Supporting Information

Iridium Complexes of New NCP Pincer ligands: Catalytic Alkane Dehydrogenation and Alkene Isomerization

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1. General information

a. Materials

All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. THF and toluene were dried with Na and distilled under argon. Hexane was dried with CaH_2 and distilled under argon. *n*-Octane and 1-octene were dried with Na, vacuum transferred, and stored under argon. *Tert*-butylethylene (TBE) was purchased from TCI (96% purity). TBE was dried with $LiAlH_4$, vacuum transferred, and stored under argon. Pinacolborane (HBPin) was purchased from TCI (97% purity) and purified according to the reported procedure.[1] The following chemicals were purchased and used as received: $IrCl_3.xH_2O$ (J&K), di-*tert*-butylchlorophosphine (Acros, 96% purity), $NaBHEt_3$ (1.0 M in toluene) (Aldrich), *trans*-3-octene (TCI, 98% purity), 2,4-hexadiene (*trans* : *cis* = 12 : 1, TCI, 95% purity), 2-hexene (*trans*: *cis* = 2 :1, Acros, 85% purity), *cis*-6-chloro-2-hexene (TCI, 90% purity). $[Ir(cod)Cl]_2$,[2] (PNN)$FeCl_2$ (**3**),[3] ($^{t\text{Bu}}$PCP)IrHCl[4] and ($^{t\text{Bu}}$POCOP)IrHCl[5] were prepared as previously reported.

b. Analytical Methods

NMR spectra were recorded on varian 300 or 400 MHz and angilent 400 MHz at ambient temperature. The residual peak of deuterated solvent was used as a reference for ^{1}H and ^{13}C chemical shifts. ^{31}P NMR chemical shifts were referenced to an external 85% H_3PO_4 standard. GC analysis was acquired on Agilent 7890A gas chromatograph equipped with a flame-ionization detector. GC-MS analysis was performed on Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert mass selective detector. Elemental analysis and high resolution mass spectrometer (HRMS) were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

c. Abbreviations

1-oct = 1-octene

Cis-2 = *cis*-2-octene

COA = cyclooctane

DME = dimethoxyethane

DMSO = dimethyl sulfoxixde

HBPin = pinacolborane

TBE = *tert*-butylethylene

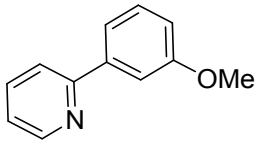
THF = tetrahydrofuran

Trans-2 = *trans*-2-octene

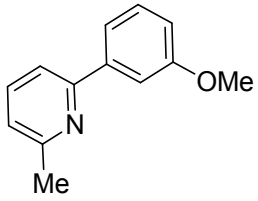
Trans-3 = *trans*-3-octene

TONs = turnover numbers

2. Procedures for preparation of iridium complexes

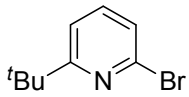


2-(3-methoxyphenyl)pyridine. To a 250 mL 3-neck flask, 2-bromopyridine (4.4 g, 27.8 mmol), 3-bromophenylboronic acid (5.0 g, 32.8 mmol), K_2CO_3 (9.4 g, 68.0 mmol), DME (50 mL) and distilled water (33 mL) were added. The reaction mixture was purged with argon for 30 min, then $Pd(PPh_3)_4$ (1.3 g, 1.1 mmol) was added and the mixture was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and the solution was filtrated. The filtrate was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After the removal of the solvent, the crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether, v/v = 1/20), affording 3.2 g (61% yield) product as colorless oil. ^{1}H NMR (400 MHz, CD_3Cl) : δ 8.69 (d, *J* = 8.0 Hz, 1H), 7.76-7.70 (m, 2H), 7.59 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.23 (td, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.98 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 3.89 (s, 3H). The spectroscopic data correspond to reported data.[6]

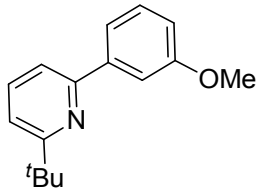


2-(3-methoxyphenyl)-6-methylpyridine. To a 250 mL 3-neck flask, 2-bromo-6-methylpyridine (5.1 g, 29.8 mmol), 3-bromophenylboronic acid (5.0 g, 32.6 mmol),

K_2CO_3 (9.8 g, 71 mmol), DME (60 mL) and distilled water (38 mL) were added. The reaction mixture was purged with argon for 30 min, then $Pd(PPh_3)_4$ (1.7 g, 1.5 mmol) was added and the mixture was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and the solution was filtrated. The filtrate was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether, v/v = 1/50), affording 3.0 g (51% yield) product as colorless oil. ^{1}H NMR (400 MHz, CD_3Cl): δ 7.63 (td, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.58 (m, 1H), 7.54 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.37 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.95 (m, 1H), 3.89 (s, 3H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3Cl): δ 159.8, 157.9, 156.3, 140.9, 136.6, 129.4, 121.5, 119.1, 117.4, 114.3, 112.1, 54.9, 24.5. HRMS (ESI) m/z (M+H+) calcd for $C_{13}H_{14}NO$: 200.1070, found: 200.1072.

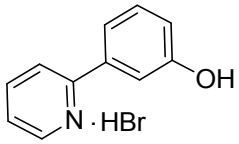


2-bromo-6-(*tert*-butyl)pyridine. Prepared according to a previously reported procedure.[7] ^{1}H NMR (400 MHz, CD_3Cl): 7.44 (t, *J* = 8.0 Hz, 1H) , 7.26 (d, *J* = 8.0 Hz, 2H), 1.34 (s, 9H).

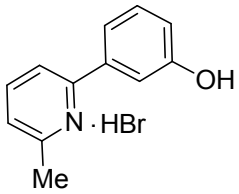


2-(*tert*-butyl)-6-(3-methoxyphenyl)pyridine. To a 250 mL 3-neck flask, 2-bromo-6-(*tert*-butyl)pyridine (3.6 g, 16.8 mmol), 3-bromophenylboronic acid (3.1 g, 20.0 mmol), K_2CO_3 (5.8 g, 42.0 mmol), DME (30 mL) and distilled water (20 mL) were added. The reaction mixture was purged with argon for 30 min, then $Pd(PPh_3)_4$ (1.0 g, 0.9 mmol) was added and the mixture was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and the solution was filtrated. The filtrate was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether, v/v = 1/100), affording

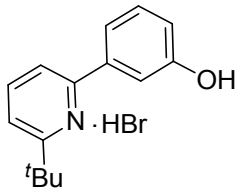
2.7 g (67% yield) product as colorless oil. ^{1}H NMR (400 MHz, CD_3Cl): δ 7.85 (m, 1H), 7.73 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.32 (m, 1H), 7.02 (m, 1H), 3.94 (s, 3H), 1.52 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CD_3Cl): δ 168.9, 160.1, 155.1, 141.5, 136.8, 129.6, 119.3, 117.6, 117.0, 114.3, 112.5, 55.3, 37.8, 30.3. HRMS (ESI) m/z (M+) calcd for $C_{16}H_{19}NO$: 241.1465, found: 241.1467.



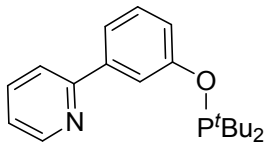
3-(pyridin-2-yl)phenol hydrobromide. To a 100 mL flask, 2-(3-methoxyphenyl)pyridine (3.2 g, 17.3 mmol) and a 40% HBr (60 mL) aqueous solution were added. The reaction was heated at 120 °C for 12 h. After removal of the volatiles, the crude product was recrystallized with ethanol, affording 3.6 g (85% yield) product as beige white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (m, 1H), 8.40 (t, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.44-7.39 (m, 3H), 7.01 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 158.1, 151.9, 145.9, 143.1, 133.0, 130.9, 125.4, 125.2, 119.0, 118.9, 114.8. Elemental analysis calcd for $C_{11}H_{10}BrNO$ (250.99): C, 52.41; H, 4.00; N, 5.56. Found: C, 52.21; H, 4.29; N, 5.56.



3-(6-methylpyridin-2-yl)phenol hydrobromide. To a 100 mL flask, 2-(3-methoxyphenyl)-6-methylpyridine (2.0 g, 10.0 mmol) and a 40% HBr (40 mL) aqueous solution were added. The reaction was heated at 120 °C for 12 h. After removal of the volatiles, the crude product was recrystallized with ethanol, affording 2.4 g (90% yield) product as beige white solid. ^{1}H NMR(400 MHz, DMSO-d_6): δ 8.44 (t, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 2H), 7.08 (m, 1H), 2.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.9, 154.9, 152.0, 145.3, 133.2, 130.5, 125.8, 122.7, 119.3, 118.5, 115.2, 20.1. Elemental analysis calcd for $C_{12}H_{12}BrNO$ (265.01): C, 54.16; H, 4.54; N, 5.26. Found: C, 53.99; H, 4.72; N, 5.28.



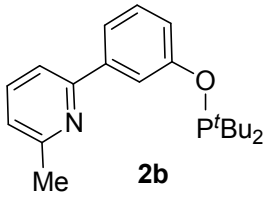
3-(6-(*tert*-butyl)pyridin-2-yl)phenol hydrobromide. To a 100 mL flask 2-(*tert*-butyl)-6-(3-methoxyphenyl)pyridine (2.7 g, 11.0 mmol) and a 40% HBr (60 mL) aqueous solution were added. The reaction was heated at 120 °C for 12 h. After removal of the volatiles, the crude product was recrystallized with ethanol/petroleum ether, affording 2.9 g (84% yield) product as beige white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.53-7.42 (m, 3H), 7.31 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 166.1, 157.7, 153.9, 142.5, 136.8, 130.3, 121.4, 120.4, 118.9, 117.4, 114.8, 37.2, 29.6. Elemental analysis calcd for $C_{15}H_{18}BrNO$ (307.06): C, 58.45; H, 5.89; N, 4.54. Found: C, 58.37; H, 5.89; N, 4.42.



2a

2-(3-((di-*tert*-butylphosphino)oxy)phenyl)pyridine 2a. Di-*tert*-butylchlorophosphine (0.42 mL, 2.2 mmol) was added to a solution of 3-(pyridin-2-yl)phenol hydrobromide (0.5 g, 2.0 mmol) and NaH (0.18 mg, 4.4 mmol, 60% purity) in 5 mL THF in a 25 mL Schlenk flask. The flask was sealed with a Teflon plug and then heated at 100 °C for 3 h. After evaporation of the solvent under vacuum, the residue was extracted with 30 mL hexane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of hexane under vacuum, the flask was heated at 70 °C for 1 h under vacuum to remove the remaining di-*tert*-butylchlorophosphine. The product was obtained as colorless viscous oil (0.5 g, 73% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 8.56 (m, 1H), 8.41 (m, 1H), 7.75 (m, 1H), 7.38 (m, 1H), 7.36 (m, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.06 (m, 1H), 6.62 (m, 1H), 1.15 (d, J = 12.0 Hz, 18H). ^{31}P NMR (162 MHz, C_6D_6): δ 152.3. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) : δ 160.9 (d, J = 10.0 Hz), 157.1, 149.9, 141.4, 136.4, 129.9, 122.2, 120.3 (d, J = 1.0 Hz), 120.2, 119.2 (d, J = 12.0 Hz), 117.4 (d, J = 10.0 Hz), 35.8 (d, J = 27.0 Hz), 27.6 (d, J = 16.0 Hz). HRMS (ESI) m/z (M+) calcd for $C_{19}H_{27}NOP$:

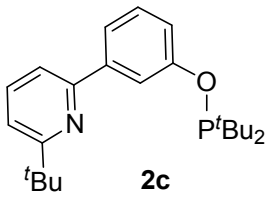
316.18248, found: 316.18353.



2b

2-(3-((di-*tert*-butylphosphino)oxy)phenyl)-6-methylpyridine 2b.

