Electronic Supplementary Material (ESI) for Dalton Transactions.

Competition between Vinylidene Rearrangement and 1,2-Insertion of Carbon Disubstituted Internal Alkynes at a Cp*Ir(III) Complex

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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 an argon atomosphere. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. Diphenylacetylene and 1-phenyl-1-propyne were purchased from Sigma-Aldrich and used as received. $[Cp^*IrCl_2]_2$,[1] [Cp*IrCl(ppy)] (**5**),[2] $NaBAr^F{}_4\cdot 2H_2O$[3], 2-(2,3,4,5-tetrafluorophenyl)pyridine,[4] p-$MeC_6H_4C{\equiv}CC_6H_4Me$-$p$[5] and p-$ClC_6H_4C{\equiv}CC_6H_4Cl$-$p$[6] were synthesized according to the literature. ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz), and $^{31}P\{^1H\}$ (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ and referenced to residual ^1H and ^{13}C signals of deuterated solvents as internal standards or to the ^{19}F signal of C_6H_5F (δ –113.15) as an external standard. 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.

[Cp*IrCl(ppy-F$_4$)] (1). The following procedure is modified from the preparation method of [Cp*IrCl(ppy)] reported by Djukic.[2] A CH_2Cl_2 (15 mL) solution containing $[Cp^*IrCl_2]_2$ (200 mg, 0.251 mmol), 2-(2,3,4,5-tetrafluorophenyl)pyridine (153.0 mg, 0.552 mmol) and $NaOAc\cdot 3H_2O$ (88.0 mg, 0.647 mmol) was stirred at room temperature for 10 h. The resulting yellow solution was concentrated in vacuo, and purification of the residue by column chromatography on silica gel (CH_2Cl_2) gave the desired complex as the first yellow band. The yellow eluate was dried up in vacuo and washed with hexane (3mL × 3) to give pure **1** (256.2 mg, 0.435 mmol, 87% yield) as yellow powder. Single crystals of **1** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. ^1H NMR ($CDCl_3$): δ 8.74 (d, $^3J_{HH}$ = 5.2 Hz, 1H, Ar), 8.19 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar), 7.75 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Ar), 7.17 (t, $^3J_{HH}$ = 6.6 Hz, 1H, Ar), 1.69 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 151.9, 138.1, 123.5, 123.4

(s, py), 89.9 (s, η^5-$C_5(CH_3)_5$), 9.30 (d, $^5J_{FC}$ = 2.4 Hz, CH_3 of Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −119.0 (m, 1F), −142.0 (m, 1F), −152.8 (m, 1F), −164.7 (m, 1F). Anal. Calcd for $C_{21}H_{19}ClF_4IrN$ (**1**): C, 42.82; H, 3.25; N, 2.38. Found: C, 42.81; H, 3.05; N, 2.29.

Synthesis of 2a. A mixture of **1** (15.5mg, 0.026 mmol), $NaBAr^F_4\cdot 2H_2O$ (26.5 mg, 0.029 mmol) and diphenylacetylene (5.9 mg, 0.033 mmol) in $C_2H_4Cl_2$ (2 mL) was stirred at 50 ˚C for 4 h. The resulting dark purple suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was dried in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane to give **2a** (36.5 mg, 0.023 mmol, 88% yield) as dark purple crystals. ^1H NMR (CD_2Cl_2): δ 8.37 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.85 (d, $^3J_{HH}$ = 5.0 Hz, 1H, Ar), 7.74–7.45 (m, 17H, Ar), 7.29–7.08 (m, 4H, Ar), 6.90 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Ar), 6.01 (br, 1H, Ar), 4.17 (br, 1H, C=C*H*Ar), 1.61 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 204.3 (s, *C*=CHAr), 94.5 (s, η^5-$C_5(CH_3)_5$), 49.3 (s, C=*C*HAr), 8.58 (s, CH_3 of Cp*). Assignment of the $^{13}C\{^1H\}$ NMR signal of carbon atom of *C*=CHAr was confirmed by using $PhC\equiv{}^{13}CPh$ (ca. 26% enriched). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −62.6 (s, 24F, CF_3 of BAr^F), −138.5 (br, 1F), −142.1 (m, 1F), −148.8 (m, 1F), −155.0 (m, 1F). Anal. Calcd for $C_{67}H_{41}BF_{28}IrN$ (**2a**): C, 50.45; H, 2.59; N, 0.88. Found: C, 50.35; H, 2.35; N, 0.82.

Synthesis of 2b. This compound was synthesized from **1** (24.8 mg, 0.042 mmol), $NaBAr^F_4\cdot 2H_2O$ (42.7 mg, 0.046 mmol) and bis(4-tolyl)acetylene (44.0 mg, 0.213 mmol) by a procedure similar to that for the synthesis of **2a** except that the reaction was performed for 30 min. Dark purple crystals (44.0 mg, 0.027 mmol, 64% yield). ^1H NMR (CD_2Cl_2): δ 8.16 (br, 1H, Ar), 7.89 (d, $^3J_{HH}$ = 5.5 Hz, 1H, Ar), 7.72 (br, 8H, BAr^F), 7.60–7.55 (m, 6H, Ar), 7.38–7.23 (m, 2H, Ar), 7.09 (br, 1H, Ar), 6.96–6.85 (m, 3H, Ar), 5.98 (br, 1H, Ar), 4.21 (s, 1H, C=C*H*Ar), 2.29, 2.22 (s, 3H each, CH_3), 1.59 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): δ 205.3 (s, *C*=CHAr), 94.7 (s, η^5-$C_5(CH_3)_5$), 45.9 (s, C=*C*HAr), 23.2, 22.0 (s, CH_3), 8.77 (s, CH_3 of Cp*).

$^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −63.1 (s, 24F, CF_3 of BAr^F), −139.8 (br, 1F), −143.3 (m, 1F), −150.8 (m, 1F), −157.8 (m, 1F). Anal. Calcd for $C_{69}H_{45}BF_{28}IrN$ (**2b**): C, 51.06; H, 2.79; N, 0.86. Found: C, 50.76; H, 2.74; N, 0.83.

Synthesis of 2c·CH_2Cl_2. This compound was synthesized from **1** (27.6 mg, 0.047 mmol), $NaBAr^F{}_4 \cdot 2H_2O$ (47.6 mg, 0.052 mmol) and bis(4-chlorophenyl)acetylene (14.5 mg, 0.059 mmol) by a procedure similar to that for the synthesis of **2a** except that the reaction was performed for 10 h. Dark purple crystals (66.0 mg, 0.038 mmol, 81% yield). ^1H NMR ($CDCl_3$): δ 8.28 (br, 1H, Ar), 7.84 (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar), 7.69 (br, 8H, BAr^F), 7.56–7.48 (m, 6H, Ar), 7.39–7.30 (m, 2H, Ar), 7.24–7.22 (m, 3H, Ar), 6.82 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Ar), 5.93 (br, 1H, Ar), 4.17 (br, 1H, C=C*H*Ar), 1.58 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): δ 201.9 (s, *C*=CHAr), 95.7 (s, η^5-$C_5(CH_3)_5$), 50.5 (s, C=*C*HAr), 8.82 (s, CH_3 of Cp*). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −63.1 (s, 24F, CF_3 of BAr^F), −138.5 (br, 1F), −142.1 (m, 1F), −149.4 (m, 1F), −155.6 (m, 1F). Anal. Calcd for $C_{68}H_{41}BCl_4F_{28}IrN$ (**2c**·CH_2Cl_2): C, 46.70; H, 2.36; N, 0.80. Found: C, 46.86; H, 2.10; N, 0.78.

Synthesis of 3. A suspension of **2a** (96.0 mg, 0.060 mmol) in MeOH (3 mL) was stirred at room temperature for 30 min. The red precipitate was collected by filtration, washed with MeOH (2 mL × 1), and dried in vacuo to give **3** (32.0 mg, 0.044 mmol, 73% yield) as a red powder. Single crystals of **3** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/hexane. ^1H NMR (CD_2Cl_2): δ 8.85 (d, $^3J_{HH}$ = 5.2 Hz, 1H, Ar), 7.88–7.84 (m, 2H, Ar), 7.68 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ar), 7.17–6.61 (m, 9H, Ar), 1.51 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 152.6, 142.2 (s, Ir–*C*=*C*(Ph)Ar), 90.0 (s, η^5-$C_5(CH_3)_5$), 8.88 (s, CH_3 of Cp*). Assignment of the $^{13}C\{^1H\}$ NMR signal of carbon atom of *C*=CHAr was confirmed by using PhC≡^{13}CPh (ca. 26% enriched). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −142.4 (m, 2F), −153.4 (m, 1F), −163.8 (m, 1F). Anal. Calcd for $C_{35}H_{28}F_4IrN$ (**3**): C, 57.52; H, 3.86; N, 1.92. Found: C, 57.44; H, 3.64; N, 1.87.

Synthesis of 4c. A mixture of **1** (28.4 mg, 0.048 mmol), $NaBAr^F{}_4 \cdot 2H_2O$ (49.0 mg, 0.053 mmol) and bis(4-chlorophenyl)acetylene (15.1 mg, 0.061 mmol) in $C_2H_4Cl_2$ (2 mL) was stirred at 50 ˚C for 30 min. The resulting dark purple suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was dried in vacuo and purified by column chromatography on silica (CH_2Cl_2) to give the desired complex as a yellow band. The yellow eluate was dried up in vacuo and recrystallized from CH_2Cl_2/hexane to afford **4c** (40.5 mg, 0.024 mmol, 50% yield) as yellow crystals. ^1H NMR (CD_2Cl_2): δ 7.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.71 (br, 9H, Ar), 7.61–7.37 (m, 10H, Ar), 7.18–7.13 (m, 2H, Ar), 6.83 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 6.28 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 1.64 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): δ 95.3 (s, η^5-$C_5(CH_3)_5$), 9.15 (s, CH_3 of Cp*). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −63.1 (s, 24F, CF_3 of BAr^F), −138.7 (m, 1F), −143.0 (m, 1F), −155.1 (m, 1F), −163.8 (m, 1F). Anal. Calcd for $C_{67}H_{39}BCl_2F_{28}IrN$ (**4c**): C, 48.36; H, 2.36; N, 0.84. Found: C, 48.11; H, 2.12; N, 0.83.

Synthesis of 6. This compound was synthesized from **5** (22.8 mg, 0.044 mmol), $NaBAr^F{}_4 \cdot 2H_2O$ (44.5 mg, 0.048 mmol) and diphenylacetylene (18.8 mg, 0.105 mmol) by a procedure similar to that for the synthesis of **2a** except that the reaction was performed for 30 min. Orange crystals (56.5 mg, 0.037 mmol, 84% yield). ^1H NMR (CD_2Cl_2): δ 7.83 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar), 7.73 (br, 8H, BAr^F), 7.64 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar), 7.58–7.42 (m, 10H, Ar), 7.98 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar), 7.14 (d, $^3J_{HH}$ = 9.5 Hz, 1H, Ar), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ar), 6.98–6.89 (m, 4H, Ar), 6.51 (br, 1H, Ar), 1.46 (s, 15H, Cp*). Selected $^{13}C\{^1H\}$ NMR data ($CDCl_3$): δ 92.1 (s, η^5-$C_5(CH_3)_5$), 78.4, 75.2 (C(Ph)=C(Ph)), 8.32 (s, CH_3 of Cp*). Assignments of the $^{13}C\{^1H\}$ NMR signals of carbon atoms of C(Ph)=C(Ph) were confirmed by using $PhC{\equiv}^{13}CPh$ (ca. 26% enriched). Anal. Calcd for $C_{67}H_{45}BF_{24}IrN$ (**6**): C, 52.84; H, 2.98; N, 0.92. Found: C, 52.87; H, 2.74; N, 0.90.

