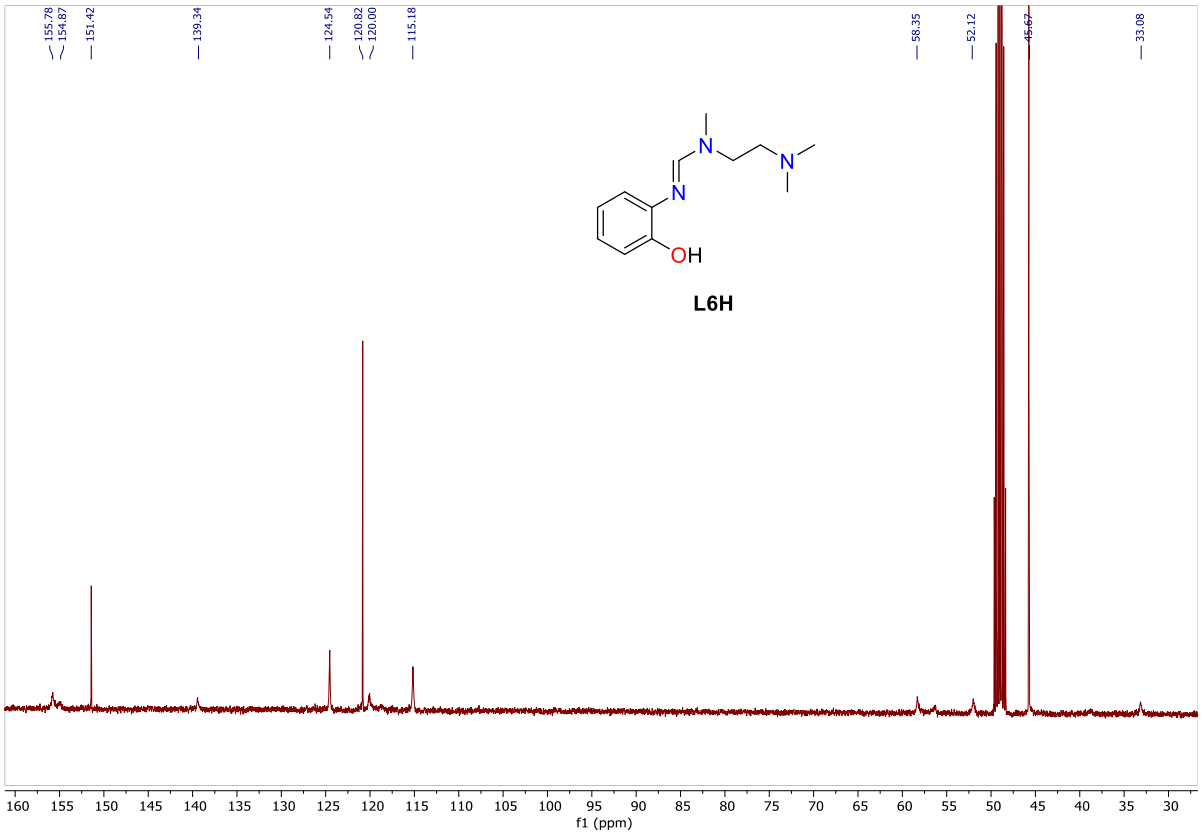


*Figure S27 {^{1}H}^{13}C NMR (101 MHz, MeOD, 298 K) of N'-(2-hydroxyphenyl)-N-methyl-N-(dimethylaminoethyl)formamidine **L6H**.*

*Figure S28 ^{1}H ^{1}H COSY (400 MHz / 400 MHz, MeOD, 298 K) of N'-(2-hydroxyphenyl)-N-methyl-N-(dimethylaminoethyl)formamidine **L6H**.*

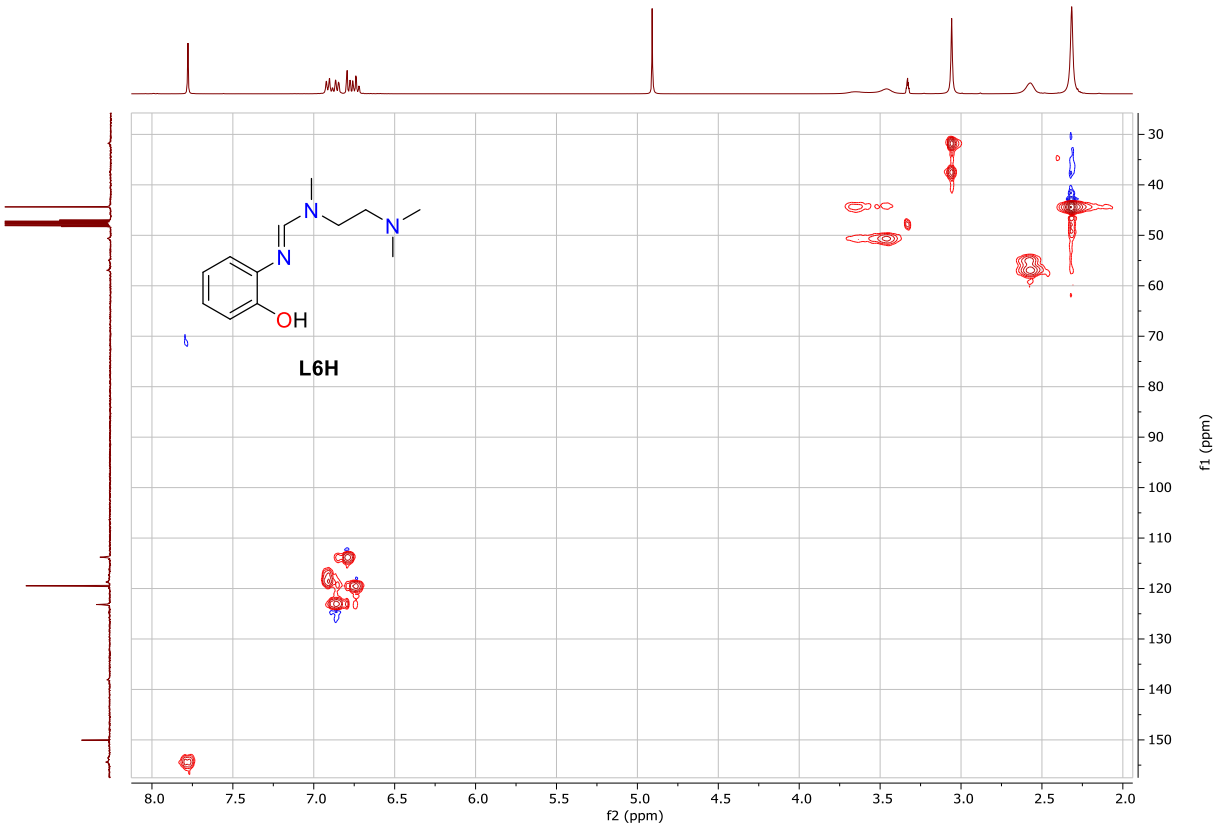


*Figure S29 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, MeOD, 298 K) of N'-(2-hydroxyphenyl)-N-methyl-N-(dimethylaminoethyl)formamidine **L6H**.*

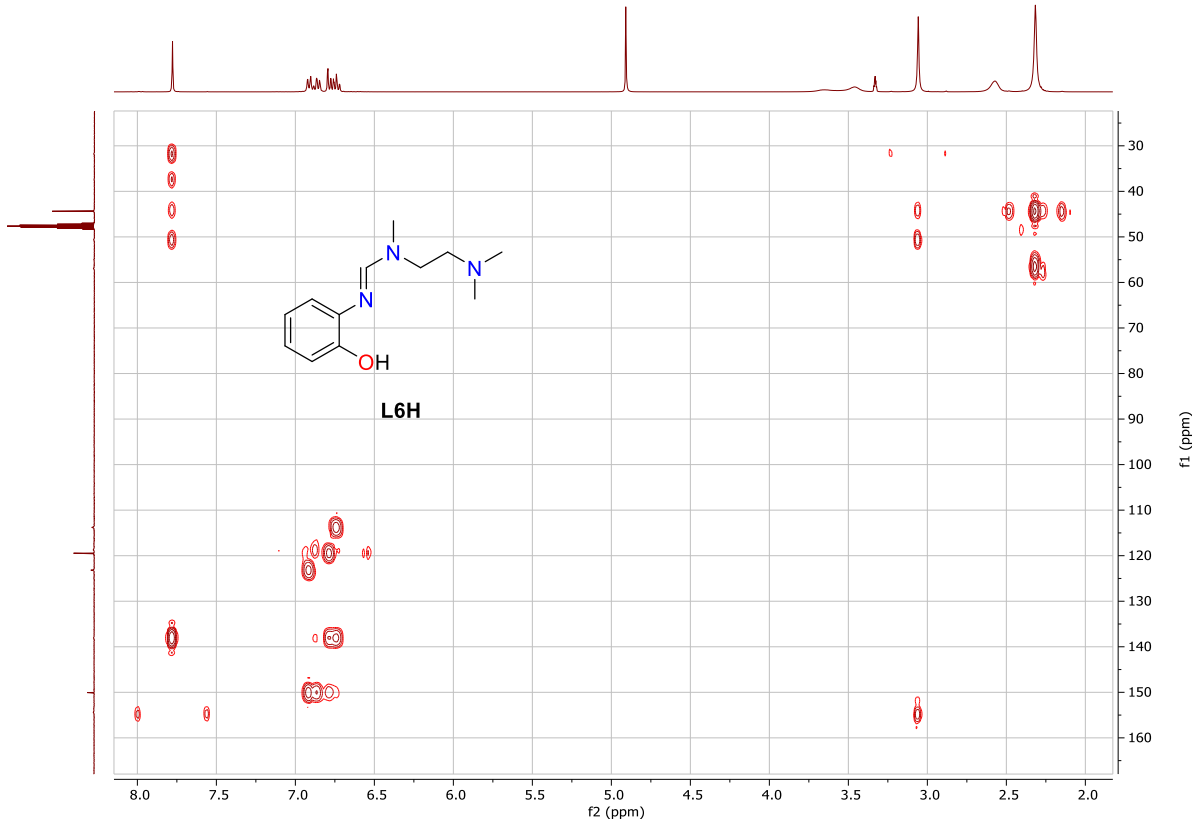


*Figure S30 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, MeOD, 298 K) of N'-(2-hydroxyphenyl)-N-methyl-N-(dimethylaminoethyl)formamidine **L6H**.*

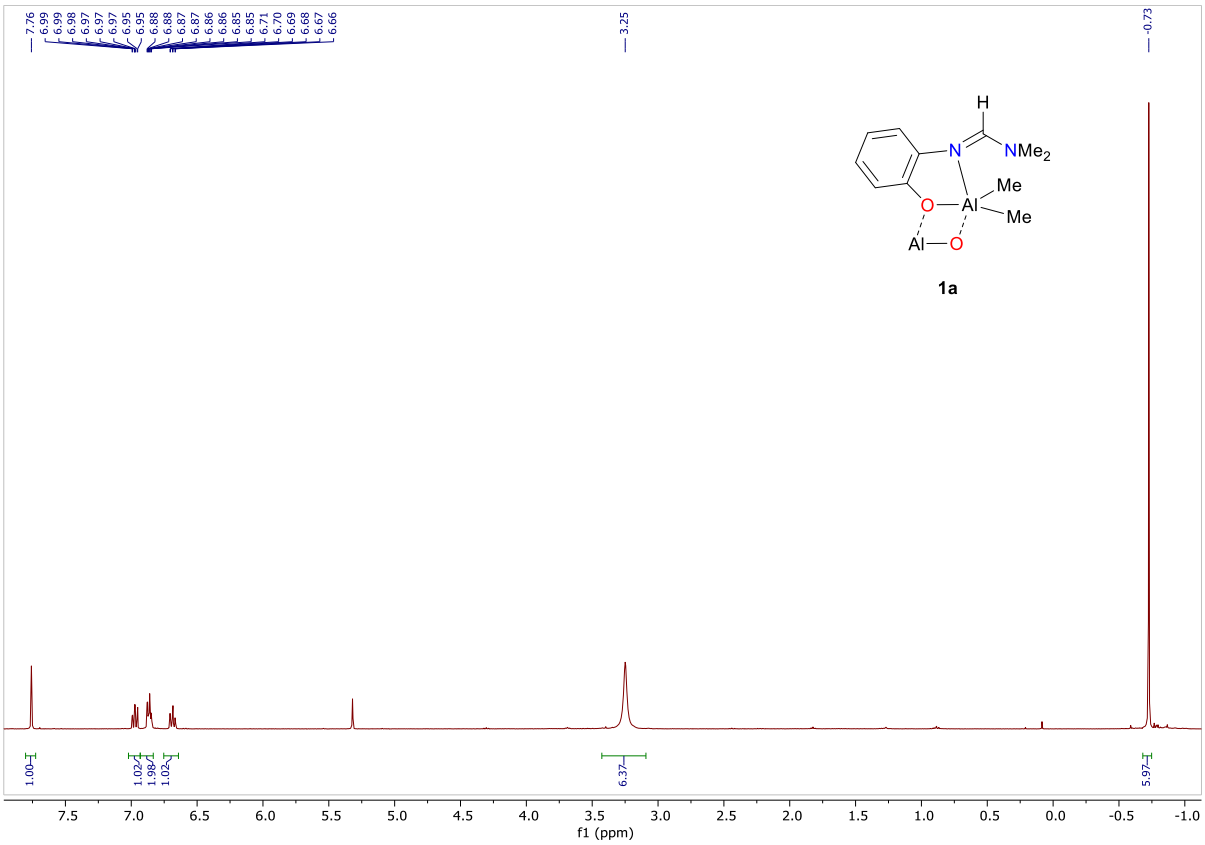


*Figure S31 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of **1a**.*

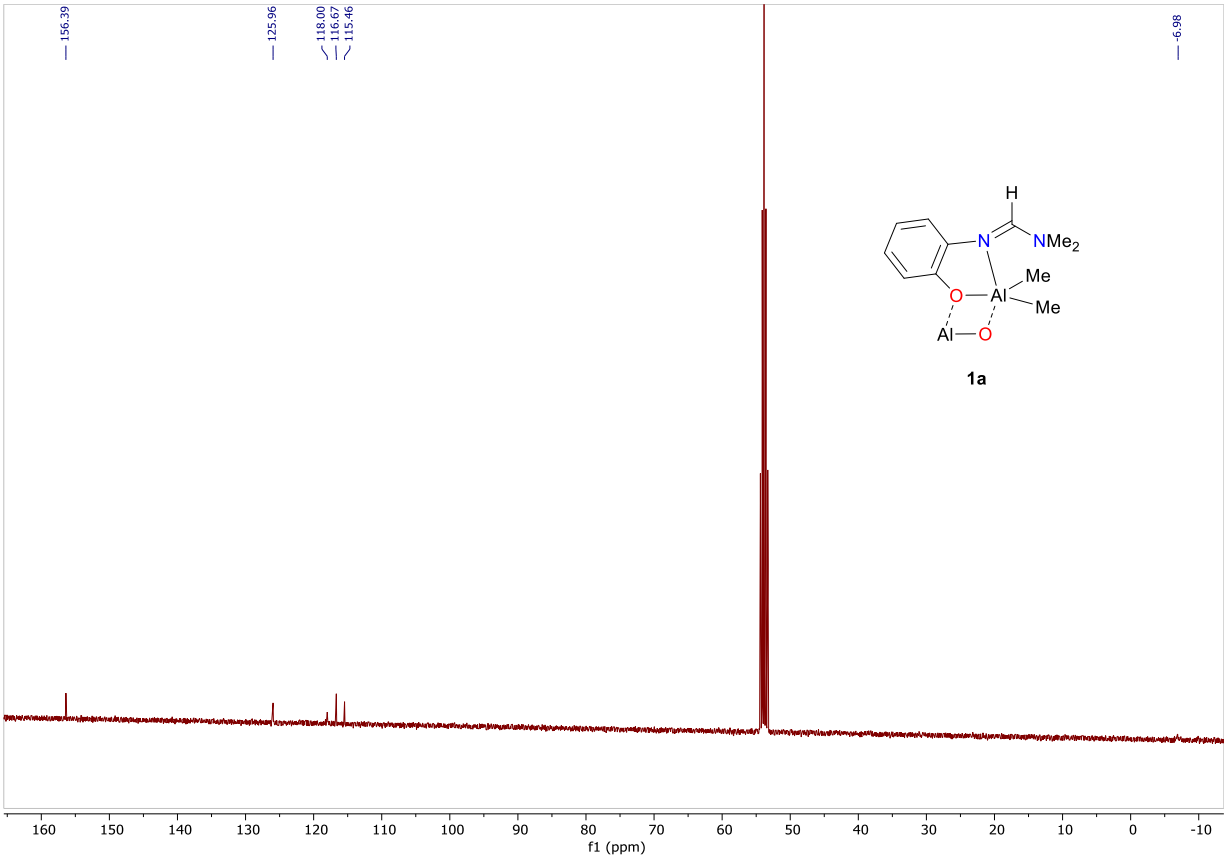


*Figure S32 $\{^{1}H\}^{13}C$ NMR (101 MHz, CD_2Cl_2, 298 K) of **1a**.*

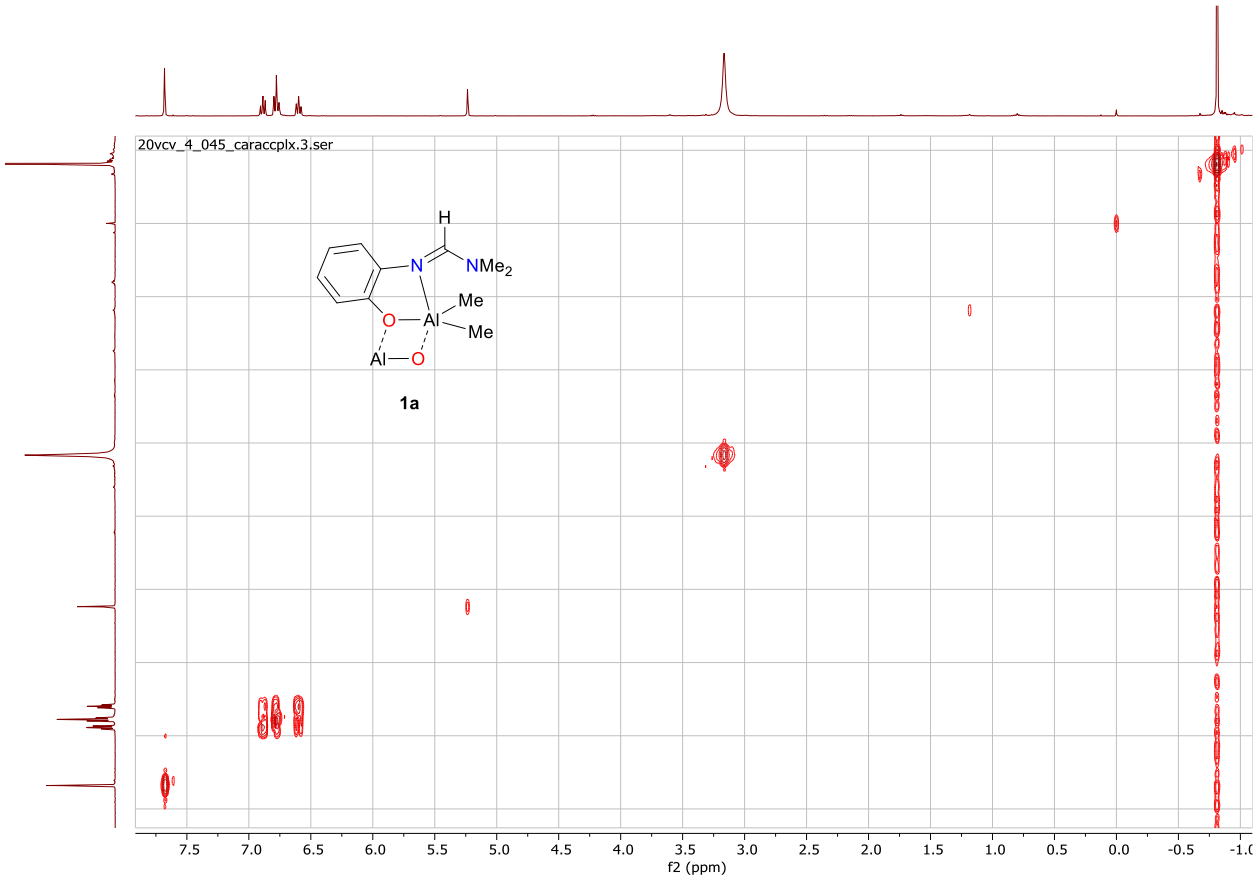


*Figure S33 ^{1}H ^{1}H COSY (400 MHz, CD_2Cl_2, 298 K) of **1a**.*

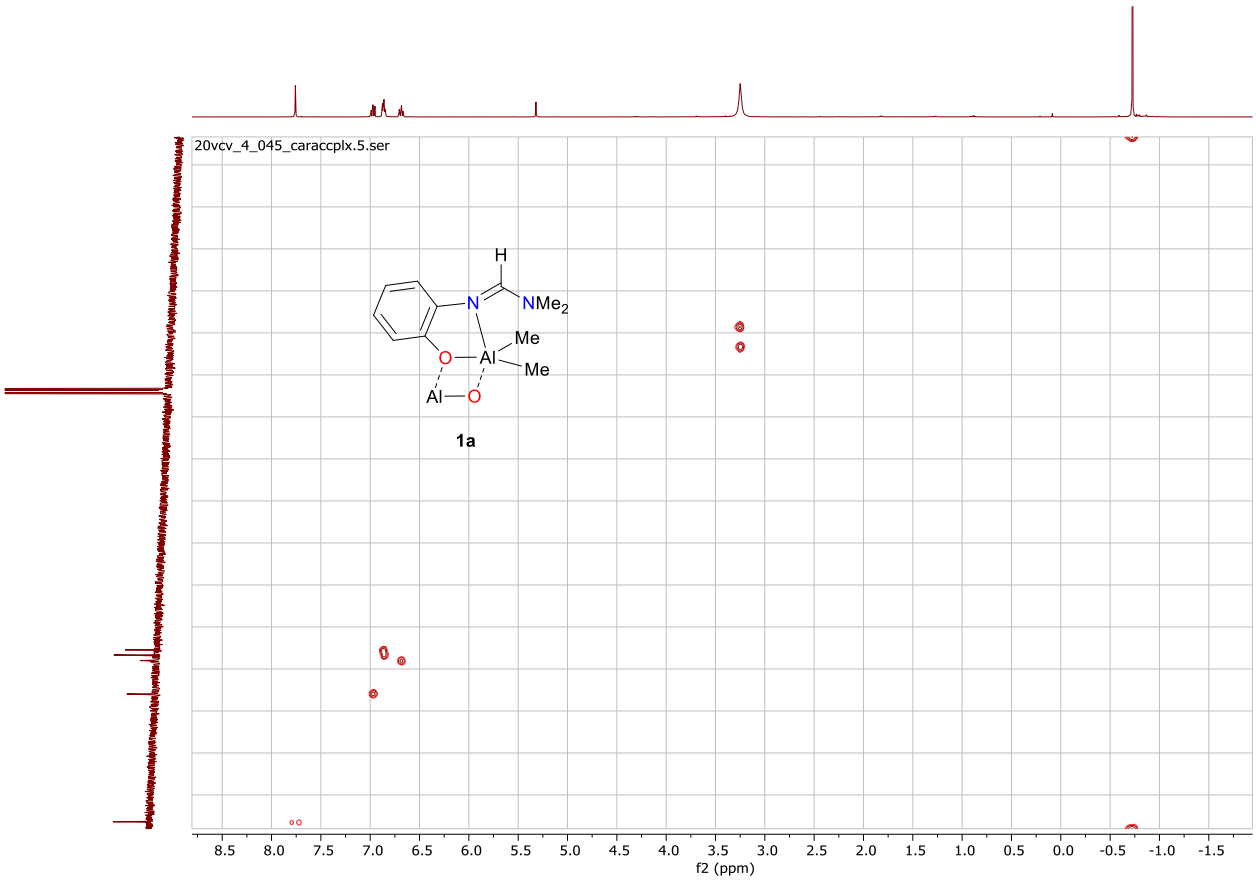


*Figure S34 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **1a**.*

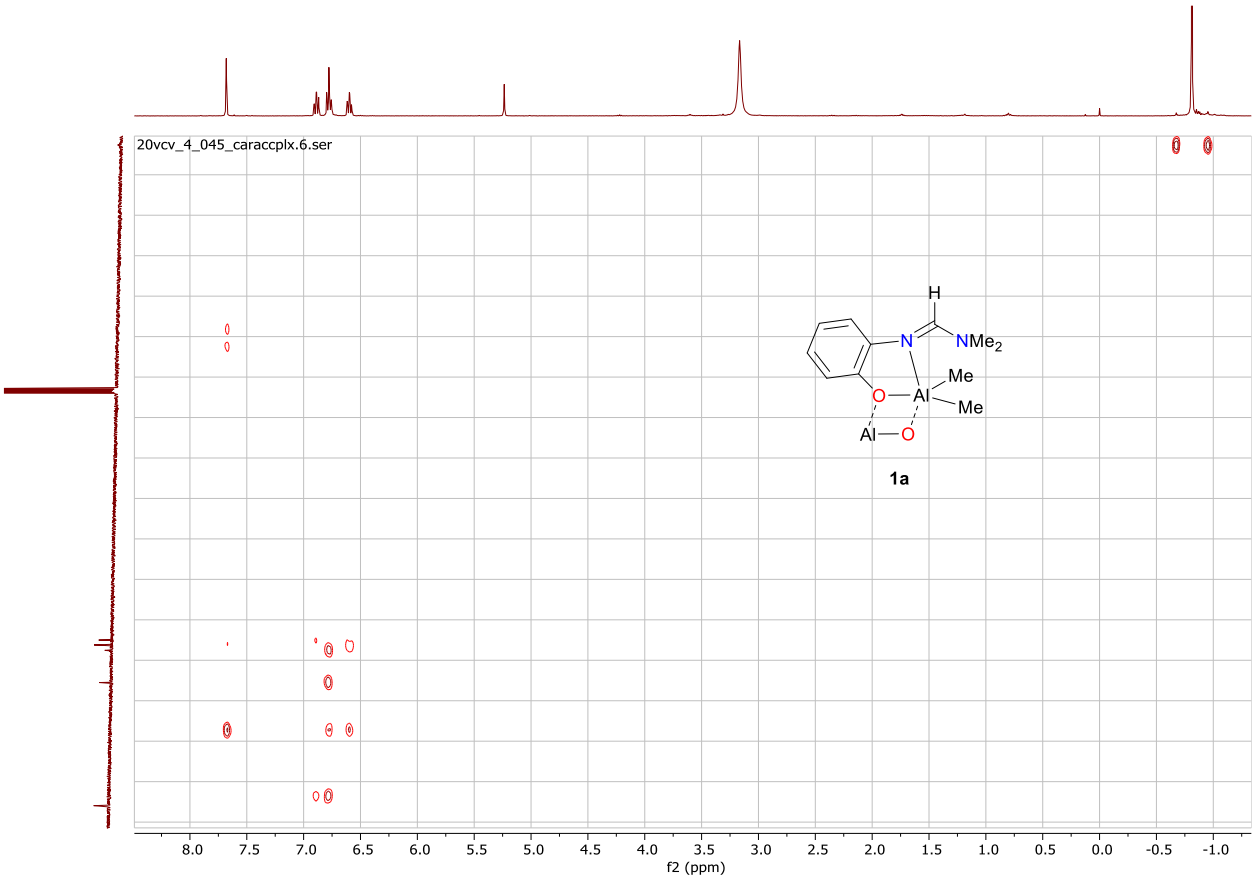


*Figure S35 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **1a**.*

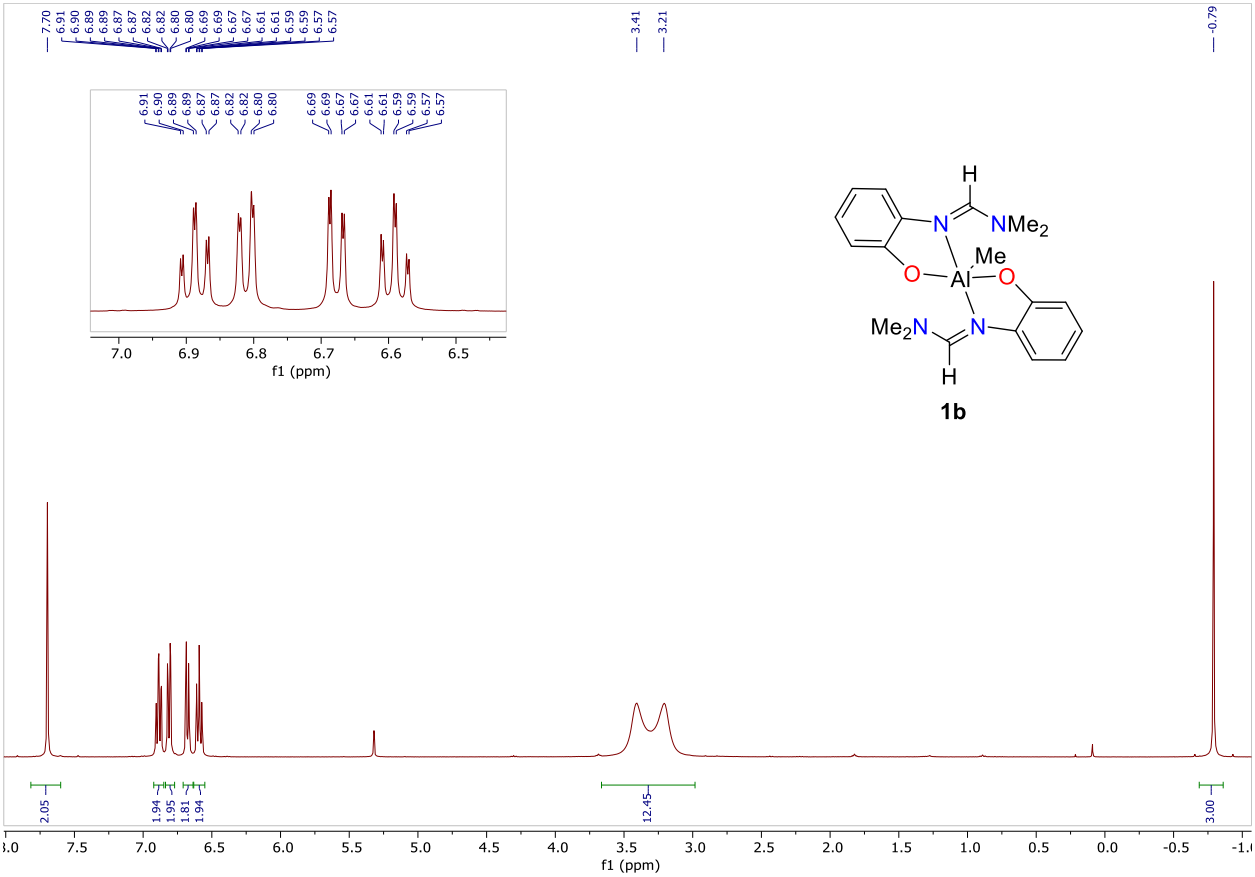


*Figure S36 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of **1b**.*

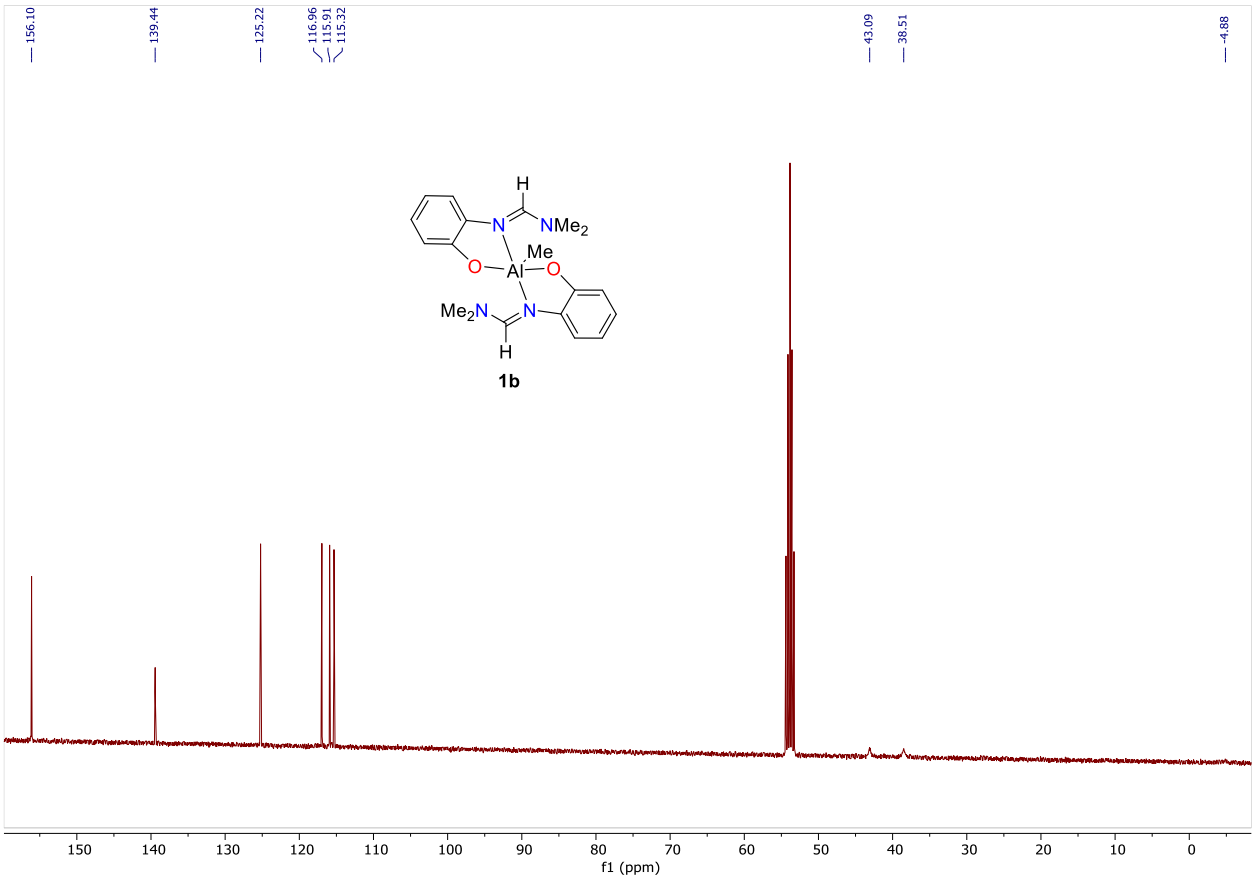


*Figure S37 {^{1}H}^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) of **1b**.*

