Supporting Information belonging to

Triazolylidene Iron(II) Piano-Stool Complexes: Synthesis and Catalytic Hydrosilylation of Carbonyl Compounds

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Content

1. NMR Spectra

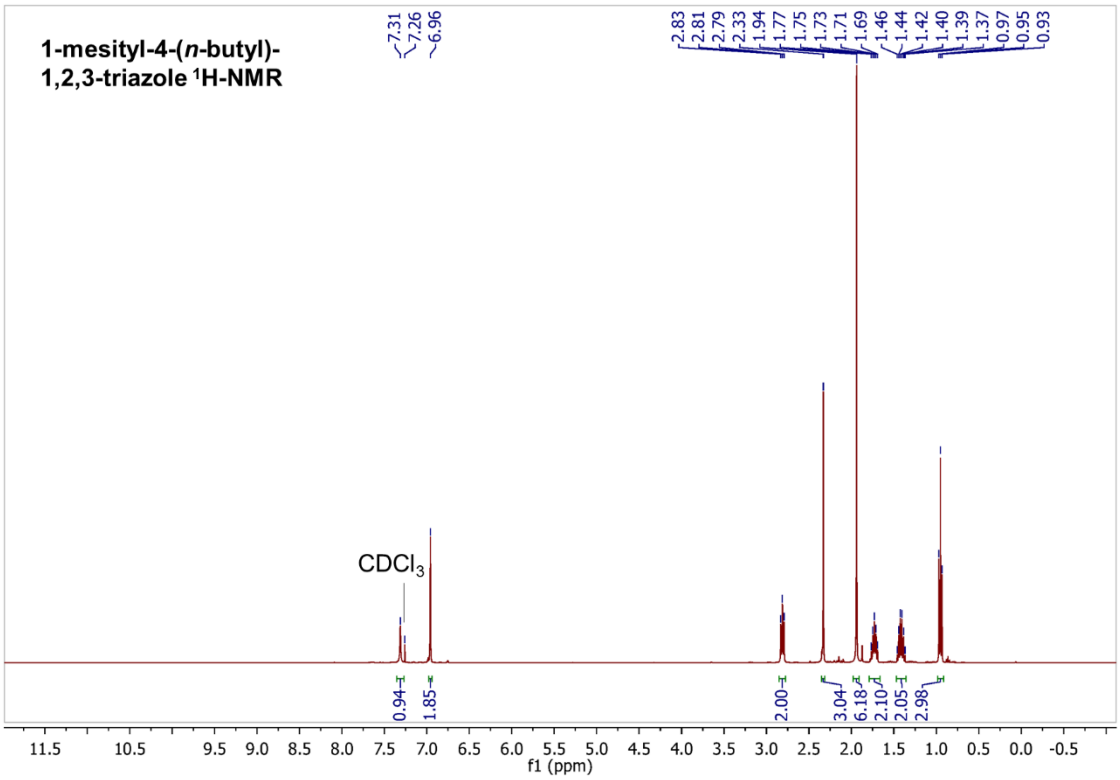


Figure S1. *[1]H NMR spectrum (400 MHz) for 1-mesityl-4-(n-butyl)-1,2,3-triazole.*

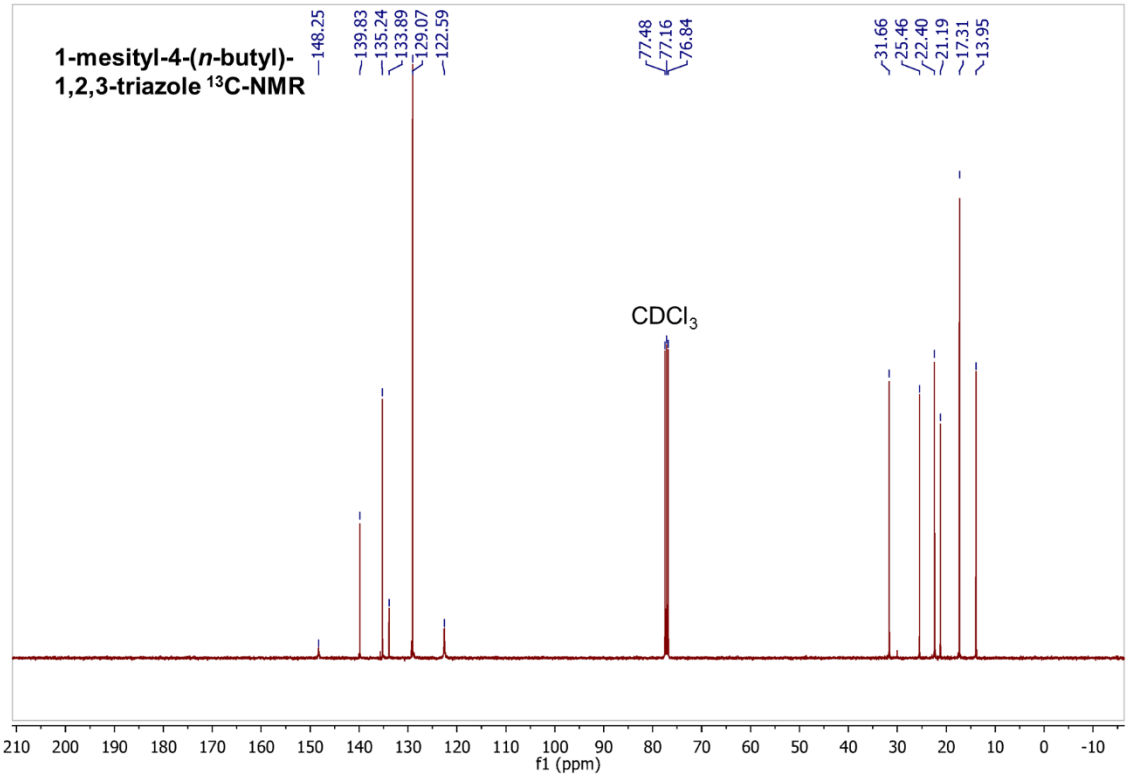


Figure S2. *[13]C{[1]H} NMR spectrum (100 MHz) for 1-mesityl-4-(n-butyl)-1,2,3-triazole.*

