

# Investigation of the properties of 4,5-dialkylated N-heterocyclic carbenes

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## Electronic supplementary information (ESI)

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## 1. General Informations

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents were purified by distillation over the drying agents indicated in parentheses and were transferred under Argon: THF (Na-benzophenone), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>).

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated. DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) and *trans*-cinnamaldehyde were freshly distilled prior to use.

Analytical thin layer chromatography was performed on Polygram SIL G/UV<sub>254</sub> plates. Visualization was accomplished with short wave UV light, KMnO<sub>4</sub> or phosphomolybdic acid staining solutions followed by heating.

Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique or using a Biotage Isolera Flash Purification System eluting with solvents as indicated.

GC Spectra were recorded on an Agilent Technologies 6890 GC-system with a HP-5MS column (0.32 mm x 30 m, Film: 0.25 μm) using H<sub>2</sub> gas as the mobile phase. The major signals are quoted in m/z with the relative intensity in parentheses. The methods used start with the injection temperature T<sub>0</sub>; after holding this temperature for 3 min, the column is heated to temperature T<sub>1</sub> (ramp) and this temperature is held for an additional time t:

Method 50\_20\_320: T<sub>0</sub> = 50 °C, T<sub>1</sub> = 320 °C, ramp = 20 °C/min, t = 3 min.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm, δ<sub>C</sub> = 77.16 ppm; d<sup>8</sup>-toluene: δ<sub>H</sub> = 7.00 ppm, δ<sub>C</sub> = 137.86 ppm).

ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

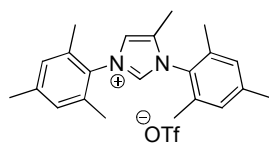
Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur and Shimadzu FTIR 8400S. The wave numbers (ν) of recorded IR-signals are quoted in cm<sup>-1</sup>.

Elemental analyses were recorded on a Vario EL III of Fa. Elementar Analysensysteme GmbH, Hanau.

## 2. General Procedure A for the Anion Exchange (6a-h)

NHC-HCl or NHC-HBr (**5**) (0.20 mmol, 1.0 eq.) and silver trifluoromethanesulfonate (AgOTf) (0.22 mmol, 1.1 eq.) were weighed in the glovebox into an oven dried, aluminum foil covered reaction vessel with Teflon screw cap under an argon atmosphere. Outside the glovebox CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) was added under an argon atmosphere and the reaction mixture was stirred at room temperature for 1 h. The resulting suspension was filtered through a celite pad and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 15:1). The products **6a-h** were dried at 110 °C under high vacuum overnight to yield the trifluoromethanesulfonates in almost quantitative yields.

### 4-Methyl-1,3-bis-(2,4,6-trimethylphenyl)-3H-imidazol-1-ium trifluoromethanesulfonate (**6a**)



Following the general procedure A, **5a** (107 mg, 0.30 mmol, 1.0 eq.) and AgOTf (86 mg, 0.33 mmol, 1.1 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) at room temperature for 1 h. The suspension was directly put on silica gel column and subjected to column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1) to furnish **6a** (140 mg, 0.298 mmol, 99 %) white solid.

IR (ATR):  $\nu$  = 2362, 1547, 1537, 1281, 1255, 1223, 1145, 1029, 863.

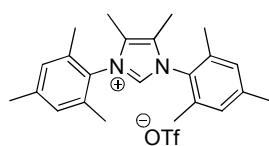
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.03 (6 H, s), 2.09 (6 H, s), 2.13 (3 H, d,  $J$  = 1.2 Hz), 2.32 (3 H, s), 2.35 (3 H, s), 6.99 (2 H, s), 7.04 (2 H, s), 7.34-7.37 (1 H, m), 9.03 (1 H, d,  $J$  = 1.8 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 9.0, 17.2, 21.1 (2 C), 121.4, 128.1, 129.7 (2 C), 129.9 (2 C), 130.5, 133.0, 133.9, 134.4, 136.9, 141.1, 141.5.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$ : -78.75.

ESI-MS: for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub><sup>+</sup> calcd: 319.2169, found: 319.2179.

### 4,5-Dimethyl-1,3-bis-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium trifluoromethanesulfonate (**6b**)



Following the general procedure A, **5b** (74 mg, 0.20 mmol, 1.0 eq.) and AgOTf (57 mg, 0.22 mmol, 1.1 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at room temperature for 1 h. The suspension was filtered over celite pad and the solvent was removed under reduced pressure. After purification by column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 15:1) **6b** was obtained in 99 % yield (96 mg, 0.199 mmol) as white powder.

Elemental analysis: for C<sub>24</sub>H<sub>29</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S calcd: C 59.73, H 6.04, N 5.76; found: C 59.73, H 6.06, N 5.81.

IR (ATR):  $\nu$  = 3116, 1541, 1488, 1260, 1223, 1145, 1030, 858, 636.

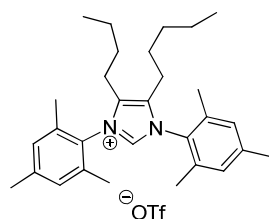
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.05 (12 H, s), 2.07 (6 H, s), 2.35 (6 H, s), 7.05 (4 H, s), 9.06 (1 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 8.7, 17.4, 21.3, 128.4, 128.7, 130.1, 134.6, 135.8, 141.6.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$ : -78.7.

ESI-MS: for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub><sup>+</sup> calcd: 333.2325, found: 333.2334.

### 5-Butyl-4-pentyl-1,3-bis-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium trifluoromethanesulfonate (**6c**)



Following the general procedure A, **5c** (154 mg, 0.30 mmol, 1.0 eq.) and AgOTf (93 mg, 0.36 mmol, 1.2 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was evaporated under reduced pressure. Column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 15:1) of the residue afforded **6c** (175 mg, 0.30 mmol, 100 %) as an yellow very viscous liquid.

Elemental analysis: for  $C_{31}H_{43}F_3N_2O_3S$  calcd: C 64.11, H 7.46, N 4.82; found: C 64.09, H 7.23, N 4.72.

IR (ATR):  $\nu = 3103, 2956, 2931, 2871, 1610, 1538, 1454, 1282, 1255, 1223, 1148, 1030, 863$ .

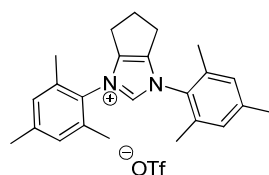
$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 0.75-0.85 (6 H, m), 1.10-1.40 (10 H, m), 2.07 (12 H, s), 2.36 (6 H, s), 2.38-2.46 (4 H, m), 7.05 (4 H, s), 9.19 (1 H, s).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 13.4, 13.6, 17.4, 17.4, 21.2, 21.9, 22.2, 22.9, 23.1, 27.9, 30.3, 31.2, 128.5, 130.0, 132.1, 132.1, 134.4, 136.8, 141.3.

$^{19}F$  NMR ( $CDCl_3$ , 282 MHz)  $\delta$ : -78.8.

ESI-MS: for  $C_{30}H_{43}N_2^+$  calcd: 431.3421, found: 431.3425.

### 1,3-Bis-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-cyclopentaimidazol-1-ium trifluoromethanesulfonate (**6d**)



Following the general procedure A, **5d** (127 mg, 0.30 mmol, 1.0 eq.) and AgOTf (93 mg, 0.36 mmol, 1.2 eq.) were stirred in  $CH_2Cl_2$  (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was evaporated under reduced pressure. Column chromatography ( $\varnothing = 2.5$  cm,  $SiO_2 = 6$  cm,  $CH_2Cl_2/MeOH$  20:1) of the residue afforded **6d** (130 mg, 0.26 mmol, 87 %) as a white powder.

Elemental analysis: for  $C_{25}H_{29}F_3N_2O_3S$  calcd: C 60.71, H 5.91, N 5.66; found: C 60.72, H 5.59, N 5.54.

IR (ATR):  $\nu = 3081, 1519, 1277, 1252, 1241, 1223, 1220, 1150, 1028, 860, 847$ .

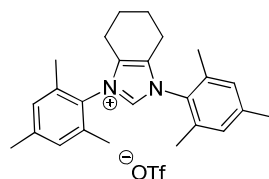
$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 2.12 (12 H, s), 2.34 (6 H, s), 2.75 (6 H, br s), 7.02 (4 H, s), 8.93 (1 H, s).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 17.4, 21.1, 23.2, 27.8, 129.3, 129.8, 133.9, 139.7, 140.0, 141.2.

$^{19}F$  NMR ( $CDCl_3$ , 282 MHz)  $\delta$ : -78.7.

ESI-MS: for  $C_{24}H_{29}N_2^+$  calcd: 345.2325, found: 345.2329.

**1,3-Bis-(2,4,6-trimethylphenyl)-4,5,6,7-tetrahydro-3*H*-benzimidazol-1-ium  
trifluoromethanesulfonate (6e)**



Following the general procedure A, **5e** (207 mg, 0.47 mmol, 1.0 eq.) and AgOTf (145 mg, 0.56 mmol, 1.2 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was evaporated under reduced pressure. Column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1) of the residue afforded **6e** (227 mg, 0.45 mmol, 95 %) as a white powder.

Elemental analysis: for C<sub>26</sub>H<sub>31</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S calcd: C 61.40, H 6.14, N 5.51; found: C 61.06, H 5.95, N 5.40.

IR (ATR):  $\nu$  = 3091, 2937, 2361, 1610, 1531, 1480, 1258, 1243, 1223, 1148, 1030, 858.

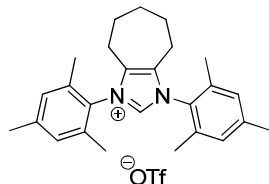
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.88-1.96 (4 H, m), 2.07 (12 H, s), 2.30-2.35 (4 H, m), 2.35 (6 H, s), 7.04 (4 H, s), 9.15 (1 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 17.29, 19.90, 21.13, 21.51, 128.35, 129.87, 130.89, 134.27, 135.89, 141.34.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$ : -78.7.

ESI-MS: for C<sub>25</sub>H<sub>31</sub>N<sub>2</sub><sup>+</sup> calcd: 359.2482, found: 359.2476.

**1,3-Bis-(2,4,6-trimethylphenyl)-3,4,5,6,7,8-hexahydro-cycloheptimidazol-1-ium  
trifluoromethanesulfonate (6f)**



Following the general procedure A, **5f** (91 mg, 0.20 mmol, 1.0 eq.) and AgOTf (57 mg, 0.22 mmol, 1.1 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was removed under reduced pressure. After purification by column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 15:1) **6f** was obtained in 99 % yield (104 mg, 0.199 mmol) as off white powder.

Elemental analysis: *found*: C 62.12, H 6.15, N 5.29, *calcd.* for C<sub>27</sub>H<sub>33</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S: C 62.05, H 6.36, N 5.36.

IR (ATR):  $\nu$  = 3105, 3034, 2926, 2857, 2359, 1611, 1542, 1446, 1279, 1253, 1222, 1149, 1030, 859, 636, 571.

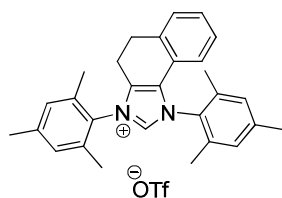
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.67-1.77 (4 H, m), 1.85-1.95 (2 H, m), 2.05 (12 H, s), 2.34 (6 H, s), 2.40-2.50 (4 H, m), 7.04 (4 H, s), 8.98 (1 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 17.4, 21.3, 23.9, 26.6, 30.2, 128.6, 130.0, 133.9, 134.8, 134.8, 141.5.

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$ : -78.7.

ESI-MS: for C<sub>26</sub>H<sub>33</sub>N<sub>2</sub><sup>+</sup> *calcd.*: 373.2638, *found*: 373.2641.

### 1,3-Bis-(2,4,6-trimethylphenyl)-4,5-dihydro-1H-naphtho[1,2-d]imidazol-3-ium trifluoromethanesulfonate (**6g**)



Following the general procedure A, **5g** (97 mg, 0.20 mmol, 1.0 eq.) and AgOTf (57 mg, 0.22 mmol, 1.1 eq.) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was removed under reduced pressure. After purification by column chromatography ( $\varnothing$  = 2.5 cm, SiO<sub>2</sub> = 6 cm, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 15:1) **6g** was obtained in 97 % yield (108 mg, 0.194 mmol) as off white powder.

Elemental analysis: *found*: C 64.50, H 5.34, N 4.92, *calcd.* for C<sub>30</sub>H<sub>31</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S: C 64.73, H 5.61, N 5.03.

IR (ATR):  $\nu$  = 3083, 3023, 2923, 2861, 2363, 1609, 1527, 1481, 1451, 1256, 1223, 1146, 1029, 855, 765, 636, 572.