Di-*tert*-butylchlorophosphine (0.36 mL, 2.1 mmol) was added to a solution of 3-(6-methylpyridin-2-yl)phenol hydrobromide (0.5 g, 1.9 mmol) and NaH (0.17 g, 4.1 mmol, 60% purity) in 5 mL THF in a 25 mL Schlenk flask. The flask was sealed with a Teflon plug and then heated at 100 °C for 3 h. After evaporation of the solvent under vacuum, the residue was extracted with 30 mL hexane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of hexane under vacuum, the flask was heated at 70 °C for 1 h under vacuum to remove the remaining di-*tert*-butylchlorophosphine. The product was obtained as colorless viscous oil (0.434 g (70% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 8.36 (m, 1H), 7.78 (m, 1H), 7.40 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 1.15 (d, *J* = 12.0 Hz, 18H). ^{31}P NMR (162 MHz, C_6D_6): δ 151.9. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 160.9 (d, *J* = 9.0 Hz), 158.5, 156.6, 141.8, 136.7, 129.9, 121.6, 120.5 (d, *J* = 1.0 Hz), 118.8 (d, *J* = 12.0 Hz), 117.5 (d, *J* = 9.0 Hz), 117.4, 35.8 (d, *J* = 27.0 Hz), 27.6 (d, *J* = 15.0 Hz), 24.8. HRMS (ESI) m/z (M+H+) calcd for $C_{20}H_{29}NOP$: 330.19813, found: 330.19885.

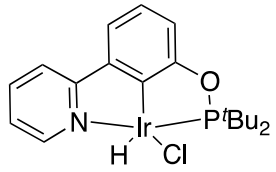


2c

2-(*tert*-butyl)-6-(3-((di-*tert*-butylphosphino)oxy)phenyl)pyridine 2c.

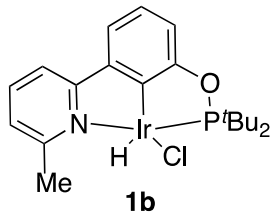
Di-*tert*-butylchlorophosphine (0.34 mL, 2.0 mmol) was added to a solution of 3-(6-(*tert*-butyl)pyridin-2-yl)phenol hydrobromide (0.5 g, 1.6 mmol) and NaH (0.14 g, 3.6 mmol, 60% purity) in 5 mL THF in a 25 mL Schlenk flask. The flask was sealed with a Teflon plug and then heated at 100 °C for 3 h. After evaporation of the solvent under vacuum, the residue was extracted with 30 mL hexane, and the extract was cannula transferred and

filtered through a pad of Celite. After removal of hexane under vacuum, the flask was heated at 70 °C for 1 h under vacuum to remove the remaining di-*tert*-butylchlorophosphine. The product was obtained as colorless viscous oil (0.452 g (75% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 8.39 (d, *J* = 1.0 Hz, 1H,), 7.81 (m, 1H), 7.36 (m, 1H), 7.31 (m, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.16 (m, 1H), 6.95 (m, 1H), 1.42 (s, 3H), 1.17 (d, *J* = 12.0 Hz, 18H). ^{31}P NMR (162 MHz, C_6D_6): δ 153.0. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 169.0, 160.8 (d, *J* = 10.0 Hz), 155.7, 142.0, 136.9, 129.9, 120.5 (d, *J* = 1.0 Hz), 119.0 (d, *J* = 10.0 Hz), 117.5, 117.4 (d, *J* = 11.0 Hz), 117.3, 37.9, 35.8 (d, *J* = 26.0 Hz), 30.4, 27.6 (d, *J* = 16.0 Hz). HRMS (ESI) m/z (M+) calcd for $C_{20}H_{34}NOP$: 371.24508, found: 371.07178.



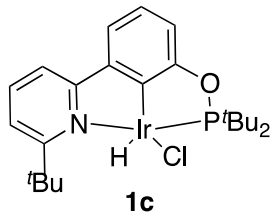
1a

Iridium Complexe 1a. In a 50 mL Schlenk flask, compound **2a** (0.37 g, 1.2 mmol) and $[Ir(cod)Cl]_2$ (0.37 g, 0.56 mmol) were dissolved in 20 mL toluene. The flask was sealed with a teflon plug and then heated at 120 °C for 12 h under hydrogen atmosphere. Toluene was then removed under vacuum, and the residue was washed with hexane. The solid was dried under vacuum to give 0.48 g (75% yield) product as red solid. The product (20 mg) was dissolved in toluene (2 mL), and pentane (1.5 mL) was added slowly. The solvents evaporated slowly at ambient temperature in the glovebox. After a few days, red crystals of **1a(H_2O)** suitable for X-ray analysis were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 9.75 (s, 1H), 7.02 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.87-6.83 (m, 2H), 6.55 (t, *J* = 6.0 Hz, 1H,), 1.34 (d, *J* = 12.0 Hz, 9H), 1.20 (d, *J* = 12.0 Hz, 9H,), -39.24 (b, 1H). ^{31}P NMR (162 MHz, C_6D_6): δ 160.8 (d, *J* = 21.1 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 167.1, 165.4, 150.3, 144.1, 143.9, 138.3, 122.9, 122.4, 118.5, 118.0, 111.2 (d, *J* = 10.0 Hz), 41.9 (d, *J* = 26.0 Hz), 39.0 (d, *J* = 31.0 Hz), 28.1 (d, *J* = 4.0 Hz), 27.9 (d, *J* = 5.0 Hz). Elemental analysis calcd for $C_{19}H_{26}ClIrNOP$ (543.11): C, 42.02; H, 4.83; N, 2.58. Found: C, 42.54; H, 5.25; N, 2.51.



1b

Iridium Complexe 1b. In a 50 mL Schlenk flask, compound **2b** (0.25 g, 0.8 mmol) and $[Ir(cod)Cl]_2$ (0.25 g, 0.4 mmol) were dissolved in 20 mL toluene. The flask was sealed with a teflon plug and then heated at 120 °C for 12 h under hydrogen atmosphere. Toluene was then removed under vacuum, and the residue was washed with hexane. The solid was dried under vacuum to give 0.3 g (71% yield) product as red solid. The product (20 mg) was dissolved in toluene (2 mL), and pentane (1.5 mL) was added slowly. The solvents evaporated slowly at ambient temperature in the glovebox. After a few days, red crystals of **1b** suitable for X-ray analysis were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.22-7.14 (m, 3H), 6.79 (d, J = 8.0 Hz, 1H), 3.49 (s, 3H), 1.79 (d, J = 12.0 Hz, 9H), 1.65 (d, J = 12.0 Hz, 9H), -33.27 (d, J = 20.0 Hz, 1H). ^{31}P NMR (162 MHz, C_6D_6): δ 156.4 (d, J = 13.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 165.3, 164.2, 162.7, 142.3, 142.3, 137.9, 123.7, 122.7, 118.1, 116.1, 110.9 (d, J = 10.0 Hz), 41.9 (d, J = 27.0 Hz), 38.9 (d, J = 31.0 Hz), 28.5 (d, J = 5.0 Hz), 27.7 (d, J = 4.0 Hz), 27.1. Elemental analysis calcd for $C_{20}H_{28}ClIrNOP$ (557.12): C, 43.12; H, 5.07; N, 2.51. Found: C, 42.70; H, 5.20; N, 2.61.



1c

Iridium Complexe 1c. In a 50 mL Schlenk flask, compound **2c** (0.44 g, 1.2 mmol) and $[Ir(cod)Cl]_2$ (0.38 g, 0.6 mmol) were dissolved in 20 mL toluene. The flask was sealed with a teflon plug and then heated at 120 °C for 12 h under hydrogen atmosphere. Toluene was then removed by vacuum, and the residue was washed with hexane. The solid was dried under vacuum to give 0.55 g (77% yield) product as light yellow-green solid. The product (30 mg) was dissolved in benzene (3 mL). The solvents evaporated slowly at ambient temperature in the glovebox. After a few days, light yellow-green

crystals of **1c** suitable for X-ray analysis were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 7.09 (d, J = 8.0 Hz, 1H), 6.99-6.92 (m, 2H), 6.85-6.79 (m, 2H), 6.69 (d, J = 8 Hz, 1H), 1.65 (d, J = 12.0 Hz, 9H), 1.28 (d, J = 16.0 Hz, 9H), 1.20 (s, 9H), -21.89 (d, J = 20.0 Hz, 1H). ^{31}P NMR (162 MHz, C_6D_6): δ 164.3 (d, J = 14.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 169.4, 162.6 (d, J = 3.0 Hz), 162.4 (d, J = 2.0 Hz), 141.8, 141.8, 137.5, 122.9, 120.1 (d, J = 3.0 Hz), 118.0, 117.3, 110.0 (d, J = 10.0 Hz), 44.4, 42.3 (d, J = 24.0 Hz), 38.6 (d, J = 31.0 Hz), 28.9 (d, J = 5.0 Hz), 28.7 (d, J = 4.0 Hz), 27.8. Elemental analysis calcd for $C_{23}H_{34}ClIrNOP$ (599.17): C, 46.11; H, 5.72; N, 2.34. Found: C, 46.06; H, 6.00; N, 2.45.

3. Crystal structures and crystallographic data for Ir complexes

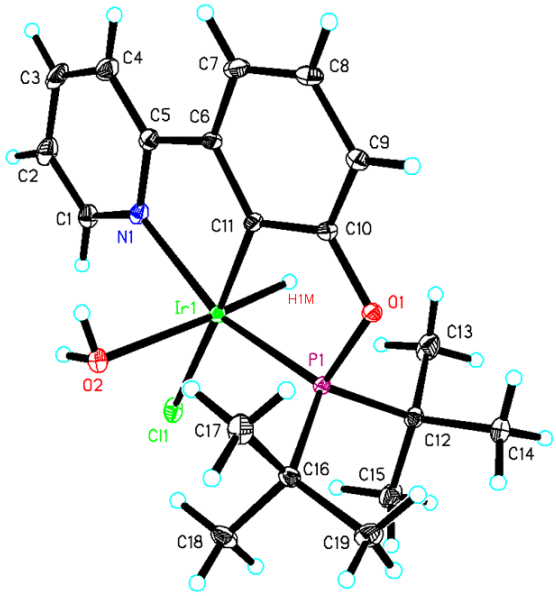


Figure S1. Crystal structure for **1a(H$_2$O)**

Table S1-1. Selected bond length for **1a(H$_2$O)**

Selected bond length	Distance (Å)
Ir(1)-C(11)	1.955(3)

Ir(1)-N(1)	2.158(3)
Ir(1)-P(1)	2.2143(8)
Ir(1)-O(2)	2.266(2)
Ir(1)-Cl(1)	2.4806(9)

Table S1-2. Selected bond angles for **1a(H_2O)**

Selected bond angles	(Deg)
C(11)-Ir(1)-N(1)	78.49(12)
C(11)-Ir(1)-P(1)	81.54(10)
N(1)-Ir(1)-P(1)	159.85(8)
C(11)-Ir(1)-Cl(1)	174.42(10)
N(1)-Ir(1)-Cl(1)	96.78(8)
P(1)-Ir(1)-Cl(1)	103.02(3)

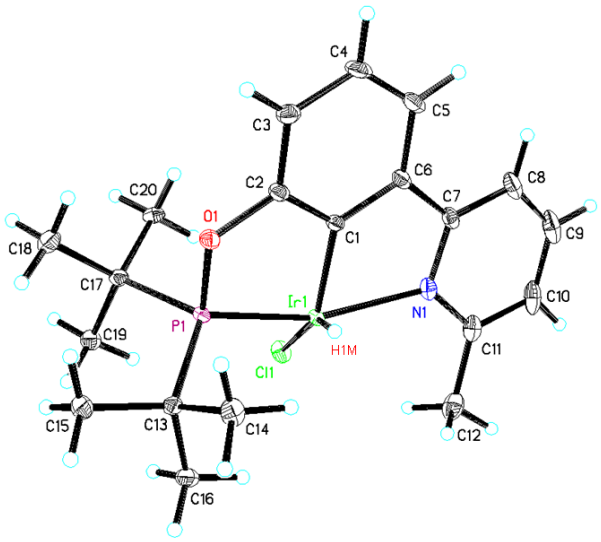


Figure S2. Crystal structure for **1b**

Table S2-1. Selected bond length for **1b**

Selected bond length	Distance (Å)

Ir(1)-C(1)	1.955(2)
Ir(1)-N(1)	2.158(2)
Ir(1)-P(1)	2.2239(7)
Ir(1)-Cl(1)	2.3929(7)