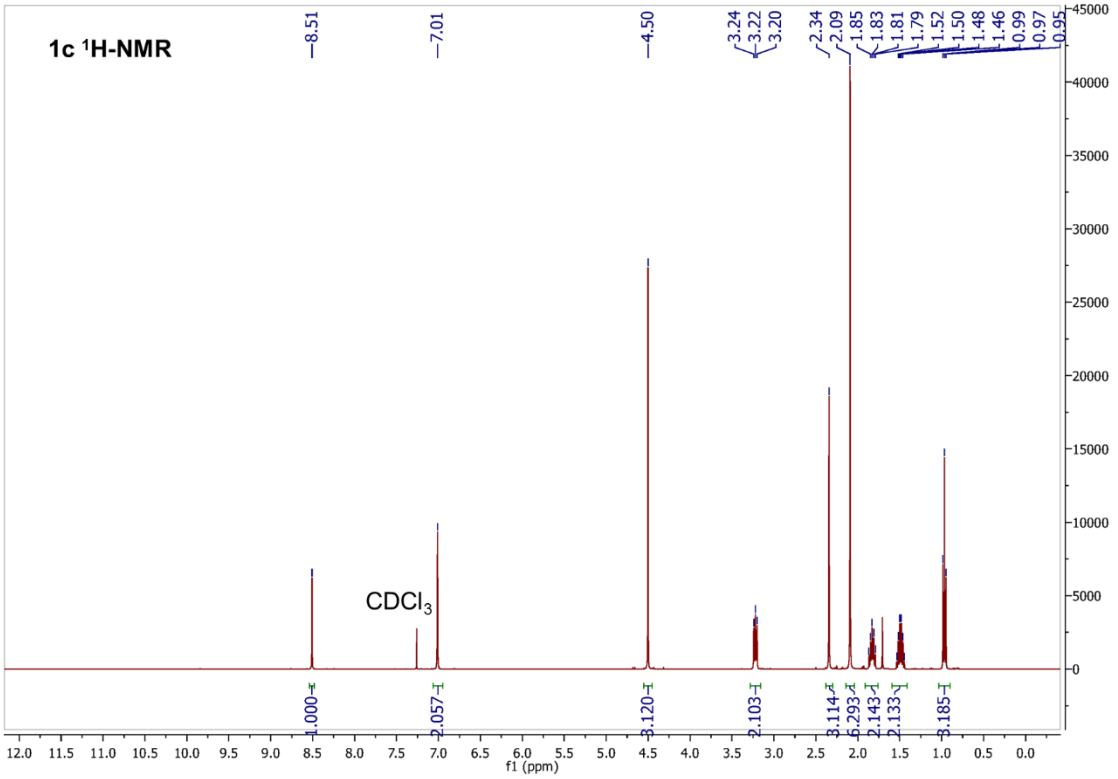


Figure S3. *[1]H NMR spectrum (400 MHz) for ligand precursor* ***1c****.*

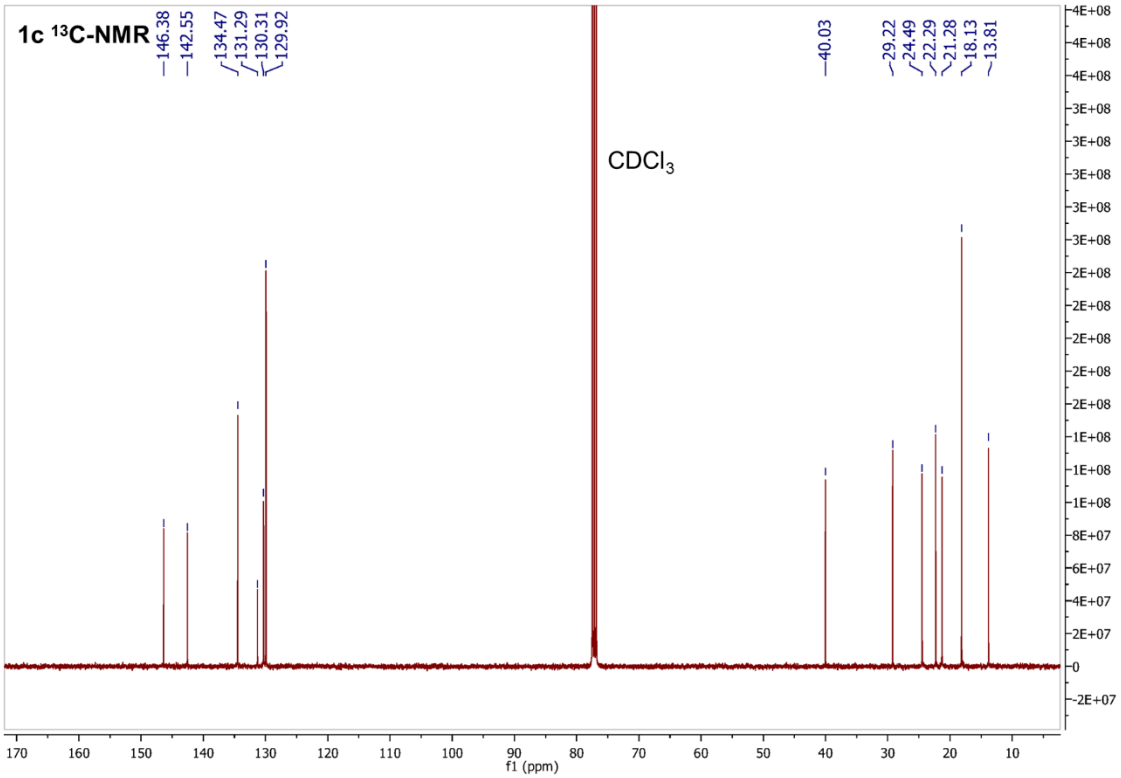


Figure S4. *[13]C{[1]H} NMR spectrum (100 MHz) for ligand precursor* ***1c****.*

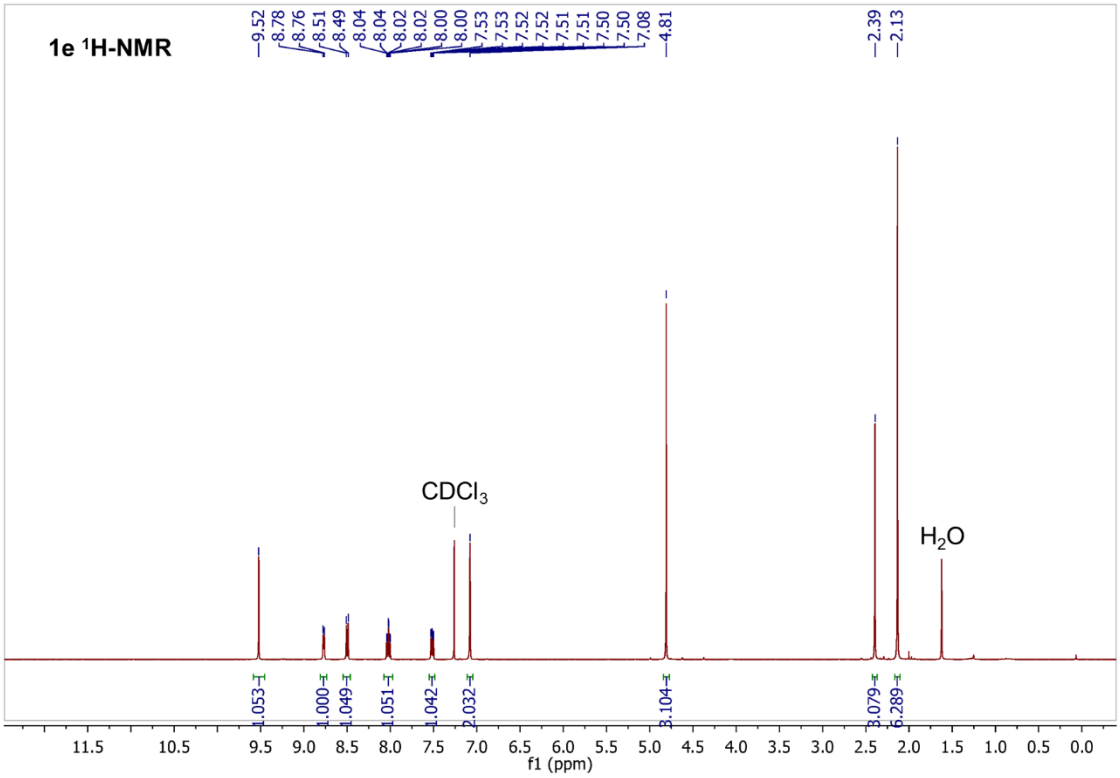


Figure S5. *[1]H NMR spectrum (400 MHz) for ligand precursor* ***1e****.*

