Electronic Supporting Information

Iridium complexes featuring a tridentate SiPSi ligand: from dimeric to monomeric 14, 16 or 18-electron species

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1. NMR and IR spectra

1.1 Complex **2**

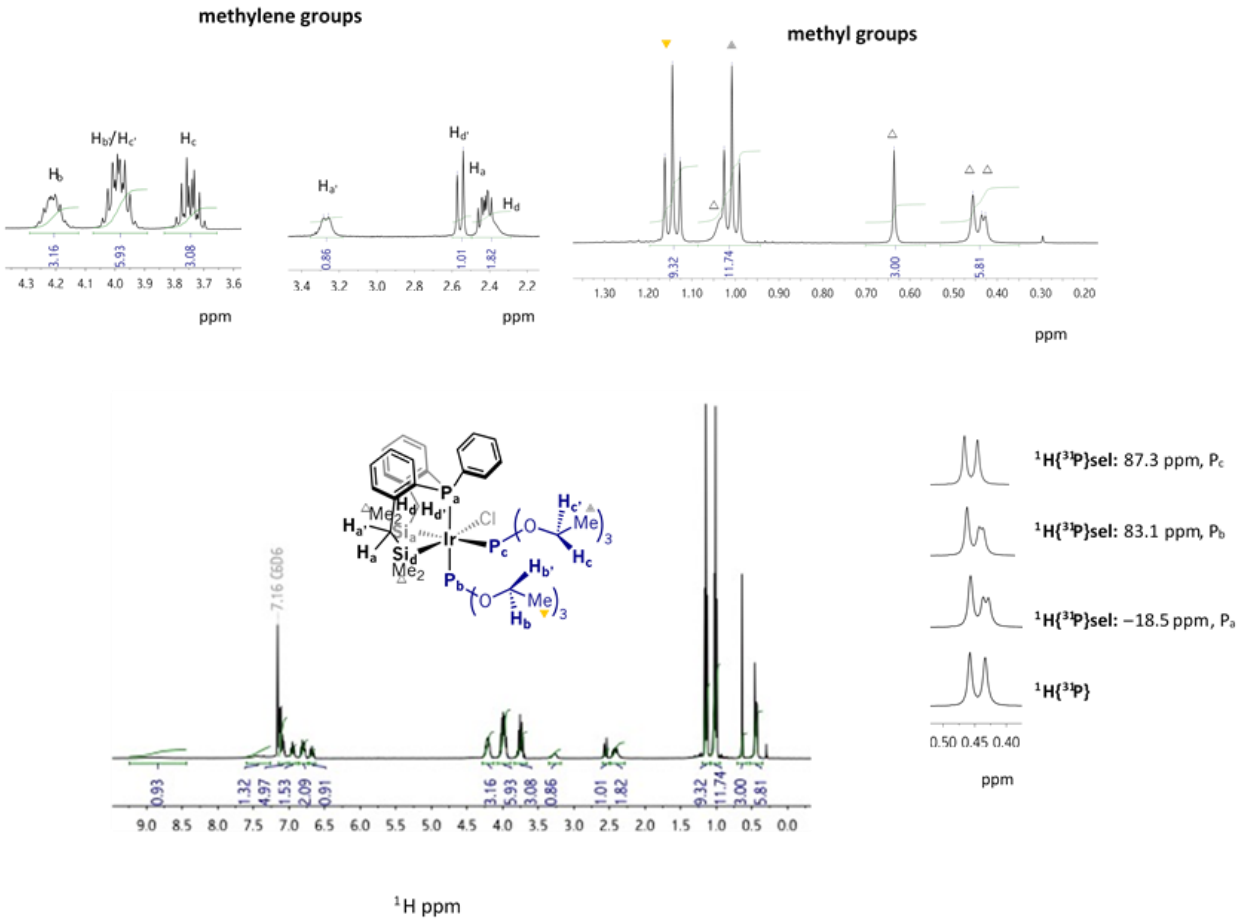


Figure S1. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of complex **2** and inlets in the methyl and methylene regions.

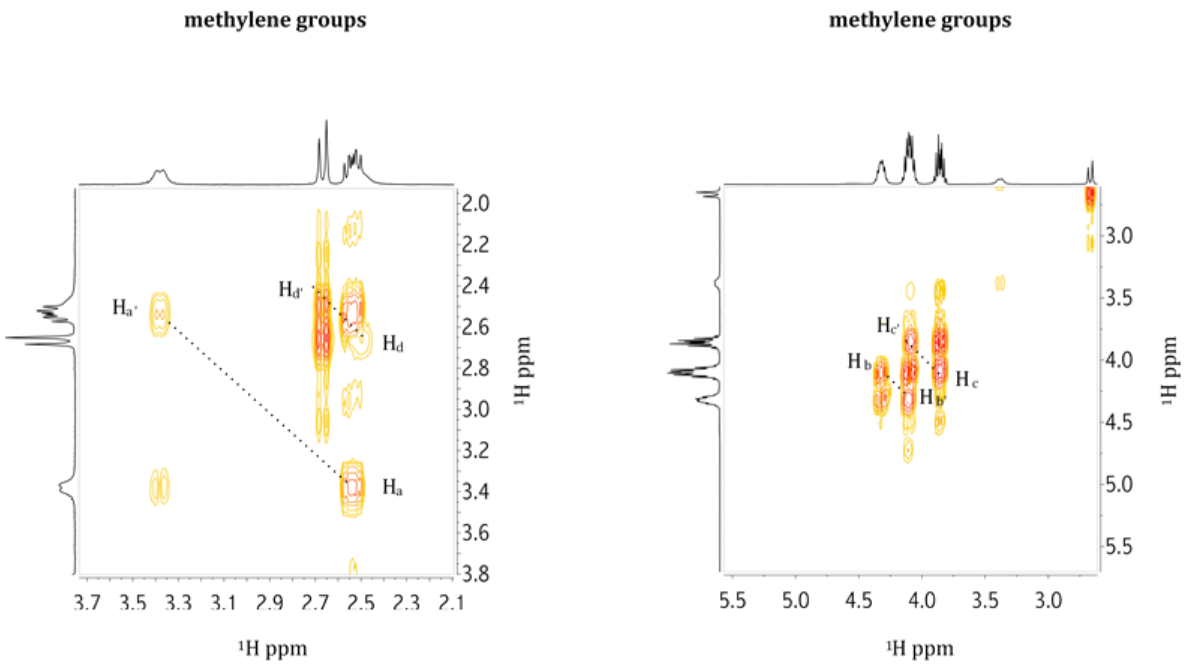


Figure S2. ^{1}H-^{1}H COSY NMR spectra (298 K, C_6D_6) of complex **2** in the methylene regions.

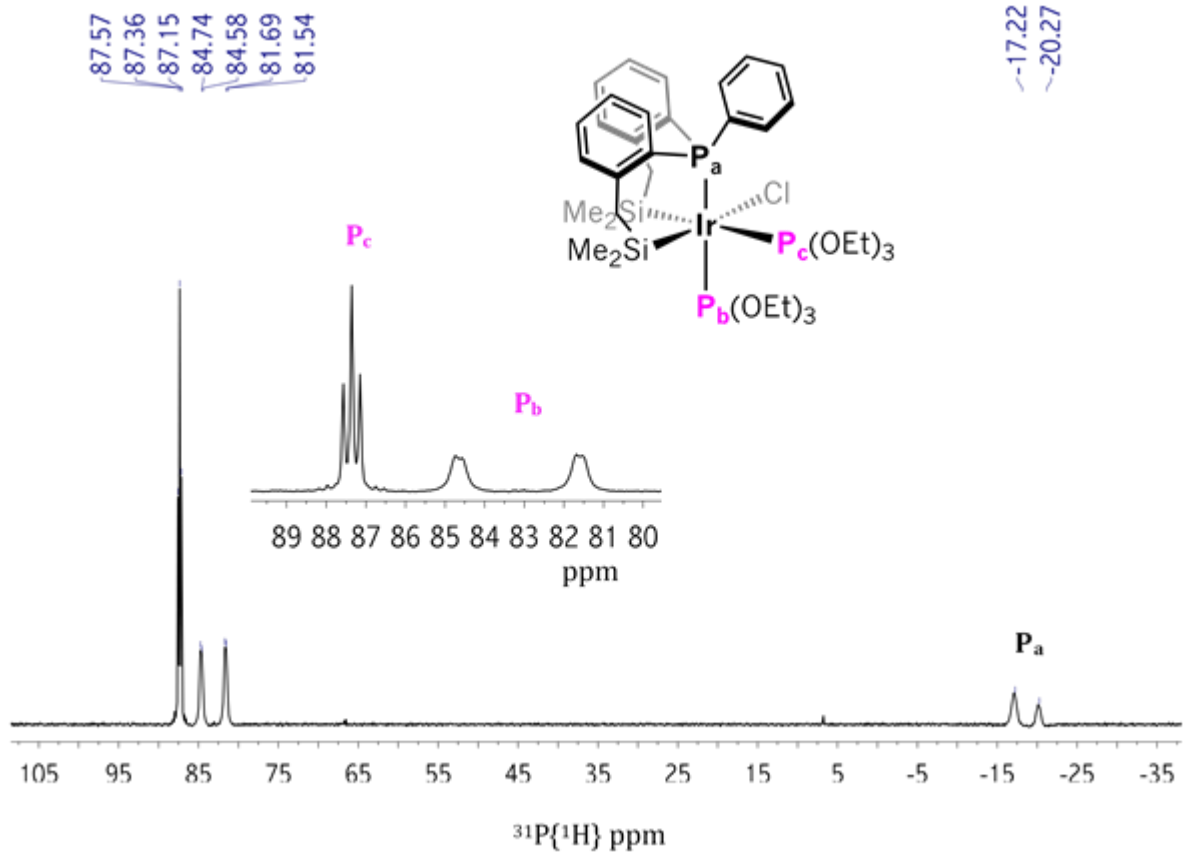


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz, 298 K, C_6D_6) of complex **2**.

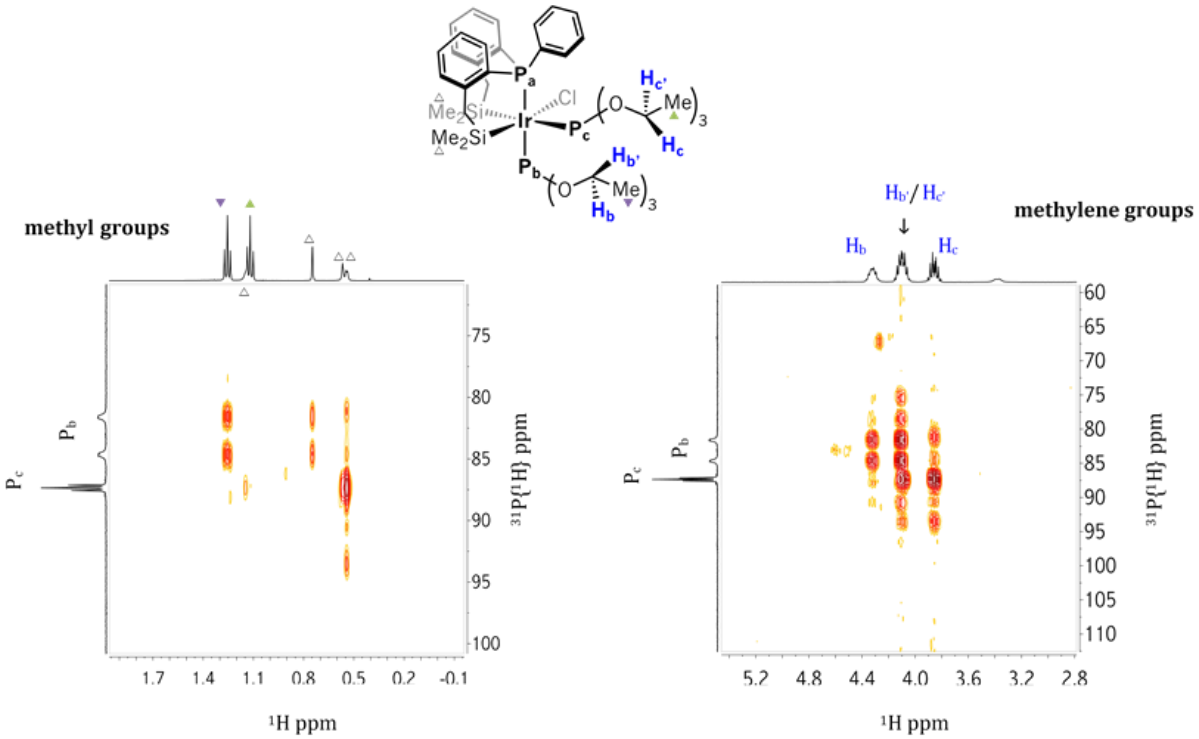


Figure S4. $^{1}H–^{31}P$ HMQC NMR spectra (298 K, C_6D_6) of complex **2**.

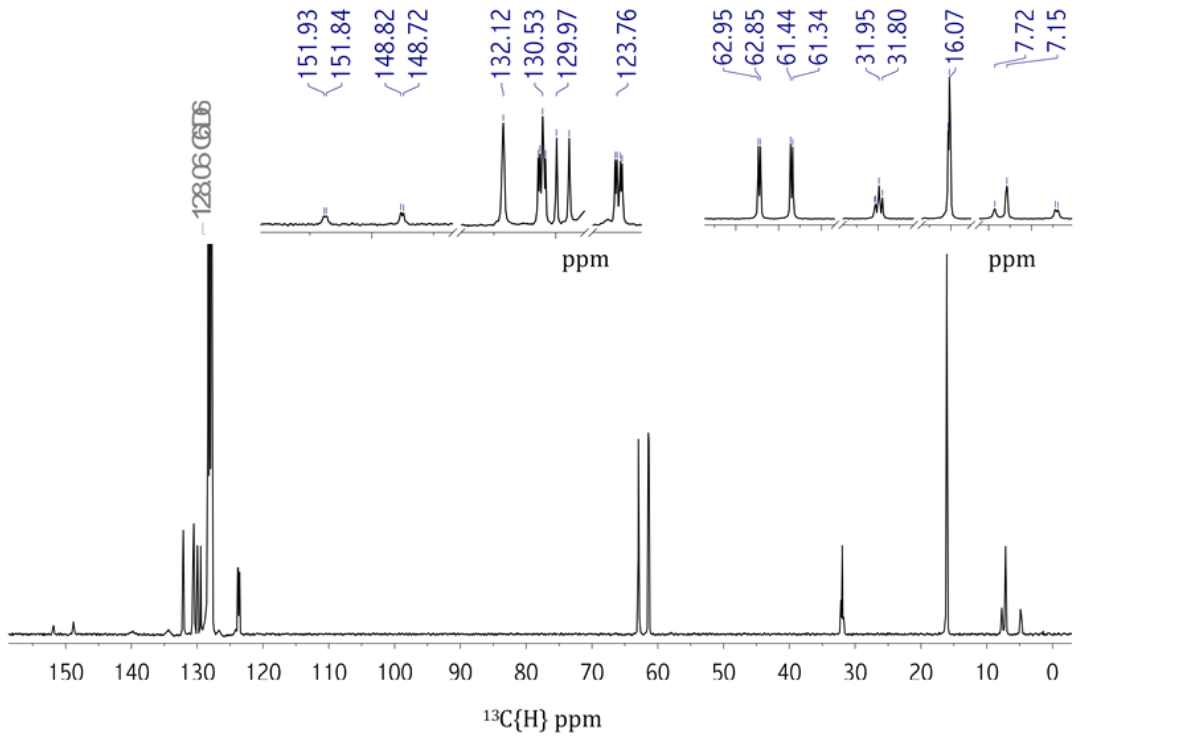


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 298 K, C_6D_6) of complex **2**.

