

Supporting Information

Fischer carbene complexes of iridium(I) for application in catalytic transfer hydrogenation.

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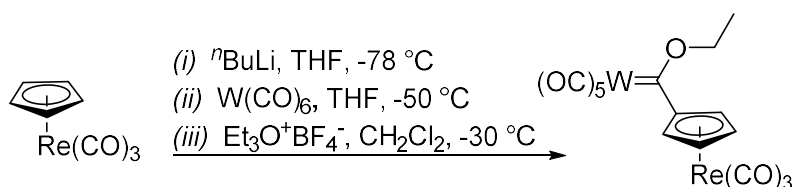
S1. Experimental

S1.1 Measurement and Methods

General procedures. The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry, oxygen-free N₂ or Ar gas using standard Schlenk techniques. All reactions were mechanically stirred and monitored by IR spectroscopy where relevant. The precursors [W(CO)₅{C(OEt)Ar}] [Ar = *p*-DMA, Fc, Cp'Re(CO)₃] and [Ir(cod)Cl]₂ were prepared according to literature procedures.^{1,2,3} Aluminum oxide 60 (particle size 0.05 – 0.15 mm) was used as resin for all column chromatography separations. Anhydrous tetrahydrofuran (THF), diethyl ether (Et₂O), and *n*-hexane were distilled over sodium metal and dichloromethane (DCM) was distilled over CaH₂. All other reagents are commercially available and were used as received.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance-III-300, Bruker Avance-III-400 and Bruker Avance-III-500 spectrometers using CDCl₃, CD₂Cl₂, and C₆D₆ as solvents at 25 °C. The NMR spectra were recorded for ¹H at 300.13, 400.13 and 500.13 MHz, and for ¹³C at 100.63 and 125.78 MHz. 2D NMR techniques (COSY, HSQC) were employed to assign signals that were otherwise ambiguous. Infrared spectroscopy was performed on a PerkinElmer Spectrum FT-IR spectrophotometer over the range 4000 – 1400 cm⁻¹. Solution IR spectra were recorded in CH₂Cl₂ using a NaCl cell with a path length of ca. 1.0 mm. Melting points were measured with a Stuart SMP10 melting point apparatus. Mass spectral analyses were performed on a Bruker Compact Q-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) with a positive electron spray as the ionization technique by direct infusion at 0.3 mL min⁻¹. The *m/z* values were measured in the range of 50 – 1000 in acetonitrile. Prior to analysis, the instrument was calibrated with sodium formate (5 mM) in resolution mode. Elemental analyses were carried out using an Elementar varioELcube CHNS-O analyser.

S1.2. Synthesis and characterization



Scheme S1. Synthesis of precursor [W(CO)₅{C(OEt)(Cp'Re(CO)₃)}] via the traditional Fischer route

Synthesis of [W(CO)₅{C(OEt)(Cp'Re(CO)₃)}]

The methoxy- analogue of this complex has been previously reported.^{4,5} *n*BuLi (3.30 mmol, 2.2 mL) was slowly added to a solution of Cp'Re(CO)₃ (3.00 mmol, 1.006 g) in THF and stirred at -78 °C for 2 hours. The reaction was warmed up to -50 °C, at which point W(CO)₆ was added in one portion and stirred for 1 hour while slowly warming to room temperature. The THF solvent was removed *in vacuo* and the resulting residue dissolved in DCM (30 mL) and cooled down to -30 °C. A DCM solution of Et₃O⁺BF₄⁻ (3.00 mmol, 0.570 g in 10 mL) was then slowly added at -30 °C and stirred for 1 hour while warming to room temperature. The resulting dark-red solution was reduced *in vacuo* and added to a silica chromatography column. Elution with *n*-hexane gave the only red band, which was collected and reduced under vacuum to give bright-red crystals. Yield = 1.200 g, 56%. ¹H NMR (300 MHz, C₆D₆) δ 5.37 (m, 2H, ReCp'-H_{α,α'}), 4.38 (q, ³J(HH) = 7.0 Hz, 2H, OCH₂CH₃), 4.28 (m, 2H, ReCp'-H_{β,β'}), 0.96 (t, ³J(HH) = 7.0 Hz, 3H, OCH₂CH₃). ¹³C{¹H} NMR (75 MHz, C₆D₆) δ 296.5 (C_{carbene}), 201.9 (W-CO_{trans}), 197.4 (W-CO_{cis}), 192.1 (Re{CO}₃), 113.1 (ReCp'-C_{ipso}), 90.1 (ReCp'-C_{α,α'}), 85.6 (ReCp'-C_{β,β'}), 78.9 (OCH₂CH₃),

Synthesis of iridium(I) carbene complexes **1 - 8**

[Ir(cod)Cl{C(OEt)*p*-DMA}], **1**. A mixture of [W(CO)₅{C(OEt)*p*-DMA}] (0.200 g, 0.40 mmol) and [Ir(cod)Cl]₂ (0.120 g, 0.20 mmol) in deoxygenated CH₂Cl₂ was stirred for 24 hours at -78 °C while slowly warming to room temperature (18 °C). The resulting dark-brown solution was reduced *in vacuo* and added to an alumina chromatography column. Elution with CH₂Cl₂ gave an orange band, which was collected and reduced under vacuum. Slow diffusion of *n*-hexane (3 mL) into the concentrated CH₂Cl₂ solution (2 mL) resulted in orange crystals. Yield = 0.186 g, 91%. Mp (dec): 149 – 151 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.36 (d, ³J(HH) = 8.8 Hz, 2H, DMA-H_{α,α'}), 6.65 (d, ³J(HH) = 9.4 Hz, 2H, DMA-H_{β,β'}), 5.67 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.2 Hz, 1H, OCH₂CH₃), 5.39 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.1 Hz, 1H, OCH₂CH₃), 4.90 – 4.86 (m, 1H, cod-CH), 4.78 – 4.74 (m, 1H, cod-CH), 3.07 (s, 6H, N(CH₃)₂), 2.99 – 2.97 (m, 1H, cod-CH), 2.92 – 2.91 (m, 1H, cod-CH), 2.41 – 2.18 (m, 4H, cod-CH₂), 2.00 – 1.78 (m, 4H, cod-CH₂), 1.60 (t, ³J(HH) = 7.1 Hz, 3H, OCH₂CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 276.7 (C_{carbene}), 154.8 (C_q), 135.7 (C_{ipso}), n.o. (DMA-C_{α,α'}), 111.1 (DMA-C_{β,β'}), 92.9 (cod-CH), 92.6 (cod-CH), 76.0 (OCH₂CH₃), 58.0 (cod-CH), 52.7 (cod-CH), 40.5 (N(CH₃)₂), 34.1 (cod-CH₂), 33.6 (cod-CH₂), 29.2 (cod-CH₂), 29.0 (cod-CH₂), 15.7 (OCH₂CH₃). Anal. Calcd for C₁₉H₂₇ONClIr: C 44.48, H 5.30, N 2.73. Found: C 44.64, H 5.20, N 2.75. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 478.1722; found 478.1588.

[Ir(cod)Cl{C(OEt)Fc}], **2**. This complex was similarly prepared from [W(CO)₅Cl{C(OEt)Fc}] (0.566 g, 1.00 mmol) and [Ir(cod)Cl]₂ (0.300 g, 0.50 mmol). The resulting red oil was dissolved in CH₂Cl₂ (2 mL) and treated with *n*-hexane (5 mL) at -30 °C to precipitate a red crystalline solid. Yield = 0.445 g, 77%. Mp: 115 – 117 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ 5.71 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.2 Hz, 1H, OCH₂CH₃), 5.32 (s, br, 1H, FeCp'), 5.25 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.1 Hz, 1H, OCH₂CH₃), 4.93 – 4.89 (m, 1H, cod-CH), 4.86 (s, br, 1H, FeCp'), 4.79 – 4.76 (m, 2H, cod-CH, FeCp'), 4.64 (s, br, 1H, FeCp'), 4.42 (s, 5H, FeCp), 3.04 – 3.01 (m, 1H, cod-CH), 2.95 – 2.91 (m, 1H, cod-CH), 2.43 – 2.04 (m, 5H, cod-CH₂), 1.88 – 1.80 (m, 3H, cod-CH₂), 1.61 (t, ³J(HH) = 7.2 Hz, 3H, OCH₂CH₃). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂) δ 286.6 (C_{carbene}), 94.3 (cod-CH), 94.1 (cod-CH), 90.3 (FeCp'-C_{ipso}), 77.2 (OCH₂CH₃), 75.4 (FeCp'), 74.8 (FeCp'), 73.7 (FeCp'), n.o. (FeCp'), 70.4 (FeCp), 59.2 (cod-CH), 52.9 (cod-CH), 34.3 (cod-CH₂), 33.5 (cod-CH₂), 29.2 (cod-CH₂), 28.7 (cod-CH₂), 15.8 (OCH₂CH₃). Anal. Calcd for C₂₁H₂₆OClFeIr: C 43.64, H 4.53. Found: C 44.00, H 4.46. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 543.0962; found 543.0967.

[Ir(cod)Cl{C(OEt)(Cp'Re(CO)₃)}], **3**. In like manner, complex **3** was synthesized from [W(CO)₅{C(OEt)(Cp'Re(CO)₃)}] (0.200 g, 0.28 mmol) and [Ir(cod)Cl]₂ (0.084 g, 0.14 mmol). The resulting orange oil was dissolved in CH₂Cl₂ (1 mL) and treated with *n*-hexane (3 mL) to precipitate an orange crystalline solid. Yield = 0.152 g, 75%. Mp: 112 – 114 °C. ¹H NMR (300 MHz, CD₂Cl₂) δ 6.20 – 6.17 (m, 2H, ReCp'-H_{α,α'}), 5.61 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.2 Hz, 1H, OCH₂CH₃), 5.53 (dt, ³J(HH) = 2.8 Hz, ⁴J(HH) = 1.8 Hz, 1H, ReCp'-H_{β,β'}), 5.47 (dt, ³J(HH) = 2.8 Hz, ⁴J(HH) = 1.8 Hz, 1H, ReCp'-H_{β,β'}), 5.25 (dq, ²J(HH) = 10.4 Hz, ³J(HH) = 7.1 Hz, 1H, OCH₂CH₃), 5.16 – 5.09 (m, 1H, cod-CH), 5.00 – 4.93 (m, 1H, cod-CH), 3.14 – 3.08 (m, 1H, cod-CH), 2.99 – 2.93 (m, 1H, cod-CH), 2.47 – 1.83 (m, 8H, cod-CH₂), 1.54 (t, ³J(HH) = 7.1 Hz, 3H, OCH₂CH₃). ¹³C NMR (126 MHz, CD₂Cl₂) δ 275.1 (C_{carbene}), 192.6 (Re(CO)₃), 108.5 (ReCp'-C_{ipso}), 98.6 (cod-CH), 98.0 (cod-CH), 91.4 (ReCp'), 90.1 (ReCp'), 87.4 (ReCp'), 85.9 (ReCp'), 78.1 (OCH₂CH₃), 61.3 (cod-CH), 55.1 (cod-CH), 34.1 (cod-CH₂), 33.1 (cod-CH₂), 29.6 (cod-CH₂), 28.1 (cod-CH₂), 15.5 (OCH₂CH₃). IR (CH₂Cl₂, ν(CO), cm⁻¹): 1937 (w), 2031 (s). Anal. Calcd for C₁₉H₂₁O₄ClReIr: C 31.38, H 2.91. Found: C 31.87, H 2.76. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 693.0627; found 693.0616.

