Electronic Supplementary Material (ESI) for Dalton Transactions.

Quasilinear 3d-Metal(I) Complexes [KM(N(Dipp)SiR$_3$)$_2$] (M = Cr – Co) – Structural Diversity, Solution State Behaviour and Reactivity

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1 NMR Spectra

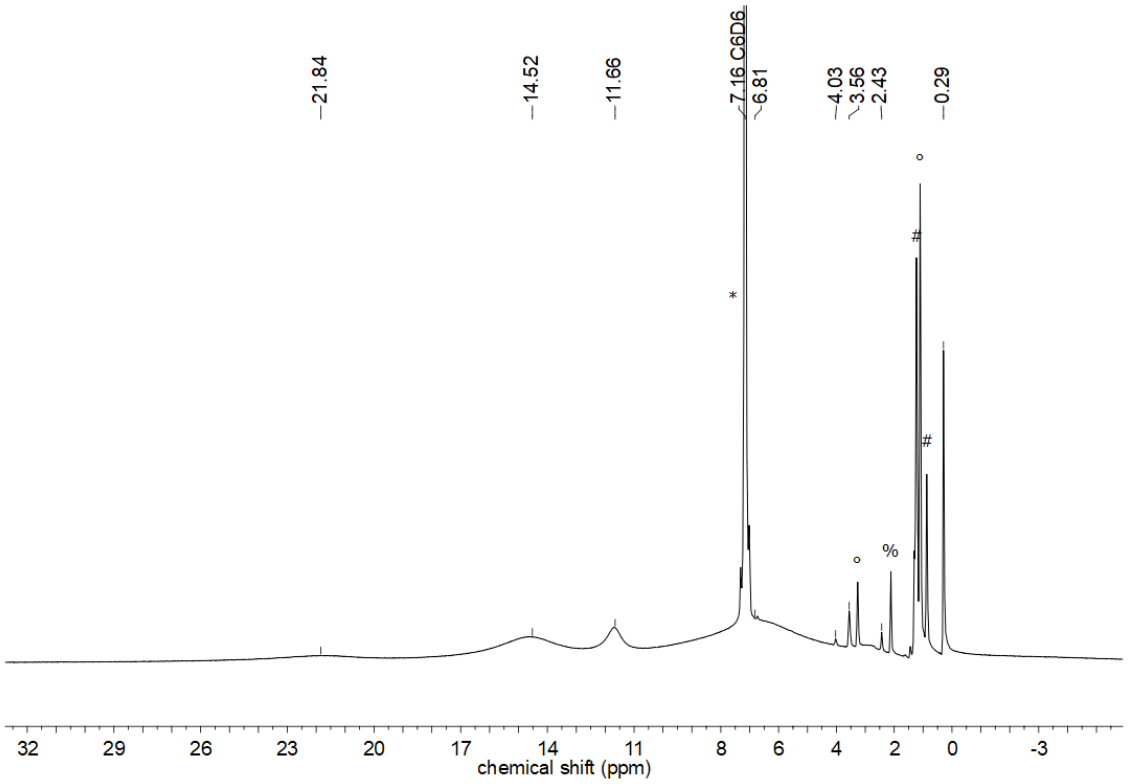

Figure S 1. ^{1}H NMR spectrum (500.1 MHz) of [KCr(L^{1})$_2$] (**1**) in C_6D_6 at 300 K. (* solvent, ° diethyl ether, $^{\#}$ *n*-pentane, $^{\%}$ toluene)

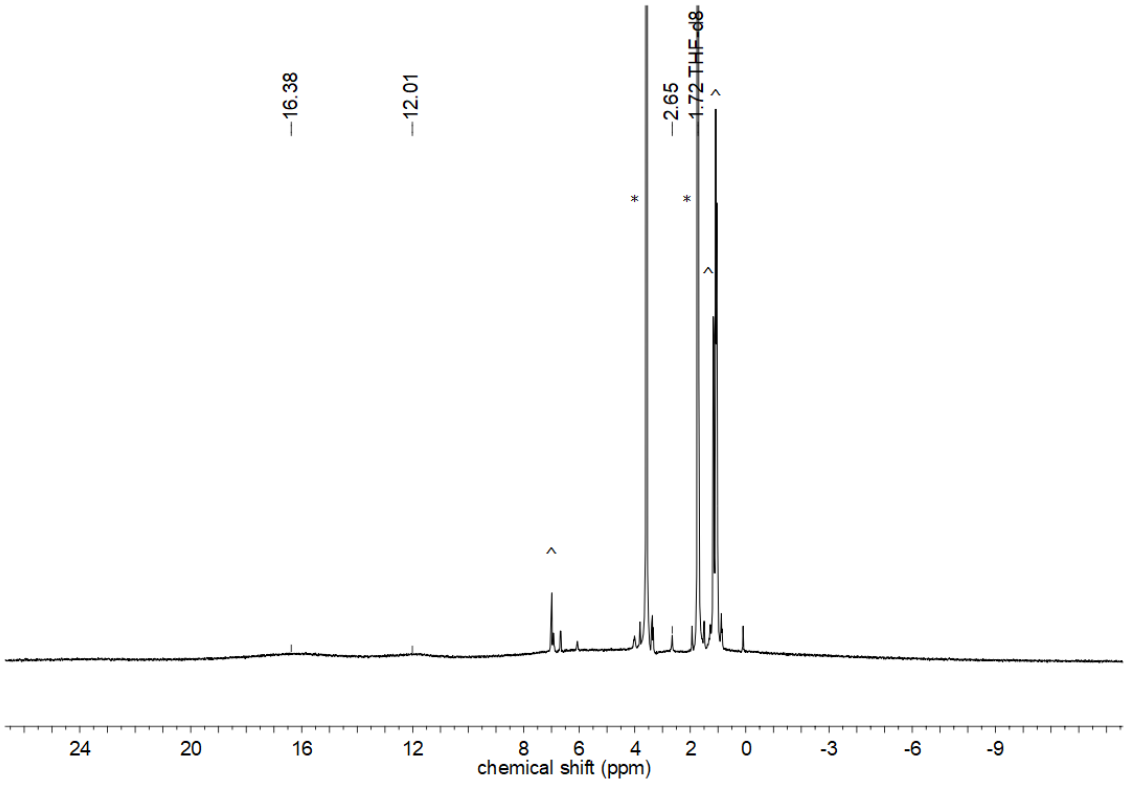

Figure S 2. ^{1}H NMR spectrum (500.1 MHz) of [KCr(L^{1})$_2$] (**1**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

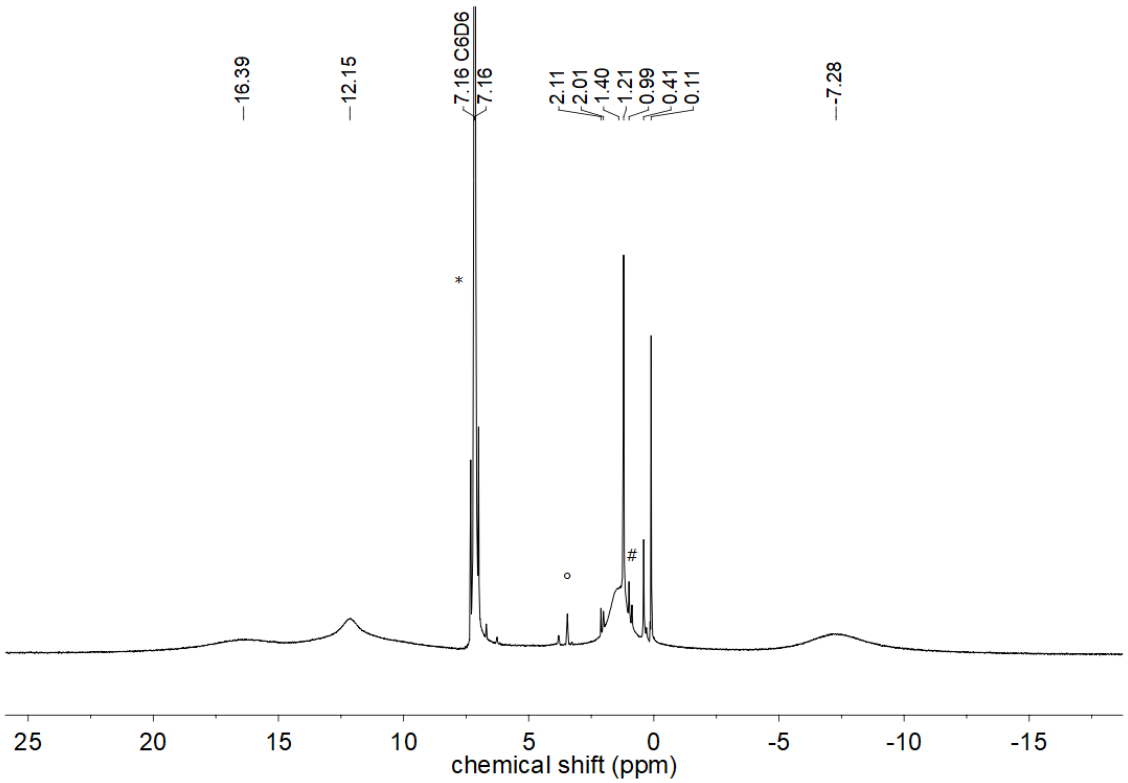

Figure S 3. ^{1}H NMR spectrum (500.1 MHz) of [KMn(L^{2})$_2$] (**2**) in C_6D_6 at 300 K. (* solvent, ° diethyl ether, $^{\#}$ *n*-pentane)

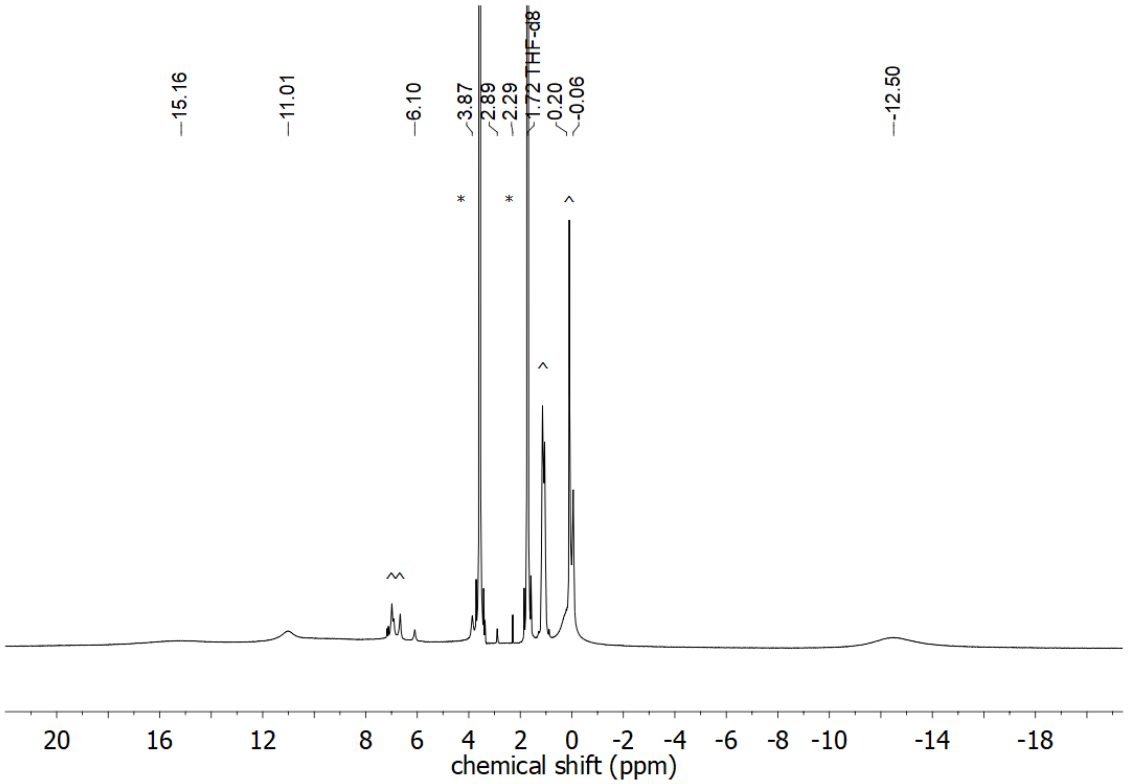

Figure S 4. ^{1}H NMR spectrum (500.1 MHz) of [KMn(L^{2})$_2$] (**2**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

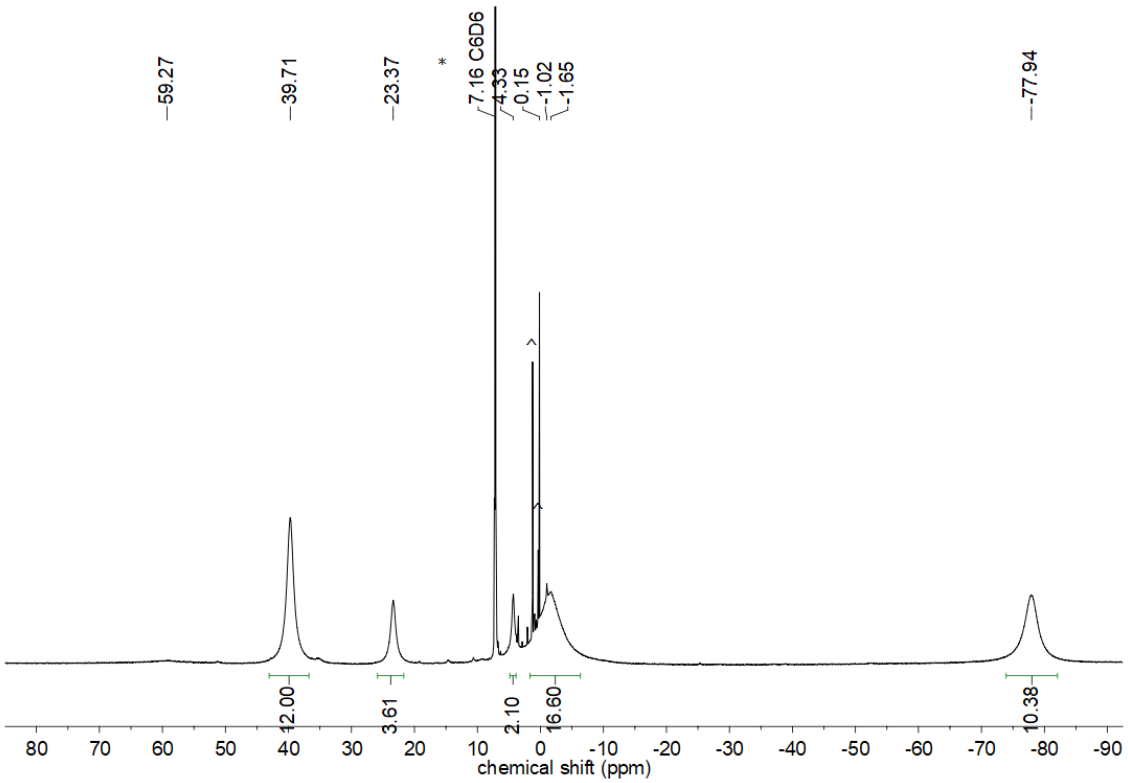

Figure S 5. ^{1}H NMR spectrum (500.1 MHz) of [KFe(L^{2})$_2$] (**3**) in C_6D_6 at 300 K. (* solvent, ^ impurities)

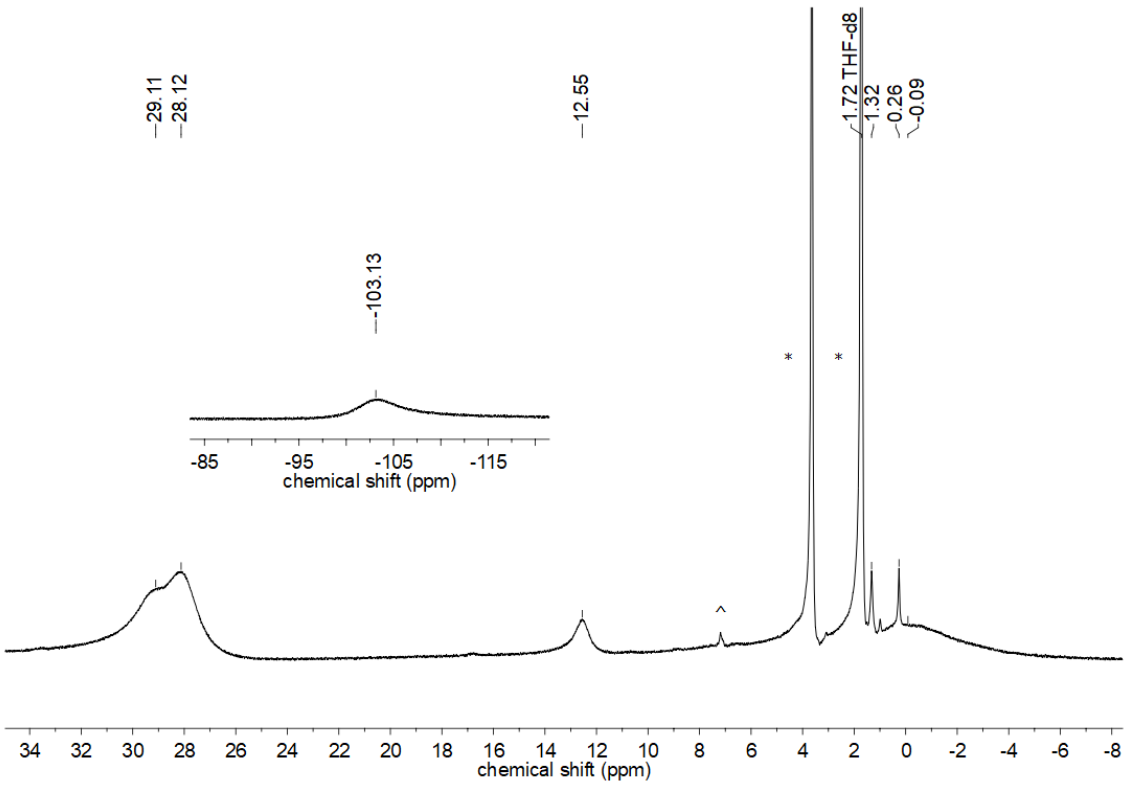

Figure S 6. ^{1}H NMR spectrum (500.1 MHz) of [KFe(L^{2})$_2$] (**3**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

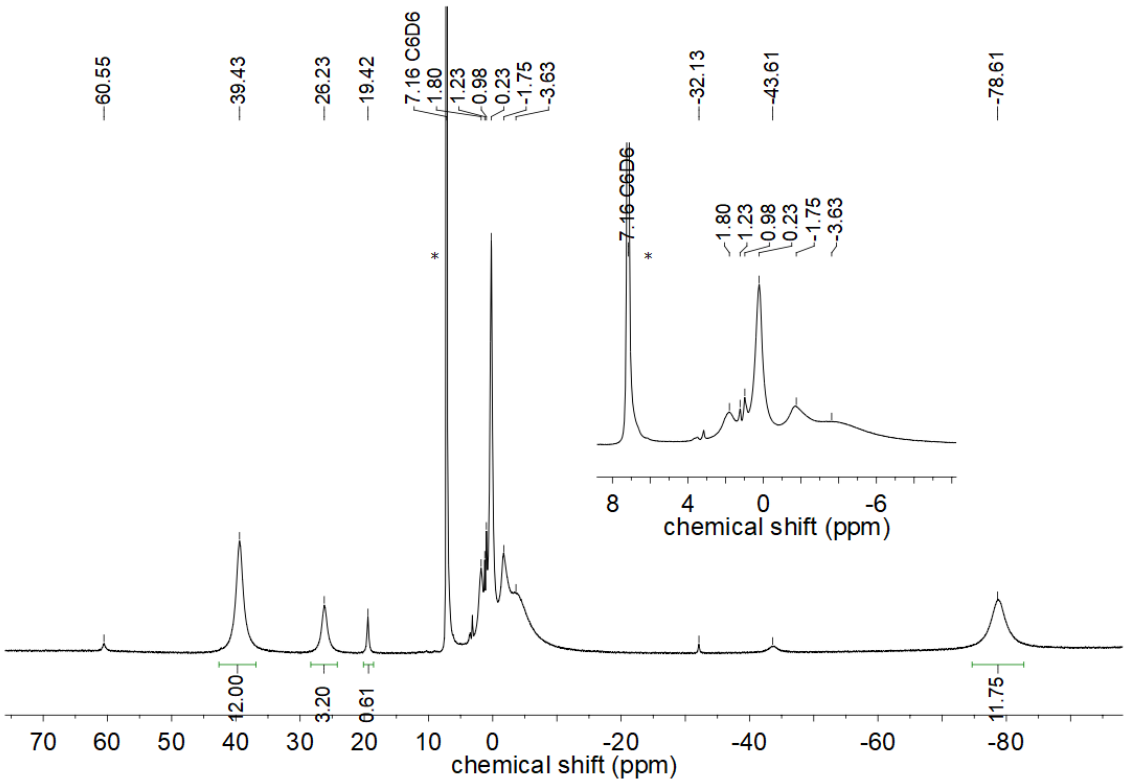

Figure S 7. ^{1}H NMR spectrum (500.1 MHz) of [K(DMAP)$_2$Fe(L^2)$_2$] (**3**.2DMAP) in C_6D_6 at 300 K. (* solvent, ^ impurities)

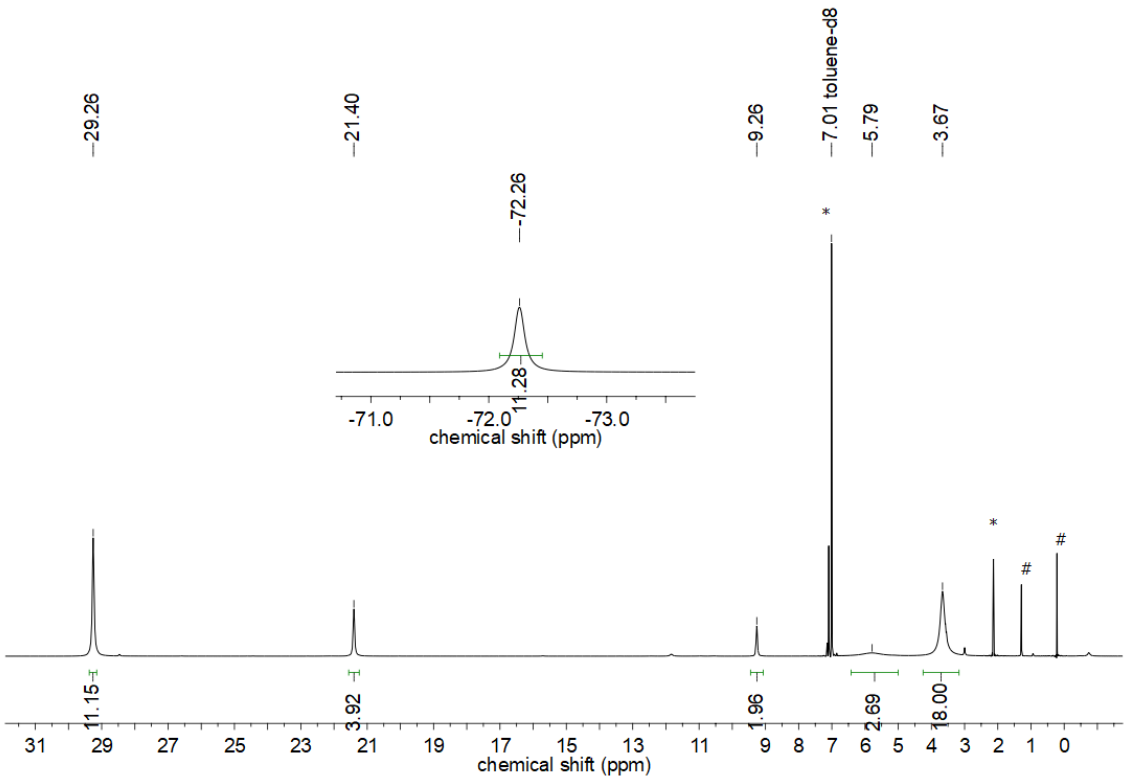

Figure S 8. ^{1}H NMR spectrum (500.1 MHz) of [KCo(L^2)$_2$] (**4**) in toluene-d_8 at 300 K. (* solvent, $^{\#}$ *n*-pentane)

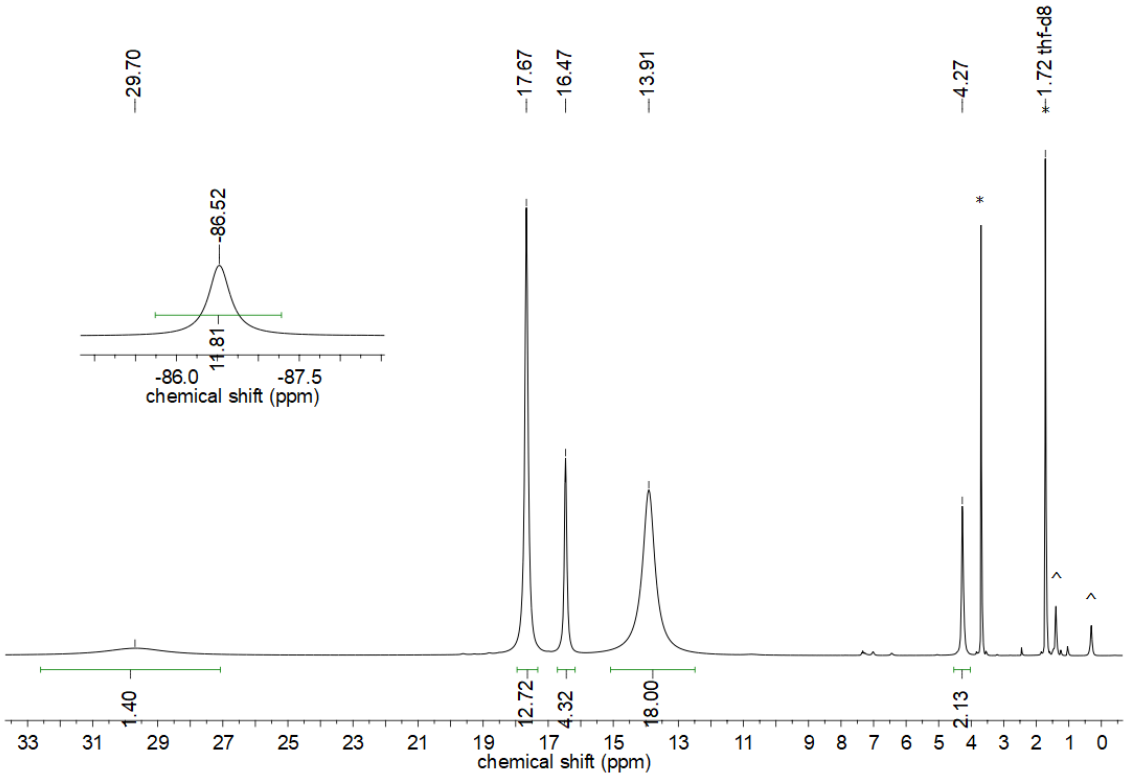

Figure S 9. ^{1}H NMR spectrum (500.1 MHz) of [KCo(L^{2})$_2$] (**4**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