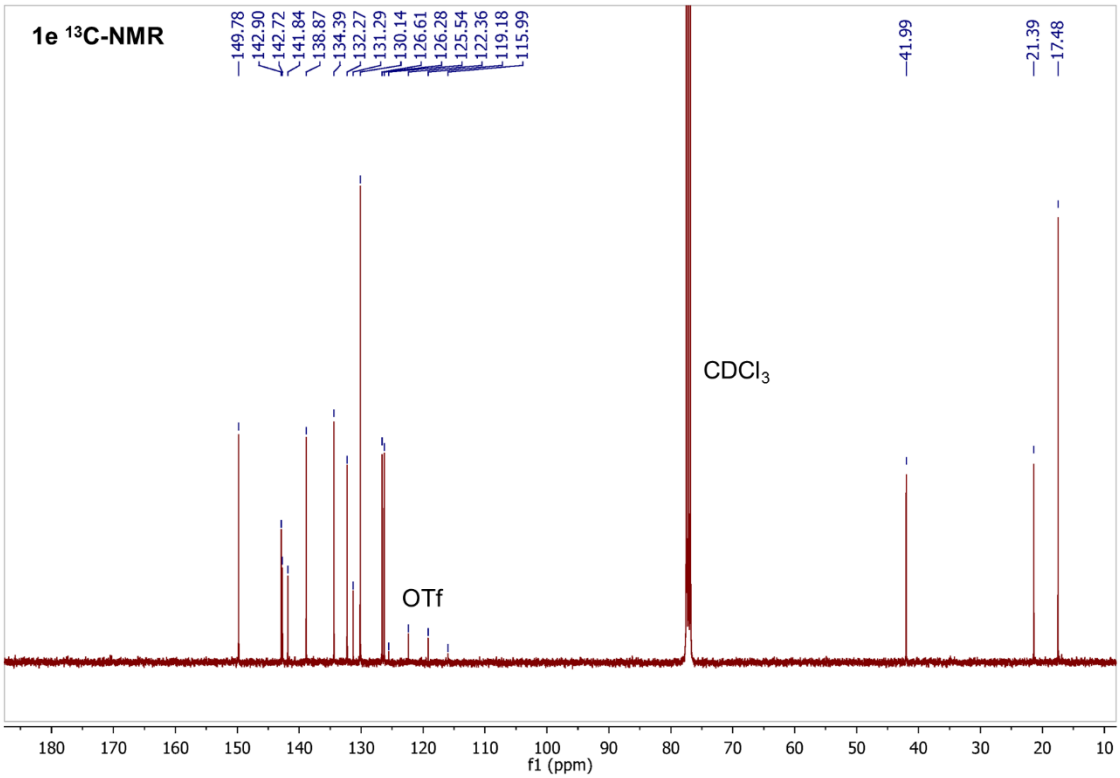


Figure S6. *[13]C{[1]H} NMR spectrum (100 MHz) for ligand precursor* ***1e****.*

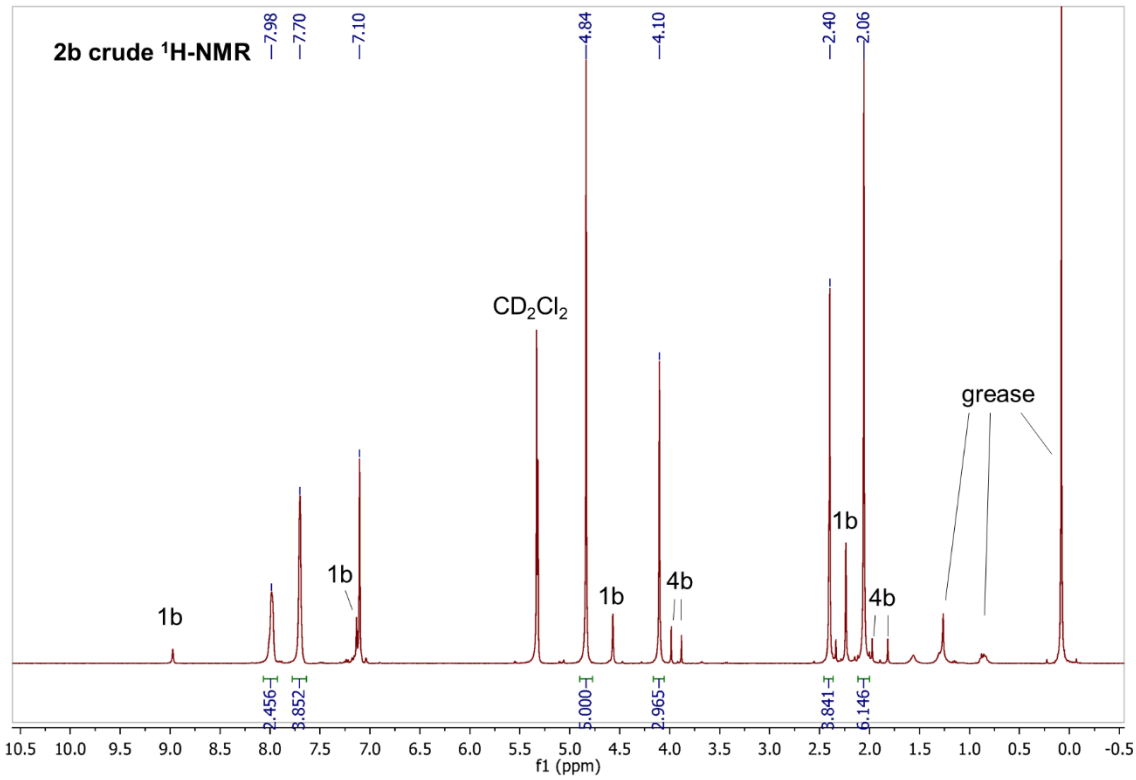


Figure S7. *^{1}H NMR spectrum (400 MHz) for crude complex* ***2b****.*

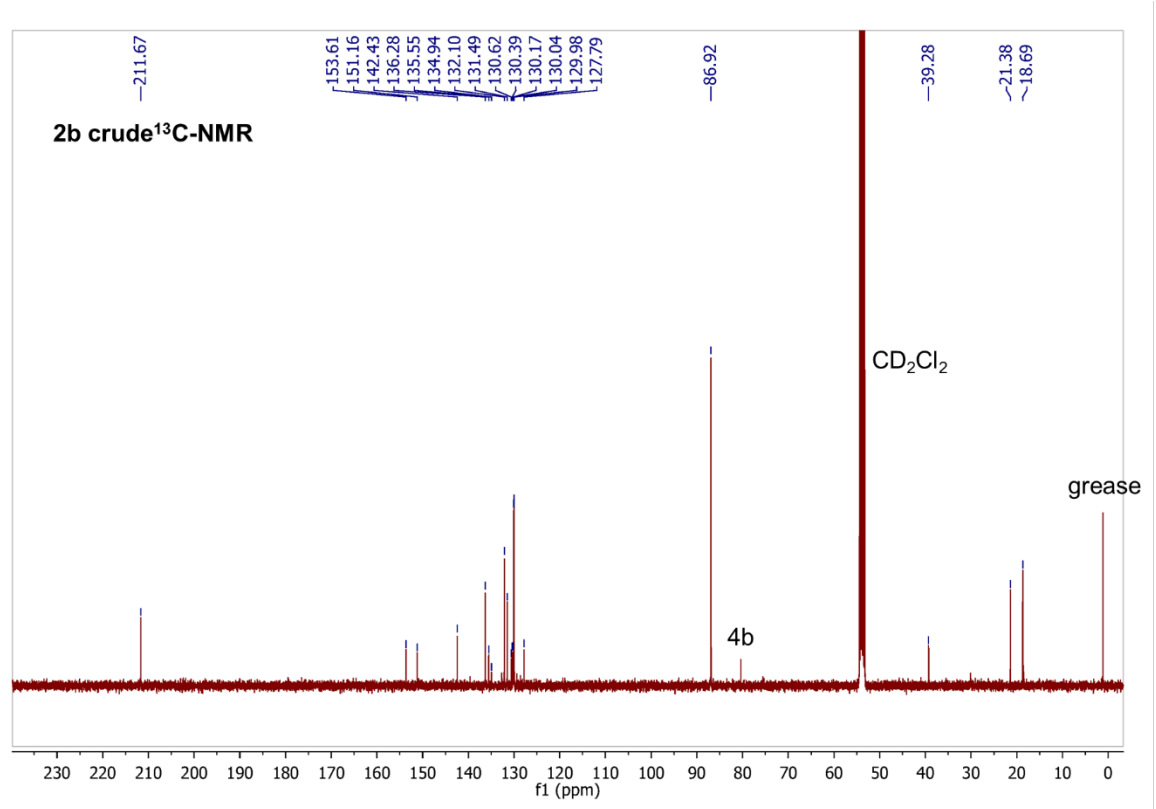


Figure S8. *$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) for crude complex* ***2b****.*

