Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information: Synthesis and Catalytic Activity of Iron Complexes with Bidentate NHC Ligands

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Magnetic Measurements

Figure S1: Temperature dependence of the χT product at 0.1 T for complex **2** (with χ being the molar susceptibility per molecule defined as *M*/*H*).

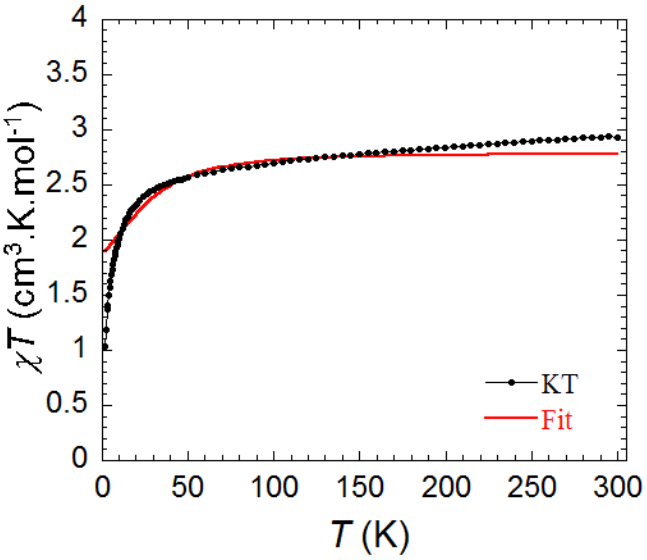


Figure S2: Temperature dependence of the χT product at 0.1 T for complex **3** (with χ being the molar susceptibility per molecule defined as *M*/*H*).

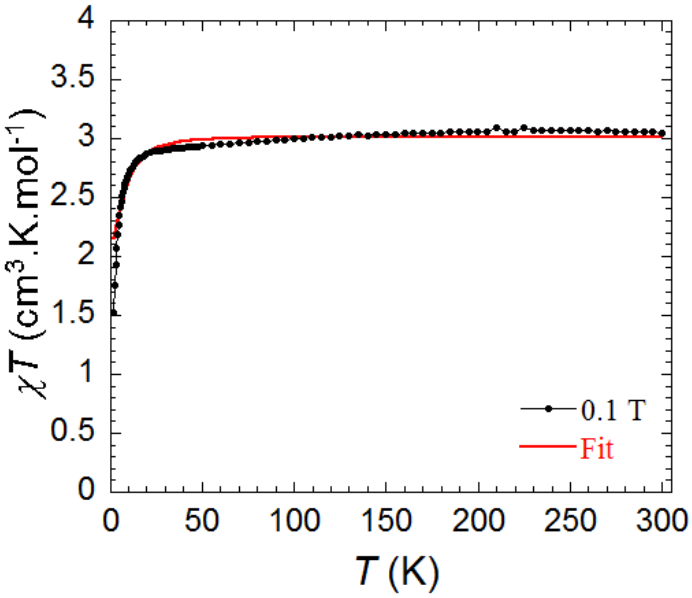


Figure S3: Temperature dependence of the χT product at 0.1 T for complex **4** (with χ being the molar susceptibility per molecule defined as *M*/*H*).

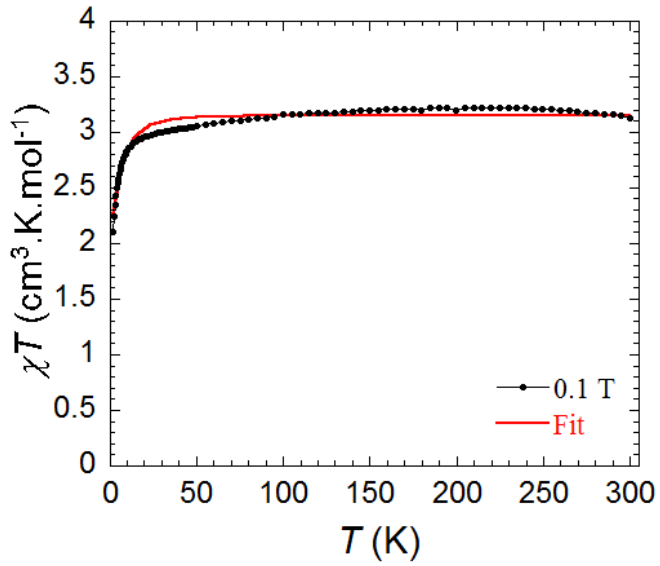


Figure S4: Field dependence of the magnetization (top) and reduced magnetization (bottom) for **2** at 1.9, 3, 5, and 8 K.

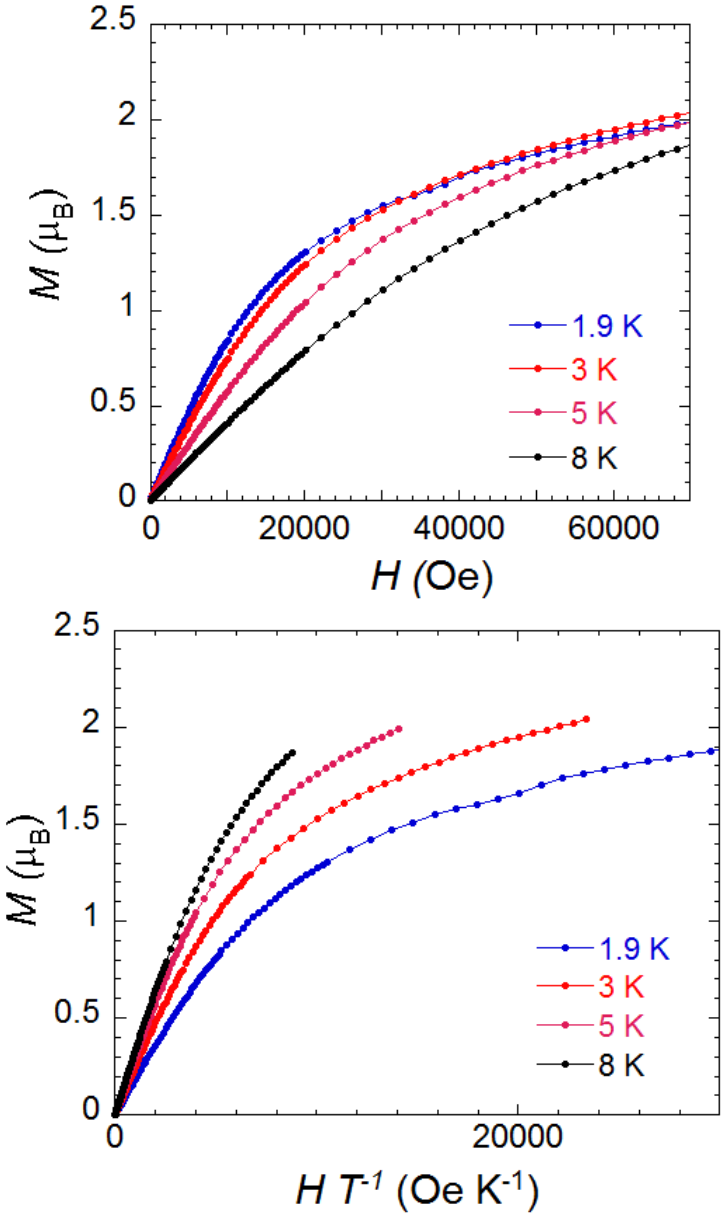


Figure S5: Field dependence of the magnetization (top) and reduced magnetization (bottom) for **3** at 1.9, 3, 5, and 8 K.

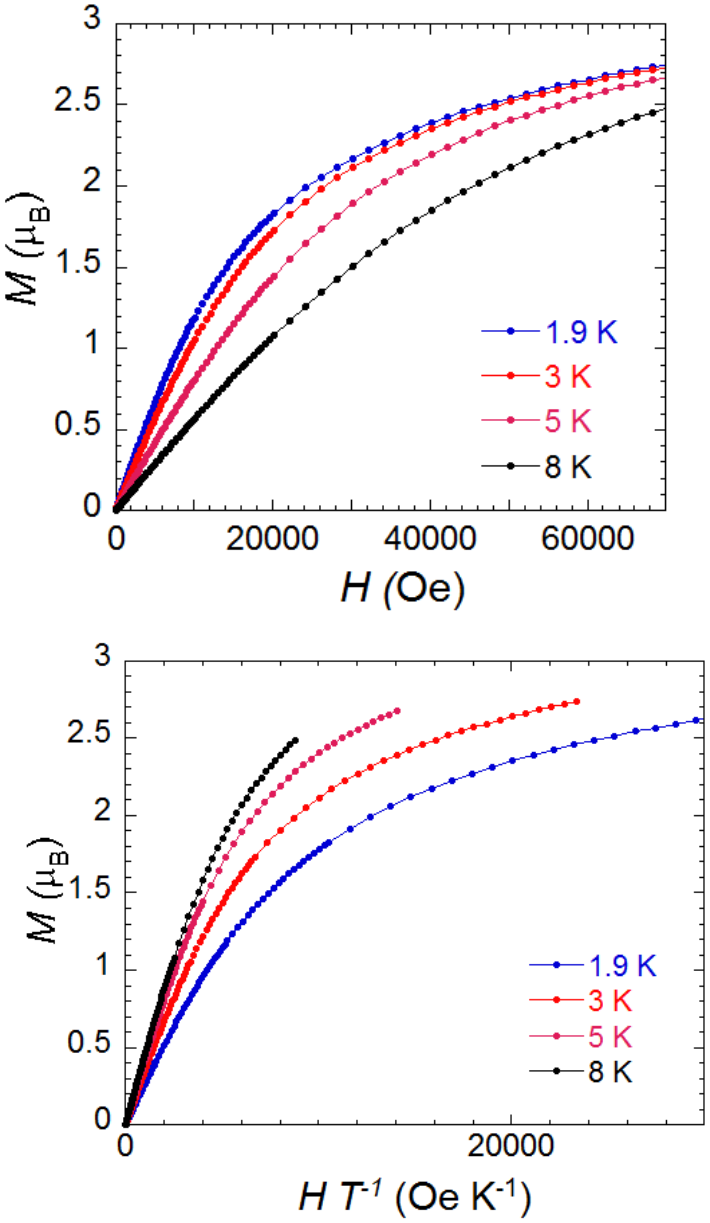
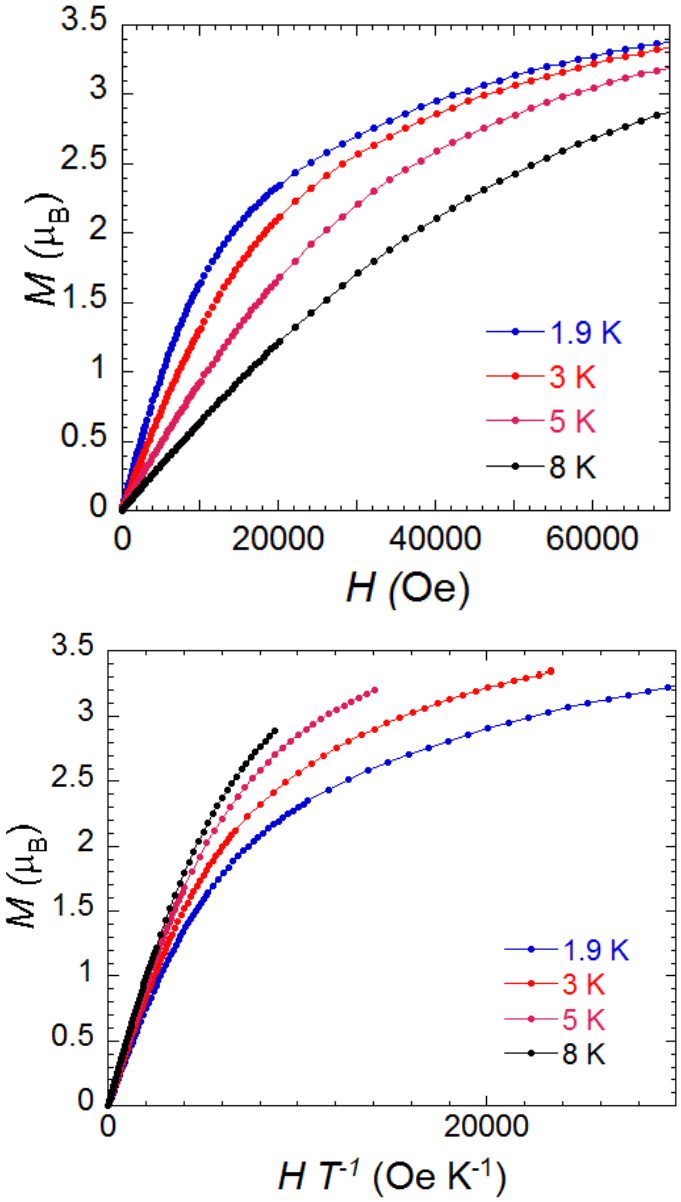


Figure S6: Field dependence of the magnetization (top) and reduced magnetization (bottom) for **4** at 1.9, 3, 5, and 8 K.



X-Ray Crystallography

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu K_α (λ = 1.54178 Å) or on a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with Mo K_α radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS[i] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[ii] using established refinement techniques.[iii] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disorders were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Compound **2** crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit along with 1.5 molecules of benzene. The phenyl group was disordered over two positions. One of the benzene molecules is disordered over two positions and the other benzene is located near an inversion center and is disordered over four positions, two of which are pairwise related to the other by the crystallographic inversion center. All benzene molecules were restrained to be flat.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit along with half a molecule of THF. The entire molecule was disordered over two positions. The THF molecule is located near an inversion center and is disordered over four positions, two of which are pairwise related to the other two by the crystallographic inversion center.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit along with one molecule of benzene. One of the phenyl groups was disordered over two positions.

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit along with one molecule of toluene. The toluene is disordered.

