Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## *$CO_2$ fixation employing an Iridium(I)- hydroxide complex*

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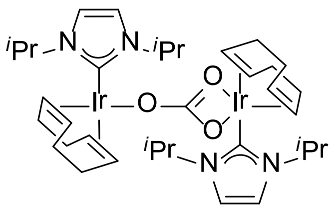
# Experimental procedures and characterization data

## General considerations

All manipulations and reactions were performed inside an Argon-filled MBraun glovebox unless stated otherwise. All reagents were supplied by Aldrich and used without further purification. $[Ir(cod)Cl]_2$ was provided by Umicore AG. Solvents were distilled and dried as required. NMR data was obtained using either a Bruker 300 MHz or 400 MHz ($^1$H observe frequency) spectrometer at 303 K in the specified deuterated solvent. All chemical shifts are given in ppm and coupling constants in Hz. Signals on the $^{13}C\{^1H\}$ spectra are singlets unless otherwise stated. Spectra were referenced to residual protonated solvent signals (for $^1$H) or solvent signals (for $^{13}$C): ($C_6D_6$: $^1$H $\delta$ 7.16 ppm, $^{13}$C $\delta$ 128.06 ppm; THF-$d_8$: $^1$H $\delta$ 1.72, 3.58 ppm, $^{13}$C $\delta$ 25.31, 67.21 ppm). Infrared spectra ($\nu$) were recorded on a Shimadzu Fourier transform IR Affinity-1 Infrared specrophotometer using a MIRacle$^{TM}$ single reflection horizontal ATR (diamond). Samples were placed directly on the crystal (ATR) in the solid state. Only characteristic peaks have been quoted. Elemental analyses were performed at the London Metropolitan University. Known compounds **7**, **10**, **15**, **18 – 22** were prepared following reported procedures.[1]

## Synthetic Procedures and Characterization data

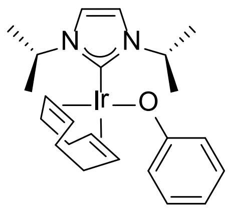



$[\{Ir(cod)(I^iPr)\}_2(\mu\text{-}\kappa^1{:}\kappa^2\text{-}CO_3)]$ **8**

*In solution:* A J. Young NMR tube was charged with $[Ir(cod)(I^iPr)(OH)]$ **7** (15.0 mg, 0.032 mmol) in $C_6D_6$ (0.6 mL). The sample was frozen in liquid $N_2$ and the Ar atmosphere was removed *in vacuo*. The sample was allowed to thaw before $CO_2$ (*ca.* 1 atm.) was added, a ppt. formed after a few minutes. The reaction mixture was allowed to mix for at least 10 mins before being placed under an Ar atmosphere *via* three vacuum-Ar purge cycles. $^1$H NMR analysis revealed full conversion to the product. The product was dried *in vacuo* to give $[\{Ir(cod)(I^iPr)\}_2(\mu\text{-}\kappa^1{:}\kappa^2\text{-}CO_3)]$ **8** (15.2 mg, 98%) as a yellow solid.

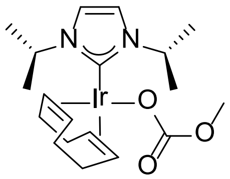
*Solid state:* $[Ir(cod)(I^iPr)(OH)]$ **7** (5 mg, 0.011) was placed in a septum sealed vial and the Ar atmosphere was replaced with $CO_2$ (1 atm.) by purging the vial for approximately 2 mins. The sample was then placed back under an Ar atmosphere *via* three vacuum-Ar purge cycles before being analysed by IR (ATR) and dissolved in $C_6D_6$ for analysis by $^1$H NMR, which indicated complete conversion to **8**. *$^{13}$C NMR analysis was conducted in THF-$d_8$ due to insufficient solubility in $C_6D_6$.

**$^1$H NMR** (500 MHz, $C_6D_6$): $\delta$ 6.30 (s, 4H, N-(C*H*)$_2$-*N*), 5.88 (sept., $J$ = 6.7, 4H, N-C*H*(CH$_3$)$_2$), 4.60 – 4.53 (m, 4H, cod-CH), 2.76 – 2.65 (m, 4H, cod-CH), 2.41 – 2.30 (m, 4H, cod-CH$_2$), 2.30 – 2.20 (m, 4H, cod-CH$_2$), 1.76 – 1.59 (m, 8H, cod-CH$_2$), 1.47 (d, $J$ = 5.3, 12H, CH$_3$), 1.91 (d, $J$ = 2.8, 12H, CH$_3$); **$^{13}$C NMR** (75 MHz, THF-$d_8$): $\delta$ 178.8 (Ir-C$_{carbene}$), 170.0 (CO), 116.9 (N-(*C*H)$_2$-N), 82.6 (cod-CH), 53.0 (N-*C*H(CH$_3$)$_2$), 38.8 (cod-CH), 35.3 (cod-CH$_2$), 30.1 (cod-CH$_2$), 24.3 (CH$_3$), 24.1 (CH$_3$). IR (ATR) $\nu$ = 1610.56 (CO$_3$), 1411.89, 1207.44 cm$^{-1}$. **Anal. Calcd.** for $C_{35}H_{56}Ir_2N_4O_3$ (MW 965.28): C, 43.55; H, 5.85; N, 5.80. Found: C, 43.44; H, 5.86; N, 5.73.



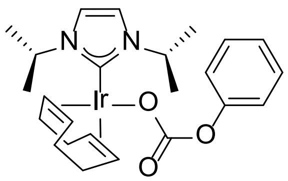
[Ir(cod)(I$^i$Pr)(OPh)] **11**

A vial was charged with [Ir(cod)(I$^i$Pr)(OH)] **7** (20.0 mg, 0.043 mmol) and phenol (4.1 mg, 0.043 mmol) in PhMe (1 mL) and the reaction mixture was stirred at rt for 16 h. Once complete, the mixture was concentrated *in vacuo* and the resultant solid was washed with cold pentane (3 x 1 mL) and dried *in vacuo* to give [Ir(cod)(I$^i$Pr)(OPh)] **11** (22.1 mg, 94%) as a yellow solid. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 7.24 (t, 2H, $J$ = 7.8, *m*-ArH), 6.96 (d, 2H, $J$ = 8.4, *o*-ArH), 6.74 (tt, 1H, $J$ = 7.2, 1.0, *p*-ArH), 6.13 (s, 2H, N-(C*H*)$_2$-N), 5.77 (sept., 2H, $J$ = 6.8, N-C*H*($CH_3$)$_2$), 4.92– 4.82 (m, 2H, cod-CH), 2.96 – 2.84 (m, 2H, cod-CH), 2.41 – 2.21 (m, 4H, cod-$CH_2$), 1.81 – 1.57 (m, 4H, cod-$CH_2$), 1.12 (d, 6H, $J$ = 6.7, $CH_3$), 1.09 (d,6 H, $J$ = 6.8, $CH_3$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 179.4 (Ir-$C_{carbene}$), 171.3 (ArC), 129.3 (ArCH), 121.4 (ArCH), 116.1 (N-(*C*H)$_2$-N), 115.6 (ArCH), 83.1 (cod-CH), 52.4 (N-*C*H($CH_3$)$_2$), 45.9 (cod-CH), 34.5 (cod-$CH_2$), 29.6 (cod-$CH_2$), 23.7 ($CH_3$), 23.5 ($CH_3$). IR (ATR) ν = 1583.56, 1479.40, 1294.24, 1209.37 cm$^{-1}$. **Anal. Calcd.** for $C_{24}H_{33}IrN_2O$ (MW 545.74): C, 50.62; H, 6.09; N, 5.13. Found: C, 50.55; H, 5.93; N, 5.17.



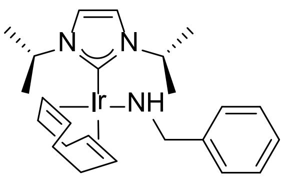
[Ir(cod)(I$^i$Pr)($OCO_2CH_3$)] **12**

A J. Young NMR tube was charged with [Ir(cod)(I$^i$Pr)(OMe)] **10** (10.0 mg, 0.021 mmol, prepared following literature procedure[1]) in $C_6D_6$ (0.6 mL). The sample was frozen in liquid $N_2$ and the Ar atmosphere was removed *in vacuo*. The sample was allowed to thaw before $CO_2$ (*ca.* 1 atm.) was added. The reaction mixture was mixed for at least 10 mins before NMR analysis was conducted. Once complete, the $CO_2$ atmosphere was removed *in vacuo* before the sample was returned to the glove-box where it was dried *in vacuo* to give [Ir(cod)(I$^i$Pr)($OCO_2CH_3$)] **12** (11 mg, 99%) as a yellow solid. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 6.22 (s, 2H, N-(C*H*)$_2$-N), 5.84 (sept., 2H, $J$ = 6.6, N-C*H*($CH_3$)$_2$), 5.03 – 4.82 (m, 2H, cod), 3.58 (s, 3H, $OCH_3$), 3.00 – 2.83 (m, 2H, cod), 2.37 – 2.12 (m, 4H, cod), 1.71 – 1.51 (m, 4H, cod), 1.31 (d, 6H, $J$ = 6.4, 6H, N-CH(C*H*$_3$)$_2$), 1.12 (d, 6H, $J$ = 6.8, N-CH(C*H*$_3$)$_2$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 178.3 (Ir-$C_{carbene}$), 160.9 (Ir-O*C*O), 116.3 (N-(*C*H)$_2$-N), 84.3 (N-*C*H($CH_3$)$_2$), 53.2 (cod-CH), 52.5 (O*C*H$_3$), 47.7 (cod-CH), 34.2 (cod-$CH_2$), 29.4 (cod-$CH_2$), 23.7 (N-CH(*C*H$_3$)$_2$), 23.6 (N-CH(*C*H$_3$)$_2$). IR (ATR) ν = 1649.14 ($CO_3$), 1624.06 ($CO_3$), 1411.89, 1207.49 cm$^{-1}$. **Anal. Calcd.** for $C_{19}H_{31}IrN_2O_3$ (MW 527.68): C, 43.25; H, 5.92; N, 5.31. Found: C, 43.17; H, 6.01; N, 5.40.



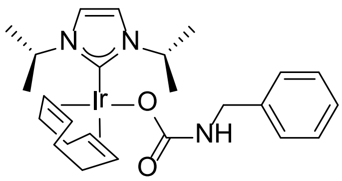

[Ir(cod)(I$^i$Pr)($OCO_2$Ph)] **13**

A J. Young NMR tube was charged with [Ir(cod)(I$^i$Pr)(OPh)] **11** (16.9 mg, 0.031 mmol) in $C_6D_6$ (0.6 mL). The sample was frozen in liquid $N_2$ and the Ar atmosphere was removed *in vacuo*. The sample was allowed to thaw before $CO_2$ (*ca.* 1 atm.) was added. The reaction mixture was mixed for at least 10 mins before NMR analysis was conducted. Once complete, the $CO_2$ atmosphere was removed *in vacuo* before the sample was returned to the glove-box where it was dried *in vacuo* to give [Ir(cod)(I$^i$Pr)($OCO_2$Ph)] **13** (18.4 mg, >99%) as a yellow solid. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 7.22 (t, 2H, *J* = 7.3, *m*-ArH), 7.09 – 6.94 (m, 2H, *o*-ArH), 6.75 (t, 1H, *J* = 7.2, *p*-ArH), 6.14 (s, 2H, N-(C*H*)$_2$-N), 5.76 (sept., 2H *J* = 6.7, N-C*H*($CH_3$)$_2$), 4.92– 4.82 (m, 2H, cod-CH), 2.95 – 2.83 (m, 2H, cod-CH), 2.39 – 2.18 (m, 4H, cod-$CH_2$), 1.77 – 1.57 (m, 4H, cod-$CH_2$), 1.13 (d, 6H, *J* = 6.7, $CH_3$), 1.09 (d, 6H, *J* = 6.8, $CH_3$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 179.2 (Ir-$C_{carbene}$), 129.1 (ArCH), 128.8 (ArCH), 124.8 (ArCH), 116.2 (N-(*C*H)$_2$-N), 83.1 (cod-CH), 52.4 (N-*C*H($CH_3$)$_2$), 46.0 (cod-CH), 34.4 (cod-$CH_2$), 29.6 (cod-$CH_2$), 23.7 ($CH_3$), 23.5 ($CH_3$). **$^{13}$C NMR** (75 MHz, THF-$d_8$): $\delta$ 179.2 (Ir-$C_{carbene}$), 176.9 (ArC), 162.9 (br., CO), 128.5 (ArCH), 121.1 (ArCH), 117.2 (N-(*C*H)$_2$-N), 114.8 (ArCH), 82.2 (cod-CH), 52.9 (N-*C*H($CH_3$)$_2$), 46.1 (cod-CH), 34.5 (cod-$CH_2$), 29.7 (cod-$CH_2$), 23.7 ($CH_3$), 23.5 ($CH_3$). IR (ATR) ν = 1583.56, 1477.47, 1296.16, 1209.37 $cm^{-1}$. **Anal. Calcd.** for $C_{24}H_{33}IrN_2O_3$ (MW 589.75): C, 48.88; H, 5.64; N, 4.75. Found: C, 48.77; H, 5.68; N, 4.79.



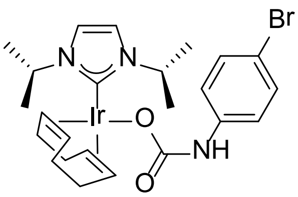

[Ir(cod)(I$^i$Pr)(NHBn)] **14**

A vial was charged with [Ir(cod)(I$^i$Pr)(OH)] **7** (20.0 mg, 0.043 mmol) and benzylamine (4.7 mg, 0.043 mmol) in PhMe (1.0 mL) and the reaction mixture was stirred at rt for 16 h. Once complete, the mixture was concentrated *in vacuo*, washed with *n*-pentane (3 x 1 mL) and dried to give [Ir(cod)(I$^i$Pr)(NHBn)] **14** (17.4 mg, 72%) as a yellow solid. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 7.61 (d, 2H, *J* = 7.4, *o*-ArH), 7.28 (t, 2H, *J* = 7.5, *m*-ArH), 7.19 – 7.08 (m, 1H, *p*-ArH), 6.17 (s, 2H, N-(C*H*)$_2$-N), 5.97 (sept., 2H, *J* = 6.7, N-C*H*($CH_3$)$_2$), 4.50 (d, 2H, *J* = 7.8, NH-C*H*$_2$), 4.50 – 4.36 (m, 2H, cod-CH), 2.63 (br., 2H, cod-CH), 2.70 – 2.35 (m, 4H, cod-$CH_2$), 2.28 – 2.10 (m, 2H, cod-$CH_2$), 2.05 – 1.90 (m, 2H, cod-$CH_2$), 1.12 (d, 6H, *J* = 6.9, $CH_3$), 1.02 (d, 6H, *J* = 6.7, $CH_3$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 182.2 (Ir-$C_{carbene}$), 149.6 (ArC), 128.1 (*m*-ArCH), 127.4 (*o*-ArCH), 125.9 (*p*-ArCH), 115.8 (N-(*C*H)$_2$-N), 76.3 (cod-CH), 59.1 (NH-*C*H$_2$), 52.4 (N-*C*H($CH_3$)$_2$), 45.4 (cod-CH), 35.0 (cod-$CH_2$), 31.2 (cod-$CH_2$), 23.6 ($CH_3$), 23.5 ($CH_3$). IR (ATR) ν = 1409.96, 1209.37 $cm^{-1}$. **Anal. Calcd.** for $C_{24}H_{36}IrN_3$ (MW 558.78): C, 51.59; H, 6.49; N, 7.52. Found: C, 51.25; H, 6.37; N, 7.38.




[Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

A vial was charged with [Ir(cod)(I$^i$Pr)(NHBn)] **14** (17.4 mg, 0.031 mmol) and in $C_6D_6$ (0.6 mL). The sample was frozen in liquid $N_2$ and the Ar atmosphere was removed *in vacuo*. The sample was allowed to thaw before $CO_2$ (*ca.* 1 atm.) was added. The reaction mixture was mixed for at least 10 mins before NMR analysis was conducted. Once complete, the $CO_2$ was removed *in vacuo* before the sample was returned to the glove-box and was dried *in vacuo* to give [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16** (17.1 mg, 92%) as a yellow solid. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 7.15 – 7.00 (m, 5H, $J$ = 7.2, *m*-ArH), 6.29 (s, 2H, N-(C*H*)$_2$-N), 5.74 (sept., 2H, $J$ = 6.7, N-C*H*($CH_3$)$_2$), 4.95 – 4.82 (m, 2H, cod-CH), 4.49 (t, 1H, $J$ = 5.8, NH), 4.30 (d, 2H, $J$ = 5.6, NH-C*H*$_2$), 2.98 – 2.86 (m, 2H, cod-CH), 2.41 – 2.19 (m, 4H, cod-$CH_2$), 1.76 – 1.59 (m, 4H, cod-$CH_2$), 1.33 (d, 6H, $J$ = 6.6, $CH_3$), 1.16 (d, 6H $J$ = 6.8, $CH_3$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 179.0 (Ir-$C_{carbene}$), 163.2 (CO), 142.7 (ArC), 128.2 (ArCH, from HSQC and HMBC), 126.4 (ArCH), 116.1 (N-(*C*H)$_2$-N), 83.7 (cod-CH), 52.5 (N-*C*H($CH_3$)$_2$), 47.0 (cod-CH), 46.5 (NH-*C*H$_2$), 34.4 (cod-$CH_2$), 29.5 (cod-$CH_2$), 23.9 ($CH_3$), 23.6 ($CH_3$). **$^1$H NMR** (400 MHz, THF-$d_8$): $\delta$ 7.18 – 7.09 (m, 5H, $J$ = 7.2, *m*-ArH), 7.06 (s, 2H, N-(C*H*)$_2$-N), 5.58 (sept., 2H, $J$ = 6.7, N-C*H*($CH_3$)$_2$), 4.91 (br., 1H, NH), 4.39 (br., 2H, cod-CH), 4.08 (d, 2H, $J$ = 6.08, NH-C*H*$_2$), 2.70 (br., 2H, cod-CH), 2.27 – 2.07 (m, 4H, cod-$CH_2$), 1.64 – 1.51 (m, 4H, cod-$CH_2$), 1.45 (d, 6H, $J$ = 6.6, $CH_3$), 1.36 (d, 6H, $J$ = 6.5, $CH_3$). **$^{13}$C NMR** (100 MHz, THF-$d_8$): $\delta$ 179.0 (Ir-$C_{carbene}$), 163.3 (CO), 143.6 (ArC), 128.3 (ArCH), 127.8 (ArCH), 126.4 (ArCH), 116.9 (N-(*C*H)$_2$-N), 82.9 (cod-CH), 52.9 (N-*C*H($CH_3$)$_2$), 46.7 (cod-CH), 46.4 (NH-*C*H$_2$), 34.4 (cod-$CH_2$), 29.6 (cod-$CH_2$), 23.9 ($CH_3$), 23.4 ($CH_3$). IR (ATR) ν = 2054.19, 1967.39 ($CO_3$), 1409.96, 1209.37 $cm^{-1}$. **Anal. Calcd.** for $C_{25}H_{36}IrN_3O_2$ (MW 602.79): C, 49.81; H, 6.02; N, 6.97. Found: C, 49.80; H, 5.87; N, 7.02.




[Ir(cod)(I$^i$Pr)($O_2$CNH-(*p*-Br$C_6H_4$)] **17**

A J. Young NMR tube was charged with [Ir(cod)(I$^i$Pr)(NH-(*p*-Br$C_6H_4$)] **15** (20.0 mg, 0.032 mmol, prepared following literature procedure[1]) in $C_6D_6$. The sample was frozen in liquid $N_2$ and the Ar atmosphere was removed *in vacuo*. The sample was allowed to thaw before $CO_2$ (*ca.* 1 atm.) was added. The reaction mixture was mixed for at least 10 mins before NMR analysis was conducted. Upon completion it was found that either bubbling Ar through the reaction mixture or concentrating the sample *in vacuo* converted the product back to **15**. **$^1$H NMR** (300 MHz, $C_6D_6$): $\delta$ 7.27 – 7.18 (m, 4H, ArH), 6.24 (s, 2H, N-(C*H*)$_2$-N), 5.68 (sept., 2H, $J$ = 6.7, N-C*H*($CH_3$)$_2$), 4.96 – 4.86 (m, 2H, cod-CH), 2.98 – 2.4 (m, 2H, cod-CH), 2.38 – 2.16 (m, 4H, cod-$CH_2$), 1.74 – 1.55 (m, 4H, cod-$CH_2$), 1.25 (d, 6H, $J$ = 6.7, $CH_3$), 1.11 (d, 6H, $J$ = 6.8, $CH_3$). **$^{13}$C NMR** (75 MHz, $C_6D_6$): $\delta$ 178.1 (Ir-$C_{carbene}$), 159.7 (CO), 142.0 (N-Ar*C*), 131.6 (ArCH), 126.4 (*m*-ArCH), 119.4 (*o*-ArCH), 116.3 (N-(*C*H)$_2$-N), 112.4 (*p*-Ar*C*Br), 83.8 (cod-CH), 52.5 (N-*C*H($CH_3$)$_2$), 47.7 (cod-CH), 34.3 (cod-$CH_2$), 29.4 (cod-$CH_2$), 23.7 ($CH_3$), 23.6 ($CH_3$).

Electronic Supplementary Material (ESI) for Chemical Communications


## NMR and IR Spectra

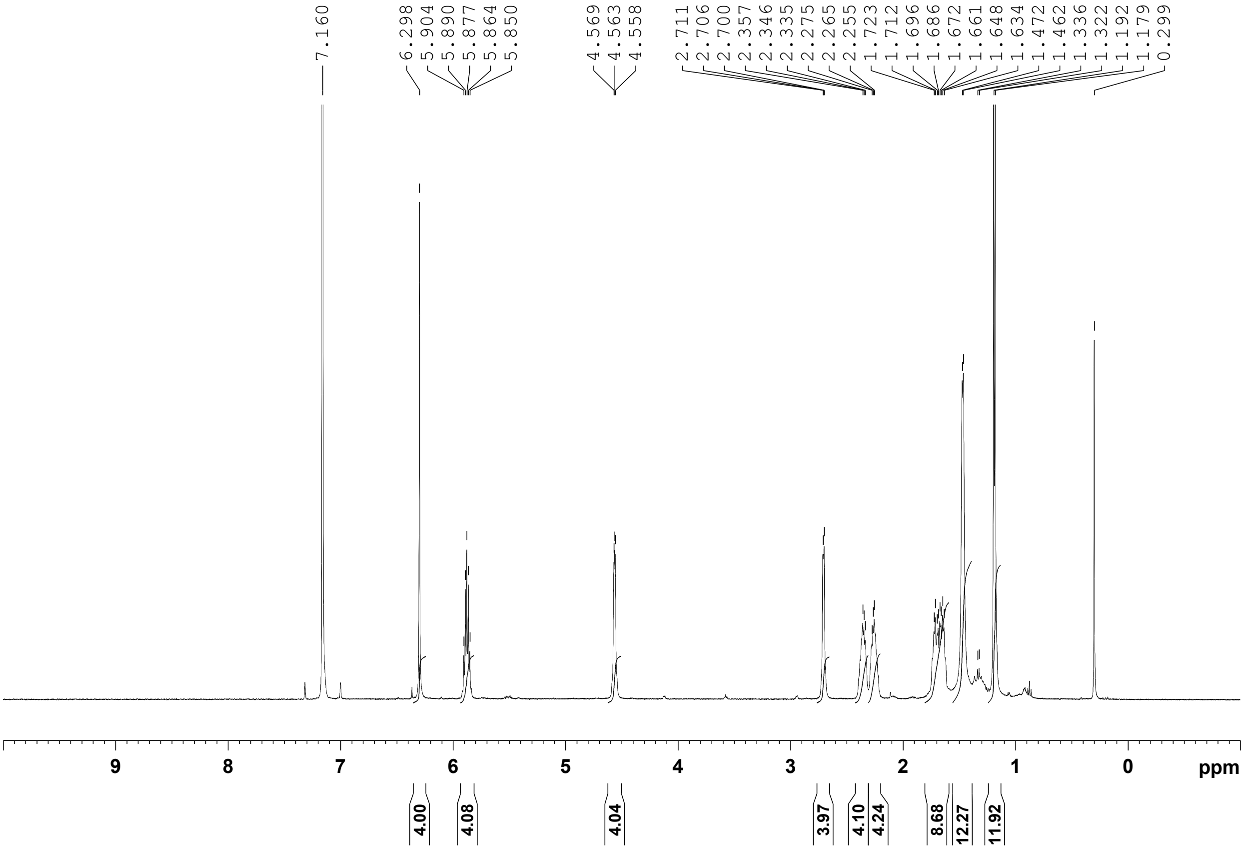



**Figure S 1** $^{1}H$ NMR (500 MHz, $C_6D_6$) spectrum for [{Ir(cod)($I^{i}Pr$)}$_2$($\mu$-$\kappa^1$:$\kappa^2$-$CO_3$)] **8**

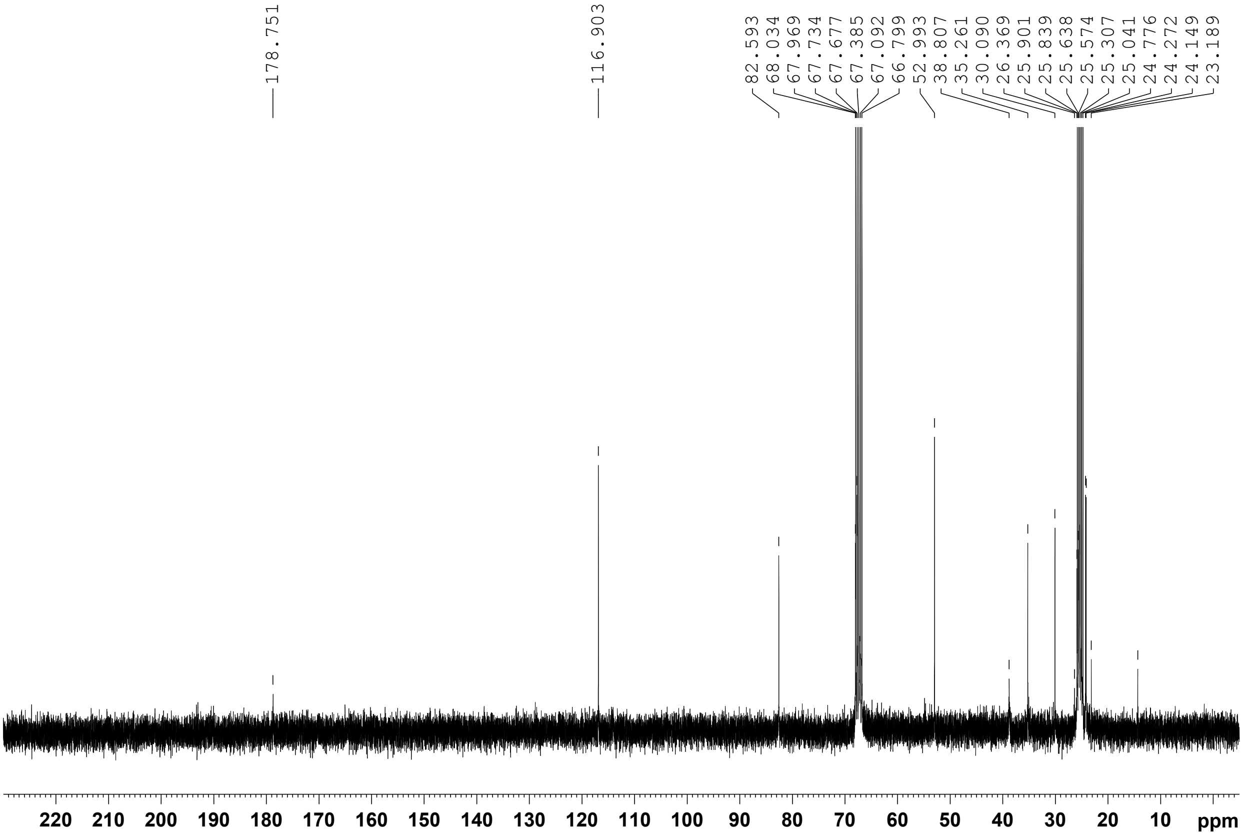



**Figure S 2** $^{13}C\{^{1}H\}$ NMR (75 MHz, THF-$d_8$) spectrum for [{Ir(cod)($I^{i}Pr$)}$_2$($\mu$-$\kappa^1$:$\kappa^2$-$CO_3$)] **8**

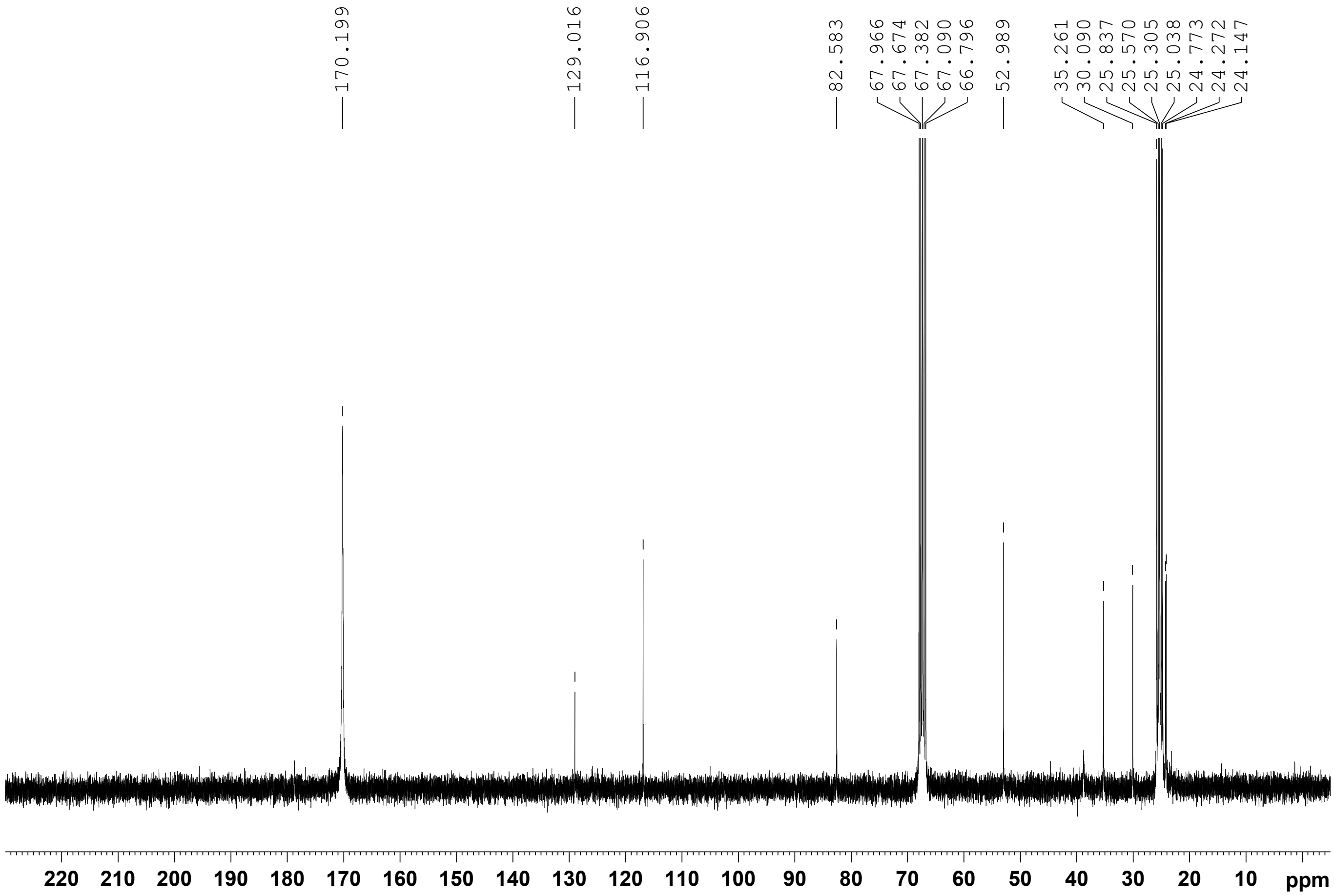



**Figure S 3** $^{13}C\{^{1}H\}$ NMR (75 MHz, THF-$d_8$) spectrum for $[\{Ir(cod)(I^{i}Pr)\}_2(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}^{13}CO_3)]$ **8**

