Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Cyclometallated iridium NHC complexes containing self-isomerised ligands as catalysts for hydrosilylation and transfer hydrogenation reactions

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Supporting Information

1. ^{1}H, ^{13}C, and selected 2D (HSQC, COSY) NMR spectra of the iridium complexes (**Figures S1-S12**).
2. Crystallographic data and structure refinement parameters (**Tables S1-S3**).
3. Conversion versus time plot for transfer hydrogenation using **3** (**Graph S1**).
4. ^{1}H NMR spectrum of catalysis reaction mixture of hydrosilylation obtained in C_6D_6 (**Figure S13**).
5. ^{1}H NMR spectrum of catalysis reaction mixture of transfer hydrogenation obtained in $CDCl_3$ (**Figure S14**).
6. ^{1}H NMR spectrum of silver biscarbene formed from **L1** (**Figure S15**).
7. Proposed mechanism for the hydrosilylation using Ir(III) catalysts (**Figure S16**).

1. ^{1}H and ^{13}C NMR spectra of **1-4** (**Figures S1-S10)**.

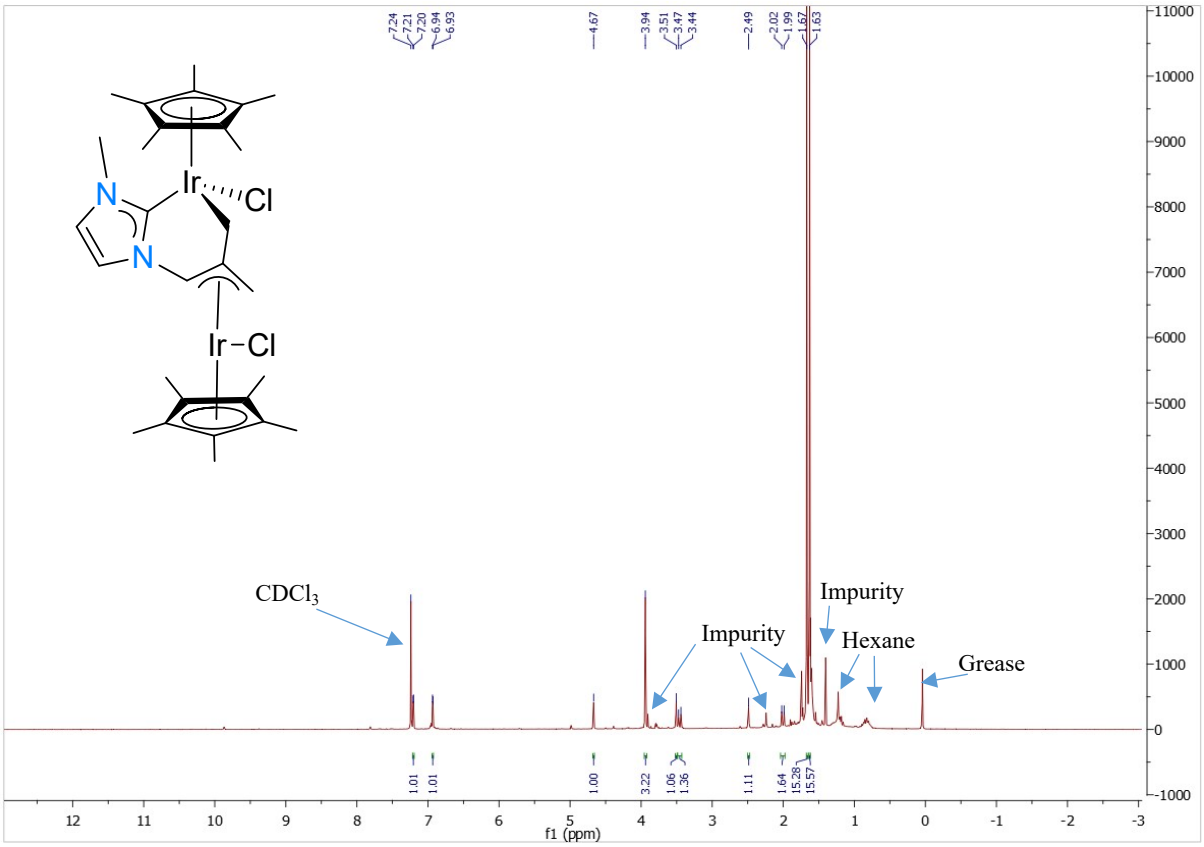


Figure S1 Complex **1**: ^{1}H NMR spectrum

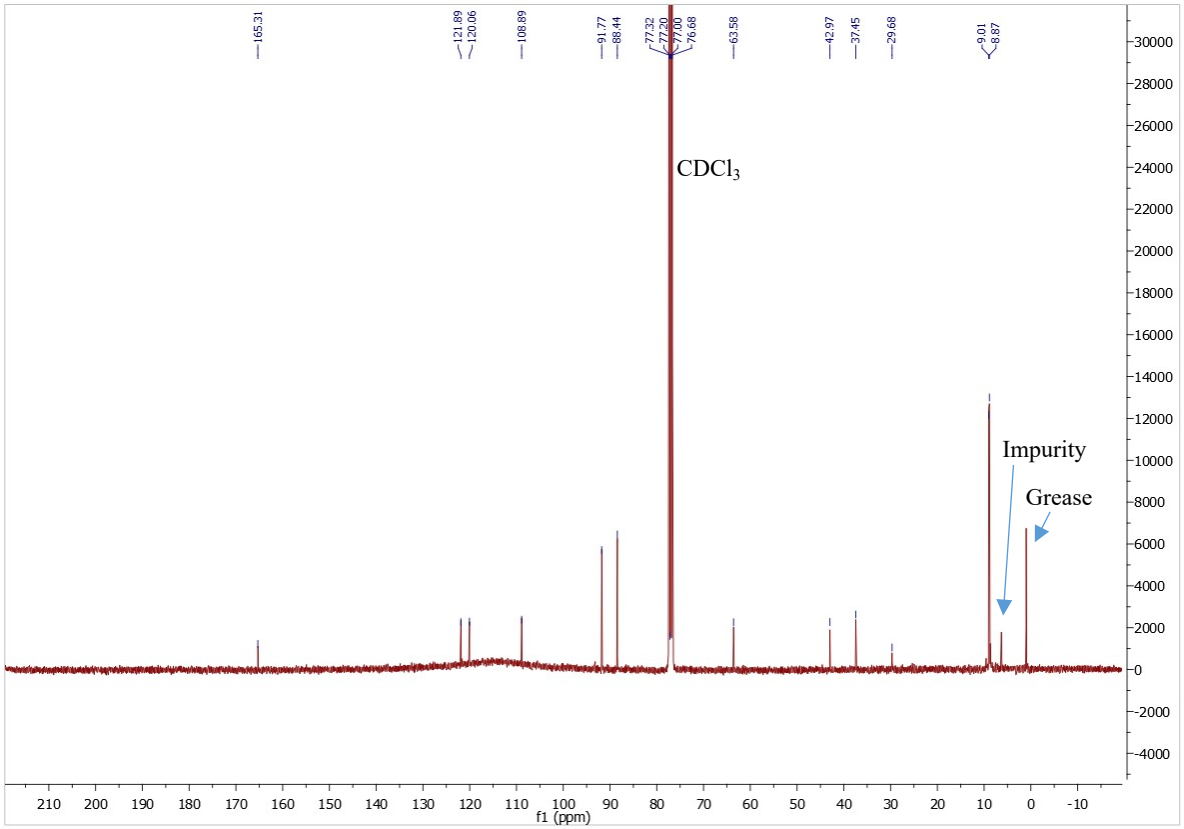


Figure S2 Complex **1**: ^{13}C NMR spectrum

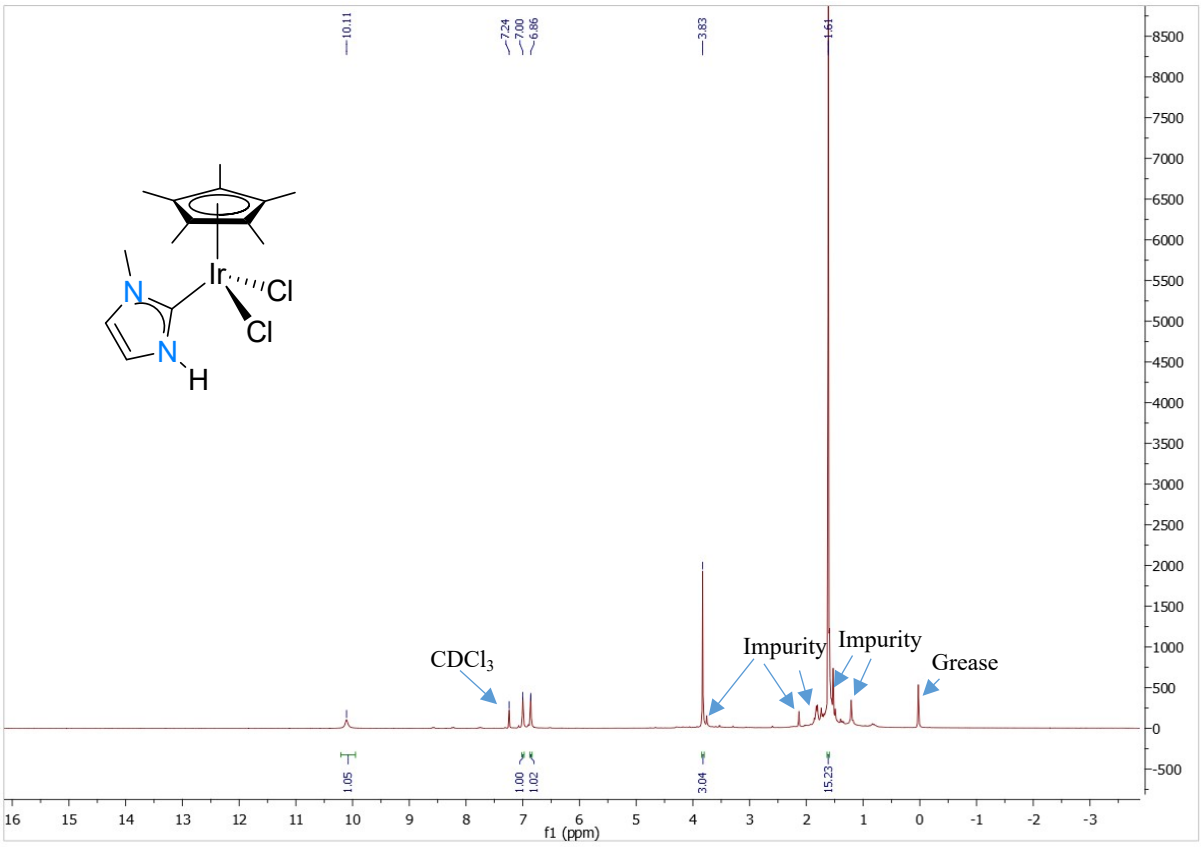


Figure S3 Complex **1b**: ^{1}H NMR spectrum

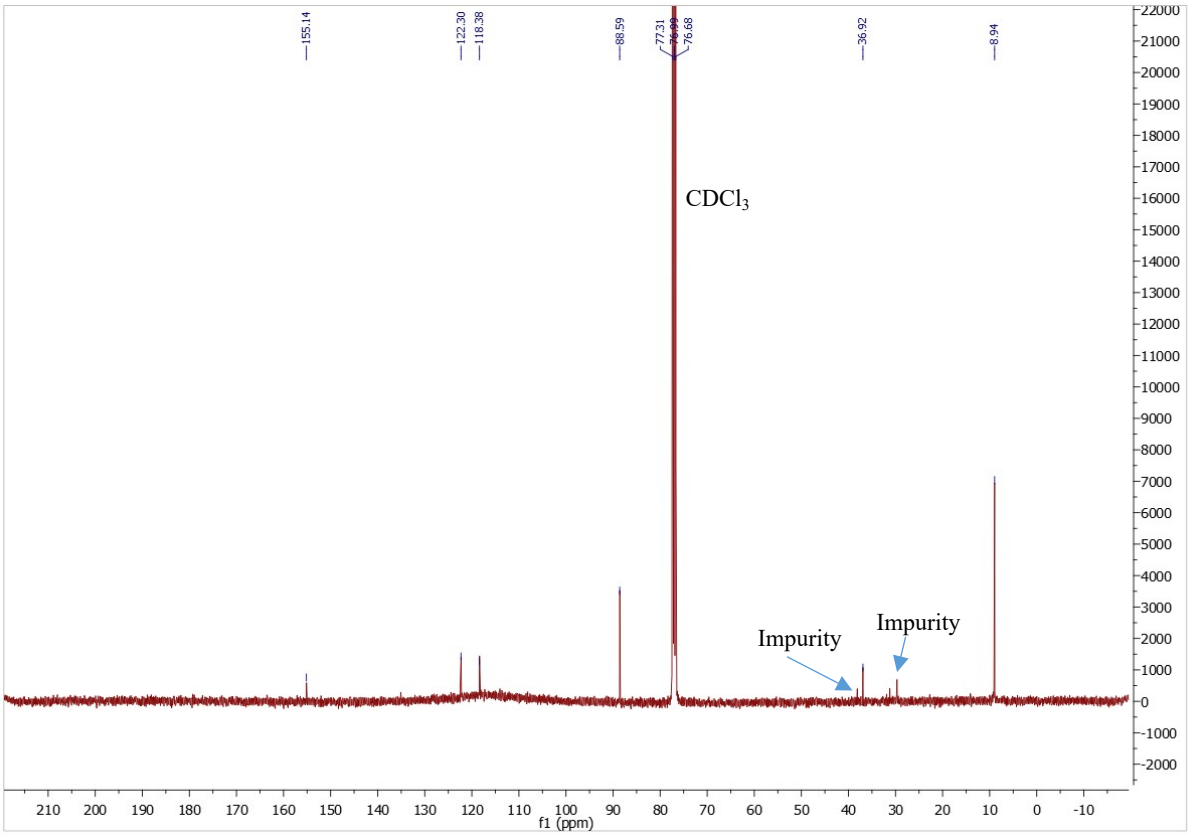


Figure S4 Complex **1b**: ^{13}C NMR spectrum

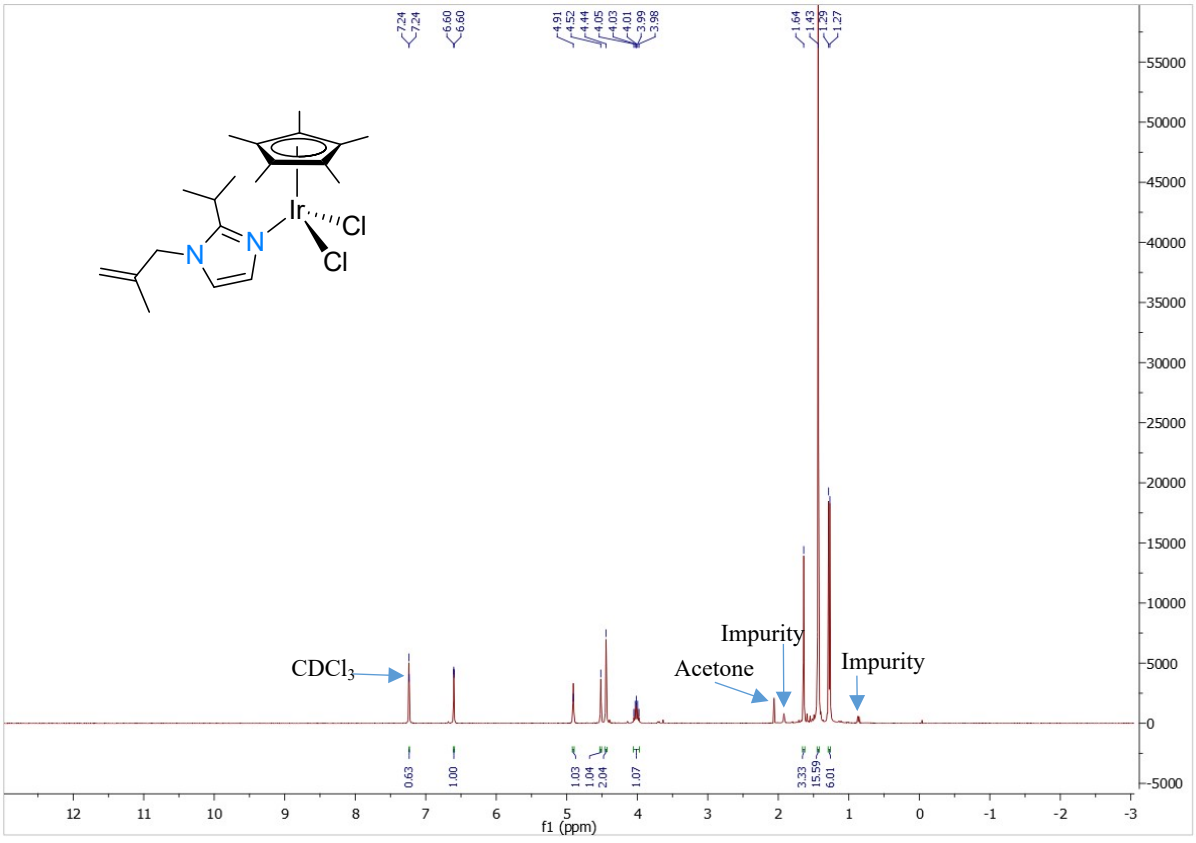


Figure S5 Complex **2**: ^{1}H NMR spectrum

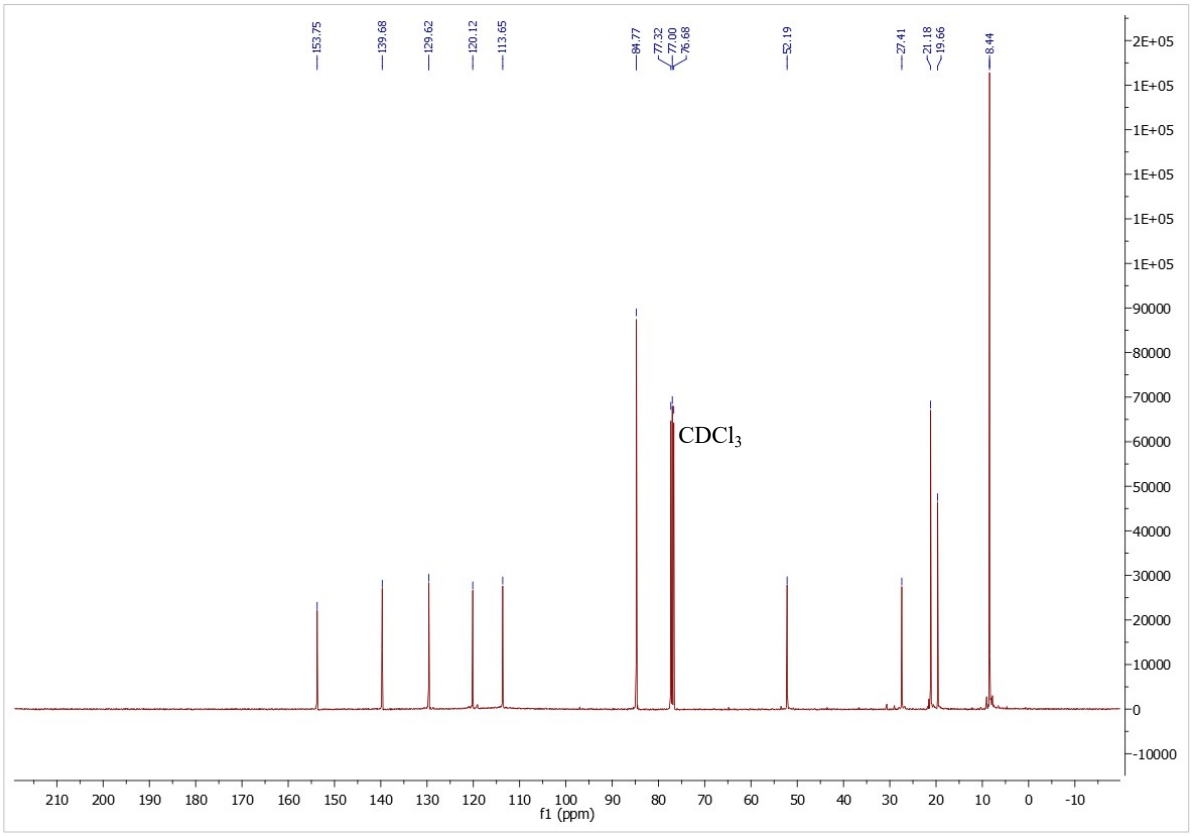


Figure S6 Complex **2**: ^{13}C NMR spectrum

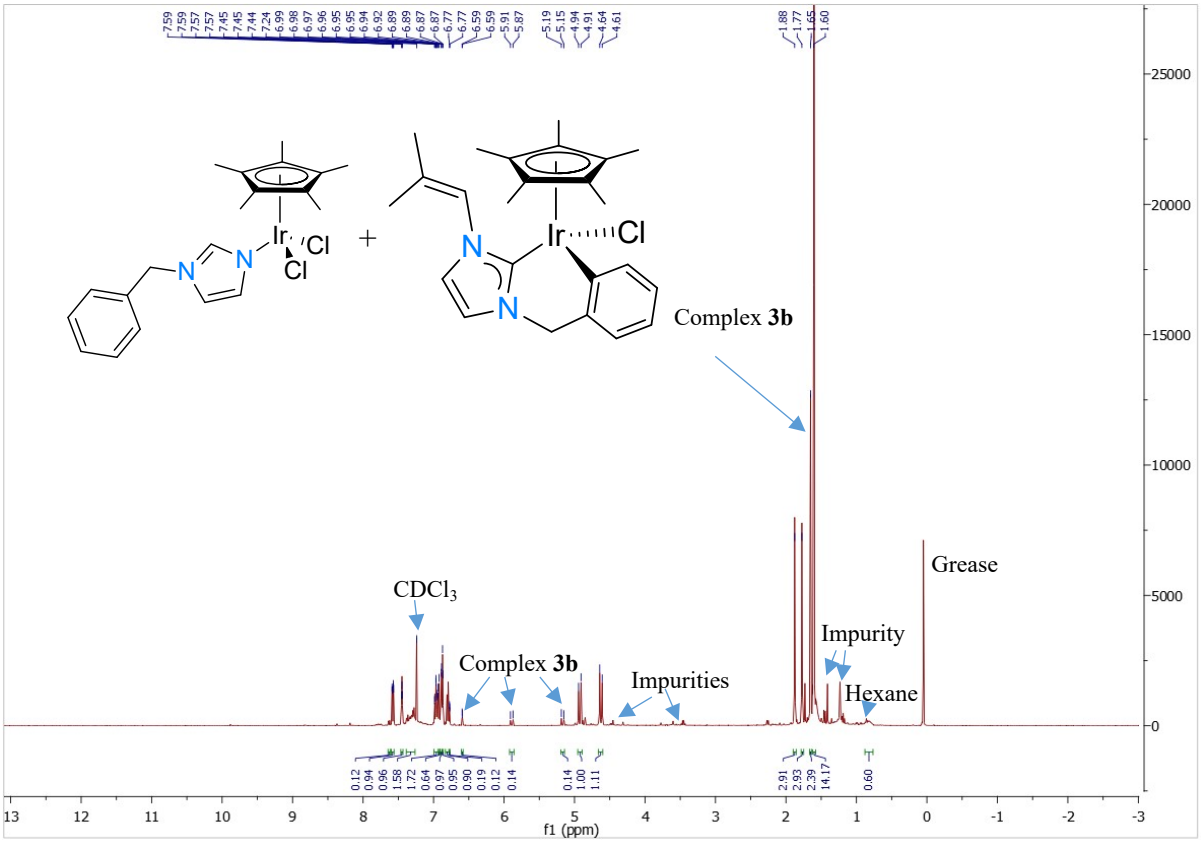


Figure S7 Complex **3**: ^{1}H NMR spectrum

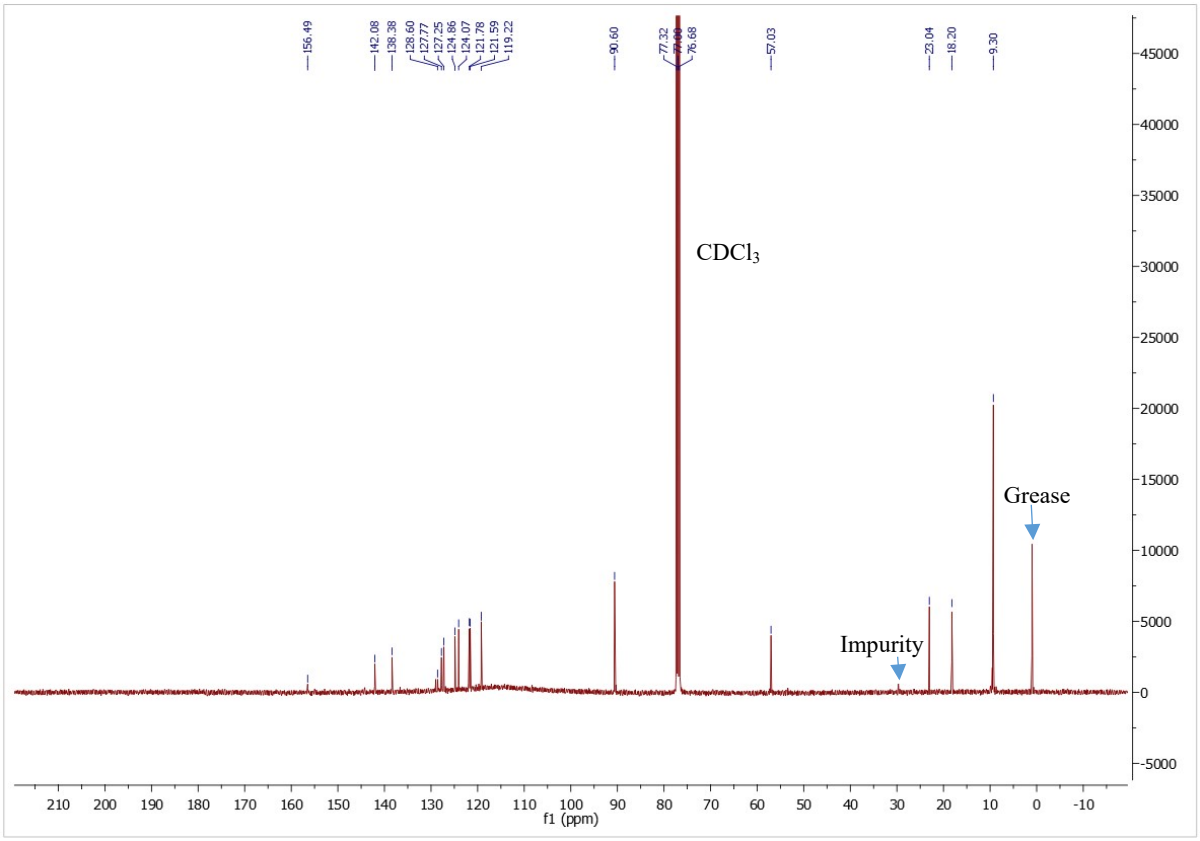


