

## Ruthenium complexes with chelating carboxylate-NHC ligands as efficient catalysts for C–H arylation in water

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### Synthetic procedures and characterization of isolated compounds

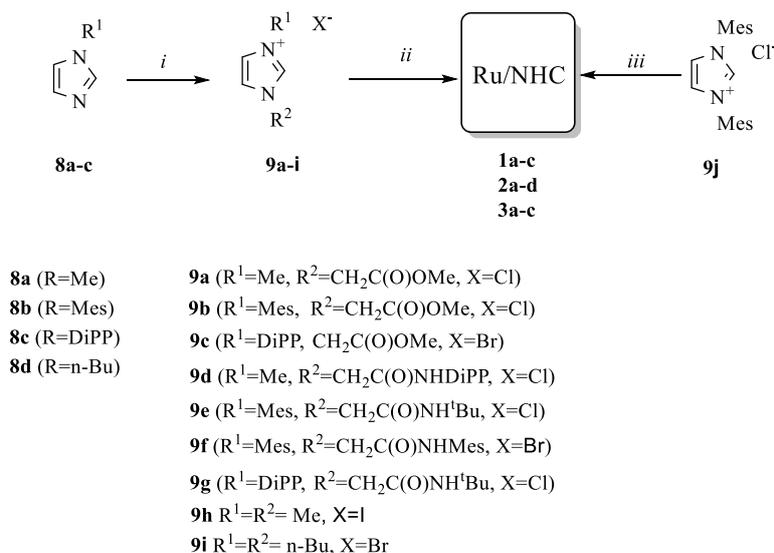
#### General Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker Avance Neo 300 spectrometer. Chemical shifts are given relative to the residual signals of protons of chloroform-*d*, dioxane-*d*<sub>8</sub>, or DMSO-*d*<sub>6</sub> (7.26, 3.53 and 2.50 ppm for <sup>1</sup>H NMR, respectively) or carbon signals in chloroform-*d*, methylene chloride-*d*<sub>2</sub>, or DMSO-*d*<sub>6</sub> (77.16, 66.66, and 39.52 ppm for <sup>13</sup>C NMR, respectively).

High-resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF instrument equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was applied for the analysed solutions at a flow rate 3 μL min<sup>–1</sup>. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 dm<sup>3</sup> min<sup>–1</sup>). The dry temperature was established at 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software package.

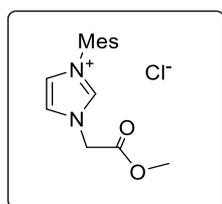
Melting points were determined in open capillary tubes using a Thiele apparatus and are uncorrected.

**Materials.** Imidazoles **8a-c**,<sup>S1</sup> azolium salts **9a**<sup>S2</sup> **f**<sup>S2</sup>, **h**<sup>S3</sup>, **i**<sup>S4</sup>, **j**<sup>S5</sup>, ruthenium complexes **1a,b**<sup>S6-7</sup>, **3a,b**<sup>S8</sup>, **3c**<sup>S9</sup> were synthesized according to previously described procedures.

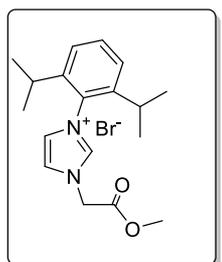


**Scheme S1.** Synthesis of imidazolium salts and Ru/NHC complexes. *Reagents and conditions:* *i:* R<sup>2</sup>X, MeCN, 80 °C, 20 h; *ii:* Ag<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C, 3 h, then [RuCl<sub>2</sub>(Cymene)]<sub>2</sub>, 25 °C, 20 h; *iii:* 1) LiHMDS, toluene 25 °C, 0.5 h, then [RuCl<sub>2</sub>(Cymene)]<sub>2</sub>, 25 °C, 20 h.

**General procedure for the synthesis of compounds 9b-e,g.** Appropriate N-substituted imidazole **8a-c** (1 mmol), corresponding alkyl halide (1.2 mmol) and acetonitrile (5 mL) were heated at 80 °C under stirring within 24 h. Then volatiles were removed in vacuo and the residue obtained was recrystallized from a MeCN-EtOAc (1:2) mixture and dried in vacuo.

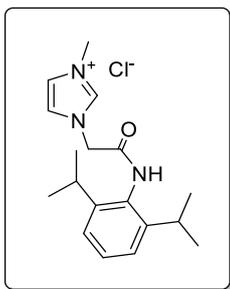


**3-Mesityl-1-(2-methoxy-2-oxoethyl)-1H-imidazol-3-ium chloride (9b).** Yield 0.215 g (73%), white crystals, mp 180-181 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 2.03 (s, 6H), 2.34 (s, 3H), 3.79 (s, 3H), 5.43 (s, 2H), 7.17 (s, 2H), 7.98 (t, *J* = 1.8 Hz, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 9.58 (t, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 16.8, 20.6, 49.9, 53.0, 123.5, 124.5, 129.3, 131.1, 134.2, 139.0, 140.4, 167.3. ESI-MS(TOF) calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M – Cl]<sup>+</sup> *m/z* 259.1441, found 259.1445

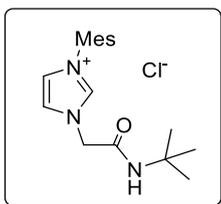


**3-(2,6-Diisopropylphenyl)-1-(2-methoxy-2-oxoethyl)-1H-imidazol-3-ium bromide (9c).** Yield 0.318 g (83%), white crystals, mp 182-183 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 1.15 (d, *J* = 6.8 Hz, 12H), 2.29 (p, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 5.40 (s, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.64 (m, 1H), 8.07 (t, *J* = 1.6 Hz, 1H), 8.13 (t, *J* = 1.7 Hz, 1H), 9.55 (d, *J* = 1.8 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 23.7, 28.1, 50.0, 53.0, 124.5, 124.6, 124.7, 130.5, 131.6, 139.3, 145.0, 167.2. ESI-MS(TOF) calcd. for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M – Br]<sup>+</sup> *m/z* 301.1911, found *m/z* 301.1923

**1-(2-((2,6-Diisopropylphenyl)amino)-2-oxoethyl)-3-methyl-1H-imidazol-3-ium chloride (9d).** Yield

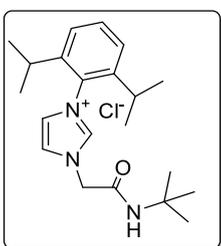


0.255 g (76%), white crystals, mp 215-216 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 1.00-1.20 (m, 12H). 3.07 (h, *J* = 6.9 Hz, 2H), 3.91 (s, 3H, CH<sub>3</sub>), 5.36 (s, 2H), 7.11-7.19 (m, 2H), 7.27 (m, 1H). 7.73 (t, *J* = 1.8 Hz, 1H); 7.78 (t, *J* = 1.8, 1H Ar); 9.22 (t, *J* = 1.7 Hz, 1H Ar); 10.15 (s, 1H, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 23.3, 23.9, 28.0, 35.9, 50.5, 123.0, 123.2, 123.7, 127.9, 131.4, 137.8, 145.9, 164.8. ESI-MS(TOF) calcd. for C<sub>18</sub>H<sub>26</sub>N<sub>3</sub>O<sup>+</sup> [M – Cl]<sup>+</sup> *m/z* 300.2070, found *m/z* 300.2071.



**1-(2-(*tert*-Butylamino)-2-oxoethyl)-3-mesityl-1H-imidazol-3-ium chloride (9e).** Yield 0.212 g (63%), white crystals, mp 191-192 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 1.29 (s, 9H); 2.03 (s, 6H, Me); 2.33 (s, 3H, Me); 5.06 (s, 2H, CH<sub>2</sub>); 7.14 (s, 2H, Ar); 7.91 (br. s, 1H); 8.01 (br. s, 1H); 8.45 (br. s, 1H, NH); 9.47 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 16.9, 20.6, 28.5, 50.8, 51.3, 123.1, 124.5, 129.2, 131.2, 134.3, 138.8, 140.2,

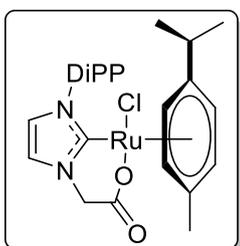
163.7. ESI-MS(TOF) calcd. for C<sub>18</sub>H<sub>26</sub>N<sub>3</sub>O<sup>+</sup> [M – Cl]<sup>+</sup> *m/z* 300.2070, found *m/z* 300.2068.



**1-(2-(*tert*-Butylamino)-2-oxoethyl)-3-(2,6-diisopropylphenyl)-1H-imidazol-3-ium chloride (9g).** Yield 0.287g (76%) mp 226-227 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 1.15 (d, *J* = 6.8 Hz, 12H), 1.30 (s, 9H), 2.30 (h, *J* = 6.8 Hz, 2H), 5.03 (s, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.69 (m, 1H), 8.04 (dt, *J* = 8.3, 1.8 Hz, 2H), 8.32 (s, 1H), 9.52 (t, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 23.76, 23.80, 28.0, 28.4, 50.8, 51.5, 124.3, 124.4, 124.6, 130.6, 131.4, 139.2, 145.2, 163.6. ESI-MS(TOF) calcd. for

C<sub>21</sub>H<sub>32</sub>N<sub>3</sub>O<sup>+</sup> [M – Cl]<sup>+</sup> 342.2540 found *m/z* 342.2553.

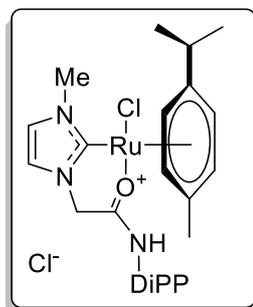
**General procedure for the synthesis of Ru/NHC complexes 1c,2a-d.** A mixture of the corresponding azolium salt **9a,d-g** (0.25 mmol), Ag<sub>2</sub>O (0.15 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was stirred at room temperature under argon atmosphere in the absence of light for 3 h. Then a solution of [RuCl<sub>2</sub>(cymene)]<sub>2</sub> (0.125 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added to the reaction mixture. Then the resulted mixture was additionally stirred within 20 h, filtered through a short pad of Celite® and evaporated in vacuo. Crude product was chromatographed on SiO<sub>2</sub> column (eluting with CH<sub>2</sub>Cl<sub>2</sub> - acetone 5:1 mixture) and recrystallized from appropriate solvent.



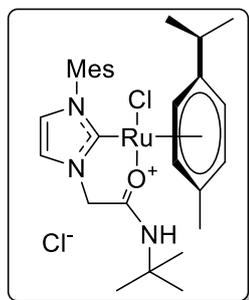
**1c:** Yield 0.078 g (56%), orange crystals, mp > 150 °C, decomp. (Et<sub>2</sub>O-benzene).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.91 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.24-1.29 (m, 6H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.81 (s, 3H), 2.57 – 2.76 (m, 2H), 3.01 (p, *J* = 6.6 Hz, 1H), 3.24 (d, *J* = 5.4 Hz, 1H), 4.28 (d, *J* = 15.5 Hz, 1H), 5.00 (d, *J* = 15.5 Hz, 1H), 5.12 (d, *J* = 5.4 Hz, 1H), 5.54 – 5.67 (m, 2H), 6.96 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 7.38-7.46 (m, 2H), 7.61 (t, *J* = 7.7 Hz, 1H). <sup>13</sup>C

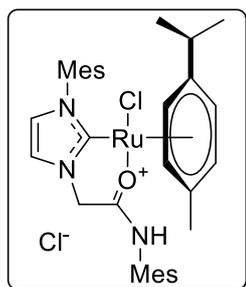
NMR (CDCl<sub>3</sub>, 75 MHz): δ 18.5, 21.2, 22.1, 22.7, 23.4, 26.5, 27.3, 28.2, 28.7, 28.8, 30.1, 54.9, 93.4, 97.0, 100.9, 122.1, 123.9, 124.7, 125.1, 131.2, 137.4, 145.7, 145.8, 148.6, 171.0, 172.3. ESI-MS(TOF) calcd. for C<sub>27</sub>H<sub>35</sub>N<sub>2</sub>O<sub>2</sub>Ru [M-Cl]<sup>+</sup> *m/z* 521.1744, found *m/z* 521.1760.



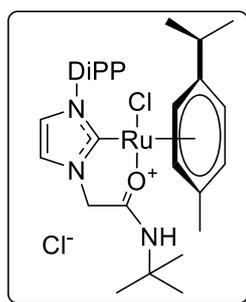
**2a:** Yield 0.114 g (76%), orange solid, mp > 200 °C, decomp. (Et<sub>2</sub>O-DCM). <sup>1</sup>H NMR (1,4-Dioxane-*d*<sub>8</sub>, 300 MHz, 70 °C) δ 1.12 (d, *J* = 6.8 Hz, 9H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.95 (s, 3H), 2.89 – 3.14 (m, 3H), 3.99 (s, 3H), 5.16 (d, *J* = 5.9 Hz, 2H), 5.45 (s, 2H), 5.51 (d, *J* = 5.9 Hz, 2H), 7.07 – 7.13 (m, 3H), 7.19 (m, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 8.94 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 18.4, 22.7, 24.0, 29.3, 31.6, 39.8, 55.4, 82.2, 87.9, 99.8, 109.5, 123.8, 123.9, 124.5, 128.5, 132.6, 147.1, 168.4 (two signals are overlapped). ESI-MS(TOF) calcd. for [M-Cl]<sup>+</sup> *m/z* 570.1824, found *m/z* 570.1827.



**2b:** Yield 0.082g (54%), orange solid, mp > 200 °C decomp. (Et<sub>2</sub>O-DCM). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.95 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.47 (s, 9H), 1.82 (s, 3H), 1.99 (s, 3H), 2.31 (s, 3H), 2.44 (s, 3H), 2.57 (p, *J* = 7.0 Hz, 1H), 3.42 – 3.53 (m, 1H), 4.96 – 5.12 (m, 2H), 5.48 (s, 1H), 5.68 (d, *J* = 6.6 Hz, 1H), 6.02 (d, *J* = 16.5 Hz, 1H), 6.91 (d, *J* = 1.7 Hz, 1H), 7.05 – 7.14 (m, 1H), 7.20 (s, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 10.45 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 18.0, 18.3, 18.6, 19.9, 20.5, 21.4, 28.8, 30.8, 51.4, 53.6, 122.7, 125.9, 129.7, 129.8, 135.0, 137.2, 137.9, 141.0, 170.3, (two signals are overlapped). ESI-MS(TOF) calcd. for C<sub>28</sub>H<sub>39</sub>ClN<sub>3</sub>ORu [M-Cl]<sup>+</sup> *m/z* 570.1824, found *m/z* 570.1823.



**2c:** Yield 0.107 g (64%), orange solid, mp > 200 °C, decomp. (Et<sub>2</sub>O-DCM). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.83 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H), 1.72 – 1.87 (m, 1H), 1.89 (s, 3H), 2.17 (s, 3H), 2.43 (d, *J* = 7.4 Hz, 12H), 2.59 (s, 3H), 3.38 (br.s., 1H), 5.02 (d, *J* = 5.4 Hz, 1H), 5.30 – 5.42 (m, 2H), 5.82 (d, *J* = 6.8 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 7.03 (br.s., 2H), 7.13 (s, 1H), 7.43 (s, 2H), 7.69 (s, 1H), 12.33 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 17.5, 18.2, 18.6, 20.1, 21.1, 21.4, 22.9, 29.5, 50.4, 92.1, 103.4, 122.6, 124.7, 125.9, 128.6, 129.6, 129.9, 130.8, 135.1, 137.2, 137.3, 137.8, 141.1, 170.4. ESI-MS(TOF) calcd. for C<sub>33</sub>H<sub>41</sub>ClN<sub>3</sub>ORu [M-Cl]<sup>+</sup> *m/z* 632.1981, found *m/z* 632.1975.



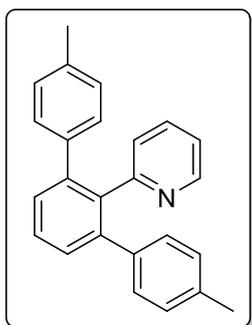
**2d:** Yield 0.091g (57%), orange crystals, mp > 200 °C, decomp. (Et<sub>2</sub>O-DCM). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.88 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.26 – 1.37 (m, 3H), 1.47 (s, 9H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.80 (s, 3H), 2.42 – 2.62 (m, 2H), 2.90 – 3.03 (m, 1H), 5.01 (d, *J* = 16.5 Hz, 1H), 5.21 – 5.48 (m, 3H), 5.67 (d, *J* = 6.6 Hz, 1H), 5.86 (d, *J* = 16.6 Hz, 1H), 7.00 (d, *J* = 1.7 Hz, 1H), 7.34 – 7.49 (m, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 10.16 (br. s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 18.5, 20.6, 22.1, 22.7, 24.3, 26.4, 27.4, 28.3, 28.7, 28.8, 30.9, 51.6, 53.6, 80.0, 81.6, 96.9, 101.2, 123.7, 124.1, 124.8, 125.4, 131.4, 137.0, 145.6, 148.5, 170.2, 170.7. ESI-MS(TOF) calcd. for C<sub>31</sub>H<sub>44</sub>ClN<sub>3</sub>ORu [M-Cl]<sup>+</sup> *m/z* 612.2294, found *m/z* 612.2295.

### General procedure for studying catalytic activity of Ru complexes.

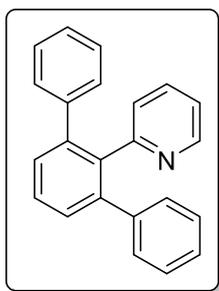
A mixture of 2-phenylpyridine (0.1 mmol), 4-chlorotoluene (0.25 mmol), appropriate base, the corresponding Ru complex and solvent (1 mL) was stirred under argon atmosphere within specified time at appropriate temperature (see Table 1 of the main text). After completion of the reaction, the mixture was cooled to room temperature and extracted with EtOAc (3×1 mL). The extract was analyzed by GC-MS using 25  $\mu$ L of 1,3-diisopropylbenzene as an internal standard.

### Synthesis of compounds 5a-g, 7a-g

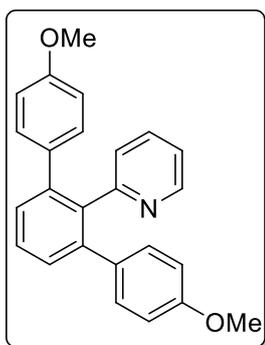
A mixture of 2-phenylpyridine **4** or 1-phenylpyrazole **6** (0.1 mmol), the corresponding aryl halide (0.25 mmol),  $K_2CO_3$  (0.25 mmol), complex **3c** (0.00625 mmol in 0.1 ml MeCN) and water (1 mL) was stirred under argon atmosphere at 120 °C within 12 h. Then the mixture was cooled to room temperature and extracted with EtOAc (3x5 mL). The extract was washed with water, dried over  $Mg_2SO_4$  and evaporated in vacuo. Crude product was purified by column chromatography on silica-gel (hexane - EtOAc 4:1 as eluent).



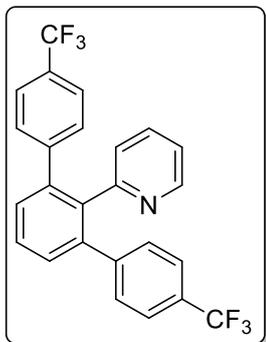
**2-(4,4''-Dimethyl-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5a).**<sup>S10</sup> Yield 0.032 g (97%), yellowish solid, mp 145-147 °C. lit<sup>S10</sup> mp 148.5-149.5 °C. <sup>1</sup>H NMR ( $CDCl_3$ , 300 MHz):  $\delta$  2.26 (s, 6H), 6.86 – 7.02 (m, 10H), 7.31 (td,  $J = 7.7, 1.8$  Hz, 1H), 7.38 – 7.44 (m, 2H), 7.49 (dd,  $J = 8.8, 6.2$  Hz, 1H), 8.33 (dt,  $J = 4.8, 1.4$  Hz, 1H). <sup>13</sup>C NMR ( $CDCl_3$ , 75 MHz):  $\delta$  21.2, 120.9, 126.9, 128.3, 128.5, 129.5, 129.6, 135.0, 135.9, 138.5, 138.8, 141.9, 148.6, 159.4.



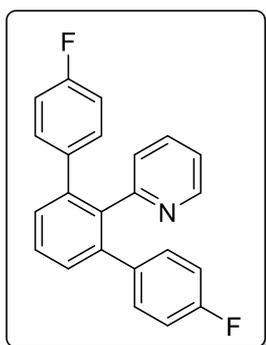
**2-([1,1':3',1''-Terphenyl]-2'-yl)pyridine (5b).**<sup>S10</sup> Yield 0.029 g (96%), white solid, mp 119-120 °C. lit<sup>S10</sup> mp 118-119.5 °C. <sup>1</sup>H NMR ( $CDCl_3$ , 300 MHz):  $\delta$  6.83 – 6.95 (m, 2H), 7.05 – 7.20 (m, 10H), 7.23 – 7.36 (m, 1H), 7.40 – 7.57 (m, 3H), 8.26 – 8.35 (m, 1H). <sup>13</sup>C NMR ( $CDCl_3$ , 75 MHz):  $\delta$  121.0, 126.4, 126.9, 127.8, 128.3, 129.6, 129.8, 135.0, 138.6, 141.7, 142.0, 148.6, 159.1.



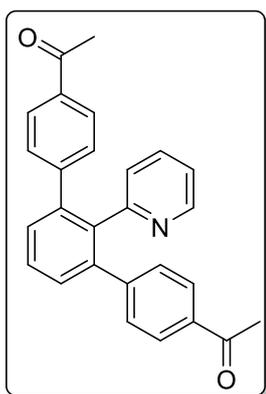
**2-(4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5c).**<sup>S11</sup> Yield 0.033 g (89%). pale green solid, mp 159-161 °C. lit<sup>S11</sup> mp 160-163 °C <sup>1</sup>H NMR ( $CDCl_3$ , 300 MHz):  $\delta$  3.74 (s, 6H), 6.65 – 6.72 (m, 4H), 6.84 – 6.95 (m, 2H), 6.97 – 7.04 (m, 4H), 7.33 (td,  $J = 7.7, 1.8$  Hz, 1H), 7.37 – 7.51 (m, 3H), 8.35 (ddd,  $J = 4.9, 1.8, 1.0$  Hz, 1H). <sup>13</sup>C NMR ( $CDCl_3$ , 75 MHz):  $\delta$  55.3, 113.2, 120.9, 126.9, 128.3, 129.3, 130.8, 134.2, 135.1, 138.6, 141.5, 148.7, 158.2, 159.4.



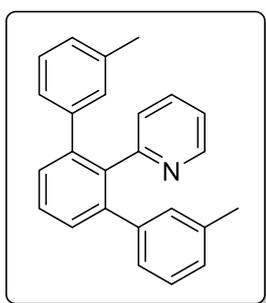
**2-(4,4''-Bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5d).**<sup>S12</sup> Yield 0.040 g (91%), yellowish solid, mp 136-137 °C. lit<sup>S12</sup> mp 138 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 6.85 (dt, *J* = 7.8, 1.1 Hz, 1H), 6.96-7.01 (m, 1H), 7.20-7.23 (m, 4H), 7.35 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 – 7.52 (m, 6H), 7.52 – 7.62 (m, 1H), 8.32 – 8.35 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 118.9, 121.7, 122.5, 124.8 (q, *J* = 3.8 Hz), 126.1, 126.8, 128.6, 128.7 128.8 (q, *J* = 32.4 Hz) 129.0, 129.4 130.0, 130.1, 135.5, 138.6, 140.9, 145.1, 149.0, 158.0.



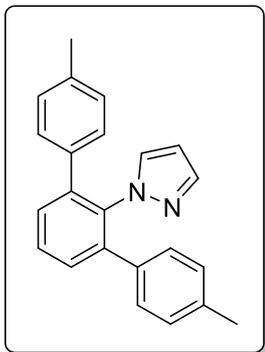
**2-(4,4''-Difluoro-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5e).**<sup>S10</sup> Yield 0.030 g (87%), yellowish solid, mp 100-101 °C. lit<sup>S10</sup> mp 100-101 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.78 – 6.89 (m, 5H), 6.95 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.99 – 7.09 (m, 4H), 7.33 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 – 7.44 (m, 2H), 7.51 (dd, *J* = 8.6, 6.5 Hz, 1H), 8.34 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 114.7 (d, *J* = 21.3 Hz), 121.2, 126.8, 128.4, 129.6, 131.2 (d, *J* = 8.1 Hz), 135.3, 137.5 (d, *J* = 3.3 Hz), 138.7, 141.0, 148.8, 158.8, 161.7 (d, *J* = 245.8 Hz) .



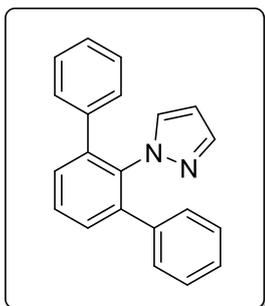
**1,1'-(2'-(Pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(ethan-1-one) (5f).**<sup>S13</sup> Yield 0.036 g (91%), yellowish solid, mp 199-201 °C. lit<sup>S13</sup> mp 200.5-201.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.55 (s, 6H), 6.87 (dt, *J* = 7.8, 1.1 Hz, 1H), 6.96 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.15 – 7.22 (m, 4H), 7.32 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 (d, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 0.7 Hz, 1H), 7.58 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.72 – 7.79 (m, 4H), 8.31 (ddd, *J* = 5.0, 1.8, 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 26.7, 121.6, 126.8, 128.0, 128.7, 129.9, 130.0, 135.3, 135.5, 138.5, 141.1, 146.5, 149.0, 158.1, 198.0.



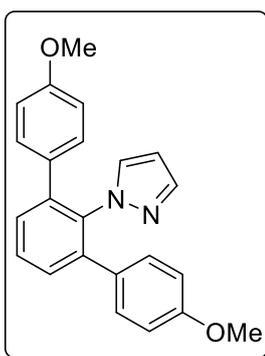
**2-(3,3''-Dimethyl-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5g).**<sup>S12</sup> Yield 0.031 g (92%), yellowish solid, mp 88-90 °C. lit<sup>S12</sup> mp 90-91 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.21 (s, 6H), 6.84 – 7.06 (m, 10H), 7.31 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 – 7.46 (m, 2H), 7.48 – 7.53 (m, 1H), 8.33 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 21.4, 120.9, 126.8, 126.9, 127.1, 127.5, 128.2, 129.4, 130.7, 134.9, 137.3, 138.6, 141.6, 142.0, 148.5, 159.3.



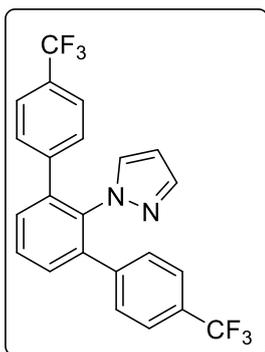
**1-(4,4''-Dimethyl-[1,1':3',1''-terphenyl]-2'-yl)-1H-pyrazole (7a).**<sup>S14</sup> Yield 0.031 g (97%), yellowish solid, mp 110-112 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.30 (s, 6H), 6.08 (t, *J* = 2.1 Hz, 1H), 6.97 – 7.05 (m, 8H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.48 (m, 2H), 7.50 – 7.59 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 21.3, 106.1, 128.2, 128.9, 129.2, 130.0, 132.6, 136.0, 136.5, 137.0, 139.4, 140.5.



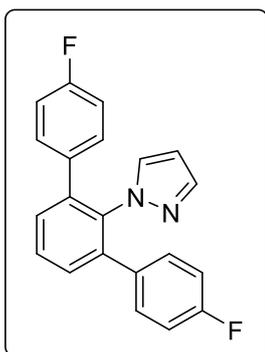
**1-([1,1':3',1''-Terphenyl]-2'-yl)-1H-pyrazole (7b).**<sup>S11</sup> Yield 0.028 g (96%), yellowish solid, mp 157-158 °C. lit<sup>S11</sup> mp 158-159 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.05 (t, *J* = 2.1 Hz, 1H), 7.05 – 7.15 (m, 5H), 7.20 – 7.25 (m, 6H), 7.36 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.44 – 7.54 (m, 2H), 7.51 – 7.64 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 106.2, 127.3, 128.2, 128.4, 129.2, 130.2, 132.5, 138.9, 139.5, 140.6, two signals overlapped.



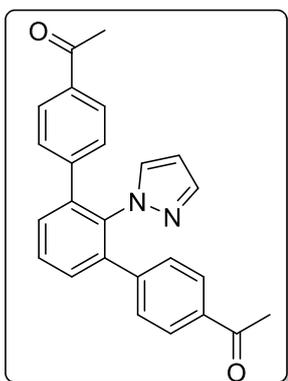
**1-(4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-1H-pyrazole (7c).**<sup>S11</sup> Yield 0.031 g (86%), yellowish solid, mp 134-135 °C. lit<sup>S13</sup> mp 132.4-133.1 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.77 (s, 6H), 6.09 (t, *J* = 2.1 Hz, 1H), 6.71 – 6.81 (m, 4H), 6.98 – 7.05 (m, 4H), 7.09 (d, *J* = 2.4, 1H), 7.40 – 7.46 (m, 3H), 7.48 – 7.58 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 55.3, 106.2, 113.6, 129.2, 129.5, 129.8, 131.3, 132.5, 136.5, 139.5, 140.2, 158.9.



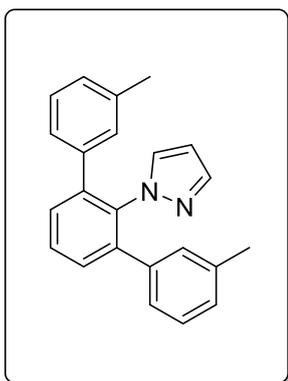
**1-(4,4''-Bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)-1H-pyrazole (7d).**<sup>S15</sup> Yield 0.040 g (92%), yellowish solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.10 (t, *J* = 2.1 Hz, 1H), 7.05 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.19 – 7.25 (m, 4H), 7.39 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.48 – 7.56 (m, 6H), 7.58 – 7.69 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 107.0, 122.4, 125.2 (q, *J* = 3.8 Hz), 126.0, 128.7, 129.7 (q, *J* = 32.5 Hz), 130.8, 132.5, 136.6, 139.4, 140.2, 142.2.



**1-(4,4''-Difluoro-[1,1':3',1''-terphenyl]-2'-yl)-1H-pyrazole (7e).**<sup>S16</sup> Yield 0.028 g (85%), yellowish solid, mp 90-91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.08 (t, *J* = 2.1 Hz, 1H), 6.88 – 6.96 (m, 4H), 7.03 – 7.11 (m, 5H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.43 – 7.48 (m, 2H), 7.52 – 7.59 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 106.5, 115.2 (d, *J* = 21.7 Hz), 129.4, 130.0 (d, *J* = 8.1 Hz), 130.2, 132.4, 134.7 (d, *J* = 3.3 Hz), 136.6, 139.8, 162.3 (d, *J* = 246.9 Hz), two signals are overlapped.

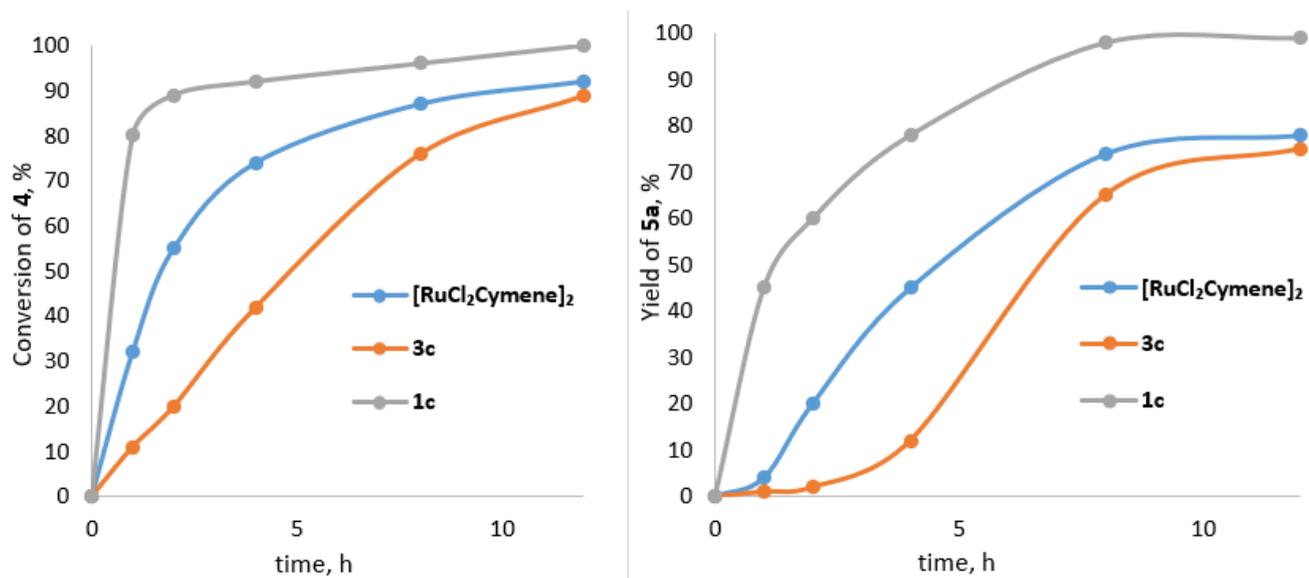


**1,1'-(2'-(1H-Pyrazol-1-yl)-[1,1':3,1''-terphenyl]-4,4''-diyl)bis(ethan-1-one) (7f).**<sup>S13</sup> Yield 0.032 g (85%), yellowish solid, mp 166-167 °C. lit<sup>S13</sup> mp 164.2-165.1 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.58 (s, 6H), 6.08 (t, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.17 – 7.22 (m, 4H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 0.7 Hz, 1H), 7.60 – 7.66 (m, 1H), 7.81 – 7.86 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 26.8, 106.9, 128.4, 128.6, 129.6, 130.7, 132.5, 136.0, 136.5, 139.6, 140.1, 143.5, 197.9.



**1-(3,3''-Dimethyl-[1,1':3,1''-terphenyl]-2'-yl)-1H-pyrazole (7g).** Yield 0.031 g (96%), white solid, mp 61-62 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.26 (s, 6H), 6.07 (t, *J* = 2.1 Hz, 1H), 6.86 – 6.92 (m, 2H), 6.95 – 6.98 (m, 2H), 7.02 – 7.14 (m, 5H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.57 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 21.5, 106.0, 125.3, 127.96, 128.03, 129.1, 129.2, 130.1, 132.6, 136.6, 137.7, 138.8, 139.3, 140.6. ESI-MS(TOF) calcd. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub><sup>+</sup> [M+ H]<sup>+</sup> *m/z* 325.1699, found *m/z* 325.1695.

# Kinetic study



**Figure S1.** Kinetic plots for the arylation of 2-phenylpyridine with 4-chlorotoluene catalyzed by different ruthenium catalysts.

## X-Ray structure determination for crystals **3c**, **4a-c**

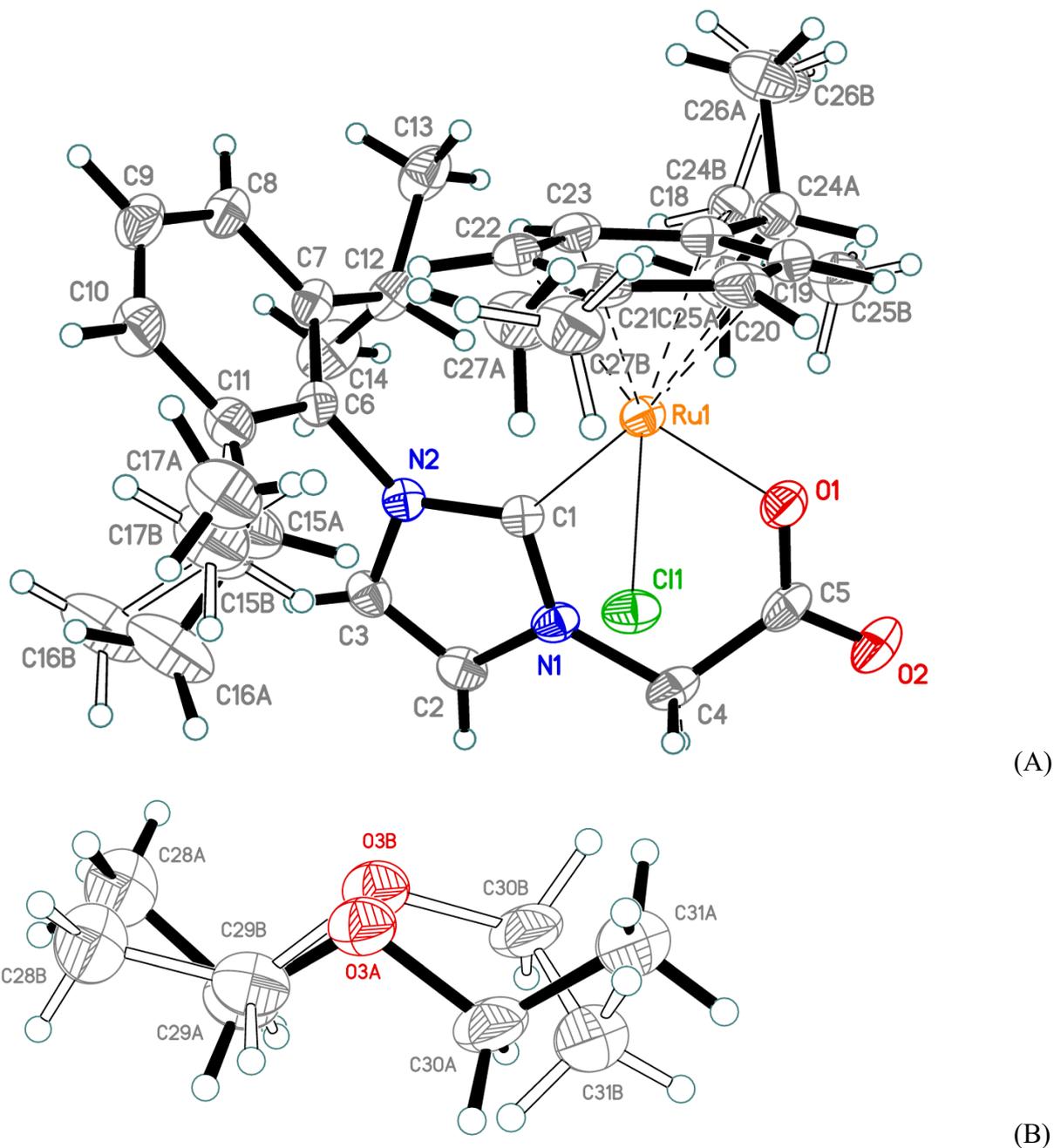
### X-ray crystallographic data and refinement details

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless  $\varphi$ -/ $\omega$ -scan technique), using Mo  $K_{\alpha}$ -radiation (crystals **1c**, **2a**, **2b**). The intensity data were integrated by the SAINT program<sup>S17</sup> and were semi-empirically corrected (basing on equivalent reflection) for absorption and decay using SADABS.<sup>S18</sup> For **2c**, X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless  $\omega$ -scan technique), using graphite monochromatized Mo  $K_{\alpha}$ -radiation. Its intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program<sup>S19</sup>. All structures were solved by direct methods using SHELXT<sup>S20</sup> and refined by full-matrix least-squares on  $F^2$  using SHELXL-2018<sup>S21</sup> in the SHELXTL program<sup>S17</sup> (**1c**, **2a**, **2b**) or in the OLEX2 program<sup>S21</sup> (**2c**). All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Locations of amido and water hydrogen atoms (H2A, H2B and H3N in **2a**; H3A, H2A and H2B in **2b**; H2A, H2B, H3, H3B and H3C in **2c**) were found from the electron density-difference map; the positions of H2A and H2B in **2b** were restrained at the distance of 0.85(2)Å from O2. These hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. Crystal channels of **2b** contained unidentified disordered non-coordinating solvent molecules, which were removed by the SQUEEZE method<sup>S24</sup> implemented in the PLATON program.<sup>S25</sup> The SHELXTL program suite was used for molecular graphics. Crystal data and structure refinement are summarized in Table S1.

