Disentangling Ligand Effects on Metathesis Catalyst Activity: Experimental and Computational Studies of Ruthenium–Aminophosphine Complexes

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Supporting Information

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I. General Information

Solvents were dried by passing through an activated alumina column (*n*-pentane, benzene, toluene, Et_2O, and THF). Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. C_6D_6 was purified by passage through a solvent purification column. Ethyl vinyl ether was degassed with argon or nitrogen gas prior to use. Amines were distilled prior to use. Catalyst **G2** was obtained from Materia, Inc. The bispyridine complex **G3** was synthesized according to literature procedure.[1] All reactions were carried out in dry glassware under a nitrogen atmosphere unless otherwise indicated.

NMR spectra were measured with Varian 500 MHz, Varian 400 MHz, and Bruker 400 MHz spectrometers. High-resolution mass spectra (HRMS) were provided by the

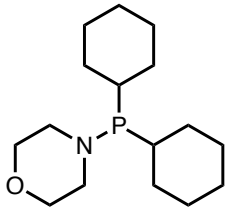
California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer.

SEC data were collected using two Agilent PLgel MIXED-B 300 × 7.5 mm columns with 10 μm beads, connected to an Agilent 1260 Series pump, a Wyatt 18-angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. The mobile phase was THF.

The crystallographic measurements were performed at 100(2) K using a Bruker APEX–II CCD area detector diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Semi-empirical absorption corrections were applied. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms.

II. Preparation of Aminosphosphine Ligands

Aminophosphine ligands were synthesized from the corresponding chlorocyclohexylphosphine or PCl_3 according to literature methods.[2] The yields have not been optimized.



4-(Dicyclohexylphosphanyl)morpholine (L1). To an Et_2O solution (50 mL) of Cy_2PCl (2.300 g, 9.883 mmol) under a nitrogen atmosphere was added freshly distilled morpholine (2.14 mL, 24.7 mmol) dropwise at ambient temperature. The mixture immediately became cloudy, and a white precipitate formed. After stirring at room temperature for one hour, the unwanted white solid was filtered off under inert atmosphere, and the filtrate was subjected to reduced pressures to remove all volatiles, affording **L1** as a colorless oil (2.52 g, 90%).

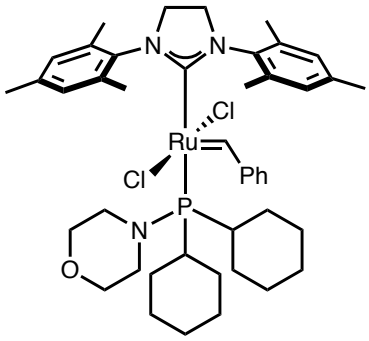
^{1}H NMR (300 MHz; C_6D_6): δ 3.42 (t, 4H, 4.8 Hz), 2.84 – 2.80 (m, 4H), 1.80 – 1.51 (m, 11H), 1.25 – 1.16 (m, 11H).

^{31}P{^{1}H} NMR (121 MHz; C_6D_6): δ 75.6 (s).

III. Preparation of Aminophosphine-Ligated Complexes

Note: Following the course of the reaction in THF, removal of volatiles occasionally resulted in some remaining bright green solid indicating unreacted **G3**. In this case, the residue was redissolved in 2 mL of THF and stirred for another 2 min, and the volatiles once again removed; this was repeated until there was no indication of unreacted **G3**.

The yields have not been optimized.



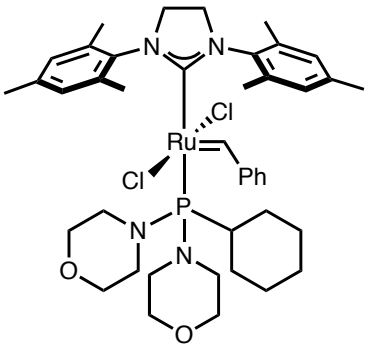
Catalyst 1. To a THF solution (2 mL) of the bispyridine complex **G3** (150 mg, 0.206 mmol), was added 2.5 equivalents (146 mg, 0.516 mmol) of the appropriate phosphine ligand, 4-(dicyclohexylphosphanyl)morpholine in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **1**, which was isolated by filtration through celite and dried under vacuum (129 mg, 73%). Dark brown crystals were obtained by slow Et_2O vapor diffusion into a THF solution of the title complex.

^{1}H NMR (500 MHz; C_7D_8): δ 19.51 (s, 1H), 9.14 (bs, 1H), 7.18 – 7.10 (m, 2H), 6.98 – 6.83 (m, 4H), 6.23 (bs, 2H), 3.61 – 3.17 (m, 9H), 2.76 (s, 6H), 2.65 – 2.25 (m, 10H), 2.21 (s, 3H), 1.79 (s, 3H), 1.70 – 1.39 (m, 11H), 1.23 – 0.98 (m, 8H), 0.76 (d, J = 12.5 Hz, 2H).

^{13}C NMR (101 MHz; C_6D_6): δ 296.25, 220.71 (d, $^2J_{C\text{-}P}$ = 84.8 Hz), 151.99, 139.39, 138.61, 137.63, 137.23, 135.59, 130.31, 129.39, 68.02, 52.11, 51.08, 49.37, 35.39 (d, $J_{C\text{-}P}$ = 19.6 Hz), 29.18, 28.74, 28.02, 27.93, 27.84, 27.72, 26.59, 21.23, 21.03, 20.57, 19.00.

^{31}P{^{1}H} NMR (162 MHz; C_6D_6): δ 92.4 (s).

MS (FAB) m/z (M^++H) calcd for $C_{44}H_{63}ON_3RuPCl_2$: 852.3130, found: 852.3153.



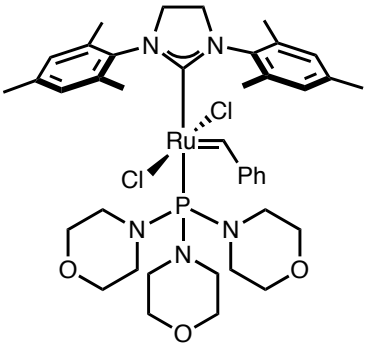
Catalyst 2. To a THF solution (2 mL) of the bispyridine complex **G3** (100 mg, 0.138 mmol), was added 1.2 equivalent (47 mg, 0.165 mmol) of the appropriate phosphine ligand, 4,4'-(cyclohexylphosphanediyl)dimorpholine in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **2**, which was isolated by filtration through celite and dried under vacuum (79 mg, 67%).

^{1}H NMR (400 MHz; C_6D_6): δ 19.40 (s, 1H), 8.17 (bs, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (s, 2H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.21 (bs, 2H), 3.50 – 3.21 (m, 12H), 3.09 (t, *J* = 12.3 Hz, 1H), 2.86 (bs, 9H), 2.66 – 2.40 (m, 13H), 1.79 (s, 3H), 1.67 – 1.51 (m, 6H), 1.17 – 1.10 (m, 2H), 0.99 (tt, *J* = 12.6 Hz, *J* = 3.5 Hz, 1H), 0.77 (q, *J* = 12.4 Hz, 2H).

^{13}C NMR (101 MHz; C_6D_6): δ 293.55, 221.10 (d, $^{2}J_{C\text{-}P}$ = 89.0 Hz), 151.59, 139.44, 139.26, 137.69, 137.49, 136.93, 135.03, 131.06, 130.55, 129.37, 67.64, 52.14, 50.97, 47.16, 37.38 (d, $J_{C\text{-}P}$ = 23.7 Hz), 27.66, 27.48, 27.36, 27.25, 21.23, 21.00, 20.63, 18.92.

^{31}P{^{1}H} NMR (161.8 MHz; C_6D_6): δ 131.9 (s).

MS (FAB) *m*/*z* (M^+) calcd for $C_{42}H_{59}O_2N_4RuPCl_2$: 854.2797, found: 854.2834.



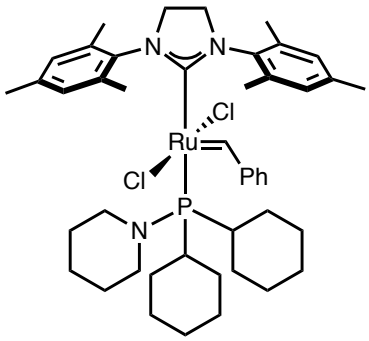
Catalyst 3. To a THF solution (2 mL) of the bispyridine complex **G3** (173 mg, 0.238 mmol), was added 1.2 equivalent (82 mg, 0.286 mmol) of the appropriate phosphine ligand, trimorpholinophosphane in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **3**, which was isolated by filtration through celite and dried under vacuum (157 mg, 77%).

^{1}H NMR (500 MHz; C_7D_8): δ 19.44 (s, 1H), 8.03 (s, 2H), 7.12 (s, 1H), 6.93 – 6.85 (m, 4H), 6.16 (s, 2H), 3.46 – 3.37 (m, 2H), 3.33 – 3.21 (m, 14H), 2.75 (s, 6H), 2.68 (q, J = 4.7 Hz, 12H), 2.35 (s, 6H), 2.28 (s, 3H), 1.77 (s, 3H).

^{13}C NMR (101 MHz; C_6D_6): δ 298.46, 219.58 (d, $^{2}J_{C\text{-}P}$ = 107.3 Hz), 151.81, 139.51, 139.07, 137.61, 137.52, 137.09, 135.33, 130.95, 130.24, 129.40, 128.80, 128.59, 67.60 (d, $J_{C\text{-}P}$ = 5.8 Hz), 51.90 (d, $J_{C\text{-}P}$ = 4.7 Hz), 50.91 (d, $J_{C\text{-}P}$ = 2.9 Hz), 46.86 (d, $J_{C\text{-}P}$ = 3.0 Hz), 21.14, 20.97, 20.65, 18.92.

^{31}P{^{1}H} NMR (162 MHz; C_6D_6): δ 116.7 (s).

MS (FAB) m/z (M^+) calcd for $C_{40}H_{56}O_3N_5RuPCl_2$: 857.2542, found: 857.2517.



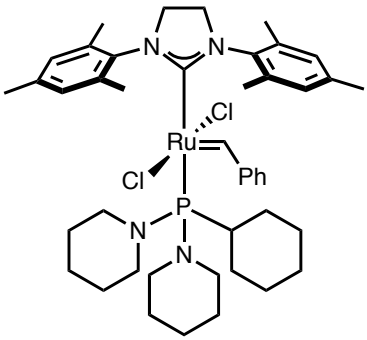
Catalyst 4. To a THF solution (2 mL) of the bispyridine complex **G3** (100 mg, 0.138 mmol), was added 1.2 equivalent (46.5 mg, 0.165 mmol) of the appropriate phosphine ligand, 1-(dicyclohexylphosphanyl)piperidine in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **4**, which was isolated by filtration through celite and dried under vacuum (93 mg, 80%). Dark brown crystals were obtained by slow Et_2O vapor diffusion into a benzene solution of the title complex.

^{1}H NMR (400 MHz; C_6D_6): δ 19.70 (s, 1H), 9.37 (bs, 1H), 7.19 – 7.12 (m, 2H), 7.06 – 6.89 (m, 4H), 6.80 – 5.56 (m, 2H), 3.50 – 3.14 (m, 5H), 3.08 – 2.75 (m, 7H), 2.73 – 2.55 (m, 7H), 2.21 (s, 3H), 1.82 (s, 3H), 1.79 – 1.04 (m, 26H), 0.95 – 0.77 (m, 2H).