Figure S8 Complex **3**: ^{13}C NMR spectrum

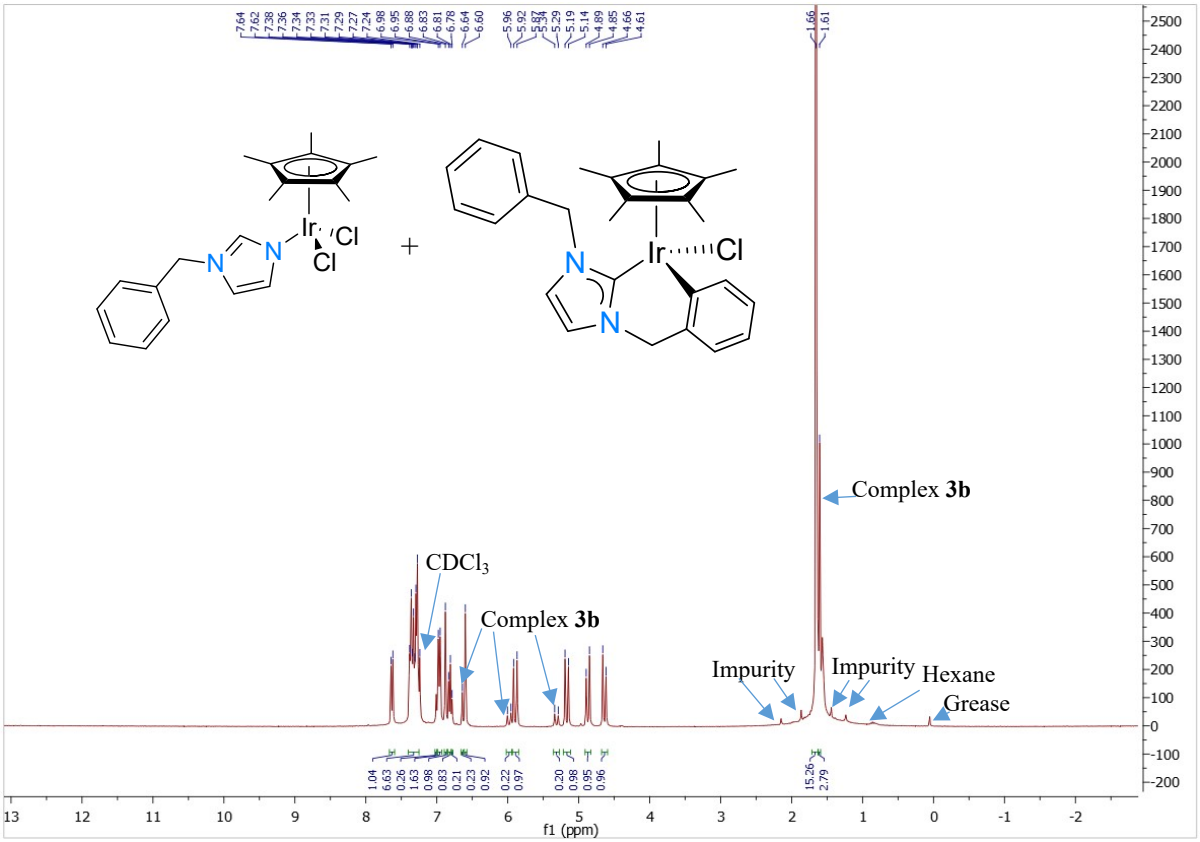


Figure S9 Complex **4**: ^{1}H NMR spectrum

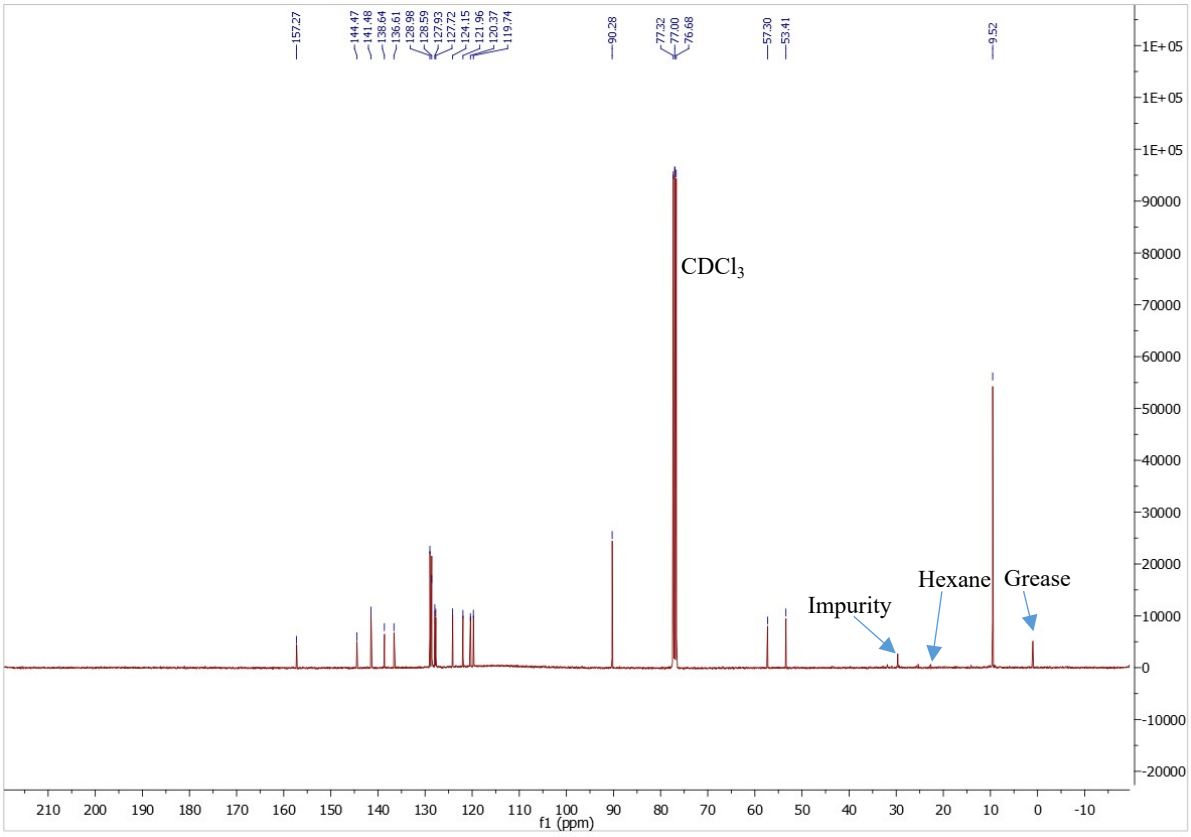


Figure S10 Complex **4**: ^{13}C NMR spectrum

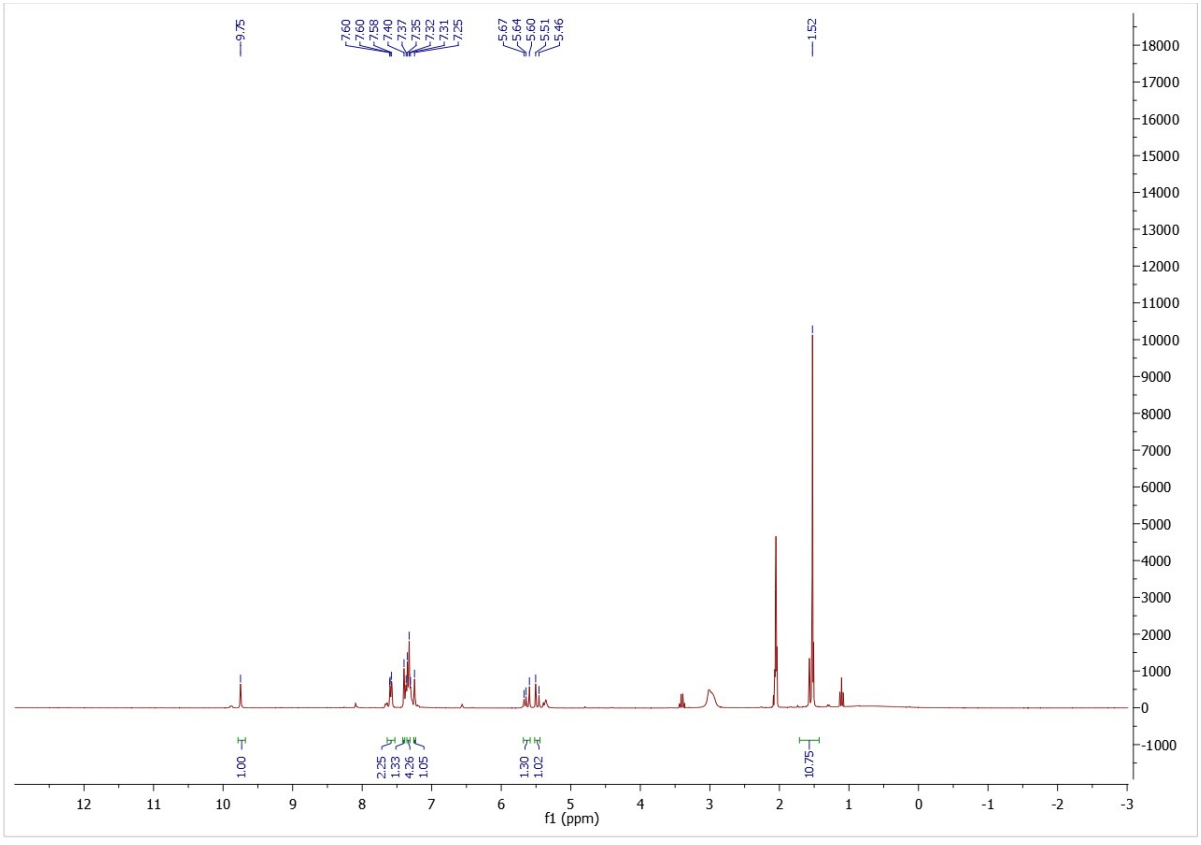


Figure S11 Complex **3b**: ^{1}H NMR spectrum

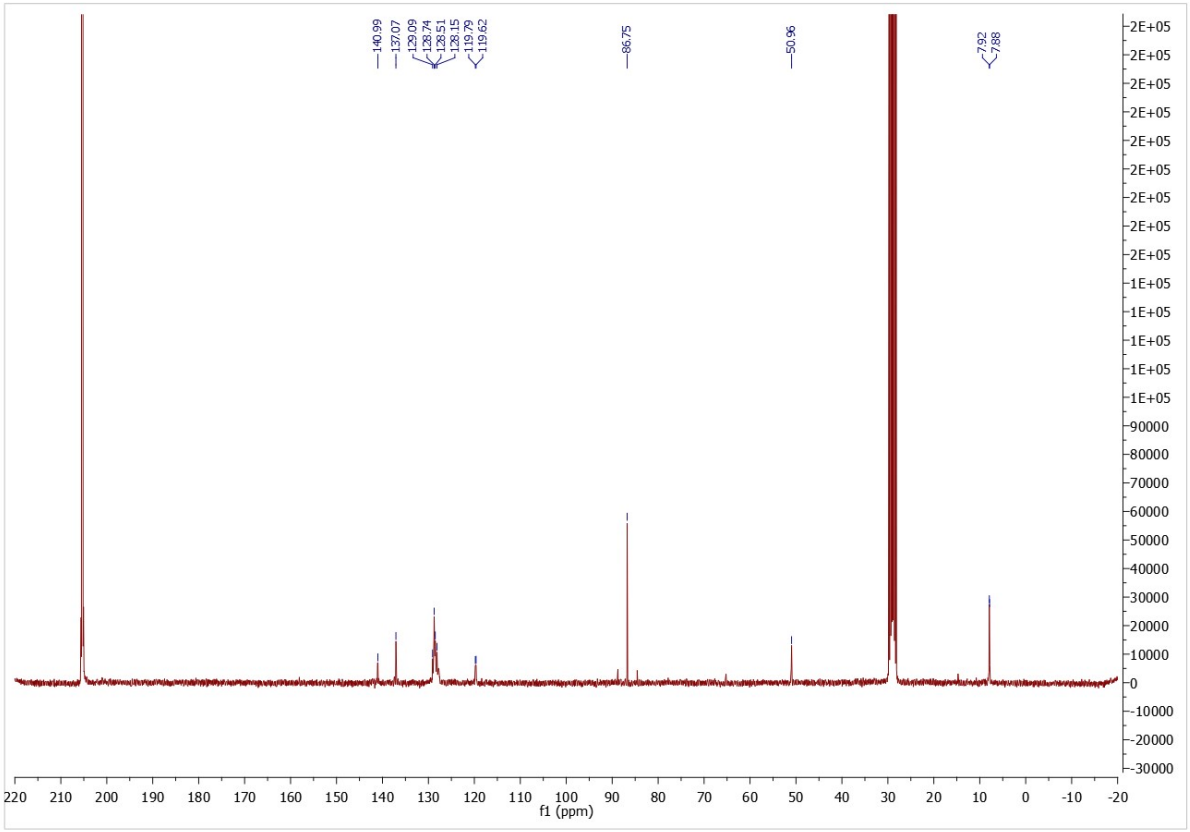


Figure 12 Complex 3b: ^{13}C NMR spectrum

2. Crystallographic data and structure refinement parameters (**Tables S1-S3**).

Table S1. Crystal data and structure refinement for **1-4** and **1b**.

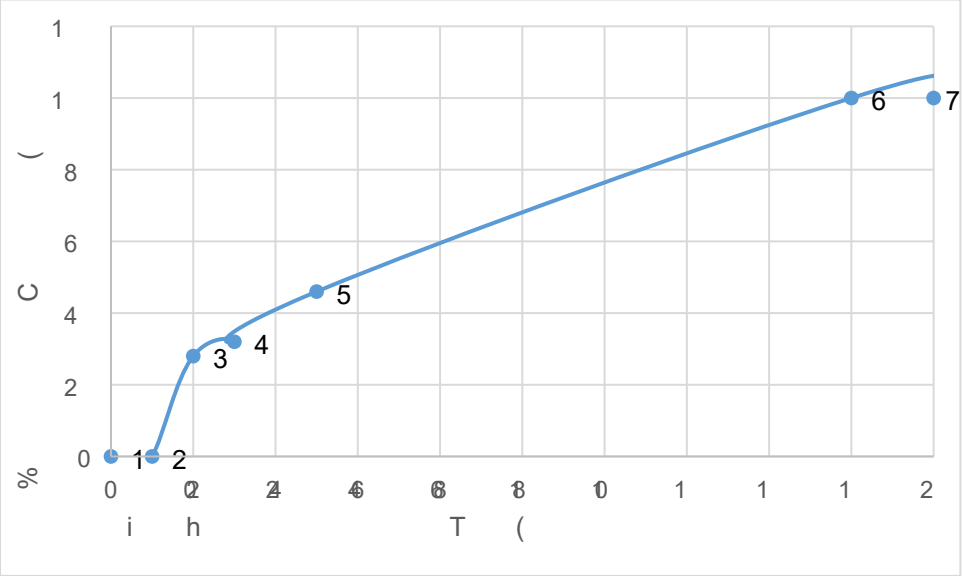
Complex	1	1b	2	3	4
Emp. formula	$C_{28}H_{40}N_2Cl_2Ir_2$	$C_{14}H_{21}N_2Cl_2Ir$	$C_{20}H_{31}N_2Cl_2Ir$	$C_{24}H_{30}N_2ClIr$	$C_{27}H_{30}N_2ClIr$
CCDC Identifier	2079421	2079420	2079418	2079419	2079422
