SUPPORTING INFORMATION

Dipyrromethene and ß-Diketiminate Zinc Hydride Complexes: Resemblances and Differences

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Contents

1) Crystal structure data

Crystal structure of ^{DIPP}DPM-H (3) – hasj180227c

A yellow crystal of ^{DIPP}DPM-H (**3**) was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on a SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro software package.[1] Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Disorder of two *iso*-propyl-groups of the molecule was observed. The relative contributions of the two orientations of each group were refined to ~ 0.50/0.50 and 0.54/0.46, respectively.

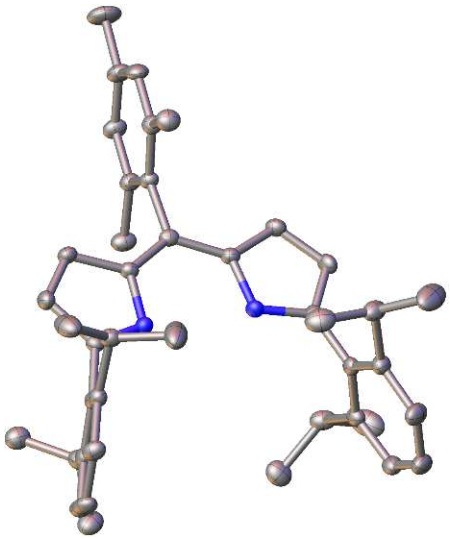


Figure S1. ORTEP plot of ^{DIPP}DPM-H (**3**) (50% probability)

Table S1. Crystal data and structure refinement for ^{DIPP}DPM-H	
Identification code	hasj180227c
Empirical formula	$C_{42}H_{50}N_2$
Formula weight	582.84
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.8415(7)
b/Å	16.59310(10)
c/Å	37.3538(12)
α/°	90
β/°	146.605(8)
γ/°	90
Volume/Å^3	7110.1(9)
Z	8
ρ_{calc}g/cm^3	1.089
μ/mm^{-1}	0.467
F(000)	2528.0
Crystal size/mm^3	0.448 × 0.293 × 0.265
Crystal color	Yellow
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.846 to 136.224
Index ranges	-25 ≤ h ≤ 25, -19 ≤ k ≤ 19, -44 ≤ l ≤ 44
Reflections collected	144252
Independent reflections	12926 [R_{int} = 0.0399, R_{sigma} = 0.0145]
Data/restraints/parameters	12926/0/857
Goodness-of-fit on F^2	1.247
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.1529
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1530
Largest diff. peak/hole / e Å^{-3}	0.47/-0.46

Crystal structure of (^{DIPP}DPM)ZnEt (4) – hasj171130a

An orange crystal of (^{DIPP}DPM)ZnEt (**4**) was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on a SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro software package.[1] Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

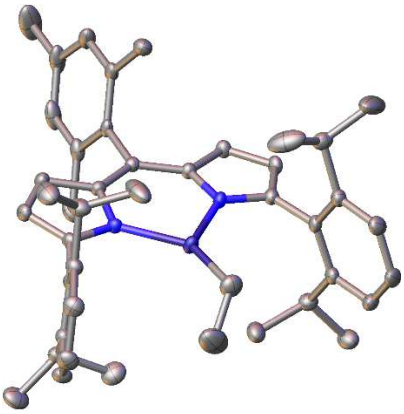


Figure S2. ORTEP plot of (^{DIPP}DPM)ZnEt (**4**) (50% probability)

Table S2. Crystal data and structure refinement for (^{DIPP}DPM)ZnEt	
Identification code	hasj171130a
Empirical formula	$C_{44}H_{54}N_2Zn$
Formula weight	676.26
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.99150(10)
b/Å	18.6458(2)
c/Å	18.5626(2)
α/°	90
β/°	93.2860(10)
γ/°	90
Volume/Å^3	3798.06(7)
Z	4
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	1.119
F(000)	1448.0
Crystal size/mm^3	0.662 × 0.499 × 0.345
Crystal color	Orange
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.724 to 136.194
Index ranges	-12 ≤ h ≤ 13, -22 ≤ k ≤ 22, -22 ≤ l ≤ 22
Reflections collected	25241
Independent reflections	6918 [R_{int} = 0.0208, R_{sigma} = 0.0170]
Data/restraints/parameters	6918/0/436
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1078
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	0.85/-0.71

Crystal structure of (^{DIPP}DPM)ZnI (5) – hasj180109b

An orange crystal of (^{DIPP}DPM)ZnEt (**5**) was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on a SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro software package.[1] Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

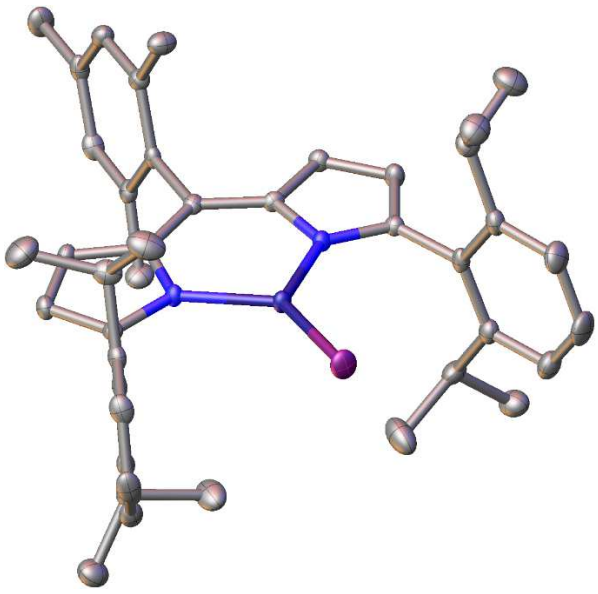


Figure S3. ORTEP plot of (^{DIPP}DPM)ZnI (**5**) (50% probability)

Table S3. Crystal data and structure refinement for (^{DIPP}DPM)ZnI	
Identification code	hasj180109b
Empirical formula	$C_{42}H_{49}IN_2Zn$
Formula weight	774.10
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.2471(5)
b/Å	23.0104(10)
c/Å	15.5386(6)
α/°	90
β/°	108.881(5)
γ/°	90
Volume/Å^3	3805.0(3)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	1.487
F(000)	1592.0
Crystal size/mm^3	0.616 × 0.498 × 0.347
Crystal color	Orange
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.99 to 56.122
Index ranges	-14 ≤ h ≤ 14, -27 ≤ k ≤ 30, -20 ≤ l ≤ 20
Reflections collected	33121
Independent reflections	8955 [R_{int} = 0.0480, R_{sigma} = 0.0446]
Data/restraints/parameters	8955/0/426
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0903
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0969
Largest diff. peak/hole / e Å^{-3}	1.22/-0.84

Crystal structure of (^{DIPP}DPM)ZnH (6) – hasj160209a

An orange crystal of (^{DIPP}DPM)ZnH **(6)** was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on a SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro software package.[1] Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. Except of the Zn-H hydrogen atom, all hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The position of the Zn-H hydrogen atom was observed from difference Fourier maps and refined.

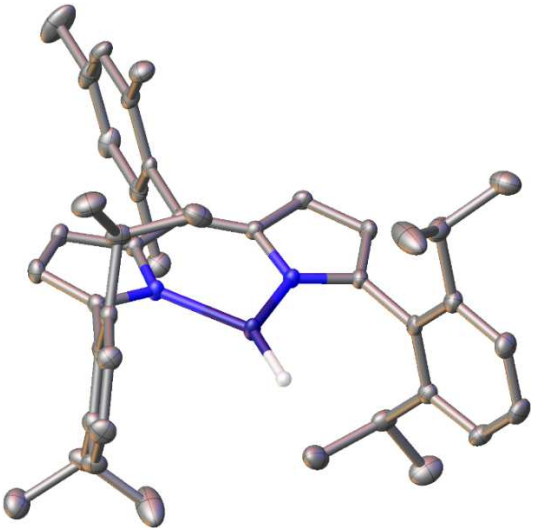


Figure S4. ORTEP plot of (^{DIPP}DPM)ZnH (**6**) (50% probability)

Table S4. Crystal data and structure refinement for (^{DIPP}DPM)ZnH	
Identification code	hasj160209a
Empirical formula	$C_{42}H_{50}N_2Zn$
Formula weight	648.21
Temperature/K	100
Crystal system	Monoclinic
Space group	C2/c
a/Å	18.87443(19)
b/Å	18.08080(19)
c/Å	10.80881(11)
α/°	90
β/°	94.9310(9)
γ/°	90
Volume/Å^3	3675.01(6)
Z	4
ρ_{calc}g/cm^3	1.172
μ/mm^{-1}	2.098
F(000)	1384.0
Crystal size/mm^3	0.431 × 0.2423 × 0.1438
Crystal color	Orange
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.782 to 136.216
Index ranges	-22 ≤ h ≤ 22, -21 ≤ k ≤ 21, -13 ≤ l ≤ 12
Reflections collected	19764
Independent reflections	3355 [R_{int} = 0.0337, R_{sigma} = 0.0165]
Data/restraints/parameters	3355/0/214
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0781
Final R indexes [all data]	R_1 = 0.0305, wR_2 = 0.0784
Largest diff. peak/hole / e Å^{-3}	0.33/-0.35

Crystal structure of (^{DIPP}DPM)ZnO$_2$CH (7) – hasj170920a

An orange crystal of (^{DIPP}DPM)ZnO$_2$CH (**7**) was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100 K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on a SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro software package.[1] Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

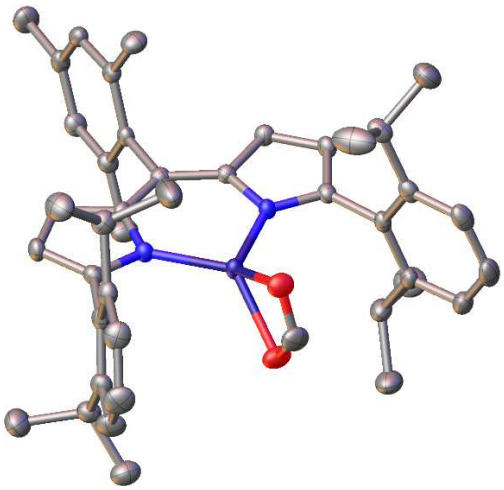


Figure S5. ORTEP plot of (^{DIPP}DPM)ZnO$_2$CH (**7**) (50% probability)

Table S5. Crystal data and structure refinement for (^{DIPP}DPM)ZnO_2CH	
Identification code	hasj170920a
Empirical formula	$C_{43}H_{50}N_2O_2Zn$
Formula weight	692.22
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.43330(10)
b/Å	22.9394(3)
c/Å	15.4127(2)
α/°	90
β/°	108.0040(10)
γ/°	90
Volume/Å^3	3844.40(8)
Z	4
ρ_{calc}g/cm^3	1.196
μ/mm^{-1}	1.159
F(000)	1472.0
Crystal size/mm^3	0.57 × 0.487 × 0.132
Crystal color	Orange
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.156 to 136.232
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 27, -18 ≤ l ≤ 15
Reflections collected	21531
Independent reflections	7024 [R_{int} = 0.0282, R_{sigma} = 0.0270]
Data/restraints/parameters	7024/0/448
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0833
Final R indexes [all data]	R_1 = 0.0367, wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	0.33/-0.41

2) Selected ^{1}H, ^{13}C, COSY, HSQC, HMBC, DOSY and temperature-dependant NMR spectra

Figure S6. ^{1}H and ^{13}C spectra of 2-(2,6-di-*iso*-propylphenyl)-1H-pyrrole (**1**) in $CDCl_3$ (*).

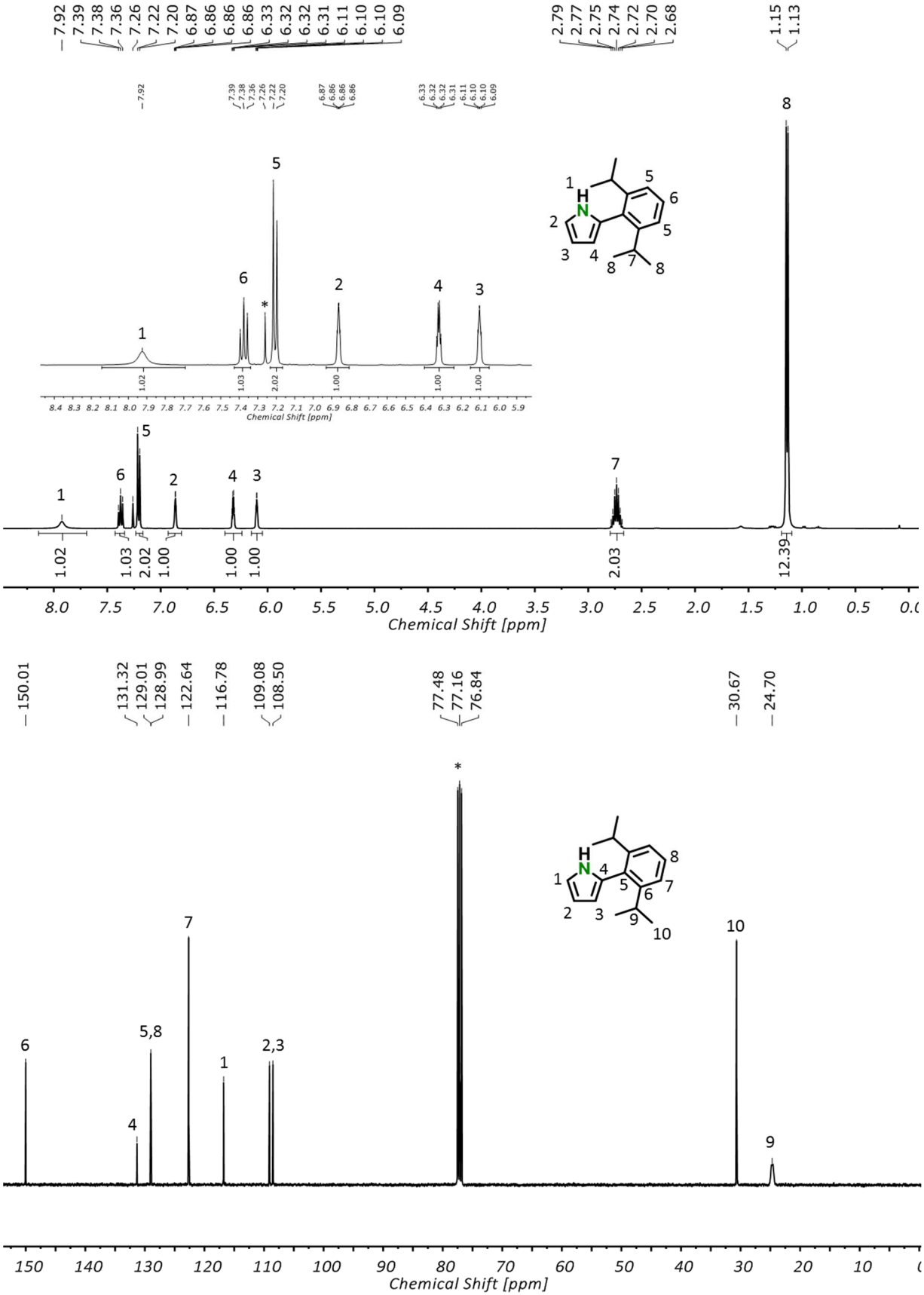
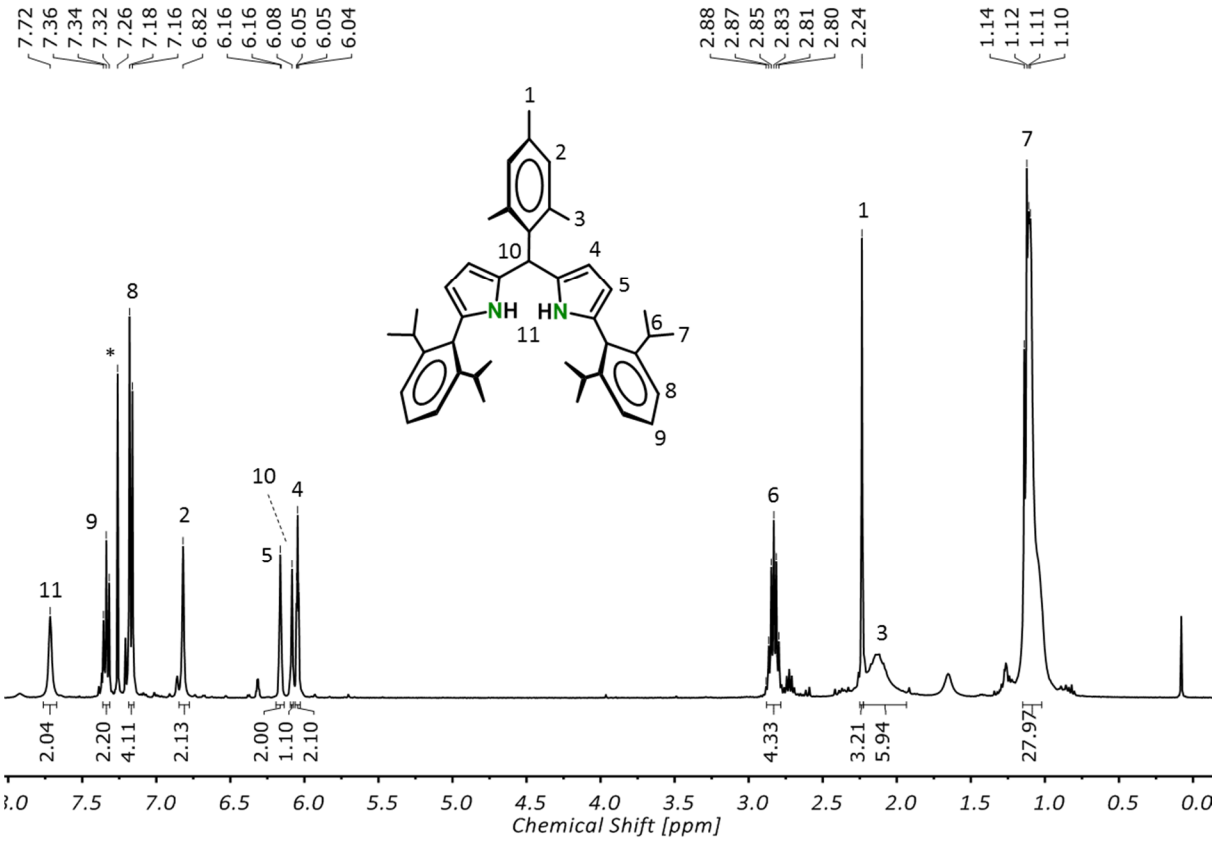


Figure S7. ^{1}H and ^{13}C NMR spectra of 1,9-di-*iso*-propylphenyl-5-mesityldipyrromethane (**2**) in $CDCl_3$ (*).



