Supporting Information

Robust Olefin Metathesis Catalyst Bearing a Tridentate Hemi-labile NHC Ligand

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General Methods

All air-sensitive manipulations were performed in oven-dried glassware under inert conditions using standard Schlenk techniques or a glovebox containing an atmosphere of purified argon (BIP). Solvents for air-sensitive reactions were dried and degassed prior to use. Tetrahydrofuran (THF) was dried using sodium / benzophenone ketyl followed by distillation. Pentane, hexanes, acetonitrile, diethyl diallylmalonate and 1-decene were dried over calcium hydride (CaH_2) followed by distillation. Solvents were degassed via freeze-pump-thaw or sparging with argon after their distillation from the drying agent, and then stored over 4 Å molecular sieves for at least 12 h prior to use (3 Å for acetonitrile). Molecular sieves were activated by heating at ~ 200 ^{o}C under vacuum. All other reagents were used as received. Elemental analysis and X-ray diffraction were performed at the Beckman Institute of the California Institute of Technology in Pasadena, California. NMR spectra were acquired on Bruker 400 MHz spectrometer running TopSpin. Chemical shifts are reported in parts per million (ppm) with reference to internal solvent for ^{1}H NMR and ^{13}C NMR spectra. Peak abbreviations are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet.

Technique for purifying samples suitable for elemental analysis

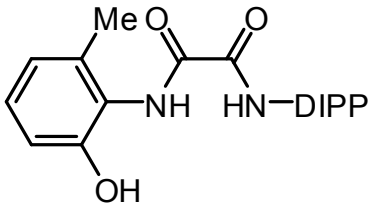
Compound **1** was recrystallized twice in hot toluene, collected and triturated on a frit using cold toluene. Finally, the filter cake was washed with pentane, and dried under vacuum over two days prior to analysis.

Compound **2** was recrystallized once with hot ethanol/toluene (~1:5), and DMSO/toluene (~1:10) the second time. Crystals were collected on a frit, washed with hexanes, and dried under vacuum overnight prior to analysis.

Compound **3** was recrystallized twice in hot isopropanol/hexanes (~1:10), collected on a frit, washed with hexanes, and dried under vacuum overnight prior to analysis.

Catalyst **5** was recrystallized twice using vapor diffusion (DCM inner / ether outer). The crystals were dried in vacuum overnight, redissolved in DCM, precipitated out of pentane, collected on a frit, and washed with pentane/toluene (1:1). The green powder was dried in vacuum for two days prior to analysis.

Synthesis



N-(2,6-diisopropylphenyl)-N'-(2-hydroxy-6-methylphenyl)-oxalamide (**1**)

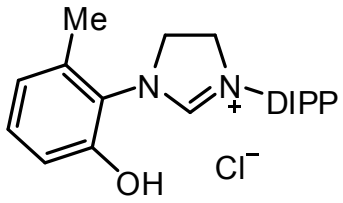
This synthetic protocol is adopted from the procedure used to make the non-methylated derivative of this molecule. For convenience, it is described here.[1]

N-(2,6- Diisopropylphenyl)-oxanilic acid ethyl ester (5.40g, 19.47mmol, 1 equiv.) and 2-amino-3-methylphenol (2.89g, 23.5mmol, 1.2 equiv.) were dissolved in ~100mL toluene. While stirring, triethylamine (5.43mL, 38.94mmol, 2 equiv.) was added via syringe. The suspension was refluxed overnight, during which the bright orange product precipitated out. The condenser was rinsed with ethyl acetate until much of the solids dissolved. It is worth mentioning that the solubility of this product in ethyl acetate is lower than the non-methylated derivative of this molecule, causing the extractions in the next step to form many emulsions. The crude mixture was washed twice with 2M HCl, followed by brine, and dried over $MgSO_4$. After filtering off the drying agent over celite, the solvent was removed via rotary evaporation. The crude orange-white solid was recrystallized in hot toluene to afford **1**, as a white flaky solid (5.48g,15.46mmol, 79.4% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (broad s, 1H), 8.80 (broad s, 1H), 8.25 (broad s, 1H), 7.38 (t, 1H), 7.25 (d, 2H), 7.15 (t, 1H), 6.97 (d, 1H), 6.84 (d, 1H), 3.04 (septet, 2H), 2.37 (s, 3H), 1.25 (d, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.48, 150.24, 145.97, 131.45, 129.37, 129.33, 128.55, 124.01, 122.98, 122.71, 118.61, 29.19, 23.82, 18.22.

CHN elemental analysis for $C_{21}H_{26}N_2O_3$ – Calculated: C 71.16 %, H 7.39 %, N 7.90 %, Found: C 71.30 %, H 7.56 %, N 7.91 %



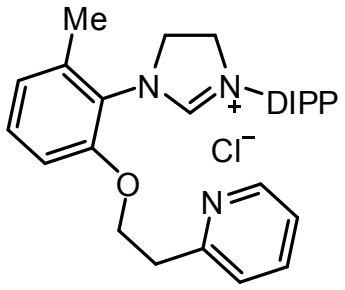
1-(2,6-diisopropylphenyl)-3-(2-hydroxy-6-methylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**3**)

N-(2,6-Diisopropylphenyl)-N'-(2-hydroxy-6-methylphenyl)-oxalamide (**1)** (5.48g, 15.46mmol, 1 eq.) was treated with 5equiv. of BH_3 (1M in THF) and refluxed overnight. The next day, the solution had turned from clear yellow to colorless. After cooling to room temperature, methanol was added slowly to the stirred solution until the bubbling ceased. The diamine (**2**) was protonated using 2.5equiv. of conc. HCl. Volatiles were removed under reduced pressure. The resulting solids were redissolved in methanol and subsequently dried under reduced pressure. This last step was conducted a total of three times to ensure the complete removal of BH_3. The resulting gel-like residue was dried under vacuum to afford a chalky white solid. To this was added 100mL triethylorthoformate and heated to 100°C for an hour, precipitating a banana yellow fine powder. The solids were collected, washed with ether, and dried overnight (4.41g, 11.8mmol, 76.5% yield).

^{1}H NMR (400 MHz, DMSO-d6) δ 11.01 (s, 1H), 9.29 (d, 1H), 7.54 (t, 1H), 7.42 (d, 2H), 7.22 (d, 1H), 7.09 (d, 1H), 6.83 (d, 1H), 4.46 (m, 4H), 3.09 (septet, 2H), 2.36 (s, 3H), 1.26 (dd, 12H).

^{13}C NMR (100 MHz, DMSO-d6): δ 161.10, 153.58, 146.27, 136.04, 130.91, 130.33, 130.19, 124.74, 122.19, 120.90, 114.31, 53.57, 50.96, 28.01, 24.81, 23.41, 17.01.