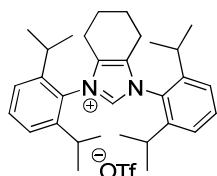
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.11 (6 H, s), 2.13 (6 H, s), 2.36 (3 H, s), 2.41 (3 H, s), 2.69 (2 H, t,  $J$  = 8.0 Hz), 3.17 (2 H, t,  $J$  = 8.0 Hz), 6.46 (1 H, d,  $J$  = 7.7 Hz), 7.00-7.08 (1 H, m), 7.06 (2 H, s), 7.11 (2 H, s), 7.22-7.33 (2 H, m), 9.31 (1 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 17.4, 17.6, 18.7, 21.3, 21.4, 28.8, 118.4, 120.6, 122.7, 123.9, 128.0, 128.1, 128.9, 129.4, 129.9, 129.9, 130.1, 130.4, 131.6, 134.4, 134.5, 134.6, 137.4, 141.7, 141.9.

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$ : -78.7.

ESI-MS: for  $C_{29}H_{31}N_2^+$  calcd: 407.2482, found: 407.2484.

**1,3-Bis-(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-3H-benzoimidazol-1-ium  
trifluoromethanesulfonate (6h)**



Following the general procedure A, **5h** (105 mg, 0.20 mmol, 1.0 eq.) and AgOTf (57 mg, 0.22 mmol, 1.1 eq.) were stirred in  $CH_2Cl_2$  (2.0 mL) at room temperature for 1 h. The suspension was filtered through celite pad and the solvent was removed under reduced pressure. After purification by column chromatography ( $\varnothing = 2.5$  cm,  $SiO_2 = 6$  cm,  $CH_2Cl_2/MeOH$  15:1) **6h** was obtained in 98 % yield (117 mg, 0.197 mmol) as white powder.

Elemental analysis: *found*: C 64.62, H 7.31, N 4.64, *calcd.* for  $C_{32}H_{43}F_3N_2O_3S$ : C 64.84, H 7.31, N 4.73.

IR (ATR):  $\nu = 3080, 2957, 2870, 1531, 1465, 1286, 1250, 1221, 1147, 1029, 805, 762, 636$ .

$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 1.20 (6 H, d,  $J = 6.9$  Hz), 1.25 (6 H, d,  $J = 6.9$  Hz), 1.90-2.00 (4 H, m), 2.30 (4 H, sep,  $J = 6.9$  Hz), 2.28 – 2.39 (4 H, m), 7.34 (4 H, d,  $J = 7.8$  Hz), 7.56 (2 H, t,  $J = 7.8$  Hz), 9.39 (1 H, s).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 20.3, 21.5, 23.4, 24.8, 29.3, 124.9, 127.7, 131.8, 132.2, 137.1, 145.2.

$^{19}F$  NMR (282 MHz,  $CDCl_3$ )  $\delta$ : -78.7.

ESI-MS: for  $C_{31}H_{43}N_2^+$  calcd: 443.3421, found: 443.3425.

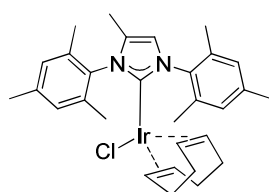


### 3. General Procedure B for the Synthesis of [(NHC)Ir(COD)Cl] complexes

#### 7a-h

According to a literature procedure,<sup>1</sup> **6** (0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of [Ir(COD)Cl]<sub>2</sub> (0.083 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, filtered over a celite pad and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 8 cm, *n*-pentane/EtOAc 10:1) to yield the complex **7** as yellow solid.

#### Preparation of [(NHC)Ir(COD)Cl] complex **7a**



According to the general procedure B, **5a** (53 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (20 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of [Ir(COD)Cl]<sub>2</sub> (55 mg, 0.083 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, filtered through celite and subjected to column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 8 cm, *n*-pentane/EtOAc 15:1) to yield **7a** (89 mg, 0.14 mmol, 91 %) as yellow solid.

Elemental analysis: for C<sub>30</sub>H<sub>38</sub>ClIrN<sub>2</sub> calcd: C 55.07, H 5.85, N 4.28; found: C 55.16, H 5.51, N 4.16.

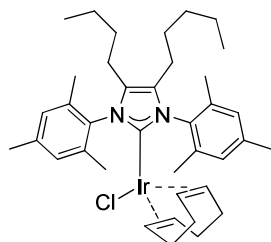
IR (ATR):  $\nu$  = 2915, 2876, 2828, 1486, 1379, 1323, 1213, 1152, 1034, 998, 969, 850, 757, 717.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 1.17-1.38 (4 H, m), 1.55-1.75 (4 H, m), 1.87 (3 H, s), 2.10 (3 H, s), 2.13 (3 H, s), 2.28 (3 H, s), 2.36 (9 H, m), 2.94-3.06 (2 H, m), 4.05-4.15 (2 H, m), 6.69 (1 H, s), 6.94-7.05 (4 H, m).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 18.3, 18.4, 19.8, 19.8, 21.2, 21.3, 28.7, 29.4, 33.3, 34.0, 50.9, 51.5, 81.7, 82.2, 128.1, 128.2, 129.6, 129.7, 130.6, 133.9, 134.5, 134.9, 136.6, 137.3, 137.9, 138.5, 138.7, 180.6.

ESI-MS: for  $C_{30}H_{38}IrN_2^+$  calcd: 619.2669, found: 619.2653  $[M-Cl]^+$ , for  $C_{30}H_{38}ClIrN_2Na^+$  calcd: 677.2245, found: 677.2229  $[M+Na]^+$ , for  $C_{31}H_{41}IrN_3^+$  calcd: 660.2930, found: 660.2920  $[M+MeCN-Cl]^+$ .

### Preparation of [(NHC)Ir(COD)Cl] complex **7c**



According to the general procedure B, **6c** (87 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (21 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of  $[Ir(COD)Cl]_2$  (55 mg, 0.081 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, adsorbed on celite and subjected to column chromatography ( $\varnothing = 2.5$  cm,  $SiO_2 = 8$  cm, *n*-pentane/EtOAc 20:1) to yield **7c** (107 mg, 0.14 mmol, 93 %) as an orange very viscous liquid.

IR (ATR):  $\nu = 2955, 2926, 2872, 2829, 1484, 1458, 1373, 1317, 1301, 852, 734$ .

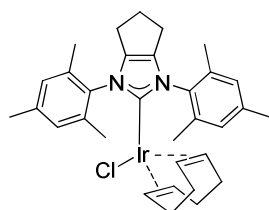
$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 0.77 (3H, t,  $J = 6.9$  Hz), 0.78 (3H, t,  $J = 6.6$  Hz), 1.05-1.30 (14 H, m), 1.50 - 1.75 (4 H, m), 2.06 (6 H, s), 2.10 - 2.25 (4 H, m), 2.29 (6 H, s), 2.34 (6 H, s), 2.85 - 2.95 (2 H, m), 3.98 - 4.08 (2 H, m), 6.95 (2 H, s), 6.99 (2 H, s).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 13.65, 13.79, 18.39, 18.41, 20.02, 20.04, 21.12, 22.11, 23.46, 23.66, 28.25, 28.83, 28.86, 30.79, 31.17, 33.52, 33.54, 51.01, 51.03, 80.95, 80.98, 128.01, 129.52, 130.66, 130.70, 134.21, 134.86, 137.61, 138.14, 178.38.

$^{19}F$  NMR ( $CDCl_3$ , 282 MHz)  $\delta$ : no signals.

ESI-MS: for  $C_{38}H_{54}IrN_2^+$  calcd: 731.3916, found: 731.3913  $[M-Cl]^+$ , for  $C_{38}H_{54}ClIrN_2Na^+$  calcd: 789.3502, found: 789.3491  $[M+Na]^+$ .

### Preparation of [(NHC)Ir(COD)Cl] complex **7d**



According to the general procedure B, **6d** (74 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (21 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of [Ir(COD)Cl]<sub>2</sub> (55 mg, 0.081 mmol, 1.1 eq.) in THF (1 mL) was added.. The resulting mixture was stirred at room temperature overnight, adsorbed on celite and subjected to column chromatography ( $\varnothing = 2.5$  cm, SiO<sub>2</sub> = 8 cm, *n*-pentane/EtOAc 20:1) to yield **7d** (75 mg, 0.11 mmol, 73 %) as an yellow solid.

Elemental analysis: for C<sub>32</sub>H<sub>40</sub>ClIrN<sub>2</sub> calcd: C 56.49, H 5.93, N 4.12; found: C 56.33, H 5.85, N 3.84.

IR (ATR):  $\nu = 2919, 1484, 1413, 1350, 1323, 1282, 1219, 1074, 1032, 852$ .

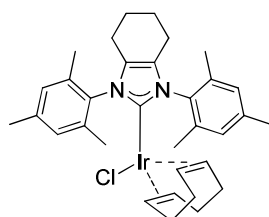
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.05-1.35 (4 H, m), 1.55-1.75 (4 H, m), 2.14 (6 H, s), 2.34 (12 H, s), 2.49 (6 H, br s), 2.95-3.04 (2 H, m), 4.05-4.15 (2 H, m), 6.95 (2 H, s), 6.98 (2 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 18.2, 19.7, 21.1, 23.8, 28.0, 28.9, 33.5, 51.1, 82.0, 127.9, 129.4, 134.2, 134.8, 137.1, 138.2, 138.2, 186.0.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$ : no signals.

ESI-MS: for C<sub>32</sub>H<sub>40</sub>IrN<sub>2</sub><sup>+</sup> calcd: 645.2821, found: 645.2824 [M-Cl]<sup>+</sup>, for C<sub>32</sub>H<sub>40</sub>ClIrN<sub>2</sub>Na<sup>+</sup> calcd: 703.2407, found: 703.2404 [M+Na]<sup>+</sup>, for C<sub>34</sub>H<sub>43</sub>IrN<sub>3</sub><sup>+</sup> calcd: 686.3086, found: 686.3082 [M+MeCN-Cl]<sup>+</sup>.

### Preparation of [(NHC)Ir(COD)Cl] complex **7e**



According to the general procedure B, **6e** (77 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (21 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of [Ir(COD)Cl]<sub>2</sub> (55 mg, 0.081 mmol, 1.1 eq.) in THF (1 mL) was added.

The resulting mixture was stirred at room temperature overnight, adsorbed on celite and subjected to column chromatography ( $\emptyset = 2.5$  cm,  $\text{SiO}_2 = 8$  cm, *n*-pentane/EtOAc 20:1) to yield **7e** (85 mg, 0.12 mmol, 80 %) as an orange solid.

Elemental analysis: for  $\text{C}_{33}\text{H}_{42}\text{ClIrN}_2$  calcd: C 57.08, H 6.10, N 4.03; found: C 57.09, H 6.21, N 3.81.

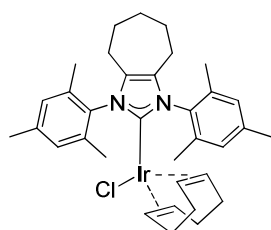
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.15-1.35 (4 H, m), 1.54-1.68 (4 H, m), 1.68-1.78 (4 H, m), 2.02-2.14 (10 H, m), 2.30 (6 H, s), 2.35 (6 H, s), 3.01-3.05 (2 H, m), 4.04-4.09 (2 H, m), 6.96 (2 H, s), 6.99 (2 H, s).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.3, 19.6, 20.7, 22.3, 28.9, 33.5, 50.8, 81.4, 128.0, 129.1, 129.5, 133.9, 134.6, 137.5, 138.2, 178.7.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$ : no signals.

ESI-MS: for  $\text{C}_{33}\text{H}_{42}\text{IrN}_2^+$  calcd: 659.2977, found: 659.2968  $[\text{M}-\text{Cl}]^+$ , for  $\text{C}_{35}\text{H}_{45}\text{IrN}_3^+$  calcd: 700.3243, found: 700.3239  $[\text{M}+\text{MeCN}-\text{Cl}]^+$ .

### Preparation of [(NHC)Ir(COD)Cl] complex **7f**



According to the general procedure B, **6f** (78 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (20 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (55 mg, 0.083 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, filtered through celite and subjected to column chromatography ( $\emptyset = 2.5$  cm,  $\text{SiO}_2 = 8$  cm, *n*-pentane/EtOAc 15:1) to yield **7f** (102 mg, 0.14 mmol, 96 %) as an yellow solid.

Elemental analysis: for  $\text{C}_{34}\text{H}_{44}\text{ClIrN}_2$  calcd: C 57.65, H 6.26, N 3.95; found: C 57.59, H 5.97, N 3.85.

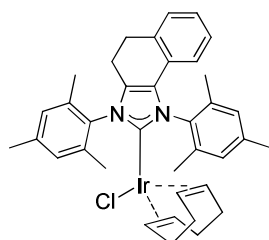
IR (ATR):  $\nu = 3014, 2915, 2877, 2852, 2830, 1484, 1446, 1362, 1307, 1212, 1033, 1000, 966, 883, 852, 576$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.15-1.29 (4 H, m), 1.52-1.68 (8 H, m), 1.70-1.79 (2 H, m), 2.02 (6 H, s), 2.20-2.26 (4 H, m), 2.30 (6 H, s), 2.35 (6 H, s), 3.01-3.05 (2 H, m), 4.00-4.06 (2 H, m), 6.96 (2 H, s), 7.00 (2 H, s).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 18.4, 19.9, 21.3, 24.8, 27.3, 29.0, 30.8, 33.6, 50.8, 80.9, 128.0, 129.6, 132.1, 134.3, 138.1, 138.4, 177.5.