^{13}C NMR (101 MHz; C_6D_6): δ 296.05, 221.10 (d, $^{2}J_{C\text{-}P}$ = 83.5 Hz), 152.07, 139.43, 138.29, 137.75, 137.54, 137.27, 135.87, 130.29, 129.39, 52.19, 51.10, 50.31, 35.88 (d, $J_{C\text{-}P}$ = 19.9 Hz), 29.31, 28.86, 28.12, 28.03, 27.94, 27.81, 27.45, 27.40, 26.68, 25.18, 21.14 (d, $J_{C\text{-}P}$ = 18.0 Hz), 20.60, 19.07.

^{31}P{^{1}H} NMR (161.8 MHz; C_6D_6): δ 92.1 (s).

MS (FAB) m/z (M^+) calcd for $C_{45}H_{64}N_3RuPCl_2$: 849.3259, found: 849.3267.



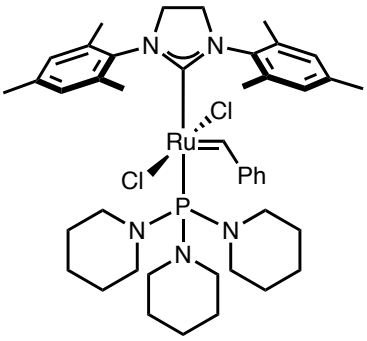
Catalyst 5. To a THF solution (2 mL) of the bispyridine complex **G3** (130 mg, 0.179 mmol), was added 4.2 equivalent (210 mg, 0.744 mmol) of the appropriate phosphine ligand, 1,1'-(cyclohexylphosphanediyl)dipiperidine in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **5**, which was isolated by filtration through celite and dried under vacuum (82 mg, 54%). Dark brown crystals were obtained by slow Et_2O vapor diffusion into a THF solution of the title complex.

^{1}H NMR (400 MHz; C_6D_6): δ 19.47 (s, 1H), 8.46 (bs, 1H), 7.19 – 7.13 (m, 2H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.94 (s, 2H), 6.77 – 5.44 (m, 2H), 3.44 – 3.17 (m, 4H), 3.04 – 2.75 (m, 11H), 2.75 – 2.56 (s, 6H), 2.22 (s, 3H), 1.82 (s, 3H), 1.69 – 1.50 (m, 5H), 1.41 (s, 11H), 1.28 (s, 7H), 1.08 – 0.75 (m, 3H).

^{13}C NMR (101 MHz; C_6D_6): δ 291.90, 222.33 (d, $^2J_{C\text{-}P}$ = 87.8 Hz), 151.79, 139.65, 138.08, 137.96, 137.35, 136.97, 135.91, 131.17, 130.35, 129.36, 52.34, 52.30, 50.97, 47.68, 38.15 (d, $J_{C\text{-}P}$ = 23.9 Hz), 27.80, 27.63, 27.50, 27.16, 27.11, 25.77, 25.22, 21.12 (d, $J_{C\text{-}P}$ = 12.9 Hz), 20.64, 19.07.

^{31}P{^{1}H} NMR (161.8 MHz; C_6D_6): δ 133.0 (s).

MS (FAB) *m/z* (M^+) calcd for $C_{44}H_{63}N_4RuPCl_2$: 850.3211, found: 850.3212.



Catalyst 6. To a THF solution (2 mL) of the bispyridine complex **G3** (100 mg, 0.138 mmol), was added 1.5 equivalent (58.7 mg, 0.207 mmol) of the appropriate phosphine ligand, tri(piperidin-1-yl)phosphane in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **6**, which was isolated by filtration through celite and dried under vacuum (92 mg, 78%). Dark

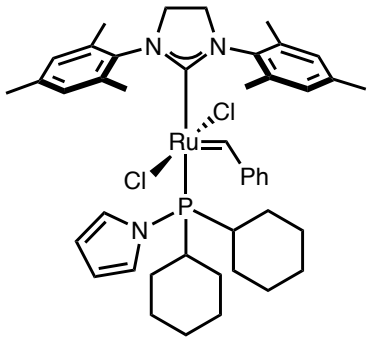
brown crystals were obtained by slow pentane vapor diffusion into a THF solution of the title complex.

^{1}H NMR (400 MHz; C_6D_6): δ 19.70 (s, 1H), 8.30 (bs, 2H), 7.21 – 7.17 (m, 1H), 7.04 – 6.98 (m, 2H), 6.93 (s, 2H), 6.25 (s, 2H), 3.43 – 3.16 (m, 4H), 2.86 (s, 6H), 2.85 – 2.77 (m, 12H), 2.48 (s, 6H), 2.22 (s, 3H), 1.82 (s, 3H), 1.48 – 1.34 (m, 6H), 1.29 (m, 12H).

^{13}C NMR (101 MHz; C_6D_6): δ 296.09, 221.30 (d, $^{2}J_{C\text{-}P}$ = 105.2 Hz), 152.12, 139.67, 138.04, 137.89, 137.38, 137.17, 136.04, 131.22, 130.18, 129.37, 52.07 (d, $J_{C\text{-}P}$ = 4.9 Hz), 50.94, 47.19 (d, $J_{C\text{-}P}$ = 4.4 Hz), 27.08 (d, $J_{C\text{-}P}$ = 4.6 Hz), 25.70, 21.09 (d, $J_{C\text{-}P}$ = 10.4 Hz), 20.72, 19.10.

^{31}P{^{1}H} NMR (161.8 MHz; C_6D_6): δ 118.7 (s).

MS (FAB) *m/z* (M^+) calcd for $C_{43}H_{62}N_5RuPCl_2$: 851.3164, found: 851.3178.



Catalyst 7. To a THF solution (2 mL) of the bispyridine complex **G3** (100 mg, 0.138 mmol), was added 2.0 equivalent (73 mg, 0.275 mmol) of the appropriate phosphine ligand, 1-(dicyclohexylphosphanyl)-1*H*-pyrrole in THF (1 mL). The resulting mixture was stirred at room temperature for 20 min. All volatiles were then removed under reduced pressure. Addition of pentane led to the formation of a pink precipitate of the desired complex, **7**, which was isolated by filtration through celite and dried under vacuum (110 mg, 96%). Dark brown crystals were obtained by slow pentane vapor diffusion into a THF solution of the title complex.

^{1}H NMR (400 MHz; C_6D_6): δ 19.82 (s, 1H), 8.24 (bs, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.94 – 6.90 (m, 4H), 6.74 (q, *J* = 2.2 Hz, 2H), 6.21 (s, 4H), 3.36 (dt, *J* = 2.3 Hz, *J* = 10.6 Hz, 2H), 3.23 (dt, *J* = 2.3 Hz, *J* = 10.6 Hz, 2H), 2.81 (s, 6H), 2.44 (s, 6H), 2.19 (s, 3H), 1.80 (s, 3H), 1.63 (d, *J* = 10.8 Hz, 2H), 1.54 (d, *J* = 11.0 Hz, 2H), 1.46 – 1.35 (m, 6H), 1.27 (qt, *J* = 12.7 Hz, *J* = 3.4 Hz, 2H), 1.12 – 0.91 (m, 6H), 0.52 (qt, *J* = 12.7 Hz, *J* = 3.4 Hz, 2H).

^{13}C NMR (101 MHz; C_6D_6): δ 301.30, 219.39 (d, $^{2}J_{C\text{-}P}$ = 89.9 Hz), 151.99, 139.40, 138.57, 137.86, 137.37, 137.25, 135.47, 131.50, 130.28, 129.44, 128.97, 128.59, 125.32 (d, $J_{C\text{-}P}$ = 2.8 Hz), 110.26 (d, $J_{C\text{-}P}$ = 4.6 Hz), 52.09 (d, $J_{C\text{-}P}$ = 4.1 Hz), 51.11 (d, $J_{C\text{-}P}$ = 2.1 Hz), 35.81 (d, $J_{C\text{-}P}$ = 18.6 Hz), 28.30 (d, $J_{C\text{-}P}$ = 4.3 Hz), 27.85 (d, $J_{C\text{-}P}$ = 2.8 Hz), 27.53, 27.44, 27.40, 27.27, 25.99, 21.25, 21.01, 20.58, 18.95.

^{31}P{^{1}H} NMR (162 MHz; C_6D_6): δ 92.3 (s).

MS (FAB) *m/z* (M^+) calcd for $C_{44}H_{58}N_3RuPCl_2$: 831.2789, found: 831.2761.

IV. Initiation Rate Studies

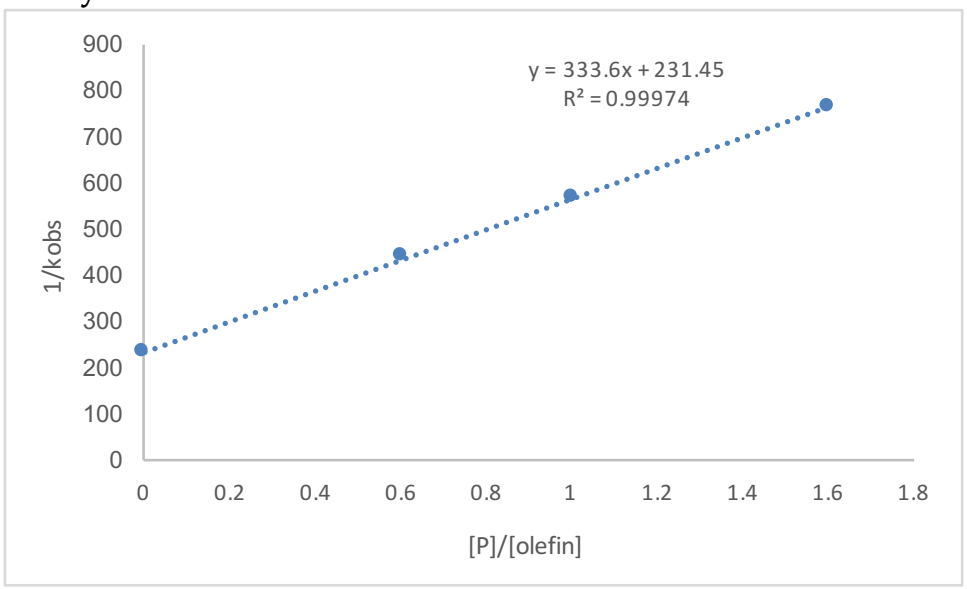
In a nitrogen-filled glovebox, the ruthenium benzylidene complex was dissolved in toluene-d_8 (600 μL, 0.017 M) in an NMR tube fitted with a septum cap. The sealed NMR tube was relocated near the NMR spectrometer. To this NMR tube was injected neat ethyl vinyl ether (30 equiv.) using a glass syringe under inert atmosphere. The tube was inverted twice and immediately loaded into a 500 MHz ^{1}H NMR spectrometer pre-warmed to 30 °C, at which point the first-order depletion of the benzylidene Ru=C*H*Ph signal was monitored. Plotting $\ln([Ru]_0/[Ru]_t)$ vs. time provided the initiation rate constant.