[Ir(cod)Cl{C(NHⁿPr)*p*-DMA}], **4**. ⁿPrNH₂ was slowly added to a brown-orange solution of **1** (0.100 g, 0.20 mmol) in THF at room temperature and the colour immediately changed to yellow. The THF solvent was removed *in vacuo*. The resulting yellow paste was washed with *n*-hexane (2 x 5 mL) and cannula-

extracted with CH₂Cl₂ to give a yellow-lime powder after drying. Yellow crystals were obtained by slow diffusion of *n*-hexane (2 mL) into a concentrated CH₂Cl₂ solution of the powder. Yield = 0.099 g, 94%. Mp (dec): 150 – 153 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.51 (s, br, 1H, NHCH₂CH₂CH₃), 7.90 (d, ³J(HH) = 9.0 Hz, 2H, DMA-H_{α,α'}), 6.69 (d, ³J(HH) = 9.0 Hz, 2H, DMA-H_{β,β'}), 4.56 – 4.49 (m, 2H, cod-CH), 4.36 – 4.20 (m, 2H, NHCH₂CH₂CH₃), 3.03 (s, 6H, N(CH₃)₂), 2.94 – 2.90 (m, 1H, cod-CH), 2.81 – 2.76 (m, 1H, cod-CH), 2.28 – 2.14 (m, 4H, cod-CH₂), 1.92 – 1.55 (m, 6H, cod-CH₂, NHCH₂CH₂CH₃), 1.07 (t, ³J(HH) = 7.2 Hz, 3H, NHCH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 240.3 (C_{carbene}), 153.1 (C_q), 132.5 (C_{ipso}), 130.4 (DMA-C_{α,α'}), 111.5 (DMA-C_{β,β'}), 86.1 (cod-CH), 85.4 (cod-CH), 55.7 (cod-CH), 54.9 (NHCH₂CH₂CH₃), 52.6 (cod-CH), 40.4 (N(CH₃)₂), 33.9 (cod-CH₂), 33.6 (cod-CH₂), 29.8 (cod-CH₂), 29.5 (cod-CH₂), 23.5 (NHCH₂CH₂CH₃), 11.9 (NHCH₂CH₂CH₃). IR (CH₂Cl₂, ν(NH), cm⁻¹): 3332. Anal. Calcd for C₂₀H₃₀N₂ClIr: C 45.66, H 5.75, N 5.32. Found: C 45.72, H 5.53, N 6.24. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 491.2038; found 491.1966.

The aminocarbene complexes; [Ir(cod)Cl{C(NH^{*n*}Pr)Fc}], **5** and [Ir(cod)Cl{C(NH(CH₂CH₂)NMe₂)Fc}], **6** were also prepared.

[Ir(cod)Cl{C(NH^{*n*}Pr)Fc}], **5**. Excess ^{*n*}PrNH₂ was added to a dark red solution of **2** (0.090 g, 0.16 mmol) in THF and stirred at 60 °C for 5 hours. The THF solvent was then evaporated to dryness, resulting in a red-orange paste. Washing with *n*-hexane (3 x 5 mL) and subsequent CH₂Cl₂ cannula-extraction resulted in a red-orange powder after the CH₂Cl₂ solvent was removed in *vacuo*. Yield = 0.082 g, 86%. Mp (dec): 171 – 173 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, br, 1H, NHCH₂CH₂CH₃), 5.16 (s, br, 1H, FeCp'), 4.71 – 4.67 (m, 1H, cod-CH), 4.66 (s, br, 1H, FeCp'), 4.59 – 4.56 (m, 1H, cod-CH), 4.54 (s, br, 1H, FeCp'), 4.45 (s, br, 1H, FeCp'), 4.35 – 4.27 (m, 1H, NHCH₂CH₂CH₃), 4.31 (s, 5H, FeCp), 4.13 – 4.05 (m, 1H, NHCH₂CH₂CH₃), 3.00 – 2.96 (m, 1H, cod-CH), 2.93 – 2.90 (m, 1H, cod-CH), 2.37 – 2.09 (m, 4H, cod-CH₂) 1.97 – 1.56 (m, 6H, cod-CH₂, NHCH₂CH₂CH₃), 1.10 (t, ³J(HH) = 7.4 Hz, 3H, NHCH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 245.4 (C_{carbene}), 86.4 (cod-CH), 86.4 (cod-CH), 85.7 (FeCp'-C_{ipso}), 73.1 (FeCp'), 72.2 (FeCp'), 71.3 (FeCp'), 70.1 (FeCp), 67.3 (FeCp'), 55.6 (cod-CH), 55.0 (cod-CH), 52.8 (NHCH₂CH₂CH₃), 34.2 (cod-CH₂), 32.8 (cod-CH₂), 28.6 (cod-CH₂), 28.9 (cod-CH₂), 23.3 (NHCH₂CH₂CH₃), 11.6 (NHCH₂CH₂CH₃). IR (CH₂Cl₂, ν(NH), cm⁻¹): 3332. Anal. Calcd for C₂₂H₂₉NCIFeIr: C 44.71, H 4.95, N 2.37. Found: C 44.82, H 4.92, N 2.46. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 556.1279; found 556.1201.

[Ir(cod)Cl{C(NH(CH₂CH₂)NMe₂)Fc}], **6**. This complex was prepared similarly to **5** using excess NH₂(CH₂CH₂)NMe₂ and **2** (0.100 g, 0.17 mmol) resulting in a yellow-orange powder. Yield = 0.082 g, 86%. Mp : 109 – 110 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.13 (s, br, 1H, NHCH₂CH₂(CH₃)₂), 5.16 (s, br, 1H, FeCp'), 4.68 – 4.59 (m, 2H, cod-CH, NHCH₂CH₂(CH₃)₂), 4.64 (s, br, 1H, FeCp'), 4.53 (s, vbr, 2H, cod-CH, FeCp'), 4.43 (s, br, 1H, FeCp'), 4.32 (s, 5H, FeCp), 3.93 – 3.89 (m, 1H, NHCH₂CH₂(CH₃)₂), 2.94 – 2.88 (m, 2H, NHCH₂CH₂(CH₃)₂), 2.84 – 2.79 (m, 1H, cod-CH), 2.70 – 2.65 (m, 1H, cod-CH), 2.38 (s, 6H, NHCH₂CH₂(CH₃)₂), 2.29 – 2.09 (m, 4H, cod-CH₂), 1.91 – 1.88 (m, 1H, cod-CH₂), 1.72 – 1.59 (m, 3H, cod-CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 245.5 (C_{carbene}), 86.6 (cod-CH), 86.5 (cod-CH), 86.1 (FeCp'-C_{ipso}), 73.4 (FeCp'), 72.1 (FeCp'), 71.0 (FeCp'), 70.1 (FeCp), 67.6 (FeCp'), 58.3 (NHCH₂CH₂(CH₃)₂), 55.4 (cod-CH), 52.5 (cod-CH), 49.1 (NHCH₂CH₂N(CH₃)₂), 45.5 (NHCH₂CH₂N(CH₃)₂), 34.2 (cod-CH₂), 32.9 (cod-CH₂), 29.6 (cod-CH₂), 28.9 (cod-CH₂). IR (CH₂Cl₂, ν(NH), cm⁻¹): 3288. Anal. Calcd for C₂₃H₃₂N₂ClFeIr: C 44.55, H 5.20, N 4.52. Found: C 44.01, H 5.30, N 4.56. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl]⁺ 585.1544; found 585.1405.

[Ir(CO)₂Cl{C(OEt)Fc}], **7**. Carbon monoxide gas was bubbled for 5 minutes through a stirred solution of **2** (0.100 g, 0.17 mmol) in CH₂Cl₂ (10 mL) at room temperature. An immediate colour change from dark-red to dark-purple was observed. The flow of CO was stopped, and black crystals were grown by slow

diffusion of *n*-hexane (2 mL) into the concentrated CH₂Cl₂ reaction mixture at -30 °C. Yield = 0.085 g 93%. Mp: 103 – 104 °C. ¹H NMR (400 MHz, C₆D₆) δ 5.11 – 5.08 (m, br, 2H, FeCp¹-H_{α,α'}), 4.96 (q, br, ³J(HH) = 8.4 Hz, 2H, OCH₂CH₃), 4.39 (d, br, ³J(HH) = 7.2 Hz, 2H, FeCp¹-H_{β,β'}), 4.18 (s, 5H, FeCp), 1.07 (t, ³J(HH) = 7.1 Hz, 3H, OCH₂CH₃). ¹³C{¹H} NMR (101 MHz, C₆D₆) δ 277.4 (C_{carbene}), 184.1 (CO_{trans}), 170.1 (CO_{cis}), 87.6 (C_{ipso}), 79.9 (OCH₂CH₃, FeCp¹-C_{α,α'}), 77.5 (FeCp¹-C_{β,β'}), 71.6 (FeCp), 14.6 (OCH₂CH₃). IR (CH₂Cl₂, ν(CO), cm⁻¹): 1989, 2069. Anal. Calcd for C₁₅H₁₄O₃ClFeIr: C 34.27, H 2.68. Found: C 34.10, H 2.66. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl] 490.9922, [M – Cl – CO]⁺ 462.9973; found [M – Cl] 490.9924, [M – Cl – CO]⁺ 462.9975.

[Ir(CO)₂Cl{C(NH^{*n*}Pr)Fc}], **8**. Carbon monoxide gas was bubbled for 10 minutes through a stirred solution of **5** (0.100 g, 0.17 mmol) in CH₂Cl₂ (15 mL) at room temperature. The flow of CO was stopped, and the CH₂Cl₂ solvent was removed under vacuum. The resulting orange-red paste was washed with *n*-hexane (3 x 10 mL) and cannula-extracted with CH₂Cl₂. Dark-red crystals were grown by slow diffusion of *n*-hexane (2 mL) into the concentrated CH₂Cl₂ solution at -30 °C. Yield = 0.085 g, 93%. Mp (dec): 173 – 175 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.79 (s, br, 1H, NHCH₂CH₂CH₃), 5.05 (s, vbr, 1H, FeCp¹-H_{α,α'}), 4.93 (s, vbr, 1H, FeCp¹-H_{α,α'}), 4.67 (s, 2H, FeCp¹-H_{β,β'}), 4.35 (s, 5H, FeCp), 4.14 (s, vbr, 1H, NHCH₂CH₂CH₃), 3.75 (s, vbr, 1H, NHCH₂CH₂CH₃), 1.79 (q, br, ³J(HH) = 7.4 Hz, 2H, NHCH₂CH₂CH₃), 1.04 (t, ³J(HH) = 7.3 Hz, 3H, NHCH₂CH₂CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 232.6 (C_{carbene}), 182.7 (CO_{trans}), 169.6 (CO_{cis}), 83.9 (C_{ipso}), n.o (FeCp¹-C_{α,α'}), 73.7 (FeCp¹-C_{β,β'}), 70.6 (FeCp), 56.2 (NHCH₂CH₂CH₃), 22.7 (NHCH₂CH₂CH₃), 11.3 (NHCH₂CH₂CH₃). IR (CH₂Cl₂, ν(CO) and ν(NH), cm⁻¹): 1980, 2063, 3323. Anal. Calcd for C₁₆H₁₇O₂NCIFeIr: C 35.67, H 3.18, N 2.60. Found: C 36.62, H 3.01, N 3.73. ESI-MS (15 V, positive mode, *m/z*): calcd for [M – Cl] 504.0238, [M – Cl – CO]⁺ 476.0289; found [M – Cl] 504.0235, [M – Cl – CO]⁺ 476.0235.

