Supporting Information for

Resting State and Kinetic Studies on the Asymmetric Allylic Substitutions Catalyzed by Iridium-Phosphoramidite Complexes

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General Methods. Elemental Analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ). GC/MS analyses were performed on an Agilent 6890N GC equipped with a 5973 MS and an HP-5ms column (30 m x 0.25 mm ID x 0.25 μm film). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. NMR spectra were acquired on 500 MHz Varian Unity or Innova instruments. Chemical shifts are reported in ppm, relative to the solvent resonance ($CDCl_3$ = 7.26 ppm for ^1H, 77.0 ppm for ^{13}C) or to an external standard ($CFCl_3$ = 0 for ^{19}F and 85% H_3PO_4 = 0 for ^{31}P). Coupling constants are given in hertz. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector). Supercritical fluid chromatography analyses were carried out on a Berger ASC-1000 instrument with a single wavelength detector (λ= 220 nm) using a chiral solid phase column.

Chromatography was conducted on Silicycle Siala-P Silica gel using hexanes/ethyl acetate, hexanes/ether, or pentane/ether mixtures. While many products were visible on TLC via UV, all products were identified by staining with $KMnO_4$ (orange).

Reaction progress was monitored by GC and GC/MS with dodecane as the internal standard (10 μL). Branched-to-linear ratios were determined by ^1H NMR (usually the olefin protons) and GC/MS analysis in all cases except for the determination of the branched-to-linear ratio of **3b** (NMR only), **3j** (GC only), and **3c**, **3e**, and **3f** (GC/MS only). Results from GC/MS and NMR spectroscopy were within 5-10% of each other in all cases.

All starting materials were purchased from Aldrich, except for $IrCl_3$, which was purchased from Pressure Chemical or obtained as a gift from Johnson-Matthey. Propylamine was stored over KOH. THF, pentane, benzene, ether, toluene, and CH_2Cl_2 were purified by passing the degassed solvent (Ar) through a column of activated alumina (Solvent purification system purchased from Innovative Technologies of Newburyport, MA). (-)-*N*-(1-phenylallyl)benzenamine, (-)-*N*-(hex-1-en-3-yl)benzenamine, (+)-*N*-(1-phenylallyl)benzenamine, [Ir(COD)(*P,C*-**L1**)(**L1**)] and [Ir(COD)(*P,C*-**L1**)Cl] were prepared by published methods.[1]. The branched to linear ratios of the allyl amines were higher than 97/3, and the ee's were higher than 96%.

Benzene-d_6 and toluene-d_8 were degassed and dried over sodium and benzophenone. Kinetic data were acquired on a 500 MHz Varian Unity instrument. A single pulse for each time point was used, and the time between data points is 120 s.

Representative Procedure for Monitoring of Reactions Catalyzed by [Ir(COD)(*P,C*-L1)(L1)] (2) and [Ir(COD)Cl]$_2$: Reactions with Aniline as Nucleophile. In screw-capped NMR tube, complex [Ir(COD)(*P,C*-**L1**)(**L1**)] (**2**) (13.8 mg, 0.0100 mmol) and $[Ir(COD)Cl]_2$ (3.4 mg, 0.0050 mmol) were added. Solutions of methyl cinnamyl carbonate (0.666 M, 64.0 mg, 0.333 mmol) and aniline (2.00 M, 93.1 mg, 1.00 mmol) in THF (0.5 ml) were then added. The reaction was monitored at room temperature by ^{31}P NMR spectroscopy. After 10 h, the ^{31}P NMR resonances corresponding to complex **4** (^{31}P NMR (161.9 MHz, THF) δ: 148.6 (s, 1P) and complex **1** (^{31}P NMR (161.9 MHz, THF) δ: 115.9 (s, 1P) were observed. The ratio of these two signals was **3**/**1**= 0.15.

Monitoring of Catalytic Reaction using Benzylamine as Nucleophile. The representative procedure was followed using a 0.5 ml THF solution of methyl cinnamyl carbonate (0.666 M, 64.0 mg, 0.333 mmol) and benzyl amine (2.000 M, 107.2 mg, 1.000 mmol). Formation of [Ir(COD)(*P,C*-**L1**)((-)-N-benzyl-1-phenylprop-2-en-1-amine)] (^{31}P NMR (161.9 MHz, THF) δ: = 149.7 (s, 1P) and compound **1** was observed. The ratio of complexes, as determined by integration of the ^{31}P NMR spectrum was [Ir(COD)(*P,C*-**L1**)((-)-N-benzyl-1-phenylprop-2-en-1-amine)]/**1**= 0.5.

Monitoring of Catalytic Reaction using Propylamine as Nucleophile for Enantioselective Allylic Amination. The representative procedure was followed using 0.5 ml THF solution of methyl cinnamyl carbonate (0.666 M, 64.0 mg, 0.333 mmol) and propylamine (2.00 M, 59.1 mg, 1.00 mmol). Formation of [Ir(COD)(*P,C*-**L1**)((-)-1-phenyl-N-propylprop-2-en-1-amine)] at δ (^{31}P NMR)= 149.9 (s, 1P) was observed. This complex was the only species observed by ^{31}P NMR spectroscopy.

Synthesis of [Ir(COD)(*P,C*-L1)(ethylene)] (5). Into a thick wall sealable reaction vessel (250 ml) containing a stir bar, was placed $[Ir(COD)Cl]_2$ (100 mg, 0.148 mmol) and **L1** (161 mg, 0.298 mmol), and the two solids were dissolved in 15 ml of THF. $PrNH_2$ (1.5 g, 25 mmol) was then added by syringe. The bomb was connected to a vacuum line and frozen with liquid nitrogen. Ethylene (9.10 mmol) was added to the reaction mixture from a bulb of known volume containing a measured pressure of ethylene. The vessel was carefully handled and thawed behind a protective shield, and the reaction mixture was stirred at room temperature for 12 h over which time the orange solution turned bright yellow. After this time, the excess of the ethylene was allowed to evaporate into a vacuum line. The vessel was brought into a glove box, and pentane was added until a precipitate ($PrNH_3Cl$) formed. The solution was the left at -35 °C for one day. The resulting suspension was filtered through a 0.25 μm nylon syringe filter. The mother liquor was evaporated, and the resulting solid product was stored at -35 °C in dry box. This procedure yielded 183 mg (71%) of **5** as a yellow solid. Material for spectroscopic and microanalytical characterization was obtained by dissolving (100 mg, 0.115 mmol) complex **5** in toluene (2 ml), layering the toluene solution with pentane (10 ml), and storing at -35 °C for 3 days. A small amount of solid forms, and this material was removed by filtering the resulting mixture through a 0.25 μm nylon syringe filter. The mother liquor contains pure product, which was isolated after evaporation of the solvent under vacuum and leaving under vacuum for 12 h. ^{1}H NMR (500.13 MHz, toluene-d_8) δ 8.00 (d, J = 8.5 Hz, 1H, ArH),7.86 (d, J = 8.5 Hz, 1H, ArH), 7.70 (d, J = 8.0 Hz, 1H, ArH), 7.64 (d, J = 8.0 Hz, 1H, ArH), 7.47 (d, J = 8.5 Hz, 1H, ArH), 7.42 (d, J = 8.5 Hz, 1H, ArH), 7.36 (d, J = 7.6 Hz, 2H, ArH), 7.26-6.80 (m, 14H, ArH), 4.48 (dq, J = 14.0, 7.1 Hz, 1H, $C\underline{H}CH_3$), 4.21 (dt, J = 24.6, 5.6 Hz, 1H, $C\underline{H}CH_2$), 3.60 (m, 1H, $=C\underline{H}$ COD), 3.16-2.80 (m, 3H,2×$=C\underline{H}$ COD, $C\underline{H_2}$ COD), 2.67 (m, 1H, $C\underline{H_2}$ COD), 2.56 (m, 1H, $C\underline{H_2}$ COD), 2.40 (m, 1H, $C\underline{H_2}$ COD), 2.04-1.77 (m, 6H, 2×$=C\underline{H_2}$ ethylene, $C\underline{H}$ COD, $C\underline{H_2}$ COD), 1.70 (m, 1H, $C\underline{H_2}$ COD), 1.45 (m, 1H, $C\underline{H_2}$ COD), 1.32 (m, 1H, $C\underline{H_2}$ COD), 1.18 (m, 1H, $C\underline{H_2}Ir$), 1.13 (d, J = 6.8 Hz, 3H, $CHC\underline{H_3}$), 0.86 (t, J = 8.8 Hz, 1H, $C\underline{H_2}Ir$). These assignments were made using COSY, HMQC and DEPT spectroscopy. ^{13}C NMR data from 110 ppm-10 ppm: ^{13}C NMR (125.7 MHz, toluene-d_8) δ 90.2, 76.8, 65.1 (d, J_{CP}= 40 Hz, $\underline{C}CH_2$), 59.3, 57.9 (d, J_{CP}= 22 Hz, $\underline{C}CH_3$), 57.5, 37.8, 33.7, 33.4, 31.6, 29.2, 28.9, 24.5, 20.3. ^{31}P NMR (161.9 MHz, THF) δ 152.4 (s, 1P). Anal. Calc. for: C 63.72%, 5.23%, N 1.62% Found: C 63.78%, 5.60%, N 1.85%.

