Supporting information for

# Ring Slippage and Dissociation of Pentamethylcyclopentadienyl Ligand in an ($\eta^5$-Cp*)Ir Complex with a $\kappa^3$-*O*,*C*,*O* Tridentate Calix[4]arene Ligand under Mild Conditions

Takuya Kuwabara, Ryogen Tezuka, Mikiya Ishikawa, Takuya Yamazaki, Shintaro Kodama, and Youichi Ishii*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551 Japan

Corresponding author's e-mail: yo-ishii@kc.chuo-u.ac.jp

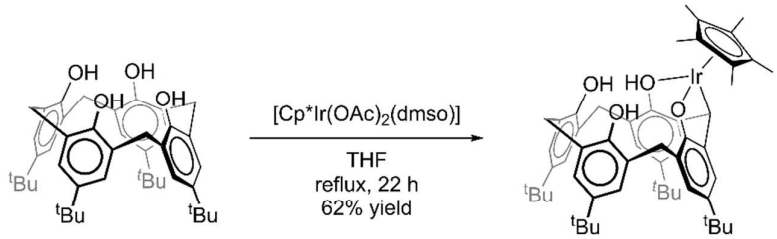
Table of contents

**1. General considerations**

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise stated. 1,2-Dichloroethane ($C_2H_4Cl_2$) and dichloromethane ($CH_2Cl_2$) were dried and distilled over $P_4O_{10}$, degassed, and stored under argon. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. Monopotassium salt of *p*-$^t$Bucalix[4]arene,[1] [Cp*Ir(OAc)$_2$(dmso)],[2] and [Cp*Rh(OAc)$_2$]$_2$[3] were synthesized according to the literatures. $^1$H (500 MHz), $^{13}$C{$^1$H} (126 MHz) and $^{31}$P{$^1$H} (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer at 20°C. Chemical shifts are reported in δ and referenced to residual $^1$H and $^{13}$C signals of deuterated solvents as internal standards. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer by using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. X-ray crystallographic analyses were performed on a Rigaku/MSC VariMax/Saturn CCD diffractometer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by $^1$H NMR spectroscopy.

**2. Synthesis and analytical data for new compounds**

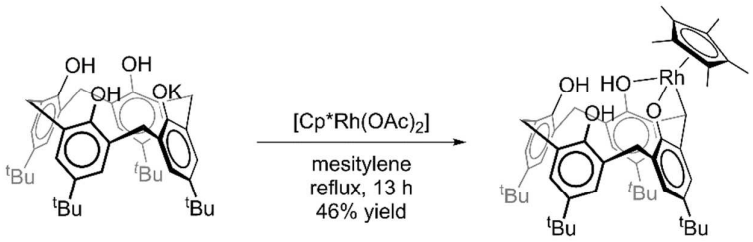
**Synthesis of [Cp*Ir{*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O*,*C*,*O*}]·0.5$CH_2Cl_2$ (1a·0.5$CH_2Cl_2$)**




**1a**

To a THF solution (65 mL) of *p*-$^t$Bucalix[4]arene (1.30 g, 2.00 mmol) was added [Cp*Ir(OAc)(dmso)] (1.04 g, 2.00 mmol), and the mixture was stirred under reflux for 22 h. The solvent was removed under reduced pressure to yield crude [Cp*Ir(*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O*,*C*,*O*)] (**1a**) as a yellow powder, which was purified by recrystallization from dichloromethane/methanol to give **1a**·0.5$CH_2Cl_2$ as yellow crystals (1.27 g, 1.25 mmol, 62% yield). Spectral data for **1a**: $^1$H NMR ($CDCl_3$): δ 13.64 (s, 2H, OH), 12.72 (s, 1H, OH), 7.14 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH), 7.01 (d, $^4J_{H–H}$ = 2.5 Hz, 4H, ArH), 6.66 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH), 4.79 (s, 1H, Ir–CH), 4.30 (d, $^2J_{H–H}$ = 13.4 Hz, 2H, $CH_2$), 4.28 (d, $^2J_{H–H}$ = 13.8 Hz, 1H, $CH_2$), 3.42 (d, $^2J_{H–H}$ = 13.4 Hz, 2H, $CH_2$), 3.37 (d, $^2J_{H–H}$ =13.8 Hz, 1H, $CH_2$), 1.75 (s, 15H, Cp*), 1.21 (s, 18H, $^t$Bu), 1.19 (s, 18H, $^t$Bu). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 157.8, 148.3, 143.7, 143.4, 143.1, 128.9, 128.3, 126.3, 126.1, 125.6, 124.4, 122.8 (Ar), 83.5 ($C_5Me_5$), 50.8 (Ir–C), 34.1 ($CH_2$), 33.97 ($C(CH_3)_3$), 33.95 ($CH_2$), 33.8 ($C(CH_3)_3$), 31.9, 31.7 (s, $C(CH_3)_3$), 9.6 (s, $C_5Me_5$). IR (KBr, cm$^{-1}$) 3430 ($\gamma_{OH}$). Anal. Calcd for $C_{54.5}H_{70}IrO_4Cl$ (**1a**·$(CH_2Cl_2)_{0.5}$): C, 60.86; H, 4.97. Found: C, 60.52; H, 4.89. Complex **1a** can be synthesized from *p*-$^t$Bucalix[4]arene and [(Cp*Ir)$_2$(OH$_2$)](OAc) in 66% isolated yield.

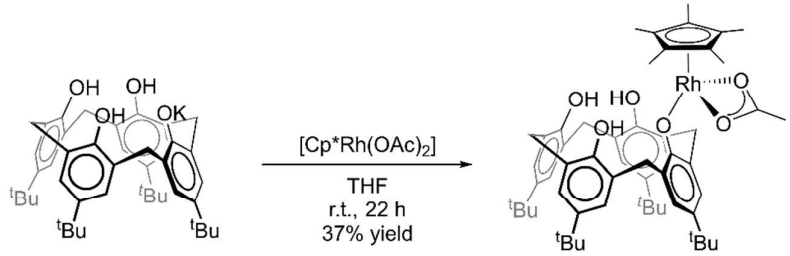
**Synthesis of [Cp*Rh{*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O*,*C*,*O*}]·$CH_2Cl_2$ (1b·$CH_2Cl_2$)**




**1b**

To a mesitylene solution (2.0 mL) of mono potassium salt of *p*-$^t$Bucalix[4]arene (20.2 mg, 0.0294 mmol) was added [Cp*Rh$(OAc)_2$] (10.6 mg, 0.0297 mmol) and the mixture was stirred under reflux (166 °C) for 13 h. The solvent was removed under reduced pressure, and the black residue was purified by column chromatography on silica gel (eluent: dichloromethane : hexane = 3 : 1). The first orange band was collected, evaporated to dryness, and recrystallized from dichloromethane/methanol to afford orange crystals of [Cp*Rh(*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O*,*C*,*O*)]·$CH_2Cl_2$ (**1b**·$CH_2Cl_2$) (13.3 mg, 0.0137 mmol, 46% yield). Similar reaction in refluxing *p*-xylene (138 °C, 22 h) resulting in lower yields (10 % yield). Spectral data for **1b**: $^1$H NMR ($CDCl_3$): δ 13.69 (br s, 2H, OH) 13.03 (br s, 1H, OH), 7.09 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH), 7.00 (s, 4H, ArH), 6.71 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH), 5.12 (s, 1H, Rh–CH), 4.32 (d, $^2J_{H–H}$ = 13.0 Hz, 2H, $CH_2$), 4.29 (d, $^2J_{H–H}$ = 13.0 Hz, 1H, $CH_2$), 3.41 (d, $^2J_{H–H}$ = 13.0 Hz, 1H, $CH_2$), 3.35 (d, $^2J_{H–H}$ = 13.0 Hz, 2H, $CH_2$), 1.71 (s, 15H, Cp*), 1.22 (s, 18H, $^t$Bu), 1.19 (s, 18H, $^t$Bu). $^{13}$C{$^1$H}3 NMR ($CDCl_3$): δ 155.7, 149.0, 142.9, 142.5, 141.5, 129.0, 128.4, 127.3, 126.0, 125.6, 124.4, 123.3 (Ar), 91.9 (d, $^1J_{Rh–C}$ = 8.4 Hz, $C_5Me_5$), 62.9 (d, $^1J_{Rh–C}$ = 25.2 Hz, Rh–C), 34.03 ($CH_2$), 34.00 (m, $CH_2$ and $C(CH_3)_3$), 31.9 (C($CH_3$)$_3$), 31.7 (C($CH_3$)$_3$), 9.3 ($C_5Me_5$). IR (KBr, cm$^{-1}$): 3445 ($\gamma_{OH}$). Anal. Calcd for $C_{55}H_{71}Cl_2O_4Rh$ (**1b**·$CH_2Cl_2$): C, 68.10; H, 7.38. Found: C, 68.10; H, 7.43.

**Synthesis of [Cp*Rh(OAc){*p*-$^t$Bucalix[4]arene(–)-*κ*-*O*}] (2)**

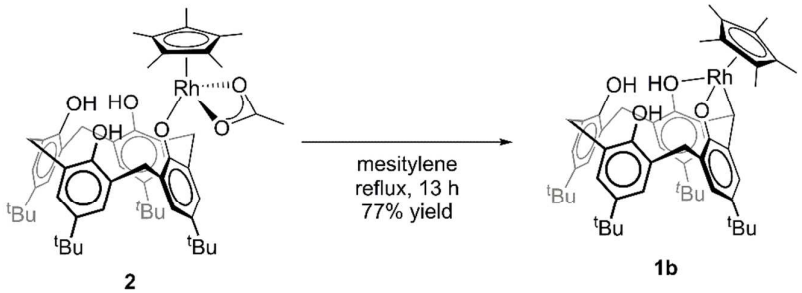



**2**

To a THF solution (10 mL) of monopotassium salt of *p*-$^t$Bucalix[4]arene (46.0 mg, 0.0699 mmol) was added [Cp*Rh$(OAc)_2$] (20.4 g, 0.0645 mmol) and the mixture was stirred for 22 h at room temperature. The resultant solution was dried up under reduced pressure to yield crude [Cp*Rh(OAc){*p*-$^t$Bucalix[4]arene(–)-*κ*-*O*}] (**2**) which was recrystallized from hexane/ether to give analytically pure **2** as an orange powder (24.7 mg, 0.0261 mmol, 37% yield). Spectral data for **2**: $^1$H NMR ($C_6D_6$): δ 10.33 (br s, 3H, OH), 7.36 (s, 2H, ArH), 7.26 (s, 2H, ArH), 7.01 (s, 2H, ArH), 6.73 (s, 2H, ArH), 5.36 (d, $^2J_{H–H}$ = 12.5 Hz, 2H, $CH_2$), 4.34 (d, $^2J_{H–H}$ = 13.5 Hz, 2H, $CH_2$), 3.57 (d, $^2J_{H–H}$ = 12.5 Hz, 2H, $CH_2$), 3.47 (d, $^2J_{H–H}$ = 13.5 Hz, 2H, $CH_2$),

1.45 (s, 18H, $^t$Bu), 1.38 (br s, 15H, Cp*), 1.12 (br s, 3H, OAc), 0.88 (s, 9H, $^t$Bu), 0.83 (s, 9H, $^t$Bu). $^{13}C\{^1H\}$ NMR ($C_6D_6$): 188.1 (br, $CH_3COO$), 151.7, 149.2, 143.7, 143.24, 142.2, 133.7, 131.30, 131.28, 130.6, 126.1, 125.4, 125.2, 124.9 (Ar; 13 distinct signals for 14 different carbons. A signal may be overlapping with the residual $C_6D_5H$ signal.), 90.8 (d, 9.3 Hz, $C_5(CH_3)_3$), 34.7, 34.2($C(CH_3)_3$), 33.7, 33.6 ($CH_2$), 33.3 ($C(CH_3)_3$), 32.1, 31.2, 31.1 ($C(CH_3)_3$), 22.1 (br s, $CH_3COO$), 8.7 ($C_5Me_5$). IR (KBr, $cm^{-1}$): 3446 ($\gamma_{OH}$). Anal. Calcd for $C_{56}H_{73}O_6Rh$ **2**: C, 71.17; H, 7.79. Found: C, 71.15; H, 8.10.

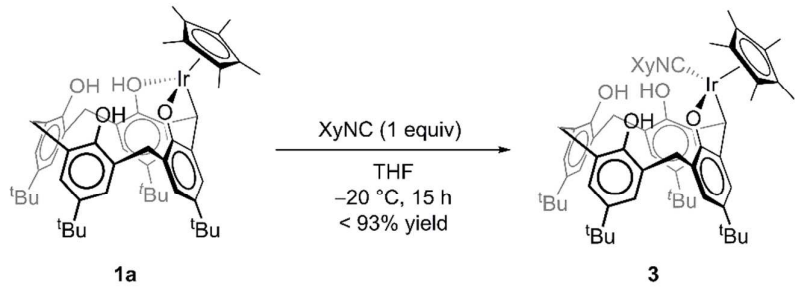
**Synthesis of 1b from 2**




2 1b

A mesitylene solution (10.0 mL) of **2** (101.7 mg, 0.107 mmol) was refluxed for 13 h. The solvent was removed under reduced pressure, and the black residue was purified by column chromatography on silica gel (eluent: dichloromethane : hexane = 3 : 1). The first orange band was collected, evaporated to dryness, and recrystallized from dichloromethane/methanol to afford orange crystals of **1b**·$CH_2Cl_2$ (80.0 mg, 0.0824 mmol, 77% yield).