X-Ray Data for {BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)

Table S1. Crystal data and structure refinement for **{BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)**

Empirical formula	C36 H50 Cl2 Fe N5	
Formula weight	679.56	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5506(2) Å	α= 85.624(6)°
	b = 14.1282(3) Å	β= 87.635(6) °
	c = 14.2614(10) Å	γ = 86.017(6) °
Volume	1912.84(15) $Å^3$	
Z	2	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	4.665 mm^{-1}	
F(000)	722	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	3.11 to 65.82°.	
Index ranges	-11<=h<=11, -16<=k<=16, -15<=l<=16	
Reflections collected	55654	
Independent reflections	6506 [R(int) = 0.0991]	
Completeness to theta = 65.82°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8002 and 0.4556	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6506 / 1051 / 595	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0832, wR2 = 0.2388	
R indices (all data)	R1 = 0.0898, wR2 = 0.2486	
Largest diff. peak and hole	1.077 and -1.022 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)**

Atom	x	y	z	U(eq)
Cl(1)	7364(1)	-1396(1)	1730(1)	49(1)
Cl(2)	4519(1)	313(1)	2511(1)	47(1)
Fe(1)	6968(1)	112(1)	2260(1)	40(1)
C(1)	7398(4)	522(3)	3641(3)	42(1)
N(1)	7564(4)	35(3)	4501(2)	44(1)
C(13)	7648(5)	-1028(3)	4680(3)	49(1)
C(14)	6231(5)	-1378(4)	4493(4)	62(1)
C(15)	8815(5)	-1450(3)	4039(3)	52(1)
C(16)	8038(6)	-1298(4)	5688(3)	66(1)
C(2)	7587(5)	659(3)	5203(3)	51(1)
C(3)	7463(5)	1540(4)	4780(3)	53(1)
N(2)	7351(4)	1444(3)	3831(2)	45(1)
C(4)	7129(5)	2255(3)	3131(3)	48(1)
C(5)	5642(5)	2705(3)	3177(3)	52(1)
C(6)	5454(5)	3530(3)	2443(3)	53(1)
N(3)	5720(4)	3268(3)	1467(3)	51(1)

C(21)	5931(5)	4132(3)	851(4)	58(1)
C(22)	7257(12)	4603(9)	968(19)	56(3)
C(23)	8552(11)	4095(9)	1011(13)	62(3)
C(24)	9763(11)	4551(8)	1064(14)	70(3)
C(25)	9711(11)	5529(7)	1046(13)	69(3)
C(26)	8436(12)	6052(7)	999(11)	63(3)
C(27)	7218(13)	5592(8)	965(13)	58(3)
C(22A)	7240(20)	4604(16)	1110(40)	60(4)
C(23A)	8500(20)	4087(16)	1320(20)	62(4)
C(24A)	9720(20)	4504(14)	1500(20)	69(4)
C(25A)	9720(20)	5486(14)	1490(20)	74(4)
C(26A)	8460(20)	6025(15)	1350(20)	72(4)
C(27A)	7260(30)	5583(16)	1180(30)	65(4)
C(7)	4522(5)	2795(3)	1159(3)	54(1)
C(8)	4751(5)	2306(3)	241(3)	51(1)
C(9)	5601(4)	1360(3)	285(3)	48(1)
N(4)	7102(4)	1431(2)	412(2)	43(1)
C(10)	7935(5)	1914(3)	-250(3)	52(1)
C(11)	9245(5)	1789(3)	44(3)	51(1)
N(5)	9214(4)	1225(2)	877(2)	41(1)
C(17)	10534(4)	968(3)	1397(3)	42(1)
C(18)	11641(5)	575(4)	715(3)	54(1)
C(19)	10291(5)	198(3)	2177(3)	48(1)
C(20)	10995(5)	1856(3)	1806(3)	54(1)
C(12)	7880(4)	999(3)	1122(3)	41(1)
C(1S)	3407(8)	7850(5)	2664(6)	58(2)
C(2S)	4378(6)	7110(4)	2508(4)	58(1)
C(3S)	3945(6)	6206(4)	2460(5)	71(2)
C(4S)	2548(6)	6058(4)	2559(7)	85(2)
C(5S)	1571(7)	6801(5)	2704(7)	80(2)
C(6S)	2009(8)	7690(5)	2781(8)	65(2)
C(1T)	3660(40)	7790(20)	2630(40)	64(4)
C(2T)	4680(30)	7110(20)	2910(30)	70(4)
C(3T)	4320(30)	6270(20)	3370(30)	81(5)
C(4T)	2930(30)	6090(20)	3500(30)	89(5)
C(5T)	1910(30)	6780(30)	3260(30)	77(4)
C(6T)	2270(40)	7630(30)	2810(50)	69(4)
C(1U)	7890(20)	4286(9)	5041(9)	128(5)
C(2U)	8800(16)	4270(9)	4287(9)	118(4)
C(3U)	8677(16)	4943(9)	3555(8)	110(4)
C(4U)	7651(17)	5667(9)	3624(9)	111(4)
C(5U)	6741(18)	5694(8)	4368(10)	115(4)
C(6U)	6790(20)	4987(11)	5075(10)	137(5)
C(1V)	10970(80)	4390(50)	5040(60)	110(9)
C(3V)	9130(100)	4750(60)	3970(40)	113(7)
C(2V)	10290(100)	4200(40)	4250(50)	115(8)
C(4V)	8620(80)	5480(50)	4480(60)	113(7)
C(5V)	9300(100)	5690(50)	5270(50)	110(9)
C(6V)	10460(100)	5140(60)	5550(40)	109(10)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S3. Anisotropic displacement parameters ($Å^2$ x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)**

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	63(1)	48(1)	40(1)	-3(1)	0(1)	-17(1)
Cl(2)	46(1)	54(1)	41(1)	5(1)	-2(1)	-13(1)
Fe(1)	46(1)	46(1)	30(1)	2(1)	0(1)	-13(1)
C(1)	43(2)	51(2)	32(2)	2(2)	-2(2)	-11(2)
N(1)	49(2)	53(2)	31(2)	3(1)	-2(1)	-12(2)
C(13)	58(2)	58(3)	32(2)	4(2)	2(2)	-9(2)
C(14)	53(3)	61(3)	72(3)	17(2)	-5(2)	-17(2)
C(15)	58(3)	57(3)	40(2)	-4(2)	2(2)	-5(2)
C(16)	85(4)	78(3)	33(2)	7(2)	-2(2)	7(3)
C(2)	59(3)	66(3)	31(2)	-4(2)	-6(2)	-14(2)
C(3)	62(3)	59(3)	40(2)	-7(2)	-4(2)	-16(2)
N(2)	54(2)	51(2)	30(2)	-2(1)	-1(1)	-15(2)
C(4)	56(2)	47(2)	40(2)	1(2)	-2(2)	-14(2)
C(5)	62(3)	50(2)	44(2)	0(2)	5(2)	-11(2)
C(6)	64(3)	46(2)	51(3)	-1(2)	-3(2)	-9(2)
N(3)	58(2)	49(2)	45(2)	5(2)	-3(2)	-13(2)
C(21)	66(2)	49(2)	57(3)	10(2)	-5(2)	-12(2)
C(22)	68(3)	46(3)	54(8)	8(4)	-2(4)	-13(3)
C(23)	66(3)	47(3)	75(8)	-1(4)	0(5)	-14(2)
C(24)	64(3)	55(3)	93(9)	0(5)	8(5)	-16(3)
C(25)	72(3)	54(3)	82(8)	8(5)	2(5)	-28(3)
C(26)	83(4)	45(3)	63(7)	9(4)	-1(5)	-19(2)
C(27)	72(3)	47(3)	56(8)	5(4)	-6(4)	-10(3)
C(22A)	66(4)	49(5)	63(10)	14(6)	9(6)	-15(4)
C(23A)	62(4)	51(5)	70(10)	13(7)	9(6)	-17(4)
C(24A)	68(5)	56(5)	83(10)	6(8)	3(7)	-17(4)
C(25A)	79(5)	58(5)	86(10)	7(8)	7(8)	-25(5)
C(26A)	87(6)	49(5)	78(11)	14(7)	7(8)	-20(4)
C(27A)	81(5)	50(4)	64(11)	8(6)	3(7)	-13(4)
C(7)	51(2)	55(3)	56(3)	0(2)	-2(2)	-14(2)
C(8)	49(2)	56(3)	48(3)	7(2)	-3(2)	-13(2)
C(9)	46(2)	53(2)	44(2)	7(2)	-4(2)	-15(2)
N(4)	48(2)	48(2)	32(2)	6(1)	0(1)	-12(2)
C(10)	54(2)	62(3)	39(2)	13(2)	0(2)	-16(2)
C(11)	52(2)	62(3)	38(2)	12(2)	-1(2)	-15(2)
N(5)	46(2)	48(2)	30(2)	4(1)	-1(1)	-13(1)
C(17)	44(2)	47(2)	34(2)	1(2)	-5(2)	-11(2)
C(18)	46(2)	75(3)	40(2)	-3(2)	2(2)	-5(2)
C(19)	49(2)	55(2)	39(2)	7(2)	-5(2)	-10(2)
C(20)	59(3)	50(2)	53(3)	-3(2)	-8(2)	-12(2)
C(12)	45(2)	46(2)	32(2)	3(2)	-2(2)	-12(2)
C(1S)	81(4)	53(3)	41(3)	-3(2)	4(3)	-19(2)
C(2S)	59(3)	61(3)	57(4)	-1(3)	-2(3)	-21(2)
C(3S)	62(3)	53(3)	101(5)	-12(3)	6(3)	-8(2)
C(4S)	67(3)	51(3)	139(6)	-9(4)	9(4)	-21(2)
C(5S)	57(3)	71(3)	113(6)	-3(4)	8(4)	-13(2)
C(6S)	74(3)	58(3)	61(4)	-4(3)	10(3)	3(3)
C(1T)	75(7)	62(8)	57(9)	-3(8)	4(8)	-16(6)
C(2T)	75(7)	62(8)	71(9)	-2(8)	4(8)	-14(6)
C(3T)	82(7)	65(8)	93(10)	8(8)	15(9)	-7(8)
C(4T)	87(9)	66(9)	112(12)	6(10)	21(11)	-16(7)
C(5T)	75(7)	66(8)	93(9)	-10(8)	16(8)	-19(6)
C(6T)	74(6)	65(7)	70(9)	-9(8)	6(9)	-13(7)
C(1U)	262(15)	66(7)	63(7)	17(6)	-42(8)	-61(8)
C(2U)	210(12)	86(7)	69(7)	8(6)	-60(7)	-68(7)

C(3U)	183(12)	86(7)	72(7)	13(6)	-41(7)	-93(7)
C(4U)	181(12)	84(7)	78(7)	32(6)	-56(7)	-90(7)
C(5U)	210(13)	60(6)	83(8)	13(5)	-47(7)	-70(7)
C(6U)	266(15)	69(7)	80(8)	16(6)	-12(9)	-63(8)
C(1V)	180(20)	89(18)	64(18)	32(16)	-35(14)	-87(16)
C(3V)	190(15)	86(12)	72(12)	27(11)	-43(11)	-87(11)
C(2V)	194(16)	92(14)	67(14)	31(13)	-41(13)	-83(12)
C(4V)	186(15)	84(12)	77(12)	26(11)	-39(12)	-92(11)
C(5V)	180(20)	84(17)	70(17)	28(13)	-34(15)	-91(16)
C(6V)	180(20)	85(19)	66(18)	34(15)	-31(15)	-91(18)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4. Bond lengths (Å) for **{BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)**

Cl(1)-Fe(1)	2.3149(12)
Cl(2)-Fe(1)	2.3521(11)
Fe(1)-C(1)	2.158(4)
Fe(1)-C(12)	2.166(4)
C(1)-N(2)	1.347(6)
C(1)-N(1)	1.368(5)
N(1)-C(2)	1.387(6)
N(1)-C(13)	1.501(6)
C(13)-C(16)	1.513(6)
C(13)-C(14)	1.513(7)
C(13)-C(15)	1.530(6)
C(2)-C(3)	1.341(7)
C(3)-N(2)	1.380(6)
N(2)-C(4)	1.471(5)
C(4)-C(5)	1.516(7)
C(5)-C(6)	1.513(6)
C(6)-N(3)	1.475(6)
N(3)-C(7)	1.463(6)
N(3)-C(21)	1.469(6)
C(21)-C(22)	1.491(10)
C(21)-C(22A)	1.528(14)
C(22)-C(23)	1.388(10)
C(22)-C(27)	1.396(9)
C(23)-C(24)	1.370(10)
C(24)-C(25)	1.378(10)
C(25)-C(26)	1.381(10)
C(26)-C(27)	1.375(10)
C(22A)-C(23A)	1.394(13)
C(22A)-C(27A)	1.397(13)
C(23A)-C(24A)	1.379(14)
C(24A)-C(25A)	1.387(13)
C(25A)-C(26A)	1.391(14)
C(26A)-C(27A)	1.381(14)
C(7)-C(8)	1.527(7)
C(8)-C(9)	1.513(7)
C(9)-N(4)	1.464(5)
N(4)-C(12)	1.363(5)
N(4)-C(10)	1.380(5)

C(10)-C(11)	1.332(6)
C(11)-N(5)	1.379(5)
N(5)-C(12)	1.360(5)
N(5)-C(17)	1.499(5)
C(17)-C(18)	1.513(6)
C(17)-C(19)	1.518(6)
C(17)-C(20)	1.523(6)
C(1S)-C(6S)	1.371(9)
C(1S)-C(2S)	1.374(8)
C(2S)-C(3S)	1.377(7)
C(3S)-C(4S)	1.365(8)
C(4S)-C(5S)	1.377(8)
C(5S)-C(6S)	1.364(9)
C(1T)-C(6T)	1.37(2)
C(1T)-C(2T)	1.369(13)
C(2T)-C(3T)	1.368(12)
C(3T)-C(4T)	1.369(12)
C(4T)-C(5T)	1.365(12)
C(5T)-C(6T)	1.372(14)
C(1U)-C(2U)	1.352(12)
C(1U)-C(6U)	1.397(19)
C(2U)-C(3U)	1.360(11)
C(3U)-C(4U)	1.373(11)
C(4U)-C(5U)	1.345(11)
C(5U)-C(6U)	1.364(11)
C(1V)-C(2V)	1.368(14)
C(1V)-C(6V)	1.38(2)
C(3V)-C(2V)	1.366(12)
C(3V)-C(4V)	1.368(12)
C(4V)-C(5V)	1.369(12)
C(5V)-C(6V)	1.366(14)

