

# SUPPORTING INFORMATION

## Fast-initiating, Ruthenium-based Catalysts for Improved Activity in Highly *E*-Selective Cross Metathesis

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## General Information

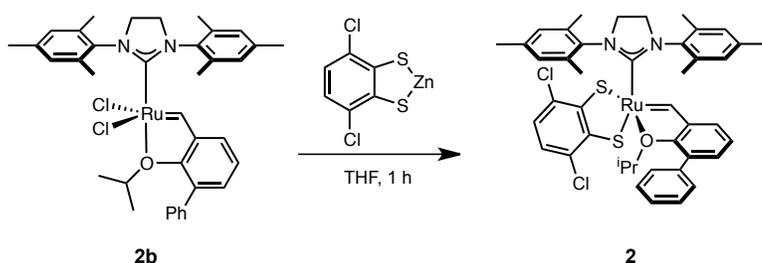
Unless otherwise specified, all manipulations were carried out under air-free conditions in dry glassware in a Vacuum Atmospheres Glovebox filled with N<sub>2</sub>. General solvents were purified by passing through solvent purification columns. Commercially available substrates were used as received. All solvents and substrates were sparged with Ar before bringing into the glovebox and filtered over basic alumina (Brockmann I) prior to use. THF-*d*<sub>8</sub> was dried over Na/benzophenone and vacuum transferred to another Schlenk flask followed by degassing via methods of freeze, pump, thaw (×3). **1**,<sup>1</sup> **2b**,<sup>2</sup> **3b**,<sup>3</sup> **4a**,<sup>4</sup> (3,6-dichlorobenzene-1,2-dithiolato)zinc(II),<sup>1</sup> and (*E/Z*)-2-isopropoxy-3-(prop-1-en-1-yl)-1,1'-biphenyl<sup>5</sup> (**A**) were synthesized according to literature procedure.

Kinetic NMR experiments were performed on a Varian 500 MHz spectrometer with an AutoX probe. Spectra were analyzed using MestReNova Ver. 8.1.2. <sup>1</sup>H and <sup>13</sup>C NMR characterization data were obtained on a Bruker 400 with Prodigy broadband cryoprobe and referenced to residual protio-solvent. <sup>19</sup>F and <sup>31</sup>P NMR data were acquired on Varian 400 MHz and 300 MHz spectrometers. <sup>1</sup>H NMR spectra for determining conversions the cross metathesis of 4-octene and 1,4-diacetoxy-2-butene was obtained using the Bruker 400 with Prodigy broadband cryoprobe.

GC conversion data was obtained using an HP-5 capillary column with an Agilent 6850 FID gas chromatograph. GC selectivity data for the self-metathesis of methyl 9-octadecanoate was also obtained on this HP-5 capillary column. GC selectivity data for the reactions of 4-octene with 1,4-diacetoxy-2-butene and with 1-decene were obtained using a DB-1 column with an Agilent 6890 FID gas chromatograph. Accurate conversion and yield data was produced by determining response factors by making solutions of varying concentrations of the desired compound to be analyzed and internal standard as described by Grubbs et. al.<sup>6</sup> 4-tridecene was synthesized as previously described for this purpose.<sup>7</sup>

High-resolution mass spectrometry (HRMS) was performed using FAB+ ionization on a JEOL MSRoute mass spectrometer.

## Synthesis of Catalyst **2**



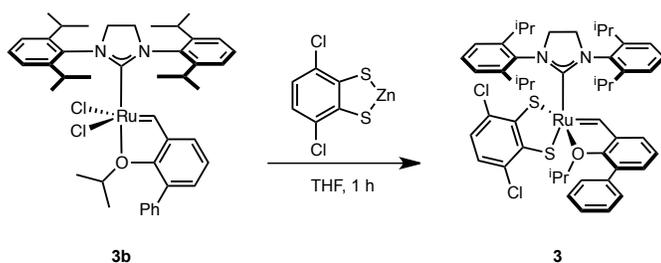
To a vial charged with a stir bar was added **2b** (40.0 mg, 0.057 mmol), (3,6-dichlorobenzene-1,2-dithiolato)zinc(II) (31.2 mg, 0.114 mmol) and 0.2 mL THF. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed *in vacuo* followed by co-evaporation with pentane. Dichloromethane was then added, and the mixture was filtered over a pad of Celite. Solvents were removed *in vacuo* followed by co-evaporation with pentane to yield the product as a brown solid (45.5 mg, 95% yield).

**$^1\text{H}$  NMR** (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  14.82 (s, 1H), 7.59 - 7.44 (m, 5H), 7.38 (d,  $J = 1.7$  Hz, 1H), 7.12 (d,  $J = 2.0$  Hz, 1H), 7.04 (t,  $J = 7.5$  Hz, 1H), 6.99 (d,  $J = 2.0$  Hz, 1H), 6.96 (d,  $J = 8.1$  Hz, 1H), 6.89 (d,  $J = 8.1$  Hz, 1H), 6.81 (d,  $J = 2.0$  Hz, 1H), 6.68 (dd,  $J = 7.5, 1.7$  Hz, 1H), 6.30 (d,  $J = 2.1$  Hz, 1H), 4.50 (hept,  $J = 6.5$  Hz, 1H), 4.20 - 4.02 (m, 2H), 3.94 - 3.80 (m, 2H), 2.76 (s, 3H), 2.61 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 2.17 (s, 3H), 1.60 (s, 3H), 1.12 - 1.05 (d, 3H), 0.83 (d,  $J = 6.4$  Hz, 3H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  255.91, 255.66, 216.74, 153.54, 152.58, 144.53, 143.09, 140.49, 140.45, 139.80, 138.03, 137.41, 137.34, 136.91, 136.04, 134.50, 132.22, 132.09, 131.92, 131.59, 130.53, 130.43, 130.38, 130.30, 130.24, 130.17, 129.73, 129.45, 129.24, 128.47, 128.36, 126.90, 125.08, 124.79, 123.53, 122.33, 79.96, 52.16, 52.05, 23.01, 21.33, 21.24, 20.08, 19.84, 19.49, 18.35.

**HRMS** (FAB<sup>+</sup>): [(M+H)-H<sub>2</sub>] C<sub>43</sub>H<sub>43</sub>N<sub>2</sub>ORuS<sub>2</sub>Cl<sub>2</sub> Calculated - 839.1238, Found - 839.1278

### Synthesis of Catalyst 3



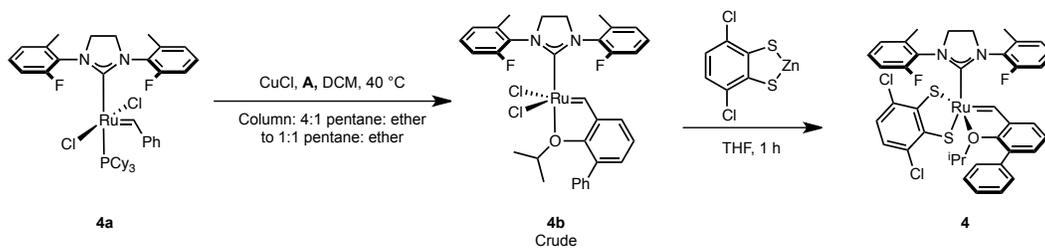
To a vial charged with a stir bar was added **3b** (35.0 mg, 0.044 mmol), (3,6-dichlorobenzene-1,2-dithiolato)zinc(II) (24.4 mg, 0.088 mmol) and 0.150 mL THF. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed *in vacuo* followed by co-evaporation with pentane. Dichloromethane was then added, and the mixture was filtered over a pad of Celite. Solvents were removed *in vacuo* followed by co-evaporation with pentane to yield the product as a brown solid (37.8 mg, 93% yield).

**$^1\text{H}$  NMR** (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  14.61 (s, 1H), 7.53 - 7.25 (m, 10H), 7.16 (dd,  $J = 7.5, 1.8$  Hz, 2H), 6.89 (t,  $J = 7.5$  Hz, 2H), 6.79 (d,  $J = 8.1$  Hz, 1H), 6.60 (dd,  $J = 7.4, 1.8$  Hz, 1H), 4.41 (hept,  $J = 6.4$  Hz, 1H), 4.13 (s, 4H), 2.05 - 1.44 (m, 10H), 1.34 (dd,  $J = 9.4, 6.1$  Hz, 6H), 1.03 (t,  $J = 6.3$  Hz, 6H), 1.02 - 0.93 (m, 3H), 0.81 (d,  $J = 6.3$  Hz, 3H), 0.41 (d,  $J = 6.9$  Hz, 6H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  261.78, 261.52, 219.77, 152.92, 152.64, 148.20, 143.84, 143.15, 141.31, 134.09, 131.95, 131.32, 129.88, 129.77, 129.73, 129.64, 129.51, 128.62, 128.62, 128.15, 126.00, 125.79, 125.53, 125.45, 125.30, 125.11, 125.01, 124.21, 123.62, 123.49, 123.47, 122.03, 78.43, 78.32, 54.46, 54.40, 32.49, 30.27, 30.24, 30.07, 29.93, 29.86, 29.66, 29.58, 29.37, 26.77, 25.72, 23.93, 23.54, 23.26, 22.25, 21.76, 20.93, 14.45.

**HRMS** (FAB<sup>+</sup>): [M]<sup>+</sup> C<sub>49</sub>H<sub>56</sub>N<sub>2</sub>ORuS<sub>2</sub>Cl<sub>2</sub> Calculated - 924.2255, Found - 924.2210

## Synthesis of Catalyst 4b/4



To a vial charged with a stir bar was added **4a** (0.100 g, 0.120 mmol), CuCl (11.9 mg, 0.120 mmol), **A** (30.4 mg, 0.120 mmol), and 1 mL dichloromethane. This mixture was stirred at 40°C for 1 hr. Pentane was added, and the reaction mixture was filtered over Celite. The filtrate was added directly to a silica gel column. Organic byproducts were eluted with 4:1 pentane:diethyl ether followed by elution of crude **4b** (24.6 mg, green solid, NMR spectrum included below) with 1:1 pentane:diethyl ether. Solvents were removed *in vacuo*. To crude **4b** was added (3,6-dichlorobenzene-1,2-dithiolato)zinc(II) (19.8 mg, 0.072 mmol) and 0.150 mL THF. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed *in vacuo* followed by co-evaporation with pentane. Dichloromethane was then added, and the mixture was filtered over a pad of Celite. Solvents were removed *in vacuo* followed by co-evaporation with pentane. The pure product was obtained upon precipitation of the compound by adding cold pentane to a concentrated solution of the crude product in diethyl ether as a brown solid (20.0 mg, 20% overall yield).

**4b**:  $^1\text{H NMR}$  (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  16.40 (s, 1H), 7.51 - 7.28 (m, 8H), 7.25 - 7.19 (m, 2H), 7.13 (q,  $J = 8.6$  Hz, 2H), 6.99 (t,  $J = 7.4$  Hz, 1H), 6.94 (dd,  $J = 7.5$ , 1.8 Hz, 1H), 4.45 - 4.34 (m, 1H), 4.33 - 4.23 (m, 2H), 4.17 (ddd,  $J = 13.3$ , 6.6, 4.2 Hz, 2H), 2.58 (s, 3H), 2.54 (s, 2H), 0.87 - 0.77 (m, 6H).