**Synthesis of [Cp*Ir{*p*-$^t$Bucalix[4]arene(2–)-κ$^2$-*O*,*C*}(CNXy)] (3)**

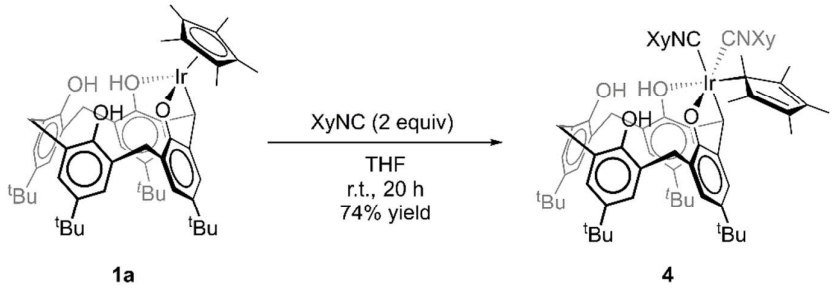



1a 3

2,6-xylyl isocyanide (4.5 mg, 0.034 mmol) was add to a THF solution (3.0 mL) of **1a**·0.5$CH_2Cl_2$ (22.9 mg, 0.0225 mmol) at –20 °C and the mixture was stirred for 15 h at this temperature. The solvent was removed under reduced pressure to yield a yellow powder, which was purified by recrystallization from dichloromethane/methanol at −20 °C to give [Cp*Ir(*p*-$^t$Bucalix[4]arene(2–)-κ$^2$-*O*,*C*)(CNXy)] (**3**) as yellow crystals (20.7 mg, 0.0200 mmol). However, this compound is not stable in solution at room temperature, and analytically pure samples could not be obtained even by repeated recrystallization at low temperatures. Spectral data for **3**: $^1$H NMR ($CDCl_3$): δ 10.48 (br s, 1H, OH), 7.07-6.98 (m, 9H, Xy (3H) + ArH of calixarene (2H) + OH (2H) + impurities), 6.94, 6.90, 6.74, 6.68, 6.65, 6.61 (d, $^4J_{H-H}$ = 2.0 Hz, 1H each, ArH of calixarene), 4.76 (d, $^2J_{H-H}$ = 12.5 Hz, 1H, $CH_2$), 4.62 (s, 1H, Ir–C*H*), 4.44 (d, $^2J_{H-H}$ = 13.0 Hz, 1H, $CH_2$), 3.31 (d, $^2J_{H-H}$ = 13.0, 1H, $CH_2$),

3.16 (d, $^2J_{H-H}$ = 12.5 Hz, $CH_2$), 3.08 (d, $^2J_{H-H}$ = 13.5 Hz, $CH_2$), 2.79 (d, $^2J_{H-H}$ = 13.5 Hz, $CH_2$), 2.10 (s, 6H, Me of XyNC), 1.63 (s, 15H, Cp*), 1.25 (s, 9H, $^t$Bu), 1.19 (s, 9H, $^t$Bu), 1.14 (s, 9H, $^t$Bu), 1.13 (s, 9H, $^t$Bu). $^{13}C\{^1H\}$ NMR data of **3** could not be obtained because of its instability. IR (KBr, $cm^{-1}$): 3430 ($\gamma_{OH}$), 2116 ($\gamma_{CN}$).

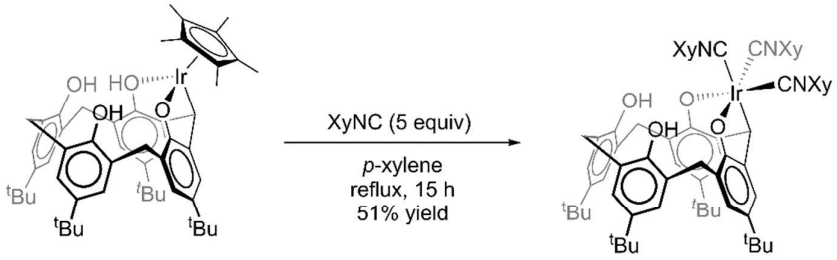
**Synthesis of [($\eta^1$-Cp*)Ir(*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O,C,O*)(CNXy)$_2$]·$CH_2Cl_2$ (4·$CH_2Cl_2$)**




**1a** **4**

To a THF solution (20.0 mL) of **1a**·0.5$CH_2Cl_2$ (201.8 g, 0.199 mmol) was added 2,6-xylyl isocyanide (54.9 mg, 0.419 mmol), and the mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure to yield crude [($\eta^1$-$C_5Me_5$)Ir(*p*-$^t$Bucalix[4]arene(2–)-$\kappa^3$-*O,C,O*)(CNXy)$_2$] (**4**) as a solid, which was further purified by recrystallization from dichloromethane/methanol to give analytically pure **4**·$CH_2Cl_2$ as yellow crystals (194.2 mg, 0.149 mmol, 74% yield). Spectral data for **4**: $^1$H NMR ($CDCl_3$): δ 14.82 (s, 1H, OH), 12.86 (s, 1H, OH), 12.50 (s, 1H, OH), 7.30-7.21 (m, 4H, (Xy (3H) + ArH of calixarene (1H)), 7.10-6.98 (m, 7H, Xy (3H) + ArH of calixarene (4H)), 6.87 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH of calixarene), 6.68 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH of calixarene), 6.58 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH of calixarene), 4.37 (d, $^2J_{H-H}$ = 13.0 Hz, 1H, $CH_2$), 4.32 (s, 1H, Ir–CH), 4.23 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 4.16 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.42 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.35 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.29 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 2.76 (s, 6H, Me of XyNC), 2.16 (s, 6H, Me of XyNC), 2.13 (s, 3H, $\eta^1$-Cp*), 1.96 (s, 3H, $\eta^1$-Cp*), 1.52 (s, 3H, $\eta^1$-Cp*), 1.37 (s, 3H, $\eta^1$-Cp*), 1.22 (s, 9H, $^t$Bu), 1.21 (s, 9H, $^t$Bu), 1.203 (s, 9H, $^t$Bu), 1.199 (s, 9H, $^t$Bu), 0.98 (s, 3H, $\eta^1$-Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 160.7, 152.2, 149.2, 147.4, 145.2, 144.9, 144.5, 144.1, 143.1, 142.8, 142.0, 139.9, 135.8, 135.0, 130.9, 129.5, 129.4, 129.1, 128.93, 128.89, 128.7, 128.5, 128.3, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 126.1, 126.0, 125.9, 125.8, 125.2, 124.3, 123.0, 122.9 (Ar + NC + C($sp^2$) of $\eta^1$-Cp*; 37 distinct signals for 38 different carbons), 51.2 (Ir–CH), 34.13, 34.09, 34.0, 33.95, 33.9, 33.8, 33.7, 33.5 ($CH_2$ and $C(CH_3)_3$), 32.1, 31.8 ($C(CH_3)_3$), 31.75 ($CH_3$ of $\eta^1$-Cp*), 31.72, 31.6 ($C(CH_3)_3$), 19.6, 18.7 ($CH_3$ of Xy), 13.8, 13.6, 11.0, 10.9 ($CH_3$ of $\eta^1$-Cp*). IR (KBr, $cm^{-1}$): 3450 ($\gamma_{OH}$), 2145, 2100 ($\gamma_{CN}$). Anal. Calcd for $C_{73}H_{89}Cl_2IrN_2O_4$ (**4**·$CH_2Cl_2$): C, 66.34; H, 6.79; N, 2.12. Found: C, 66.22; H, 6.68; N, 2.14.

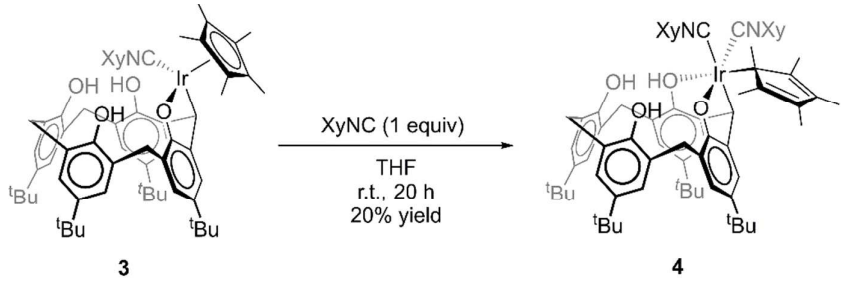
**Synthesis of [Ir(p-$^t$Bucalix[4]arene(3–)-$\kappa^3$-*O,C,O*)(CNXy)$_3$]·0.5$CH_2Cl_2$ (5·0.7$CH_2Cl_2$)**




**1a** **5**

To a *p*-xylene solution (22.0 mL) of **1a**·0.5$CH_2Cl_2$ (100.5 mg, 0.989 mmol) was added 2,6-xylyl isocyanide (67.3 mg, 0.514 mmol), and the mixture was stirred under reflux for 15 h. The solvent was removed under reduced pressure, and the residue was washed with methanol to yield [Ir(*p*-$^t$Bucalix[4]arene(3–)-$\kappa^3$-*O,C,O*)(CNXy)$_3$]·0.7$CH_2Cl_2$ (**5**·0.7$CH_2Cl_2$) as a white powder (66.1 mg, 0.0511 mmol, 51% yield). Analytically pure sample was obtained by recrystallization from dichloromethane. Spectral data for **5**·0.7$CH_2Cl_2$: $^1$H NMR ($C_6D_6$): δ 11.15 (s, 2H, OH), 7.39 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH of calixarene), 7.37 (d, $^4J_{H–H}$ = 2.0 Hz, 2H, ArH of calixarene), 7.16 (d, $^4J_{H–H}$ = 2.5 Hz, 2H, ArH of calixarene), 6.99 (d, $^4J_{H–H}$ = 2.0 Hz, 2H, ArH of calixarene), 6.83 (t, $^3J_{H–H}$ = 7.5 Hz, 1H, Xy), 6.70 (d, $^3J_{H–H}$ = 7.5 Hz, 2H, Xy), 6.67 (t, $^3J_{H–H}$ = 7.5 Hz, 2H, Xy), 6.54 (d, $^3J_{H–H}$ = 7.5 Hz, 4H, Xy), 5.72 (d, $^2J_{H–H}$ = 11.5 Hz, 1H, $CH_2$), 5.32 (s, 1H, Ir–CH), 5.18 (d, $^2J_{H–H}$ = 12.5 Hz, 2H, $CH_2$), 3.62 (d, $^2J_{H–H}$ = 12.5 Hz, 2H, $CH_2$), 3.59 (d, $^2J_{H–H}$ = 11.5 Hz, 1H, $CH_2$), 2.69 (s, 6H, Me of Xy), 1.86 (s, 12H, Me of Xy), 1.33 (s, 18H, $^t$Bu), 1.27 (s, 18H, $^t$Bu). $^{13}$C{$^1$H} NMR ($C_6D_6$): δ 164.6, 151.2, 141.0, 139.2, 138.6, 137.0, 135.6, 134.8, 132.3, 130.1, 129.9, 129.1, 128.3, 128.1, 128.0, 127.2, 125.3, 124.4, 123.8, 122.6, 121.0 (Ar + NC; 21 distinct signals for 22 different carbons), 47.0 (Ir–CH), 34.3, 33.9, 33.8 ($CH_2$ and *C*$(CH_3)_3$, two *C*$(CH_3)_3$ signals are overlapping), 32.1, 31.8 (C(*C*$H_3)_3$), 19.4, 18.1 (Me of Xy). IR (KBr, cm$^{-1}$): 3426($\gamma_{OH}$), 2205, 2155 ($\gamma_{CN}$). Anal. Calcd for $C_{71.7}H_{81.4}IrN_3O_4Cl_{1.4}$ (**5**·0.7$CH_2Cl_2$): C, 66.70; H, 6.35; N, 3.25. Found C, 66.95; H, 6.80; N, 3.19.

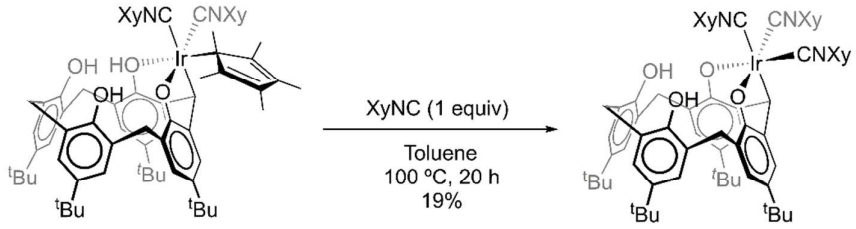
**Synthesis of 4 from 3**




**3** **4**

To a THF solution (2.0 mL) of **3** (10.3 mg, 9.3 μmol) was added 2,6-xylyl isocyanide (1.1 mg, 8.3 μmol), and the mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure to yield crude **4**, which was purified by recrystallization from dichloromethane/methanol to give **4**·$CH_2Cl_2$ (2.5 mg, 1.9 μmol, 20% yield).

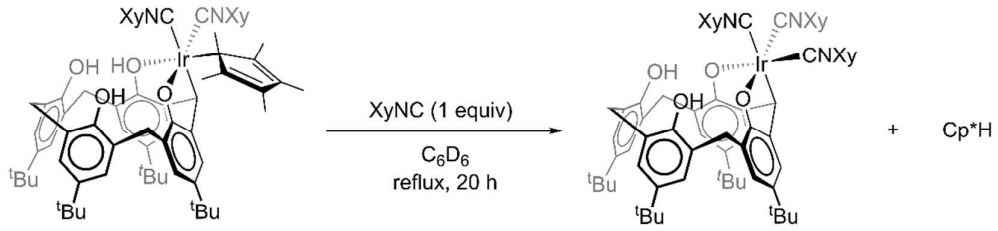
**Synthesis of 5 from 4**




**4** **5**

To a toluene solution (10.0 mL) of **4**·$CH_2Cl_2$ (100.4 mg, 0.0760 mmol) was added 2,6-xylyl isocyanide (13.7 mg, 0.104 mmol), and the mixture was stirred for 20 h at 100 °C. The solvent was removed under reduced pressure, and the residue was washed with methanol to yield **5**·0.7$CH_2Cl_2$ as a white powder (18.3 mg, 0.0142 mmol, 19% yield).