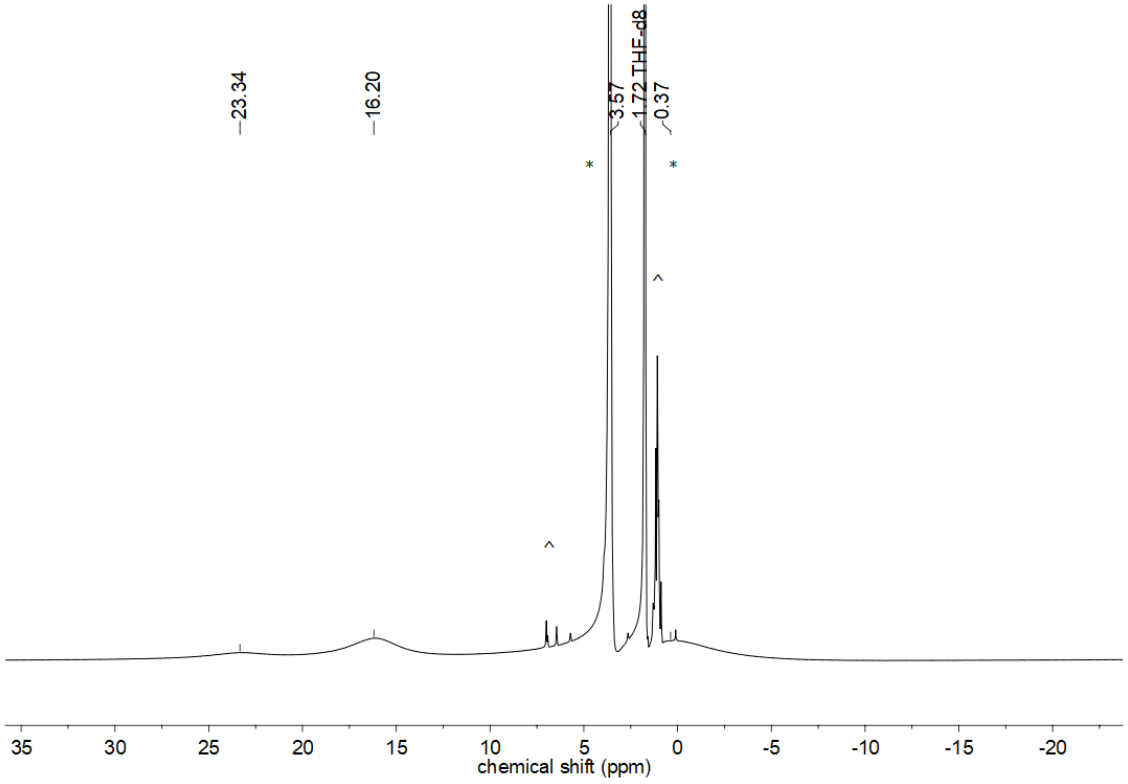

Figure S 10. ^{1}H NMR spectrum (500.1 MHz) of [K{18c6}][Cr(L^{1})$_2$] (**5**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

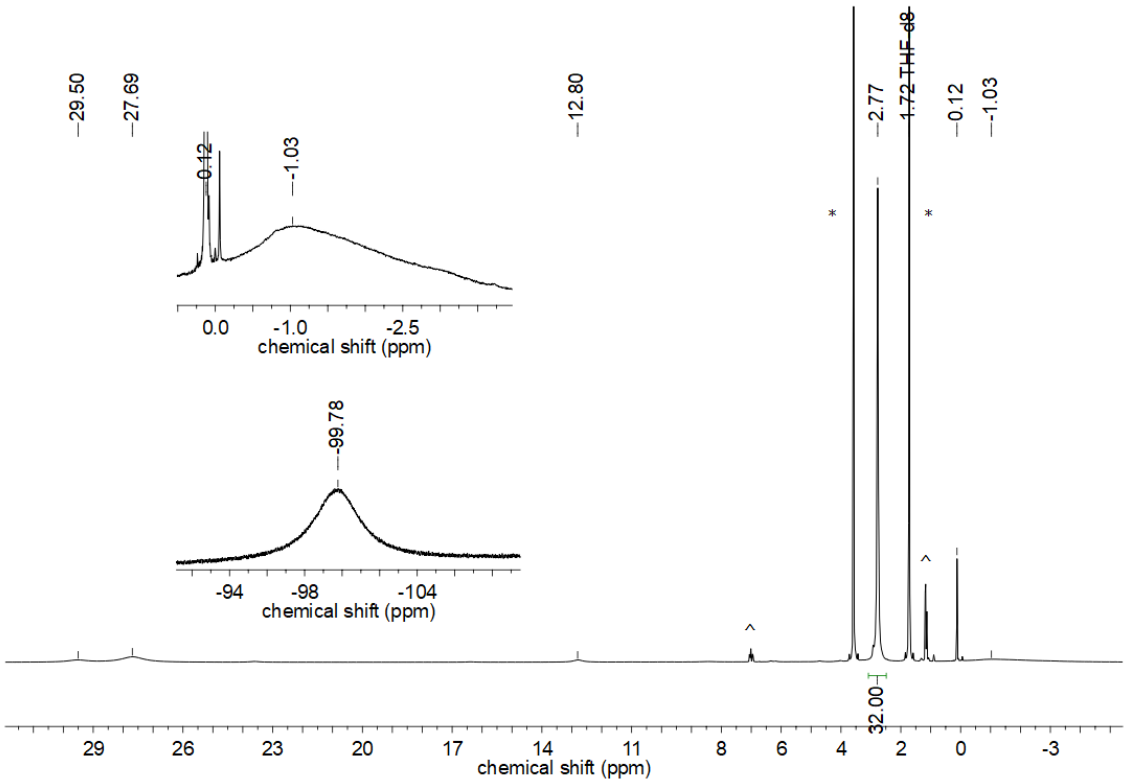

Figure S 11. ^{1}H NMR spectrum (500.1 MHz) of [Li{12c4}$_2$][Fe(L^2)$_2$] (**6**) in THF-d_8 at 300 K. (* solvent, ^ impurities)

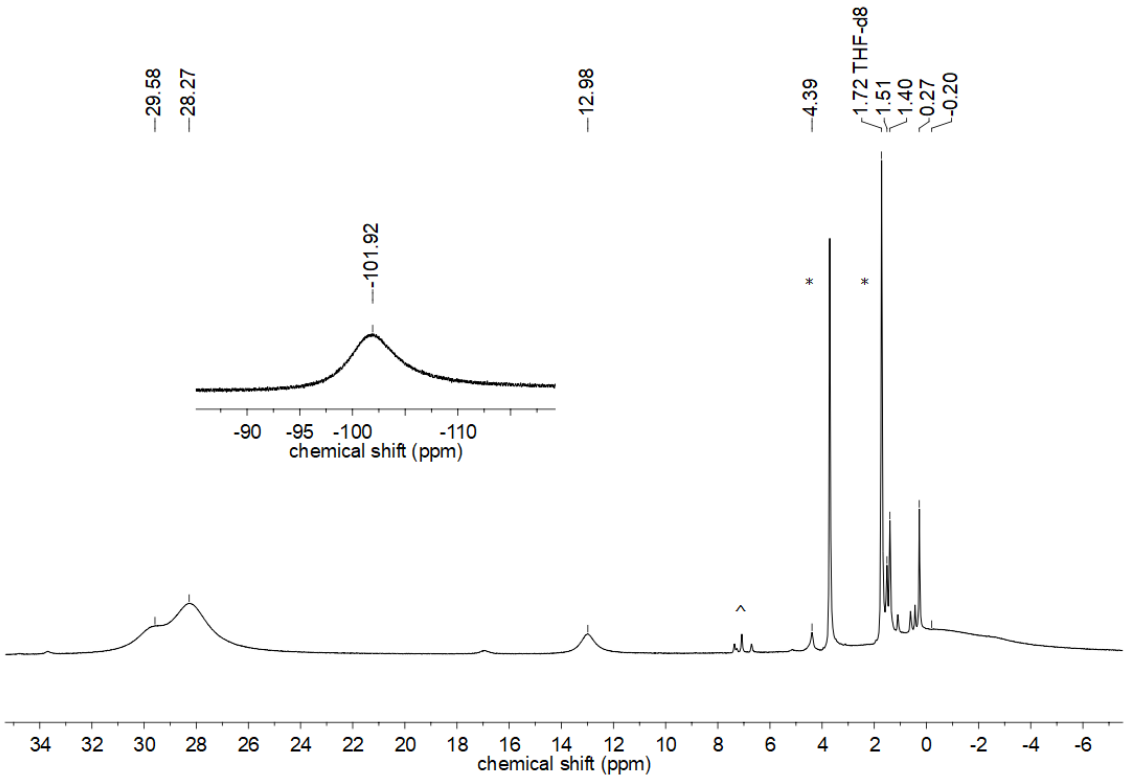

Figure S 12. *In Situ* ^{1}H NMR spectrum (300.2 MHz) of [LiFe(L^2)$_2$] in THF-d_8 at 300 K. (* solvent, ^ impurities)

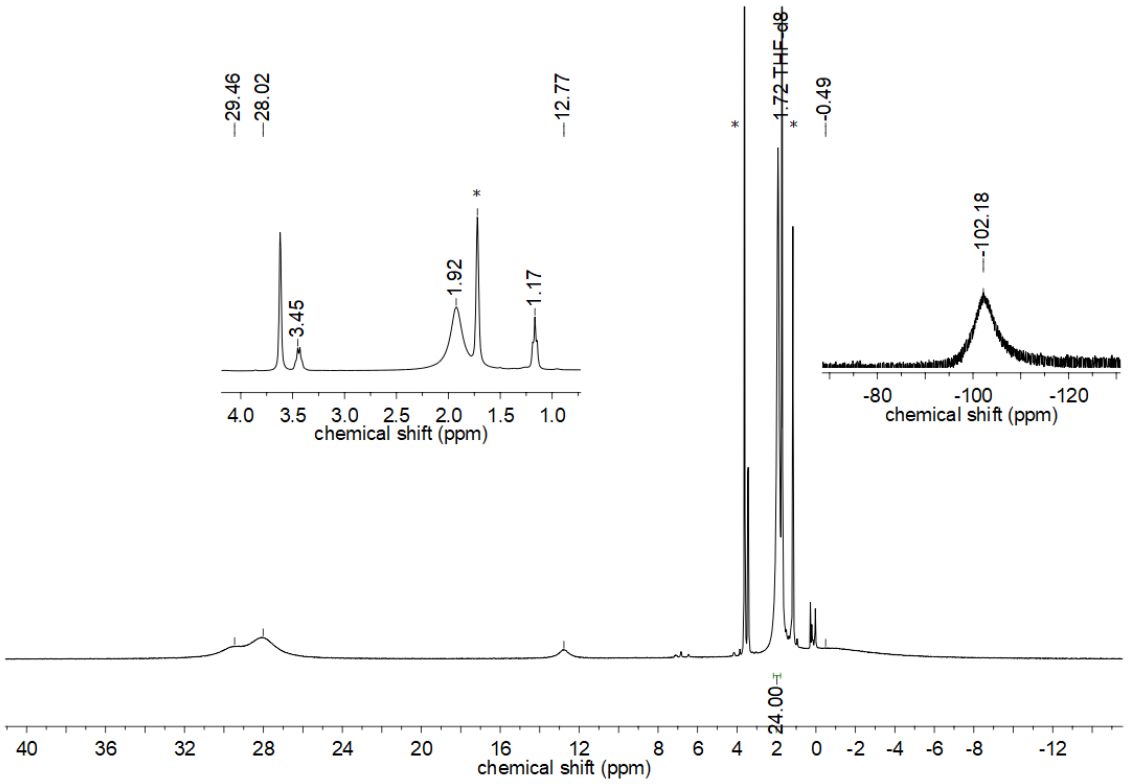

Figure S 13. ^{1}H NMR spectrum (500.1 MHz) of [Na{18c6}][Fe(L^{2})$_2$] (**7**) in THF-d_8 at 300 K. (* solvent)

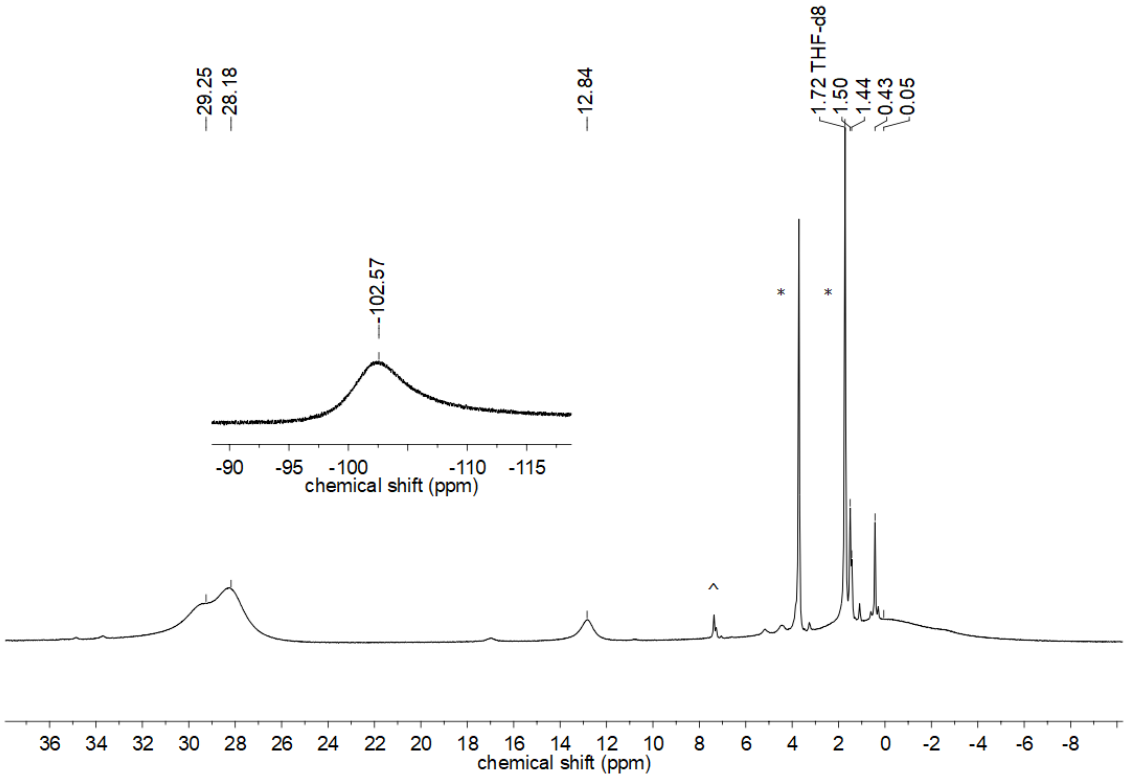

Figure S 14. *In Situ* ^{1}H NMR spectrum (300.2 MHz) of [NaFe(L^{2})$_2$] in THF-d_8 at 300 K. (* solvent, ^ impurities)

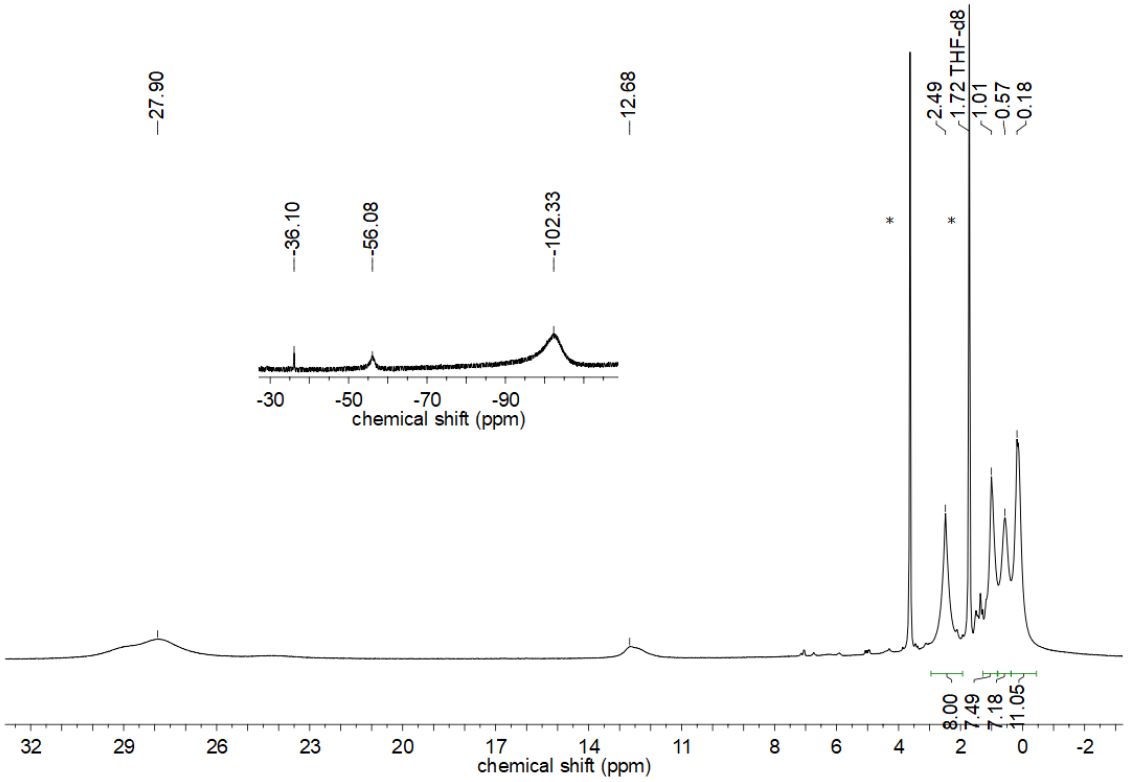

Figure S 15. ^{1}H NMR spectrum (500.1 MHz) of [NBu$_4$][Fe(L^2)$_2$] (**8**) in THF-d_8 at 300 K. (* solvent)

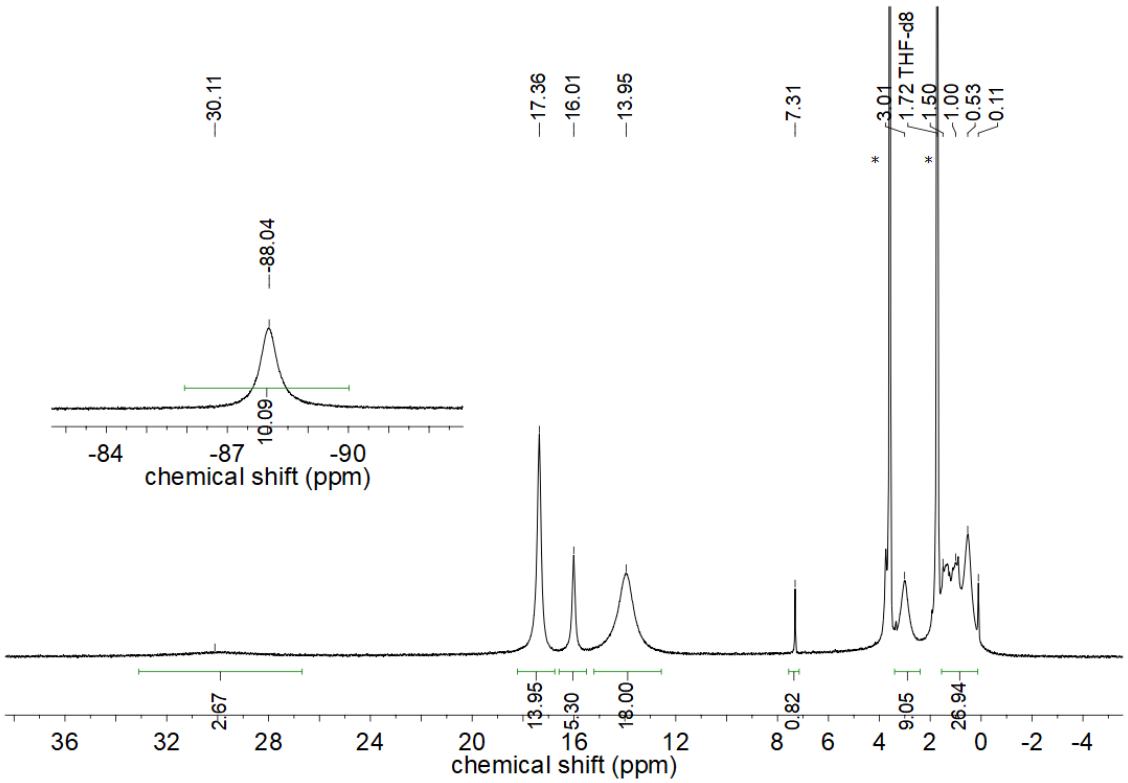

Figure S 16. ^{1}H NMR spectrum (500.1 MHz) of [Bu$_4$N][Co(L^2)$_2$] (**9**) in THF-d_8 at 300 K. (* solvent)

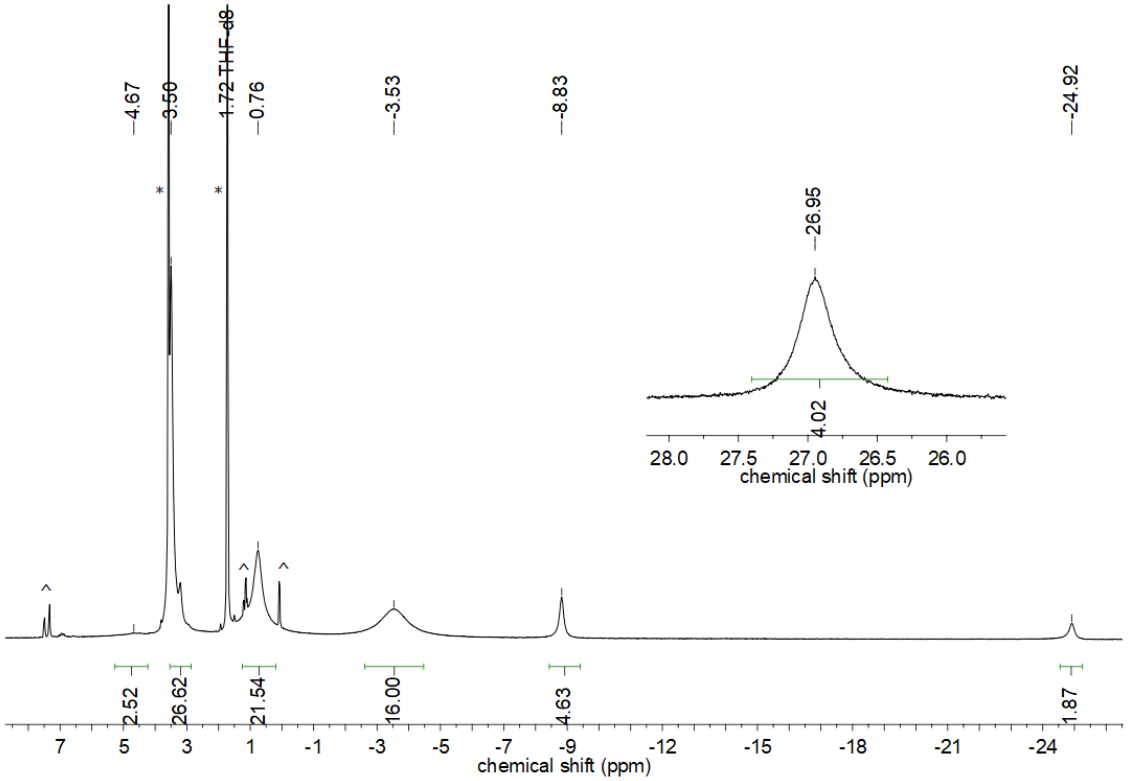

Figure S 17. ^{1}H NMR spectrum (300.2 MHz) of [K{18c6}][Fe(L^{2})$_2$)(η^{2}-PhCCPh)] (**10**) in THF-d_8 at 300 K. (* solvent, ^ impurities and residual diphenyl acetylene)

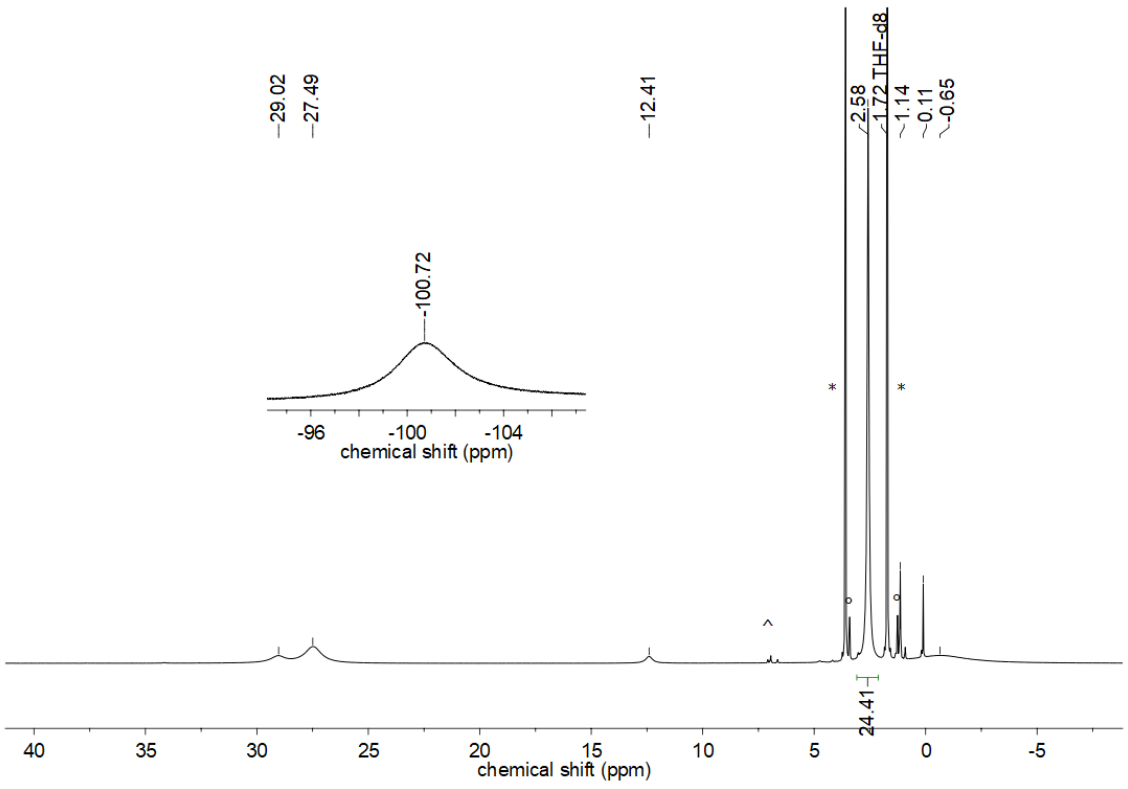

Figure S 18. ^{1}H NMR spectrum (500.1 MHz) of [K{18c6}][Fe(L^{2})$_2$] in THF-d_8 at 300 K. (* solvent, ° diethyl ether, ^ impurities)

