Supporting information

Highly selective ethenolysis with acyclic-aminooxycarbene ruthenium catalysts

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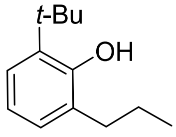
1. General Remarks

All the reactions were conducted in flame-dried glassware under an argon atmosphere using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox with a high capacity recirculator (<1 ppm of O_2). NMR spectra were recorded using a JEOL spectrometer, operating at 400 MHz for ^{1}H NMR, at 101 MHz for ^{13}C NMR, at 376 MHz for ^{19}F NMR and 76 MHz for ^{77}Se NMR. All chemical shifts for ^{1}H, ^{13}C NMR, and ^{19}F NMR spectroscopy were referenced to residual signals from $CDCl_3$ (^{1}H) 7.26 ppm and (^{13}C) 77.16 ppm, CD_2Cl_2 (^{1}H) 5.32 ppm and (^{13}C) 53.84 ppm, and C_6D_6 (^{1}H) 7.16 ppm and (^{13}C) 128.06 ppm. Gas Chromatographic analyses were conducted using an Agilent 7890 GC. Elemental analysis were carried out using a UNICUBE Elementar Analyser at Gwangju Institute of Science and Technology (GIST) Central Research Facilities. High-resolution mass spectra (HR-MS) were obtained at the Korea Basic Science Institute (KBSI) in Daegu, Korea. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated silica gel 60 Ǻ (F254) glass plates and visualization on TLC was achieved by UV light. Flash chromatography was performed with 230-400 Mesh 60 Ǻ Silica Gel purchased from Merck Inc. Yield refers to isolated yield of analytically pure material unless otherwise noted. THF, CH_2Cl_2 and Et_2O were dried under a positive pressure of dry nitrogen by a J. C. Meyer Solvent Purification System prior to use. Hexane, benzene, toluene, DMF, DMSO and acetonitrile were dried over calcium hydride (CaH_2), distilled atmosphere prior to use and stored over 4 Å molecular sieves. $CDCl_3$, CD_2Cl_2, and C_6D_6 were dried over CaH_2 and distilled into a Schlenk tube, freeze/pump/thawed 3 times and stored over 4 Å molecular sieves. Unless specified, all the other chemicals were purchased from Sigma-Aldrich Co., Acros Organics, TCI, Alfa Aesar and were used as received without further purification.

2. Experimental details

2.1. Preparation of 2-(*tert*-butyl)-6-propylphenol



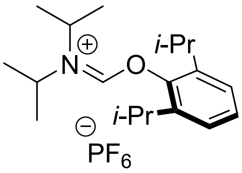
S1

2-allyl-6-(*tert*-butyl)phenol (1 equiv.)[1] was dissolved in EtOH. Pd/C (10 wt%) was added to this solution. The reaction was purged with hydrogen. The mixture was stirred for 24h at room temperature. The mixture was filtered through a sintered funnel. The solvent was removed in vacuo to leave a light yellow oil as the desired product in quantitative yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (1H, dd, J = 7.8, 1.7 Hz, Ar*H*), 7.00 (1H, dd, J = 7.5, 1.7 Hz, Ar*H*), 6.82 (1H, t, J = 7.6 Hz, Ar*H*), 4.86 (1H, s, O*H*), 2.61 – 2.51 (2H, m, CH_2), 1.73 – 1.61 (2H, m, CH_2), 1.43 (9H, s, $(CH_3)_3$), 1.02 (3H, t, J = 7.3 Hz, C*H*3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 135.8, 127.7, 125.0, 120.0, 34.6, 32.3, 29.9, 22.9, 14.2. HRMS (EI): Calcd. for $C_{13}H_{20}O$ $[M]^+$:191.1514; found: 192.1511.

2.2. Preparation of AAOC salts[2]

General procedure

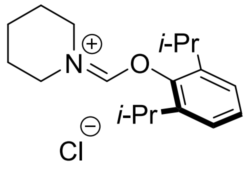
$(COCl)_2$ (1.5 equiv.) was added dropwise to a solution of formamide **2** (0.95 equiv.) in CH_2Cl_2 at –78 °C. The reaction mixture was stirred for 1 h at room temperature. After evaporation of all the volatiles by vacuum, CH_2Cl_2 was added. A solution of aryloxysilane **1** in CH_2Cl_2 was added dropwise to the reaction mixture of **2** at –78 °C. After stirring for 3 h at room temperature, the reaction solution was concentrated to 2 mL and the precipitated solid was washed with additional hexanes. The chloride salt (1 eq) was added to a solution of KPF_6 (1.1 eq) in a minimal amount of H_2O. The resulting precipitate was extracted with CH_2Cl_2 and the organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The resulting solid was recrystallized from hexane.



3a

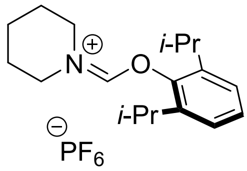
Following the **GP 2.2**, **3a** (82%, 1.6 g) was obtained from N,N-diisopropylformamide (4.5 mmol, 0.65 mL), $(COCl)_2$ (6.75 mmol, 0.84 mL), (2,6-diisopropylphenoxy)trimethylsilane (5 mmol) and CH_2Cl_2 (10 mL). The chloride salt (1 eq) was added to a solution of KPF_6 (1.1 eq) in a minimal amount of H_2O. The resulting precipitate was extracted with CH_2Cl_2 and the organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The resulting solid was recrystallized from hexane. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.29 (1H, s, NC*H*O), 7.33 (1H, t, J = 7.6 Hz, Ar*H*), 7.23 (2H, t, J = 8.0 Hz, Ar*H*), 4.43-4.31 (2H, m, NC*H*), 2.85-2.75

(2H, m, ArC*H*), 1.62 (6H, d, J = 5.7 Hz, CHC*H*$_3$), 1.47 (6H, d, J = 5.7 Hz, CHC*H*$_3$), 1.24 (12H, d, J = 6.9 Hz, CHC*H*$_3$). ^{13}C NMR (CDCl$_3$, 101 MHz), δ (ppm): 165.3, 149.7, 139.1, 129.3, 125.3, 58.5, 52.6, 27.7, 23.2, 20.8, 19.7. HRMS (FAB): Calcd. for $C_{19}H_{32}NO$ [M–PF$_6$]$^+$:290.2484; found: 290.2484. Anal. Calcd (%) for $C_{19}H_{32}F_6NOP$: C, 52.41; H, 7.41; N, 3.22; found: C, 52.33; H, 7.50; N, 3.32.



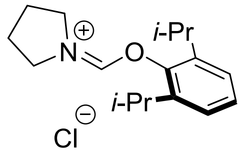
3b•Cl

Following the **GP 2.2**, **3b•Cl** (85%, 748 mg) was obtained from piperidine-1-carbaldehyde (2.85 mmol, 322 mg), (COCl)$_2$ 4 mmol, 0.34 mL), (2,6-diisopropylphenoxy)trimethylsilane (3 mmol) and CH$_2$Cl$_2$ (10 mL). ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 10.39 (1H, s, NC*H*O), 7.29 (1H, t, J = 7.6 Hz, Ar*H*), 7.20 (2H, d, J = 7.2 Hz, Ar*H*), 4.46 (2H, t, J = 5.3 Hz, C*H*$_2$), 4.01 (2H, t, J = 5.3 Hz, C*H*$_2$), 3.04-2.87 (2H, m, C*H*), 1.97-1.80 (m, 7H), 1.26 (12H, d, J = 6.9 Hz, C*H*$_3$). ^{13}C NMR (CDCl$_3$, 101 MHz), δ (ppm): 165.1, 148.7, 139.2, 128.9, 125.1, 52.5, 46.9, 27.7, 26.5, 26.0, 23.1, 22.8. HRMS (FAB): Calcd. for $C_{18}H_{28}NO$ [M–Cl]$^+$: 274.2165; found 274.2170.



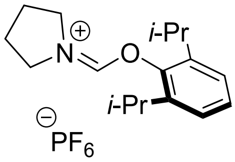
3*b*

3b (70 mg, 32%) was obtained. The chloride salt **3b•Cl** (160 mg, 1 eq) was added to a solution of KPF$_6$ (95 mg, 1.1 eq) in a minimal amount of H$_2$O. The resulting precipitate was extracted with CH$_2$Cl$_2$ and the organic layers were combined and dried over Na$_2$SO$_4$, filtered, and concentrated. The resulting solid was recrystallized from hexane. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 8.32 (1H, s, NC*H*O), 7.33 (1H, dd, J = 8.2, 7.3 Hz, Ar*H*), 7.21 (2H, d, J = 7.7 Hz, Ar*H*), 4.12 – 3.95 (4H, m, NC*H*$_2$), 2.89 (2H, hept, J = 6.8 Hz, C*H*), 1.99 – 1.78 (6H, m, C*H*$_2$), 1.23 (12H, d, J = 6.8 Hz, C*H*$_3$). ^{13}C NMR (CDCl$_3$, 101 MHz), δ (ppm): 162.8, 149.0, 139.3, 129.2, 125.2, 53.2, 47.3, 27.5, 26.4, 25.9, 22.9, 22.8. Anal. Calcd (%) for $C_{18}H_{28}F_6NOP$: C, 51.55; H, 6.73; N, 3.34; found: C, 51.69; H, 7.06; N, 3.40.



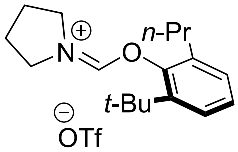
***3c*•Cl**

Following the **GP 2.2**, **3c•Cl** (91%, 1.54 g) was obtained from pyrrolidine-1-carbaldehyde (5.7 mmol, 565 mg), (COCl)$_2$ (8.6 mmol, 0.73 mL), (2,6-diisopropylphenoxy)trimethylsilane (6 mmol) and CH$_2$Cl$_2$ (20 mL). ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 10.27 (1H, s, NC*H*O), 7.29 (1H, t, J = 7.8 Hz, Ar*H*), 7.19 (2H, d, J = 7.6 Hz, Ar*H*), 4.58 (2H, t, J = 6.1 Hz, C*H*$_2$), 3.95 (2H, t, J = 6.1 Hz, C*H*), 3.15-2.93 (2H, m, C*H*), 2.26-2.19 (4H, m, C*H*$_2$), 1.25 (12H, d, J = 6.9 Hz, C*H*$_3$). ^{13}C NMR (CDCl$_3$, 101 MHz), δ (ppm): 164.9, 149.1, 139.3, 128.8, 125.0, 52.8, 49.2, 27.6, 24.9, 24.0, 23.2. HRMS (FAB): Calcd. for $C_{17}H_{26}NO$ [M–Cl]$^+$: 260.2009; found 260.2010.



3c

3c (70 mg, 51%) was obtained. The chloride salt **3c•Cl** (100 mg, 1 eq) was added to a solution of KPF_6 (62 mg, 1.1 eq) in a minimal amount of H_2O. The resulting precipitate was extracted with CH_2Cl_2 and the organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The resulting solid was recrystallized from hexane. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.41 (1H, s, NC*H*O), 7.36 – 7.28 (1H, m, Ar*H*), 7.21 (2H, d, J = 7.7 Hz, Ar*H*), 4.20 (2H, t, J = 6.7 Hz, NC*H₂*), 3.99 (2H, t, J = 6.9 Hz, NC*H₂*), 2.91 (2H, hept, J = 6.8 Hz, CC*H*), 2.34 – 2.14 (4H, m, CH_2), 1.21 (12H, d, J = 6.8 Hz, C*H₃*). ^{13}C NMR ($CDCl_3$, 101 MHz), δ (ppm): 163.0, 149.3, 139.5, 129.1, 125.1, 77.4, 77.1, 76.8, 52.6, 49.6, 27.4, 24.6, 23.9, 23.0. Anal. Calcd (%) for $C_{17}H_{26}F_6NOP$: C, 50.37; H, 6.47; N, 3.46; found: C, 50.62; H, 5.98; N, 3.56.



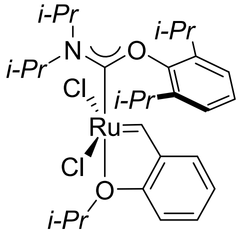
3d

A formamide (5 mmol, 496 mg) was dissolved in CH_2Cl_2 (0.02 M), and Tf_2O (5 mmol, 0.84 mL) was added carefully dropwise at –78 °C. The solution was warmed to room temperature and stirred for 1 h. 2-(*tert*-butyl)-6-propylphenol (5 mmol, 961 mg) and Et_3N (5.5 mmol, 0.77 mL) in CH_2Cl_2 (10 mL) were added dropwise to the solution at – 78 °C. The reaction mixture was stirred for 4 h at room temperature. Product was purified by passing a short plug of silica and this residue was triturated by the additional hexane to precipitate a solid (52%, 1.11 g). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): δ 9.19 (1H, s, NC*H*O), 7.30-7.17 (2H, m, Ar*H*), 4.35 (2H, t, J = 6.5 Hz, C*H₂*), 3.99 (2H, t, J = 6.7 Hz, C*H₂*), 3.18-3.11 (3H, m, C*H₂*), 2.50 (2H, t, J = 7.4 Hz, C*H₂*), 2.25 (4H, dq, J = 28.6, 6.7 Hz, C*H₂*), 1.61 (2H, td, J = 14.9, 7.4 Hz, C*H₂*), 1.36-1.33 (12H, m, C*H₃*), 0.90 (3H, t, J = 7.2 Hz, C*H₃*). ^{13}C NMR (CD_2Cl_2, 101 MHz), δ (ppm): 164.9, 151.7, 140.8, 133.8, 129.4, 128.4, 126.2, 49.8, 46.0, 34.8, 32.0, 30.7, 24.9, 24.1, 22.9, 13.5. HRMS (FAB): Calcd. for $C_{18}H_{28}NO$ [M–OTf]$^+$: 274.2165; found 274.2170. Anal. Calcd (%) for $C_{19}H_{28}F_3NO_4S$: C, 53.89; H, 6.66; N, 3.31; found: C, 54.07; H, 6.40; N, 3.40.

2.3. Synthesis of AAOC–ruthenium catalysts

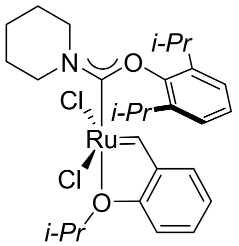
General procedure

To AAOC salt (2 equiv.) and KHMDS (2.2 equiv.), THF was added and stirred at –78 °C for 0.5 h. 1G Grubbs-Hoveyda catalyst (1 equiv.) in benzene was added and stirred for 2 h. The solution was concentrated. The crude mixture was dissolved in CH_2Cl_2. Amberlyst 15 resin (4 eq.) was added. The reaction was heated at 50 °C. The mixture was filtered over a pad of Celite, eluted with CH_2Cl_2 and the filtrate was concentrated. Product was purified silica gel chromatography.



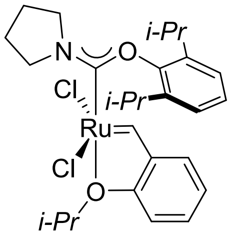
4a

Following the **GP 2.3**, **4a** (70%, 43 mg) was obtained from **3a** (0.2 mmol, 87 mg), KHMDS (0.22 mmol, 44 mg), **HG1** (0.1 mmol, 60 mg) and THF and benzene (2 mL). ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 15.64 (1H, s, Ru=C*H*), 7.56-7.52 (1H, m, Ar*H*), 7.48 (1H, t, J = 7.6 Hz, Ar*H*), 7.33 (2H, d, J = 8.0 Hz, Ar*H*), 6.94 (1H, d, J = 8.4 Hz, Ar*H*), 6.89 (2H, t, J = 2.9 Hz, Ar*H*), 5.25 (1H, m, J = 6.3 Hz, C*H*), 5.13-5.04 (1H, m, C*H*), 3.79-3.69 (1H, m, C*H*), 3.19-3.09 (2H, m, C*H*), 1.67 (12H, d, J = 6.1 Hz, C*H*$_3$), 1.55 (6H, d, J = 6.9 Hz, C*H*$_3$), 1.12 (6H, d, J = 6.7 Hz, C*H*$_3$), 0.86 (6H, d, J = 6.9 Hz, C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 101 MHz), δ (ppm): 223.6, 152.1, 151.4, 144.0, 142.5, 130.4, 127.2, 124.6, 122.9, 122.5, 112.9, 74.9, 56.8, 50.3, 26.4, 25.4, 22.4, 22.0, 21.8, 20.1. HRMS (FAB): Calcd. for $C_{29}H_{43}Cl_2NO_2Ru$ $[M]^+$: 609.1709; found 609.1717. Anal. Calcd (%) for $C_{29}H_{43}Cl_2NO_2Ru$: C, 57.14; H, 7.11; N, 2.30; found: C, 56.97; H, 6.81; N, 2.19.



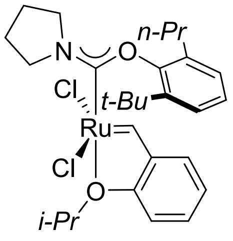
4b

Following the **GP 2.3**, **4b** (38%, 22 mg) was obtained from **3b** (0.4 mmol, 124 mg), KHMDS (0.44 mmol, 88 mg), **HG1** (0.1 mmol, 60 mg) and THF and benzene (2 mL). ^{1}H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 15.67 (1H, s, Ru=C*H*), 7.56-7.52 (1H, m, Ar*H*), 7.45 (1H, t, J = 7.6 Hz, Ar*H*), 7.30 (2H, d, J = 7.6 Hz, Ar*H*), 6.96-6.87 (3H, m, Ar*H*), 5.16-5.07 (1H, m, OC*H*), 4.51 (2H, t, J = 5.5 Hz, C*H*$_2$), 4.01 (2H, t, J = 5.5 Hz, C*H*$_2$), 3.24-3.13 (2H, m, C*H*$_2$), 2.13-2.07 (2H, m, C*H*$_2$), 1.88-1.82 (2H, m, C*H*$_2$), 1.74-1.68 (8H, m, C*H*$_2$, and C*H*$_3$), 1.11 (6H, d, J = 6.9 Hz, C*H*$_3$), 0.95 (6H, d, J = 6.9 Hz, C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 101 MHz), δ (ppm): 220.0, 152.1, 152.0, 143.6, 141.8, 130.4, 127.0, 124.1, 122.7, 122.5, 112.9, 75.2, 47.7, 26.8, 26.3, 24.3, 24.1, 21.9, 21.1. HRMS (FAB): Calcd. for $C_{28}H_{39}Cl_2NO_2Ru$ $[M]^+$: 593.1396; found 593.1405. Anal. Calcd (%) for $C_{28}H_{39}Cl_2NO_2Ru$: C, 56.66; H, 6.62; N, 2.36; found: C, 56.96; H, 6.17; N, 2.22.