1.2 Complex 3

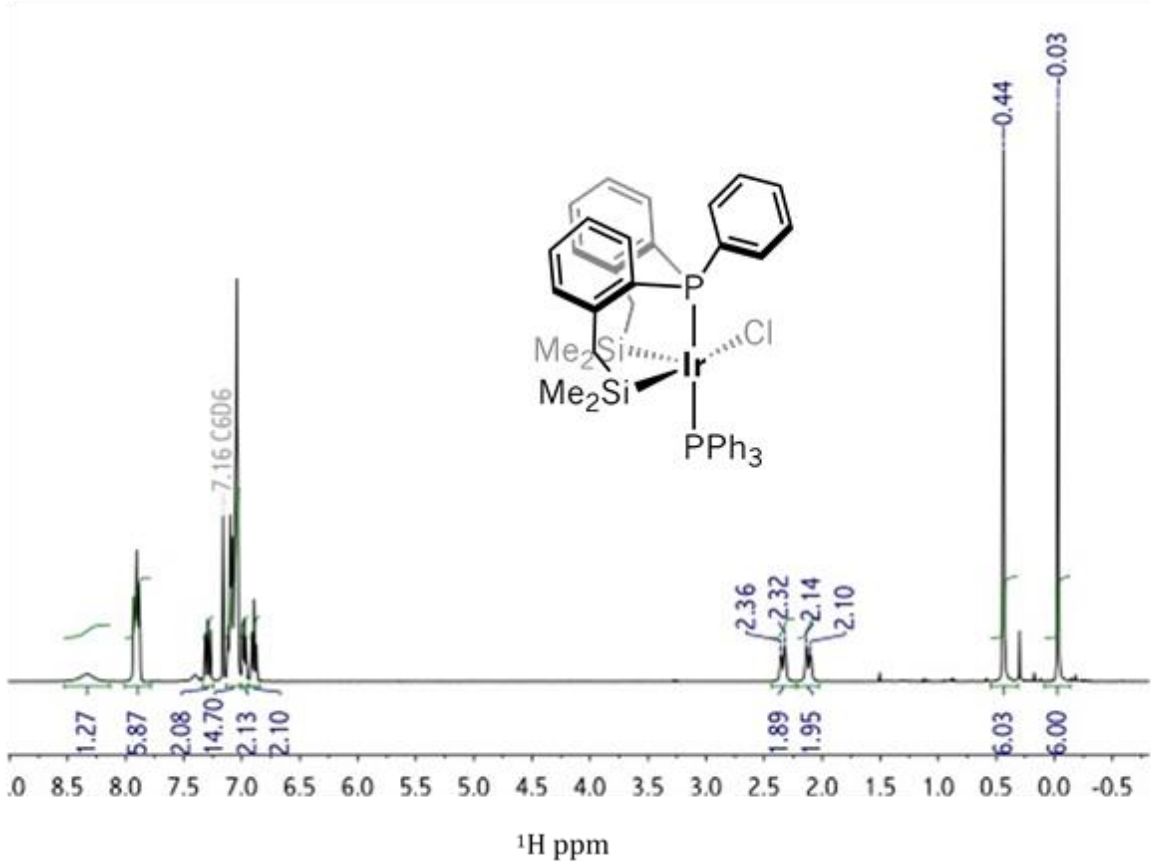


Figure S6. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of complex **3**.

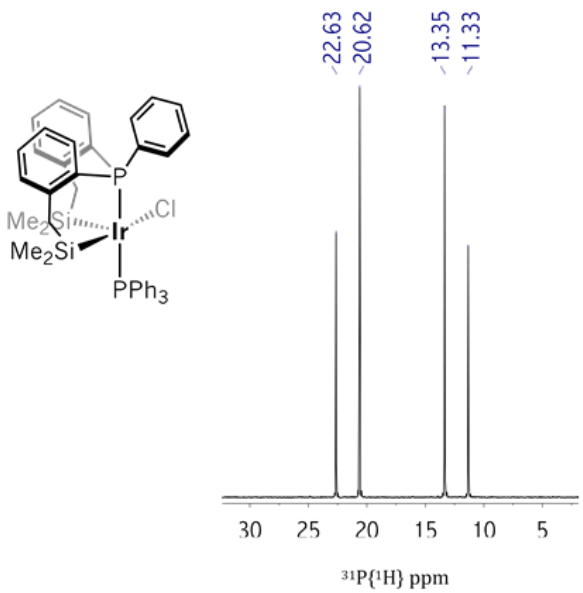


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz, 298 K, C_6D_6) of complex **3**.

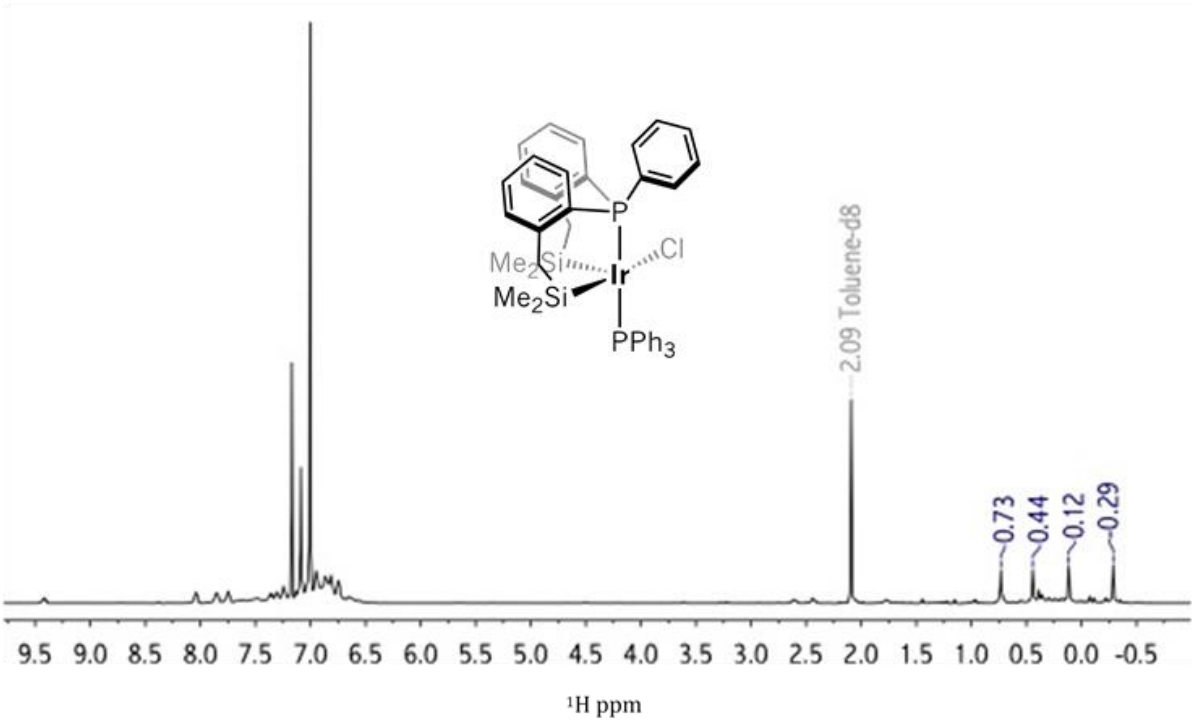


Figure S8. ^{1}H NMR spectrum (600 MHz, 193 K, tol–d_8) of complex **3**.

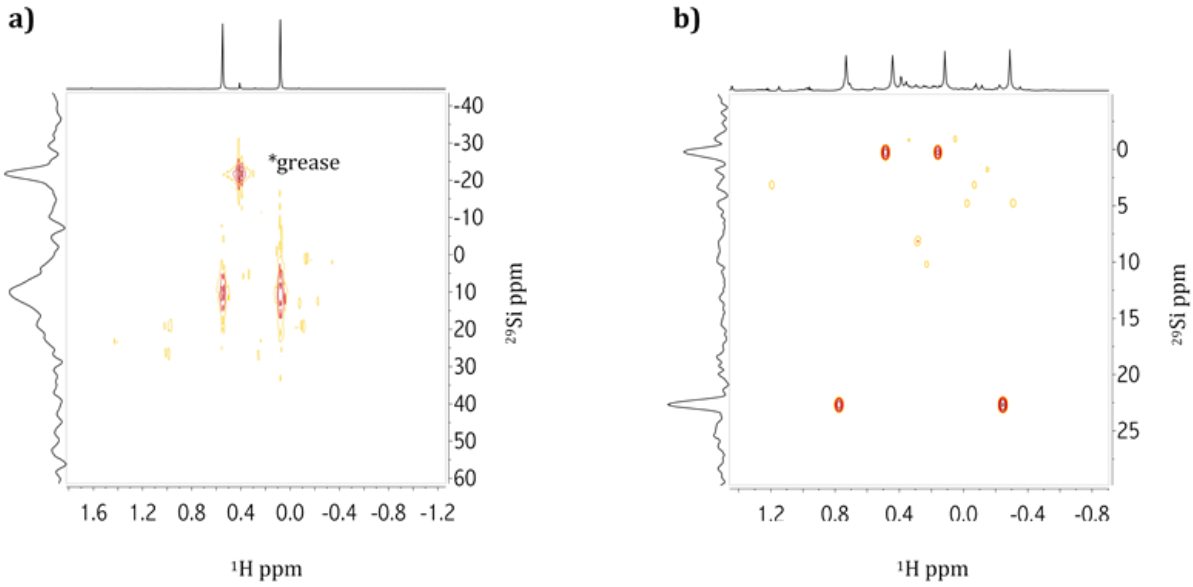


Figure S9. ^{1}H–^{29}Si HMQC NMR spectra **a)** at 298 K in C_6D_6 ; **b)** at 193 K in tol–d_8 of complex **3**.

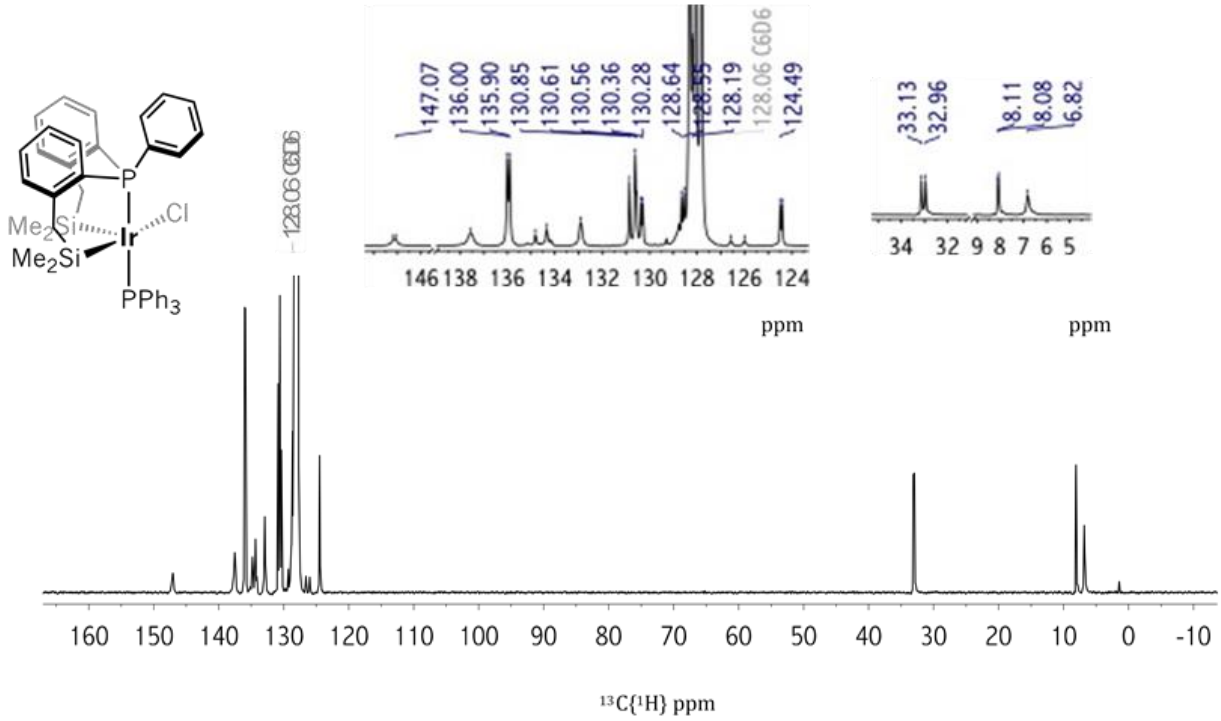


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 298 K, C_6D_6) of complex **3**.

1.3 Complex 4

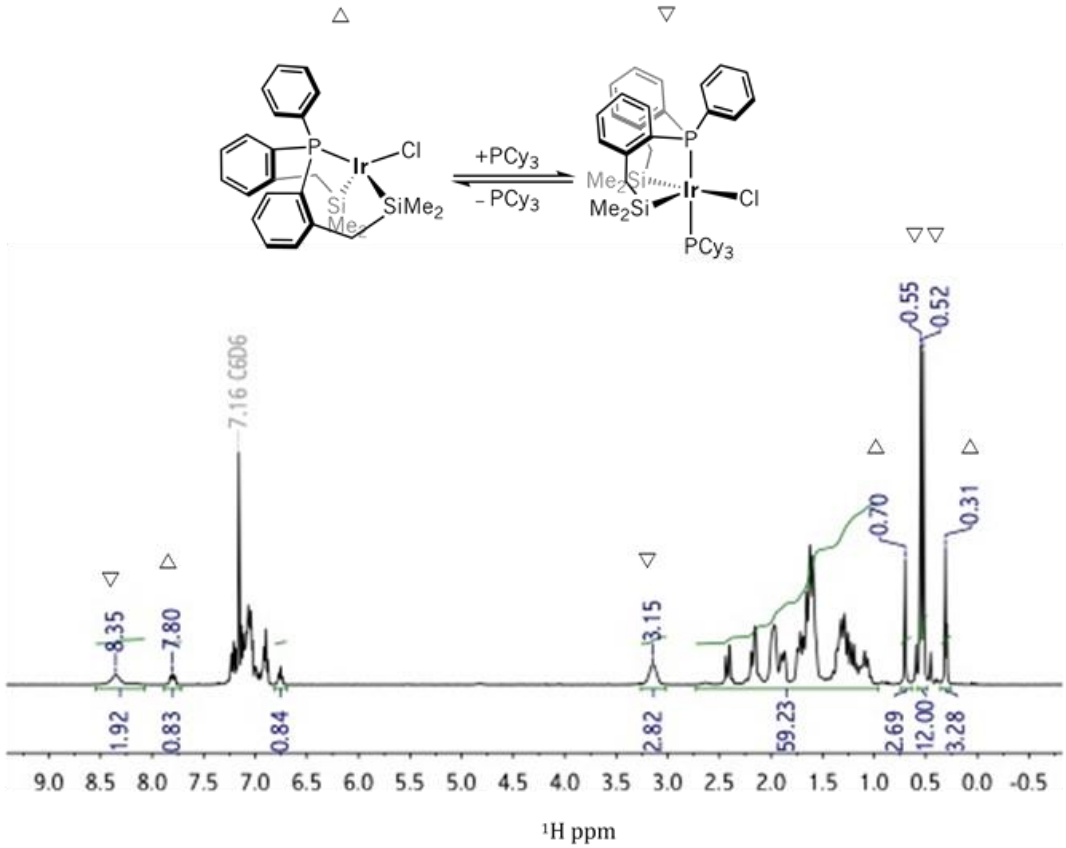


Figure S11. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of the equilibrium mixture containing **1'** and **4**.