Form. weight (g.mol^{-1})	859.96	480.43	562.57	574.17	610.20
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	*C*2/c	*C*2/c	*P*-1	$Pca2_1$	$P2_1/c$
Crystal descr.	yellow blade	yellow block	yellow blade	yellow block	yellow rod
a (Å)	35.6540(4)	8.44700(10)	8.9646(2)	23.81220(10)	8.89560(10)
b (Å)	8.49960(10)	15.3306(2)	9.4002(2)	8.6736(10)	26.1325(3)
c (Å)	22.7872(2)	24.2878(3)	13.4196(3)	21.15360(10)	20.4863(2)
α (°)	90	90	73.897(2)	90	90
β (°)	127.3400(10)	94.4640(10)	86.405(2)	90	90.2520(10)
γ (°)	90	90	78.889(2)	90	90
Volume (Å^3)	5490.25(12)	3135.67(7)	1066.07(4)	4369.21(3)	4762.29(9)
Z	8	8	2	8	8
Abs. coeff. (m.mm^{-1})	20.424	19.517	14.454	13.031	11.993
F(000)	3279.0	1840.0	552.0	2256.0	2396.0
Independent refl.	5402	3098	4436	8500	9253
Completeness (%)	99.8	100	100	99.2	95.9
Data/Restr/Para	5402/0/318	3098/30/178	4436/0/234	8500/1/520	9253/245/665
