Supporting Information for:

Synthesis and Activity of 6-Membered Cyclic Alkyl Amino Carbene–Ruthenium Olefin Metathesis Catalysts

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General considerations.

Unless otherwise stated, all manipulations were carried out in dry solvents under an atmosphere of argon, using either standard Schlenk techniques or a glovebox. Pentane, toluene, benzene, and diethyl ether were dried using a custom solvent purification system. 4-iodo-2-methylbut-1-ene,[1] **1a**[2], and **1b**[2] were prepared by literature procedures or slight modifications thereof. Compounds **S1**, **S2**, **S3**, **S4**, **S5**, **S6**, **1d**, **1c**, **1e**, **3a**, **3b**, **3d**, **3c**, and **7** were prepared using the following procedures (Figure S1). 2-isopropyl-6-methylaniline and 2,6-diisopropylaniline were distilled under argon prior to use, Hoveyda-Grubbs 1st generation catalyst (**HG1**) was received from Materia Inc. and used as is. Methyl oleate was purchased from Nu-Chek Prep and subjected to further purification by passing through an activated neutral alumina plug, then storing over fresh activated neutral alumna for at least 3 days in a glovebox. To activate, neutral alumina was heated to 200 °C for 48 h under high vacuum. Ultra-high purity (99.95%) ethylene gas was purchased and used as received from Matheson, all other reagents and solvents were purchased from various commercial suppliers and used as received. "Room temperature" or "RT" refers to ~22 °C. Reaction temperatures represent the oil bath temperature unless otherwise stated. Mass spectrometry was performed by the Multi User Mass Spectrometry Laboratory at the California Institute of Technology. Gas chromatography was carried out using an Agilent 6850 GC equipped with an HP-1 column. Integrations performed on GC traces were normalized using experimentally determined response factors and dodecane as an internal standard. Unless otherwise noted, NMR spectra were acquired at 25 °C using Varian 300, 400, 500, 600, and Bruker 400 spectrometers. Chemical shifts (δ) are given in ppm and referenced to residual solvent peaks for ^{1}H NMR spectra (δ = 7.26 ppm for chloroform-*d*, and δ = 7.16 ppm for benzene-*d6*) and for ^{13}C{^{1}H} NMR spectra (δ = 77.16 ppm for chloroform-*d*, and δ = 128.06 ppm for benzene-*d6*).

Synthetic Procedures and Characterization of Compounds

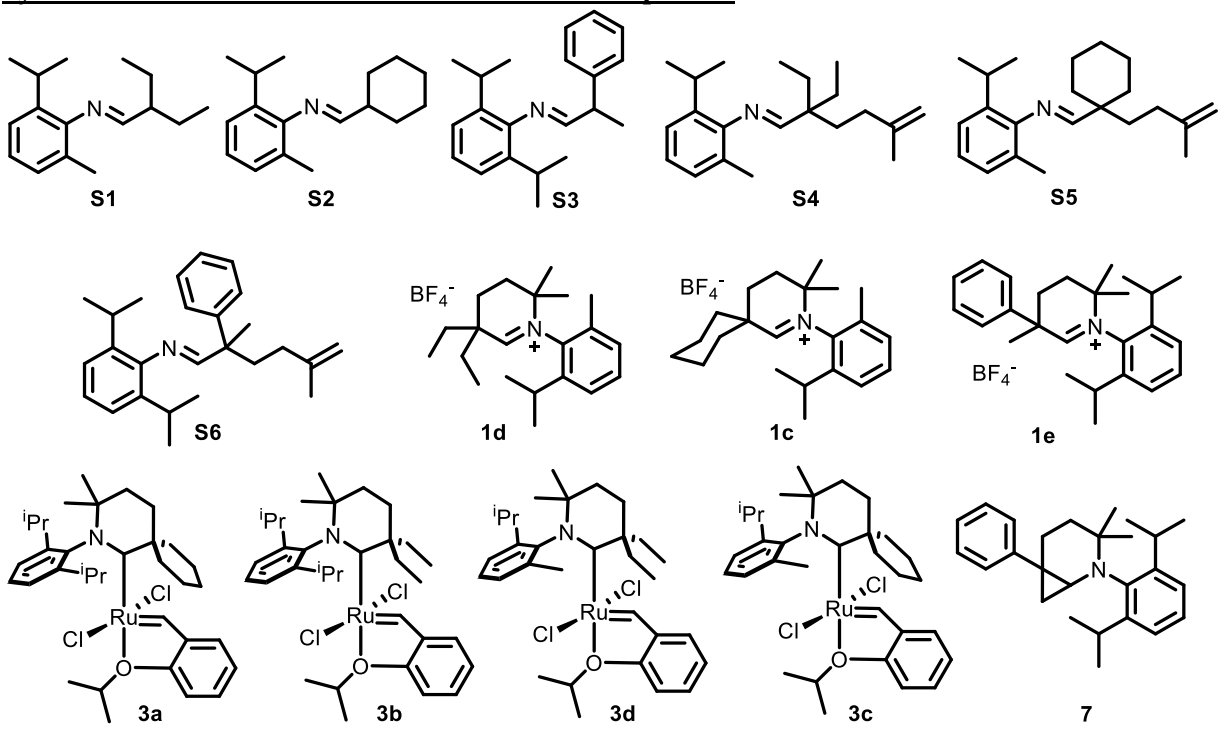
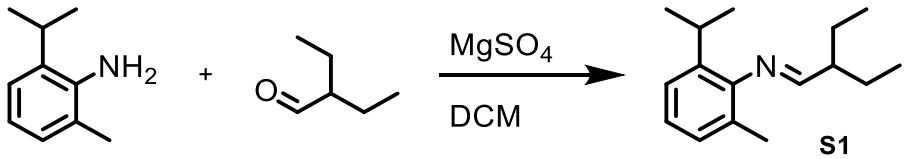
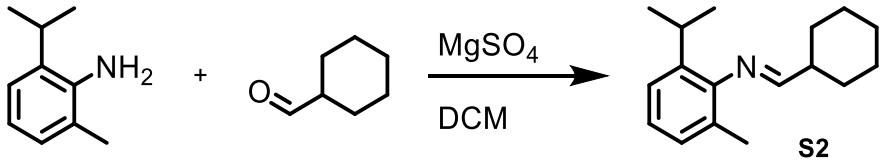


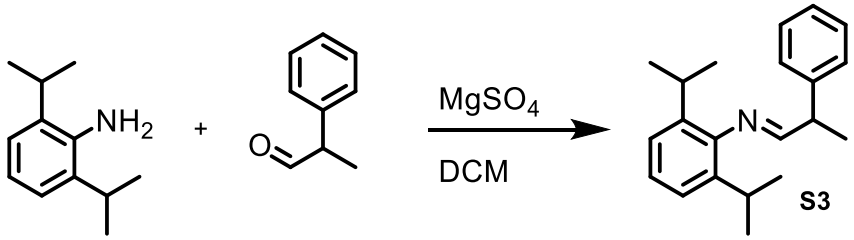
Figure S1. Compounds synthesized for this study.



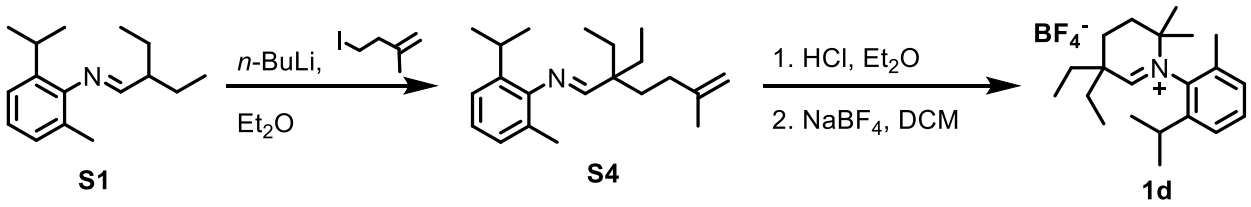
2-ethyl-*N*-(2-isopropyl-6-methylphenyl)butan-1-imine (S1). A procedure was adapted from the literature[2] as follows: A 20 mL vial was charged with 2-isopropyl-6-methylaniline (3.04 g, 20.4 mmol, 1.0 equiv), 2-ethylbutanal (2.04 g, 20.4 mmol, 1.0 equiv), magnesium sulfate (2.0 g, 16.6 mmol, 0.80 equiv), and CH_2Cl_2 (10 mL) in air. The vial was sealed and stirred vigorously at RT for 24 h. The reaction was filtered over celite and concentrated under reduced pressure. The residual oil was taken up in hexanes (20 mL) and passed through a plug of neutral alumina with hexanes. The solution was concentrated under reduced pressure and dried *in vacuo* to furnish **S1** (3.1 g, 66%) as a viscous oil. ^{1}H NMR (benzene-*d6*, 500 MHz): δ = 7.14 (d, *J* = 0.7 Hz, 1H), 7.06 – 7.00 (m, 2H), 3.22 (hept, *J* = 6.9 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.11 (s, 3H), 1.55 – 1.44 (m, 2H), 1.44 – 1.33 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 6H), 0.44 (s, 1H). This compound was used directly in the next step without further purification.



1-cyclohexyl-*N*-(2-isopropyl-6-methylphenyl)methanimine (S2). Prepared following a nearly identical procedure as **S1** with cyclohexanecarbaldehyde (2.29 g, 20.4 mmol, 1.0 equiv) to afford **S2** (4.90 g, 98%) as a yellow oil. ^{1}H NMR (chloroform-*d*, 400 MHz): δ = 7.50 (d, *J* = 4.8 Hz, 1H), 7.10 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.02 – 6.94 (m, 2H), 2.95 (hept, *J* = 6.7 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.06 (s, 3H), 1.97 (p, *J* = 4.3, 3.7 Hz, 2H), 1.83 (tq, *J* = 6.0, 3.4, 2.5 Hz, 2H), 1.76 – 1.68 (m, 1H), 1.40 (ddt, *J* = 11.5, 6.1, 2.8 Hz, 4H), 1.28 – 1.28 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 6H). This compound was used directly in the next step without further purification.

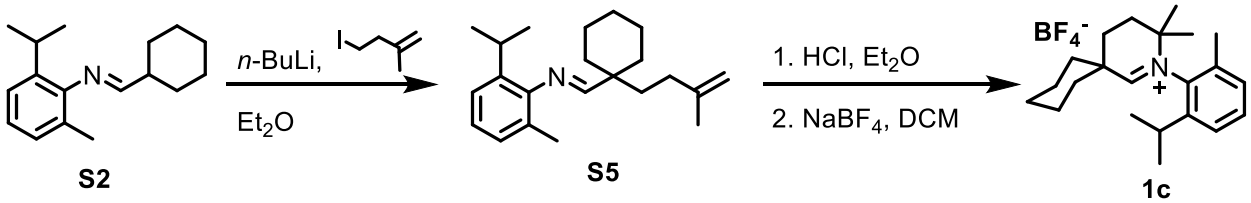


***N*-(2,6-diisopropylphenyl)-2-phenylpropan-1-imine (S3).** Prepared following a nearly identical procedure as **S1** with 2-phenylpropanal (4.02 g, 30 mmol, 1.0 equiv), 2,6-diisopropylaniline (5.32 g, 30 mmol, 1.0 equiv), magnesium sulfate (3.0 g, 25 mmol, 0.80 equiv), CH_2Cl_2 (15 mL) to afford **S3** (5.50 g, 63%) as a colorless oil. ^{1}H NMR (benzene-*d6*, 400 MHz): δ = 7.44 (d, *J* = 4.8 Hz, 1H), 7.15 (s, 3H), 7.13 – 7.03 (m, 5H), 3.65 (qd, *J* = 7.1, 4.7 Hz, 1H), 3.06 (h, *J* = 6.9 Hz, 2H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 12H). This compound was used directly in the next step without further purification.



5,5-diethyl-1-(2-isopropyl-6-methylphenyl)-2,2-dimethyl-2,3,4,5-tetrahydropyridin-1-ium tetrafluoroborate (1d). A procedure was adapted from the literature[2] as follows: To a 100 mL schlenk flask under Ar was added **S1** (3.14 g, 13.58 mmol, 1.0 equiv) and Et_2O (24 mL). The reaction was cooled to -78 °C using a dry ice/acetone bath and *n*-BuLi (6.0 mL, 2.37M in hexane, 14.26 mmol, 1.05 equiv) was added dropwise over 5 minutes with stirring. The flask was left to stir at -78 °C for a further 10 minutes then warmed to RT and stirred for 3 h. The flask was then cooled to -78 °C again, and a solution of 4-iodo-2-methylbut-1-ene (3.20 g, 16.3 mmol, 1.2 equiv) in Et_2O (10 mL) was added slowly. The reaction was left to warm to RT overnight and then quenched with concentrated $NaHSO_3$ (2 x 40 mL), then H_2O (3 x 20 mL). The organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to yield crude **S4** (3.66 g) as a yellow oil which was dried *in vacuo* and used directly in the next step without further purification.