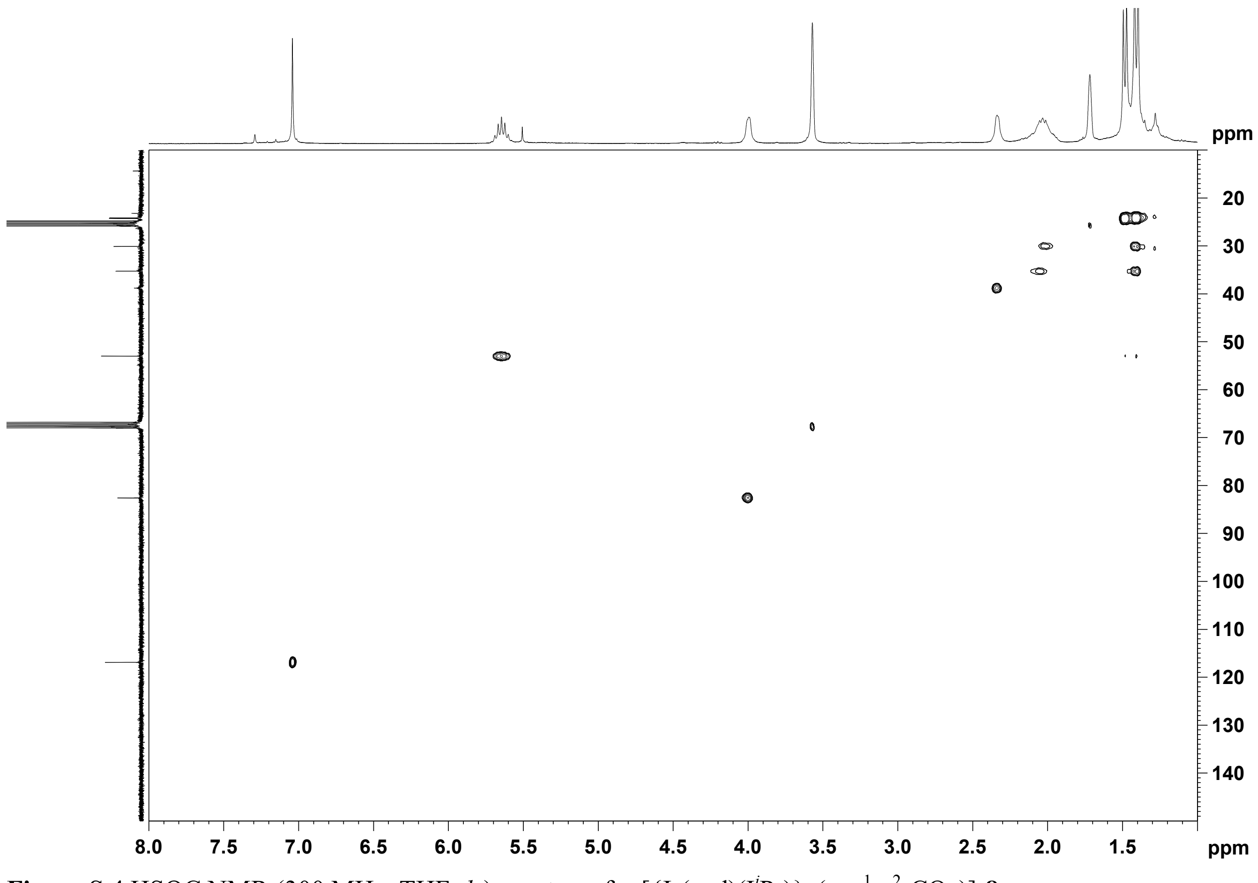



**Figure S 4** HSQC NMR (300 MHz, THF-$d_8$) spectrum for $[\{Ir(cod)(I^{i}Pr)\}_2(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)]$ **8**

