Supporting Information

Iron(II) β-ketiminate complexes as mediators of controlled radical polymerisation

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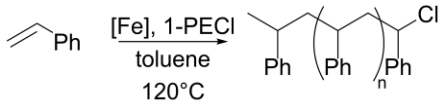
CONTENT

GPC DATA

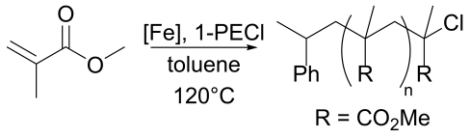
Table S1 ATRP of styrene[a]



Entry	Complex	Conv. (%)	$M_{n,th}$ (Da)	M_n (Da)	Đ
S1	**1a**	34	3541	8362	1.78
S2	**2a**	24	2500	9377	1.76
S3	**3a**	22	2291	5366	1.66
S4	**4a**	23	2395	5892	1.74
S5	**1b**	23	2395	5057	1.69
S6	**3b**	19	1979	4935	1.70
S7	**1c**	21	2187	9312	1.74
S8	**3c**	24	2500	4661	1.81

[a] Conditions: [styrene]:[Fe^{II}]:[1-PECl] = 100:1.00:1.00, styrene:toluene = 1:1 (v/v), 120°C, 1 hour. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th}$ = $[styrene]_0/[1\text{-}PECl]_0$ × M(styrene) × conversion.

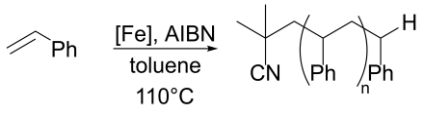
Table S2 ATRP of MMA[a]



Entry	Complex	Conv. (%)	$M_{n,th}$ (Da)	M_n (Da)	Đ
S9	**1a**	70	7008	14792	1.81
S10	**2a**	57	5707	19283	2.18
S11	**3a**	40	4005	12368	1.45
S12	**4a**	43	4305	13386	1.61
S13	**1b**	54	5406	15021	1.60
S14	**3b**	35	3504	15184	1.41
S15	**1c**	37	3704	28168	2.22
S16	**3c**	41	4105	15288	1.78

[a] Conditions: [MMA]:[Fe^{II}]:[1-PECl] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 120°C, 1 hour. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th}$ = $[MMA]_0/[1\text{-}PECl]_0$ × M(MMA) × conversion.

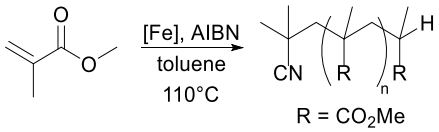
Table S3 OMRP of styrene[a]



Entry	Complex	Conv. (%)	$M_{n,th\ [AIBN]}$ (Da)	$M_{n,th\ [Fe]}$ (Da)	M_n (Da)	Đ
S17	**1a**	45	2343	4686	8254	2.16
S18	**2a**	49	2552	5104	8294	2.27
S19	**3a**	35	1823	3646	6213	1.58
S20	**4a**	36	1875	3750	6561	1.61
S21	**1b**	43	2239	4478	8786	2.06
S22	**3b**	31	1614	3228	6881	1.86
S23	**1c**	41	2135	4270	8361	2.32
S24	**3c**	39	2031	4062	7104	1.92

[a] Conditions: [styrene]:[Fe^{II}]:[AIBN] = 100:1.00:1.00, styrene:toluene = 1:1 (v/v), 110°C, 1 hour. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th\ [AIBN]}$ = $[styrene]_0/(2 \times [AIBN]_0) \times M(styrene) \times conversion$. $M_{n,th\ [Fe]}$ = $[styrene]_0/[Fe] \times M(styrene) \times conversion$.

Table S4 OMRP of MMA[a]

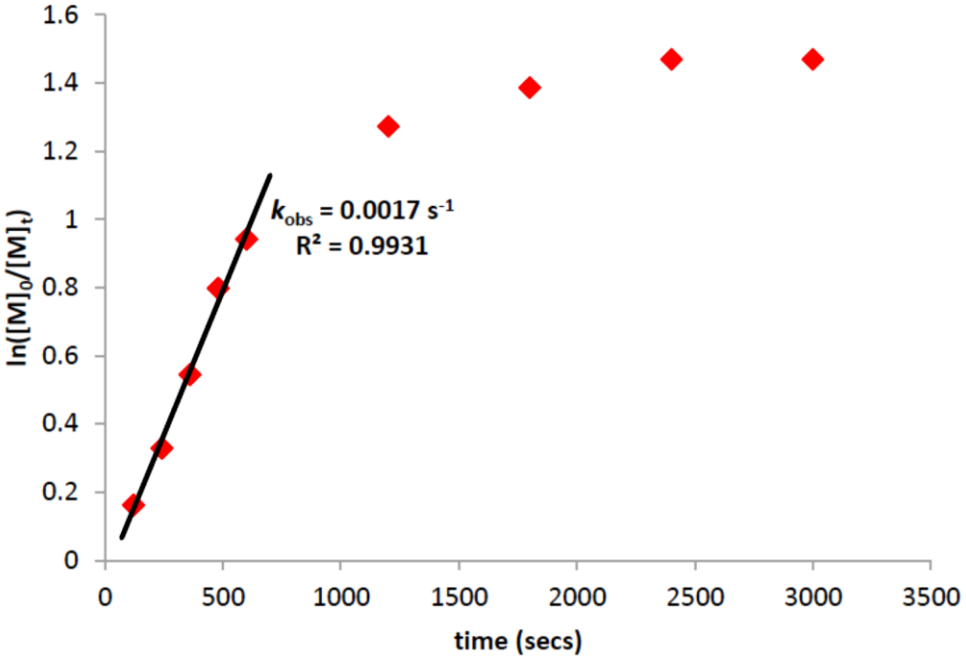


Entry	Complex	Conv. (%)	$M_{n,th\ [AIBN]}$ (Da)	$M_{n,th\ [Fe]}$ (Da)	M_n (Da)	Đ
S25	**1a**	73	3654	7308	11764	1.47
S26	**2a**	69	3454	6908	11704	1.37
S27	**3a**	13	651	1302	13862	1.49
S28	**4a**	22	1101	2202	11128	1.53
S29	**1b**	56	2803	5606	10229	1.45
S30	**3b**	36	1802	3604	10123	1.41
S31	**1c**	54	2703	5406	10734	1.33
S32	**3c**	9	451	902	[b]	[b]

[a] Conditions: [MMA]:[Fe^{II}]:[AIBN] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 110°C, 1 hour. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th\ [AIBN]}$ = $[MMA]_0/(2 \times [AIBN]_0) \times M(MMA) \times conversion$. $M_{n,th\ [Fe]}$ = $[MMA]_0/[Fe] \times M(MMA) \times conversion$. [b] Too little polymer obtained for GPC analysis.

KINETIC DATA

Figure S1 First-order kinetic plot for the OMRP of MMA mediated by complex **1a**[a]



[a] Conditions: [MMA]:[**1a**]:[AIBN] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 110°C. Conversion determined by ^{1}H NMR spectroscopy.