Table S5. Bond angles (°) for **{BnN($CH_2CH_2CH_2$-*N*-*tert*-butyl-imidazole-2-ylidene)$_2$}$FeCl_2$ (2)**

C(1)-Fe(1)-C(12)	113.71(15)
C(1)-Fe(1)-Cl(1)	126.20(12)
C(12)-Fe(1)-Cl(1)	102.35(12)
C(1)-Fe(1)-Cl(2)	93.44(11)
C(12)-Fe(1)-Cl(2)	116.57(11)
Cl(1)-Fe(1)-Cl(2)	104.91(4)
N(2)-C(1)-N(1)	104.1(3)
N(2)-C(1)-Fe(1)	121.3(3)
N(1)-C(1)-Fe(1)	133.9(3)
C(1)-N(1)-C(2)	110.7(4)
C(1)-N(1)-C(13)	125.5(3)
C(2)-N(1)-C(13)	123.8(3)
N(1)-C(13)-C(16)	109.7(4)
N(1)-C(13)-C(14)	108.2(4)
C(16)-C(13)-C(14)	110.7(4)
N(1)-C(13)-C(15)	108.6(4)
C(16)-C(13)-C(15)	107.7(4)
C(14)-C(13)-C(15)	112.0(4)
C(3)-C(2)-N(1)	106.7(4)
C(2)-C(3)-N(2)	106.9(4)

C(1)-N(2)-C(3)	111.5(4)
C(1)-N(2)-C(4)	124.9(3)
C(3)-N(2)-C(4)	123.4(4)
N(2)-C(4)-C(5)	112.6(4)
C(6)-C(5)-C(4)	111.0(4)
N(3)-C(6)-C(5)	114.0(4)
C(7)-N(3)-C(21)	109.7(4)
C(7)-N(3)-C(6)	109.8(4)
C(21)-N(3)-C(6)	109.2(4)
N(3)-C(21)-C(22)	116.1(9)
N(3)-C(21)-C(22A)	111.1(17)
C(22)-C(21)-C(22A)	7(3)
C(23)-C(22)-C(27)	118.4(8)
C(23)-C(22)-C(21)	122.0(8)
C(27)-C(22)-C(21)	119.4(9)
C(24)-C(23)-C(22)	120.9(8)
C(23)-C(24)-C(25)	120.1(9)
C(24)-C(25)-C(26)	120.1(8)
C(27)-C(26)-C(25)	119.8(8)
C(26)-C(27)-C(22)	120.7(9)
C(23A)-C(22A)-C(27A)	114.5(14)
C(23A)-C(22A)-C(21)	122.6(15)
C(27A)-C(22A)-C(21)	122.8(15)
C(24A)-C(23A)-C(22A)	123.5(15)
C(23A)-C(24A)-C(25A)	120.1(15)
C(24A)-C(25A)-C(26A)	118.3(15)
C(27A)-C(26A)-C(25A)	120.0(15)
C(26A)-C(27A)-C(22A)	123.3(16)
N(3)-C(7)-C(8)	116.0(4)
C(9)-C(8)-C(7)	116.9(4)
N(4)-C(9)-C(8)	114.1(4)
C(12)-N(4)-C(10)	111.2(4)
C(12)-N(4)-C(9)	126.8(3)
C(10)-N(4)-C(9)	121.8(3)
C(11)-C(10)-N(4)	106.7(4)
C(10)-C(11)-N(5)	107.5(4)
C(12)-N(5)-C(11)	110.8(3)
C(12)-N(5)-C(17)	128.7(3)
C(11)-N(5)-C(17)	120.5(3)
N(5)-C(17)-C(18)	108.3(3)
N(5)-C(17)-C(19)	110.5(3)
C(18)-C(17)-C(19)	107.8(4)
N(5)-C(17)-C(20)	108.7(3)
C(18)-C(17)-C(20)	111.2(4)
C(19)-C(17)-C(20)	110.3(4)
N(5)-C(12)-N(4)	103.8(3)
N(5)-C(12)-Fe(1)	133.8(3)
N(4)-C(12)-Fe(1)	122.3(3)
C(6S)-C(1S)-C(2S)	120.2(5)
C(1S)-C(2S)-C(3S)	119.9(5)
C(4S)-C(3S)-C(2S)	119.4(5)
C(3S)-C(4S)-C(5S)	120.8(5)
C(6S)-C(5S)-C(4S)	119.6(6)
C(5S)-C(6S)-C(1S)	120.1(6)
C(6T)-C(1T)-C(2T)	120.4(11)
C(3T)-C(2T)-C(1T)	119.6(12)

C(2T)-C(3T)-C(4T)	119.9(10)
C(5T)-C(4T)-C(3T)	120.3(10)
C(4T)-C(5T)-C(6T)	119.6(12)
C(1T)-C(6T)-C(5T)	119.9(11)
C(2U)-C(1U)-C(6U)	120.5(9)
C(1U)-C(2U)-C(3U)	121.1(10)
C(2U)-C(3U)-C(4U)	118.1(9)
C(5U)-C(4U)-C(3U)	121.6(8)
C(4U)-C(5U)-C(6U)	120.8(10)
C(5U)-C(6U)-C(1U)	117.7(10)
C(2V)-C(1V)-C(6V)	119.9(12)
C(2V)-C(3V)-C(4V)	120.0(11)
C(3V)-C(2V)-C(1V)	120.2(12)
C(3V)-C(4V)-C(5V)	119.9(11)
C(6V)-C(5V)-C(4V)	120.3(12)
C(5V)-C(6V)-C(1V)	119.7(12)

X-Ray Data for {BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)

Table S6. Crystal data and structure refinement for **{BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)**

Empirical formula	C29 H33 Cl2 Fe N5 O0.50	
Formula weight	586.35	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.9406(3) Å	α= 90°
	b = 9.3355(2) Å	β= 91.132(6) °
	c = 22.9686(16) Å	γ = 90 °
Volume	2774.2(2) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	6.362 mm^{-1}	
F(000)	1224	
Crystal size	0.07 x 0.03 x 0.03 mm^3	
Theta range for data collection	3.85 to 65.09°.	
Index ranges	-12<=h<=14, -10<=k<=10, -26<=l<=27	
Reflections collected	47039	
Independent reflections	4496 [R(int) = 0.0852]	
Completeness to theta = 65.09°	95.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8321 and 0.6644	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4496 / 1595 / 723	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0832, wR2 = 0.1768	
R indices (all data)	R1 = 0.0939, wR2 = 0.1818	
Largest diff. peak and hole	0.387 and -0.468 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and Biso/Beq ($Å^2$x 10^3) for **{BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)**

Atom	x	y	z	U(eq)
Cl(1)	11484(9)	10752(9)	883(5)	59(2)
Cl(2)	13040(3)	7567(5)	1240(2)	62(1)
Fe(1)	11438(5)	8558(7)	1345(4)	54(1)
C(1)	11070(14)	8840(18)	2229(5)	48(2)
N(1)	10425(15)	9850(20)	2462(6)	57(3)
C(8)	9819(15)	10936(19)	2151(9)	91(5)
C(2)	10360(20)	9690(20)	3064(6)	60(3)
C(3)	9825(18)	10460(20)	3464(6)	72(3)
C(4)	9936(16)	10040(19)	4040(6)	74(4)
C(5)	10593(17)	8922(18)	4206(6)	73(4)
C(6)	11120(20)	8140(20)	3801(7)	65(3)
C(7)	10990(20)	8550(30)	3216(6)	57(2)
N(2)	11400(20)	8050(20)	2694(6)	55(2)
C(9)	12005(14)	6740(17)	2638(9)	65(3)
C(10)	11278(7)	5435(11)	2736(4)	61(2)
N(3)	10553(6)	5198(8)	2247(3)	52(2)
C(21)	9530(7)	4770(10)	2439(4)	57(2)
C(22)	8933(8)	5989(11)	2694(4)	50(2)
C(23)	8545(10)	7077(14)	2355(5)	55(2)
C(24)	7975(9)	8179(12)	2582(5)	71(2)
C(25)	7790(10)	8242(13)	3162(5)	81(3)
C(26)	8173(11)	7175(13)	3521(5)	85(3)
C(27)	8776(11)	6067(14)	3300(5)	74(3)
C(11)	10951(8)	4207(10)	1796(4)	58(2)
C(12)	11240(12)	4992(16)	1221(7)	47(3)
N(4)	10356(11)	5763(12)	989(8)	37(2)
C(13)	9471(10)	5128(13)	734(8)	35(2)
C(14)	9206(10)	3723(13)	578(9)	40(3)
C(15)	8280(10)	3505(15)	282(9)	42(3)
C(16)	7640(10)	4666(14)	153(8)	44(3)
C(17)	7892(11)	6049(14)	307(8)	40(3)
C(18)	8813(9)	6265(13)	593(8)	35(2)
N(5)	9313(8)	7505(13)	771(8)	38(2)
C(19)	10250(9)	7221(11)	1014(8)	36(2)
C(20)	8839(10)	8925(15)	716(7)	46(3)
Cl(1A)	11204(13)	10774(13)	934(9)	53(3)
Cl(2A)	13132(5)	8116(8)	1373(4)	70(2)
Fe(1A)	11419(7)	8600(11)	1389(5)	50(2)
C(1A)	11010(20)	8630(30)	2276(7)	52(3)
N(1A)	11440(30)	7850(30)	2723(9)	52(3)
C(8A)	12130(30)	6600(30)	2705(15)	78(6)
C(2A)	11070(40)	8300(40)	3253(9)	54(3)
C(3A)	11290(30)	7830(40)	3799(9)	60(4)
C(4A)	10750(30)	8460(30)	4240(9)	61(4)
C(5A)	10080(20)	9610(30)	4149(8)	61(4)
C(6A)	9890(30)	10140(30)	3595(9)	63(4)
C(7A)	10410(30)	9440(40)	3139(8)	55(3)
N(2A)	10410(20)	9620(30)	2532(8)	53(3)
C(9A)	9761(16)	10570(20)	2188(13)	63(4)
C(10A)	8651(10)	9979(14)	2109(6)	54(3)
N(3A)	8536(9)	8730(11)	1729(4)	51(2)
C(21A)	7876(11)	7635(15)	1989(6)	60(3)
C(22A)	8379(17)	6870(20)	2494(7)	57(3)
C(23A)	9170(12)	5916(17)	2429(6)	51(3)

C(24A)	9614(12)	5200(16)	2894(6)	57(3)
C(25A)	9284(14)	5428(19)	3450(6)	70(3)
C(26A)	8462(17)	6350(20)	3531(7)	82(4)
C(27A)	8005(14)	7090(20)	3065(6)	77(3)
C(11A)	8218(10)	9033(14)	1114(5)	44(3)
C(12A)	9121(16)	8740(20)	692(9)	41(3)
N(4A)	9538(13)	7297(19)	751(12)	33(2)
C(13A)	9035(14)	6040(20)	554(13)	34(3)
C(14A)	8095(16)	5760(20)	256(13)	38(3)
C(15A)	7886(15)	4340(20)	119(12)	39(3)
C(16A)	8567(15)	3250(20)	275(13)	39(4)
C(17A)	9493(16)	3510(20)	570(14)	38(3)
C(18A)	9697(15)	4913(19)	696(13)	33(3)
N(5A)	10527(18)	5512(18)	998(13)	38(3)
C(19A)	10454(12)	6984(17)	1022(13)	34(3)
C(20A)	11330(20)	4650(20)	1275(12)	48(4)
O(1S)	8922(12)	3827(17)	4661(8)	83(4)
C(1S)	9927(16)	3670(20)	4501(11)	86(5)
C(2S)	10545(16)	4860(30)	4845(14)	84(5)
C(3S)	9654(16)	5960(20)	4979(12)	74(4)
C(4S)	8715(16)	4910(20)	5043(13)	81(5)
O(1T)	10150(30)	4430(40)	4643(16)	85(5)
C(1T)	11000(30)	4770(50)	4990(30)	82(6)
C(2T)	10720(30)	6310(50)	5220(30)	74(6)
C(3T)	9510(30)	6390(40)	5120(20)	70(6)
C(4T)	9250(30)	4810(50)	4920(20)	81(5)

$Beq = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for **{BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)**

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	77(6)	57(2)	43(3)	1(2)	10(3)	-25(2)
Cl(2)	51(2)	76(3)	61(2)	-8(2)	3(1)	-21(2)
Fe(1)	61(2)	63(2)	38(2)	5(2)	2(2)	-19(2)
C(1)	48(5)	56(6)	39(3)	8(3)	-5(3)	-18(4)
N(1)	61(5)	72(7)	38(4)	3(4)	-2(4)	-10(4)
C(8)	108(10)	98(11)	68(7)	22(8)	11(8)	28(7)
C(2)	64(5)	77(8)	37(4)	0(4)	-1(4)	-21(5)
C(3)	82(7)	94(9)	39(5)	1(5)	2(6)	-10(6)
C(4)	90(8)	95(10)	37(5)	-3(6)	-3(6)	-15(6)
C(5)	86(9)	93(11)	38(4)	0(5)	-11(5)	-22(7)
C(6)	70(8)	85(9)	40(3)	3(4)	-14(4)	-24(5)
C(7)	55(6)	77(7)	37(3)	5(4)	-9(4)	-28(5)
N(2)	53(5)	72(5)	39(3)	10(4)	-8(4)	-16(4)
C(9)	67(7)	83(6)	44(6)	19(5)	-15(5)	0(3)
C(10)	64(5)	72(5)	47(4)	21(4)	-3(4)	10(4)
N(3)	50(4)	61(4)	45(3)	11(3)	3(3)	16(3)
C(21)	60(4)	56(5)	56(5)	-2(4)	14(4)	5(4)
C(22)	48(5)	49(4)	54(4)	-5(4)	8(4)	-3(3)
C(23)	45(6)	58(5)	61(5)	2(4)	7(4)	1(4)
C(24)	69(6)	64(5)	79(4)	6(4)	15(5)	15(4)
C(25)	95(7)	71(6)	79(5)	-9(5)	11(6)	28(5)
C(26)	110(8)	82(7)	63(5)	-10(4)	17(5)	35(6)