**Reaction of 4 and 1 equiv. of xylyl isocyanide in a J. Young NMR tube**




**4** **5**

In a J. Young NMR tube, a mixture of **4**·$CH_2Cl_2$ (9.9 mg, 7.5 μmol) and XyNC (1.1 mg, 8.4 μmol) dissolved in $C_6D_6$ (0.5 mL) was heated at 100 °C for 20 h. $^1$H NMR of the reaction mixture revealed relatively clean formation of **5** and generation of Cp* as shown in Figure S3.

**3. Details for X-ray diffraction analysis and crystallographic data of 1a-b, 2 and 4**

**1a**: Since one of the solvent molecules contained in the unit cell could not be modeled correctly, the contribution from disordered solvent molecules were removed by the program SQUEEZE[4] (PLATON[5]).

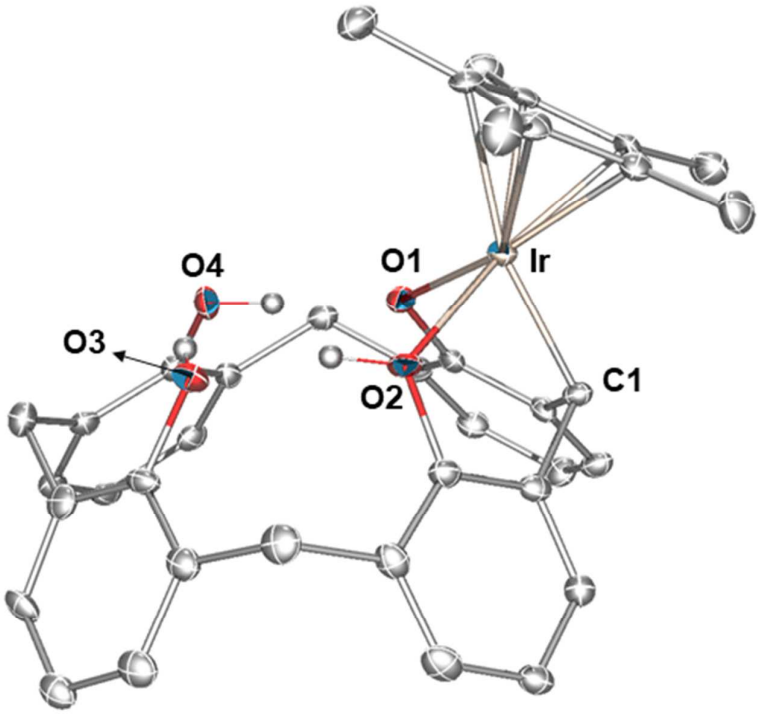



Figure S1. ORTEP drawing of **1a** with 50% probability. All hydrogen atoms except for the OH groups, $^{t}$Bu groups and a $CH_2Cl_2$ inside the cavity were omitted for clarity. Selected bond lengths [Å]: Ir–C(1): 2.106(4), Ir–O(1): 2.103(3), Ir–O(2): 2.171(3).

**1b**: Two independent molecules (molecule A and B) with similar structural characteristics were found in the unit cell. One of the $^{t}$Bu groups in molecule B is disordered over two positions in the ratio of 0.6 : 0.4.

**2**: one of the diethyl ether molecules encapsulated in the cavity of calix[4]arene is disordered over two positions in the ratio of 0.76 : 0.24. One of the $^{t}$Bu groups is disordered over two positions in the ratio of 0.7 : 0.3. The minor part was refined isotropically and the $^{t}$Bu group was refined without hydrogen atoms.

**4**: One of the $^{t}$Bu groups is disordered over two positions in the ratio of 0.56 : 0.44. Two THF molecules (inside and outside the cavity) are disordered over two positions in the ratio of 0.56 : 0.44.

Table S1. Crystarographical data for **1a**-**b**, **2** and **4**.

| | **1a** | **1b** | **2** | **4** |
|---|---|---|---|---|
| CCDC | 1824327 | 1824328 | 1824329 | 1824330 |
| formula | $C_{55}H_{71}O_4Cl_2Ir$ | $C_{56}H_{73}O_4Cl_4Rh$ | $C_{64}H_{84}O_8Rh$ | $C_{80}H_{86}IrN_2O_6$ |
| fw | 1059.21 | 1054.85 | 1084.22 | 1363.4 |
| crystal dimension | 0.21 × 0.19 × 0.17 | 0.24 × 0.20 × 0.17 | 0.23 × 0.22 × 0.19 | 0.19 × 0.07 × 0.05 |
| crystal system | monoclinic | triclinic | monoclinic | triclinic |
| space group | $P2_1/c$ | $P$-1 | $P2_1/c$ | $P$-1 |
| $a$, Å | 17.8177(18) | 13.1501(15) | 13.185(2) | 12.3197(18) |
| $b$, Å | 12.7252(11) | 16.8753(18) | 17.320(3) | 16.414(3) |
| $c$, Å | 25.120(3) | 25.342(3) | 28.330(4) | 17.365(3) |
| $a$, deg | 90 | 79.270(5) | 90 | 89.767(4) |
| $b$, deg | 102.6659(14) | 87.480(5) | 95.905(2) | 87.594(5) |
| $g$, deg | 90 | 75.877(3) | 90 | 87.488(4) |
| $V$, Å$^3$ | 5557.0(9) | 5358.3(10) | 6435.4(17) | 3505.1(10) |
| $Z$ | 4 | 4 | 4 | 2 |
| $r_{calcd}$, g cm$^{-3}$ | 1.266 | 1.308 | 1.119 | 1.292 |
| $F$(000) | 2176 | 2216 | 2308 | 1398 |
| $m$, cm$^{-1}$ | 25.38 | 5.61 | 3.13 | 19.57 |
| transmission factors range | 0.883 – 1 | 0.9231 – 1 | 0.8741 – 1 | 0.6706 – 0.9169 |
| index range | -23 ≤ h ≤ 23<br>-16 ≤ k ≤ 14<br>-32 ≤ l ≤ 32 | -17 ≤ h ≤ 17<br>-21 ≤ k ≤ 20<br>-26 ≤ l ≤ 32 | -16 ≤ h ≤ 14<br>-21 ≤ k ≤ 21<br>-29 ≤ l ≤ 34 | -15 ≤ h ≤ 12<br>-21 ≤ k ≤ 15<br>-22 ≤ l ≤ 22 |
| no. reflections total | 44753 | 44281 | 45881 | 29078 |
| unique ($R_{int}$) | 12592 (0.0504) | 23584 (0.0449) | 12515 (0.0555) | 15456 (0.0554) |
| $I > 2\sigma(I)$ | 11076 | 16643 | 10746 | 13495 |
| no. parameters | 582 | 1248 | 733 | 900 |
| *R1* (I > 2σ(I))[a] | 0.0439 | 0.0614 | 0.073 | 0.06 |
| *wR2* (all data)[b] | 0.0869 | 0.1778 | 0.2073 | 0.1189 |
| GOF [c] | 1.096 | 1.052 | 1.095 | 1.061 |
| max diff peak / hole, e Å$^{-3}$ | 1.305/-1.257 | 1.115/-1.002 | 1.832/-0.974 | 1.519/-2.066 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, w = $1/[\sigma^2F_o^2 + (aP)^2 + bP]$ ($a$ and $b$ are constants suggested by the refinement program; P = $[\max(F_o^2,0) + 2F_c^2]/3$). [c] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} -$

$N_{params}$)]$^{1/2}$.

**4. Preliminary X-ray diffraction analysis of 3 and 5**

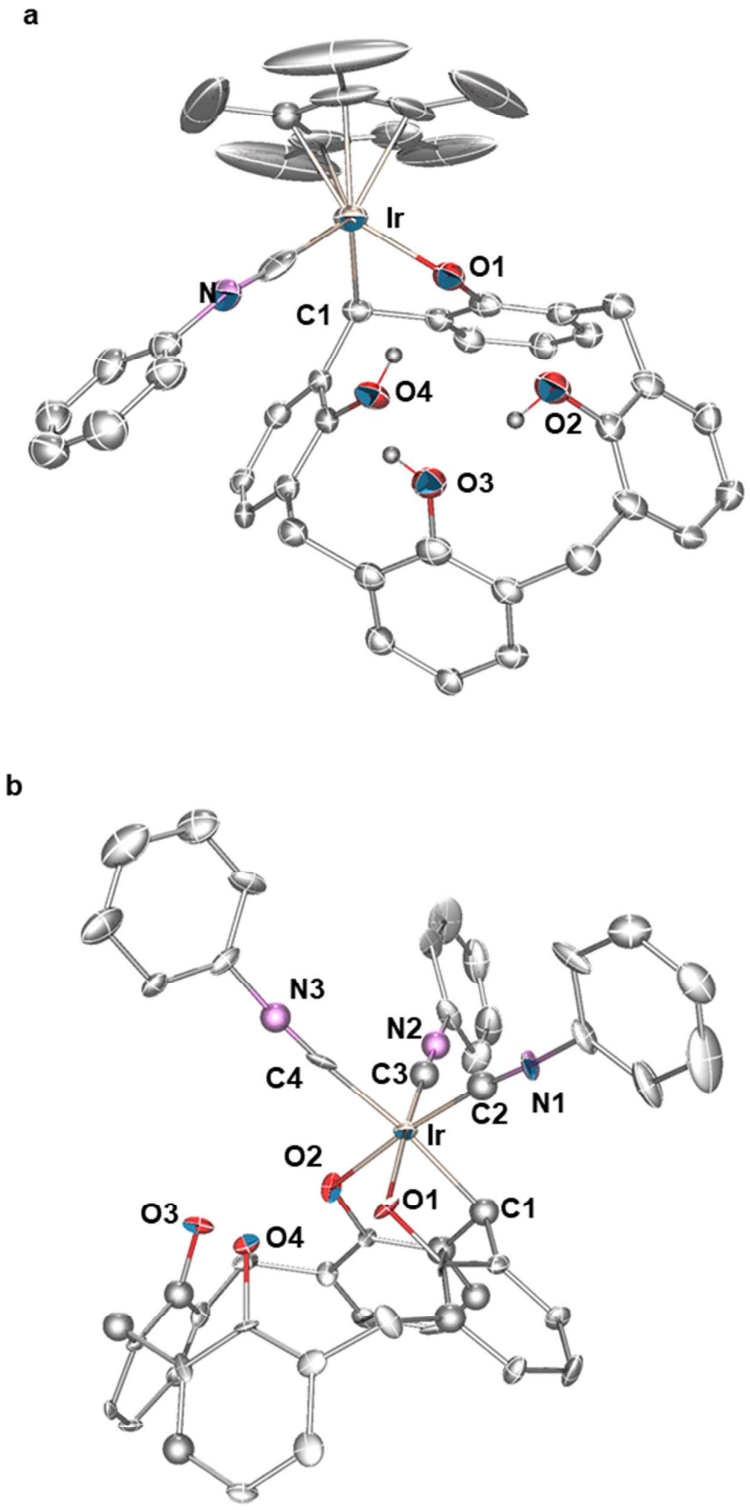



Figure S2. Preliminary molecular structures of **4** (a; top) and **5** (b; bottom) with thermal ellipsoid plot at 50% probability.

**5. Direct observation of Cp*H in the reaction of 4 and 1 equiv. of XyNC**

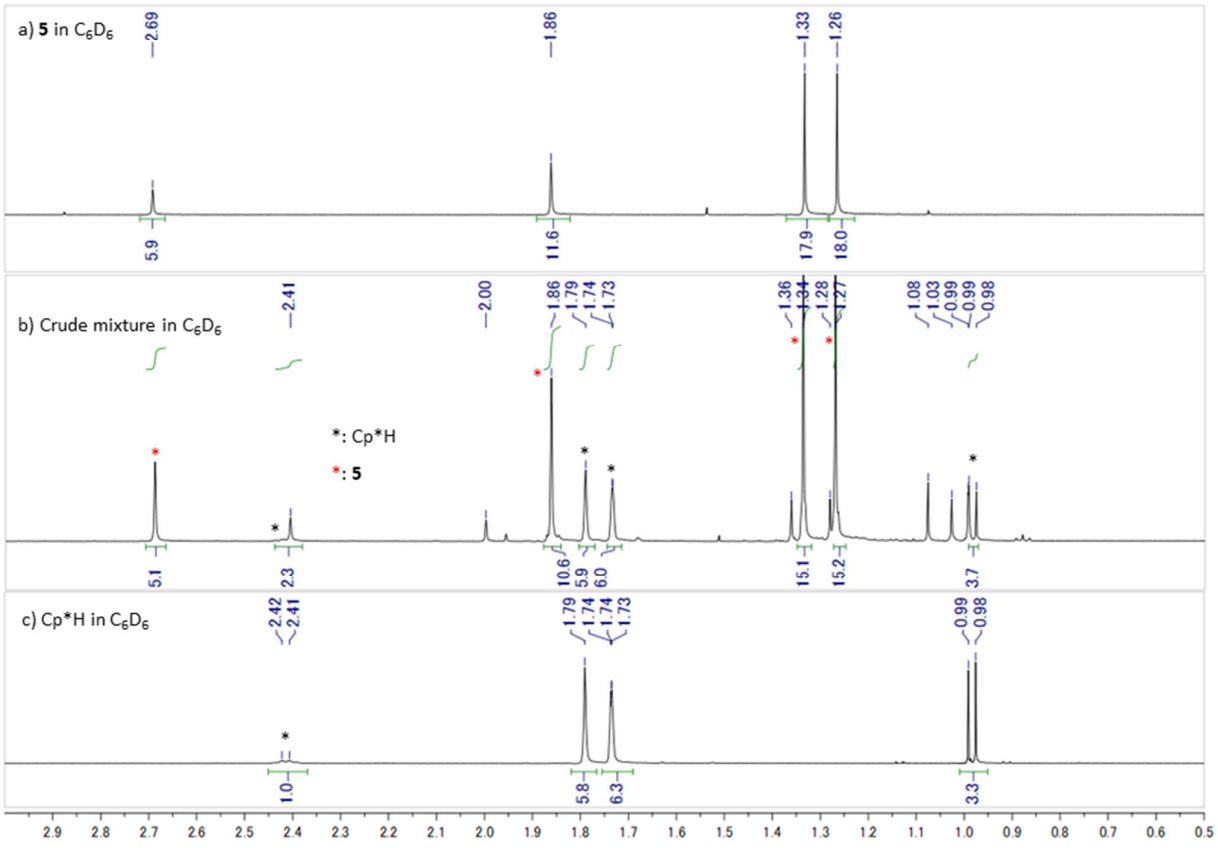
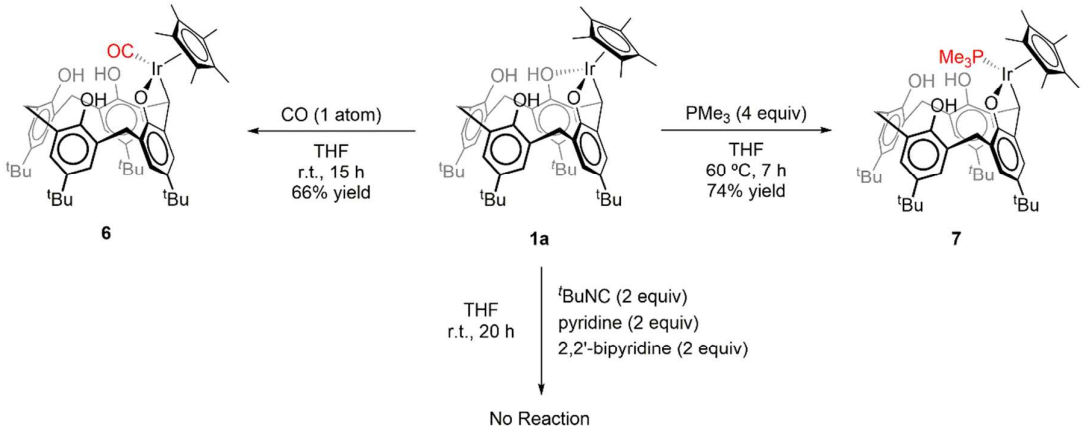