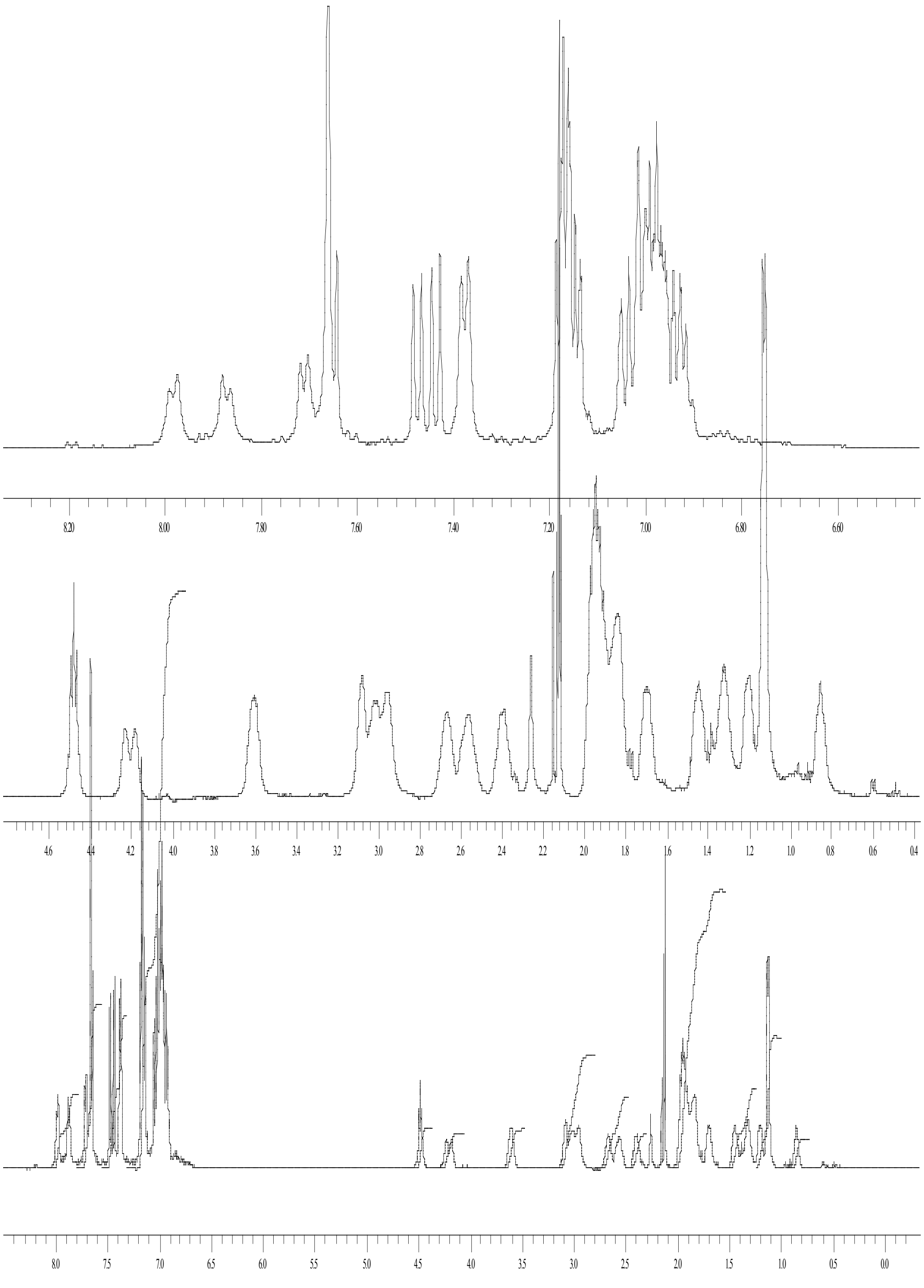


Figure S1. ^{1}H NMR spectrum of [Ir(COD)(*P,C*-**L1**)(ethylene)] (**5**).

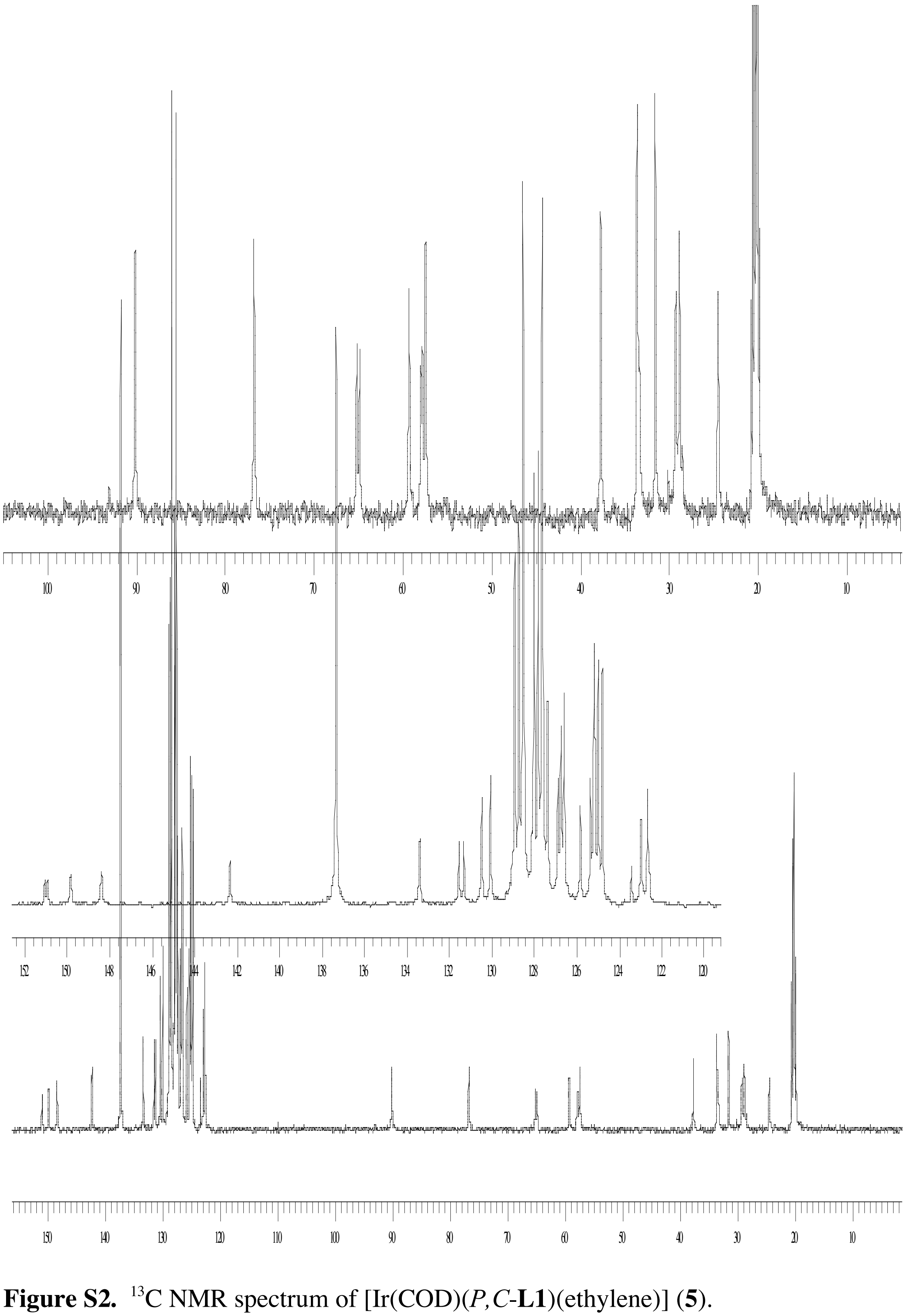


Figure S2. ^{13}C NMR spectrum of [Ir(COD)(*P,C*-**L1**)(ethylene)] (**5**).