NMR SPECTRA

Figure S2 ^{1}H NMR spectrum of complex **1a** (500 MHz, C_6D_6)

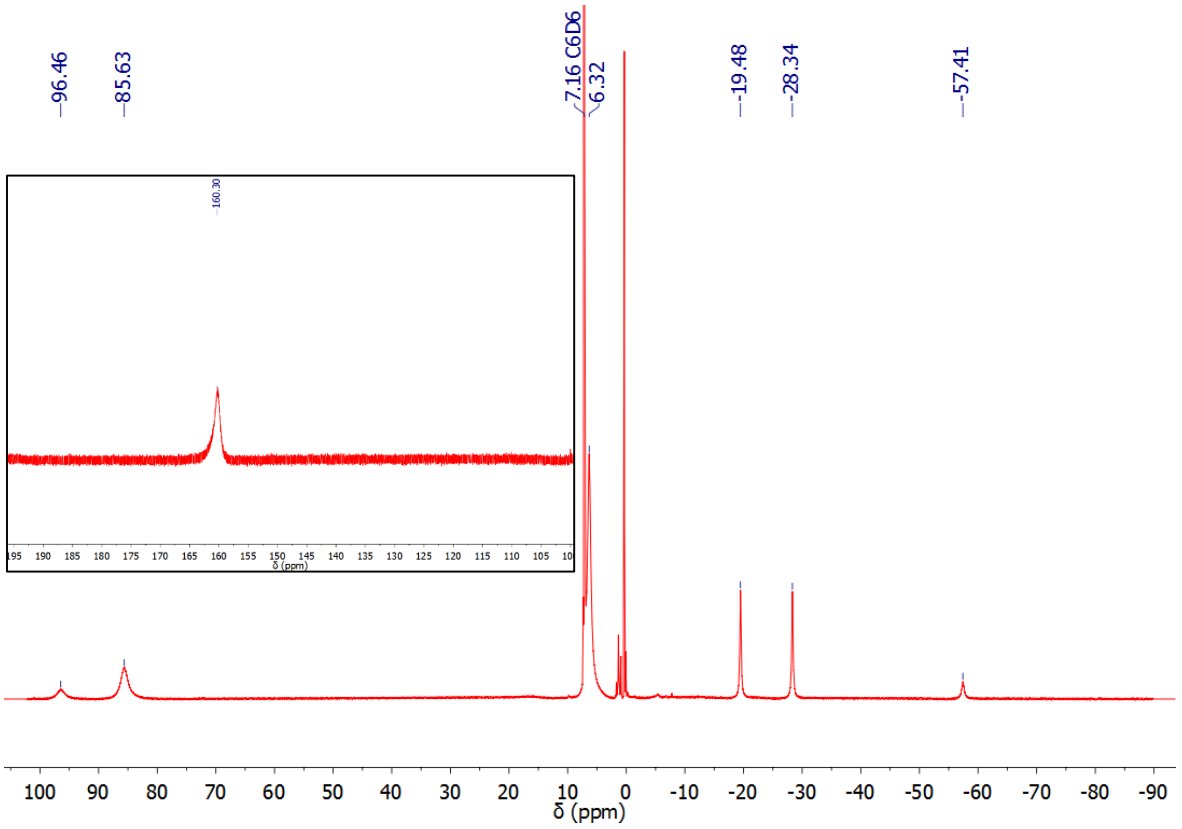


Figure S3 ^{1}H NMR spectrum of complex **2a** (500 MHz, C_6D_6)

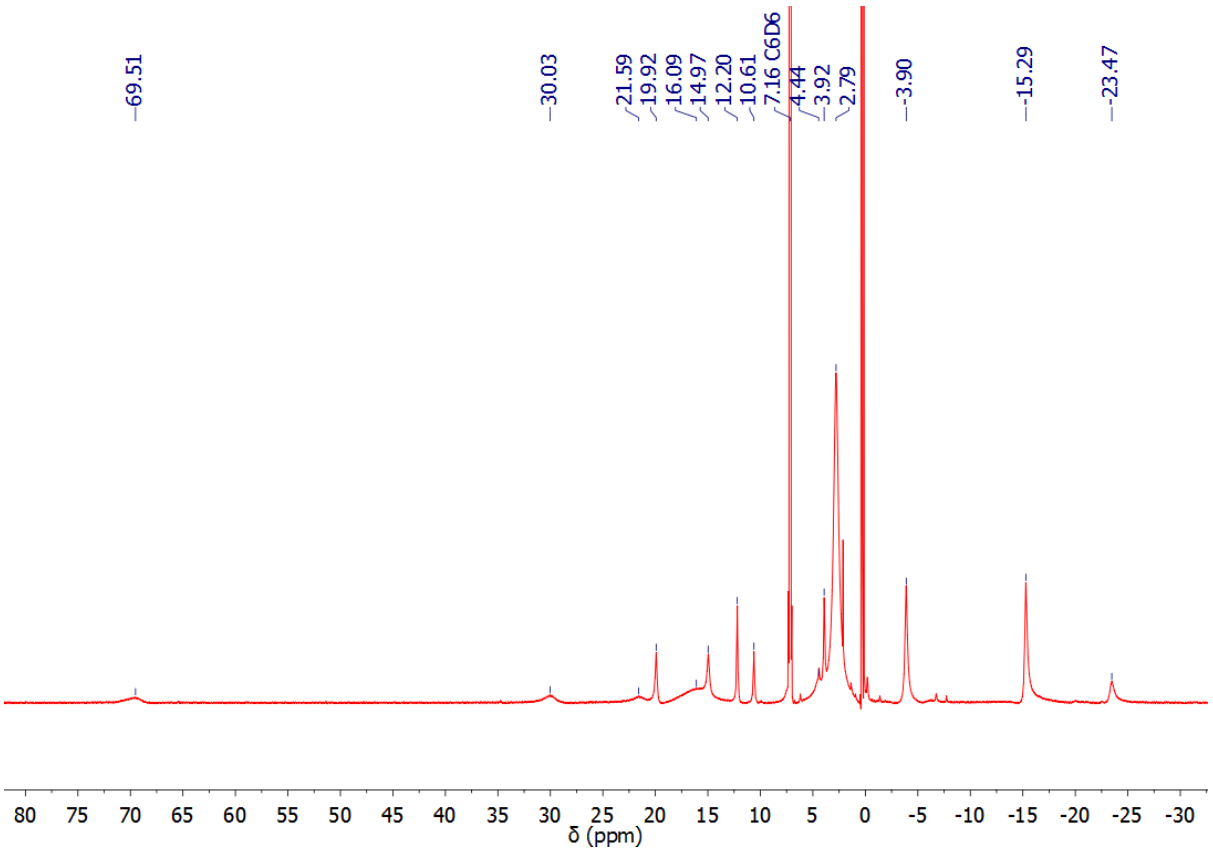


Figure S4 ^{1}H NMR spectrum of complex **3a** (500 MHz, THF-d_8)