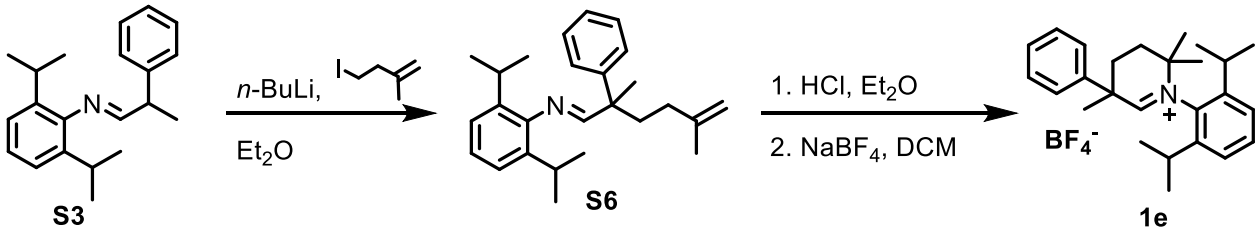
To an oven dried Fischer-porter flask with a stir bar and valve assembly was added a solution of **S4** (3.66 g, 12.2 mmol, 1.0 equiv) in Et_2O (25 mL), and HCl (24.4 mL, 1M in Et_2O, 24.4 mmol, 2.0 equiv) under Ar. The valves were sealed, and the flask was heated to 90 °C with stirring in an oil bath behind a blast shield for 18 h. The reaction was then cooled during which time a brown oil settled out. The supernatant was poured off, and the brown oil was dried *in vacuo* to give an amorphous solid. The solid was added to a 20 mL vial with CH_2Cl_2 (5 mL) and $NaBF_4$ (1.0 g) and stirred overnight. The solution was then loaded onto a neutral alumina plug and flushed with CH_2Cl_2 (150 mL) to remove impurities. The plug is then flushed with 10% MeOH in CH_2Cl_2 (100 mL) to recover the product. The eluent was concentrated under reduced pressure, sonicated with pentane (2 mL), and filtered to afford **1d** (219 mg, 6%) as a fine white powder. ^{1}H NMR (chloroform-*d*, 500 MHz): δ = 8.86 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.26 – 7.23 (m, 1H), 2.62 (hept, *J* = 6.7 Hz, 1H), 2.32 (s, 3H), 2.20 (t, *J* = 6.4 Hz, 2H), 2.03 (t, *J* = 6.8 Hz, 2H), 2.09 – 1.88 (m, 4H), 1.47 (d, *J* = 5.5 Hz, 6H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.11 (dt, *J* = 15.1, 7.5 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-d, 101 MHz): δ = 243.92, 182.17, 181.22, 176.28, 128.38, 128.06, 127.74, 119.63, 96.91, 84.87, 80.73, 80.00, 79.86, 78.49, 78.16, 76.99, 73.22, 73.16, 70.67, 59.72, 59.67; $[M]^+$ calcd. for $[C_{21}H_{34}N]^+$, 300.2691; found, 300.2684.



2-(2-isopropyl-6-methylphenyl)-3,3-dimethyl-2-azaspiro[5.5]undec-1-en-2-ium tetrafluoroborate (1c). Was setup nearly identically to **1d**, but using **S2** (4.97 g, 20.12 mmol, 1.0 equiv), Et_2O (78 mL), *n*-BuLi (8.75 mL, 2.45M in hexane, 21.44 mmol, 1.05 equiv), and a solution of 4-iodo-2-methylbut-1-ene (4.73 g, 24.14 mmol, 1.2 equiv) in Et_2O (10 mL). This gave an oil which was taken up in hexanes (20 mL)

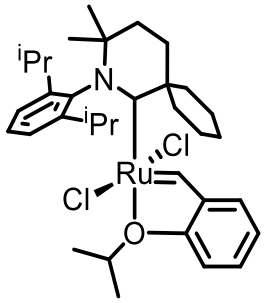
and passed through a plug of basic alumina to afford crude **S5** (5.0 g) as a light yellow oil which was dried *in vacuo* and directly used in the next step without further purification.

S5 (5.0 g, 16.05 mmol, 1.0 equiv), Et_2O (64 mL), and HCl (16 mL, 2M in Et_2O, 32.1 mmol, 2.0 equiv) formed a white solid instead of a brown oil, which was filtered, washed with Et_2O, and subjected to stirring in a 20 mL vial with $NaBF_4$ (1.04 g) and CH_2Cl_2 (10 mL) overnight. The mixture was then filtered, and the filtrate concentrated under reduced pressure to afford **1c** (103 mg, 2%) as an off-white solid. ^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.59 (s, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.27 (dd, *J* = 26.0, 6.8 Hz, 2H), 2.59 (s, 1H), 2.29 (s, 3H), 2.16 (s, 4H), 1.86 (d, *J* = 81.6 Hz, 10H), 1.48 (s, 3H), 1.43 (s, 3H), 1.41 – 1.34 (m, 3H), 1.13 (s, 3H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 191.94, 143.68, 136.75, 132.95, 131.37, 130.43, 125.32, 68.76, 42.46, 34.26, 32.06, 31.95, 29.95, 28.19, 27.44, 26.15, 24.33, 24.10, 22.30, 20.11, 19.98, 19.78; $[M]^+$ calcd. for $[C_{22}H_{34}N]^+$, 312.2691; found, 312.2699.



1-(2,6-diisopropylphenyl)-2,2,5-trimethyl-5-phenyl-2,3,4,5-tetrahydropyridin-1-ium tetrafluoroborate (1e). Was setup nearly identically to **3d**, but using **S3** (5.5 g, 18.74 mmol, 1.0 equiv), Et_2O (80 mL), *n*-BuLi (8.0 mL, 2.45M in hexane, 19.68 mmol, 1.05 equiv), and a solution of 4-iodo-2-methylbut-1-ene (4.4 g, 22.48 mmol, 1.2 equiv) in Et_2O (10 mL) which afforded crude **S6** (6.63 g) as a light-yellow oil which was dried *in vacuo* and used directly in the next step.

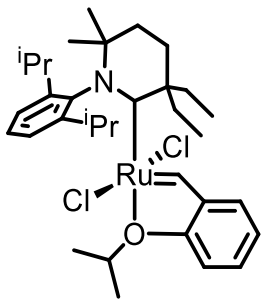
S6 (6.63 g, 18.33 mmol, 1.0 equiv), Et_2O (75 mL), and HCl (18.3 mL, 2M in Et_2O, 36.67 mmol, 2.0 equiv) formed a brown oil, which was washed with Et_2O, and subjected to stirring in a 20 mL vial with $NaBF_4$ (0.85 g) and CH_2Cl_2 (10 mL) overnight. The solution was then loaded onto a neutral alumina plug and flushed with CH_2Cl_2 (150 mL) to remove impurities. The plug is then flushed with 10% MeOH in CH_2Cl_2 (100 mL) to recover the product. The eluent was concentrated under reduced pressure, sonicated with pentane (2 mL), and filtered to afford **1e** (459 mg, 5%) as a fine white powder. ^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.54 (s, 1H), 7.53 – 7.40 (m, 5H), 7.39 – 7.28 (m, 3H), 2.70 (p, *J* = 6.7 Hz, 1H), 2.66 – 2.55 (m, 2H), 2.55 – 2.45 (m, 1H), 2.39 – 2.29 (m, 2H), 1.92 (s, 3H), 1.58 (d, *J* = 22.7 Hz, 3H), 1.49 (s, 3H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.34 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 187.56, 144.13, 143.30, 138.98, 135.11, 132.07, 130.14, 129.10, 126.31, 125.80, 125.79, 69.69, 46.27, 33.86, 29.97, 29.82, 29.23, 27.65, 26.85, 26.04, 26.00, 25.04, 22.51, 22.19; $[M]^+$ calcd. for $[C_{26}H_{36}N]^+$, 362.2848; found, 362.2847.



3a

3a. To a 4 mL vial in a glovebox was added **1a** (107 mg, 0.25 mmol, 3.0 equiv), LiHMDS (39 mg, 0.232 mmol, 2.8 equiv), and C_6D_6 (2.7 mL). The vial was sealed and stirred for 1 h at RT. The solution of **2a** was filtered using a PTFE syringe filter into another 4 mL vial with **HG1** (50 mg, 0.083 mmol, 1.0 equiv) and heated to 40 °C on an aluminum heating block for 48 h. The reaction was then cooled to RT and the solvent removed *in vacuo*. The residue was re-dissolved in benzene (0.3 mL). Upon addition of pentane (2 mL), the product was precipitated and collected through filtration (**3a**, 37 mg, 67%) as green solid. The product can be further purified by recrystallization from CH_2Cl_2/EtOH. ^{1}H NMR (benzene-*d6*, 500 MHz): δ = 16.24 (s, 1H), 7.32 (dd, J = 8.3, 7.0 Hz, 1H), 7.23 (d, J = 7.7 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.12 (dd, J = 7.5, 1.7 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.42 (d, J = 8.3 Hz, 1H), 4.60 (hept, J = 6.1 Hz, 1H), 4.26 – 4.19 (m, 2H), 3.29 (p, J = 6.6 Hz, 2H), 2.66 (d, J = 12.1 Hz, 2H), 2.08 – 2.02 (m, 3H), 1.93 (d, J = 13.4 Hz, 2H), 1.74 – 1.52 (m, 11H), 1.17 – 1.10 (m, 12H), 1.01 (s, 3H), 1.00 (s, 3H); ^{13}C{^{1}H} NMR (benzene-*d*6, 101 MHz): δ = 301.64, 271.89, 153.31, 148.67, 144.54, 143.02, 130.69, 129.00, 126.17, 124.77, 121.89, 113.64, 74.63, 66.55, 55.90, 35.96, 31.58, 31.09, 28.53, 26.21, 25.61, 25.40, 24.77, 22.35, 22.19; $[M]^+$ calcd. for $[C_{34}H_{49}NOCl_2Ru]^+$, 659.2235; found, 659.2245.

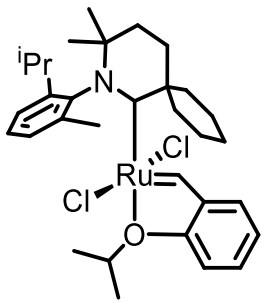
Note: The free carbenes can be successfully generated through the base treatment and seemed to be stable in solution, at least for several hours. However, under less-optimized conditions (for example, with KHMDS or ^{t}AmylOK as the bases), upon the addition of HG1, the decomposition of the free carbene **2a** took place rapidly to unknown species, resulting in lower yield of the transmetalation.



3b

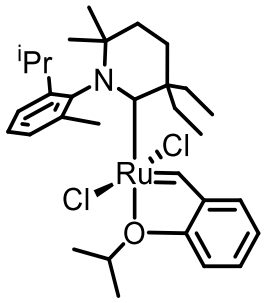
3b. Was setup nearly identically to **3a**, but with **1b** (41.4 mg, 0.010 mmol, 3.0 equiv), LiHMDS (15.6 mg, 0.093 mmol, 2.8 equiv), **HG1** (20 mg, 0.033 mmol, 1.0 equiv), and C_6D_6 (0.8 mL). After adding **HG1**, the reaction was heated for 72 h and concentrated *in vacuo*. The residue was dissolved in benzene (0.4 mL) and precipitated by adding pentane (2 mL). The crude solid was filtered and recrystallized from CH_2Cl_2/EtOH to afford **3b** (5.3 mg, 25%) as a green solid. ^{1}H NMR (benzene-*d*6, 400 MHz): δ = 16.20 (s, 1H), 7.31 (dd, J = 8.5, 6.8 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.17 (m, 1H), 7.12 – 7.06 (m, 1H), 6.69 (td, J = 7.4, 0.7

Hz, 1H), 6.41 (d, J = 8.3 Hz, 1H), 4.59 (hept, J = 6.2 Hz, 1H), 3.84 (dq, J = 14.5, 7.3 Hz, 2H), 3.32 (hept, J = 6.5 Hz, 2H), 3.08 (dq, J = 14.6, 7.4 Hz, 2H), 1.96 – 1.91 (m, 2H), 1.66 – 1.63 (m, 2H), 1.64 (d, J = 6.1 Hz, 6H), 1.24 (t, J = 7.4 Hz, 6H), 1.13 (d, J = 6.7 Hz, 6H), 1.10 (s, 6H), 1.00 (d, J = 6.4 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (benzene-*d*6, 101 MHz): δ = 300.99, 273.31, 153.19, 148.83, 144.55, 143.04, 130.71, 126.29, 124.77, 121.87, 113.63, 74.59, 66.32, 57.55, 36.28, 31.14, 28.70, 28.68, 26.37, 25.46, 23.87, 22.16, 10.59; $[M]^+$ calcd. for $[C_{33}H_{49}NOCl_2Ru]^+$, 647.2235; found, 647.2228.



