

## Supporting information for:

### A $D_{3h}$ symmetry hexaazatriphenylene-tris-N-heterocyclic carbene ligand and its coordination to iridium and gold. Preliminary catalytic studies

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**General methods.** 1,3-Dibutyl-5,6-diaminobenzimidazolium iodide<sup>1</sup> and N, N'-dibutylbenzimidazol-2-ylidene)gold(I) chloride (**7**)<sup>2</sup> were prepared according to literature methods. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 MHz or 500 MHz, using DMSO-*d*<sub>6</sub>, CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> as solvents. *J* values are given in Hz. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quattro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series.

## 1. Synthesis and characterization of the compounds

**1.1. Synthesis of compound [1](I)<sub>3</sub>.** Hexaketocyclohexane octahydrate (80 mg, 0.275 mmol, 1 equiv.) and 1,3-dibutyl-5,6-diaminobenzimidazolium iodide (300 mg, 0.772 mmol, 3 equiv.) were placed together in an oven-dried Schlenk flask and suspended in glacial acetic acid (15 mL) under inert atmosphere and heated at 140° C for 24 h. The mixture was filtered and the solid was subsequently washed with glacial acetic acid (5 mL), and ethanol (50 mL) until the filtrate was colorless. Compound [1](I)<sub>3</sub> (284.9 mg, 81%) was isolated as a brown solid after filtration.  $\delta$ H NMR (500 MHz, DMSO-*d*<sub>6</sub>) 10.33 (s, 1H, NCHN), 9.32 (s, 2H, CH<sub>Ar</sub>), 4.85-4.67 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.18-1.99 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.60-1.43 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.04 (t, <sup>3</sup>J<sub>H-H</sub> = 10 Hz, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).  $\delta$ C NMR (126 MHz, DMSO-*d*<sub>6</sub>) 149.23 (NCHN), 145.16 (C<sub>q</sub> Ar), 139.26 (C<sub>q</sub> Ar), 134.42 (C<sub>q</sub> Ar), 113.38 (CH<sub>Ar</sub>), 47.21 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.45 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.26 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.49 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Electrospray MS (20 V, *m/z*): 281 (M<sup>3+</sup>, 100%). Found: C, 48.3; H, 5.2; N, 13.6. C<sub>51</sub>H<sub>63</sub>N<sub>12</sub>I<sub>3</sub>·2H<sub>2</sub>O requires C, 48.6; H, 5.35; N, 13.3.

**1.2. Synthesis of compound [1](BF<sub>4</sub>)<sub>3</sub>.** Under aerobic conditions, a suspension of [1](I)<sub>3</sub> (100 mg, 0.082 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was treated with [Et<sub>3</sub>O](BF<sub>4</sub>) (38.1 mg, 0.245 mmol). The mixture was stirred at room temperature for 1 h. The solution was concentrated and diethyl ether (5 mL) was added for precipitation. The product was filtrated and washed with diethyl ether (5 mL). Compound [1](BF<sub>4</sub>)<sub>3</sub> (78.4 mg, 87%) was isolated as a green solid.  $\delta$ H NMR (500 MHz, DMSO-*d*<sub>6</sub>) 10.31 (s, 1H, NCHN), 9.32 (s, 2H, CH<sub>Ar</sub>), 4.96-4.63 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.25-1.96 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.67-1.42 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.16-0.89 (m, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).  $\delta$ F NMR (282 MHz, DMSO-*d*<sub>6</sub>) -148.40.  $\delta$ C NMR (126 MHz, DMSO-*d*<sub>6</sub>) 149.25 (NCHN), 145.18 (C<sub>q</sub> Ar), 139.27 (C<sub>q</sub> Ar), 134.44 (C<sub>q</sub> Ar), 113.38 (CH<sub>Ar</sub>),

47.17 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.46 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.25 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.47 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Electrospray MS (20 V, *m/z*): 281 (M<sup>3+</sup>, 100%). Found: C, 52.8; H, 6.1; N, 14.6. C<sub>51</sub>H<sub>63</sub>N<sub>12</sub>B<sub>3</sub>F<sub>12</sub>·3H<sub>2</sub>O requires C, 52.8; H, 6.0; N, 14.5.

**1.3. Synthesis of compound [1][RuCl<sub>2</sub>I(*p*-cymene)]<sub>3</sub>.** A suspension of compound **1**(I)<sub>3</sub> (50 mg, 0.041 mmol) and [RuCl(*p*-cymene)]<sub>2</sub> (37.5 mg, 0.061 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at room temperature overnight. Then the volatiles were removed nearly to dryness and *n*-hexane (5 mL) was added. The product was collected by filtration and washed with *n*-hexane (5 mL). Compound [1][RuCl<sub>2</sub>I(*p*-cymene)]<sub>3</sub> (52.2 mg, 60%) was isolated as a red solid.  $\delta$ H NMR (300 MHz, CDCl<sub>3</sub>) 10.85 (br s, 1H, NCHN), 8.95 (br s, 2H, CH<sub>Ar</sub>), 5.54 (br s, 2H, CH<sub>*p*-cym</sub>), 5.31 (br s, 2H, CH<sub>*p*-cym</sub>), 5.08-4.76 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.32-3.09 (m, 1H, CH<sub>isop *p*-cym</sub>), 2.32 (br s, 3H, CH<sub>3 *p*-cym</sub>), 2.22-1.97 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.69-1.47 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.37 (d, <sup>3</sup>J<sub>H-H</sub> = 5 Hz, 6H, CH<sub>3 isop *p*-cym</sub>), 1.04 (t, <sup>3</sup>J<sub>H-H</sub> = 6 Hz, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).  $\delta$ C NMR (75 MHz, CDCl<sub>3</sub>) 151.41 (NCHN), 144.11 (C<sub>q Ar</sub>), 140.36 (C<sub>q Ar</sub>), 135.25 (C<sub>q Ar</sub>), 113.64 (CH<sub>Ar</sub>), 96.71 (C<sub>q *p*-cym</sub>), 81.85 (CH *p*-cym), 79.92 (CH *p*-cym), 48.50 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.39 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.05 (CH<sub>isop *p*-cym</sub>), 22.48 (CH<sub>3 isop *p*-cym</sub>), 20.16 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.07 (CH<sub>3 *p*-cym</sub>), 13.84 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Electrospray MS (20 V, *m/z*): 281 (M<sup>3+</sup>, 100%) and 312 ([RuCl(*p*-cymene)(NCMe)]<sup>+</sup>, 30%). Electrospray negative MS (20 V, *m/z*): 433 ([RuCl<sub>2</sub>(*p*-cymene)(I)]<sup>-</sup>, 30%). Found: C, 45.5; H, 4.95; N, 7.8. C<sub>81</sub>H<sub>105</sub>N<sub>12</sub>Cl<sub>6</sub>I<sub>3</sub>Ru<sub>3</sub> requires C, 45.4; H, 4.9; N, 7.8.

**1.4. Synthesis of complex 2.** NaO<sup>t</sup>Bu (40.8  $\mu$ L, 0.082 mmol) was added dropwise to suspension of compound [1](I)<sub>3</sub> (100 mg, 0.082 mmol), NaH (6.5 mg, 0.269 mmol) and [IrCl(cod)]<sub>2</sub> (82.2 mg, 0.122 mmol) in THF (20 mL) at -78°C. The mixture was allowed to reach room temperature overnight. Then the volatiles were removed and the solid residue was suspended in CH<sub>2</sub>Cl<sub>2</sub>. The suspension was then filtered through a pad of Celite to remove insoluble solids. The solvent was removed under reduced pressure. The product was purified by column chromatography. Elution with a mixture CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane afforded a band that contained complex **2**. Complex **2** (45.7 mg, 27%) was isolated as a yellow solid.  $\delta$ H NMR (300 MHz, CDCl<sub>3</sub>) 8.50 (s, 2H, CH<sub>Ar</sub>), 5.14 (br s, 2H, CH<sub>cod</sub>), 5.02-4.85 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.85-4.68 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.15 (br s, 2H, CH<sub>cod</sub>), 2.46-2.16 (m, 8H, CH<sub>2 cod</sub>), 1.78-1.44 (m, 8H; 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.16 (t, <sup>3</sup>J<sub>H-H</sub> = 6 Hz, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).  $\delta$ C NMR (75 MHz, CDCl<sub>3</sub>) 205.60 (Ir-C<sub>carbene</sub>), 142.91 (C<sub>q Ar</sub>), 139.87 (C<sub>q Ar</sub>), 139.29 (C<sub>q Ar</sub>), 107.72 (CH<sub>Ar</sub>),

88.07 ( $\text{CH}_{\text{cod}}$ ), 56.98 ( $\text{CH}_{\text{cod}}$ ), 49.05 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 33.08 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 30.71 ( $\text{CH}_2_{\text{cod}}$ ), 30.27 ( $\text{CH}_2_{\text{cod}}$ ), 20.76 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.97 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ). Electrospray MS (20 V,  $m/z$ ): 2123 ( $[\text{M}+\text{H}]^+$ , 20%). Found: C, 42.4; H, 4.55; N, 7.9.  $\text{C}_{75}\text{H}_{96}\text{N}_{12}\text{I}_3\text{Ir}_3$  requires C, 42.4; H, 4.6; N, 7.9.