4c

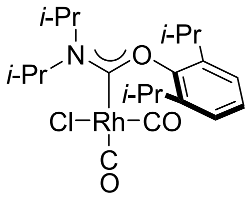
Following the **GP 2.3**, **4c** (51%, 30 mg) was obtained from **3c** (0.4 mmol, 118 mg), KHMDS (0.44 mmol, 88 mg), **HG1** (0.1 mmol, 60 mg) and THF and benzene (2 mL). ^1H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 15.70 (1H, s, Ru=CH), 7.56-7.51 (1H, m, Ar*H*), 7.46 (1H, t, J = 7.8 Hz, Ar*H*), 7.30 (2H, d, J = 7.6 Hz, Ar*H*), 6.98-6.87 (3H, m, Ar*H*), 5.20-5.10 (1H, m, OC*H*), 4.81 (2H, t, J = 6.7 Hz, CH_2), 4.04 (2H, t, J = 7.2 Hz, CH_2), 3.24-3.13 (2H, m, CH_2), 2.24-2.18 (2H, m, CH_2), 2.09-2.02 (2H, m, CH_2), 1.72 (6H, d, J = 6.1 Hz, CH_3), 1.12 (6H, d, J = 7.2 Hz, CH_3), 0.93 (6H, d, J = 6.5 Hz, CH_3). ^{13}C NMR (CD_2Cl_2, 101 MHz), δ (ppm): 221.1, 152.3, 152.2, 143.5, 141.8, 130.2, 127.0, 124.1, 122.4, 112.8, 75.4, 50.5, 50.3, 26.8, 26.1, 24.5, 23.8, 21.9, 21.2. HRMS (FAB): Calcd. for $C_{27}H_{37}Cl_2NO_2Ru$ $[M]^+$: 579.1239; found 579.1247. Anal. Calcd (%) for $C_{27}H_{37}Cl_2NO_2Ru$: C, 55.95; H, 6.44; N, 2.42; found: C, 56.34; H, 5.90; N, 2.31.



4d

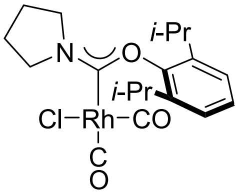
Following the **GP 2.3**, **4d** (37%, 195 mg) was obtained from **3d** (0.6 mmol, 254 mg), KHMDS (0.66 mmol, 180 mg), **HG1** (0.1 mmol, 180 mg) and THF and benzene (10 mL). ^1H NMR (CD_2Cl_2, 400 MHz), δ (ppm): 15.90 (1H, s, Ru=C*H*), 7.55-7.47 (2H, m, Ar*H*), 7.33 (1H, t, J = 7.6 Hz, Ar*H*), 7.09 (1H, dd, J = 7.4, 1.3 Hz, Ar*H*), 6.99-6.92 (3H, m, Ar*H*), 5.21-5.12 (1H, m, OC*H*), 4.92-4.80 (2H, m, CH_2), 3.99 (2H, ddd, J = 27.9, 12.7, 7.2 Hz, CH_2), 2.66-2.58 (1H, m, CH_2), 2.32-1.99 (5H, m, CH_2, CH_2 CH_2), 1.65-1.81 (6H, m, CH_3), 1.51-1.39 (2H, m, CH_2), 1.30 (9H, s, (CH_3)$_3$), 0.82 (3H, t, J = 7.2 Hz, CH_3). ^{13}C NMR (CD_2Cl_2, 101 MHz), δ (ppm): 221.8, 154.1, 152.6, 143.1, 142.1, 137.3, 130.2, 128.5, 126.3, 125.9, 122.5, 122.4, 112.9, 75.4, 51.0, 50.7, 35.6, 33.3, 31.6, 25.9, 24.1, 23.6, 21.9, 21.8, 13.6. HRMS (FAB): Calcd. for $C_{28}H_{39}Cl_2NO_2Ru$ $[M]^+$: 593.1396; found 593.1404. Anal. Calcd (%) for $C_{28}H_{39}Cl_2NO_2Ru$: C, 56.66; H, 6.62; N, 2.36; found: C, 56.90; H, 6.46; N, 2.40.

2.4. Preparation of Rh complexes



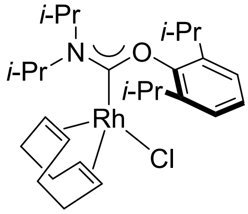
5a

[Rh(COD)(**3a**)Cl] **5c** (0.025 mmol, 13 mg) was treated with carbon monoxide in CH_2Cl_2 (2 mL). The mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure. The volatiles were further removed under high vacuum. The complex **5a** was washed with cold hexane and obtained quantitatively. ^1H NMR (400 MHz, CD_2Cl_2), δ 7.27 (1H, t, J = 7.8 Hz, Ar*H*), 7.19 (2H, d, J = 7.3 Hz, Ar*H*), 5.79-5.69 (1H, m, C*H*), 3.84-3.74 (1H, m, C*H*), 3.38-3.28 (1H, m, C*H*), 2.99-2.89 (1H, m, C*H*), 1.56 (6H, dd, J = 10.1, 6.9 Hz, CH_3), 1.36 (9H, q, J = 6.6 Hz, CH_3), 1.25 (3H, d, J = 6.9 Hz, CH_3), 1.07 (3H, d, J = 6.9 Hz, CH_3), 0.99 (3H, d, J = 6.9 Hz, CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2), δ 219.7, 186.0, 182.6, 150.3, 142.2, 140.6, 127.3, 123.9, 123.2, 59.0, 49.9, 27.6, 26.5, 26.1, 21.3, 20.7, 20.2, 19.9, 19.0. IR (ATR): 2078.6 (CO) 1984.3 (CO). HRMS (FAB): Calcd. for $C_{21}H_{31}NO_3Rh$ $[M–Cl]^+$: 448.1353; found 448.1361.



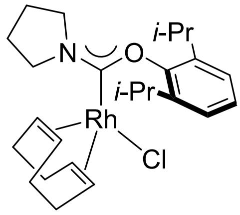
5b

[Rh(COD)(**3a**)Cl] **5d** (0.04 mmol, 20 mg) was treated with carbon monoxide in CH_2Cl_2 (2 mL). The mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure. The volatiles were further removed under high vacuum. The complex **5b** was used without further purification and obtained quantitatively. Due to the presence of conformational and rotational isomers, the ^1H, ^{13}C spectra of **5b** was highly complex, which precluded further assignment. IR (ATR): 2074.9 (CO) 1993.1 (CO).



5c

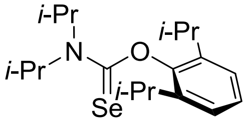
AAOC **3a** salt (0.5 mmol, 1 equiv), KHMDS (0.6 mmol, 1.1 equiv) and THF (5 mL) were mixed and stirred at –78 °C for 0.5 h. $[RhCl(COD)]_2$ (0.25 mmol, 0.5 equiv) was added and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure. Product was purified by silica gel column chromatography to afford the desired product [Rh(COD)(**3a**)Cl] **5a** as a yellow solid (95 mg, 35%). ^1H-NMR (400 MHz, CD_2Cl_2), δ 7.34-7.26 (2H, m, Ar*H*), 7.15 (1H, dd, J = 7.2, 1.9 Hz, Ar*H*), 6.50-6.40 (1H, m, C*H*), 4.61 (1H, t, J = 7.6 Hz, C*H*), 4.49 (1H, q, J = 8.0 Hz, C*H*), 3.81-3.58 (3H, m, CH), 2.82-2.68 (2H, m, CH_2), 2.49-2.38 (1H, m, C*H*), 2.01 (1H, q, J = 7.6 Hz, C*H*), 1.90-1.77 (2H, m, CH_2), 1.70-1.59 (1H, m, C*H*), 1.50-1.39 (12H, m, CH_3), 1.32 (3H, d, J = 6.5 Hz, CH_3), 1.24 (6H, d, J = 6.9 Hz, CH_3), 1.05 (3H, d, J = 6.9 Hz, CH_3), 0.95 (3H, d, J = 6.9 Hz, CH_3). ^{13}C NMR (101 MHz, $CDCl_2$), δ 228.4, 150.2, 143.0, 140.7, 126.6, 124.2, 122.4, 99.6, 96.4, 69.5, 65.5, 58.2, 49.2, 35.6, 30.3, 28.8, 27.6, 27.3, 26.8, 26.3, 25.7, 21.7, 21.1, 20.4, 19.7. HRMS (FAB): Calcd. for $C_{27}H_{43}ClNORh$ $[M]^+$: 535.2083; found 535.2090.



5d

AAOC **3c** salt (0.4 mmol, 1 equiv, 118 mg), KHMDS (0.48 mmol, 1.2 equiv, 96 mg) and THF (4 mL) were mixed and stirred at –78 °C for 0.5 h. $[RhCl(COD)]_2$ (0.2 mmol, 0.5 equiv, 98 mg) was added and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure. Product was purified by silica gel column chromatography to afford the desired product [Rh(COD)(**3c**)Cl] **5d** as a yellow solid (127 mg, 62%). ^{1}H-NMR (400 MHz, CD_2Cl_2), δ 7.32 (1H, dd, J = 7.7, 1.4 Hz, Ar*H*), 7.24 (1H, t, J = 7.6 Hz, Ar*H*), 7.07 (1H, dd, J = 7.6, 1.4 Hz, Ar*H*), 4.74 (3H, m, C*H*, C*H₂*), 4.27 (1H, J = 12.1, 6.5 Hz, C*H*), 4.10 – 3.93 (1H, m, C*H*), 3.75 (1H, m, C*H*), 3.64 – 3.46 (2H, m, C*H₂*), 2.59 (1H, m, C*H*₂), 2.54 – 2.36 (2H, m, C*H₂*), 2.13 – 1.91 (6H, m, C*H₂*), 1.90 – 1.73 (1H, m), 1.58 – 1.43 (3H, m, C*H₃*), 1.39 (3H, d, J = 6.7 Hz, C*H₃*), 1.33 – 1.22 (2H, m, C*H₂*), 1.22 – 1.12 (3H, d, J = 6.9 Hz, C*H₃*), 1.07 (3H, d, J = 6.8 Hz, C*H₃*), 1.00 (3H, d, J = 6.9 Hz, C*H₃*). ^{13}C NMR (101 MHz, $CDCl_2$), δ 225.0, 224.8 (due to the presence of conformational and rotational isomers), 150.7, 142.3, 140.4, 126.4, 124.4, 122.2, 100.1, 99.1, 69.3, 66.0, 52.7, 48.0, 35.0, 30.1, 29.6, 28.0, 7.1, 26.5, 25.0, 24.9, 21.8, 20.4 Due to the presence of conformational and rotational isomers, the ^{13}C NMR spectra of rhodium complex was highly complex, which precluded further assignment.

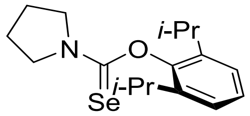
2.5. Preparation of Se adduct



6a

To AAOC **3a** salt (0.2 mmol, 87 mg), KHMDS (0.24 mmol, 48 mg) and selenium (0.4 mmol, 32 mg) was added THF (2 mL) at –78 °C. The mixture was warmed to rt and then stirred 12 h. The volatiles were removed under reduced pressure and Se adducts were purified by column chromatography afforded the desired product as a yellow solid (74 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.27 (1H, dd, J = 8.6, 7.1 Hz, Ar*H*), 7.18 (2H, d, J = 7.6 Hz, Ar*H*), 5.84 (1H, m, C*H*), 3.88 (1H, m, C*H*), 2.96-2.86 (2H, m, C*H*), 1.56 (6H, t, J = 6.7 Hz, C*H₃*), 1.31 (12H, dd, J = 6.7, 2.5 Hz, C*H₃*), 1.17 (6H, d, J = 6.9 Hz, C*H₃*). ^{13}C NMR (101 MHz, $CDCl_3$), δ 191.6, 149.2, 141.4, 126.6, 124.2, 58.4, 49.1, 27.4, 24.9, 23.0, 21.5, 19.5. ^{77}Se NMR (76 MHz, $CDCl_3$), δ 284.4. HRMS (FAB): Calcd. for

$C_{19}H_{32}NOSe$ [M+H]$^+$: 370.1649; found 370.1645. Anal. Calcd (%) for $C_{19}H_{31}NOSe$: C, 61.94; H, 8.48; N, 3.80; found: C, 62.31; H, 8.28; N, 3.62.



6**b**

To AAOC **3c** salt (0.2 mmol, 59 mg), KHMDS (0.24 mmol, 48 mg) and selenium (0.4 mmol, 32 mg) was added THF (2 mL) at –78 °C. The mixture was warmed to rt and then stirred 12 h. The volatiles were removed under reduced pressure and Se adducts were purified by column chromatography afforded the desired product as a yellow solid (32 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.25 (2H, dd, J = 8.5, 6.7 Hz, Ar*H*), 7.20 – 7.13 (3H, m, Ar*H*), 3.89 (2H, t, J = 6.9 Hz, C*H*$_2$), 3.76 (2H, t, J = 6.9 Hz, C*H*$_2$), 2.95 (2H, hept, J = 6.9 Hz, C*H*), 2.19 – 2.10 (3H, m, C*H*), 2.09 – 2.00 (3H, m, C*H*$_2$), 1.29 (6H, d, J = 6.9 Hz, C*H*$_3$), 1.15 (6H, d, J = 6.9 Hz, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$), δ 187.1, 149.5, 141.0, 126.7, 123.9, 77.4, 77.1, 76.8, 55.0, 49.0, 27.7, 26.1, 24.6, 24.5, 22.2. ^{77}Se NMR (76 MHz, $CDCl_3$), δ 286.3. Anal. Calcd (%) for $C_{17}H_{25}NOSe$: C, 60.35; H, 7.45; N, 4.14; found: C, 60.83; H, 7.64; N, 4.00.

3. Electronic Properties of Ligands by TEP and 77Se NMR Study.

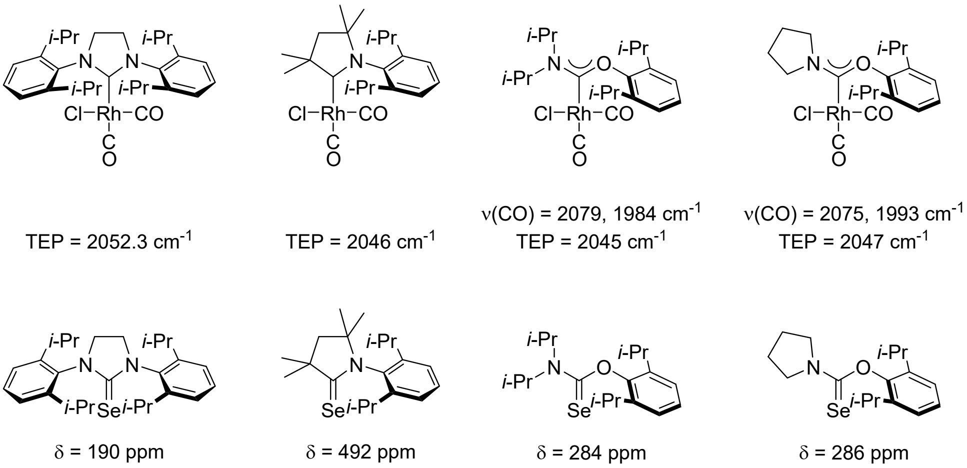


Figure S1. Tolman Electronic Parameters (TEP) and ^{77}Se NMR Shifts of Selected carbenes [a]The IR spectra of complexes were measured in CH$_2$Cl$_2$, and TEP values were calculated from the symmetric and antisymmetric CO stretching frequencies of the corresponding [Rh(carbene)(CO)$_2$Cl] complexes, using the equation TEP = 0.8001 × νav(CO) + 420cm^{-1}. [b] ^{77}Se-NMR spectra in CDCl$_3$.

4.1. Ethenolysis of Methyl Oleate using AAOC-Ru Catalysts

Reactions were setup analogously to those described in the literature.[3] A vial was charged with (Ru complex and toluene) to prepare a stock solution (0.0005 M). A reactor was charged with methyl oleate (1 mmol, 1 equiv.), tridecane (10 – 20 mg) as an internal standard and ruthenium catalyst (ppm) in a glovebox. The reactor was then purged three times with ethylene and pressurized to 150 psi. The mixture was stirred at 40 °C for 3 h. The reaction was cooled to rt, quenched with 0.1 mL of a 3 M solution of ethyl vinyl ether in MC, and diluted with hexane. The samples were analyzed by GC.

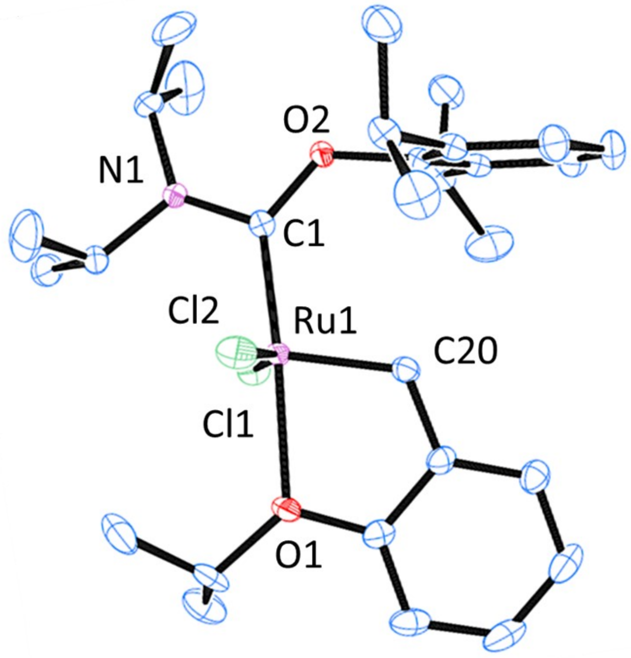
4.2. Ethenolysis of *cis*-Cyclooctene using AAOC-Ru Catalysts

Reactions were setup analogously to those described in the literature.[3b] A vial was charged with Ru catalyst and toluene to prepare a stock solution (0.0005 M). A reactor was charged with *cis*-cyclooctene (1 equiv.), tridecane (30 – 50 mg) as an internal standard and a solution of the catalyst in a glovebox. The vessel was then purged three times with ethylene and pressurized to 300 psi. The mixture was stirred at 30 °C for 5 h. The reaction was cooled to rt, quenched with 0.1 mL of a 3 M solution of ethyl vinyl ether in MC, and diluted with hexane. The samples were analyzed by GC.