**Table S1. Crystal data and structure refinement of compounds 1c, 2a-c**

Code	<b>1c</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>
Empirical formula	C <sub>31</sub> H <sub>45</sub> ClN <sub>2</sub> O <sub>3</sub> Ru	C <sub>28</sub> H <sub>38</sub> ClN <sub>3</sub> ORu·HCl·H <sub>2</sub> O	C <sub>28</sub> H <sub>39</sub> ClN <sub>3</sub> ORu·Cl·H <sub>2</sub> O	C <sub>33</sub> H <sub>41</sub> ClN <sub>3</sub> ORu·Cl·1.817(H <sub>2</sub> O)
Formula weight	630.21	623.61	623.61	700.40
Temperature, K	100(2)	100(2)	100(2)	100.0(1)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P2 <sub>1</sub> /n
Unit cell dimensions				
a, Å	10.4819(2)	10.1277(2)	9.8425(5)	9.76421(13)
b, Å	10.8202(2)	10.3823(2)	11.2449(6)	21.3530(3)
c, Å	14.2449(3)	15.5175(3)	15.3995(8)	15.6948(2)
$\alpha$ , °	107.7390(10)	90.5393(5)	78.8930(10)	90
$\beta$ , °	96.5280(10)	92.7864(5)	76.7820(10)	97.3468(13)
$\gamma$ , °	99.7020(10)	116.7548(5)	87.6790(10)	90
Volume, Å <sup>3</sup>	1493.16(5)	1454.35(5)	1628.14(15) Å <sup>3</sup>	3245.43(8)
Z	2	2	2	4
Calculated density, g/cm <sup>3</sup>	1.402	1.424	1.272	1.433
Absorption coefficient, mm <sup>-1</sup>	0.648	0.752	0.672	0.684
F(000)	660	648	648	1456.7
Crystal size, mm	0.185x0.105x0.048	0.24 x 0.20 x 0.08	0.12 x 0.05 x 0.03	0.17x0.09x0.04
$\theta$ range for data collection, °	2.002 to 32.499	2.198 to 36.324	2.087 to 32.500	1.907 to 34.498
Completeness to $\theta_{\text{full}} / \theta_{\text{max}}$	1.000 / 1.000	0.998 / 0.999	1.000 / 1.000	1.000/ 0.963
Index ranges	-15<=h<=15, -16<=k<=16, -21<=l<=21	-16<=h<=16, -17<=k<=17, -25<=l<=25	-14<=h<=14, -16<=k<=16, -23<=l<=23	-15<=h<=15, -34<=k<=33, -24<=l<=24
Reflections				
Collected	72541	143979	79315	58895
Independent [ $R_{\text{int}}$ ]	10812 [0.0782]	14087 [0.0307]	11766 [0.0545]	13264 [0.0301]
Observed (with $I > 2\sigma(I)$ )	8156	12943	9354	11678
Data / restraints / parameters	10812 / 11 / 398	14087 / 27 / 381	11766 / 2 / 347	13264 / 4 / 409
Goodness-of-fit on $F^2$	1.020	1.052	1.029	1.040
Final R1/wR2 indices (with $I > 2\sigma(I)$ )	0.0446 / 0.0868	0.0262 / 0.0600	0.0566 / 0.1335	0.0247 / 0.0613
Final R1/wR2 indices (all data)	0.0724 / 0.1007	0.0303 / 0.0630	0.0750 / 0.1481	0.0300 / 0.0631
Largest diff. peak / hole, e $\cdot$ Å <sup>-3</sup>	0.877 / -1.072	0.765 / -1.476	0.881 / -2.194	0.764 / -0.388
CCDC number	2109279	2109280	2109281	2109282

## The structure of 1c.



**Figure S2.** (A) The structure of 1c (p=50%). (B) A disordered non-coordinating Et<sub>2</sub>O solvent molecule.

**Table S2. Bond lengths (Å) in 1c**

Ru(1)-C(1)	2.069(2)	N(1)-C(1)	1.357(3)
Ru(1)-O(1)	2.0856(18)	N(1)-C(2)	1.384(3)
Ru(1)-C(23)	2.157(2)	N(1)-C(4)	1.468(3)
Ru(1)-C(18)	2.188(3)	N(2)-C(1)	1.373(3)
Ru(1)-C(22)	2.202(2)	N(2)-C(3)	1.383(3)
Ru(1)-C(21)	2.228(3)	N(2)-C(6)	1.450(3)
Ru(1)-C(19)	2.230(3)	C(2)-C(3)	1.343(4)
Ru(1)-C(20)	2.250(2)	C(2)-H(2)	0.9500
Ru(1)-Cl(1)	2.4360(6)	C(3)-H(3)	0.9500
O(1)-C(5)	1.273(3)	C(4)-C(5)	1.520(4)
O(2)-C(5)	1.234(3)	C(4)-H(4A)	0.9900

C(4)-H(4B)	0.9900	C(23)-H(23)	1.0000
C(6)-C(7)	1.398(4)	C(24A)-C(25A)	1.520(5)
C(6)-C(11)	1.398(3)	C(24A)-C(26A)	1.567(11)
C(7)-C(8)	1.396(3)	C(24A)-H(24A)	1.0000
C(7)-C(12)	1.521(4)	C(25A)-H(25A)	0.9800
C(8)-C(9)	1.388(4)	C(25A)-H(25B)	0.9800
C(8)-H(8)	0.9500	C(25A)-H(25C)	0.9800
C(9)-C(10)	1.368(4)	C(26A)-H(26A)	0.9800
C(9)-H(9)	0.9500	C(26A)-H(26B)	0.9800
C(10)-C(11)	1.399(4)	C(26A)-H(26C)	0.9800
C(10)-H(10)	0.9500	C(27A)-H(27A)	0.9800
C(11)-C(15B)	1.516(4)	C(27A)-H(27B)	0.9800
C(11)-C(15A)	1.517(5)	C(27A)-H(27C)	0.9800
C(12)-C(13)	1.531(4)	C(24B)-C(25B)	1.518(5)
C(12)-C(14)	1.531(4)	C(24B)-C(26B)	1.567(11)
C(12)-H(12)	1.0000	C(24B)-H(24B)	1.0000
C(13)-H(13A)	0.9800	C(25B)-H(25D)	0.9800
C(13)-H(13B)	0.9800	C(25B)-H(25E)	0.9800
C(13)-H(13C)	0.9800	C(25B)-H(25F)	0.9800
C(14)-H(14A)	0.9800	C(26B)-H(26D)	0.9800
C(14)-H(14B)	0.9800	C(26B)-H(26E)	0.9800
C(14)-H(14C)	0.9800	C(26B)-H(26F)	0.9800
C(15A)-C(17A)	1.527(6)	C(27B)-H(27D)	0.9800
C(15A)-C(16A)	1.531(6)	C(27B)-H(27E)	0.9800
C(15A)-H(15A)	1.0000	C(27B)-H(27F)	0.9800
C(16A)-H(16A)	0.9800	C(28A)-C(29A)	1.507(5)
C(16A)-H(16B)	0.9800	C(28A)-H(28A)	0.9800
C(16A)-H(16C)	0.9800	C(28A)-H(28B)	0.9800
C(17A)-H(17A)	0.9800	C(28A)-H(28C)	0.9800
C(17A)-H(17B)	0.9800	C(29A)-O(3A)	1.429(4)
C(17A)-H(17C)	0.9800	C(29A)-H(29A)	0.9900
C(15B)-C(17B)	1.527(5)	C(29A)-H(29B)	0.9900
C(15B)-C(16B)	1.531(5)	O(3A)-C(30A)	1.430(4)
C(15B)-H(15B)	1.0000	C(30A)-C(31A)	1.492(5)
C(16B)-H(16D)	0.9800	C(30A)-H(30A)	0.9900
C(16B)-H(16E)	0.9800	C(30A)-H(30B)	0.9900
C(16B)-H(16F)	0.9800	C(31A)-H(31A)	0.9800
C(17B)-H(17D)	0.9800	C(31A)-H(31B)	0.9800
C(17B)-H(17E)	0.9800	C(31A)-H(31C)	0.9800
C(17B)-H(17F)	0.9800	C(28B)-C(29B)	1.507(6)
C(18)-C(23)	1.410(4)	C(28B)-H(28D)	0.9800
C(18)-C(19)	1.422(4)	C(28B)-H(28E)	0.9800
C(18)-C(24B)	1.529(5)	C(28B)-H(28F)	0.9800
C(18)-C(24A)	1.531(4)	C(29B)-O(3B)	1.428(5)
C(19)-C(20)	1.386(4)	C(29B)-H(29C)	0.9900
C(19)-H(19)	1.0000	C(29B)-H(29D)	0.9900
C(20)-C(21)	1.425(4)	O(3B)-C(30B)	1.431(5)
C(20)-H(20)	1.0000	C(30B)-C(31B)	1.492(6)
C(21)-C(22)	1.402(4)	C(30B)-H(30C)	0.9900
C(21)-C(27A)	1.524(4)	C(30B)-H(30D)	0.9900
C(21)-C(27B)	1.524(5)	C(31B)-H(31D)	0.9800
C(22)-C(23)	1.425(4)	C(31B)-H(31E)	0.9800
C(22)-H(22)	1.0000	C(31B)-H(31F)	0.9800

**Table S3. Bond angles (°) in 1c**

C(1)-Ru(1)-O(1)	85.01(8)	C(11)-C(6)-N(2)	117.4(2)
C(1)-Ru(1)-C(23)	96.60(9)	C(8)-C(7)-C(6)	117.7(2)
O(1)-Ru(1)-C(23)	120.80(10)	C(8)-C(7)-C(12)	120.3(2)
C(1)-Ru(1)-C(18)	116.40(9)	C(6)-C(7)-C(12)	121.9(2)
O(1)-Ru(1)-C(18)	89.16(9)	C(9)-C(8)-C(7)	120.4(3)
C(23)-Ru(1)-C(18)	37.86(10)	C(9)-C(8)-H(8)	119.8
C(1)-Ru(1)-C(22)	102.45(10)	C(7)-C(8)-H(8)	119.8
O(1)-Ru(1)-C(22)	157.72(9)	C(10)-C(9)-C(8)	120.4(3)
C(23)-Ru(1)-C(22)	38.14(11)	C(10)-C(9)-H(9)	119.8
C(18)-Ru(1)-C(22)	68.67(10)	C(8)-C(9)-H(9)	119.8
C(1)-Ru(1)-C(21)	129.69(10)	C(9)-C(10)-C(11)	121.9(3)
O(1)-Ru(1)-C(21)	144.73(9)	C(9)-C(10)-H(10)	119.0
C(23)-Ru(1)-C(21)	67.76(11)	C(11)-C(10)-H(10)	119.0
C(18)-Ru(1)-C(21)	80.81(10)	C(6)-C(11)-C(10)	116.6(3)
C(22)-Ru(1)-C(21)	36.89(11)	C(6)-C(11)-C(15B)	122.4(3)
C(1)-Ru(1)-C(19)	152.13(10)	C(10)-C(11)-C(15B)	120.8(3)
O(1)-Ru(1)-C(19)	84.99(9)	C(6)-C(11)-C(15A)	120.6(14)
C(23)-Ru(1)-C(19)	66.86(9)	C(10)-C(11)-C(15A)	121.2(13)
C(18)-Ru(1)-C(19)	37.53(10)	C(7)-C(12)-C(13)	114.5(2)
C(22)-Ru(1)-C(19)	78.73(10)	C(7)-C(12)-C(14)	110.0(2)
C(21)-Ru(1)-C(19)	66.55(11)	C(13)-C(12)-C(14)	108.2(2)
C(1)-Ru(1)-C(20)	166.80(10)	C(7)-C(12)-H(12)	108.0
O(1)-Ru(1)-C(20)	108.04(9)	C(13)-C(12)-H(12)	108.0
C(23)-Ru(1)-C(20)	78.65(9)	C(14)-C(12)-H(12)	108.0
C(18)-Ru(1)-C(20)	67.00(10)	C(12)-C(13)-H(13A)	109.5
C(22)-Ru(1)-C(20)	66.20(10)	C(12)-C(13)-H(13B)	109.5
C(21)-Ru(1)-C(20)	37.11(11)	H(13A)-C(13)-H(13B)	109.5
C(19)-Ru(1)-C(20)	36.03(10)	C(12)-C(13)-H(13C)	109.5
C(1)-Ru(1)-Cl(1)	84.24(6)	H(13A)-C(13)-H(13C)	109.5
O(1)-Ru(1)-Cl(1)	89.01(5)	H(13B)-C(13)-H(13C)	109.5
C(23)-Ru(1)-Cl(1)	150.17(8)	C(12)-C(14)-H(14A)	109.5
C(18)-Ru(1)-Cl(1)	159.02(7)	C(12)-C(14)-H(14B)	109.5
C(22)-Ru(1)-Cl(1)	112.44(8)	H(14A)-C(14)-H(14B)	109.5
C(21)-Ru(1)-Cl(1)	88.73(7)	C(12)-C(14)-H(14C)	109.5
C(19)-Ru(1)-Cl(1)	121.50(7)	H(14A)-C(14)-H(14C)	109.5
C(20)-Ru(1)-Cl(1)	93.79(7)	H(14B)-C(14)-H(14C)	109.5
C(5)-O(1)-Ru(1)	132.00(18)	C(11)-C(15A)-C(17A)	115(2)
C(1)-N(1)-C(2)	111.8(2)	C(11)-C(15A)-C(16A)	109(2)
C(1)-N(1)-C(4)	127.1(2)	C(17A)-C(15A)-C(16A)	111(3)
C(2)-N(1)-C(4)	120.9(2)	C(11)-C(15A)-H(15A)	107.1
C(1)-N(2)-C(3)	111.6(2)	C(17A)-C(15A)-H(15A)	107.1
C(1)-N(2)-C(6)	127.54(19)	C(16A)-C(15A)-H(15A)	107.1
C(3)-N(2)-C(6)	120.6(2)	C(15A)-C(16A)-H(16A)	109.5
N(1)-C(1)-N(2)	103.12(19)	C(15A)-C(16A)-H(16B)	109.5
N(1)-C(1)-Ru(1)	122.63(17)	H(16A)-C(16A)-H(16B)	109.5
N(2)-C(1)-Ru(1)	134.19(17)	C(15A)-C(16A)-H(16C)	109.5
C(3)-C(2)-N(1)	106.8(2)	H(16A)-C(16A)-H(16C)	109.5
C(3)-C(2)-H(2)	126.6	H(16B)-C(16A)-H(16C)	109.5
N(1)-C(2)-H(2)	126.6	C(15A)-C(17A)-H(17A)	109.5
C(2)-C(3)-N(2)	106.6(2)	C(15A)-C(17A)-H(17B)	109.5
C(2)-C(3)-H(3)	126.7	H(17A)-C(17A)-H(17B)	109.5
N(2)-C(3)-H(3)	126.7	C(15A)-C(17A)-H(17C)	109.5
N(1)-C(4)-C(5)	115.1(2)	H(17A)-C(17A)-H(17C)	109.5
N(1)-C(4)-H(4A)	108.5	H(17B)-C(17A)-H(17C)	109.5
C(5)-C(4)-H(4A)	108.5	C(11)-C(15B)-C(17B)	112.2(3)
N(1)-C(4)-H(4B)	108.5	C(11)-C(15B)-C(16B)	110.7(3)
C(5)-C(4)-H(4B)	108.5	C(17B)-C(15B)-C(16B)	109.6(3)
H(4A)-C(4)-H(4B)	107.5	C(11)-C(15B)-H(15B)	108.1
O(2)-C(5)-O(1)	123.8(3)	C(17B)-C(15B)-H(15B)	108.1
O(2)-C(5)-C(4)	117.4(2)	C(16B)-C(15B)-H(15B)	108.1
O(1)-C(5)-C(4)	118.7(2)	C(15B)-C(16B)-H(16D)	109.5
C(7)-C(6)-C(11)	123.0(2)	C(15B)-C(16B)-H(16E)	109.5
C(7)-C(6)-N(2)	119.4(2)	H(16D)-C(16B)-H(16E)	109.5

C(15B)-C(16B)-H(16F)	109.5	C(24A)-C(26A)-H(26B)	109.5
H(16D)-C(16B)-H(16F)	109.5	H(26A)-C(26A)-H(26B)	109.5
H(16E)-C(16B)-H(16F)	109.5	C(24A)-C(26A)-H(26C)	109.5
C(15B)-C(17B)-H(17D)	109.5	H(26A)-C(26A)-H(26C)	109.5
C(15B)-C(17B)-H(17E)	109.5	H(26B)-C(26A)-H(26C)	109.5
H(17D)-C(17B)-H(17E)	109.5	C(21)-C(27A)-H(27A)	109.5
C(15B)-C(17B)-H(17F)	109.5	C(21)-C(27A)-H(27B)	109.5
H(17D)-C(17B)-H(17F)	109.5	H(27A)-C(27A)-H(27B)	109.5
H(17E)-C(17B)-H(17F)	109.5	C(21)-C(27A)-H(27C)	109.5
C(23)-C(18)-C(19)	117.2(2)	H(27A)-C(27A)-H(27C)	109.5
C(23)-C(18)-C(24B)	109.7(3)	H(27B)-C(27A)-H(27C)	109.5
C(19)-C(18)-C(24B)	133.0(3)	C(25B)-C(24B)-C(18)	110.3(4)
C(23)-C(18)-C(24A)	129.9(3)	C(25B)-C(24B)-C(26B)	102(2)
C(19)-C(18)-C(24A)	112.8(3)	C(18)-C(24B)-C(26B)	110(3)
C(23)-C(18)-Ru(1)	69.87(15)	C(25B)-C(24B)-H(24B)	111.5
C(19)-C(18)-Ru(1)	72.83(15)	C(18)-C(24B)-H(24B)	111.5
C(24B)-C(18)-Ru(1)	129.2(4)	C(26B)-C(24B)-H(24B)	111.5
C(24A)-C(18)-Ru(1)	129.9(3)	C(24B)-C(25B)-H(25D)	109.5
C(20)-C(19)-C(18)	121.6(2)	C(24B)-C(25B)-H(25E)	109.5
C(20)-C(19)-Ru(1)	72.81(15)	H(25D)-C(25B)-H(25E)	109.5
C(18)-C(19)-Ru(1)	69.64(14)	C(24B)-C(25B)-H(25F)	109.5
C(20)-C(19)-H(19)	118.4	H(25D)-C(25B)-H(25F)	109.5
C(18)-C(19)-H(19)	118.4	H(25E)-C(25B)-H(25F)	109.5
Ru(1)-C(19)-H(19)	118.4	C(24B)-C(26B)-H(26D)	109.5
C(19)-C(20)-C(21)	120.9(2)	C(24B)-C(26B)-H(26E)	109.5
C(19)-C(20)-Ru(1)	71.16(15)	H(26D)-C(26B)-H(26E)	109.5
C(21)-C(20)-Ru(1)	70.58(14)	C(24B)-C(26B)-H(26F)	109.5
C(19)-C(20)-H(20)	118.7	H(26D)-C(26B)-H(26F)	109.5
C(21)-C(20)-H(20)	118.7	H(26E)-C(26B)-H(26F)	109.5
Ru(1)-C(20)-H(20)	118.7	C(21)-C(27B)-H(27D)	109.5
C(22)-C(21)-C(20)	118.7(3)	C(21)-C(27B)-H(27E)	109.5
C(22)-C(21)-C(27A)	114.4(4)	H(27D)-C(27B)-H(27E)	109.5
C(20)-C(21)-C(27A)	126.9(3)	C(21)-C(27B)-H(27F)	109.5
C(22)-C(21)-C(27B)	133.8(5)	H(27D)-C(27B)-H(27F)	109.5
C(20)-C(21)-C(27B)	107.5(4)	H(27E)-C(27B)-H(27F)	109.5
C(22)-C(21)-Ru(1)	70.55(15)	C(29A)-C(28A)-H(28A)	109.5
C(20)-C(21)-Ru(1)	72.30(15)	C(29A)-C(28A)-H(28B)	109.5
C(27A)-C(21)-Ru(1)	127.7(4)	H(28A)-C(28A)-H(28B)	109.5
C(27B)-C(21)-Ru(1)	127.8(6)	C(29A)-C(28A)-H(28C)	109.5
C(21)-C(22)-C(23)	119.8(2)	H(28A)-C(28A)-H(28C)	109.5
C(21)-C(22)-Ru(1)	72.56(15)	H(28B)-C(28A)-H(28C)	109.5
C(23)-C(22)-Ru(1)	69.21(14)	O(3A)-C(29A)-C(28A)	106.8(4)
C(21)-C(22)-H(22)	119.5	O(3A)-C(29A)-H(29A)	110.4
C(23)-C(22)-H(22)	119.5	C(28A)-C(29A)-H(29A)	110.4
Ru(1)-C(22)-H(22)	119.5	O(3A)-C(29A)-H(29B)	110.4
C(18)-C(23)-C(22)	121.7(2)	C(28A)-C(29A)-H(29B)	110.4
C(18)-C(23)-Ru(1)	72.27(14)	H(29A)-C(29A)-H(29B)	108.6
C(22)-C(23)-Ru(1)	72.65(15)	C(29A)-O(3A)-C(30A)	109.5(3)
C(18)-C(23)-H(23)	118.7	O(3A)-C(30A)-C(31A)	109.5(3)
C(22)-C(23)-H(23)	118.7	O(3A)-C(30A)-H(30A)	109.8
Ru(1)-C(23)-H(23)	118.7	C(31A)-C(30A)-H(30A)	109.8
C(25A)-C(24A)-C(18)	113.5(3)	O(3A)-C(30A)-H(30B)	109.8
C(25A)-C(24A)-C(26A)	110(2)	C(31A)-C(30A)-H(30B)	109.8
C(18)-C(24A)-C(26A)	103.1(17)	H(30A)-C(30A)-H(30B)	108.2
C(25A)-C(24A)-H(24A)	110.1	C(30A)-C(31A)-H(31A)	109.5
C(18)-C(24A)-H(24A)	110.1	C(30A)-C(31A)-H(31B)	109.5
C(26A)-C(24A)-H(24A)	110.1	H(31A)-C(31A)-H(31B)	109.5
C(24A)-C(25A)-H(25A)	109.5	C(30A)-C(31A)-H(31C)	109.5
C(24A)-C(25A)-H(25B)	109.5	H(31A)-C(31A)-H(31C)	109.5
H(25A)-C(25A)-H(25B)	109.5	H(31B)-C(31A)-H(31C)	109.5
C(24A)-C(25A)-H(25C)	109.5	C(29B)-C(28B)-H(28D)	109.5
H(25A)-C(25A)-H(25C)	109.5	C(29B)-C(28B)-H(28E)	109.5
H(25B)-C(25A)-H(25C)	109.5	H(28D)-C(28B)-H(28E)	109.5
C(24A)-C(26A)-H(26A)	109.5	C(29B)-C(28B)-H(28F)	109.5

H(28D)-C(28B)-H(28F)	109.5	C(31B)-C(30B)-H(30C)	109.7
H(28E)-C(28B)-H(28F)	109.5	O(3B)-C(30B)-H(30D)	109.7
O(3B)-C(29B)-C(28B)	129(3)	C(31B)-C(30B)-H(30D)	109.7
O(3B)-C(29B)-H(29C)	105.1	H(30C)-C(30B)-H(30D)	108.2
C(28B)-C(29B)-H(29C)	105.1	C(30B)-C(31B)-H(31D)	109.5
O(3B)-C(29B)-H(29D)	105.1	C(30B)-C(31B)-H(31E)	109.5
C(28B)-C(29B)-H(29D)	105.1	H(31D)-C(31B)-H(31E)	109.5
H(29C)-C(29B)-H(29D)	105.9	C(30B)-C(31B)-H(31F)	109.5
C(29B)-O(3B)-C(30B)	125(3)	H(31D)-C(31B)-H(31F)	109.5
O(3B)-C(30B)-C(31B)	110(2)	H(31E)-C(31B)-H(31F)	109.5
O(3B)-C(30B)-H(30C)	109.7		

**Table S4. Torsion angles (°) of compound 1c**

C(2)-N(1)-C(1)-N(2)	-1.6(3)	C(10)-C(11)-C(15B)-C(16B)	69.5(5)
C(4)-N(1)-C(1)-N(2)	-177.3(2)	C(23)-C(18)-C(19)-C(20)	2.4(4)
C(2)-N(1)-C(1)-Ru(1)	176.02(17)	C(24B)-C(18)-C(19)-C(20)	178.6(5)
C(4)-N(1)-C(1)-Ru(1)	0.3(3)	C(24A)-C(18)-C(19)-C(20)	-180.0(3)
C(3)-N(2)-C(1)-N(1)	1.9(3)	Ru(1)-C(18)-C(19)-C(20)	-53.3(2)
C(6)-N(2)-C(1)-N(1)	175.3(2)	C(23)-C(18)-C(19)-Ru(1)	55.7(2)
C(3)-N(2)-C(1)-Ru(1)	-175.35(19)	C(24B)-C(18)-C(19)-Ru(1)	-128.1(5)
C(6)-N(2)-C(1)-Ru(1)	-1.9(4)	C(24A)-C(18)-C(19)-Ru(1)	-126.7(3)
C(1)-N(1)-C(2)-C(3)	0.8(3)	C(18)-C(19)-C(20)-C(21)	-0.3(4)
C(4)-N(1)-C(2)-C(3)	176.8(2)	Ru(1)-C(19)-C(20)-C(21)	-52.1(2)
N(1)-C(2)-C(3)-N(2)	0.4(3)	C(18)-C(19)-C(20)-Ru(1)	51.9(2)
C(1)-N(2)-C(3)-C(2)	-1.5(3)	C(19)-C(20)-C(21)-C(22)	-2.6(4)
C(6)-N(2)-C(3)-C(2)	-175.4(2)	Ru(1)-C(20)-C(21)-C(22)	-55.0(2)
C(1)-N(1)-C(4)-C(5)	-39.7(3)	C(19)-C(20)-C(21)-C(27A)	176.7(5)
C(2)-N(1)-C(4)-C(5)	144.9(2)	Ru(1)-C(20)-C(21)-C(27A)	124.3(5)
Ru(1)-O(1)-C(5)-O(2)	-175.42(18)	C(19)-C(20)-C(21)-C(27B)	177.4(6)
Ru(1)-O(1)-C(5)-C(4)	2.2(3)	Ru(1)-C(20)-C(21)-C(27B)	125.0(6)
N(1)-C(4)-C(5)-O(2)	-144.7(2)	C(19)-C(20)-C(21)-Ru(1)	52.4(2)
N(1)-C(4)-C(5)-O(1)	37.5(3)	C(20)-C(21)-C(22)-C(23)	3.4(4)
C(1)-N(2)-C(6)-C(7)	94.3(3)	C(27A)-C(21)-C(22)-C(23)	-176.0(5)
C(3)-N(2)-C(6)-C(7)	-92.7(3)	C(27B)-C(21)-C(22)-C(23)	-176.7(8)
C(1)-N(2)-C(6)-C(11)	-90.8(3)	Ru(1)-C(21)-C(22)-C(23)	-52.5(2)
C(3)-N(2)-C(6)-C(11)	82.1(3)	C(20)-C(21)-C(22)-Ru(1)	55.9(2)
C(11)-C(6)-C(7)-C(8)	3.9(4)	C(27A)-C(21)-C(22)-Ru(1)	-123.5(5)
N(2)-C(6)-C(7)-C(8)	178.5(2)	C(27B)-C(21)-C(22)-Ru(1)	-124.2(8)
C(11)-C(6)-C(7)-C(12)	-172.5(2)	C(19)-C(18)-C(23)-C(22)	-1.6(4)
N(2)-C(6)-C(7)-C(12)	2.0(3)	C(24B)-C(18)-C(23)-C(22)	-178.7(4)
C(6)-C(7)-C(8)-C(9)	-1.8(4)	C(24A)-C(18)-C(23)-C(22)	-178.8(3)
C(12)-C(7)-C(8)-C(9)	174.7(2)	Ru(1)-C(18)-C(23)-C(22)	55.5(2)
C(7)-C(8)-C(9)-C(10)	-1.1(4)	C(19)-C(18)-C(23)-Ru(1)	-57.2(2)
C(8)-C(9)-C(10)-C(11)	2.1(4)	C(24B)-C(18)-C(23)-Ru(1)	125.8(4)
C(7)-C(6)-C(11)-C(10)	-2.9(4)	C(24A)-C(18)-C(23)-Ru(1)	125.7(4)
N(2)-C(6)-C(11)-C(10)	-177.6(2)	C(21)-C(22)-C(23)-C(18)	-1.3(4)
C(7)-C(6)-C(11)-C(15B)	170.9(3)	Ru(1)-C(22)-C(23)-C(18)	-55.4(2)
N(2)-C(6)-C(11)-C(15B)	-3.8(4)	C(21)-C(22)-C(23)-Ru(1)	54.1(2)
C(7)-C(6)-C(11)-C(15A)	-168.3(13)	C(23)-C(18)-C(24A)-C(25A)	-48.1(6)
N(2)-C(6)-C(11)-C(15A)	17.0(14)	C(19)-C(18)-C(24A)-C(25A)	134.6(4)
C(9)-C(10)-C(11)-C(6)	-0.2(4)	Ru(1)-C(18)-C(24A)-C(25A)	48.4(5)
C(9)-C(10)-C(11)-C(15B)	-174.1(3)	C(23)-C(18)-C(24A)-C(26A)	70.5(18)
C(9)-C(10)-C(11)-C(15A)	165.2(14)	C(19)-C(18)-C(24A)-C(26A)	-106.8(18)
C(8)-C(7)-C(12)-C(13)	34.8(3)	Ru(1)-C(18)-C(24A)-C(26A)	167.0(18)
C(6)-C(7)-C(12)-C(13)	-148.9(2)	C(23)-C(18)-C(24B)-C(25B)	-146.4(5)
C(8)-C(7)-C(12)-C(14)	-87.3(3)	C(19)-C(18)-C(24B)-C(25B)	37.1(9)
C(6)-C(7)-C(12)-C(14)	89.0(3)	Ru(1)-C(18)-C(24B)-C(25B)	-66.8(7)
C(6)-C(11)-C(15A)-C(17A)	135(3)	C(23)-C(18)-C(24B)-C(26B)	102(2)
C(10)-C(11)-C(15A)-C(17A)	-30(3)	C(19)-C(18)-C(24B)-C(26B)	-74(2)
C(6)-C(11)-C(15A)-C(16A)	-99(3)	Ru(1)-C(18)-C(24B)-C(26B)	-178(2)
C(10)-C(11)-C(15A)-C(16A)	96(3)	C(28A)-C(29A)-O(3A)-C(30A)	-174.5(4)
C(6)-C(11)-C(15B)-C(17B)	133.2(3)	C(29A)-O(3A)-C(30A)-C(31A)	175.8(4)
C(10)-C(11)-C(15B)-C(17B)	-53.3(5)	C(28B)-C(29B)-O(3B)-C(30B)	-164(4)
C(6)-C(11)-C(15B)-C(16B)	-104.0(4)	C(29B)-O(3B)-C(30B)-C(31B)	-73(5)



**Table S5. Bond lengths (Å) of compound 2a**

Ru(1)-C(1)	2.0542(10)	C(15B)-H(15E)	0.9800
Ru(1)-O(1)	2.1092(8)	C(15B)-H(15F)	0.9800
Ru(1)-C(21)	2.1689(12)	C(16A)-C(18A)	1.526(3)
Ru(1)-C(20)	2.1742(11)	C(16A)-C(17A)	1.526(3)
Ru(1)-C(24)	2.1827(10)	C(16A)-H(16A)	1.0000
Ru(1)-C(19)	2.1908(10)	C(17A)-H(17A)	0.9800
Ru(1)-C(23)	2.2059(11)	C(17A)-H(17B)	0.9800
Ru(1)-C(22)	2.2475(12)	C(17A)-H(17C)	0.9800
Ru(1)-Cl(1)	2.4080(3)	C(18A)-H(18A)	0.9800
N(1)-C(1)	1.3570(13)	C(18A)-H(18B)	0.9800
N(1)-C(3)	1.3841(13)	C(18A)-H(18C)	0.9800
N(1)-C(4)	1.4525(13)	C(16B)-C(17B)	1.526(3)
C(1)-N(2)	1.3502(13)	C(16B)-C(18B)	1.527(3)
N(2)-C(2)	1.3860(14)	C(16B)-H(16B)	1.0000
N(2)-C(6)	1.4613(15)	C(17B)-H(17D)	0.9800
C(2)-C(3)	1.3508(16)	C(17B)-H(17E)	0.9800
C(2)-H(2)	0.9500	C(17B)-H(17F)	0.9800
C(3)-H(3)	0.9500	C(18B)-H(18D)	0.9800
C(4)-C(5)	1.5098(14)	C(18B)-H(18E)	0.9800
C(4)-H(4A)	0.9900	C(18B)-H(18F)	0.9800
C(4)-H(4B)	0.9900	C(19)-C(24)	1.4147(15)
C(5)-O(1)	1.2519(13)	C(19)-C(20)	1.4287(15)
C(5)-N(3)	1.3238(13)	C(19)-C(25)	1.4927(15)
N(3)-C(7)	1.4417(13)	C(20)-C(21)	1.4148(18)
N(3)-H(3N)	0.80(2)	C(20)-H(20)	1.0000
C(6)-H(6A)	0.9800	C(21)-C(22)	1.429(2)
C(6)-H(6B)	0.9800	C(21)-H(21)	1.0000
C(6)-H(6C)	0.9800	C(22)-C(23)	1.395(2)
C(7)-C(8)	1.3960(15)	C(22)-C(26B)	1.527(2)
C(7)-C(12)	1.3972(14)	C(22)-C(26A)	1.577(2)
C(8)-C(9)	1.3993(16)	C(23)-C(24)	1.4249(16)
C(8)-C(13A)	1.526(2)	C(23)-H(23)	1.0000
C(8)-C(13B)	1.529(3)	C(24)-H(24)	1.0000
C(9)-C(10)	1.3816(17)	C(25)-H(25A)	0.9800
C(9)-H(9)	0.9500	C(25)-H(25B)	0.9800
C(10)-C(11)	1.3837(17)	C(25)-H(25C)	0.9800
C(10)-H(10)	0.9500	C(26A)-C(27A)	1.530(2)
C(11)-C(12)	1.3959(15)	C(26A)-C(28A)	1.539(2)
C(11)-H(11)	0.9500	C(26A)-H(26A)	1.0000
C(12)-C(16A)	1.522(2)	C(27A)-H(27A)	0.9800
C(12)-C(16B)	1.522(2)	C(27A)-H(27B)	0.9800
C(13A)-C(15A)	1.520(2)	C(27A)-H(27C)	0.9800
C(13A)-C(14A)	1.521(2)	C(28A)-H(28A)	0.9800
C(13A)-H(13A)	1.0000	C(28A)-H(28B)	0.9800
C(14A)-H(14A)	0.9800	C(28A)-H(28C)	0.9800
C(14A)-H(14B)	0.9800	C(26B)-C(28B)	1.525(2)
C(14A)-H(14C)	0.9800	C(26B)-C(27B)	1.532(2)
C(15A)-H(15A)	0.9800	C(26B)-H(26B)	1.0000
C(15A)-H(15B)	0.9800	C(27B)-H(27D)	0.9800
C(15A)-H(15C)	0.9800	C(27B)-H(27E)	0.9800
C(13B)-C(14B)	1.521(3)	C(27B)-H(27F)	0.9800
C(13B)-C(15B)	1.521(3)	C(28B)-H(28D)	0.9800
C(13B)-H(13B)	1.0000	C(28B)-H(28E)	0.9800
C(14B)-H(14D)	0.9800	C(28B)-H(28F)	0.9800
C(14B)-H(14E)	0.9800	O(2)-H(2A)	0.88(3)
C(14B)-H(14F)	0.9800	O(2)-H(2B)	0.95(3)
C(15B)-H(15D)	0.9800		

**Table S6. Bond angles (°) of compound 2a**

C(1)-Ru(1)-O(1)	83.80(4)	C(7)-N(3)-H(3N)	121.9(14)
C(1)-Ru(1)-C(21)	133.05(5)	N(2)-C(6)-H(6A)	109.5
O(1)-Ru(1)-C(21)	142.14(5)	N(2)-C(6)-H(6B)	109.5
C(1)-Ru(1)-C(20)	101.42(4)	H(6A)-C(6)-H(6B)	109.5
O(1)-Ru(1)-C(20)	164.78(4)	N(2)-C(6)-H(6C)	109.5
C(21)-Ru(1)-C(20)	38.02(5)	H(6A)-C(6)-H(6C)	109.5
C(1)-Ru(1)-C(24)	109.55(4)	H(6B)-C(6)-H(6C)	109.5
O(1)-Ru(1)-C(24)	96.63(4)	C(8)-C(7)-C(12)	122.29(9)
C(21)-Ru(1)-C(24)	80.31(4)	C(8)-C(7)-N(3)	119.71(9)
C(20)-Ru(1)-C(24)	68.15(4)	C(12)-C(7)-N(3)	117.98(9)
C(1)-Ru(1)-C(19)	91.03(4)	C(7)-C(8)-C(9)	117.92(10)
O(1)-Ru(1)-C(19)	128.34(3)	C(7)-C(8)-C(13A)	119.78(15)
C(21)-Ru(1)-C(19)	68.76(4)	C(9)-C(8)-C(13A)	122.12(16)
C(20)-Ru(1)-C(19)	38.21(4)	C(7)-C(8)-C(13B)	122.9(3)
C(24)-Ru(1)-C(19)	37.74(4)	C(9)-C(8)-C(13B)	118.0(3)
C(1)-Ru(1)-C(23)	144.99(5)	C(10)-C(9)-C(8)	120.86(10)
O(1)-Ru(1)-C(23)	87.82(5)	C(10)-C(9)-H(9)	119.6
C(21)-Ru(1)-C(23)	66.58(6)	C(8)-C(9)-H(9)	119.6
C(20)-Ru(1)-C(23)	79.72(5)	C(9)-C(10)-C(11)	120.04(10)
C(24)-Ru(1)-C(23)	37.89(4)	C(9)-C(10)-H(10)	120.0
C(19)-Ru(1)-C(23)	68.06(4)	C(11)-C(10)-H(10)	120.0
C(1)-Ru(1)-C(22)	169.93(5)	C(10)-C(11)-C(12)	121.20(10)
O(1)-Ru(1)-C(22)	106.06(5)	C(10)-C(11)-H(11)	119.4
C(21)-Ru(1)-C(22)	37.70(6)	C(12)-C(11)-H(11)	119.4
C(20)-Ru(1)-C(22)	68.53(6)	C(11)-C(12)-C(7)	117.68(10)
C(24)-Ru(1)-C(22)	67.94(4)	C(11)-C(12)-C(16A)	123.0(3)
C(19)-Ru(1)-C(22)	81.29(5)	C(7)-C(12)-C(16A)	119.2(3)
C(23)-Ru(1)-C(22)	36.49(5)	C(11)-C(12)-C(16B)	118.7(3)
C(1)-Ru(1)-Cl(1)	85.95(3)	C(7)-C(12)-C(16B)	123.3(3)
O(1)-Ru(1)-Cl(1)	84.85(2)	C(15A)-C(13A)-C(14A)	112.3(4)
C(21)-Ru(1)-Cl(1)	89.04(3)	C(15A)-C(13A)-C(8)	106.61(16)
C(20)-Ru(1)-Cl(1)	109.63(3)	C(14A)-C(13A)-C(8)	114.8(4)
C(24)-Ru(1)-Cl(1)	164.50(3)	C(15A)-C(13A)-H(13A)	107.6
C(19)-Ru(1)-Cl(1)	146.18(3)	C(14A)-C(13A)-H(13A)	107.6
C(23)-Ru(1)-Cl(1)	127.12(3)	C(8)-C(13A)-H(13A)	107.6
C(22)-Ru(1)-Cl(1)	96.77(3)	C(13A)-C(14A)-H(14A)	109.5
C(1)-N(1)-C(3)	111.33(9)	C(13A)-C(14A)-H(14B)	109.5
C(1)-N(1)-C(4)	124.90(8)	H(14A)-C(14A)-H(14B)	109.5
C(3)-N(1)-C(4)	123.76(9)	C(13A)-C(14A)-H(14C)	109.5
N(2)-C(1)-N(1)	104.74(8)	H(14A)-C(14A)-H(14C)	109.5
N(2)-C(1)-Ru(1)	132.77(8)	H(14B)-C(14A)-H(14C)	109.5
N(1)-C(1)-Ru(1)	122.38(7)	C(13A)-C(15A)-H(15A)	109.5
C(1)-N(2)-C(2)	110.65(9)	C(13A)-C(15A)-H(15B)	109.5
C(1)-N(2)-C(6)	125.72(9)	H(15A)-C(15A)-H(15B)	109.5
C(2)-N(2)-C(6)	123.63(9)	C(13A)-C(15A)-H(15C)	109.5
C(3)-C(2)-N(2)	107.28(9)	H(15A)-C(15A)-H(15C)	109.5
C(3)-C(2)-H(2)	126.4	H(15B)-C(15A)-H(15C)	109.5
N(2)-C(2)-H(2)	126.4	C(14B)-C(13B)-C(15B)	110.9(6)
C(2)-C(3)-N(1)	106.00(9)	C(14B)-C(13B)-C(8)	105.2(7)
C(2)-C(3)-H(3)	127.0	C(15B)-C(13B)-C(8)	119.1(3)
N(1)-C(3)-H(3)	127.0	C(14B)-C(13B)-H(13B)	107.0
N(1)-C(4)-C(5)	111.54(8)	C(15B)-C(13B)-H(13B)	107.0
N(1)-C(4)-H(4A)	109.3	C(8)-C(13B)-H(13B)	107.0
C(5)-C(4)-H(4A)	109.3	C(13B)-C(14B)-H(14D)	109.5
N(1)-C(4)-H(4B)	109.3	C(13B)-C(14B)-H(14E)	109.5
C(5)-C(4)-H(4B)	109.3	H(14D)-C(14B)-H(14E)	109.5
H(4A)-C(4)-H(4B)	108.0	C(13B)-C(14B)-H(14F)	109.5
O(1)-C(5)-N(3)	121.16(9)	H(14D)-C(14B)-H(14F)	109.5
O(1)-C(5)-C(4)	122.35(9)	H(14E)-C(14B)-H(14F)	109.5
N(3)-C(5)-C(4)	116.44(9)	C(13B)-C(15B)-H(15D)	109.5
C(5)-O(1)-Ru(1)	125.93(7)	C(13B)-C(15B)-H(15E)	109.5
C(5)-N(3)-C(7)	121.56(9)	H(15D)-C(15B)-H(15E)	109.5
C(5)-N(3)-H(3N)	116.6(14)	C(13B)-C(15B)-H(15F)	109.5