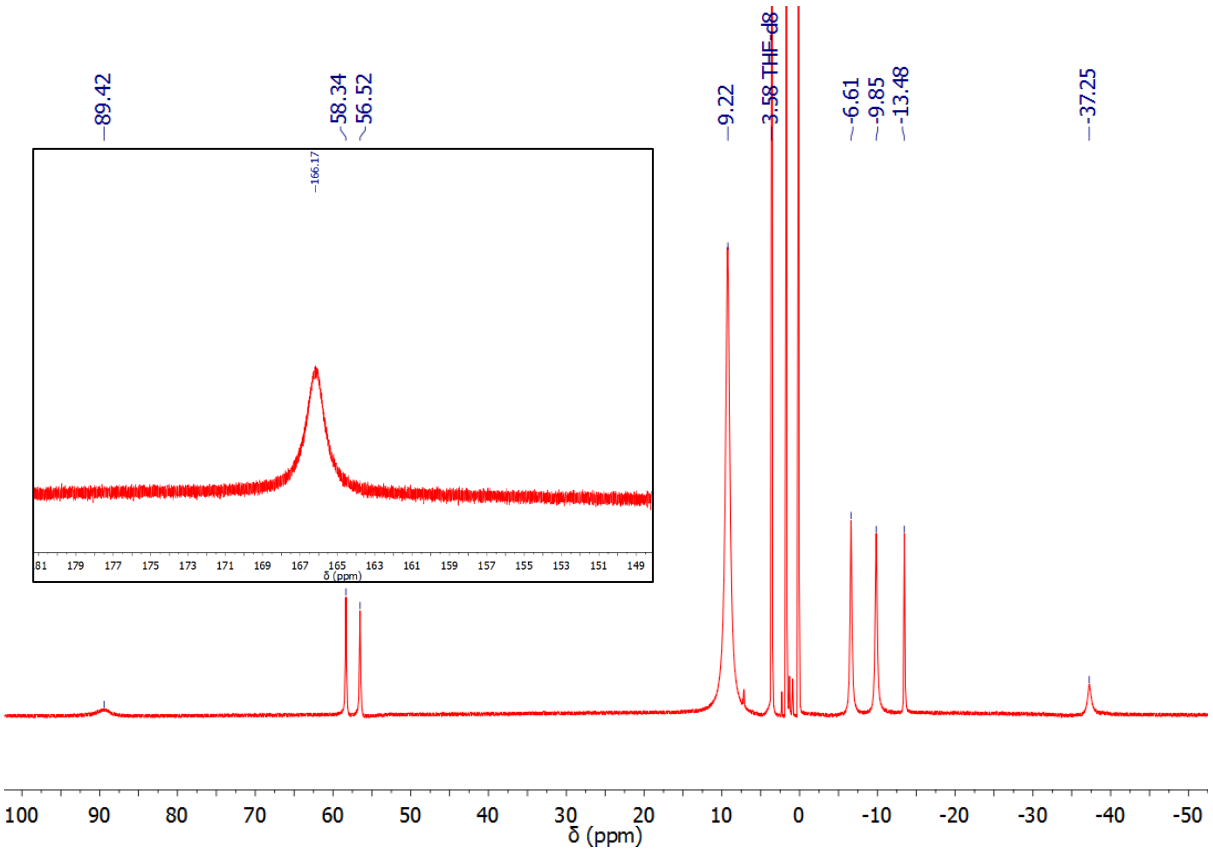


Figure S5 ^{1}H NMR spectrum of complex **4a** (500 MHz, C_6D_6)

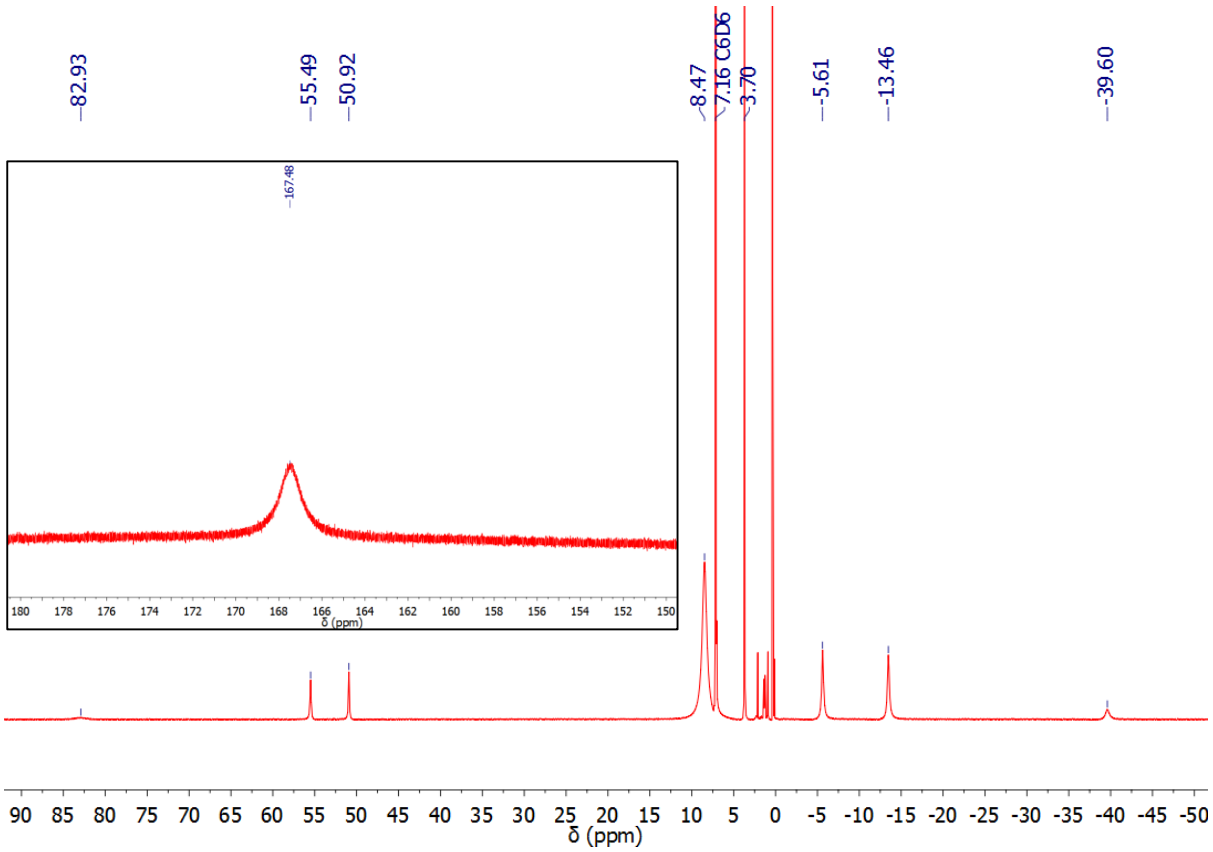
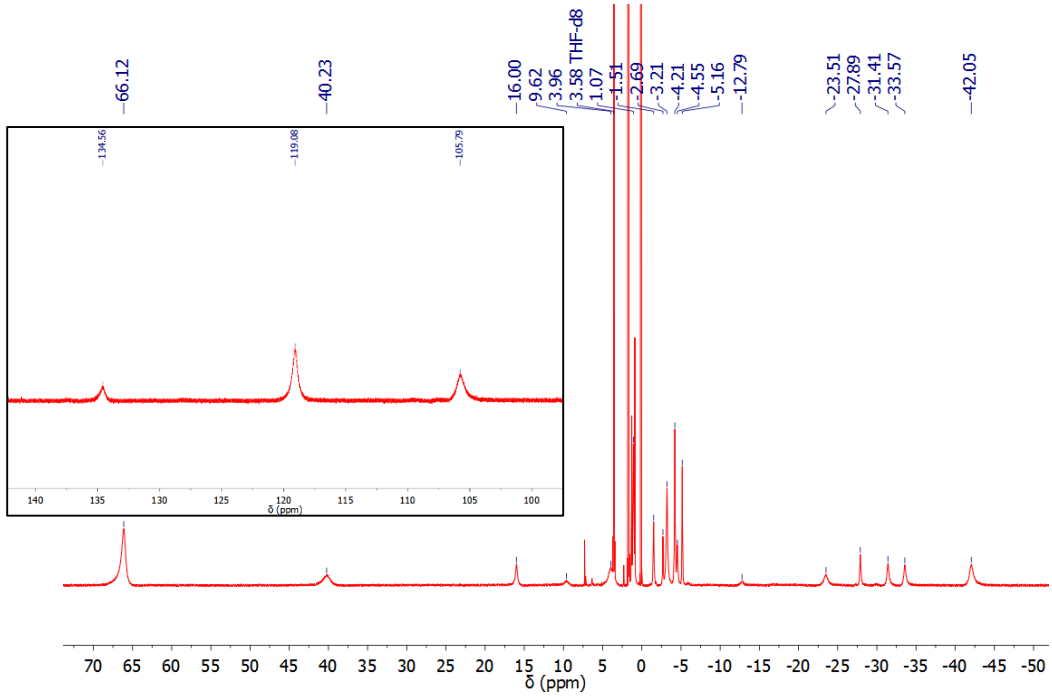
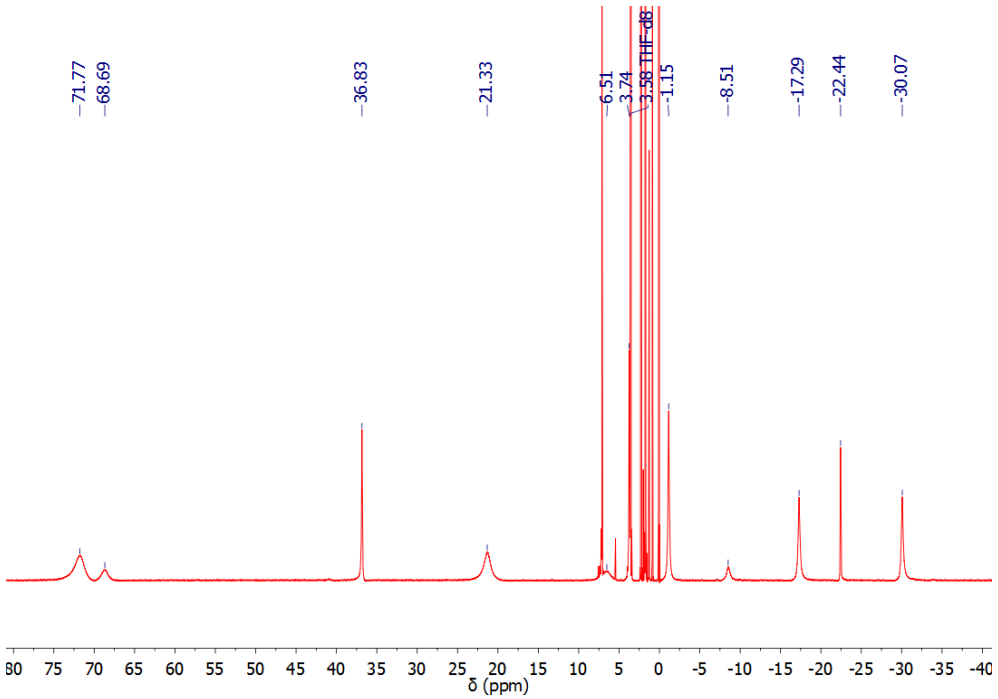


