

Supporting Information

Ruthenium Olefin Metathesis Catalysts Featuring a Labile Carbodicarbene Ligand

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General Considerations.

All experiments were conducted using standard Schlenk techniques or in a nitrogen atmosphere glovebox. All solvents were dried by passage through solvent purification columns, further degassed with argon, and stored over activated 3Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratory and were degassed and dried prior to use. Ethyl vinyl ether was degassed and stored over 3Å molecular sieves.

$(\text{H}_2\text{IMes})(\text{py})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$,¹ $(\text{H}_2\text{IPr})(\text{py})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$,² carbodicarbene **1**,³ *endo,exo*-norbornenyl diethyl diester,⁴ and 2-isopropoxy- β -methylstyrene⁵ were prepared according to literature procedures.

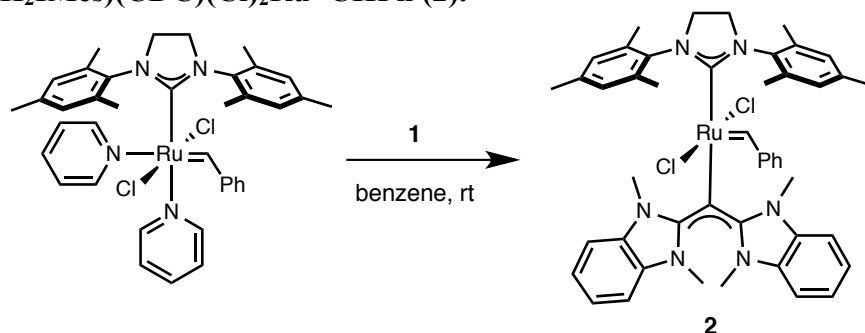
Standard NMR spectroscopic experiments were performed using a Varian Inova 400 MHz spectrometer, and kinetics experiments were conducted on a Varian 600 MHz spectrometer with an AutoX probe. ^1H were calibrated internally to the residual proteo solvent relative to tetramethylsilane. Spectra were analyzed using MestReNova Ver. 10.0 software.

SEC data were collected using two Agilent PLgel MIXED-B 300×7.5 mm columns with 10 μm beads, connected to an Agilent 1260 Series pump, a Wyatt 18- angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. The SEC mobile phase was THF. Online determination of dn/dc assumed 100% mass elution under the peak of interest.

High-resolution mass spectrometry (HRMS) data was obtained using an Autoflex MALDI-TOF instrument for solvent free samples with a benzyldiene malononitrile matrix (complexes **2** and **3**) or on a JEOL MSRoute mass spectrometer using FAB+ ionization (complexes **4** and **5**).

The purity of complexes **2** and **3** was established by NMR spectroscopy.

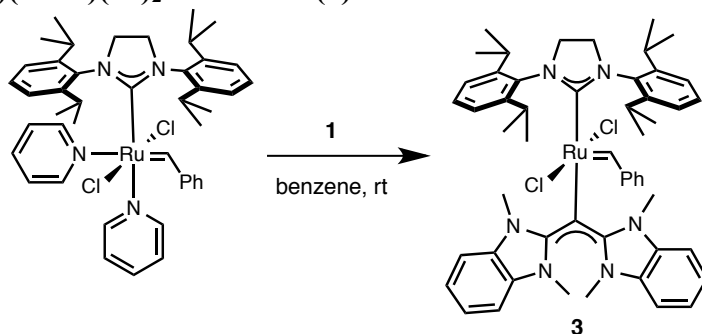
Synthesis of $(\text{H}_2\text{IMes})(\text{CDC})(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**2**).



In a glovebox, a 20 mL scintillation vial was charged with $(\text{H}_2\text{IMes})(\text{py})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (68.2 mg, 0.094 mmol), carbodicarbene **1** (31.4 mg, 0.103 mmol) and benzene (8 mL). Over 5 minutes, the solution changed in color from green to orange. After stirring at 25 °C for 3 hours, the solution was concentrated *in vacuo* to afford an orange solid and was triturated twice with pentane (5 mL). The orange powder was dissolved in 2 mL of THF, filtered through Celite, layered with diethyl ether (8 mL), and stored at -30 °C to afford orange crystals of $(\text{H}_2\text{IMes})(\text{CDC})(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**2**, 76.1 mg, 93% yield). ^1H NMR (400 MHz, C_6D_6) δ 19.62 (s, 1H, $\text{Ru}=\text{CHPh}$), 9.17 (br s, 1H, *o*-Ph), 6.91 (overlapping m, 4H, CDC and *m*-Mes), 6.81 (s, 1H, *m*-Mes), 6.65 (overlapping m, 4H, CDC and Ph), 6.43 (overlapping m, 4H, CDC and Ph), 6.18 (br s, 2H, CDC), 5.84 (s, 1H, *m*-Mes), 3.36 (m, 4H, $\text{H}_2\text{IMes NCH}_2\text{CH}_2\text{N}$), 3.25 (br, 12H, CDC),

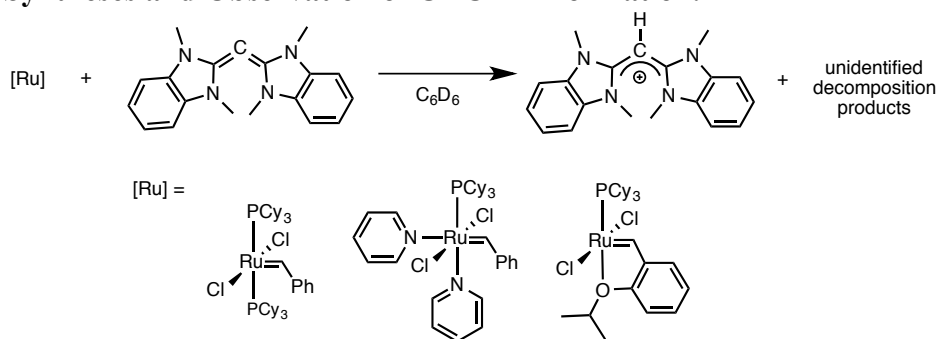
3.10 (s, 3H, Mes), 2.86 (s, 3H, Mes), 2.71 (s, 3H, Mes), 2.23 (s, 3H, Mes), 2.05 (s, 3H, Mes), 1.89 (s, 3H, Mes); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ 291.80 (Ru=CHPh), 224.58 ($\text{H}_2\text{IMes NCN}$), 163.40 (CDC NCN), 151.62 (Ph), 148.05 (Ph), 139.75 (Mes), 139.37 (Mes), 138.96 (Mes), 138.92 (Mes), 138.26 (Mes), 138.06 (Mes), 137.66 (Mes), 137.15 (Mes), 131.14 (Ph), 130.65 (*m*-Mes), 130.30 (*m*-Mes), 129.61 (*m*-Mes), 129.08 (*m*-Mes), 122.38 (Ph), 119.37 (CDC), 109.61 (CDC), 104.05 (CDC), 73.01 (CDC central carbon), 51.74 ($\text{H}_2\text{IMes NCH}_2\text{CH}_2\text{N}$), 51.46 ($\text{H}_2\text{IMes NCH}_2\text{CH}_2\text{N}$), 31.23 (CDC N-CH₃), 21.16 (Mes), 21.05 (Mes), 20.43 (Mes), 20.13 (Mes), 19.32 (Mes), 18.74 (Mes). HRMS (MALDI-TOF) m/z Calculated for $\text{C}_{47}\text{H}_{52}\text{N}_6\text{RuCl}$ [$\text{M}-\text{HCl}$]: 837.299; Found: 837.299.

Synthesis of $(\text{H}_2\text{IPr})(\text{CDC})(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**3**).



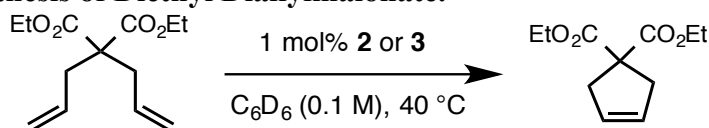
In a glovebox, a 20 mL scintillation vial was charged with $(\text{H}_2\text{IPr})(\text{py})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (58.6 mg, 0.0722 mmol), carbodicarbene **1** (25.2 mg, 0.0828 mmol) and benzene (8 mL). Over 5 minutes, the solution changed in color from green to orange. After stirring at 25 °C for 2 hours, the solution was concentrated *in vacuo* and triturated twice with pentane (5 mL). The orange powder was dissolved in benzene (4 mL) and additional carbodicarbene **1** (10.2 mg, 0.0316 mmol) was added. After 30 minutes, volatile components were removed *in vacuo*. The solid was dissolved in a mixture of diethyl ether (10 mL) and THF (3 mL), filtered through Celite, and stored at -30 °C to afford orange crystals of $(\text{H}_2\text{IPr})(\text{CDC})(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**3**, 52.2 mg, 75% yield). ^1H NMR (400 MHz, C_6D_6) δ 19.67 (s, 1H, Ru=CHPh), 7.39 (s, 4H, Ph and DIPP), 7.22 (br d, 1H, DIPP), 6.97 (t, $J = 8\text{Hz}$, 1H, Ph), 6.87 (m, 2H, CDC), 6.64 (m, 3H, CDC and Ph), 6.53 (br d, 1H, DIPP), 6.46 (t, $J = 8\text{Hz}$, 2H, DIPP), 6.38 (br m, 2H, CDC), 6.17 (m, 2H, CDC), 4.77 (br s, 1H, $\text{CH}(\text{CH}_3)_2$), 4.39 (br s, 1H, $\text{CH}(\text{CH}_3)_2$), 3.97 (s, 2H, $\text{H}_2\text{IPr NCH}_2\text{CH}_2\text{N}$), 3.85 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.76 (m, 1H, $\text{H}_2\text{IPr NCH}_2\text{CH}_2\text{N}$), 3.52 (m, 1H, $\text{H}_2\text{IPr NCH}_2\text{CH}_2\text{N}$), 3.28 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.17 (s, 6H, CDC N-CH₃), 2.75 (br s, 6H, CDC N-CH₃), 2.01 (s, 3H, $\text{CH}(\text{CH}_3)_2$), 1.71 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.36 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 1.28 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 1.19 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 1.05 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 0.98 (m, 3H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ 294.30 (Ru=CHPh), 227.09 ($\text{H}_2\text{IPr NCN}$), 162.36 (CDC NCN), 150.85 (Ph), 149.74 (DIPP), 147.54 (Ph), 139.89 (DIPP), 139.29 (DIPP), 136.43 (DIPP), 130.97 (CDC), 129.27 (Ph), 125.62 (DIPP), 124.87 (Ph), 124.22 (DIPP), 123.91 (DIPP), 121.89 (CDC), 119.34 (CDC), 108.90 (CDC), 104.23 (CDC), 73.37 (CDC central C), 54.70 ($\text{H}_2\text{IMes NCH}_2\text{CH}_2\text{N}$), 54.21 ($\text{H}_2\text{IMes NCH}_2\text{CH}_2\text{N}$), 30.65 (CDC N-CH₃), 30.24 (CDC N-CH₃), 28.64 ($\text{CH}(\text{CH}_3)_2$), 28.24 ($\text{CH}(\text{CH}_3)_2$), 27.61 ($\text{CH}(\text{CH}_3)_2$), 26.91 ($\text{CH}(\text{CH}_3)_2$), 26.58 ($\text{CH}(\text{CH}_3)_2$), 26.56 ($\text{CH}(\text{CH}_3)_2$), 26.40 ($\text{CH}(\text{CH}_3)_2$), 26.32 ($\text{CH}(\text{CH}_3)_2$), 26.08 ($\text{CH}(\text{CH}_3)_2$), 24.59 ($\text{CH}(\text{CH}_3)_2$), 24.10 ($\text{CH}(\text{CH}_3)_2$), 22.97 ($\text{CH}(\text{CH}_3)_2$). HRMS (MALDI-TOF) m/z Calculated for $\text{C}_{53}\text{H}_{64}\text{N}_6\text{RuCl}$ [$\text{M}-\text{HCl}$]: 921.392; Found: 921.394.