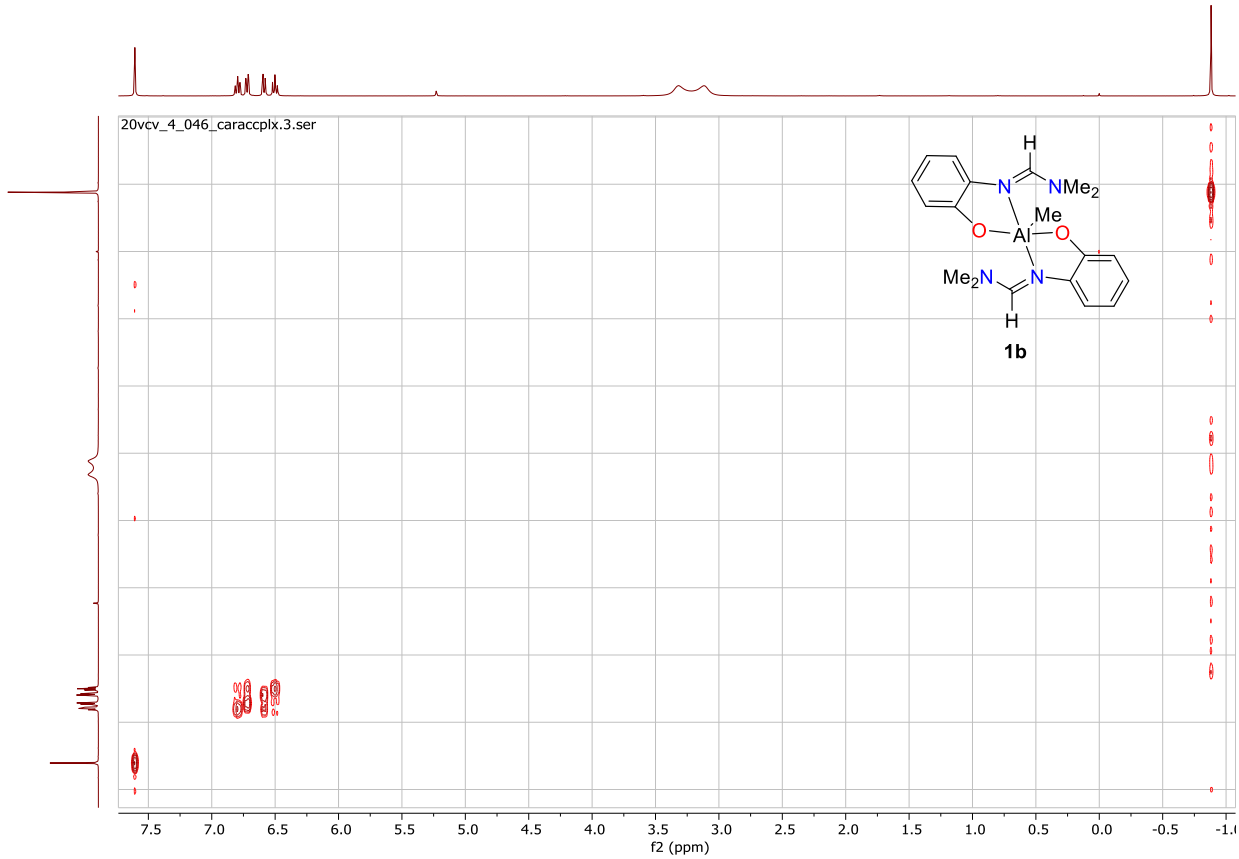


*Figure S38 ^{1}H ^{1}H COSY (400 MHz, CD_2Cl_2, 298 K) of **1b**.*

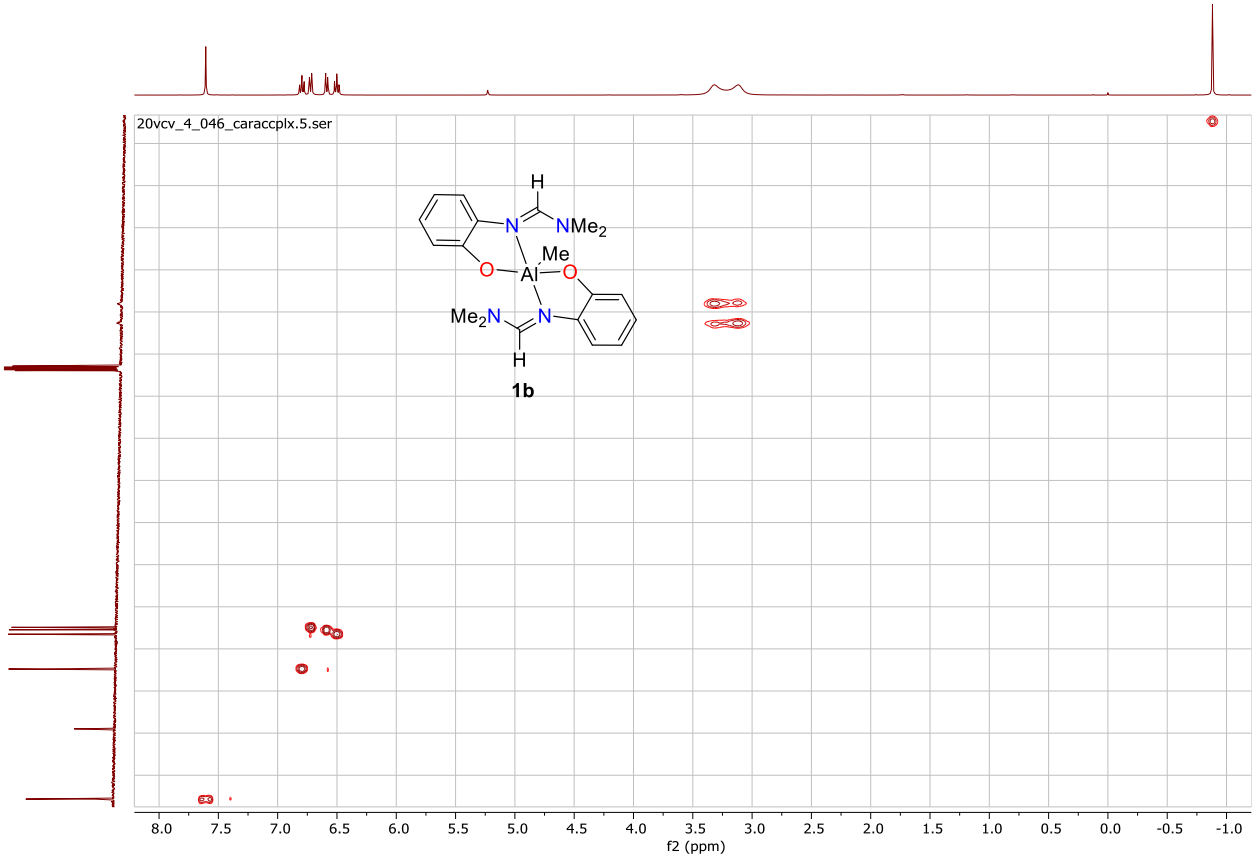


*Figure S39 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **1b**.*

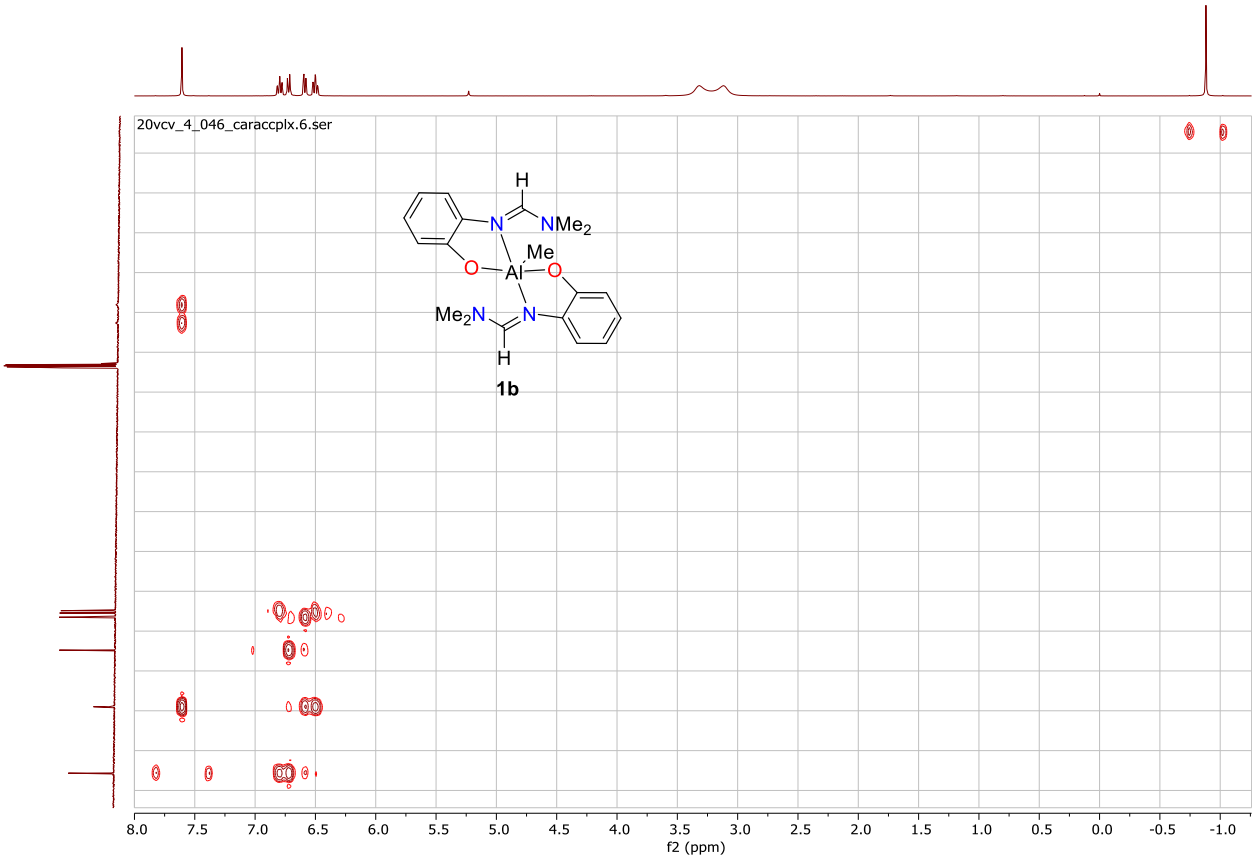


*Figure S40 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **1b**.*

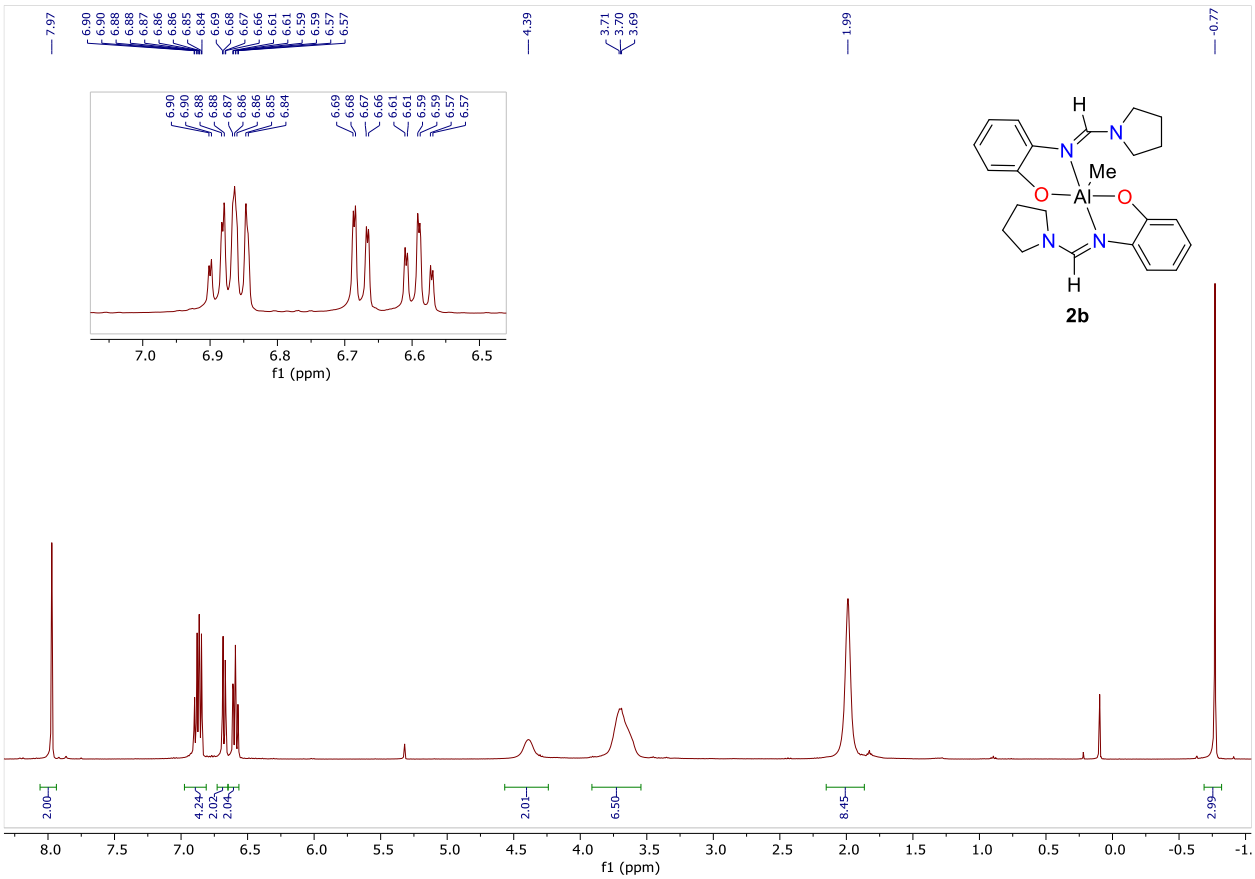


*Figure S41 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) of **2b**.*

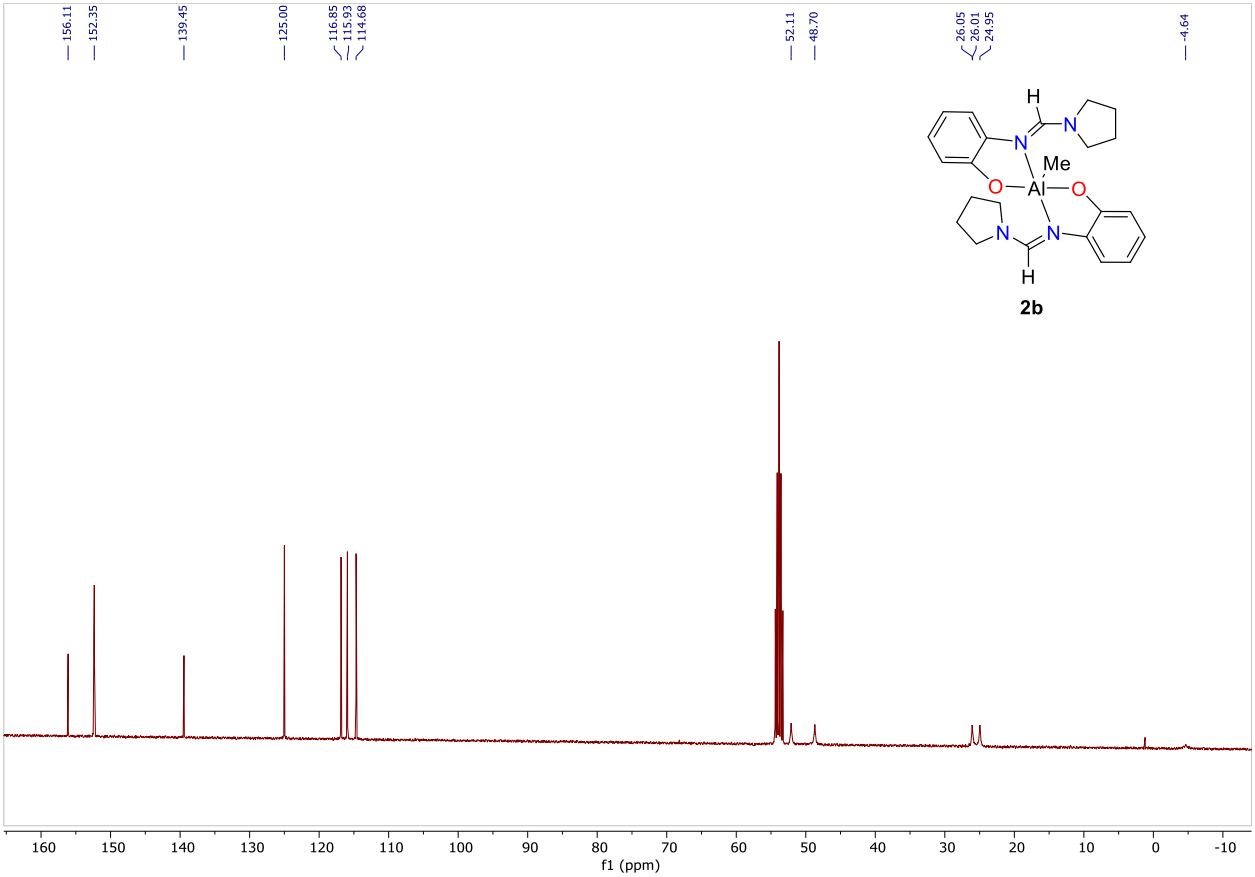


*Figure S42 $\{^{1}H\}^{13}C$ NMR (101 MHz, CD_2Cl_2, 298 K) of **2b**.*

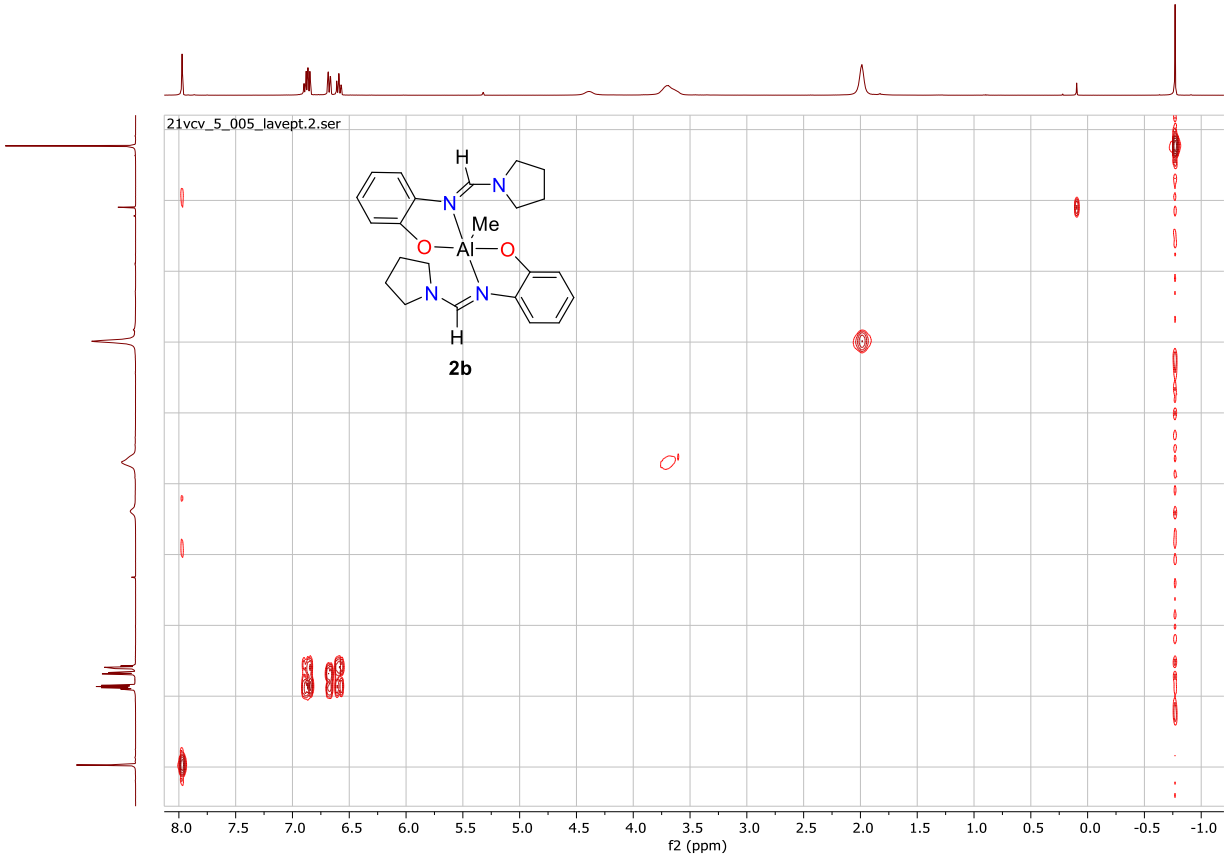


*Figure S43 ^{1}H ^{1}H COSY (400 MHz, CD_2Cl_2, 298 K) of **2b**.*

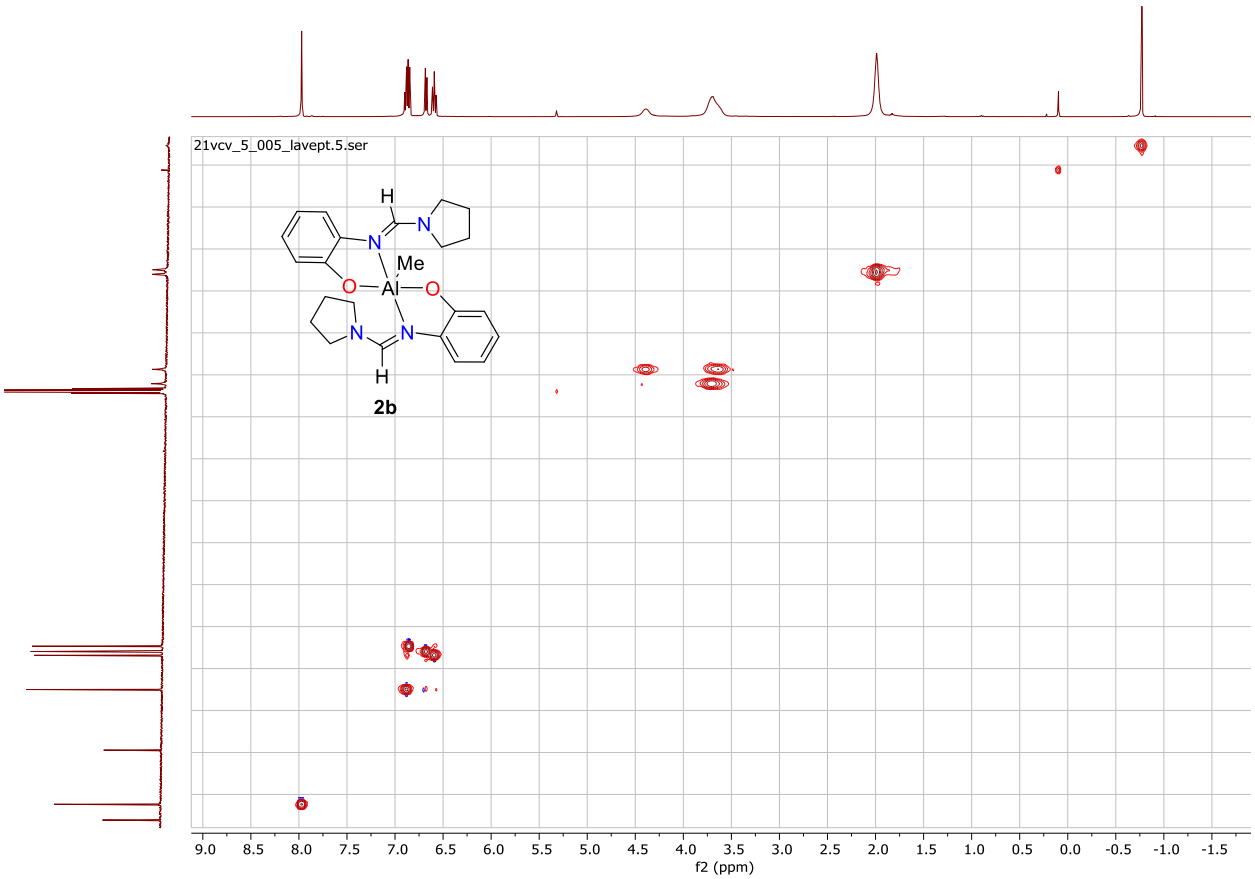


*Figure S44 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **2b**.*

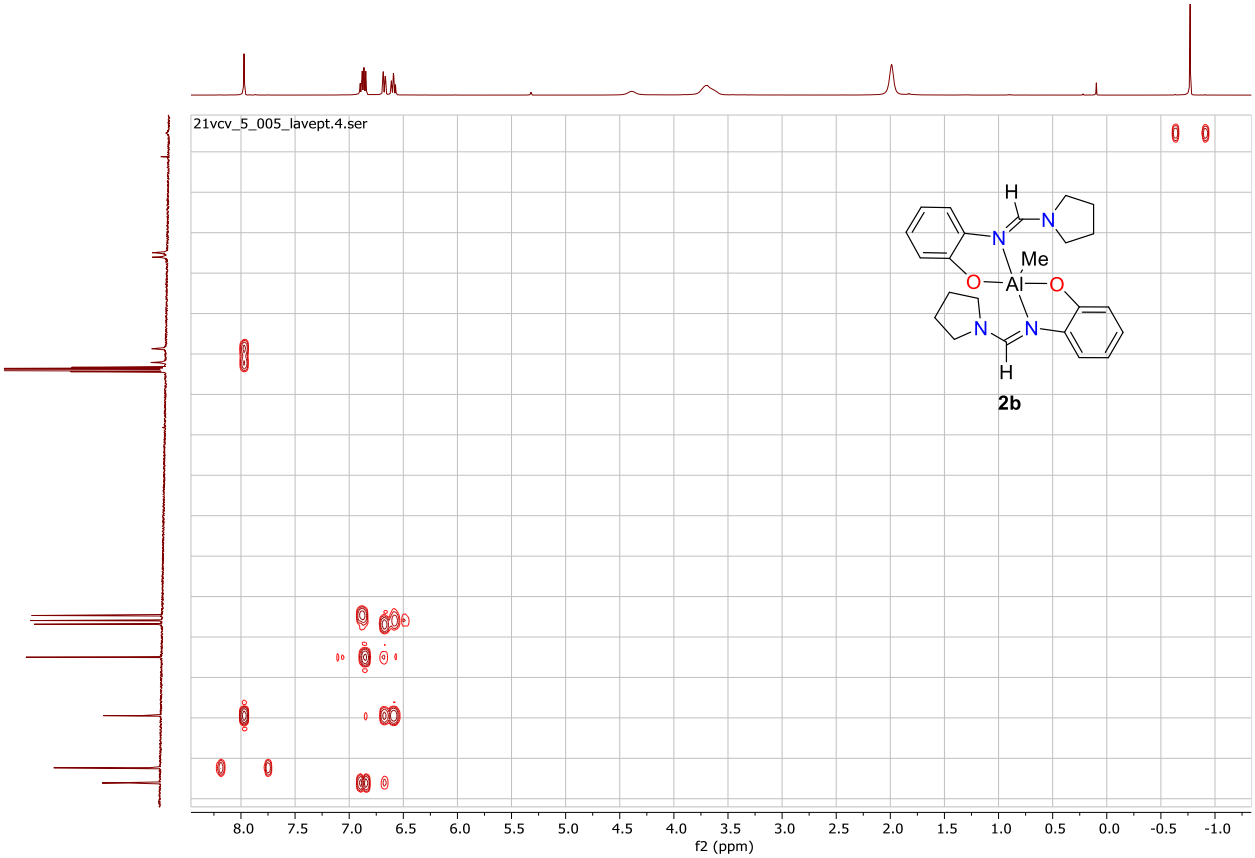


*Figure S45 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) of **2b**.*

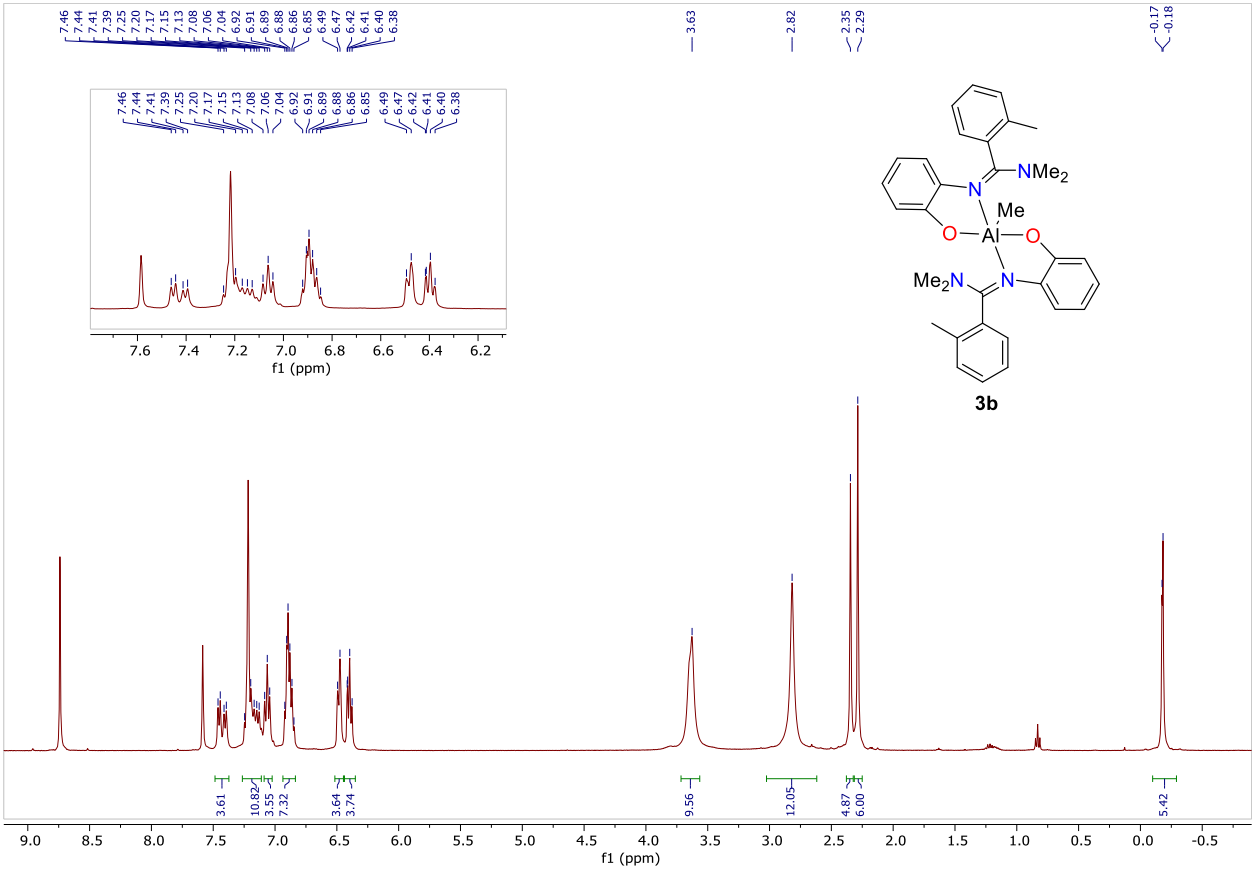


*Figure S46 ^{1}H NMR (400 MHz, C_5D_5N, 298 K) of **3b**.*

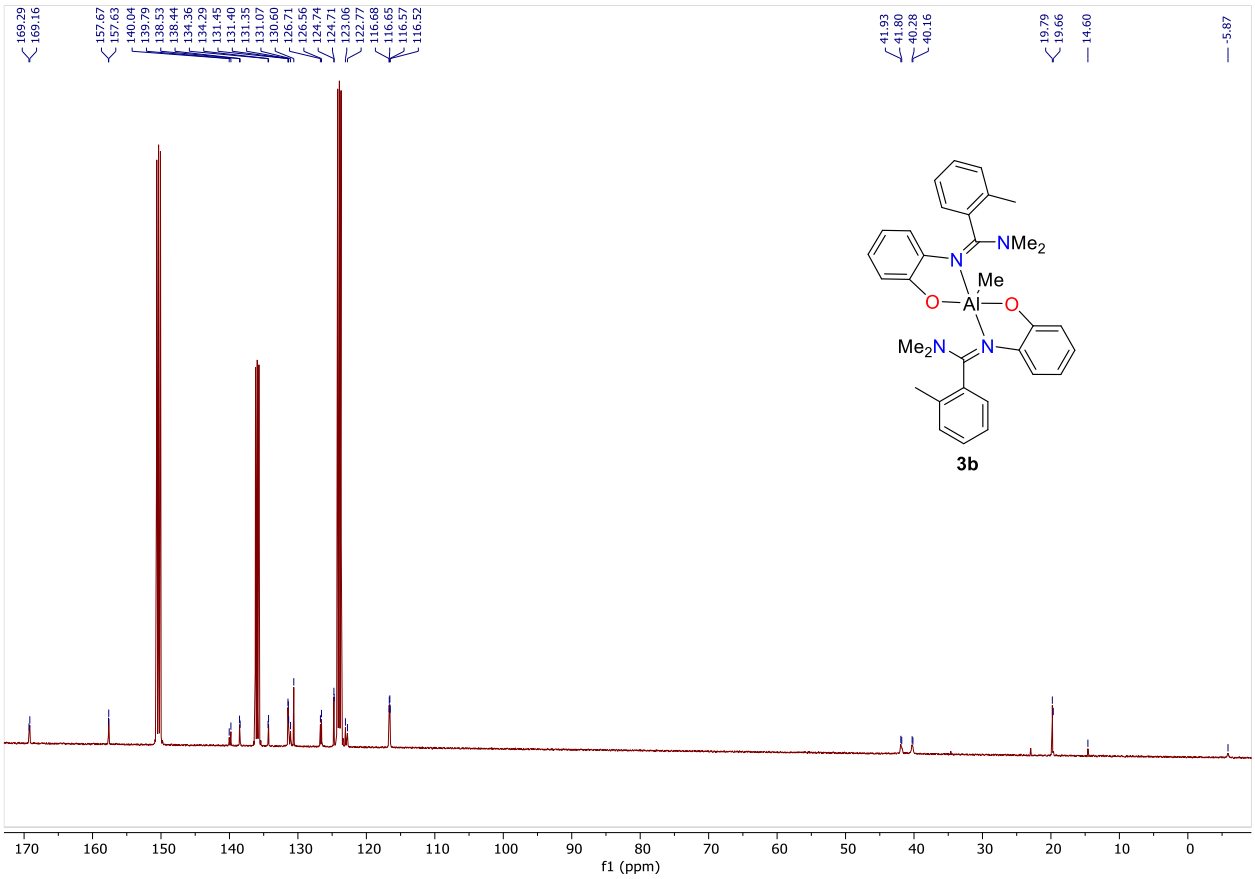


*Figure S47 {^{1}H}^{13}C NMR (101 MHz, C_5D_5N, 298 K) of **3b.***

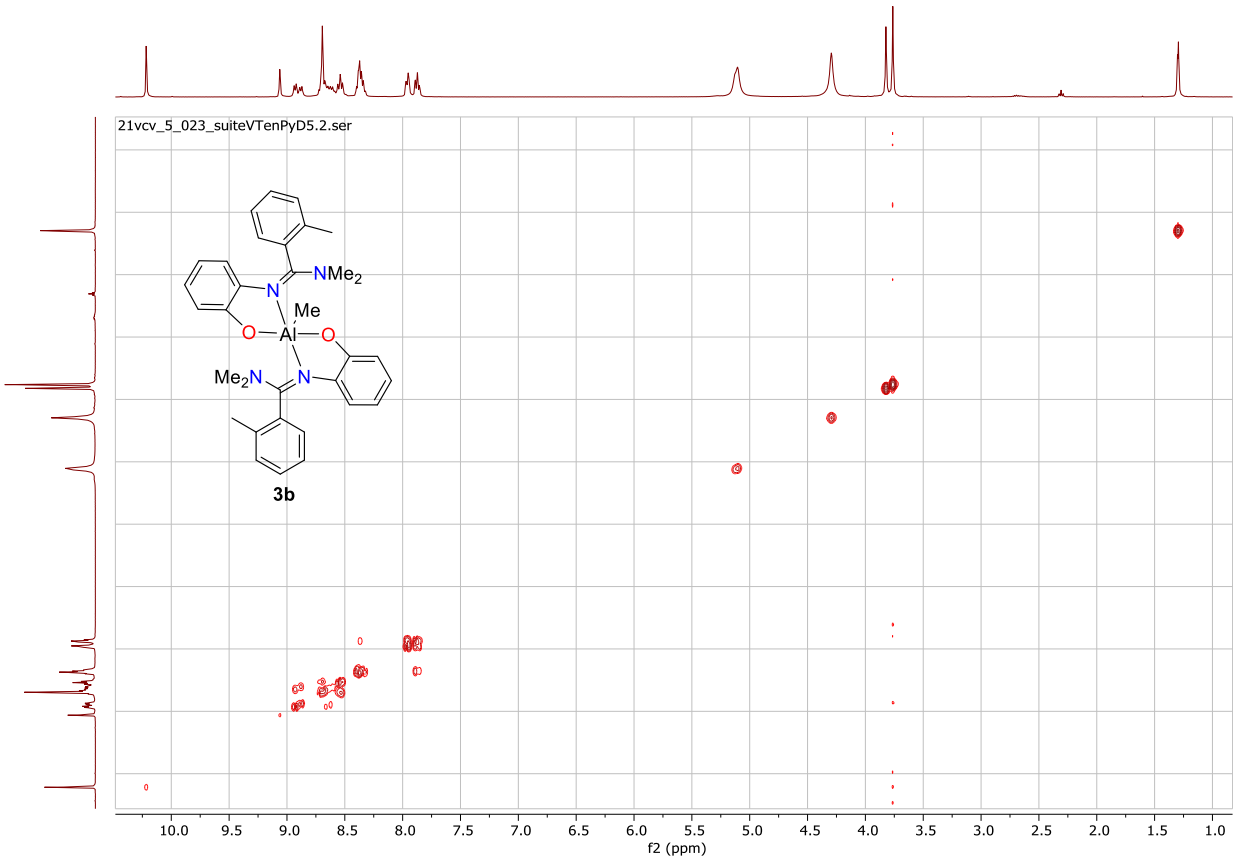


*Figure S48 ^{1}H ^{1}H COSY (400 MHz, C_5D_5N, 298 K) of **3b**.*

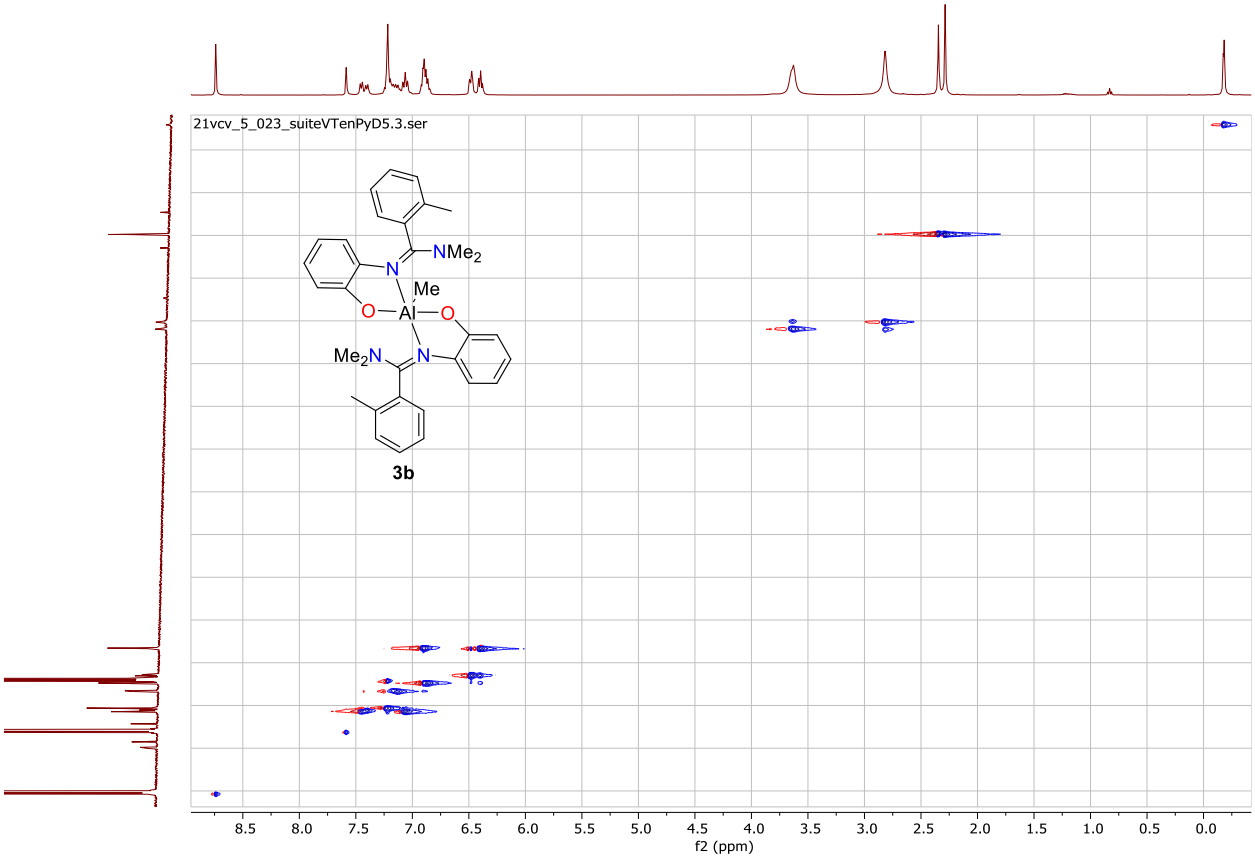


*Figure S49 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **3b**.*

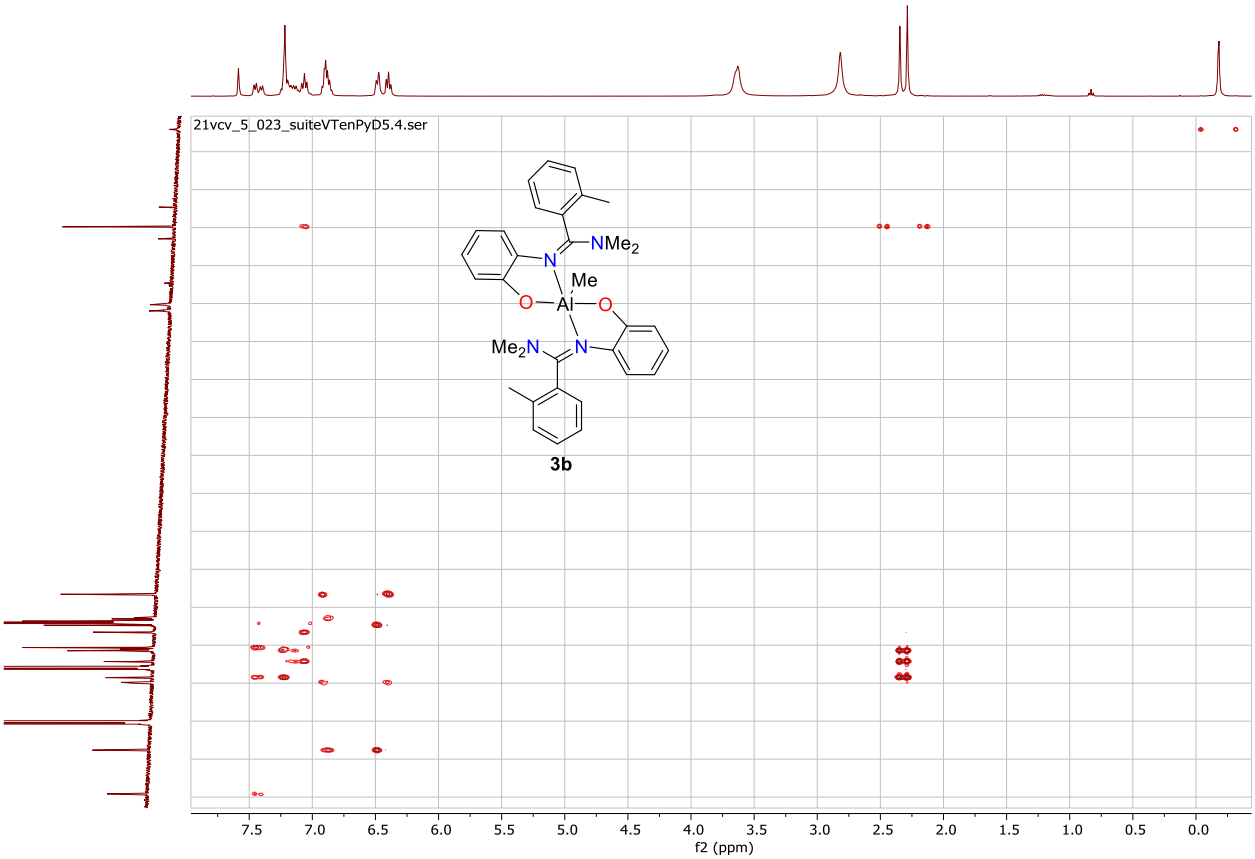


*Figure S50 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **3b**.*

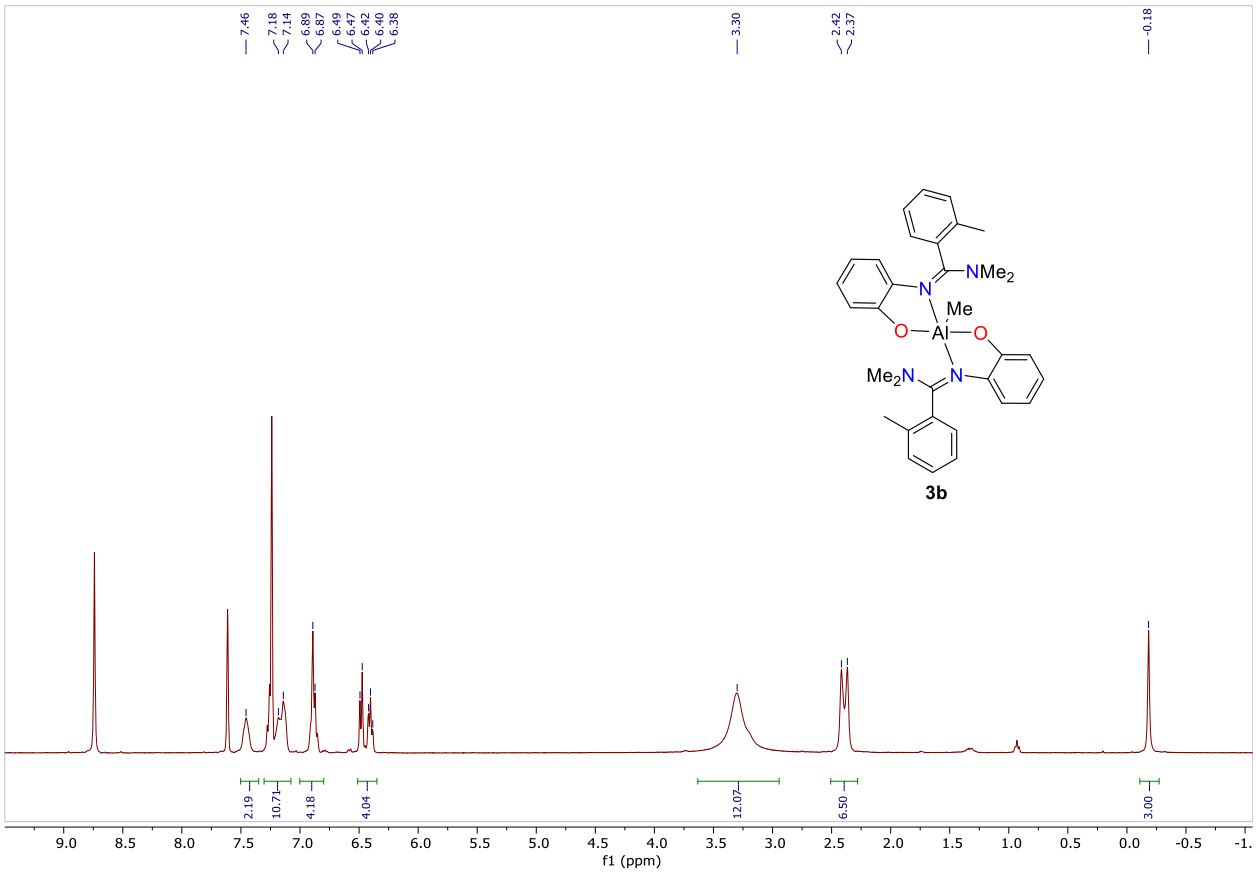


*Figure S51 ^{1}H NMR (400 MHz, C_5D_5N, 383 K) of **3b**.*

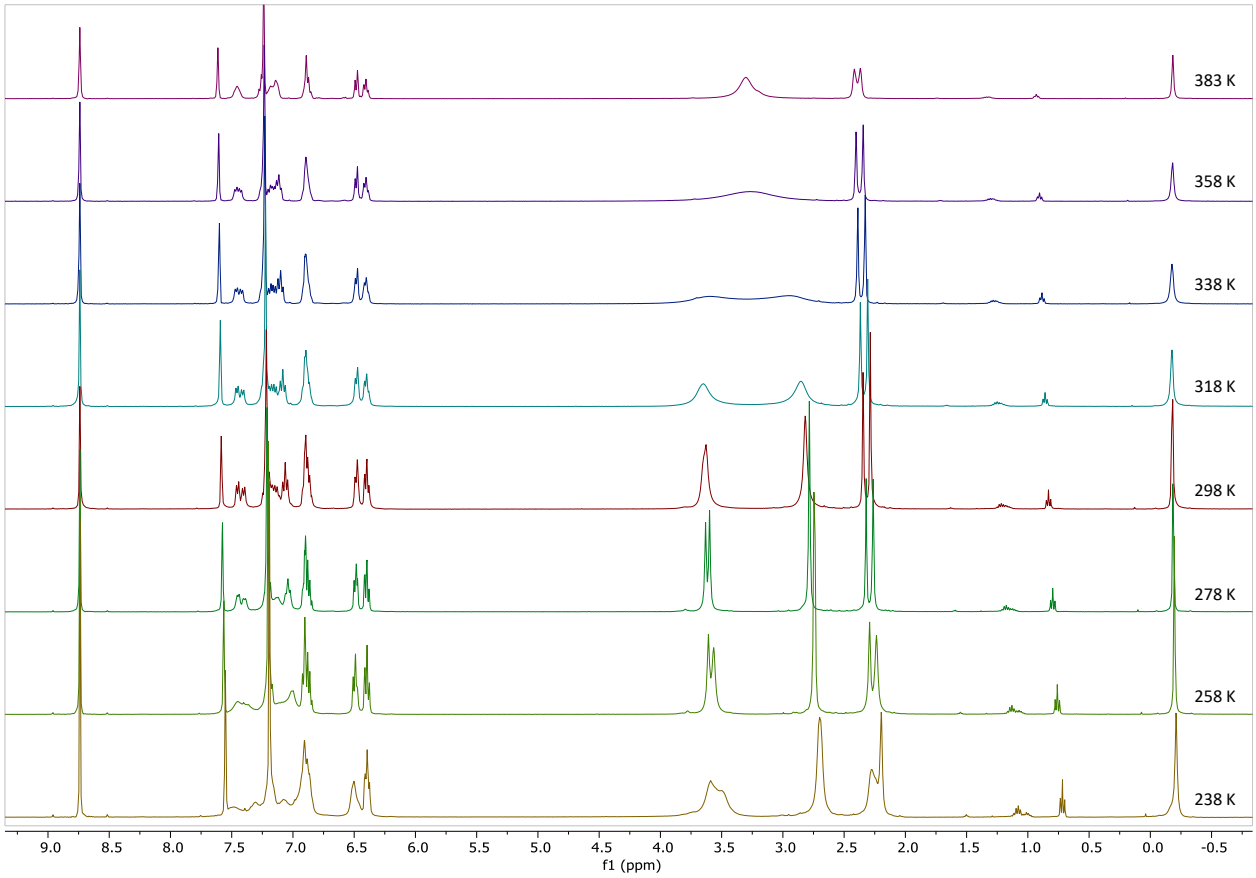


*Figure S52 Variable Temperature ^{1}H NMR (400 MHz, C_5D_5N) of **3b**.*

