Two-Coordinate, Late First-Row Transition Metal Amido Derivatives of the Bulky Ligand -N(SiPr$^i_3$)Dipp (Dipp = 2,6-di-isopropylphenyl): Ligand Effects on the Stability of Two-Coordinate Copper(II) Complexes

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Supporting Information

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Synthetic Details of 4 and 5:

[(Pr^i_3Si)N(*c*-C_6H_2-2,6-Pr^i_2)]$_2$ (**4**): LiN($SiPr^i_3$)Dipp (1.0 g, 3.0 mmol) was dissolved in *ca*. 30 ml of hexanes and added to CuCl (0.30 g, 3.0 mmol) at room temperature. After stirring for 18 hrs., the volatiles were removed under reduced pressure. The remaining oil was extracted with *ca*. 20 ml of toluene. This green solution was concentrated to a volume of *ca*. 5 ml and placed in a *ca*. -30 °C freezer. Rectangular, green crystals that were suitable for single crystal X-ray diffraction were grown after 48 hrs.

HN($SiPr^i_3$)Dipp-4-Ad (**5**): 2.5 M n-Butyl Lithium in hexanes (10 ml, 25 mmol) was added dropwise to a *ca*. 50 ml solution of H_2NDipp-4-Ad (7.8 g, 25 mmol) in THF at 0 °C in a thick-walled Teflon tapped flask. After the addition, the reaction mixture was allowed to warm to room temperature. Cl$SiPr^i_3$ (4.8 g, 25 mmol) was then added to this solution at room temperature. The reaction flask was then warmed to *ca*. 100 °C and allowed to stir for 40 hrs. After the reaction was allowed to cool to room temperature, the volatiles were removed under reduced pressure. The remaining solid was extracted with *ca*. 40 ml of hexanes. This hexanes solution was stored *ca*. -18 °C to give colorless rods suitable for single crystal X-ray diffraction. Yield: (2.0 g, 17%)