Table S2-2. Selected bond angles for **1b**

Selected bond angles	(Deg)
C(1)-Ir(1)-N(1)	78.82(10)
C(1)-Ir(1)-P(1)	81.83(8)
N(1)-Ir(1)-P(1)	160.61(7)
C(1)-Ir(1)-Cl(1)	140.23(8)
N(1)-Ir(1)-Cl(1)	93.32(6)
P(1)-Ir(1)-Cl(1)	102.49(2)

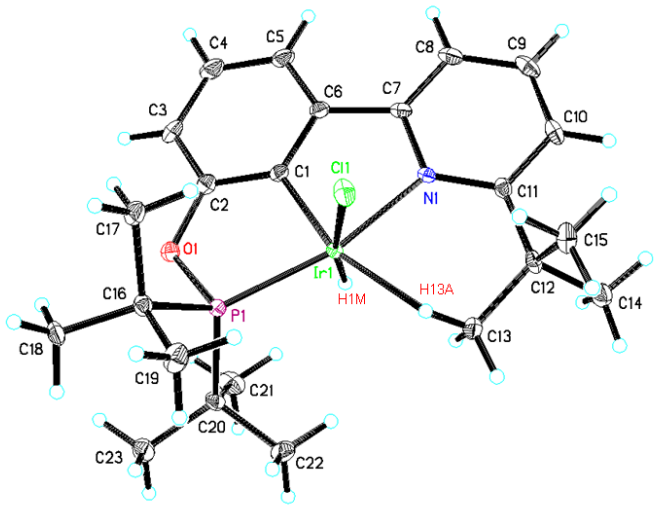


Figure S3. Crystal structure for **1c**

Table S3-1. Selected bond length for **1c**

Selected bond length	Distance (Å)

Ir(1)-C(1)	1.939(4)
Ir(1)-N(1)	2.114(3)
Ir(1)-P(1)	2.2374(10)
Ir(1)-Cl(1)	2.4769(9)

Table S3-2. Selected bond angles for **1c**

Selected bond angles	(Deg)
C(1)-Ir(1)-N(1)	80.90(13)
C(1)-Ir(1)-P(1)	81.24(11)
N(1)-Ir(1)-P(1)	161.52(8)
C(1)-Ir(1)-Cl(1)	103.38(11)
N(1)-Ir(1)-Cl(1)	85.18(8)
P(1)-Ir(1)-Cl(1)	103.54(3)

Table S4. Crystal data and structure refinement for **1a(H_2O)**

Empirical formula	C19 H30 Cl Ir N O3 P
Formula weight	579.06
Temperature	140(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.0810(8) Å alpha = 79.849(2) b = 8.7266(8) Å beta = 79.048(2)° c = 15.7699(15) Å gamma = 79.265(2)°
Volume	1061.23(18) $Å^3$
Z, Calculated density	2, 1.812 Mg/m^3
Absorption coefficient	6.510 mm^{-1}
F(000)	568
Crystal size	0.20 x 0.04 x 0.03 mm^3
Theta range for data collection	2.40 to 30.90°.
Limiting indices	-11<=h<=11, -12<=k<=8, -22<=l<=22
Reflections collected / unique	10752 / 6602 [R(int) = 0.0250]
Completeness to theta = 30.90°	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8287 and 0.3559
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6602 / 0 / 245
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0251, wR2 = 0.0594
R indices (all data)	R1 = 0.0311, wR2 = 0.0611
Largest diff. peak and hole	0.895 and -1.101 e. $Å^{-3}$

Table S5. Crystal data and structure refinement for **1b**

Empirical formula	C20 H28 Cl Ir N O P
Formula weight	557.05
Temperature	140(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.1303(10) A alpha = 90°
	b = 13.7700(14) A beta = 105.782(2)°
	c = 15.0040(15) A gamma = 90°
Volume	2014.1(3) $Å^3$
Z, Calculated density	4, 1.837 Mg/m^3
Absorption coefficient	6.849 mm^{-1}
F(000)	1088
Crystal size	0.30 x 0.25 x 0.16 mm^3
Theta range for data collection	2.04 to 30.60°.
Limiting indices	-14<=h<=14, -16<=k<=19, -21<=l<=21
Reflections collected / unique	19210 / 6175 [R(int) = 0.0283]
Completeness to theta = 30.60°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4070 and 0.2331
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6175 / 0 / 233
Goodness-of-fit on F^2	0.989
Final R indices [I>2sigma(I)]	R1 = 0.0221, wR2 = 0.0511
R indices (all data)	R1 = 0.0312, wR2 = 0.0544
Largest diff. peak and hole	2.315 and -1.768 e. $Å^{-3}$

Table S6. Crystal data and structure refinement for **1c**

Empirical formula	C26 H37 Cl Ir N O P
Formula weight	638.19
Temperature	133(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2
Unit cell dimensions	a = 15.6237(15) A alpha = 90°
	b = 16.1007(16) A beta = 90°
	c = 9.9759(10) A gamma = 90°
Volume	2509.5(4) $Å^3$
Z, Calculated density	4, 1.689 Mg/m^3
Absorption coefficient	5.509 mm^{-1}
F(000)	1268
Crystal size	0.15 x 0.08 x 0.05 mm^3
Theta range for data collection	1.82 to 30.78°.
Limiting indices	-22<=h<=22, -15<=k<=23, -14<=l<=14
Reflections collected / unique	24962 / 7798 [R(int) = 0.0469]
Completeness to theta = 30.78°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7702 and 0.4921
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7798 / 6 / 320
Goodness-of-fit on F^2	0.880
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0507
R indices (all data)	R1 = 0.0327, wR2 = 0.0528
Absolute structure parameter	-0.016(6)
Largest diff. peak and hole	0.860 and -0.922 e. $Å^{-3}$

4. Procedures for alkane dehydrogenation

Table 1. In an argon-filled glovebox, 5.0 μmol of the iridium complex (**1a**, **1b** or **1c**) and 11.0 μmol of sodium *tert*-butyloxide were dissolved in 4.7 mL of cyclooctane (COA). *Tert*-butylethylene (2.5 mmol) was added to the solution. The solution was transfered into a 10 mL thick-wall tube. The tube was sealed with a teflon plug under an argon atmosphere, and the solution stirred in a 150 °C oil bath. Periodically, the flask was removed from the bath and cooled to room temperature. An aliquot was removed from the flask and analyzed by GC.

The effect of different concentration of *tert*-butylethylene for transfer dehydrogenation of cyclooctane

In an argon-filled glovebox, iridium complexe **1a** (2.7 mg, 5.0 μmol) and sodium *tert*-butyloxide (1.1 mg, 11.0 μmol) were dissolved in cyclooctane. *Tert*-butylethylene (2.5 mmol, 5.0 mmol, 10.0 mmol or 12.5 mmol, respectively) was added to the solution. The solution was transfered into a 10 mL thick-wall tube. The tube was sealed with a teflon plug under an argon atmosphere, and the solution stirred in a 150 °C oil bath. Periodically, the flask was removed from the bath and cooled to room temperature. An aliquot was removed from the flask and analyzed by GC.

Table S7. Transfer-dehydrogenation of COA with 0.5 M, 1.0 M, 2.0 M or 2.5 M of TBE catalyzed by **1a/** NaO^{t}Bu at 150 °C

[Ir]/TBE / Time	1/500 (TONs)	1/1000 (TONs)	1/2000 (TONs)	1/2500 (TONs)
10 min	168	123	101	71
30 min	257	238	188	150
1 h	333	326	270	220
5 h	446	514	438	364

12 h	466	582	510	420

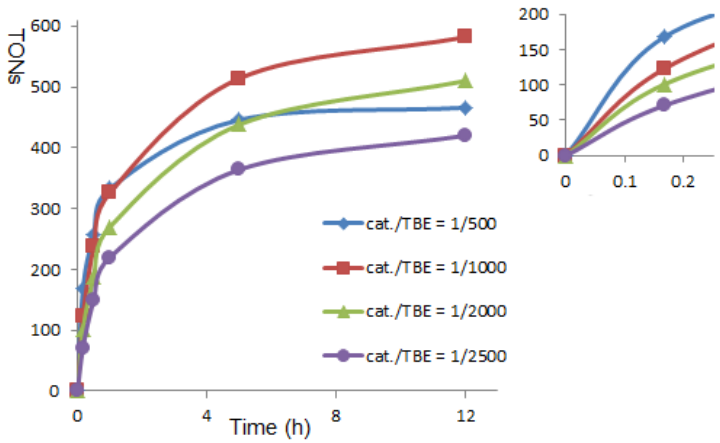


Figure S4. TONs vs time for transfer-dehydrogenations of COA with 0.5 M, 1.0 M, 2.0 M or 2.5 M of TBE

Table 2. In an argon-filled glovebox, 5.0 μmol of the iridium complexe (**1a**, **1b** or **1c**) and 11.0 μmol of sodium *tert*-butyloxide were dissolved in *n*-octane (4.7mL). *Tert*-butylethylene (330 μL, 2.5 mmol) and mesitylene (10 μL) as internal standard were added to the solution. Then the solution was transfered into a 10 mL thick-wall tube. The tube was sealed with a teflon plug under an argon atmosphere, and the solution stirred in a 150 °C oil bath. Periodically, the flask was removed from the bath and cooled to room temperature. An aliquot was removed from the flask and analyzed by GC.

5. Procedures for alkene isomerization

Isomerization of 1-octene. In an argon-filled glovebox, 5.0 μmol of iridium complex (**1a**, **1b**, **1c**, ($^{t\text{Bu}}$PCP)IrHCl or ($^{t\text{Bu}}$POCOP)IrHCl), 11.0 μmol of sodium *tert*-butyloxide, 2.5 mmol of 1-octene (392 μL), and 1.6 mL of mesitylene were added to a 10 mL tube. The tube was sealed with a teflon plug under an argon atmosphere, and the solution stirred in a 60 °C oil bath. Periodically, the flask was removed from the bath and cooled to room temperature. An aliquot was removed from the flask and analyzed by GC.

Table S8. Octene distributions (concentration in mM) from **1b**/NaO^{t}Bu-catalyzed isomerization of 1-octene at 60 °C

Octenes	5 min	10 min	30 min	1 h	2 h	4 h
3- and 4-octenes	132	228	312	371	378	391
Cis-2-octene	125	140	220	207	202	197
Trans-2-octene	287	407	595	645	653	645
1-Octene	705	475	123	27	17	17

Table S9. Octene distributions (concentration in mM) from **1a**/NaO^{t}Bu-catalyzed isomerization of 1-octene at 60 °C

Octenes	5 min	10 min	30 min	1 h	2 h	4 h	15 h	32 h
3- and 4-octenes	53	80	125	145	155	157	217	384
Cis-2-octene	130	177	242	260	265	258	248	218
Trans-2-octene	253	355	545	655	770	810	760	635
1-Octene	815	637	337	190	60	25	25	13

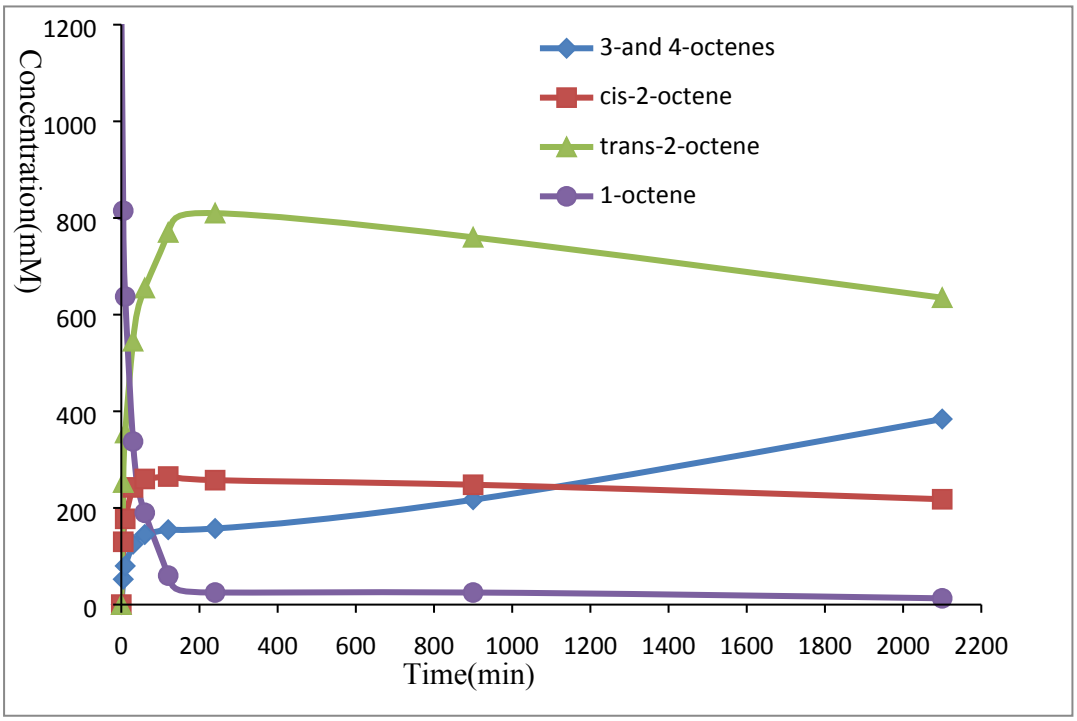


Figure S5. Isomerization of 1-octene catalyzed by **1a**/NaO^{t}Bu at 60 °C

Table S10. Octene distributions (concentration in mM) from **1c**/NaO^{t}Bu-catalyzed isomerization of 1-octene at 60 °C