Synthesis of 7 and 8. A mixture of **1** (31.9 mg, 0.054 mmol), $NaBAr^F_4 \cdot 2H_2O$ (55.1 mg, 0.060 mmol) and 1,3-diphenyl-2-propyne-1-one (36.3 mg, 0.176 mmol) in $C_2H_4Cl_2$ (2 mL) was stirred at 50 ˚C for 30 min. The resulting reddish orange suspension was filtered through a plug of Celite, and the plug was rinsed with $C_2H_4Cl_2$. The combined filtrate was dried in vacuo, and the residue was purified by column chromatography on silica (CH_2Cl_2) to give **7** and **8** as yellow and red bands, respectively. Each eluate was dried up in vacuo and recrystallized from CH_2Cl_2/hexane to afford **7** (31.9 mg, 0.020 mmol, 37% yield) as yellow crystals and **8** (33.2 mg, 0.021 mmol, 39% yield) as red crystals. **7**: ^{1}H NMR (CD_2Cl_2): δ 9.40 (d, $^3J_{HH}$ = 6.0 Hz, 1H, Ar), 8.14 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 7.95–7.94 (m, 1H, Ar), 7.84 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ar), 7.73 (br, 8H, BAr^F), 7.56 (br, 4H, BAr^F), 7.44–7.37 (m, 2H, Ar), 7.14 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar), 6.90 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar), 6.84 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar), 6.67 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar), 5.95 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 5.42 (br, 1H, C=C*H*C(=O)Ar), 1.34 (s, 15H, Cp*). Selected ^{13}C{^{1}H} NMR data (CD_2Cl_2): δ 197.1 (s, *C*=O), 104.5 (s, η^5-$C_5(CH_3)_5$), 81.3 (d, $^4J_{FC}$ = 4.8 Hz, C=*C*HC(=O)Ar), 8.72 (s, CH_3 of Cp*). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −63.0 (s, 24F, CF_3 of BAr^F), −139.2 (m, 1F), −141.4 (m, 1F), −146.2 (m, 1F), −153.0 (m, 1F). IR (cm^{-1}): 1682 (s, $\nu_{C=O}$). Anal. Calcd for $C_{68}H_{41}BF_{28}IrNO$ (**7**): C, 50.32; H, 2.55; N, 0.86. Found: C, 50.43; H, 2.29; N, 0.84. **8**: ^{1}H NMR (CD_2Cl_2): δ 8.83 (d, $^3J_{HH}$ = 5.7 Hz, 1H, Ar), 8.04–7.98 (m, 2H, Ar), 7.74 (br, 8H, BAr^F), 7.56 (br, 4H, BAr^F), 7.50–7.42 (m, 4H, Ar), 7.25–7.18 (m, 5H, Ar), 6.70 (br, 2H, Ar), 1.58 (s, 15H, Cp*). Selected ^{13}C{^{1}H} NMR data (CD_2Cl_2): δ 207.5 (s, *C*=O), 205.7 (s, Ir–*C*=CPh), 92.5 (s, η^5-$C_5(CH_3)_5$), 8.96 (s, CH_3 of Cp*). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −63.1 (s, 24F, CF_3 of BAr^F), −138.6 (m, 1F), −138.9 (m, 1F), −148.9 (m, 1F), −156.3 (m, 1F). IR (cm^{-1}): 1601 (s, $\nu_{C=O}$). Anal. Calcd for $C_{68}H_{41}BF_{28}IrNO$ (**8**): C, 50.32; H, 2.55; N, 0.86. Found: C, 50.71; H, 2.29; N, 0.85.

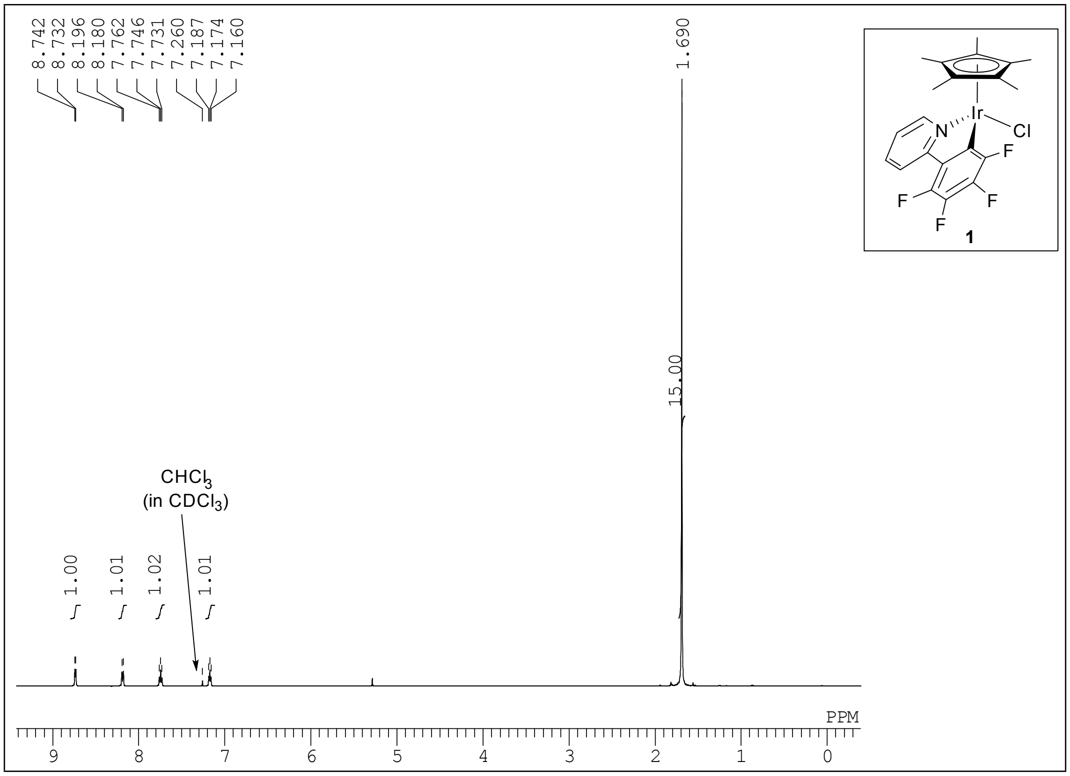

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 500.16 MHz) of **1**.

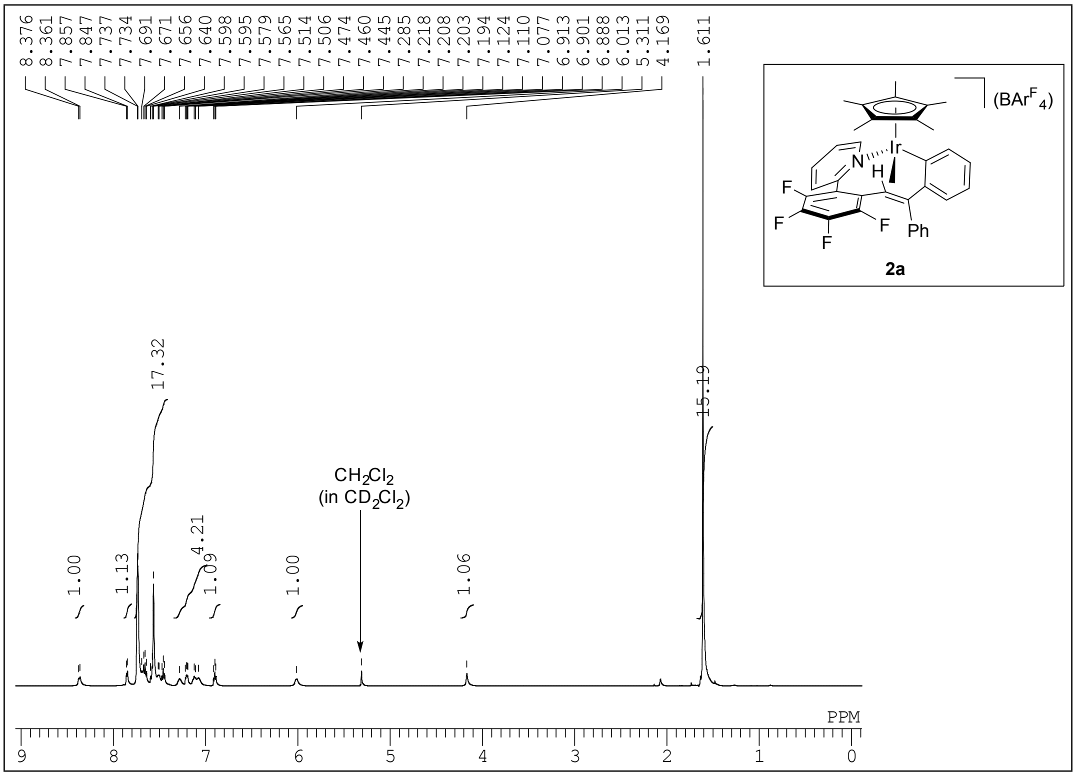

Figure S2. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **2a**.

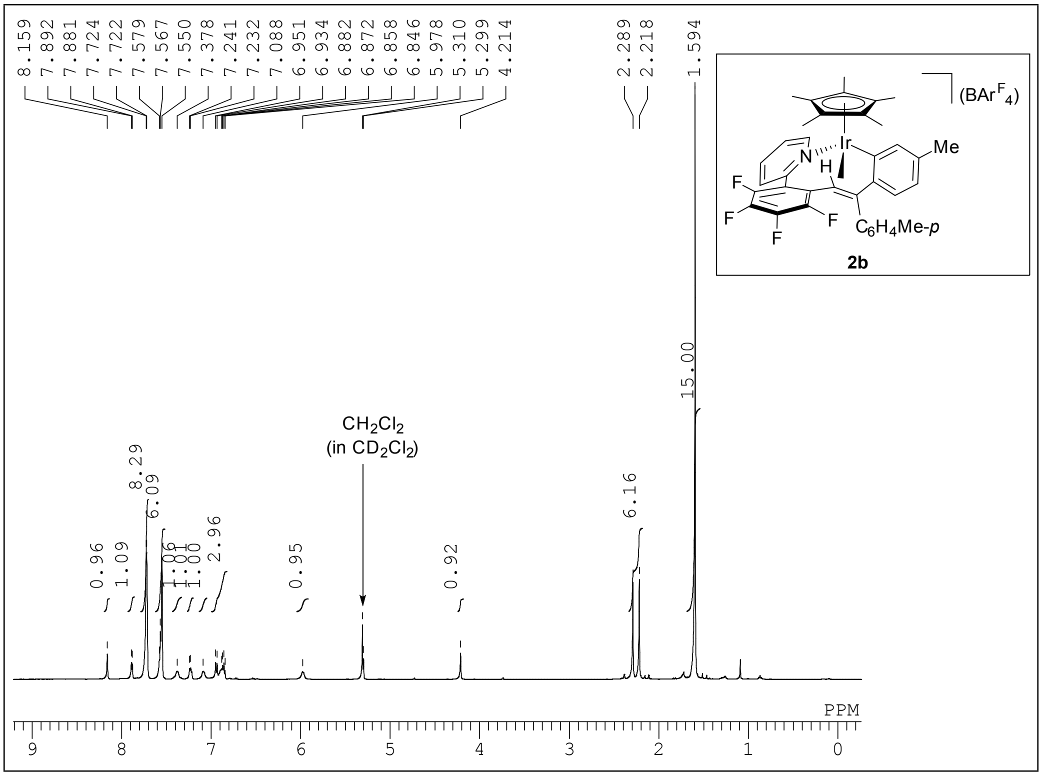

Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **2b**.

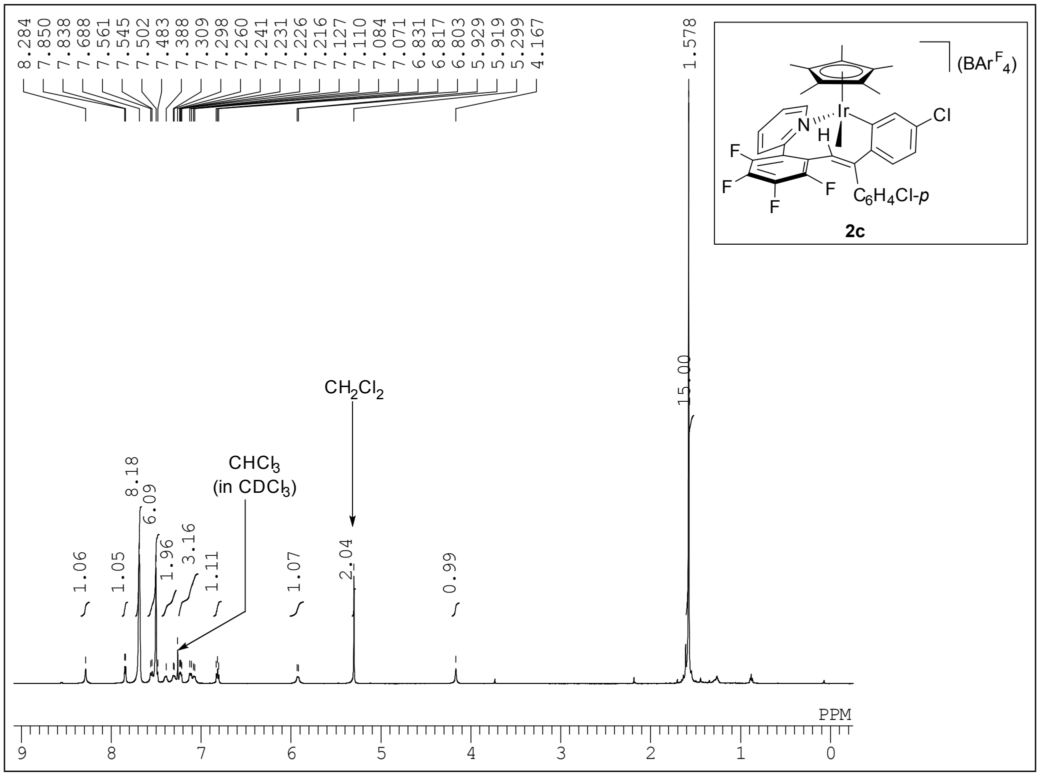

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 500.16 MHz) of **2c**.