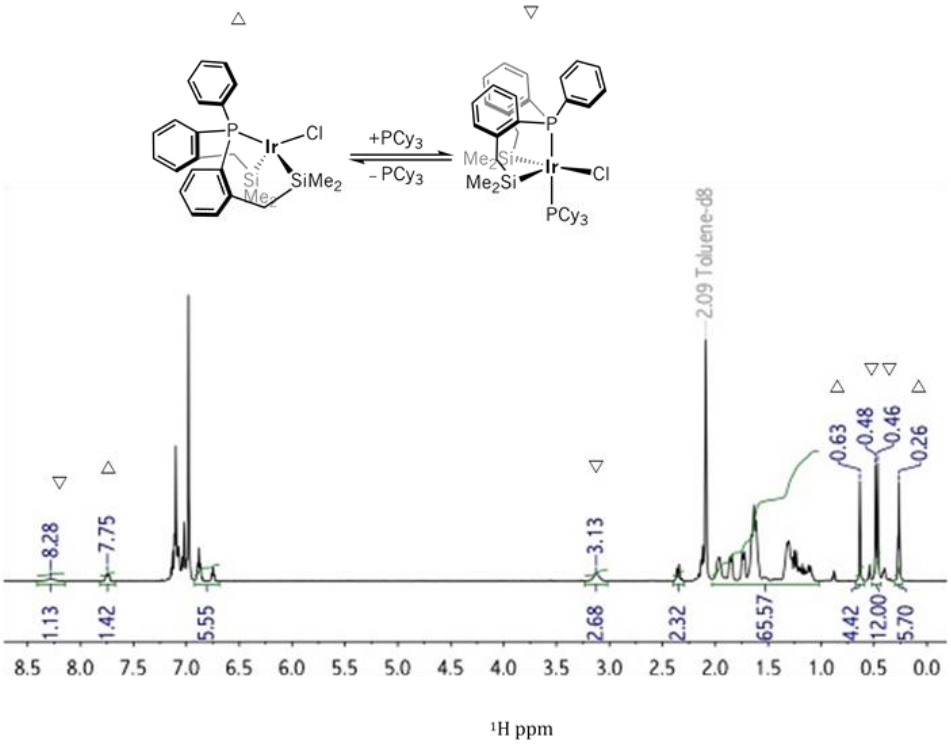


Figure S12. ^{1}H NMR spectrum (600 MHz, 298 K, tol–d_8) of the equilibrium mixture containing **1'** and **4**.

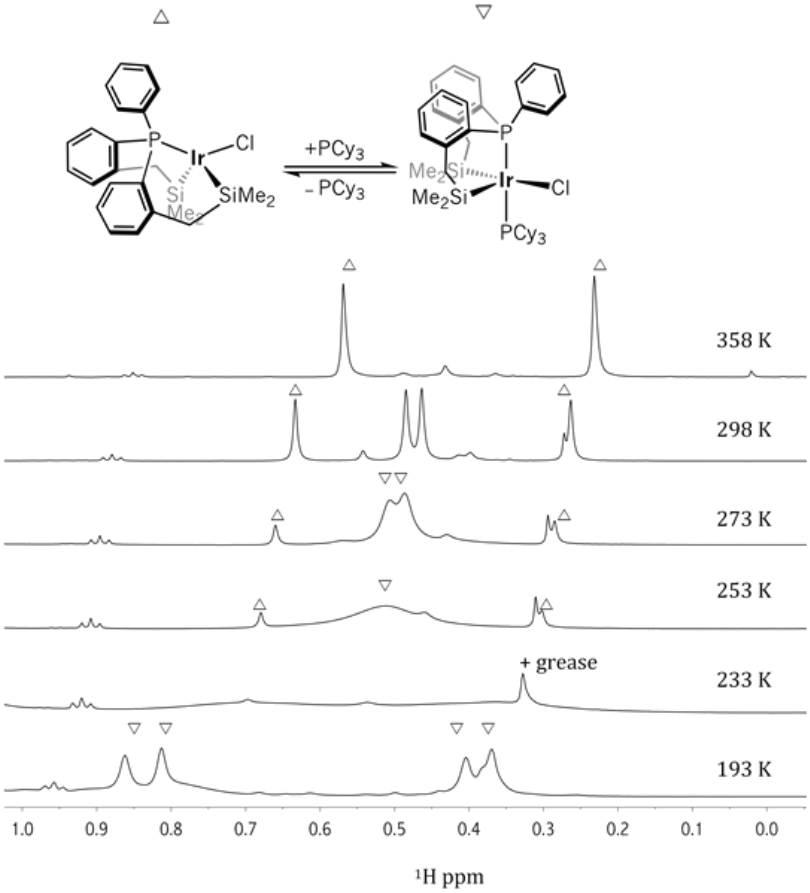


Figure S13. ^{1}H NMR spectra (600 MHz, tol–d_8) in the region of 0.0–1.0 ppm at different temperatures of the equilibrium mixture containing **1'** and **4**.

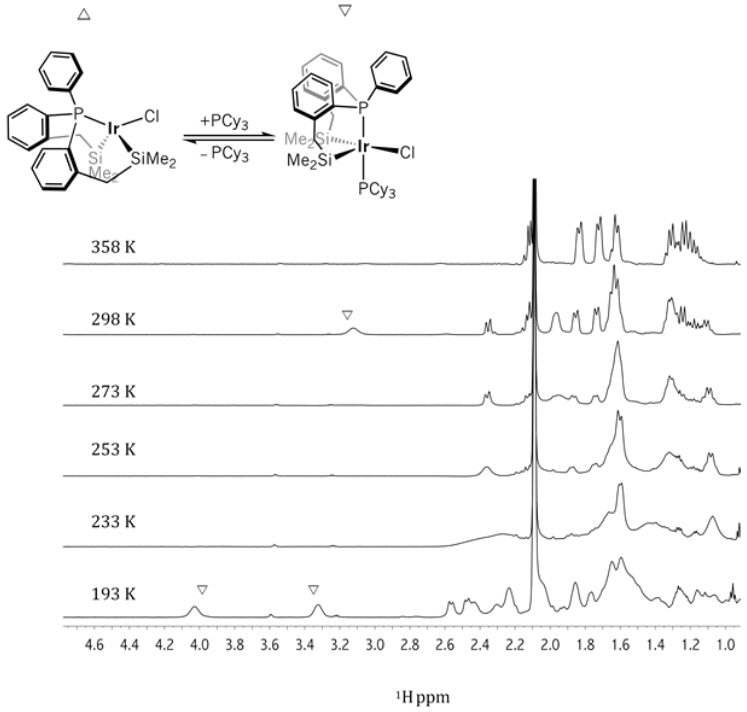


Figure S14. ^{1}H NMR spectra (600 MHz, tol–d_8) in the region of 1.0–4.6 ppm at different temperatures of the equilibrium mixture containing **1'** and **4**.

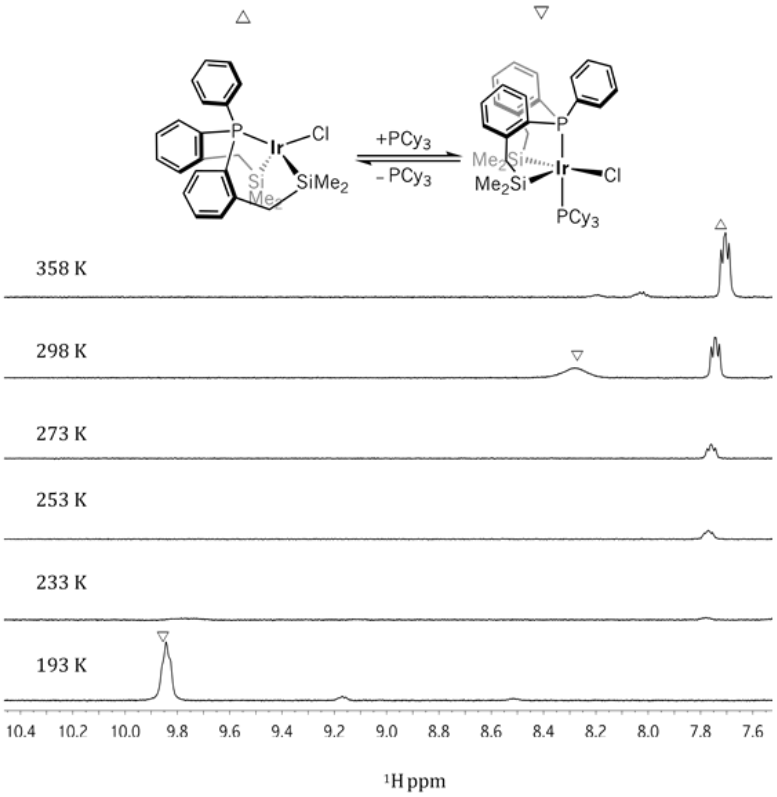


Figure S15. ^{1}H NMR spectra (600 MHz, tol–d_8) in the region of 7.6–10.4 ppm at different temperatures of the equilibrium mixture containing **1'** and **4**.

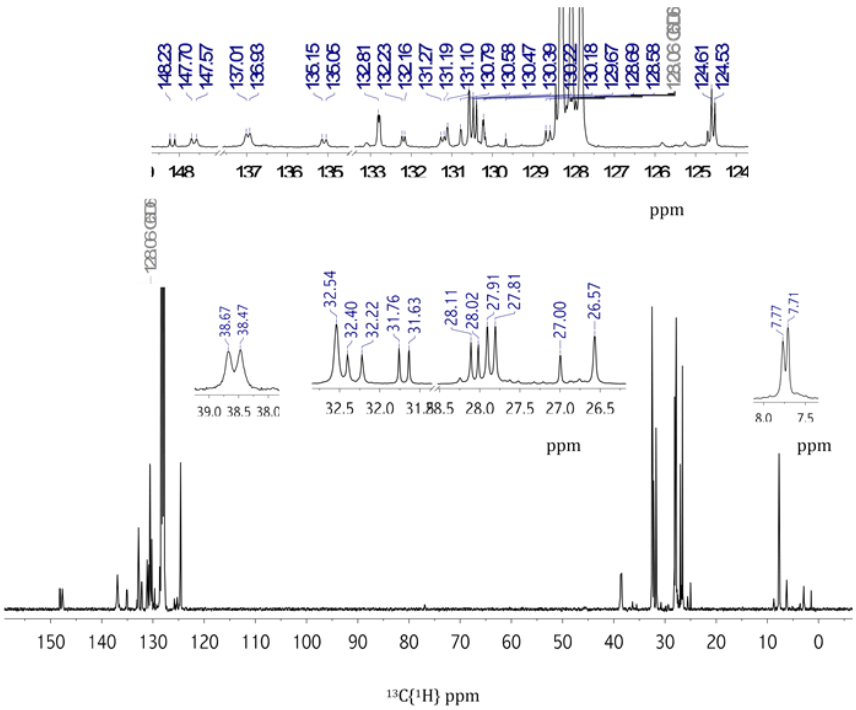


Figure S16. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, 298 K, C_6D_6) of the equilibrium mixture containing **1'** and **4**.

1.3 Complexes 5a-d

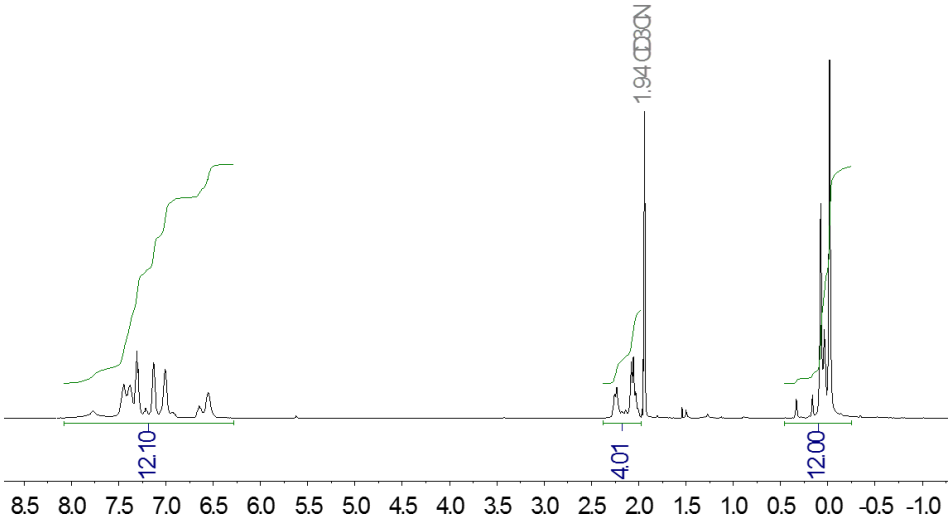
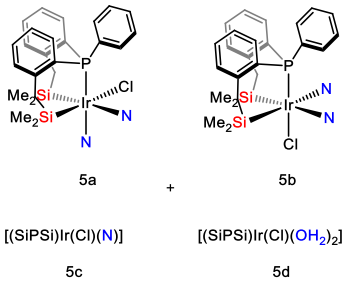


Figure S17. ^{1}H NMR spectrum (500 MHz, 298 K, CD_3CN) of the equilibrium mixture containing **5a-d**.



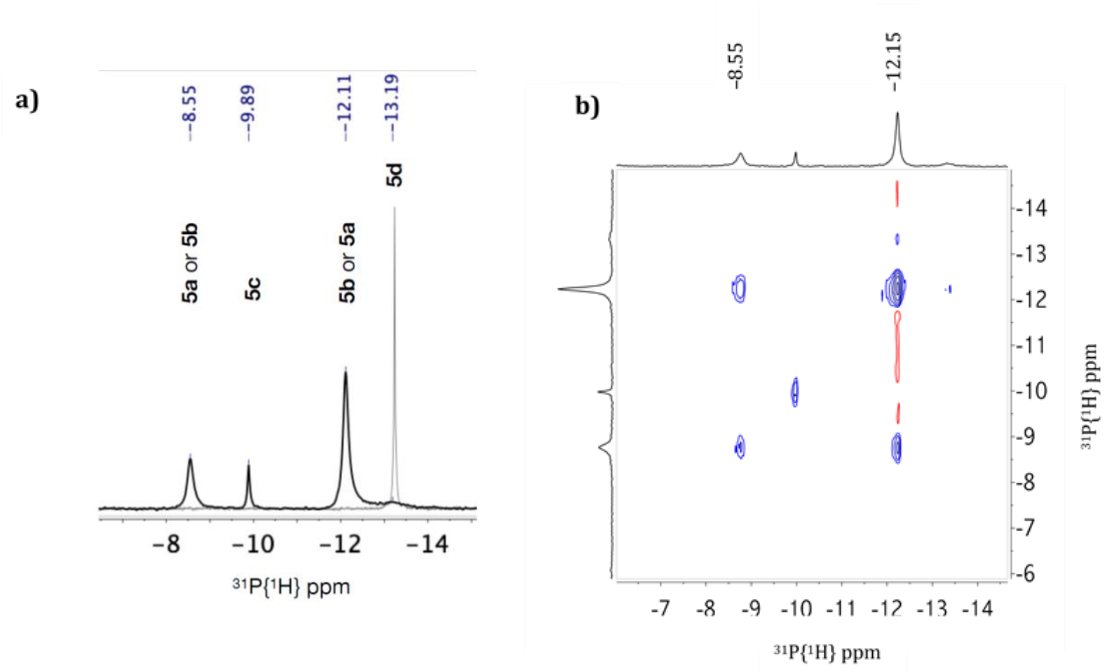


Figure S18. NMR spectra of the equilibrium mixture containing **5a-d** in CD_3CN: **a)** $^{31}P\{^{1}H\}$ (161.9 MHz, 298 K) and in grey, same mixture after addition of an excess of water. **b)** ^{31}P–^{31}P EXSY (tm = 150 ms, 263 K).

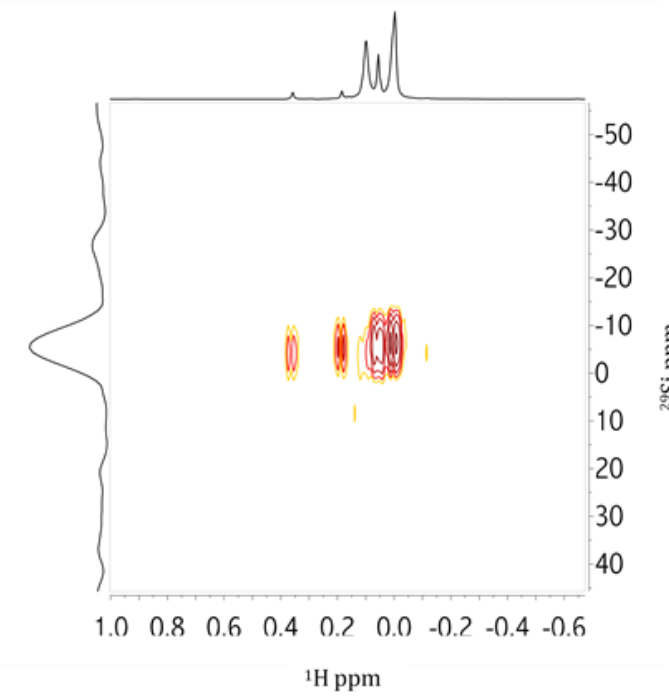


Figure S19. ^{1}H–^{29}Si HMQC NMR spectrum (298 K, CD_3CN) of the equilibrium mixture containing **5a-d**.