Figure S6 ^{1}H NMR spectrum of complex **1b** (500 MHz, THF-d_8)



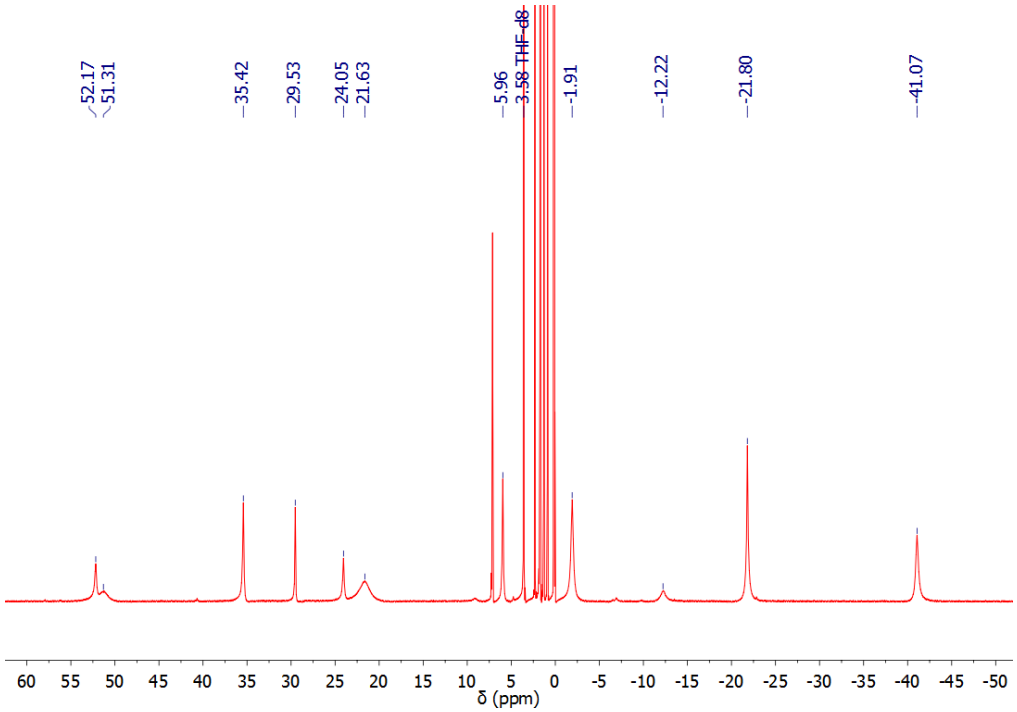
*Note. The number of resonances observed in the ^{1}H NMR spectrum of **1b** is double what would be expected based on the solid state structure. It is possible that multiple spectroscopically distinct species (e.g. monomers, dimers, etc.) are present in solution, thus giving rise to the higher than expected number of resonances. Combustion analysis and solution magnetic moment data together confirm the expected empirical formula of this complex.*

Figure S7 ^{1}H NMR spectrum of complex **1c** (500 MHz, THF-d_8)



Note. A number of resonances corresponding to residual solvent (toluene and n-hexane) are apparent in the above spectrum, despite the spectrum being obtained from a 'dry' crystalline sample of complex ***1c****. The appearance of residual solvent presumably arises through release of crystal lattice solvent on dissolution in THF-d_8 (see* ***Figure S15*** *for x-ray structure).*