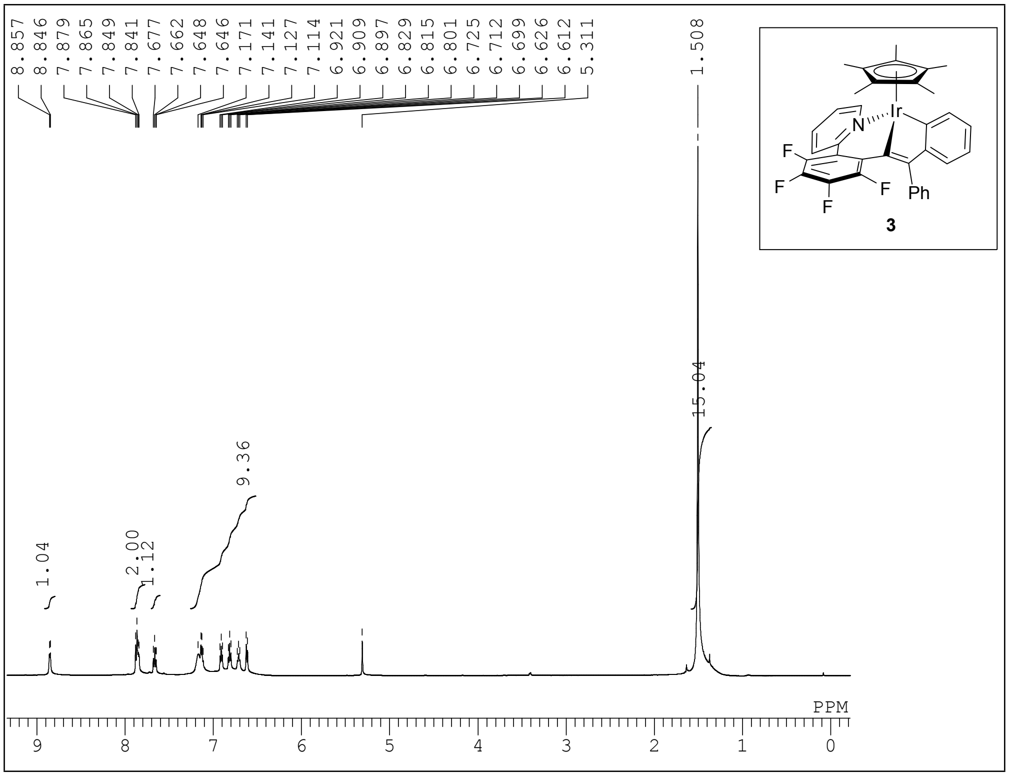

Figure S5. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **3**.

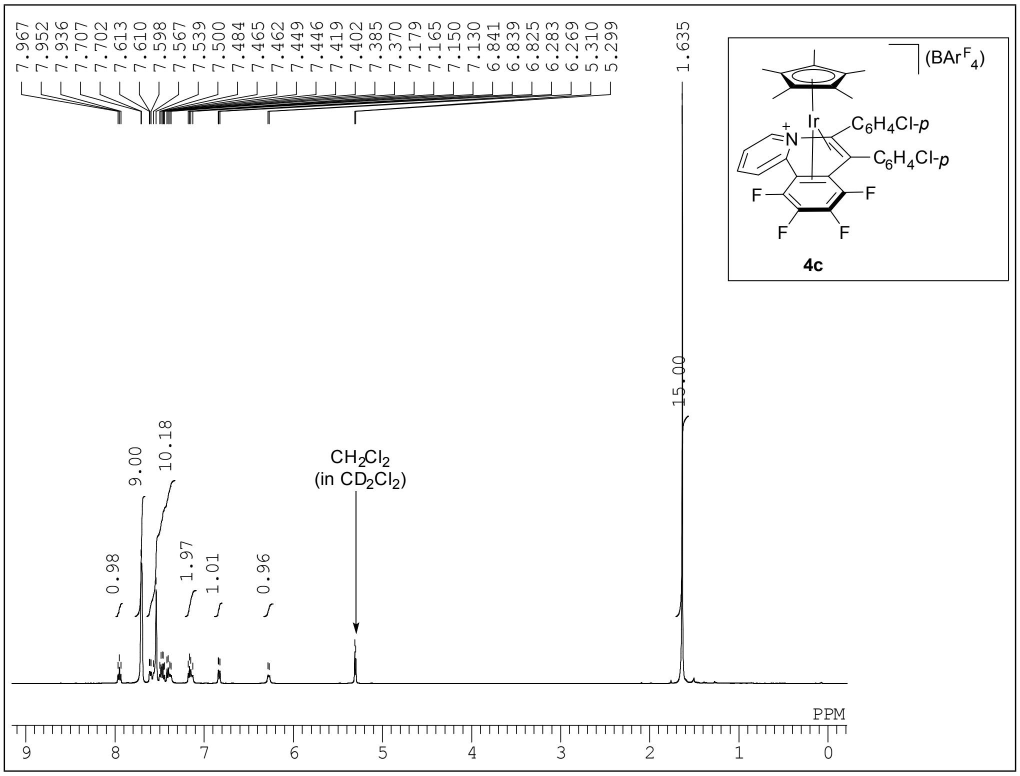

Figure S6. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **4c**.

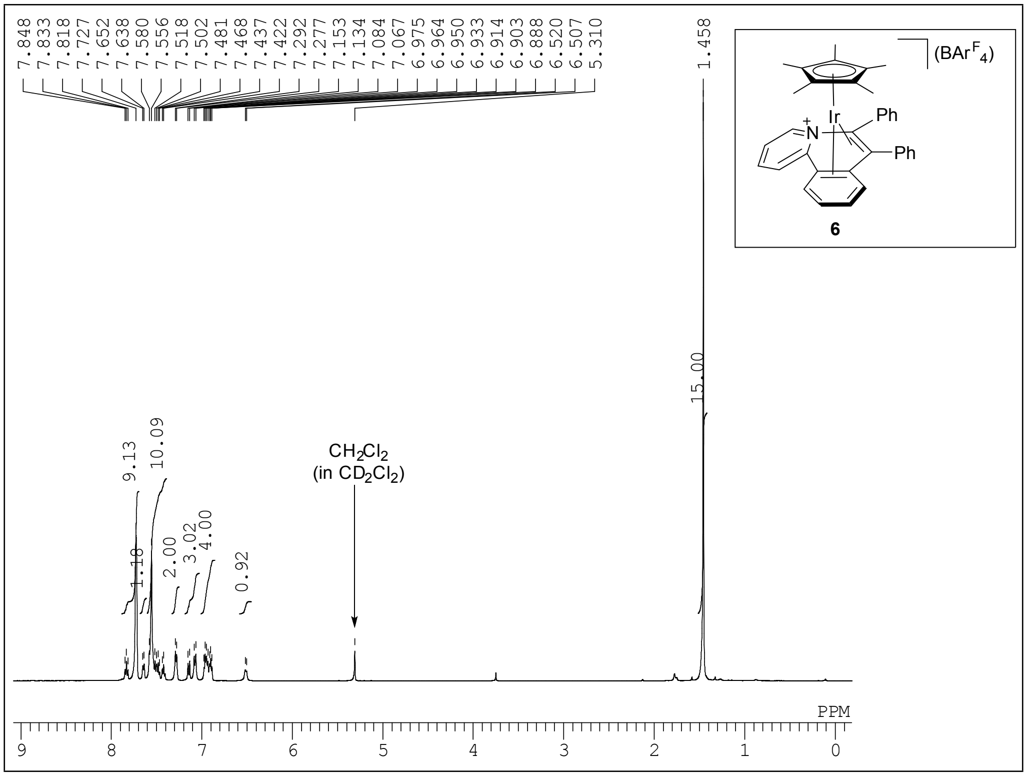

Figure S7. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **6**.

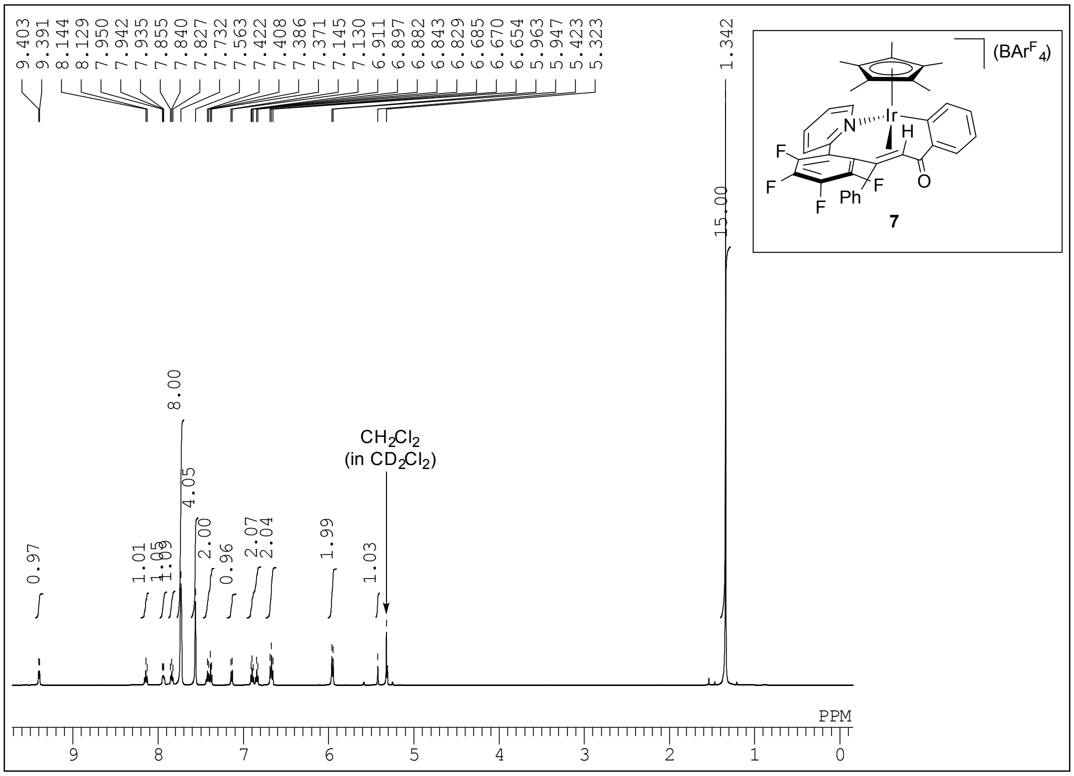

Figure S8. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **7**.

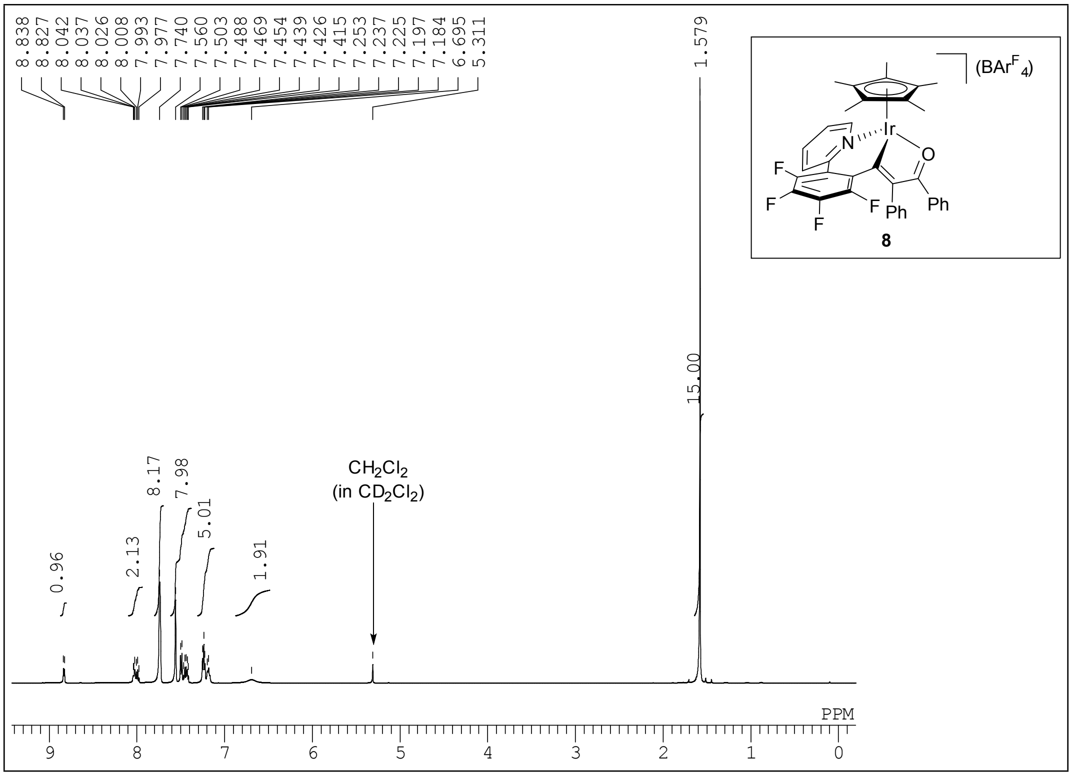

Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 500.16 MHz) of **8**.