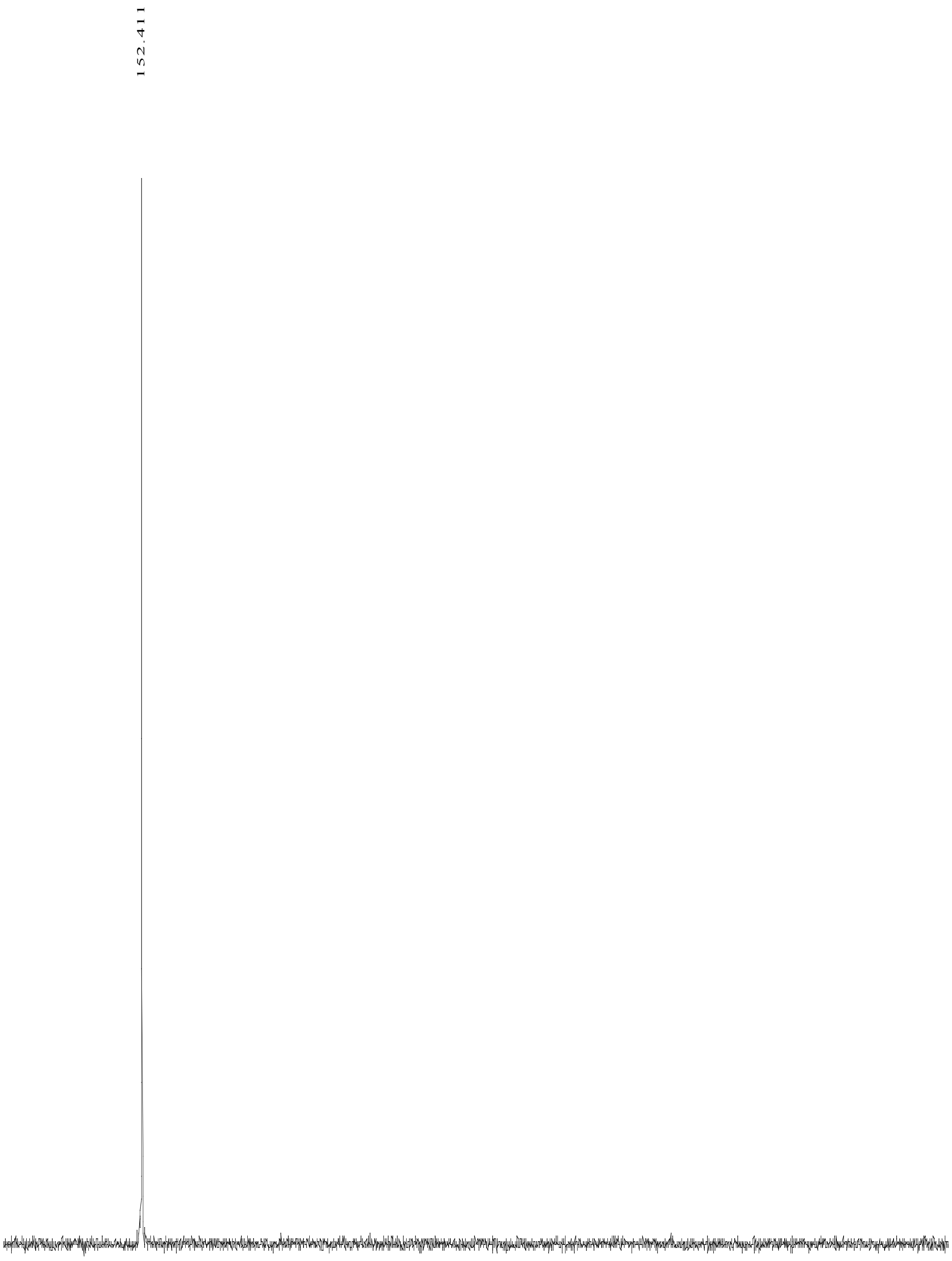


Figure S3. ^{31}P NMR Spectrum of [Ir(COD)(*P,C*-**L1**)(ethylene)] (**5**).

Synthesis of [Ir(COD)(*P,C*-L1)(4)] (3) In a drybox, [Ir(COD)(*P,C*-**L1**)(ethylene)] (100 mg, 0.115 mmol) and allylamine **4** (24.1 mg, 0.115 mmol) were dissolved in 10 ml of toluene in a vial. A small magnetic stirbar was added, and the vial was connected to vacuum. The solution was stirred and evaporated. Three portions of toluene (10 ml) were added and evaporated sequentially. After the third cycle, 1 ml of toluene was added, and the resulting solution was layered with pentane (ca 5 ml). The layered mixture was left for one day at -35 °C, over which time a small amount of solid formed. Pure complex **3** was contained in the mother liquor and was isolated by evaporation under vacuum for 12 h. This procedure yielded in 94 mg of yellow **3** (78%). ^{1}H NMR (500.13 MHz, benzene-d_6) δ 8.02-6.54 (m, 30H, ArH), 6.43 (d, J = 7.6 Hz, 2H, ArH), 5.31 (s, 1H, NH), 4.13 (dq, J = 21.2, 7.3 Hz, 1H, $C\underline{H}CH_3$), 4.03-3.89 (m, 2H, $C\underline{H}CH_2$, $C\underline{H}$ COD), 3.82 (d, J = 9.5 Hz, 1H, $NHC\underline{H}CH$ allylamine), 3.59 (m, 1H, $C\underline{H}CH_2$ allylamine), 3.89-3.60 (m, 3H, $C\underline{H}$ COD, $C\underline{H_2}$ COD, $C\underline{H_2}$ COD), 2.90 (m, 1H, $C\underline{H}$ COD), 2.11 (m, 1H, $C\underline{H_2}$ COD), 1.84 (m, 1H, $C\underline{H_2}$ COD), 1.77-1.47 (m, 4H, $C\underline{H_2}$ COD, $C\underline{H_2}$ COD, $C\underline{H_2}Ir$, $CHC\underline{H_2}$ allylamine), 1.44-1.24 (m, 2H, $C\underline{H}$ COD, $C\underline{H_2}$ COD), 1.15-1.02 (m, 2H, $C\underline{H_2}$ COD, $C\underline{H_2}Ir$), 0.93 (t, J = 9.5 Hz, 1H, $CHC\underline{H_2}$ allylamine), 0.76 (d, J = 7.6 Hz, 3H, $C\underline{H_3}$). These assignments were made by COSY, HMQC and DEPT spectroscopy. ^{13}C NMR spectrum from 110 ppm-10 ppm: ^{13}C NMR (125.7 MHz, benzene-d_6) δ 90.5, 76.5, 67.7 (d, J_{CP}= 41, $\underline{C}CH_2Ir$), 63.4, 62.1, 60.1, 54.4 (d, J_{CP} = 23, $\underline{C}CH_3$), 51.7 (d, J_{CP} = 26, $CH\underline{CH}CH_2$ allylamine), 41.7, 36.1, 28.8, 28.1, 27.2, 19.7, 16.3. ^{31}P NMR (161.9 MHz, THF) δ 148.6 (s, 1P). Anal. Calc. for: C 67.60%, 5.38%, N 2.67% Found: C 67.80%, 5.58%, N 2.97%.

Generation of Allylamine Complex 3 by Reaction of Allyl Amine 4 with the Combination of [Ir(COD)(*P,C*-L1)(L1)] and [Ir(COD)Cl]$_2$. To a screw-capped NMR tube, [Ir(COD)(*P,C*-**L1**)(**L1**)] (**2**) (13.8 mg, 0.0100 mmol), [Ir(COD)Cl]$_2$ (3.4 mg, 0.0050 mmol) and allyl amine **4** (209.3 mg, 1.000 mmol) in THF (0.5 ml) were added. A sealed capillary tube containing $PO(OPh)_3$ as external standard as placed into the tube. After 10 h, complex **3** and complex **1** were observed by ^{31}P NMR spectroscopy in a ratio of 1:1. To the solution was added an additional 0.5 ml of THF, and the resulting mixture was used for the reactions of **3** with **L1** and ethylene.

Reaction of Complex 3 with L1: To the solution of **3** in THF prepared by the above procedure (0.5 ml) was added **L1** (3.3 mg, 0.0061 mmol). The reaction was monitored by ^{31}P NMR spectroscopy. After 2 h, complete formation of complex **2** (^{31}P NMR (161.9 MHz, THF) δ: 152.6 (d, J = 46.3 Hz, 1P), 127.8 (d, J = 46.2 Hz, 1P), complex **1** (^{31}P NMR (161.9 MHz, THF) δ: 115.9 (s, 1P) ppm) and free ligand **L1** ((^{31}P NMR (161.9 MHz, THF) δ: 151.2 (s, 1P) ppm) were observed in a ratio of 1/1/0.2.

Reaction of Complex 3 with Ethylene: Into a J. Young NMR tube was added 0.5 ml of the solution of **3** in THF prepared by the above procedure. A sealed capillary tube containing $PO(OPh)_3$ as external standard was placed into the tube. The tube was connected to vacuum line and frozen with liquid nitrogen. Ethylene (10.8 mg, 0.3857 mmol) was condensed into the tube, and a ^{31}P NMR spectrum was recorded. The reaction was monitored by ^{31}P NMR spectroscopy, and after 15 min, complete formation of complex **5** (^{31}P NMR (161.9 MHz, THF)) δ 152.4 (s, 1P) ppm), complex **1** (^{31}P NMR (161.9 MHz, THF)) δ 115.9 (s, 1P) ppm) and free ligand **L1** were observed in a ratio of 1/1/0.2 .