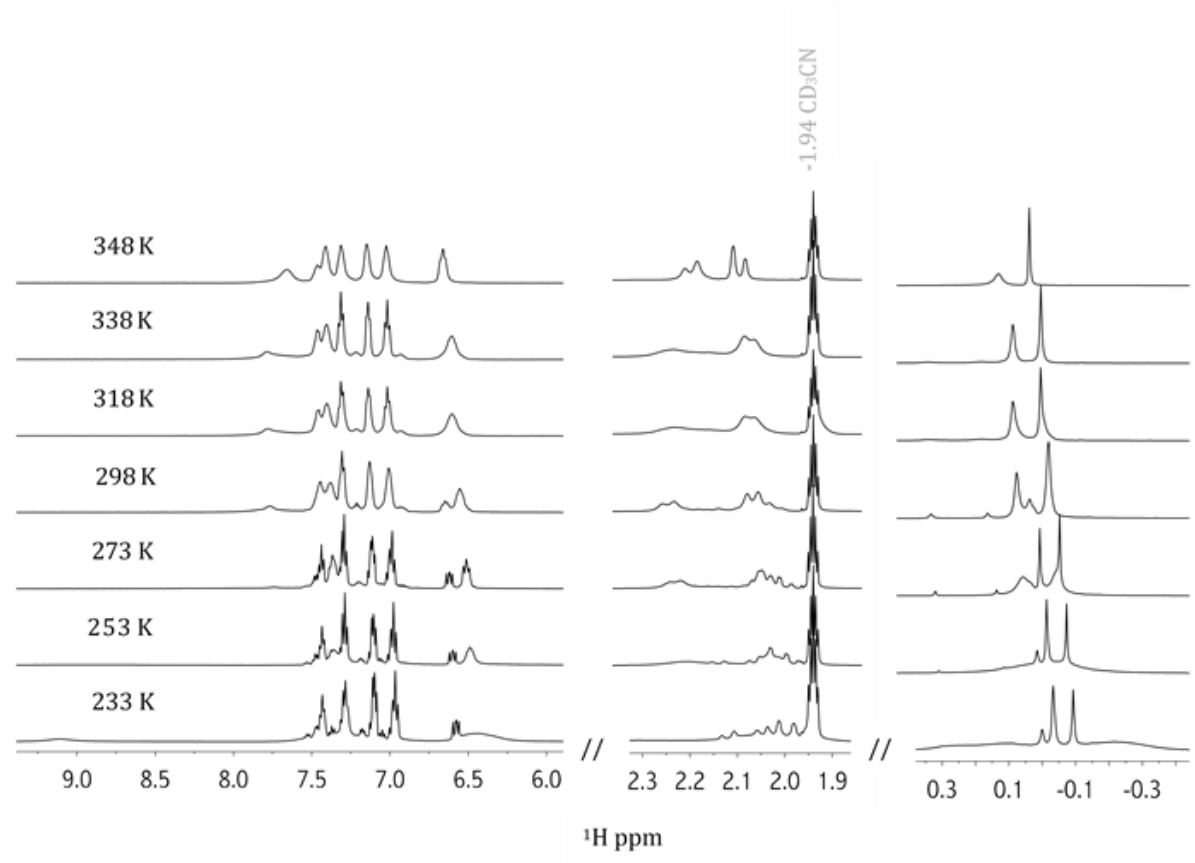


Figure S20. ^{1}H NMR spectra (500 MHz) at different temperatures of the equilibrium mixture containing **5a-d** in CD_3CN.

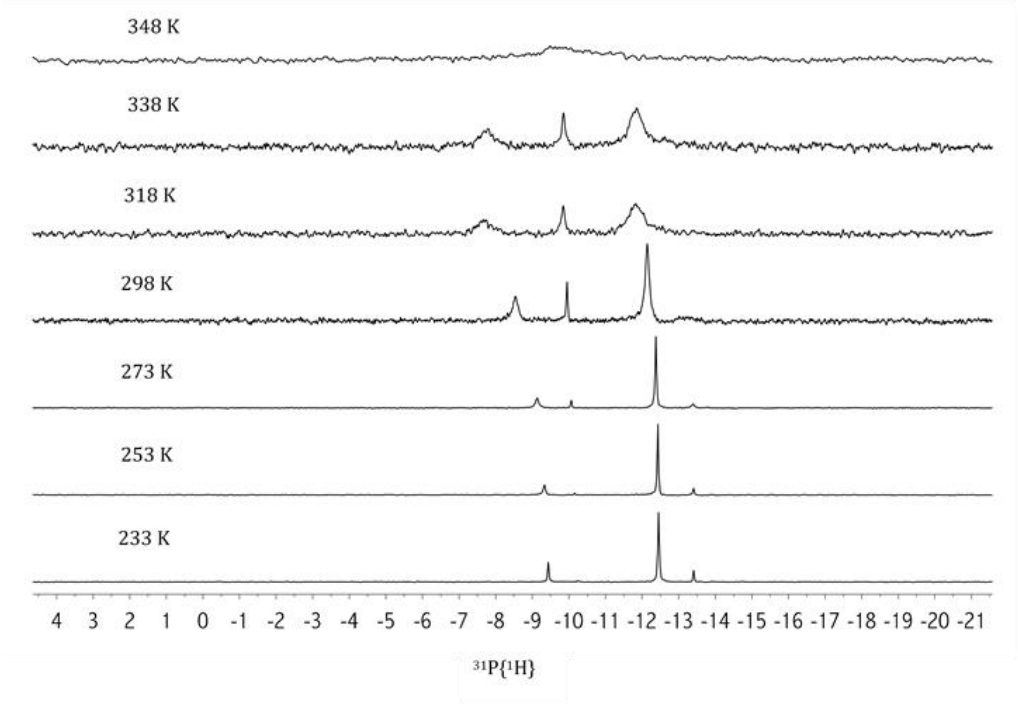


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (202.5 MHz) at different temperatures of the equilibrium mixture containing **5a-d** in CD_3CN.

1.4 Complex 6b

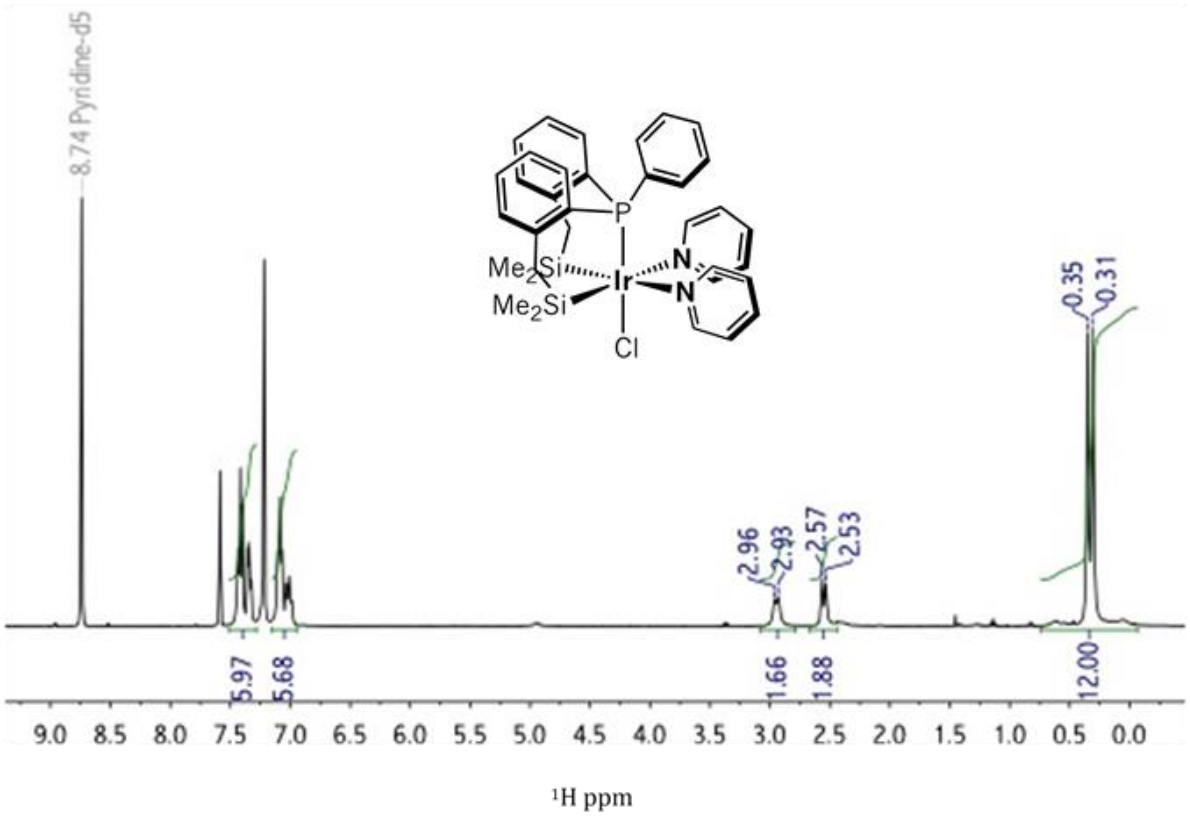


Figure S22. ^{1}H NMR spectrum (400 MHz, 298 K, pyr–d_5) of complex **6b**.

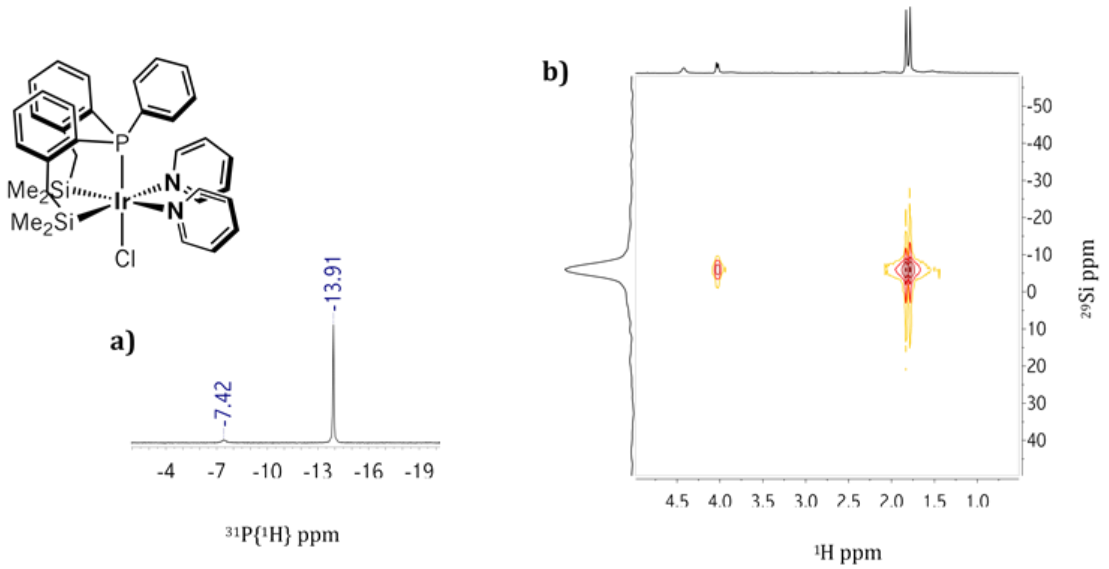


Figure S23. **a)** $^{31}P\{^{1}H\}$ NMR (161.9 MHz) and **b)** ^{1}H–^{29}Si HMQC spectrums of complex **6b** in pyr–d_5 at 298 K. Traces of isomer **6a** at –7.42 ppm.

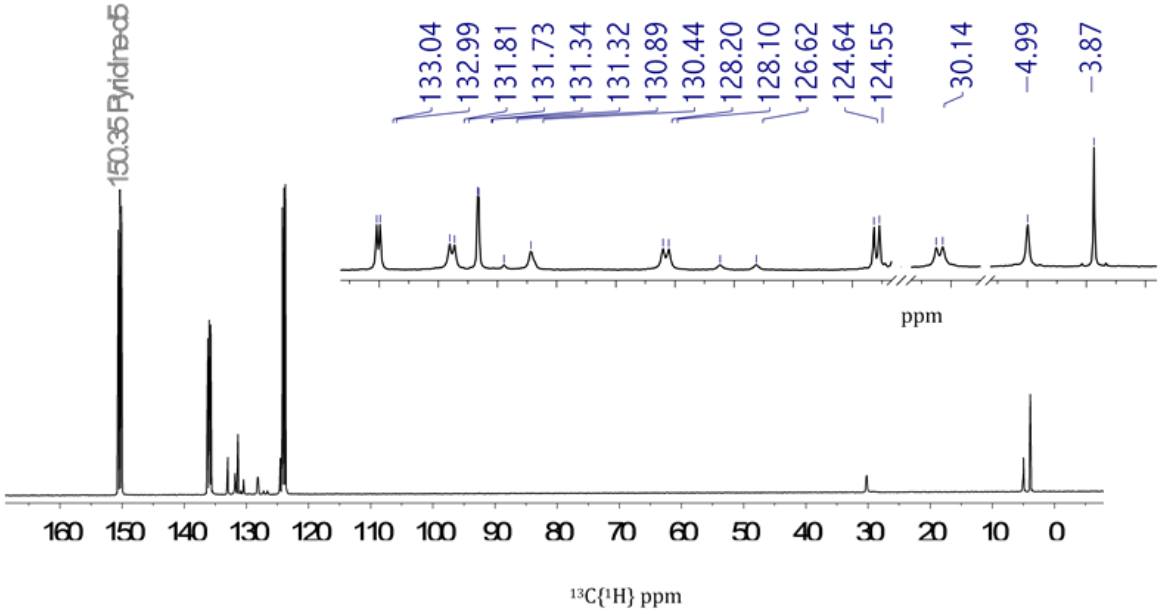
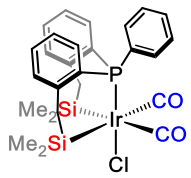


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 298 K, pyr–d_5) of complex **6b**.

1.4 Complex 7b



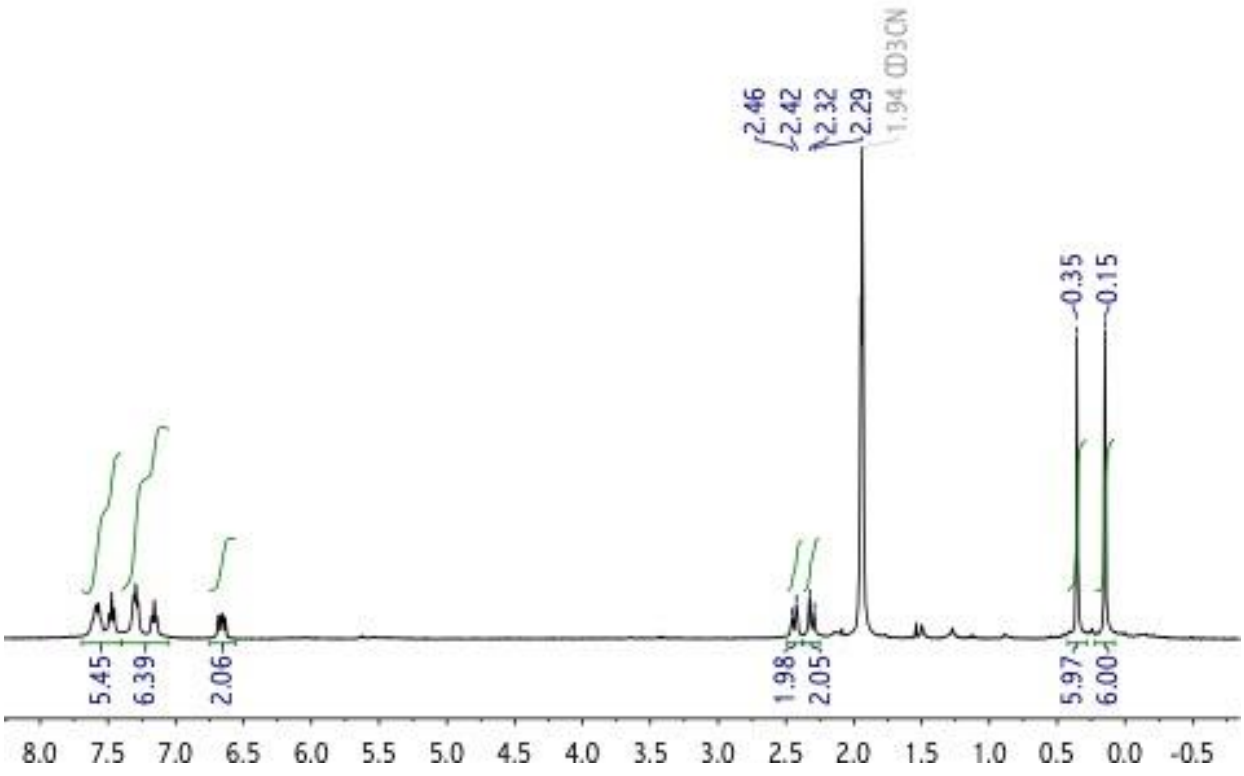


Figure S25. ^{1}H NMR spectrum (400 MHz, 298 K, CD_3CN) of complex **7b**.