**1.5. Synthesis of complex 3.** CO gas was bubbled through a solution of complex **2** (70 mg, 0.033 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) for 1h at  $0^\circ\text{C}$ . The solution was then concentrated nearly to dryness and *n*-hexane was added for precipitation. The crude solid was washed three times with *n*-hexane to remove the released 1,5-cylooctadiene. Complex **3** (56.1 mg, 87 %) was collected by filtration.  $\nu_{\text{max}}/\text{cm}^{-1}$  2069 and 1992 (CO).  $\delta\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 8.75 (s, 2H,  $\text{CH}_{\text{Ar}}$ ), 5.01-4.82 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.82-4.60 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.31-2.05 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.75-1.62 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.12 (t,  $^3J_{\text{H-H}} = 9$  Hz, 6H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).  $\delta\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  194.27 (Ir-CO), 181.54 (Ir-CO), 167.71 (Ir- $\text{C}_{\text{carbene}}$ ), 143.57 ( $\text{C}_{\text{q Ar}}$ ), 139.92 ( $\text{C}_{\text{q Ar}}$ ), 138.38 ( $\text{C}_{\text{q Ar}}$ ), 110.10 ( $\text{CH}_{\text{Ar}}$ ), 49.79 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 30.65 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 20.50 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.94 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ). Electrospray MS (20 V,  $m/z$ ): 1967 ( $[\text{M}+\text{H}]^+$ , 20%). Found: C, 34.85; H, 3.05; N, 8.55.  $\text{C}_{57}\text{H}_{60}\text{N}_{12}\text{I}_3\text{Ir}_3\text{O}_6$  requires C, 34.8; H, 3.1; N, 8.55.

**1.6. Synthesis of complex 4.**  $\text{NaO}^t\text{Bu}$  (40.8  $\mu\text{L}$ , 0.082 mmol) was added dropwise to a suspension of compound **[1](I)<sub>3</sub>** (100 mg, 0.082 mmol), NaH (6.5 mg, 0.269 mmol) and  $\text{AuCl}(\text{SMe})_2$  (72.1 mg, 0.245 mmol) in THF (20 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to reach room temperature overnight. Then a spatula of charcoal was added and the mixture was stirred for further 15 minutes. The volatiles were removed and the solid residue was suspended in  $\text{CH}_2\text{Cl}_2$ . The suspension was filtered through a pad of Celite to remove insoluble solids. The solvent was evaporated under reduced pressure. The product was purified by column chromatography. Elution with a mixture  $\text{CH}_2\text{Cl}_2/n$ -hexane afforded a band that contained complex **4**. Complex **4** (34.1 mg, 23%) was isolated as a yellow solid.  $\delta\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) 8.71 (s, 2H,  $\text{CH}_{\text{Ar}}$ ), 4.84-4.67 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.23-2.08 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.68-1.61 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.09 (t,  $^3J_{\text{H-H}} = 5$  Hz, 6H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).  $\delta\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) 197.23 (Au- $\text{C}_{\text{carbene}}$ ), 144.18 ( $\text{C}_{\text{q Ar}}$ ), 140.76 ( $\text{C}_{\text{q Ar}}$ ), 137.80 ( $\text{C}_{\text{q Ar}}$ ), 111.35 ( $\text{CH}_{\text{Ar}}$ ), 49.90 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.25 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 20.82 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 14.17 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ). Electrospray MS (20 V,  $m/z$ ): 1813

([M+H]<sup>+</sup>, 30%). Found: C, 33.35; H, 3.4; N, 9.2. C<sub>51</sub>H<sub>60</sub>N<sub>12</sub>I<sub>3</sub>Au<sub>3</sub> requires C, 33.8; H, 3.3; N, 9.3.

**1.7. Synthesis of complex 5.** NaO<sup>t</sup>Bu (22.6 μL, 0.041 mmol) was added dropwise to a suspension of compound [1](I)<sub>3</sub> (50 mg, 0.041 mmol), NaH (3.3 mg, 0.137 mmol) and [Au(CNC)Cl] (56.5 mg, 0.122 mmol) in THF (20 mL) at -78°C. The mixture was allowed to reach room temperature overnight. Under air, a spatula of charcoal was added and the mixture was stirred for further 15 minutes. Then the volatiles were removed and the solid residue was suspended in CH<sub>2</sub>Cl<sub>2</sub>. The suspension was filtered through a pad of Celite to remove insoluble solids. The volatiles were removed nearly to dryness and diethyl ether (5 mL) was for precipitation. The solid so formed was filtrated and washed with diethyl ether (5 mL). Complex 5 (20.5 mg, 24%) was isolated as a brown solid. δH NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 9.16 (s, 2H, CH<sub>Ar</sub>), 8.20 (t, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 1H, CH<sub>pyridyl</sub>), 7.83 (d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 2H, CH<sub>pyridyl</sub>), 7.79 (d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, 2H, CH<sub>phenyl</sub>), 7.48-7.30 (m, 4H, CH<sub>phenyl</sub>), 7.22-7.10 (m, 2H, CH<sub>phenyl</sub>), 4.96-4.82 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.15-2.13 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.56-1.43 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.89 (t, <sup>3</sup>J<sub>H-H</sub> = 5 Hz, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). δC NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 172.33 (Au-C<sub>carbene</sub>), 165.28 (C<sub>q</sub> CNC), 164.26 (C<sub>q</sub> CNC), 149.94 (C<sub>q</sub> CNC), 145.16 (C<sub>q</sub> Ar), 140.77 (C<sub>q</sub> Ar), 137.64 (C<sub>q</sub> Ar), 136.40 (CH<sub>pyridyl</sub>), 133.57 (CH<sub>phenyl</sub>), 129.06 (CH<sub>phenyl</sub>), 127.31 (CH<sub>phenyl</sub>), 118.94 (CH<sub>phenyl</sub>), 113.24 (CH<sub>Ar</sub>), 104.52 (CH<sub>pyridyl</sub>), 50.80 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.84 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.67 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.77 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Electrospray MS (20 V, *m/z*): 707 (M<sup>3+</sup>, 100%). Found: C, 49.0; H, 3.75; N, 8.4. C<sub>102</sub>H<sub>93</sub>N<sub>15</sub>Au<sub>3</sub>I<sub>3</sub> requires C, 49.0; H, 3.75; N, 8.4.

**1.8. Synthesis of compound 6.** A suspension of compound [1](I)<sub>3</sub> (100 mg, 0.082 mmol) and Ag<sub>2</sub>O (97.5 mg, 0.408 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), was stirred at room temperature overnight under the exclusion of light. Then the mixture was filtered through a pad of Celite to remove insoluble salts. The solution was concentrated nearly to dryness and diethyl ether (5 mL) was added to precipitate the complex, which was collected by filtration and further washed with diethyl ether. Complex 6 (28.2 mg, 39%) was isolated as a red solid.  $\nu_{\max}/\text{cm}^{-1}$  1735 (CO). δH NMR (300 MHz, CDCl<sub>3</sub>) 8.11 (s, 2H, CH<sub>Ar</sub>), 4.14-4.01 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.04-1.82 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.59-1.44 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.35-1.18 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.05 (t, <sup>3</sup>J<sub>H-H</sub> = 6 Hz, 6H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). δC NMR (75 MHz, CDCl<sub>3</sub>) 154.98 (NCON), 141.33 (C<sub>q</sub> Ar), 141.06 (C<sub>q</sub> Ar), 135.92 (C<sub>q</sub> Ar), 104.72 (CH<sub>Ar</sub>), 41.86 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.07

(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.84 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20.40 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.90 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Electrospray MS (20 V, *m/z*): 889 ([M+H]<sup>+</sup>, 20%). Found: C, 68.9; H, 6.9; N, 18.7. C<sub>51</sub>H<sub>63</sub>N<sub>12</sub>O<sub>3</sub> requires C, 68.9; H, 6.8; N, 18.9.