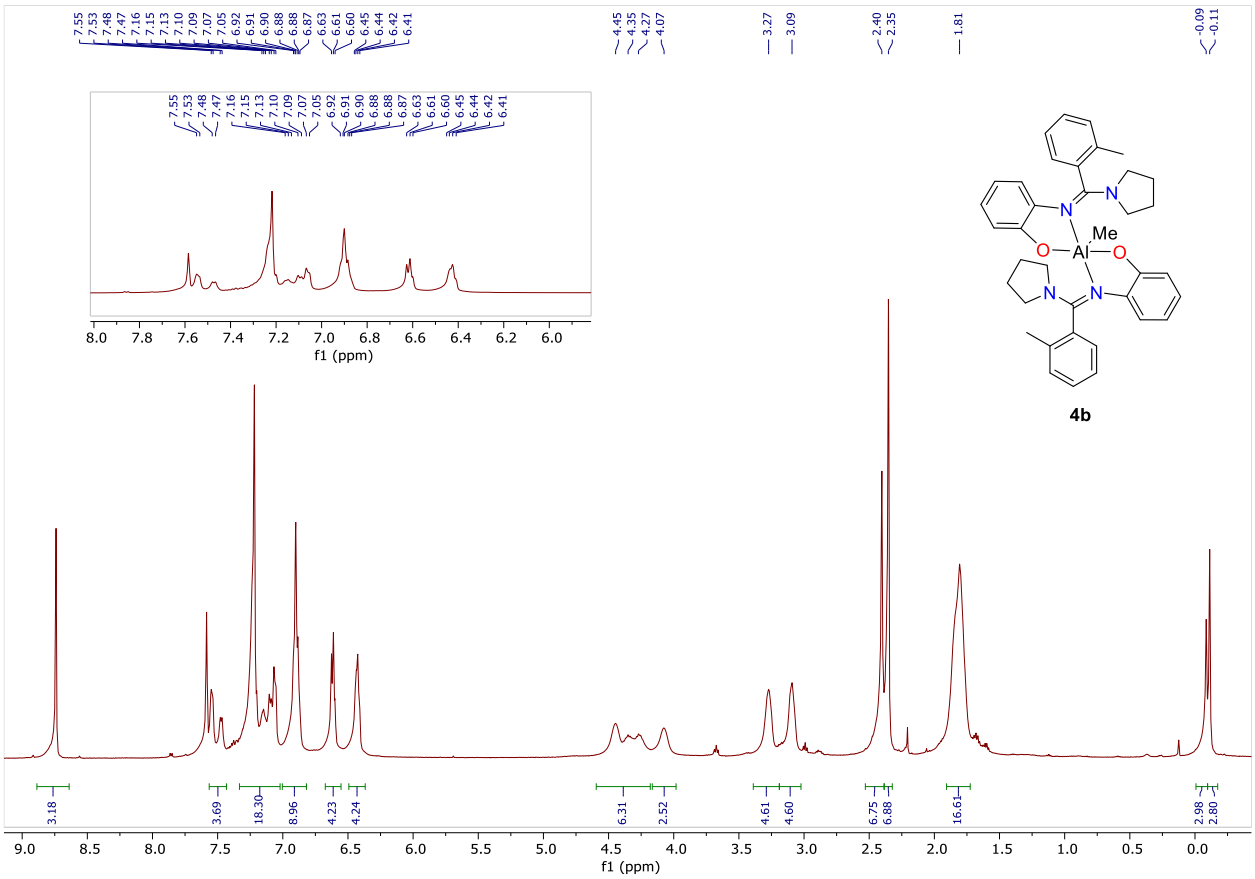


*Figure S53 ^{1}H NMR (400 MHz, C_5D_5N, 298 K) of **4b**.*

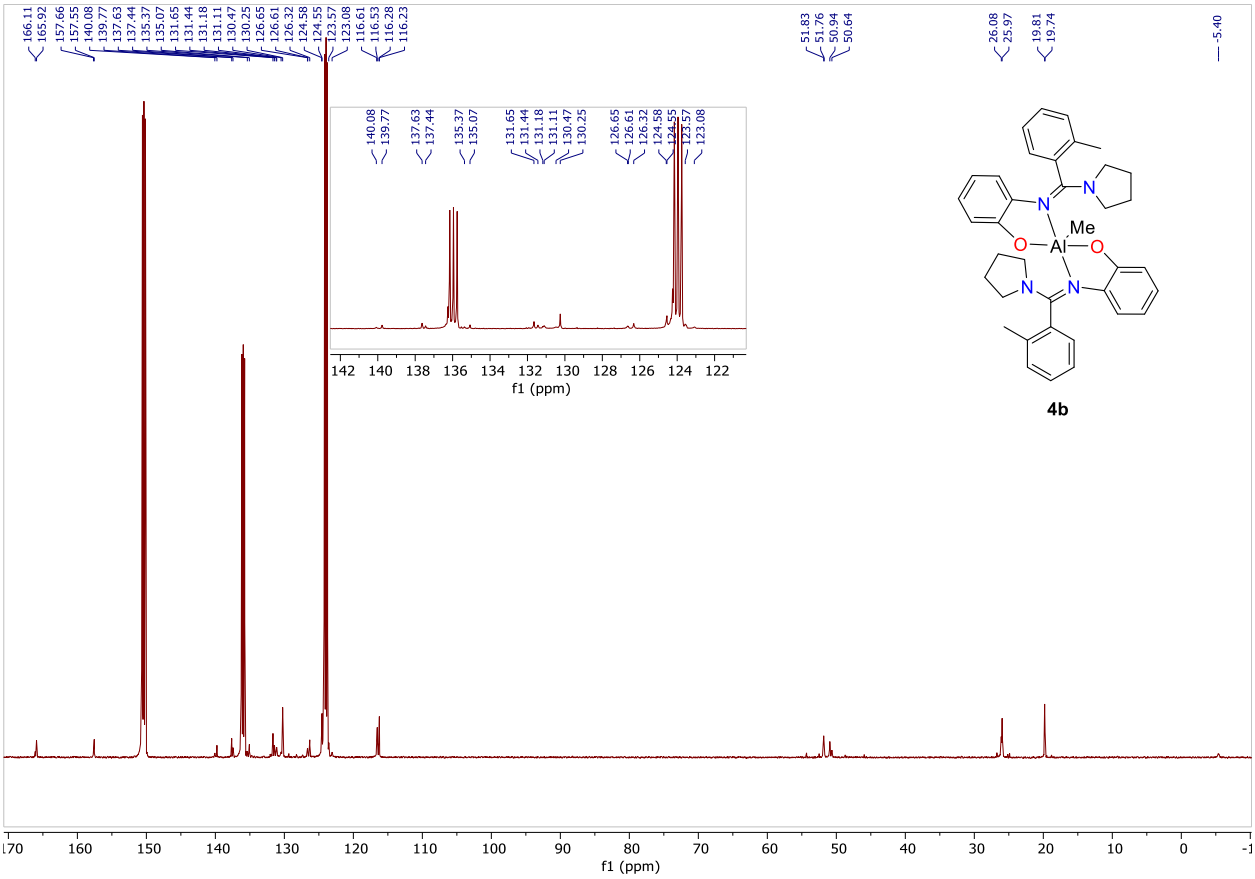


*Figure S54 $\{^{1}H\}^{13}C$ NMR (101 MHz, C_5D_5N, 298 K) of **4b.***

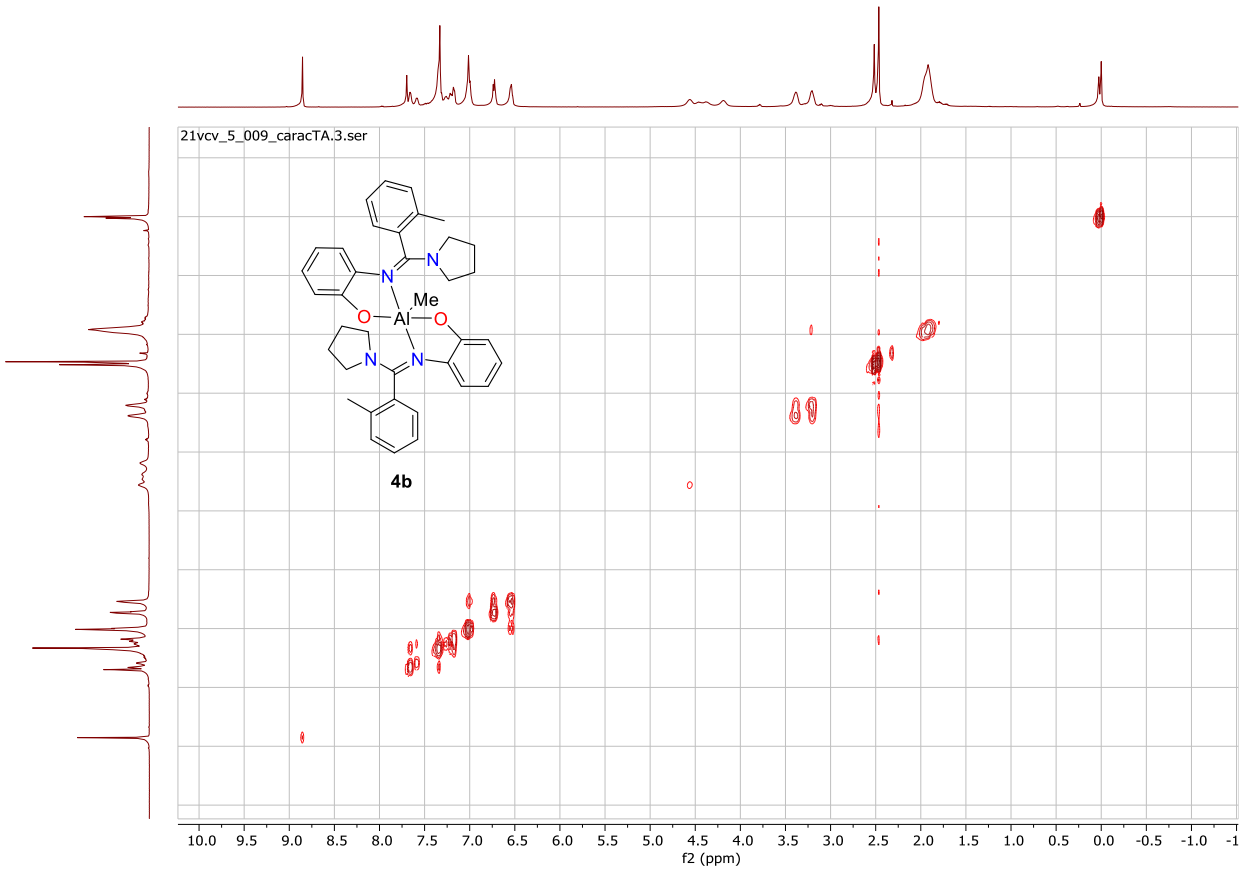


*Figure S55 ^{1}H ^{1}H COSY (400 MHz, C_5D_5N, 298 K) of **4b**.*

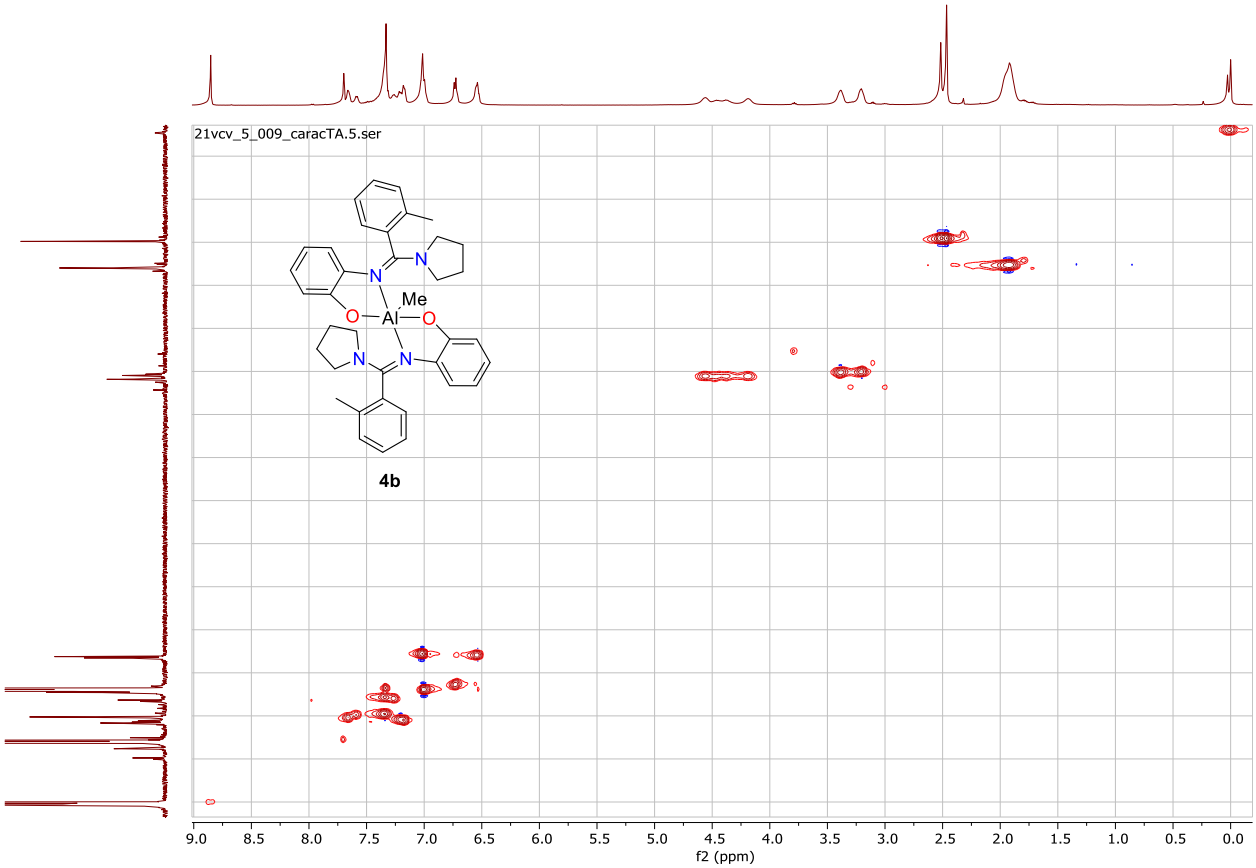


*Figure S56 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **4b**.*

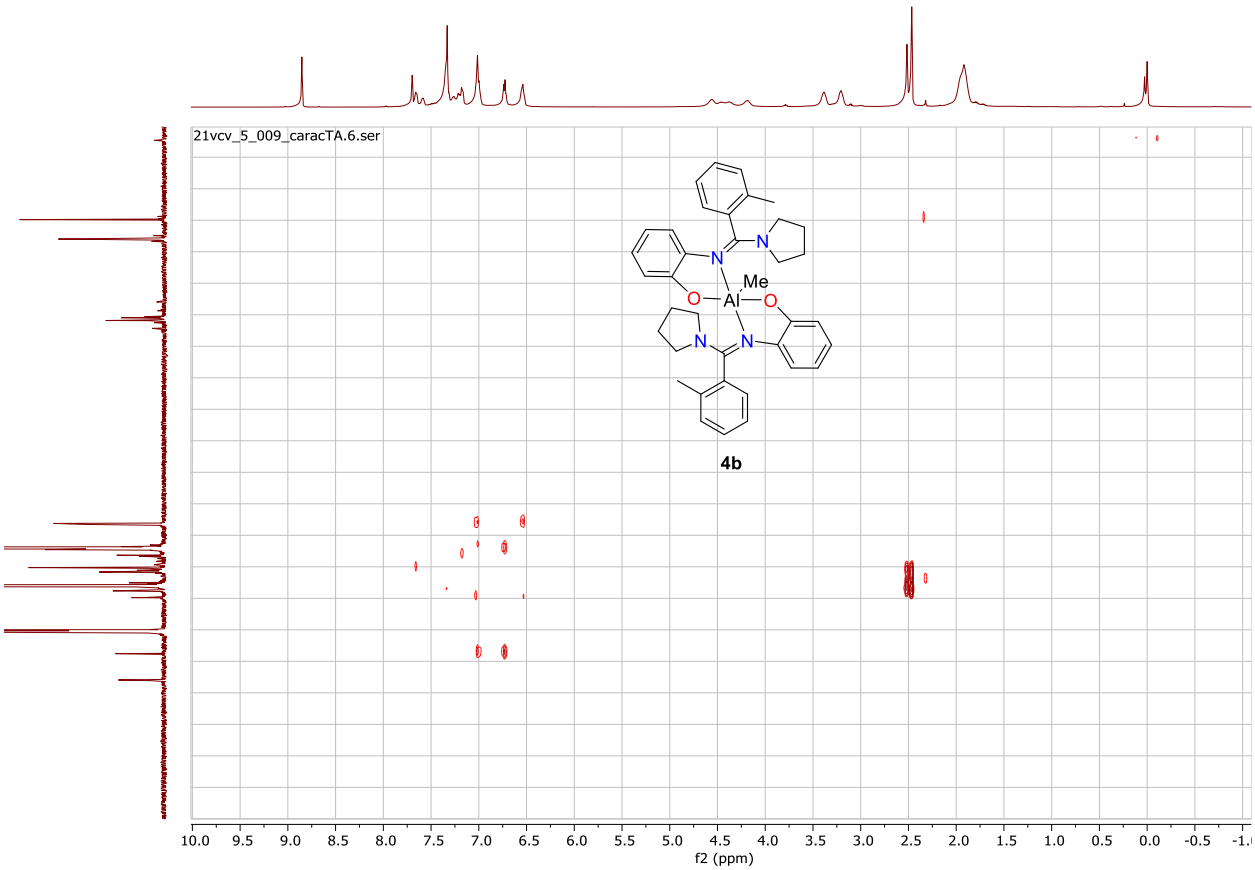


*Figure S57 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **4b**.*

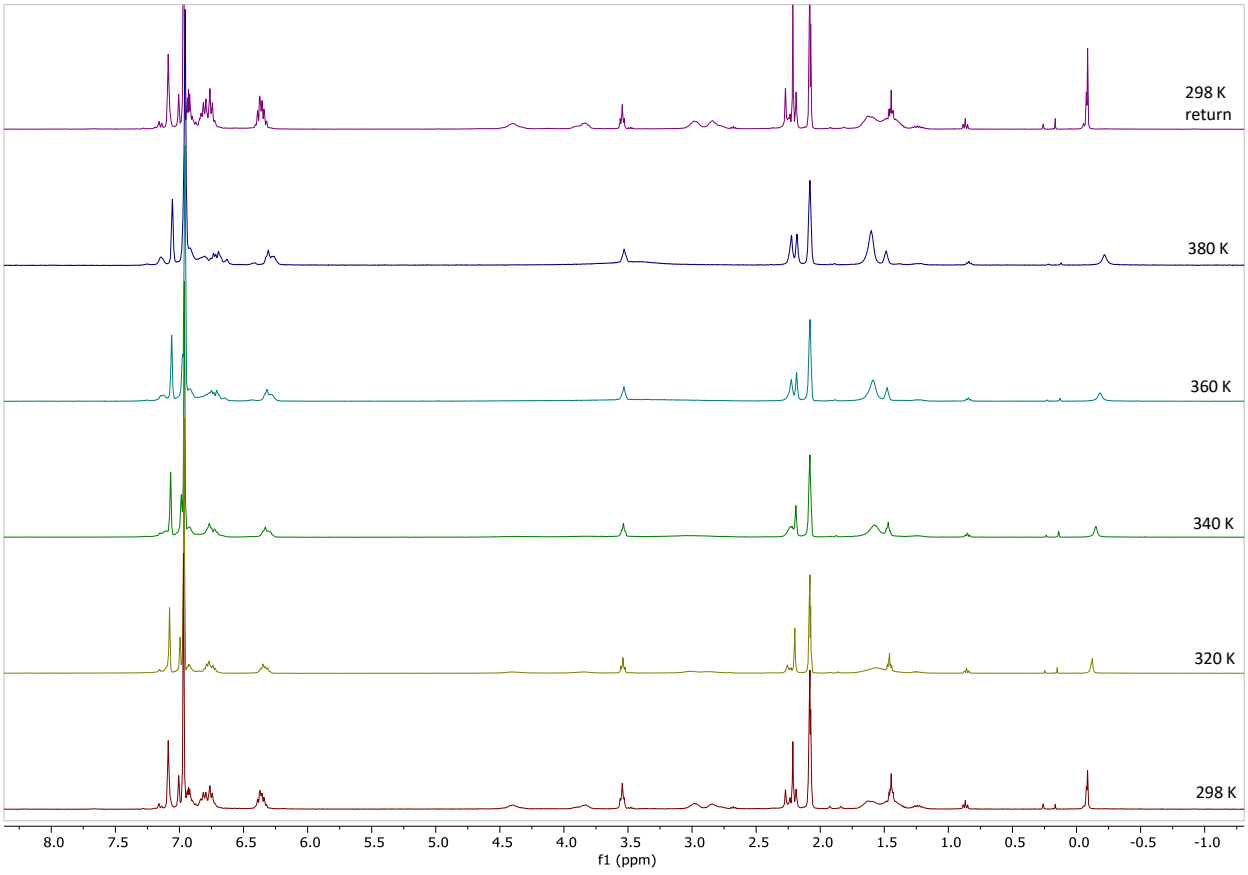


*Figure S58 Variable Temperature ^{1}H NMR (400 MHz, Toluene-d_8) of **4b**.*

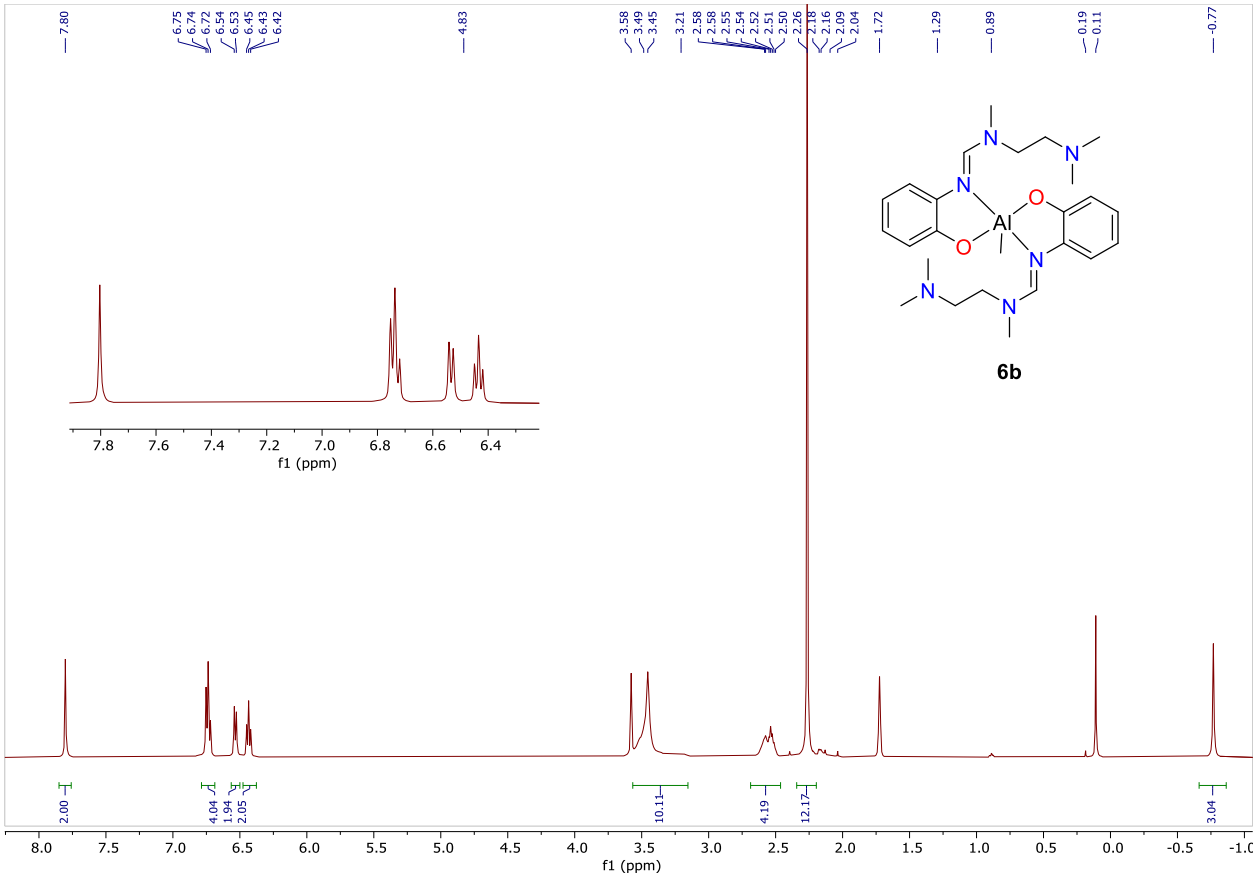


*Figure S59 ^{1}H NMR (500 MHz, THF-d8, 298 K) of **6b**.*

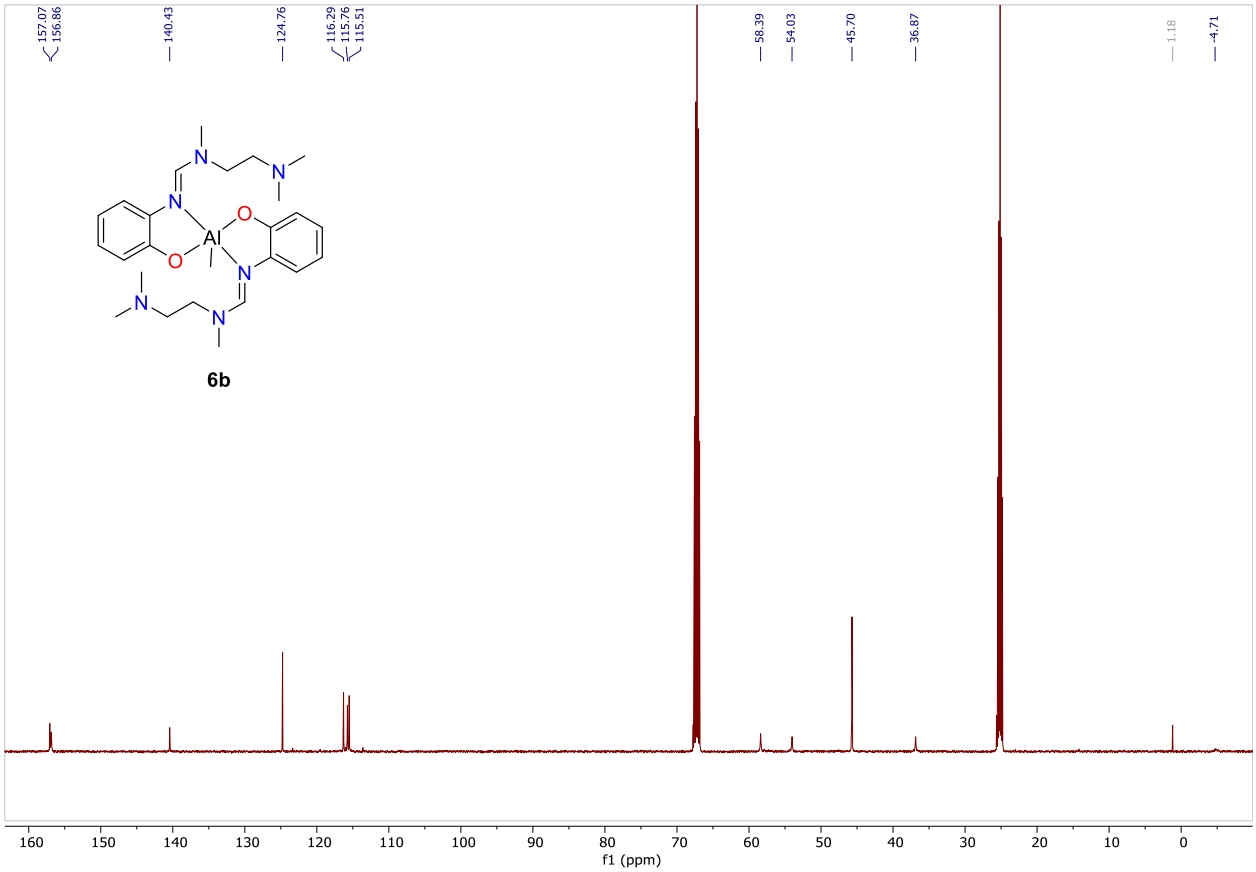


*Figure S60 $\{^{1}H\}^{13}C$ (125 MHz, THF-d8, 298 K) of **6b**.*

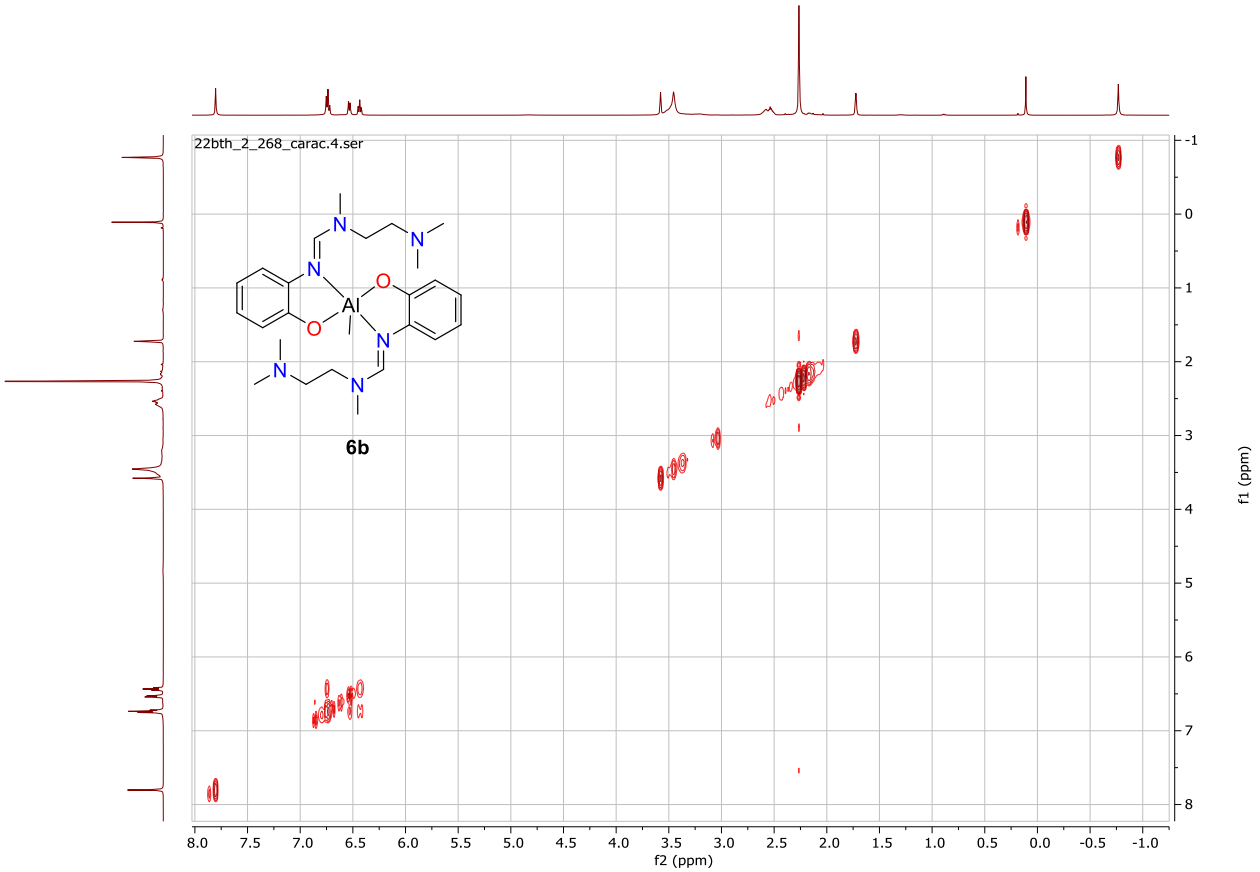


*Figure S61 ^{1}H ^{1}H COSY (500 MHz / 500 MHz, THF-d8, 298 K) of **6b**.*

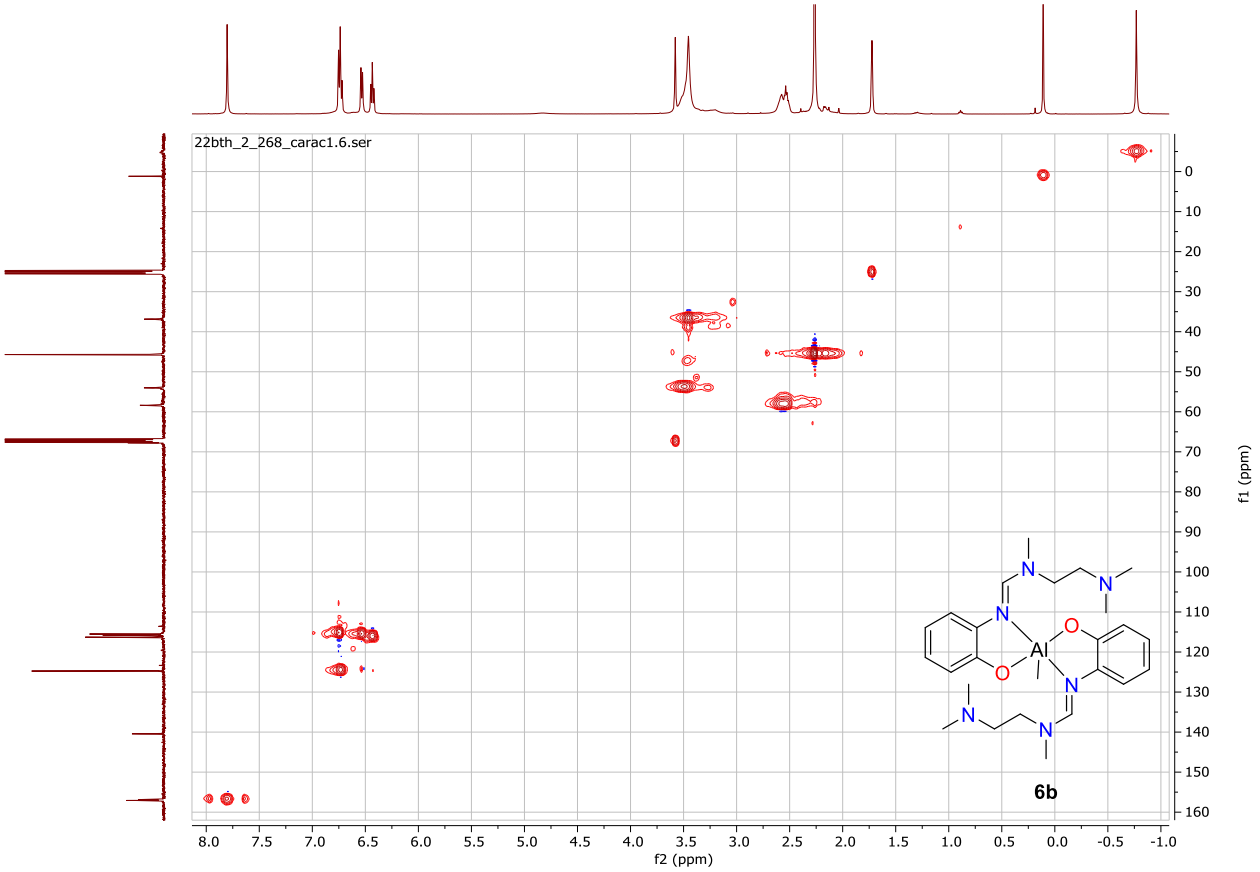


*Figure S62 ^{1}H ^{13}C HSCQ (500 MHz / 125 MHz, THF-d8, 298 K) of **6b**.*

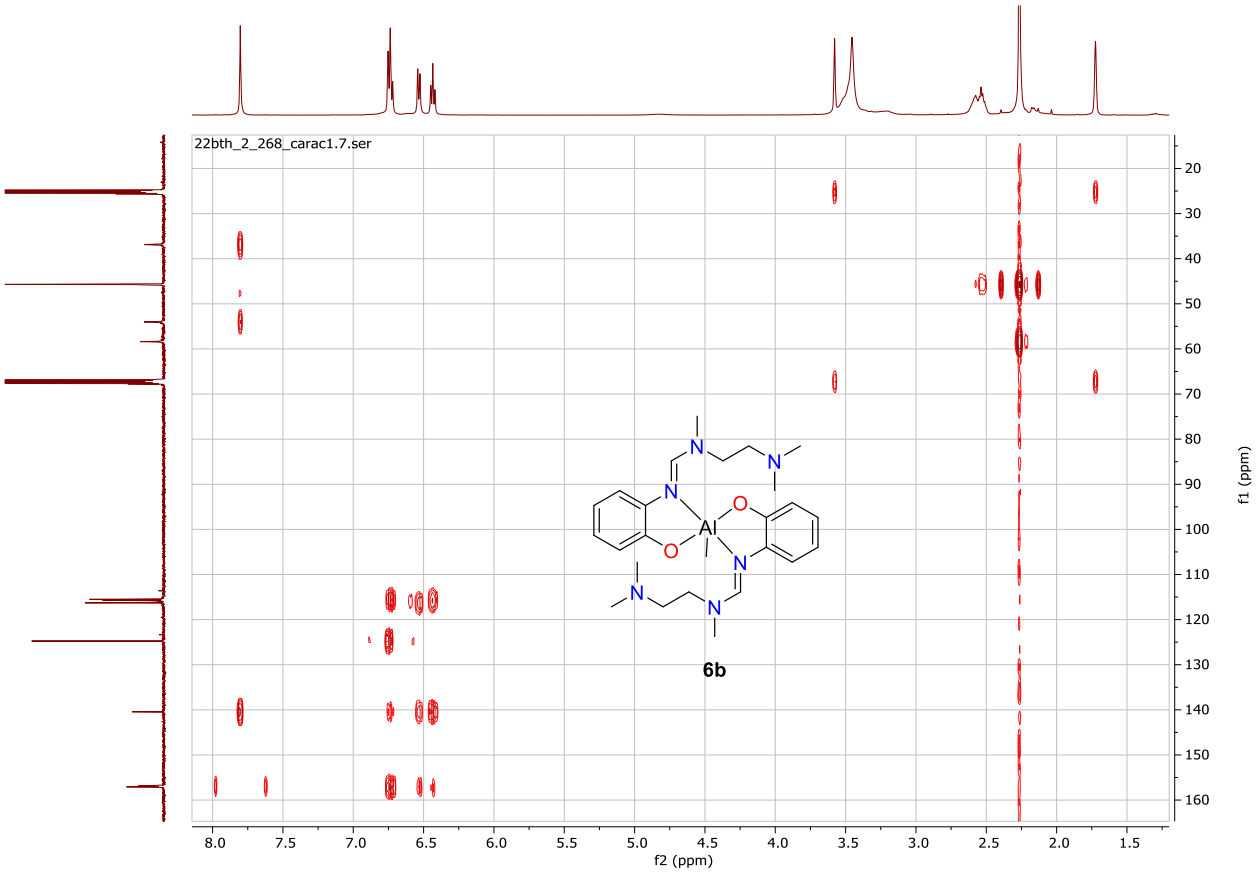


*Figure S63 ^{1}H ^{13}C HMBC (500 MHz / 125 MHz, THF-d8, 298 K) of **6b.***

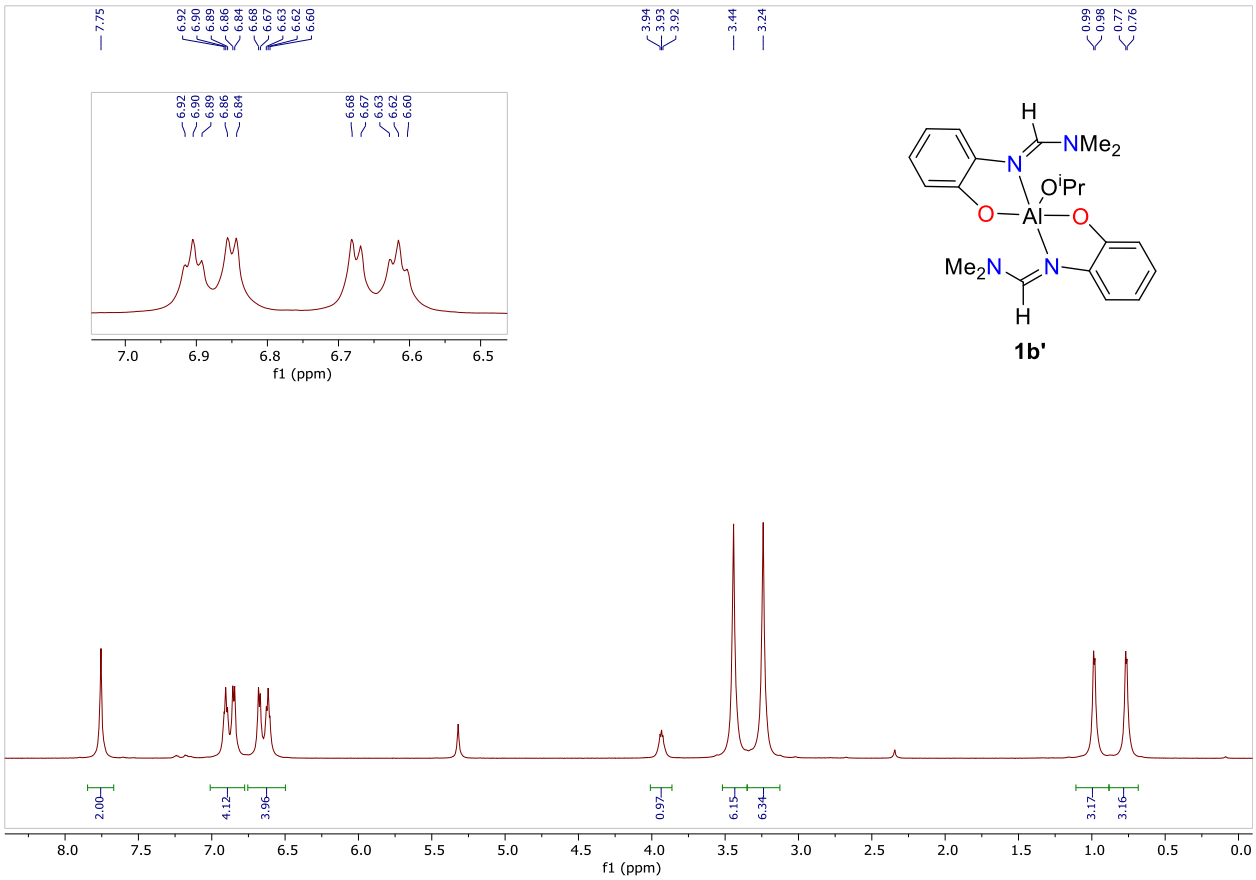


*Figure S64 ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) of **1b'**.*

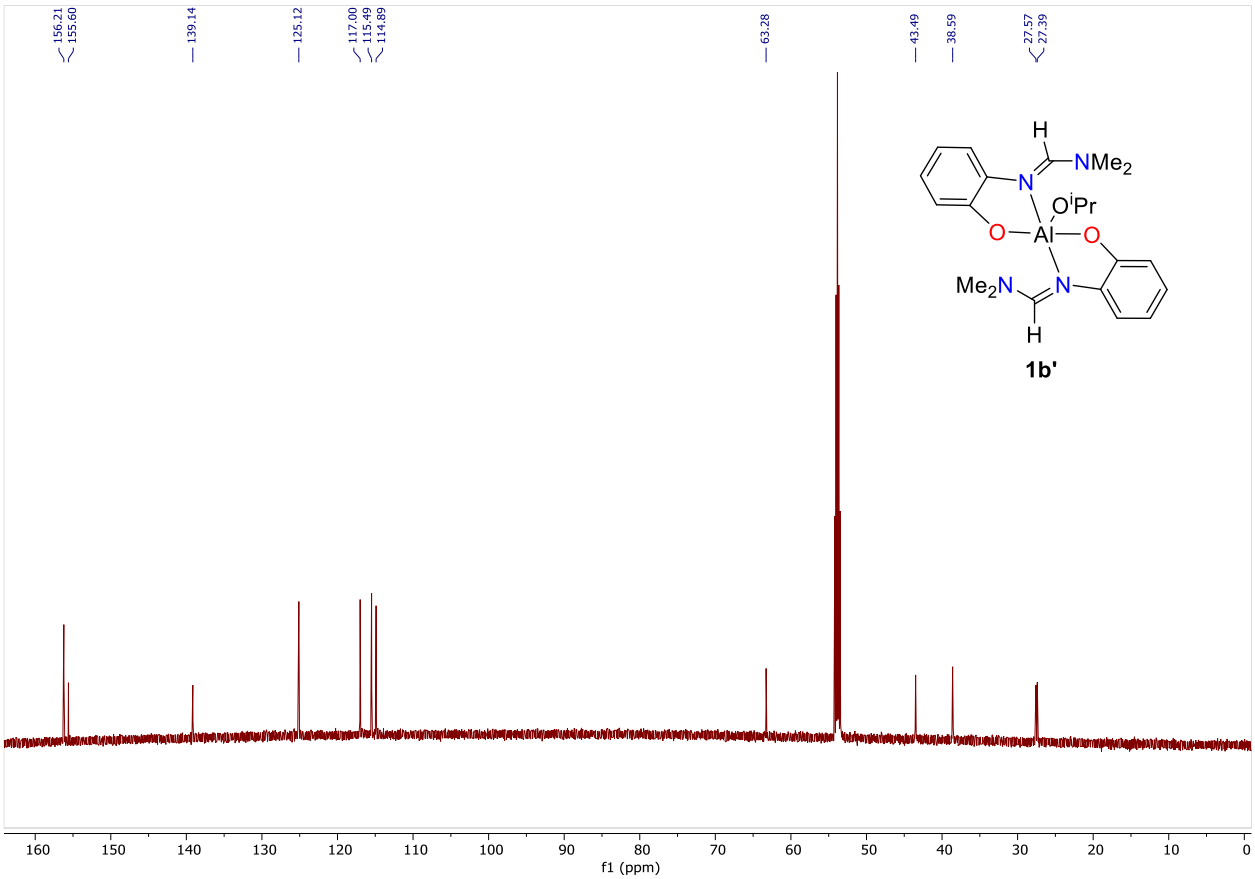


*Figure S65 {^{1}H}^{13}C NMR (151 MHz, CD_2Cl_2, 298 K) of **1b'**.*

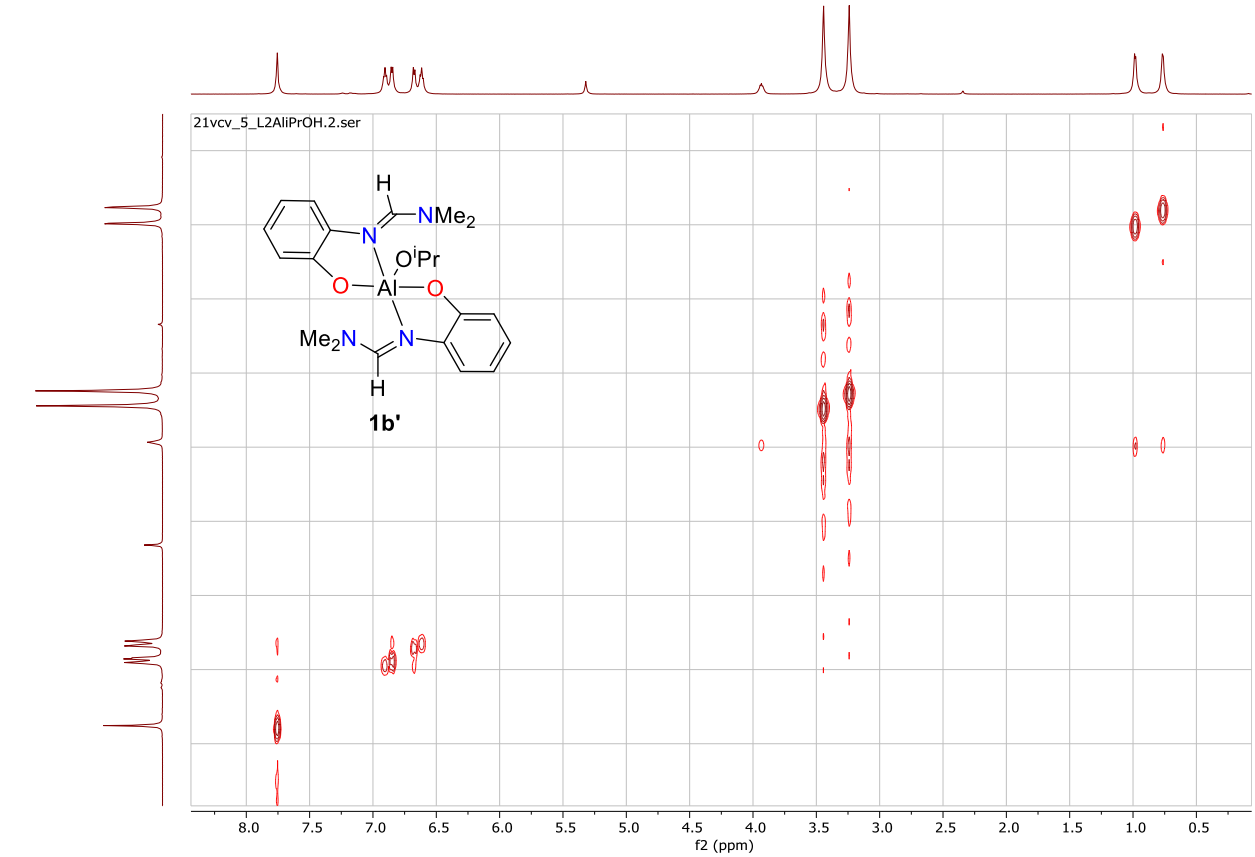


*Figure S66 ^{1}H ^{1}H COSY (600 MHz, CD_2Cl_2, 298 K) of **1b'**.*

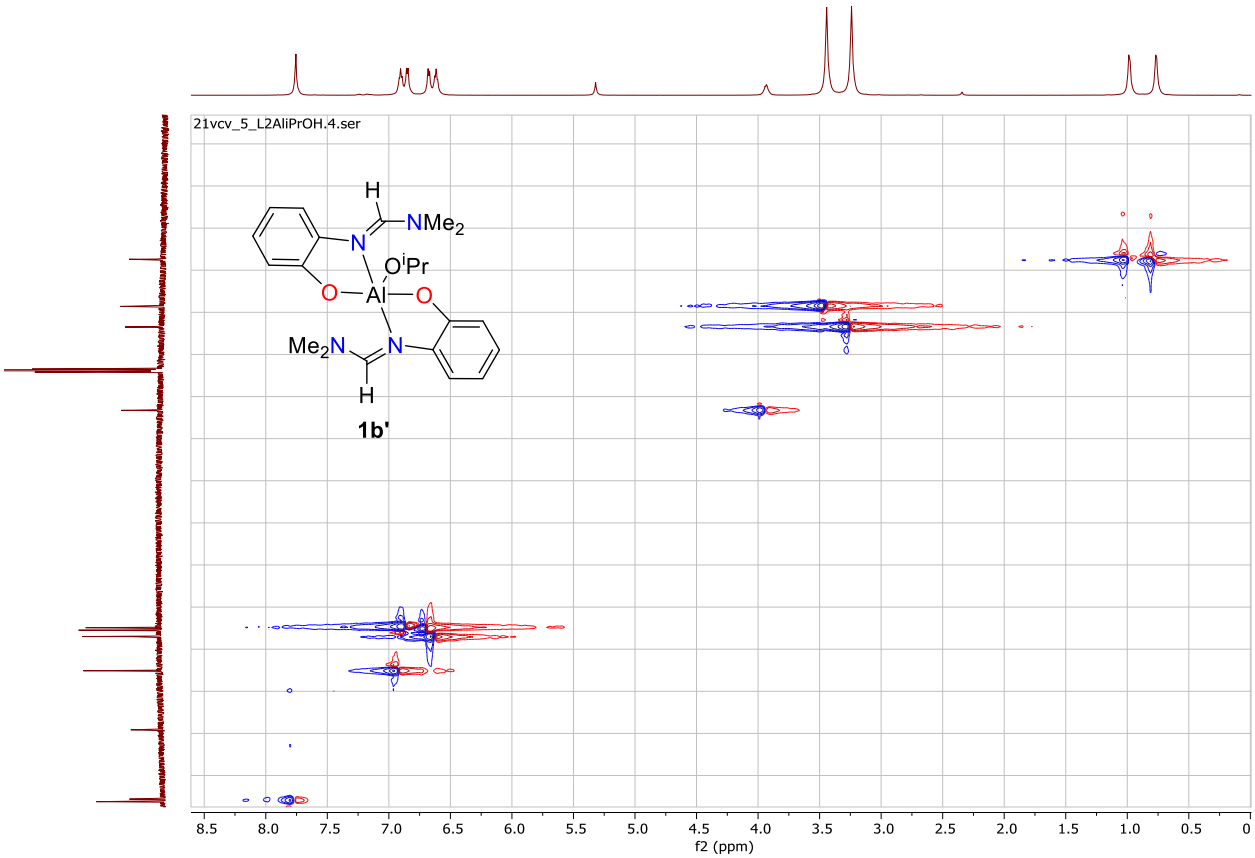


*Figure S67 ^{1}H ^{13}C HSQC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of **1b'**.*

