

## ***Supporting Information for***

### **Effect of $\beta$ -ketoiminato ancillary ligand modification on emissive properties of new iridium complexes**

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## 1. Synthesis of ligands and complexes

**4-Phenylimino-2-pentanone (3a)**<sup>1</sup>: To a solution of 0.05 mol of acetylacetone (5.0 g) in benzene, 0.045 mol of aniline (4.2 g) and 20 mg of *p*-toluenesulfonic acid were added. The obtained mixture was refluxed using Dean-Stark apparatus, until no more water was generated (ca. 10 h). Then the solvent was evaporated and the oily residue was crystallized from hexane. The product was filtered off and dried in vacuum at r.t. Yield: 7.1 g (90%), m.p. 47-49°C. Yield: 7.1 g (90%); m.p. 47-49°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 12.47 (bs, 1H; NH); 7.32 (t, 2H, 7.7 Hz; C<sub>Ar3,5</sub>H); 7.17 (t, 1H, 7.7 Hz; C<sub>Ar4</sub>H); 7.09 (d, 2H, 7.7 Hz; C<sub>Ar2,6</sub>H); 5.18 (s, 1H; =CH); 2.09 (s, 3H; C(=O)CH<sub>3</sub>); 1.98 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 196.0 (C=O); 160.1 (=C-N); 138.7 (N-C<sub>Ar1</sub>); 129.0 (C<sub>Ar2,6</sub>); 125.5 (C<sub>Ar4</sub>); 124.7 (C<sub>Ar3,5</sub>); 97.5 (=CH); 29.1 (C(=O)CH<sub>3</sub>); 19.8 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>11</sub>H<sub>13</sub>NO<sup>+</sup>: 175.0992, found: 175.0971.

Compounds **3b-3i** have been synthesized using the same method as for **3a**:

**4-(4-Methoxyphenyl) imino-2-pentanone (3b)**: 0.07 mol (8.6 g) of 4-methoxyaniline was used. Yield: 10.2 g (71%); m.p. 40-42°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = δ 12.27 (bs, 1H; NH); 7.01 (m, 2H; C<sub>Ar2</sub>H); 6.84 (m, 2H; C<sub>Ar3</sub>H); 5.13 (s, 1H; =CH); 2.06 (s, 3H; C(=O)CH<sub>3</sub>); 1.88 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 195.7 (C=O); 161.3 (=C-N); 157.6 (C<sub>Ar4</sub>O); 131.4 (N-C<sub>Ar1</sub>); 126.5 (C<sub>Ar2,6</sub>); 114.2 (C<sub>Ar3,5</sub>); 96.7 (=CH); 28.5 (C(=O)CH<sub>3</sub>); 19.5 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub><sup>+</sup>: 205.1097, found: 205.1109.

**4-(4-cyanophenyl) imino-2-pentanone (3c)**: 0.05 mol (5.5 g) of 4-aminobenzonitrile was used. Yield: 8.2 g (88%); m.p. 85-88°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = δ 12.67 (bs, 1H; NH); 7.59 (m, 2H; C<sub>Ar3</sub>H); 7.14 (m, 2H; C<sub>Ar2</sub>H); 5.28 (s, 1H; =CH); 2.12 (s, 3H;

C(=O)CH<sub>3</sub>); 2.11 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 197.5 (C=O); 157.5 (=C-N); 143.3 (N-C<sub>Ar1</sub>); 133.2 (C<sub>Ar3,5</sub>); 122.8 (C<sub>Ar2,6</sub>); 118.6 (C≡N); 107.2 (C<sub>Ar4</sub>CN); 99.9 (=CH); 29.5 (C(=O)CH<sub>3</sub>); 20.3 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sup>+</sup>: 200.0944, found: 200.0938.

**4-(4-Nitrophenyl) imino-2-pentanone (3d)**: 0.04 mol (6.1 g) of 4-nitroaniline was used. Yield: 7.1 g (73%); m.p. 140–142°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.75 (bs, 1H; NH); 8.16 (m, 2H; C<sub>Ar3</sub>H); 7.15 (m, 2H; C<sub>Ar2</sub>H); 5.31 (s, 1H; =CH); 2.17 (s, 3H; C(=O)CH<sub>3</sub>); 2.11 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 197.8 (C=O); 156.9 (=C-N); 145.2 (N-C<sub>Ar1</sub>); 143.4 (C<sub>Ar4</sub>NO<sub>2</sub>); 125.1 (C<sub>Ar3,5</sub>); 121.8 (C<sub>Ar2,6</sub>); 101.1 (=CH); 29.5 (C(=O)CH<sub>3</sub>); 20.5 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 220.0842, found: 220.0840.

**4-(3-Nitrophenyl) imino-2-pentanone (3e)**: 0.05 mol (6.8 g) of 3-nitroaniline was used. Yield: 7.8 g (72%); m.p. 76–78°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.64 (bs, 1H; NH); 7.99 (ddd, 1H, 8.1, 2.1 & 0.9 Hz; C<sub>Ar4</sub>H); 7.96 (t, 1H, 2.1 Hz; C<sub>Ar2</sub>H); 7.50 (t, 1H, 8.1 Hz; C<sub>Ar5</sub>H); 7.40 (ddm, 1H, 8.1 & 2.1 Hz; C<sub>Ar6</sub>H); 5.28 (s, 1H; =CH); 2.12 (s, 3H; C(=O)CH<sub>3</sub>); 2.09 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 197.4 (C=O); 158.3 (=C-N); 148.7 (C<sub>Ar3</sub>NO<sub>2</sub>); 140.3 (N-C<sub>Ar1</sub>); 130.0 (C<sub>Ar5</sub>); 129.6 (C<sub>Ar6</sub>); 119.5 (C<sub>Ar2</sub>); 118.3 (C<sub>Ar4</sub>); 99.6 (=CH); 29.4 (C(=O)CH<sub>3</sub>); 19.4 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 220.0842, found: 220.0857.

**4-(2-Nitrophenyl) imino-2-pentanone (3f)**: 0.04 mol (5.2 g) of 2-nitroaniline was used. Yield: 7.3 g (88%); m.p. 58–60°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.89 (bs, 1H; NH); 8.02 (dd, 1H, 8.2 & 1.5 Hz; C<sub>Ar3</sub>H); 7.54 (ddd, 1H, 8.4, 7.0 & 1.5 Hz; C<sub>Ar5</sub>H); 7.22 (dd, 1H, 8.4 & 1.2 Hz; C<sub>Ar6</sub>H); 7.23 (ddd, 1H, 8.2, 7.0 & 1.2 Hz; C<sub>Ar4</sub>H); 5.37 (s, 1H; =CH); 2.14 (s, 3H; C(=O)CH<sub>3</sub>); 2.03 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = δ 197.3 (C=O); 156.2 (=C-N); 142.5 (C<sub>Ar2</sub>NO<sub>2</sub>); 134.0 (N-C<sub>Ar1</sub>); 133.4 (C<sub>Ar5</sub>); 126.4 (C<sub>Ar3</sub>); 125.7

(C<sub>Ar4</sub>); 124.5 (C<sub>Ar6</sub>); 101.9 (=CH); 29.5 (C(=O)CH<sub>3</sub>); 19.9 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 220.0842, found: 220.0861.

**4-(4-(5-Methyl-2-benzothiazyl)phenyl)imino-2-pentanone (3g):**

0.03 mol (7.8 g) of 2-(4-aminophenyl)-5-methylbenzothiazole was used. Yield: 9.4 g (90%); m.p. 156–158°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.65 (bs, 1H; NH); 8.01 (m, 2H; C<sub>Ph3,5</sub>H); 7.91 (d, 1H, 8.3 Hz; C<sub>Bt7</sub>H); 7.66 (s, 1H; C<sub>Bt4</sub>H); 7.28 (d, 1H, 8.2 Hz; C<sub>Bt6</sub>H); 7.18 (m, 2H; C<sub>Ph2,6</sub>H); 5.24 (s, 1H; =CH); 2.48 (s, 3H; BtCH<sub>3</sub>); 2.12 (s, 3H; C(=O)CH<sub>3</sub>); 2.09 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 196.7 (C=O); 165.9 (C<sub>Bt2</sub>); 158.8 (=C-N); 152.2 (C<sub>Bt3a</sub>); 141.2 (N-C<sub>Ar1</sub>); 135.3 (C<sub>Bt5</sub>); 135.1 (C<sub>Bt7a</sub>); 130.2 (C<sub>Ar4</sub>Bt); 128.2 (C<sub>Ar3,5</sub>); 127.9 (C<sub>Bt6</sub>); 123.7 (C<sub>Ar2,6</sub>); 122.6 (C<sub>Bt7</sub>); 121.3 (C<sub>Bt4</sub>); 100.0 (=CH); 29.3 (C(=O)CH<sub>3</sub>); 21.5 (BtCH<sub>3</sub>); 20.1 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>OS<sup>+</sup>: 322.1134, found: 322.1153.

**4-(1-Naphthyl)imino-2-pentanone (3h):** 0.04 mol (5.8 g) of 1-aminonaphthalene was used. Yield: 6.8 g (75%); m.p. 74–75°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.75 (bs, 1H; NH); 8.03 (d, 1H, 7.9 Hz; C<sub>Nph8</sub>H); 7.87 (d, 1H, 7.5 Hz; C<sub>Nph5</sub>H); 7.77 (d, 1H, 8.2 Hz; C<sub>Nph4</sub>H); 7.53 (m, 2H; C<sub>Nph6,7</sub>H); 7.44 (t, 1H, 7.4 Hz; C<sub>Nph3</sub>H); 7.28 (d, 1H, 7.4 Hz; C<sub>Nph2</sub>H); 5.31 (s, 1H; =CH); 2.18 (s, 3H; C(=O)CH<sub>3</sub>); 1.88 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 196.4 (C=O); 161.8 (=C-N); 134.8 (N-C<sub>Nph1</sub>); 134.2 (C<sub>Nph10</sub>); 129.9 (C<sub>Nph9</sub>); 128.2 (C<sub>Nph5</sub>); 126.9 (C<sub>Nph6</sub>); 126.8 (C<sub>Nph3</sub>); 126.5 (C<sub>Nph7</sub>); 125.2 (C<sub>Nph8</sub>); 123.4 (C<sub>Nph4</sub>); 122.7 (C<sub>Nph2</sub>); 97.4 (=CH); 29.1 (C(=O)CH<sub>3</sub>); 19.6 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>15</sub>H<sub>15</sub>NO<sup>+</sup>: 225.1148, found: 225.1157.

**4-(2-Naphthyl)imino-2-pentanone (3i):** 0.04 mol (5.7 g) of 2-aminonaphthalene was used. Yield: 6.3 g (70%); m.p. 95–97°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.66 (bs, 1H; NH); 7.82 (d, 1H, 7.2 Hz; C<sub>Nph5</sub>H); 7.81 (d, 1H, 8.6 Hz; C<sub>Nph4</sub>H); 7.77 (d, 1H, 8.1 Hz;

$C_{Nph8}H$ ); 7.54 (d, 1H, 1.9 Hz;  $C_{Nph1}H$ ); 7.49 (t, 1H, 7.2 Hz;  $C_{Nph7}H$ ); 7.45 (d, 1H, 7.2 Hz;  $C_{Nph6}H$ ); 7.25 (dd, 1H, 8.6 & 1.9 Hz;  $C_{Nph3}H$ ); 5.31 (s, 1H; =CH); 2.18 (s, 3H; C(=O)CH<sub>3</sub>); 1.88 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 196.2 (C=O); 160.1 (=C-N); 136.3 (N-C<sub>Nph1</sub>); 133.5 (C<sub>Nph9</sub>); 131.1 (C<sub>Nph10</sub>); 129.0 (C<sub>Nph4</sub>); 127.6 (C<sub>Nph5</sub>); 127.4 (C<sub>Nph7</sub>); 126.6 (C<sub>Nph7</sub>); 125.6 (C<sub>Nph8</sub>); 123.9 (C<sub>Nph6</sub>); 121.7 (C<sub>Nph3</sub>); 97.9 (=CH); 29.2 (C(=O)CH<sub>3</sub>); 20.0 (=CCH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>15</sub>H<sub>15</sub>NO<sup>+</sup>: 225.1148, found: 225.1141.

**4-(1-Anthracenyl) imino-2-pentanone (3j):** to a pressure glass vessel of 10 mL capacity equipped with a magnetic stirrer, 400 mg (2.070 mmol; 1.00 eq.) of 1-aminoanthracene, 2.125 mL of pentane-2,4-dione (20.70 mmol; 10.00 eq.) and a drop of acetic acid were added. The reactor was sealed by a plastic cap equipped with elastic membrane and then placed in the chamber of a microwave radiation source. The thus prepared reaction system was sealed with an encapsulating head, equipped with a pressure sensor. The reaction was conducted for 1 hour at 150 °C, irradiating the mixture with microwaves (150 W and frequency 2445 MHz). Afterwards, the solvent was fully evaporated from the post-reaction mixture under reduced pressure. The remaining crude product was purified by flash chromatography using silica treated with triethylamine as the solid phase (gradient elution from pure n-hexane to n-hexane:AcOEt = 4:1, v/v). The purified material was dried *in vacuo* for 4 hours. The desired product was obtained in 79 % yield (450.35 mg, 1.637 mmol); m.p. 157-158°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.86 (bs, 1H; NH); 8.58 (s, 1H; C<sub>Ant10</sub>H); 8.45 (s, 1H; C<sub>Ant9</sub>H); 8.06 (m, 1H; C<sub>Ant8</sub>H); 8.00 (m, 1H; C<sub>Ant5</sub>H); 7.92 (d, 1H, 8.5 Hz; C<sub>Ant4</sub>H); 7.49 (m, 2H; C<sub>Ant6,7</sub>H); 7.42 (dd, 1H, 8.5 & 7.0 Hz; C<sub>Ant3</sub>H); 7.25 (dt, 1H, 7.0 & 1.0 Hz; C<sub>Ant2</sub>H); 5.37 (s, 1H; =CH); 2.23 (s, 3H; C(=O)CH<sub>3</sub>); 1.92 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 196.5 (C=O); 161.9 (=C-N); 134.8 (N-C<sub>Ant1</sub>); 132.2 (C<sub>Ant4a</sub>); 132.0 (C<sub>Ant10a</sub>); 131.9 (C<sub>Ant8a</sub>); 128.7 (C<sub>Ant8</sub>); 128.6

(C<sub>Ant9a</sub>); 127.9 (C<sub>Ant5</sub>); 127.2 (C<sub>Ant10</sub>); 126.8 (C<sub>Ant7</sub>); 126.0 (C<sub>Ant3</sub>); 125.8 (C<sub>Ant6</sub>); 124.4 (C<sub>Ant9</sub>); 122.6 (C<sub>Ant4</sub>); 121.6 (C<sub>Ant2</sub>); 97.7 (=CH); 29.2 (C(=O)CH<sub>3</sub>); 19.6 (=CCH<sub>3</sub>); HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>18</sub>NO<sup>+</sup> ([M+H]<sup>+</sup>): 276.1383, found: 276.1384.

**4-(2-Anthracenyl) imino-2-pentanone (3k):** Following the procedure used for preparation of **3j**, the reaction was carried out with 0.726 mmol (140 mg) of 1-aminoanthracene and 7.26 mmol pentane-2,4-dione. Yield: 150.17 mg (0.545 mmol, 75%); m.p. 185–188°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.71 (bs, 1H; NH); 8.39 (s, 1H; C<sub>Ant9</sub>H); 8.33 (s, 1H; C<sub>Ant10</sub>H); 7.99 (dm, 1H, 8.7 Hz; C<sub>Ant4</sub>H); 7.97 (dm, 2H, 8.9 Hz; C<sub>Ant5,8</sub>H); 7.67 (d, 1H, 2.1 Hz; C<sub>Ant1</sub>H); 7.47 (m, 2H; C<sub>Ant6,7</sub>H); 7.24 (dd, 1H, 8.7 & 2.1 Hz; C<sub>Ant3</sub>H); 5.27 (s, 1H; =CH); 2.16 (s, 3H; =CCH<sub>3</sub>); 2.15 (s, 3H; C(=O)CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 196.4 (C=O); 159.9 (=C-N); 135.7 (N-C<sub>Ant2</sub>); 132.2 (C<sub>Ant9a</sub>); 131.5 (C<sub>Ant8a,10a</sub>); 129.5 (C<sub>Ant4</sub>); 129.4 (C<sub>Ant4a</sub>); 128.2 (C<sub>Ant5</sub>); 127.9 (C<sub>Ant8</sub>); 126.3 (C<sub>Ant10</sub>); 125.8 (C<sub>Ant7</sub>); 125.6 (C<sub>Ant6</sub>); 125.4 (C<sub>Ant9</sub>); 124.1 (C<sub>Ant3</sub>); 120.5 (C<sub>Ant1</sub>); 98.3 (=CH); 29.3 (C(=O)CH<sub>3</sub>); 20.2 (=CCH<sub>3</sub>); HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>18</sub>NO<sup>+</sup> ([M+H]<sup>+</sup>): 276.1383, found: 276.1473.

**4-(9-Anthracenyl) imino-2-pentanone (3l):** Following the procedure used for preparation of **3j**, the reaction was carried out with 2.070 mmol (400 mg) of 9-aminoanthracene and 20.70 mmol (2.125 mL) of pentane-2,4-dione. Yield: 399.04 mg (1.450 mmol, 70%); m.p. 147–149°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 12.67 (bs, 1H; NH); 8.44 (s, 1H; C<sub>Ant10</sub>H); 8.08 (dq, 2H, 8.5 & 0.9 Hz; C<sub>Ant1,8</sub>H); 8.03 (ddt, 2H, 8.3, 1.4 & 0.9 Hz; C<sub>Ant4,5</sub>H); 7.52 (m, 2H; C<sub>Ant2,7</sub>H); 7.49 (m, 2H; C<sub>Ant3,6</sub>H); 5.42 (s, 1H; =CH); 2.25 (s, 3H; C(=O)CH<sub>3</sub>); 1.57 (s, 3H; =CCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 196.7 (C=O); 163.8 (=C-N); 131.6 (C<sub>Ant5a,10a</sub>); 130.3 (N-C<sub>Ant9</sub>); 129.1 (C<sub>Ant10</sub>); 128.5 (C<sub>Ant3,6</sub>); 126.7 (C<sub>Ant4,5</sub>); 126.6 (C<sub>Ant8a,9a</sub>); 125.6 (C<sub>Ant2,7</sub>); 127.2 (C<sub>Ant1,8</sub>); 96.7 (=CH); 29.3 (C(=O)CH<sub>3</sub>); 19.3

(=CCH<sub>3</sub>); HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>18</sub>NO<sup>+</sup> ([M+H]<sup>+</sup>): 276.1383, found: 276.1410.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(C<sub>6</sub>H<sub>5</sub>))Me}]** (5a): Complex was synthesized according to previously published procedure.<sup>1</sup>

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(4-MeO-C<sub>6</sub>H<sub>4</sub>))Me}]** (5b): In a Schlenk vessel equipped with a magnetic stirrer, 100 mg (0.0856 mmol, 1.00 eq.) of [Ir(bzq)<sub>2</sub>(μ-Cl)]<sub>2</sub> (4), 70.15 mg (0.342 mmol, 4.00 eq.) of 4-(4-methoxyphenyl)imino-2-pentanone (3b) were placed and then 5 mL of dried and deoxygenated THF was introduced. In the next step, to the stirred mixture 41.13 mg (0.428 mmol, 5 eq.) of NaO<sup>t</sup>Bu was added. The reaction was conducted at ambient condition for 12 hours. Then the solvent was evaporated from the red-orange solution under reduced pressure. The remaining crude product was purified by flash chromatography using silica as the solid phase and chloroform as eluent. After evaporation of the solvent the remaining solid was dried *in vacuo* for 4 hours. The desired product was obtained in 62 % yield (78.90 mg, 0.103 mmol). Elemental anal. calcd for C<sub>38</sub>H<sub>30</sub>IrN<sub>3</sub>O<sub>2</sub>, C 60.62; H 4.02; found C 60.70; H 4.06. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.28 (dd, *J* = 5.3&1.4 Hz, 1H); 9.11 (dd, *J* = 5.3&1.4 Hz, 1H); 8.23 (dd, *J* = 8.0&1.4 Hz, 1H); 8.14 (dd, *J* = 8.0&1.4 Hz, 1H); 7.75 (d, *J* = 9.2 Hz, 1H); 7.60 (d, *J* = 8.8 Hz, 1H); 7.56 (dd, *J* = 8.0&5.3 Hz, 2H); 7.45 (d, *J* = 1.5 Hz, 2H); 6.93 (ddd, *J* = 7.6&4.0&3.2 Hz, 2H); 6.63 (t, *J* = 7.5 Hz, 1H); 6.34 (dd, *J* = 7.2&0.9 Hz, 1H); 6.19 (dd, *J* = 8.7&2.6 Hz, 1H); 5.96 (dd, *J* = 7.3&0.9 Hz, 1H); 5.89 (dd, *J* = 8.6&2.9 Hz, 1H); 5.48 (dd, *J* = 8.6&2.9 Hz, 1H); 4.85 (s, 1H, =CH-); 4.59 (dd, *J* = 8.6&2.6 Hz, 1H); 3.41 (s, 3H, -OCH<sub>3</sub>); 1.68 (s, 3H, -CH<sub>3</sub>); 1.61 (s, 3H, -CH<sub>3</sub>). HRMS (EI): *m/z* calcd for C<sub>38</sub>H<sub>30</sub>IrN<sub>3</sub>O<sub>2</sub><sup>+</sup>: [M]<sup>+</sup> 753.1962, found 753.1975.

**[Ir (bzq)<sub>2</sub>{MeC(O)=CHC(=N(4-CN-C<sub>6</sub>H<sub>4</sub>))Me}]** (**5c**): In a Schlenk vessel equipped with a magnetic stirrer, 27.27 mg (0.668 mmol, 10.00 eq.) of NaH (60% dispersion in mineral oil) was placed and washed with anhydrous and deoxygenated toluene (3 x 1.5 mL). In the next step, to the stirred NaH powder, 30.00 mg (0.147 mmol, 2.20 eq.) 4-(4-cyanophenyl)imino-2-pentanone (**3c**) and 4 mL of dried and deoxygenated THF was introduced. The reaction was conducted until hydrogen evolution ceased. The mixture obtained was transferred by a syringe equipped with a syringe-filter disc to a Schlenk vessel of 25 mL capacity, in which a portion of 78.00 mg (0.0667 mmol, 1.00 eq.) of [ $\text{Ir}(\text{bzq})_2(\mu\text{-Cl})_2$ ] (**4**) and 2 mL of anhydrous and deoxygenated THF were placed under inert atmosphere. The reaction was conducted at 65°C for 24 hours. After that, mixture was filtered and concentrated. The remaining crude product was purified by flash chromatography using silica as the solid phase (gradient elution from pure n-hexane to n-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2, v/v). Solid material was dried *in vacuo* for 4 hours. The desired product was obtained in 68 % yield (67.87 mg, 0.091 mmol). Elemental anal. calcd for C<sub>38</sub>H<sub>27</sub>IrN<sub>4</sub>O, C 61.03; H 3.64; found C 61.10; H 3.69. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.22 (d, *J* = 5 Hz, 1H); 9.06 (d, *J* = 5 Hz, 1H); 8.26 (d, *J* = 8.0 Hz, 1H); 8.17 (d, *J* = 8 Hz, 1H); 7.75 (d, *J* = 9Hz, 1H); 7.60 (m, 3H); 7.53 (d, *J* = 9 Hz, 1H); 7.48 (d, *J* = 9Hz, 1H); 6.99 (d, *J* = 8 Hz, 1H); 6.94 (t, *J* = 8 Hz, 1H); 6.66 (t, *J* = 8Hz, 1H); 6.60 (d, *J* = 8Hz, 1H); 6.35 (dd, *J* = 8 & 2 Hz, 1H); 6.30 (d, *J* = 7 Hz, 1H); 6.23 (dd, *J* = 8.2 & 1.9 Hz, 1H); 5.94 (d, *J* = 7 Hz, 1H); 4.91 (s, 1H); 4.78 (dd, *J* = 8.1, 2.1 Hz, 1H); 1.70 (s, 3H, -CH<sub>3</sub>); 1,59 (s, 3H, -CH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>38</sub>H<sub>27</sub>IrN<sub>4</sub>O<sup>+</sup>: [M]<sup>+</sup> 748.1809, found 748.1825.

**[Ir (bzq)<sub>2</sub>{MeC(O)=CHC(=N(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))Me}]** (**5d**): Following the procedure used for preparation of **5c**, the reaction was carried out with 200.00 mg (0.171 mmol, 1.00 eq.) of [ $\text{Ir}(\text{bzq})_2(\mu\text{-}$

Cl)<sub>2</sub>] (**4**), 68.18 mg (1.713 mmol, 10.00 eq.) of NaH and 82.00 mg (0.377 mmol, 2.20 eq.) of 4-(4-nitrophenyl)imino-2-pentanone (**3d**). Mixture was filtered and the solvent was fully evaporated from the post-reaction mixture under reduced pressure. The remaining crude product was purified by flash chromatography using silica as the solid phase (gradient elution from pure n-hexane to n-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2, v/v). The desired product was obtained in 67 % yield (176.02 mg, 0.229 mmol). Elemental anal. calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub>, C 57.88; H 3.54; found C 57.99; H 3.59. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.23 (d, J = 6 Hz; 1H); 9.07 (d, J = 6 Hz, 1H); 8.27 (d, J = 9 Hz, 1H); 8.18 (d, J = 6Hz, 1H); 7.75 (d, J = 9Hz, 1H); 7.61 (m, 3H); 7.44 (q, J = 9 Hz, 2H); 7.17 (m, 2H); 6.97 (d, J = 9 Hz, 1H); 6.92 (d, J = 9 Hz, 1H); 6.81 (m, 1H); 6.68 (t, J = 9 Hz, 1H); 6.34 (m, 2H); 5.96 (d, J = 6Hz, 1H); 4.94 (s, 1H, =CH-); 4.80 (dd, 1H); 1.72 (s, 3H, -CH<sub>3</sub>); 1.62 (s, 3H, -CH<sub>3</sub>); HRMS (EI): m/z calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub><sup>+</sup>: [M]<sup>+</sup> 768.1707, found 768.1723.