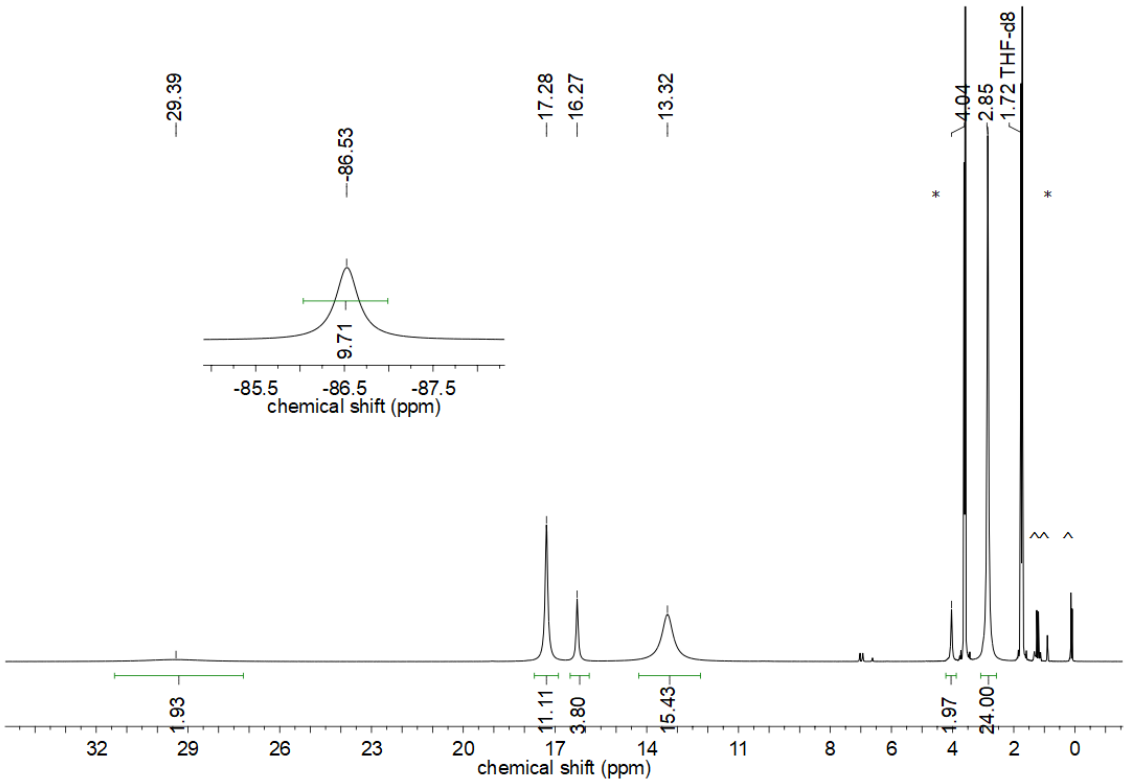

Figure S 19. ^{1}H NMR spectrum (500.1 MHz) of [K{18c6}][Co(L^{2})$_2$] in THF-d_8 at 300 K. (* solvent, ^ impurities)

Temperature-dependent ^{1}H NMR spectra of 4

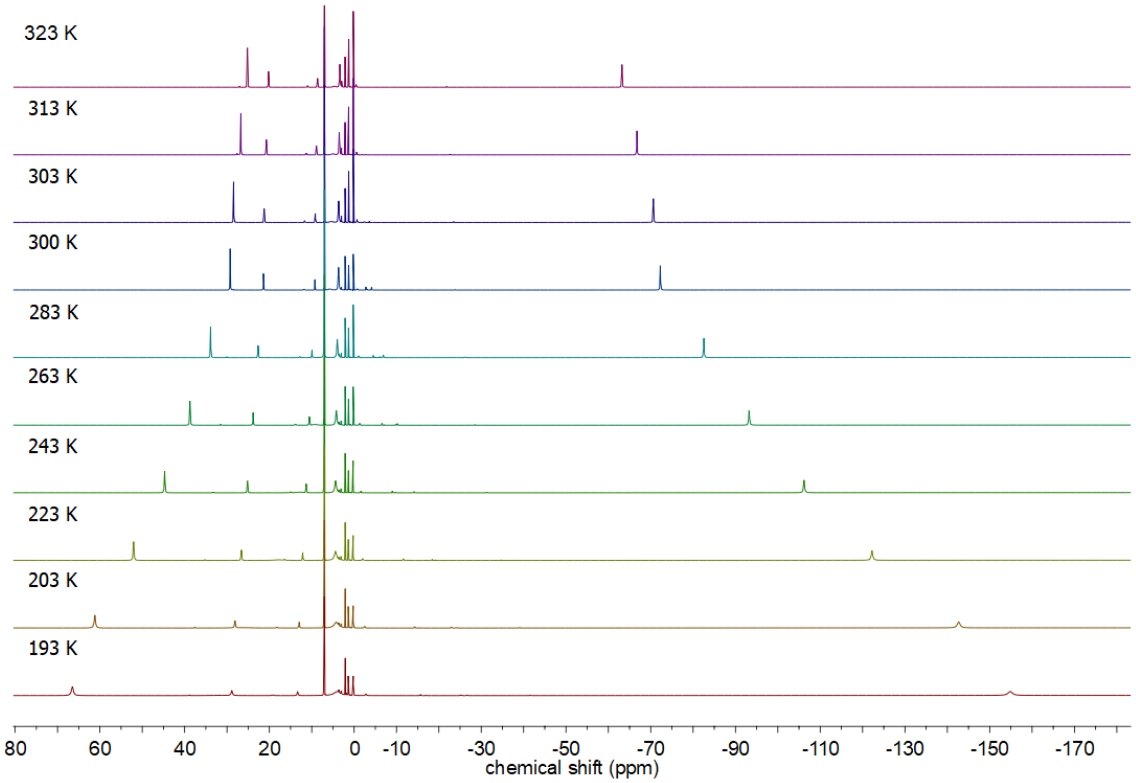

Figure S 20. Temperature-dependent ^{1}H NMR spectrum (500.1 MHz) of [KCo(L^{2})$_2$] (**4**) in toluene-d_8 from 323 K to 193 K.

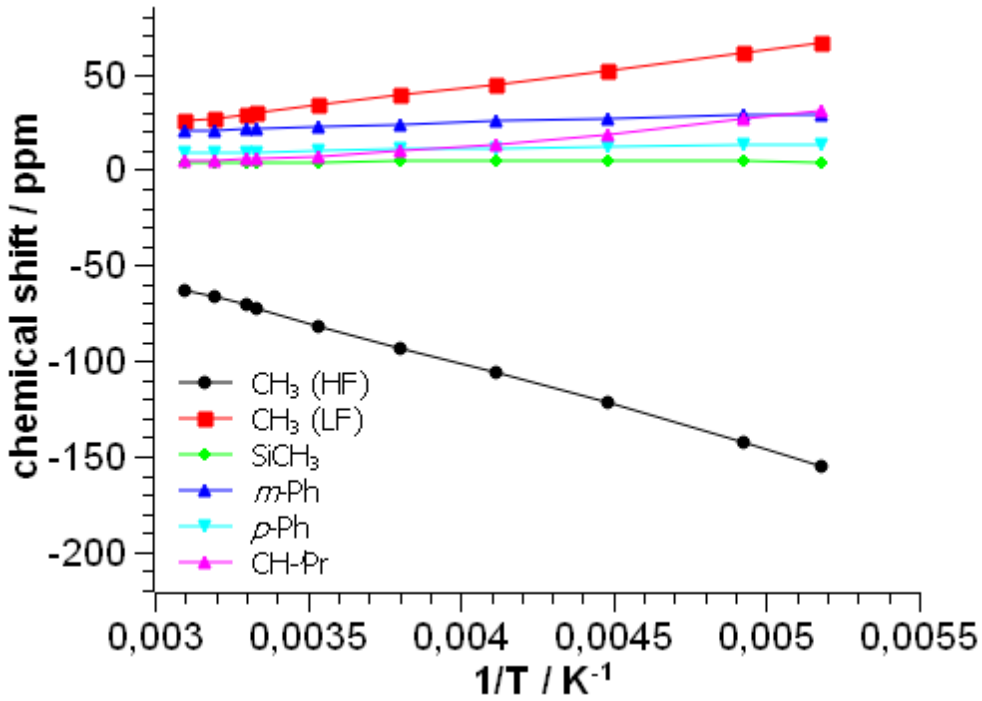

Figure S 21. Curie-Weiss plot of the temperature dependent ^{1}H NMR spectrum of [KCo(L^{2})$_2$] (**4**) in toluene-d_8 (HF: high field; LF: low field).

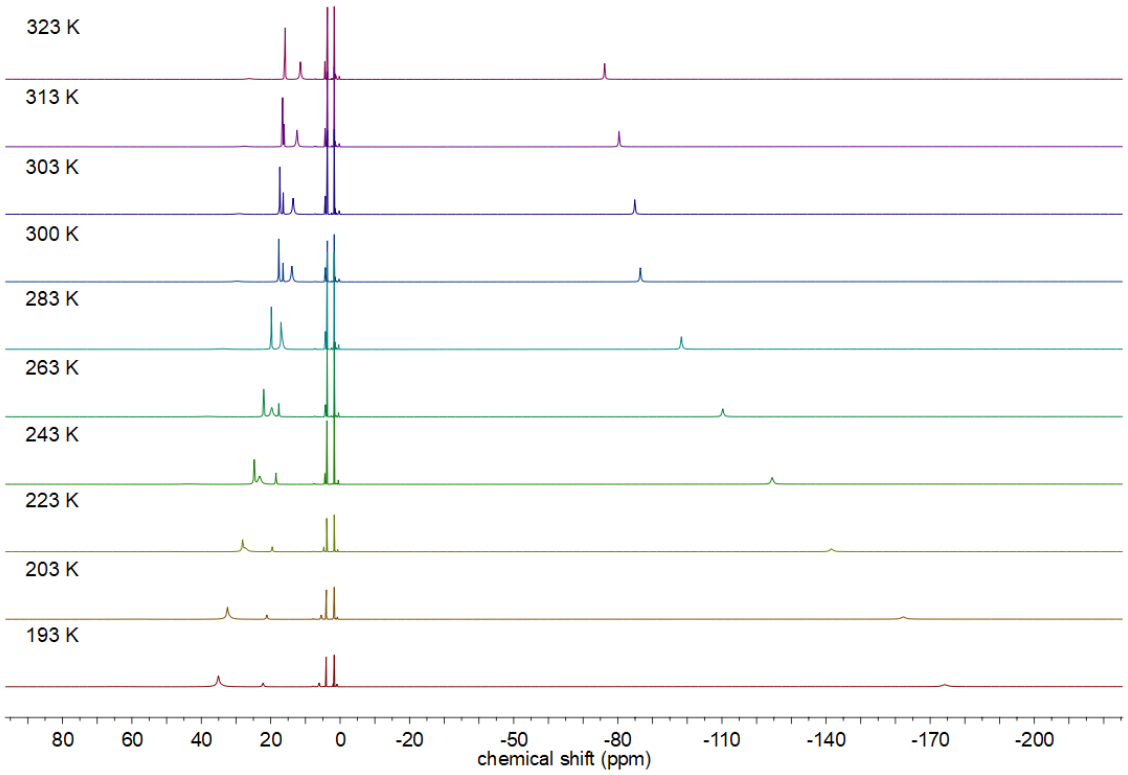

Figure S 22. Temperature-dependent ^{1}H NMR spectrum (500.1 MHz) of [KCo(L^{2})$_2$] (**4**) in THF-d_8 from 323 K to 193 K.

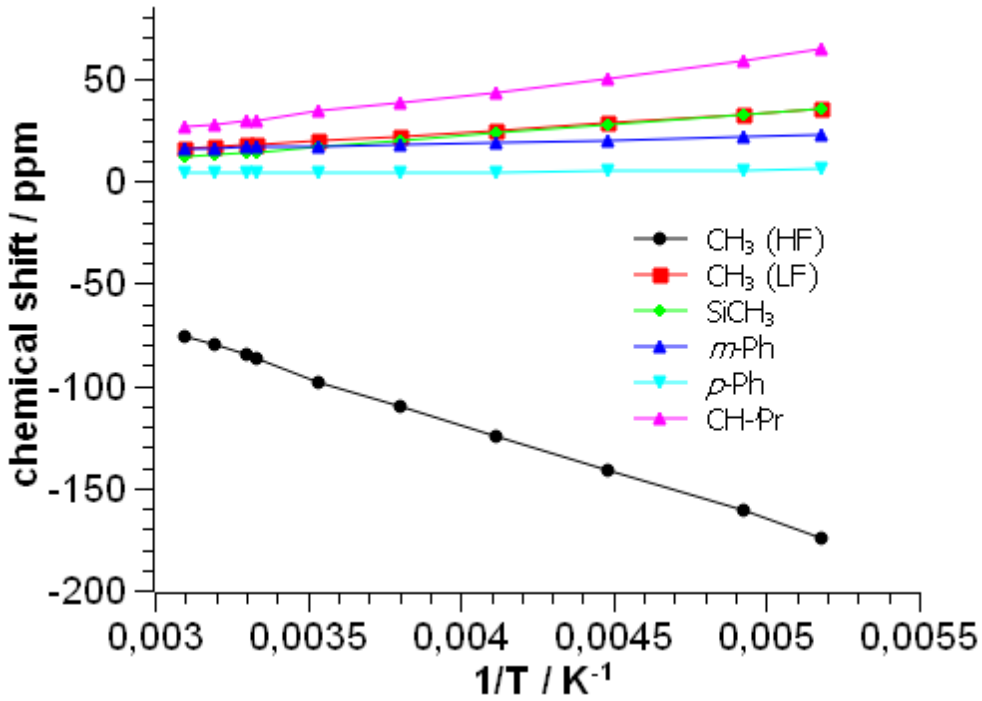

Figure S 23. Curie-Weiss plot of the temperature dependent ^{1}H NMR spectrum of [KCo(L^{2})$_2$] (**4**) in THF-d_8 (HF: high field; LF: low field).

Gradual addition of coordinating solvent to 4 in toluene-d_8

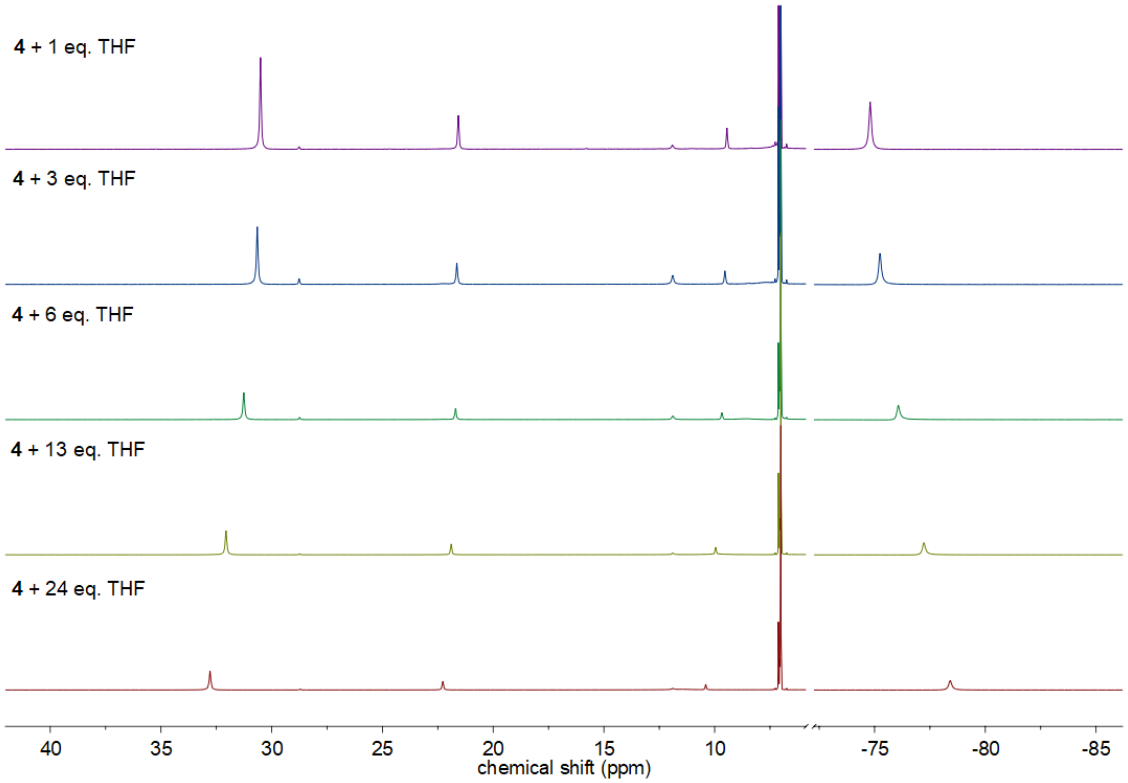

Figure S 24. Paramagnetic region of the ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^2)$_2$] (**4**) in toluene-d_8 at 300 K by gradual addition of THF.

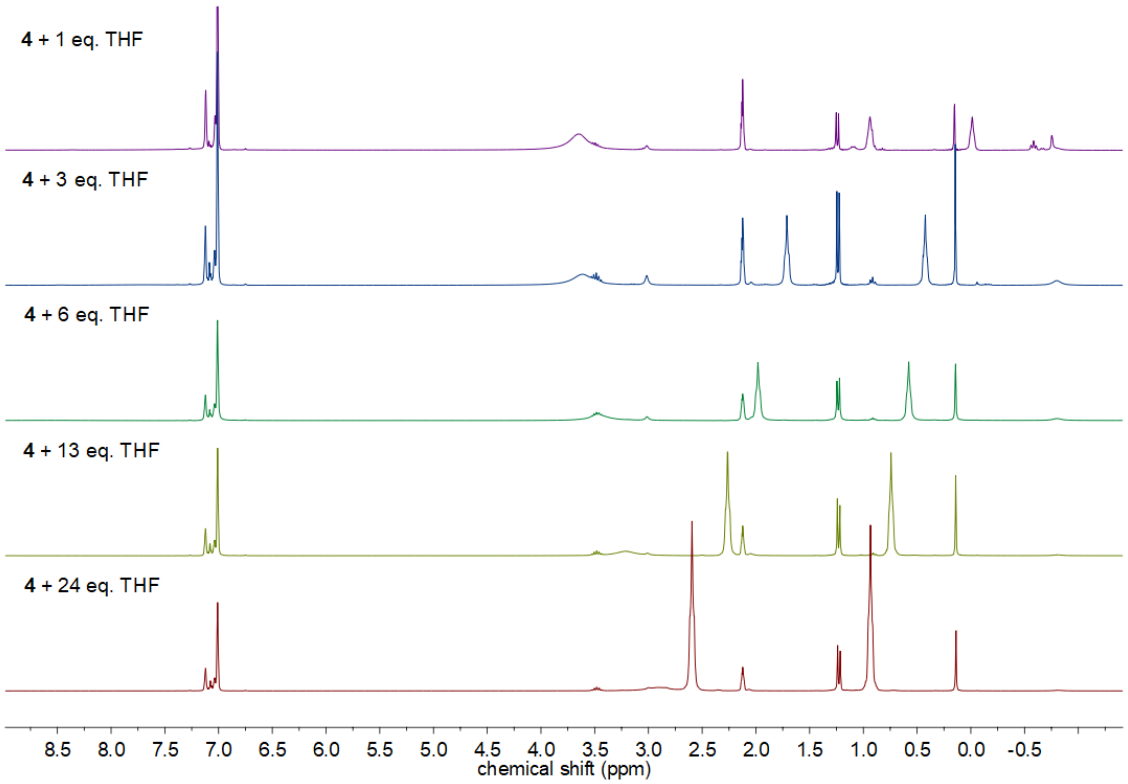

Figure S 25. Diamagnetic region of the ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^2)$_2$] (**4**) in toluene-d_8 at 300 K by gradual addition of THF.

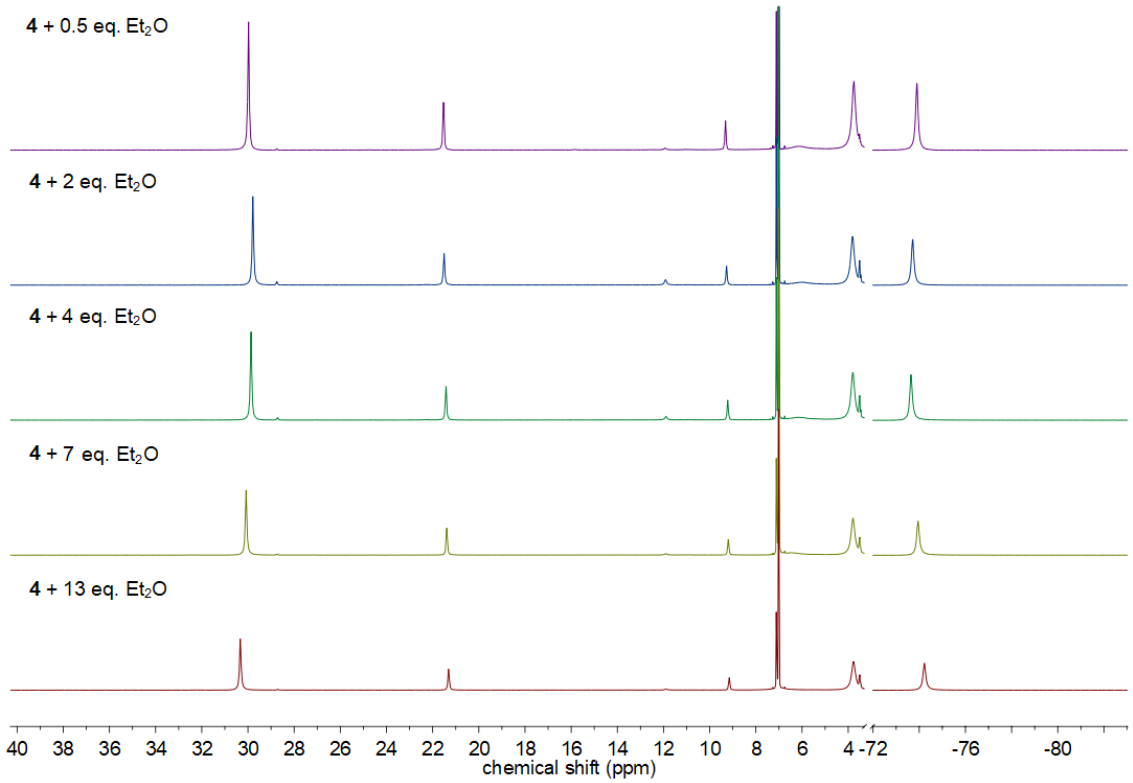

Figure S 26. Paramagnetic region of the ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^{2})$_2$] (**4**) in toluene-d_8 at 300 K by gradual addition of Et_2O.

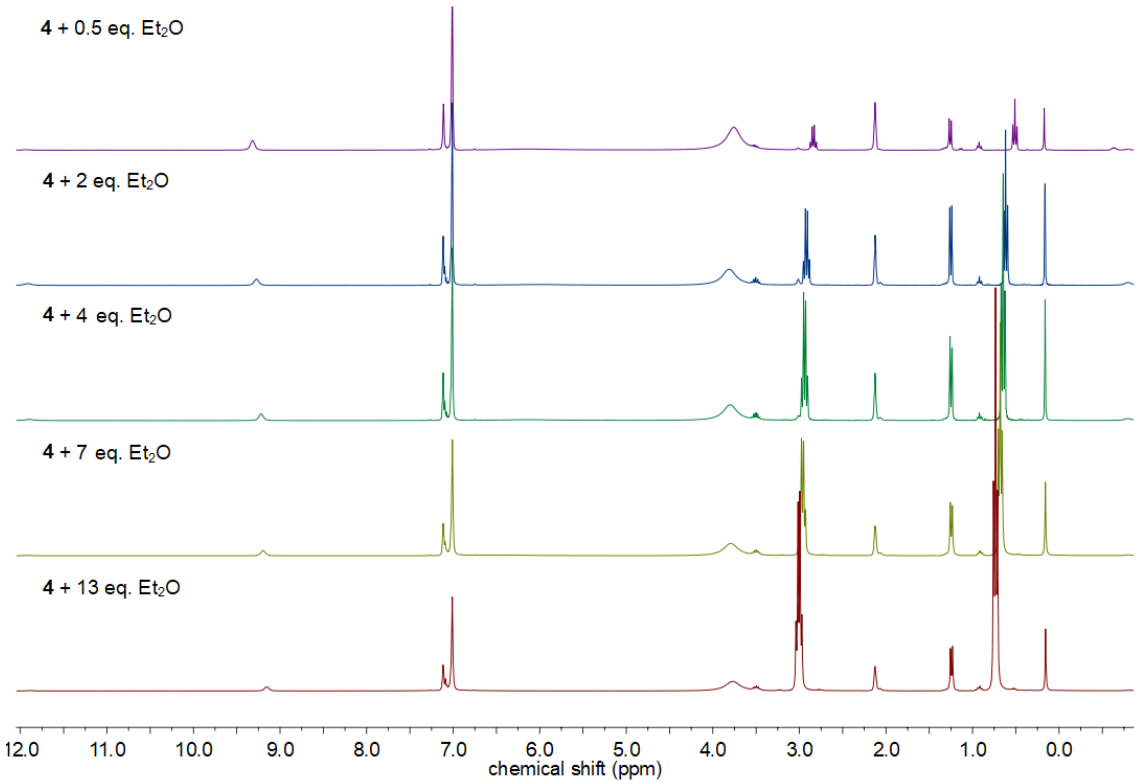

Figure S 27. Diamagnetic region of the ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^{2})$_2$] (**4**) in toluene-d_8 at 300 K by gradual addition of Et_2O.