**4b**:  $^{13}\text{C NMR}$  (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  293.88, 215.19, 214.26, 191.20, 162.66, 162.55, 160.16, 160.04, 150.51, 149.75, 149.72, 148.31, 148.29, 142.34, 142.30, 139.63, 137.78, 133.94, 133.91, 133.10, 132.08, 131.13, 130.87, 130.82, 130.78, 130.73, 129.78, 129.71, 129.48, 129.39, 129.25, 129.04, 128.95, 128.61, 128.47, 128.31, 128.12, 127.48, 127.26, 126.87, 126.84, 125.43, 124.49, 124.19, 124.08, 121.80, 114.77, 114.68, 114.57, 114.48, 78.23, 78.20, 53.07, 52.88, 30.23, 27.48, 27.37, 26.83, 26.70, 22.24, 22.01, 20.61, 20.57, 19.15, 18.99.

**4b**: **HRMS** (FAB+): [(M+H)-H<sub>2</sub>] C<sub>33</sub>H<sub>31</sub>F<sub>2</sub>N<sub>2</sub>ORuCl<sub>2</sub> Calculated – 681.0826, Found – 681.0831

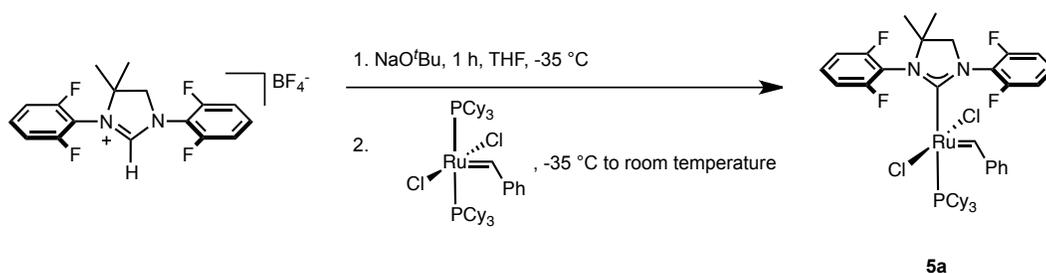
**4**:  $^1\text{H NMR}$  (400 MHz, Methylene Chloride- $d_2$ ) (three conformers in solution)  $\delta$  14.99 (s, 0.31H), 14.92 (s, 0.17H), 14.86 (s, 0.53H), 7.75 - 7.65 (m, 1H), 7.61 - 7.48 (m, 2H), 7.44 (t,  $J = 6.9$  Hz, 1H), 7.37 (d,  $J = 7.5$  Hz, 1H), 7.28 - 7.20 (m, 3H), 7.12 (d,  $J = 7.6$  Hz, 1H), 7.01 (d,  $J = 7.8$  Hz, 1H), 6.94 (d,  $J = 7.5$  Hz, 1H), 6.87 (q,  $J = 7.4$  Hz, 3H), 6.57 (t,  $J = 7.6$  Hz, 1H), 6.20 (t,  $J = 9.0$  Hz, 1H), 4.69 - 4.47 (m, 1H), 4.00 (ddd,  $J = 19.3$ , 15.1, 9.2 Hz, 4H), 2.77 - 2.62 (m, 3H), 2.23 (d,  $J = 24.1$  Hz, 3H), 1.58 (s, 1H), 1.26 (s, 1H), 1.23 - 1.02 (m, 2H), 0.77 (dd,  $J = 9.2$ , 6.0 Hz, 2H).

4:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  254.03, 253.83, 220.96, 220.45, 220.04, 161.69, 160.33, 159.22, 157.86, 154.90, 152.58, 144.51, 141.30, 139.91, 139.73, 139.38, 131.66, 131.45, 130.82, 130.73, 130.11, 130.03, 129.81, 129.54, 129.37, 128.87, 128.30, 127.12, 126.68, 125.48, 123.59, 123.32, 122.37, 122.19, 115.17, 114.97, 114.73, 114.64, 114.53, 114.45, 114.28, 114.08, 113.83, 81.40, 76.51, 74.85, 68.29, 53.33, 52.91, 52.33, 30.24, 26.12, 23.17, 22.49, 21.59, 20.12, 19.39, 19.06, 18.63, 16.74.

4:  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -113.32, -116.93, -118.23, -119.84, -121.75, -123.33.

4: HRMS (FAB+):  $[\text{M}]^+$   $\text{C}_{39}\text{H}_{34}\text{F}_2\text{N}_2\text{ORuS}_2\text{Cl}_2$  Calculated – 820.0502, Found – 820.0493

### Synthesis of Catalyst 5a



This reaction was performed just as previously described in the literature.<sup>4</sup> However, the product of this first step was isolated as a pure product. The crude solution was filtered over Celite, and solvents were removed *in vacuo*. 10 mL of pentane were added, and the product was sonicated for 10 minutes. Solids were collected on a medium frit and washed with methanol ( $3 \times 5$  mL) to generate the pure product as a maroon solid (236.2 mg, 45% yield)

$^1\text{H}$  NMR (400 MHz, Methylene Chloride- $d_2$ ) (two conformers in solution)  $\delta$  19.53 (d,  $J = 29.2$  Hz, 0.5H), 19.45 (m, 0.5H), 7.57 - 7.33 (m, 4H), 7.33 - 7.10 (m, 4H), 6.95 - 6.67 (m, 1H), 6.44 (s, 2H), 3.96 (s, 1H), 3.82 (s, 1H), 2.22 - 2.00 (m, 3H), 1.75 (d,  $J = 12.9$  Hz, 3H), 1.56 - 1.19 (m, 18H), 1.03 (dq,  $J = 21.2, 11.4$  Hz, 15H).

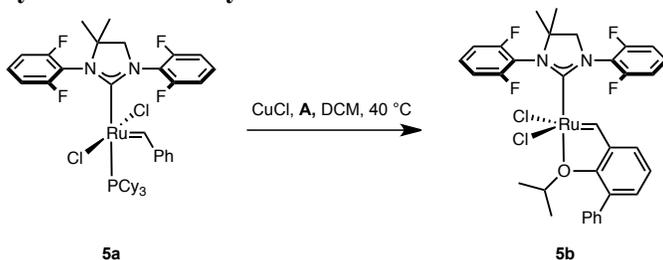
Due to multiple conformers being present in solution and extensive fluorine coupling, fluorine splitting resonances are reported as peaks:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  296.81, 296.68, 296.60, 296.54, 296.45, 224.29, 224.16, 223.51, 223.37, 162.63, 162.60, 161.99, 161.95, 161.38, 161.35, 160.72, 160.69, 160.08, 160.05, 159.44, 159.40, 158.87, 158.83, 158.20, 158.16, 157.72, 155.76, 152.64, 151.76, 151.59, 148.52, 137.27, 134.37, 133.87, 133.77, 133.67, 132.13, 132.03, 131.94, 131.57, 131.47, 131.37, 131.16, 131.06, 130.97, 130.91, 130.81, 130.76, 130.71, 130.57, 130.23, 130.13, 130.03, 129.88, 129.78, 129.68, 129.54, 129.08, 128.98, 128.83, 128.67, 128.65, 128.62, 128.49, 128.13, 127.61, 126.41, 120.79, 119.38, 119.04, 118.88, 118.72, 117.97, 117.82, 117.66, 115.63, 115.47, 115.31, 114.43, 114.27, 114.11, 113.83, 113.63, 113.20, 113.16, 113.12, 112.99, 112.96, 112.92, 112.68, 112.64, 112.57, 112.54, 112.47, 112.43, 112.37, 112.34, 112.22, 112.15, 112.12, 111.99, 111.82, 111.79, 111.76, 111.69, 111.65, 111.61, 111.58, 111.55, 111.50, 111.47, 111.38, 111.30, 111.25, 111.20, 111.12, 71.91, 67.94, 67.91, 67.73, 67.71, 66.94, 66.15, 66.13, 66.01, 65.77, 64.10, 35.46, 35.40, 35.21, 34.85, 33.26, 33.10, 32.13, 32.05,

31.97, 31.86, 31.81, 29.69, 29.57, 29.13, 28.85, 28.76, 28.73, 27.85, 27.80, 27.75, 27.69, 27.59, 27.46, 27.41, 27.32, 27.17, 27.07, 26.99, 26.96, 26.84, 26.72, 26.60, 26.53, 26.42, 26.31, 26.28, 26.18, 26.16, 25.89, 25.78, 25.74, 25.69, 25.59, 25.53, 25.37, 24.83, 24.77, 24.29.

$^{31}\text{P}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  26.22, 26.11.

HRMS (FAB+):  $[\text{M}]^+$   $\text{C}_{42}\text{H}_{53}\text{Cl}_2\text{F}_4\text{N}_2\text{PRu}$  Calculated – 864.2304, Found – 864.2311

### Synthesis of Catalyst 5b



To a vial charged with a stir bar was added **5a** (0.100 g, 0.120 mmol),  $\text{CuCl}$  (11.9 mg, 0.120 mmol), **A** (30.4 mg, 0.120 mmol), and 1 mL dichloromethane. This mixture was stirred at  $40\text{ }^\circ\text{C}$  for 1 hr. Pentane was added, and the reaction mixture was filtered over Celite. The filtrate was added directly to a silica gel column. Organic byproducts were eluted with 4:1 pentane:diethyl ether followed by elution of the product with 1:1 pentane:diethyl ether. Solvents were removed *in vacuo* to yield the product as a green solid (20.3 mg, 24% yield).

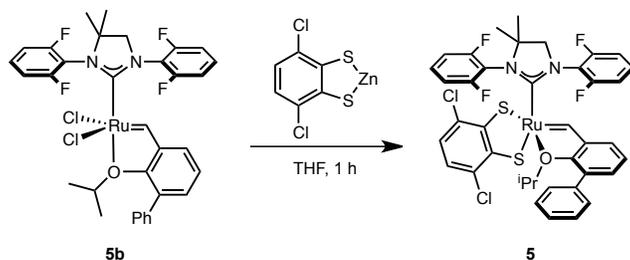
$^1\text{H}$  NMR (400 MHz, Methylene Chloride- $d_2$ )  $\delta$  16.80 (s, 1H), 7.66 - 7.21 (m, 9H), 7.16 - 7.06 (m, 3H), 7.08 - 6.97 (m, 2H), 4.46 (hept,  $J = 6.3\text{ Hz}$ , 1H), 4.08 (s, 2H), 1.49 (d,  $J = 2.9\text{ Hz}$ , 6H), 0.92 (d,  $J = 6.2\text{ Hz}$ , 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  292.04, 291.83, 215.42, 163.33, 163.30, 161.97, 161.93, 160.81, 160.78, 159.46, 159.42, 150.33, 148.26, 139.58, 137.78, 133.94, 132.35, 131.69, 131.66, 131.59, 131.50, 131.49, 130.49, 130.39, 130.29, 129.78, 129.48, 129.34, 129.26, 129.12, 128.96, 128.53, 128.35, 128.13, 127.26, 125.51, 124.49, 124.24, 121.20, 120.22, 120.07, 119.92, 116.66, 116.50, 116.34, 113.03, 113.00, 112.98, 112.94, 112.92, 112.89, 112.83, 112.81, 112.78, 112.75, 112.73, 112.71, 108.16, 78.36, 77.38, 68.21, 66.05, 26.51, 26.49, 26.46, 20.69.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -108.17, -115.14.