CHN elemental analysis for $C_{22}H_{29}ClN_2O$ – Calculated: C 70.85 %, H 7.84 %, N 7.51 %, Found: C 70.95 %, H 7.79 %, N 7.75 %



1-(2,6-diisopropylphenyol)-3-(2-methyl-6-(2-(pyridin-2-yl)ethoxy)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**4**)

Synthesis of Tosylate Salt

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-6-methylphenyl)-4,5-dihydro-imidazolium chloride (**3**) (1.78g, 4.77 mmol, 1 equiv.) was charged into a 250-mL oven-dried round-bottom flask equipped with a football shaped magnetic stir bar in an argon filled glovebox. To this was added 2-(Pyridin-3-yl)ethyl 4-methylbenzenesulfonate (3.97g, 14.3 mmol, 3 equiv.) dissolved in acetonitrile (20 mL). 3Ä molecular sieves (~ .5g) was added to this suspension followed by crushed and oven-dried K_2CO_3 (.824g, 5.96 mmol, 1.25 equiv.). A total of ~120 mL acetonitrile was added to the round-bottom flask. The flask was sealed with a rubber septum, removed from the glovebox, and heated to 80°C, vented to an oil bubbler while stirring overnight. The reaction changed from a white/pale yellow slurry in clear brown solution to a cappuccino-brown slurry underneath a supernatant dark brown solution. Solids were filtered off over celite, and solvent was removed from the filtrate under reduced pressure and heat (50°C) followed by a strong vacuum via Schlenk manifold (20 mtorr), affording a deep dark brown goop. As this goop was stirred for a couple of hours in ethyl acetate, a pale grey solid was precipitated out. The solid was collected on a frit and washed with hexanes to provide the tosylate salt of the desired product as a pale grey powdery solid (2.07g, 3.37 mmol, 70.61% yield).

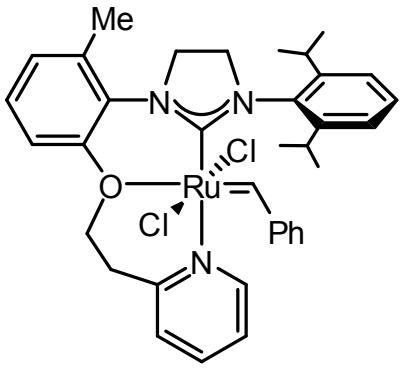
Anion Exchange from OTs^- to Cl^-.

1.62g (2.64 mmol, 1 equiv.) of the above solid and LiCl (1.17g, 27.6 mmol, 10 equiv.) were dissolved in tetrahydrofuran (80 mL) and heated to 60°C for 2 hr. Solvent was removed and solids were dried in vacuo overnight. Resulting solids were dissolved in minimal dichloromethane, resulting in the precipitation of LiOTs salts, which were filtered off over celite. Removal of the solvent from the resulting filtrate afforded a dark orange/brown oil. The desired chloride salt of the product was precipitated with ethyl acetate as a tan pink/brown solid. This anion exchange procedure was repeated once more to ensure complete anion exchange. The resulting solids appeared whiter in color after the second exchange. The solids were recrystallized in hot isopropanol/hexanes (~1:10) (1.24g, 2.59 mmol, 98.2% yield) to afford white crystals which were dried overnight. Product was confirmed by ^1H and ^{13}C NMR spectroscopy.

^{1}H NMR (400 MHz, CDCl3) δ 8.80 (s, 1H), 8.28 (d, 1H), 7.63 (t of d, 1H), 7.45 (t, 1H), 7.27 (m, 4H), 7.09 (m, 1H), 6.90 (d, 2H), 4.57 (s, 2H), 4.51 (t, 4H), 3.27 (t, 2H), 3.02 (septet, 2H), 2.47 (s, 3H), 1.28 (dd, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.22, 158.07, 153.61, 149.47, 146.44, 137.23, 136.99, 131.45, 131.17, 129.95, 125.10, 123.65, 123.61, 122.89, 122.24, 110.39, 67.89, 54.97, 52.39, 37.43, 29.01, 25.22, 24.32, 18.24.

CHN elemental analysis for $C_{29}H_{36}ClN_3O$ – Calculated: C 72.86 %, H 7.59 %, N 8.79 %, Found: C 72.62 %, H 7.58 %, N 8.41 %



Catalyst (**5**)

In an Argon filled glovebox, 1-(2,6-diisopropylphenyol)-3-(2-methyl-6-(2-(pyridin-2-yl)ethoxy)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**3**) (1.363g, 2.221 mmol, 2 equiv.) and potassium hexamethyldisilazide (.4431g, 2.221 mmol, 2 equiv.) were dissolved in toluene (30 mL) and charged into a round-bottom flask equipped with a football-shaped magnetic stir bar. The mixture was stirred for 30min at room temperature, generating the active N-heterocyclic carbene. The carbene mixture was added slowly into a stirred oven-dried 250-mL round-bottom flask containing $RuCl_2(PCy_3)_2(=CHPh)$ (.914g, 1.111 mmol, 1 equiv.) dissolved in toluene (50mL). An additional 2x10mL of toluene was used to rinse the carbene residue and added to the reaction flask which was then septum capped and stirred for 3hr at 45°C. Volatiles were removed under reduced pressure at 50°C and subsequently dried via Schlenk vacuum manifold (20 mtorr) affording a sticky dark brown solid. Salts were precipitated with dichloromethane and filtered off over celite. The filtrate was concentrated down to approximately 5mL. The crude material was purified through flash column chromatography (gradient: 1:1 ethyl acetate:hexanes, 100% ethyl acetate) eluting the product as an emerald-green band. The product was purified via vapor diffusion recrystallization using an inner flask containing product dissolved in minimal dichloromethane placed in a larger closed jar containing a reservoir of diethyl ether. The product was collected and washed with pentane, affording small crystals with a fuzzy appearance (.3425g, .487 mmol, 44% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 19.34 (s, 1H), 7.48 (m, 4H), 7.37 (t, 2H), 7.20 (m, 5H) 7.02 (t, 2H), 6.85 (broad s, 1H), 6.60 (t, 1H), 5.84 (broad s, 1H), 4.874 (broad s, 2H), 4.41 (broad s, 1H), 3.93 (broad s, 2H), 3.64 (broad d, 2H), 3.32 (broad d, 2H), 2.62 (s, 3H), 1.6-0.41 (broad q, 12H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 320.15, 225.22, 162.52, 158.77, 154.95, 151.96, 148.71, 137.65, 137.24, 134.72, 131.99, 131.34, 130.37. 129.34, 127.96, 126.11, 125.83, 125.36, 125.12, 124.32, 122.35, 111.01, 70.34, 50.55, 36.54, 28.84, 27.73, 26.38, 24.15, 23.51, 19.81.