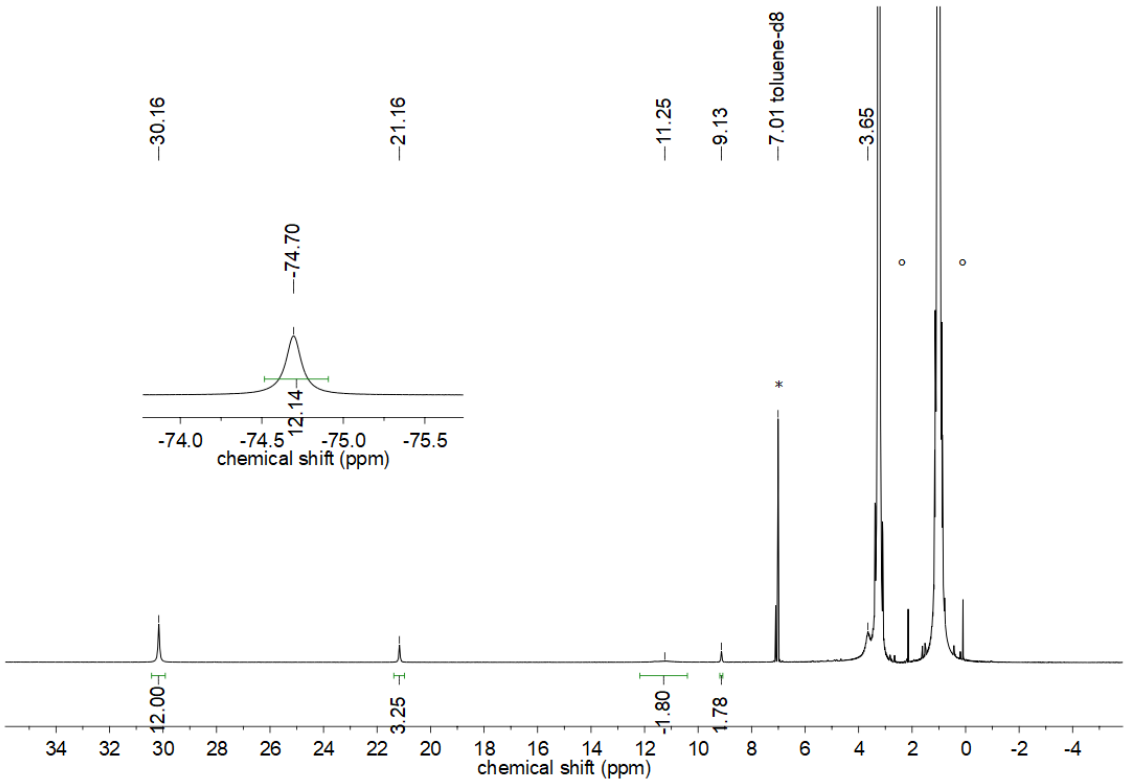

Figure S 28. ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^{2})$_2$] (**4**) in toluene-d_8/Et$_2$O (1:1 v/v) at 300 K. (* solvent, ° diethyl ether)

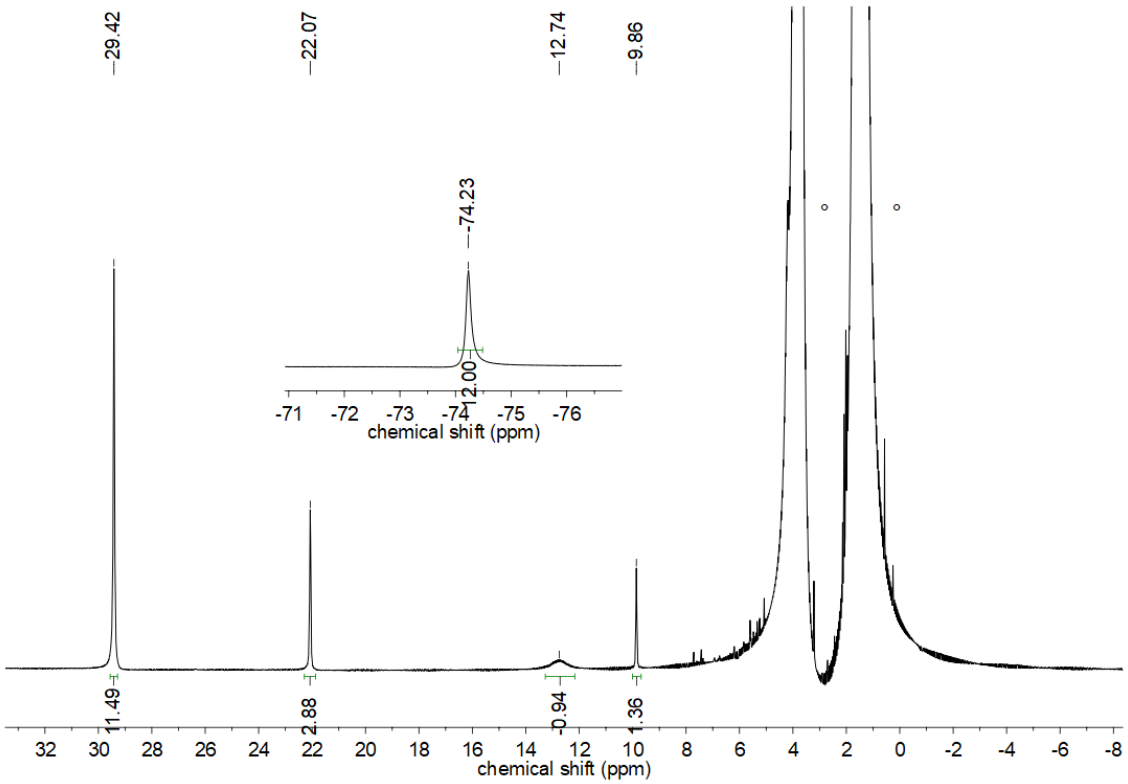

Figure S 29. ^{1}H NMR spectrum (300.2 MHz) of [KCo(L^{2})$_2$] (**4**) in Et$_2$O at 300 K. (° diethyl ether)

^{1}H NMR studies of 3 with diethyl ether

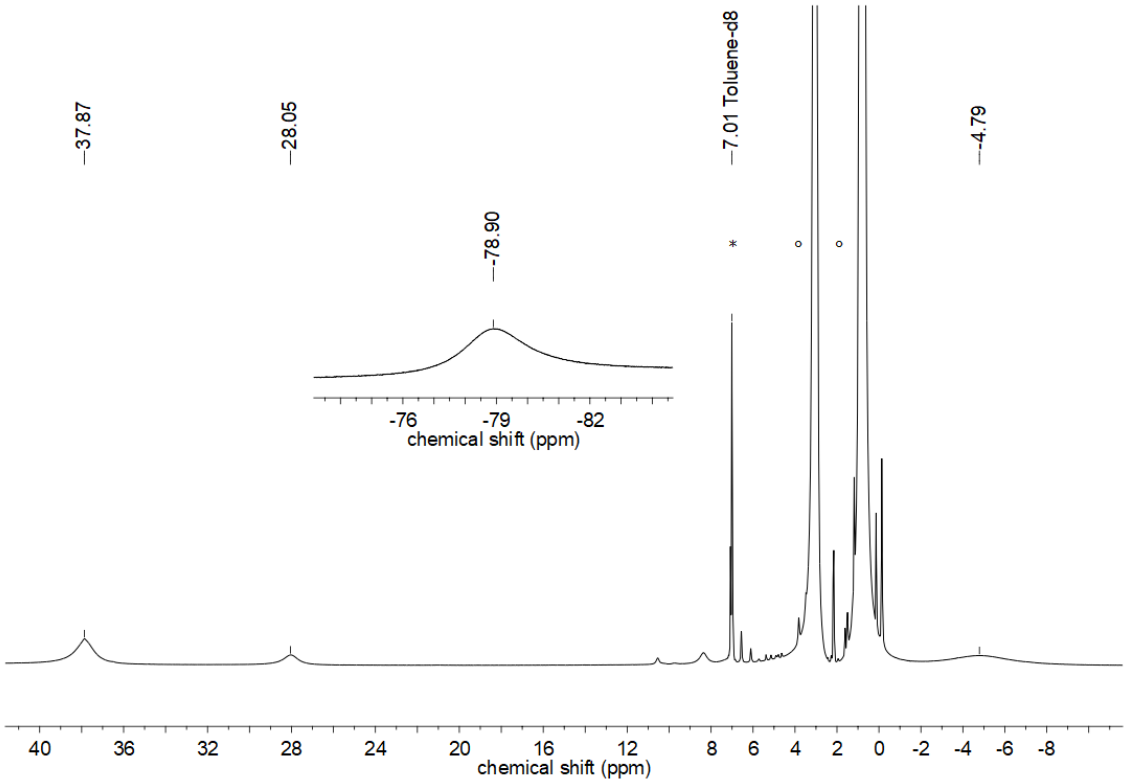

Figure S 30. ^{1}H NMR spectrum (300.2 MHz) of [KFe(L^2)$_2$] (**3**) in toluene-d_8/Et_2O (1:1 v/v) at 300 K. (* solvent, ° diethyl ether)

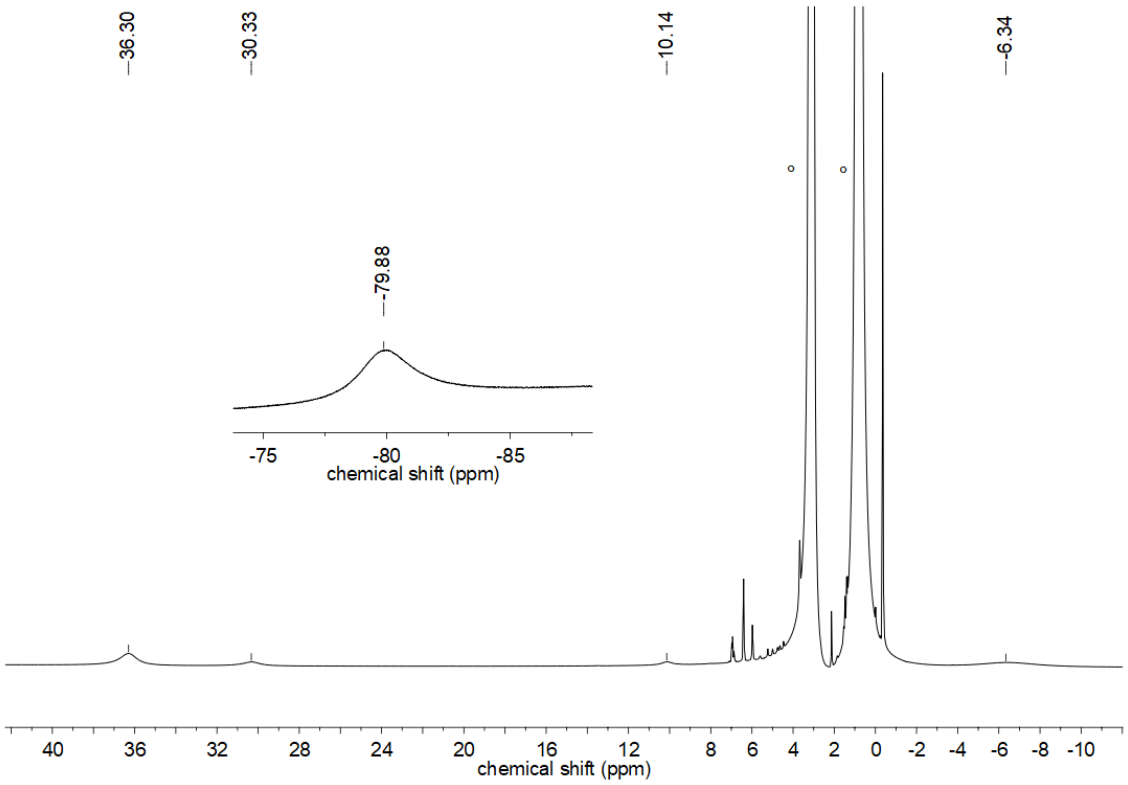

Figure S 31. ^{1}H NMR spectrum (300.2 MHz) of [KFe(L^2)$_2$] (**3**) in Et_2O at 300 K. (° diethyl ether)

***In Situ* ^{1}H NMR's of reacting 2 and 3 with diphenyl acetylene**

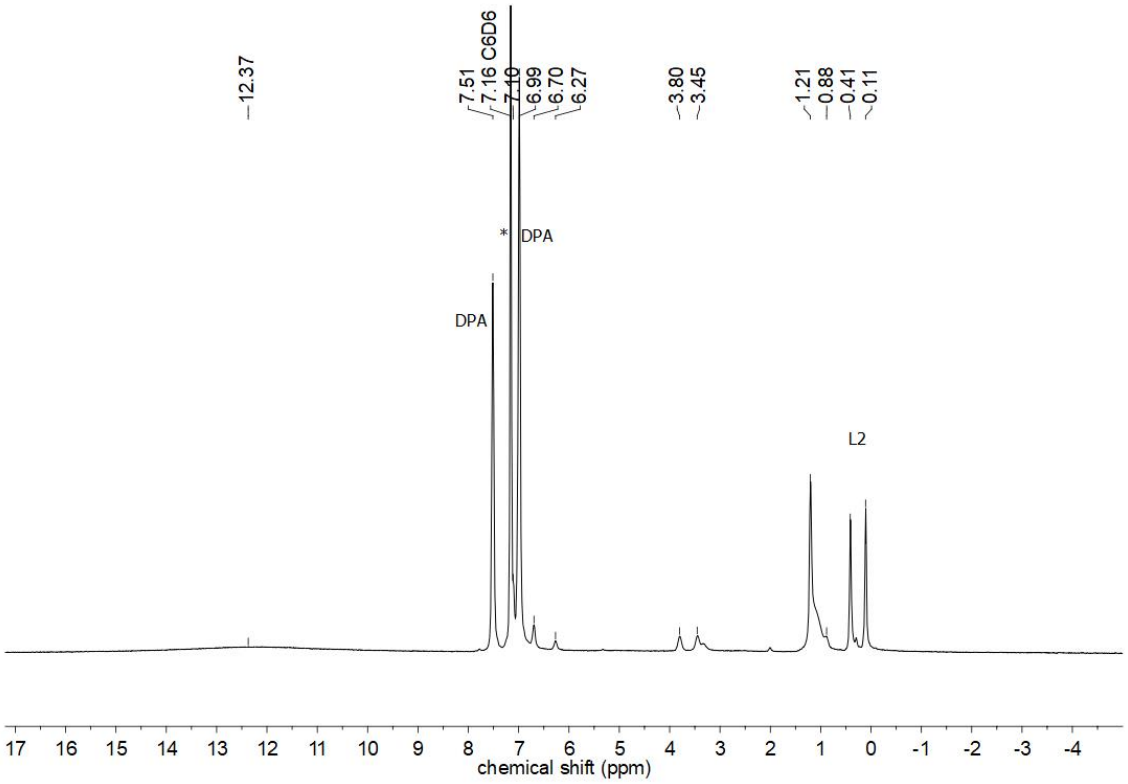

Figure S 32. *In Situ* ^{1}H NMR spectrum (300.2 MHz) of [KMn(L^2)$_2$] (**2**) with diphenyl acetylene in C_6D_6 at 300 K. (* solvent, ^{DPA} diphenyl acetylene, ^{L2} released KL^2 during the reaction)

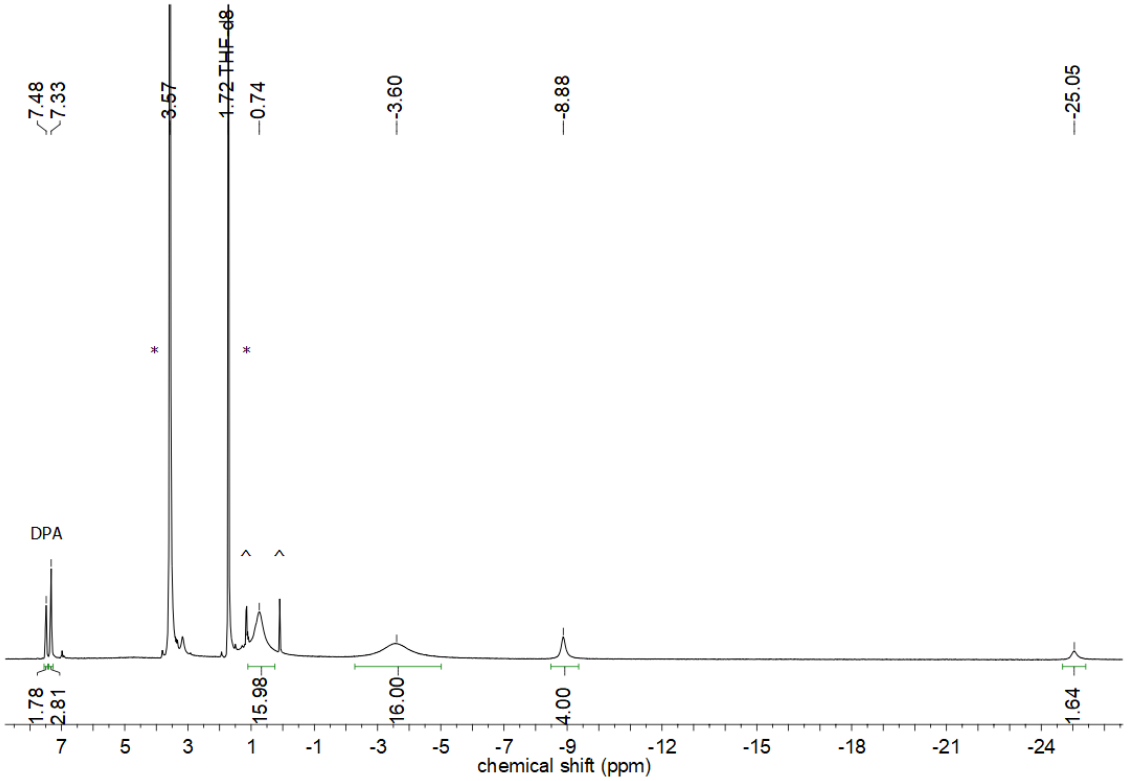

Figure S 33. *In Situ* ^{1}H NMR spectrum (300.2 MHz) of [K{18c6}][Fe(L^{2})$_2$] with diphenyl acetylene in THF-d_8 at 300 K. (* solvent, ^{DPA} diphenyl acetylene, ^ impurities)

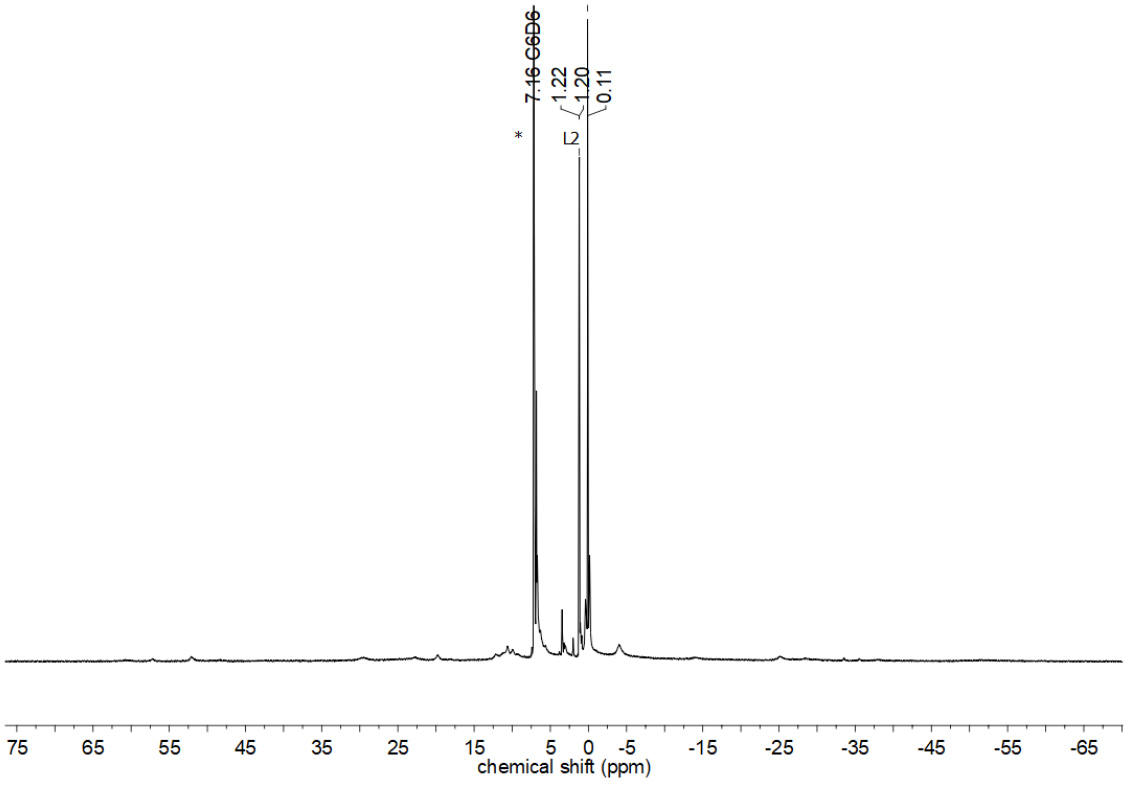

Figure S 34. *In Situ* ^{1}H NMR spectrum (300.2 MHz) of [KFe(L^{2})$_2$] (**3**) with diphenyl acetylene in C_6D_6 at 300 K. (* solvent, ^{L2} released KL^{2} during the reaction)

2 UV/Vis spectra

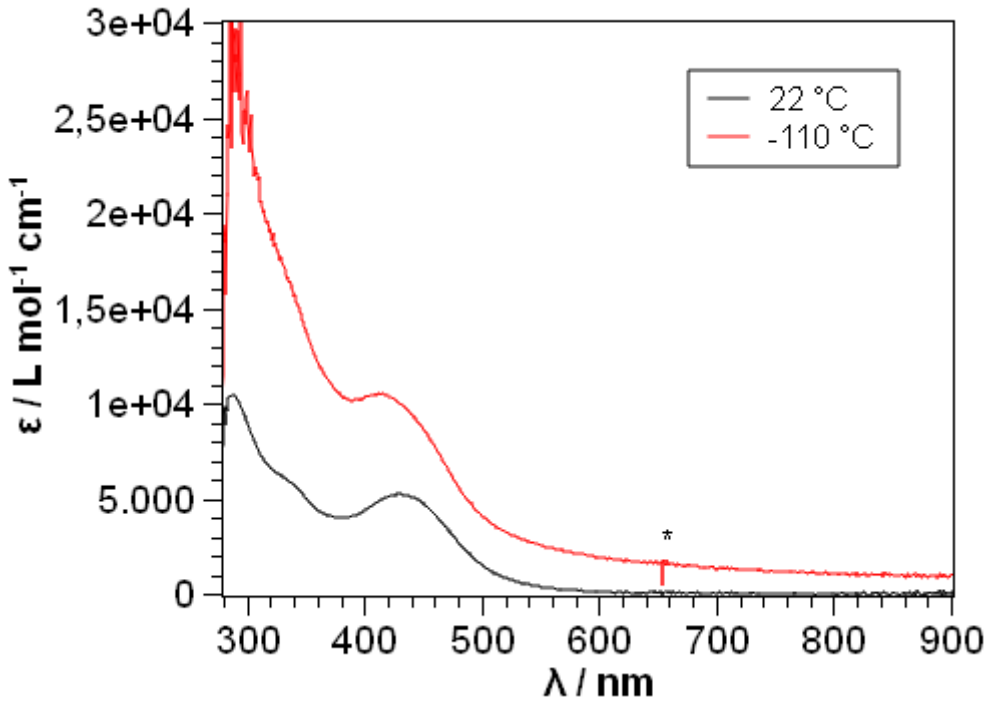

Figure S 35. UV/Vis spectrum of [KCr(L^1)$_2$] (**1**) in toluene. The signal caused by detector exchange is indicated by *.

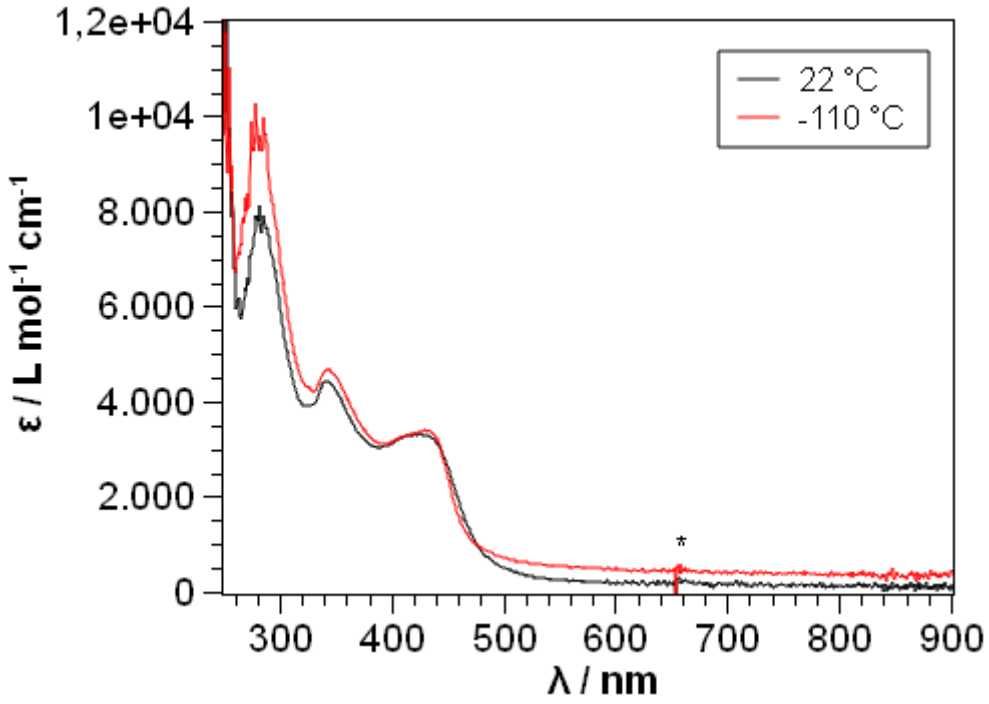

Figure S 36. UV/Vis spectrum of [KCr(L^1)$_2$] (**1**) in THF. The signal caused by detector exchange is indicated by *.