Attempted Syntheses and Observation of CDC-H⁺ Formation.



Representative procedure: A solution of (PCy₃)₂(Cl)₂Ru=CHPh (6.6 mg, 0.0080 mmol) and CDC **1** (2.5 mg, 0.0080 mmol) was prepared in benzene-*d*₆ (0.8 mL). After 24 hours, CDC-H⁺ had precipitated as a pale yellow powder, and was washed with Et₂O (5 mL) and dried *in vacuo*. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.38 (m, 8H), 5.23 (s, 1H), 3.64 (s, 12H); ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 153.89, 133.58, 124.53, 110.43, 51.47, 33.06. HRMS (FAB⁺) : *m/z* Calculated for C₁₉H₂₁N₄ [M⁺]: 305.1766; Found: 305.1762.

Ring-Closing Metathesis of Diethyl Diallylmalonate.



In a glovebox, a solution of catalyst **2** or **3** (0.00080 mmol) in 0.80 mL of benzene-*d*₆ was prepared in a J. Young NMR tube and frozen using a glovebox cold well. An internal standard, 1,3,5-tris(trifluoromethyl)benzene (1 μL) and diethyl diallylmalonate (19.3 μL, 0.0800 mmol) were added, and the NMR tube was stored at 0 °C before use. The tube was placed in an NMR spectrometer with the temperature pre-equilibrated to 40 °C. Disappearance of diethyl diallylmalonate and appearance of 4,4-dicarbethoxy-1-cyclopentene were monitored by comparing the ratio of integrals for the methylene protons of these compounds (δ = 2.86 (dt) and 3.16 (s), respectively).

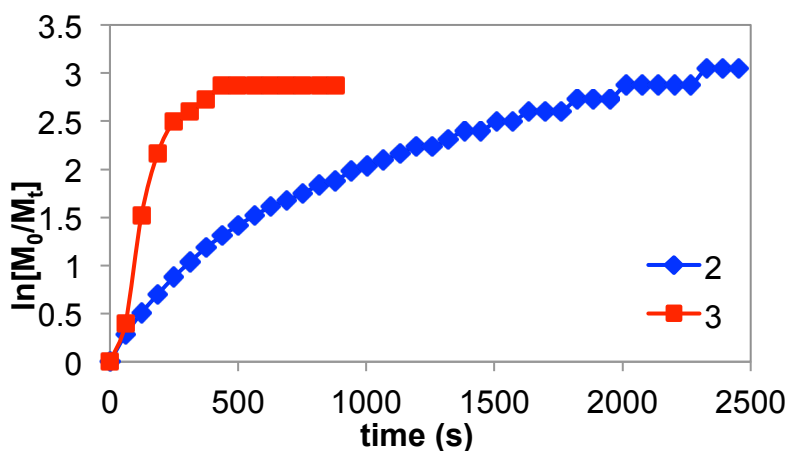
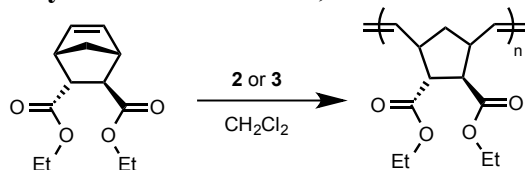


Figure S1. Log plots for the ring-closing metathesis of diethyl diallylmalonate with catalysts **2** and **3**.

Ring-Opening Metathesis Polymerization of *endo,exo*-Norbornenyl Diethyl Diester (DEE)



A solution of **DEE** (23.8 mg, 0.100 mmol) in dichloromethane (1.75 mL) was prepared in a glovebox. While stirring, a solution of catalyst **2** or **3** (0.00080 mmol) in dichloromethane (0.25 mL) was added. Aliquots (~50 μL) were taken at different time points throughout the reaction and immediately quenched in separate vials containing ethyl vinyl ether (0.1 mL) in THF (0.9 mL). The quenched aliquots were analyzed by SEC and ^1H NMR spectroscopy.

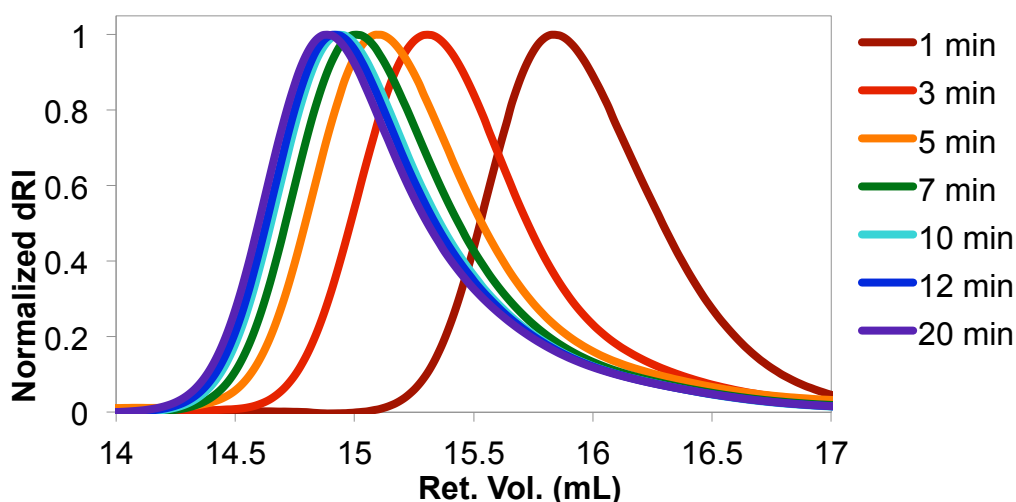


Figure S2. Size exclusion chromatograms for ROMP of **DEE** by catalyst **2**.

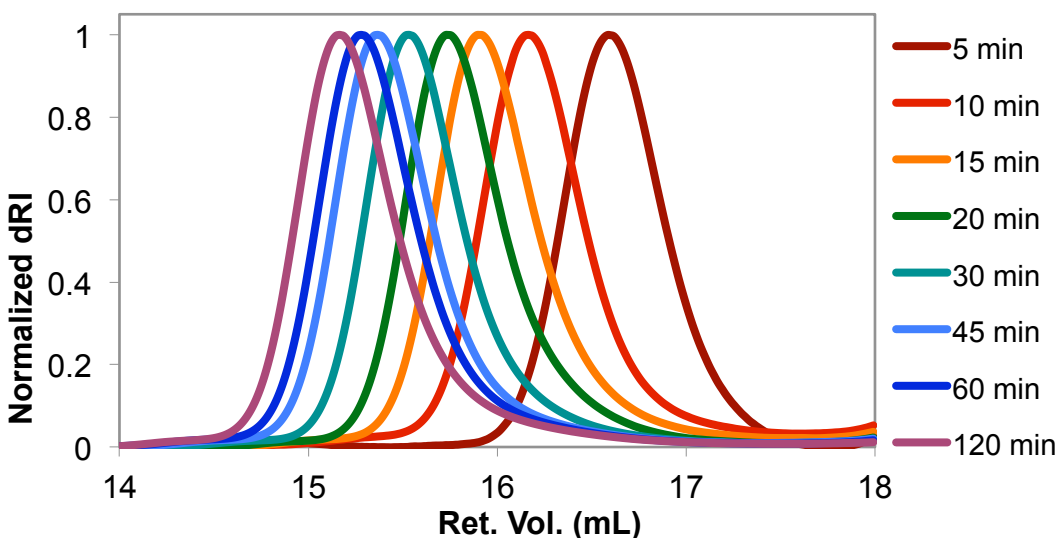
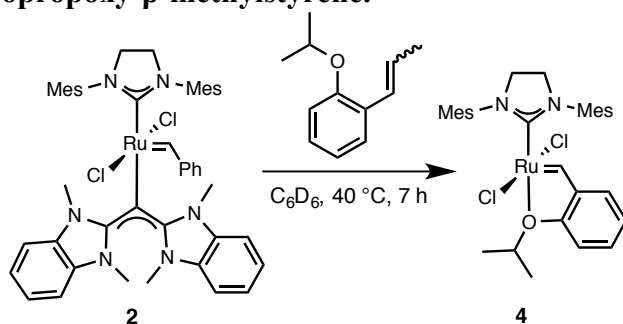


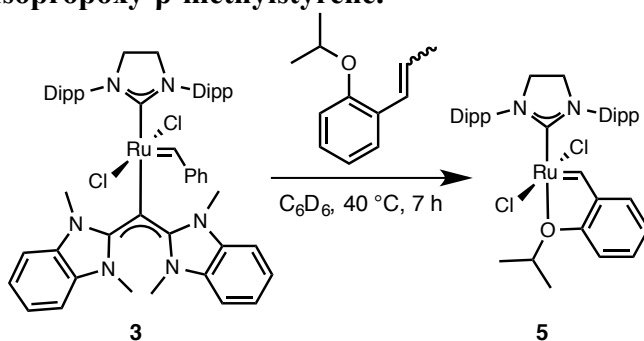
Figure S3. Size exclusion chromatograms for ROMP of **DEE** by catalyst **3**.

Reaction of **2** with 2-Isopropoxy- β -methylstyrene.



In a glovebox, a solution of complex **2** (2.6 mg, 0.0030 mmol), 2-isopropoxy- β -methylstyrene (1.6 μ L, 0.0090 mmol), and 1,3,5-tris(trifluoromethyl)benzene (1 μ L) as an internal standard was prepared in 0.60 mL of benzene- d_6 and transferred to a J. Young NMR tube. The NMR tube was heated to 40 $^{\circ}$ C in a temperature-controlled oil bath. After 7 hours, complete conversion of **2** to **4** was observed by ^1H NMR spectroscopy.⁶ The identity of **4** was verified by HRMS (FAB+): m/z Calculated for $\text{C}_{31}\text{H}_{38}\text{ON}_2\text{RuCl}_2$ $[\text{M}+\text{H}]-\text{H}_2$: 626.1405; Found: 626.1397.

Reaction of **3** with 2-Isopropoxy- β -methylstyrene.



In a glovebox, a solution of complex **3** (2.9 mg, 0.0030 mmol), 2-isopropoxy- β -methylstyrene (1.6 μ L, 0.0090 mmol), and 1,3,5-tris(trifluoromethyl)benzene (1 μ L) as an internal standard was prepared in 0.60 mL of benzene- d_6 and transferred to a J. Young NMR tube. The NMR tube was heated to 40 $^{\circ}$ C in a temperature-controlled oil bath. After 7 hours, complete conversion of **3** to **5** was observed by ^1H NMR spectroscopy.⁷ The identity of **5** was verified by HRMS (FAB+): m/z Calculated for $\text{C}_{37}\text{H}_{50}\text{ON}_2\text{RuCl}_2$ $[\text{M}+\text{H}]-\text{H}_2$: 710.2344; Found: 710.2362.

Reaction of **2** and **3** with Excess Tricyclohexylphosphine.

Complex **2** or **3** (0.0013 mmol) and tricyclohexylphosphine (0.0065 mmol) were dissolved in benzene- d_6 in a J. Young tube. Exchange of CDC **1** for PCy_3 was monitored by ^1H and ^{31}P NMR spectroscopy at 25 $^{\circ}$ C.⁸ After 12 hours, 50% conversion of **2** or **3** was observed, along with concomitant formation of the analogous $(\text{NHC})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}$ complex and free CDC **1**.

NMR Kinetics of Initiation Rates.