V. Estimation of k_{-1}/k_2

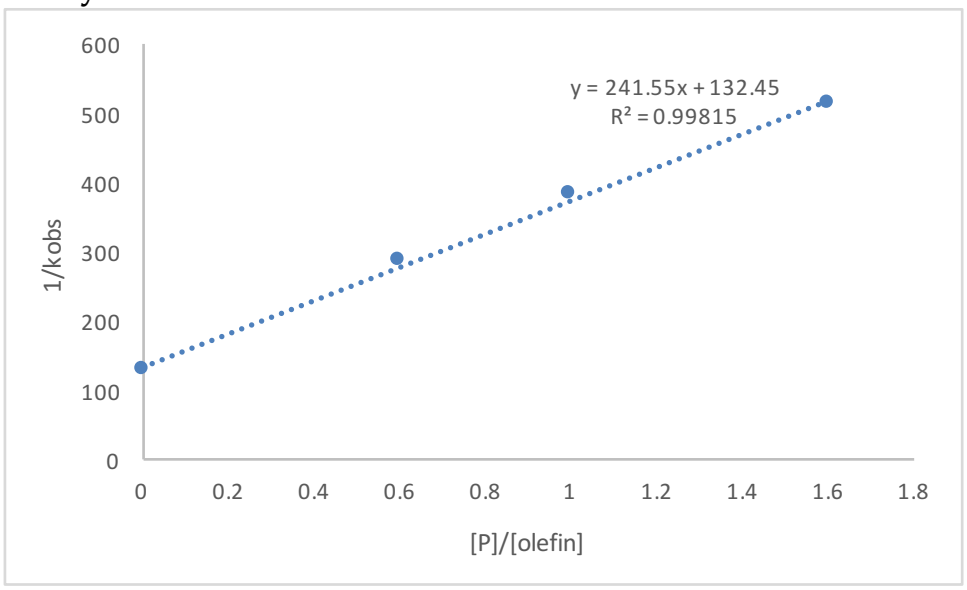
In a nitrogen-filled glovebox, a solution of toluene-d_8 (600 μL) containing the ruthenium benzylidene complex (0.017 M) and free aminophosphine ([P]/[ethyl vinyl ether] = 0.6, 1.0, 1.6; mass of phosphine calculated based upon 15 μL ethyl vinyl ether) was added to an NMR tube fitted with a septum cap. The sealed NMR tube was relocated near the NMR spectrometer. To this NMR tube was injected neat ethyl vinyl ether (15 μL) using a glass syringe under inert atmosphere. The tube was inverted twice and immediately loaded into a 500 MHz ^{1}H NMR spectrometer pre-warmed to 30 °C, at which point the first-order depletion of the benzylidene Ru=C*H*Ph signal was monitored. In order to determine k_{obs}, the data from each array with a specific [P]/[ethyl vinyl ether] ratio were analyzed in the same way as described above in the initiation rate studies. Due to poor solubility of the aminophosphine in toluene, the experiment for catalyst **3** and ligand **L3** was performed with $[Ru]_0$ = 0.005 M and 4.4 μL ethyl vinyl ether.

The values of $1/k_{obs}$ were plotted vs. [P]/[ethyl vinyl ether], including the data from initiation rate studies where [P]/[olefin] = 0. The graph for each catalyst is shown below. The ratio of k_{-1}/k_2 was calculated by dividing the slope of the line of best fit by the y-intercept.

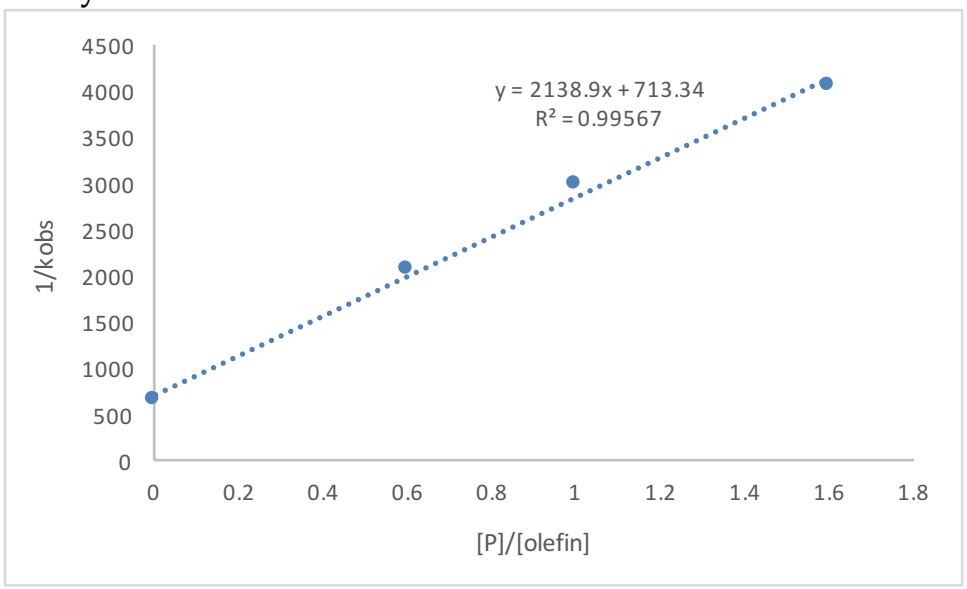
Catalyst 1



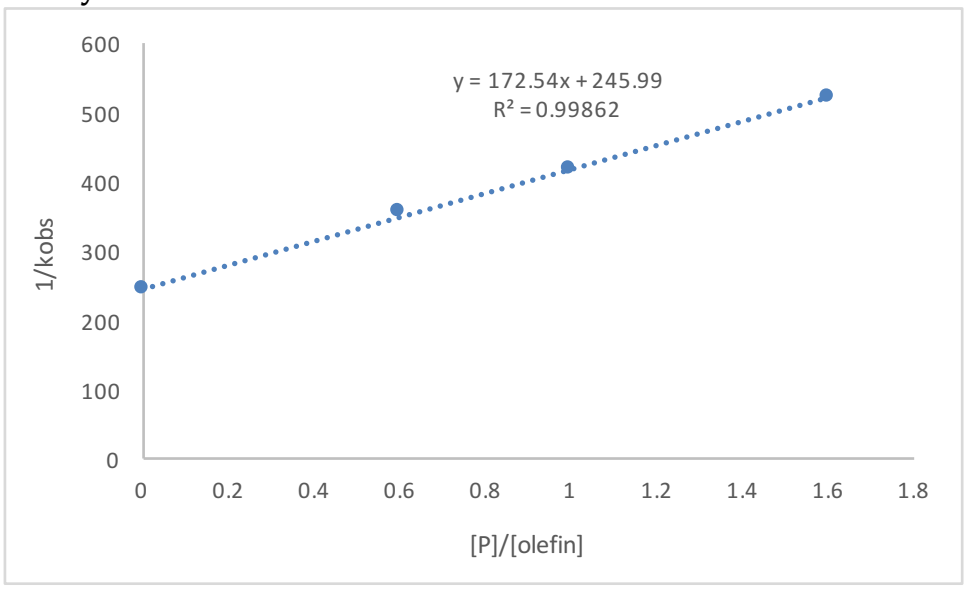
Catalyst 2



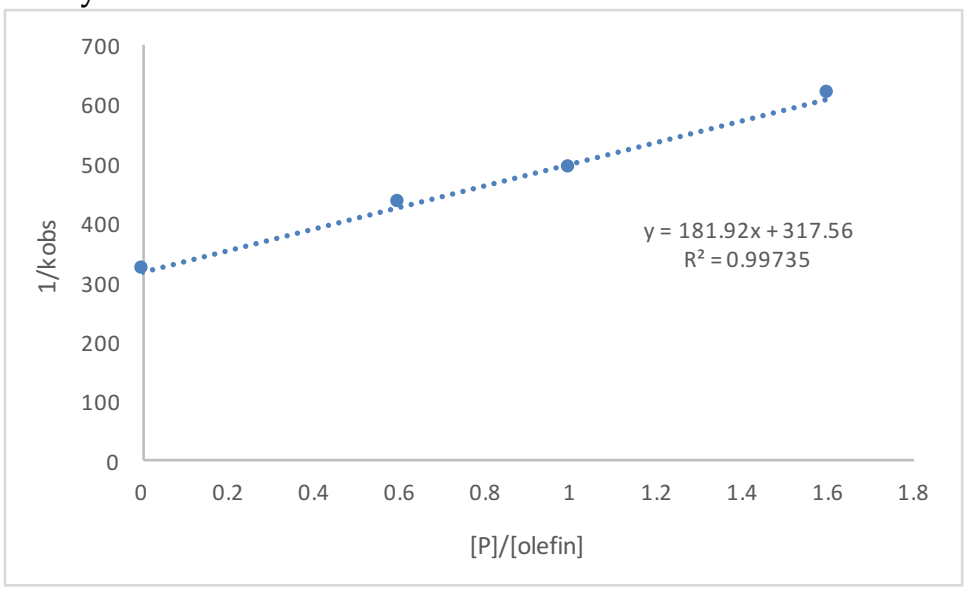
Catalyst 3



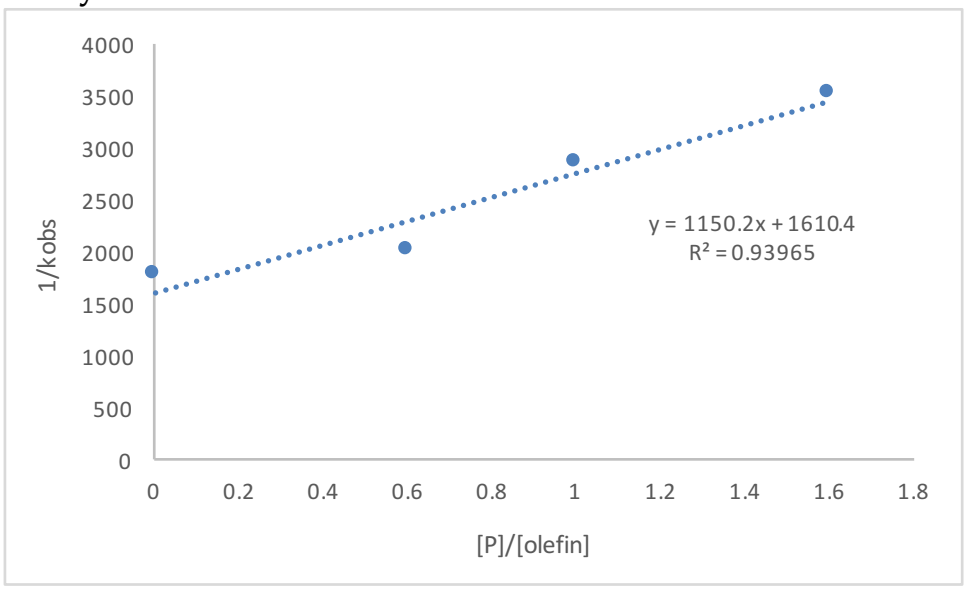
Catalyst 4



Catalyst 5



Catalyst 6



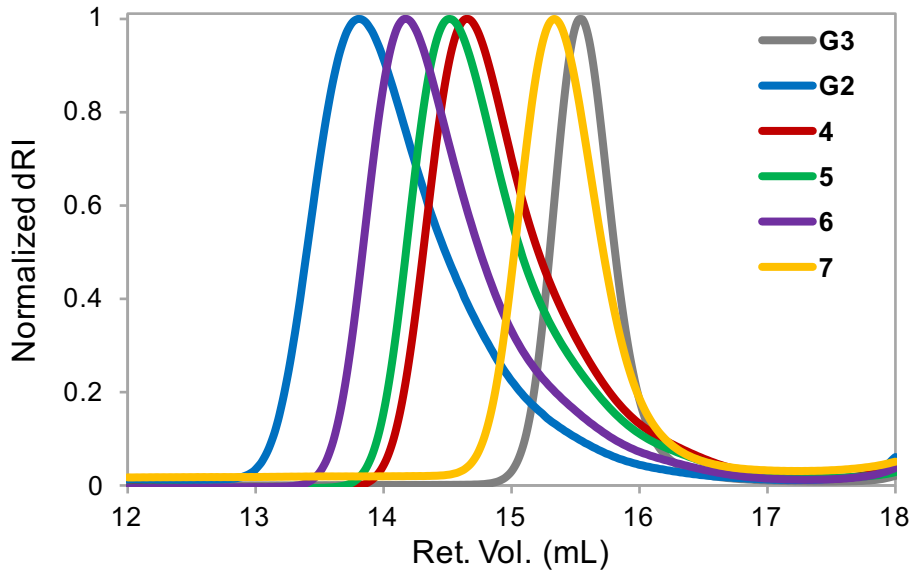
VI. Evaluation of Selected Catalysts in ROMP

In an argon-filled glovebox, a solution of **8** (21.0 mg, 0.100 mmol) was prepared in 2 mL of dichloromethane at 298 K. While stirring, the polymerization was initiated by addition of a CH_2Cl_2 solution of catalyst (0.0500 M, 20.0 μL, 0.100 μmol). During the course of the reaction, aliquots (~50 μL) were extracted and quenched in separate vials containing a large excess of ethyl vinyl ether (0.1 mL) in THF (0.9 mL). The quenched reaction mixtures were analyzed by SEC and ^{1}H NMR spectroscopy to determine norbornene conversion, molecular weight (M_n), and dispersity ($Đ$).