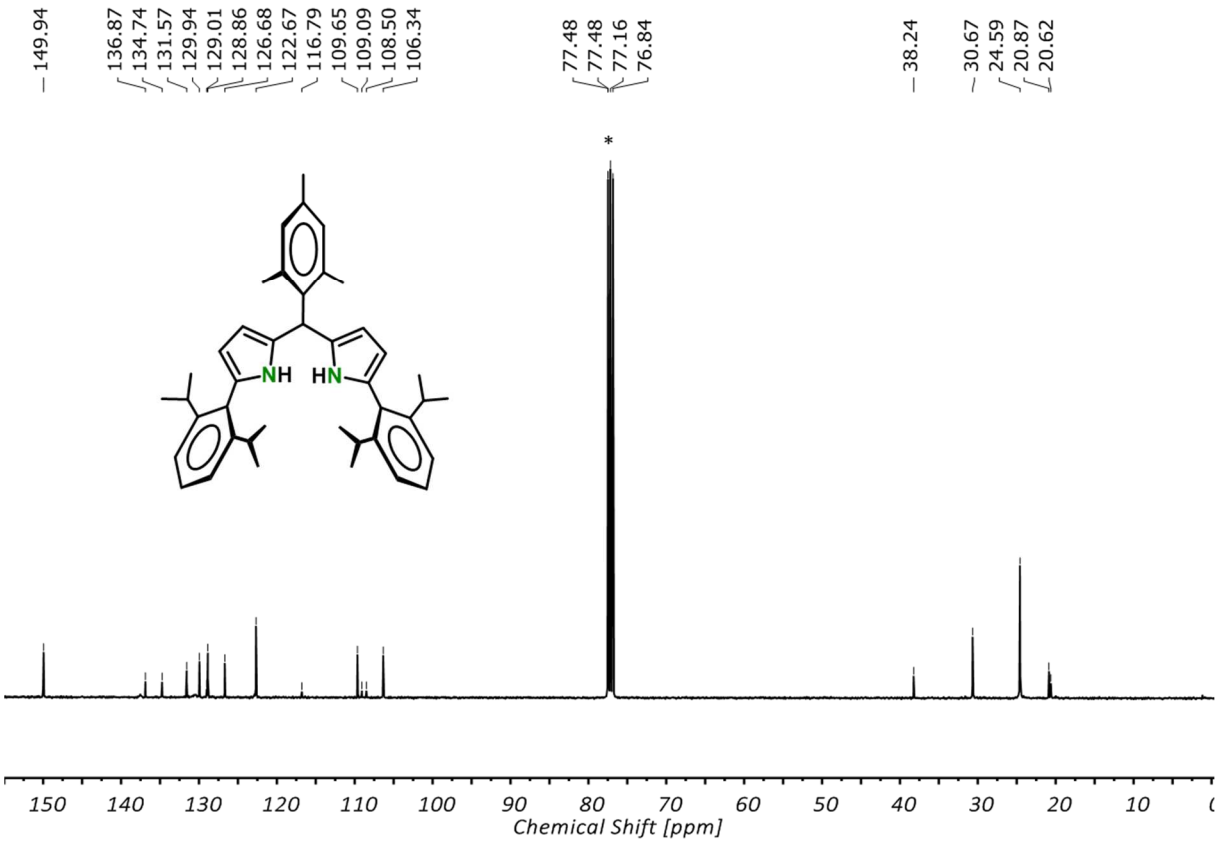
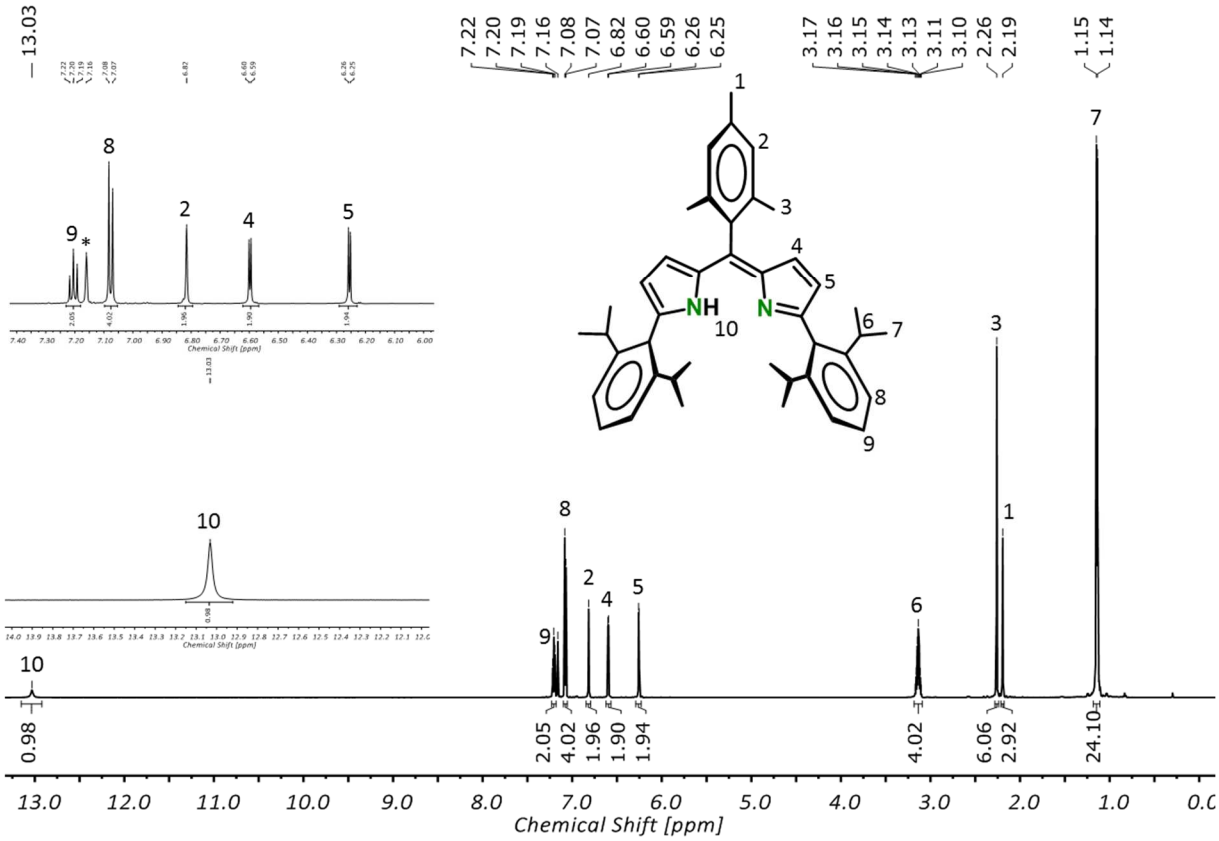


Figure S8. ^{1}H and ^{13}C spectra of ^{DIPP}DPM-H (**3**) in benzene-d_6 (*).



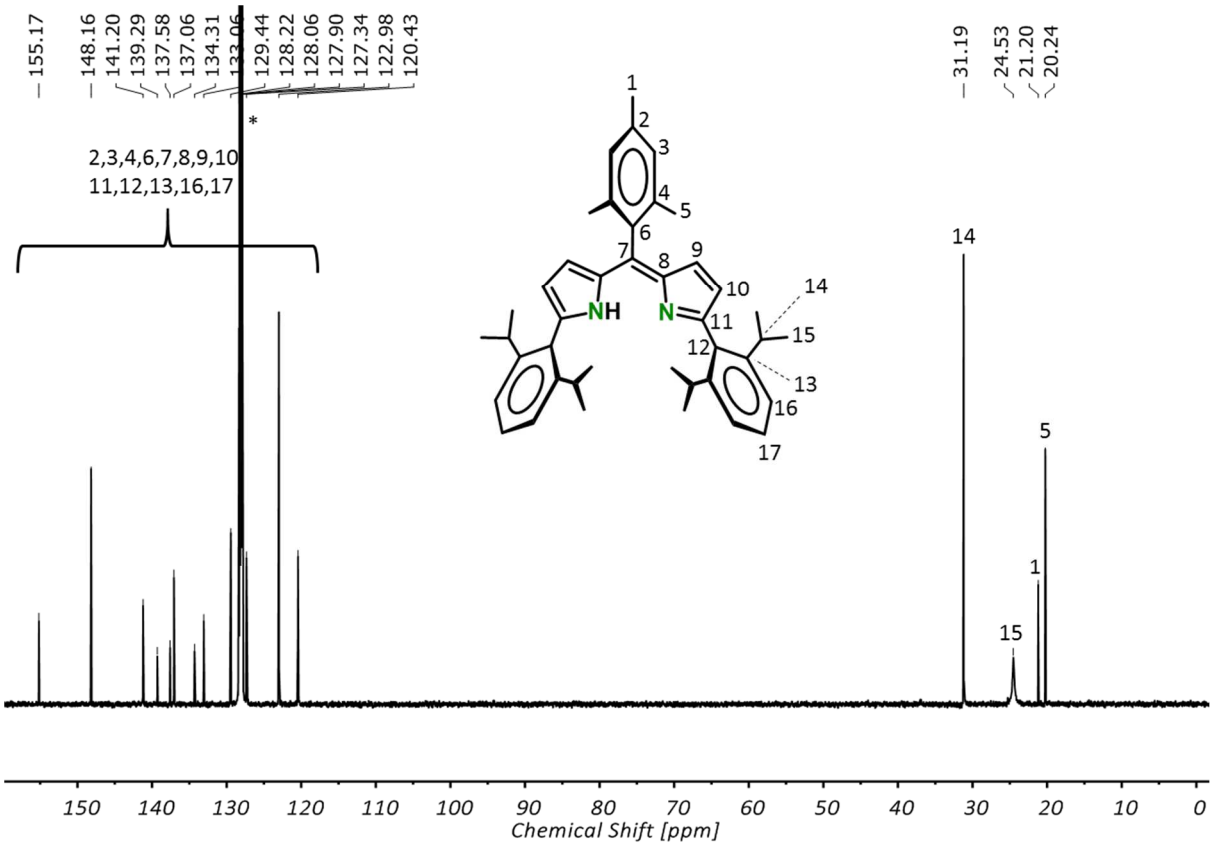
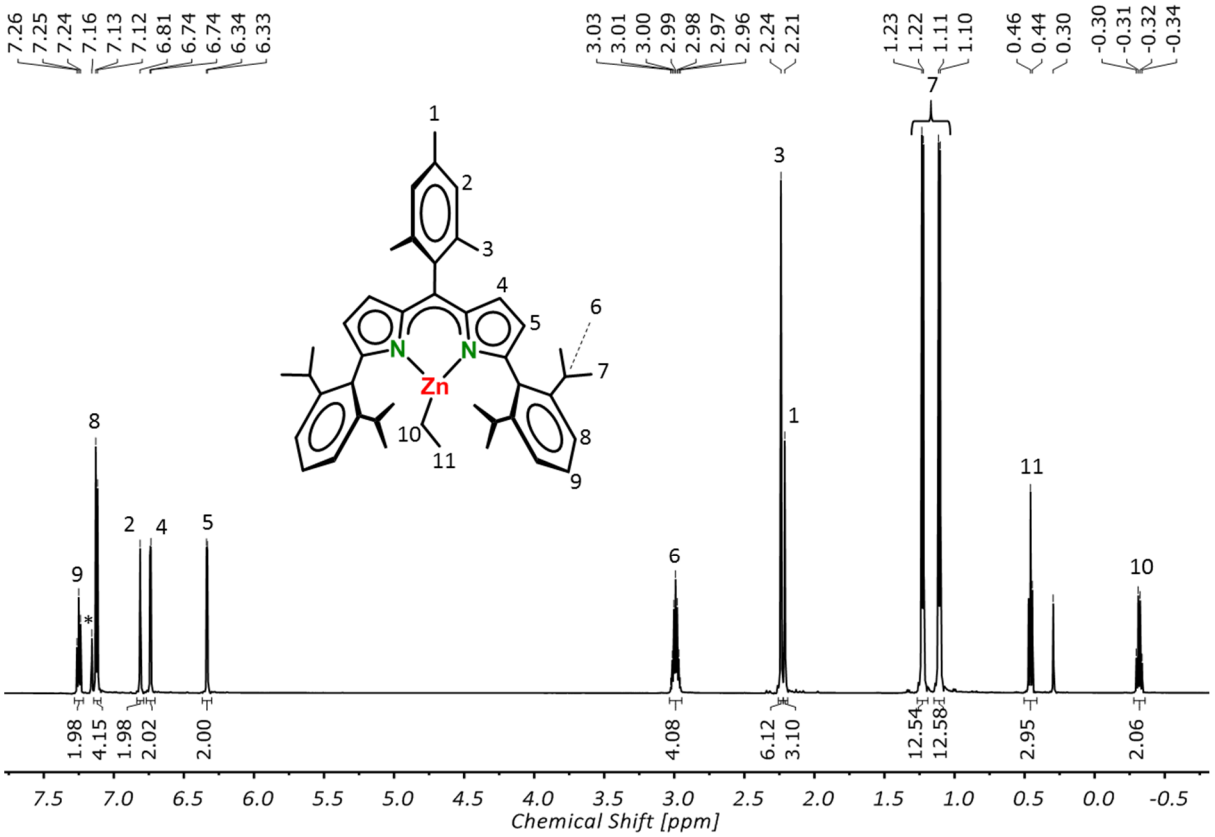
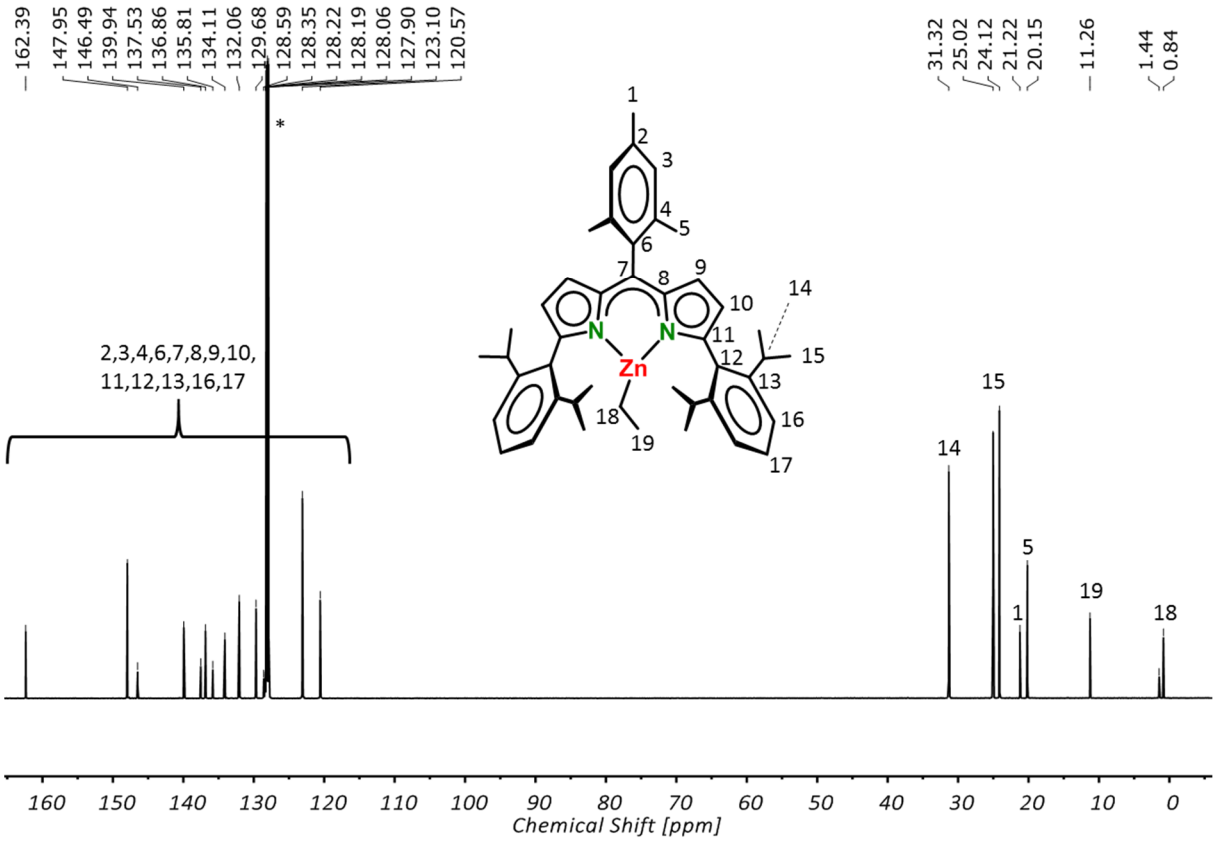
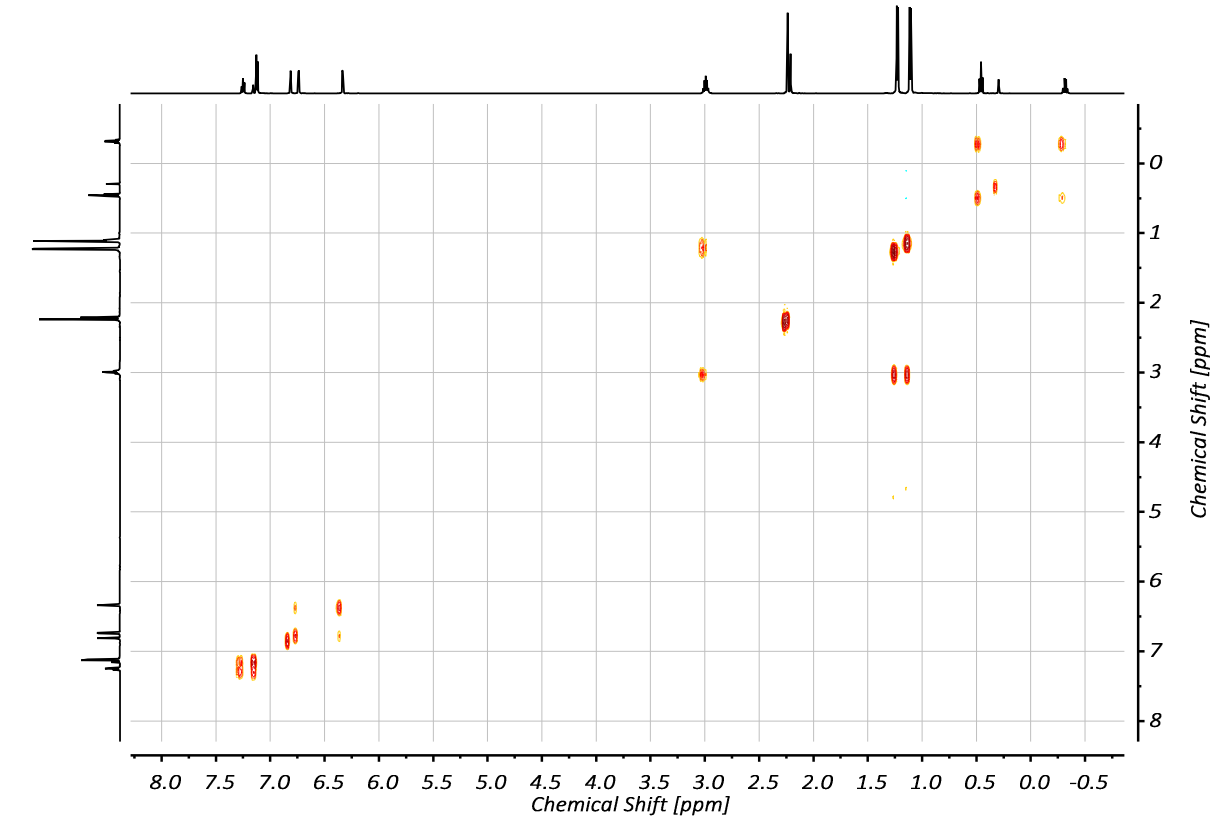