H(15D)-C(15B)-H(15F)	109.5	C(21)-C(22)-C(26A)	130.53(13)
H(15E)-C(15B)-H(15F)	109.5	C(23)-C(22)-Ru(1)	70.13(7)
C(12)-C(16A)-C(18A)	106.4(2)	C(21)-C(22)-Ru(1)	68.16(6)
C(12)-C(16A)-C(17A)	114.5(8)	C(26B)-C(22)-Ru(1)	137.84(12)
C(18A)-C(16A)-C(17A)	113.4(6)	C(26A)-C(22)-Ru(1)	123.53(12)
C(12)-C(16A)-H(16A)	107.4	C(22)-C(23)-C(24)	122.82(12)
C(18A)-C(16A)-H(16A)	107.4	C(22)-C(23)-Ru(1)	73.38(7)
C(17A)-C(16A)-H(16A)	107.4	C(24)-C(23)-Ru(1)	70.17(6)
C(16A)-C(17A)-H(17A)	109.5	C(22)-C(23)-H(23)	117.8
C(16A)-C(17A)-H(17B)	109.5	C(24)-C(23)-H(23)	117.8
H(17A)-C(17A)-H(17B)	109.5	Ru(1)-C(23)-H(23)	117.8
C(16A)-C(17A)-H(17C)	109.5	C(19)-C(24)-C(23)	120.11(11)
H(17A)-C(17A)-H(17C)	109.5	C(19)-C(24)-Ru(1)	71.44(6)
H(17B)-C(17A)-H(17C)	109.5	C(23)-C(24)-Ru(1)	71.94(6)
C(16A)-C(18A)-H(18A)	109.5	C(19)-C(24)-H(24)	119.5
C(16A)-C(18A)-H(18B)	109.5	C(23)-C(24)-H(24)	119.5
H(18A)-C(18A)-H(18B)	109.5	Ru(1)-C(24)-H(24)	119.5
C(16A)-C(18A)-H(18C)	109.5	C(19)-C(25)-H(25A)	109.5
H(18A)-C(18A)-H(18C)	109.5	C(19)-C(25)-H(25B)	109.5
H(18B)-C(18A)-H(18C)	109.5	H(25A)-C(25)-H(25B)	109.5
C(12)-C(16B)-C(17B)	109.5(9)	C(19)-C(25)-H(25C)	109.5
C(12)-C(16B)-C(18B)	114.8(2)	H(25A)-C(25)-H(25C)	109.5
C(17B)-C(16B)-C(18B)	108.9(6)	H(25B)-C(25)-H(25C)	109.5
C(12)-C(16B)-H(16B)	107.8	C(27A)-C(26A)-C(28A)	107.3(2)
C(17B)-C(16B)-H(16B)	107.8	C(27A)-C(26A)-C(22)	108.93(16)
C(18B)-C(16B)-H(16B)	107.8	C(28A)-C(26A)-C(22)	118.64(16)
C(16B)-C(17B)-H(17D)	109.5	C(27A)-C(26A)-H(26A)	107.1
C(16B)-C(17B)-H(17E)	109.5	C(28A)-C(26A)-H(26A)	107.1
H(17D)-C(17B)-H(17E)	109.5	C(22)-C(26A)-H(26A)	107.1
C(16B)-C(17B)-H(17F)	109.5	C(26A)-C(27A)-H(27A)	109.5
H(17D)-C(17B)-H(17F)	109.5	C(26A)-C(27A)-H(27B)	109.5
H(17E)-C(17B)-H(17F)	109.5	H(27A)-C(27A)-H(27B)	109.5
C(16B)-C(18B)-H(18D)	109.5	C(26A)-C(27A)-H(27C)	109.5
C(16B)-C(18B)-H(18E)	109.5	H(27A)-C(27A)-H(27C)	109.5
H(18D)-C(18B)-H(18E)	109.5	H(27B)-C(27A)-H(27C)	109.5
C(16B)-C(18B)-H(18F)	109.5	C(26A)-C(28A)-H(28A)	109.5
H(18D)-C(18B)-H(18F)	109.5	C(26A)-C(28A)-H(28B)	109.5
H(18E)-C(18B)-H(18F)	109.5	H(28A)-C(28A)-H(28B)	109.5
C(24)-C(19)-C(20)	118.30(10)	C(26A)-C(28A)-H(28C)	109.5
C(24)-C(19)-C(25)	121.47(9)	H(28A)-C(28A)-H(28C)	109.5
C(20)-C(19)-C(25)	120.18(10)	H(28B)-C(28A)-H(28C)	109.5
C(24)-C(19)-Ru(1)	70.82(6)	C(28B)-C(26B)-C(22)	102.32(18)
C(20)-C(19)-Ru(1)	70.27(6)	C(28B)-C(26B)-C(27B)	112.3(2)
C(25)-C(19)-Ru(1)	128.63(7)	C(22)-C(26B)-C(27B)	109.89(18)
C(21)-C(20)-C(19)	119.96(11)	C(28B)-C(26B)-H(26B)	110.7
C(21)-C(20)-Ru(1)	70.79(7)	C(22)-C(26B)-H(26B)	110.7
C(19)-C(20)-Ru(1)	71.52(6)	C(27B)-C(26B)-H(26B)	110.7
C(21)-C(20)-H(20)	119.4	C(26B)-C(27B)-H(27D)	109.5
C(19)-C(20)-H(20)	119.4	C(26B)-C(27B)-H(27E)	109.5
Ru(1)-C(20)-H(20)	119.4	H(27D)-C(27B)-H(27E)	109.5
C(20)-C(21)-C(22)	122.25(11)	C(26B)-C(27B)-H(27F)	109.5
C(20)-C(21)-Ru(1)	71.19(6)	H(27D)-C(27B)-H(27F)	109.5
C(22)-C(21)-Ru(1)	74.13(8)	H(27E)-C(27B)-H(27F)	109.5
C(20)-C(21)-H(21)	118.4	C(26B)-C(28B)-H(28D)	109.5
C(22)-C(21)-H(21)	118.4	C(26B)-C(28B)-H(28E)	109.5
Ru(1)-C(21)-H(21)	118.4	H(28D)-C(28B)-H(28E)	109.5
C(23)-C(22)-C(21)	116.50(11)	C(26B)-C(28B)-H(28F)	109.5
C(23)-C(22)-C(26B)	132.63(17)	H(28D)-C(28B)-H(28F)	109.5
C(21)-C(22)-C(26B)	110.36(16)	H(28E)-C(28B)-H(28F)	109.5
C(23)-C(22)-C(26A)	112.14(15)	H(2A)-O(2)-H(2B)	108(2)

**Table S7. Torsion angles (°)of compound 2a**

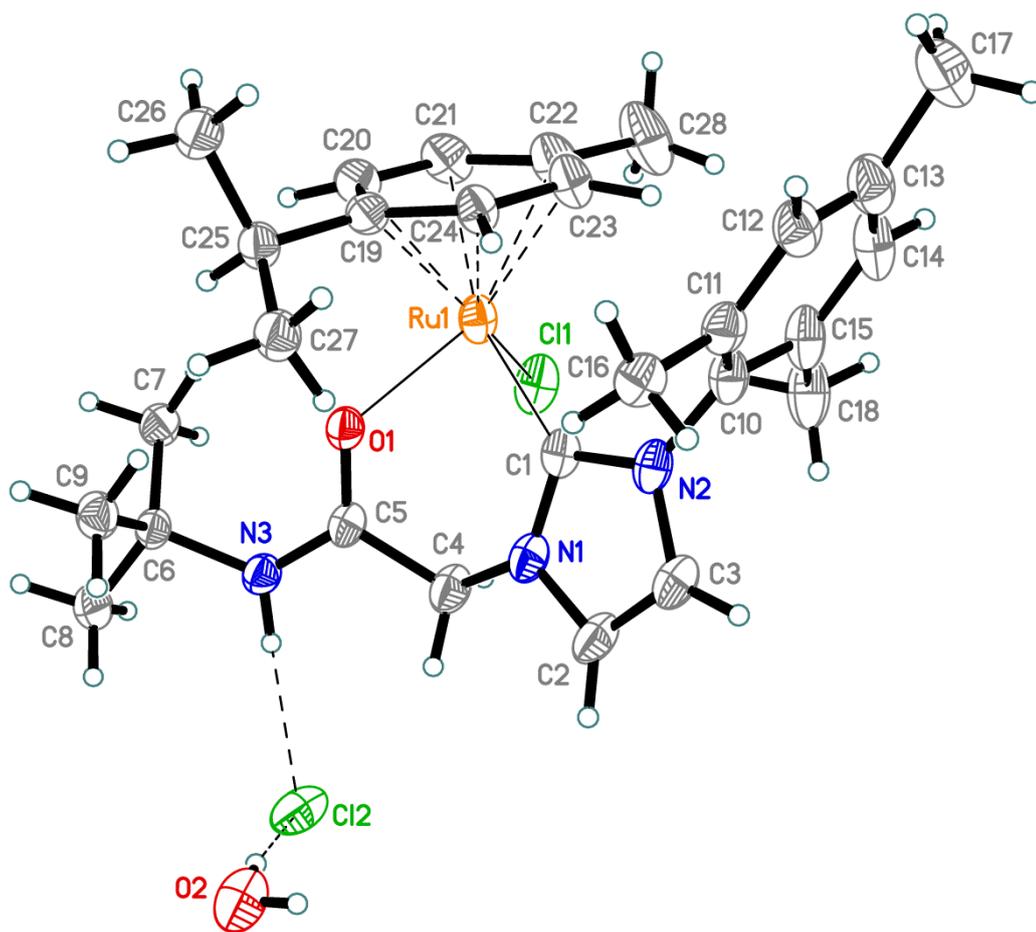
C(3)-N(1)-C(1)-N(2)	0.10(11)	C(11)-C(12)-C(16A)-C(18A)	93.6(5)
C(4)-N(1)-C(1)-N(2)	178.92(9)	C(7)-C(12)-C(16A)-C(18A)	-90.1(4)
C(3)-N(1)-C(1)-Ru(1)	176.75(7)	C(11)-C(12)-C(16A)-C(17A)	-32.5(5)
C(4)-N(1)-C(1)-Ru(1)	-4.43(13)	C(7)-C(12)-C(16A)-C(17A)	143.8(5)
N(1)-C(1)-N(2)-C(2)	0.07(11)	C(11)-C(12)-C(16B)-C(17B)	-64.9(5)
Ru(1)-C(1)-N(2)-C(2)	-176.07(8)	C(7)-C(12)-C(16B)-C(17B)	121.8(6)
N(1)-C(1)-N(2)-C(6)	180.00(9)	C(11)-C(12)-C(16B)-C(18B)	58.0(6)
Ru(1)-C(1)-N(2)-C(6)	3.85(15)	C(7)-C(12)-C(16B)-C(18B)	-115.4(5)
C(1)-N(2)-C(2)-C(3)	-0.22(12)	C(24)-C(19)-C(20)-C(21)	-0.24(15)
C(6)-N(2)-C(2)-C(3)	179.85(10)	C(25)-C(19)-C(20)-C(21)	177.59(10)
N(2)-C(2)-C(3)-N(1)	0.27(12)	Ru(1)-C(19)-C(20)-C(21)	53.62(9)
C(1)-N(1)-C(3)-C(2)	-0.24(12)	C(24)-C(19)-C(20)-Ru(1)	-53.86(8)
C(4)-N(1)-C(3)-C(2)	-179.07(9)	C(25)-C(19)-C(20)-Ru(1)	123.96(9)
C(1)-N(1)-C(4)-C(5)	48.46(13)	C(19)-C(20)-C(21)-C(22)	2.22(17)
C(3)-N(1)-C(4)-C(5)	-132.87(10)	Ru(1)-C(20)-C(21)-C(22)	56.19(11)
N(1)-C(4)-C(5)-O(1)	-40.44(14)	C(19)-C(20)-C(21)-Ru(1)	-53.97(9)
N(1)-C(4)-C(5)-N(3)	142.17(9)	C(20)-C(21)-C(22)-C(23)	-2.36(19)
N(3)-C(5)-O(1)-Ru(1)	167.93(8)	Ru(1)-C(21)-C(22)-C(23)	52.49(12)
C(4)-C(5)-O(1)-Ru(1)	-9.34(14)	C(20)-C(21)-C(22)-C(26B)	170.47(13)
O(1)-C(5)-N(3)-C(7)	-9.58(16)	Ru(1)-C(21)-C(22)-C(26B)	-134.68(13)
C(4)-C(5)-N(3)-C(7)	167.84(9)	C(20)-C(21)-C(22)-C(26A)	-170.98(15)
C(5)-N(3)-C(7)-C(8)	84.33(13)	Ru(1)-C(21)-C(22)-C(26A)	-116.13(17)
C(5)-N(3)-C(7)-C(12)	-94.59(12)	C(20)-C(21)-C(22)-Ru(1)	-54.85(10)
C(12)-C(7)-C(8)-C(9)	-0.31(17)	C(21)-C(22)-C(23)-C(24)	0.6(2)
N(3)-C(7)-C(8)-C(9)	-179.19(10)	C(26B)-C(22)-C(23)-C(24)	-170.25(16)
C(12)-C(7)-C(8)-C(13A)	174.98(13)	C(26A)-C(22)-C(23)-C(24)	171.29(14)
N(3)-C(7)-C(8)-C(13A)	-3.89(18)	Ru(1)-C(22)-C(23)-C(24)	52.13(12)
C(12)-C(7)-C(8)-C(13B)	-168.2(2)	C(21)-C(22)-C(23)-Ru(1)	-51.53(11)
N(3)-C(7)-C(8)-C(13B)	13.0(2)	C(26B)-C(22)-C(23)-Ru(1)	137.6(2)
C(7)-C(8)-C(9)-C(10)	0.67(18)	C(26A)-C(22)-C(23)-Ru(1)	119.15(13)
C(13A)-C(8)-C(9)-C(10)	-174.51(14)	C(20)-C(19)-C(24)-C(23)	-1.46(15)
C(13B)-C(8)-C(9)-C(10)	169.1(2)	C(25)-C(19)-C(24)-C(23)	-179.25(11)
C(8)-C(9)-C(10)-C(11)	-0.81(19)	Ru(1)-C(19)-C(24)-C(23)	-55.05(10)
C(9)-C(10)-C(11)-C(12)	0.57(19)	C(20)-C(19)-C(24)-Ru(1)	53.60(8)
C(10)-C(11)-C(12)-C(7)	-0.21(17)	C(25)-C(19)-C(24)-Ru(1)	-124.20(9)
C(10)-C(11)-C(12)-C(16A)	176.15(17)	C(22)-C(23)-C(24)-C(19)	1.29(19)
C(10)-C(11)-C(12)-C(16B)	-174.0(2)	Ru(1)-C(23)-C(24)-C(19)	54.82(9)
C(8)-C(7)-C(12)-C(11)	0.08(16)	C(22)-C(23)-C(24)-Ru(1)	-53.53(12)
N(3)-C(7)-C(12)-C(11)	178.98(10)	C(23)-C(22)-C(26A)-C(27A)	-175.23(16)
C(8)-C(7)-C(12)-C(16A)	-176.42(17)	C(21)-C(22)-C(26A)-C(27A)	-6.2(3)
N(3)-C(7)-C(12)-C(16A)	2.48(19)	Ru(1)-C(22)-C(26A)-C(27A)	-95.05(18)
C(8)-C(7)-C(12)-C(16B)	173.5(2)	C(23)-C(22)-C(26A)-C(28A)	-52.1(2)
N(3)-C(7)-C(12)-C(16B)	-7.6(2)	C(21)-C(22)-C(26A)-C(28A)	116.9(2)
C(7)-C(8)-C(13A)-C(15A)	89.8(2)	Ru(1)-C(22)-C(26A)-C(28A)	28.1(3)
C(9)-C(8)-C(13A)-C(15A)	-95.1(2)	C(23)-C(22)-C(26B)-C(28B)	-58.3(3)
C(7)-C(8)-C(13A)-C(14A)	-145.2(4)	C(21)-C(22)-C(26B)-C(28B)	130.4(2)
C(9)-C(8)-C(13A)-C(14A)	29.9(4)	Ru(1)-C(22)-C(26B)-C(28B)	50.8(3)
C(7)-C(8)-C(13B)-C(14B)	-123.9(7)	C(23)-C(22)-C(26B)-C(27B)	61.2(3)
C(9)-C(8)-C(13B)-C(14B)	68.3(6)	C(21)-C(22)-C(26B)-C(27B)	-110.1(2)
C(7)-C(8)-C(13B)-C(15B)	111.1(5)	Ru(1)-C(22)-C(26B)-C(27B)	170.32(18)
C(9)-C(8)-C(13B)-C(15B)	-56.8(6)		

**Table S8.** Hydrogen bonds for **2a**, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...Cl(2)	0.80(2)	2.33(2)	3.1102(9)	165.6(19)
O(2)-H(2A)...Cl(1)#1	0.88(3)	2.53(3)	3.3756(12)	162(2)
O(2)-H(2B)...Cl(2)	0.95(3)	2.23(3)	3.1531(12)	164(2)

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

### The structure of **2b**.



**Figure S5.** The structure of **2b** (p=50%).

**Table S9. Bond lengths (Å) of compound 2b**

Ru(1)-C(1)	2.061(3)	C(12)-H(12)	0.9500
Ru(1)-O(1)	2.118(2)	C(13)-C(14)	1.391(5)
Ru(1)-C(19)	2.179(3)	C(13)-C(17)	1.508(5)
Ru(1)-C(24)	2.190(3)	C(14)-C(15)	1.391(5)
Ru(1)-C(23)	2.201(3)	C(14)-H(14)	0.9500
Ru(1)-C(22)	2.208(3)	C(15)-C(18)	1.502(5)
Ru(1)-C(20)	2.242(3)	C(16)-H(16A)	0.9800
Ru(1)-C(21)	2.249(3)	C(16)-H(16B)	0.9800
Ru(1)-Cl(1)	2.4125(8)	C(16)-H(16C)	0.9800
O(1)-C(5)	1.252(3)	C(17)-H(17A)	0.9800
N(1)-C(1)	1.354(4)	C(17)-H(17B)	0.9800
N(1)-C(2)	1.394(4)	C(17)-H(17C)	0.9800
N(1)-C(4)	1.460(4)	C(18)-H(18A)	0.9800
N(2)-C(1)	1.362(3)	C(18)-H(18B)	0.9800
N(2)-C(3)	1.397(4)	C(18)-H(18C)	0.9800
N(2)-C(10)	1.427(4)	C(19)-C(24)	1.411(4)
N(3)-C(5)	1.317(4)	C(19)-C(20)	1.433(4)
N(3)-C(6)	1.485(3)	C(19)-C(25)	1.510(4)
N(3)-H(3A)	0.90(4)	C(20)-C(21)	1.383(4)
C(2)-C(3)	1.338(5)	C(20)-H(20)	1.0000
C(2)-H(2)	0.9500	C(21)-C(22)	1.433(5)
C(3)-H(3)	0.9500	C(21)-H(21)	1.0000
C(4)-C(5)	1.512(4)	C(22)-C(23)	1.406(4)
C(4)-H(4A)	0.9900	C(22)-C(28)	1.502(5)
C(4)-H(4B)	0.9900	C(23)-C(24)	1.427(4)
C(6)-C(8)	1.523(4)	C(23)-H(23)	1.0000
C(6)-C(7)	1.529(4)	C(24)-H(24)	1.0000
C(6)-C(9)	1.529(4)	C(25)-C(27)	1.523(4)
C(7)-H(7A)	0.9800	C(25)-C(26)	1.537(4)
C(7)-H(7B)	0.9800	C(25)-H(25)	1.0000
C(7)-H(7C)	0.9800	C(26)-H(26A)	0.9800
C(8)-H(8A)	0.9800	C(26)-H(26B)	0.9800
C(8)-H(8B)	0.9800	C(26)-H(26C)	0.9800
C(8)-H(8C)	0.9800	C(27)-H(27A)	0.9800
C(9)-H(9A)	0.9800	C(27)-H(27B)	0.9800
C(9)-H(9B)	0.9800	C(27)-H(27C)	0.9800
C(9)-H(9C)	0.9800	C(28)-H(28A)	0.9800
C(10)-C(11)	1.396(4)	C(28)-H(28B)	0.9800
C(10)-C(15)	1.402(4)	C(28)-H(28C)	0.9800
C(11)-C(12)	1.395(4)	O(2)-H(2A)	0.87(2)
C(11)-C(16)	1.508(4)	O(2)-H(2B)	0.86(2)
C(12)-C(13)	1.391(5)		

**Table S10. Bond angles (°) of compound 2b**

C(1)-Ru(1)-O(1)	83.44(9)	O(1)-C(5)-C(4)	121.4(2)
C(1)-Ru(1)-C(19)	121.42(10)	N(3)-C(5)-C(4)	115.6(2)
O(1)-Ru(1)-C(19)	86.14(9)	N(3)-C(6)-C(8)	106.0(2)
C(1)-Ru(1)-C(24)	98.27(10)	N(3)-C(6)-C(7)	111.0(2)
O(1)-Ru(1)-C(24)	113.99(9)	C(8)-C(6)-C(7)	109.3(2)
C(19)-Ru(1)-C(24)	37.69(10)	N(3)-C(6)-C(9)	108.3(2)
C(1)-Ru(1)-C(23)	100.02(11)	C(8)-C(6)-C(9)	110.3(2)
O(1)-Ru(1)-C(23)	151.86(10)	C(7)-C(6)-C(9)	111.8(2)
C(19)-Ru(1)-C(23)	68.10(11)	C(6)-C(7)-H(7A)	109.5
C(24)-Ru(1)-C(23)	37.92(10)	C(6)-C(7)-H(7B)	109.5
C(1)-Ru(1)-C(22)	124.13(12)	H(7A)-C(7)-H(7B)	109.5
O(1)-Ru(1)-C(22)	152.32(10)	C(6)-C(7)-H(7C)	109.5
C(19)-Ru(1)-C(22)	81.17(12)	H(7A)-C(7)-H(7C)	109.5
C(24)-Ru(1)-C(22)	68.32(11)	H(7B)-C(7)-H(7C)	109.5
C(23)-Ru(1)-C(22)	37.20(11)	C(6)-C(8)-H(8A)	109.5
C(1)-Ru(1)-C(20)	158.48(11)	C(6)-C(8)-H(8B)	109.5
O(1)-Ru(1)-C(20)	88.44(9)	H(8A)-C(8)-H(8B)	109.5
C(19)-Ru(1)-C(20)	37.80(10)	C(6)-C(8)-H(8C)	109.5
C(24)-Ru(1)-C(20)	66.97(10)	H(8A)-C(8)-H(8C)	109.5
C(23)-Ru(1)-C(20)	78.21(11)	H(8B)-C(8)-H(8C)	109.5
C(22)-Ru(1)-C(20)	66.59(12)	C(6)-C(9)-H(9A)	109.5
C(1)-Ru(1)-C(21)	161.08(12)	C(6)-C(9)-H(9B)	109.5
O(1)-Ru(1)-C(21)	114.84(10)	H(9A)-C(9)-H(9B)	109.5
C(19)-Ru(1)-C(21)	67.36(11)	C(6)-C(9)-H(9C)	109.5
C(24)-Ru(1)-C(21)	79.27(11)	H(9A)-C(9)-H(9C)	109.5
C(23)-Ru(1)-C(21)	66.45(11)	H(9B)-C(9)-H(9C)	109.5
C(22)-Ru(1)-C(21)	37.48(12)	C(11)-C(10)-C(15)	122.6(3)
C(20)-Ru(1)-C(21)	35.88(11)	C(11)-C(10)-N(2)	119.8(3)
C(1)-Ru(1)-Cl(1)	85.18(8)	C(15)-C(10)-N(2)	117.5(3)
O(1)-Ru(1)-Cl(1)	88.68(6)	C(12)-C(11)-C(10)	117.7(3)
C(19)-Ru(1)-Cl(1)	151.98(7)	C(12)-C(11)-C(16)	120.3(3)
C(24)-Ru(1)-Cl(1)	157.29(7)	C(10)-C(11)-C(16)	122.0(3)
C(23)-Ru(1)-Cl(1)	119.37(8)	C(13)-C(12)-C(11)	121.3(3)
C(22)-Ru(1)-Cl(1)	91.08(9)	C(13)-C(12)-H(12)	119.4
C(20)-Ru(1)-Cl(1)	114.61(8)	C(11)-C(12)-H(12)	119.4
C(21)-Ru(1)-Cl(1)	90.19(9)	C(12)-C(13)-C(14)	119.1(3)
C(5)-O(1)-Ru(1)	128.69(17)	C(12)-C(13)-C(17)	120.1(3)
C(1)-N(1)-C(2)	111.8(2)	C(14)-C(13)-C(17)	120.8(3)
C(1)-N(1)-C(4)	126.9(2)	C(15)-C(14)-C(13)	121.9(3)
C(2)-N(1)-C(4)	120.6(3)	C(15)-C(14)-H(14)	119.1
C(1)-N(2)-C(3)	110.8(3)	C(13)-C(14)-H(14)	119.1
C(1)-N(2)-C(10)	125.6(2)	C(14)-C(15)-C(10)	117.1(3)
C(3)-N(2)-C(10)	123.2(2)	C(14)-C(15)-C(18)	122.0(3)
C(5)-N(3)-C(6)	126.0(2)	C(10)-C(15)-C(18)	120.9(3)
C(5)-N(3)-H(3A)	115(2)	C(11)-C(16)-H(16A)	109.5
C(6)-N(3)-H(3A)	118(2)	C(11)-C(16)-H(16B)	109.5
N(1)-C(1)-N(2)	104.0(2)	H(16A)-C(16)-H(16B)	109.5
N(1)-C(1)-Ru(1)	122.88(19)	C(11)-C(16)-H(16C)	109.5
N(2)-C(1)-Ru(1)	133.1(2)	H(16A)-C(16)-H(16C)	109.5
C(3)-C(2)-N(1)	106.2(3)	H(16B)-C(16)-H(16C)	109.5
C(3)-C(2)-H(2)	126.9	C(13)-C(17)-H(17A)	109.5
N(1)-C(2)-H(2)	126.9	C(13)-C(17)-H(17B)	109.5
C(2)-C(3)-N(2)	107.2(3)	H(17A)-C(17)-H(17B)	109.5
C(2)-C(3)-H(3)	126.4	C(13)-C(17)-H(17C)	109.5
N(2)-C(3)-H(3)	126.4	H(17A)-C(17)-H(17C)	109.5
N(1)-C(4)-C(5)	112.1(2)	H(17B)-C(17)-H(17C)	109.5
N(1)-C(4)-H(4A)	109.2	C(15)-C(18)-H(18A)	109.5
C(5)-C(4)-H(4A)	109.2	C(15)-C(18)-H(18B)	109.5
N(1)-C(4)-H(4B)	109.2	H(18A)-C(18)-H(18B)	109.5
C(5)-C(4)-H(4B)	109.2	C(15)-C(18)-H(18C)	109.5
H(4A)-C(4)-H(4B)	107.9	H(18A)-C(18)-H(18C)	109.5
O(1)-C(5)-N(3)	123.0(2)	H(18B)-C(18)-H(18C)	109.5

C(24)-C(19)-C(20)	118.6(2)	C(19)-C(24)-Ru(1)	70.76(16)
C(24)-C(19)-C(25)	122.6(2)	C(23)-C(24)-Ru(1)	71.47(17)
C(20)-C(19)-C(25)	118.8(2)	C(19)-C(24)-H(24)	119.7
C(24)-C(19)-Ru(1)	71.55(16)	C(23)-C(24)-H(24)	119.7
C(20)-C(19)-Ru(1)	73.47(17)	Ru(1)-C(24)-H(24)	119.7
C(25)-C(19)-Ru(1)	128.53(19)	C(19)-C(25)-C(27)	114.0(2)
C(21)-C(20)-C(19)	121.4(3)	C(19)-C(25)-C(26)	108.5(2)
C(21)-C(20)-Ru(1)	72.36(19)	C(27)-C(25)-C(26)	111.0(2)
C(19)-C(20)-Ru(1)	68.73(15)	C(19)-C(25)-H(25)	107.7
C(21)-C(20)-H(20)	118.3	C(27)-C(25)-H(25)	107.7
C(19)-C(20)-H(20)	118.3	C(26)-C(25)-H(25)	107.7
Ru(1)-C(20)-H(20)	118.3	C(25)-C(26)-H(26A)	109.5
C(20)-C(21)-C(22)	120.3(3)	C(25)-C(26)-H(26B)	109.5
C(20)-C(21)-Ru(1)	71.76(17)	H(26A)-C(26)-H(26B)	109.5
C(22)-C(21)-Ru(1)	69.69(18)	C(25)-C(26)-H(26C)	109.5
C(20)-C(21)-H(21)	119.1	H(26A)-C(26)-H(26C)	109.5
C(22)-C(21)-H(21)	119.1	H(26B)-C(26)-H(26C)	109.5
Ru(1)-C(21)-H(21)	119.1	C(25)-C(27)-H(27A)	109.5
C(23)-C(22)-C(21)	118.4(3)	C(25)-C(27)-H(27B)	109.5
C(23)-C(22)-C(28)	121.2(3)	H(27A)-C(27)-H(27B)	109.5
C(21)-C(22)-C(28)	120.3(3)	C(25)-C(27)-H(27C)	109.5
C(23)-C(22)-Ru(1)	71.13(18)	H(27A)-C(27)-H(27C)	109.5
C(21)-C(22)-Ru(1)	72.83(18)	H(27B)-C(27)-H(27C)	109.5
C(28)-C(22)-Ru(1)	129.4(3)	C(22)-C(28)-H(28A)	109.5
C(22)-C(23)-C(24)	121.3(3)	C(22)-C(28)-H(28B)	109.5
C(22)-C(23)-Ru(1)	71.68(19)	H(28A)-C(28)-H(28B)	109.5
C(24)-C(23)-Ru(1)	70.61(16)	C(22)-C(28)-H(28C)	109.5
C(22)-C(23)-H(23)	118.6	H(28A)-C(28)-H(28C)	109.5
C(24)-C(23)-H(23)	118.6	H(28B)-C(28)-H(28C)	109.5
Ru(1)-C(23)-H(23)	118.6	H(2A)-O(2)-H(2B)	115(7)
C(19)-C(24)-C(23)	119.6(2)		

**Table S11. Torsion angles (°) of compound 2b**

C(2)-N(1)-C(1)-N(2)	0.8(3)	C(15)-C(10)-C(11)-C(16)	-175.1(3)
C(4)-N(1)-C(1)-N(2)	-170.0(3)	N(2)-C(10)-C(11)-C(16)	4.8(4)
C(2)-N(1)-C(1)-Ru(1)	-176.6(2)	C(10)-C(11)-C(12)-C(13)	-1.5(4)
C(4)-N(1)-C(1)-Ru(1)	12.5(4)	C(16)-C(11)-C(12)-C(13)	179.0(3)
C(3)-N(2)-C(1)-N(1)	-0.3(3)	C(11)-C(12)-C(13)-C(14)	-3.1(5)
C(10)-N(2)-C(1)-N(1)	172.2(3)	C(11)-C(12)-C(13)-C(17)	176.9(3)
C(3)-N(2)-C(1)-Ru(1)	176.7(2)	C(12)-C(13)-C(14)-C(15)	4.0(5)
C(10)-N(2)-C(1)-Ru(1)	-10.8(4)	C(17)-C(13)-C(14)-C(15)	-175.9(3)
C(1)-N(1)-C(2)-C(3)	-1.1(4)	C(13)-C(14)-C(15)-C(10)	-0.3(5)
C(4)-N(1)-C(2)-C(3)	170.5(3)	C(13)-C(14)-C(15)-C(18)	178.5(3)
N(1)-C(2)-C(3)-N(2)	0.8(4)	C(11)-C(10)-C(15)-C(14)	-4.6(5)
C(1)-N(2)-C(3)-C(2)	-0.3(4)	N(2)-C(10)-C(15)-C(14)	175.5(3)
C(10)-N(2)-C(3)-C(2)	-173.0(3)	C(11)-C(10)-C(15)-C(18)	176.6(3)
C(1)-N(1)-C(4)-C(5)	-48.2(4)	N(2)-C(10)-C(15)-C(18)	-3.3(4)
C(2)-N(1)-C(4)-C(5)	141.6(3)	C(24)-C(19)-C(20)-C(21)	5.7(4)
Ru(1)-O(1)-C(5)-N(3)	-161.0(2)	C(25)-C(19)-C(20)-C(21)	-177.1(3)
Ru(1)-O(1)-C(5)-C(4)	17.2(4)	Ru(1)-C(19)-C(20)-C(21)	-51.8(3)
C(6)-N(3)-C(5)-O(1)	-0.2(4)	C(24)-C(19)-C(20)-Ru(1)	57.5(2)
C(6)-N(3)-C(5)-C(4)	-178.4(2)	C(25)-C(19)-C(20)-Ru(1)	-125.3(3)
N(1)-C(4)-C(5)-O(1)	31.1(4)	C(19)-C(20)-C(21)-C(22)	-1.8(5)
N(1)-C(4)-C(5)-N(3)	-150.6(3)	Ru(1)-C(20)-C(21)-C(22)	-52.0(3)
C(5)-N(3)-C(6)-C(8)	170.6(3)	C(19)-C(20)-C(21)-Ru(1)	50.2(3)
C(5)-N(3)-C(6)-C(7)	52.0(4)	C(20)-C(21)-C(22)-C(23)	-3.6(5)
C(5)-N(3)-C(6)-C(9)	-71.1(3)	Ru(1)-C(21)-C(22)-C(23)	-56.5(3)
C(1)-N(2)-C(10)-C(11)	103.2(3)	C(20)-C(21)-C(22)-C(28)	179.0(4)
C(3)-N(2)-C(10)-C(11)	-85.2(4)	Ru(1)-C(21)-C(22)-C(28)	126.1(4)
C(1)-N(2)-C(10)-C(15)	-76.9(4)	C(20)-C(21)-C(22)-Ru(1)	52.9(3)
C(3)-N(2)-C(10)-C(15)	94.7(3)	C(21)-C(22)-C(23)-C(24)	5.0(5)
C(15)-C(10)-C(11)-C(12)	5.5(4)	C(28)-C(22)-C(23)-C(24)	-177.6(4)
N(2)-C(10)-C(11)-C(12)	-174.6(2)	Ru(1)-C(22)-C(23)-C(24)	-52.4(3)

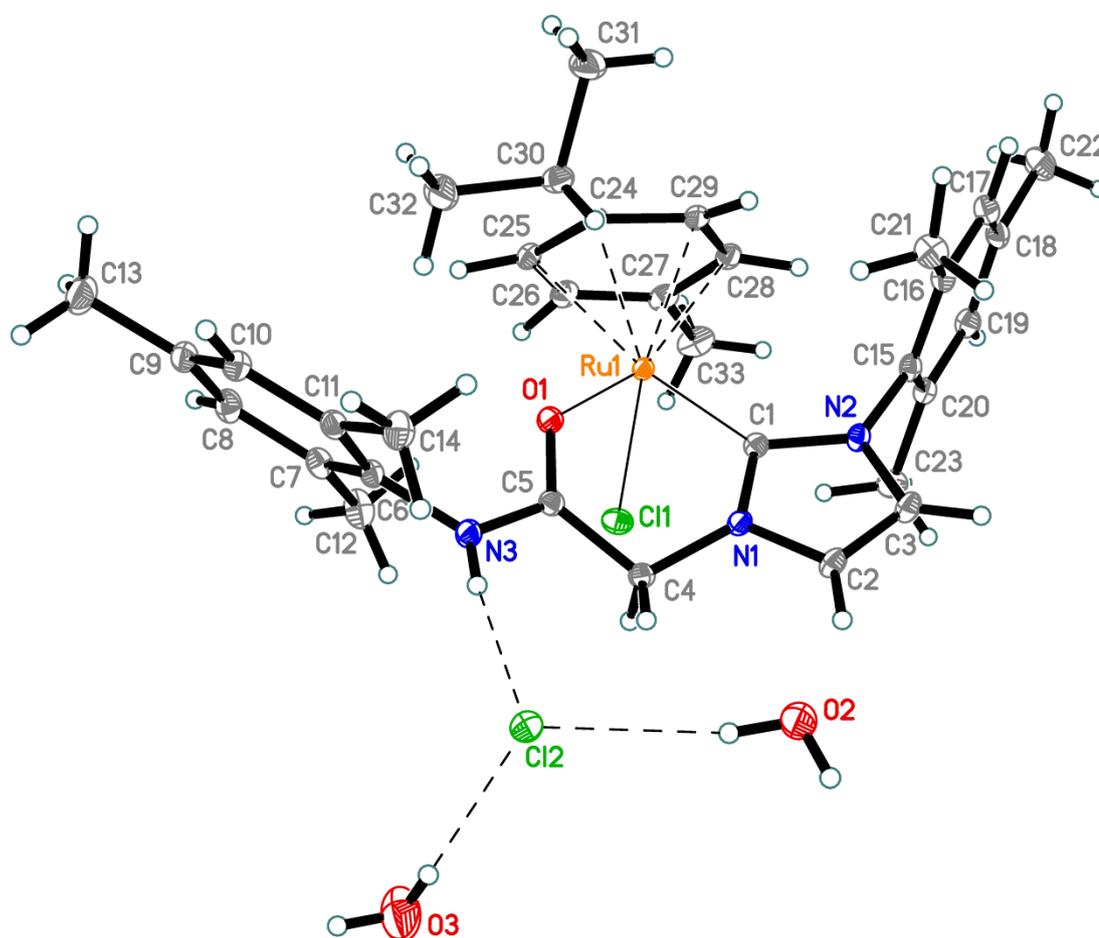
C(21)-C(22)-C(23)-Ru(1)	57.3(3)	Ru(1)-C(23)-C(24)-C(19)	-53.8(2)
C(28)-C(22)-C(23)-Ru(1)	-125.3(4)	C(22)-C(23)-C(24)-Ru(1)	52.8(3)
C(20)-C(19)-C(24)-C(23)	-4.3(4)	C(24)-C(19)-C(25)-C(27)	-31.4(4)
C(25)-C(19)-C(24)-C(23)	178.7(3)	C(20)-C(19)-C(25)-C(27)	151.5(3)
Ru(1)-C(19)-C(24)-C(23)	54.2(3)	Ru(1)-C(19)-C(25)-C(27)	60.2(3)
C(20)-C(19)-C(24)-Ru(1)	-58.5(2)	C(24)-C(19)-C(25)-C(26)	92.8(3)
C(25)-C(19)-C(24)-Ru(1)	124.5(3)	C(20)-C(19)-C(25)-C(26)	-84.3(3)
C(22)-C(23)-C(24)-C(19)	-1.0(5)	Ru(1)-C(19)-C(25)-C(26)	-175.59(19)

**Table S12.** Hydrogen bonds for **2b**, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3A)...Cl(2)	0.90(4)	2.29(4)	3.186(3)	176(3)
O(2)-H(2A)...Cl(2)	0.87(2)	2.27(3)	3.131(3)	168(7)
O(2)-H(2B)...Cl(2)#1	0.86(2)	2.38(3)	3.212(3)	162(7)

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

### The structure of **2c**.



**Figure S6.** The structure of **2c** (p=50%).

**Table S13. Bond lengths (Å) of compound 2c**

Ru(1)-Cl(1)	2.4305(3)	C(16)-C(17)	1.3958(15)
Ru(1)-O(1)	2.0931(7)	C(16)-C(21)	1.5068(15)
Ru(1)-C(1)	2.0714(10)	C(17)-H(17)	0.9500
Ru(1)-C(24)	2.2036(10)	C(17)-C(18)	1.3940(15)
Ru(1)-C(25)	2.2432(10)	C(18)-C(19)	1.4002(16)
Ru(1)-C(26)	2.2373(10)	C(18)-C(22)	1.5065(16)
Ru(1)-C(27)	2.2000(10)	C(19)-H(19)	0.9500
Ru(1)-C(28)	2.2029(10)	C(19)-C(20)	1.3907(15)
Ru(1)-C(29)	2.1883(10)	C(20)-C(23)	1.5045(15)
O(1)-C(5)	1.2480(12)	C(21)-H(21A)	0.9800
N(1)-C(1)	1.3603(13)	C(21)-H(21B)	0.9800
N(1)-C(2)	1.3906(13)	C(21)-H(21C)	0.9800
N(1)-C(4)	1.4598(13)	C(22)-H(22A)	0.9800
N(2)-C(1)	1.3630(13)	C(22)-H(22B)	0.9800
N(2)-C(3)	1.3894(13)	C(22)-H(22C)	0.9800
N(2)-C(15)	1.4354(13)	C(23)-H(23A)	0.9800
N(3)-H(3)	0.812(17)	C(23)-H(23B)	0.9800
N(3)-C(5)	1.3293(13)	C(23)-H(23C)	0.9800
N(3)-C(6)	1.4396(13)	C(24)-C(25)	1.4364(15)
C(2)-H(2)	0.9500	C(24)-C(29)	1.4164(14)
C(2)-C(3)	1.3493(15)	C(24)-C(30)	1.5227(15)
C(3)-H(3A)	0.9500	C(25)-H(25)	1.0000
C(4)-H(4A)	0.9900	C(25)-C(26)	1.3968(15)
C(4)-H(4B)	0.9900	C(26)-H(26)	1.0000
C(4)-C(5)	1.5051(14)	C(26)-C(27)	1.4321(16)
C(6)-C(7)	1.4019(15)	C(27)-C(28)	1.4050(16)
C(6)-C(11)	1.4009(15)	C(27)-C(33)	1.5022(16)
C(7)-C(8)	1.3996(15)	C(28)-H(28)	1.0000
C(7)-C(12)	1.5081(16)	C(28)-C(29)	1.4261(15)
C(8)-H(8)	0.9500	C(29)-H(29)	1.0000
C(8)-C(9)	1.3917(17)	C(30)-H(30)	1.0000
C(9)-C(10)	1.3942(15)	C(30)-C(31)	1.5309(16)
C(9)-C(13)	1.5080(16)	C(30)-C(32)	1.5246(17)
C(10)-H(10)	0.9500	C(31)-H(31A)	0.9800
C(10)-C(11)	1.3926(14)	C(31)-H(31B)	0.9800
C(11)-C(14)	1.5045(15)	C(31)-H(31C)	0.9800
C(12)-H(12A)	0.9800	C(32)-H(32A)	0.9800
C(12)-H(12B)	0.9800	C(32)-H(32B)	0.9800
C(12)-H(12C)	0.9800	C(32)-H(32C)	0.9800
C(13)-H(13A)	0.9800	C(33)-H(33A)	0.9800
C(13)-H(13B)	0.9800	C(33)-H(33B)	0.9800
C(13)-H(13C)	0.9800	C(33)-H(33C)	0.9800
C(14)-H(14A)	0.9800	O(2)-H(2A)	0.813(15)
C(14)-H(14B)	0.9800	O(2)-H(2B)	0.845(14)
C(14)-H(14C)	0.9800	O(3)-H(3B)	0.813(17)
C(15)-C(16)	1.3928(15)	O(3)-H(3C)	0.831(17)
C(15)-C(20)	1.4020(14)		