HRMS (FAB+):  $[\text{M}]^+$   $\text{C}_{33}\text{H}_{30}\text{Cl}_2\text{F}_4\text{N}_2\text{ORu}$  Calculated – 718.0715, Found – 718.0718

## Synthesis of Catalyst 5



To a vial charged with a stir bar was added **5b** (20.3 mg, 0.0283 mmol), (3,6-dichlorobenzene-1,2-dithiolato)zinc(II) (15.5 mg, 0.0566 mmol) and 0.1 mL THF. After the reaction mixture was stirred at room temperature for 1 hour, the solvent was removed *in vacuo* followed by co-evaporation with pentane. Dichloromethane was then added, and the mixture was filtered over a pad of Celite. Solvents were removed *in vacuo* followed by co-evaporation with pentane to yield the product as a brown solid (23.0 mg, 95% yield).

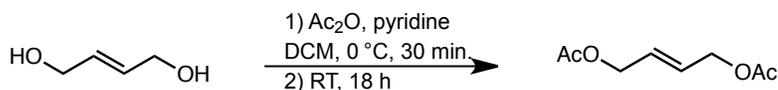
**<sup>1</sup>H NMR** (400 MHz, Methylene Chloride-*d*<sub>2</sub>)  $\delta$  14.93 (s, 0.56H), 14.62 (s, 0.44H), 7.66 (d,  $J = 7.5$  Hz, 1H), 7.62 (d,  $J = 7.5$  Hz, 1H), 7.52 (td,  $J = 7.7, 3.3$  Hz, 2H), 7.47 - 7.39 (m, 2H), 7.33 - 7.29 (m, 1H), 7.25 (dt,  $J = 6.3, 2.1$  Hz, 1H), 7.19 - 7.06 (m, 3H), 6.99 (dq,  $J = 8.7, 4.4, 4.0$  Hz, 1H), 6.94 (t,  $J = 8.0$  Hz, 1H), 6.85 - 6.76 (m, 2H), 6.71 (d,  $J = 8.2$  Hz, 0.47H), 6.65 (dd,  $J = 7.6, 1.7$  Hz, 0.61H), 6.57 (dd,  $J = 7.4, 1.7$  Hz, 1H), 6.40 (dd,  $J = 14.5, 8.9$  Hz, 1H), 4.73 (p,  $J = 6.4$  Hz, 0.47H), 4.61 (p,  $J = 6.6$  Hz, 0.53H), 3.95 - 3.74 (m, 2H), 3.28 (dt,  $J = 12.3, 6.1$  Hz, 0.33H), 3.01 (s, 0.76H), 2.48 (q,  $J = 7.1$  Hz, 0.43H), 2.29 (t,  $J = 7.6$  Hz, 0H), 1.43 - 1.33 (m, 3H), 1.38 - 1.28 (m, 3H), 0.93 (d,  $J = 6.2$  Hz, 2H), 0.83 (d,  $J = 6.3$  Hz, 2H), 0.72 (d,  $J = 6.1$  Hz, 1H), 0.48 (t,  $J = 6.5$  Hz, 1H).

Due to multiple conformers being present in solution an extensive fluorine coupling, fluorine splitting resonances are reported as peaks: **<sup>13</sup>C NMR** (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  252.42, 252.14, 222.64, 221.58, 173.61, 161.94, 161.53, 160.61, 159.39, 158.99, 158.11, 158.03, 156.03, 154.77, 154.46, 153.99, 153.80, 151.14, 144.56, 143.74, 142.85, 142.77, 140.20, 139.69, 139.54, 136.93, 135.39, 134.54, 134.14, 132.29, 132.23, 132.19, 132.09, 131.61, 131.55, 131.52, 131.41, 131.36, 131.28, 131.18, 131.14, 131.08, 130.71, 130.69, 130.59, 130.49, 130.40, 130.10, 129.78, 129.74, 129.71, 129.49, 129.34, 129.30, 129.22, 128.98, 128.96, 128.91, 128.63, 128.61, 128.54, 128.36, 128.30, 128.22, 127.16, 125.74, 125.67, 125.56, 125.44, 125.35, 124.61, 124.20, 124.16, 123.65, 123.59, 122.96, 122.67, 122.55, 122.38, 122.34, 121.94, 120.97, 119.50, 117.16, 116.52, 114.58, 113.10, 113.07, 112.95, 112.92, 112.89, 112.85, 112.81, 112.76, 112.72, 112.64, 112.61, 112.57, 112.02, 108.16, 82.19, 80.80, 77.65, 76.20, 75.01, 69.62, 69.27, 68.50, 66.78, 66.40, 65.72, 62.56, 60.00, 48.96, 48.76, 38.65, 34.66, 34.48, 32.69, 32.48, 31.96, 31.65, 30.24, 29.92, 29.77, 29.66, 29.61, 29.30, 28.44, 28.41, 27.63, 26.97, 26.66, 26.62, 26.51, 26.48, 26.32, 25.93, 25.88, 25.38, 23.73, 23.25, 22.99, 22.49, 22.43, 22.39, 22.35, 22.31, 22.29, 22.24, 21.65, 21.55, 20.83, 20.22, 14.44, 14.35, 10.13.

**<sup>19</sup>F NMR** (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -102.19, -107.21, -109.43, -110.03, -110.92, -113.88, -114.12, -114.92, -115.37, -115.39, -116.50, -119.15, -119.17, -119.19.

**HRMS** (FAB<sup>+</sup>): [M]<sup>+</sup> C<sub>39</sub>H<sub>32</sub>Cl<sub>2</sub>F<sub>4</sub>N<sub>2</sub>ORu Calculated – 856.03134, Found – 856.03090

## Synthesis of *trans*-1,4-diacetoxy-2-butene



To a vial charged with a stir bar under argon atmosphere was added *trans*-2-butene-1,4-diol (5.00 g, 56.7 mmol), 4.9 mL dichloromethane, and Ac<sub>2</sub>O (18.2 mL, 0.192 mol) at 0 °C. Pyridine (14.0 mL, 0.174 mol) was then added dropwise to the reaction mixture. After 30 minutes, the reaction mixture was allowed to rise to room temperature and was stirred for an additional 18 h. Extraction of the product with DCM was followed by washing of the organic layer with 2M HCl, saturated aq. NaCl, and 2M aq. Na<sub>2</sub>CO<sub>3</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and solvents were removed *in vacuo*. The product was distilled at 120 mtorr at 110 °C (7.45 g, 76% yield). Spectroscopic data matched those previously reported in the literature.<sup>8</sup>

### General procedure for NMR initiation experiments.

*Trans*: To a vial containing catalyst (0.00275 mmol) was added THF-*d*<sub>8</sub> (506.5 μL) and *trans*-2-hexenyl acetate (43.5 μL, 0.275 mmol). This solution was transferred to a J. Young Tube and monitored by observing the disappearance of the benzyldene signal by <sup>1</sup>H NMR using an array at 45 °C.

### General procedure for cross metathesis of methyl 9-octadecenoate experiments.

To a vial charged with a stir bar, the appropriate amount of catalyst was added and dissolved in 383.1 μL THF. Tridecane (48.8 μL, 0.2 mmol) and methyl 9-octadecenoate (68.1 μL, 0.2 mmol) were then added and the vial was capped. At the specified time points, 5 μL aliquots were taken and quenched with butyl vinyl ether, and the product distribution was analyzed by GC.

**Table S1.** Time needed to reach equilibrium for reactions with methyl 9-octadecenoate with varying concentrations of catalysts, showing first-order with respect to catalyst.

entry	Starting Material	Ru	mol %	Time
1	<i>E</i>	2	2.0	1.5 h
			1.0	3 h
2	<i>E</i>	3	2.0	1.25 h
			1.0	2.5 h
3	<i>E</i>	4	1.0	30 min
			0.5	1 h
4	<i>E</i>	5	1.0	20 min
			0.5	40 min
5	<i>Z</i>	2	0.2	15 min
			0.1	30 min
6	<i>Z</i>	3	0.5	90 s
			0.05	15 min
7	<i>Z</i>	4	0.1	40 min
			0.2	20 min
8	<i>Z</i>	5	0.1	50 min
			0.2	25 min

**General procedure for cross metathesis of *trans*-4-octene and *trans*-1,4-diacetoxy-2-butene experiments.**

To a vial charged with a stir bar, catalyst (0.0192 mmol) was added and dissolved in 294.8  $\mu\text{L}$  THF. 147.4  $\mu\text{L}$  THF of this catalyst stock solution was added to a vial containing *trans*-1,4-diacetoxy-2-butene (30.6  $\mu\text{L}$ , 0.128 mmol), *trans*-4-octene (120.4  $\mu\text{L}$ , 0.512 mmol), and a stir bar. The vial was capped, and the reaction mixture was stirred. At the specified time points, 3  $\mu\text{L}$  aliquots were added to a septum-capped NMR tube to which was added  $\text{CDCl}_3$ , and the product distribution was analyzed by  $^1\text{H}$  NMR. Stereoselectivity of the product was determined by GC.

**General procedure for cross metathesis of *cis*-4-octene and *cis*-1,4-diacetoxy-2-butene experiments.**

To a vial was added catalyst (0.0128 mmol) that was dissolved in 294.8  $\mu\text{L}$  THF. 147.4  $\mu\text{L}$  of this catalyst stock solution was added to a vial containing *cis*-1,4-diacetoxy-2-butene (30.6  $\mu\text{L}$ , 0.128 mmol), *cis*-4-octene (120.4  $\mu\text{L}$ , 0.512 mmol), and stir bar. The vial was capped, and the reaction mixture was stirred. At the specified time points, 3  $\mu\text{L}$  aliquots were added to a septum-capped NMR tube to which was added  $\text{CDCl}_3$ , and the product distribution was analyzed by  $^1\text{H}$  NMR. Stereoselectivity of the product was determined by GC.

**General procedure for cross metathesis of *cis/trans*-4-octene and 1-decene.**

To a vial was added catalyst (0.0072 mmol) that was dissolved in 870.8  $\mu\text{L}$  THF. 435.4  $\mu\text{L}$  of the catalyst stock solution was added to a vial containing tetradecane (15.6  $\mu\text{L}$ , 0.06 mmol), 4-octene (37.6  $\mu\text{L}$ , 0.24 mmol), 1-decene (11.4  $\mu\text{L}$ , 0.06 mmol), and a stir bar. The vial was capped, and the reaction mixture was stirred. At the specified time points, 20  $\mu\text{L}$  aliquots were quenched with butyl vinyl ether, and the product distribution was analyzed by GC.

**GC Methods**

Self-Metathesis of MO (Conversion and Selectivity) and Cross Metathesis of 4-Octene and 1-Decene (Conversion)

HP-5 Agilent Column 30m  $\times$  0.25mm (ID)  $\times$  0.25 $\mu\text{m}$  film thickness

Injector temperature: 250  $^\circ\text{C}$

Detector temperature: 350  $^\circ\text{C}$

Oven temperature: Starting temperature: 50  $^\circ\text{C}$ , hold time: 2 min.