Table S.1. Molecular Weights and Dispersities of Polymers 9.

Catalyst	M_n (kDa)	*Đ*
G2	96.1	1.50
G3	23.1	1.02
4	46.3	1.17
5	55.2	1.22
6	70.1	1.41
7	25.9	1.03

SEC Traces for ROMP Studies



VII. X-Ray Crystallography Methods[3]

Table S.2. Crystal Data and Structure Analysis Details for Catalyst 4.
(Structure shown in Figure 3)

Empirical formula	C100 H144 Cl4 N6 O P2 Ru2	
Formula weight	1852.08	
Crystal shape	block	
Crystal color	brown	
Crystal size	0.050 x 0.080 x 0.100 mm^3	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å	
Data collection temperature	100(2) K	
Theta range for 9838 reflections used in lattice determination	4.655 to 65.411°	
Unit cell dimensions	a = 12.5478(5) Å	α = 90°
	b = 14.1495(6) Å	β = 92.828(2)°
	c = 26.7547(11) Å	γ = 90°
Volume	4744.4(3) $Å^3$	
Z	2	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.296 g/cm^3	
F(000)	1960	
Theta range for data collection	1.6 to 37.7º	
Completeness to theta = 25.242°	100.0%	
Index ranges	$-21 \le h \le 21$, $-24 \le k \le 23$, $-45 \le l \le 45$	
Reflections collected	180275	
Independent reflections	24676 [R_{int}= 0.0782]	
Reflections > 2s(I)	17555	
Average s(I)/(net I)	0.0619	
Absorption coefficient	0.51 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6876 and 0.6876	
Structure Solution and Refinement		
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	24676 / 17 / 520
Treatment of hydrogen atoms	constr
Goodness-of-fit on F^2	1.07
Final R indices [I>2s(I), 17555 reflections]	R1 = 0.0561, *w*R2 = 0.1214
R indices (all data)	R1 = 0.0959, *w*R2 = 0.1363
Type of weighting scheme used	calc
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	2.49 and -1.63 e/Å^{-3}

Programs Used

Structure refinement	SHELXL-2013 (Sheldrick, 2013)

Table S.3. Crystal Data and Structure Analysis Details for Catalyst 5.
(Structure shown in Figure 4)

Empirical formula	C100 H152 Cl4 N8 O3 P2 Ru2 Si0	
Formula weight	1920.17	
Crystal shape	block	
Crystal color	brown	
Crystal size	0.020 x 0.150 x 0.150 mm^3	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å	
Data collection temperature	100(2) K	
Theta range for 9872 reflections used in lattice determination	4.877 to 60.270°	
Unit cell dimensions	a = 12.582(4) Å	α = 90°
	b = 14.694(4) Å	β = 102.711(9)°
	c = 26.929(9) Å	γ = 90°
Volume	4856(3) $Å^3$	
Z	2	
Crystal system	monoclinic	
Space group	P $2_1/n$	
Density (calculated)	1.313 g/cm^3	
F(000)	2036	
Theta range for data collection	2.1 to 31.3º	
Completeness to theta = 25.242°	99.9%	
Index ranges	$-18 \le h \le 17$, $-21 \le k \le 21$, $-39 \le l \le 39$	
Reflections collected	109331	
Independent reflections	14689 [R_{int}= 0.0561]	
Reflections > 2s(I)	10910	
Average s(I)/(net I)	0.0580	
Absorption coefficient	0.51 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9533	
Structure Solution and Refinement		
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14689 / 2 / 538	
Treatment of hydrogen atoms	constr	

Goodness-of-fit on F^2	1.04
Final R indices [I>2s(I), 10910 reflections]	R1 = 0.0645, *w*R2 = 0.1465
R indices (all data)	R1 = 0.1013, *w*R2 = 0.1643
Type of weighting scheme used	calc
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	2.26 and -1.25 e/$Å^{-3}$

Programs Used

Structure refinement	SHELXL-2013 (Sheldrick, 2013)

Table S.4. Crystal Data and Structure Analysis Details for Catalyst 6.
(Structure shown in Figure 5)

Empirical formula	C43 H62 Cl2 N5 P Ru	
Formula weight	851.91	
Crystal shape	block	
Crystal color	brown	
Crystal size	0.030 x 0.120 x 0.140 mm^3	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å	
Data collection temperature	100(2) K	
Theta range for 9656 reflections used in lattice determination	5.207 to 62.321°	
Unit cell dimensions	a = 12.685(4) Å	α = 90°
	b = 14.502(4) Å	β = 99.043(12)°
	c = 22.983(7) Å	γ = 90°
Volume	4176(2) $Å^3$	
Z	4	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.355 g/cm^3	
F(000)	1792	
Theta range for data collection	2.3 to 33.6º	
Completeness to theta = 25.000°	99.9%	
Index ranges	$-18 \le h \le 19$, $-22 \le k \le 22$, $-34 \le l \le 30$	
Reflections collected	100488	
Independent reflections	15279 [R_{int}= 0.0733]	
Reflections > 2s(I)	10188	
Average s(I)/(net I)	0.0882	
Absorption coefficient	0.58 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9954 and 0.9389	
Structure Solution and Refinement		
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15279 / 138 / 704	
Treatment of hydrogen atoms	constr	

Goodness-of-fit on F^2	1.16
Final R indices [I>2s(I), 10188 reflections]	R1 = 0.0820, *w*R2 = 0.1464
R indices (all data)	R1 = 0.1400, *w*R2 = 0.1609
Type of weighting scheme used	calc
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	1.13 and -1.50 e/$Å^{-3}$

Programs Used

Structure refinement SHELXL-2013 (Sheldrick, 2013)

Table S.5. Crystal Data and Structure Analysis Details for Catalyst 7.
(Structure shown in Figure 2)

Empirical formula	C44 H58 Cl2 N3 P Ru	
Formula weight	831.87	
Crystal shape	block	
Crystal color	brown	
Crystal size	0.050 x 0.090 x 0.100 mm^3	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å	
Data collection temperature	100(2) K	
Theta range for 9838 reflections used in lattice determination	4.655 to 65.411°	
Unit cell dimensions	a = 12.1351(9) Å	α = 90°
	b = 14.8021(10) Å	β = 98.642(3)°
	c = 22.944(2) Å	γ = 90°
Volume	4074.6(6) $Å^3$	
Z	4	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.356 g/cm^3	
F(000)	1744	
Theta range for data collection	2.2 to 33.2º	
Completeness to theta = 25.242°	99.9%	
Index ranges	$-17 \le h \le 18$, $-21 \le k \le 22$, $-34 \le l \le 34$	
Reflections collected	125473	
Independent reflections	14290 [R_{int}= 0.1065]	
Reflections > 2s(I)	9560	
Average s(I)/(net I)	0.1029	
Absorption coefficient	0.59 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7466 and 0.7034	
Structure Solution and Refinement		
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14290 / 0 / 460	
Treatment of hydrogen atoms	constr	

Goodness-of-fit on F^2	1.08
Final R indices [I>2s(I), 9560 reflections]	R1 = 0.0641, *w*R2 = 0.1225
R indices (all data)	R1 = 0.1239, *w*R2 = 0.1426
Type of weighting scheme used	calc
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	2.73 and -0.90 e/$Å^{-3}$

Programs Used

Structure refinement SHELXL-2013 (Sheldrick, 2013)

VIII. Computational Methods

Geometry optimizations of complexes **G2**, **1-3**, and the phosphine ligands were performed using M06[4], with the def2SVP basis set.[5] Single point energies were calculated using M06 with the def2TZVP basis set. Solvation effects were considered by performing single point calculations with the SMD model in toluene.[6] All calculations were performed with Gaussian 09.[7] The reported Gibbs free energies and enthalpies include zero-point vibrational energies and thermal corrections at 298K. The quasiharmonic approximation from Cramer and Truhlar[8] was applied to compute the vibrational entropies. In the quasiharmonic approximation, vibrational frequencies lower than 100 cm^{-1} were raised to 100 cm^{-1} as a way to avoid spurious results associated with the harmonic-oscillator model for very low-frequency vibrations.[9]

Tolman electronic parameters[10] were calculated with model complex $Ni(CO)_3L$ using B3LYP[11] and a mixed basis set of LANL2DZ for Ni and 6-31G(d) for other atoms.[12] The computed A_1 stretch frequency was reported with a scaling factor of 0.962.

To reduce computational cost, structures in the reaction coordinates (Figure 12) were optimized using B3LYP and a mixed basis set of SDD for Ru and 6-31G(d) for other atoms. Single point energies were performed using M06 and a mixed basis set of SDD for Ru and 6-311+G(d,p) for other atoms.