Figure S9. ^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of (^{DIPP}DPM)ZnEt (**4**) in benzene-d_6 (*).



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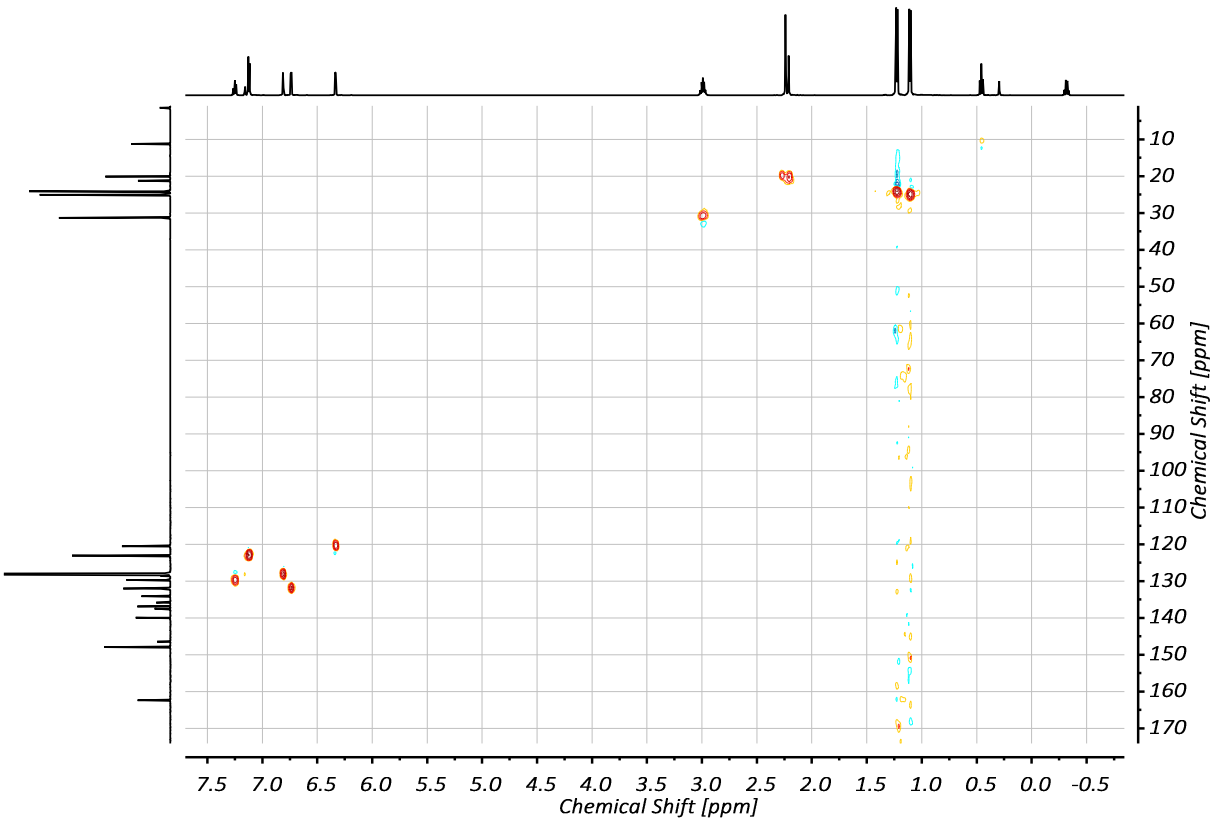
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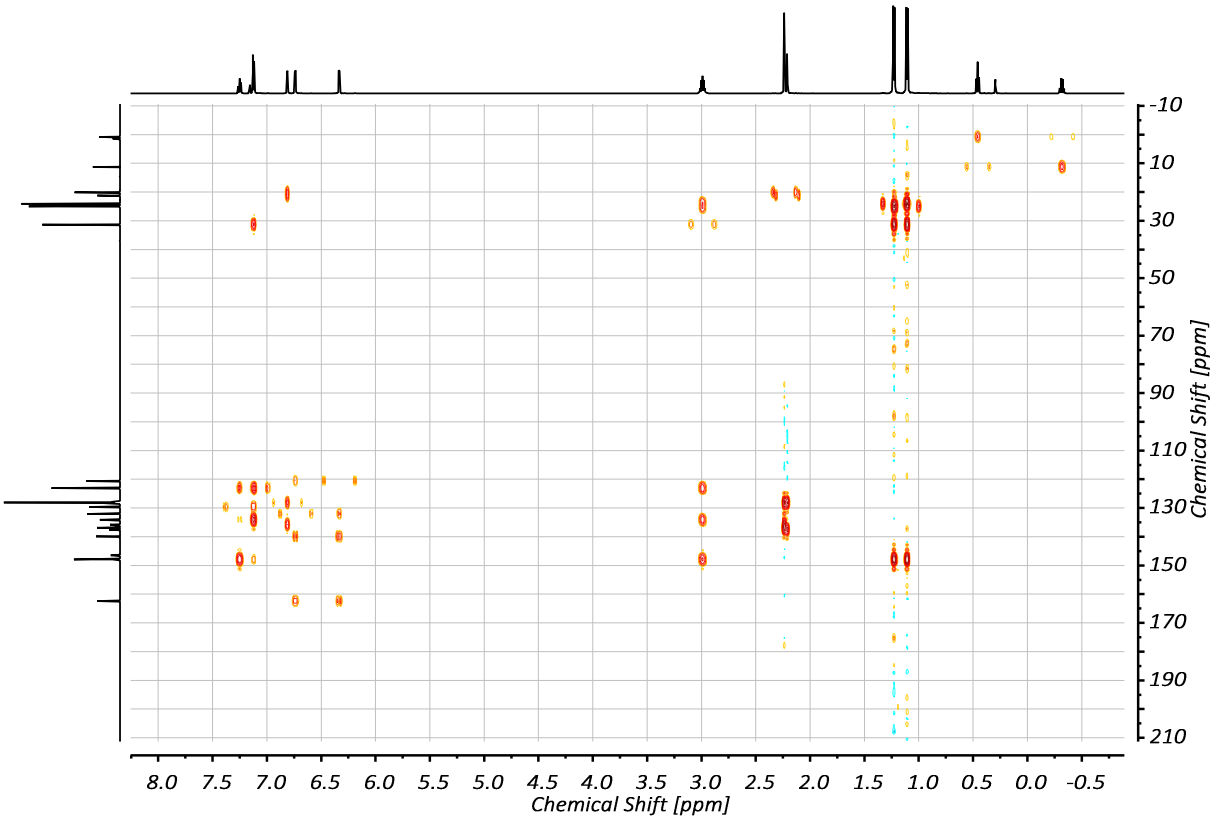
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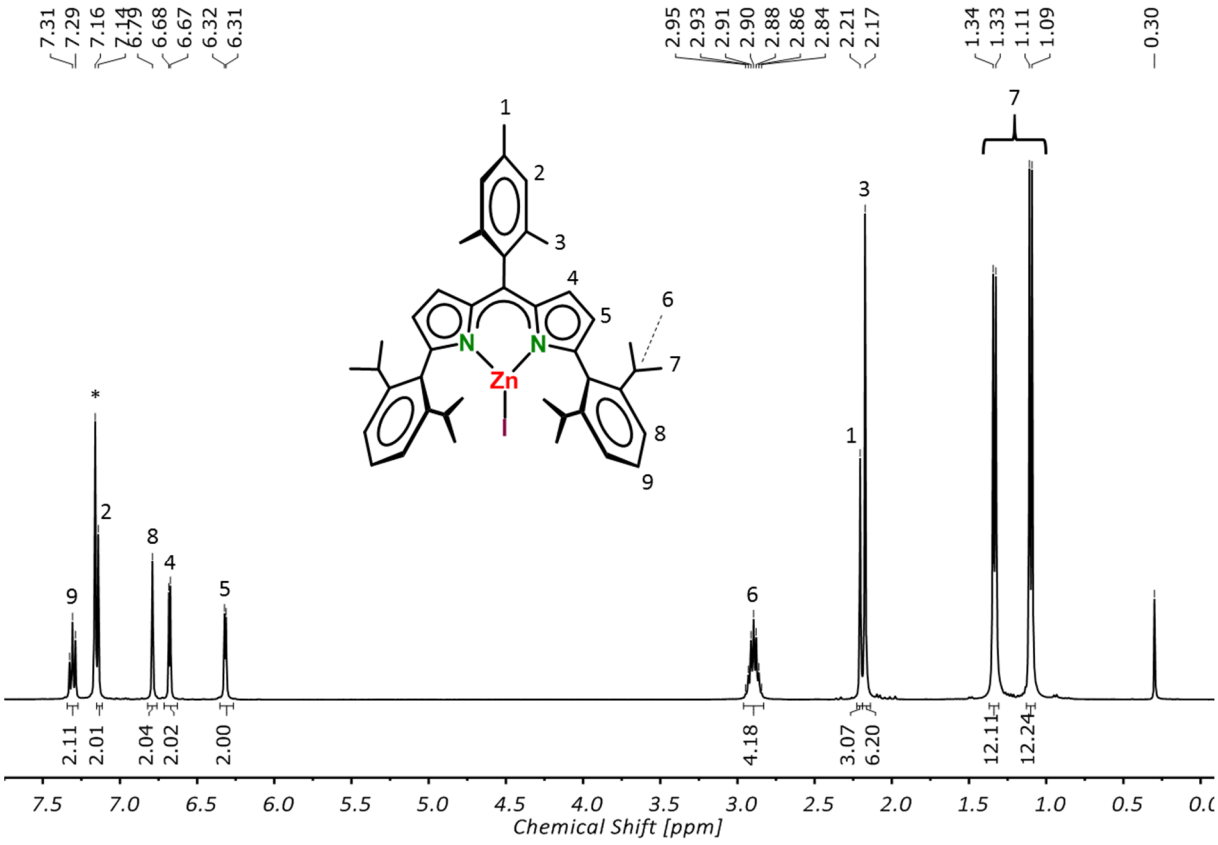
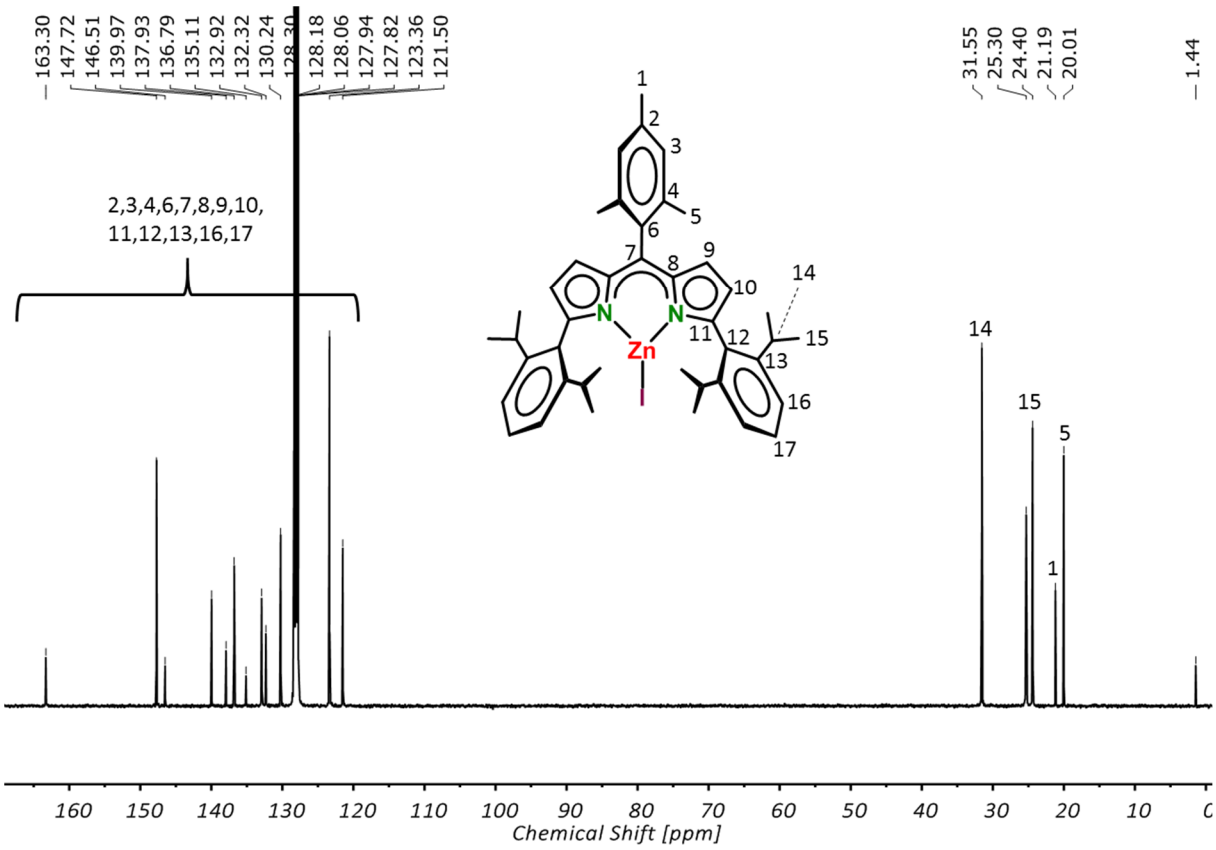
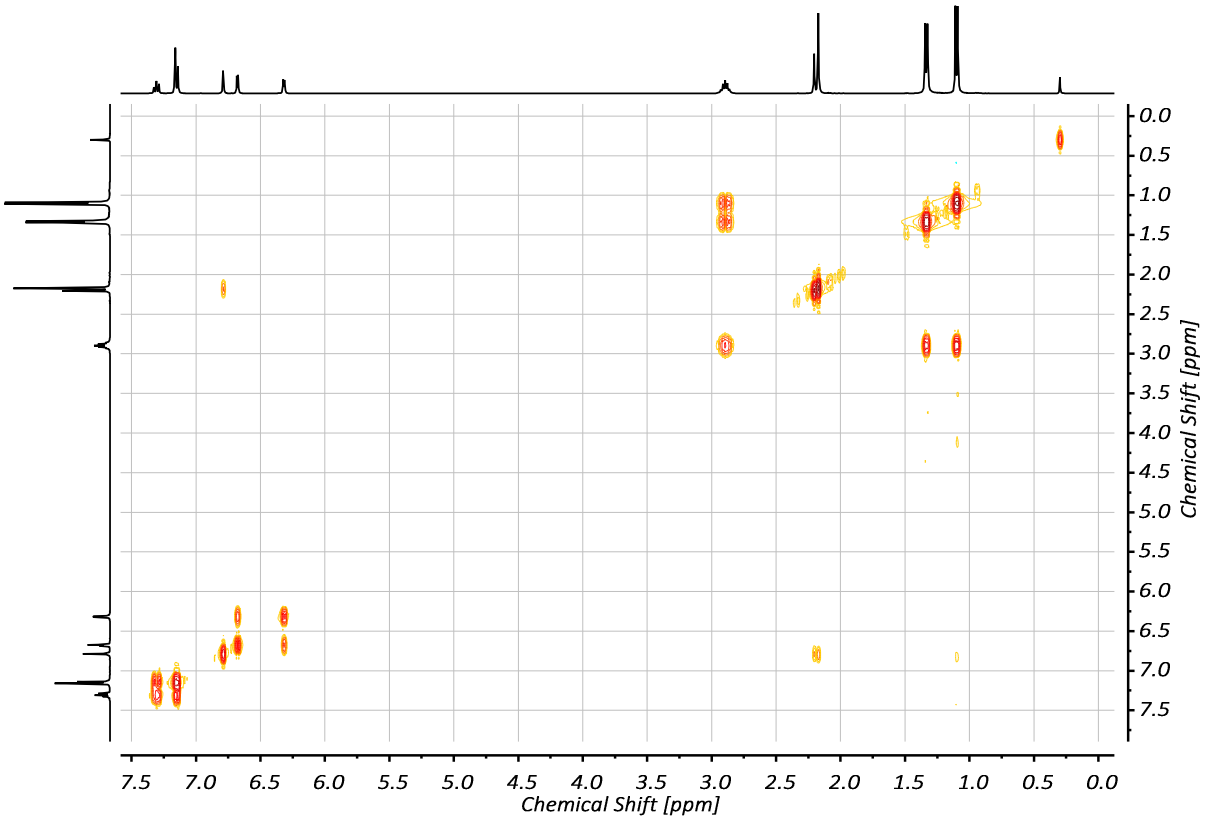
Figure S10. ^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of (^{DIPP}DPM)ZnI (**5**) in benzene-d_6 (*).



