Supplementary Material

pertaining to

Facial triad modeling using ferrous pyridinyl prolinate complexes: synthesis and catalytic applications

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Table S1. Selected bond lengths (Å) and angles (°) for complex **10**.

Bond length		Angle	
Fe1-N32	2.132(5)	N32-Fe1-N22	76.90(17)
Fe1-N22	2.197(5)	N32-Fe1-O12	151.82(18)
Fe1-O12	2.146(4)	N22-Fe1-O12	75.13(17)
Fe1-N31	2.148(5)	N31-Fe1-N21	77.26(18)
Fe1-N21	2.183(5)	N31-Fe1-O11	150.70(17)
Fe1-O11	2.164(4)	N21-Fe1-O11	74.09(17)
		N31-Fe1-N22	124.41(19)
		N22-Fe1-N21	154.94(16)

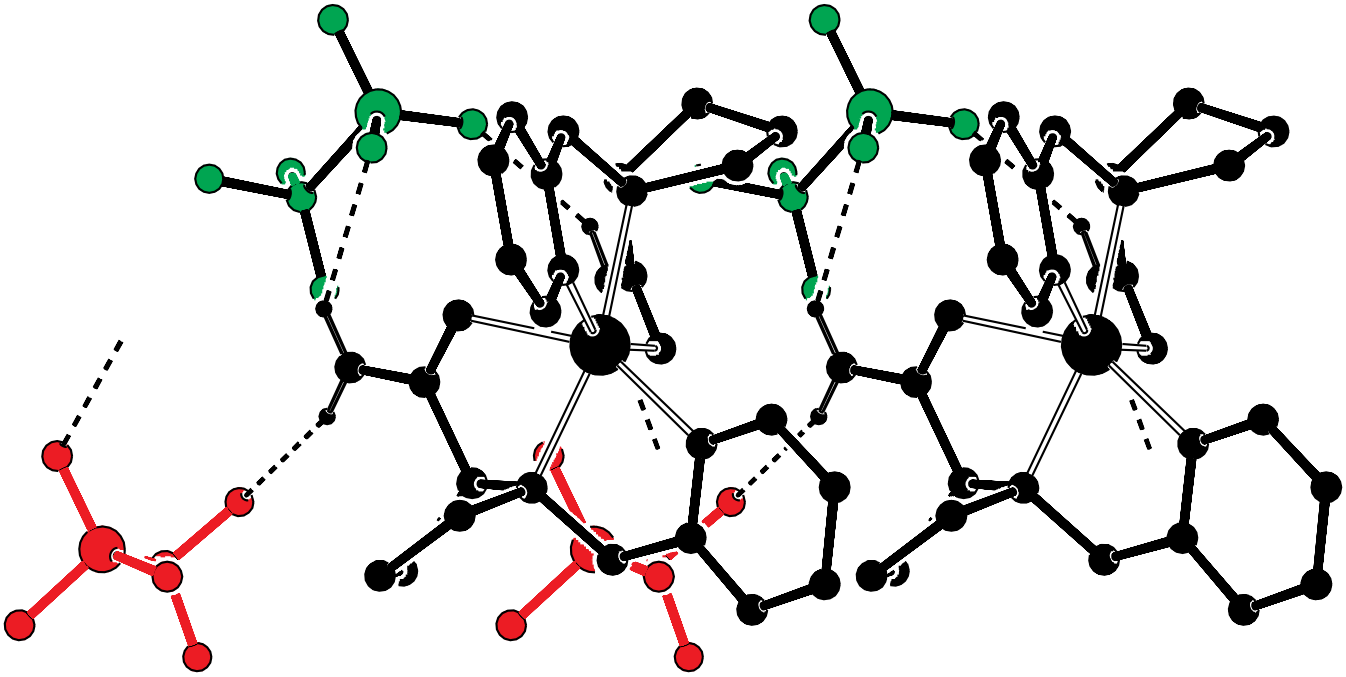


Fig. S1 Hydrogen-bonded one-dimensional chain in the direction of the a-axis (compound **10**). View along the c-axis. C-H hydrogen atoms are omitted for clarity. Only the major form of the disordered triflate is shown.

Table S2 Hydrogen bonding details in **10**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [º]
N11-H11A...O1^{i}	0.88	2.33	3.051(7)	139
N11-H11B...F6a^{ii}	0.88	2.45	3.290(13)	159
N12-H12A...O4a	0.88	2.09	2.876(9)	149
N12-H12B...O3^{i}	0.88	2.19	2.983(7)	150

Symmetry operations. i: -x, y+0.5, 1-z; ii: x-1, y, z.

Table S3. Selected bond lengths (Å) and angles (°) for **12b** (from MeOH) and **12a** (from CH_2Cl_2).