IX. Cartesian Coordinates of Optimized Catalyst Structures

Catalyst G2

M06/def2SVP SCF energy: -3255.08587815 a.u.
M06/def2SVP enthalpy: -3254.017016 a.u.
M06/def2SVP free energy: -3254.155540 a.u.
M06/def2TZVP SCF energy in solution: -3257.59943330 a.u.
M06/def2TZVP enthalpy in solution: -3256.530571 a.u.
M06/def2TZVP free energy in solution: -3256.669095 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.038148	-0.408366	0.132840
Cl	-0.213729	-0.507936	-2.285132
Cl	-0.231280	-0.403305	2.557522
P	-0.986221	1.836871	0.114061
C	0.380184	-2.437817	0.230718
N	1.551204	-3.088272	0.421064
C	1.376149	-4.526015	0.644494
H	1.577486	-4.776237	1.702450

H	2.084268	-5.103039	0.026807
C	-0.077672	-4.742833	0.263934
H	-0.194256	-5.229434	-0.723783
H	-0.641591	-5.342697	0.997545
N	-0.595783	-3.374924	0.207179
C	2.871890	-2.553387	0.397649
C	3.514260	-2.406607	-0.846332
C	4.829297	-1.945430	-0.857841
H	5.333476	-1.806486	-1.822661
C	5.514097	-1.640284	0.321465
C	4.852599	-1.817294	1.537073
H	5.378448	-1.587634	2.471967
C	3.534748	-2.279254	1.603792
C	2.798838	-2.719584	-2.121807
H	3.472181	-2.614803	-2.985376
H	1.932706	-2.051006	-2.282435
H	2.401762	-3.750619	-2.129804
C	6.918214	-1.125760	0.265453
H	6.958048	-0.149457	-0.248528
H	7.574999	-1.807548	-0.299804
H	7.347839	-0.996483	1.270266
C	2.852661	-2.460728	2.923196
H	1.840065	-2.020027	2.924325
H	3.431983	-1.990436	3.731580
H	2.747437	-3.529172	3.183344
C	-1.970880	-3.182983	-0.128384
C	-2.371046	-3.261631	-1.472250
C	-3.735386	-3.146493	-1.761440
H	-4.054921	-3.189175	-2.809865
C	-4.694609	-3.017151	-0.759934
C	-4.264021	-2.999082	0.571504
H	-5.009353	-2.936399	1.374625
C	-2.915285	-3.084805	0.913783
C	-1.411327	-3.559734	-2.580776
H	-0.372012	-3.316379	-2.321472
H	-1.660888	-2.982306	-3.483341
H	-1.466014	-4.630480	-2.850739
C	-6.153130	-2.927080	-1.084776
H	-6.590040	-1.985066	-0.710217
H	-6.719831	-3.745901	-0.610777

H	-6.332856	-2.974797	-2.169227
C	-2.491392	-3.123493	2.346458
H	-3.365141	-3.132302	3.014596
H	-1.855130	-2.260201	2.609860
H	-1.891539	-4.024670	2.562790
C	1.749880	0.168527	0.393850
H	2.083276	0.096119	1.451763
C	2.790121	0.789687	-0.429594
C	2.779402	0.878098	-1.834164
H	1.930227	0.459937	-2.383213
C	3.824252	1.496923	-2.509422
H	3.803024	1.550398	-3.602189
C	4.886934	2.067723	-1.806214
H	5.697022	2.568684	-2.345149
C	4.907675	2.003328	-0.414004
H	5.732422	2.454029	0.146723
C	3.879146	1.356673	0.262138
H	3.901469	1.290438	1.355705
C	-0.662635	2.843765	-1.429871
H	-0.527457	2.043742	-2.187183
C	-1.777494	3.768651	-1.922216
H	-2.731392	3.223909	-2.026893
H	-1.953825	4.572021	-1.179149
C	-1.410181	4.392002	-3.265151
H	-1.344832	3.587230	-4.023159
H	-2.216630	5.066983	-3.600859
C	-0.080023	5.127451	-3.207394
H	0.174751	5.547743	-4.195633
H	-0.171292	5.989974	-2.517401
C	1.021949	4.207038	-2.706110
H	1.986012	4.741195	-2.640147
H	1.172479	3.382974	-3.431449
C	0.657718	3.614716	-1.352207
H	0.559114	4.441507	-0.621488
H	1.473537	2.968753	-0.986866
C	-0.664566	2.873100	1.626401
H	-1.057569	2.193530	2.409259
C	0.805438	3.076476	1.989768
H	1.338494	2.113563	1.937589
H	1.294318	3.758366	1.269322

C	0.922797	3.661159	3.390731
H	0.521172	2.924759	4.114368
H	1.984281	3.808877	3.654842
C	0.153750	4.969262	3.510450
H	0.229115	5.377410	4.533211
H	0.617341	5.722602	2.842181
C	-1.303345	4.788321	3.112270
H	-1.847557	5.746957	3.171653
H	-1.796699	4.106322	3.833368
C	-1.430351	4.194274	1.714007
H	-1.022328	4.912108	0.974884
H	-2.497110	4.061271	1.460275
C	-2.843741	1.657771	0.153546
H	-3.243505	2.660155	-0.100445
C	-3.338509	0.672958	-0.907941
H	-2.880348	0.864793	-1.893982
H	-3.005748	-0.348873	-0.630968
C	-4.858329	0.700113	-0.994087
H	-5.183364	1.700432	-1.346459
H	-5.208286	-0.022978	-1.752706
C	-5.493820	0.403390	0.356620
H	-6.594391	0.477830	0.296322
H	-5.260090	-0.644154	0.627965
C	-4.953843	1.314002	1.447858
H	-5.383046	1.039802	2.427106
H	-5.276546	2.356855	1.252751
C	-3.431686	1.276419	1.513081
H	-3.078734	0.265551	1.798542
H	-3.084768	1.954161	2.311235

Catalyst 1

M06/def2SVP SCF energy: -3306.97822735 a.u.
M06/def2SVP enthalpy: -3305.945320 a.u.
M06/def2SVP free energy: -3306.085609 a.u.
M06/def2TZVP SCF energy in solution: -3309.55916664 a.u.
M06/def2TZVP enthalpy in solution: -3308.526259 a.u.
M06/def2TZVP free energy in solution: -3308.666548 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.076566	-0.384937	0.123572
Cl	-0.147991	-0.432361	-2.297369
Cl	-0.222979	-0.536396	2.533674
P	-1.026497	1.821851	0.108283
C	0.512922	-2.400132	0.151332
N	1.711015	-2.996542	0.349404
C	1.601307	-4.448470	0.517891
H	1.774523	-4.725142	1.574483
H	2.360249	-4.967147	-0.090721
C	0.175638	-4.723227	0.075389
H	0.119691	-5.171341	-0.935167
H	-0.380861	-5.383373	0.761131
N	-0.411970	-3.381888	0.060402
C	3.005382	-2.400059	0.364876
C	3.651795	-2.172113	-0.864672
C	4.943708	-1.650013	-0.843099
H	5.450257	-1.450952	-1.795986
C	5.603068	-1.362256	0.354946
C	4.940588	-1.622746	1.554968
H	5.446373	-1.409578	2.504655
C	3.646120	-2.149858	1.588479
C	2.963648	-2.467948	-2.158901
H	3.631714	-2.276427	-3.011635
H	2.056909	-1.848984	-2.291933
H	2.635953	-3.521449	-2.219062
C	6.979757	-0.776206	0.335416
H	6.967971	0.235979	-0.105208
H	7.666331	-1.381227	-0.279383
H	7.407046	-0.698684	1.346438
C	2.964794	-2.420273	2.892990
H	1.930362	-2.033148	2.902843
H	3.513611	-1.954942	3.725276
H	2.913725	-3.502327	3.109290
C	-1.798683	-3.250286	-0.258021
C	-2.203199	-3.314799	-1.604059
C	-3.571187	-3.256799	-1.885569
H	-3.892806	-3.287114	-2.933623
C	-4.532311	-3.196115	-0.877534

C	-4.096669	-3.191018	0.449860
H	-4.839663	-3.181187	1.257658
C	-2.742605	-3.220342	0.788073
C	-1.234489	-3.527022	-2.725485
H	-0.238033	-3.114483	-2.514245
H	-1.591533	-3.037874	-3.644161
H	-1.135599	-4.605268	-2.949332
C	-5.994175	-3.150884	-1.196181
H	-6.444584	-2.197807	-0.866886
H	-6.543646	-3.953654	-0.677352
H	-6.179687	-3.254029	-2.275731
C	-2.342377	-3.234641	2.228296
H	-3.142462	-3.665270	2.849035
H	-2.128159	-2.215102	2.594473
H	-1.415069	-3.801577	2.405468
C	1.762030	0.243734	0.427226
H	2.111922	0.095529	1.472005
C	2.763580	0.975248	-0.350323
C	2.767366	1.113470	-1.751039
H	1.955670	0.661843	-2.329970
C	3.781499	1.820551	-2.385061
H	3.775960	1.909731	-3.475616
C	4.791653	2.435421	-1.642612
H	5.576424	3.005012	-2.149682
C	4.793641	2.325266	-0.253259
H	5.577079	2.809685	0.337484
C	3.801318	1.585768	0.381291
H	3.812836	1.479632	1.471931
C	-0.721702	2.862396	-1.414103
H	-0.498048	2.103476	-2.191977
C	-1.872035	3.735531	-1.919343
H	-2.780393	3.135245	-2.100640
H	-2.140898	4.486886	-1.149969
C	-1.478758	4.459370	-3.202524
H	-1.307352	3.706447	-3.996487
H	-2.313490	5.091822	-3.551739
C	-0.215393	5.286744	-3.018298
H	0.062925	5.786749	-3.962076
H	-0.413554	6.094939	-2.286063
C	0.925276	4.421580	-2.504570

H	1.840156	5.019855	-2.349572
H	1.177292	3.661265	-3.270312
C	0.534908	3.714354	-1.214598
H	0.343769	4.471879	-0.429094
H	1.375090	3.099989	-0.849912
C	0.428548	2.839973	2.249011
H	0.917853	1.858467	2.161145
H	1.136660	3.625015	1.899589
C	0.089341	3.096615	3.700684
H	-0.531984	2.254279	4.074243
H	1.003338	3.151413	4.313321
C	-1.786263	4.323348	3.128249
H	-2.266970	5.303721	3.282727
H	-2.475697	3.540359	3.515431
C	-1.539339	4.086830	1.648759
H	-0.979150	4.960195	1.243767
H	-2.507019	4.047732	1.121690
C	-2.861775	1.554413	0.129387
H	-3.320398	2.542626	-0.078345
C	-3.329972	0.594391	-0.965369
H	-2.892973	0.835479	-1.950207
H	-2.964993	-0.425808	-0.727267
C	-4.851785	0.580510	-1.019363
H	-5.211383	1.585976	-1.319658
H	-5.200435	-0.115231	-1.803782
C	-5.449757	0.203007	0.329730
H	-6.552881	0.248565	0.293287
H	-5.183342	-0.850382	0.542945
C	-4.912540	1.069415	1.460546
H	-5.308444	0.722891	2.430884
H	-5.275648	2.109589	1.334667
C	-3.390030	1.075993	1.479706
H	-3.001282	0.057089	1.675281
H	-3.001293	1.697847	2.303154
N	-0.788200	2.856795	1.451757
O	-0.592490	4.318718	3.856279

Catalyst 2

M06/def2SVP SCF energy: -3358.87522324 a.u.