Goodness of fit on F^2	1.066	1.084	1.127	1.042	1.296
Final R_1 indexes	0.0485	0.0453	0.0265	0.0223	0.0584
wR_2 indices (all data)	0.1437	0.1098	0.0687	0.0575	0.1495
Largest diffr. peak and hole (e.Å^{-3})	3.94/-1.96	2.11/-1.46	1.14/-1.95	1.36/-0.81	2.36/-1.47

Table S3. Selected bond lengths (Å) and angles (°) for **1-4** and **1b**.

Description	1	1b	2	3	4
Cp*$_{cent}$-Ir1[a]	1.837(6)[b]	1.812(8)	1.775(5)	1.854(9)	1.857(10)
Ir1-Cl1	2.4134(17)[c]	2.411(2)[e]	2.4171(9)[f]	2.4273(14)	2.423(3)
Ir1-C2	2.026(8)	2.031(7)	-	1.997(6)	1.999(11)
Ir1-C7	2.117(6)	-	-	2.073(6)	2.058(11)
Ir1-N1	-	-	2.120(3)	-	-
C6-C7	1.459(9)	-	1.319(6)	1.394(10)	1.410(17)
C6-C8	1.432(9)	-	1.503(6)	-	-
C6-C5	1.447(8)	-	1.510(5)	1.501(10)	1.512(18)
Ir2-C5[d]	2.124(5)	-	-	-	-
Ir1-C7-C6	107.5(4)	-	-	124.1(5)	122.5(8)