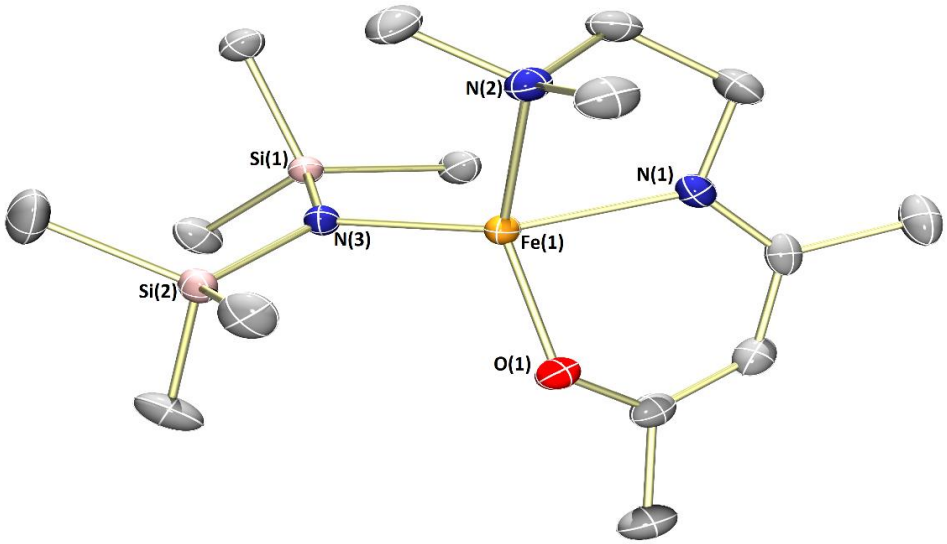
Figure S8 ^{1}H NMR spectrum of complex **3c** (500 MHz, THF-d_8)



Note. A number of resonances corresponding to residual solvent (toluene and n-hexane) are apparent in the above spectrum, despite the spectrum being obtained from a 'dry' crystalline sample of complex ***3c****. The appearance of residual solvent presumably arises through release of crystal lattice solvent on dissolution in THF-d_8 (see* ***Figure S16*** *for x-ray structure).*

X-RAY CRYSTALLOGRAPHIC DATA

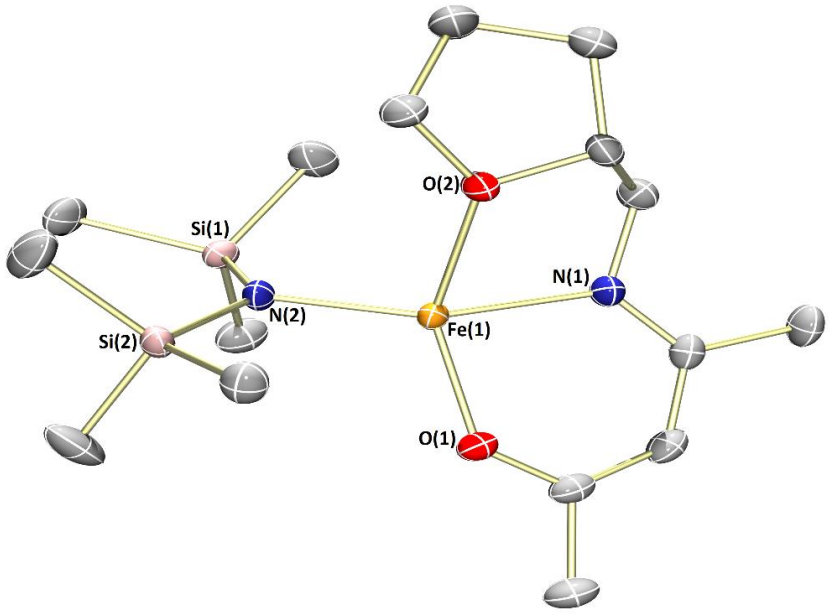
Figure S9 Complex **1a**



CCDC Code	1470307	
Formula	$C_{15}H_{35}FeN_3OSi_2$	
Formula weight	385.49	
Size	0.3657 x 0.2421 x 0.125 mm	
Crystal morphology	Green block	
Temperature	119.97(18) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.3546(6) Å	α = 90°
	b = 15.0837(4) Å	β = 127.970(9)°
	c = 17.2714(10) Å	γ = 90°
Volume	2126.6(3) Å^3	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.827 mm^{-1}	
F(000)	832	
Data collection range	2.837 ≤ θ ≤ 31.076°	
Index ranges	-14 ≤ h ≤14, -21 ≤ k ≤ 21, -24 ≤ l ≤ 23	
Reflections collected	44800	
Independent reflections	6463 [R(int) = 0.0539]	
Observed reflections	5349 [I >2σ(I)]	
Absorption correction	Gaussian	
Max. and min. transmission	0.975 and 0.95	

Refinement method	Full
Data / restraints / parameters	6463 / 0 / 209
Goodness of fit	1.055
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0393$, $wR_2 = 0.0773$
R indices (all data)	$R_1 = 0.0537$, $wR_2 = 0.0826$
Largest diff. peak and hole	0.4 and -0.261e.Å^{-3}

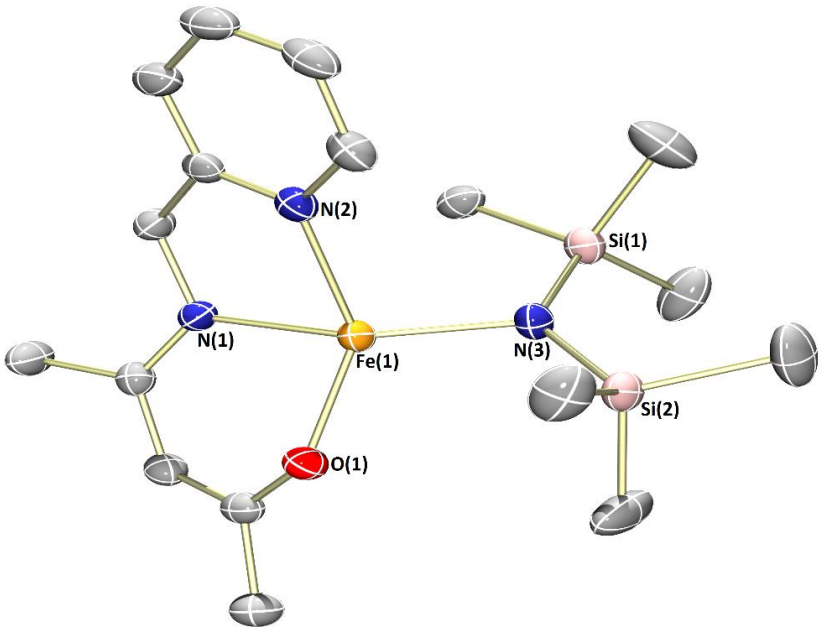
Figure S10 Complex **2a**



CCDC Code	1470308	
Formula	$C_{16}H_{34}FeN_2O_2Si_2$	
Formula weight	398.48	
Size	0.5458 x 0.4191 x 0.1544 mm	
Crystal morphology	Green plate	
Temperature	120.00(10) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.06239(9) Å	α = 90°
	b = 9.46682(8) Å	β = 91.0690(7)°
	c = 18.89946(16) Å	γ = 90°
Volume	2157.80(3) Å^3	
Z	4	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.819 mm^{-1}	