**Table S14. Bond angles (°) of compound 2c**

O(1)-Ru(1)-Cl(1)	88.33(2)	N(3)-C(5)-C(4)	117.11(9)
O(1)-Ru(1)-C(24)	85.38(3)	C(7)-C(6)-N(3)	119.69(9)
O(1)-Ru(1)-C(25)	87.14(3)	C(11)-C(6)-N(3)	118.56(9)
O(1)-Ru(1)-C(26)	114.04(4)	C(11)-C(6)-C(7)	121.75(9)
O(1)-Ru(1)-C(27)	151.69(4)	C(6)-C(7)-C(12)	122.59(10)
O(1)-Ru(1)-C(28)	151.59(4)	C(8)-C(7)-C(6)	117.63(10)
O(1)-Ru(1)-C(29)	113.77(3)	C(8)-C(7)-C(12)	119.78(10)
C(1)-Ru(1)-Cl(1)	84.00(3)	C(7)-C(8)-H(8)	119.0
C(1)-Ru(1)-O(1)	84.23(3)	C(9)-C(8)-C(7)	122.06(10)
C(1)-Ru(1)-C(24)	122.21(4)	C(9)-C(8)-H(8)	119.0
C(1)-Ru(1)-C(25)	158.97(4)	C(8)-C(9)-C(10)	118.58(10)
C(1)-Ru(1)-C(26)	160.86(4)	C(8)-C(9)-C(13)	121.62(10)
C(1)-Ru(1)-C(27)	123.91(4)	C(10)-C(9)-C(13)	119.79(11)
C(1)-Ru(1)-C(28)	100.46(4)	C(9)-C(10)-H(10)	119.2
C(1)-Ru(1)-C(29)	99.38(4)	C(11)-C(10)-C(9)	121.53(10)
C(24)-Ru(1)-Cl(1)	152.10(3)	C(11)-C(10)-H(10)	119.2
C(24)-Ru(1)-C(25)	37.68(4)	C(6)-C(11)-C(14)	121.29(9)
C(24)-Ru(1)-C(26)	67.48(4)	C(10)-C(11)-C(6)	118.43(10)
C(25)-Ru(1)-Cl(1)	114.93(3)	C(10)-C(11)-C(14)	120.24(10)
C(26)-Ru(1)-Cl(1)	90.65(3)	C(7)-C(12)-H(12A)	109.5
C(26)-Ru(1)-C(25)	36.33(4)	C(7)-C(12)-H(12B)	109.5
C(27)-Ru(1)-Cl(1)	91.51(3)	C(7)-C(12)-H(12C)	109.5
C(27)-Ru(1)-C(24)	81.61(4)	H(12A)-C(12)-H(12B)	109.5
C(27)-Ru(1)-C(25)	67.33(4)	H(12A)-C(12)-H(12C)	109.5
C(27)-Ru(1)-C(26)	37.65(4)	H(12B)-C(12)-H(12C)	109.5
C(27)-Ru(1)-C(28)	37.22(4)	C(9)-C(13)-H(13A)	109.5
C(28)-Ru(1)-Cl(1)	119.93(3)	C(9)-C(13)-H(13B)	109.5
C(28)-Ru(1)-C(24)	68.30(4)	C(9)-C(13)-H(13C)	109.5
C(28)-Ru(1)-C(25)	78.60(4)	H(13A)-C(13)-H(13B)	109.5
C(28)-Ru(1)-C(26)	66.44(4)	H(13A)-C(13)-H(13C)	109.5
C(29)-Ru(1)-Cl(1)	157.82(3)	H(13B)-C(13)-H(13C)	109.5
C(29)-Ru(1)-C(24)	37.63(4)	C(11)-C(14)-H(14A)	109.5
C(29)-Ru(1)-C(25)	66.80(4)	C(11)-C(14)-H(14B)	109.5
C(29)-Ru(1)-C(26)	78.99(4)	C(11)-C(14)-H(14C)	109.5
C(29)-Ru(1)-C(27)	68.30(4)	H(14A)-C(14)-H(14B)	109.5
C(29)-Ru(1)-C(28)	37.90(4)	H(14A)-C(14)-H(14C)	109.5
C(5)-O(1)-Ru(1)	130.50(7)	H(14B)-C(14)-H(14C)	109.5
C(1)-N(1)-C(2)	111.71(8)	C(16)-C(15)-N(2)	118.20(9)
C(1)-N(1)-C(4)	126.76(8)	C(16)-C(15)-C(20)	122.61(9)
C(2)-N(1)-C(4)	120.71(8)	C(20)-C(15)-N(2)	119.19(9)
C(1)-N(2)-C(3)	111.59(9)	C(15)-C(16)-C(17)	118.22(9)
C(1)-N(2)-C(15)	125.25(8)	C(15)-C(16)-C(21)	121.40(9)
C(3)-N(2)-C(15)	123.13(8)	C(17)-C(16)-C(21)	120.38(10)
C(5)-N(3)-H(3)	116.0(12)	C(16)-C(17)-H(17)	119.5
C(5)-N(3)-C(6)	121.56(9)	C(18)-C(17)-C(16)	121.07(10)
C(6)-N(3)-H(3)	122.1(12)	C(18)-C(17)-H(17)	119.5
N(1)-C(1)-Ru(1)	123.49(7)	C(17)-C(18)-C(19)	118.81(10)
N(1)-C(1)-N(2)	103.62(8)	C(17)-C(18)-C(22)	120.35(10)
N(2)-C(1)-Ru(1)	132.87(7)	C(19)-C(18)-C(22)	120.84(10)
N(1)-C(2)-H(2)	126.8	C(18)-C(19)-H(19)	119.0
C(3)-C(2)-N(1)	106.46(9)	C(20)-C(19)-C(18)	122.02(10)
C(3)-C(2)-H(2)	126.8	C(20)-C(19)-H(19)	119.0
N(2)-C(3)-H(3A)	126.7	C(15)-C(20)-C(23)	121.18(9)
C(2)-C(3)-N(2)	106.61(9)	C(19)-C(20)-C(15)	117.19(10)
C(2)-C(3)-H(3A)	126.7	C(19)-C(20)-C(23)	121.61(9)
N(1)-C(4)-H(4A)	109.0	C(16)-C(21)-H(21A)	109.5
N(1)-C(4)-H(4B)	109.0	C(16)-C(21)-H(21B)	109.5
N(1)-C(4)-C(5)	112.86(8)	C(16)-C(21)-H(21C)	109.5
H(4A)-C(4)-H(4B)	107.8	H(21A)-C(21)-H(21B)	109.5
C(5)-C(4)-H(4A)	109.0	H(21A)-C(21)-H(21C)	109.5
C(5)-C(4)-H(4B)	109.0	H(21B)-C(21)-H(21C)	109.5
O(1)-C(5)-N(3)	120.59(9)	C(18)-C(22)-H(22A)	109.5
O(1)-C(5)-C(4)	122.24(9)	C(18)-C(22)-H(22B)	109.5

C(18)-C(22)-H(22C)	109.5	C(27)-C(28)-H(28)	118.7
H(22A)-C(22)-H(22B)	109.5	C(27)-C(28)-C(29)	120.94(10)
H(22A)-C(22)-H(22C)	109.5	C(29)-C(28)-Ru(1)	70.49(6)
H(22B)-C(22)-H(22C)	109.5	C(29)-C(28)-H(28)	118.7
C(20)-C(23)-H(23A)	109.5	Ru(1)-C(29)-H(29)	119.0
C(20)-C(23)-H(23B)	109.5	C(24)-C(29)-Ru(1)	71.78(6)
C(20)-C(23)-H(23C)	109.5	C(24)-C(29)-C(28)	120.97(10)
H(23A)-C(23)-H(23B)	109.5	C(24)-C(29)-H(29)	119.0
H(23A)-C(23)-H(23C)	109.5	C(28)-C(29)-Ru(1)	71.60(6)
H(23B)-C(23)-H(23C)	109.5	C(28)-C(29)-H(29)	119.0
C(25)-C(24)-Ru(1)	72.65(6)	C(24)-C(30)-H(30)	107.5
C(25)-C(24)-C(30)	122.69(9)	C(24)-C(30)-C(31)	110.42(9)
C(29)-C(24)-Ru(1)	70.60(6)	C(24)-C(30)-C(32)	113.75(10)
C(29)-C(24)-C(25)	117.56(9)	C(31)-C(30)-H(30)	107.5
C(29)-C(24)-C(30)	119.75(9)	C(32)-C(30)-H(30)	107.5
C(30)-C(24)-Ru(1)	127.04(7)	C(32)-C(30)-C(31)	109.87(10)
Ru(1)-C(25)-H(25)	118.5	C(30)-C(31)-H(31A)	109.5
C(24)-C(25)-Ru(1)	69.67(6)	C(30)-C(31)-H(31B)	109.5
C(24)-C(25)-H(25)	118.5	C(30)-C(31)-H(31C)	109.5
C(26)-C(25)-Ru(1)	71.61(6)	H(31A)-C(31)-H(31B)	109.5
C(26)-C(25)-C(24)	121.07(9)	H(31A)-C(31)-H(31C)	109.5
C(26)-C(25)-H(25)	118.5	H(31B)-C(31)-H(31C)	109.5
Ru(1)-C(26)-H(26)	118.6	C(30)-C(32)-H(32A)	109.5
C(25)-C(26)-Ru(1)	72.06(6)	C(30)-C(32)-H(32B)	109.5
C(25)-C(26)-H(26)	118.6	C(30)-C(32)-H(32C)	109.5
C(25)-C(26)-C(27)	121.08(10)	H(32A)-C(32)-H(32B)	109.5
C(27)-C(26)-Ru(1)	69.76(6)	H(32A)-C(32)-H(32C)	109.5
C(27)-C(26)-H(26)	118.6	H(32B)-C(32)-H(32C)	109.5
C(26)-C(27)-Ru(1)	72.59(6)	C(27)-C(33)-H(33A)	109.5
C(26)-C(27)-C(33)	120.19(10)	C(27)-C(33)-H(33B)	109.5
C(28)-C(27)-Ru(1)	71.50(6)	C(27)-C(33)-H(33C)	109.5
C(28)-C(27)-C(26)	118.07(10)	H(33A)-C(33)-H(33B)	109.5
C(28)-C(27)-C(33)	121.74(10)	H(33A)-C(33)-H(33C)	109.5
C(33)-C(27)-Ru(1)	126.86(8)	H(33B)-C(33)-H(33C)	109.5
Ru(1)-C(28)-H(28)	118.7	H(2A)-O(2)-H(2B)	105.5(19)
C(27)-C(28)-Ru(1)	71.28(6)	H(3B)-O(3)-H(3C)	110(2)

**Table S15. Torsion angles (°)of compound 2c**

Ru(1)-O(1)-C(5)-N(3)	-165.90(7)	C(1)-N(1)-C(4)-C(5)	-45.20(14)
Ru(1)-O(1)-C(5)-C(4)	11.24(15)	C(1)-N(2)-C(3)-C(2)	0.68(12)
Ru(1)-C(24)-C(25)-C(26)	-51.96(9)	C(1)-N(2)-C(15)-C(16)	95.06(12)
Ru(1)-C(24)-C(29)-C(28)	54.19(9)	C(1)-N(2)-C(15)-C(20)	-84.20(13)
Ru(1)-C(24)-C(30)-C(31)	147.33(8)	C(2)-N(1)-C(1)-Ru(1)	-178.03(7)
Ru(1)-C(24)-C(30)-C(32)	-88.61(11)	C(2)-N(1)-C(1)-N(2)	0.82(11)
Ru(1)-C(25)-C(26)-C(27)	-51.71(9)	C(2)-N(1)-C(4)-C(5)	146.03(9)
Ru(1)-C(26)-C(27)-C(28)	-57.04(9)	C(3)-N(2)-C(1)-Ru(1)	177.78(8)
Ru(1)-C(26)-C(27)-C(33)	123.01(10)	C(3)-N(2)-C(1)-N(1)	-0.91(11)
Ru(1)-C(27)-C(28)-C(29)	-52.11(9)	C(3)-N(2)-C(15)-C(16)	-82.79(13)
Ru(1)-C(28)-C(29)-C(24)	-54.27(9)	C(3)-N(2)-C(15)-C(20)	97.94(12)
N(1)-C(2)-C(3)-N(2)	-0.15(12)	C(4)-N(1)-C(1)-Ru(1)	12.36(14)
N(1)-C(4)-C(5)-O(1)	32.15(14)	C(4)-N(1)-C(1)-N(2)	-168.79(9)
N(1)-C(4)-C(5)-N(3)	-150.62(9)	C(4)-N(1)-C(2)-C(3)	169.89(9)
N(2)-C(15)-C(16)-C(17)	-176.01(9)	C(5)-N(3)-C(6)-C(7)	64.46(14)
N(2)-C(15)-C(16)-C(21)	3.88(14)	C(5)-N(3)-C(6)-C(11)	-114.75(11)
N(2)-C(15)-C(20)-C(19)	176.62(9)	C(6)-N(3)-C(5)-O(1)	4.21(15)
N(2)-C(15)-C(20)-C(23)	-1.87(14)	C(6)-N(3)-C(5)-C(4)	-173.06(9)
N(3)-C(6)-C(7)-C(8)	179.89(10)	C(6)-C(7)-C(8)-C(9)	0.07(17)
N(3)-C(6)-C(7)-C(12)	-0.85(16)	C(7)-C(6)-C(11)-C(10)	1.38(15)
N(3)-C(6)-C(11)-C(10)	-179.43(9)	C(7)-C(6)-C(11)-C(14)	-176.46(10)
N(3)-C(6)-C(11)-C(14)	2.73(15)	C(7)-C(8)-C(9)-C(10)	0.31(17)
C(1)-N(1)-C(2)-C(3)	-0.43(12)	C(7)-C(8)-C(9)-C(13)	-178.80(11)

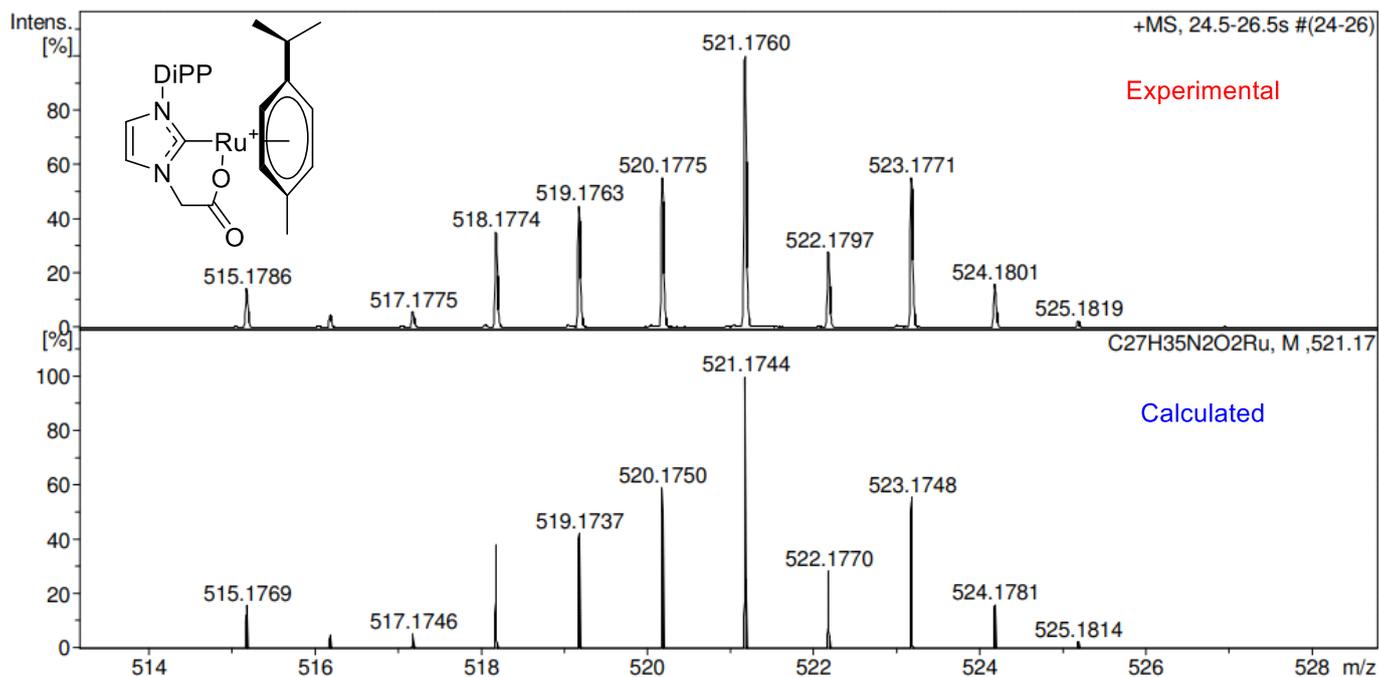
C(8)-C(9)-C(10)-C(11)	0.15(17)	C(24)-C(25)-C(26)-C(27)	-0.60(16)
C(9)-C(10)-C(11)-C(6)	-0.97(16)	C(25)-C(24)-C(29)-Ru(1)	-57.29(8)
C(9)-C(10)-C(11)-C(14)	176.89(10)	C(25)-C(24)-C(29)-C(28)	-3.10(15)
C(11)-C(6)-C(7)-C(8)	-0.93(16)	C(25)-C(24)-C(30)-C(31)	-120.35(11)
C(11)-C(6)-C(7)-C(12)	178.33(10)	C(25)-C(24)-C(30)-C(32)	3.71(15)
C(12)-C(7)-C(8)-C(9)	-179.21(11)	C(25)-C(26)-C(27)-Ru(1)	52.74(9)
C(13)-C(9)-C(10)-C(11)	179.28(10)	C(25)-C(26)-C(27)-C(28)	-4.30(16)
C(15)-N(2)-C(1)-Ru(1)	-0.29(16)	C(25)-C(26)-C(27)-C(33)	175.75(10)
C(15)-N(2)-C(1)-N(1)	-178.98(9)	C(26)-C(27)-C(28)-Ru(1)	57.59(9)
C(15)-N(2)-C(3)-C(2)	178.80(9)	C(26)-C(27)-C(28)-C(29)	5.48(15)
C(15)-C(16)-C(17)-C(18)	-1.39(15)	C(27)-C(28)-C(29)-Ru(1)	52.46(9)
C(16)-C(15)-C(20)-C(19)	-2.61(15)	C(27)-C(28)-C(29)-C(24)	-1.80(15)
C(16)-C(15)-C(20)-C(23)	178.91(10)	C(29)-C(24)-C(25)-Ru(1)	56.25(8)
C(16)-C(17)-C(18)-C(19)	-0.90(16)	C(29)-C(24)-C(25)-C(26)	4.28(15)
C(16)-C(17)-C(18)-C(22)	179.03(10)	C(29)-C(24)-C(30)-C(31)	60.09(13)
C(17)-C(18)-C(19)-C(20)	1.53(16)	C(29)-C(24)-C(30)-C(32)	-175.85(10)
C(18)-C(19)-C(20)-C(15)	0.17(15)	C(30)-C(24)-C(25)-Ru(1)	-123.32(10)
C(18)-C(19)-C(20)-C(23)	178.65(10)	C(30)-C(24)-C(25)-C(26)	-175.28(10)
C(20)-C(15)-C(16)-C(17)	3.22(15)	C(30)-C(24)-C(29)-Ru(1)	122.29(9)
C(20)-C(15)-C(16)-C(21)	-176.89(10)	C(30)-C(24)-C(29)-C(28)	176.48(9)
C(21)-C(16)-C(17)-C(18)	178.72(10)	C(33)-C(27)-C(28)-Ru(1)	-122.46(10)
C(22)-C(18)-C(19)-C(20)	-178.40(10)	C(33)-C(27)-C(28)-C(29)	-174.58(10)
C(24)-C(25)-C(26)-Ru(1)	51.11(9)		

**Table S16.** Hydrogen bonds for **2c** [ $\text{\AA}$  and  $^\circ$ ].

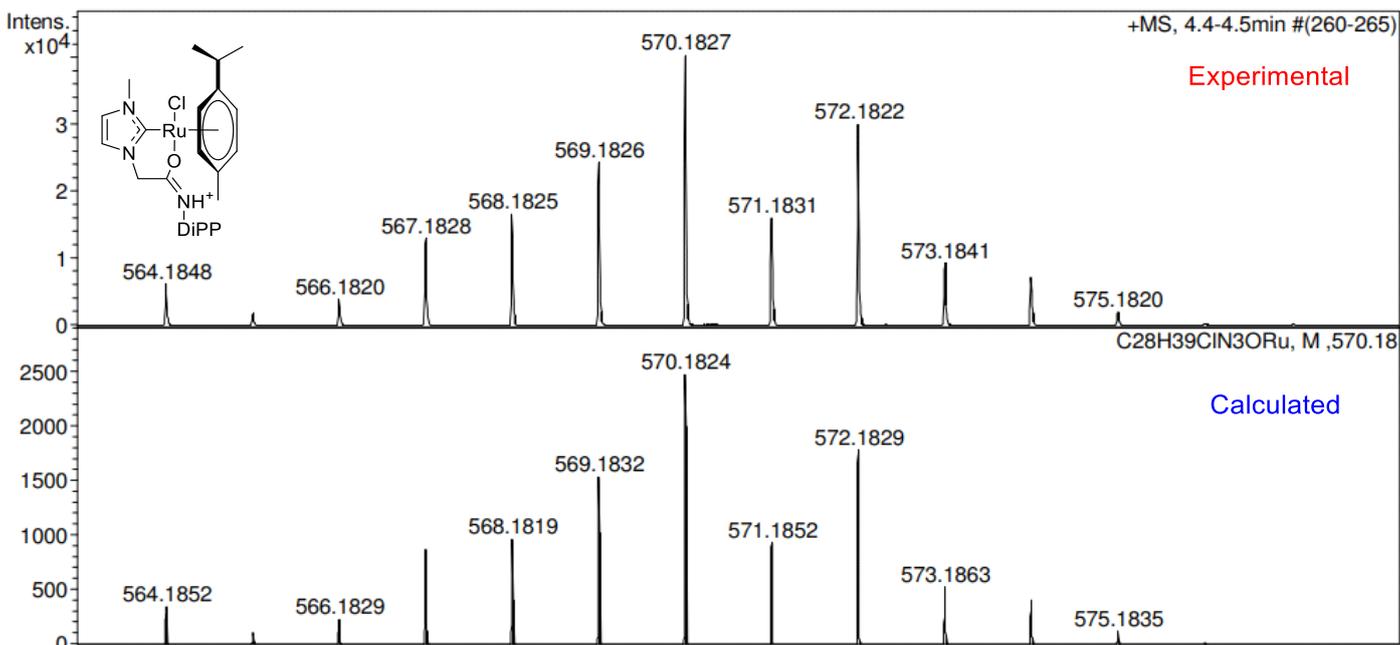
D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
N(3)-H(3)...Cl(2)	0.812(17)	2.359(17)	3.1638(10)	170.9(16)
O(2)-H(2A)...Cl(1)#1	0.813(15)	2.694(16)	3.4723(10)	160.9(19)
O(2)-H(2B)...Cl(2)	0.845(14)	2.439(15)	3.2634(10)	165.3(18)
O(3)-H(3B)...Cl(1)#2	0.813(17)	2.876(18)	3.6731(15)	167(2)
O(3)-H(3C)...Cl(2)	0.831(17)	2.420(18)	3.2272(15)	164(2)

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

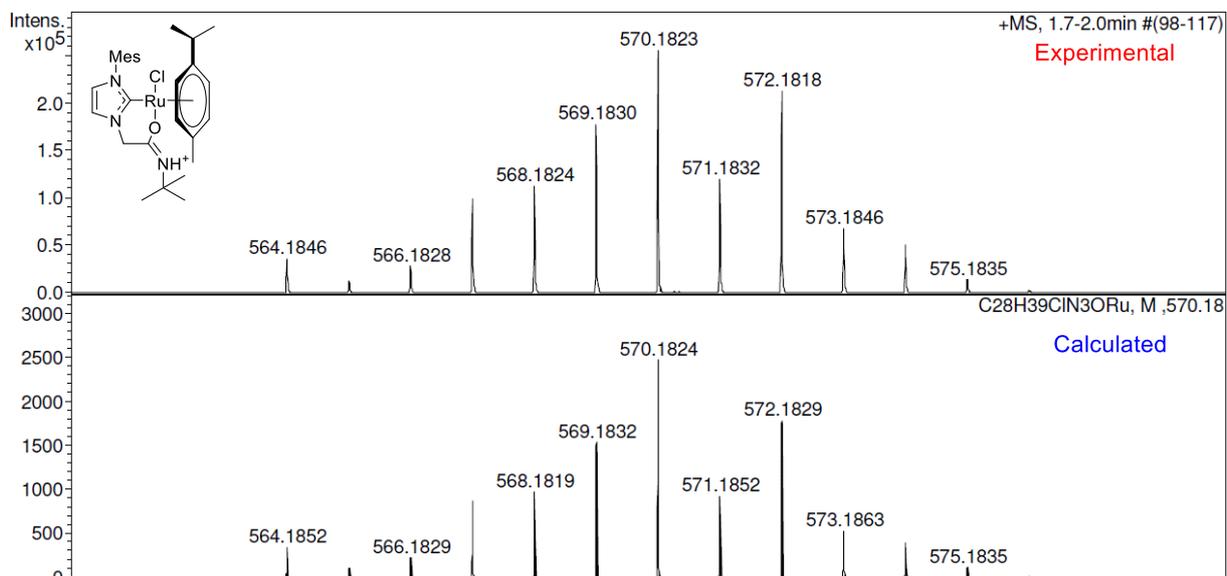
# HRMS spectra of ruthenium complexes



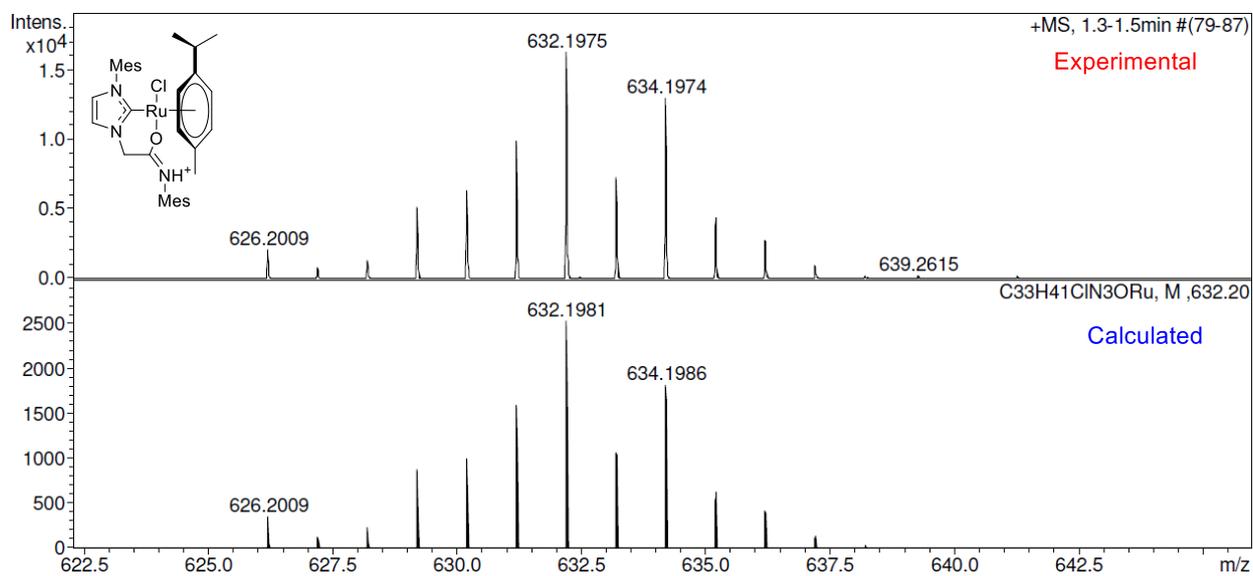
**Figure S7.** HRMS spectrum of compound **1c**.



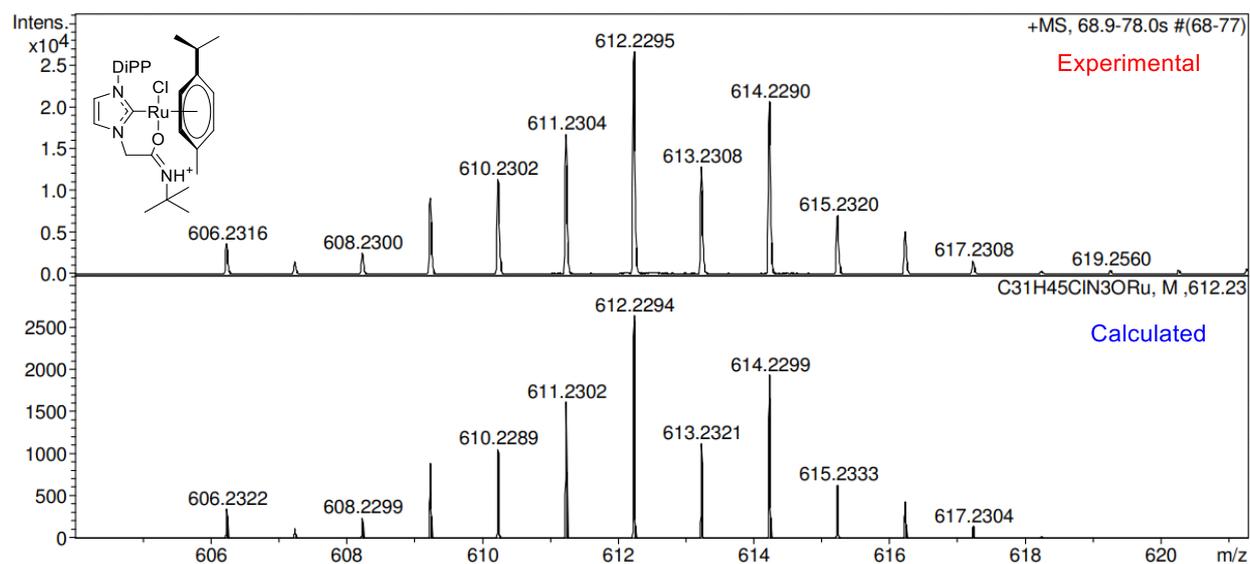
**Figure S8.** HRMS spectrum of compound **2a**.



**Figure S9.** HRMS spectrum of compound **2b**.

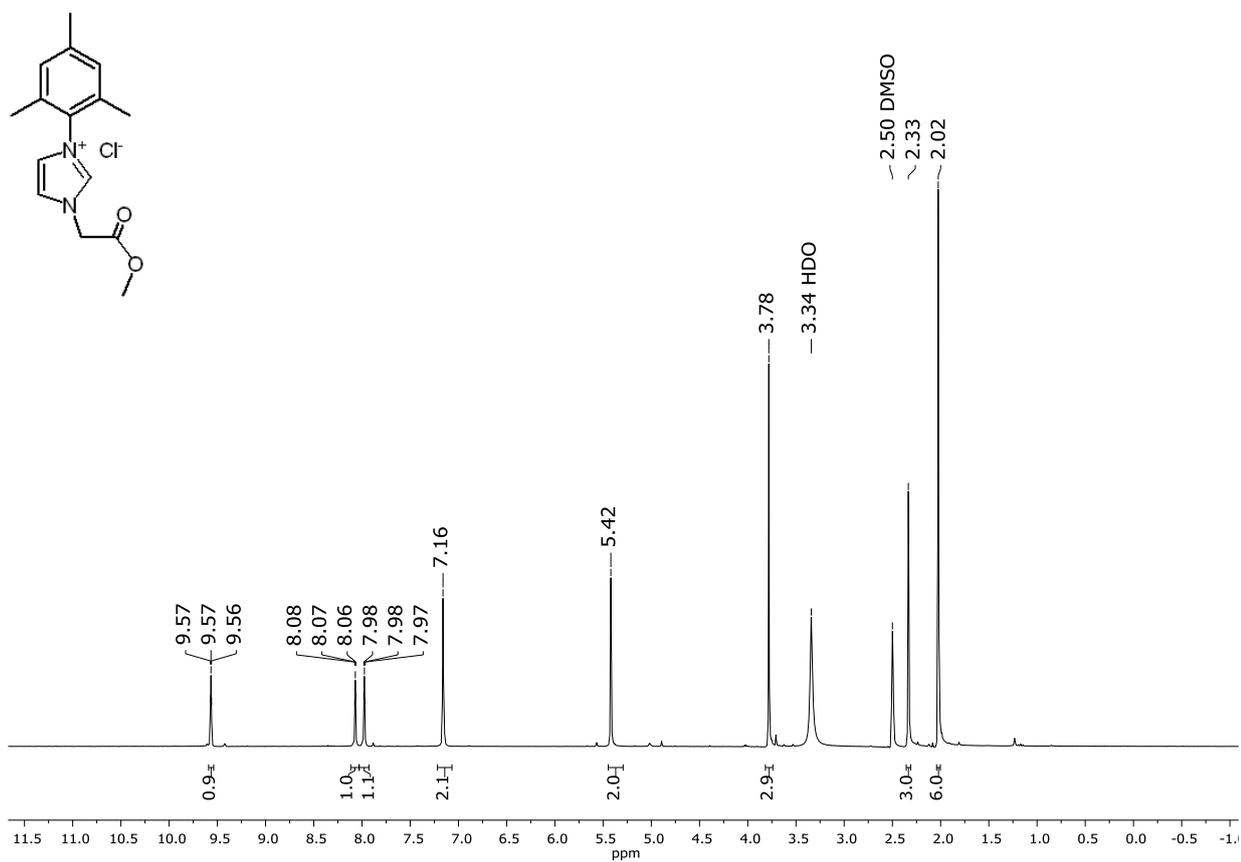


**Figure S10.** HRMS spectrum of compound **2c**.

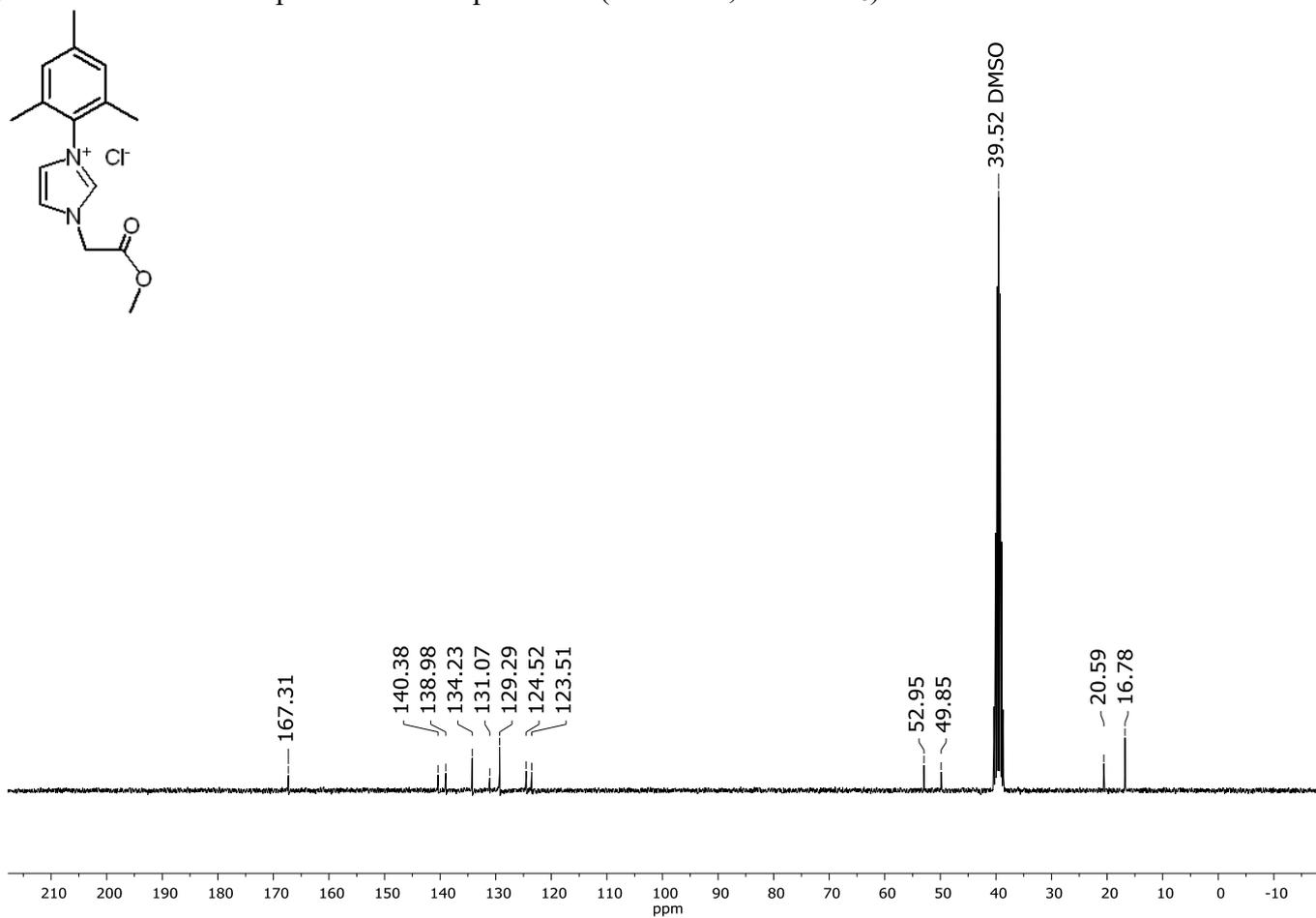


**Figure S11.** HRMS spectrum of compound **2d**.

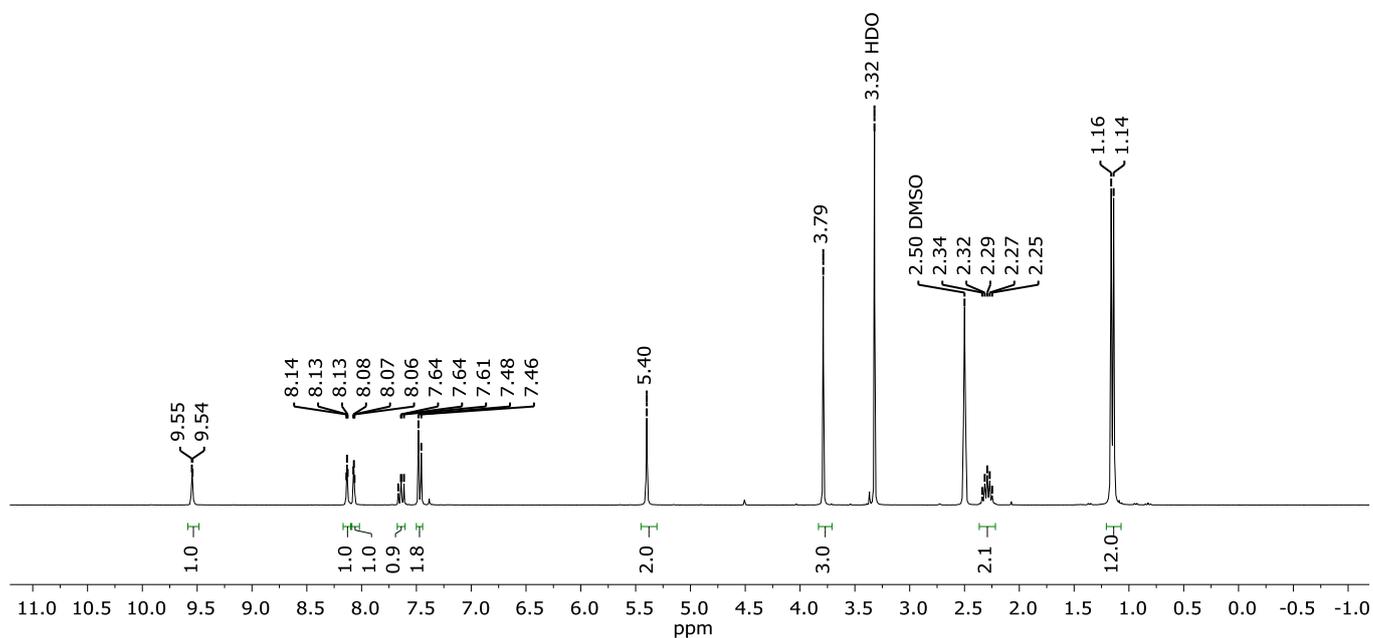
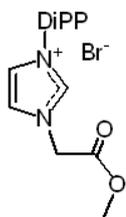
# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra



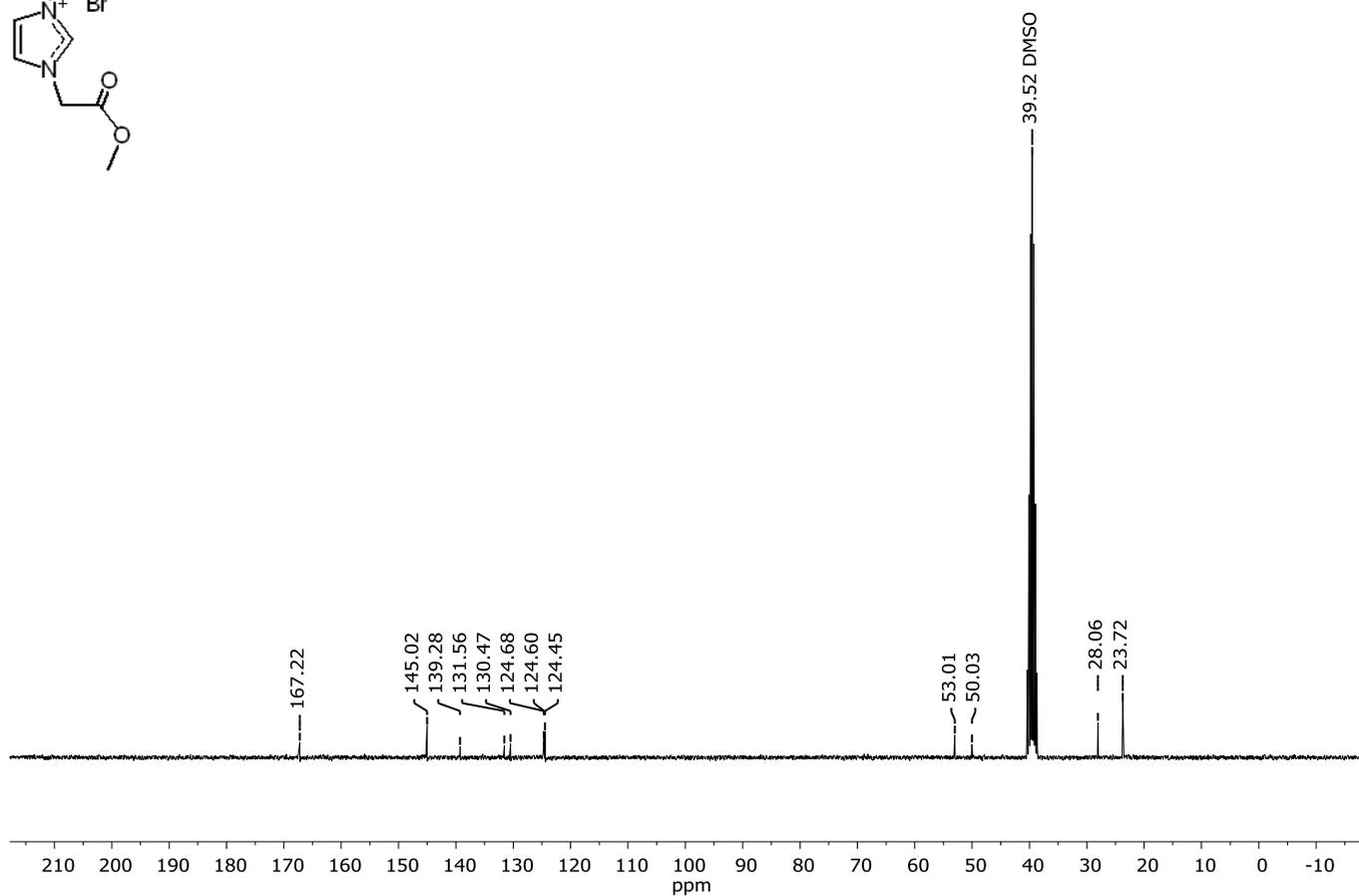
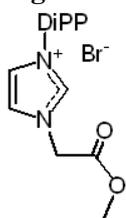
**Figure S12.**  $^1\text{H}$  NMR spectrum of compound **9b** (300 MHz,  $\text{DMSO-}d_6$ ).