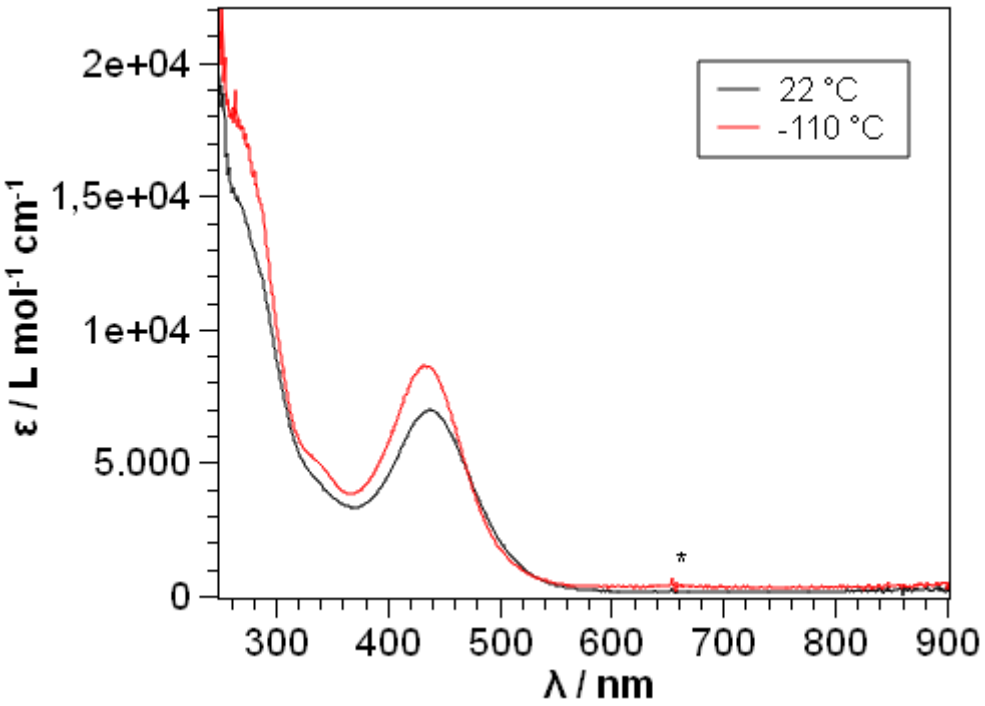

Figure S 37. UV/Vis spectrum of [KCr(L^1)$_2$] (**1**) in Et_2O. The signal caused by detector exchange is indicated by *.

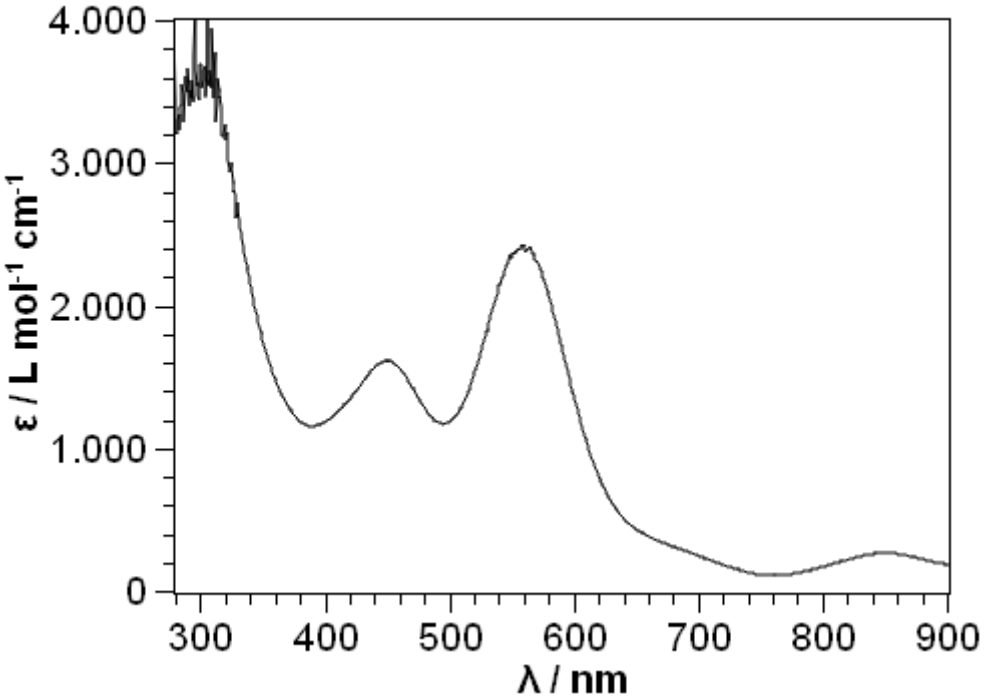

Figure S 38. UV/Vis spectrum of [KMn(L^2)$_2$] (**2**) in Et_2O.

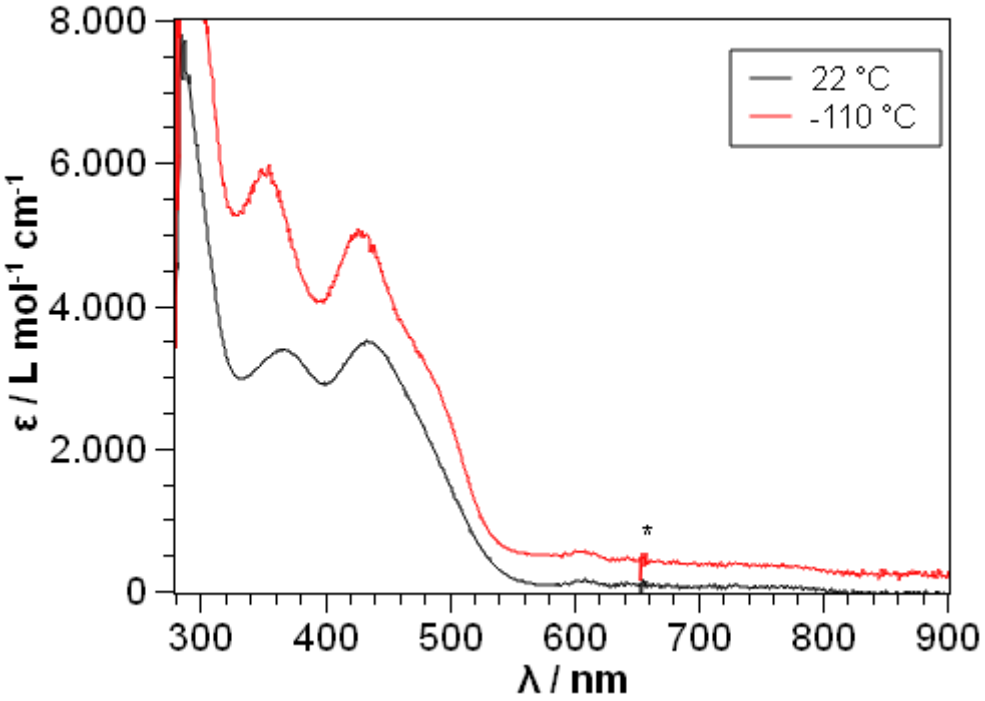

Figure S 39. UV/Vis spectrum of [KFe(L^2)$_2$] (**3**) in toluene. The signal caused by detector exchange is indicated by *.

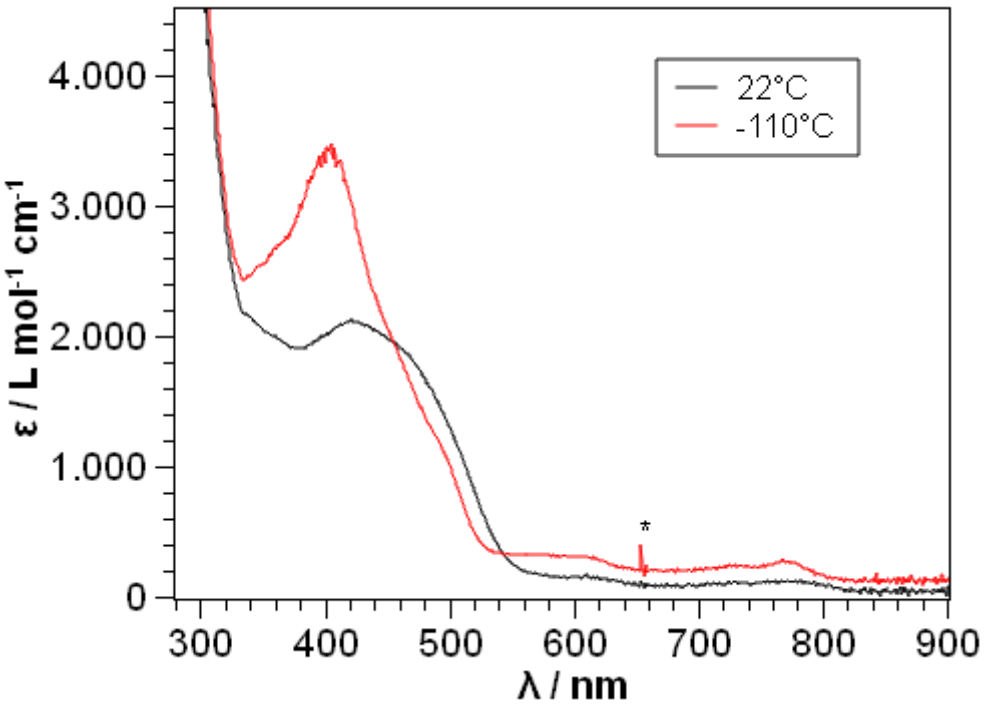

Figure S 40. UV/Vis spectrum of [KFe(L^2)$_2$] (**3**) in THF. The signal caused by detector exchange is indicated by *.

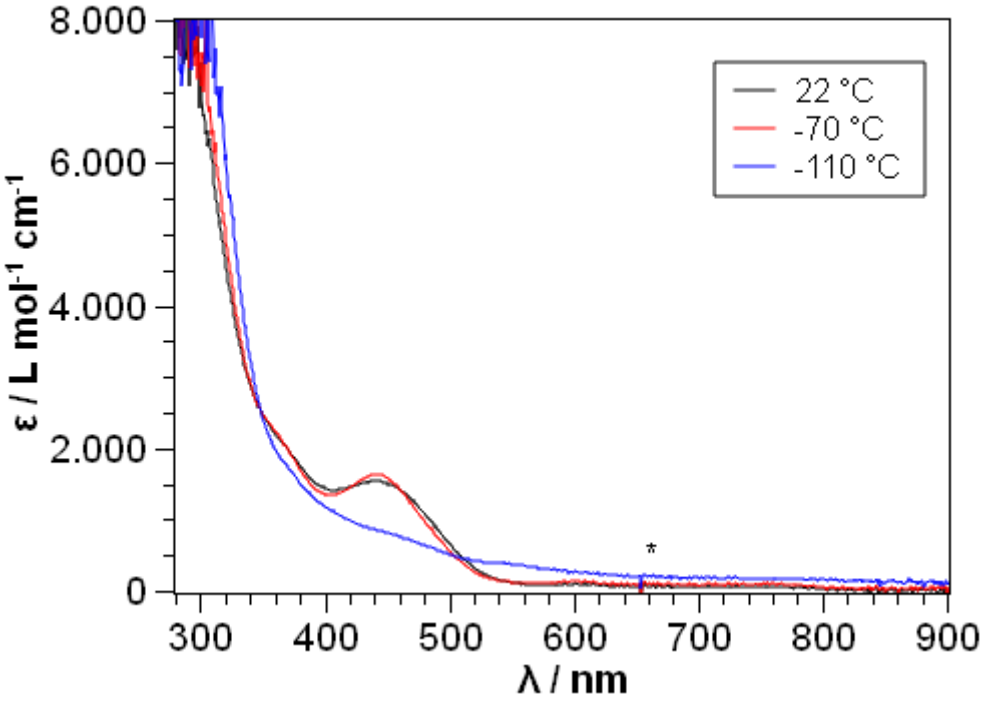

Figure S 41. UV/Vis spectrum of [KFe(L^2)$_2$] (**3**) in Et_2O. The signal caused by detector exchange is indicated by *.

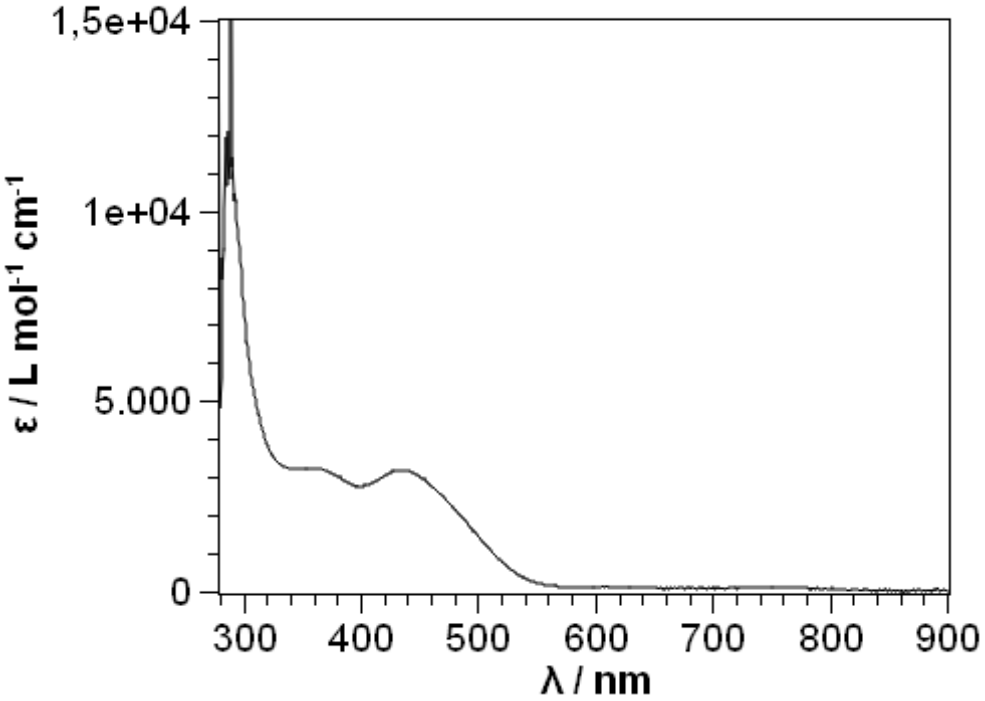

Figure S 42. UV/Vis spectrum of [K(DMAP)$_2$Fe(L^2)$_2$] (**3**.2DMAP) in toluene.

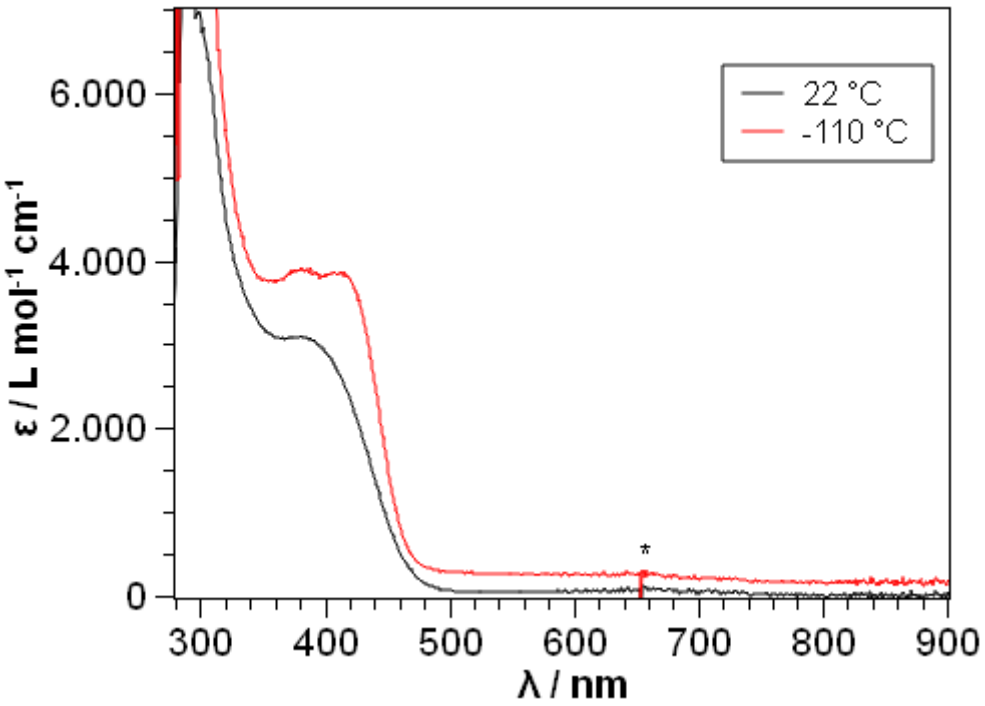

Figure S 43. UV/Vis spectrum of [KCo(L^2)$_2$] (**4**) in toluene. The signal caused by detector exchange is indicated by *.

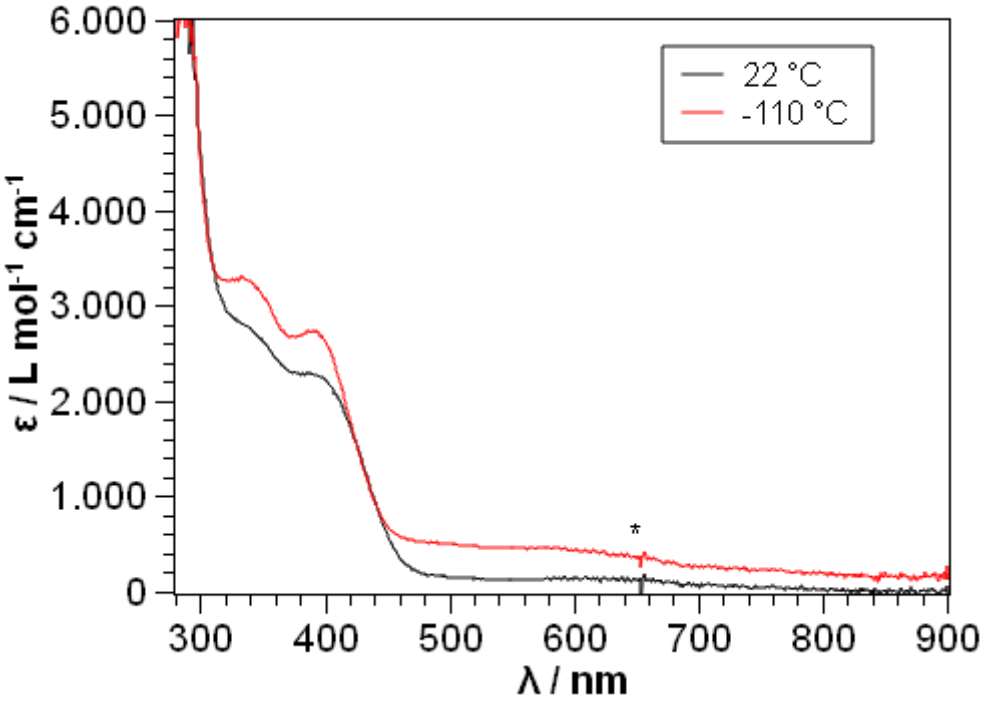

Figure S 44. UV/Vis spectrum of [KCo(L^2)$_2$] (**4**) in THF. The signal caused by detector exchange is indicated by *.

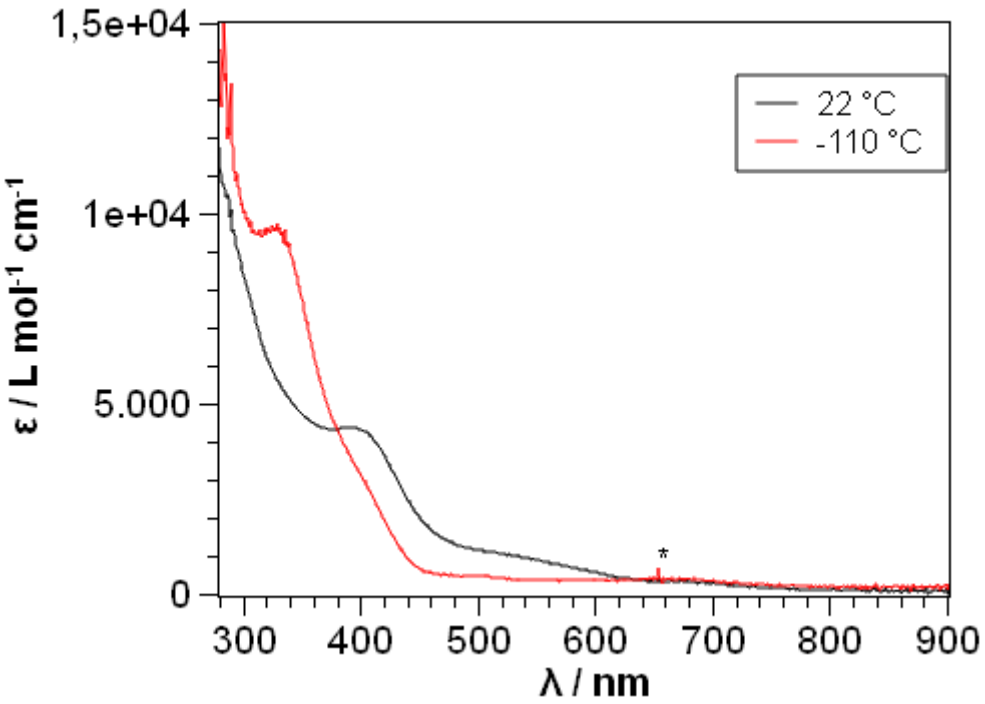

Figure S 45. UV/Vis spectrum of [KCo(L^2)$_2$] (**4**) in Et_2O. The signal caused by detector exchange is indicated by *.

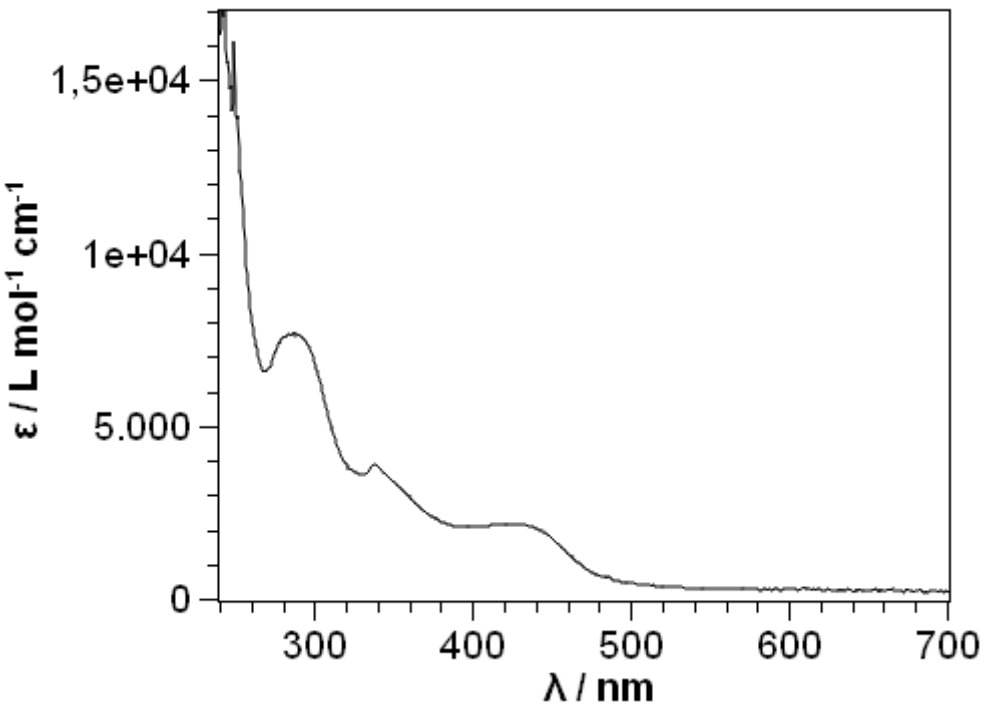

Figure S 46. UV/Vis spectrum of [K{18c6}][Cr(L^1)$_2$] (**5**) in THF.

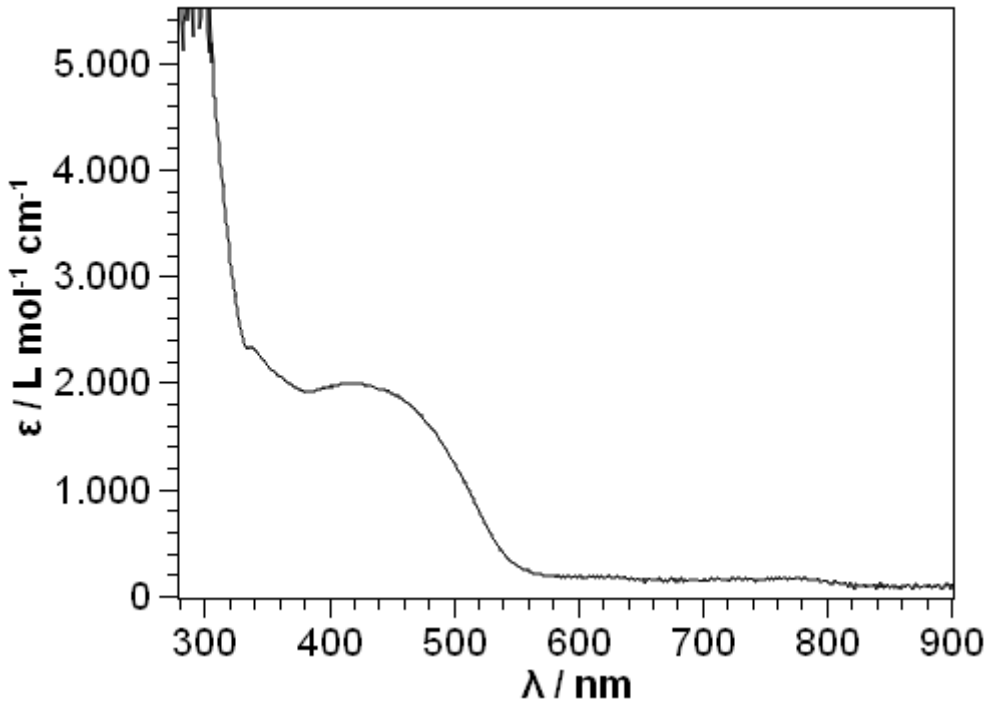

Figure S 47. UV/Vis spectrum of [Li{12c4}$_2$][Fe(L^2)$_2$] (**6**) in THF.