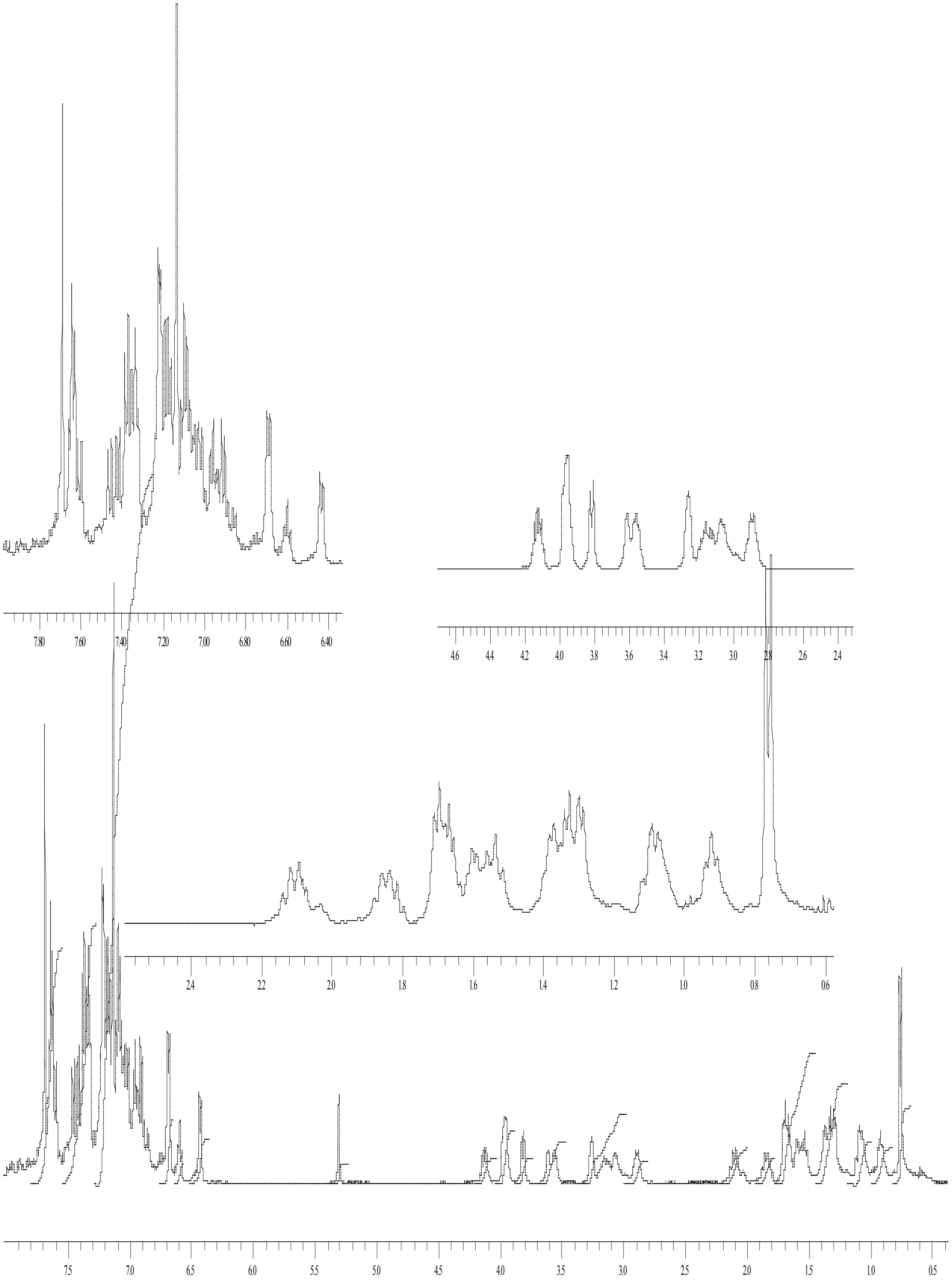


Figure S4. ^{1}H NMR spectrum of [Ir(COD)(*P,C*-**L1**)(**4**)] (**3**).

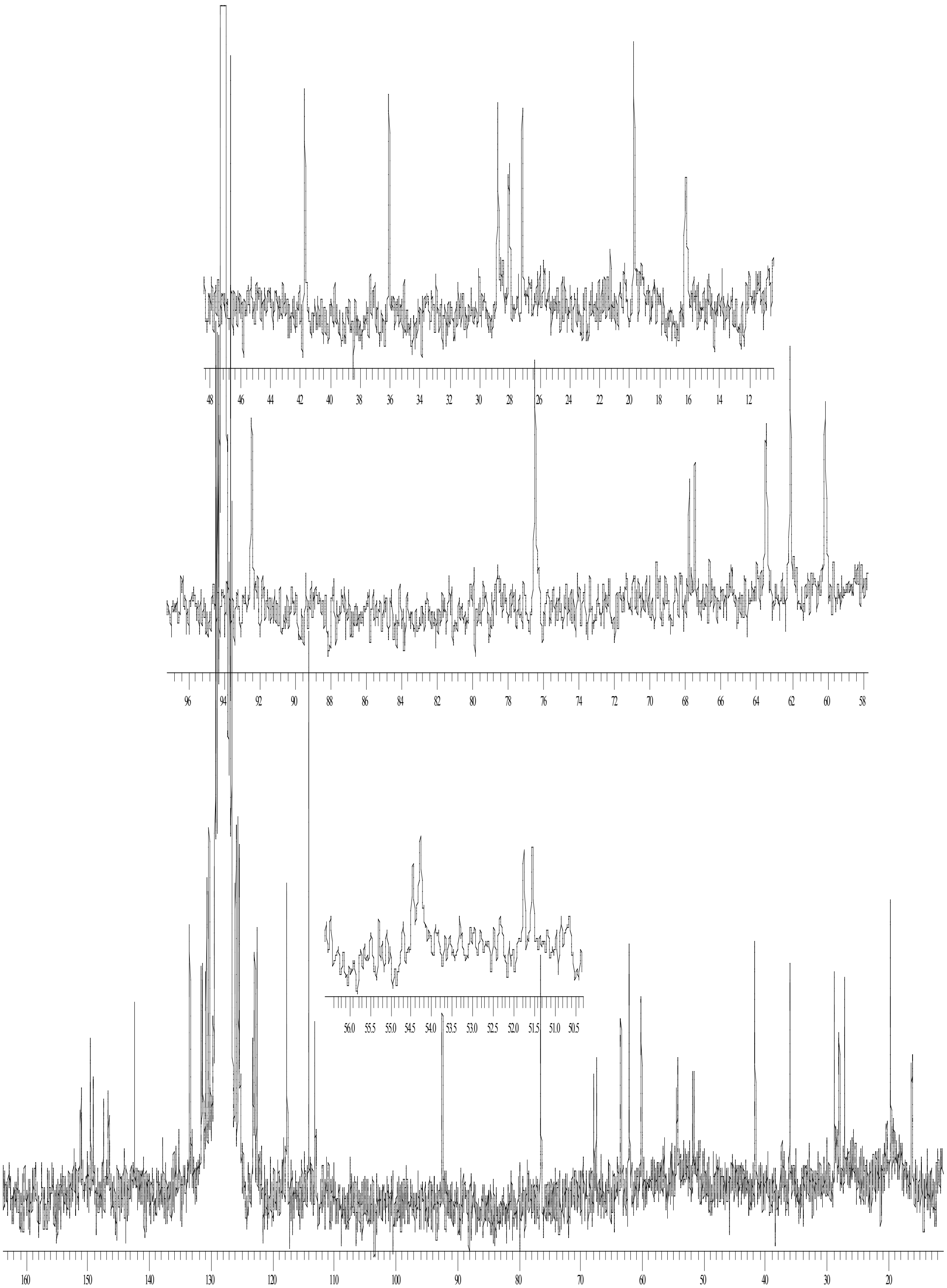


Figure S5. ^{13}C NMR Spectrum of [Ir(COD)(*P,C*-**L1**)(**4**)] (**3**).

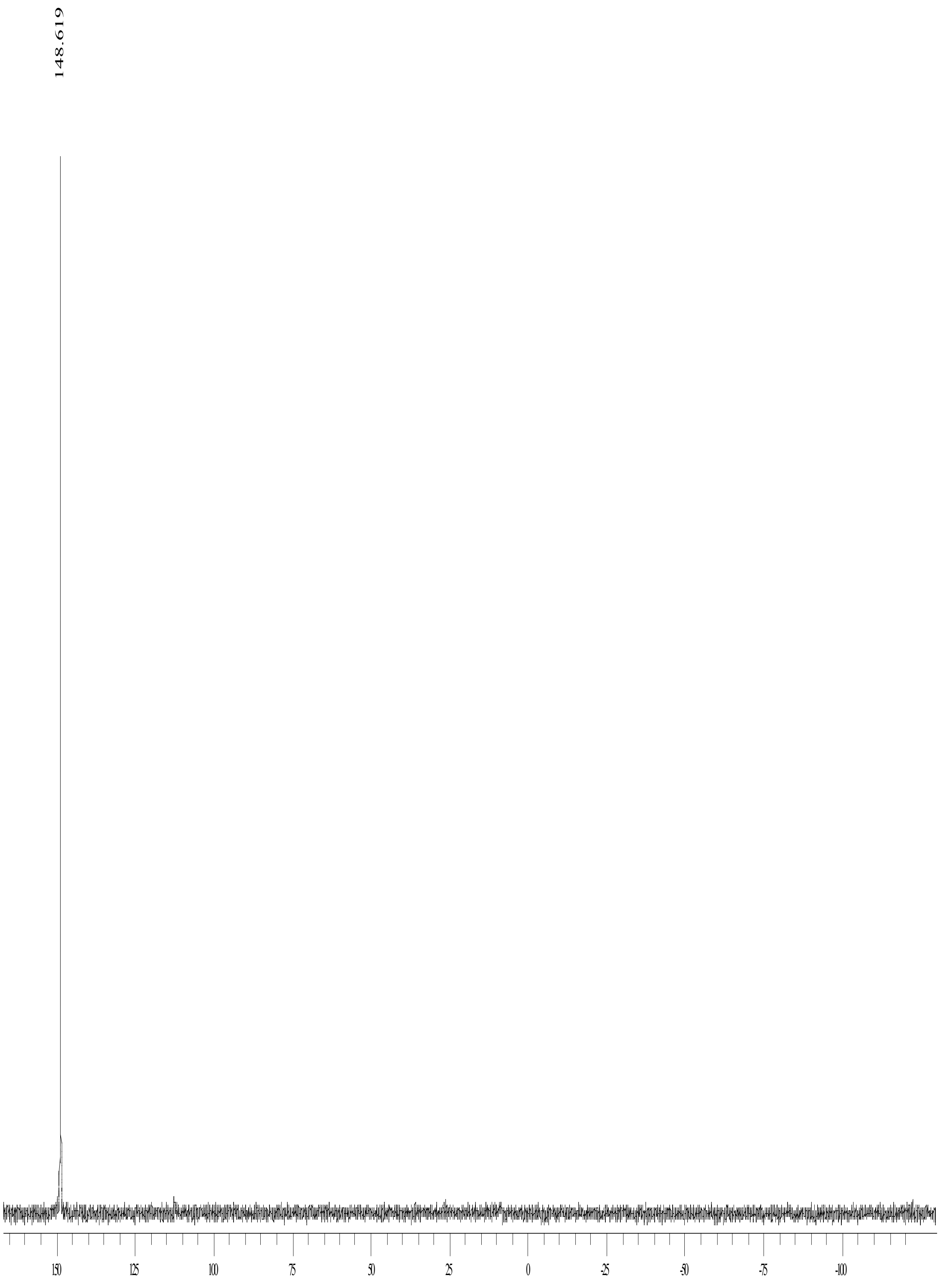


Figure S6. ^{31}P NMR Spectrum of [Ir(COD)(*P*,*C*-**L1**)(**4**)] (**3**).