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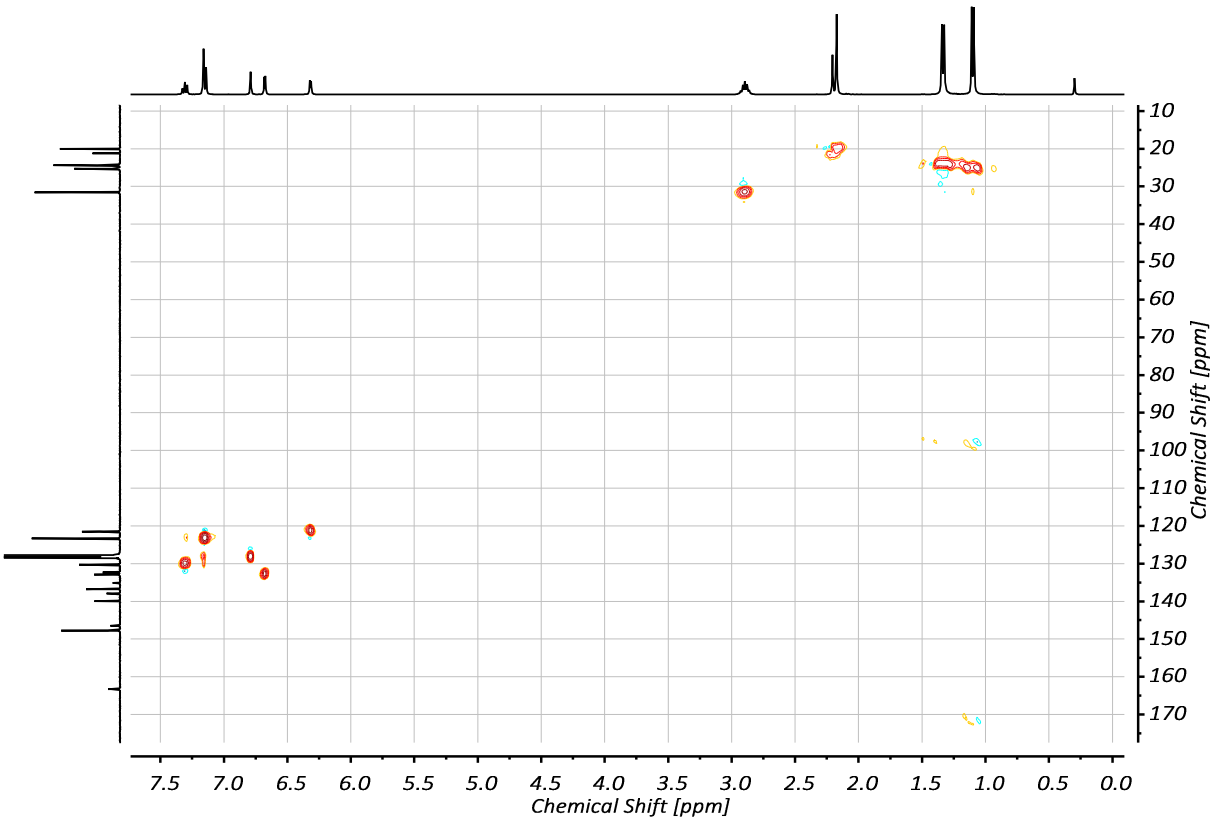
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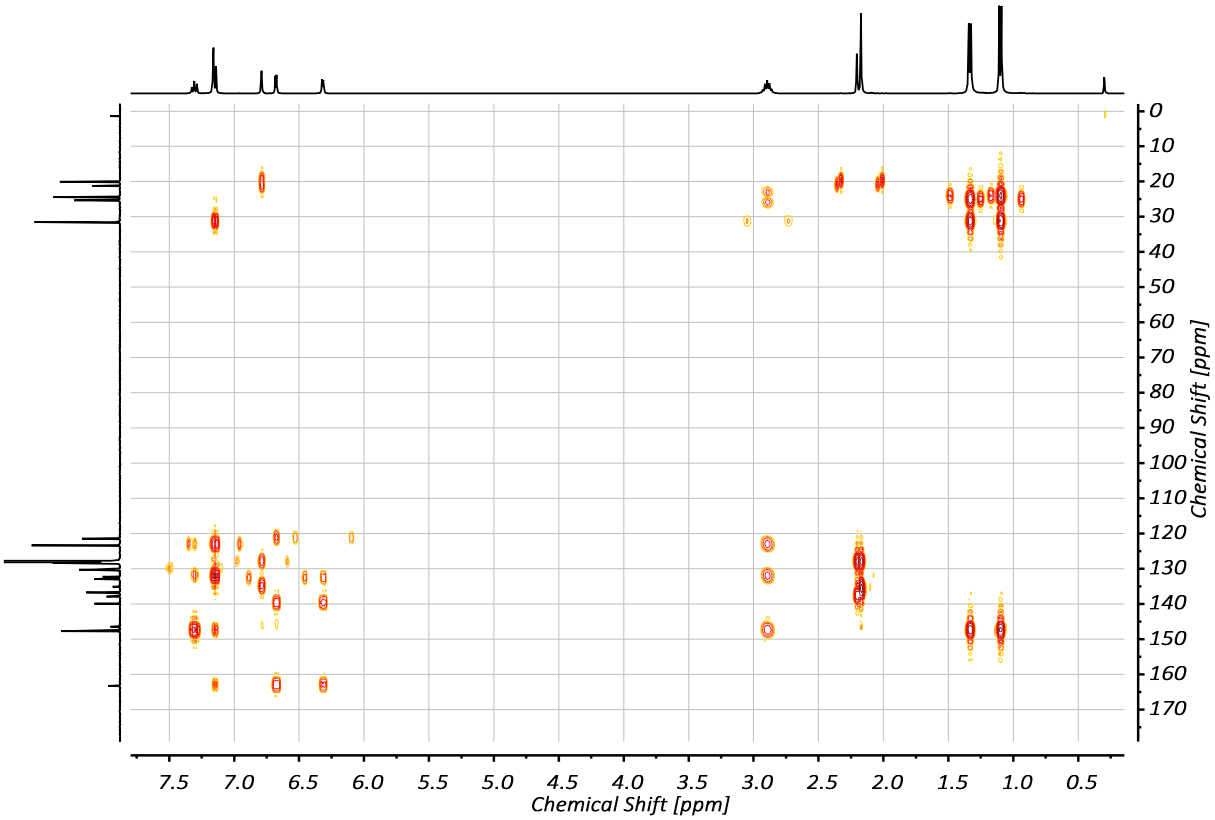
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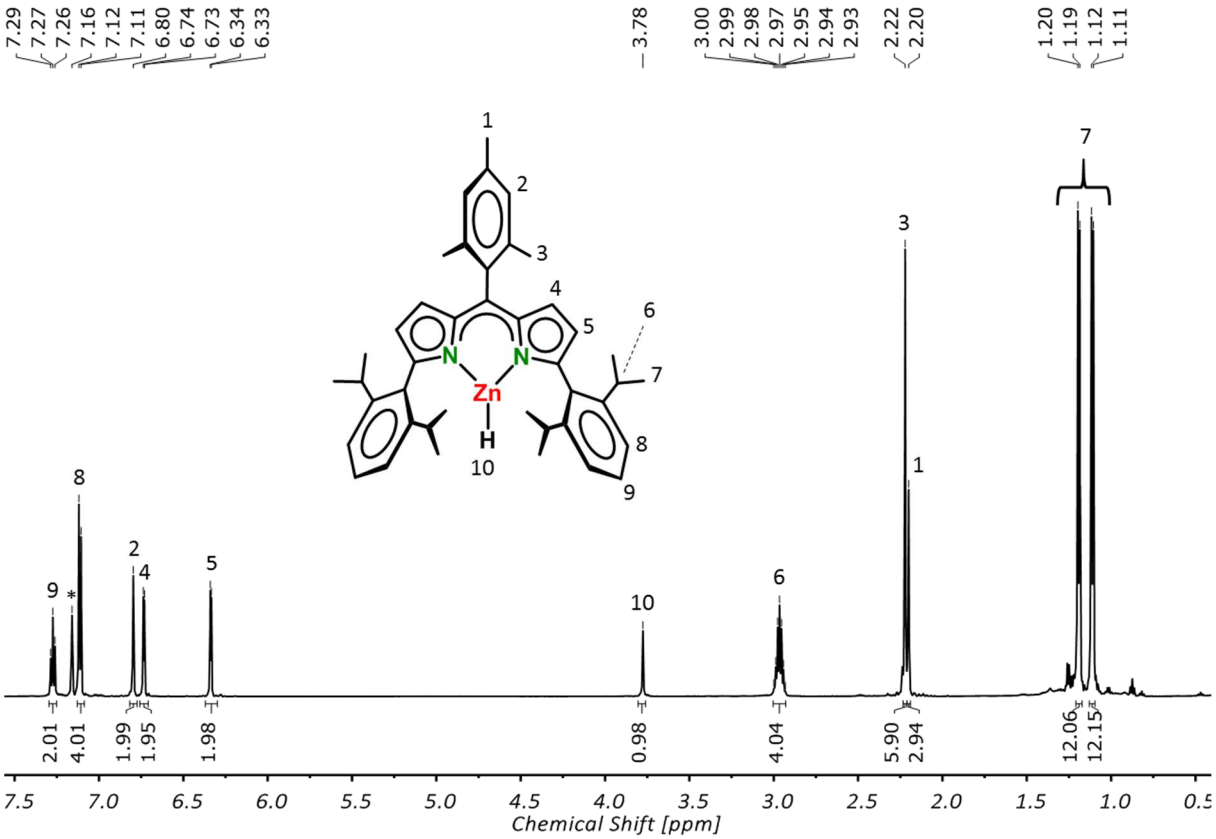
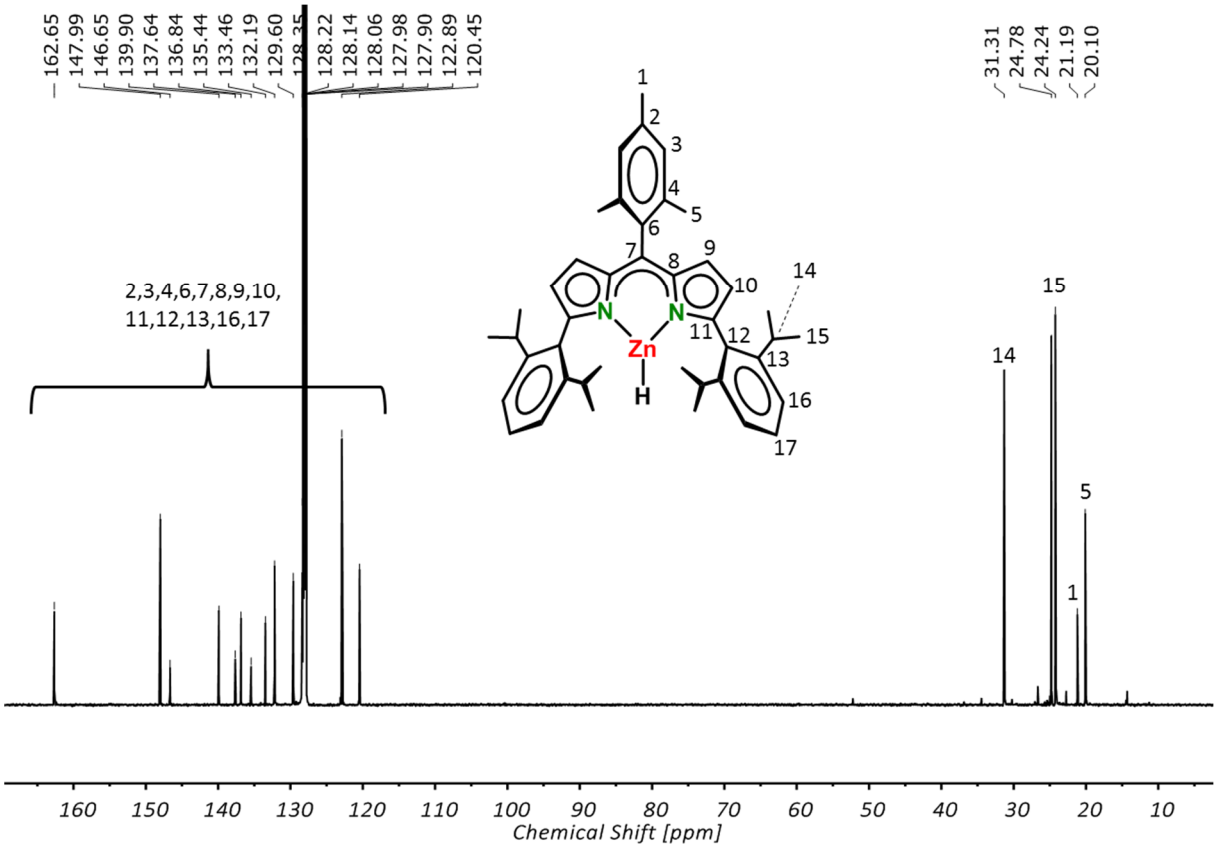
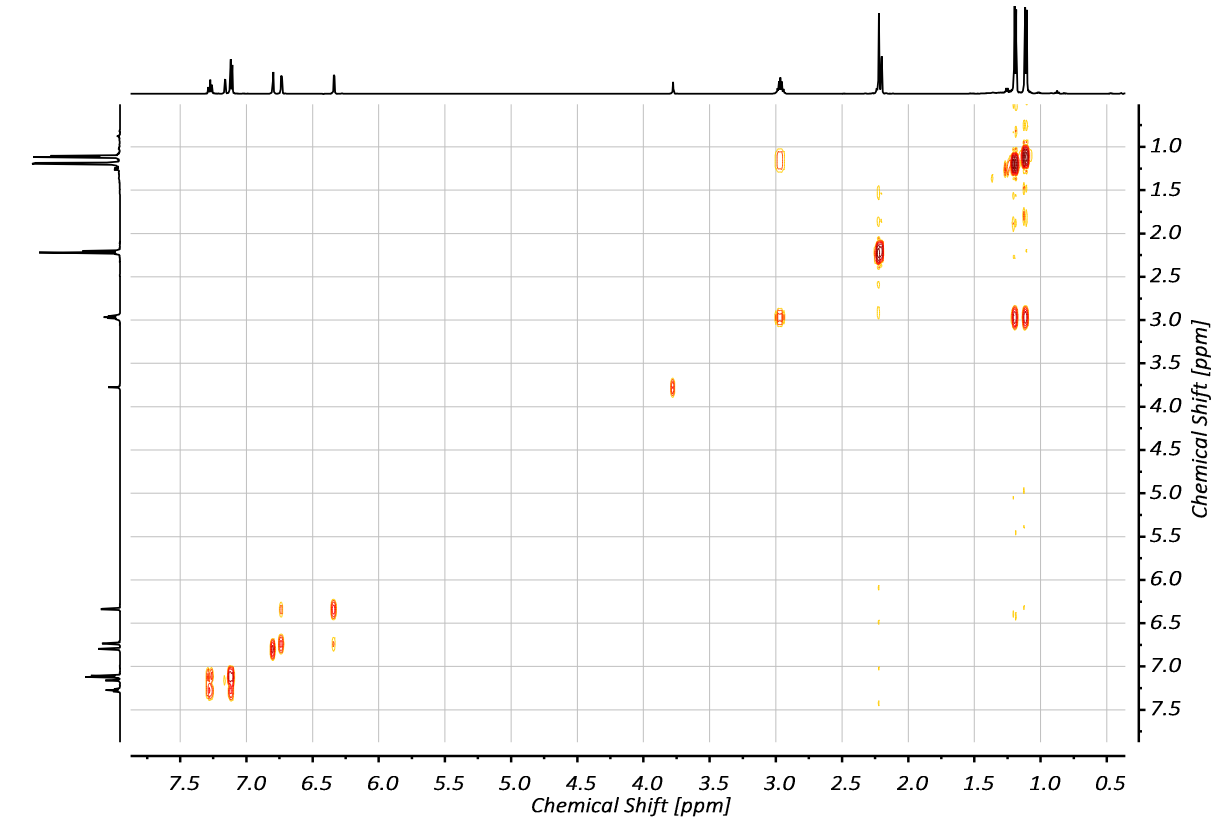
Chemical Shift [ppm]