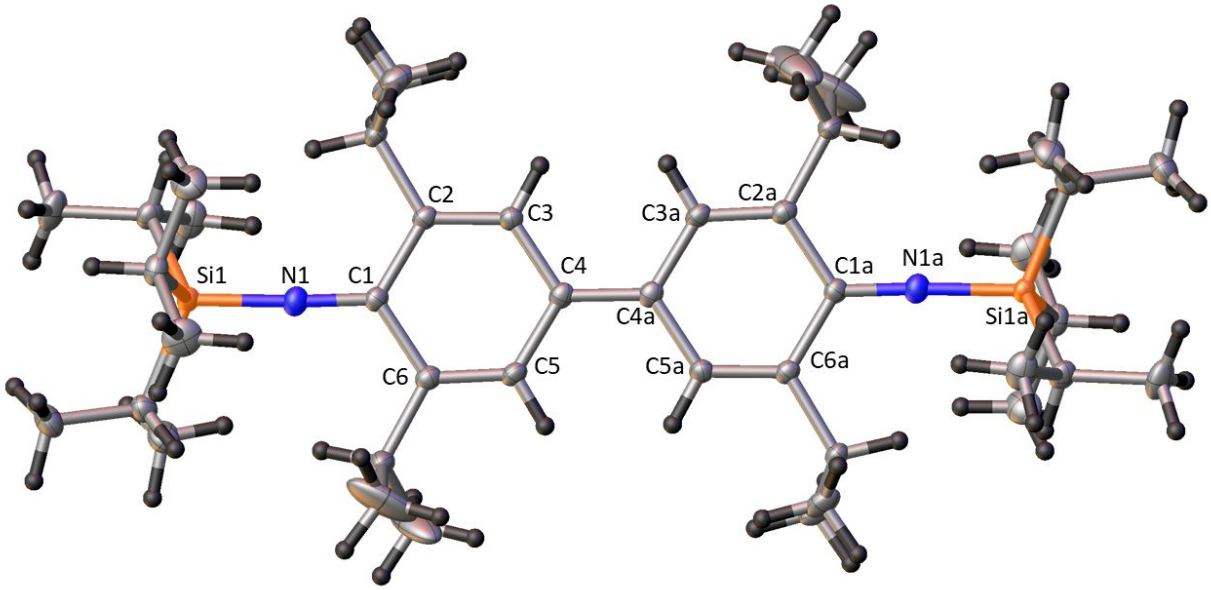


Figure S1. Molecular structure of $[(Pri_3Si)N(c\text{-}C_6H_2\text{-}2,6\text{-}Pri_2)]_2$ (4). The thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): C4-C4a 