C(27)	87(7)	78(6)	57(4)	-1(4)	18(5)	29(5)
C(11)	64(6)	62(5)	48(4)	18(3)	14(4)	27(4)
C(12)	49(5)	48(6)	45(5)	14(5)	4(4)	24(4)
N(4)	30(5)	42(4)	39(4)	4(4)	5(4)	12(3)
C(13)	32(5)	38(4)	35(4)	-8(4)	15(4)	14(3)
C(14)	31(7)	37(4)	53(5)	-4(4)	18(6)	12(4)
C(15)	35(7)	39(5)	53(5)	-16(5)	15(6)	10(5)
C(16)	33(6)	46(6)	51(5)	-15(5)	6(5)	10(4)
C(17)	36(6)	39(5)	45(5)	-14(4)	5(5)	15(4)
C(18)	30(5)	38(4)	36(4)	-3(4)	8(5)	12(3)
N(5)	37(5)	36(4)	39(4)	4(4)	-1(4)	11(3)
C(19)	39(4)	37(4)	33(4)	6(4)	0(4)	11(3)
C(20)	42(8)	38(4)	57(6)	2(5)	-2(6)	18(5)
Cl(1A)	69(7)	45(2)	47(4)	5(2)	17(4)	-15(3)
Cl(2A)	47(3)	84(5)	78(5)	23(3)	0(2)	-15(3)
Fe(1A)	48(3)	65(4)	37(3)	12(3)	-9(3)	-8(3)
C(1A)	57(6)	61(7)	37(3)	5(3)	-7(4)	-16(5)
N(1A)	55(6)	63(7)	36(3)	8(4)	-4(5)	-16(5)
C(8A)	86(13)	84(11)	63(12)	17(8)	9(10)	12(8)
C(2A)	57(6)	69(8)	37(3)	3(5)	-8(5)	-17(5)
C(3A)	68(9)	75(10)	37(4)	-3(5)	-15(5)	-10(6)
C(4A)	73(9)	74(11)	37(5)	2(6)	-14(6)	-2(8)
C(5A)	76(9)	73(11)	33(5)	10(6)	-8(7)	-2(7)
C(6A)	81(7)	73(9)	35(6)	14(6)	2(7)	-1(6)
C(7A)	62(6)	68(8)	36(4)	4(5)	-3(5)	-16(5)
N(2A)	57(5)	64(7)	38(4)	8(5)	-2(4)	-15(5)
C(9A)	76(7)	65(8)	49(7)	9(6)	-4(6)	-5(5)
C(10A)	59(6)	60(6)	42(6)	-8(5)	-1(5)	18(5)
N(3A)	55(6)	52(5)	44(4)	-5(3)	-5(4)	22(4)
C(21A)	55(7)	67(6)	59(5)	-6(5)	-2(5)	9(4)
C(22A)	57(7)	58(6)	57(5)	-3(4)	1(5)	2(5)
C(23A)	50(6)	50(6)	53(5)	1(6)	1(5)	-4(5)
C(24A)	61(7)	53(6)	57(5)	4(5)	0(5)	-2(5)
C(25A)	85(9)	71(8)	54(5)	8(6)	2(6)	7(6)
C(26A)	104(9)	85(9)	57(5)	1(7)	11(6)	21(7)
C(27A)	90(7)	80(7)	62(5)	-1(6)	10(5)	24(6)
C(11A)	38(7)	46(6)	49(5)	-11(4)	-10(4)	24(5)
C(12A)	40(8)	40(5)	42(5)	-3(6)	-9(5)	21(6)
N(4A)	33(5)	36(4)	31(5)	0(4)	2(5)	15(4)
C(13A)	26(6)	39(5)	37(6)	-8(5)	10(5)	17(4)
C(14A)	28(7)	41(6)	44(7)	-12(6)	8(6)	17(5)
C(15A)	28(7)	41(7)	48(6)	-14(6)	14(6)	13(6)
C(16A)	28(8)	39(6)	50(6)	-4(6)	20(7)	13(5)
C(17A)	30(8)	38(5)	47(6)	-6(5)	19(7)	15(5)
C(18A)	27(6)	37(4)	35(6)	-3(5)	16(6)	18(4)
N(5A)	36(6)	40(4)	39(5)	1(5)	2(5)	19(4)
C(19A)	35(5)	37(4)	31(5)	4(5)	1(5)	16(4)
C(20A)	52(8)	42(9)	51(9)	18(8)	-5(7)	19(7)
O(1S)	86(9)	81(7)	85(9)	-21(6)	35(7)	-18(7)
C(1S)	83(9)	84(9)	92(10)	-30(7)	28(9)	-10(8)
C(2S)	81(8)	89(9)	85(10)	-33(8)	31(9)	-10(7)
C(3S)	78(9)	75(8)	70(10)	-13(7)	31(8)	-13(7)
C(4S)	83(9)	78(9)	84(10)	-17(7)	39(9)	-17(8)
O(1T)	82(10)	86(10)	88(11)	-34(8)	31(9)	-13(9)
C(1T)	80(10)	86(12)	80(13)	-36(11)	33(11)	-7(10)
C(2T)	74(11)	77(10)	72(12)	-24(9)	36(11)	-11(9)

C(3T)	74(11)	77(10)	59(13)	-14(10)	37(11)	-13(9)
C(4T)	80(9)	83(9)	81(10)	-24(8)	32(9)	-16(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S9. Bond lengths (Å) for **{BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)**

Cl(1)-Fe(1)	2.308(7)
Cl(2)-Fe(1)	2.287(7)
Fe(1)-C(19)	2.110(8)
Fe(1)-C(1)	2.113(8)
C(1)-N(2)	1.360(12)
C(1)-N(1)	1.373(13)
N(1)-C(2)	1.394(13)
N(1)-C(8)	1.462(12)
C(2)-C(3)	1.369(14)
C(2)-C(7)	1.383(11)
C(3)-C(4)	1.386(13)
C(4)-C(5)	1.394(12)
C(5)-C(6)	1.373(14)
C(6)-C(7)	1.402(13)
C(7)-N(2)	1.400(13)
N(2)-C(9)	1.457(13)
C(9)-C(10)	1.559(18)
C(10)-N(3)	1.466(9)
N(3)-C(21)	1.459(11)
N(3)-C(11)	1.489(9)
C(21)-C(22)	1.501(12)
C(22)-C(23)	1.369(11)
C(22)-C(27)	1.412(14)
C(23)-C(24)	1.375(14)
C(24)-C(25)	1.358(13)
C(25)-C(26)	1.379(14)
C(26)-C(27)	1.399(13)
C(11)-C(12)	1.562(16)
C(12)-N(4)	1.445(11)
N(4)-C(19)	1.369(11)
N(4)-C(13)	1.406(12)
C(13)-C(18)	1.395(9)
C(13)-C(14)	1.401(13)
C(14)-C(15)	1.381(12)
C(15)-C(16)	1.393(10)
C(16)-C(17)	1.376(12)
C(17)-C(18)	1.364(13)
C(18)-N(5)	1.385(12)
N(5)-C(19)	1.350(11)
N(5)-C(20)	1.465(10)
Cl(1A)-Fe(1A)	2.297(10)
Cl(2A)-Fe(1A)	2.263(9)
Fe(1A)-C(1A)	2.112(11)
Fe(1A)-C(19A)	2.123(11)
C(1A)-N(2A)	1.354(15)
C(1A)-N(1A)	1.369(15)

N(1A)-C(2A)	1.383(17)
N(1A)-C(8A)	1.466(15)
C(2A)-C(3A)	1.356(16)
C(2A)-C(7A)	1.382(12)
C(3A)-C(4A)	1.377(16)
C(4A)-C(5A)	1.399(14)
C(5A)-C(6A)	1.379(15)
C(6A)-C(7A)	1.414(16)
C(7A)-N(2A)	1.406(15)
N(2A)-C(9A)	1.443(15)
C(9A)-C(10A)	1.546(19)
C(10A)-N(3A)	1.463(11)
N(3A)-C(21A)	1.467(14)
N(3A)-C(11A)	1.489(11)
C(21A)-C(22A)	1.499(16)
C(22A)-C(23A)	1.370(14)
C(22A)-C(27A)	1.421(17)
C(23A)-C(24A)	1.376(16)
C(24A)-C(25A)	1.370(16)
C(25A)-C(26A)	1.385(17)
C(26A)-C(27A)	1.394(16)
C(11A)-C(12A)	1.557(17)
C(12A)-N(4A)	1.458(13)
N(4A)-C(19A)	1.359(14)
N(4A)-C(13A)	1.411(16)
C(13A)-C(18A)	1.392(11)
C(13A)-C(14A)	1.409(16)
C(14A)-C(15A)	1.385(15)
C(15A)-C(16A)	1.389(13)
C(16A)-C(17A)	1.387(15)
C(17A)-C(18A)	1.362(16)
C(18A)-N(5A)	1.384(16)
N(5A)-C(19A)	1.378(14)
N(5A)-C(20A)	1.453(13)
O(1S)-C(1S)	1.37(2)
O(1S)-C(4S)	1.37(2)
C(1S)-C(2S)	1.57(2)
C(2S)-C(3S)	1.58(2)
C(3S)-C(4S)	1.57(2)
O(1T)-C(1T)	1.38(2)
O(1T)-C(4T)	1.39(2)
C(1T)-C(2T)	1.58(2)
C(2T)-C(3T)	1.57(2)
C(3T)-C(4T)	1.58(2)

Table S10. Bond angles (°) for **{BnN(CH_2CH_2-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (3)**

C(19)-Fe(1)-C(1)	104.1(6)
C(19)-Fe(1)-Cl(2)	112.2(4)
C(1)-Fe(1)-Cl(2)	111.9(5)
C(19)-Fe(1)-Cl(1)	112.6(5)
C(1)-Fe(1)-Cl(1)	109.9(5)
Cl(2)-Fe(1)-Cl(1)	106.2(3)
N(2)-C(1)-N(1)	104.5(7)

N(2)-C(1)-Fe(1)	127.8(9)
N(1)-C(1)-Fe(1)	127.6(8)
C(1)-N(1)-C(2)	111.2(9)
C(1)-N(1)-C(8)	127.5(11)
C(2)-N(1)-C(8)	121.2(11)
C(3)-C(2)-C(7)	122.9(11)
C(3)-C(2)-N(1)	130.5(11)
C(7)-C(2)-N(1)	106.6(11)
C(2)-C(3)-C(4)	116.5(11)
C(3)-C(4)-C(5)	121.6(12)
C(6)-C(5)-C(4)	121.4(11)
C(5)-C(6)-C(7)	117.1(11)
C(2)-C(7)-N(2)	105.8(10)
C(2)-C(7)-C(6)	120.4(12)
N(2)-C(7)-C(6)	133.8(11)
C(1)-N(2)-C(7)	111.9(9)
C(1)-N(2)-C(9)	123.2(11)
C(7)-N(2)-C(9)	124.5(11)
N(2)-C(9)-C(10)	108.6(15)
N(3)-C(10)-C(9)	112.7(9)
C(21)-N(3)-C(10)	112.3(7)
C(21)-N(3)-C(11)	111.6(7)
C(10)-N(3)-C(11)	113.7(7)
N(3)-C(21)-C(22)	112.7(8)
C(23)-C(22)-C(27)	117.7(10)
C(23)-C(22)-C(21)	121.8(10)
C(27)-C(22)-C(21)	120.5(9)
C(22)-C(23)-C(24)	122.1(11)
C(25)-C(24)-C(23)	120.7(11)
C(24)-C(25)-C(26)	119.2(10)
C(25)-C(26)-C(27)	120.8(10)
C(26)-C(27)-C(22)	119.3(10)
N(3)-C(11)-C(12)	112.9(9)
N(4)-C(12)-C(11)	110.3(13)
C(19)-N(4)-C(13)	110.8(7)
C(19)-N(4)-C(12)	124.0(9)
C(13)-N(4)-C(12)	125.1(9)
C(18)-C(13)-C(14)	120.5(10)
C(18)-C(13)-N(4)	105.3(9)
C(14)-C(13)-N(4)	134.0(9)
C(15)-C(14)-C(13)	118.0(9)
C(14)-C(15)-C(16)	119.8(10)
C(17)-C(16)-C(15)	122.6(10)
C(18)-C(17)-C(16)	117.6(9)
C(17)-C(18)-N(5)	131.6(9)
C(17)-C(18)-C(13)	121.6(10)
N(5)-C(18)-C(13)	106.7(9)
C(19)-N(5)-C(18)	111.6(7)
C(19)-N(5)-C(20)	125.7(9)
C(18)-N(5)-C(20)	122.6(9)
N(5)-C(19)-N(4)	105.5(7)
N(5)-C(19)-Fe(1)	132.4(7)
N(4)-C(19)-Fe(1)	122.0(7)
C(1A)-Fe(1A)-C(19A)	103.7(9)
C(1A)-Fe(1A)-Cl(2A)	106.3(8)
C(19A)-Fe(1A)-Cl(2A)	114.8(7)