Figure S11. ^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of (^{DIPP}DPM)ZnH (**6**) in benzene-d_6 (*).



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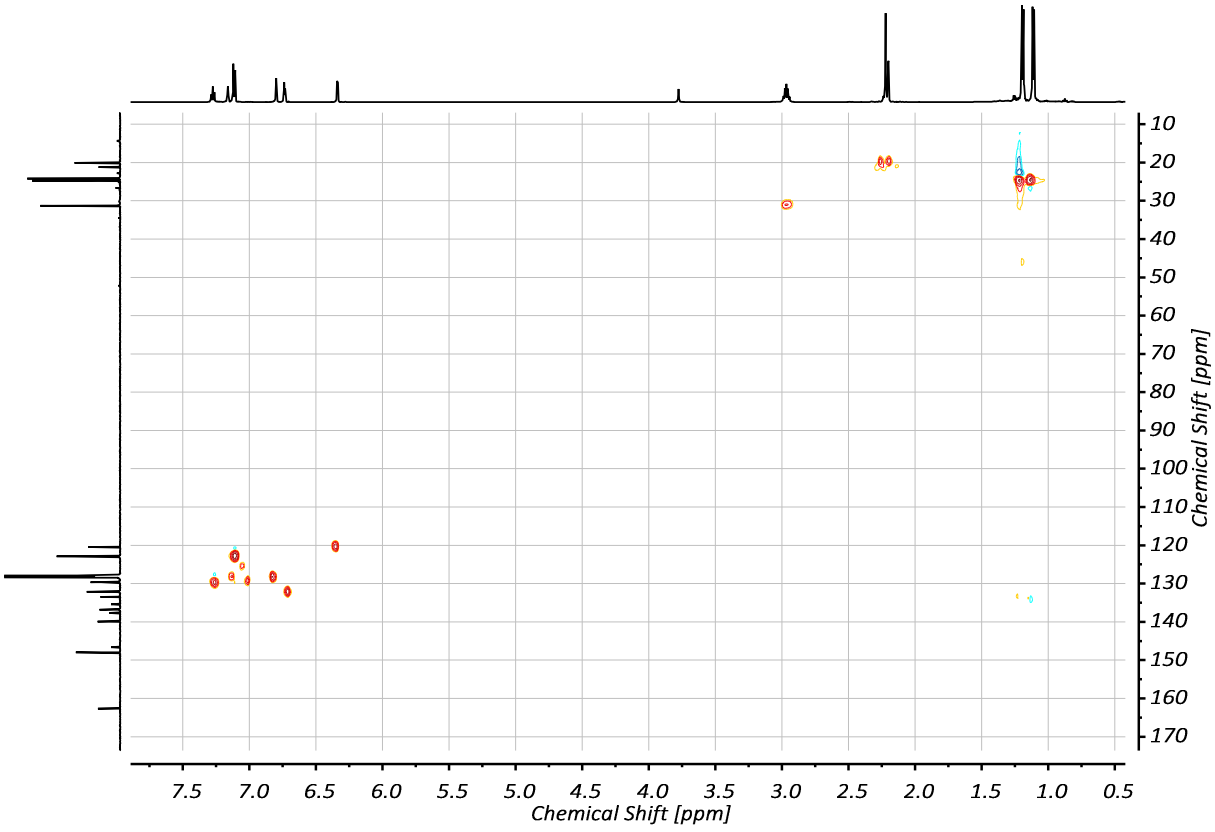
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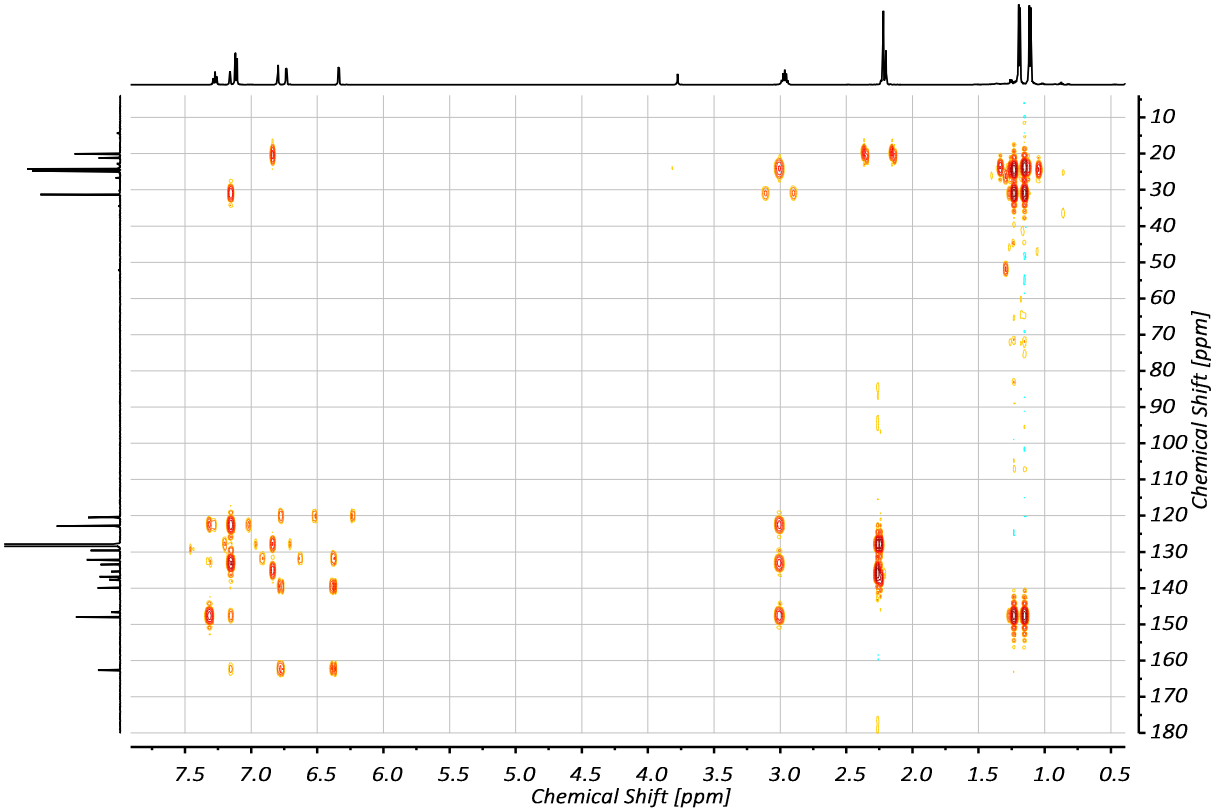
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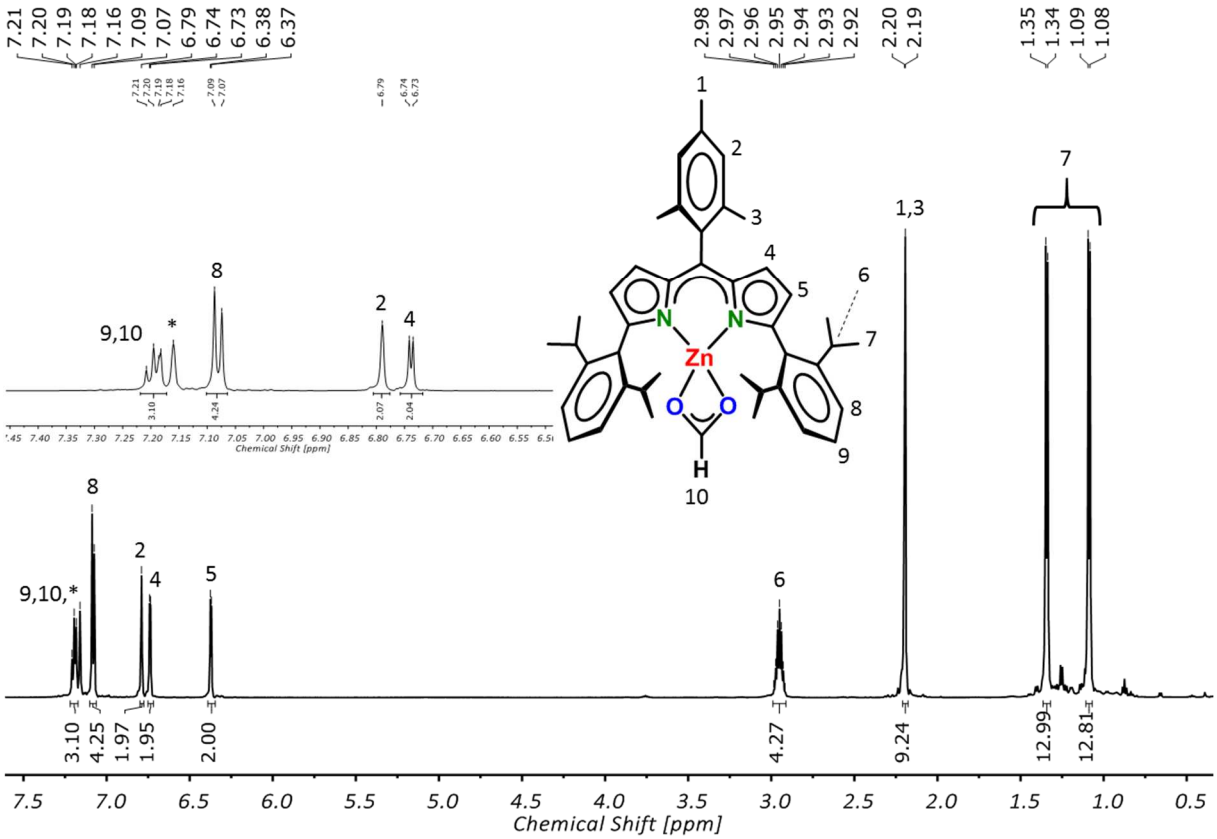
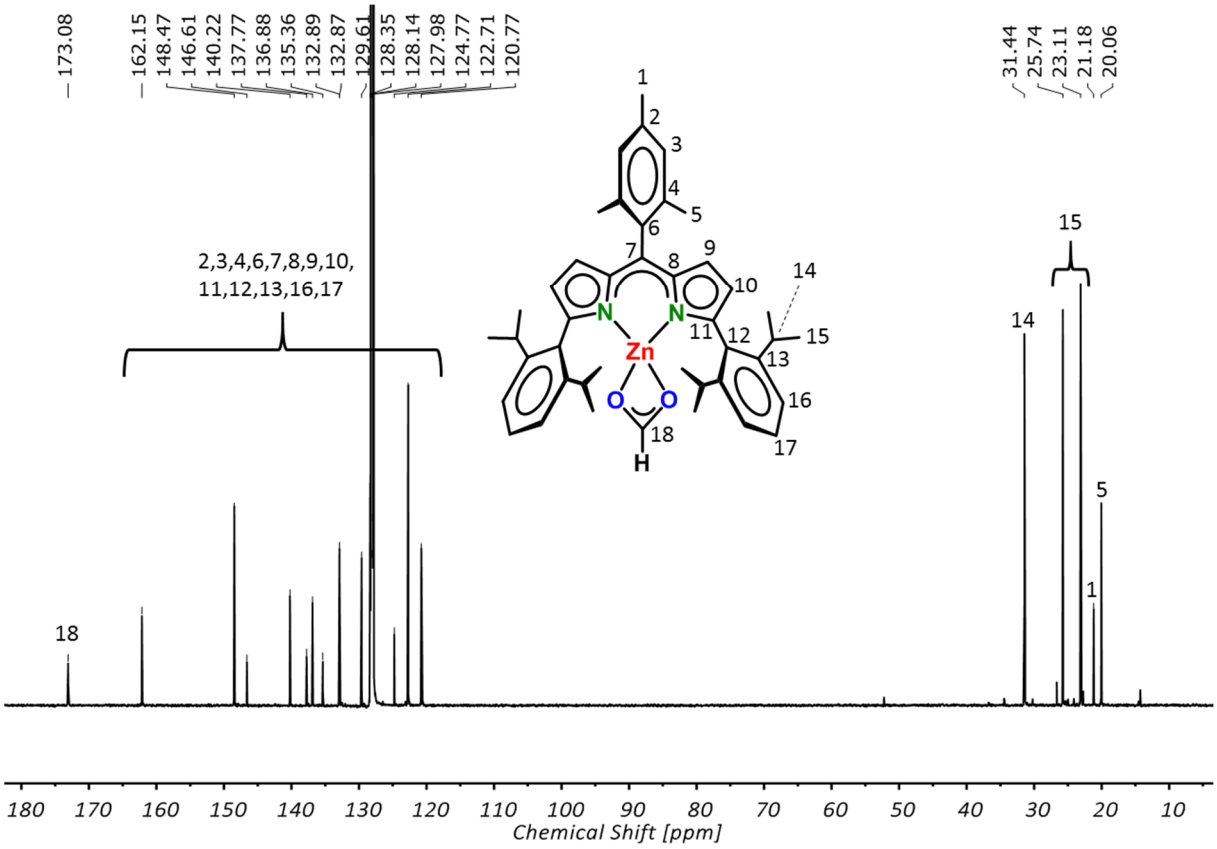
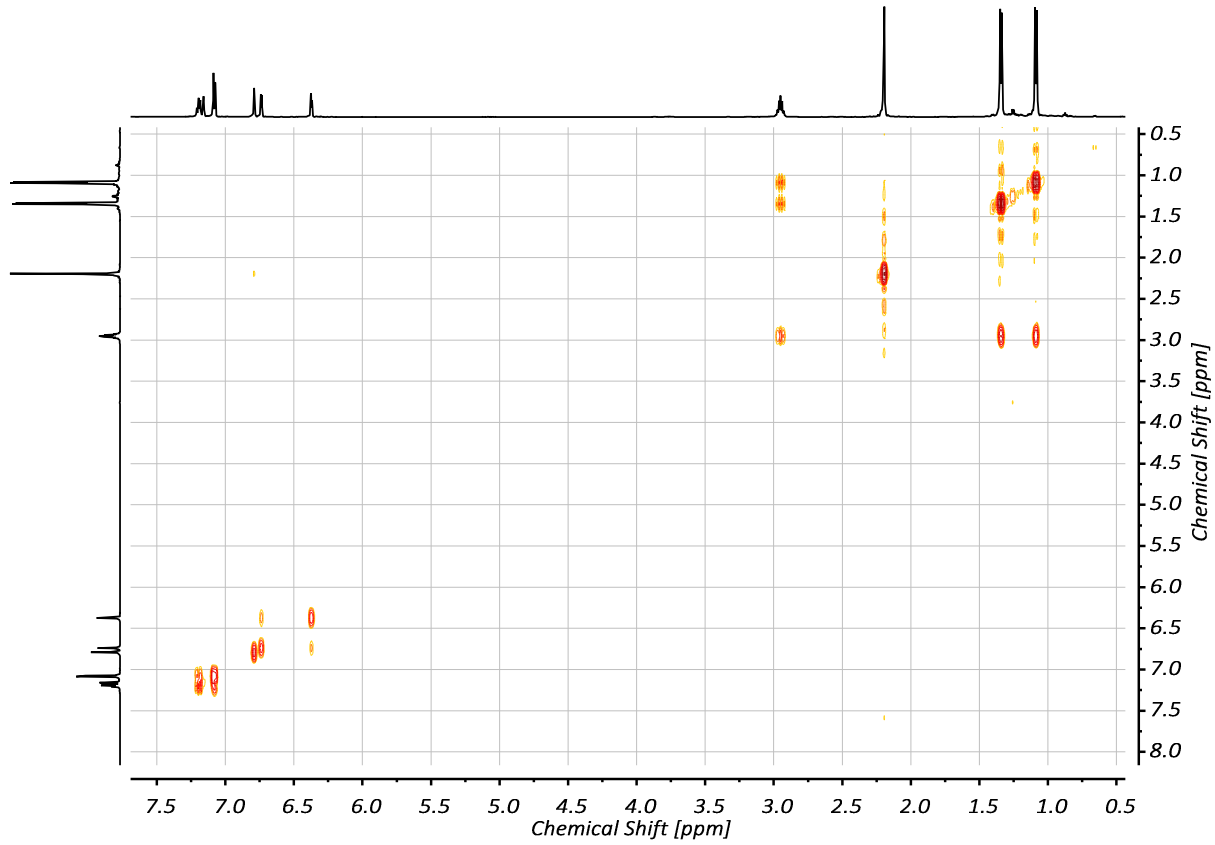
Figure S12. ^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of (^{DIPP}DPM)Zn(O_2CH) (**7**) in benzene-d_6 (*).