[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))Me}] (**5e**): Following the procedure used for preparation of **5c**, the reaction was carried out with 200.00 mg (0.171 mmol, 1.00 eq.) of [Ir(bzq)<sub>2</sub>(μ-Cl)<sub>2</sub>] (**4**), 68.18 mg (1.713 mmol, 10.00 eq.) of NaH and 82.00 mg (0.377 mmol, 2.20 eq) of 4-(3-nitrophenyl)imino-2-pentanone (**3e**). Mixture was filtered and the solvent was fully evaporated from the post-reaction mixture under reduced pressure. The remaining crude product was purified by flash chromatography using silica as the solid phase (gradient elution from pure n-hexane to n-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2, v/v). The desired product was obtained in 80 % yield (210.17 mg, 0.274 mmol). Elemental anal. calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub>, C 57.88; H 3.54; found C 58.02; H 3.59. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.24 (m, 1H); 9.09 (m, 1H); 8.27 (t, J = 6 Hz, 1H); 8.18 (m, 1H); 7.75 (m, 1H); 7.62 (m, 4H); 7.64 (s, 1H); 7.73 (m, 1H); 7.08 (m, 1H); 6.93 (m, 2H); 6.63 (m, 1H); 6.33 (dd, J = 6 Hz, 1H); 6.07

(m, 1H); 4.93 (s, 1H, =CH-); 1.71 (s, 3H, -CH<sub>3</sub>); 1.61 (s, 3H, -CH<sub>3</sub>); HRMS (EI): *m/z* calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub><sup>+</sup>: [M]<sup>+</sup> 768.1707, found 768.1725.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(2-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))Me}] (5f):** In a Schlenk vessel equipped with a magnetic stirrer, 100 mg (0.0856 mmol, 1.00 eq.) of [{Ir(bzq)<sub>2</sub>(μ-Cl)}<sub>2</sub>] (**4**), 75.36 mg (0.342 mmol, 4.00 eq.) of 4-(2-nitrophenyl)imino-2-pentanone (**3f**) were placed and then 5 mL of dried and deoxygenated THF was introduced. In the next step, to the stirred mixture 41.13 mg (0.428 mmol, 5 eq.) of NaO<sup>t</sup>Bu was added. The reaction was conducted at ambient condition for 12 hours. After that, solvent was evaporated under reduced pressure. The remaining crude product was purified by flash chromatography using silica as the solid phase and chloroform as eluent. After evaporation of the solvent the remaining solid was dried *in vacuo* for 4 hours. The desired product was obtained in 60 % yield (78.90 mg, 0.103 mmol). Elemental anal. calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub>, C 57.88; H 3.54; found C 57.96; H 3.57. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.50 (d, *J* = 5.5 Hz, 1H); 9.18 (d, *J* = 5.5 Hz, 1H); 8.24 (d, *J* = 8.1 Hz, 1H); 8.18 (d, *J* = 8.0 Hz, 1H); 7.76 – 7.56 (m, 4H); 7.47 (d, *J* = 5.0 Hz, 2H); 7.21 (d, *J* = 7.8 Hz, 1H); 7.02 (d, *J* = 7.8 Hz, 1H); 6.96 (d, *J* = 8.2 Hz, 1H); 6.87 (t, *J* = 7.5 Hz, 1H); 6.76 (t, *J* = 7.5 Hz, 1H); 6.24 (t, *J* = 7.8 Hz, 1H); 6.14 – 5.99 (m, 3H); 5.09 (s, 1H); 4.93 (d, *J* = 7.9 Hz, 1H); 1.81 (s, 3H), 1.71 (s, 3H); HRMS (EI): *m/z* calcd for C<sub>37</sub>H<sub>27</sub>IrN<sub>4</sub>O<sub>3</sub><sup>+</sup>: [M]<sup>+</sup> 768.1707, found 768.1729.

**[Ir(bzq)<sub>2</sub>{4-(4-(5-Methyl-2-benzothiazyl)phenyl)imino-2-pentanolato}] (5g):** Following the procedure used for preparation of **5c**, the reaction was carried out with 134 mg (0.115 mmol, 1 eq.) of [{Ir(bzq)<sub>2</sub>(μ-Cl)}<sub>2</sub>] (**4**), 46.1 mg (1.149 mmol; 10 eq.) of KH and 82 mg (0.253 mmol; 2.2 eq.) of 4-(4-(5-Methyl-2-benzothiazyl)phenyl)imino-2-pentanone (**3g**). The crude product was purified by precipitation from DCM/*n*-hexane

mixture and then dried *in vacuo* for 4 hours. The desired product was obtained in 51 % yield (102.07 mg, 0.117 mmol). Elemental anal. calcd for  $C_{45}H_{33}IrN_4OS$ , C 63.12; H 3.82; found C 62.21; H 3.89.  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ )  $\delta$  = 9.35 (dd, 1H,  $J$  = 5.3 & 1.4 Hz); 9.07 (dd, 1H,  $J$  = 5.3 & 1.3 Hz); 8.33 (dd, 1H,  $J$  = 8.0 & 1.4 Hz); 8.25 (dd, 1H,  $J$  = 8.1 & 1.3 Hz); 7.81 - 7.75 (m, 2H); 7.71 - 7.62 (m, 4H); 7.49 (d, 1H,  $J$  = 8.8 Hz); 7.35 - 7.23 (m, 3H); 7.02 (dd, 1H,  $J$  = 8.3 & 2.2 Hz); 6.94 (t, 1H,  $J$  = 7.5 Hz); 6.85 (d, 1H,  $J$  = 7.7 Hz); 6.65 (t, 1H,  $J$  = 7.5 Hz); 6.60 (dd, 1H,  $J$  = 8.2 & 2.2 Hz); 6.43 (dd, 1H,  $J$  = 8.3 & 2.2 Hz); 6.31 (dd, 1H,  $J$  = 7.2 & 1.0 Hz); 5.98 - 5.94 (m, 1H); 4.96 (s, 1H, =CH-); 4.77 (dd, 1H,  $J$  = 8.2 & 2.2 Hz); 2.47 (s, 3H, -CH<sub>3</sub>); 1.72 (s, 3H, -CH<sub>3</sub>); 1.66 (s, 3H, -CH<sub>3</sub>); HRMS (EI):  $m/z$  calcd for  $C_{45}H_{33}IrN_4OS^+$ :  $[M]^+$  870.1999, found 870.2019.

**[Ir (bzq)<sub>2</sub> {MeC(O)=CHC(=N(1-Naph) ) Me}]** (**5h**): Following the procedure used for preparation of **5c**, the reaction was carried out with 189 mg (0.162 mmol, 1 eq.) of [ $\{Ir(bzq)_2(\mu-Cl)\}_2$ ] (**4**), 64.97 mg (1.620 mmol; 10 eq.) of KH and 80.29 mg (0.356 mmol; 2.2 eq.) of 4-(1-naphthyl)imino-2-pentanone (**3h**). The remaining crude product was purified by flash chromatography using silica as the solid phase (gradient elution from pure n-hexane to n-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2, v/v). The desired product was obtained in 64 % yield (160.33 mg, 0.207 mmol). Elemental anal. calcd for  $C_{41}H_{30}IrN_3O$ , C 63.71; H 3.91; found C 63.86; H 3.97.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  = 9.47 (d,  $J$  = 6 Hz, 1H); 9.35 (d,  $J$  = 6 Hz, 1H); 9.17 (d,  $J_H$  = 6 Hz, 1H); 8.27 (d,  $J$  = 9 Hz, 2H); 7.74 (m, 4H); 7.48 (m, 1H); 7.22 (m, 2H); 6.90 (m, 2H); 6.67 (t,  $J_H$  = 9 Hz, 2H); 6.16 (d,  $J$  = 6 Hz, 1H); 5.98 (d,  $J$  = 9 Hz, 1H); 5.92 (d,  $J$  = 6 Hz, 1H); 4.97 (s, 1H, =CH-); 1.78 (s, 3H, -CH<sub>3</sub>); 1.59 (s, 3H, -CH<sub>3</sub>); HRMS (EI):  $m/z$  calcd for  $C_{41}H_{30}IrN_3O^+$ :  $[M]^+$  773.2013, found 773.2033.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(2-Naph))Me}]** (**5i**): Following the procedure used for preparation of **5c**, the reaction was carried out with 189 mg (0.162 mmol, 1 eq.) of [{Ir(bzq)<sub>2</sub>(μ-Cl)}<sub>2</sub>] (**4**), 64.97 mg (1.620 mmol; 10 eq.) of KH and 80.29 mg (0.356 mmol; 2.2 eq.) of 4-(2-naphthyl)imino-2-pentanone (**3i**). The remaining crude product was purified by flash chromatography using silica as the solid phase (gradient elution from pure n-hexane to n-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2, v/v). The desired product was obtained in 70 % yield (174.74 mg, 0.226 mmol). Elemental anal. calcd for C<sub>41</sub>H<sub>30</sub>IrN<sub>3</sub>O, C 63.71; H 3.91; found C 63.83; H 3.96. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 9.44 (d, *J* = 4.8 Hz); 9.37 (d, *J* = 5.2 Hz, 2H); 9.18 (d, *J* = 5.2 Hz, 2H); 9.13 (d, *J* = 4.8 Hz); 8.27 (m, *J* = 6.9 Hz); 8.14 (d, *J* = 7.9 Hz); 7.74 (m); 7.69-7.55 (m); 7.37 (d, *J* = 8.8 Hz); 7.31 (d, *J* = 7.9 Hz); 7.24 - 7.20 (m); 7.18 - 7.13 (m); 7.07 (m); 6.99 (d, *J* = 8.8 Hz); 6.96 - 6.87 (m); 6.78 (d, *J* = 8.8 Hz); 6.66 (m); 6.56 (m); 6.46 - 6.34 (m); 6.30 (d, *J* = 7.2 Hz); 5.98 - 5.91 (m); 4.99 (d, *J* = 2.0 Hz); 4.96 (dd, *J* = 8.6 & 2.1 Hz); 4.91 (s), 4.89 (s, 1H), 1.72 (s), 1.71 (s, 3H), 1.65 (s, 3H), 1.64 (s); HRMS (EI): *m/z* calcd for C<sub>41</sub>H<sub>30</sub>IrN<sub>3</sub>O<sup>+</sup>: [M]<sup>+</sup> 773.2013, found 773.2029.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(1-anthracenyl))Me}]** (**5j**): Following the procedure used for preparation of **5c**, the reaction was carried out with 142 mg (0.121 mmol, 1 eq.) of [{Ir(bzq)<sub>2</sub>(μ-Cl)}<sub>2</sub>] (**4**), 48.5 mg (1.214 mmol; 10 eq.) of KH and 73.5 mg (0.267 mmol; 2.2 eq.) of 4-(1-anthracenyl)imino-2-pentanone (**3j**). The remaining crude product was purified by flash chromatography using silica treated with triethylamine as the solid phase (gradient elution from pure n-hexane to n-hexane: AcOEt = 6:4, v/v). The purified material was dried *in vacuo* for 4 hours. The desired product was obtained in 25% yield (50.0 mg, 0.061 mmol). Elemental anal. calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O, C 65.67; H 3.92; found C 65.80; H 3.97. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) = 9.55

(dd, 1H,  $J = 5.4$  &  $1.3$  Hz); 9.22 (dd, 1H,  $J = 5.4$  &  $1.4$  Hz); 8.35 (dd, 1H,  $J = 8.0$  &  $1.3$  Hz); 7.80 - 7.66 (m, 5H); 7.47 - 7.40 (m, 2H); 7.37 - 7.24 (m, 4H); 7.20 (s, 1H); 7.01 (d, 1H,  $J = 8.8$  Hz); 6.97 (d, 1H,  $J = 8.4$  Hz); 6.86 (t, 1H,  $J = 7.5$  Hz); 6.81 - 6.76 (m, 1H); 6.70 - 6.52 (m, 4H); 6.05 (dd, 1H,  $J = 7.2$  &  $1.0$  Hz); 5.86 (dd, 1H,  $J = 7.2$  &  $1.0$  Hz); 5.09 (s, 1H, =CH-); 1.85 (s, 3H, -CH<sub>3</sub>); 1.68 (s, 3H, CH<sub>3</sub>); HRMS (EI):  $m/z$  calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O<sup>+</sup>: [M]<sup>+</sup> 823.2169, found 823.2197.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(2-anthracenyl))Me}]** (**5k**): Following the procedure used for preparation of **5c**, the reaction was carried out with 142 mg (0.121 mmol, 1 eq.) of [{Ir(bzq)<sub>2</sub>( $\mu$ -Cl)}<sub>2</sub>] (**4**), 48.5 mg (1.214 mmol; 10 eq.) of KH and 73.5 mg (0.267 mmol; 2.2 eq.) of 4-(2-anthracenyl)imino-2-pentanone (**3k**). The remaining crude product was purified by flash chromatography using silica treated with triethylamine as the solid phase (gradient elution from pure n-hexane to n-hexane: AcOEt = 6:4, v/v). The purified material was dried *in vacuo* for 4 hours. The desired product was obtained in 38 % yield (74.8 mg, 0.091 mmol). Elemental anal. calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O, C 65.67; H 3.92; found C 65.77; H 3.96. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta =$  6.49 (d,  $J = 6.0$ ); 9.39 (d,  $J = 5.1$  Hz, 1H); 9.21 (d,  $J = 5.1$  Hz, 1H); 9.15 (d,  $J = 5.2$  Hz), 8.30-8.23 (m); 8.20 - 8.13 (m, 1H); 7.89 (s, 1H); 7.83 - 7.78 (m); 7.77 - 7.71 (m); 7.70 - 7.65 (m); 7.65 - 7.59 (m); 7.39 - 7.31 (m); 7.24 - 7.20 (m); 7.16 (s, 1H); 7.08 (d,  $J = 8.7$  Hz, 1H); 6.95 (d,  $J = 8.8$  Hz, 1H); 6.92 (t,  $J = 7.5$  Hz, 1H); 6.87 (s, 1H); 6.79 (d,  $J = 8.7$  Hz, 1H); 6.61 (d,  $J = 8.7$  Hz, 1H); 6.58 - 6.53 (m); 6.46 (s); 6.39 (s); 6.28 (t,  $J = 7.0$  Hz, 1H); 6.14 (d,  $J = 7.7$  Hz, 0H), 5.99 - 5.97 (d,  $J = 7.3$  Hz, 1H), 5.12 (s, 1H); 5.01 (dd,  $J = 8.9$ , 2.0 Hz); 4.94 (s); 4.92 (s, 1H); 1.75 (s); 1.72 (s, 3H); 1.70 (s, 3H); 1.68 (s); HRMS (EI):  $m/z$  calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O<sup>+</sup>: [M]<sup>+</sup> 823.2169, found 823.2198.

**[Ir(bzq)<sub>2</sub>{MeC(O)=CHC(=N(9-anthracenyl))Me}] (51)**: Following the procedure used for preparation of **5c**, the reaction was carried out with 142 mg (0.121 mmol, 1 eq.) of [Ir(bzq)<sub>2</sub>(μ-Cl)]<sub>2</sub> (**4**), 48.5 mg (1.214 mmol; 10 eq.) of KH and 73.5 mg (0.267 mmol; 2.2 eq.) of 4-(9-anthracenyl)imino-2-pentanone (**31**). The remaining crude product was purified by flash chromatography using silica treated with triethylamine as the solid phase (gradient elution from pure n-hexane to n-hexane: AcOEt = 6:4, v/v). The purified material was dried *in vacuo* for 4 hours. The desired product was obtained in 63 % yield (127.0 mg, 0.154 mmol). Elemental anal. calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O, C 65.67; H 3.92; found C 65.82; H 3.97. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = δ 10.08 (d, *J* = 5.3 Hz); 9.98 (d, *J* = 5.5 Hz, 1H); 9.23 (d, *J* = 5.3 Hz); 9.14 (d, *J* = 5.5 Hz, 1H); 8.45 – 8.30 (m, 3H); 7.93 – 7.82 (m); 7.79 – 7.66 (m); 7.65 – 7.53 (m); 7.47 – 7.38 (m); 7.32 (s, 1H); 7.26 (d, *J* = 8.6 Hz); 7.18 (d, *J* = 7.3 Hz); 7.14 – 7.08 (m); 7.01 – 6.88 (m); 6.83 – 6.73 (m); 6.59 (t, *J* = 7.5 Hz, 1H); 6.52 (d, *J* = 8.0 Hz); 6.44 (d, *J* = 7.8 Hz, 1H); 5.94 (t, *J* = 7.2 Hz, 1H); 5.86 (d, *J* = 7.4 Hz, 1H); 5.81 (t, *J* = 7.5 Hz, 1H); 5.61 (s); 5.44 (t, *J* = 6.3 Hz, 1H); 5.24 (s, 1H), 5.02 (s); 2.50 (s), 2.05 (s), 1.85 (s, 3H), 1.62 (s, 3H); HRMS (EI): *m/z* calcd for C<sub>45</sub>H<sub>32</sub>IrN<sub>3</sub>O<sup>+</sup>: [M]<sup>+</sup> 823.2169, found 823.2193.

## References

- (1) Witkowska, E.; Wiosna-Salyga, G.; Głowacki, I.; Orwat, B.; Oh, M-j.; Kownacki, I.; Kubicki, M.; Gierczyk, B.; Dutkiewicz, M.; Cieszko, P.; Luszczynska, B.; Ulanski, J.; Grzelak, I.; Hoffmann, M.; Ledwon, P.; Lapkowski, M. Effect of fluorine substitution of the β-ketoiminate ancillary ligand on photophysical properties and electroluminescence ability of new iridium(III) complexes. *J. Mater. Chem. C* **2018**, *6*, 8688–8708.

## 2. NMR spectra of 4-arylimino-2-pentanones

### $^1\text{H}$ NMR



### $^{13}\text{C}$ NMR

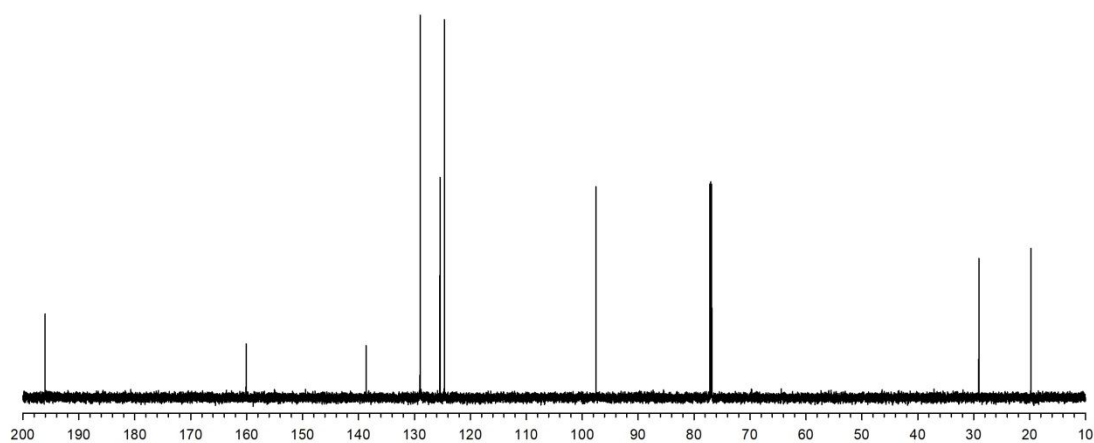
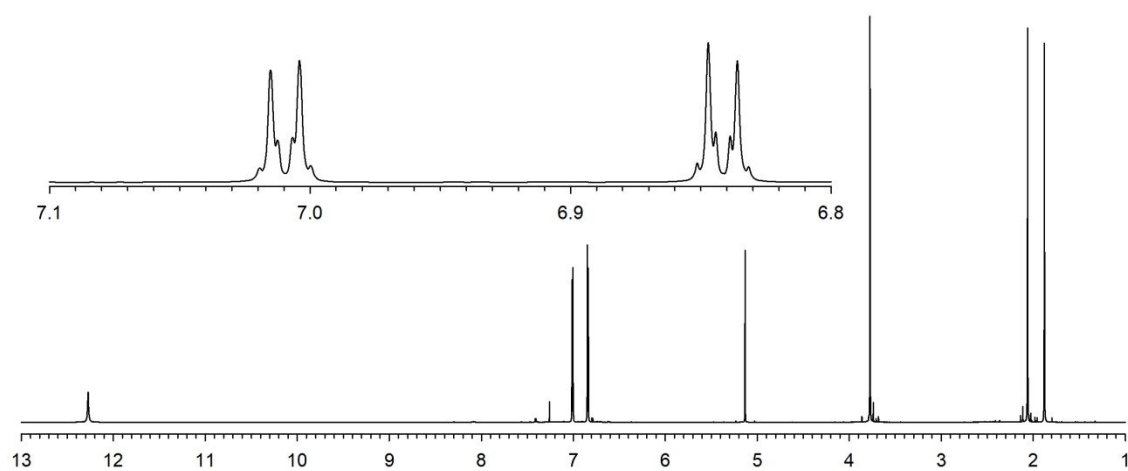


Fig. 1S. NMR spectra of 4-phenylimino-2-pentanone (**3a**)

**<sup>1</sup>H NMR**



**<sup>13</sup>C NMR**

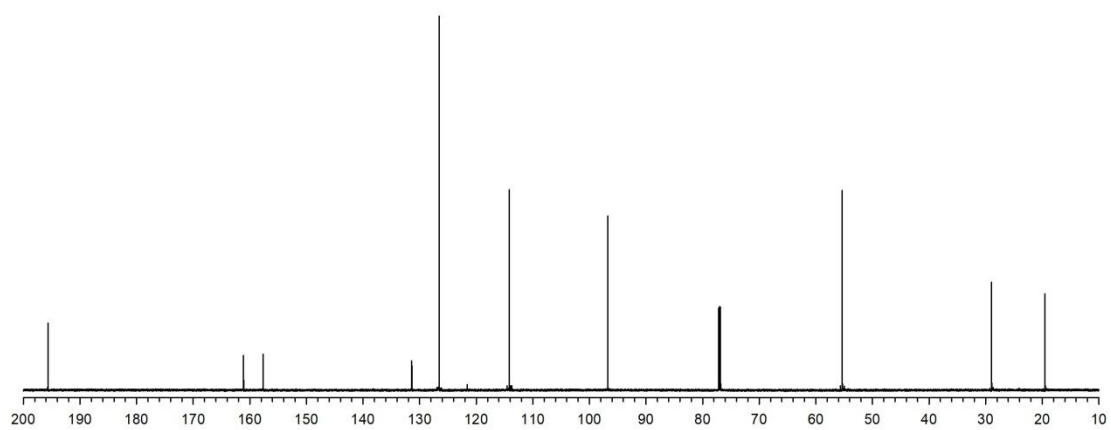
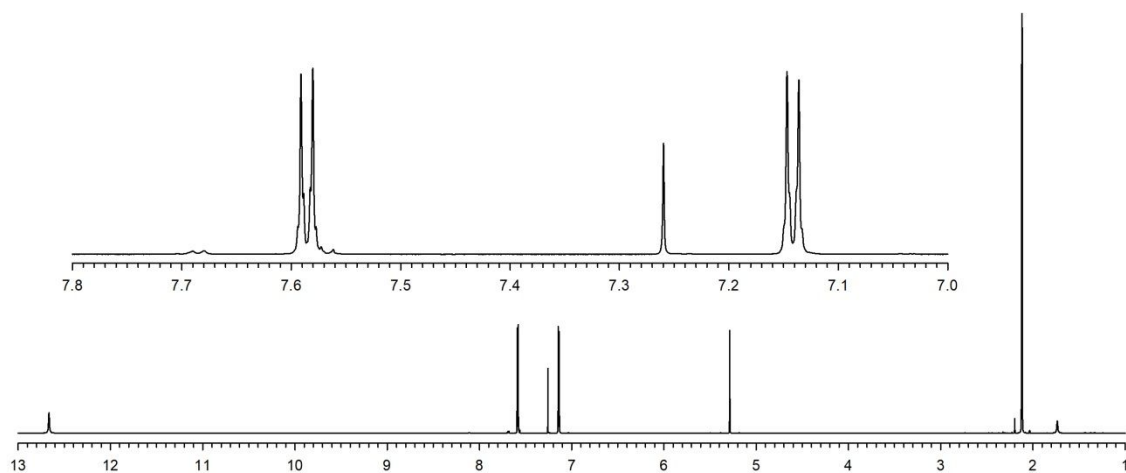


Fig. 2S. NMR spectra of 4-(4-methoxyphenyl)imino-2-pentanone (**3b**)