C(1A)-Fe(1A)-Cl(1A)	113.3(7)
C(19A)-Fe(1A)-Cl(1A)	112.4(7)
Cl(2A)-Fe(1A)-Cl(1A)	106.2(5)
N(2A)-C(1A)-N(1A)	105.5(10)
N(2A)-C(1A)-Fe(1A)	125.8(12)
N(1A)-C(1A)-Fe(1A)	127.7(13)
C(1A)-N(1A)-C(2A)	110.9(12)
C(1A)-N(1A)-C(8A)	129.7(16)
C(2A)-N(1A)-C(8A)	119.2(16)
C(3A)-C(2A)-C(7A)	123.1(15)
C(3A)-C(2A)-N(1A)	129.9(15)
C(7A)-C(2A)-N(1A)	106.9(13)
C(2A)-C(3A)-C(4A)	115.9(14)
C(3A)-C(4A)-C(5A)	123.1(15)
C(6A)-C(5A)-C(4A)	120.4(14)
C(5A)-C(6A)-C(7A)	116.4(13)
C(2A)-C(7A)-N(2A)	105.8(13)
C(2A)-C(7A)-C(6A)	120.9(14)
N(2A)-C(7A)-C(6A)	133.3(14)
C(1A)-N(2A)-C(7A)	110.9(11)
C(1A)-N(2A)-C(9A)	121.0(15)
C(7A)-N(2A)-C(9A)	127.5(15)
N(2A)-C(9A)-C(10A)	111.8(18)
N(3A)-C(10A)-C(9A)	115.9(14)
C(10A)-N(3A)-C(21A)	111.4(10)
C(10A)-N(3A)-C(11A)	115.9(10)
C(21A)-N(3A)-C(11A)	111.4(10)
N(3A)-C(21A)-C(22A)	113.5(14)
C(23A)-C(22A)-C(27A)	117.5(13)
C(23A)-C(22A)-C(21A)	122.6(14)
C(27A)-C(22A)-C(21A)	119.8(13)
C(22A)-C(23A)-C(24A)	122.2(14)
C(25A)-C(24A)-C(23A)	121.0(14)
C(24A)-C(25A)-C(26A)	118.5(14)
C(25A)-C(26A)-C(27A)	121.3(15)
C(26A)-C(27A)-C(22A)	119.4(14)
N(3A)-C(11A)-C(12A)	111.1(11)
N(4A)-C(12A)-C(11A)	112.6(15)
C(19A)-N(4A)-C(13A)	111.1(10)
C(19A)-N(4A)-C(12A)	124.0(13)
C(13A)-N(4A)-C(12A)	124.8(13)
C(18A)-C(13A)-C(14A)	119.5(13)
C(18A)-C(13A)-N(4A)	106.0(12)
C(14A)-C(13A)-N(4A)	134.5(12)
C(15A)-C(14A)-C(13A)	116.9(12)
C(14A)-C(15A)-C(16A)	121.4(14)
C(17A)-C(16A)-C(15A)	122.2(14)
C(18A)-C(17A)-C(16A)	115.9(12)
C(17A)-C(18A)-N(5A)	129.7(13)
C(17A)-C(18A)-C(13A)	124.0(14)
N(5A)-C(18A)-C(13A)	106.2(12)
C(19A)-N(5A)-C(18A)	111.7(10)
C(19A)-N(5A)-C(20A)	125.8(13)
C(18A)-N(5A)-C(20A)	122.4(13)
N(4A)-C(19A)-N(5A)	104.8(9)
N(4A)-C(19A)-Fe(1A)	122.0(10)

N(5A)-C(19A)-Fe(1A)	133.2(10)
C(1S)-O(1S)-C(4S)	116.8(15)
O(1S)-C(1S)-C(2S)	105.5(13)
C(1S)-C(2S)-C(3S)	101.0(13)
C(4S)-C(3S)-C(2S)	100.5(14)
O(1S)-C(4S)-C(3S)	103.8(14)
C(1T)-O(1T)-C(4T)	110(3)
O(1T)-C(1T)-C(2T)	102.4(19)
C(3T)-C(2T)-C(1T)	103.2(14)
C(2T)-C(3T)-C(4T)	101.9(15)
O(1T)-C(4T)-C(3T)	100.7(19)

X-Ray Data for {BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)

Table S11. Crystal data and structure refinement for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)**

Empirical formula	C32 H36 Cl2 Fe N5	
Formula weight	617.41	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.3137(2) Å	α = 90°
	b = 29.3333(5) Å	β = 98.700(7)°
	c = 22.4626(16) Å	γ = 90°
Volume	6066.2(5) Å3	
Z	8	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	5.835 mm^{-1}	
F(000)	2584	
Crystal size	0.20 x 0.05 x 0.05 mm^3	
Theta range for data collection	6.51 to 55.99°	
Index ranges	-10<=h<=10, -31<=k<=31, -24<=l<=24	
Reflections collected	74851	
Independent reflections	7859 [R(int) = 0.1618]	
Completeness to theta	= 55.99° 99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7591 and 0.3882	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	7859 / 254 / 741	
Goodness-of-fit on F2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1619	
R indices (all data)	R1 = 0.0766, wR2 = 0.1716	
Largest diff. peak and hole	0.769 and -0.542 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and Biso/Beq ($Å^2$x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)**

Atom	x	y	z	U(eq)
Cl(1)	3033(1)	5824(1)	1382(1)	46(1)
Cl(2)	451(1)	5378(1)	2339(1)	41(1)
Fe(1)	2786(1)	5346(1)	2160(1)	36(1)
C(1)	3414(5)	4673(2)	2005(2)	44(1)

N(1)	4105(4)	4496(1)	1559(2)	48(1)
C(21)	4369(7)	4736(2)	1019(2)	65(2)
C(2)	4500(5)	4045(2)	1675(2)	51(1)
C(3)	5222(5)	3733(2)	1360(3)	57(1)
C(4)	5423(6)	3306(2)	1596(3)	59(2)
C(5)	4946(5)	3188(2)	2138(3)	58(2)
C(6)	4241(5)	3502(2)	2460(3)	51(1)
C(7)	4029(5)	3934(2)	2215(2)	42(1)
N(2)	3377(4)	4324(1)	2402(2)	39(1)
C(8)	2718(5)	4357(2)	2954(2)	42(1)
C(9)	3791(5)	4350(2)	3526(2)	44(1)
C(10)	3006(5)	4393(2)	4071(2)	44(1)
N(3)	2324(4)	4845(1)	4098(2)	39(1)
C(22)	1059(5)	4815(2)	4418(2)	44(1)
C(23)	-153(5)	4530(2)	4102(2)	41(1)
C(24)	-700(5)	4597(2)	3493(2)	44(1)
C(25)	-1822(5)	4330(2)	3207(2)	51(1)
C(26)	-2448(5)	3993(2)	3524(3)	51(1)
C(27)	-1926(5)	3928(2)	4123(2)	47(1)
C(28)	-781(5)	4186(2)	4407(2)	40(1)
C(11)	3381(5)	5172(2)	4399(2)	45(1)
C(12)	2974(5)	5668(2)	4292(2)	41(1)
C(13)	2969(5)	5842(2)	3655(2)	38(1)
N(4)	4333(4)	5754(1)	3418(2)	34(1)
C(14)	5708(4)	5884(2)	3698(2)	34(1)
C(15)	6189(5)	6143(2)	4204(2)	38(1)
C(16)	7658(5)	6222(2)	4337(2)	42(1)
C(17)	8636(5)	6057(2)	3972(2)	41(1)
C(18)	8163(5)	5803(2)	3464(2)	39(1)
C(19)	6680(5)	5725(1)	3330(2)	35(1)
N(5)	5842(4)	5510(1)	2849(2)	36(1)
C(29)	6432(5)	5300(2)	2343(2)	48(1)
C(20)	4403(5)	5530(1)	2890(2)	36(1)
Cl(3)	3588(1)	7161(1)	3917(1)	46(1)
Cl(4)	685(1)	7043(1)	4931(1)	50(1)
Fe(2)	1277(1)	7328(1)	4056(1)	36(1)
C(101)	1153(5)	8050(2)	4088(2)	38(1)
N(101)	1833(4)	8311(1)	4552(2)	41(1)
C(121)	2710(6)	8122(2)	5089(2)	55(1)
C(102)	1576(5)	8772(2)	4442(2)	43(1)
C(103)	1990(6)	9157(2)	4782(2)	55(1)
C(104)	1512(7)	9576(2)	4536(2)	64(2)
C(105)	640(7)	9603(2)	3973(3)	68(2)
C(106)	232(6)	9218(2)	3635(2)	59(1)
C(107)	698(5)	8803(2)	3883(2)	44(1)
N(102)	475(4)	8356(1)	3683(2)	39(1)
C(108)	-306(5)	8233(2)	3084(2)	40(1)
C(109)	550(5)	8360(2)	2589(2)	50(1)
C(110)	-154(5)	8185(2)	1972(2)	49(1)
N(103)	-301(4)	7687(1)	1925(2)	40(1)
C(122)	-1041(2)	7586(1)	1311(1)	46(1)
C(123)	-2631(2)	7745(1)	1192(1)	42(3)
C(124)	-3129(2)	8082(1)	777(1)	50(3)
C(125)	-4608(2)	8172(1)	643(1)	54(3)
C(126)	-5588(2)	7926(1)	924(1)	53(3)
C(127)	-5091(2)	7589(1)	1340(1)	46(3)

C(128)	-3612(2)	7498(1)	1474(1)	42(2)
C(23A)	-2641(2)	7711(1)	1197(1)	39(2)
C(24A)	-3204(2)	7901(1)	644(1)	50(2)
C(25A)	-4689(2)	7976(1)	500(1)	58(2)
C(26A)	-5611(2)	7861(1)	908(1)	50(2)
C(27A)	-5048(2)	7671(1)	1462(1)	46(2)
C(28A)	-3563(2)	7596(1)	1606(1)	38(2)
C(111)	1136(2)	7470(1)	2009(1)	51(1)
C(112)	1139(5)	6952(2)	2017(2)	49(1)
C(113)	1031(5)	6733(2)	2626(2)	44(1)
N(104)	-308(4)	6844(1)	2867(2)	37(1)
C(114)	-1694(5)	6722(2)	2593(2)	36(1)
C(115)	-2175(5)	6461(2)	2086(2)	43(1)
C(116)	-3654(5)	6404(2)	1947(2)	44(1)
C(117)	-4621(5)	6584(2)	2303(2)	41(1)
C(118)	-4130(5)	6836(2)	2813(2)	38(1)
C(119)	-2651(4)	6901(1)	2948(2)	33(1)
N(105)	-1799(4)	7129(1)	3418(2)	34(1)
C(129)	-2398(5)	7386(2)	3882(2)	41(1)
C(120)	-353(5)	7094(2)	3383(2)	40(1)
C(1S)	6435(7)	6184(3)	296(3)	77(2)
C(2S)	7337(8)	5859(2)	603(3)	74(2)
C(3S)	8799(7)	5932(2)	722(3)	68(2)
C(4S)	9364(7)	6334(2)	538(3)	67(2)
C(5S)	8491(8)	6654(2)	232(3)	74(2)
C(6S)	7040(7)	6585(2)	110(3)	75(2)

Beq = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Table S13. Anisotropic displacement parameters (Å^2 x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)**

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	50(1)	56(1)	34(1)	3(1)	6(1)	-5(1)
Cl(2)	37(1)	51(1)	37(1)	-1(1)	9(1)	1(1)
Fe(1)	38(1)	42(1)	31(1)	-2(1)	9(1)	-1(1)
C(1)	38(3)	59(3)	37(3)	-8(3)	10(2)	0(2)
N(1)	49(2)	54(3)	42(3)	-13(2)	12(2)	1(2)
C(21)	87(4)	73(4)	42(3)	-7(3)	28(3)	2(3)
C(2)	43(3)	47(3)	61(4)	-21(3)	5(3)	0(2)
C(3)	49(3)	61(4)	62(4)	-20(3)	12(3)	2(3)
C(4)	51(3)	52(4)	76(4)	-27(3)	10(3)	7(3)
C(5)	39(3)	45(3)	87(4)	-15(3)	-3(3)	-1(2)
C(6)	40(3)	43(3)	69(4)	-9(3)	7(3)	4(2)
C(7)	39(3)	38(3)	49(3)	-7(2)	7(2)	2(2)
N(2)	42(2)	34(2)	43(2)	0(2)	15(2)	3(2)
C(8)	41(3)	41(3)	46(3)	4(2)	17(2)	0(2)
C(9)	39(3)	47(3)	47(3)	5(2)	13(2)	6(2)
C(10)	42(3)	45(3)	47(3)	9(2)	14(2)	6(2)
N(3)	38(2)	43(2)	39(2)	6(2)	15(2)	0(2)
C(22)	43(3)	50(3)	42(3)	1(2)	16(2)	0(2)
C(23)	38(3)	42(3)	45(3)	-1(2)	12(2)	4(2)
C(24)	43(3)	46(3)	45(3)	8(2)	13(2)	7(2)
C(25)	48(3)	62(4)	42(3)	-1(3)	2(3)	15(3)
C(26)	34(3)	54(3)	65(4)	-8(3)	9(3)	4(2)