	Bond lengths			Angles	
	12b	**12a**		**12b**	**12a**
Fe1-N1	2.1856(14)	2.1749(18)	N1-Fe1-N2	74.86(5)	76.28(6)
Fe1-N2	2.2880(13)	2.1686(16)	N2-Fe1-O1	75.27(5)	73.55(6)
Fe1-O1	2.2210(12)	2.2830(15)	N1-Fe1-Cl1	94.71(4)	100.95(5)
Fe1-Cl1	2.4742(5)	2.3187(6)	N1-Fe1-Cl2	98.48(4)	99.25(5)
Fe1-Cl2	2.3303(5)	2.2810(6)	O1-Fe1-Cl1	163.93(3)	92.60(4)
Fe1-O3	2.1554(12)		O1-Fe1-Cl2	98.63(3)	100.05(4)
			N1-Fe1-O1	86.63(5)	149.78(6)
			Cl1-Fe1-Cl2	97.011(18)	113.01(2)
			N2-Fe1-Cl2	171.04(4)	126.96(5)

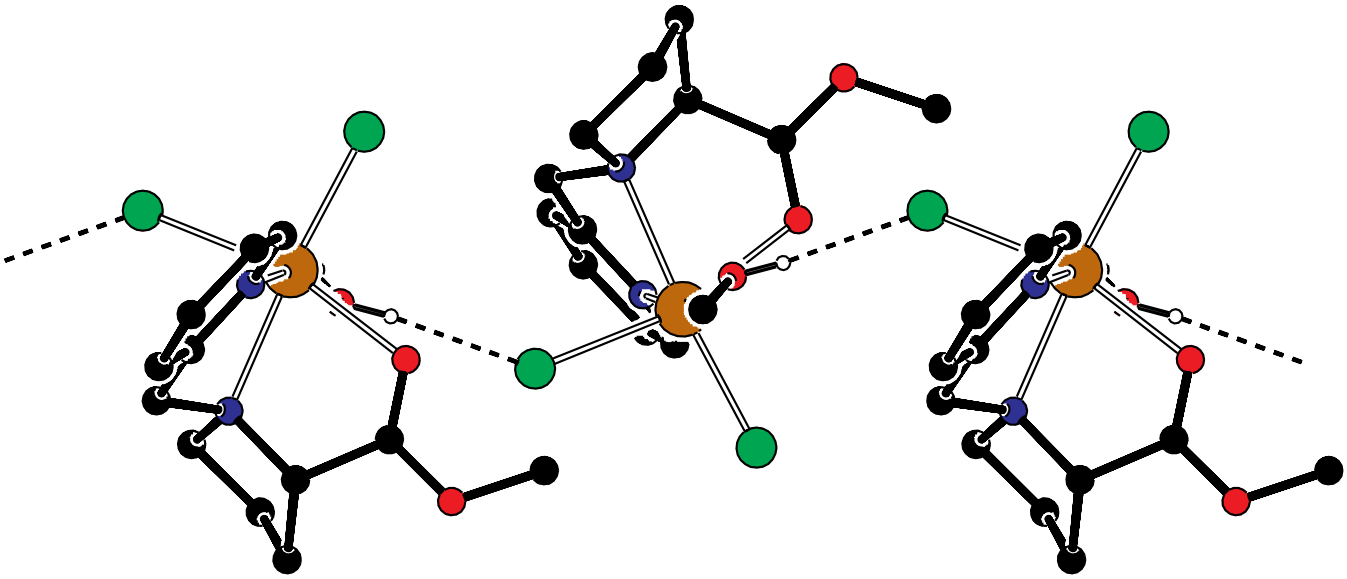


Fig. S2 Hydrogen-bonded one-dimensional chain in the direction of the b-axis (compound **12b**). View along the a-axis. C-H hydrogen atoms are omitted for clarity.

Table S4 Hydrogen bonding details in **12b**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [°]
O3-H3O...Cl1^{i}	0.77(2)	2.37(2)	3.1221(14)	165(2)

Symmetry operations. i: 1-x, y+0.5, 0.5-z.

Table S5. Selected bond lengths (Å) and angles (°) for complex **13**.

Bond length		Angle	
Fe1-N1	2.1866(17)	N1-Fe1-N2	78.53(6)
Fe1-N2	2.1512(17)	N2-Fe1-O1	75.33(6)
Fe1-O1	2.2610(15)	N1-Fe1-Cl1	99.88(5)
Fe1-Cl1	2.3011(6)	N1-Fe1-Cl2	102.73(5)
Fe1-Cl2	2.2804(6)	O1-Fe1-Cl1	88.83(4)
		O1-Fe1-Cl2	91.23(4)
		N1-Fe1-O1	153.71(6)
		Cl1-Fe1-Cl2	127.01(2)

Table S6. Selected bond lengths (Å) and angles (°) for complex **14** and **15**.