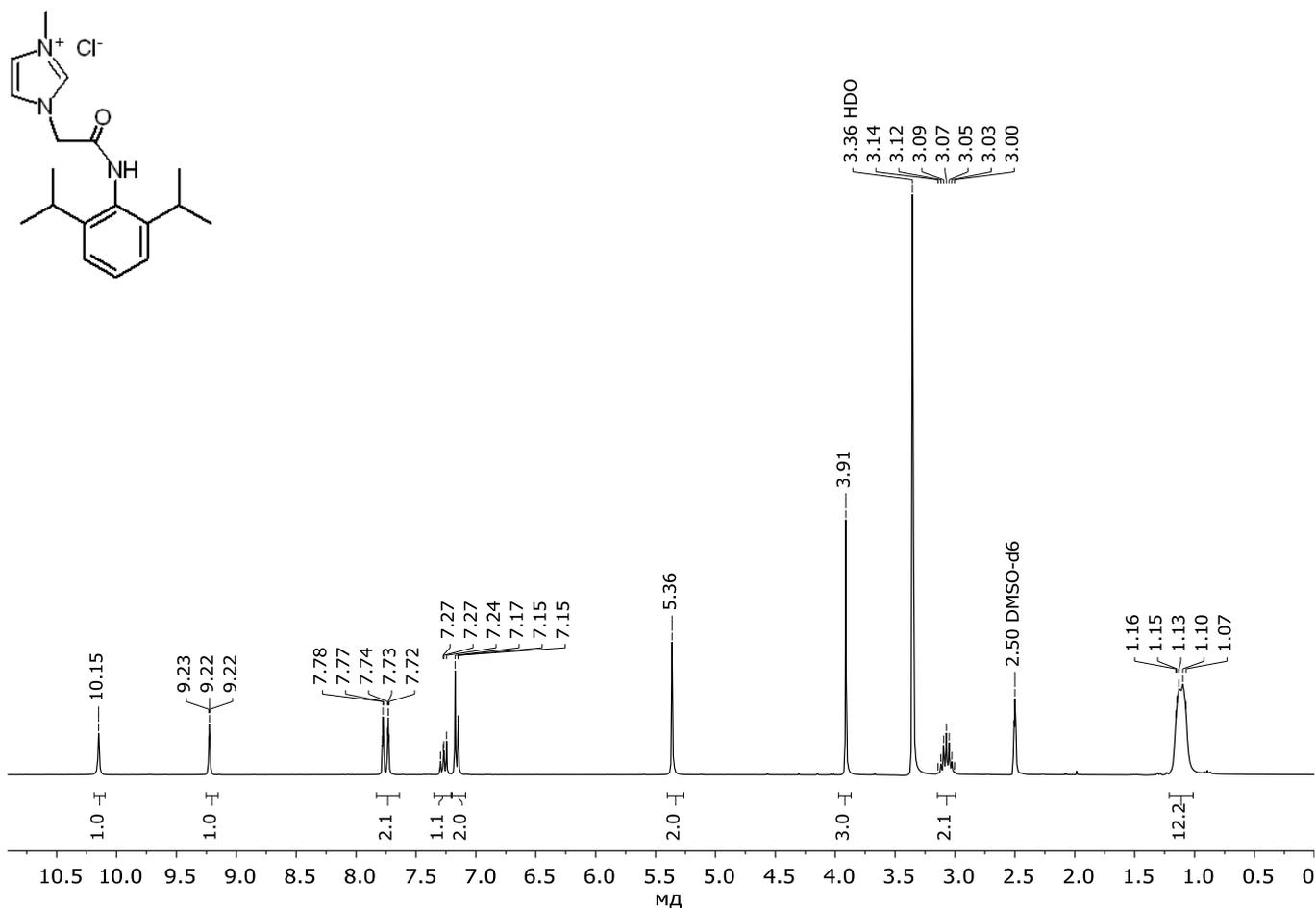
**Figure S13.**  $^{13}\text{C}$  NMR spectrum of compound **9b** (75 MHz,  $\text{DMSO-}d_6$ ).



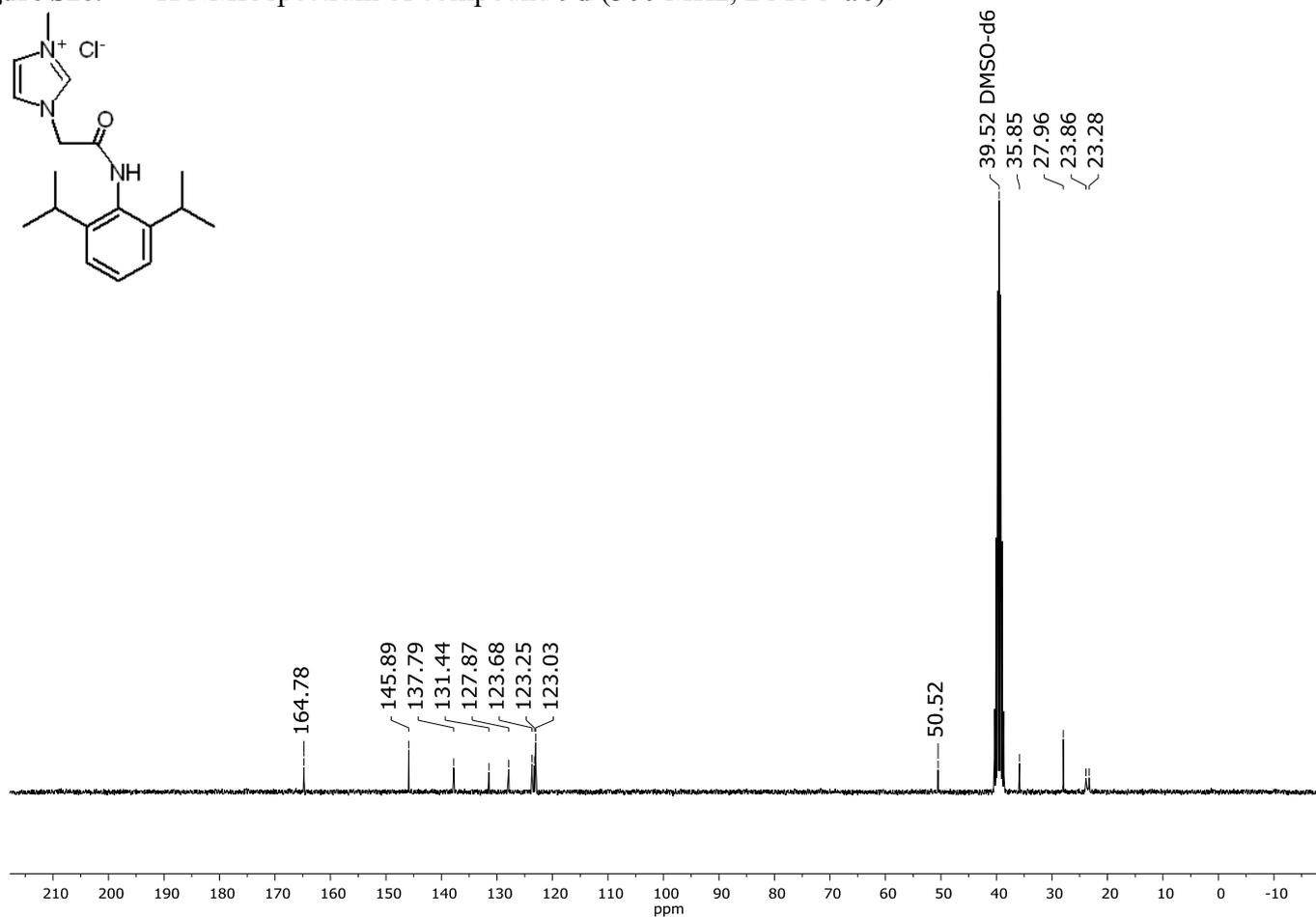
**Figure S14.**  $^1\text{H}$  NMR spectrum of compound **9c** (300 MHz,  $\text{DMSO-}d_6$ ).



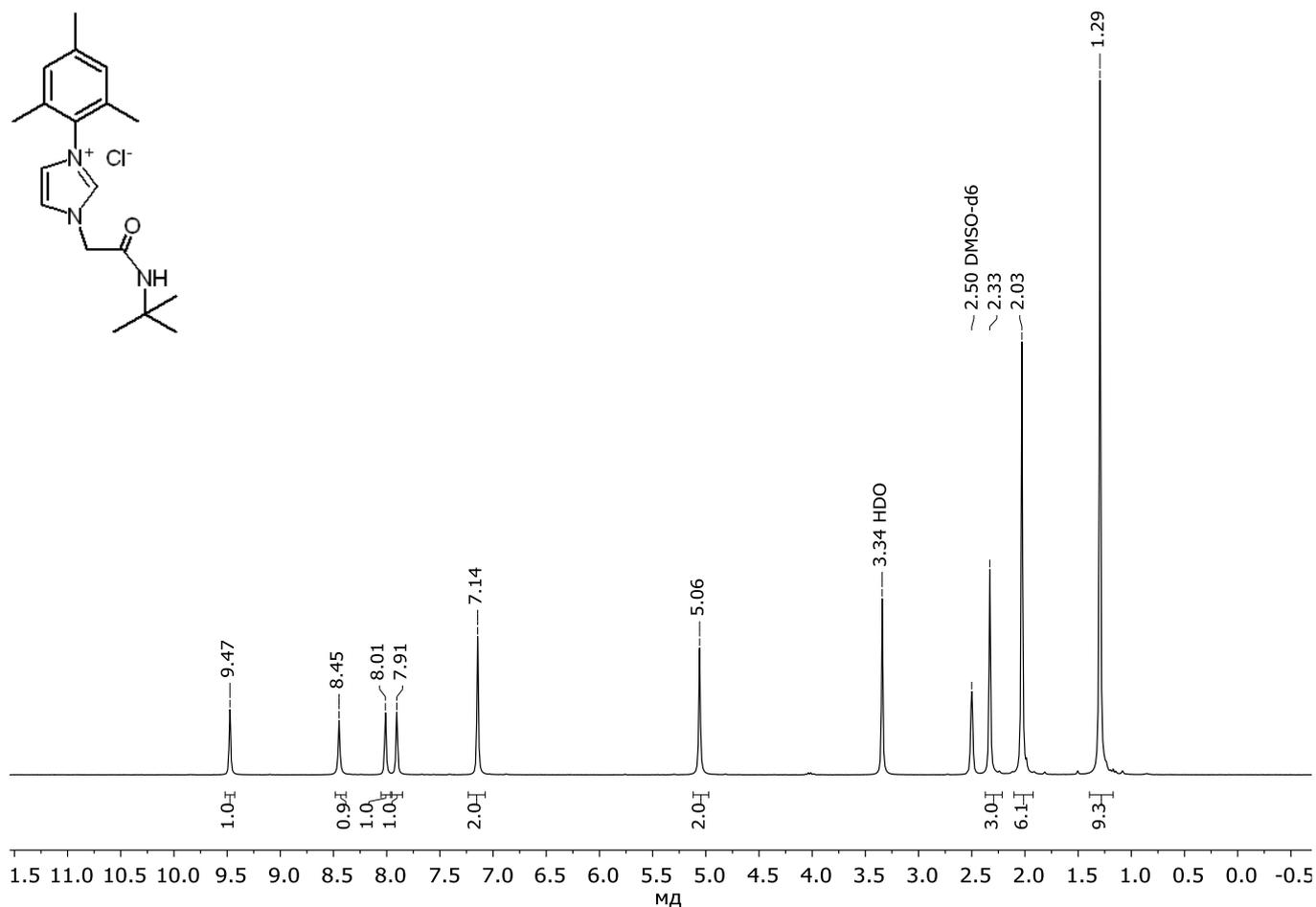
**Figure S15.**  $^{13}\text{C}$  NMR spectrum of compound **9c** (75 MHz,  $\text{DMSO-}d_6$ ).



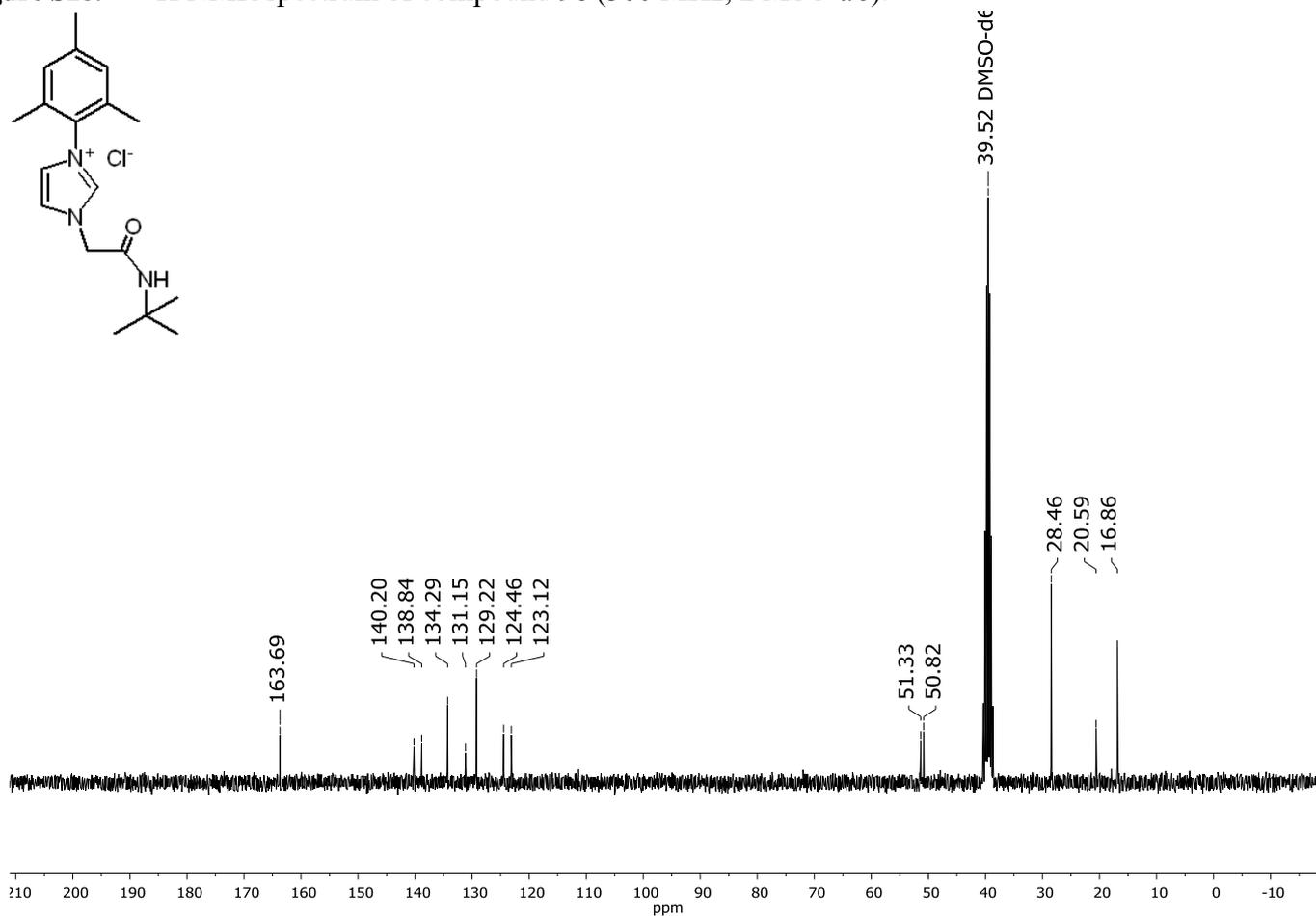
**Figure S16.** <sup>1</sup>H NMR spectrum of compound **9d** (300 MHz, DMSO-*d*<sub>6</sub>).



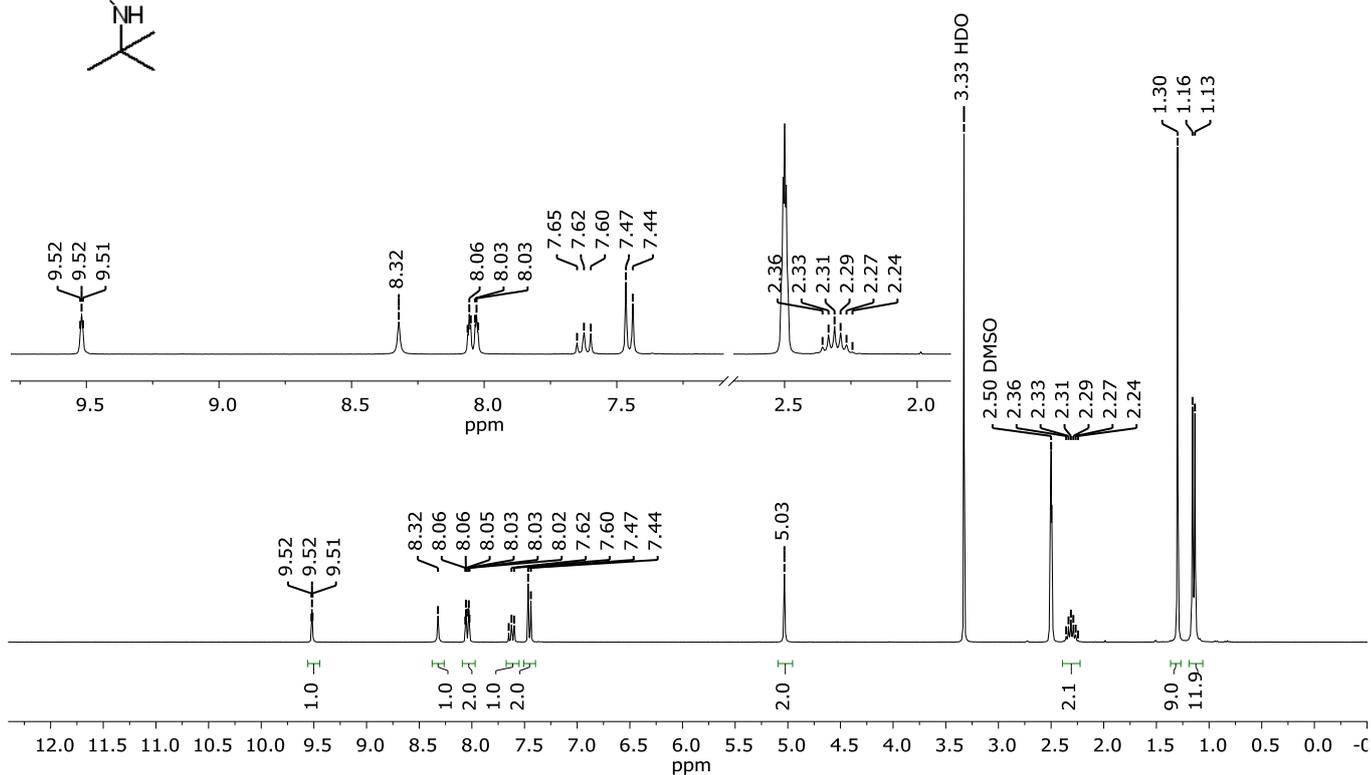
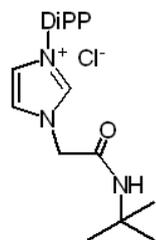
**Figure S17.** <sup>13</sup>C NMR spectrum of compound **9d** (75 MHz, DMSO-*d*<sub>6</sub>).



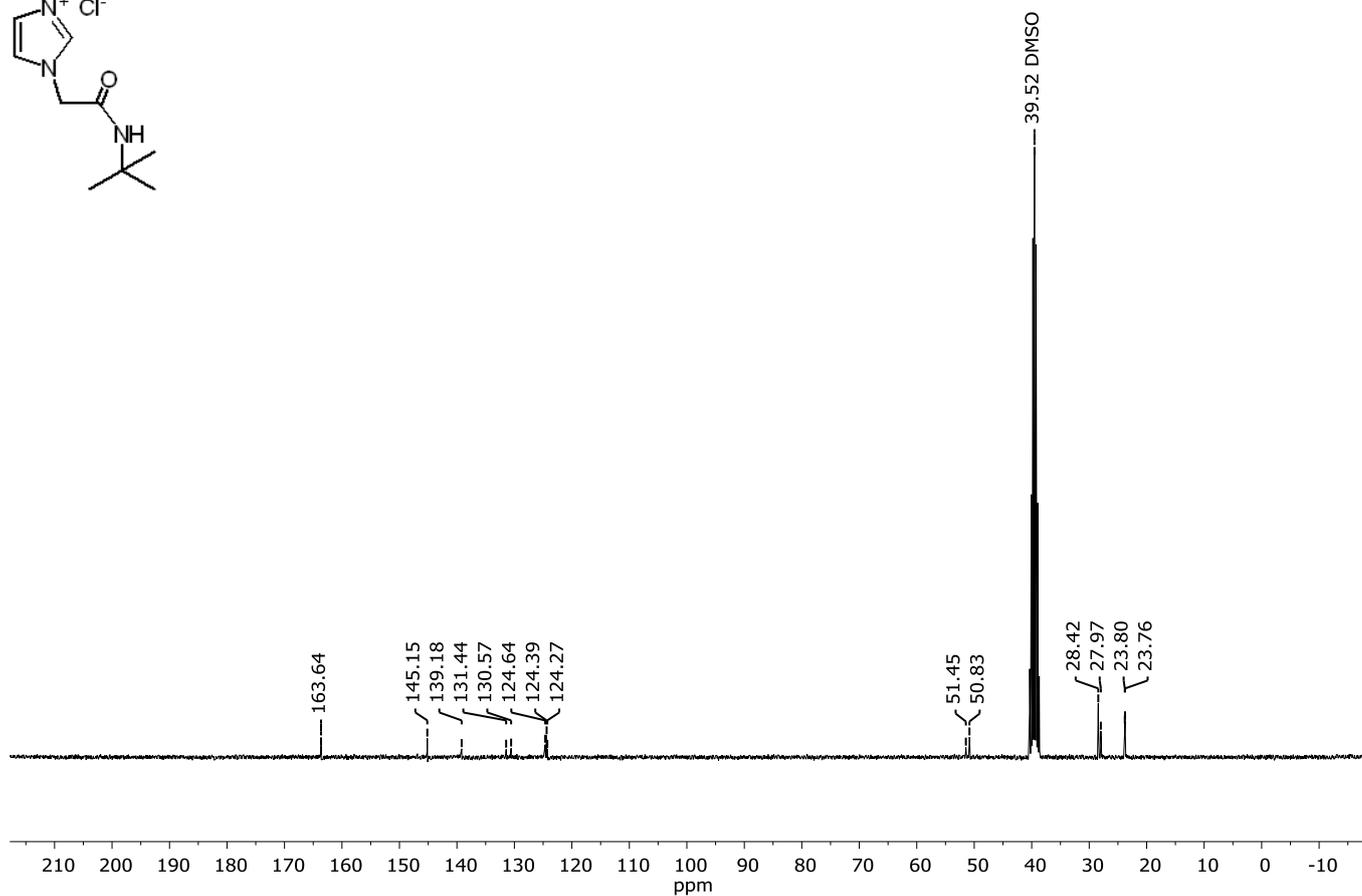
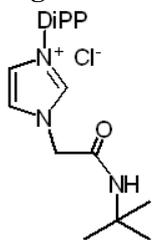
**Figure S18.** <sup>1</sup>H NMR spectrum of compound **9e** (300 MHz, DMSO-d<sub>6</sub>).



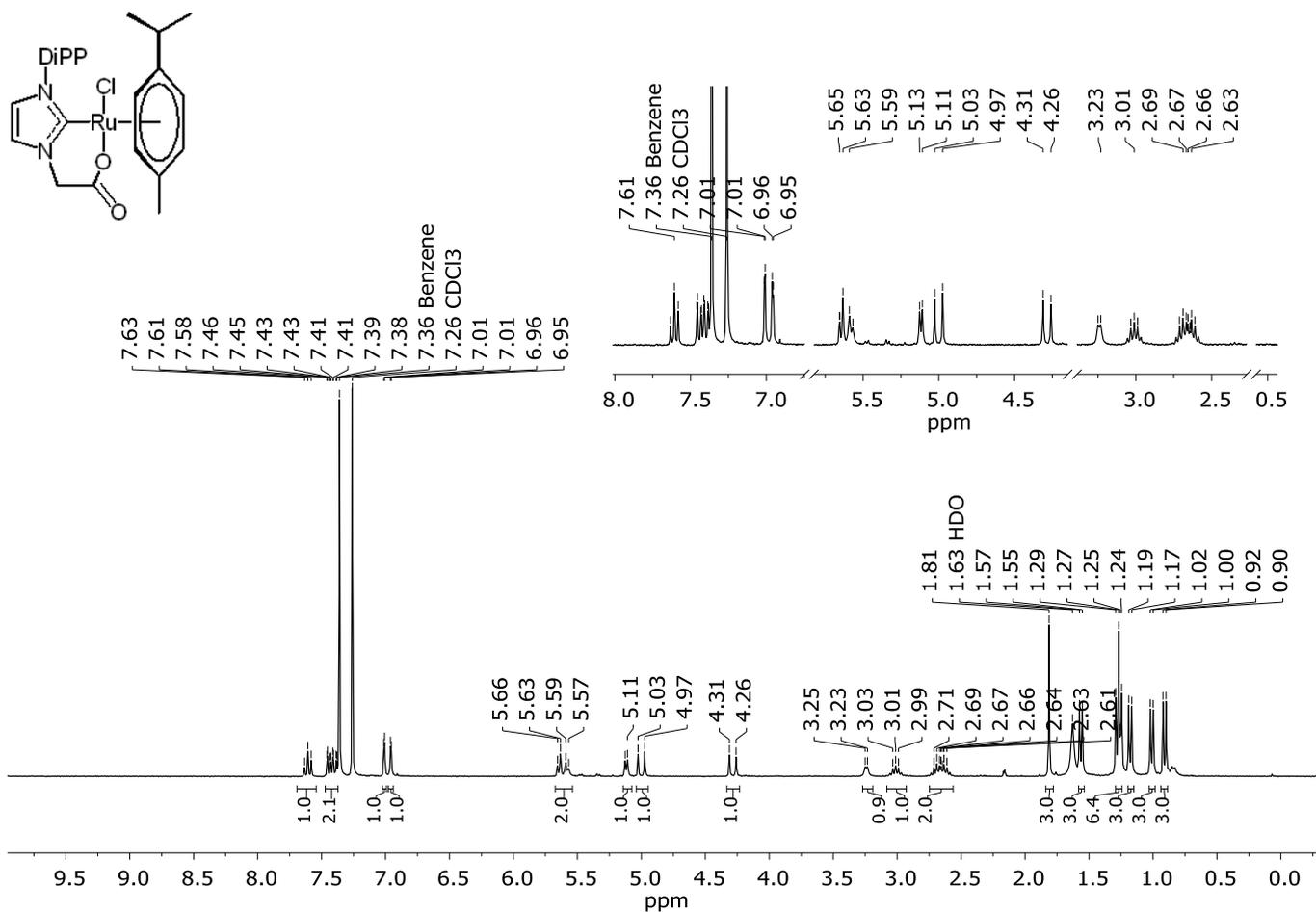
**Figure S19.** <sup>13</sup>C NMR spectrum of compound **9e** (75 MHz, DMSO-d<sub>6</sub>).



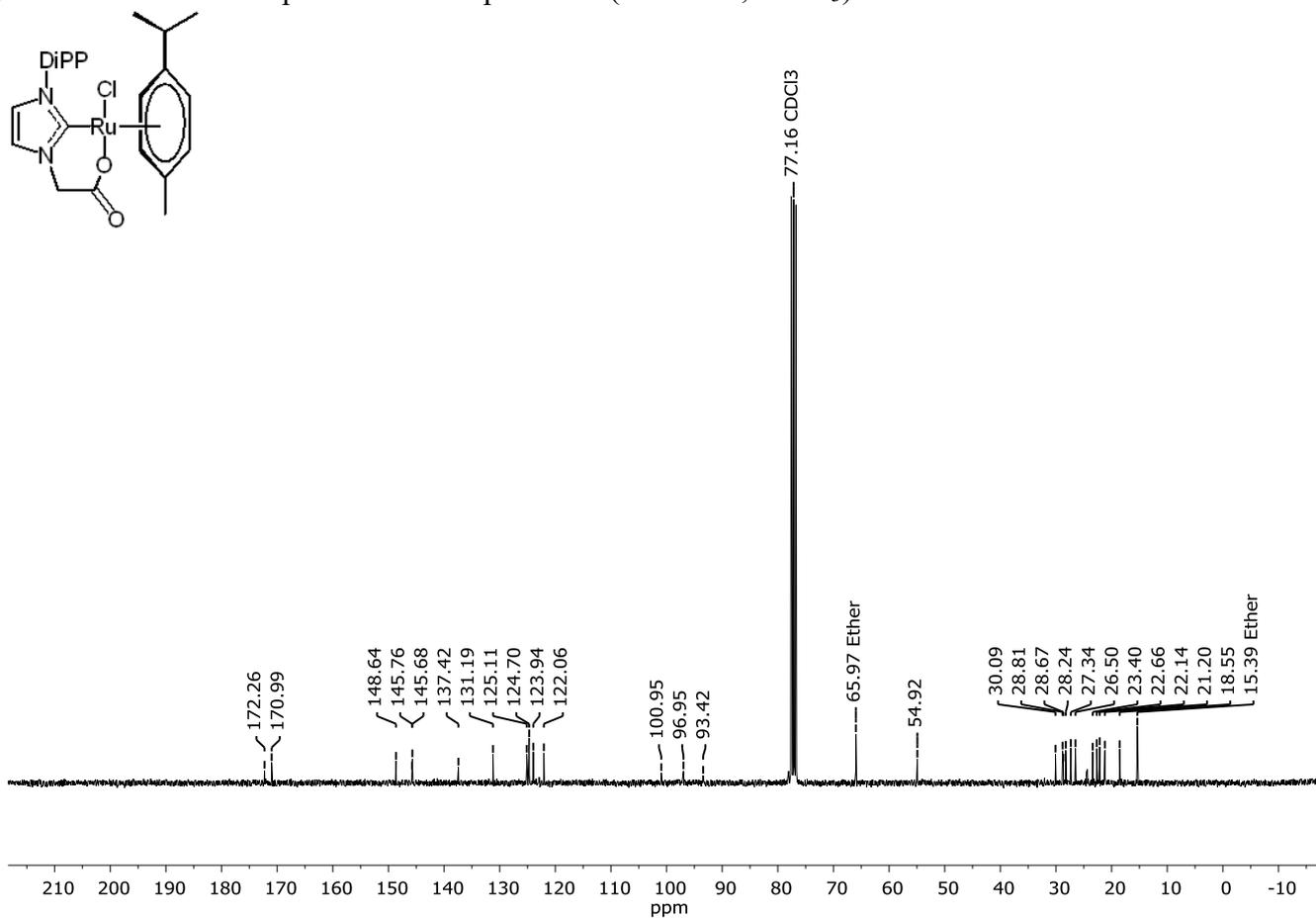
**Figure S20.** <sup>1</sup>H NMR spectrum of compound **9g** (300 MHz, DMSO-*d*<sub>6</sub>).



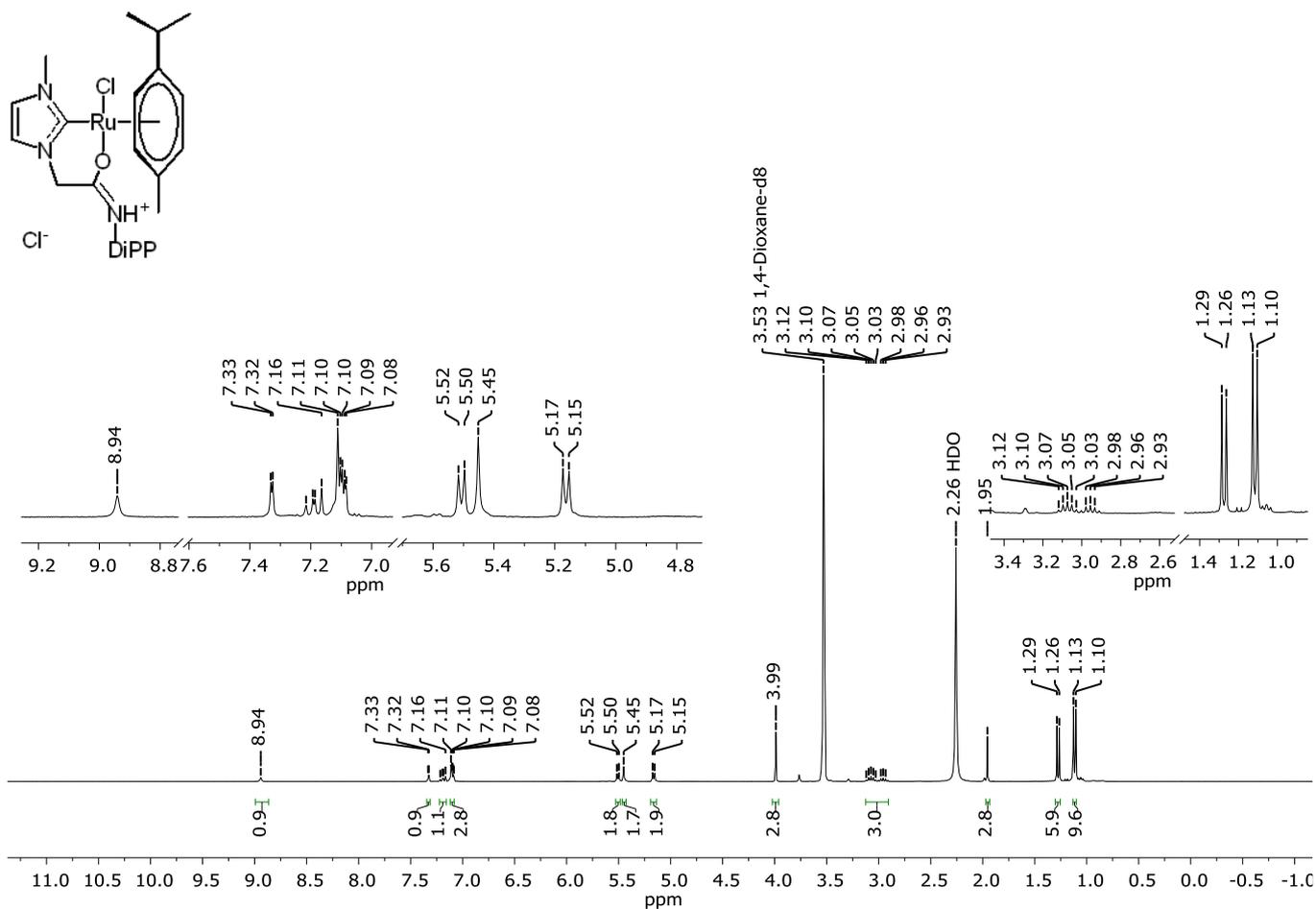
**Figure S21.** <sup>13</sup>C NMR spectrum of compound **9g** (75 MHz, DMSO-*d*<sub>6</sub>).



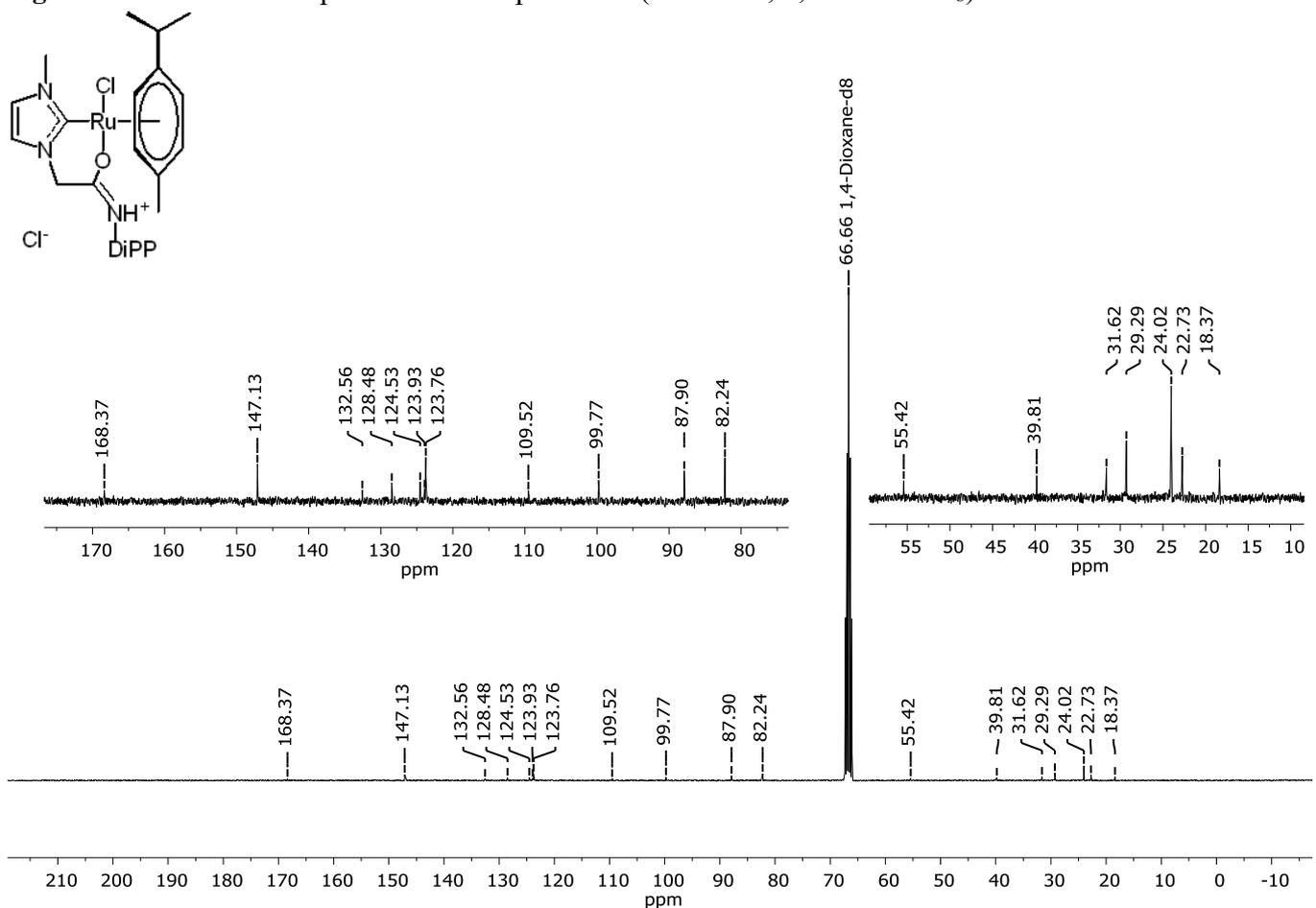
**Figure S22.**  $^1\text{H}$  NMR spectrum of compound **1c** (300 MHz,  $\text{CDCl}_3$ ).



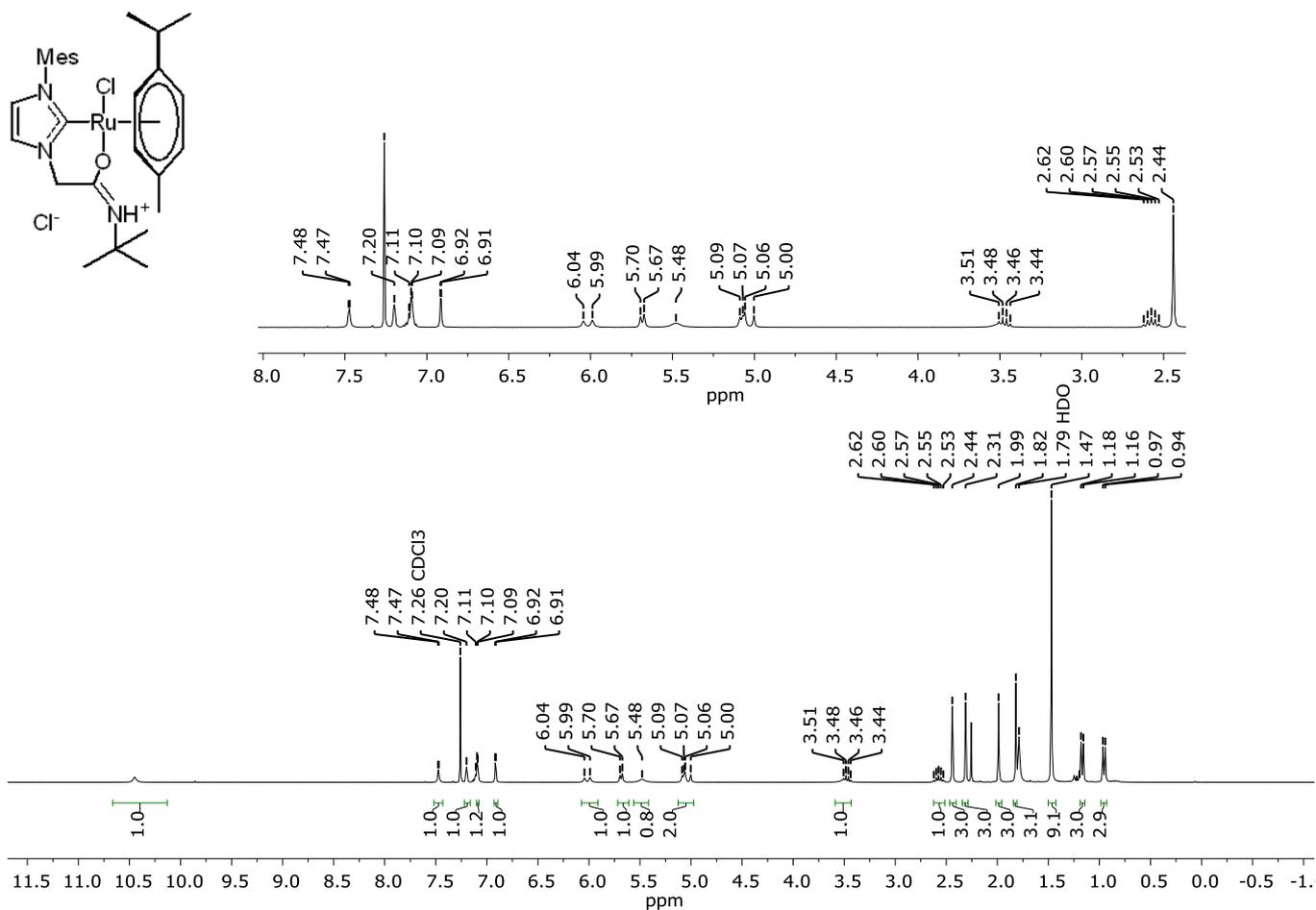
**Figure S23.**  $^{13}\text{C}$  NMR spectrum of compound **1c** (75 MHz,  $\text{CDCl}_3$ ).