CHN elemental analysis for $C_{36}H_{41}Cl_2N_3ORu$ – Calculated: C 61.44 %, H 5.87 %, N 5.97 %, Found: C 61.54 %, H 6.04 %, N 5.61 %

Metathesis Reactions

Self-metathesis of 1-decene

Sample Protocol for 10,000 equiv. of 1-decene

Catalyst stock solutions were prepared outside of the glovebox, in Ar sparged and dry DCM. A 10-mL round-bottom flask was charged with 1-decene (5.00 mL, 26.41 mmol) and a stir bar. A water-cooled reflux condenser was attached and vented to an oil bubbler. The headspace was purged with Ar for several minutes at a rate of ~2 bubbles/second while stirring. After equilibrating to the desired temperature in an oil bath, the condenser was temporarily removed, ensuring a positive pressure of Ar, and catalyst **5** stock solution (.00582 M, 45.4 µL, .000265 mmol, .001 mol%) was injected, followed by immediate replacement of the condenser. A steady flow of Ar was kept throughout the duration of the experiment. After 24hr, the condenser was rinsed with hexanes and removed. The reaction was quenched with .1 mL of 1 M tris(hydroxymethyl)phosphine, followed by vigorous stirring overnight at 60-65°C. The crude mixture was repeatedly washed with H_2O until the aqueous phase was colorless, followed by .5 M HCl, saturated $NaHCO_3$, and brine, to ensure complete removal of the catalyst before GC analysis. For the kinetic experiments, aliquots of .1 mL were taken from the reaction at various times, each worked up separately. The purified product mixture was diluted further with hexanes (~1:100) before analysis via GC. The experiments conducted with different catalyst loadings followed the same protocol with different molar amounts of catalyst and substrate.

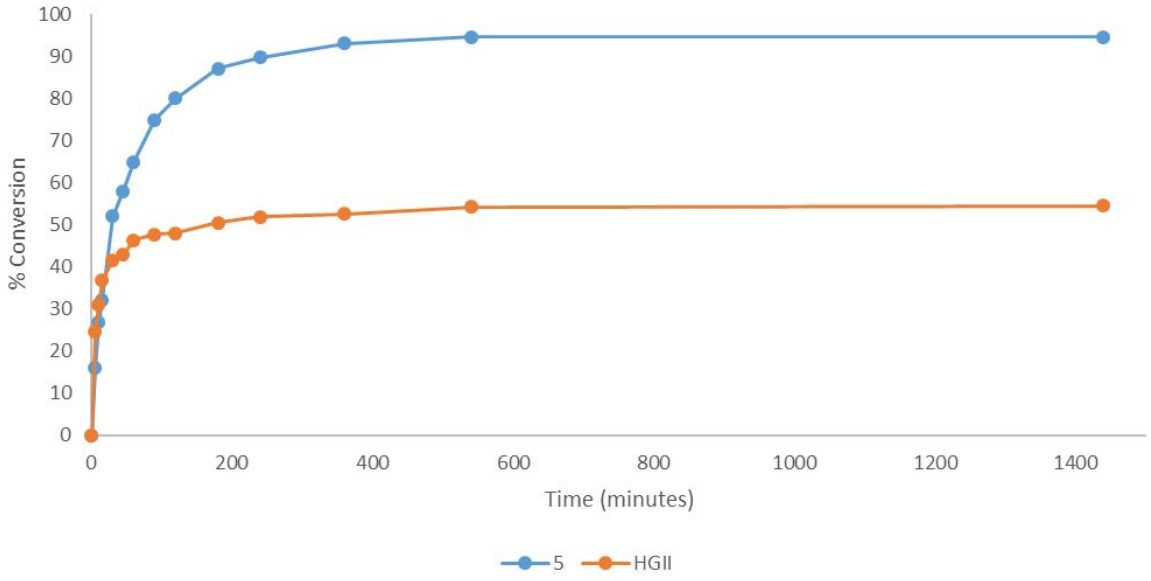
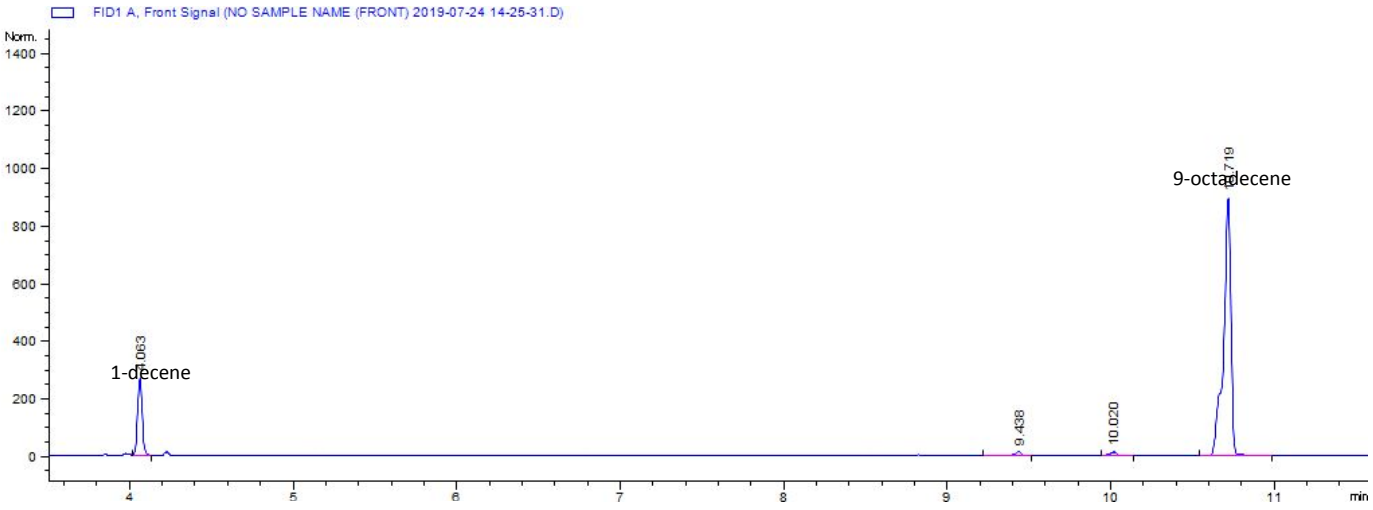


Figure S1. SM of 1-decene kinetic plots of **5** and HGII catalysts with 10,000 equivalents of substrate at room temperature.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.063	VV	0.0293	525.01355	274.32968	15.15205
2	9.438	VB	0.0371	44.74145	16.80018	1.29125
3	10.020	VV	0.0465	45.75456	13.84881	1.32049
4	10.719	VV	0.0460	2849.45728	899.25281	82.23621
Totals :				3464.96684	1204.23148	

*** End of Report ***

Figure S2. Sample gas chromatogram for the SM of 1-decene with 100,000 equivalents of substrate at 70°C using catalyst **5** after 24hr of reaction.