Complex **2** or **3** (0.0020 mmol) and 0.5 μL of 1,3,5-tris(trifluoromethyl)benzene as an internal standard were dissolved in benzene- d_6 (0.60 mL) in a screw-capped NMR tube. The temperature of the NMR tube was allowed to equilibrate in the NMR probe at 40 $^{\circ}\text{C}$. Ethyl vinyl ether (26 μL , 0.27 mmol) was injected into the NMR tube, and disappearance of the ^1H NMR signal for the ruthenium benzylidene was monitored as a function of time for three half lives. Reactions performed in triplicate provided rate constants ($k_{\text{obs}} = k_1$) of $(4.04 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ for complex **2** and $(9.48 \pm 0.07) \times 10^{-3} \text{ s}^{-1}$ for **3**.

Table S1. Temperature dependence of k_{obs} for the reaction of **2** (0.0020 mmol) with ethyl vinyl ether (0.27 mmol) in benzene- d_6 (0.60 mL).

Temp. ($^{\circ}\text{C}$)	$1/T$ (K^{-1})	k_{obs} (s^{-1})	$\ln(k/T)$
40	0.00319	4.04×10^{-4}	-13.56
50	0.00309	1.73×10^{-3}	-12.14
58	0.00302	5.48×10^{-3}	-11.01
64	0.00297	1.59×10^{-2}	-9.96
70	0.00291	2.54×10^{-2}	-9.51

The plot of $\ln(k/T)$ as a function of T^{-1} (Figure S3) was linearly fit to the expression

$$\ln \frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \ln \frac{k_{\text{B}}}{h} + \frac{\Delta S^{\ddagger}}{R}$$

The enthalpy and entropy of activation were extracted from the slope and intercept, respectively. Standard deviations for ΔH^{\ddagger} and ΔS^{\ddagger} were evaluated using the LINEST routine in Excel.

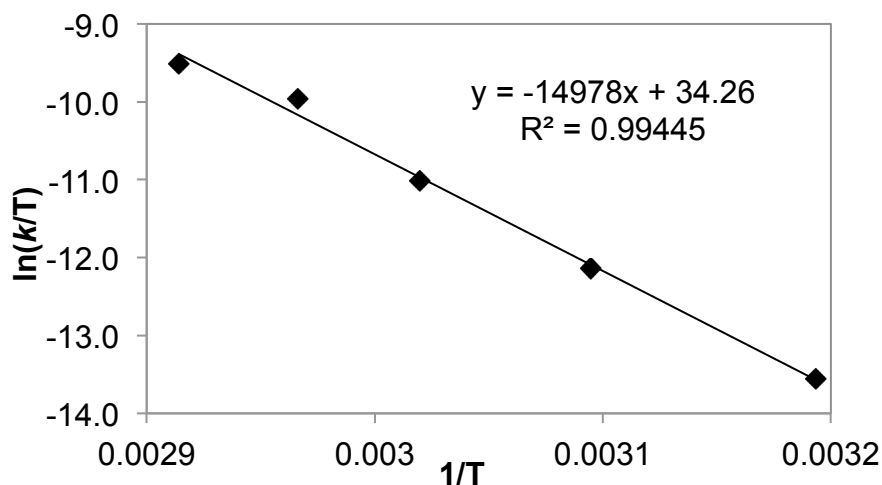


Figure S4. Eyring plot for the reaction of **2** with ethyl vinyl ether.

Table S2. Temperature dependence of k_{obs} for the reaction of **3** (0.0020 mmol) with ethyl vinyl ether (0.27 mmol) in benzene- d_6 (0.60 mL).

Temp. (°C)	1/T (K ⁻¹)	k_{obs} (s ⁻¹)	ln(k/T)
25	0.00335	1.05×10^{-3}	-12.56
35	0.00325	5.17×10^{-3}	-11.00
40	0.00319	9.48×10^{-3}	-10.41
55	0.00305	5.42×10^{-2}	-8.71
48	0.00311	2.89×10^{-2}	-9.32

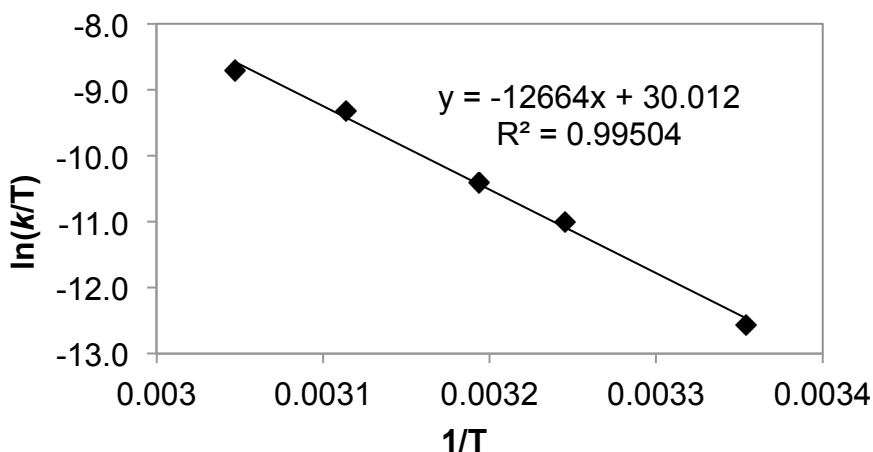


Figure S5. Eyring plot for the reaction of **3** with ethyl vinyl ether.

CDC Dependence Experiments to Determine k_{-1}/k_2 .

Complex **2** or **3** (0.0020 mmol), CDC (**1**, 0.0040 to 0.011 mmol), and 1 μL of 1,3,5-tris(trifluoromethyl)benzene as an internal standard were dissolved in benzene- d_6 (0.60 mL) in a screw-capped NMR tube. Each sample was thermally equilibrated in the NMR probe, and olefin (ethyl vinyl ether, 0.021 to 0.26 mmol) was injected into the NMR tube. Disappearance of the ^1H NMR signal for the ruthenium benzylidene was monitored as a function of time for three half lives.

Table S3. [CDC]/[olefin] experiments for **2** at 60 °C.

[CDC] (mmol)	[olefin] (mmol)	[CDC]/[olefin]	k_{obs} (s ⁻¹)	1/ k_{obs} (s)
0.011	0.22	0.050	7.86×10^{-3}	127
0.011	0.094	0.12	7.37×10^{-3}	136
0.011	0.057	0.19	6.65×10^{-3}	150
0.011	0.031	0.35	5.91×10^{-3}	169
0.011	0.021	0.53	5.39×10^{-3}	186

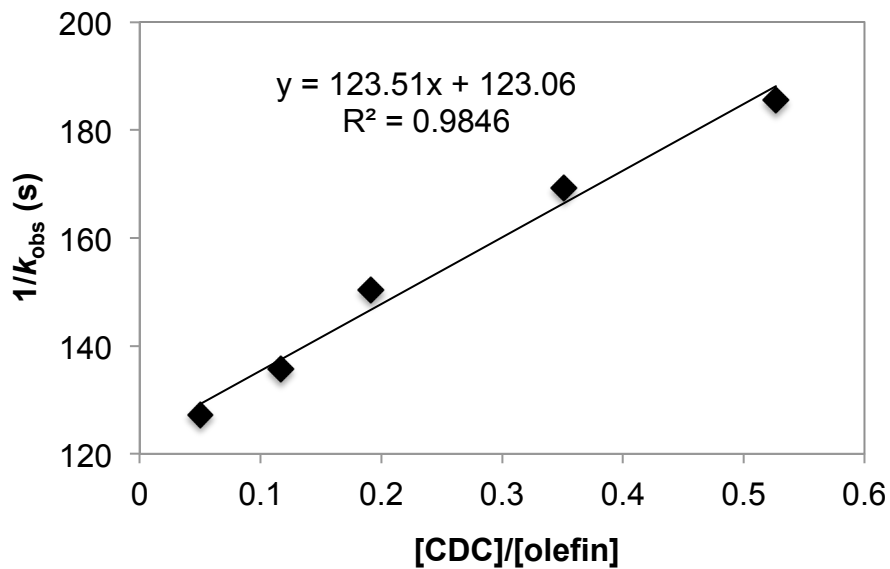


Figure S6. $1/k_{\text{obs}}$ versus $[\text{CDC}]/[\text{olefin}]$ for complex **2**.

Table S4. $[\text{CDC}]/[\text{olefin}]$ experiments for **3** at 40 °C.

[CDC] (mmol)	[olefin] (mmol)	[CDC]/[olefin]	k_{obs} (s ⁻¹)	1/ k_{obs} (s)
0.0040	0.26	0.015	9.49×10^{-3}	105
0.011	0.09	0.12	6.58×10^{-3}	152
0.011	0.031	0.35	3.77×10^{-3}	265
0.015	0.035	0.43	3.02×10^{-3}	331
0.011	0.021	0.52	2.79×10^{-3}	358

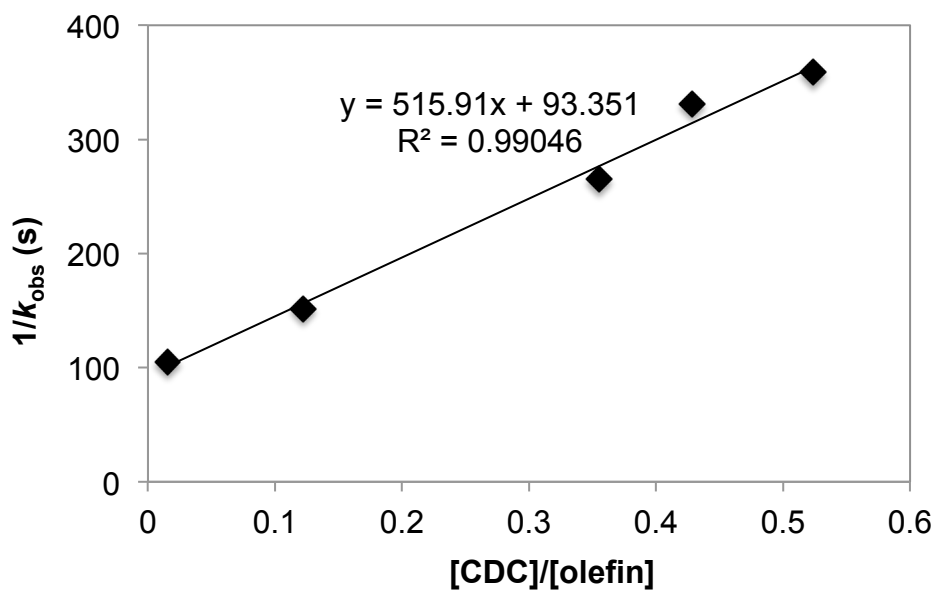


Figure S7. $1/k_{\text{obs}}$ versus $[\text{CDC}]/[\text{olefin}]$ for complex **3**.

X-Ray Structure Determination.

Complex 2. Low-temperature diffraction data (ϕ - and ω -scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo K_α radiation ($\lambda = 0.71073$ Å) from an I μ S micro-source for the structure of compound **2**. The structure was solved by direct methods using SHELXS⁹ and refined against F^2 on all data by full-matrix least squares with SHELXL-2016¹⁰ using established refinement techniques.¹¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit.

Complex 3. Low-temperature diffraction data (ϕ - and ω -scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Cu K_α radiation ($\lambda = 1.54178$ Å) from an I μ S micro-source for the structure of compound **3**. The structure was solved by direct methods using SHELXS⁹ and refined against F^2 on all data by full-matrix least squares with SHELXL-2016¹⁰ using established refinement techniques.¹¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as enhanced rigid bond restraints for anisotropic displacement parameters.

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit along with 2.588 molecules of diethyl ether. The crystal was pseudomerohedrally twinned. The structure was refined using the twin matrix $[-1\ 0\ 0\ 0\ -1\ 0\ 0\ 0\ 1]$ and the twin ratio converged at a value of 0.400(2).

Table S5. Crystal data and structure refinement for complex **2**.

