Supporting Information

Challenges in Cyclometalation: Steric Effects Leading to Competing Pathways and η^1,η^2-Cyclometalated Iridium(III) Complexes

Houguang Jeremy Chen, Ronald Hong Xiang Teo, Jonathan Wong, Yongxin Li, Sumod A. Pullarkat, and Pak-Hing Leung*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Email: pakhing@ntu.edu.sg

TABLE OF CONTENTS

A GENERAL CONSIDERATIONS

Reactions involving air- or moisture-sensitive compounds were carried out by means of conventional Schlenk techniques under a positive pressure of nitrogen gas. Unless stated otherwise, chemicals and solvents were used as received from commercial vendors without further purification. When required, anhydrous solvents were freshly distilled and dried according to standard procedures prior to use.

Nuclear magnetic resonance (NMR) spectroscopy were recorded at Nanyang Technological University Division of Chemistry and Biological Chemistry Central Facilities Laboratory on the Bruker Avance III 400 (BBFO 400) spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts (δ) are quoted in ppm, and referenced to chemical shifts of residual solvent peaks for ^{1}H and ^{13}C NMR.

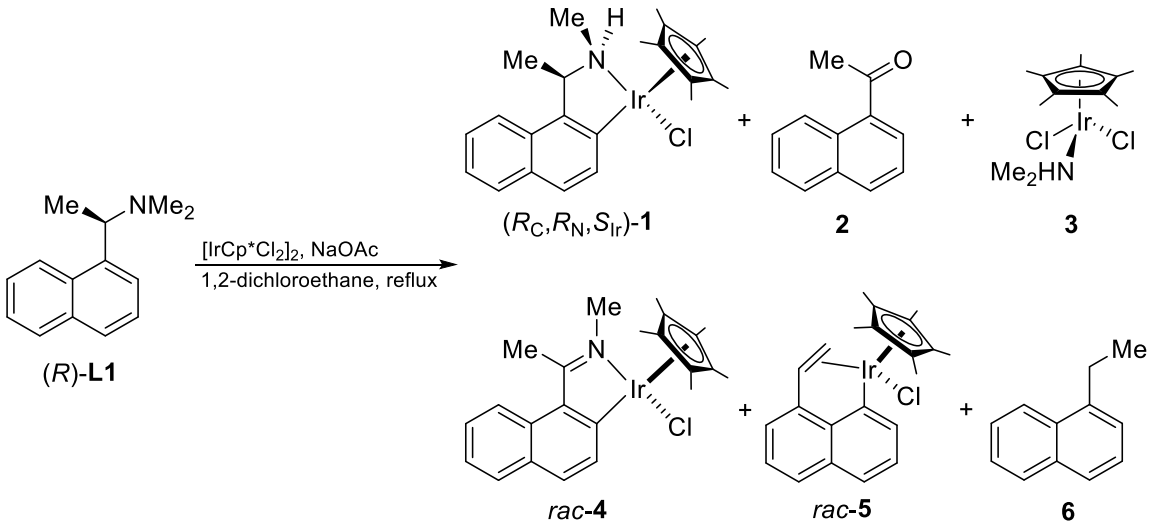
High resolution mass spectrometry *via* electrospray ionization (ESI) was performed on the Waters Q-Tof Premier spectrometer. Unless stated otherwise, acetonitrile was used as the solvent for the dissolution of compounds.

Elemental analysis was performed on the EuroVector Euro EA elemental analyzer at Nanyang Technological University Division of Chemistry and Biological Chemistry Central Facilities Laboratory.

Optical rotation studies were measured on the Jasco P-1030 polarimeter in a 0.1 dm polarimetry cell at the specified temperature using the D-line of sodium (589 nm) as the source of light. Unless stated otherwise, dichloromethane was used as the solvent for the dissolution of compounds.

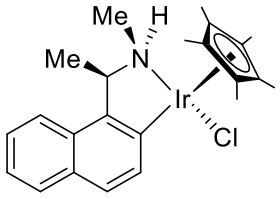
B EXPERIMENTAL

B1 The Iridation Reaction of (*R*)-*N*,*N*-Dimethyl-1-Naphthylethylamine (*R*)-L1



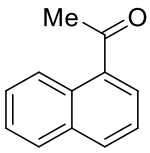
$[IrCp^*Cl_2]_2$ (100 mg, 0.125 mmol) and NaOAc (41 mg, 0.50 mmol) were added to a stirring solution of (*R*)-*N*,*N*-dimethyl-1-naphthylethylamine (*R*)-**L1** (50 mg, 0.25 mmol) in 1,2-dichloroethane (5 mL). The reaction mixture was then reflux for 48 h. The crude reaction mixture was evaporated to dryness and purified directly by column chromatography on silica gel (*refer to products on eluent system for column chromatography*).

(R_C,R_N,S_{Ir})-(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-1-[1-(N-methylamino)ethyl]naphthyl}iridium(III) chloride (R_C,R_N,S_{Ir})-1



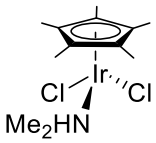
Eluent System (Chromatography): CH_2Cl_2; Yield: 5.5 mg (4%); $[\alpha]_D$ (22 °C, *c* 0.5) = –102.1°; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.24 (d, $^3J_{HH}$ = 6.5 Hz, 3H, ArCH(C*H*$_3$)), 1.67 (s, 15H, Cp(C*H*$_3$)), 3.02 (d, $^3J_{HH}$ = 6.4 Hz, 3H, NH(C*H*$_3$)), 4.69 (dq, $^3J_{HH}$ = 4.2 Hz and 6.4 Hz, 1H, ArC*H*(CH$_3$)), 5.02 (br s, 1H, N*H*(CH$_3$)), 7.20-7.74 (m, 6H, Ar*H*); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 9.36 (C_5(*C*H$_3$)$_5$), 17.39 (ArCH(*C*H$_3$)N), 39.57 (N*C*H$_3$), 66.89 (Ar*C*H(CH$_3$)N), 87.35 (C_5(CH$_3$)$_5$), 122.66 (aromatic carbon), 123.41 (aromatic carbon), 125.41 (aromatic carbon), 126.05 (aromatic carbon), 127.92 (aromatic carbon), 128.38 (aromatic carbon), 131.07 (aromatic carbon), 136.07 (aromatic carbon), 144.65 (aromatic carbon), 153.10 (aromatic carbon); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{23}H_{29}ClIrN$ 547.1618, found 547.1619; Anal. calcd for $C_{23}H_{29}ClIrN$: C, 50.49; H, 5.34; N, 2.56. Found: C, 50.02; H, 5.56; N, 2.31.

1-Acetonaphthone 2



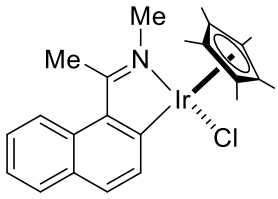
Eluent System (Chromatography): *n*-hexane:CH_2Cl_2 (2:1); Yield: 20.4 mg (48%; *two-day reaction*); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 3H, Ar(C=O)C*H*$_3$), 7.48-8.74 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.93 (C(=O)*C*H$_3$), 124.29 (aromatic carbon), 126.00 (aromatic carbon), 126.41 (aromatic carbon), 128.01 (aromatic carbon), 128.37 (aromatic carbon), 128.58 (aromatic carbon), 130.15 (aromatic carbon), 132.97 (aromatic carbon), 133.98 (aromatic carbon), 135.52 (aromatic carbon), 201.76 (*C*(=O)CH$_3$); HRMS (ESI) *m*/*z* $[(M+H)]^+$ calcd for $C_{12}H_{11}O$ 171.0810, found 170.0814; Anal. calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.93; H, 5.59.

Dichloro(dimethylamino)-1,2,3,4,5-pentamethylcyclopentadienyl iridium(III) 3



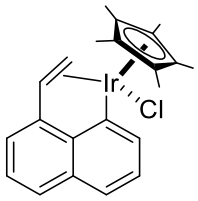
Eluent System (Chromatography): CH_2Cl_2:EtOAc (1:1); Yield: 24.4 mg (22%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64 (s, 15H, Cp(C*H*$_3$)), 2.89 (d, $^3J_{HH}$ = 5.4 Hz, 6H, HN(C*H*$_3$)$_2$), 3.90 (br s, 1H, *H*N(CH$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.20 (C_5(*C*H$_3$)$_5$), 43.94 (N*C*H$_3$), 84.76 (*C*$_5$(CH$_3$)$_5$); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{12}H_{22}ClIrN$ 443.0759, found 443.0747.

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-1-[1-(N-methylimino)ethyl]naphthyl}iridium(III) chloride rac-4



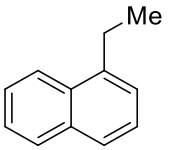
Eluent System (Chromatography): CH_2Cl_2:EtOAc (10:1); Yield: 2.7 mg (2%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73 (s, 15H, Cp(C*H*$_3$)), 2.98 (s, 3H, C(=NMe) (C*H*$_3$)Ar)), 3.98 (s, 3H, NC*H*$_3$), 7.32-8.22 (m, 6H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.16 (C_5(*C*H$_3$)$_5$), 20.65 (C(=N)*C*H$_3$), 45.68 (N*C*H$_3$)), 89.34 (*C*$_5$(CH$_3$)$_5$), 122.11 (aromatic carbon), 122.46 (aromatic carbon), 125.92 (aromatic carbon), 129.57 (aromatic carbon), 130.95 (aromatic carbon), 131.17 (aromatic carbon), 132.80 (aromatic carbon), 134.49 (aromatic carbon), 140.83 (aromatic carbon), 174.92 ((*C*(=N)CH$_3$)), 180.39 (aromatic carbon); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{23}H_{27}ClIrN$ 545.1461, found 545.1451; Anal. Calcd for $C_{23}H_{27}ClIrN$: C, 50.68; H, 4.99; N, 2.57. Found: C, 50.50; H, 5.07; N, 2.73.