**<sup>1</sup>H NMR**



**<sup>13</sup>C NMR**

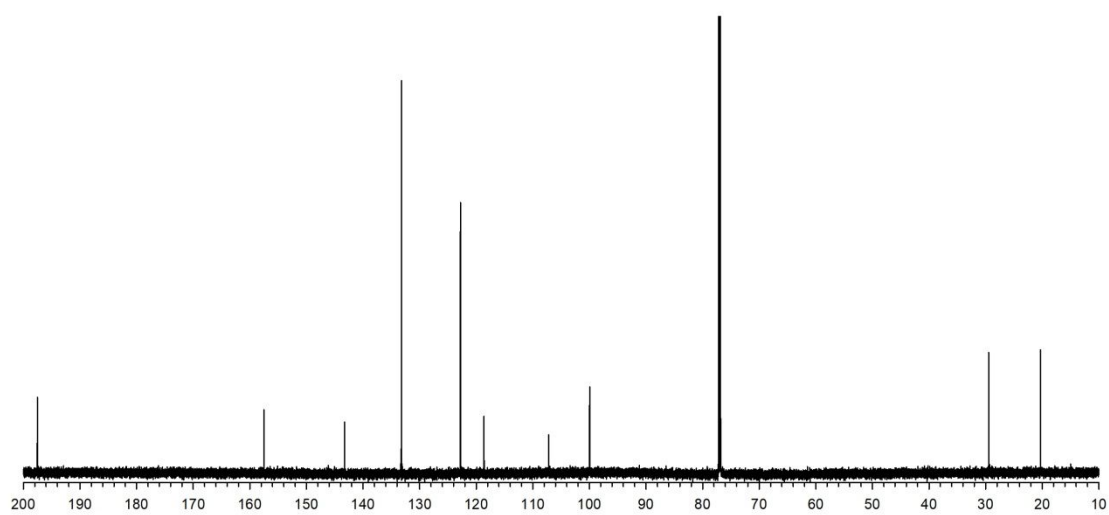
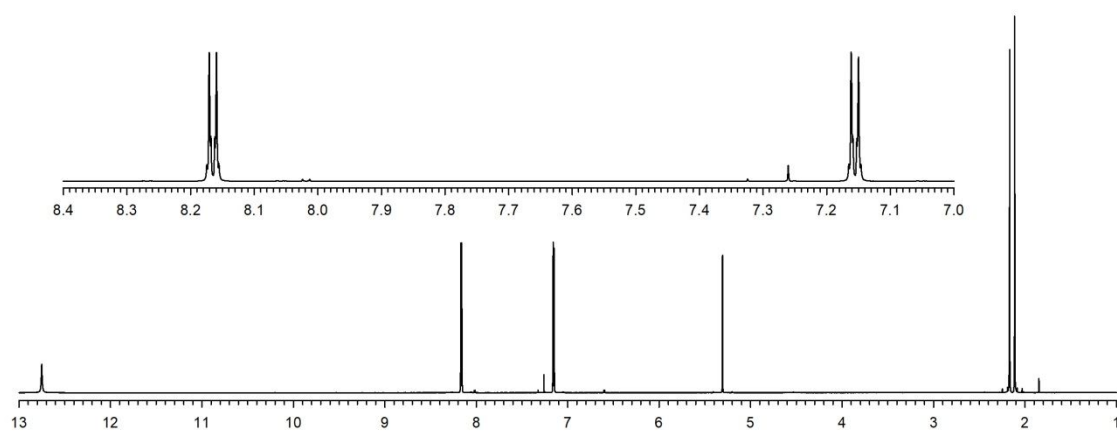


Fig. 3S. NMR spectra of 4-(4-cyanophenyl)imino-2-pentanone (**3c**)

<sup>1</sup>H NMR



<sup>13</sup>C NMR

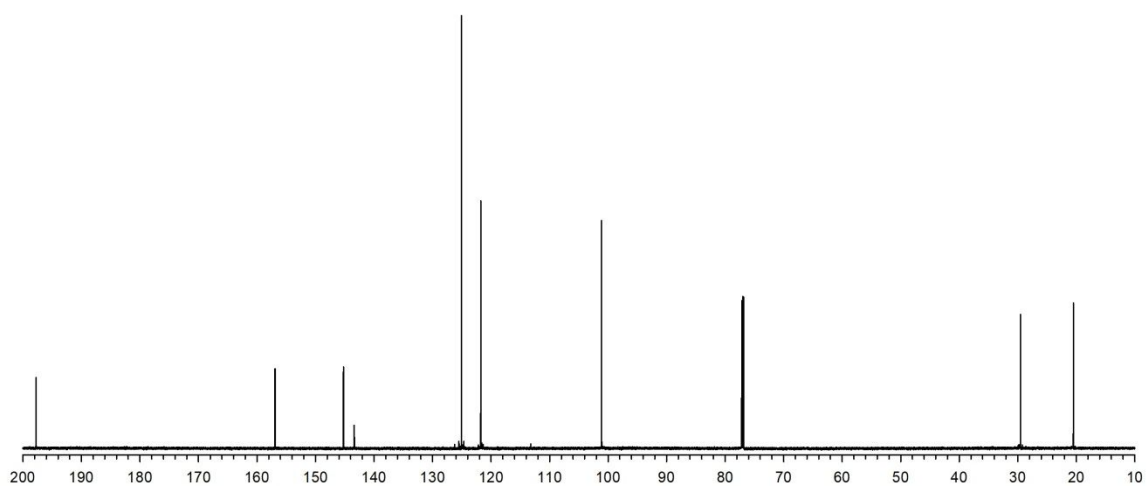
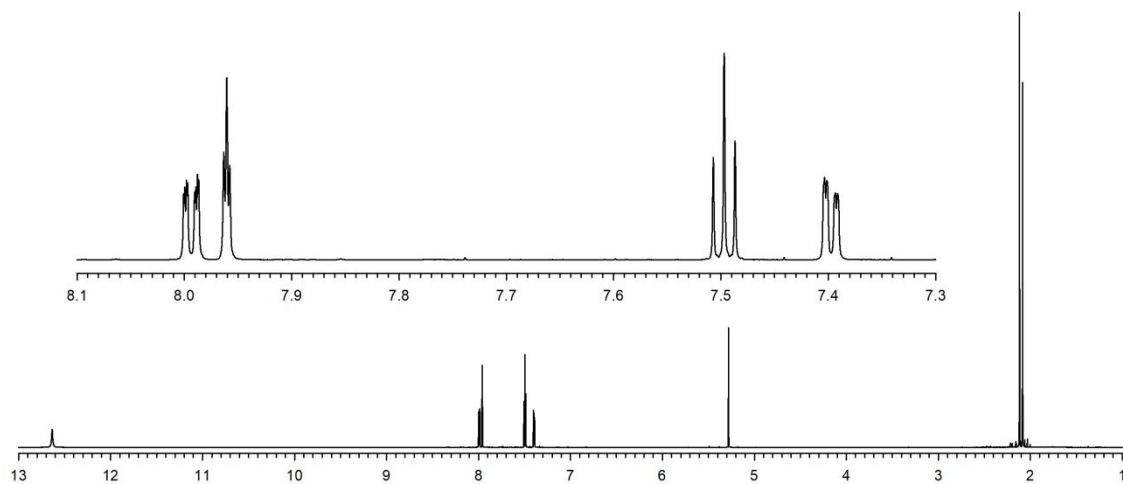


Fig. 4S. NMR spectra of 4-(4-nitrophenyl)imino-2-pentanone (**3d**)

**$^1\text{H}$  NMR**



**$^{13}\text{C}$  NMR**

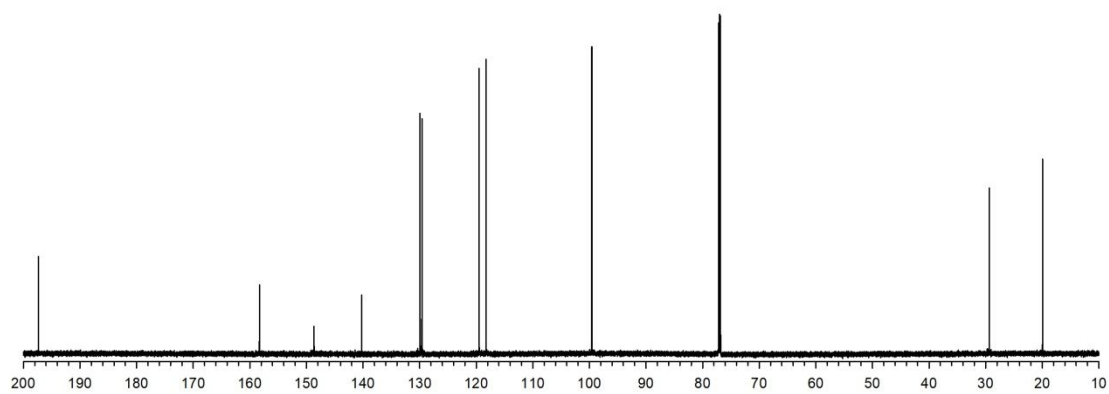
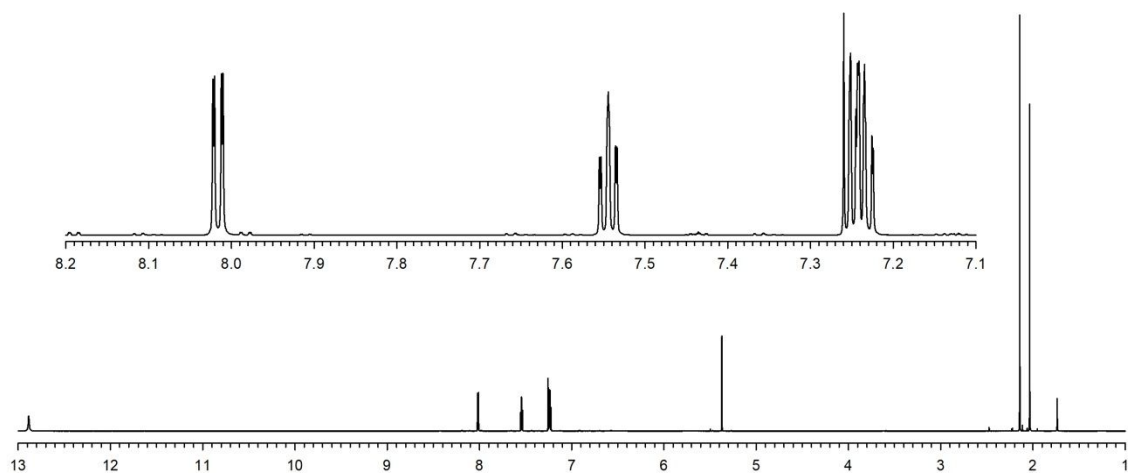


Fig. 5S. NMR spectra of 4-(3-nitrophenyl)imino-2-pentanone (**3e**)

<sup>1</sup>H NMR



<sup>13</sup>C NMR

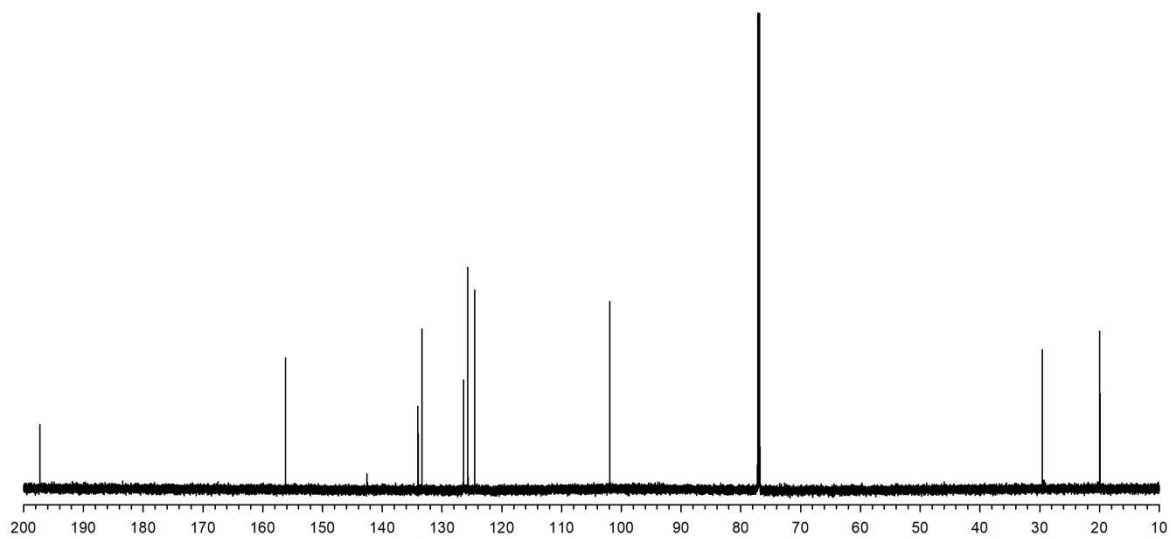
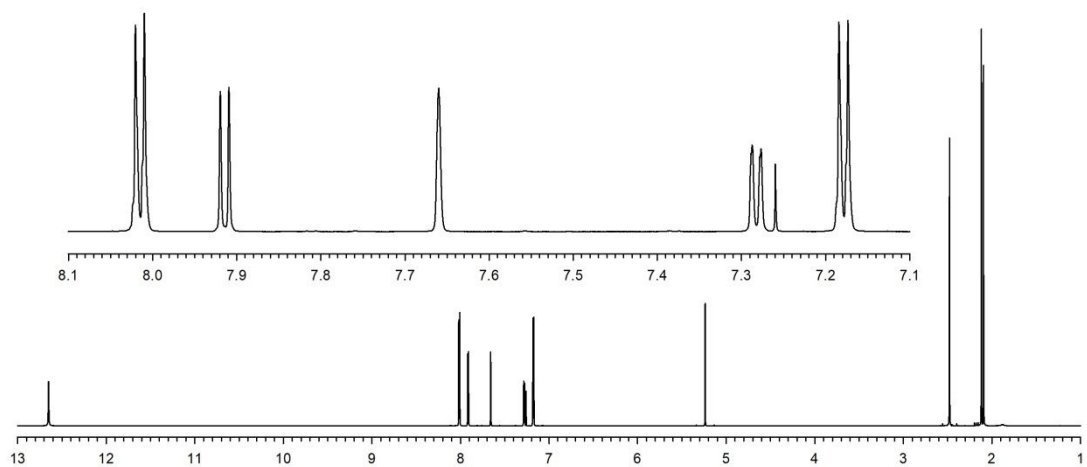


Fig. 6S. NMR spectra of 4-(2-nitrophenyl)imino-2-pentanone (**3f**)

**<sup>1</sup>H NMR**



**<sup>13</sup>C NMR**

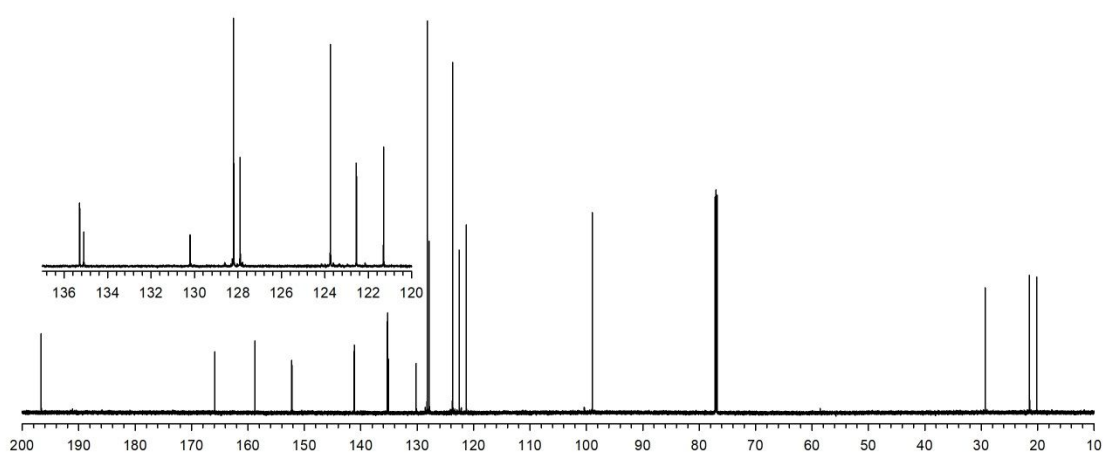
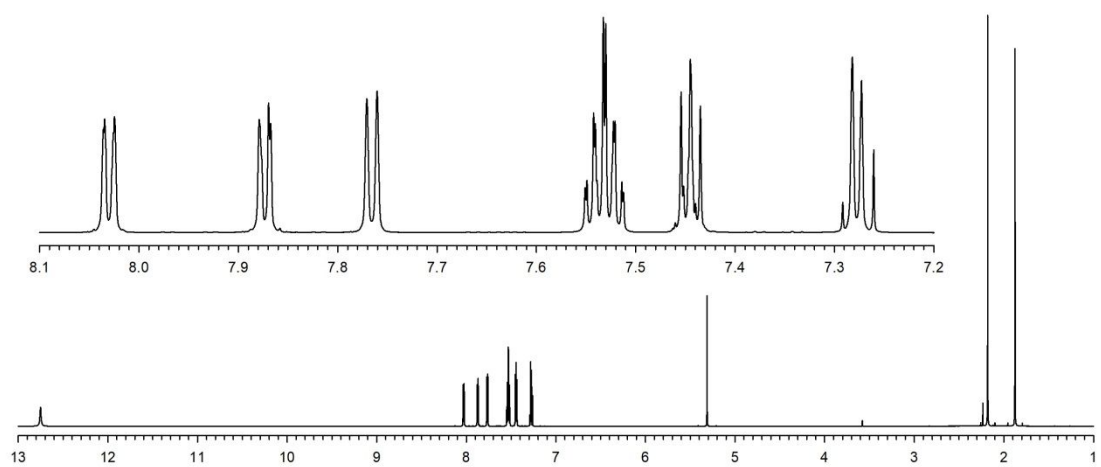


Fig. 7S. NMR spectra of 4-(4-(5-methyl-2-benzothiazyl)phenyl)imino-2-pentanone (**3g**)

**<sup>1</sup>H NMR**



**<sup>13</sup>C NMR**

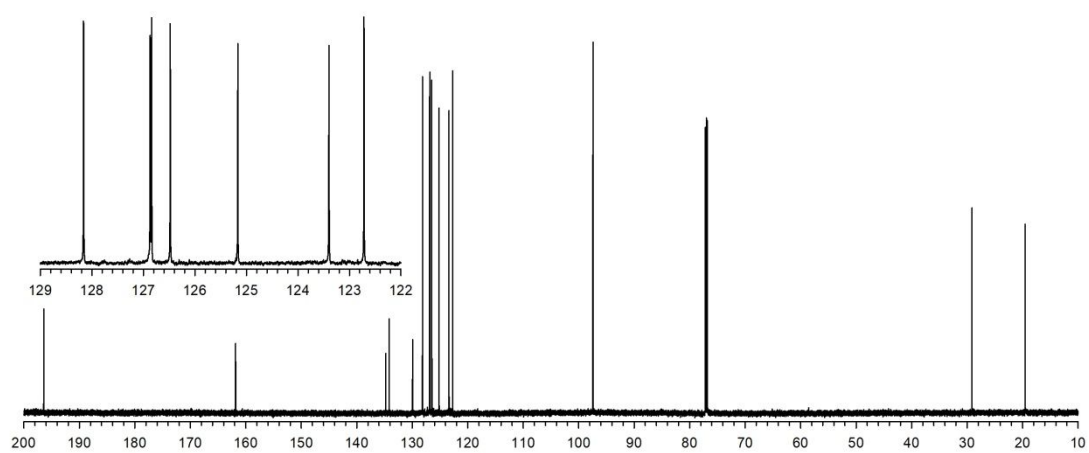
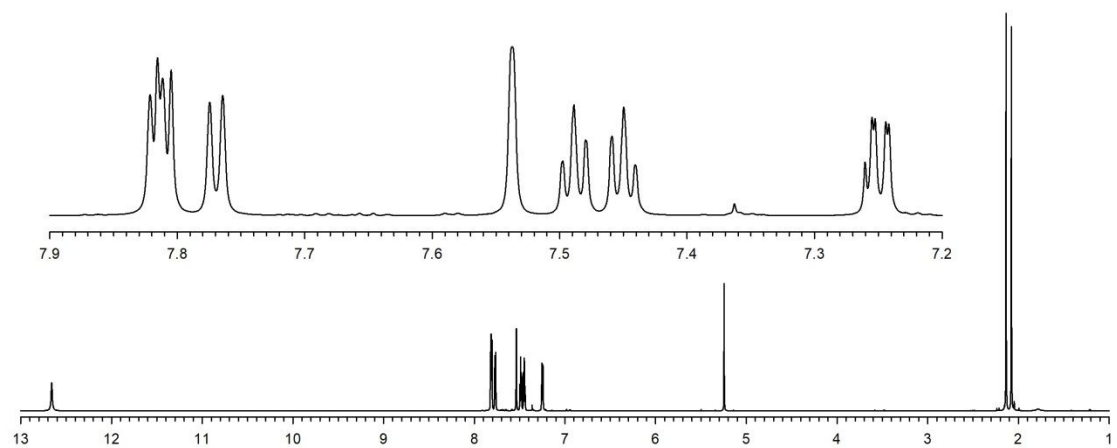


Fig. 8S. NMR spectra of 4-(1-naphthyl)imino-2-pentanone (**3h**)

**$^1\text{H}$  NMR**



**$^{13}\text{C}$  NMR**

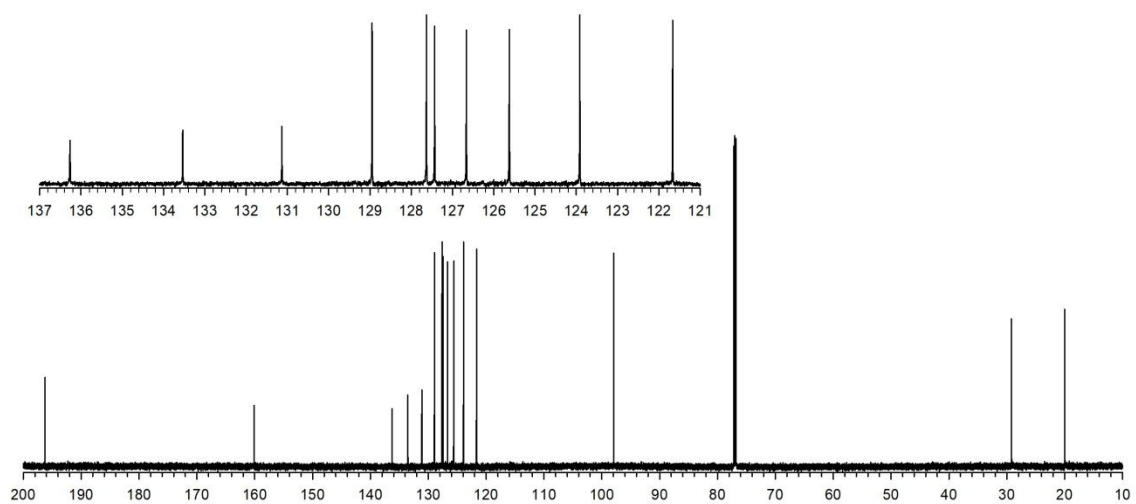
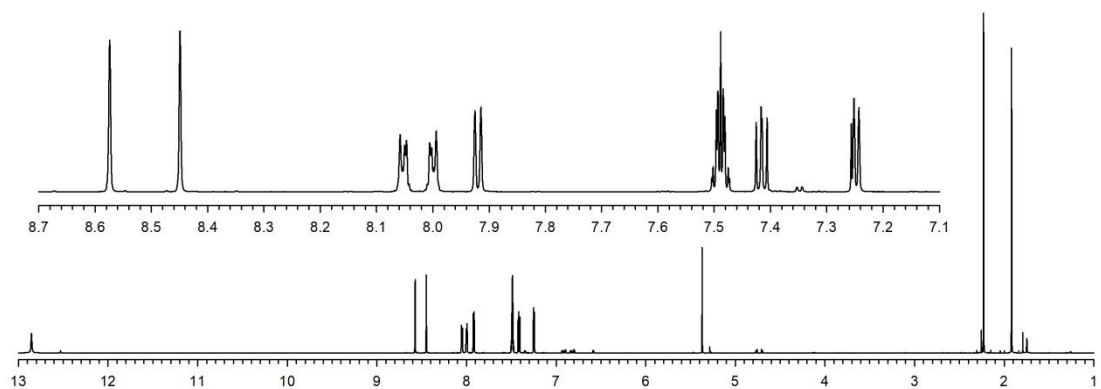


Fig. 9S. NMR spectra of 4-(2-naphthyl)imino-2-pentanone (**3i**)