## 2. Catalytic experiments

### 2.1. Hydroamination of alkynes

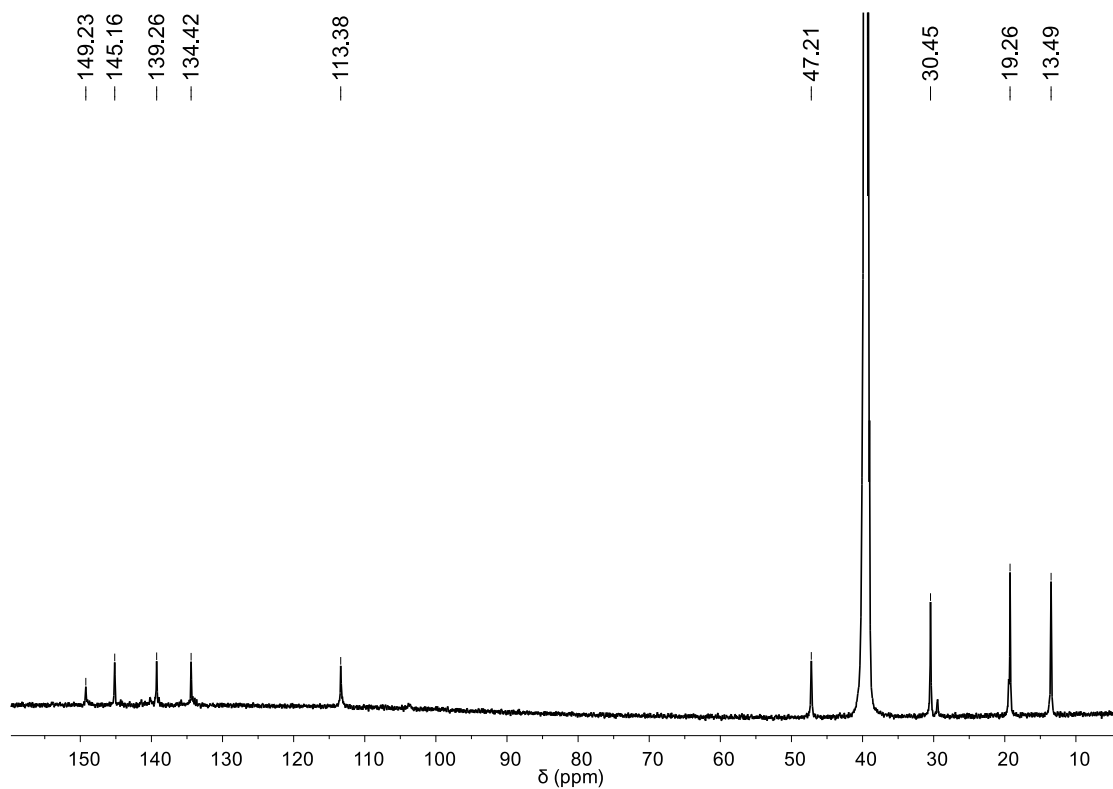
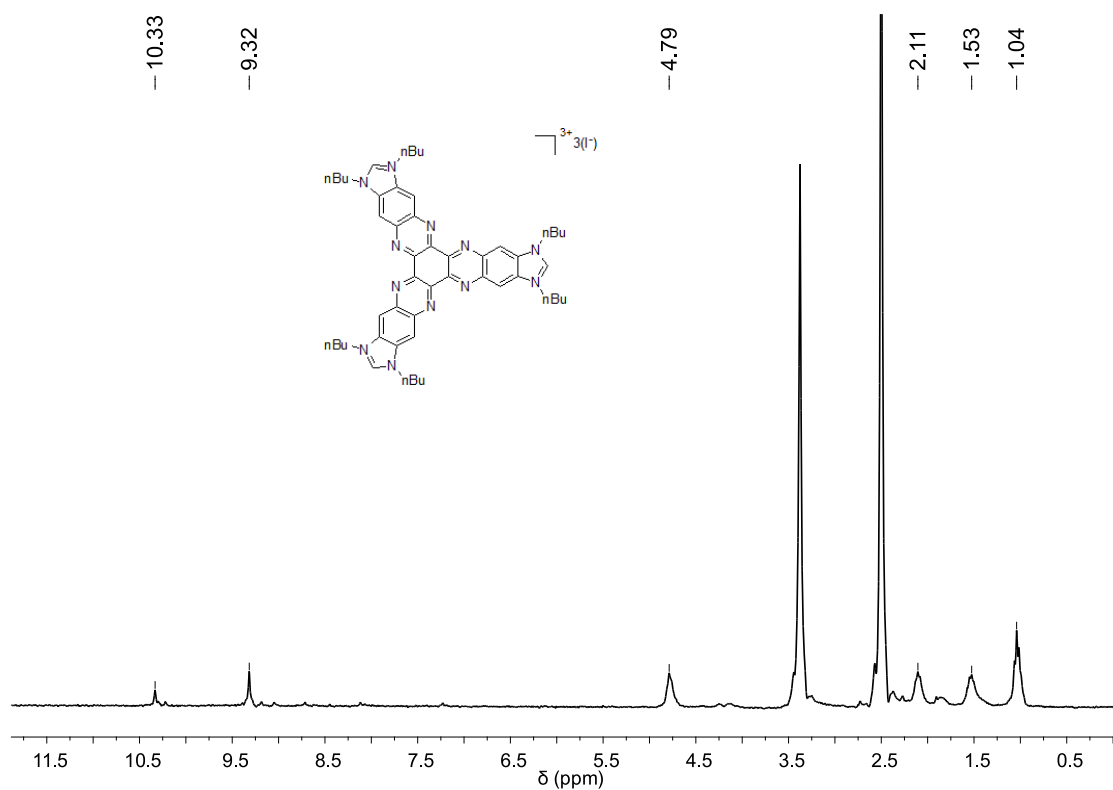
Typical procedure for catalysis hydroamination of alkynes: complex **4** (0.0016 mmol) or **7** (0.005 mmol) and AgBF<sub>4</sub> (0.01 mmol) were dissolved in MeCN (1 mL) in a thick-walled Schlenk tube fitted with a Teflon cap and stirred for 5 minutes. Then the corresponding arylamine (0.55 mmol), phenylacetylene (0.50 mmol) and anisole as internal standard (0.50 mmol) were subsequently added. The resulting mixture was stirred at 90 °C for the appropriate time. The evolution of the reactions and yields were determined by GC analysis.

### 2.2. Synthesis of $\alpha$ -aminonitriles (three-component Strecker reaction)

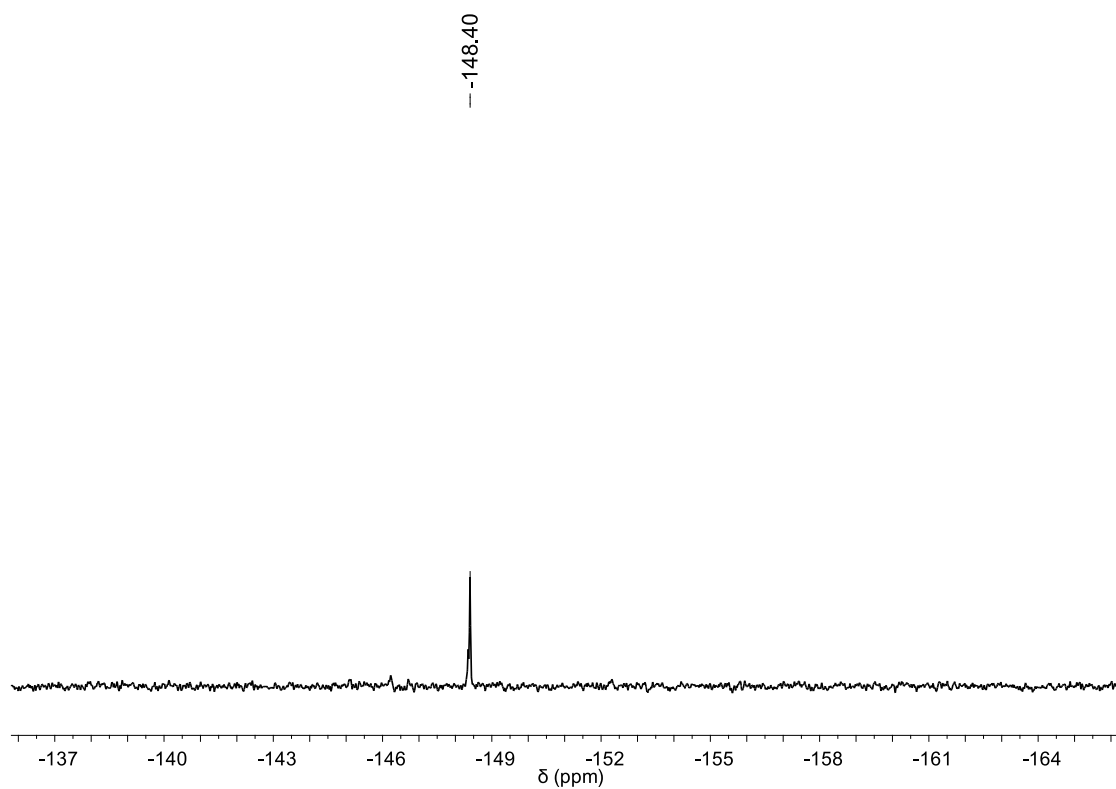
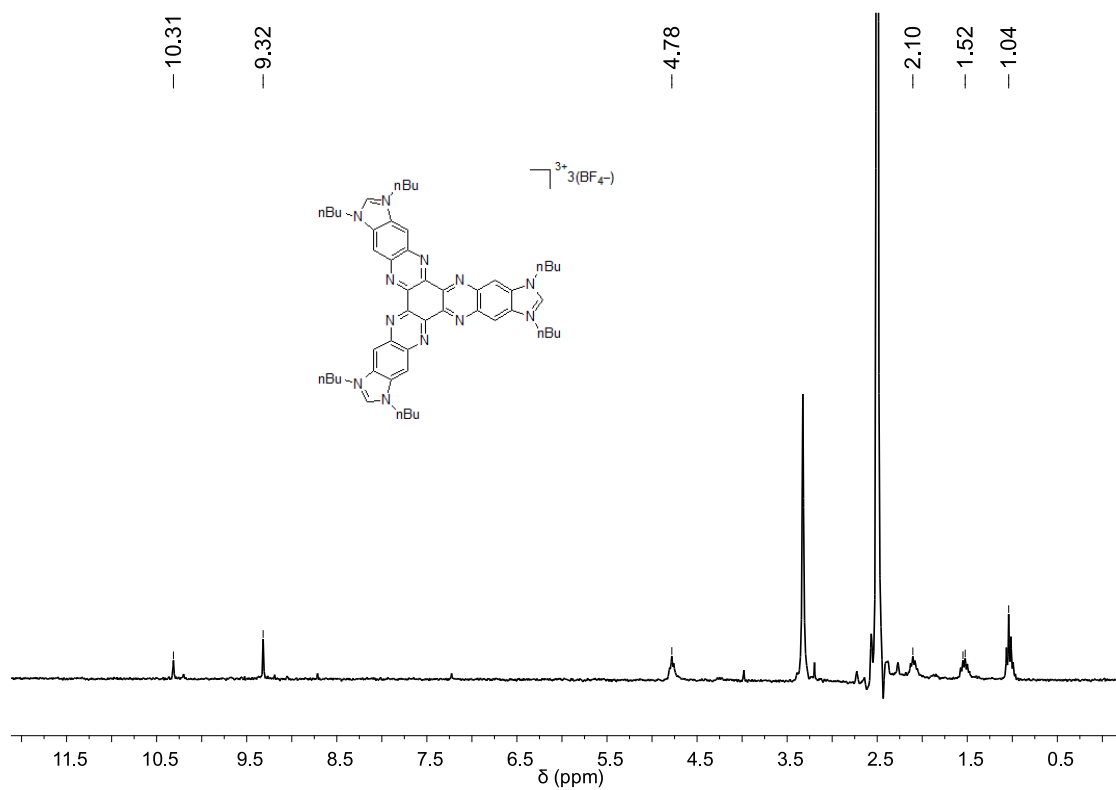
A capped vessel containing a stirrer was charged with the corresponding ketone (0.5 mmol), aniline (0.55 mmol), TMS-CN (1 mmol), anisole as internal standard (0.5 mmol), complex **4** (0.0066 mmol) or **7** (0.02 mmol), and 2 mL of dichloromethane. The resulting mixture was stirred for 24 h at room temperature. The evolution of the reactions, yields and conversions were determined by GC analysis.