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ²-C,[η²-ethylene])-1-naphthylethene}iridium(III) chloride rac-5



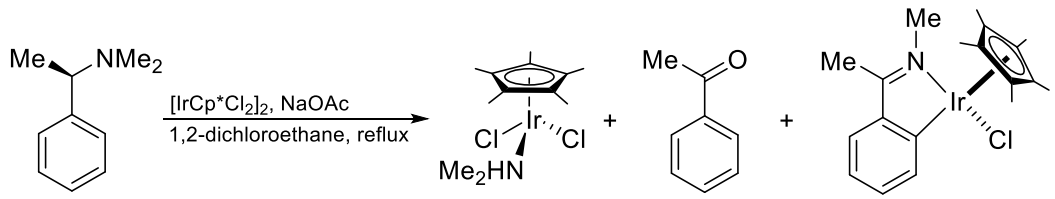
Eluent System (Chromatography): CH_2Cl_2; Yield: 2.6 mg (2%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 15H, Cp(C*H*$_3$)), 4.04 (d, $^3J_{HH}$ = 11.3 Hz, 1H, ArCHCH*H*), 4.10 (d, $^3J_{HH}$ = 8.8 Hz, 1H, ArCHC*H*H), 5.32 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 11.2 Hz, ArC*H*CH$_2$), 7.02-7.49 (m, 6H, Ar*H*) ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.29 (C$_5$(*C*H$_3$)$_5$), 56.16 (ArCH=*C*H$_2$), 80.82 (Ar*C*H=CH$_2$), 99.36 (*C*$_5$(CH$_3$)$_5$), 121.11 (aromatic carbon), 121.43 (aromatic carbon), 124.84 (aromatic carbon), 125.38 (aromatic carbon), 127.98 (aromatic carbon), 131.70 (aromatic carbon), 133.83 (aromatic carbon), 143.47 (aromatic carbon), 146.03 (aromatic carbon), 148.17 (aromatic carbon); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{22}H_{24}ClIr$ 516.1196, found 516.1188; Anal. calcd for $C_{22}H_{24}ClIr$: C, 51.20; H, 4.69. Found: C, 51.45; H, 4.11.

1-Ethylnaphthalene 6



Eluent System (Chromatography): *n*-hexane; Yield: 0.3 mg (<1%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (t, $^3J_{HH}$ = 7.5 Hz, 3H, ArCH$_2$C*H*$_3$), 3.13 (q, $^3J_{HH}$ = 7.5 Hz, 2H, ArC*H*$_2$CH$_3$), 7.34-8.08 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.03 (ArCH$_2$*C*H$_3$), 25.88 (Ar*C*H$_2$CH$_3$), 123.72 (aromatic carbon), 124.83 (aromatic carbon), 125.37 (aromatic carbon), 125.65 (aromatic carbon), 126.37 (aromatic carbon), 128.73 (aromatic carbon), 131.77 (aromatic carbon), 133.81 (aromatic carbon), 140.27 (aromatic carbon); HRMS (ESI) *m*/*z* [(M+H)]$^+$ calcd for $C_{12}H_{13}$ 157.1017, found 157.1017; Anal. calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.57; H, 7.50.

B2 The Iridation Reaction of (*R*)-*N*,*N*-Dimethyl-1-Phenylethylamine (*R*)-L2

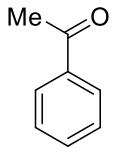


$[IrCp^*Cl_2]_2$ (100 mg, 0.125 mmol) and NaOAc (41 mg, 0.50 mmol) were added to a stirring solution of (*R*)-*N*,*N*-dimethyl-1-phenylethylamine (*R*)-**L2** (50 mg, 0.25 mmol) in 1,2-dichloroethane (5 mL). The reaction mixture was then reflux for 2 days. The crude reaction mixture was evaporated to dryness and purified directly by column chromatography on silica gel with hexane/ethyl acetate as the eluent.

Dichloro(dimethylamino)-1,2,3,4,5-pentamethylcyclopentadienyl iridium(III) 3

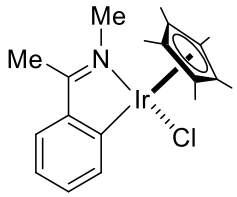
Yield: 17% (*refer to Page S5 for characterization*).

Acetophenone 7



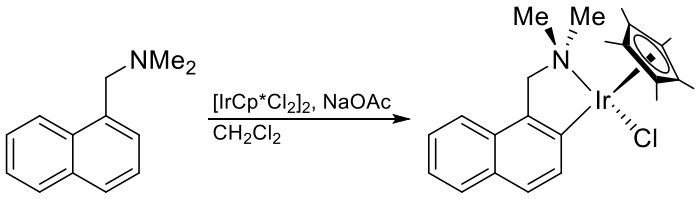
Yield: 12.3 mg (41%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 3H, C*H*$_3$), 7.44-7.97 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.57 (C(=O)*C*H$_3$), 128.27 (aromatic carbon), 128.54 (aromatic carbon), 133.07 (aromatic carbon), 137.12 (aromatic carbon), 198.12 (*C*(=O)CH$_3$); HRMS (ESI) *m*/*z* $[(M+H)]^+$ calcd for C_8H_8O 121.0653, found 121.0649; ; Anal. calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 80.13; H, 6.78.

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-1-[1-(N-methylimino)ethyl]phenyl}iridium (III) chloride rac-8



Yield: 16.1 mg (13%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67 (s, 15H, Cp(C*H*$_3$)), 2.51 (s, 3H, Ar(CN)C*H*$_3$), 3.84 (s, 3H, N(C*H*$_3$)), 6.95-7.76 (m, 4H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.99 (C_5(*C*H$_3$)$_5$), 14.65 (C(=N)*C*H$_3$), 45.09 (N*C*H$_3$), 88.67 (*C*$_5$(CH$_3$)$_5$), 121.07 (aromatic carbon), 127.34 (aromatic carbon), 130.77 (aromatic carbon), 135.10 (aromatic carbon), 148.18 (aromatic carbon), 167.89 (aromatic carbon), 180.04 (Ar*C*(=N)CH$_3$); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{19}H_{25}ClIrN$ 495.1305, found 495.1292; Anal. calcd for $C_{19}H_{25}ClIrN$: C, 46.10; H, 5.09; N, 2.83. Found: C, 45.62; H, 5.38; N, 2.83.

B3 The Cycloiridation of *N*,*N*-Dimethyl-1-Naphthylmethylamine L3

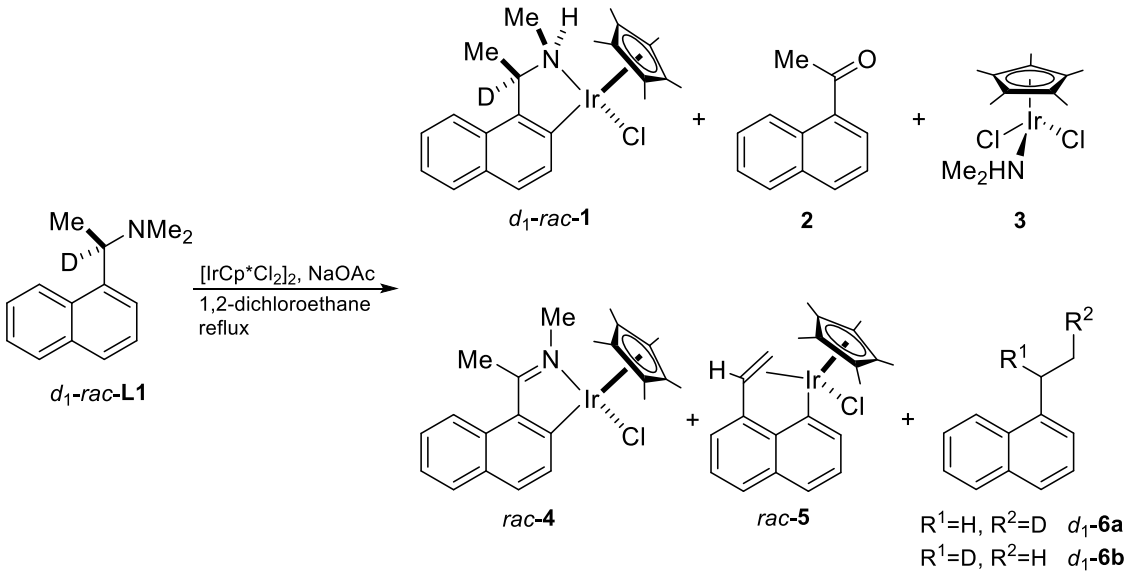


$[IrCp^*Cl_2]_2$ (40 mg, 0.05 mmol) and NaOAc (10 mg, 0.12 mmol) were added to a stirring solution of *N*,*N*-dimethyl-1-naphthylmethylamine **L3** (0.10 mmol) in dichloromethane (3 mL). The reaction mixture was then stirred at room temperature for 24 h. The crude reaction mixture was evaporated to dryness and purified by column chromatography on silica gel with dichloromethane as the eluent.

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-(N,N-dimethylamino)methylnaphthyl}iridium(III) chloride rac-9

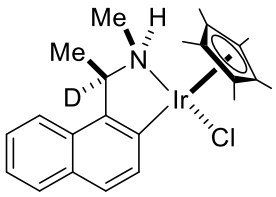
Yield: 40 mg (73%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.65 (s, 15H, Cp(C*H*$_3$)), 2.96 (s, 3H, ArCH$_2$NMe(C*H*$_3$)), 3.11 (s, 3H, ArCH$_2$N(C*H*$_3$)Me), 3.99 (d, $^2J_{HH}$ = 13.1 Hz, 1H, ArC*H*HNMe$_2$), 4.48 (d, $^2J_{HH}$ = 13.0 Hz, 1H, ArCH*H*NMe$_2$), 7.24-7.84 (m, 6H, Ar*H*); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 9.11 (C$_5$(*C*H$_3$)$_5$), 51.83 (N*C*H$_3$), 57.90 (N*C*H$_3$), 70.92 (Ar*C*H$_2$N), 87.85 (*C*$_5$(CH$_3$)$_5$), 122.56 (aromatic carbon), 123.18 (aromatic carbon), 124.74 (aromatic carbon), 125.06 (aromatic carbon), 128.09 (aromatic carbon), 129.82 (aromatic carbon), 130.72 (aromatic carbon), 134.48 (aromatic carbon), 141.10 (aromatic carbon), 150.86 (aromatic carbon); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{23}H_{29}ClIrN$ 547.1618, found 547.1608; Anal. calcd for $C_{23}H_{29}ClIrN$: C, 50.49; H, 5.34; N, 2.56. Found: C, 50.52; H, 5.15; N, 2.59.