Comparison of Catalysts:

General Procedure for Enantioselective Allylic Amination Catalyzed by Complex 3 (eq 3): In a drybox, allylamine complex **3** (10.7 mg, 0.0100 mmol) was dissolved in 1 mL of THF in a screw-capped vial. *t*-Butylbenzene (134.1 mg, 1.000 mmol) was added as internal standard. A small magnetic stirbar was added, and the vial was sealed with a cap containing a PTFE septum. Aniline (111.7 mg, 1.200 mmol) and methyl cinnamyl carbonate (192.2 mg, 1.000 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at room temperature for 10 h and monitored by GC every 2 h. ^{1}H-NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers was greater than 99/1. The mixture was then purified by flash column chromatography on silica gel (1.5% ethyl acetate in hexanes) to give 165.3 mg of the allylamine product (79% yield). HPLC analysis indicated that the enantiomeric excess of the product was 96% [Diacel Chiralcel® OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.75/0.25; flow rate = 0.6 mL/min; detection wavelength = 254 nm; TR = 32.1 (major) min., 34.3 min. (minor)]. ^{1}H NMR spectrum was recorded and was similar to published before.

Enantioselective Allylic Amination Catalyzed by Complex 5: The general procedure was followed using ethylene complex **5** (8.7 mg, 0.010 mmol) as catalyst. After 10 h, ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers was greater than 99/1. Flash column chromatography on silica gel gave 171.6 mg of the allylamine product in (82% yield). HPLC analysis indicated that the enantiomeric excess of the product was 96%.

Enantioselective Allylic Amination Catalyzed by the combination of complex 2 and $[Ir(COD)Cl]_2$ (eq 3): The general procedure was followed using the combination of complex **2** (13.8 mg, 0.0100 mmol) and $[Ir(COD)Cl]_2$ (3.4 mg, 0.0050 mmol) as catalyst. After 10 h, ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers was greater than 99/1. Flash column chromatography on silica gel gave 167.4 mg of the allylamine product (80% yield). HPLC analysis indicated that the enantiomeric excess of the product was 96%.

Enantioselective Allylic Amination Catalyzed by the combination of $[Ir(COD)Cl]_2$ and L1 (eq 3): In a drybox, $[Ir(COD)Cl]_2$ (6.7 mg, 0.010 mmol) and **L1** (*Sa*,*Sc*,*Sc*) (10.8 mg, 0.0200 mmol) were dissolved in 0.5 mL of THF in a screw-capped vial. Propylamine (59 mg, 1 mmol) was added, and reaction mixture was mixed for 2 h at room temperature. The THF was evaporated, and the general procedure was followed using the solid resulting from evaporation of the THF as catalyst. After 10 h ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers was greater than 99/1. Flash column chromatography on silica gel gave 161.2 mg of allylamine (77% yield). HPLC analysis indicated that the enantiomeric excess of the product was 96%.

(-)-1-phenyl-*N*-propylprop-2-en-1-amine Preparation of this allylic amine was conducted by published methods using ([Ir(COD)(*P,C*-**L1**)(**L1**)] (**2**) (13.8 mg, 0.0100 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0050 mmol)) methyl cinnamyl carbonate (192 mg, 1.00 mmol) and propylamine (82.8 mg, 1.40 mmol) in 1 mL of THF solvent and an 8 h reaction time at room temperature.[1] ^{1}H NMR analysis of the crude reaction mixture indicated the ratio of regioisomers (b/l) to be 98/2. The mixture was purified by flash column chromatography on silica gel (hexanes/ethylacetate 10:1) to give the title compound (126 mg, 72%). HPLC analysis indicated that the enantiomeric excess of the product was 94% [Diacel CHIRALCEL ODH (0.46 cm x 25 cm); hexanes/2-propanol = 99.0/1.0; flow rate = 0.5 mL/min; detection wavelength = 230 nm; TR = 11.9 (major), 13.3 (minor) min]. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.40–7.20 (m, 3H), 7.22–7.28 (m, 2H), 5.96 (ddd, *J* = 17.1, 10.0, 7.1 Hz, 1H), 5.23 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.12 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.20 (d, *J* = 7.3 Hz, 1H), 2.62-244 (m, 2H), 1.54 (tq, *J* = 7.3, 2.9 Hz, 2H), 1.64 (brs, 1H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.3, 141.5, 128.7, 127.5, 127.3, 115.0, 66.5, 49.8, 23.5, 12.1.

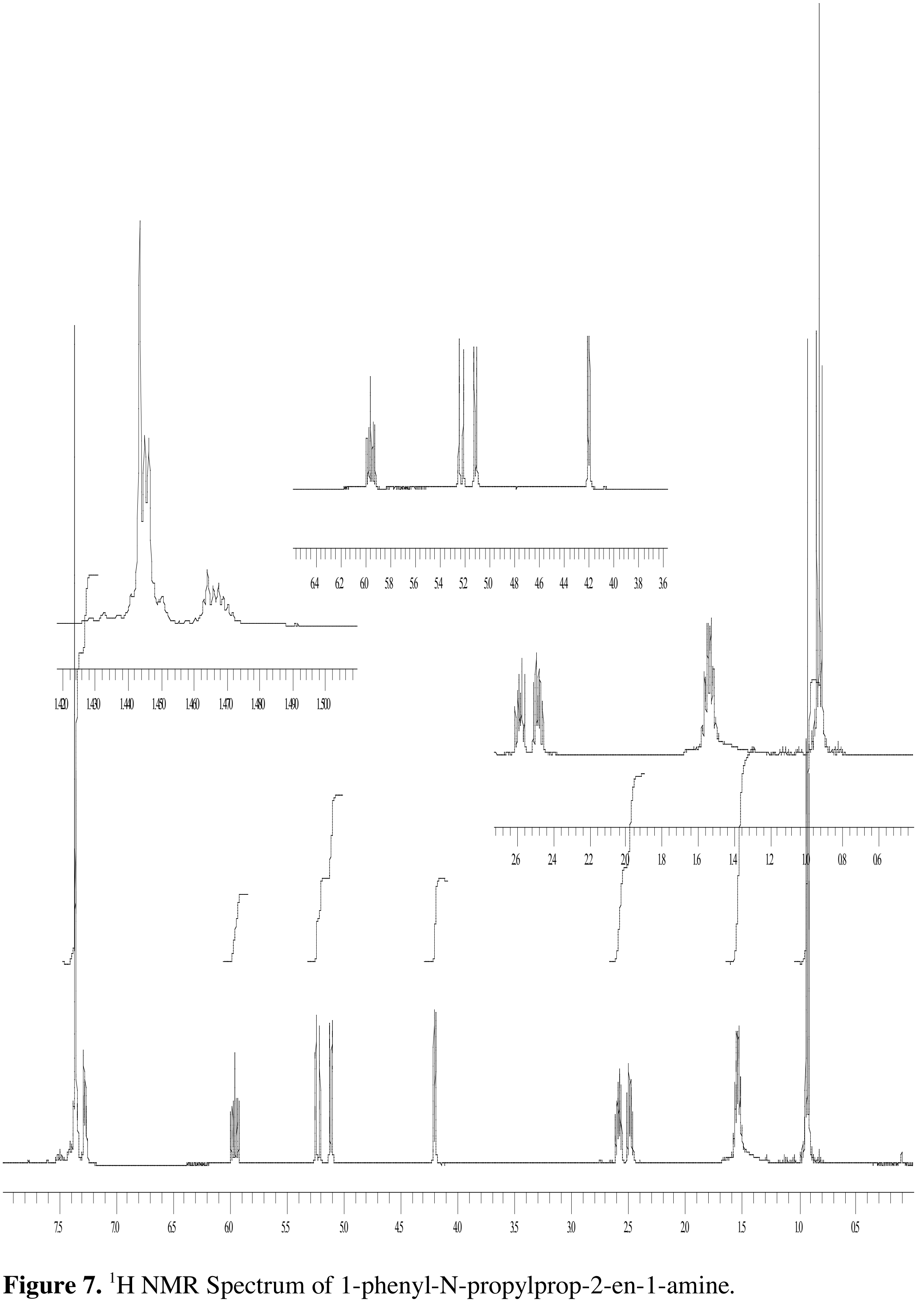


Figure 7. ^{1}H NMR Spectrum of 1-phenyl-N-propylprop-2-en-1-amine.