S2. NMR and IR spectra of complexes

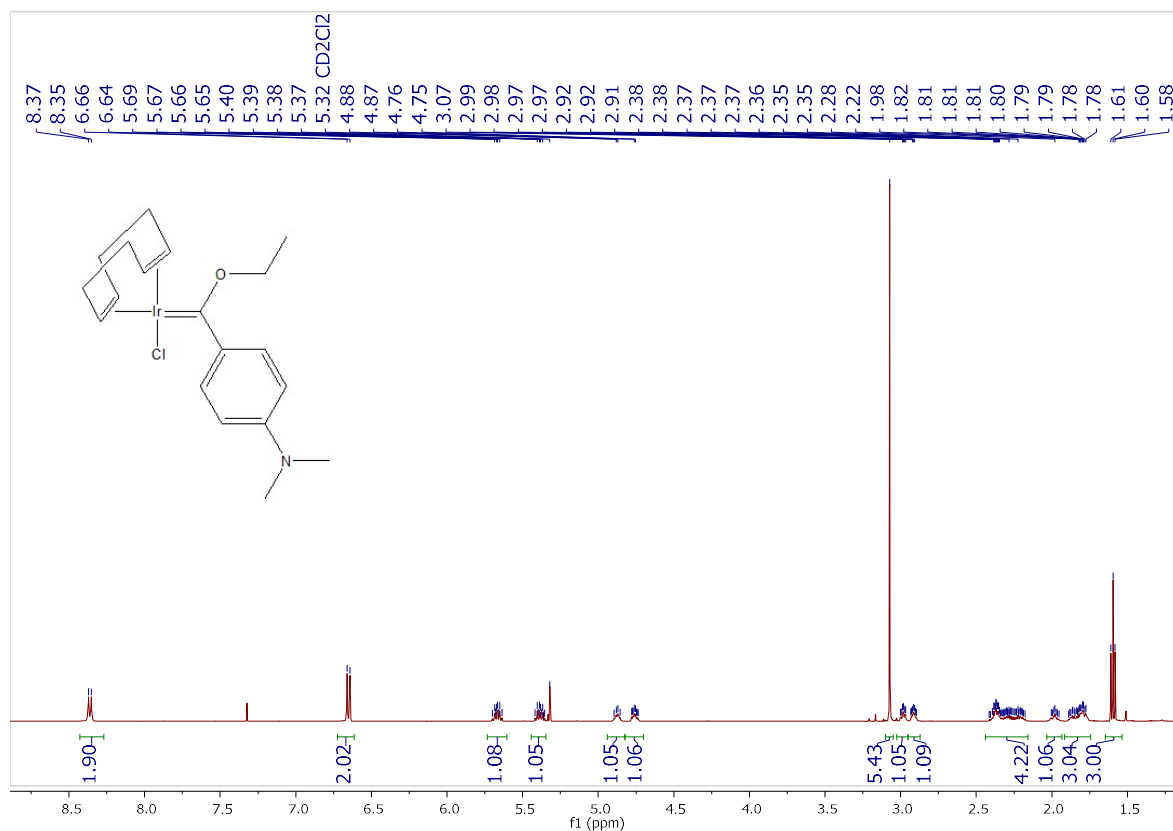


Figure S3. ^1H NMR spectrum of **1** in CD_2Cl_2

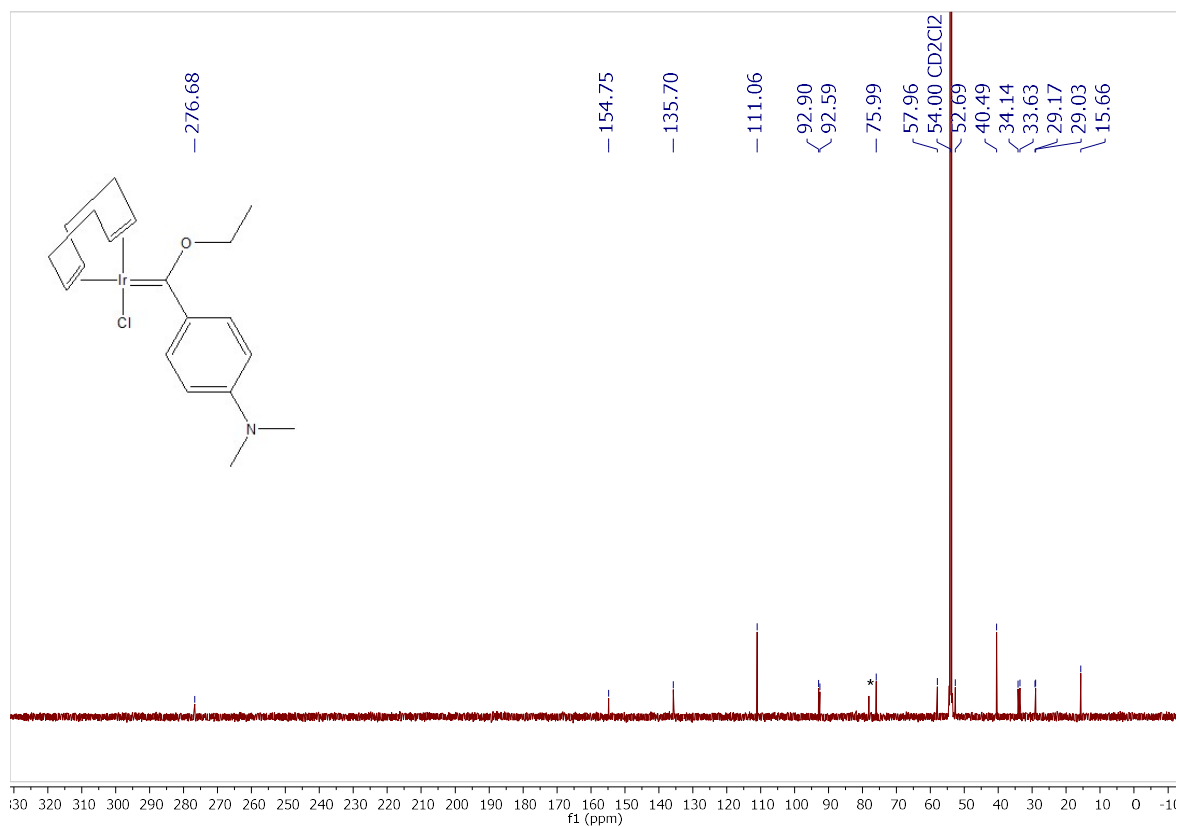


Figure S4. ^{13}C NMR spectrum of **1** in CD_2Cl_2 . *Residual CHCl_3