B4 The Iridation Reaction of Deuterated *d*$_1$-*rac*-*N*,*N*-Dimethyl-1-Naphthylethylamine *d*$_1$-*rac*-L1



$[IrCp^*Cl_2]_2$ (100 mg, 0.125 mmol) and NaOAc (41 mg, 0.50 mmol) were added to a stirring solution of *d*$_1$-*rac*-dimethyl-1-naphthylethylamine *d*$_1$-(*R*)-**L1** (50 mg, 0.25 mmol) in 1,2-dichloroethane (5 mL). The reaction mixture was then reflux for 48 h. The crude reaction mixture was evaporated to dryness and purified directly by column chromatography on silica gel.

***d*$_1$-*rac*-(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-1-[1-(*N*-methylamino)-ethyl]naphthyl}iridium(III) chloride *d*$_1$-*rac*-1**



^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.25 (s, 3H, ArCD(C*H*$_3$)), 1.68 (s, 15H, Cp(C*H*$_3$)), 3.02 (d, $^3J_{HH}$ = 6.3 Hz, 3H, NH(C*H*$_3$)), 5.03 (br s, 1H, N*H*(CH$_3$)), 7.21-7.75 (m, 6H, Ar*H*); ^{2}H NMR (400 MHz, CD_2Cl_2): δ 4.72 (ArC*D*(CH$_3$)); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 9.37 (C_5(*C*H$_3$)$_5$), 17.28 (ArCD(*C*H$_3$)N), 39.54 (N*C*H$_3$), 66.51 ($^1J_{CD}$ = 20.5 Hz, Ar*C*D(CH$_3$)N), 87.35 (*C*$_5$(CH$_3$)$_5$), 122.66 (aromatic carbon), 123.41 (aromatic carbon), 125.41 (aromatic carbon), 126.05 (aromatic carbon), 127.95 (aromatic carbon), 128.39 (aromatic carbon), 131.09 (aromatic carbon), 136.09 (aromatic carbon), 144.64 (aromatic carbon), 153.13 (aromatic carbon); HRMS (ESI) *m*/*z* [*negative mode*] calcd for $C_{23}H_{28}DClIrN$ 548.1681, found 548.1675.

1-Acetonaphthone 2

Refer to Page S5 for characterization data.

Dichloro(dimethylamino)-1,2,3,4,5-pentamethylcyclopentadienyl iridium(III) 3

Refer to Page S5 for characterization data.

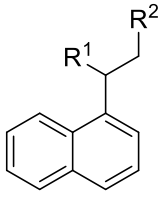
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-1-[1-(N-methylimino)ethyl]naphthyl}iridium(III) chloride rac-4

Refer to Page S5 for characterization data.

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,[η^2-ethylene])-1-naphthylethene}iridium(III) chloride rac-5

Refer to Page S6 for characterization data.

d$_1$-1-Ethylnaphthalene 6a and 6b

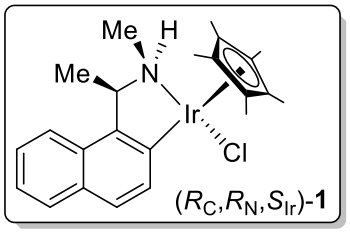


R^1=H, R^2=D d_1-**6a**
R^1=D, R^2=H d_1-**6b**

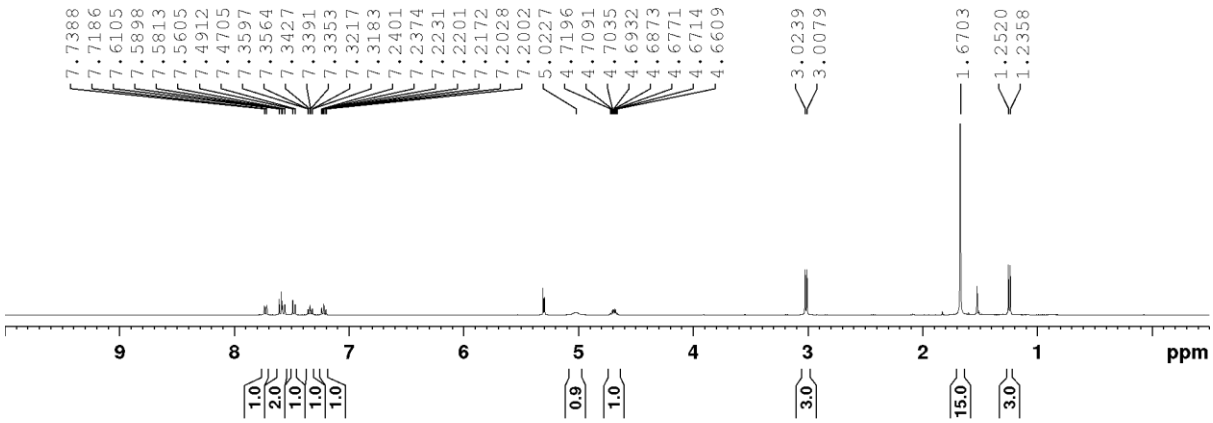
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (t, $^3J_{HH}$ = 7.5 Hz, 2.86H, $ArCH_2CH_3$), 3.13 (q, $^3J_{HH}$ = 7.5 Hz, 1.62H, $ArCH_2CH_3$), 7.34-8.08 (m, 7H, Ar*H*); ^{2}H NMR (400 MHz, $CDCl_3$): δ 1.41 ($ArCH_2CH_2D$), 3.13 ($ArCHDCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.73 ($^1J_{CD}$ = 20.6 Hz, $ArCH_2CH_2D$) 15.01 ($ArCH_2CH_3$), 25.55 ($^1J_{CD}$ = 19.3 Hz, $ArCHDCH_3$), 25.87 ($ArCH_2CH_3$), 123.72 (aromatic carbon), 124.83 (aromatic carbon), 125.36 (aromatic carbon), 125.65 (aromatic carbon), 126.36 (aromatic carbon), 128.72 (aromatic carbon), 131.78 (aromatic carbon), 133.83 (aromatic carbon), 140.27 (aromatic carbon); HRMS (ESI) *m*/*z* $[(M–H)]^+$ calcd for $C_{12}H_{11}D$ 156.0924, found 156.0919.

C NMR SPECTROSCOPY DATA

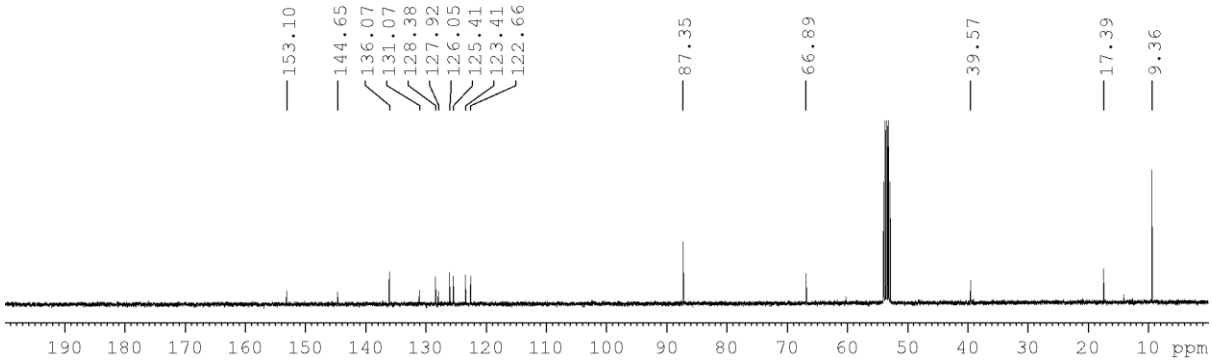
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-1-[1-(*N*-methylamino)ethyl]naphthyl}-iridium(III) chloride



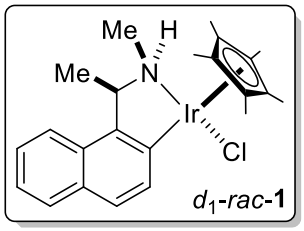
^{1}H NMR spectrum (400 MHz, CD_2Cl_2)



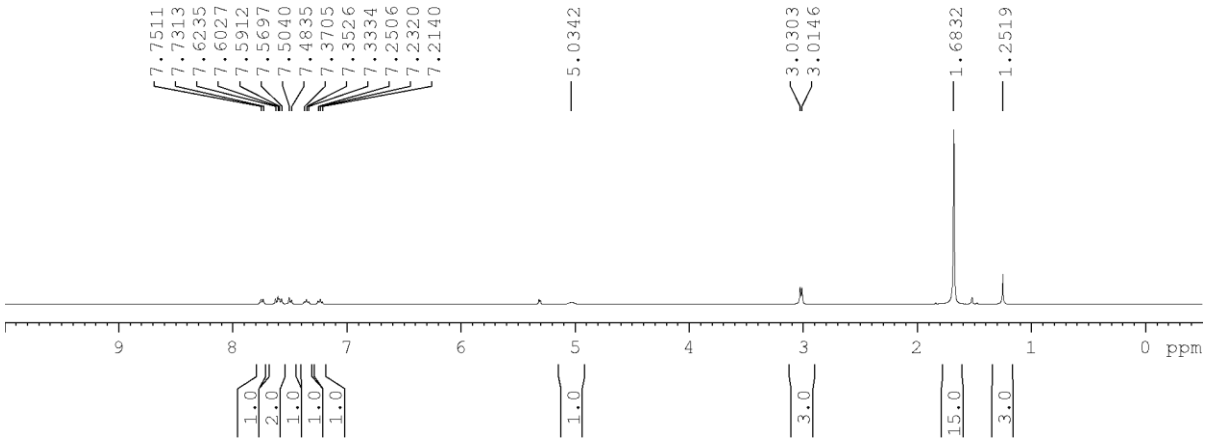
^{13}C NMR spectrum (100 MHz, CD_2Cl_2)