Empirical formula	C ₄₇ H ₅₂ Cl ₂ N ₆ Ru	
Formula weight	872.91	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 14.1398(7) Å	α = 90°.
	b = 23.1163(12) Å	β = 115.3760(19)°.
	c = 14.2265(8) Å	γ = 90°.
Volume	4201.4(4) Å ³	
Z	4	
Density (calculated)	1.380 Mg/m ³	
Absorption coefficient	0.541 mm ⁻¹	
F(000)	1816	
Crystal size	0.300 x 0.150 x 0.050 mm ³	
Theta range for data collection	2.370 to 33.142°.	
Index ranges	-21 ≤ h ≤ 21, -35 ≤ k ≤ 35, -21 ≤ l ≤ 21	
Reflections collected	74416	
Independent reflections	16014 [R(int) = 0.1090]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6445	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16014 / 0 / 515	
Goodness-of-fit on F ²	1.009	
Final R indices [I > 2σ(I)]	R1 = 0.0534, wR2 = 0.0858	
R indices (all data)	R1 = 0.1149, wR2 = 0.0979	
Largest diff. peak and hole	1.264 and -0.774 e.Å ⁻³	

Figure S8. X-ray crystal structure of complex **2**. Displacement ellipsoids are drawn at 50% probability, and hydrogen atoms have been omitted for clarity.

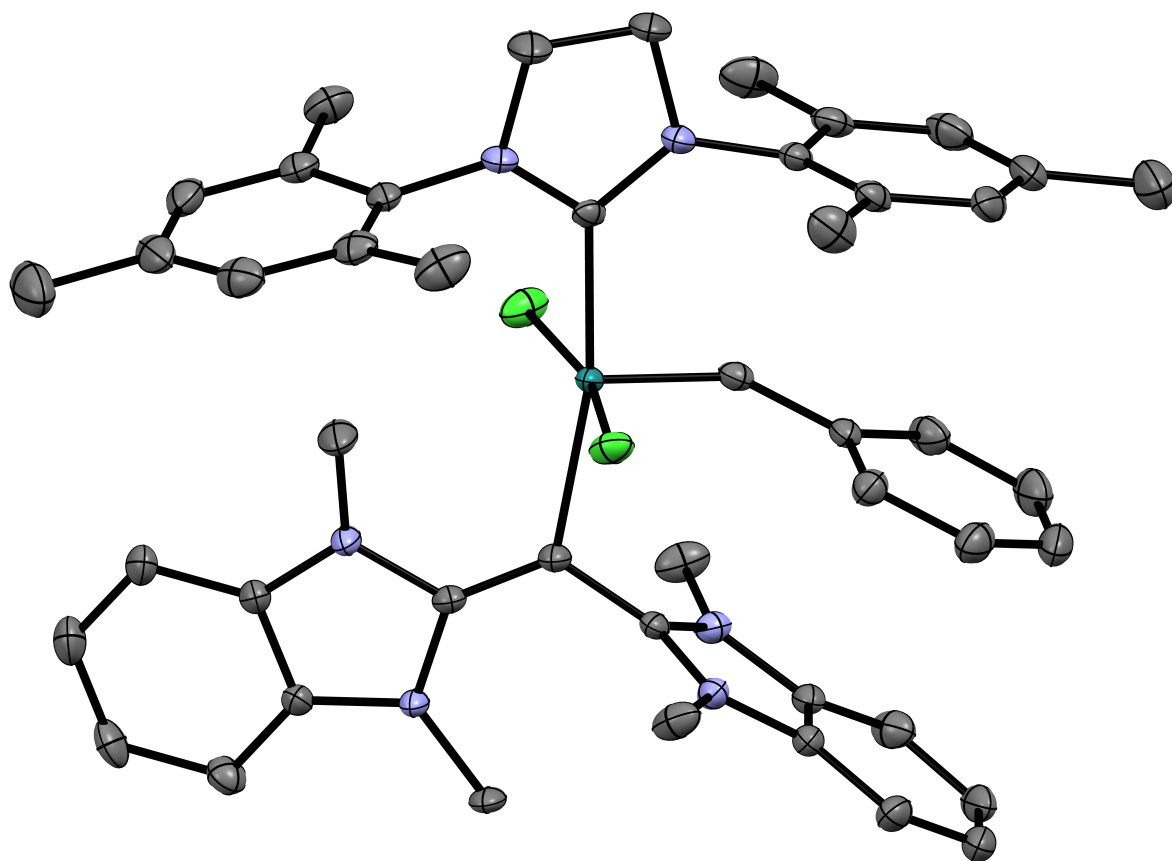


Table S6. Crystal data and structure refinement for complex **3**.

Empirical formula	C63.35 H89.88 Cl2 N6 O2.59 Ru	
Formula weight	1148.85	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 12.7525(4) Å	α = 90°.
	b = 32.6167(12) Å	β = 90.0724(18)°.
	c = 14.4122(5) Å	γ = 90°.
Volume	5994.7(4) Å ³	
Z	4	
Density (calculated)	1.273 Mg/m ³	
Absorption coefficient	3.307 mm ⁻¹	
F(000)	2443	
Crystal size	0.300 x 0.100 x 0.050 mm ³	
Theta range for data collection	2.709 to 74.488°.	
Index ranges	-15 ≤ h ≤ 15, -40 ≤ k ≤ 40, -18 ≤ l ≤ 17	
Reflections collected	86257	
Independent reflections	12234 [R(int) = 0.0709]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3827 and 0.2333	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12234 / 675 / 753	
Goodness-of-fit on F ²	1.294	
Final R indices [I > 2σ(I)]	R1 = 0.0826, wR2 = 0.1954	
R indices (all data)	R1 = 0.0865, wR2 = 0.1974	
Largest diff. peak and hole	0.774 and -1.539 e.Å ⁻³	

Figure S9. X-ray crystal structure of complex **3**. Displacement ellipsoids are drawn at 50% probability, and hydrogen atoms and diethyl ether molecules have been omitted for clarity.

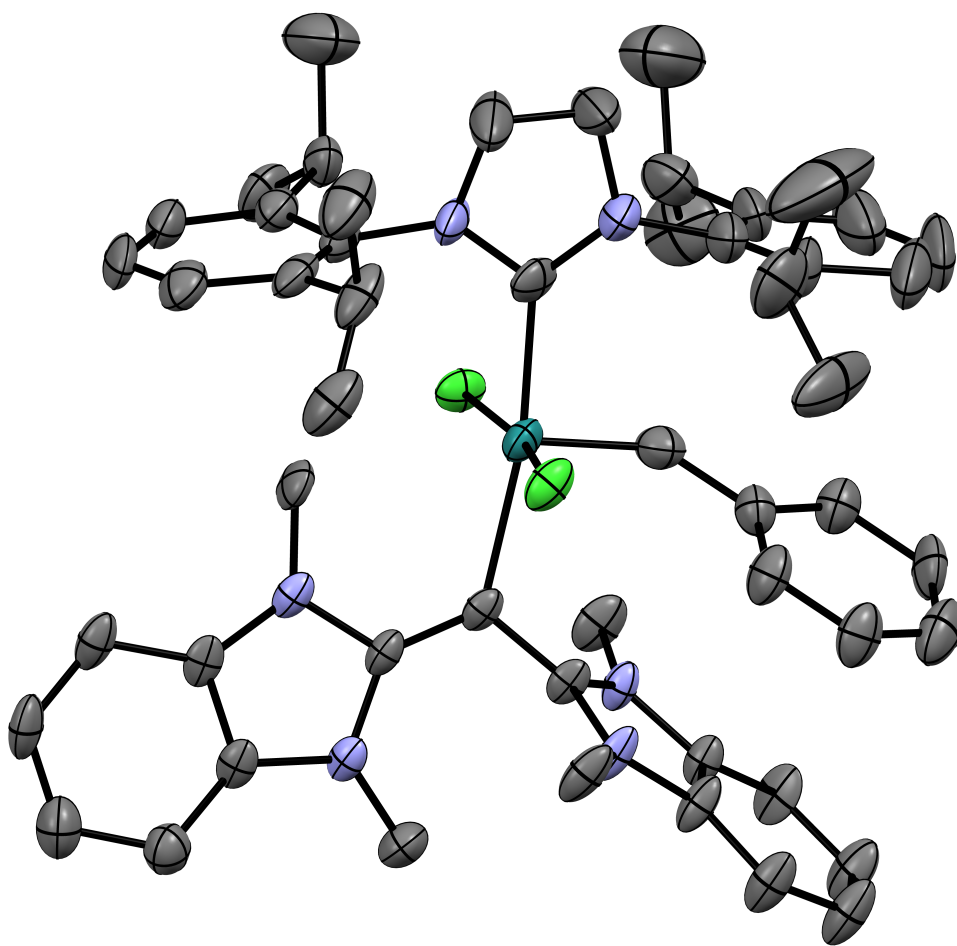


Figure S10. ^1H NMR spectrum of **2** (in C_6D_6).

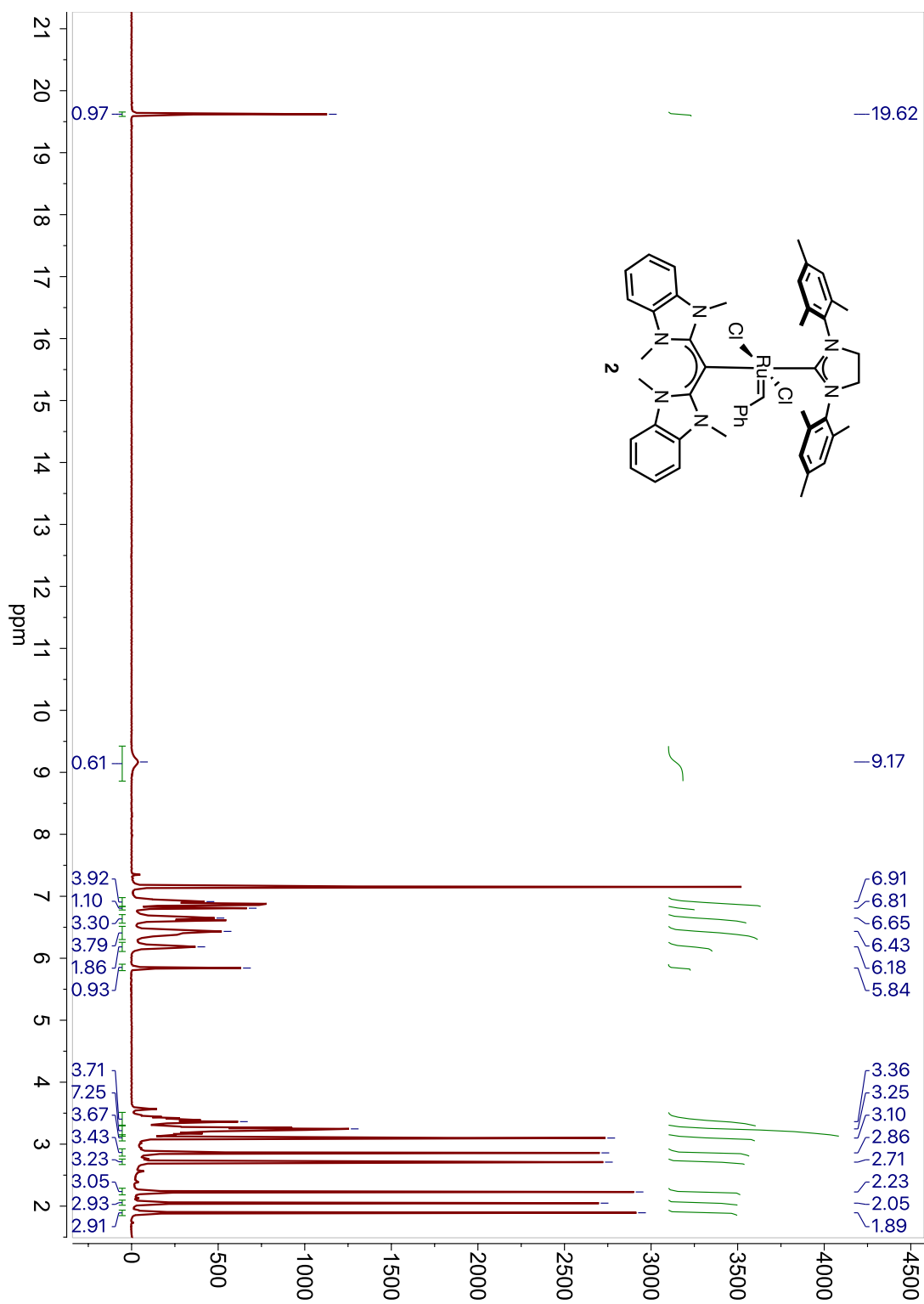


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** (in C_6D_6). Signals for trace diethyl ether are observed at 15.63 and 65.94 ppm.