Octenes	5 min	10 min	30 min	1 h	2 h	4 h
3- and 4-octenes	145	205	313	355	380	388
Cis-2-octene	150	192	242	255	250	243
Trans-2-octene	332	430	530	570	580	592
1-Octene	622	422	165	70	40	25

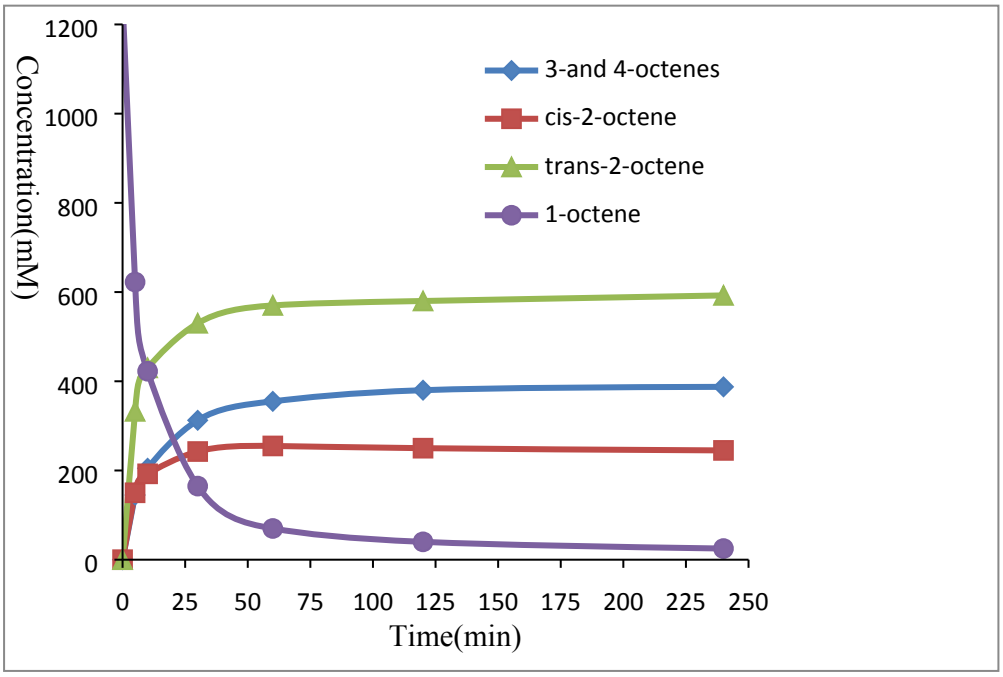


Figure S6. Isomerization of 1-octene catalyzed by **1c**/NaO^{t}Bu at 60 °C

Table S11. Octene distributions (concentration in mM) from ($^{t\text{Bu}}$PCP)IrHCl/NaO^{t}Bu-catalyzed isomerization of 1-octene at 60 °C

Octenes	5 min	10 min	30 min	1 h	2 h	4 h
3- and 4-octenes	28	37	72	120	250	327
Cis-2-octene	30	41	63	94	120	191
Trans-2-octene	66	107	200	315	542	613
1-Octene	1125	1065	915	721	538	119

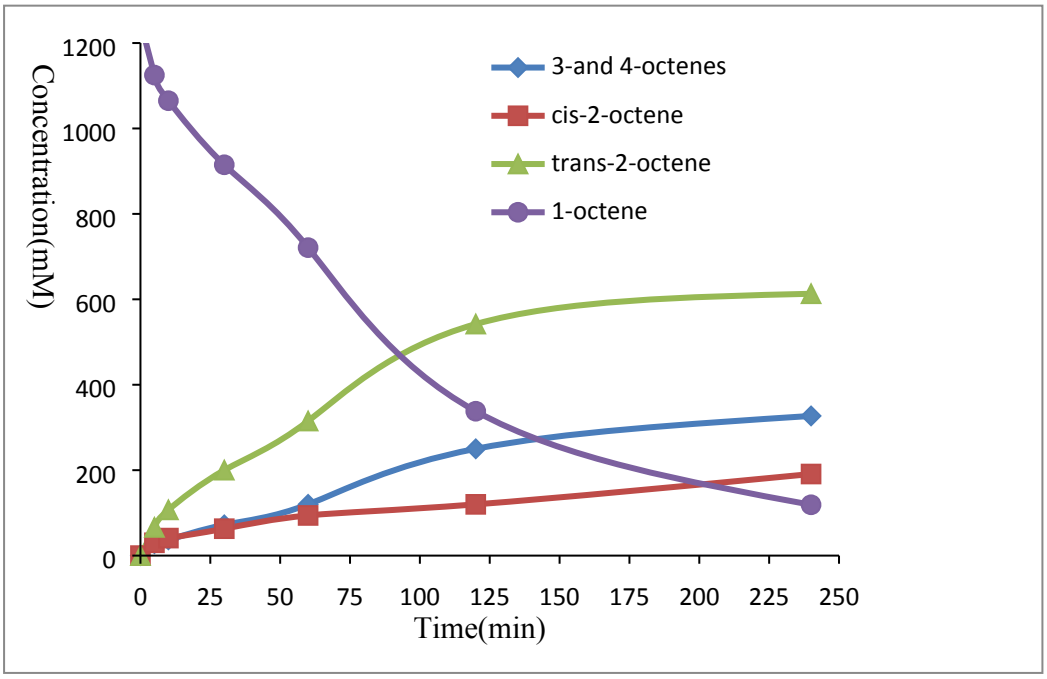


Figure S7. Isomerization of 1-octene catalyzed by ($^{t\text{Bu}}$PCP)IrHCl/NaO^{t}Bu at 60 °C

Table S12. Octene distributions (concentration in mM) from ($^{t\text{Bu}}$POCOP)IrHCl/NaO^{t}Bu-catalyzed isomerization of 1-octene at 60 °C

Octenes	5 min	10 min	30 min	1 h	2 h	4 h
3- and 4-octenes	22	28	44	60	83	117
Cis-2-octene	23	32	53	68	95	127
Trans-2-octene	32	43	68	88	120	173
1-Octene	1173	1147	1085	1034	952	833

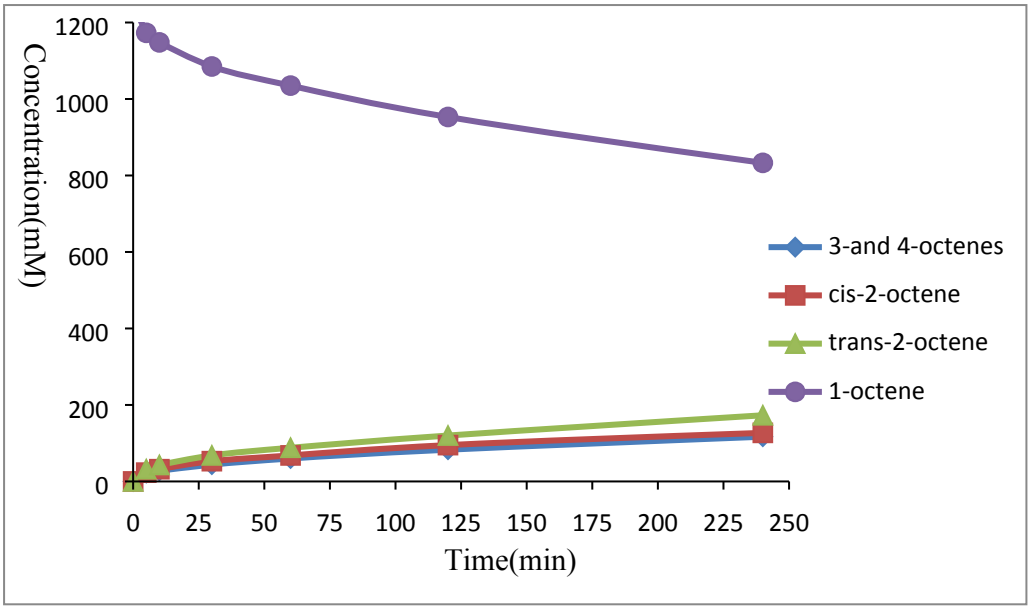
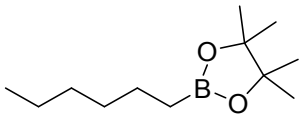


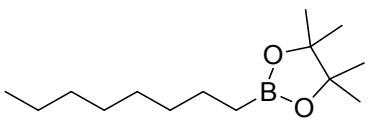
Figure S8. Isomerization of 1-octene catalyzed by ($^{t\text{Bu}}$POCOP)IrHCl/NaO^{t}Bu at 60 °C

6. Procedures for isomerization/hydroboration of internal olefins

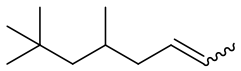
Table 3, entry 1-7, entry 9. In an argon-filled glovebox, complex **1b** (2.2 mg, 4.0 μmol), complex (PNN)$FeCl_2$ **3** (18.0 mg, 40.0 μmol), 1 mL toluene, $NaBHEt_3$ (88.0 μmol, 88.0 μL, 1.0 M in toluene), HBPin (116.0 μL, 0.8 mmol), and the olefin substrate (0.8 mmol) were added to a 10 mL tube. The solution stirred at room temperature for 0.5-4 h, and then the reaction was quenched by exposing the solution to air. The resulting solution was concentrated under vacuum and the residue was purified by elution through a silica gel plug with hexane and ethyl acetate.



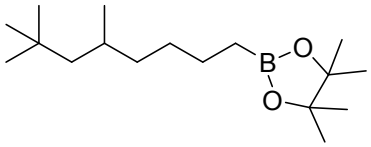
2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4. ^{1}H NMR (400 MHz, CD_3Cl): δ 1.41-1.38 (m, 2H), 1.31-1.26 (m, 6H), 1.24 (s, 12H), 0.87 (t, 3H), 0.76 (t, 2H). The spectroscopic data correspond to reported data.[8]



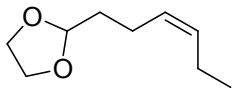
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane 5. ^{1}H NMR (400 MHz, CD_3Cl): δ 1.41-1.38 (m, 2H), 1.29-1.26 (m, 10H), 1.24 (m, 12H), 0.87 (t, 3H), 0.76 (t, 2H). The spectroscopic data correspond to reported data.[9]



5,7,7-trimethyloct-2-ene This olefin was prepared by wittig olefination: aldehyde with ethyltriphenylphosphonium bromide and *n*-BuLi in THF. The Z/E was determinated by GC. The complex NMR spectra see below.

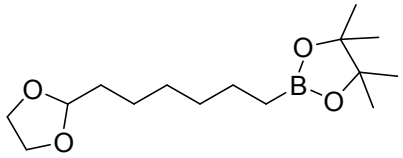


4,4,5,5-tetramethyl-2-(5,7,7-trimethyloctyl)-1,3,2-dioxaborolane 6 ^{1}H NMR (400 MHz, CD_3Cl): δ 1.40-1.34 (m, 4H), 1.24-1.11 (m, 15H), 1.02-0.97 (m, 2H), 0.87 (s, 12H), 0.77 (t, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3Cl): δ 82.9, 51.4, 39.5, 31.2, 30.2, 30.1, 29.3, 24.9, 24.5, 22.8. HRMS (EI) m/z (M+) calcd for $C_{17}H_{35}{}^{10}BO_2$: 281.2766, found: 281.2763.