	Complex **14**	Complex **15**		Complex **14**	Complex **15**
	Bond Lengths			Angles	
Fe1-N1	2.2264(15)	2.1598(11)	N1-Fe1-N2	75.37(5)	76.51(4)
Fe1-N2	2.2319(14)	2.2767(11)	N2-Fe1-O1	79.18(5)	74.81(4)
Fe1-O1	2.1176(13)	2.0941(11)	N1-Fe1-Cl1	168.72(4)	104.37(3)
Fe1-Cl1	2.4809(5)	2.3147(4)	N1-Fe1-Cl2	92.76(4)	98.98(3)
Fe1-Cl2	2.3873(5)	2.3660(4)	O1-Fe1-Cl1	87.97(4)	121.53(4)
Fe1-N4	2.1900(16)		O1-Fe1-Cl2	174.14(4)	84.99(3)
			N1-Fe1-O1	83.01(5)	130.66(4)
			Cl1-Fe1-Cl2	95.723(17)	106.956(15)
			N2-Fe1-Cl2	95.86(4)	147.29(3)

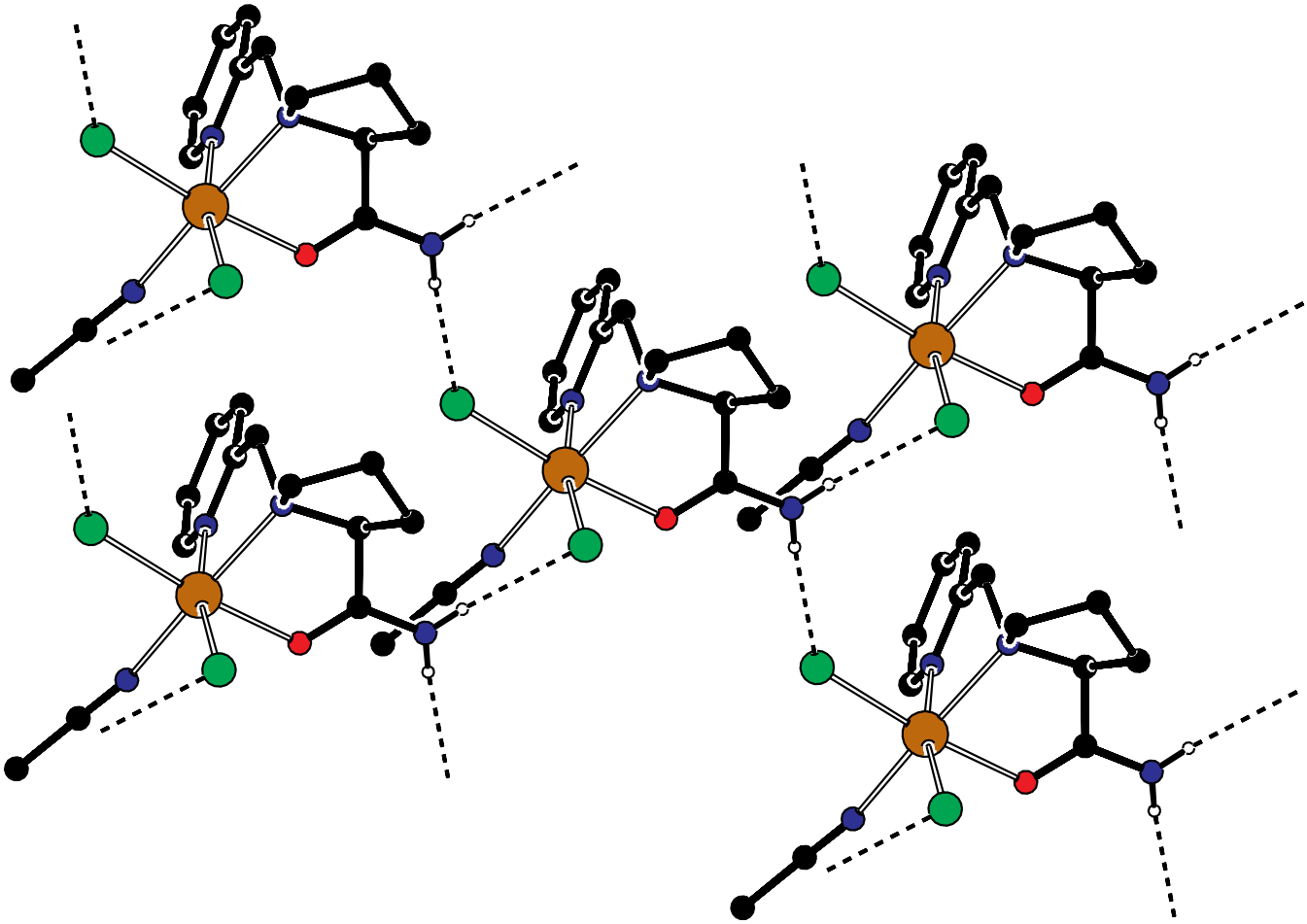


Fig. S3 Hydrogen-bonded two-dimensional network in the crystallographic *a,b*-plane (compound **14**). View along the c-axis. C-H hydrogen atoms are omitted for clarity.