Ring-closing metathesis of DEDAM

In an Ar filled glovebox, an NMR tube was charged with DEDAM (181.3 μL, .750 mmol), 570 μL of toluene-d8, then catalyst **5** stock solution (.01 M, 1.5 μL, $1.5x10^{-5}$ mmol, .002 mol%). The tube was promptly capped and inverted. An 18G needle was used to vent the system prior to heating to the desired temperature outside of the glovebox. ^{1}H NMR spectra were acquired until the activity ceased. The degree of conversion was determined by comparing the ratio of the integrals of the methylene protons in the substrate (δ 2.72) to those in the product (δ 3.05).

Table S1. RCM of *neat* DEDAM at 55˚C using catalyst **5** varying the venting conditions.

Equivalents of substrate	Venting condition	Conversion (%)	TON
50,000	Closed	23	11,700
	Vented to oil bubbler	25	12,300
	Ar sparged	18	8,900
1,000,000	Closed	1.1	11,300
	Vented to oil bubbler	1.3	12,500
	Ar sparged	1.1	11,200

ROMP of 1,5-cyclooctadiene

Sample Protocol for 1,000 equiv. of COD

In an Ar glovebox, a J-young NMR tube was charged with 1,5-cyclooctadiene (49.1 µL, .40 mmol, .5 M) and .75mL of CD_2Cl_2. For the experiments run at 80˚C, bromobenzene-d5 was used as the solvent. The sample was equilibrated in the spectrometer to the desired temperature before injection of catalyst **5** stock solution (.01844 M, 21.7 µL, .0004 mmol, 0.1 mol%). Conversion of COD starting material to poly-COD was determined by comparing the ratio of the integrals of the methylene protons in the substrate (δ 2.36) to those in the product (δ 2.09 & 2.04). For kinetic experiments, the sample was kept in the spectrometer throughout the duration of the experiment, and data points were collected at various time intervals. The experiments conducted with different catalyst loadings followed the same protocol with different amounts of catalyst.

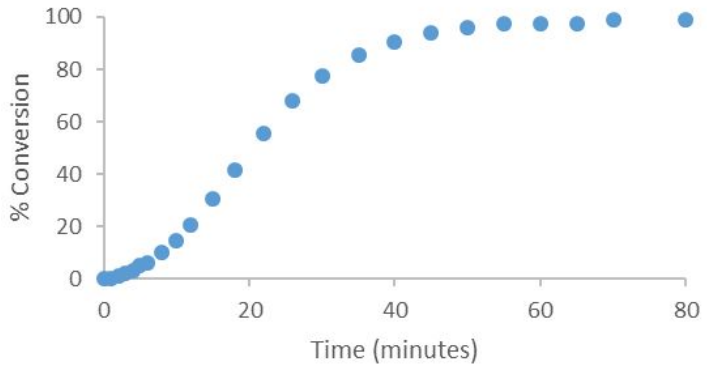


Figure S3. ROMP of COD kinetic plot with catalyst **5** at 1,000 equivalents of substrate and 30 ˚C.

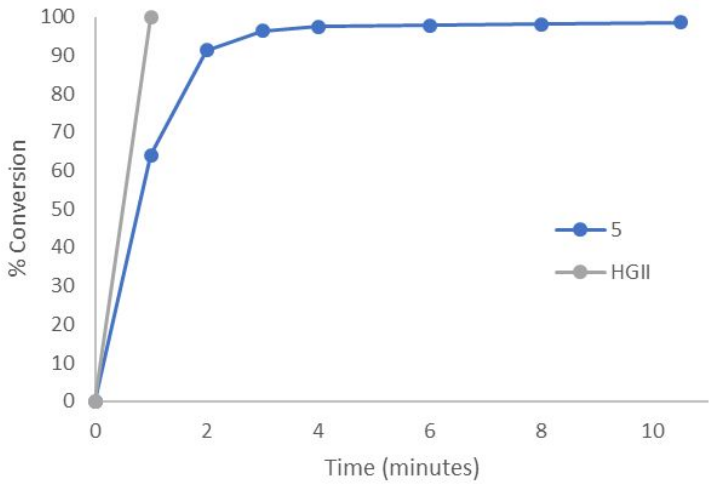


Figure S4. ROMP of COD kinetic plot of **5** and **HGII** catalysts at 5,000 equivalents of substrate and 80˚C.

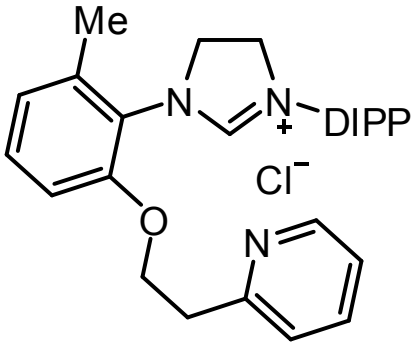
X-ray Crystallography

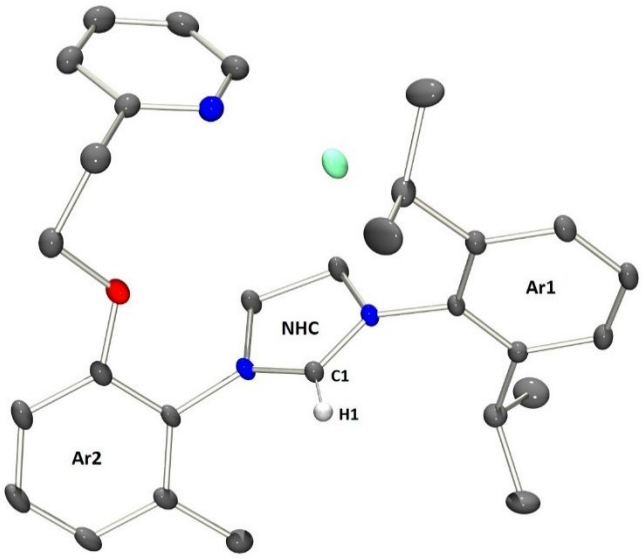
General remarks

All crystal structures are shown with thermal ellipsoids at 50 % probability. Counterions, solvent molecules, and hydrogen atoms are omitted for clarity with the exception of those deemed significant. The structures were drawn by obtaining coordinates with ORTEP 3 followed by image creation with POVray using the following parameters: style (ORTEP ellipsoids), ellipse style (plain), finish (shiny), and resolution of [1600 × 1200, AA 0.3], with the following color scheme: bonds (wheat), C (dark grey 30), H (light grey), Cl (aquamarine), N (blue), O (red), and Ru (orchid). Crystal structure measurements of angle and distance were obtained with the program Mercury.

Table S2. Crystal structure measurements for **4.**

C1–H1	0.950 Å
NHC plane × Ar1 plane	89.90°
NHC plane × Ar2 plane	74.72°





Special refinement details for compound **4**

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Mo K_α radiation (λ = 0.71073 Å) from an IμS micro-source for the structure of compound V18143. The structure was solved by direct methods using SHELXS[ii] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[iii] using established refinement techniques.[iv] 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).