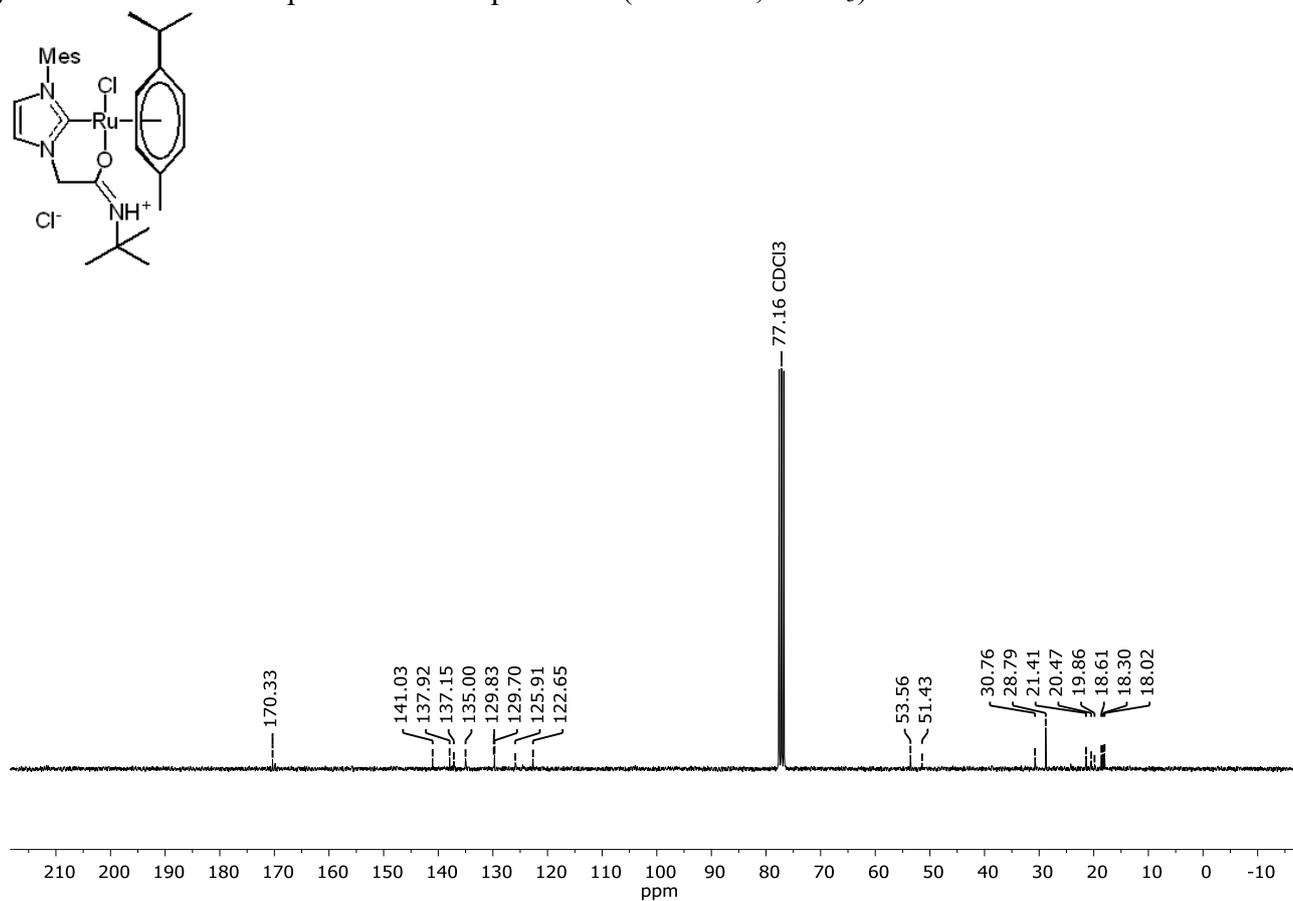
**Figure S24.**  $^1\text{H}$  NMR spectrum of compound **2a** (300 MHz,  $1,4\text{-dioxane-}d_8$ ).



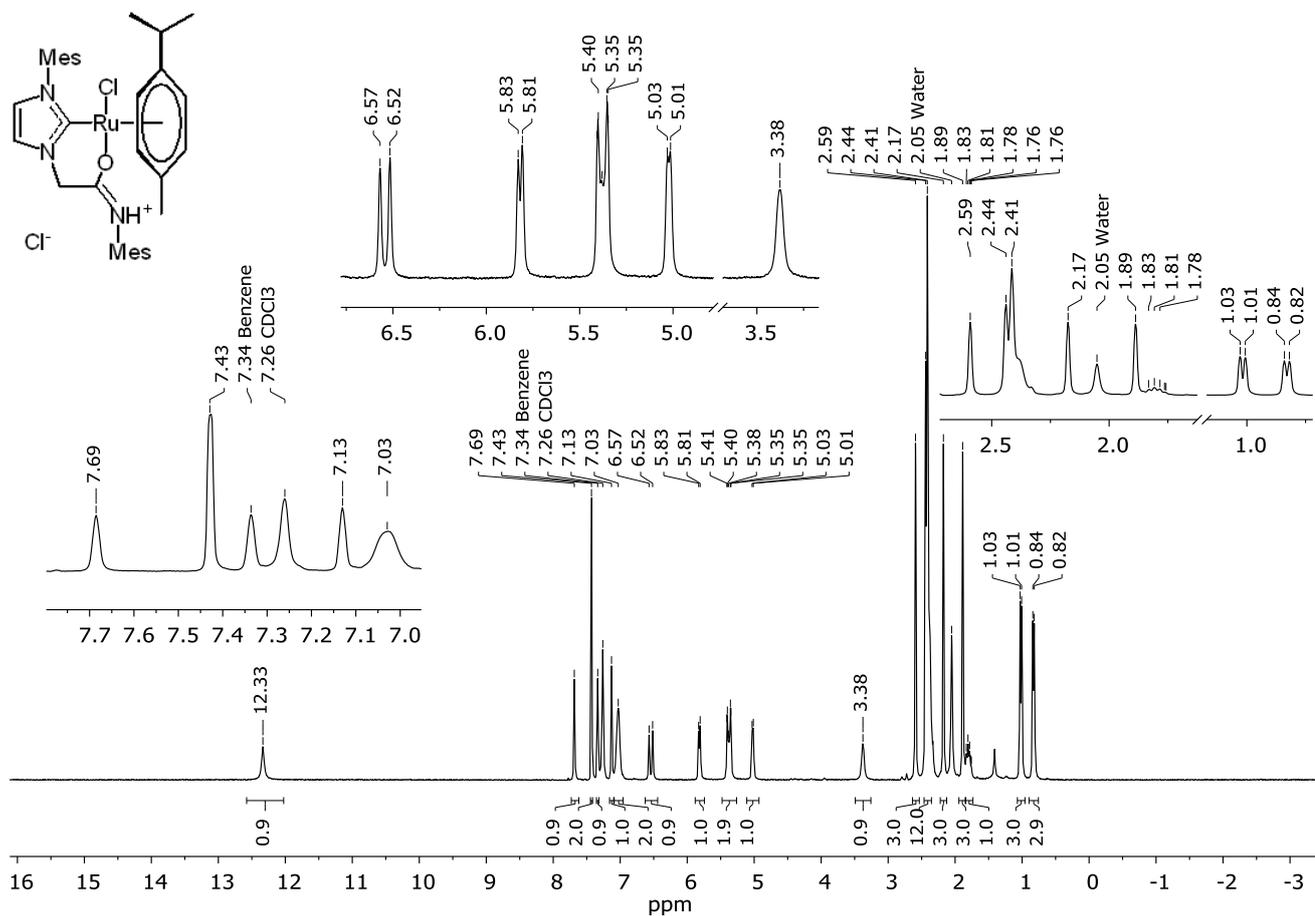
**Figure S25.**  $^{13}\text{C}$  NMR spectrum of compound **2a** (300 MHz,  $1,4\text{-dioxane-}d_8$ ).



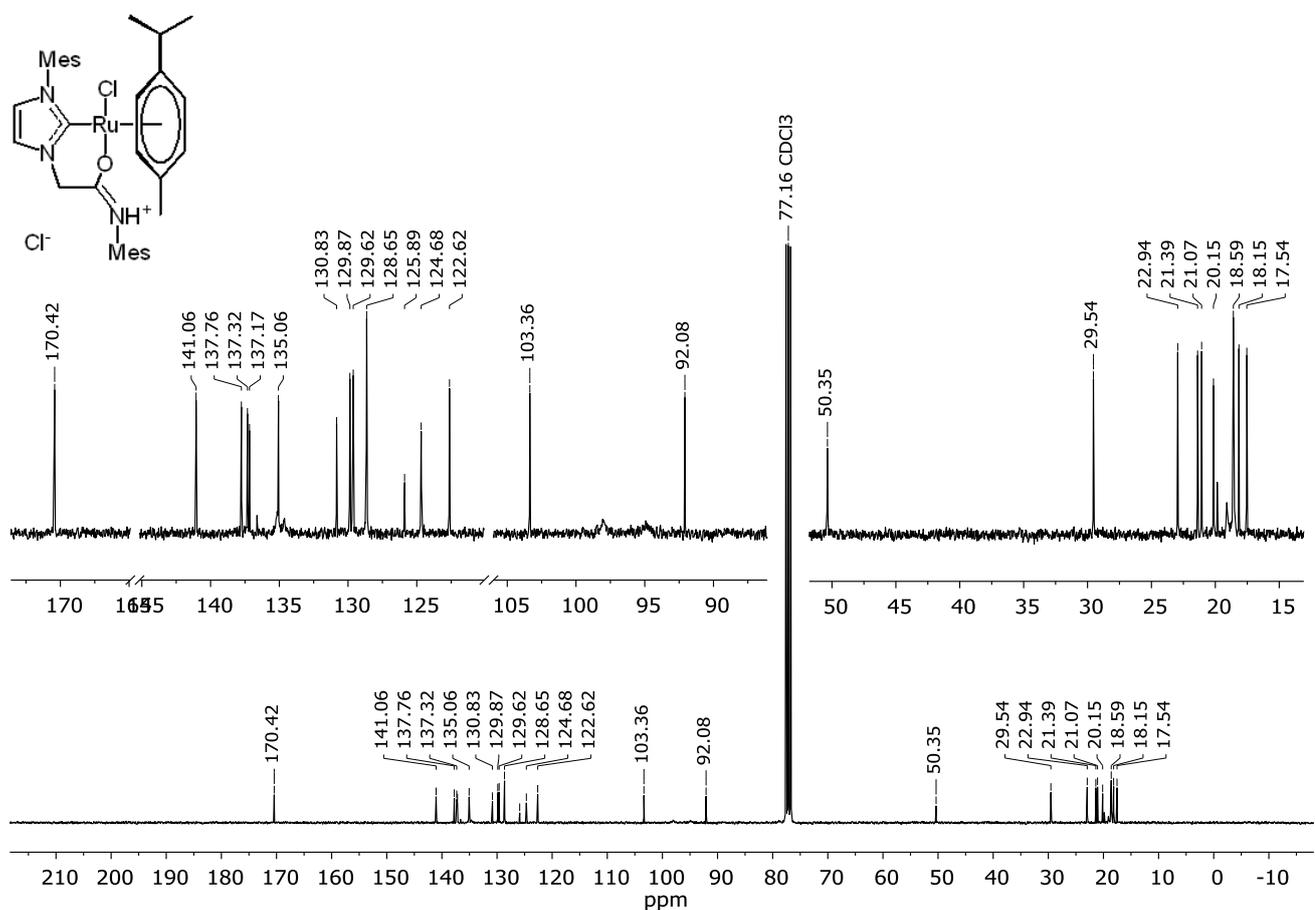
**Figure S26.**  $^1\text{H}$  NMR spectrum of compound **2b** (300 MHz,  $\text{CDCl}_3$ ).



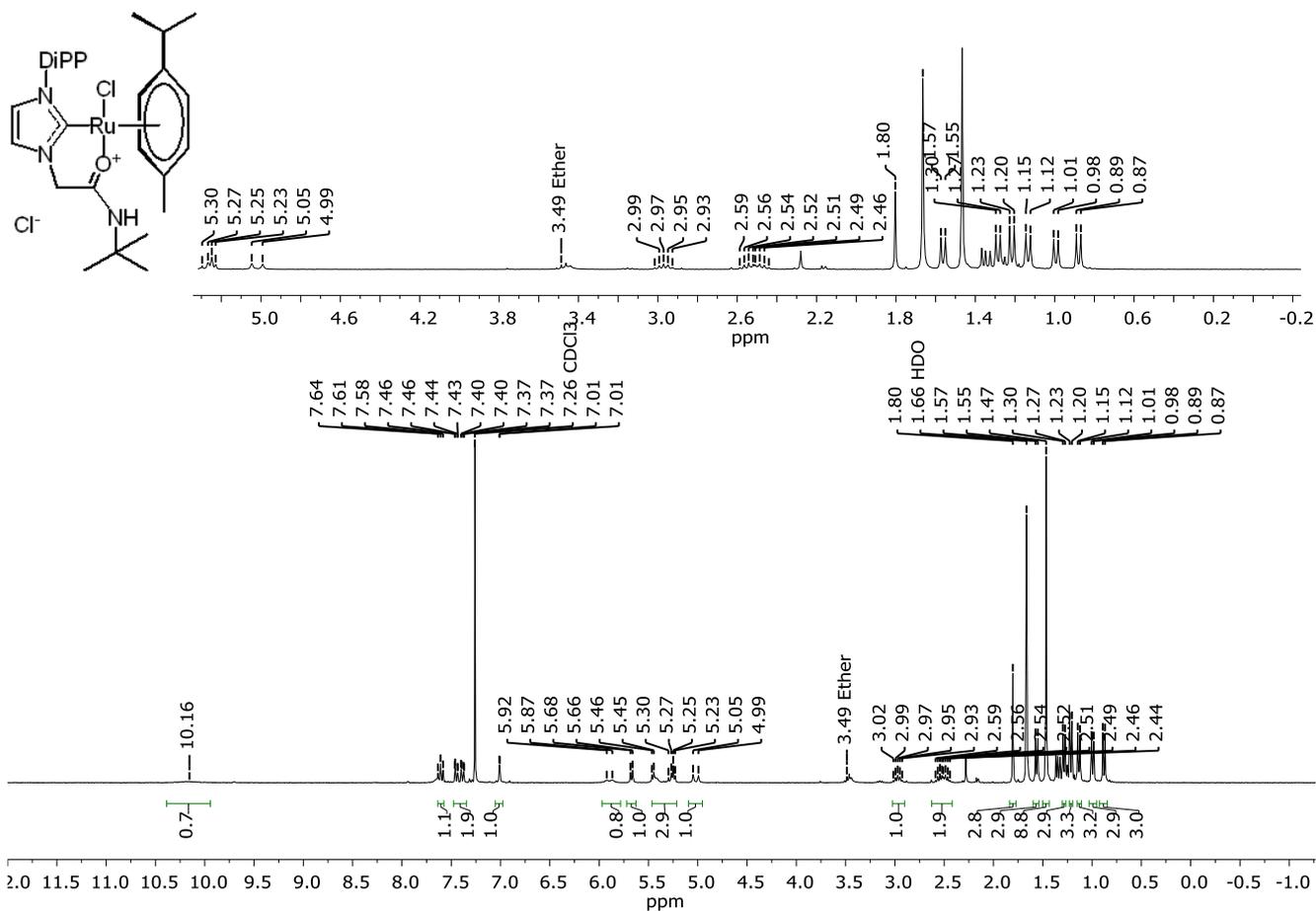
**Figure S27.**  $^{13}\text{C}$  NMR spectrum of compound **2b** (75 MHz,  $\text{CDCl}_3$ ).



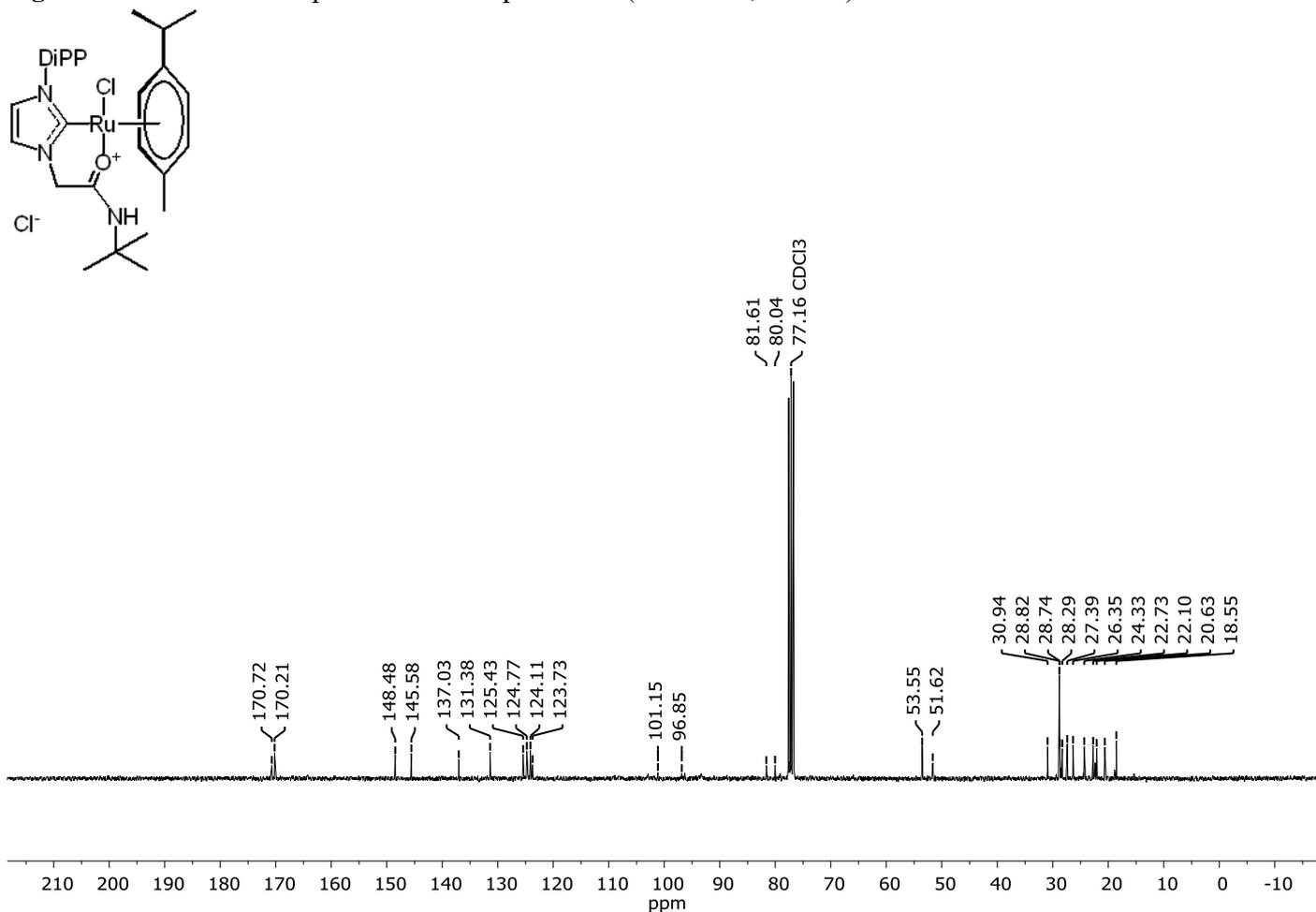
**Figure S28.** <sup>1</sup>H NMR spectrum of compound 2c (300 MHz, CDCl<sub>3</sub>).



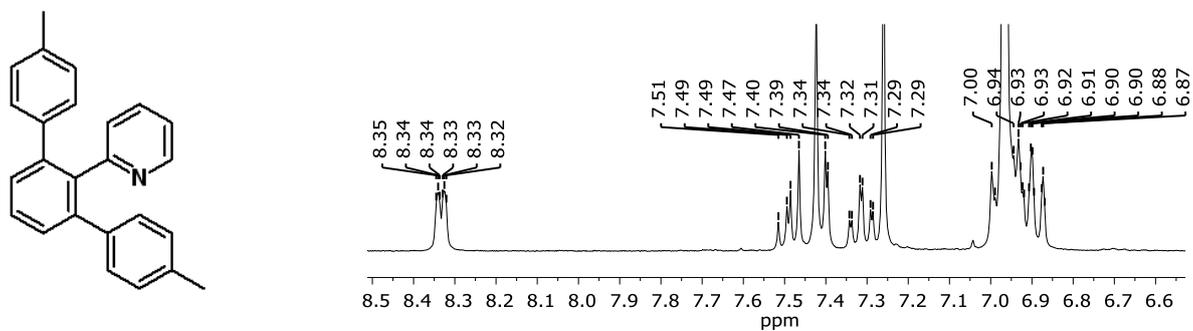
**Figure S29.** <sup>13</sup>C NMR spectrum of compound 2c (75 MHz, CDCl<sub>3</sub>).



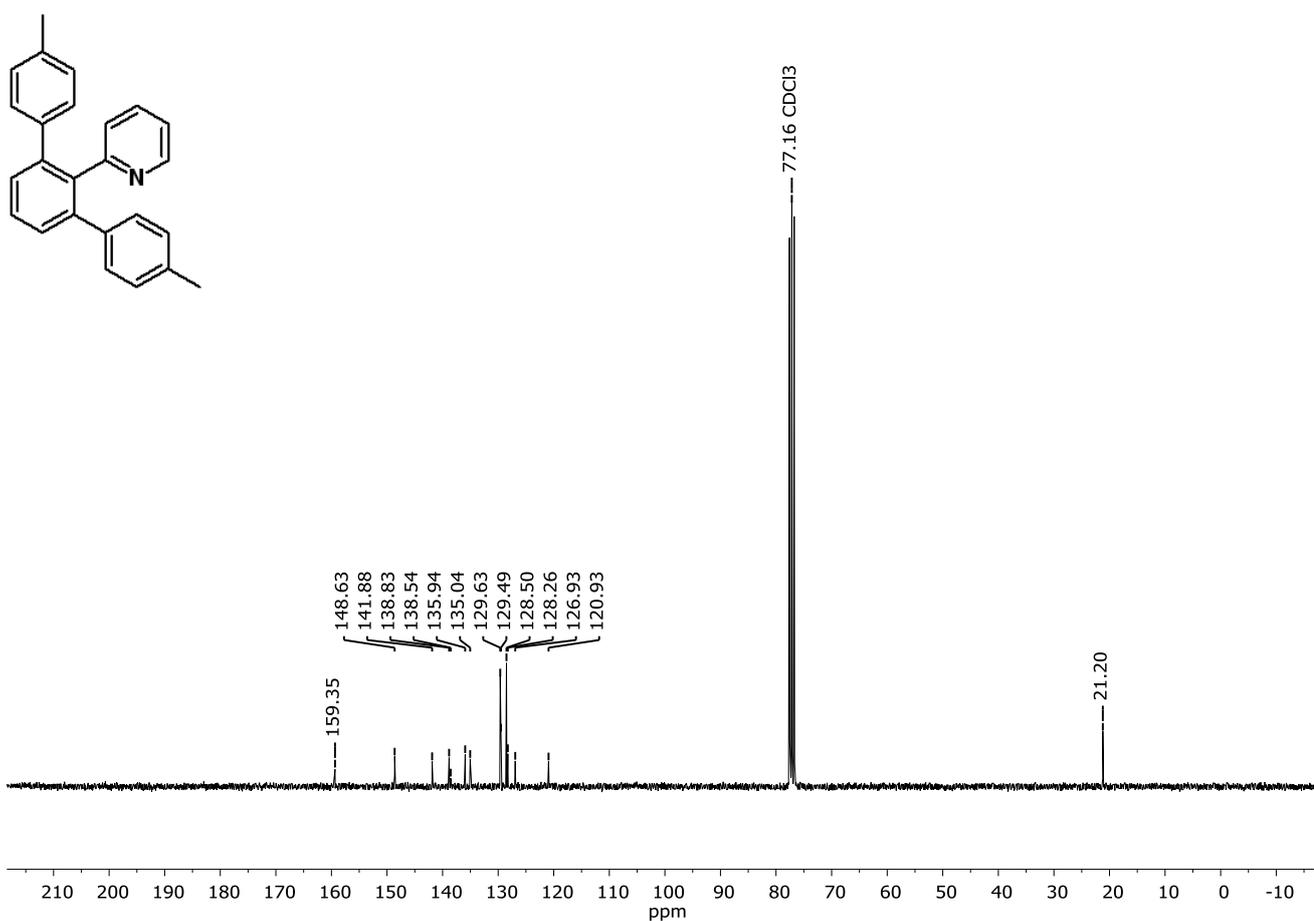
**Figure S30.**  $^1\text{H}$  NMR spectrum of compound **2d** (300 MHz,  $\text{CDCl}_3$ ).



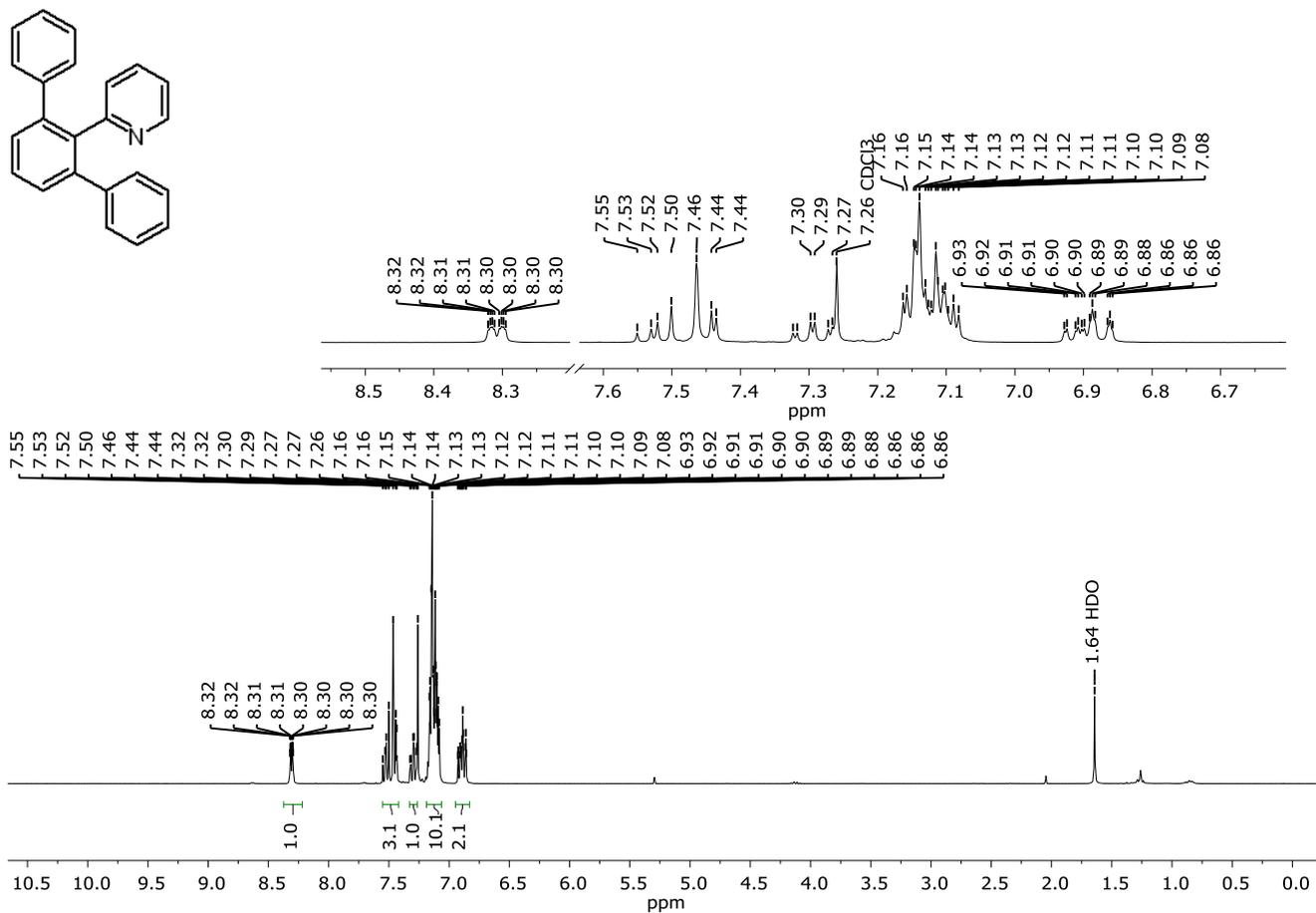
**Figure S31.**  $^{13}\text{C}$  NMR spectrum of compound **2d** (75 MHz,  $\text{CDCl}_3$ ).



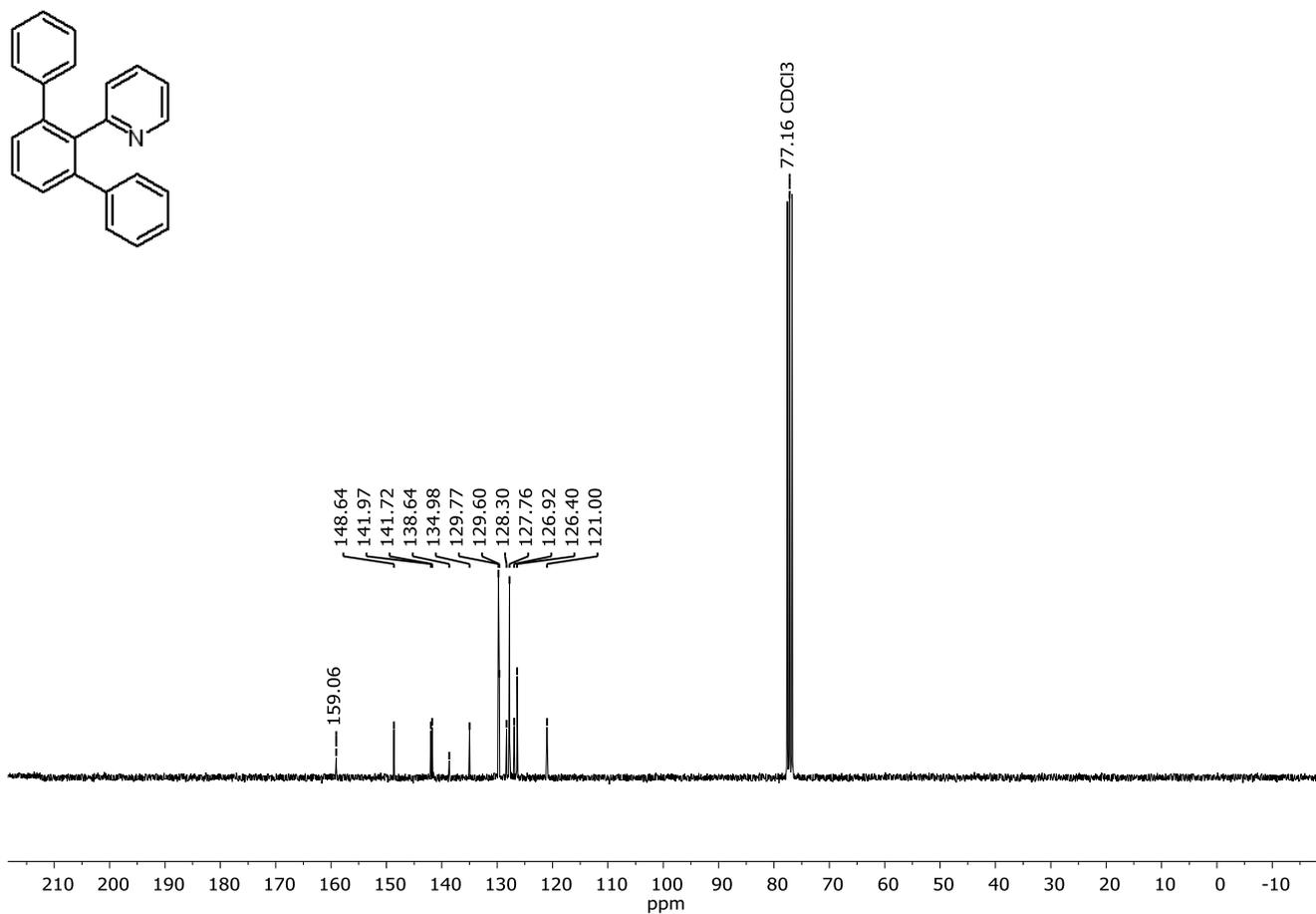
**Figure S32.**  $^1\text{H}$  NMR spectrum of compound **5a** (300 MHz,  $\text{CDCl}_3$ ).



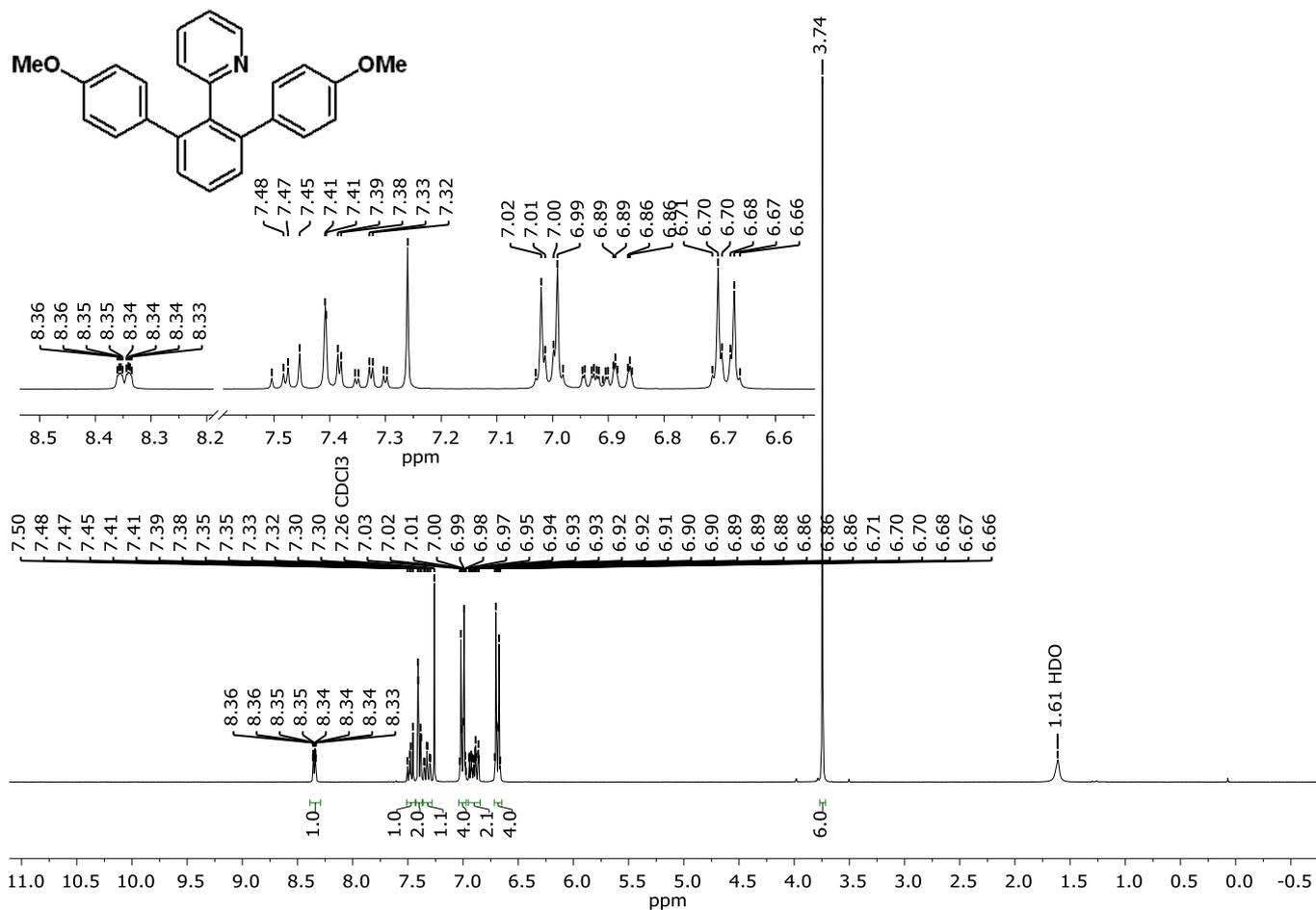
**Figure S33.**  $^{13}\text{C}$  NMR spectrum of compound **5a** (75 MHz,  $\text{CDCl}_3$ ).



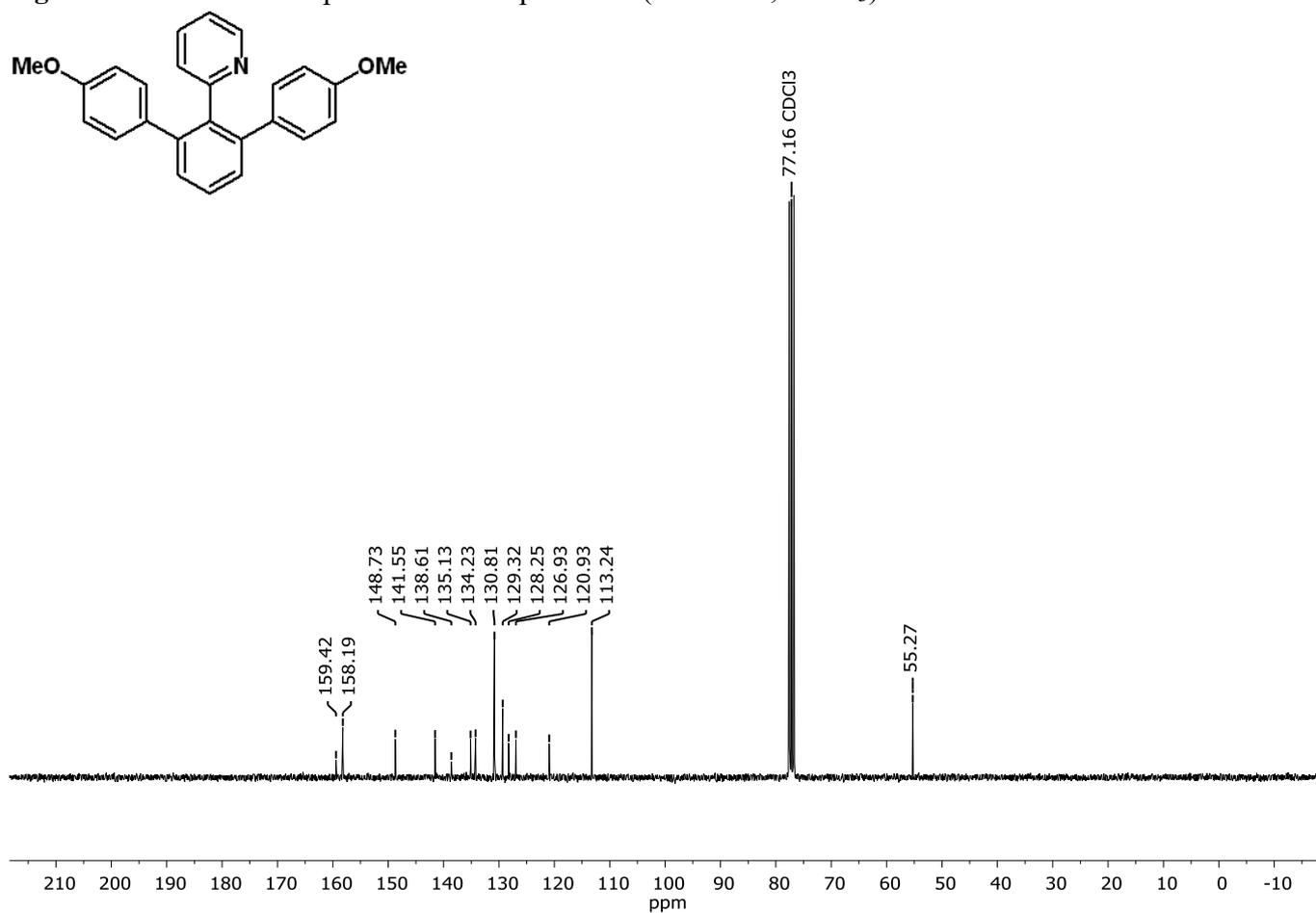
**Figure S34.** <sup>1</sup>H NMR spectrum of compound **5b** (300 MHz, CDCl<sub>3</sub>).