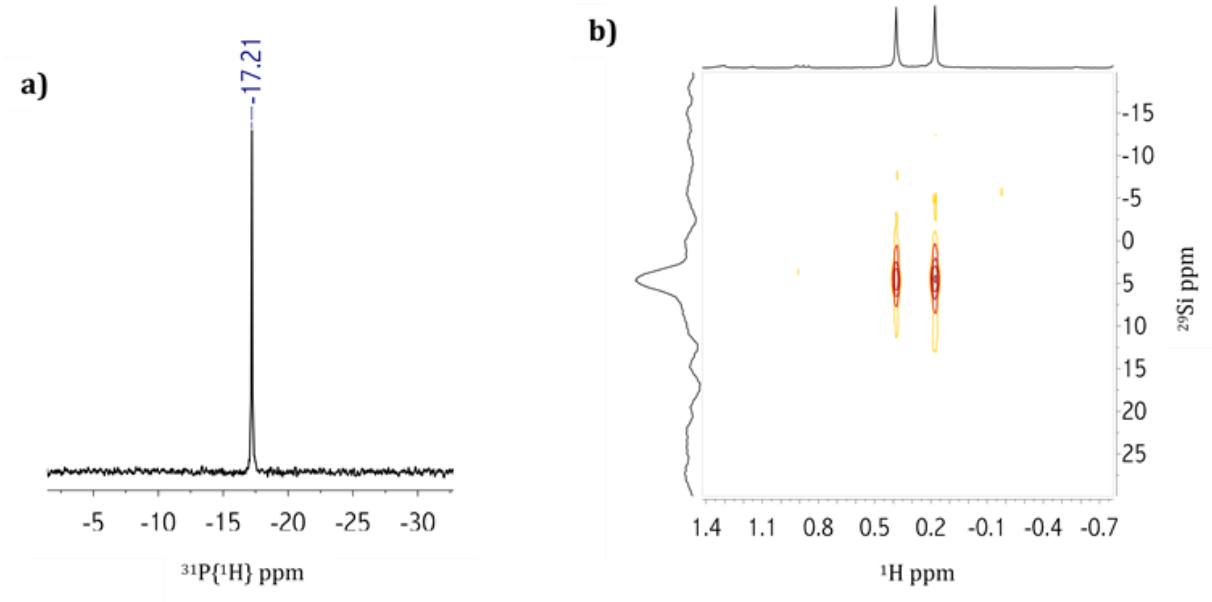


Figure S26. **a)** $^{31}P\{^{1}H\}$ (161.9 MHz) and **b)** ^{1}H–^{29}Si HMQC NMR spectra of complex **7b** at 298 K in CD_3CN.

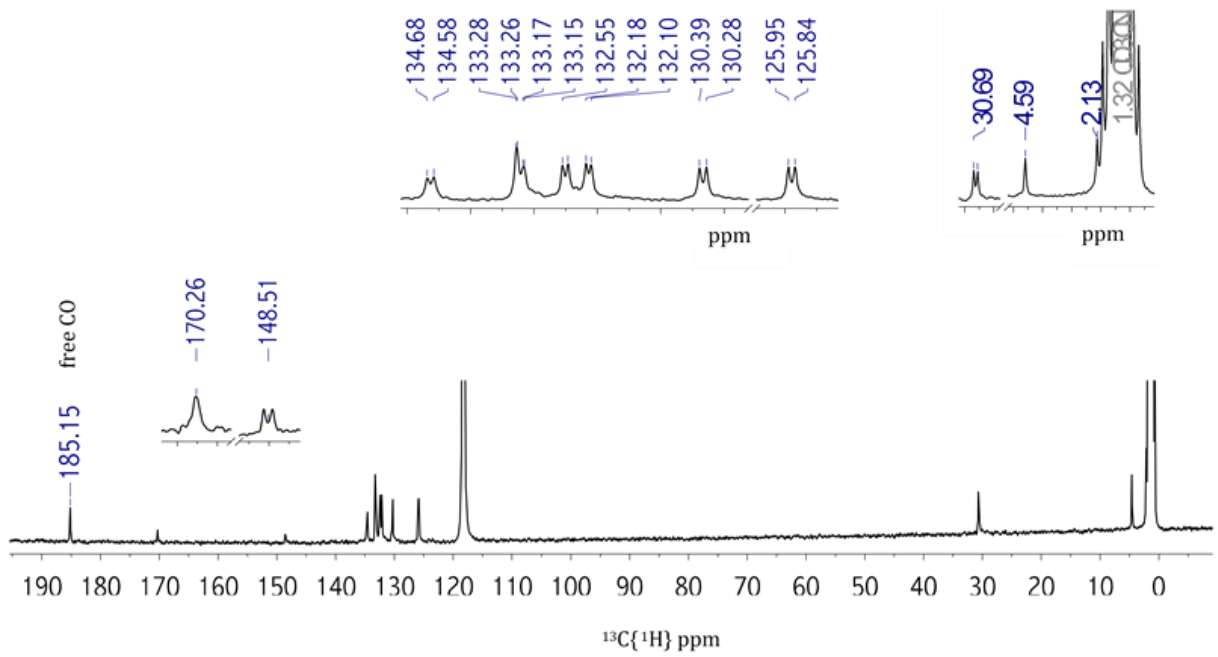


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 298 K, CD_3CN) of complex **7b**.

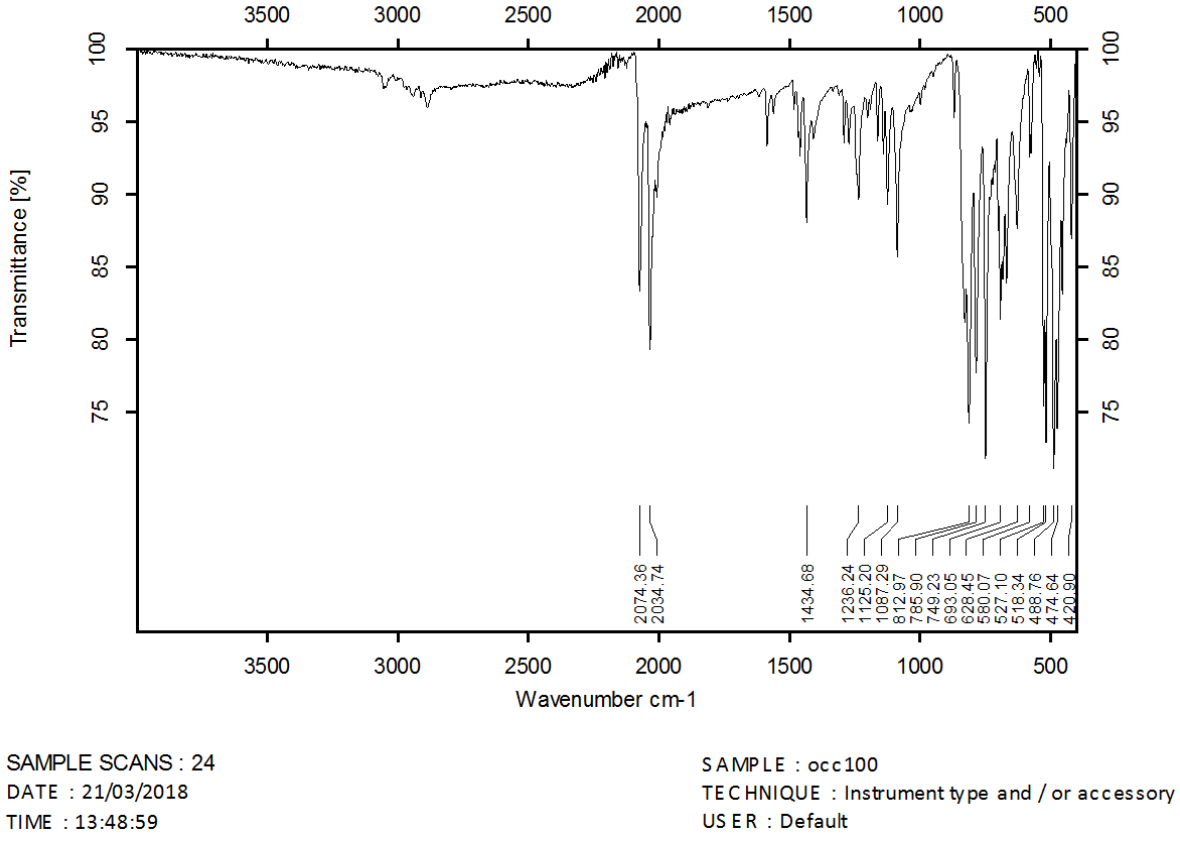


Figure S28. IR–ATR spectrum of complex **7b**.

1.5 Complexes 7a,b,c

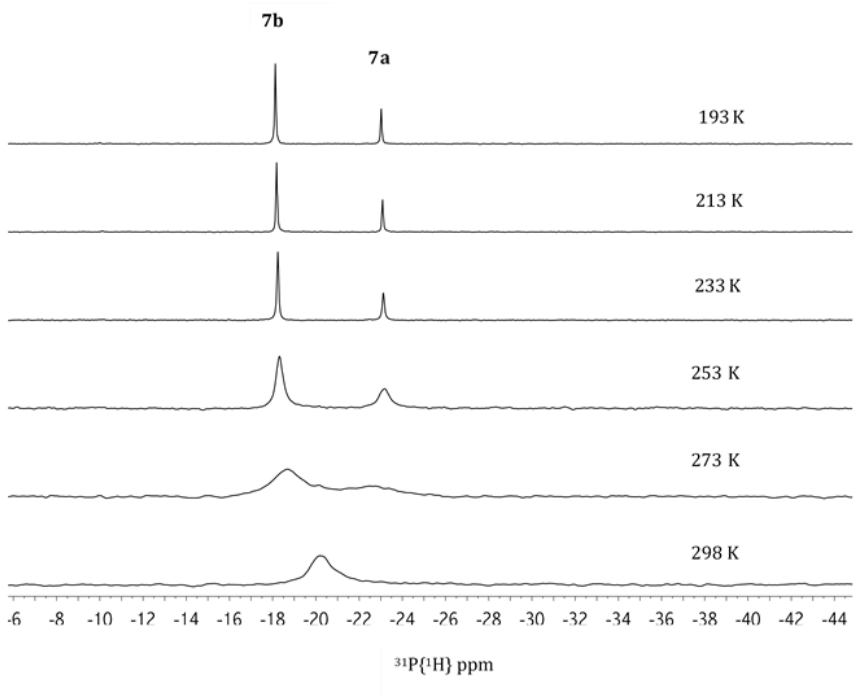


Figure S29. $^{31}P\{^{1}H\}$ NMR spectra (202.5 MHz, tol–d_8) at different temperatures corresponding to the equilibrium mixture of isomers **7b** and **7a**.

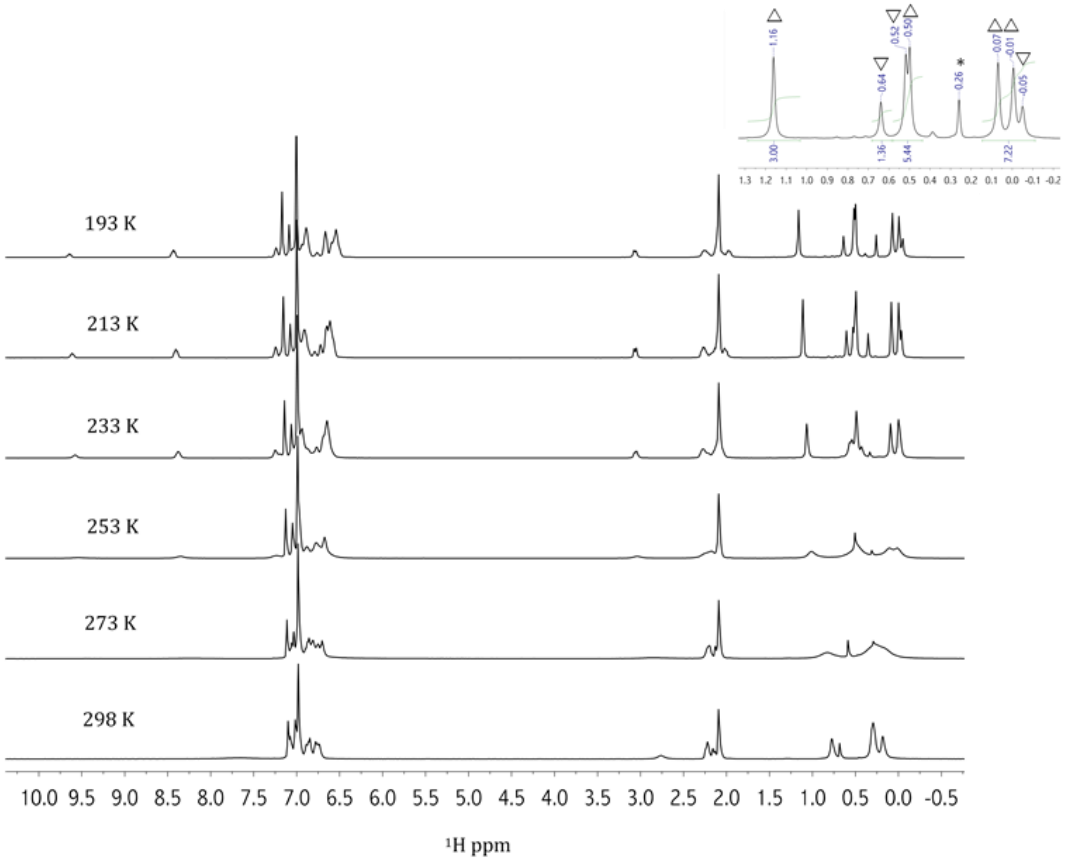


Figure S30. ^{1}H NMR spectRA (500 MHz, tol–d_8) at different temperatures corresponding to the equilibrium mixture of isomers **7b** △and **7a** ▽and inlet of the region from –0.2 ppm to 1.3 ppm at 193 K. * grease.