5. Crystallographic Data

Reflection data for **4a** and **4d** were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoKα radiation (λ = 0.7107 Å). The hemisphere of reflection data were collected as ω scan frames with 0.5°/frame and an exposure time of 10s/frame. Cell parameters were determined and refined by the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.

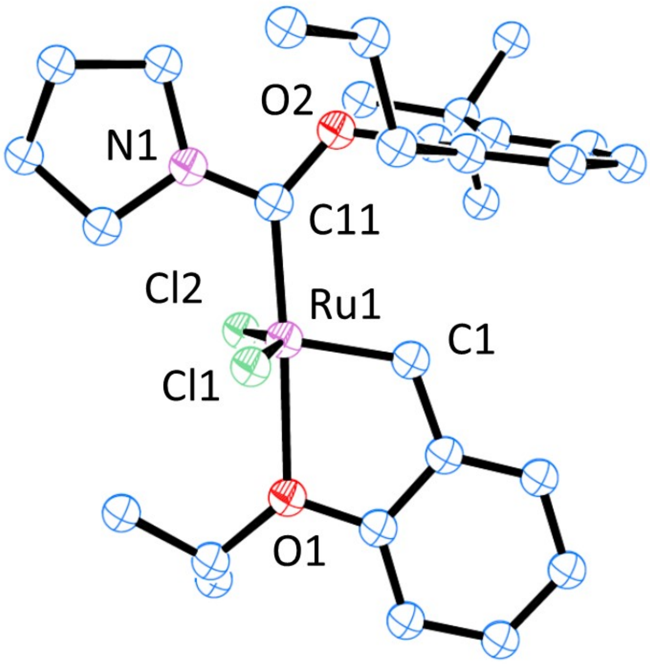
Table S2. X-ray crystallography data for **4a**



Identification code	**4a**	
CCDC number	1902240	
Empirical formula	C29 H43 Cl2 N O2 Ru	
Formula weight	609.61	
Temperature	296.15 *T* (K)	
Wavelength	0.71073	
Crystal system	orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 34.7471(5)Å	α= 90°
	b = 11.0709(2) Å	β= 90°
	c = 15.4792(2)Å	γ=90°
Volume	5954.56(16)Å^3	

Z	8
Density (calculated)	1.360 g cm^{-3}
Absorption coefficient	0.731
F(000)	2544
θ range for data collection	2.336 to 25.578°
Index ranges	$-42 \leq h \leq 42$, $-13 \leq k \leq 12$, $-18 \leq l \leq 18$
Reflections collected	74178
Independent reflections	4984 [R(int) = 0.0299]
Completeness to θ = 25.24°	99.9%
Data / restraints /parameters	5562/ 0 / 326
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma((I)$]	$R_1 = 0.0219$, $wR_2 = 0.0474$
R indices (all data)	$R_1 = 0.0264$, $wR_2 = 0.0490$
Largest diff. peak and hole	

Table S3. X-ray crystallography data for **4d**



Identification code	**4d**	
CCDC number	1987567	
Empirical formula	C28 H39 Cl2 N O2 Ru	
Formula weight	593.57	
Temperature	296(2) *T* (K)	
Wavelength	0.71073	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.4974(2)Å	α = 90°
	b = 22.8652(3)Å	β = 111.0221 (7)°
	c = 11.6035(2)Å	γ = 90°
Volume	2847.42(8)Å^3	
Z	4	

Density (calculated)	1.385 g cm^{-3}
Absorption coefficient	0.762
F(000)	1232
θ range for data collection	2.603 to 25.338°
Index ranges	-13 ≤ h ≤ 13, -27 ≤ k ≤274, -13 ≤ l ≤13
Reflections collected	36876
Independent reflections	5174 [R(int) = 0.0328]
Completeness to θ = 25.242°	99.8%
Data / restraints /parameters	5174 / 6 / 343
Goodness-of-fit on F^2	1.040
Final R indices [I > 2σ((I)]	$R_1 = 0.0284$, $wR_2 = 0.0744$
R indices (all data)	$R_1 = 0.0363$, $wR_2 = 0.0783$
Largest diff. peak and hole	

6. ^{1}H, ^{13}C and ^{77}Se NMR spectra

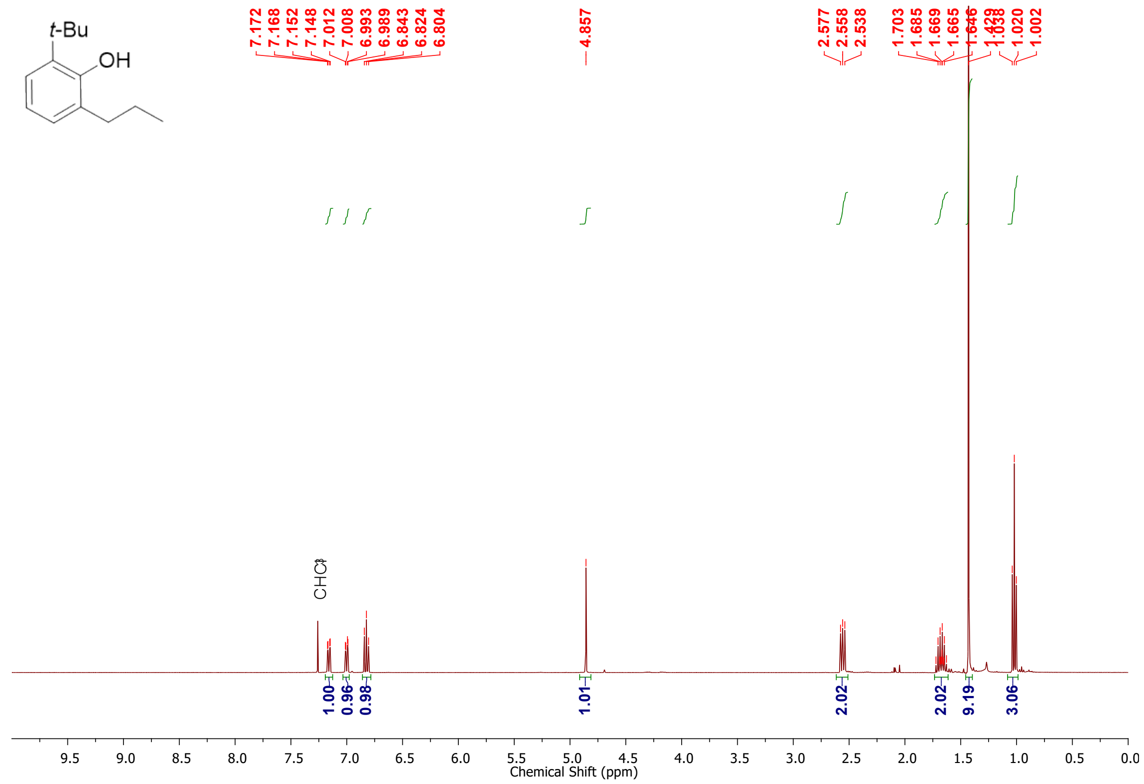


Figure S2. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **S1**, δ 7.16 (1H, dd, J = 7.8, 1.7 Hz, Ar*H*), 7.00 (1H, dd, J = 7.5, 1.7 Hz, Ar*H*), 6.82 (1H, t, J = 7.6 Hz, Ar*H*), 4.86 (1H, s, O*H*), 2.61 – 2.51 (2H, m, C*H$_2$*), 1.73 – 1.61 (2H, m, C*H$_2$*), 1.43 (9H, s, (C*H$_3$*)$_3$), 1.02 (3H, t, J = 7.3 Hz, C*H$_3$*)

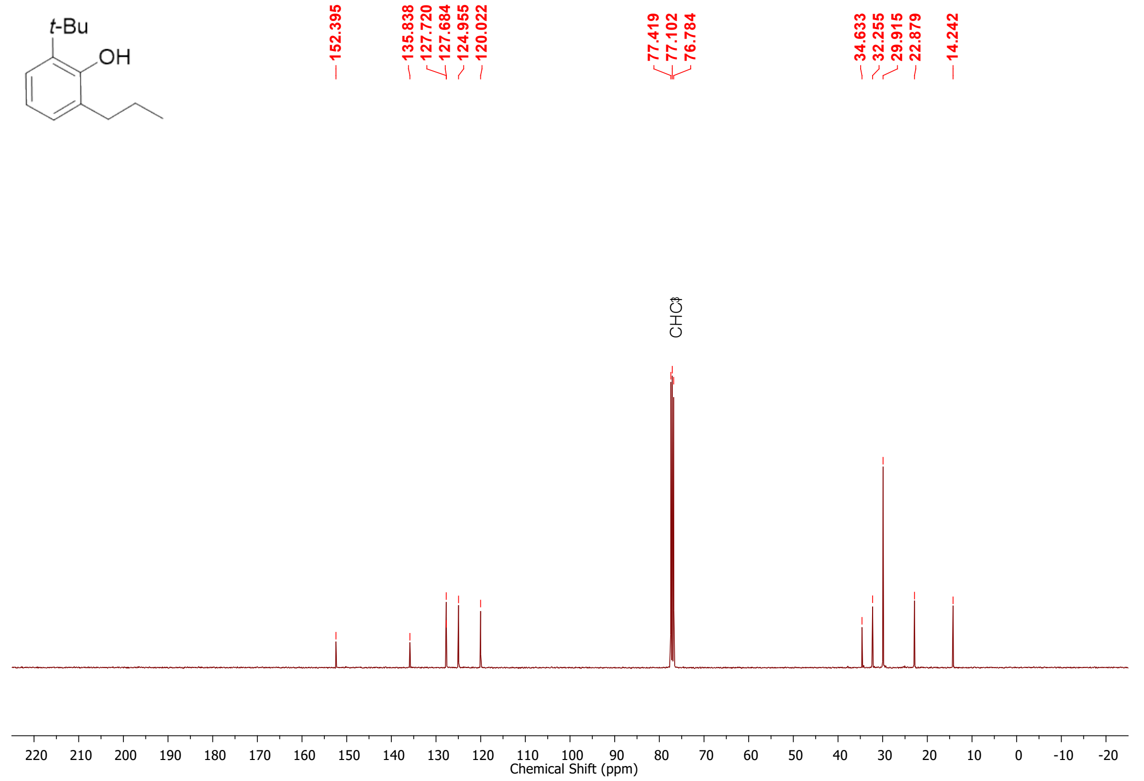


Figure S3. ^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **S1**, δ 152.4, 135.8, 127.7, 125.0, 120.0, 34.6, 32.3, 29.9, 22.9, 14.2

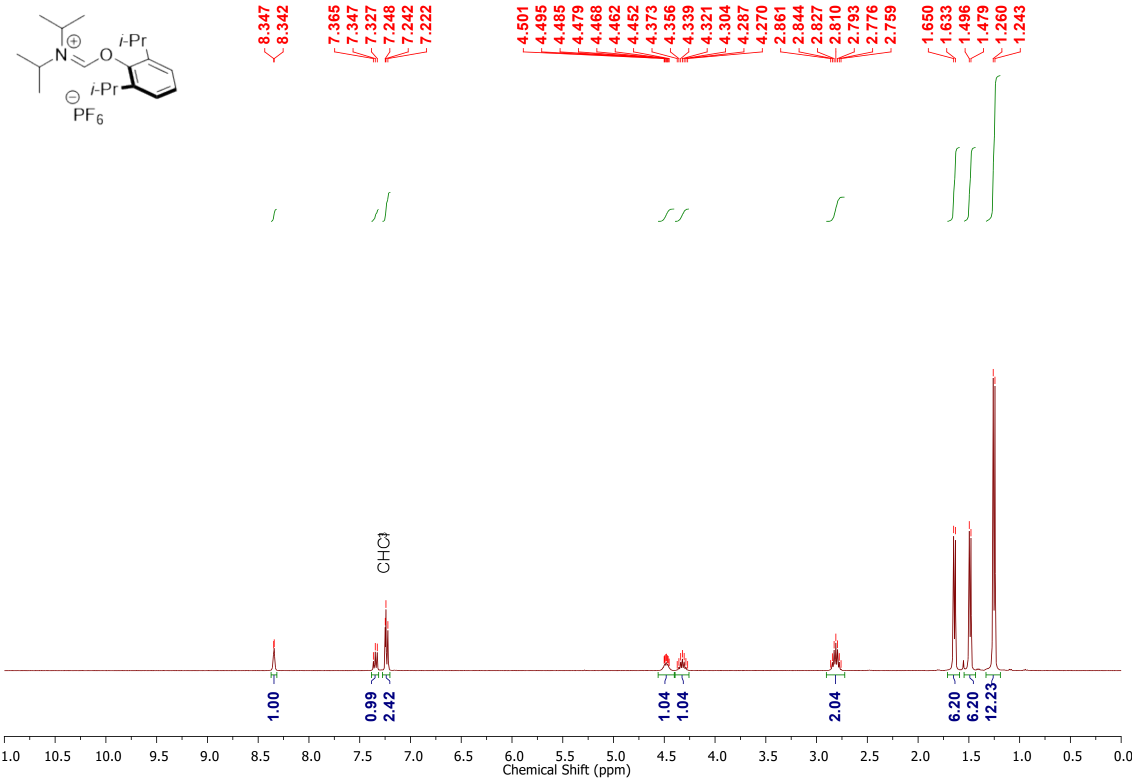


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a,** δ (ppm): 8.29 (1H, s, C*H*), 7.33 (1H, t, J = 7.6 Hz, Ar*H*), 7.23 (2H, t, J = 8.0 Hz, Ar*H*), 4.43-4.31 (2H, m, NC*H*), 2.85-2.75 (2H, m, ArC*H*), 1.62 (6H, d, J = 5.7 Hz, CH_3), 1.47 (6H, d, J = 5.7 Hz, CH_3), 1.24 (12H, d, J = 6.9 Hz, CH_3)

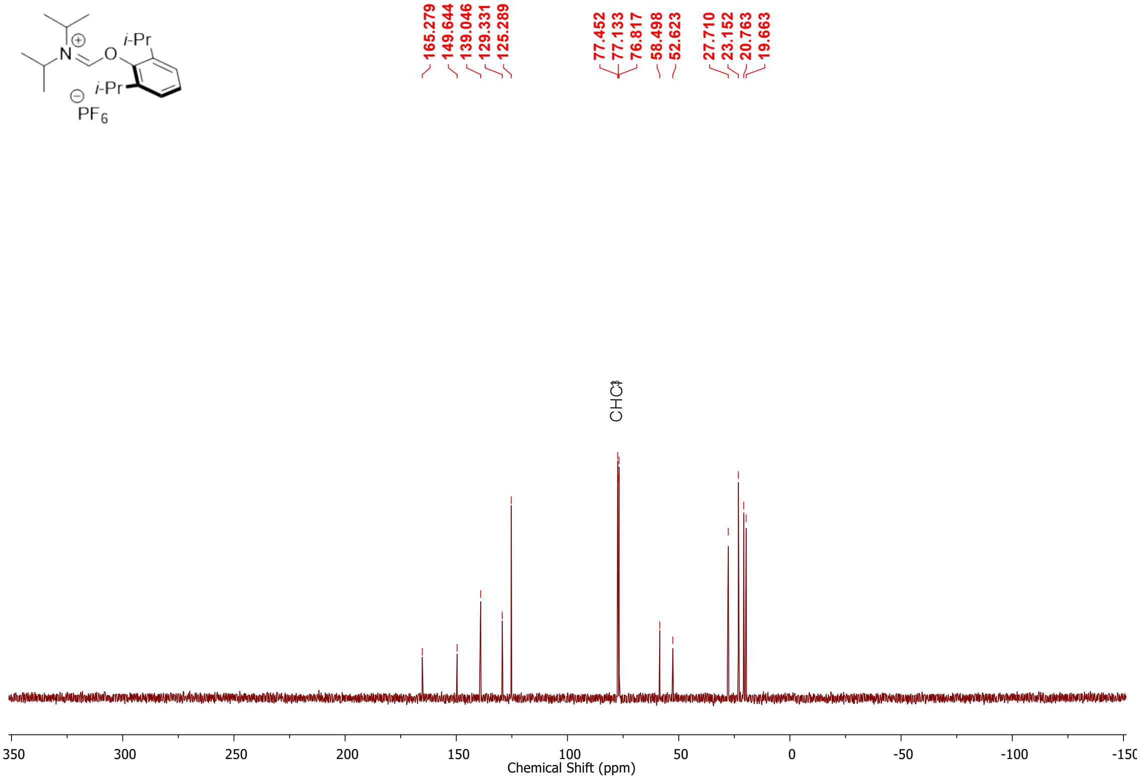


Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**, δ (ppm): 165.3, 149.7, 139.1, 129.3, 125.3, 58.5, 52.6, 27.7, 23.2, 20.8, 19.7

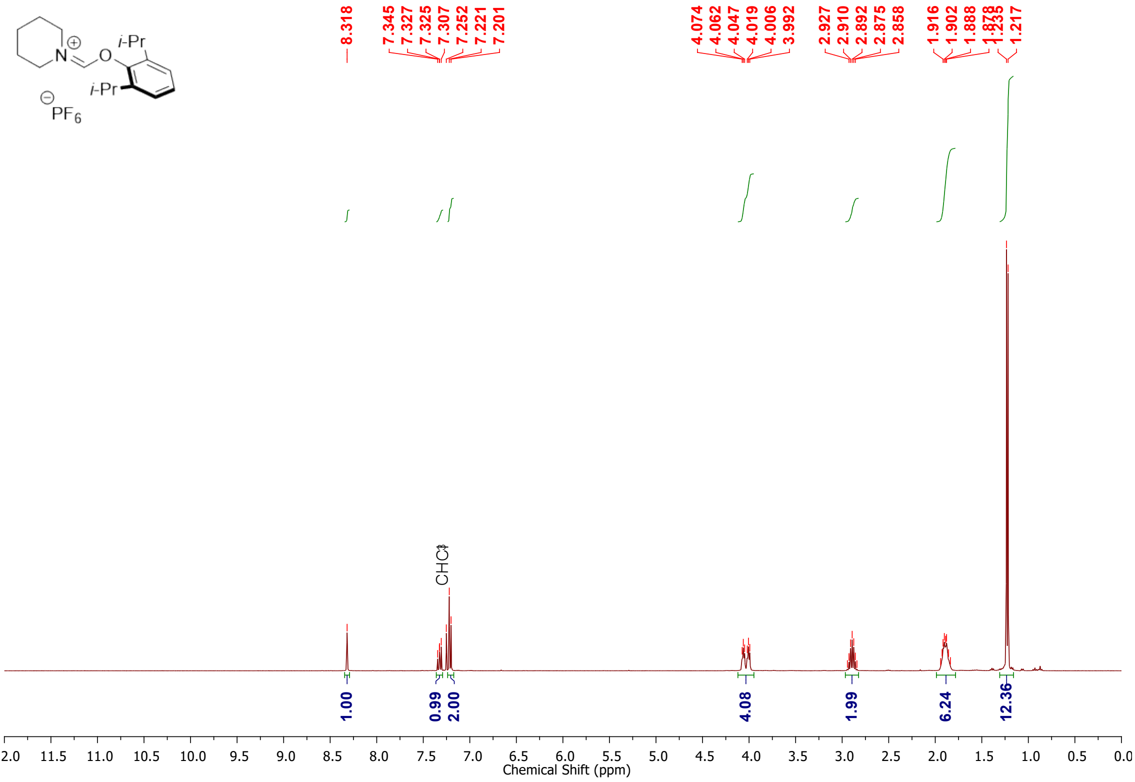


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**, δ (ppm): 8.32 (1H, s, NC*H*O), 7.33 (1H, dd, J = 8.2, 7.3 Hz, Ar*H*), 7.21 (2H, d, J = 7.7 Hz, Ar*H*), 4.12 – 3.95 (4H, m, NC*H$_2$*), 2.89 (2H, hept, J = 6.8 Hz, C*H*), 1.99 – 1.78 (6H, m, C*H$_2$*), 1.23 (12H, d, J = 6.8 Hz, C*H$_3$*).