1.407(3), C1-N1 1.2766(17), C2-C3 1.3539(18), C5-C6 1.3515(18), Si1-N1-C1 177.22(11), Si1-N1 1.6891(12).

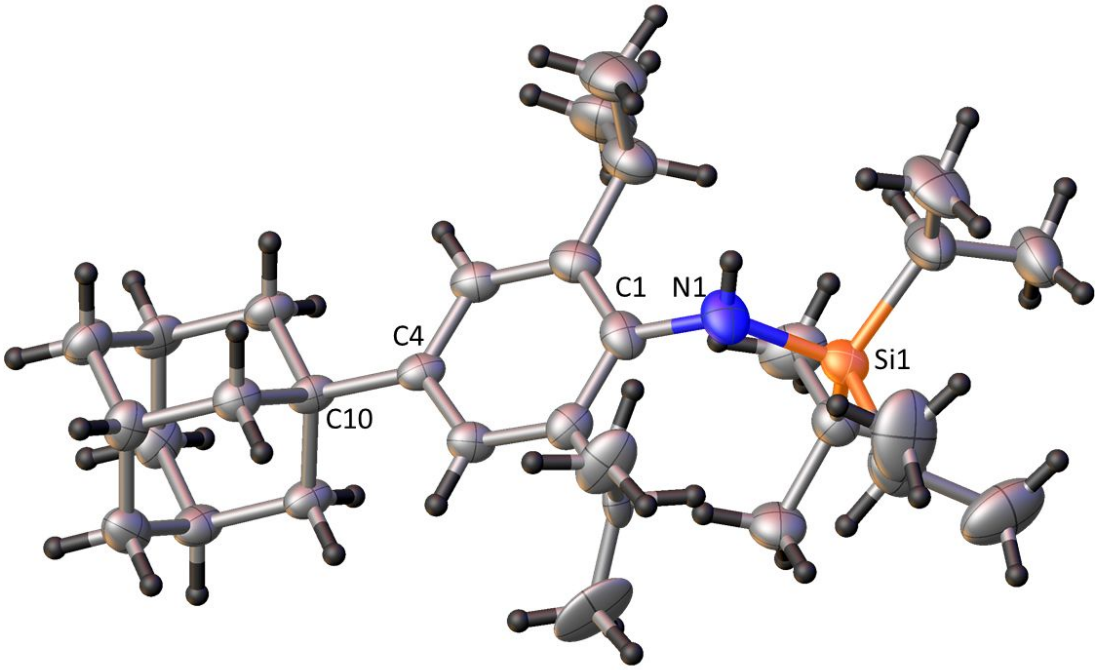
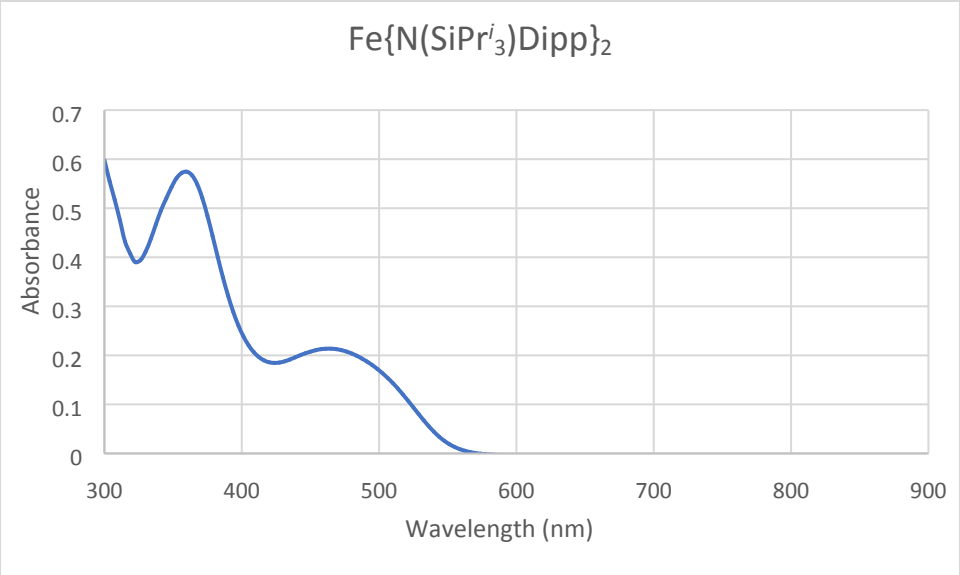