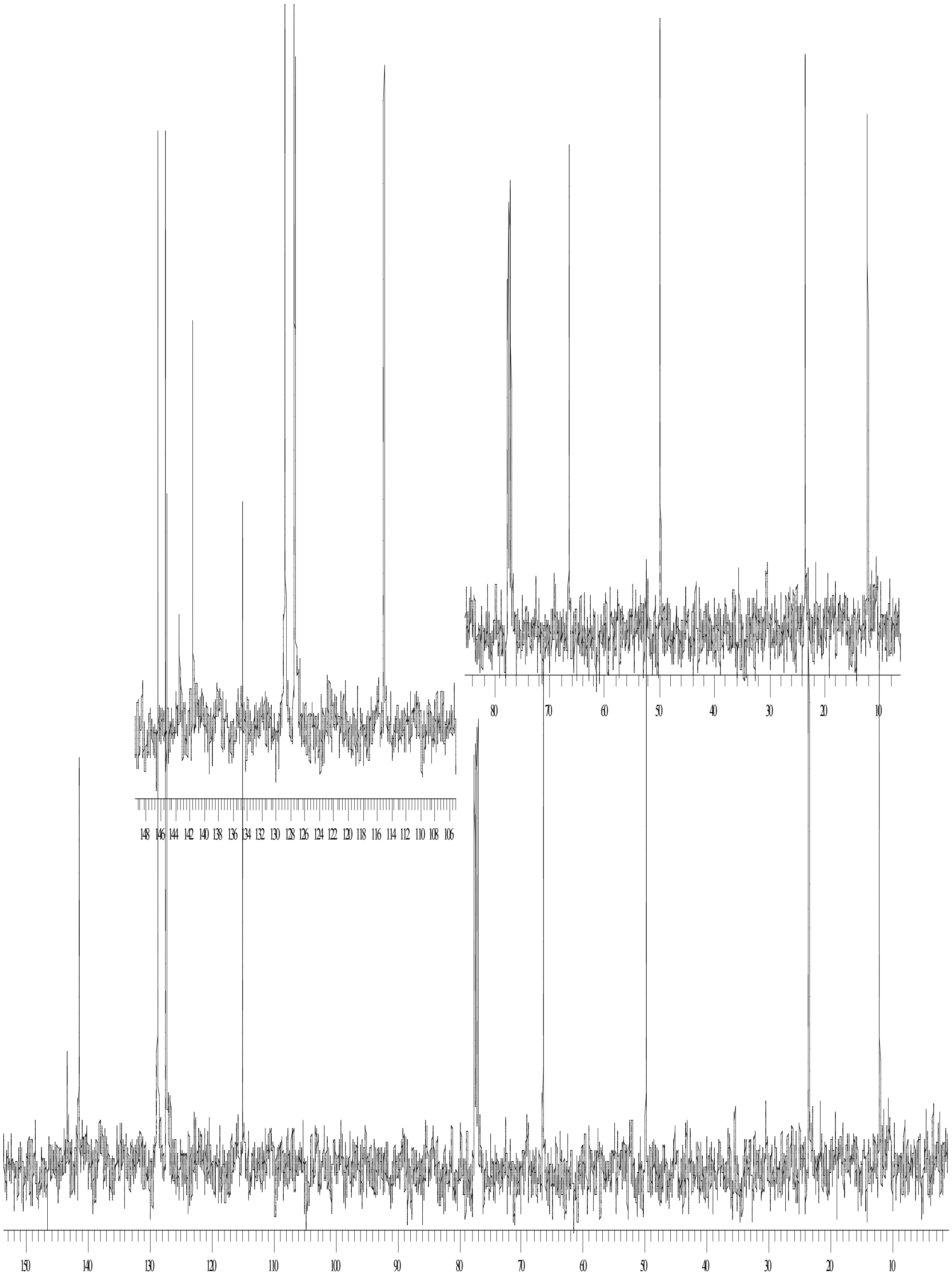


Figure 8. ^{13}C NMR Spectrum of (-)-1-phenyl-N-propylprop-2-en-1-amine.

Measurement of Equilibrium Constants for Table 2:

Representative Procedure: Equation 3, Entry 1. Into a J. Young NMR tube was added a solution of ethylene complex **5** (0.0231 M) and *t*-butylbenzene (0.236 M) in benzene-d_6 (0.5 ml). A sealed capillary tube containing $PO(OPh)_3$ as external standard was then added. The J Young valve was closed, and the tube was inserted into preequilibrated NMR probe at 25° C. A ^{31}P NMR spectrum was recorded. To the NMR tube was then added allyl amine **4** (118.1 mg, 0.5643 mmol). The tube was connected to a vacuum line and frozen with liquid nitrogen. Ethylene was added from a bulb with known volume and measured pressure. The sample was thawed, and a ^{31}P NMR spectrum was obtained. ^{31}P (5 delay times, 100 scans) and ^{1}H NMR spectra (15 s delay time, 32 scans) were recorded at 25 °C. After 2 h, the ratio of complex **3** (δ 148.6 (s, 1P)) to complex **5** (δ 152.4 (s, 1P)) was measured by ^{31}P NMR spectroscopy to be 0.20. The ratio of ethylene (δ 5.22) to allyl amine **4** (C-H signal at δ 5.75) was measured by ^{1}H NMR spectroscopy to be 0.11. After 6 h, the ratio was unchanged, indicating that equilibrium was reached.

Entry 2: The general procedure was followed using (-)-1-phenyl-N-propylprop-2-en-1-amine (184.8 mg, 1.054 mmol). After acquisition of an initial ^{31}P NMR spectrum, the ethylene concentration was reduced by freeze/thaw cycles using an acetone/dry ice bath until both the allylamine complex and the ethylene complex **5** were observed. The ^{31}P NMR chemical shift of [Ir(COD)(*P,C*-**L1**)((-)-1-phenyl-N-propylprop-2-en-1-amine)] was 149.8 ppm. After 2 h, the ratio of this allylamine complex to ethylene complex **5** determined by ^{31}P NMR spectroscopy was 0.17. The ratio of ethylene and (-)-1-phenyl-*N*-propylprop-2-en-1-amine was determined to be 0.028 by integration of the ^{1}H NMR signal for one of the vinyl hydrogens of (-)-1-phenyl-*N*-propylprop-2-en-1-amine at δ 5.83 of and the ethylene signal at δ 5.22. After 6 h, the ratio was unchanged, indicating that equilibrium was reached.

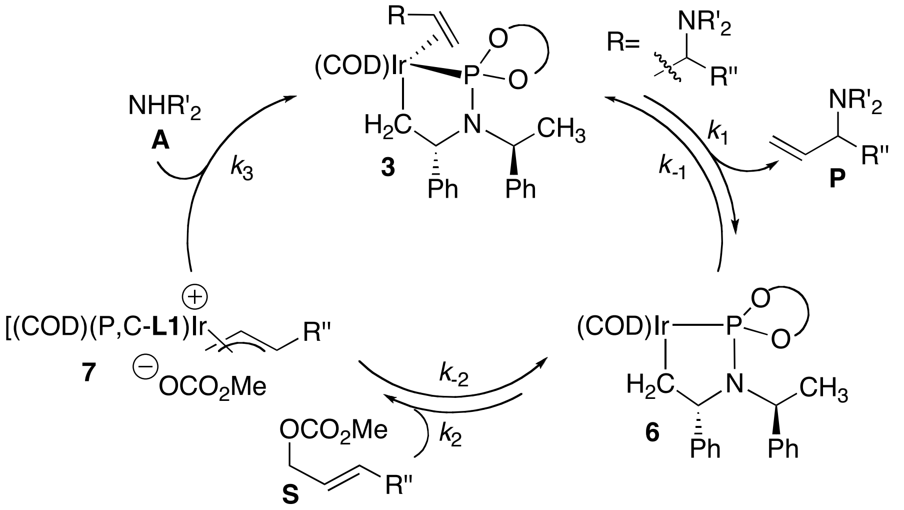
Entry 3: The general procedure was followed using (-)-*N*-(hex-1-en-3-yl)benzenamine (219.1 mg, 1.250 mmol). After acquisition of an initial ^{31}P NMR spectrum, the ethylene concentration was reduced by freeze/thaw cycles using an acetone/dry ice bath until both the allylamine complex and the ethylene complex **5** were both observed. The ^{31}P NMR chemical shift of [Ir(COD)(*P,C*-**L1**)((-)-*N*-(hex-1-en-3-yl)benzenamine)] was δ148.8. The ratio of this allylamine complex to **5**, as determined by ^{31}P NMR spectroscopy was 0.090. The ratio of ethylene to (-)-*N*-(hex-1-en-3-yl)benzenamine was calculated to be 0.0031 by integration of the ^{1}H NMR signal for one of the vinyl hydrogens of (-)-*N*-(hex-1-en-3-yl)benzenamine at δ 5.83 of and the ethylene signal at δ 5.22.