3c

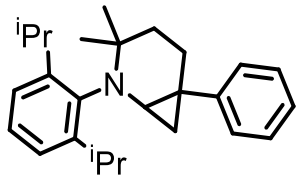
3c. Was setup nearly identically to **3a**, but with **1c** (80 mg, 0.20 mmol, 3.0 equiv), LiHMDS (29 mg, 0.173 mmol, 2.6 equiv), **HG1** (40 mg, 0.066 mmol, 1.0 equiv), and C_6D_6 (2.5 mL). After adding **HG1**, the reaction was heated for 72 h, then concentrated *in vacuo*. The residue was purified by crystallization from CH_2Cl_2/pentane to afford **3c** (12.5 mg, 30%) as a green solid. ^1H NMR (benzene-*d6*, 400 MHz): δ = 16.25 (d, *J* = 0.9 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.13 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.96 (dd, *J* = 6.8, 2.4 Hz, 1H), 6.71 (td, *J* = 7.4, 0.8 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.62 (hept, *J* = 6.1 Hz, 1H), 4.40 (td, *J* = 12.3, 3.9 Hz, 1H), 4.03 (td, *J* = 12.8, 3.9 Hz, 1H), 3.16 (hept, *J* = 6.6 Hz, 1H), 2.91 (dd, *J* = 12.1, 3.1 Hz, 1H), 2.49 (dd, *J* = 12.4, 3.0 Hz, 1H), 2.23 (s, 3H), 1.96 – 1.44 (m, 10H), 1.66 (d, *J* = 6.1 Hz, 3H), 1.64 (d, *J* = 6.1 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H), 1.05 (s, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 3H); $^{13}C\{^{1}H\}$ NMR (benzene-*d6*, 101 MHz): δ = 302.91, 269.2, 152.96, 149.24, 145.23, 143.51, 138.93, 130.81, 130.00, 128.58, 126.06, 124.61, 121.93, 113.59, 74.66, 68.29, 54.97, 35.09, 31.21, 31.19, 30.35, 29.89, 28.60, 26.69, 25.30, 24.69, 23.57, 23.49, 22.21, 22.20, 22.04, 21.75; $[M]^+$ calcd. for $[C_{32}H_{45}NOCl_2Ru]^+$, 631.1922; found, 631.1932.



3d

3d. Was setup nearly identically to **3a**, but with **1d** (100 mg, 0.26 mmol, 2.2 equiv), LiHMDS (39 mg, 0.232 mmol, 2.0 equiv), **HG1** (70 mg, 0.117 mmol, 1.0 equiv), and C_6D_6 (3.5 mL). After adding **HG1**, the reaction was heated for 48 h then concentrated *in vacuo*. The residue purified by column chromatography (silica, benzene/Et_2O) and recrystallized from pentane to afford **3d** (50 mg, 68%) as a green solid. ^1H NMR (benzene-*d*6, 400 MHz): δ = 16.16 (s, 1H), 7.24 – 7.20 (m, 3H), 7.14 – 7.10 (m, 2H) 6.71 (t, J = 7.4 Hz,

1H), 6.43 (d, J = 8.4 Hz, 1H), 4.61 (p, J = 6.3 Hz, 1H), 3.91 (dt, J = 14.4, 7.2 Hz, 1H), 3.75 (dd, J = 14.3, 7.3 Hz, 1H), 3.62 (dd, J = 13.9, 6.9 Hz, 1H), 3.19 (p, J = 6.6 Hz, 1H), 2.59 (dd, J = 14.2, 7.2 Hz, 1H), 2.28 (s, 3H), 1.84 – 1.53 (m, 4H), 1.65 (d, J = 6.1 Hz, 6H), 1.28 (t, J = 7.3 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H), 1.03 (s, 3H), 1.02 (d, J = 6.7 Hz, 3H), 0.93 (s, 3H); $^{13}C\{^{1}H\}$ NMR (benzene-*d*6, 101 MHz): δ = 302.74, 270.77, 149.52, 145.35, 143.60, 138.89, 130.89, 130.23, 128.57, 126.07, 124.76, 121.91, 113.58, 74.56, 68.21, 56.72, 35.41, 31.10, 30.53, 28.90, 28.77, 27.82, 26.68, 24.62, 24.10, 22.36, 22.20, 22.14, 10.30, 9.79; $[M]^+$ calcd. for $[C_{31}H_{45}NOCl_2Ru]^+$, 619.1922; found, 619.1941.



7

2-(2,6-diisopropylphenyl)-3,3-dimethyl-6-phenyl-2-azabicyclo[4.1.0]heptane (7) To a 4 mL vial in a glovebox was added **1e** (20 mg, 0.045 mmol, 1 equiv), KHMDS (7.7 mg, 0.039 mmol, 0.87 equiv) and benzene-*d6* (0.55 mL). The reaction was stirred for an hour at RT, then analyzed by ^{1}H NMR, which showed complete conversion to **7**. The solvent was removed under reduced pressure and the residue was purified by column chromatography (basic alumina, hexanes) to yield **7** as a waxy, white solid**.** ^{1}H NMR (benzene-*d6*, 600 MHz): δ = 7.39 – 7.34 (m, 2H), 7.18 – 7.13 (m, 3H), 7.11 – 6.98 (m, 3H), 3.63 (hept, *J* = 6.9 Hz, 1H), 3.47 (hept, *J* = 6.9 Hz, 1H), 2.86 (dd, *J* = 6.2, 3.9 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.12 (ddd, *J* = 13.8, 5.6, 2.2 Hz, 1H), 1.64 (td, *J* = 13.1, 5.6 Hz, 1H), 1.34 (ddd, *J* = 13.1, 5.8, 2.2 Hz, 1H), 1.28 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 4.2 Hz, 1H), 0.78 (ddd, *J* = 6.2, 4.4, 0.8 Hz, 1H), 0.74 (s, 3H); $^{13}C\{^{1}H\}$ NMR (benzene-*d6*, 101 MHz); δ = 152.21, 150.87, 128.97, 127.53, 127.21, 126.24, 124.89, 124.13, 52.29, 43.34, 39.14, 29.25, 28.46, 28.38, 27.73, 27.43, 27.26, 25.54, 25.48, 25.12, 23.32, 20.57; $[M]^+$ calcd. for $[C_{26}H_{35}N]^+$, 361.2769; found, 361.2769. The conversion to **7** was rapid with or without the presence of **HG1**.

^{1}H and ^{13}C NMR Spectra

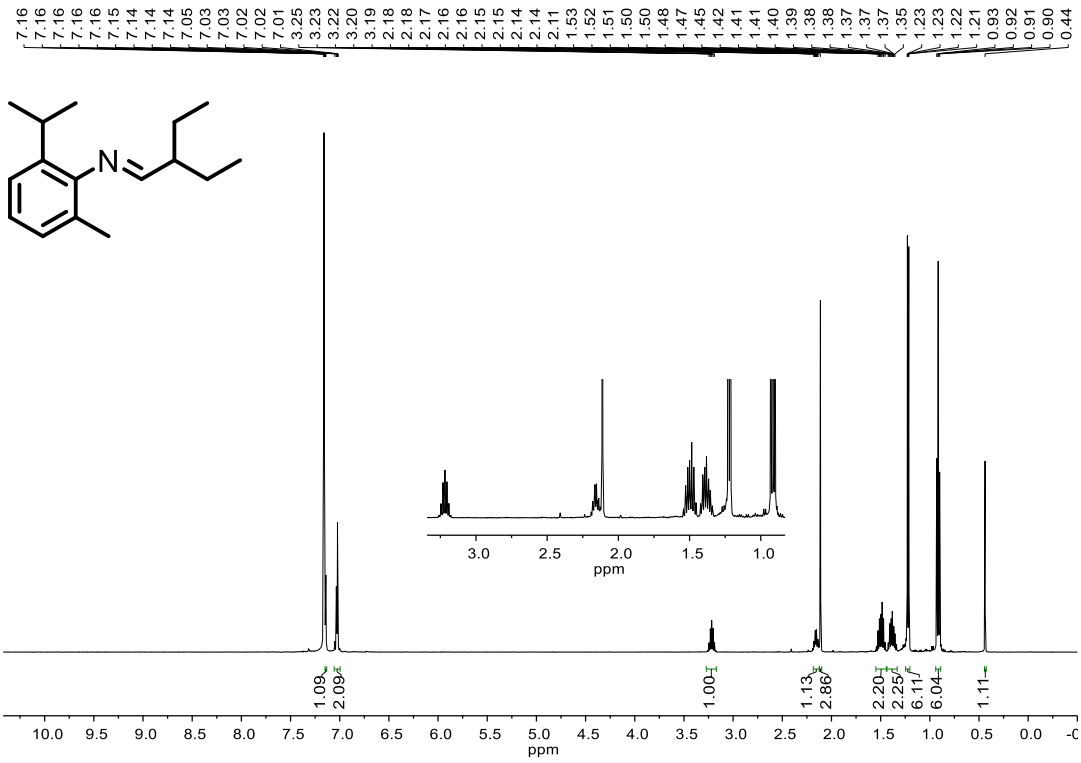


Figure S2. ^{1}H NMR Spectrum (400 MHz, benzene-*d6*) of **S1** (crude).

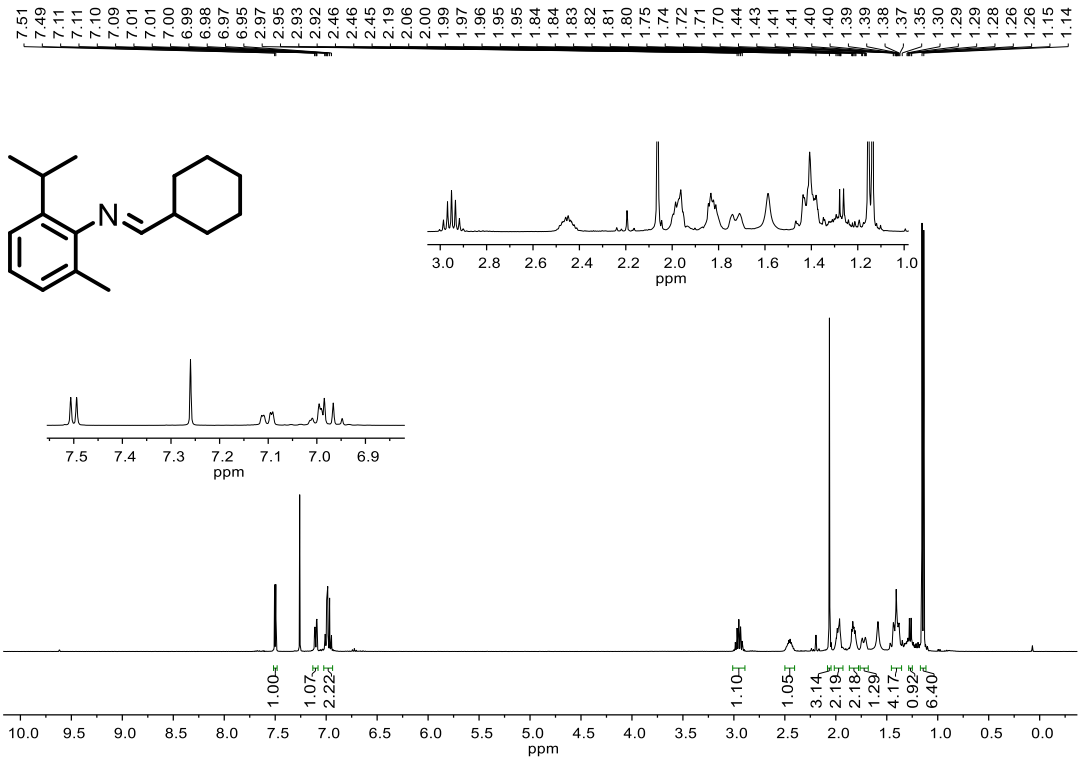


Figure S3. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **S2** (crude)**.**