### 3. Spectroscopic data

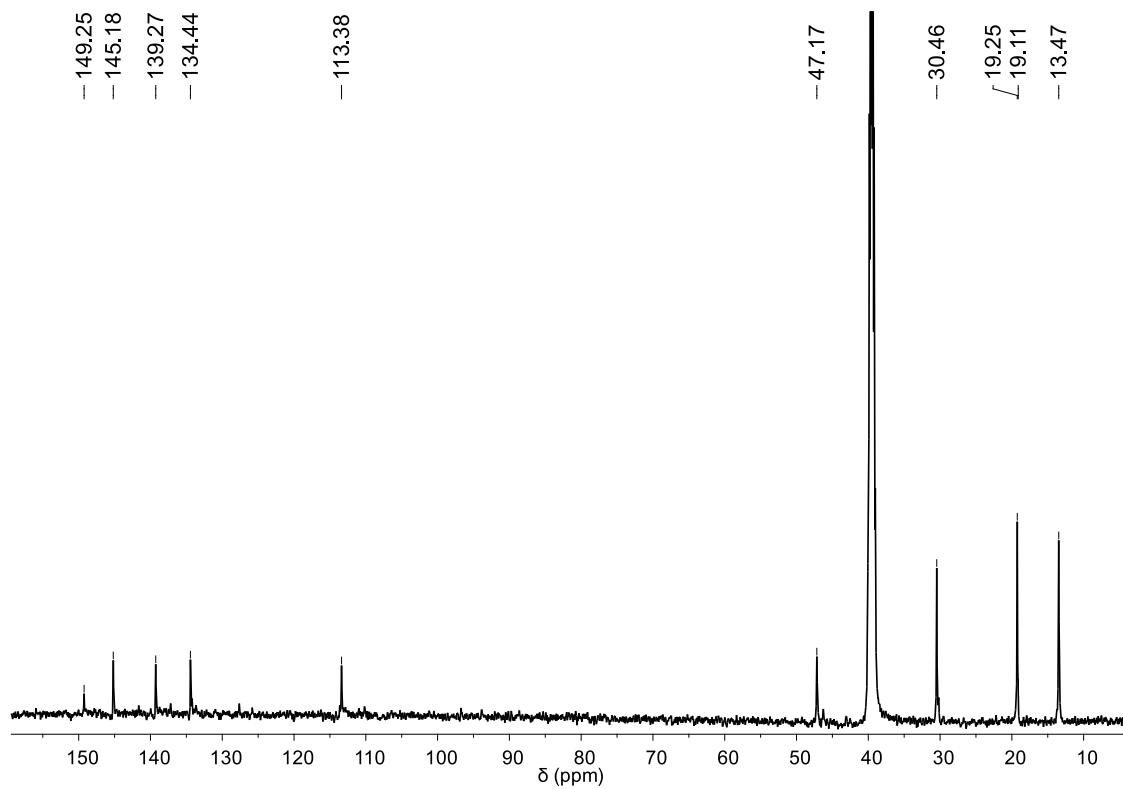
#### 3.1. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of [1](I)<sub>3</sub>



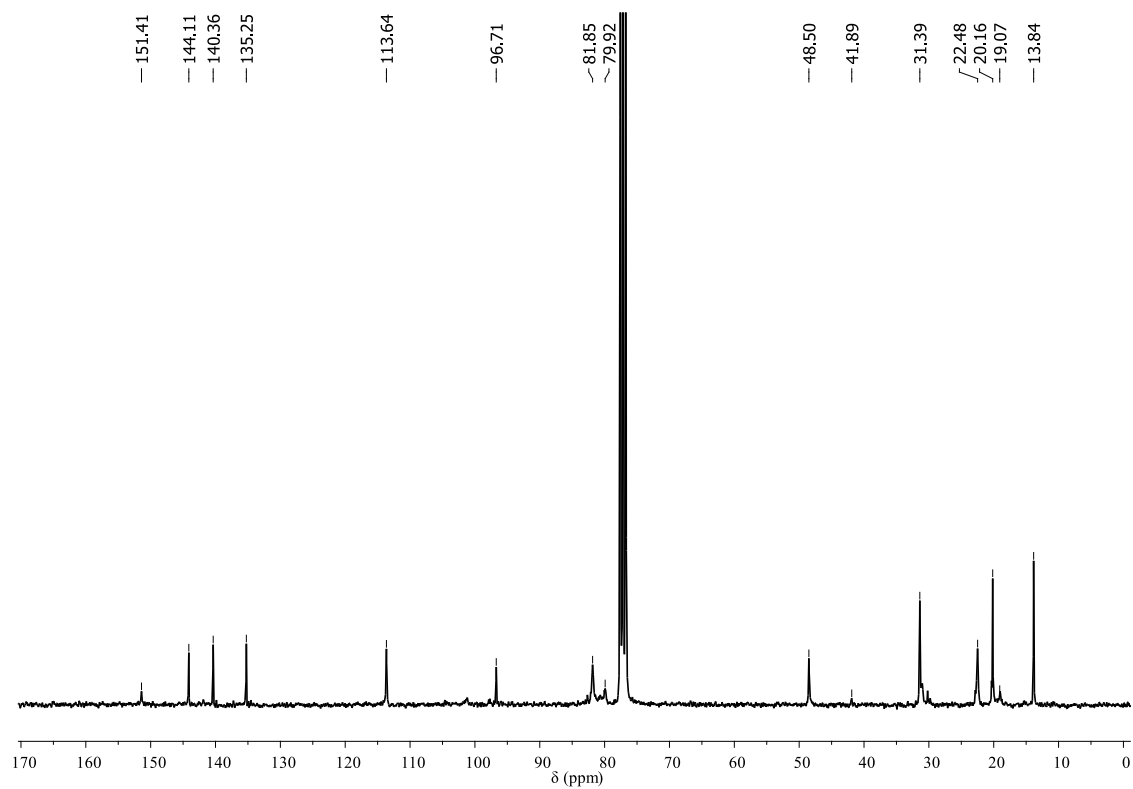
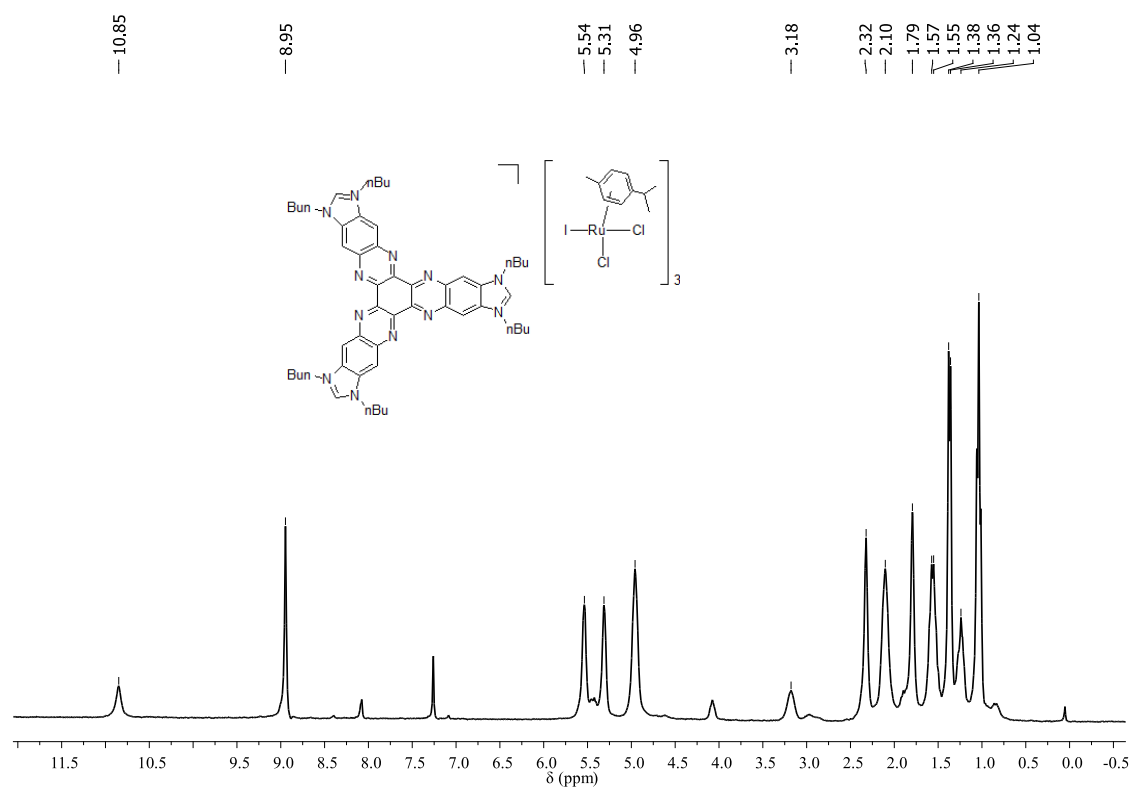
### 3.2. $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR spectra of $[1](\text{BF}_4)_3$