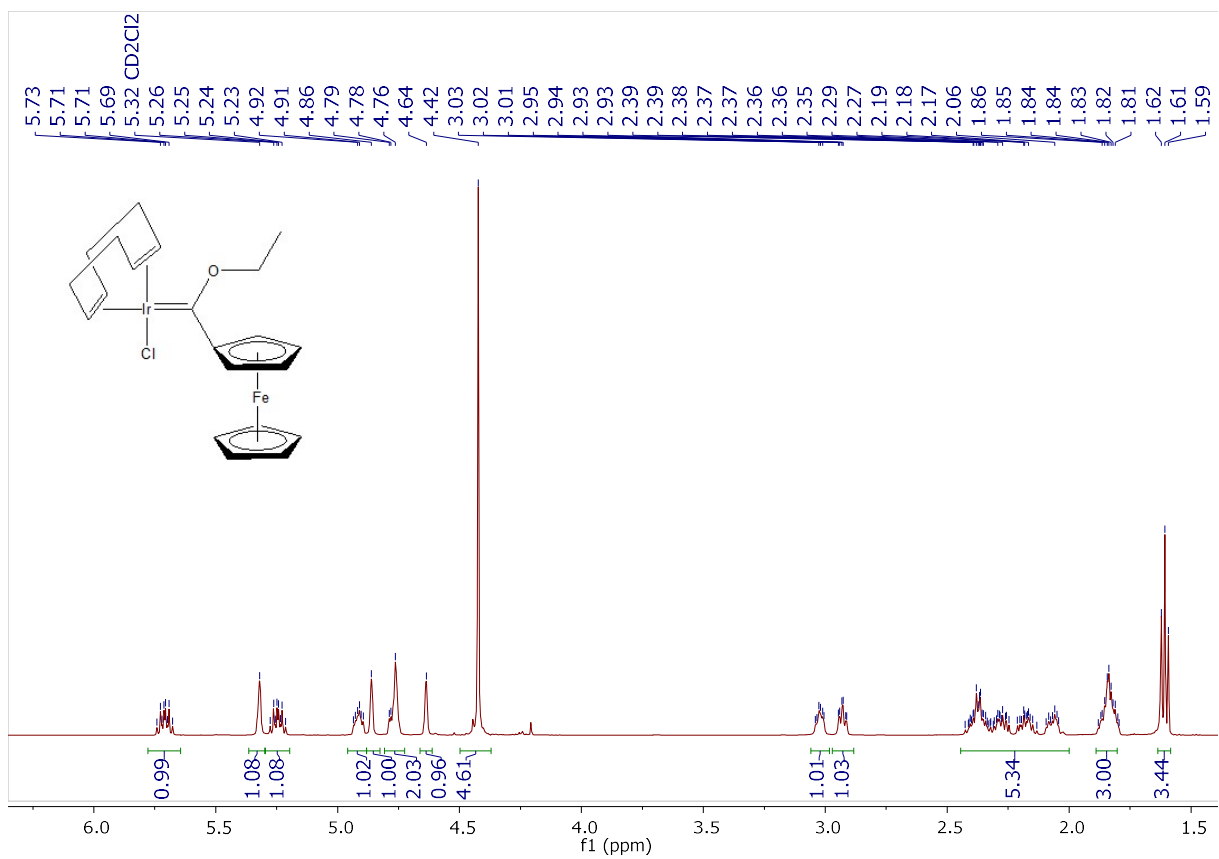


Figure S5. ^1H NMR spectrum of **2** in CD_2Cl_2

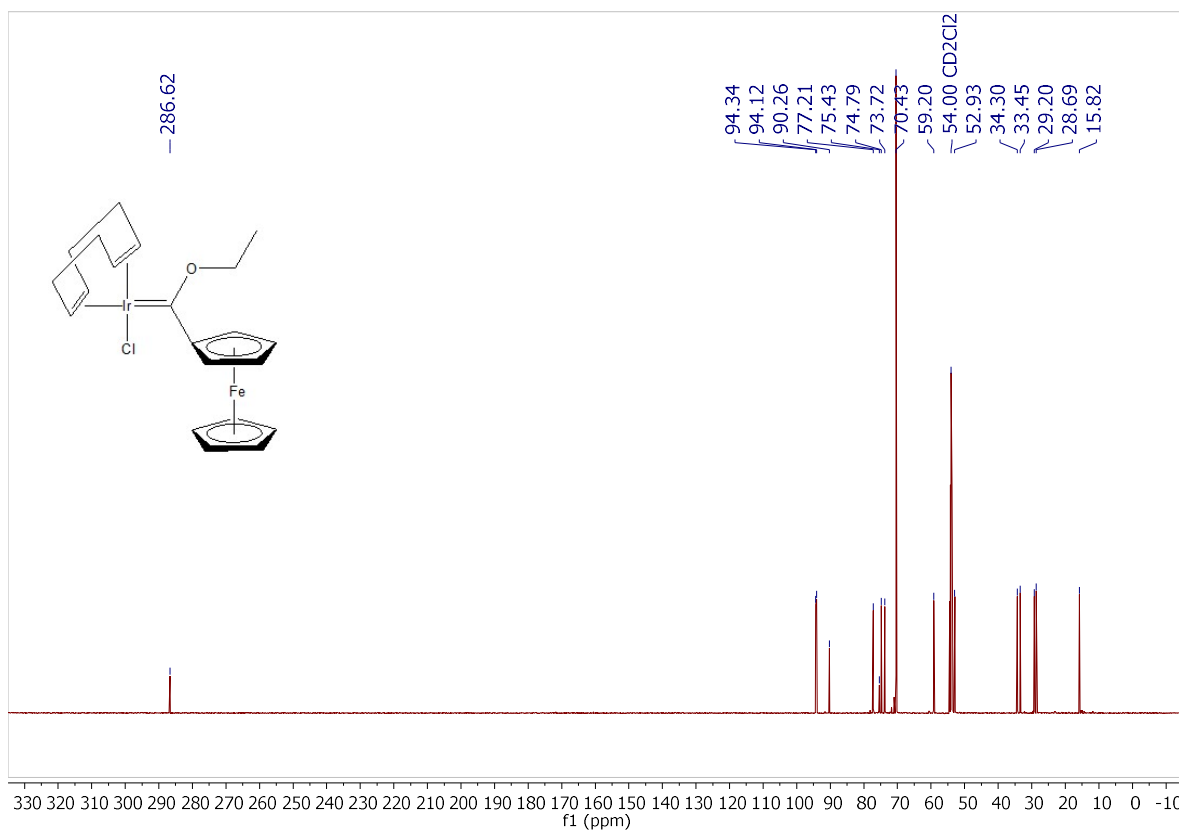
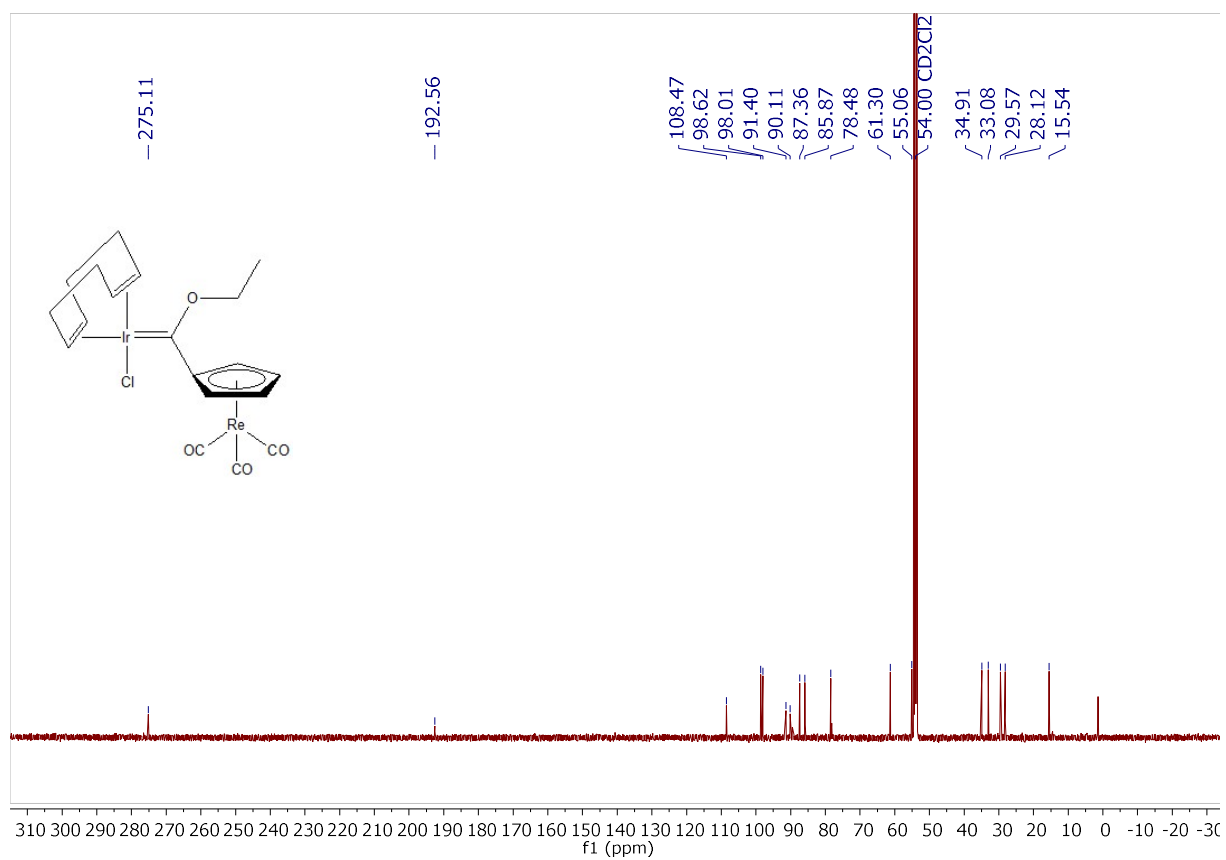
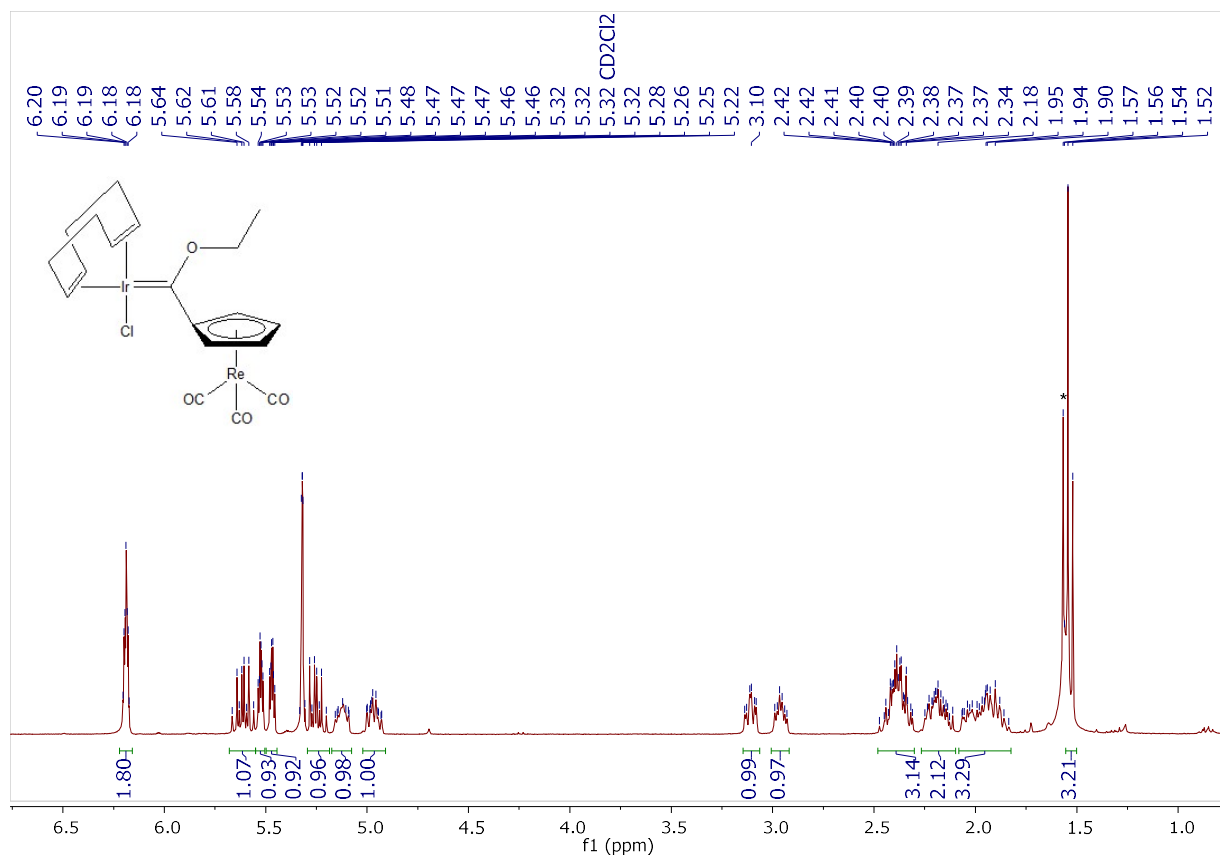