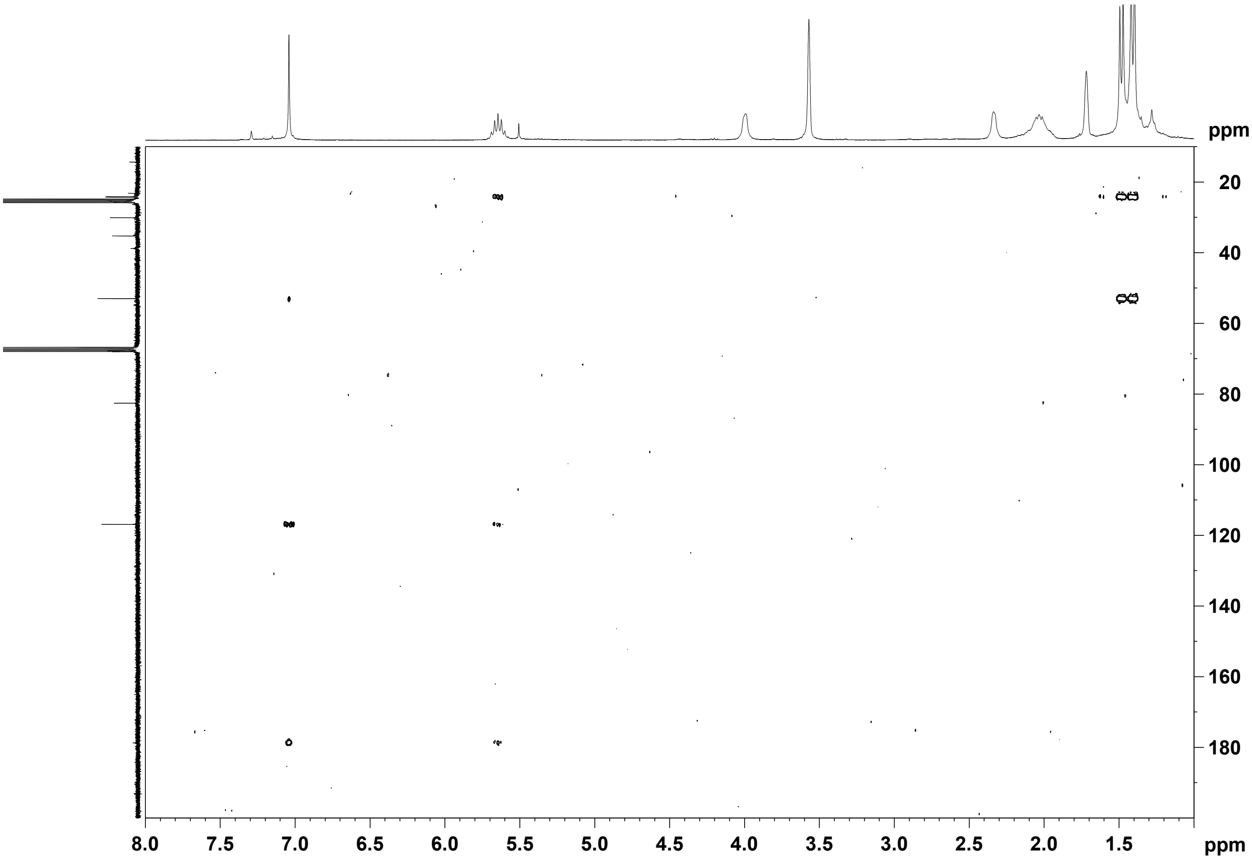



**Figure S 5** HMBC NMR (300 MHz, THF-$d_8$) spectrum for [{Ir(cod)(I$^i$Pr)}$_2$(μ-κ$^1$:κ$^2$-CO$_3$)] **8**

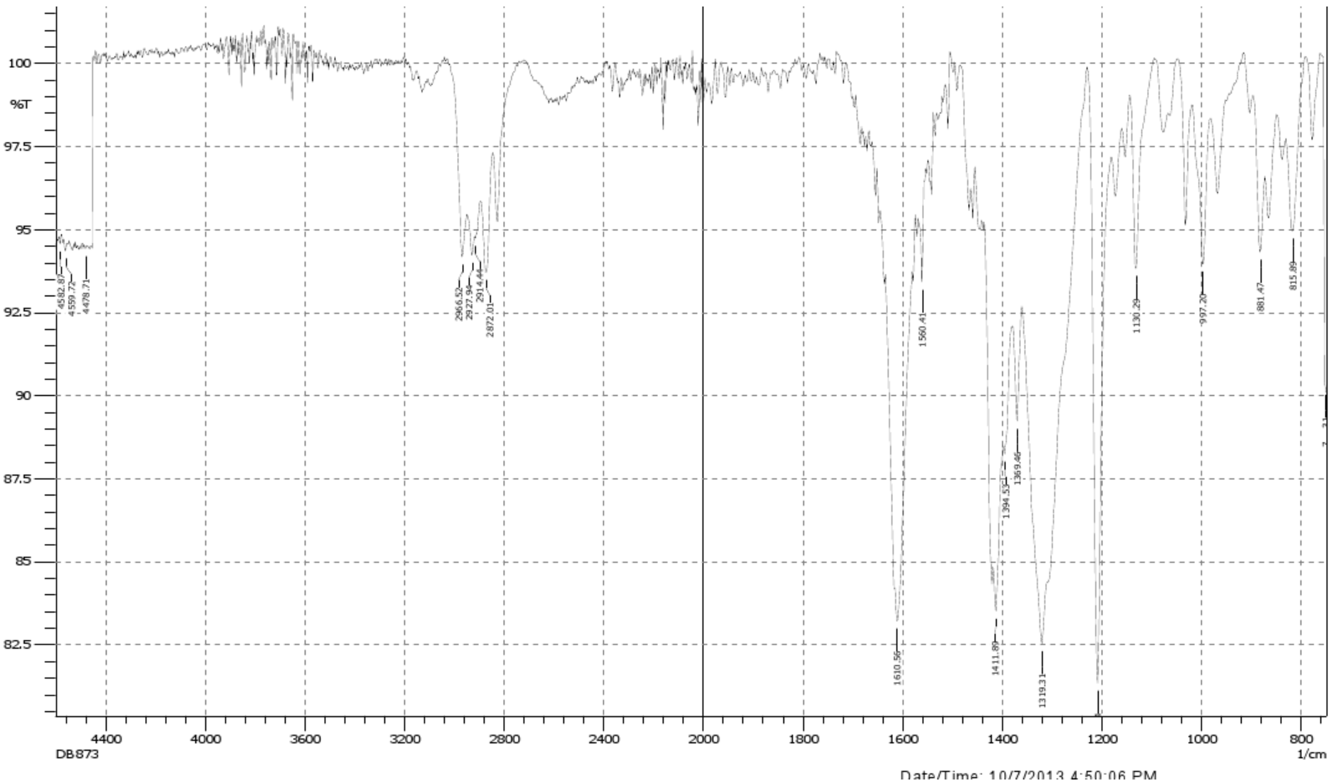



**Figure S 6** IR (ATR) spectrum for [{Ir(cod)(I$^i$Pr)}$_2$(μ-κ$^1$:κ$^2$-CO$_3$)] **8**

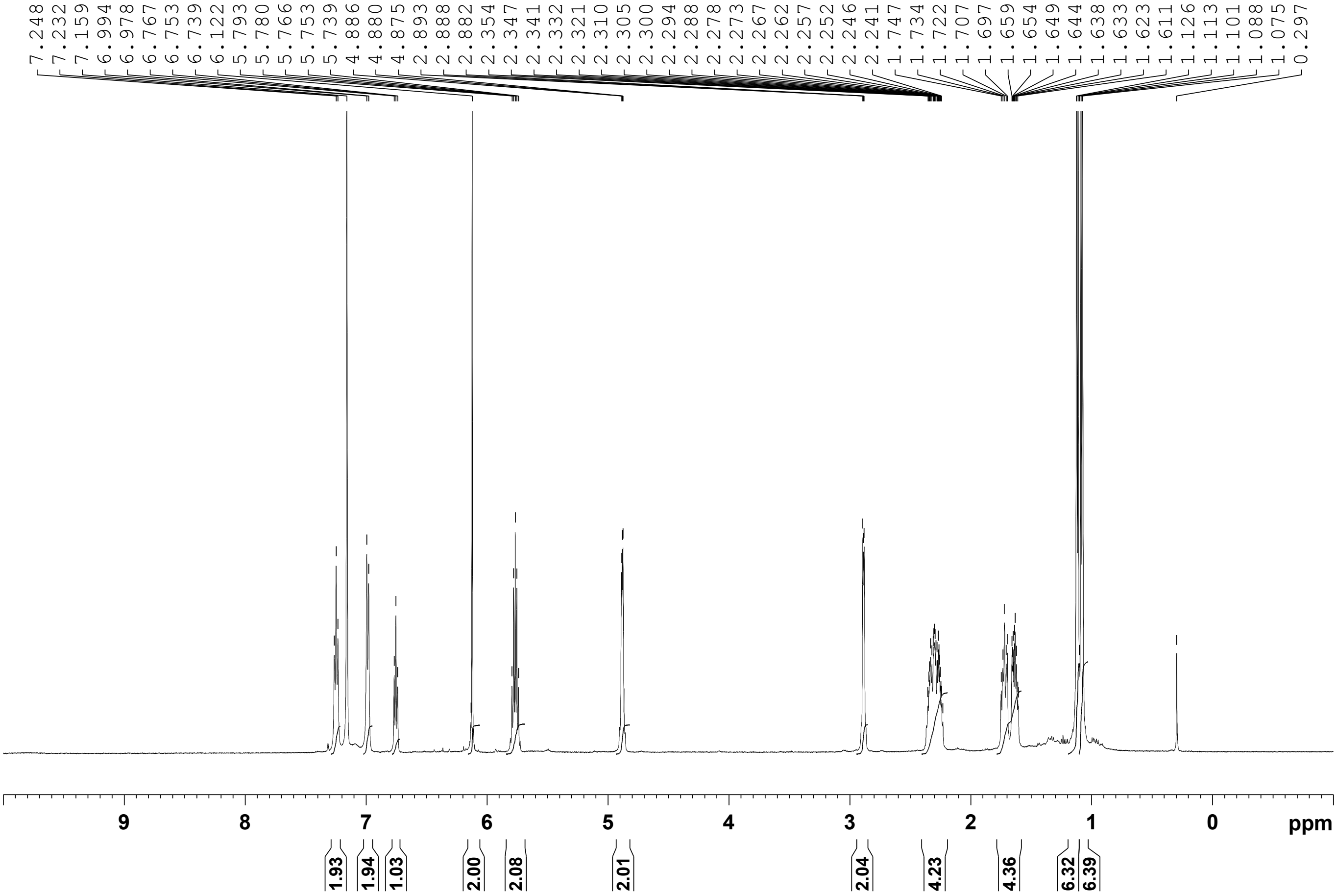



**Figure S 7** $^{1}$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)(OPh)] **11**

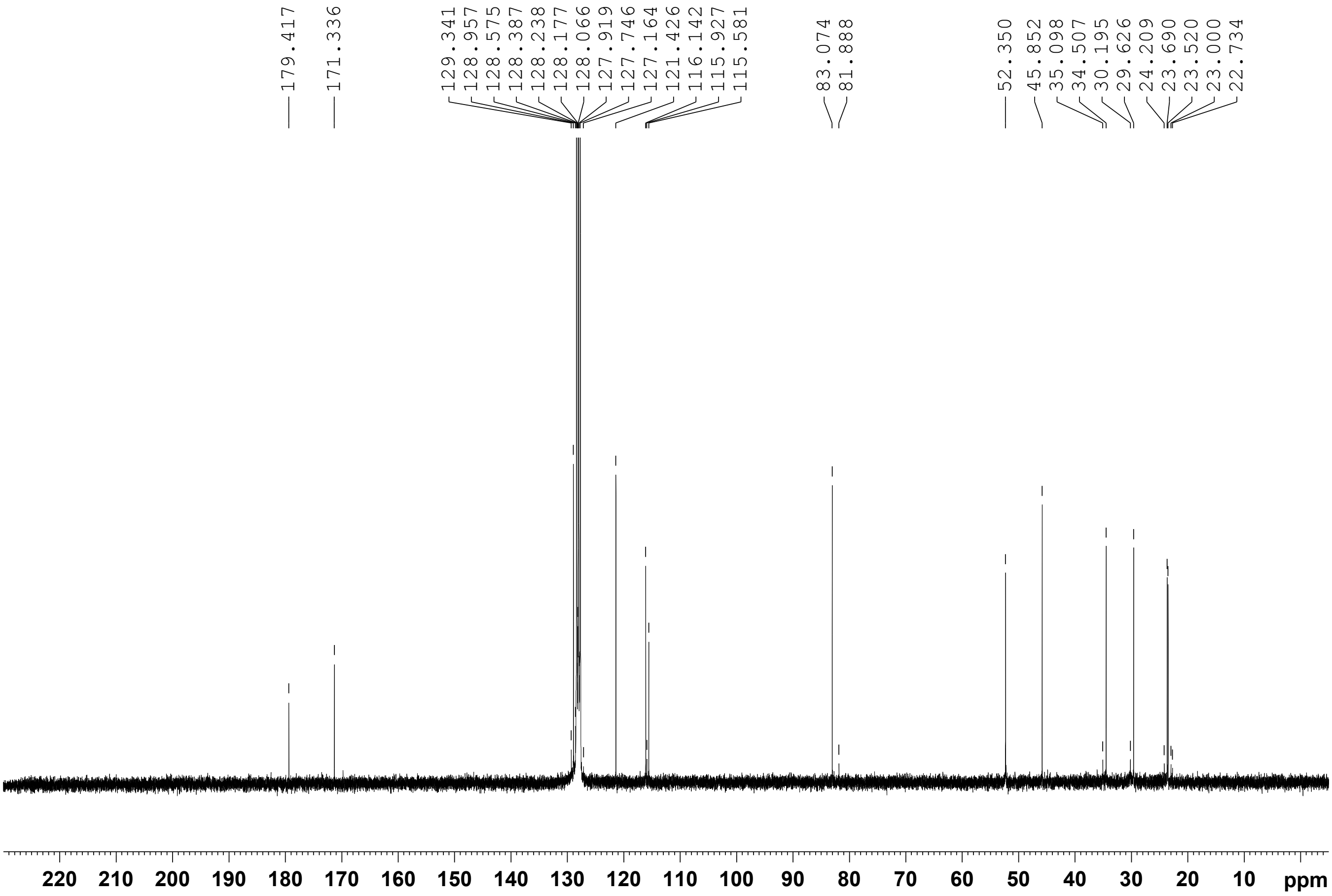



**Figure S 8** $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)(OPh)] **11**

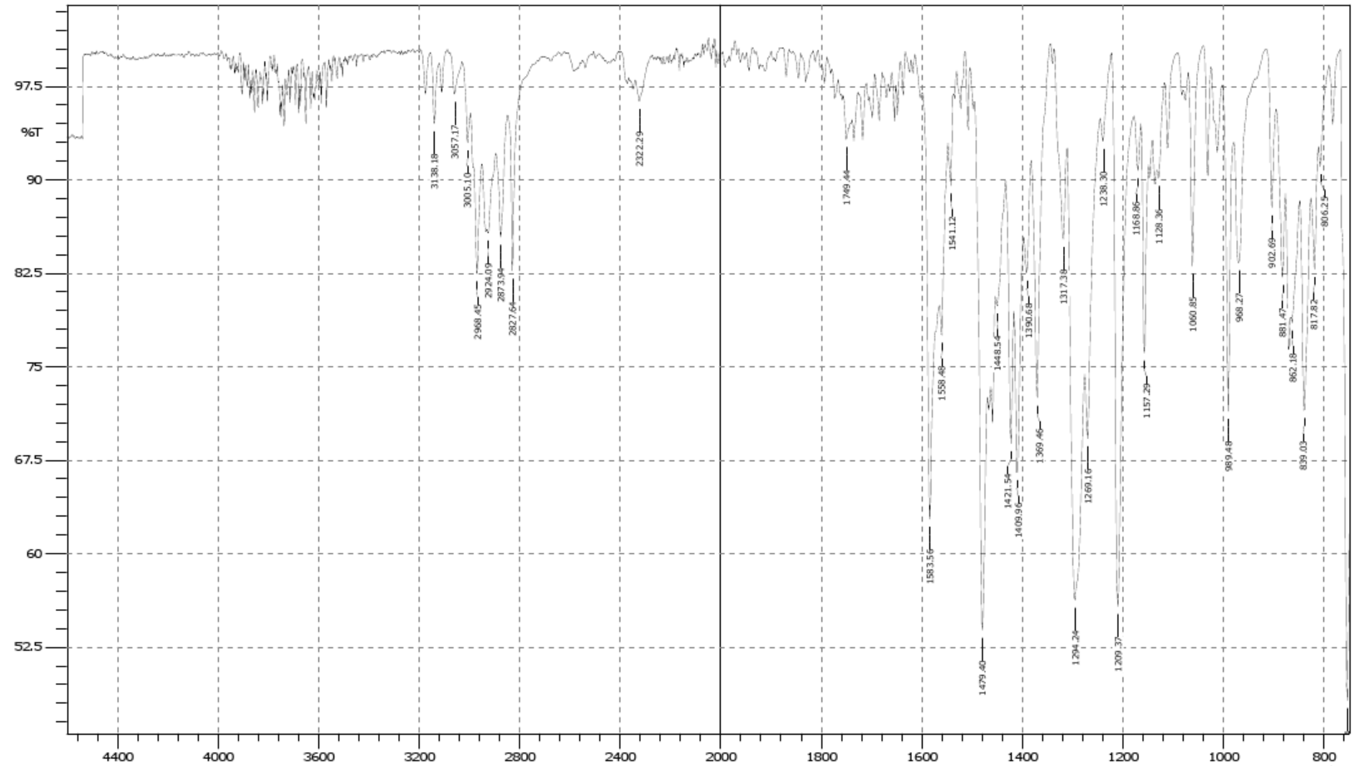


**Figure S 9** IR (ATR) spectrum for [Ir(cod)(I$^i$Pr)(OPh)] **11**

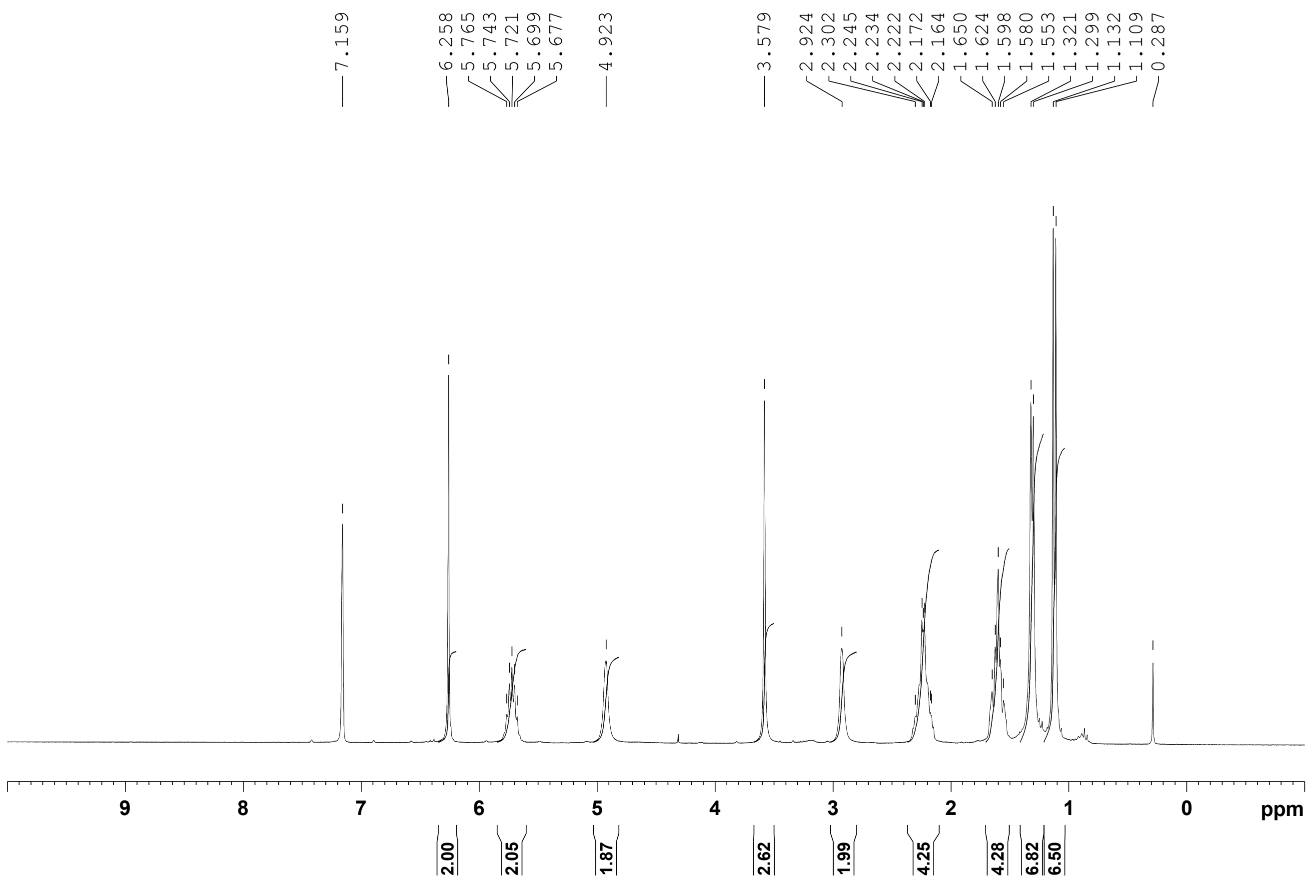


**Figure S 10** $^1$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($OCO_2CH_3$)] **12**

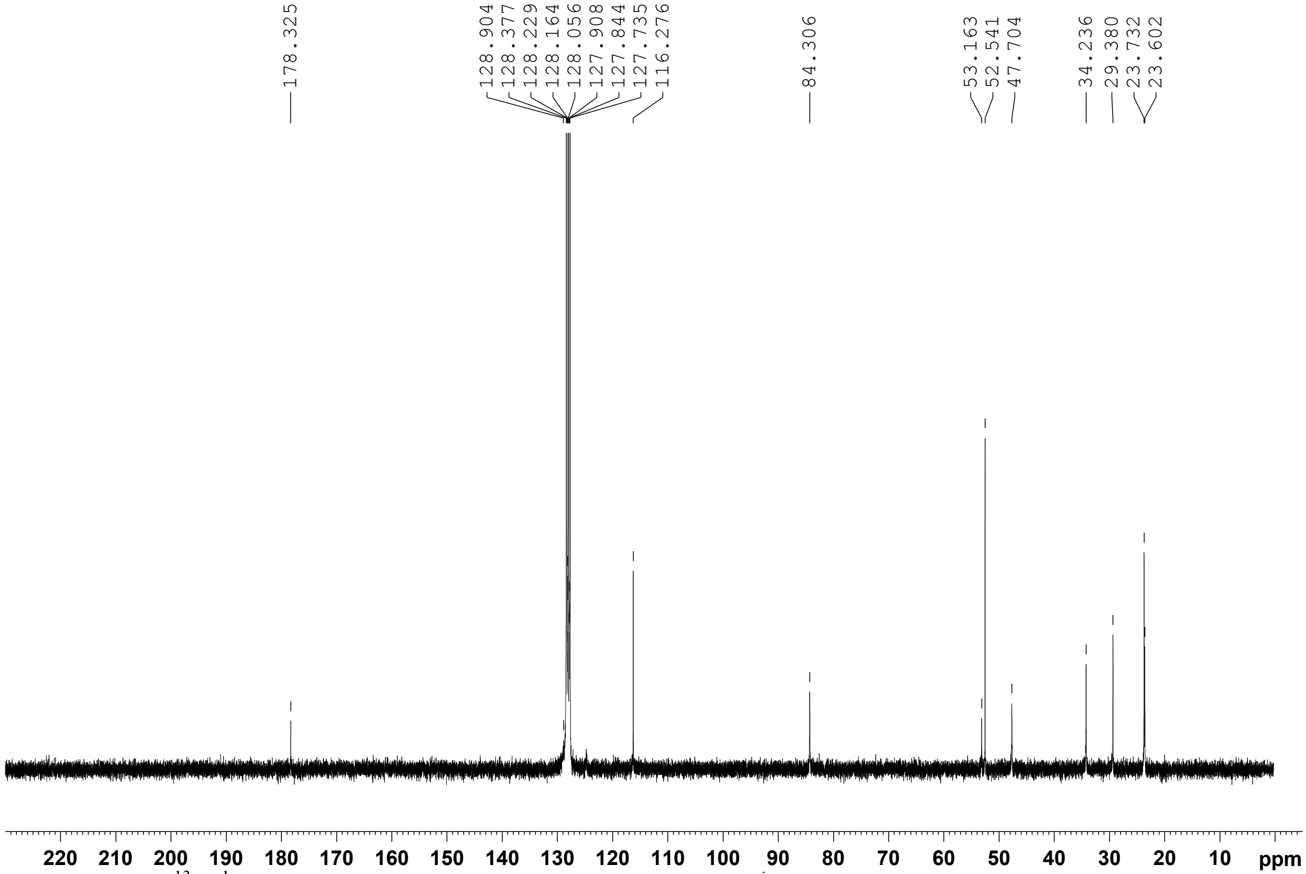