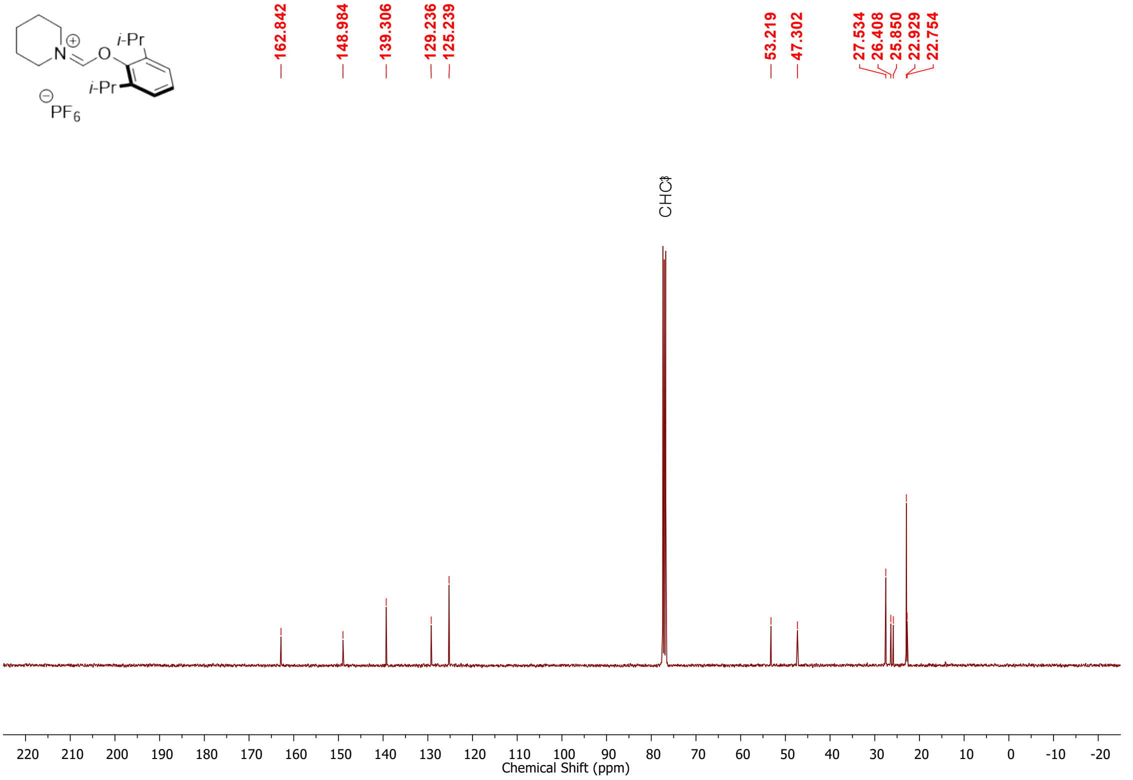


Figure S7. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**, δ (ppm): 162.8, 149.0, 139.3, 129.2, 125.2, 53.2, 47.3, 27.5, 26.4, 25.9, 22.9, 22.8.

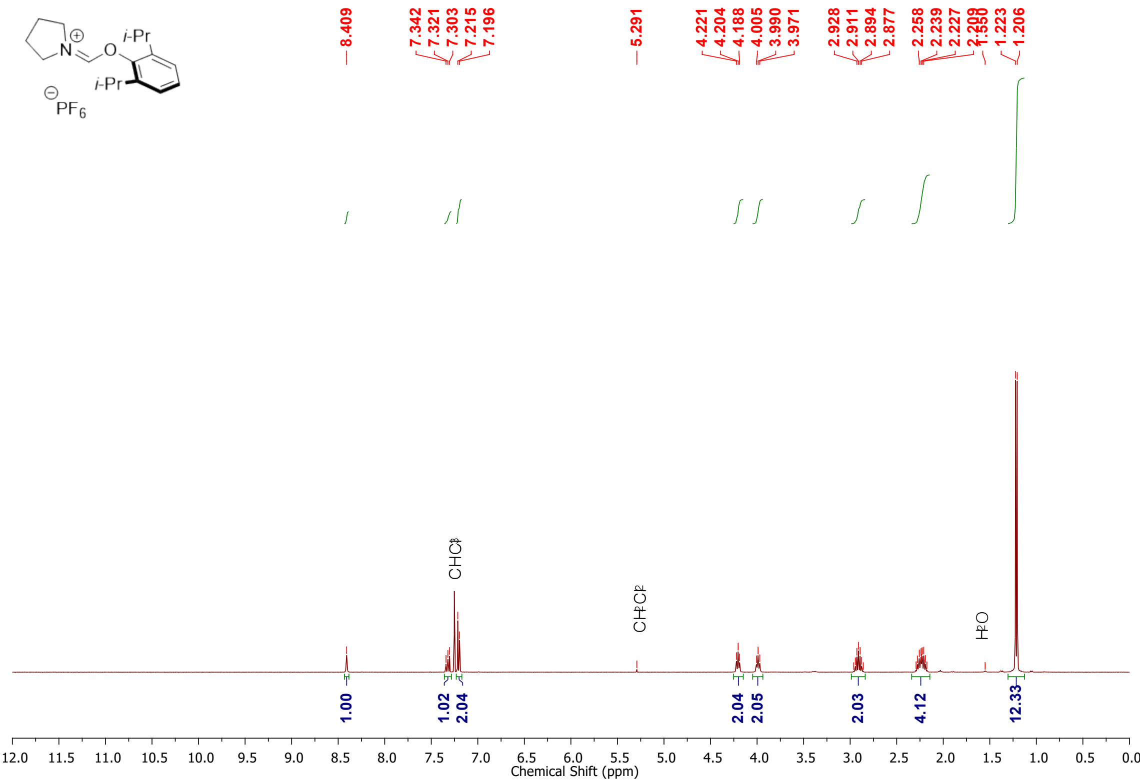


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**, 8.41 (1H, s, NC*H*O), 7.36 – 7.28 (1H, m, Ar*H*), 7.21 (2H, d, J = 7.7 Hz, Ar*H*), 4.20 (2H, t, J = 6.7 Hz, NCH_2), 3.99 (2H, t, J = 6.9 Hz, NCH_2), 2.91 (2H, hept, J = 6.8 Hz, CC*H*), 2.34 – 2.14 (4H, m, CH_2), 1.21 (12H, d, J = 6.8 Hz, CH_3).

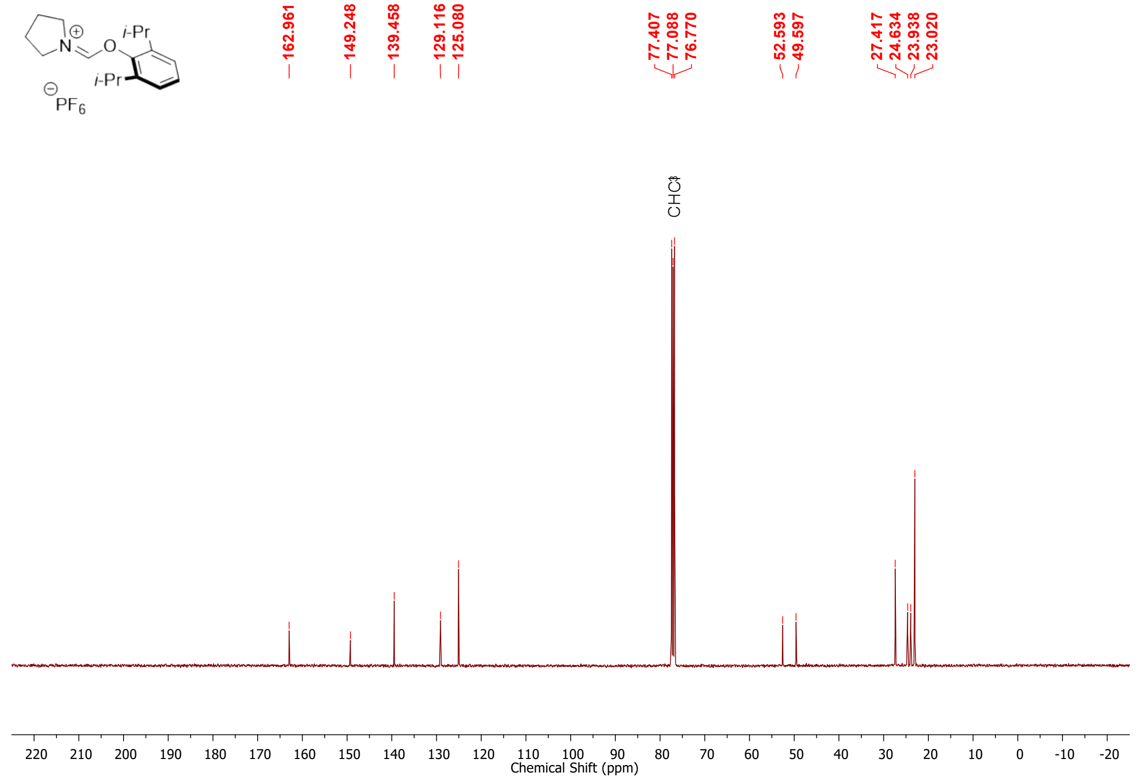


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3c**, δ (ppm): 163.0, 149.3, 139.5, 129.1, 125.1, 77.4, 77.1, 76.8, 52.6, 49.6, 27.4, 24.6, 23.9, 23.0.

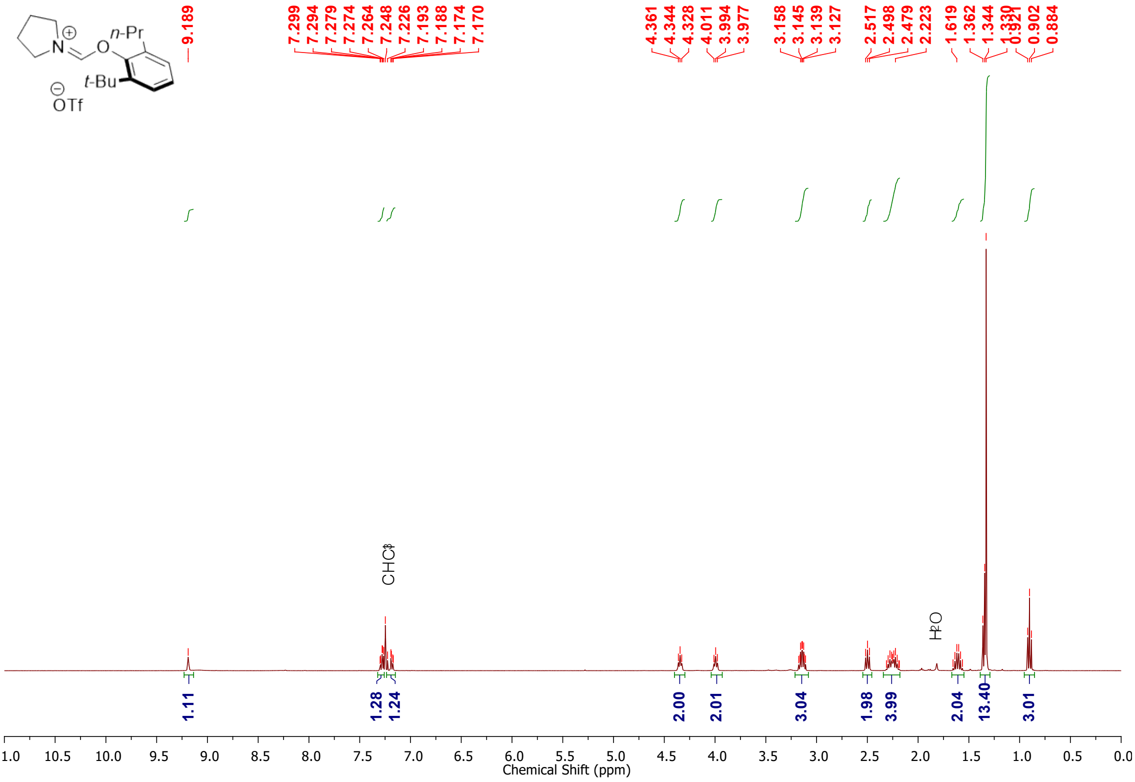


Figure S10. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of **3d**, δ (ppm): δ 9.19 (1H, s, C*H*), 7.30-7.17 (2H, m, Ar*H*), 4.35 (2H, t, J = 6.5 Hz, CH_2), 3.99 (2H, t, J = 6.7 Hz, CH_2), 3.18-3.11 (3H, m, CH_2), 2.50 (2H, t, J = 7.4 Hz, CH_2), 2.25 (4H, dq, J = 28.6, 6.7 Hz, CH_2), 1.61 (2H, td, J = 14.9, 7.4 Hz, CH_2), 1.36-1.33 (12H, m, CH_3), 0.90 (3H, t, J = 7.2 Hz, CH_3)

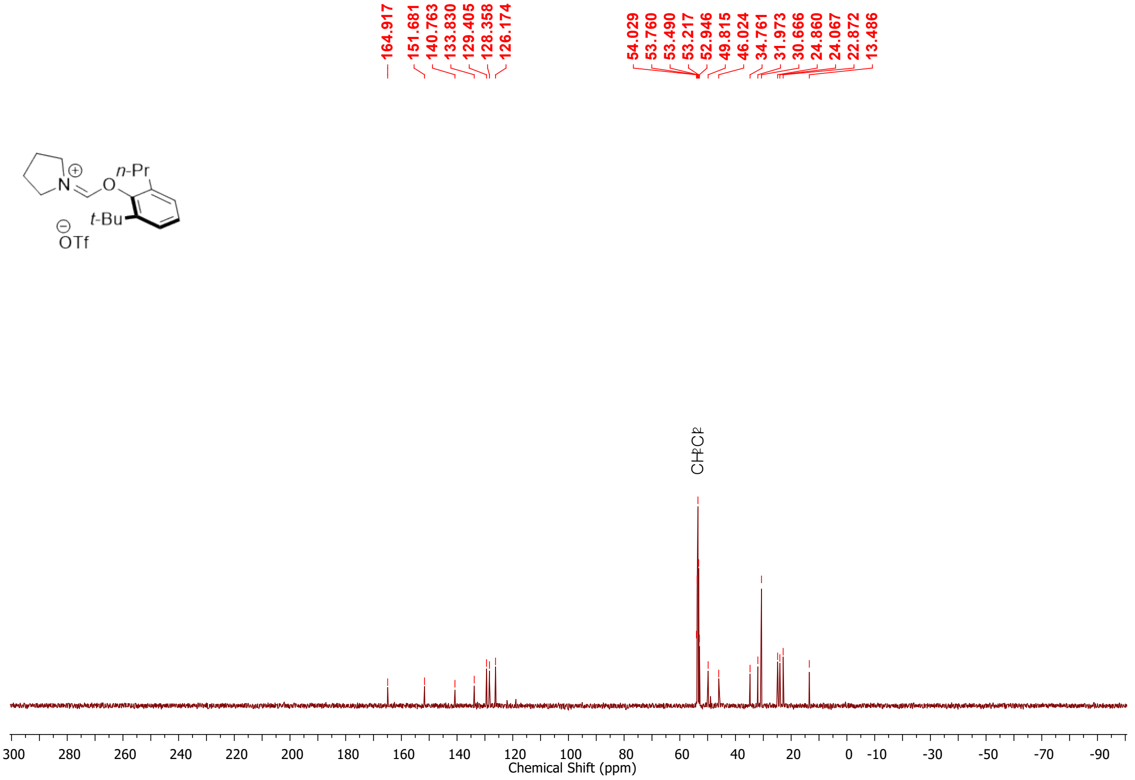


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Figure S11. ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) spectrum of **3d**, δ (ppm): 164.9, 151.7, 140.8, 133.8, 129.4, 128.4, 126.2, 49.8, 46.0, 34.8, 32.0, 30.7, 24.9, 24.1, 22.9, 13.5