ESI-MS: for  $\text{C}_{34}\text{H}_{44}\text{IrN}_2^+$  calcd: 673.3134, found: 673.3124  $[\text{M}-\text{Cl}]^+$ , for  $\text{C}_{34}\text{H}_{44}\text{ClIrN}_2^+$  calcd: 731.2714, found: 731.2699  $[\text{M}+\text{Na}]^+$ .

### Preparation of $[(\text{NHC})\text{Ir}(\text{COD})\text{Cl}]$ complex **7g**



According to the general procedure B, **6g** (84 mg, 0.125 mmol, 1 eq.) was added to a solution of *t*-BuOK (17 mg, 0.15 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (46 mg, 0.069 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, filtered through celite and subjected to column chromatography ( $\text{Ø} = 2.5$  cm,  $\text{SiO}_2 = 8$  cm, *n*-pentane/EtOAc 15:1) to yield **7g** (88 mg, 0.12 mmol, 95 %) as an yellow solid.

Elemental analysis: for  $\text{C}_{37}\text{H}_{42}\text{ClIrN}_2$  calcd: C 59.86, H 5.70, N 3.77; found: C 59.47, H 5.36, N 3.61.

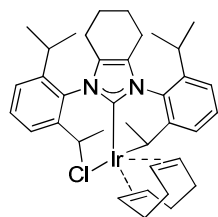
IR (ATR):  $\nu = 2913, 2875, 1486, 1357, 1324, 1305, 1237, 1034, 967, 851, 758, 720, 563$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 1.15-1.39 (4 H, m), 1.57-1.74 (4 H, m), 2.06 (3 H, s), 2.11 (3 H, s), 2.35 (6 H, s), 2.37 (3 H, s), 2.40-2.47 (2 H, m), 2.41 (3 H, s), 2.96 (2 H, t,  $J = 7.8$  Hz), 3.00-3.14 (2 H, m), 4.00-4.15 (2 H, m), 6.28 (1 H, d,  $J = 7.6$  Hz), 6.91 (2 H, t,  $J = 7.4$  Hz), 6.96-7.09 (5 H, m), 7.16 (1 H, d,  $J = 7.2$  Hz).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 18.3, 18.6, 19.8, 19.8, 20.0, 21.3, 21.4, 28.8, 29.2, 29.8, 33.5, 33.9, 51.2, 51.6, 82.1, 82.6, 119.8, 126.7, 127.4, 128.2, 128.4, 128.5, 128.6, 129.8, 130.0, 131.8, 133.6, 133.8, 134.8, 135.2, 135.4, 137.7, 137.9, 138.9, 139.0, 181.7.

ESI-MS: for  $\text{C}_{37}\text{H}_{42}\text{IrN}_2^+$  calcd: 707.2907, found: 707.2958  $[\text{M}-\text{Cl}]^+$ , for  $\text{C}_{37}\text{H}_{42}\text{ClIrN}_2\text{Na}^+$  calcd: 765.2558, found: 765.2530  $[\text{M}+\text{Na}]^+$ .

## Preparation of [(NHC)Ir(COD)Cl] complex **7h**



According to the general procedure B, **6h** (89 mg, 0.15 mmol, 1 eq.) was added to a solution of *t*-BuOK (20 mg, 0.18 mmol, 1.2 eq.) in THF (1 mL). After stirring at room temperature for 20 min, a solution of [Ir(COD)Cl]<sub>2</sub> (55 mg, 0.083 mmol, 1.1 eq.) in THF (1 mL) was added. The resulting mixture was stirred at room temperature overnight, filtered through celite and subjected to column chromatography (Ø = 2.5 cm, SiO<sub>2</sub> = 8 cm, *n*-pentane/EtOAc 15:1) to yield **7h** (93 mg, 0.12 mmol, 80 %) as an yellow solid.

Elemental analysis: for C<sub>39</sub>H<sub>54</sub>ClIrN<sub>2</sub> calcd: C 60.17, H 6.99, N 3.60; found: C 60.05, H 6.69, N 3.50.

IR (ATR):  $\nu$  = 2960, 2929, 2867, 2364, 2343, 1444, 1355, 1303, 806.

Room temperature <sup>1</sup>H NMR in CDCl<sub>3</sub> of complex **7h** gave broad signals due to rotamers resulting from restricted rotation of the N-2,6-diisopropylphenyl bonds. Therefore high temperature NMR was required to obtain free rotation.

<sup>1</sup>H NMR (toluene-d<sub>8</sub>, 500 MHz, 100 °C)  $\delta$ : 1.08 (12 H, d, 6.76 Hz), 1.23-1.30 (2 H, m), 1.31-1.38 (4 H, m), 1.46 (12 H, d, *J* = 6.76), 1.46-1.54 (2 H, m), 1.59-1.67 (2 H, m), 1.68-1.76 (2 H, m), 2.11-2.18 (4 H, brs), 3.11-3.18 (2 H, m), 3.28 (4 H, brs), 4.53-4.60 (2 H, m), 7.22 (4 H, d, *J* = 8.0 Hz), 7.30 (2 H, t, *J* = 8.0 Hz).

<sup>13</sup>C NMR (toluene-d<sub>8</sub>, 125 MHz)  $\delta$ : 22.7, 23.1, 25.5, 26.0, 29.1, 29.5, 34.5, 50.6, 83.0, 124.9, 130.2, 131.4, 135.3, 148.2, 185.1.

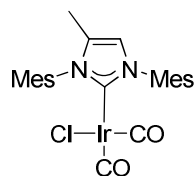
ESI-MS: for C<sub>39</sub>H<sub>54</sub>IrN<sub>2</sub><sup>+</sup> calcd: 743.3911, found: 743.3904 [M-Cl]<sup>+</sup>, for C<sub>39</sub>H<sub>54</sub>ClIrN<sub>2</sub>Na<sup>+</sup> calcd: 801.3497, found: 801.3477 [M+Na]<sup>+</sup>.

## 4. General Procedure C for the Formation of [(NHC)Ir(CO)<sub>2</sub>Cl] complexes

### 8a-h

According to a literature procedure,<sup>1</sup> a solution of [(NHC)Ir(COD)Cl] complex (**7**, 1 eq.) in CH<sub>2</sub>Cl<sub>2</sub> was cooled in an ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. The colour changed from bright yellow to pale yellow. The solvent was evaporated, *n*-pentane was added and the collected precipitate was washed with *n*-pentane (3 × 1 mL). Drying in vacuo afforded the product **8** as a pale yellow solid.

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8a**



According to the general procedure C, solution of **7a** (50 mg, 0.076 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4.5 mL) was cooled in ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was washed with *n*-pentane (3 × 1 mL). Drying in vacuo afforded 42 mg (0.07 mmol, 91 %) of **8a** as pale yellow solid.

Elemental analysis: for C<sub>24</sub>H<sub>26</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 47.87, H 4.35, N 4.65; found: C 48.05, H 4.09, N 4.53.

IR (ATR):  $\nu$  = 2922, 2860, 2050, 1969, 1610, 1485, 1399, 1378, 1337, 1223, 1200, 1036, 852.

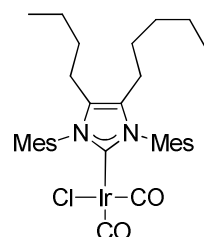
IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  = 2064.4, 1978.0.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 1.95 (3 H, s), 2.16 (6 H, s), 2.22 (6 H, s), 2.35 (3 H, s), 2.37 (3 H, s), 6.84 (1 H, brs), 6.99 (2 H, s), 7.02 (2 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 9.8, 18.5, 18.6, 21.3, 21.4, 120.7, 129.3, 129.5, 131.5, 132.8, 135.1, 135.3, 135.5, 139.3, 139.6, 168.8, 175.3, 180.3.

ESI-MS: for C<sub>24</sub>H<sub>26</sub>IrN<sub>2</sub>O<sub>2</sub><sup>+</sup> calcd: 567.1619, found: 567.1625 [M-Cl]<sup>+</sup>, for C<sub>24</sub>H<sub>26</sub>ClIrN<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> calcd: 625.1197, found: 625.1207 [M+Na]<sup>+</sup>.

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8c**



According to the general procedure C, solution of **7c** (50 mg, 0.084 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was cooled in ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure. The residue was very well soluble in *n*-pentane. Complex **8c** was obtained after three times repeated lyophilisation from benzene as yellow powder (42 mg, 0.058 mmol, 89 %).

Elemental analysis: for C<sub>32</sub>H<sub>42</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 53.80, H 5.93, N 3.92; found: C 53.45, H 5.73, N 3.76.

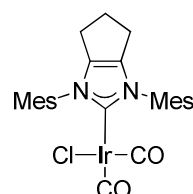
IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> = 2062.2, 1976.1.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 0.80 (6 H, t, *J* = 6.9 Hz), 1.10-1.30 (10 H, m), 2.15 (12 H, s), 2.23-2.31 (4 H, m), 2.36 (6 H, s), 6.99 (4 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 13.6, 13.8, 18.7, 18.7, 21.2, 22.1, 22.2, 23.4, 23.6, 28.1, 30.6, 31.2, 129.3, 131.4, 131.5, 133.2, 135.4, 139.0, 168.6, 173.3, 180.3.

ESI-MS: for C<sub>32</sub>H<sub>42</sub>IrN<sub>2</sub>O<sub>2</sub><sup>+</sup> calcd: 679.2876, found: 679.2872 [M-Cl]<sup>+</sup>, for C<sub>32</sub>H<sub>42</sub>ClIrN<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> calcd: 737.2462, found: 737.2449 [M+Na]<sup>+</sup>.

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8d**



According to the general procedure C, a solution of **7d** (59 mg, 0.087 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was cooled in ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was washed with



*n*-pentane (3 × 1 mL). Drying in vacuo afforded 44 mg (0.07 mmol, 80 %) of **8d** as a pale yellow solid.

Elemental analysis: for C<sub>26</sub>H<sub>30</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 49.55, H 4.80, N 4.45; found: C 49.78, H 4.34, N 4.30.

IR (ATR):  $\nu$  = 2946, 2865, 2055, 1969, 1484, 1364, 1071, 1037, 857.

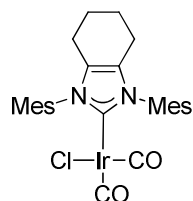
IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  = 2063.2, 1977.3.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.22 (12 H, s), 2.35 (6 H, s), 2.50-2.65 (6 H, m), 6.98 (4 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 18.5, 21.2, 23.7, 28.2, 129.2, 133.7, 135.0, 138.9, 139.1, 168.6, 180.2, 180.4.

ESI-MS: for C<sub>26</sub>H<sub>28</sub>IrN<sub>2</sub>O<sub>2</sub><sup>+</sup> calcd: 593.1780, found: 593.1776 [M-Cl]<sup>+</sup>, for C<sub>26</sub>H<sub>28</sub>ClIrN<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> calcd: 651.1366, found: 651.1353 [M+Na]<sup>+</sup>.

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8e**



According to the general procedure C, solution of **7e** (55 mg, 0.08 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was cooled ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was washed with *n*-pentane (3 × 1 mL). Drying in vacuo afforded 44 mg (0.068 mmol, 85 %) of **8e** as yellow solid.

Elemental analysis: for C<sub>27</sub>H<sub>30</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 50.50, H 4.71, N 4.36; found: C 50.44, H 4.82, N 4.19.

IR (ATR):  $\nu$  = 2948, 2924, 2854, 2055, 1963, 1484, 1399, 1377, 1107, 1034, 857.

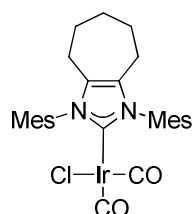
IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  = 2062.9, 1976.7.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.80 (4 H, br s), 2.16 (16 H, s), 2.35 (6 H, s), 6.99 (4 H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 18.4, 20.6, 21.2, 22.1, 129.2, 129.9, 132.8, 135.3, 139.1, 168.8, 172.9, 180.5.

ESI-MS: for  $C_{27}H_{30}IrN_2O_2^+$  calcd: 607.1937, found: 607.1932  $[M-Cl]^+$ , for  $C_{27}H_{30}ClIrN_2O_2Na^+$  calcd: 665.1523, found: 665.1510  $[M+Na]^+$ .

### Preparation of $[(NHC)Ir(CO)_2Cl]$ complex **8f**



According to the general procedure C, solution of **7f** (60 mg, 0.084 mmol) in dry  $CH_2Cl_2$  (4 mL) was cooled in ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was washed with *n*-pentane ( $3 \times 1$  mL). The complex precipitated as a yellow solid which was twice lyophilised from benzene to give 38 mg (0.058 mmol, 69 %) of **8f**.