**Figure S 11** $^{13}C\{^{1}H\}$ NMR (75 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)($OCO_2CH_3$)] **12**

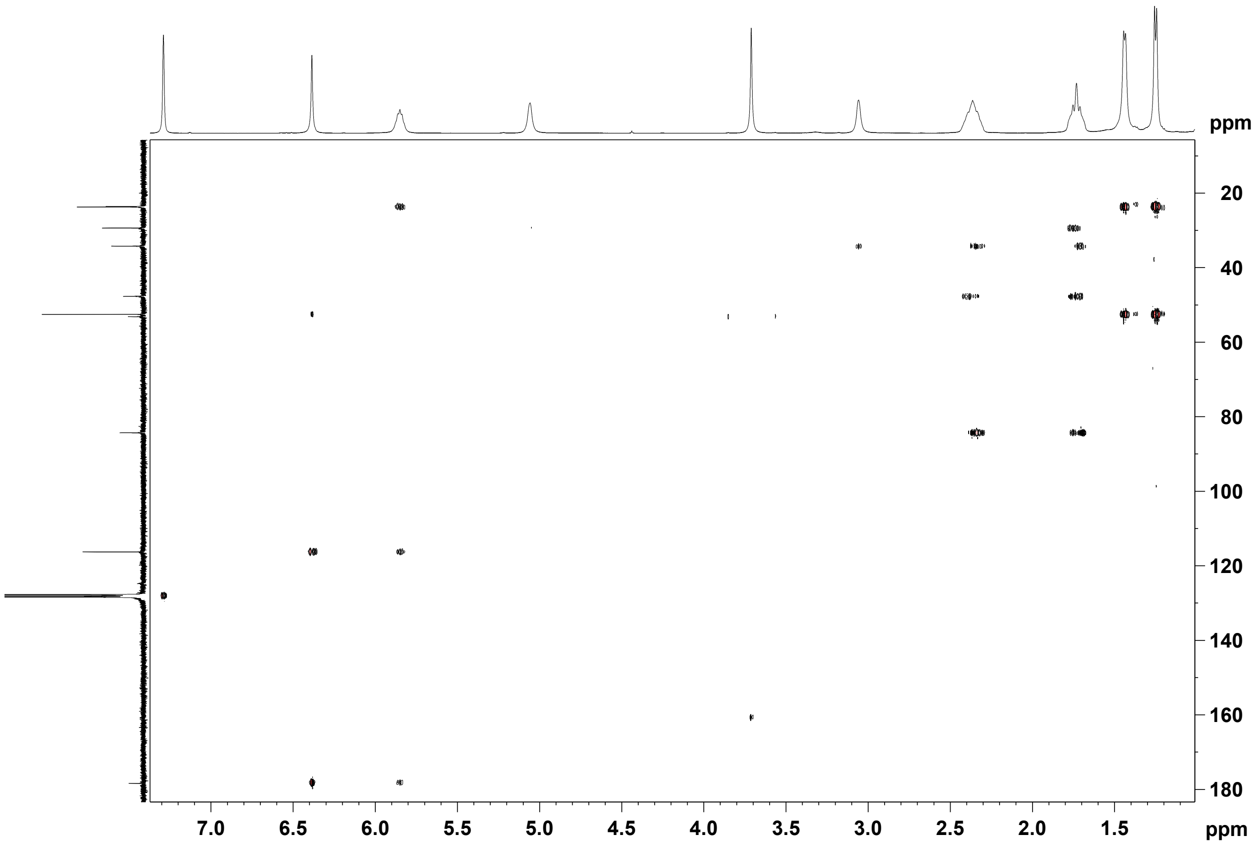



**Figure S 12** HMBC NMR (500 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)($OCO_2CH_3$)] **12**

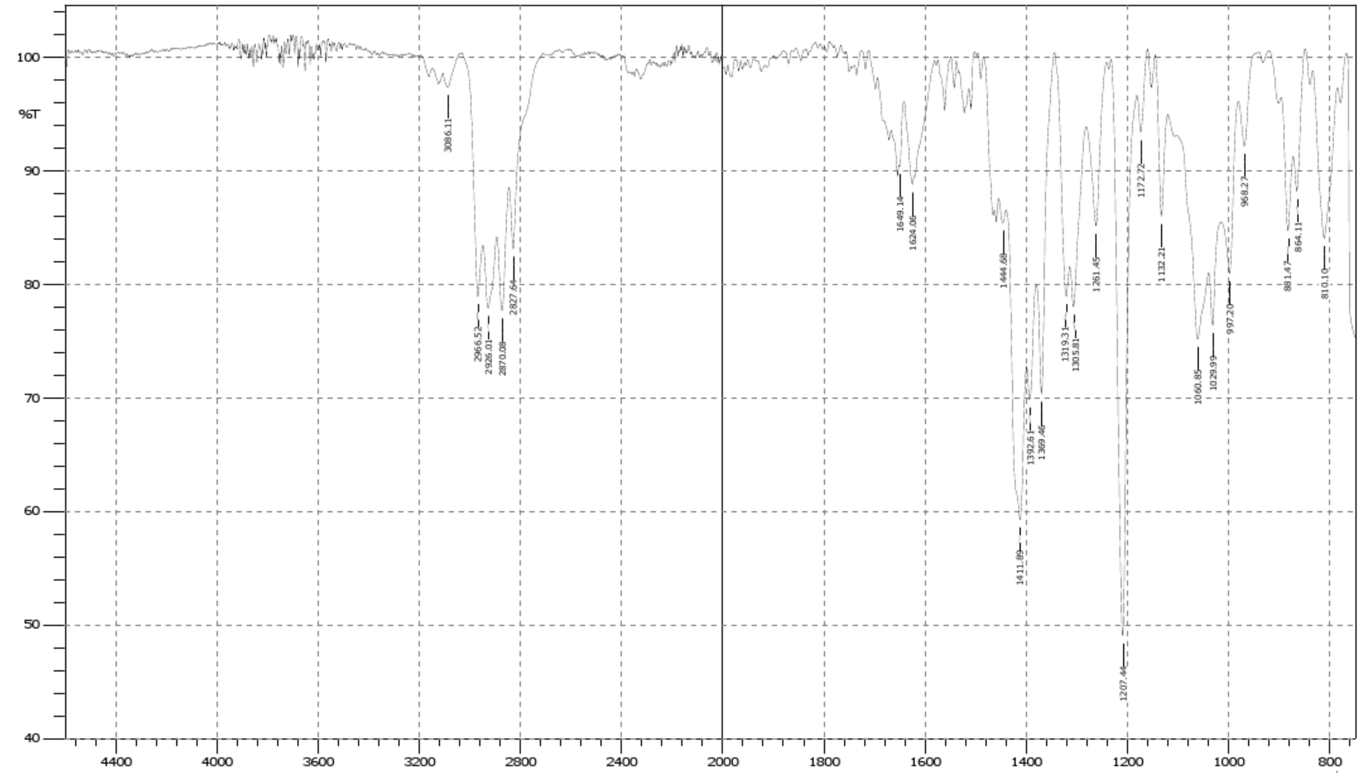


**Figure S 13** IR (ATR) spectrum for [Ir(cod)(I$^{i}$Pr)($OCO_2CH_3$)] **12**

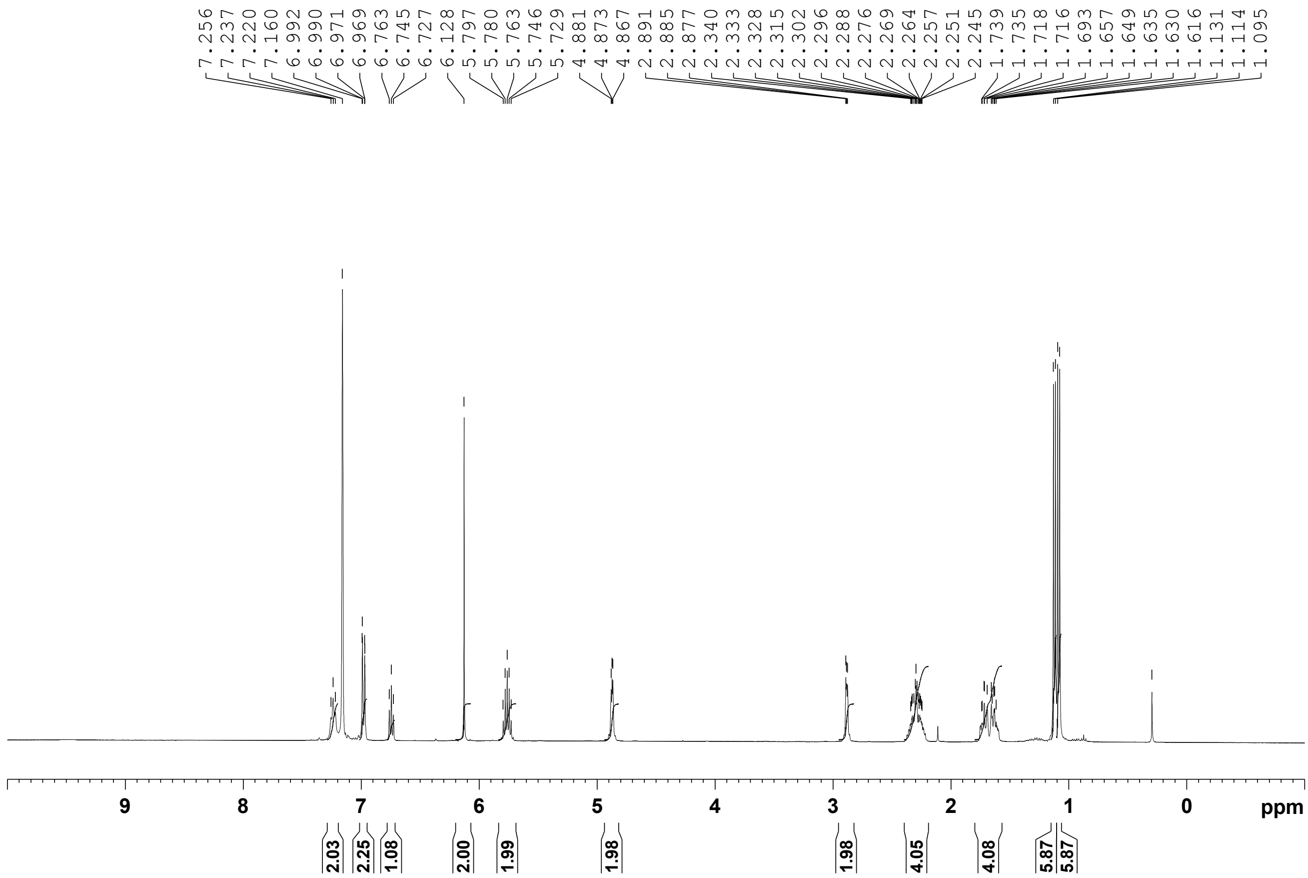


**Figure S 14** $^{1}$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)($OCO_2$Ph)] **13**

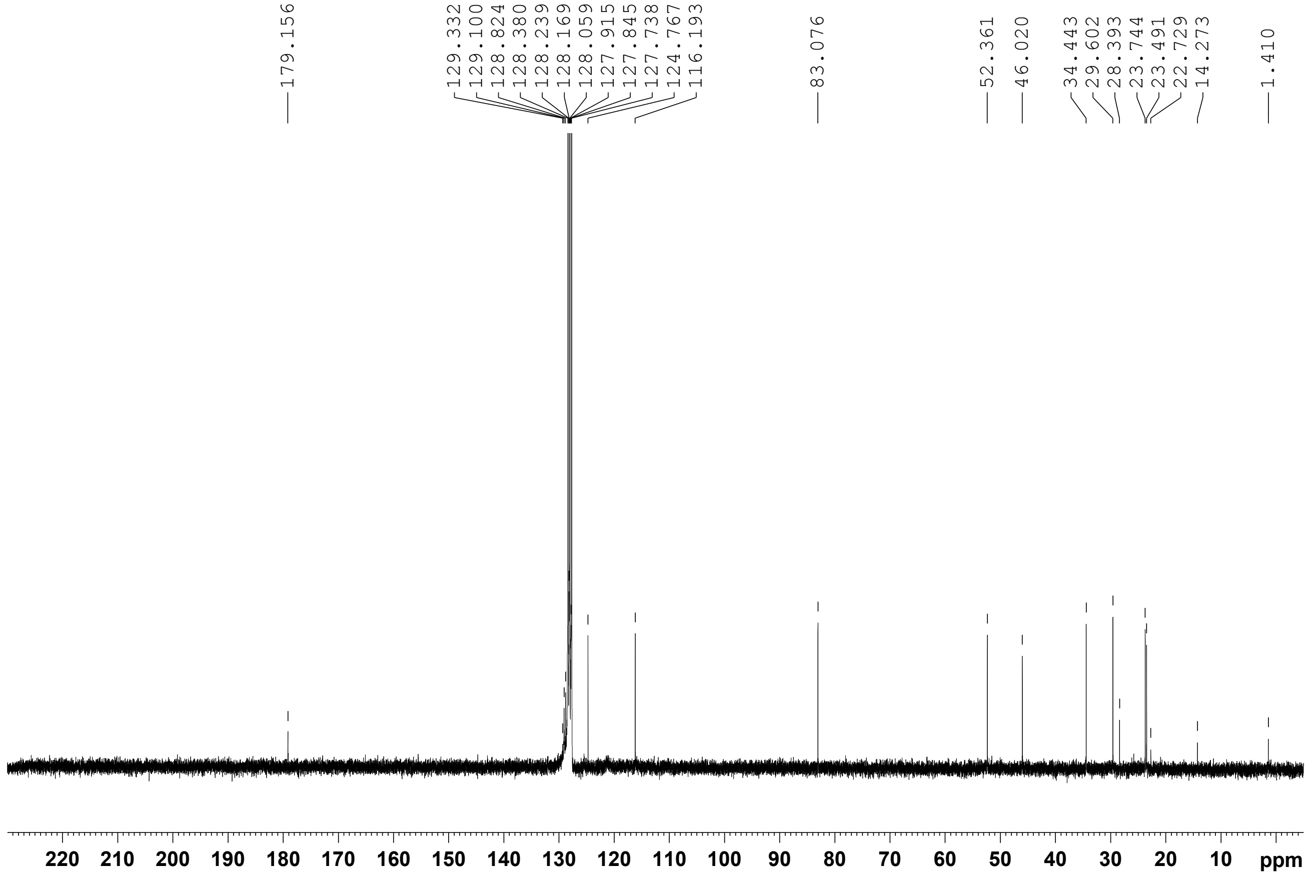



**Figure S 15** $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($OCO_2$Ph)] **13**

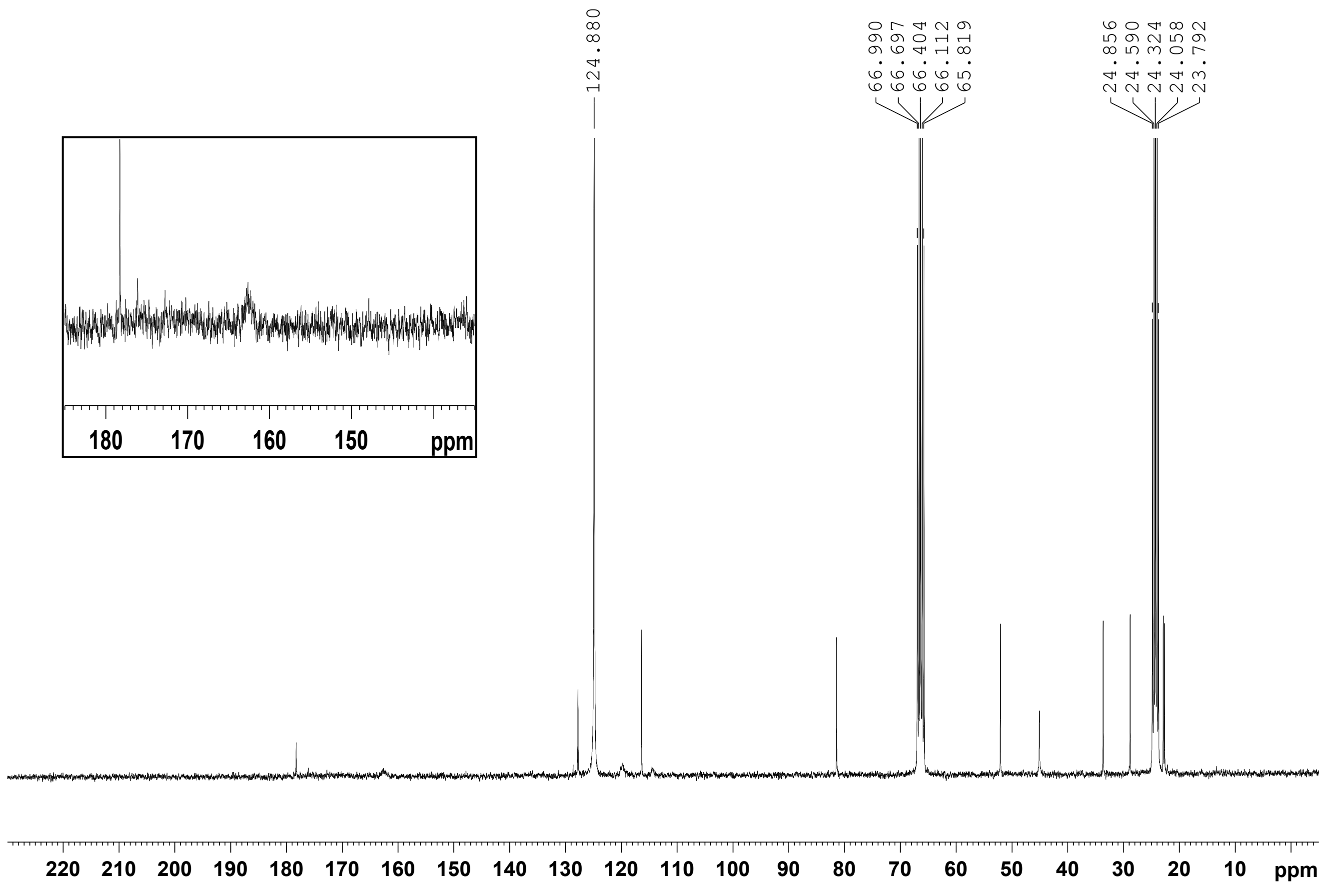



**Figure S 16** $^{13}C\{^1H\}$ NMR (75 MHz, THF-$d_8$) spectrum for [Ir(cod)(I$^i$Pr)($OCO_2$Ph)] **13**. Inset: expanded region showing CO signal after $^{13}CO_2$ insertion .