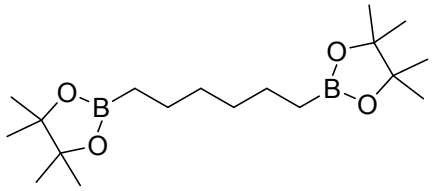
(Z)-2-(hex-3-en-1-yl)-1,3-dioxolane *cis*-4-heptenal (5.0 mL, 37.9 mmol), ethylene glycol (6.3 mL, 113 mmol), *p*-toluenesulfonic acid (130 mg, 0.56 mmol) in 100 mL of toluene refluxed for 10 h with continus removal of water as toluene azeotrope. After cooling, evaporated of the solvent under vacuum, the crude product was purified with silica gel column chromatography by petroleum ether, affording 4.7 g (80% yield) product as colorless oil.

^{1}H NMR (400 MHz, CD_3Cl): δ 5.42-5.30 (m, 2H), 4.86 (t, 1H), 4.04-3.92 (m, 2H), 3.89-3.81 (m, 2H), 2.19-2.14 (m, 2H), 2.09-2.01 (m, 2H), 1.73-1.68 (m, 2H), 0.95 (t, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3Cl): δ 132.3, 128.0, 104.2, 64.9, 33.9, 21.9, 20.5, 14.3. HRMS (EI) m/z (M-H+) calcd for $C_9H_{15}O_2$: 155.1072, found: 155.1076.



2-(6-(1,3-dioxolan-2-yl)hexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 ^{1}H NMR (400 MHz, CD_3Cl): δ 4.83 (t, 1H), 3.99-3.91 (m, 2H), 3.88-3.80 (m, 2H), 1.64-1.58 (m, 2H), 1.42-1.38 (m, 4H), 1.31-1.23 (m, 16H), 0.76 (t, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3Cl): δ 104.8, 82.9, 64.9, 34.0, 32.4, 29.4, 24.9, 24.1, 24.0. HRMS (EI) m/z (M-H+) calcd for $C_{15}H_{28}{}^{10}BO_4$: 282.2117, found: 282.2121.

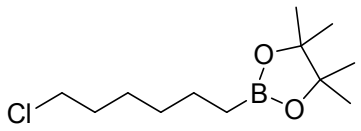
Table 3, entry 8. In an argon-filled glovebox, complex **1b** (2.2 mg, 4.0 μmol), complex (PNN)$FeCl_2$ **3** (18.0 mg, 40.0 μmol), 1 mL toluene, $NaBHEt_3$ (88.0 μL, 88.0 μmol, 1.0 M in toluene), HBPin (232.0 μL, 1.6 mmol), and 2,4-hexadiene (*trans* : *cis* = 12 :1, 0.8 mmol) were added to a 10 mL tube. The solution stirred at room temperature for 3 h and then the reaction was quenched by exposing the solution to air. The resulting solution was concentrated under vacuum and the residue was purified by elution through a silica gel plug with hexane and ethyl acetate. The hydroboration product **7** was obtained in 80% isolated yield.



1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane 7. ^{1}H NMR (400 MHz, CD_3Cl): δ 1.38 (m, 4H), 1.29-1.21 (m, 28H), 0.75 (t, 4H). The spectroscopic data correspond to reported data.[10]

Table 3, entry 10. In an argon-filled glovebox, complex **1b** (1.1 mg, 2.0 μmol), complex (PNN)$FeCl_2$ **3** (36.0 mg, 80.0 μmol), 1 mL toluene, HBPin (58.0 μL, 0.4 mmol), and *cis*-6-chloro-2-hexene (57μL, 0.4 mmol, 90% purity) were added to a 10 mL tube. The solution of $NaBHEt_3$ (164.0 μL, 164.0 μmol, 1.0 M in toluene) was dropped slowly into the tube. After 10 min, all $NaBHEt_3$ was added. The solution stirred continuesly at room temperature for 20 min and then the reaction was quenched by exposing the solution to air. The resulting solution was concentrated under vacuum and the residue was purified

by elution through a silica gel plug with hexane and ethyl acetate. The hydroboration product **9** was obtained in 74% isolated yield.



2-(6-chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9. ^{1}H NMR (400 MHz, CD_3Cl): δ 3.52 (t, 2H), 1.76 (t, 2H), 1.44-1.40 (m, 4H), 1.34-1.29(m, 2H), 1.24 (s, 12H), 0.77 (t, 2H). The spectroscopic data correspond to reported data.[9]

7. Reference.

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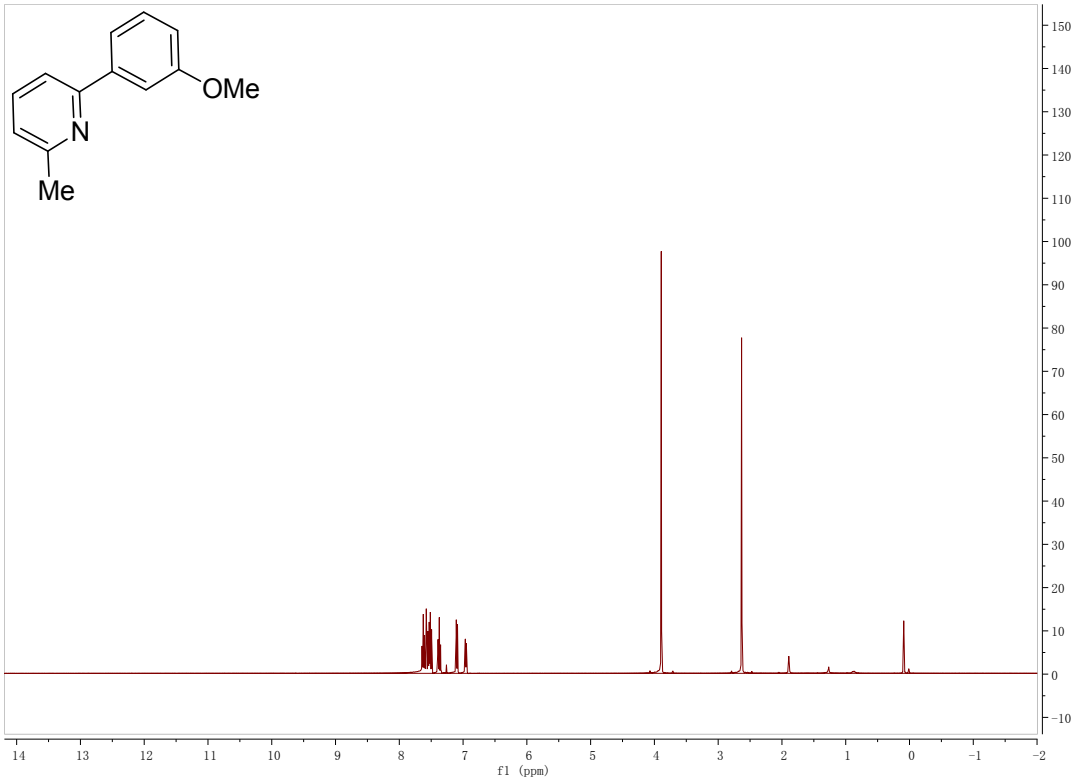
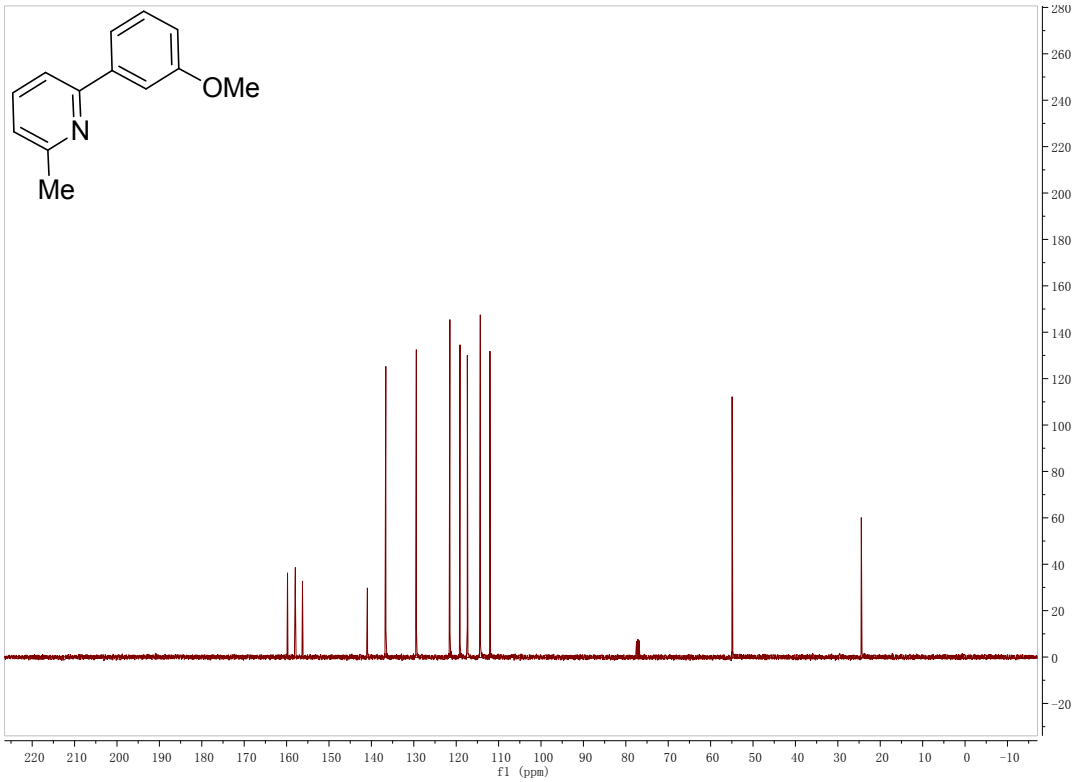
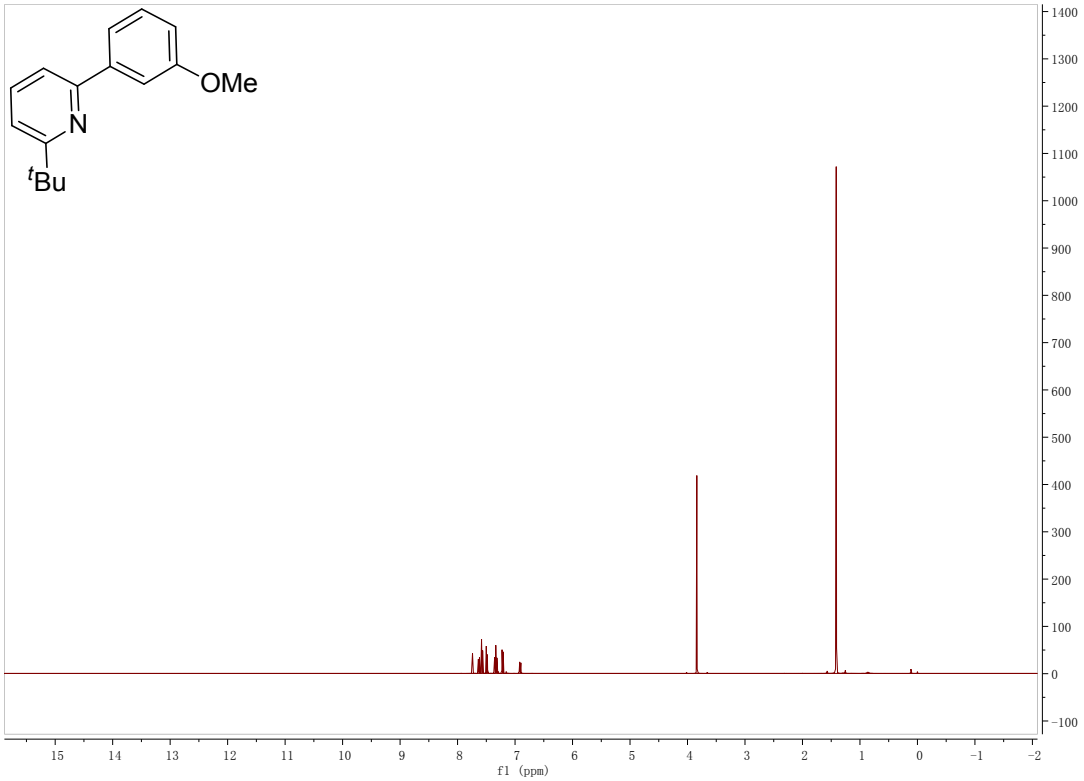
8. NMR spectra.