### <sup>1</sup>H NMR



### <sup>13</sup>C NMR

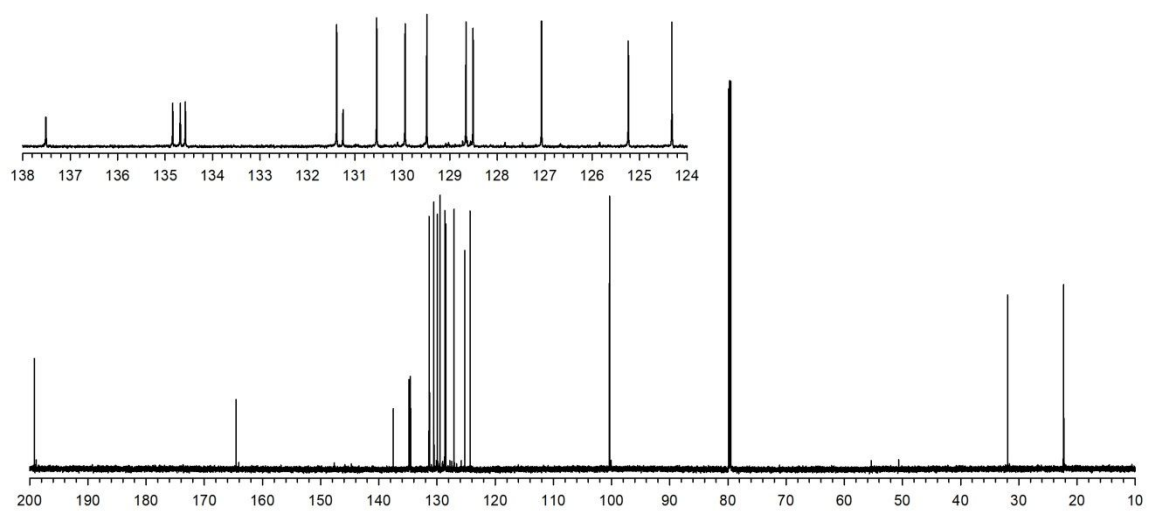
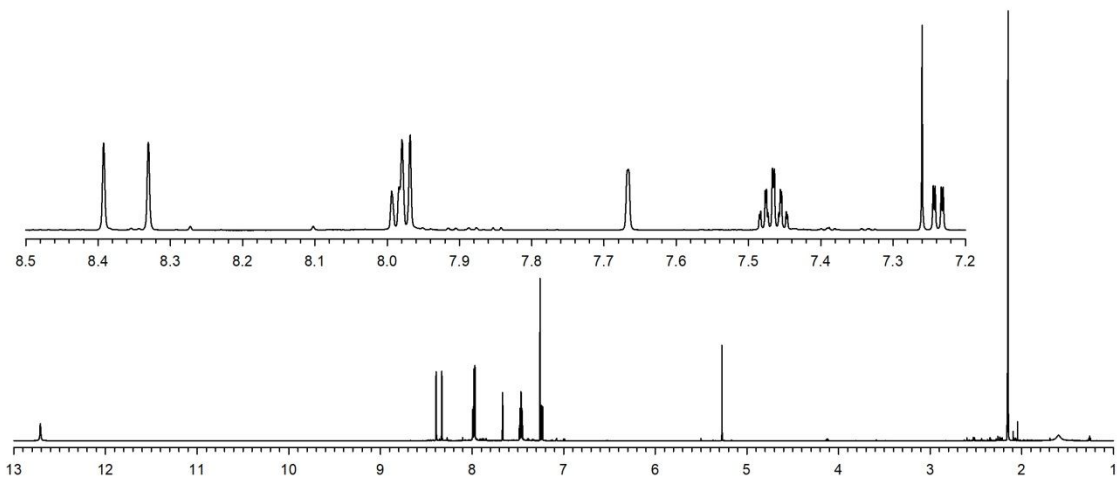


Fig. 10S. NMR spectra of 4-(1-anthracenyl)imino-2-pentanone (**3j**)

### $^1\text{H}$ NMR



### $^{13}\text{C}$ NMR

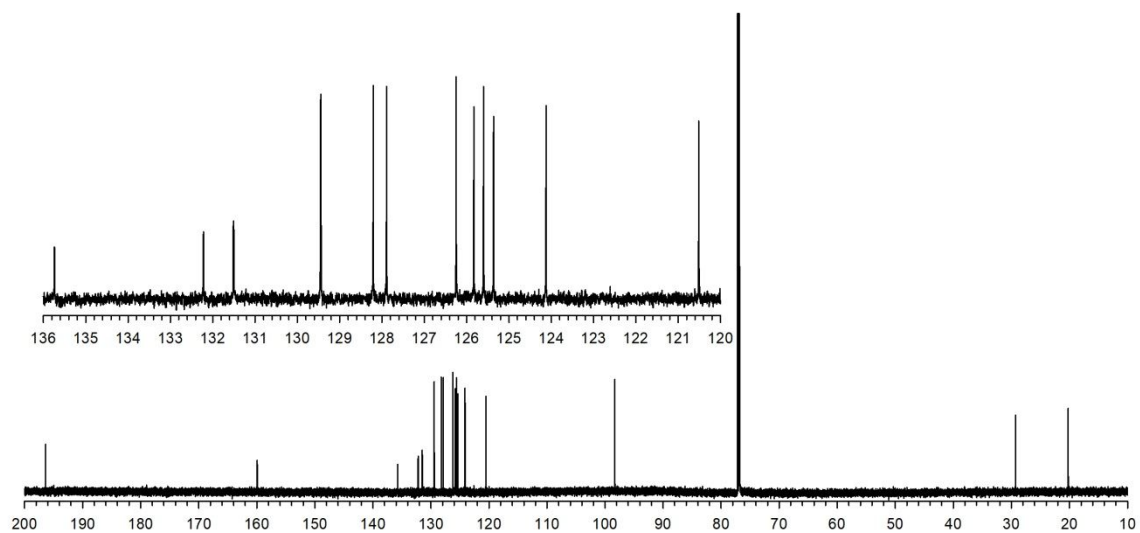
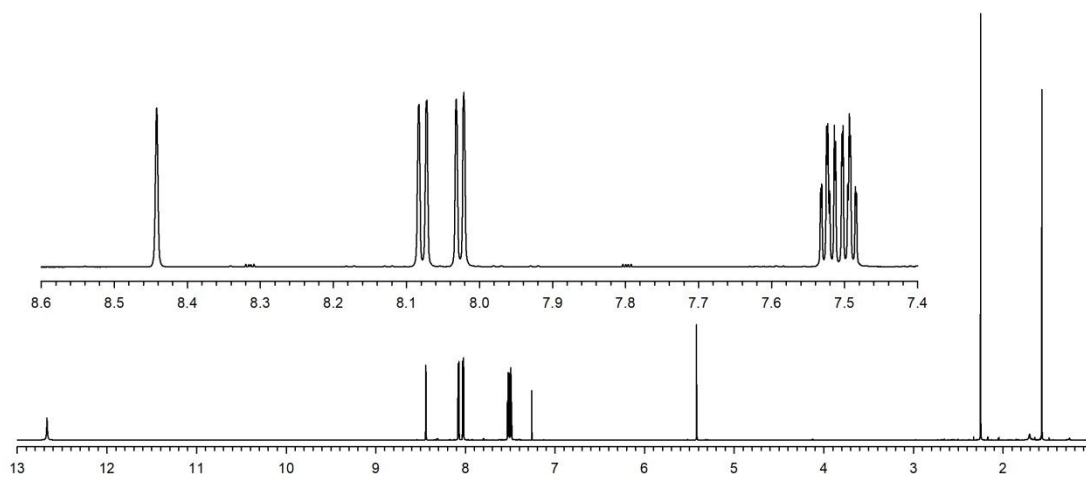


Fig. 11S. NMR spectra of 4-(2-anthracenyl)imino-2-pentanone (**3k**)

**$^1\text{H}$  NMR**



**$^{13}\text{C}$  NMR**

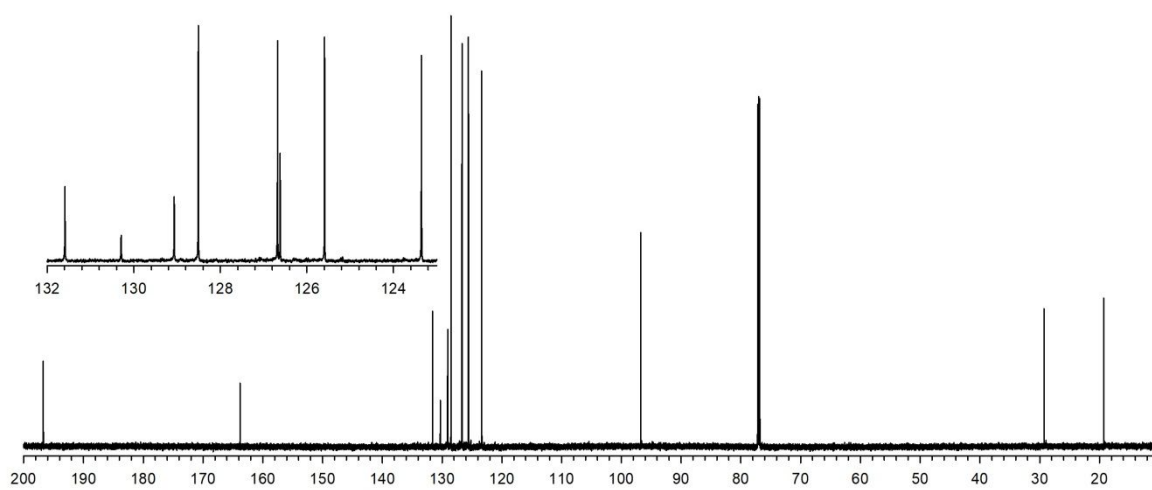


Fig. 12S. NMR spectra of 4-(9-anthracenyl)imino-2-pentanone (**3I**)