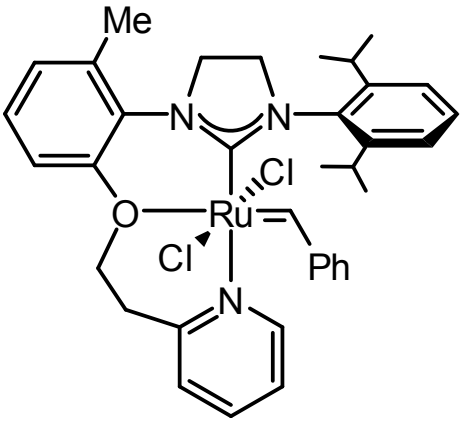
Compound **4** (V18143) crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit along with one molecule of isopropyl alcohol.

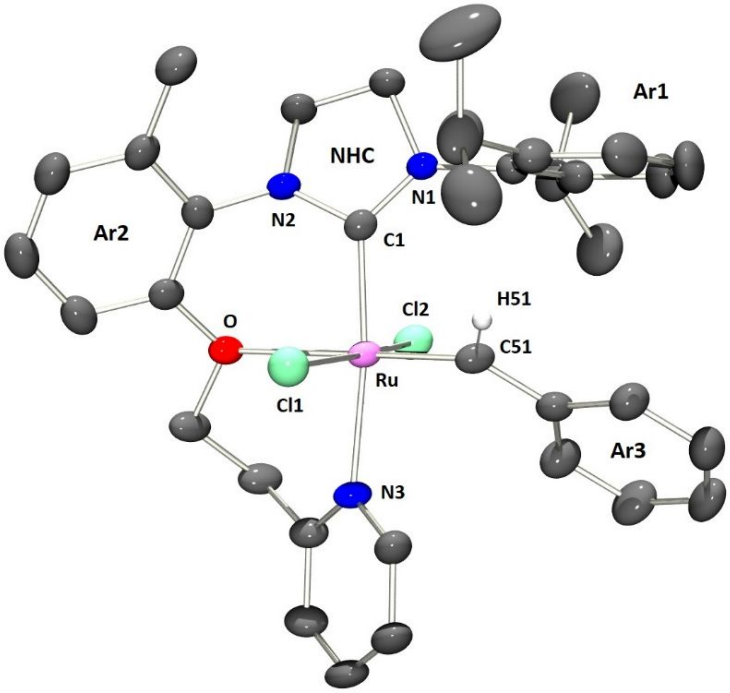
Table S3. Crystal data and structure refinement for **4** (V18143).

Empirical formula	C32 H44 Cl N3 O2	
Formula weight	538.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.9580(5) Å	a= 90°.
	b = 14.0367(5) Å	b= 105.0675(17)°.
	c = 20.2453(8) Å	g = 90°.
Volume	3007.0(2) $Å^3$	
Z	4	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.159 mm^{-1}	
F(000)	1160	
Crystal size	0.600 x 0.600 x 0.600 mm^3	
Theta range for data collection	2.410 to 36.329°.	
Index ranges	-18<=h<=18, -23<=k<=19, -33<=l<=33	
Reflections collected	55658	
Independent reflections	14508 [R(int) = 0.0280]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6872	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14508 / 0 / 351	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.1064	
R indices (all data)	R1 = 0.0494, wR2 = 0.1127	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.559 and -0.241 $e.Å^{-3}$	

Table S4. Crystal structure measurements for **5.**

Ru–C1	1.998 Å
Ru=C51	1.846 Å
Ru-Cl1	2.398 Å
Ru-Cl2	2.381 Å
Ru–O	2.366 Å
Ru–N3	2.187 Å
C51-H51	.950 Å
NHC plane × Ar1 plane	75.22°
NHC plane × Ar2 plane	51.57°
Ar1 plane × Ar3 plane	35.88°





Special refinement details for catalyst **5**

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound V19207. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2018 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, 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).

Compound **5** (V19207) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit along with two partially occupied water molecules. The coordinates for the hydrogen atoms bound to O1S and O2S were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the O-H distance (0.84(4) Å).

Table S5. Crystal data and structure refinement for **5** (V19207).

Empirical formula	C72 H84.50 Cl4 N6 O3.25 Ru2	
Formula weight	1429.89	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.3434(12) Å	a= 90°.
	b = 15.6537(13) Å	b= 91.843(5)°.
	c = 42.617(4) Å	g = 90°.
Volume	6896.7(12) $Å^3$	
Z	4	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	5.366 mm^{-1}	
F(000)	2962	
Crystal size	0.150 x 0.150 x 0.050 mm^3	
Theta range for data collection	3.008 to 74.696°.	
Index ranges	-12<=h<=12, -19<=k<=19, -52<=l<=53	
Reflections collected	76063	
Independent reflections	14027 [R(int) = 0.0737]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6160	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14027 / 4 / 815	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.0990	
R indices (all data)	R1 = 0.0655, wR2 = 0.1061	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.700 and -1.301 $e.Å^{-3}$	