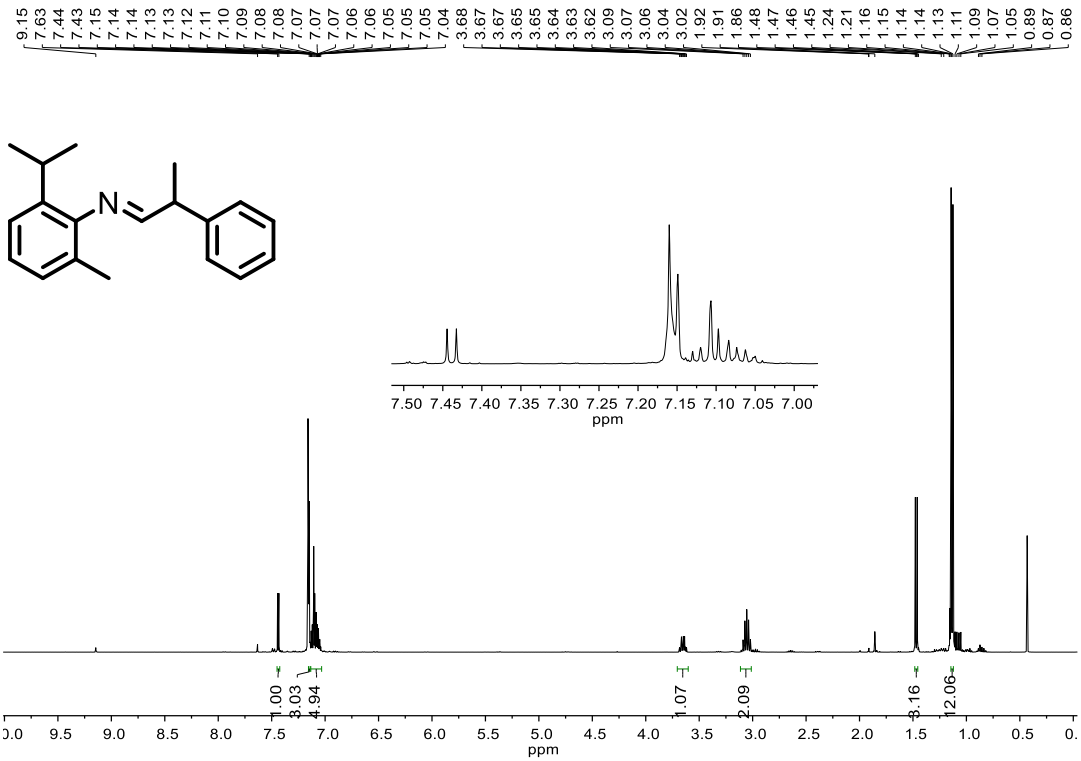


Figure S4. ^{1}H NMR Spectrum (500 MHz, benzene-*d6*) of **S3** (crude)**.**

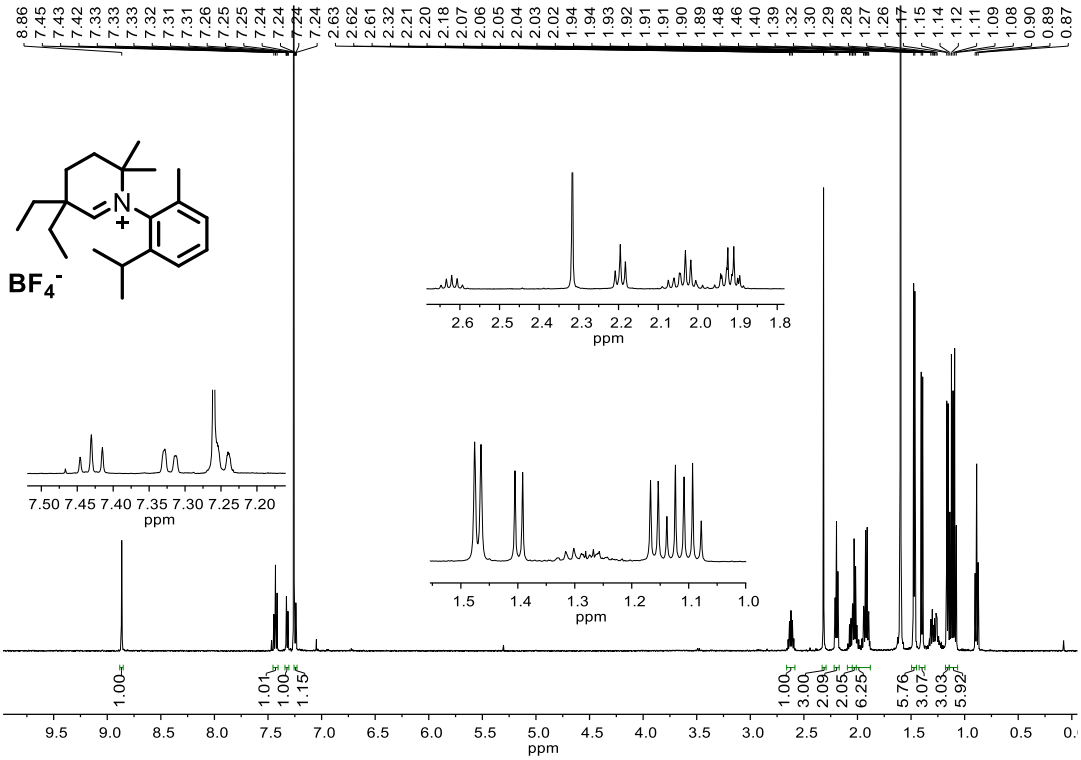


Figure S5. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **1d.**

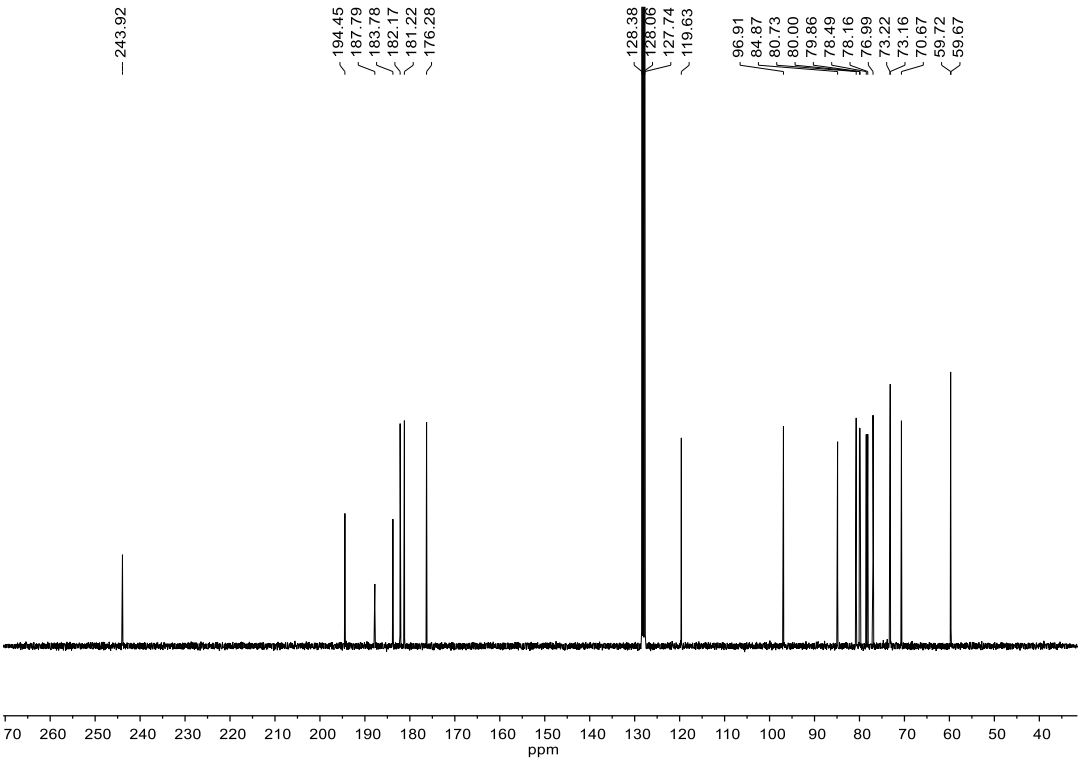


Figure S6. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-*d*) of **1d**.

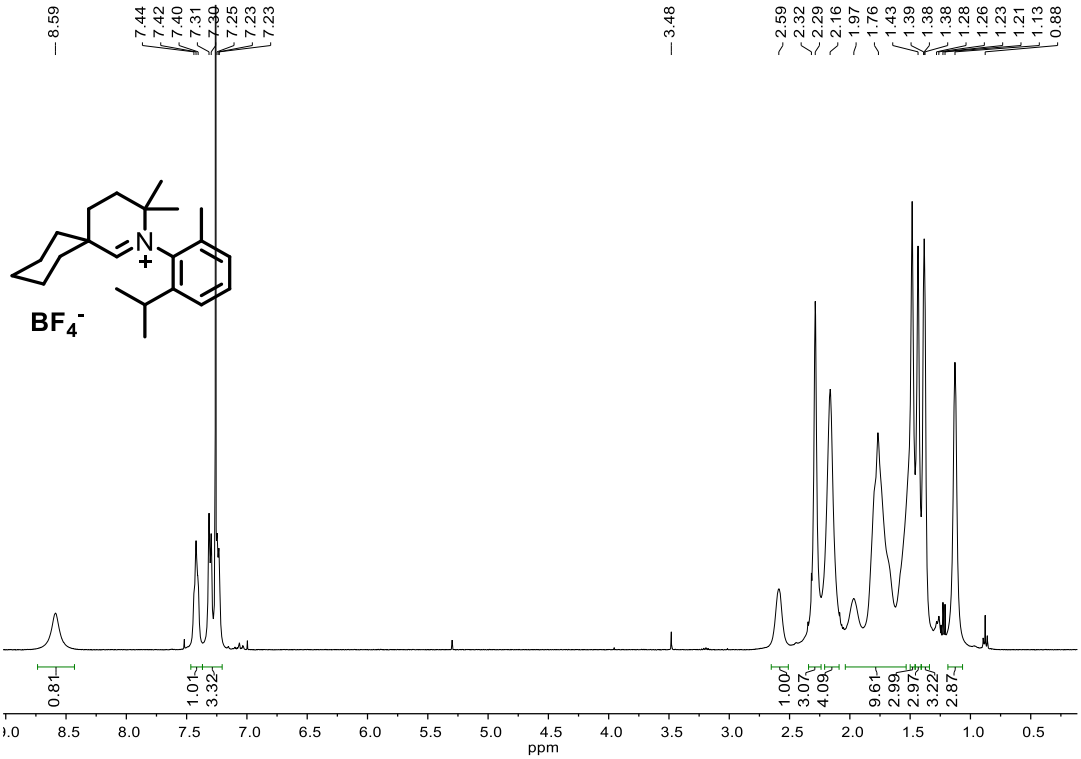


Figure S7. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **1c**.

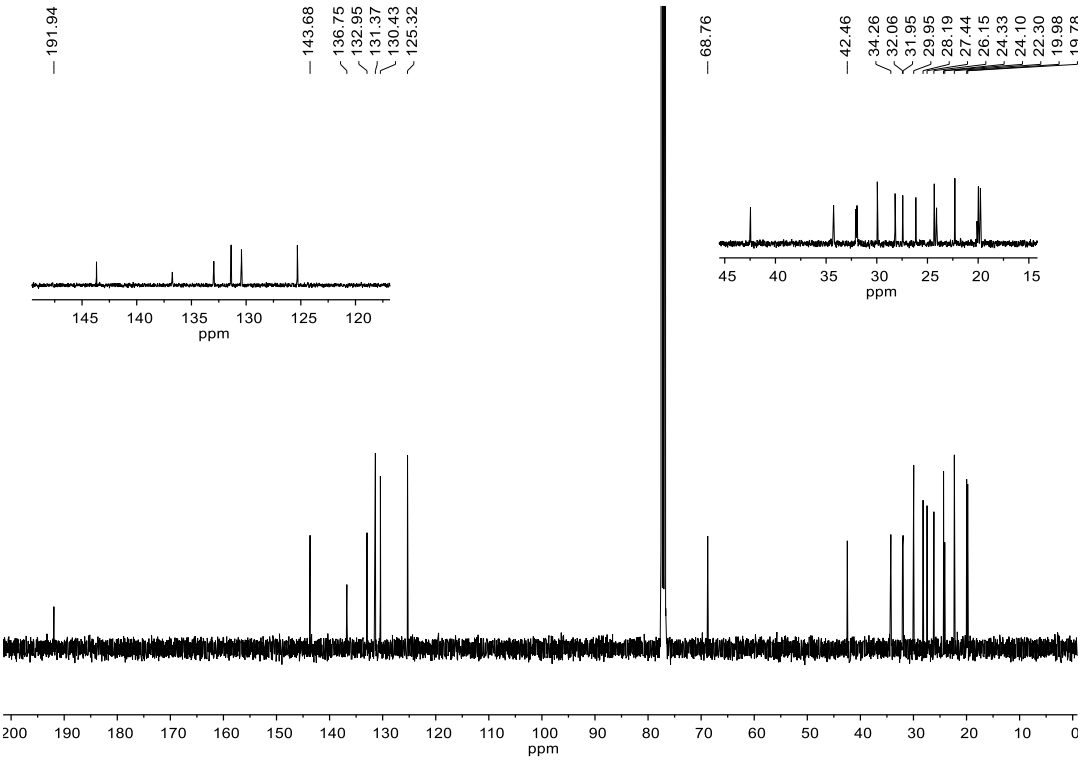


Figure S8. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-*d*) of **1c**.