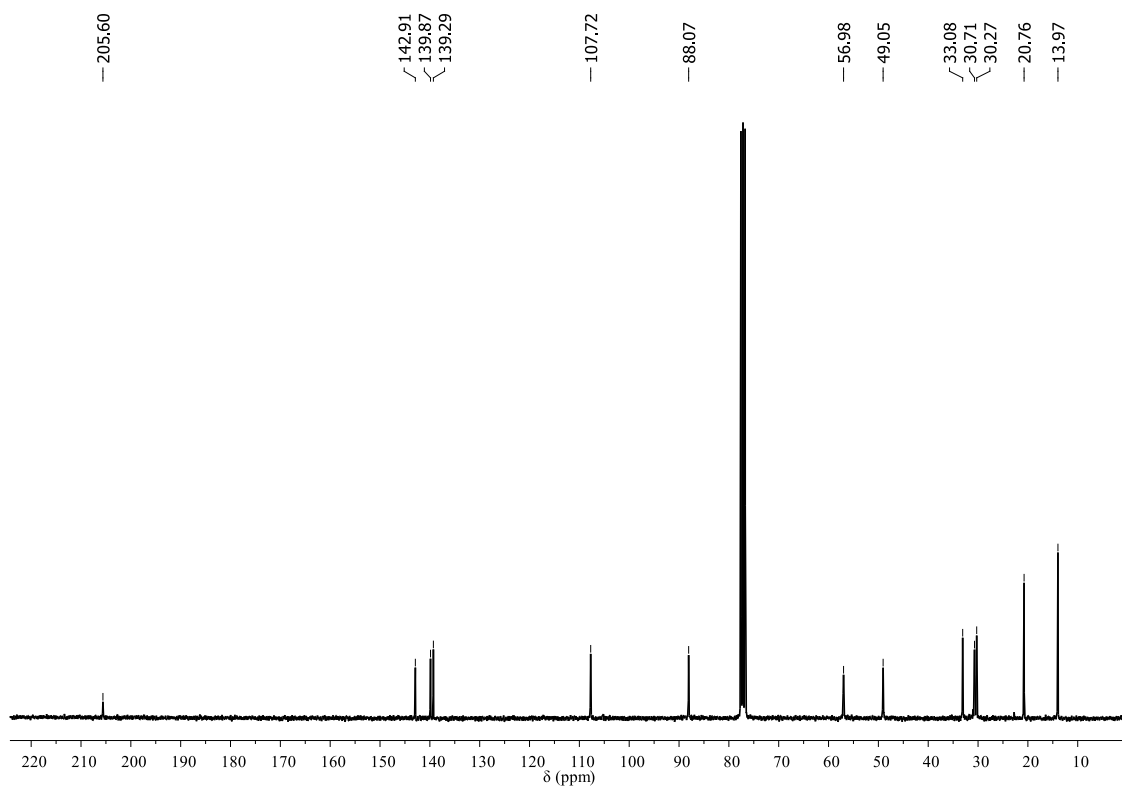
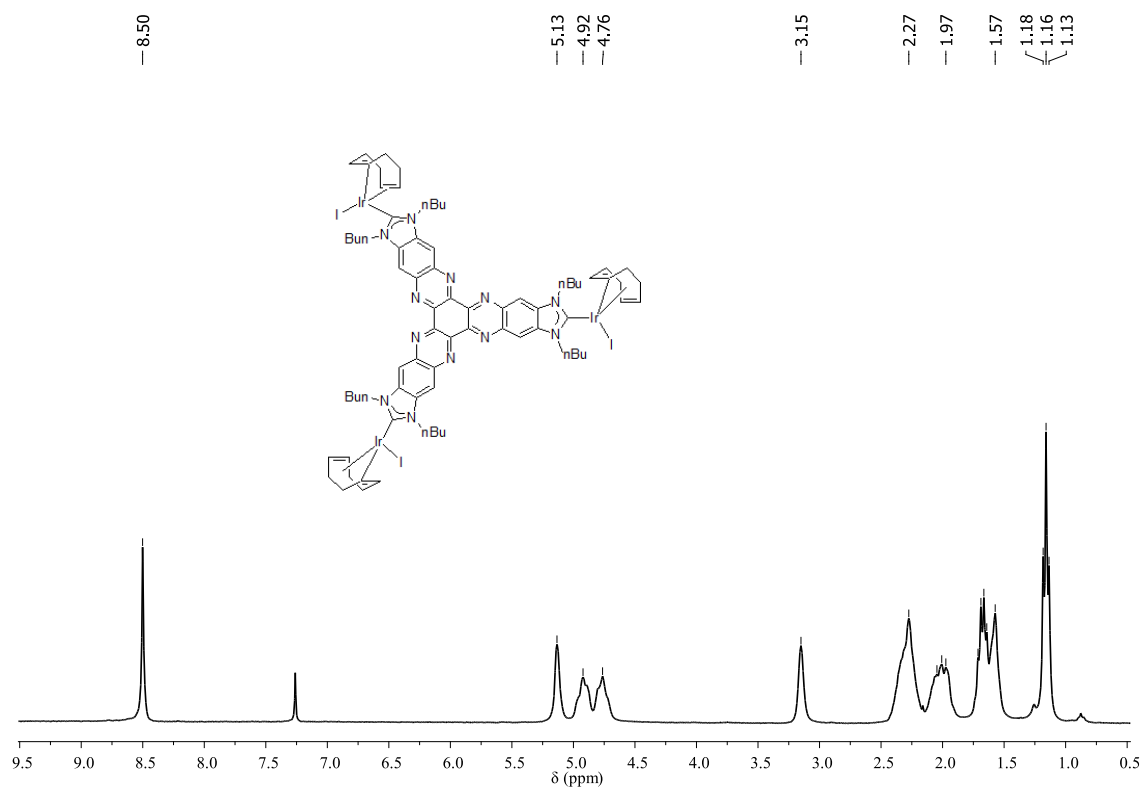