X-ray Diffraction Studies. Diffraction data for **1**, **2a**, **3**, **4c**, **7**, and **8** were collected on a VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). at –160 ˚C. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (REQAB).[7] All calculations were performed using the *CrystalStructure*[8] crystallographic software package except for refinements, which were performed using SHELXL-97.[9] The positions of the non-hydrogen atoms were determined by direct methods (SIR-2008)[10] and subsequent Fourier syntheses (DIRDIF-99).[11] All non-hydrogen atoms were refined on $F_o{}^2$ anisotropically by full-matrix least-square techniques. All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Details of the X-ray diffraction study are summarized in Tables S1 and S2.

Table S1. X-ray Crystallographic Data for **1**, **2a**, and **3**.

	1	**2a**	**3**
CCDC	1052465	1052466	1052467
formula	$C_{21}H_{19}ClF_4IrN$	$C_{67}H_{41}BF_{28}IrN$	$C_{35}H_{28}F_4IrN$
fw	589.05	1595.05	730.83
crystal dimension	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.05	0.13 × 0.13 × 0.05
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (#14)	P-1 (#2)	$P2_1/c$ (#14)
a, Å	8.4111(10)	12.134(2)	15.070(3)
b, Å	16.132(2)	15.328(3)	15.505(3)
c, Å	13.860(2)	17.215(3)	11.975(2)
α, deg	90	107.564(4)	90
β, deg	94.166(2)	90.620(3)	104.628(2)
γ, deg	90	91.975(3)	90
V, Å^3	1875.7(4)	3050.2(10)	2707.2(7)
Z	4	2	4
ρ_{calcd}, g cm^{-3}	2.086	1.737	1.793
$F(000)$	1128	1568	1432
μ, cm^{-1}	73.250	23.247	49.996
transmission factors range	0.365 – 0.481	0.623 – 0.890	0.471 – 0.779
index range	$-10 \le h \le 10$ $-20 \le k \le 20$ $-12 \le l \le 17$	$-15 \le h \le 15$ $-19 \le k \le 18$ $-17 \le l \le 22$	$-19 \le h \le 19$ $-19 \le k \le 20$ $-15 \le l \le 11$
no. reflections total	15136	25269	22004
unique (R_{int})	4284 (0.0330)	13472 (0.0459)	6202 (0.0426)
$I > 2\sigma(I)$	3650	11732	5535
no. parameters	253	875	370
$R1$ ($I > 2\sigma(I)$)[a]	0.0240	0.0586	0.0333
$wR2$ (all data)[b]	0.0532	0.1238	0.0669
GOF [c]	1.073	1.058	1.110
max diff peak / hole, e Å^{-3}	1.54/−1.45	1.95/−2.00	2.05/−0.86

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

Table S2. X-ray Crystallographic Data for **4c**, **7**, and **8**.

	4c	**7**	**8**
CCDC	1052468	1052469	1052470
formula	$C_{67}H_{39}BCl_2F_{28}IrN$	$C_{68}H_{41}BF_{28}IrNO$	$C_{68}H_{41}BF_{28}IrNO$
fw	1663.94	1623.06	1623.06
crystal dimension	0.15 × 0.15 × 0.15	0.25 × 0.15 × 0.10	0.20 × 0.20 × 0.10
crystal system	triclinic	monoclinic	monoclinic
space group	P-1 (#2)	Pn (#7)	$P2_1/c$ (#14)
a, Å	13.610(2)	15.420(2)	12.878(2)
b, Å	14.167(2)	13.028(2)	27.452(3)
c, Å	17.544(2)	16.333(2)	18.947(2)
α, deg	88.498(4)	90	90
β, deg	73.243(4)	109.541(2)	102.694(2)
γ, deg	79.690(3)	90	90
V, Å^3	3185.8(7)	3092.4(7)	6534.8(13)
Z	2	2	4
ρ_{calcd}, g cm^{-3}	1.734	1.743	1.650
F(000)	1632	1596	3192
μ, cm^{-1}	23.107	22.958	21.729
transmission factors range	0.594 – 0.707	0.393 – 0.795	0.698 – 0.805
index range	$-17 \le h \le 17$ $-14 \le k \le 18$ $-22 \le l \le 16$	$-20 \le h \le 15$ $-16 \le k \le 16$ $-21 \le l \le 21$	$-16 \le h \le 16$ $-35 \le k \le 35$ $-22 \le l \le 24$
no. reflections total	26414	24931	53570
unique (R_{int})	14095 (0.0341)	11444 (0.0384)	14976 (0.0472)
$I > 2\sigma(I)$	12349	9657	13049
no. parameters	887	894	893
$R1$ ($I > 2\sigma(I)$)[a]	0.0442	0.0668	0.0473
$wR2$ (all data)[b]	0.1078	0.1917	0.1125
GOF [c]	1.046	1.033	1.072
max diff peak / hole, e Å^{-3}	2.60/−1.26	3.01/−1.36	2.22/−1.43

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

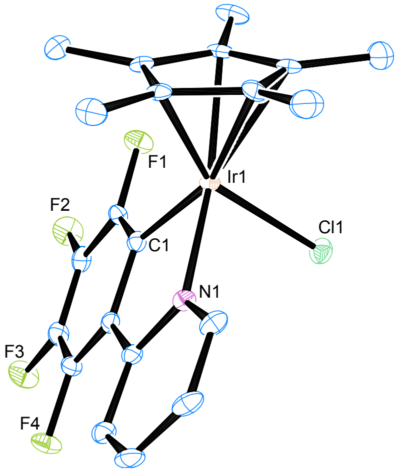

Figure S10. ORTEP drawing of **1** (50% probability). Anionic part and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1–Cl1, 2.4078(9); Ir1–N1, 2.103(3); Ir1–C1, 2.046(4); Cl1–Ir1–N1, 87.61(8); N1–Ir1–C1, 77.42(12); Cl1–Ir1–C1, 85.34(10).

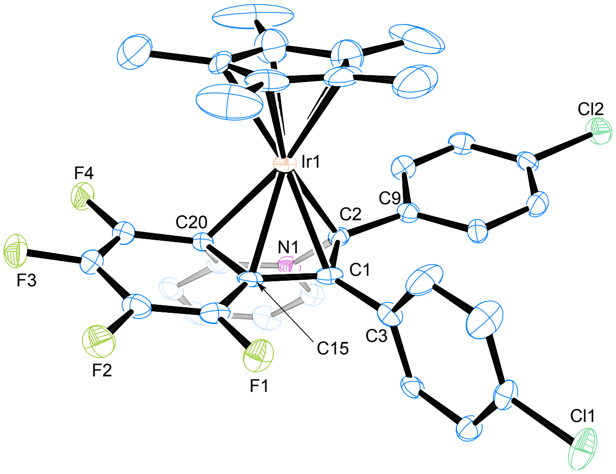

Figure S11. ORTEP drawing of **4c** (50% probability). Anionic part and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1–C1, 2.144(5); Ir1–C2, 2.115(5); Ir1–C15, 2.155(4); Ir1–C20, 2.161(4); C1–C2, 1.483(6); C15–C20, 1.480(6); C1–C15, 1.434(7); C2–C1–C3, 127.0(4); C2–C1–C15, 110.6(4); C3–C1–C15, 122.2(4).

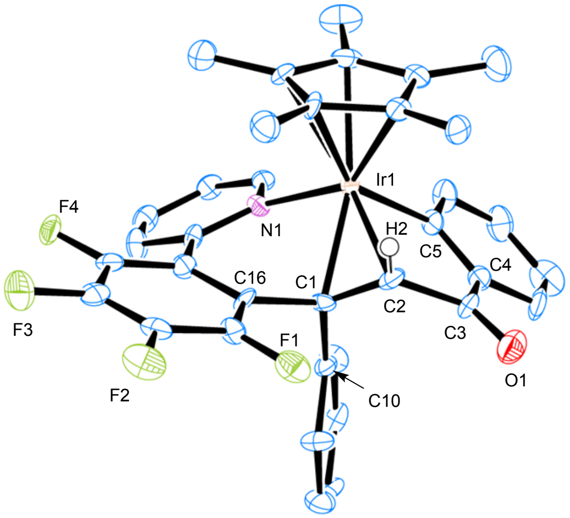

Figure S12. ORTEP drawing of **7** (50% probability). Anionic part and hydrogen atoms except for H2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1–N1, 2.131(10); Ir1–C1, 2.161(11); Ir1–C2, 2.128(11); Ir1–C5, 2.059(13); C1–C2, 1.430(17); C1–C2–C3, 117.3(12); C2–C1–C10, 120.8(10); C2–C1–C16, 119.0(13); C10–C1–C16, 111.4(10).

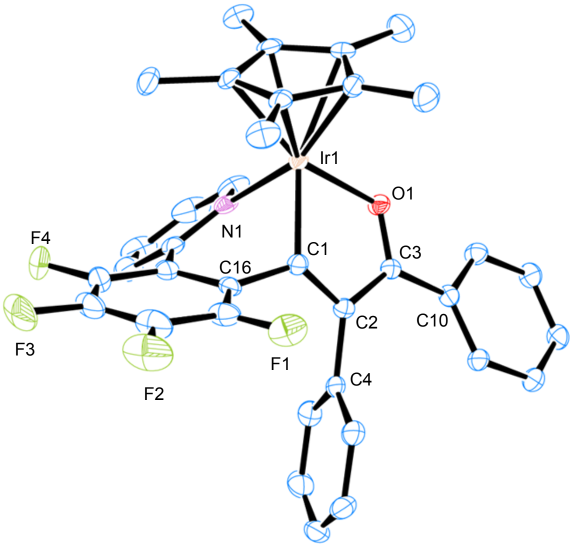

Figure S13. ORTEP drawing of **8** (50% probability). Anionic part and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1–O1, 2.083(3); Ir1–N1, 2.102(4); Ir1–C1, 2.161(11); 2.016(5); C1–C2, 1.364(6); Ir1–C1–C2, 118.8(3); Ir1–C1–C16, 112.4(3); C2–C1–C16, 126.0(4); C1–C2–C3, 111.1(4); C1–C2–C4, 123.5(4); C3–C2–C4, 124.1(4).

Computational Details. All density functional theory (DFT) calculations were performed using the Gaussian 09 package.[12] The computers used in the present study are the computer facilities at the Research Center for Computational Science in Okazaki and Kyoto University ACCMS, Japan. Geometries of the cationic part of **2a**, **4a**, **INT1**–**4** and **TS1**–**4** were fully optimized using the B3PW91[13] density functional with the effective core potential (ECP) and basis sets: the Stuttgart/Dresden (SDD) ECP with the corresponding basis set for Ir[14] and the 6-31G(d) basis set[15] for the remaining non-metal atoms. The combined basis set is denoted as BS throughout this article. All the stationary points were characterized by vibrational analysis as local minima (LM), transition states (TS), or higher-order saddle points. Optimized Cartesian coordinates were summarized in Tables S3–12. The optimized structure of the cationic part of **2a** in the ground state along with the selected calculated structural parameters and the experimental values obtained by X-ray crystallography are summarized in Table S13. The local minimum structures of complexes **4a**, **INT1**–**4** and **TS1**–**4** with the selected structural parameters are summarized in Tables S14–22. The potential energy difference of **2a** relative to **4a** is described in the main text of this paper.

Table S3. Optimized Cartesian Coordinates for the Cationic Part of **2a** at B3PW91/BS level.

Atomic	Coordinates (angstrom)		
Number	X	Y	Z
6	-3.405449	-2.552442	0.280607
6	-3.170019	-2.367838	-1.076041
6	-4.352458	2.492391	-1.498241
6	-2.713392	-1.774910	1.205820
6	-4.605949	3.513513	-0.579746
6	-2.237996	-1.413713	-1.474792
6	-3.095972	1.904739	-1.558052
6	-1.780884	-0.808365	0.813802
6	-3.592452	3.956831	0.270781
6	-1.535742	-0.628504	-0.568009
6	-1.733793	0.424600	2.984094
6	-2.055943	2.352699	-0.718147
6	0.540367	-3.570924	-0.293687
6	-1.061257	-0.015311	1.835472
6	-2.325049	3.391283	0.196227
6	-1.059051	1.121771	3.974867
6	-0.493339	0.327483	-1.023904
6	-0.722437	1.766486	-0.820046
6	1.577786	-2.493945	-0.311708
6	1.567307	-2.004740	-2.882073
6	0.296634	1.382936	3.802325
6	2.283596	-2.576626	2.193487
6	2.048355	-1.785594	-1.482257
6	0.905026	0.955473	2.633879
6	0.462207	2.528194	-0.722759
6	2.391726	-2.076914	0.787698
6	0.527904	3.935906	-0.943946
6	1.637359	1.758076	-0.401781
6	3.182574	-0.975868	-1.102679
6	3.400166	-1.156967	0.315544
6	1.733723	4.584405	-0.843192
6	2.845588	2.480016	-0.297598
6	4.084943	-0.256861	-2.055132
6	4.573905	-0.672545	1.106510
6	2.891536	3.849345	-0.504591
1	-5.137060	2.157749	-2.170780
1	-5.593516	3.963547	-0.528291
1	-2.897256	1.128336	-2.290184
1	-2.790169	0.213290	3.087979
1	-3.791388	4.745381	0.990977
1	0.070185	-3.668439	0.688619
1	-0.250390	-3.385832	-1.025502
1	-1.585408	1.457750	4.863377

1	0.990724	-4.541790	-0.538783
1	0.495189	-2.213682	-2.920728
1	-1.540201	3.725496	0.868708
1	-0.200046	0.159815	-2.066433
1	1.265397	-2.888965	2.438988
1	2.938709	-3.446243	2.332201
1	1.767875	-1.140389	-3.520965
1	2.086232	-2.866368	-3.321906
1	-0.368064	4.478038	-1.231306
1	0.877159	1.920989	4.544298
1	2.589901	-1.818850	2.920419
1	1.949186	1.162811	2.433983
1	3.526232	0.201918	-2.874729
1	1.805312	5.651288	-1.032341
1	4.320899	-0.507312	2.157862
1	4.659033	0.531385	-1.563333
1	5.382146	-1.415841	1.080338
1	3.762041	1.963642	-0.029089
1	4.803425	-0.963085	-2.490659
1	4.983933	0.259794	0.709131
1	3.840599	4.372459	-0.408902
9	-4.267656	-3.473011	0.693244
9	-3.824376	-3.090118	-1.973894
9	-2.948386	-2.030175	2.498068
9	-2.046741	-1.239699	-2.794258
77	1.376222	-0.211124	-0.078076
7	0.256790	0.278891	1.663440

Gibbs free energy = −1908.415446 a.u.