Table S7 Hydrogen bonding details in **14**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [º]
N3-H1N...Cl1^{i}	0.78(2)	2.46(2)	3.237(2)	171(2)
N3-H2N...Cl2^{ii}	0.80(3)	2.44(3)	3.237(2)	174(2)

Symmetry operations. i: x, y+1, z; ii: x+1, y+1, z.

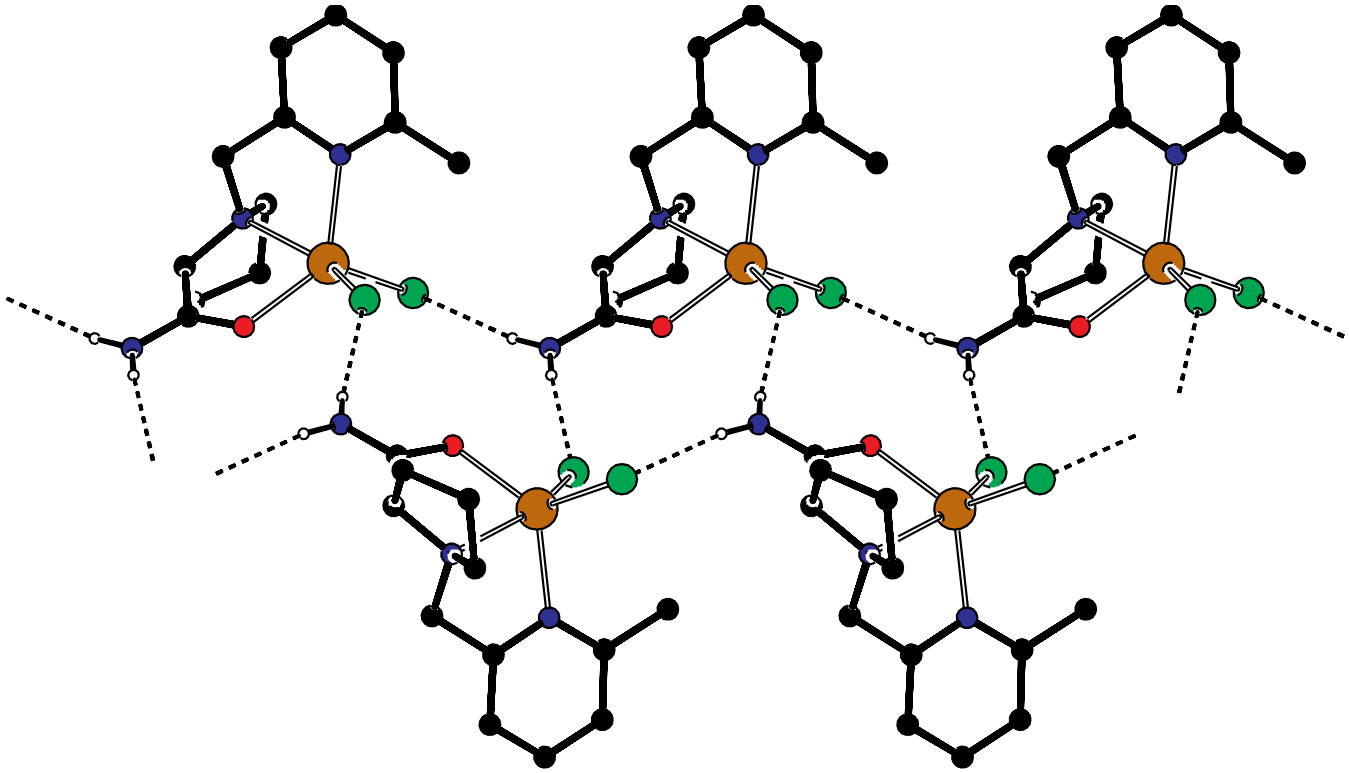


Fig. S4 Hydrogen-bonded one-dimensional chain in the direction of the b-axis (compound **15**). View along the c-axis. C-H hydrogen atoms are omitted for clarity.

Table S8 Hydrogen bonding details in **15**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [º]
N3-H1N...Cl2^{i}	0.79(2)	2.50(2)	3.2748(15)	168(2)
N3-H2N...Cl1^{ii}	0.84(2)	2.48(2)	3.3117(14)	170.1(18)

Symmetry operations. i: 2-x, y-0.5, 2-z; ii: x, y-1, z.