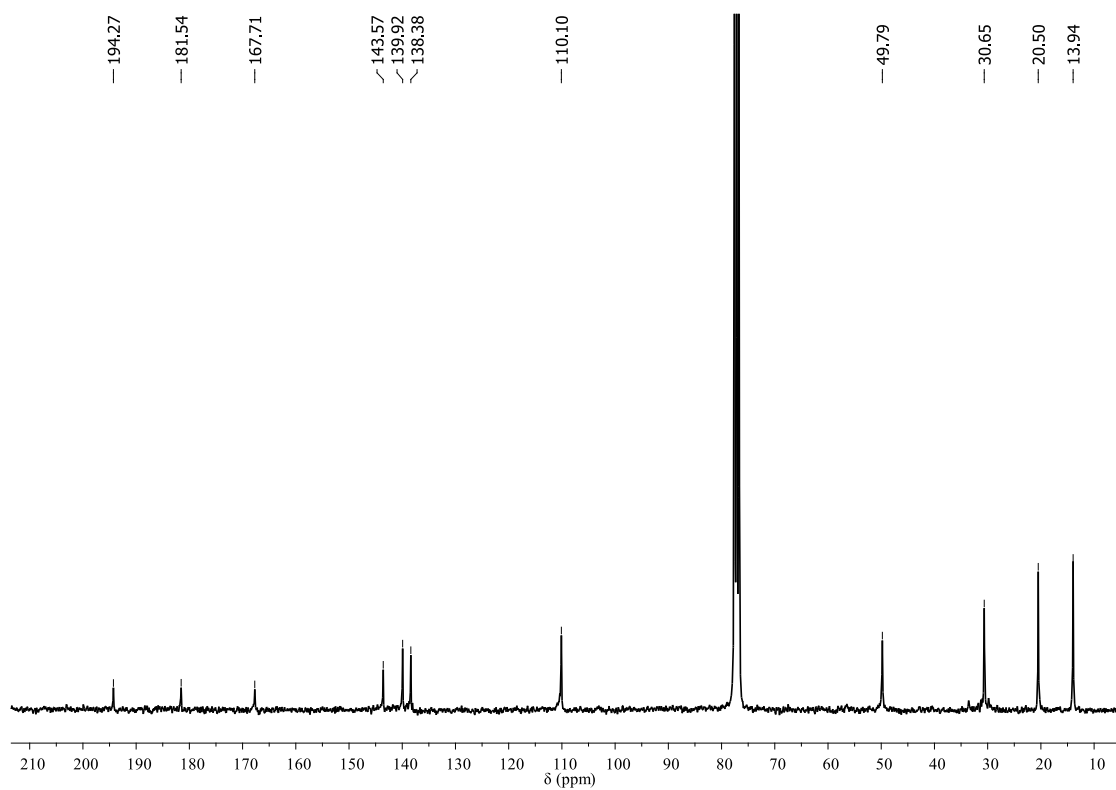
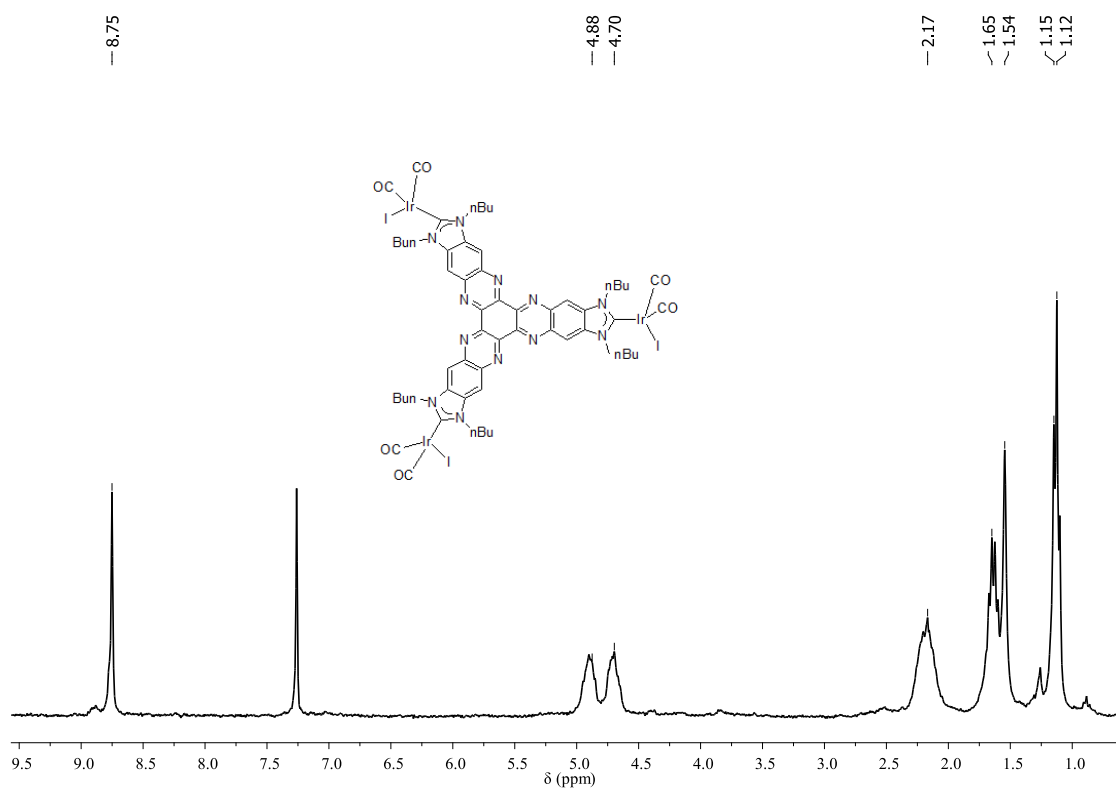
### 3.3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of $[\mathbf{1}](\text{RuCl}_2\text{I}(p\text{-cymene)})_3$



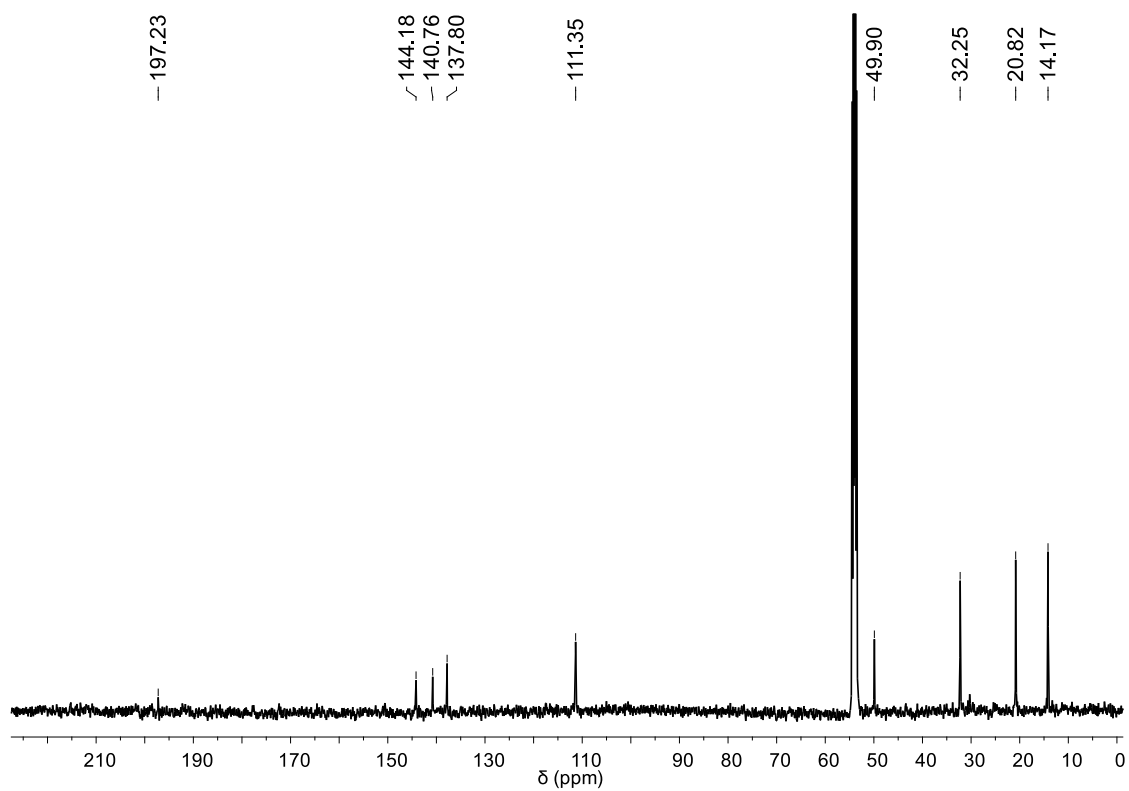
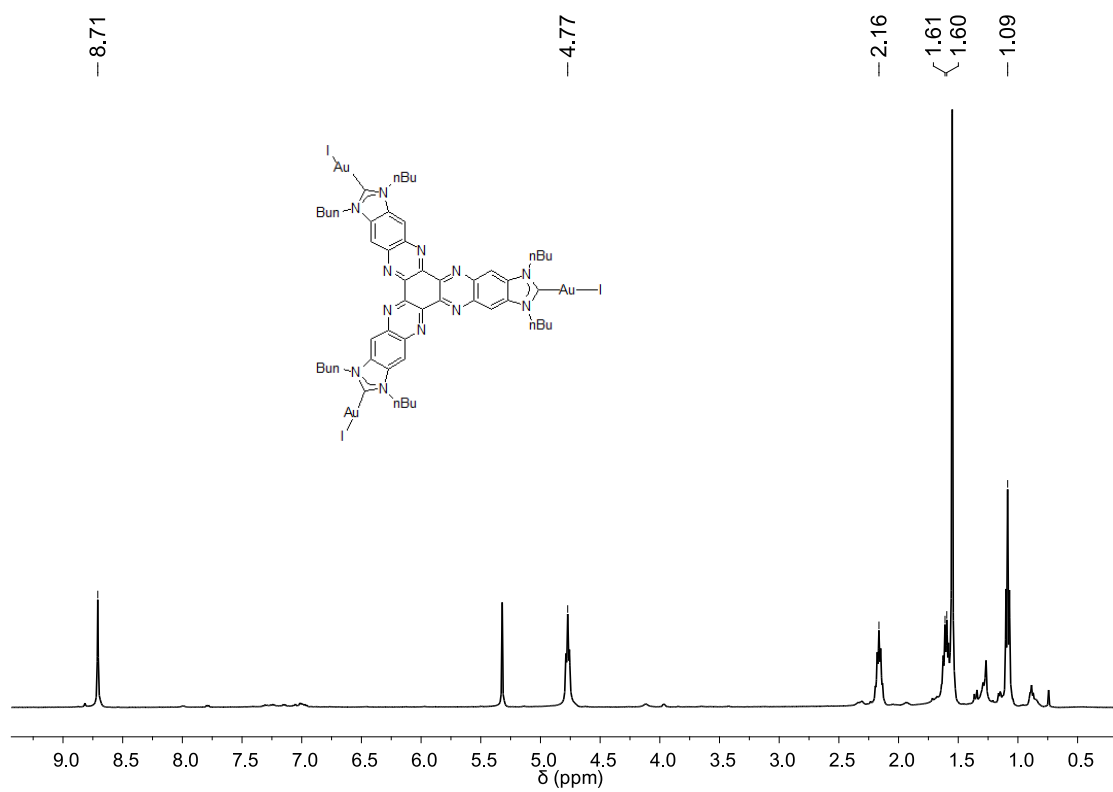
### 3.4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of **2**