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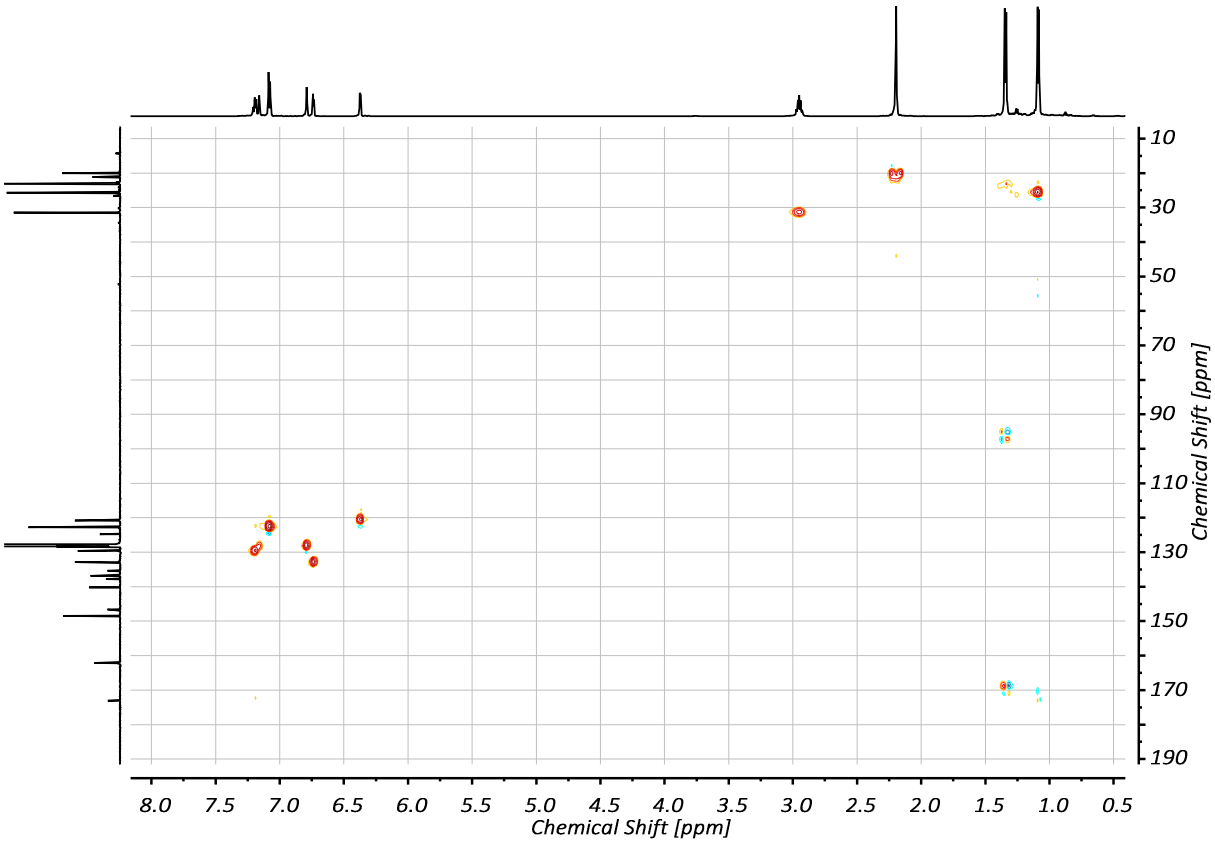
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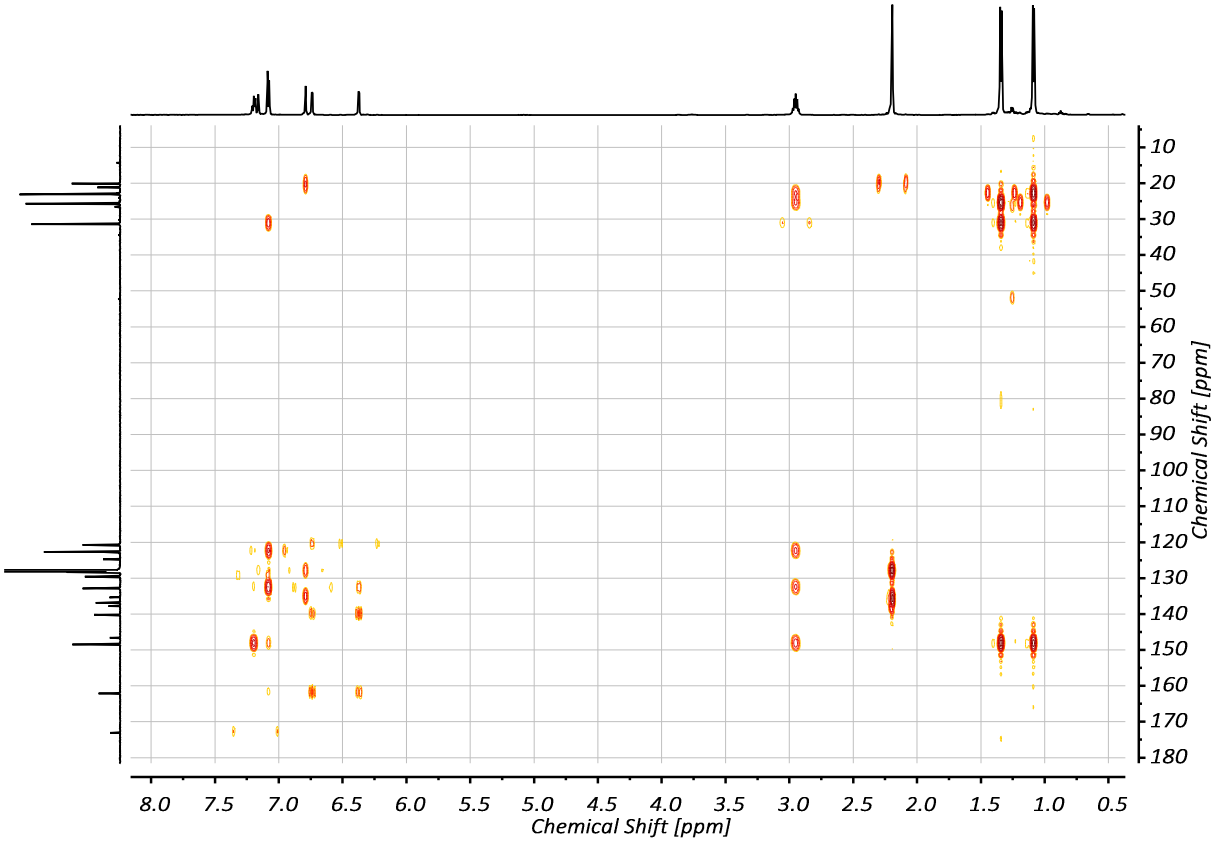
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Chemical Shift [ppm]
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Chemical Shift [ppm]

Figure S13. Temperature dependent ^{1}H-NMR spectra (^{DIPP}DPM)ZnH (**6**) in toluene-d_8.

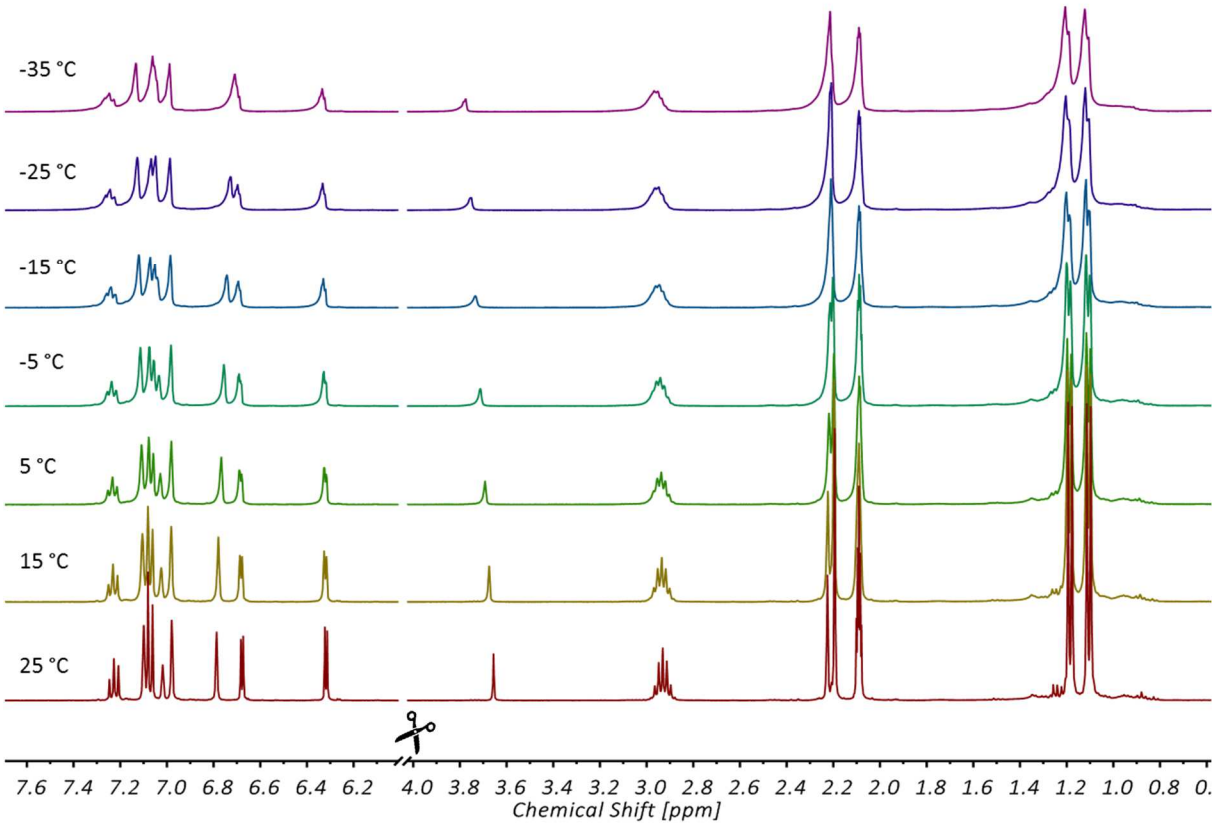
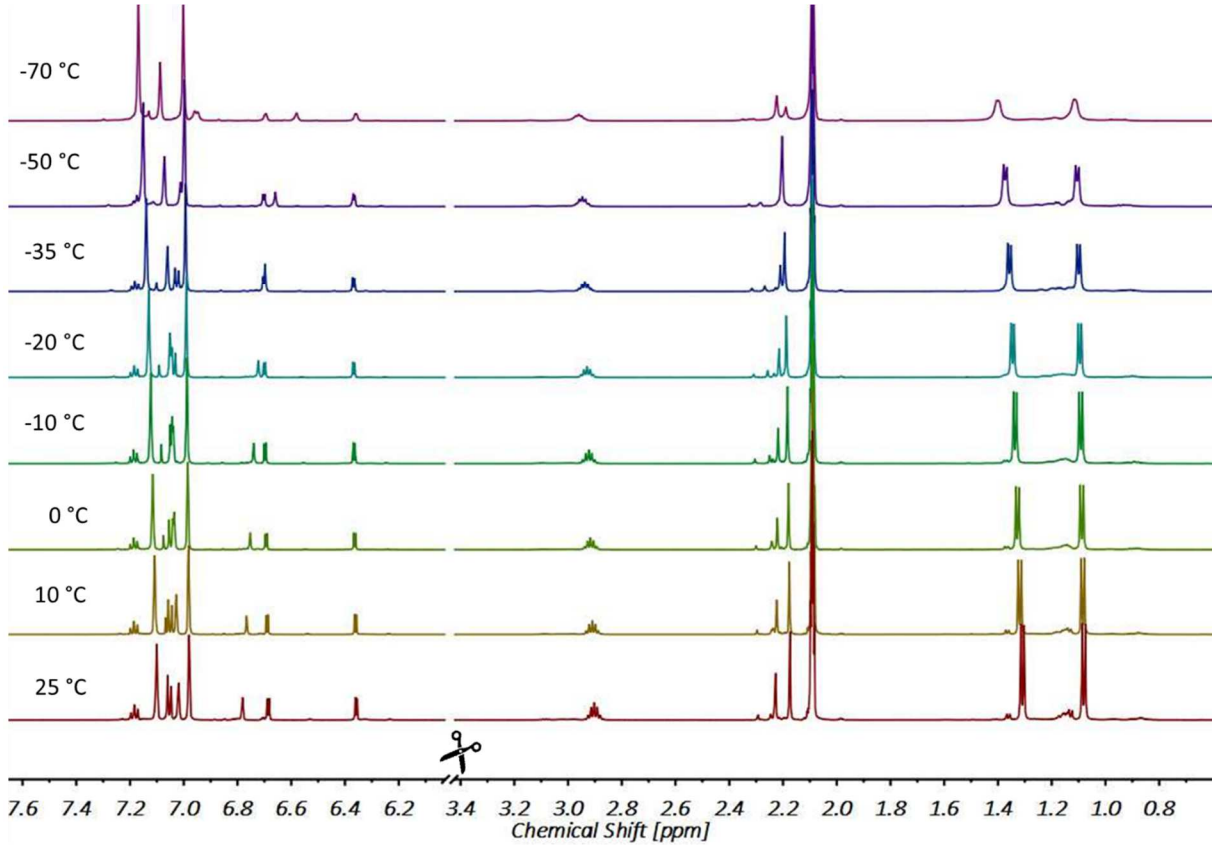


Figure S14. Temperature dependent ^{1}H-NMR spectra (^{DIPP}DPM)ZnO_2CH (**7**) in toluene-d_8.