Ramp rate: 11  $^\circ\text{C}/\text{min}$  to 300  $^\circ\text{C}$ , hold time: 3 min.

Carrier gas: He

Average velocity: 31 cm/s

Split ratio: 48.9:1

Cross Metathesis of 4-Octene and 1,4-Diacetoxy-2-butene (Selectivity) and Cross Metathesis of 4-Octene and 1-Decene (Selectivity)

DB-1 Agilent Column 10 m × 0.100mm (ID) × 0.40µm film thickness

Injector temperature: 250 °C

Detector temperature: 350 °C

Oven temperature: Starting temperature: 35 °C, hold time: 0.5 min.

Ramp rate: 10 °C/min to 135 °C, hold time: 0 min., 20 °C/min to 290 °C

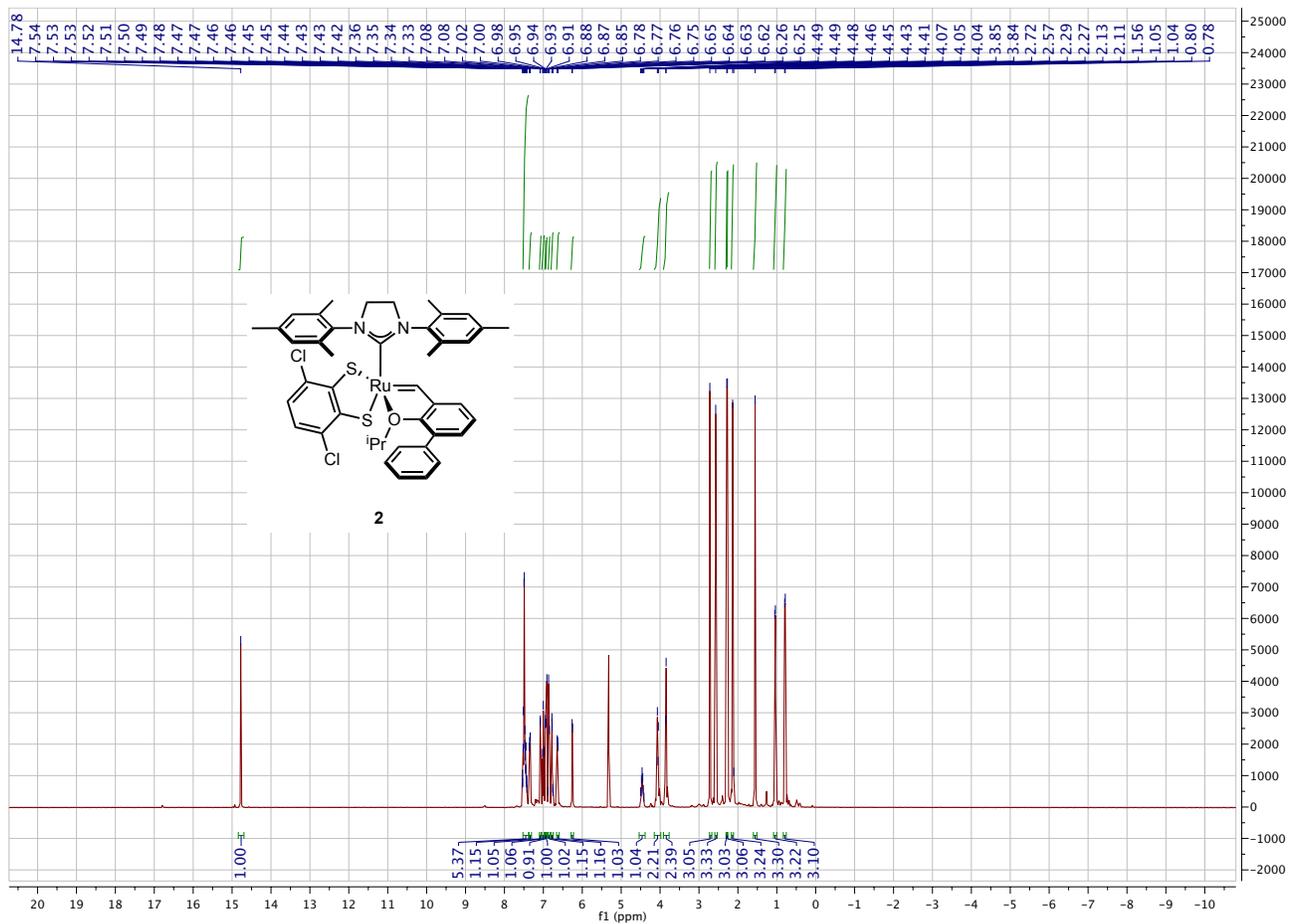
Carrier gas: He

Average velocity: 20 cm/s

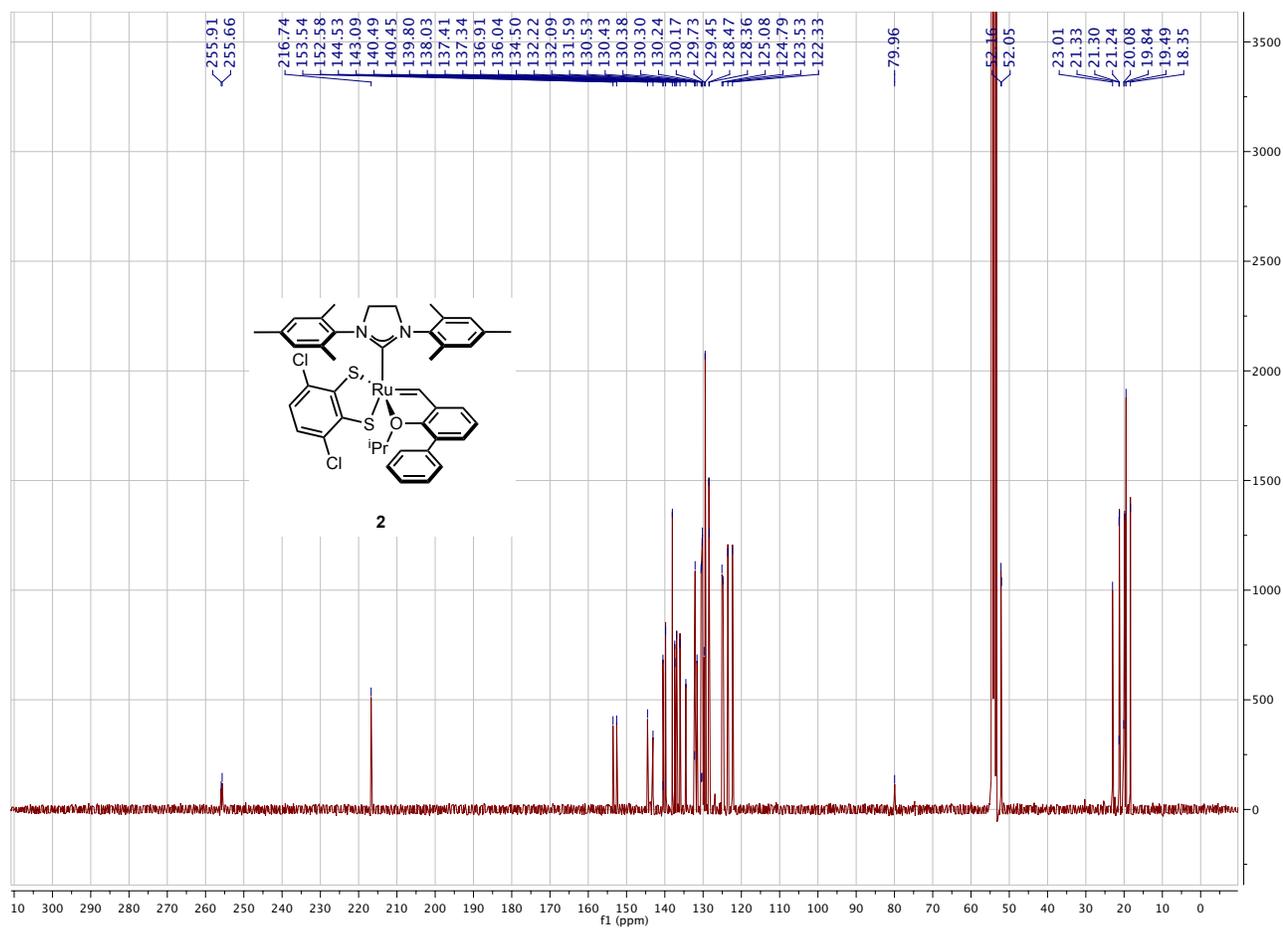
Split ratio: 103:1

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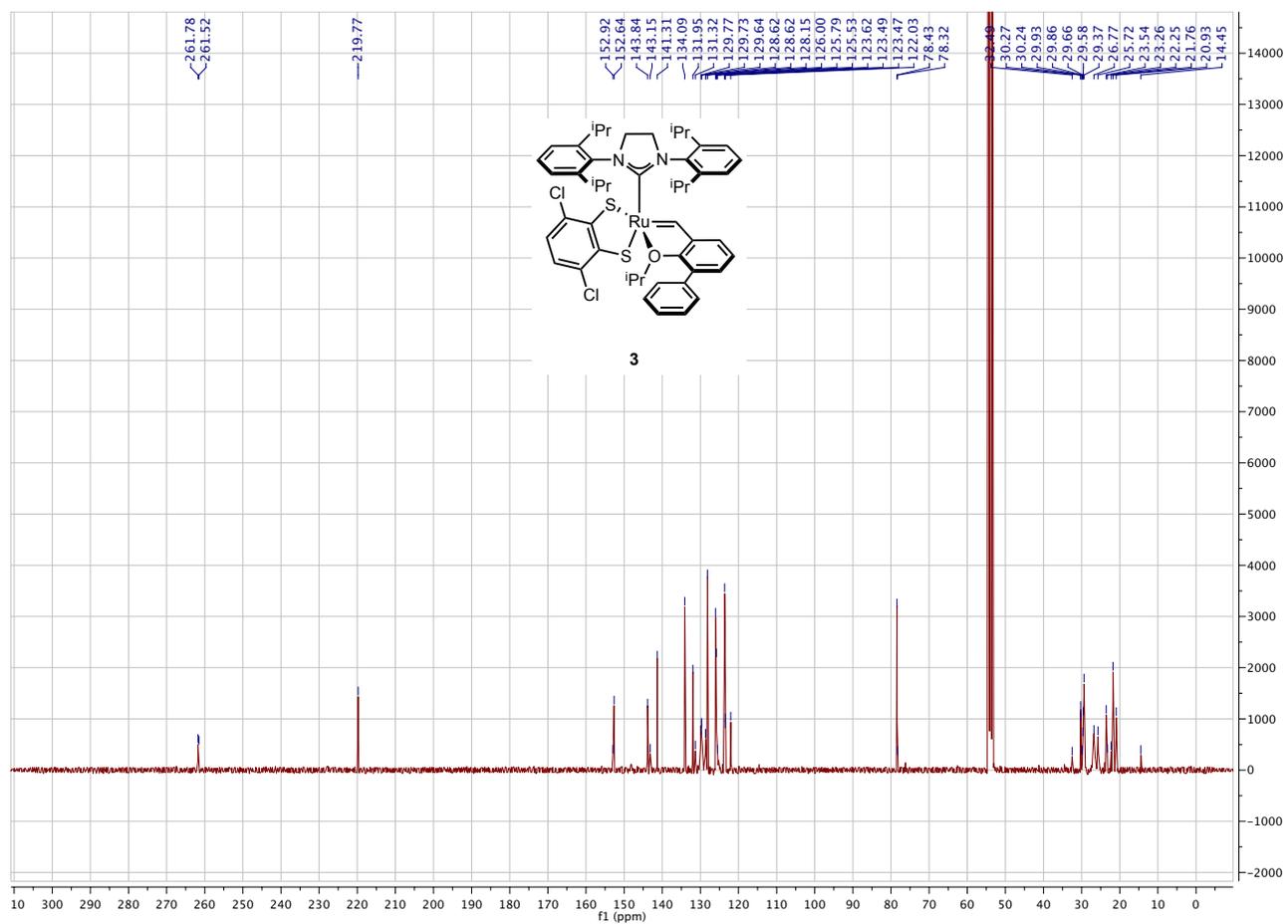