Figure S2. Molecular structure of HN(SiPri$_3$)Dipp-4-Ad (5) (Dipp-4-Ad = 2,6-diisopropyl-4-adamantyl-phenyl). The thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): C4-C10 1.522(4), N1-C1 1.436(5), N1-Si1 1.732(3), Si1-N1-C1 130.6(2).

Electronic Spectra of 1 and 2 as 0.3 mM solutions in hexanes at 25 °C



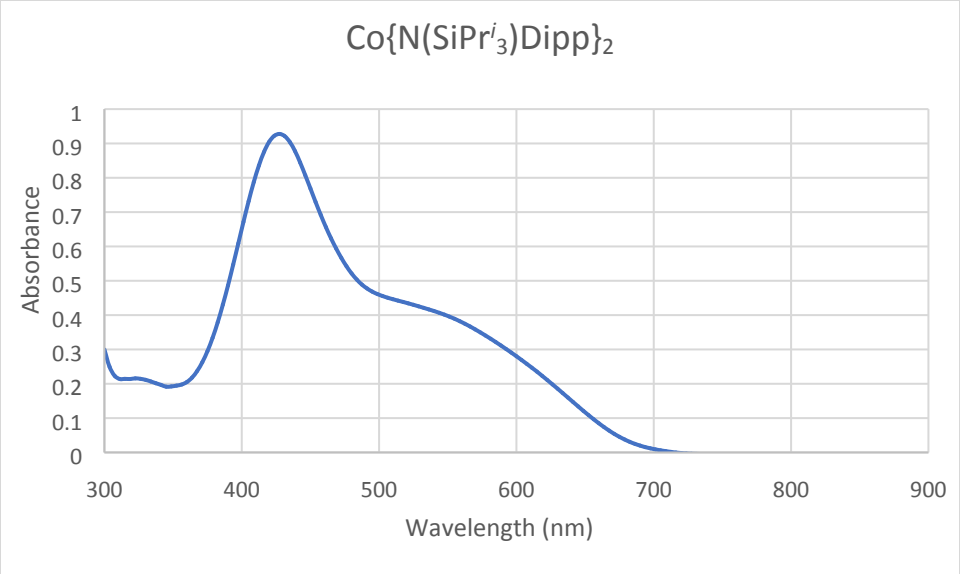
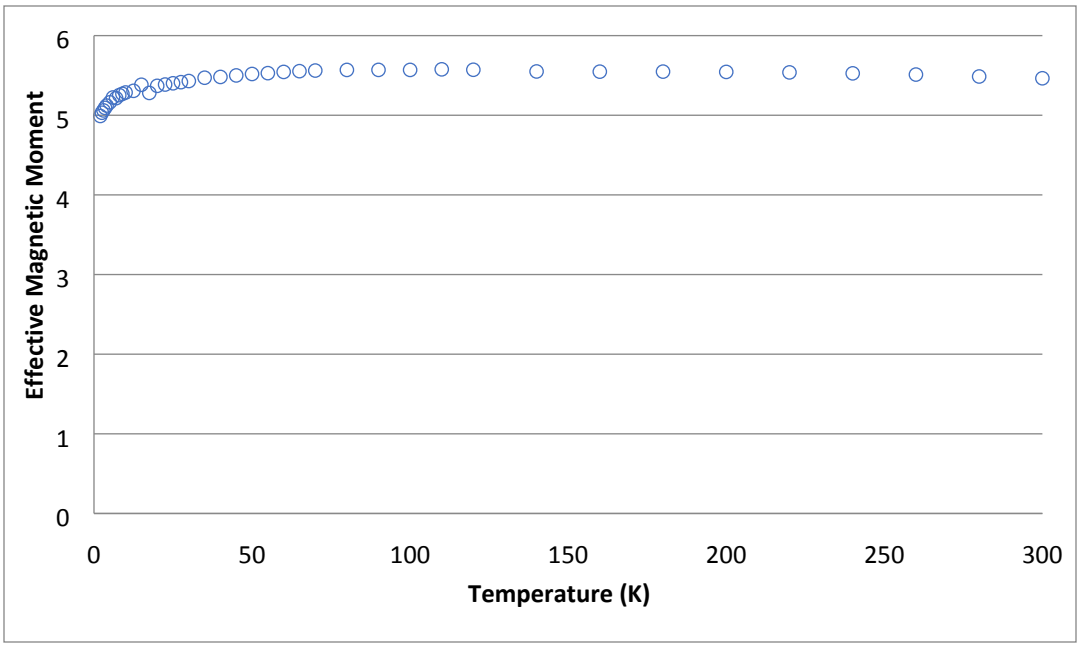