C7-C6-C8	127.6(6)	-	123.8(4)	117.0(6)[g]	116.6(11)[g]
C5-C6-C7	120.8(5)	-	123.7(4)	120.4(6)	120.8(10)
N2-C5-C6	115.4(5)	-	113.7(3)	111.8(6)	112.0(9)
C2-Ir1-C7	81.0(3)	-	-	85.4(3)	85.5(4)
Cl1-Ir1-Cl2	-	87.43(10)	87.45(3)	-	-
Cl1-Ir1-C2	90.15(19)	89.0(2)	-	90.59(17)	89.5(3)
Cl1-Ir1-C7	86.76(19)	-	-	87.26(18)	87.9(3)
Ir1-C7-C6-C5	60.2(7)	-	-	1.0(9)	8.2(15)
C7-C6-C5-N2	-3.5(8)	-	0.7(6)	-47.1(9)	41.6(15)
Ir1-C2-N2-C5	6.2(9)	-	-	-1.2(9)	0.6(15)
C2-N2-C5-C6	-35.8(9)	-	-99.2(5)	48.7(9)	-47.8(15)
N2-C5-C6-C8	-179.4(5)	-	-179.5(4)	134.4(7)[h]	-139.6(11)[h]

[a] Cp*$_{cent}$ = centroid of Cp* ligand. [b] Ir2-Cp*$_{cent}$ = 1.826(6) Å. [c] Ir2-Cl2 = 2.4052(17) Å. [d] Ir2-C6 = 2.213(6) Å. Ir2-C8 = 2.191(6) Å. [e] Ir1-Cl2 = 2.422(2) Å. [f] Ir-Cl2 = 2.4115(9) Å. [g] Refers to the C6-C7-C8 bond angle. [h] Refers to the N2-C5-C6-C11 torsion angle.