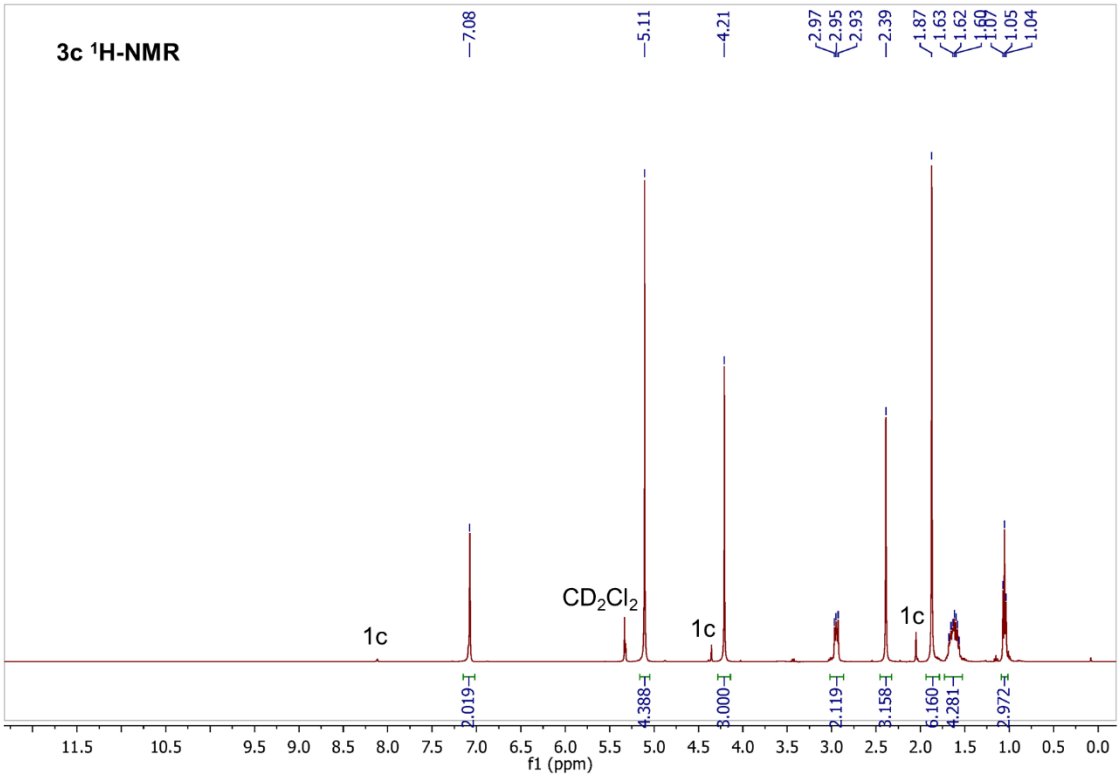


Figure S9. *[1]H NMR spectrum (400 MHz) for crude complex* ***3c****.*

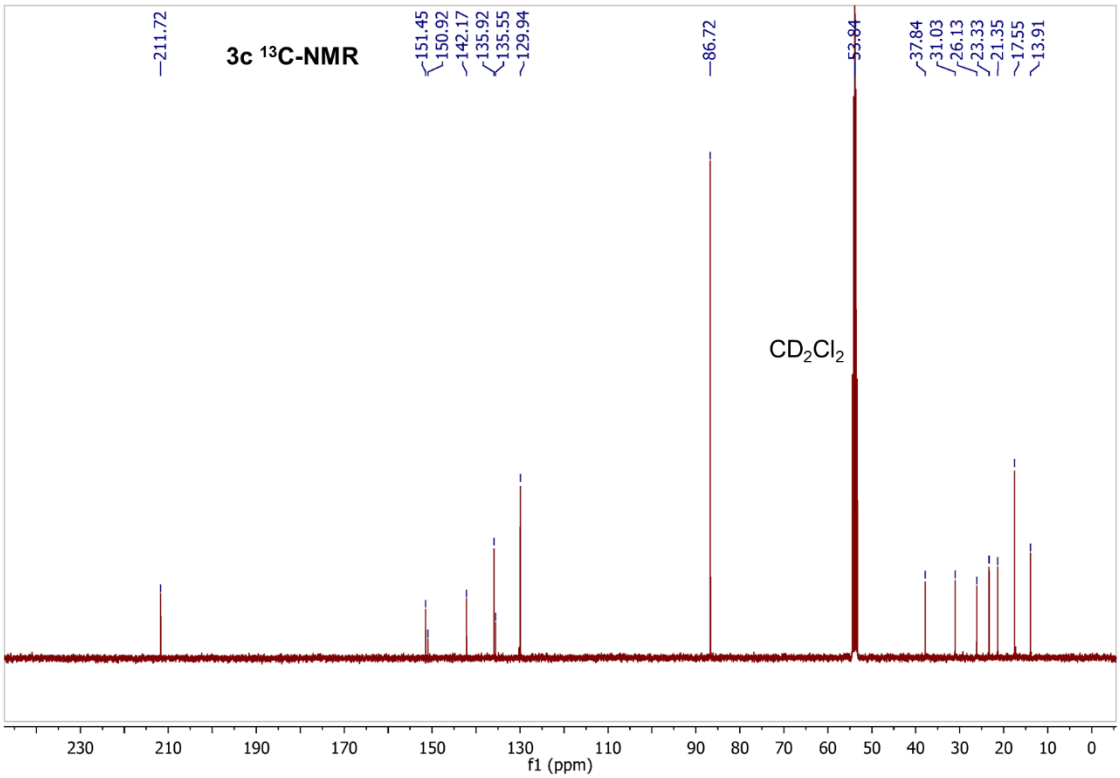


Figure S10. *[13]C{[1]H} NMR spectrum (100 MHz) for crude complex* ***3c****.*

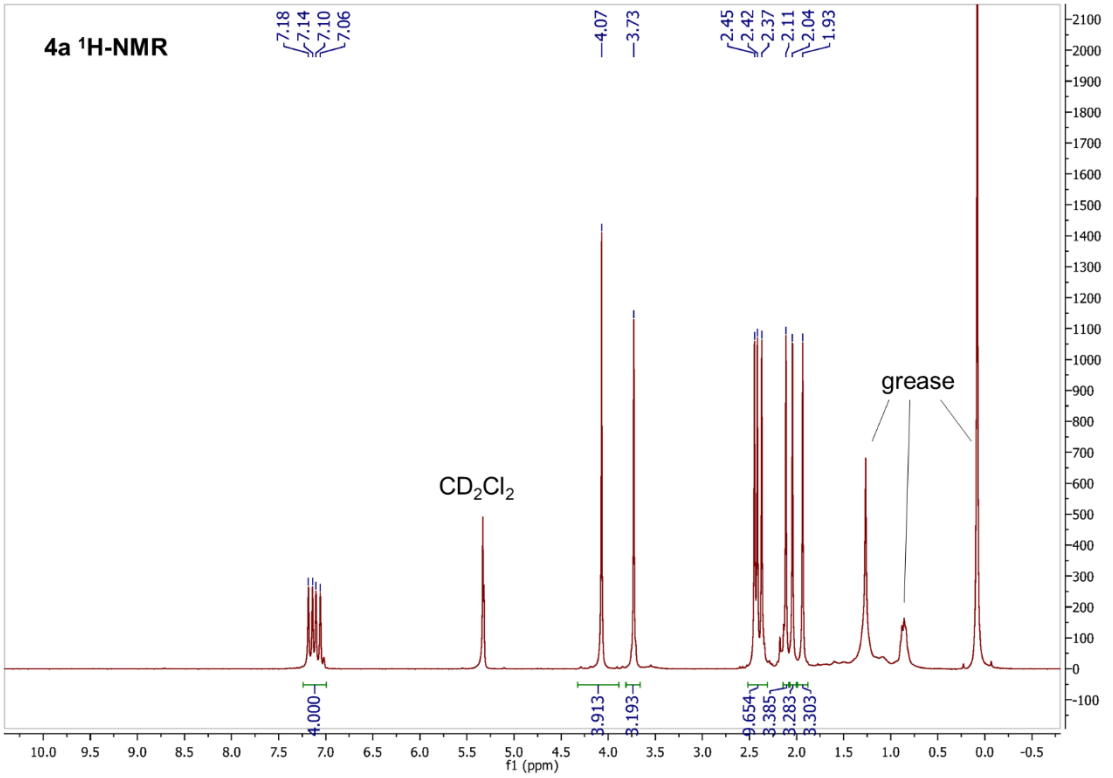


Figure S11. *^{1}H NMR spectrum (400 MHz) for complex* ***4a****.*

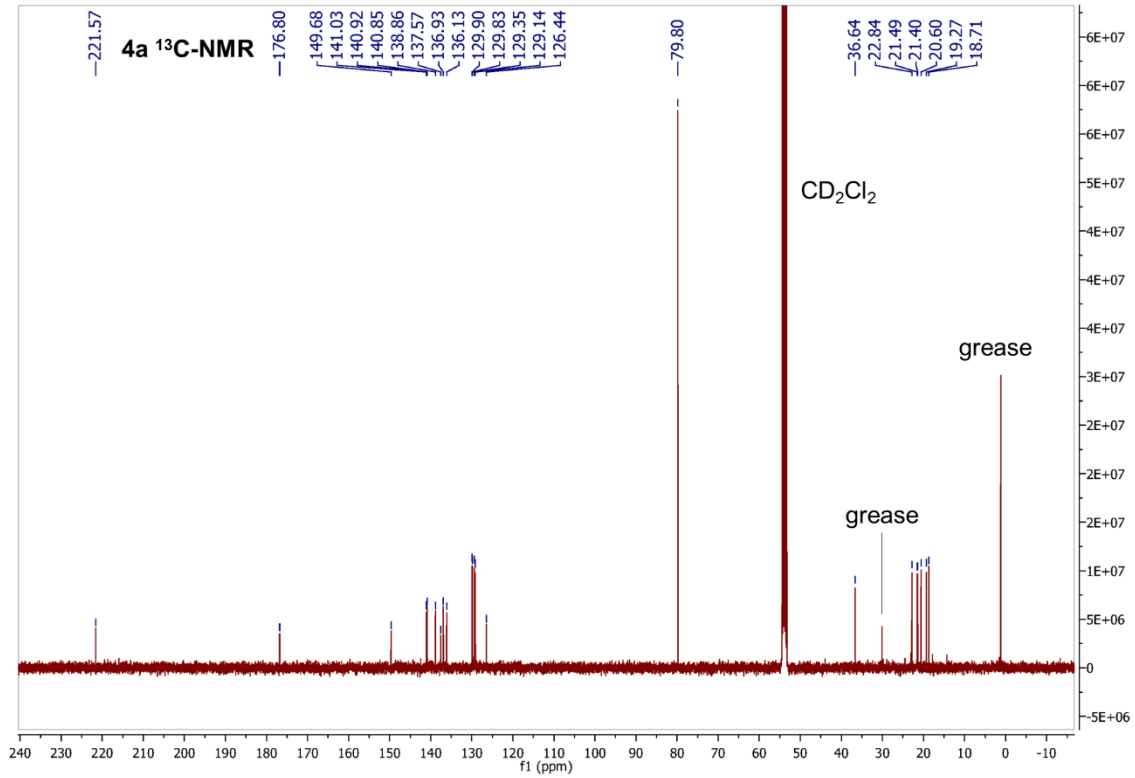


Figure S12. *$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) for complex* ***4a****.*

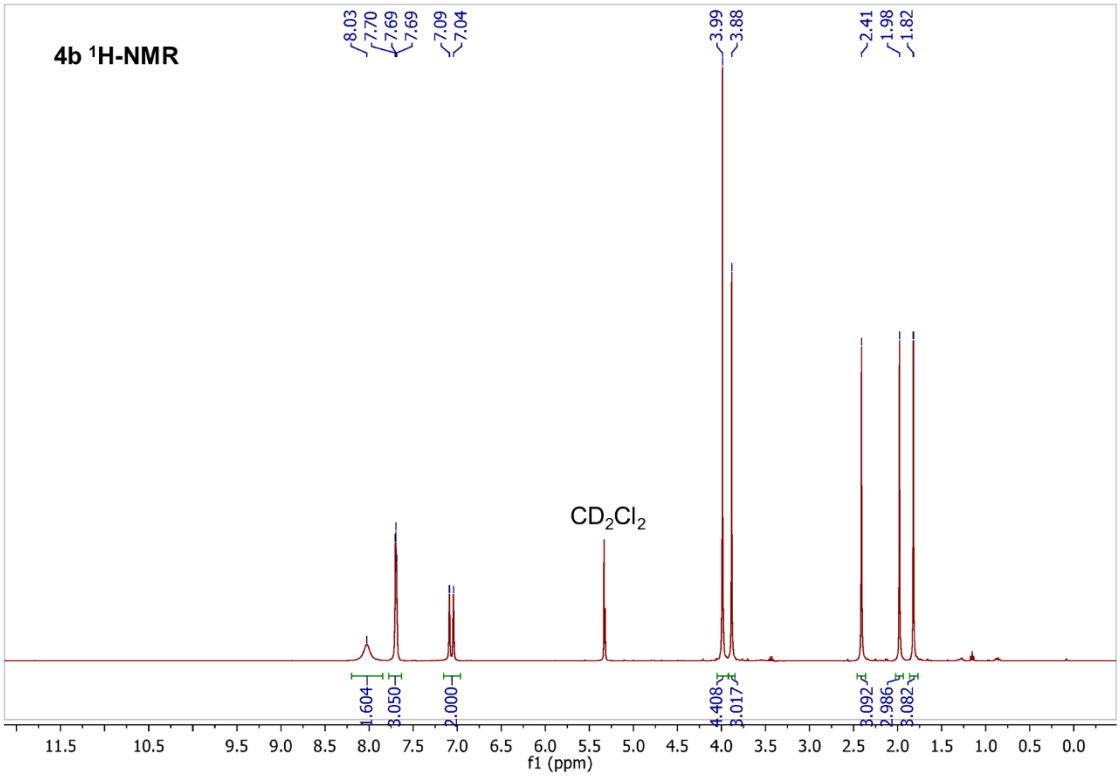


Figure S13. *^{1}H NMR spectrum (400 MHz) for complex* ***4b****.*

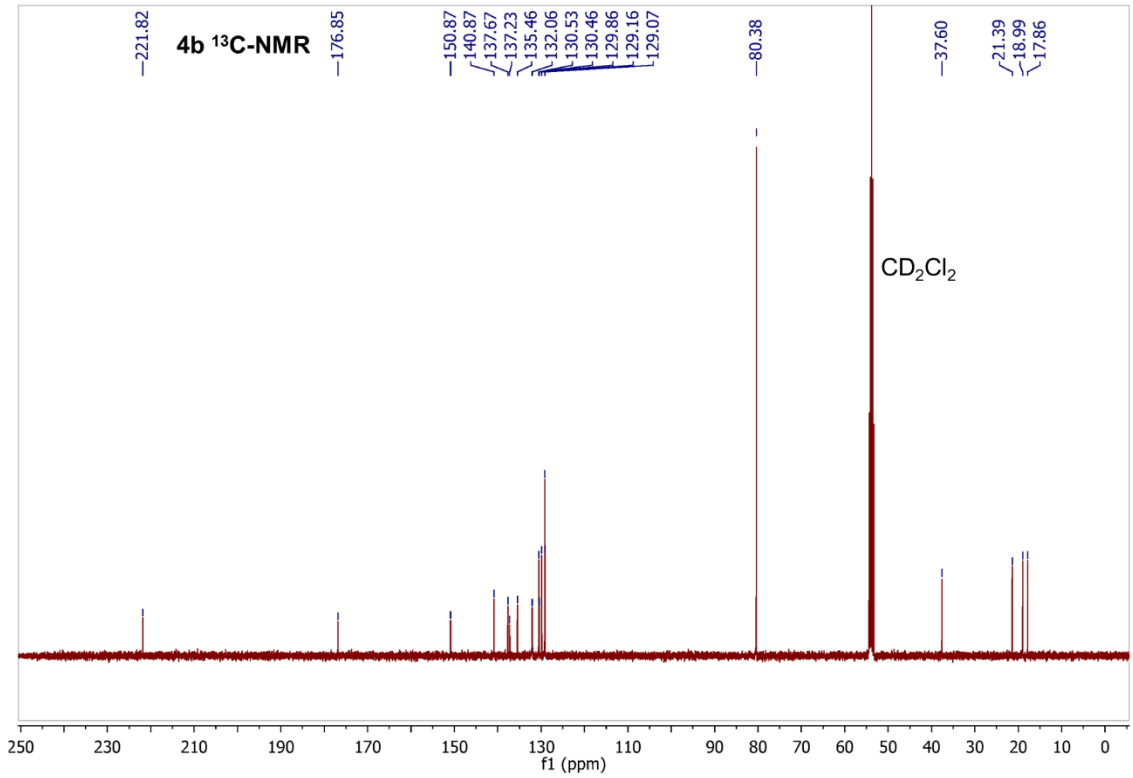


Figure S14. *$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) for complex* ***4b****.*