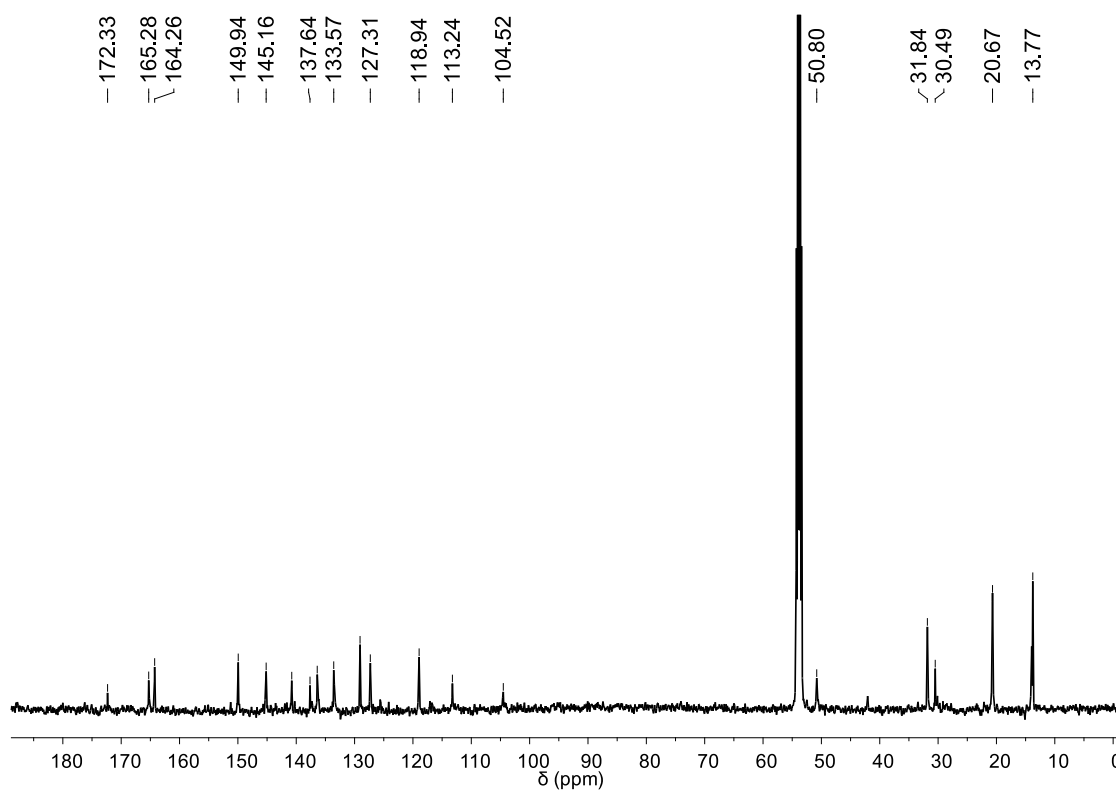
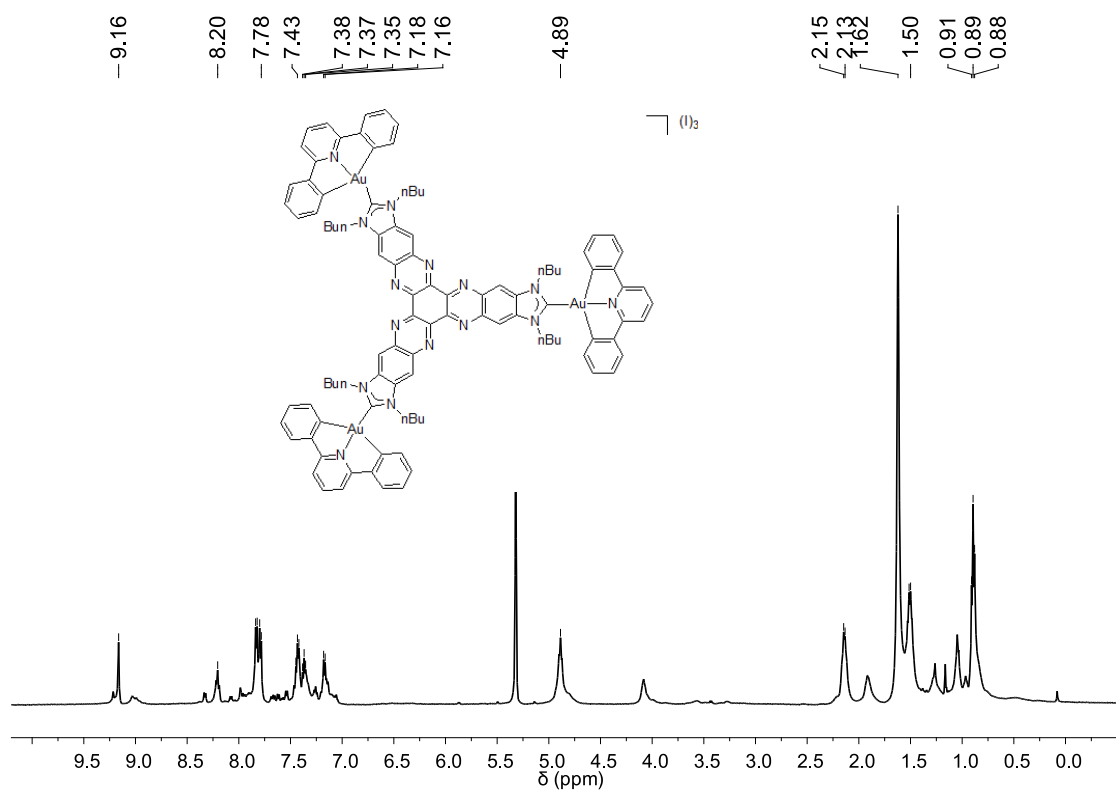
### 3.5. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 3