$^1\text{H}$  NMR of Catalyst **2** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )

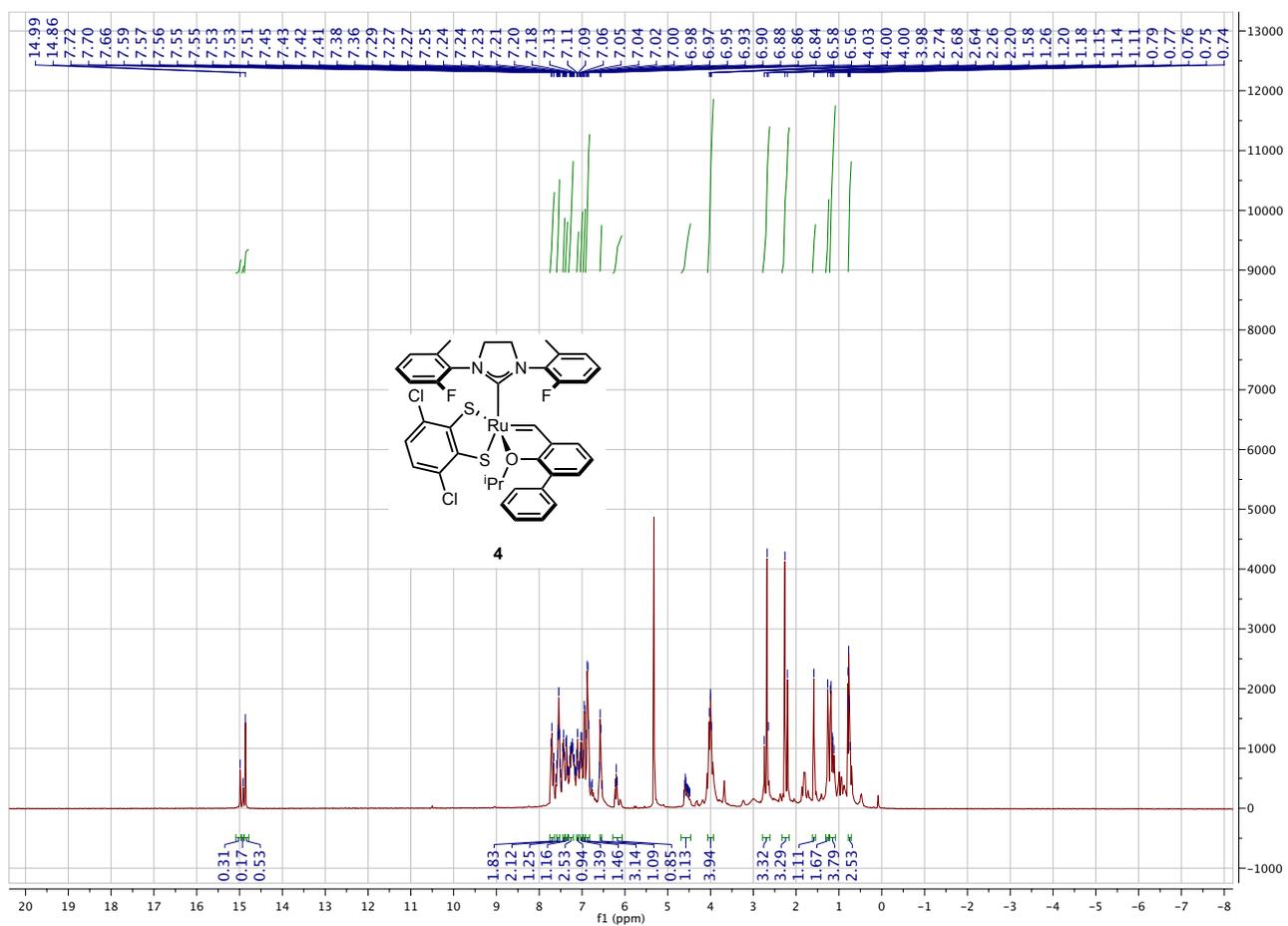


$^{13}\text{C}$  NMR of Catalyst 2 in (101 MHz,  $\text{CD}_2\text{Cl}_2$ )

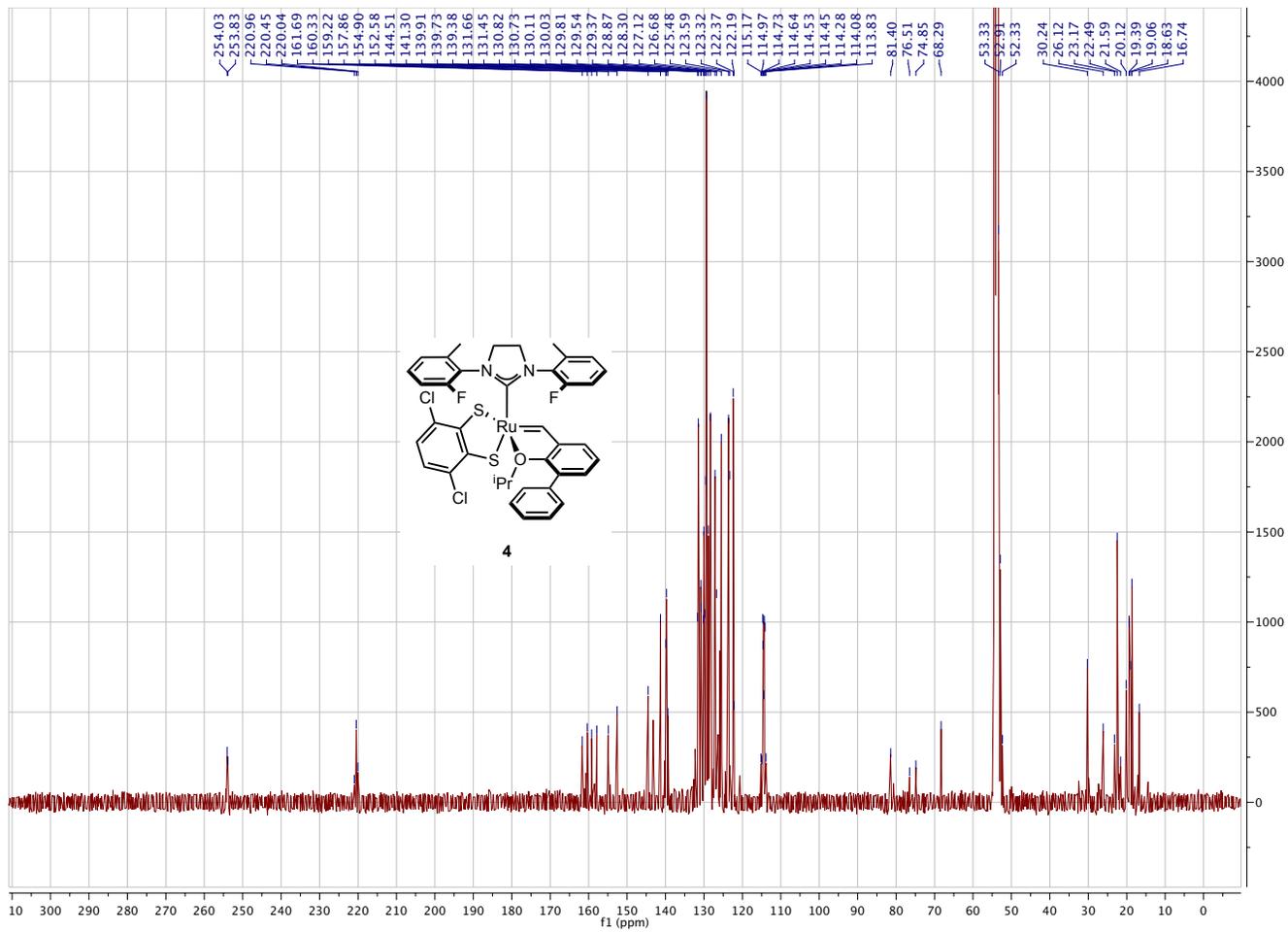




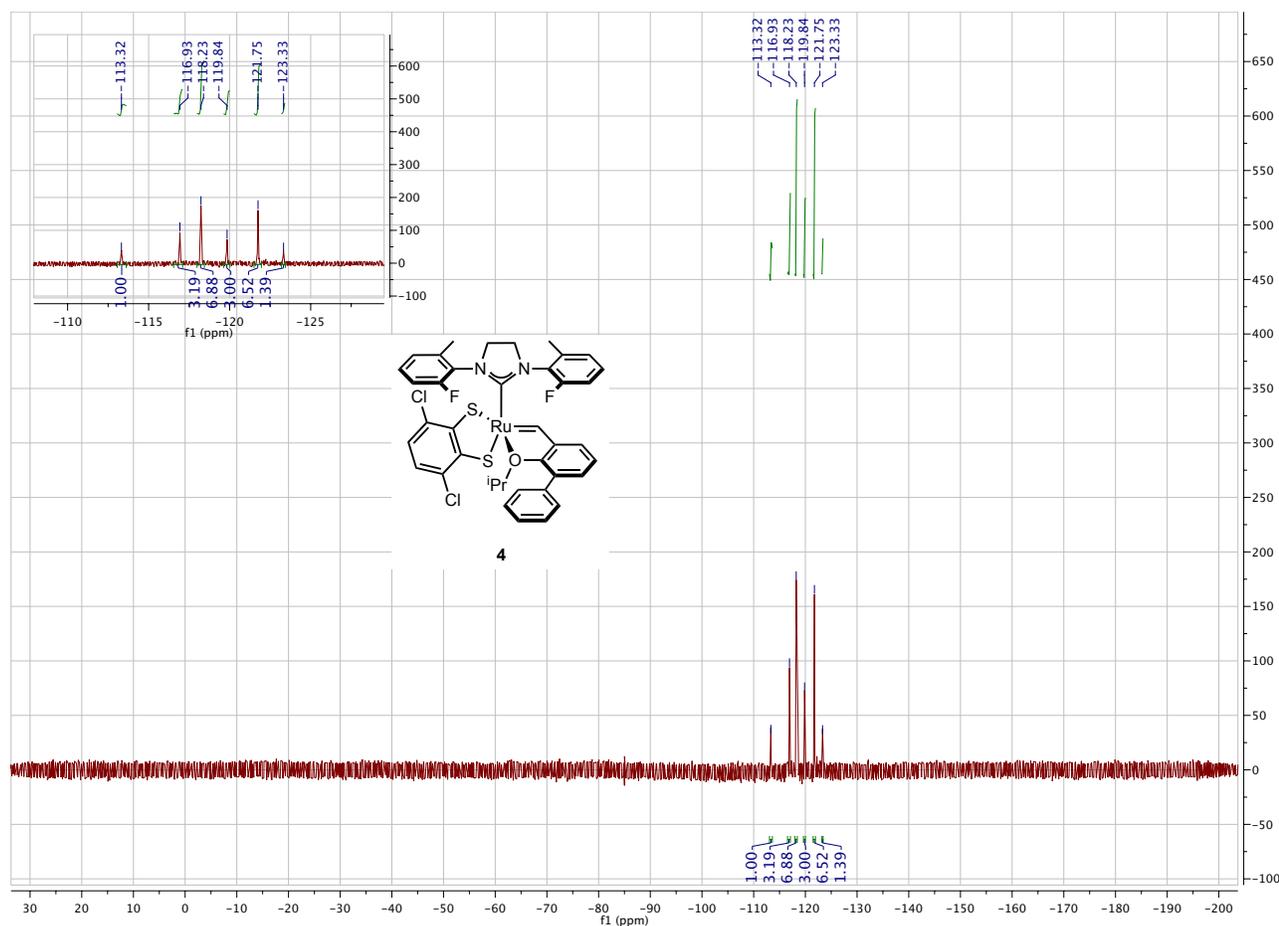
$^{13}\text{C}$  NMR of Catalyst **3** in (101 MHz,  $\text{CD}_2\text{Cl}_2$ )