F(000)	856
Data collection range	$2.735 \leq \theta \leq 31.12°$
Index ranges	$-17 \leq h \leq 17, -13 \leq k \leq 13, -26 \leq l \leq 27$
Reflections collected	44886
Independent reflections	6597 [*R*(int) = 0.0339]
Observed reflections	5798 [$I > 2\sigma(I)$]
Absorption correction	Gaussian
Max. and min. transmission	0.878 and 0.702
Refinement method	Full
Data / restraints / parameters	6597 / 0 / 216
Goodness of fit	1.074
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0282$, $wR_2 = 0.0661$
R indices (all data)	$R_1 = 0.035$, $wR_2 = 0.0697$
Largest diff. peak and hole	0.366 and -0.232e.Å^{-3}

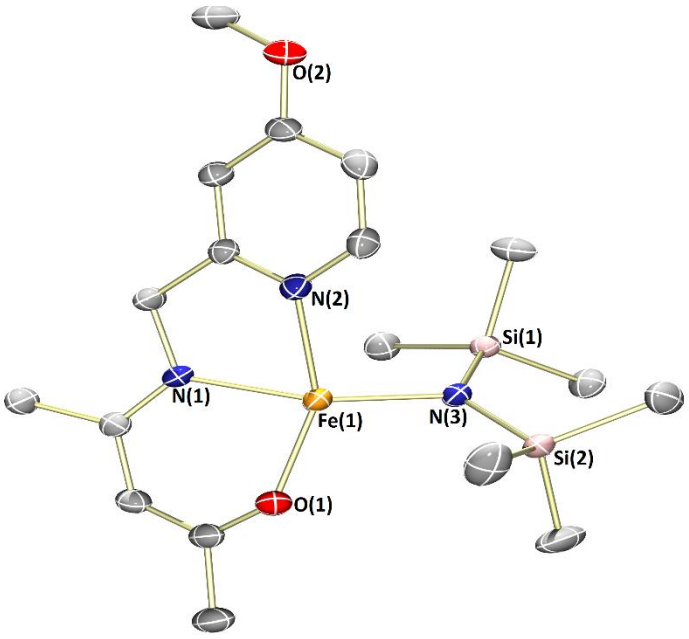
Figure S11 Complex **3a**



CCDC Code	1470309
Formula	$C_{17}H_{31}FeN_3OSi_2$
Formula weight	405.48
Size	0.4586 x 0.1651 x 0.109 mm
Crystal morphology	Intense green plate
Temperature	120.01(10) K
Wavelength	0.71073 Å [Mo-K_α]
Crystal system	Monoclinic

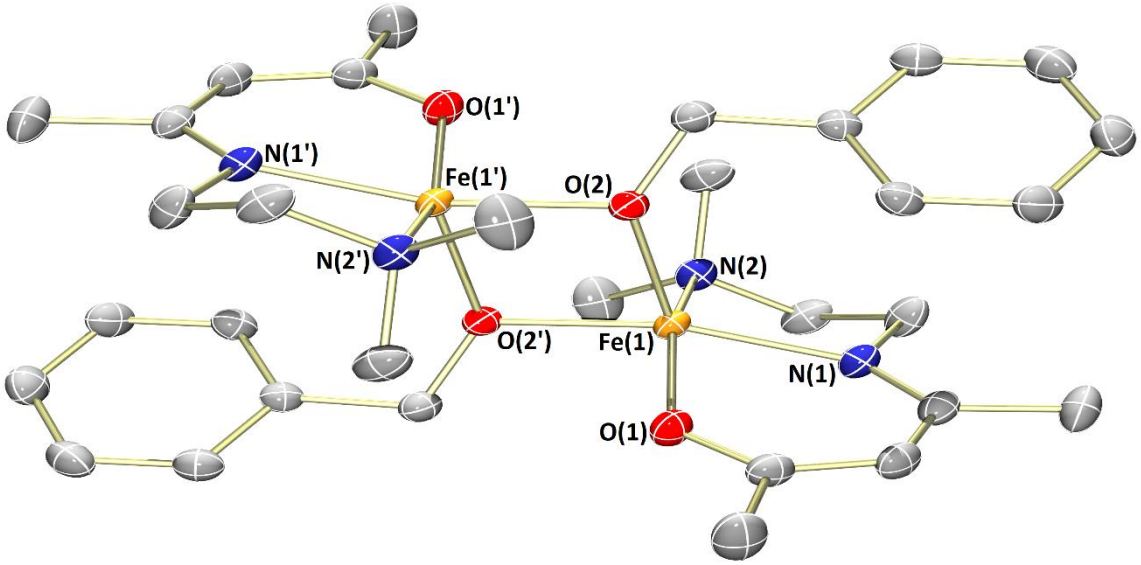
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.8709(5) Å	α = 90°
	b = 16.3660(5) Å	β = 103.421(3)°
	c = 8.6899(3) Å	γ = 90°
Volume	2195.50(12) Å^3	
Z	4	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.805 mm^{-1}	
F(000)	864	
Data collection range	$2.712 \leq \theta \leq 29.665°$	
Index ranges	$-21 \leq h \leq 21$, $-22 \leq k \leq 22$, $-12 \leq l \leq 10$	
Reflections collected	38643	
Independent reflections	5793 [R(int) = 0.0574]	
Observed reflections	4655 [$I > 2\sigma(I)$]	
Absorption correction	Gaussian	
Max. and min. transmission	0.977 and 0.905	
Refinement method	Full	
Data / restraints / parameters	5793 / 0 / 225	
Goodness of fit	1.063	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0434, wR_2 = 0.0845	
R indices (all data)	R_1 = 0.0615, wR_2 = 0.0915	
Largest diff. peak and hole	0.435 and -0.311e.Å^{-3}	

Figure S12 Complex **4a**



CCDC Code	1470310	
Formula	$C_{18}H_{33}FeN_3O_2Si_2$	
Formula weight	435.5	
Size	0.4065 x 0.174 x 0.1573 mm	
Crystal morphology	Green block	
Temperature	120.00(10) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 8.8657(6) Å	α = 90.425(4)°
	b = 10.8724(6) Å	β = 100.153(5)°
	c = 12.2568(5) Å	γ = 97.601(5)°
Volume	1152.16(11) Å^3	
Z	2	
Density (calculated)	1.255 Mg/m^3	
Absorption coefficient	0.774 mm^{-1}	
F(000)	464	
Data collection range	$2.814 \leq \theta \leq 31.03°$	
Index ranges	$-12 \leq h \leq 11$, $-15 \leq k \leq 14$, $-17 \leq l \leq 17$	
Reflections collected	24682	
Independent reflections	6749 [*R*(int) = 0.0535]	
Observed reflections	5501 [$I > 2\sigma(I)$]	
Absorption correction	Gaussian	
Max. and min. transmission	0.952 and 0.905	
Refinement method	Full	
Data / restraints / parameters	6749 / 0 / 244	
Goodness of fit	1.06	
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0428, wR_2 = 0.0996	
R indices (all data)	R_1 = 0.0555, wR_2 = 0.1088	
Largest diff. peak and hole	0.715 and -0.491e.Å^{-3}	