### 3. NMR spectra of iridium(III) complexes

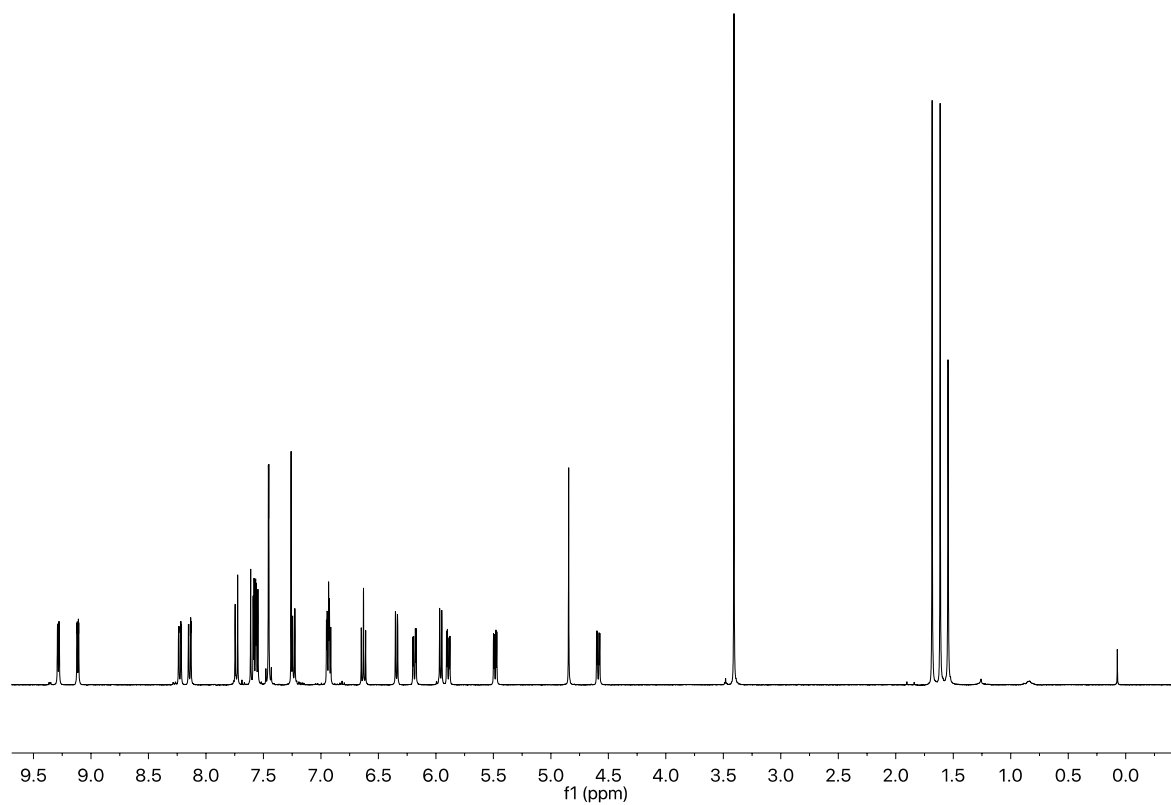


Fig. 13S.  $^1\text{H}$  NMR spectrum of **5b**

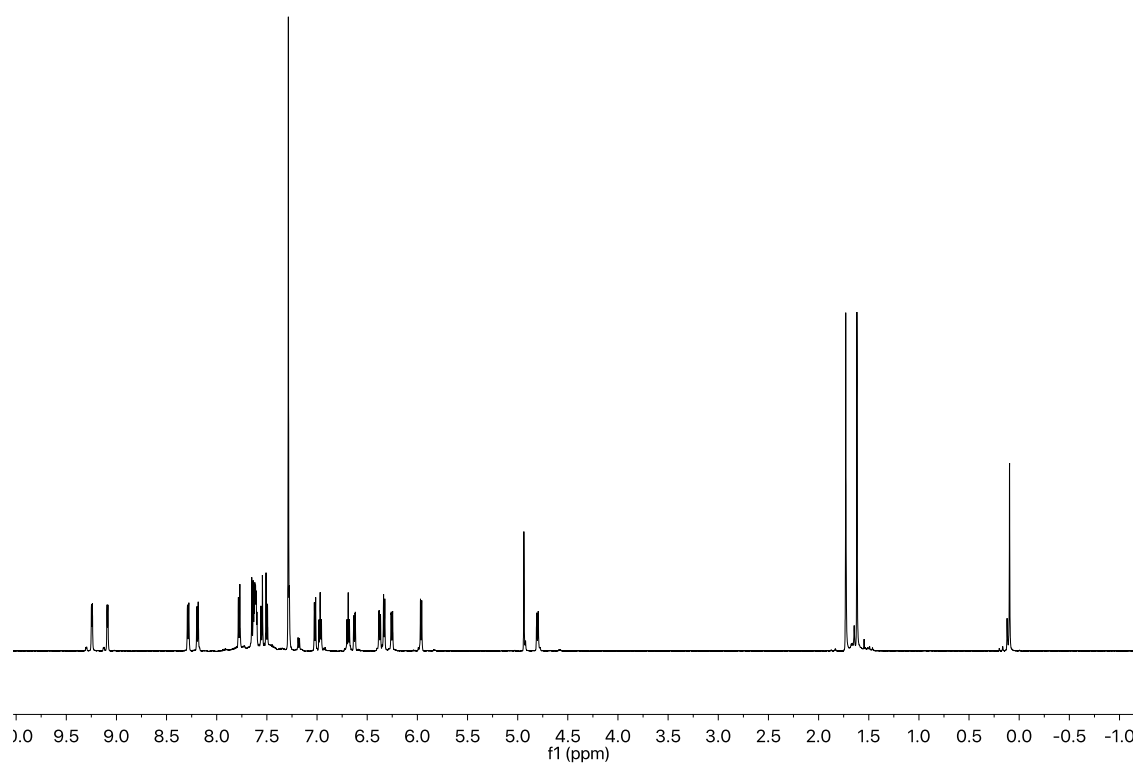


Fig. 14S.  $^1\text{H}$  NMR spectrum of **5c**

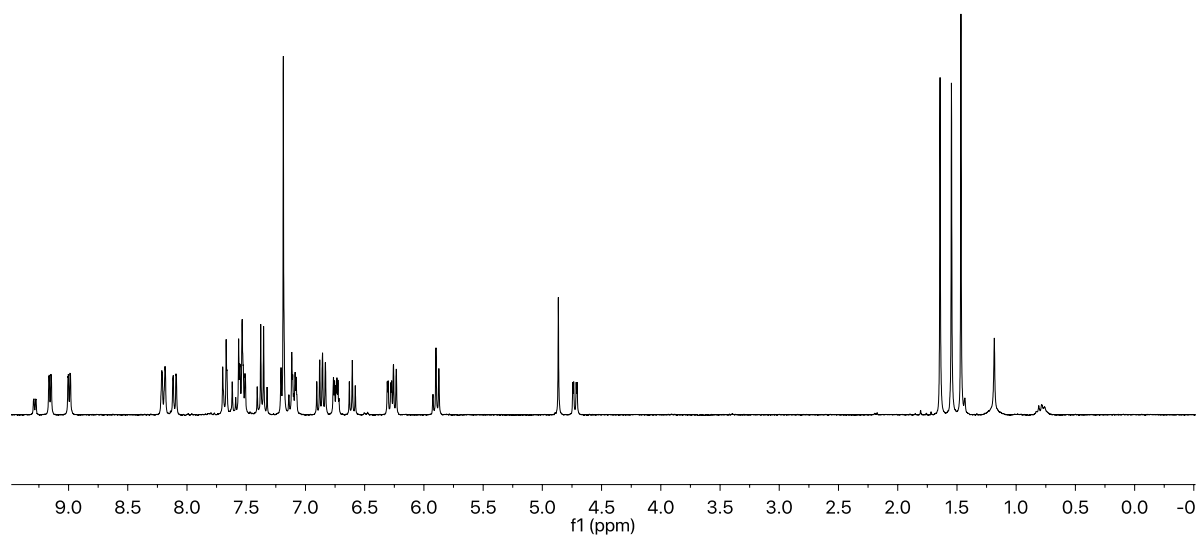


Fig. 15S. <sup>1</sup>H NMR spectrum of **5d**

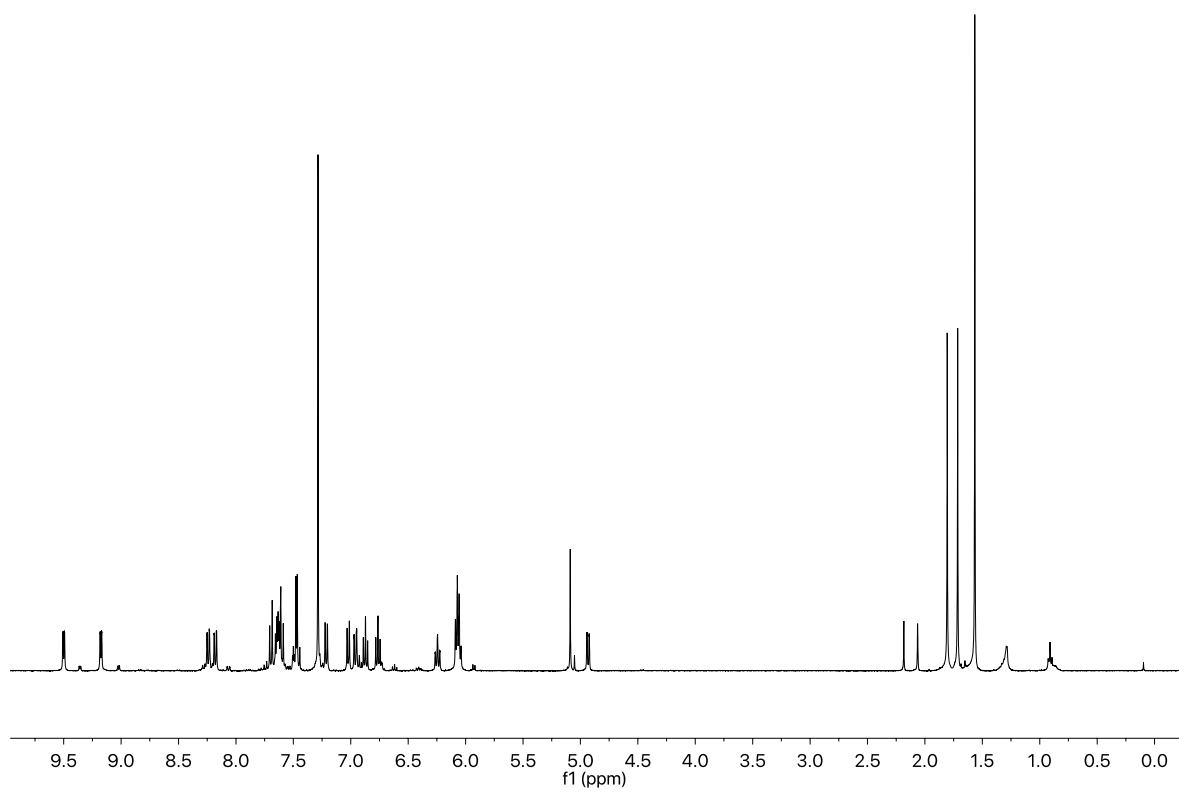


Fig. 16S. <sup>1</sup>H NMR spectrum of **5f**

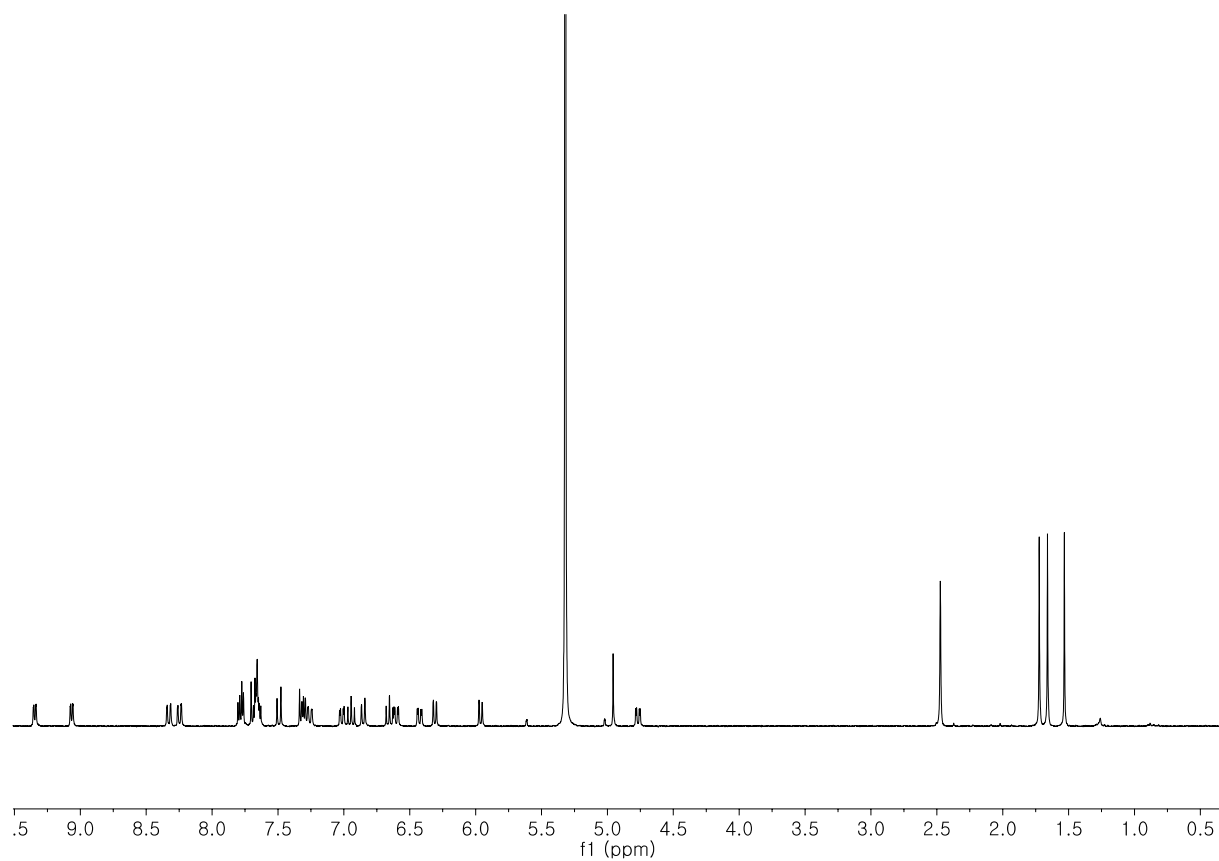


Fig. 17S. <sup>1</sup>H NMR spectrum of **5g**

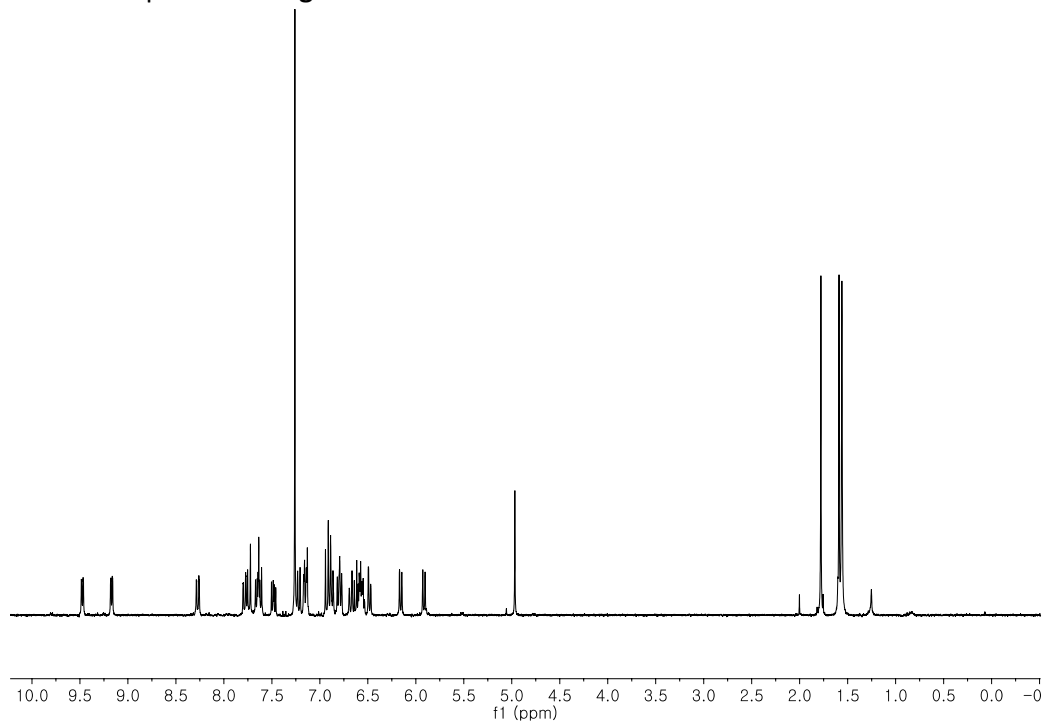


Fig. 18S. <sup>1</sup>H NMR spectrum of **5h**

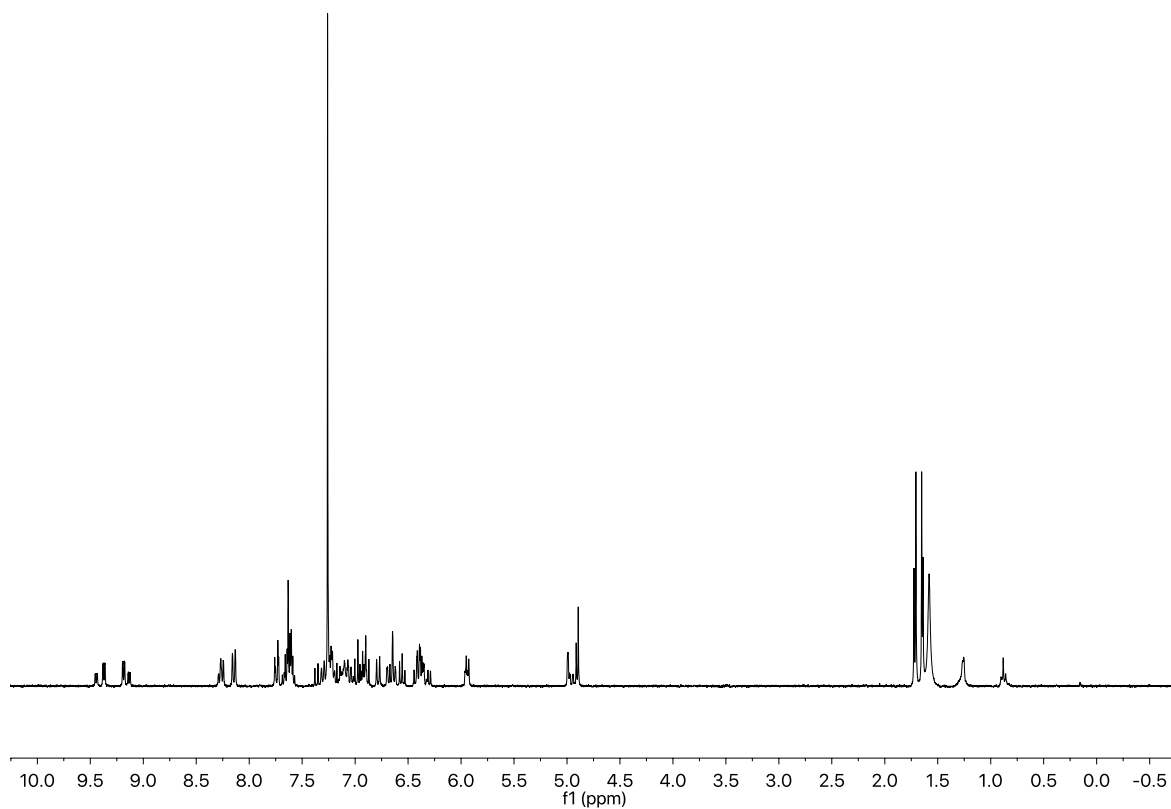


Fig. 19S. <sup>1</sup>H NMR spectrum of **5i**

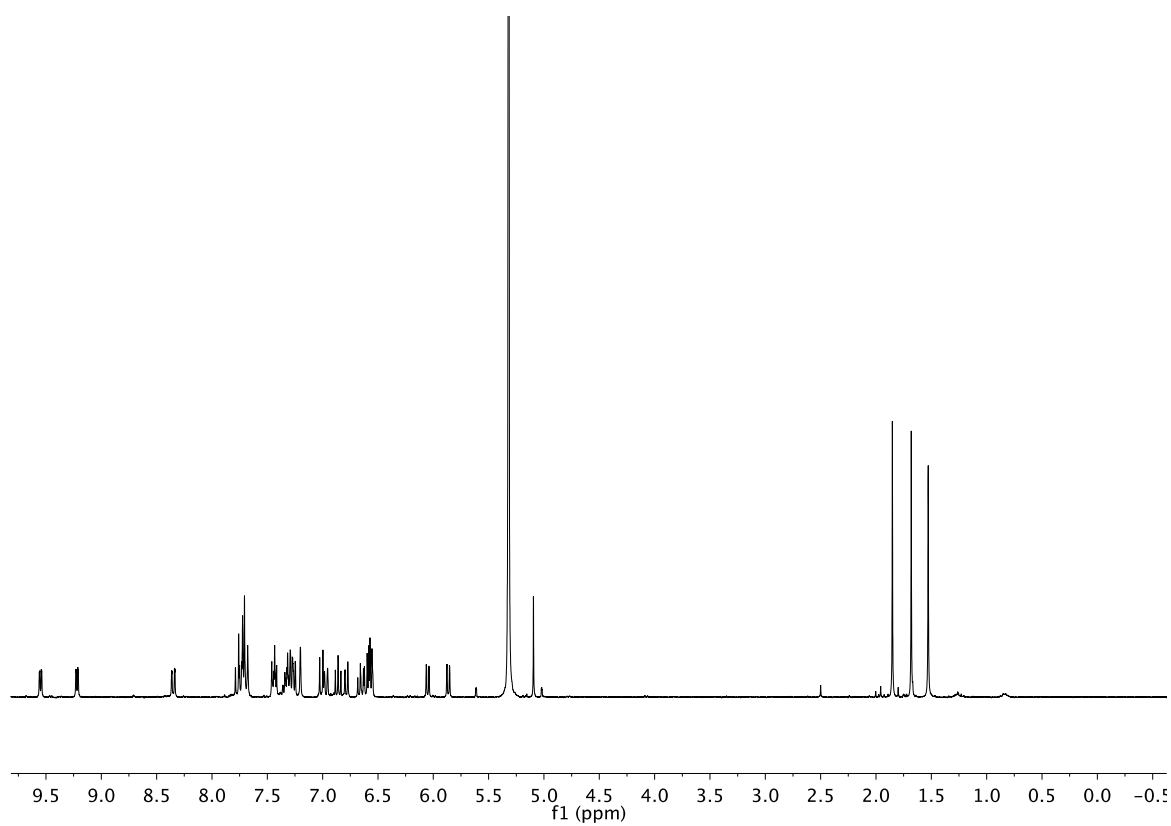


Fig. 20S. <sup>1</sup>H NMR spectrum of **5j**

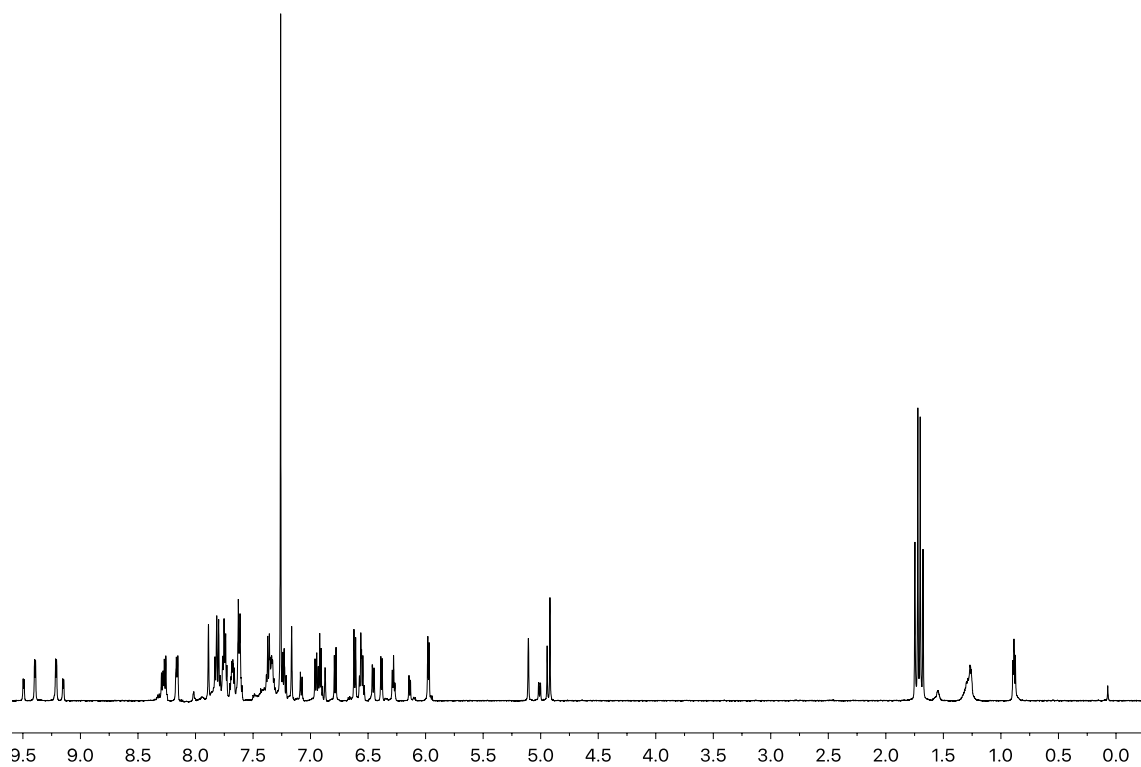


Fig. 21S.  $^1\text{H}$  NMR spectrum of **5k**

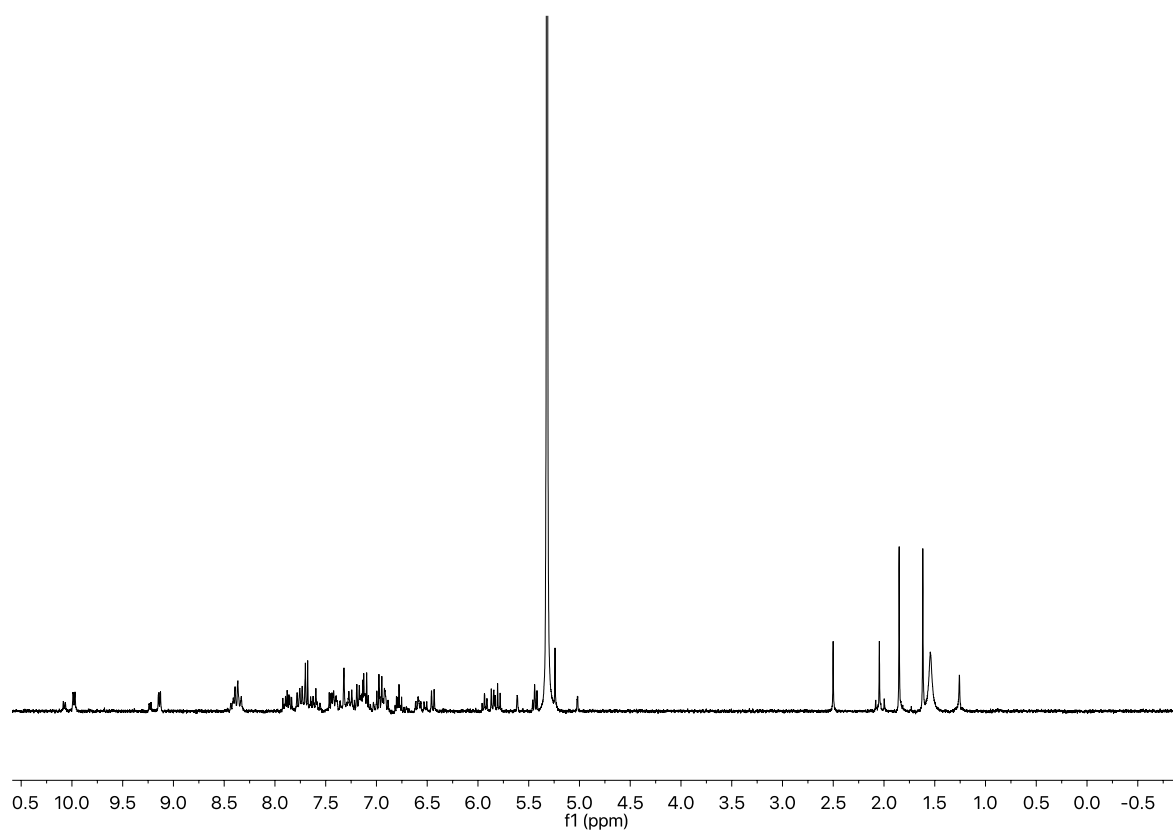


Fig. 22S.  $^1\text{H}$  NMR spectrum of **5l**

#### 4. X-Ray analysis data

**Table 1S.** Crystal data, data collection and structure refinement

Compound	3d	3h	3j	3l	5g	5j	5l
Formula	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	2(C <sub>15</sub> H <sub>15</sub> NO)·H <sub>2</sub> O	C <sub>19</sub> H <sub>17</sub> NO	C <sub>19</sub> H <sub>17</sub> NO	C <sub>45</sub> H <sub>33</sub> IrN <sub>4</sub> OS	C <sub>45</sub> H <sub>32</sub> IrN <sub>3</sub> O	C <sub>45</sub> H <sub>32</sub> IrN <sub>3</sub> O
Formula weight	220.23	468.58	275.33	275.33 /c	870.01	822.93	822.93
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /n	I2/a	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
a(Å)	4.3661(7)	16.8762(4)	7.7643(3)	8.8402(4)	8.7504(2)	15.39264(9)	9.53788(14)
b(Å)	13.1478(18)	8.2994(2)	14.0865(8)	15.0895(4)	32.0328(12)	12.27706(7)	19.5224(3)
c(Å)	18.853(3)	18.2491(5)	13.5190(6)	22.5145(8)	13.1546(5)	19.49316(13)	17.3966(4)
β(°)	93.000(15)	103.665(2)	101.690(4)	97.237(4)	92.144(3)	109.5070(7)	95.4280(17)
V(Å <sup>3</sup> )	1080.8(3)	2483.66(11)	1447.93(12)	2979.38(19)	3684.7(2)	3472.30(4)	3224.76(10)
Z	4	4	4	8	4	4	4
D <sub>x</sub> (g cm <sup>-3</sup> )	1.353	1.253	1.263	1.228	1.568	1.574	1.695
F(000)	464	1000	584	1168	1728	1632	1632
μ(mm <sup>-1</sup> )	0.100	0.081	0.078	0.076	3.721	7.752	4.184
Reflections:							
collected	4926	12884	6148	27337	21762	33752	14603
unique (R <sub>int</sub> )	1897 (0.019)	2720 (0.013)	2904 (0.016)	5242 (0.035)	7479 (0.057)	7195 (0.035)	6553 (0.029)
with I>2σ(I)	1507	2452	2464	4961	5645	7017	5427
R(F) [I>2σ(I)]	0.0452	0.0350	0.0362	0.0637	0.0529	0.0283	0.0278
wR(F <sup>2</sup> ) [I>2σ(I)]	0.1296	0.0914	0.0917	0.1679	0.1395	0.0803	0.0517
R(F) [all data]	0.0565	0.0389	0.0443	0.1239	0.0786	0.0288	0.0398
wR(F <sup>2</sup> ) [all data]	0.1375	0.0945	0.0981	0.1990	0.153	0.0809	0.0553
Goodness of fit	1.079	1.020	1.057	0.882	1.039	1.105	1.033
max/min Δρ (e·Å <sup>-3</sup> )	0.18/-0.17	0.24/-0.24	0.22/-0.18	0.27/-0.18	0.31/-0.22	2.79/-1.43	1.08/-0.61

**Table 2S.** Relevant geometrical features (Å, °). Max(A) is the maximum deviation from the least-squares plane through C1 – N5 atoms, A is the least-squares plane of keto-iminato fragment, A' – of Ir-ketoiminato group, B – of aromatic substituent at N5, and C and D – of two bzq planes.

	<b>3d</b>	<b>3h</b>	<b>3j</b>	<b>3l</b>	<b>5g</b>	<b>5j</b>	<b>5l</b>
C2=O2	1.237(2)	1.2571(13)	1.2553(15)	1.231(3) 1.231(3)	1.280(10)	1.265(4)	1.283(4)
C4-N5	1.357(2)	1.3430(13)	1.3523(16)	1.327(3) 1.328(3)	1.302(10)	1.313(4)	1.314(4)
N5-C6	1.388(2)	1.4277(13)	1.4169(15)	1.427(3) 1.431(3)	1.424(10)	1.437(4)	1.444(4)
O2-C2-C3-C4	-2.9(3)	1.23(17)	1.0(2)	-4.8(5) 3.5(5)	3.2(6)	4.5(5)	7.9(7)
C2-C3-C4-N5	1.7(3)	1.98(16)	-0.57(19)	2.7(5) -1.3(5)	-9.0(2)	-10.8(5)	-11.9(6)
C3-C4-N5-C6	-178.72(17)	-167.93(9)	176.23(12)	-175.2(3) 177.1(3)	171.8(5)	172.9(3)	165.7(4)
Ir1-O2A					2.135(6)	2.156(2)	2.137(2)
Ir1-N5A					2.157(6)	2.171(3)	2.183(3)
Ir1-N1B					2.028(7)	2.045(2)	2.061(3)
Ir1-N1C					2.050(7)	2.064(3)	2.045(3)
Ir1-C12B					2.006(9)	2.018(3)	2.018(4)
Ir1-C12C					2.009(8)	2.015(3)	2.005(4)
C-N-C	133.27(15)	125.26(9)	129.01(11)	126.2(2) 126.4(2)	118.8(7)	119.3(3)	118.3(3)
angles					175.2(3) 174.3(3) 173.8(3)	175.34(9) 173.97(9) 173.31(10)	176.51(13) 174.72(12) 172.38(11)
Max(A)	0.0216(12)	-0.1224(7)	0.0341(9)	0.057(3) 0.042(3)	0.116(6)	0.118(2)	0.196(3)
A/B	12.36(11)	61.29(5)	47.36(4)	85.10(11) 83.06(11)	89.8(4)	79.17(19)	89.11(14)
A'/B					89.3	80.2	89.9
A'/C					86.2	79.2	85.8
A'/D					72.1	86.9	84.3
B/C					60.3	66.5	78.0
B/D					25.7	30.6	16.5
C/D					82.8	89.2	89.9

**Table 3S.** Intramolecular hydrogen bonds in the ligand molecules.

D	H	A	D-H	H···A	D···A	D-H···A
<b>3d</b>						
N5	H5	O2	0.90(2)	1.88(2)	2.6497(19)	141.9(17)
<b>3h</b>						
N5	H5	O2	0.911(15)	1.925(15)	2.6716(12)	137.9(12)
<b>3j</b>						
N5	H5	O2	0.918(16)	1.877(16)	2.6496(14)	140.4(14)

31						
N5A	H5A	O2A	0.86	1.97	2.642(3)	134
N5B	H5B	O2B	0.86	1.98	2.650(3)	134

**Table 4S.** Crystal data, data collection and structure refinement

Compound	<b>5f</b>	<b>5i</b>
Formula	C <sub>37</sub> H <sub>27</sub> IrN <sub>4</sub> O <sub>3</sub>	C <sub>41</sub> H <sub>30</sub> IrN <sub>3</sub> O
Formula weight	767.82	772.88
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 <sub>1</sub> /c
a(Å)	35.389(2)	16.7335(11)
b(Å)	10.0534(4)	18.7126(16)
c(Å)	19.4276(11)	20.7091(16)
β(°)	105.773(6)	108.945(8)
V(Å <sup>3</sup> )	6651.7(6)	6133.3(9)
Z	8	8
D <sub>x</sub> (g cm <sup>-3</sup> )	1.533	1.674
F(000)	3024	3056
μ(mm <sup>-1</sup> )	4.055	4.393
Reflections:		
collected	21762	25025
unique (R <sub>int</sub> )	7479 (0.057)	10773 (0.074)
with I>2σ(I)	5645	5738
R(F) [I>2σ(I)]	0.1118	0.0847
wR(F <sup>2</sup> ) [I>2σ(I)]	0.3216	0.1838
R(F) [all data]	0.1359	0.1693
wR(F <sup>2</sup> ) [all data]	0.3654	0.2162
Goodness of fit	1.414	0.971
max/min Δρ (e·Å <sup>-3</sup> )	3.06/-4.81	7.13/-1.35
CCDC number	1865883	1865886

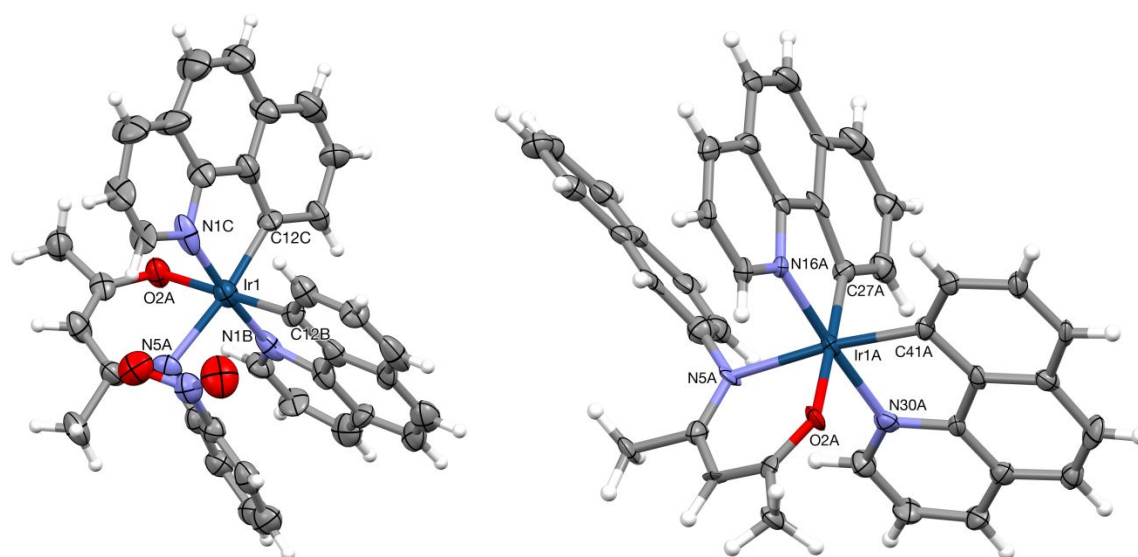
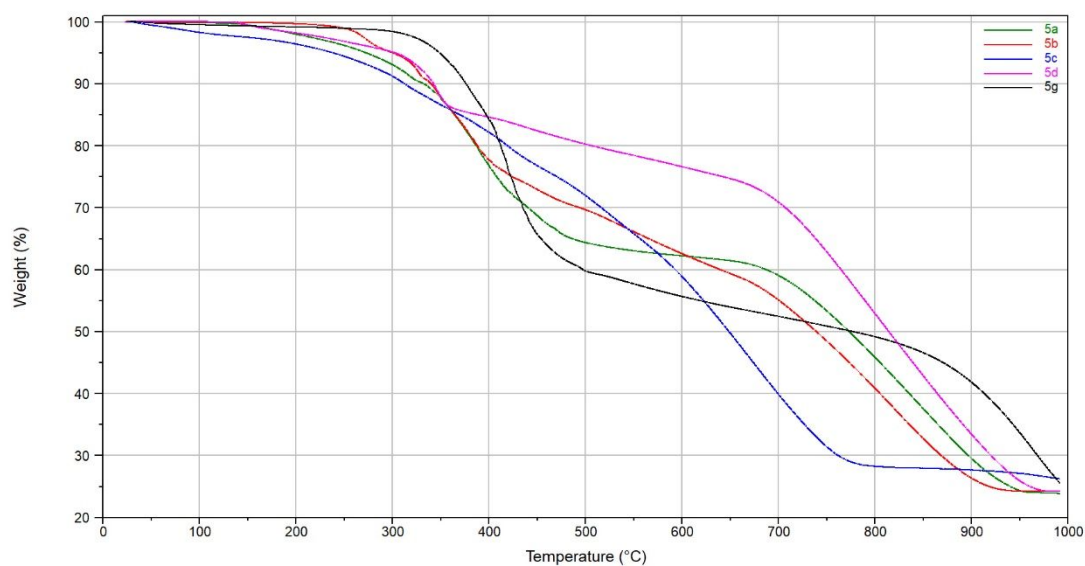
**Fig. 23S.** Perspective views of the complexes **5f** and **5i**.