3. Conversion versus time plot using **3** (**Graph S1**).



Graph S1. Conversion versus time plot in the transfer hydrogenation using ^{i}PrOH as hydrogen source at 110°C utilising **3** with acetophenone. General reaction conditions: Ketone/Aldehyde (0.6 mmol), ^{i}PrOH (10 mL), base (10 mol%), anisole (0.6 mmol), reflux.

4. ^{1}H NMR spectrum of catalysis reaction mixtures

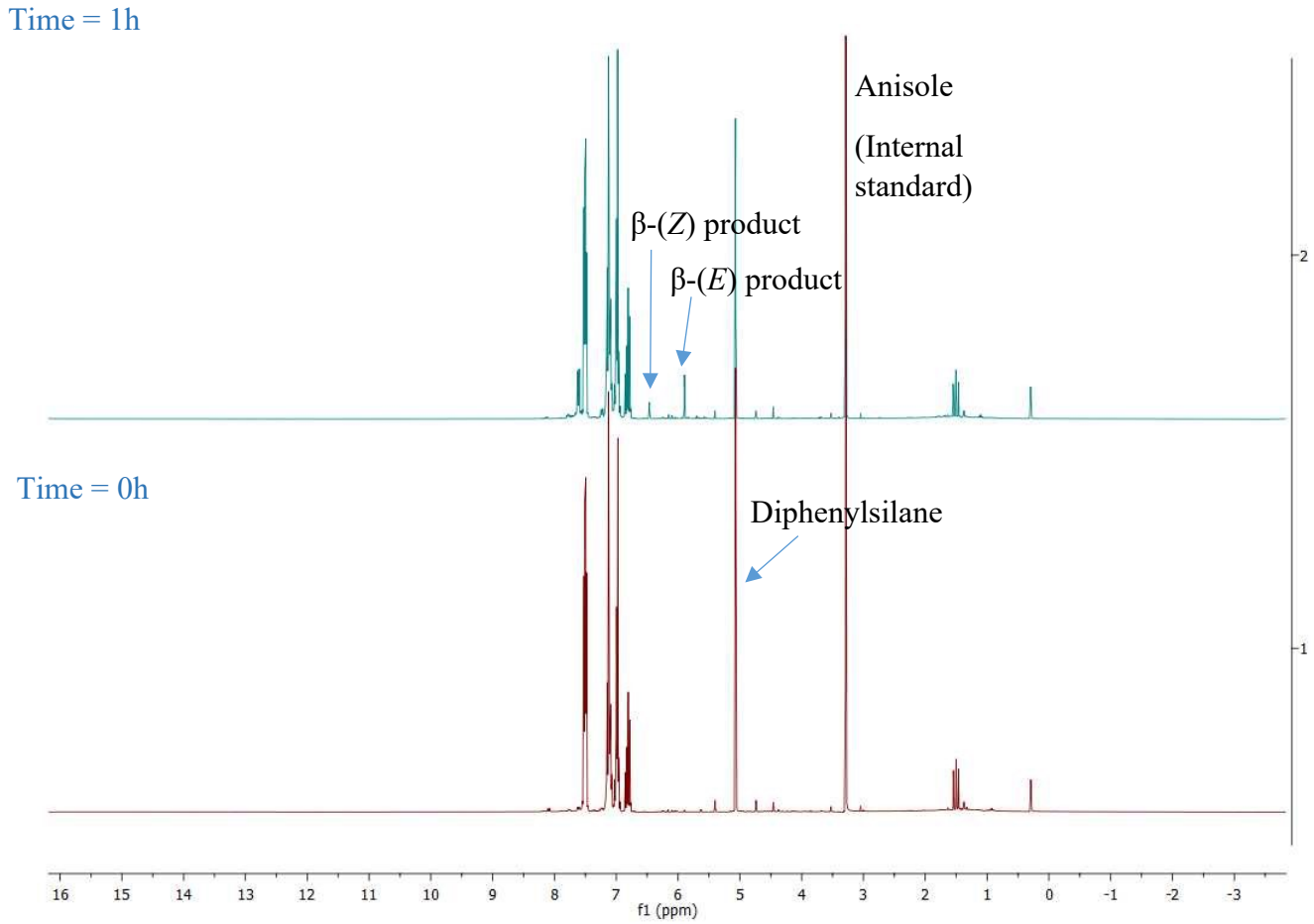


Figure S13 ^{1}H NMR spectrum of hydrosilylation catalysis of diphenylacetylene using **3** + **3b** obtained in C_6D_6. General conditions: PhCCPh (18 mg, 0.1 mmol), H_2SiPh_2 (20 µL, 0.1 mmol), **3** + **3b** (4 mol%), anisole (11 µl, 0.11 mmol), C_6D_6, 80 °C, 1 hour.