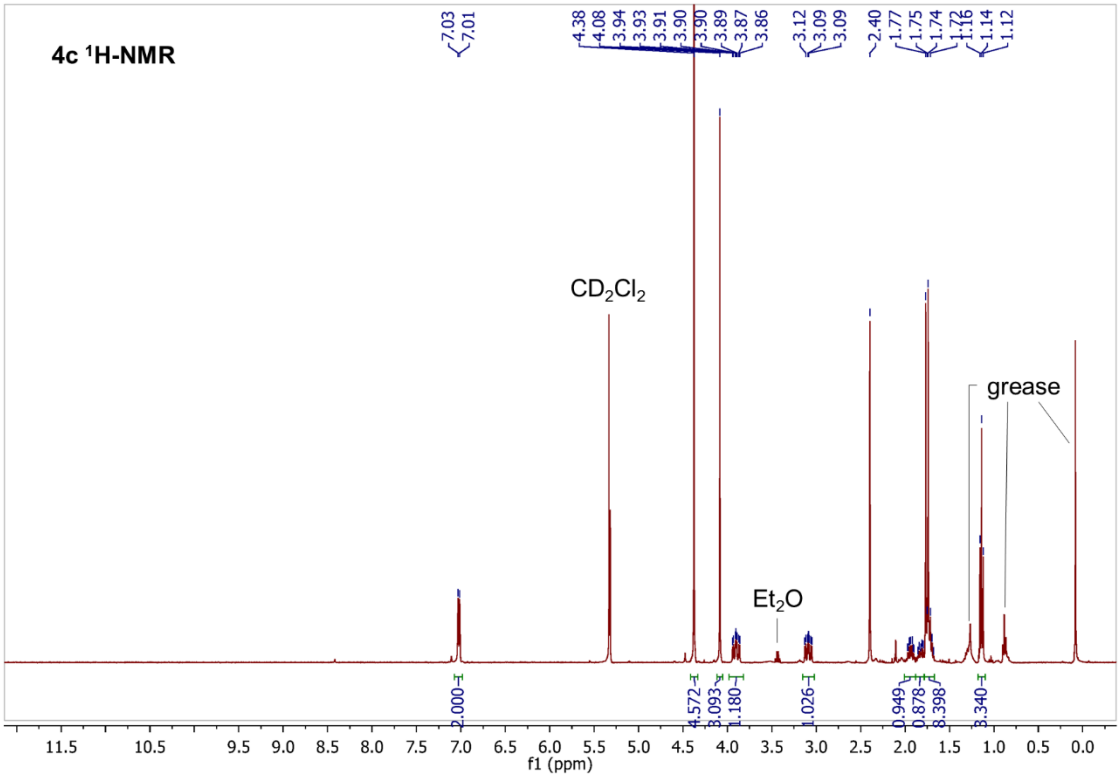


Figure S15. *[1]H NMR spectrum (400 MHz) for complex* ***4c****.*

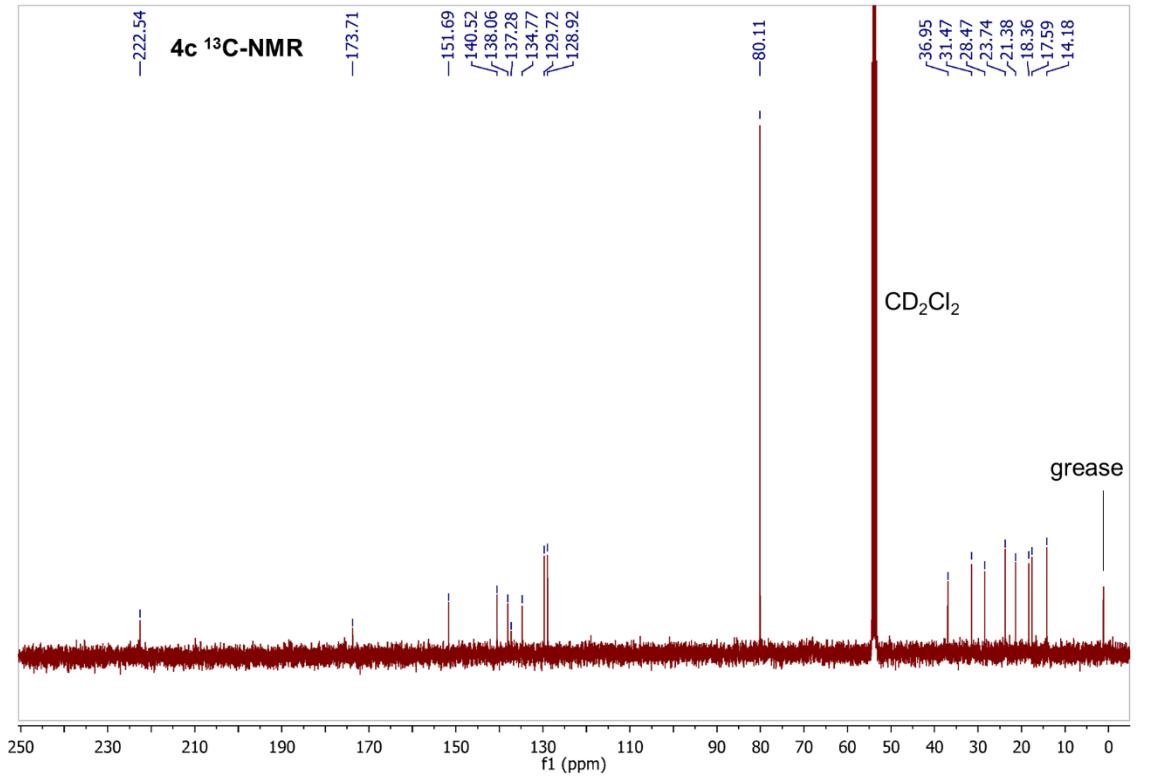


Figure S16. *[13]C{[1]H} NMR spectrum (100 MHz) for complex* ***4c****.*

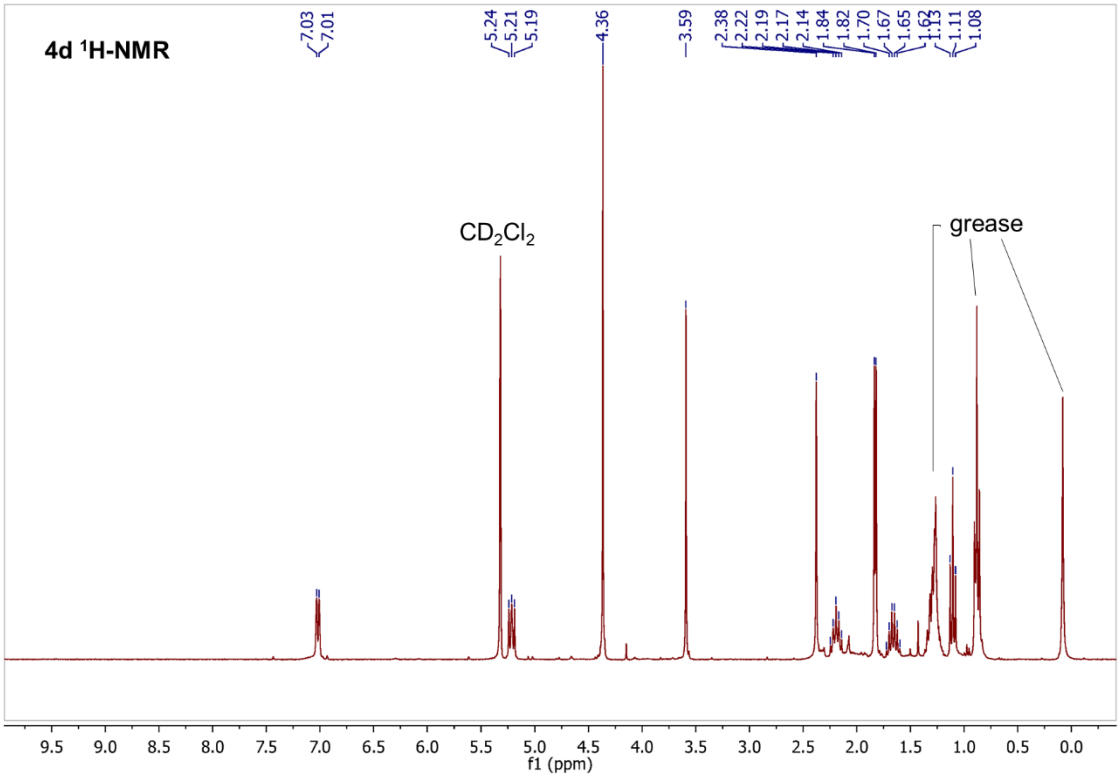


Figure S17. *^{1}H NMR spectrum (300 MHz) for complex* ***4d****.*