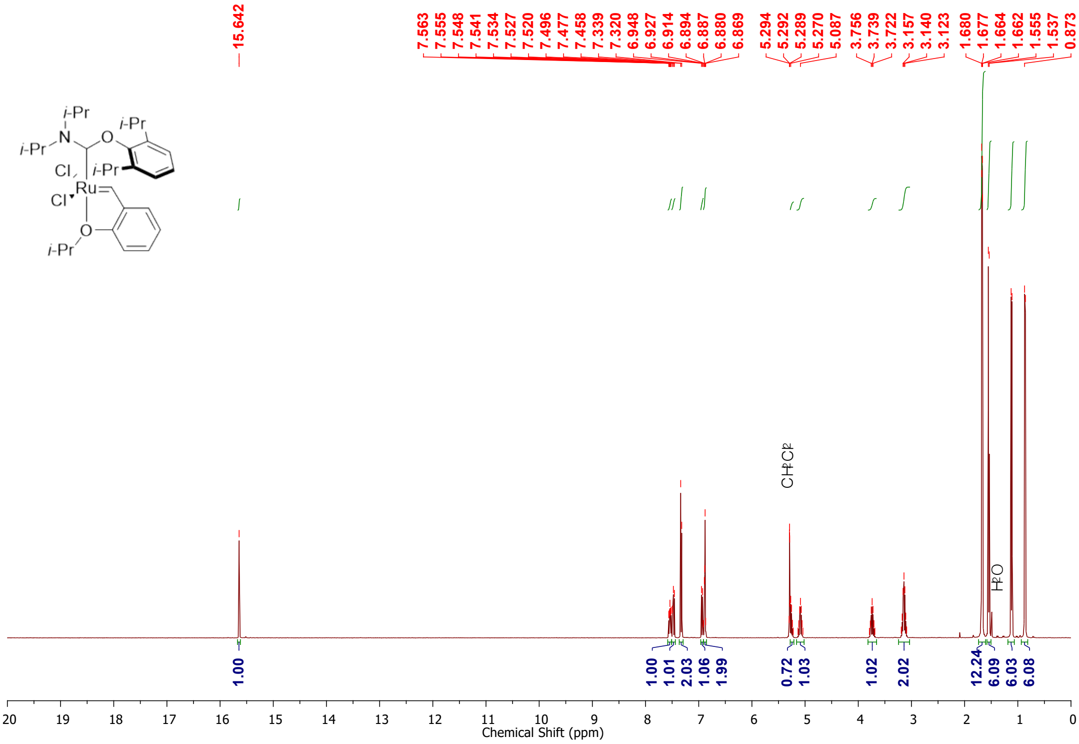

Figure S12. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **4a**, δ (ppm): 15.64 (1H, s, Ru=C*H*), 7.56-7.52 (1H, m, Ar*H*), 7.48 (1H, t, J = 7.6 Hz, Ar*H*), 7.33 (2H, d, J = 8.0 Hz, Ar*H*), 6.94 (1H, d, J = 8.4 Hz, Ar*H*), 6.89 (2H, t, J = 2.9 Hz, Ar*H*), 5.25 (1H, m, J = 6.3 Hz, C*H*), 5.13-5.04 (1H, m, C*H*), 3.79-3.69 (1H, m, C*H*), 3.19-3.09 (2H, m, C*H*), 1.67 (12H, d, J = 6.1 Hz, CH_3), 1.55 (6H, d, J = 6.9 Hz, CH_3), 1.12 (6H, d, J = 6.7 Hz, CH_3), 0.86 (6H, d, J = 6.9 Hz, CH_3)

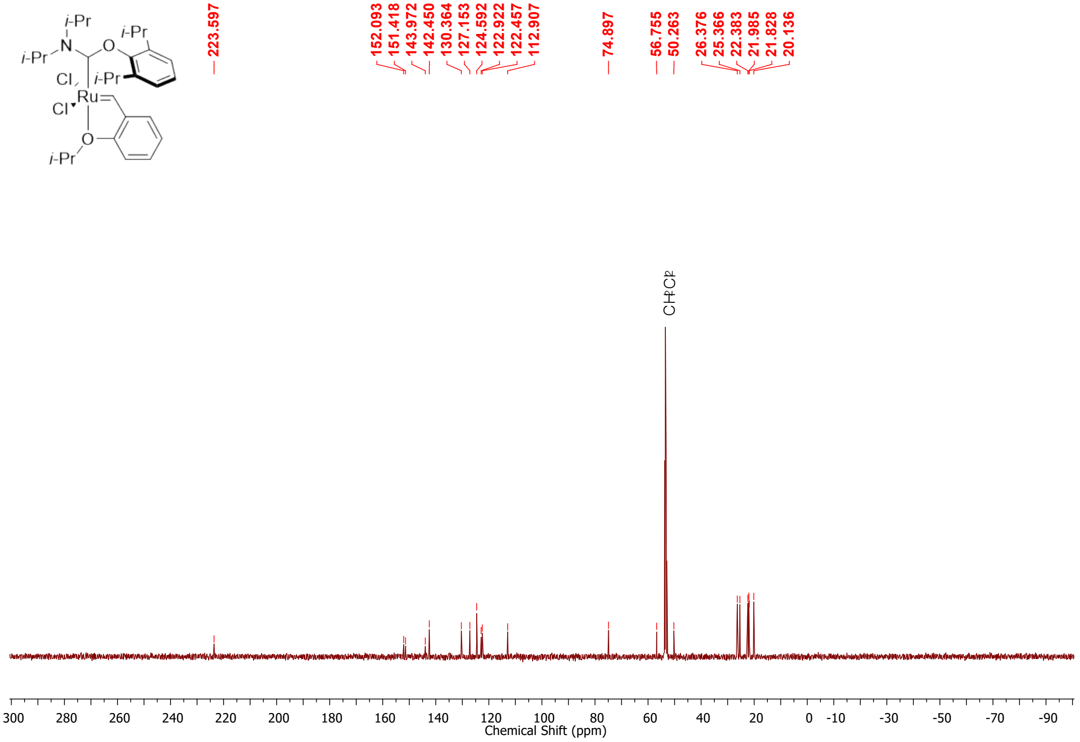

Figure S13. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **4a**, δ (ppm): 223.6, 152.1, 151.4, 144.0, 142.5, 130.4, 127.2, 124.6, 122.9, 122.5, 112.9, 74.9, 56.8, 50.3, 26.4, 25.4, 22.4, 22.0, 21.8, 20.1

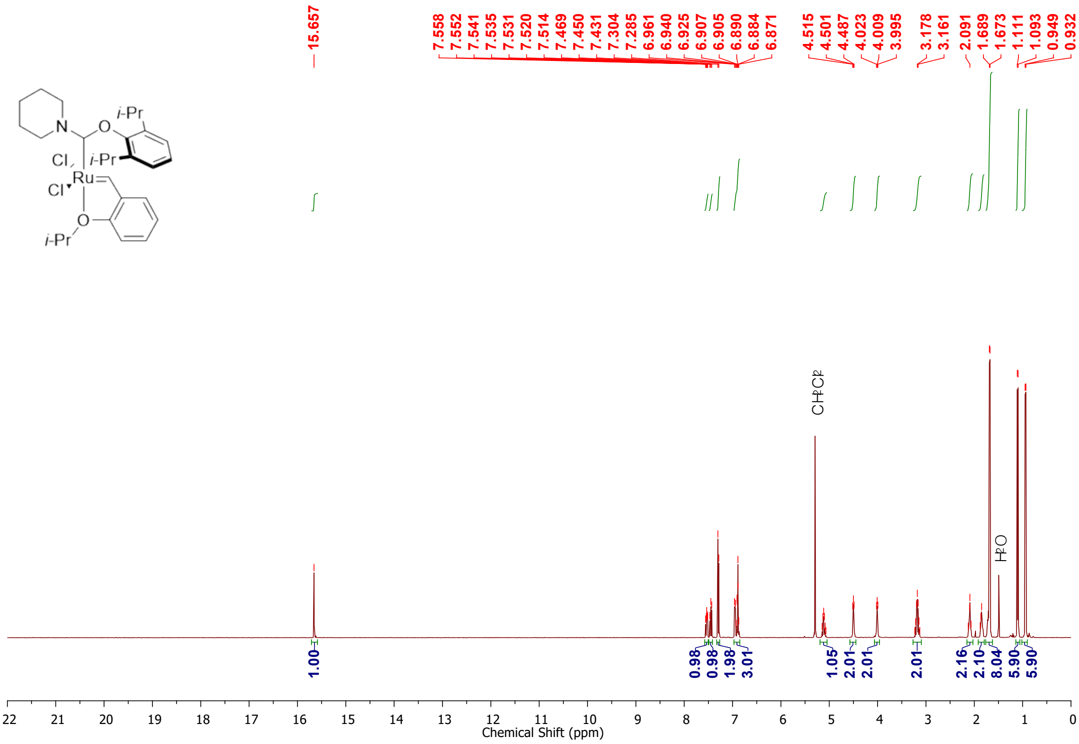

Figure S14. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **4b**, δ (ppm): 15.67 (1H, s, Ru=C*H*), 7.56-7.52 (1H, m, Ar*H*), 7.45 (1H, t, J = 7.6 Hz, Ar*H*), 7.30 (2H, d, J = 7.6 Hz, Ar*H*), 6.96-6.87 (3H, m, Ar*H*), 5.16-5.07 (1H, m, OC*H*), 4.51 (2H, t, J = 5.5 Hz, C*H₂*), 4.01 (2H, t, J = 5.5 Hz, C*H₂*), 3.24-3.13 (2H, m, C*H₂*), 2.13-2.07 (2H, m, C*H₂*), 1.88-1.82 (2H, m, C*H₂*), 1.74-1.68 (8H, m, C*H₂*, and C*H₃*), 1.11 (6H, d, J = 6.9 Hz, C*H₃*), 0.95 (6H, d, J = 6.9 Hz, C*H₃*)

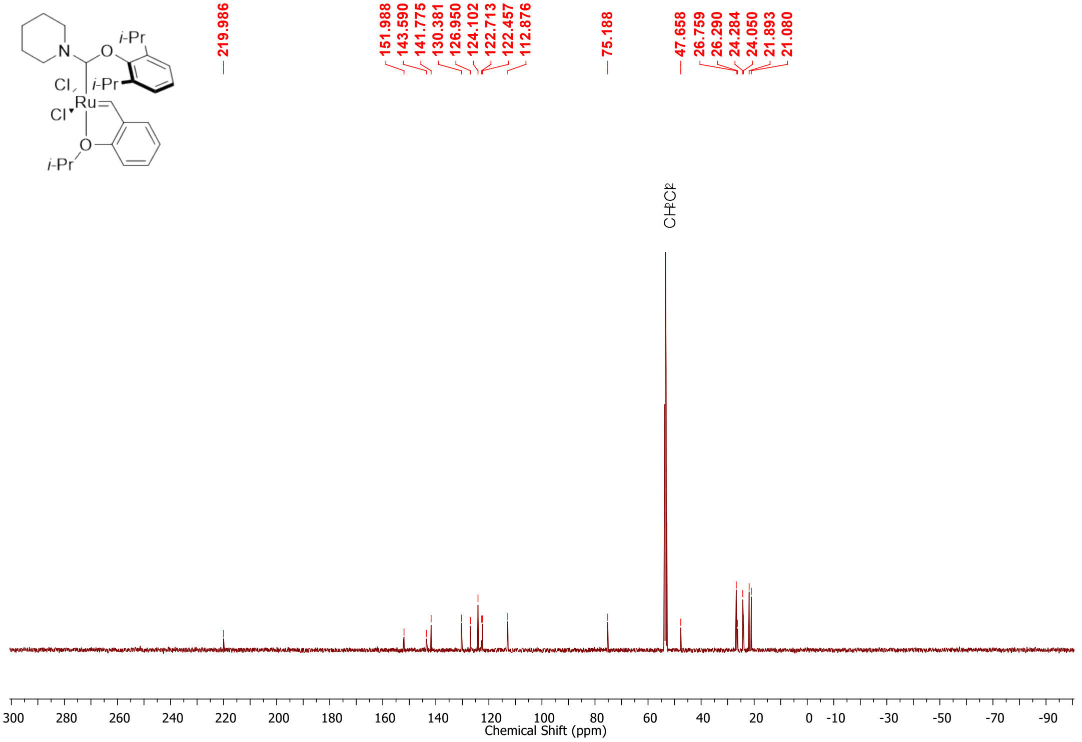

Figure S15. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **4b**, δ (ppm): 220.0, 152.1, 152.0, 143.6, 141.8, 130.4, 127.0, 124.1, 122.7, 122.5, 112.9, 75.2, 47.7, 26.8, 26.3, 24.3, 24.1, 21.9, 21.1

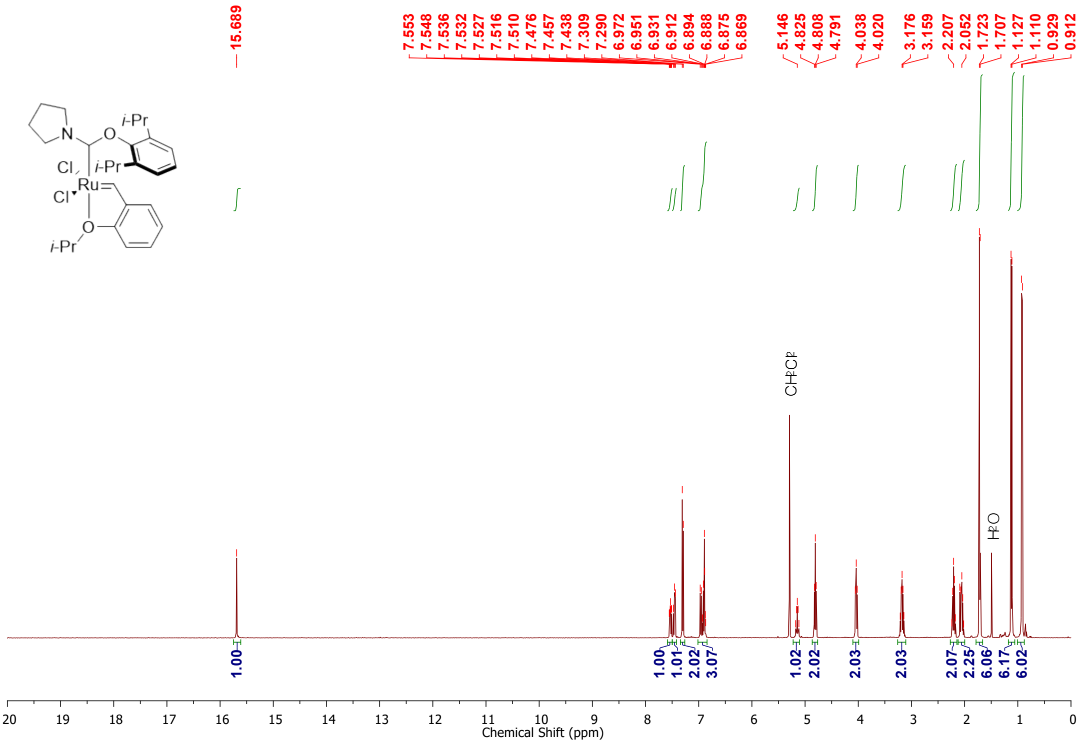

Figure S16. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **4c**, δ (ppm): 15.70 (1H, s, Ru=CH), 7.56-7.51 (1H, m, Ar*H*), 7.46 (1H, t, J = 7.8 Hz, Ar*H*), 7.30 (2H, d, J = 7.6 Hz, Ar*H*), 6.98-6.87 (3H, m, Ar*H*), 5.20-5.10 (1H, m, OC*H*), 4.81 (2H, t, J = 6.7 Hz, C*H₂*), 4.04 (2H, t, J = 7.2 Hz, C*H₂*), 3.24-3.13 (2H, m, C*H₂*), 2.24-2.18 (2H, m, C*H₂*), 2.09-2.02 (2H, m, C*H₂*), 1.72 (6H, d, J = 6.1 Hz, C*H₃*), 1.12 (6H, d, J = 7.2 Hz, C*H₃*), 0.93 (6H, d, J = 6.5 Hz, C*H₃*)

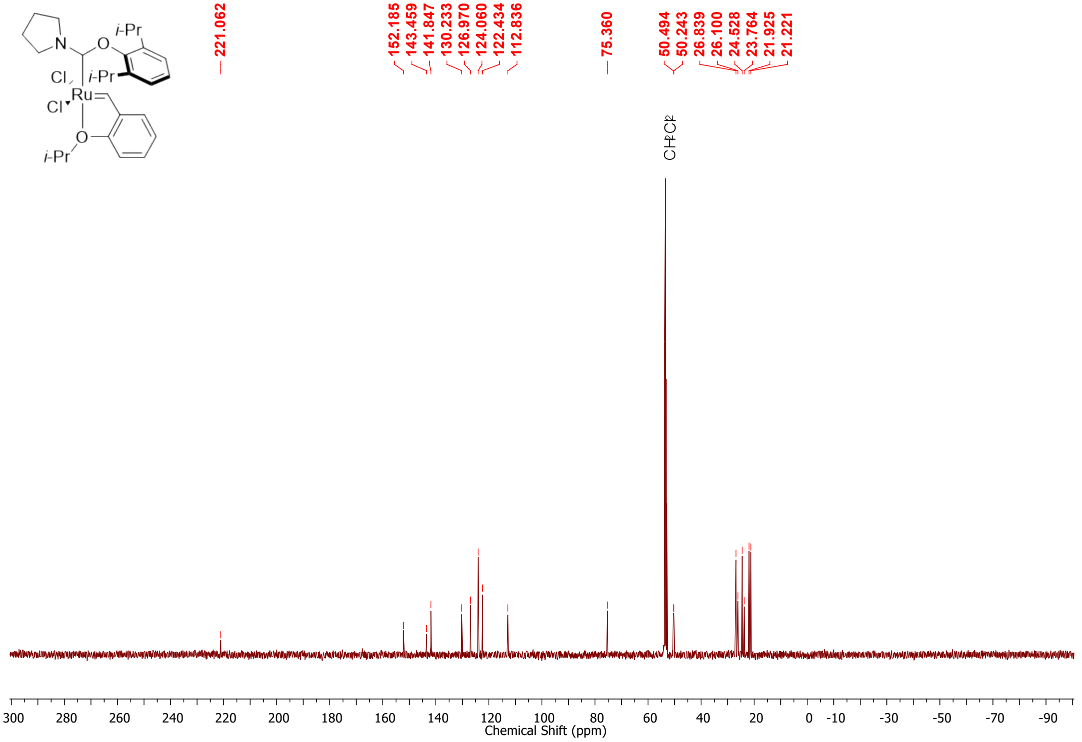

Figure S17. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **4c**, δ (ppm): 221.1, 152.3, 152.2, 143.5, 141.8, 130.2, 127.0, 124.1, 122.4, 112.8, 75.4, 50.5, 50.3, 26.8, 26.1, 24.5, 23.8, 21.9, 21.2