Figure S3. Partial $^{1}$H NMR spectra (0.5-3 ppm) of complex **5** in $C_6D_6$ (a), the crude mixture after refluxing for 20 h (b) and Cp*H in $C_6D_6$ (c). The black * and red * in (b) indicate the signals derived from Cp*H and **5**, respectively.

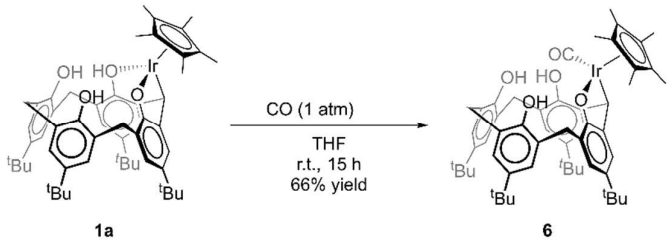
**6. Reactions of 1a with other donors**

Reactions of **1a** with other donors such as CO, $PMe_3$, $^t$BuNC, pyridine and 2,2'-bipyridine were investigated under similar conditions to that for the XyNC cases (Scheme S1). In the reactions with CO and $PMe_3$, only mono-CO adduct **6** and mono-$PMe_3$ adduct **7** were obtained in 66 and 74% yields, respectively, but no further product accompanied by ring slippage was observed. Details for these experiments and spectroscopic data are shown below. In contrast, In the case of $^t$BuNC, pyridine and 2,2'-bipyridine, no reaction took place judging from the $^1$H NMR spectra of crude reaction mixtures. The reason of the different reactivities of **1a** toward XyNC and other donors is still unclear.




**Scheme S1.** Reactions of **1a** with various donors.

**Reaction of 1a with CO (1 atom)**




A THF solution (3.0 mL) of **1a**·0.5$CH_2Cl_2$ (29.9 mg, 29.4 μmol) was stirred for 15 h under a CO atmosphere. The solvent was removed under reduced pressure and the residual solvent was recrystallized from dichloromethane/methanol to give [Cp*Ir{*p*-$^t$Bucalix[4]arene(2–)-$\kappa^2$-*O*,*C*}(CO)] (**6**) as yellow crystals (20.3 mg, 16.4 μmol, 56%). $^1$H NMR ($CDCl_3$) δ 9.63 (br, 2H, OH), 7.07 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 7.06 (s, OH), 7.03 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 6.98 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 6.95 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 6.90 (m, 2H, ArH), 6.68 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 6.61 (d, $^4J_{H–H}$ = 2.0 Hz, 1H, ArH), 4.68 (s, 1H, Ir–CH), 4.64 (d, $^2J_{H–H}$ = 12.4 Hz, 1H, $CH_2$), 4.36 (d, $^2J_{H–H}$ = 13.8 Hz, 1H, $CH_2$), 4.01 (d, $^2J_{H–H}$ = 13.8 Hz, 1H, $CH_2$), 3.52 (d, $^2J_{H–H}$ = 14.3 Hz, 1H, $CH_2$), 3.49 (d, $^2J_{H–H}$ = 14.3 Hz, 1H, $CH_2$), 3.17 (d, $^2J_{H–H}$ = 12.4 Hz, 1H, $CH_2$), 1.69 (s, 15H, Cp*), 1.28 (s, 9H, $^t$Bu), 1.23 (s, 9H, $^t$Bu), 1.18 (s, 9H, $^t$Bu), 1.12 (s, 9H, $^t$Bu).

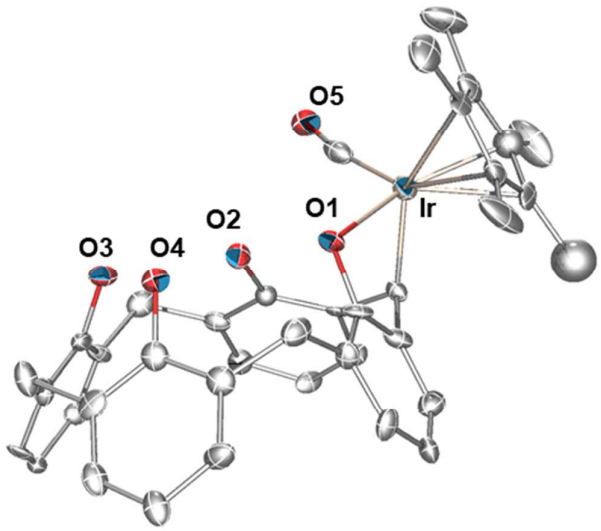



Figure S4. Preliminary molecular structure of [Cp*Ir{*p*-$^{t}$Bucalix[4]arene(2–)-κ$^{2}$-*O,C*}(CO)] (**6**). All the hydrogen atoms and the $^{t}$Bu groups were omitted for clarity.

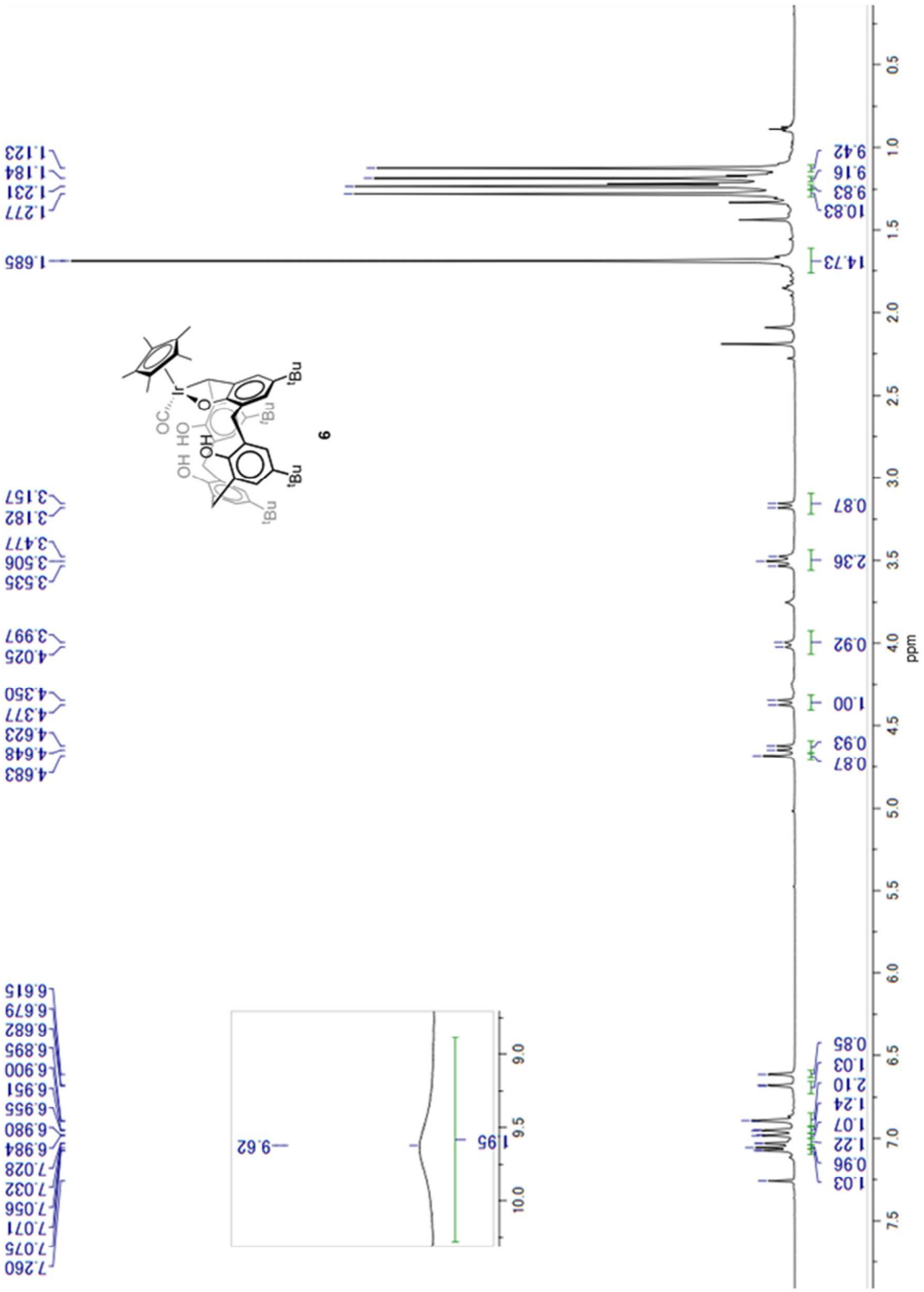
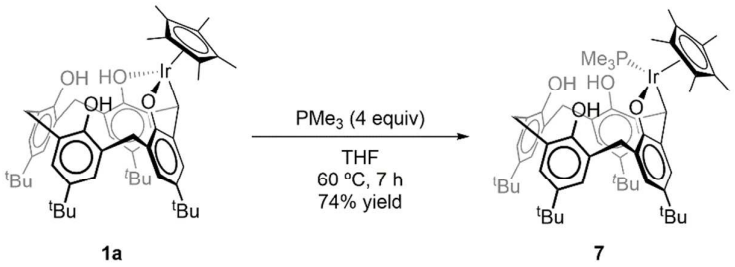


Figure S5. $^{1}$H NMR of [Cp*Ir{*p*-$^{t}$Bucalix[4]arene(2–)-κ$^{2}$-*O,C*}(CO)] (**6**) recorded in $CDCl_3$.

**Reaction of 1a with $PMe_3$**




**1a** **7**

In this reaction, *in situ* generated **1a** was used. A THF solution (3 mL) of *p*-$^t$Bucalix[4]arene (30.0 mg, 0.0313 mmol) and $[(Cp^*Ir)_2(OH)_3](OAc)$ (25.0 mg, 0.0214 mmol) was heated at 60 °C for 6 h. After removing the solvent under reduced pressure, the resulting yellow solid was washed by MeOH and dried well under vacuum to give **1a** as a yellow solid. To a THF solution (3 mL) of thus obtained **1a** $PMe_3$ (1. 0 M in THF, 80 µL, 0.080 mmol) was added and the mixture was heated at 60 °C for 7 h to give yellow suspension. After removing the insoluble material by filtration through Celite, the solution was dried up. Recrystallization of the resulting solid by $CH_2Cl_2$/MeOH afforded mono-$PMe_3$ adduct **7** as yellow needle crystals (24.3 mg, 0.0231 mmol, 74% yield). Spectral data for **7**: $^1$H NMR ($CDCl_3$): δ 7.91, 7.43 (s, 1H each, OH), 7.07 (d, $^4J_{H-H}$ = 2.5 Hz, 1H, ArH), 7.05 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH), 6.99 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 6.97 (s, 1H, ArH), 6.83 (s, 2H, ArH), 6.75 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, ArH), 5.91 (s, 1H, OH), 5.69 (s, 1H, Ir–CH), 4.25 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.84 (d, $^2J_{H-H}$ = 13.9 Hz, 2H, $CH_2$), 3.75 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.36 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, $CH_2$), 3.25 (d, $^2J_{H-H}$ = 13.9 Hz, 1H, $CH_2$), 1.57 (s, 15H, Cp*), 1.29, 1.24, 1.23, 1.19 (s, 9H each, $^t$Bu), –0.11 (d, $^2J_{P-H}$ = 10.2 Hz, 9H, $PMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.9, 150.6, 148.0, 147.0, 143.9, 141.8, 141.3, 139.45, 139.40, 136.0, 135.5, 131.5, 129.6, 129.0, 128.4, 128.0, 127.5, 127.0, 125.4, 125.3, 124.8, 124.3, 121.5 (s, Ar), 90.4 (d, $^2J_{P-C}$ = 3.4 Hz, $C_5Me_5$), 39.0, 34.1, 33.9, 33.7, 32.9, 32.3, 32.1, 31.9, 31.8 (s, $CH_2$ and $^t$Bu; 9 distinct signals for 11 different carbons), 27.2 (d, $^2J_{P-C}$ = 4.9 Hz, Ir–CH), 13.1 (d, $^1J_{P-C}$ = 35.2 Hz, $PMe_3$), 9.1 (s, $C_5Me_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –34.5 (s). Anal. Calcd for $C_{57.5}H_{79}O_4IrPCl$ (**7**·0.5$CH_2Cl_2$): C, 63.19; H, 7.29. Found C, 63.16; H, 7.22.