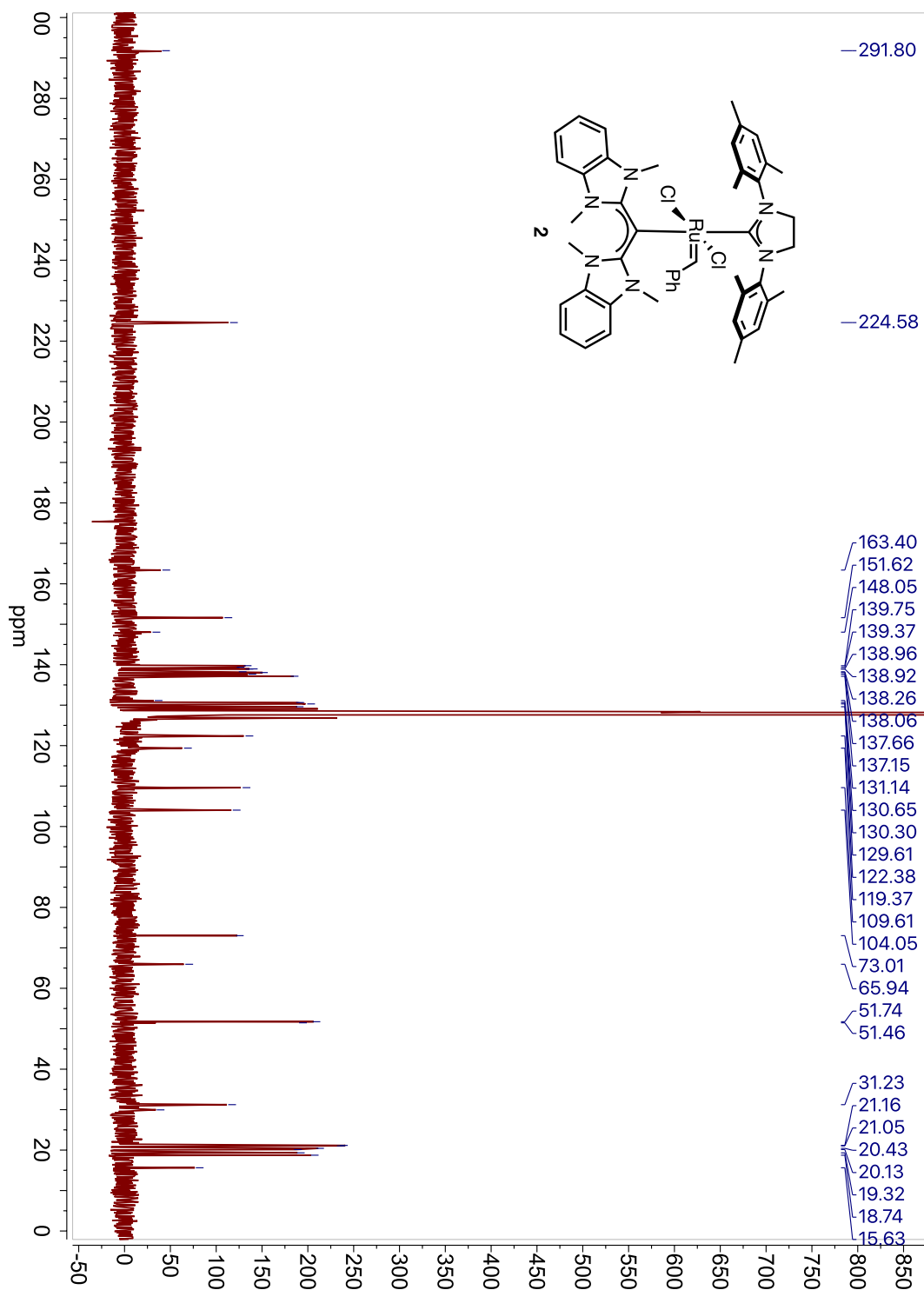


Figure S12. COSY NMR spectrum of **2** (in C₆D₆).

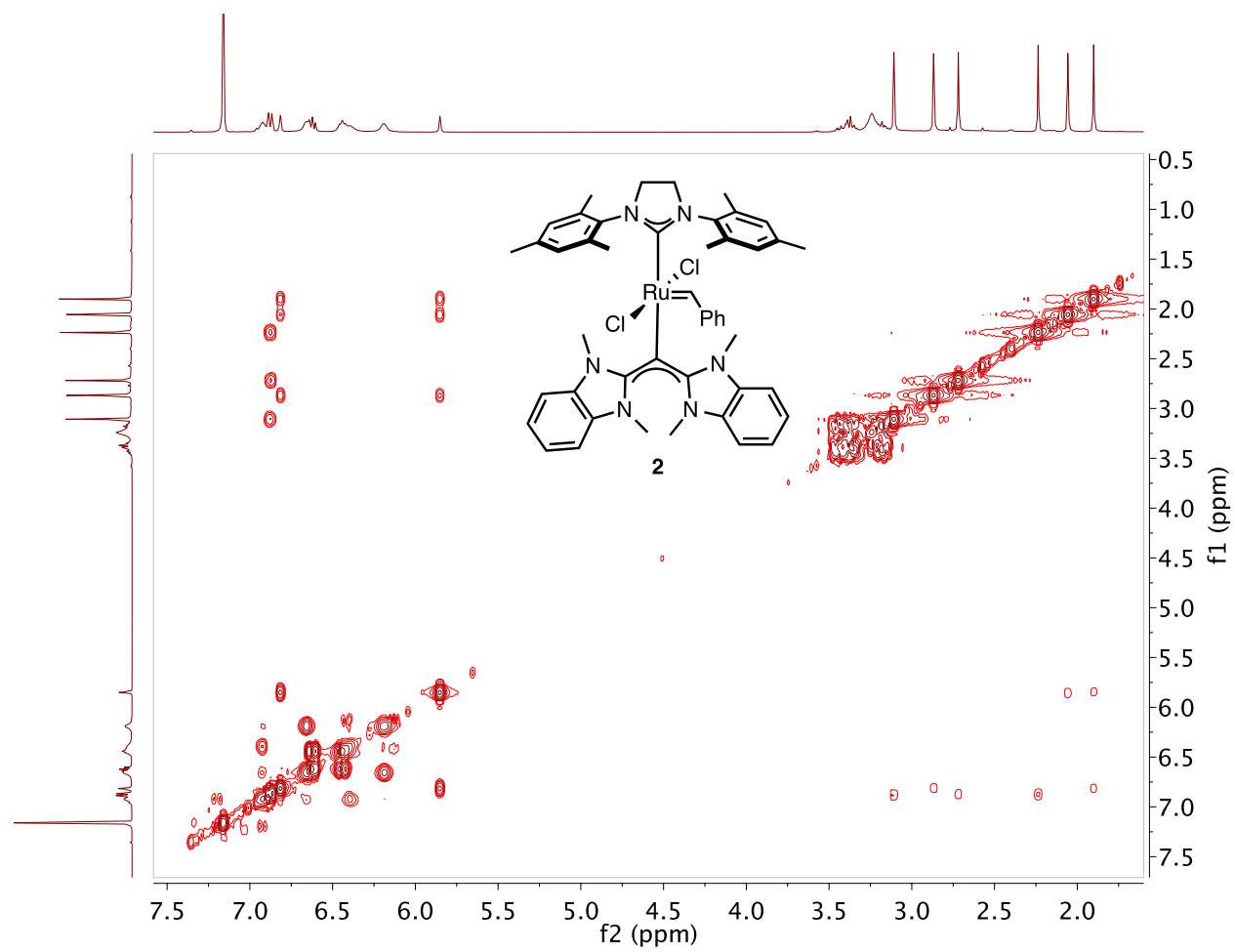


Figure S13. NOESY NMR spectrum of **2** (in C₆D₆).

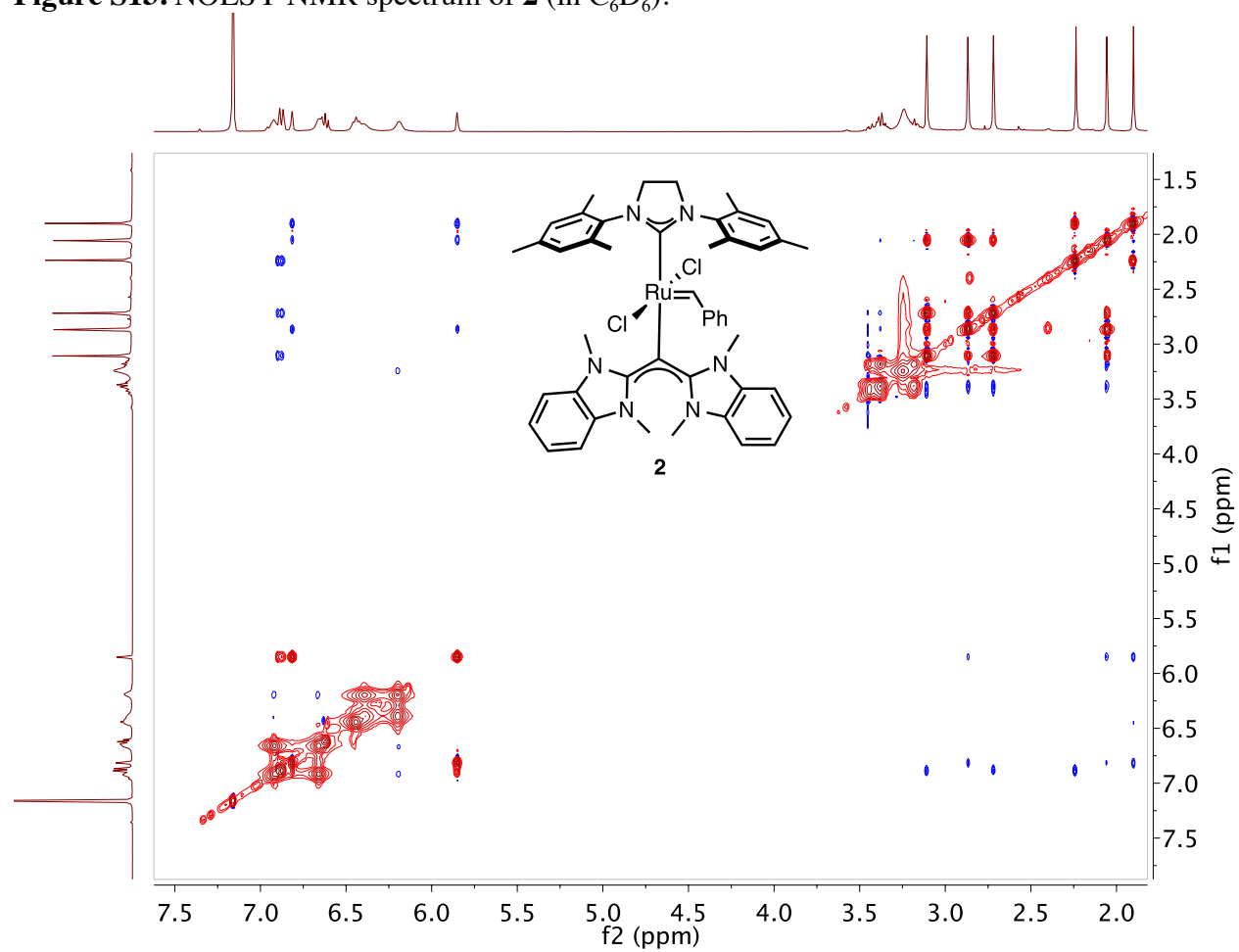


Figure S14. ^1H - ^{13}C HSQC NMR spectrum of **2** (in C_6D_6).