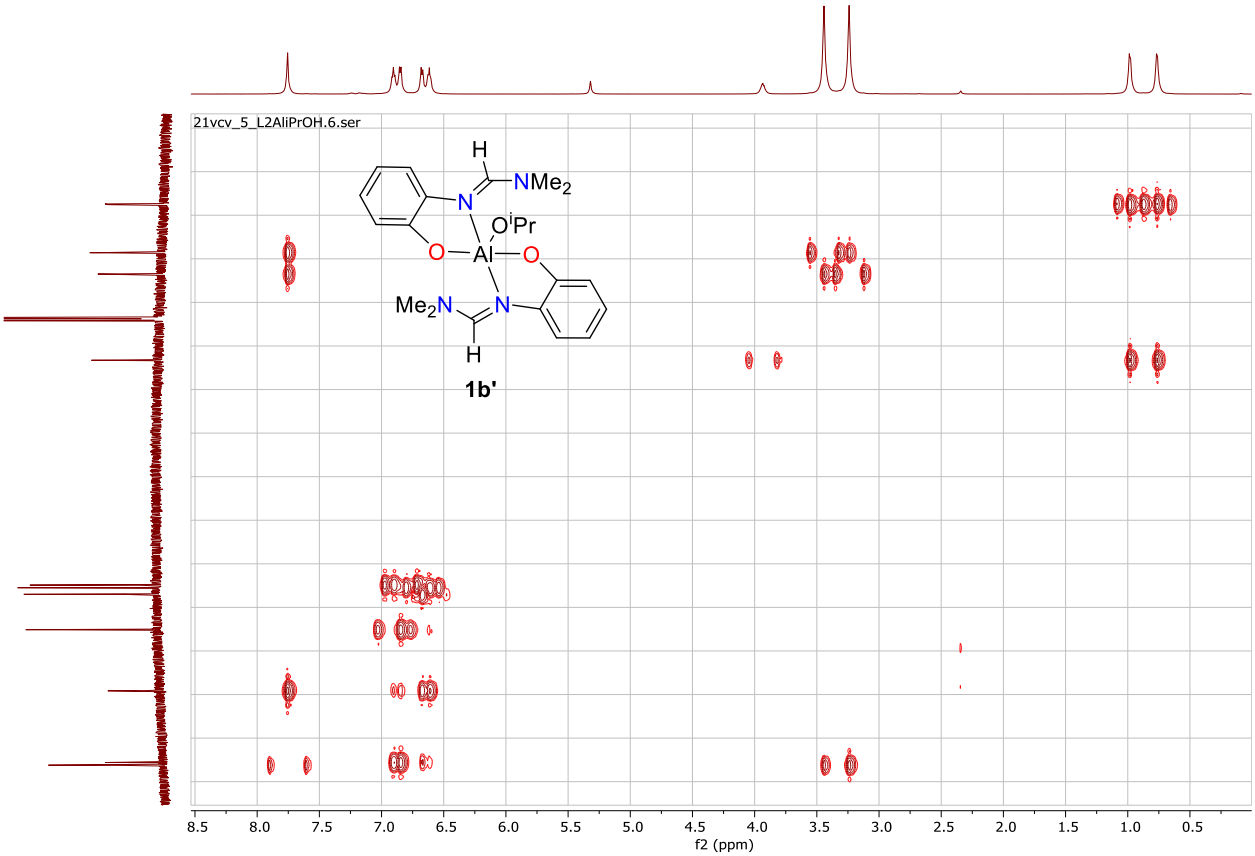


*Figure S68 ^{1}H ^{13}C HMBC (600 MHz / 151 MHz, CD_2Cl_2, 298 K) of **1b'**.*

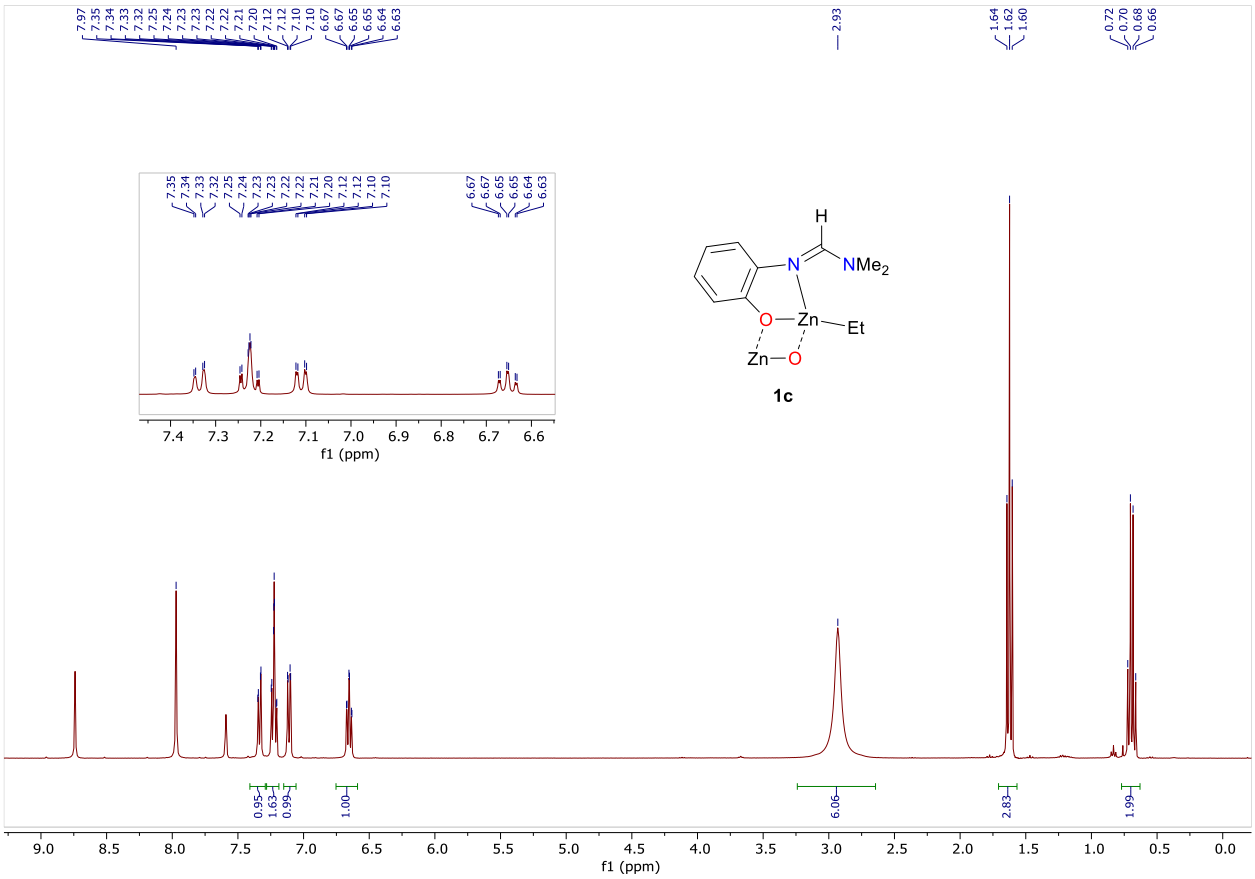


*Figure S69 ^{1}H NMR (400 MHz, C_5D_5N, 298 K) of **1c**.*

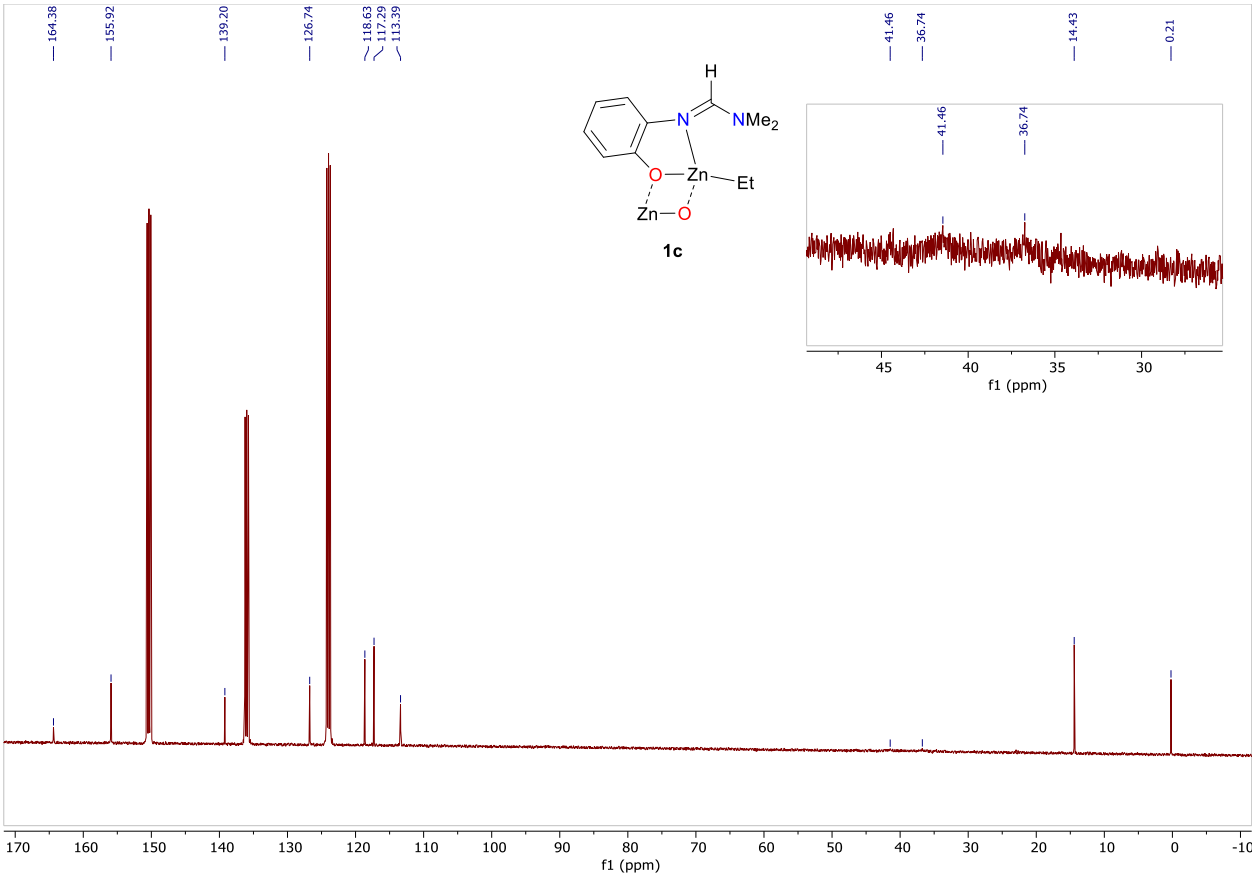


*Figure S70 {^{1}H}^{13}C NMR (101 MHz, C_5D_5N, 298 K) of **1c**.*

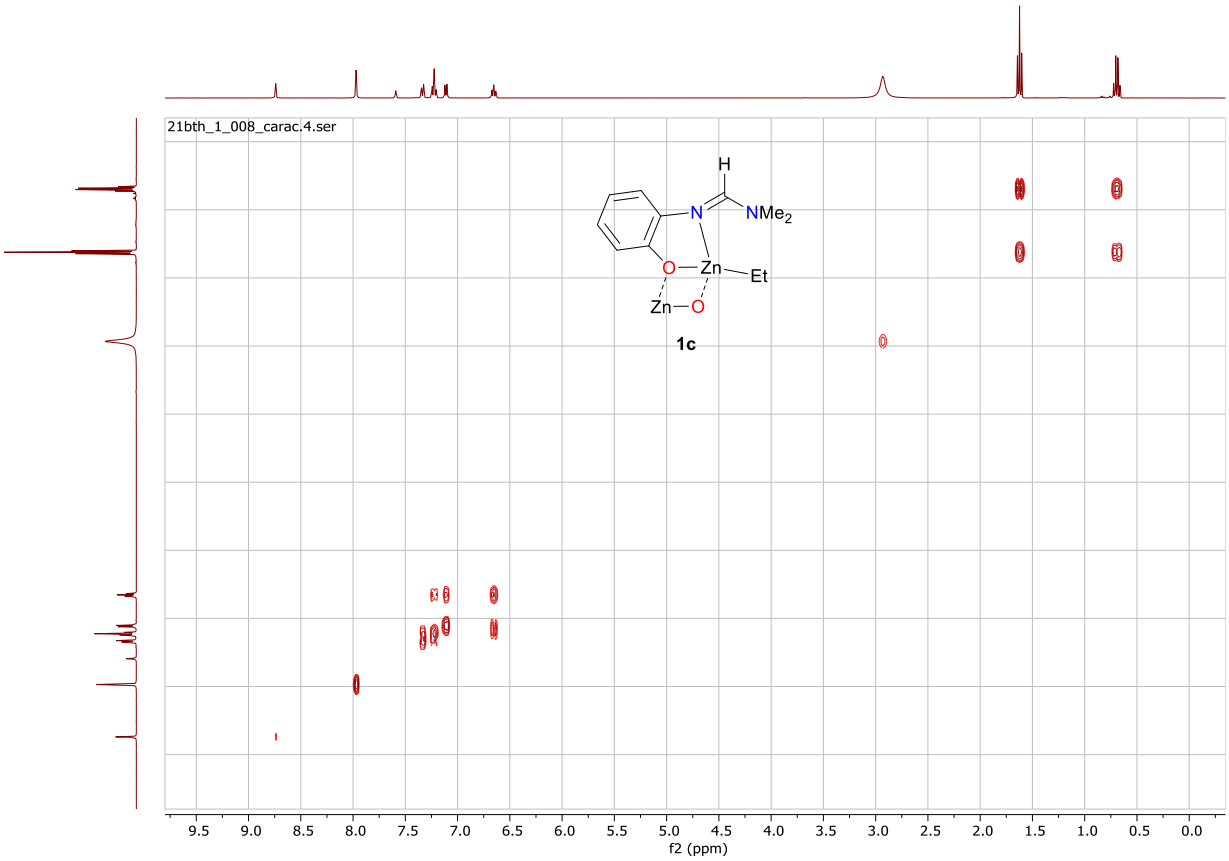


*Figure S71 ^{1}H ^{1}H COSY (400 MHz, C_5D_5N) of **1c**.*

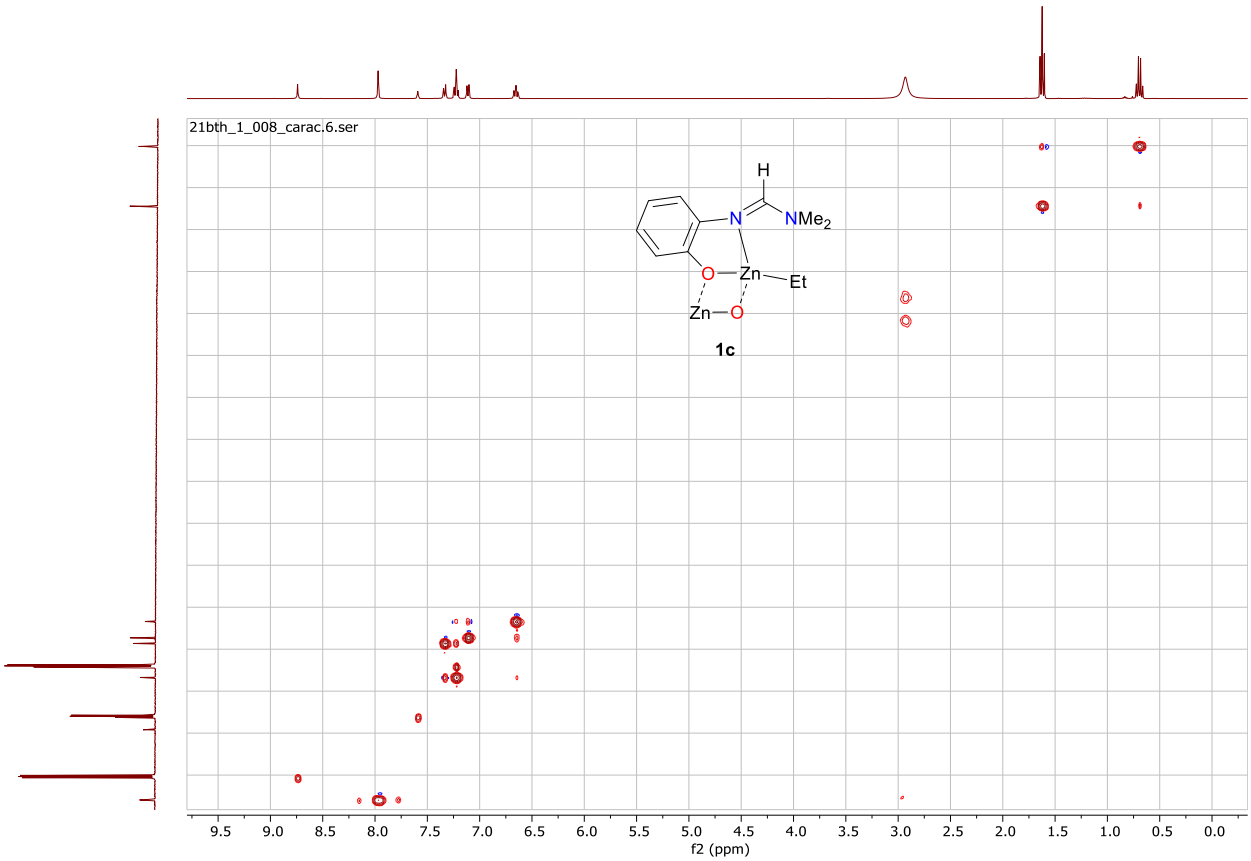


*Figure S72 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **1c**.*

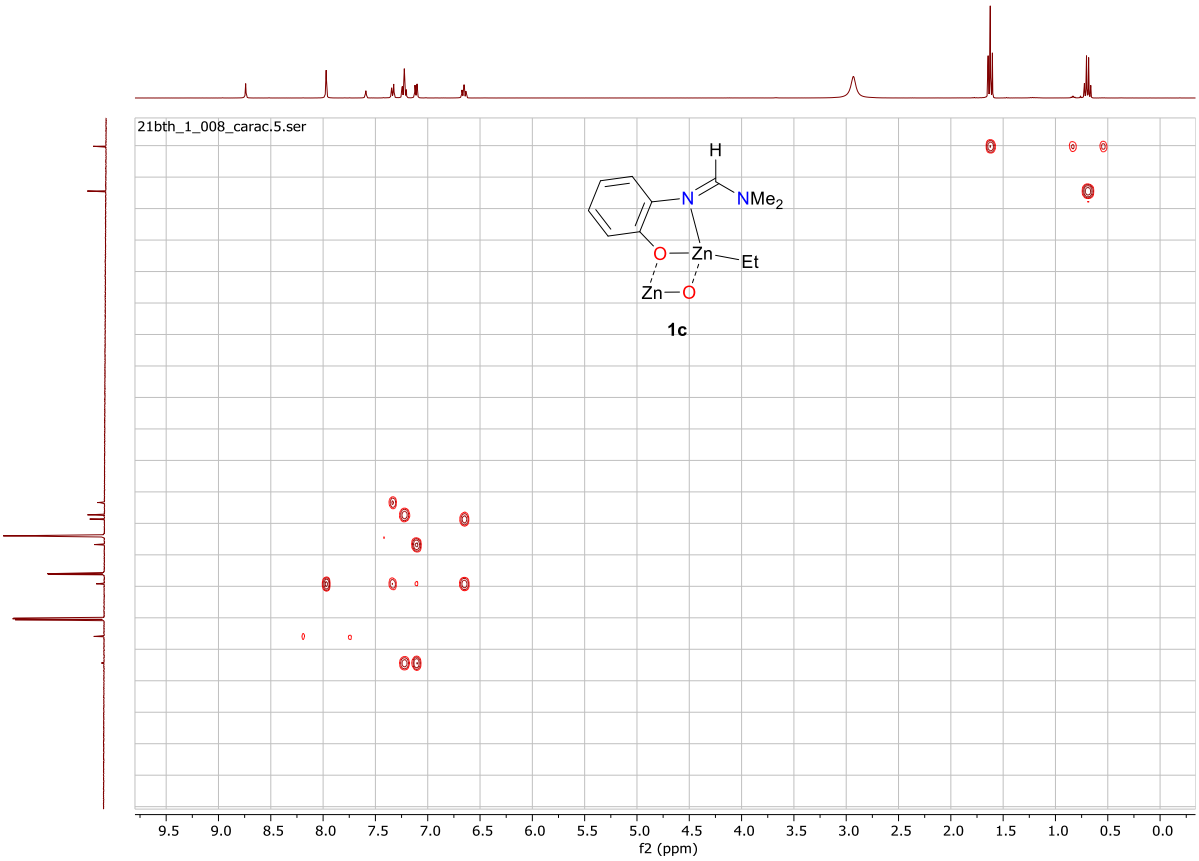


*Figure S73 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **1c**.*

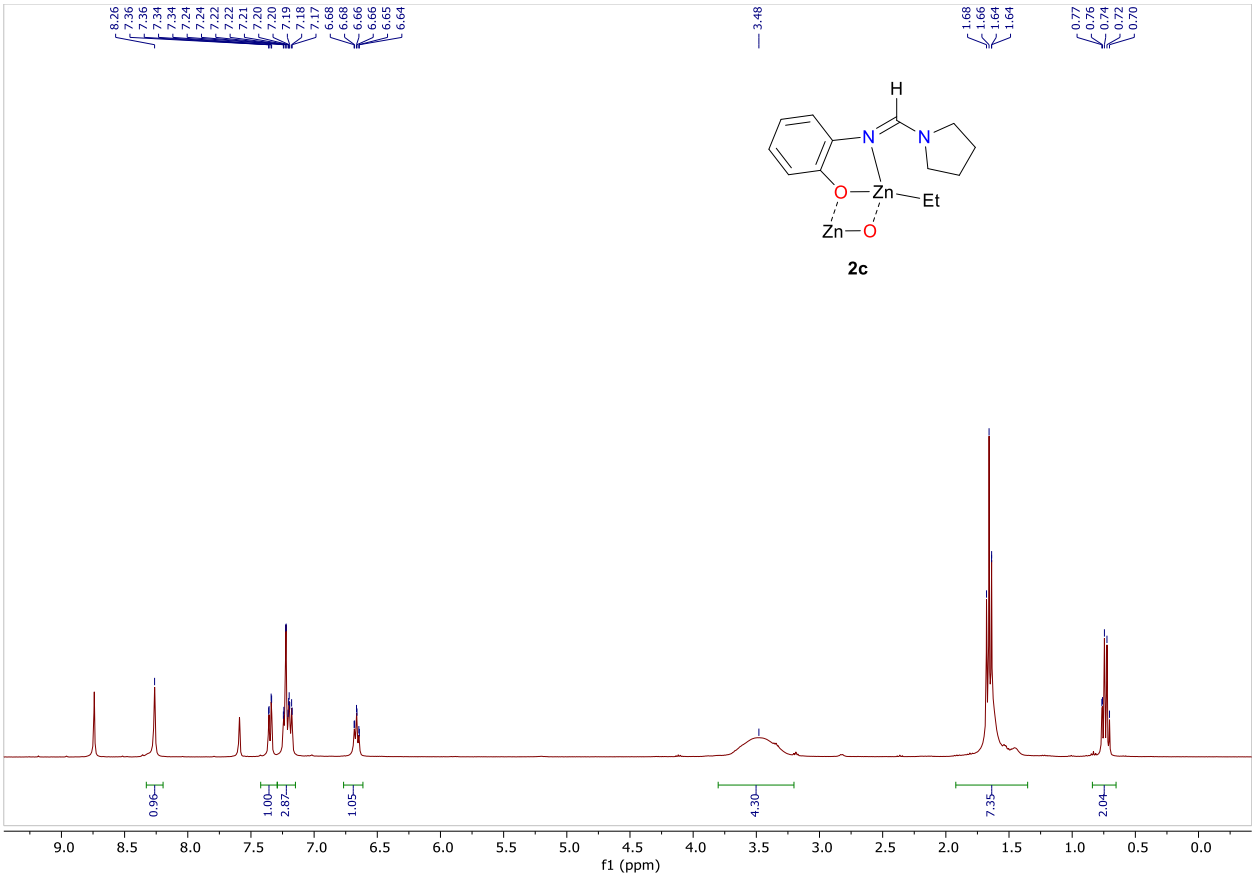


*Figure S74 ^{1}H NMR (400 MHz, C_5D_5N, 298 K) of **2c**.*

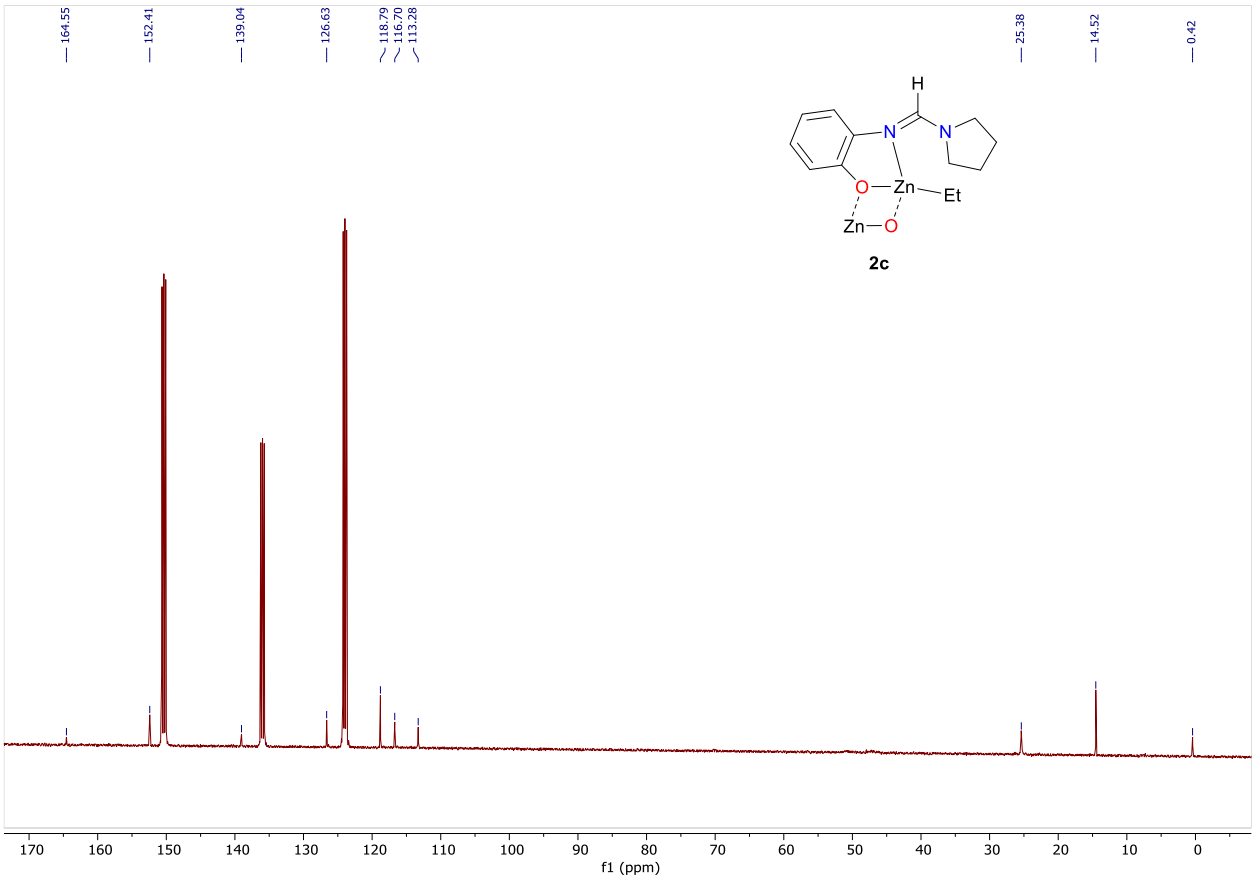


*Figure S75 {^{1}H}^{13}C NMR (101 MHz, C_5D_5N, 298 K) of **2c**.*

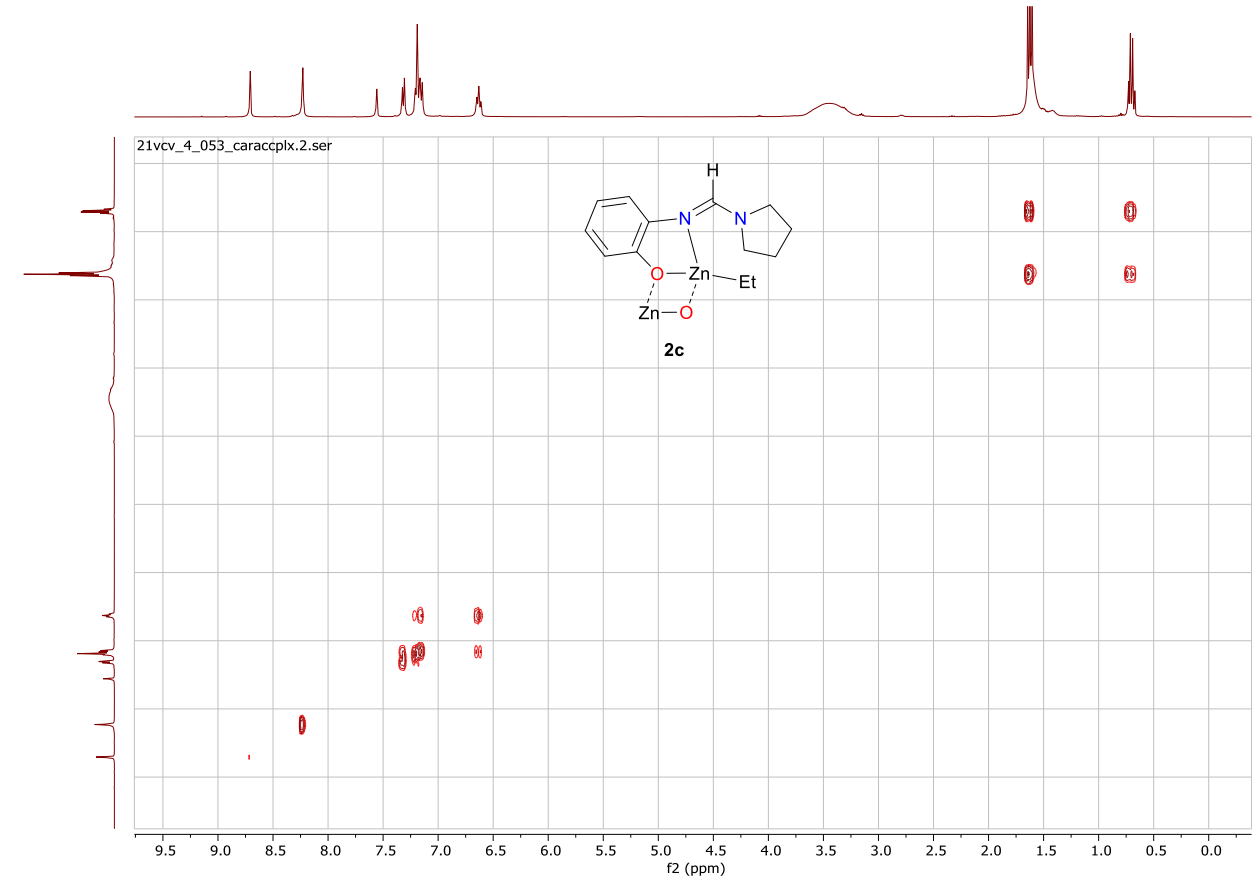


*Figure S76 ^{1}H ^{1}H COSY (400 MHz, C_5D_5N) of **2c**.*

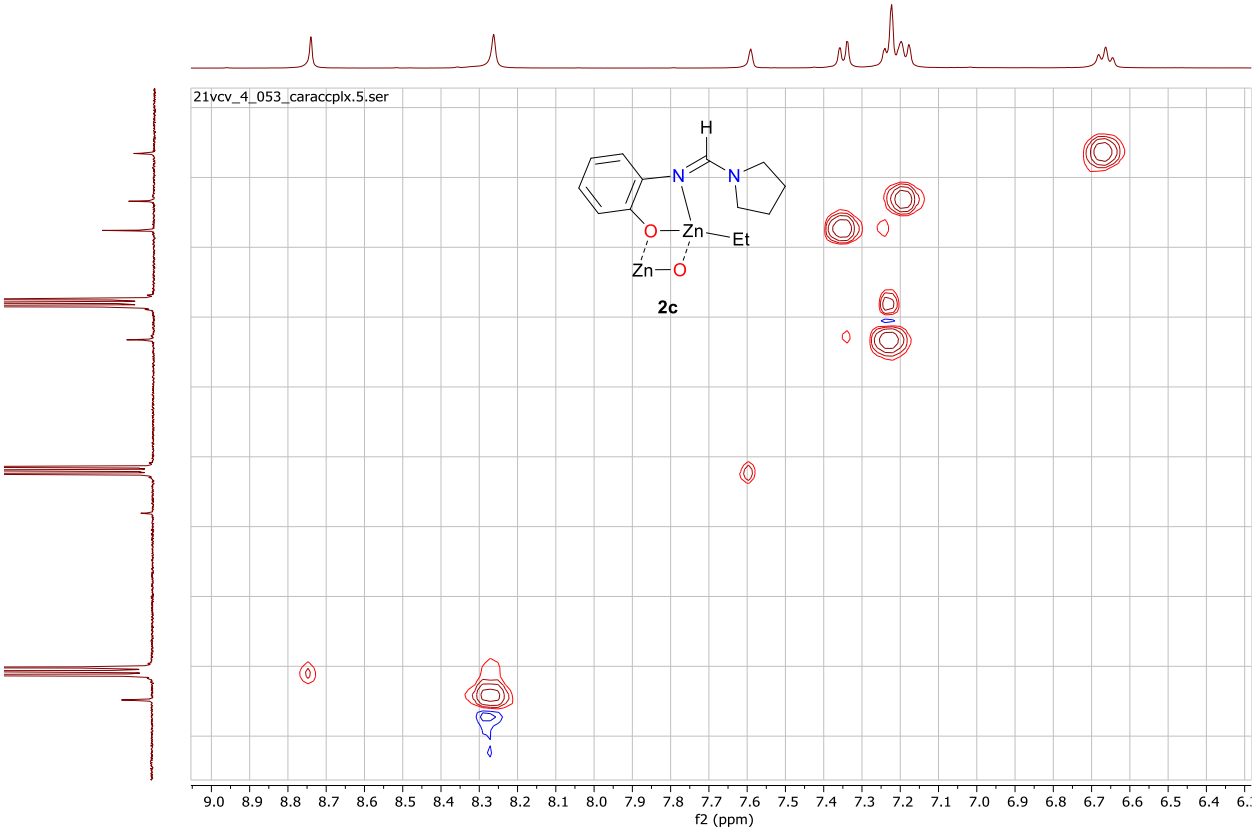


*Figure S77 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **2c**.*

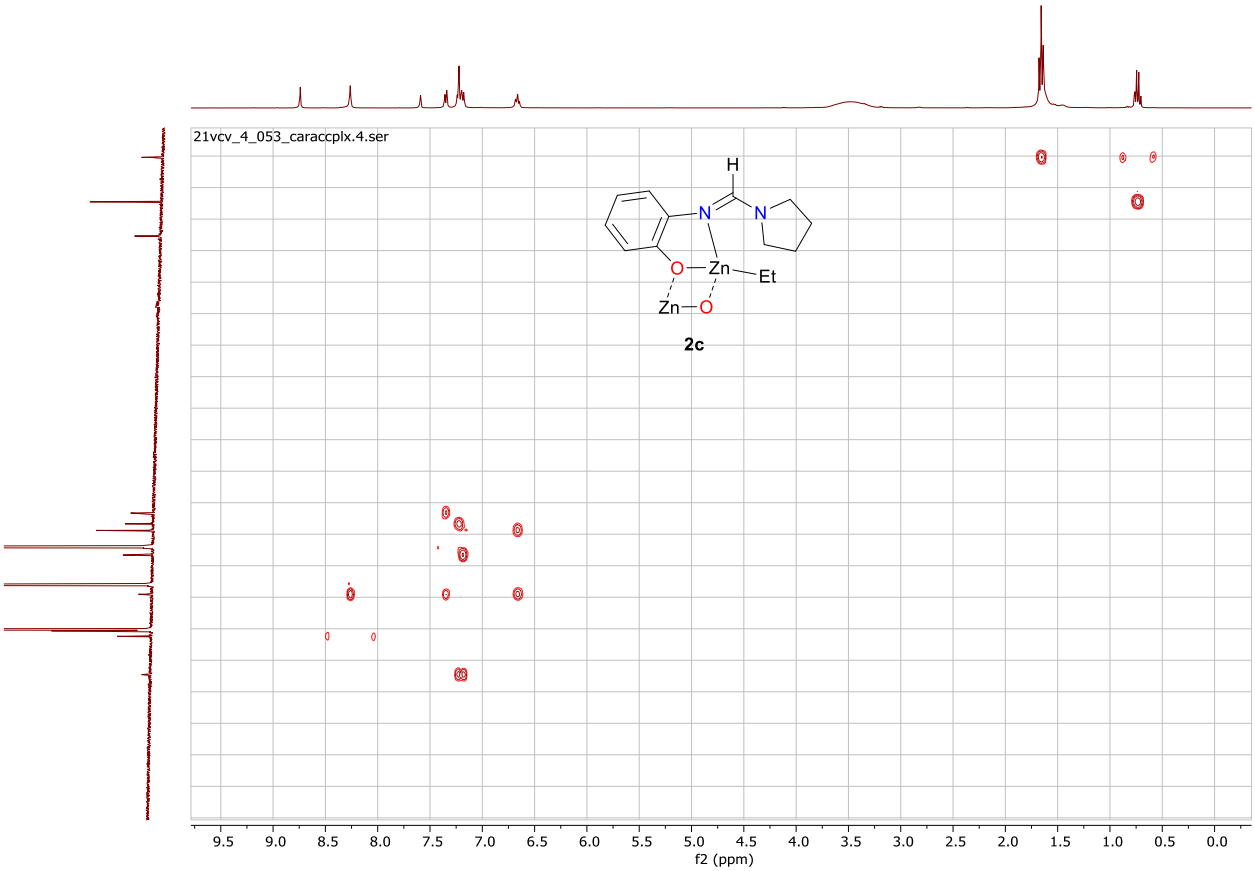


*Figure S 78 ^{1}H ^{13}C HMBC (400 MHz / 101 MHz, C_5D_5N, 298 K) of **2c**.*

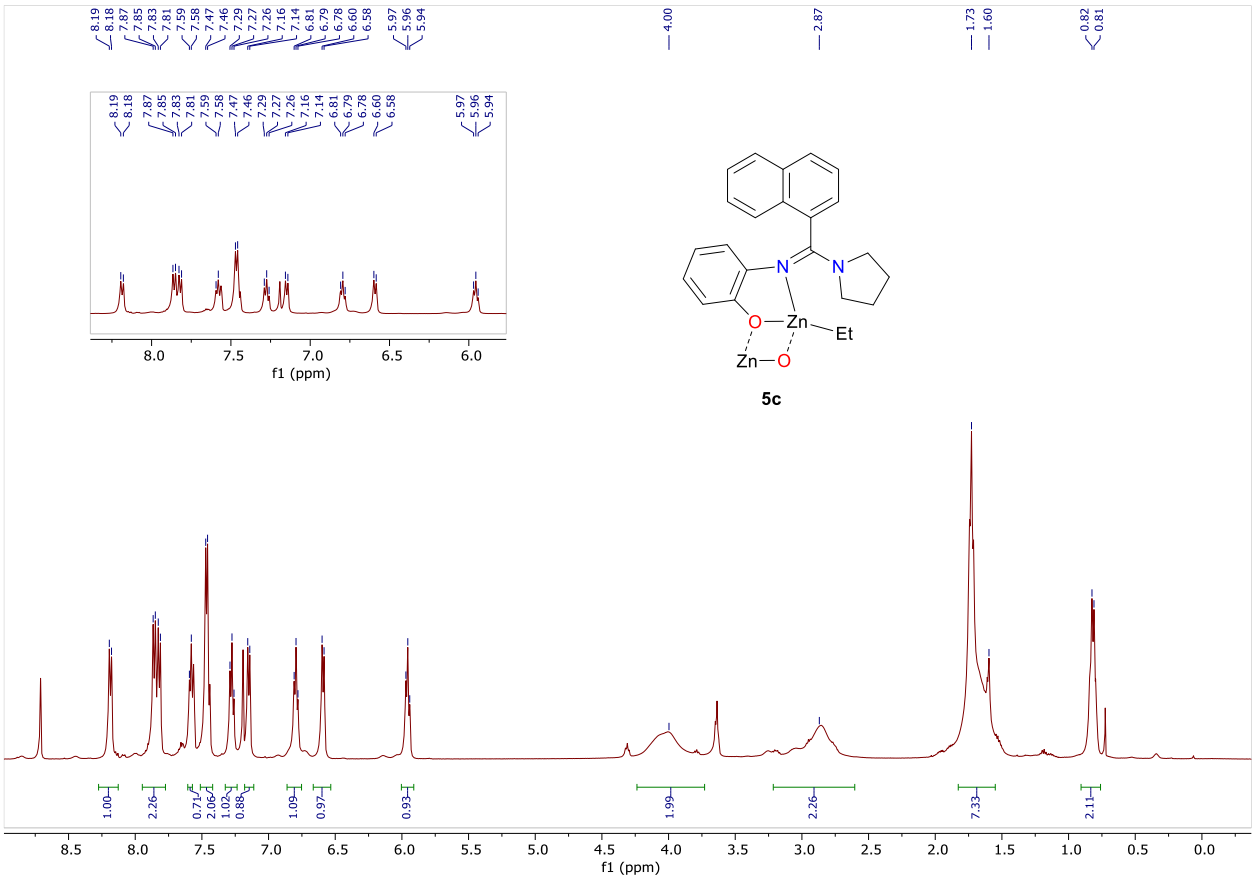


*Figure S79 ^{1}H NMR (500 MHz, C_5D_5N, 298 K) of **5c**.*

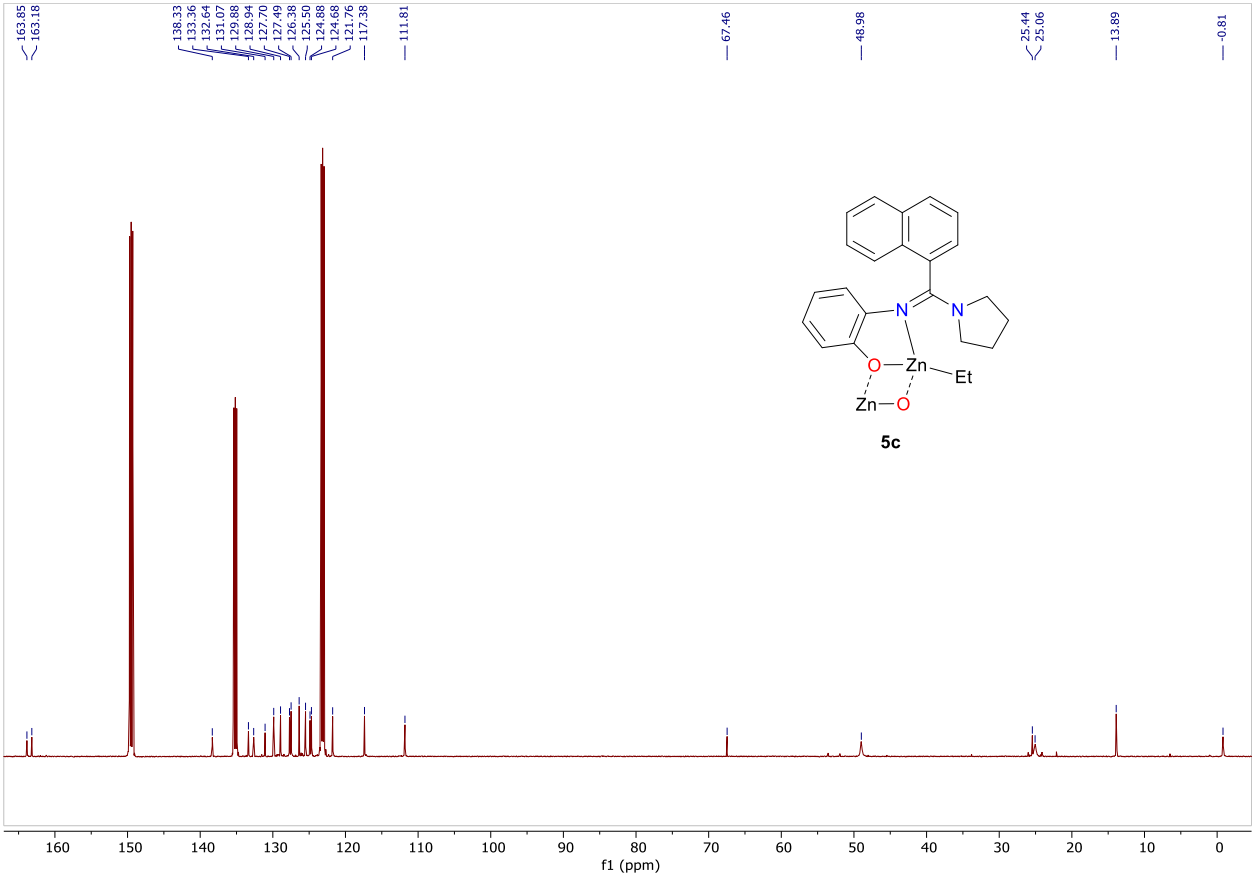


*Figure S80 $\{^{1}H\}^{13}C$ NMR (125 MHz, C_5D_5N, 298 K) of **5c**.*

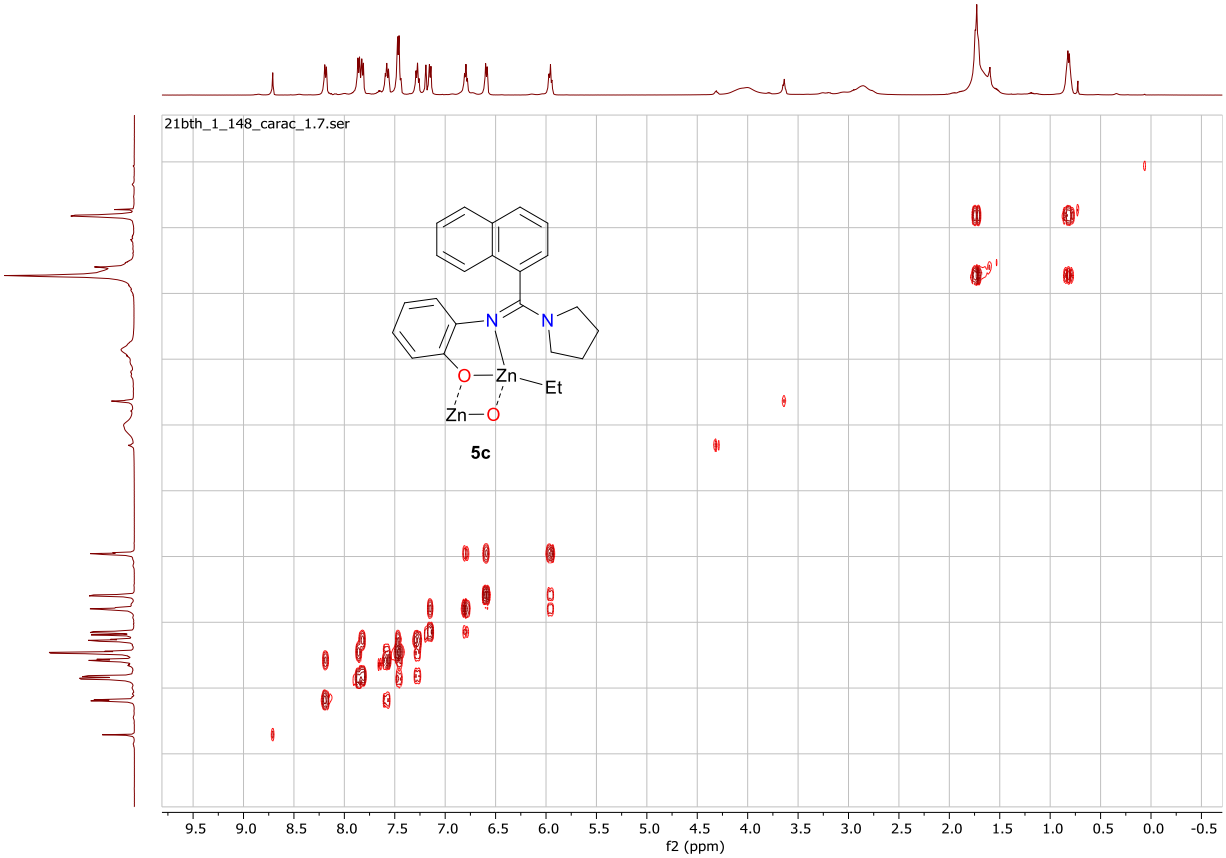


*Figure S81 ^{1}H ^{1}H COSY (500 MHz, C_5D_5N, 298 K) of **5c**.*

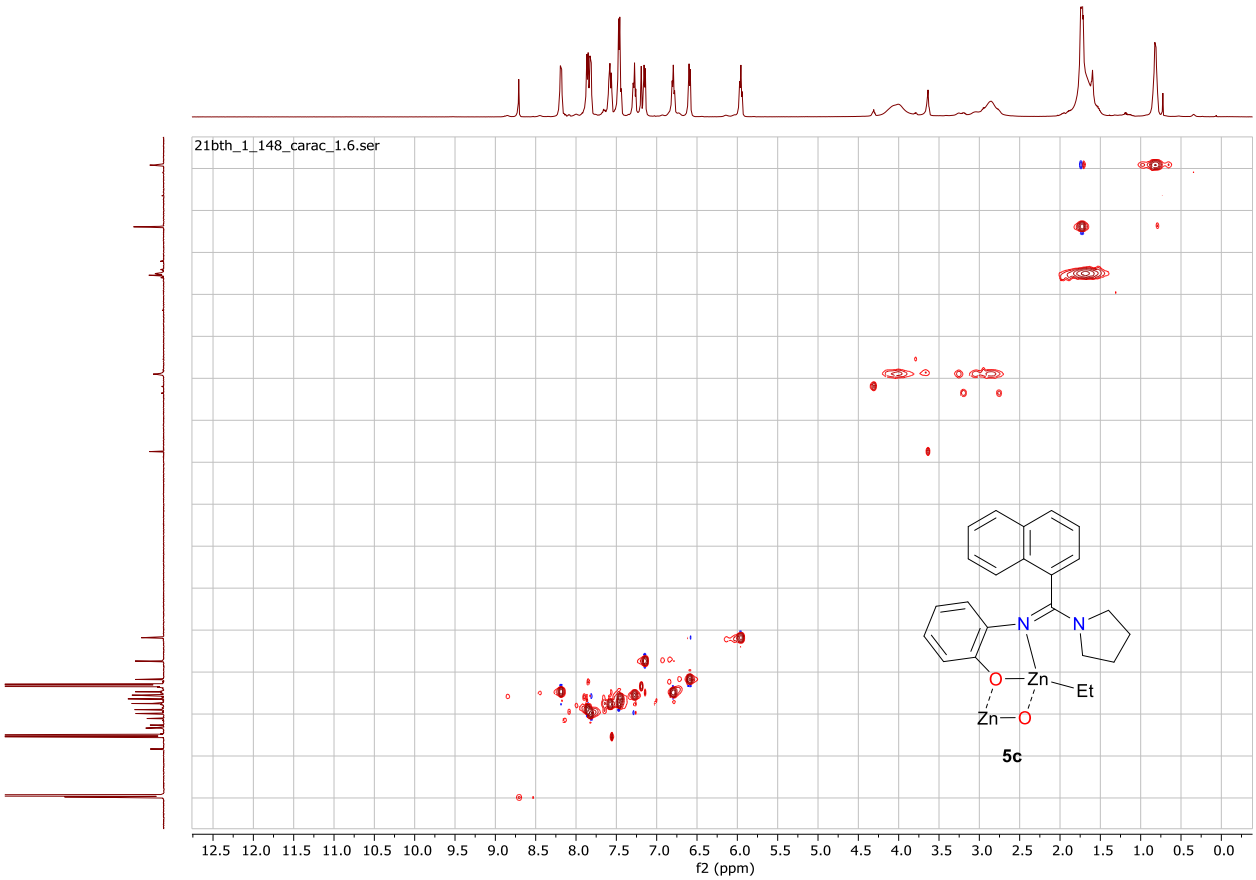


*Figure S82 ^{1}H ^{13}C HSQC (500 MHz / 125 MHz, C_5D_5N, 298 K) of **5c**.*

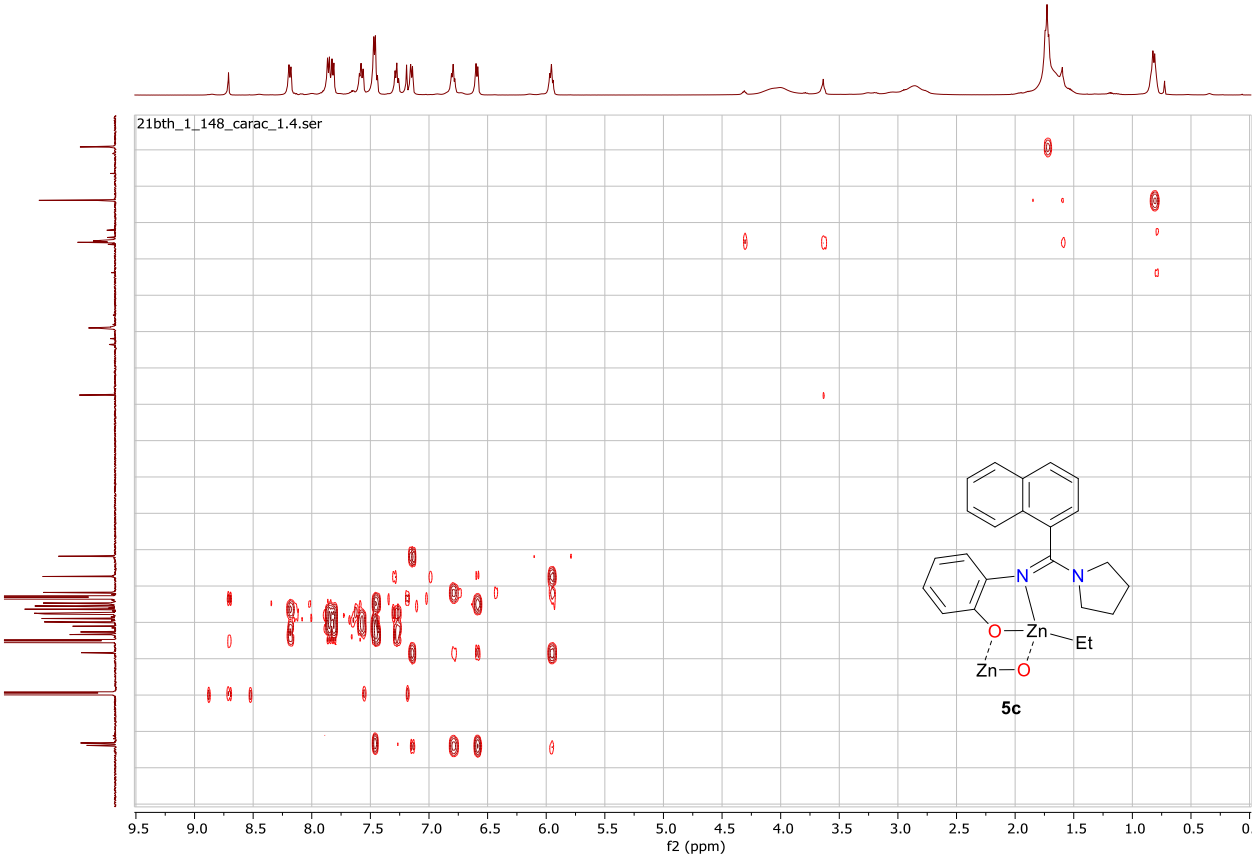


*Figure S83 ^{1}H ^{13}C HMBC (500 MHz / 125 MHz, C_5D_5N, 298 K) of **5c**.*

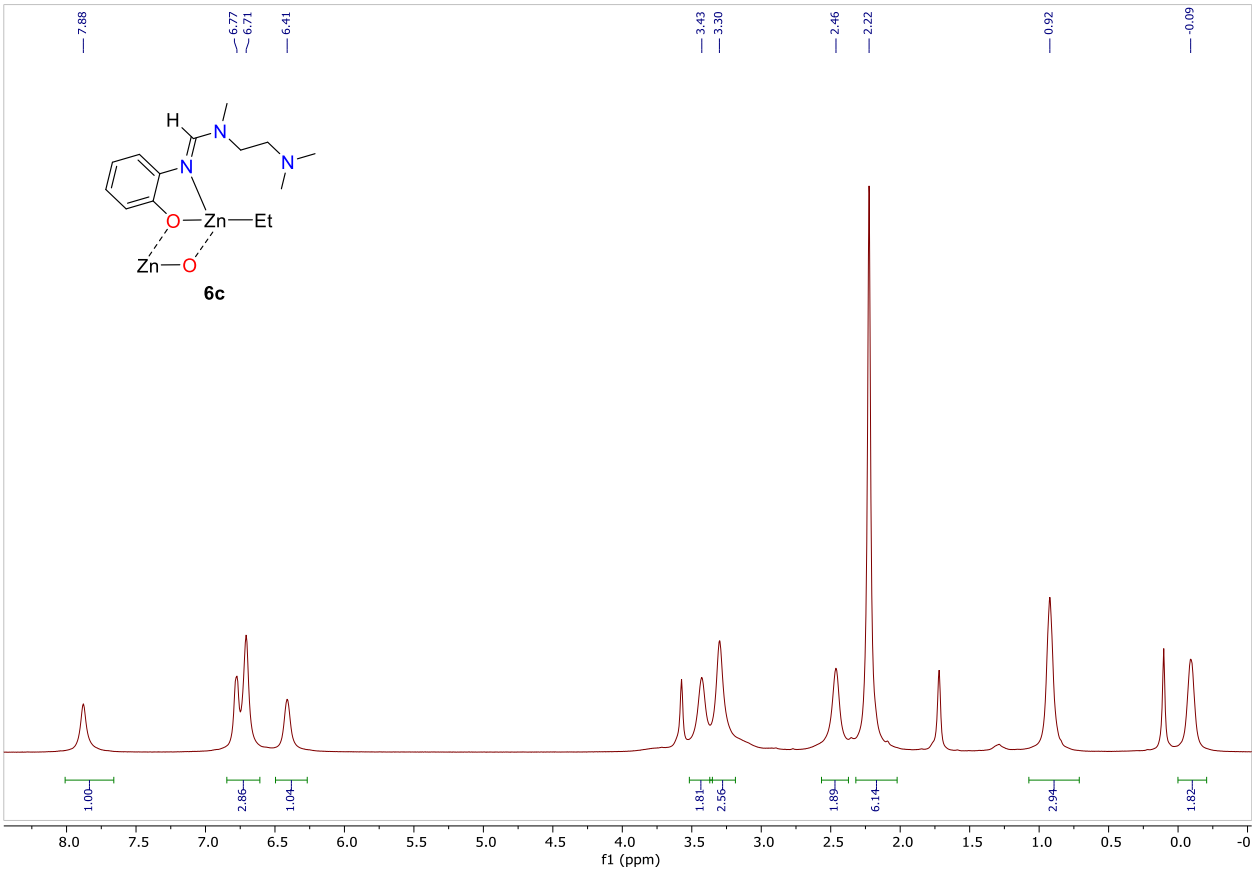


*Figure S84 ^{1}H (500 MHz, THF-d8, 298 K) of **6c**.*

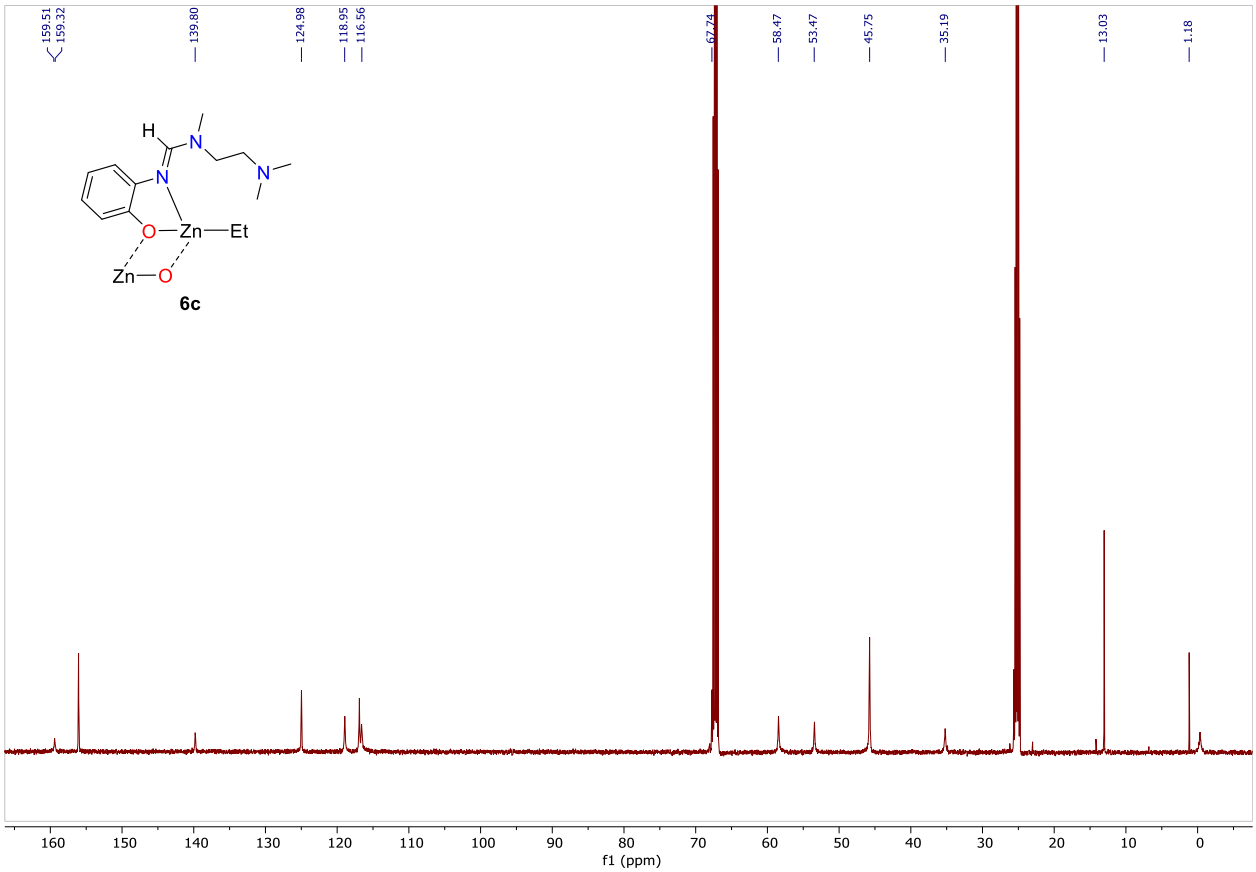


*Figure S85 ^{13}C (125 MHz, THF-d8, 298 K) of **6c**.*

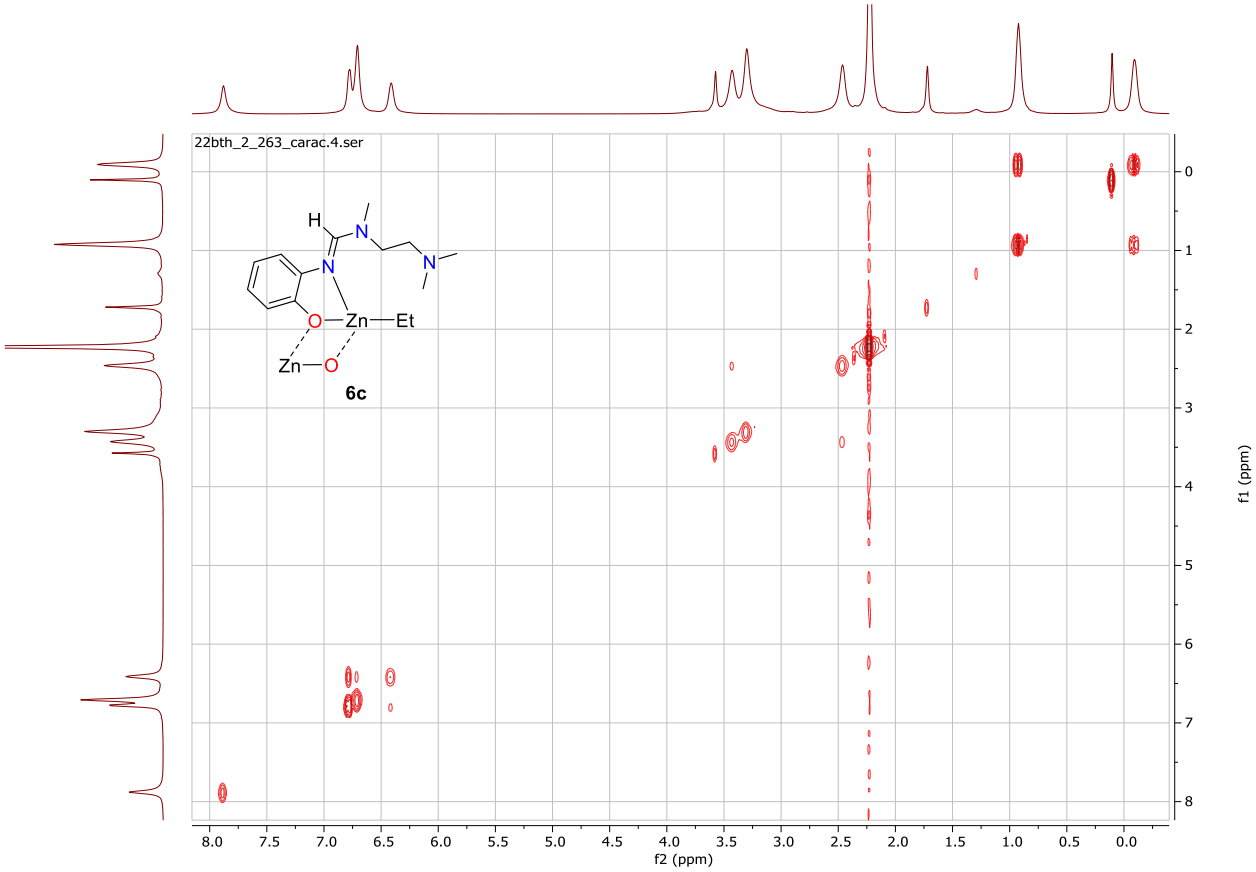


*Figure S86 ^{1}H ^{1}H HMBC (500 MHz / 500 MHz, THF-d8, 298 K) of **6c**.*

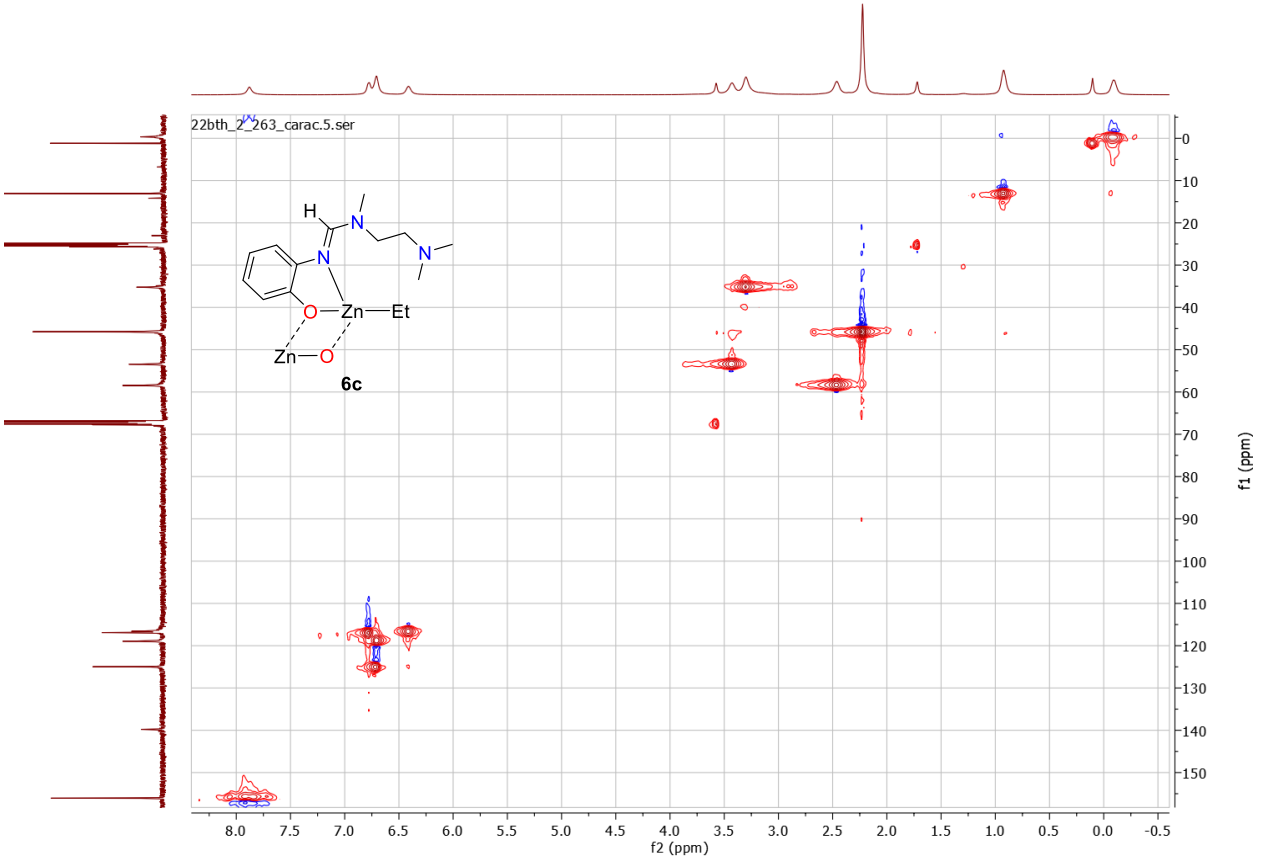


*Figure S87 ^{1}H ^{13}C HSQC (500 MHz / 125 MHz, THF-d8, 298 K) of **6c**.*

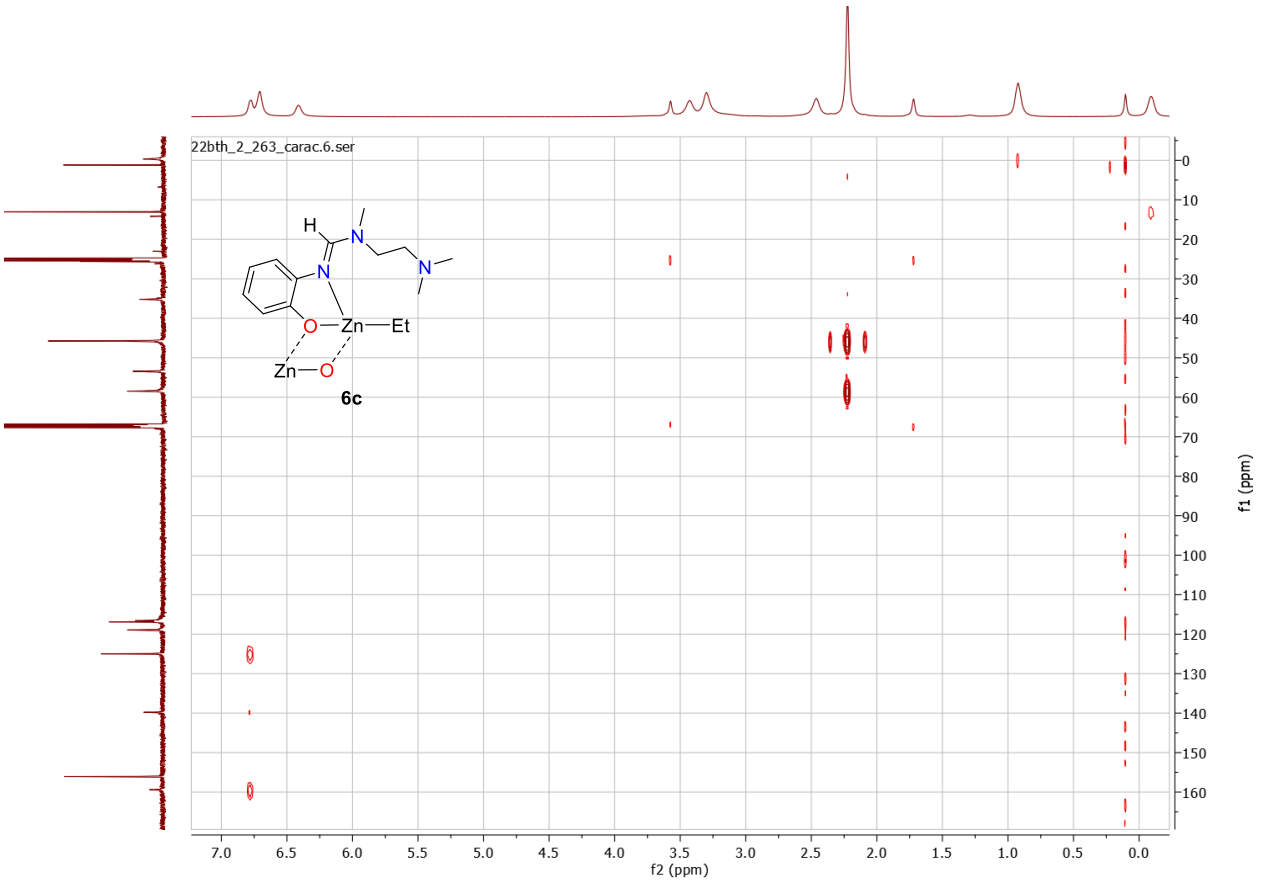


*Figure S88 ^{1}H ^{13}C HMBC (500 MHz / 125 MHz, THF-d8, 298 K) of **6c**.*

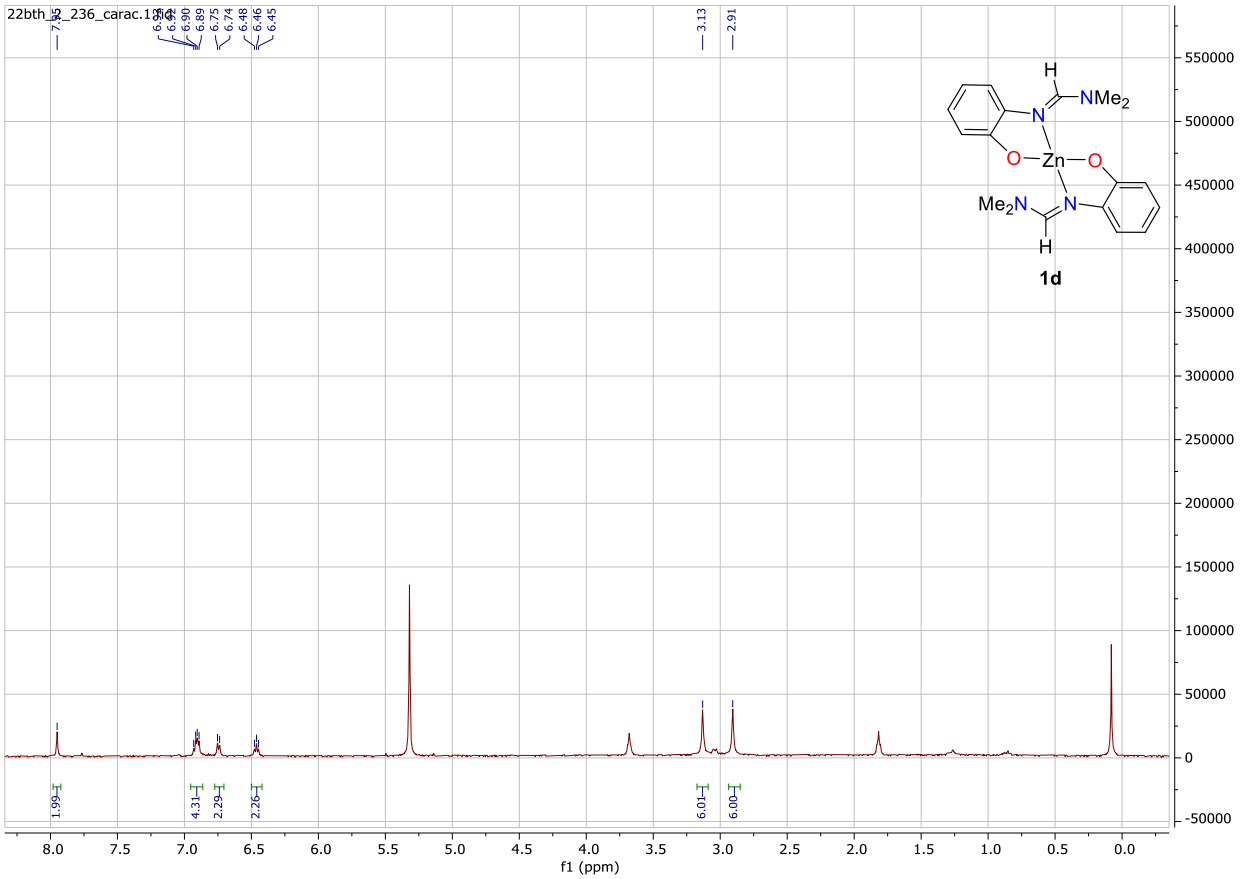


*Figure S89 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of **1d**.*

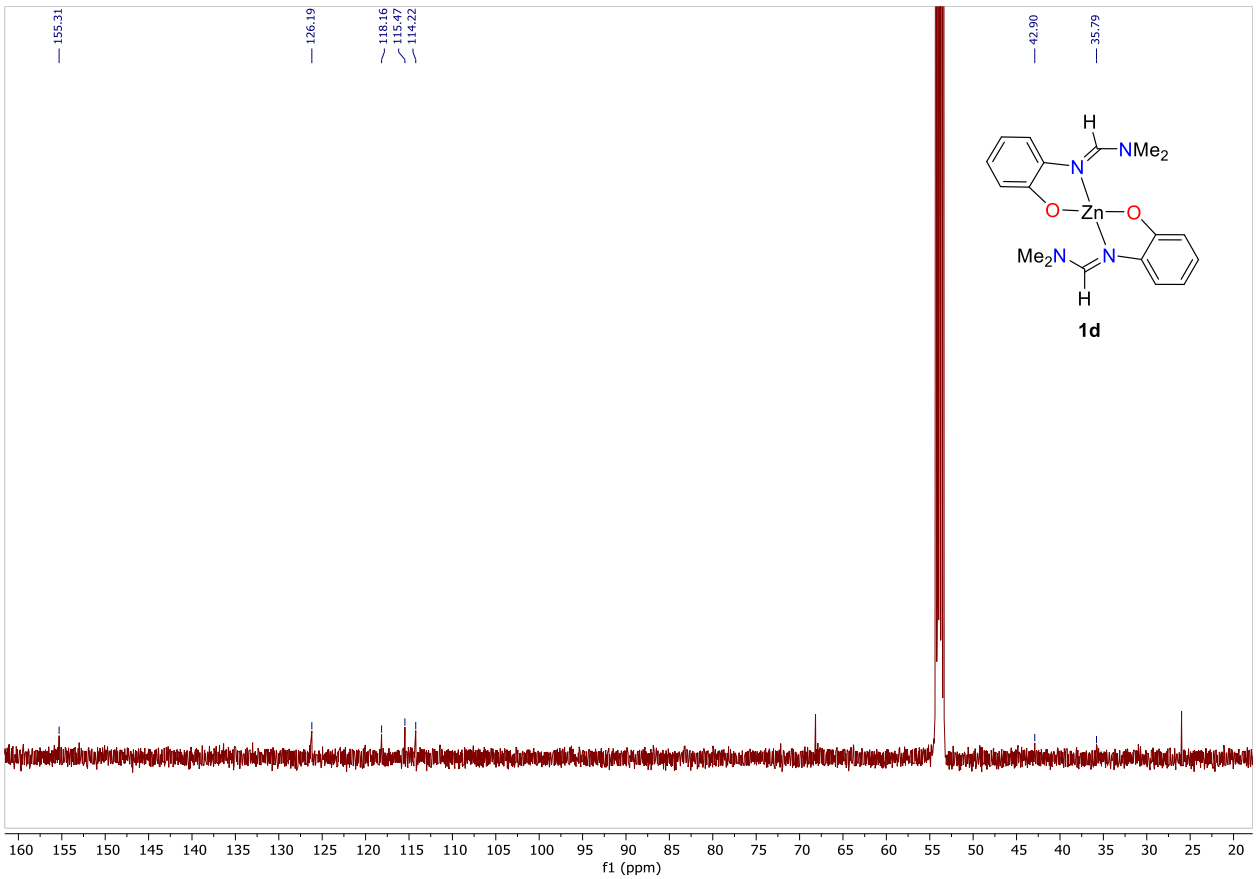


*Figure S90 $\{^{1}H\}^{13}C$ NMR (125 MHz, CD_2Cl_2, 298 K) of **1d**.*

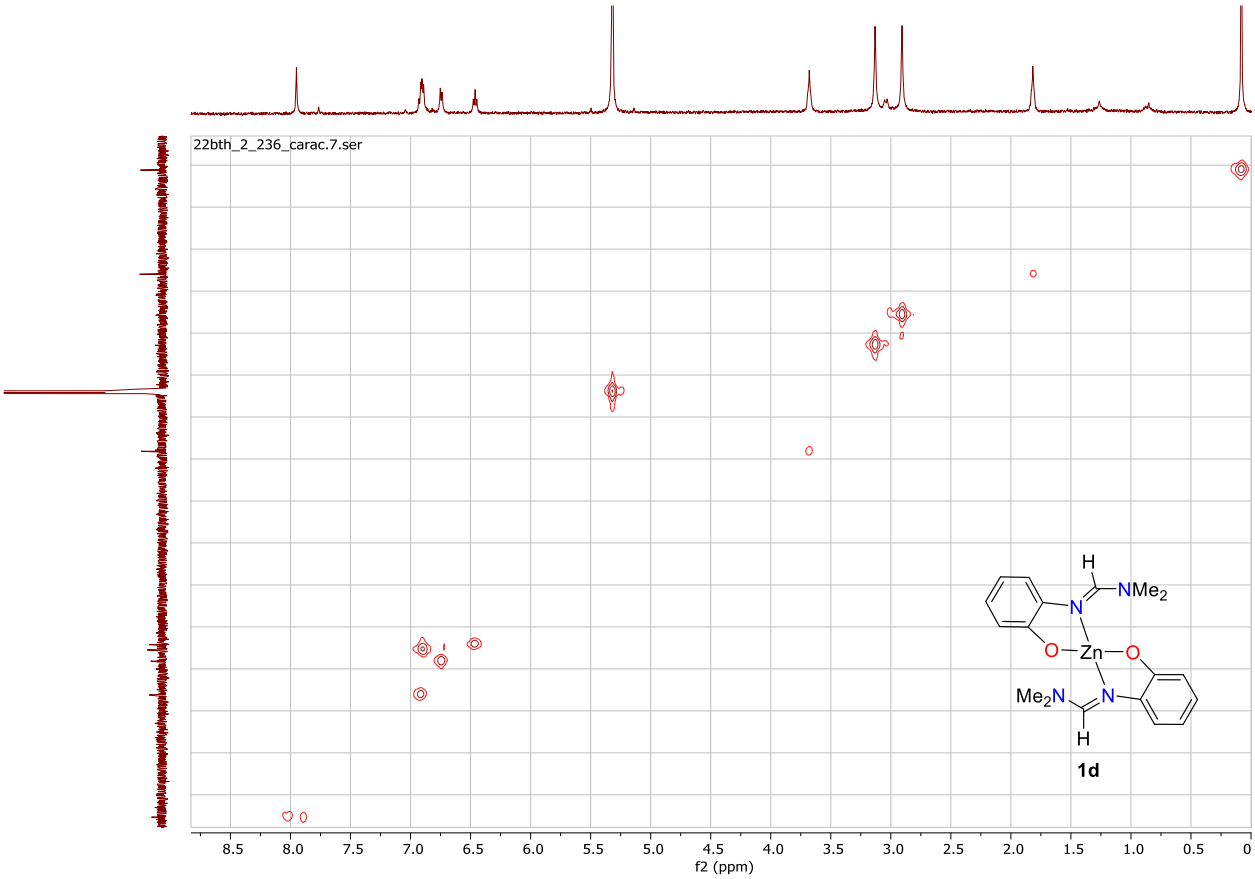


*Figure S91 ^{1}H ^{13}C HSQC (500 MHz / 125 MHz, CD_2Cl_2, 298 K) of **1d**.*

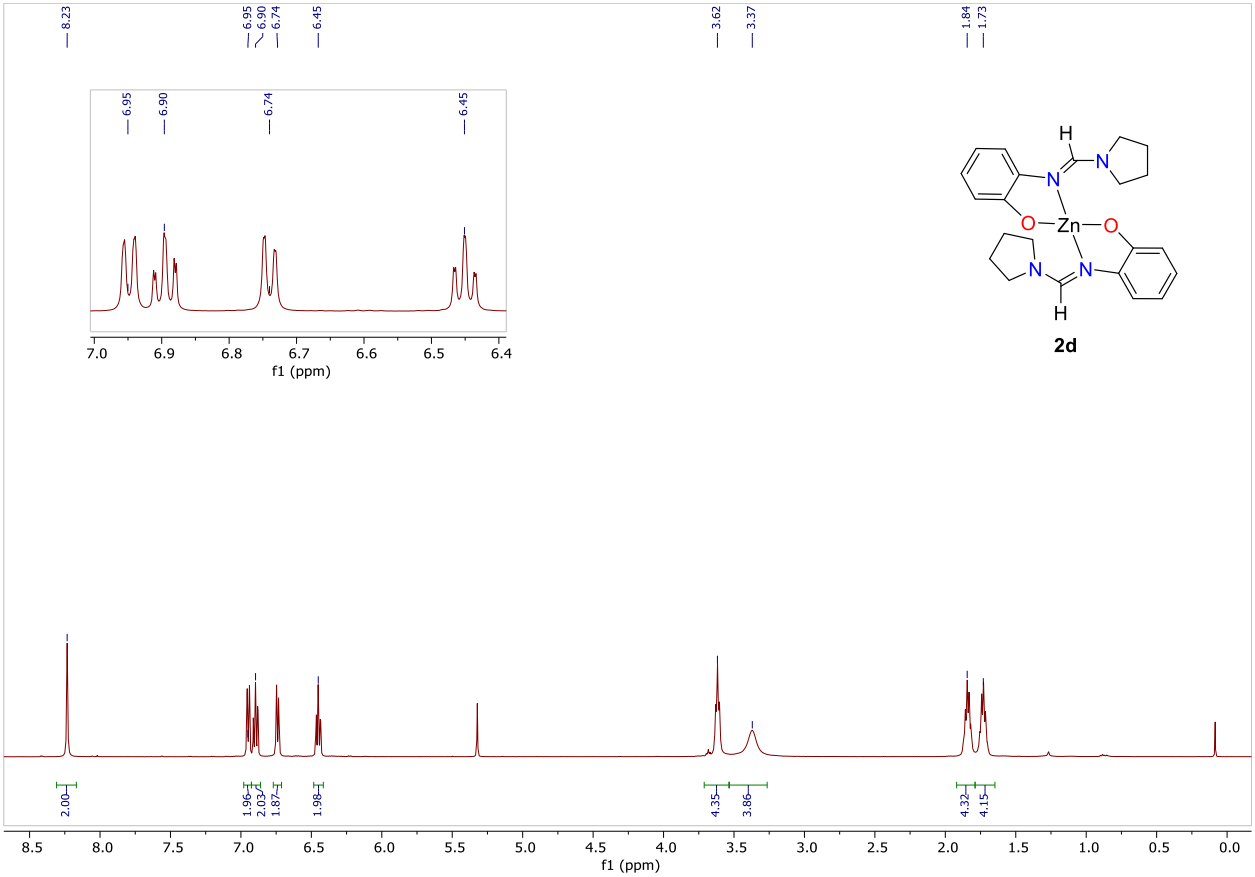


*Figure S92 ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of **2d**.*

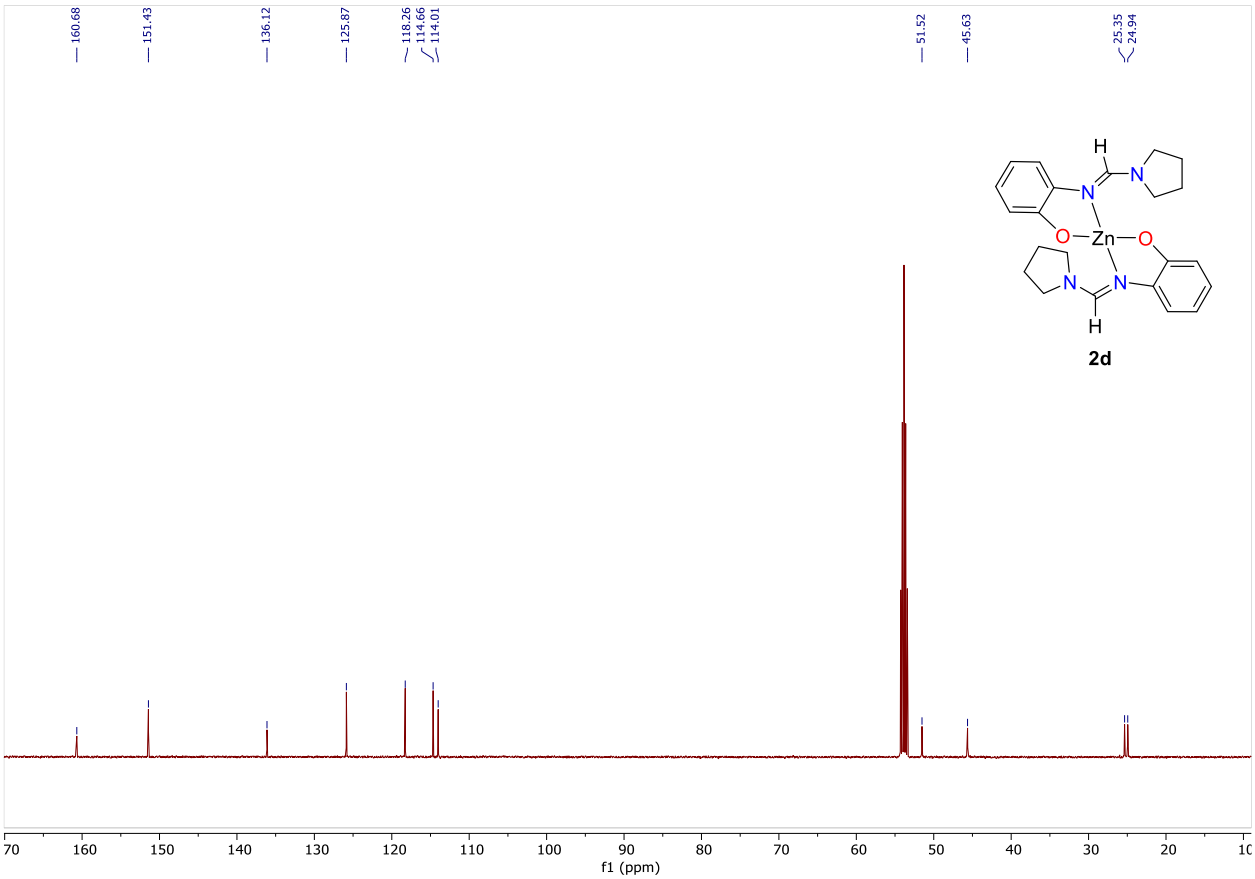


*Figure S93 {^{1}H}^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) of **2d**.*