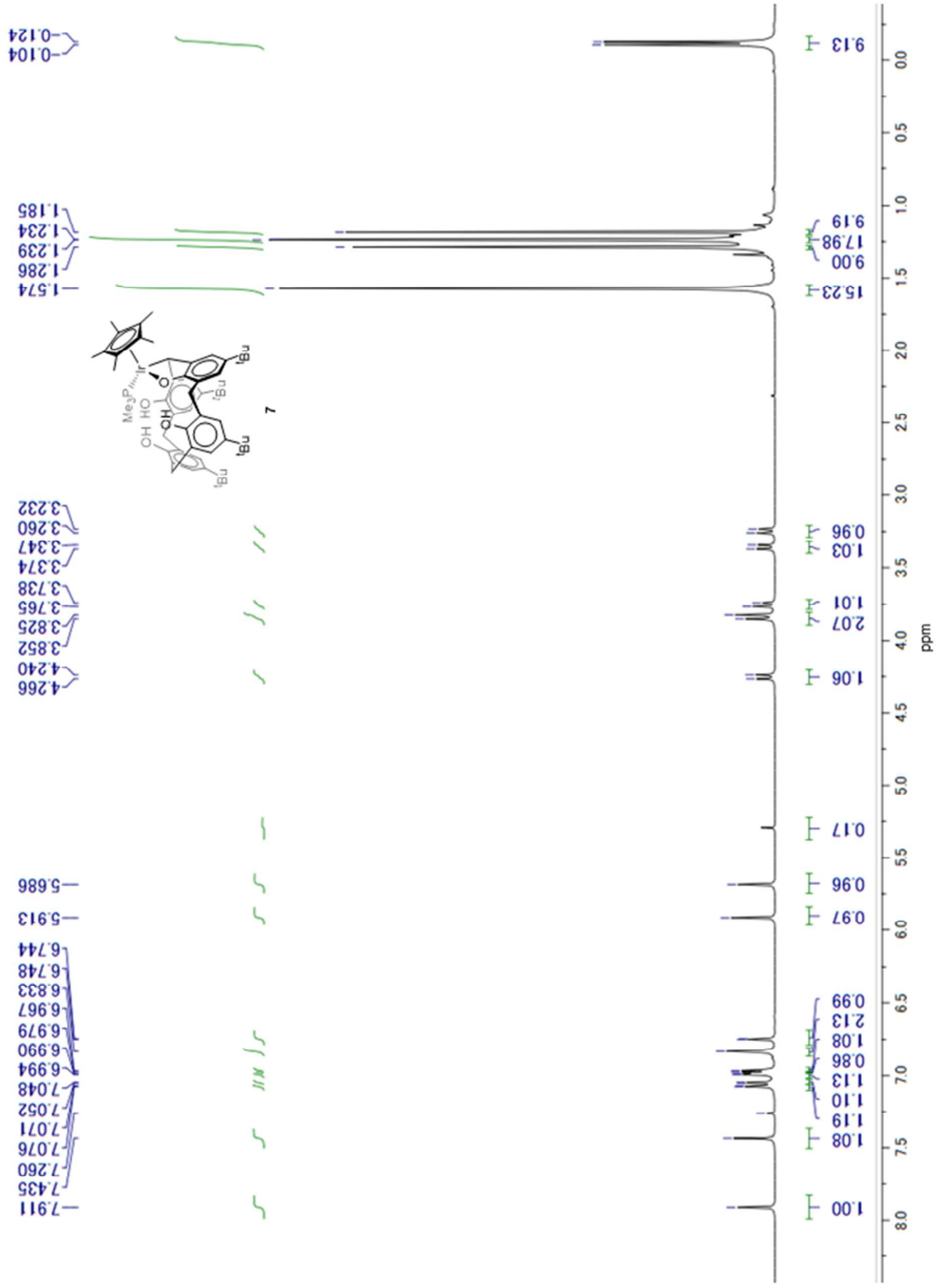


Figure S6. $^{1}$H NMR of [Cp*Ir{*p*-$^{t}$Bucalix[4]arene(2–)-κ$^{2}$-*O*,*C*}(PMe$_3$)] (**7**) recorded in $CDCl_3$.

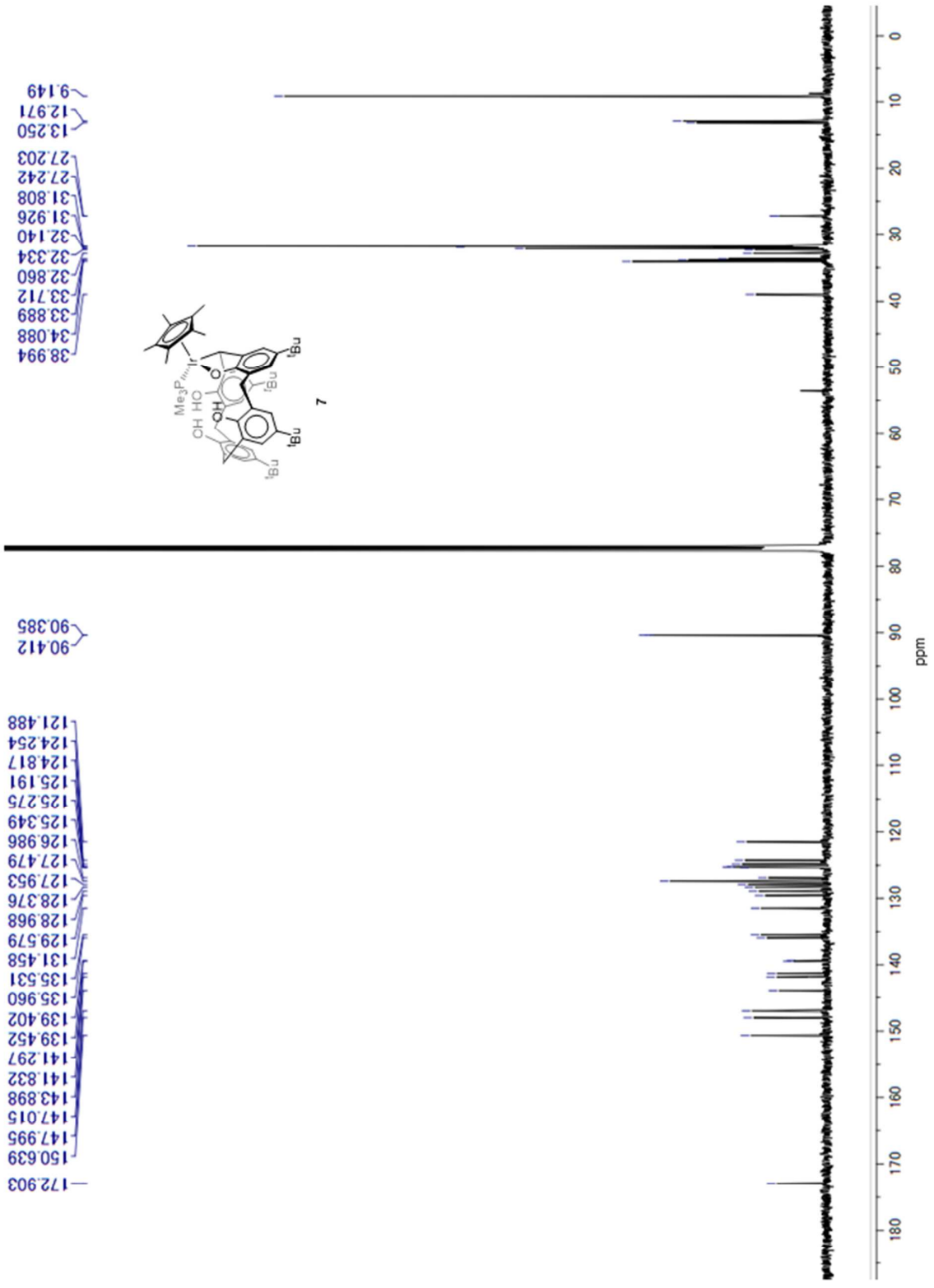



Figure S7. $^{13}$C NMR of [Cp*Ir{*p*-$^{t}$Bucalix[4]arene(2–)-κ$^{2}$-*O*,*C*}(PMe$_3$)] (**7**) recorded in $CDCl_3$.

## 7. $^{1}H$ and $^{13}C$ NMR charts for the new compounds

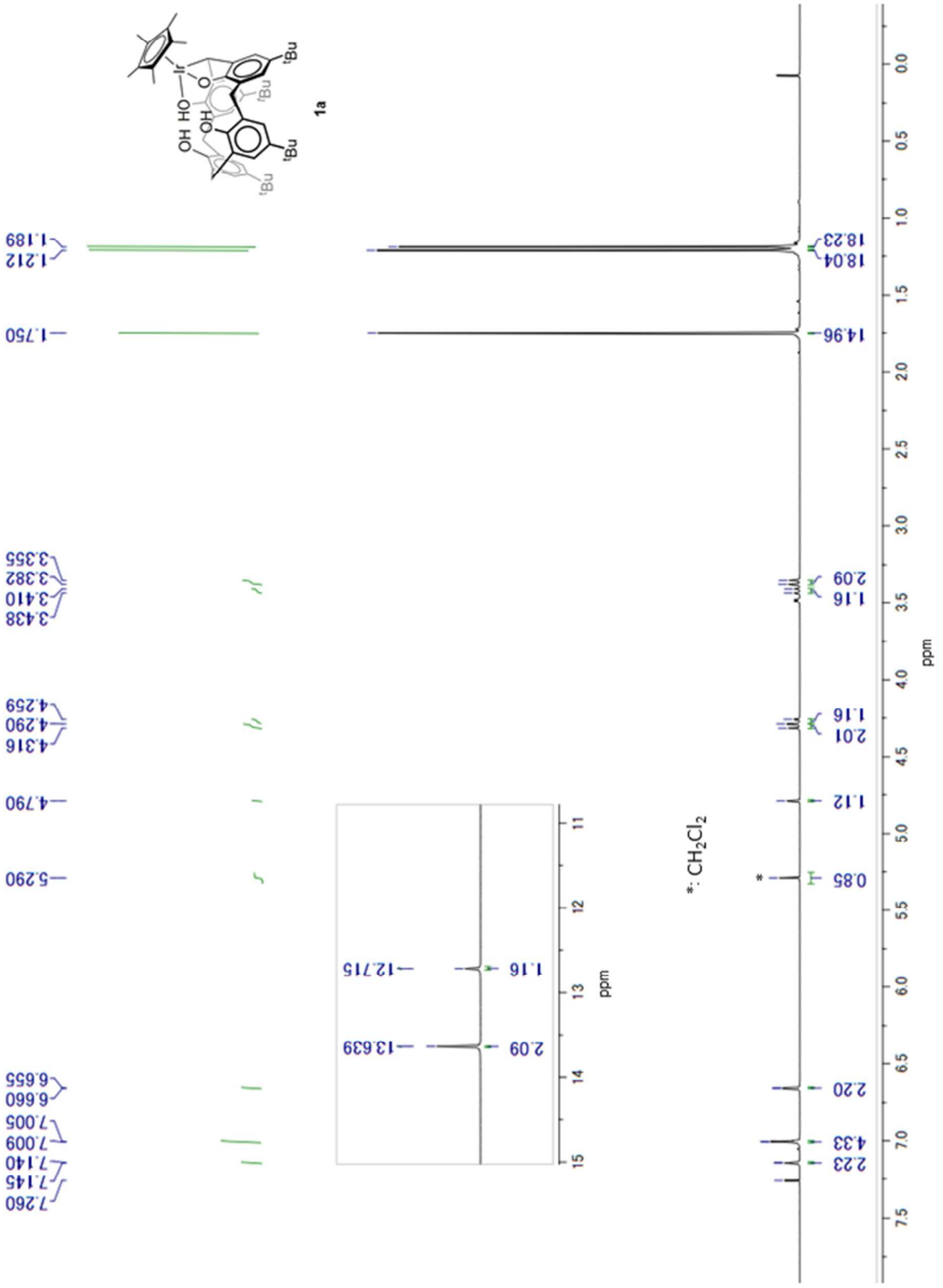



Figure S8. $^{1}H$ NMR spectrum of **1a** recorded in $CDCl_3$.