Table S4. Optimized Cartesian Coordinates for the Cationic Part of **4a** at B3PW91/BS level.

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 ---------------------------------------------------------------------
 Atomic              Coordinates (angstrom)
 Number        X           Y           Z
 ---------------------------------------------------------------------
    6      5.036469   -0.242174    0.470242
    6      5.300000   -1.526960    0.002636
    6      2.970549    4.550102   -0.047757
    6      2.796056    3.639293   -1.088250
    6      3.725446    0.166914    0.719951
    6      2.375296    4.308735    1.190136
    6      4.242068   -2.412305   -0.207676
    6      2.032898    2.490853   -0.892254
    6      1.609576    3.162385    1.385290
    6      2.650669   -0.699954    0.476123
    6      2.933939   -1.999176    0.025979
    6      1.432532    2.240524    0.343857
    6      1.783173   -0.918456   -3.233249
    6      1.708618   -1.479775    2.990031
    6      1.223268   -0.361281    0.793802
    6      1.282384   -2.066095    4.165526
    6      0.651638    1.001695    0.615227
    6      0.390390   -0.935041   -2.688924
    6     -0.413770    1.426322   -3.529362
    6      0.296409   -3.483808   -2.032570
    6     -0.084581   -2.122632    4.436046
    6     -0.601320    0.103169   -2.856906
    6     -0.760728    1.017034    0.912473
    6     -0.274316   -2.104010   -2.132336
    6     -0.510410   -1.001610    2.348973
    6     -1.667449    2.128303    0.769494
    6     -0.981134   -1.566346    3.532381
    6     -1.305730   -0.298161    1.329001
    6     -1.844371   -0.389770   -2.350179
    6     -1.643088   -1.755065   -1.908541
    6     -3.007969    1.953368    0.917125
    6     -2.746708   -0.395386    1.423878
    6     -3.152392    0.332686   -2.400352
    6     -2.715521   -2.688525   -1.446223
    6     -3.560963    0.666955    1.219820
    1      5.854132    0.449166    0.654663
    1      6.322511   -1.841717   -0.186344
    1      3.564706    5.446534   -0.201173
    1      3.255035    3.823310   -2.055876
    1      2.501919    5.016661    2.004529
    1      3.548819    1.162745    1.109723
    1      4.436668   -3.423779   -0.554611
    1      2.751943   -1.400739    2.715774
    1      2.166548    0.098727   -3.344761
```

1	1.903603	1.773082	-1.694869
1	1.143386	2.981882	2.351262
1	2.479094	-1.465780	-2.592962
1	1.799017	-1.386969	-4.226141
1	2.017805	-2.474462	4.849627
1	2.109503	-2.689633	-0.125284
1	0.640524	1.692495	-3.627605
1	1.388244	-3.472582	-2.033539
1	-0.913390	2.236146	-2.989856
1	-0.838189	1.390929	-4.541157
1	-0.043249	-4.008230	-1.134640
1	-0.448409	-2.584881	5.348651
1	-0.020895	-4.077340	-2.900251
1	-2.045822	-1.574557	3.727385
1	-3.024737	1.411665	-2.276726
1	-2.320158	-3.470459	-0.793022
1	-3.635253	0.170224	-3.372946
1	-3.173904	-3.179861	-2.314816
1	-3.846383	-0.018640	-1.632375
1	-3.512320	-2.169852	-0.908733
9	-1.205891	3.327920	0.417288
9	-3.854416	2.956676	0.727144
9	-3.276766	-1.591439	1.724477
9	-4.885110	0.552611	1.255800
77	-0.335371	-0.430205	-0.656772
7	0.819554	-0.993008	2.096387

Gibbs free energy = −1908.401867 a.u.

Table S5. Optimized Cartesian Coordinates for the Cationic Part of **INT1** at B3PW91/BS level.

Atomic Coordinates

Number	X	Y	Z
6	4.363470	-2.031818	-1.644096
6	4.584523	-3.051525	-0.718138
6	4.774315	3.639989	0.135918
6	3.650407	4.054001	-0.574771
6	3.308671	-1.139855	-1.470597
6	4.787033	2.372689	0.718849
6	3.738189	-3.175034	0.383398
6	2.551627	3.208863	-0.707485
6	3.690550	1.528186	0.589532
6	2.442614	-1.254816	-0.368985
6	2.672900	-2.292662	0.548739
6	2.552606	1.926283	-0.135450
6	0.252131	-2.908700	-2.460584
6	-0.029361	-1.032532	3.063055
6	1.311624	-0.324618	-0.219792
6	0.175922	-0.482647	4.322461
6	1.377617	1.028093	-0.223039
6	-0.817788	-2.416472	-1.544361
6	-1.915157	-0.634094	-3.093423
6	-0.454691	-4.123308	0.407877
6	0.059611	0.895335	4.484234
6	-1.790028	-1.409534	-1.822465
6	-0.004422	1.630319	-0.265543
6	-1.122755	-2.945534	-0.220823
6	-0.444901	1.064806	2.151278
6	-0.492735	2.195620	-1.455095
6	-0.259203	1.683565	3.380812
6	-0.828421	1.744905	0.891157
6	-2.794437	-1.415438	-0.747338
6	-2.400608	-2.359871	0.215975
6	-1.699875	2.878566	-1.512809
6	-2.043257	2.430664	0.823811
6	-4.026955	-0.572845	-0.738692
6	-3.125687	-2.733574	1.467548
6	-2.481528	3.003058	-0.362882
1	5.018652	-1.927090	-2.504821
1	5.411361	-3.743232	-0.852732
1	5.631439	4.299558	0.239059
1	3.626974	5.038452	-1.034345
1	5.653037	2.042234	1.286334
1	3.146638	-0.341287	-2.189348
1	3.909472	-3.959446	1.116361
1	0.050207	-2.098106	2.881066
1	0.538609	-2.148387	-3.190754
1	1.698711	3.553864	-1.282865
1	3.708217	0.552182	1.063665

1	1.151465	-3.205431	-1.916458
1	-0.117473	-3.783327	-3.011832
1	0.424010	-1.130503	5.156644
1	2.022708	-2.392672	1.413736
1	-0.943620	-0.457084	-3.559767
1	0.615642	-4.140539	0.189502
1	-2.398973	0.333161	-2.935322
1	-2.533371	-1.194553	-3.807042
1	-0.588042	-4.139255	1.493552
1	0.214897	1.352096	5.456940
1	-0.894769	-5.049625	0.013987
1	-0.362306	2.759984	3.464350
1	-3.821579	0.449734	-1.069544
1	-2.436144	-2.943065	2.290878
1	-4.773963	-0.989327	-1.426857
1	-3.716802	-3.643683	1.302838
1	-4.481839	-0.522121	0.253328
1	-3.809297	-1.946555	1.795253
9	0.218908	2.096008	-2.577823
9	-2.130001	3.392412	-2.656904
9	-2.834845	2.502646	1.896731
9	-3.646671	3.629645	-0.420108
77	-0.667613	-0.872543	-0.008178
7	-0.339452	-0.272421	2.003887

Gibbs free energy = -1908.398054 a.u.

Table S6. Optimized Cartesian Coordinates for the Cationic Part of **INT2** at B3PW91/BS level.

Atomic	Coordinates		
Number	X	Y	Z

6	3.565758	-0.213778	3.807082
6	4.811161	0.178466	3.316955
6	-3.062155	3.705672	2.728274
6	-2.073275	4.319831	1.960137
6	2.412343	0.028861	3.067578
6	-3.019314	2.328741	2.945992
6	4.899733	0.820219	2.081494
6	-1.052272	3.560880	1.398997
6	-2.001147	1.562089	2.389241
6	2.492614	0.672025	1.819851
6	3.750747	1.061753	1.335138
6	-1.009686	2.171503	1.601824
6	2.322477	2.843095	-1.666643
6	2.288979	-2.078259	0.182513
6	1.266315	0.943661	1.096201
6	2.676768	-3.311047	0.678521
6	0.089216	1.397877	1.075447
6	1.510337	1.661483	-2.087339
6	-0.736037	2.961706	-2.324201
6	3.414888	-0.078887	-2.485002
6	1.687963	-4.189379	1.117430
6	0.082401	1.710641	-2.336178
6	-1.371644	-0.692025	-0.171979
6	1.985620	0.360406	-2.417552
6	0.019035	-2.547038	0.529166
6	-2.620839	-0.104487	-0.304324
6	0.358161	-3.803427	1.049748
6	-1.318860	-1.993059	0.389801
6	-0.305399	0.440690	-2.895136
6	0.845193	-0.417180	-2.887597
6	-3.796623	-0.751855	0.069072
6	-2.500900	-2.641797	0.771967
6	-1.628668	0.101236	-3.499888
6	0.913591	-1.796196	-3.463385