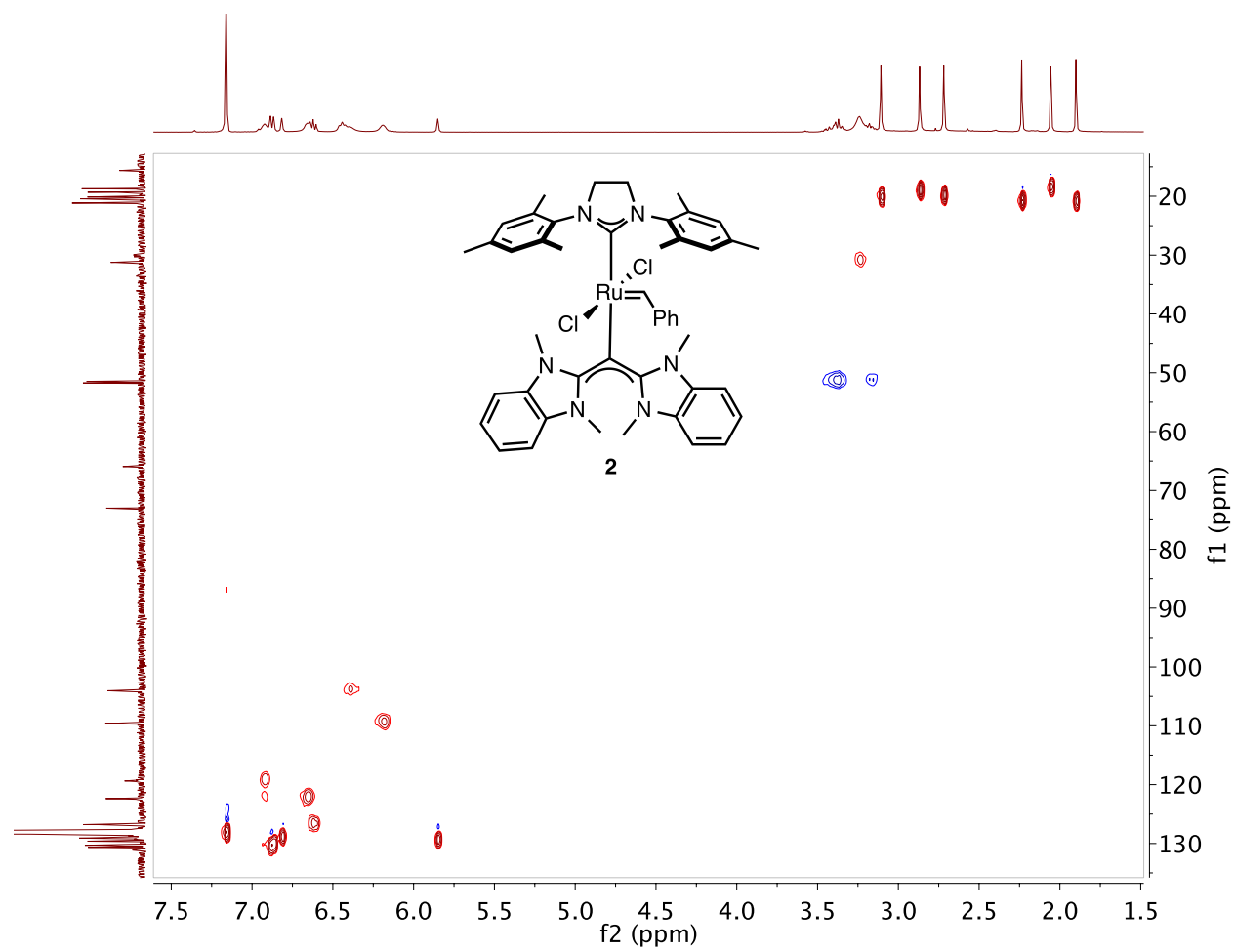


Figure S15. ^1H - ^{13}C HMBC NMR spectrum of **2** (in C_6D_6).

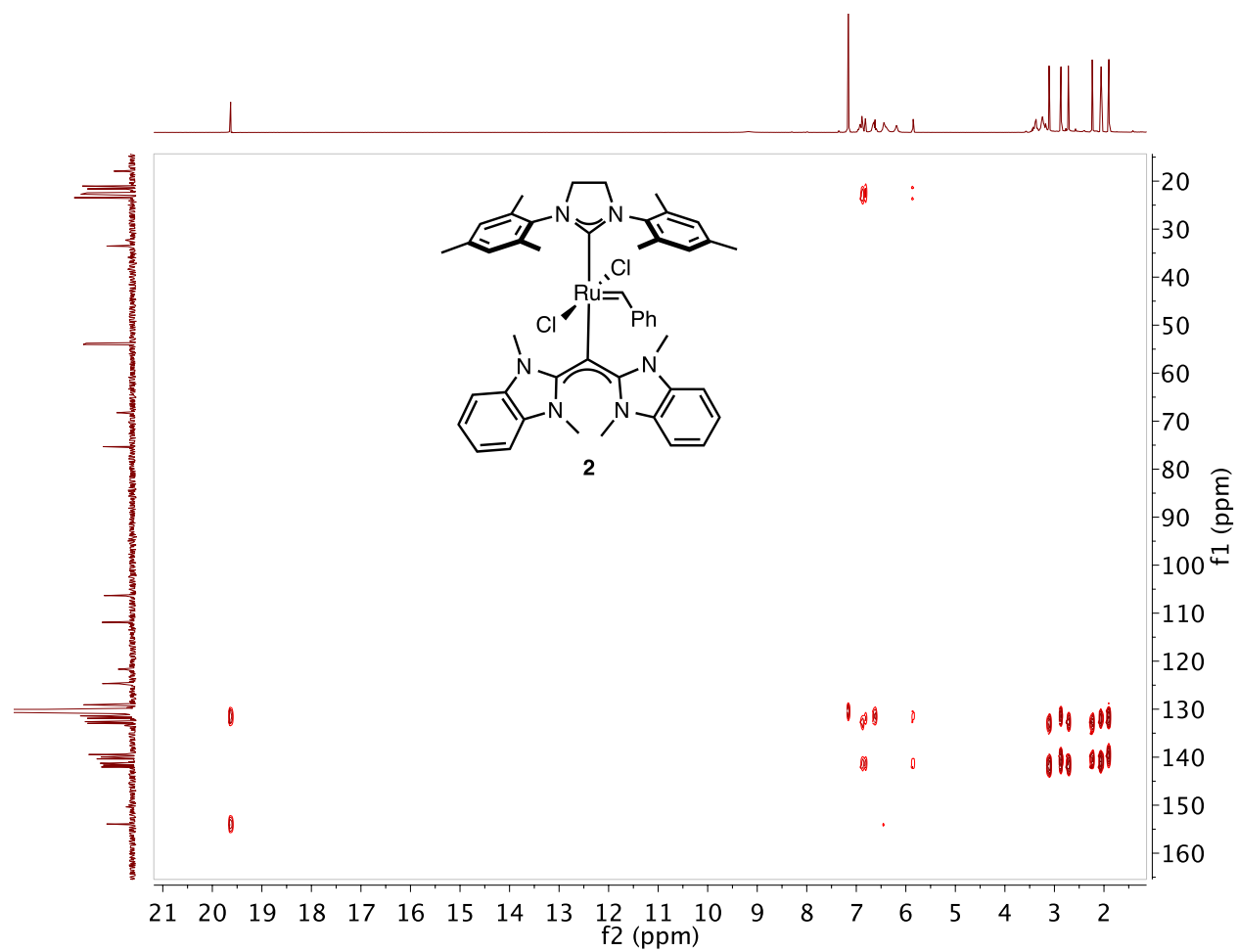


Figure S16. ^1H NMR spectrum of **3** (in C_6D_6).

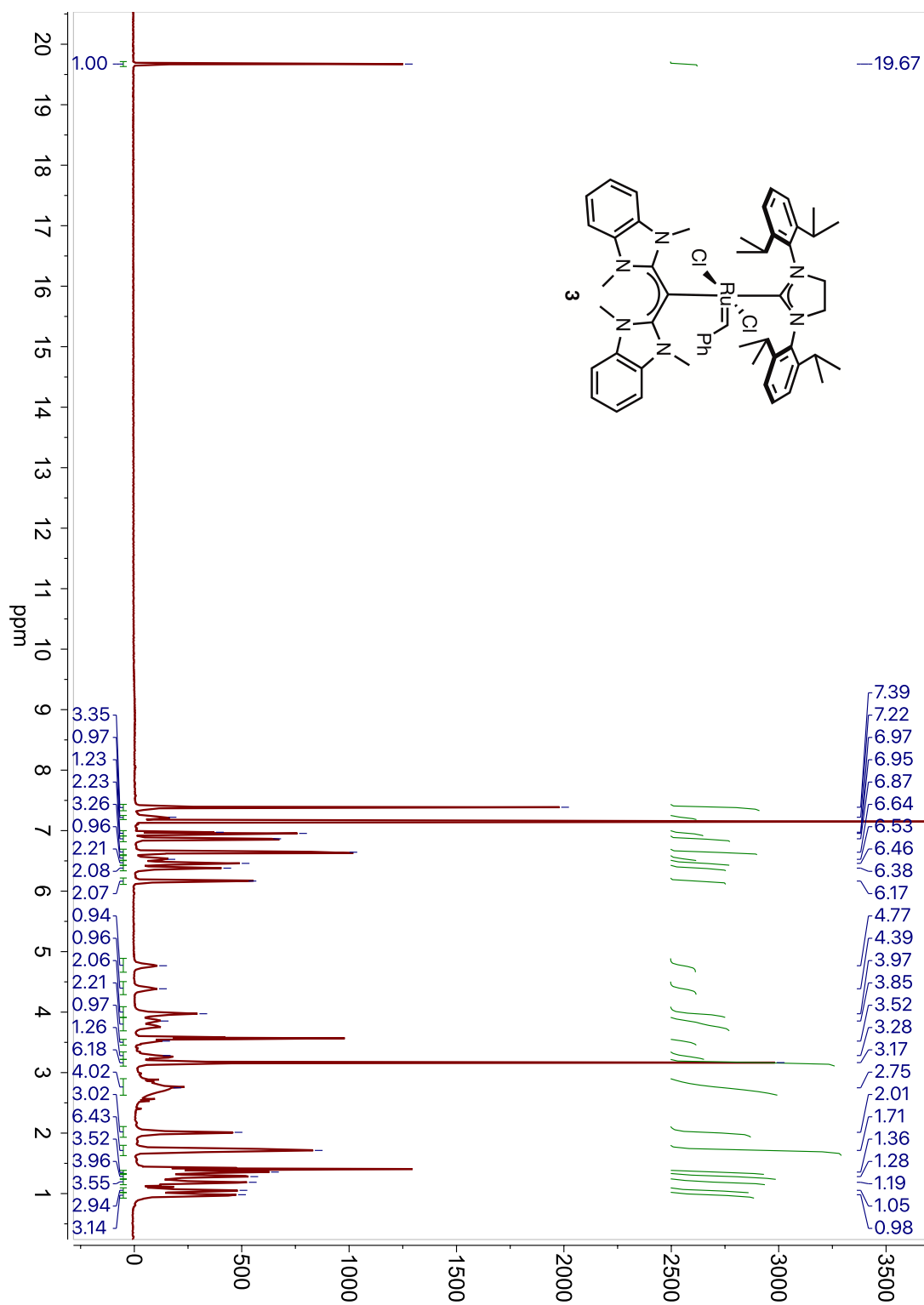


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** (in C_6D_6). Signals for trace tetrahydrofuran are observed at 25.45 and 67.45 ppm.