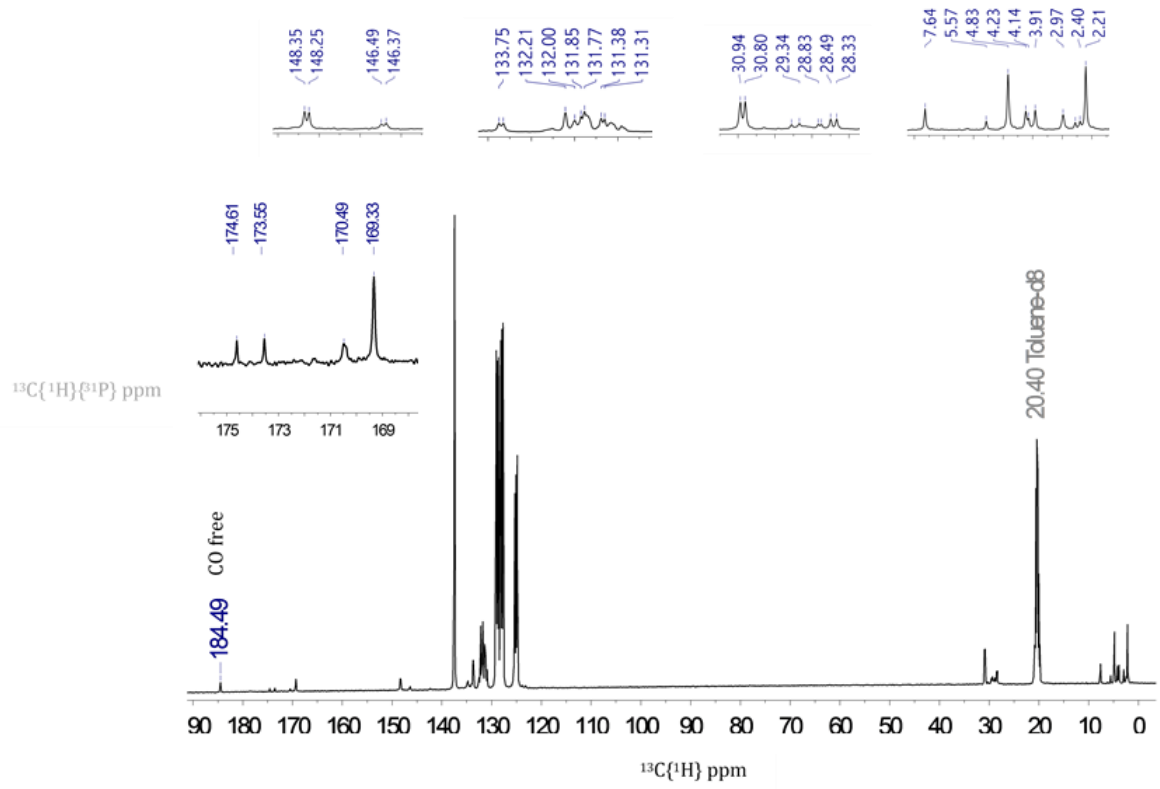


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, 298 K, tol–d_8) corresponding to the equilibrium mixture of isomers **7b** and **7a**. Inlets of methyl, methylene, aromatic and CO regions.

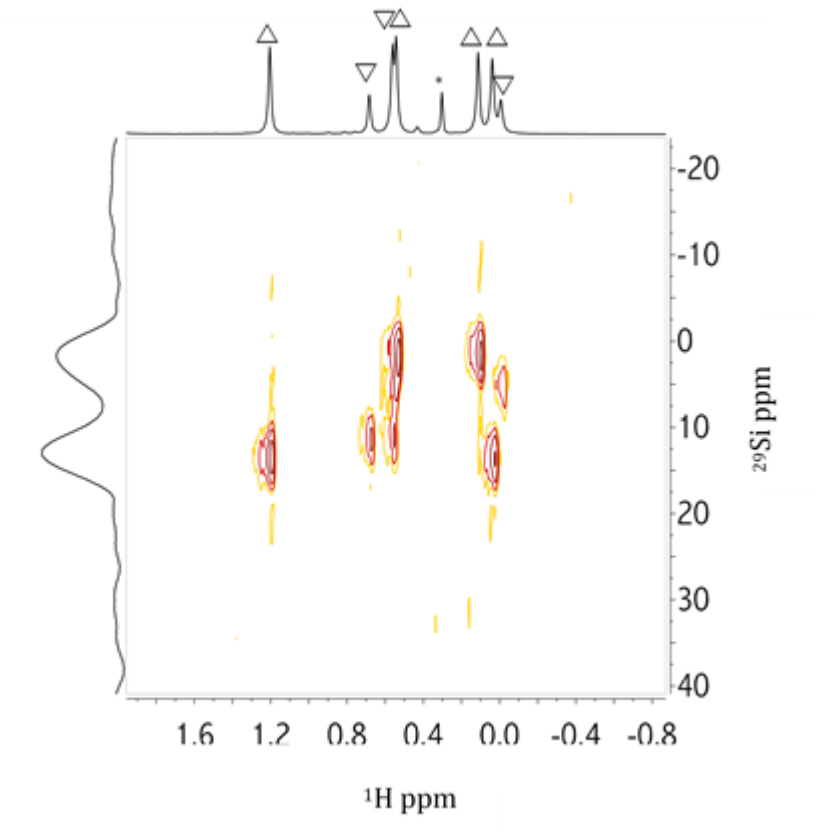


Figure S32. $^{1}H–^{29}Si$ HMQC NMR spectra of the equilibrium mixture of isomers **7b** △and **7a**▽ in tol–d_8.

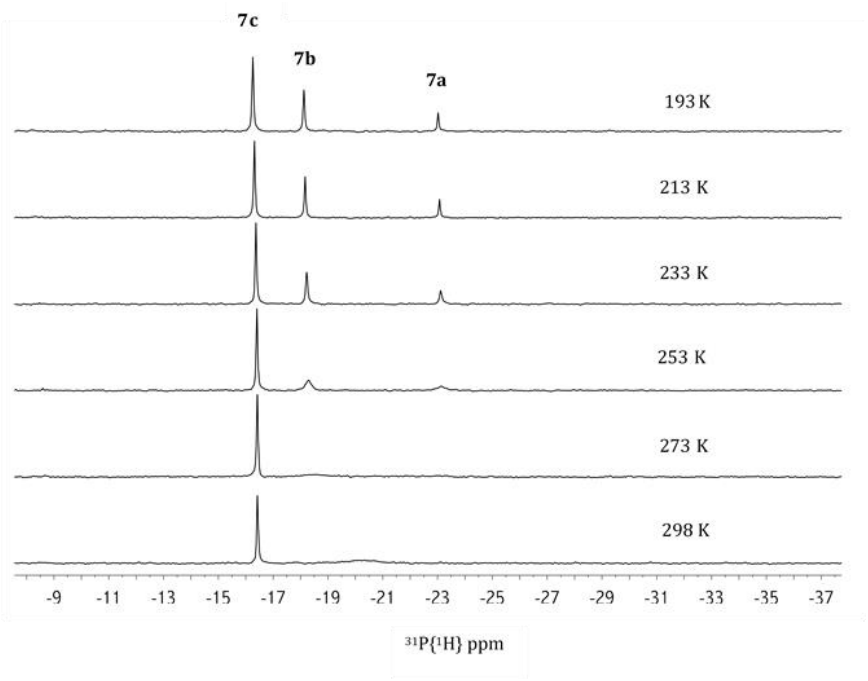


Figure S33. $^{31}P\{^{1}H\}$ NMR spectra (202.5 MHz, tol–d_8) at different temperatures of the reaction of **1** with 1 bar of CO leading to the NMR characterization of the monocarbonyl complex **7c**.

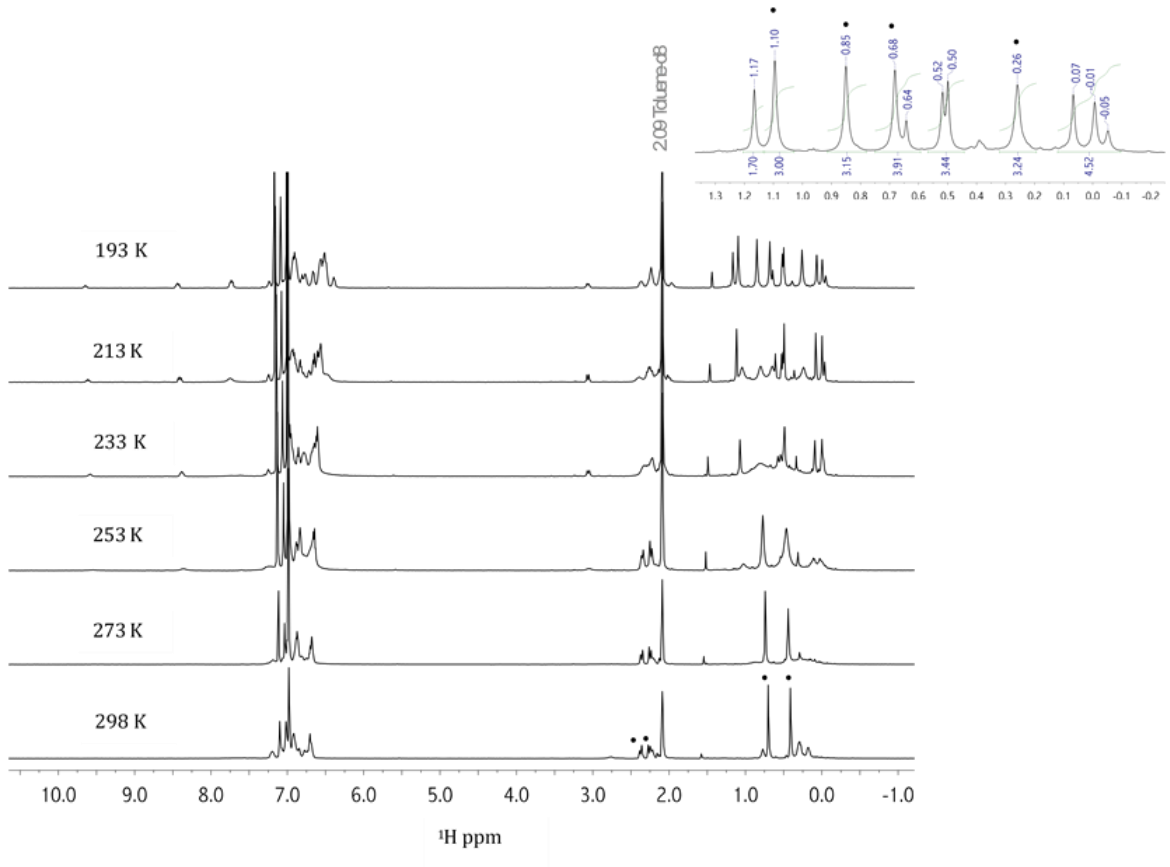


Figure S34. ^{1}H NMR spectra (500 MHz, tol–d_8) at different temperatures of the reaction of **1** with 1 bar of CO leading to the NMR characterization of the monocarbonyl complex **7c•**. Inlet of the region from –0.2 ppm to 1.3 ppm at 193 K.

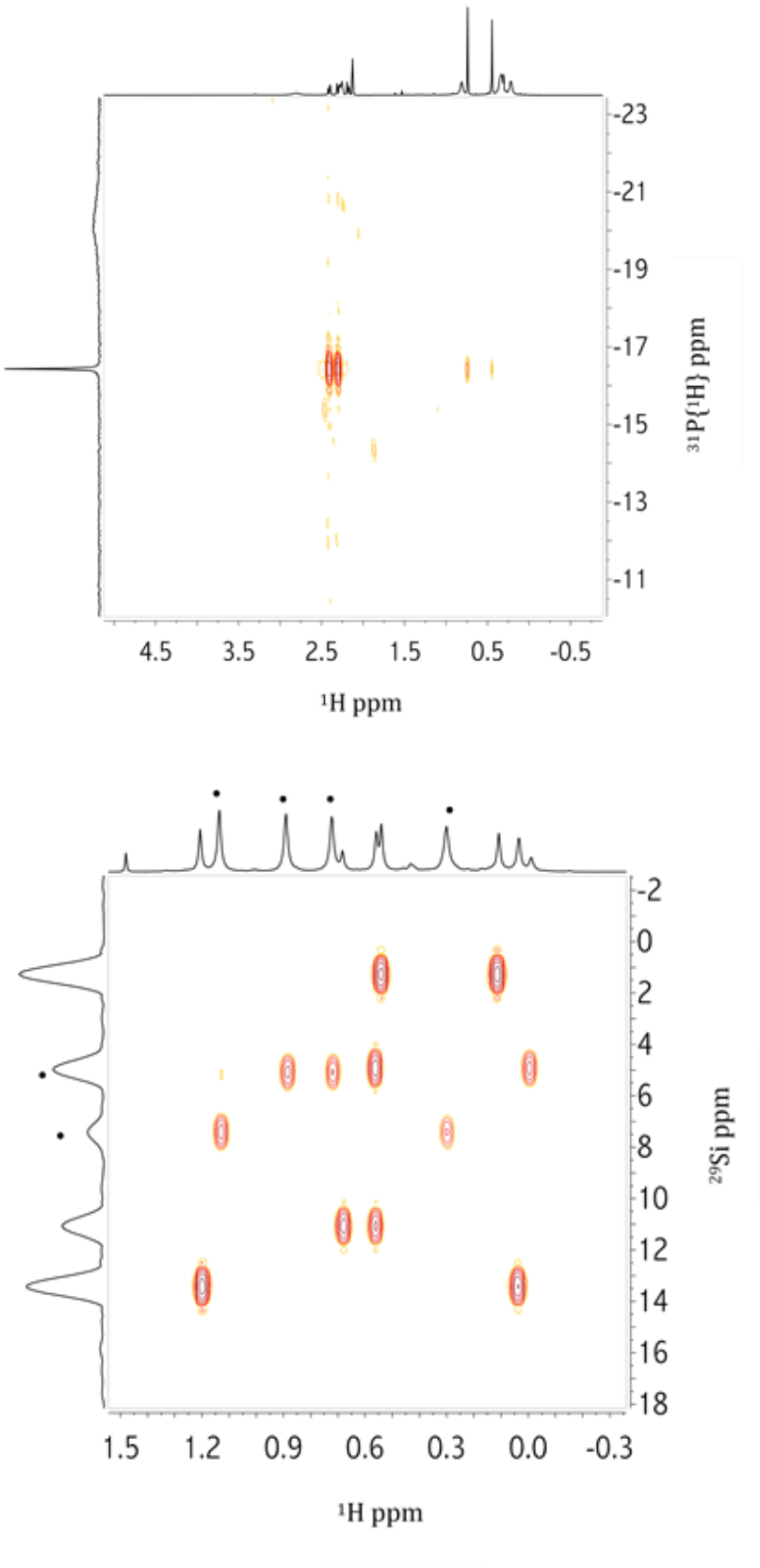


Figure S35. **(Top)** ^{1}H–^{31}P{^{1}H} HMQC and **(Bottom)** ^{1}H–^{29}Si HMQC NMR spectrums of the reaction of **1** with 1 bar of CO leading to the NMR characterization of the monocarbonyl complex **7c•** in tol–d_8 at 298 and 193 K, respectively.

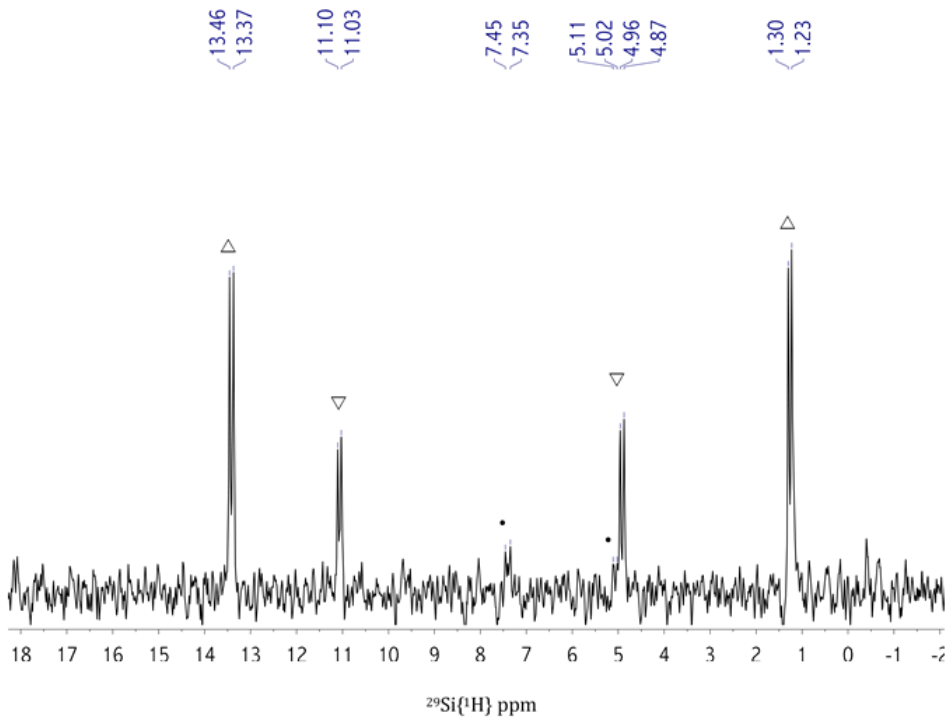


Figure S36. $^{29}Si\{^{1}H\}$ DEPT NMR spectrum (119.2 MHz, 193 K, tol–d_8) of the reaction of **1** with 1 bar of CO leading to the NMR characterization of the monocarbonyl complex **7c•** and the equilibrium mixture of isomers **7b**△ and **7a**▽.