Table of Crystallographic Parameters for 1-5

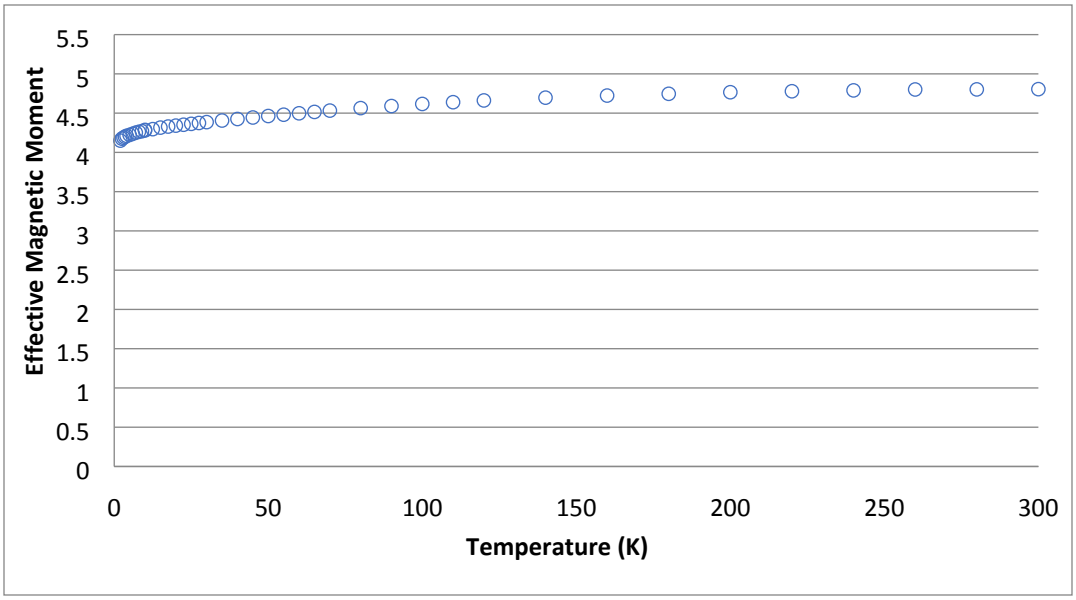
	Fe{N(SiPr$^i_3$)Dipp}$_2$ (1)	Co{N(SiPr$^i_3$)Dipp}$_2$ (2)	Zn{N(SiPr$^i_3$)Dipp}$_2$ (3)	[(Pr$^i_3$Si)N(*c*-C$_6$H$_2$-2,6-Pr$^i_2$)]$_2$ (4)	HN(SiPr$^i_3$)Dipp-4-Ad (5)
formula	$C_{42}H_{76}FeN_2Si_2$	$C_{42}H_{76}CoN_2Si_2$	$C_{42}H_{76}ZnN_2Si_2$	$C_{42}H_{74}N_2Si_2$	$C_{31}H_{51}NSi$
fw	721.07	724.15	730.59	663.21	467.83
color, habit	Red, shard	brown, plate	colorless, plate	Green, block	Colorless, rod
cryst. system	$P2_1/n$	*P-1*	*P-1*	$P2_1/n$	*P-1*
***a*, Å**	10.7637(7)	13.9034(8)	13.9424(8)	9.6832(4)	11.3543(18)
***b*, Å**	22.9265(14)	18.4138(10)	18.3952(10)	16.0500(6)	13.365(2)
***c*, Å**	17.6984(11)	18.8778(10)	18.8483(11)	14.2959(5)	19.908(3)
***α*, °**	90	71.1443(9)	71.5709(8)	90	76.881(2)
***β*, °**	98.4030(9)	79.4930(9)	79.3129(8)	107.5645(15)	88.290(2)
***γ*, °**	90	72.6926(10)	73.0352(8)	90	85.758(2)
***V*, Å^3**	4320.6(5)	4346.6(4)	4363.4(4)	2118.22(14)	2933.9(8)
Z	4	4	4	2	4
cryst. size, mm	0.273 x 0.107 x 0.087	0.319 x 0.207 x 0.042	0.322 x 0.224 x 0.084	0.223 x 0.195 x 0.155	0.227 x 0.084 x 0.048
T, K	90(2)	90(2)	90(2)	90(2)	90(2)
***d*$_{calc}$, g cm^{-3}**	1.109	1.107	1.112	1.040	1.059
abs. μ, mm^{-1}	0.433	0.478	0.646	0.995	0.098
***Θ*, °**	1.463 to 27.545	1.541 to 27.545	1.205 to 27.543	4.255 to 72.474	1.568 to 25.245
***R*(int)**	0.0442	0.0488	0.0252	0.0463	0.0473
obs. reflns. [$I > 2\sigma(I)$]	8014	13304	16470	3774	6720
data/restraints/parameters	9937/6/469	20001/36/938	20060/17/936	4110/0/218	10619/97/792
***R*$_1$, obsd. reflns.**	0.0411	0.0566	0.0388	0.0403	0.0686

Magnetic Measurements: The powdered samples of **1**, **2** and **4** used for magnetic measurements were sealed under vacuum in 6 mm outer and 4 mm inner diameter quartz tubes with a thin shelf, and the sample moment was measured using a Quantum Design MPMSXL7 superconducting quantum interference magnetometer. For each compound was zero-field cooled to 2 K and the moment was measured upon warming to 300 K in an applied field of 0.01 T. Inorder to ensure thermal equilibrium between the powdered sample sealed under vacuum in the quartz tube and the temperature sensor, the moment was measured at a given sensor temperature until a constant value moment was observed; ca. 20 h were required for the measurements between 2 and 300 K. Diamagnetic corrections of 0.0005305 emu/mol (**1**), 0.0005295 emu/mol (**2**), and 0.0006110 (**4**) obtained from tables of Pascal's constants, have been applied to the molar susceptibility of **1**, **2** and **4**.