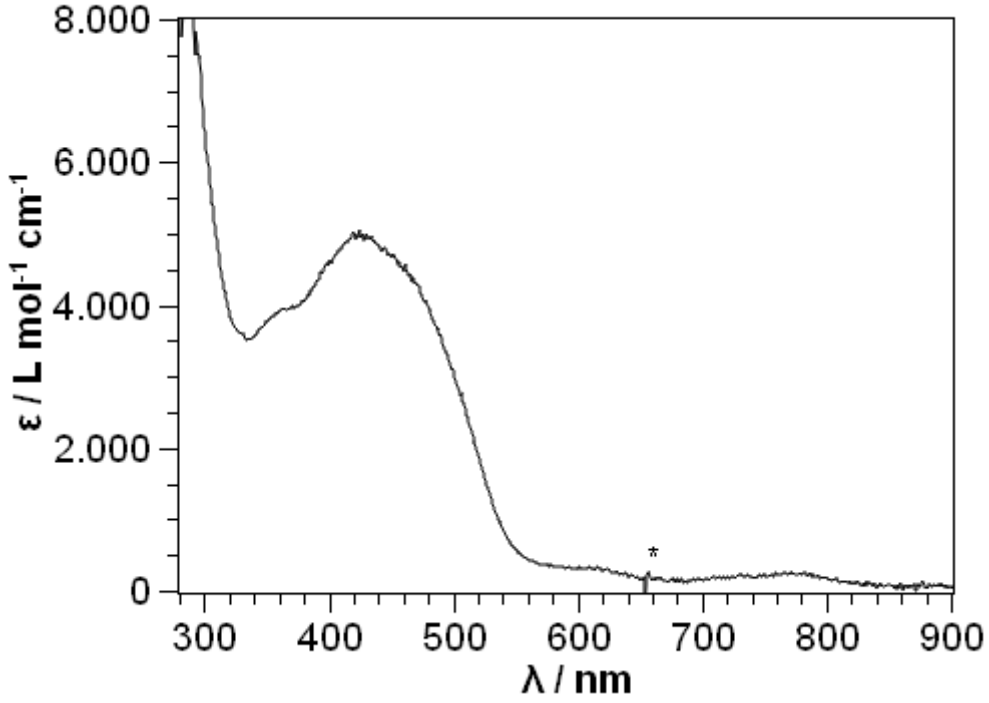

Figure S 48. UV/Vis spectrum of [Na{18c6}][Fe(L^2)$_2$] (**7**) in THF. The signal caused by detector exchange is indicated by *.

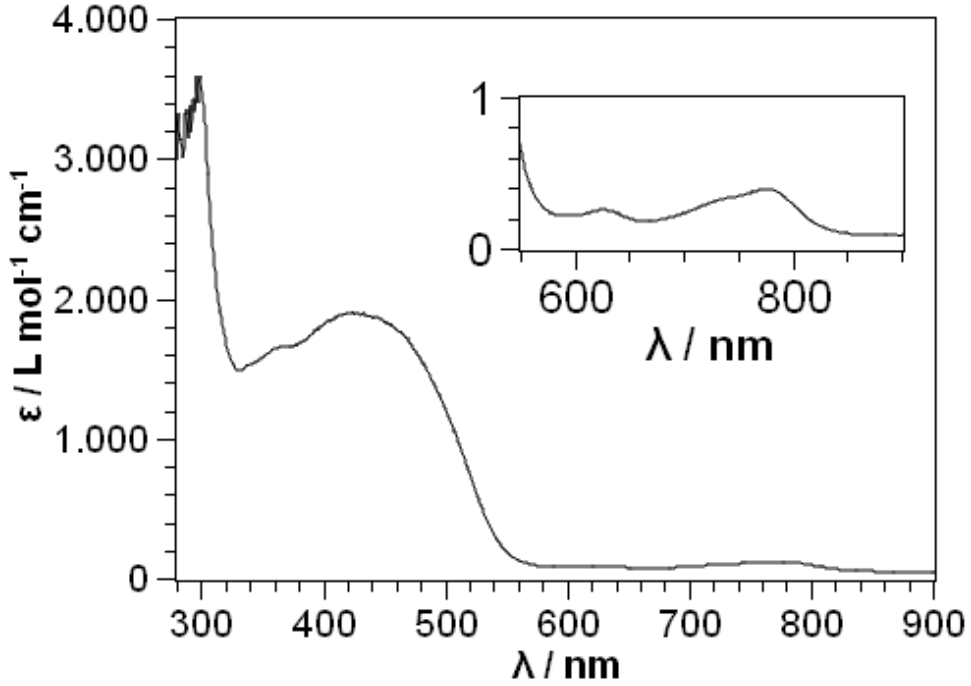

Figure S 49. UV/Vis spectrum of $[NBu_4][Fe(L^2)_2]$ (**8**) in THF.

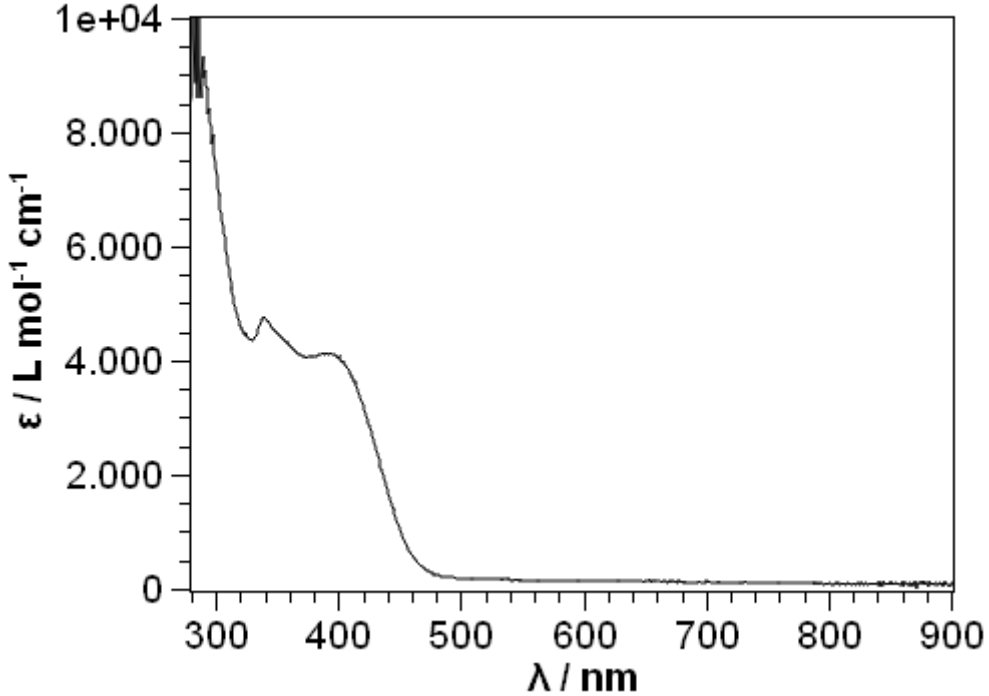

Figure S 50. UV/Vis spectrum of $[NBu_4][Co(L^2)_2]$ (**9**) in THF.

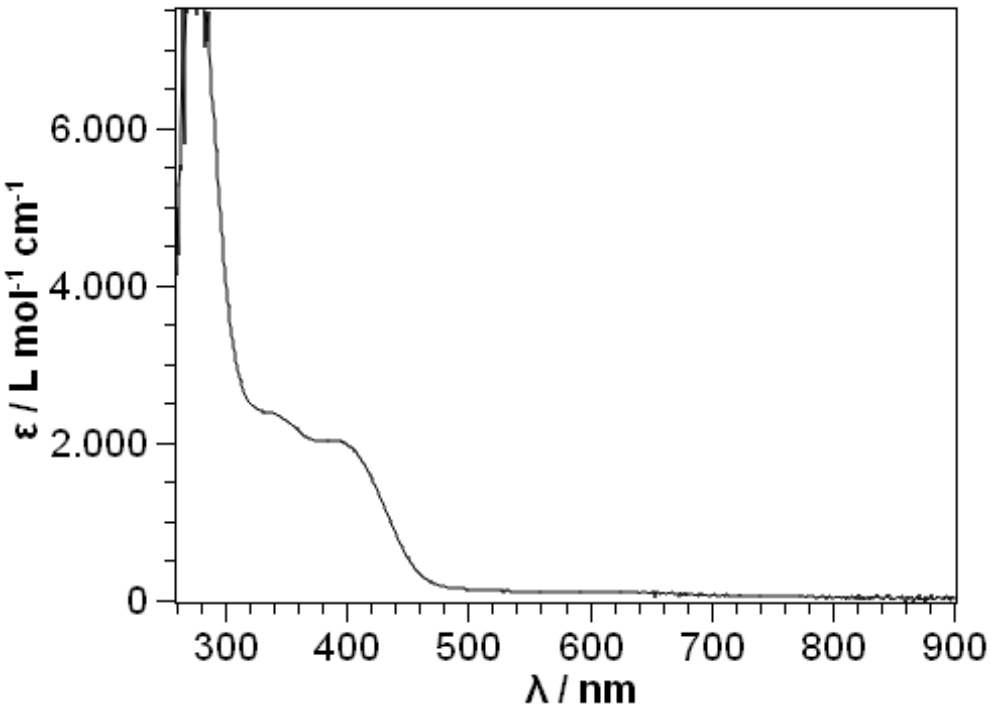

Figure S 51. UV/Vis spectrum of [K{18c6}][Co(L^2)$_2$] in THF.

Table S 1. Location of UV/Vis absorption maxima in compounds **1** − **9** and [K{18c6}][M(L^2)$_2$] (M = Fe, Co, L^2 = −N(Dipp)SiMe$_3$)) in the range from 280 − 900 nm. *UV/Vis spectrum was recorded but no absorption coefficients were given in the original report.

		solvent	T	λ(ε) / nm(Lmol^{-1}cm^{-1})
Cr	**1**	toluene	r.t.	431 (5210)
			−100 °C	419 (10430)
		THF	r.t.	286 (>7930), 343 (4440), 426 (3320)
			−100 °C	286 (9980), 343 (4680), 428 (3370)
		Et_2O	r.t.	435 (6940)
			−100 °C	433 (8670)
	5	THF	r.t.	288 (7710), 338 (3880), 421 (2160)
Mn	**2**	Et_2O	r.t.	448 (1610), 565 (2410), 849 (2650)
Fe	**3**	toluene	r.t.	368 (3380), 432 (3490), 602 (140)
			−100 °C	355 (5970), 430 (5040), 606 (560)
		THF	r.t.	421 (2120), 610 (160), 773 (120)
			−100 °C	408 (3430), 610 (310), 771 (480)
		Et_2O	r.t.	442 (1540), 601 (100)
			−100 °C	no maximum
	3.2DMAP	toluene	r.t.	360 (3230), 434 (3190), 607 (130)
	6	THF	r.t.	422 (1990), 771 (170)
	7	THF	r.t.	420 (5020), 613 (320), 771 (260)
	8	THF	r.t.	364 (1660), 420 (1900)
	K{18c6}[Fe(L^2)$_2$][1]	THF	r.t.	428 (4000), 626 (100)
Co	**4**	toluene	r.t.	385 (3080)
			−100 °C	387 (3910), 410 (3850)
		THF	r.t.	336 (2800), 385 (2300)
			−100 °C	334 (3300), 388 (2740)
		Et_2O	r.t.	393 (3560)
			−100 °C	334 (9540)
	9	THF	r.t.	340 (4770), 390 (4120)
	K{18c6}[Co(L^2)$_2$]* [1]	THF	r.t.	337 (2380), 391 (2030), 629 (100)

3 IR spectra

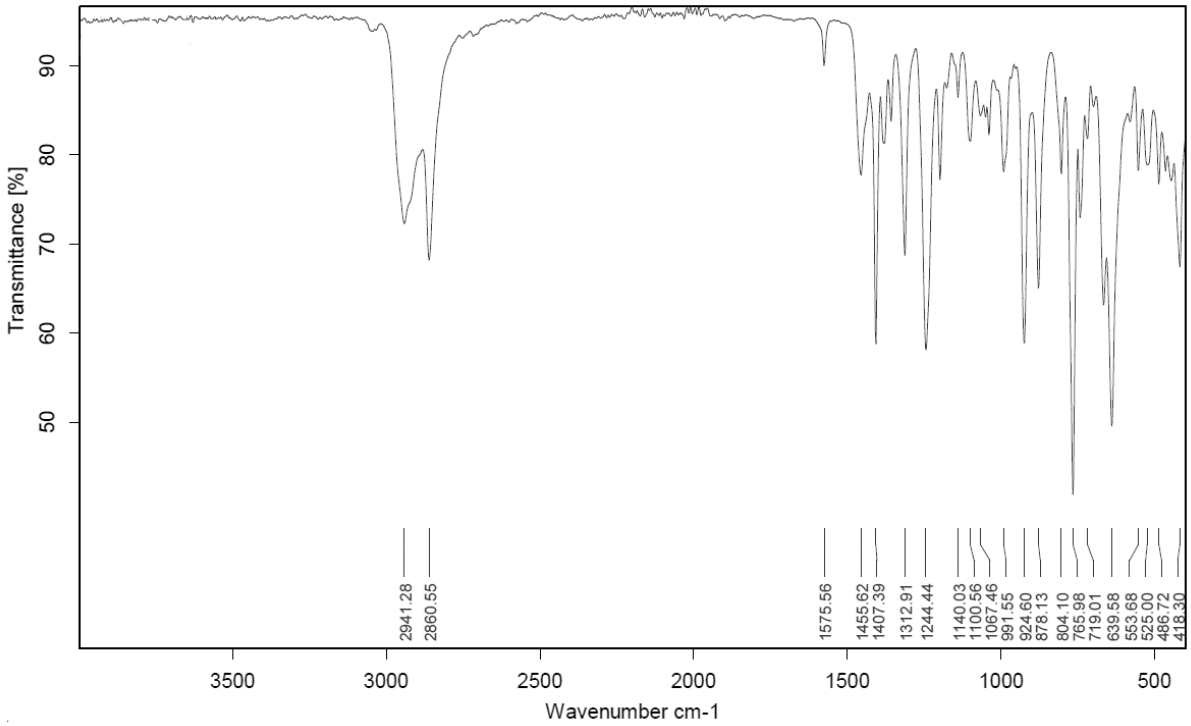

Figure S 52. IR spectrum of $[KCr(L^1)_2]_n$ (**1**).

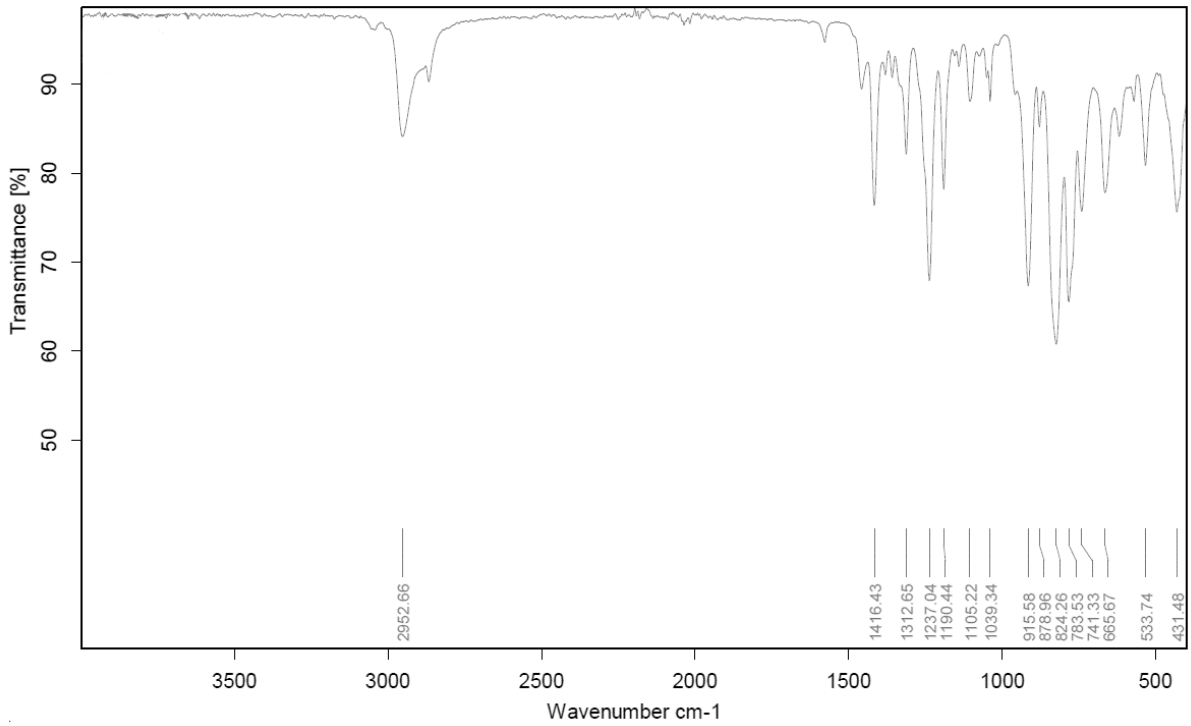

Figure S 53. IR spectrum of $[KMn(L^2)_2]$ (**2**).

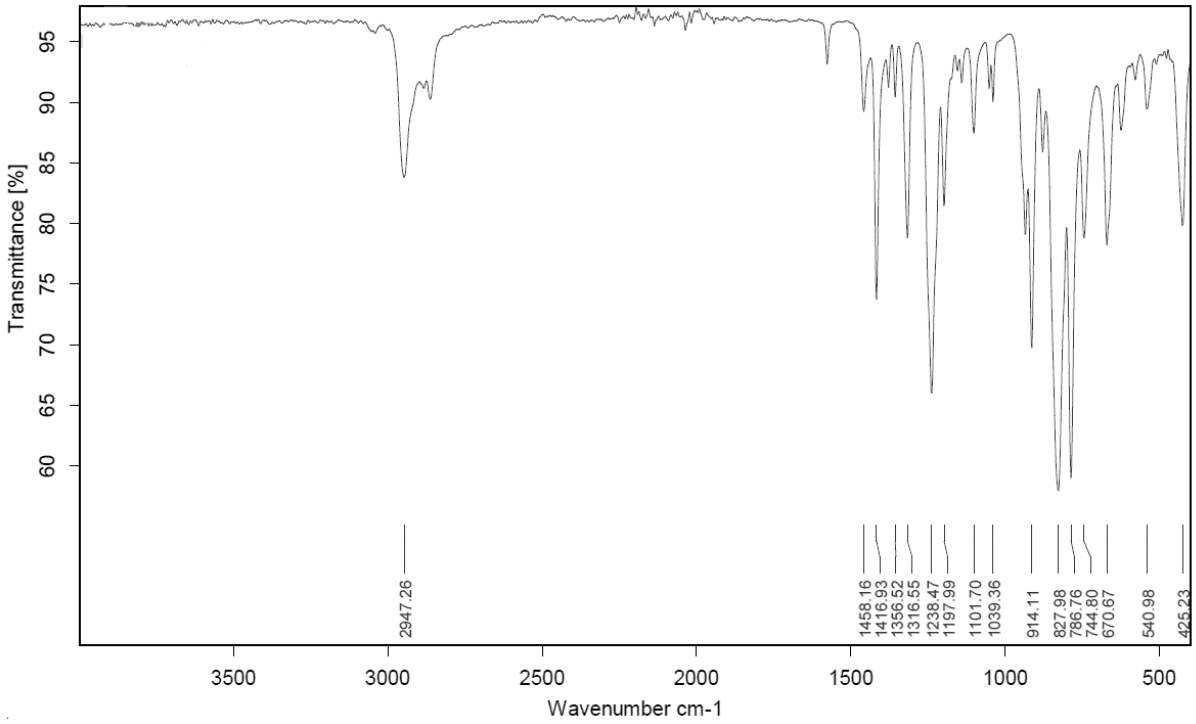

Figure S 54. IR spectrum of [KFe(L^2)$_2$] (**3**).

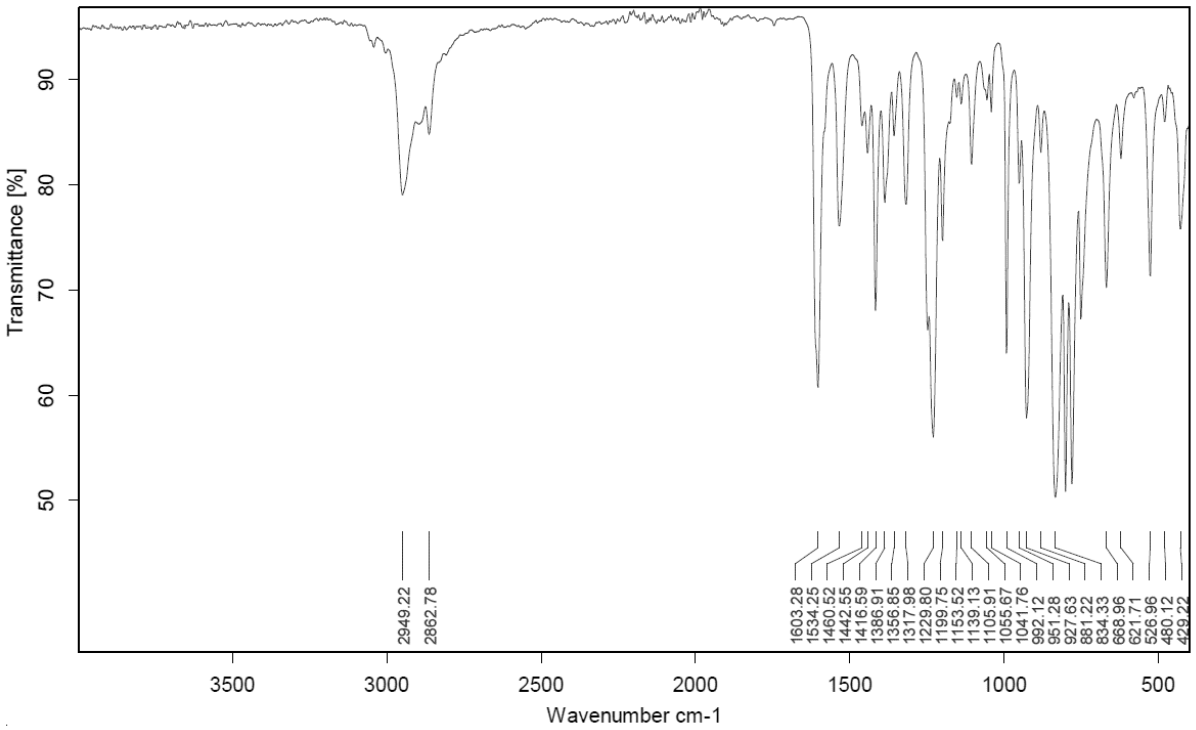

Figure S 55. IR spectrum of [K(DMAP)$_2$Fe(L^2)$_2$] (**3**.2DMAP).

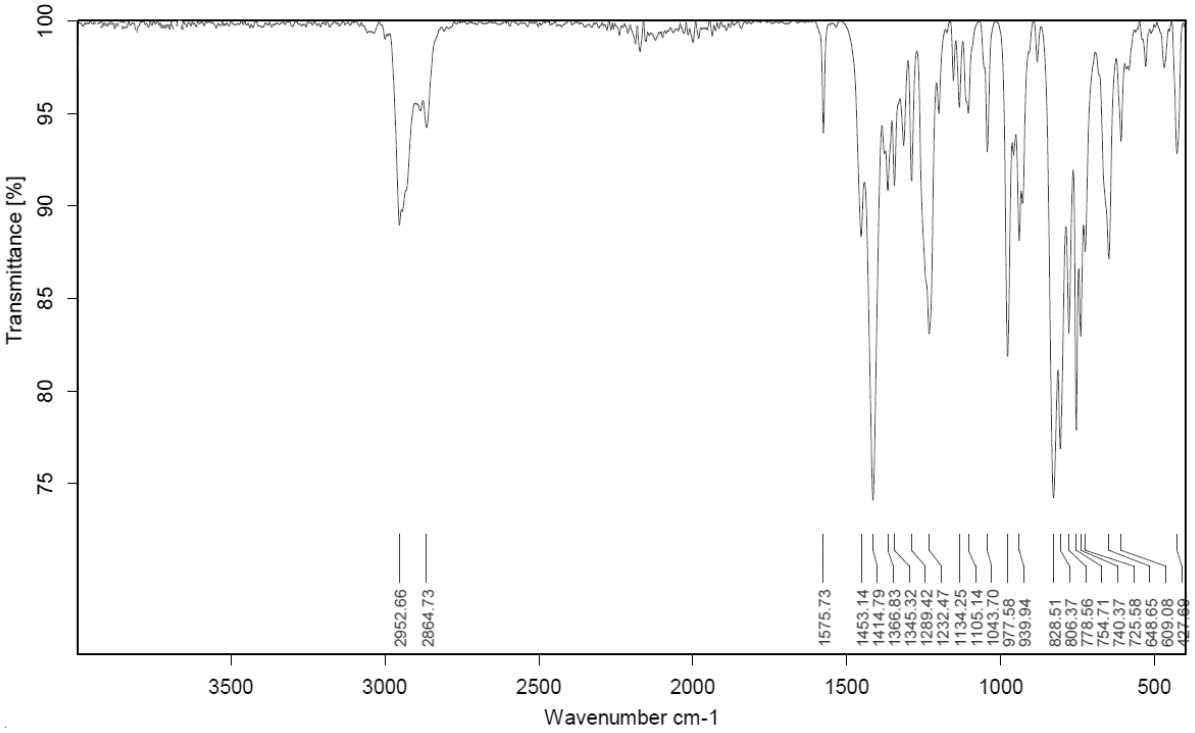

Figure S 56. IR spectrum of [KCo(L^2)$_2$] (**4**).

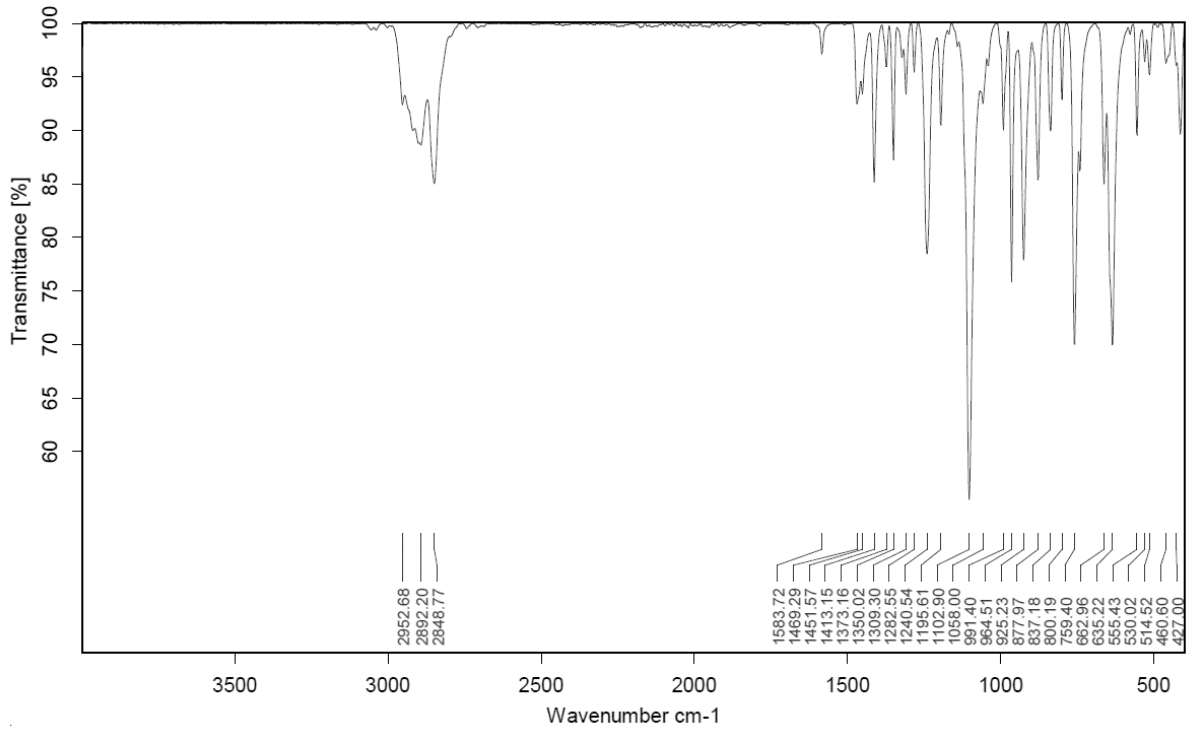

Figure S 57. IR spectrum of [K{18c6}(thf)$_2$][Cr(L^1)$_2$] (**5**).