NMR Spectra

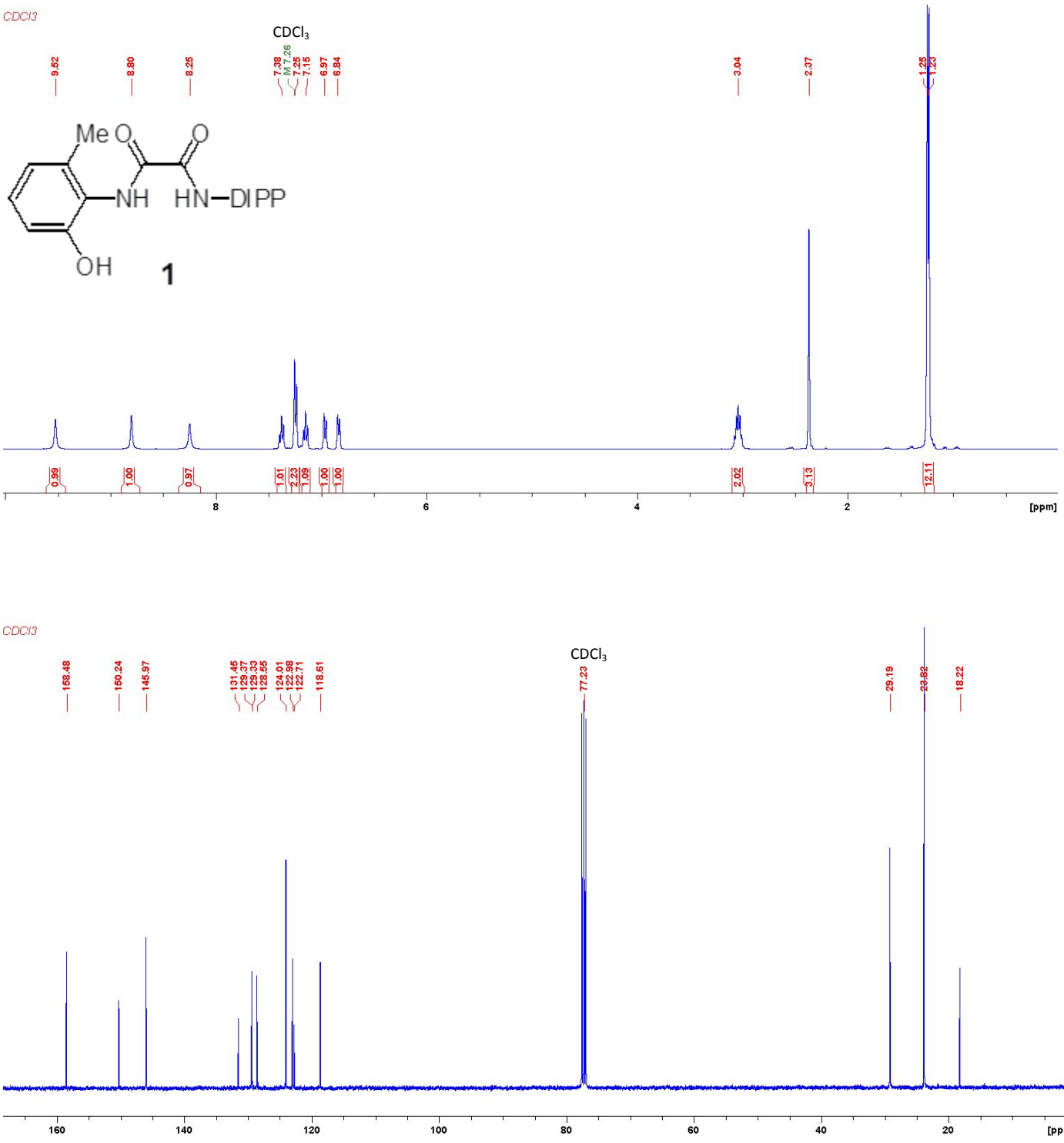


Figure S5. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR (bottom) (400MHz, $CDCl_3$) of **1**.

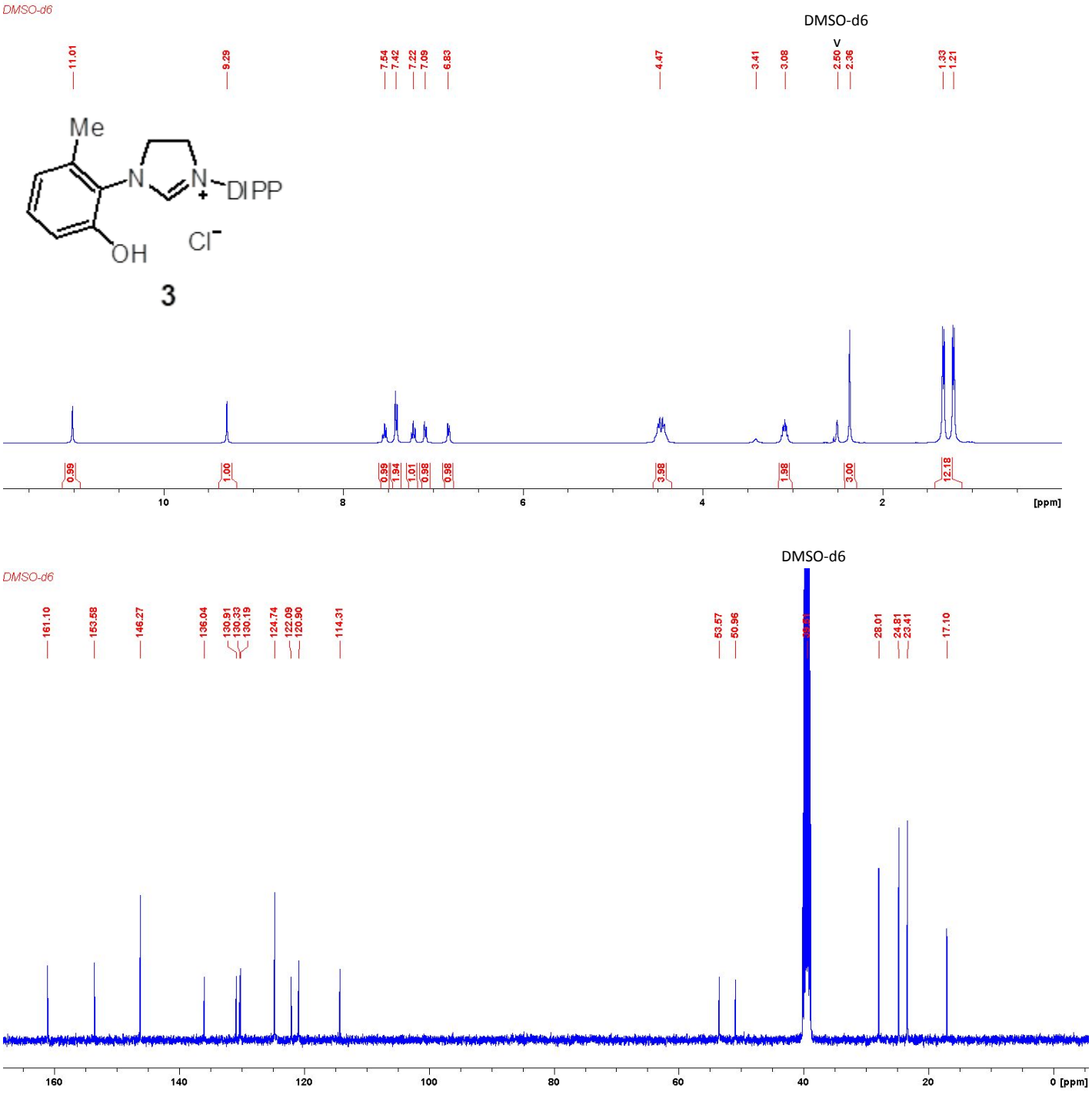


Figure S6. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR (bottom) (400MHz, DMSO-d6) of **3**.