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2



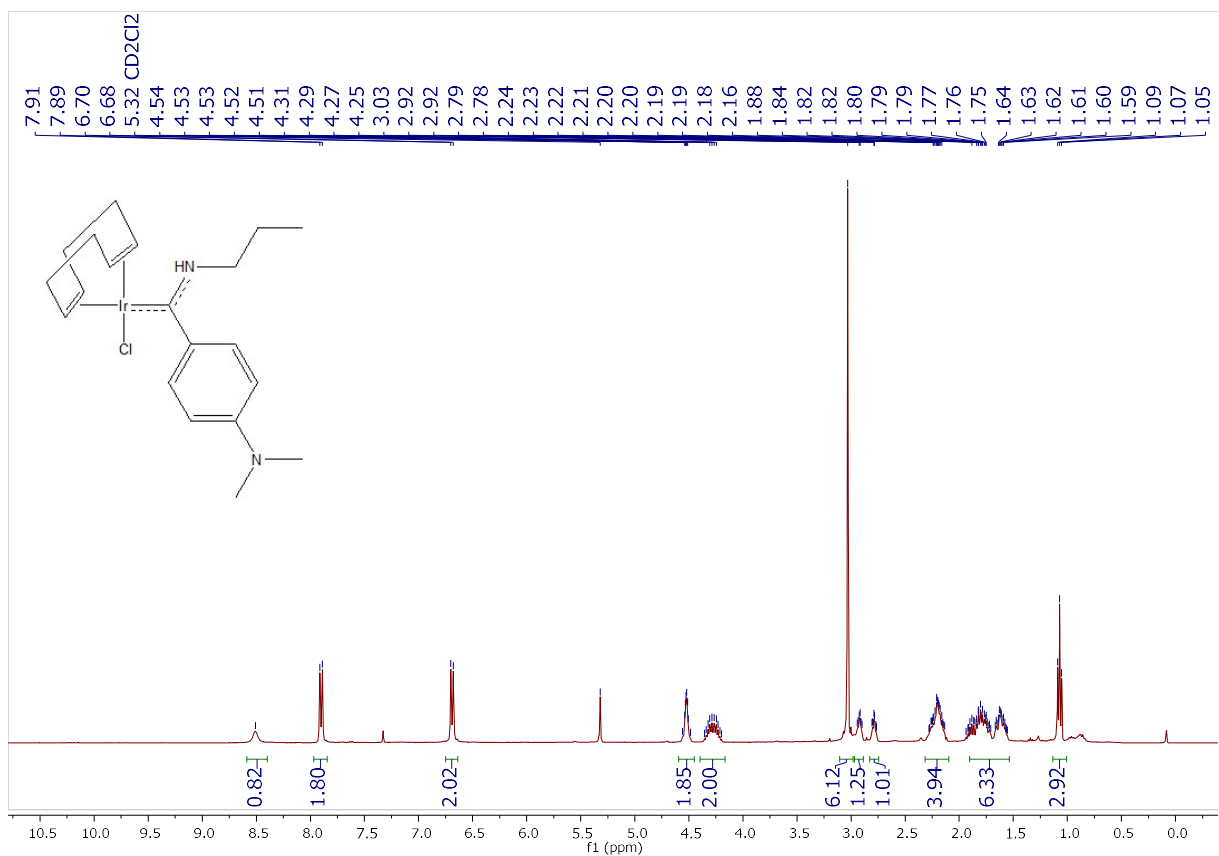


Figure S9. ^1H NMR spectrum of **4** in CD_2Cl_2

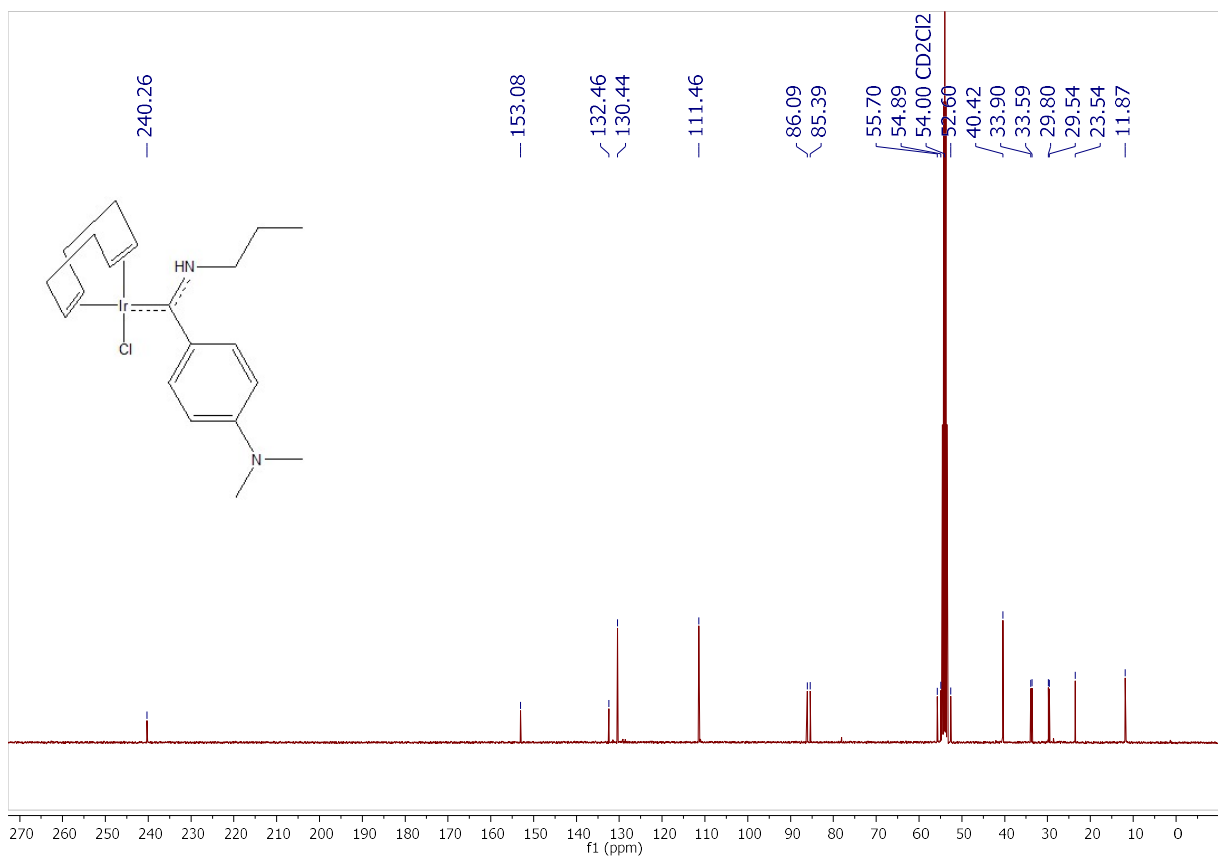


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2

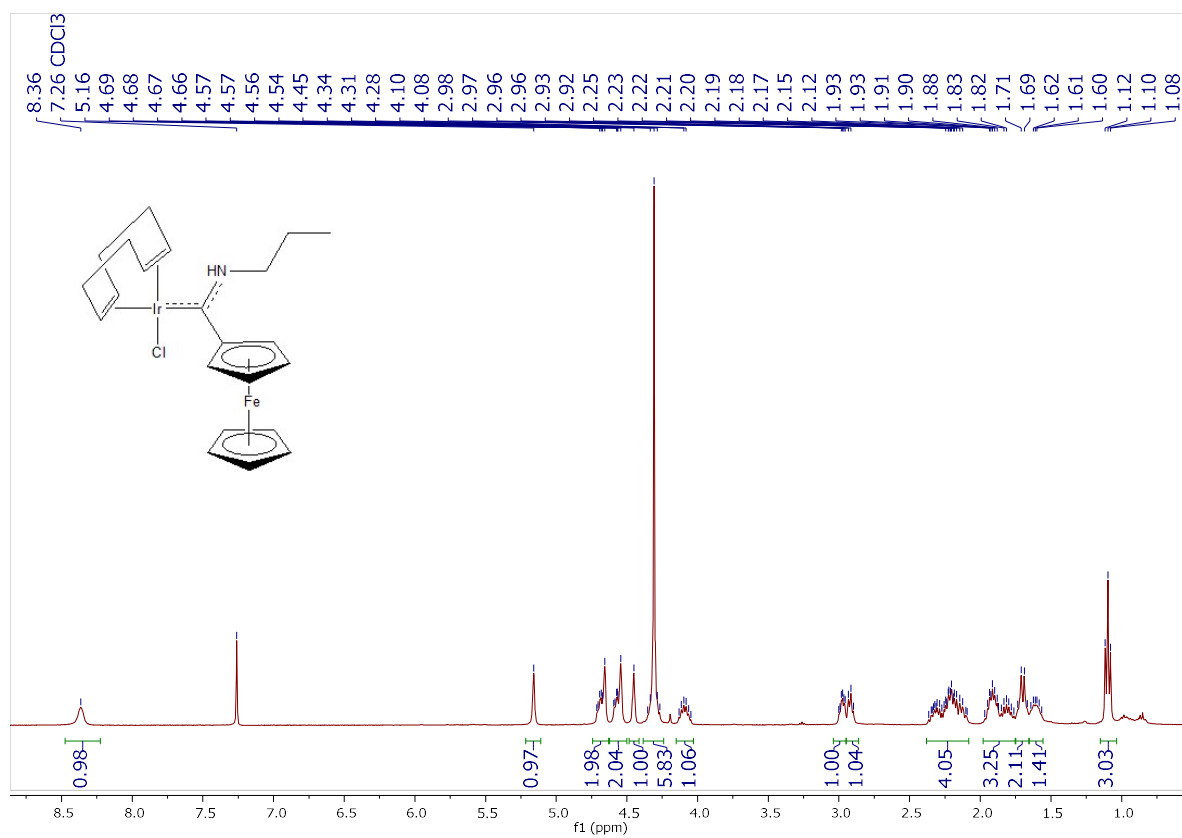


Figure S11. ^1H NMR spectrum of 5 in CDCl_3

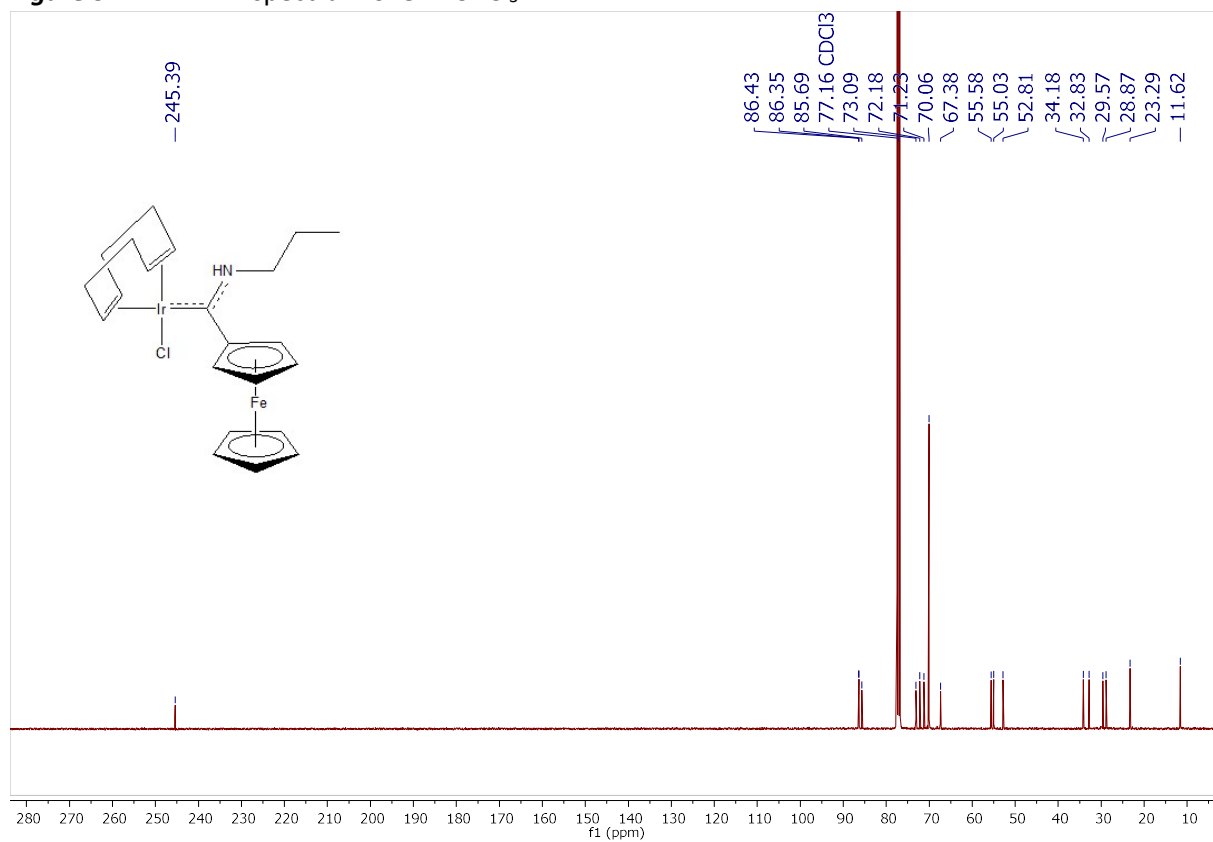


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5 in CDCl_3

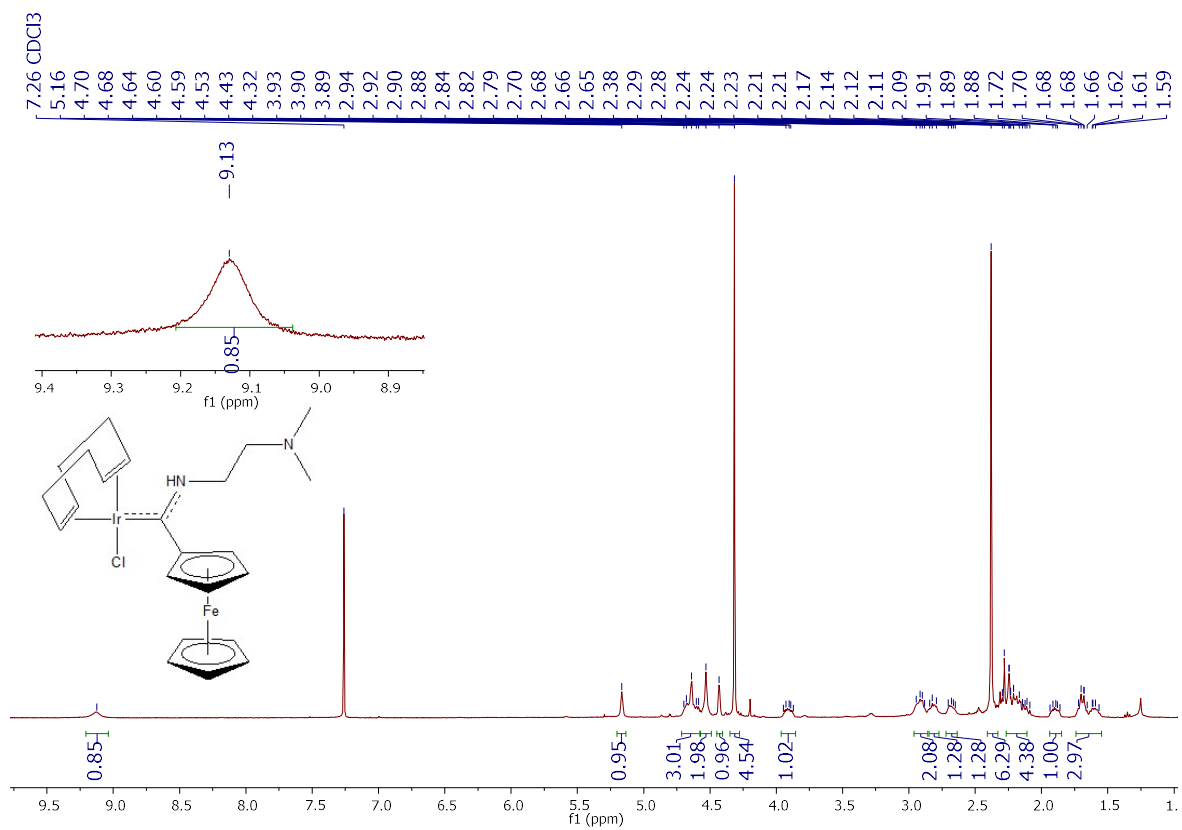


Figure S13. ¹H NMR spectrum of 6 in CDCl₃

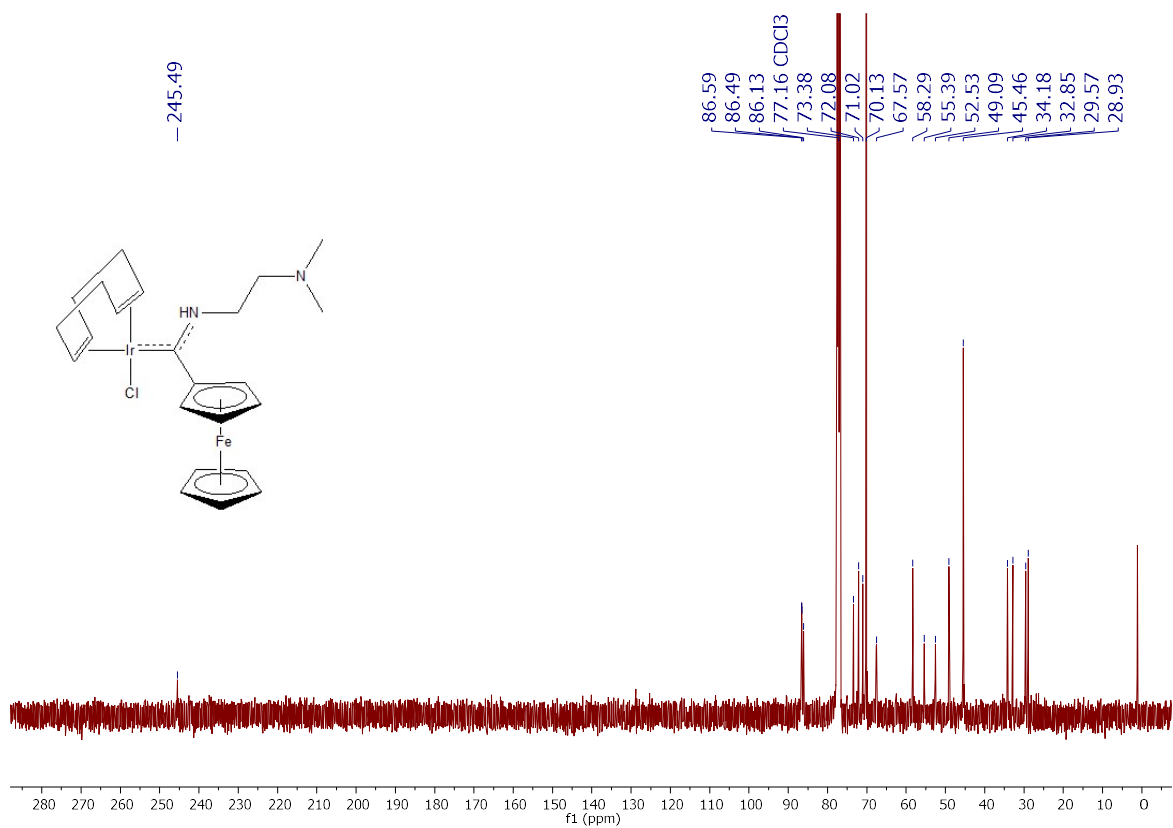


Figure S14. ¹³C{¹H} NMR spectrum of 6 in CDCl₃

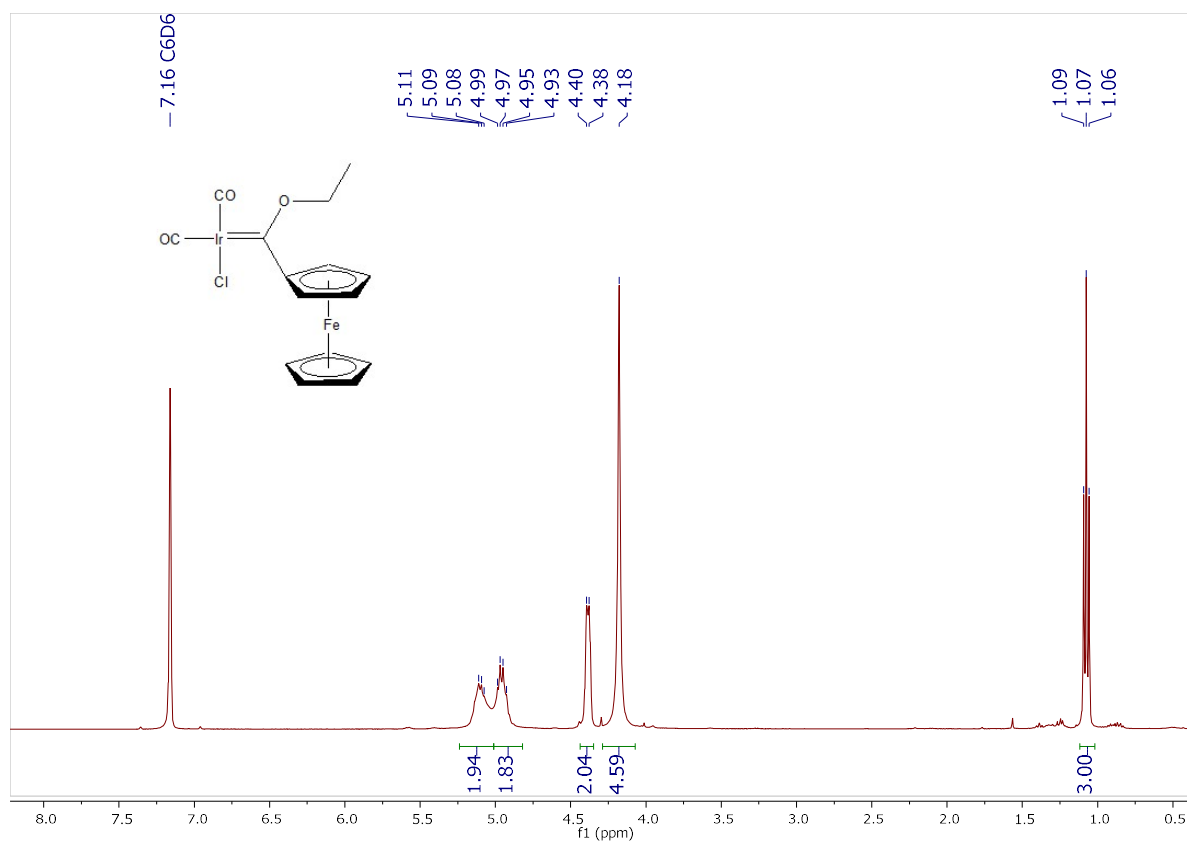


Figure S15. ^1H NMR spectrum of **7** in C_6D_6

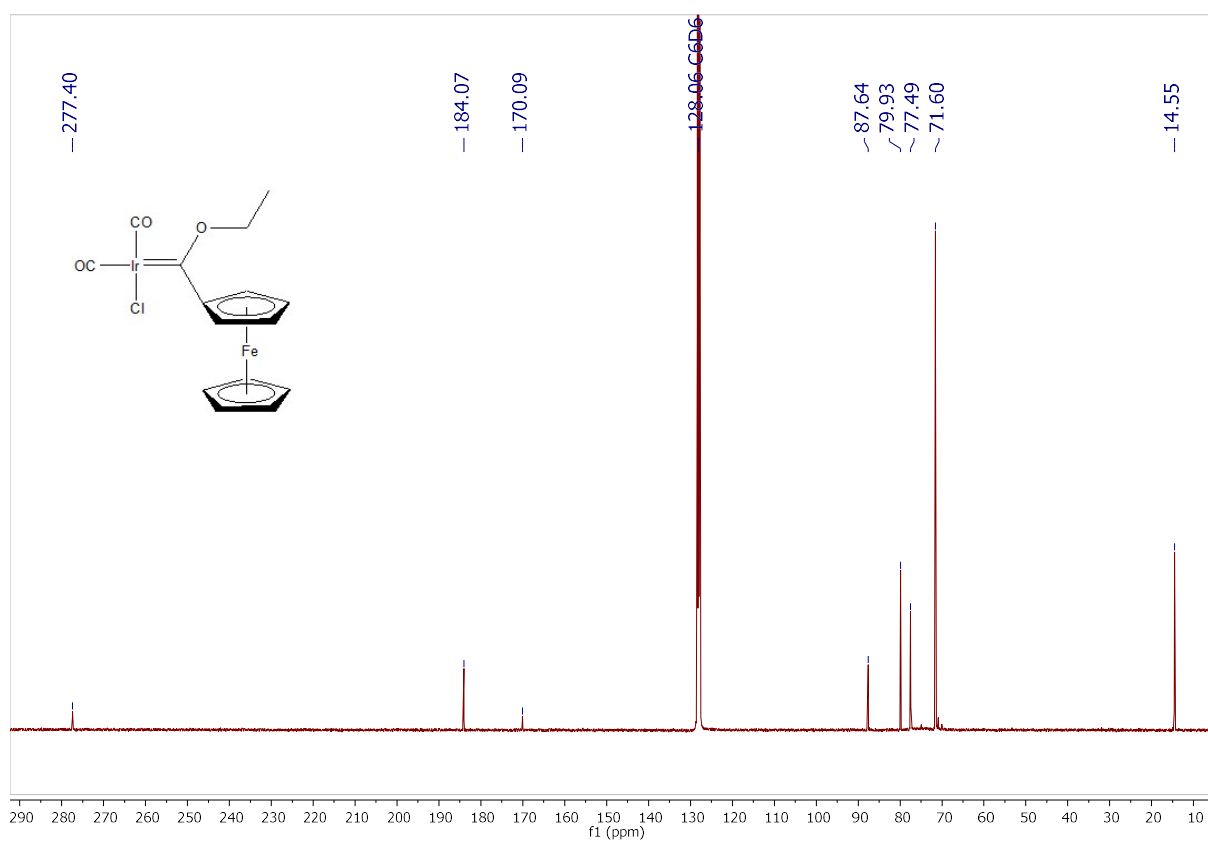


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in C_6D_6

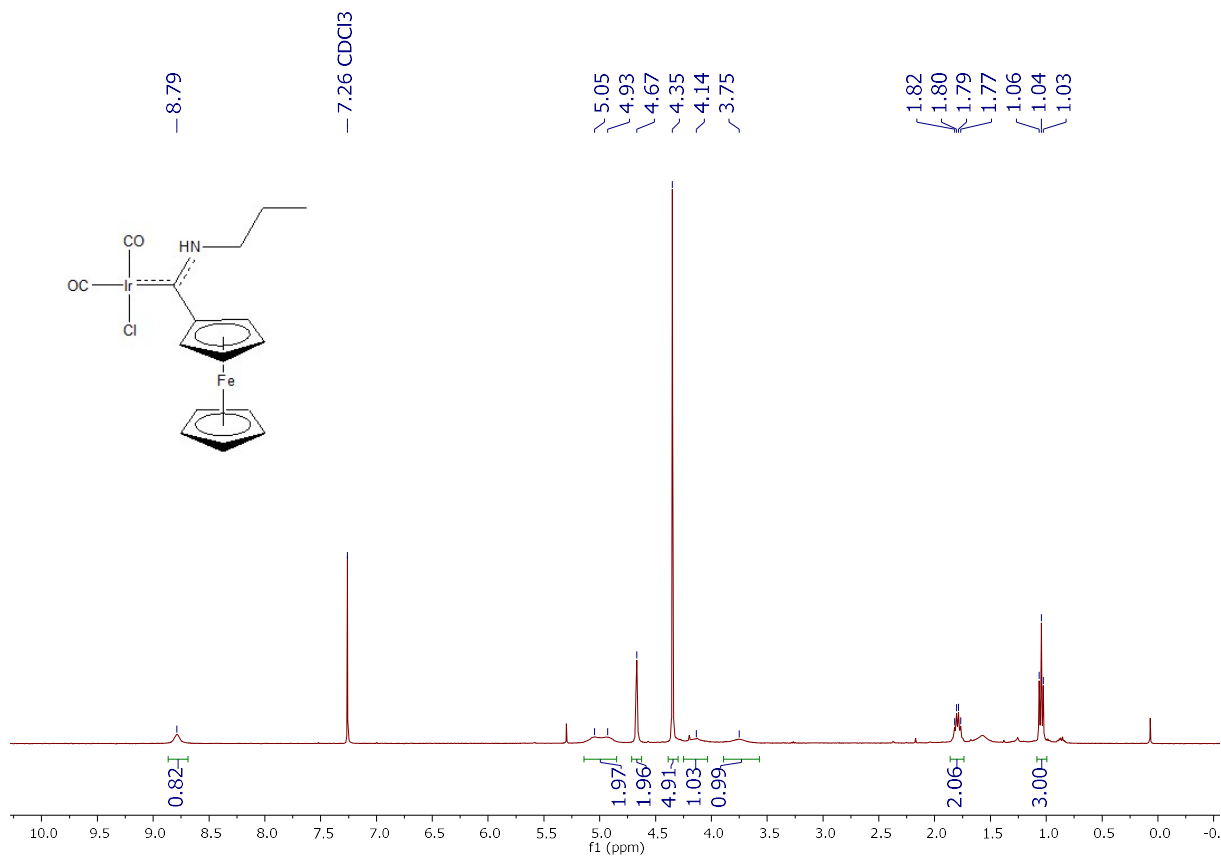


Figure S17. ^1H NMR spectrum of **8** in CDCl_3

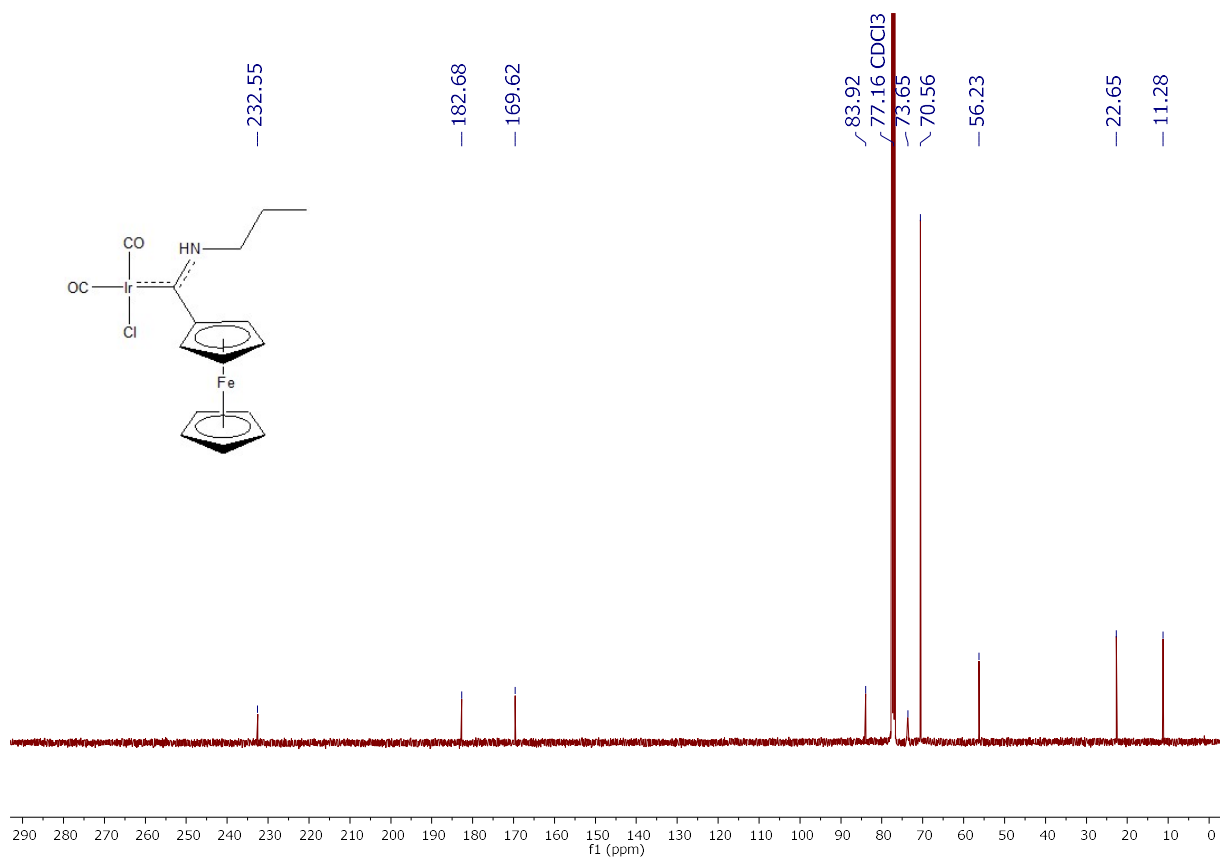


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3

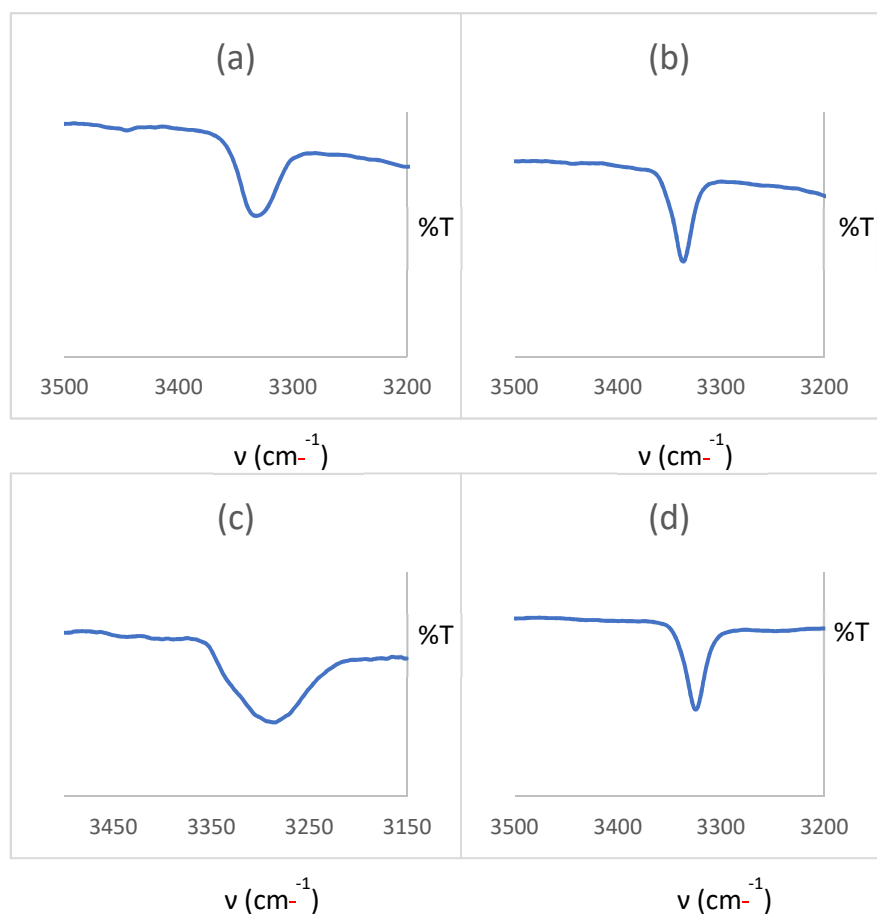


Figure S19. IR spectra in the $\nu(\text{NH})$ region of aminocarbene complexes $[\text{Ir}(\text{cod})\text{Cl}\{\text{C}(\text{NH}^n\text{Pr})(p\text{-DMA})\}]$ **4** (a), $[\text{Ir}(\text{cod})\text{Cl}\{\text{C}(\text{NH}^n\text{Pr})\text{Fc}\}]$ **5** (b), $[\text{Ir}(\text{cod})\text{Cl}\{\text{C}(\text{NH}(\text{CH}_2\text{CH}_2)\text{N}(\text{Me})_2)\text{Fc}\}]$ **6** (c), and $[\text{Ir}(\text{CO})_2\text{Cl}\{\text{C}(\text{NH}^n\text{Pr})\text{Fc}\}]$ **8**