Table S9. Selected bond lengths (Å) and angles (°) for complex **16** and **17**.[a]

	Complex **16**		Complex **17**	
	Res 1	Res 2	Res 1	Res 2
	Bond lengths			
Fex-N1x	2.1227(18)	2.1354(18)	2.160(2)	2.153(3)
Fex-N2x	2.2800(18)	2.2125(17)	2.240(3)	2.193(3)
Fex-O1x	2.0858(15)	2.1347(14)	2.123(2)	2.1431(19)
Fex-Cl1x	2.3890(6)	2.3666(6)	2.2565(9)	2.2580(9)
Fex-Cl2x	2.2542(6)	2.2604(6)	2.3825(9)	2.3663(9)
	Angles			
N1x-Fex-N2x	76.41(7)	74.96(7)	77.51(10)	75.63(10)
N2x-Fex-O1x	74.73(6)	73.38(6)	73.40(9)	73.47(8)
N1x-Fex-Cl1x	92.30(6)	90.88(5)	111.38(8)	113.58(7)
N1x-Fex-Cl2x	112.82(6)	113.09(6)	92.17(8)	90.34(7)
O1x-Fex-Cl1x	90.17(4)	91.84(4)	119.52(6)	115.03(6)
O1x-Fex-Cl2x	120.13(5)	119.68(5)	85.67(6)	89.86(6)
N1x-Fex-O1x	124.63(7)	124.56(7)	126.54(9)	128.07(9)
Cl1x-Fex-Cl2x	103.77(2)	104.17(2)	109.76(4)	109.71(3)

[a] x = residue 1 or 2.

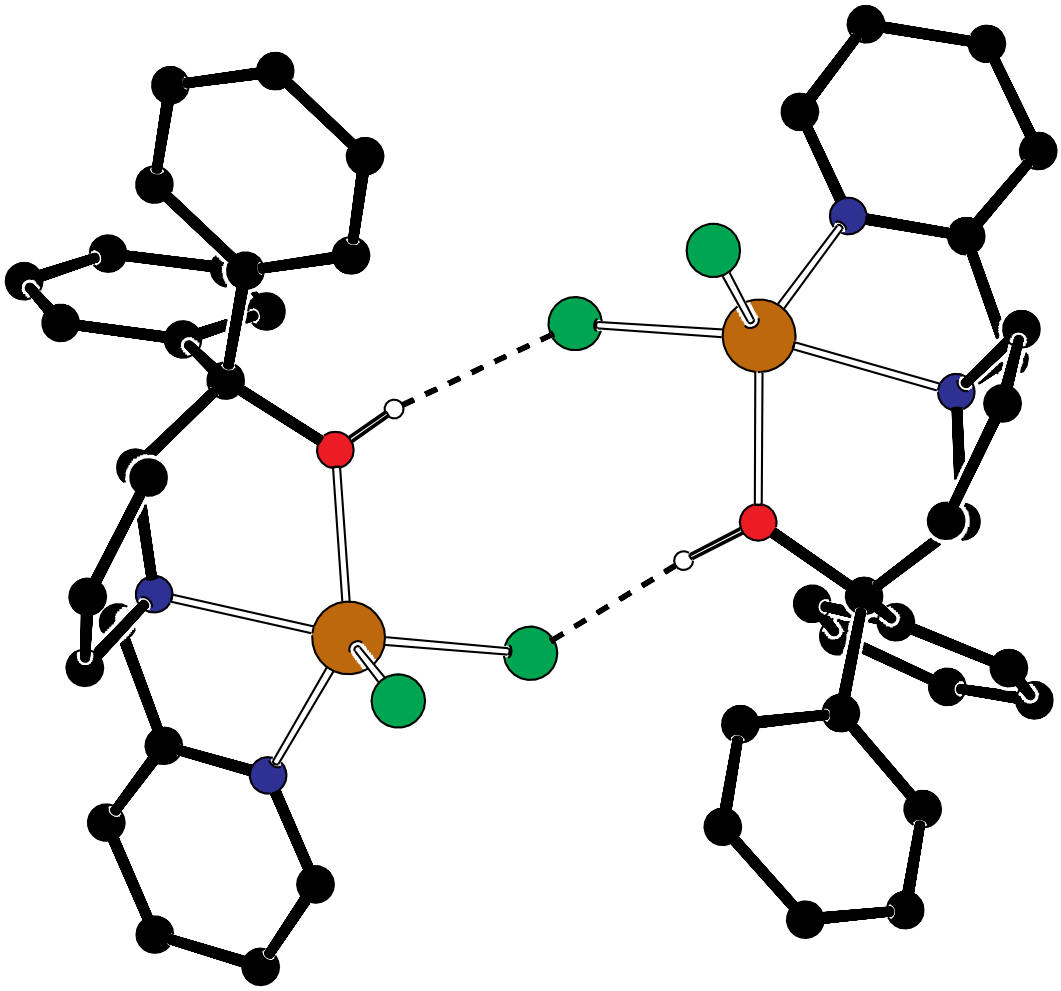


Fig. S5 Hydrogen-bonded dimer between the two independent molecules of **16**. C-H hydrogen atoms and CH_2Cl_2 solvent molecules are omitted for clarity.