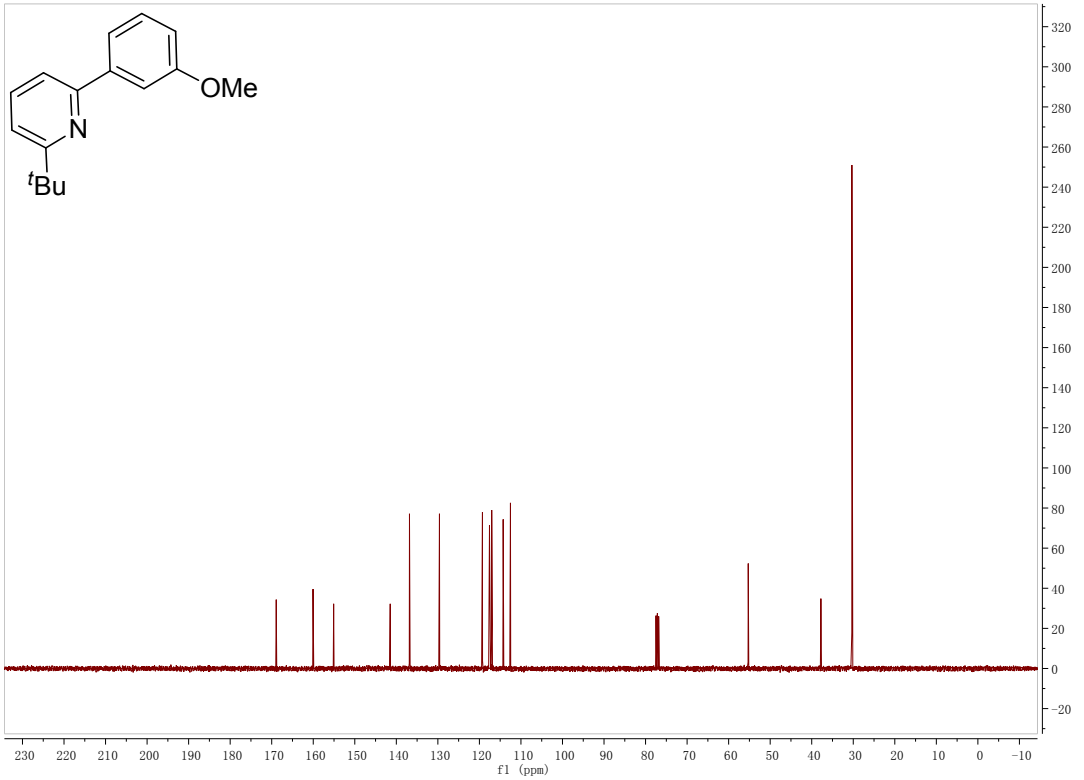
^{1}H NMR (400 MHz, CD_3Cl) for 2-(3-methoxyphenyl)-6-methylpyridine



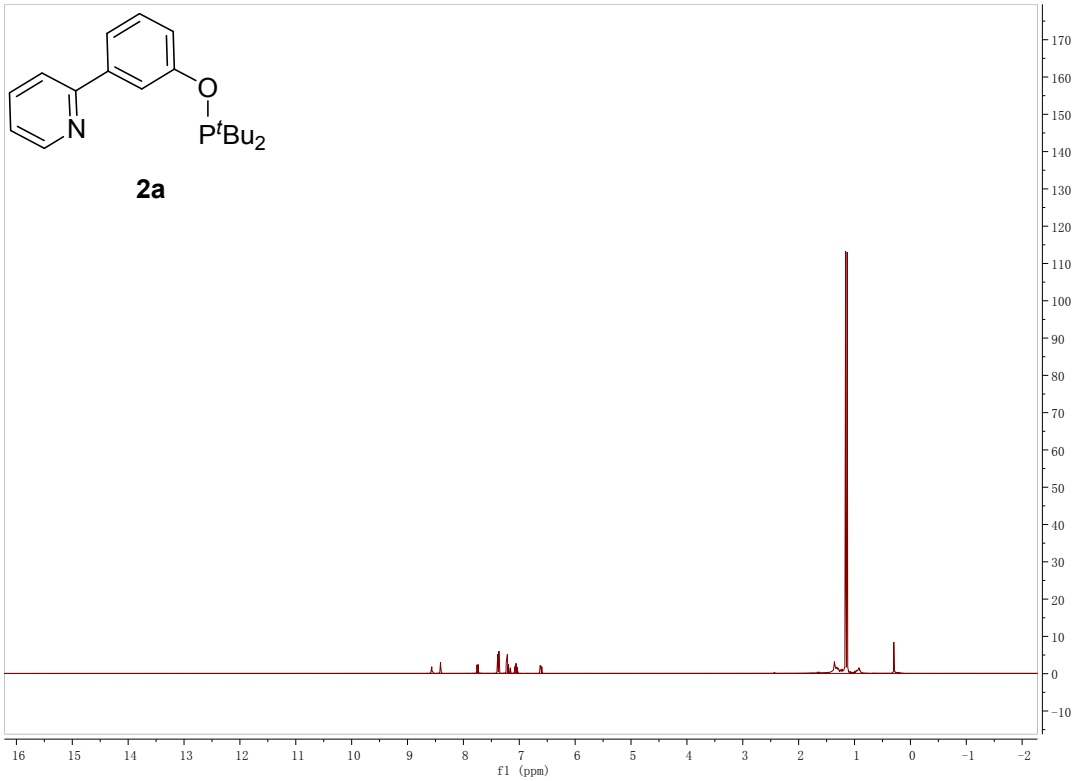
^{13}C NMR (100 MHz, CD_3Cl) for 2-(3-methoxyphenyl)-6-methylpyridine



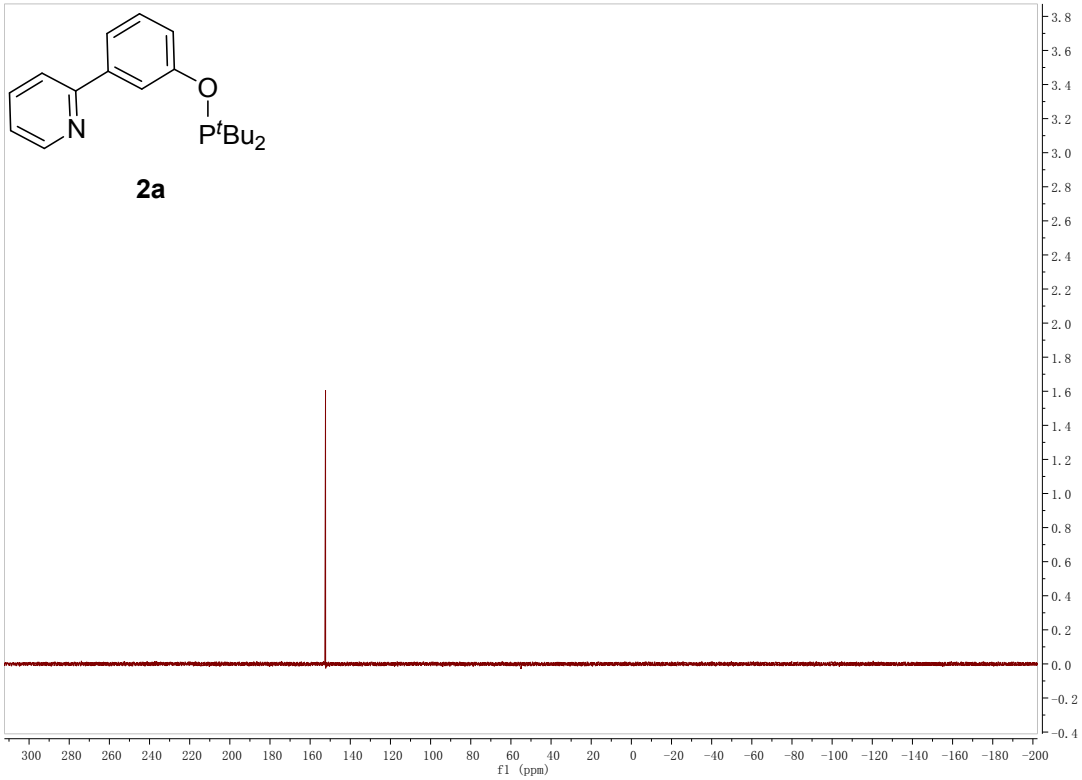
^{1}H NMR (400 MHz, CD_3Cl) for 2-(*tert*-butyl)-6-(3-methoxyphenyl)pyridine



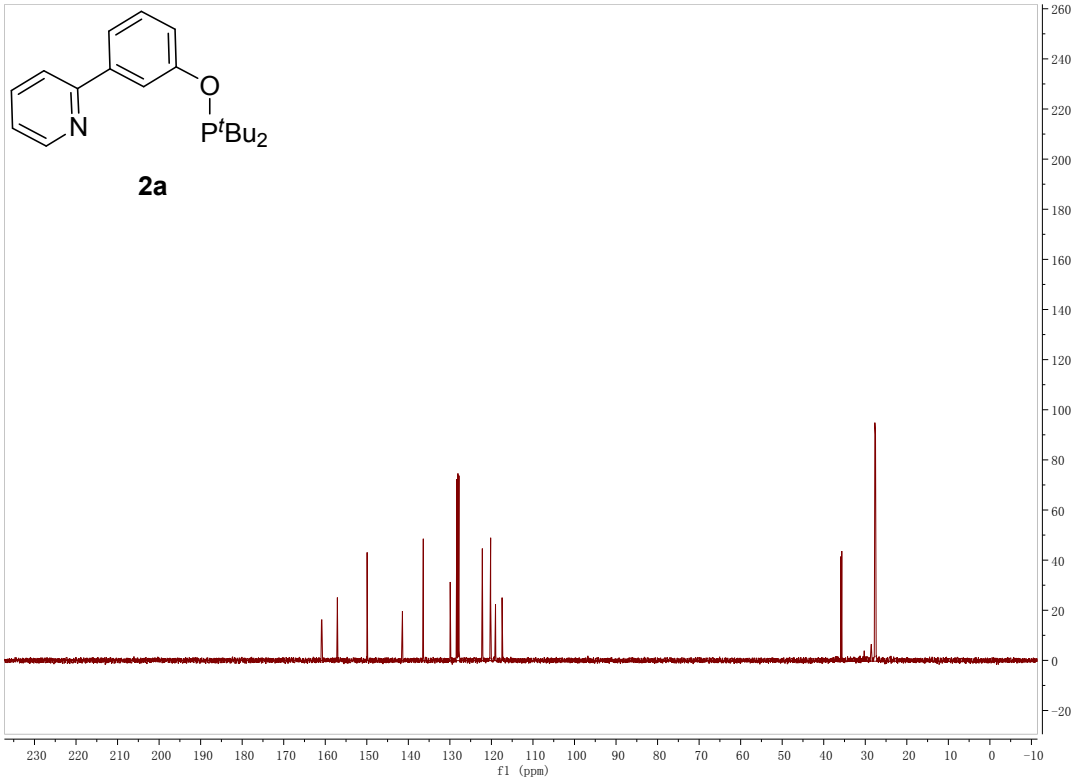
^{13}C NMR (100 MHz, CD_3Cl) for 2-(*tert*-butyl)-6-(3-methoxyphenyl)pyridine