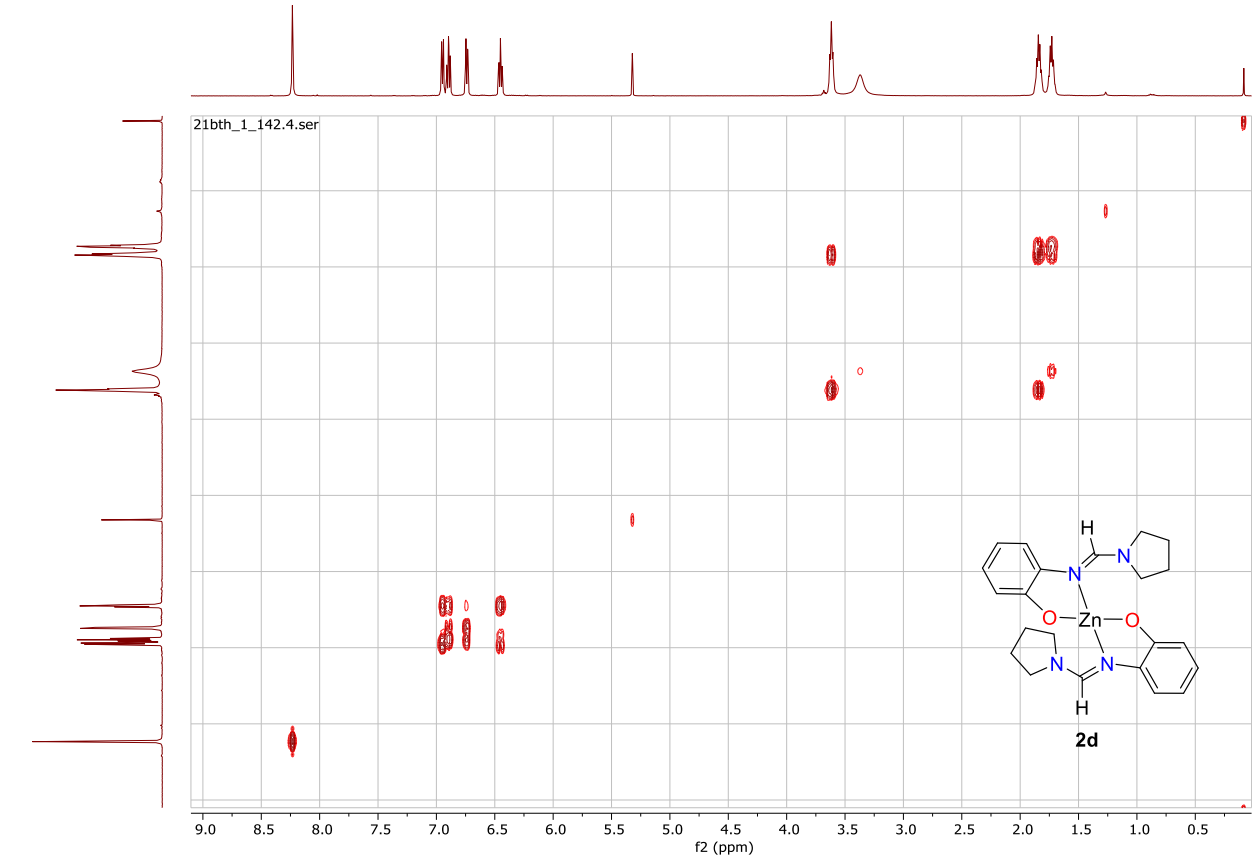


*Figure S94 ^{1}H ^{1}H COSY (500 MHz, CD_2Cl_2, 298 K) of **2d**.*

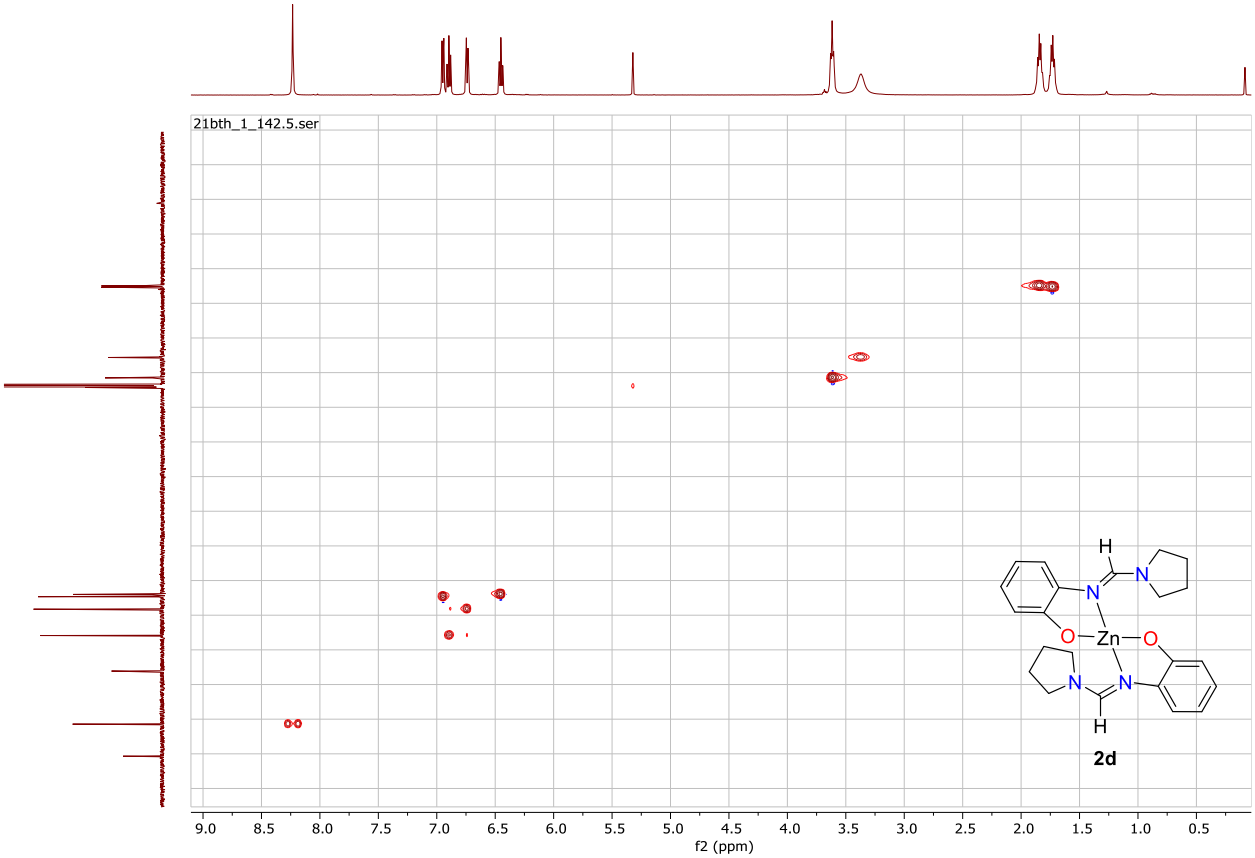


*Figure S95 ^{1}H ^{13}C HSQC (500 MHz / 125 MHz, CD_2Cl_2, 298 K) of **2d**.*

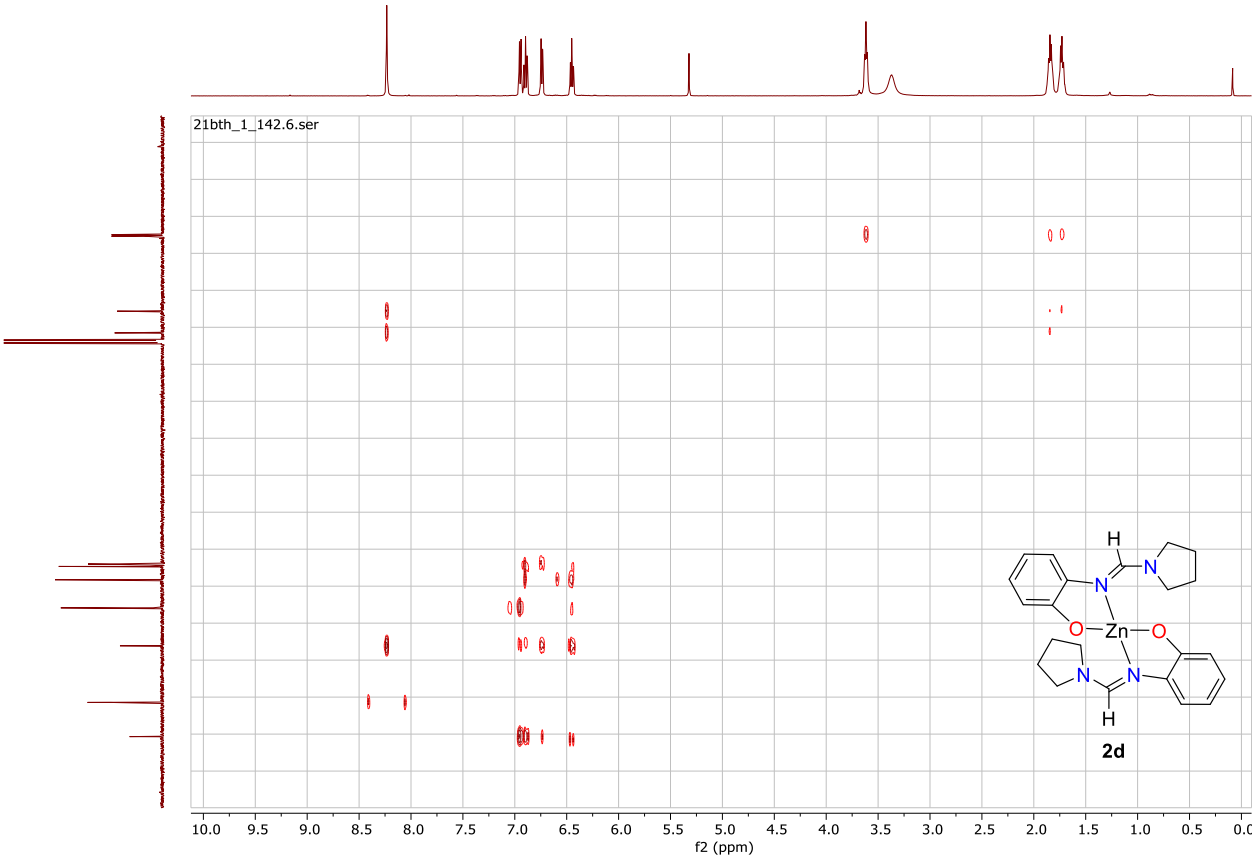


*Figure S96 ^{1}H ^{13}C HMBC (500 MHz / 125 MHz, CD_2Cl_2, 298 K) of **2d**.*

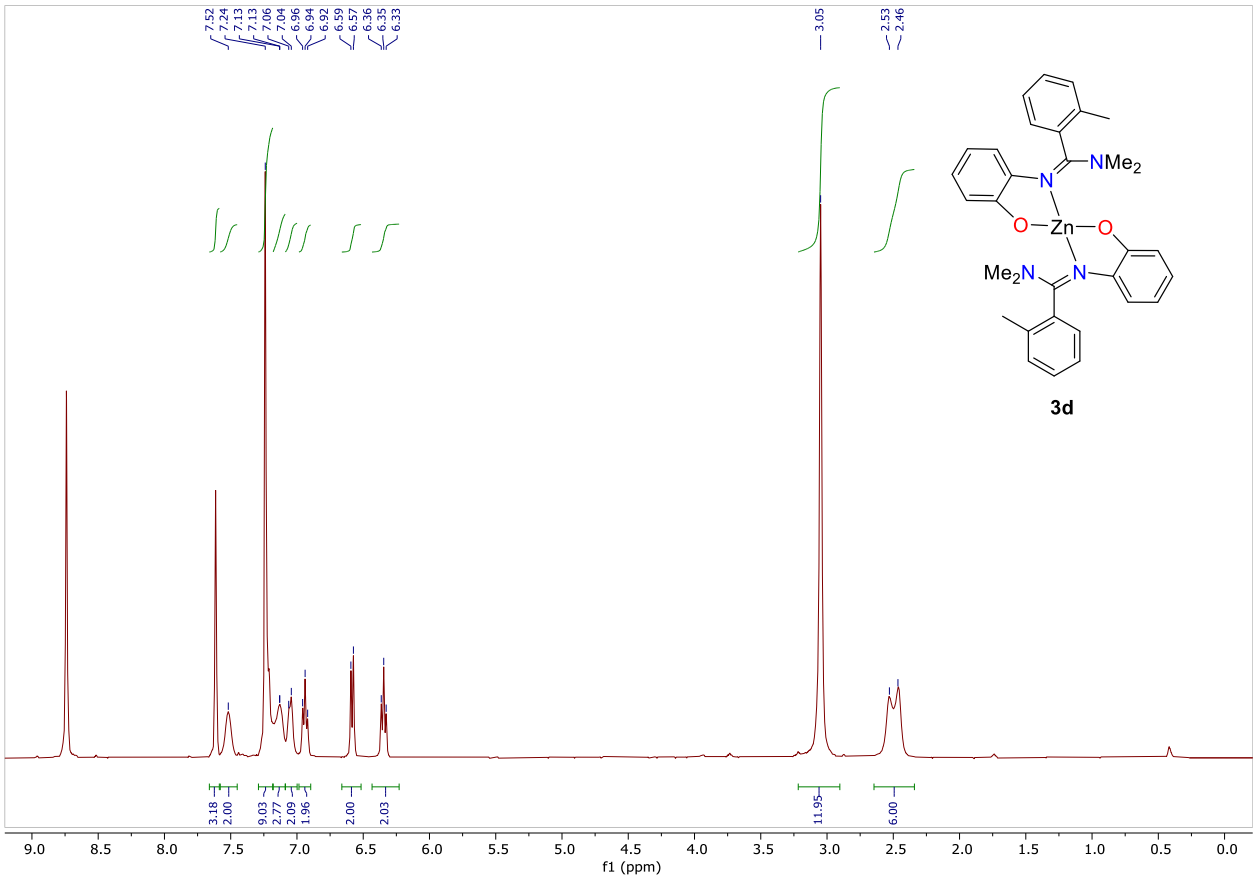


*Figure S97 ^{1}H NMR (400 MHz, C_5D_5N, 378 K) of **3d**.*

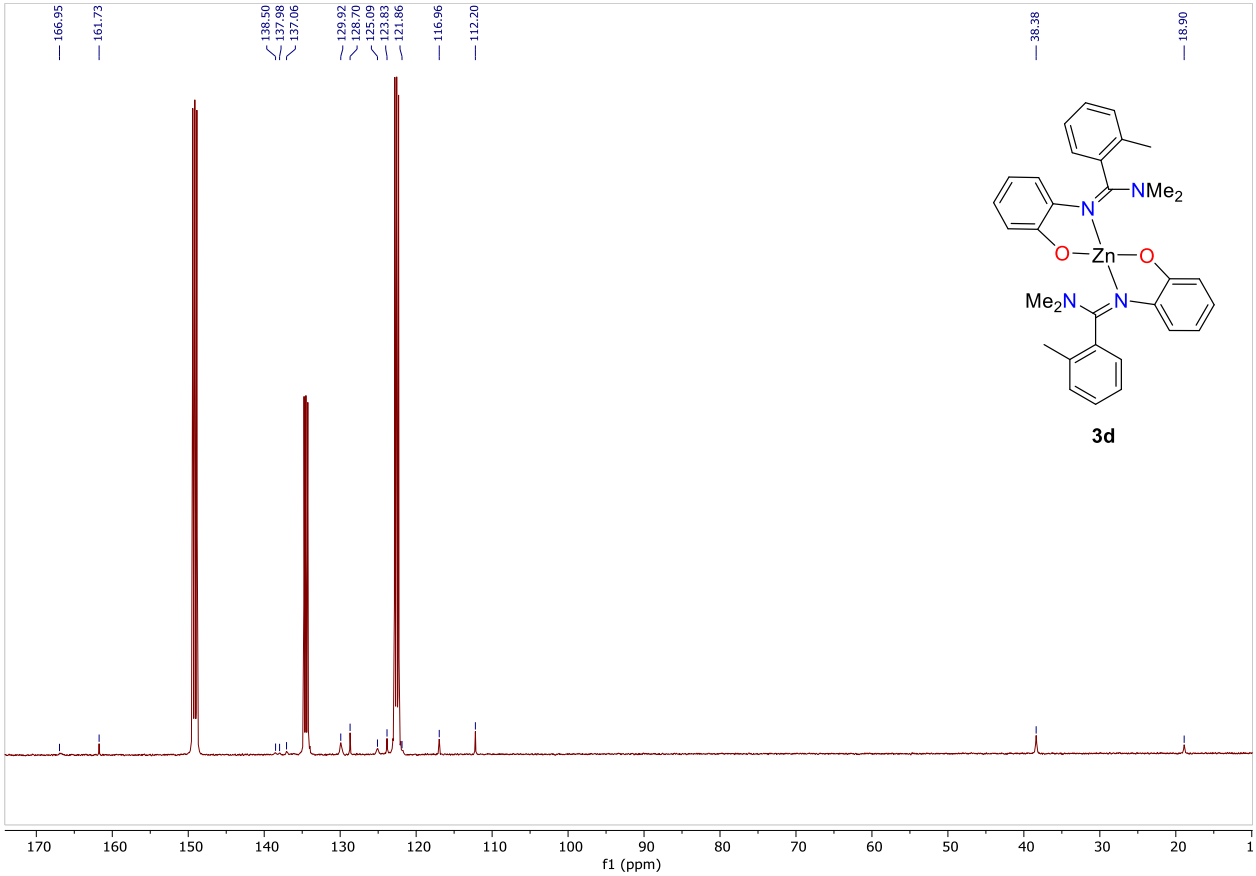


*Figure S98 {^{1}H}^{13}C NMR (101 MHz, C_5D_5N, 378 K) of **3d**.*

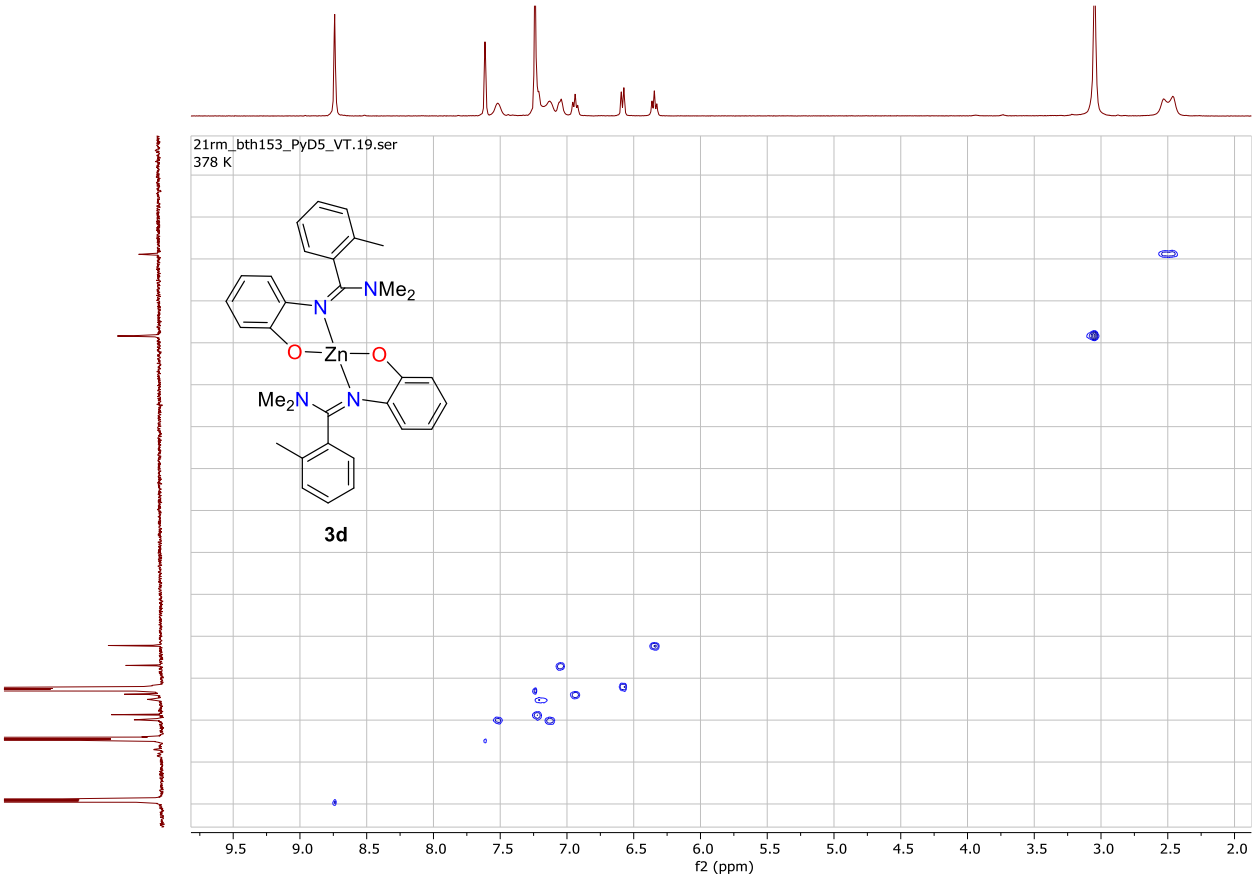


*Figure S99 ^{1}H ^{13}C HSQC (400 MHz / 101 MHz, C_5D_5N, 378 K) of **3d**.*

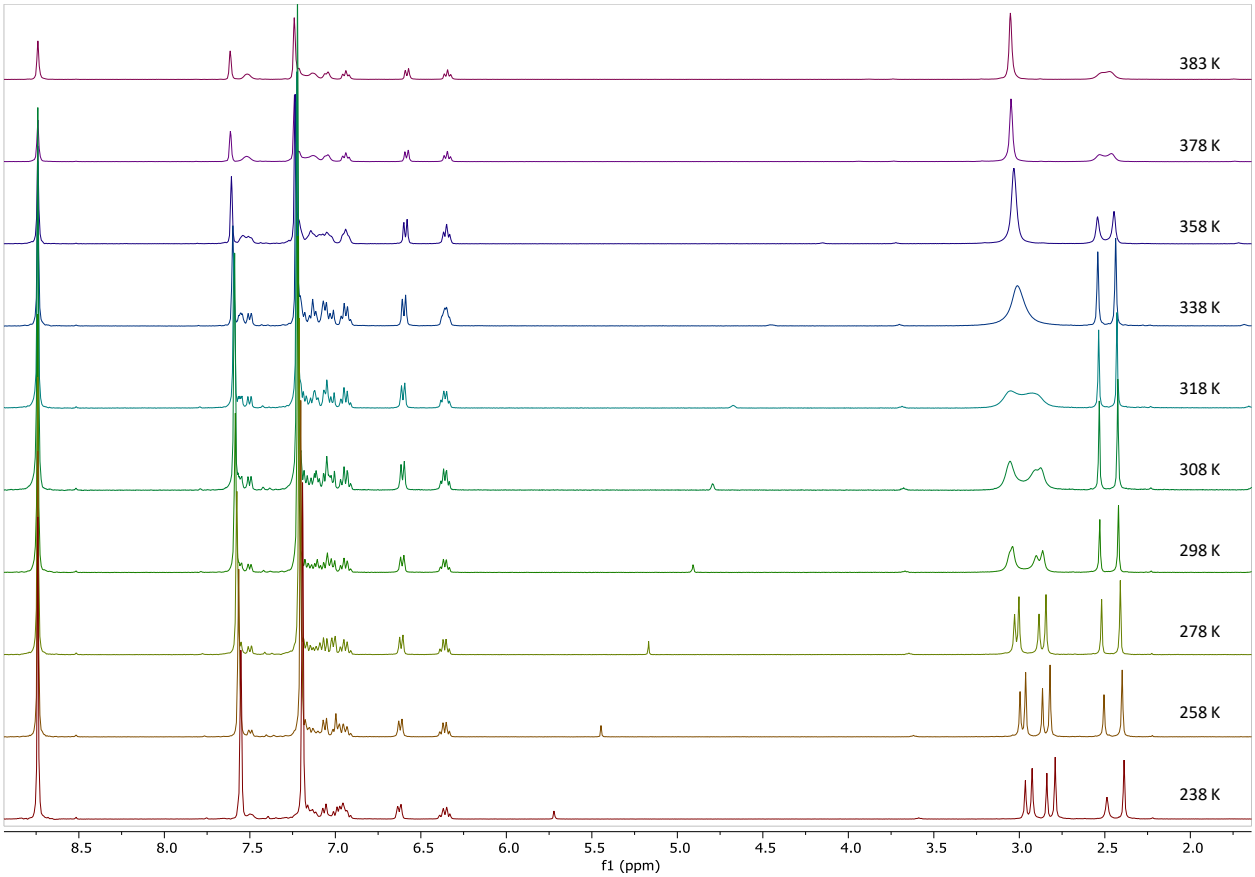


*Figure S100 Variable Temperature ^{1}H NMR (400 MHz, C_5D_5N) of **3d**.*

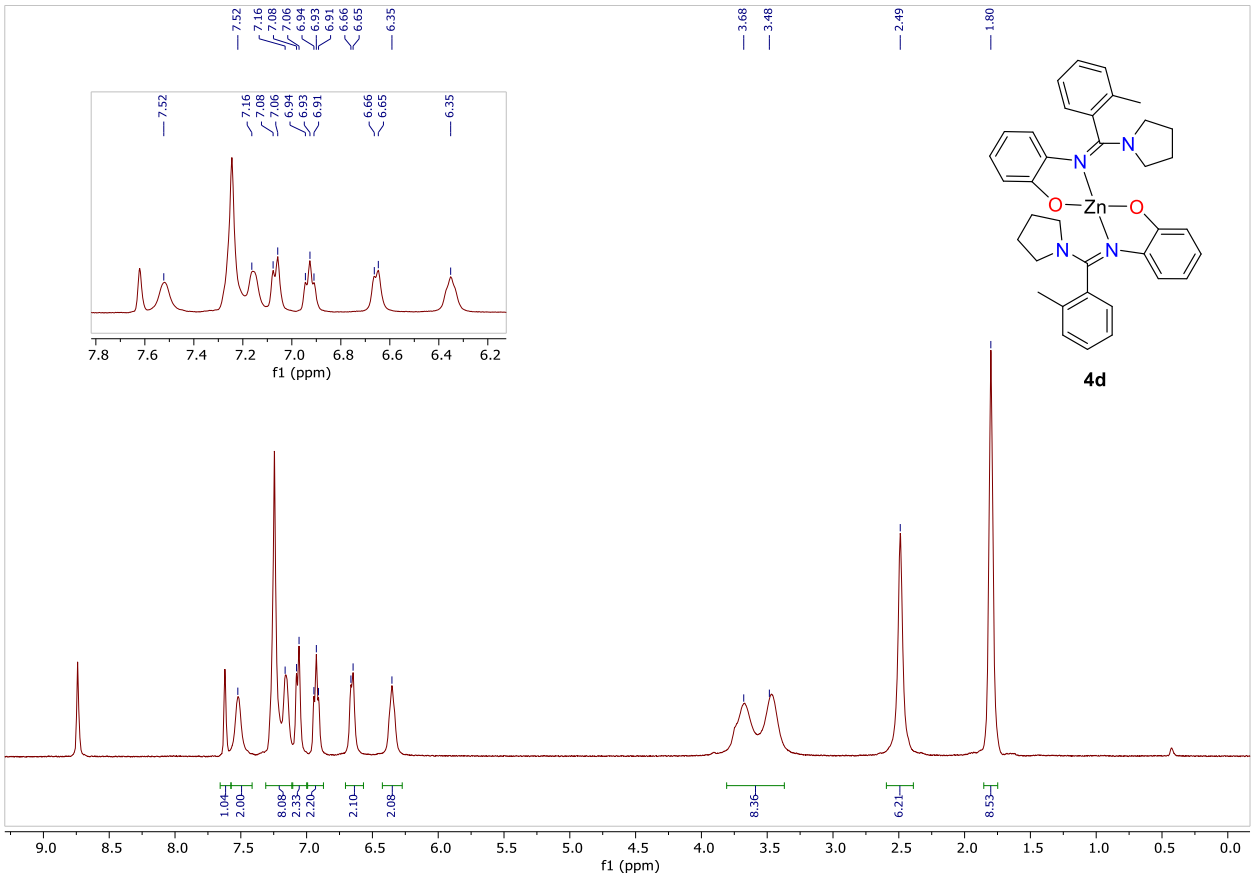


*Figure S101 ^{1}H NMR (400 MHz, C_5D_5N, 383 K) of **4d**.*

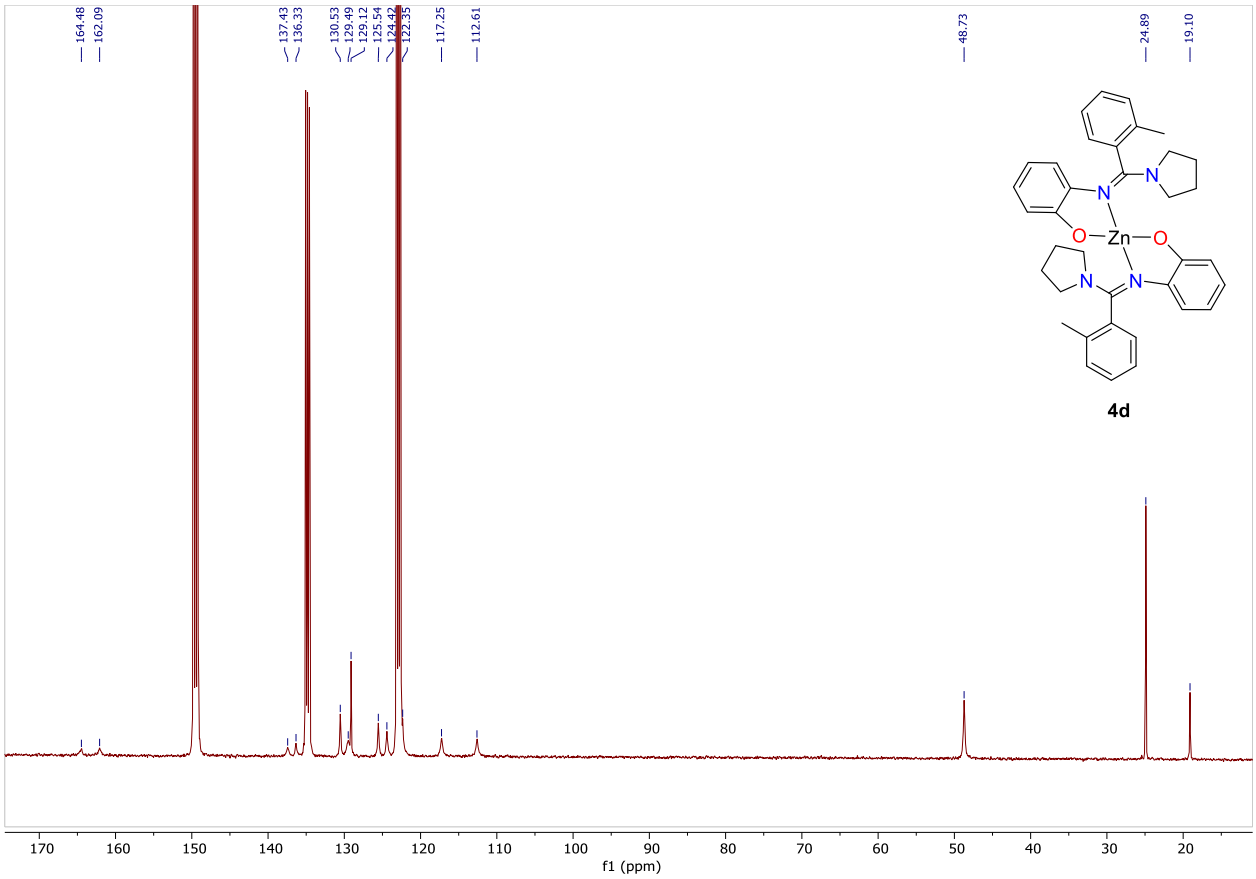


*Figure S102 $\{^{1}H\}^{13}C$ NMR (101 MHz, C_5D_5N, 383 K) of **4d**.*

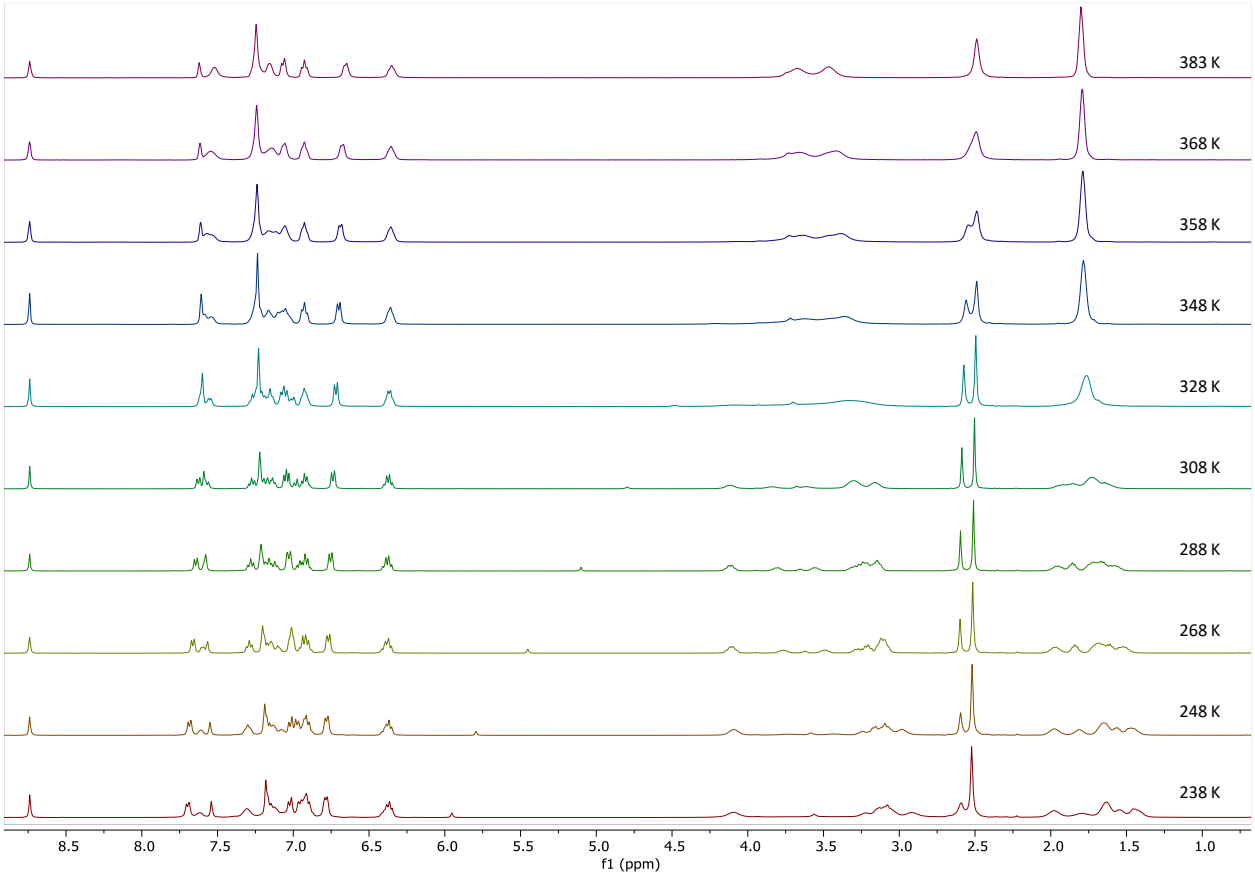


*Figure S103 Variable Temperature ^{1}H NMR (400 MHz, C_5D_5N) of **4d**.*

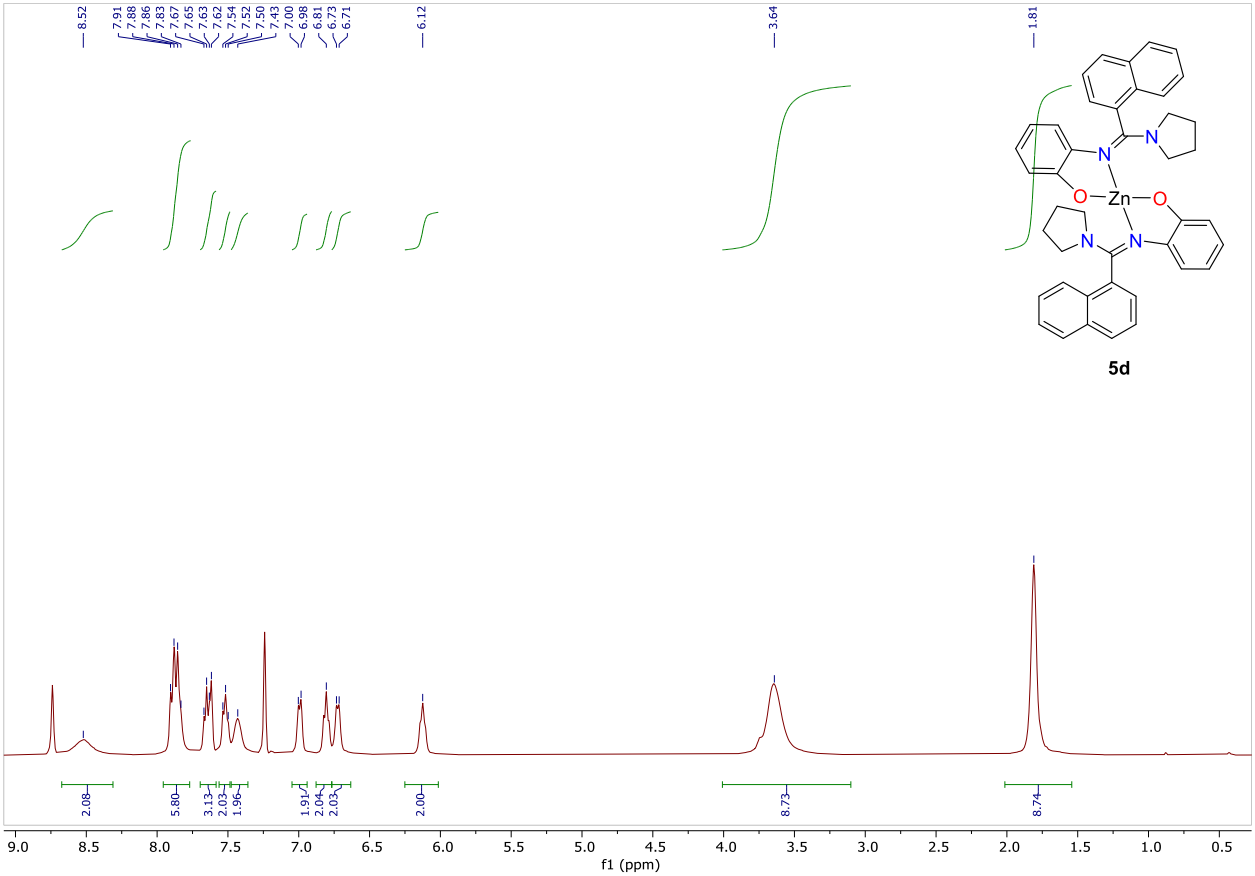


*Figure S104 ^{1}H NMR (400 MHz, C_5D_5N, 383 K) of **5d**.*

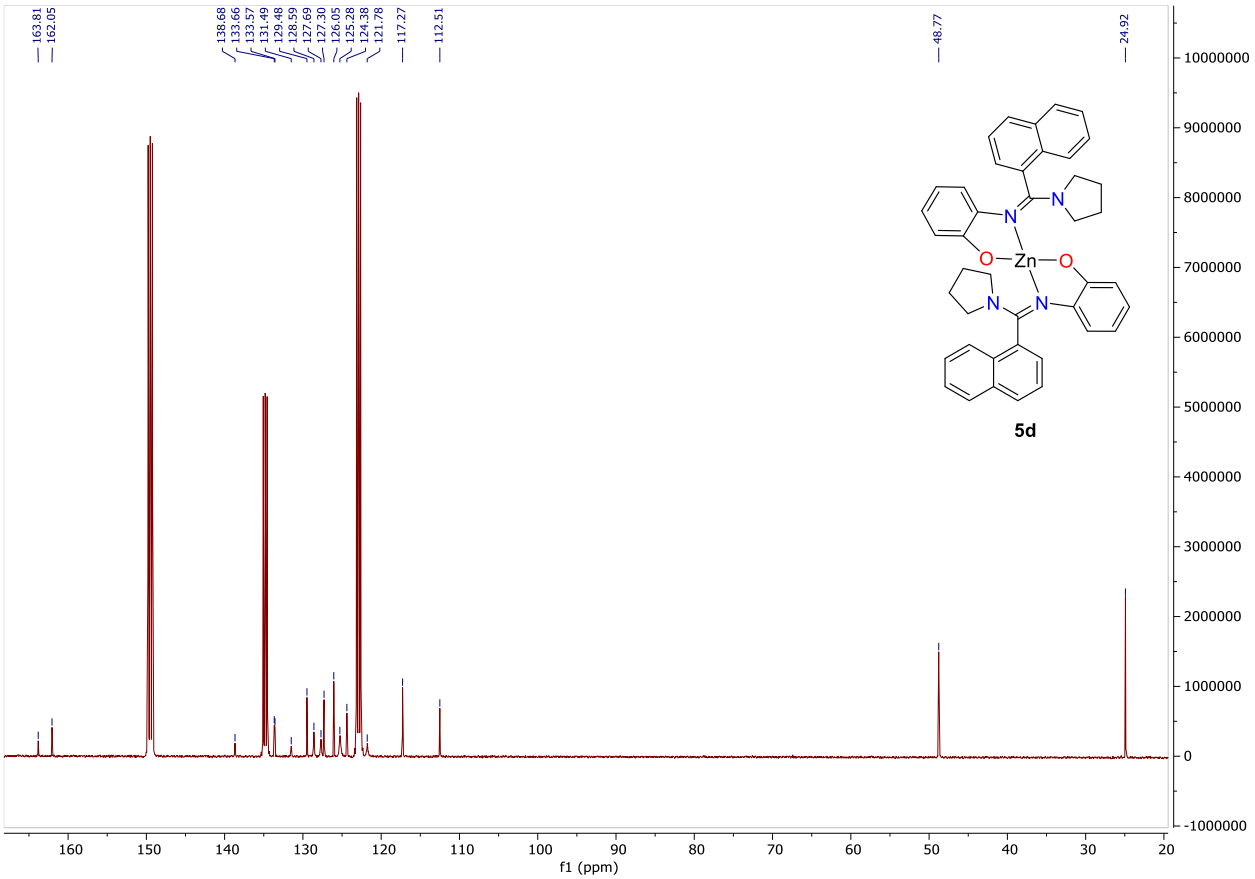


*Figure S105 {^{1}H}^{13}C NMR (101 MHz, C_5D_5N, 383 K) of **5d**.*

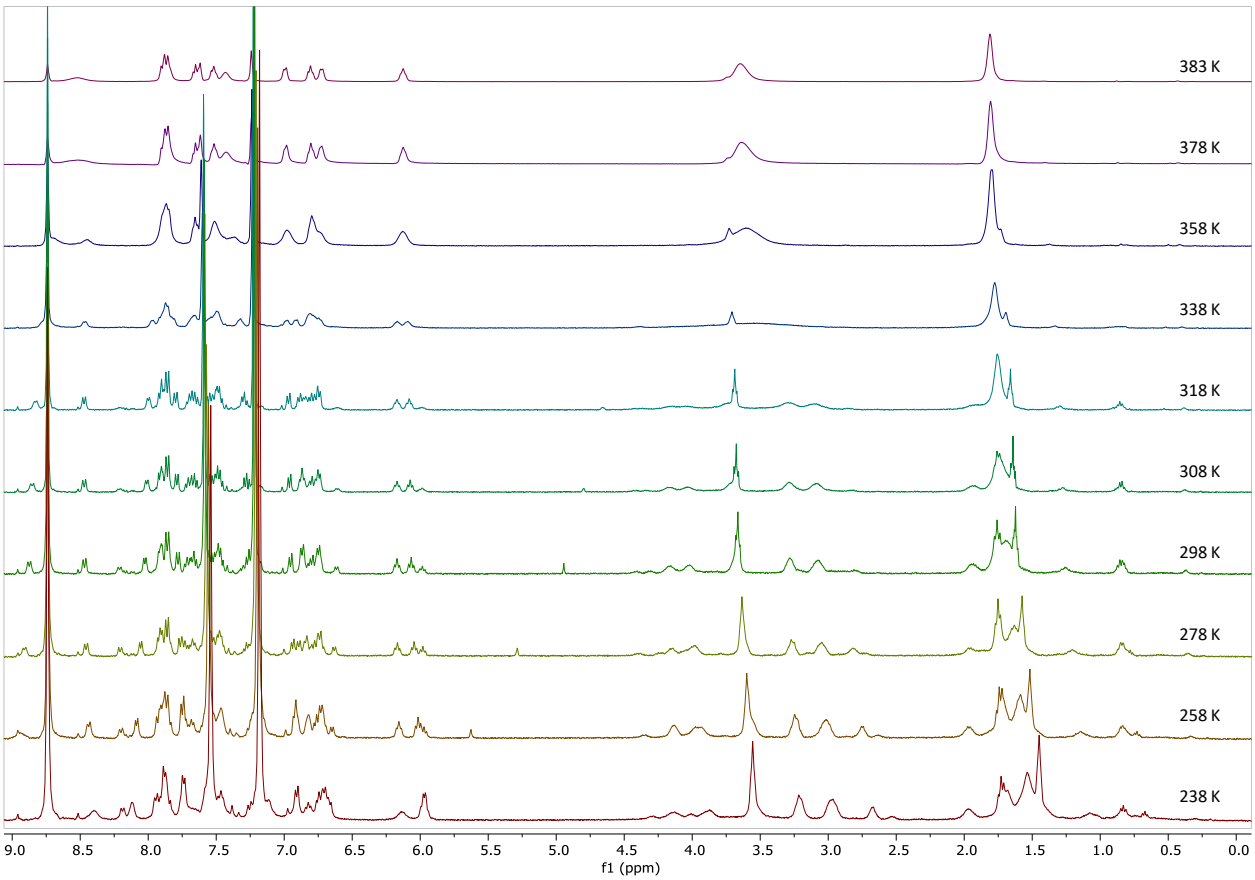


*Figure S106 Variable Temperature ^{1}H NMR (400 MHz, C_5D_5N) of **5d**.*

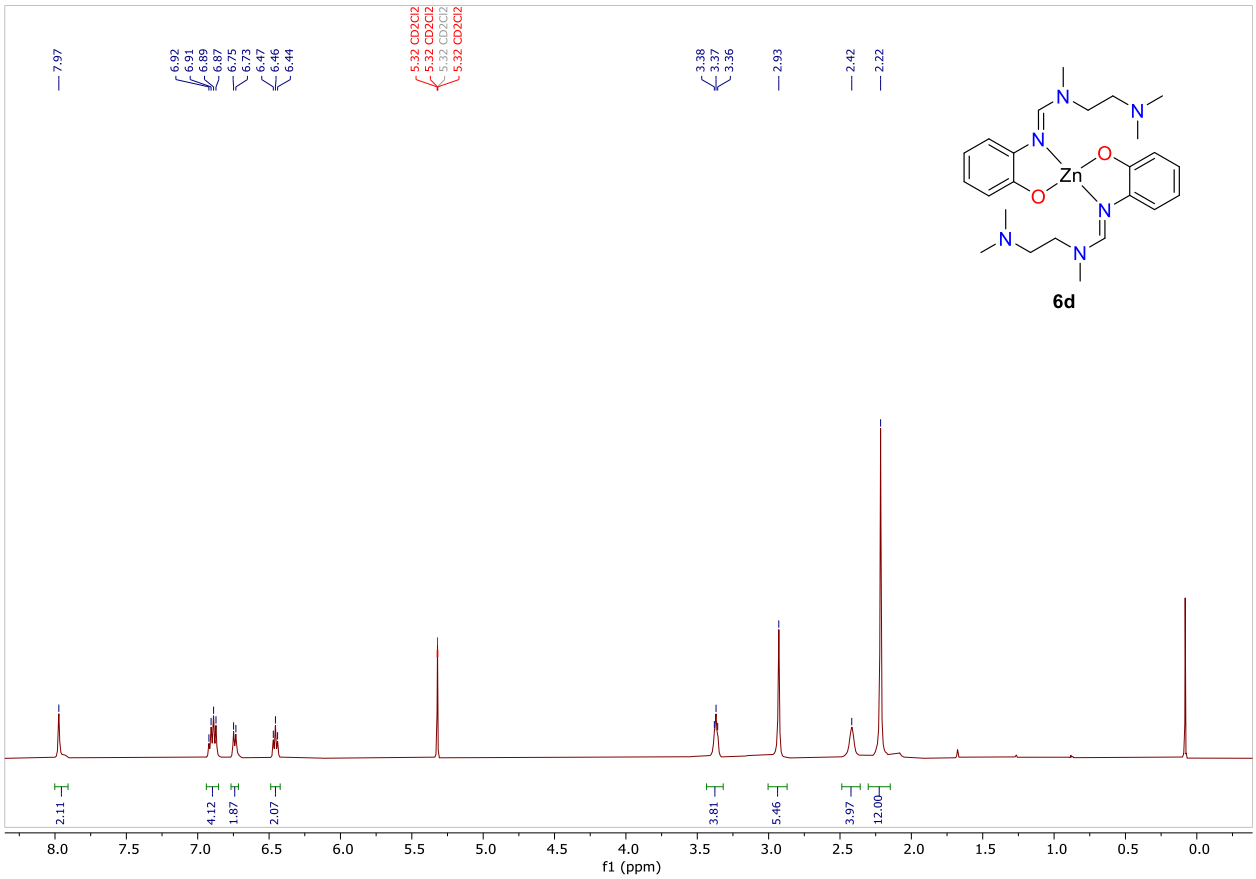


*Figure S107 ^{1}H (500 MHz, CD_2Cl_2, 298 K) of **6d**.*

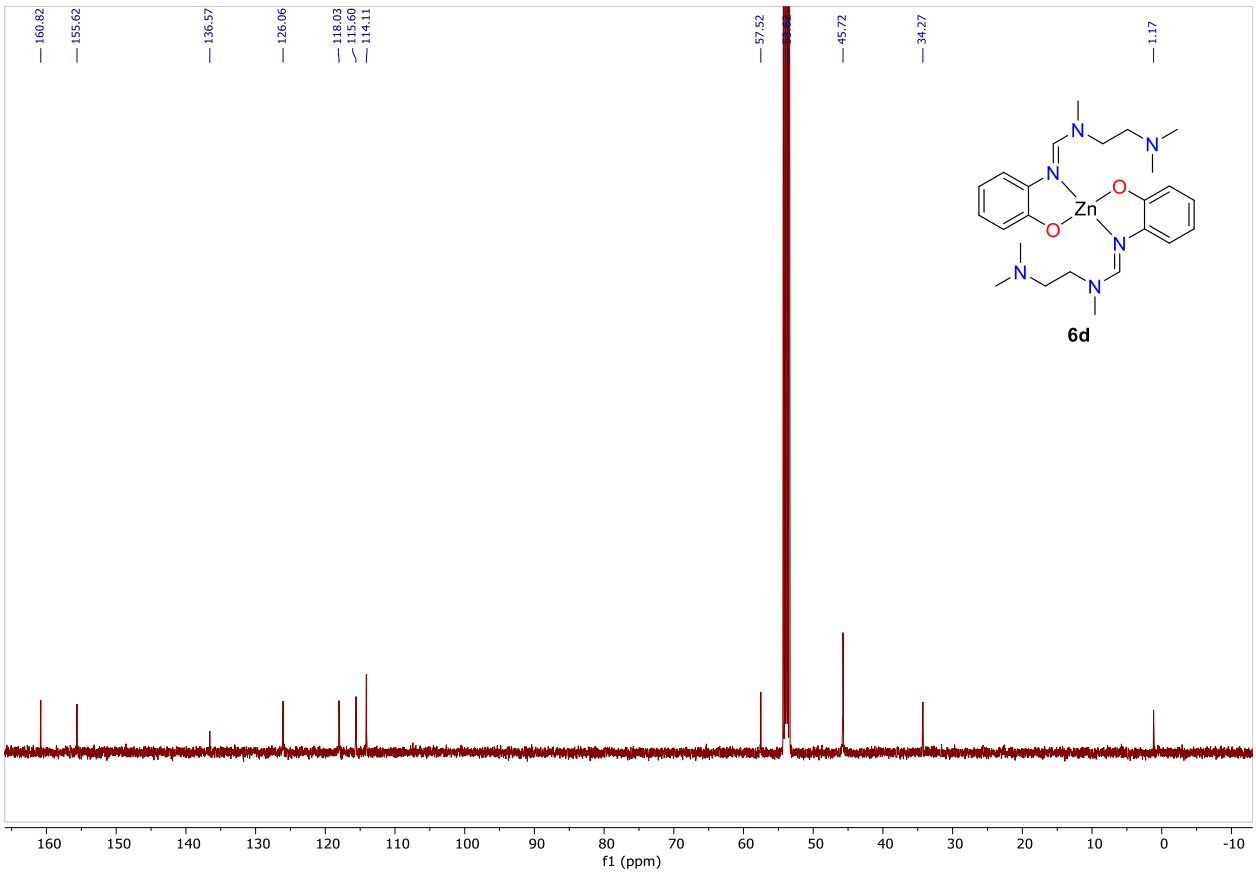


*Figure S108 ^{13}C (500 MHz, CD_2Cl_2, 298 K) of **6d**.*

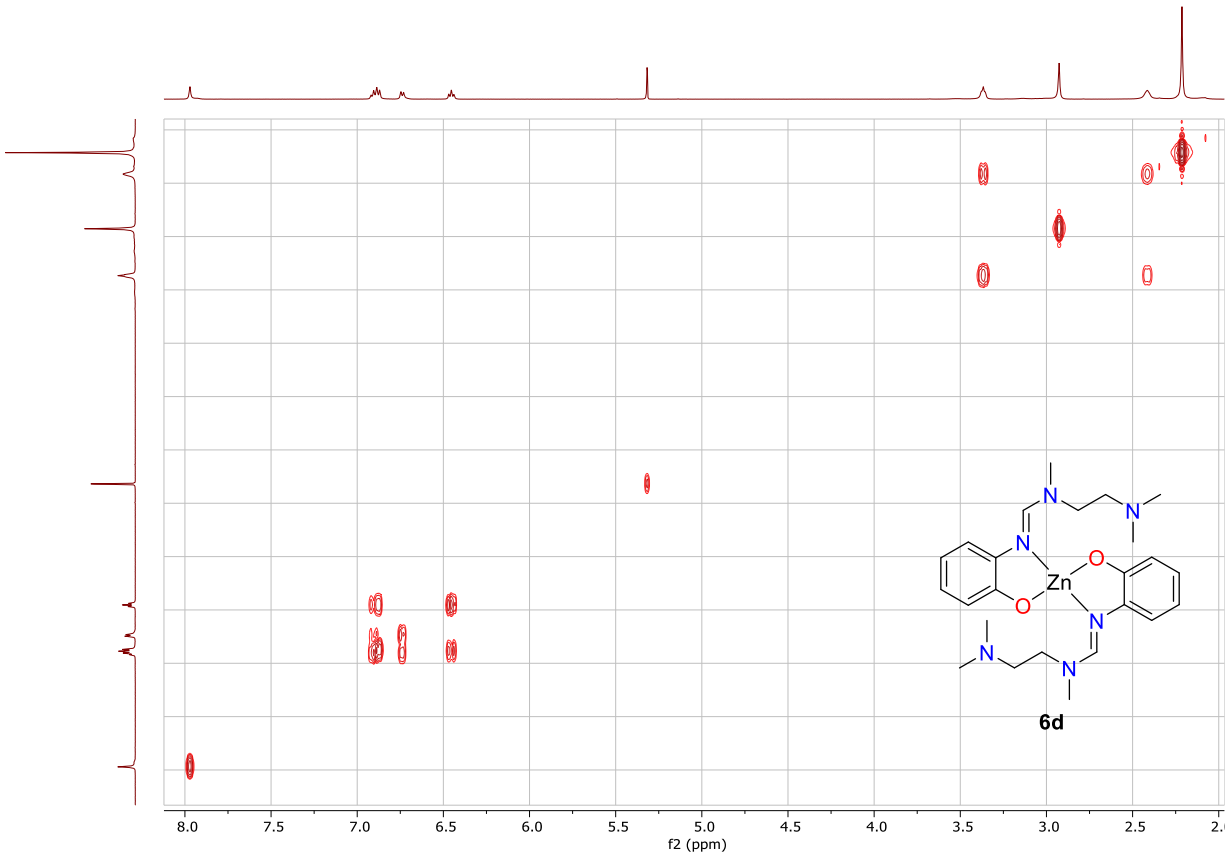


*Figure S109 ^{1}H ^{1}H COSY (125 MHz / 125 MHz, CD_2Cl_2, 298 K) of **6d**.*

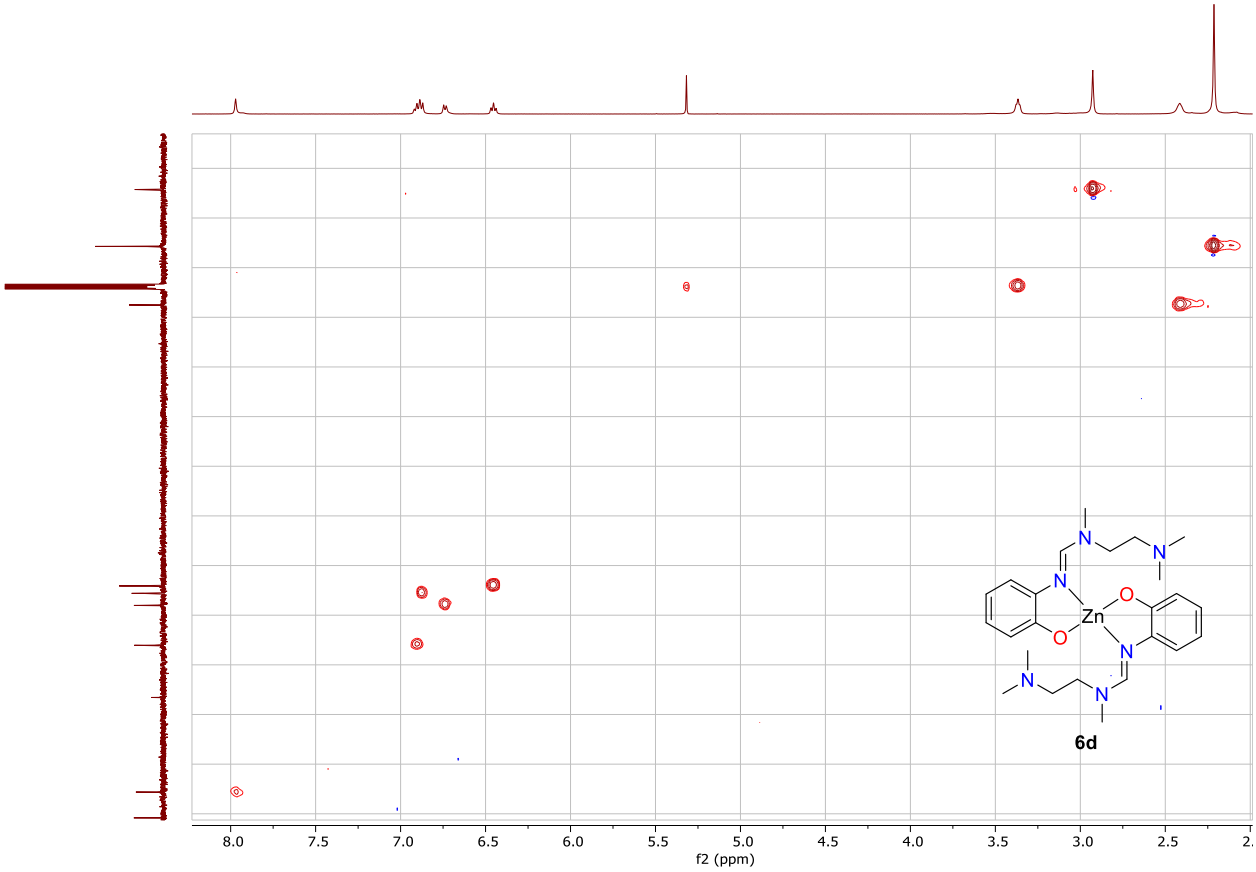


*Figure S110 ^{1}H ^{13}C HSQC (500 MHz / 125 MHz, CD_2Cl_2, 298 K) of **6d**.*

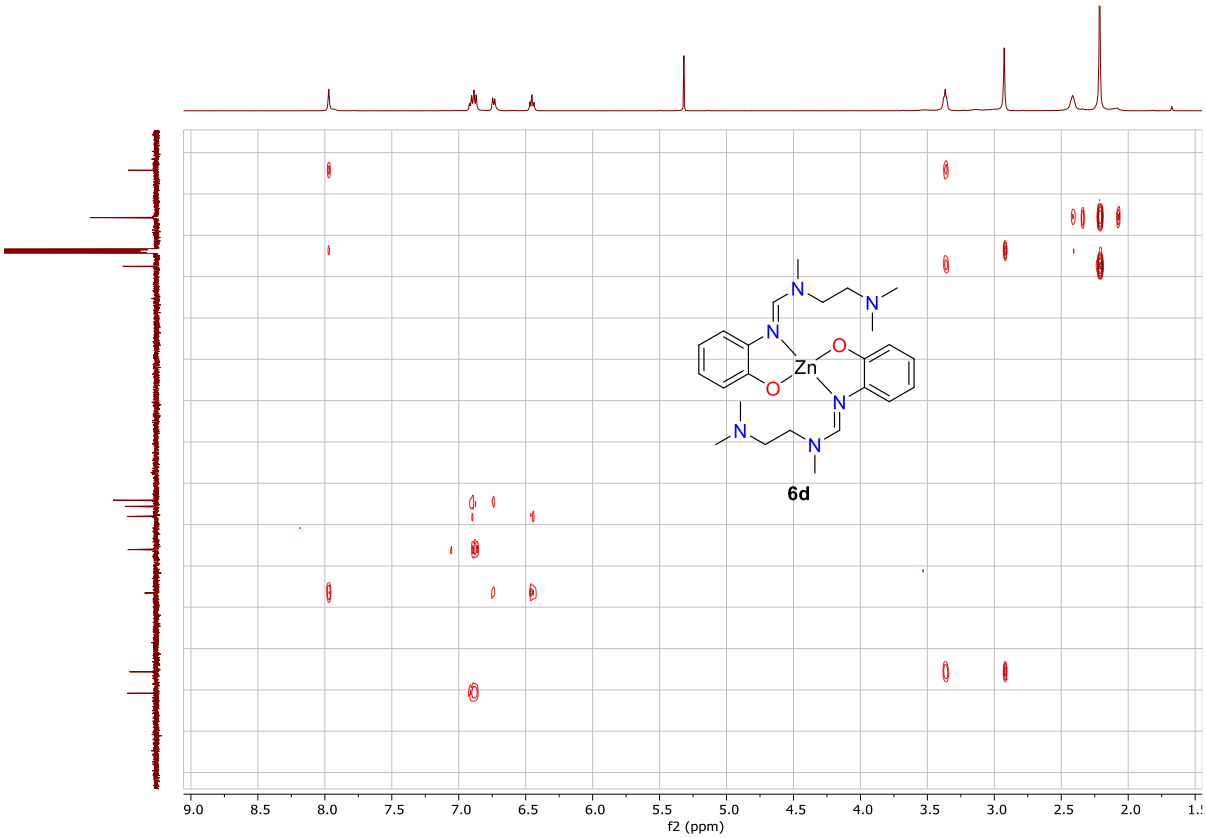


*Figure S111 ^{1}H ^{13}C HMBC (500 MHz / 125 MHz, CD_2Cl_2, 298 K) of **6d**.*

DOSY analyses

All spectra were recorded on an Avance III HD 600 MHz Bruker spectrometer equipped with a 5 mm Prodigy probe, and using 5 mm NMR tubes at 298K. The samples were prepared as follow: 15 µmol of the analyte were dissolved in 500 µL of CD_2Cl_2 (or Pyridine-D_5) then introduced in a 5 mm NMR tube and finally introduced in the magnet. The specific parameters of each sample (d1, p1, ns, rg) were optimized on a standard 1D acquisition (^{1}H sequence zg30, 16 scans), and recalled in the dosy experiment (ledbpgp2s, 32 points, linear gradient from 95% to 5%). The diffusion delay d20 was fixed at 0,01 s, while the diffusion gradient length p30 was adapted to get a 95% intensity decrease between the first spectrum and the last one. DOSY data were processed using Topspin 3.5 pl7 with the dosy2d exponential processing method. All diffusion coefficients were read on the two-dimensional spectrum obtained after processing.

The Stokes–Einstein equation (1) for diffusion of spherical particles was used to calculate the hydrodynamic radius of spherical particle.

$rH = kT/6\pi\eta D$ (equation 1)

D is the diffusion coefficient ($m^2\ s^{-1}$)

k is the Boltzmann constant ($k = 1.38065 \times 10^{-23}\ kg\ m^2\ s^{-2}\ K^{-1}$)

T is the absolute temperature (T = 298 K)

η is the dynamic viscosity (CD_2Cl_2 : $\eta = 4.13 \times 10^{-4}\ kg\ m^{-1}\ s^{-1}$)

r_H is the hydrodynamic radius of the spherical particle (m)

OLEX2 was used to determine the hydrodynamic radius (r'_H) from the molecular volume based on the XRD structure (equation 2).

$r'H = \sqrt[3]{(3V/4\pi)}$ (equation 2)

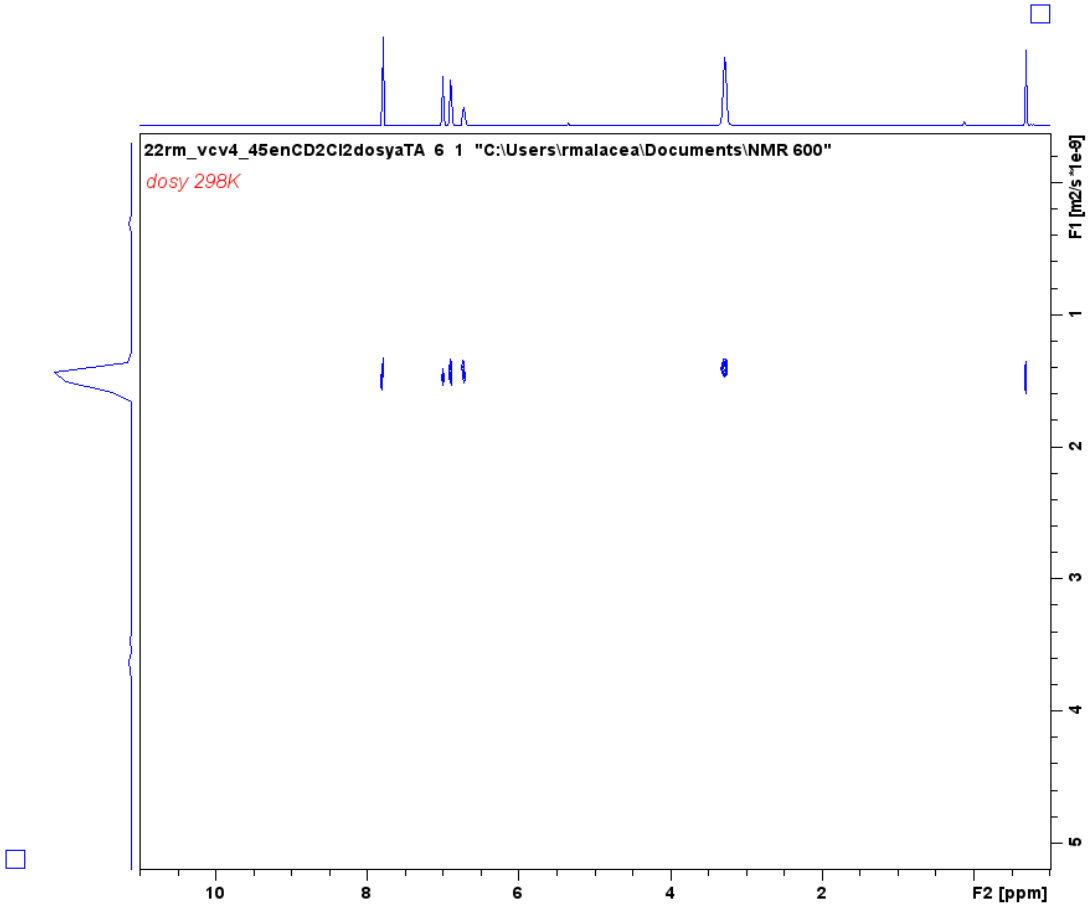


*Figure S112 Processed DOSY spectrum for **1a** in CD_2Cl_2 ($1.45*10^{-9} m^2/s$)*

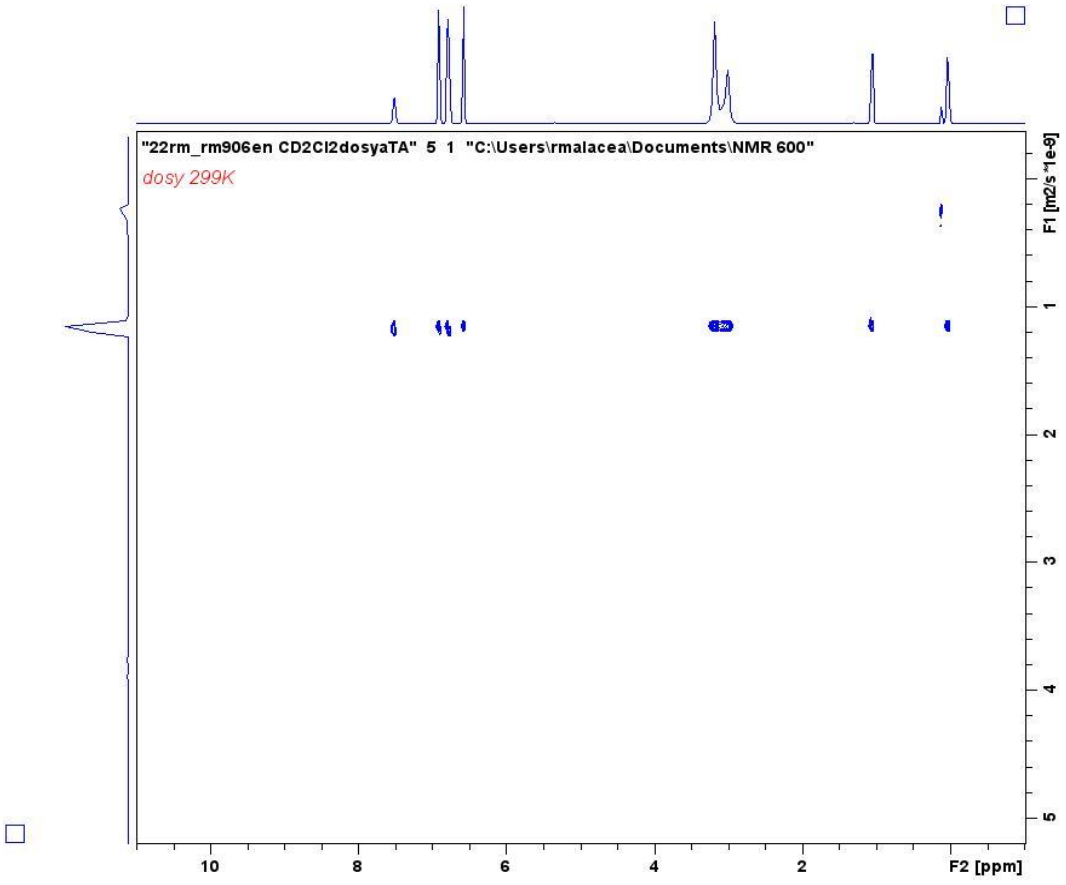


*Figure S113 Processed DOSY spectrum for **1c** in CD_2Cl_2 ($1.15*10^{-9} m^2/s$)*

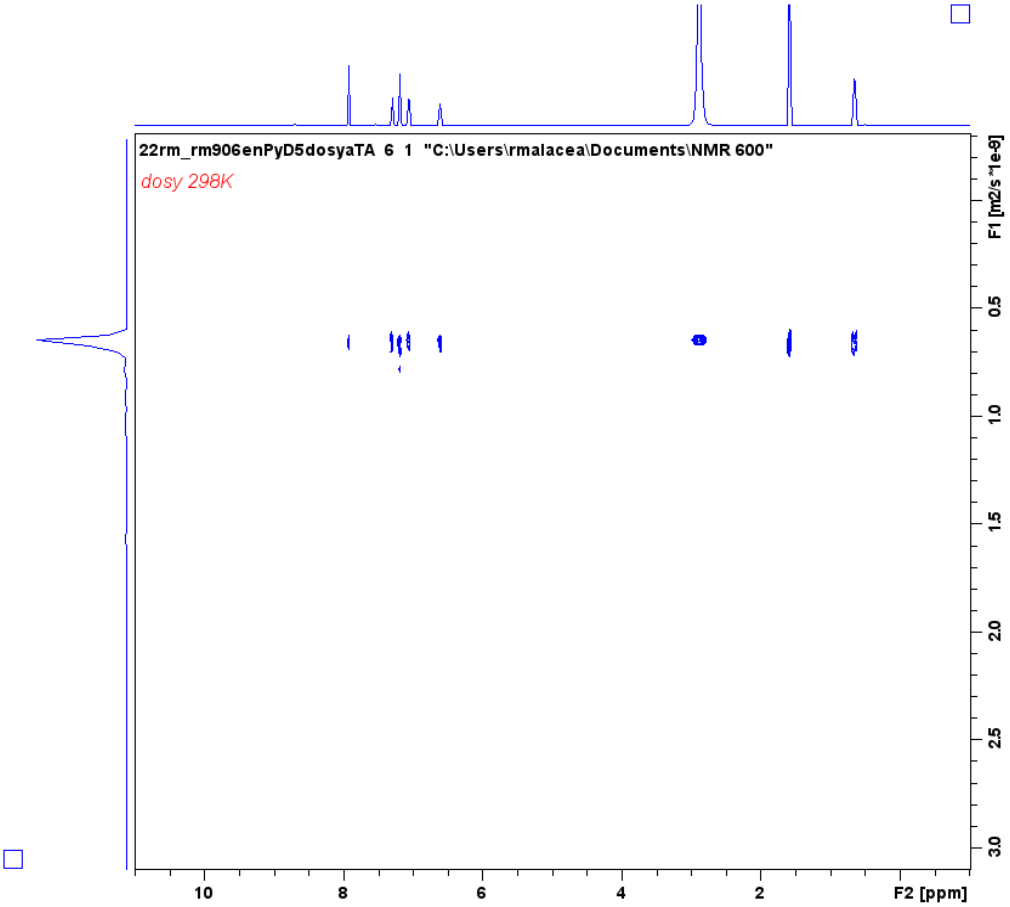
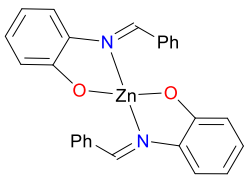


*Figure S114 Processed DOSY spectrum for **1c** in CD_2Cl_2 ($0.66*10^{-9} m^2/s$)*

Table S1 Comparison of the hydrodynamic radius (r_H) estimated from the diffusion coefficients with the hydrodynamic radius (r'H) determined from the XRD structure for complexes **1a** and **1c**.

Complex	D (m^2/s)	Radius (Å) r_H	Complex	Volume (Å^3)	Radius (Å) r'_H
1a in CD_2Cl_2	$1.45*10^{-9}$	3.64	**1a** (dimer)	388.14	4.53
			1a (monomer)	198.96	**3.62**
1c in CD_2Cl_2	$1.15*10^{-9}$	4.60	**1c** (dimer)	371.45	**4.46**
			1c (monomer)	187.51	3.55
1c in Pyridine -D5	$0.66*10^{-9}$	3.76	**1c** in (dimer)	371.45	4.46
			1c (monomer)	187.51	**3.55**

Experimental procedure for the synthesis of 7d



7d

In a glovebox, 197.24 mg (1 mmol) of *N*-benzylidene-2-hydroxyaniline were solubilized in 10 mL of dried THF. 0.5 mL (0.5 mmol, 0.5 equiv.) of a 1 M solution of $ZnEt_2$ in hexane was added and the mixture was stirred at r.t. for 2 h. The volatiles were evaporated under vacuum and the solid obtained was washed with 4 mL of pentane before being dried under vacuum affording **7d** as a reddish powder (115 mg, 50% yield). **Elemental Analysis:** calcd for $C_{26}H_{20}N_2O_2Zn$: C, 68.21; H, 4.40; N, 6.12. Found: C, 68.08; H, 4.36; N, 5.81. **^{1}H NMR (500 MHz, CD_2Cl_2, 298 K):** δ(ppm) = 8.27 (s, 2H), 7.62-7.47 (broad signal, 4H), 7.37-7.25 (broad signal, 2H), 7.22-7.02 (broad signal, 8H), 6.94-6.80 (broad signal, 2H), 6.57 (t, *J* = 7.4 Hz, 2H).**{^{1}H}^{13}C NMR (126 MHz, CD_2Cl_2, 298 K):** δ(ppm) = 163.08, 158.54, 135.50, 134.15, 132.62, 131.37, 129.38, 128.99, 120.70, 116.68, 115.41.