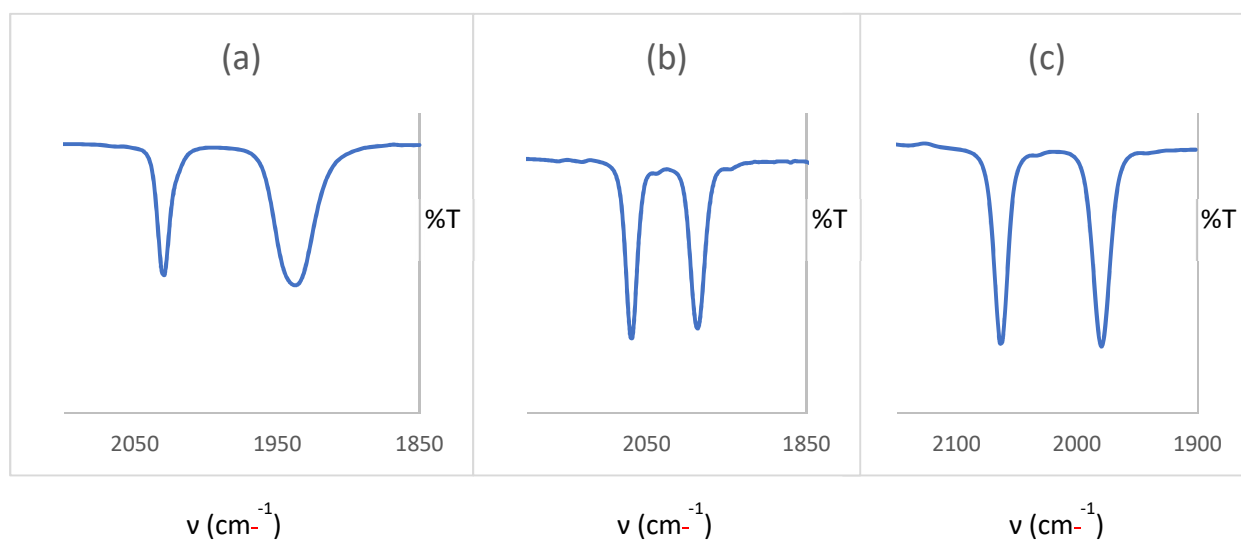
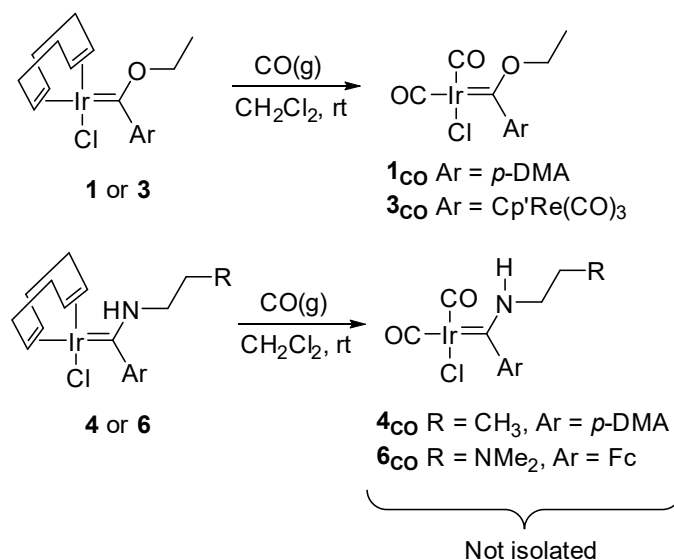


Figure S20. IR spectra in the $\nu(\text{CO})$ region of carbonyl complexes $[\text{Ir}(\text{cod})\text{Cl}\{\text{C}(\text{OEt})(\text{Cp}'\text{Re}(\text{CO})_3)\}]$ **3** (a), $[\text{Ir}(\text{CO})_2\text{Cl}\{\text{C}(\text{OEt})\text{Fc}\}]$ **7** (b), and $[\text{Ir}(\text{CO})_2\text{Cl}\{\text{C}(\text{NH}^n\text{Pr})\text{Fc}\}]$ **8** (c)

S3. TEP calculation

Complexes **1**, **3**, **4** and **6** were dissolved in solvent CH_2Cl_2 and $\text{CO}(\text{g})$ passed through the solution for approximately 10-20 minutes, for substitution of the cod-ligand with two carbonyl ligands (Scheme S2). The resultant dicarbonyl complexes were not purified and isolated, but the FT-IR spectra of the reaction mixtures in solution CH_2Cl_2 were recorded (Figure S21), in order to obtain the two carbonyl stretching vibration frequencies required for TEP calculation.



Scheme S2. Substitution of cod-ligands by CO.

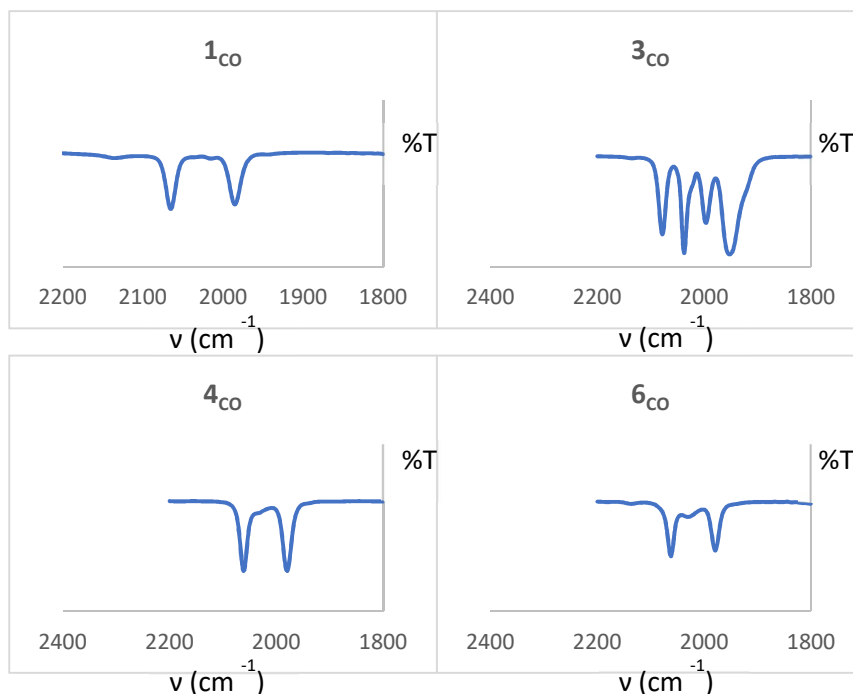


Figure S21. IR spectra of the carbonyl-substituted complexes **1**_{CO}, **3**_{CO}, **4**_{CO} and **6**_{CO}

Table S1. Calculated TEP for the Fischer carbene ligands, using formula $TEP = 0.8475\nu(\text{CO})_{\text{ave}}\text{Ir} + 336.2 \text{ cm}^{-1}$

FC ligand						
TEP (cm ⁻¹)	2055	2050	2052	2063	2049	2043

S4. X-ray crystallography

All crystals for single-crystal X-ray diffraction were grown by slow diffusion of *n*-hexane into a concentrated CH₂Cl₂ solution of the carbene complex at 4 °C. Single crystal X-ray diffraction data for complexes **1**, **3** and **7** were collected at 173 K on a Bruker Apex II CCD diffractometer, while data for complexes **2**, **4** and **5** were collected at 173 K using a Bruker Venture D8 Photon CMOS diffractometer, with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation using an Oxford Cryostream 600 cooler. All data reductions were carried out using the program SAINT+, version 6.02⁶ and empirical absorption corrections were made using SADABS.⁶ Space group assignments were made using XPREP.⁶ The structures were solved in the WinGX⁷ Suite of programs, using intrinsic phasing through SHELXT⁸ and refined using full-matrix least-squares/difference Fourier techniques on F² using SHELXL-2017.⁸ All C-bound H atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of their parent atoms. The amine-H atom positions in **4** and **5** were located and were refined. All diagrams and publication material were generated using OLEX2, ORTEP-3,⁷ and PLATON.⁹ Experimental details of the X-Ray analyses are provided in Table S2 below.