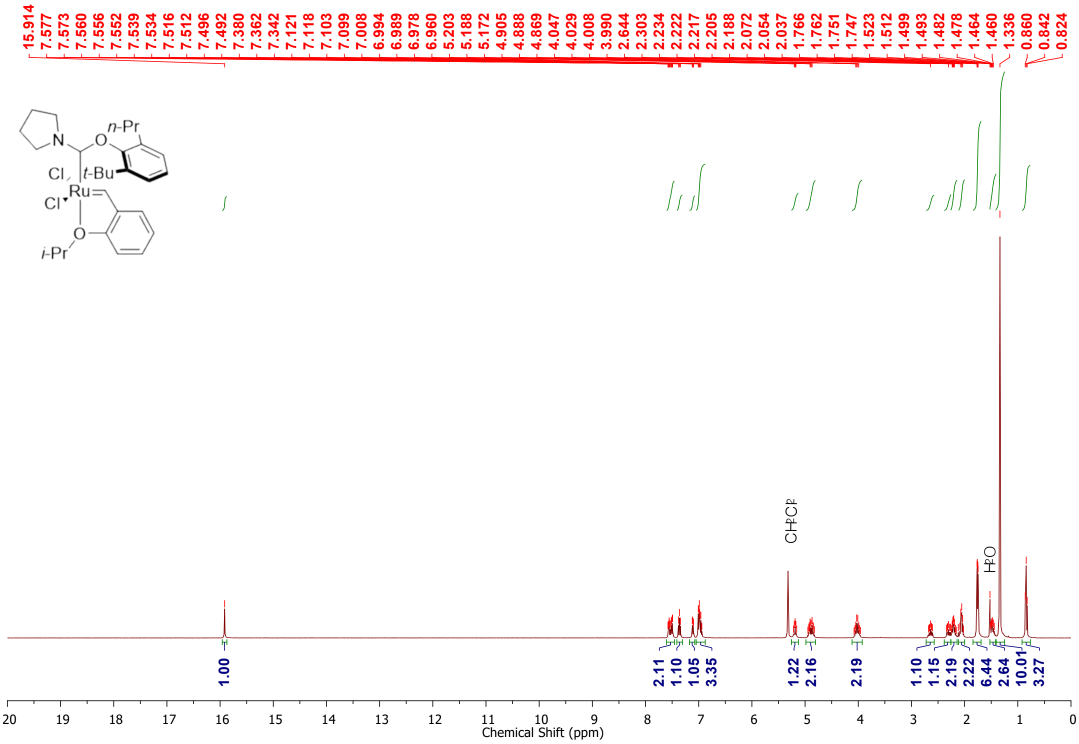

Figure S18. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **4d**, δ (ppm): 15.90 (1H, s, Ru=C*H*), 7.55-7.47 (2H, m, Ar*H*), 7.33 (1H, t, J = 7.6 Hz, Ar*H*), 7.09 (1H, dd, J = 7.4, 1.3 Hz, Ar*H*), 6.99-6.92 (3H, m, Ar*H*), 5.21-5.12 (1H, m, OC*H*), 4.92-4.80 (2H, m, NCH_2), 3.99 (2H, ddd, J = 27.9, 12.7, 7.2 Hz, NCH_2), 2.66-2.58 (1H, m, CH_2), 2.32-1.99 (5H, m, CH_2, CH_2 CH_2), 1.65-1.81 (6H, m, CH_3), 1.51-1.39 (2H, m, CH_2), 1.30 (9H, s, (CH_3)$_3$), 0.82 (3H, t, J = 7.2 Hz, CH_3)

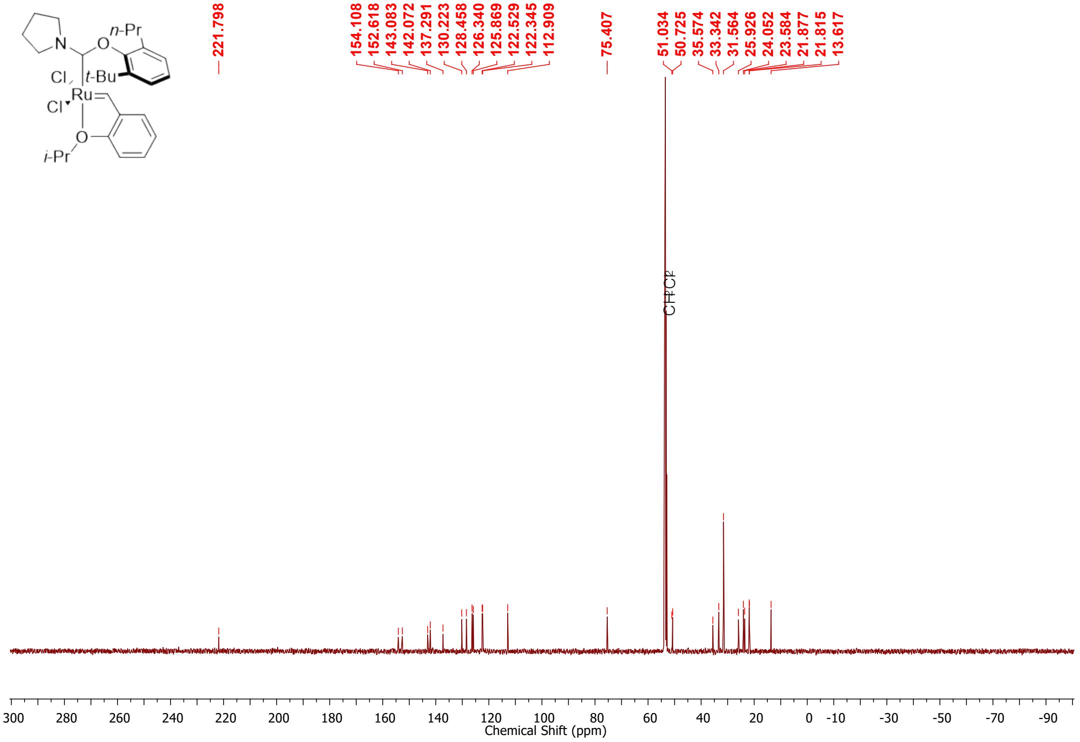

Figure S19. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **4d,** δ (ppm): 221.8, 154.1, 152.6, 143.1, 142.1, 137.3, 130.2, 128.5, 126.3, 125.9, 122.5, 122.4, 112.9, 75.4, 51.0, 50.7, 35.6, 33.3, 31.6, 25.9, 24.1, 23.6, 21.9, 21.8, 13.6.

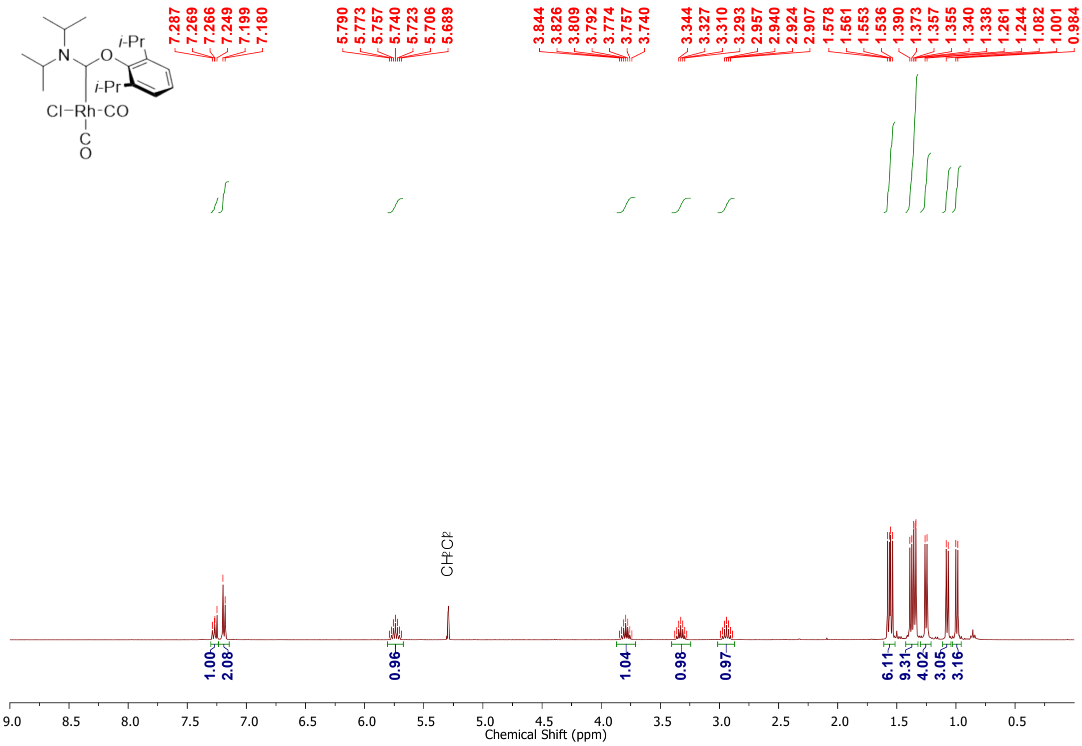

Figure S20. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **5a**, δ 7.19 (2H, d, J = 7.3 Hz, Ar*H*), 5.79-5.69 (1H, m, C*H*), 3.84-3.74 (1H, m, C*H*), 3.38-3.28 (1H, m, C*H*), 2.99-2.89 (1H, m, C*H*), 1.56 (6H, dd, J = 10.1, 6.9 Hz, C*H₃*), 1.36 (9H, q, J = 6.6 Hz, C*H₃*), 1.25 (3H, d, J = 6.9 Hz, C*H₃*), 1.07 (3H, d, J = 6.9 Hz, C*H₃*), 0.99 (3H, d, J = 6.9 Hz, C*H₃*).

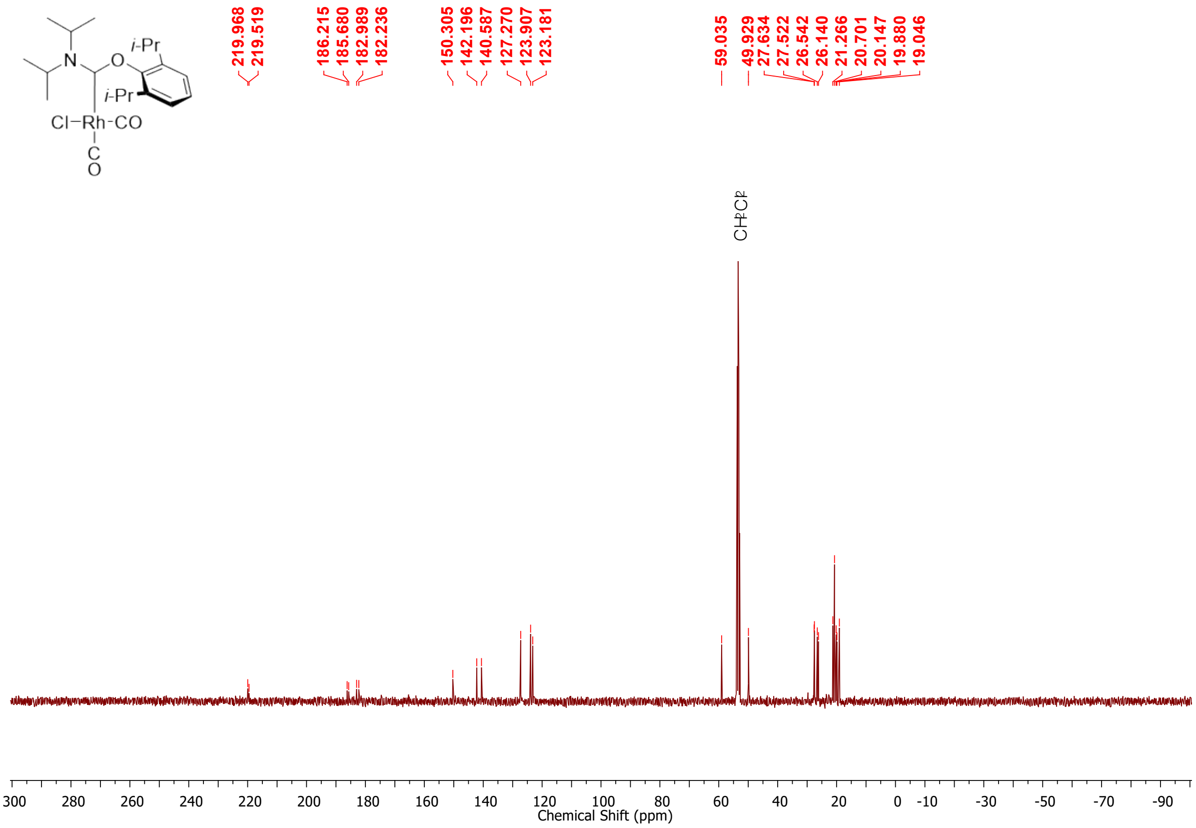

Figure S21. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **5a**, δ 219.7, 186.0, 182.6, 150.3, 142.2, 140.6, 127.3, 123.9, 123.2, 59.0, 49.9, 27.6, 26.5, 26.1, 21.3, 20.7, 20.2, 19.9, 19.0.

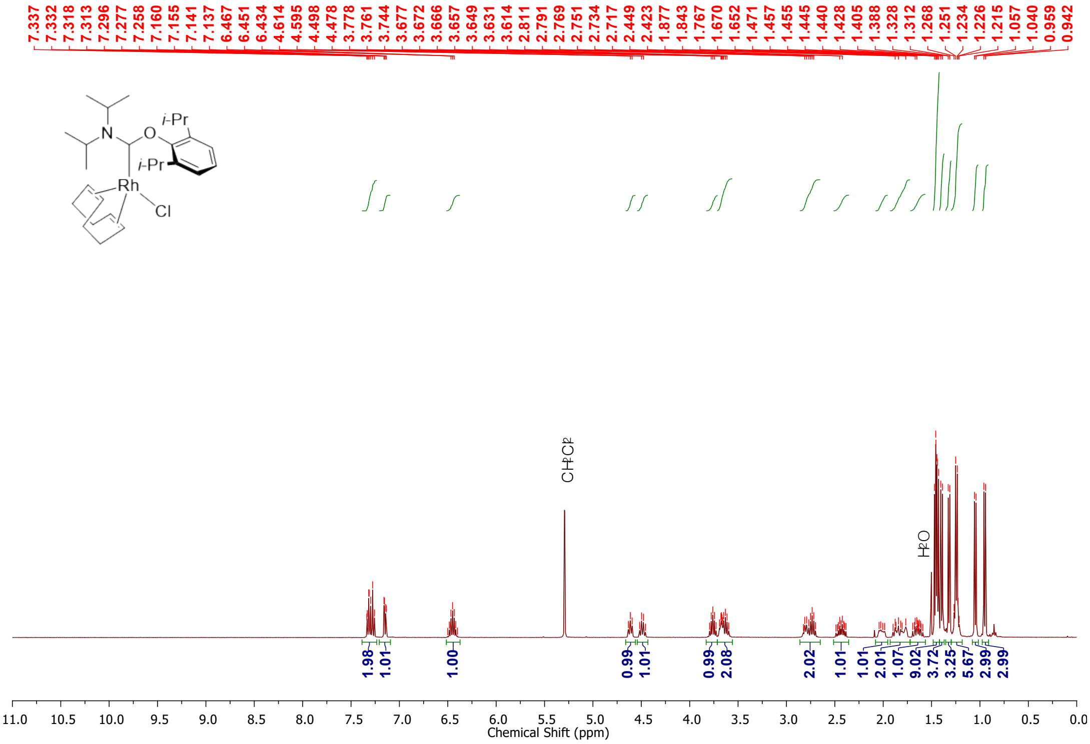

Figure S22. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **5c**, δ 7.34-7.26 (2H, m, Ar*H*), 7.15 (1H, dd, J = 7.2, 1.9 Hz, Ar*H*), 6.50-6.40 (1H, m, C*H*), 4.61 (1H, t, J = 7.6 Hz, C*H*), 4.49 (1H, q, J = 8.0 Hz, C*H*), 3.81-3.58 (3H, m, CH), 2.82-2.68 (2H, m, C*H₂*), 2.49-2.38 (1H, m, C*H*), 2.01 (1H, q, J = 7.6 Hz, C*H*), 1.90-1.77 (2H, m, C*H₂*), 1.70-1.59 (1H, m, C*H*), 1.50-1.39 (12H, m, C*H₃*), 1.32 (3H, d, J = 6.5 Hz, C*H₃*), 1.24 (6H, d, J = 6.9 Hz, C*H₃*), 1.05 (3H, d, J = 6.9 Hz, C*H₃*), 0.95 (3H, d, J = 6.9 Hz, C*H₃*).

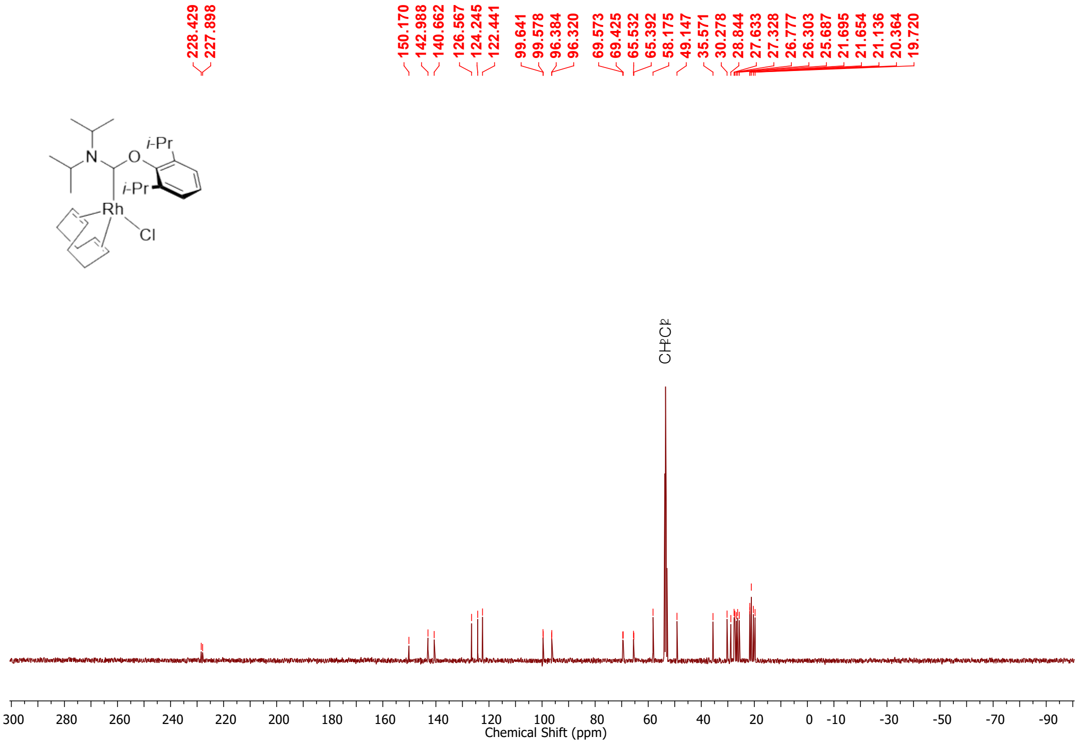

Figure S23. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **5c**, δ 228.4, 150.2, 143.0, 140.7, 126.6, 124.2, 122.4, 99.6, 96.4, 69.5, 65.5, 58.2, 49.2, 35.6, 30.3, 28.8, 27.6, 27.3, 26.8, 26.3, 25.7, 21.7, 21.1, 20.4, 19.7.