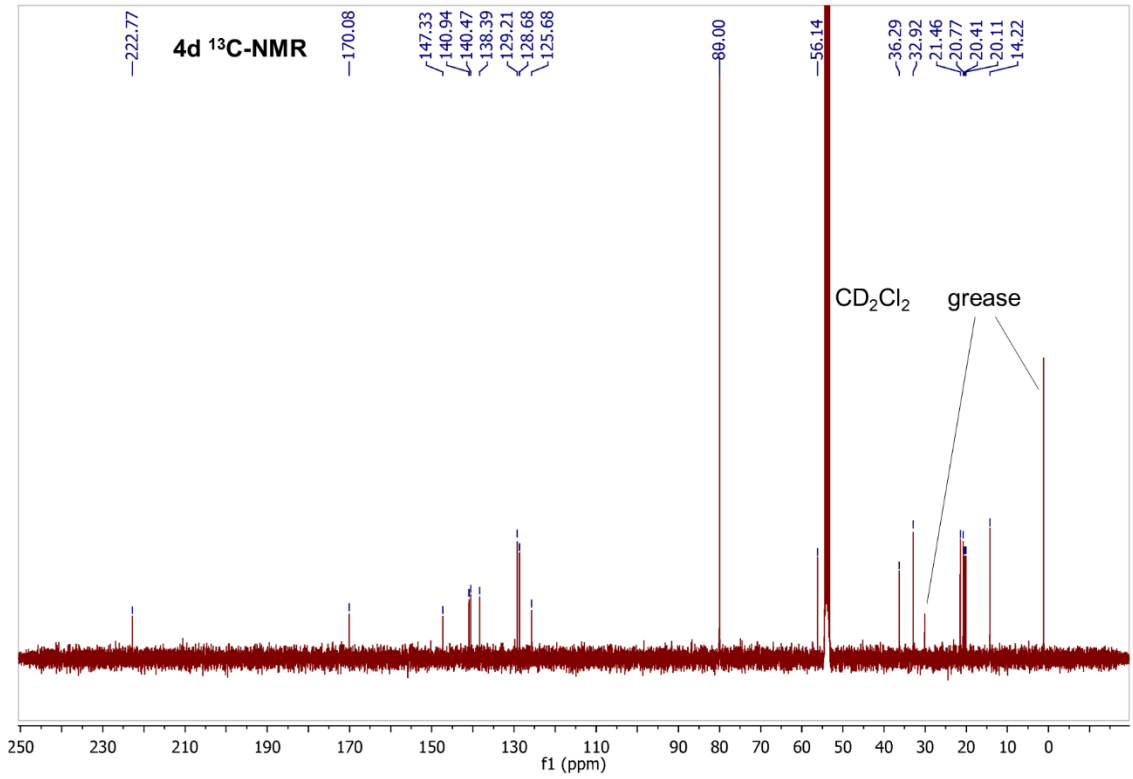


Figure S18. *$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) for complex* ***4d****.*

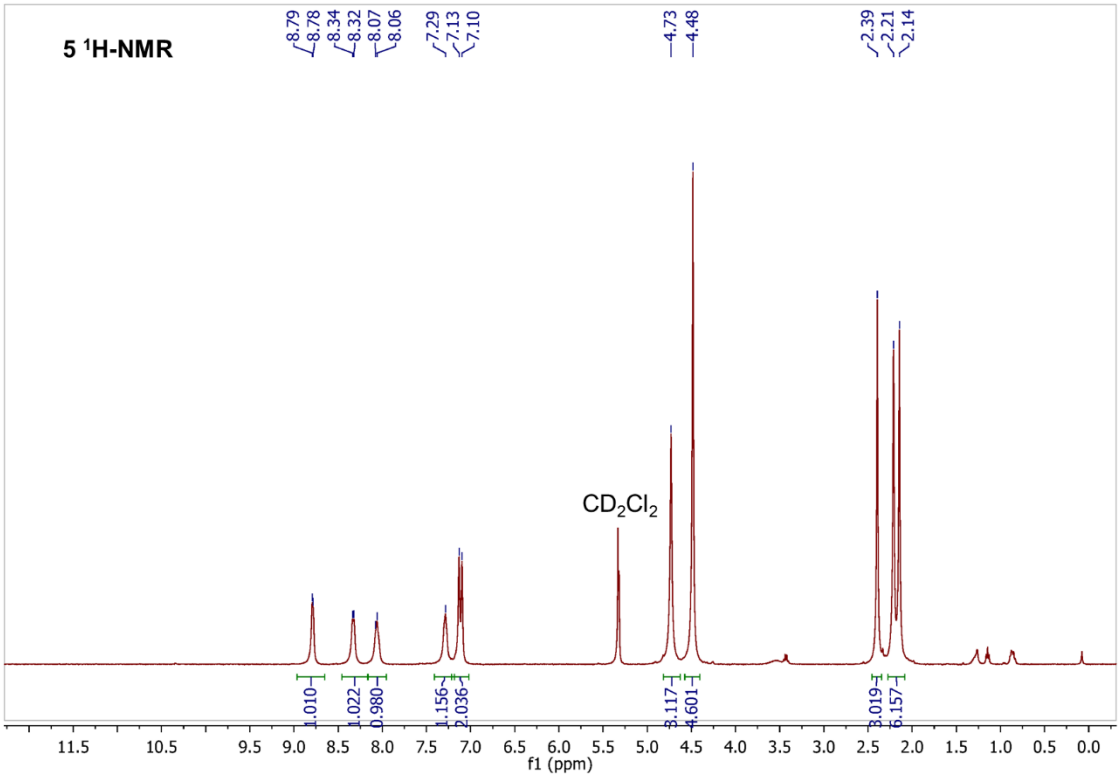


Figure S19. *^{1}H NMR spectrum (300 MHz) for complex **5**.*

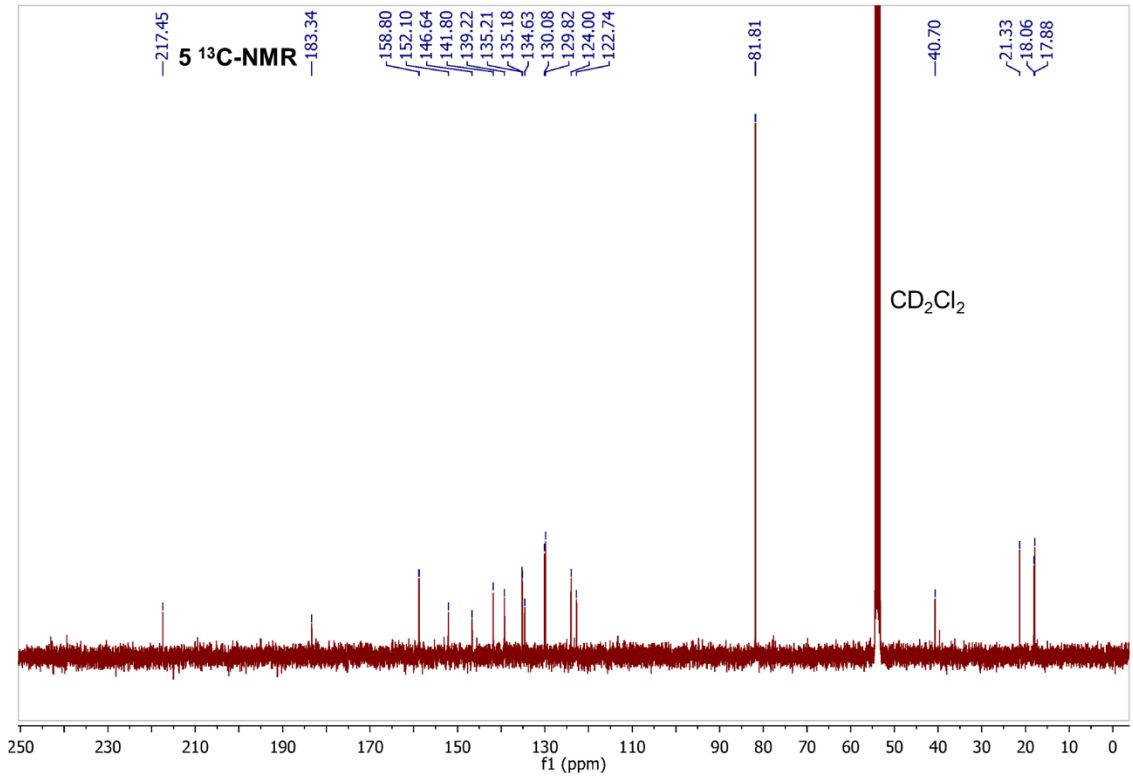


Figure S20. *$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) for complex **5**.*