Elemental analysis: for  $C_{28}H_{32}ClIrN_2O_2$  calcd: C 51.25, H 4.92, N 4.27; found: C 51.74, H 4.74, N 4.01.

IR (ATR):  $\nu = 2925, 2855, 2054, 1965, 1484, 1383, 1215, 1034, 856$ .

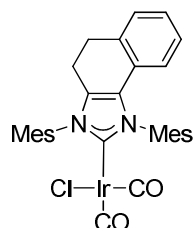
IR ( $CH_2Cl_2$ ):  $\nu_{CO} = 2062.2, 1975.9$ .

$^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 1.57-1.85 (6 H, m), 2.14 (12 H, s), 2.25-2.33 (4 H, m), 2.35 (6 H, s), 6.99 (4 H, s).

$^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 18.4, 21.2, 24.6, 27.1, 30.6, 129.2, 132.7, 133.1, 135.7, 139.1, 168.9, 171.5, 180.3.

ESI-MS: for  $C_{28}H_{32}IrN_2O_2^+$  calcd: 621.2093, found: 621.2089  $[M-Cl]^+$ , for  $C_{28}H_{32}ClIrN_2O_2Na^+$  calcd: 679.1679, found: 679.1666  $[M+Na]^+$ .

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8g**



According to the general procedure C, solution of **7g** (49 mg, 0.07 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was cooled ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was washed with *n*-pentane (3 × 1 mL). Drying in vacuo afforded 39 mg (0.056 mmol, 80 %) of **8g** as pale yellow solid.

Elemental analysis: for C<sub>31</sub>H<sub>30</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 53.94, H 4.38, N 4.06; found: C 54.10, H 4.30, N 3.85.

IR (ATR):  $\nu$  = 2919, 2052, 1965, 1487, 1375, 1339, 1014, 856.

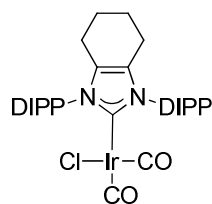
IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  = 2064.2, 1978.4.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 2.18 (6 H, s), 2.21 (6 H, s), 2.37 (3 H, s), 2.42 (3 H, s), 2.52 (2 H, dd,  $J$  = 7.8, 7.8 Hz), 3.03 (2 H, dd,  $J$  = 7.8, 7.8 Hz), 6.32 (1 H, d,  $J$  = 7.8 Hz), 6.96 (1 H, dd,  $J$  = 7.5, 7.5 Hz), 7.02 (2 H, s), 7.05 (2 H, s), 7.11 (1 H, ddd,  $J$  = 0.9, 7.5, 7.5 Hz), 7.21 (1 H, d,  $J$  = 6.9 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 18.5, 18.6, 19.4, 21.2, 21.4, 29.5, 119.9, 126.5, 127.4, 128.6, 129.4, 129.6, 132.0, 133.9, 134.2, 135.4, 135.5, 139.5, 139.7, 168.6, 175.4, 180.2.

ESI-MS: for C<sub>31</sub>H<sub>30</sub>IrN<sub>2</sub>O<sub>2</sub><sup>+</sup> calcd: 655.1937, found: 655.1932 [M-Cl]<sup>+</sup>, for C<sub>31</sub>H<sub>30</sub>ClIrN<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> calcd: 713.1523, found: 713.1510 [M+Na]<sup>+</sup>.

### Preparation of [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8h**



According to the general procedure C, solution of **7h** (62 mg, 0.08 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4.5 mL) was cooled ice-water bath and exposed to an atmosphere of CO (balloon) for 1 h.

Then the solvent was evaporated under reduced pressure, and the residue was washed with *n*-pentane (3 × 1 mL). Drying in vacuo afforded 54 mg (0.074 mmol, 93 %) of **8h** as pale yellow solid.

Elemental analysis: for C<sub>33</sub>H<sub>42</sub>ClIrN<sub>2</sub>O<sub>2</sub> calcd: C 54.57, H 5.83, N 3.86; found: C 54.09, H 5.39, N 3.69.

IR (ATR):  $\nu$  = 2964, 2931, 2868, 2054, 1970, 1456, 1370, 805, 773, 619.

IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  = 2064.7, 1978.3.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 1.14 (12 H, d,  $J$  = 6.8 Hz), 1.38 (12 H, d,  $J$  = 6.8 Hz), 1.75 (4 H, m), 2.24 (4 H, m), 2.89 (4 H, sep,  $J$  = 6.8), 7.32 (4 H, d,  $J$  = 7.7 Hz), 7.49 (2 H, t,  $J$  = 7.7 Hz)

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 21.9, 22.2, 24.7, 25.4, 28.6, 124.6, 130.4, 131.7, 132.9, 146.4, 169.3, 176.1, 179.9.

ESI-MS: for C<sub>33</sub>H<sub>42</sub>IrN<sub>2</sub>O<sub>2</sub><sup>+</sup> calcd: 691.2872, found: 691.2882 [M-Cl]<sup>+</sup>, for C<sub>33</sub>H<sub>42</sub>ClIrN<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> calcd: 749.2456, found: 749.2456 [M+Na]<sup>+</sup>.

## 5. General Procedure D for the Formation of $\gamma$ -butyrolactones 11a+11b

According to a literature procedure,<sup>2</sup> *para*-chlorobenzaldehyde (**11**) (141 mg, 1.0 mmol, 1 eq.) and NHC-HOTf (**6a-h**) or IMes-HCl (**6i**) (0.1 mmol, 10 mol%) were weighed in the glovebox into an oven dried (140 °C) crimp vial under an argon atmosphere and sealed. Outside the glovebox THF (2.5 mL), *trans*-cinnamaldehyde (**10**) (126  $\mu$ L, 1.0 mmol, 1 eq.) and DBU (15  $\mu$ L, 0.1 mmol, 10 mol%) were added via syringe and the reaction mixture was stirred at room temperature for 16 h. After a reaction time of 16 h mesitylene was added as internal standard. A sample of the well mixed reaction mixture was then passed through SiO<sub>2</sub> ( $\varnothing$  = 0.5 cm, high = 1 cm, ethyl acetate) to quench the reaction and remove the NHC-HX salt. The eluent was analysed on a calibrated GC.

**Table 1.** Yields and Diastereomeric ratio of 11a+11b catalyzed by **6a-i**, IMes·HCl and IPr·HCl

entry	imidazolium salts employed as catalysts	<i>cis</i> -lactone average P/S <sup>a</sup>	<i>trans</i> -lactone average P/S <sup>a</sup>	ratio <b>11a/11b</b> [%] <sup>b</sup>	yield of <b>11a+11b</b> [%] <sup>b</sup>
1	<b>6a</b>	0,82622939	0,16236026	84:16	49
2	<b>6b</b>	0,8923186	0,16737521	84:16	52
3	<b>6c</b>	0,71474334	0,1747639	80:20	44
4	<b>6d</b>	1,13502645	0,23229675	83:17	68
5	<b>6e</b>	0,96368937	0,1942418	83:17	57
6	<b>6f</b>	0,93896733	0,18951612	83:17	56
7	<b>6g</b>	0,92767301	0,22786183	80:20	57
8	<b>6h</b>	0,6158024	0,92160171	40:60	81
9	IMes·HCl	1,26711259	0,30470637	81:19	78

<sup>a</sup> Product/standard ratio of peak area obtained from GC. Mesitylene was used as internal standard. Each reaction sample was measured three times.

<sup>b</sup> Linear regression ( $y = 0,4884x - 0,0125$ ) was used to calculate the yield of *cis*-lactone.

<sup>c</sup> Linear regression ( $y = 0,5658x + 0,0027$ ) was used to calculate the yield of *trans*-lactone.

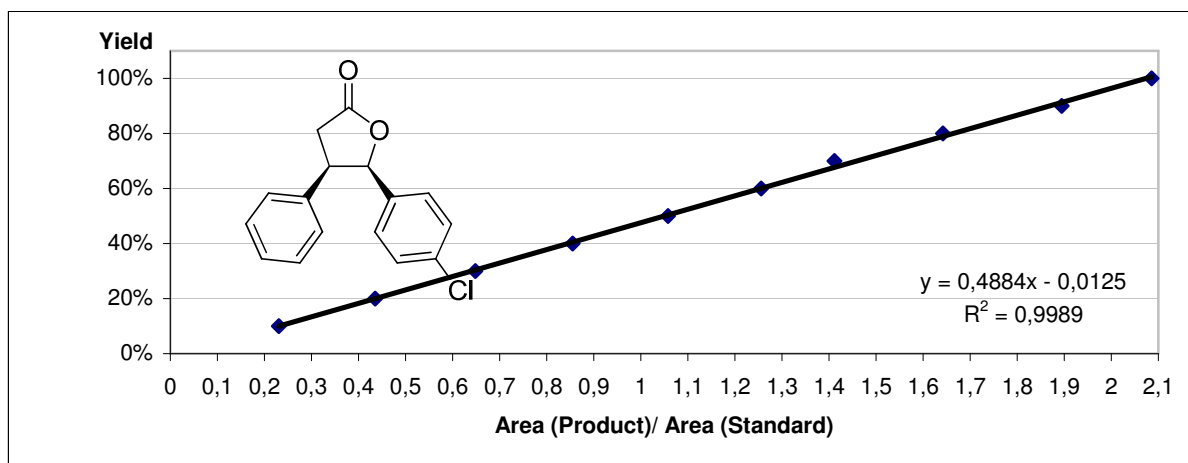
## 6. Calibration for GC yield determination of 11a and 11b

Both diastereomers **11a** and **11b** were prepared according to literature procedure and used for calibration.<sup>2</sup>

**Table 2.** Calibration for *cis*-5-(4-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (**11a**)

	<b>11a</b>	<b>standard<sup>a</sup></b>	<b>P/S<sup>b</sup></b>	<b>average P/S<sup>c</sup></b>
<b>10%</b>	38,78708	169,15924	0,2292933	0,230373206
	38,5386	165,59195	0,23273233	
	37,03159	161,643654	0,22909399	
<b>20%</b>	57,71704	133,56735	0,43211938	0,435549864
	48,17566	110,85153	0,43459626	
	53,58023	121,79153	0,43993396	
<b>30%</b>	73,5526	113,826	0,64618453	0,648070624
	77,54283	117,23074	0,66145475	
	73,69028	115,761	0,63657259	
<b>40%</b>	93,78533	111,62705	0,8401667	0,855068767
	85,34971	99,92532	0,85413497	
	86,00961	98,75893	0,87090464	
<b>50%</b>	91,2021	87,42583	1,04319399	1,05813571
	83,19336	78,5564	1,05902714	
	95,51792	89,08708	1,072186	
<b>60%</b>	82,60355	65,15086	1,26788119	1,256037406
	111,70008	88,51244	1,26197041	
	102,71461	82,95072	1,23826062	
<b>70%</b>	94,34582	67,49354	1,39784963	1,41142912
	98,9976	69,67037	1,42094265	
	86,63808	61,20691	1,41549508	
<b>80%</b>	101,80565	62,20863	1,63651972	1,642123458
	110,00319	64,96514	1,69326488	
	100,94099	63,22303	1,59658577	
<b>90%</b>	114,18093	61,95873	1,84285459	1,894751525
	109,11241	57,9702	1,88221552	
	120,75216	61,63389	1,95918447	
<b>100%</b>	136,52699	65,96317	2,06974574	2,08542688
	138,47121	67,13167	2,06268085	
	140,62866	66,2139	2,12385405	

Areas of peaks are given. <sup>a</sup> Mesitylene was used as internal standard. <sup>b</sup> Product/standard ratio.  
<sup>c</sup> Each calibration sample was measured three times.