M06/def2SVP enthalpy: -3357.877635 a.u.
M06/def2SVP free energy: -3358.015620 a.u.
M06/def2TZVP SCF energy in solution: -3361.52127892 a.u.
M06/def2TZVP enthalpy in solution: -3360.523691 a.u.
M06/def2TZVP free energy in solution: -3360.661676 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.211847	-0.345047	0.139967
Cl	-0.052579	-0.370080	-2.279489
Cl	-0.029326	-0.589494	2.552449
P	-1.260704	1.587362	0.136594
C	0.878736	-2.305907	0.127406
N	2.136770	-2.761479	0.307619
C	2.205987	-4.223730	0.405615
H	2.496759	-4.524811	1.428526
H	2.972025	-4.619844	-0.282422
C	0.790854	-4.651610	0.047521
H	0.724277	-5.137265	-0.944418
H	0.342073	-5.340427	0.783249
N	0.066034	-3.379627	0.026418
C	3.345390	-2.003281	0.329322
C	3.940041	-1.650373	-0.895630
C	5.151466	-0.959285	-0.864736
H	5.617148	-0.666772	-1.814106
C	5.781689	-0.628904	0.337240
C	5.175106	-1.018217	1.532781
H	5.663677	-0.778591	2.485081
C	3.960054	-1.708805	1.556766
C	3.289063	-1.998370	-2.196193
H	3.935315	-1.728001	-3.044405
H	2.321575	-1.478786	-2.326546
H	3.072162	-3.078878	-2.271846
C	7.062596	0.144894	0.335120
H	6.873190	1.214172	0.133143
H	7.749577	-0.209558	-0.449825
H	7.582661	0.077953	1.302760
C	3.327032	-2.099866	2.854109
H	2.309935	-1.678234	2.952330
H	3.930017	-1.753163	3.706145

H	3.226618	-3.194764	2.949435
C	-1.321673	-3.372684	-0.320808
C	-1.692611	-3.409773	-1.675267
C	-3.057713	-3.424695	-1.982625
H	-3.356803	-3.436425	-3.038031
C	-4.040632	-3.453030	-0.994960
C	-3.632172	-3.483022	0.341985
H	-4.393213	-3.531636	1.131063
C	-2.286064	-3.460574	0.704014
C	-0.690197	-3.535854	-2.779715
H	0.287829	-3.106180	-2.524040
H	-1.037439	-3.018106	-3.686198
H	-0.548330	-4.600563	-3.042678
C	-5.495539	-3.472557	-1.339055
H	-5.997984	-2.596513	-0.897601
H	-5.991148	-4.369423	-0.931150
H	-5.658524	-3.462052	-2.427482
C	-1.878416	-3.573959	2.137934
H	-2.759917	-3.653159	2.791465
H	-1.275311	-2.710771	2.467645
H	-1.260099	-4.473945	2.304122
C	1.787105	0.529458	0.438264
H	2.148735	0.442151	1.485788
C	2.671264	1.395450	-0.341998
C	2.628576	1.557571	-1.739844
H	1.882297	1.000101	-2.314376
C	3.510599	2.422571	-2.374986
H	3.469448	2.532236	-3.462907
C	4.432918	3.166332	-1.635444
H	5.112917	3.858017	-2.141748
C	4.480565	3.028650	-0.249501
H	5.196054	3.611889	0.338249
C	3.620834	2.138915	0.385893
H	3.668077	2.014597	1.473553
C	-1.186857	2.760045	-1.298821
H	-0.905544	2.113571	-2.155087
C	-2.447481	3.547442	-1.659378
H	-3.317982	2.886519	-1.802493
H	-2.713556	4.223531	-0.825588
C	-2.200023	4.387855	-2.908212

H	-1.990957	3.712525	-3.760896
H	-3.110909	4.951244	-3.175714
C	-1.022695	5.334164	-2.717052
H	-0.837983	5.915410	-3.636889
H	-1.279194	6.072401	-1.931402
C	0.229817	4.579878	-2.294551
H	1.066657	5.276802	-2.113424
H	0.554575	3.912704	-3.117377
C	-0.032554	3.738334	-1.053741
H	-0.303029	4.406713	-0.212187
H	0.885601	3.209544	-0.744601
C	-0.213527	2.780862	2.403049
H	0.529594	1.982674	2.256940
H	0.264502	3.757814	2.168634
C	-0.669367	2.789800	3.846032
H	-1.034317	1.773826	4.108447
H	0.165767	3.042425	4.518498
C	-2.798454	3.482022	3.257540
H	-3.552509	4.257181	3.472052
H	-3.237751	2.495420	3.527661
C	-2.443076	3.487587	1.782487
H	-2.143326	4.521916	1.500904
H	-3.322505	3.208034	1.178294
C	-3.307107	0.292068	-1.164544
H	-2.989530	0.862958	-2.051082
H	-2.853768	-0.716728	-1.272467
C	-4.816586	0.178886	-1.141504
H	-5.260436	1.199101	-1.180447
H	-5.172732	-0.386847	-2.018903
C	-4.826746	0.090316	1.190523
H	-5.197250	-0.532439	2.021004
H	-5.264020	1.108671	1.300298
C	-3.319088	0.184321	1.226023
H	-2.890868	-0.840555	1.219963
H	-2.970988	0.667212	2.153031
O	-5.276549	-0.501598	-0.002163
N	-2.866514	0.949463	0.064731
N	-1.355340	2.553613	1.530079
O	-1.680051	3.747620	4.055164

Catalyst 3

M06/def2SVP SCF energy: -3410.76821041 a.u.
M06/def2SVP enthalpy: -3409.807147 a.u.
M06/def2SVP free energy: -3409.946210 a.u.
M06/def2TZVP SCF energy in solution: -3413.48279955 a.u.
M06/def2TZVP enthalpy in solution: -3412.521736 a.u.
M06/def2TZVP free energy in solution: -3412.660799 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ru	0.234089	-0.251532	0.127814
Cl	0.047381	-0.290047	-2.290456
Cl	-0.072599	-0.446476	2.539150
P	-1.282371	1.642154	0.136007
C	0.871981	-2.211751	0.177720
N	2.120862	-2.686267	0.374356
C	2.143632	-4.139241	0.577106
H	2.319196	-4.371799	1.644674
H	2.958692	-4.600023	-0.004361
C	0.757728	-4.551181	0.116972
H	0.756127	-4.984402	-0.902328
H	0.264650	-5.273040	0.788356
N	0.039814	-3.274271	0.113660
C	3.344777	-1.955076	0.371310
C	3.959331	-1.694097	-0.866961
C	5.185470	-1.031494	-0.866064
H	5.670306	-0.812596	-1.825725
C	5.806923	-0.632639	0.320383
C	5.178173	-0.927884	1.530653
H	5.658150	-0.631258	2.471225
C	3.951350	-1.596947	1.584844
C	3.307237	-2.107550	-2.147582
H	3.950872	-1.876964	-3.009526
H	2.338462	-1.595285	-2.298639
H	3.093961	-3.191471	-2.169662
C	7.106319	0.108254	0.277705
H	6.964769	1.120563	-0.140866
H	7.840581	-0.401575	-0.367142
H	7.549467	0.218308	1.278922
C	3.306277	-1.911573	2.897651

H	2.248499	-1.592953	2.923914
H	3.836061	-1.415432	3.724392
H	3.324135	-2.995441	3.109075
C	-1.364280	-3.266880	-0.156538
C	-1.807237	-3.367763	-1.488074
C	-3.183964	-3.422408	-1.724627
H	-3.535667	-3.485681	-2.761844
C	-4.115165	-3.419677	-0.686393
C	-3.637902	-3.371403	0.624766
H	-4.357366	-3.386661	1.453520
C	-2.275105	-3.313374	0.919632
C	-0.858921	-3.494045	-2.639320
H	0.108082	-3.007221	-2.450490
H	-1.278843	-3.027070	-3.542897
H	-0.680107	-4.559033	-2.876303
C	-5.585910	-3.473945	-0.950473
H	-6.079193	-2.590245	-0.512934
H	-6.044169	-4.363193	-0.486098
H	-5.807887	-3.504311	-2.028157
C	-1.833833	-3.321332	2.348804
H	-2.520585	-3.925924	2.960941
H	-1.804342	-2.298567	2.763781
H	-0.811156	-3.709087	2.474205
C	1.820162	0.594218	0.463956
H	2.129860	0.536735	1.530328
C	2.772964	1.399000	-0.302132
C	2.826921	1.485800	-1.706479
H	2.099647	0.919322	-2.296955
C	3.783156	2.279565	-2.327574
H	3.815162	2.330320	-3.420109
C	4.694894	3.017803	-1.569632
H	5.436734	3.650255	-2.066577
C	4.653115	2.949996	-0.178461
H	5.360820	3.527847	0.423662
C	3.711663	2.137974	0.444816
H	3.686903	2.069656	1.538156
C	-2.574894	3.336715	-1.731152
H	-3.491169	2.818517	-1.408743
H	-2.627374	4.376140	-1.337456
C	-2.481049	3.401241	-3.243391

H	-2.511631	2.366772	-3.653971
H	-3.328814	3.965192	-3.666026
C	-0.155583	3.395642	-3.168453
H	0.716128	3.971642	-3.519517
H	-0.091996	2.364474	-3.576597
C	-0.173228	3.308196	-1.657299
H	-0.112937	4.334187	-1.227608
H	0.703135	2.745253	-1.297136
C	-0.112050	2.937581	2.268179
H	0.566562	2.072897	2.234395
H	0.410633	3.822586	1.839442
C	-0.490334	3.226085	3.703592
H	-0.909779	2.295504	4.145000
H	0.391024	3.523196	4.293656
C	-2.593106	3.982253	3.080876
H	-3.269817	4.846157	3.183497
H	-3.099029	3.097251	3.528852
C	-2.308577	3.699141	1.618160
H	-1.937106	4.628685	1.130726
H	-3.239867	3.397507	1.108823
C	-3.299226	0.192854	-1.001681
H	-2.933331	0.644802	-1.936777
H	-2.877553	-0.833139	-0.968526
C	-4.810146	0.110973	-1.001028
H	-5.240585	1.124511	-1.166413
H	-5.161070	-0.544013	-1.816181
C	-4.873432	0.310657	1.320456
H	-5.286088	-0.186449	2.213221
H	-5.285412	1.344596	1.279131
C	-3.364387	0.378950	1.391859
H	-2.953673	-0.644790	1.529000
H	-3.030949	0.972532	2.257628
N	-2.868372	0.980170	0.155103
N	-1.319937	2.636967	1.514270
N	-1.397314	2.655899	-1.222083
O	-5.304041	-0.422433	0.200929
O	-1.422065	4.277370	3.787099
O	-1.305718	4.049421	-3.649101

PCy3

M06/def2SVP SCF energy: -1045.97560506 a.u.
M06/def2SVP enthalpy: -1045.475919 a.u.
M06/def2SVP free energy: -1045.542283 a.u.
M06/def2TZVP SCF energy in solution: -1046.86684783 a.u.
M06/def2TZVP enthalpy in solution: -1046.367162 a.u.
M06/def2TZVP free energy in solution: -1046.433526 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-0.220734	-0.054617	-1.081234
C	0.552375	1.550097	-0.469882
H	-0.051768	2.299496	-1.027309
C	0.476864	1.937399	1.007111
H	-0.556883	1.854404	1.387166
H	1.083351	1.236142	1.610521
C	1.001614	3.353699	1.222950
H	0.339747	4.068226	0.693927
H	0.950585	3.622321	2.292517
C	2.422262	3.506628	0.698359
H	2.784088	4.538666	0.847225
H	3.096049	2.855389	1.290325
C	2.512220	3.109450	-0.767511
H	3.551130	3.192729	-1.131143
H	1.913956	3.816311	-1.375582
C	1.984739	1.697651	-0.983216
H	2.636904	0.988893	-0.435716
H	2.042933	1.412791	-2.049833
C	0.755514	-1.481878	-0.349081
H	0.051726	-2.323316	-0.528599
C	1.997592	-1.805008	-1.184016
H	1.739287	-1.813069	-2.257924
H	2.753064	-1.005591	-1.055927
C	2.613865	-3.133257	-0.763270
H	1.897417	-3.949703	-0.982715
H	3.516369	-3.346964	-1.361871
C	2.939762	-3.143052	0.723393
H	3.369261	-4.114569	1.023254
H	3.722250	-2.384579	0.925902
C	1.709311	-2.819004	1.557926