Table S10 Hydrogen bonding details in **16**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [°]
O11-H11O...Cl12	1.00	2.09	3.0818(15)	175
O12-H12O...Cl11	0.82	2.32	3.1319(15)	170

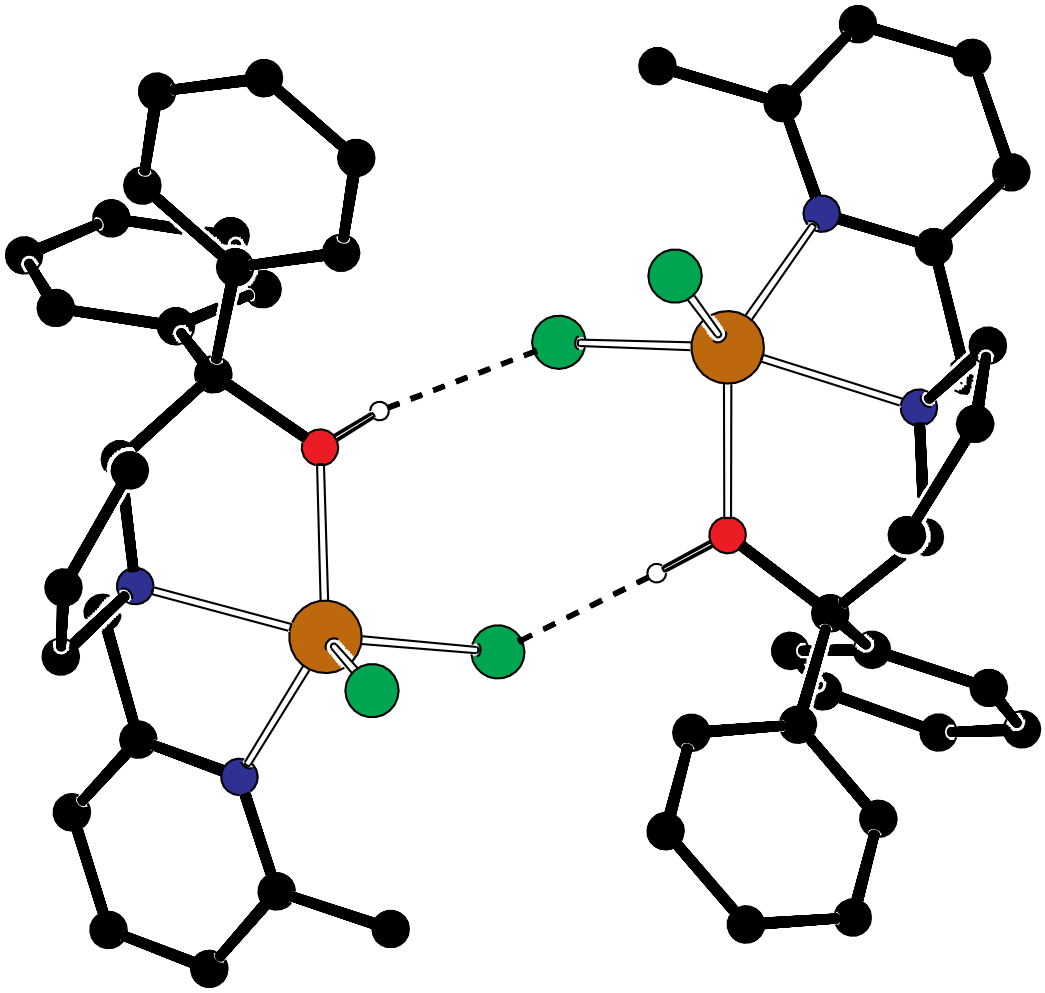


Fig. S6 Hydrogen-bonded dimer between the two independent molecules of **17**. C-H hydrogen atoms are omitted for clarity.