C(27)	46(3)	49(3)	50(3)	0(3)	21(3)	-3(2)
C(28)	37(3)	44(3)	41(3)	-3(2)	15(2)	4(2)
C(11)	33(3)	60(3)	43(3)	6(2)	10(2)	-4(2)
C(12)	35(3)	54(3)	34(3)	-4(2)	9(2)	-5(2)
C(13)	38(3)	42(3)	36(3)	-4(2)	9(2)	0(2)
N(4)	31(2)	40(2)	33(2)	0(2)	7(2)	0(2)
C(14)	32(2)	38(3)	31(3)	5(2)	5(2)	0(2)
C(15)	43(3)	42(3)	29(3)	3(2)	8(2)	-1(2)
C(16)	41(3)	48(3)	35(3)	1(2)	0(2)	-5(2)
C(17)	33(3)	46(3)	43(3)	5(2)	3(2)	-1(2)
C(18)	37(3)	45(3)	35(3)	4(2)	8(2)	-1(2)
C(19)	37(3)	38(3)	29(3)	3(2)	3(2)	-2(2)
N(5)	36(2)	45(2)	31(2)	-1(2)	11(2)	3(2)
C(29)	41(3)	59(3)	45(3)	-7(2)	13(2)	3(2)
C(20)	43(3)	32(3)	33(3)	4(2)	12(2)	3(2)
Cl(3)	36(1)	53(1)	50(1)	-6(1)	14(1)	1(1)
Cl(4)	46(1)	68(1)	36(1)	7(1)	9(1)	-9(1)
Fe(2)	35(1)	42(1)	33(1)	1(1)	11(1)	-1(1)
C(101)	36(3)	45(3)	35(3)	1(2)	12(2)	5(2)
N(101)	50(2)	40(2)	32(2)	-1(2)	4(2)	-2(2)
C(121)	70(3)	57(3)	35(3)	3(2)	-3(3)	2(3)
C(102)	55(3)	40(3)	35(3)	-1(2)	5(2)	-2(2)
C(103)	79(4)	52(4)	33(3)	-2(3)	5(3)	-5(3)
C(104)	95(4)	49(4)	43(3)	-2(3)	-2(3)	-7(3)
C(105)	94(4)	45(3)	58(4)	2(3)	-9(3)	2(3)
C(106)	78(4)	48(4)	47(3)	-1(3)	-5(3)	-1(3)
C(107)	56(3)	37(3)	39(3)	-1(2)	2(2)	0(2)
N(102)	43(2)	40(2)	33(2)	2(2)	2(2)	0(2)
C(108)	42(3)	42(3)	34(3)	2(2)	-2(2)	-3(2)
C(109)	58(3)	54(3)	38(3)	2(2)	5(2)	-14(2)
C(110)	52(3)	53(3)	41(3)	7(2)	3(2)	-13(2)
N(103)	36(2)	50(3)	35(2)	3(2)	2(2)	-3(2)
C(122)	46(2)	57(3)	36(3)	-5(2)	5(2)	-3(2)
C(123)	44(4)	52(6)	28(6)	-2(5)	4(5)	-7(5)
C(124)	61(4)	56(6)	30(6)	2(4)	5(5)	-6(4)
C(125)	67(5)	57(7)	36(6)	6(5)	-2(5)	3(5)
C(126)	46(5)	54(6)	54(7)	0(5)	-9(5)	1(5)
C(127)	42(4)	53(6)	41(6)	-2(4)	3(5)	-3(5)
C(128)	44(4)	50(6)	31(5)	1(4)	4(4)	1(4)
C(23A)	45(3)	43(5)	28(4)	-2(4)	2(3)	-5(4)
C(24A)	56(3)	53(5)	37(4)	10(4)	1(3)	-19(4)
C(25A)	63(4)	55(6)	48(4)	15(4)	-16(3)	-8(4)
C(26A)	42(4)	46(5)	56(5)	-8(4)	-10(3)	0(4)
C(27A)	44(3)	49(5)	45(4)	-9(3)	4(4)	-5(4)
C(28A)	45(3)	37(4)	31(4)	-3(3)	3(3)	-1(3)
C(111)	42(3)	71(4)	44(3)	11(3)	13(2)	-5(3)
C(112)	34(3)	74(4)	43(3)	2(3)	18(2)	8(2)
C(113)	37(3)	54(3)	41(3)	-1(2)	11(2)	12(2)
N(104)	38(2)	40(2)	32(2)	2(2)	8(2)	4(2)
C(114)	36(3)	39(3)	32(3)	6(2)	1(2)	1(2)
C(115)	43(3)	48(3)	37(3)	0(2)	7(2)	3(2)
C(116)	47(3)	52(3)	33(3)	-5(2)	6(2)	-1(2)
C(117)	36(3)	41(3)	44(3)	7(2)	1(2)	-4(2)
C(118)	40(3)	43(3)	33(3)	3(2)	9(2)	-1(2)
C(119)	33(3)	38(3)	29(2)	4(2)	7(2)	-1(2)
N(105)	32(2)	40(2)	32(2)	2(2)	10(2)	1(2)

C(129)	38(3)	50(3)	37(3)	-5(2)	11(2)	1(2)
C(120)	43(3)	39(3)	39(3)	4(2)	13(2)	2(2)
C(1S)	67(4)	98(5)	65(4)	-24(4)	7(3)	-6(4)
C(2S)	87(5)	71(4)	68(4)	-16(3)	26(4)	-9(4)
C(3S)	81(5)	68(4)	58(4)	-9(3)	21(3)	11(3)
C(4S)	78(4)	75(4)	50(4)	-4(3)	19(3)	8(4)
C(5S)	91(5)	73(4)	60(4)	-5(3)	19(4)	-4(4)
C(6S)	72(5)	84(5)	66(4)	-7(4)	-1(3)	10(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S14. Bond lengths (Å) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)**

Cl(1)-Fe(1)	2.2790(13)
Cl(2)-Fe(1)	2.2727(12)
Fe(1)-C(1)	2.103(5)
Fe(1)-C(20)	2.123(5)
C(1)-N(2)	1.361(6)
C(1)-N(1)	1.372(6)
N(1)-C(2)	1.389(6)
N(1)-C(21)	1.456(7)
C(2)-C(7)	1.390(7)
C(2)-C(3)	1.391(7)
C(3)-C(4)	1.360(8)
C(4)-C(5)	1.401(8)
C(5)-C(6)	1.396(7)
C(6)-C(7)	1.384(7)
C(7)-N(2)	1.390(5)
N(2)-C(8)	1.467(6)
C(8)-C(9)	1.504(7)
C(9)-C(10)	1.524(6)
C(10)-N(3)	1.475(6)
N(3)-C(11)	1.466(6)
N(3)-C(22)	1.473(5)
C(22)-C(23)	1.494(6)
C(23)-C(28)	1.398(6)
C(23)-C(24)	1.400(7)
C(24)-C(25)	1.384(7)
C(25)-C(26)	1.396(7)
C(26)-C(27)	1.373(7)
C(27)-C(28)	1.381(6)
C(11)-C(12)	1.513(6)
C(12)-C(13)	1.520(6)
C(13)-N(4)	1.473(5)
N(4)-C(20)	1.364(5)
N(4)-C(14)	1.393(5)
C(14)-C(15)	1.385(6)
C(14)-C(19)	1.394(6)
C(15)-C(16)	1.375(6)
C(16)-C(17)	1.400(6)
C(17)-C(18)	1.377(6)
C(18)-C(19)	1.387(6)
C(19)-N(5)	1.386(5)
N(5)-C(20)	1.359(5)

N(5)-C(29)	1.472(6)
Cl(3)-Fe(2)	2.2745(12)
Cl(4)-Fe(2)	2.2786(13)
Fe(2)-C(120)	2.090(5)
Fe(2)-C(101)	2.125(5)
C(101)-N(102)	1.363(5)
C(101)-N(101)	1.369(5)
N(101)-C(102)	1.389(6)
N(101)-C(121)	1.459(6)
C(102)-C(103)	1.385(7)
C(102)-C(107)	1.393(7)
C(103)-C(104)	1.392(7)
C(104)-C(105)	1.399(8)
C(105)-C(106)	1.382(7)
C(106)-C(107)	1.379(7)
C(107)-N(102)	1.391(6)
N(102)-C(108)	1.474(6)
C(108)-C(109)	1.510(6)
C(109)-C(110)	1.531(7)
C(110)-N(103)	1.469(6)
N(103)-C(111)	1.468(4)
N(103)-C(122)	1.476(4)
C(111)-C(112)	1.519(5)
C(112)-C(113)	1.528(6)
C(113)-N(104)	1.469(6)
N(104)-C(120)	1.376(6)
N(104)-C(114)	1.390(5)
C(114)-C(119)	1.384(6)
C(114)-C(115)	1.390(6)
C(115)-C(116)	1.376(6)
C(116)-C(117)	1.395(6)
C(117)-C(118)	1.381(6)
C(118)-C(119)	1.379(6)
C(119)-N(105)	1.393(5)
N(105)-C(120)	1.365(5)
N(105)-C(129)	1.464(5)
C(1S)-C(2S)	1.385(9)
C(1S)-C(6S)	1.395(9)
C(2S)-C(3S)	1.365(8)
C(3S)-C(4S)	1.380(8)
C(4S)-C(5S)	1.358(8)
C(5S)-C(6S)	1.353(9)

Table S15. Bond angles (°) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeCl_2$ (4)**

C(1)-Fe(1)-C(20)	100.59(17)
C(1)-Fe(1)-Cl(2)	111.46(13)
C(20)-Fe(1)-Cl(2)	116.01(12)
C(1)-Fe(1)-Cl(1)	112.87(14)
C(20)-Fe(1)-Cl(1)	107.07(12)
Cl(2)-Fe(1)-Cl(1)	108.71(5)
N(2)-C(1)-N(1)	104.8(4)
N(2)-C(1)-Fe(1)	124.3(3)
N(1)-C(1)-Fe(1)	130.4(4)

C(1)-N(1)-C(2)	111.4(4)
C(1)-N(1)-C(21)	125.7(4)
C(2)-N(1)-C(21)	122.9(4)
N(1)-C(2)-C(7)	106.0(4)
N(1)-C(2)-C(3)	131.9(5)
C(7)-C(2)-C(3)	122.1(5)
C(4)-C(3)-C(2)	117.1(5)
C(3)-C(4)-C(5)	121.7(5)
C(6)-C(5)-C(4)	121.4(5)
C(7)-C(6)-C(5)	116.7(5)
C(6)-C(7)-N(2)	132.5(5)
C(6)-C(7)-C(2)	121.1(4)
N(2)-C(7)-C(2)	106.4(4)
C(1)-N(2)-C(7)	111.4(4)
C(1)-N(2)-C(8)	123.9(4)
C(7)-N(2)-C(8)	124.6(4)
N(2)-C(8)-C(9)	114.3(3)
C(8)-C(9)-C(10)	110.4(4)
N(3)-C(10)-C(9)	111.6(4)
C(11)-N(3)-C(22)	110.1(3)
C(11)-N(3)-C(10)	110.1(3)
C(22)-N(3)-C(10)	110.3(3)
N(3)-C(22)-C(23)	113.8(4)
C(28)-C(23)-C(24)	117.5(4)
C(28)-C(23)-C(22)	120.9(4)
C(24)-C(23)-C(22)	121.6(4)
C(25)-C(24)-C(23)	120.8(5)
C(24)-C(25)-C(26)	120.6(5)
C(27)-C(26)-C(25)	118.9(5)
C(26)-C(27)-C(28)	120.8(5)
C(27)-C(28)-C(23)	121.4(4)
N(3)-C(11)-C(12)	115.0(4)
C(11)-C(12)-C(13)	115.9(4)
N(4)-C(13)-C(12)	113.7(4)
C(20)-N(4)-C(14)	111.3(3)
C(20)-N(4)-C(13)	123.7(4)
C(14)-N(4)-C(13)	125.0(3)
C(15)-C(14)-N(4)	133.1(4)
C(15)-C(14)-C(19)	120.8(4)
N(4)-C(14)-C(19)	106.0(4)
C(16)-C(15)-C(14)	117.2(4)
C(15)-C(16)-C(17)	121.9(4)
C(18)-C(17)-C(16)	121.1(4)
C(17)-C(18)-C(19)	116.9(4)
N(5)-C(19)-C(18)	132.0(4)
N(5)-C(19)-C(14)	106.0(4)
C(18)-C(19)-C(14)	122.0(4)
C(20)-N(5)-C(19)	111.8(3)
C(20)-N(5)-C(29)	124.0(4)
C(19)-N(5)-C(29)	124.1(3)
N(5)-C(20)-N(4)	104.9(4)
N(5)-C(20)-Fe(1)	121.9(3)
N(4)-C(20)-Fe(1)	132.3(3)
C(120)-Fe(2)-C(101)	108.40(17)
C(120)-Fe(2)-Cl(3)	115.40(13)
C(101)-Fe(2)-Cl(3)	106.06(12)

C(120)-Fe(2)-Cl(4)	105.05(13)
C(101)-Fe(2)-Cl(4)	108.35(12)
Cl(3)-Fe(2)-Cl(4)	113.36(5)
N(102)-C(101)-N(101)	104.8(4)
N(102)-C(101)-Fe(2)	131.0(3)
N(101)-C(101)-Fe(2)	124.2(3)
C(101)-N(101)-C(102)	111.1(4)
C(101)-N(101)-C(121)	123.5(4)
C(102)-N(101)-C(121)	125.3(4)
C(103)-C(102)-N(101)	131.9(4)
C(103)-C(102)-C(107)	121.4(5)
N(101)-C(102)-C(107)	106.7(4)
C(102)-C(103)-C(104)	117.0(5)
C(103)-C(104)-C(105)	121.1(5)
C(106)-C(105)-C(104)	121.6(5)
C(107)-C(106)-C(105)	117.0(5)
C(106)-C(107)-N(102)	132.6(5)
C(106)-C(107)-C(102)	121.8(5)
N(102)-C(107)-C(102)	105.5(4)
C(101)-N(102)-C(107)	111.9(4)
C(101)-N(102)-C(108)	124.2(4)
C(107)-N(102)-C(108)	123.7(4)
N(102)-C(108)-C(109)	111.7(3)
C(108)-C(109)-C(110)	112.5(4)
N(103)-C(110)-C(109)	114.9(4)
C(111)-N(103)-C(110)	110.4(3)
C(111)-N(103)-C(122)	108.7(3)
C(110)-N(103)-C(122)	106.9(3)
N(103)-C(122)-C(23A)	114.61(16)
N(103)-C(122)-C(123)	113.77(16)
N(103)-C(111)-C(112)	115.8(3)
C(111)-C(112)-C(113)	115.6(4)
N(104)-C(113)-C(112)	114.3(4)
C(120)-N(104)-C(114)	111.4(4)
C(120)-N(104)-C(113)	124.3(4)
C(114)-N(104)-C(113)	124.2(4)
C(119)-C(114)-N(104)	106.5(4)
C(119)-C(114)-C(115)	121.6(4)
N(104)-C(114)-C(115)	131.9(4)
C(116)-C(115)-C(114)	116.1(4)
C(115)-C(116)-C(117)	122.4(4)
C(118)-C(117)-C(116)	121.1(4)
C(119)-C(118)-C(117)	116.8(4)
C(118)-C(119)-C(114)	122.0(4)
C(118)-C(119)-N(105)	132.0(4)
C(114)-C(119)-N(105)	106.0(3)
C(120)-N(105)-C(119)	111.9(3)
C(120)-N(105)-C(129)	124.5(4)
C(119)-N(105)-C(129)	123.6(3)
N(105)-C(120)-N(104)	104.2(4)
N(105)-C(120)-Fe(2)	123.2(3)
N(104)-C(120)-Fe(2)	132.3(3)
C(2S)-C(1S)-C(6S)	119.2(6)
C(3S)-C(2S)-C(1S)	120.0(6)
C(2S)-C(3S)-C(4S)	119.4(6)
C(5S)-C(4S)-C(3S)	121.0(6)