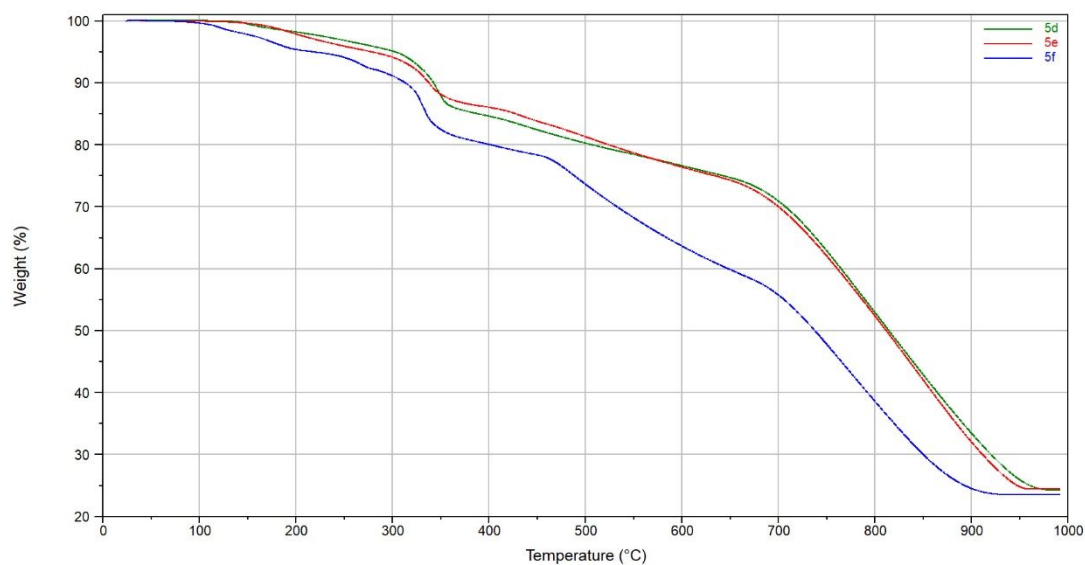
Table 5S. Conformations of the **5g** and **5i** complexes; plane codes as in Table 2S.

	<b>5g</b>	<b>5i(A)</b>	<b>5i(B)</b>
A'/B	83.5	81.4	86.3
A'/C	85.9	83.1	83.4
A'/D	84.8	89.2	87.6
B/C	60.9	57.8	56.1
B/D	26.8	32.5	30.1
C/D	87.1	87.0	85.6

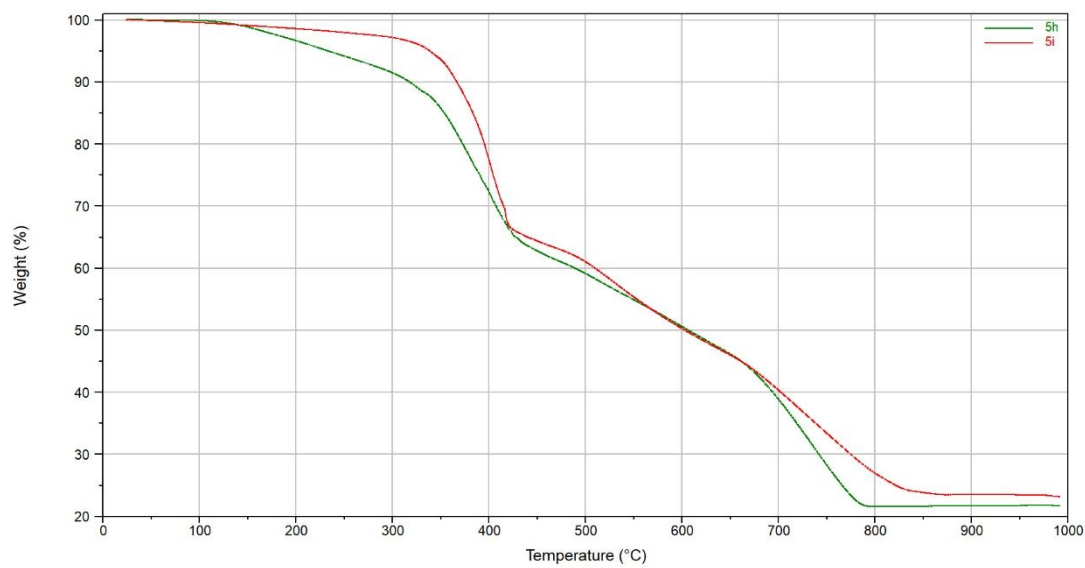
## 5. Thermal analysis curves



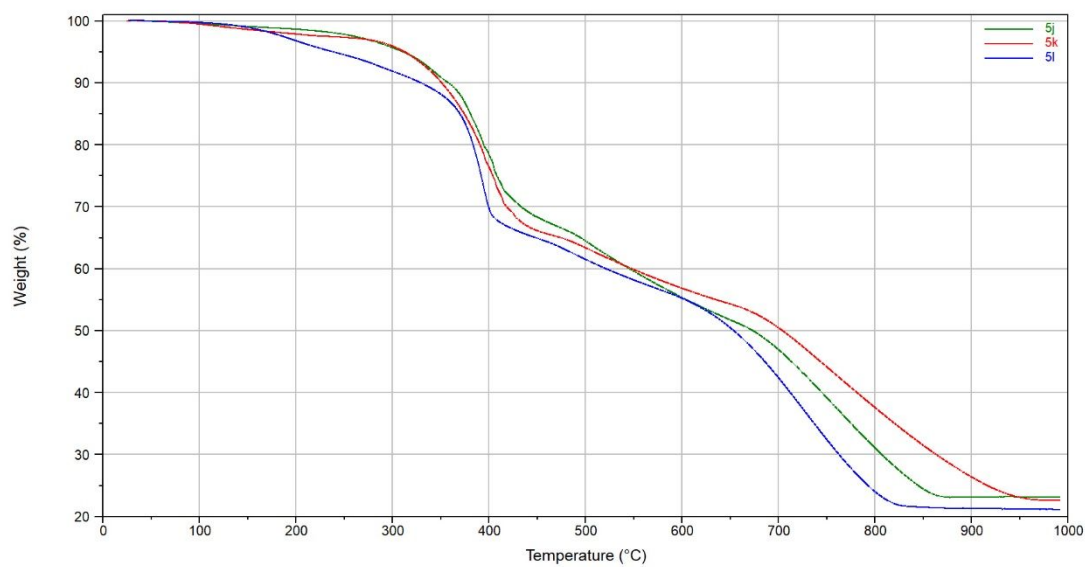
**Figure 24S.** TG curves of **5a**, **5b**, **5c**, **5d** and **5g** complexes in N<sub>2</sub> atmosphere.



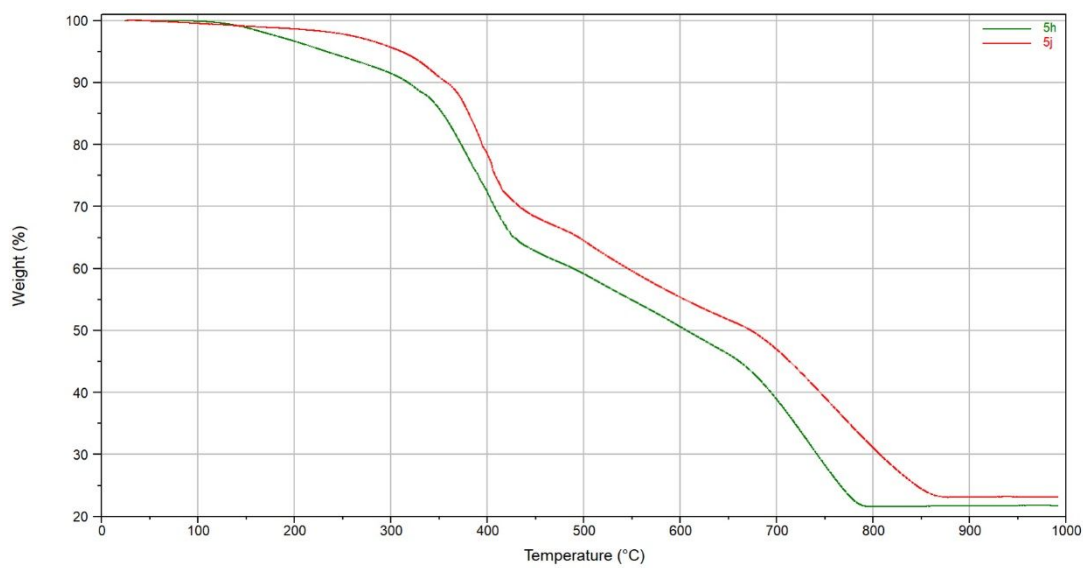
**Figure 25S.** TG curves of **5d**, **5e** and **5f** complexes in N<sub>2</sub> atmosphere.



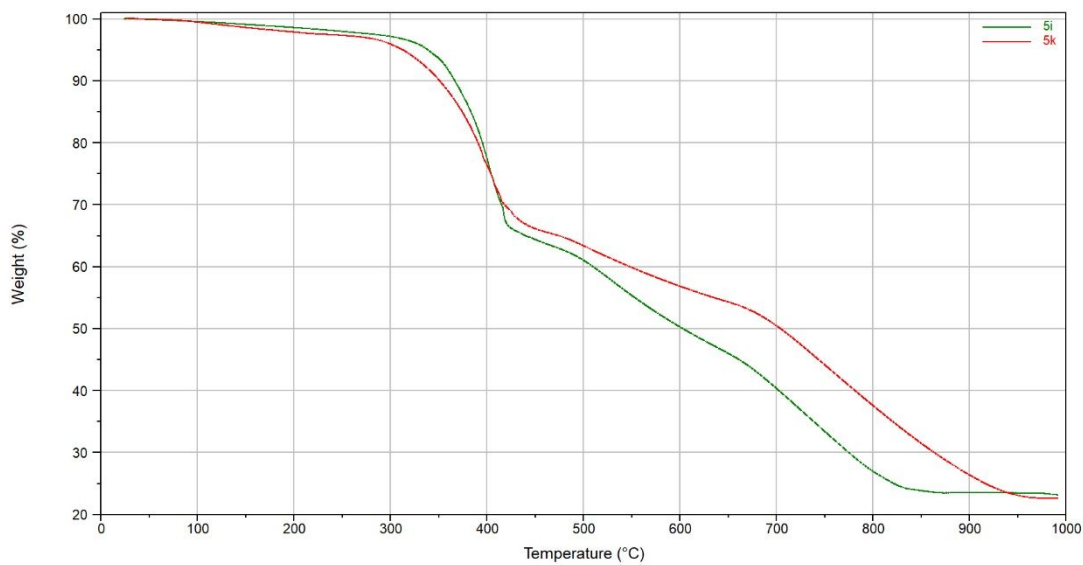
**Figure 26S.** TG curves of **5h** and **5i** complexes in N<sub>2</sub> atmosphere.



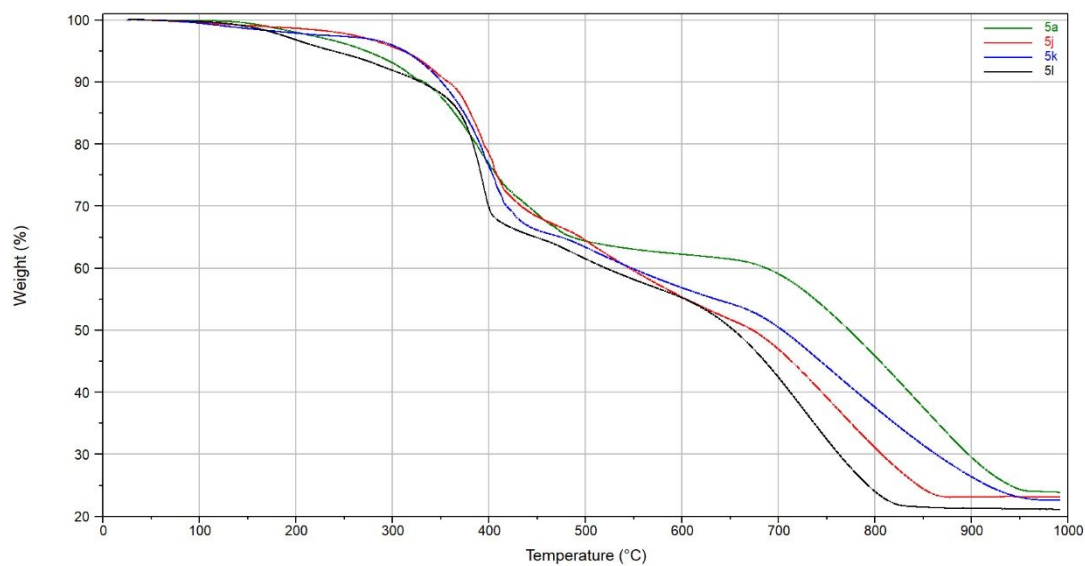
**Figure 27S.** TG curves of **5j**, **5k** and **5l** complexes in N<sub>2</sub> atmosphere.



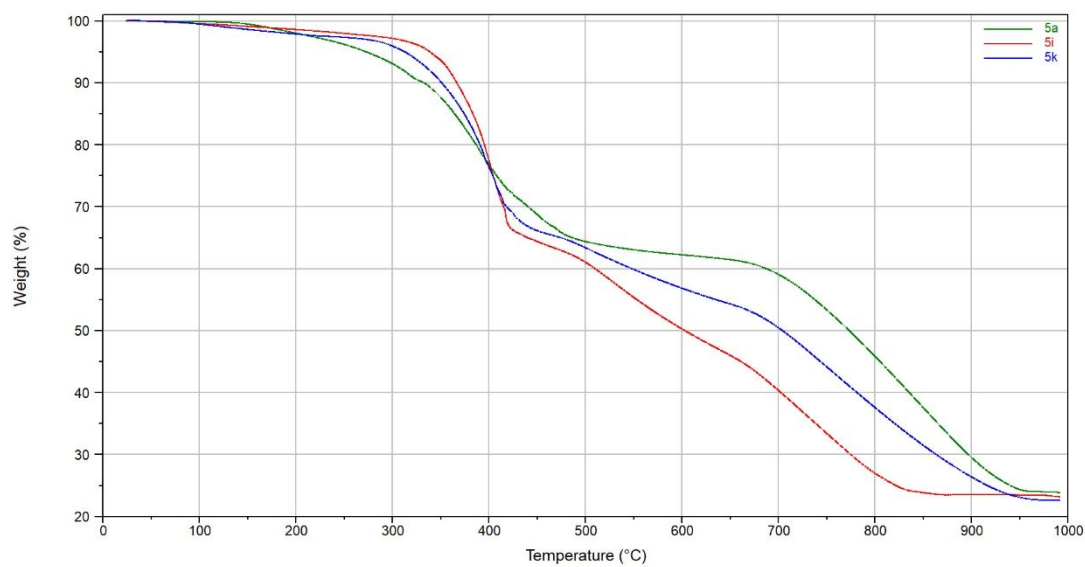
**Figure 28S.** TG curves of **5h** and **5j** complexes in N<sub>2</sub> atmosphere.



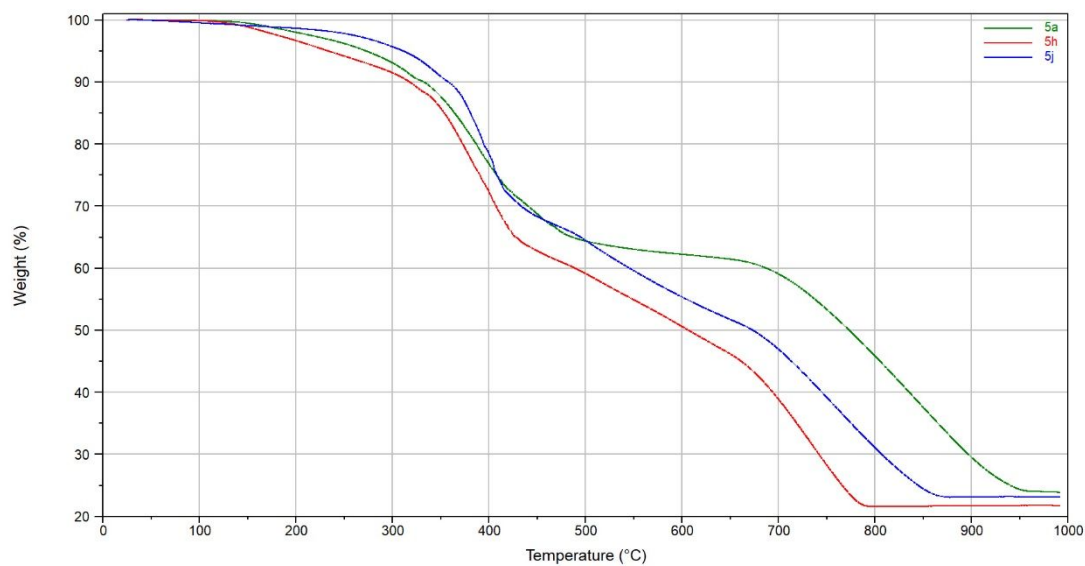
**Figure 29S.** TG curves of **5i** and **5k** complexes in N<sub>2</sub> atmosphere.



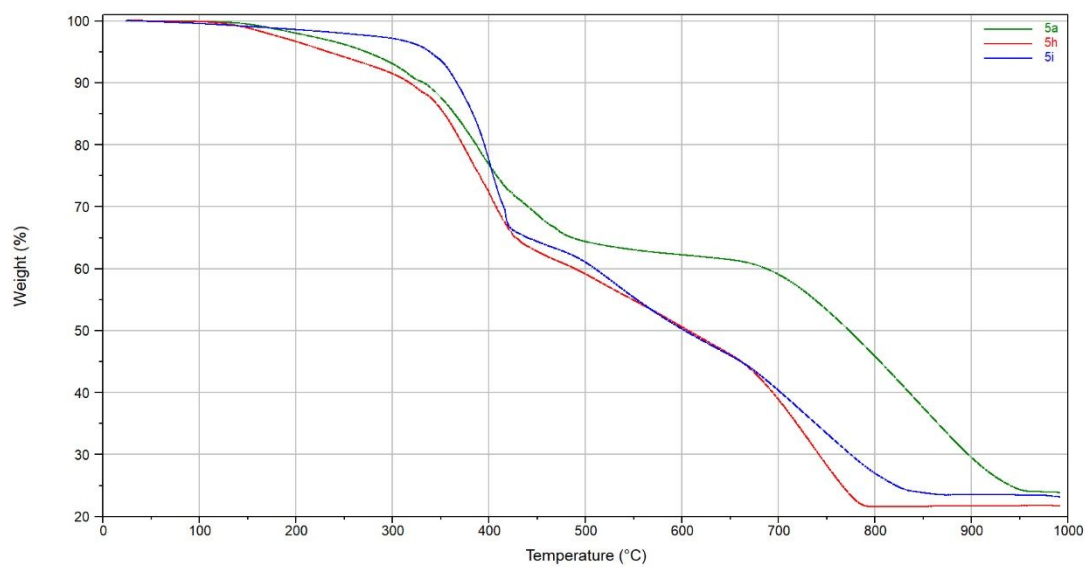
**Figure 30S.** TG curves of **5a**, **5j**, **5k** and **5l** complexes in N<sub>2</sub> atmosphere.



**Figure 31S.** TG curves of **5a**, **5i** and **5k** complexes in N<sub>2</sub> atmosphere.



**Figure 32S.** TG curves of **5a**, **5h** and **5j** complexes in N<sub>2</sub> atmosphere.



**Figure 33S.** TG curves of **5a**, **5h** and **5i** complexes in N<sub>2</sub> atmosphere.

## 6. Cyclic voltammetry measurements

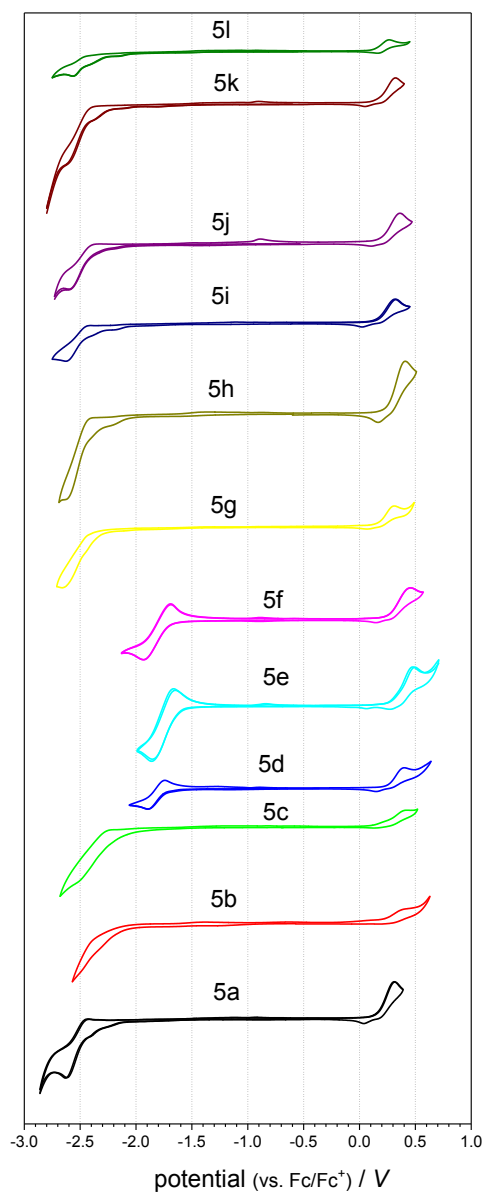


Fig. 34S. Cyclic voltammetry of compounds recorded in THF/0.1 M Bu<sub>4</sub>NBF<sub>4</sub> electrolyte; scan rate 100 mV/s; concentration 2 mM.

## 7. DFT calculation data

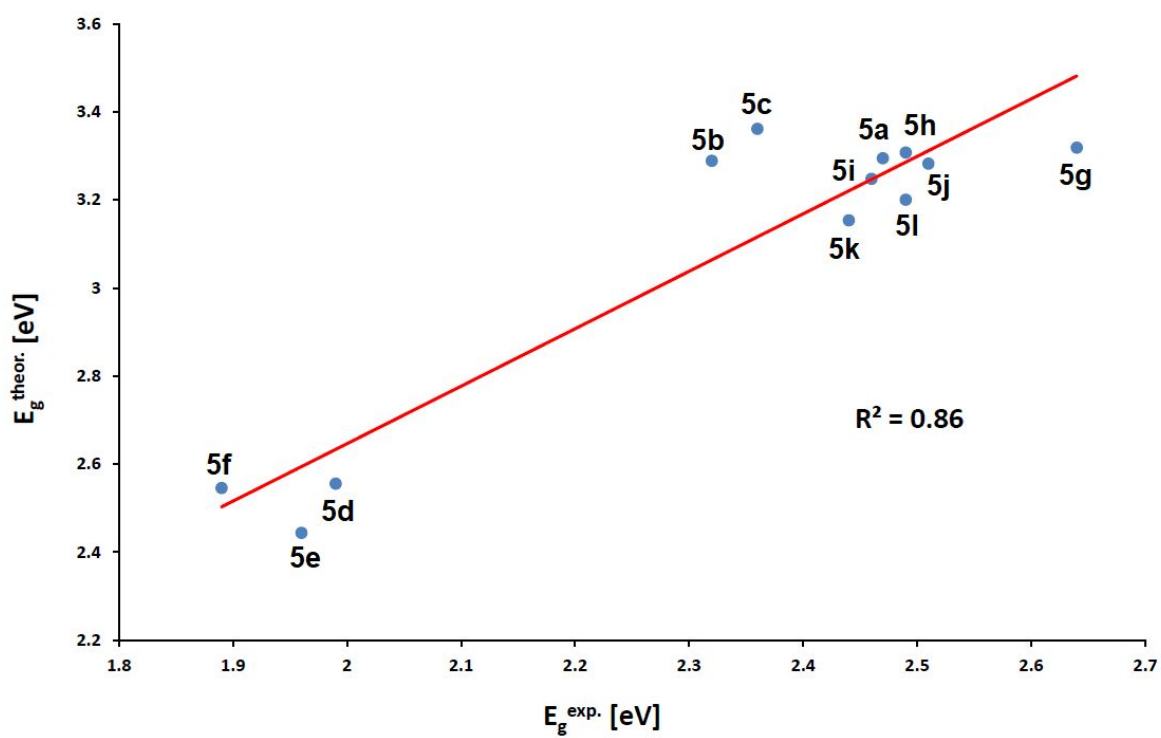


Fig. 35S. Theoretical  $E_g^{\text{theor.}}$  calculated at the B3LYP/SDD/6-311++G(d,p) level of theory vs experimental values  $E_g^{\text{exp.}}$ .