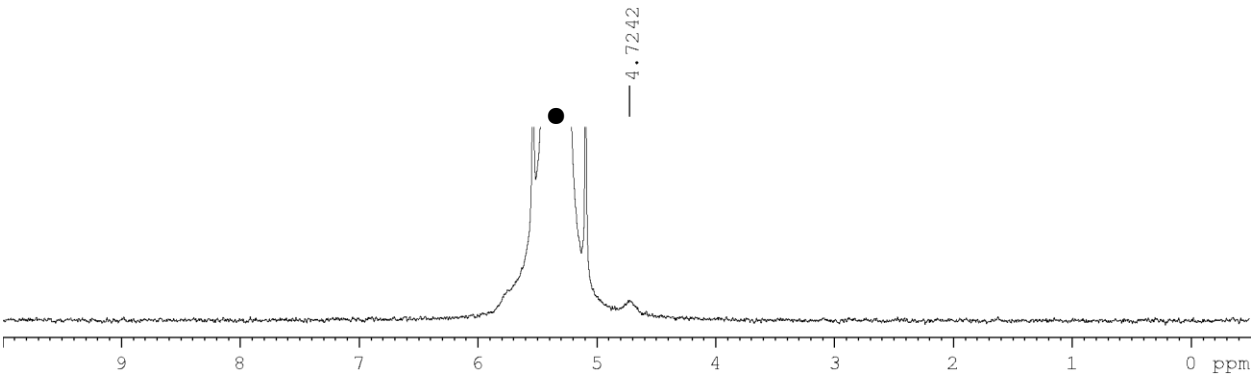
***d*$_1$-*rac*-(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-1-[1-(*N*-methylamino)ethyl]naphthyl}iridium(III) chloride**



^{1}H NMR spectrum (400 MHz, CD_2Cl_2)

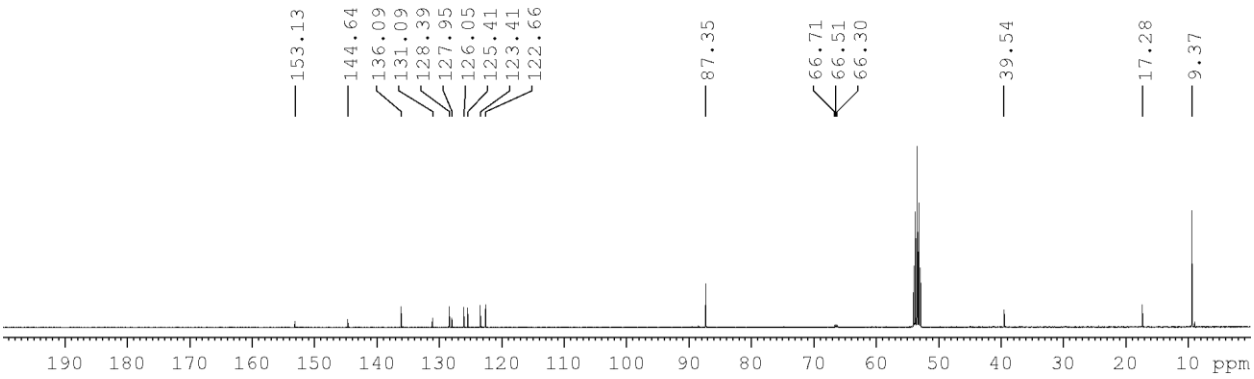


^{2}H NMR spectrum (400 MHz, CD_2Cl_2)

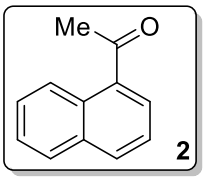


Note: The spectrum has been enlarged for clarity (● (*5.32 ppm*): *CD_2Cl_2*).

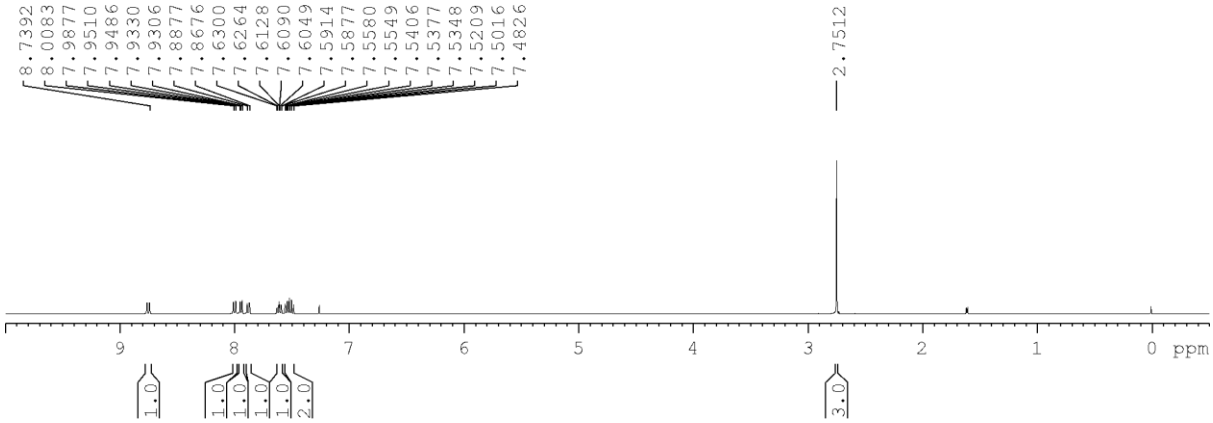
^{13}C NMR spectrum (100 MHz, CD_2Cl_2)



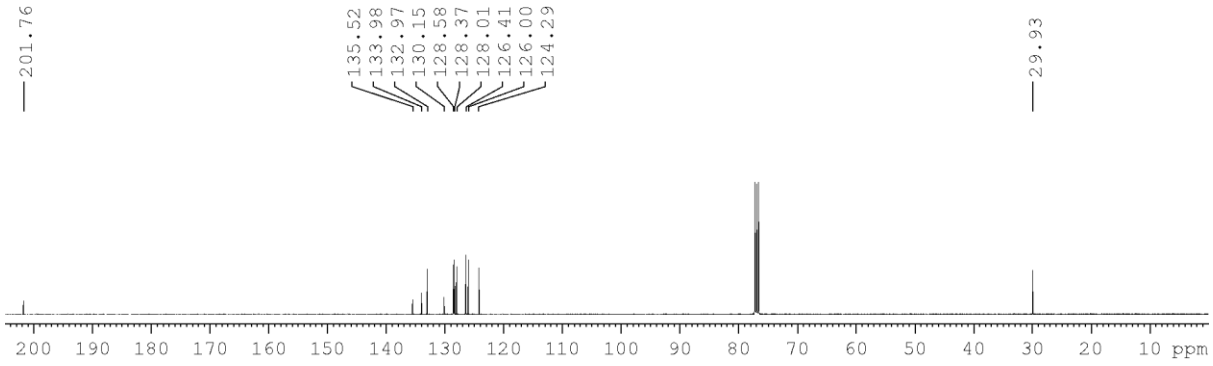
1-Acetonaphthone



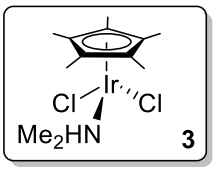
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



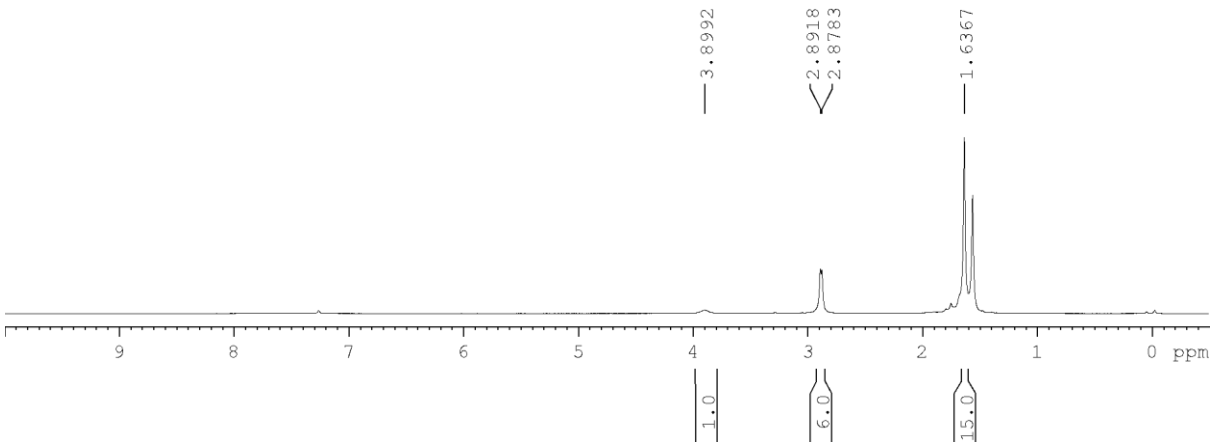
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



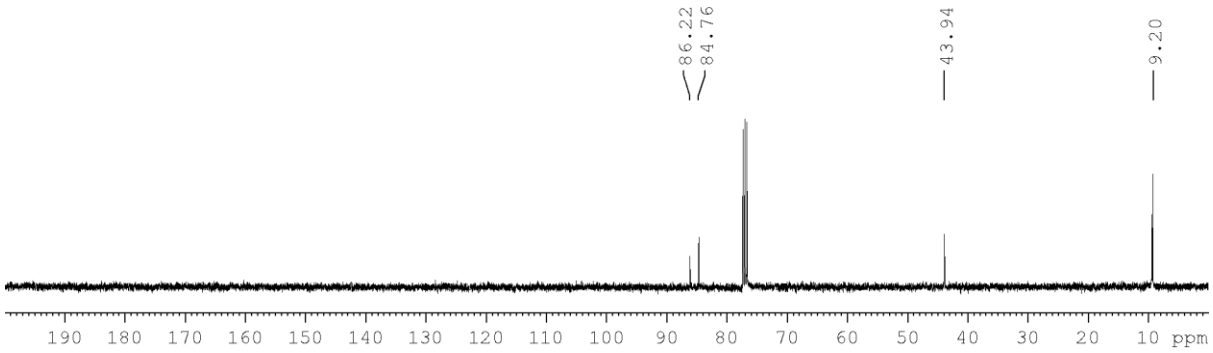
Dichloro(dimethylamino)-1,2,3,4,5-pentamethylcyclopentadienyl iridium(III)