6	-3.737313	-2.031352	0.612495
1	3.489917	-0.704405	4.773488
1	5.709144	-0.007630	3.899271
1	-3.859465	4.300512	3.164685
1	-2.093597	5.394548	1.802795
1	-3.779093	1.850250	3.557593
1	1.440954	-0.267244	3.452351
1	5.865914	1.142449	1.702938
1	3.017502	-1.347798	-0.144086
1	1.973477	3.258797	-0.715905
1	-0.269276	4.042691	0.821069
1	-1.959082	0.492601	2.570941
1	3.381185	2.594798	-1.566205
1	2.241007	3.634411	-2.421705

1	3.730610	-3.563098	0.726084
1	3.820074	1.583223	0.386475
1	-0.422984	3.640707	-1.528476
1	4.021976	0.347301	-1.681915
1	-1.796756	2.755141	-2.186680
1	-0.611332	3.489555	-3.279106
1	3.508306	-1.167044	-2.442166
1	1.949989	-5.165145	1.515761
1	3.856405	0.242150	-3.437329
1	-0.424549	-4.464530	1.393646
1	-2.429796	0.726998	-3.107422
1	1.632411	-2.425282	-2.931053
1	-1.573557	0.262118	-4.584521
1	1.229129	-1.749802	-4.513711
1	-1.897403	-0.945144	-3.334957
1	-0.057951	-2.295142	-3.430507
9	-2.759300	1.139657	-0.796370
9	-4.970960	-0.152878	-0.080006
9	-2.494434	-3.869923	1.306280
9	-4.850965	-2.657345	0.976534
77	0.416051	0.117757	-0.762039
7	0.999548	-1.706476	0.091931

Gibbs free energy = -1908.395284 a.u.

Table S7. Optimized Cartesian Coordinates for the Cationic Part of **INT3** at B3PW91/BS level.

Atomic Number	Coordinates		
	X	Y	Z
6	5.395927	0.933512	2.160073
6	5.812549	-0.390315	2.028065

6	1.904006	5.086063	-1.163056
6	2.931007	4.282433	-1.661831
6	4.244934	1.377861	1.514904
6	0.987650	4.558399	-0.256356
6	5.072326	-1.270917	1.239446
6	3.037892	2.954037	-1.262626
6	1.091225	3.228510	0.149289
6	3.492647	0.497569	0.724931
6	3.923449	-0.830239	0.589832
6	2.114955	2.417312	-0.353504
6	2.035712	-1.962640	-2.769639
6	0.325061	-2.335049	2.119476
6	1.211759	0.207143	-0.157750
6	0.171064	-2.697553	3.446362
6	2.247942	0.985877	0.072645
6	0.620025	-1.991981	-2.291358
6	-0.230480	-0.037500	-3.789027
6	0.680572	-4.182716	-0.871423
6	-0.804135	-2.047012	4.201206
6	-0.413917	-1.076447	-2.727709
6	-1.579895	0.513861	0.189531
6	0.017239	-2.965490	-1.434617
6	-1.365747	-0.714503	2.269205
6	-2.085323	1.577617	-0.536560
6	-1.569290	-1.050789	3.614065
6	-2.027397	0.347034	1.523461
6	-1.677930	-1.566906	-2.209973
6	-1.415336	-2.695290	-1.385431
6	-3.042999	2.445470	-0.012681
6	-2.990687	1.218130	2.048492
6	-3.026877	-1.027503	-2.557369
6	-2.431692	-3.544415	-0.688978
6	-3.503654	2.260641	1.287172
1	5.970113	1.627525	2.767742
1	6.714798	-0.731421	2.527790
1	1.824704	6.123322	-1.476269
1	3.652576	4.693056	-2.362854
1	0.194424	5.184047	0.143750
1	3.924741	2.409852	1.623785
1	5.401816	-2.299435	1.116373
1	1.075825	-2.791946	1.487065
1	2.441596	-0.947417	-2.773451
1	3.842360	2.331147	-1.644822
1	0.392621	2.818428	0.872800
1	2.688805	-2.589405	-2.158504
1	2.081208	-2.341958	-3.798394
1	0.808441	-3.464755	3.872374
1	3.366413	-1.508655	-0.051251

1	0.711893	0.501311	-3.664444
1	1.740325	-4.014354	-0.660944
1	-1.035870	0.696111	-3.784837
1	-0.215319	-0.520217	-4.775051
1	0.196567	-4.525239	0.047049
1	-0.958810	-2.304664	5.244757
1	0.617497	-5.006681	-1.593931
1	-2.317270	-0.520617	4.186340
1	-2.990560	0.036083	-2.796289
1	-2.049660	-3.947388	0.253445
1	-3.405238	-1.555152	-3.442584
1	-2.712813	-4.397113	-1.320282
1	-3.749583	-1.175888	-1.751439
1	-3.342555	-2.982782	-0.467577
9	-1.666410	1.829575	-1.787746
9	-3.512192	3.448577	-0.742182
9	-3.453390	1.091372	3.298022
9	-4.417504	3.078372	1.795547
77	-0.250648	-0.897733	-0.490345
7	-0.434173	-1.389521	1.539128

Gibbs free energy = -1908.397274 a.u.

Table S8. Optimized Cartesian Coordinates for the Cationic Part of **INT4** at B3PW91/BS level.

Atomic Number	Coordinates		
	X	Y	Z
6	1.255931	-5.142844	-0.942953
6	0.274438	-5.543591	-0.036383
6	5.828528	-0.933030	-0.048173
6	5.119858	-0.400211	-1.121751

6	1.672874	-3.815245	-0.984445
6	5.147219	-1.637903	0.945015
6	-0.286547	-4.603946	0.827848
6	3.735610	-0.554961	-1.198281
6	3.768648	-1.803798	0.863700
6	1.093035	-2.852446	-0.143688
6	0.115475	-3.269759	0.769536
6	3.038595	-1.248035	-0.200315
6	-1.812894	-2.257213	-2.359797
6	-1.288562	-0.355439	2.975729
6	0.685888	-0.408977	-0.233234
6	-0.863895	-0.197861	4.289502
6	1.555411	-1.438807	-0.220778
6	-2.311313	-1.060902	-1.618581
6	-1.678025	0.798142	-3.333524
6	-3.471169	-2.305545	0.370069
6	0.196767	0.663119	4.549586
6	-2.246643	0.301798	-2.043895
6	0.988576	1.044870	-0.211587
6	-3.045360	-1.074152	-0.357974
6	0.317948	1.136308	2.198358
6	1.341761	1.747248	-1.376281
6	0.797170	1.337393	3.489181
6	0.850436	1.803141	0.992703
6	-3.042379	1.116755	-1.112644
6	-3.554049	0.275999	-0.105846
6	1.638838	3.104276	-1.363435
6	1.141486	3.163521	0.992168
6	-3.273963	2.583449	-1.271000
6	-4.460653	0.659439	1.018954
6	1.544479	3.817743	-0.170730
1	1.708218	-5.869581	-1.612410
1	-0.036840	-6.583586	0.009289
1	6.906821	-0.812278	0.009592
1	5.644911	0.129738	-1.912276
1	5.693194	-2.067230	1.780983
1	2.454141	-3.515273	-1.677797
1	-1.024845	-4.916139	1.563070
1	-2.105401	-1.019835	2.718810
1	-0.933998	-2.017716	-2.962555
1	3.201060	-0.164754	-2.056918
1	3.245368	-2.368910	1.631065
1	-1.542596	-3.071070	-1.683789
1	-2.598298	-2.620536	-3.035981
1	-1.360011	-0.745218	5.083968
1	-0.306970	-2.543050	1.456872
1	-0.871346	0.157239	-3.693795
1	-2.695432	-3.074416	0.349795

1	-1.288998	1.815638	-3.245479
1	-2.465011	0.812203	-4.098982
1	-3.734821	-2.098155	1.411068
1	0.556886	0.808723	5.563531
1	-4.367939	-2.719694	-0.110942
1	1.627696	2.013264	3.654565
1	-2.371183	3.100186	-1.609226
1	-4.213419	0.132082	1.945327
1	-4.050683	2.758619	-2.027080
1	-5.499363	0.405816	0.771205
1	-3.604623	3.051386	-0.340813
1	-4.421830	1.731583	1.226576
9	1.410884	1.115516	-2.548927
9	1.992492	3.725954	-2.478584
9	1.001379	3.895553	2.099482
9	1.801006	5.114517	-0.151761
77	-1.259776	0.086143	-0.104397
7	-0.719274	0.300412	1.955247

Gibbs free energy = -1908.401166 a.u.

Table S9. Optimized Cartesian Coordinates for the Cationic Part of **TS1** at B3PW91/BS level.

Atomic Number	Coordinates		
	X	Y	Z
6	2.928621	4.186375	1.371040
6	4.238380	3.706078	1.301048
6	-2.762523	4.603599	-1.362249
6	-1.587940	4.291569	-2.046374
6	1.863270	3.378991	0.995121
6	-3.155578	3.838019	-0.263502

6	4.476142	2.405881	0.858017
6	-0.807287	3.215260	-1.636717
6	-2.384209	2.755329	0.143777
6	2.090444	2.065861	0.534574
6	3.410808	1.592747	0.485466
6	-1.199293	2.434559	-0.537302
6	3.146321	-0.142703	-2.652376
6	1.854073	-0.995832	2.412095
6	0.972125	1.233513	0.146579
6	1.906047	-1.008132	3.796077
6	-0.312235	1.377241	-0.051659
6	2.129780	-1.078441	-2.080115
6	0.243944	-0.499667	-3.771078
6	3.629124	-2.404130	-0.395687
6	0.718612	-0.846794	4.507915
6	0.783404	-1.221645	-2.577455
6	-1.335630	-0.237769	0.184857