Entry 4: The general procedure was followed using (+)-*N*-(1-phenylallyl)benzenamine (261 mg, 1.25 mmol). After acquisition of an initial ^{31}P NMR spectrum, the ethylene concentration was reduced by freeze/thaw cycles using an acetone/dry ice bath until both the allylamine complex and the ethylene complex **5** were both observed. The ^{31}P NMR chemical shift of [Ir(COD)(*P,C*-**L1**)((+)-*N*-(1-phenylallyl)benzenamine)] was δ 149.2 The ratio of this allylamine complex and the ethylene complex **5** was calculated by ^{31}P NMR spectroscopy to be 0.10. The ratio of ethylene to (+)-*N*-(1-phenylallyl)benzenamine was calculated as 0.0032 from integration of the ^{1}H NMR signal for one of the vinyl hydrogens of (+)-*N*-(1-phenylallyl)benzenamine at δ 5.83 of and the ethylene signal at δ 5.22.

Addition of methyl cinnamyl carbonate to complex 3 and 5: In a drybox, a solution of complex **3** (12.7 mg, 0.0121 mmol) or **5** (10.5 mg, 0.0121 mmol), and a capillary tube containing

$PO(OPh)_3$ as external standard were added to screw-capped NMR tube. A solution of methyl cinnamyl carbonate 2.8 mg, 0.015 mmol) in 0.5 ml of THF was added the NMR tube by syringe. The NMR tube was sealed with a cap, and a ^{31}P NMR spectrum was recorded. The sample was allowed to react in a drybox for 6 h at room temperature, and a second ^{31}P NMR spectrum was recorded. No new resonances in the ^{31}P or ^{1}H NMR spectrum were observed.

Derivation of Kinetic Equations.



Using the method of determinants[2] the full rate equation for the catalytic cycle is:

$$rate = \frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2k_3[\mathbf{S}][\mathbf{A}][\mathrm{Ir}]_{\mathrm{tot}}}{k_1k_3[\mathbf{A}] + k_1k_{-2} + k_1k_2[\mathbf{S}] + k_2k_3[\mathrm{S}][\mathrm{A}] + k_{-1}k_3[\mathbf{A}][\mathbf{P}] + k_{-1}k_{-2}[\mathbf{P}]}$$

The following approximations were made, based on experimental data:
$k_1k_3[\mathbf{A}] << k_{-1}k_3[\mathbf{A}][\mathbf{P}]$ and $k_1k_{-2} << k_{-1}k_{-2}[\mathbf{P}]$ because $k_1 << k_{-1}[\mathbf{P}]$

The approximation $k_1 << k_{-1}[\mathbf{P}]$ is valid because a solution of **3** does not contain free allylamine or four-coordinate complex **6** in concentrations that can be measured by ^{1}H NMR spectroscopy.

$k_1k_2[\mathbf{S}] << k_{-1}k_{-2}$ because a solution of **3** and the allylic carbonate does not generate a new species, such as allyl complex **7**, at the temperatures of the catalytic process.

$[\mathrm{Ir}]_{\mathrm{tot}}=[\mathbf{3}]$ because this is the only iridium complex observed by ^{31}P NMR spectroscopy in the reactions initiated with **3** as catalyst.

These approximations lead to the simplified rate equation:

$$rate = \frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2k_3[\mathbf{S}][\mathbf{A}][\mathrm{Ir}]_{\mathrm{tot}}}{k_2k_3[\mathrm{S}][\mathrm{A}] + k_{-1}k_3[\mathbf{A}][\mathbf{P}] + k_{-1}k_{-2}[\mathbf{P}]}$$

As presented in the text, if dissociation of amine and addition of the allylic carbonate are reversible, then the $k_{-1}k_{-2}$[P] term in the denominator is larger than the other two terms, and the rate equation simplifies to

$$\frac{d[\mathrm{P}]}{dt} = \frac{k[\mathbf{S}][\mathbf{A}][\mathrm{Ir}]_{tot}}{[\mathbf{P}]} \quad \text{in which} \quad k = \frac{k_1 k_2 k_3}{k_{-1}k_{-2}}$$

Kinetic Measurements

Preparation of Stock Solutions.

Preparation of Solution 1. In 2.00 mL volumetric flask was added **5** (10.8 mg, 0.0125 mmol), and the complex was dissolved in benzene-d_6. To this vial was added allylamine **4** (1.3081 g, 6.2500 mmol) by syringe. Benzene-d_6 was then added to the 2 ml mark. This solution was allowed to stand in an inert atmosphere glove box at room temperature for 6 h and was then stored in an inert atmosphere freezer at -35 C. The final concentrations were [**5**]=0.0063 M, [**4**]=3.13 M.

Preparation of Solution 2. In a 5.00 ml volumetric flask was added methyl cinnamyl carbonate (480.5 mg, 2.500 mmol) and *t*-butylbenzene (134.2 mg, 1.000 mmol). Benzene-d_6 was added to the 5 ml mark. This solution was mixed and stored in an inert atmosphere freezer at -35 C. The final concentrations were [methyl cinnamyl carbonate]=0.500 M, [*t*-butylbenzene]=0.200 M.

Preparation of Solution 3. In a 1.00 ml volumetric flask was added **4** (392.3 mg, 1.875 mmol) and benzene-d_6 to the 1 ml mark. The resulting solution was stored in an inert atmosphere freezer at -35 C. The final concentration was [**4**]=1.88 M.

Preparation of Solution 4. In a 2.00 ml volumetric flask was added methyl cinnamyl carbonate (120 mg, 0.625 mmol), *t*-butylbenzene (33.6 mg, 0.250 mmol), aniline (1.1641 g, 12.500 mmol) and benzene-d_6 to the 2 ml mark. The resulting solution was mixed and stored in an inert atmosphere freezer at -35 C. The final concentrations were [methyl cinnamyl carbonate]=0.312 M, [*t*-butylbenzene]= 0.125 M, [aniline]=6.25 M.

Preparation of Solution 5. Into a 2.00 ml volumetric flask was added **4** (1.3081 g, 6.2500 mmol) and benzene-d_6 to the 2 ml mark. The resulting solution was stored in inert atmosphere freezer at -35 C. The final concentration was [**4**]=3.12 M

Preparation of Solution 6. In 2.00 mL volumetric flask was added **5** (10.8 mg, 0.0125 mmol), and the complex was dissolved in benzene-d_6. Benzene-d_6 was then added to the 2 ml mark. This solution was stored in an inert atmosphere freezer at -35 C. The final concentration was [**5**]=0.00625 M.

Determination of the Order in Aniline. Into a 1.00 mL volumetric flask was added solution 2 (0.250 ml), aniline (58.2 mg 0.625 mmol, 116.4 mg 1.250 mmol, 232.8 mg 2.500 mmol, 349.2 mg 3.750 mmol, or 465.7 mg 5.000 mmol) and benzene-d_6 to the 1 ml mark. Into a screw-capped NMR tube was added 0.500 ml of this solution by syringe. To this tube was then added 0.100 ml of Solution 1, and the resulting solution was mixed. The final concentrations were [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.00104 M, [**4**]=0.521 M, and 0.521 M, 1.04 M, 2.08 M, 3.12 M and 4.17 M of aniline. The NMR tube was inserted into the NMR probe, which had been pre-equilibrated to 50 °C. Automated data acquisition was then started.

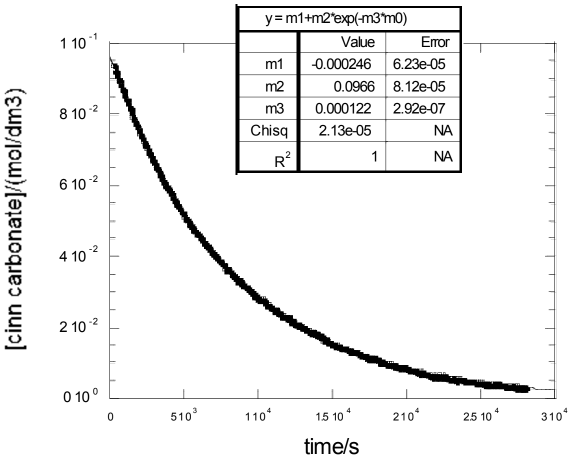


Figure S10. Representative curve for the decay of methyl cinnamyl carbonate during the reaction in eq 3 with [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.0010 M, [**4**]=0.521 M and [aniline]=0.521 M.

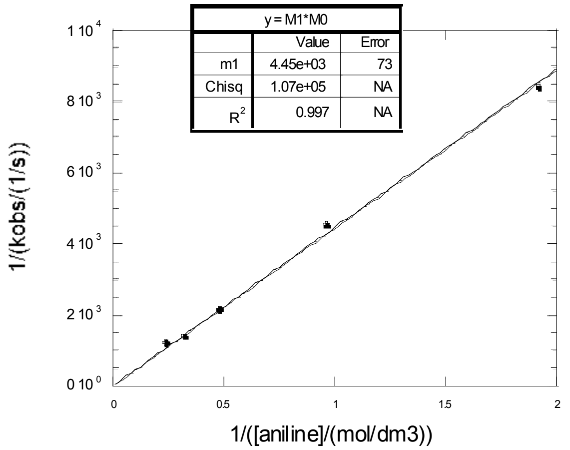


Figure S11. Kinetic data plotted as $1/(k_{obs}/s^{-1})$ vs $1/([\text{aniline}]/\text{moldm}^{-3})$ collected for the reaction in eq 3 conducted with [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.0010 M, [**4**]=0.521 M and 0.521 M, 1.04 M, 2.08 M, 3.12 M and 4.17 M concentrations of aniline.