H	1.959142	-2.806373	2.633170
H	0.956759	-3.621900	1.425809
C	1.095165	-1.487542	1.138476
H	1.826357	-0.681200	1.343703
H	0.203582	-1.261294	1.751268
C	-1.797223	-0.106000	-0.059445
H	-1.562098	0.000126	1.020482
C	-2.700220	1.059864	-0.470534
H	-2.198359	2.027323	-0.290762
H	-2.870377	1.002678	-1.565487
C	-4.041596	1.031152	0.249740
H	-3.873676	1.173935	1.336015
H	-4.668829	1.878344	-0.077785
C	-4.756952	-0.291026	0.024562
H	-5.723748	-0.310241	0.556457
H	-4.992573	-0.395789	-1.053068
C	-3.879592	-1.454160	0.458158
H	-4.388266	-2.417605	0.280454
H	-3.711368	-1.392007	1.551677
C	-2.532826	-1.433102	-0.253603
H	-2.686796	-1.598650	-1.340217
H	-1.915446	-2.277137	0.101874

Ligand L1_B

M06/def2SVP SCF energy: -1097.87188163 a.u.
M06/def2SVP enthalpy: -1097.408515 a.u.
M06/def2SVP free energy: -1097.474747 a.u.
M06/def2TZVP SCF energy in solution: -1098.83025239 a.u.
M06/def2TZVP enthalpy in solution: -1098.366886 a.u.
M06/def2TZVP free energy in solution: -1098.433118 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	0.057904	-0.052395	-1.052677
C	-1.360619	-1.153046	-0.496240
H	-1.214033	-2.072304	-1.106224
C	-1.470194	-1.581633	0.965442
H	-0.539913	-2.067541	1.309558
H	-1.609162	-0.687337	1.603174

C	-2.654852	-2.518472	1.176911
H	-2.482407	-3.452644	0.606030
H	-2.724371	-2.815349	2.237916
C	-3.955027	-1.879820	0.711258
H	-4.802556	-2.571964	0.854704
H	-4.168842	-0.994558	1.342982
C	-3.859689	-1.439525	-0.742229
H	-4.794384	-0.947625	-1.062875
H	-3.743571	-2.333177	-1.386728
C	-2.670718	-0.513701	-0.959903
H	-2.829718	0.423129	-0.387159
H	-2.596083	-0.213906	-2.021677
C	-0.683872	2.582346	-1.103731
H	-0.451525	2.386150	-2.164298
H	-1.789092	2.696893	-1.021077
C	-0.038267	3.873627	-0.647438
H	1.057988	3.816815	-0.831184
H	-0.437505	4.736938	-1.203913
C	0.216173	3.061350	1.507707
H	-0.010455	3.306361	2.558343
H	1.322382	3.002054	1.401450
C	-0.394286	1.724725	1.124340
H	-1.476679	1.744708	1.389787
H	0.076770	0.924388	1.719553
C	1.492431	-0.718223	-0.067297
H	1.253298	-0.734905	1.017234
C	1.807104	-2.149981	-0.505127
H	0.943013	-2.815867	-0.332201
H	1.984047	-2.154102	-1.600607
C	3.037476	-2.697661	0.207011
H	2.820950	-2.774527	1.291231
H	3.251997	-3.724497	-0.136389
C	4.245927	-1.796590	0.002103
H	5.124838	-2.195189	0.537382
H	4.513392	-1.791243	-1.073153
C	3.942637	-0.372337	0.443831
H	4.812401	0.284474	0.270031
H	3.761432	-0.361448	1.537042
C	2.716145	0.174617	-0.272356
H	2.924912	0.239339	-1.360330

H	2.493853	1.206227	0.052435
N	-0.209577	1.475607	-0.292138
O	-0.286841	4.102914	0.716050

Ligand L2_A

M06/def2SVP SCF energy: -1149.76073370 a.u.
M06/def2SVP enthalpy: -1149.332689 a.u.
M06/def2SVP free energy: -1149.397860 a.u.
M06/def2TZVP SCF energy in solution: -1150.78660904 a.u.
M06/def2TZVP enthalpy in solution: -1150.358564 a.u.
M06/def2TZVP free energy in solution: -1150.423735 a.u.

Cartesian coordinates

ATOM	X	Y	Z
P	-0.023302	-0.001295	-1.202675
C	-1.642709	-0.674488	-0.538697
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C	-1.768264	-1.025880	0.941161
H	-0.970248	-1.718038	1.260967
H	-1.629372	-0.107525	1.541553
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H	-3.280155	-2.547482	0.686324
H	-3.230776	-1.857426	2.314238
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H	-5.242141	-1.048523	1.047920
H	-4.163342	0.286110	1.473936
C	-4.123738	-0.221767	-0.619585
H	-4.896851	0.519717	-0.885304
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H	-2.573710	1.264329	-0.370527
H	-2.651549	0.584871	-2.004072
C	0.134199	2.720407	-0.964277
H	0.162151	2.577763	-2.058636
H	-0.842463	3.194533	-0.717275
C	1.245268	3.648641	-0.518471
H	2.219815	3.249684	-0.880349
H	1.111999	4.658603	-0.938856
C	1.462456	2.533610	1.502836

H	1.479803	2.710799	2.590345
H	2.452486	2.115304	1.211338
C	0.372076	1.543992	1.137110
H	-0.586996	1.895640	1.580738
H	0.605971	0.552627	1.560579
C	0.956317	-2.489655	-0.590853
H	-0.085481	-2.800522	-0.408970
H	1.207606	-2.772678	-1.640435
C	1.871183	-3.242821	0.354336
H	1.538045	-3.050011	1.399053
H	1.815911	-4.328163	0.172156
C	3.378400	-1.479547	0.379126
H	4.444901	-1.255585	0.216561
H	3.121110	-1.196131	1.424881
C	2.507008	-0.687453	-0.569730
H	2.834070	-0.886723	-1.617351
H	2.628511	0.394180	-0.389167
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N	0.265177	1.434246	-0.306474
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Ligand L2_B

M06/def2SVP SCF energy: -1149.76691886 a.u.
M06/def2SVP enthalpy: -1149.338335 a.u.
M06/def2SVP free energy: -1149.404376 a.u.
M06/def2TZVP SCF energy in solution: -1150.79324075 a.u.
M06/def2TZVP enthalpy in solution: -1150.364657 a.u.
M06/def2TZVP free energy in solution: -1150.430698 a.u.

Cartesian coordinates

ATOM	X	Y	Z
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H	3.646162	-0.154083	1.052362
H	3.429622	-1.298631	2.414784

C	3.471736	-2.035412	-0.757429
H	3.943864	-2.888472	-1.270899
H	3.929953	-1.098267	-1.144600
C	1.980742	-1.992774	-1.019340
H	1.543996	-2.977225	-0.732679
H	1.782308	-1.841310	-2.094482
C	-2.066744	-1.900960	-1.010547
H	-1.852044	-1.777202	-2.086181
H	-1.665097	-2.893426	-0.700499
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H	-4.053633	-2.739679	-1.266568
C	-3.266609	-0.941014	1.330373
H	-3.531102	-1.086687	2.390321
H	-3.691479	0.033174	0.999510
C	-1.760295	-0.910141	1.148177
H	-1.334173	-1.834561	1.600116
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C	1.318298	2.246222	-0.409980
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H	2.280205	4.158718	-0.064073
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H	-1.239607	2.426699	-1.497144
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O	3.738844	-2.173214	0.614345
N	1.380173	-0.909571	-0.259085

Ligand L3

M06/def2SVP SCF energy: -1201.66004663 a.u.
M06/def2SVP enthalpy: -1201.266869 a.u.
M06/def2SVP free energy: -1201.332408 a.u.
M06/def2TZVP SCF energy in solution: -1202.75322621 a.u.
M06/def2TZVP enthalpy in solution: -1202.360049 a.u.
M06/def2TZVP free energy in solution: -1202.425588 a.u.

Cartesian coordinates

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H	1.285057	-1.627911	1.695810
C	3.169384	-0.658480	1.365506
H	3.553864	0.293350	0.933680
H	3.399315	-0.656166	2.443258
C	3.612185	-1.835902	-0.584694
H	4.185140	-2.698938	-0.960098
H	3.989480	-0.920565	-1.093469
C	2.134371	-1.988163	-0.880635
H	1.790038	-2.964873	-0.471521
H	1.956612	-2.004663	-1.970158
C	-2.134430	-1.988154	-0.880594
H	-1.956692	-2.004640	-1.970121
H	-1.790129	-2.964885	-0.471505
C	-3.612233	-1.835843	-0.584625
H	-3.989507	-0.920487	-1.093381
H	-4.185225	-2.698855	-0.960030
C	-3.169358	-0.658466	1.365585
H	-3.399268	-0.656164	2.443342
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C	-1.672958	-0.749223	1.134226
H	-1.285063	-1.627964	1.695845
H	-1.169134	0.151946	1.522917
C	1.188272	2.110346	-0.657528
H	2.095355	1.511902	-0.477227
H	1.231253	2.463967	-1.713809
C	1.161114	3.314630	0.259262
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H	-1.230958	2.464056	-1.714023
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N	-0.000009	1.302404	-0.418321
N	-1.401879	-0.884312	-0.286446
N	1.401875	-0.884282	-0.286492
O	0.000050	4.078400	0.071294
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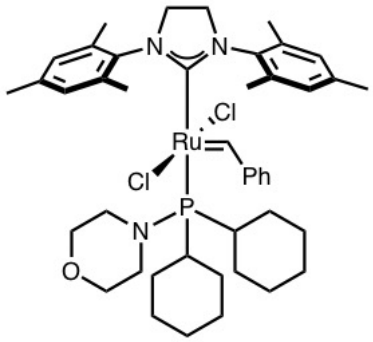
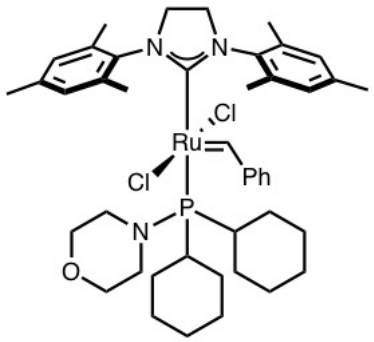


Catalyst 1

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



Catalyst 1

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137.63
137.23
135.59
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128.06
68.02
52.11
51.08
49.37
35.49
35.29
29.18
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28.02
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21.03
20.57
19.00