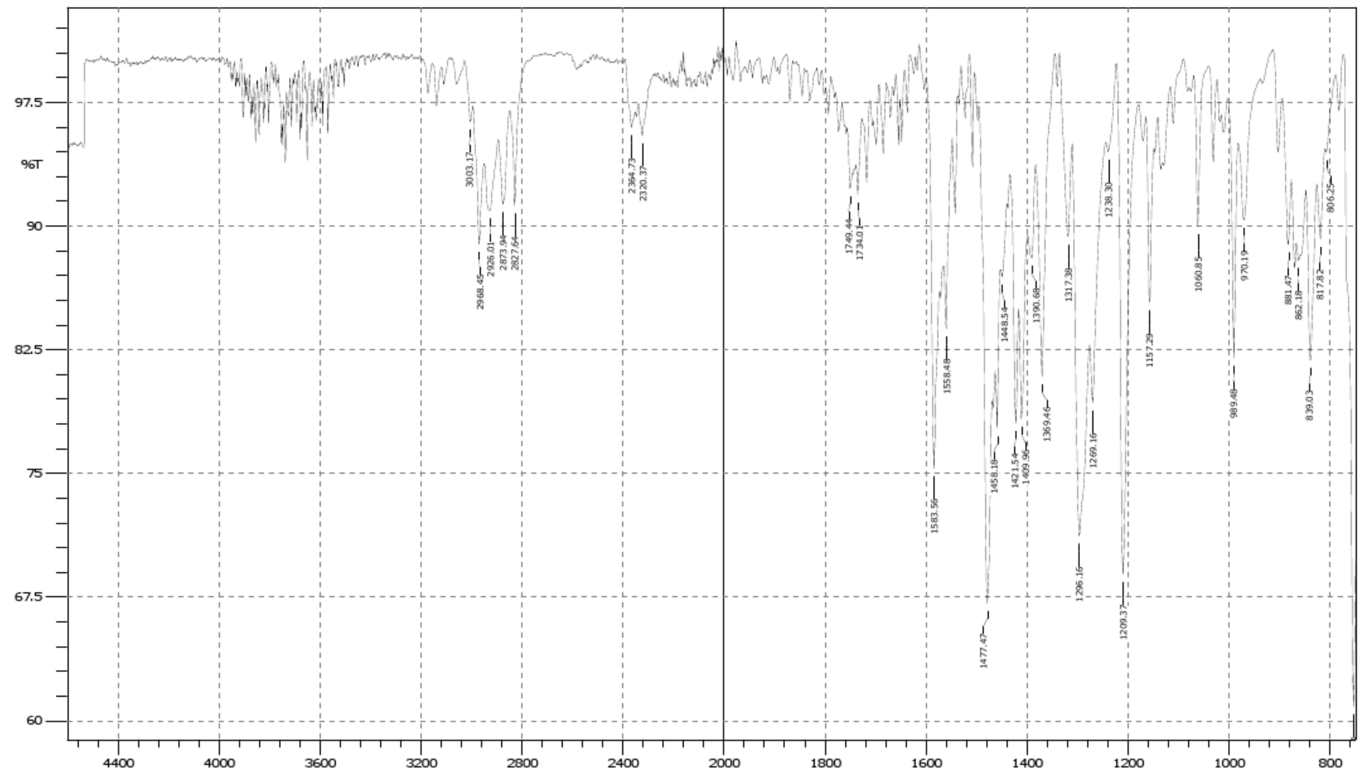



**Figure S 17** IR (ATR) spectrum for [Ir(cod)(I$^i$Pr)(OCO$_2$Ph)] **13**

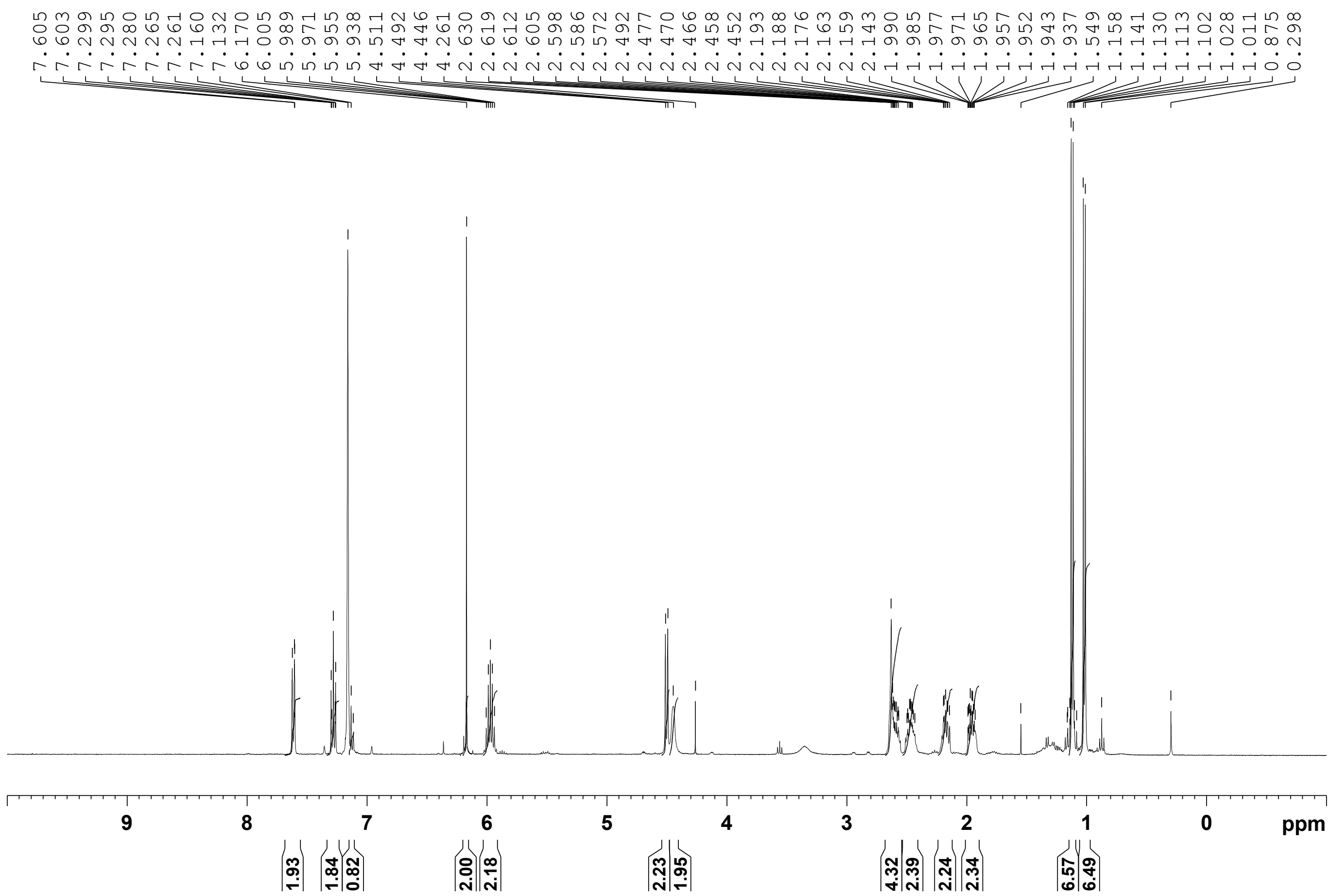



**Figure S 18** $^1$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)(NHBn)] **14**

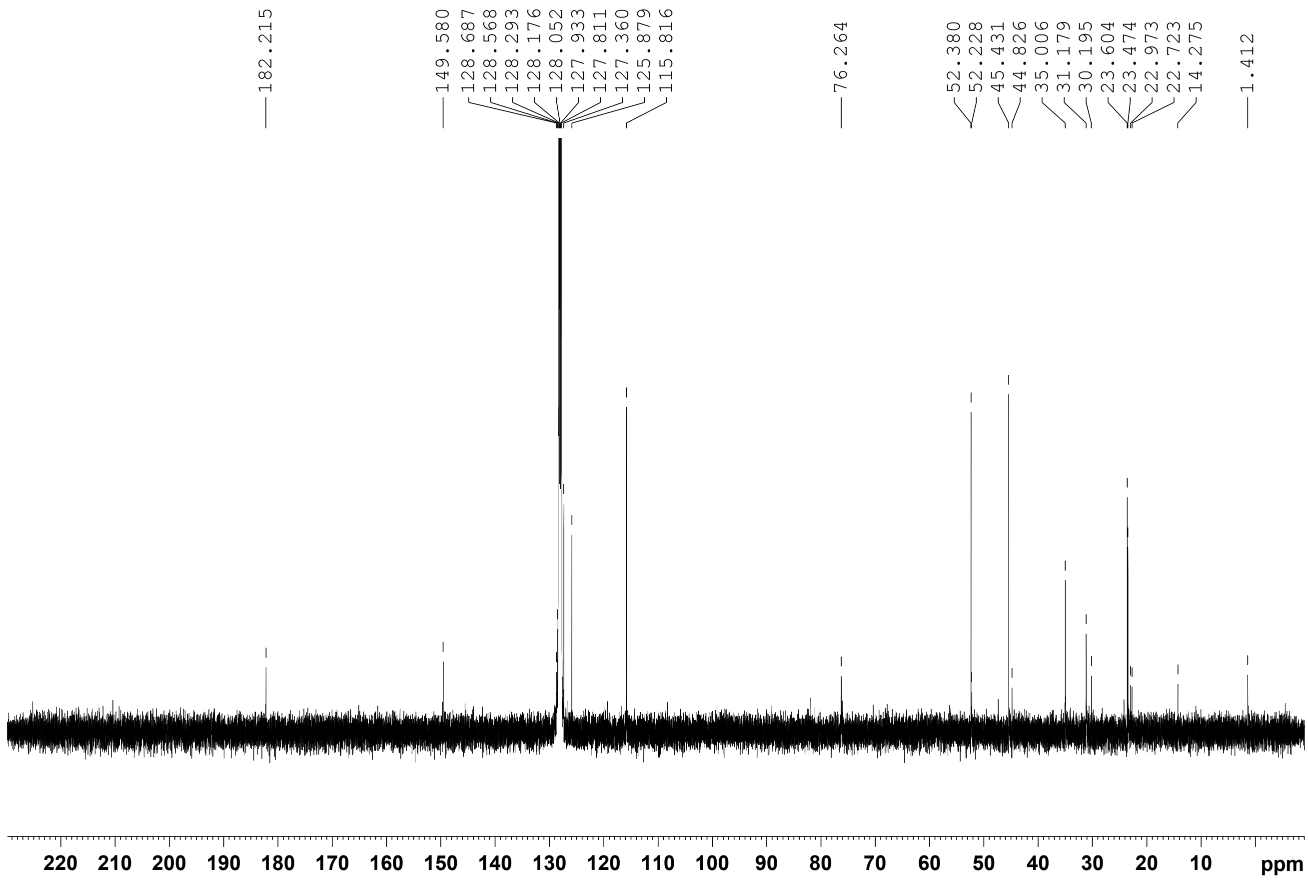



**Figure S 19** $^{13}C\{^{1}H\}$ NMR (100 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)(NHBn)] **14**

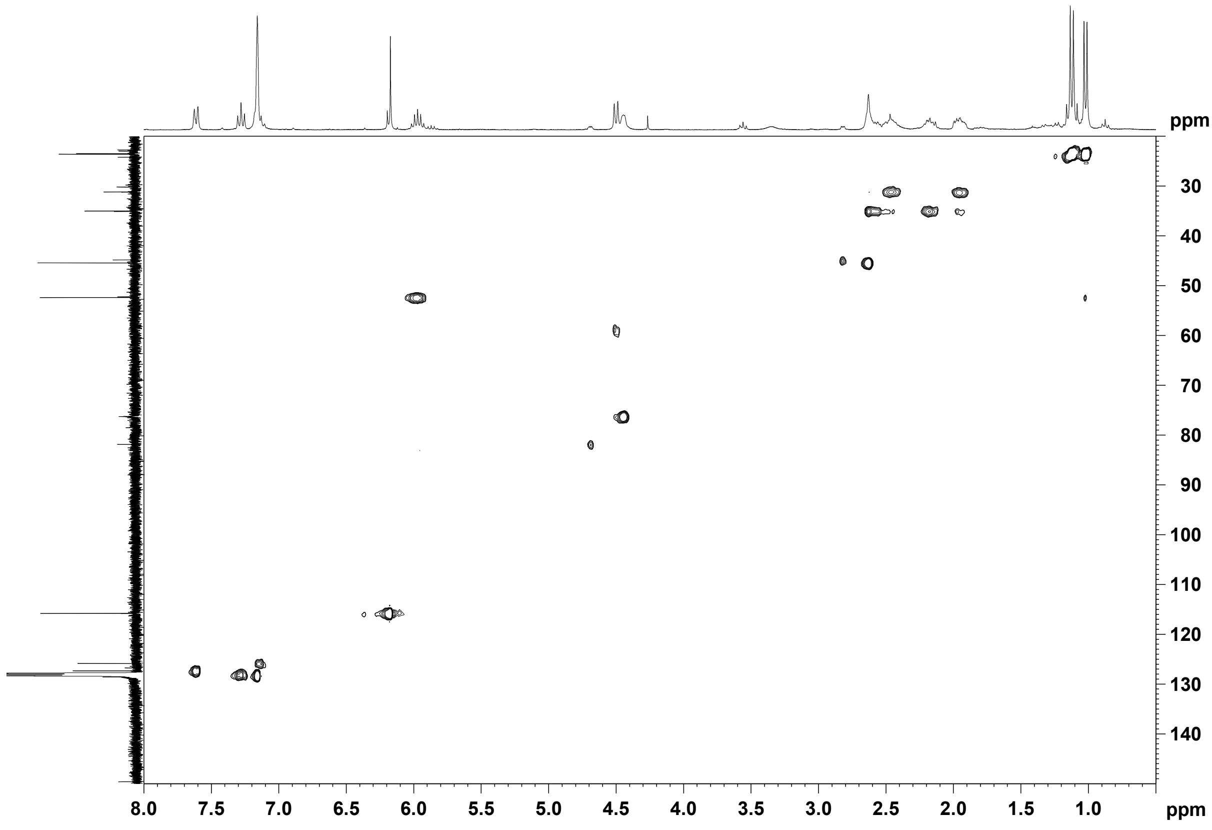



**Figure S 20** HSQC NMR (400 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)(NHBn)] **14**

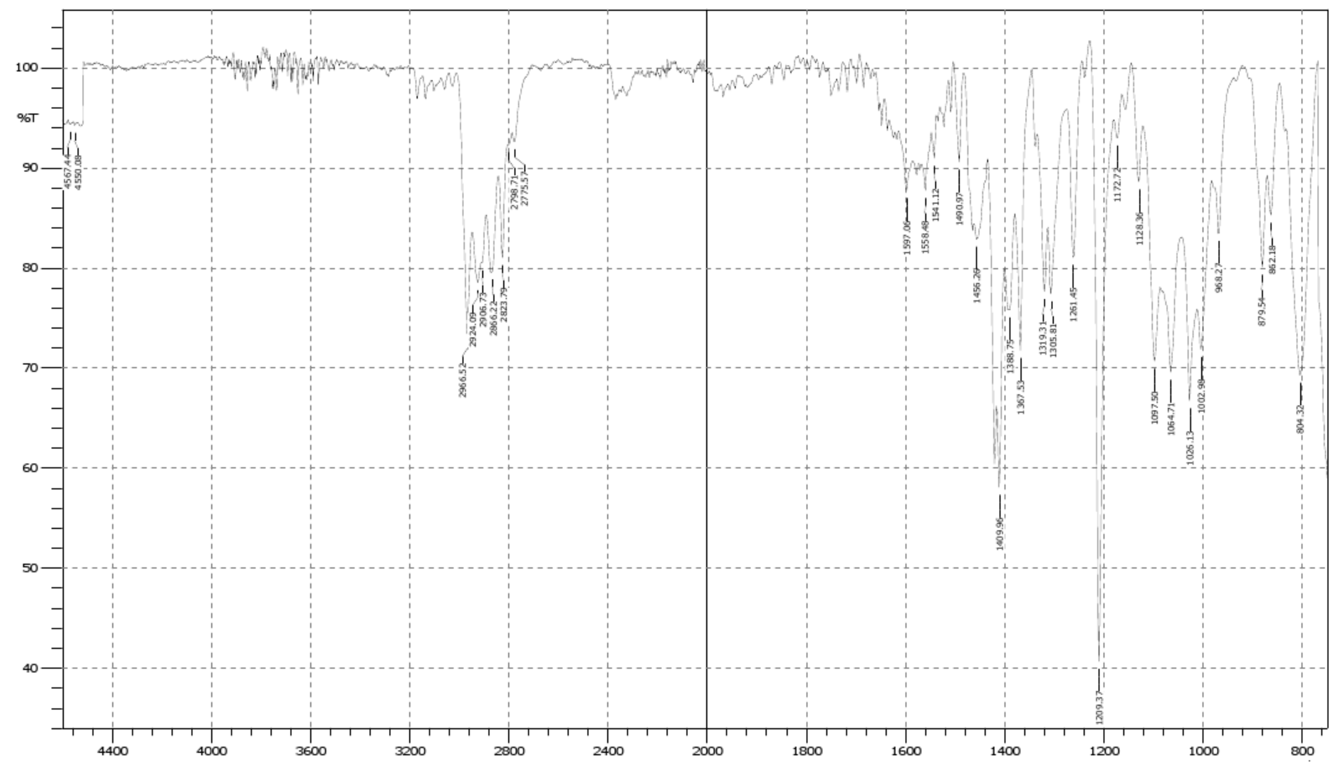


**Figure S 21** IR (ATR) spectrum for [Ir(cod)(I$^i$Pr)(NHBn)] **14**

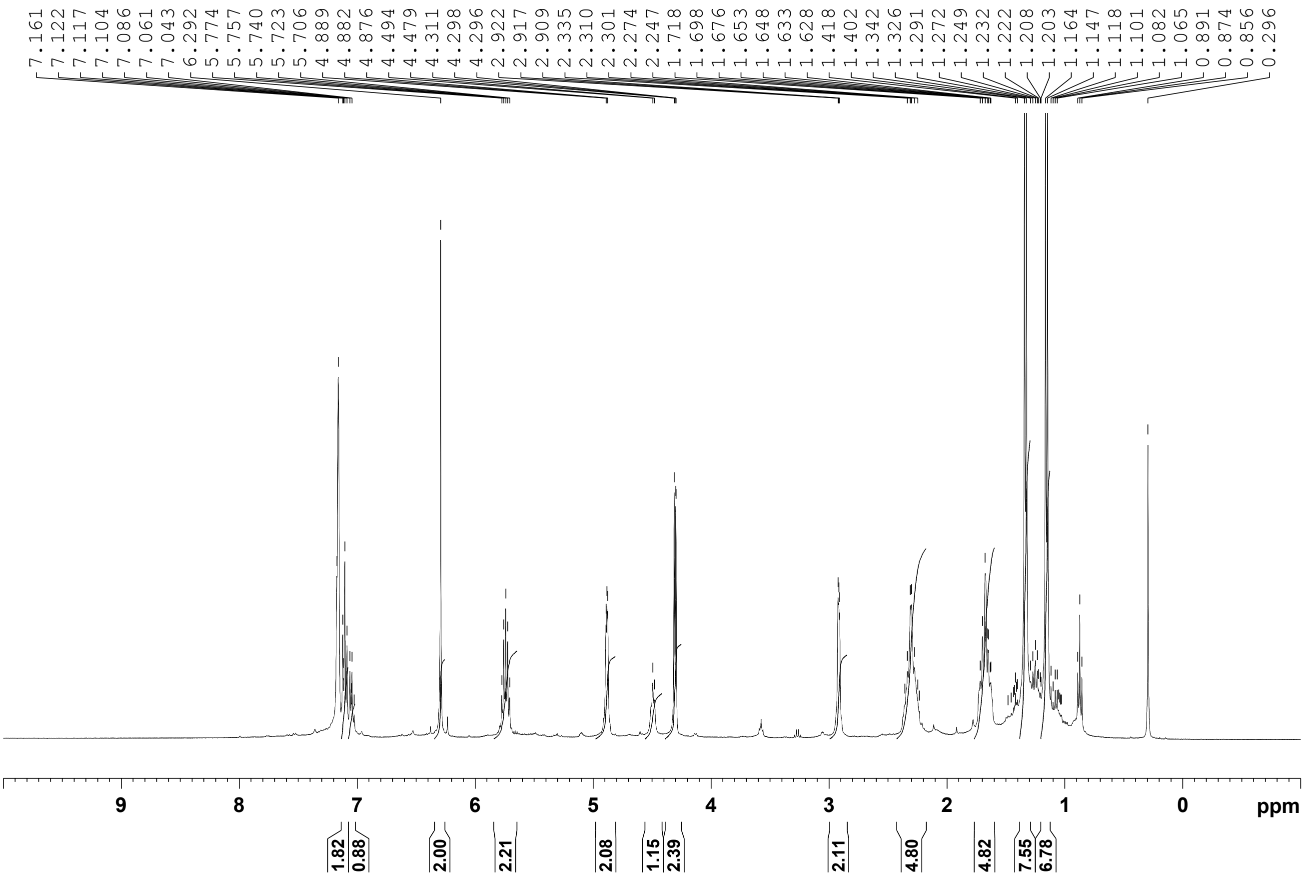