<sup>1</sup>H NMR of Catalyst 4 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

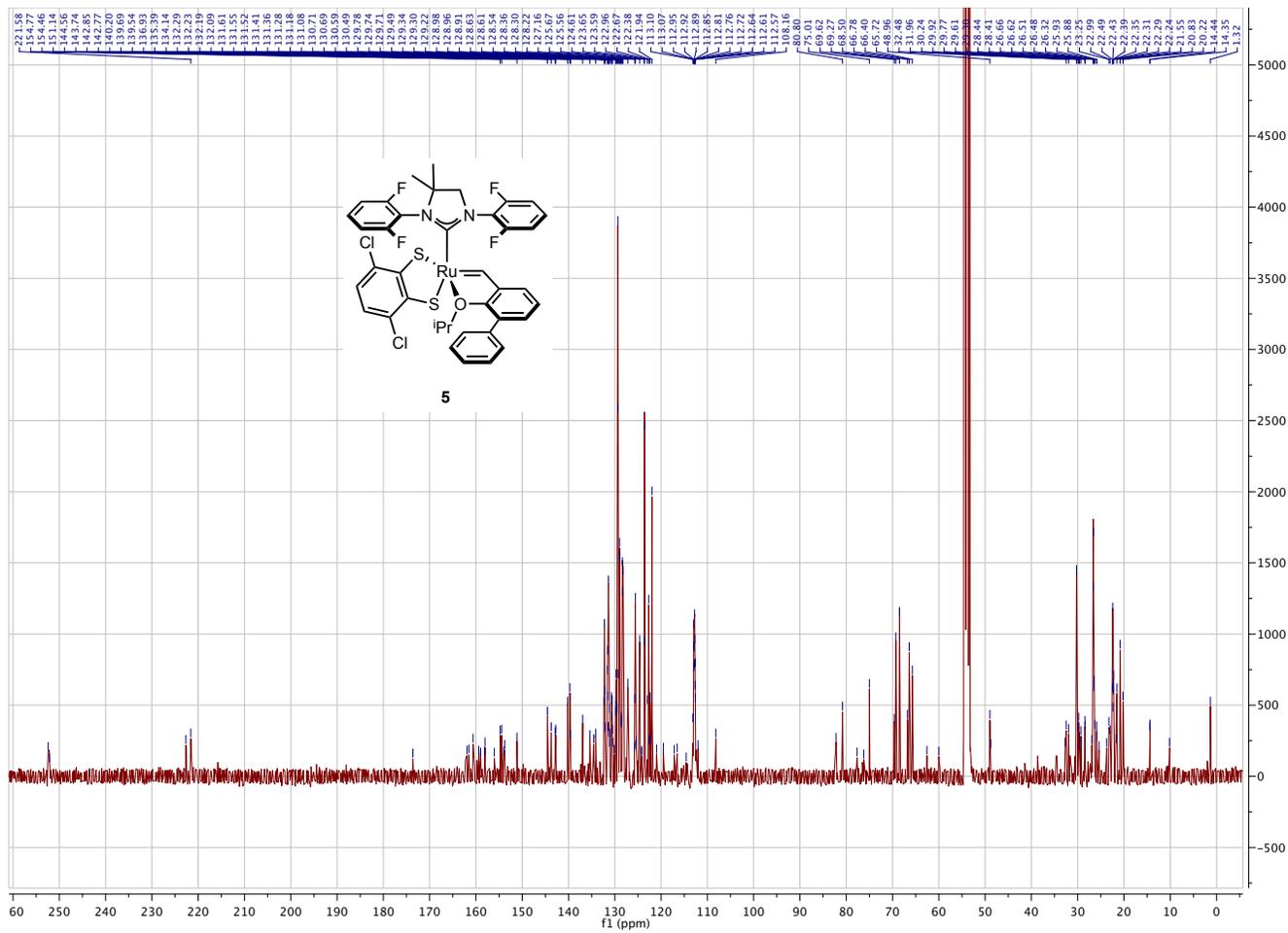


<sup>13</sup>C NMR of Catalyst **4** in (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

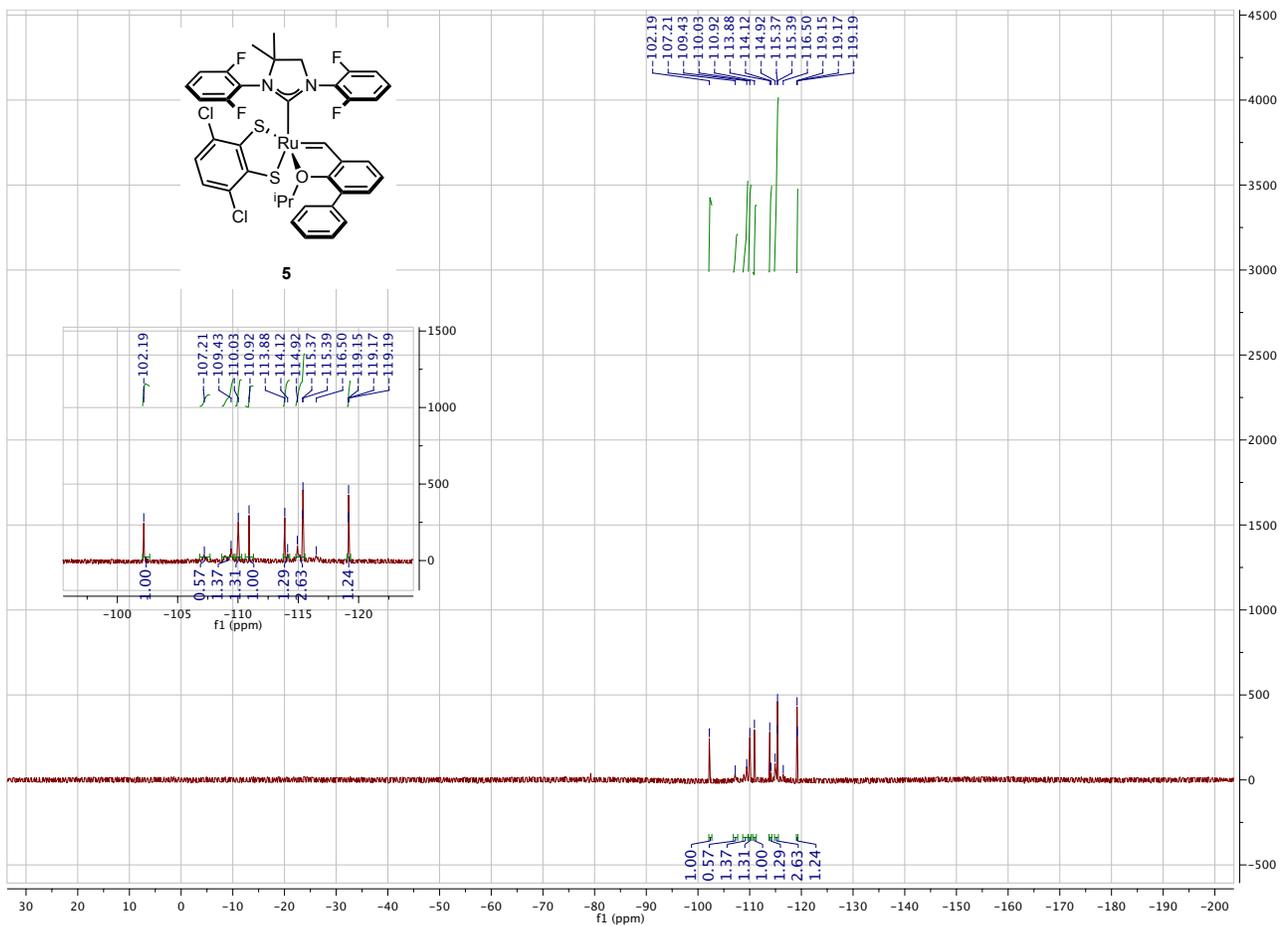


$^{19}\text{F}$  NMR of Catalyst **4** in (376 MHz,  $\text{CD}_2\text{Cl}_2$ )