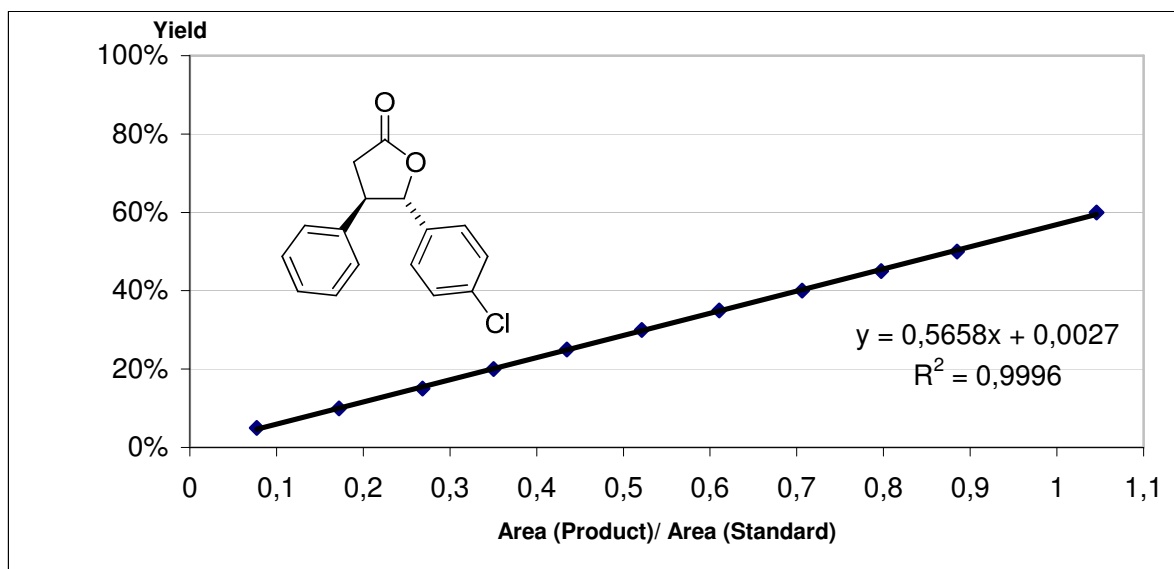


**Table 3** Calibration for *trans*-5-(4-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (**11b**)

	<b>11b</b>	<b>Standard<sup>a</sup></b>	<b>P/S<sup>b</sup></b>	<b>average P/S<sup>c</sup></b>
<b>5%</b>	16	209,32205	0,0760015	0,077184829
	15,50672	201,23259	0,07705869	
	14,36544	183,01254	0,07849429	
<b>10%</b>	28,03439	162,10942	0,17293498	0,171974454
	18,57855	112,18476	0,16560672	
	21,25938	119,85106	0,17738166	
<b>15%</b>	28,24328	103,68209	0,27240269	0,268532809
	26,5931	101,96393	0,2608089	
	28,32006	103,97	0,27238684	
<b>20%</b>	34,01339	96,0491	0,35412503	0,350182681
	34,05926	98,04539	0,34738257	
	36,14874	103,56605	0,34904044	
<b>25%</b>	42,81116	98,23946	0,43578375	0,434753644
	38,43085	88,54968	0,43400326	
	38,83281	89,37892	0,43447392	
<b>30%</b>	43,28186	81,90004	0,52847178	0,521124714
	42,98491	81,70162	0,52612066	
	42,26732	83,07555	0,50878171	
<b>35%</b>	44,83279	72,11813	0,62165769	0,6106916
	44,95681	74,82277	0,60084397	
	49,043	80,45466	0,60957314	
<b>40%</b>	49,18633	73,45325	0,66962769	0,70629981
	52,27581	70,18405	0,74483889	
	52,0802	73,9321	0,70443285	
<b>45%</b>	54,22944	66,0066	0,82157602	0,797319406
	55,18089	69,7985	0,79057415	
	57,15249	73,29046	0,77980804	
<b>50%</b>	52,71395	60,02415	0,87821235	0,884759588
	51,82401	58,40738	0,88728531	
	56,49498	63,56456	0,888781	
<b>60%</b>	57,45392	55,48422	1,035500	1,0457116
	58,33465	55,22586	1,056292	
	57,45549	54,96333	1,045342	

Areas of peaks are given. <sup>a</sup> Mesitylene was used as internal standard. <sup>b</sup> Product/standard ratio.  
<sup>c</sup> Each calibration sample was measured three times.





## 7. Single-crystal X-ray Analysis

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, 276, 307-326), absorption correction SORTAV (R. H. Blessing, *Acta Cryst.* **1995**, A51, 33-37; R. H. Blessing, *J. Appl. Cryst.* **1997**, 30, 421-426), and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, A59, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 2001).

## Single-crystal X-ray analysis of **8f**:

**Table 4.** Crystal data and structure refinement for **8f**.

Empirical formula	C <sub>31</sub> H <sub>35</sub> Cl Ir N <sub>2</sub> O <sub>2</sub>
Formula weight	695.26
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 <sub>1</sub> /c (No.14)
Unit cell dimensions	a = 7.9293(1) Å b = 19.9537(3) Å     β = 94.594(1)°. c = 18.4870(3) Å
Volume	2915.59(7) Å <sup>3</sup>
Z, Calculated density	4, 1.584 Mg/m <sup>3</sup>
Absorption coefficient	4.700 mm <sup>-1</sup>
F(000)	1380
Crystal size	0.40 x 0.20 x 0.10 mm
Theta range for data collection	2.32 to 28.26°.
Limiting indices	-7<=h<=10, -26<=k<=24, -24<=l<=20
Reflections collected / unique	20121 / 7105 [R(int) = 0.029]
Completeness to theta = 28.26	98.3 %
Max. and min. transmission	0.6507 and 0.2550
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7105 / 0 / 337
Goodness-of-fit on F <sup>2</sup>	1.026
Final R indices [I>2σ(I)]	R1 = 0.0263, wR <sup>2</sup> = 0.0627
R indices (all data)	R1 = 0.0357, wR <sup>2</sup> = 0.0672
Largest diff. peak and hole	1.122 and -1.109 eÅ <sup>-3</sup>

**Table 5.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8f**.  
U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Ir(1)	4764(1)	6836(1)	7210(1)	26(1)
Cl(2)	2598(1)	7161(1)	6338(1)	51(1)
C(3)	3143(5)	6836(2)	7904(2)	39(1)
O(4)	2168(4)	6830(2)	8316(2)	64(1)
C(5)	6443(5)	6567(2)	7909(2)	39(1)
O(6)	7378(4)	6413(2)	8314(2)	62(1)
N(7)	7013(3)	7333(1)	6013(1)	25(1)
C(8)	6456(4)	6817(1)	6408(2)	24(1)
N(9)	7217(3)	6270(1)	6154(1)	25(1)
C(10)	8248(3)	6436(2)	5599(2)	27(1)
C(11)	8125(4)	7108(2)	5513(2)	28(1)
C(12)	9296(4)	5922(2)	5257(2)	37(1)
C(13)	9553(5)	6036(2)	4461(2)	45(1)
C(14)	10417(5)	6689(2)	4286(2)	48(1)
C(15)	9302(5)	7308(2)	4297(2)	44(1)
C(16)	9021(4)	7578(2)	5048(2)	36(1)
C(17)	7010(4)	5599(1)	6426(2)	28(1)
C(18)	8264(4)	5327(2)	6903(2)	33(1)
C(19)	8026(5)	4681(2)	7155(2)	42(1)
C(20)	6605(5)	4311(2)	6949(2)	46(1)
C(21)	5384(4)	4600(2)	6468(2)	44(1)
C(22)	5550(4)	5246(2)	6193(2)	33(1)
C(23)	9863(4)	5703(2)	7147(2)	47(1)
C(24)	6380(6)	3607(2)	7236(3)	72(1)
C(25)	4217(4)	5546(2)	5667(2)	49(1)
C(26)	6631(4)	8031(1)	6115(2)	28(1)
C(27)	5488(4)	8355(2)	5622(2)	37(1)
C(28)	5210(5)	9035(2)	5736(2)	50(1)
C(29)	6031(5)	9383(2)	6310(2)	51(1)
C(30)	7158(5)	9043(2)	6780(2)	44(1)
C(31)	7494(4)	8368(2)	6696(2)	33(1)
C(32)	4615(5)	7998(2)	4983(2)	52(1)
C(34)	8773(5)	8018(2)	7211(2)	46(1)
C(33)	5699(7)	10124(2)	6413(3)	85(2)
C(41)	10452(6)	5571(2)	10366(2)	91(2)
C(42)	9926(6)	5601(2)	9668(2)	90(2)
C(43)	9414(9)	5040(3)	9297(3)	97(2)

**Table 6.** Bond lengths [Å] and angles [°] for **8f**.

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Ir(1)-C(5)	1.859(4)
Ir(1)-C(3)	1.887(4)
Ir(1)-C(8)	2.079(3)
Ir(1)-Cl(2)	2.3501(9)
C(3)-O(4)	1.128(4)
C(5)-O(6)	1.055(4)
N(7)-C(8)	1.356(4)
N(7)-C(11)	1.402(4)
N(7)-C(26)	1.440(4)
C(8)-N(9)	1.349(4)
N(9)-C(10)	1.402(3)
N(9)-C(17)	1.443(4)
C(10)-C(11)	1.354(4)
C(10)-C(12)	1.493(4)
C(11)-C(16)	1.490(4)
C(12)-C(13)	1.519(5)
C(13)-C(14)	1.519(5)
C(14)-C(15)	1.519(5)
C(15)-C(16)	1.522(5)
C(17)-C(18)	1.385(4)
C(17)-C(22)	1.394(4)
C(18)-C(19)	1.389(4)
C(18)-C(23)	1.511(5)
C(19)-C(20)	1.375(5)
C(20)-C(21)	1.386(6)
C(20)-C(24)	1.516(5)
C(21)-C(22)	1.395(5)
C(22)-C(25)	1.503(5)
C(26)-C(27)	1.393(4)
C(26)-C(31)	1.399(4)
C(27)-C(28)	1.392(5)
C(27)-C(32)	1.500(5)
C(28)-C(29)	1.387(6)
C(29)-C(30)	1.374(6)
C(29)-C(33)	1.516(5)
C(30)-C(31)	1.383(5)
C(31)-C(34)	1.506(5)
C(41)-C(42)	1.3258
C(41)-C(43)#1	1.369(7)
C(42)-C(43)	1.358(7)
C(43)-C(41)#1	1.369(7)
C(5)-Ir(1)-C(3)	90.94(15)
C(5)-Ir(1)-C(8)	91.37(13)
C(3)-Ir(1)-C(8)	177.10(13)
C(5)-Ir(1)-Cl(2)	178.73(10)
C(3)-Ir(1)-Cl(2)	88.03(12)
C(8)-Ir(1)-Cl(2)	89.64(8)
O(4)-C(3)-Ir(1)	179.3(3)
O(6)-C(5)-Ir(1)	178.9(3)
C(8)-N(7)-C(11)	111.2(2)
C(8)-N(7)-C(26)	125.6(2)
C(11)-N(7)-C(26)	123.1(2)
N(9)-C(8)-N(7)	104.7(2)
N(9)-C(8)-Ir(1)	126.5(2)
N(7)-C(8)-Ir(1)	128.8(2)
C(8)-N(9)-C(10)	111.5(2)
C(8)-N(9)-C(17)	124.3(2)
C(10)-N(9)-C(17)	124.3(2)
C(11)-C(10)-N(9)	106.3(2)
C(11)-C(10)-C(12)	132.0(3)
N(9)-C(10)-C(12)	121.7(3)
C(10)-C(11)-N(7)	106.4(2)
C(10)-C(11)-C(16)	131.2(3)
N(7)-C(11)-C(16)	122.2(3)
C(10)-C(12)-C(13)	115.5(3)

**Table 6.** Bond lengths [Å] and angles [°] for **8f** (continued).

C(12)–C(13)–C(14)	115.6(3)
C(15)–C(14)–C(13)	114.9(3)
C(14)–C(15)–C(16)	115.3(3)
C(11)–C(16)–C(15)	114.5(3)
C(18)–C(17)–C(22)	122.3(3)
C(18)–C(17)–N(9)	119.2(3)
C(22)–C(17)–N(9)	118.5(3)
C(17)–C(18)–C(19)	117.9(3)
C(17)–C(18)–C(23)	122.6(3)
C(19)–C(18)–C(23)	119.6(3)
C(20)–C(19)–C(18)	122.4(3)
C(19)–C(20)–C(21)	117.9(3)
C(19)–C(20)–C(24)	121.2(4)
C(21)–C(20)–C(24)	120.9(4)
C(20)–C(21)–C(22)	122.5(3)
C(17)–C(22)–C(21)	117.1(3)
C(17)–C(22)–C(25)	121.4(3)
C(21)–C(22)–C(25)	121.5(3)
C(27)–C(26)–C(31)	122.1(3)
C(27)–C(26)–N(7)	119.7(3)
C(31)–C(26)–N(7)	118.1(3)
C(28)–C(27)–C(26)	117.1(3)
C(28)–C(27)–C(32)	120.9(3)
C(26)–C(27)–C(32)	122.0(3)
C(29)–C(28)–C(27)	122.3(3)
C(30)–C(29)–C(28)	118.5(3)
C(30)–C(29)–C(33)	120.9(4)
C(28)–C(29)–C(33)	120.6(4)
C(29)–C(30)–C(31)	122.1(3)
C(30)–C(31)–C(26)	117.9(3)
C(30)–C(31)–C(34)	120.4(3)
C(26)–C(31)–C(34)	121.7(3)
C(42)–C(41)–C(43) #1	119.4(3)
C(41)–C(42)–C(43)	120.8(3)
C(42)–C(43)–C(41) #1	119.6(4)

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Symmetry transformations used to generate equivalent atoms:  
#1 -x+2,-y+1,-z+2