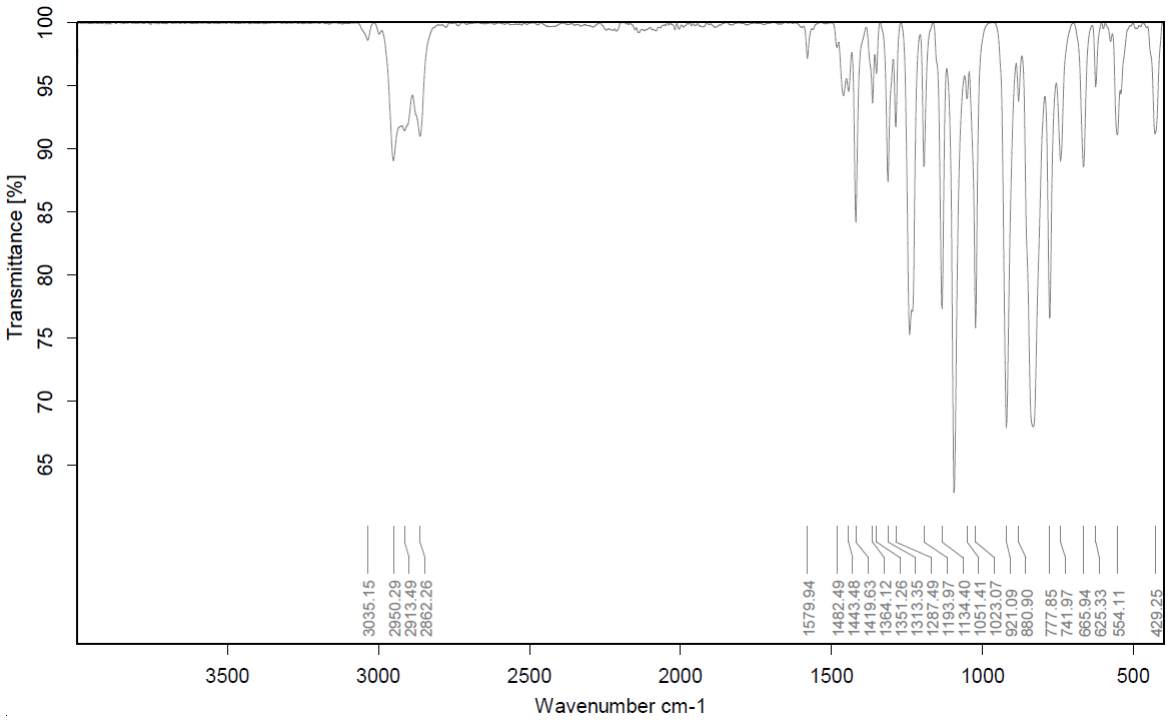

Figure S 58. IR spectrum of [Li{12c4}$_2$][Fe(L^2)$_2$] (**6**).

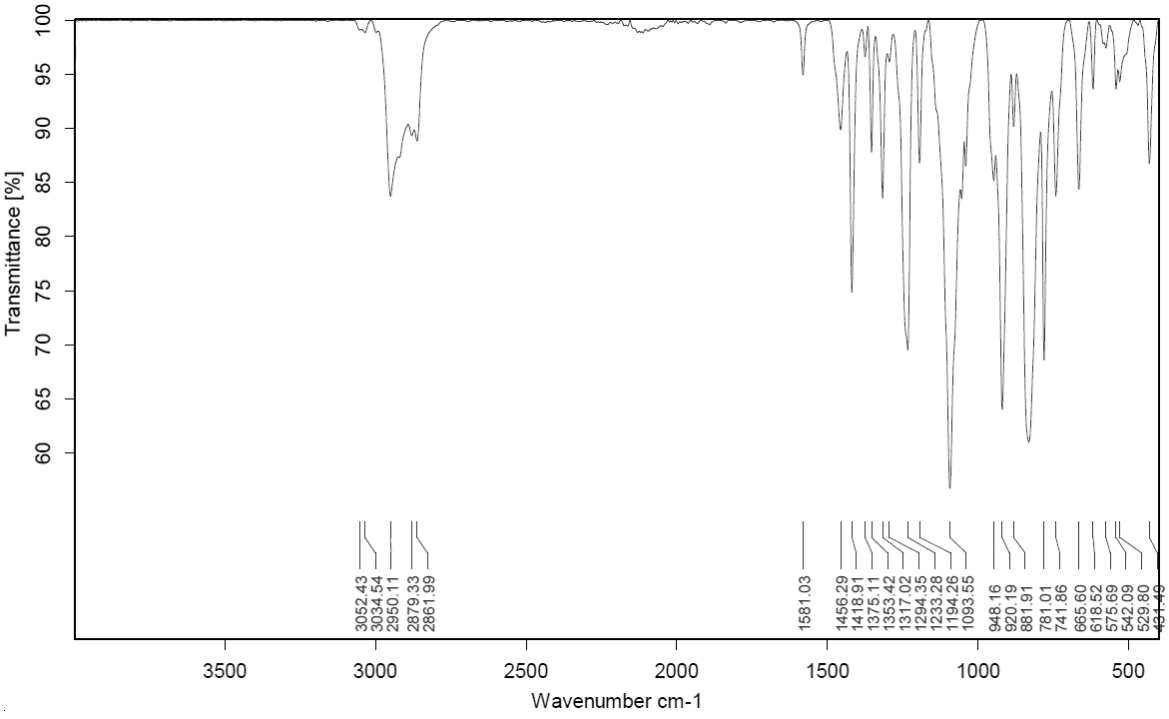

Figure S 59. IR spectrum of [Na{18c6}][Fe(L^2)$_2$] (**7**).

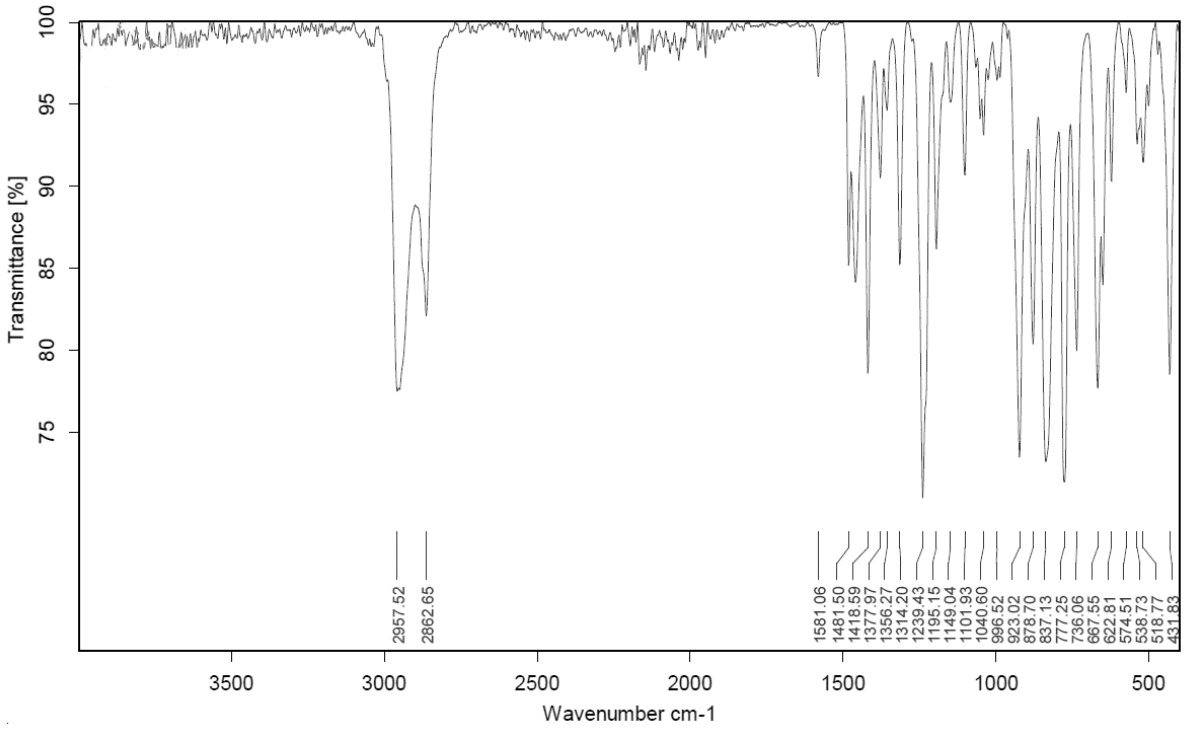

Figure S 60. IR spectrum of $[NBu_4][Fe(L^2)_2]$ (**8**).

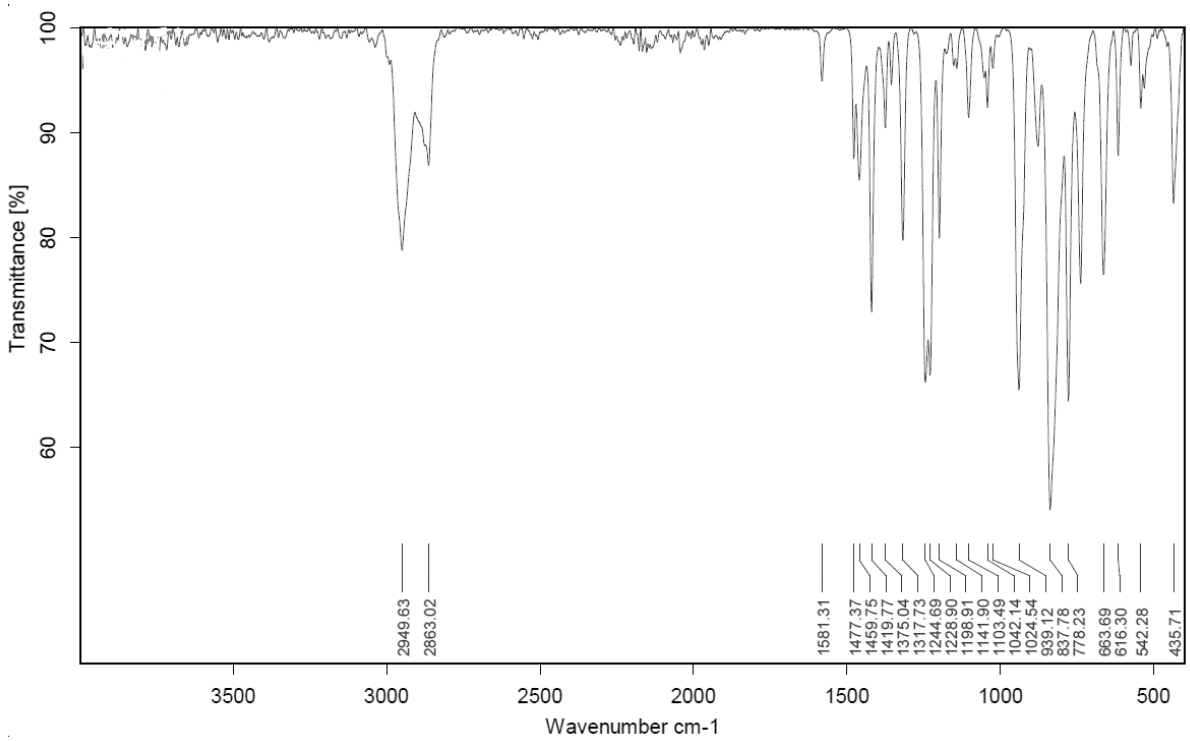

Figure S 61. IR spectrum of $[NBu_4][Co(L^2)_2]$ (**9**).

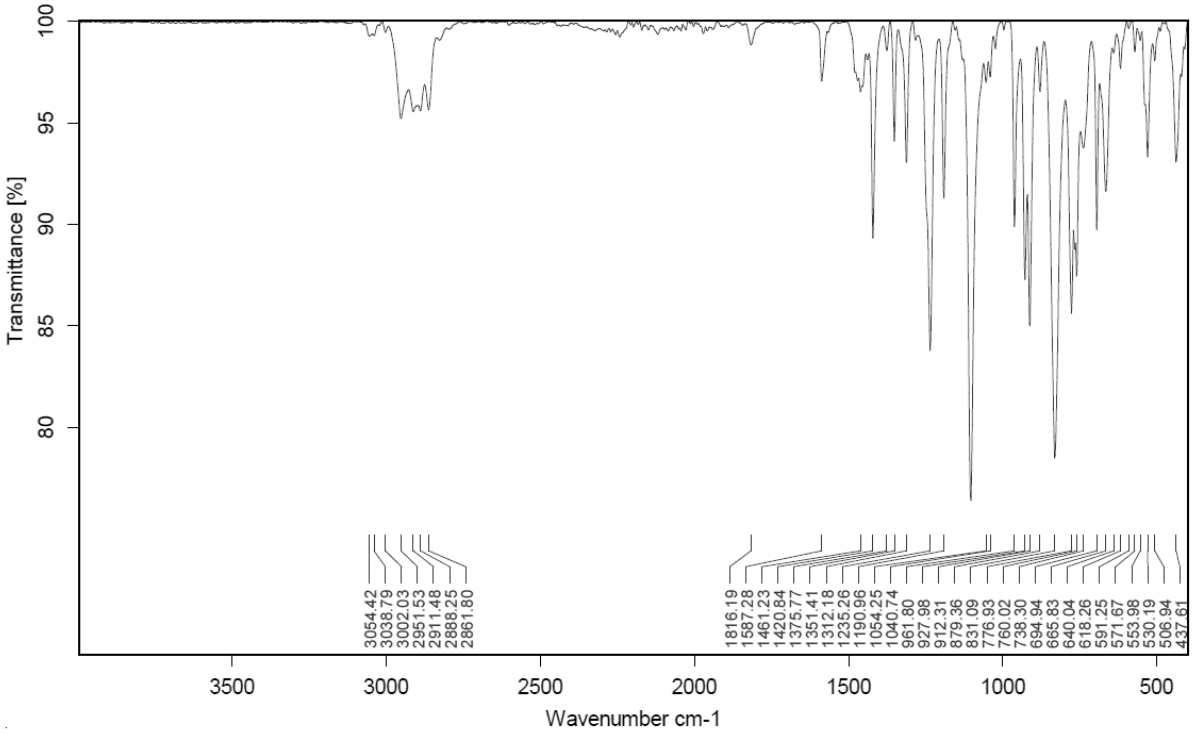

Figure S 62. IR spectrum of [K{18c6}][Fe(L^2)$_2$)(η^2-PhCCPh)] (**10**).

4 X-Ray Diffraction Analysis and Molecular Structures

$[KCr(L^1)_2]$ (1)

Table S 2. Crystal data and structure refinement of **1**

Empirical formula	$C_{42}H_{76}CrKN_2Si_2$
Formula weight	756.32
Temperature/K	99.99
Crystal system	orthorhombic
Space group	Pbcn
a/Å	22.7750(14)
b/Å	22.3023(13)
c/Å	17.1996(10)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	8736.3(9)
Z	8
$\rho_{calc}g/cm^3$	1.150
μ/mm^{-1}	0.441
F(000)	3304.0
Crystal size/mm^3	0.157 × 0.124 × 0.109
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.354 to 49.998
Index ranges	−27 ≤ h ≤ 27, −26 ≤ k ≤ 26, −20 ≤ l ≤ 20
Reflections collected	119181
Independent reflections	7685 [R_{int} = 0.1694, R_{sigma} = 0.0597]
Data/restraints/parameters	7685/36/453
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.1112
Largest diff. peak/hole / e $Å^{-3}$	0.35/−0.41

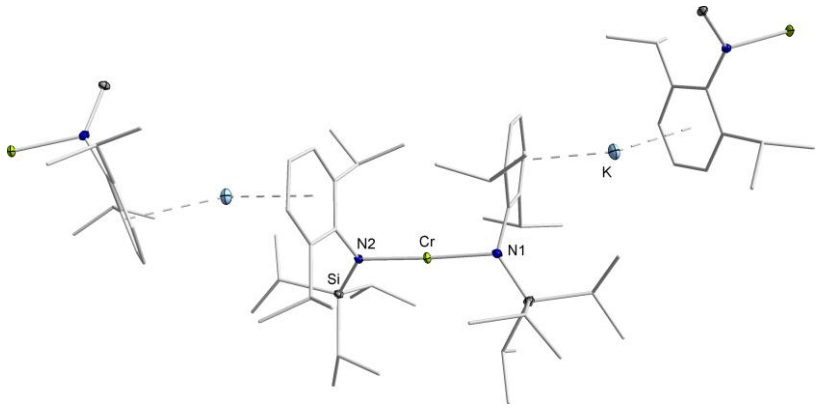

Figure S 63. Molecular structure of $[KCr^{I}(L^1)_2]_n$ (**1**). All hydrogen atoms are omitted for clarity.

Table S 3. Crystal data and structure refinement of **1**.3THF

Empirical formula	$C_{54}H_{98}CrKN_2O_3Si_2$
Formula weight	970.62
Temperature/K	100.0
Crystal system	triclinic
Space group	P−1
a/Å	11.886(2)
b/Å	14.190(2)
c/Å	17.464(3)
α/°	93.330(5)
β/°	95.457(5)
γ/°	97.740(5)
Volume/Å^3	2898.0(8)
Z	2
ρ_{calc}g/cm^3	1.112
μ/mm^{-1}	0.350
F(000)	1062.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.394 to 29.706
Index ranges	−8 ≤ h ≤ 8, −10 ≤ k ≤ 10, −12 ≤ l ≤ 11
Reflections collected	23343
Independent reflections	2232 [R_{int} = 0.0445, R_{sigma} = 0.0224]
Data/restraints/parameters	2232/1424/433
Goodness-of-fit on F^2	1.182
Final R indexes [I>=2σ (I)]	R_1 = 0.1311, wR_2 = 0.2766
Final R indexes [all data]	R_1 = 0.1331, wR_2 = 0.2776
Largest diff. peak/hole / e Å^{-3}	0.69/−0.39

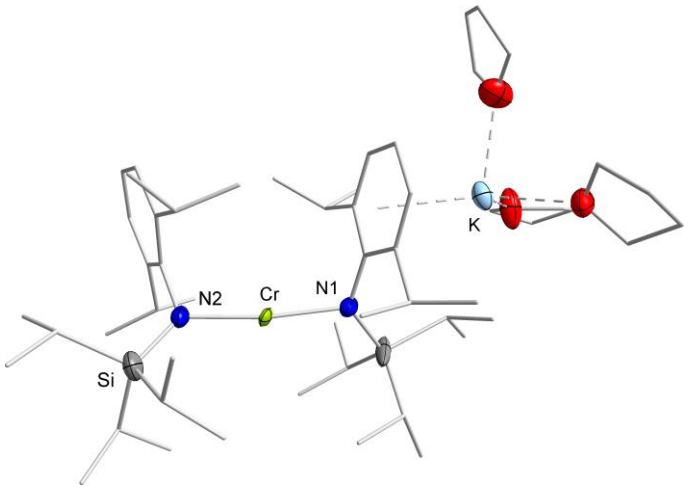

Figure S 64. Molecular structure of [K(THF)$_3$Cr^{I}(L^1)$_2$] (**1**.3THF). All hydrogen atoms are omitted for clarity. Disorders were found for one THF molecule (part 1: 63%, part 2: 37%) and two *iso*-propyl groups of a Si(^{i}Pr)$_3$ unit (part 1/2: 50%).

[KMn(L^2)$_2$] (2)

Table S 4. Crystal data and structure refinement of **2**

Empirical formula	$C_{30}H_{52}KMnN_2Si_2$
Formula weight	590.97
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6778(6)
b/Å	17.5423(9)
c/Å	17.8495(8)
α/°	90
β/°	108.652(2)
γ/°	90
Volume/Å^3	3464.5(3)
Z	4
ρ_{calc}g/cm^3	1.1329
μ/mm^{-1}	0.590
F(000)	1275.2
Crystal size/mm^3	0.236 × 0.179 × 0.132
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 53.36
Index ranges	−14 ≤ h ≤ 14, −22 ≤ k ≤ 22, −22 ≤ l ≤ 22
Reflections collected	76754
Independent reflections	7299 [R_{int} = 0.1314, R_{sigma} = 0.0575]
Data/restraints/parameters	7299/0/533
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0767
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.0824
Largest diff. peak/hole / e Å^{-3}	0.84/−0.51

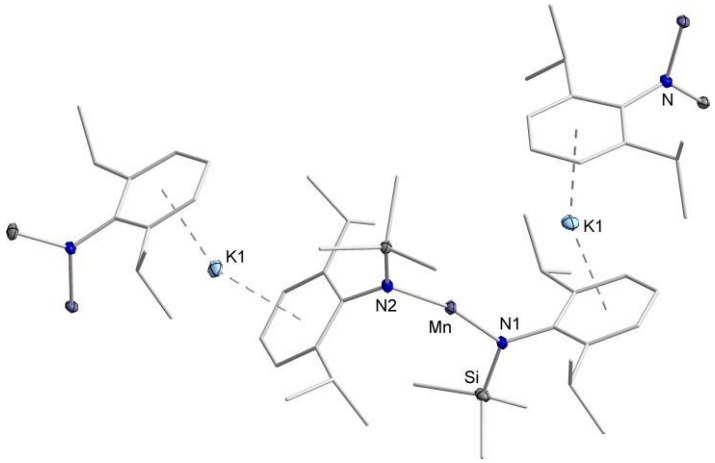

Figure S 65. Molecular structure of [KMn^I(L^2)$_2$]$_n$ (**2**). All hydrogen atoms are omitted for clarity.

[KFe(L^2)$_2$] (3)

Table S 5. Crystal data and structure refinement of **3**

Empirical formula	$C_{30}H_{52}FeKN_2Si_2$
Formula weight	591.86
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.8776(6)
b/Å	14.0736(7)
c/Å	14.4037(7)
α/°	115.309(2)
β/°	91.001(2)
γ/°	110.473(2)
Volume/Å^3	1999.11(18)
Z	2
ρ_{calc}g/cm^3	0.983
μ/mm^{-1}	0.558
F(000)	638.0
Crystal size/mm^3	0.5 × 0.386 × 0.278
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.734 to 52
Index ranges	−14 ≤ h ≤ 14, −17 ≤ k ≤ 17, −17 ≤ l ≤ 17
Reflections collected	72350
Independent reflections	7861 [R_{int} = 0.0405, R_{sigma} = 0.0193]
Data/restraints/parameters	7861/0/363
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0836
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.0851
Largest diff. peak/hole / e Å^{-3}	0.31/−0.26

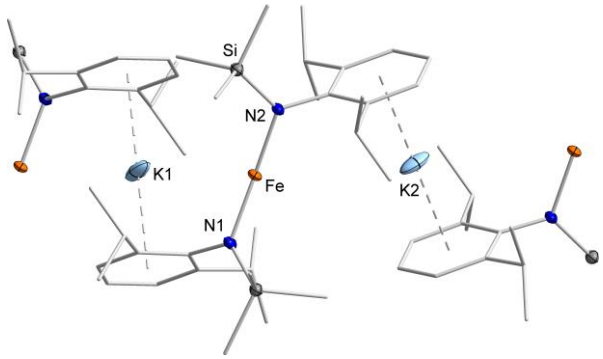

Figure S 66. Molecular structure of [KFe(L^2)$_2$]$_n$ (**3**). All hydrogen atoms are omitted for clarity. Disordering the potassium ion over two positions did not lead to a better, stable structure refinement. one free *n*-pentane molecule is heavily disordered over multiple positions. Attempts to model the disorders did not lead to satisfactory. It was thus squeezed.

Table S 6. Crystal data and structure refinement of **3**.Et_2O

Empirical formula	$C_{34}H_{62}Fe_1K_1N_2O_1Si_2$
Formula weight	666.00
Temperature/K	100
Crystal system	monoclinic
Space group	P 1 2_1/n 1
a/Å	10.4002(6)
b/Å	16.5542(9)
c/Å	22.9563(13)
α/°	90
β/°	95.379(2)
γ/°	90
Volume/$Å^3$	3934.9(4)
Z	4
$\rho_{calc}g/cm^3$	1.124
μ/mm^{-1}	0.576
F(000)	1444.000
Crystal size/mm^3	0.15 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2 to 32
Index ranges	−15 ≤ h ≤ 15, 0 ≤ k ≤ 24, 0 ≤ l ≤ 16
Reflections collected	98693
Independent reflections	8758
Data/restraints/parameters	7182/0/370
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0299, wR2 = 0.0296
Final R indexes [all data]	R1 = 0.0405, wR2 = 0.0439
Largest diff. peak/hole / e $Å^{-3}$	0.84/−0.36

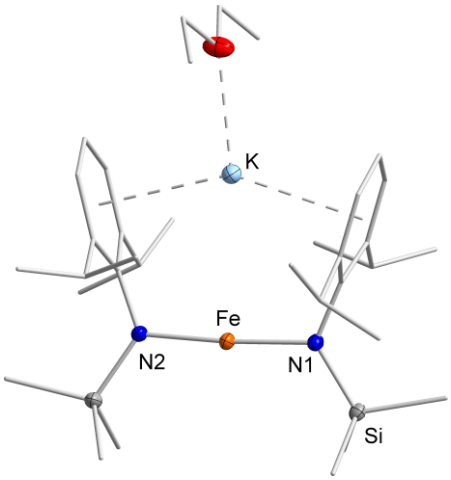

Figure S 67. Molecular structure of [K(Et_2O)Fe(L^2)$_2$] (**3**.Et_2O). All hydrogen atoms are omitted for clarity. Some data are probably incomplete due to strategy errors.