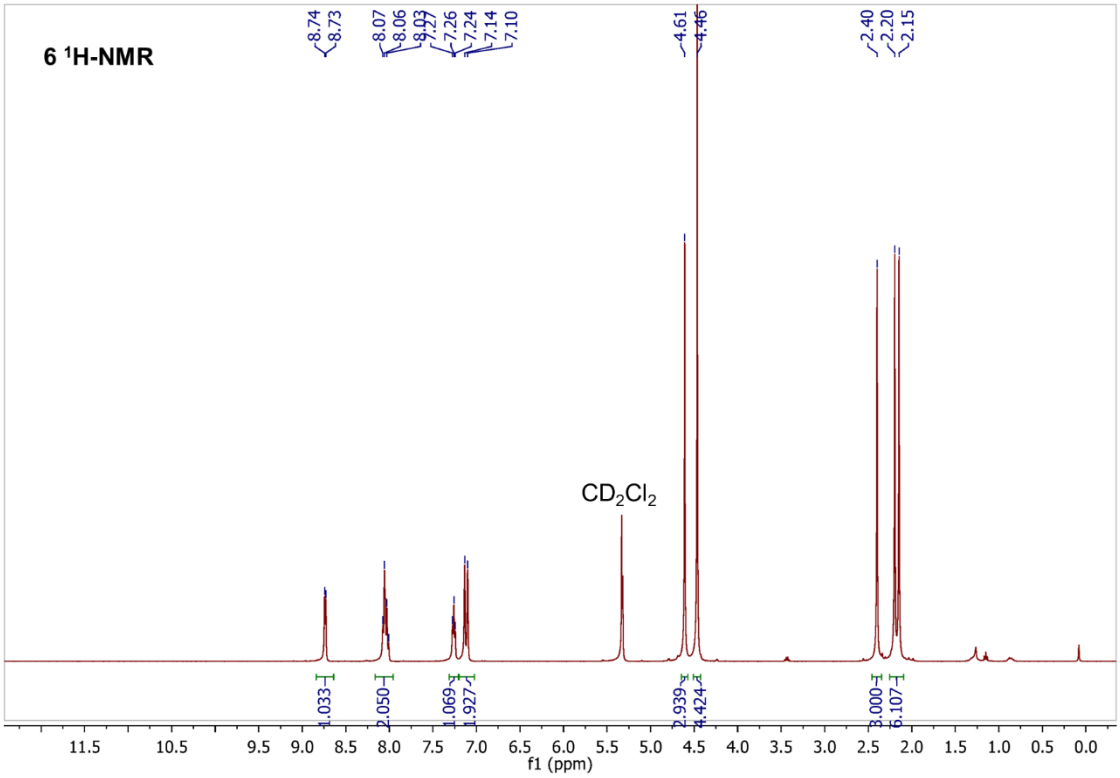


Figure S21. *[1]H NMR spectrum (400 MHz) for complex* ***6****.*

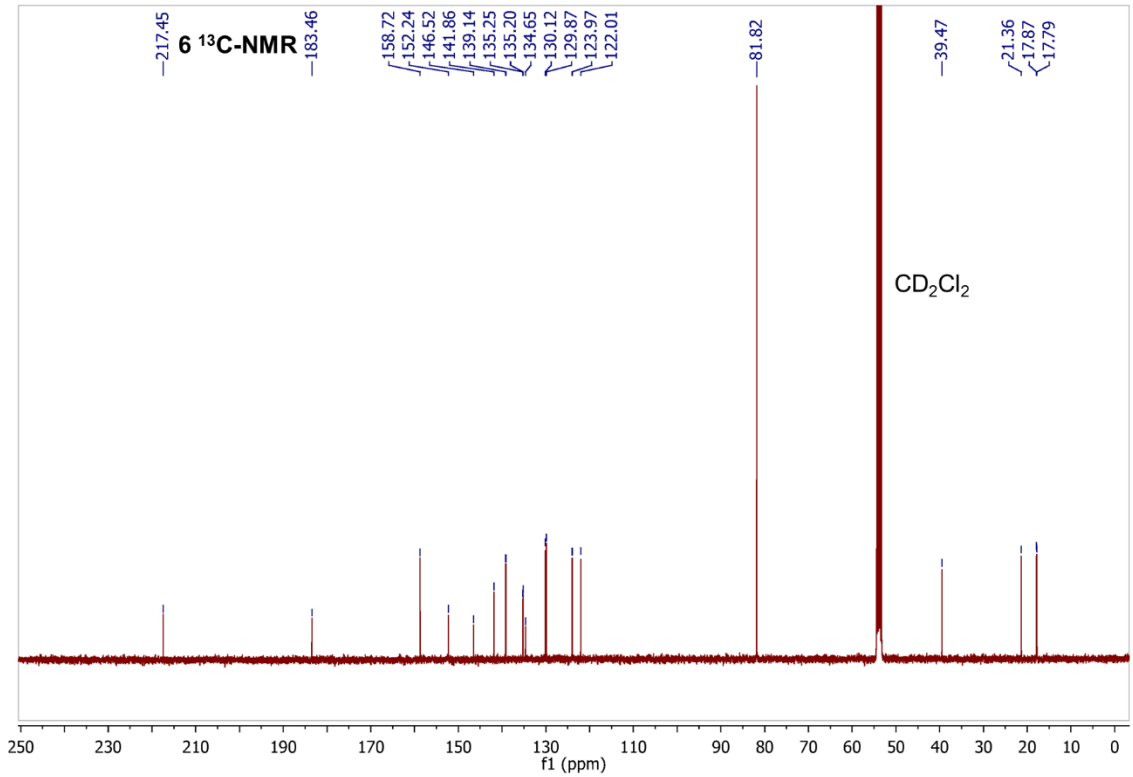


Figure S22. *[13]C{[1]H} NMR spectrum (100 MHz) for complex* ***6****.*

2. Cyclic Voltammetry

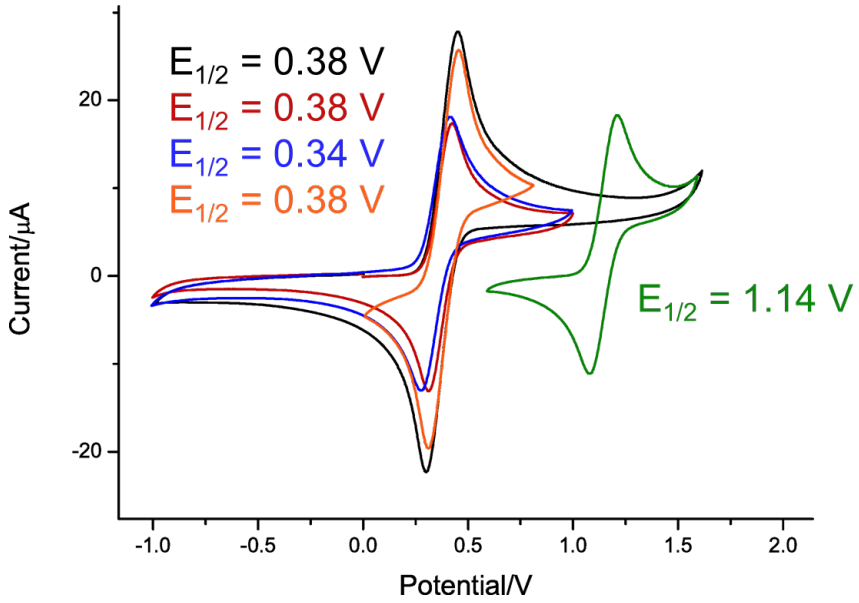


Figure S23. *Cyclic voltammograms for iron complexes* ***4a*** *(blue),* ***4b*** *(black),* ***4c*** *(red),* ***4d*** *(orange) and* ***6*** *(green). Scan rate: 250 mV* s^{-1}*; in* CH_2Cl_2 *solution vs. SCE using Fc+/Fc as reference.*

3. Crystallographic Information

Table S1. *Crystallographic data for cationic iron complexes* ***2a,b*** *and* ***3c****.*

	2a	**2b**	**3c**
CCDC No	1546613	1546614	1546615
colour, shape	yellow, plate	yellow, plate	yellow, plate
crystal size/mm	0.23 x 0.18 x 0.12	0.15 x 0.14 x 0.07	0.22 x 0.18 x 0.14
empirical formula	$C_{28}H_{30}FeIN_3O_2$	$C_{25}H_{24}FeIN_3O_2$	$C_{23}H_{28}BF_4FeN_3O_2$
F_w	623.3	581.22	521.14
T/K	173(2)	173(2)	173(2)
crystal system	trigonal	monoclinic	monoclinic
space group	P 32	P 21/c	P 21/c
unit cell			
a/Å	12.2824(2)	11.93567(11)	11.03020(8)
b/Å	12.2824(2)	15.01702(9)	14.44351(10)
c/Å	15.5277(2)	14.38590(11)	15.46764(9)
α/deg	90	90	90
β/deg	90	107.3764(9)	99.3532(6)
γ/deg	120	90	90
V/Å^3	2028.64(7)	2460.83(3)	2431.46(3)
Z	3	4	4
D_{calc}/g cm^{-3}	1.531	1.569	1.424
μ/mm^{-1} (Mo K_α)	1.728	1.893	0.676
reflections collected	29027	37531	42151
independent reflections	6216	6093	6049
R_{int}	0.0318	0.027	0.0278
transm. range	0.857–1.000	0.778–0.889	0.891–0.92
no. params, restrainsts	324, 1	293, 0	312, 0
R,[a] R_w[b]	0.0398, 0.0949	0.0281, 0.0634	0.0307, 0.0804
GOF	1.067	1.037	1.036
min, max resid density/e Å^{-3}	-0.658, 0.975	-0.707, 0.825	-0.286, 0.36

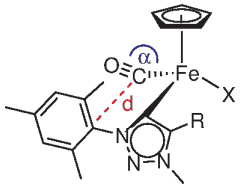
[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ *for all* $I > 2\sigma(I)$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$

Table S2. *Crystallographic data for neutral iron complexes* ***4a,b*** *and pyridine chelate* ***5****.*

	4a	**4b**	**5**
CCDC No	1546616	1546617	1546618
colour, shape	green, plate	green, needle	green, needle
crystal size/mm	0.24 x 0.17 x 0.11	0.28 x 0.10 x 0.026	0.22 x 0.13 x 0.02
empirical formula	$C_{27}H_{30}FeIN_3O$	$C_{24}H_{24}FeIN_3O$	$C_{22}H_{25}FeIN_4O$ x CH_2Cl_2
F_w	595.29	553.21	639.13
T/K	173(2)	173(2)	173(2)
crystal system	triclinic	monoclinic	orthorhombic
space group	P -1	P 21/c	P n a 21
unit cell			
a/Å	8.3021(2)	19.47364(15)	10.1301(2)
b/Å	9.6264(2)	7.34149(10)	37.9500(7)
c/Å	17.9578(6)	16.21349(12)	6.89680(10)
α/deg	94.073(2)	90	90
β/deg	97.588(2)	96.6717(7)	90
γ/deg	113.158(2)	90	90
V/Å^3	1296.02(6)	2302.27(4)	2651.39(8)
Z	2	4	4
D_{calc}/g cm^{-3}	1.525	1.596	1.601
μ/mm^{-1} (Mo K_α)	1.796	2.016	1.958
reflections collected	18511	31979	44618
independent reflections	5236	5720	6590
R_{int}	0.0302	0.0321	0.0292
transm. range	0.718–0.836	0.679–0.949	0.779–0.962
no. params, restrainsts	305, 0	275, 0	331, 70
R, R_w[a]	0.0312, 0.0694	0.025, 0.0573	0.028, 0.056
GOF	1.046	1.057	1.176
min, max resid density/e Å^{-3}	-0.417, 0.635	-0.438, 1.595	-1.272, 0.574

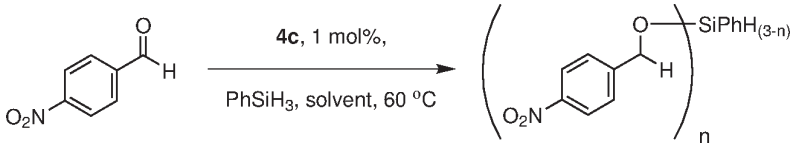
[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ *for all* $I > 2\sigma(I)$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$