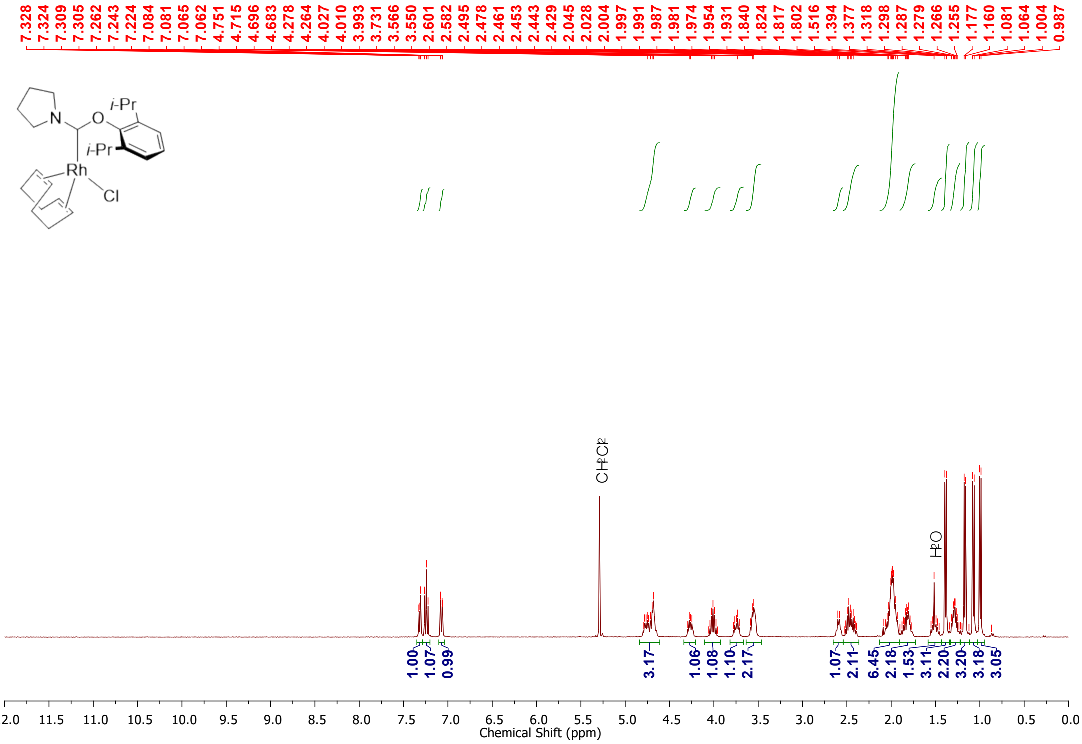

Figure S24. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **5d**, δ 7.32 (1H, dd, J = 7.7, 1.4 Hz, Ar*H*), 7.24 (1H, t, J = 7.6 Hz, Ar*H*), 7.07 (1H, dd, J = 7.6, 1.4 Hz, Ar*H*), 4.74 (3H, m, C*H*, C*H*$_2$), 4.27 (1H, J = 12.1, 6.5 Hz, C*H*), 4.10 – 3.93 (1H, m, C*H*), 3.75 (1H, m, C*H*), 3.64 – 3.46 (2H, m, C*H*$_2$), 2.59 (1H, m, C*H*$_2$), 2.54 – 2.36 (2H, m, C*H*$_2$), 2.13 – 1.91 (6H, m, C*H*$_2$), 1.90 – 1.73 (1H, m), 1.58 – 1.43 (3H, m, C*H*$_3$), 1.39 (3H, d, J = 6.7 Hz, C*H*$_3$), 1.33 – 1.22 (2H, m, C*H*$_2$), 1.22 – 1.12 (3H, d, J = 6.9 Hz, C*H*$_3$), 1.07 (3H, d, J = 6.8 Hz, C*H*$_3$), 1.00 (3H, d, J = 6.9 Hz, C*H*$_3$).

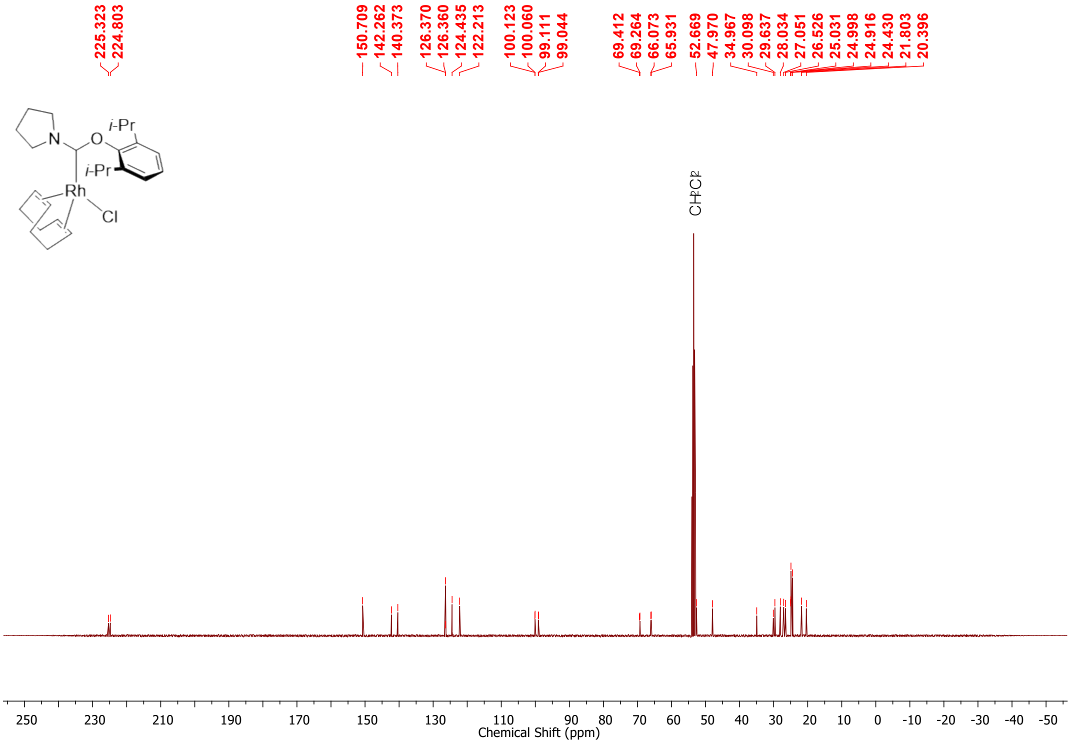

Figure S25. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **5d**, δ 225.0 (d), 150.7, 142.3, 140.4, 126.4, 124.4, 122.2, 100.1 (d, J = 6.4 Hz), 99.1 (d, J = 6.7 Hz), 69.3 (d, J = 14.9 Hz), 66.0 (d, J = 14.3 Hz), 52.7, 48.0, 35.0, 30.1, 29.6, 28.0, 27.1, 26.5, 25.0 (d, J = 3.4 Hz), 24.9, 21.8, 20.4.

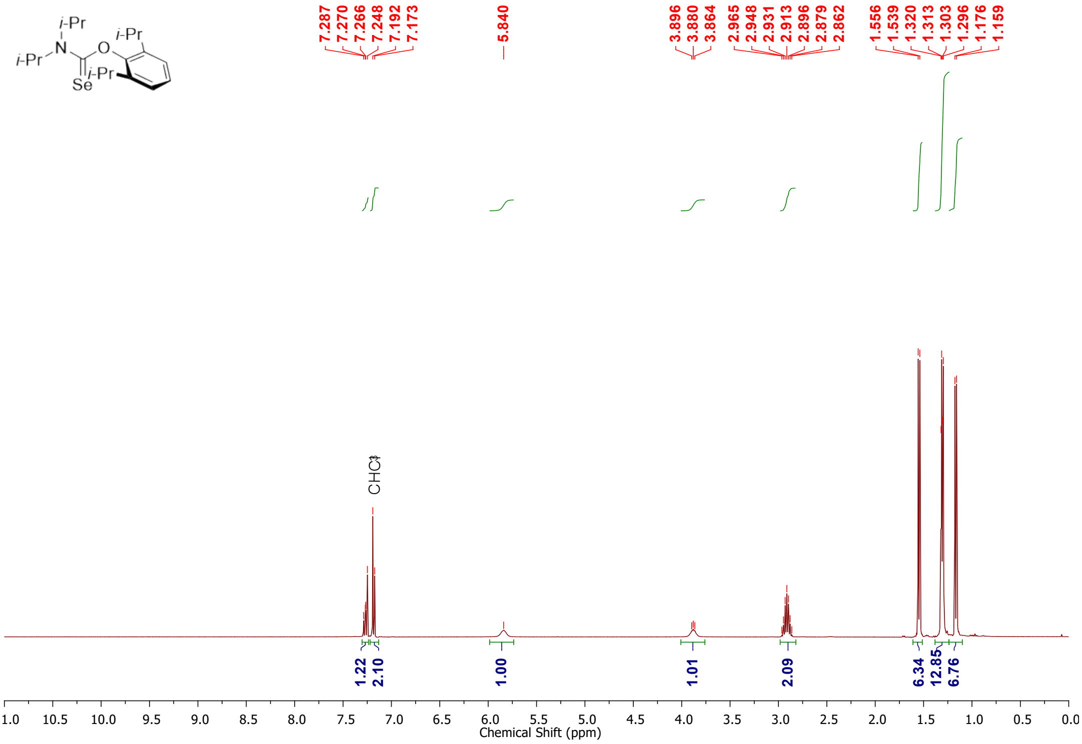

Figure S26. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **6a**, δ 7.27 (1H, dd, J = 8.6, 7.1 Hz, Ar*H*), 7.18 (2H, d, J = 7.6 Hz, Ar*H*), 5.84 (1H, m, C*H*), 3.88 (1H, m, C*H*), 2.96-2.86 (2H, m, C*H*), 1.56 (6H, t, J = 6.7 Hz, C*H$_3$*), 1.31 (12H, dd, J = 6.7, 2.5 Hz, C*H$_3$*), 1.17 (6H, d, J = 6.9 Hz, C*H$_3$*)

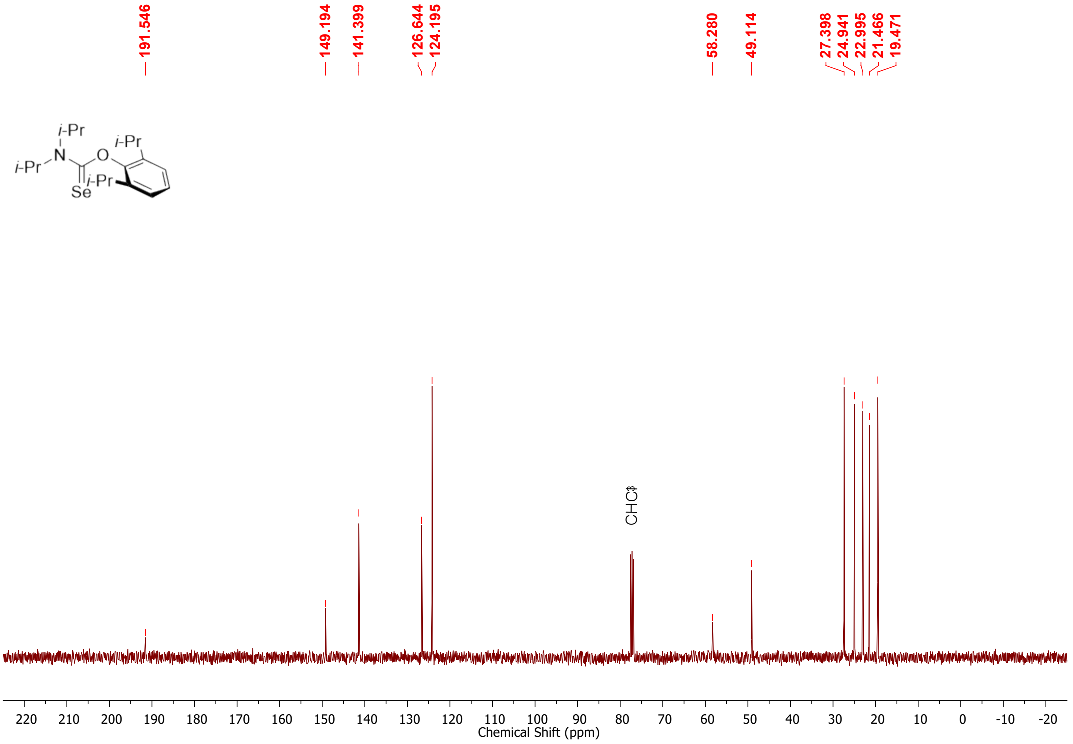

Figure S27. ^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **6a**, δ 191.6, 149.2, 141.4, 126.6, 124.2, 58.4, 49.1, 27.4, 24.9, 23.0, 21.5, 19.5

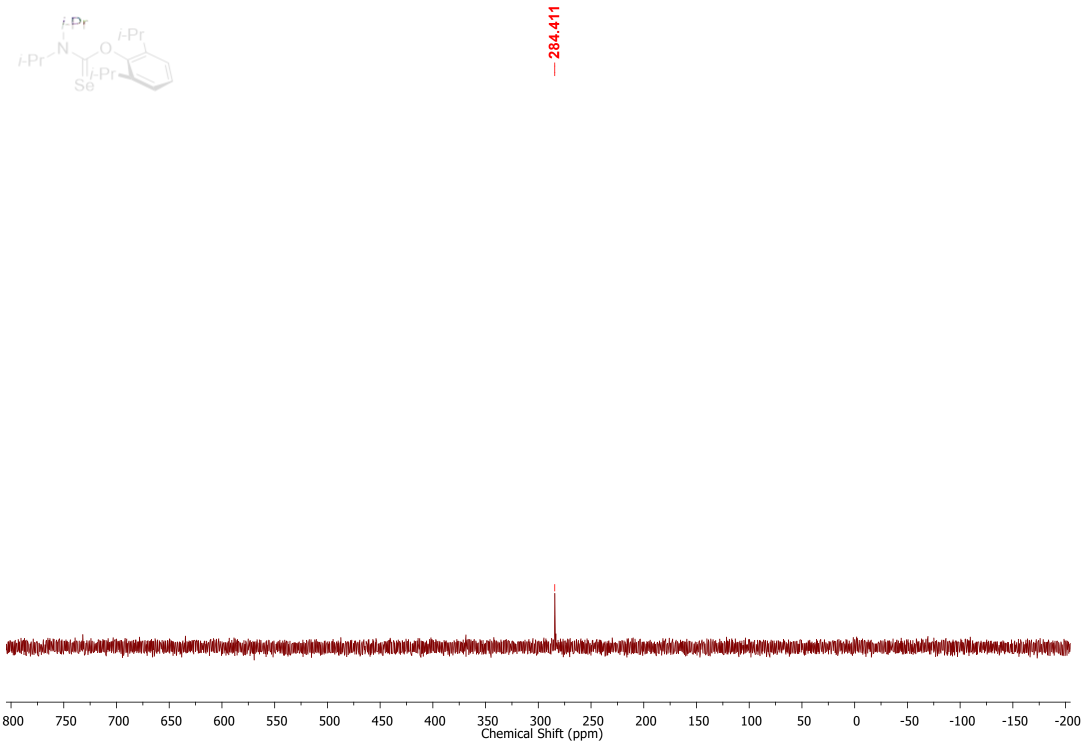

Figure S28. ^{77}Se NMR (76 MHz, CDCl$_3$) spectrum of **6a**, δ 284.4

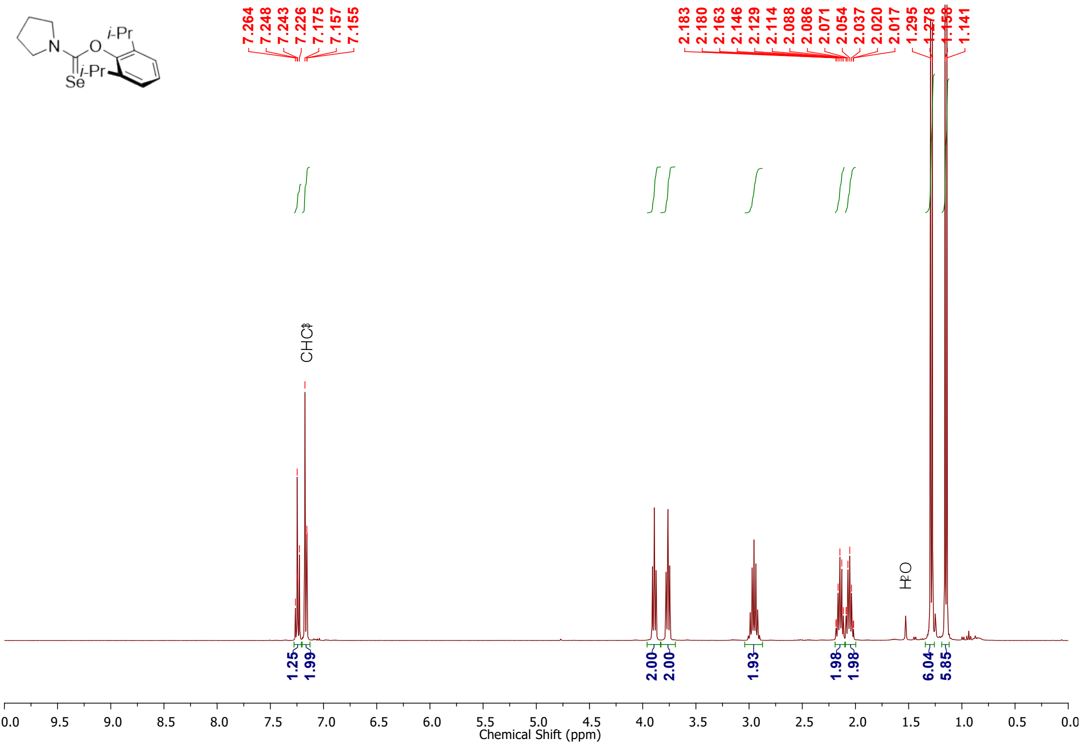

Figure S29. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **6c**, δ 7.25 (2H, dd, J = 8.5, 6.7 Hz, Ar*H*), 7.20 – 7.13 (3H, m, Ar*H*), 3.89 (2H, t, J = 6.9 Hz, C*H*$_2$), 3.76 (2H, t, J = 6.9 Hz, C*H*$_2$), 2.95 (2H, hept, J = 6.9 Hz, C*H*), 2.19 – 2.10 (3H, m, C*H*), 2.09 – 2.00 (3H, m, C*H*$_2$), 1.29 (6H, d, J = 6.9 Hz, C*H*$_3$), 1.15 (6H, d, J = 6.9 Hz, C*H*$_3$)