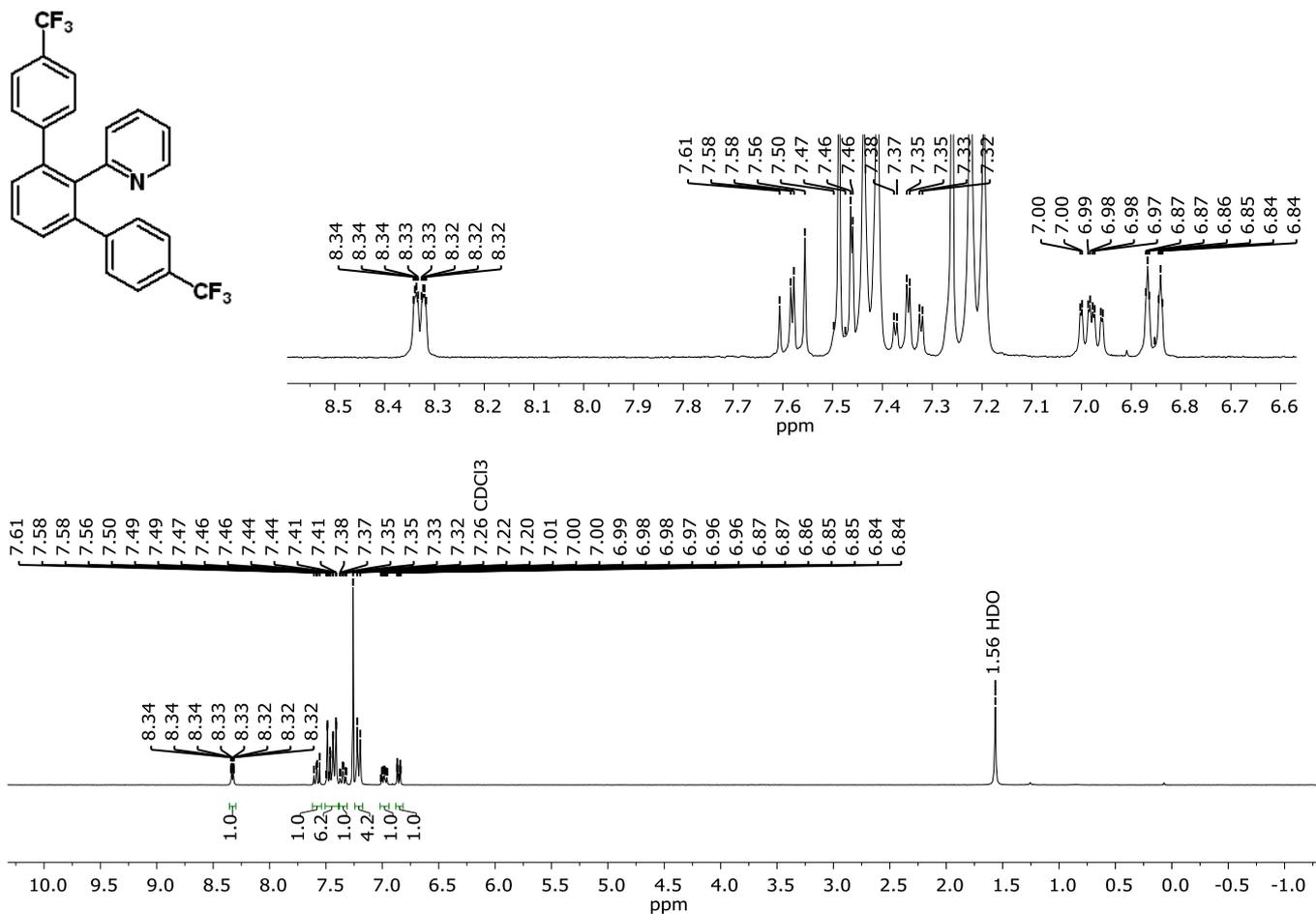
**Figure S35.** <sup>13</sup>C NMR spectrum of compound **5b** (75 MHz, CDCl<sub>3</sub>).



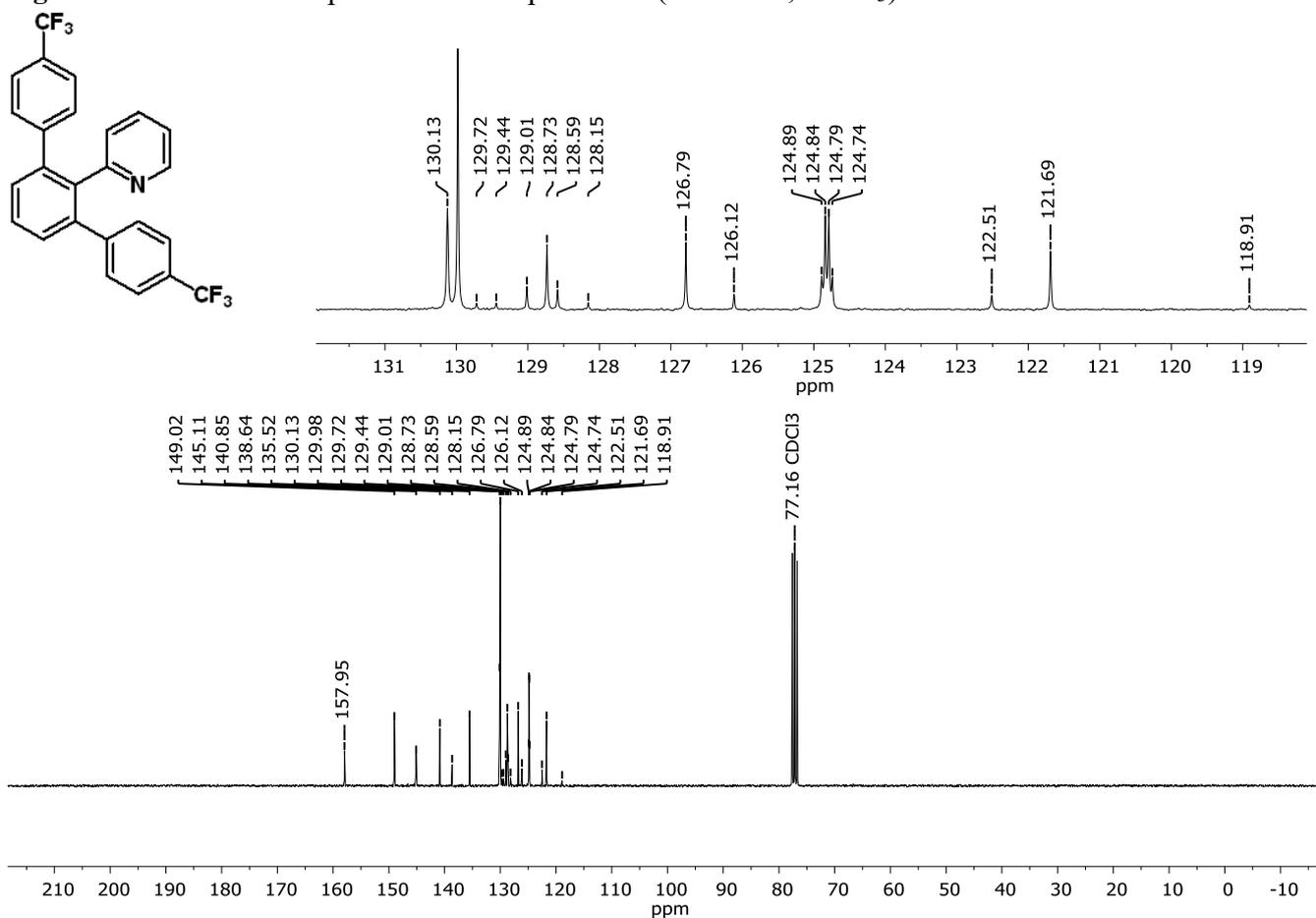
**Figure S36.** <sup>1</sup>H NMR spectrum of compound **5c** (300 MHz, CDCl<sub>3</sub>).



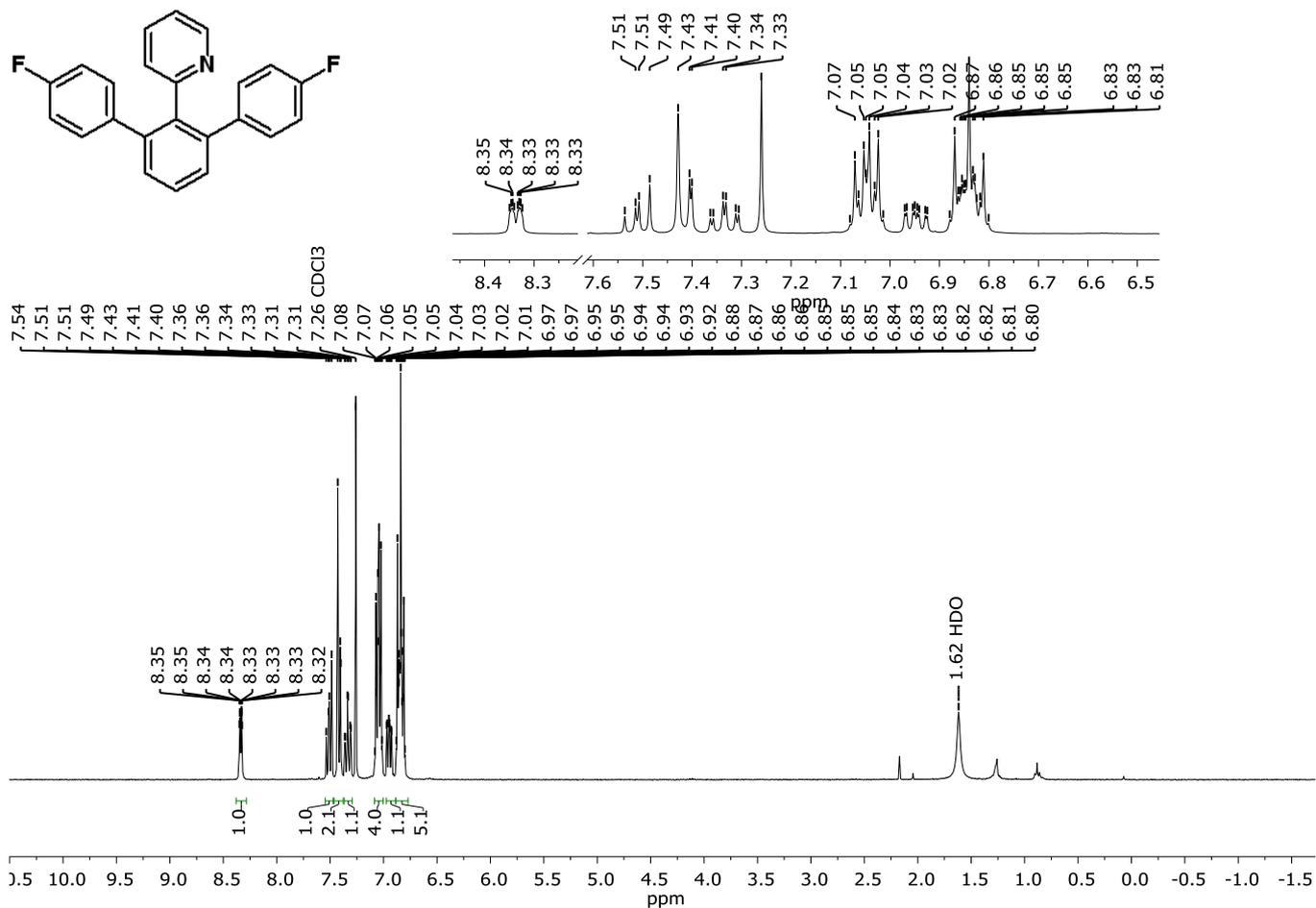
**Figure S37.** <sup>13</sup>C NMR spectrum of compound **5c** (75 MHz, CDCl<sub>3</sub>).



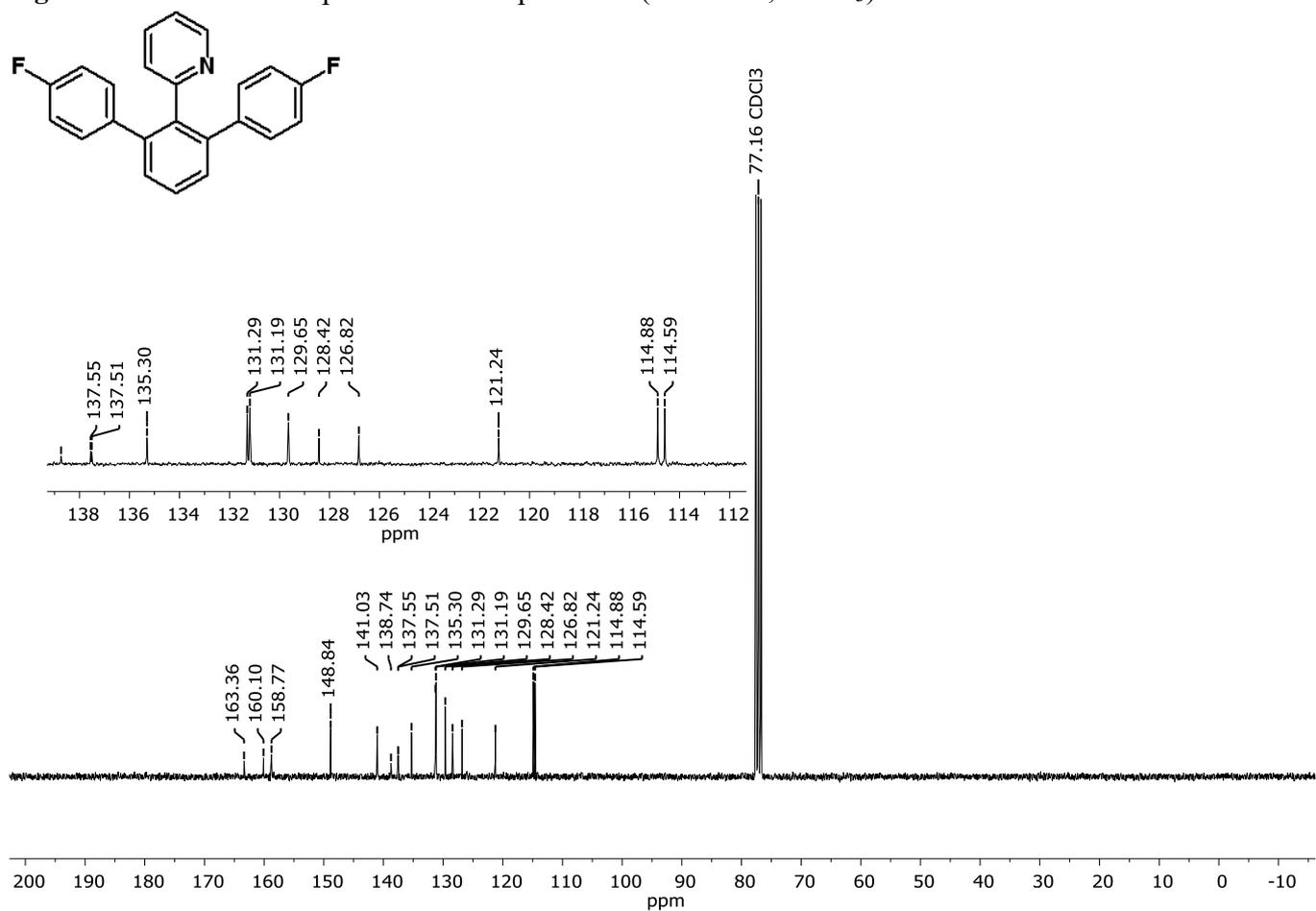
**Figure S38.** <sup>1</sup>H NMR spectrum of compound **5d** (300 MHz, CDCl<sub>3</sub>).



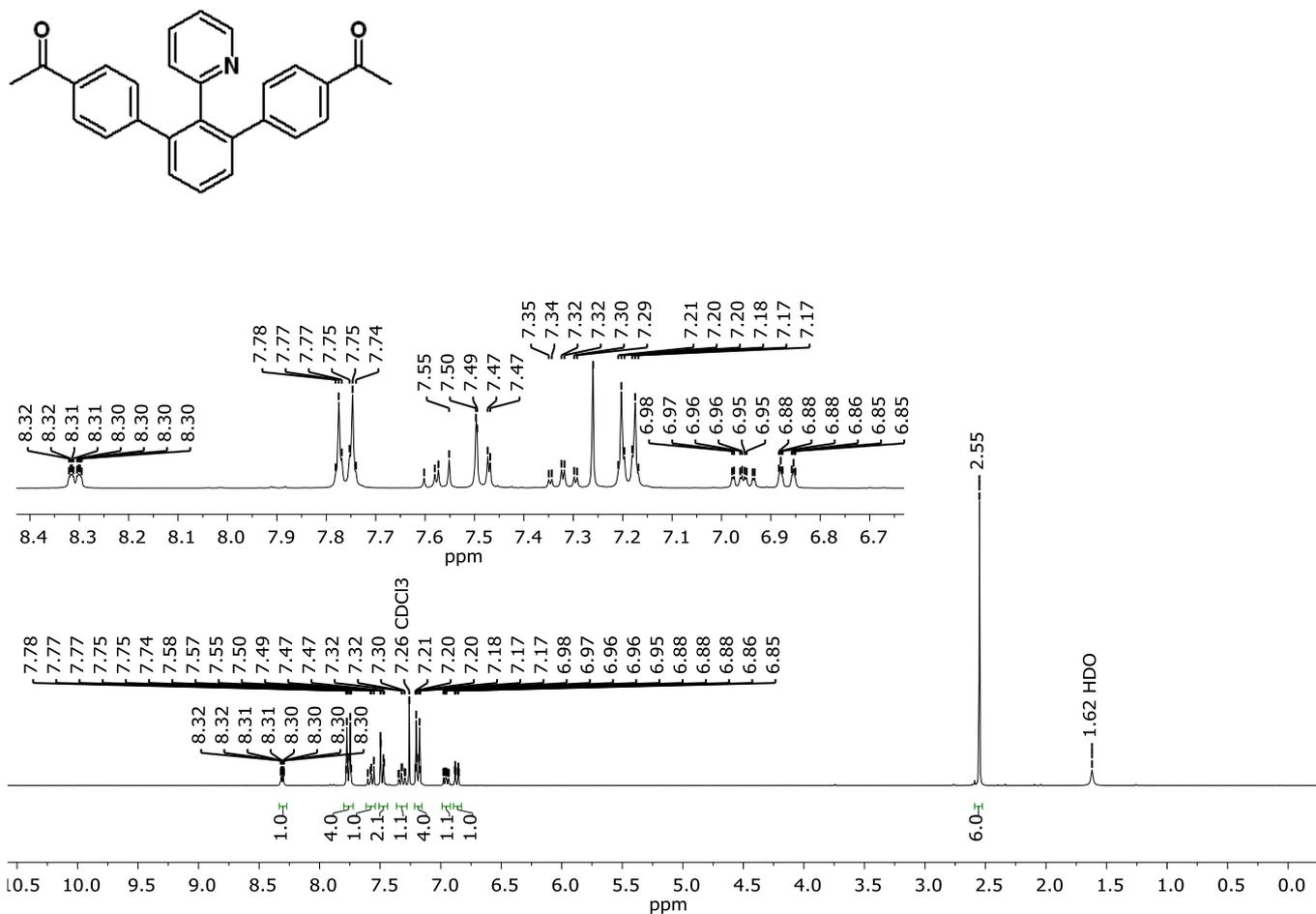
**Figure S39.** <sup>13</sup>C NMR spectrum of compound **5d** (75 MHz, CDCl<sub>3</sub>).



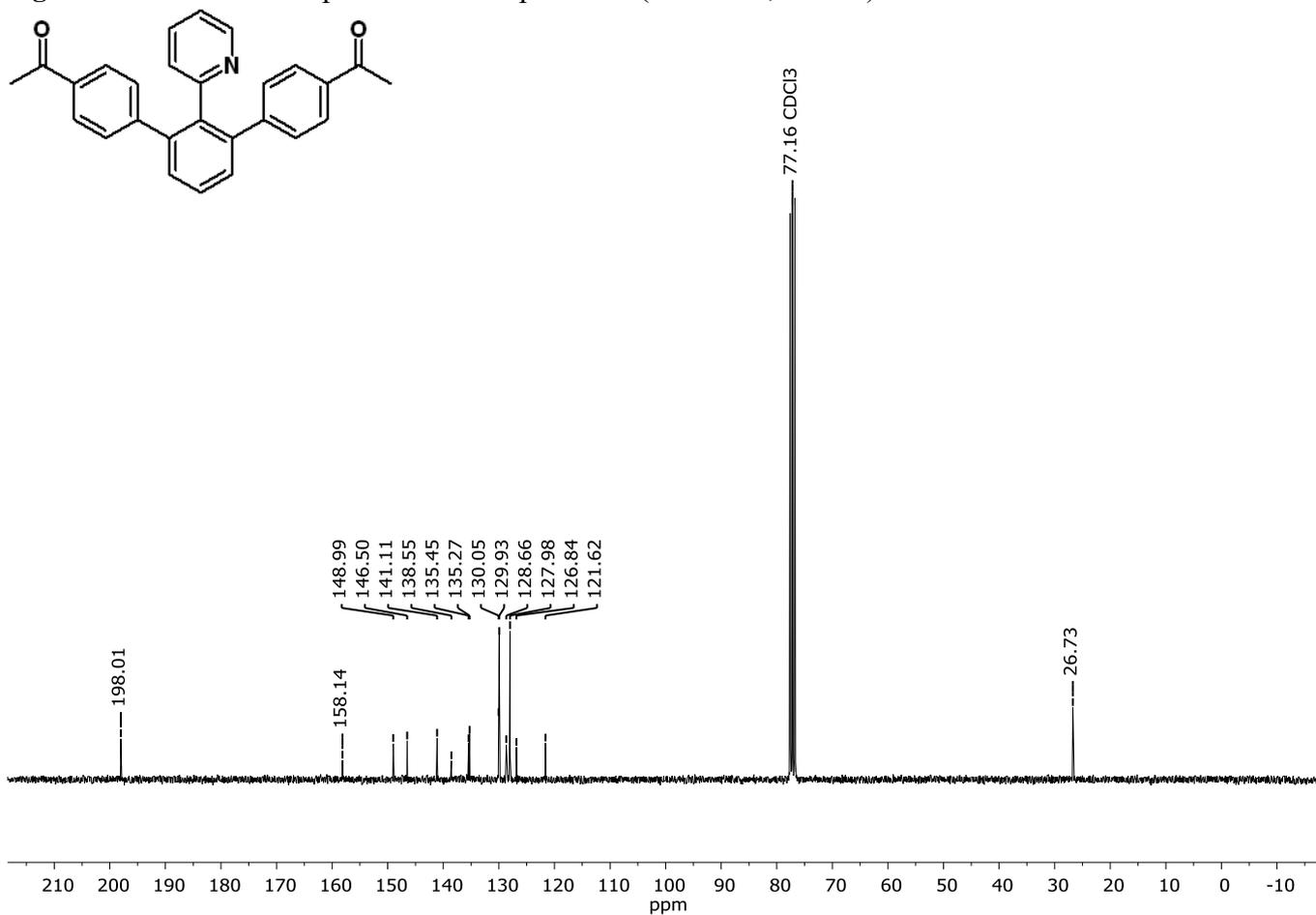
**Figure S40.** <sup>1</sup>H NMR spectrum of compound **5e** (300 MHz, CDCl<sub>3</sub>).



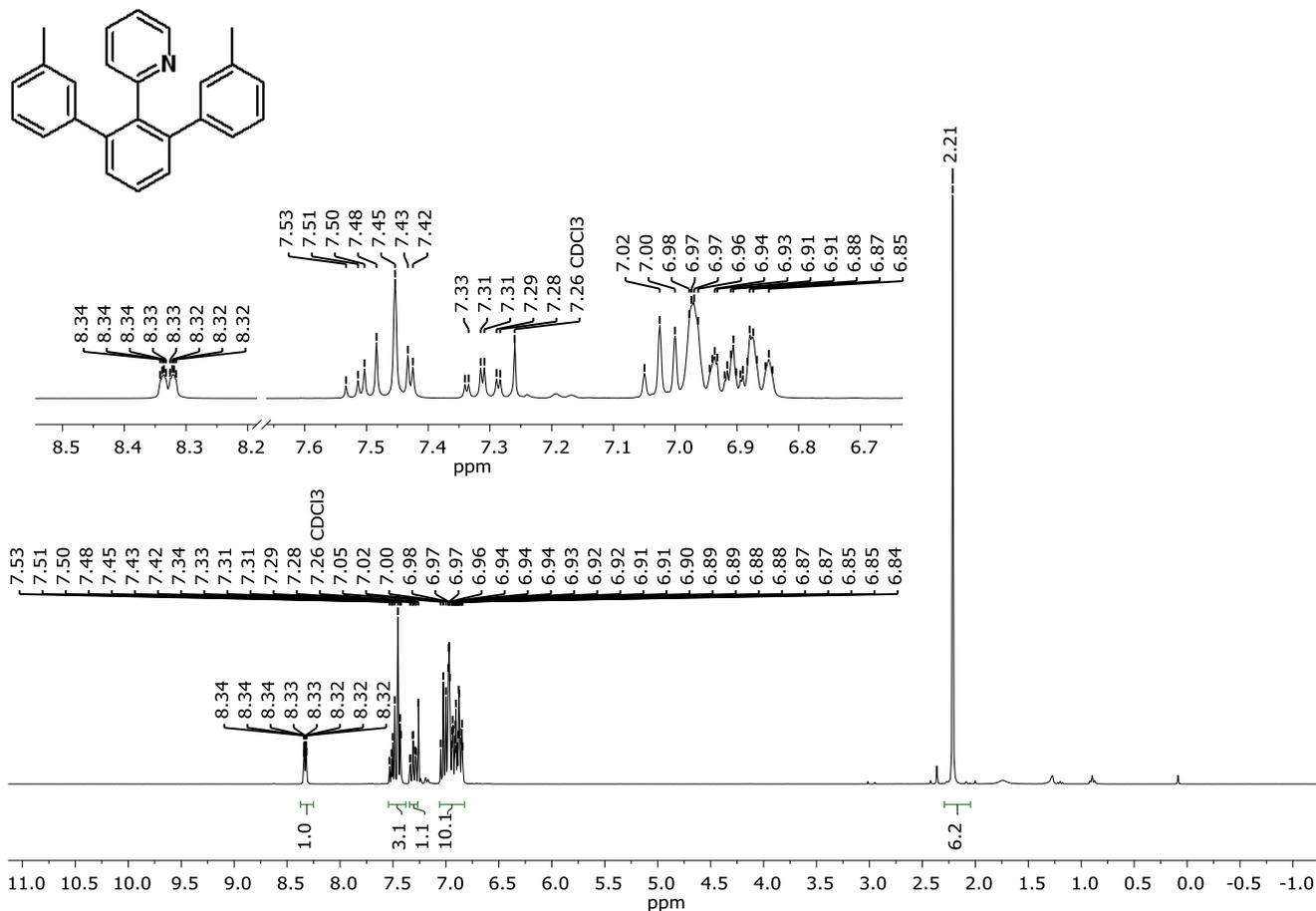
**Figure S41.** <sup>13</sup>C NMR spectrum of compound **5e** (75 MHz, CDCl<sub>3</sub>).



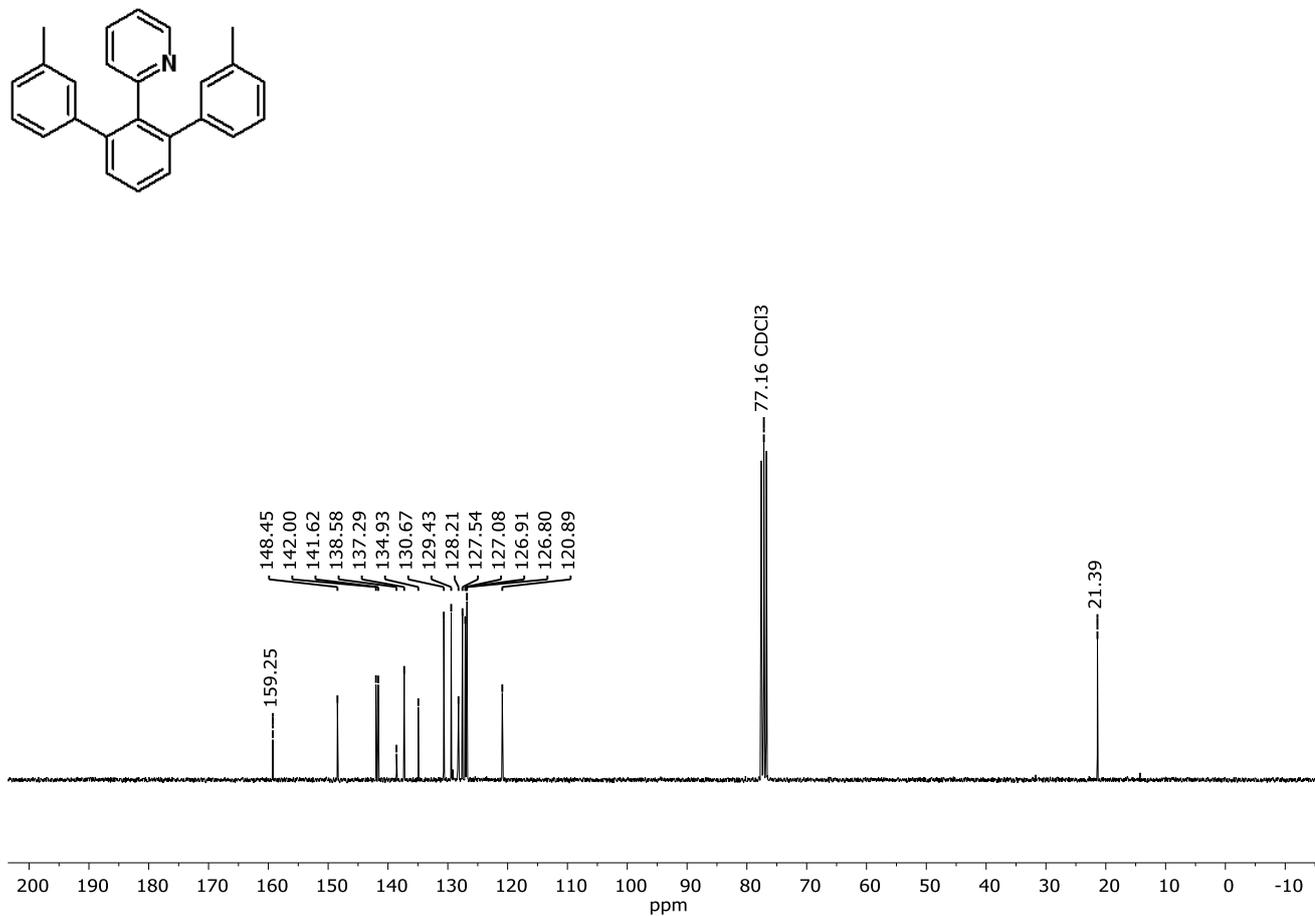
**Figure S42.** <sup>1</sup>H NMR spectrum of compound **5f** (300 MHz, CDCl<sub>3</sub>).



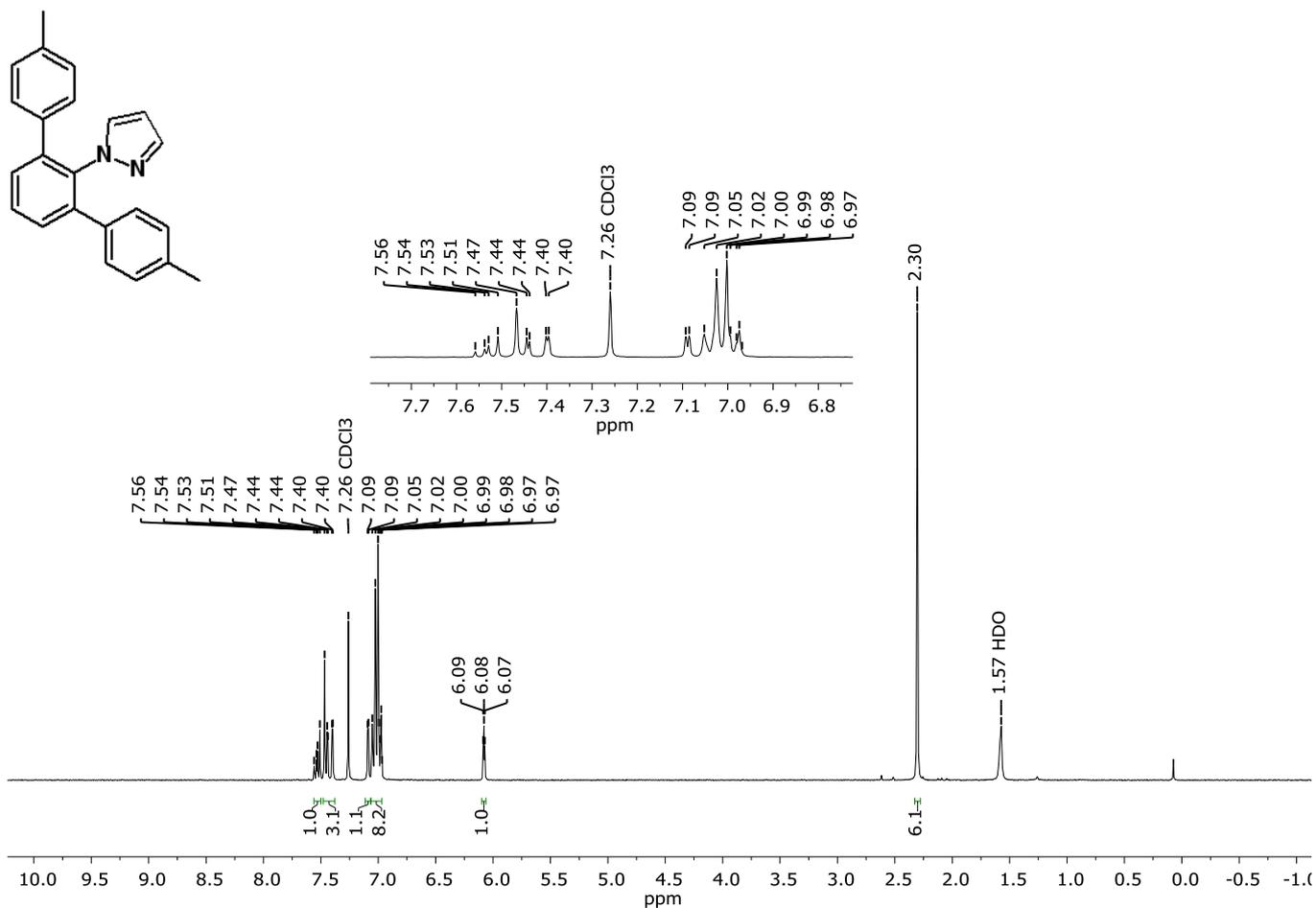
**Figure S43.** <sup>13</sup>C NMR spectrum of compound **5f** (75 MHz, CDCl<sub>3</sub>).



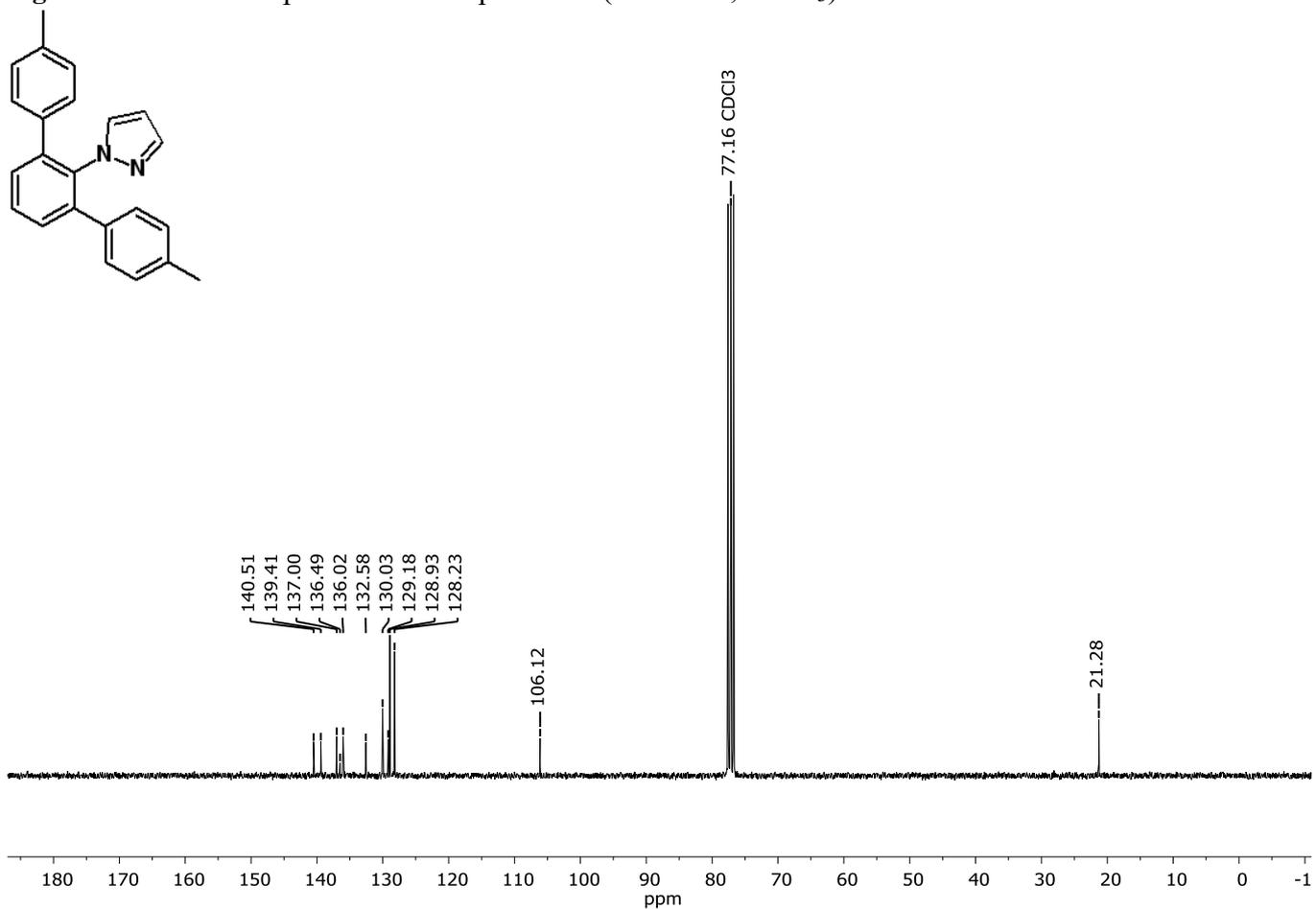
**Figure S44.**  $^1\text{H}$  NMR spectrum of compound **5g** (300 MHz,  $\text{CDCl}_3$ ).



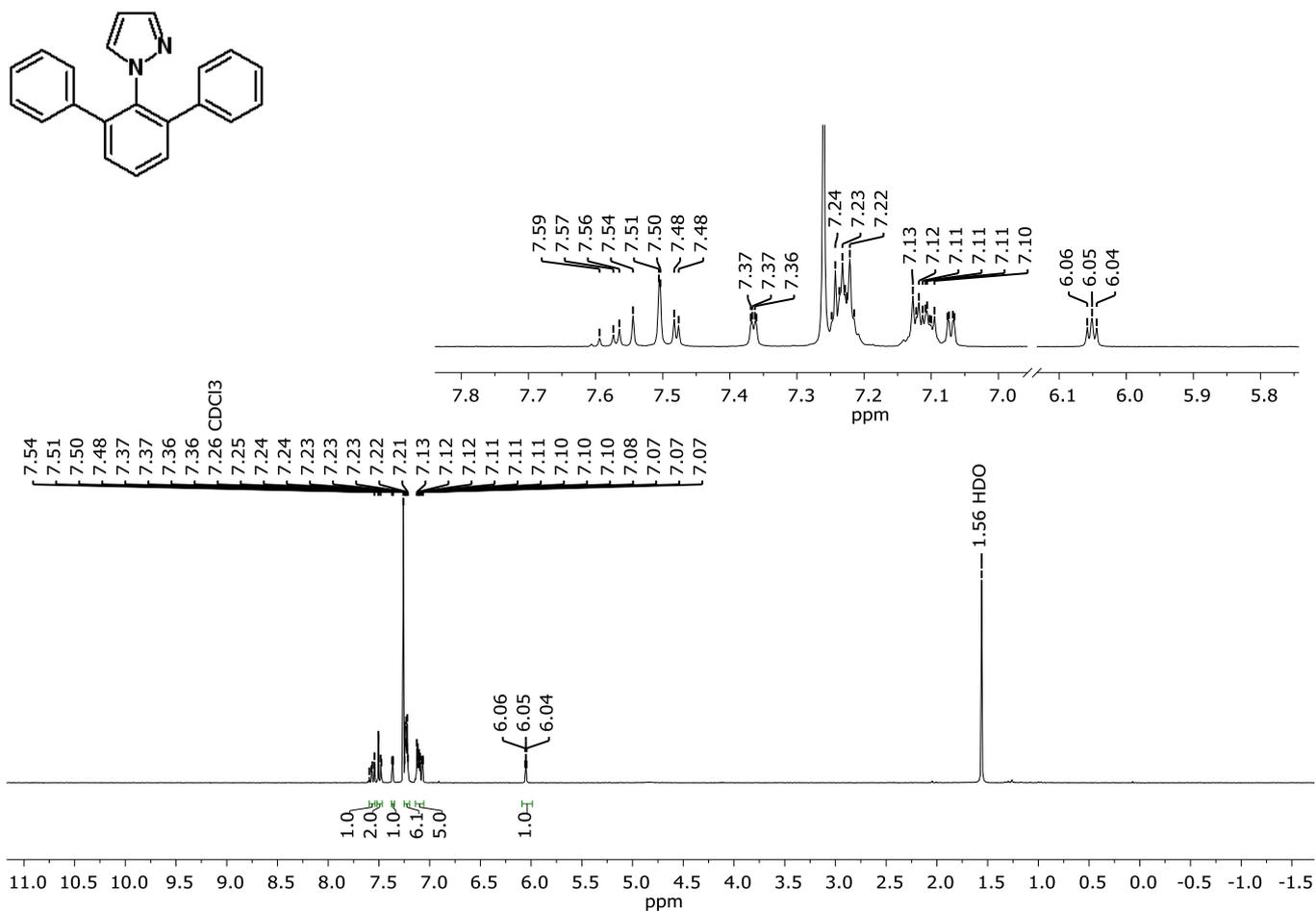
**Figure S45.**  $^{13}\text{C}$  NMR spectrum of compound **5g** (75 MHz,  $\text{CDCl}_3$ ).