Polymer characterization

Representative homonuclear decoupled ^{1}H NMR spectrum:

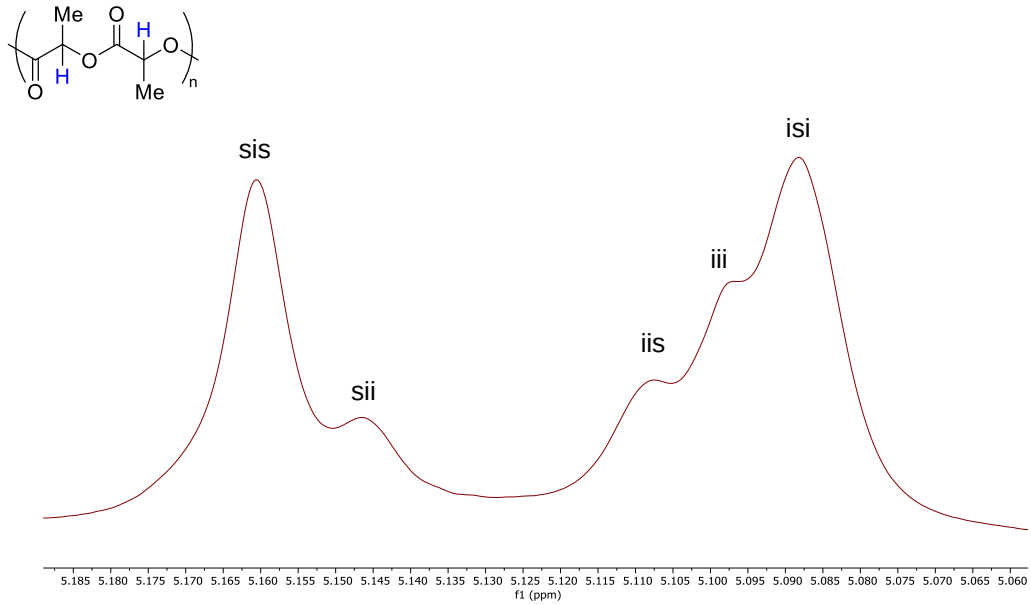


*Figure S115 Homonuclear decoupled ^{1}H NMR ($CDCl_3$) spectra of purified PLA (Pr = 0.77) product from the solution polymerisation of rac-LA at 20 °C for 2 h using **1c**, displaying the five tetrad possibilities in the methine region (blue)*

MALDI-ToF spectra

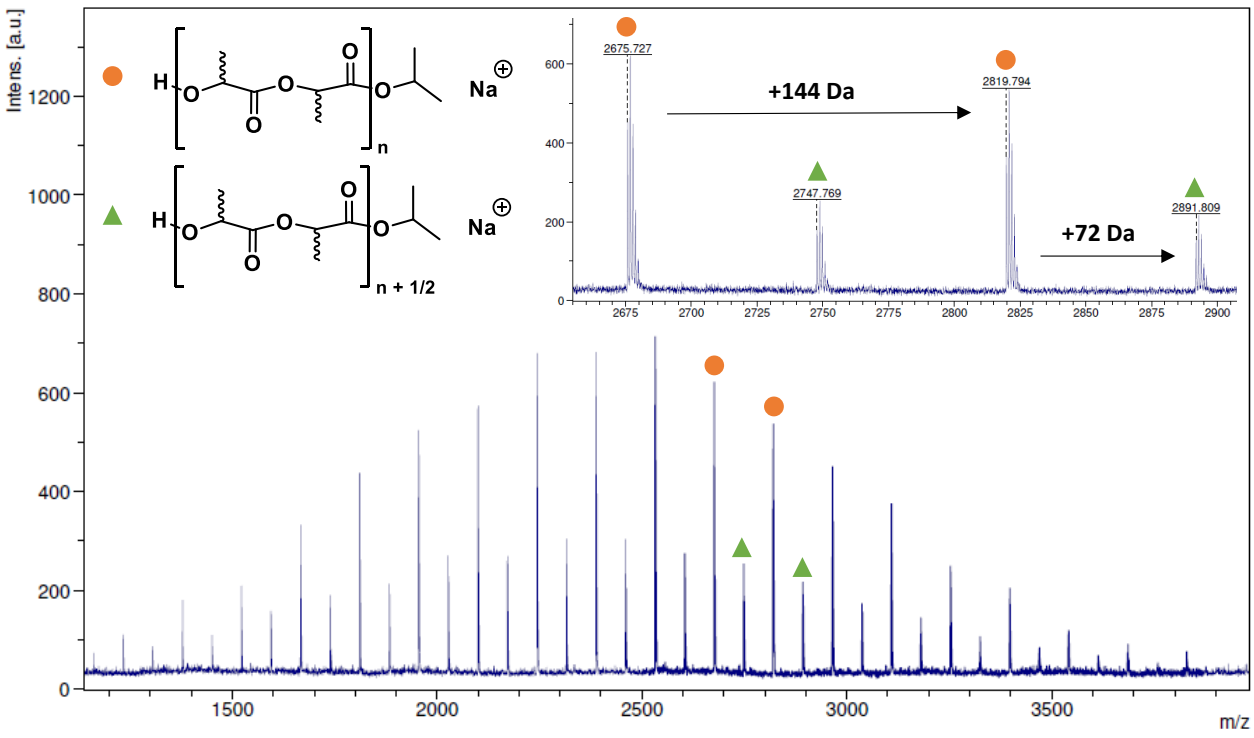


*Figure S116 MALDI-ToF spectrum of PLA produced using **1b'** (90 °C, 4 h, 25% conv., 100:1:1). Magnified version is provided to assist in identifying the repeat unit.*

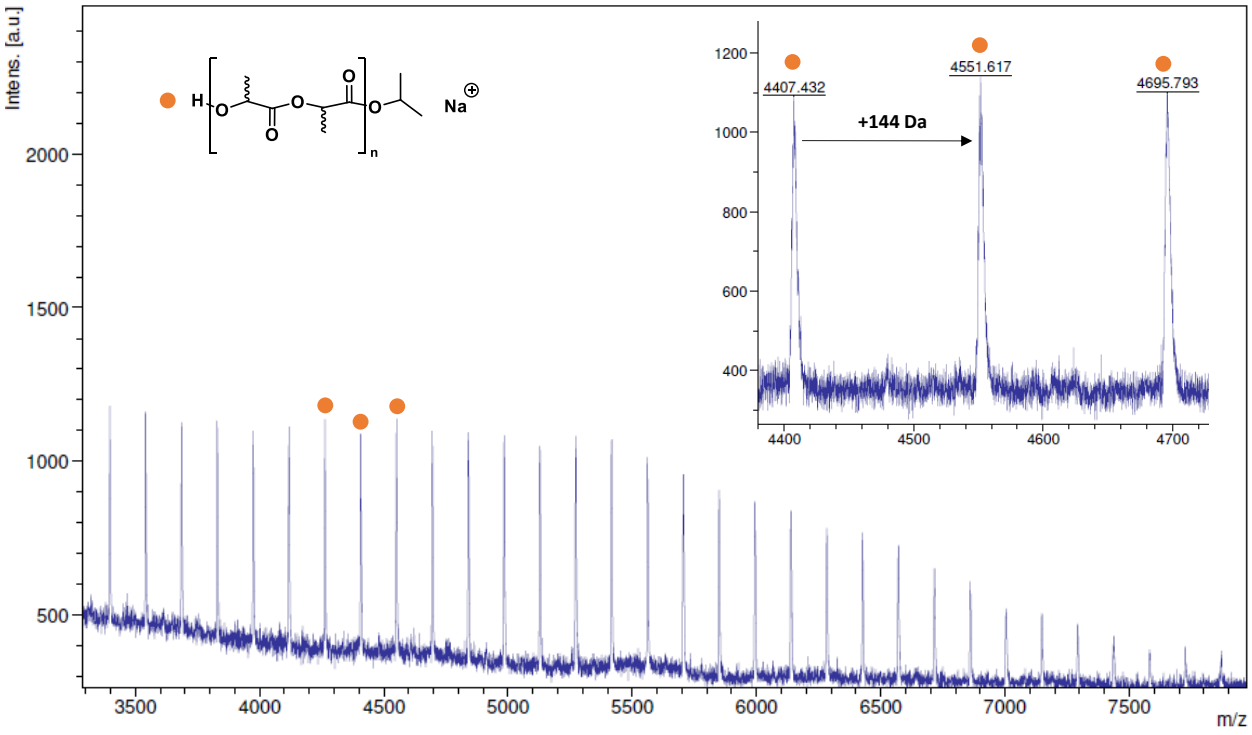


*Figure S117 MALDI-ToF spectrum of PLA produced using **6c** with ^{i}PrOH as co-initiator (20 °C, 40 min, 42% conv., 100:1:1). Magnified version is provided to assist in identifying the repeat unit.*

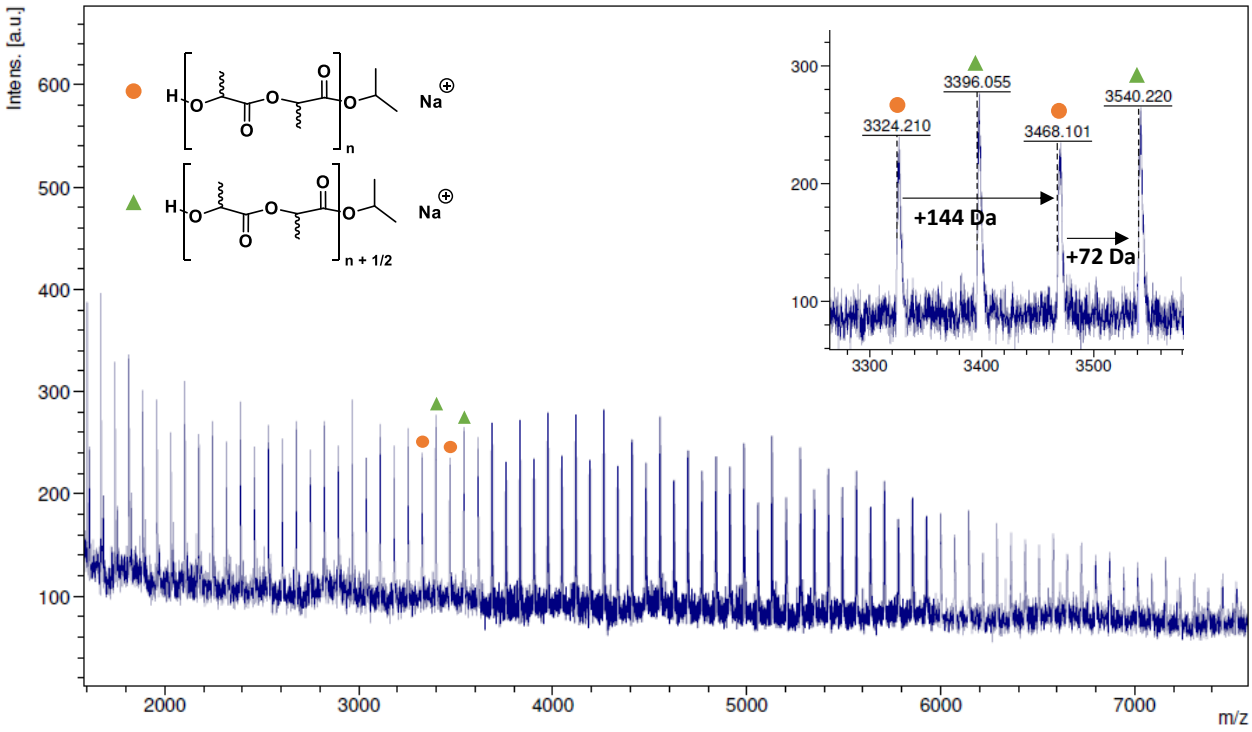


*Figure S118 MALDI-ToF spectrum of PLA produced using **6c** with ^{i}PrOH as co-initiator (20 °C, 2 h, 100% conv., 25:1:1). Magnified version is provided to assist in identifying the repeat unit.*

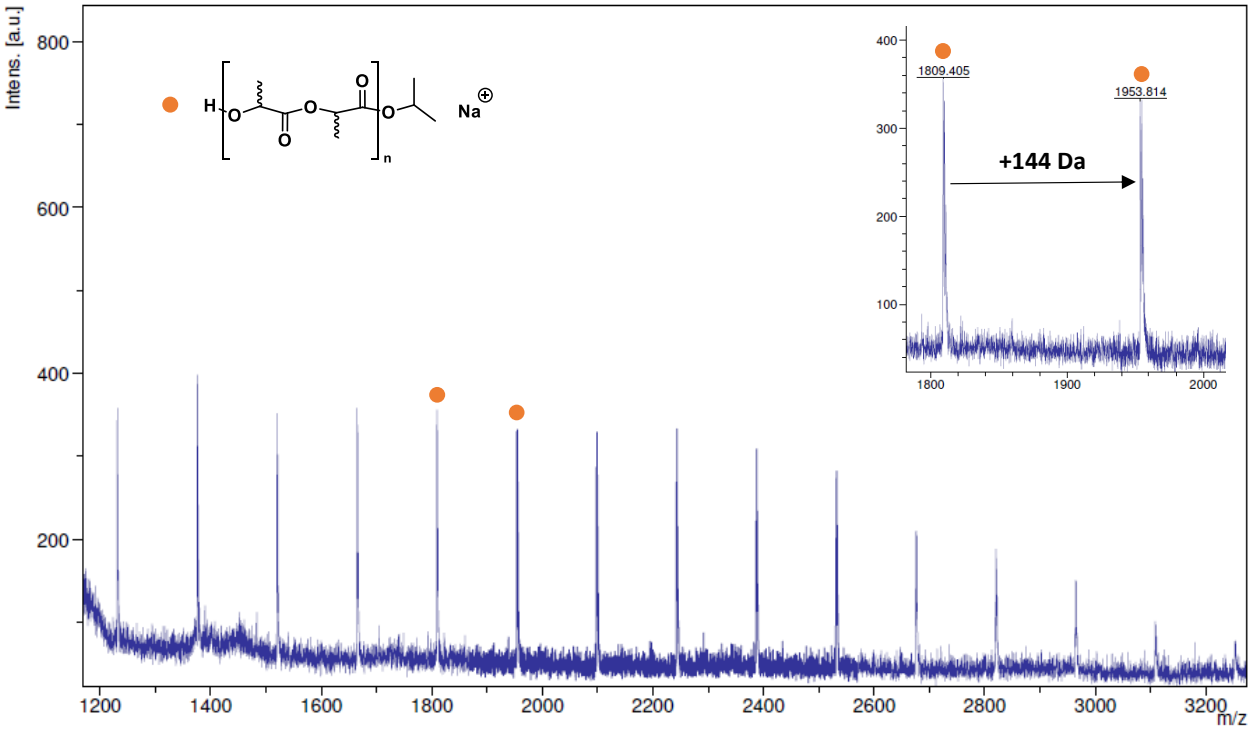


*Figure S119 MALDI-ToF spectrum of PLA produced using **6d** with ^{i}PrOH as co-initiator (30 °C, 40 min, 20% conv., 100:1:1). Magnified version is provided to assist in identifying the repeat unit.*

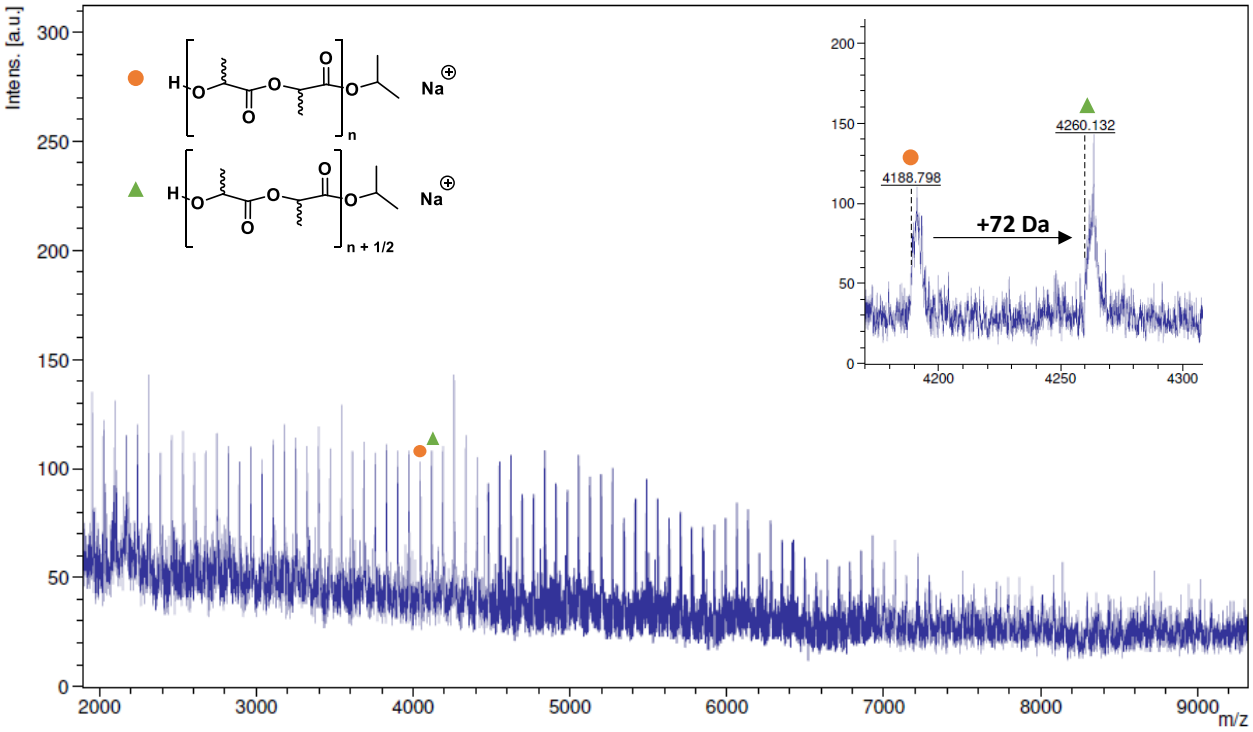


*Figure S120 MALDI-ToF spectrum of PLA produced using **6d** with ^{i}PrOH as co-initiator (30 °C, 2 h, 100% conv., 25:1:1). Magnified version is provided to assist in identifying the repeat unit.*

X-ray data for compounds

L1H, L3H, L4H, L5H, 1a, 1b, 1b’, 2b, 3b, 1c, 5c, 6c, 1d, 2d, 3d, 4d, 6d

Compound L1H

Pacsmub PLATEFORME Analyse Chimique Synthèse Moléculaire UNIVERSITÉ DE BOURGOGNE

R_1=3.27%

Crystal Data and Experimental

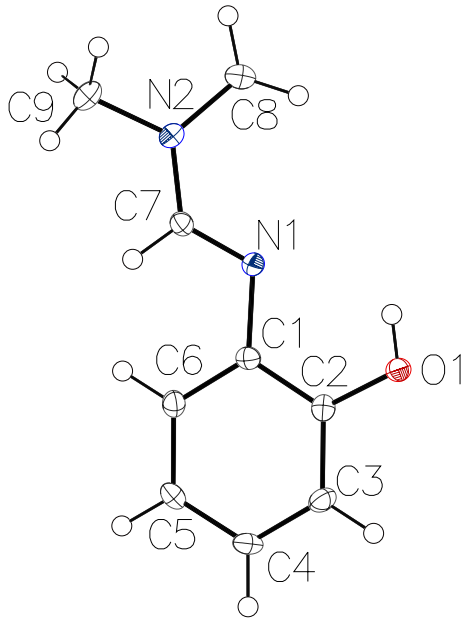


Figure S121: ORTEP view of compound **L1H**.

Experimental. Single clear light colourless prism crystals of **compound L1H** recrystallized from DCM by slow evaporation. A suitable crystal with dimensions 0.69 x 0.09 x 0.08 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture (Cu) diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] as the graphical interface. The model was refined with ShelXL[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_9H_{12}N_2O$, M_r = 164.21, orthorhombic, *Fdd*2 (No. 43), a = 21.7702(6) Å, b = 21.9570(6) Å, c = 7.2513(2) Å, α = β = γ = 90°, V = 3466.18(17) Å^3, T = 100.0(1) K, Z = 16, Z' = 1, μ(CuK$_\alpha$) = 0.677, 15105 reflections measured, 1510 unique (R_{int} = 0.0498) which were used in all calculations. The final wR_2 was 0.0794 (all data) and R_1 was 0.0327 (I≥2 σ(I)).

Table S2: Experimental parameters

Compound	**L1H**
CCDC	**2182070**
Formula	$C_9H_{12}N_2O$
$D_{calc.}$/ g cm^{-3}	1.259
μ/mm^{-1}	0.677
Formula Weight	164.21
Colour	clear light colourless
Shape	prism
Size/mm^3	0.69x0.09x0.08
T/K	100.0(1)
Crystal System	orthorhombic
Flack Parameter	unknown
Space Group	*Fdd*2
a/Å	21.7702(6)
b/Å	21.9570(6)
c/Å	7.2513(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	3466.18(17)
Z	16
Z'	1
Wavelength/Å	1.54178
Radiation type	CuK$_\alpha$
Θ_{min}/°	5.724
Θ_{max}/°	66.855
Measured Refl's.	15105
Indep't Refl's	1510
Refl's I≥2 σ(I)	1429
R_{int}	0.0498
Parameters	112
Restraints	1
Largest Peak	0.138
Deepest Hole	-0.187
GooF	1.072
wR_2 (all data)	0.0794
wR_2	0.0778
R_1 (all data)	0.0354
R_1	0.0327

Table S3: Structure Quality Indicators

Reflections:	d min (Cu) 0.84	I/σ(I) 38.0	Rint 4.98%	complete 98%
Refinement:	Shift 0.000	Max Peak 0.1	Min Peak -0.2	GooF 1.072

A clear light colourless prism-shaped crystal with dimensions 0.69 x 0.09 x 0.08 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture (Cu) diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans using CuK_α radiation. The maximum resolution that was achieved was Θ = 66.855° (0.84 Å). The unit cell was refined using **SAINT**[4] on 9915 reflections, 66% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT**[4]. The final completeness is 99.90 % out to 66.855° in Θ. A multi-scan absorption correction was performed using **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0868 before and 0.0704 after correction. The Ratio of minimum to maximum transmission is 0.8195. The absorption coefficient μ of this material is 0.677 mm^{-1} at this wavelength (λ = 1.54178Å) and the minimum and maximum transmissions are 0.739 and 0.902. The structure was solved and the space group *Fdd*2 (# 43) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 16 and Z' is 1.

Table S4: Bond Lengths in Å for **compound L1H**.

Atom	Atom	Length/Å
O1	C2	1.362(3)
N1	C1	1.416(3)
N1	C7	1.290(3)
N2	C7	1.335(3)
N2	C8	1.448(3)
N2	C9	1.452(3)

Atom	Atom	Length/Å
C1	C2	1.405(3)
C1	C6	1.399(3)
C2	C3	1.390(3)
C3	C4	1.383(3)
C4	C5	1.384(3)
C5	C6	1.389(3)

Table S5: Bond Angles in ° for **compound L1H**.

Atom	Atom	Atom	Angle/°
C7	N1	C1	116.17(18)
C7	N2	C8	121.2(2)
C7	N2	C9	121.0(2)
C8	N2	C9	117.4(2)
C2	C1	N1	118.43(18)
C6	C1	N1	123.19(19)
C6	C1	C2	118.3(2)
O1	C2	C1	122.7(2)

Atom	Atom	Atom	Angle/°
O1	C2	C3	117.41(19)
C3	C2	C1	119.88(19)
C4	C3	C2	120.8(2)
C3	C4	C5	120.1(2)
C4	C5	C6	119.5(2)
C5	C6	C1	121.4(2)
N1	C7	N2	124.7(2)

Table S6: Torsion Angles in ° for **compound L1H**.

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	178.5(2)
N1	C1	C2	O1	4.1(3)
N1	C1	C2	C3	-176.6(2)
N1	C1	C6	C5	177.1(2)
C1	N1	C7	N2	-174.9(2)

Atom	Atom	Atom	Atom	Angle/°
C1	C2	C3	C4	-0.9(3)
C2	C1	C6	C5	0.2(3)
C2	C3	C4	C5	0.5(4)
C3	C4	C5	C6	0.3(4)
C4	C5	C6	C1	-0.6(4)
C6	C1	C2	O1	-178.8(2)
C6	C1	C2	C3	0.5(3)
C7	N1	C1	C2	-143.1(2)
C7	N1	C1	C6	40.0(3)
C8	N2	C7	N1	5.0(3)
C9	N2	C7	N1	177.5(2)

Table S7: Hydrogen Bond information for **compound L1H**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	N1[1]	0.84	2.07	2.837(2)	151.9

––––

[1]1/2-x,3/2-y,+z

Compound L3H

R_1=3.96%

Crystal Data and Experimental

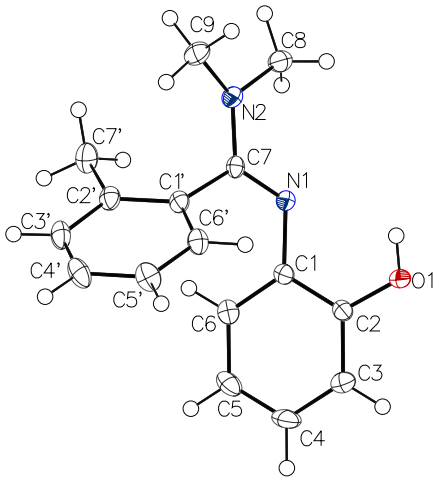


Figure S122: ORTEP view of compound **L3H**

Experimental. Single clear light colourless block-shaped crystals of **compound L3H** recrystallised from a mixture of DCM and pentane by slow evaporation. A suitable crystal with dimensions 0.33 x 0.25 x 0.19 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] 2018/2 solution program using dual methods and by using **Olex2**[2] **1.5** as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{16}H_{18}N_2O$, M_r = 254.32, orthorhombic, *Pccn* (No. 56), a = 16.7113(6) Å, b = 10.8251(4) Å, c = 15.6437(6) Å, α = β = γ = 90°, V = 2829.97(18) Å^3, T = 110.0(1) K, Z = 8, Z' = 1, μ(Mo K$_{\alpha1}$) = 0.075, 50670 reflections measured, 3246 unique (R_{int} = 0.0548) which were used in all calculations. The final wR_2 was 0.1016 (all data) and R_1 was 0.0396 (I≥2 σ(I)).

Table S8: Experimental parameters

Compound	**L3H**
CCDC	**2182071**
Formula	$C_{16}H_{18}N_2O$
$D_{calc.}$/ g cm^{-3}	1.194
μ/mm^{-1}	0.075
Formula Weight	254.32
Colour	clear light colourless
Shape	block-shaped
Size/mm^3	0.33x0.25x0.19
T/K	110.0(1)
Crystal System	orthorhombic
Space Group	*Pccn*
a/Å	16.7113(6)
b/Å	10.8251(4)
c/Å	15.6437(6)
α/°	90
β/°	90
γ/°	90
V/Å^3	2829.97(18)
Z	8
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.592
Θ_{max}/°	27.511
Measured Refl's.	50670
Indep't Refl's	3246
Refl's I≥2 σ(I)	2378
R_{int}	0.0548
Parameters	176
Restraints	0
Largest Peak	0.242
Deepest Hole	-0.242
GooF	1.056
wR_2 (all data)	0.1016
wR_2	0.0867
R_1 (all data)	0.0662
R_1	0.0396

Table S9: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.0°	0.77	I/σ(I)	37.9	Rint	5.48%	Full 50.5°	99.9
Refinement:	Shift	0.000	Max Peak	0.2	Min Peak	-0.2	GooF	1.056

A clear light colourless block-shaped-shaped crystal with dimensions 0.33 x 0.25 x 0.19 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6] . The maximum resolution that was achieved was Θ = 27.511° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 8989 reflections, 18% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4] . The final completeness is 99.90 % out to 27.511° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0568 before and 0.0538 after correction. The Ratio of minimum to maximum transmission is 0.9385. The absorption coefficient μ of this material is 0.075 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.911 and 0.971. The structure was solved and the space group *Pccn* (# 56) determined by the **ShelXT**[1] **2018/2** structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Table S10: Bond Lengths in Å for **compound L3H**.

Atom	Atom	Length/Å
O1	C2	1.3613(16)
N1	C7	1.3039(16)
N1	C1	1.4212(16)
N2	C7	1.3559(17)
N2	C9	1.4585(17)
N2	C8	1.4531(18)
C7	C1'	1.5012(18)
C1	C2	1.4054(18)
C1	C6	1.3963(19)
C2	C3	1.3897(19)

Atom	Atom	Length/Å
C1'	C2'	1.4034(19)
C1'	C6'	1.396(2)
C6	C5	1.386(2)
C2'	C3'	1.399(2)
C2'	C7'	1.507(2)
C3	C4	1.385(2)
C6'	C5'	1.383(2)
C3'	C4'	1.380(2)
C5	C4	1.386(2)
C4'	C5'	1.385(2)

Table S11: Bond Angles in ° for **compound L3H**.

Atom	Atom	Atom	Angle/°
C7	N1	C1	119.56(11)
C7	N2	C9	122.91(12)
C7	N2	C8	119.49(11)
C8	N2	C9	115.44(12)
N1	C7	N2	119.70(12)
N1	C7	C1'	123.17(12)
N2	C7	C1'	117.13(11)
C2	C1	N1	118.13(12)
C6	C1	N1	123.60(12)
C6	C1	C2	118.22(12)
O1	C2	C1	123.09(12)
O1	C2	C3	116.77(12)
C3	C2	C1	120.12(12)

Atom	Atom	Atom	Angle/°
C2'	C1'	C7	121.14(12)
C6'	C1'	C7	118.52(12)
C6'	C1'	C2'	120.22(13)
C5	C6	C1	121.46(13)
C1'	C2'	C7'	122.68(13)
C3'	C2'	C1'	118.02(13)
C3'	C2'	C7'	119.29(13)
C4	C3	C2	120.54(13)
C5'	C6'	C1'	120.59(13)
C4'	C3'	C2'	121.30(13)
C6	C5	C4	119.57(13)
C3	C4	C5	120.02(13)
C3'	C4'	C5'	120.32(14)

Atom	Atom	Atom	Angle/°
C6'	C5'	C4'	119.52(14)

Table S12: Torsion Angles in ° for **compound L3H**.

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	179.27(13)
N1	C7	C1'	C2'	-116.88(15)
N1	C7	C1'	C6'	59.25(18)
N1	C1	C2	O1	1.66(19)
N1	C1	C2	C3	179.63(12)
N1	C1	C6	C5	179.57(13)
N2	C7	C1'	C2'	62.65(17)
N2	C7	C1'	C6'	-121.21(13)
C7	N1	C1	C2	-128.40(13)
C7	N1	C1	C6	54.23(18)
C7	C1'	C2'	C3'	176.65(12)
C7	C1'	C2'	C7'	-2.1(2)
C7	C1'	C6'	C5'	-177.52(13)
C1	N1	C7	N2	-171.60(11)
C1	N1	C7	C1'	7.93(19)
C1	C2	C3	C4	1.2(2)
C1	C6	C5	C4	0.2(2)
C2	C1	C6	C5	2.2(2)
C2	C3	C4	C5	1.3(2)
C1'	C2'	C3'	C4'	0.9(2)
C1'	C6'	C5'	C4'	0.6(2)
C6	C1	C2	O1	179.17(12)
C6	C1	C2	C3	-2.86(19)
C6	C5	C4	C3	-1.9(2)
C2'	C1'	C6'	C5'	-1.4(2)
C2'	C3'	C4'	C5'	-1.7(2)
C6'	C1'	C2'	C3'	0.58(19)
C6'	C1'	C2'	C7'	-178.12(13)
C3'	C4'	C5'	C6'	0.9(2)
C9	N2	C7	N1	-155.50(13)
C9	N2	C7	C1'	24.95(18)
C7'	C2'	C3'	C4'	179.70(13)
C8	N2	C7	N1	7.04(19)
C8	N2	C7	C1'	-172.51(12)

Table S13: Hydrogen Bond information for **compound L3H**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	N1[1]	0.84	2.01	2.7509(14)	146.5

––––

[1]3/2-x,3/2-y,+z

Compound L4H

Pacsmub PLATEFORME Analyse Chimique Synthèse Moléculaire UNIVERSITÉ DE BOURGOGNE

R_1=8.68%

Crystal Data and Experimental

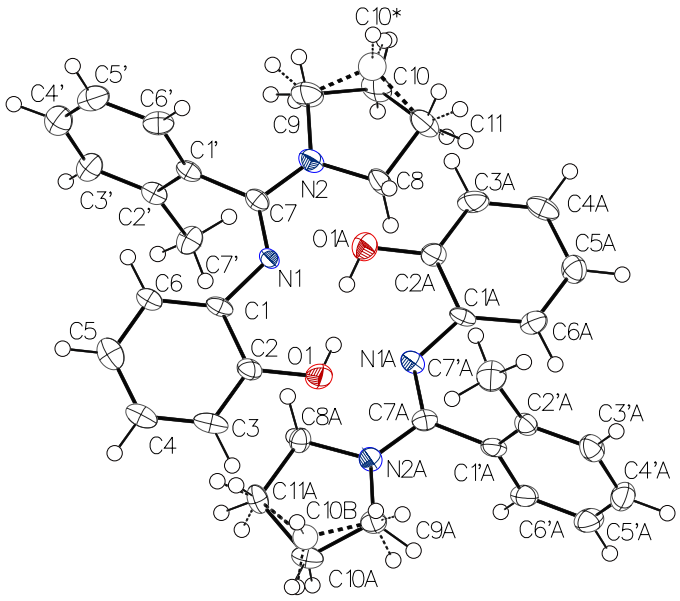


Figure S123: ORTEP view of compound **L4H**

Experimental. Single clear light colourless block-shaped crystals of **compound L4H** recrystallised from a mixture of DCM and pentane by slow evaporation. A suitable crystal with dimensions 0.66 x 0.56 x 0.47 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{18}H_{20}N_2O$, M_r = 280.36, orthorhombic, $Pna2_1$ (No. 33), a = 19.8302(12) Å, b = 8.1178(5) Å, c = 18.3922(12) Å, α = β = γ = 90°, V = 2960.7(3) Å^3, T = 110.0(1) K, Z = 8, Z' = 2, μ(Mo $K_{\alpha1}$) = 0.079, 68139 reflections measured, 5224 unique (R_{int} = 0.0728) which were used in all calculations. The final wR_2 was 0.2340 (all data) and R_1 was 0.0868 (I≥2 σ(I)).

Table S14: Experimental parameters

Compound	**L4H**
CCDC	**2182072**
Formula	$C_{18}H_{20}N_2O$
$D_{calc.}$/ g cm^{-3}	1.258
μ/mm^{-1}	0.079
Formula Weight	280.36
Colour	clear light colourless
Shape	block-shaped
Size/mm^3	0.66x0.56x0.47
T/K	110.0(1)
Crystal System	orthorhombic
Flack Parameter	1(4)
Hooft Parameter	-0.2(7)
Space Group	$Pna2_1$
a/Å	19.8302(12)
b/Å	8.1178(5)
c/Å	18.3922(12)
α/°	90
β/°	90
γ/°	90
V/Å^3	2960.7(3)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	Mo $K_{\alpha1}$
Θ_{min}/°	2.054
Θ_{max}/°	24.998
Measured Refl's.	68139
Indep't Refl's	5224
Refl's I≥2 σ(I)	4631
R_{int}	0.0728
Parameters	394
Restraints	1
Largest Peak	0.743
Deepest Hole	-0.410
GooF	1.192
wR_2 (all data)	0.2340
wR_2	0.2210
R_1 (all data)	0.0971
R_1	0.0868

Table S15: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=50.0° 0.84	I/σ(I) 25.9	Rint 7.28%	Full 50.0° 99.9
Refinement:	Shift 0.000	Max Peak 0.7	Min Peak -0.4	GooF 1.192

A clear light colourless block-shaped-shaped crystal with dimensions 0.66 x 0.56 x 0.47 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6] . The maximum resolution that was achieved was Θ = 24.998° (0.84 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9903 reflections, 15% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4] . The final completeness is 99.90 % out to 24.998° in Θ. **SADABS-2016/2**[5] (Bruker, 2016/2) was used for absorption correction. wR_2(int) was 0.1013 before and 0.0904 after correction. The Ratio of minimum to maximum transmission is 0.8389. The absorption coefficient μ of this material is 0.079 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.804 and 0.958. The structure was solved and the space group $Pna2_1$ (# 33) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically, excepted minor disordered part on each pyrrolidine (**Table**). Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table S16: Bond Lengths in Å for **compound L4H**.

Atom	Atom	Length/Å
O1	C2	1.372(8)
N1	C1	1.426(8)
N1	C7	1.293(9)
N2	C7	1.348(8)
N2	C8	1.433(9)
N2	C9	1.469(9)
C1	C2	1.401(9)
C1	C6	1.388(9)
C1'	C2'	1.417(8)
C1'	C6'	1.402(9)
C1'	C7	1.489(9)
C2	C3	1.377(10)
C2'	C3'	1.388(9)
C2'	C7'	1.488(9)
C3	C4	1.369(11)
C3'	C4'	1.396(10)
C4	C5	1.393(11)
C4'	C5'	1.394(10)
C5	C6	1.393(9)
C5'	C6'	1.387(10)
C8	C11	1.537(10)
C9	C10	1.494(12)
C9	C10*	1.39(4)
C10	C11	1.517(12)
C10*	C11	1.52(4)

Atom	Atom	Length/Å
O1A	C2A	1.360(8)
N1A	C1A	1.395(8)
N1A	C7A	1.316(8)
N2A	C7A	1.348(8)
N2A	C8A	1.459(8)
N2A	C9A	1.480(9)
C1'A	C2'A	1.376(9)
C1'A	C6'A	1.395(9)
C1'A	C7A	1.500(9)
C1A	C2A	1.407(9)
C1A	C6A	1.400(9)
C2'A	C3'A	1.396(9)
C2'A	C7'A	1.498(10)
C2A	C3A	1.393(11)
C3'A	C4'A	1.396(10)
C3A	C4A	1.368(11)
C4'A	C5'A	1.372(10)
C4A	C5A	1.389(10)
C5'A	C6'A	1.380(10)
C5A	C6A	1.396(10)
C8A	C11A	1.527(10)
C9A	C10A	1.505(12)
C9A	C10B	1.42(3)
C10A	C11A	1.512(11)
C11A	C10B	1.52(3)

Table S17: Bond Angles in ° for **compound L4H**.

Atom	Atom	Atom	Angle/°
C7	N1	C1	126.5(5)
C7	N2	C8	122.4(6)
C7	N2	C9	125.3(6)
C8	N2	C9	112.3(6)
C2	C1	N1	111.8(5)
C6	C1	N1	129.9(6)
C6	C1	C2	118.2(6)
C2'	C1'	C7	119.5(5)
C6'	C1'	C2'	120.5(6)
C6'	C1'	C7	120.0(5)
O1	C2	C1	118.2(6)
O1	C2	C3	120.2(6)
C3	C2	C1	121.6(6)
C1'	C2'	C7'	119.6(6)
C3'	C2'	C1'	118.2(6)
C3'	C2'	C7'	122.1(6)
C4	C3	C2	120.0(7)
C2'	C3'	C4'	121.4(6)
C3	C4	C5	119.6(7)
C5'	C4'	C3'	119.9(7)
C4	C5	C6	120.7(6)
C6'	C5'	C4'	120.1(6)
C1	C6	C5	119.9(6)
C5'	C6'	C1'	119.9(6)
N1	C7	N2	117.9(6)
N1	C7	C1'	126.8(6)
N2	C7	C1'	115.4(6)
N2	C8	C11	104.6(6)
N2	C9	C10	102.6(7)
C10*	C9	N2	104.8(17)
C9	C10	C11	104.5(7)
C9	C10*	C11	110(3)
C10	C11	C8	103.3(6)
C10*	C11	C8	102.9(16)

Atom	Atom	Atom	Angle/°
C7A	N1A	C1A	125.1(5)
C7A	N2A	C8A	122.9(5)
C7A	N2A	C9A	125.1(5)
C8A	N2A	C9A	111.7(5)
C2'A	C1'A	C6'A	121.5(6)
C2'A	C1'A	C7A	120.4(6)
C6'A	C1'A	C7A	118.2(6)
N1A	C1A	C2A	111.2(5)
N1A	C1A	C6A	132.6(6)
C6A	C1A	C2A	116.2(6)
C1'A	C2'A	C3'A	117.9(6)
C1'A	C2'A	C7'A	121.5(6)
C3'A	C2'A	C7'A	120.6(6)
O1A	C2A	C1A	117.9(6)
O1A	C2A	C3A	120.2(6)
C3A	C2A	C1A	121.8(6)
C4'A	C3'A	C2'A	120.8(6)
C4A	C3A	C2A	120.2(6)
C5'A	C4'A	C3'A	120.2(6)
C3A	C4A	C5A	120.1(7)
C4'A	C5'A	C6'A	119.7(6)
C4A	C5A	C6A	119.3(6)
C5'A	C6'A	C1'A	119.8(6)
C5A	C6A	C1A	122.3(6)
N1A	C7A	N2A	117.6(6)
N1A	C7A	C1'A	126.2(6)
N2A	C7A	C1'A	116.2(5)
N2A	C8A	C11A	103.8(5)
N2A	C9A	C10A	102.5(6)
C10B	C9A	N2A	106.6(14)
C9A	C10A	C11A	103.9(7)
C10A	C11A	C8A	105.9(6)
C10B	C11A	C8A	105.8(13)
C9A	C10B	C11A	108(2)

Table S18: Torsion Angles in ° for **compound L4H**.

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	-179.6(6)
N1	C1	C2	O1	-2.2(8)
N1	C1	C2	C3	179.8(6)
N1	C1	C6	C5	-178.5(6)
N2	C8	C11	C10	-22.0(8)
N2	C8	C11	C10*	12.3(19)
N2	C9	C10	C11	-33.6(9)
N2	C9	C10*	C11	24(3)
C1	N1	C7	N2	179.2(6)
C1	N1	C7	C1'	-1.0(10)
C1	C2	C3	C4	-1.6(10)
C1'	C2'	C3'	C4'	-0.4(11)
C2	C1	C6	C5	-1.4(9)
C2	C3	C4	C5	0.1(10)
C2'	C1'	C6'	C5'	0.9(10)
C2'	C1'	C7	N1	-80.0(9)

Atom	Atom	Atom	Atom	Angle/°
C2'	C1'	C7	N2	99.8(7)
C2'	C3'	C4'	C5'	1.3(11)
C3	C4	C5	C6	0.6(10)
C3'	C4'	C5'	C6'	-1.1(11)
C4	C5	C6	C1	0.0(9)
C4'	C5'	C6'	C1'	0.0(11)
C6	C1	C2	O1	-179.7(6)
C6	C1	C2	C3	2.2(9)
C6'	C1'	C2'	C3'	-0.7(10)
C6'	C1'	C2'	C7'	175.7(6)
C6'	C1'	C7	N1	98.1(8)
C6'	C1'	C7	N2	-82.1(8)
C7	N1	C1	C2	169.7(6)
C7	N1	C1	C6	-13.1(10)
C7	N2	C8	C11	178.6(6)
C7	N2	C9	C10	-156.9(7)
C7	N2	C9	C10*	167(2)
C7	C1'	C2'	C3'	177.5(6)
C7	C1'	C2'	C7'	-6.2(10)
C7	C1'	C6'	C5'	-177.2(6)
C7'	C2'	C3'	C4'	-176.7(6)
C8	N2	C7	N1	0.8(9)
C8	N2	C7	C1'	-179.0(6)
C8	N2	C9	C10	20.4(9)
C8	N2	C9	C10*	-16(2)
C9	N2	C7	N1	177.9(6)
C9	N2	C7	C1'	-1.9(9)
C9	N2	C8	C11	1.2(8)
C9	C10	C11	C8	34.7(9)
C9	C10*	C11	C8	-23(3)
O1A	C2A	C3A	C4A	176.4(6)
N1A	C1A	C2A	O1A	3.2(8)
N1A	C1A	C2A	C3A	-178.2(6)
N1A	C1A	C6A	C5A	179.1(6)
N2A	C8A	C11A	C10A	-17.1(7)
N2A	C8A	C11A	C10B	15.9(15)
N2A	C9A	C10A	C11A	-34.2(8)
N2A	C9A	C10B	C11A	19(2)
C1'A	C2'A	C3'A	C4'A	-3.1(11)
C1A	N1A	C7A	N2A	-178.2(5)
C1A	N1A	C7A	C1'A	1.8(10)
C1A	C2A	C3A	C4A	-2.2(10)
C2'A	C1'A	C6'A	C5'A	-1.4(10)
C2'A	C1'A	C7A	N1A	81.1(9)
C2'A	C1'A	C7A	N2A	-98.9(7)
C2'A	C3'A	C4'A	C5'A	1.5(11)
C2A	C1A	C6A	C5A	2.2(9)
C2A	C3A	C4A	C5A	3.5(10)
C3'A	C4'A	C5'A	C6'A	0.3(11)
C3A	C4A	C5A	C6A	-1.9(10)
C4'A	C5'A	C6'A	C1'A	-0.4(10)
C4A	C5A	C6A	C1A	-1.0(10)
C6'A	C1'A	C2'A	C3'A	3.1(10)
C6'A	C1'A	C2'A	C7'A	-175.9(7)
C6'A	C1'A	C7A	N1A	-97.9(8)
C6'A	C1'A	C7A	N2A	82.1(8)
C6A	C1A	C2A	O1A	-179.3(6)
C6A	C1A	C2A	C3A	-0.6(9)
C7'A	C2'A	C3'A	C4'A	175.8(7)
C7A	N1A	C1A	C2A	-170.1(6)

Atom	Atom	Atom	Atom	Angle/°
C7A	N1A	C1A	C6A	12.9(10)
C7A	N2A	C8A	C11A	-179.6(6)
C7A	N2A	C9A	C10A	-160.7(7)
C7A	N2A	C9A	C10B	165.7(16)
C7A	C1'A	C2'A	C3'A	-175.9(6)
C7A	C1'A	C2'A	C7'A	5.2(10)
C7A	C1'A	C6'A	C5'A	177.6(6)
C8A	N2A	C7A	N1A	0.8(9)
C8A	N2A	C7A	C1'A	-179.3(6)
C8A	N2A	C9A	C10A	24.8(8)
C8A	N2A	C9A	C10B	-8.8(17)
C8A	C11A	C10B	C9A	-22(2)
C9A	N2A	C7A	N1A	-173.1(6)
C9A	N2A	C7A	C1'A	6.9(9)
C9A	N2A	C8A	C11A	-5.0(7)
C9A	C10A	C11A	C8A	32.3(8)

Table S19: Hydrogen Bond information for **compound L4H**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H	N1	0.84	2.11	2.581(7)	115.0
O1A	H1A	N1A	0.84	2.06	2.552(8)	116.9

Table S20: Atomic Occupancies for all atoms that are not fully occupied in **compound L4H**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
HN	0.8	C10*	0.2	H9AA	0.81(8)	H11A	0.81(8)
HO	0.8	HT	0.2	H9AB	0.81(8)	H11B	0.81(8)
HP	0.2	HU	0.2	H9AC	0.19(8)	H11C	0.19(8)
HQ	0.2	HV	0.95(12)	H9AD	0.19(8)	H11D	0.19(8)
C10	0.8	HW	0.95(12)	C10A	0.77	C10B	0.23
HR	0.8	HX	0.05(12)	H10A	0.77	H10C	0.23
HS	0.8	HY	0.05(12)	H10B	0.77	H10D	0.23

Compound L5H

R_1=4.36%

Crystal Data and Experimental

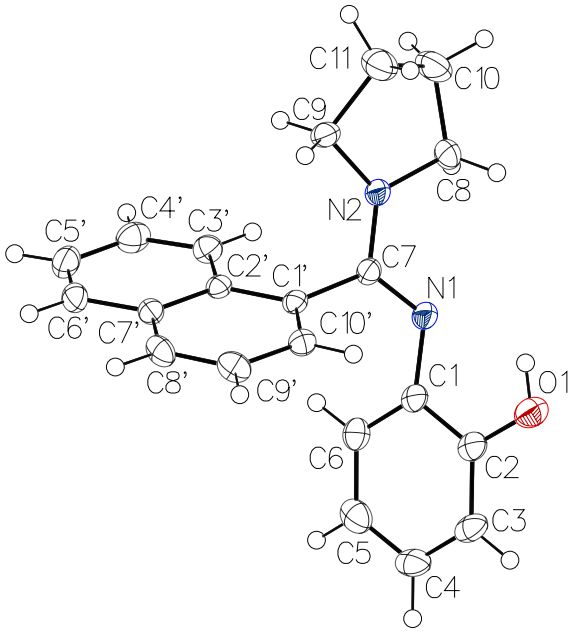


Figure S124: ORTEP view of compound **L5H**

Experimental. Single clear light colourless prism-shaped crystals of **compound L5H** recrystallised from a mixture of DCM and pentane by slow evaporation. A suitable crystal with dimensions 0.87 x 0.62 x 0.53 mm^3 was selected and mounted on a glass fibre oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] 2018/2 solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{21}H_{20}N_2O$, M_r = 316.39, triclinic, P-1 (No. 2), a = 8.7993(2) Å, b = 9.5600(3) Å, c = 11.0330(4) Å, α = 92.371(2)°, β = 100.401(2)°, γ = 114.782(2)°, V = 821.64(5) Å^3, T = 110.0(1) K, Z = 2, Z' = 1, μ(Mo K$_{\alpha1}$) = 0.079, 20523 reflections measured, 3792 unique (R_{int} = 0.0220) which were used in all calculations. The final wR_2 was 0.1193 (all data) and R_1 was 0.0436 (I≥2 σ(I)).

Table S21: Experimental parameters

Compound	**L5H**
CCDC	**2182073**
Formula	$C_{21}H_{20}N_2O$
$D_{calc.}$/ g cm^{-3}	1.279
μ/mm^{-1}	0.079
Formula Weight	316.39
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.87x0.62x0.53
T/K	110.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	8.7993(2)
b/Å	9.5600(3)
c/Å	11.0330(4)
α/°	92.371(2)
β/°	100.401(2)
γ/°	114.782(2)
V/Å^3	821.64(5)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	1.893
Θ_{max}/°	27.532
Measured Refl's.	20523
Indep't Refl's	3792
Refl's I≥2 σ(I)	3047
R_{int}	0.0220
Parameters	218
Restraints	0
Largest Peak	0.296
Deepest Hole	-0.218
GooF	1.055
wR_2 (all data)	0.1193
wR_2	0.1061
R_1 (all data)	0.0587
R_1	0.0436

Table S22: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.1° 0.77	I/σ(I) 57.9	Rint 2.20%	Full 50.5° 100
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.2	GooF 1.055

A clear light colourless prism-shaped-shaped crystal with dimensions 0.87 x 0.62 x 0.53 mm^3 was mounted on a glass fibre oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6] . The maximum resolution that was achieved was Θ = 27.532° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 6361 reflections, 31% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4] . The final completeness is 100.00 % out to 27.532° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0529 before and 0.0389 after correction. The Ratio of minimum to maximum transmission is 0.8878. The absorption coefficient μ of this material is 0.079 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.851 and 0.958. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] **2018/2** structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] **2018/3** . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table S23: Bond Lengths in Å for **compound L5H**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.3723(18)	C3	C4	1.386(2)
N1	C1	1.4087(17)	C3'	C4'	1.368(2)
N1	C7	1.2978(17)	C4	C5	1.380(2)
N2	C7	1.3419(17)	C4'	C5'	1.409(2)
N2	C8	1.4684(16)	C5	C6	1.392(2)
N2	C9	1.4680(17)	C5'	C6'	1.360(2)
C1	C2	1.399(2)	C6'	C7'	1.4165(19)
C1	C6	1.390(2)	C7'	C8'	1.4101(19)
C1'	C2'	1.4235(18)	C8	C10	1.519(2)
C1'	C7	1.5013(17)	C8'	C9'	1.360(2)
C1'	C10'	1.3743(18)	C9	C11	1.510(2)
C2	C3	1.383(2)	C9'	C10'	1.4142(19)
C2'	C3'	1.4180(18)	C10	C11	1.519(2)
C2'	C7'	1.4224(17)			

Table S24: Bond Angles in ° for **compound L5H**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C1	120.92(11)	C3	C2	C1	121.34(14)
C7	N2	C8	121.89(11)	C3'	C2'	C1'	122.79(11)
C7	N2	C9	125.92(11)	C3'	C2'	C7'	118.57(12)
C9	N2	C8	111.90(11)	C7'	C2'	C1'	118.63(11)
C2	C1	N1	116.43(12)	C2	C3	C4	119.49(14)
C6	C1	N1	124.95(13)	C4'	C3'	C2'	120.58(13)
C6	C1	C2	118.30(13)	C5	C4	C3	120.09(14)
C2'	C1'	C7	121.17(11)	C3'	C4'	C5'	120.73(14)
C10'	C1'	C2'	120.12(11)	C4	C5	C6	120.34(15)
C10'	C1'	C7	118.66(11)	C6'	C5'	C4'	120.08(13)
O1	C2	C1	119.51(12)	C1	C6	C5	120.41(14)
O1	C2	C3	119.15(13)	C5'	C6'	C7'	120.93(13)

Atom	Atom	Atom	Angle/°
N1	C7	N2	118.95(12)
N1	C7	C1'	125.09(12)
N2	C7	C1'	115.86(11)
C6'	C7'	C2'	119.12(13)
C8'	C7'	C2'	119.57(12)
C8'	C7'	C6'	121.29(12)
N2	C8	C10	103.47(11)
C9'	C8'	C7'	120.71(12)
N2	C9	C11	102.83(11)
C8'	C9'	C10'	120.41(13)
C11	C10	C8	104.44(12)
C1'	C10'	C9'	120.52(12)
C9	C11	C10	103.21(13)

Table S25: Torsion Angles in ° for **compound L5H**.

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	-178.30(12)
N1	C1	C2	O1	4.93(18)
N1	C1	C2	C3	-175.52(12)
N1	C1	C6	C5	173.53(13)
N2	C8	C10	C11	25.23(17)
N2	C9	C11	C10	34.25(16)
C1	N1	C7	N2	-172.87(12)
C1	N1	C7	C1'	10.8(2)
C1	C2	C3	C4	2.1(2)
C1'	C2'	C3'	C4'	178.25(13)
C1'	C2'	C7'	C6'	-178.86(12)
C1'	C2'	C7'	C8'	-0.66(18)
C2	C1	C6	C5	0.2(2)
C2	C3	C4	C5	-1.2(2)
C2'	C1'	C7	N1	-117.34(15)
C2'	C1'	C7	N2	66.23(17)
C2'	C1'	C10'	C9'	-2.1(2)
C2'	C3'	C4'	C5'	0.5(2)
C2'	C7'	C8'	C9'	-1.0(2)
C3	C4	C5	C6	-0.2(2)
C3'	C2'	C7'	C6'	-0.20(18)
C3'	C2'	C7'	C8'	178.00(12)
C3'	C4'	C5'	C6'	0.0(2)
C4	C5	C6	C1	0.7(2)
C4'	C5'	C6'	C7'	-0.5(2)
C5'	C6'	C7'	C2'	0.6(2)
C5'	C6'	C7'	C8'	-177.53(13)
C6	C1	C2	O1	178.82(12)
C6	C1	C2	C3	-1.63(19)
C6'	C7'	C8'	C9'	177.11(13)
C7	N1	C1	C2	-126.45(14)
C7	N1	C1	C6	60.12(19)
C7	N2	C8	C10	-177.89(13)
C7	N2	C9	C11	154.58(14)
C7	C1'	C2'	C3'	6.34(19)
C7	C1'	C2'	C7'	-175.05(11)
C7	C1'	C10'	C9'	175.23(12)
C7'	C2'	C3'	C4'	-0.4(2)
C7'	C8'	C9'	C10'	1.2(2)
C8	N2	C7	N1	1.8(2)
C8	N2	C7	C1'	178.50(12)
C8	N2	C9	C11	-19.39(16)
C8	C10	C11	C9	-37.36(18)
C8'	C9'	C10'	C1'	0.4(2)
C9	N2	C7	N1	-171.57(13)
C9	N2	C7	C1'	5.09(19)
C9	N2	C8	C10	-3.64(16)
C10'	C1'	C2'	C3'	-176.38(12)
C10'	C1'	C2'	C7'	2.23(18)

Atom	Atom	Atom	Atom	Angle/°
C10'	C1'	C7	N1	65.34(18)
C10'	C1'	C7	N2	-111.09(14)

Table S26: Hydrogen Bond information for **compound L5H**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	N1	0.84	2.23	2.7045(15)	116.2

Compound 1a

R_1=3.55%

Crystal Data and Experimental

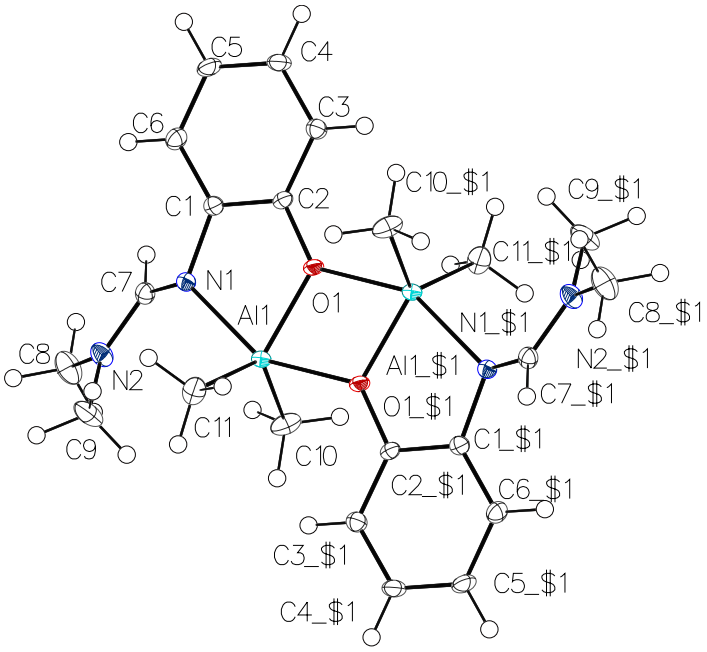


Figure S125: ORTEP view of compound **1a**

Experimental. Single clear light colourless prism-shaped crystals of **compound 1a** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.27 x 0.22 x 0.17 mm³ was selected and mounted on a MITIGEN holder oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{22}H_{34}Al_2N_4O_2$, M_r = 440.49, monoclinic, $P2_1/n$ (No. 14), a = 8.7561(7) Å, b = 10.6856(7) Å, c = 12.8516(9) Å, β = 99.758(3)°, α = γ = 90°, V = 1185.05(15) Å³, T = 100.0(1) K, Z = 2, Z' = 0.5, μ(Mo $K_{\alpha1}$) = 0.148, 35086 reflections measured, 2733 unique (R_{int} = 0.0600) which were used in all calculations. The final wR_2 was 0.0915 (all data) and R_1 was 0.0355 (I≥2 σ(I)).

Table S27: Experimental parameters

Compound	**1a**
CCDC	**2182074**
Formula	$C_{22}H_{34}Al_2N_4O_2$
$D_{calc.}$/ g cm^{-3}	1.234
μ/mm^{-1}	0.148
Formula Weight	440.49
Colour	clear light colourless
Shape	prism-shaped
Size/mm³	0.27x0.22x0.17
T/K	100.0(1)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	8.7561(7)
b/Å	10.6856(7)
c/Å	12.8516(9)
α/°	90
β/°	99.758(3)
γ/°	90
V/Å³	1185.05(15)
Z	2
Z'	0.5
Wavelength/Å	0.71073
Radiation type	Mo $K_{\alpha1}$
Θ_{min}/°	3.034
Θ_{max}/°	27.549
Measured Refl's.	35086
Indep't Refl's	2733
Refl's I≥2 σ(I)	2337
R_{int}	0.0600
Parameters	140
Restraints	0
Largest Peak	0.301
Deepest Hole	-0.274
GooF	1.063
wR_2 (all data)	0.0915
wR_2	0.0859
R_1 (all data)	0.0464
R_1	0.0355

Table S28: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.1° 0.77	I/σ(I) 44.8	Rint 6.00%	Full 50.5° 99.9
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.3	GooF 1.063

A clear light colourless prism-shaped-shaped crystal with dimensions 0.27 x 0.22 x 0.17 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 VENTURE diffractometer operating at T = 100.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 27.549° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9909 reflections, 28% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 27.549° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0636 before and 0.0591 after correction. The Ratio of minimum to maximum transmission is 0.9215. The absorption coefficient μ of this material is 0.148 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.894 and 0.971. The structure was solved, and the space group $P2_1/n$ (# 14) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S29: Bond Lengths in Å for **compound 1a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Al1	O1	1.8509(10)	N1	C1	1.4205(17)
Al1	O1[1]	2.0254(11)	C2	C1	1.4009(19)
Al1	N1	2.1742(12)	C2	C3	1.3881(19)
Al1	C10	1.9751(15)	C1	C6	1.3942(19)
Al1	C11	1.9789(15)	C5	C4	1.387(2)
O1	C2	1.3565(16)	C5	C6	1.394(2)
N2	C7	1.3260(18)	C4	C3	1.396(2)
N2	C9	1.454(2)	----		
N2	C8	1.4594(19)	[1]1-x,1-y,1-z		
N1	C7	1.3091(18)			

Table S30: Bond Angles in ° for **compound 1a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Al1	O1[1]	73.25(5)	C7	N2	C8	120.78(13)
O1[1]	Al1	N1	152.62(5)	C9	N2	C8	116.58(13)
O1	Al1	N1	79.64(4)	C7	N1	Al1	130.63(10)
O1	Al1	C10	118.82(6)	C7	N1	C1	115.16(12)
O1	Al1	C11	116.20(6)	C1	N1	Al1	108.29(9)
C10	Al1	O1[1]	94.94(6)	N1	C7	N2	125.27(13)
C10	Al1	N1	94.74(6)	O1	C2	C1	116.18(12)
C10	Al1	C11	124.45(7)	O1	C2	C3	123.25(12)
C11	Al1	O1[1]	93.50(5)	C3	C2	C1	120.57(13)
C11	Al1	N1	101.93(6)	C2	C1	N1	114.50(12)
Al1	O1	Al1[1]	106.75(5)	C6	C1	N1	125.98(13)
C2	O1	Al1[1]	132.28(9)	C6	C1	C2	119.43(13)
C2	O1	Al1	120.92(9)	C4	C5	C6	120.04(13)
C7	N2	C9	122.57(13)	C5	C4	C3	120.47(13)

Atom	Atom	Atom	Angle/°
C2	C3	C4	119.40(13)
C1	C6	C5	120.02(13)

––––
[1]1-x,1-y,1-z

Table S31: Torsion Angles in ° for **compound 1a**.

Atom	Atom	Atom	Atom	Angle/°
Al1	O1	C2	C1	-5.15(16)
Al1[1]	O1	C2	C1	177.75(9)
Al1	O1	C2	C3	174.33(10)
Al1[1]	O1	C2	C3	-2.8(2)
Al1	N1	C7	N2	44.2(2)
Al1	N1	C1	C2	4.93(14)
Al1	N1	C1	C6	-171.61(12)
O1[1]	Al1	O1	Al1[1]	-0.001(1)
O1[1]	Al1	O1	C2	-177.76(13)
O1	C2	C1	N1	-0.72(17)
O1	C2	C1	C6	176.07(12)
O1	C2	C3	C4	-176.92(13)
N1	Al1	O1	Al1[1]	-176.13(6)
N1	Al1	O1	C2	6.12(10)
N1	C1	C6	C5	178.65(13)
C7	N1	C1	C2	-150.99(12)
C7	N1	C1	C6	32.5(2)
C2	C1	C6	C5	2.3(2)
C1	N1	C7	N2	-166.45(13)
C1	C2	C3	C4	2.5(2)
C5	C4	C3	C2	-0.5(2)
C4	C5	C6	C1	-0.2(2)
C3	C2	C1	N1	179.78(12)
C3	C2	C1	C6	-3.4(2)
C6	C5	C4	C3	-0.7(2)
C10	Al1	O1	Al1[1]	-86.39(7)
C10	Al1	O1	C2	95.85(11)
C11	Al1	O1	Al1[1]	85.58(7)
C11	Al1	O1	C2	-92.18(11)
C9	N2	C7	N1	6.9(2)
C8	N2	C7	N1	-169.98(14)

––––
[1]1-x,1-y,1-z

Compound 1b

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R_1=3.78%

Crystal Data and Experimental

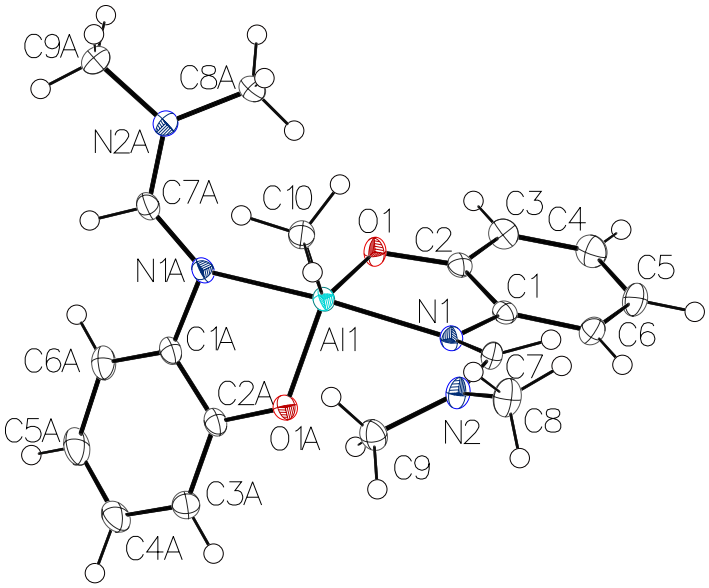

Figure S126: ORTEP view of compound **1b**

Experimental. Single clear light colourless prism-shaped crystals of **compound 1b** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.63 x 0.22 x 0.22 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 120.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{19}H_{25}AlN_4O_2$, M_r = 368.41, monoclinic, $P2_1/c$ (No. 14), a = 12.0344(13) Å, b = 13.1284(16) Å, c = 12.6875(15) Å, β = 107.976(4)°, α = γ = 90°, V = 1906.7(4) Å^3, T = 120.0(1) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.127, 49921 reflections measured, 4390 unique (R_{int} = 0.0620) which were used in all calculations. The final wR_2 was 0.0971 (all data) and R_1 was 0.0378 (I≥2 σ(I)).

Table S32: Experimental parameters

Compound	**1b**
CCDC	**2182075**
Formula	$C_{19}H_{25}AlN_4O_2$
$D_{calc.}$/ g cm^{-3}	1.283
μ/mm^{-1}	0.127
Formula Weight	368.41
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.63x0.22x0.22
T/K	120.0(1)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	12.0344(13)
b/Å	13.1284(16)
c/Å	12.6875(15)
α/°	90
β/°	107.976(4)
γ/°	90
V/Å^3	1906.7(4)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.563
Θ_{max}/°	27.584
Measured Refl's.	49921
Indep't Refl's	4390
Refl's I≥2 σ(I)	3550
R_{int}	0.0620
Parameters	240
Restraints	0
Largest Peak	0.338
Deepest Hole	-0.386
GooF	1.038
wR_2 (all data)	0.0971
wR_2	0.0867
R_1 (all data)	0.0559
R_1	0.0378

Table S33: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.2° 0.77	I/σ(I) 38.2	Rint 6.20%	Full 50.5° 99% to 55.2° 99.9
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.4	GooF 1.038

A clear light colourless prism-shaped-shaped crystal with dimensions 0.63 x 0.22 x 0.22 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 120.0(1) K. Data were measured using ϕ and ω scans with MoK_α radiation. The maximum resolution that was achieved was Θ = 27.584° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9714 reflections, 19% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 27.584° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0681 before and 0.0568 after correction. The Ratio of minimum to maximum transmission is 0.9196. The absorption coefficient μ of this material is 0.127 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.892 and 0.971. The structure was solved, and the space group $P2_1/c$ (# 14) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

Table S34: Bond Lengths in Å for **compound 1b**.

Atom	Atom	Length/Å
Al1	O1	1.8000(11)
Al1	O1A	1.7905(11)
Al1	N1	2.1109(13)
Al1	N1A	2.1604(13)
Al1	C10	1.9802(16)
O1	C2	1.3418(17)
O1A	C2A	1.3414(18)
N1	C1	1.4221(18)
N1	C7	1.3147(19)
N1A	C1A	1.4233(18)
N1A	C7A	1.3062(19)
N2	C7	1.3199(19)
N2	C8	1.4644(19)
N2	C9	1.4600(19)
N2A	C7A	1.3275(19)
N2A	C8A	1.4526(19)
N2A	C9A	1.458(2)
C1	C2	1.408(2)
C1	C6	1.393(2)
C1A	C2A	1.404(2)
C1A	C6A	1.395(2)
C2	C3	1.388(2)
C2A	C3A	1.391(2)
C3	C4	1.395(2)
C3A	C4A	1.394(2)
C4	C5	1.383(2)
C4A	C5A	1.382(3)
C5	C6	1.395(2)
C5A	C6A	1.394(2)

Table S35: Bond Angles in ° for **compound 1b**.

Atom	Atom	Atom	Angle/°
O1	Al1	N1	82.74(5)
O1	Al1	N1A	85.97(5)
O1	Al1	C10	123.06(6)
O1A	Al1	O1	116.74(5)
O1A	Al1	N1	93.66(5)
O1A	Al1	N1A	81.99(5)
O1A	Al1	C10	120.04(6)
N1	Al1	N1A	164.53(5)
C10	Al1	N1	97.49(6)
C10	Al1	N1A	97.53(6)
C2	O1	Al1	118.45(9)
C2A	O1A	Al1	118.90(9)
C1	N1	Al1	107.64(9)
C7	N1	Al1	133.01(10)
C7	N1	C1	115.74(12)
C1A	N1A	Al1	105.89(9)
C7A	N1A	Al1	136.70(10)
C7A	N1A	C1A	115.50(12)
C7	N2	C8	120.26(13)
C7	N2	C9	123.73(13)
C9	N2	C8	115.95(12)
C7A	N2A	C8A	123.89(13)

Atom	Atom	Atom	Angle/°
C7A	N2A	C9A	120.42(13)
C8A	N2A	C9A	115.66(12)
C2	C1	N1	112.96(12)
C6	C1	N1	127.34(13)
C6	C1	C2	119.67(13)
C2A	C1A	N1A	113.30(12)
C6A	C1A	N1A	126.59(14)
C6A	C1A	C2A	120.06(14)
O1	C2	C1	117.98(13)
O1	C2	C3	122.14(13)
C3	C2	C1	119.88(14)
O1A	C2A	C1A	118.26(13)
O1A	C2A	C3A	122.34(14)
C3A	C2A	C1A	119.40(14)
C2	C3	C4	120.13(15)
C2A	C3A	C4A	119.95(16)
C5	C4	C3	119.93(14)
C5A	C4A	C3A	120.37(15)
C4	C5	C6	120.61(15)
C4A	C5A	C6A	120.23(15)
C1	C6	C5	119.74(14)
C5A	C6A	C1A	119.54(16)
N1	C7	N2	126.25(14)
N1A	C7A	N2A	126.98(14)

Table S36: Torsion Angles in ° for **compound 1b**.