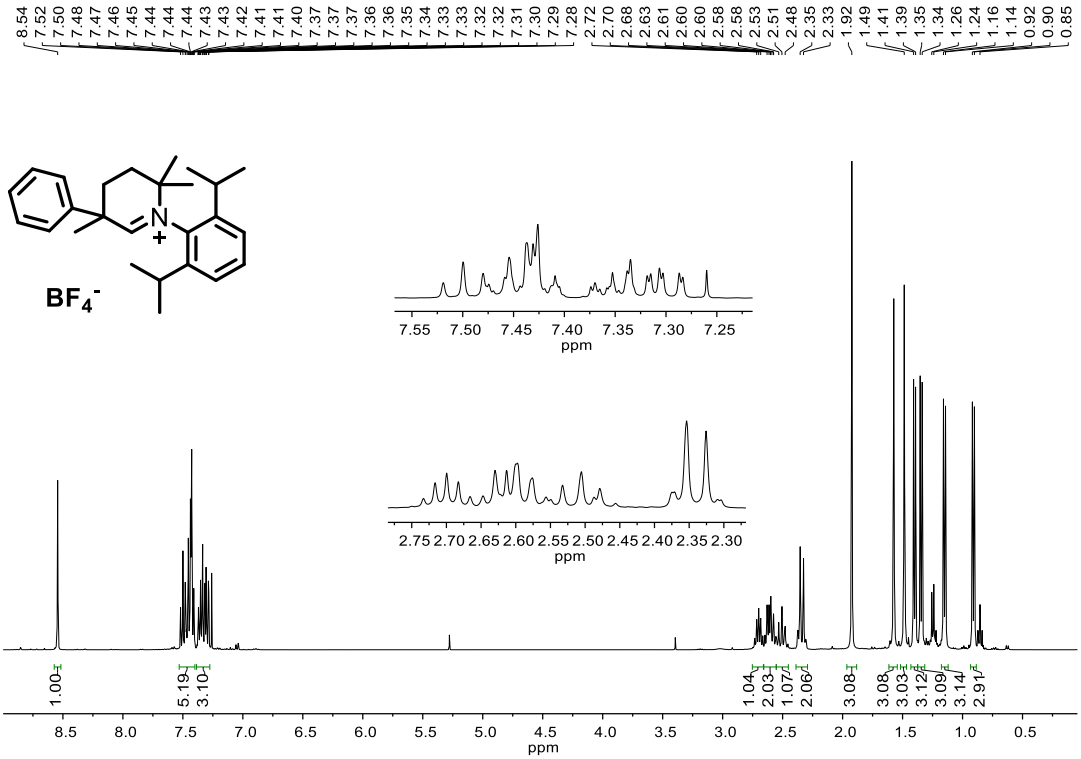


Figure S9. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **1e**.

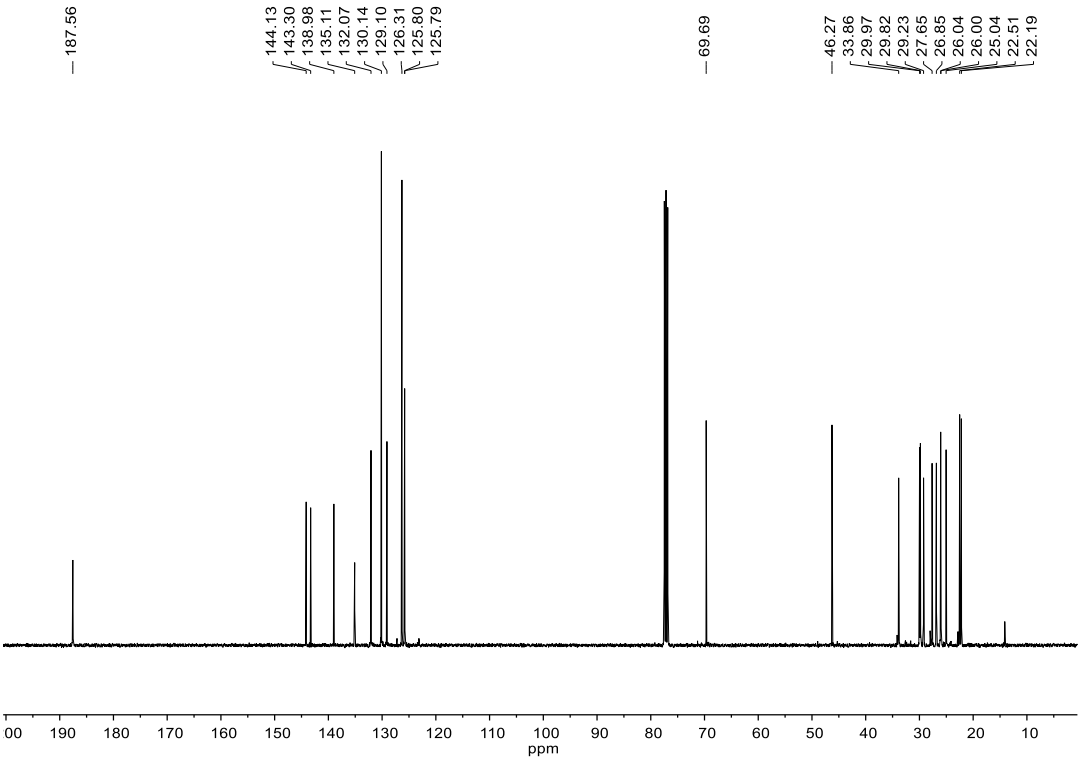


Figure S10. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-*d*) of **1e**.

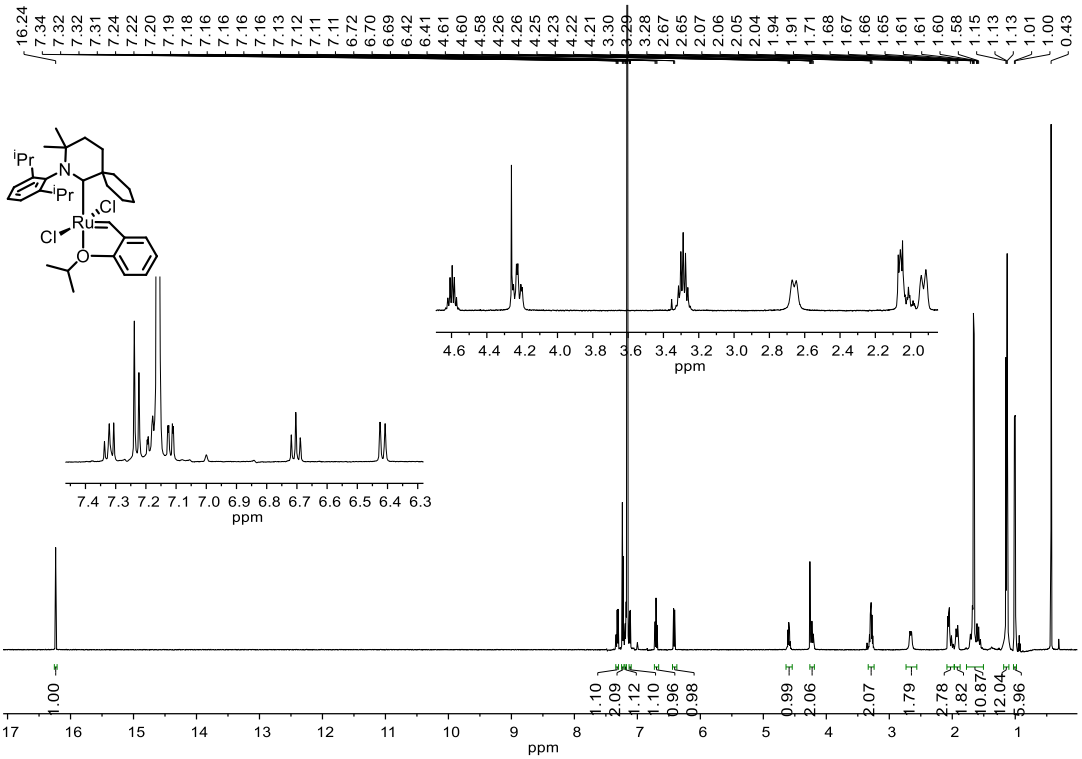


Figure S11. ^{1}H NMR Spectrum (500 MHz, benzene-*d6*) of **3a.**

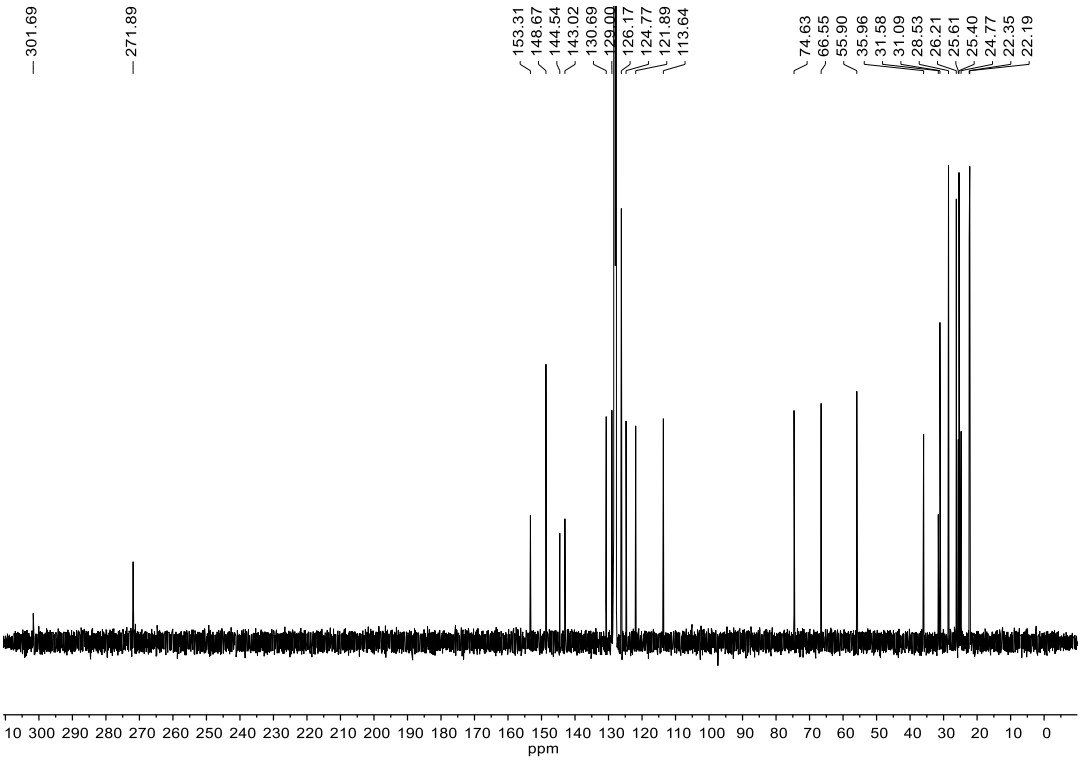


Figure S12. ^{13}C{^{1}H} NMR Spectrum (101 MHz, benzene-*d6*) of **3a**.