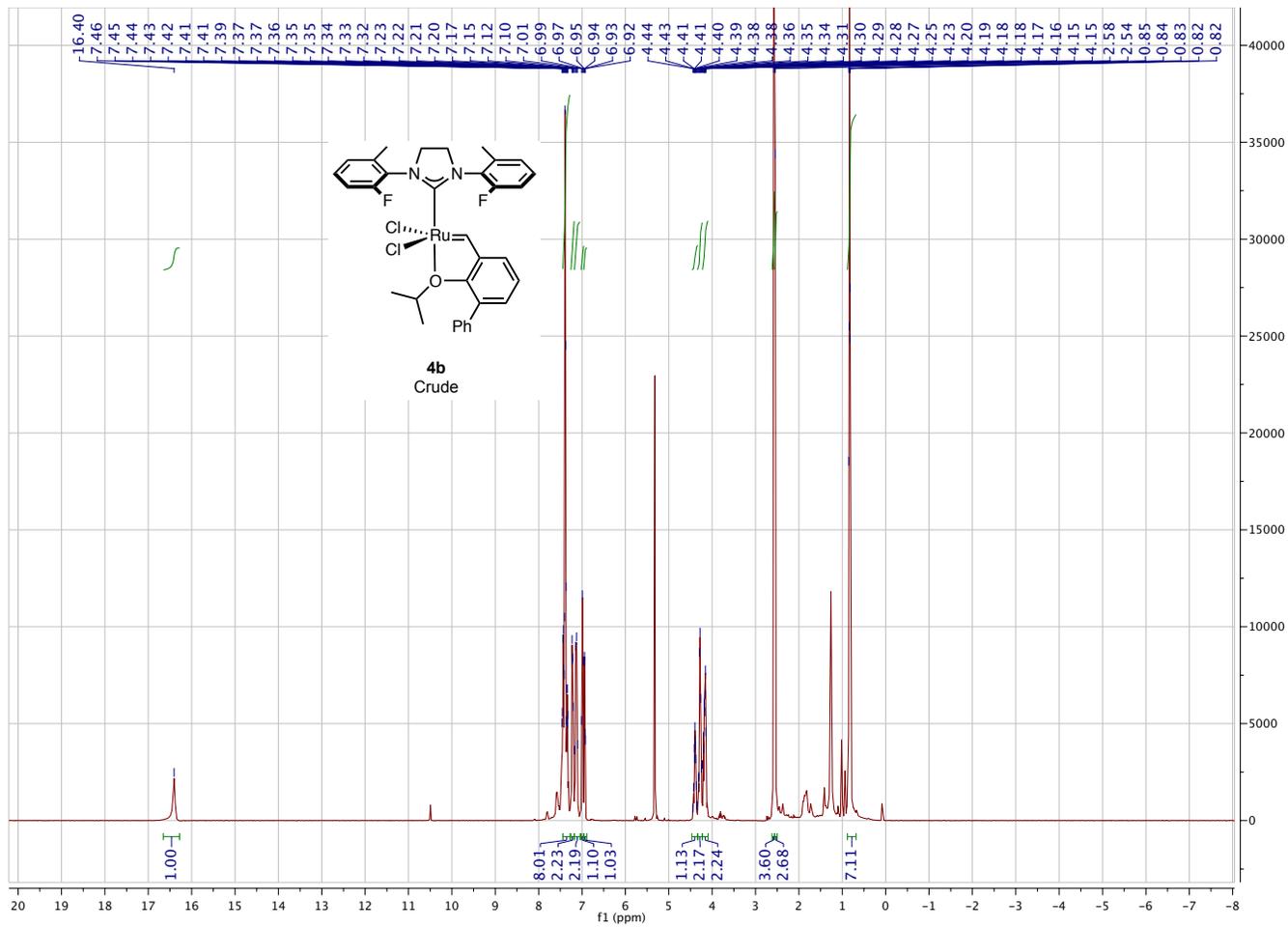




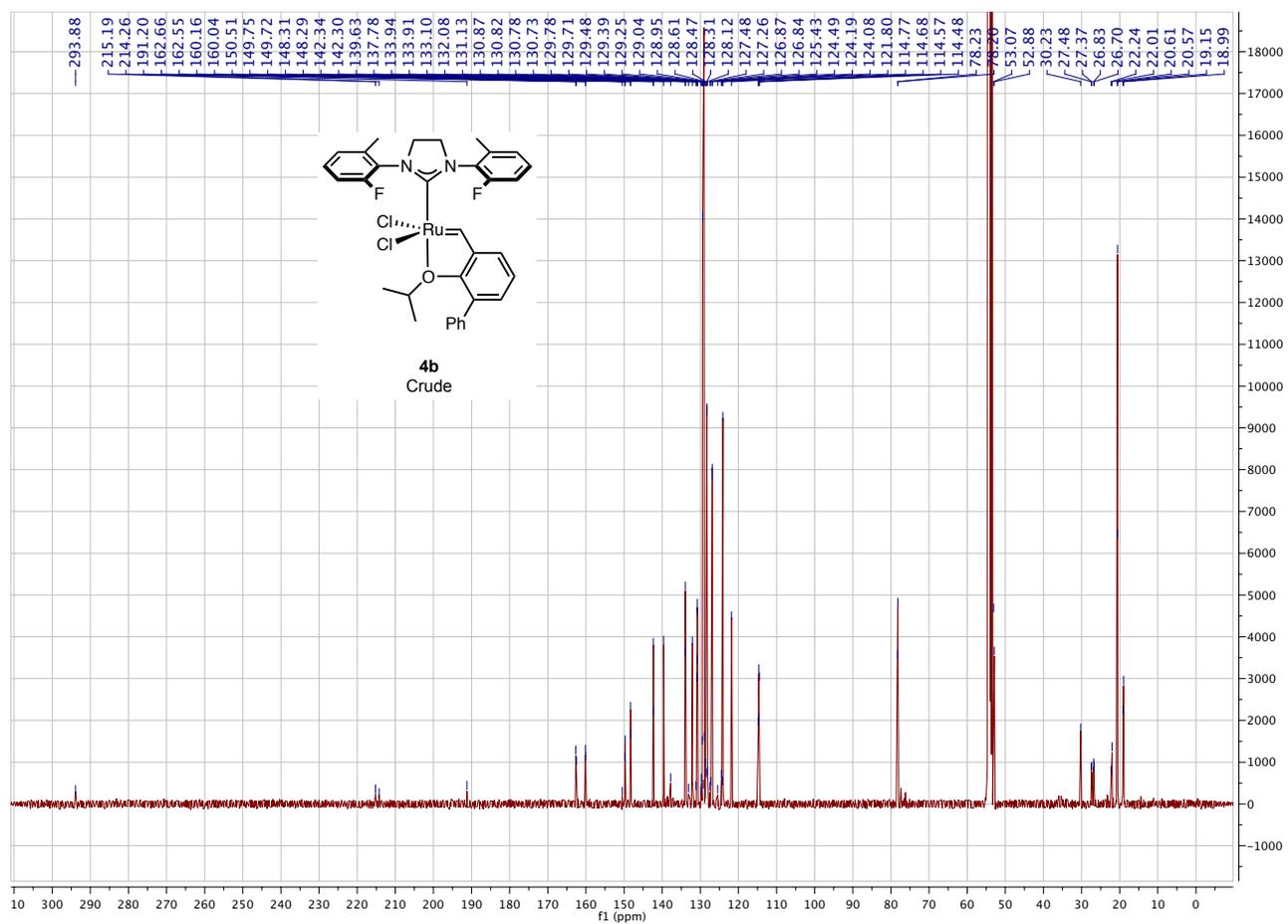
$^{13}\text{C}$  NMR of Catalyst **5** in (101 MHz,  $\text{CD}_2\text{Cl}_2$ )



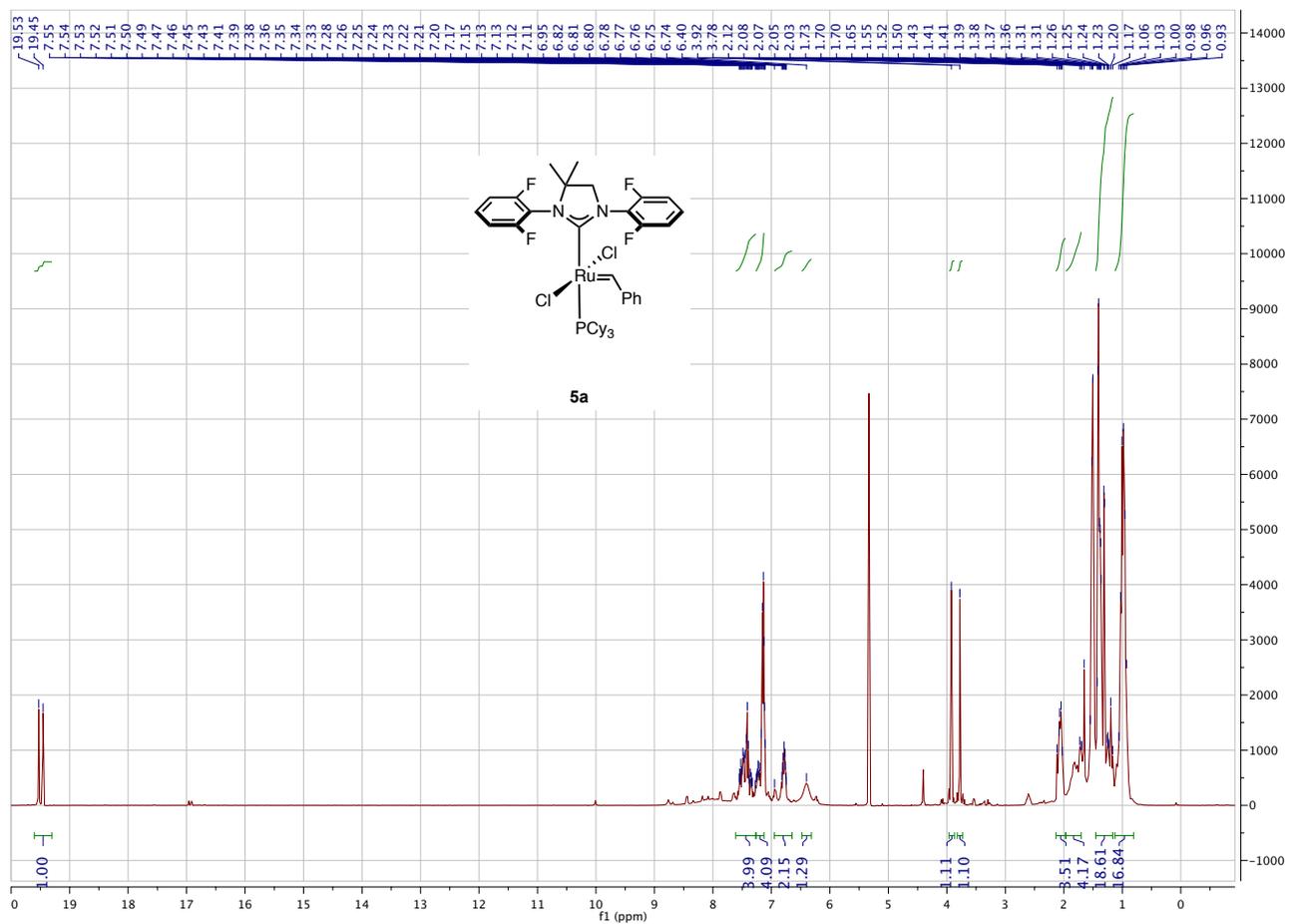
<sup>19</sup>F NMR of Catalyst **5** in (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



<sup>1</sup>H NMR of Catalyst Crude **4b** in (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