1.6 Complex 8

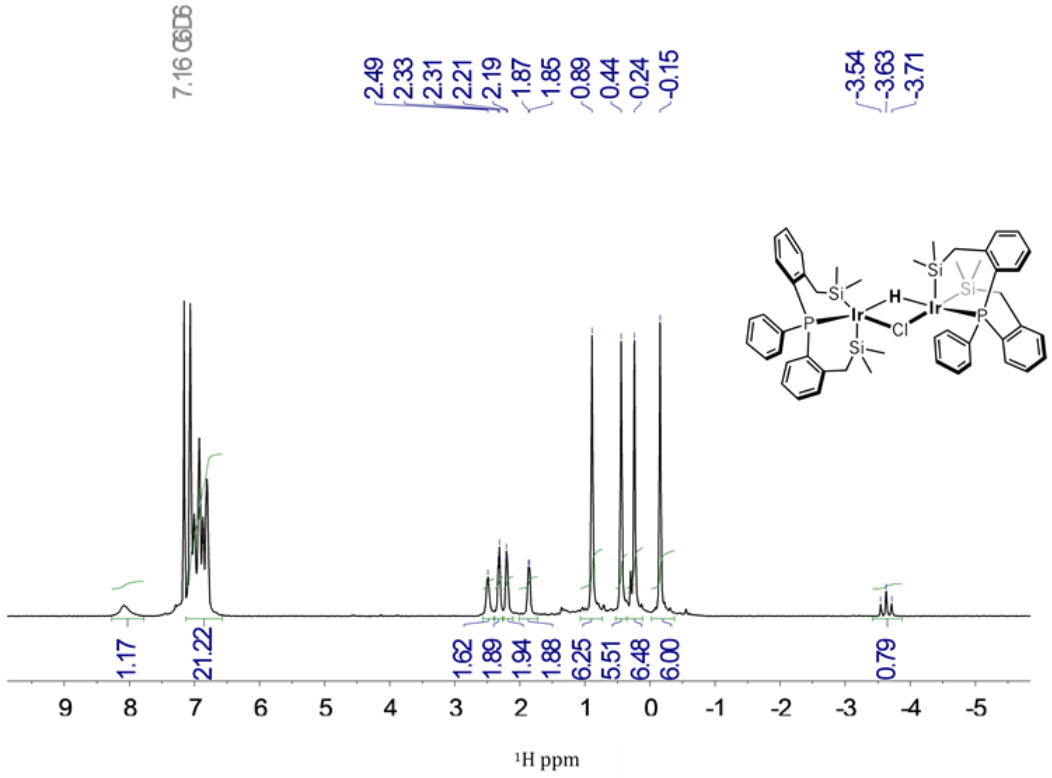


Figure S37. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of complex **8**.

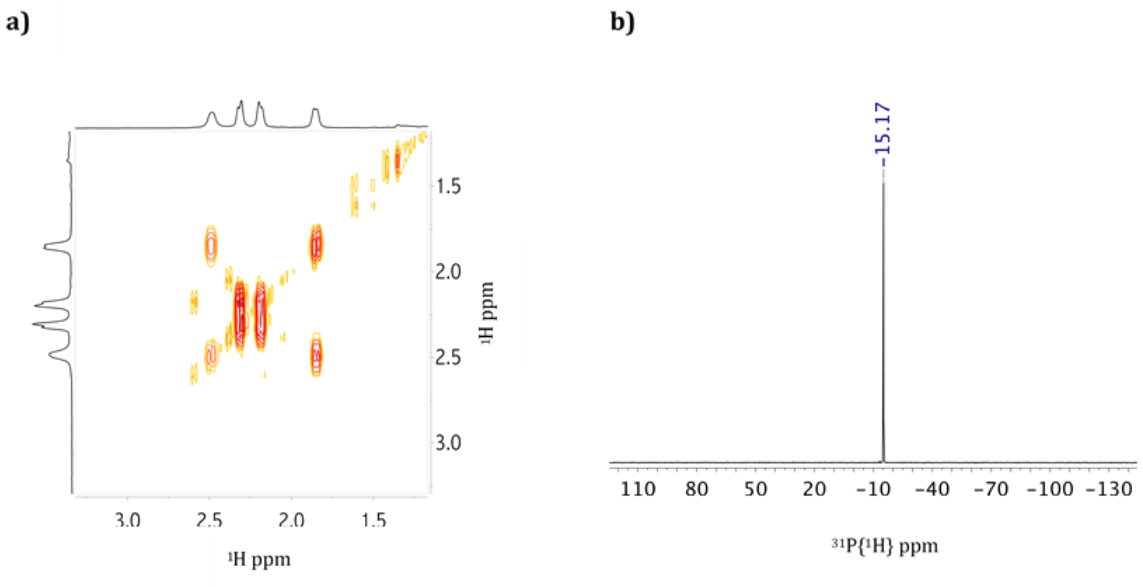


Figure S38. **a)** ^{1}H–^{1}H COSY in the region of 1.0 to 3.5 ppm and **b)** ^{31}P{^{1}H} NMR spectrum (243 MHz) of complex **8** in C_6D_6 at 298 K.

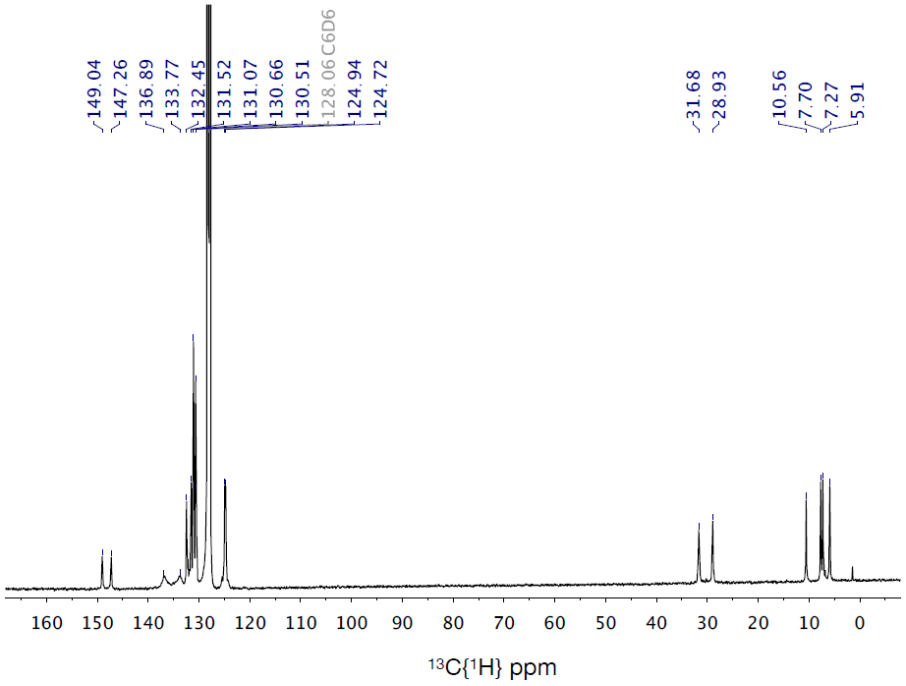


Figure S39. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, 298 K, C_6D_6) of complex **8.**

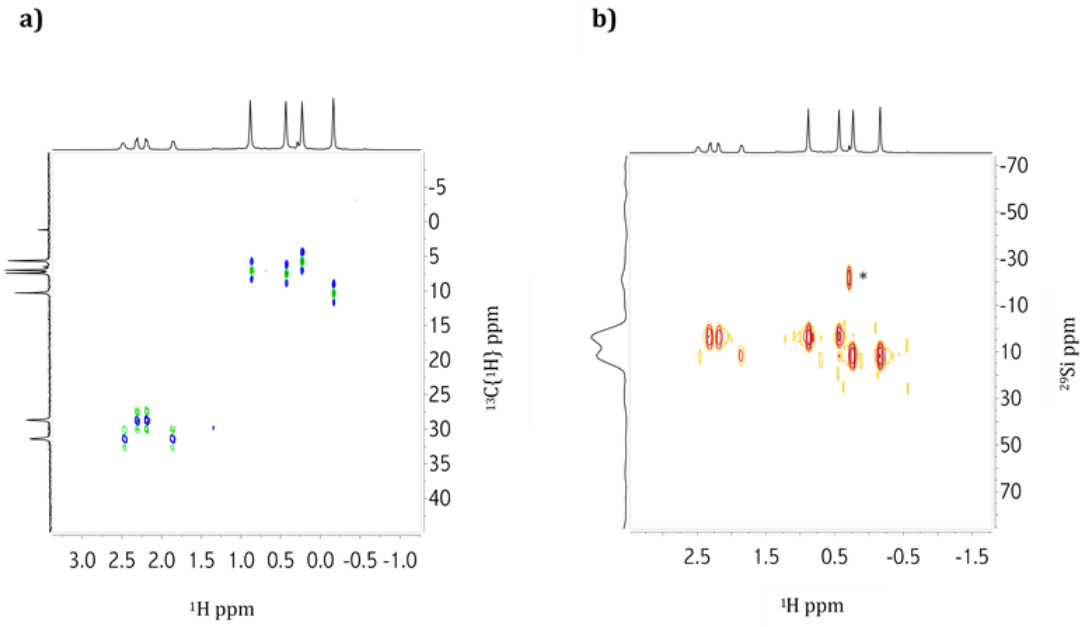


Figure S40. **a)** $^{1}H–^{13}C\{^{1}H\}$ HSQC of methyl and methylene region and **b)** $^{1}H–^{29}Si$ HMQC NMR spectra of complex **8** in C_6D_6 at 298 K. * grease.

1.7 Complex 9

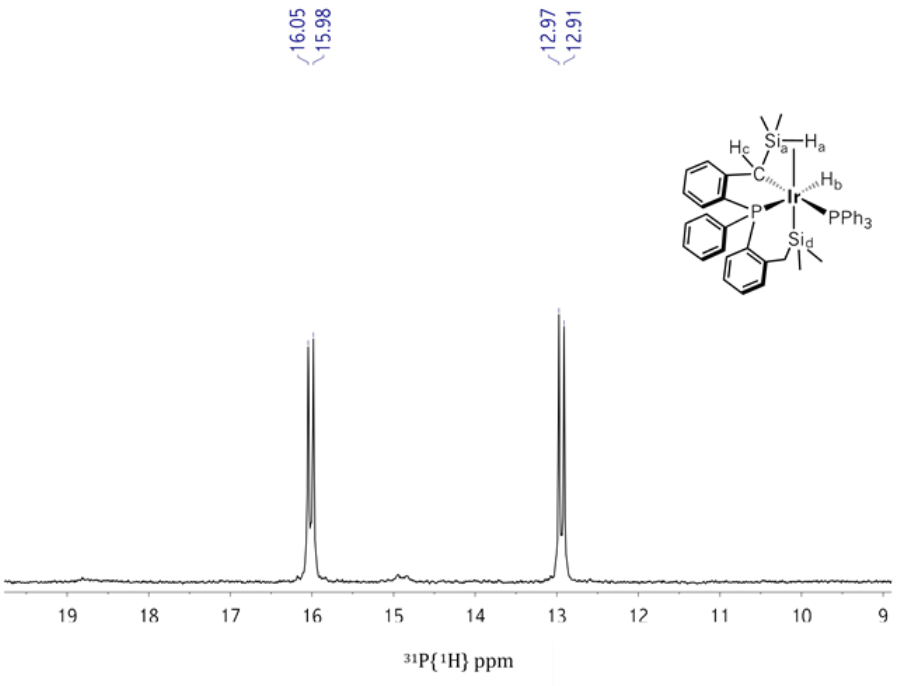


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz) of the reaction of **3** with $LiBHEt_3$ in C_6D_6 at 298 K leading to the NMR characterization of complex **9**.

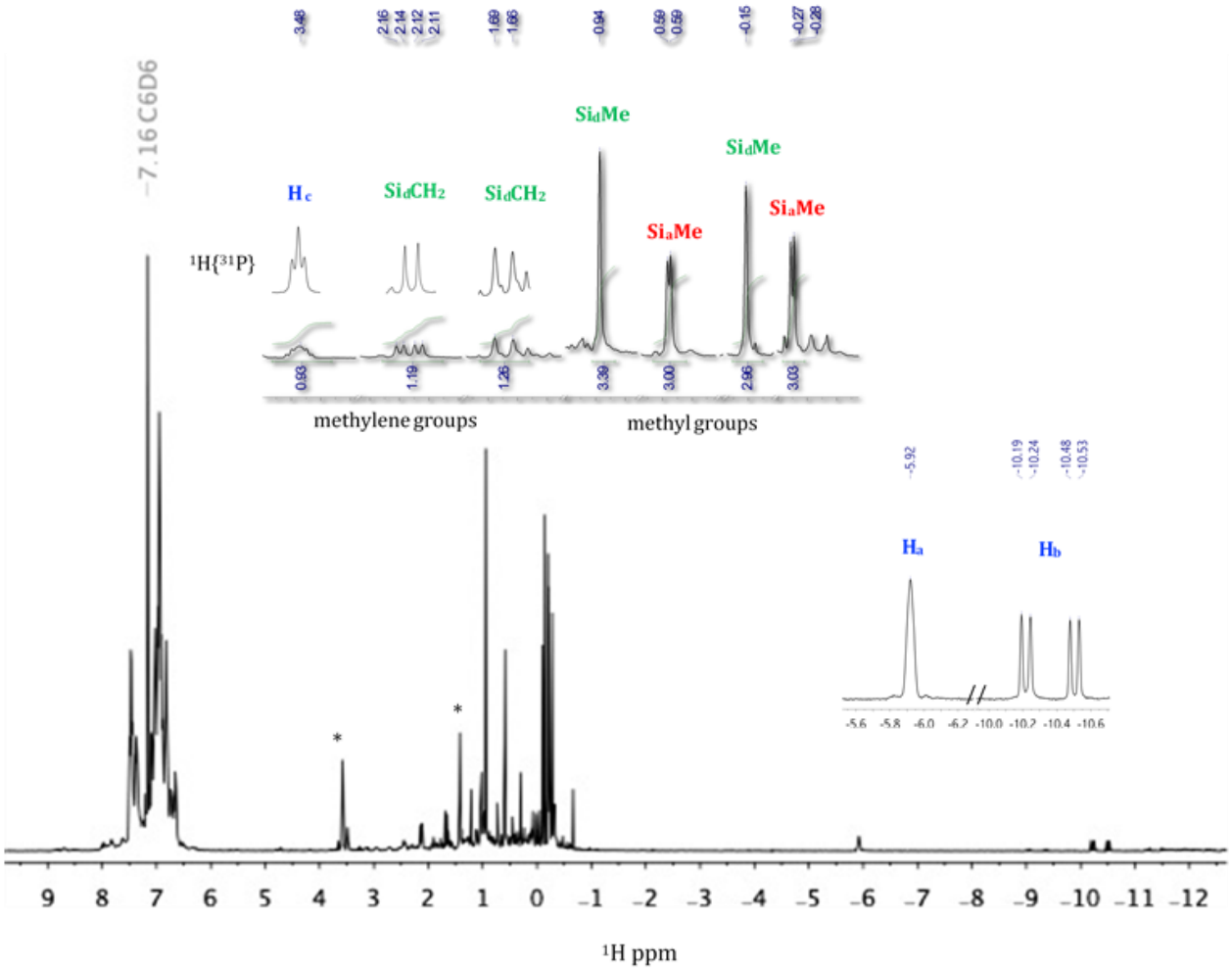


Figure S42. ^{1}H NMR spectrum (400 MHz) of the reaction of **3** with $LiBHEt_3$ in C_6D_6 at 298 K leading to the NMR characterization of complex **9**. * THF

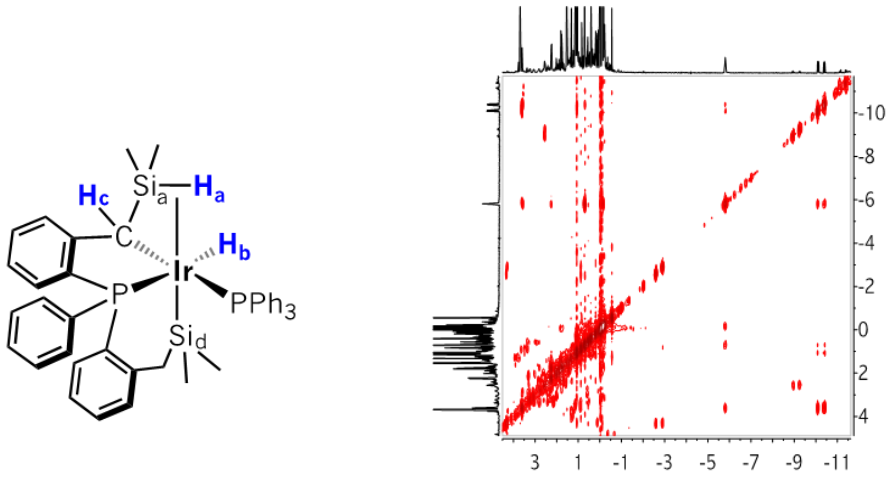


Figure S43. $^{1}H–^{1}H$ COSY NMR spectrum of the reaction of **3** with $LiBHEt_3$ in C_6D_6 at 298 K leading to the NMR characterization of complex **9**.