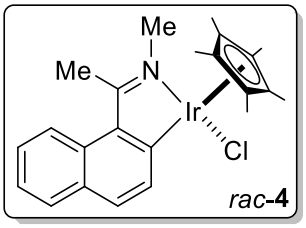
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



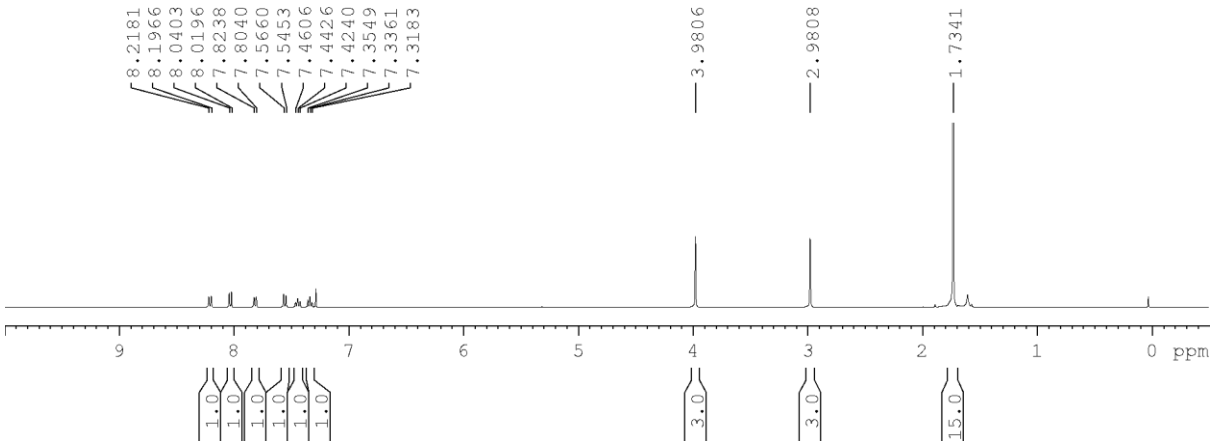
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



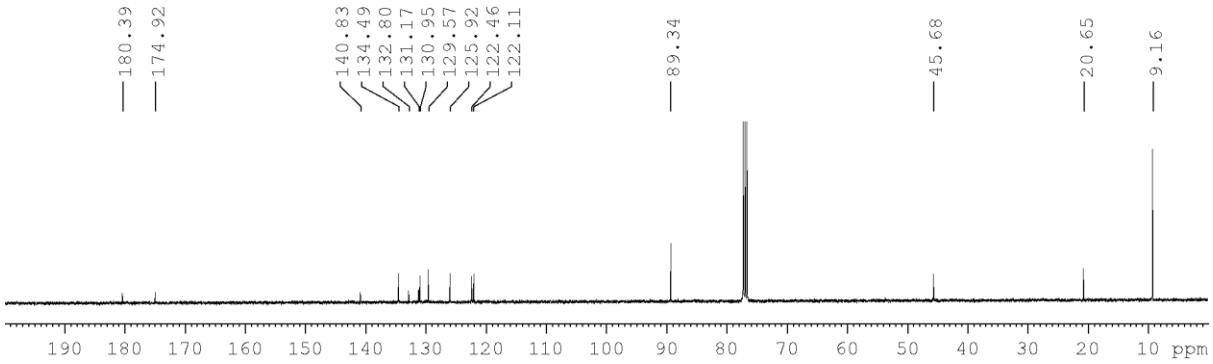
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-1-[1-(*N*-methylimino)ethyl]naphthyl}iridium(III) chloride



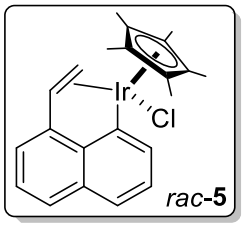
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



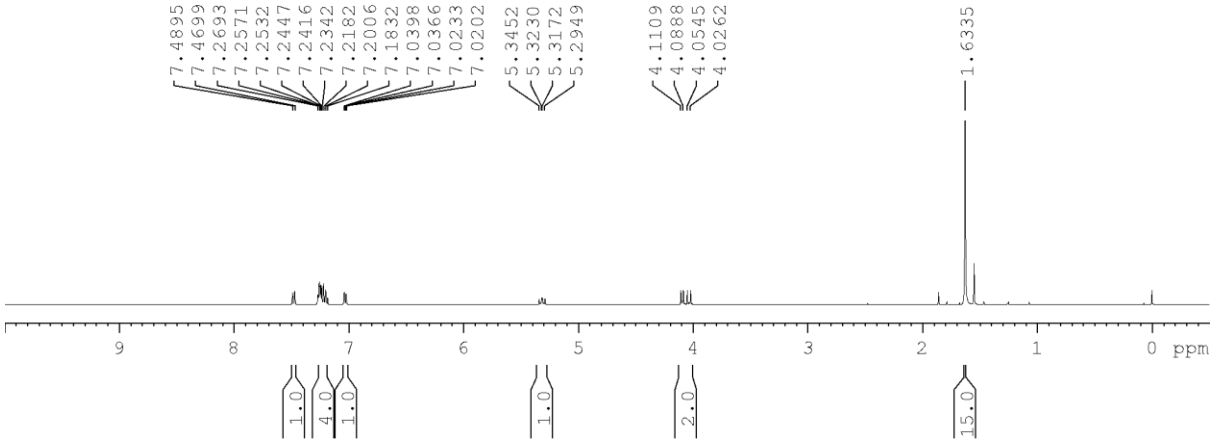
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



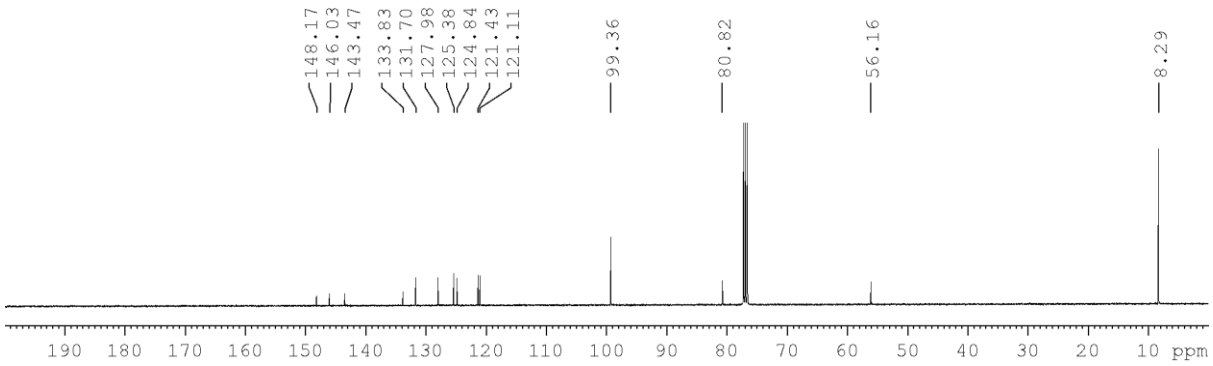
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,[η^2-ethylene])-1-naphthylethene}iridium(III) chloride



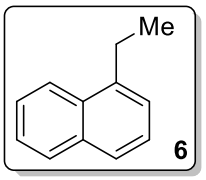
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



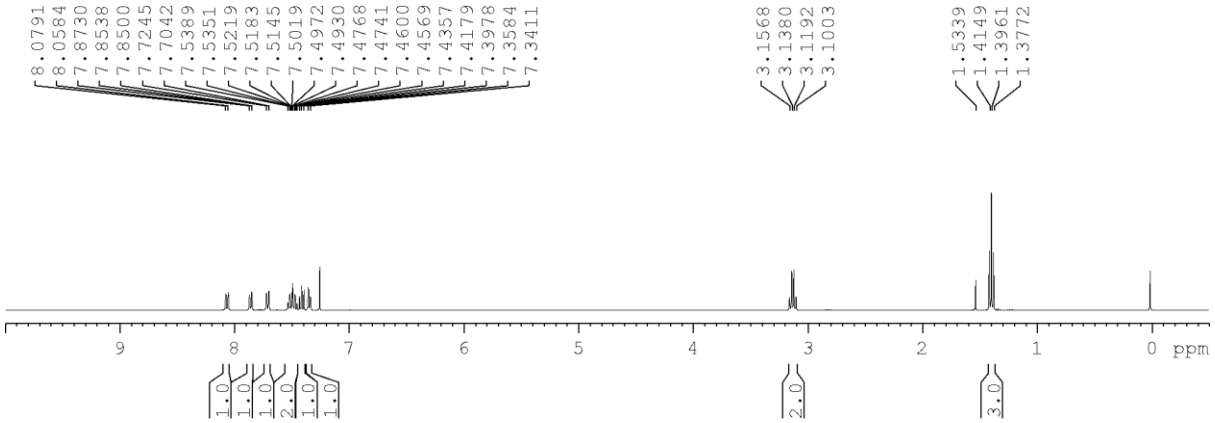
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