**Table 6S.** The energy levels and HOMO-LUMO energy gaps for the studied complexes (in eV) calculated at the B3LYP/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	LUMO+1 [eV]	LUMO+2 [eV]	$E_g^{\text{theor.}}$ [eV]	$E_g^{\text{exp.}}$ [eV]
5a	-5.28	-1.97	-1.95	-1.34	3.31	2.49
5b	-5.25	-1.96	-1.94	-1.33	3.29	2.32
5c	-5.39	-2.03	-2.02	-1.62	3.36	2.36
5d	-5.43	-2.87	-2.05	-2.03	2.56	1.99
5e	-5.39	-2.94	-2.03	-2.00	2.44	1.96
5f	-5.34	-2.79	-2.04	-1.92	2.55	1.89
5g	-5.32	-2.00	-1.98	-1.90	3.32	2.64
5h	-5.26	-1.98	-1.95	-1.40	3.28	2.51
5i	-5.27	-1.97	-1.95	-1.40	3.30	2.47
5j	-5.24	-2.04	-1.98	-1.92	3.20	2.49
5k	-5.24	-1.99	-1.99	-1.90	3.25	2.44
5l	-5.18	-2.03	-1.96	-1.94	3.15	2.46

**Table 7S.** The energy levels and HOMO-LUMO energy gaps for the studied complexes (in eV) calculated at the M06/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	LUMO+1 [eV]	LUMO+2 [eV]	$E_g^{\text{theor.}}$ [eV]	$E_g^{\text{exp.}}$ [eV]
5a	-5.55	-1.86	-1.86	-1.24	3.69	2.49
5b	-5.52	-1.86	-1.85	-1.24	3.66	2.32
5c	-5.67	-1.94	-1.92	-1.46	3.73	2.36
5d	-5.71	-2.62	-1.96	-1.94	3.09	1.99
5e	-5.66	-2.70	-1.92	-1.92	2.96	1.96
5f	-5.64	-2.54	-1.95	-1.82	3.10	1.89
5g	-5.60	-1.93	-1.92	-1.79	3.67	2.64
5h	-5.54	-1.88	-1.85	-1.28	3.66	2.51
5i	-5.54	-1.87	-1.86	-1.33	3.67	2.47
5j	-5.55	-1.90	-1.87	-1.83	3.65	2.49
5k	-5.49	-1.89	-1.86	-1.82	3.60	2.44
5l	-5.48	-1.88	-1.86	-1.83	3.60	2.46

**Table 8S.** The energy levels and HOMO-LUMO energy gaps for the studied complexes (in eV) calculated at the WB97XD/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	LUMO+1 [eV]	LUMO+2 [eV]	E <sub>g</sub> <sup>theor.</sup> [eV]	E <sub>g</sub> <sup>exp.</sup> [eV]
5a	-7.06	-0.76	-0.74	-0.11	6.30	2.49
5b	-7.01	-0.82	-0.80	-0.17	6.19	2.32
5c	-7.17	-0.92	-0.90	-0.42	6.25	2.36
5d	-7.19	-1.39	-0.79	-0.77	5.80	1.99
5e	-7.23	-1.48	-0.74	-0.72	5.75	1.96
5f	-7.14	-1.05	-0.56	-0.42	6.09	1.89
5g	-7.16	-0.83	-0.83	-0.76	6.33	2.64
5h	-7.06	-0.76	-0.70	-0.14	6.30	2.51
5i	-7.02	-0.75	-0.72	-0.20	6.27	2.47
5j	-7.06	-0.81	-0.70	-0.64	6.25	2.49
5k	-6.97	-0.80	-0.70	-0.61	6.17	2.44
5l	-7.06	-0.89	-0.82	-0.79	6.17	2.46

**Table 9S.** Set of numerical orbital distributions.

Complex	Orbital	MO composition			
		Ir	Bzq1	Bzq2	Bzq-R
<b>5a</b>	LUMO+1	3	6	91	0
	LUMO	4	91	5	0
	HOMO	31	18	18	33
	HOMO-1	29	16	10	45
<b>5b</b>	LUMO+1	4	13	83	0
	LUMO	4	82	14	0
	HOMO	30	17	17	36
	HOMO-1	28	17	10	45
<b>5c</b>	LUMO+1	4	15	80	1
	LUMO	4	80	16	0
	HOMO	32	23	22	23
	HOMO-1	27	13	6	54
<b>5d</b>	LUMO+1	4	49	47	0
	LUMO	1	1	0	98
	HOMO	32	24	23	21
	HOMO-1	27	14	6	53
<b>5e</b>	LUMO+1	4	0	96	0
	LUMO	1	1	0	98
	HOMO	33	22	22	23
	HOMO-1	28	13	7	52
<b>5f</b>	LUMO+1	3	97	0	0
	LUMO	0	1	1	98
	HOMO	31	20	25	24
	HOMO-1	27	11	10	52
<b>5g</b>	LUMO+1	4	92	1	3
	LUMO	4	0	95	1
	HOMO	31	21	19	29
	HOMO-1	27	16	8	49
<b>5h</b>	LUMO+1	3	97	0	0
	LUMO	4	0	95	1
	HOMO	30	20	17	33
	HOMO-1	25	21	9	45
<b>5i</b>	LUMO+1	4	78	18	0
	LUMO	4	17	78	1
	HOMO	30	21	17	32
	HOMO-1	28	16	9	47
<b>5j</b>	LUMO+1	4	8	79	9
	LUMO	0	37	19	44
	HOMO	27	18	16	39
	HOMO-1	7	27	5	61
<b>5k</b>	LUMO+1	2	35	27	36
	LUMO	3	19	69	9
	HOMO	23	25	14	38
	HOMO-1	11	17	7	65
<b>5l</b>	LUMO+1	4	80	16	0
	LUMO	4	14	77	5
	HOMO	25	24	15	36
	HOMO-1	25	21	13	41

**Table 10S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for **5a**.

Atom symbol	X	Y	Z
C	-5.13087	-1.75439	-0.73518
C	-3.92862	-2.08424	-0.01784
C	-2.84487	-1.17188	-0.05963
C	-2.97823	0.03526	-0.80396
C	-4.16643	0.34877	-1.50314
C	-5.24777	-0.59542	-1.44419
N	-1.89195	0.86826	-0.80074
C	-4.20955	1.56718	-2.20558
C	-3.10691	2.40174	-2.18295
C	-1.96501	2.02085	-1.46760
C	-3.76375	-3.26913	0.72934
C	-2.56545	-3.49660	1.38667
C	-1.49987	-2.57398	1.32889
C	-1.60768	-1.38743	0.60794
H	-5.10307	1.84429	-2.75437
H	-3.10755	3.34880	-2.70705
C	1.02043	-1.97794	-3.28502
C	2.11622	-2.68103	-2.80870
C	0.26475	-1.12499	-2.45490
C	2.48442	-2.54990	-1.45382
C	3.59532	-3.24058	-0.85469
C	1.70787	-1.69054	-0.63843
C	3.90642	-3.09427	0.46555
C	3.12888	-2.23844	1.31884
N	1.23305	-0.71845	1.46463
C	3.36853	-2.03735	2.69088
C	1.47874	-0.54612	2.76440
C	2.54150	-1.19082	3.40937
C	0.58991	-0.94637	-1.11185
H	4.19396	-2.54676	3.17632
H	0.80393	0.11445	3.29324
H	2.69735	-1.01819	4.46652
Ir	-0.29323	0.15171	0.34947
O	-1.19862	1.16275	2.06902
N	0.95791	1.98947	0.09734
C	-1.11158	2.41090	2.32893
C	-0.26558	3.33764	1.71712
C	0.75269	3.12250	0.74643
H	-0.33903	4.35092	2.08824
C	-2.02529	2.88680	3.44151
H	-1.81169	2.32255	4.35404

H	-3.06495	2.67967	3.17162
H	-1.91620	3.95168	3.64896
C	1.64303	4.32593	0.47768
H	1.17909	5.23486	0.85913
H	1.84350	4.44874	-0.58779
H	2.61035	4.20786	0.97389
C	2.03944	-1.55077	0.73821
C	2.11920	1.88948	-0.73275
C	2.01870	2.00244	-2.12365
C	3.37506	1.64640	-0.16423
C	4.50858	1.53820	-0.96841
C	4.40430	1.66732	-2.35299
C	3.15324	1.89731	-2.92551
H	3.45793	1.54396	0.91191
H	5.47390	1.35098	-0.51058
H	5.28541	1.58278	-2.97888
H	-1.08996	2.65377	-1.42419
H	-6.16400	-0.36543	-1.97696
H	-5.96034	-2.45355	-0.70275
H	-4.57185	-3.99065	0.78411
H	-2.44017	-4.40920	1.96147
H	-0.58584	-2.81168	1.86262
H	0.73357	-2.08625	-4.32672
H	-0.58252	-0.60305	-2.88715
H	2.68587	-3.33089	-3.46425
H	4.19394	-3.89526	-1.48012
H	4.74731	-3.62772	0.89529
H	1.04905	2.17380	-2.57504
H	3.05781	1.99197	-4.00176

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**Table 11S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5b.

Atom symbol	X	Y	Z
C	5.38782	1.07344	-1.62332
C	4.34957	1.63274	-0.80004
C	3.18677	0.85887	-0.55961
C	3.08235	-0.43991	-1.13513
C	4.11052	-0.97827	-1.94278
C	5.27709	-0.17088	-2.16998
N	1.93278	-1.1308	-0.86018
C	3.92249	-2.27095	-2.46549
C	2.75946	-2.95857	-2.17018
C	1.78702	-2.35813	-1.36128
C	4.42071	2.91389	-0.21449
C	3.36626	3.36542	0.56273
C	2.21793	2.57713	0.78613
C	2.09508	1.3038	0.23593
H	4.68773	-2.71873	-3.09009
H	2.58452	-3.95718	-2.54935
C	-1.07153	1.70078	-3.26899
C	-1.99293	2.59075	-2.73866
C	-0.27799	0.87256	-2.44931
C	-2.14115	2.67768	-1.33906
C	-3.06036	3.56971	-0.6835
C	-1.331	1.83752	-0.5361
C	-3.16374	3.62627	0.67578
C	-2.34876	2.79142	1.51504
N	-0.6191	1.08147	1.5878
C	-2.38068	2.78852	2.92194
C	-0.66595	1.09799	2.92065
C	-1.53866	1.94016	3.62067
C	-0.38763	0.90818	-1.06053
H	-3.05964	3.45028	3.44868
H	0.01673	0.42807	3.42679
H	-1.53718	1.91694	4.70284
Ir	0.61394	-0.09288	0.39546
O	1.68766	-0.964	2.09645
N	-0.82274	-1.78895	0.59973
C	1.52327	-2.14617	2.55396
C	0.50801	-3.04102	2.2145
C	-0.62401	-2.84196	1.37316
H	0.54008	-3.99626	2.72097
C	2.54729	-2.56753	3.59011
H	2.50976	-1.87838	4.4392

H	3.55083	-2.49403	3.16132
H	2.38626	-3.58361	3.9516
C	-1.65087	-3.96344	1.41443
H	-1.20437	-4.87098	1.81998
H	-2.05627	-4.17679	0.42464
H	-2.49417	-3.69001	2.05506
C	-1.44487	1.91048	0.88013
C	-2.08421	-1.67281	-0.07008
C	-2.20792	-1.97381	-1.43295
C	-3.21558	-1.22453	0.6102
C	-4.44874	-1.09048	-0.03397
C	-4.55867	-1.40753	-1.38905
C	-3.42708	-1.85134	-2.08354
H	-3.13798	-0.97416	1.66226
H	0.87282	-2.87353	-1.10297
H	6.07239	-0.57431	-2.78726
H	6.27803	1.66671	-1.80657
H	5.29563	3.53434	-0.37628
H	3.42239	4.35245	1.01173
H	1.42486	2.98771	1.40214
H	-0.9557	1.63847	-4.34689
H	0.42588	0.19771	-2.9256
H	-2.59443	3.21827	-3.38755
H	-3.68257	4.21234	-1.29833
H	-3.86319	4.30829	1.14702
H	-3.51945	-2.08853	-3.13708
H	-1.3396	-2.30858	-1.98717
H	-5.30177	-0.73769	0.53015
O	-5.71354	-1.31422	-2.11909
C	-6.88941	-0.84216	-1.46656
H	-7.18367	-1.50553	-0.64688
H	-7.6703	-0.838	-2.22496
H	-6.74995	0.17345	-1.08297

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**Table 12S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5c.

Atom symbol	X	Y	Z
C	5.29474	1.2289	-1.58222
C	4.24221	1.73885	-0.74506
C	3.09763	0.93103	-0.53166
C	3.02452	-0.35146	-1.1466
C	4.0669	-0.84195	-1.96627
C	5.21457	-0.00086	-2.166
N	1.8906	-1.07593	-0.89602
C	3.90989	-2.12325	-2.52619
C	2.7625	-2.84604	-2.25417
C	1.77424	-2.29183	-1.43175
C	4.28186	3.00278	-0.12036
C	3.2162	3.40529	0.66808
C	2.08602	2.58398	0.86479
C	1.99551	1.3267	0.27464
H	4.6867	-2.53564	-3.16076
H	2.61228	-3.83729	-2.66207
C	-1.17571	1.75304	-3.2287
C	-2.12938	2.59353	-2.67598
C	-0.35662	0.92814	-2.43032
C	-2.28428	2.63489	-1.27484
C	-3.23394	3.47709	-0.59728
C	-1.44869	1.79934	-0.49359
C	-3.34051	3.49267	0.76275
C	-2.4997	2.66228	1.58051
N	-0.71905	1.00379	1.61043
C	-2.53291	2.62025	2.98679
C	-0.76783	0.98289	2.94329
C	-1.66599	1.77969	3.66396
C	-0.47417	0.91756	-1.04219
H	-3.23261	3.24609	3.52987
H	-0.06693	0.3202	3.4338
H	-1.66475	1.72775	4.74509
Ir	0.54671	-0.10432	0.38619
O	1.63762	-1.00751	2.05953
N	-0.85218	-1.8491	0.54824
C	1.49871	-2.19931	2.49291
C	0.49926	-3.10972	2.13478
C	-0.63387	-2.91629	1.30263
H	0.55309	-4.07536	2.61882
C	2.52983	-2.62234	3.5204
H	2.47709	-1.95224	4.38366

H	3.53159	-2.51851	3.09411
H	2.38937	-3.64894	3.85955
C	-1.63867	-4.05725	1.30917
H	-1.17523	-4.96825	1.68616
H	-2.03853	-4.25008	0.31244
H	-2.48675	-3.82193	1.95853
C	-1.56767	1.82789	0.92403
C	-2.1077	-1.71665	-0.10223
C	-2.21967	-1.90478	-1.48702
C	-3.25001	-1.34753	0.62383
C	-4.47494	-1.18864	-0.00798
C	-4.58002	-1.39457	-1.39205
C	-3.43968	-1.75331	-2.12807
H	-3.16957	-1.1824	1.6915
H	0.87202	-2.83667	-1.19076
H	6.02046	-0.36664	-2.79282
H	6.17103	1.84809	-1.74536
H	5.14208	3.64825	-0.26121
H	3.24828	4.37897	1.14731
H	1.28236	2.95648	1.49089
H	-1.05329	1.72801	-4.3073
H	0.37273	0.29357	-2.92309
H	-2.75035	3.21871	-3.30836
H	-3.87687	4.11482	-1.19544
H	-4.06292	4.13777	1.25082
H	-3.51552	-1.9094	-3.19713
H	-1.34224	-2.17407	-2.06022
H	-5.35017	-0.90486	0.56356
C	-5.83828	-1.23757	-2.04821
N	-6.85894	-1.11369	-2.57941

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**Table 13S.** Cartesian coordinates from the optimized structures of S<sub>0</sub> in C<sub>6</sub>H<sub>5</sub>Cl media for 5d.

Atom symbol	X	Y	Z
C	5.4145	1.04992	-1.80968
C	4.4129	1.61383	-0.94523
C	3.25635	0.84609	-0.66049
C	3.12088	-0.4504	-1.23429
C	4.11229	-0.99255	-2.08385
C	5.27447	-0.1923	-2.35436
N	1.97857	-1.13438	-0.91579
C	3.89369	-2.28161	-2.60359
C	2.7375	-2.96155	-2.26639
C	1.80245	-2.35793	-1.41682
C	4.51378	2.89361	-0.36098
C	3.49361	3.35026	0.45746
C	2.35037	2.56828	0.72576
C	2.20152	1.29716	0.17895
H	4.63021	-2.73251	-3.25961
H	2.53986	-3.95664	-2.6435
C	-1.10299	1.71095	-3.19205
C	-2.02179	2.57999	-2.62464
C	-0.26577	0.89361	-2.40474
C	-2.11881	2.66212	-1.21997
C	-3.02438	3.54028	-0.52798
C	-1.26564	1.83385	-0.45007
C	-3.06993	3.59908	0.83426
C	-2.20716	2.77958	1.63999
N	-0.45652	1.08885	1.64391
C	-2.17607	2.78396	3.04695
C	-0.44305	1.11359	2.97752
C	-1.29259	1.95074	3.71143
C	-0.33045	0.91992	-1.01344
H	-2.83952	3.43965	3.60019
H	0.26845	0.45477	3.45781
H	-1.24165	1.93453	4.79246
Ir	0.72446	-0.0891	0.39861
O	1.87117	-0.97651	2.04666
N	-0.70924	-1.7942	0.68565
C	1.73021	-2.15379	2.51471
C	0.69347	-3.0504	2.22935
C	-0.47663	-2.84868	1.45603
H	0.7535	-4.00703	2.73026
C	2.8047	-2.57793	3.49604
H	2.82177	-1.88042	4.33866

H	3.78294	-2.51863	3.01057
H	2.65382	-3.58894	3.87498
C	-1.50408	-3.96622	1.53681
H	-1.03592	-4.88501	1.88838
H	-1.97175	-4.15534	0.56918
H	-2.30209	-3.71093	2.23968
C	-1.32116	1.9069	0.96994
C	-1.99459	-1.6247	0.1185
C	-2.18771	-1.75861	-1.26599
C	-3.08831	-1.26042	0.92273
C	-4.34124	-1.05018	0.36854
C	-4.50475	-1.20502	-1.00775
C	-3.43617	-1.559	-1.83197
H	-2.9441	-1.134	1.9887
H	-5.18385	-0.76729	0.98384
H	0.8949	-2.86854	-1.12676
H	6.04234	-0.5992	-3.00313
H	6.3004	1.63809	-2.02658
H	5.38507	3.50952	-0.55598
H	3.57264	4.33642	0.90459
H	1.5843	2.98181	1.37282
H	-1.02361	1.65627	-4.27352
H	0.4341	0.23485	-2.90839
H	-2.65822	3.19799	-3.24865
H	-3.68251	4.17114	-1.11675
H	-3.75905	4.27173	1.33306
H	-3.5902	-1.67075	-2.89599
H	-1.34835	-2.0208	-1.89566
N	-5.82262	-0.98986	-1.59895
O	-6.74878	-0.66027	-0.85792
O	-5.95175	-1.14786	-2.81274

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**Table 14S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5e.

Atom symbol	X	Y	Z
C	-5.63961	-1.34235	-0.72232
C	-4.47168	-1.76361	0.0038
C	-3.30859	-0.9565	-0.06005
C	-3.33033	0.2374	-0.83614
C	-4.48458	0.63962	-1.54671
C	-5.64937	-0.19731	-1.46267
N	-2.17198	0.96663	-0.85275
C	-4.4143	1.83571	-2.28408
C	-3.23865	2.56436	-2.28375
C	-2.1376	2.10092	-1.55351
C	-4.4146	-2.94011	0.77951
C	-3.24061	-3.26224	1.44098
C	-2.09475	-2.44316	1.36174
C	-2.09676	-1.26814	0.6152
H	-5.27856	2.17849	-2.84247
H	-3.1515	3.49157	-2.83534
C	0.54741	-2.15399	-3.23529
C	1.58657	-2.92003	-2.73084
C	-0.16001	-1.23613	-2.43154
C	1.94459	-2.79003	-1.37265
C	2.9962	-3.54486	-0.74471
C	1.21754	-1.86471	-0.58434
C	3.29665	-3.39712	0.57785
C	2.56762	-2.47478	1.4042
N	0.78327	-0.82149	1.49388
C	2.79924	-2.2682	2.77699
C	1.01861	-0.6471	2.79534
C	2.02198	-1.35523	3.46833
C	0.15935	-1.05519	-1.08736
H	3.58024	-2.82461	3.28351
H	0.38486	0.06833	3.303
H	2.17308	-1.17631	4.52501
Ir	-0.65268	0.14365	0.3354
O	-1.49149	1.27549	2.01457
N	0.75386	1.86471	0.06438
C	-1.2953	2.51294	2.25535
C	-0.36169	3.35098	1.63623
C	0.64337	3.02851	0.68823
H	-0.35014	4.37388	1.98725
C	-2.16988	3.08929	3.35125
H	-1.99976	2.5356	4.27926

H	-3.2221	2.95444	3.08498
H	-1.97854	4.14764	3.52973
C	1.63861	4.14157	0.40182
H	1.23276	5.10203	0.71725
H	1.89223	4.19576	-0.65813
H	2.57078	3.97836	0.95039
C	1.53901	-1.72235	0.79476
C	1.9118	1.62188	-0.7257
C	1.84093	1.61208	-2.12595
C	3.13355	1.33094	-0.11441
C	4.24343	1.05652	-0.90862
C	4.18846	1.05439	-2.29948
C	2.9663	1.33769	-2.8997
H	3.22152	1.31024	0.96237
H	-1.20905	2.65356	-1.52447
H	-6.54097	0.10284	-2.00219
H	-6.53037	-1.96024	-0.67127
H	-5.28556	-3.58254	0.85198
H	-3.19841	-4.16916	2.03638
H	-1.20483	-2.75066	1.90031
H	0.26728	-2.2628	-4.27872
H	-0.96529	-0.66724	-2.88478
H	2.11904	-3.61934	-3.36636
H	3.55733	-4.25002	-1.34949
H	4.09276	-3.97867	1.02947
H	2.88932	1.34136	-3.98018
H	0.89428	1.8223	-2.60684
H	5.0717	0.83473	-2.88145
N	5.52219	0.75114	-0.24627
O	5.56636	0.79314	0.98059
O	6.4871	0.46791	-0.95142

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**Table 15S.** Cartesian coordinates from the optimized structures of S<sub>0</sub> in C<sub>6</sub>H<sub>5</sub>Cl media for 5f.

Atom symbol	X	Y	Z
C	5.2489	1.41453	-1.2605
C	4.07328	1.98497	-0.66044
C	2.96623	1.13781	-0.40468
C	3.04857	-0.24221	-0.74413
C	4.21431	-0.79206	-1.32389
C	5.31942	0.0903	-1.57726
N	1.94209	-1.00018	-0.46603
C	4.21735	-2.1712	-1.60421
C	3.10038	-2.92498	-1.29878
C	1.98065	-2.30743	-0.7259
C	3.9582	3.34526	-0.30551
C	2.785	3.79951	0.27356
C	1.69643	2.93674	0.52099
C	1.75729	1.58503	0.19345
H	5.09271	-2.6307	-2.05034
H	3.06784	-3.98905	-1.49397
C	-1.07991	1.03961	-3.59849
C	-2.10032	1.93393	-3.31544
C	-0.3037	0.44756	-2.58079
C	-2.3739	2.26773	-1.97272
C	-3.39873	3.19321	-1.56838
C	-1.5836	1.65831	-0.96793
C	-3.6181	3.49673	-0.25632
C	-2.82779	2.89762	0.78362
N	-1.01855	1.3562	1.30796
C	-2.97741	3.15553	2.15889
C	-1.17592	1.62083	2.6061
C	-2.14958	2.51605	3.06614
C	-0.53638	0.73078	-1.23711
H	-3.73496	3.85326	2.499
H	-0.50255	1.10983	3.28201
H	-2.23656	2.69723	4.1297
Ir	0.39472	0.09357	0.44955
O	1.35499	-0.432	2.34794
N	-0.9714	-1.68136	0.82733
C	1.26132	-1.55869	2.93969
C	0.33886	-2.57671	2.67252
C	-0.76465	-2.5774	1.78141
H	0.40993	-3.44559	3.31248
C	2.24909	-1.75958	4.07186
H	2.10913	-0.97369	4.81992

H	3.2672	-1.65791	3.6855
H	2.14489	-2.73158	4.55444
C	-1.76451	-3.70092	1.98552
H	-1.34343	-4.47907	2.62086
H	-2.05894	-4.1434	1.03314
H	-2.66912	-3.32424	2.47192
C	-1.82403	1.9815	0.39668
C	-2.23534	-1.66256	0.18033
C	-2.49418	-2.16655	-1.11029
C	-3.30425	-1.00156	0.80529
C	-4.54084	-0.84772	0.19049
C	-4.75294	-1.331	-1.10097
C	-3.71994	-1.98486	-1.75385
H	-3.13763	-0.59722	1.79588
H	-5.33891	-0.3388	0.71869
H	-5.71063	-1.20599	-1.5905
H	1.09656	-2.87535	-0.479
H	6.21671	-0.32203	-2.02569
H	6.09576	2.0639	-1.45792
H	4.78554	4.02285	-0.48707
H	2.69741	4.84689	0.54577
H	0.80557	3.35431	0.97674
H	-0.86825	0.78704	-4.63288
H	0.48472	-0.24	-2.8673
H	-2.68364	2.37986	-4.11378
H	-4.00531	3.65975	-2.3381
H	-4.39371	4.20119	0.02368
H	-3.85074	-2.38414	-2.75055
N	-1.51103	-2.97744	-1.83543
O	-1.46535	-2.87748	-3.0576
O	-0.80918	-3.75199	-1.18889

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**Table 16S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5g.