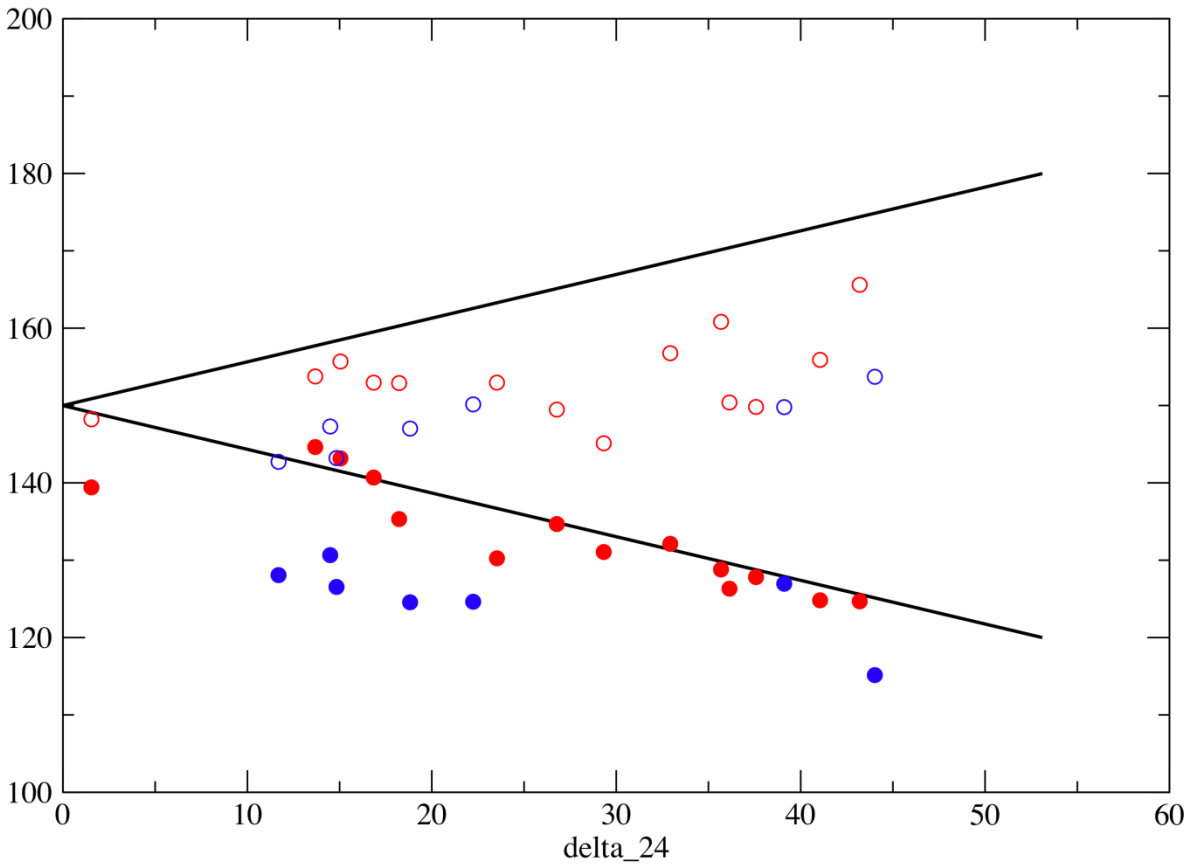
Table S11 Hydrogen bonding details in **17**.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [°]
O11-H11O...Cl22	0.97	2.10	3.069(2)	177
O12-H12O...Cl21	0.87	2.24	3.094(2)	167

Table S12 Berry pseudorotation.

	δ_{24}[a]	θ_{24}[a]	θ_{15}[a]
12a	39.11	126.96(5)	149.78(6)
13	44.02	115.14(5)	153.71(6)
15	14.49	130.66(4)	147.29(3)
16_mol1	22.24	124.63(7)	150.14(5)
16_mol2	18.82	124.56(7)	147.02(5)
17_mol1	14.83	126.54(9)	143.20(8)
17_mol2	11.69	128.07(9)	142.72(7)

a) for a definition of δ_{24}, θ_{24}, and θ_{15} see Holmes, R. R. *Progress in Inorganic Chemistry* **1984**, *32*, 119-235.



Graph S1 Graphical representation of the Berry pseudo-rotation pathway screening.

In Graph S1 the results on the Berry pseudo-rotation pathway screening are depicted. The seven structures reported here are represented as the blue dots. The 14 structures extracted from the CSD-database are represented as the red dots.[33] The open circles correspond to the 1,5-angle and the filled circles to the 2,4-angle. Furthermore the theoretical Berry pathway is draw as the black lines.

Table S13 Experimental details of crystal structure **10**.

	10
formula	$[C_{22}H_{30}FeN_6O_2](CF_3O_3S)_2$
Fw	764.51
crystal colour	yellow
crystal size [mm^3]	0.54x0.08x0.06
T [K]	150(2)
crystal system	monoclinic
space group	$P2_1$ (No. 4)
a [Å]	7.0198(6)
b [Å]	18.956(2)
c [Å]	11.9392(7)
β [°]	107.114(3)
V [$Å^3$]	1518.4(2)
Z	2
D_{calc} [g/cm^3]	1.672
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.61
refl. measured/unique	20320 / 5667
parameters / restraints	517 / 454
R1/wR2 [I>2σ (I)]	0.0317 / 0.0568
R1/wR2 [all refl.)]	0.0394 / 0.0595
Flack x[49]	0.00(2)
S	1.068
ρ (min/max) [$eÅ^{-3}$]	-0.26 / 0.27

Table S14 Experimental details of crystal structures **12a** and **12b**.