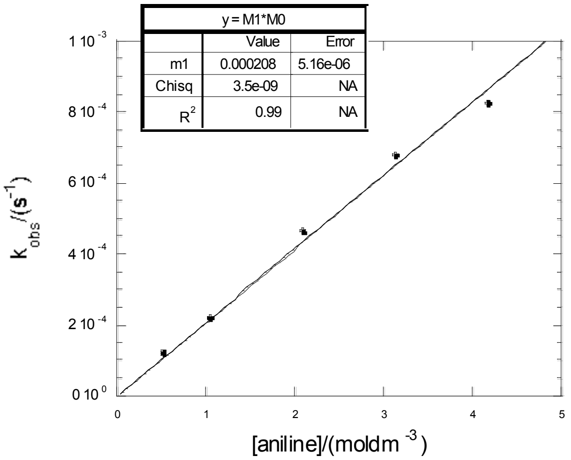
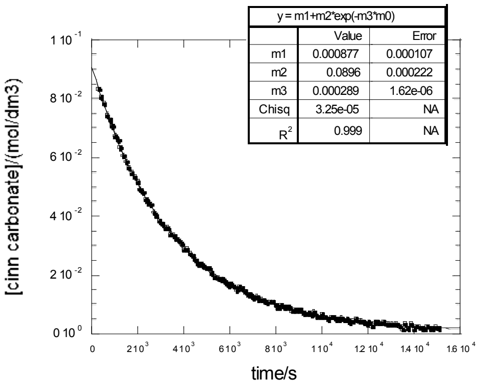


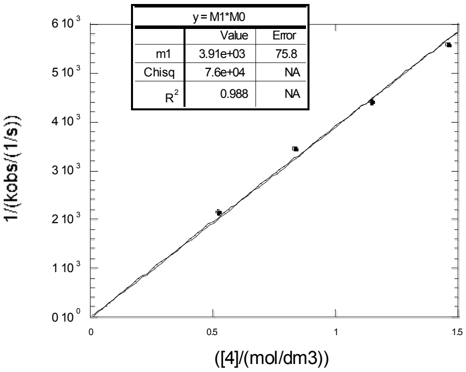
Figure S12. Kinetic data plotted as k_{obs}/s^{-1} vs [aniline]/moldm^{-3} collected for the reaction in eq 3 conducted with [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.0010 M, [**4**]=0.521 M and 0.521 M, 1.04 M, 2.08 M, 3.12 M and 4.17 M concentrations of aniline.

Determination of the Order in Allylamine 4. Into screw cap NMR tube was added solution 1 (0.100 ml), solution 3 (0.100, 0.200, 0.300 ml) and benzene-d_6 (0.200, 0.100, 0 ml). The NMR tube was kept at room temperature for 6 h, after which time solution 4 (0.200 ml) was added to the NMR tube by syringe. The final concentrations were [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]= 0.0417 M, [**5**]=0.00100 M, [**4**]=0.833, 1.15, and 1.46 M and [aniline]=2.08 M. The NMR tube was inserted in the NMR spectrometer probe, which had been preequilibrated to 50 °C. Automated data acquisition was than started. The fourth data point in the plot was obtained from the experiments to determine the order in aniline.



y = m1+m2*exp(-m3*m0)		
	Value	Error
m1	0.000877	0.000107
m2	0.0896	0.000222
m3	0.000289	1.62e-06
Chisq	3.25e-05	NA
R^2	0.999	NA

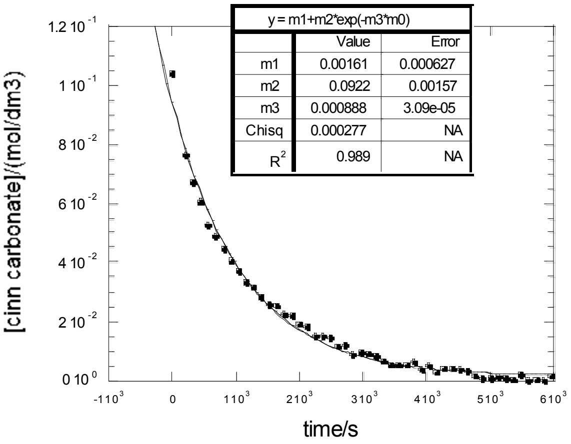
Figure S13. Representative curve for the decay of methyl cinnamyl carbonate during the reaction of eq 3 with [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.00100 M, and [**4**]=0.833 M.



y = M1*M0		
	Value	Error
m1	3.91e+03	75.8
Chisq	7.6e+04	NA
R^2	0.988	NA

Figure S14. Kinetic data for the reaction in eq 3 with [aniline]=2.08 M [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.00100 M, and 0.521, 0.833, 1.15, and 1.46 M concentrations of **4**.

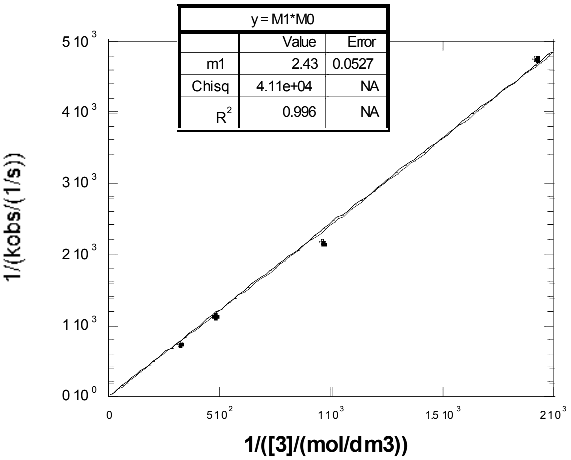
Determination of the Order in Catalyst. Into a screw capped NMR tube was added solution 6 (0.050, 0.200, 0.300 ml), Solution 5 (0.100 ml) and bezene-d_6 (0.250, 0.100, 0 ml). The NMR tube was kept at room temperature for 6 h after which time, solution 4 (0.200 ml) was added to the NMR tube by syringe. The concentrations were [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]= 0.0417 M, [**5**]=0.00050, 0.00210, and 0.00320 M, [**4**]=0.521 M and [aniline]=2.08 M. The NMR tube was inserted in an NMR spectrometer probe, which had been preequilibrated to 50 °C. Automated data collection was than started. The fourth data point in the plot was obtained from the experiments to determine the order in aniline



y = m1+m2*exp(-m3*m0)

	Value	Error
m1	0.00161	0.000627
m2	0.0922	0.00157
m3	0.000888	3.09e-05
Chisq	0.000277	NA
R^2	0.989	NA

Figure S15. Decay of methyl cinnamyl carbonate during the reaction in eq 3 with [aniline]=2.08 M, [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**5**]=0.00200 M, [**4**]=0.521 M.



y = M1*M0

	Value	Error
m1	2.43	0.0527
Chisq	4.11e+04	NA
R^2	0.996	NA

Figure S16. Kinetic data plotted as $1/(k_{obs}/s^{-1})$ vs $1/([\mathbf{3}]/\text{moldm}^{-3})$ collected for reaction in eq 3 with 2.083 M [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**4**]=0.521 M and [**5**]=0.000500, 0.00100, 0.00210, and 0.00320 M concentrations of catalyst **3**.

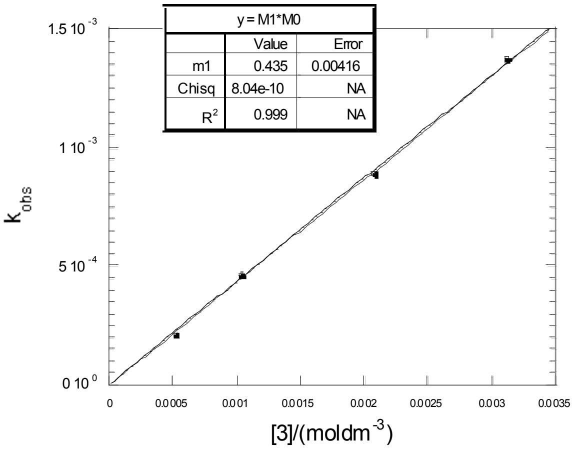


Figure S17. Kinetic data plotted as k$_{obs}$/s^{-1} vs [**3**]/moldm^{-3} collected for reaction in eq 3 with 2.083 M [methyl cinnamyl carbonate]=0.104 M, [*t*-butylbenzene]=0.0417 M, [**4**]=0.521 M and [**5**]=0.000500, 0.00100, 0.00210, and 0.00320 M concentrations of catalyst **3**.

Table S1. Rate constants from three sets of data under pseudo first- order conditions for the reaction in eq 3 catalyzed by 1 mol % **3**

Concentration varied	k/(mol^{-1}dm^{3}s^{-1}
Aniline	0.10±0.01
Allyl amine **4**	0.12±0.01
Ir complex **5**	0.10±0.01

[a] All rate constants were calculated from the pseudo first-order rate constants using the concentrations of aniline, allyl amine **4** and Ir complex **5**.

References

(1) Kiener, C. A.; Shu, C.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14272-14273.

(2) King, E. L.; Altman, C. *J. Phys. Chem.* **1956**, *60*, 1375-1378.