Table S2. Selected bond lengths (Å) and angles (°) for complexes **1** – **5**, and **7**

	1	2	3	4	5	7
Ir-C _{carbene}	1.972(2)	1.963(9)	1.954(7)	2.0145(17)	2.029(3)	2.065(9)
C _{carbene} -O/N	1.349(2)	1.317(11)	1.319(10)	1.315(2)	1.305(5)	1.311(10)
C _{carbene} -C _{ipso}	1.443(3)	1.458(13)	1.449(12)	1.475(2)	1.458(5)	1.430(12)
Ir-Cl	2.3653(6)	2.361(2)	2.357(2)	2.3684(4)	2.3770(9)	2.350(2)
Ir-Y ^{a-e} or Ir-CO _{trans}	2.092(2) ^a	2.132(10) ^b	2.113(8) ^c	2.088(18) ^d	2.076(4) ^e	1.914(10)
Ir-Y ^{f-j} or Ir-CO _{cis}	1.983(2) ^f	1.991(8) ^g	1.998(9) ^h	1.979(17) ⁱ	1.981(3) ^j	1.832(12)
C _{carbene} -Ir-Cl	89.40(6)	93.10(3)	90.8(2)	89.13(5)	88.08(11)	86.0(2)
O/N-C _{carbene} -C _{ipso}	110.37(17)	110.2(8)	107.9(6)	115.08(15)	114.7(3)	111.8(7)
C _α -C _{ipso} -C _{carbene} -	8.4(3)	3.1(13)	2.7(12)	27.4(2)	2.4(6)	9.7(12)
O/N						

^aY = midpoint of C(5)-C(6). ^bY = midpoint of C(4)-C(5). ^cY = midpoint of C(4)-C(5). ^dY = midpoint of C(5)-C(6). ^eY = midpoint of C(1)-C(2). ^fY = midpoint of C(1)-C(2). ^gY = midpoint of C(1)-C(8). ^hY = midpoint of C(1)-C(8). ⁱY = midpoint of C(1)-C(2). ^jY = midpoint of C(5)-C(8).

Table S3. Crystal data and summary of data collection and refinement for complexes **1** – **5**, and **7**

Crystal data for:	1	2	3	4	5	7
Chemical formula	C ₁₉ H ₂₇ ClIrN O	C ₂₁ H ₂₆ ClFeIr O	C ₁₉ H ₂₁ ClIr O ₄ Re	C ₂₀ H ₃₀ ClIr N ₂	C ₂₂ H ₂₉ ClFe IrN	C ₁₅ H ₁₄ ClFe IrO ₃
<i>M_r</i>	513.06	577.92	727.423	526.11	590.96	525.76
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	Pca2 ₁	P2 ₁ 2 ₁ 2 ₁	<i>P</i> -1	<i>P</i> -1	P2 ₁ /c
Temp.(K)	173	173	173	173	173	173
<i>a</i> (Å)	15.0771(4)	23.4785(9)	7.1772(2)	9.7515(7)	7.621(4)	9.5567(4)
<i>b</i> (Å)	9.4273(2)	7.3046(3)	13.6484(4)	10.6457(7)	10.8953(6)	7.4257(3)
<i>c</i> (Å)	12.7543(3)	22.6327(9)	20.3481(6)	11.2922(8)	12.7852(7)	22.3102(9)
α (°)	90	90	90	64.293(2)	109.228(2)	90
β (°)	92.1530	90	90	82.960(2)	93.019(2)	95.626(2)
γ (°)	90	90	90	71.201(2)	95.009(2)	90
<i>V</i> (Å ³)	1811.57(7)	3881.5(3)	1993.24(10)	999.69(12)	994.89(9)	1575.54(11)
<i>Z</i>	4	8	4	2	2	4
Radiation type	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
μ (mm ⁻¹)	7.522	7.741	12.891	6.815	7.550	9.532
Crystal size (mm)	0.311 × 0.296 × 0.086	0.261 × 0.087 × 0.064	0.182 × 0.167 × 0.053	0.426 × 0.228 × 0.183	0.263 × 0.202 × 0.106	0.291 × 0.216 × 0.102
<i>T_{min}</i> , <i>T_{max}</i>	0.206, 0.697	0.341, 0.845	0.177, 0.629	0.185, 0.405	0.621, 0.948	0.097, 0.272
Measured	29663	73073	36910	45043	30244	30710
Independent	4376	9376	4825	4811	4788	8184
observed [<i>I</i> > 2 σ (<i>I</i>)]	3859	8669	4261	4628	4537	6656
<i>R_{int}</i>	0.0343	0.0628	0.0750	0.0269	0.0280	0.0741
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.660	0.660	0.661	0.661	0.660	0.665
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0144	0.0309	0.0245	0.0115	0.0154	0.0502
<i>wR</i> (<i>F</i> ²)	0.0324	0.0633	0.0522	0.0267	0.0357	0.1414
<i>S</i>	1.042	1.032	1.005	1.115	1.139	1.078
No. of reflections	4376	9376	4825	4628	4788	8184
No. of parameters	211	454	237	225	274	182
No. of restraints	0	1	0	0	96	0
H-atom treatment	Constrained	Constrained	Constrained	Mixed	Constrained	Constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.63, -0.55	1.67, -1.11	1.78, -0.88	1.90, -0.60	2.29, -1.80	2.68, -1.65
CCDC numbers	1970902	1970903	1970904	1970905	1970906	1970907

S5. Stability test

10 mg of complex **6** was dissolved in *i*PrOH (3 mL), excess KOH (0.05 mL of a 0.24 M *i*PrOH solution) was added in a Schlenk tube under argon gas. The reaction was stirred in the sealed Schlenk tube at 82 °C for 16 hours. The *i*PrOH solvent was removed under vacuum, the crude reaction mixture was immediately dissolved in 0.5 mL CDCl₃ and NMR spectra were recorded.

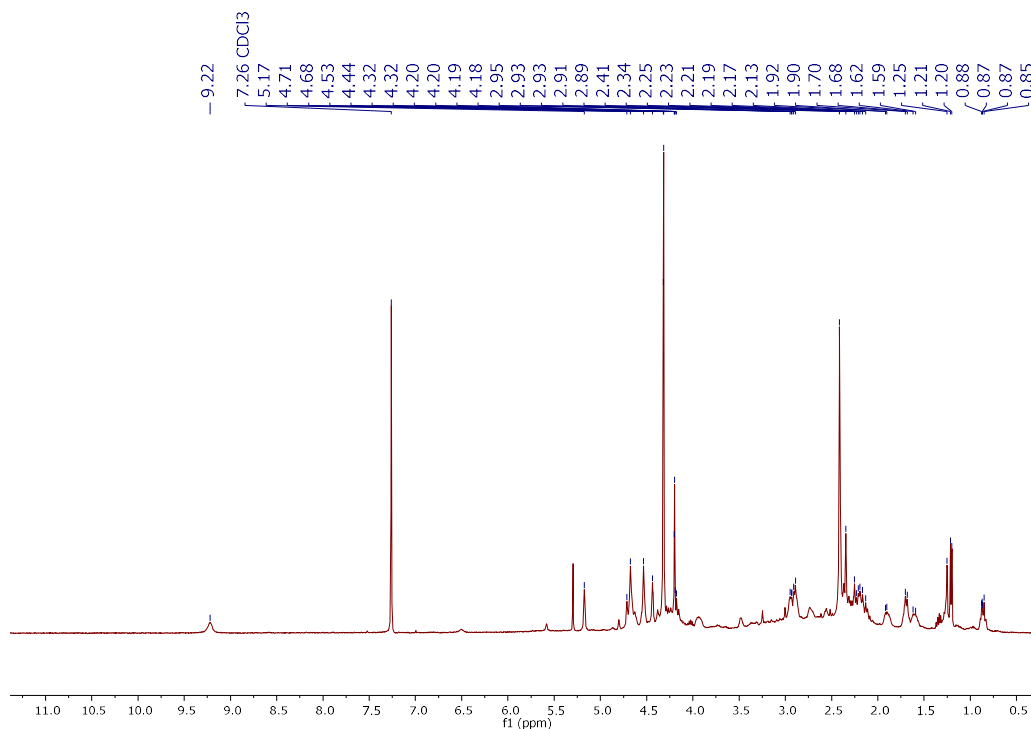


Figure S22. ¹H NMR spectrum in CDCl₃ of the stability test reaction mixture for catalyst **6**

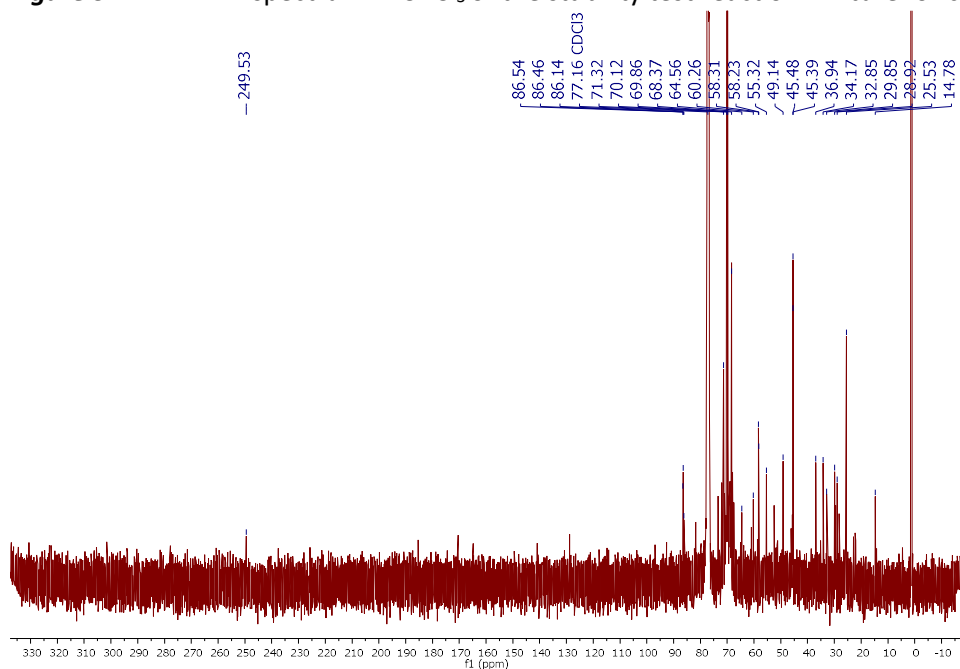


Figure S23. ¹³C{¹H} NMR spectrum of the stability test reaction mixture of **6** in CDCl₃

S6. Catalytic transfer hydrogenation

General procedure for transfer hydrogenation reactions.

The catalytic transfer hydrogenation reactions were done under an argon atmosphere in thick glass reaction tubes fitted with a greaseless high-vacuum stopcock. In a typical reaction, the schlenk tube was charged with a solution of acetophenone (2.0 mmol, 230 μ L) in *iso*-propanol (4 mL), base (42 μ L, 0.01 mmol of a 0.24 M KOH solution in *iso*-propanol), internal standard (*n*-decane, 100 μ L), and the Iridium complex (0.002 mmol, 0.1 mol %). The mixture was stirred at 82 $^{\circ}$ C for the required number of hours. Conversions were determined by gas chromatography analysis under the following conditions: oven temperature 35 $^{\circ}$ C (2 min) to 220 $^{\circ}$ C at 20 $^{\circ}$ C/min with a flow rate of 1 mL/min using ultrapure He as carrier gas and Supelco Equity 1 capillary column, L x I.D. 30m x 0.32mm, d_f 0.25mm.

Table S4. Optimization results from the transfer hydrogenation reactions

Entry	Ir Comp.	Loading (mol %)	KOH (mol %)	Time (h)	Conversion (%)	TOF ^a (hr ⁻¹)
1	2	0.5	0.5	24	31	03
2	2	0.5	0.25	24	79	07
3	2	0.1	0.5	24	67	28
4 ^b	2	0.1	0.5	16	65(1.6) ^b	41(1.3)
5	2	0.05	0.25	16	27	34
6	2	0.1	0.5	8	18	23
7	2	0.1	0.5	4	11	29
8 ^b	-	-	0.5	24	3(0.6) ^b	
9 ^b	-	-	10	24	8(2.2) ^b	
10 ^b	-	-	20	24	23(4.7) ^b	
11 ^b	-	-	100	24	47(8.4) ^b	

All reactions were done in condenser-fitted round-bottomed flasks at 82 $^{\circ}$ C under argon gas atmosphere. ^aAverage turnover frequency ((mol of product)/((mmol of catalyst) h)) determined at the reaction time. ^bThese reactions were performed in triplicate, with standard deviations indicated in parentheses.

S7. References

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