Diffusion-Ordered-Spectroscopy (DOSY)

Table S6. DOSY parameter for (^{DIPP}DPM)ZnH (**6**) and (^{DIPP}DPM)ZnO$_2$CH (**7**) in benzene-*d6*.

Compound	**Formula**	**D [m^2/s]**	$\mathbf{MW}^{Exp.}_{Monomer}$ **[g/mol]**	$\mathbf{MW}^{Calc.}_{Monomer}$ **[g/mol]**
(^{DIPP}DPM)ZnH	**$C_{42}H_{50}N_2Zn$**	5,738*10^{-10}	631	648
(^{DIPP}DPM)ZnO$_2$CH	**$C_{43}H_{50}N_2O_2Zn$**	5,661*10^{-10}	591	691

Diffusion measurements were conducted on a Bruker AVANCE NMR spectrometer operating at 600.13 MHz for proton resonance equipped with a 5 mm PABDO BB/19F-1H/D probe with Z-GRD and actively shielded gradient coil with a maximum gradient strength of 5.3500094 G/mm (at 10 A).

Parameter optimization was carried out empirically employing the pulse programme ledbpgp2s1D using stimulated echo and LED (D21 = 5 ms, longitudinal eddy current delay as a Z-filter) with bipolar gradient pulses (P30) and two spoiling gradients (P19 = 600 µs) leading to values for gradient pulse length (P30 = 1250 µs, in case of bipolar gradients *little DELTA*0.5*) and diffusion time (D20 = 60 ms, *big DELTA*). Delay for gradient recovery was set to 200 µs.

The diffusion experiment was executed with variable gradients from 2% to 98% gradient strength with 32 increment values (difframp calculated with the AU-program *DOSY*). In this case the pulse program ledbpgp2s was applied for data aquiring of this pseudo-2D Experiment. Data processing was performed with the T1/T2 software package (SimFit) of TopSpin (version 3.2, Bruker Biospin) by fitting area data (integration of all peaks of interest of the same molecule) of diffusion decays. From these Stejskal-Tanner fitting curves calculated diffusion constants were obtained and assimilated statistically.

For molecular weight estimation Stalke´s method was applied (external calibration curves **ECC**´s under assumption of DSE-shaped molecules (dissipated spheres and ellipsoides) with residual signal of deuterated benzene as internal reference with normalized diffusion coefficients.[5,6]

4) Selected infrared spectra

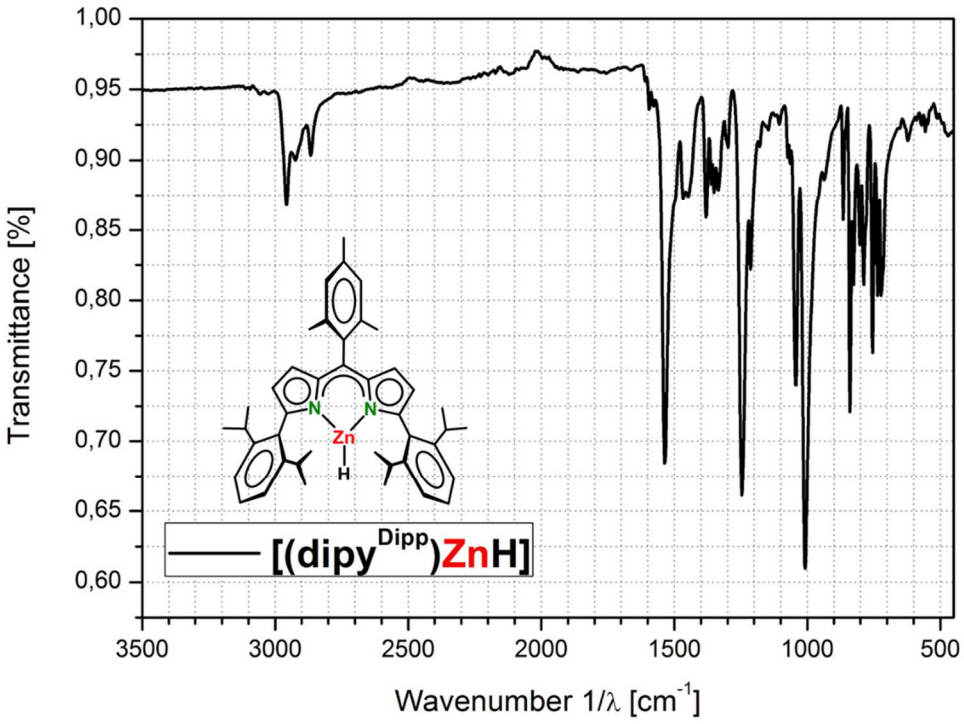


Figure S15. Infrared spectrum of (^{DIPP}DPM)ZnH (**6**).

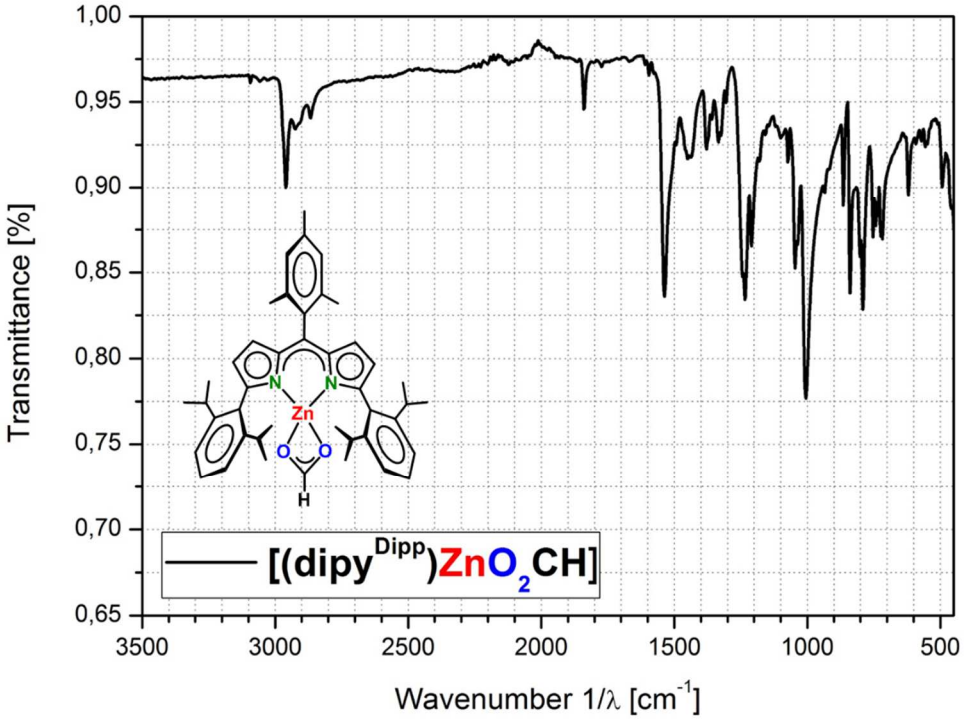


Figure S16. Infrared spectrum of (^{DIPP}DPM)ZnO_2CH (**7**).

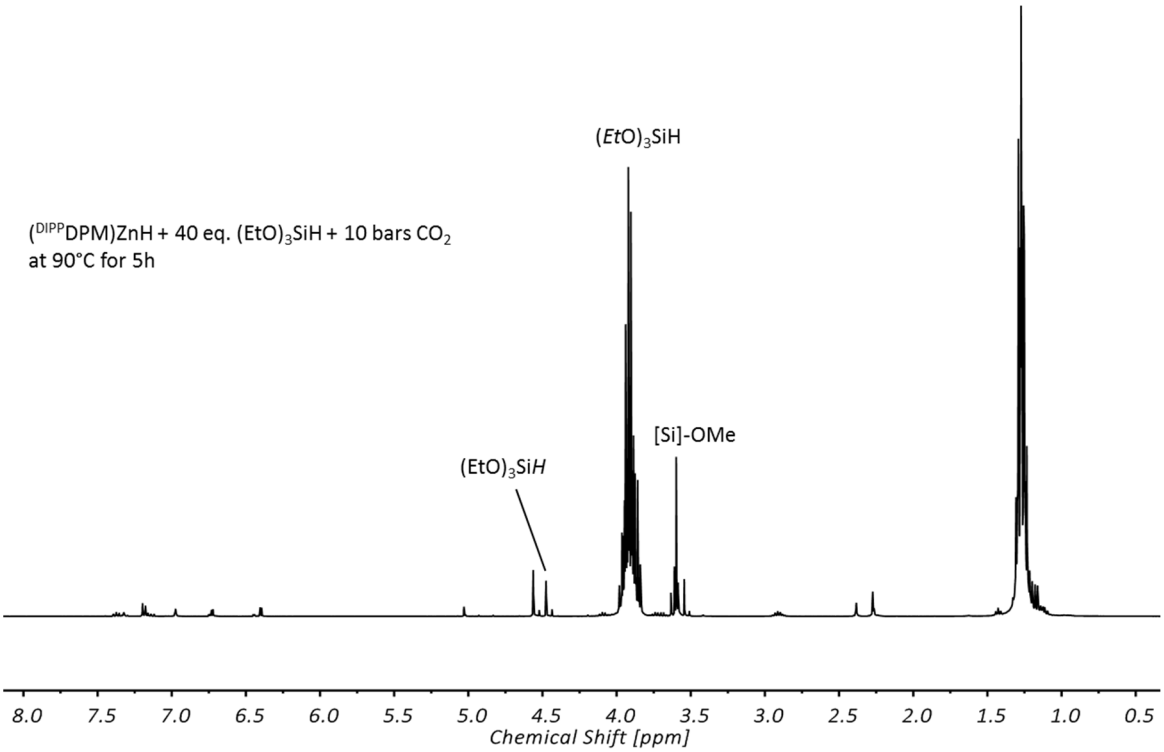
4) Catalytic experiments

Experimental procedure

In a nitrogen-filled glovebox, a 10 mL high-pressure reactor was charged with (^{DIPP}DPM)ZnH (37 mg, 0.057 mmol, 1.0 eq) and $(EtO)_3SiH$ (0.38 g, 2.3 mmol, 40 eq.). The reactor was taken out of the glovebox, pressurized with 10 bars of CO_2 and sealed. The reaction mixture in the reactor was stirred vigorously at 90 °C for 5h. The reactor was placed in cold water to cool down and excess CO_2 was released. The reaction mixture was analyzed by NMR and GC-MS. Under the given reaction conditions, $HSi(OEt)_3$ partially disproportionated into SiH_4 and $Si(OEt)_4$. The conversion of $(EtO)_3SiH$ and the yields of $H_3COSi(OEt)_3$, $HCO_2Si(OEt)_3$ and $Si(OEt)_4$ (or that of its disproportionation products) were determined by quantitative ^{13}C NMR.[7]

NMR measurements

Figure S17. ^{1}H and quantitative ^{13}C NMR spectra of the products of CO_2 hydrosilyation with (^{DIPP}DPM)ZnH (**6**) in benzene-d_6.



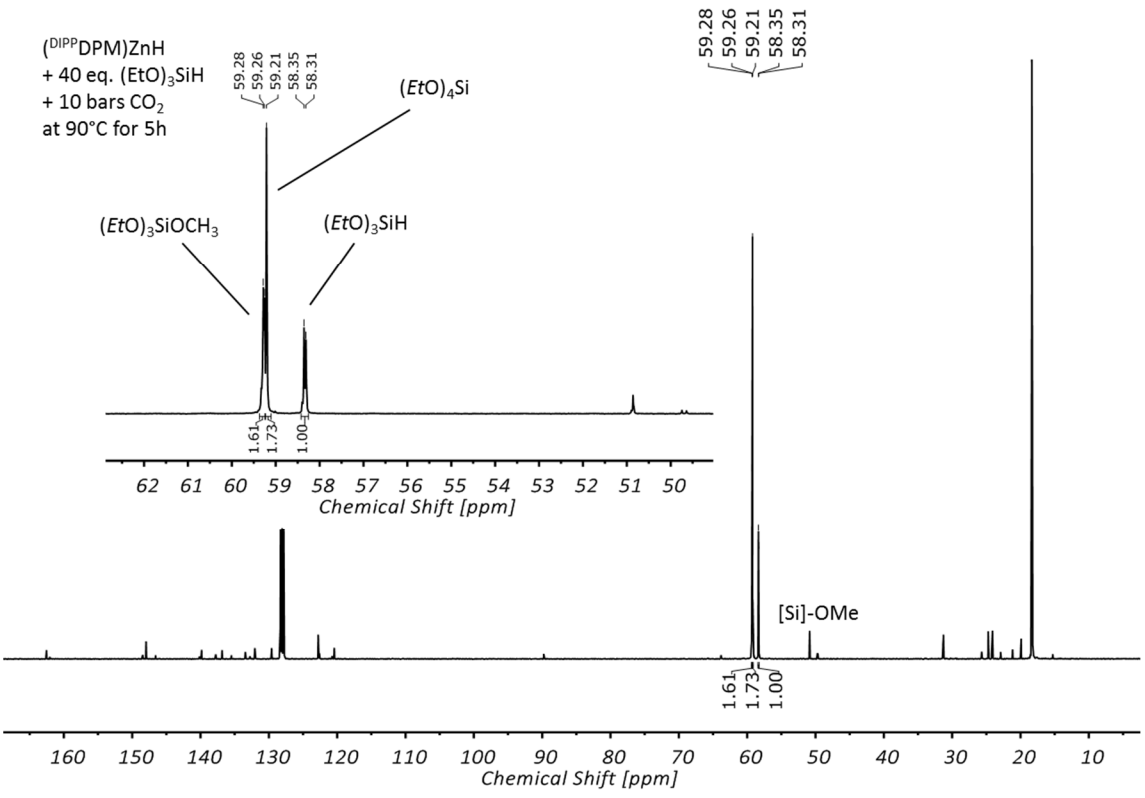
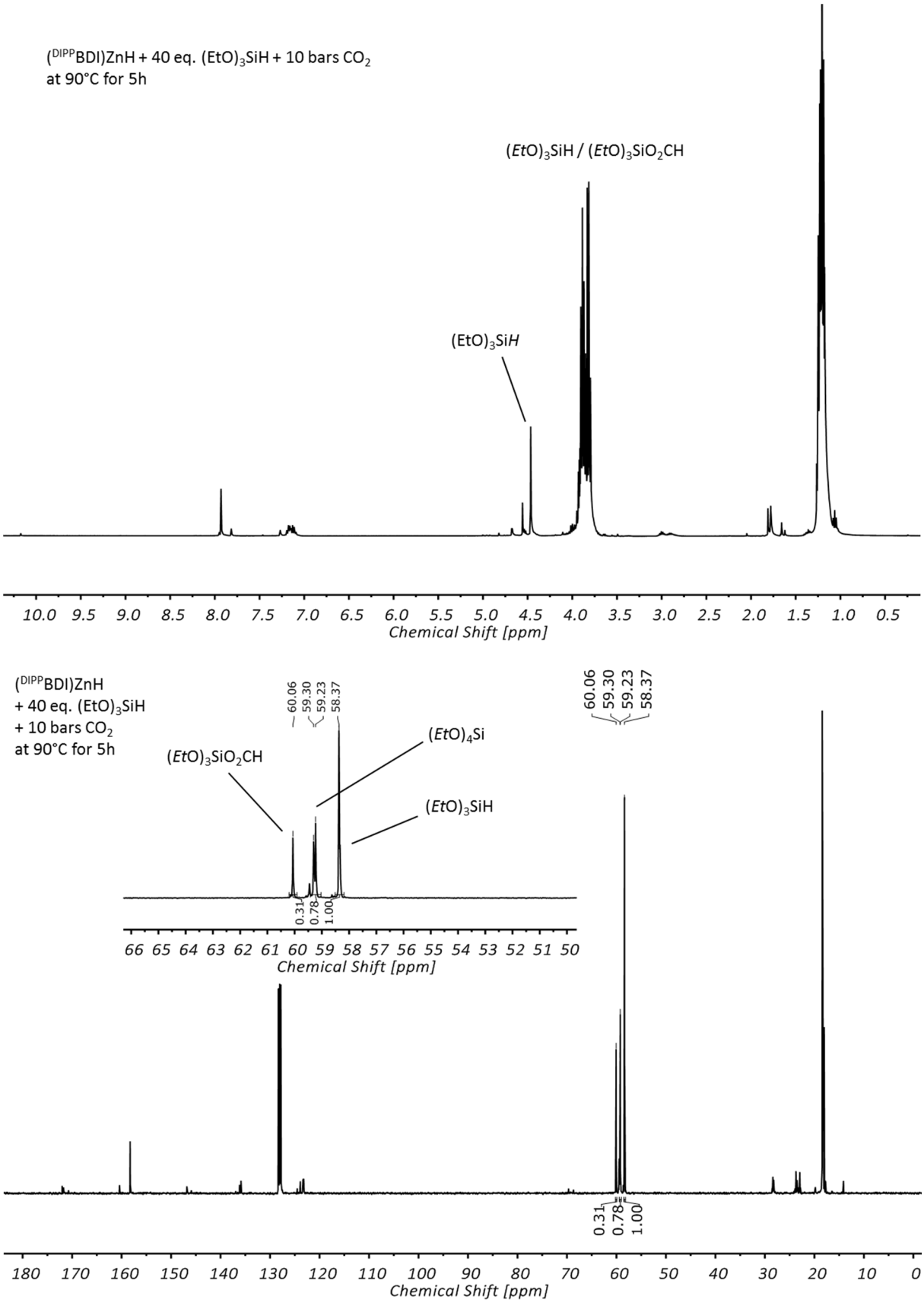


Figure S18. ^{1}H and quantitative ^{13}C NMR spectra of the products of CO_2 hydrosilylation with (^{DIPP}BDI)ZnH (**II**) in benzene-d_6.