Table S3. *Selected bond angles and distances to investigate potential $C_{ipso}\cdots C_{CO}$ interligand interactions.*



complex	d/Å	α/°	ν(CO)/cm^{-1}
2a	2.911	170.53	2047, 2002
2b	2.969	172.64	2041, 1994
3c	3.066	173.91	2041, 1994
4a	2.901	169.80	1933
4b	2.926	170.02	1935

4. Catalytic Details



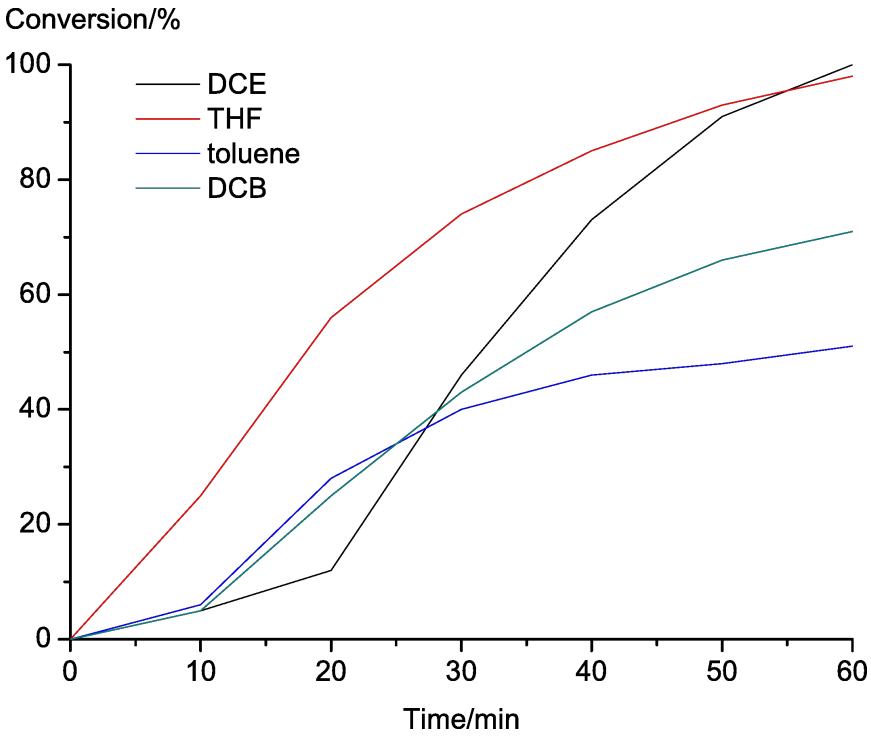
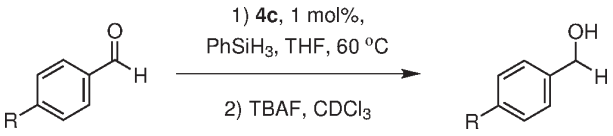


Figure S24. *Time-dependent conversion of 4-nitrobenzaldehyde in various solvents.*

Table S4. *Conversion of aldehydes in THF catalysed by complex* ***4c****.*



entry	R	time/ min	conv./ %[b]	yield/ %[c]	σ_p[d]	induction time/min	TOF_{max} /h^{-1}
1	NO_2	60	98	98	0.71	0	190
2	CN	6	100	94	0.66	0	2,070
3	CF_3	25	100	93	0.54	10	940
4	Br	9	100	100	0.23	3	2,280
5	H	18	99	99	0	<10	1,260
6	CH_3	50	100	100	−0.17	20	360
7	OMe	40	100	100	−0.27	10	410
8	NMe_2	45	100	89	−0.87	5	500

[a] *General conditions: substrate (0.5 mmol), phenylsilane (0.6 mmol), [Fe] precatalyst (1 mol%; 5 µmol),* C_6Me_6 *(50 µmol) and THF (2.5 mL);* [b] *conversion determined by* ^{1}*H-NMR using* C_6Me_6 *as internal standard;* [c] *spectroscopic (*^{1}*H-NMR) yield of alcohol product after silyl deprotection.* [d] *From reference S1*

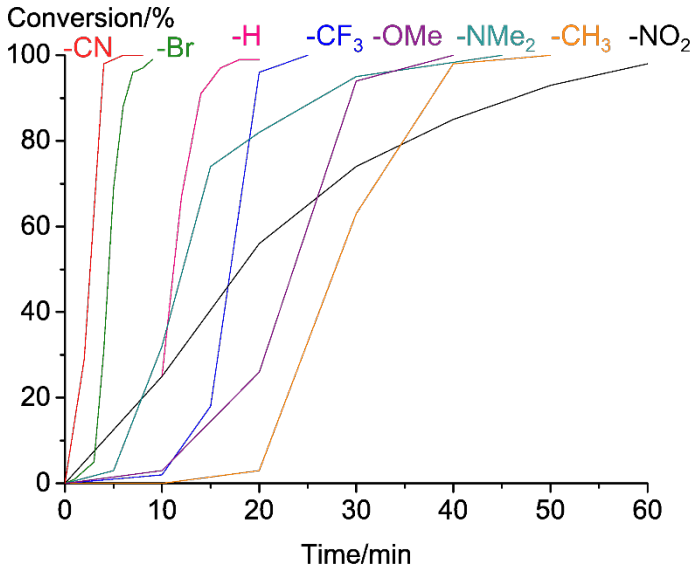


Figure S25. *Time-dependent conversion of para-substituted benzaldehydes catalysed by* ***4c*** *in THF. Para-substituents are indicated in the figure.*

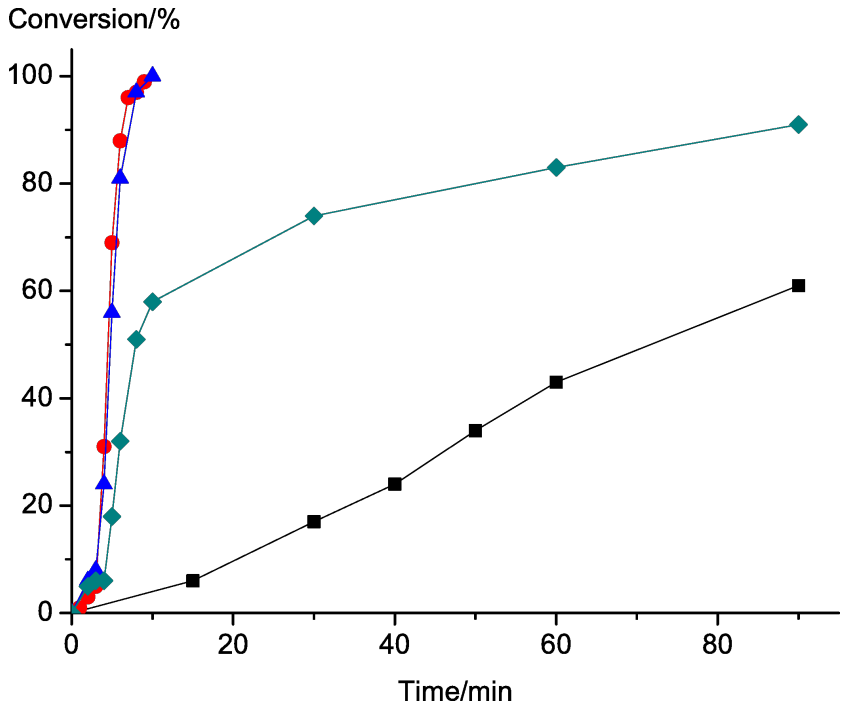
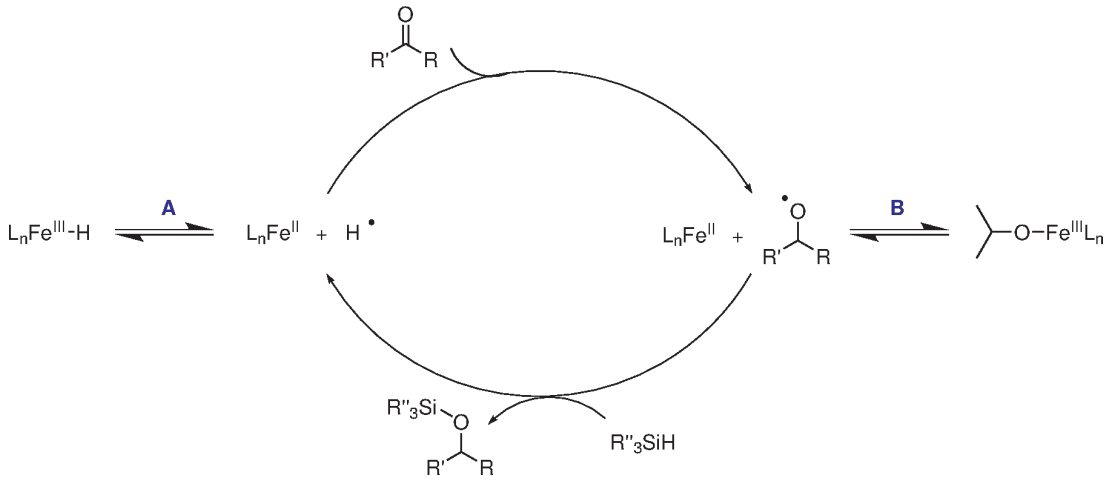


Figure S26. *Time-dependent conversion of 4-bromoacetophenone (0.2 M) in the presence (cyan diamonds) and absence (black squares) of 4-bromobenzaldehyde (0.2 M; conversion represented by blue triangles) catalysed by* ***4c*** *(2 mM) under standard conditions (cf. Table S4). Conversion of 4-bromobenzaldehyde in the absence of ketone substrate is indicated by red circles.*



Scheme S1. *Tentative proposal for a radical mechanism of the iron-catalyzed hydrosilylation with triazolylidene iron complexes with the persistent iron(III) radical, either as hydride (left) or as oxo radical which may rearrange to the carbon-centered radical species..*

References.

(S1) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.