**Figure S 22** $^1$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

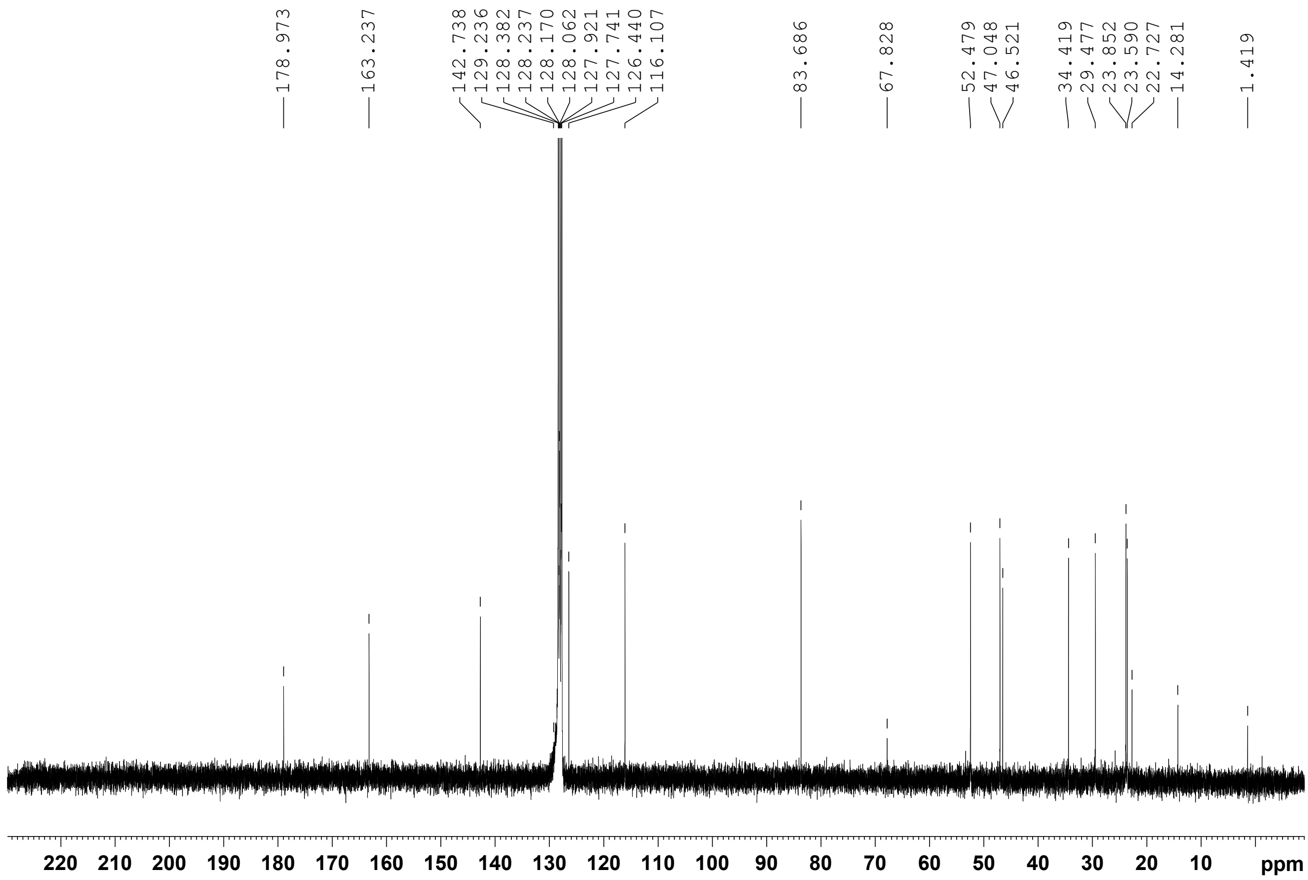



**Figure S 23** $^{13}C\{^{1}H\}$ NMR (75 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

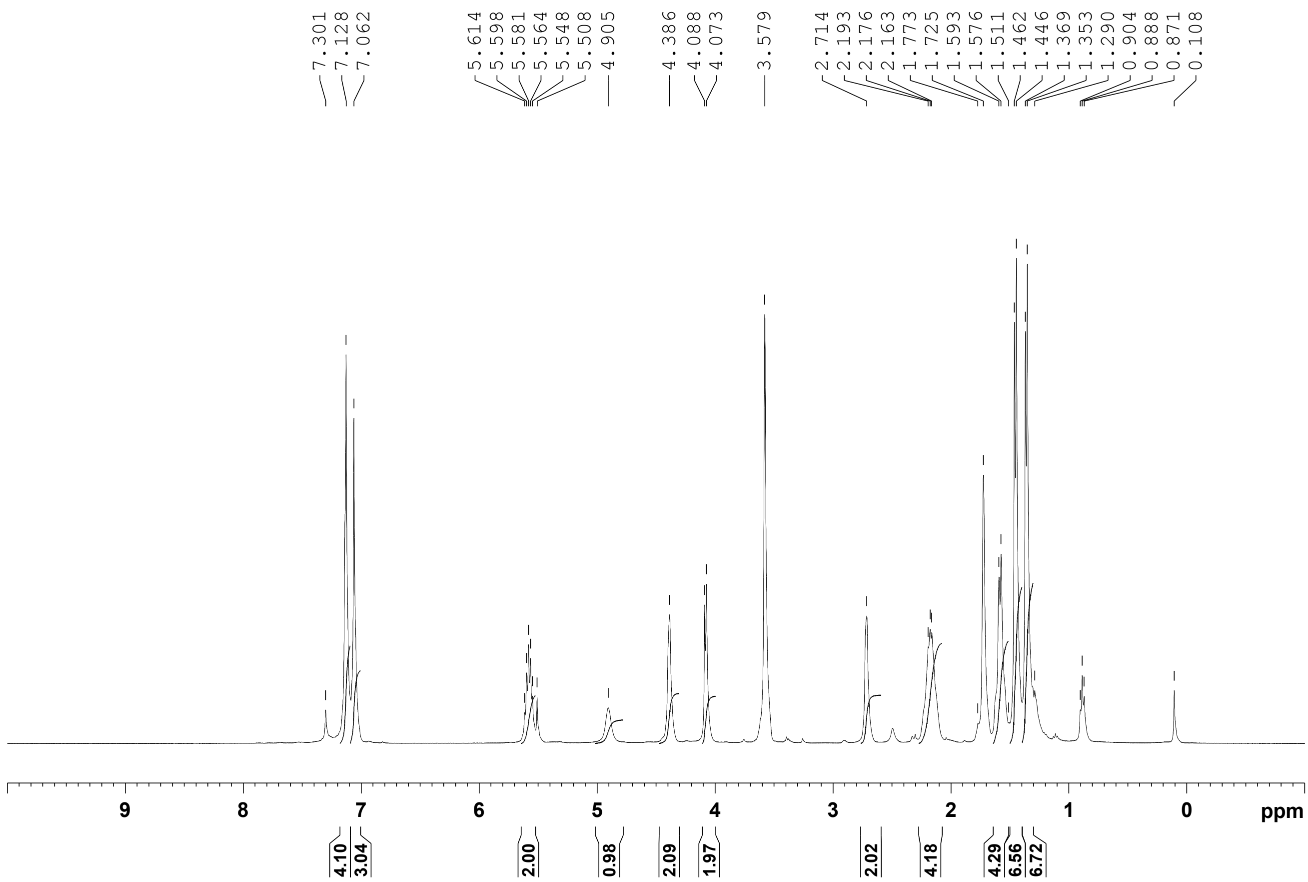



**Figure S 24** $^1$H NMR (400 MHz, THF$d_8$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

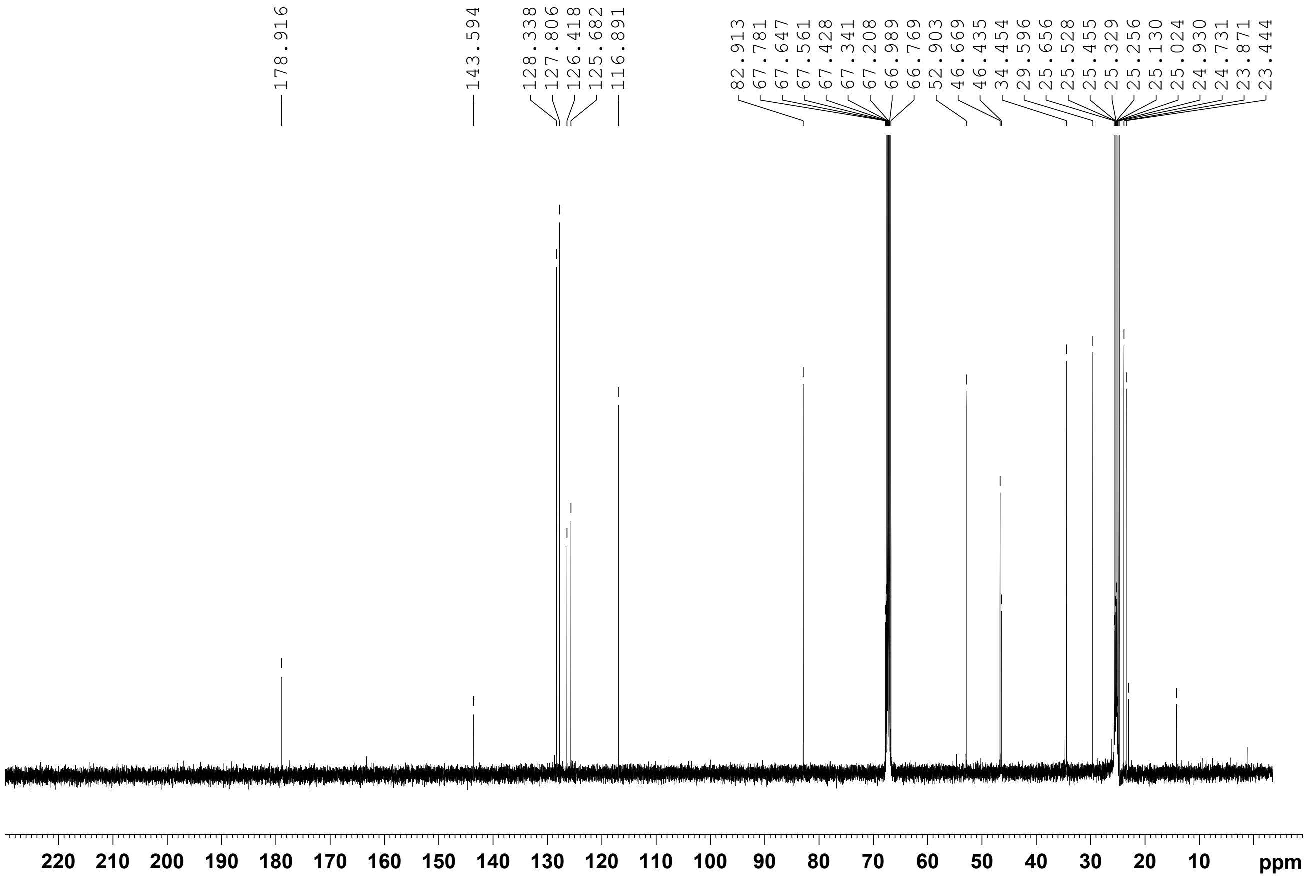



**Figure S 25** $^{13}C\{^{1}H\}$ NMR (100 MHz, THF$d_8$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

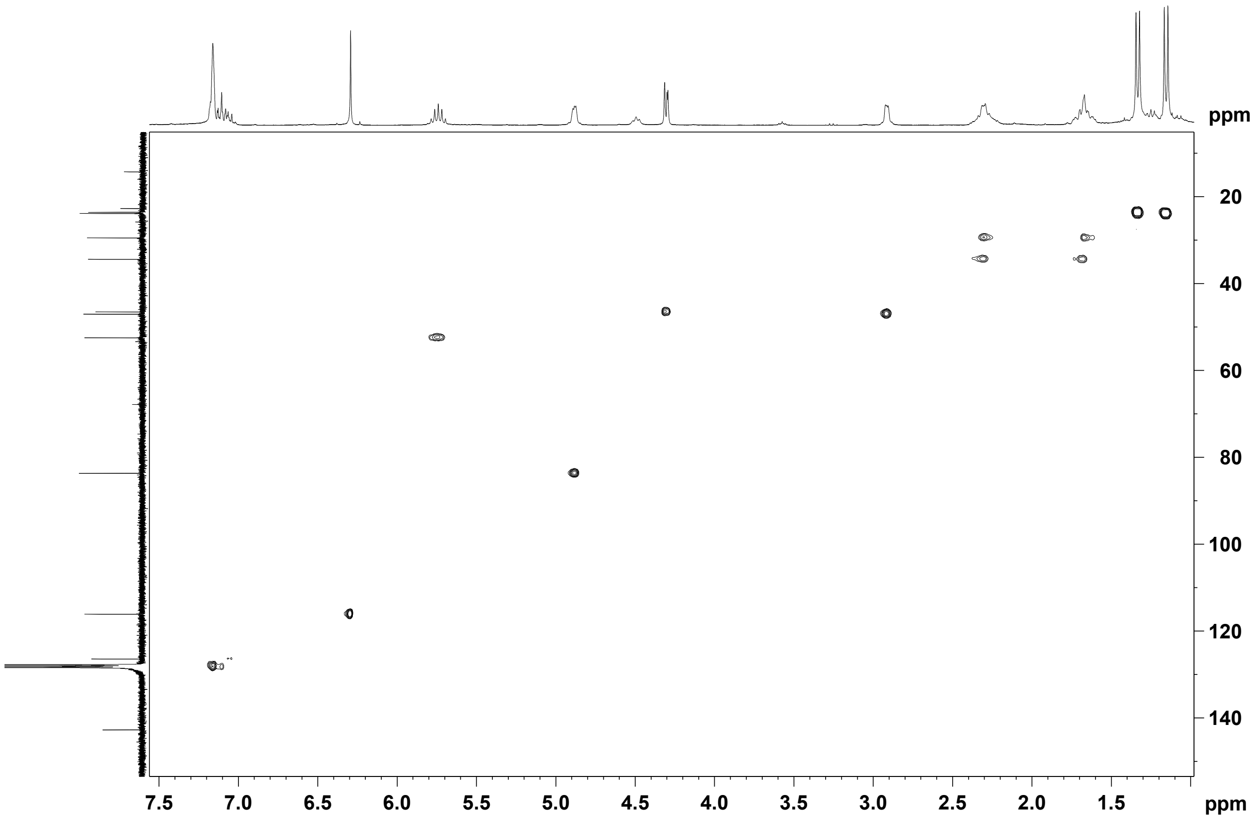



**Figure S 26** HSQC NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

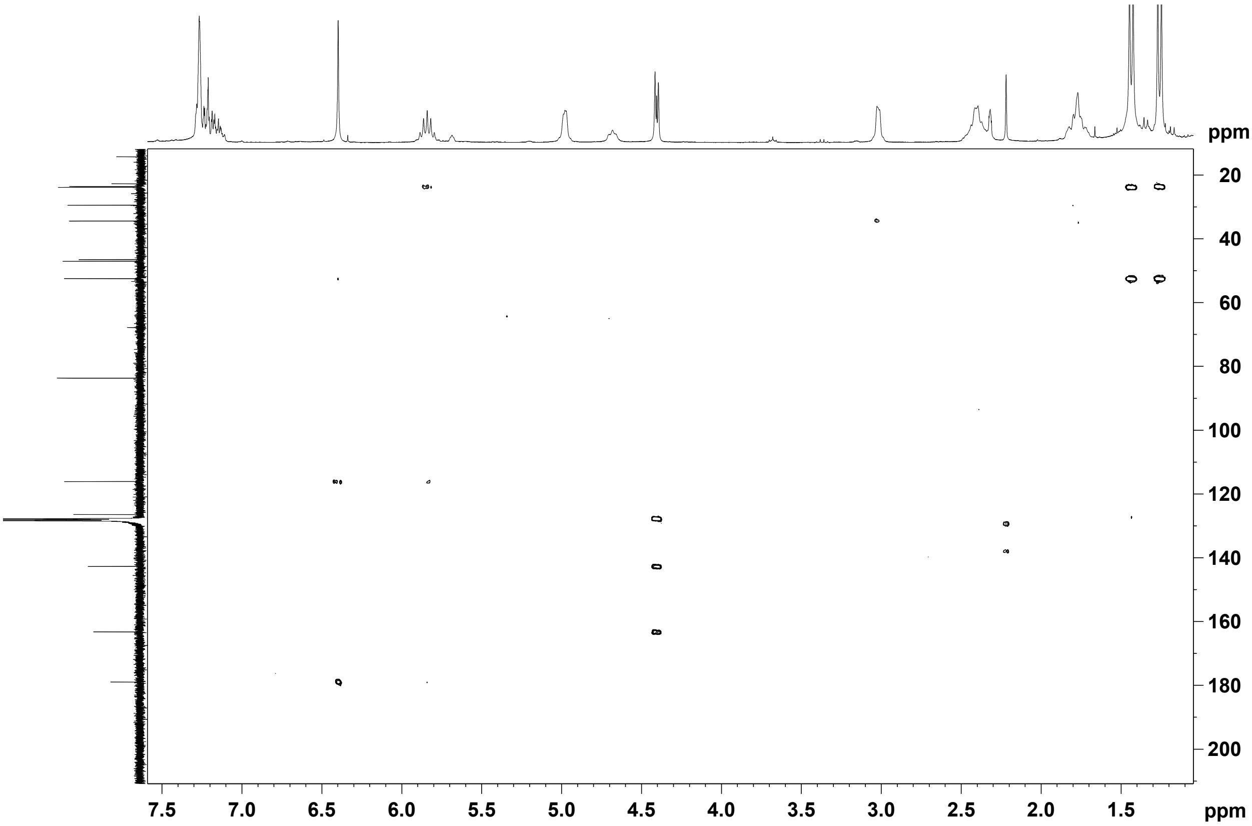