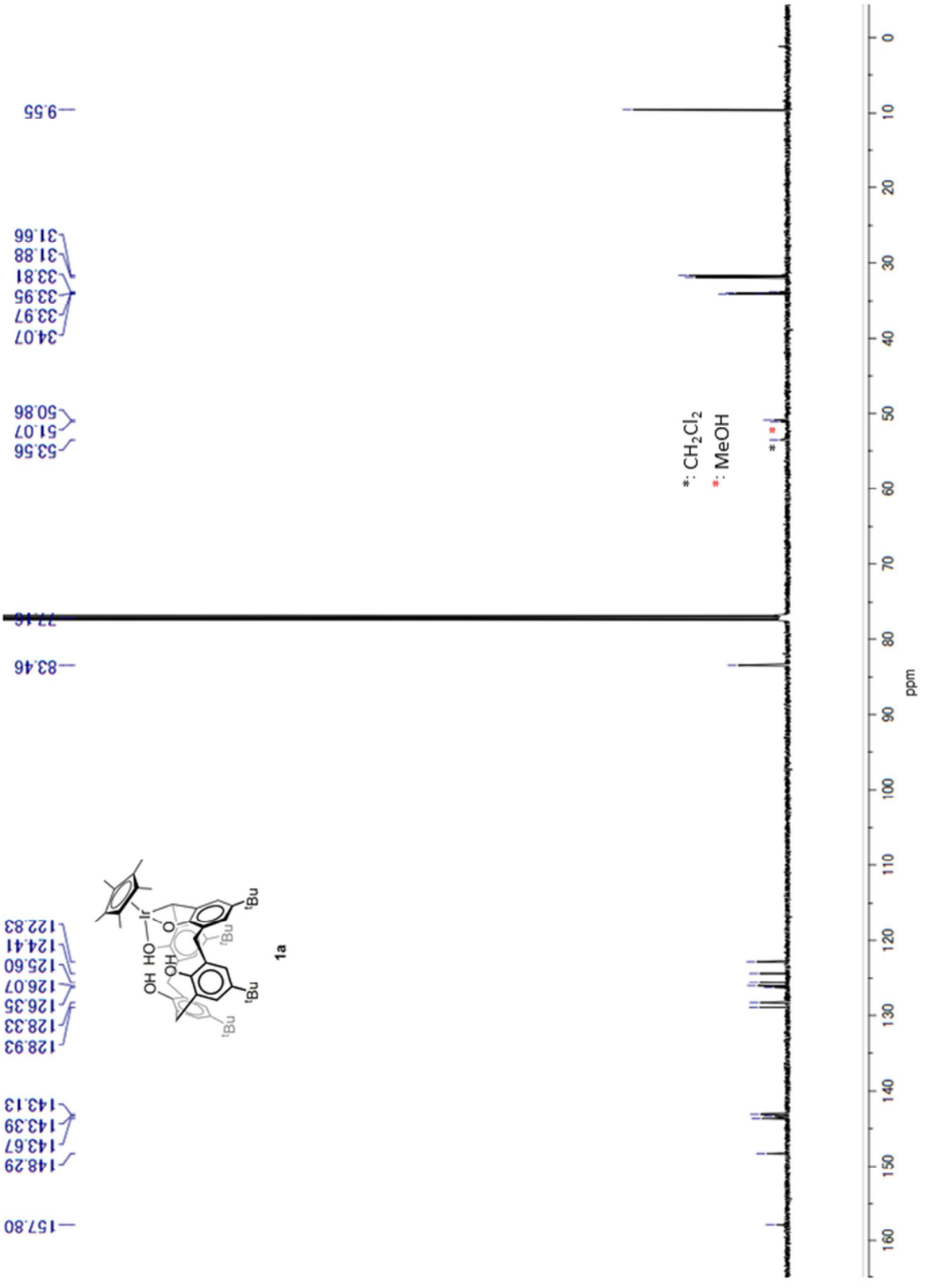



Figure S9. $^{13}C$ NMR spectrum of **1a** recorded in $CDCl_3$.

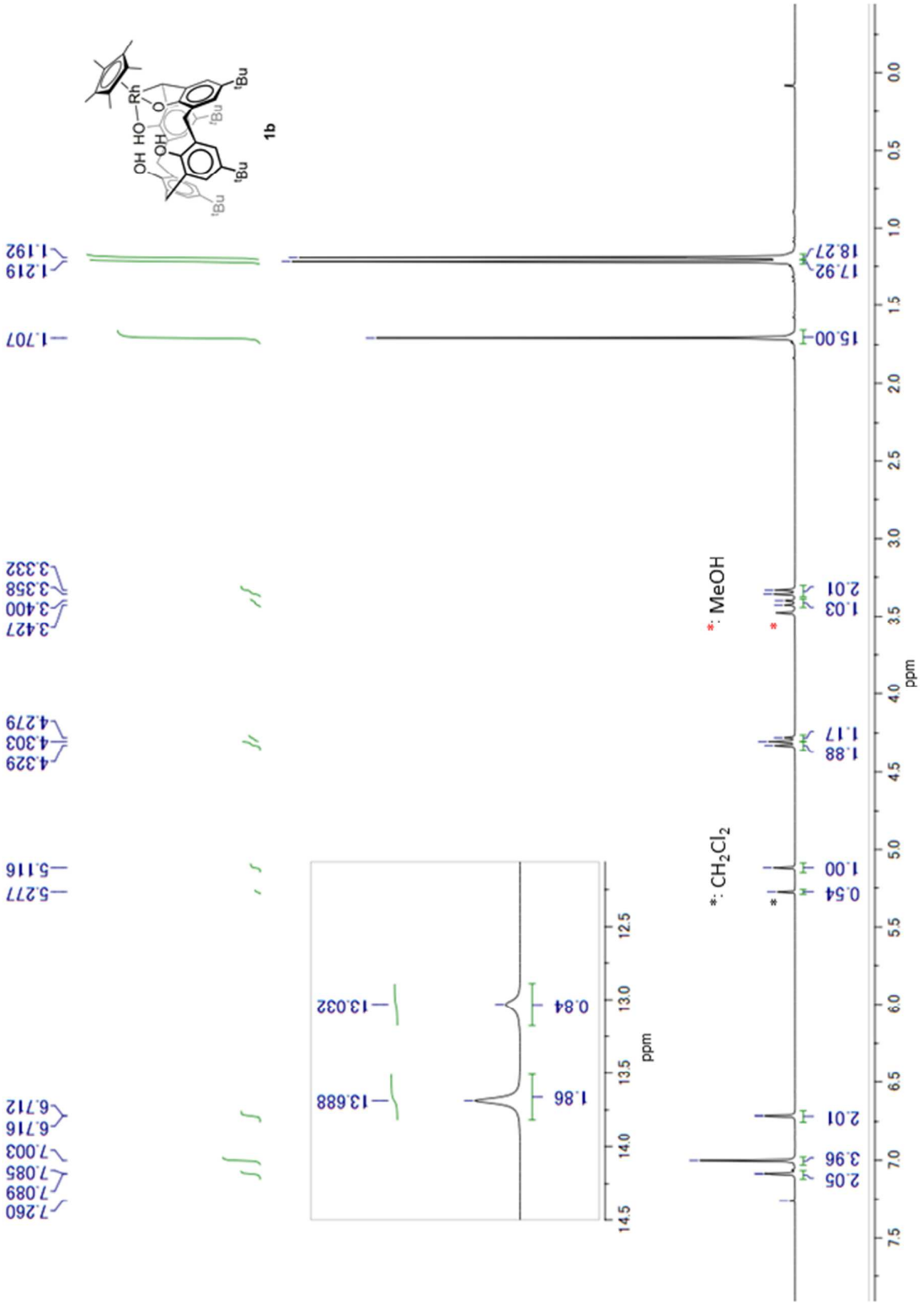



Figure S10. $^{1}$H NMR spectrum of **1b** recorded in $CDCl_3$.

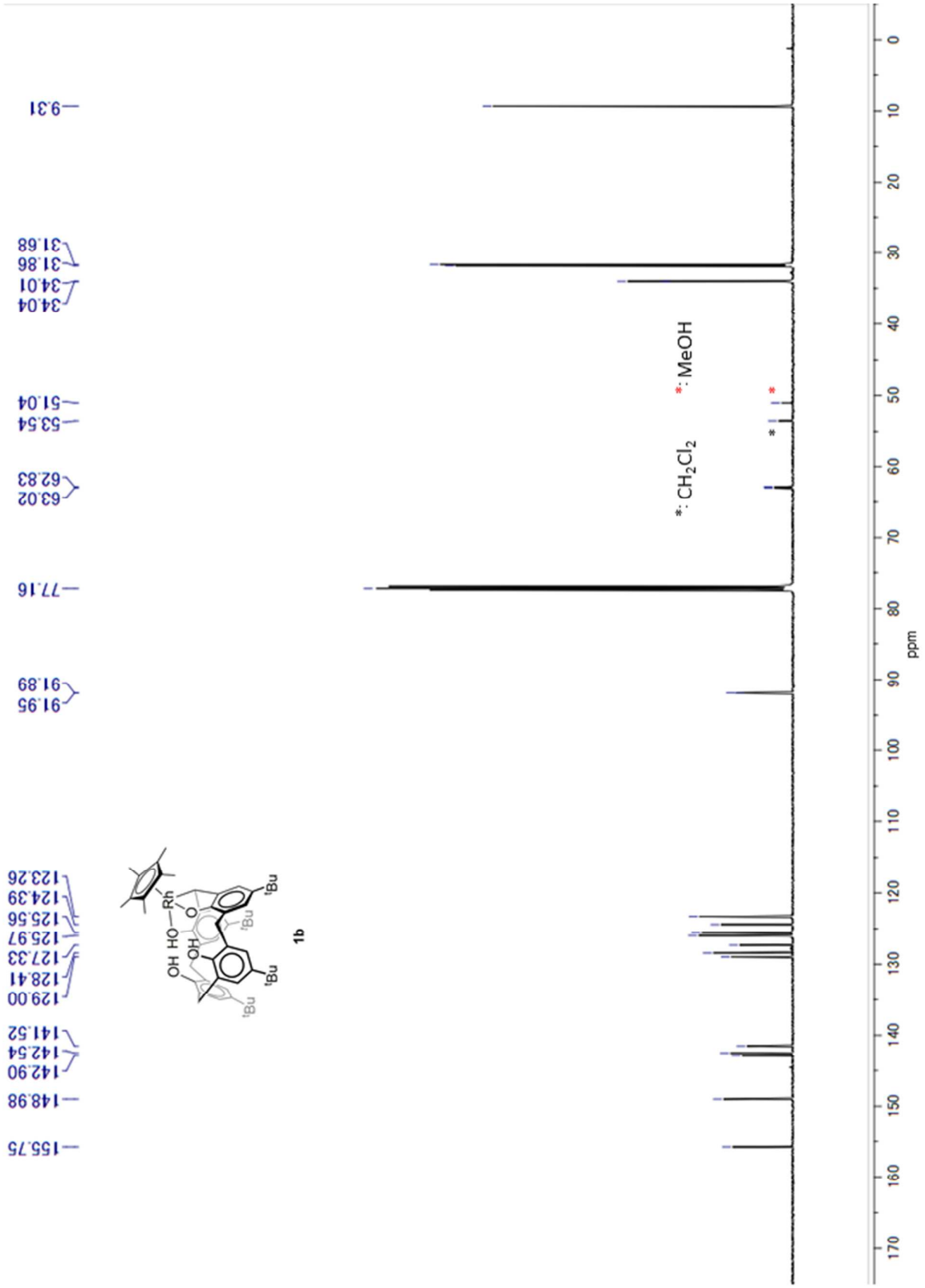



Figure S11. $^{13}C$ NMR spectrum of **1b** recorded in $CDCl_3$.

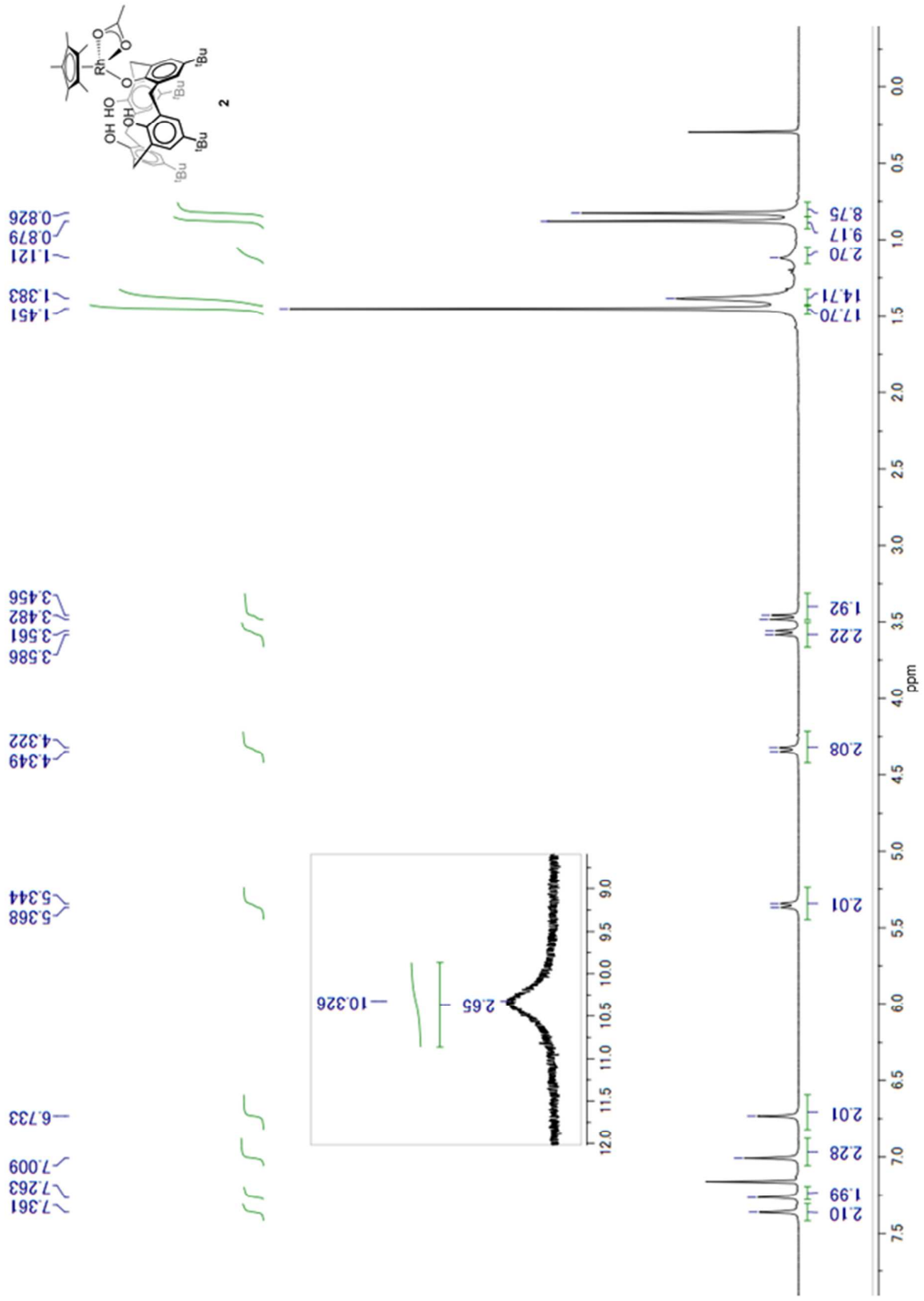



Figure S12. $^{1}$H NMR spectrum of **2** recorded in $C_6D_6$.