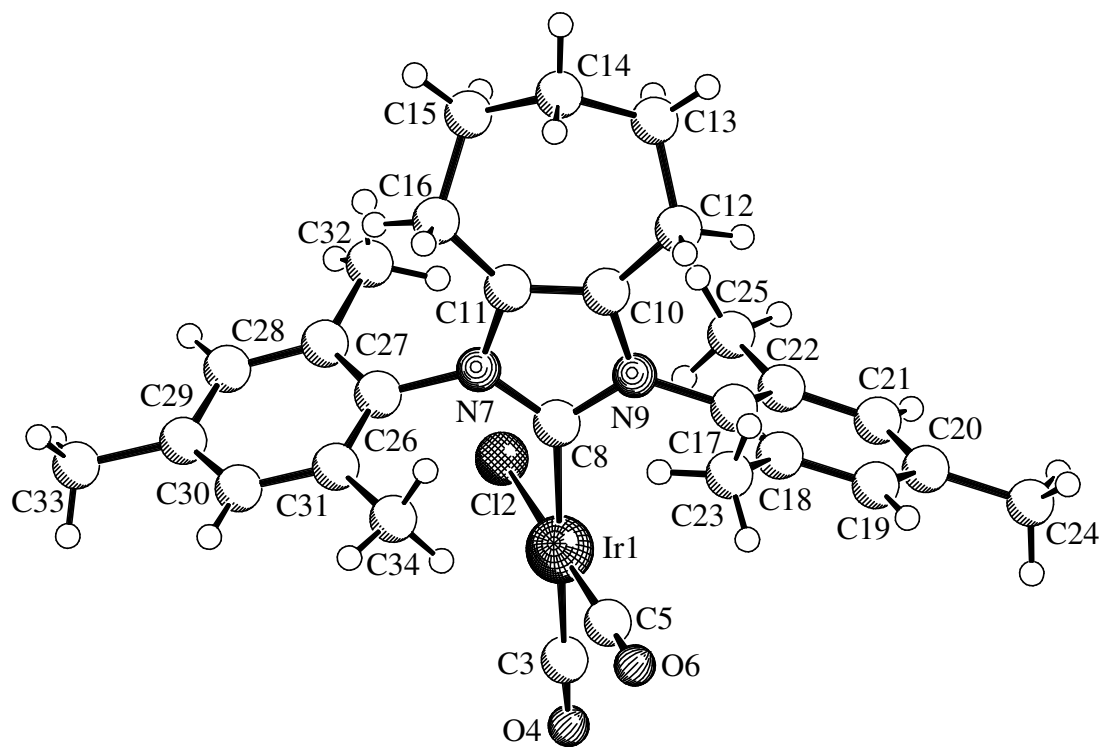
**Table 7.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8f**.  
 The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ir(1)	29(1)	22(1)	27(1)	-2(1)	8(1)	0(1)
Cl(2)	39(1)	63(1)	50(1)	1(1)	4(1)	11(1)
C(3)	43(2)	38(2)	38(2)	-6(1)	14(2)	0(1)
O(4)	61(2)	82(2)	53(2)	-9(1)	35(2)	0(1)
C(5)	49(2)	28(2)	43(2)	3(2)	17(2)	-5(2)
O(6)	62(2)	66(2)	56(2)	4(2)	-6(1)	-6(2)
N(7)	29(1)	20(1)	26(1)	2(1)	7(1)	2(1)
C(8)	24(1)	23(1)	26(1)	1(1)	3(1)	-1(1)
N(9)	27(1)	18(1)	30(1)	1(1)	6(1)	2(1)
C(10)	26(1)	27(2)	30(1)	0(1)	8(1)	0(1)
C(11)	29(1)	27(2)	28(1)	2(1)	6(1)	2(1)
C(12)	41(2)	28(2)	44(2)	-1(1)	15(1)	9(1)
C(13)	49(2)	43(2)	46(2)	-10(2)	18(2)	4(2)
C(14)	50(2)	53(2)	44(2)	3(2)	24(2)	7(2)
C(15)	51(2)	47(2)	37(2)	10(2)	19(2)	3(2)
C(16)	37(2)	32(2)	41(2)	7(1)	14(1)	-1(1)
C(17)	31(2)	21(1)	35(2)	-1(1)	10(1)	1(1)
C(18)	35(2)	27(2)	39(2)	3(1)	8(1)	3(1)
C(19)	45(2)	30(2)	51(2)	13(2)	16(2)	13(2)
C(20)	47(2)	24(2)	70(2)	4(2)	34(2)	3(2)
C(21)	39(2)	28(2)	68(2)	-7(2)	23(2)	-9(1)
C(22)	30(2)	26(2)	46(2)	-10(1)	11(1)	-3(1)
C(23)	37(2)	47(2)	54(2)	11(2)	-5(2)	-1(2)
C(24)	72(3)	29(2)	122(4)	21(2)	49(3)	4(2)
C(25)	36(2)	44(2)	66(2)	-17(2)	-7(2)	0(2)
C(26)	32(2)	19(1)	34(2)	3(1)	9(1)	1(1)
C(27)	40(2)	37(2)	36(2)	10(1)	6(1)	6(1)
C(28)	54(2)	32(2)	64(2)	18(2)	12(2)	16(2)
C(29)	59(2)	27(2)	70(3)	0(2)	26(2)	5(2)
C(30)	52(2)	27(2)	56(2)	-9(2)	15(2)	-8(2)
C(31)	35(2)	28(2)	38(2)	-2(1)	10(1)	-6(1)
C(32)	58(2)	58(2)	39(2)	9(2)	-6(2)	9(2)
C(34)	43(2)	49(2)	46(2)	-3(2)	-6(2)	-8(2)
C(33)	109(4)	21(2)	128(5)	-3(2)	31(3)	11(2)
C(41)	125(5)	69(4)	78(4)	-11(3)	-3(3)	17(3)
C(42)	136(5)	63(4)	73(4)	20(3)	19(3)	24(3)
C(43)	144(6)	91(4)	53(3)	3(3)	-6(3)	40(4)

**Table 8.** Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8f**.

	x	y	z	U(eq)
H(12A)	8762	5483	5305	44
H(12B)	10409	5905	5528	44
H(13A)	8445	6022	4185	54
H(13B)	10226	5664	4291	54
H(14A)	11398	6753	4637	58
H(14B)	10839	6650	3804	58
H(15A)	8198	7201	4047	53
H(15B)	9811	7663	4020	53
H(16A)	10123	7689	5297	43
H(16B)	8366	7994	4993	43
H(19)	8866	4490	7479	50
H(21)	4409	4352	6322	53
H(23A)	10776	5555	6867	70
H(23B)	10157	5616	7658	70
H(23C)	9681	6180	7074	70
H(24A)	7329	3331	7119	108
H(24B)	5339	3417	7013	108
H(24C)	6330	3622	7758	108
H(25A)	3602	5888	5911	74
H(25B)	3439	5199	5486	74
H(25C)	4751	5746	5265	74
H(28)	4438	9265	5413	60
H(30)	7719	9276	7170	53
H(32A)	5319	8014	4578	78
H(32B)	3540	8214	4847	78
H(32C)	4420	7534	5112	78
H(34A)	9362	8346	7525	70
H(34B)	9582	7783	6936	70
H(34C)	8200	7699	7502	70
H(33A)	6610	10382	6230	127
H(33B)	5638	10218	6925	127
H(33C)	4636	10245	6149	127
H(41)	10730	5965	10627	110
H(42)	9907	6016	9427	108
H(43)	8970	5071	8811	116





Single-crystal X-ray structure of **8f**

## Single-crystal X-ray analysis of **8h**:

**Table 9.** Crystal data and structure refinement for **8h**.

Empirical formula	C <sub>33</sub> H <sub>42</sub> Cl Ir N <sub>2</sub> O <sub>2</sub>
Formula weight	726.34
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Pnma (No. 62)
Unit cell dimensions	a = 19.4679(3) Å b = 17.5361(2) Å c = 9.5159(1) Å
Volume	3248.64(7) Å <sup>3</sup>
Z, Calculated density	4, 1.485 Mg/m <sup>3</sup>
Absorption coefficient	4.222 mm <sup>-1</sup>
F(000)	1456
Crystal size	0.20 x 0.20 x 0.05 mm
Theta range for data collection	2.09 to 28.28°.
Limiting indices	-25<=h<=18, -17<=k<=23, -9<=l<=12
Reflections collected / unique	22070 / 4104 [R(int) = 0.043]
Completeness to theta = 28.28	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8167 and 0.4856
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4104 / 0 / 210
Goodness-of-fit on F <sup>2</sup>	1.030
Final R indices [I>2σ(I)]	R1 = 0.0334, wR <sup>2</sup> = 0.0708
R indices (all data)	R1 = 0.0469, wR <sup>2</sup> = 0.0774
Largest diff. peak and hole	1.878 and -2.281 eÅ <sup>-3</sup>

**Table 10.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**.  
U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Ir(1)	9624(1)	2500	1051(1)	34(1)
Cl(2)	10516(1)	2500	-558(2)	55(1)
C(3)	10292(4)	2500	2493(8)	69(2)
O(4)	10688(4)	2500	3343(7)	118(3)
C(5)	8932(4)	2500	2348(6)	50(2)
O(6)	8514(3)	2500	3183(5)	76(2)
N(7)	8633(2)	1889(2)	-1235(3)	27(1)
C(8)	8922(2)	2500	-619(5)	25(1)
C(9)	8145(2)	2118(2)	-2224(3)	29(1)
C(10A)	7622(14)	1676(15)	-2970(30)	32(4)
C(11A)	7333(10)	2146(10)	-4142(18)	41(3)
C(10B)	7754(15)	1581(17)	-3210(30)	33(4)
C(11B)	7128(10)	2064(10)	-3700(30)	53(5)
C(12)	8810(2)	1094(2)	-1041(4)	31(1)
C(13)	9298(2)	776(2)	-1933(4)	39(1)
C(14)	9427(3)	-8(2)	-1789(5)	55(1)
C(15)	9074(3)	-438(2)	-818(5)	64(1)
C(16)	8598(3)	-109(2)	28(5)	57(1)
C(17)	8447(2)	668(2)	-43(4)	40(1)
C(18)	9682(2)	1224(2)	-3060(5)	47(1)
C(19)	9376(3)	1076(4)	-4513(5)	88(2)
C(20)	10454(3)	1064(3)	-3081(6)	68(1)
C(21)	7914(3)	1006(3)	931(4)	51(1)
C(22)	8047(3)	782(3)	2470(5)	78(2)
C(23)	7179(3)	776(4)	524(7)	86(2)

**Table 11.** Bond lengths [Å] and angles [°] for **8h**.

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Ir(1)-C(5)	1.828(7)
Ir(1)-C(3)	1.890(7)
Ir(1)-C(8)	2.096(5)
Ir(1)-Cl(2)	2.3147(17)
C(3)-O(4)	1.119(8)
C(5)-O(6)	1.138(8)
N(7)-C(8)	1.346(4)
N(7)-C(9)	1.396(4)
N(7)-C(12)	1.448(4)
C(8)-N(7)#1	1.346(4)
C(9)-C(9)#1	1.339(6)
C(9)-C(10A)	1.46(3)
C(9)-C(10B)	1.54(3)
C(10A)-C(11A)	1.50(4)
C(10A)-H(10A)	0.9800
C(10A)-H(10B)	0.9800
C(11A)-C(11A)#1	1.24(4)
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(10B)-C(11B)	1.55(3)
C(10B)-H(10C)	0.9800
C(10B)-H(10D)	0.9800
C(11B)-C(11B)#1	1.53(3)
C(11B)-H(11C)	0.9800
C(11B)-H(11D)	0.9800
C(12)-C(13)	1.391(5)
C(12)-C(17)	1.399(5)
C(13)-C(14)	1.404(5)
C(13)-C(18)	1.526(6)
C(14)-C(15)	1.375(7)
C(14)-H(14)	0.9400
C(15)-C(16)	1.357(7)
C(15)-H(15)	0.9400
C(16)-C(17)	1.396(5)
C(16)-H(16)	0.9400
C(17)-C(21)	1.513(6)
C(18)-C(19)	1.527(7)
C(18)-C(20)	1.529(6)
C(18)-H(18)	0.9900
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(20)-H(20C)	0.9700
C(21)-C(23)	1.537(7)
C(21)-C(22)	1.538(6)
C(21)-H(21)	0.9900
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(22)-H(22C)	0.9700
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(23)-H(23C)	0.9700
C(5)-Ir(1)-C(3)	90.9(3)
C(5)-Ir(1)-C(8)	91.8(2)
C(3)-Ir(1)-C(8)	177.3(3)
C(5)-Ir(1)-Cl(2)	178.90(19)
C(3)-Ir(1)-Cl(2)	88.0(3)
C(8)-Ir(1)-Cl(2)	89.31(14)
O(4)-C(3)-Ir(1)	179.8(9)
O(6)-C(5)-Ir(1)	178.2(6)
C(8)-N(7)-C(9)	110.4(3)
C(8)-N(7)-C(12)	127.8(3)
C(9)-N(7)-C(12)	121.7(3)