**Figure S 27** HMBC NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

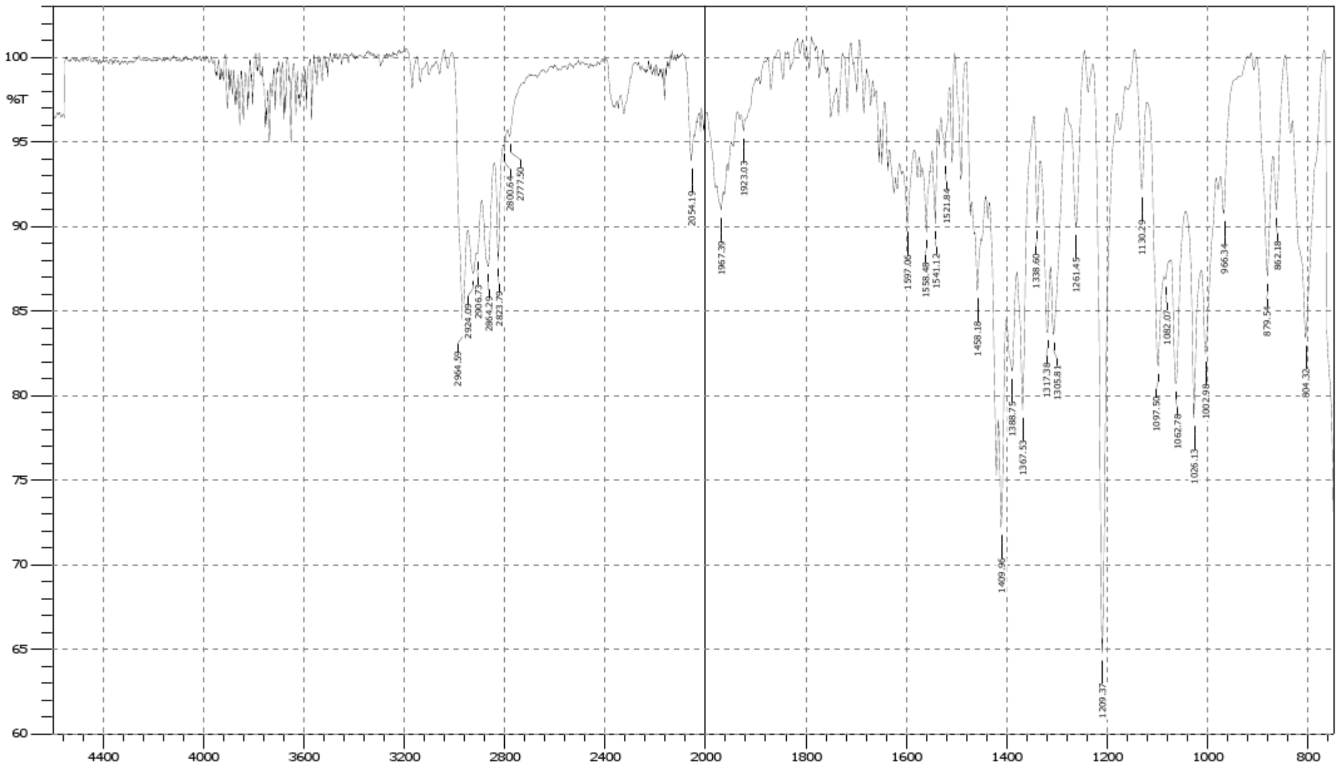



**Figure S 28** IR (ATR) spectrum for [Ir(cod)(I$^i$Pr)($O_2$CNHBn)] **16**

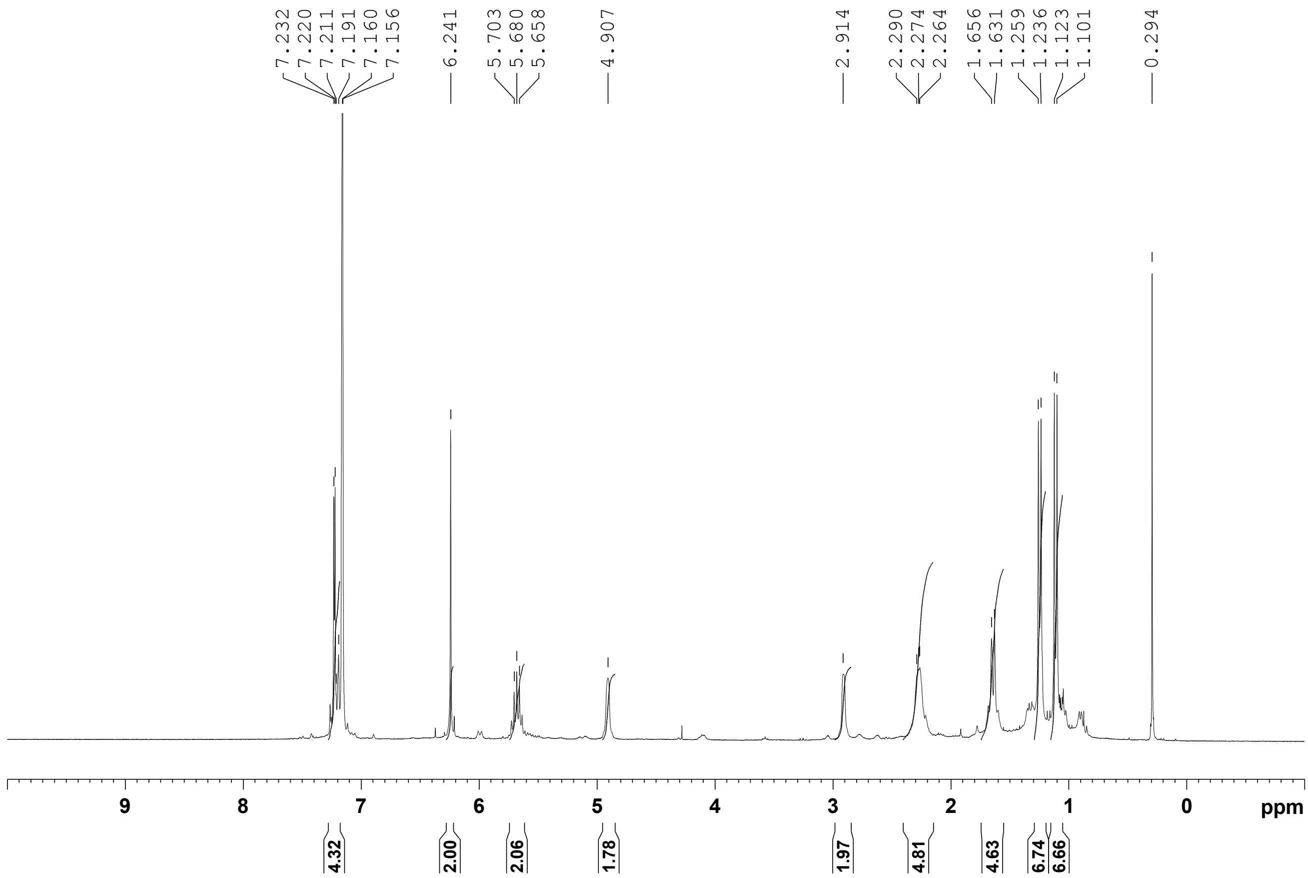



**Figure S 29** $^{1}$H NMR (300 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)($O_2$CNH(-*p*-Br$C_6H_4$))] **17**

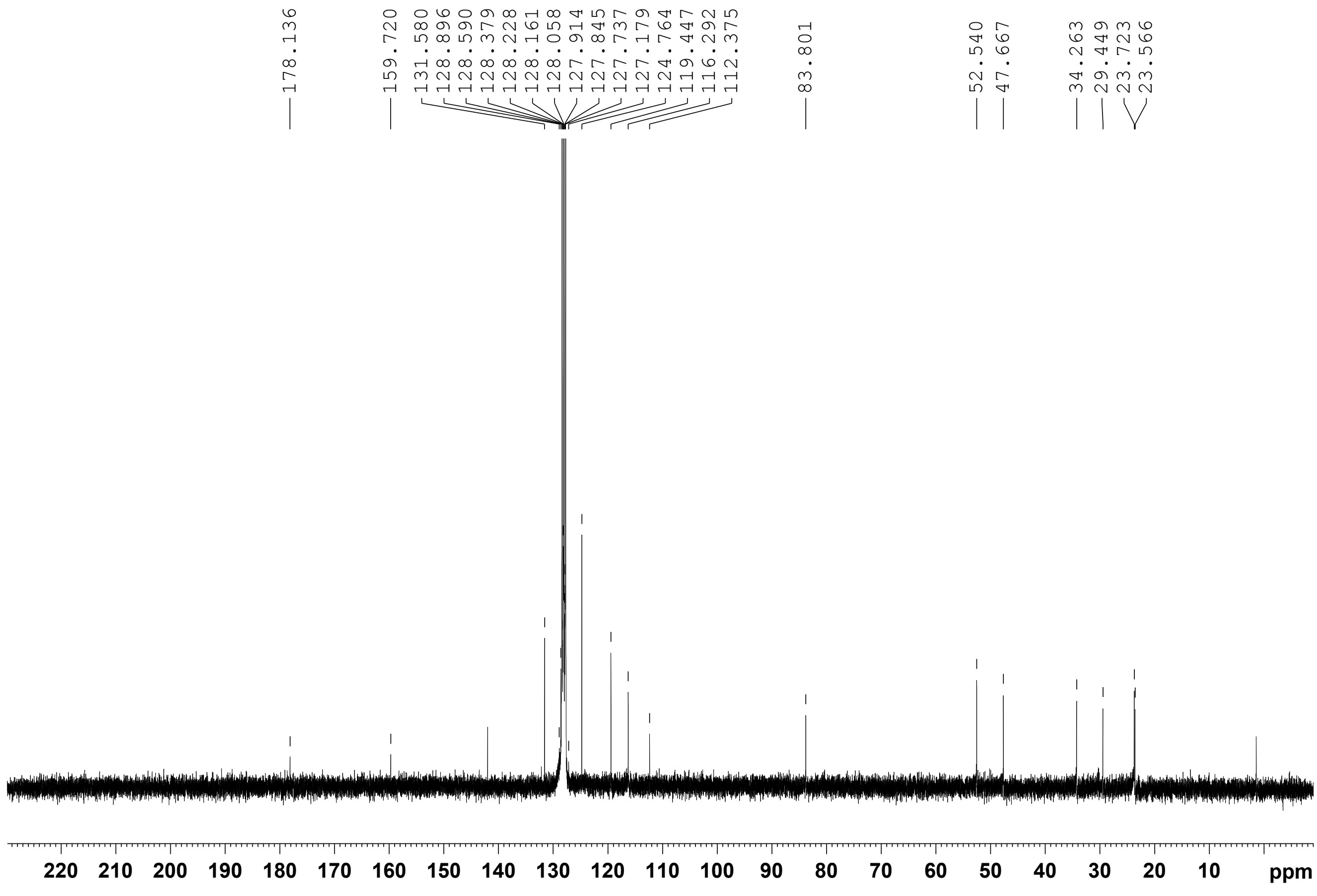



**Figure S 30** $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$) spectrum for [Ir(cod)(I$^{i}$Pr)($O_2$CNH(-*p*-Br$C_6H_4$))] **17**

**References**

1. B. J. Truscott, D. J. Nelson, C. Lujan, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2013, **19**, 7904-7916.