6	2.331265	-2.057563	-1.055103
6	-0.465068	-0.713775	2.412005
6	-2.424793	-0.228898	-0.699693
6	-0.470664	-0.688631	3.813008
6	-1.623539	-0.564752	1.547599
6	0.180472	-2.367832	-1.917004
6	1.108633	-2.860399	-0.957675
6	-3.728219	-0.471189	-0.294951
6	-2.941644	-0.787152	1.953170
6	-1.149599	-2.969406	-2.238823
6	0.940453	-4.069743	-0.094031
6	-3.994727	-0.746829	1.046055
1	2.738168	5.196824	1.722050
1	5.068392	4.342204	1.595270
1	-3.370813	5.444633	-1.683079
1	-1.279507	4.887006	-2.901131
1	-4.063186	4.088581	0.278350
1	0.846953	3.756948	1.054071
1	5.492743	2.025134	0.807098
1	2.751857	-1.080812	1.813796
1	2.743036	0.864326	-2.787734
1	0.112057	2.971551	-2.161200
1	-2.683814	2.167904	1.007199
1	4.038564	-0.067222	-2.028318
1	3.461430	-0.508222	-3.638292
1	2.860472	-1.129155	4.297201
1	3.586432	0.577160	0.146597
1	0.555673	0.547953	-3.784263
1	4.269991	-1.531091	-0.244884
1	-0.844796	-0.526820	-3.811950
1	0.626459	-0.970924	-4.686195

1	3.479621	-2.893490	0.570534
1	0.720678	-0.833114	5.593728
1	4.185351	-3.109472	-1.027021
1	-1.402966	-0.540007	4.340337
1	-1.836327	-2.235002	-2.661748
1	1.417652	-3.943105	0.882011
1	-1.022312	-3.770715	-2.977985
1	1.398052	-4.944252	-0.574338
1	-1.622133	-3.407441	-1.355552
1	-0.114050	-4.299386	0.077125
9	-2.235602	0.075036	-1.991141
9	-4.722430	-0.444390	-1.172098
9	-3.239378	-1.105284	3.217910
9	-5.236298	-0.986386	1.444656
77	0.652200	-0.747840	-0.399129
7	0.702351	-0.869930	1.731095

Gibbs free energy = -1908.367918 a.u.

Table S10. Optimized Cartesian Coordinates for the Cationic Part of **TS2** at B3PW91/BS level.

Atomic		Coordinates	
Number	X	Y	Z
6	0.999649	-3.658193	-1.760389
6	1.217106	-3.462534	-3.127234
6	6.472281	-1.026604	0.844726
6	6.195435	-0.530081	-0.431574
6	1.107393	-2.588891	-0.880480
6	5.434597	-1.299162	1.737889
6	1.542256	-2.195268	-3.620518
6	4.881526	-0.300099	-0.817732

6	4.115031	-1.084983	1.357401
6	1.427021	-1.305231	-1.368113
6	1.651897	-1.120727	-2.747899
6	3.828631	-0.575509	0.075211
6	2.030277	3.398049	-0.547787
6	-1.520840	0.590665	-2.807014
6	1.236561	-0.030006	-0.417185
6	-2.337372	0.049505	-3.786697
6	2.469556	-0.316722	-0.282901
6	0.687036	3.076487	0.024592
6	1.507754	2.424526	2.425463
6	-0.811516	3.914821	-1.933618
6	-3.172178	-1.011450	-3.438399
6	0.454204	2.568321	1.371548
6	-1.157566	-0.583066	0.924812
6	-0.570602	3.285221	-0.597855
6	-2.293641	-0.917836	-1.190991
6	-0.830529	-1.029366	2.195785
6	-3.143184	-1.501620	-2.141083
6	-2.106037	-1.343212	0.191690
6	-0.975104	2.544739	1.580937
6	-1.615015	2.928952	0.356851
6	-1.440023	-2.135984	2.783326
6	-2.723261	-2.454127	0.781384
6	-1.671031	2.262668	2.873874
6	-3.084115	3.124718	0.145889
6	-2.403119	-2.848568	2.073632
1	0.757604	-4.647866	-1.383917
1	1.143538	-4.304137	-3.810491
1	7.501970	-1.202392	1.143523
1	7.007187	-0.320121	-1.121847
1	5.655148	-1.683983	2.729284
1	0.953458	-2.726935	0.185389
1	1.721333	-2.054124	-4.682591
1	-0.849510	1.414108	-3.018898
1	2.783178	2.661846	-0.253042
1	4.657593	0.087204	-1.807333
1	3.298566	-1.295735	2.041801
1	2.007731	3.440375	-1.639941
1	2.367435	4.377364	-0.183929
1	-2.315279	0.454436	-4.792950
1	1.916020	-0.131827	-3.112341
1	2.438995	2.024920	2.014351
1	0.014804	3.740299	-2.629255
1	1.185615	1.758807	3.226898
1	1.734903	3.403696	2.867620
1	-1.734772	3.555085	-2.396619
1	-3.835502	-1.458955	-4.172834

1	-0.913826	5.001775	-1.817716
1	-3.771476	-2.332749	-1.853363
1	-1.089061	1.595550	3.511110
1	-3.379729	2.909066	-0.885333
1	-1.819939	3.204716	3.417526
1	-3.367100	4.164328	0.358221
1	-2.654291	1.812074	2.716407
1	-3.674944	2.480652	0.802228
9	0.121464	-0.412003	2.927348
9	-1.107249	-2.521551	4.010517
9	-3.632505	-3.192782	0.128937
9	-2.995030	-3.905082	2.623763
77	-0.403479	1.068358	-0.012613
7	-1.510052	0.142158	-1.540157

Gibbs free energy = -1908.370410 a.u.

Table S11. Optimized Cartesian Coordinates for the Cationic Part of **TS3** at B3PW91/BS level.

Atomic Number	Coordinates		
	X	Y	Z
6	-0.909829	5.469504	-0.531566
6	0.093591	5.769658	0.389576
6	-5.400246	1.103378	-0.766122
6	-4.523414	0.848526	-1.818592
6	-1.321606	4.153409	-0.719636
6	-4.902813	1.551148	0.458214
6	0.680129	4.743759	1.129013
6	-3.150952	1.028163	-1.646680
6	-3.534409	1.740824	0.630794
6	-0.729768	3.114334	0.013527

6	0.270905	3.425200	0.944889
6	-2.644961	1.464219	-0.416464
6	3.025587	1.982428	-1.916556
6	1.792036	0.123729	2.805801
6	-0.227893	0.789356	-0.238501
6	1.548484	0.080375	4.170406
6	-1.185532	1.705141	-0.214136
6	2.901108	0.551912	-1.501076
6	1.573776	-0.304572	-3.570732
6	4.483259	0.625894	0.562059
6	0.369193	-0.509407	4.615256
6	2.195026	-0.479953	-2.220621
6	-0.647156	-1.123485	-0.082872
6	3.523594	-0.056997	-0.361063
6	-0.212032	-0.972099	2.319913
6	-1.389668	-1.596755	-1.156755
6	-0.519266	-1.029567	3.683919
6	-1.059135	-1.467806	1.235230
6	2.467130	-1.750036	-1.553932
6	3.272786	-1.495320	-0.415002
6	-2.522198	-2.389708	-0.980735
6	-2.191519	-2.259251	1.404268
6	2.008102	-3.087773	-2.038559
6	3.839548	-2.505996	0.531710
6	-2.923362	-2.719028	0.306577
1	-1.379094	6.264584	-1.104587
1	0.407250	6.799035	0.538967
1	-6.469268	0.964578	-0.901555
1	-4.905948	0.516392	-2.779948
1	-5.583272	1.761487	1.278912
1	-2.108441	3.927539	-1.433541
1	1.446849	4.973219	1.864730
1	2.681800	0.595883	2.409856
1	2.154211	2.313813	-2.485635
1	-2.470868	0.845373	-2.473245
1	-3.149374	2.109510	1.578108
1	3.136962	2.649076	-1.058028
1	3.909860	2.105050	-2.555951
1	2.268367	0.510388	4.858734
1	0.708306	2.629643	1.541147
1	0.979133	0.610763	-3.626125
1	4.163006	1.643005	0.807576
1	0.927234	-1.141362	-3.835609
1	2.363056	-0.238183	-4.330543
1	4.629544	0.068827	1.491337
1	0.136149	-0.556892	5.674732
1	5.466688	0.701433	0.080203
1	-1.450235	-1.475692	4.004032

1	1.039638	-3.024659	-2.539483
1	3.855566	-2.137684	1.562104
1	2.729872	-3.486575	-2.762892
1	4.873419	-2.750174	0.255651
1	1.922919	-3.809937	-1.222943
1	3.265962	-3.436117	0.521363
9	-1.046379	-1.304011	-2.415320
9	-3.209982	-2.825796	-2.025183
9	-2.626213	-2.638150	2.609672
9	-3.993591	-3.472129	0.498367
77	1.316662	-0.312947	-0.194512
7	0.951757	-0.401974	1.900413

Gibbs free energy = -1908.377816 a.u.

Table S12. Optimized Cartesian Coordinates for the Cationic Part of **TS4** at B3PW91/BS level.

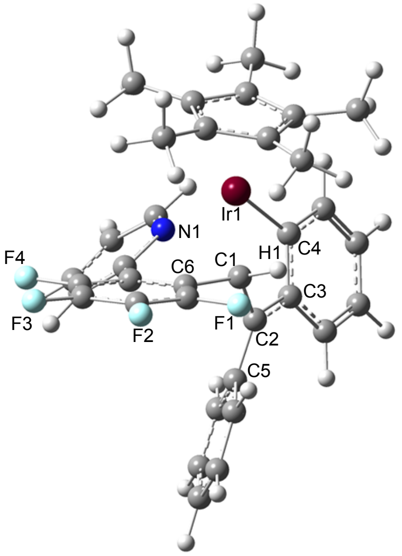
Atomic		Coordinates	
Number	X	Y	Z
6	-3.291684	-2.691162	0.285774
6	-3.240734	-2.193883	-1.012521
6	-4.385408	2.759619	-1.582865
6	-2.467464	-2.141202	1.263750
6	-4.819772	3.485106	-0.475101
6	-2.366130	-1.150957	-1.315624
6	-3.098349	2.224917	-1.612040
6	-1.593042	-1.089340	0.977396
6	-3.958800	3.677701	0.605652
6	-1.553271	-0.576272	-0.345803
6	-1.222277	-0.337545	3.332730
6	-2.226164	2.409414	-0.531245