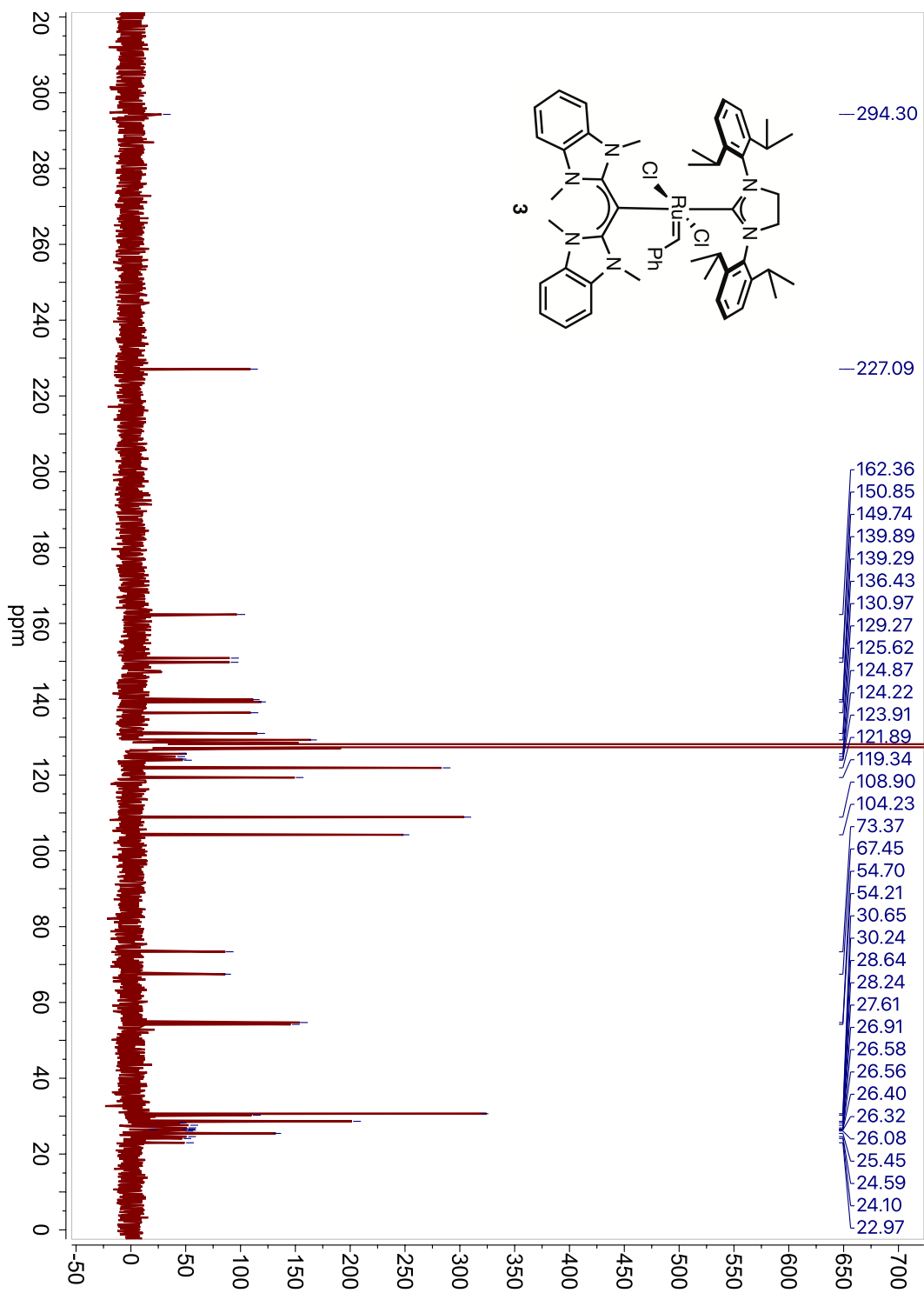


Figure S18. COSY NMR spectrum of **3** (in C_6D_6).

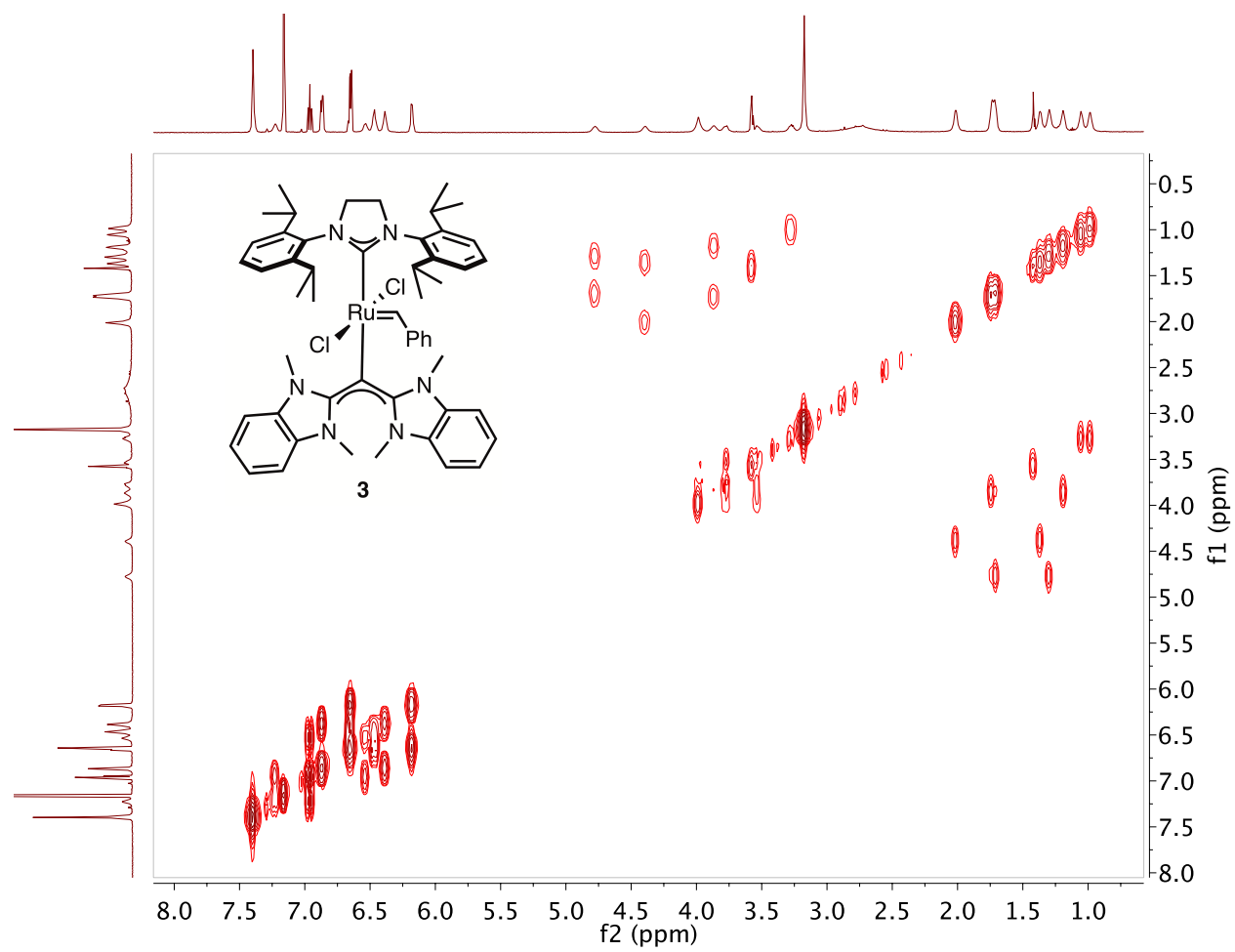


Figure S20. ^1H - ^{13}C HSQC NMR spectrum of **3** (in C_6D_6).

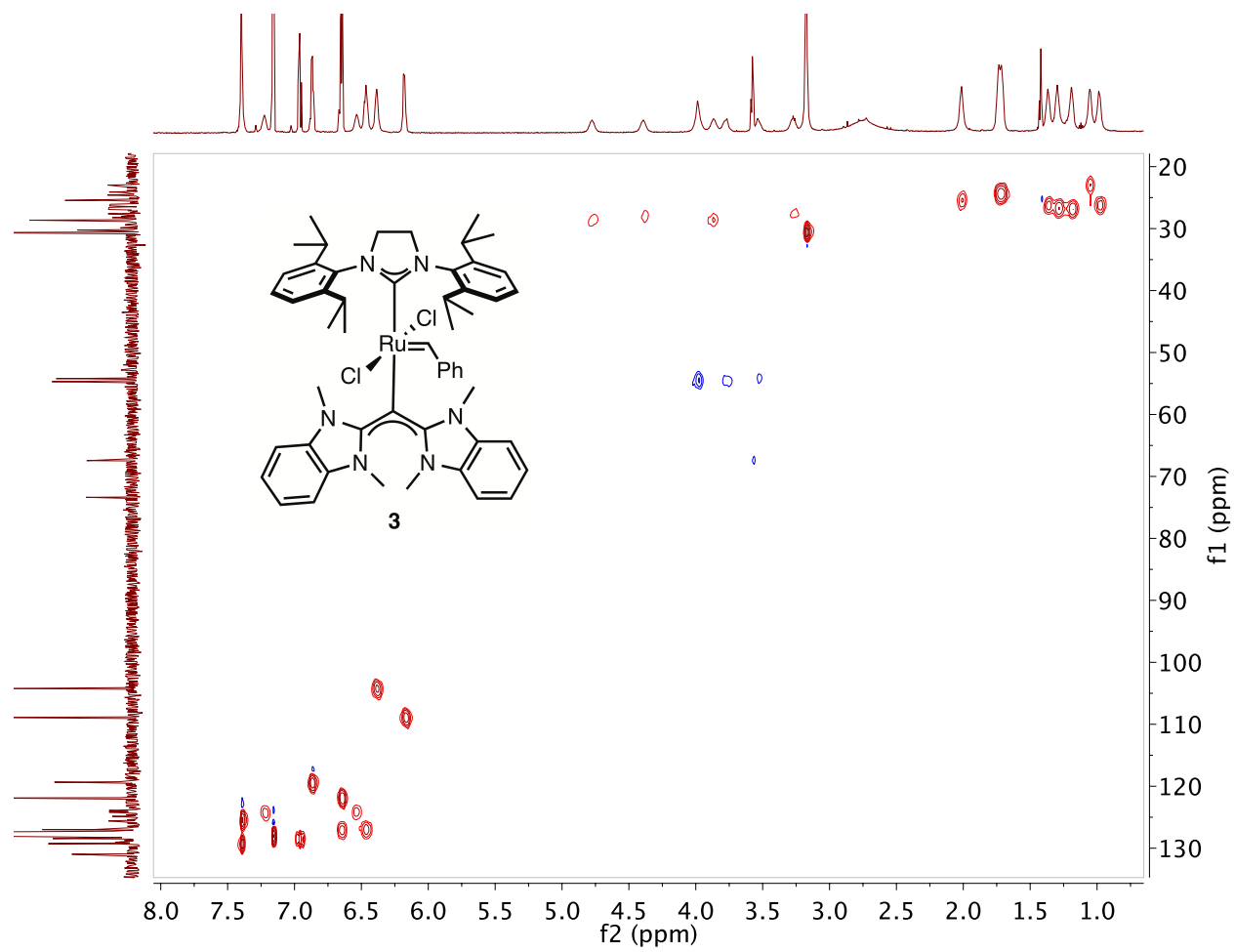


Figure S21. ^1H - ^{13}C HMBC NMR spectrum of **3** (in C_6D_6).