GC-MS measurements

GC-MS measurements were performed on a Thermo Scientic™ Trace™ 1310 gas chromatography system (carrier gas Helium) with detection by a Thermo Scientic™ ISQ™ LT Single Quadrupole mass spectrometer. A Phenomenex® ZebronTMZB-5 GC column of the dimensions 0.25mm x 30m with a film thickness of 0.25 µm was used. The samples (1 µL) were injected with an Instant Connect-SSL Module in the split mode (injector temperature: 280 °C). Temperature programs were started at 40 °C followed by heating ramps, optimized for the separation problem, until 280°. Baseline separation of each analyte was achieved by choosing the different temperature programs.

The molecular formulas were assigned by comparison with entries in the NIST/EPA/NIH mass spectral library (version 2.2, built June 10 2014). Retention time and mass spectra of redistilled $(EtO)_3SiH$ (received from Alpha Aesar in 96% purity) were verified by GC-MS measurements.

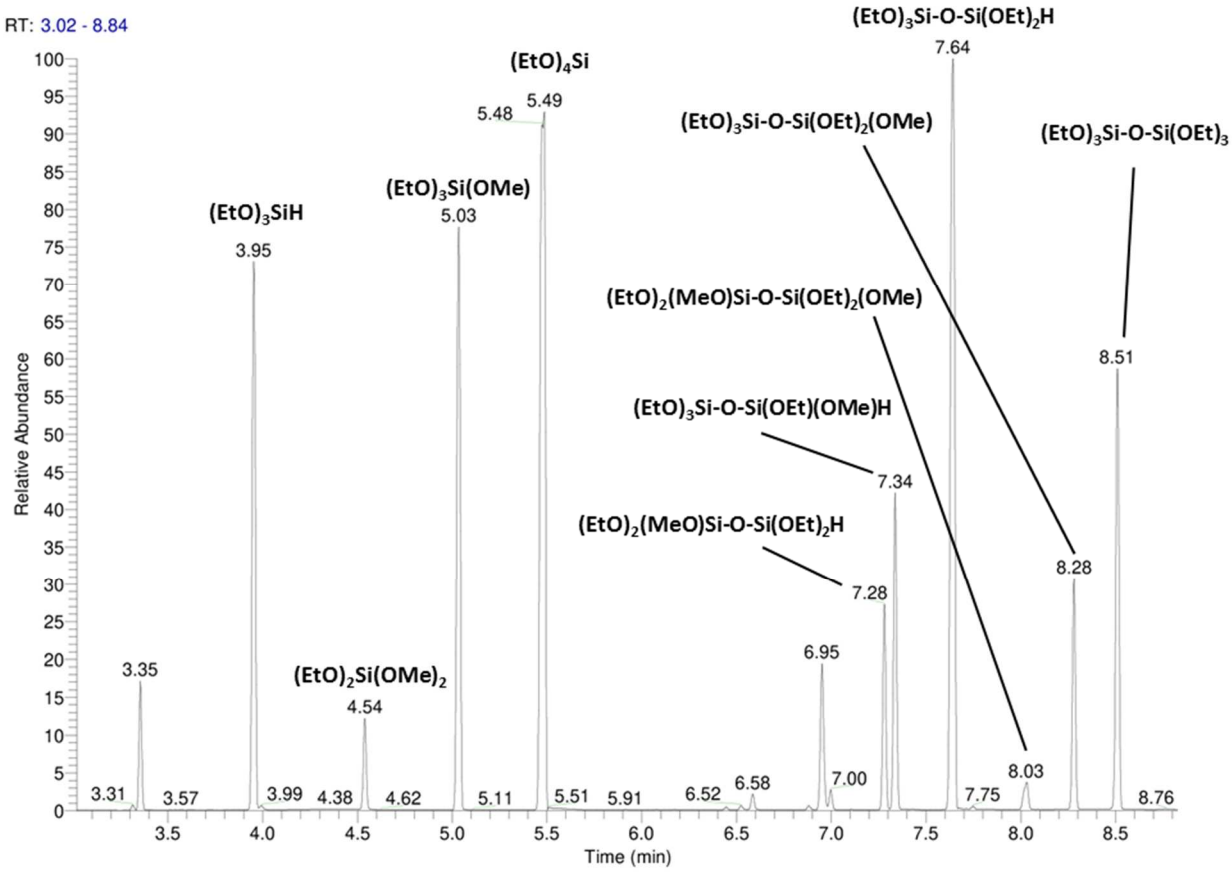


Figure S19. Chromatogram of products formed by catalytic conversions with (^{DIPP}DPM)ZnH (**6**). Depicted retention times correspond to a highly concentrated sample. All spectrometric data given below derive from diluted samples to ensure prevention of incorrect data from saturated peaks.

GC-MS (EI-MS, 70 eV): m/z (%): RT: 3.95 min $(EtO)_3SiH$: 163.08 (78) $[M]^+$, 149.07 (100), 119.07 (95), 91.03 (47).

GC-MS (EI-MS, 70 eV): m/z (%): RT: 5.03 min $(EtO)_3Si(OMe)$: 193.09 (5) $[M]^+$, 179.06 (100), 149.07 (58), 135.06 (82), 105.05 (34).

GC-MS (EI-MS, 70 eV): m/z (%): RT: 5.48 min $(EtO)_4Si$: 207.10 (5) $[M]^+$, 193.07 (87), 179.07 (31), 163.07 (51), 149.07 (100), 135.07 (7), 119.06 (41).

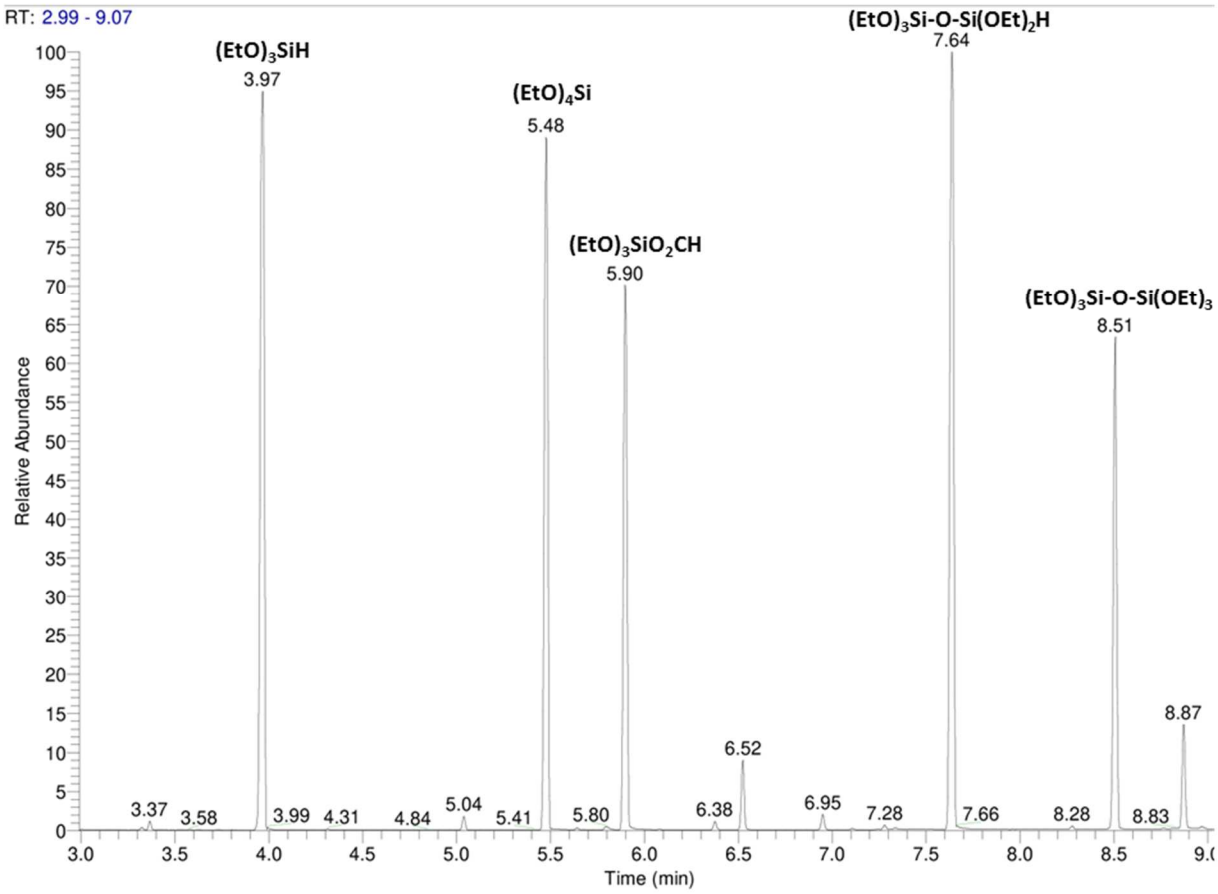


Figure S20. Chromatogram of products formed by catalytic conversions with (^{DIPP}BDI)ZnH (**II**). Depicted retention times correspond to a highly concentrated sample. All spectrometric data given below derive from diluted samples to ensure prevention of incorrect data from saturated peaks.

GC-MS (EI-MS, 70 eV): m/z (%): RT: 3.97 min $(EtO)_3SiH$: 163.08 (87) $[M]^+$, 149.05 (100), 119.06 (97), 105.04 (78), 91.04 (46).

GC-MS (EI-MS, 70 eV): m/z (%): RT: 5.48 min $(EtO)_4Si$: 207.10 (6) $[M]^+$, 193.07 (100), 179.07 (36), 149.06 (97), 135.04 (22), 119.05 (40).

GC-MS (EI-MS, 70 eV): m/z (%): RT: 5.90 min $(EtO)_3SiO_2CH$: 207.04 (2) $[M]^+$, 193.06 (7), 179.03 (13), 163.03 (100), 135.01 (53), 107.01 (26).

5) Theoretical calculations

All calculations were carried out using Gaussian 09 Rev. D.[8] All methods were used as implemented. All structures were fully optimized as true minima on a B3PW91/6-311++G** level of theory and characterized as true minima (NIMAG=0) by frequency calculations on the same level of theory.[9-12] Charges were calculated by NBO analysis.[13] Structures were drawn and evaluated using Molecule V2.3.[14]

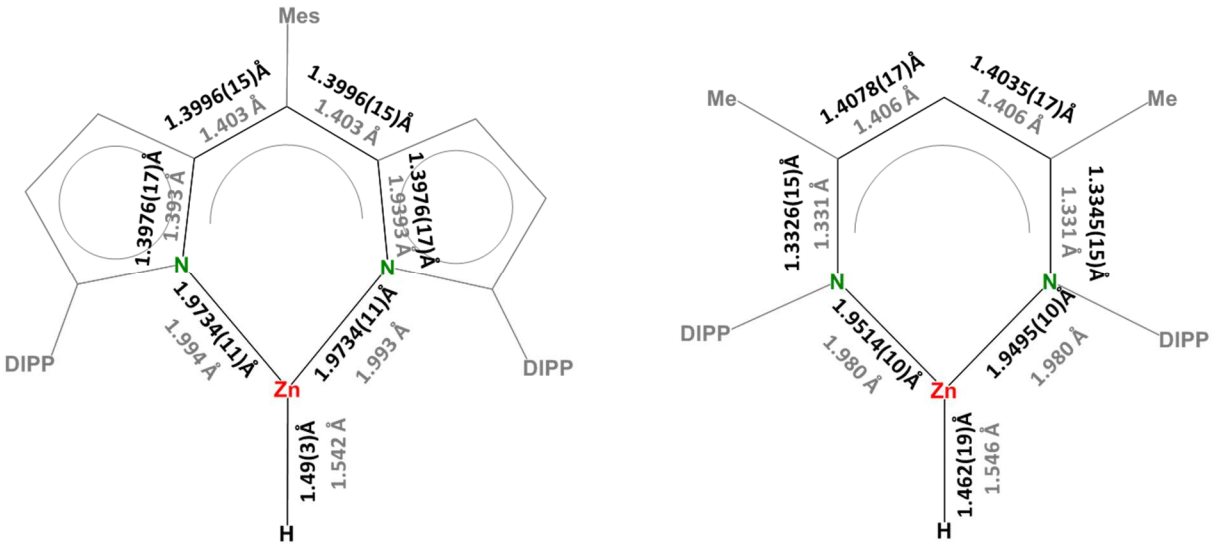


Figure S21. Comparison of calculated geometries (grey) with crystal structures (black): (^{DIPP}DPM)ZnH (left) and (^{DIPP}BDI)ZnH (right). The Zn-H distances in the crystal structure are substantially shorter than the calculated values. This is due to the fact that the maximum of the H electron density does not coincide with its nucleus.

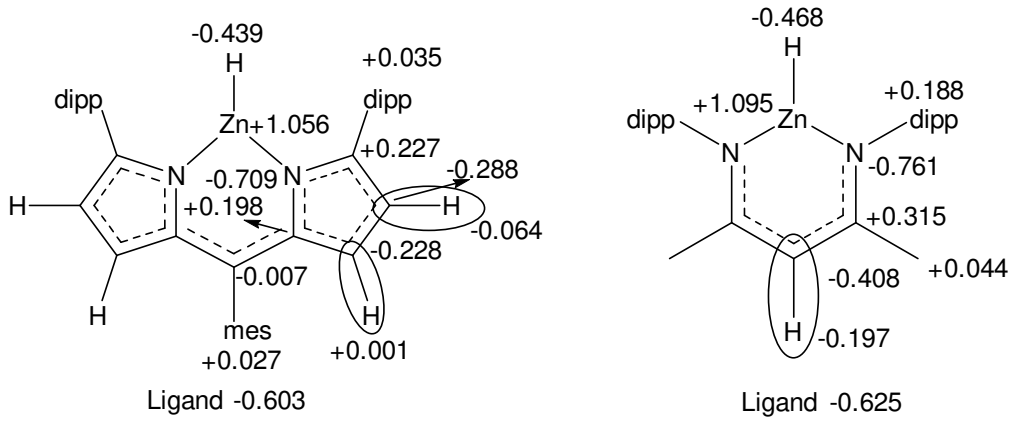


Figure S22. Distribution of NPA charges in (^{DIPP}DPM)ZnH (left) and (^{DIPP}BDI)ZnH (right).

5) References

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