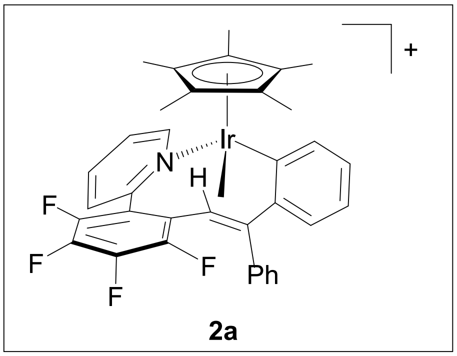
6	0.601739	-3.483910	-0.059793
6	-0.746919	-0.479280	2.022837
6	-2.670892	3.149063	0.576626
6	-0.446985	0.281023	4.304369
6	-0.598251	0.502584	-0.597776
6	-0.855440	1.834567	-0.542330
6	1.568154	-2.400726	-0.416939
6	0.953788	-2.115254	-2.935587
6	0.807378	0.770878	3.954863
6	2.894890	-2.370174	1.837276
6	1.730620	-1.803933	-1.697626
6	1.230534	0.615731	2.644491
6	0.328160	2.684785	-0.354661
6	2.653247	-1.917966	0.434869
6	0.318539	4.084328	-0.294465
6	1.550347	1.991518	-0.187546
6	2.896111	-0.919322	-1.624583
6	3.493149	-1.053108	-0.312655
6	1.501729	4.782758	-0.066857
6	2.733348	2.700427	0.023618
6	3.533627	-0.226562	-2.789063
6	4.800428	-0.473750	0.126219
6	2.704845	4.095873	0.098697
1	-5.047187	2.613527	-2.432408
1	-5.822397	3.903315	-0.454951
1	-2.760461	1.671150	-2.481949
1	-2.213024	-0.699684	3.573780
1	-4.290097	4.243345	1.472571
1	0.336481	-3.464371	1.000444
1	-0.320484	-3.405292	-0.640585
1	-0.827892	0.393186	5.315194
1	1.043063	-4.467089	-0.269637
1	-0.072656	-2.407937	-2.705899
1	-2.003579	3.304551	1.421099
1	1.447991	0.937253	-1.482309
1	1.962549	-2.556893	2.376707
1	3.456616	-3.313726	1.822623
1	0.911847	-1.260762	-3.615091
1	1.428143	-2.947862	-3.471277
1	-0.614731	4.622312	-0.433155
1	1.447490	1.275591	4.670608
1	3.485080	-1.647058	2.406046
1	2.184242	1.005034	2.309039
1	2.807566	0.006652	-3.571413
1	1.487689	5.868435	-0.029852
1	4.798717	-0.205608	1.186957
1	4.020593	0.705601	-2.490982
1	5.607681	-1.202218	-0.025585

1	3.680868	2.179446	0.131676
1	4.299260	-0.880127	-3.226015
1	5.061603	0.419185	-0.447331
1	3.626992	4.644616	0.271792
9	-4.100097	-3.700266	0.583661
9	-4.007485	-2.722016	-1.954540
9	-2.519710	-2.692375	2.482502
9	-2.312914	-0.729422	-2.583878
77	1.342206	-0.110123	-0.276074
7	0.490813	-0.002011	1.703336

Gibbs free energy = -1908.380812 a.u.

Table S13. Optimized Structure for the Cationic Part of **2a**.





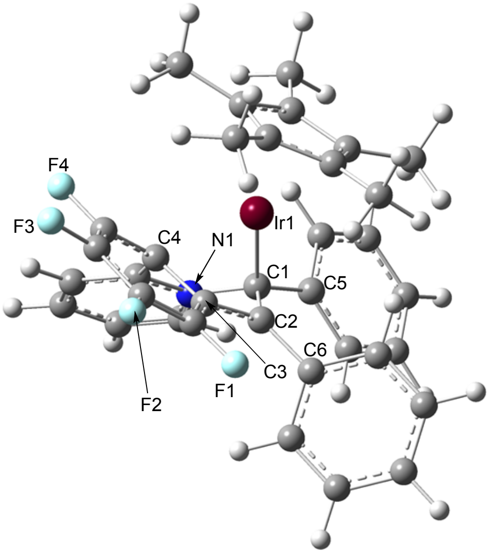
2a

ΔG = −8.52 kcal/mol

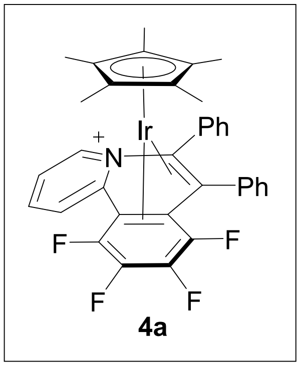
		B3PW91/BS	Experimental
Bond distances (Å)	Ir1–C1	2.163	2.213(5)
	Ir1–H1	2.564	1.893
	Ir1–C4	2.013	2.026(6)
	Ir1–N1	2.217	2.121(5)
	C1–C2	1.471	1.461(9)
	C1–H1	1.096	0.950
Bond angles (deg)	N1–Ir1–C4	88.5	89.5(2)
	Ir1–C1–C2	108.5	104.8(4)
	Ir1–C1–C6	108.2	106.1(4)
	C2–C1–C6	118.5	119.3(5)
	C1–C2–C3	114.0	114.0(5)
	C1–C2–C5	123.0	123.0(6)
	C3–C2–C5	123.0	122.5(6)

*The position of the H1 atom was not refined.

Table S14. Optimized Structure for the Cationic Part of **4a**.



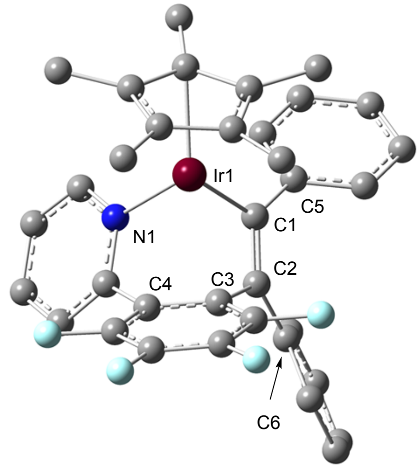
ΔG = 0 kcal/mol

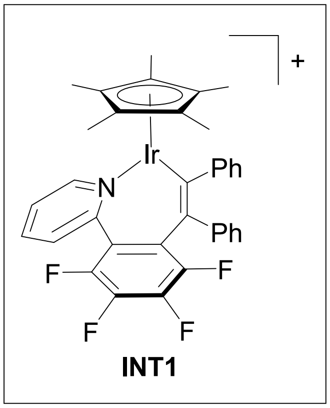


4a

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.130
	Ir1–C2	2.155
	Ir1–C3	2.177
	Ir1–C4	2.214
	C1–C2	1.489
	C2–C3	1.443
	C3–C4	1.483
Bond angles (deg)	C1–Ir1–C2	40.7
	C2–Ir1–C3	38.9
	C3–Ir1–C4	39.4
	C2–C1–C5	123.1
	C2–C1–N1	112.7
	C5–C1–N1	110.1
	C1–C2–C3	111.1
	C1–C2–C6	125.6
	C3–C2–C6	122.8

Table S15. Optimized Structure for the Cationic Part of **INT1**.

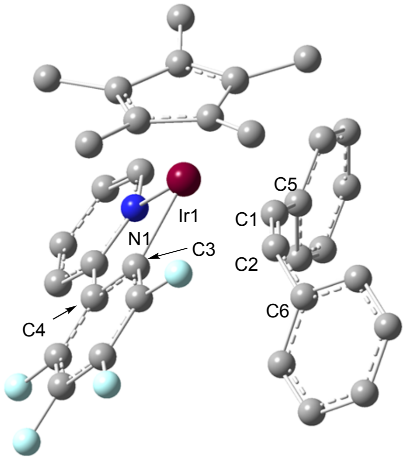


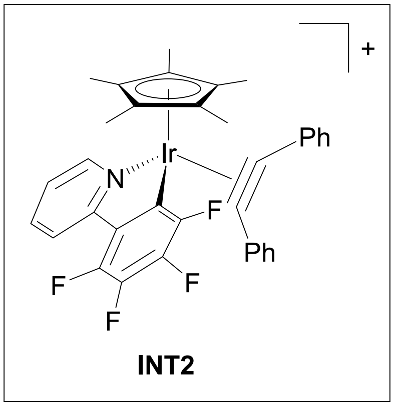


ΔG = 2.39 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.065
	Ir1–C2	2.800
	Ir1–C3	2.602
	Ir1–C4	2.772
	Ir1–N1	2.125
	C1–C2	1.354
	C2–C3	1.508
	C3–C4	1.425
Bond angles (deg)	C1–Ir1–C2	27.4
	C2–Ir1–C3	32.2
	C3–Ir1–C4	30.5
	C1–Ir1–N1	82.8
	C2–C1–C5	126.4
	C2–C1–N1	90.7
	C5–C1–N1	123.5
	C1–C2–C3	110.7
	C1–C2–C6	130.1
	C3–C2–C6	119.1

Table S16. Optimized Structure for the Cationic Part of **INT2**.

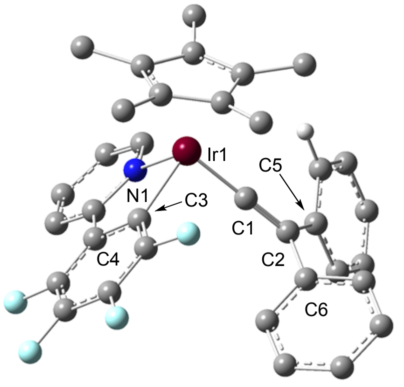


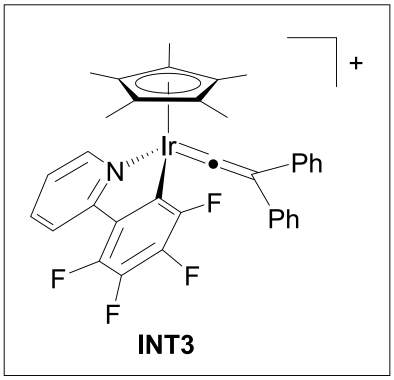


ΔG = 4.13 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.204
	Ir1–C2	2.263
	Ir1–C3	2.049
	Ir1–N1	2.097
	C1–C2	1.262
	C2–C3	2.839
	C1–N1	2.847
Bond angles (deg)	C1–Ir1–C2	32.8
	C2–Ir1–C3	82.2
	C1–Ir1–N1	82.8
	C3–Ir1–N1	77.4
	C2–C1–C5	149.9
	C1–C2–C6	153.8

Table S17. Optimized Structure for the Cationic Part of **INT3**.



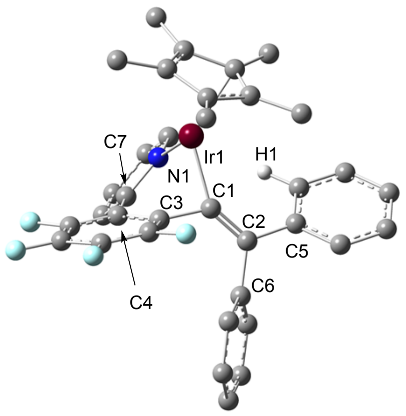


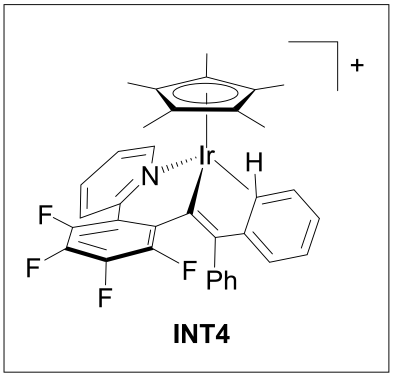
INT3

ΔG = 2.88 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	1.863
	Ir1–C3	2.055
	Ir1–N1	2.096
	C1–C2	1.317
	C1–C3	2.830
	C1–N1	2.853
	C2–C5	1.488
	C2–C6	1.499
Bond angles (deg)	C1–Ir1–C3	92.4
	C1–Ir1–N1	92.0
	C3–Ir1–N1	77.5
	C1–C2–C5	57.6
	C1–C2–C6	116.4

Table S18. Optimized Structure for the Cationic Part of **INT4**.



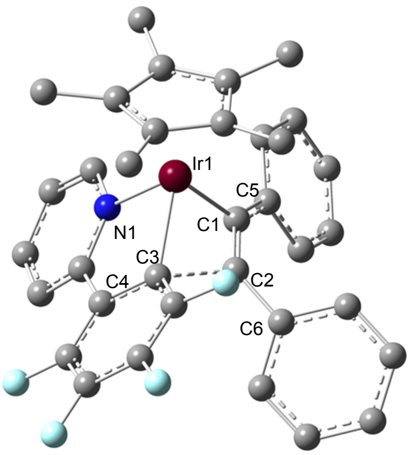


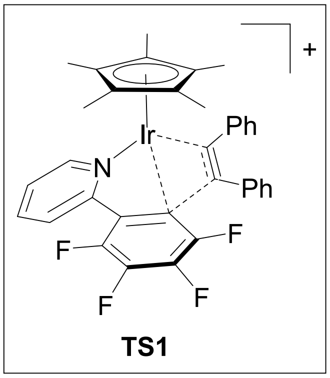
INT4

ΔG = 0.44 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.012
	Ir1–N1	2.140
	Ir1–H1	3.203
	C1–C2	1.348
	C1–C3	1.485
	C1–N1	2.140
	C2–C5	1.489
	C2–C6	1.496
	C4–C7	1.477
Bond angles (deg)	Ir–C1–C2	144.2
	C1–Ir1–N1	80.9
	C1–Ir1–H1	62.7
	C1–C3–C4	120.8
	C1–C2–C5	121.7
	C1–C2–C6	122.9
	C3–C4–C7	118.9
	C4–C7–N1	114.1

Table S19. Optimized Structure for the Cationic Part of **TS1**.



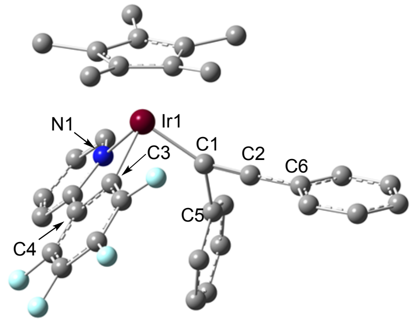


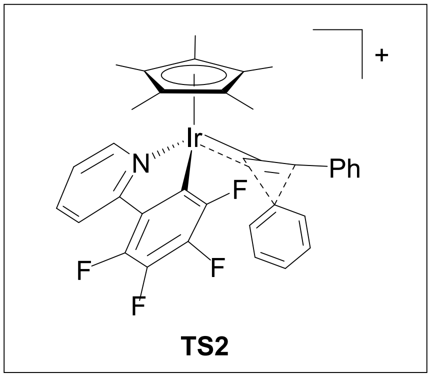
TS1

ΔG = 21.3 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.080
	Ir1–C2	2.359
	Ir1–C3	2.134
	Ir1–N1	2.134
	C1–C2	1.307
	C2–C3	1.927
	C1–N1	2.647
Bond angles (deg)	C1–Ir1–C2	33.5
	C2–Ir1–C3	50.5
	C1–Ir1–N1	77.8
	C3–Ir1–N1	76.3
	C2–C1–C5	137.4
	C1–C2–C6	136.5
	C1–C2–C3	114.3
	C2–C3–C4	114.5

Table S20. Optimized Structure for the Cationic Part of **TS2**.



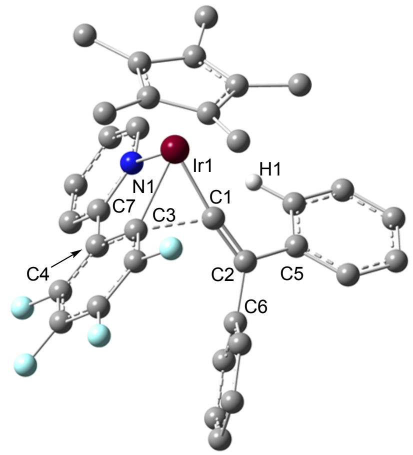


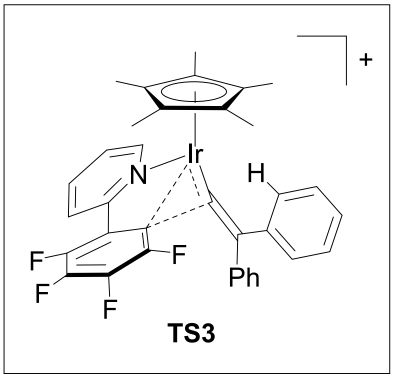
TS2

ΔG = 19.74 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.015
	Ir1–C3	2.043
	Ir1–N1	2.101
	C1–C2	1.273
	C1–C3	2.800
	C1–N1	2.101
	C1–C5	1.602
	C2–C5	1.800
	C2–C6	1.429
Bond angles (deg)	C1–Ir1–C3	87.2
	C1–Ir1–N1	92.4
	C3–Ir1–N1	77.5
	C1–C2–C5	60.0
	C1–C2–C6	171.2

Table S21. Optimized Structure for the Cationic Part of **TS3**.



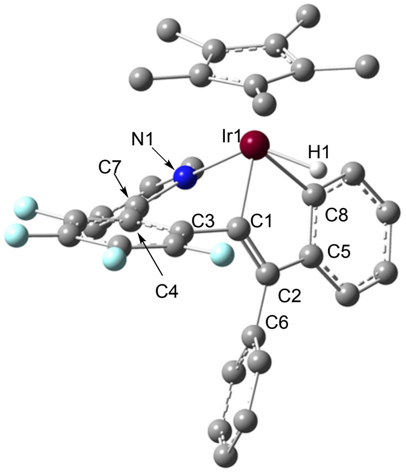


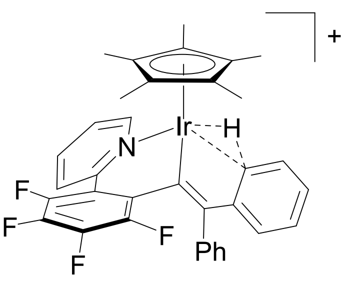
TS3

ΔG = 15.09 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	1.898
	Ir1–C3	2.127
	Ir1–N1	2.128
	Ir1–H1	3.470
	C1–C2	1.325
	C1–C3	1.964
	C1–N1	2.718
	C2–C5	1.489
	C2–C6	1.493
Bond angles (deg)	Ir–C1–C2	171.5
	C1–Ir1–C3	58.1
	C1–Ir1–H1	51.4
	C1–Ir1–N1	84.7
	C3–C4–C7	115.9
	C4–C7–N1	114.1

Table S22. Optimized Structure for the Cationic Part of **TS4**.





TS4

ΔG = 13.21 kcal/mol

		B3PW91/BS
Bond distances (Å)	Ir1–C1	2.060
	Ir1–C8	2.114
	Ir1–N1	2.157
	Ir1–H1	1.601
	C1–C2	1.358
	C1–C3	1.462
	C2–C5	1.469
	C1–H1	2.271
	C8–H1	1.673
Bond angles (deg)	C1–It1–C8	78.7
	C1–Ir1–N1	75.9
	C1–Ir1–H1	75.5
	C8–Ir1–H1	51.3
	C1–C3–C4	116.4
	C3–C4–C7	119.6

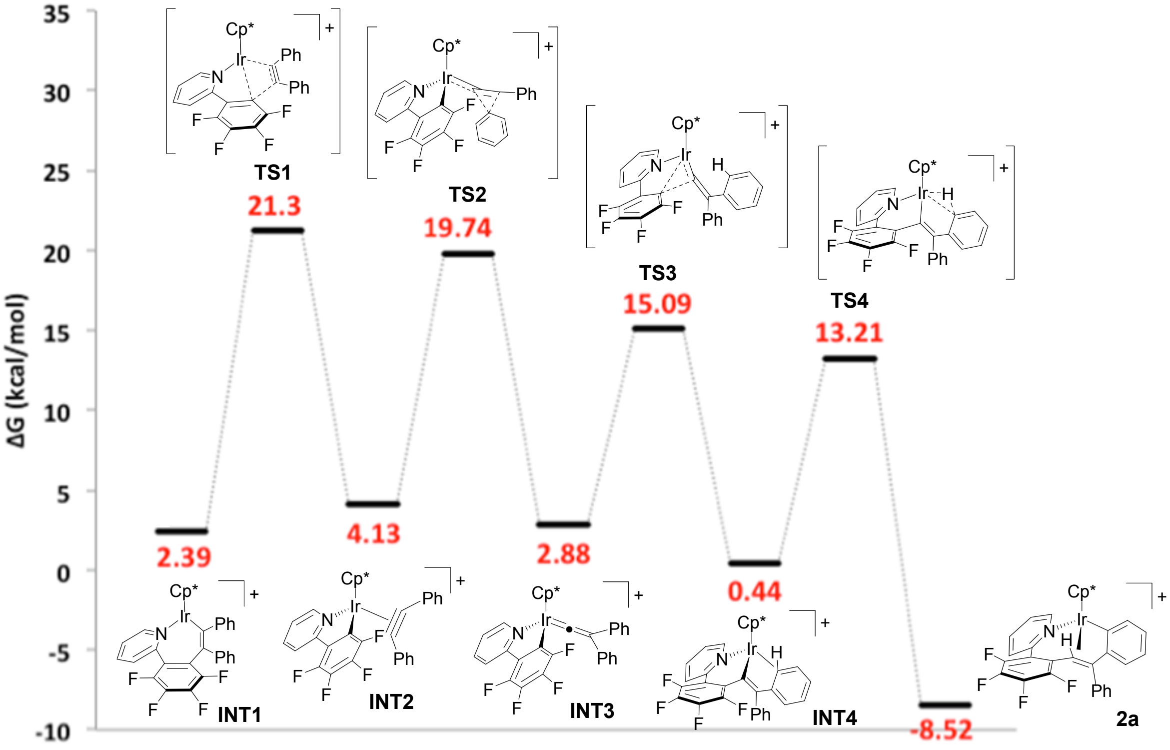


Figure S14. Free energy profiles for the formation of **2a** from the seven-membered iridacyle **INT1**.

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