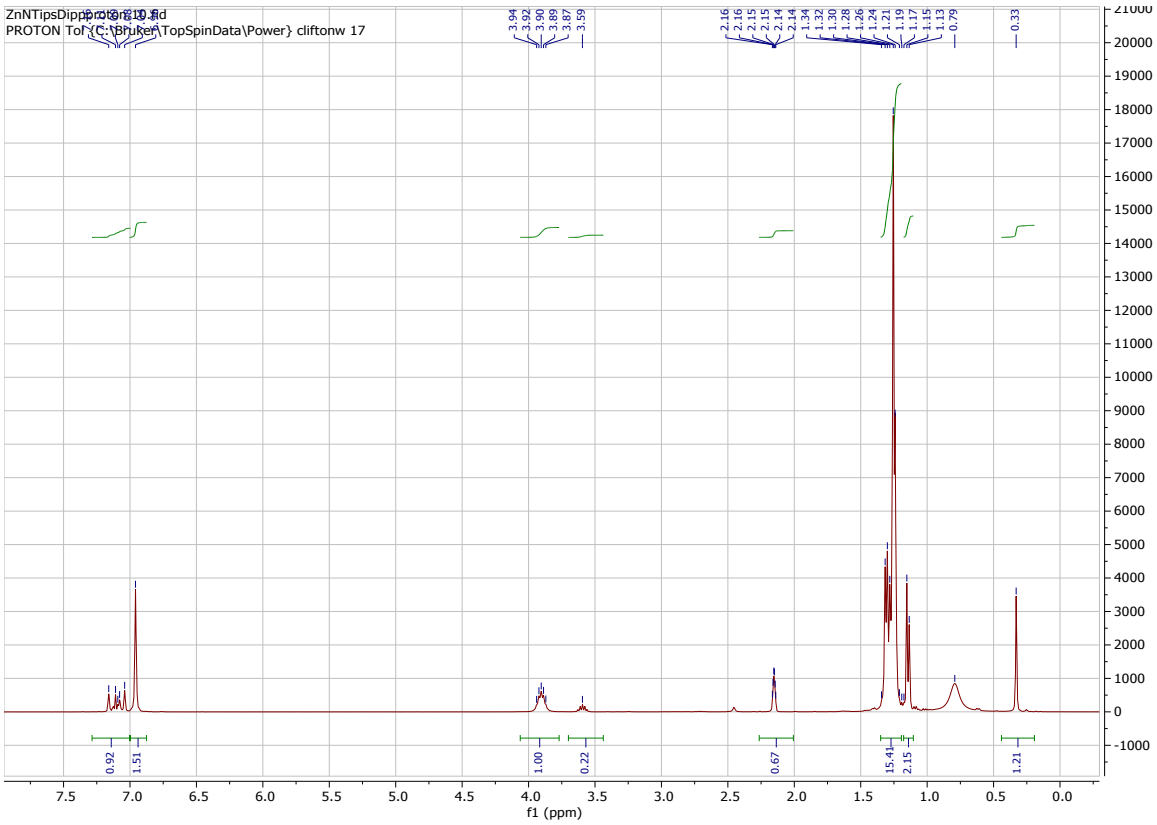
SQUID measurements for 24.5 mg Fe{N(SiPr$^{i}_{3}$)Dipp}$_2$