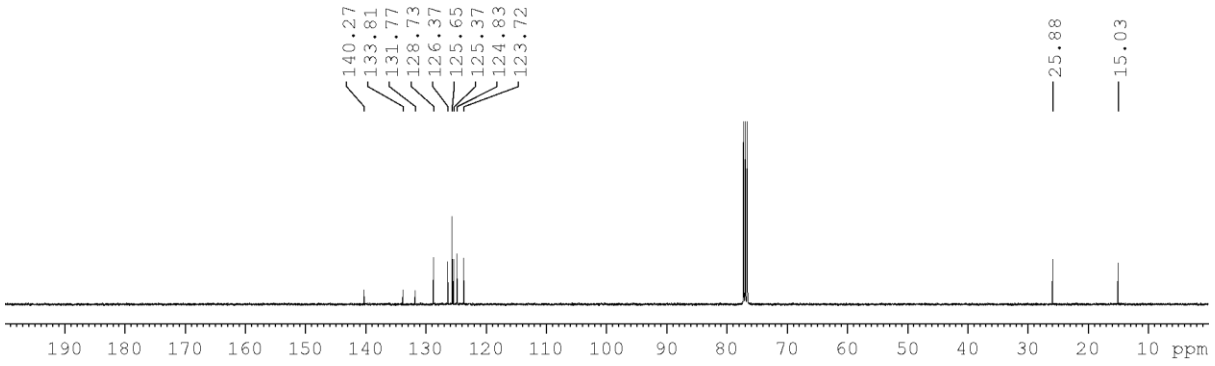
1-Ethylnaphthalene



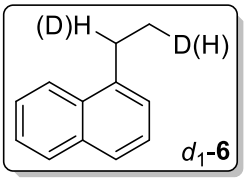
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



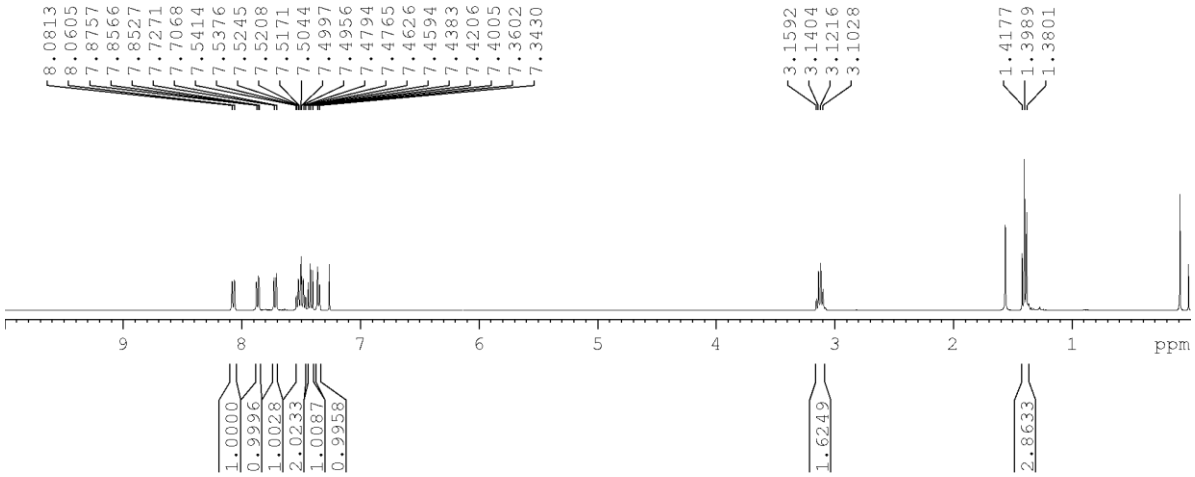
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



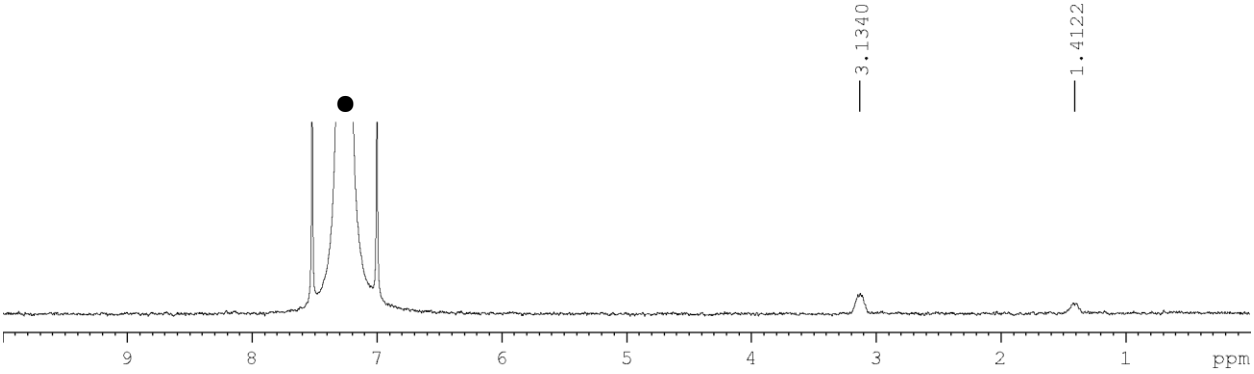
***d*$_1$-1-Ethylnaphthalene Mixture**



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

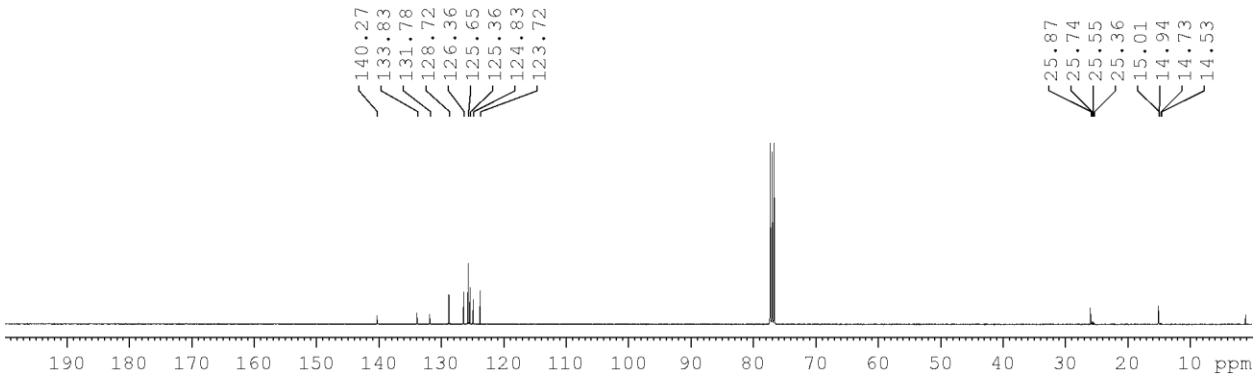


^{2}H NMR spectrum (400 MHz, $CDCl_3$)

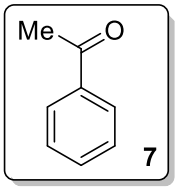


Note: The spectrum has been enlarged for clarity (● (*7.26 ppm*): *$CDCl_3$*).

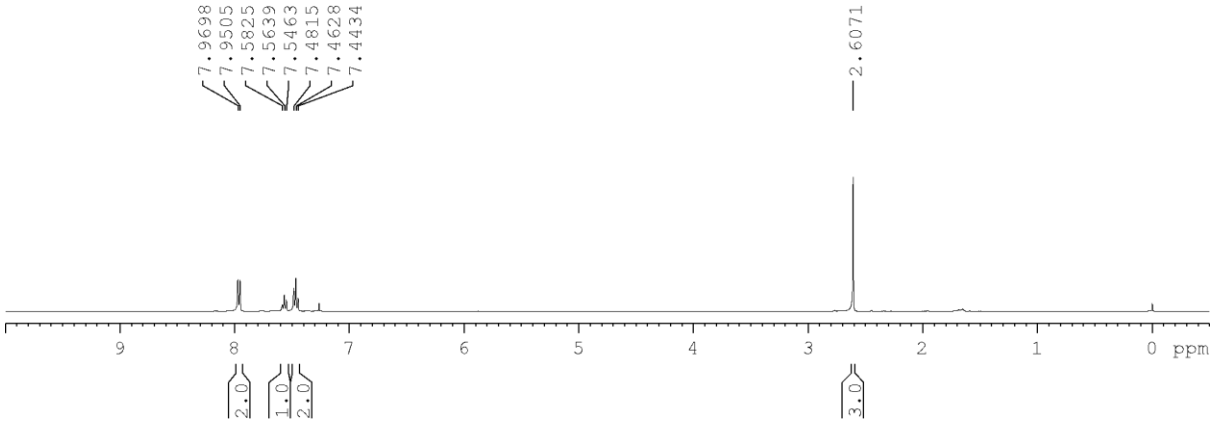
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



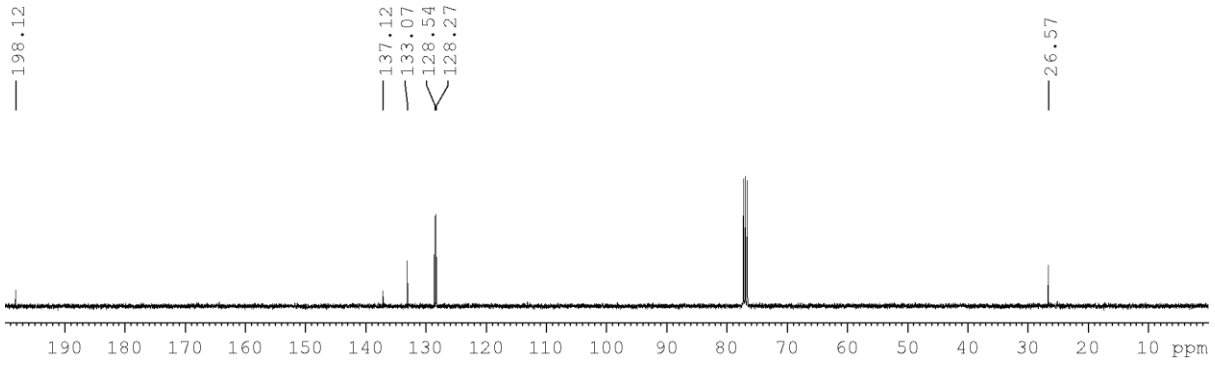
Acetophenone



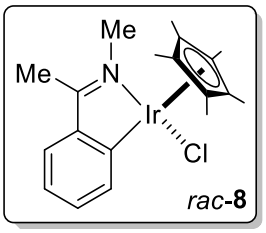
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