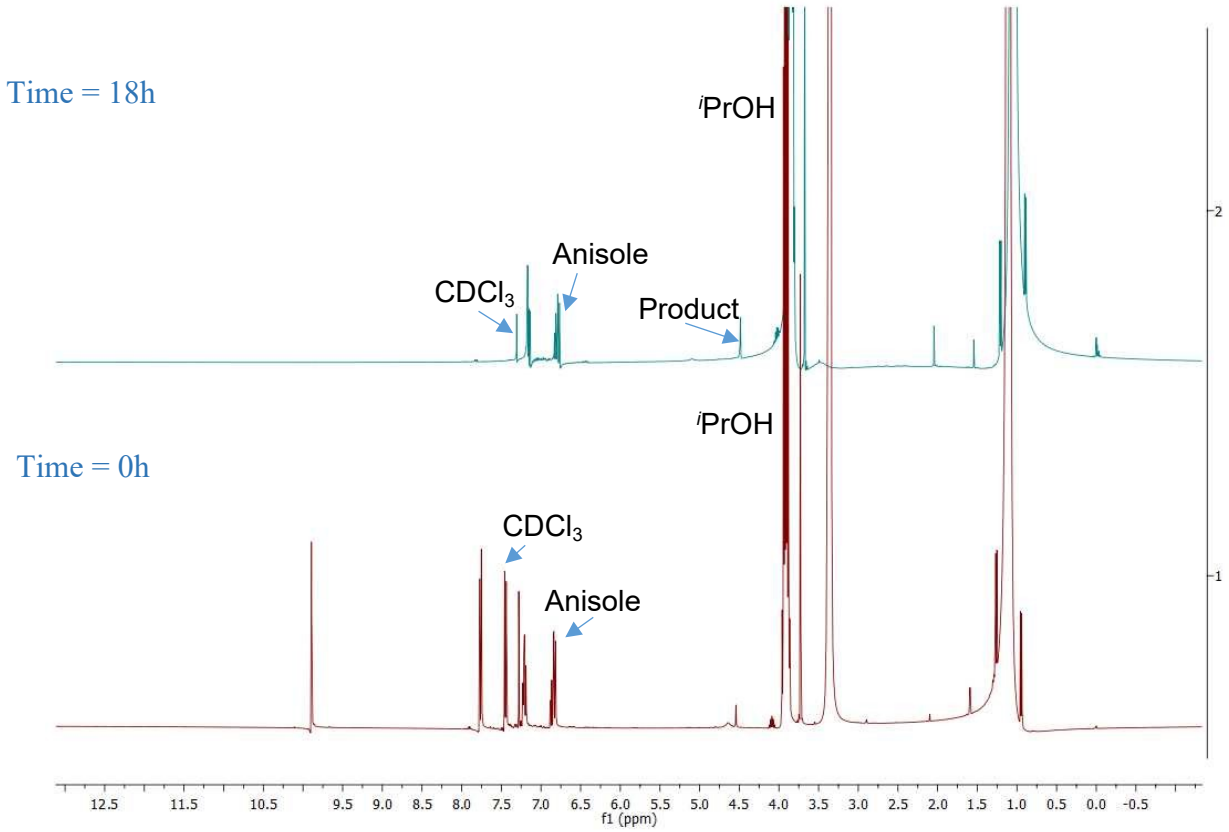


Figure S14 ^{1}H NMR spectrum of transfer hydrogenation catalysis of nitrobenzaldehyde using **3** obtained in $CDCl_3$. General reaction conditions: Ketone/Aldehyde (0.6 mmol), ^{i}PrOH (10 mL), base (10 mol%), anisole (0.6 mmol), reflux.

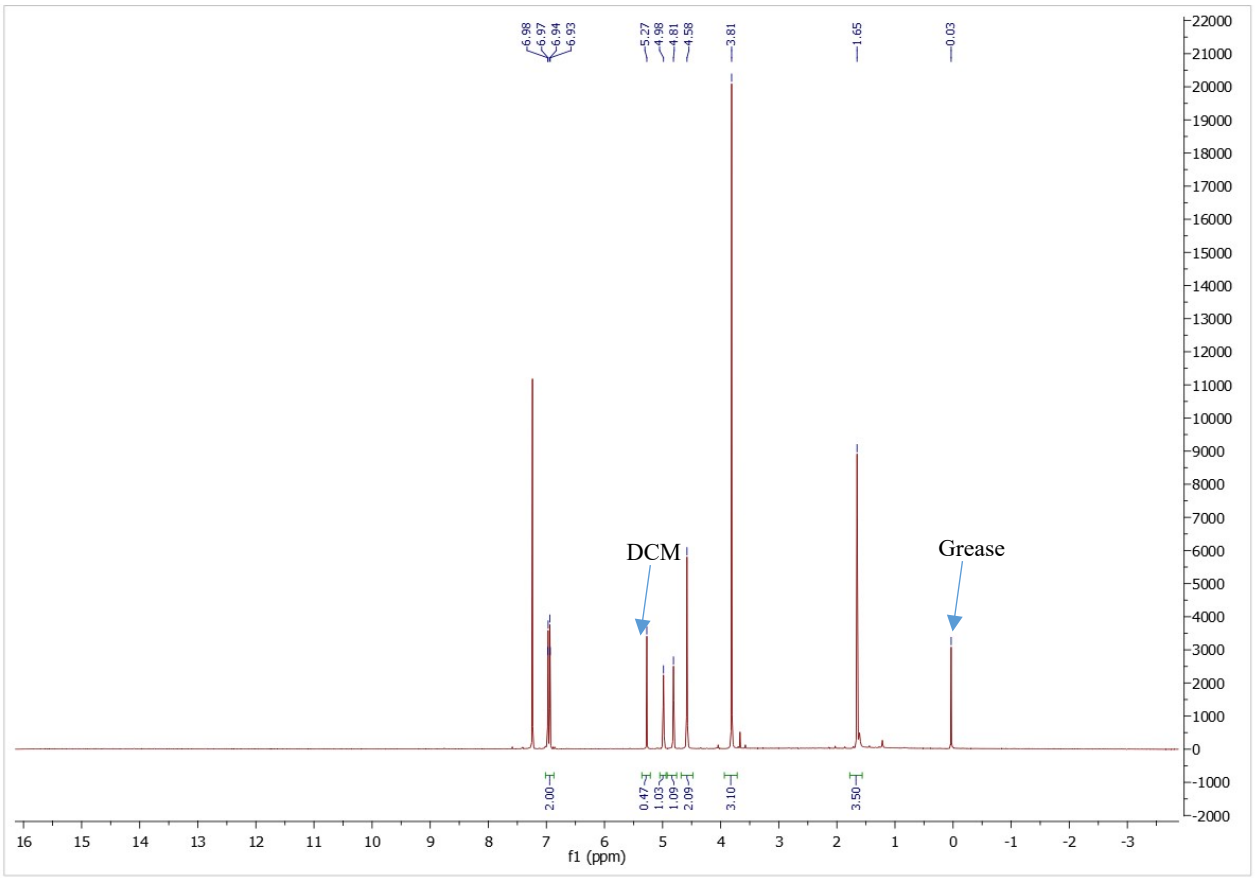


Figure S15 ^{1}H NMR spectrum of silver biscarbene formed from **L1**

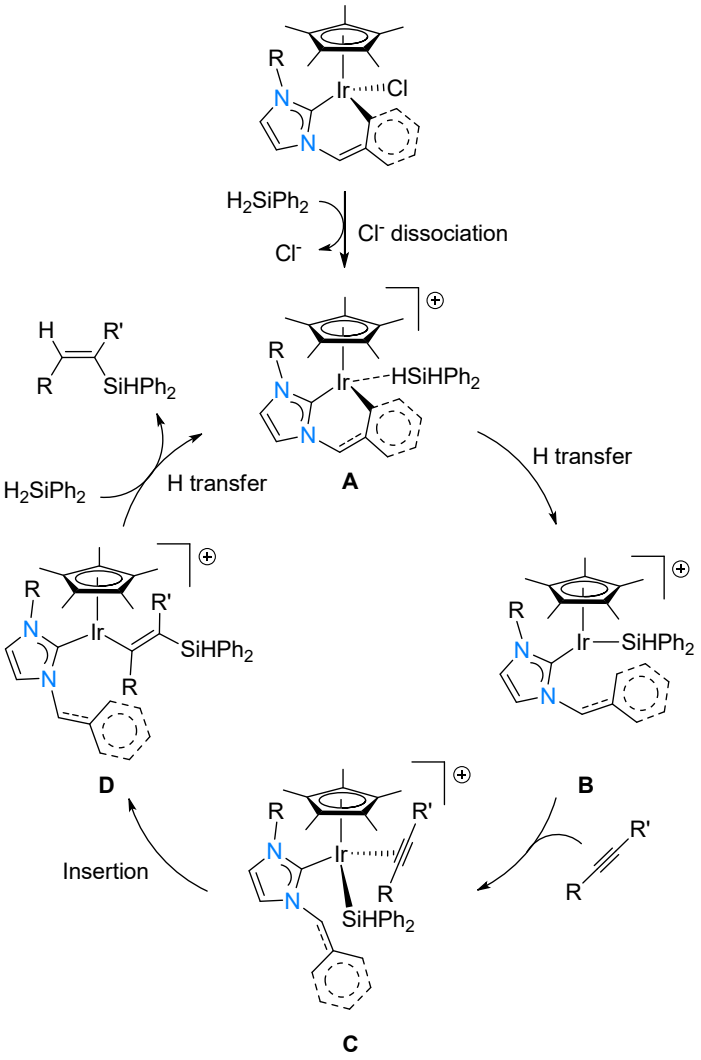


Figure S16 Proposed mechanism for the hydrosilylation using Ir(III) catalysts