Figure S13 Complex **1b**

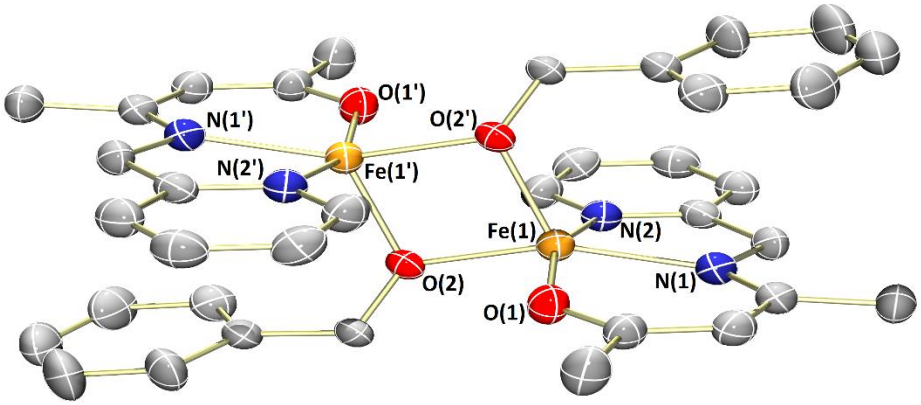


CCDC Code	1470323	
Formula	$C_{32}H_{48}Fe_2N_4O_4$	
Formula weight	664.44	
Size	0.6512 x 0.1049 x 0.1016 mm	
Crystal morphology	Orange plate	
Temperature	120.00(10) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 7.8337(3) Å	α = 84.382(3)°
	b = 10.2379(3) Å	β = 72.596(4)°
	c = 10.7448(4) Å	γ = 86.906(3)°
Volume	818.06(6) Å^3	
Z	1	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	0.927 mm^{-1}	
F(000)	352	
Data collection range	2.862 ≤ θ ≤ 31.142°	
Index ranges	-11 ≤ *h* ≤10, -14 ≤ *k* ≤ 14, -15 ≤ *l* ≤ 15	
Reflections collected	35409	
Independent reflections	4970 [*R*(int) = 0.0382]	
Observed reflections	4603 [$I > 2\sigma(I)$]	
Absorption correction	Gaussian	
Max. and min. transmission	0.926 and 0.709	
Refinement method	Full	

Data / restraints / parameters	4970 / 0 / 194
Goodness of fit	1.086
Final *R* indices [*I* >2σ(*I*)]	R_1 = 0.0318, wR_2 = 0.0707
R indices (all data)	R_1 = 0.0359, wR_2 = 0.0723
Largest diff. peak and hole	0.494 and -0.284e.Å^{-3}

Figure S14 Complex **3b**

*Note. Crystals of complex **3b** were generally observed to be of very poor quality. However, a suitable single crystal was eventually found and a data set obtained. The asymmetric unit of complex **3b** was found to contain two crystallographically-distinct [Fe(L)OBn] units, with each representing half of a (μ^2-OBn)$_2$ bridged dimer. The two halves of each dimer are crystallographically related through inversion. After some preliminary structural refinement, a very large residual electron density peak was observed in the vicinity of Fe2, along with further, more diffuse electron density. Therefore, the [Fe(L)OBn] unit initially containing Fe2 was modelled as being split over two positions with SOFs of 0.75 for the major component (containing Fe2A) and 0.25 for the minor component (containing Fe2B). One of the β-ketiminate methyl groups (C23) was best modelled as being common to both disorder components. Unfortunately, the OBn group of the minor disorder component appeared disordered further, and could not be satisfactorily refined without the use of EADP constraints. Therefore, this group was refined isotropically. The disordered nature of this structure accounts for the large number of checkCIF alerts.*

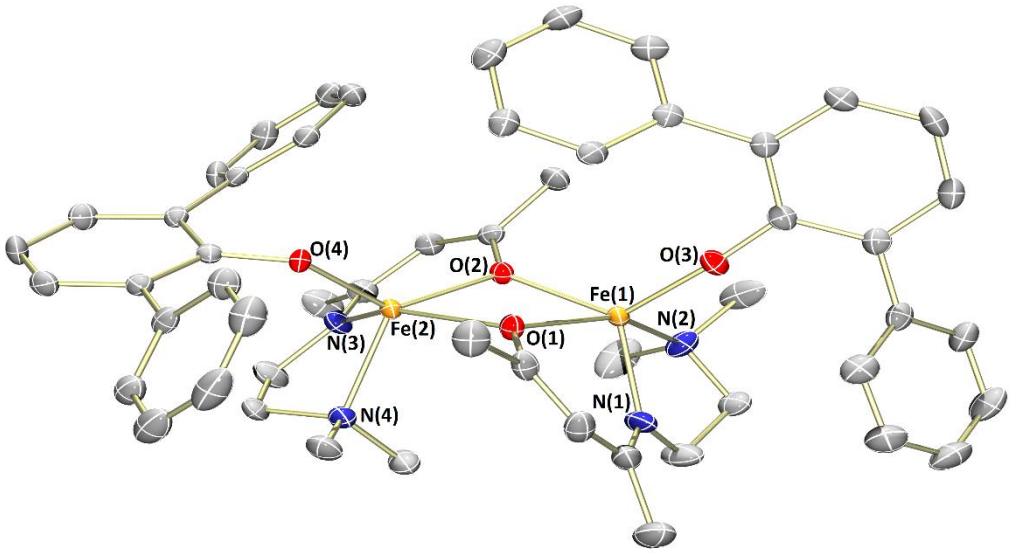


CCDC Code	1470324	
Formula	$C_{36}H_{40}Fe_2N_4O_4$	
Formula weight	704.42	
Size	0.1677 x 0.1112 x 0.0678 mm	
Crystal morphology	Dark red plate	
Temperature	120.00(10) K	
Wavelength	1.54184 Å [Cu-K_α]	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	*a* = 8.2528(4) Å	α = 90°
	b = 18.5226(6) Å	β = 119.539(7)°
	c = 24.7956(13) Å	γ = 90°
Volume	3297.7(3) Å^3	

Z	4
Density (calculated)	1.419 Mg/m^3
Absorption coefficient	7.42 mm^{-1}
F(000)	1472
Data collection range	$3.145 \leq \theta \leq 76.889°$
Index ranges	$-6 \leq h \leq 10$, $-23 \leq k \leq 23$, $-31 \leq l \leq 30$
Reflections collected	53543
Independent reflections	6864 [*R*(int) = 0.1062]
Observed reflections	5515 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	1 and 0.54604
Refinement method	Full
Data / restraints / parameters	6864 / 5 / 553
Goodness of fit	1.2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0861$, $wR_2 = 0.1848$
R indices (all data)	$R_1 = 0.102$, $wR_2 = 0.1922$
Largest diff. peak and hole	0.689 and -0.506e.$Å^{-3}$

Figure S15 Complex **1c**

*Note. The asymmetric unit of complex **1c** was found to consist of two structurally analogous dimers (only one shown below), and two regions of co-crystallised solvent. One region could be easily modelled as a molecule of toluene with an SOF of 1. The contents of the additional solvent region were a little less clear, though could be modelled as containing either one molecule of toluene (SOF = 0.66) or one molecule of hexane (SOF = 0.33) (this explains the non-integer value in the chemical formula shown below). A number of geometric and ADP constraints/restraints were required to generate chemically sensible structures of the disordered solvent.*