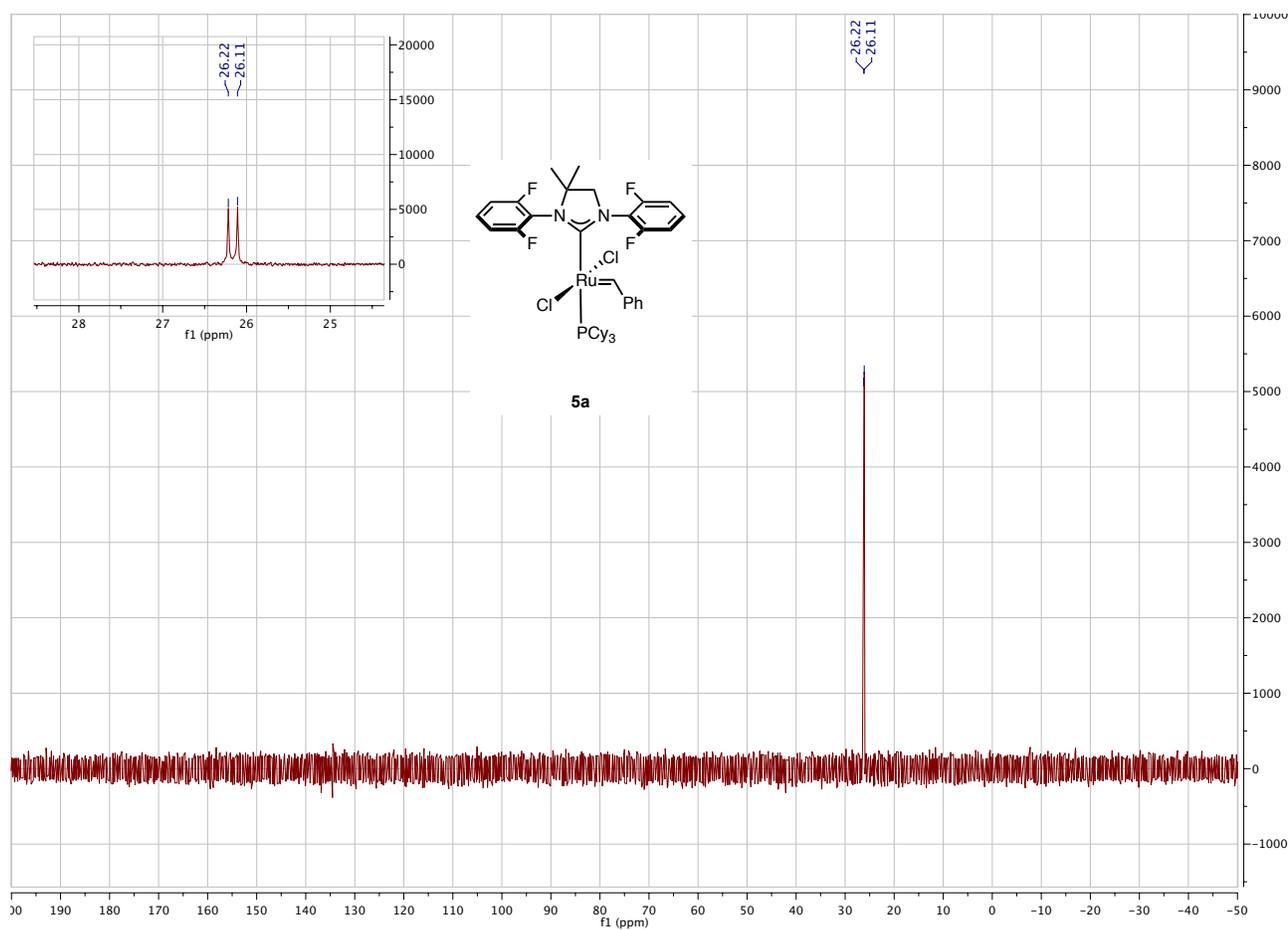


$^{13}\text{C}$  NMR of Catalyst Crude **4b** in (101 MHz,  $\text{CD}_2\text{Cl}_2$ )



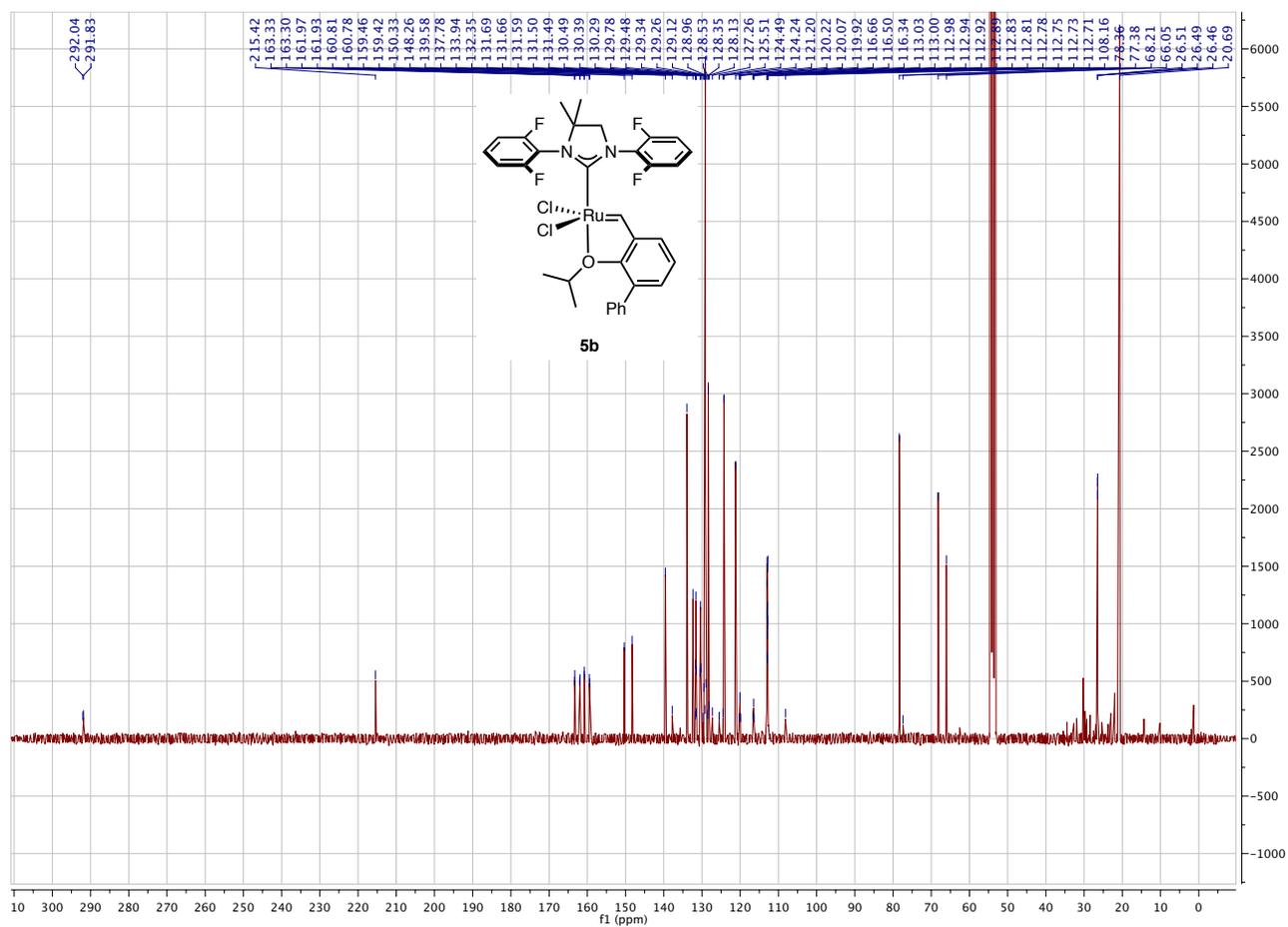
$^1\text{H}$  NMR of Catalyst **5a** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )



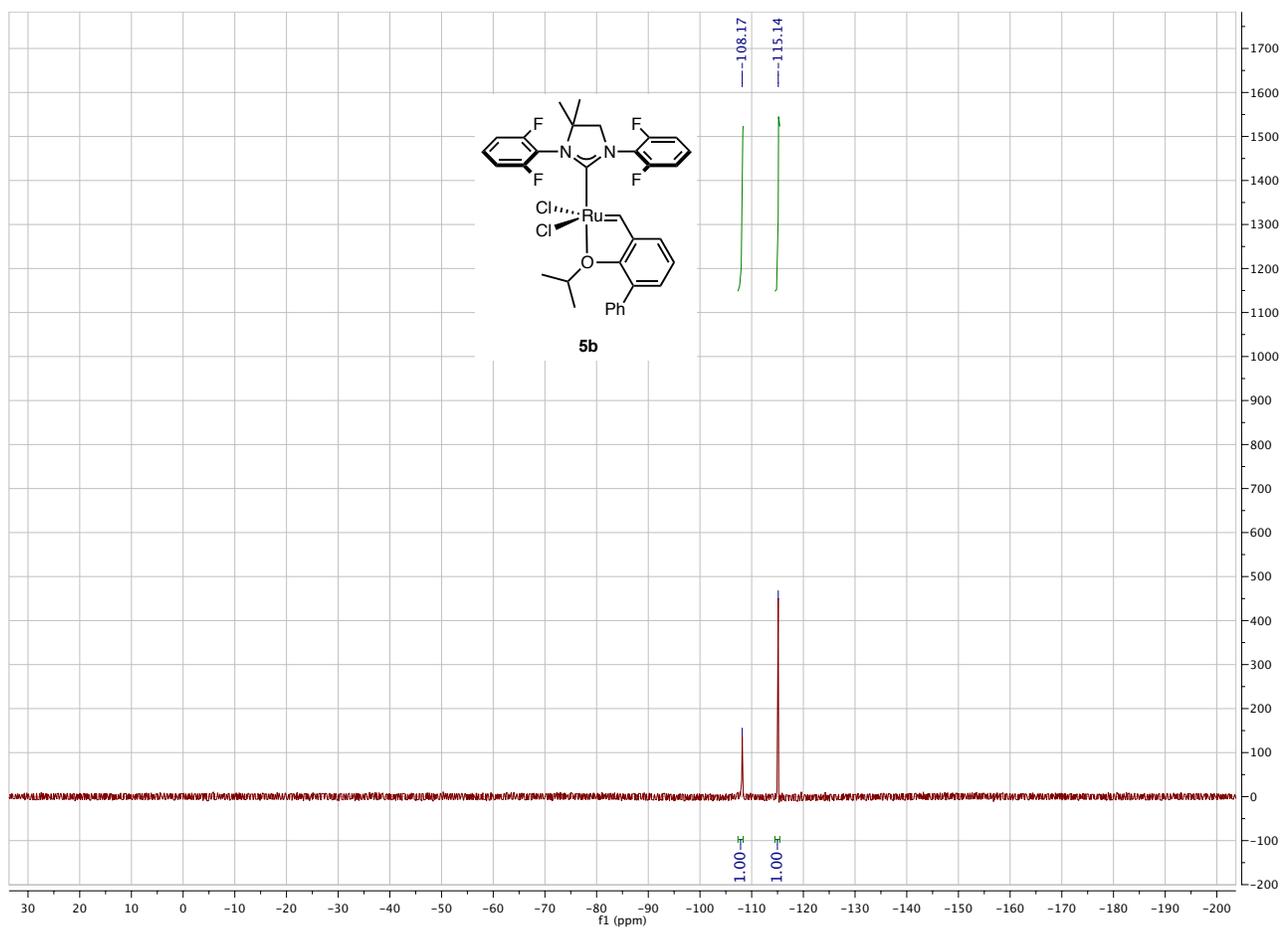


$^{31}\text{P}$  NMR of Catalyst **5a** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )





$^{13}\text{C}$  NMR of Catalyst **5b** in (101 MHz,  $\text{CD}_2\text{Cl}_2$ )



$^{19}\text{F}$  NMR of Catalyst **5b** in (376 MHz,  $\text{CD}_2\text{Cl}_2$ )