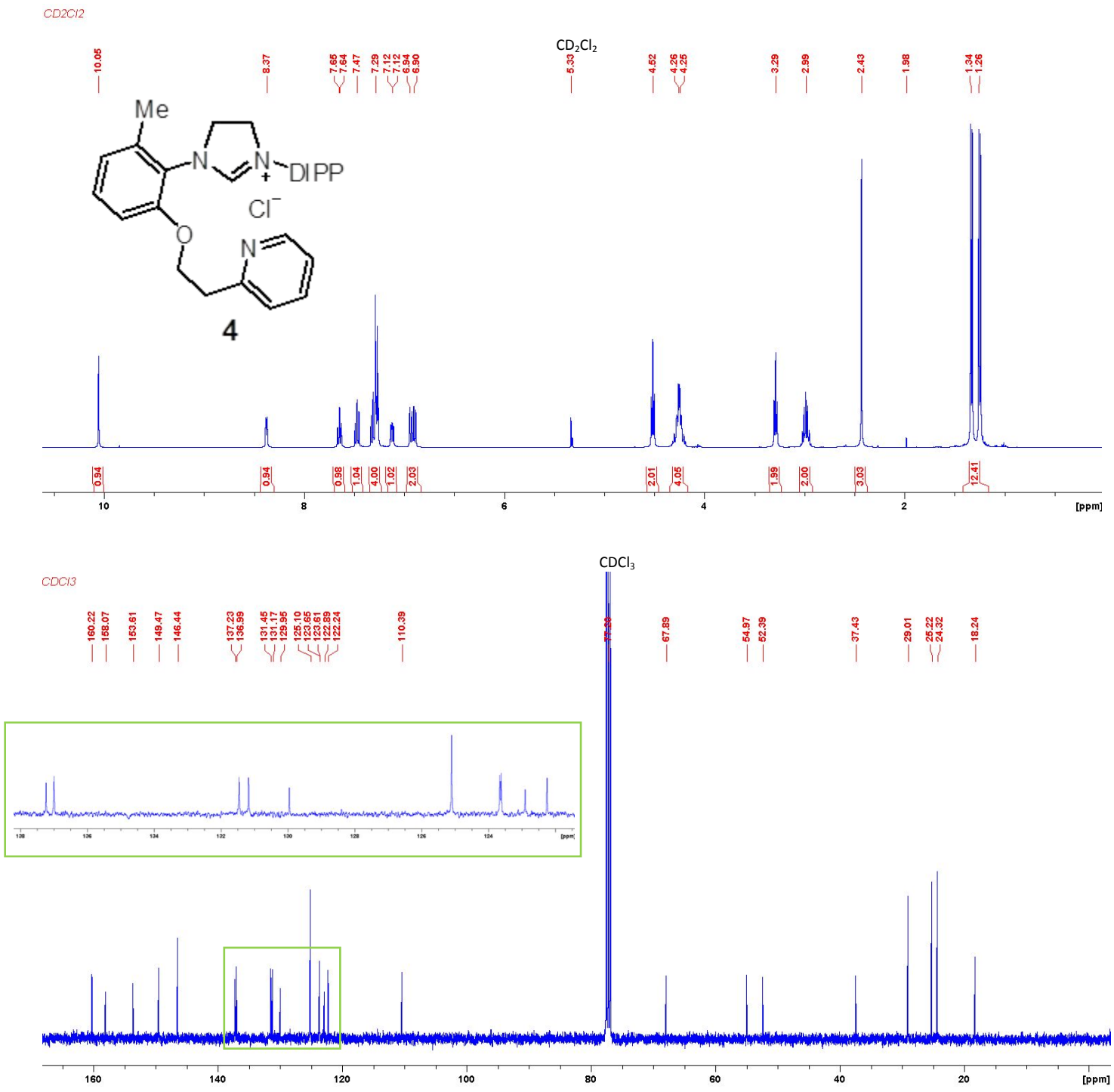
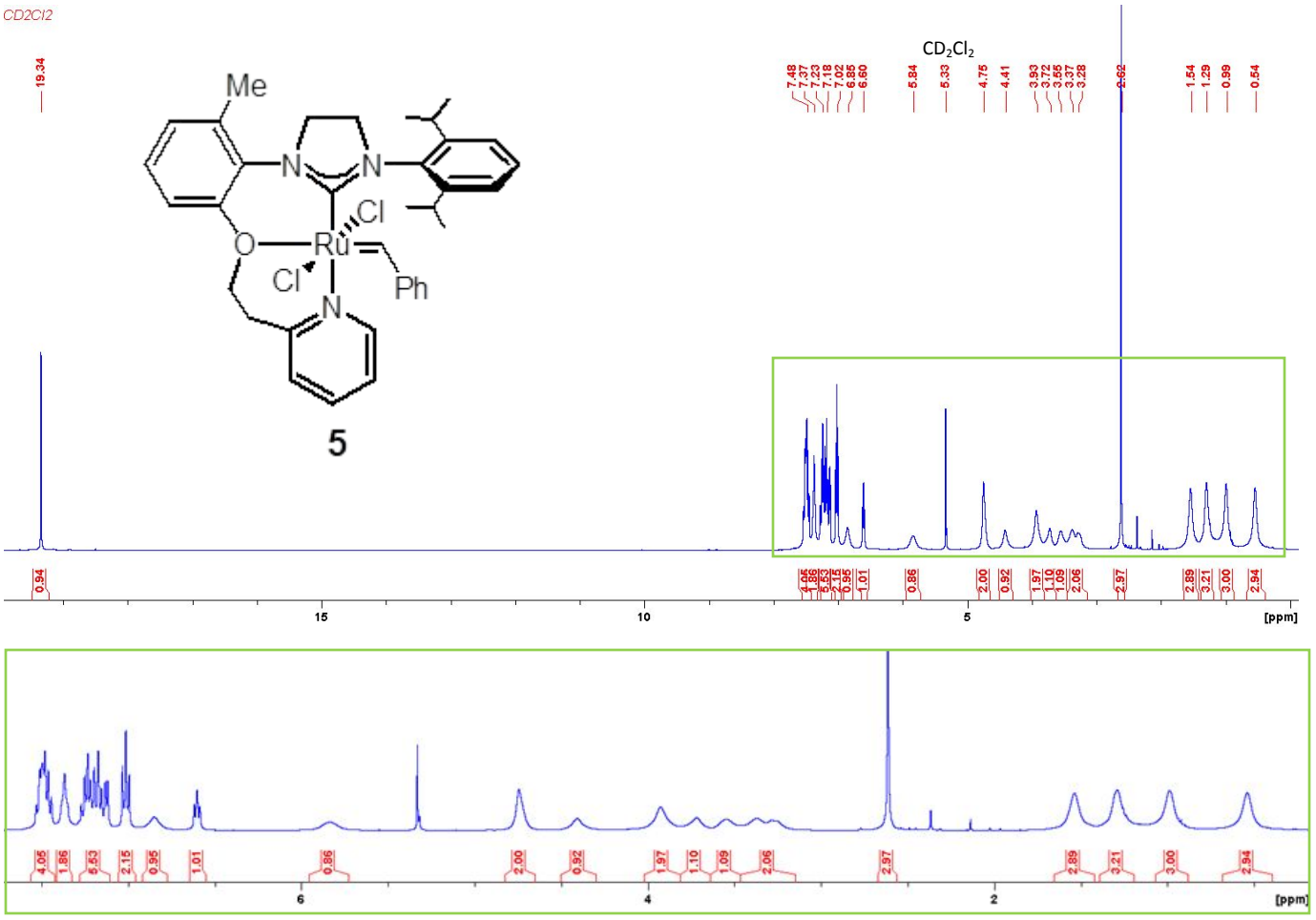
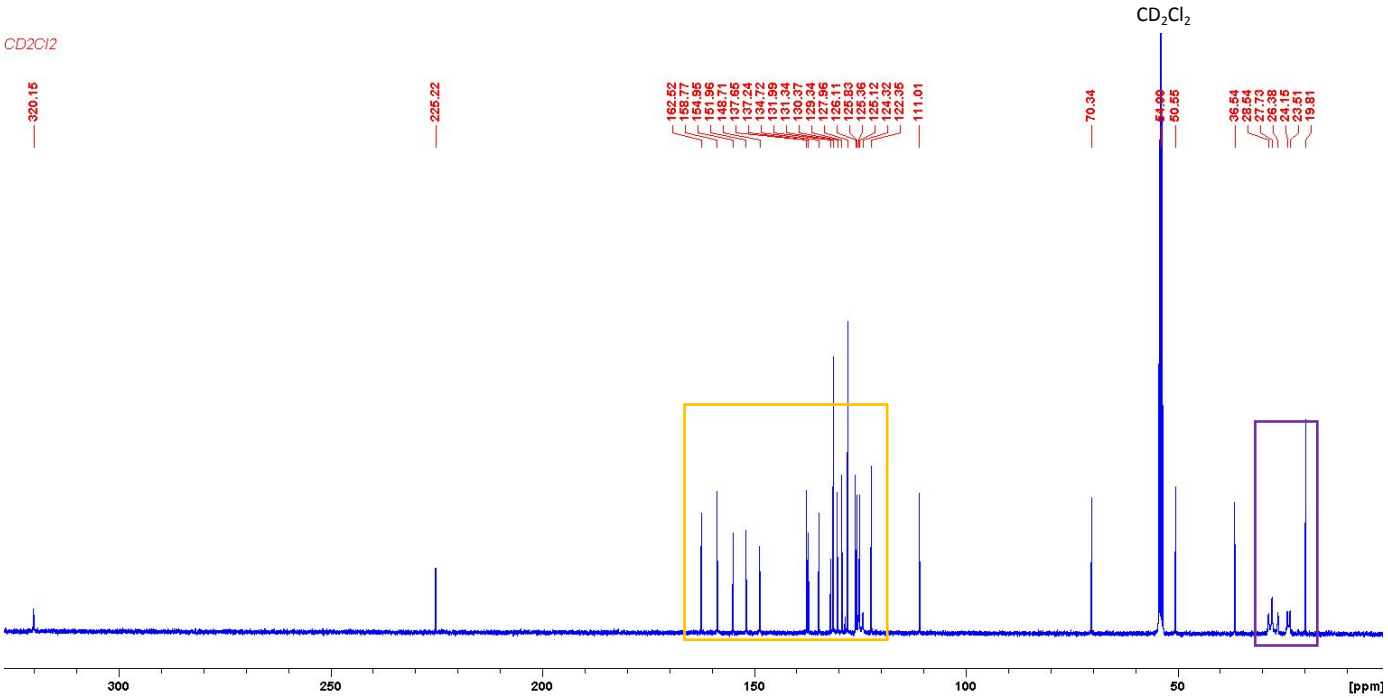