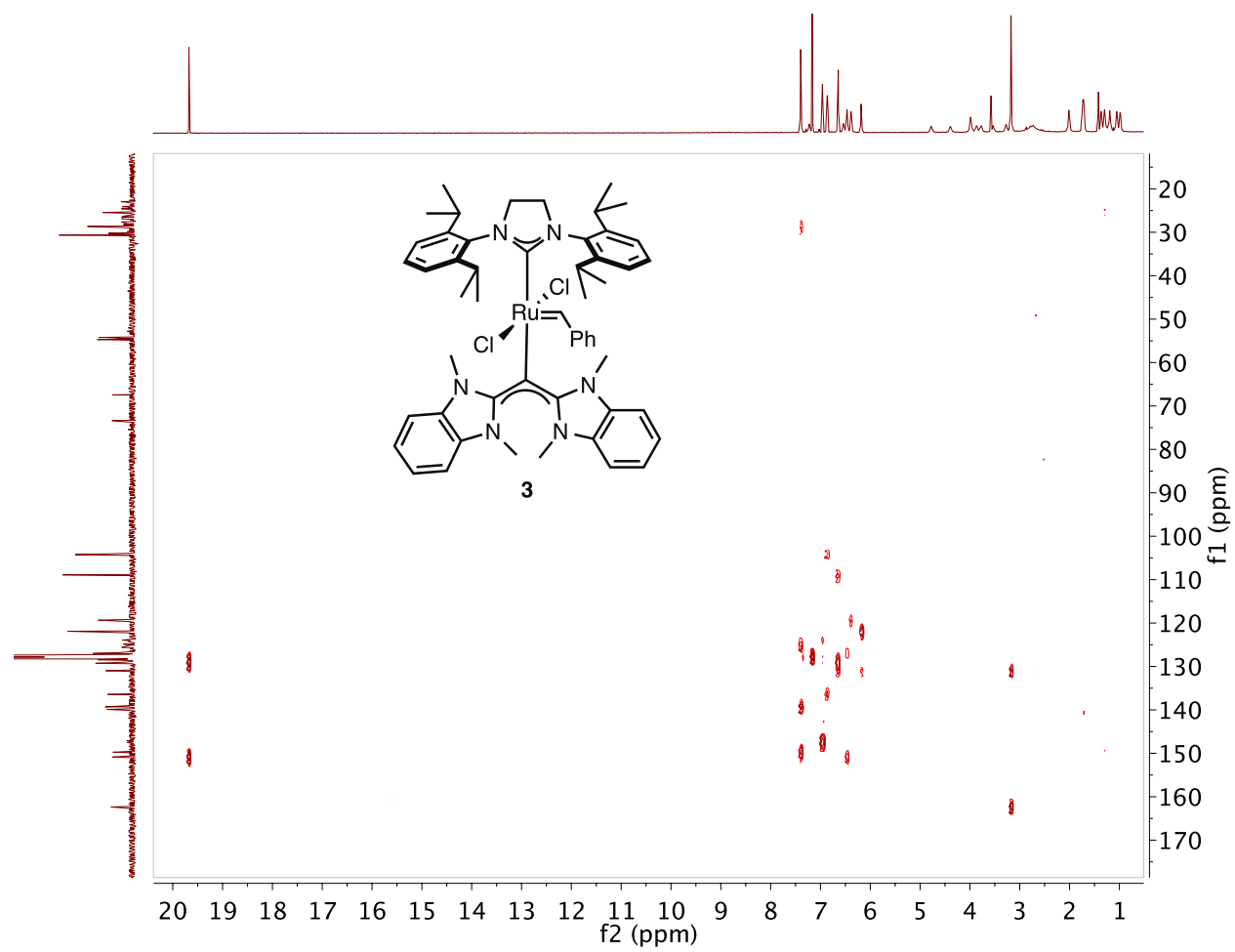


Figure S22. ^1H NMR spectrum of CDC-H^+ (in CD_2Cl_2).

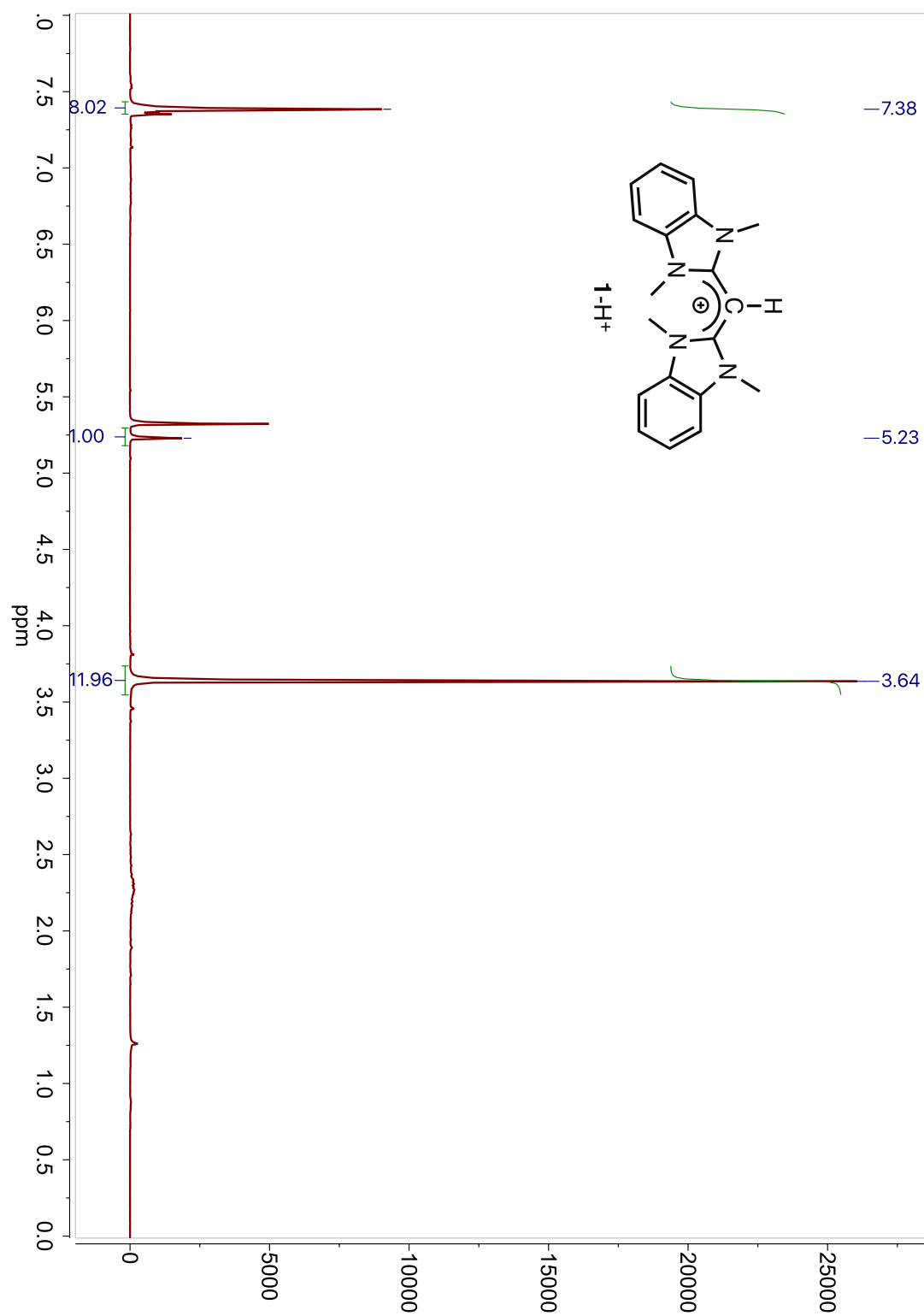
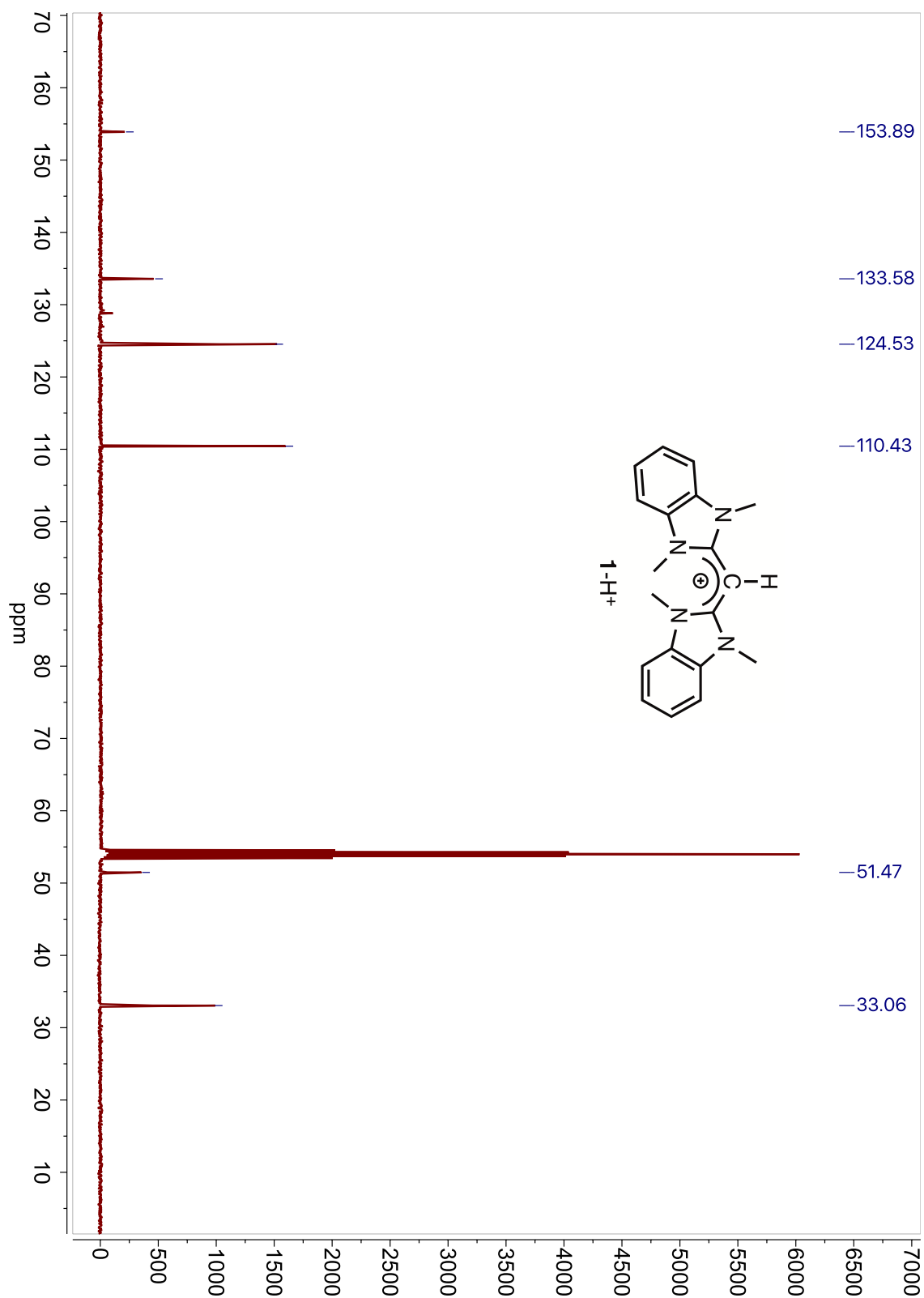


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of CDC-H^+ (in CD_2Cl_2).



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