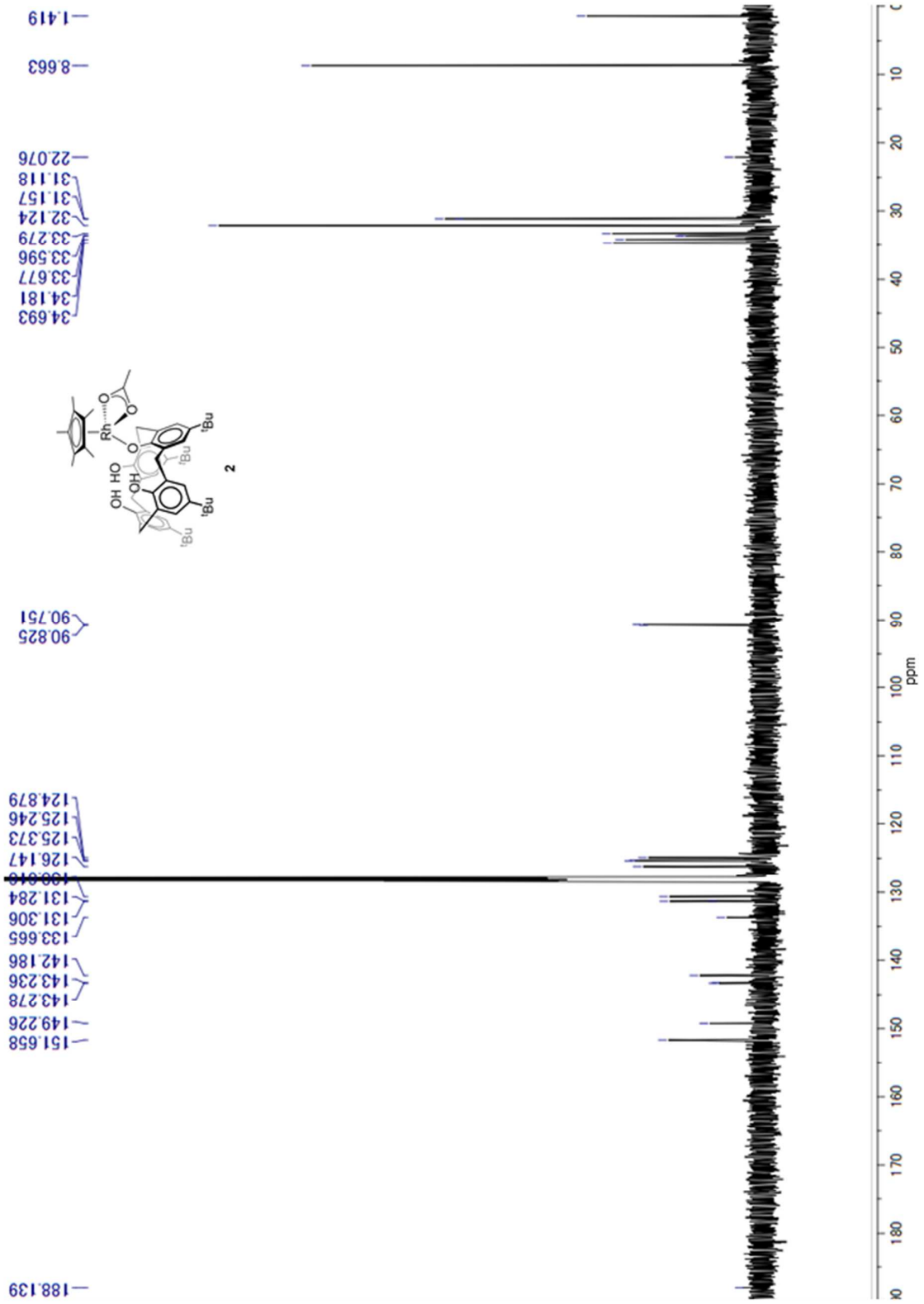



Figure S13. $^{13}C$ NMR spectrum of **2** recorded in $C_6D_6$.

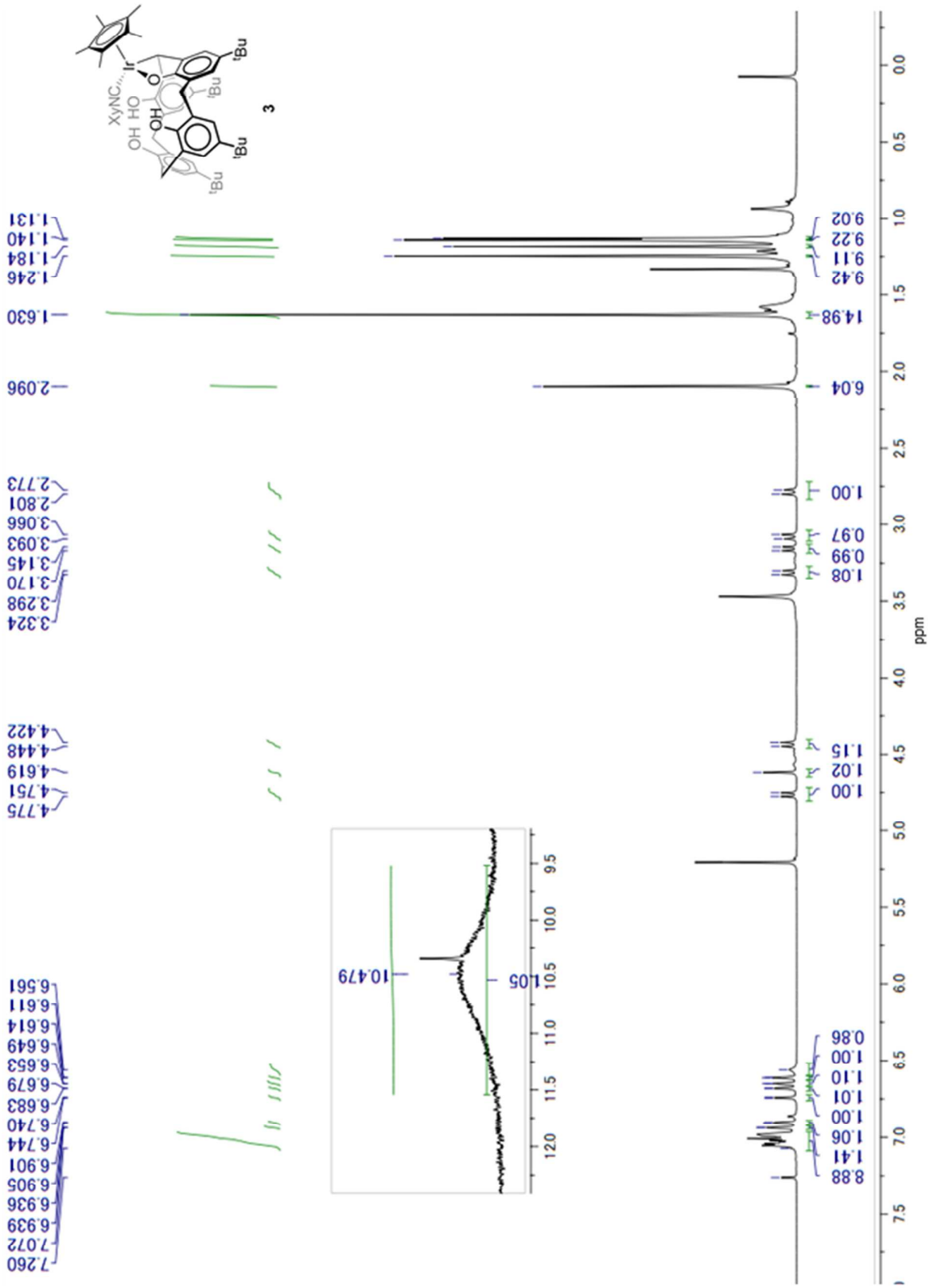


Figure S14. $^{1}H$ spectrum of **3** recorded in $CDCl_3$.

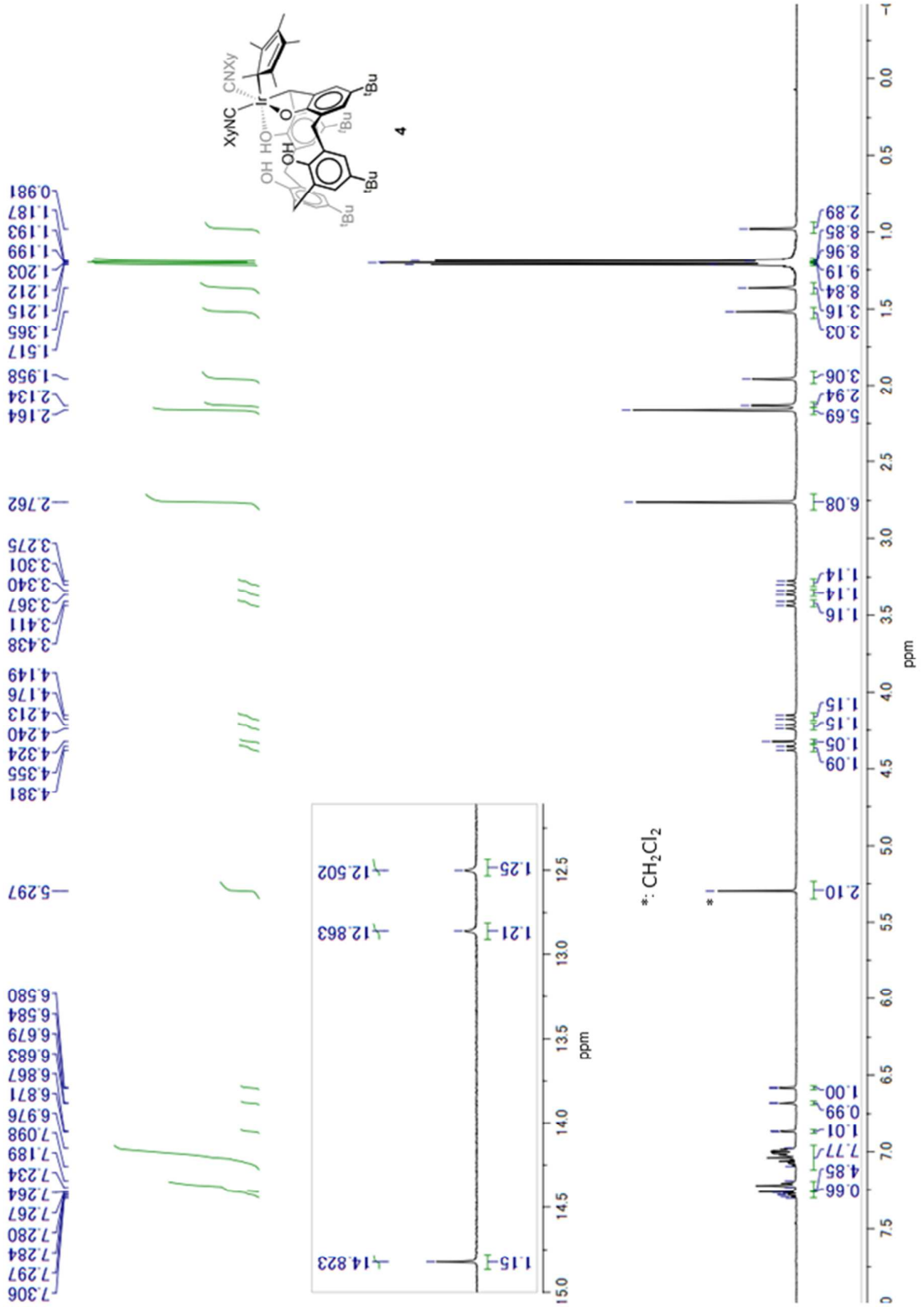



Figure S15. $^{1}$H spectrum of **4**·$CH_2Cl_2$ recorded in $CDCl_3$.