Atom	Atom	Atom	Atom	Angle/°
Al1	O1	C2	C1	-2.74(17)
Al1	O1	C2	C3	177.11(11)
Al1	O1A	C2A	C1A	-6.26(18)
Al1	O1A	C2A	C3A	174.31(12)
Al1	N1	C1	C2	3.82(14)
Al1	N1	C1	C6	-174.42(13)
Al1	N1	C7	N2	35.7(2)
Al1	N1A	C1A	C2A	11.06(14)
Al1	N1A	C1A	C6A	-166.37(13)
Al1	N1A	C7A	N2A	28.4(2)
O1	Al1	O1A	C2A	-71.49(12)
O1	C2	C3	C4	-178.47(14)
O1A	Al1	O1	C2	-86.60(11)
O1A	C2A	C3A	C4A	-176.38(15)
N1	Al1	O1	C2	3.85(10)
N1	Al1	O1A	C2A	-155.20(11)
N1	C1	C2	O1	-1.25(18)
N1	C1	C2	C3	178.90(13)
N1	C1	C6	C5	-179.51(14)
N1A	Al1	O1	C2	-165.54(10)
N1A	Al1	O1A	C2A	9.87(11)
N1A	C1A	C2A	O1A	-4.89(19)
N1A	C1A	C2A	C3A	174.56(13)
N1A	C1A	C6A	C5A	-177.09(14)
C1	N1	C7	N2	-168.84(14)
C1	C2	C3	C4	1.4(2)
C1A	N1A	C7A	N2A	-170.05(14)
C1A	C2A	C3A	C4A	4.2(2)
C2	C1	C6	C5	2.4(2)
C2	C3	C4	C5	0.3(2)
C2A	C1A	C6A	C5A	5.6(2)
C2A	C3A	C4A	C5A	1.6(3)
C3	C4	C5	C6	-0.7(3)
C3A	C4A	C5A	C6A	-3.8(3)
C4	C5	C6	C1	-0.7(2)
C4A	C5A	C6A	C1A	0.2(2)
C6	C1	C2	O1	177.14(13)
C6	C1	C2	C3	-2.7(2)
C6A	C1A	C2A	O1A	172.73(13)
C6A	C1A	C2A	C3A	-7.8(2)
C7	N1	C1	C2	-157.61(13)
C7	N1	C1	C6	24.1(2)
C7A	N1A	C1A	C2A	-155.91(13)

Atom	Atom	Atom	Atom	Angle/°
C7A	N1A	C1A	C6A	26.7(2)
C8	N2	C7	N1	-171.65(15)
C8A	N2A	C7A	N1A	7.3(2)
C9	N2	C7	N1	11.3(2)
C9A	N2A	C7A	N1A	-174.47(16)
C10	Al1	O1	C2	98.09(11)
C10	Al1	O1A	C2A	103.97(11)

Compound 1b'

R_1=5.47%

Crystal Data and Experimental

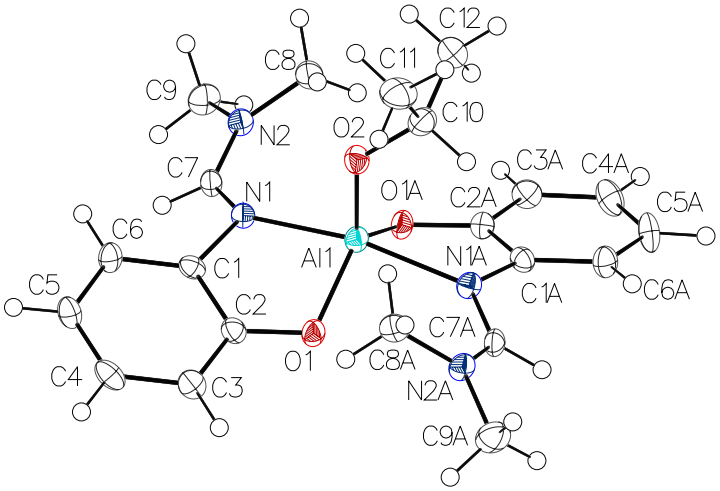

Figure S127: ORTEP view of compound **1b'**

Experimental. Single clear light colourless prism-shaped crystals of **compound 1bp'** recrystallised from a mixture of DCM and pentane by slow evaporation. A suitable crystal with dimensions 0.22 x 0.21 x 0.11 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 115.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{21}H_{29}AlN_4O_3$, M_r = 412.46, monoclinic, $P2_1/n$ (No. 14), a = 10.6976(5) Å, b = 7.7241(4) Å, c = 25.9622(11) Å, β = 95.4237(15)°, α = γ = 90°, V = 2135.63(17) Å^3, T = 115.0(1) K, Z = 4, Z' = 1, μ(Mo K$_{\alpha1}$) = 0.124, 19967 reflections measured, 3760 unique (R_{int} = 0.0870) which were used in all calculations. The final wR_2 was 0.1373 (all data) and R_1 was 0.0547 (I≥2 σ(I)).

Table S37: Experimental parameters

Compound	**1b'**
CCDC	**2182076**
Formula	$C_{21}H_{29}AlN_4O_3$
$D_{calc.}$/ g cm^{-3}	1.283
μ/mm^{-1}	0.124
Formula Weight	412.46
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.22x0.21x0.11
T/K	115.0(1)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.6976(5)
b/Å	7.7241(4)
c/Å	25.9622(11)
α/°	90
β/°	95.4237(15)
γ/°	90
V/Å^3	2135.63(17)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.752
Θ_{max}/°	24.995
Measured Refl's.	19967
Indep't Refl's	3760
Refl's I≥2 σ(I)	2304
R_{int}	0.0870
Parameters	268
Restraints	0
Largest Peak	0.262
Deepest Hole	-0.443
GooF	1.013
wR_2 (all data)	0.1373
wR_2	0.1125
R_1 (all data)	0.1115
R_1	0.0547

Table S38: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=50.0° 0.84	I/σ(I) 11.6	Rint 8.70%	Full 50.0° 99.9
Refinement:	Shift -0.001	Max Peak 0.3	Min Peak -0.4	GooF 1.013

A clear light colourless prism-shaped-shaped crystal with dimensions 0.22 x 0.21 x 0.11 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 24.995° (0.84 Å). The unit cell was refined using **SAINT V8.40B**[4] on 5488 reflections, 27% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 24.995° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0733 before and 0.0615 after correction. The Ratio of minimum to maximum transmission is 0.8675. The absorption coefficient μ of this material is 0.124 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.832 and 0.959. The structure was solved, and the space group $P2_1/n$ (# 14) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] **2018/3**. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

Table S39: Bond Lengths in Å for **compound 1b'**.

Atom	Atom	Length/Å
Al1	O1	1.795(2)
Al1	O1A	1.787(2)
Al1	O2	1.739(2)
Al1	N1	2.053(2)
Al1	N1A	2.092(2)
O1	C2	1.344(3)
O1A	C2A	1.342(3)
O2	C10	1.415(4)
N1	C1	1.422(4)
N1	C7	1.315(4)
N1A	C1A	1.427(4)
N1A	C7A	1.309(4)
N2	C7	1.322(4)
N2	C8	1.457(4)
N2	C9	1.466(4)
N2A	C7A	1.320(4)
N2A	C8A	1.460(4)
N2A	C9A	1.457(4)
C1	C2	1.409(4)
C1	C6	1.391(4)
C1A	C2A	1.409(4)
C1A	C6A	1.385(4)
C2	C3	1.386(4)
C2A	C3A	1.387(4)
C3	C4	1.391(4)
C3A	C4A	1.390(4)
C4	C5	1.380(4)
C4A	C5A	1.388(5)
C5	C6	1.389(4)
C5A	C6A	1.383(4)
C10	C11	1.519(5)
C10	C12	1.517(4)

Table S40: Bond Angles in ° for **compound 1b'**.

Atom	Atom	Atom	Angle/°
O1	Al1	N1	83.66(10)
O1	Al1	N1A	88.44(10)
O1A	Al1	O1	122.92(11)
O1A	Al1	N1	94.04(10)
O1A	Al1	N1A	83.30(10)
O2	Al1	O1	118.86(11)
O2	Al1	O1A	118.20(11)
O2	Al1	N1	93.98(11)
O2	Al1	N1A	97.09(10)
N1	Al1	N1A	168.55(11)
C2	O1	Al1	114.24(18)
C2A	O1A	Al1	116.25(18)
C10	O2	Al1	129.38(19)
C1	N1	Al1	105.24(17)

Atom	Atom	Atom	Angle/°
C7	N1	Al1	136.3(2)
C7	N1	C1	115.9(2)
C1A	N1A	Al1	106.07(18)
C7A	N1A	Al1	134.9(2)
C7A	N1A	C1A	116.7(2)
C7	N2	C8	123.6(2)
C7	N2	C9	120.1(3)
C8	N2	C9	116.3(2)
C7A	N2A	C8A	125.0(3)
C7A	N2A	C9A	120.4(3)
C9A	N2A	C8A	114.7(2)
C2	C1	N1	113.0(3)
C6	C1	N1	126.4(3)
C6	C1	C2	120.5(3)
C2A	C1A	N1A	112.9(2)
C6A	C1A	N1A	127.1(3)
C6A	C1A	C2A	120.0(3)
O1	C2	C1	116.8(3)
O1	C2	C3	123.8(3)
C3	C2	C1	119.4(3)
O1A	C2A	C1A	117.5(3)
O1A	C2A	C3A	123.2(3)
C3A	C2A	C1A	119.3(3)
C2	C3	C4	119.8(3)
C2A	C3A	C4A	120.2(3)
C5	C4	C3	120.6(3)
C5A	C4A	C3A	120.4(3)
C4	C5	C6	120.6(3)
C6A	C5A	C4A	119.8(3)
C5	C6	C1	119.1(3)
C5A	C6A	C1A	120.4(3)
N1	C7	N2	126.4(3)
N1A	C7A	N2A	127.2(3)
O2	C10	C11	110.2(3)
O2	C10	C12	110.4(3)
C12	C10	C11	111.3(3)

Table S41: Torsion Angles in ° for **compound 1b'**.

Atom	Atom	Atom	Atom	Angle/°
Al1	O1	C2	C1	20.0(3)
Al1	O1	C2	C3	-157.5(3)
Al1	O1A	C2A	C1A	17.7(3)
Al1	O1A	C2A	C3A	-161.9(3)
Al1	O2	C10	C11	-146.7(2)
Al1	O2	C10	C12	90.0(3)
Al1	N1	C1	C2	-17.2(3)
Al1	N1	C1	C6	159.3(3)
Al1	N1	C7	N2	-35.3(5)
Al1	N1A	C1A	C2A	-10.6(3)
Al1	N1A	C1A	C6A	166.5(3)
Al1	N1A	C7A	N2A	-31.8(5)
O1	Al1	O1A	C2A	-102.2(2)
O1	Al1	O2	C10	113.3(2)
O1	C2	C3	C4	176.9(3)
O1A	Al1	O1	C2	-114.3(2)
O1A	Al1	O2	C10	-65.0(3)
O1A	C2A	C3A	C4A	-179.3(3)
O2	Al1	O1	C2	67.5(2)
O2	Al1	O1A	C2A	76.1(2)
N1	Al1	O1	C2	-23.5(2)
N1	Al1	O1A	C2A	172.8(2)
N1	Al1	O2	C10	-161.8(2)
N1	C1	C2	O1	0.6(4)
N1	C1	C2	C3	178.2(3)
N1	C1	C6	C5	-178.3(3)
N1A	Al1	O1	C2	164.8(2)
N1A	Al1	O1A	C2A	-18.4(2)
N1A	Al1	O2	C10	21.1(3)
N1A	C1A	C2A	O1A	-2.6(4)
N1A	C1A	C2A	C3A	177.0(3)
N1A	C1A	C6A	C5A	-178.3(3)
C1	N1	C7	N2	166.1(3)
C1	C2	C3	C4	-0.5(5)
C1A	N1A	C7A	N2A	168.2(3)
C1A	C2A	C3A	C4A	1.2(5)
C2	C1	C6	C5	-2.0(5)

Atom	Atom	Atom	Atom	Angle/°
C2	C3	C4	C5	0.2(5)
C2A	C1A	C6A	C5A	-1.4(5)
C2A	C3A	C4A	C5A	-0.2(5)
C3	C4	C5	C6	-0.8(5)
C3A	C4A	C5A	C6A	-1.5(5)
C4	C5	C6	C1	1.7(5)
C4A	C5A	C6A	C1A	2.3(5)
C6	C1	C2	O1	-176.2(3)
C6	C1	C2	C3	1.4(5)
C6A	C1A	C2A	O1A	-179.9(3)
C6A	C1A	C2A	C3A	-0.3(5)
C7	N1	C1	C2	147.7(3)
C7	N1	C1	C6	-35.8(4)
C7A	N1A	C1A	C2A	154.8(3)
C7A	N1A	C1A	C6A	-28.1(5)
C8	N2	C7	N1	-8.4(5)
C8A	N2A	C7A	N1A	-7.0(5)
C9	N2	C7	N1	171.6(3)
C9A	N2A	C7A	N1A	173.4(3)

Compound 2b

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R_1=4.65%

Crystal Data and Experimental

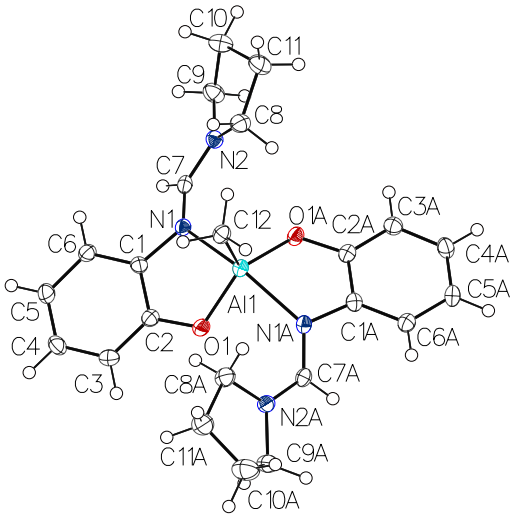

Figure S128: ORTEP view of compound **2b**

Experimental. Single clear light colourless prism-shaped crystals of **compound 2b** recrystallised from a mixture of DCM and pentane by slow evaporation. A suitable crystal with dimensions 0.21 x 0.21 x 0.15 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] 2018/2 solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{23}H_{29}AlN_4O_2$, M_r = 420.48, monoclinic, $P2_1/c$ (No. 14), a = 11.5025(6) Å, b = 17.2998(10) Å, c = 11.5070(6) Å, β = 107.584(2)°, α = γ = 90°, V = 2182.8(2) Å^3, T = 110.0(1) K, Z = 4, Z' = 1, μ(Mo K$_{\alpha1}$) = 0.120, 44219 reflections measured, 5007 unique (R_{int} = 0.0556) which were used in all calculations. The final wR_2 was 0.1292 (all data) and R_1 was 0.0465 (I≥2 σ(I)).

Table S42: Experimental parameters

Compound	**2b**
CCDC	**2182077**
Formula	$C_{23}H_{29}AlN_4O_2$
$D_{calc.}$/ g cm^{-3}	1.280
μ/mm^{-1}	0.120
Formula Weight	420.48
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.21x0.21x0.15
T/K	110.0(1)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	11.5025(6)
b/Å	17.2998(10)
c/Å	11.5070(6)
α/°	90
β/°	107.584(2)
γ/°	90
V/Å^3	2182.8(2)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.490
Θ_{max}/°	27.532
Measured Refl's.	44219
Indep't Refl's	5007
Refl's I≥2 σ(I)	3463
R_{int}	0.0556
Parameters	272
Restraints	0
Largest Peak	1.029
Deepest Hole	-0.382
GooF	1.036
wR_2 (all data)	0.1292
wR_2	0.1096
R_1 (all data)	0.0814
R_1	0.0465

Table S43: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.1° 0.77	I/σ(I) 25.1	Rint 5.56%	Full 50.5° 99.9
Refinement:	Shift 0.000	Max Peak 1.0	Min Peak -0.4	GooF 1.036

A clear light colourless prism-shaped-shaped crystal with dimensions 0.21 x 0.21 x 0.15 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 27.532° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 6983 reflections, 16% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 27.532° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0542 before and 0.0520 after correction. The Ratio of minimum to maximum transmission is 0.9504. The absorption coefficient μ of this material is 0.120 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.922 and 0.971. The structure was solved, and the space group $P2_1/c$ (# 14) determined by the **ShelXT**[1] 2018/2 structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table S44: Bond Lengths in Å for **compound 2b**.

Atom	Atom	Length/Å
Al1	O1A	1.7951(14)
Al1	O1	1.7984(15)
Al1	N1	2.1200(17)
Al1	N1A	2.1224(17)
Al1	C12	1.973(2)
O1A	C2A	1.338(2)
O1	C2	1.342(2)
N1	C7	1.308(2)
N1	C1	1.420(2)
N2	C7	1.325(2)
N2	C8	1.472(2)
N2	C9	1.471(3)
N2A	C7A	1.319(2)
N2A	C9A	1.470(3)
N2A	C8A	1.471(3)
N1A	C1A	1.419(2)
N1A	C7A	1.311(2)
C1A	C2A	1.407(3)

Atom	Atom	Length/Å
C1A	C6A	1.385(3)
C2	C1	1.405(3)
C2	C3	1.390(3)
C2A	C3A	1.386(3)
C1	C6	1.389(3)
C3	C4	1.392(3)
C4	C5	1.386(3)
C6	C5	1.397(3)
C6A	C5A	1.395(3)
C5A	C4A	1.381(3)
C3A	C4A	1.392(3)
C8	C11	1.523(3)
C9A	C10A	1.508(3)
C8A	C11A	1.525(3)
C9	C10	1.514(3)
C11	C10	1.522(3)
C11A	C10A	1.522(3)

Table S45: Bond Angles in ° for **compound 2b**.

Atom	Atom	Atom	Angle/°
O1A	Al1	O1	126.79(7)
O1A	Al1	N1	89.04(6)
O1A	Al1	N1A	82.43(6)
O1A	Al1	C12	116.16(8)
O1	Al1	N1	82.30(6)
O1	Al1	N1A	86.13(6)
O1	Al1	C12	117.06(8)

Atom	Atom	Atom	Angle/°
N1	Al1	N1A	157.40(7)
C12	Al1	N1	99.90(8)
C12	Al1	N1A	102.65(8)
C2A	O1A	Al1	118.34(12)
C2	O1	Al1	116.47(12)
C7	N1	Al1	135.20(13)
C7	N1	C1	116.70(16)

Atom	Atom	Atom	Angle/°
C1	N1	Al1	106.00(12)
C7	N2	C8	124.97(17)
C7	N2	C9	122.40(17)
C9	N2	C8	111.03(15)
C7A	N2A	C9A	123.07(17)
C7A	N2A	C8A	124.56(16)
C9A	N2A	C8A	111.36(15)
C1A	N1A	Al1	106.94(12)
C7A	N1A	Al1	132.57(13)
C7A	N1A	C1A	116.01(16)
C2A	C1A	N1A	113.37(17)
C6A	C1A	N1A	126.55(18)
C6A	C1A	C2A	120.04(18)
O1	C2	C1	117.43(17)
O1	C2	C3	122.69(18)
C3	C2	C1	119.86(18)
N1	C7	N2	126.10(18)
O1A	C2A	C1A	117.56(17)
O1A	C2A	C3A	122.87(18)
C3A	C2A	C1A	119.57(18)

Atom	Atom	Atom	Angle/°
C2	C1	N1	113.32(17)
C6	C1	N1	126.61(18)
C6	C1	C2	119.90(18)
N1A	C7A	N2A	125.28(18)
C2	C3	C4	119.84(19)
C5	C4	C3	120.49(19)
C1	C6	C5	119.93(19)
C1A	C6A	C5A	119.71(19)
C4A	C5A	C6A	120.30(19)
C2A	C3A	C4A	120.06(19)
C4	C5	C6	119.94(19)
C5A	C4A	C3A	120.23(19)
N2	C8	C11	103.57(16)
N2A	C9A	C10A	103.28(17)
N2A	C8A	C11A	103.70(16)
N2	C9	C10	103.31(17)
C10	C11	C8	104.14(17)
C10A	C11A	C8A	105.60(18)
C9	C10	C11	102.16(17)
C9A	C10A	C11A	102.98(19)

Table S46: Torsion Angles in ° for **compound 2b**.

Atom	Atom	Atom	Atom	Angle/°
Al1	O1A	C2A	C1A	12.1(2)
Al1	O1A	C2A	C3A	-169.21(15)
Al1	O1	C2	C1	20.5(2)
Al1	O1	C2	C3	-157.85(16)
Al1	N1	C7	N2	-34.3(3)
Al1	N1	C1	C2	-9.27(18)
Al1	N1	C1	C6	165.98(17)
Al1	N1A	C1A	C2A	-4.27(19)
Al1	N1A	C1A	C6A	173.53(17)
Al1	N1A	C7A	N2A	-43.0(3)
O1A	Al1	O1	C2	-102.78(14)
O1A	C2A	C3A	C4A	-175.90(18)
O1	Al1	O1A	C2A	-90.47(15)
O1	C2	C1	N1	-5.2(2)
O1	C2	C1	C6	179.25(17)
O1	C2	C3	C4	-179.68(18)
N1	Al1	O1A	C2A	-170.11(13)
N1	Al1	O1	C2	-19.79(13)
N1	C1	C6	C5	-174.20(18)
N2	C8	C11	C10	27.0(2)
N2	C9	C10	C11	36.0(2)
N2A	C9A	C10A	C11A	34.9(2)
N2A	C8A	C11A	C10A	19.4(2)
N1A	Al1	O1A	C2A	-11.10(13)
N1A	Al1	O1	C2	179.66(14)
N1A	C1A	C2A	O1A	-3.8(2)
N1A	C1A	C2A	C3A	177.38(17)
N1A	C1A	C6A	C5A	-179.65(19)
C1A	N1A	C7A	N2A	164.31(18)
C1A	C2A	C3A	C4A	2.8(3)
C1A	C6A	C5A	C4A	2.3(3)
C2	C1	C6	C5	0.8(3)
C2	C3	C4	C5	-0.1(3)
C7	N1	C1	C2	156.79(17)
C7	N1	C1	C6	-28.0(3)

Atom	Atom	Atom	Atom	Angle/°
C7	N2	C8	C11	-170.13(18)
C7	N2	C9	C10	146.14(19)
C2A	C1A	C6A	C5A	-2.0(3)
C2A	C3A	C4A	C5A	-2.5(3)
C1	N1	C7	N2	164.86(18)
C1	C2	C3	C4	2.0(3)
C1	C6	C5	C4	1.2(3)
C7A	N2A	C9A	C10A	144.8(2)
C7A	N2A	C8A	C11A	-165.85(19)
C7A	N1A	C1A	C2A	155.02(17)
C7A	N1A	C1A	C6A	-27.2(3)
C3	C2	C1	N1	173.25(17)
C3	C2	C1	C6	-2.4(3)
C3	C4	C5	C6	-1.5(3)
C6A	C1A	C2A	O1A	178.20(17)
C6A	C1A	C2A	C3A	-0.6(3)
C6A	C5A	C4A	C3A	-0.1(3)
C8	N2	C7	N1	-15.5(3)
C8	N2	C9	C10	-20.1(2)
C8	C11	C10	C9	-39.3(2)
C9A	N2A	C7A	N1A	179.63(18)
C9A	N2A	C8A	C11A	2.9(2)
C8A	N2A	C7A	N1A	-12.9(3)
C8A	N2A	C9A	C10A	-24.1(2)
C8A	C11A	C10A	C9A	-34.0(2)
C9	N2	C7	N1	-179.77(19)
C9	N2	C8	C11	-4.3(2)
C12	Al1	O1A	C2A	89.32(15)
C12	Al1	O1	C2	77.43(15)

Compound 3b

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R_1=5.81%

Crystal Data and Experimental

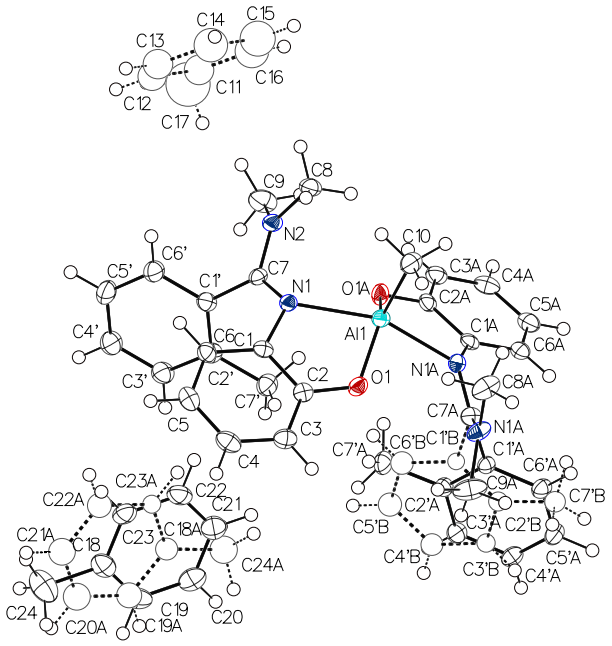

Figure S129: ORTEP view of compound **3b**

Experimental. Single clear light colourless prism-shaped crystals of **compound 3b** recrystallised from toluene by slow evaporation. A suitable crystal with dimensions 0.42 x 0.34 x 0.33 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 120.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{87}H_{98}Al_2N_8O_4$, M_r = 1373.69, triclinic, P-1 (No. 2), a = 12.4063(12) Å, b = 13.7450(12) Å, c = 14.0446(13) Å, α = 110.884(3)°, β = 110.057(3)°, γ = 104.529(4)°, V = 1902.5(3) Å^3, T = 120.0(1) K, Z = 1, Z' = 0.5, μ(MoK$_\alpha$) = 0.095, 90466 reflections measured, 8806 unique (R_{int} = 0.0689) which were used in all calculations. The final wR_2 was 0.1547 (all data) and R_1 was 0.0581 (I≥2 σ(I)).

Table S47: Experimental parameters

Compound	**3b**
CCDC	**2182078**
Formula	$C_{87}H_{98}Al_2N_8O_4$
$D_{calc.}$/ g cm^{-3}	1.199
μ/mm^{-1}	0.095
Formula Weight	1373.69
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.42x0.34x0.33
T/K	120.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	12.4063(12)
b/Å	13.7450(12)
c/Å	14.0446(13)
α/°	110.884(3)
β/°	110.057(3)
γ/°	104.529(4)
V/Å^3	1902.5(3)
Z	1
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.554
Θ_{max}/°	27.606
Measured Refl's.	90466
Indep't Refl's	8806
Refl's I≥2 σ(I)	6546
R_{int}	0.0689
Parameters	461
Restraints	0
Largest Peak	0.906
Deepest Hole	-0.551
GooF	1.025
wR_2 (all data)	0.1547
wR_2	0.1340
R_1 (all data)	0.0858
R_1	0.0581

Table S48: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.2° 0.77	I/σ(I) 31.1	Rint 6.89%	Full 50.5° 99.9
Refinement:	Shift -0.001	Max Peak 0.9	Min Peak -0.6	GooF 1.025

A clear light colourless prism-shaped-shaped crystal with dimensions 0.42 x 0.34 x 0.33 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 120.0(1) K. Data were measured using ϕ and ω scans with MoK_α radiation. The maximum resolution that was achieved was Θ = 27.606° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9955 reflections, 11% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 27.606° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0628 before and 0.0576 after correction. The Ratio of minimum to maximum transmission is 0.9397. The absorption coefficient μ of this material is 0.095 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.912 and 0.971. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3]. All non-hydrogen atoms were refined anisotropically, excepted minor disordered parts. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S49: Bond Lengths in Å for **compound 3b**.

Atom	Atom	Length/Å
Al1	O1	1.7940(15)
Al1	O1A	1.7969(15)
Al1	N1	2.1703(17)
Al1	N1A	2.1555(17)
Al1	C10	1.970(2)
O1	C2	1.340(2)
O1A	C2A	1.341(2)
N1	C1	1.418(2)
N1	C7	1.321(2)
N1A	C1A	1.415(2)
N1A	C7A	1.319(3)
N2	C7	1.342(2)
N2	C8	1.455(3)
N2	C9	1.459(3)
N2A	C7A	1.337(3)
N2A	C8A	1.456(3)
N2A	C9A	1.455(3)
C1	C2	1.409(3)
C1	C6	1.389(3)
C1'	C2'	1.394(3)
C1'	C6'	1.409(3)
C1'	C7	1.502(3)
C1'A	C2'A	1.3900
C1'A	C6'A	1.3900
C1'A	C7A	1.530(2)
C2'A	C3'A	1.3900
C2'A	C7'A	1.513(4)
C3'A	C4'A	1.3900
C4'A	C5'A	1.3900

Atom	Atom	Length/Å
C5'A	C6'A	1.3900
C1'B	C6'B	1.3900
C1'B	C2'B	1.3900
C1'B	C7A	1.503(4)
C6'B	C5'B	1.3900
C5'B	C4'B	1.3900
C4'B	C3'B	1.3900
C3'B	C2'B	1.3900
C2'B	C7'B	1.486(11)
C1A	C2A	1.411(3)
C1A	C6A	1.389(3)
C2	C3	1.390(3)
C2'	C3'	1.399(3)
C2'	C7'	1.486(3)
C2A	C3A	1.392(3)
C3	C4	1.388(3)
C3'	C4'	1.376(3)
C3A	C4A	1.389(3)
C4	C5	1.386(3)
C4'	C5'	1.385(3)
C4A	C5A	1.389(3)
C5	C6	1.391(3)
C5'	C6'	1.385(3)
C5A	C6A	1.389(3)
C14	C13	1.3900
C14	C15	1.3900
C13	C12	1.3900
C12	C11	1.3900
C11	C16	1.3900

Atom	Atom	Length/Å
C11	C17	1.486(12)
C16	C15	1.3900
C24	C18	1.510(4)
C24A	C18A	1.501(15)
C21	C22	1.3900
C21	C20	1.3900
C22	C23	1.3900
C23	C18	1.3900
C18	C19	1.3900
C19	C20	1.3900
C19A	C18A	1.3900
C19A	C20A	1.3900
C18A	C23A	1.3900
C23A	C22A	1.3900
C22A	C21A	1.3900
C21A	C20A	1.3900

Table S50: Bond Angles in ° for **compound 3b**.

Atom	Atom	Atom	Angle/°
O1	Al1	O1A	128.60(7)
O1	Al1	N1	81.42(6)
O1	Al1	N1A	86.33(7)
O1	Al1	C10	115.64(9)
O1A	Al1	N1	87.10(7)
O1A	Al1	N1A	81.66(7)
O1A	Al1	C10	115.76(9)
N1A	Al1	N1	152.73(7)
C10	Al1	N1	103.55(8)
C10	Al1	N1A	103.71(8)
C2	O1	Al1	119.16(12)
C2A	O1A	Al1	118.55(12)
C1	N1	Al1	106.41(12)
C7	N1	Al1	126.19(13)
C7	N1	C1	119.65(16)
C1A	N1A	Al1	106.77(12)
C7A	N1A	Al1	125.44(14)
C7A	N1A	C1A	119.85(17)
C7	N2	C8	121.42(17)
C7	N2	C9	122.64(18)
C8	N2	C9	114.51(17)
C7A	N2A	C8A	121.00(18)
C7A	N2A	C9A	123.46(18)
C9A	N2A	C8A	114.54(18)
C2	C1	N1	113.37(17)
C6	C1	N1	126.69(18)
C6	C1	C2	119.65(18)
C2'	C1'	C6'	120.36(19)
C2'	C1'	C7	120.89(18)
C6'	C1'	C7	118.66(18)
C2'A	C1'A	C6'A	120.0
C2'A	C1'A	C7A	119.80(13)
C6'A	C1'A	C7A	120.13(13)
C1'A	C2'A	C7'A	120.89(16)
C3'A	C2'A	C1'A	120.0
C3'A	C2'A	C7'A	119.09(16)
C2'A	C3'A	C4'A	120.0
C3'A	C4'A	C5'A	120.0
C6'A	C5'A	C4'A	120.0
C5'A	C6'A	C1'A	120.0
C6'B	C1'B	C2'B	120.0
C6'B	C1'B	C7A	121.7(4)
C2'B	C1'B	C7A	118.3(4)
C1'B	C6'B	C5'B	120.0
C4'B	C5'B	C6'B	120.0
C5'B	C4'B	C3'B	120.0
C2'B	C3'B	C4'B	120.0
C1'B	C2'B	C7'B	120.3(6)
C3'B	C2'B	C1'B	120.0
C3'B	C2'B	C7'B	119.7(5)
C2A	C1A	N1A	113.18(17)
C6A	C1A	N1A	126.50(18)
C6A	C1A	C2A	119.96(18)
O1	C2	C1	117.84(17)
O1	C2	C3	122.66(18)
C3	C2	C1	119.50(18)
C1'	C2'	C3'	118.1(2)
C1'	C2'	C7'	121.57(19)
C3'	C2'	C7'	120.33(19)
O1A	C2A	C1A	117.80(17)
O1A	C2A	C3A	122.83(18)
C3A	C2A	C1A	119.37(19)
C4	C3	C2	120.2(2)
C4'	C3'	C2'	121.4(2)
C4A	C3A	C2A	120.04(19)
C5	C4	C3	120.4(2)
C3'	C4'	C5'	120.7(2)
C3A	C4A	C5A	120.50(19)
C4	C5	C6	119.9(2)
C6'	C5'	C4'	119.3(2)
C4A	C5A	C6A	120.0(2)
C1	C6	C5	120.30(19)
C5'	C6'	C1'	120.2(2)
C1A	C6A	C5A	120.11(19)
N1	C7	N2	119.64(17)
N1	C7	C1'	125.00(17)
N2	C7	C1'	115.35(17)
N1A	C7A	N2A	120.08(18)
N1A	C7A	C1'A	126.38(17)
N1A	C7A	C1'B	115.4(3)
N2A	C7A	C1'A	113.26(17)
N2A	C7A	C1'B	120.6(3)
C13	C14	C15	120.0
C12	C13	C14	120.0
C13	C12	C11	120.0
C12	C11	C17	115.6(6)
C16	C11	C12	120.0
C16	C11	C17	124.4(6)
C15	C16	C11	120.0
C16	C15	C14	120.0
C22	C21	C20	120.0
C21	C22	C23	120.0
C18	C23	C22	120.0
C23	C18	C24	120.4(2)

Atom	Atom	Atom	Angle/°
C23	C18	C19	120.0
C19	C18	C24	119.6(2)
C18	C19	C20	120.0
C19	C20	C21	120.0
C18A	C19A	C20A	120.0
C19A	C18A	C24A	118.7(8)

Atom	Atom	Atom	Angle/°
C19A	C18A	C23A	120.0
C23A	C18A	C24A	121.2(8)
C22A	C23A	C18A	120.0
C23A	C22A	C21A	120.0
C20A	C21A	C22A	120.0
C21A	C20A	C19A	120.0

Table S51: Torsion Angles in ° for **compound 3b**.

Atom	Atom	Atom	Atom	Angle/°
Al1	O1	C2	C1	13.4(2)
Al1	O1	C2	C3	-166.58(15)
Al1	O1A	C2A	C1A	14.8(2)
Al1	O1A	C2A	C3A	-165.81(15)
Al1	N1	C1	C2	-5.77(18)
Al1	N1	C1	C6	167.95(16)
Al1	N1	C7	N2	-56.9(2)
Al1	N1	C7	C1'	124.14(18)
Al1	N1A	C1A	C2A	-5.14(18)
Al1	N1A	C1A	C6A	167.89(16)
Al1	N1A	C7A	N2A	-59.0(2)
Al1	N1A	C7A	C1'A	127.59(18)
Al1	N1A	C7A	C1'B	98.7(3)
O1	Al1	O1A	C2A	-91.96(15)
O1	C2	C3	C4	178.14(19)
O1A	Al1	O1	C2	-91.97(15)
O1A	C2A	C3A	C4A	179.09(18)
N1	Al1	O1	C2	-12.68(14)
N1	Al1	O1A	C2A	-168.58(14)
N1	C1	C2	O1	-3.3(2)
N1	C1	C2	C3	176.67(17)
N1	C1	C6	C5	-175.09(18)
N1A	Al1	O1	C2	-168.25(14)
N1A	Al1	O1A	C2A	-13.49(14)
N1A	C1A	C2A	O1A	-4.7(2)
N1A	C1A	C2A	C3A	175.92(17)
N1A	C1A	C6A	C5A	-174.36(18)
C1	N1	C7	N2	158.12(18)
C1	N1	C7	C1'	-20.9(3)
C1	C2	C3	C4	-1.8(3)
C1'	C2'	C3'	C4'	0.0(3)
C1'A	C2'A	C3'A	C4'A	0.0
C2'A	C1'A	C6'A	C5'A	0.0
C2'A	C1'A	C7A	N1A	-67.6(2)
C2'A	C1'A	C7A	N2A	118.55(17)
C2'A	C3'A	C4'A	C5'A	0.0
C3'A	C4'A	C5'A	C6'A	0.0
C4'A	C5'A	C6'A	C1'A	0.0
C6'A	C1'A	C2'A	C3'A	0.0
C6'A	C1'A	C2'A	C7'A	178.8(2)
C6'A	C1'A	C7A	N1A	115.5(2)
C6'A	C1'A	C7A	N2A	-58.4(2)
C1'B	C6'B	C5'B	C4'B	0.0
C6'B	C1'B	C2'B	C3'B	0.0
C6'B	C1'B	C2'B	C7'B	-177.1(7)
C6'B	C1'B	C7A	N1A	-46.6(4)
C6'B	C1'B	C7A	N2A	111.0(4)
C6'B	C5'B	C4'B	C3'B	0.0
C5'B	C4'B	C3'B	C2'B	0.0

Atom	Atom	Atom	Atom	Angle/°
C4'B	C3'B	C2'B	C1'B	0.0
C4'B	C3'B	C2'B	C7'B	177.1(7)
C2'B	C1'B	C6'B	C5'B	0.0
C2'B	C1'B	C7A	N1A	132.4(3)
C2'B	C1'B	C7A	N2A	-70.0(4)
C1A	N1A	C7A	N2A	156.29(18)
C1A	N1A	C7A	C1'A	-17.2(3)
C1A	N1A	C7A	C1'B	-46.0(3)
C1A	C2A	C3A	C4A	-1.6(3)
C2	C1	C6	C5	-1.7(3)
C2	C3	C4	C5	0.4(3)
C2'	C1'	C6'	C5'	1.1(3)
C2'	C1'	C7	N1	-59.4(3)
C2'	C1'	C7	N2	121.6(2)
C2'	C3'	C4'	C5'	-0.3(4)
C2A	C1A	C6A	C5A	-1.8(3)
C2A	C3A	C4A	C5A	0.1(3)
C3	C4	C5	C6	0.4(3)
C3'	C4'	C5'	C6'	0.9(4)
C3A	C4A	C5A	C6A	0.5(3)
C4	C5	C6	C1	0.3(3)
C4'	C5'	C6'	C1'	-1.3(4)
C4A	C5A	C6A	C1A	0.3(3)
C6	C1	C2	O1	-177.47(17)
C6	C1	C2	C3	2.5(3)
C6'	C1'	C2'	C3'	-0.5(3)
C6'	C1'	C2'	C7'	177.5(2)
C6'	C1'	C7	N1	124.1(2)
C6'	C1'	C7	N2	-54.9(3)
C6A	C1A	C2A	O1A	-178.24(17)
C6A	C1A	C2A	C3A	2.4(3)
C7	N1	C1	C2	145.40(18)
C7	N1	C1	C6	-40.9(3)
C7	C1'	C2'	C3'	-176.93(19)
C7	C1'	C2'	C7'	1.1(3)
C7	C1'	C6'	C5'	177.7(2)
C7'	C2'	C3'	C4'	-178.0(2)
C7'A	C2'A	C3'A	C4'A	-178.8(2)
C7A	N1A	C1A	C2A	145.45(18)
C7A	N1A	C1A	C6A	-41.5(3)
C7A	C1'A	C2'A	C3'A	-176.93(17)
C7A	C1'A	C2'A	C7'A	1.9(2)
C7A	C1'A	C6'A	C5'A	176.92(17)
C7A	C1'B	C6'B	C5'B	179.1(5)
C7A	C1'B	C2'B	C3'B	-179.1(5)
C7A	C1'B	C2'B	C7'B	3.8(7)
C8	N2	C7	N1	-15.6(3)
C8	N2	C7	C1'	163.53(18)
C8A	N2A	C7A	N1A	-15.3(3)
C8A	N2A	C7A	C1'A	158.99(19)
C8A	N2A	C7A	C1'B	-171.8(3)
C9	N2	C7	N1	150.0(2)
C9	N2	C7	C1'	-30.9(3)
C9A	N2A	C7A	N1A	152.7(2)
C9A	N2A	C7A	C1'A	-33.0(3)
C9A	N2A	C7A	C1'B	-3.8(4)
C10	Al1	O1	C2	88.30(16)
C10	Al1	O1A	C2A	87.77(16)
C14	C13	C12	C11	0.0
C13	C14	C15	C16	0.0

Atom	Atom	Atom	Atom	Angle/°
C13	C12	C11	C16	0.0
C13	C12	C11	C17	-180.0(9)
C12	C11	C16	C15	0.0
C11	C16	C15	C14	0.0
C15	C14	C13	C12	0.0
C17	C11	C16	C15	180.0(10)
C24	C18	C19	C20	179.7(2)
C24A	C18A	C23A	C22A	-178.1(9)
C21	C22	C23	C18	0.0
C22	C21	C20	C19	0.0
C22	C23	C18	C24	-179.7(3)
C22	C23	C18	C19	0.0
C23	C18	C19	C20	0.0
C18	C19	C20	C21	0.0
C20	C21	C22	C23	0.0
C19A	C18A	C23A	C22A	0.0
C18A	C19A	C20A	C21A	0.0
C18A	C23A	C22A	C21A	0.0
C23A	C22A	C21A	C20A	0.0
C22A	C21A	C20A	C19A	0.0
C20A	C19A	C18A	C24A	178.2(9)
C20A	C19A	C18A	C23A	0.0

Table S52: Atomic Occupancies for all atoms that are not fully occupied in **compound 3b**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
C1'A	0.760(4)	C2'B	0.240(4)	H15	0.5	C18	0.793(4)
C2'A	0.760(4)	C7'A	0.760(4)	C17	0.5	C19	0.793(4)
C3'A	0.760(4)	H7'D	0.760(4)	H17A	0.5	H19	0.793(4)
H3'A	0.760(4)	H7'E	0.760(4)	H17B	0.5	C20	0.793(4)
C4'A	0.760(4)	H7'F	0.760(4)	H17C	0.5	H20	0.793(4)
H4'A	0.760(4)	C7'B	0.240(4)	C24	0.793(4)	C19A	0.207(4)
C5'A	0.760(4)	H7'G	0.240(4)	H24A	0.793(4)	H19A	0.207(4)
H5'A	0.760(4)	H7'H	0.240(4)	H24B	0.793(4)	C18A	0.207(4)
C6'A	0.760(4)	H7'I	0.240(4)	H24C	0.793(4)	C23A	0.207(4)
H6'A	0.760(4)	C14	0.5	C24A	0.207(4)	H23A	0.207(4)
C1'B	0.240(4)	H14	0.5	H24D	0.207(4)	C22A	0.207(4)
C6'B	0.240(4)	C13	0.5	H24E	0.207(4)	H22A	0.207(4)
H6'B	0.240(4)	H13	0.5	H24F	0.207(4)	C21A	0.207(4)
C5'B	0.240(4)	C12	0.5	C21	0.793(4)	H21A	0.207(4)
H5'B	0.240(4)	H12	0.5	H21	0.793(4)	C20A	0.207(4)
C4'B	0.240(4)	C11	0.5	C22	0.793(4)	H20A	0.207(4)
H4'B	0.240(4)	C16	0.5	H22	0.793(4)		
C3'B	0.240(4)	H16	0.5	C23	0.793(4)		
H3'B	0.240(4)	C15	0.5	H23	0.793(4)		

Compound 1c

R_1=3.31%

Crystal Data and Experimental

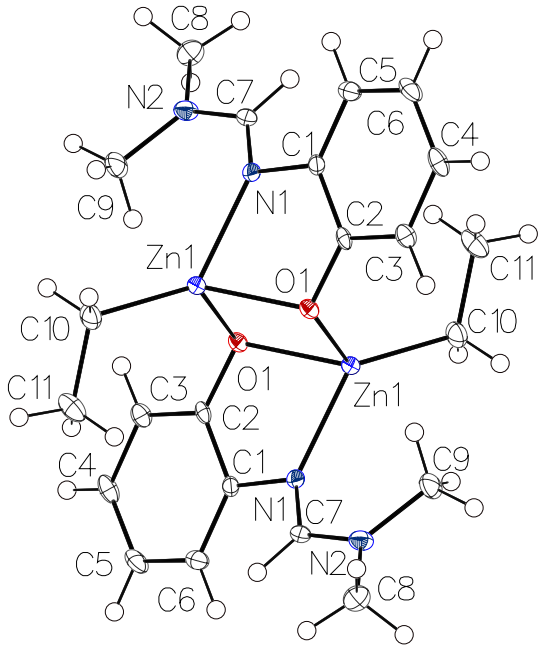

Figure S130: ORTEP view of compound **1c**

Experimental. Single clear light colorless plate crystals of **compound 1c** recrystallized from DCM by slow evaporation. A suitable crystal with dimensions 0.18 x 0.11 x 0.10 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using Olex2[2] as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimization on F^2.

Crystal Data. $C_{22}H_{32}N_4O_2Zn_2$, M_r = 515.25, orthorhombic, *Cmce* (No. 64), a = 10.3231(6) Å, b = 14.4461(9) Å, c = 15.2624(10) Å, α = β = γ = 90°, V = 2276.1(2) Å^3, T = 100.0(1) K, Z = 4, Z' = 0.25, μ(Mo K$_{\alpha1}$) = 2.133, 19802 reflections measured, 1888 unique (R_{int} = 0.0684) which were used in all calculations. The final wR_2 was 0.0579 (all data) and R_1 was 0.0331 (I≥2 σ(I)).

Table S53: Experimental parameters

Compound	**1c**
CCDC	**2182079**
Formula	$C_{22}H_{32}N_4O_2Zn_2$
$D_{calc.}$/ g cm^{-3}	1.504
μ/mm^{-1}	2.133
Formula Weight	515.25
Color	clear light colorless
Shape	plate
Size/mm^3	0.18x0.11x0.10
T/K	100.0(1)
Crystal System	orthorhombic
Space Group	*Cmce*
a/Å	10.3231(6)
b/Å	14.4461(9)
c/Å	15.2624(10)
α/°	90
β/°	90
γ/°	90
V/Å^3	2276.1(2)
Z	4
Z'	0.25
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.669
Θ_{max}/°	31.580
Measured Refl's.	19802
Indep't Refl's	1888
Refl's I≥2 σ(I)	1456
R_{int}	0.0684
Parameters	136
Restraints	0
Largest Peak	0.511
Deepest Hole	-0.611
GooF	1.056
wR_2 (all data)	0.0579
wR_2	0.0511
R_1 (all data)	0.0620
R_1	0.0331

Table S54: Structure Quality Indicators

Reflections:	d min (Mo) 0.68	I/σ(I) 22.8	Rint 6.84%	complete 100%
Refinement:	Shift 0.000	Max Peak 0.5	Min Peak -0.6	GooF 1.056

A clear light colorless plate-shaped crystal with dimensions 0.18 x 0.11 x 0.10 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans' using Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX3**[7]. The maximum resolution that was achieved was Θ = 31.580° (0.68 Å). The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX3**[7]. The unit cell was refined using **SAINT** V8.40A[8] on 6420 reflections, 32% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** V8.40A[8], The final completeness is 99.90 % out to 31.580° in Θ. A multi-scan absorption correction was performed using **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0643 before and 0.0576 after correction. The Ratio of minimum to maximum transmission is 0.8731. The absorption coefficient μ of this material is 2.133 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.690 and 0.790. The structure was solved and the space group *Cmce* (# 64) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimization on F^2 using version 2018/3 of ShelXL[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.25.

Table S55: Bond Lengths in Å for **compound 1c**.

Atom	Atom	Length/Å
Zn1	Zn1[1]	2.9829(5)
Zn1	O1	2.064(2)
Zn1	N1	2.089(2)
Zn1	C10	1.970(3)
O1	C2	1.343(3)
N1	C1	1.427(4)
N1	C7	1.304(4)
N2	C7	1.328(4)
N2	C8	1.452(4)
N2	C9	1.452(4)

Atom	Atom	Length/Å
C1	C2	1.409(4)
C1	C6	1.391(4)
C2	C3	1.395(4)
C3	C4	1.390(4)
C4	C5	1.387(5)
C5	C6	1.389(4)
C10	C11	1.527(5)

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[1]1-x,1-y,1-z

Table S56: Bond Angles in ° for **compound 1c**.

Atom	Atom	Atom	Angle/°
O1	Zn1	Zn1[1]	43.45(6)
O1	Zn1	N1	80.41(9)
N1	Zn1	Zn1[1]	89.07(7)
C10	Zn1	Zn1[1]	138.61(10)
C10	Zn1	O1	125.76(12)
C10	Zn1	N1	131.83(12)
C2	O1	Zn1	109.58(19)
C1	N1	Zn1	107.92(18)
C7	N1	Zn1	133.8(2)
C7	N1	C1	117.3(3)
C7	N2	C8	120.8(3)
C7	N2	C9	121.7(3)
C8	N2	C9	117.2(3)

Atom	Atom	Atom	Angle/°
C2	C1	N1	115.3(3)
C6	C1	N1	124.4(3)
C6	C1	C2	120.2(3)
O1	C2	C1	119.4(3)
O1	C2	C3	121.9(3)
C3	C2	C1	118.6(3)
C4	C3	C2	121.0(3)
C5	C4	C3	119.8(3)
C4	C5	C6	120.2(3)
C5	C6	C1	120.2(3)
N1	C7	N2	125.1(3)
C11	C10	Zn1	115.1(2)

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[1]1-x,1-y,1-z

Table S57: Torsion Angles in ° for **compound 1c**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	-20.0(3)
Zn1	O1	C2	C3	158.5(2)
Zn1	N1	C1	C2	18.8(3)
Zn1	N1	C1	C6	-158.2(3)
Zn1	N1	C7	N2	19.8(5)
O1	C2	C3	C4	-177.2(3)
N1	C1	C2	O1	0.5(4)
N1	C1	C2	C3	-178.0(3)
N1	C1	C6	C5	176.9(3)
C1	N1	C7	N2	-173.3(3)
C1	C2	C3	C4	1.2(5)
C2	C1	C6	C5	0.1(5)
C2	C3	C4	C5	-0.7(5)
C3	C4	C5	C6	-0.2(5)
C4	C5	C6	C1	0.5(5)
C6	C1	C2	O1	177.6(3)
C6	C1	C2	C3	-0.9(5)
C7	N1	C1	C2	-151.4(3)
C7	N1	C1	C6	31.7(4)
C8	N2	C7	N1	-173.2(3)
C9	N2	C7	N1	1.3(5)

Table S58: Atomic Occupancies for all atoms that are not fully occupied in **compound 1c**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
O1	0.5	H4	0.5	H8A	0.5	H10A	0.5
N1	0.5	C5	0.5	H8B	0.5	H10B	0.5
N2	0.5	H5	0.5	H8C	0.5	C11	0.5
C1	0.5	C6	0.5	C9	0.5	H11A	0.5
C2	0.5	H6	0.5	H9A	0.5	H11B	0.5
C3	0.5	C7	0.5	H9B	0.5	H11C	0.5
H3	0.5	H7	0.5	H9C	0.5		
C4	0.5	C8	0.5	C10	0.5		

Compound 5c

R_1=11.86%

Crystal Data and Experimental

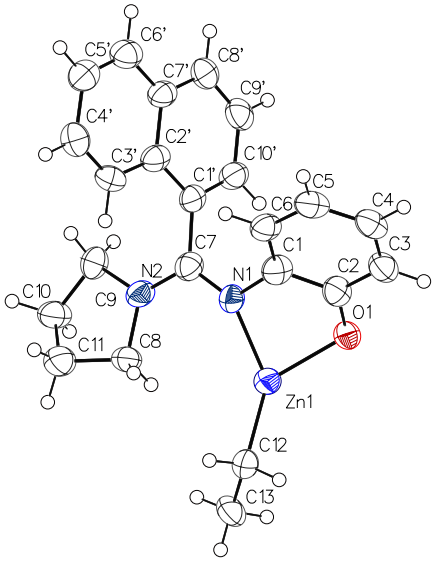

Figure S131: ORTEP view of compound **5c**

Experimental. Single clear light colourless plate-shaped crystals of **compound 5c** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.12 x 0.08 x 0.04 mm^3 was selected and mounted on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{46}H_{48}N_4O_2Zn_2$, M_r = 819.62, triclinic, P-1 (No. 2), a = 8.5813(6) Å, b = 9.6302(7) Å, c = 12.5497(9) Å, α = 97.970(4)°, β = 99.773(4)°, γ = 102.037(4)°, V = 983.15(12) Å^3, T = 110.0(1) K, Z = 1, Z' = 0.5, μ(Cu K$_{\alpha1}$) = 1.836, 11389 reflections measured, 3446 unique (R_{int} = 0.1034) which were used in all calculations. The final wR_2 was 0.3283 (all data) and R_1 was 0.1186 (I≥2 σ(I)).

Table S59: Experimental parameters

Compound	**5c**
CCDC	**2182080**
Formula	$C_{46}H_{48}N_4O_2Zn_2$
$D_{calc.}$/ g cm^{-3}	1.384
μ/mm^{-1}	1.836
Formula Weight	819.62
Colour	clear light colourless
Shape	plate-shaped
Size/mm^3	0.12x0.08x0.04
T/K	110.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	8.5813(6)
b/Å	9.6302(7)
c/Å	12.5497(9)
α/°	97.970(4)
β/°	99.773(4)
γ/°	102.037(4)
V/Å^3	983.15(12)
Z	1
Z'	0.5
Wavelength/Å	1.54178
Radiation type	Cu K$_{\alpha1}$
Θ_{min}/°	3.633
Θ_{max}/°	66.845
Measured Refl's.	11389
Indep't Refl's	3446
Refl's I≥2 σ(I)	2739
R_{int}	0.1034
Parameters	245
Restraints	0
Largest Peak	1.047
Deepest Hole	-1.181
GooF	1.069
wR_2 (all data)	0.3283
wR_2	0.3100
R_1 (all data)	0.1420
R_1	0.1186

Table S60: Structure Quality Indicators

Reflections:	d min (Cu\a) 2Θ=133.7°	0.84	I/σ(I)	11.8	Rint	10.34%	Full 133.7°	98.4
Refinement:	Shift	0.000	Max Peak	1.1	Min Peak	-1.2	GooF	1.069

A clear light colourless plate-shaped-shaped crystal with dimensions 0.12 x 0.08 x 0.04 mm^3 was mounted. Data were collected using a Bruker D8 VENTURE diffractometer operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Cu $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 66.845° (0.84 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9069 reflections, 80% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 98.40 % out to 66.845° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.1523 before and 0.1083 after correction. The Ratio of minimum to maximum transmission is 0.5663. The absorption coefficient μ of this material is 1.836 mm^{-1} at this wavelength (λ = 1.54178Å) and the minimum and maximum transmissions are 0.426 and 0.753. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

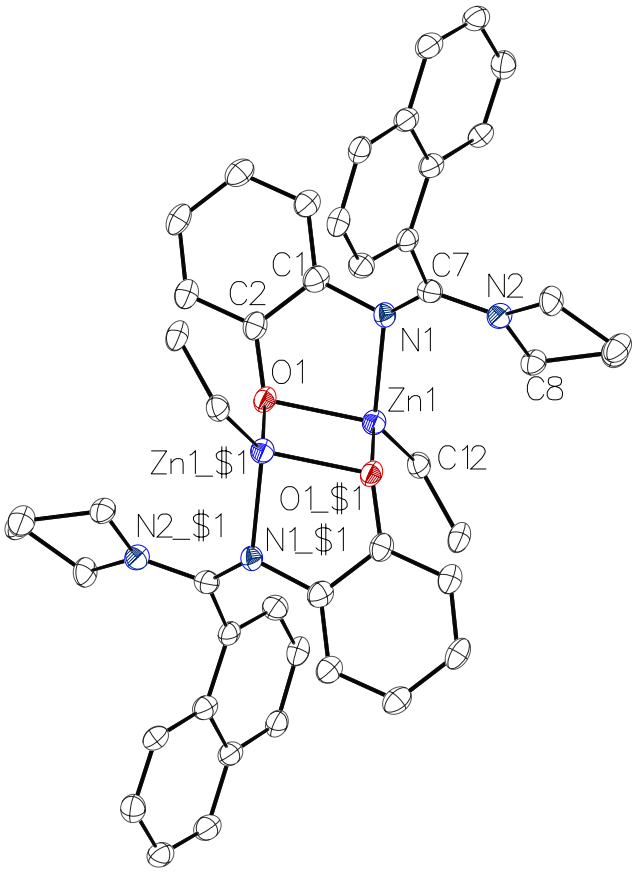

Figure S132: ORTEP view of complex **5c**. Thermal ellipsoids are drawn 25% probability level. Hydrogen atoms are omitted for clarity.

Table S61: Bond Lengths in Å for **compound 5c**.

Atom	Atom	Length/Å
Zn1	Zn1[1]	3.009(2)
Zn1	O1[1]	2.042(6)
Zn1	O1	2.051(6)
Zn1	N1	2.082(7)
Zn1	C12	1.985(9)
O1	C2	1.354(11)
N1	C1	1.423(11)
N1	C7	1.307(12)
N2	C7	1.344(12)
N2	C8	1.479(11)
N2	C9	1.474(11)
C1	C2	1.411(14)
C1	C6	1.390(13)
C1'	C2'	1.416(13)
C1'	C7	1.507(12)
C1'	C10'	1.362(14)
C2	C3	1.401(13)
C2'	C3'	1.424(13)
C2'	C7'	1.435(12)
C3	C4	1.367(14)
C3'	C4'	1.346(14)
C4	C5	1.399(15)
C4'	C5'	1.433(14)
C5	C6	1.385(13)
C5'	C6'	1.369(15)
C6'	C7'	1.404(14)
C7'	C8'	1.408(14)
C8	C11	1.516(14)
C8'	C9'	1.372(14)
C9	C10	1.513(13)
C9'	C10'	1.379(14)
C10	C11	1.513(14)
C12	C13	1.514(13)

––––

[1]1-x,1-y,-z

Table S62: Bond Angles in ° for **compound 5c**.

Atom	Atom	Atom	Angle/°
O1[1]	Zn1	Zn1[1]	42.81(16)
O1	Zn1	Zn1[1]	42.57(17)
O1[1]	Zn1	O1	85.4(2)
O1	Zn1	N1	81.0(3)
O1[1]	Zn1	N1	97.4(3)
N1	Zn1	Zn1[1]	88.9(2)
C12	Zn1	Zn1[1]	143.1(3)
C12	Zn1	O1	127.7(3)
C12	Zn1	O1[1]	124.3(3)
C12	Zn1	N1	127.5(4)
Zn1[1]	O1	Zn1	94.6(2)
C2	O1	Zn1	108.6(5)
C2	O1	Zn1[1]	119.5(5)
C1	N1	Zn1	107.2(6)
C7	N1	Zn1	127.4(6)
C7	N1	C1	120.4(8)
C7	N2	C8	123.8(7)
C7	N2	C9	124.6(8)
C9	N2	C8	111.6(7)
C2	C1	N1	115.7(8)
C6	C1	N1	124.8(9)
C6	C1	C2	119.3(8)
C2'	C1'	C7	121.4(8)
C10'	C1'	C2'	119.9(8)
C10'	C1'	C7	118.7(8)
O1	C2	C1	118.9(8)
O1	C2	C3	122.4(9)
C3	C2	C1	118.7(9)
C1'	C2'	C3'	123.3(8)
C1'	C2'	C7'	118.4(8)
C3'	C2'	C7'	118.3(8)
C4	C3	C2	121.0(10)
C4'	C3'	C2'	122.6(8)
C3	C4	C5	120.8(9)
C3'	C4'	C5'	118.5(9)
C6	C5	C4	118.6(9)
C6'	C5'	C4'	120.9(9)
C5	C6	C1	121.6(10)
C5'	C6'	C7'	121.3(9)
N1	C7	N2	120.3(8)
N1	C7	C1'	123.9(8)
N2	C7	C1'	115.6(8)
C6'	C7'	C2'	118.3(9)
C6'	C7'	C8'	122.6(9)
C8'	C7'	C2'	119.0(9)
N2	C8	C11	101.5(7)
C9'	C8'	C7'	120.5(9)
N2	C9	C10	103.3(8)
C8'	C9'	C10'	120.0(9)
C9	C10	C11	103.4(8)
C1'	C10'	C9'	122.1(9)
C10	C11	C8	103.3(8)
C13	C12	Zn1	117.2(7)

––––

[1]1-x,1-y,-z

Table S63: Torsion Angles in ° for **compound 5c**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	-22.2(9)

Atom	Atom	Atom	Atom	Angle/°
Zn1[1]	O1	C2	C1	84.6(9)
Zn1[1]	O1	C2	C3	-97.5(9)
Zn1	O1	C2	C3	155.8(8)
Zn1	N1	C1	C2	19.3(9)
Zn1	N1	C1	C6	-154.6(8)
Zn1	N1	C7	N2	40.7(12)
Zn1	N1	C7	C1'	-134.8(7)
O1	C2	C3	C4	-178.0(8)
N1	C1	C2	O1	1.7(12)
N1	C1	C2	C3	-176.3(8)
N1	C1	C6	C5	175.1(9)
N2	C8	C11	C10	36.4(10)
N2	C9	C10	C11	28.8(11)
C1	N1	C7	N2	-167.8(8)
C1	N1	C7	C1'	16.7(14)
C1	C2	C3	C4	-0.1(14)
C1'	C2'	C3'	C4'	-179.6(8)
C1'	C2'	C7'	C6'	-179.0(8)
C1'	C2'	C7'	C8'	0.8(12)
C2	C1	C6	C5	1.4(14)
C2	C3	C4	C5	3.0(14)
C2'	C1'	C7	N1	-109.1(10)
C2'	C1'	C7	N2	75.2(10)
C2'	C1'	C10'	C9'	-1.9(13)
C2'	C3'	C4'	C5'	-0.6(14)
C2'	C7'	C8'	C9'	-0.2(13)
C3	C4	C5	C6	-3.7(14)
C3'	C2'	C7'	C6'	2.8(12)
C3'	C2'	C7'	C8'	-177.5(8)
C3'	C4'	C5'	C6'	1.3(14)
C4	C5	C6	C1	1.5(14)
C4'	C5'	C6'	C7'	0.1(14)
C5'	C6'	C7'	C2'	-2.2(14)
C5'	C6'	C7'	C8'	178.1(9)
C6	C1	C2	O1	175.9(8)
C6	C1	C2	C3	-2.1(13)
C6'	C7'	C8'	C9'	179.5(9)
C7	N1	C1	C2	-137.4(9)
C7	N1	C1	C6	48.8(13)
C7	N2	C8	C11	161.5(9)
C7	N2	C9	C10	173.4(9)
C7	C1'	C2'	C3'	-3.5(13)
C7	C1'	C2'	C7'	178.3(8)
C7	C1'	C10'	C9'	179.9(8)
C7'	C2'	C3'	C4'	-1.5(13)
C7'	C8'	C9'	C10'	-1.5(13)
C8	N2	C7	N1	8.4(14)
C8	N2	C7	C1'	-175.7(8)
C8	N2	C9	C10	-6.0(11)
C8'	C9'	C10'	C1'	2.6(14)
C9	N2	C7	N1	-170.9(9)
C9	N2	C7	C1'	4.9(13)
C9	N2	C8	C11	-19.0(10)
C9	C10	C11	C8	-41.2(11)
C10'	C1'	C2'	C3'	178.4(8)
C10'	C1'	C2'	C7'	0.3(12)
C10'	C1'	C7	N1	69.0(12)
C10'	C1'	C7	N2	-106.7(10)

––––

[1]1-x,1-y,-z

Compound 6c

Pacsmub PLATEFORME Analyse Chimique Synthèse Moléculaire UNIVERSITÉ DE BOURGOGNE

R_1=1.98%

Crystal Data and Experimental

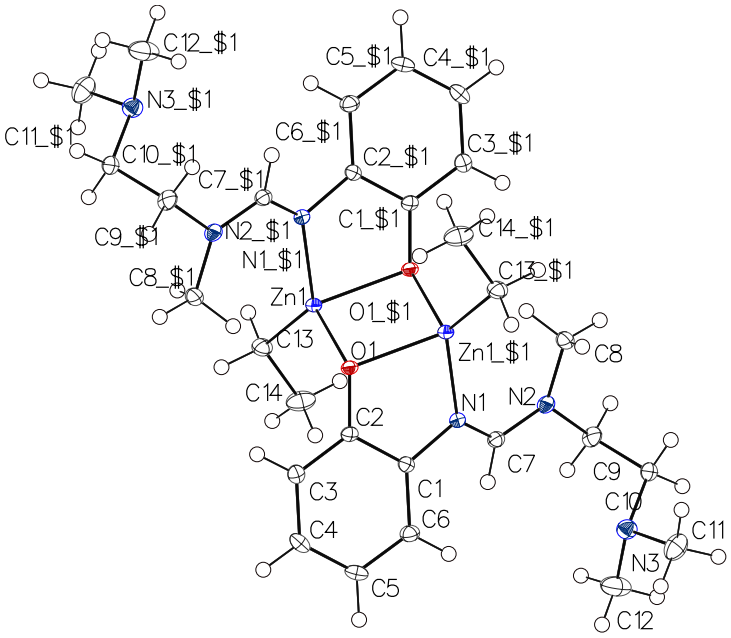

Figure S132: ORTEP view of compound **6c**

Experimental. Single clear light colourless prism crystals of **compound 6c** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.42 x 0.20 x 0.16 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{28}H_{46}N_6O_2Zn_2$, M_r = 629.45, monoclinic, $P2_1/n$ (No. 14), a = 10.0934(6) Å, b = 14.4079(8) Å, c = 11.0432(7) Å, β = 107.793(2)°, α = γ = 90°, V = 1529.14(16) Å^3, T = 100.0(1) K, Z = 2, Z' = 0.5, μ(MoK$_\alpha$) = 1.603, 81240 reflections measured, 3525 unique (R_{int} = 0.0410) which were used in all calculations. The final wR_2 was 0.0500 (all data) and R_1 was 0.0198 (I≥2 σ(I)).