Atom symbol	X	Y	Z
C	6.02788	-0.22221	-2.82368
C	5.23471	0.72711	-2.08987
C	4.1218	0.25075	-1.35293
C	3.82414	-1.14207	-1.3615
C	4.6097	-2.06453	-2.09009
C	5.73268	-1.55349	-2.82655
N	2.73607	-1.53013	-0.62731
C	4.23813	-3.42076	-2.04151
C	3.13848	-3.7961	-1.29125
C	2.41184	-2.82334	-0.59379
C	5.49969	2.11211	-2.06085
C	4.67413	2.94718	-1.32551
C	3.57065	2.44985	-0.60071
C	3.26558	1.09159	-0.59052
H	4.8141	-4.15944	-2.58821
H	2.82732	-4.83088	-1.22816
C	-0.6265	0.59236	-3.26826
C	-1.37714	1.70878	-2.93425
C	0.31464	0.0341	-2.37874
C	-1.19191	2.31297	-1.6736
C	-1.90768	3.48013	-1.23125
C	-0.23962	1.73605	-0.79819
C	-1.68436	4.04082	-0.00784
C	-0.71544	3.48427	0.89562
N	0.93163	1.72896	1.25591
C	-0.40968	4.00257	2.16782
C	1.20721	2.24112	2.45629
C	0.55227	3.37872	2.94397
C	0.5289	0.57942	-1.11466
H	-0.92491	4.88556	2.53007
H	1.97237	1.7308	3.02675
H	0.81308	3.75568	3.92456
Ir	1.80075	0.05525	0.37732
O	3.20324	-0.28229	2.02901
N	0.37608	-1.2551	1.50934
C	3.10749	-1.19776	2.91391
C	2.00372	-2.02103	3.15205
C	0.7114	-1.98256	2.56286
H	2.11992	-2.73553	3.95565
C	4.33348	-1.35648	3.79145
H	4.54325	-0.4089	4.29635

H	5.20082	-1.58557	3.16563
H	4.21681	-2.13966	4.54096
C	-0.32448	-2.87172	3.23278
H	0.16567	-3.64007	3.83
H	-0.9776	-3.3521	2.50265
H	-0.96211	-2.28659	3.90146
C	-0.01387	2.33257	0.4738
C	-0.99766	-1.17445	1.14469
C	-1.48075	-1.83029	0.00633
C	-1.88927	-0.39108	1.8925
C	-3.22196	-0.27951	1.52462
C	-3.71073	-0.94709	0.38985
C	-2.81523	-1.72276	-0.36092
H	-1.52568	0.13619	2.76691
H	-3.89943	0.32944	2.10942
H	1.55291	-3.0852	0.00821
H	6.3442	-2.25219	-3.38695
H	6.881	0.1427	-3.38669
H	6.34324	2.51262	-2.61276
H	4.87901	4.01323	-1.30594
H	2.96087	3.15395	-0.04477
H	-0.76479	0.13309	-4.24248
H	0.87179	-0.83972	-2.70011
H	-2.09734	2.12188	-3.63215
H	-2.64219	3.91895	-1.89899
H	-2.2352	4.92187	0.30281
H	-0.80439	-2.42544	-0.59356
H	-3.15607	-2.25013	-1.24501
C	-5.12336	-0.81183	0.02228
S	-5.77573	-1.60194	-1.44388
N	-5.99676	-0.13253	0.70164
C	-7.25276	-0.17565	0.12797
C	-7.34755	-0.93387	-1.06186
C	-8.39615	0.4608	0.63165
C	-9.59686	0.32995	-0.05287
C	-9.67598	-0.42639	-1.23385
C	-8.55344	-1.06589	-1.75086
H	-8.32605	1.0426	1.54309
H	-10.4866	0.8179	0.32781
H	-10.6239	-0.5145	-1.75189
H	-8.61806	-1.64783	-2.66219

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**Table 17S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5h.

Atom symbol	X	Y	Z
C	-5.72531	1.06077	0.45312
C	-4.54302	1.55796	-0.19747
C	-3.33794	0.82341	-0.06464
C	-3.33329	-0.37587	0.70387
C	-4.50229	-0.85113	1.34208
C	-5.70927	-0.08712	1.18855
N	-2.13585	-1.03478	0.78888
C	-4.40484	-2.04255	2.08366
C	-3.18876	-2.69678	2.15722
C	-2.07606	-2.16559	1.49372
C	-4.51224	2.74193	-0.96314
C	-3.32204	3.14216	-1.54852
C	-2.13447	2.3955	-1.40103
C	-2.10837	1.21619	-0.66103
H	-5.27942	-2.43839	2.58844
H	-3.07791	-3.61734	2.71566
C	0.26367	2.19384	3.35116
C	1.26646	3.04304	2.9091
C	-0.33739	1.24429	2.49971
C	1.69556	2.96516	1.56792
C	2.70859	3.81421	0.99924
C	1.0787	2.00212	0.73229
C	3.06906	3.72444	-0.31339
C	2.44738	2.76881	-1.18814
N	0.81082	0.97742	-1.38204
C	2.73448	2.62648	-2.55836
C	1.09371	0.8683	-2.68111
C	2.05229	1.67849	-3.30138
C	0.05833	1.11051	1.17043
H	3.48044	3.26163	-3.02373
H	0.53422	0.12216	-3.23056
H	2.24441	1.54965	-4.35883
Ir	-0.60118	-0.11059	-0.3084
O	-1.28427	-1.25207	-2.04914
N	0.86257	-1.78398	0.03228
C	-1.06704	-2.49411	-2.25334
C	-0.18402	-3.31624	-1.54969
C	0.7618	-2.97093	-0.54482
H	-0.15597	-4.34965	-1.86798
C	-1.85931	-3.09291	-3.39914
H	-1.63311	-2.5484	-4.32064

H	-2.92878	-2.96788	-3.2064
H	-1.64471	-4.15105	-3.55106
C	1.70656	-4.09464	-0.14905
H	1.28475	-5.05985	-0.42809
H	1.90932	-4.09153	0.92265
H	2.667	-3.98896	-0.6615
C	1.46588	1.91654	-0.63434
C	1.96638	-1.54223	0.90831
C	1.77235	-1.51071	2.2742
C	3.27536	-1.28614	0.37935
C	4.35243	-1.02429	1.28953
C	4.10316	-1.01383	2.68593
C	2.8371	-1.2514	3.1629
H	-1.11623	-2.66112	1.52404
H	-6.61157	-0.44469	1.67239
H	-6.64759	1.62335	0.34926
H	-5.41584	3.32911	-1.08695
H	-3.29996	4.0546	-2.13663
H	-1.23469	2.76185	-1.88317
H	-0.07183	2.26205	4.3817
H	-1.12101	0.61157	2.90378
H	1.71517	3.7676	3.58011
H	3.18765	4.54723	1.64052
H	3.83099	4.37965	-0.72121
C	5.65258	-0.78353	0.76766
C	5.88881	-0.79803	-0.58576
C	4.82626	-1.05101	-1.48459
C	3.55598	-1.28784	-1.01345
H	6.46157	-0.58724	1.46392
H	6.88668	-0.61414	-0.9682
H	2.74994	-1.4751	-1.71069
H	5.01596	-1.05557	-2.55222
H	2.64448	-1.24057	4.22997
H	0.7804	-1.68676	2.66972
H	4.92406	-0.81419	3.36635

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**Table 18S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5i.

Atom symbol	X	Y	Z
C	5.62667	1.07315	-1.41368
C	4.56941	1.60935	-0.59913
C	3.38842	0.84337	-0.43418
C	3.28574	-0.42533	-1.07361
C	4.33274	-0.94166	-1.87124
C	5.51718	-0.14242	-2.02191
N	2.11813	-1.10996	-0.86964
C	4.14417	-2.20608	-2.45913
C	2.96221	-2.8883	-2.23476
C	1.97137	-2.31059	-1.43167
C	4.639	2.86027	0.04871
C	3.56575	3.29112	0.81168
C	2.39936	2.51148	0.95956
C	2.27719	1.26782	0.34547
H	4.92366	-2.63694	-3.07801
H	2.78614	-3.86546	-2.66577
C	-0.73301	1.87912	-3.25558
C	-1.66847	2.75302	-2.72319
C	0.0158	1.00308	-2.44354
C	-1.87672	2.77525	-1.32861
C	-2.81263	3.64805	-0.67078
C	-1.11134	1.88756	-0.53329
C	-2.97227	3.64253	0.68399
C	-2.2025	2.75935	1.51626
N	-0.49484	1.02698	1.58123
C	-2.29233	2.69313	2.91902
C	-0.59623	0.98388	2.91041
C	-1.48866	1.80381	3.61197
C	-0.15603	0.97278	-1.06119
H	-2.98558	3.33863	3.44731
H	0.05823	0.28396	3.4133
H	-1.53187	1.73187	4.69113
Ir	0.77136	-0.10895	0.38531
O	1.76385	-1.07851	2.08366
N	-0.70104	-1.7918	0.46209
C	1.58144	-2.28624	2.45873
C	0.577	-3.1544	2.02672
C	-0.53232	-2.89256	1.17464
H	0.59068	-4.14116	2.46973
C	2.56509	-2.77629	3.50339
H	2.49302	-2.14416	4.39359

H	3.58447	-2.67554	3.11996
H	2.39112	-3.81348	3.79112
C	-1.56906	-4.00456	1.12298
H	-1.12336	-4.94846	1.43654
H	-1.98877	-4.12394	0.12344
H	-2.40078	-3.78805	1.79933
C	-1.28289	1.89657	0.87916
C	-1.94649	-1.60385	-0.21253
C	-2.02221	-1.77976	-1.62083
C	-3.07728	-1.22401	0.47874
C	-4.31713	-1.0287	-0.18361
C	-4.39023	-1.22687	-1.59858
C	-3.20815	-1.60506	-2.28895
H	1.04121	-2.82292	-1.22923
H	6.32686	-0.52855	-2.63146
H	6.53059	1.66056	-1.53966
H	5.52757	3.47368	-0.05485
H	3.62082	4.25468	1.30909
H	1.59211	2.90501	1.5681
H	-0.56979	1.86813	-4.32911
H	0.73438	0.34481	-2.92095
H	-2.23464	3.41829	-3.36616
H	-3.40188	4.32594	-1.28007
H	-3.68408	4.31016	1.15714
C	-5.49552	-0.64773	0.51373
C	-5.63231	-1.03688	-2.25885
C	-6.75574	-0.66868	-1.55503
C	-6.68514	-0.47275	-0.15462
H	-3.25203	-1.75106	-3.36338
H	-1.12704	-2.05894	-2.16235
H	-3.02496	-1.07454	1.55197
H	-5.68209	-1.18663	-3.33261
H	-7.69925	-0.52666	-2.07
H	-7.57644	-0.18276	0.3908
H	-5.4432	-0.49722	1.58719

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**Table 19S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5j.

Atom symbol	X	Y	Z
C	-6.22089	0.74609	-0.41467
C	-4.98129	1.22677	-0.96309
C	-3.7742	0.60918	-0.54969
C	-3.82401	-0.46046	0.38954
C	-5.04941	-0.91842	0.92668
C	-6.25693	-0.27556	0.48749
N	-2.62092	-1.01141	0.74175
C	-5.0028	-1.9742	1.85536
C	-3.77948	-2.51873	2.20064
C	-2.60907	-2.01405	1.62133
C	-4.89609	2.28506	-1.8914
C	-3.65318	2.68188	-2.35745
C	-2.46474	2.05431	-1.92925
C	-2.49023	1.00077	-1.01911
H	-5.92112	-2.35225	2.29143
H	-3.70626	-3.3339	2.90898
C	-0.80291	2.70396	3.1041
C	0.21241	3.55103	2.6881
C	-1.22186	1.60509	2.3259
C	0.84214	3.31675	1.44805
C	1.88765	4.14626	0.91033
C	0.4063	2.20549	0.68558
C	2.44736	3.89866	-0.30885
C	2.0111	2.79013	-1.11217
N	0.51162	0.87955	-1.2692
C	2.5059	2.48044	-2.39252
C	0.99025	0.61171	-2.48498
C	1.98861	1.39444	-3.07715
C	-0.6238	1.31438	1.10158
H	3.28206	3.09493	-2.83541
H	0.55618	-0.24224	-2.98917
H	2.34259	1.13518	-4.06662
Ir	-0.98784	-0.14636	-0.25666
O	-1.32724	-1.57517	-1.88783
N	0.49139	-1.64925	0.53675
C	-1.05146	-2.8214	-1.84586
C	-0.26913	-3.47363	-0.8894
C	0.51397	-2.91813	0.15968
H	-0.16662	-4.54248	-1.0206
C	-1.63451	-3.63541	-2.98445
H	-1.25379	-3.25184	-3.93584

H	-2.72123	-3.51292	-3.00053
H	-1.39396	-4.6962	-2.90952
C	1.43364	-3.90564	0.85955
H	1.0883	-4.92611	0.69585
H	1.48633	-3.71518	1.93224
H	2.45115	-3.82981	0.46561
C	0.99929	1.95747	-0.5839
C	1.46039	-1.19902	1.48475
C	1.1005	-0.95733	2.78759
C	2.8208	-0.94537	1.06777
C	3.76702	-0.45424	2.0448
C	3.33298	-0.22812	3.38567
C	2.03599	-0.47397	3.74054
H	-1.6404	-2.42645	1.8644
H	-7.20228	-0.62169	0.89084
H	-7.14464	1.2184	-0.73324
H	-5.79954	2.78026	-2.23073
H	-3.58921	3.49875	-3.06986
H	-1.52248	2.41236	-2.32955
H	-1.2934	2.89167	4.05459
H	-2.02632	0.98292	2.70412
H	0.5191	4.39168	3.30113
H	2.2284	4.99308	1.49761
H	3.23047	4.54134	-0.69607
C	5.09102	-0.21537	1.65599
C	5.53139	-0.44309	0.34886
C	4.58958	-0.93395	-0.62569
C	3.26353	-1.16544	-0.24135
H	5.79544	0.15535	2.39453
H	2.56347	-1.52623	-0.98454
H	1.70602	-0.30156	4.75899
H	0.07787	-1.13449	3.09471
H	4.04859	0.14143	4.11213
C	6.88252	-0.20976	-0.05794
C	7.27916	-0.44906	-1.3455
C	6.34869	-0.93731	-2.30953
C	5.04637	-1.17064	-1.95986
H	7.59022	0.1606	0.67664
H	8.3067	-0.26942	-1.64146
H	6.68241	-1.12296	-3.32436
H	4.33789	-1.54265	-2.69258

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**Table 20S.** Cartesian coordinates from the optimized structures of  $S_0$  in  $C_6H_5Cl$  media for 5k.

Atom symbol	X	Y	Z
C	6.12929	1.03506	-1.61793
C	5.10923	1.58137	-0.7637
C	3.93065	0.82427	-0.54875
C	3.79273	-0.4452	-1.18012
C	4.80305	-0.97094	-2.01781
C	5.98668	-0.18136	-2.21751
N	2.62853	-1.12015	-0.92874
C	4.58101	-2.23426	-2.59615
C	3.40264	-2.90586	-2.3255
C	2.4492	-2.31928	-1.48438
C	5.2129	2.83411	-0.12397
C	4.17399	3.27506	0.67969
C	3.00929	2.50396	0.87742
C	2.85471	1.25896	0.27341
H	5.33209	-2.67222	-3.24447
H	3.20111	-3.88146	-2.74882
C	-0.29637	1.88921	-3.19704
C	-1.21369	2.75927	-2.62792
C	0.48358	1.01307	-2.41537
C	-1.36826	2.77969	-1.22636
C	-2.27963	3.64995	-0.53187
C	-0.57069	1.89328	-0.46176
C	-2.38393	3.64534	0.82824
C	-1.57771	2.76609	1.62966
N	0.13429	1.03638	1.62675
C	-1.60794	2.70372	3.0351
C	0.08889	0.99675	2.9592
C	-0.774	1.81774	3.69573
C	0.36316	0.97954	-1.02761
H	-2.27915	3.34966	3.59061
H	0.76385	0.29835	3.43636
H	-0.77127	1.74877	4.77595
Ir	1.34321	-0.10781	0.37998
O	2.40402	-1.0844	2.03261
N	-0.13895	-1.77739	0.53041
C	2.22827	-2.28906	2.41975
C	1.19639	-3.14889	2.03799
C	0.05251	-2.87921	1.23618
H	1.22258	-4.13538	2.48102
C	3.25766	-2.78705	3.41534
H	3.25406	-2.13803	4.29609

H	4.25524	-2.7199	2.97162
H	3.07504	-3.81462	3.73087
C	-0.99158	-3.98568	1.22815
H	-0.53309	-4.93462	1.50645
H	-1.46427	-4.09202	0.25104
H	-1.78493	-3.77513	1.95065
C	-0.68388	1.90347	0.95658
C	-1.411	-1.57244	-0.08325
C	-1.53491	-1.70426	-1.50332
C	-2.51085	-1.21888	0.65659
C	-3.78342	-1.00391	0.04527
C	-3.904	-1.1567	-1.38396
C	-2.73493	-1.51246	-2.12527
H	1.52305	-2.8231	-1.24592
H	6.76846	-0.57527	-2.85775
H	7.03167	1.61546	-1.78169
H	6.10061	3.44127	-0.2652
H	4.25534	4.24012	1.17057
H	2.22971	2.90504	1.51643
H	-0.17358	1.88068	-4.27596
H	1.18426	0.35637	-2.9206
H	-1.80578	3.42387	-3.24784
H	-2.89547	4.3254	-1.11708
H	-3.07835	4.31116	1.32897
C	-4.91843	-0.65684	0.7878
C	-5.14506	-0.95205	-1.99392
C	-6.2803	-0.60402	-1.25174
C	-6.16288	-0.45385	0.17892
H	-2.81471	-1.62318	-3.20171
H	-0.65548	-1.96302	-2.07916
H	-2.42207	-1.10185	1.73131
H	-5.23081	-1.0654	-3.07048
H	-4.83278	-0.54359	1.8643
C	-7.55579	-0.39285	-1.86132
C	-8.64874	-0.05629	-1.10928
C	-8.53375	0.09075	0.30383
C	-7.33008	-0.10186	0.92628
H	-7.6415	-0.50508	-2.93727
H	-9.61042	0.10057	-1.58478
H	-9.41015	0.35709	0.8841
H	-7.24331	0.00992	2.00221

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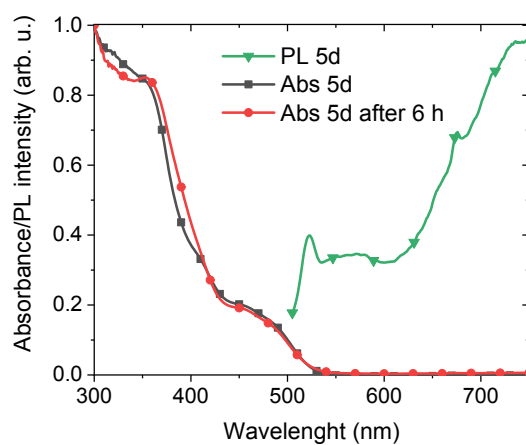
**Table 21S.** Cartesian coordinates from the optimized structures of S<sub>0</sub> in C<sub>6</sub>H<sub>5</sub>Cl media for 5I.

Atom symbol	X	Y	Z
C	5.82823	0.46734	-1.16893
C	4.70355	1.30314	-0.84667
C	3.49211	0.68446	-0.44627
C	3.42815	-0.73542	-0.36233
C	4.55134	-1.5439	-0.65584
C	5.7592	-0.89097	-1.07806
N	2.23144	-1.26489	0.04428
C	4.41843	-2.93493	-0.49489
C	3.21894	-3.45013	-0.0412
C	2.15131	-2.58395	0.22361
C	4.7404	2.71172	-0.89781
C	3.609	3.43285	-0.55376
C	2.41499	2.79601	-0.15697
C	2.32032	1.40765	-0.0918
H	5.25706	-3.58762	-0.71162
H	3.08544	-4.51241	0.11778
C	-0.20712	0.14174	-3.88126
C	-1.1419	1.16177	-3.96625
C	0.39851	-0.2141	-2.65862
C	-1.49162	1.87614	-2.80186
C	-2.41617	2.97851	-2.78333
C	-0.87467	1.4957	-1.58489
C	-2.68081	3.67735	-1.64188
C	-2.04616	3.33265	-0.39962
N	-0.51214	1.81669	0.72722
C	-2.21476	4.02836	0.81177
C	-0.67817	2.50022	1.86066
C	-1.52166	3.61458	1.93621
C	0.07245	0.43838	-1.47265
H	-2.87671	4.88646	0.85469
H	-0.11933	2.14529	2.7171
H	-1.6216	4.13503	2.88003
Ir	0.76073	0.20294	0.42455
O	1.44357	0.13963	2.5093
N	-0.8373	-1.28113	1.08711
C	1.23936	-0.83208	3.3123
C	0.31221	-1.86718	3.15766
C	-0.72544	-2.00096	2.19377
H	0.29526	-2.5992	3.95401
C	2.09187	-0.80593	4.56587
H	1.90737	0.12482	5.11049

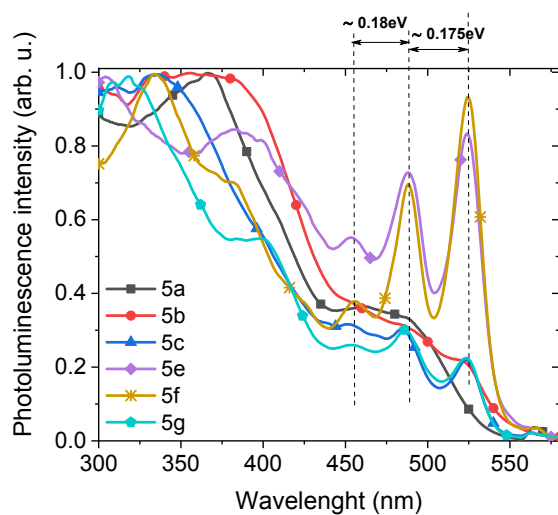
H	3.14939	-0.81038	4.28648
H	1.89199	-1.64908	5.22754
C	-1.76991	-3.05329	2.52966
H	-1.35388	-3.79131	3.21544
H	-2.13507	-3.56318	1.6377
H	-2.63198	-2.59282	3.02123
C	-1.16733	2.2265	-0.39993
C	-2.08069	-1.34055	0.37662
C	-2.21518	-2.11828	-0.79691
C	-3.19117	-0.60879	0.86593
C	-4.44007	-0.63062	0.1412
C	-4.54704	-1.37934	-1.03178
C	-3.47254	-2.13349	-1.50646
H	1.21375	-2.96128	0.60253
H	6.62143	-1.5045	-1.31557
H	6.75207	0.94233	-1.48317
H	5.65048	3.21787	-1.20119
H	3.63836	4.51757	-0.59082
H	1.56534	3.41932	0.09742
H	0.06921	-0.39968	-4.78093
H	1.12664	-1.01803	-2.65757
H	-1.5947	1.4206	-4.91733
H	-2.90015	3.26153	-3.71278
H	-3.36995	4.5147	-1.65606
C	-3.60265	-2.95206	-2.67223
C	-2.56977	-3.73439	-3.10803
C	-1.33322	-3.73119	-2.40466
C	-1.16416	-2.94426	-1.29775
H	-0.51595	-4.35022	-2.75807
H	-0.21553	-2.93574	-0.78625
H	-4.55124	-2.94658	-3.19905
H	-2.68698	-4.35715	-3.98788
C	-5.55662	0.09927	0.65786
C	-5.46584	0.79655	1.82989
C	-3.14439	0.13801	2.08482
C	-4.24035	0.8111	2.5534
H	-6.48648	0.07781	0.09894
H	-6.32309	1.33851	2.21349
H	-2.21998	0.16386	2.64459
H	-4.1763	1.36559	3.48303
H	-5.48932	-1.39523	-1.57025

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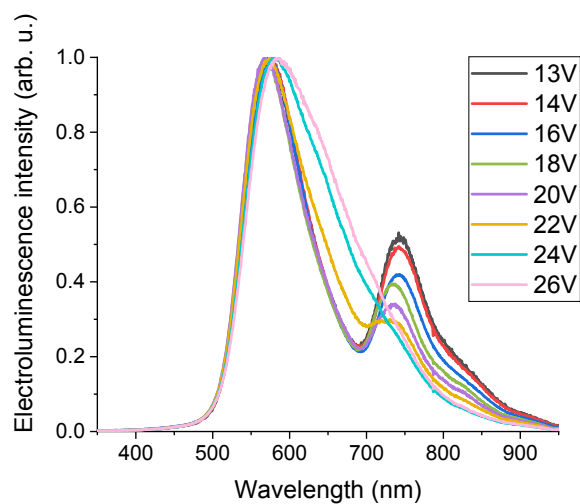
## 8. Photophysical measurements



**Figure 36S.** Normalized absorption and photoluminescence spectra of **5d** in chlorobenzene.

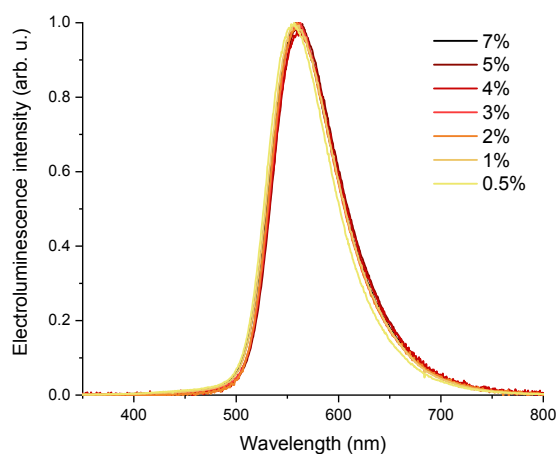


**Figure 37S.** Normalized photoluminescence excitation spectra (measured at emission band) of the first group (**5a–5g**) of investigated complexes in chlorobenzene.



**Figure 38S.** Normalized EL spectra of PhOLEDs based on PVK/PBD doped with **5I** under incensement of applied voltage.

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**Figure 39S.** Normalized EL spectra of PhOLEDs based on PVK/PBD doped with **5h** in different concentrations (from 0.5 to 7 wt%).

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