C(6S)-C(5S)-C(4S)	120.1(6)
C(5S)-C(6S)-C(1S)	120.2(6)

X-Ray Data for {BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)

Table S16. Crystal data and structure refinement for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)**

Empirical formula	C65 H74 Br4 Fe2 N10	
Formula weight	1426.68	
Temperature	150(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.434(4) Å	α= 90°
	b = 30.1020(7) Å	β= 101.188(15)°
	c = 23.0220(16) Å	γ = 90°
Volume	6414(3) Å^3	
Z	4	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	2.992 mm^{-1}	
F(000)	2904	
Crystal size	0.25 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.99 to 26.37°.	
Index ranges	-11<=h<=11, -37<=k<=37, -28<=l<=28	
Reflections collected	130163	
Independent reflections	13093 [R(int) = 0.0657]	
Completeness to theta = 26.37°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7541 and 0.5217	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13093 / 249 / 798	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0904	
R indices (all data)	R1 = 0.0688, wR2 = 0.1015	
Largest diff. peak and hole	0.807 and -0.679 e.Å^{-3}	

Table S17. Atomic coordinates (x 10^4) and Biso/Beq (Å^{2}x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)**

Atom	x	y	z	U(eq)
Fe(1)	7402(1)	297(1)	2212(1)	30(1)
Br(1)	4930(1)	329(1)	2324(1)	41(1)
Br(2)	7579(1)	782(1)	1390(1)	47(1)
C(1)	9023(3)	522(1)	2918(1)	28(1)
N(1)	10437(3)	509(1)	2871(1)	28(1)
C(21)	10981(4)	297(1)	2389(2)	36(1)
C(2)	11295(3)	736(1)	3332(1)	30(1)
C(3)	12782(4)	818(1)	3457(2)	35(1)
C(4)	13285(4)	1078(1)	3945(2)	39(1)
C(5)	12367(4)	1254(1)	4291(2)	40(1)
C(6)	10891(4)	1169(1)	4166(2)	36(1)
C(7)	10373(3)	901(1)	3684(1)	28(1)

N(2)	8989(3)	755(1)	3421(1)	28(1)
C(8)	7668(3)	839(1)	3654(2)	30(1)
C(9)	7765(4)	700(1)	4296(2)	33(1)
C(10)	8303(4)	229(1)	4452(2)	34(1)
N(3)	7306(3)	-119(1)	4182(1)	32(1)
C(11)	8093(4)	-544(1)	4177(2)	36(1)
C(12)	8753(4)	-588(1)	3630(2)	34(1)
C(13)	7572(4)	-629(1)	3080(2)	34(1)
N(4)	8111(3)	-683(1)	2532(1)	33(1)
C(14)	8728(3)	-1074(1)	2375(2)	35(1)
C(15)	9007(4)	-1483(1)	2653(2)	43(1)
C(16)	9654(4)	-1800(1)	2354(2)	51(1)
C(17)	10004(4)	-1714(1)	1809(2)	56(1)
C(18)	9719(4)	-1310(1)	1532(2)	53(1)
C(19)	9069(4)	-991(1)	1827(2)	41(1)
N(5)	8619(3)	-559(1)	1675(1)	40(1)
C(29)	8715(6)	-356(2)	1108(2)	61(1)
C(20)	8048(4)	-364(1)	2111(2)	33(1)
C(22)	6105(4)	-170(1)	4500(2)	40(1)
C(23)	4884(4)	-448(1)	4161(2)	37(1)
C(24)	4302(4)	-800(1)	4418(2)	41(1)
C(25)	3161(4)	-1041(1)	4103(2)	51(1)
C(26)	2607(4)	-943(1)	3521(2)	52(1)
C(27)	3199(4)	-600(1)	3254(2)	54(1)
C(28)	4312(4)	-349(1)	3570(2)	48(1)
Fe(2)	3736(1)	7298(1)	1046(1)	31(1)
Br(3)	1288(1)	7212(1)	1181(1)	50(1)
Br(4)	4194(1)	6921(1)	172(1)	50(1)
C(101)	3999(4)	7991(1)	949(2)	35(1)
N(101)	3532(3)	8235(1)	449(1)	42(1)
C(121)	2842(6)	8055(1)	-122(2)	66(1)
C(102)	3789(4)	8686(1)	553(2)	46(1)
C(103)	3533(5)	9055(1)	187(2)	60(1)
C(104)	3931(6)	9462(1)	441(2)	66(1)
C(105)	4562(5)	9499(1)	1038(2)	63(1)
C(106)	4829(5)	9134(1)	1401(2)	50(1)
C(107)	4436(4)	8721(1)	1145(2)	39(1)
C(108)	5152(4)	8182(1)	1988(2)	36(1)
N(102)	4560(3)	8291(1)	1369(1)	34(1)
C(109)	4054(5)	8255(1)	2380(2)	50(1)
C(110)	4660(5)	8129(1)	3021(2)	53(1)
N(103)	4995(3)	7654(1)	3117(1)	37(1)
C(111)	3650(4)	7389(2)	3032(2)	50(1)
C(112)	3868(4)	6889(1)	3028(2)	47(1)
C(113)	3985(4)	6680(1)	2441(2)	39(1)
N(104)	5297(3)	6803(1)	2221(1)	32(1)
C(114)	6678(4)	6679(1)	2506(2)	32(1)
C(115)	7173(4)	6415(1)	2996(2)	40(1)
C(116)	8658(4)	6356(1)	3154(2)	44(1)
C(117)	9596(4)	6550(1)	2832(2)	46(1)
C(118)	9111(4)	6811(1)	2335(2)	37(1)
C(119)	7621(3)	6870(1)	2184(2)	32(1)
N(105)	6766(3)	7099(1)	1720(1)	29(1)
C(129)	7343(4)	7350(1)	1279(2)	37(1)
C(120)	5336(3)	7059(1)	1741(2)	30(1)
C(122)	5780(4)	7602(1)	3733(2)	47(1)

C(123)	7325(4)	7758(1)	3845(2)	40(1)
C(124)	8344(4)	7525(1)	3616(2)	49(1)
C(125)	9795(5)	7633(1)	3760(2)	58(1)
C(126)	10234(6)	7984(2)	4135(2)	69(2)
C(127)	9220(7)	8231(2)	4348(2)	76(2)
C(128)	7756(6)	8122(2)	4205(2)	60(1)
C(7S)	1850(12)	1866(2)	-87(3)	108(3)
C(1S)	1846(9)	1405(2)	157(3)	78(2)
C(2S)	620(8)	1171(3)	127(3)	75(2)
C(3S)	621(8)	730(3)	350(3)	81(2)
C(4S)	1895(8)	540(2)	611(4)	83(2)
C(5S)	3164(8)	773(3)	631(3)	86(2)
C(6S)	3141(8)	1201(3)	410(4)	83(2)
C(7T)	3180(80)	1837(14)	40(20)	89(10)
C(1T)	2630(50)	1383(15)	130(20)	84(5)
C(2T)	1170(50)	1310(18)	10(30)	82(5)
C(3T)	550(50)	990(20)	320(30)	84(5)
C(4T)	1390(60)	637(19)	570(30)	84(5)
C(5T)	2830(60)	740(20)	770(30)	85(5)
C(6T)	3450(40)	1090(20)	500(40)	83(5)

$Beq = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Table S18. Anisotropic displacement parameters ($Å^2$ x 10^3) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)**

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	32(1)	32(1)	26(1)	-2(1)	5(1)	-3(1)
Br(1)	34(1)	52(1)	38(1)	2(1)	8(1)	4(1)
Br(2)	57(1)	53(1)	31(1)	7(1)	5(1)	-9(1)
C(1)	35(2)	25(2)	25(2)	2(1)	7(1)	-2(1)
N(1)	26(1)	33(2)	26(2)	-1(1)	8(1)	-2(1)
C(21)	34(2)	44(2)	32(2)	-7(2)	10(2)	-1(2)
C(2)	31(2)	30(2)	26(2)	4(1)	4(1)	-3(1)
C(3)	30(2)	40(2)	36(2)	4(2)	9(2)	-1(1)
C(4)	31(2)	48(2)	37(2)	5(2)	3(2)	-11(2)
C(5)	43(2)	45(2)	31(2)	-2(2)	4(2)	-13(2)
C(6)	44(2)	37(2)	29(2)	-2(2)	11(2)	-7(2)
C(7)	33(2)	29(2)	23(2)	3(1)	8(1)	-4(1)
N(2)	28(1)	32(2)	22(1)	1(1)	7(1)	-5(1)
C(8)	28(2)	32(2)	32(2)	0(1)	9(1)	0(1)
C(9)	35(2)	36(2)	29(2)	-3(2)	10(2)	-5(1)
C(10)	32(2)	41(2)	31(2)	3(2)	8(2)	-3(1)
N(3)	30(2)	32(2)	36(2)	2(1)	16(1)	0(1)
C(11)	42(2)	35(2)	34(2)	5(2)	13(2)	3(2)
C(12)	32(2)	38(2)	33(2)	0(2)	7(2)	7(1)
C(13)	36(2)	36(2)	32(2)	0(2)	9(2)	0(1)
N(4)	33(2)	33(2)	32(2)	-4(1)	5(1)	-1(1)
C(14)	28(2)	34(2)	40(2)	-11(2)	2(2)	0(1)
C(15)	40(2)	40(2)	46(2)	-8(2)	0(2)	2(2)
C(16)	49(2)	40(2)	57(3)	-10(2)	-8(2)	7(2)
C(17)	52(3)	47(3)	65(3)	-24(2)	0(2)	11(2)
C(18)	55(3)	57(3)	46(3)	-24(2)	12(2)	0(2)
C(19)	39(2)	41(2)	40(2)	-14(2)	2(2)	-1(2)

N(5)	53(2)	38(2)	31(2)	-8(1)	10(1)	-4(1)
C(29)	96(4)	55(3)	40(3)	-6(2)	29(2)	2(2)
C(20)	32(2)	38(2)	29(2)	-7(2)	6(2)	-6(1)
C(22)	47(2)	40(2)	40(2)	-3(2)	24(2)	-7(2)
C(23)	38(2)	33(2)	43(2)	-1(2)	19(2)	1(2)
C(24)	52(2)	36(2)	38(2)	0(2)	17(2)	-4(2)
C(25)	54(2)	38(2)	63(3)	-1(2)	19(2)	-9(2)
C(26)	34(2)	50(2)	70(3)	-5(2)	7(2)	6(2)
C(27)	42(2)	59(3)	58(3)	10(2)	1(2)	10(2)
C(28)	43(2)	48(2)	54(3)	14(2)	12(2)	3(2)
Fe(2)	27(1)	34(1)	31(1)	-4(1)	4(1)	2(1)
Br(3)	30(1)	53(1)	68(1)	-1(1)	14(1)	1(1)
Br(4)	52(1)	60(1)	34(1)	-10(1)	2(1)	23(1)
C(101)	34(2)	38(2)	30(2)	-5(2)	0(2)	3(1)
N(101)	58(2)	37(2)	27(2)	-2(1)	-5(1)	4(1)
C(121)	102(4)	49(3)	33(2)	-12(2)	-17(2)	14(2)
C(102)	61(3)	36(2)	36(2)	-1(2)	0(2)	3(2)
C(103)	89(3)	50(3)	37(2)	5(2)	-3(2)	8(2)
C(104)	101(4)	38(2)	53(3)	7(2)	2(3)	8(2)
C(105)	83(3)	36(2)	62(3)	-2(2)	-7(2)	-7(2)
C(106)	62(3)	39(2)	44(2)	-1(2)	-8(2)	-2(2)
C(107)	42(2)	38(2)	35(2)	0(2)	-1(2)	1(2)
C(108)	35(2)	38(2)	30(2)	-1(2)	-4(2)	3(2)
N(102)	34(2)	34(2)	30(2)	0(1)	-2(1)	0(1)
C(109)	57(3)	56(3)	39(2)	0(2)	11(2)	22(2)
C(110)	70(3)	55(3)	34(2)	-7(2)	14(2)	17(2)
N(103)	41(2)	43(2)	27(2)	-3(1)	6(1)	2(1)
C(111)	30(2)	79(3)	44(2)	-11(2)	16(2)	5(2)
C(112)	35(2)	68(3)	43(2)	-1(2)	17(2)	-15(2)
C(113)	33(2)	45(2)	40(2)	-2(2)	8(2)	-14(2)
N(104)	31(2)	32(2)	31(2)	-1(1)	4(1)	-3(1)
C(114)	34(2)	28(2)	32(2)	-5(1)	1(2)	-1(1)
C(115)	50(2)	32(2)	37(2)	0(2)	7(2)	-6(2)
C(116)	54(2)	35(2)	38(2)	4(2)	-7(2)	3(2)
C(117)	39(2)	43(2)	48(2)	-4(2)	-8(2)	7(2)
C(118)	31(2)	40(2)	40(2)	-2(2)	6(2)	4(2)
C(119)	31(2)	31(2)	32(2)	-5(1)	1(2)	1(1)
N(105)	26(1)	32(2)	29(2)	1(1)	7(1)	2(1)
C(129)	28(2)	44(2)	40(2)	7(2)	10(2)	0(2)
C(120)	30(2)	30(2)	29(2)	-2(1)	6(1)	-3(1)
C(122)	58(3)	54(2)	28(2)	-1(2)	9(2)	0(2)
C(123)	54(2)	43(2)	19(2)	-1(2)	1(2)	-7(2)
C(124)	54(3)	41(2)	49(3)	-7(2)	-2(2)	-5(2)
C(125)	50(3)	49(3)	72(3)	6(2)	1(2)	-3(2)
C(126)	67(3)	62(3)	62(3)	11(3)	-24(3)	-28(3)
C(127)	105(4)	67(3)	45(3)	-14(2)	-8(3)	-30(3)
C(128)	88(3)	57(3)	34(2)	-14(2)	9(2)	-11(2)
C(7S)	185(9)	74(4)	55(4)	-9(3)	1(5)	-5(4)
C(1S)	115(5)	85(3)	35(3)	-11(3)	15(3)	9(3)
C(2S)	100(4)	95(4)	38(3)	6(3)	30(3)	24(3)
C(3S)	94(4)	98(4)	61(4)	7(4)	36(3)	23(3)
C(4S)	103(5)	90(4)	64(4)	9(3)	37(4)	32(3)
C(5S)	99(4)	105(4)	61(4)	5(4)	34(3)	28(3)
C(6S)	104(4)	100(4)	46(4)	-6(3)	15(4)	8(3)
C(7T)	130(20)	93(14)	50(20)	-16(15)	20(20)	9(14)
C(1T)	110(9)	98(9)	45(10)	-5(8)	17(9)	12(8)