Table S64: Experimental parameters

Compound	**6c**
CCDC	**2182081**
Formula	$C_{28}H_{46}N_6O_2Zn_2$
$D_{calc.}$/ g cm^{-3}	1.367
μ/mm^{-1}	1.603
Formula Weight	629.45
Colour	clear light colourless
Shape	prism
Size/mm^3	0.42x0.20x0.16
T/K	100.0(1)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.0934(6)
b/Å	14.4079(8)
c/Å	11.0432(7)
α/°	90
β/°	107.793(2)
γ/°	90
V/Å^3	1529.14(16)
Z	2
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.548
Θ_{max}/°	27.543
Measured Refl's.	81240
Indep't Refl's	3525
Refl's I≥2 σ(I)	3108
R_{int}	0.0410
Parameters	176
Restraints	0
Largest Peak	0.360
Deepest Hole	-0.294
GooF	1.054
wR_2 (all data)	0.0500
wR_2	0.0477
R_1 (all data)	0.0253
R_1	0.0198

Table S65: Structure Quality Indicators

Reflections:	d min (Mo) 2θ=55.1° 0.77	I/σ(I) 86.6	Rint 4.10%	Full 50.5° 99.9
Refinement:	Shift -0.001	Max Peak 0.4	Min Peak -0.3	GooF 1.054

A clear light colourless prism-shaped crystal with dimensions 0.42 x 0.20 x 0.16 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans using MoK_α radiation. The maximum resolution that was achieved was Θ = 27.543° (0.77 Å). The unit cell was refined using **SAINT** V8.40B[4] on 9889 reflections, 12% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** V8.40B[4]. The final completeness is 99.90 % out to 27.543° in Θ. A multi-scan absorption correction was performed using **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0629 before and 0.0527 after correction. The Ratio of minimum to maximum transmission is 0.8625. The absorption coefficient μ of this material is 1.603 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.616 and 0.714. The structure was solved, and the space group $P2_1/n$ (# 14) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] **2018/3**. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S66: Bond Lengths in Å for **compound 6c**.

Atom	Atom	Length/Å
Zn1	Zn1[1]	3.0242(3)
Zn1	O1[1]	2.0689(9)
Zn1	O1	2.0610(9)
Zn1	N1[1]	2.0714(10)
Zn1	C13	1.9778(13)
O1	C2	1.3489(15)
N1	C1	1.4259(15)
N1	C7	1.3022(16)
N2	C7	1.3296(16)
N2	C8	1.4603(16)
N2	C9	1.4659(16)
N3	C10	1.4563(17)
N3	C11	1.4565(18)
N3	C12	1.4559(18)
C14	C13	1.5311(19)
C1	C2	1.4165(17)
C1	C6	1.3931(17)
C2	C3	1.3964(17)
C3	C4	1.3920(18)
C4	C5	1.3857(19)
C5	C6	1.3954(18)
C9	C10	1.5250(19)

[1]-x,1-y,1-z

Table S67: Bond Angles in ° for **compound 6c**.

Atom	Atom	Atom	Angle/°
O1	Zn1	Zn1[1]	43.02(2)
O1[1]	Zn1	Zn1[1]	42.82(2)
O1	Zn1	O1[1]	85.84(3)
O1	Zn1	N1[1]	101.91(4)
O1[1]	Zn1	N1[1]	80.90(4)
N1[1]	Zn1	Zn1[1]	91.85(3)
C13	Zn1	Zn1[1]	135.17(4)
C13	Zn1	O1[1]	126.58(5)
C13	Zn1	O1	116.26(5)
C13	Zn1	N1[1]	132.63(5)
Zn1	O1	Zn1[1]	94.16(3)
C2	O1	Zn1	120.56(7)
C2	O1	Zn1[1]	109.57(7)
C1	N1	Zn1[1]	107.86(8)
C7	N1	Zn1[1]	134.49(9)
C7	N1	C1	117.33(10)
C7	N2	C8	121.33(11)
C7	N2	C9	119.09(11)
C8	N2	C9	118.13(10)
C10	N3	C11	110.47(11)
C12	N3	C10	111.11(11)
C12	N3	C11	109.12(12)

Atom	Atom	Atom	Angle/°
C2	C1	N1	115.50(10)
C6	C1	N1	124.58(11)
C6	C1	C2	119.90(11)
O1	C2	C1	118.92(11)
O1	C2	C3	122.31(11)
C3	C2	C1	118.75(11)
C4	C3	C2	120.69(12)
C5	C4	C3	120.33(12)
C4	C5	C6	119.90(12)
C1	C6	C5	120.32(12)
N1	C7	N2	125.36(12)
N2	C9	C10	112.39(11)
C14	C13	Zn1	113.33(10)
N3	C10	C9	112.46(11)

––––
[1]-x,1-y,1-z

Table S68: Torsion Angles in ° for **compound 6c**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	91.04(12)
Zn1[1]	O1	C2	C1	-16.38(13)
Zn1[1]	O1	C2	C3	162.24(10)
Zn1	O1	C2	C3	-90.35(12)
Zn1[1]	N1	C1	C2	21.63(12)
Zn1[1]	N1	C1	C6	-156.44(11)
Zn1[1]	N1	C7	N2	7.2(2)
O1	C2	C3	C4	-175.58(11)
N1	C1	C2	O1	-3.80(16)
N1	C1	C2	C3	177.53(11)
N1	C1	C6	C5	-179.10(12)
N2	C9	C10	N3	68.27(14)
C1	N1	C7	N2	179.81(12)
C1	C2	C3	C4	3.03(18)
C2	C1	C6	C5	2.91(19)
C2	C3	C4	C5	-0.3(2)
C3	C4	C5	C6	-1.1(2)
C4	C5	C6	C1	-0.2(2)
C6	C1	C2	O1	174.36(11)
C6	C1	C2	C3	-4.30(18)
C7	N1	C1	C2	-152.84(11)
C7	N1	C1	C6	29.09(18)
C7	N2	C9	C10	-87.20(14)
C8	N2	C7	N1	3.7(2)
C8	N2	C9	C10	79.26(14)
C9	N2	C7	N1	169.69(12)
C11	N3	C10	C9	-160.32(12)
C12	N3	C10	C9	78.41(14)

––––
[1]-x,1-y,1-z

Compound 1d

R_1=2.53%

Crystal Data and Experimental

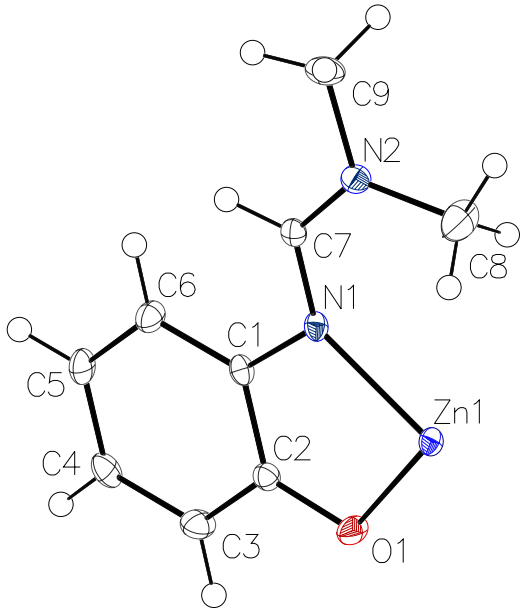

Figure S133: ORTEP view of compound **1d**

Experimental. Single clear light colourless prism-shaped crystals of **compound 1d** recrystallised from chloroform by slow evaporation. A suitable crystal with dimensions 0.31 x 0.14 x 0.07 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{18}H_{22}N_4O_2Zn$, M_r = 391.76, monoclinic, $C2/c$ (No. 15), a = 13.8168(15) Å, b = 11.5315(13) Å, c = 11.4556(11) Å, β = 110.176(3)°, α = γ = 90°, V = 1713.2(3) Å^3, T = 100.0(1) K, Z = 4, Z' = 0.5, μ(Mo K$_{\alpha1}$) = 1.453, 60525 reflections measured, 1977 unique (R_{int} = 0.0725) which were used in all calculations. The final wR_2 was 0.0616 (all data) and R_1 was 0.0253 (I≥2 σ(I)).

Table S69: Experimental parameters

Compound	**1d**
CCDC	**2182082**
Formula	$C_{18}H_{22}N_4O_2Zn$
$D_{calc.}$/ g cm^{-3}	1.519
μ/mm^{-1}	1.453
Formula Weight	391.76
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.31x0.14x0.07
T/K	100.0(1)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	13.8168(15)
b/Å	11.5315(13)
c/Å	11.4556(11)
α/°	90
β/°	110.176(3)
γ/°	90
V/Å^3	1713.2(3)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.363
Θ_{max}/°	27.585
Measured Refl's.	60525
Indep't Refl's	1977
Refl's I≥2 σ(I)	1689
R_{int}	0.0725
Parameters	116
Restraints	0
Largest Peak	0.385
Deepest Hole	-0.357
GooF	1.086
wR_2 (all data)	0.0616
wR_2	0.0578
R_1 (all data)	0.0345
R_1	0.0253

Table S70: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.2° 0.77	I/σ(I) 60.5	Rint 7.25%	Full 50.5° 100
Refinement:	Shift 0.000	Max Peak 0.4	Min Peak -0.4	GooF 1.086

A clear light colourless prism-shaped-shaped crystal with dimensions 0.31 x 0.14 x 0.07 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 27.585° (0.77 Å). The unit cell was refined using **SAINT V8.40A**[8] on 9800 reflections, 16% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40A**[8]. The final completeness is 100.00 % out to 27.585° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0725 before and 0.0616 after correction. The Ratio of minimum to maximum transmission is 0.8721. The absorption coefficient μ of this material is 1.453 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.720 and 0.825. The structure was solved, and the space group $C2/c$ (# 15) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S71: Bond Lengths in Å for **compound 1d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1[1]	1.9339(12)	N2	C8	1.451(2)
Zn1	O1	1.9339(12)	C1	C2	1.420(2)
Zn1	N1[1]	2.0240(14)	C1	C6	1.392(2)
Zn1	N1	2.0240(14)	C2	C3	1.398(2)
O1	C2	1.329(2)	C5	C4	1.385(3)
N1	C7	1.306(2)	C5	C6	1.391(2)
N1	C1	1.433(2)	C4	C3	1.388(2)
N2	C7	1.323(2)	----		
N2	C9	1.458(2)	[1]1-x,+y,1/2-z		

Table S72: Bond Angles in ° for **compound 1d**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Zn1	O1	117.76(8)	N1	C7	N2	125.90(15)
O1	Zn1	N1	86.49(5)	C2	C1	N1	115.02(14)
O1[1]	Zn1	N1[1]	86.49(5)	C6	C1	N1	125.54(15)
O1[1]	Zn1	N1	119.77(5)	C6	C1	C2	119.44(15)
O1	Zn1	N1[1]	119.77(5)	O1	C2	C1	120.84(14)
N1	Zn1	N1[1]	130.19(8)	O1	C2	C3	120.95(15)
C2	O1	Zn1	110.62(10)	C3	C2	C1	118.21(15)
C7	N1	Zn1	134.23(11)	C4	C5	C6	119.55(15)
C7	N1	C1	118.42(13)	C5	C4	C3	120.02(16)
C1	N1	Zn1	107.02(10)	C4	C3	C2	121.54(16)
C7	N2	C9	120.67(15)	C5	C6	C1	121.23(16)
C7	N2	C8	123.01(15)	----			
C8	N2	C9	116.21(15)	[1]1-x,+y,1/2-z			

Table S73: Torsion Angles in ° for **compound 1d**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	-1.22(19)
Zn1	O1	C2	C3	179.52(13)
Zn1	N1	C7	N2	10.8(3)
Zn1	N1	C1	C2	-0.21(16)
Zn1	N1	C1	C6	179.90(14)
O1	C2	C3	C4	178.57(16)
N1	C1	C2	O1	1.0(2)
N1	C1	C2	C3	-179.74(14)
N1	C1	C6	C5	-179.29(16)
C7	N1	C1	C2	-174.52(14)
C7	N1	C1	C6	5.6(2)
C1	N1	C7	N2	-176.78(15)
C1	C2	C3	C4	-0.7(3)
C2	C1	C6	C5	0.8(3)
C5	C4	C3	C2	0.3(3)
C4	C5	C6	C1	-1.3(3)
C6	C1	C2	O1	-179.12(15)
C6	C1	C2	C3	0.2(2)
C6	C5	C4	C3	0.7(3)
C9	N2	C7	N1	175.60(16)
C8	N2	C7	N1	-0.4(3)

Compound 2d

pacsmub PLATEFORME Analyse Chimique Synthèse Moléculaire UNIVERSITÉ DE BOURGOGNE

R_1=2.38%

Crystal Data and Experimental

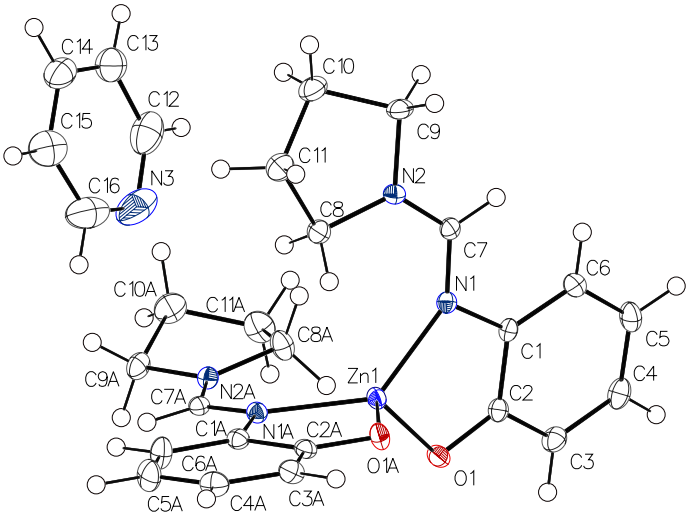

Figure S134: ORTEP view of compound **2d**

Experimental. Single clear light colourless prism-shaped crystals of **compound 2d** recrystallised from a mixture of cyclohexane and pyridine by slow evaporation. A suitable crystal with dimensions 0.29 x 0.27 x 0.27 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] 2018/2 solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{27}H_{31}N_5O_2Zn$, M_r = 522.94, triclinic, P-1 (No. 2), a = 10.7763(3) Å, b = 11.2517(3) Å, c = 12.6240(3) Å, α = 93.987(2)°, β = 111.8620(10)°, γ = 115.4340(10)°, V = 1233.90(6) Å^3, T = 110.0(1) K, Z = 2, Z' = 1, μ(Mo K$_{\alpha1}$) = 1.030, 32448 reflections measured, 5666 unique (R_{int} = 0.0245) which were used in all calculations. The final wR_2 was 0.0591 (all data) and R_1 was 0.0238 (I≥2 σ(I)).

Table S74: Experimental parameters

Compound	**2d**
CCDC	**2182083**
Formula	$C_{27}H_{31}N_5O_2Zn$
$D_{calc.}$/ g cm^{-3}	1.407
μ/mm^{-1}	1.030
Formula Weight	522.94
Colour	clear light colourless
Shape	prism-shaped
Size/mm^3	0.29x0.27x0.27
T/K	110.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	10.7763(3)
b/Å	11.2517(3)
c/Å	12.6240(3)
α/°	93.987(2)
β/°	111.8620(10)
γ/°	115.4340(10)
V/Å^3	1233.90(6)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.339
Θ_{max}/°	27.509
Measured Refl's.	32448
Indep't Refl's	5666
Refl's I≥2 σ(I)	5056
R_{int}	0.0245
Parameters	316
Restraints	0
Largest Peak	0.581
Deepest Hole	-0.241
GooF	1.021
wR_2 (all data)	0.0591
wR_2	0.0564
R_1 (all data)	0.0294
R_1	0.0238

Table S75: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.0° 0.77	I/σ(I) 52.8	Rint 2.45%	Full 50.5° 99.9
Refinement:	Shift -0.002	Max Peak 0.6	Min Peak -0.2	GooF 1.021

A clear light colourless prism-shaped-shaped crystal with dimensions 0.29 x 0.27 x 0.27 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 27.509° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9862 reflections, 30% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 99.90 % out to 27.509° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0401 before and 0.0347 after correction. The Ratio of minimum to maximum transmission is 0.9273. The absorption coefficient μ of this material is 1.030 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.575 and 0.620. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] 2018/2 structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Table S76: Bond Lengths in Å for **compound 2d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	1.9397(10)	C1A	C6A	1.3915(19)
Zn1	O1A	1.9446(10)	C2	C1	1.4213(19)
Zn1	N1A	2.0043(11)	C2	C3	1.4007(18)
Zn1	N1	2.0133(11)	C1	C6	1.3944(19)
O1	C2	1.3296(16)	N3	C12	1.333(3)
O1A	C2A	1.3290(16)	N3	C16	1.334(3)
N2	C7	1.3203(17)	C8	C11	1.5289(19)
N2	C8	1.4681(18)	C9	C10	1.521(2)
N2	C9	1.4778(17)	C4	C5	1.385(2)
N2A	C7A	1.3207(17)	C4	C3	1.384(2)
N2A	C9A	1.4763(17)	C10	C11	1.521(2)
N2A	C8A	1.4647(18)	C5	C6	1.3893(19)
N1A	C1A	1.4319(17)	C5A	C6A	1.390(2)
N1A	C7A	1.3074(17)	C9A	C10A	1.518(2)
N1	C1	1.4314(16)	C14	C13	1.372(3)
N1	C7	1.3114(17)	C14	C15	1.376(3)
C3A	C4A	1.384(2)	C8A	C11A	1.530(2)
C3A	C2A	1.4007(19)	C11A	C10A	1.518(2)
C4A	C5A	1.386(2)	C13	C12	1.380(3)
C1A	C2A	1.4208(19)	C15	C16	1.377(3)

Table S77: Bond Angles in ° for **compound 2d**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Zn1	O1A	118.09(4)	O1	Zn1	N1	86.81(4)
O1	Zn1	N1A	120.15(4)	O1A	Zn1	N1A	86.71(4)

Atom	Atom	Atom	Angle/°
O1A	Zn1	N1	115.57(4)
N1A	Zn1	N1	132.83(4)
C2	O1	Zn1	109.82(8)
C2A	O1A	Zn1	110.00(8)
C7	N2	C8	125.60(11)
C7	N2	C9	122.29(12)
C8	N2	C9	112.00(11)
C7A	N2A	C9A	121.73(12)
C7A	N2A	C8A	125.50(12)
C8A	N2A	C9A	112.26(11)
C1A	N1A	Zn1	107.37(8)
C7A	N1A	Zn1	133.22(9)
C7A	N1A	C1A	119.35(11)
C1	N1	Zn1	106.81(8)
C7	N1	Zn1	133.82(9)
C7	N1	C1	119.04(11)
C4A	C3A	C2A	121.48(13)
C3A	C4A	C5A	119.93(13)
C2A	C1A	N1A	115.03(11)
C6A	C1A	N1A	125.51(12)
C6A	C1A	C2A	119.44(12)
O1A	C2A	C3A	120.99(12)
O1A	C2A	C1A	120.76(12)
C3A	C2A	C1A	118.25(12)
O1	C2	C1	121.04(12)
O1	C2	C3	121.00(12)

Atom	Atom	Atom	Angle/°
C3	C2	C1	117.95(12)
N1A	C7A	N2A	125.20(12)
C2	C1	N1	114.96(11)
C6	C1	N1	125.34(12)
C6	C1	C2	119.70(12)
C12	N3	C16	116.45(16)
N1	C7	N2	125.00(12)
N2	C8	C11	103.38(11)
N2	C9	C10	102.44(11)
C3	C4	C5	120.26(13)
C9	C10	C11	103.15(12)
C4	C5	C6	119.61(13)
C4	C3	C2	121.45(13)
C4A	C5A	C6A	119.82(14)
C5	C6	C1	120.93(13)
N2A	C9A	C10A	103.28(12)
C10	C11	C8	103.75(12)
C13	C14	C15	119.11(17)
N2A	C8A	C11A	103.31(12)
C5A	C6A	C1A	121.06(14)
C10A	C11A	C8A	103.85(12)
C14	C13	C12	118.36(18)
C11A	C10A	C9A	104.19(12)
C14	C15	C16	118.31(19)
N3	C12	C13	123.85(19)
N3	C16	C15	123.91(19)

Table S78: Torsion Angles in ° for **compound 2d**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	-1.60(15)
Zn1	O1	C2	C3	177.09(10)
Zn1	O1A	C2A	C3A	-175.96(10)
Zn1	O1A	C2A	C1A	3.83(15)
Zn1	N1A	C1A	C2A	-0.87(13)
Zn1	N1A	C1A	C6A	177.43(12)
Zn1	N1A	C7A	N2A	-7.4(2)
Zn1	N1	C1	C2	7.45(13)
Zn1	N1	C1	C6	-172.20(11)
Zn1	N1	C7	N2	-12.7(2)
O1	C2	C1	N1	-4.32(18)
O1	C2	C1	C6	175.35(12)
O1	C2	C3	C4	-176.43(13)
N2	C8	C11	C10	27.86(15)
N2	C9	C10	C11	34.56(14)
N2A	C9A	C10A	C11A	29.46(15)
N2A	C8A	C11A	C10A	29.25(15)
N1A	C1A	C2A	O1A	-2.02(18)
N1A	C1A	C2A	C3A	177.78(11)
N1A	C1A	C6A	C5A	-177.40(13)
N1	C1	C6	C5	-178.64(13)
C3A	C4A	C5A	C6A	-0.9(2)
C4A	C3A	C2A	O1A	179.46(13)
C4A	C3A	C2A	C1A	-0.3(2)
C4A	C5A	C6A	C1A	-0.1(2)
C1A	N1A	C7A	N2A	175.95(12)
C2A	C3A	C4A	C5A	1.1(2)
C2A	C1A	C6A	C5A	0.8(2)
C2	C1	C6	C5	1.7(2)

Atom	Atom	Atom	Atom	Angle/°
C7A	N2A	C9A	C10A	160.93(13)
C7A	N2A	C8A	C11A	176.86(13)
C7A	N1A	C1A	C2A	176.55(12)
C7A	N1A	C1A	C6A	-5.1(2)
C1	N1	C7	N2	174.86(12)
C1	C2	C3	C4	2.3(2)
C7	N2	C8	C11	177.39(13)
C7	N2	C9	C10	158.69(13)
C7	N1	C1	C2	-178.23(12)
C7	N1	C1	C6	2.1(2)
C8	N2	C7	N1	-0.8(2)
C8	N2	C9	C10	-17.84(15)
C9	N2	C7	N1	-176.89(12)
C9	N2	C8	C11	-6.21(15)
C9	C10	C11	C8	-39.17(15)
C4	C5	C6	C1	1.1(2)
C5	C4	C3	C2	0.5(2)
C3	C2	C1	N1	176.95(12)
C3	C2	C1	C6	-3.38(19)
C3	C4	C5	C6	-2.3(2)
C9A	N2A	C7A	N1A	-175.02(12)
C9A	N2A	C8A	C11A	-11.21(15)
C14	C13	C12	N3	-1.3(3)
C14	C15	C16	N3	-0.6(3)
C8A	N2A	C7A	N1A	-3.8(2)
C8A	N2A	C9A	C10A	-11.35(15)
C8A	C11A	C10A	C9A	-36.80(16)
C6A	C1A	C2A	O1A	179.57(12)
C6A	C1A	C2A	C3A	-0.63(19)
C13	C14	C15	C16	0.2(3)
C15	C14	C13	C12	0.7(3)
C12	N3	C16	C15	0.1(3)
C16	N3	C12	C13	0.9(3)

Compound 3d

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R_1=3.85%

Crystal Data and Experimental

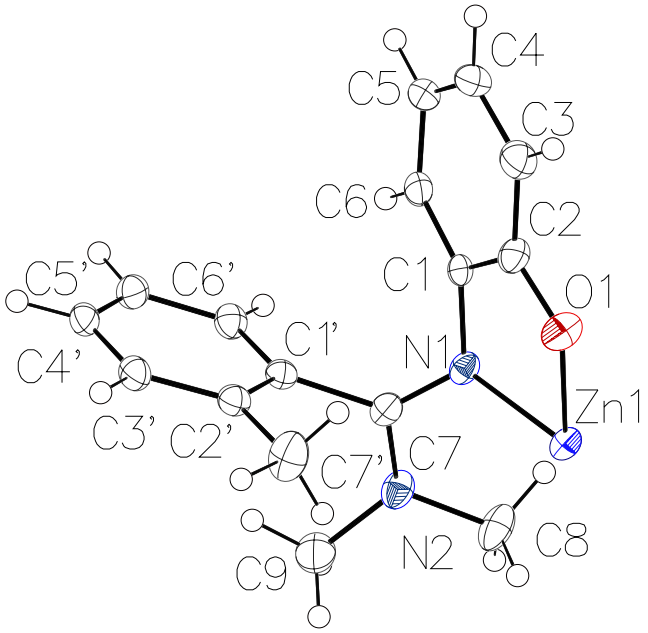

Figure S135: ORTEP view of compound **3d**

Experimental. Single clear light colourless plate-shaped crystals of **compound 3d** recrystallised from DCM by slow evaporation. A suitable crystal with dimensions 0.19 x 0.16 x 0.09 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at a steady T = 110.0(0) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{32}H_{34}N_4O_2Zn$, M_r = 572.00, monoclinic, $C2/c$ (No. 15), a = 9.5932(7) Å, b = 12.3033(9) Å, c = 24.3137(19) Å, β = 99.317(2)°, α = γ = 90°, V = 2831.8(4) Å^3, T = 110.0(0) K, Z = 4, Z' = 0.5, μ(Mo K$_{\alpha1}$) = 0.903, 24097 reflections measured, 3244 unique (R_{int} = 0.0577) which were used in all calculations. The final wR_2 was 0.0929 (all data) and R_1 was 0.0385 (I≥2 σ(I)).

Table S79: Experimental parameters

Compound	**3d**
CCDC	**2182084**
Formula	$C_{32}H_{34}N_4O_2Zn$
$D_{calc.}$/ g cm^{-3}	1.342
μ/mm^{-1}	0.903
Formula Weight	572.00
Colour	clear light colourless
Shape	plate-shaped
Size/mm^3	0.19x0.16x0.09
T/K	110.0(0)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	9.5932(7)
b/Å	12.3033(9)
c/Å	24.3137(19)
α/°	90
β/°	99.317(2)
γ/°	90
V/Å^3	2831.8(4)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.715
Θ_{max}/°	27.518
Measured Refl's.	24097
Indep't Refl's	3244
Refl's I≥2 σ(I)	2621
R_{int}	0.0577
Parameters	180
Restraints	0
Largest Peak	0.887
Deepest Hole	-0.451
GooF	1.046
wR_2 (all data)	0.0929
wR_2	0.0862
R_1 (all data)	0.0563
R_1	0.0385

Table S80: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.0° 0.77	I/σ(I) 23.4	Rint 5.77%	Full 50.5° 99.9
Refinement:	Shift 0.001	Max Peak 0.9	Min Peak -0.5	GooF 1.046

A clear light colourless plate-shaped-shaped crystal with dimensions 0.19 x 0.16 x 0.09 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius Kappa Apex II diffractometer operating at T = 110.0(0) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 27.518° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 5183 reflections, 22% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B[4] . The final completeness is 99.90 % out to 27.518° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0650 before and 0.0579 after correction. The Ratio of minimum to maximum transmission is 0.9186. The absorption coefficient μ of this material is 0.903 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.816 and 0.888. The structure was solved, and the space group $C2/c$ (# 15) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S81: Bond Lengths in Å for **compound 3d**.

Atom	Atom	Length/Å
Zn1	O1	1.9195(15)
Zn1	O1[1]	1.9195(15)
Zn1	N1[1]	2.0422(17)
Zn1	N1	2.0422(17)
O1	C2	1.334(3)
N1	C1	1.433(3)
N1	C7	1.316(3)
N2	C7	1.339(3)
N2	C8	1.460(3)
N2	C9	1.463(3)
C1	C2	1.415(3)
C1	C6	1.392(3)
C1'	C2'	1.400(3)
C1'	C6'	1.387(3)
C1'	C7	1.504(3)
C2	C3	1.400(3)
C2'	C3'	1.394(3)
C2'	C7'	1.497(3)
C3	C4	1.388(3)
C3'	C4'	1.377(3)
C4	C5	1.386(4)
C4'	C5'	1.382(3)
C5	C6	1.386(3)
C5'	C6'	1.393(3)

––––

[1]1-x,+y,3/2-z

Table S82: Bond Angles in ° for **compound 3d**.

Atom	Atom	Atom	Angle/°
O1	Zn1	O1[1]	120.87(10)
O1[1]	Zn1	N1	120.16(7)
O1[1]	Zn1	N1[1]	86.24(7)
O1	Zn1	N1	86.24(7)
O1	Zn1	N1[1]	120.16(7)
N1	Zn1	N1[1]	127.45(10)
C2	O1	Zn1	110.58(13)
C1	N1	Zn1	105.72(13)
C7	N1	Zn1	124.25(14)
C7	N1	C1	121.50(17)
C7	N2	C8	121.29(18)
C7	N2	C9	123.77(18)
C8	N2	C9	114.52(18)
C2	C1	N1	115.64(18)
C6	C1	N1	123.9(2)
C6	C1	C2	119.9(2)
C2'	C1'	C7	118.18(19)
C6'	C1'	C2'	120.6(2)
C6'	C1'	C7	121.17(19)
O1	C2	C1	120.19(19)
O1	C2	C3	121.5(2)
C3	C2	C1	118.3(2)
C1'	C2'	C7'	120.91(19)
C3'	C2'	C1'	117.9(2)

Atom	Atom	Atom	Angle/°
C3'	C2'	C7'	121.2(2)
C4	C3	C2	120.9(2)
C4'	C3'	C2'	121.9(2)
C5	C4	C3	120.3(2)
C3'	C4'	C5'	119.7(2)
C4	C5	C6	119.7(2)
C4'	C5'	C6'	119.8(2)
C5	C6	C1	120.7(2)
C1'	C6'	C5'	120.1(2)
N1	C7	N2	119.81(19)
N1	C7	C1'	123.53(18)
N2	C7	C1'	116.59(18)

––––

[1]1-x,+y,3/2-z

Table S83: Torsion Angles in ° for **compound 3d**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	10.8(2)
Zn1	O1	C2	C3	-166.97(18)
Zn1	N1	C1	C2	-7.1(2)
Zn1	N1	C1	C6	164.54(17)
Zn1	N1	C7	N2	-52.6(3)
Zn1	N1	C7	C1'	124.24(18)
O1	C2	C3	C4	176.4(2)
N1	C1	C2	O1	-2.1(3)
N1	C1	C2	C3	175.78(19)
N1	C1	C6	C5	-174.74(19)
C1	N1	C7	N2	164.13(18)
C1	N1	C7	C1'	-19.1(3)
C1	C2	C3	C4	-1.4(3)
C1'	C2'	C3'	C4'	-2.4(3)
C2	C1	C6	C5	-3.5(3)
C2	C3	C4	C5	-1.3(4)
C2'	C1'	C6'	C5'	1.5(3)
C2'	C1'	C7	N1	-77.2(3)
C2'	C1'	C7	N2	99.8(2)
C2'	C3'	C4'	C5'	0.9(3)
C3	C4	C5	C6	1.7(4)
C3'	C4'	C5'	C6'	1.9(3)
C4	C5	C6	C1	0.7(3)
C4'	C5'	C6'	C1'	-3.1(3)
C6	C1	C2	O1	-174.04(19)
C6	C1	C2	C3	3.8(3)
C6'	C1'	C2'	C3'	1.3(3)
C6'	C1'	C2'	C7'	-179.3(2)
C6'	C1'	C7	N1	105.9(2)
C6'	C1'	C7	N2	-77.2(3)
C7	N1	C1	C2	142.0(2)
C7	N1	C1	C6	-46.3(3)
C7	C1'	C2'	C3'	-175.73(18)
C7	C1'	C2'	C7'	3.7(3)
C7	C1'	C6'	C5'	178.35(19)
C7'	C2'	C3'	C4'	178.1(2)
C8	N2	C7	N1	-5.8(3)
C8	N2	C7	C1'	177.17(19)
C9	N2	C7	N1	166.3(2)
C9	N2	C7	C1'	-10.7(3)

Compound 4d

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R_1=6.25%

Crystal Data and Experimental

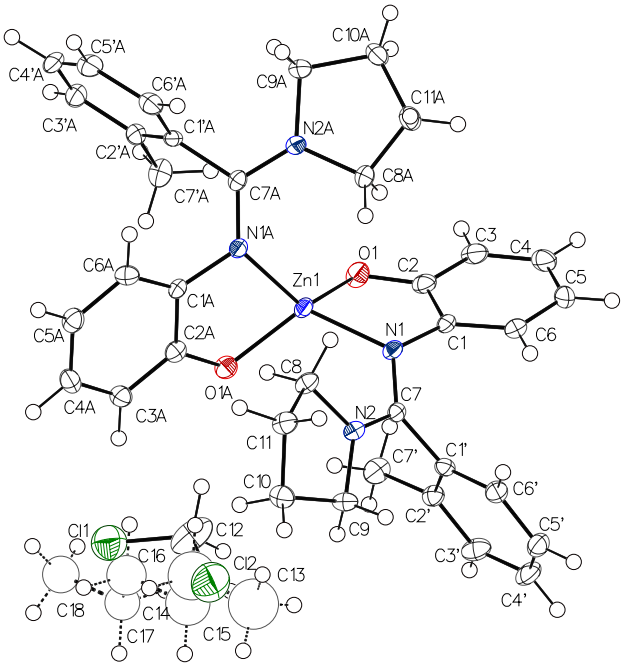

Figure S136: ORTEP view of compound **4d**

Experimental. Single clear light colourless prism-shaped crystals of **compound 4d** recrystallised from a mixture of DCM and hexane by slow evaporation. A suitable crystal with dimensions 0.25 x 0.13 x 0.09 mm³ was selected and mounted on a MITIGEN holder oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{76.5}H_{86}Cl_3N_8O_4Zn_2$, M_r = 1418.62, triclinic, P-1 (No. 2), a = 8.2841(6) Å, b = 10.5138(8) Å, c = 19.9849(15) Å, α = 89.305(3)°, β = 80.720(4)°, γ = 82.276(4)°, V = 1702.2(2) Å³, T = 100.0(1) K, Z = 1, Z' = 0.5, μ(Cu K$_{\alpha1}$) = 2.399, 10719 reflections measured, 10719 unique which were used in all calculations. The final wR_2 was 0.1636 (all data) and R_1 was 0.0625 (I≥2 σ(I)).

Table S84: Experimental parameters

Compound	**4d**
CCDC	**2182085**
Formula	$C_{76.5}H_{86}Cl_3N_8O_4Zn_2$
$D_{calc.}$/ g cm^{-3}	1.384
μ/mm^{-1}	2.399
Formula Weight	1418.62
Colour	clear light colourless
Shape	prism-shaped
Size/mm³	0.25x0.13x0.09
T/K	100.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	8.2841(6)
b/Å	10.5138(8)
c/Å	19.9849(15)
α/°	89.305(3)
β/°	80.720(4)
γ/°	82.276(4)
V/Å³	1702.2(2)
Z	1
Z'	0.5
Wavelength/Å	1.54178
Radiation type	Cu K$_{\alpha1}$
Θ_{min}/°	4.781
Θ_{max}/°	66.897
Measured Refl's.	10719
Indep't Refl's	10719
Refl's I≥2 σ(I)	9531
R_{int}	.
Parameters	432
Restraints	5
Largest Peak	0.895
Deepest Hole	-1.007
GooF	1.078
wR_2 (all data)	0.1636
wR_2	0.1573
R_1 (all data)	0.0716
R_1	0.0625

Table S85: Structure Quality Indicators

Reflections:	d min (Cu\a) 2Θ=133.8° 0.84	I/σ(I) 34.5	Rint 6.13%	Full 133.8° 98.1
Refinement:	Shift 0.000	Max Peak 0.9	Min Peak -1.0	GooF 1.078

A clear light colourless prism-shaped-shaped crystal with dimensions 0.25 x 0.13 x 0.09 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 VENTURE diffractometer operating at T = 100.0(1) K. Data were measured using ϕ and ω scans with Cu $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6]. The maximum resolution that was achieved was Θ = 66.897° (0.84 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9989 reflections, 93% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B**[4]. The final completeness is 98.10 % out to 66.897° in Θ. A multi-scan absorption correction was performed using **TWINABS-2012/1**[9] was used for absorption correction. For component 1: wR_2(int) was 0.1178 before and 0.0638 after correction. For component 2: wR_2(int) was 0.1014 before and 0.0772 after correction. The Ratio of minimum to maximum transmission is 0.80. Final HKLF 4 output contains 44641 reflections, R_{int} = 0.0510 (34520 with I > 3sig(I), R_{int} = 0.0474). The absorption coefficient μ of this material is 2.399 mm^{-1} at this wavelength (λ = 1.54178Å) and the minimum and maximum transmissions are 0.570 and 0.710. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically excepted disordered hexane solvent. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms. An idealized molecular geometry has been used to model disordered hexane part. Both solvent hexane/DCM were found disordered on the same site 25.0(1)%/75.0(1)%. Several crystals examined proved to have multiple domains. The final data crystal, while still a multiple, could be described having primarily two domains and was treated as such. Orientation matrices for the two domains were determined using the program **CELL_NOW**[10] and the data were processed further using **TWINABS**[9]. HKLF 5 was employed, BASF specifies the fractional volume contributions of the various twin components. The crystal was refined as a non-merohedral twin with a minor twin component of 0.1940 (9). The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table S86: Bond Lengths in Å for **compound 4d**.

Atom	Atom	Length/Å
Zn1	O1	1.923(3)
Zn1	O1A	1.927(3)
Zn1	N1	2.049(3)
Zn1	N1A	2.045(3)
O1	C2	1.334(5)
O1A	C2A	1.329(5)
N1	C1	1.423(5)
N1	C7	1.324(5)
N1A	C1A	1.436(5)
N1A	C7A	1.326(5)
N2	C7	1.330(5)
N2	C8	1.467(5)
N2	C9	1.480(5)
N2A	C7A	1.335(5)
N2A	C8A	1.472(5)
N2A	C9A	1.487(5)

Atom	Atom	Length/Å
C1	C2	1.431(6)
C1	C6	1.388(6)
C1'	C2'	1.395(6)
C1'	C6'	1.396(6)
C1'	C7	1.501(5)
C1'A	C2'A	1.398(6)
C1'A	C6'A	1.392(6)
C1'A	C7A	1.498(5)
C1A	C2A	1.424(5)
C1A	C6A	1.387(6)
C2	C3	1.398(6)
C2'	C3'	1.396(6)
C2'	C7'	1.499(6)
C2'A	C3'A	1.390(6)
C2'A	C7'A	1.531(6)
C2A	C3A	1.398(6)

Atom	Atom	Length/Å
C3	C4	1.391(7)
C3'	C4'	1.388(6)
C3'A	C4'A	1.369(7)
C3A	C4A	1.372(6)
C4	C5	1.385(7)
C4'	C5'	1.380(7)
C4'A	C5'A	1.379(7)
C4A	C5A	1.393(6)
C5	C6	1.391(6)
C5'	C6'	1.384(6)
C5'A	C6'A	1.403(6)
C5A	C6A	1.385(6)
C8	C11	1.519(6)
C8A	C11A	1.519(6)
C9	C10	1.514(6)
C9A	C10A	1.530(6)
C10	C11	1.524(6)
C10A	C11A	1.526(6)
Cl1	C12	1.712(10)
Cl2	C12	1.748(8)
C18	C17	1.5341
C13	C14	1.5333
C14	C15	1.5348
C15	C16	1.5348
C16	C17	1.5349

Table S87: Bond Angles in ° for **compound 4d**.

Atom	Atom	Atom	Angle/°
O1	Zn1	O1A	121.16(13)
O1	Zn1	N1	86.44(13)
O1	Zn1	N1A	124.54(12)
O1A	Zn1	N1	118.27(12)
O1A	Zn1	N1A	86.17(12)
N1A	Zn1	N1	124.41(13)
C2	O1	Zn1	110.2(2)
C2A	O1A	Zn1	110.2(2)
C1	N1	Zn1	106.1(2)
C7	N1	Zn1	123.7(3)
C7	N1	C1	120.9(3)
C1A	N1A	Zn1	105.7(2)
C7A	N1A	Zn1	128.9(3)
C7A	N1A	C1A	121.5(3)
C7	N2	C8	123.6(3)
C7	N2	C9	124.9(3)
C8	N2	C9	111.3(3)
C7A	N2A	C8A	124.4(3)
C7A	N2A	C9A	124.4(3)
C8A	N2A	C9A	111.2(3)
N1	C1	C2	115.1(3)
C6	C1	N1	124.4(4)
C6	C1	C2	120.1(4)
C2'	C1'	C6'	121.5(4)
C2'	C1'	C7	118.2(3)
C6'	C1'	C7	120.1(4)
C2'A	C1'A	C7A	118.2(3)
C6'A	C1'A	C2'A	120.8(4)
C6'A	C1'A	C7A	121.0(4)
C2A	C1A	N1A	115.3(3)
C6A	C1A	N1A	124.7(4)
C6A	C1A	C2A	119.5(4)
O1	C2	C1	120.8(4)
O1	C2	C3	121.4(4)
C3	C2	C1	117.8(4)
C1'	C2'	C3'	117.3(4)
C1'	C2'	C7'	121.9(4)
C3'	C2'	C7'	120.8(4)
C1'A	C2'A	C7'A	120.6(4)
C3'A	C2'A	C1'A	118.1(4)
C3'A	C2'A	C7'A	121.4(4)
O1A	C2A	C1A	120.4(3)
O1A	C2A	C3A	121.5(4)
C3A	C2A	C1A	118.1(4)
C4	C3	C2	121.2(4)
C4'	C3'	C2'	121.6(4)
C4'A	C3'A	C2'A	121.4(4)
C4A	C3A	C2A	121.5(4)
C5	C4	C3	120.4(4)
C5'	C4'	C3'	120.1(4)
C3'A	C4'A	C5'A	121.0(4)
C3A	C4A	C5A	120.3(4)
C4	C5	C6	119.9(4)
C4'	C5'	C6'	119.7(4)
C4'A	C5'A	C6'A	119.0(4)
C6A	C5A	C4A	119.4(4)
C1	C6	C5	120.6(4)
C5'	C6'	C1'	119.8(4)
C1'A	C6'A	C5'A	119.7(4)
C5A	C6A	C1A	121.2(4)
N1	C7	N2	120.0(3)
N1	C7	C1'	124.1(3)
N2	C7	C1'	115.8(3)
N1A	C7A	N2A	120.6(3)
N1A	C7A	C1'A	123.6(3)
N2A	C7A	C1'A	115.7(3)
N2	C8	C11	102.7(3)
N2A	C8A	C11A	103.6(3)
N2	C9	C10	103.4(3)
N2A	C9A	C10A	103.4(3)
C9	C10	C11	103.3(3)
C11A	C10A	C9A	103.3(3)
C8	C11	C10	102.4(3)
C8A	C11A	C10A	103.4(3)
Cl1	C12	Cl2	115.2(6)
C13	C14	C15	113.3
C16	C15	C14	113.7
C15	C16	C17	113.7
C18	C17	C16	113.3

Table S88: Torsion Angles in ° for **compound 4d**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	10.0(5)
Zn1	O1	C2	C3	-169.1(3)
Zn1	O1A	C2A	C1A	13.5(4)
Zn1	O1A	C2A	C3A	-164.4(3)
Zn1	N1	C1	C2	-6.6(4)
Zn1	N1	C1	C6	166.6(3)
Zn1	N1	C7	N2	-52.3(5)
Zn1	N1	C7	C1'	124.6(3)
Zn1	N1A	C1A	C2A	-7.2(4)
Zn1	N1A	C1A	C6A	164.1(3)
Zn1	N1A	C7A	N2A	-39.2(5)
Zn1	N1A	C7A	C1'A	137.3(3)
O1	C2	C3	C4	176.8(4)
O1A	C2A	C3A	C4A	177.5(4)
N1	C1	C2	O1	-1.9(5)
N1	C1	C2	C3	177.2(4)
N1	C1	C6	C5	-175.5(4)
N1A	C1A	C2A	O1A	-3.8(5)
N1A	C1A	C2A	C3A	174.1(3)
N1A	C1A	C6A	C5A	-173.8(4)
N2	C8	C11	C10	-35.9(4)
N2	C9	C10	C11	-29.7(4)
N2A	C8A	C11A	C10A	-33.1(5)
N2A	C9A	C10A	C11A	-29.8(4)
C1	N1	C7	N2	165.6(3)
C1	N1	C7	C1'	-17.5(6)
C1	C2	C3	C4	-2.3(6)
C1'	C2'	C3'	C4'	-0.1(6)
C1'A	C2'A	C3'A	C4'A	-0.5(6)
C1A	N1A	C7A	N2A	166.5(4)
C1A	N1A	C7A	C1'A	-17.1(6)
C1A	C2A	C3A	C4A	-0.4(6)
C2	C1	C6	C5	-2.6(6)
C2	C3	C4	C5	-0.1(7)
C2'	C1'	C6'	C5'	1.3(6)
C2'	C1'	C7	N1	-68.7(5)
C2'	C1'	C7	N2	108.3(4)
C2'	C3'	C4'	C5'	1.0(7)
C2'A	C1'A	C6'A	C5'A	1.6(6)
C2'A	C1'A	C7A	N1A	-66.9(5)
C2'A	C1'A	C7A	N2A	109.7(4)
C2'A	C3'A	C4'A	C5'A	1.1(6)
C2A	C1A	C6A	C5A	-2.8(6)
C2A	C3A	C4A	C5A	-1.0(6)
C3	C4	C5	C6	1.3(7)
C3'	C4'	C5'	C6'	-0.7(7)
C3'A	C4'A	C5'A	C6'A	-0.4(6)
C3A	C4A	C5A	C6A	0.6(6)
C4	C5	C6	C1	0.1(6)
C4'	C5'	C6'	C1'	-0.4(6)
C4'A	C5'A	C6'A	C1'A	-0.9(6)
C4A	C5A	C6A	C1A	1.4(6)
C6	C1	C2	O1	-175.5(4)
C6	C1	C2	C3	3.7(6)
C6'	C1'	C2'	C3'	-1.0(6)

Atom	Atom	Atom	Atom	Angle/°
C6'	C1'	C2'	C7'	178.2(4)
C6'	C1'	C7	N1	116.1(4)
C6'	C1'	C7	N2	-66.9(5)
C6'A	C1'A	C2'A	C3'A	-0.8(6)
C6'A	C1'A	C2'A	C7'A	-179.7(4)
C6'A	C1'A	C7A	N1A	113.6(4)
C6'A	C1'A	C7A	N2A	-69.7(5)
C6A	C1A	C2A	O1A	-175.6(4)
C6A	C1A	C2A	C3A	2.3(6)
C7	N1	C1	C2	141.3(4)
C7	N1	C1	C6	-45.5(6)
C7	N2	C8	C11	-165.8(4)
C7	N2	C9	C10	-168.8(4)
C7	C1'	C2'	C3'	-176.2(4)
C7	C1'	C2'	C7'	3.1(6)
C7	C1'	C6'	C5'	176.4(4)
C7'	C2'	C3'	C4'	-179.4(4)
C7'A	C2'A	C3'A	C4'A	178.4(4)
C7A	N1A	C1A	C2A	152.3(4)
C7A	N1A	C1A	C6A	-36.4(6)
C7A	N2A	C8A	C11A	-164.2(4)
C7A	N2A	C9A	C10A	-171.5(4)
C7A	C1'A	C2'A	C3'A	179.7(3)
C7A	C1'A	C2'A	C7'A	0.9(5)
C7A	C1'A	C6'A	C5'A	-179.0(4)
C8	N2	C7	N1	-7.2(6)
C8	N2	C7	C1'	175.6(3)
C8	N2	C9	C10	7.3(4)
C8A	N2A	C7A	N1A	-4.6(6)
C8A	N2A	C7A	C1'A	178.7(4)
C8A	N2A	C9A	C10A	9.5(5)
C9	N2	C7	N1	168.4(4)
C9	N2	C7	C1'	-8.8(5)
C9	N2	C8	C11	18.1(4)
C9	C10	C11	C8	41.1(4)
C9A	N2A	C7A	N1A	176.5(4)
C9A	N2A	C7A	C1'A	-0.2(6)
C9A	N2A	C8A	C11A	14.7(5)
C9A	C10A	C11A	C8A	39.2(5)
C13	C14	C15	C16	180.0
C14	C15	C16	C17	180.0
C15	C16	C17	C18	180.0

Table S89: Atomic Occupancies for all atoms that are not fully occupied in **compound 4d**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Cl1	0.75	H18B	0.25	H14A	0.25	H16B	0.25
Cl2	0.75	H18C	0.25	H14B	0.25	C17	0.25
C12	0.75	C13	0.25	C15	0.25	H17A	0.25
H12A	0.75	H13A	0.25	H15A	0.25	H17B	0.25
H12B	0.75	H13B	0.25	H15B	0.25		
C18	0.25	H13C	0.25	C16	0.25		
H18A	0.25	C14	0.25	H16A	0.25		

Compound 6d

Pacsmub LATEFORME Analyse Chimique Synthèse Moléculaire UNIVERSITÉ DE BOURGOGNE

R_1=2.59%

Crystal Data and Experimental

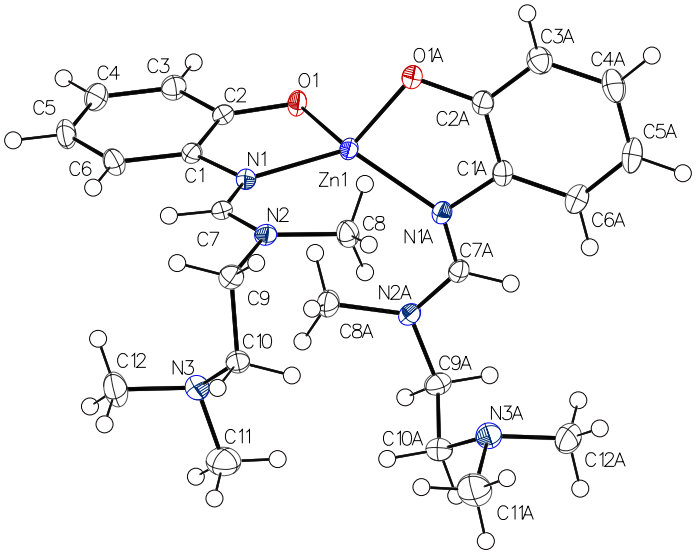

Figure S137: ORTEP view of compound **6d**

Experimental. Single clear light colourless needle-shaped crystals of **compound 6d** recrystallised from a mixture of DCM and cyclohexane by slow evaporation. A suitable crystal with dimensions 0.80 x 0.15 x 0.12 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius APEX-II CCD diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT**[1] solution program using dual methods and by using **Olex2**[2] 1.5 as the graphical interface. The model was refined with **ShelXL**[3] 2018/3 using full matrix least squares minimisation on F^2.

Crystal Data. $C_{24}H_{36}N_6O_2Zn$, M_r = 505.96, triclinic, P-1 (No. 2), a = 10.6168(3) Å, b = 11.2860(4) Å, c = 11.5396(4) Å, α = 75.743(2)°, β = 89.755(2)°, γ = 71.855(2)°, V = 1269.52(7) Å^3, T = 110.0(1) K, Z = 2, Z' = 1, μ(Mo K$_{\alpha1}$) = 0.999, 86013 reflections measured, 5840 unique (R_{int} = 0.0553) which were used in all calculations. The final wR_2 was 0.0655 (all data) and R_1 was 0.0259 (I≥2 σ(I)).

Table S90: Experimental parameters

Compound	**6d**
CCDC	**2182086**
Formula	$C_{24}H_{36}N_6O_2Zn$
$D_{calc.}$/ g cm^{-3}	1.324
μ/mm^{-1}	0.999
Formula Weight	505.96
Colour	clear light colourless
Shape	needle-shaped
Size/mm^3	0.80x0.15x0.12
T/K	110.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	10.6168(3)
b/Å	11.2860(4)
c/Å	11.5396(4)
α/°	75.743(2)
β/°	89.755(2)
γ/°	71.855(2)
V/Å^3	1269.52(7)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_{\alpha1}$
Θ_{min}/°	2.313
Θ_{max}/°	27.576
Measured Refl's.	86013
Indep't Refl's	5840
Refl's I≥2 σ(I)	4799
R_{int}	0.0553
Parameters	304
Restraints	0
Largest Peak	0.357
Deepest Hole	-0.304
GooF	1.038
wR_2 (all data)	0.0655
wR_2	0.0589
R_1 (all data)	0.0408
R_1	0.0259

Table S91: Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.2°	0.77	I/σ(I)	40.1	Rint	5.53%	Full 50.5°	99.9
Refinement:	Shift	-0.002	Max Peak	0.4	Min Peak	-0.3	GooF	1.038

A clear light colourless needle-shaped-shaped crystal with dimensions 0.80 x 0.15 x 0.12 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius APEX-II CCD diffractometer operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4**[6] . The maximum resolution that was achieved was Θ = 27.576° (0.77 Å). The unit cell was refined using **SAINT V8.40B**[4] on 9904 reflections, 12% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B[4] . The final completeness is 99.90 % out to 27.576° in Θ. **SADABS-2016/2**[5] was used for absorption correction. wR_2(int) was 0.0663 before and 0.0530 after correction. The Ratio of minimum to maximum transmission is 0.8031. The absorption coefficient μ of this material is 0.999 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.644 and 0.801. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT**[1] structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL**[3] 2018/3 . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Table S92: Bond Lengths in Å for **compound 6d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	1.9337(11)	N3	C12	1.459(2)
Zn1	O1A	1.9370(11)	N3A	C10A	1.458(2)
Zn1	N1	2.0172(12)	N3A	C11A	1.462(2)
Zn1	N1A	2.0072(13)	N3A	C12A	1.457(2)
O1	C2	1.3278(18)	C1	C2	1.422(2)
O1A	C2A	1.3342(18)	C1	C6	1.388(2)
N1	C1	1.4326(19)	C1A	C2A	1.418(2)
N1	C7	1.305(2)	C1A	C6A	1.394(2)
N1A	C1A	1.4390(19)	C2	C3	1.401(2)
N1A	C7A	1.309(2)	C2A	C3A	1.397(2)
N2	C7	1.3289(19)	C3	C4	1.386(2)
N2	C8	1.453(2)	C3A	C4A	1.387(2)
N2	C9	1.4621(19)	C4	C5	1.384(2)
N2A	C7A	1.328(2)	C4A	C5A	1.386(3)
N2A	C8A	1.457(2)	C5	C6	1.390(2)
N2A	C9A	1.463(2)	C5A	C6A	1.388(2)
N3	C10	1.458(2)	C9	C10	1.520(2)
N3	C11	1.455(2)	C9A	C10A	1.523(2)

Table S93: Bond Angles in ° for **compound 6d**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Zn1	O1A	112.07(5)	C2	O1	Zn1	110.35(9)
O1	Zn1	N1	86.72(5)	C2A	O1A	Zn1	110.06(9)
O1	Zn1	N1A	122.65(5)	C1	N1	Zn1	107.00(9)
O1A	Zn1	N1	122.19(5)	C7	N1	Zn1	133.65(10)
O1A	Zn1	N1A	87.14(5)	C7	N1	C1	119.12(12)
N1A	Zn1	N1	128.83(5)	C1A	N1A	Zn1	106.79(9)

Atom	Atom	Atom	Angle/°
C7A	N1A	Zn1	133.90(11)
C7A	N1A	C1A	118.21(13)
C7	N2	C8	122.78(13)
C7	N2	C9	119.00(13)
C8	N2	C9	117.29(12)
C7A	N2A	C8A	122.71(13)
C7A	N2A	C9A	117.89(13)
C8A	N2A	C9A	118.31(13)
C10	N3	C12	111.34(14)
C11	N3	C10	111.52(14)
C11	N3	C12	110.12(15)
C10A	N3A	C11A	110.97(14)
C12A	N3A	C10A	111.88(15)
C12A	N3A	C11A	109.57(15)
C2	C1	N1	114.97(13)
C6	C1	N1	125.51(14)
C6	C1	C2	119.52(14)
C2A	C1A	N1A	115.34(13)
C6A	C1A	N1A	125.17(15)
C6A	C1A	C2A	119.49(15)

Atom	Atom	Atom	Angle/°
O1	C2	C1	120.91(13)
O1	C2	C3	120.83(14)
C3	C2	C1	118.25(14)
O1A	C2A	C1A	120.66(14)
O1A	C2A	C3A	120.94(15)
C3A	C2A	C1A	118.39(14)
C4	C3	C2	121.37(15)
C4A	C3A	C2A	121.39(16)
C5	C4	C3	119.89(15)
C5A	C4A	C3A	119.85(16)
C4	C5	C6	119.95(15)
C4A	C5A	C6A	119.97(16)
C1	C6	C5	121.02(15)
C5A	C6A	C1A	120.85(16)
N1	C7	N2	125.43(14)
N1A	C7A	N2A	125.87(14)
N2	C9	C10	111.96(13)
N2A	C9A	C10A	112.35(13)
N3	C10	C9	112.35(13)
N3A	C10A	C9A	112.59(14)

Table S94: Torsion Angles in ° for **compound 6d**.

Atom	Atom	Atom	Atom	Angle/°
Zn1	O1	C2	C1	2.37(17)
Zn1	O1	C2	C3	-179.10(12)
Zn1	O1A	C2A	C1A	0.30(17)
Zn1	O1A	C2A	C3A	179.13(12)
Zn1	N1	C1	C2	-0.10(15)
Zn1	N1	C1	C6	-179.48(13)
Zn1	N1	C7	N2	-4.4(2)
Zn1	N1A	C1A	C2A	-1.08(15)
Zn1	N1A	C1A	C6A	178.64(13)
Zn1	N1A	C7A	N2A	-15.2(2)
O1	C2	C3	C4	-177.86(15)
O1A	C2A	C3A	C4A	-178.58(15)
N1	C1	C2	O1	-1.5(2)
N1	C1	C2	C3	179.88(14)
N1	C1	C6	C5	179.51(15)
N1A	C1A	C2A	O1A	0.6(2)
N1A	C1A	C2A	C3A	-178.28(13)
N1A	C1A	C6A	C5A	177.43(15)
N2	C9	C10	N3	-63.33(17)
N2A	C9A	C10A	N3A	-61.44(19)
C1	N1	C7	N2	-177.99(14)
C1	C2	C3	C4	0.7(2)
C1A	N1A	C7A	N2A	178.61(14)
C1A	C2A	C3A	C4A	0.3(2)
C2	C1	C6	C5	0.2(2)
C2	C3	C4	C5	-0.2(3)
C2A	C1A	C6A	C5A	-2.9(2)
C2A	C3A	C4A	C5A	-1.7(3)
C3	C4	C5	C6	-0.4(3)
C3A	C4A	C5A	C6A	0.8(3)
C4	C5	C6	C1	0.4(3)
C4A	C5A	C6A	C1A	1.4(3)
C6	C1	C2	O1	177.87(14)
C6	C1	C2	C3	-0.7(2)
C6A	C1A	C2A	O1A	-179.17(14)

Atom	Atom	Atom	Atom	Angle/°
C6A	C1A	C2A	C3A	2.0(2)
C7	N1	C1	C2	175.07(13)
C7	N1	C1	C6	-4.3(2)
C7	N2	C9	C10	96.29(16)
C7A	N1A	C1A	C2A	168.57(14)
C7A	N1A	C1A	C6A	-11.7(2)
C7A	N2A	C9A	C10A	85.72(17)
C8	N2	C7	N1	-3.7(2)
C8	N2	C9	C10	-72.95(17)
C8A	N2A	C7A	N1A	-2.8(2)
C8A	N2A	C9A	C10A	-82.71(18)
C9	N2	C7	N1	-172.27(14)
C9A	N2A	C7A	N1A	-170.65(14)
C11	N3	C10	C9	160.91(14)
C11A	N3A	C10A	C9A	165.69(15)
C12	N3	C10	C9	-75.65(17)
C12A	N3A	C10A	C9A	-71.59(18)

Table S95: Continuous shape measure values SQ(P) calculated for the coordination polyhedra found in the crystal structures of complexes **1a**, **1b**, **1b'**, **2**, and **3b**.

ML5 structure	PP-5-D5h-Pentagon	vOC-5-C4v-Vacant octahedron	**TBPY-5-D3h-Trigonal bipyramid**	**SPY-5-C4v-Spherical square pyramid**	JTBPY-5-D3h-Johnson trigonal bipyramid J12
1a	33.899	7.322	**2.015**	4.462	4.006
1b	33.873	7.198	**1.348**	4.402	2.062
1b'	32.956	5.552	**1.055**	3.908	1.436
2b	33.393	4.916	2.204	**2.180**	3.180
3b	34.054	4.678	3.062	**1.812**	3.830

Bold-faced numbers correspond to the lowest SQ(P) values calculated by the SHAPE 2.1 program[11]

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