Table S 7. Crystal data and structure refinement of **3**.2DMAP

Empirical formula	$C_{176}H_{288}Fe_4K_4N_{24}Si_8$
Formula weight	3344.81
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	20.857(3)
b/Å	13.086(2)
c/Å	19.863(3)
α/°	90
β/°	117.192(10)
γ/°	90
Volume/Å^3	4822.1(14)
Z	1
ρ_{calc}g/cm^3	1.152
μ/mm^{-1}	0.483
F(000)	1804.0
Crystal size/mm^3	0.687 × 0.104 × 0.098
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.808 to 50
Index ranges	−24 ≤ h ≤ 21, −15 ≤ k ≤ 15, −23 ≤ l ≤ 23
Reflections collected	18133
Independent reflections	4259 [R_{int} = 0.0940, R_{sigma} = 0.0594]
Data/restraints/parameters	4259/0/254
Goodness-of-fit on F^2	0.938
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1572
Final R indexes [all data]	R_1 = 0.0848, wR_2 = 0.1679
Largest diff. peak/hole / e Å^{-3}	0.54/−0.78

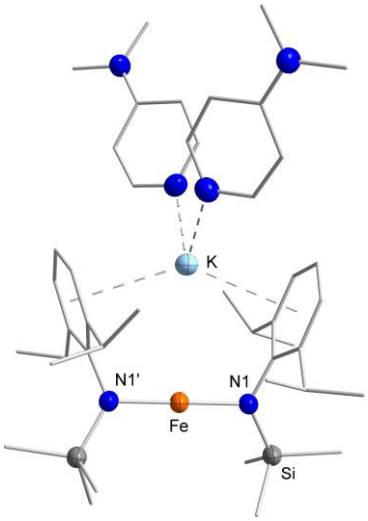

Figure S 68. Molecular structure of [K(DMAP)$_2$Fe(L^2)$_2$] (**3**.2DMAP). All hydrogen atoms are omitted for clarity.

[K(C$_7$H$_8$)Co(L^2)$_2$] (4)

Table S 8. Crystal data and structure refinement of **4**

Empirical formula	$C_{37}H_{60}CoKN_2Si_2$
Formula weight	687.08
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	24.6815(11)
b/Å	25.6246(11)
c/Å	15.9053(7)
α/°	90
β/°	128.3810(10)
γ/°	90
Volume/Å^3	7885.5(6)
Z	8
ρ_{calc}g/cm^3	1.157
μ/mm^{-1}	0.627
F(000)	2960.0
Crystal size/mm^3	0.567 × 0.191 × 0.143
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.558 to 52.212
Index ranges	−30 ≤ h ≤ 30, −31 ≤ k ≤ 31, −17 ≤ l ≤ 19
Reflections collected	141451
Independent reflections	7826 [R_{int} = 0.0701, R_{sigma} = 0.0234]
Data/restraints/parameters	7826/0/414
Goodness-of-fit on F^2	1.211
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.0817
Largest diff. peak/hole / e Å^{-3}	0.28/−0.31

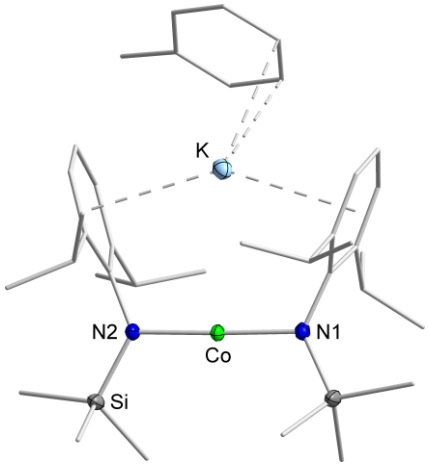

Figure S 69. Molecular structure of [K(C$_7$H$_8$)Co(L^2)$_2$] (**4**). All hydrogen atoms are omitted for clarity.

[K{18c6}(THF)$_2$][Cr(L^1)$_2$] (5)

Table S 9. Crystal data and structure refinement of **5**

Empirical formula	$C_{62}H_{116}CrKN_2O_8Si_2$
Formula weight	1164.82
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	17.2978(7)
b/Å	23.0874(9)
c/Å	34.2506(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	13678.4(10)
Z	8
ρ_{calc}g/cm^3	1.131
μ/mm^{-1}	0.312
F(000)	5096.0
Crystal size/mm^3	0.338 × 0.243 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.256 to 52.23
Index ranges	−21 ≤ h ≤ 21, −28 ≤ k ≤ 28, −41 ≤ l ≤ 42
Reflections collected	239756
Independent reflections	13578 [R_{int} = 0.0914, R_{sigma} = 0.0297]
Data/restraints/parameters	13578/2/722
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.0782
Largest diff. peak/hole / e Å^{-3}	0.28/−0.24

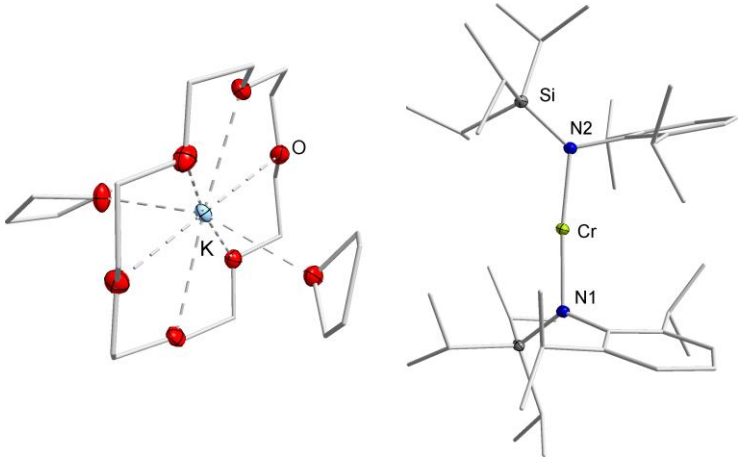

Figure S 70. Molecular structure of [K{18c6}(THF)$_2$][Cr(L^1)$_2$] (**5**). All hydrogen atoms and a disorder in one THF molecule are omitted for clarity.

[Li{12c4}$_2$][Fe(L^2)$_2$] (6)

Table S 10. Crystal data and structure refinement of **6**

Empirical formula	$C_{46}H_{84}FeLiN_2O_8Si_2$
Formula weight	912.12
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.6888(8)
b/Å	14.5127(10)
c/Å	16.4126(12)
α/°	70.550(2)
β/°	83.481(2)
γ/°	77.315(2)
Volume/Å^3	2558.7(3)
Z	2
ρ_{calc}g/cm^3	1.184
μ/mm^{-1}	0.390
F(000)	990.0
Crystal size/mm^3	0.395 × 0.248 × 0.242
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.346 to 61.008
Index ranges	−14 ≤ h ≤ 16, −20 ≤ k ≤ 20, −23 ≤ l ≤ 23
Reflections collected	50692
Independent reflections	14042 [R_{int} = 0.0418, R_{sigma} = 0.0499]
Data/restraints/parameters	14042/471/564
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0826, wR_2 = 0.1912
Final R indexes [all data]	R_1 = 0.0979, wR_2 = 0.1996
Largest diff. peak/hole / e Å^{-3}	1.46/−0.85

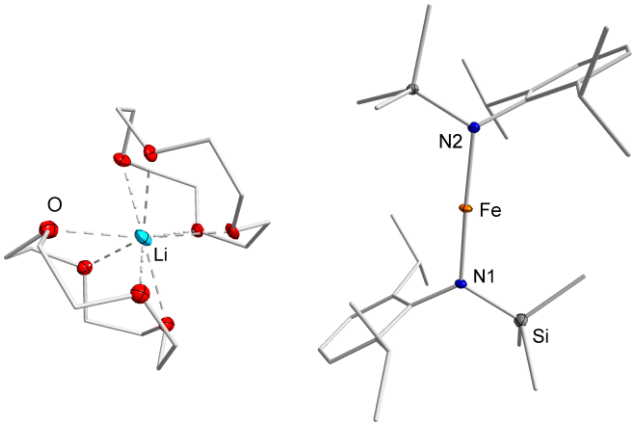

Figure S 71. Molecular structure of [Li{12c4}$_2$][Fe(L^2)$_2$] (**6**). All hydrogen atoms are omitted for clarity. The structure was refined as a twin, twin ratio refined to 0.0863(9).

[Na{18c6}(Et_2O)][Fe(L^2)$_2$] (7)

Table S 11. Crystal data and structure refinement of **7**

Empirical formula	$C_{46}H_{86}FeN_2NaO_7Si_2$
Formula weight	914.18
Temperature/K	100.0
Crystal system	triclinic
Space group	P−1
a/Å	12.392(3)
b/Å	13.002(3)
c/Å	18.053(3)
α/°	71.086(15)
β/°	76.889(16)
γ/°	70.636(15)
Volume/Å^3	2572.7(10)
Z	2
ρ_{calc}g/cm^3	1.180
μ/mm^{-1}	0.395
F(000)	994.0
Crystal size/mm^3	0.893 × 0.503 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.45 to 53.888
Index ranges	−15 ≤ h ≤ 14, −16 ≤ k ≤ 16, −23 ≤ l ≤ 22
Reflections collected	23621
Independent reflections	10961 [R_{int} = 0.2177, R_{sigma} = 0.1943]
Data/restraints/parameters	10961/54/578
Goodness-of-fit on F^2	0.909
Final R indexes [I>=2σ (I)]	R_1 = 0.0828, wR_2 = 0.2018
Final R indexes [all data]	R_1 = 0.1415, wR_2 = 0.2306
Largest diff. peak/hole / e Å^{-3}	1.03/−0.86

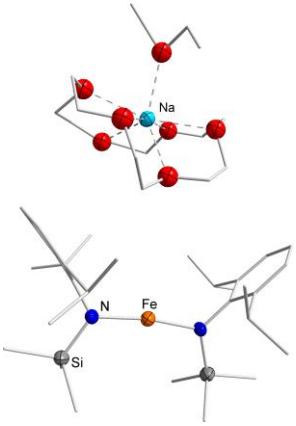

Figure S 72. Molecular structure of [Na{18c6}(Et_2O)][Fe(L^2)$_2$] (**7**). All hydrogen atoms are omitted for clarity. A disorder of the 18-crown-6 unit with occupations of 50% for both part 1 (depicted) and part 2 is found.

[NBu$_4$][Fe(L^2)$_2$] (8)

Table S 12. Crystal data and structure refinement of **8**

Empirical formula	$C_{184}H_{352}Fe_4N_{12}Si_8$
Formula weight	3180.87
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.298(2)
b/Å	13.8270(10)
c/Å	21.446(3)
α/°	90
β/°	114.323(10)
γ/°	90
Volume/Å^3	4944.3(10)
Z	1
ρ_{calc}g/cm^3	1.068
μ/mm^{-1}	0.385
F(000)	1756.0
Crystal size/mm^3	0.372 × 0.246 × 0.173
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.862 to 53.478
Index ranges	−23 ≤ h ≤ 23, −17 ≤ k ≤ 17, −26 ≤ l ≤ 27
Reflections collected	44120
Independent reflections	10436 [R_{int} = 0.0915, R_{sigma} = 0.0680]
Data/restraints/parameters	10436/0/487
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0746
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.0839
Largest diff. peak/hole / e Å^{-3}	0.24/−0.35

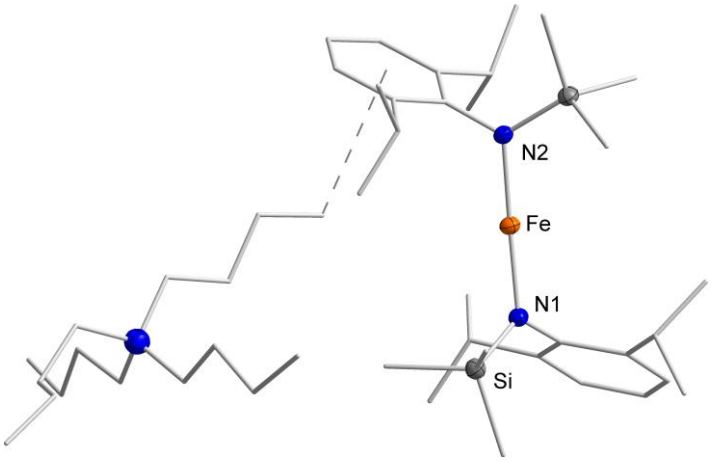

Figure S 73. Molecular structure of [NBu$_4$][Fe(L^2)$_2$] (**8**). All hydrogen atoms are omitted for clarity.

[NBu$_4$][Co(L^2)$_2$] (9)

Table S 13. Crystal data and structure refinement of **9**

Empirical formula	$C_{184}H_{352}Co_4N_{12}Si_8$
Formula weight	3193.20
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.7553(6)
b/Å	19.9389(8)
c/Å	22.5989(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4846.3(4)
Z	1
ρ_{calc}g/cm^3	1.094
μ/mm^{-1}	0.435
F(000)	1760.0
Crystal size/mm^3	0.432 × 0.293 × 0.185
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.604 to 49.998
Index ranges	−12 ≤ h ≤ 12, −23 ≤ k ≤ 23, −26 ≤ l ≤ 26
Reflections collected	36221
Independent reflections	8508 [R_{int} = 0.0503, R_{sigma} = 0.0302]
Data/restraints/parameters	8508/0/488
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0286, wR_2 = 0.0720
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0731
Largest diff. peak/hole / e Å^{-3}	0.25/−0.20
Flack parameter	0.152(12)

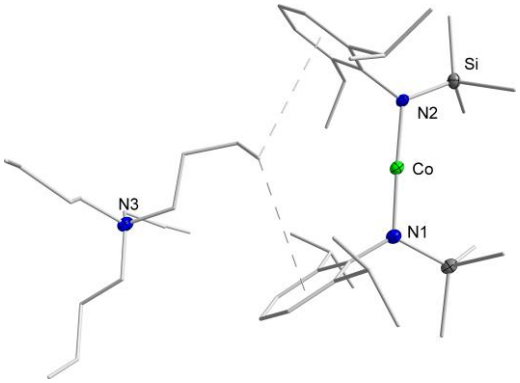

Figure S 74. Molecular structure of [NBu$_4$][Co(L^2)$_2$] (**9**). All hydrogen atoms are omitted for clarity. The structure was refined as an inversion twin, twin ratio refined to 0.152(12).

[K{18c6}(THF)$_2$][Fe(L^2)$_2$)(η^{2}-PhCCPh)] (10)

Table S 17. Crystal data and structure refinement of **10**

Empirical formula	$C_{64}H_{102}N_2O_8Si_2KFe$
Formula weight	1178.60
Temperature/K	100.0
Crystal system	triclinic
Space group	P−1
a/Å	11.0677(6)
b/Å	13.4596(7)
c/Å	22.1320(11)
α/°	83.532(2)
β/°	88.471(2)
γ/°	87.653(2)
Volume/Å^3	3272.4(3)
Z	2
ρ_{calc}g/cm^3	1.196
μ/mm^{-1}	0.383
F(000)	1274.0
Crystal size/mm^3	0.312 × 0.239 × 0.072
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.528 to 50.626
Index ranges	−12 ≤ h ≤ 13, −16 ≤ k ≤ 16, −26 ≤ l ≤ 26
Reflections collected	117177
Independent reflections	11928 [R_{int} = 0.0554, R_{sigma} = 0.0299]
Data/restraints/parameters	11928/0/720
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.0773
Largest diff. peak/hole / e Å^{-3}	0.36/−0.33

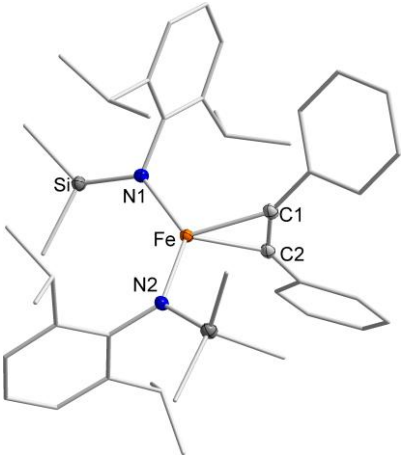

Figure S 75. Molecular structure of [K{18c6}(THF)$_2$][Fe(L^2)$_2$)(η^{2}-PhCCPh)] (**10**). All hydrogen atoms and the K{18c6}(THF)$_2$ cation are omitted for clarity.

[K(Et$_2$O)Fe(η^6-HPB)(η^{2-}PhCCPh)] (11.Et$_2$O**)**

Table S 15. Crystal data and structure refinement of **11**.Et2O

Empirical formula	$C_{60}H_{50}FeKO$
Formula weight	881.95
Temperature/K	110.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	19.3467(7)
b/Å	11.2945(4)
c/Å	21.4705(9)
α/°	90
β/°	102.4730(13)
γ/°	90
Volume/Å^3	4580.8(3)
Z	4
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	0.462
F(000)	1852.0
Crystal size/mm^3	0.26 × 0.08 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.312 to 50.652
Index ranges	−23 ≤ h ≤ 23, −13 ≤ k ≤ 13, −25 ≤ l ≤ 25
Reflections collected	115901
Independent reflections	8348 [R_{int} = 0.0574, R_{sigma} = 0.0218]
Data/restraints/parameters	8348/0/594
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0870
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.0920
Largest diff. peak/hole / e Å^{-3}	0.59/−0.50

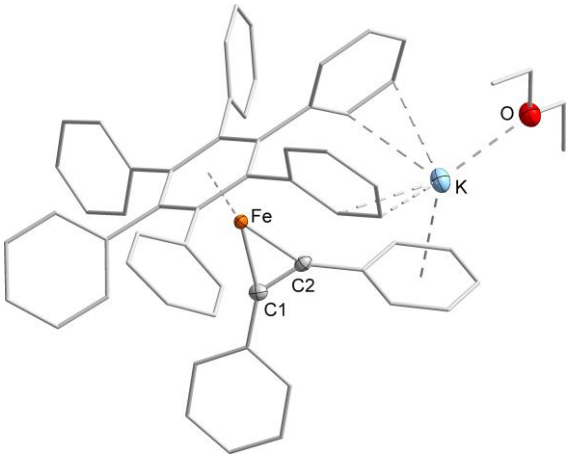

Figure S 76. Molecular structure of [K(Et$_2$O)Fe(η^6-HPB)(η^{2-}PhCCPh)] (**11**.Et$_2$O). All hydrogen atoms are omitted for clarity.

[KFe(η^6-HPB)(η^{2-}PhCCPh)] (11)

Table S 16. Crystal data and structure refinement of **11**

Empirical formula	$C_{56}H_{40}FeK$
Formula weight	807.83
Temperature/K	99.99
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4506(4)
b/Å	18.1974(7)
c/Å	23.8299(9)
α/°	90
β/°	97.1120(10)
γ/°	90
Volume/Å^3	4497.0(3)
Z	4
ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	0.463
F(000)	1684.0
Crystal size/mm^3	0.194 × 0.135 × 0.075
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.476 to 52.172
Index ranges	−11 ≤ h ≤ 12, −22 ≤ k ≤ 22, −29 ≤ l ≤ 29
Reflections collected	70523
Independent reflections	8887 [R_{int} = 0.0621, R_{sigma} = 0.0363]
Data/restraints/parameters	8887/0/550
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.0897
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.0952
Largest diff. peak/hole / e Å^{-3}	0.31/−0.36

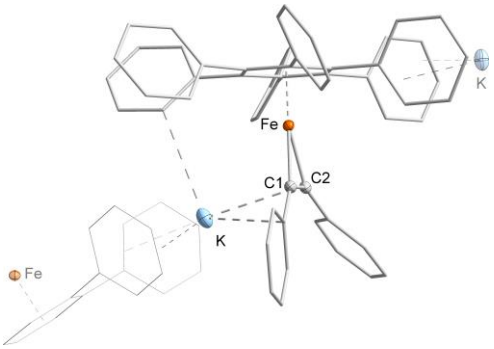

Figure S 77. Molecular structure of [KFe(η^6-HPB)(η^{2-}PhCCPh)] (**11**). All hydrogen atoms and a disorder in one phenyl ring (part 1: 75%, depicted; part 2: 25%) are omitted for clarity. A free diethyl ether molecule is located on a symmetry element and is heavily disordered over multiple positions. Attempts to model the disorder did not lead to satisfactory results and further gave higher R-values. It was thus squeezed.

Table S 19. Crystal data and structure refinement of **12**

Empirical formula	$C_{74}H_{103}K_2Mn_2N_2O_4Si_2$
Formula weight	1328.84
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	12.905(11)
b/Å	13.215(8)
c/Å	14.360(9)
α/°	104.35(5)
β/°	107.84(6)
γ/°	105.11(6)
Volume/Å^3	2103(3)
Z	1
ρ_{calc}g/cm^3	1.049
μ/mm^{-1}	0.468
F(000)	709.0
Crystal size/mm^3	0.942 × 0.456 × 0.229
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.188 to 49.994
Index ranges	−15 ≤ h ≤ 15, −15 ≤ k ≤ 15, −17 ≤ l ≤ 17
Reflections collected	15985
Independent reflections	7390 [R_{int} = 0.1069, R_{sigma} = 0.0991]
Data/restraints/parameters	7390/3/409
Goodness-of-fit on F^2	0.949
Final R indexes [I>=2σ (I)]	R_1 = 0.0868, wR_2 = 0.2314
Final R indexes [all data]	R_1 = 0.1224, wR_2 = 0.2483
Largest diff. peak/hole / e Å^{-3}	0.86/−0.64

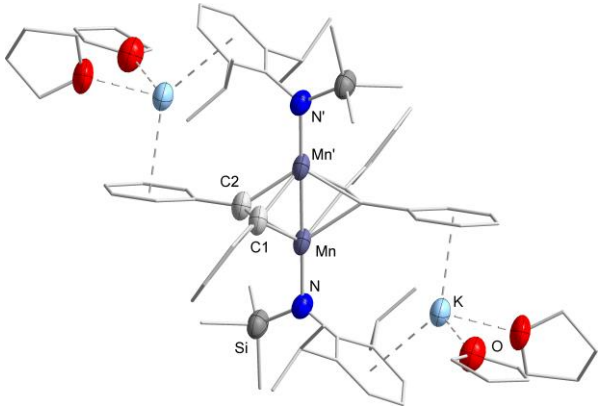

Figure S 78. Molecular structure of **12**. All hydrogen atoms and disorders in one *iso*-propyl group and one trimethylsilyl group are omitted for clarity. Two free toluene molecules are heavily disordered over multiple positions. Attempts to model the disorders did not lead to satisfactory results and further gave higher R-values. They were thus squeezed.

Table S 18. Crystal data and structure refinement of **13**

Empirical formula	$C_{78}H_{70}K_2Mn_2O_2$
Formula weight	1227.42
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.6490(9)
b/Å	18.4355(9)
c/Å	19.6687(11)
α/°	90
β/°	93.540(2)
γ/°	90
Volume/Å^3	6387.4(6)
Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.573
F(000)	2568.0
Crystal size/mm^3	0.729 × 0.113 × 0.103
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.418 to 50.202
Index ranges	−18 ≤ h ≤ 21, −21 ≤ k ≤ 21, −23 ≤ l ≤ 23
Reflections collected	37162
Independent reflections	11297 [R_{int} = 0.0750, R_{sigma} = 0.0891]
Data/restraints/parameters	11297/1548/879
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0829, wR_2 = 0.1868
Final R indexes [all data]	R_1 = 0.1366, wR_2 = 0.2107
Largest diff. peak/hole / e Å^{-3}	0.70/−0.77

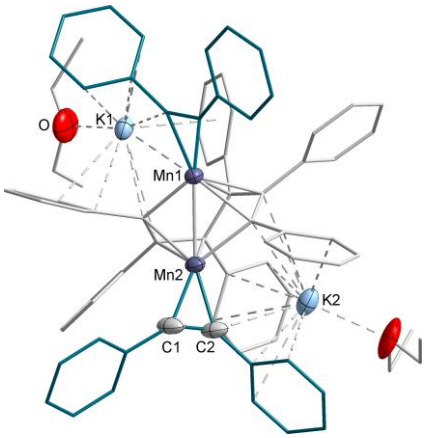

Figure S 79. Molecular structure of **13**. All hydrogen atoms are omitted for clarity. Disorders in both diethyl ether adducts and two phenyl rings with occupations of 50% for both part 1 (depicted) and part 2 are found.

[K{18c6}][Fe(L^2)$_2$] x Et$_2$O

Table S 14. Crystal data and structure refinement of [K{18c6}][Fe(L^2)$_2$] x Et$_2$O

Empirical formula	$C_{184}H_{344}Fe_4K_4N_8O_{28}Si_8$
Formula weight	3721.17
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.3333(7)
b/Å	34.0397(14)
c/Å	15.5254(9)
α/°	90
β/°	95.062(5)
γ/°	90
Volume/Å^3	5439.6(5)
Z	1
ρ_{calc}g/cm^3	1.136
μ/mm^{-1}	0.442
F(000)	2020.0
Crystal size/mm^3	0.888 × 0.304 × 0.225
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.944 to 53.622
Index ranges	−13 ≤ h ≤ 13, −43 ≤ k ≤ 43, −19 ≤ l ≤ 18
Reflections collected	42532
Independent reflections	11480 [R_{int} = 0.0441, R_{sigma} = 0.0347]
Data/restraints/parameters	11480/0/548
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0648, wR_2 = 0.1172
Largest diff. peak/hole / e Å^{-3}	0.59/−0.69

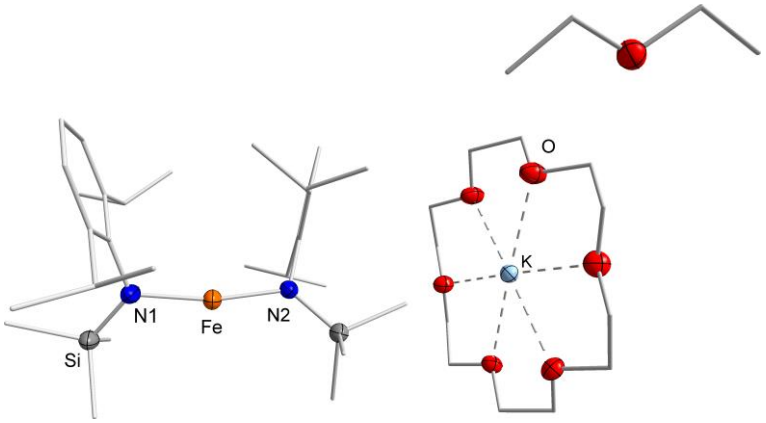

Figure S 80. Molecular structure of [K{18c6}][Fe(L^2)$_2$] x Et$_2$O. All hydrogen atoms are omitted for clarity.

References

(1) Lin, C.-Y.; Fettinger, J. C.; Grandjean, F.; Long, G. J.; Power, P. P. Synthesis, Structure, and Magnetic and Electrochemical Properties of Quasi-Linear and Linear Iron(I), Cobalt(I), and Nickel(I) Amido Complexes // Synthesis, structure, and magnetic and electrochemical properties of quasi-linear and linear iron(I), cobalt(I), and nickel(I) amido complexes. *Inorg. Chem.* **2014**, *53*, 9400–9406.