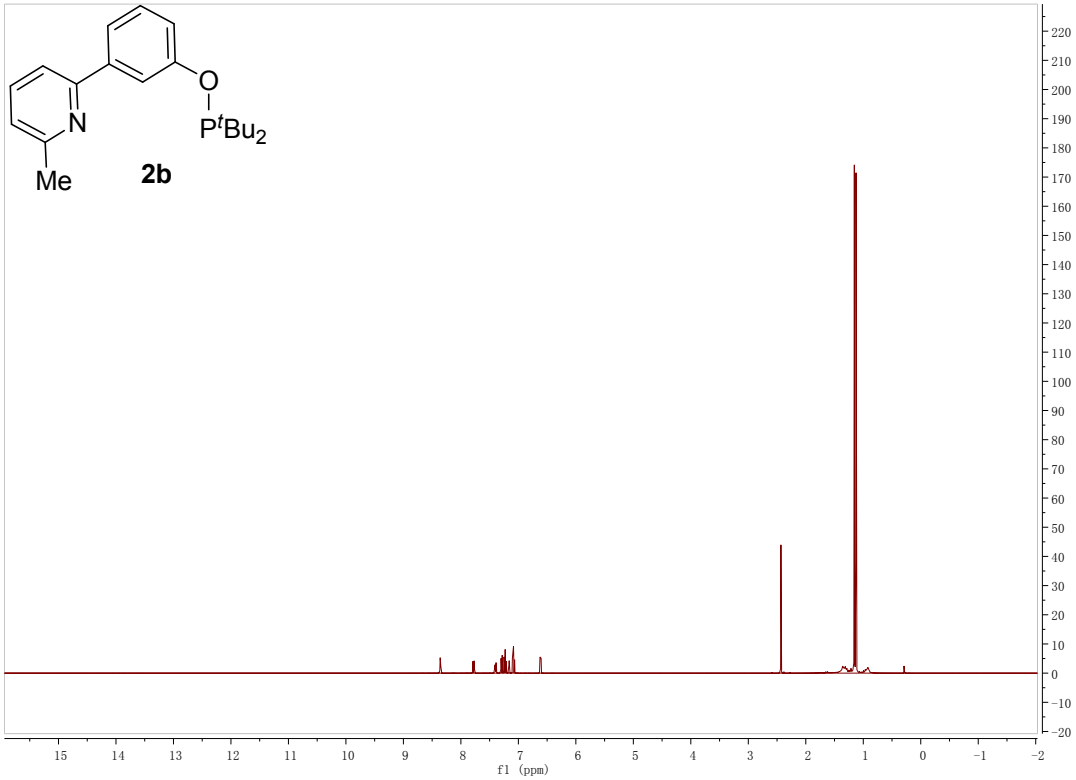
^{1}H NMR (400 MHz, C_6D_6) for **2a**



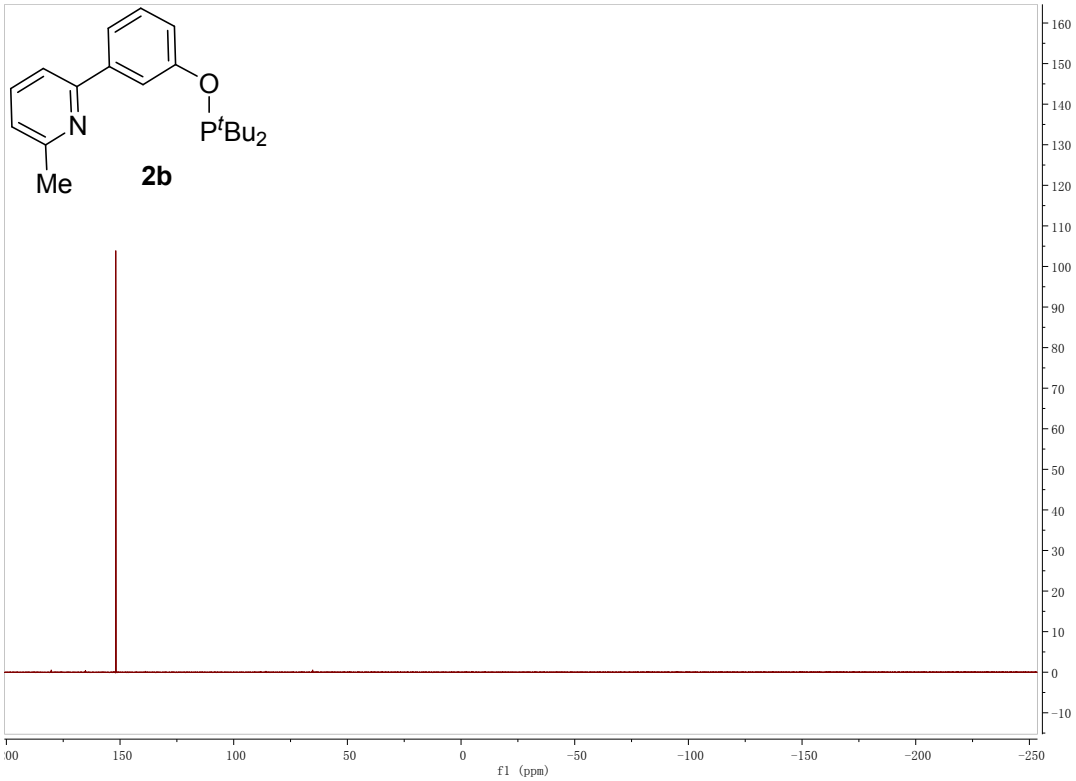
^{31}P NMR (162 MHz, C_6D_6) for **2a**



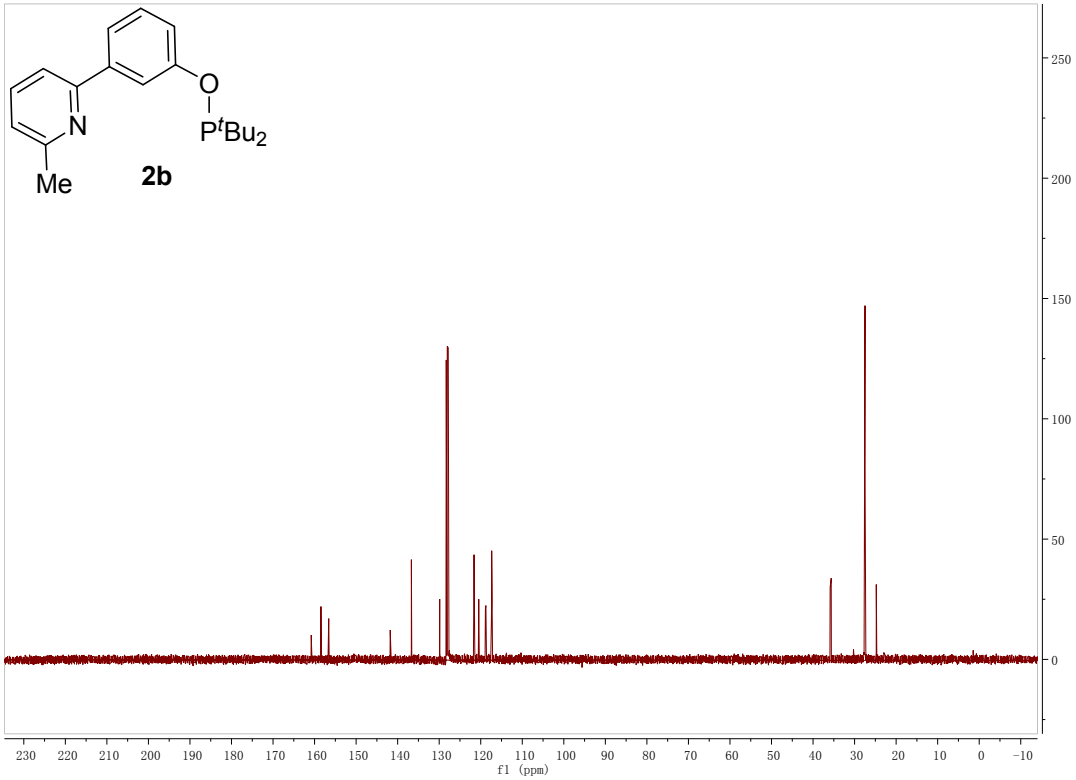
^{13}C NMR (100 MHz, C_6D_6) for **2a**



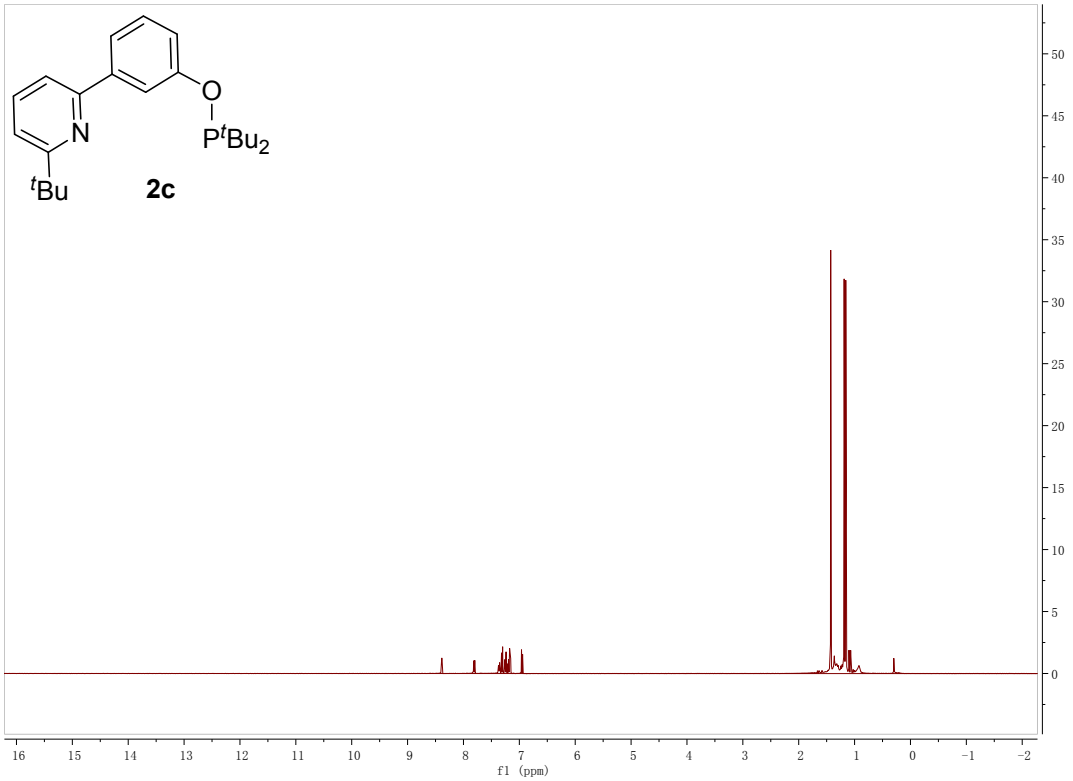
^{1}H NMR (400 MHz, C_6D_6) for **2b**



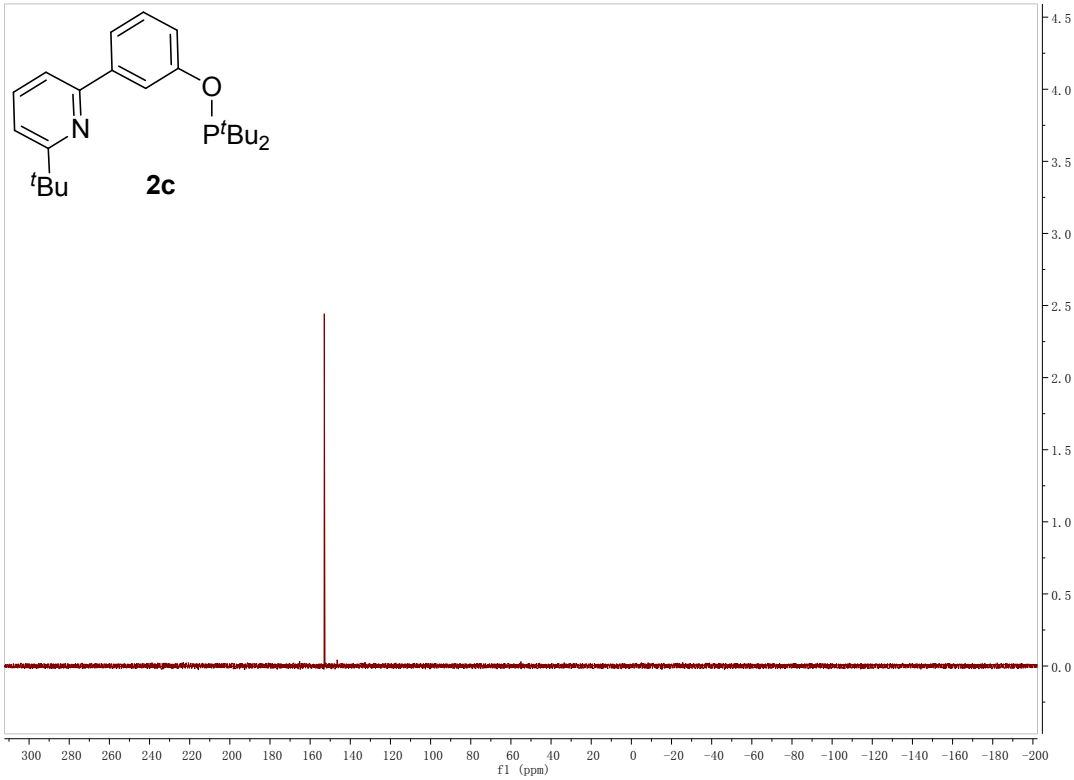