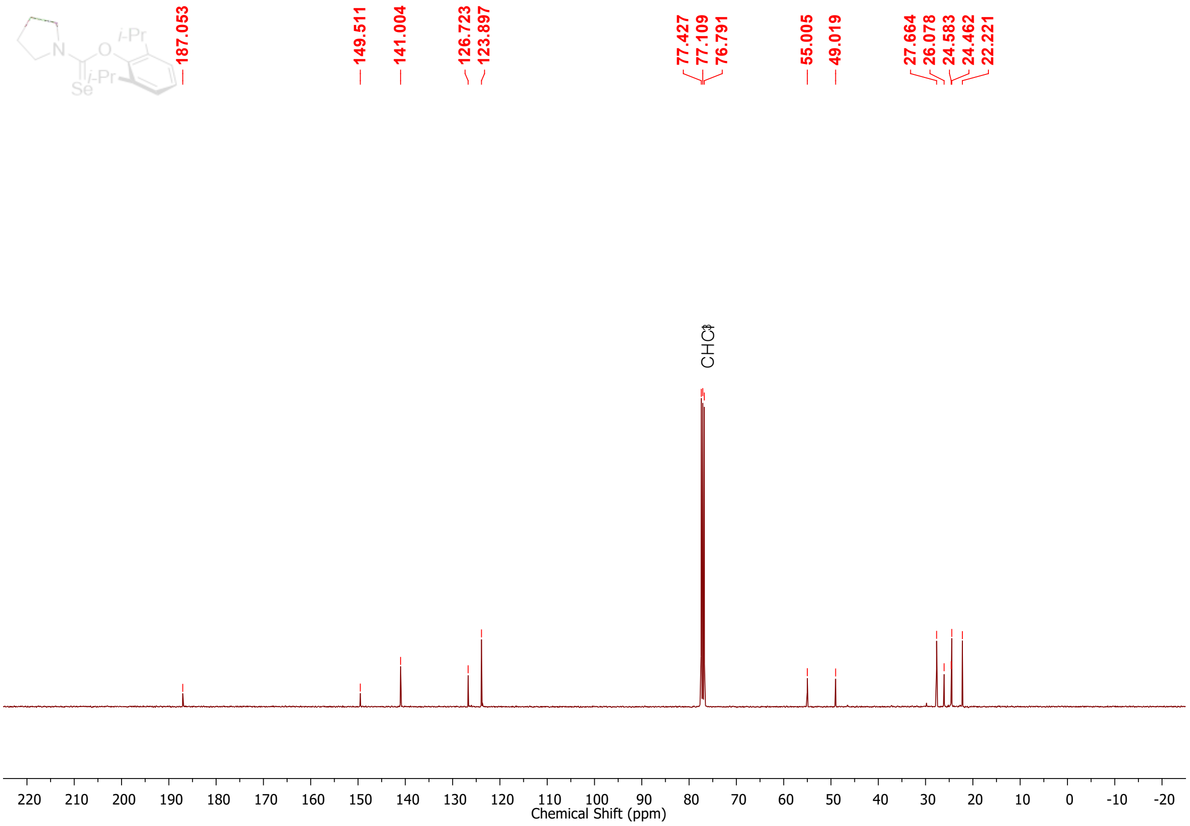

Figure S30. ^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **6b**, δ 187.1, 149.5, 141.0, 126.7, 123.9, 77.4, 77.1, 76.8, 55.0, 49.0, 27.7, 26.1, 24.6, 24.5, 22.2

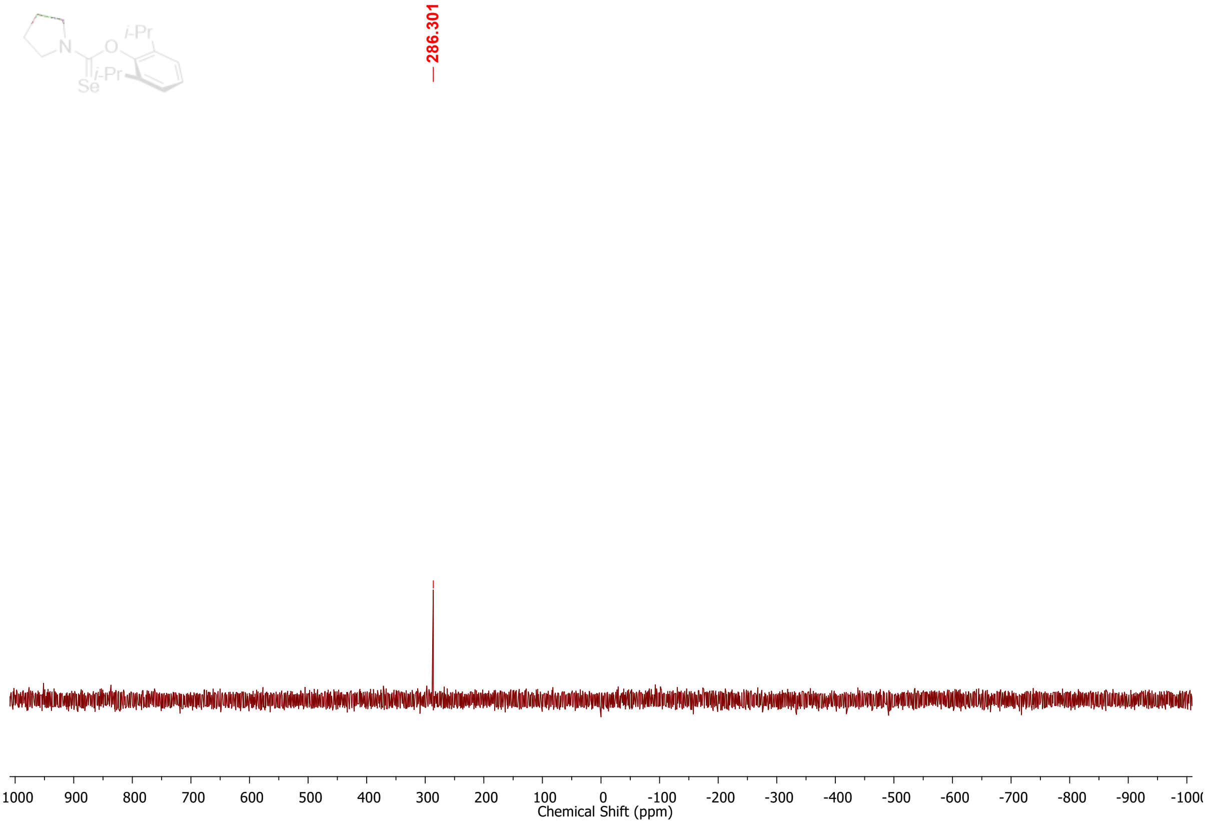

Figure S31. ^{77}Se NMR (76 MHz, CDCl$_3$) spectrum of **6b**, δ 286.3

7. Computational Results

All DFT calculations were performed with the Gaussian 09 program.[4] All calculations were performed with the B3LYP functional and employing the def2-TZVPP basis set.[5] The ground states were fully optimized without constraints at the corresponding level of theory, were uniquely characterized by the occurrence of no imaginary frequencies, and were verified by the corresponding frequency calculation. The Gibbs free reaction energies and enthalpies were calculated for standard conditions (*p* = 1 atm, *T* = 298 K) and were unscaled.

Cartesian coordinates of optimized geometries

NHC-5 (singlet)

C	-0.76723	-1.23413	0.00002
C	0.767227	-1.23413	-0.00002
C	0	1.012022	0
N	-1.07266	0.207683	-2.1E-05
H	-1.19032	-1.72188	-0.88221
H	1.190322	-1.72188	0.882209
N	1.072662	0.207682	0.000021
C	-2.43892	0.663045	-3E-06
H	-2.97691	0.307601	-0.88522
H	-2.97688	0.307642	0.88525
H	-2.43681	1.749239	-2.7E-05
C	2.438922	0.663045	0.000003
H	2.976908	0.307602	0.885219
H	2.976875	0.30764	-0.88525
H	2.436811	1.749239	0.000026
H	1.190272	-1.72182	-0.88231
H	-1.19027	-1.72182	0.882312
C	-0.76723	-1.23413	0.00002
C	0.767227	-1.23413	-0.00002
C	0	1.012022	0
N	-1.07266	0.207683	-2.1E-05
H	-1.19032	-1.72188	-0.88221
H	1.190322	-1.72188	0.882209

NHC-5 (triplet)

C	-0.77714	-1.20085	0.000129
C	0.777136	-1.20085	-0.00013
C	0	0.987618	0
N	-1.1447	0.19888	-0.00032
H	-1.17168	-1.72059	-0.88415
H	1.171682	-1.72059	0.884145
N	1.144703	0.19888	0.000321
C	-2.49706	0.652568	-0.00013
H	-3.04837	0.309189	-0.88671
H	-3.04807	0.309464	0.886755
H	-2.5127	1.740904	-0.0003
C	2.497057	0.652567	0.000132
H	3.048371	0.30919	0.886714
H	3.048076	0.309462	-0.88675
H	2.512697	1.740903	0.000294
H	1.171389	-1.71998	-0.88491
H	-1.17139	-1.71998	0.884911
C	-0.77714	-1.20085	0.000129
C	0.777136	-1.20085	-0.00013
C	0	0.987618	0
N	-1.1447	0.19888	-0.00032
H	-1.17168	-1.72059	-0.88415
H	1.171682	-1.72059	0.884145

NHC-6 (singlet)

C	-0.54224	-1.70381	-0.20116
N	-1.23879	-0.56348	-0.06764
N	-1.24273	-2.84368	-0.0855
C	-0.55707	-4.10605	-0.29063
H	0.490435	-3.89476	-0.48158
H	-0.64447	-4.74908	0.591054
H	-0.97613	-4.64741	-1.14584
C	-0.54875	0.699548	-0.2531
H	-0.63405	1.329114	0.638465
H	0.498048	0.487637	-0.44722
H	-0.96582	1.255581	-1.09982
C	-2.68484	-2.94605	0.158725
H	-2.87546	-3.84115	0.755052
H	-3.21907	-3.0757	-0.79052
C	-3.18033	-1.7078	0.888962
H	-2.80234	-1.7166	1.913433
H	-4.26953	-1.7063	0.939623
C	-2.68049	-0.45987	0.178452
H	-3.2144	-0.31315	-0.76849
H	-2.86781	0.426286	0.789026

NHC-6 (triplet)

C	-0.78567	-1.70192	-0.36444
N	-1.1793	-0.50093	0.208258
N	-1.18427	-2.91055	0.187904
C	-0.55184	-4.10017	-0.35239
H	0.530508	-3.99429	-0.29312
H	-0.85016	-4.96394	0.241731
H	-0.82488	-4.28583	-1.40122
C	-0.54448	0.694753	-0.31587
H	-0.83914	1.550527	0.291501
H	0.537671	0.584979	-0.26032
H	-0.81913	0.896488	-1.3613
C	-2.65542	-2.9733	0.260051
H	-2.92802	-3.85952	0.837057
H	-3.08981	-3.07183	-0.74682
C	-3.17914	-1.70863	0.944257
H	-2.86782	-1.71851	1.990592
H	-4.27051	-1.70614	0.920599
C	-2.65038	-0.43428	0.282342
H	-3.08462	-0.3163	-0.72251
H	-2.91941	0.442676	0.874979

CAAC (singlet)

C	-0.61088	0.751801	-0.78237
C	-0.58862	-0.77912	-1.06174
C	0.479114	-1.35468	-0.14453
N	0.840899	-0.39689	0.662333
C	0.169168	0.955658	0.52982
C	1.207417	2.075294	0.422711
C	-0.74877	1.204284	1.733893
C	-0.23966	-1.08858	-2.52314
C	-1.92533	-1.45742	-0.70759
C	1.83799	-0.60312	1.708635
H	-0.11181	1.285407	-1.59256
H	-1.62287	1.151278	-0.71174
H	0.708039	3.018255	0.195574
H	1.92122	1.871018	-0.37617
H	1.758837	2.214081	1.353486
H	-1.49588	0.417478	1.832599
H	-1.27083	2.154373	1.61147
H	-0.18603	1.259323	2.666641
H	0.731012	-0.66988	-2.79447
H	-0.99052	-0.66635	-3.19595
H	-0.19465	-2.1653	-2.6858
H	-2.22157	-1.25995	0.323588
H	-1.84693	-2.53775	-0.8281
H	-2.71943	-1.09164	-1.36275
H	1.424609	-0.37545	2.692208
H	2.711032	0.029948	1.545817
H	2.135781	-1.6455	1.674128

CAAC (triplet)

C	-0.55461	0.723166	-0.7825

C	-0.6717	-0.82612	-1.02711
C	0.299915	-1.28684	0.009489
N	1.079766	-0.29387	0.56592
C	0.263773	0.958261	0.518987
C	1.171049	2.181765	0.395485
C	-0.64947	1.093505	1.746308
C	-0.24148	-1.18776	-2.46253
C	-2.09644	-1.35148	-0.78181
C	1.910804	-0.59843	1.710793
H	-0.02567	1.1743	-1.62221
H	-1.53709	1.191286	-0.71979
H	0.570292	3.076456	0.221668
H	1.864602	2.064125	-0.43695
H	1.748977	2.349795	1.305685
H	-1.27022	0.206185	1.869954
H	-1.30554	1.958734	1.638775
H	-0.06848	1.231785	2.65952
H	0.776926	-0.85146	-2.65731
H	-0.90491	-0.72478	-3.19847
H	-0.27584	-2.26794	-2.61179
H	-2.46149	-1.07038	0.205541
H	-2.11798	-2.44033	-0.84716
H	-2.78849	-0.95654	-1.52997
H	1.333195	-0.84892	2.610837
H	2.560635	0.246133	1.935925
H	2.540809	-1.45406	1.468708

AAOC1 (singlet)

C	0.354458	0.720869	-0.27674
C	-1.94202	0.300665	-0.45326
H	-2.39406	-0.13246	-1.346
H	-2.52082	0.004768	0.422448
H	-1.90994	1.385666	-0.53399
C	2.73432	1.044619	-0.08533
H	3.413858	0.575432	0.632404
N	1.544682	0.155474	-0.14037
C	3.432911	1.09578	-1.44667
H	4.352753	1.678845	-1.38141
H	3.694386	0.100378	-1.8077
H	2.778623	1.565025	-2.18274
C	2.421272	2.443859	0.43041
H	1.907631	2.40387	1.389921
H	3.359574	2.987902	0.558081
H	1.784722	2.990448	-0.26072
O	-0.61606	-0.20995	-0.32133
C	1.85507	-1.30558	-0.06401
H	2.944814	-1.34973	-0.04453
C	1.354025	-1.92174	1.244516
H	0.267399	-1.92807	1.285584
H	1.708353	-2.9509	1.328454
H	1.728059	-1.36542	2.104844
C	1.404381	-2.09364	-1.29676
H	1.838649	-3.09474	-1.26123
H	0.323256	-2.18966	-1.34061
H	1.742791	-1.61156	-2.214

AAOC1 (triplet)

C	0.389153	0.303578	-0.78659
C	-1.8932	0.85381	-0.64419
H	-2.67287	0.921319	0.111073
H	-1.7585	1.827315	-1.12212
H	-2.17828	0.122021	-1.40399
C	2.637579	0.932907	-0.01031
H	3.357054	0.423551	0.636656
N	1.589604	-0.07214	-0.31238
C	3.363598	1.376044	-1.28381
H	4.179864	2.060851	-1.04697
H	3.783859	0.522484	-1.81756
H	2.667699	1.885218	-1.95189
C	2.067571	2.119159	0.760213
H	1.57039	1.792372	1.672796
H	2.869258	2.809428	1.027248
H	1.34034	2.661446	0.155326
O	-0.70796	0.451113	0.03014
C	2.017244	-1.49457	-0.26967
H	3.080894	-1.50607	-0.52587

C	1.85454	-2.05199	1.148654
H	0.8017	-2.05633	1.433598
H	2.233324	-3.07455	1.207184
H	2.398964	-1.4497	1.876925
C	1.280597	-2.34899	-1.29473
H	1.671911	-3.3672	-1.26953
H	0.212894	-2.38864	-1.07944
H	1.405849	-1.95229	-2.30152

AAOC2 (singlet)

C	-0.06355	0.581814	0.677613
C	-2.21098	0.677036	-0.26282
H	-2.5653	1.556248	-0.8014
H	-2.68761	-0.21308	-0.67429
H	-2.43591	0.768362	0.798176
O	-0.80022	0.567045	-0.44896
C	1.791131	0.416441	-1.01083
C	2.267541	0.485307	1.375653
C	3.302177	0.308039	-0.77406
H	1.523317	1.321916	-1.55761
H	1.377938	-0.42938	-1.55828
C	3.505625	0.944728	0.608507
H	2.410315	-0.52532	1.769738
H	1.980328	1.133094	2.199214
H	3.604358	-0.7408	-0.74668
H	3.878941	0.795015	-1.55924
H	4.433668	0.638114	1.088687
H	3.5121	2.033722	0.526655
N	1.212507	0.482707	0.353256

AAOC2 (triplet)

C	-0.07027	0.959466	0.086116
C	-2.3576	0.431104	-0.05108
H	-2.98437	-0.44085	-0.22337
H	-2.58372	0.859638	0.928307
H	-2.54976	1.181593	-0.82175
O	-1.01077	-0.02046	-0.10801
C	2.072983	0.897954	-1.16709
C	2.080306	0.431676	1.226968
C	3.445676	0.36972	-0.75344
H	2.116094	1.959881	-1.42982
H	1.638432	0.360339	-2.01014
C	3.509601	0.692261	0.746934
H	1.946034	-0.60784	1.543544
H	1.7785	1.074838	2.053049
H	3.492508	-0.71025	-0.90623
H	4.256472	0.823704	-1.32202
H	4.245528	0.092419	1.280726
H	3.767743	1.74321	0.892331
N	1.243004	0.702607	0.038304

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