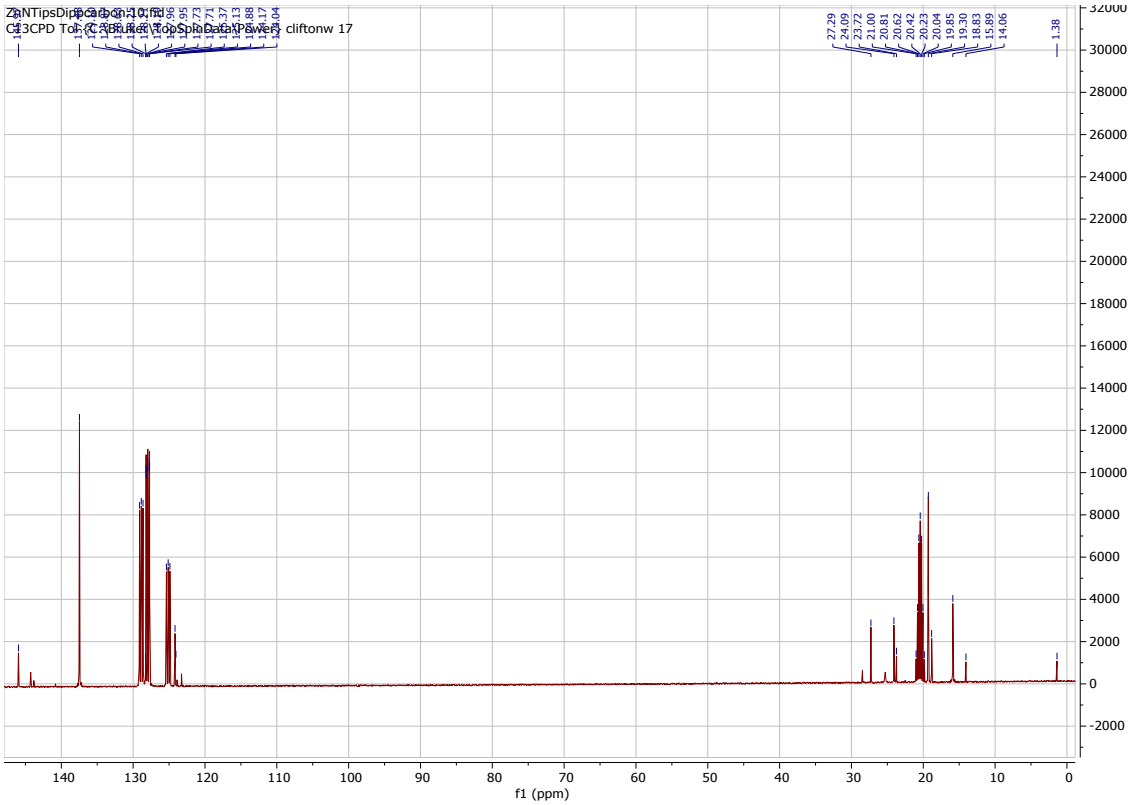
SQUID measurements for 34.8 mg Co{N(SiPr$^{i}_{3}$)Dipp}$_2$



^{1}H NMR Spectrum of Zn{N(SiPr$^i_3$)Dipp}$_2$ in C_6D_6 at 25 °C

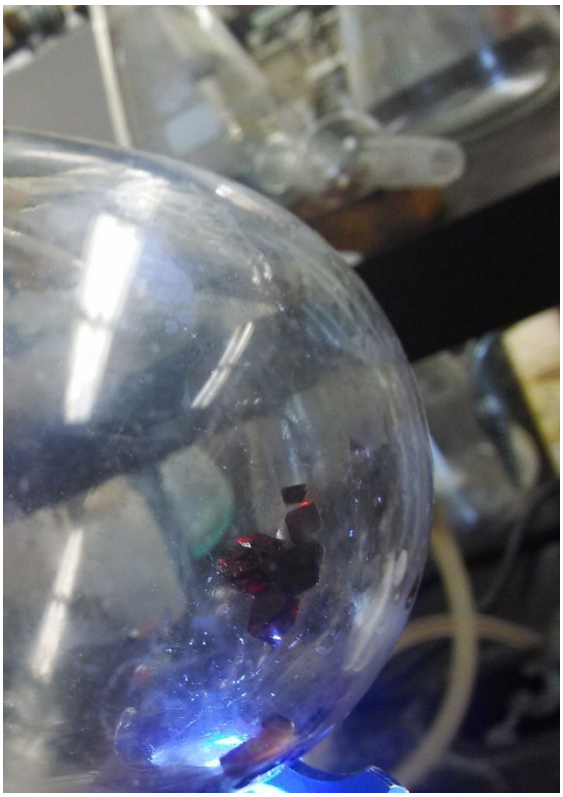


13C NMR Spectrum of Zn{N(SiPri3)Dipp}2 in C6D6 at 25 °C



Pictures of Samples

Picture of **1**



Picture of "Cu{N(SiPr$^{i}_{3}$)Dipp}$_2$"

Picture of **4**