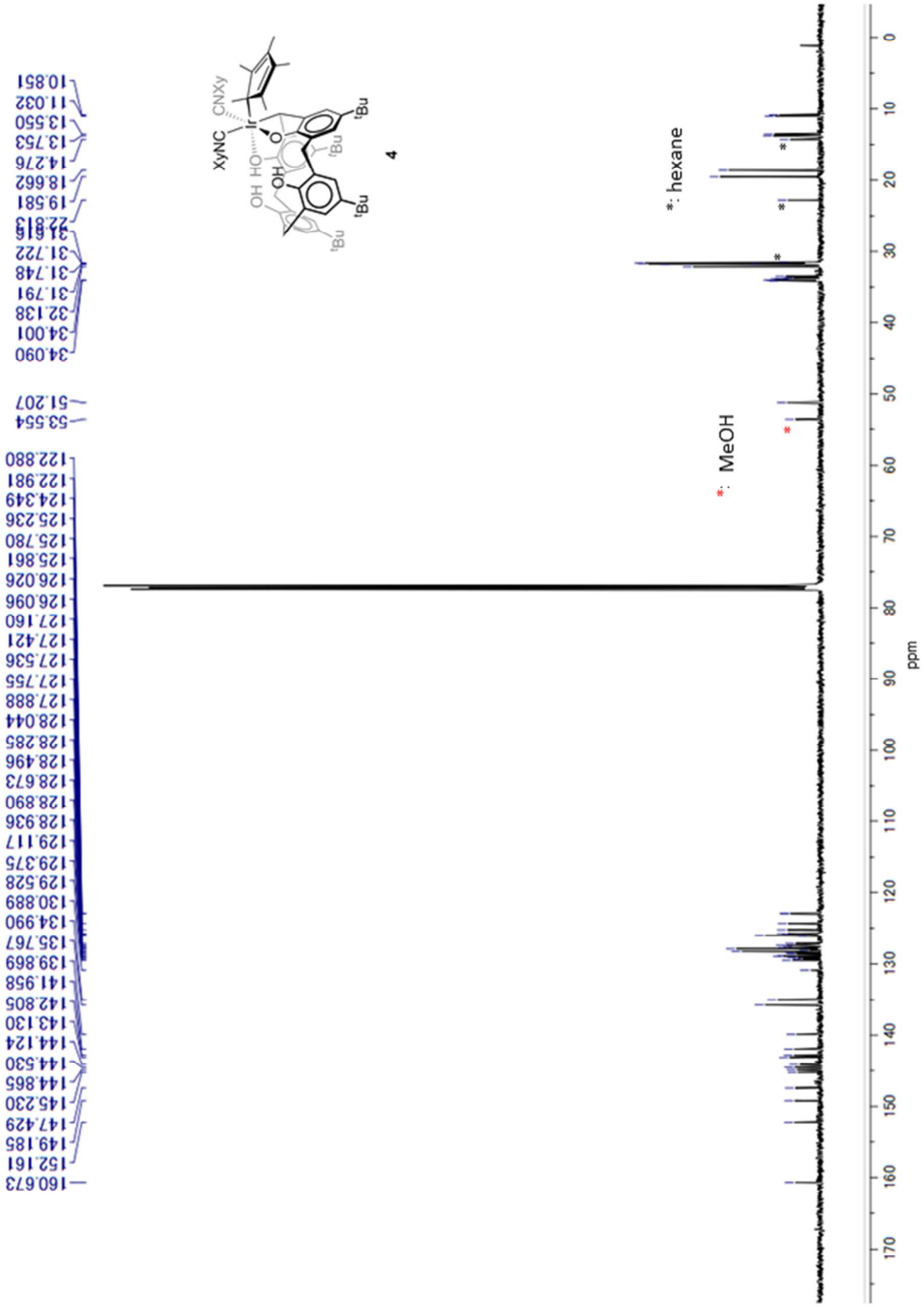



Figure S16. $^{13}C$ NMR spectrum of **4** recorded in $CDCl_3$.

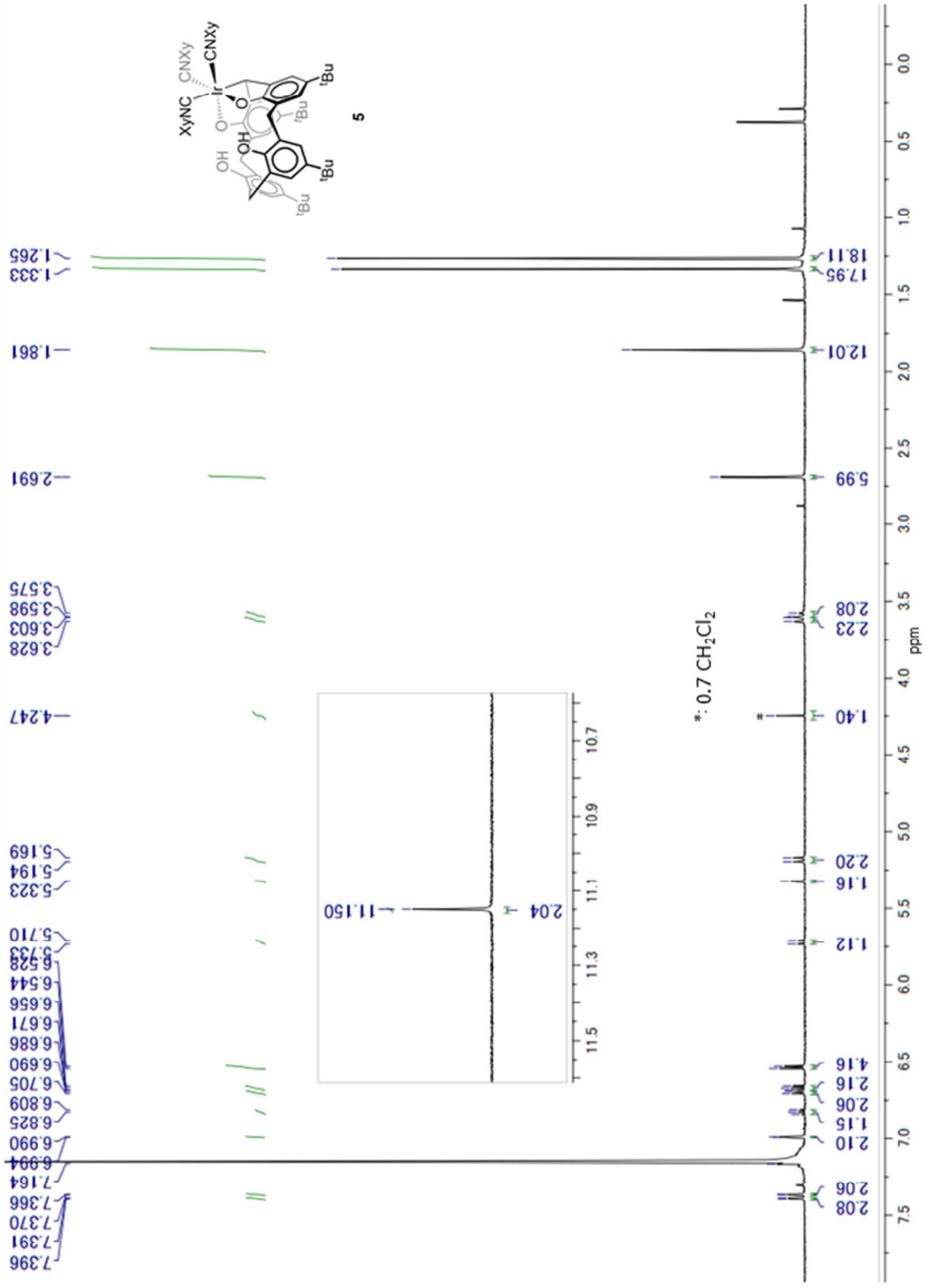



Figure S17. $^{1}$H NMR spectrum of **5** recorded in $C_6D_6$.

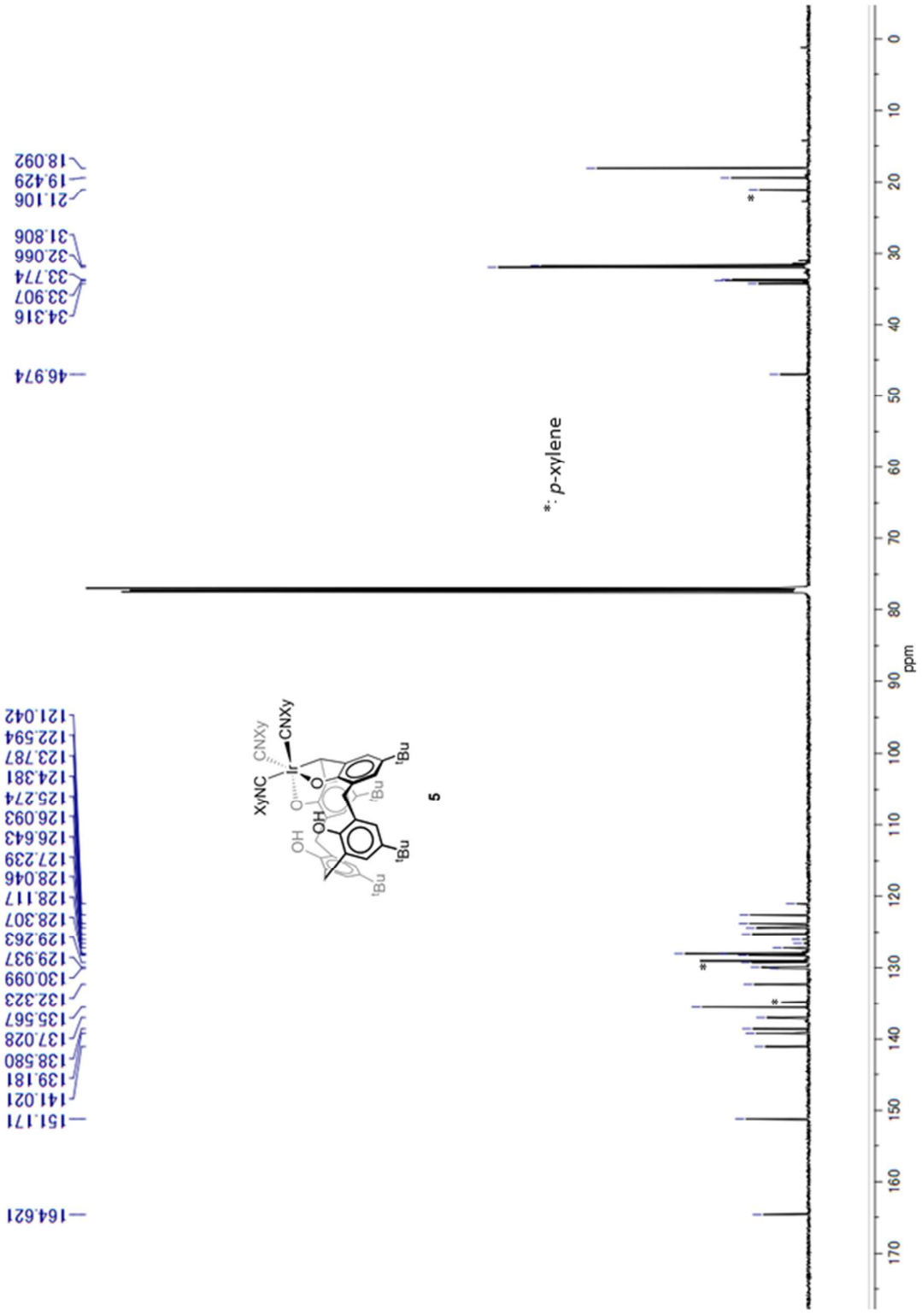



Figure S18. $^{13}C$ NMR spectrum of **5** recorded in $CDCl_3$.

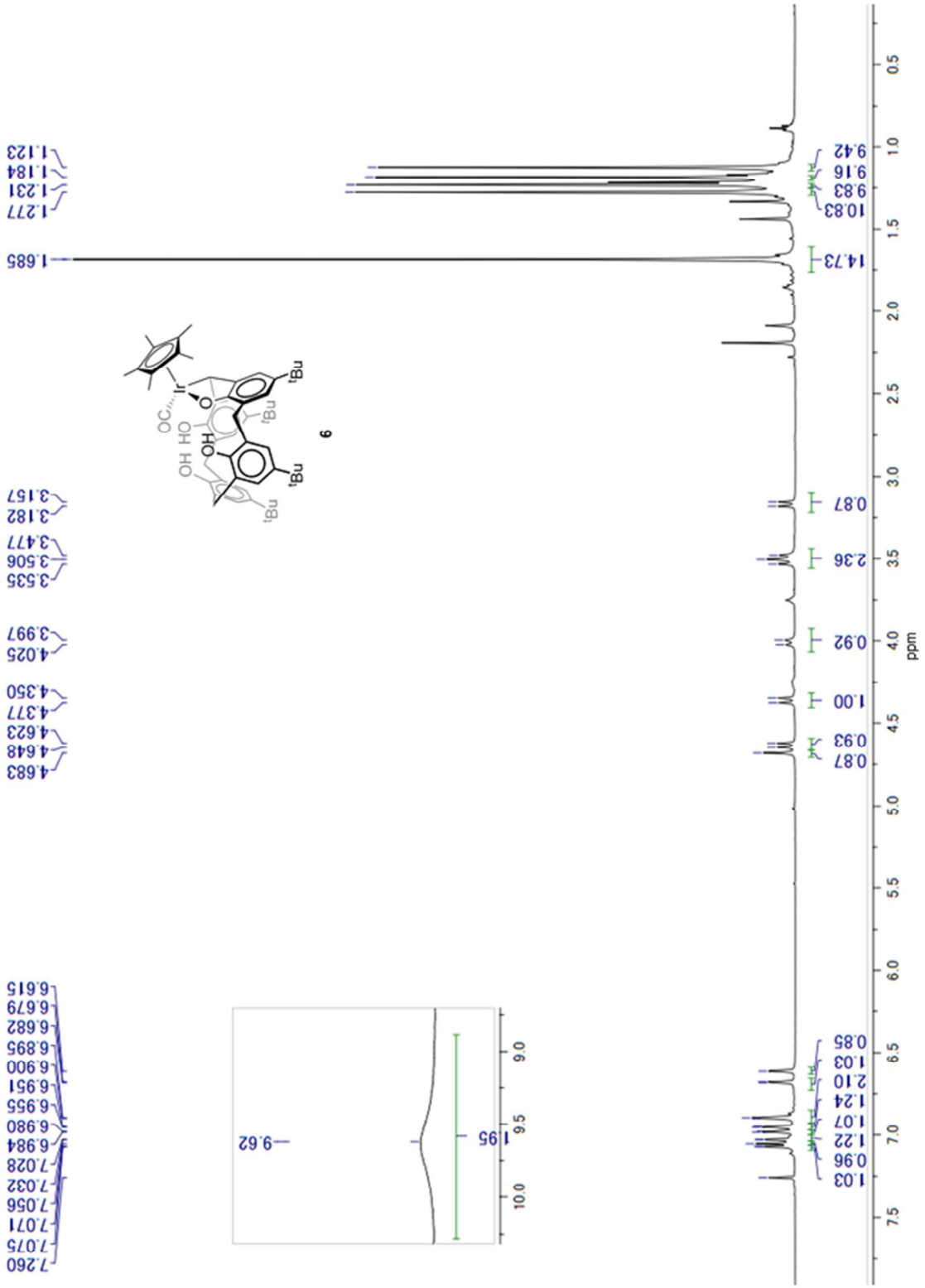



Figure S19. Preliminary $^{1}$H NMR spectrum of **6** recorded in $CDCl_3$.

## 8. References

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