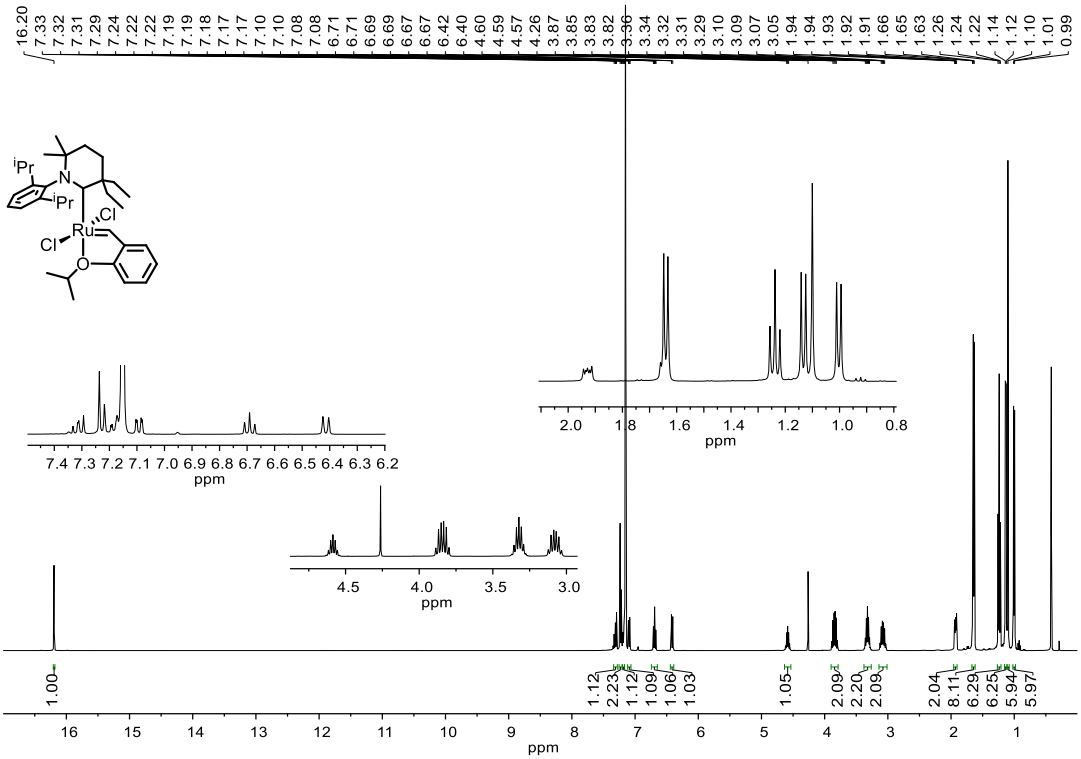


Figure S13. ^{1}H NMR Spectrum (400 MHz, benzene-*d6*) of **3b.**

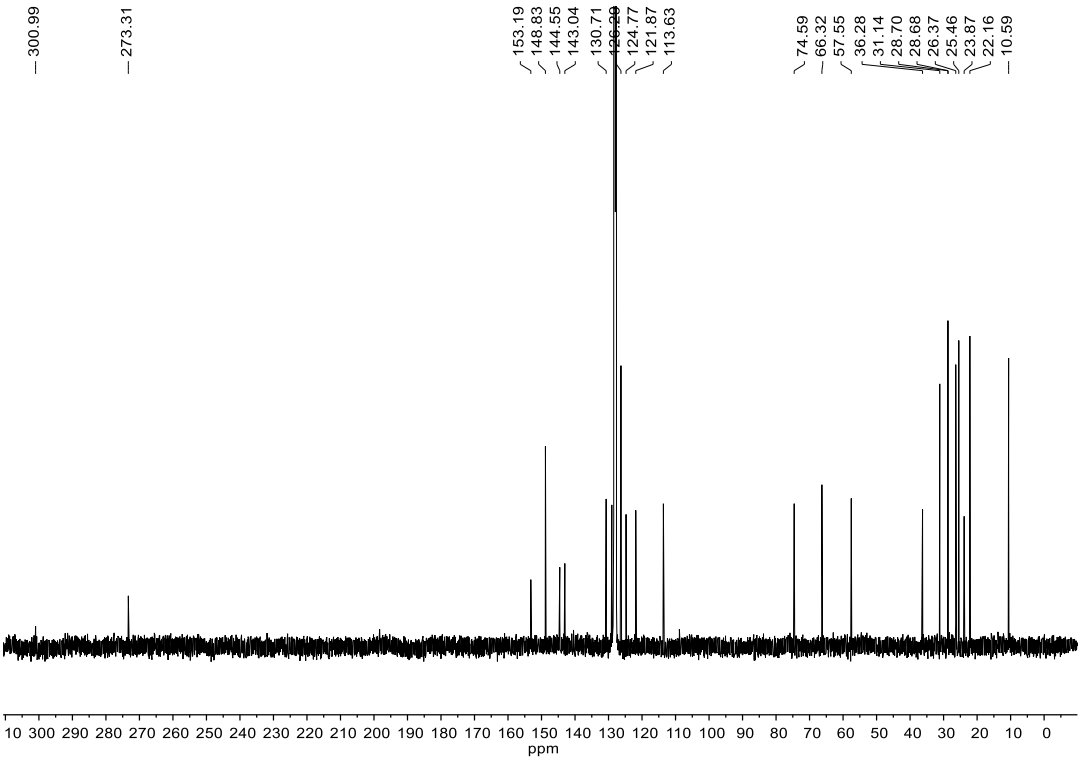


Figure S14. ^{13}C{^{1}H} NMR Spectrum (101 MHz, benzene-*d6*) of **3b**.

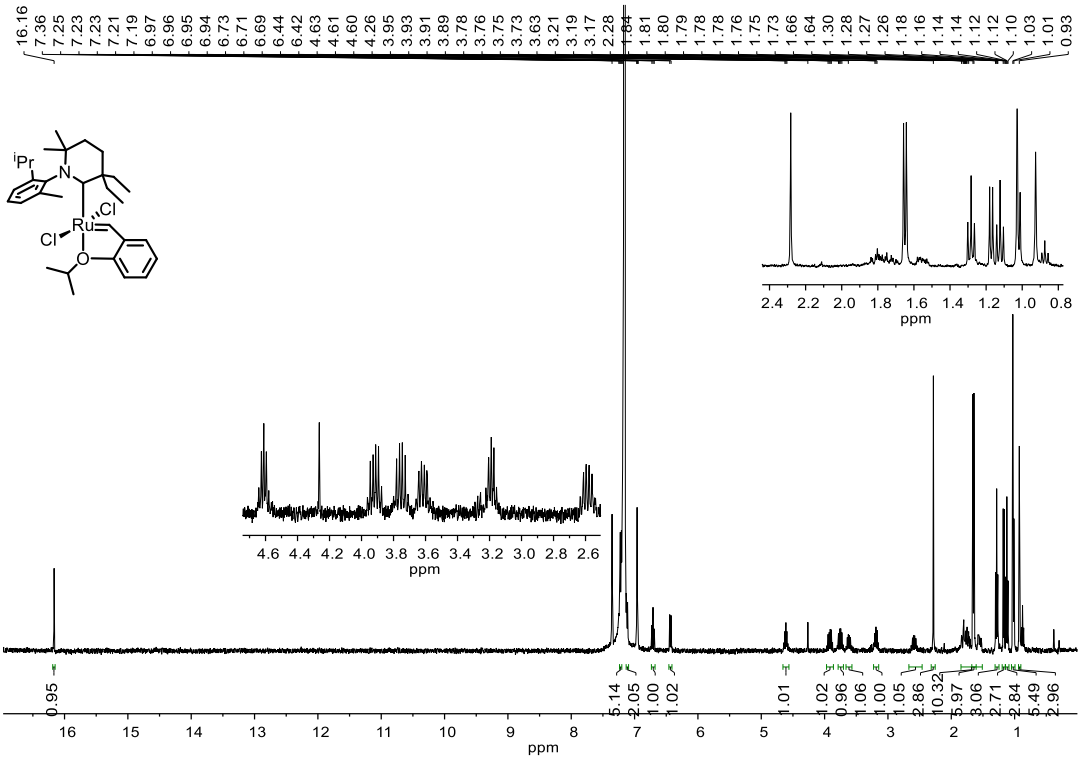


Figure S15. ^{1}H NMR Spectrum (400 MHz, benzene-*d6*) of **3d.**

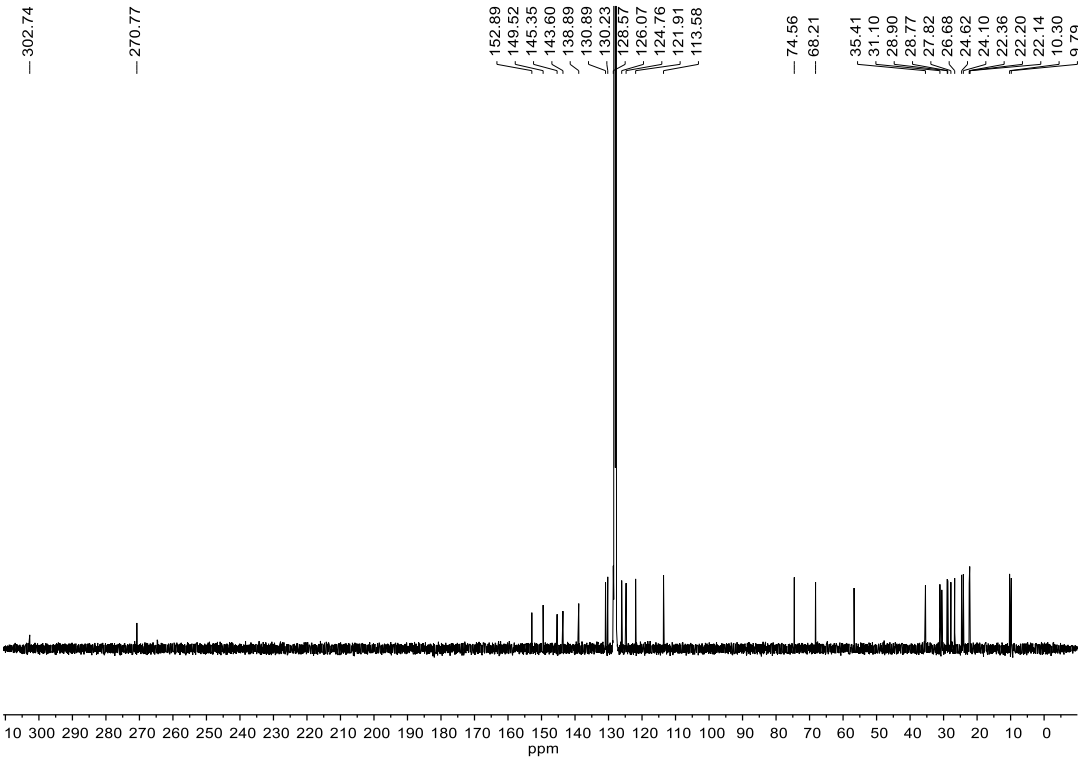


Figure S16. ^{13}C{^{1}H} NMR Spectrum (101 MHz, benzene-*d6*) of **3d**.

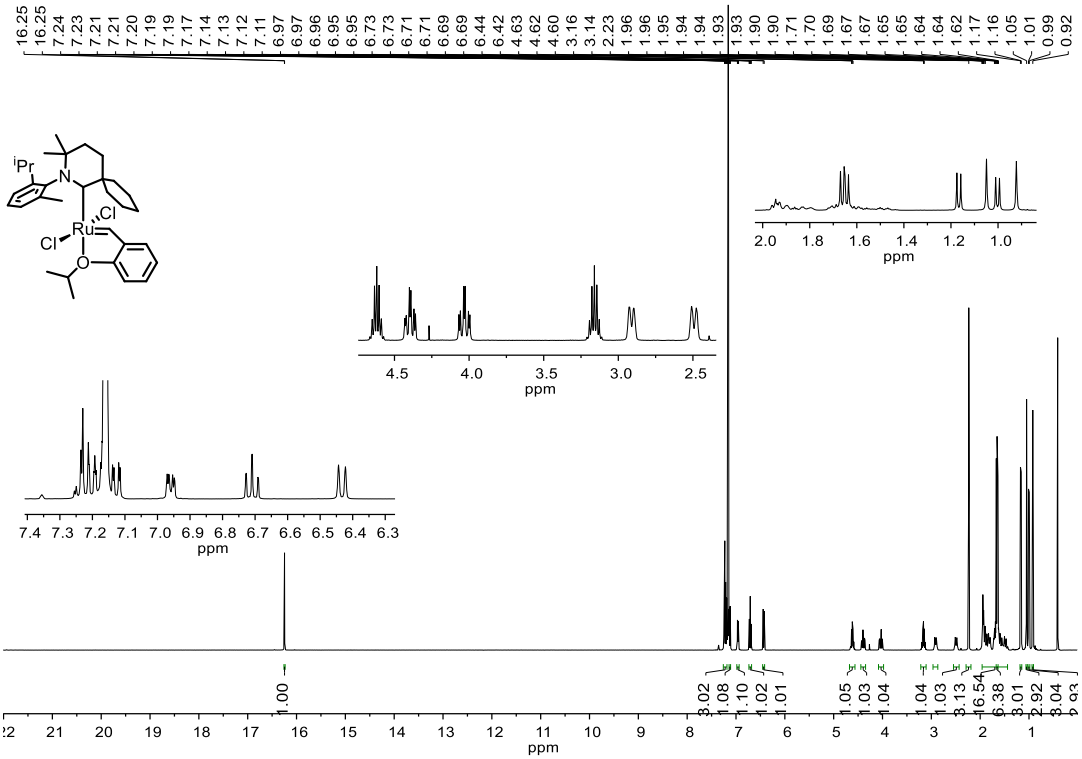


Figure S17. ^{1}H NMR Spectrum (400 MHz, benzene-*d6*) of **3c.**

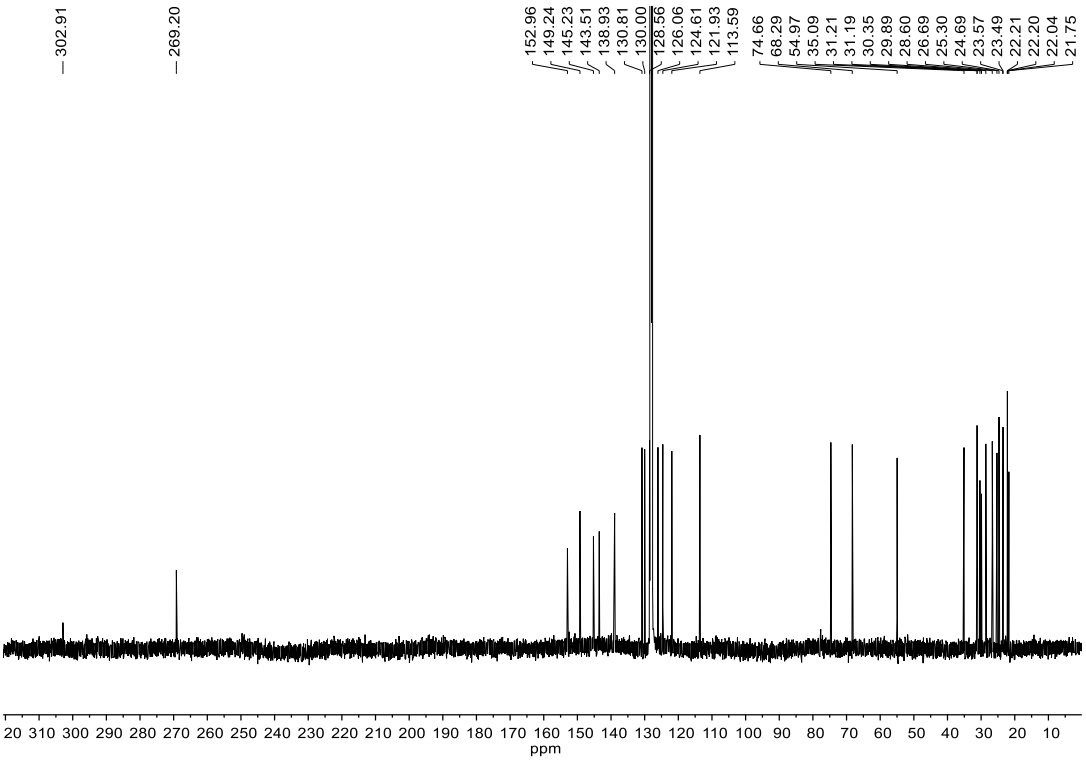


Figure S18. ^{13}C{^{1}H} NMR Spectrum (101 MHz, benzene-*d6*) of **3c**.