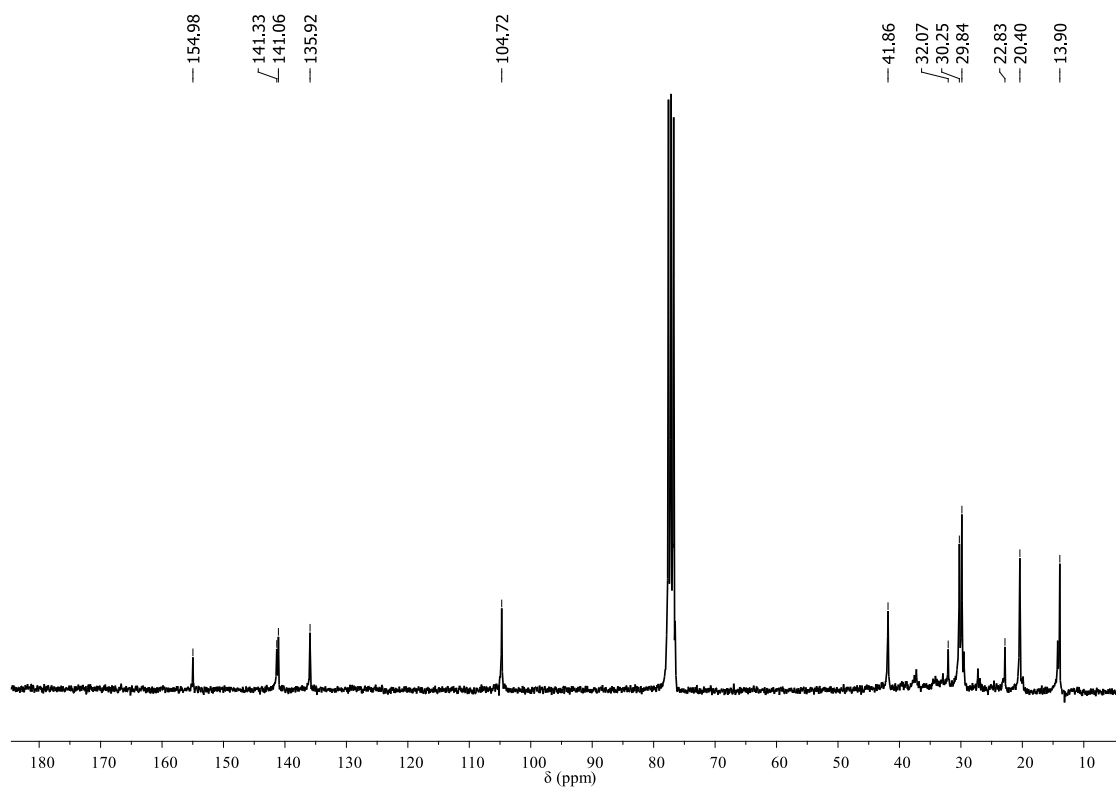
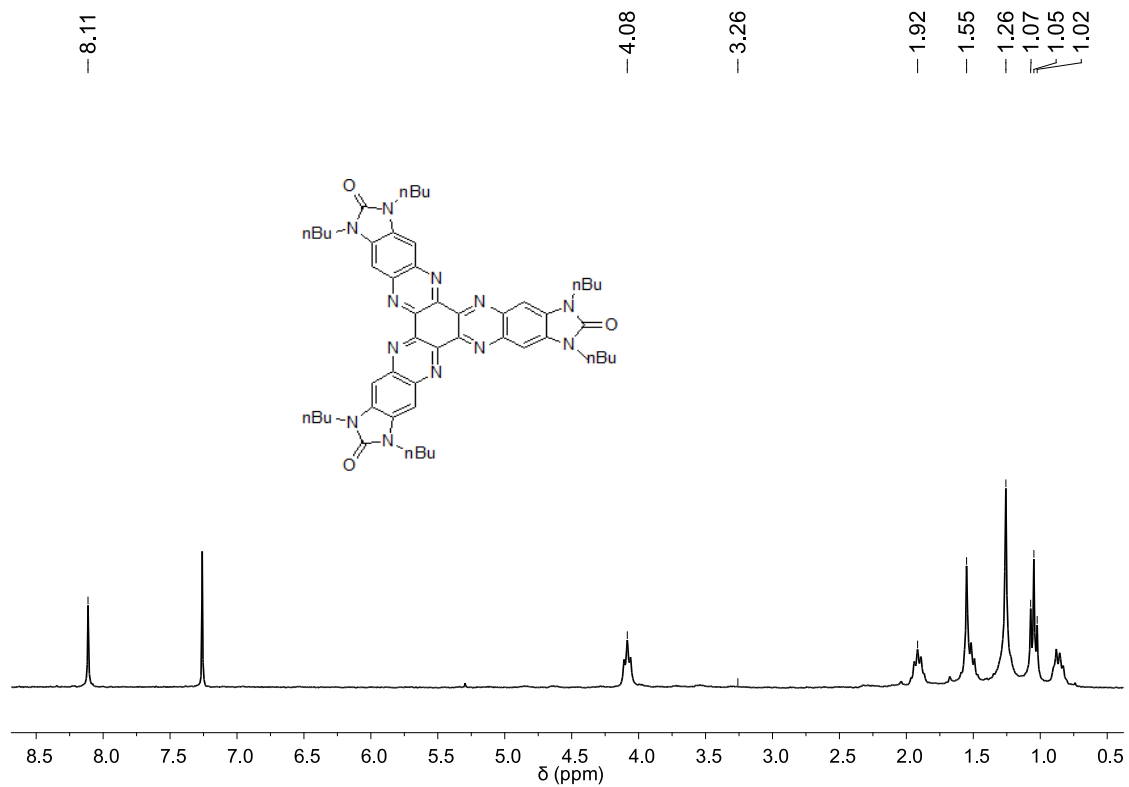
### 3.6. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 4



### 3.7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 5



### 3.7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of **6**



#### 4. X-Ray Crystallography

**X-Ray Diffraction studies for compound [1][RuCl<sub>2</sub>I(*p*-cymene)]<sub>3</sub>.** Crystals suitable for X-Ray studies of complex [1][RuCl<sub>2</sub>I(*p*-cymene)]<sub>3</sub> were obtained by slow diffusion of hexane into a concentrated solution of dichloromethane and methanol. Diffraction data was collected on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multi-scan method were applied. Using Olex2,<sup>2</sup> the structure of the complex was solved using Charge Flipping<sup>3</sup> in Superflip and refined with ShelXL<sup>4</sup> refinement package using Least Squares minimisation. Key details of the crystals and structure refinement data are summarized in Supplementary Table S1.

The structure model exhibits significant disorder in the lattice solvent region and in the cation environment. The occupancy of these disordered components was refined. One of the *n*-butyl groups exhibits disorder; bond distance restraints (ShelX DFIX and SADI) were applied. The crystal contains a mixture of [RuCl<sub>3</sub>(*p*-cymene)] and [RuCl<sub>2</sub>I(*p*-cymene)] cations, which were refined with a 40% and 60% occupancy, respectively. The lattice solvent region has been treated using PLATON/SQUEEZE<sup>5</sup> procedure. H-atoms were introduced and refined on a riding model. Non-hydrogen atoms were refined anisotropically. A global, enhanced rigid bond restraint (ShelX RIGU) was applied. CCDC- 1528547 contains the supplementary crystallographic data for this paper.

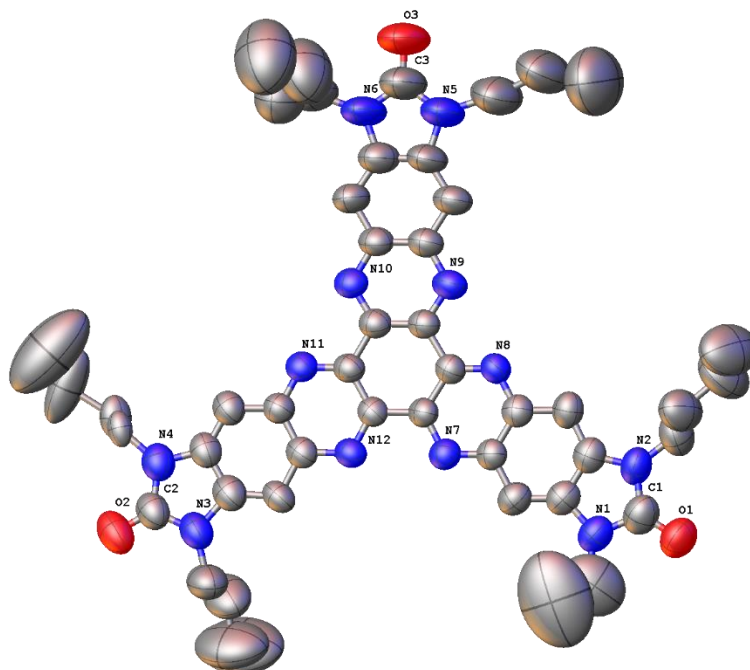
**Supplementary Table S1.** Summary of crystal data, data collection, and structure refinement details of [1][RuCl<sub>2</sub>I(*p*-cymene)]<sub>3</sub>

Empirical formula	C <sub>84.56</sub> H <sub>83.22</sub> Cl <sub>12.57</sub> I <sub>1.8</sub> N <sub>12</sub> O <sub>2.95</sub> Ru <sub>3</sub>
Formula weight	2292.12
Temperature/K	293
Crystal system	trigonal
Space group	R3
a/Å	17.7983(7)
b/Å	17.7983(7)
c/Å	32.0239(18)
$\alpha$ /°	90.0
$\beta$ /°	90.0



$\gamma/^\circ$	120.0
Volume/ $\text{\AA}^3$	8785.4(7)
Z	3
$\rho_{\text{calc}}/\text{g/cm}^3$	1.300
$\mu/\text{mm}^{-1}$	1.185
F(000)	3418.0
Crystal size/ $\text{mm}^3$	0.2212 x 0.1837 x 0.0356
2 $\Theta$ range for data collection/ $^\circ$	6.89 to 51.992
Index ranges	$-21 \leq h \leq 19, -17 \leq k \leq 19, -39 \leq l \leq 34$
Reflections collected	15067
Independent reflections	6958 [Rint = 0.0447, Rsigma = 0.0579]
Data/restraints/parameters	6958/405/369
Goodness-of-fit on $F^2$	1.027
Final R indexes [ $I \geq 2\sigma(I)$ ]	R1 = 0.0830, wR2 = 0.2163
Final R indexes [all data]	R1 = 0.0998, wR2 = 0.2426
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.90/-0.87
Flack parameter	0.043(18)

### Preliminary molecular structure of compound 6



**Figure S1.** Molecular structure of compound 6. Ellipsoids are at 50% probability. Hydrogen atoms and solvent (dichloromethane) have been omitted for clarity.

## 5. References

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