**Table 11.** Bond lengths [Å] and angles [°] for **8h**. (Continued)

N(7)-C(8)-N(7)#1	105.7(4)
N(7)-C(8)-Ir(1)	127.10(19)
N(7)#1-C(8)-Ir(1)	127.10(19)
C(9)#1-C(9)-N(7)	106.76(17)
C(9)#1-C(9)-C(10A)	122.0(11)
N(7)-C(9)-C(10A)	130.3(12)
C(9)#1-C(9)-C(10B)	127.9(12)
N(7)-C(9)-C(10B)	125.1(12)
C(10A)-C(9)-C(10B)	14.5(12)
C(9)-C(10A)-C(11A)	109(2)
C(9)-C(10A)-H(10A)	109.8
C(11A)-C(10A)-H(10A)	109.8
C(9)-C(10A)-H(10B)	109.8
C(11A)-C(10A)-H(10B)	109.8
H(10A)-C(10A)-H(10B)	108.2
C(11A)#1-C(11A)-C(10A)	123.3(12)
C(11A)#1-C(11A)-H(11A)	106.5
C(10A)-C(11A)-H(11A)	106.5
C(11A)#1-C(11A)-H(11B)	106.5
C(10A)-C(11A)-H(11B)	106.5
H(11A)-C(11A)-H(11B)	106.5
C(9)-C(10B)-C(11B)	103.6(18)
C(9)-C(10B)-H(10C)	111.0
C(11B)-C(10B)-H(10C)	111.0
C(9)-C(10B)-H(10D)	111.0
C(11B)-C(10B)-H(10D)	111.0
H(10C)-C(10B)-H(10D)	109.0
C(11B)#1-C(11B)-C(10B)	123.0(13)
C(11B)#1-C(11B)-H(11C)	106.6
C(10B)-C(11B)-H(11C)	106.6
C(11B)#1-C(11B)-H(11D)	106.6
C(10B)-C(11B)-H(11D)	106.6
H(11C)-C(11B)-H(11D)	106.5
C(13)-C(12)-C(17)	123.1(3)
C(13)-C(12)-N(7)	118.1(3)
C(17)-C(12)-N(7)	118.6(3)
C(12)-C(13)-C(14)	117.1(4)
C(12)-C(13)-C(18)	123.8(3)
C(14)-C(13)-C(18)	119.1(4)
C(15)-C(14)-C(13)	120.9(4)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(16)-C(15)-C(14)	120.4(4)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	122.0(4)
C(15)-C(16)-H(16)	119.0
C(17)-C(16)-H(16)	119.0
C(16)-C(17)-C(12)	116.5(4)
C(16)-C(17)-C(21)	119.8(4)
C(12)-C(17)-C(21)	123.6(3)
C(19)-C(18)-C(13)	111.0(4)
C(19)-C(18)-C(20)	109.9(4)
C(13)-C(18)-C(20)	113.3(4)
C(19)-C(18)-H(18)	107.5
C(13)-C(18)-H(18)	107.5
C(20)-C(18)-H(18)	107.5
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

**Table 11.** Bond lengths [Å] and angles [°] for **8h**. (Continued)

C(17)–C(21)–C(23)	112.4(4)
C(17)–C(21)–C(22)	111.6(4)
C(23)–C(21)–C(22)	109.3(4)
C(17)–C(21)–H(21)	107.8
C(23)–C(21)–H(21)	107.8
C(22)–C(21)–H(21)	107.8
C(21)–C(22)–H(22A)	109.5
C(21)–C(22)–H(22B)	109.5
H(22A)–C(22)–H(22B)	109.5
C(21)–C(22)–H(22C)	109.5
H(22A)–C(22)–H(22C)	109.5
H(22B)–C(22)–H(22C)	109.5
C(21)–C(23)–H(23A)	109.5
C(21)–C(23)–H(23B)	109.5
H(23A)–C(23)–H(23B)	109.5
C(21)–C(23)–H(23C)	109.5
H(23A)–C(23)–H(23C)	109.5
H(23B)–C(23)–H(23C)	109.5

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Symmetry transformations used to generate equivalent atoms:  
#1  $x, -y+1/2, z$

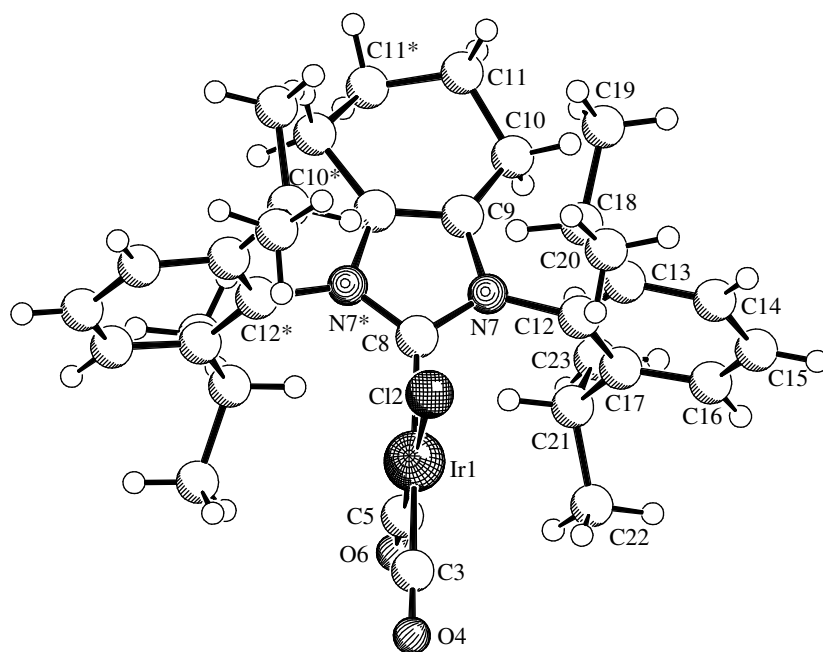
**Table 12.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**.  
 The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ir(1)	36(1)	30(1)	36(1)	0	-10(1)	0
Cl(2)	33(1)	58(1)	76(1)	0	5(1)	0
C(3)	69(5)	77(5)	61(4)	0	-25(4)	0
O(4)	97(5)	165(7)	92(5)	0	-67(4)	0
C(5)	64(4)	50(4)	36(3)	0	-11(3)	0
O(6)	85(4)	97(4)	46(3)	0	23(3)	0
N(7)	32(2)	19(1)	31(2)	0(1)	-8(1)	-1(1)
C(8)	24(2)	23(2)	27(2)	0	-1(2)	0
C(9)	33(2)	22(2)	33(2)	1(1)	-7(1)	-1(1)
C(10A)	34(9)	20(8)	43(8)	-12(6)	-6(5)	2(6)
C(11A)	40(8)	34(6)	50(8)	-6(5)	-20(5)	-3(5)
C(10B)	37(10)	17(6)	46(10)	-13(7)	-12(6)	9(6)
C(11B)	35(8)	29(5)	94(15)	12(7)	-32(7)	-10(5)
C(12)	43(2)	17(1)	34(2)	-1(1)	-12(2)	2(1)
C(13)	51(2)	26(2)	39(2)	-2(2)	-11(2)	6(2)
C(14)	76(3)	31(2)	57(3)	-7(2)	-9(2)	17(2)
C(15)	95(4)	22(2)	74(3)	5(2)	-8(3)	13(2)
C(16)	83(4)	27(2)	61(3)	15(2)	-9(3)	-4(2)
C(17)	52(2)	27(2)	40(2)	4(2)	-10(2)	-4(2)
C(18)	53(3)	40(2)	47(2)	0(2)	3(2)	12(2)
C(19)	92(4)	130(6)	43(3)	17(3)	-8(3)	2(4)
C(20)	60(3)	74(4)	69(3)	-9(3)	6(3)	16(3)
C(21)	66(3)	41(2)	46(2)	5(2)	2(2)	-9(2)
C(22)	120(5)	67(3)	46(3)	11(2)	8(3)	-11(3)
C(23)	64(4)	105(5)	90(4)	-11(4)	0(3)	-15(4)

**Table 13.** Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **8h**.

	x	y	z	U(eq)
H(10A)	7255	1532	-2316	39
H(10B)	7827	1208	-3346	39
H(11A)	7573	1987	-4998	50
H(11B)	6853	1987	-4254	50
H(10C)	7605	1119	-2721	40
H(10D)	8040	1434	-4018	40
H(11C)	7022	1904	-4659	63
H(11D)	6739	1904	-3113	63
H(14)	9758	-242	-2363	66
H(15)	9164	-963	-741	76
H(16)	8362	-414	681	68
H(18)	9620	1773	-2851	56
H(19A)	9390	534	-4712	133
H(19B)	9641	1349	-5215	133
H(19C)	8904	1252	-4533	133
H(20A)	10640	1134	-2144	101
H(20B)	10678	1413	-3725	101
H(20C)	10533	544	-3386	101
H(21)	7947	1568	864	61
H(22A)	7960	241	2591	117
H(22B)	7744	1071	3079	117
H(22C)	8521	892	2709	117
H(23A)	7069	983	-395	129
H(23B)	6858	975	1213	129
H(23C)	7144	224	496	129





SCHAKAL

Single-crystal X-ray structure of **8h**.

## 8. Calculation of the Buried Volume using SambVa (Web Application)<sup>3,4</sup>

The buried volume ( $\%V_{\text{Bur}}$ ; the fraction of the space buried by the NHC ligand of a sphere around the metal) of the NHC-ligands was calculated using the web application SambVca developed by Cavallo et al. for the calculation of the buried volume of any type of ligands. As an input file for this computer program, only the coordinates of the ligand must be supplied. This program positions the putative metal atom at 2.10 Å from the coordinating atom of the ligand; a value of 3.5 Å is taken for the radius of the sphere around this metal atom. For our calculations of the buried volumes, we took the coordinates from the crystal structure analyses of the [(NHC)Ir(CO)<sub>2</sub>Cl] complex **8f** and **8h**.

## Calculation of the Buried Volume of Ligand 1f from complex 8f

### SambVca @ MoLNaC Results page

```
|
|           S A M B V C A
|
|           Buried Volume in Salerno
|
|           http://www.molnac.unisa.it/OM-tools/SambVca
|
|           L. Cavallo et al. email: lcavallo@unisa.it
|
```

#### Molecule from input :

```
Molecule from input :
./temp/752e429f6b2dfd68d8badd2e92c73971.cif
```

```
Number of atoms           :    60
Atom that is coordinated   :     1
Atoms that define the axis :     2
ID of these atoms         :     2   3

Radius of sphere (Angs)   :     3.500
Distance from sphere (Angs) :    2.100
Mesh step (Angs)         :     0.050
H atoms omitted in the V_bur calculation
```

#### Cartesian coordinates from input :

```
Cartesian coordinates from input :
C      -4.17039   13.60224   11.80749
N      -4.67047   14.63205   11.08052
N      -4.81130   12.51037   11.34090
C      -5.71107   12.84180   10.31725
C      -5.62627   14.18349   10.15877
C      -6.59273   11.81578    9.68665
H      -6.16214   10.94061    9.77584
H      -7.43507   11.78266   10.18678
C      -6.91439   12.04365    8.21963
H      -6.07662   12.01612    7.71195
H      -7.47313   11.30177    7.90729
C      -7.62532   13.34703    7.89807
H      -8.35121   13.47473    8.54488
```

H	-8.03131	13.26921	7.00986
C	-6.73954	14.58156	7.91871
H	-5.90120	14.36866	7.45765
H	-7.18419	15.29052	7.40790
C	-6.40556	15.12071	9.30226
H	-7.24250	15.34240	9.76110
H	-5.89433	15.95099	9.20090
C	-4.60694	11.17227	11.84158
C	-5.53067	10.62993	12.72021
C	-5.30458	9.34052	13.18532
H	-5.92270	8.95921	13.78201
C	-4.20836	8.60124	12.80534
C	-3.31141	9.17830	11.91897
H	-2.55992	8.68385	11.64993
C	-3.48370	10.46671	11.41295
C	-6.76236	11.37959	13.17076
H	-7.52781	11.08428	12.65424
H	-6.91986	11.20600	14.11186
H	-6.62890	12.33138	13.03569
C	-3.98745	7.19730	13.33421
H	-4.75727	6.64658	13.11861
H	-3.19503	6.81818	12.92328
H	-3.87051	7.22723	14.29614
C	-2.50467	11.06652	10.44292
H	-1.98089	11.74874	10.89256
H	-1.91457	10.37393	10.10938
H	-2.98762	11.46539	9.70213
C	-4.35247	16.02382	11.26848
C	-3.51922	16.67151	10.35908
C	-3.28183	18.02717	10.57007
H	-2.71751	18.48710	9.97486
C	-3.84783	18.72256	11.62782
C	-4.67187	18.04313	12.49392
H	-5.05896	18.50905	13.21259
C	-4.95075	16.69725	12.33894
C	-2.92153	15.95897	9.18248
H	-3.53973	15.99089	8.43616
H	-2.08927	16.38997	8.93186
H	-2.74781	15.03312	9.42019
C	-5.88864	15.99888	13.28815
H	-6.30918	16.65336	13.86677
H	-6.57084	15.52996	12.78139
H	-5.39120	15.36235	13.82439
C	-3.56933	20.20112	11.81762
H	-4.31879	20.71593	11.48040
H	-3.44515	20.38869	12.76112
H	-2.76554	20.44256	11.33113