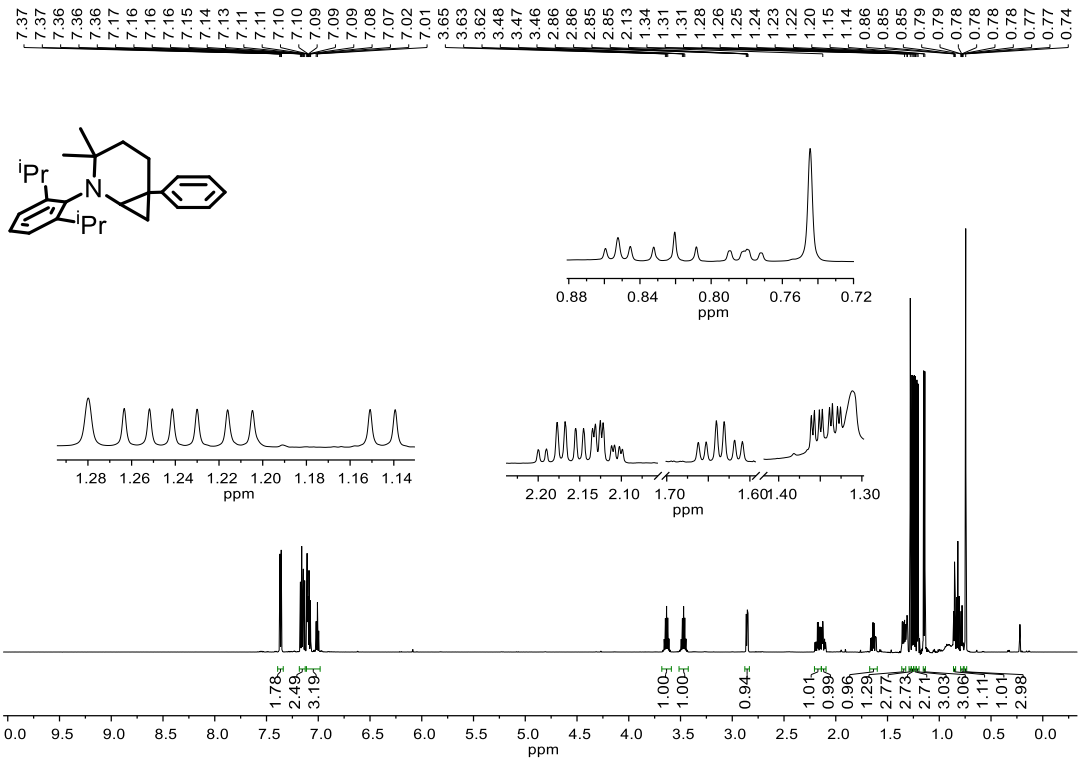


Figure S19. ^{1}H NMR Spectrum (600 MHz, benzene-*d6*) of **7.**

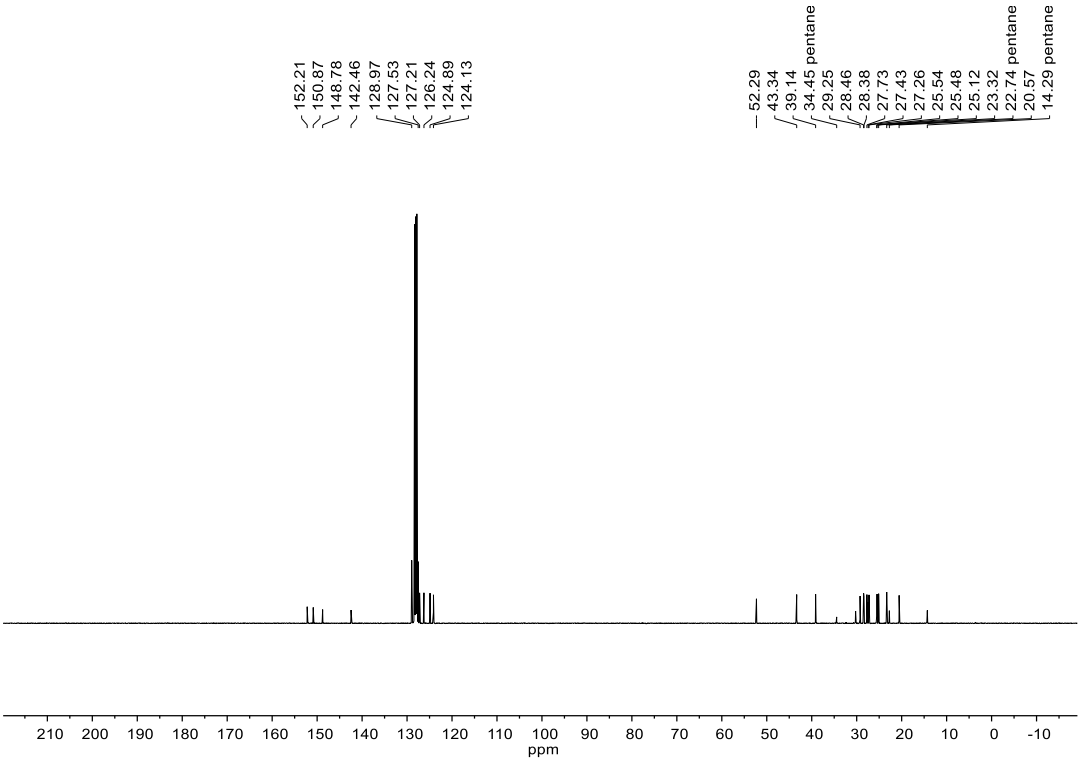
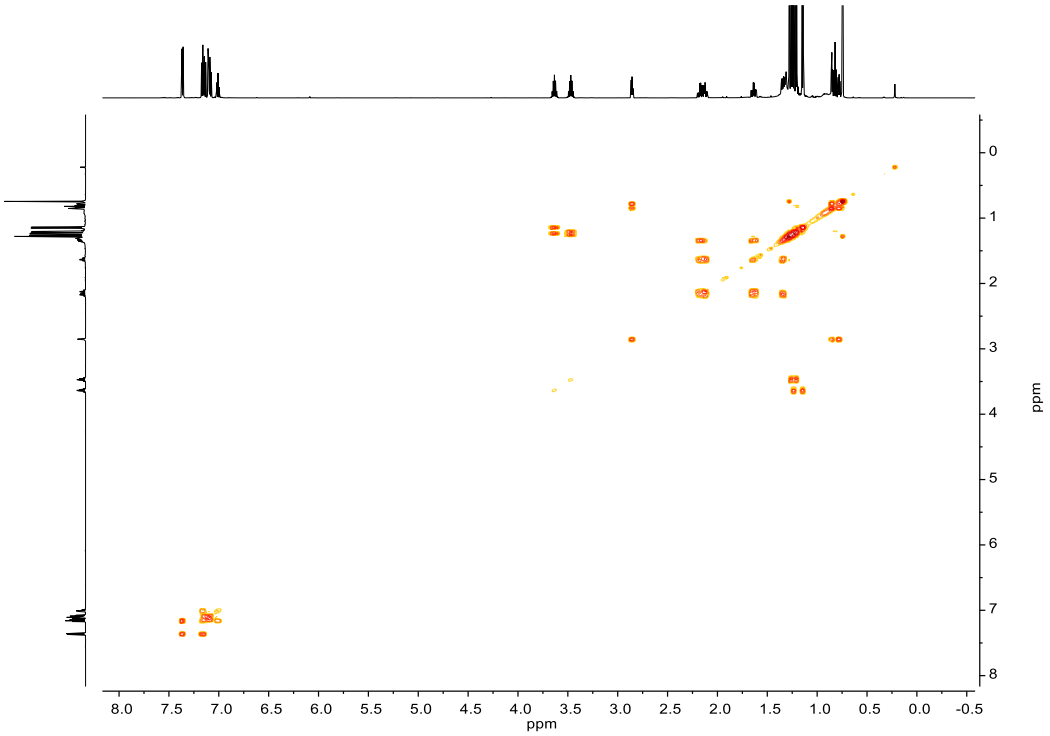


Figure S20. ^{13}C{^{1}H} NMR Spectrum (101 MHz, benzene-*d6*) of **7**.

2d COSY spectrum of 7

S22a:



S21b:

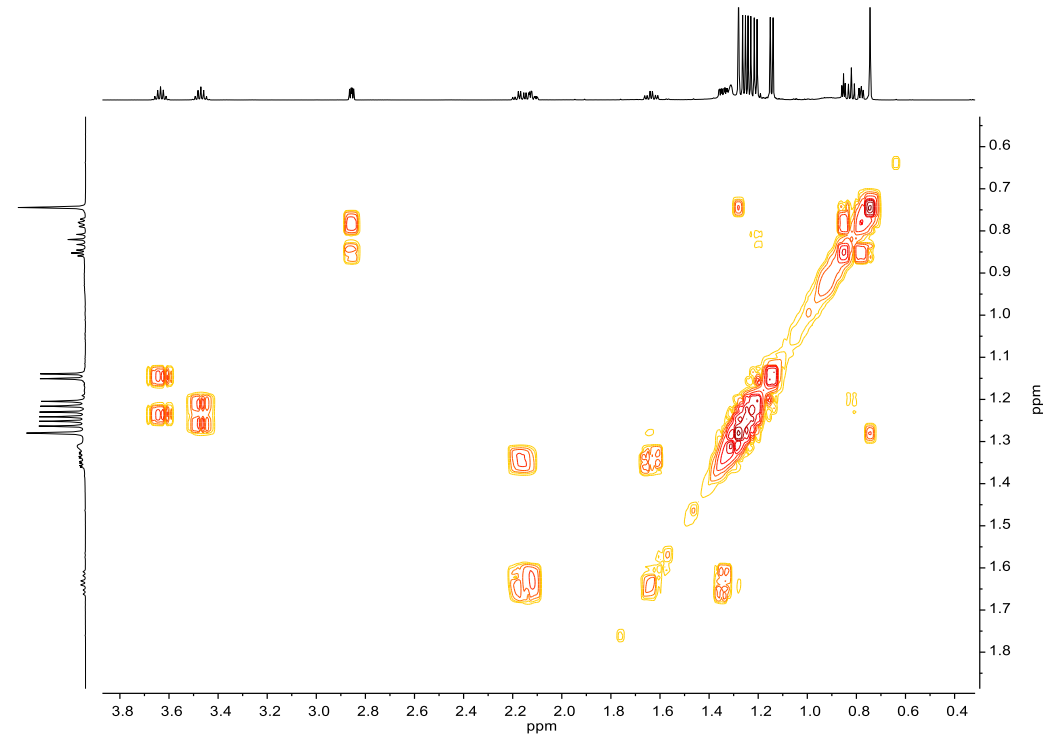


Figure S21. 2D-COSY NMR Spectra (600 MHz, benzene-*d6*) of **7**.