C(2T)	107(8)	101(10)	41(10)	2(8)	21(10)	21(9)
C(3T)	104(8)	99(10)	55(11)	6(10)	29(9)	28(8)
C(4T)	99(8)	99(9)	59(9)	6(8)	31(9)	28(8)
C(5T)	102(8)	99(9)	58(10)	0(8)	26(9)	26(8)
C(6T)	101(9)	100(10)	50(10)	-7(9)	22(9)	19(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S19. Bond lengths (Å) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)**

Fe(1)-C(20)	2.109(3)
Fe(1)-C(1)	2.115(3)
Fe(1)-Br(1)	2.3969(12)
Fe(1)-Br(2)	2.4209(6)
C(1)-N(2)	1.358(4)
C(1)-N(1)	1.359(4)
N(1)-C(2)	1.384(4)
N(1)-C(21)	1.458(4)
C(2)-C(7)	1.390(5)
C(2)-C(3)	1.398(5)
C(3)-C(4)	1.376(5)
C(4)-C(5)	1.391(5)
C(5)-C(6)	1.390(5)
C(6)-C(7)	1.382(5)
C(7)-N(2)	1.400(4)
N(2)-C(8)	1.472(4)
C(8)-C(9)	1.524(5)
C(9)-C(10)	1.526(5)
C(10)-N(3)	1.465(4)
N(3)-C(22)	1.471(4)
N(3)-C(11)	1.480(4)
C(11)-C(12)	1.516(5)
C(12)-C(13)	1.521(5)
C(13)-N(4)	1.456(4)
N(4)-C(20)	1.359(4)
N(4)-C(14)	1.391(4)
C(14)-C(19)	1.383(5)
C(14)-C(15)	1.390(5)
C(15)-C(16)	1.385(5)
C(16)-C(17)	1.384(6)
C(17)-C(18)	1.375(6)
C(18)-C(19)	1.388(5)
C(19)-N(5)	1.391(5)
N(5)-C(20)	1.359(4)
N(5)-C(29)	1.461(5)
C(22)-C(23)	1.511(5)
C(23)-C(24)	1.380(5)
C(23)-C(28)	1.395(5)
C(24)-C(25)	1.382(5)
C(25)-C(26)	1.373(6)
C(26)-C(27)	1.373(6)
C(27)-C(28)	1.380(6)
Fe(2)-C(120)	2.102(3)

Fe(2)-C(101)	2.117(4)
Fe(2)-Br(3)	2.4034(12)
Fe(2)-Br(4)	2.4210(6)
C(101)-N(102)	1.354(4)
C(101)-N(101)	1.365(4)
N(101)-C(102)	1.392(5)
N(101)-C(121)	1.453(5)
C(102)-C(107)	1.384(5)
C(102)-C(103)	1.389(5)
C(103)-C(104)	1.377(6)
C(104)-C(105)	1.393(6)
C(105)-C(106)	1.373(6)
C(106)-C(107)	1.395(5)
C(107)-N(102)	1.390(4)
C(108)-N(102)	1.463(4)
C(108)-C(109)	1.515(5)
C(109)-C(110)	1.524(5)
C(110)-N(103)	1.472(5)
N(103)-C(122)	1.476(5)
N(103)-C(111)	1.480(5)
C(111)-C(112)	1.518(6)
C(112)-C(113)	1.514(5)
C(113)-N(104)	1.473(4)
N(104)-C(120)	1.354(4)
N(104)-C(114)	1.392(4)
C(114)-C(115)	1.384(5)
C(114)-C(119)	1.389(5)
C(115)-C(116)	1.389(5)
C(116)-C(117)	1.387(6)
C(117)-C(118)	1.389(5)
C(118)-C(119)	1.392(5)
C(119)-N(105)	1.390(4)
N(105)-C(120)	1.364(4)
N(105)-C(129)	1.455(4)
C(122)-C(123)	1.505(5)
C(123)-C(124)	1.375(6)
C(123)-C(128)	1.385(5)
C(124)-C(125)	1.383(6)
C(125)-C(126)	1.377(6)
C(126)-C(127)	1.376(7)
C(127)-C(128)	1.396(7)
C(7S)-C(1S)	1.499(9)
C(1S)-C(2S)	1.344(9)
C(1S)-C(6S)	1.390(9)
C(2S)-C(3S)	1.424(9)
C(3S)-C(4S)	1.362(8)
C(4S)-C(5S)	1.380(9)
C(5S)-C(6S)	1.383(9)
C(7T)-C(1T)	1.49(2)
C(1T)-C(6T)	1.362(16)
C(1T)-C(2T)	1.373(17)
C(2T)-C(3T)	1.397(17)
C(3T)-C(4T)	1.383(17)
C(4T)-C(5T)	1.380(17)
C(5T)-C(6T)	1.399(17)

Table S20. Bond angles (°) for **{BnN($CH_2CH_2CH_2$-*N*-methylbenzimidazole-2-ylidene)$_2$}$FeBr_2$ (5)**

C(20)-Fe(1)-C(1)	101.90(13)
C(20)-Fe(1)-Br(1)	110.93(9)
C(1)-Fe(1)-Br(1)	118.58(9)
C(20)-Fe(1)-Br(2)	114.63(10)
C(1)-Fe(1)-Br(2)	104.96(9)
Br(1)-Fe(1)-Br(2)	106.06(2)
N(2)-C(1)-N(1)	105.5(3)
N(2)-C(1)-Fe(1)	133.3(2)
N(1)-C(1)-Fe(1)	120.3(2)
C(1)-N(1)-C(2)	111.2(3)
C(1)-N(1)-C(21)	124.7(3)
C(2)-N(1)-C(21)	124.1(3)
N(1)-C(2)-C(7)	106.5(3)
N(1)-C(2)-C(3)	131.2(3)
C(7)-C(2)-C(3)	122.3(3)
C(4)-C(3)-C(2)	116.2(3)
C(3)-C(4)-C(5)	122.0(3)
C(6)-C(5)-C(4)	121.5(3)
C(7)-C(6)-C(5)	117.2(3)
C(6)-C(7)-C(2)	120.8(3)
C(6)-C(7)-N(2)	133.4(3)
C(2)-C(7)-N(2)	105.7(3)
C(1)-N(2)-C(7)	110.9(3)
C(1)-N(2)-C(8)	124.2(3)
C(7)-N(2)-C(8)	124.9(3)
N(2)-C(8)-C(9)	114.2(3)
C(8)-C(9)-C(10)	116.0(3)
N(3)-C(10)-C(9)	114.1(3)
C(10)-N(3)-C(22)	110.8(3)
C(10)-N(3)-C(11)	109.8(3)
C(22)-N(3)-C(11)	110.5(3)
N(3)-C(11)-C(12)	111.7(3)
C(11)-C(12)-C(13)	110.2(3)
N(4)-C(13)-C(12)	114.0(3)
C(20)-N(4)-C(14)	111.9(3)
C(20)-N(4)-C(13)	124.4(3)
C(14)-N(4)-C(13)	123.6(3)
C(19)-C(14)-C(15)	121.6(3)
C(19)-C(14)-N(4)	105.5(3)
C(15)-C(14)-N(4)	132.9(4)
C(16)-C(15)-C(14)	116.3(4)
C(17)-C(16)-C(15)	121.8(4)
C(18)-C(17)-C(16)	121.8(4)
C(17)-C(18)-C(19)	116.8(4)
C(14)-C(19)-C(18)	121.7(4)
C(14)-C(19)-N(5)	106.6(3)
C(18)-C(19)-N(5)	131.8(4)
C(20)-N(5)-C(19)	111.2(3)
C(20)-N(5)-C(29)	125.5(3)
C(19)-N(5)-C(29)	123.2(3)
N(4)-C(20)-N(5)	104.7(3)
N(4)-C(20)-Fe(1)	124.2(2)

N(5)-C(20)-Fe(1)	130.8(3)
N(3)-C(22)-C(23)	112.6(3)
C(24)-C(23)-C(28)	118.1(4)
C(24)-C(23)-C(22)	122.1(3)
C(28)-C(23)-C(22)	119.9(3)
C(23)-C(24)-C(25)	120.8(4)
C(26)-C(25)-C(24)	120.7(4)
C(25)-C(26)-C(27)	119.1(4)
C(26)-C(27)-C(28)	120.7(4)
C(27)-C(28)-C(23)	120.6(4)
C(120)-Fe(2)-C(101)	109.61(13)
C(120)-Fe(2)-Br(3)	115.53(10)
C(101)-Fe(2)-Br(3)	104.77(10)
C(120)-Fe(2)-Br(4)	104.72(9)
C(101)-Fe(2)-Br(4)	109.30(10)
Br(3)-Fe(2)-Br(4)	112.88(3)
N(102)-C(101)-N(101)	105.1(3)
N(102)-C(101)-Fe(2)	128.3(3)
N(101)-C(101)-Fe(2)	126.5(2)
C(101)-N(101)-C(102)	111.2(3)
C(101)-N(101)-C(121)	125.2(3)
C(102)-N(101)-C(121)	123.5(3)
C(107)-C(102)-C(103)	121.8(4)
C(107)-C(102)-N(101)	105.9(3)
C(103)-C(102)-N(101)	132.2(4)
C(104)-C(103)-C(102)	117.0(4)
C(103)-C(104)-C(105)	121.3(4)
C(106)-C(105)-C(104)	122.0(4)
C(105)-C(106)-C(107)	117.0(4)
C(102)-C(107)-N(102)	106.4(3)
C(102)-C(107)-C(106)	121.0(3)
N(102)-C(107)-C(106)	132.6(3)
N(102)-C(108)-C(109)	111.8(3)
C(101)-N(102)-C(107)	111.3(3)
C(101)-N(102)-C(108)	124.7(3)
C(107)-N(102)-C(108)	123.9(3)
C(108)-C(109)-C(110)	111.7(3)
N(103)-C(110)-C(109)	114.6(3)
C(110)-N(103)-C(122)	107.5(3)
C(110)-N(103)-C(111)	110.6(3)
C(122)-N(103)-C(111)	109.1(3)
N(103)-C(111)-C(112)	115.0(3)
C(113)-C(112)-C(111)	116.7(3)
N(104)-C(113)-C(112)	114.5(3)
C(120)-N(104)-C(114)	111.6(3)
C(120)-N(104)-C(113)	125.6(3)
C(114)-N(104)-C(113)	122.8(3)
C(115)-C(114)-C(119)	121.5(3)
C(115)-C(114)-N(104)	132.5(3)
C(119)-C(114)-N(104)	105.9(3)
C(114)-C(115)-C(116)	116.7(4)
C(117)-C(116)-C(115)	121.5(4)
C(116)-C(117)-C(118)	122.3(4)
C(117)-C(118)-C(119)	115.6(4)
C(114)-C(119)-N(105)	106.2(3)
C(114)-C(119)-C(118)	122.3(3)

N(105)-C(119)-C(118)	131.5(3)
C(120)-N(105)-C(119)	111.2(3)
C(120)-N(105)-C(129)	125.2(3)
C(119)-N(105)-C(129)	123.6(3)
N(104)-C(120)-N(105)	105.2(3)
N(104)-C(120)-Fe(2)	133.4(2)
N(105)-C(120)-Fe(2)	120.9(2)
N(103)-C(122)-C(123)	114.8(3)
C(124)-C(123)-C(128)	119.1(4)
C(124)-C(123)-C(122)	120.1(3)
C(128)-C(123)-C(122)	120.7(4)
C(123)-C(124)-C(125)	121.4(4)
C(126)-C(125)-C(124)	119.6(5)
C(127)-C(126)-C(125)	119.6(5)
C(126)-C(127)-C(128)	120.8(4)
C(123)-C(128)-C(127)	119.4(5)
C(2S)-C(1S)-C(6S)	117.9(7)
C(2S)-C(1S)-C(7S)	122.0(7)
C(6S)-C(1S)-C(7S)	120.1(7)
C(1S)-C(2S)-C(3S)	122.0(6)
C(4S)-C(3S)-C(2S)	119.3(7)
C(3S)-C(4S)-C(5S)	119.2(7)
C(4S)-C(5S)-C(6S)	120.6(7)
C(5S)-C(6S)-C(1S)	121.0(7)
C(6T)-C(1T)-C(2T)	117(2)
C(6T)-C(1T)-C(7T)	121(2)
C(2T)-C(1T)-C(7T)	119(2)
C(1T)-C(2T)-C(3T)	120(2)
C(4T)-C(3T)-C(2T)	119(3)
C(5T)-C(4T)-C(3T)	114(3)
C(4T)-C(5T)-C(6T)	119(2)
C(1T)-C(6T)-C(5T)	122(2)

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