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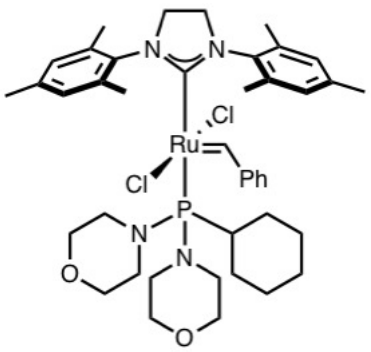
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Cl
Ph
P
N
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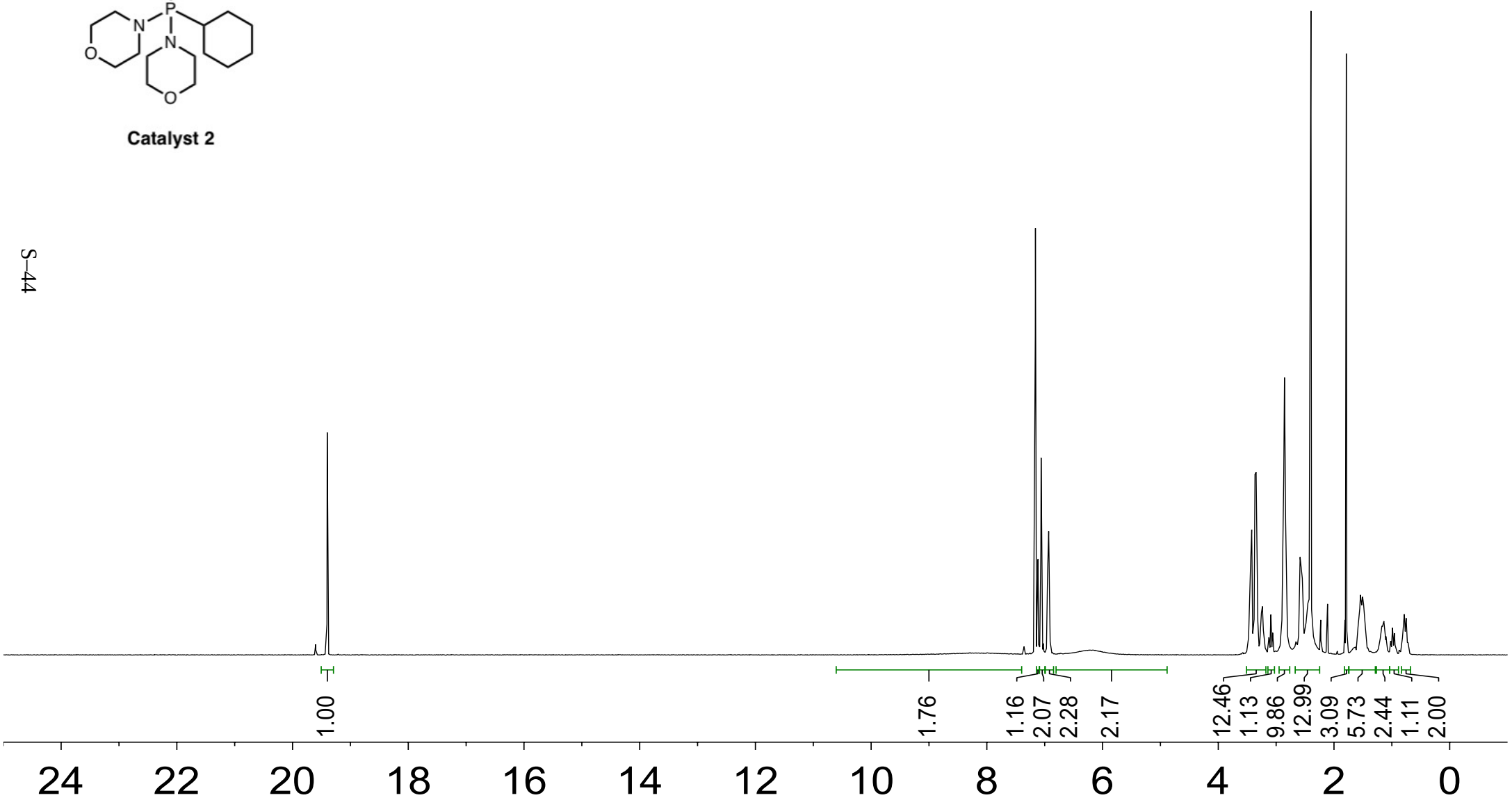
N
O
O

Catalyst 2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2.00
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14
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6
4
2
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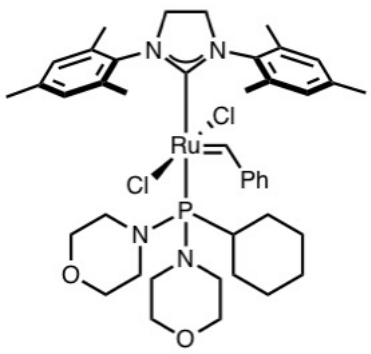

Catalyst 2

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139.26
137.69
137.49
136.93
135.03
131.06
130.55
129.37
67.64
52.14
50.97
47.16
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21.23
21.00
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18.92

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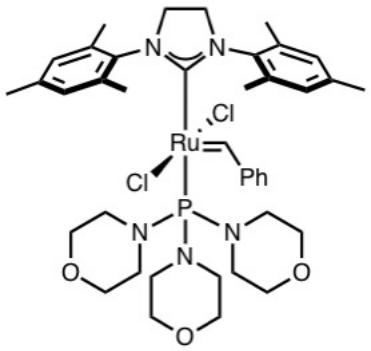
Cl
Ru
Cl
Ph
P
N
N
N
N
O
O
O

Catalyst 3

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2.47
15.37
6.50
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14
12
10
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6
4
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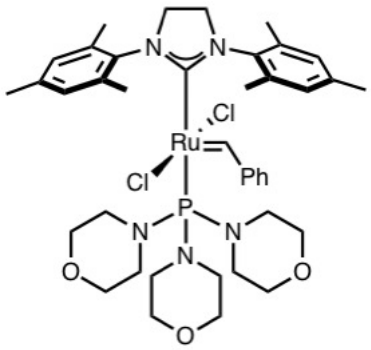

Catalyst 3

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129.40
128.80
128.59
67.63
67.57
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20.97
20.65
18.92

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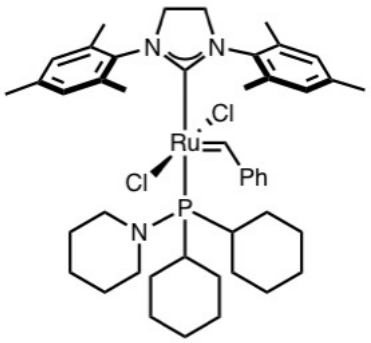
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N
Cl
Ru
Cl
Ph
P
N

Catalyst 4

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0.31
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1.65
4.99
7.83
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3.89
26.64
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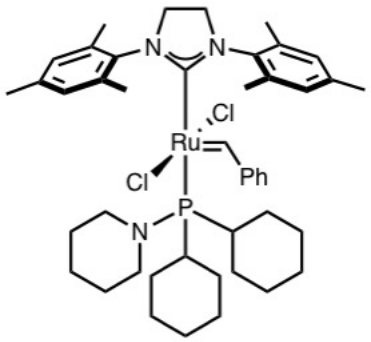
f1 (ppm)



Catalyst 4

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137.27
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129.39
52.19
51.10
50.31
35.97
35.78
29.31
28.86
28.12
28.03
27.94
27.81
27.45
27.40
26.68
25.18
21.23
21.05
20.60
19.07

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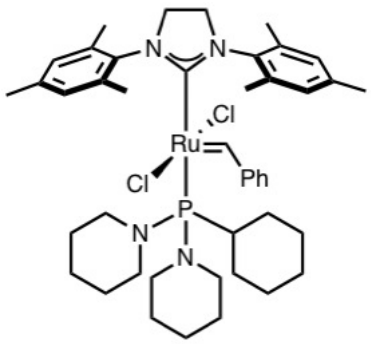
f1 (ppm)


N
N
Cl
Ru
Cl
Ph
P
N
N

Catalyst 5

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0.50
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11.29
5.55
3.31
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6.61
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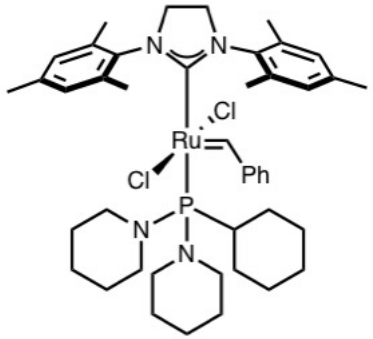
f1 (ppm)


Cl
Ru
Cl
Ph
P
N
N
N
N

Catalyst 5

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131.17
130.35
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38.03
27.80
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27.50
27.16
27.11
25.77
25.22
21.18
21.05
20.64
19.07
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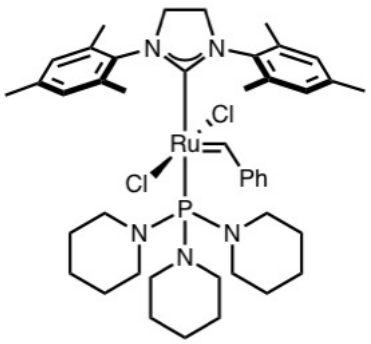
150
130
110
90
70
50
30
10
f1 (ppm)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N
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Catalyst 6

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1.80
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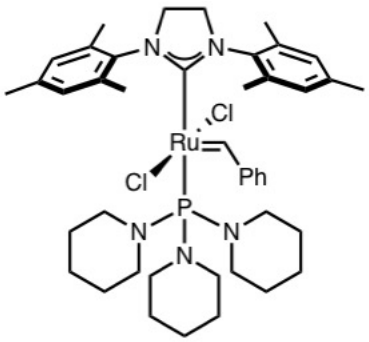
f1 (ppm)



Catalyst 6

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137.17
136.04
131.22
130.18
129.37
52.09
52.05
50.94
47.21
47.16
27.10
27.05
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21.14
21.04
20.72
19.10

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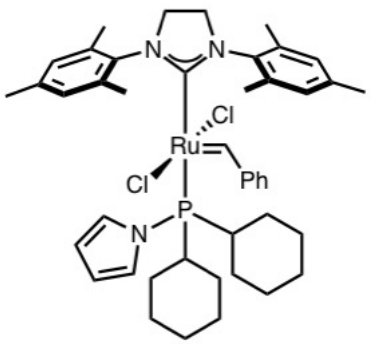
f1 (ppm)


N
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Cl
Ru
Cl
Ph
P
N

Catalyst 7

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2.11
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2.09
5.98
6.04
3.20
3.10
2.23
2.36
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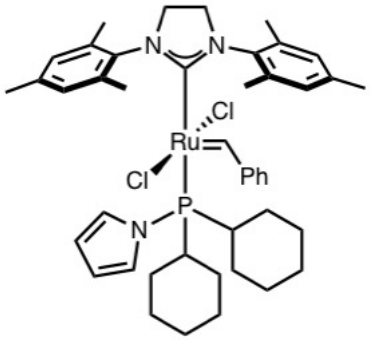

Catalyst 7

XI. References

1. Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314–5318.
2. Fetz, M.; Gerber, R.; Blacque, O.; Frech. C. M. *Chem. Eur. J.* **2011**, *17*, 4732–4736.
3. CCDC 1825659 (**4**), 1825660 (**5**), 1825661 (**6**), 1825662 (**7**), contain supplementary crystallographic data, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
4. Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
5. (a) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577. (b) Schaefer, A.; Huber, C.; Ahlrichs, R.; *J. Chem. Phys.* **1994**, *100*, 5829–5835.
6. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.
7. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
8. R. F. Ribeiro, A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.* **2011**, *115*, 14556–14562.
9. S. Grimme, *Chem. Eur. J.* **2012,** *18*, 9955–9964.
10. Tolman, C. A.; *Chem. Rev.* **1997**, *77*, 313–348.
11. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789. (b) Bechke, A. D. *Phys. Rev. A.*, **1988**, *38*, 3098–3100. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem.Phys. Lett.* **1989**, *157*, 200–206. (d) Becke, A. D.; *J. Chem. Phys.* **1993**, *98*, 5648–5652.
12. Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.