### Atoms and radius in the parameter file

Atoms and radius in the parameter file	
C2	1.99
C3	1.99
C	1.99
N2	1.81
N3	1.81
N	1.81
O	1.78
P	2.11
H	1.40

F 1.72

## Coordinates scaled to put the metal at the origin

Coordinates scaled to put the metal at the origin

C	-1.45009	-0.07887	-1.51691
N	-1.95017	0.95094	-2.24388
N	-2.09100	-1.17074	-1.98350
C	-2.99077	-0.83931	-3.00715
C	-2.90597	0.50238	-3.16563
C	-3.87243	-1.86533	-3.63775
H	-3.44184	-2.74050	-3.54856
H	-4.71477	-1.89845	-3.13762
C	-4.19409	-1.63746	-5.10477
H	-3.35632	-1.66499	-5.61245
H	-4.75283	-2.37934	-5.41711
C	-4.90502	-0.33408	-5.42633
H	-5.63091	-0.20638	-4.77952
H	-5.31101	-0.41190	-6.31454
C	-4.01924	0.90045	-5.40569
H	-3.18090	0.68755	-5.86675
H	-4.46389	1.60941	-5.91650
C	-3.68526	1.43960	-4.02214
H	-4.52220	1.66129	-3.56330
H	-3.17403	2.26988	-4.12350
C	-1.88664	-2.50884	-1.48282
C	-2.81037	-3.05118	-0.60419
C	-2.58428	-4.34059	-0.13908
H	-3.20240	-4.72190	0.45761
C	-1.48806	-5.07987	-0.51906
C	-0.59111	-4.50281	-1.40543
H	0.16038	-4.99726	-1.67447
C	-0.76340	-3.21440	-1.91145
C	-4.04206	-2.30152	-0.15364
H	-4.80751	-2.59683	-0.67016
H	-4.19956	-2.47511	0.78746
H	-3.90860	-1.34973	-0.28871
C	-1.26715	-6.48381	0.00981
H	-2.03697	-7.03453	-0.20579
H	-0.47473	-6.86293	-0.40112
H	-1.15021	-6.45388	0.97174
C	0.21563	-2.61459	-2.88148
H	0.73941	-1.93237	-2.43184
H	0.80573	-3.30718	-3.21502
H	-0.26732	-2.21572	-3.62227
C	-1.63217	2.34271	-2.05592
C	-0.79892	2.99040	-2.96532
C	-0.56153	4.34606	-2.75433
H	0.00279	4.80599	-3.34954
C	-1.12753	5.04145	-1.69658
C	-1.95157	4.36202	-0.83048
H	-2.33866	4.82794	-0.11181
C	-2.23045	3.01614	-0.98546
C	-0.20123	2.27786	-4.14192
H	-0.81943	2.30978	-4.88824
H	0.63103	2.70886	-4.39254

H	-0.02751	1.35201	-3.90421
C	-3.16834	2.31777	-0.03625
H	-3.58888	2.97225	0.54237
H	-3.85054	1.84885	-0.54301
H	-2.67090	1.68124	0.49999
C	-0.84903	6.52001	-1.50678
H	-1.59849	7.03482	-1.84400
H	-0.72485	6.70758	-0.56328
H	-0.04524	6.76145	-1.99327
XX	0.00000	0.00000	0.00000

### Results : Volumes in Angs^3

Results : Volumes in Angs^3

N of voxels examined :	1436277
Volume of voxel :	0.125E-03

V Free	V Buried	V Total	V Exact
119.651	59.884	179.535	179.594

%V_Free	%V_Bur	% Tot/Ex
66.645	33.355	99.967

**The %V\_Bur of your molecule is: 33.4**

## Calculation of the Buried Volume of ligand 1h from complex 8h

# SambVca @ MoLNaC

## Results page

```
-----  
|                                     |  
|               S A M B V C A       |  
|                                     |  
|           Buried Volume in Salerno |  
|                                     |  
| http://www.molnac.unisa.it/OM-tools/SambVca |  
|                                     |  
|           L. Cavallo et al. email: lcavallo@unisa.it |  
|                                     |  
|-----|
```

### Molecule from input :

Molecule from input :

./temp/752e429f6b2dfd68d8badd2e92c73971.cif

```
Number of atoms           :    75  
Atom that is coordinated   :     1  
Atoms that define the axis :     2  
ID of these atoms         :     2   3  
  
Radius of sphere (Angs)   :    3.500  
Distance from sphere (Angs) :    2.100  
Mesh step (Angs)         :    0.050  
H atoms omitted in the V_bur calculation
```

### Cartesian coordinates from input :

```
Cartesian coordinates from input :  
C    -17.36926    4.38403   -0.58903  
N    -16.80644    3.31169   -1.17521  
N    -16.80644    5.45636   -1.17521  
C    -15.85660    3.71432   -2.11634  
C    -15.85660    5.05373   -2.11634  
C    -14.83843    2.93905   -2.82622  
H    -14.12396    2.68653   -2.20388  
H    -15.23752    2.11836   -3.18402  
C    -14.83843    5.82900   -2.82622  
H    -14.12396    6.08152   -2.20388  
H    -15.23752    6.64969   -3.18402  
C    -14.27581    3.76325   -3.94149  
H    -14.74304    3.48442   -4.75605  
H    -13.34135    3.48442   -4.04806  
C    -14.27581    5.00480   -3.94149  
H    -14.74304    5.28363   -4.75605
```

H	-13.34135	5.28363	-4.04806
C	-17.15122	1.91775	-0.99061
C	-17.15122	6.85030	-0.99061
C	-18.10125	1.36080	-1.83942
C	-18.10125	7.40725	-1.83942
C	-18.35239	-0.01403	-1.70239
H	-18.99678	-0.42437	-2.24861
C	-18.35239	8.78208	-1.70239
H	-18.99677	9.19242	-2.24861
C	-17.66517	-0.76808	-0.77840
H	-17.84038	-1.68873	-0.70513
C	-17.66517	9.53613	-0.77840
H	-17.84038	10.45678	-0.70513
C	-16.73850	-0.19114	0.02664
H	-16.27906	-0.72599	0.64803
C	-16.73850	8.95919	0.02664
H	-16.27906	9.49405	0.64803
C	-16.44453	1.17141	-0.04092
C	-16.44453	7.59664	-0.04092
C	-18.84882	2.14642	-2.91187
H	-18.72812	3.10915	-2.71298
C	-18.84882	6.62163	-2.91187
H	-18.72812	5.65890	-2.71298
C	-18.25310	1.88688	-4.29453
H	-18.28036	0.93643	-4.48389
H	-18.76900	2.36562	-4.96254
H	-17.33422	2.19552	-4.31356
C	-18.25310	6.88117	-4.29453
H	-18.28036	7.83162	-4.48389
H	-18.76900	6.40243	-4.96254
H	-17.33422	6.57253	-4.31356
C	-20.35174	1.86584	-2.93185
H	-20.71384	1.98859	-2.04021
H	-20.78782	2.47785	-3.54467
H	-20.50554	0.95396	-3.22208
C	-20.35174	6.90221	-2.93185
H	-20.71384	6.77946	-2.04021
H	-20.78782	6.29020	-3.54467
H	-20.50554	7.81409	-3.22208
C	-15.40690	1.76413	0.88593
H	-15.47114	2.74966	0.82217
C	-15.40690	7.00392	0.88593
H	-15.47114	6.01839	0.82217
C	-15.66582	1.37132	2.35043
H	-15.49645	0.42262	2.46557
H	-15.07594	1.87812	2.92995
H	-16.58860	1.56422	2.57786
C	-15.66582	7.39673	2.35043
H	-15.49645	8.34543	2.46557
H	-15.07594	6.88993	2.92995
H	-16.58860	7.20383	2.57786
C	-13.97600	1.36080	0.49863
H	-13.76186	1.72380	-0.37588
H	-13.35109	1.70977	1.15428
H	-13.90787	0.39281	0.47199
C	-13.97600	7.40725	0.49863
H	-13.76186	7.04425	-0.37588
H	-13.35109	7.05828	1.15428
H	-13.90787	8.37524	0.47199



## Atoms and radius in the parameter file

Atoms and radius in the parameter file

C2	1.99
C3	1.99
C	1.99
N2	1.81
N3	1.81
N	1.81
O	1.78
P	2.11
H	1.40
F	1.72

## Coordinates scaled to put the metal at the origin

Coordinates scaled to put the metal at the origin

C	1.45443	-0.00001	-1.51480
N	2.01725	-1.07235	-2.10098
N	2.01725	1.07232	-2.10098
C	2.96709	-0.66972	-3.04211
C	2.96709	0.66969	-3.04211
C	3.98526	-1.44499	-3.75199
H	4.69973	-1.69751	-3.12965
H	3.58617	-2.26568	-4.10979
C	3.98526	1.44496	-3.75199
H	4.69973	1.69748	-3.12965
H	3.58617	2.26565	-4.10979
C	4.54788	-0.62079	-4.86726
H	4.08065	-0.89962	-5.68182
H	5.48234	-0.89962	-4.97383
C	4.54788	0.62076	-4.86726
H	4.08065	0.89959	-5.68182
H	5.48234	0.89959	-4.97383
C	1.67247	-2.46629	-1.91638
C	1.67247	2.46626	-1.91638
C	0.72244	-3.02324	-2.76519
C	0.72244	3.02321	-2.76519
C	0.47130	-4.39807	-2.62816
H	-0.17309	-4.80841	-3.17438
C	0.47130	4.39804	-2.62816
H	-0.17308	4.80838	-3.17438
C	1.15852	-5.15212	-1.70417
H	0.98331	-6.07277	-1.63090
C	1.15852	5.15209	-1.70417
H	0.98331	6.07274	-1.63090
C	2.08519	-4.57518	-0.89913
H	2.54463	-5.11003	-0.27774
C	2.08519	4.57515	-0.89913
H	2.54463	5.11001	-0.27774
C	2.37916	-3.21263	-0.96669
C	2.37916	3.21260	-0.96669
C	-0.02513	-2.23762	-3.83764
H	0.09557	-1.27489	-3.63875
C	-0.02513	2.23759	-3.83764

H	0.09557	1.27486	-3.63875
C	0.57059	-2.49716	-5.22030
H	0.54333	-3.44761	-5.40966
H	0.05469	-2.01842	-5.88831
H	1.48947	-2.18852	-5.23933
C	0.57059	2.49713	-5.22030
H	0.54333	3.44758	-5.40966
H	0.05469	2.01839	-5.88831
H	1.48947	2.18849	-5.23933
C	-1.52805	-2.51820	-3.85762
H	-1.89015	-2.39545	-2.96598
H	-1.96413	-1.90619	-4.47044
H	-1.68185	-3.43008	-4.14785
C	-1.52805	2.51817	-3.85762
H	-1.89015	2.39542	-2.96598
H	-1.96413	1.90616	-4.47044
H	-1.68185	3.43005	-4.14785
C	3.41679	-2.61991	-0.03984
H	3.35255	-1.63438	-0.10360
C	3.41679	2.61988	-0.03984
H	3.35255	1.63435	-0.10360
C	3.15787	-3.01272	1.42466
H	3.32724	-3.96142	1.53980
H	3.74775	-2.50592	2.00418
H	2.23509	-2.81982	1.65209
C	3.15787	3.01269	1.42466
H	3.32724	3.96139	1.53980
H	3.74775	2.50589	2.00418
H	2.23509	2.81979	1.65209
C	4.84769	-3.02324	-0.42714
H	5.06183	-2.66024	-1.30165
H	5.47260	-2.67427	0.22851
H	4.91582	-3.99123	-0.45378
C	4.84769	3.02321	-0.42714
H	5.06183	2.66021	-1.30165
H	5.47260	2.67424	0.22851
H	4.91582	3.99120	-0.45378
XX	0.00000	0.00000	0.00000

### Results : Volumes in Angs^3

Results : Volumes in Angs^3

N of voxels examined : 1436277  
Volume of voxel : 0.125E-03

V Free	V Buried	V Total	V Exact
119.827	59.707	179.535	179.594

%V_Free	%V_Bur	% Tot/Ex
66.743	33.257	99.967

**The %V\_Bur of your molecule is: 33.3**

## 9. References

- (1) R. A. Kelly III., H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* 2008, **27**, 202.
- (2) S. S. Sohn, E. L. Rosen and J. W. Bode, *J. Am. Chem. Soc.* 2004, **126**, 14370.
- (3) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* 2009, 1759.
- (4) [www.molnac.unisa.it/OMtools/sambvca.php](http://www.molnac.unisa.it/OMtools/sambvca.php) (retrieved 4<sup>th</sup> May 2009).