General procedures for metathesis reactions

General procedure for ring-closing metathesis of diethyl diallyl malonate

A procedure was followed from the literature[3]: in a glovebox, diethyl diallyl malonate (19.2 mg, 0.08 mmol) and anthracene (1 mg, internal standard) was dissolved in 0.4 mL C_6D_6 and added to a J. Young tube. To this was added a solution of catalyst (1.6 µmol, 2 mol%) in C_6D_6 (0.35 mL). The tube was sealed, and NMR spectra were taken with regular intervals at 38 °C using the Varian array function. Yields were calculated using the starting material and product peaks (at 3.16 ppm and 2.86 ppm respectively) normalized to anthracene. *Note: A lower catalyst loading at 0.4 mol% was further tested. The RCM reaction progressed in a slower kinetics but ultimately reached the same conversion.*

General procedure for homodimerization of 1-decene

A procedure was adapted from the literature[4]: a solution of 1-decene (13.5 mg, 0.08 mmol) and anthracene (2 mg, internal standard) in C_6D_6 (0.5 mL) was added to a NMR tube with a screw cap with a septum in a glovebox. A solution of catalyst (8 µmol, 1 mol%) in C_6D_6 (0.15 mL) was injected into the tube immediately prior to starting an NMR acquisition taken at regular intervals at 38 °C using the Varian array function. The yield of products was calculated using the products' allylic protons normalized to anthracene.

General procedure for ethenolysis of methyl oleate

Following a procedure from the literature[3], methyl oleate (2.97 g, 10 mmol) was added to a Fischer porter flask fitted with a stainless-steel dip tube connected to a rotary valve in a glovebox. A solution of catalyst (0.2 µmol, 20 ppm) in toluene (0.1 mL) was added to the flask. The flask was sealed, brought out of the glove box, and purged several times with ethylene and then pressurized to 150 psi with ethylene. The flask was lowered into an oil bath set to either 40 °C or 60 °C. Reaction progress was followed *via* the dip tube, aliquots being taken until the increase in product formation ceased. The aliquots were immediately diluted with hexane, and either cooled to -78 °C or analyzed with GC immediately. Conversion and selectivity were calculated using dodecane as an internal standard according to the equations below.

Conversion = (final moles **MO**) / (initial moles **MO**)
Selectivity = (moles **6a** + **6b**) / [(moles **6a** + **6b**) + (2 × moles **6c** + **6d**)]
Yield = Conversion × Selectivity
TON = Yield × (initial moles **MO** / moles catalyst)

Table S1. Compiled ethenolysis data.

Catalyst	Temp	Conversion	Yield	TON	Selectivity
3a	40 °C	0.3%	0.2%	116	81%
3b	40 °C	0.7%	0.5%	257	80%
3c	40 °C	3.7%	3.4%	1720	93%
3c	60 °C	1.0%	0.8%	407	80%
3d	40 °C	4.4%	3.4%	1705	77%

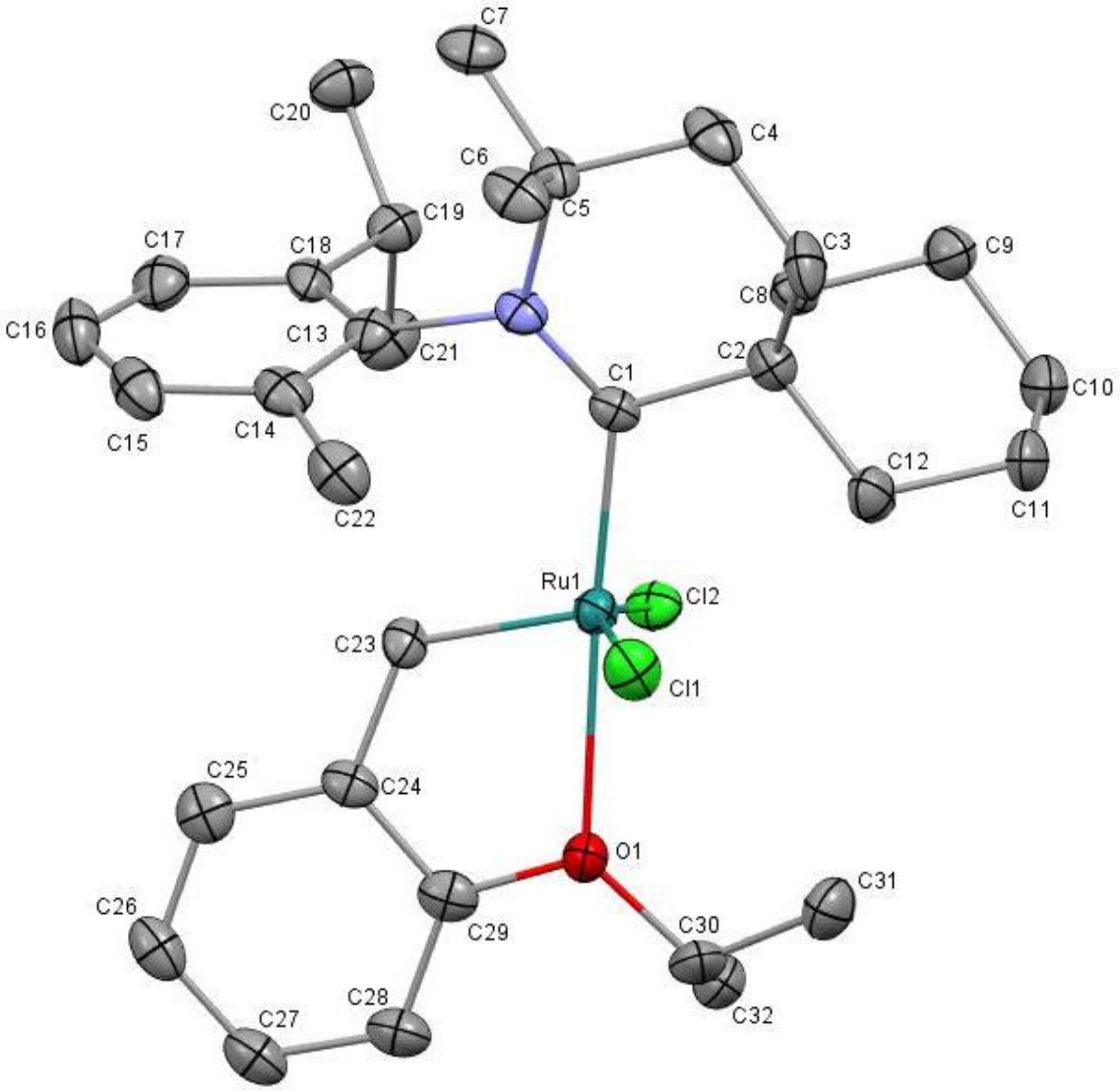


Figure S22. X-Ray Structure for Catalyst **3c** (CCDC 1972386)

Table S2. X-Ray Crystallography Data for Catalyst **3c** (CCDC 1972386)

Bond precision:	C-C = 0.0080 A	Wavelength=1.54178	
Cell:	a=8.9895(9)	b=34.186(3)	c=10.3393(10)
	alpha=90	beta=111.188(7)	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	2962.6(5)	2962.7(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C32 H45 Cl2 N O Ru	C32 H45 Cl2 N O Ru
Sum formula	C32 H45 Cl2 N O Ru	C32 H45 Cl2 N O Ru
Mr	631.66	631.66
Dx,g cm-3	1.416	1.416
Z	4	4
Mu (mm-1)	6.125	6.125
F000	1320.0	1320.0
F000'	1325.77	
h,k,lmax	11,42,12	11,42,12
Nref	6066	5881
Tmin,Tmax	0.569,0.542	0.630,0.753
Tmin'	0.516	

Correction method= # Reported T Limits: Tmin=0.630 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.970 Theta(max)= 74.619

R(reflections)= 0.0569(5311) wR2(reflections)= 0.1319(5881)

S = 1.220 Npar= 341

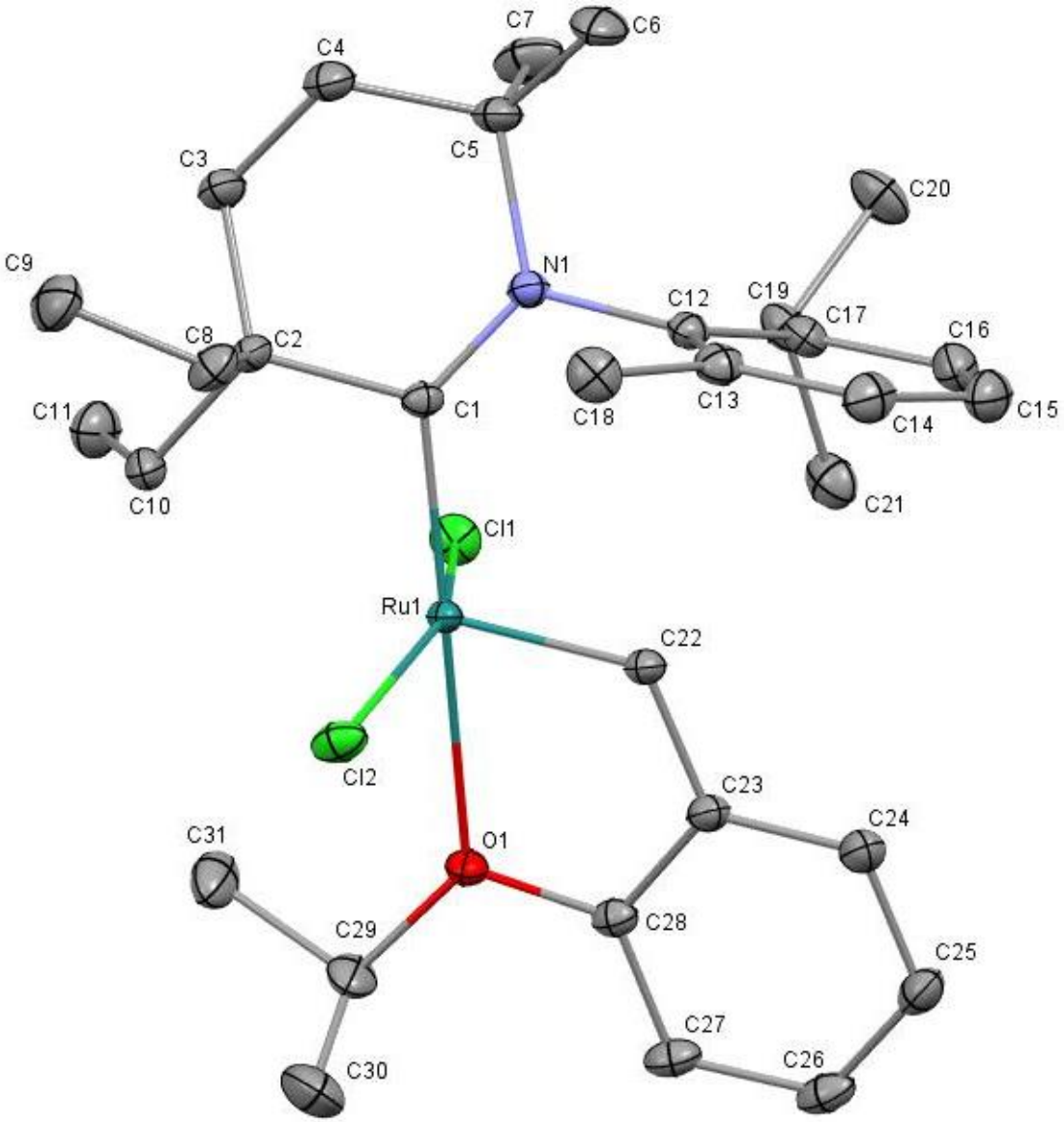


Figure S23. X-Ray Structure for Catalyst **3d** (CCDC 1972385)

Table S3. X-Ray Crystallography Data for Catalyst **3d** (CCDC 1972385)

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=12.875(3) b=12.398(4) c=18.186(6)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2902.9(15)	2903.0(14)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C31 H45 Cl2 N O Ru	C31 H45 Cl2 N O Ru
Sum formula	C31 H45 Cl2 N O Ru	C31 H45 Cl2 N O Ru
Mr	619.65	619.65
Dx,g cm-3	1.418	1.418
Z	4	4
Mu (mm-1)	0.749	0.749
F000	1296.0	1296.0
F000'	1292.49	
h,k,lmax	18,17,26	18,17,26
Nref	8969[4617]	8925
Tmin,Tmax	0.894,0.928	0.681,0.746
Tmin'	0.894	

Correction method= # Reported T Limits: Tmin=0.681 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.93/1.00 Theta(max)= 30.638

R(reflections)= 0.0182(8424) wR2(reflections)= 0.0497(8925)

S = 1.053 Npar= 334

References

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(2) Weinstein, C. M.; Junor, G. P.; Tolentino, D. R.; Jazzar, R.; Melaimi, M.; Bertrand, G. Highly Ambiphilic Room Temperature Stable Six-Membered Cyclic (Alkyl)(Amino)Carbenes. *J. Am. Chem. Soc.* **2018**, *140*, 9255–9260.

(3) Marx, V. M.; Sullivan, A. H.; Melaimi, M.; Virgil, S. C.; Keitz, B. K.; Weinberger, D. S.; Bertrand, G.; Grubbs, R. H. Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 1919–1923.

(4) Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. Kinetic Selectivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl)(Amino)Carbenes. *Organometallics* **2008**, *27*, 563–566.