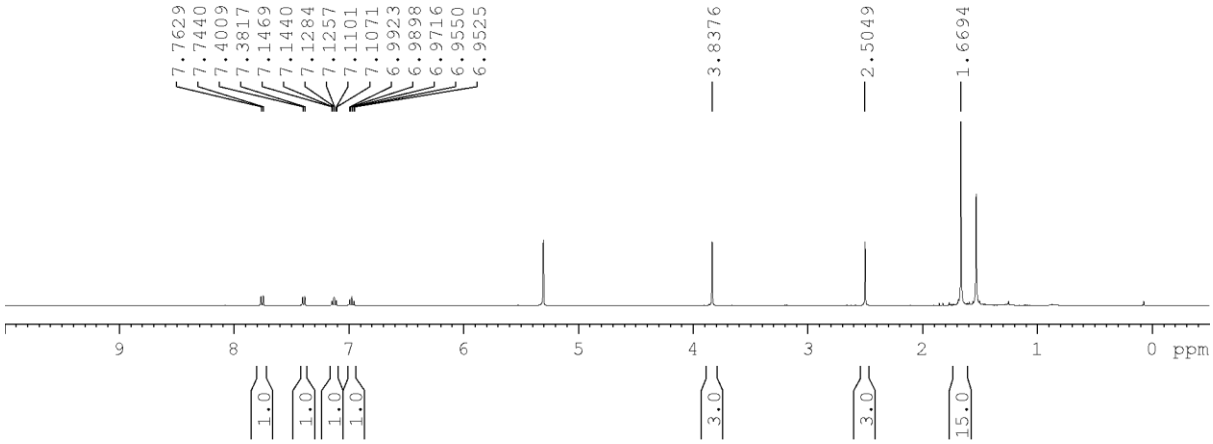
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



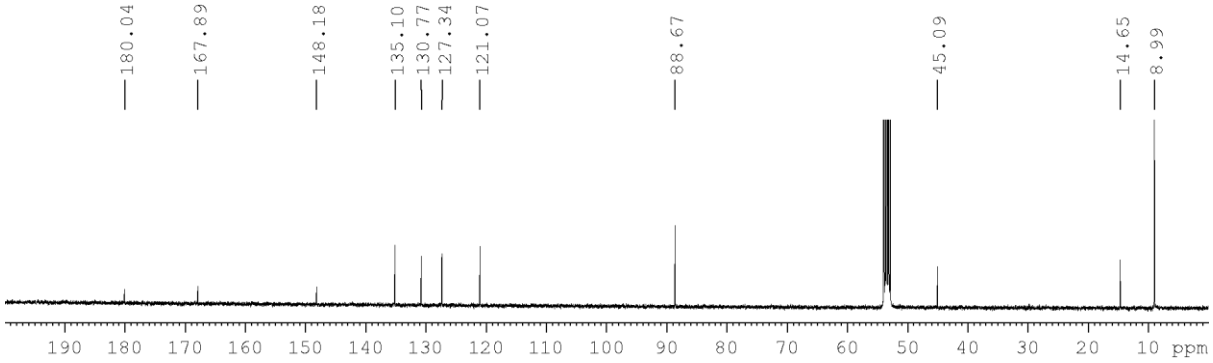
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-1-[1-(*N*-methylimino)ethyl]phenyl}iridium(III) chloride



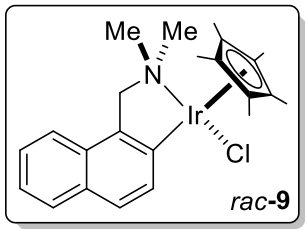
^{1}H NMR spectrum (400 MHz, CD_2Cl_2)



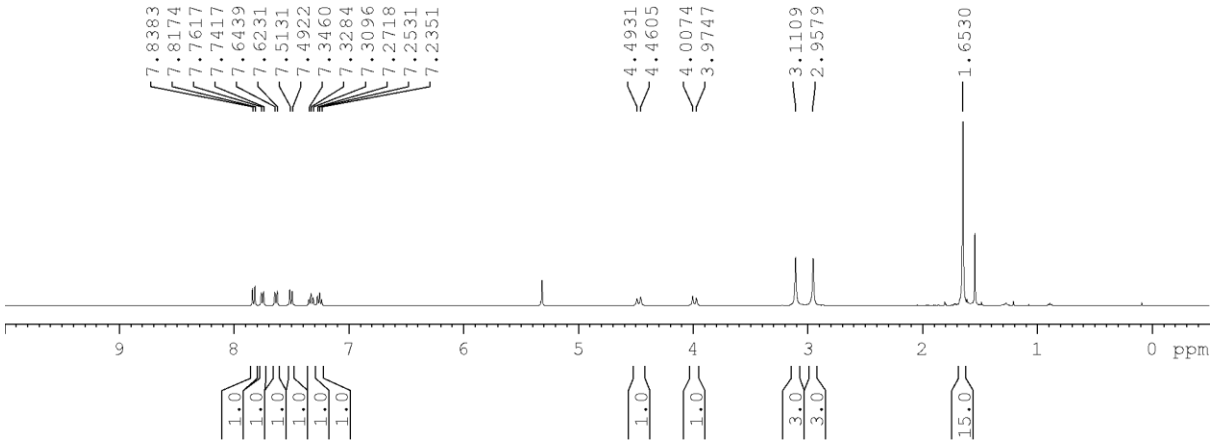
^{13}C NMR spectrum (100 MHz, CD_2Cl_2)



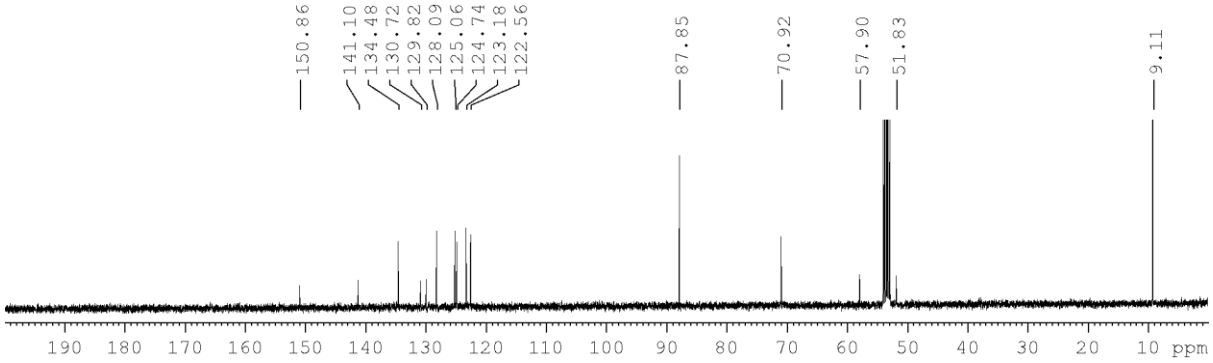
(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-*C*,*N*)-(*N*,*N*-dimethylamino)methylnaphthyl}iridium(III) chloride



^{1}H NMR spectrum (400 MHz, CD_2Cl_2)

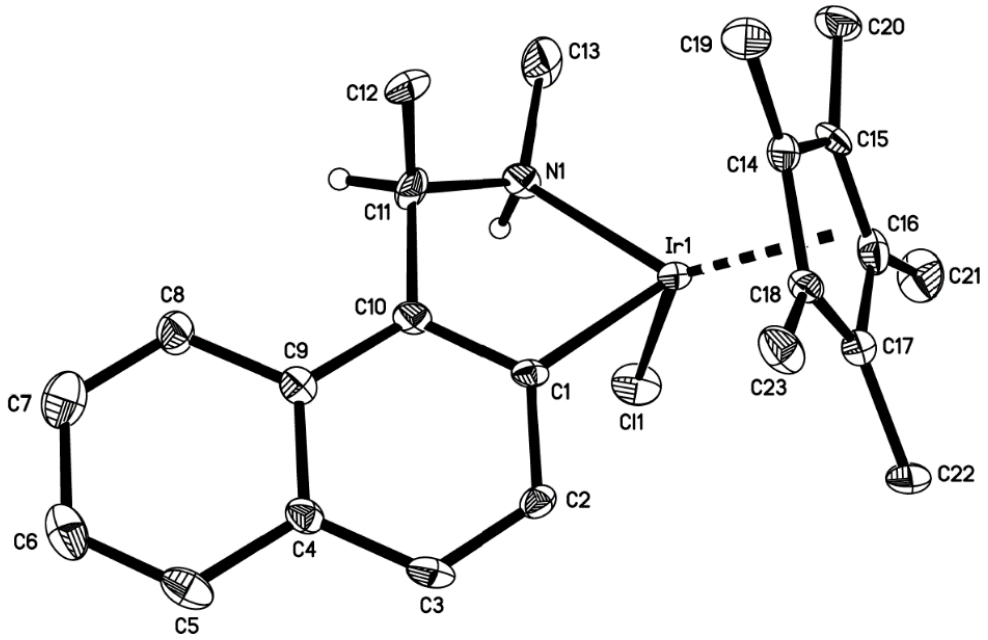


^{13}C NMR spectrum (100 MHz, CD_2Cl_2)



D X-RAY CRYSTALLOGRAPHIC DATA

(R_C,R_N,S_{Ir})-(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ^2-C,N)-1-[1-(N-methylamino)ethyl]naphthyl}iridium(III) chloride



Molecular structure of cycloiridated complex (R_C,R_N,S_{Ir})-**1** with thermal ellipsoids shown at 50% probability. Hydrogen atoms except H(C11) and H(N1) are omitted for clarity. Selected bond lengths and angles: N−Ir (2.134(5) Å), C_1−Ir (2.035(7) Å), Cl−Ir (2.4339(18) Å), N−Ir−C_1 (76.8(2)°), N−Ir−Cl (81.94(17)°), C_1−Ir−Cl (86.20(19)°).