	12a	**12b**
formula	$C_{12}H_{16}Cl_2FeN_2O_2$	$C_{13}H_{20}Cl_2FeN_2O_3$
Fw	347.02	379.06
crystal colour	yellow	yellow
crystal size [mm^3]	0.36x0.18x0.09	0.42x0.18x0.12
T [K]	150(2)	150(2)
crystal system	hexagonal	orthorhombic
space group	$P6_5$ (No. 170)	$P2_12_12_1$ (No. 19)
a [Å]	8.3897(1)	11.5923(1)
b [Å]	-	11.6358(1)
c [Å]	35.4893(5)	12.1043(2)
V [$Å^3$]	2163.32(5)	1632.70(3)
Z	6	4
D_{calc} [g/cm^3]	1.598	1.542
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.65	0.65
refl. measured/unique	11159 / 3256	28909 / 3728
parameters / restraints	173 / 1	196 / 0
R1/wR2 [$I>2\sigma(I)$]	0.0252 / 0.0507	0.0223 / 0.0491
R1/wR2 [all refl.)]	0.0300 / 0.0528	0.0251 / 0.0503
Flack x[49]	-0.015(11)	0.000(10)
S	1.072	1.071
ρ (min/max) [$eÅ^{-3}$]	-0.21 / 0.21	-0.22 / 0.21

Table S15 Experimental details of crystal structure **13**.

	13
formula	$C_{13}H_{18}Cl_2FeN_2O_2$
Fw	361.04
crystal colour	yellow
crystal size [mm^3]	0.36x0.09x0.09
T [K]	150(2)
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a [Å]	8.0901(1)
b [Å]	12.9326(2)
c [Å]	14.6255(2)
V [$Å^3$]	1530.21(4)
Z	4
D_{calc} [g/cm^3]	1.567
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.65
refl. measured/unique	27410 / 3509
parameters / restraints	183 / 0
R1/wR2 [$I>2\sigma(I)$]	0.0271 / 0.0615
R1/wR2 [all refl.)]	0.0337 / 0.0647
Flack x[49]	-0.012(13)
S	1.075
ρ (min/max) [$eÅ^{-3}$]	-0.29 / 0.29

Table S16 Experimental details of crystal structures **14** and **15**.

	14	**15**
formula	$C_{13}H_{18}Cl_2FeN_4O$	$C_{12}H_{17}Cl_2FeN_3O$
Fw	373.06	346.04
crystal colour	yellow	yellow
crystal size [mm^3]	0.42x0.18x0.06	0.60x0.27x0.18
T [K]	110(2)	150(2)
crystal system	triclinic	monoclinic
space group	P1 (No. 1)	$P2_1$ (No. 4)
a [Å]	6.8899(1)	8.89008(11)
b [Å]	7.4891(1)	8.19097(10)
c [Å]	9.0561(1)	10.05615(16)
α [º]	113.7230(8)	-
β [º]	92.0237(7)	90.575(1)
γ [º]	107.1842(6)	-
V [$Å^3$]	402.305(9)	732.236(17)
Z	1	2
D_{calc} [g/cm^3]	1.540	1.569
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.65	0.65
refl. measured/unique	9765 / 3636	26417 / 3374
parameters / restraints	199 / 3	181 / 1
R1/wR2 [$I>2\sigma$ (I)]	0.0215 / 0.0488	0.0154 / 0.0401
R1/wR2 [all refl.)]	0.0229 / 0.0496	0.0157 / 0.0404
Flack x[49]	0.000(9)	-0.008(8)
S	1.084	1.069
ρ (min/max) [$eÅ^{-3}$]	-0.21 / 0.25	-0.27 / 0.26

Table S17 Experimental details of crystal structures **16** and **17**.

	16	**17**
formula	$C_{23}H_{24}Cl_2FeN_2O \cdot 0.5CH_2Cl_2$	$C_{24}H_{26}Cl_2FeN_2O$
Fw	513.66	485.22
crystal colour	yellow	yellow
crystal size [mm^3]	0.48x0.27x0.24	0.36x0.18x0.15
T [K]	150(2)	150(2)
crystal system	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a [Å]	11.2439(1)	11.1681(2)
b [Å]	12.5035(1)	12.3970(2)
c [Å]	16.7671(2)	16.8766(3)
β [º]	101.8532(4)	103.6971(8)
V [$Å^3$]	2306.99(4)	2270.13(7)
Z	4	4
D_{calc} [g/cm^3]	1.479	1.420
$(\sin\theta/\lambda)_{max}$ [$Å^{-1}$]	0.65	0.65
refl. measured/unique	38678 / 10555	34625 / 10331
parameters / restraints	550 / 1	543 / 1
R1/wR2 [I>2σ (I)]	0.0286 / 0.0712	0.0409 / 0.0846
R1/wR2 [all refl.)]	0.0308 / 0.0728	0.0546 / 0.0914
Flack x[49]	-0.012(8)	-0.005(11)
S	1.030	1.051
ρ (min/max) [$eÅ^{-3}$]	-0.61 / 0.44	-0.33 / 0.54