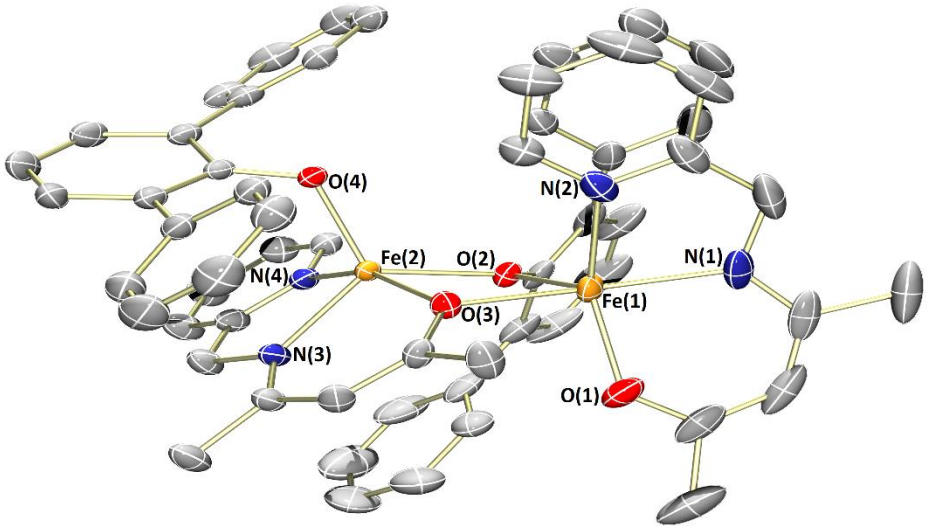


CCDC Code	1470383
Formula	$C_{60.83}H_{69}Fe_2N_4O_4$

Formula weight	1031.9	
Size	0.47 x 0.27 x 0.06 mm	
Crystal morphology	Orange plate	
Temperature	120.00(10) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 34.0413(13) Å	α = 90°
	b = 15.5968(6) Å	β = 98.031(3)°
	c = 20.4395(7) Å	γ = 90°
Volume	10745.7(7) Å^3	
Z	8	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.59 mm^{-1}	
F(000)	4368	
Data collection range	2.747 ≤ θ ≤ 25.351°	
Index ranges	-41 ≤ h ≤40, -18 ≤ k ≤ 18, -24 ≤ l ≤ 23	
Reflections collected	157681	
Independent reflections	19635 [R(int) = 0.0987]	
Observed reflections	15942 [I >2σ(I)]	
Absorption correction	Gaussian	
Max. and min. transmission	0.998 and 0.99	
Refinement method	Full	
Data / restraints / parameters	19635 / 17 / 1311	
Goodness of fit	1.121	
Final R indices [I >2σ(I)]	R_1 = 0.0608, wR_2 = 0.1085	
R indices (all data)	R_1 = 0.0819, wR_2 = 0.1158	
Largest diff. peak and hole	0.747 and -0.487e.Å^{-3}	

Figure S16 Complex **3c**

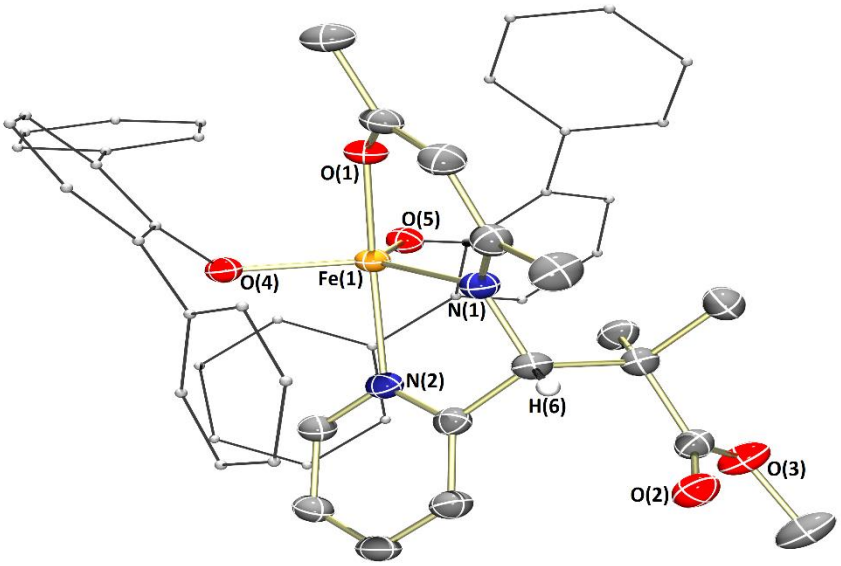
Note. Regions of diffuse, poorly resolved electron density were observed in the crystalline lattice, but could not be modelled satisfactorily as solvent (toluene or hexane). This residual electron density was removed using the SQUEEZE routine in PLATON. In all, electron density (125 electrons) pertaining to 2.5 molecules of toluene (or hexane) per unit cell was removed. This is included in the chemical formula and as a result produces many errors in checkCIF which should be ignored.



CCDC Code	1470384	
Formula	$C_{62.38}H_{57}Fe_2N_4O_4$	
Formula weight	1038.32	
Size	0.3462 x 0.2548 x 0.0594 mm	
Crystal morphology	Orange block	
Temperature	120.00(10) K	
Wavelength	0.71073 Å [Mo-K_α]	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.7953(2) Å	α = 90°
	b = 14.0417(3) Å	β = 91.2680(17)°
	c = 30.0899(6) Å	γ = 90°
Volume	5404.83(18) Å^3	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.588 mm^{-1}	
F(000)	2173	
Data collection range	2.937 ≤ θ ≤ 28.281°	
Index ranges	-17 ≤ h ≤17, -18 ≤ k ≤ 18, -40 ≤ l ≤ 40	
Reflections collected	140618	
Independent reflections	13322 [R(int) = 0.0579]	
Observed reflections	11966 [I >2σ(I)]	
Absorption correction	Multi-scan	
Max. and min. transmission	1 and 0.89445	
Refinement method	Full	
Data / restraints / parameters	13322 / 0 / 617	

Goodness of fit	1.191
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0749$, $wR_2 = 0.1619$
R indices (all data)	$R_1 = 0.086$, $wR_2 = 0.1672$
Largest diff. peak and hole	0.794 and -0.641e.Å^{-3}

Figure S17 Complex **3c'**



CCDC Code	1470385	
Formula	$C_{52}H_{47}FeN_2O_5$	
Formula weight	835.76	
Size	0.1631 x 0.113 x 0.0591 mm	
Crystal morphology	Black fragment	
Temperature	120.00(10) K	
Wavelength	1.54184 Å [Cu-K_α]	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 11.8082(3) Å	α = 84.253(2)°
	b = 12.0560(4) Å	β = 75.270(2)°
	c = 15.9552(4) Å	γ = 75.487(2)°
Volume	2125.01(11) Å^3	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	3.254 mm^{-1}	
F(000)	878	
Data collection range	$3.79 \leq \theta \leq 76.13°$	
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-20 \leq l \leq 19$	

Reflections collected	52301
Independent reflections	8832 [R(int) = 0.0691]
Observed reflections	8288 [I >2σ(I)]
Absorption correction	multi-scan
Max. and min. transmission	1 and 0.77371
Refinement method	Full
Data / restraints / parameters	8832 / 0 / 546
Goodness of fit	1.046
Final R indices [I >2σ(I)]	R_1 = 0.0471, wR_2 = 0.1214
R indices (all data)	R_1 = 0.0498, wR_2 = 0.1251
Largest diff. peak and hole	0.624 and -0.916e.Å^{-3}