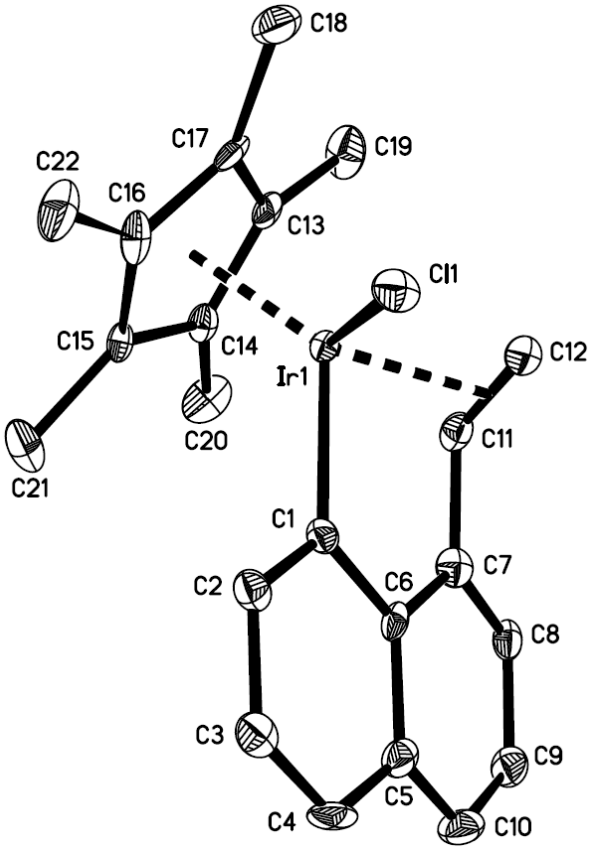
Depository Number	
CCDC Number	1815863

Crystal Data	
Chemical Formula	$C_{23}H_{29}ClIrN$
Formula Weight (FW), g mol^{-1}	547.12
Crystal System	orthorhombic
Space Group	P 21 21 21
Temperature (K)	103(2)
a,b,c (Å)	7.8309(9), 18.449(2), 28.858(3)
α,β,γ (°)	90, 90, 90
V (Å^3)	4169.2(8)
Z	8
F(000)	2144
Radiation Type (Wavelength)	Mo (0.71073 Å)
Absorption Coefficient (mm^{-1})	6.539
Crystal Size (mm)	0.260 × 0.340 × 0.400

Data Collection	
Theta Range for Data Collection	5.10° to 31.08°
Index Ranges	$-8 \leq h \leq 11$, $-26 \leq k \leq 22$, $-37 \leq l \leq 41$
Reflections Collected	35193
Independent Reflections	13198 [R(int) = 0.0516]
T_{min}, T_{max}	0.1800, 0.2810

Refinement	
Refinement Method	Full-matrix least-squares on F^2
Refinement Program	SHELXL-2016/6 (Sheldrick, 2016)
Function Minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
No. of Reflections	13198
No. of Restraints	595
No. of Parameters	571
Goodness-of-Fit on F^2	0.985
Δ/σ_{max}	0.003
Final R Indices	11509 data; $I>2\sigma(I)$
	(R1 = 0.0378, wR2 = 0.0623)
	all data
	(R1 = 0.0474, wR2 = 0.0646)
Weighting Scheme	$w = 1 / [\sigma^2(F_o^2) + (0.0117P)^2]$,
	where $P = (F_o^2 + 2F_c^2) / 3$
Absolute Structure Parameter	0.021(8)
r_{max}, r_{min} (e Å^{-3})	2.375, -1.503
R.M.S. Deviation from Mean (e Å^{-3})	0.166

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ²-C,[η²-ethylene])-1-naphthylethene}iridium(III) chloride



Molecular structure of cycloiridated complex *rac*-**5** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Ir–C_1 (2.050(6) Å), Ir–C_{11} (2.171(7) Å), Ir–C_{12} (2.131(7) Å), Ir–Cl (2.4057(16) Å), C_{11}–C_{12} (1.407(10) Å), C_1–Ir–Cl (83.66(18)°), C_{11}–Ir–C_{12} (38.2(3)°), C_7–C_{11}–C_{12} (122.1(6)°).

Depository Number	
CCDC Number	1830655

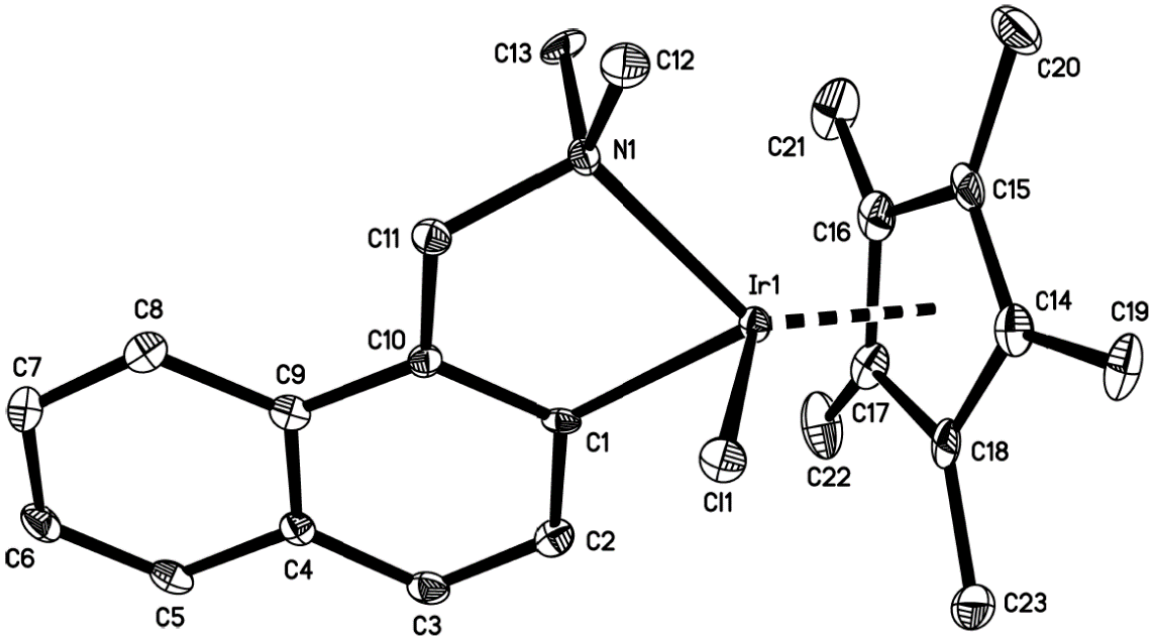
Crystal Data	
Chemical Formula	$C_{22}H_{24}ClIr$
Formula Weight (FW), g mol^{-1}	516.06
Crystal System	orthorhombic
Space Group	P n a 2 1
Temperature (K)	100(2)
a,b,c (Å)	17.0801(5), 7.2442(2), 14.5460(5)
α,β,γ (°)	90, 90, 90
V (Å^3)	1799.80(10)
Z	4
F(000)	1000

Crystal Data (con't)	
Radiation Type (Wavelength)	Mo (0.71073 Å)
Absorption Coefficient (mm^{-1})	7.567
Crystal Size (mm)	0.060 × 0.080 × 0.100

Data Collection	
Theta Range for Data Collection	2.38° to 34.00°
Index Ranges	$-26 \le h \le 26$, $-11 \le k \le 11$, $-22 \le l \le 22$
Reflections Collected	26362
Independent Reflections	7323 [R(int) = 0.0562]
T_{min}, T_{max}	0.5180, 0.6600

Refinement	
Refinement Method	Full-matrix least-squares on F^2
Refinement Program	SHELXL-2016/6 (Sheldrick, 2016)
Function Minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
No. of Reflections	7323
No. of Restraints	1
No. of Parameters	223
Goodness-of-Fit on F^2	1.069
Final R Indices	5966 data; $I>2\sigma(I)$ (R1 = 0.0328, wR2 = 0.0558) all data (R1 = 0.0490, wR2 = 0.0604)
Weighting Scheme	$w = 1 / [\sigma^2(F_o^2) + 1.6661P]$, where $P = (F_o^2 + 2F_c^2) / 3$
r_{max}, r_{min} (e $Å^{-3}$)	1.934, -1.385
R.M.S. Deviation from Mean (e $Å^{-3}$)	0.178

(1,2,3,4,5-Pentamethylcyclopentadienyl){(κ²-C,N)-(N,N-dimethylamino)methylnaphthyl}iridium(III) chloride



Molecular structure of cycloiridated complex *rac*-**9** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: N−Ir (2.192(5) Å), C_1−Ir (2.043(6)Å), Cl−Ir (2.4380(15) Å), N−Ir−C_1 (78.5(2)°), N−Ir−Cl (85.90(14)°), C_1−Ir−Cl (87.82(16)°).

Depository Number	
CCDC Number	1815864

Crystal Data	
Chemical Formula	$C_{23}H_{29}ClIrN$
Formula Weight (FW), g mol^{-1}	547.12
Crystal System	monoclinic
Space Group	P 1 21 1
Temperature (K)	103(2)
a,b,c (Å)	8.5640(5), 13.4034(8), 9.7175(6)
α,β,γ (°)	90, 114.7655(8), 90
V (Å^3)	1012.85(11)
Z	2
F(000)	536
Radiation Type (Wavelength)	Mo (0.71073 Å)
Absorption Coefficient (mm^{-1})	6.730
Crystal Size (mm)	0.120 × 0.180 × 0.200

Data Collection	
Theta Range for Data Collection	2.76° to 30.50°
Index Ranges	$-12 \leq h \leq 12$, $-19 \leq k \leq 19$, $-13 \leq l \leq 13$
Reflections Collected	5788
T_{min}, T_{max}	0.3460, 0.4990

Refinement	
Refinement Method	Full-matrix least-squares on F^2
Refinement Program	SHELXL-2013 (Sheldrick, 2013)
Function Minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
No. of Reflections	5788
No. of Restraints	1
No. of Parameters	243
Goodness-of-Fit on F^2	0.894
Final R Indices	5524 data; $I>2\sigma(I)$
	(R1 = 0.0253, wR2 = 0.0533)
	all data
	(R1 = 0.0267, wR2 = 0.0538)
Weighting Scheme	$w = 1 / [\sigma^2(F_o^2)]$, where $P = (F_o^2 + 2F_c^2) / 3$
r_{max}, r_{min} (e Å^{-3})	1.447, -1.865
R.M.S. Deviation from Mean (e Å^{-3})	0.145