Figure S7. ^{1}H NMR (top) (400MHz, CD_2Cl_2) and $^{13}C\{^{1}H\}$ NMR (bottom) ($CDCl_3$) of **4.**


CD2Cl2
CD2Cl2
Me
N
N
Cl
O
Ru
Cl
Ph
N
5
[ppm]
[ppm]


CD2Cl2
CD2Cl2
[ppm]

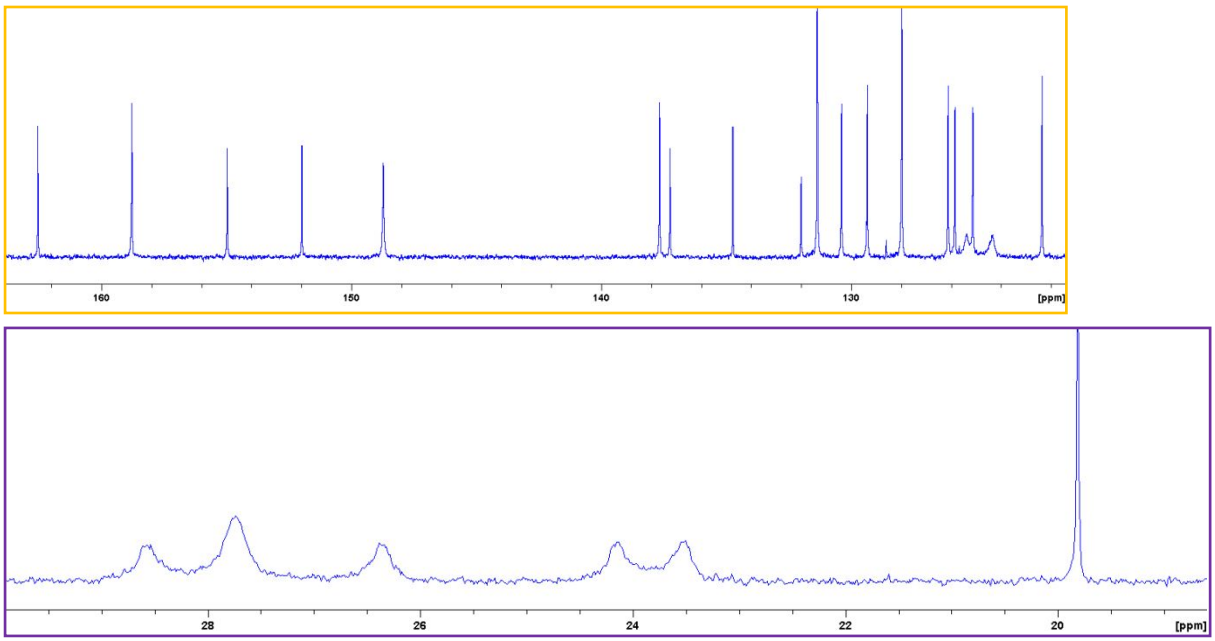


Figure S8. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR (bottom) (400MHz, CD_2Cl_2) of **5.**

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[ii] Sheldrick, G. M. Phase annealing in SHELX-90: direct methods for larger structures *Acta Cryst.* **1990**, A46, 467-473.

[iii] Sheldrick, G. M. *SHELXT*–Integrated space-group and crystal-structure determination *Acta Cryst.* **2015**, C71, 3-8.

[iv] Müller, P. Practical suggestions for better crystal structures *Crystallography Reviews* **2009**, *15*, 57-83.