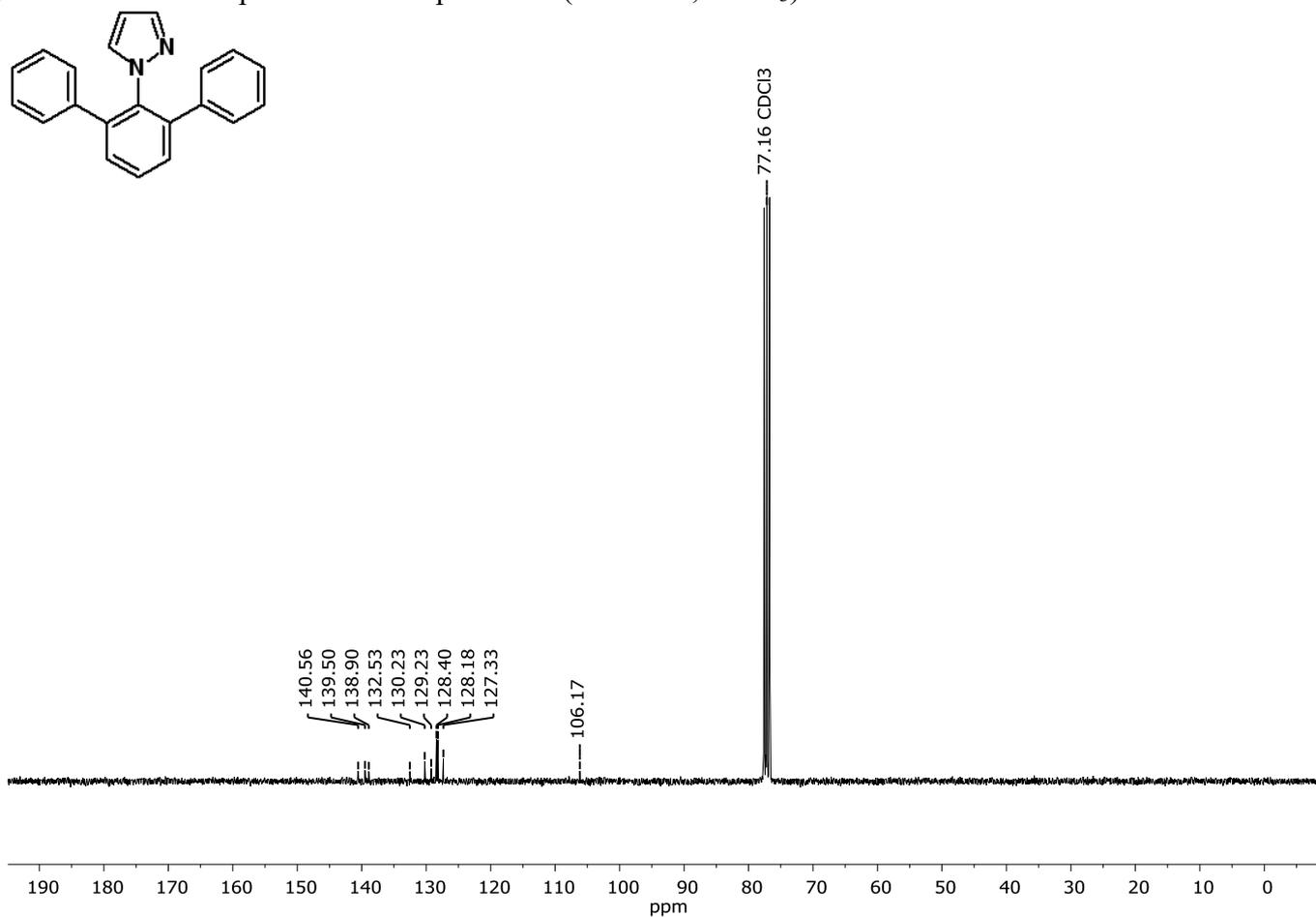
**Figure S46.**  $^1\text{H}$  NMR spectrum of compound **7a** (300 MHz,  $\text{CDCl}_3$ ).



**Figure S47.**  $^{13}\text{C}$  NMR spectrum of compound **7a** (75 MHz,  $\text{CDCl}_3$ ).



**Figure S48.**  $^1\text{H}$  NMR spectrum of compound **7b** (300 MHz,  $\text{CDCl}_3$ ).



**Figure S49.**  $^{13}\text{C}$  NMR spectrum of compound **7b** (75 MHz,  $\text{CDCl}_3$ ).

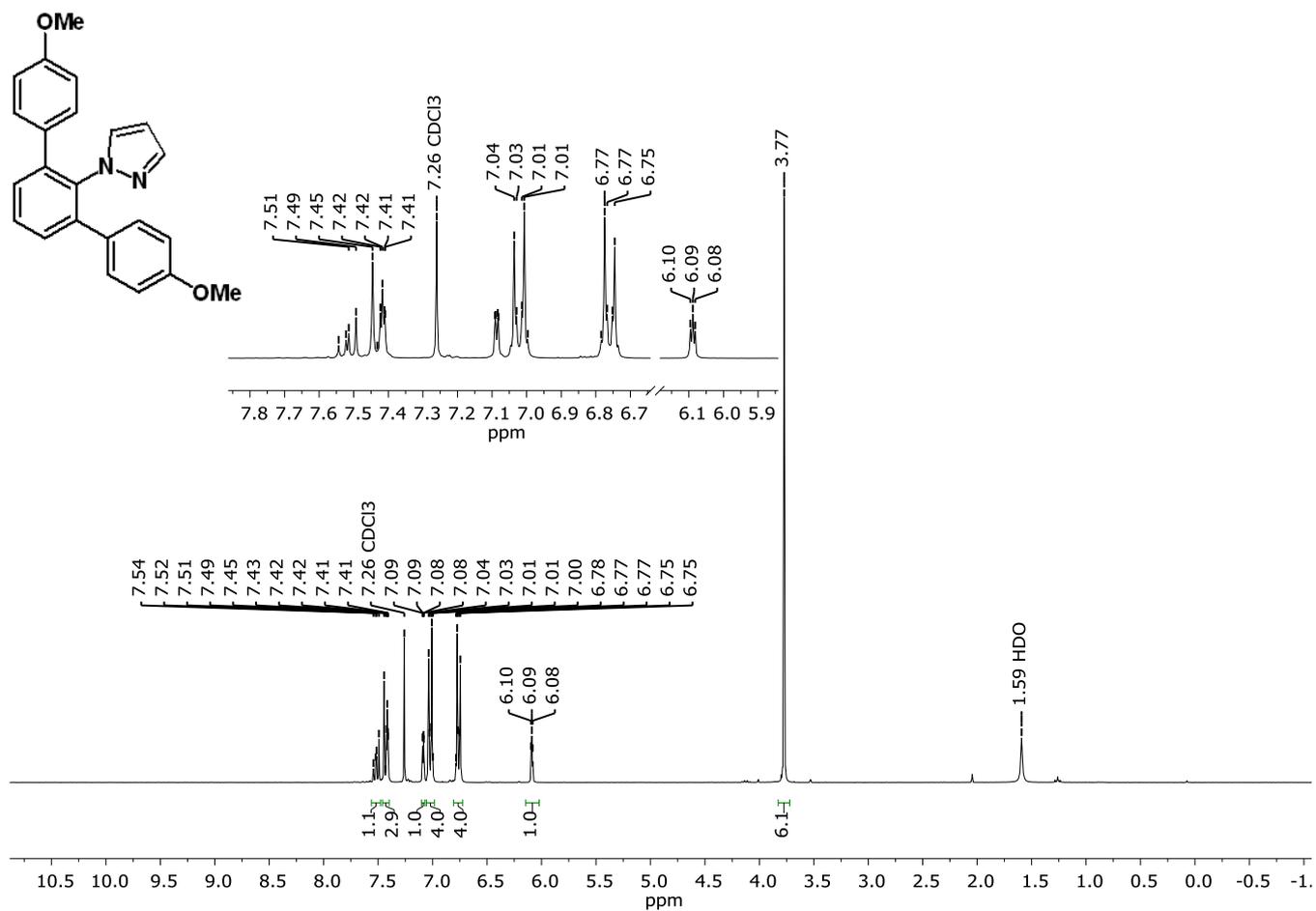


Figure S50.  $^1\text{H}$  NMR spectrum of compound **7c** (300 MHz,  $\text{CDCl}_3$ ).

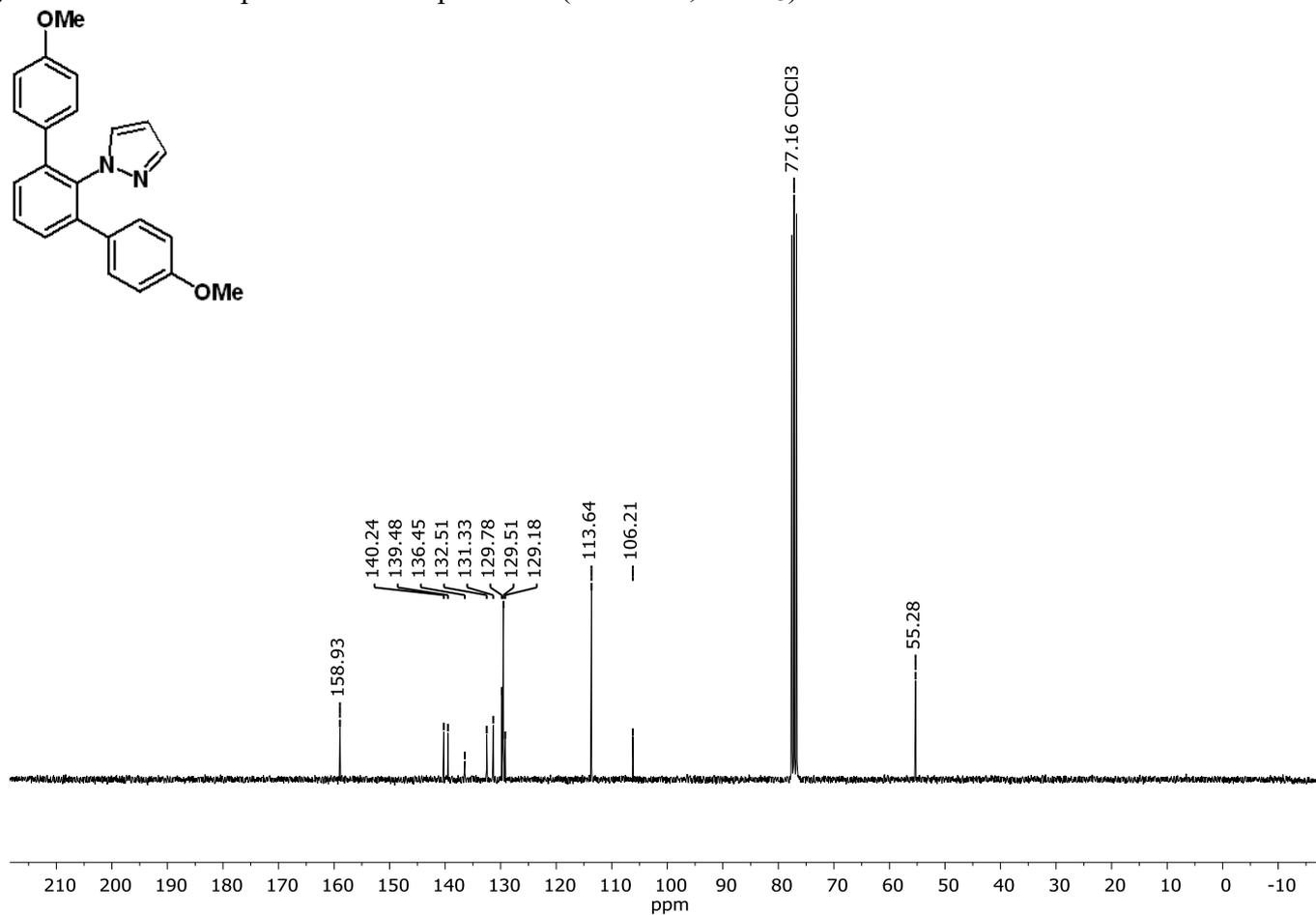
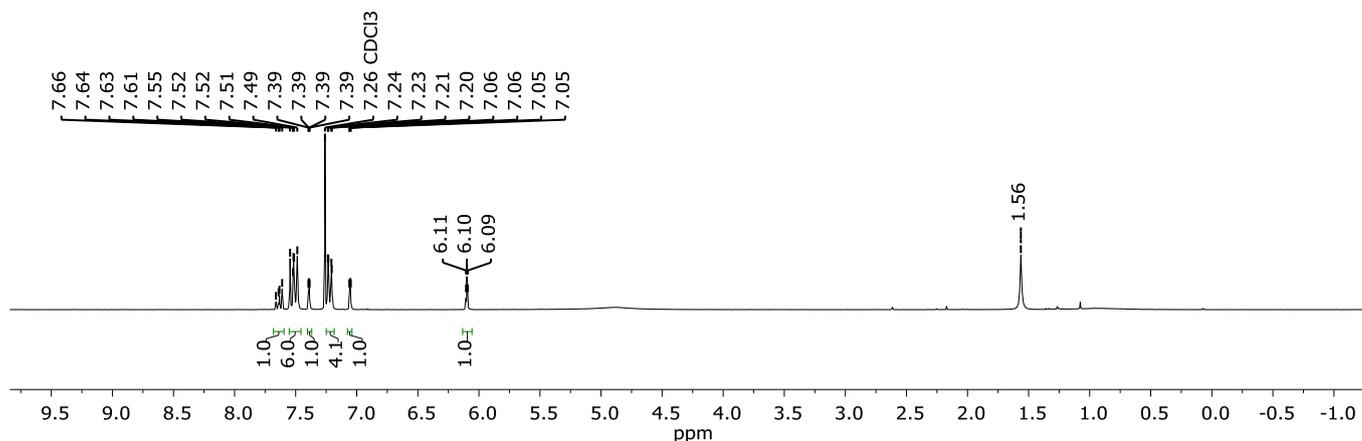
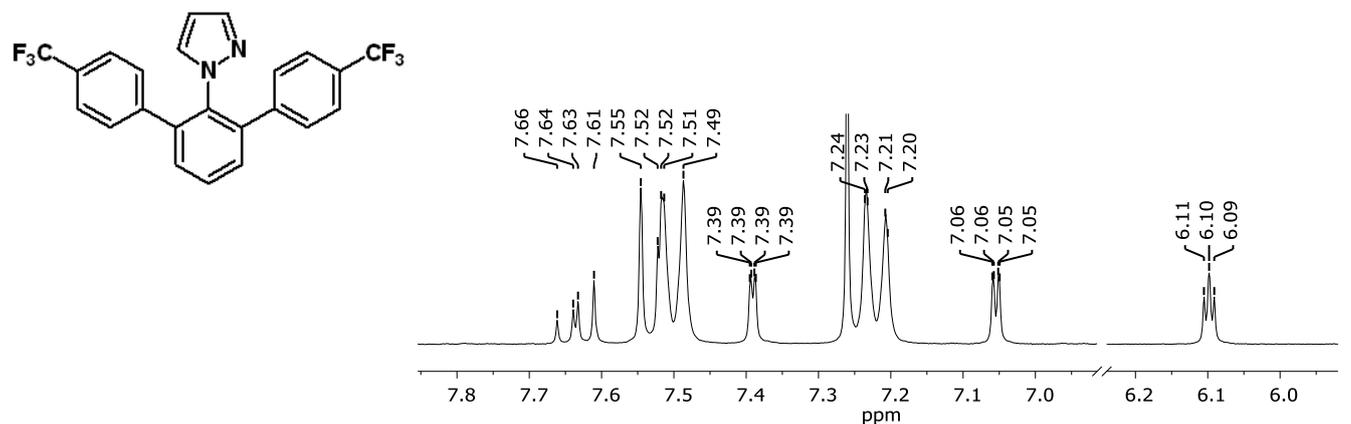
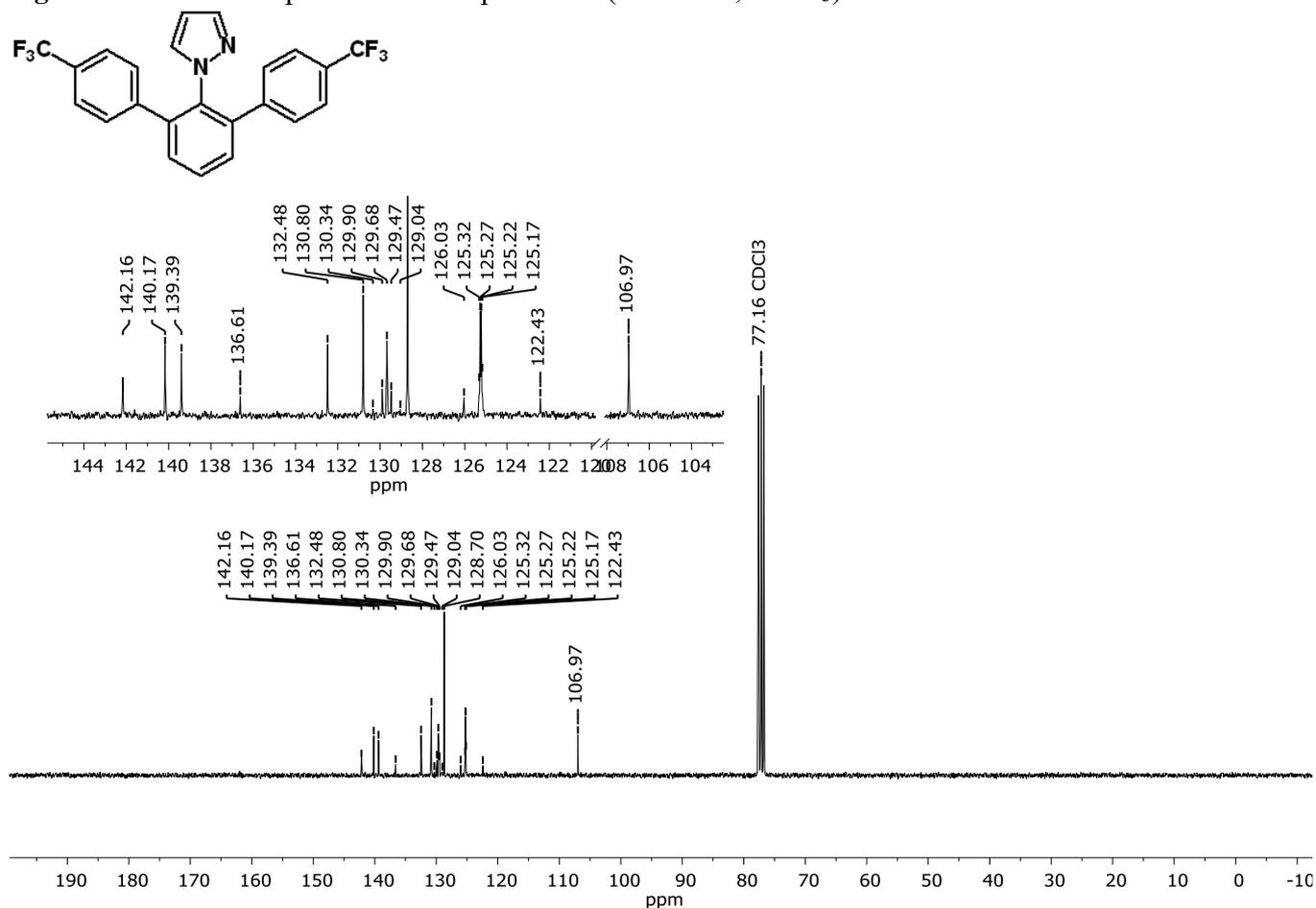


Figure S51.  $^{13}\text{C}$  NMR spectrum of compound **7c** (75 MHz,  $\text{CDCl}_3$ ).



**Figure S52.** <sup>1</sup>H NMR spectrum of compound **7d** (300 MHz, CDCl<sub>3</sub>).



**Figure S53.** <sup>13</sup>C NMR spectrum of compound **7d** (75 MHz, CDCl<sub>3</sub>).

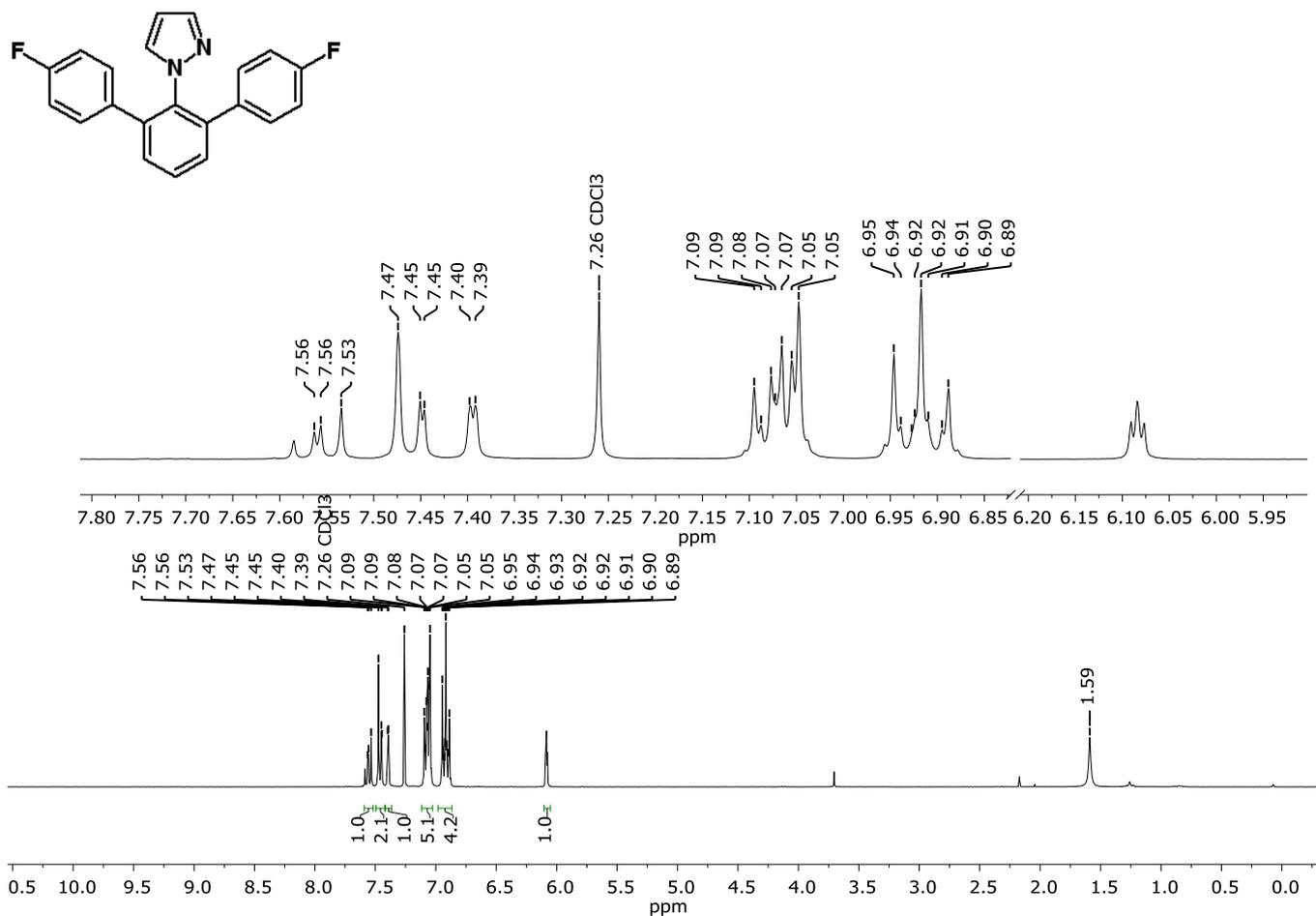


Figure S54. <sup>1</sup>H NMR spectrum of compound 7e (300 MHz, CDCl<sub>3</sub>).

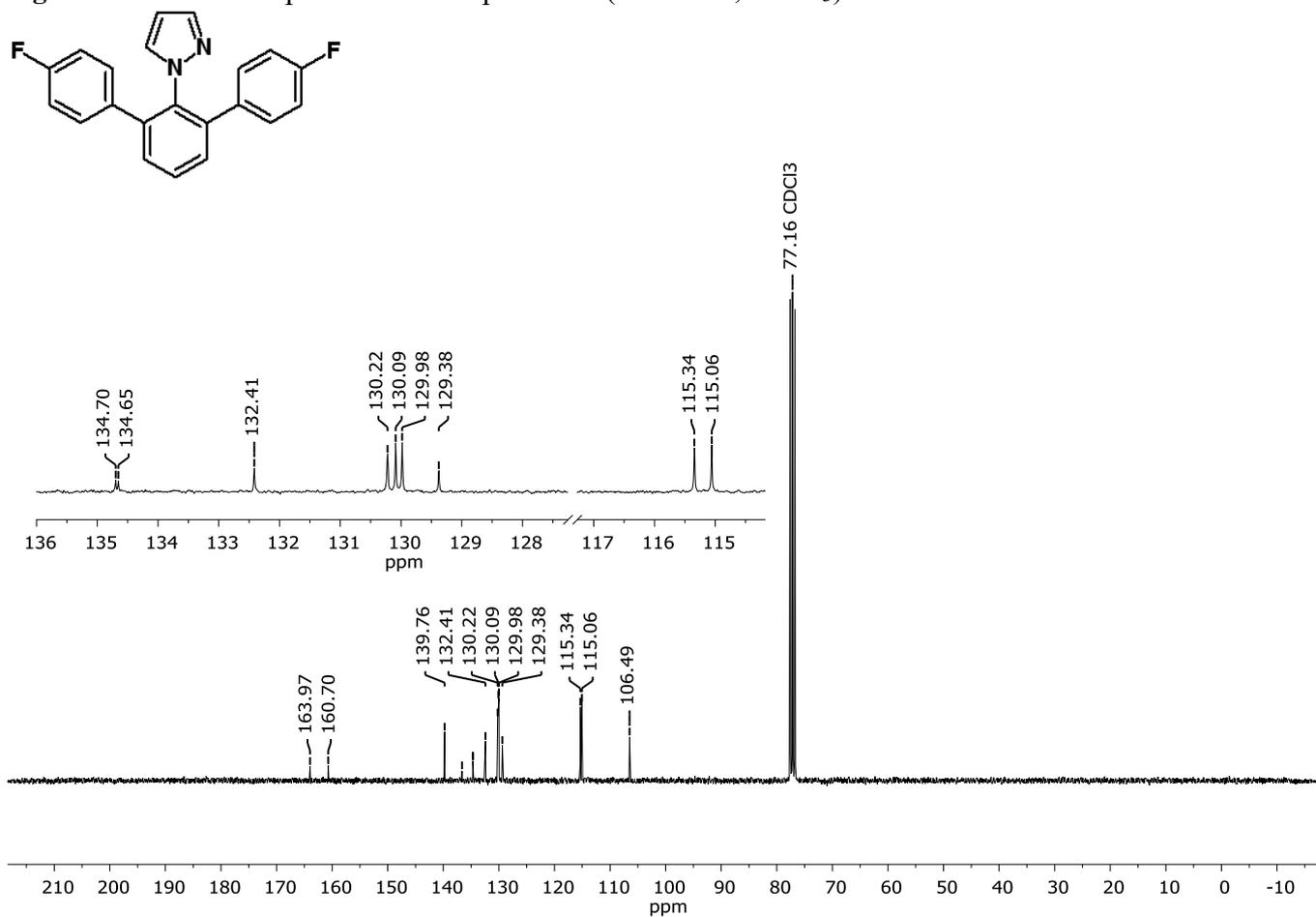
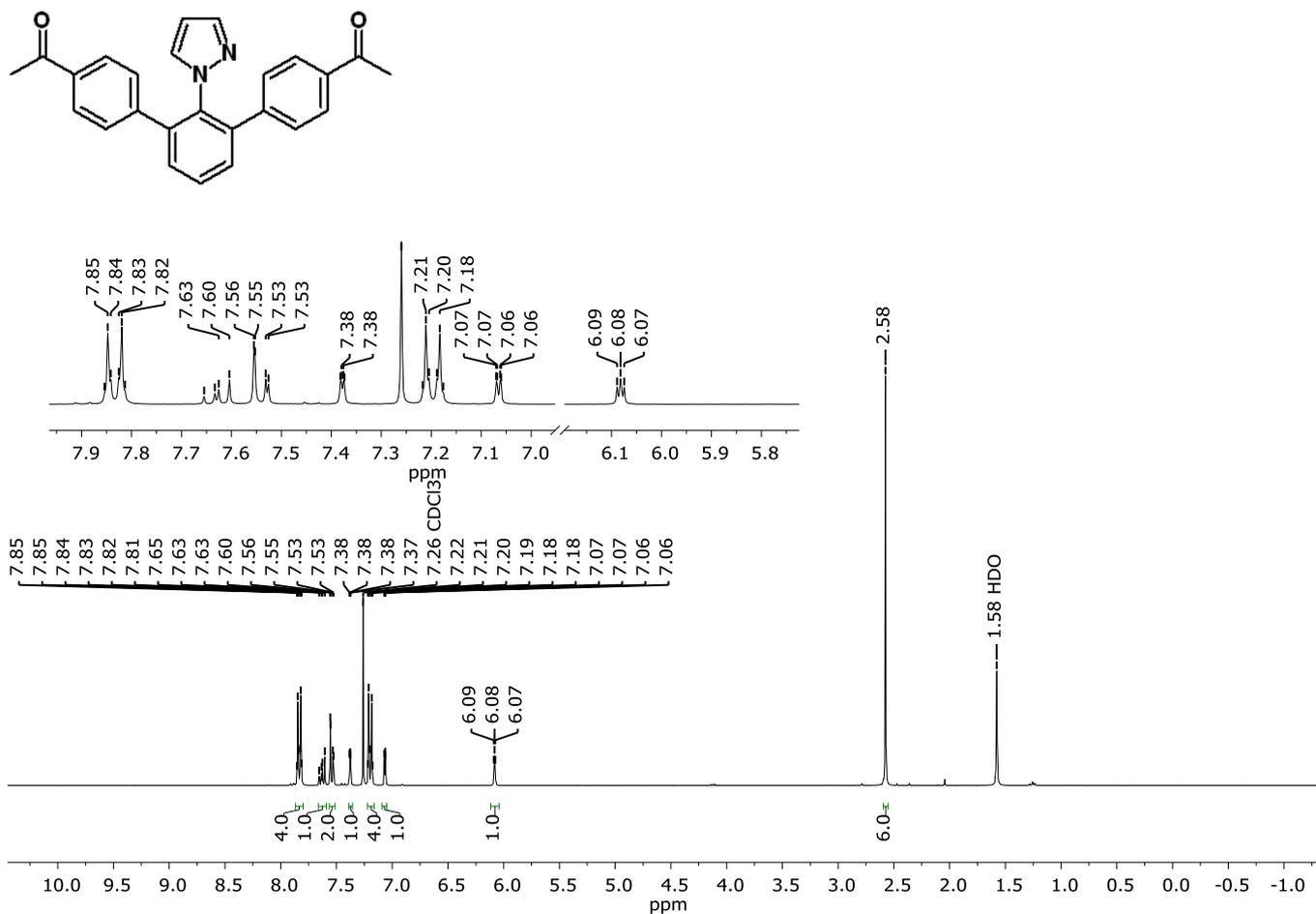
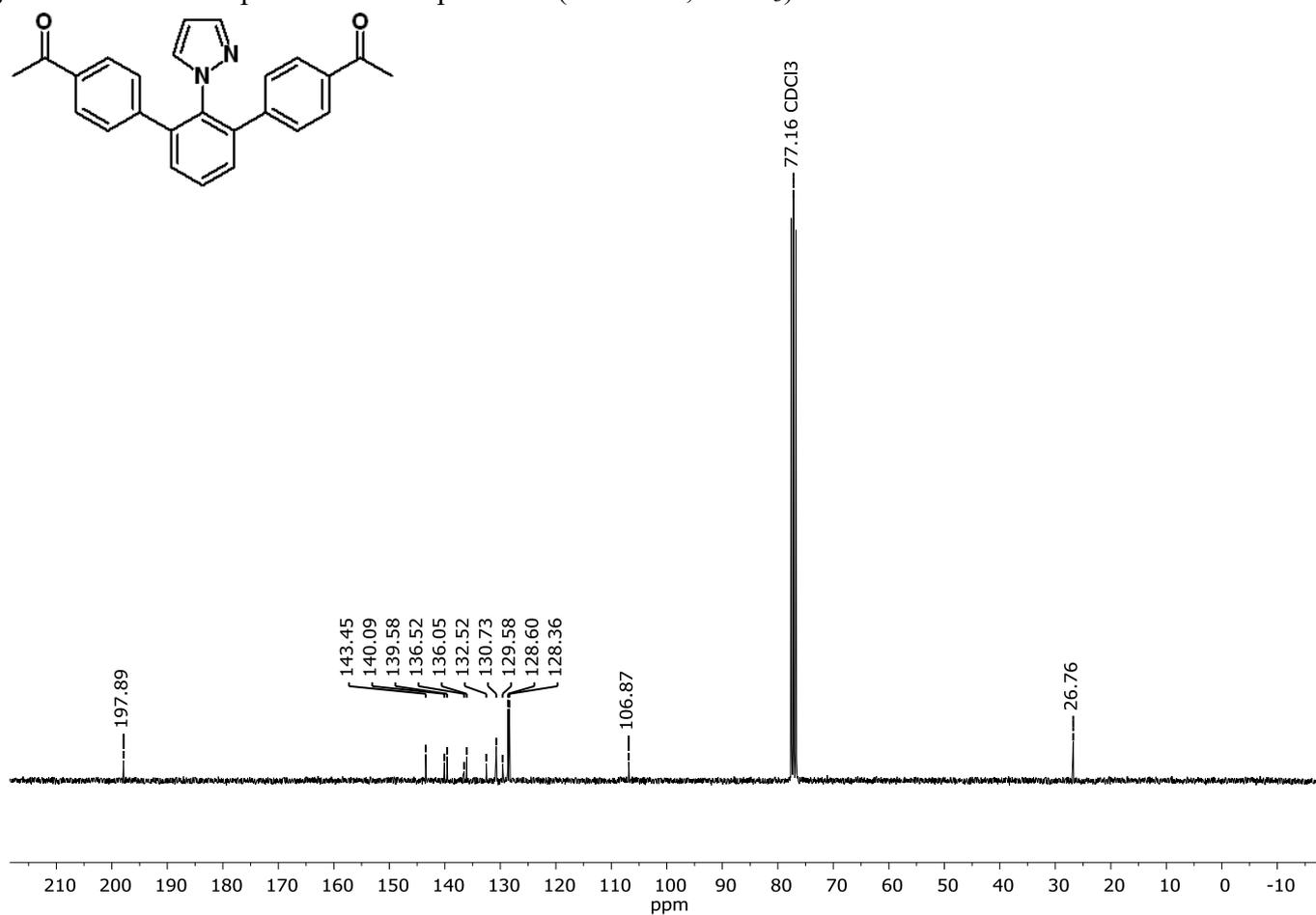


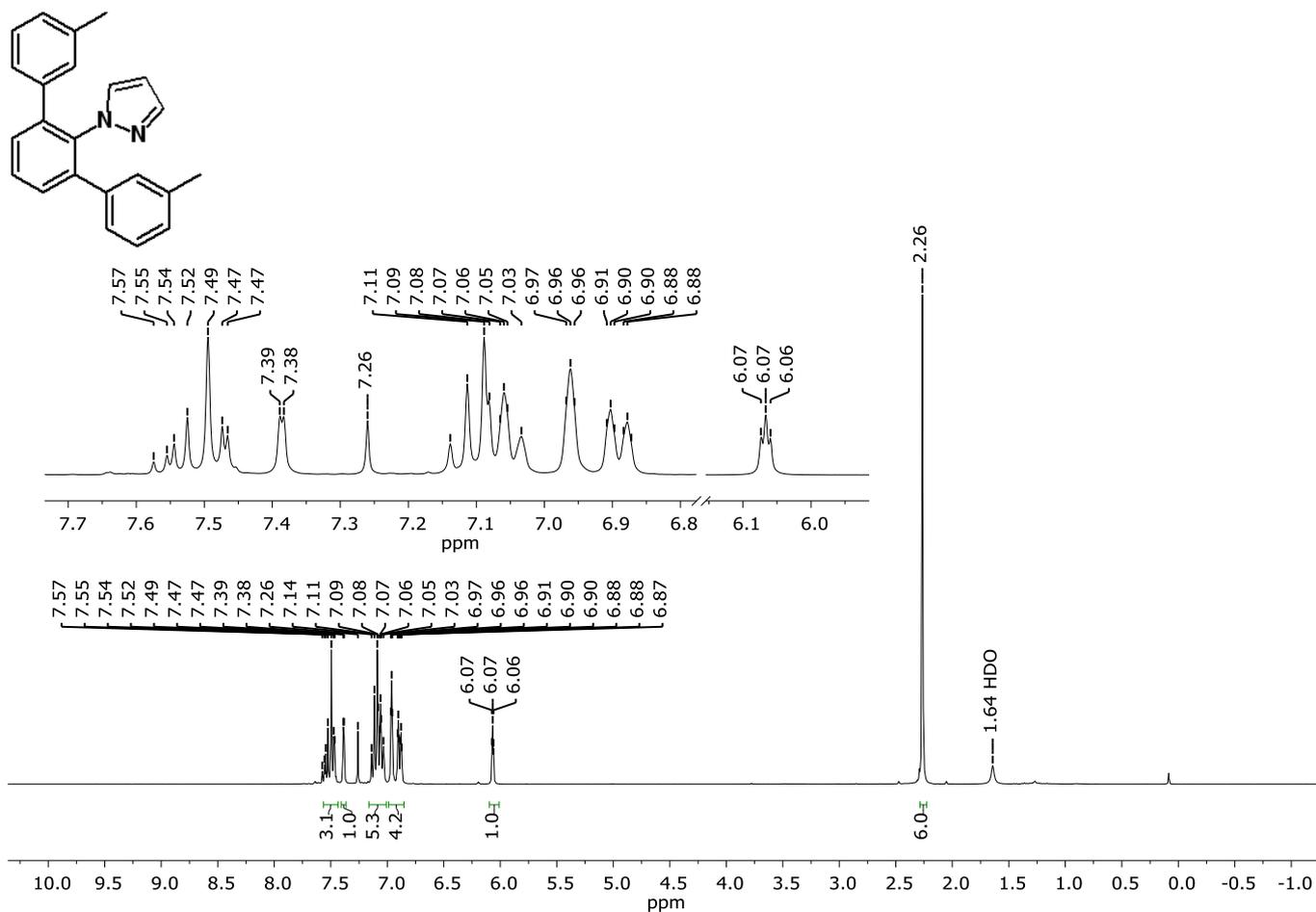
Figure S55. <sup>13</sup>C NMR spectrum of compound 7e (75 MHz, CDCl<sub>3</sub>).



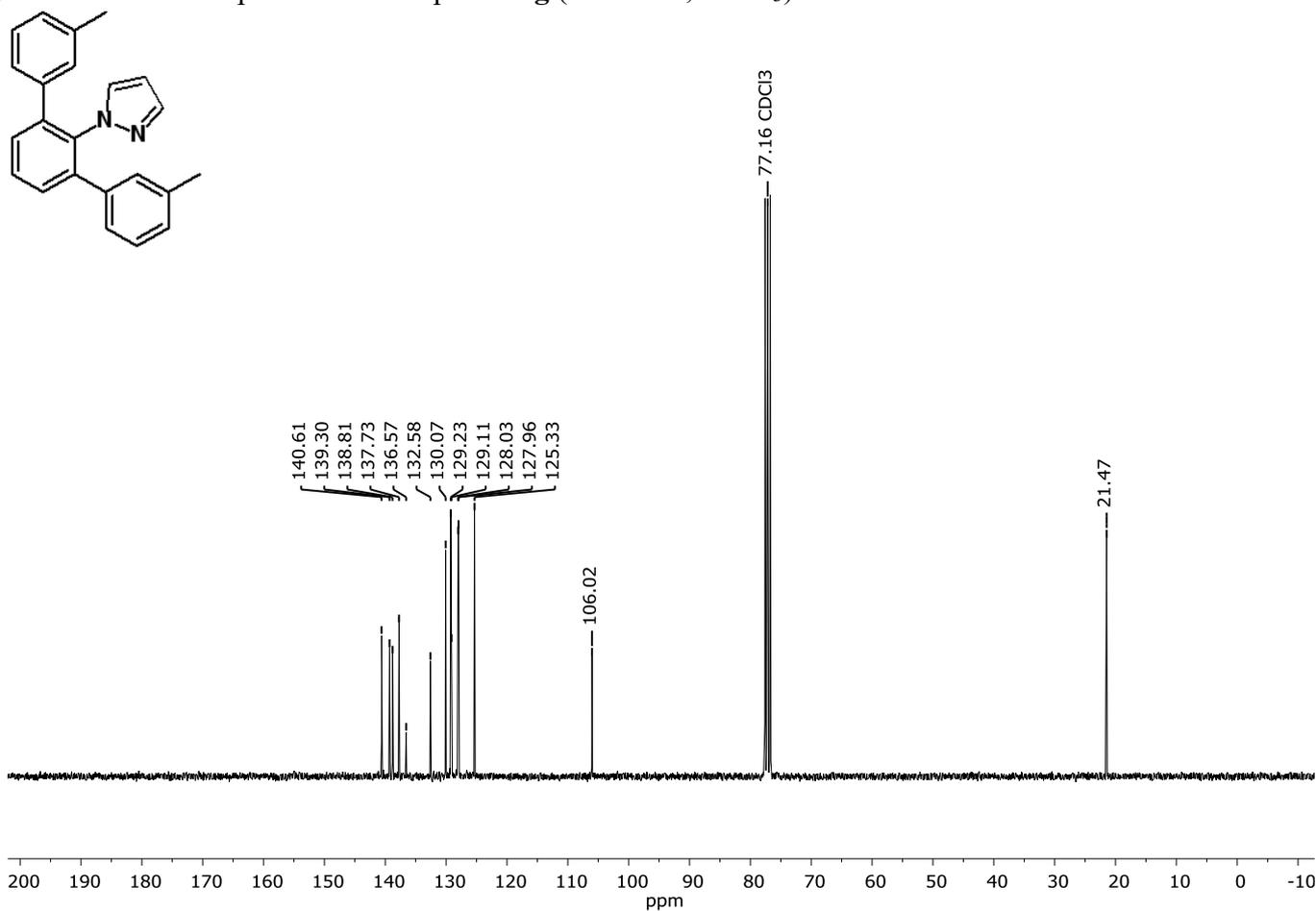
**Figure S56.**  $^1\text{H}$  NMR spectrum of compound **7f** (300 MHz,  $\text{CDCl}_3$ ).



**Figure S57.**  $^{13}\text{C}$  NMR spectrum of compound **7f** (75 MHz,  $\text{CDCl}_3$ ).



**Figure S58.**  $^1\text{H}$  NMR spectrum of compound **7g** (300 MHz,  $\text{CDCl}_3$ ).



**Figure S59.**  $^{13}\text{C}$  NMR spectrum of compound **7g** (75 MHz,  $\text{CDCl}_3$ ).

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