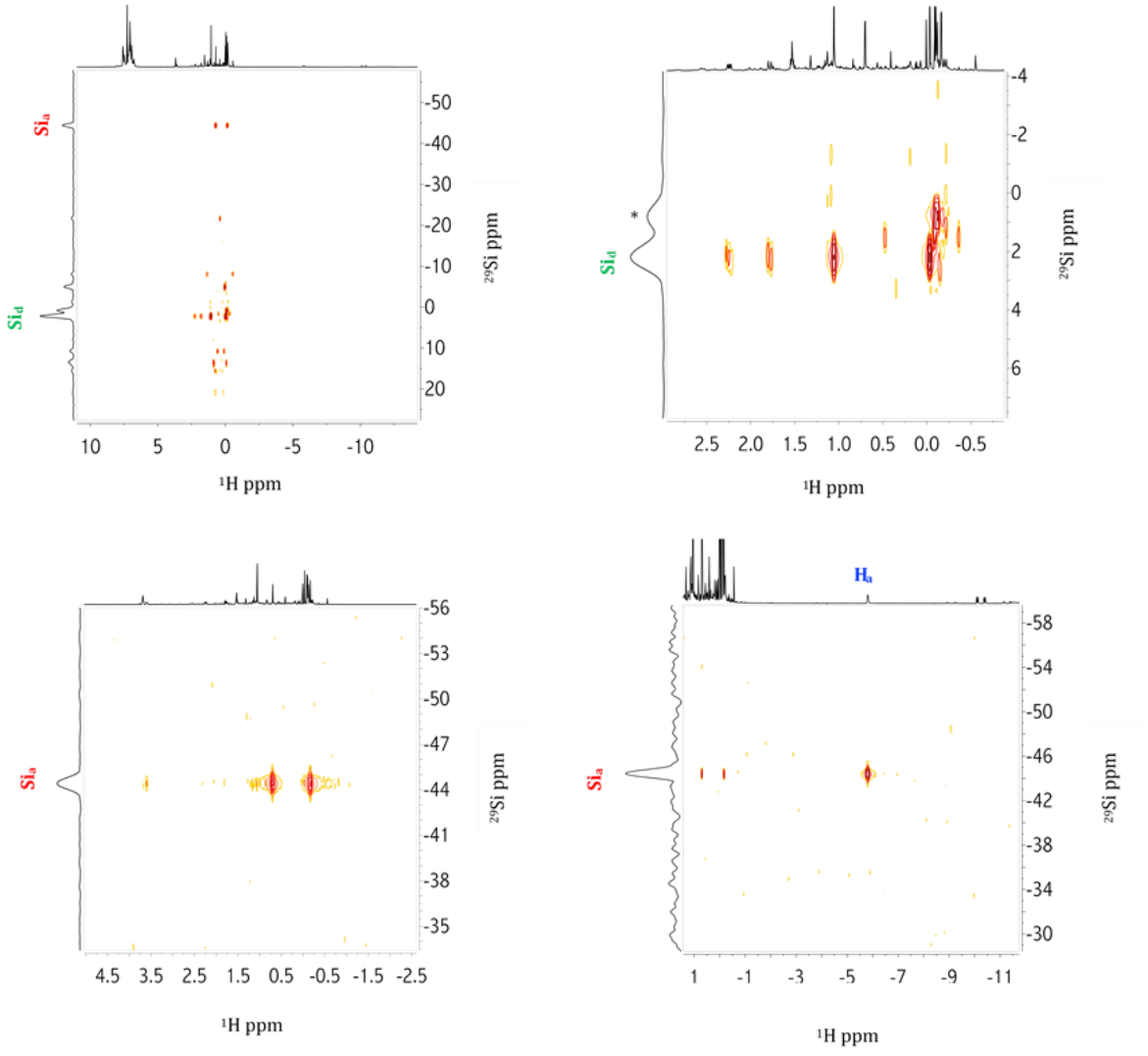


Figure S44. $^{1}H–^{29}Si$ HMQC NMR spectra of the reaction of **3** with $LiBHEt_3$ in C_6D_6 at 298 K leading to the NMR characterization of complex **9**. * grease

2. X-ray Data

X-ray data for complex 1

$C_{48}H_{58}Cl_2Ir_2P_2Si_4 \cdot C_6H_6$	$F(000)$ = 662
M_r = 1342.65	
Triclinic, P -1	D_x = 1.643 Mg m^{-3}
Hall symbol: -P 1	
a = 10.4849 (8) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 11.5765 (9) Å	Cell parameters from 9827 reflections
c = 12.4188 (9) Å	θ = 2.5–26.5°
α = 68.798 (2)°	μ = 5.18 mm^{-1}
β = 78.844 (2)°	T = 100 K
γ = 76.585 (3)°	Plate, yellow
V = 1356.98 (18) Å^3	0.15 × 0.1 × 0.02 mm
Z = 1	

Bruker Kappa APEX II diffractometer	5046 reflections with $I > 2\sigma(I)$
Radiation source: micro-source	R_{int} = 0.039
Graphite monochromator	θ_{max} = 26.4°, θ_{min} = 2.0°
ω–φ scans	h = −13 13
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	k = −11 14
T_{min} = 0.529, T_{max} = 0.754	l = −15 15
27827 measured reflections	Standard reflections: 0
5538 independent reflections	

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.020	H-atom parameters constrained
$wR(F^2)$ = 0.044	$w = 1/[\sigma^2(F_o^2) + 1.9163P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max}$ = 0.001
5538 reflections	$\Delta\rho_{max}$ = 0.93 e Å^{-3}

293 parameters	$\Delta\rho_{min}$ = −1.11 e Å^{-3}
0 restraints	Extinction correction: none

X-ray data for complex 2

M_r = 1036.67	D_x = 1.512 Mg m^{-3}
Monoclinic, $P2_1/c$	
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.171 (3) Å	Cell parameters from 9831 reflections
b = 15.591 (5) Å	θ = 2.3–30.5°
c = 28.733 (9) Å	μ = 3.19 mm^{-1}
β = 92.251 (8)°	T = 100 K
V = 4553 (2) Å^3	Parallelepiped, colourless
Z = 4	0.12 × 0.08 × 0.02 mm
F(000) = 2120	

Radiation source: Mo micro-source	R_{int} = 0.056
Graphite monochromator	θ_{max} = 29.9°, θ_{min} = 1.5°
ω–φ scans	h = −14 14
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	k = −21 21
T_{min} = 0.670, T_{max} = 0.746	l = −36 40
106334 measured reflections	Standard reflections: 0
13093 independent reflections	

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.027	H-atom parameters constrained
$wR(F^2)$ = 0.059	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 6.4502P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max}$ = 0.004
13093 reflections	$\Delta\rho_{max}$ = 1.75 e Å^{-3}
497 parameters	$\Delta\rho_{min}$ = −1.35 e Å^{-3}
0 restraints	Extinction correction: none

X-ray Data for complex 3

M_r = 1038.77	D_x = 1.514 Mg m^{-3}
Monoclinic, $P2_1/c$	

Hall symbol: -P 2ybc	Mo *Kα* radiation, λ = 0.71073 Å
a = 10.2493 (14) Å	Cell parameters from 9606 reflections
b = 22.784 (3) Å	θ = 2.3–30.6°
c = 19.998 (3) Å	μ = 3.15 mm^{-1}
β = 102.638 (3)°	*T* = 100 K
V = 4556.8 (11) $Å^3$	Block, orange
Z = 4	0.18 × 0.14 × 0.09 mm
F(000) = 2112	

Bruker Kappa APEX II diffractometer	8863 reflections with $I > 2\sigma(I)$
Radiation source: micro-source	R_{int} = 0.042
Graphite monochromator	θ_{max} = 26.4°, θ_{min} = 1.4°
ω–φ scans	*h* = −12 12
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	*k* = −28 28
T_{min} = 0.668, T_{max} = 0.746	*l* = −24 24
88526 measured reflections	Standard reflections: 0
9289 independent reflections	

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.021	H-atom parameters constrained
$wR(F^2)$ = 0.046	$w = 1/[\sigma^2(F_o^2) + 7.9453P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.18	$(\Delta/\sigma)_{max}$ = 0.007
9289 reflections	$\Delta\rho_{max}$ = 0.66 e $Å^{-3}$
527 parameters	$\Delta\rho_{min}$ = −0.75 e $Å^{-3}$
0 restraints	Extinction correction: none

X-ray Data for complex 4

$C_{42}H_{62}ClIrP_2Si_2 \cdot 2(CH_2Cl_2)$	
M_r = 1082.61	D_x = 1.446 Mg m^{-3}
Monoclinic, *C*2/*c*	

Hall symbol: -C 2yc	Mo *Kα* radiation, λ = 0.71073 Å
a = 46.882 (14) Å	Cell parameters from 9156 reflections
b = 10.431 (3) Å	θ = 2–30°
c = 22.858 (7) Å	μ = 3.10 mm^{-1}
β = 117.182 (6)°	*T* = 100 K
V = 9943 (5) $Å^3$	Plate, yellow
Z = 8	0.15 × 0.10 × 0.02 mm
F(000) = 4400	

Bruker Kappa Apex2 diffractometer	11555 reflections with $I > 2.0\sigma(I)$
Radiation source: Mo micro-source	R_{int} = 0.057
Graphite monochromator	θ_{max} = 30.0°, θ_{min} = 1.0°
φ & ω scans	*h* = −64 65
Absorption correction: multi-scan *SADABS* (Siemens, 1996)	*k* = −14 14
T_{min} = 0.76, T_{max} = 0.94	*l* = −31 31
141996 measured reflections	Standard reflections: 0
14265 independent reflections	

Refinement on *F*	
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.047	H-atom parameters not refined
$wR(F^2)$ = 0.052	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ⋯ + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 1.48 -0.824E-01 0.970
S = 1.15	$(\Delta/\sigma)_{max}$ = 0.004
11555 reflections	$\Delta\rho_{max}$ = 5.59 e $Å^{-3}$
496 parameters	$\Delta\rho_{min}$ = −3.19 e $Å^{-3}$
0 restraints	Extinction correction: None

X-ray Data for complex 5a

$C_{28}H_{35}ClIrN_2PSi_2 \cdot 2(C_2H_3N)$	
M_r = 796.52	D_x = 1.513 Mg m^{-3}
Monoclinic, $P2_1/n$	

Hall symbol: -P 2yn	Mo *Kα* radiation, λ = 0.71073 Å
a = 14.0609 (6) Å	Cell parameters from 9908 reflections
b = 9.4670 (4) Å	θ = 2–26°
c = 27.1645 (11) Å	μ = 4.04 mm^{-1}
β = 104.790 (1)°	*T* = 100 K
V = 3496.2 (3) $Å^3$	Plate, yellow
Z = 4	0.15 × 0.10 × 0.03 mm
F(000) = 1591.991	

Bruker Kappa Apex2 diffractometer	6137 reflections with $I > 2.0\sigma(I)$
Radiation source: ?	R_{int} = 0.063
Graphite monochromator	θ_{max} = 26.4°, θ_{min} = 1.6°
φ & ω scans	*h* = −17 16
Absorption correction: multi-scan *SADABS* (Siemens, 1996)	*k* = −11 11
T_{min} = 0.73, T_{max} = 0.89	*l* = −30 33
61092 measured reflections	Standard reflections: 0
7152 independent reflections	

Refinement on *F*	
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.024	H-atom parameters not refined
$wR(F^2)$ = 0.024	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ⋯ + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.203 0.522E-01 0.937E-01
S = 1.10	$(\Delta/\sigma)_{max}$ = 0.002
5830 reflections	$\Delta\rho_{max}$ = 0.69 e $Å^{-3}$
370 parameters	$\Delta\rho_{min}$ = −0.48 e $Å^{-3}$
0 restraints	Extinction correction: None

X-ray Data for complex 7b

$C_{26}H_{29}ClIrO_2PSi_2$	*F*(000) = 676

M_r = 688.33	
Triclinic, *P*-1	D_x = 1.728 Mg m^{-3}
Hall symbol: -P 1	
a = 9.7364 (12) Å	Mo *K*α radiation, λ = 0.71073 Å
b = 9.9162 (14) Å	Cell parameters from 9757 reflections
c = 14.706 (2) Å	θ = 2–26°
α = 82.877 (5)°	μ = 5.32 mm^{-1}
β = 72.789 (4)°	*T* = 293 K
γ = 77.865 (4)°	Needle, colourless
V = 1323.0 (3) Å^3	0.20 × 0.03 × 0.02 mm
Z = 2	

Bruker Kappa Apex2 diffractometer	4978 reflections with $I > 2.0\sigma(I)$
Radiation source: Mo micro-source	R_{int} = 0.061
Graphite monochromator	θ_{max} = 26.5°, θ_{min} = 1.5°
φ & ω scans	*h* = −12 12
Absorption correction: multi-scan *SADABS* (Siemens, 1996)	*k* = −12 12
T_{min} = 0.68, T_{max} = 0.90	*l* = −18 18
54275 measured reflections	Standard reflections: 0
5457 independent reflections	

Refinement on *F*	
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.026	H-atom parameters not refined
$wR(F^2)$ = 0.028	Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ⋯ + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (Prince, 1982) W = [weight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 1.46 -0.668 0.987
S = 1.09	$(\Delta/\sigma)_{max}$ = 0.002
4865 reflections	$\Delta\rho_{max}$ = 2.36 e Å^{-3}
298 parameters	$\Delta\rho_{min}$ = −0.78 e Å^{-3}
0 restraints	Extinction correction: None

X-ray Data for complex 8

$C_{48}H_{59}ClIr_2P_2Si_4 \cdot 2(C_6H_6)$	$F(000)$ = 1376
M_r = 1386.31	
Triclinic, P -1	D_x = 1.64 Mg m^{-3}
Hall symbol: -P 1	
a = 12.2965 (6) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 12.8675 (6) Å	Cell parameters from 9239 reflections
c = 18.4988 (9) Å	θ = 2.6–28.3°
α = 84.086 (1)°	μ = 4.96 mm^{-1}
β = 87.716 (1)°	T = 100 K
γ = 74.647 (1)°	Parallelepiped, yellow
V = 2807.3 (2) Å^3	0.08 × 0.05 × 0.02 mm
Z = 2	

Radiation source: ?	R_{int} = 0.038
Graphite monochromator	θ_{max} = 28.3°, θ_{min} = 2.9°
ω–φ scans	h = −16 16
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	k = −17 17
T_{min} = 0.654, T_{max} = 0.746	l = −24 24
62177 measured reflections	Standard reflections: 0
13948 independent reflections	

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.016	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.006P)^2 + 1.8867P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ = 0.007
13948 reflections	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
634 parameters	$\Delta\rho_{min}$ = −0.38 e Å^{-3}
0 restraints	Extinction correction: none