^{31}P NMR (162 MHz, C_6D_6) for **2b**



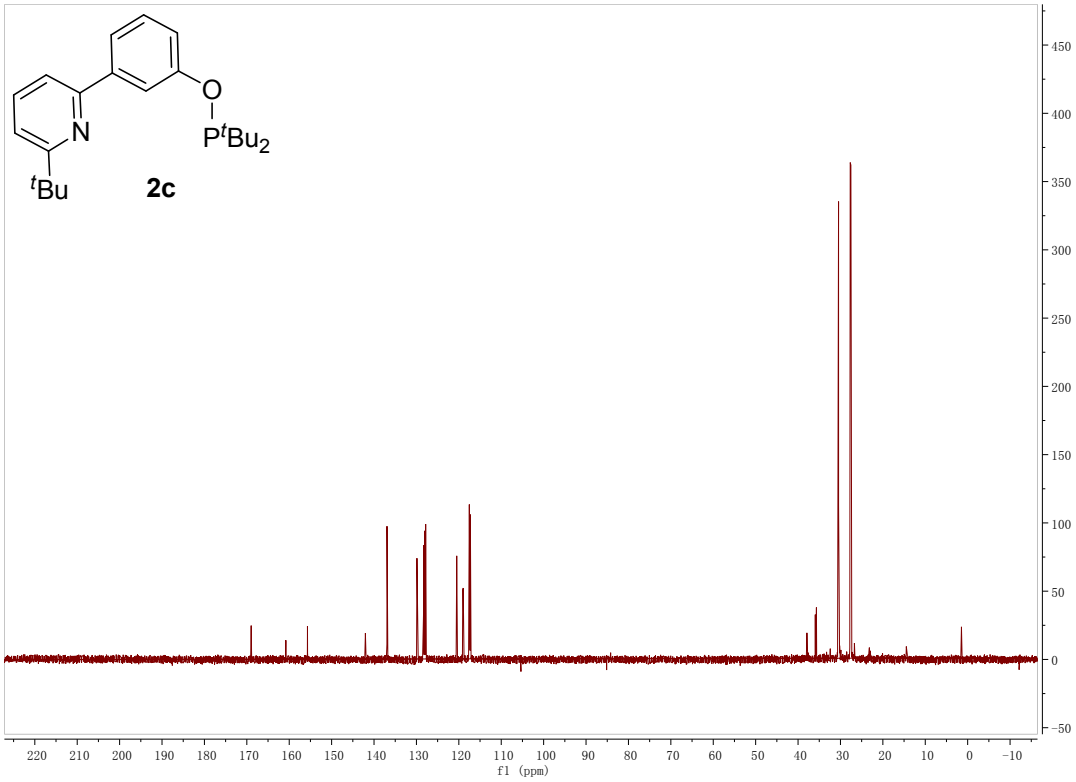
^{13}C NMR (100 MHz, C_6D_6) for **2b**



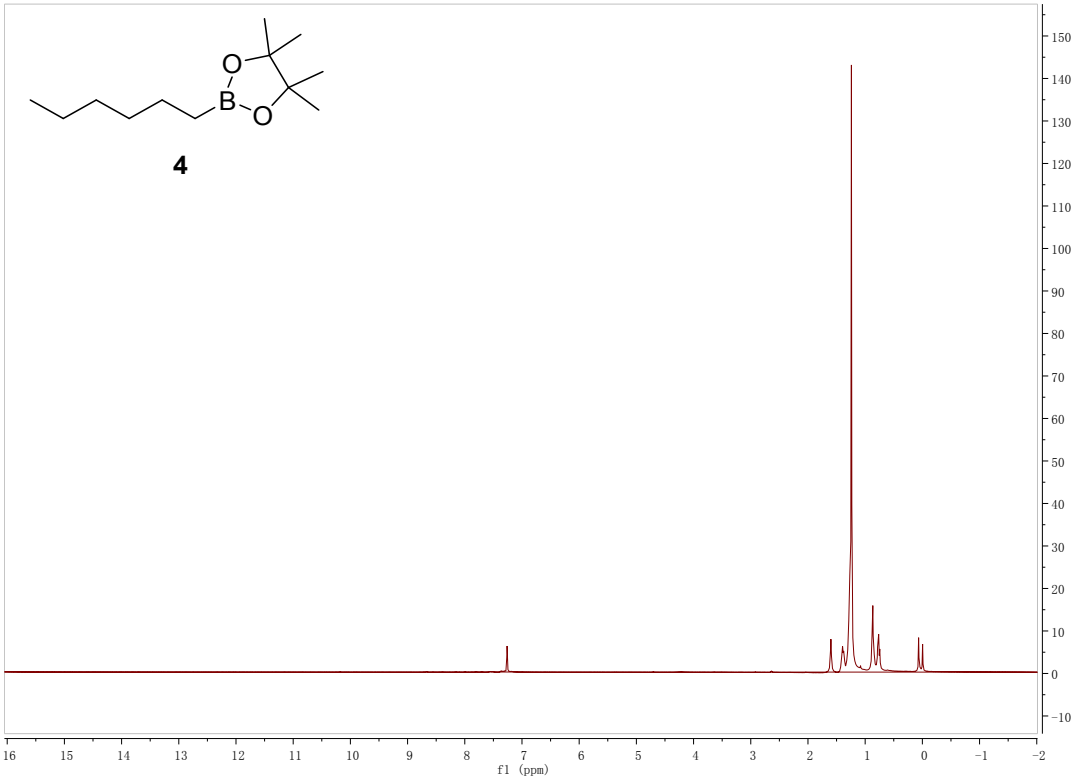
^{1}H NMR (400 MHz, C_6D_6) for **2c**



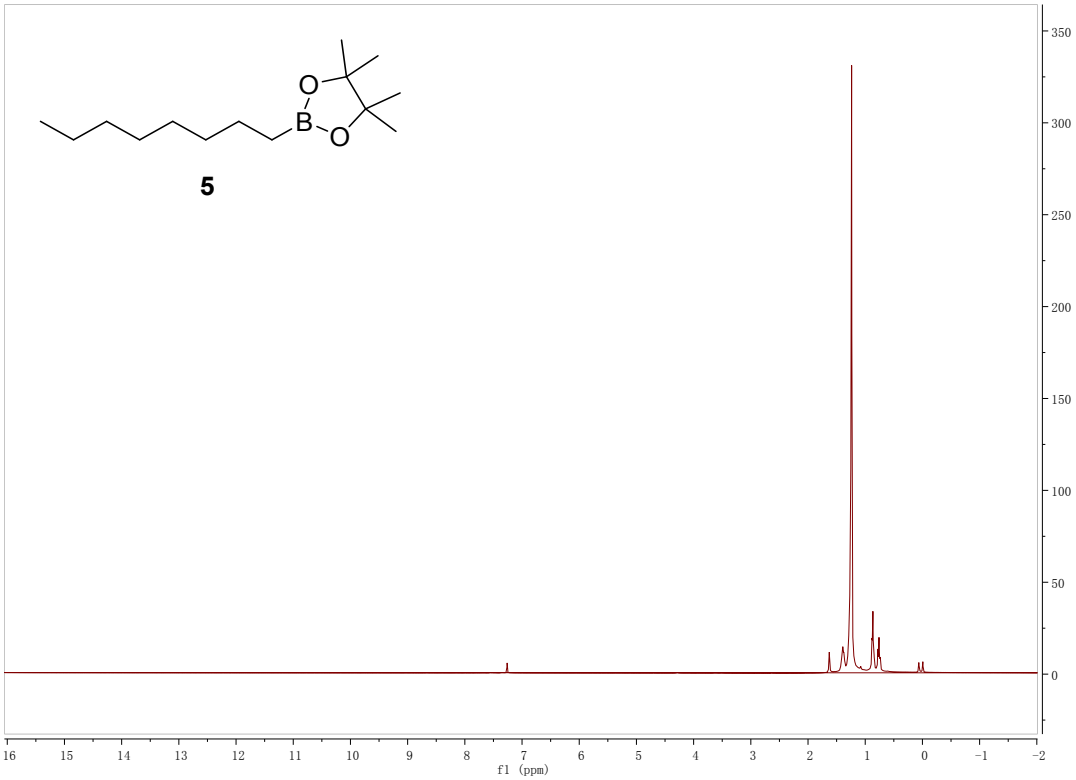
^{31}P NMR (162 MHz, C_6D_6) for **2c**



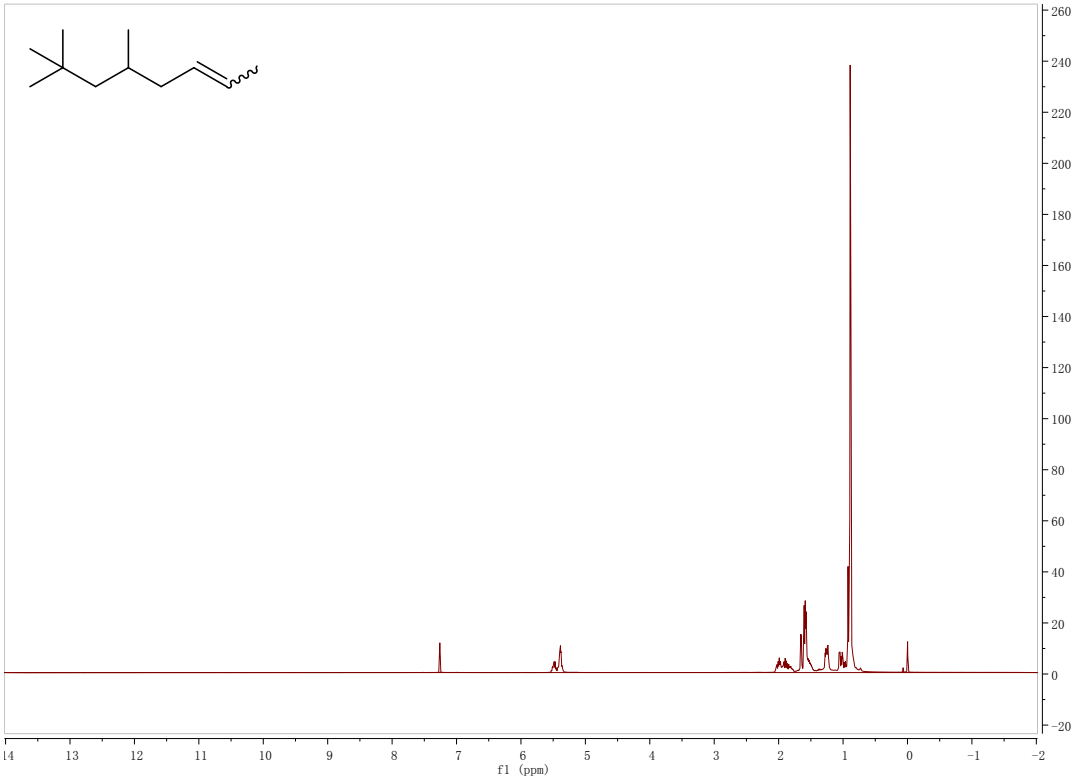
^{13}C NMR (100 MHz, C_6D_6) for **2c**



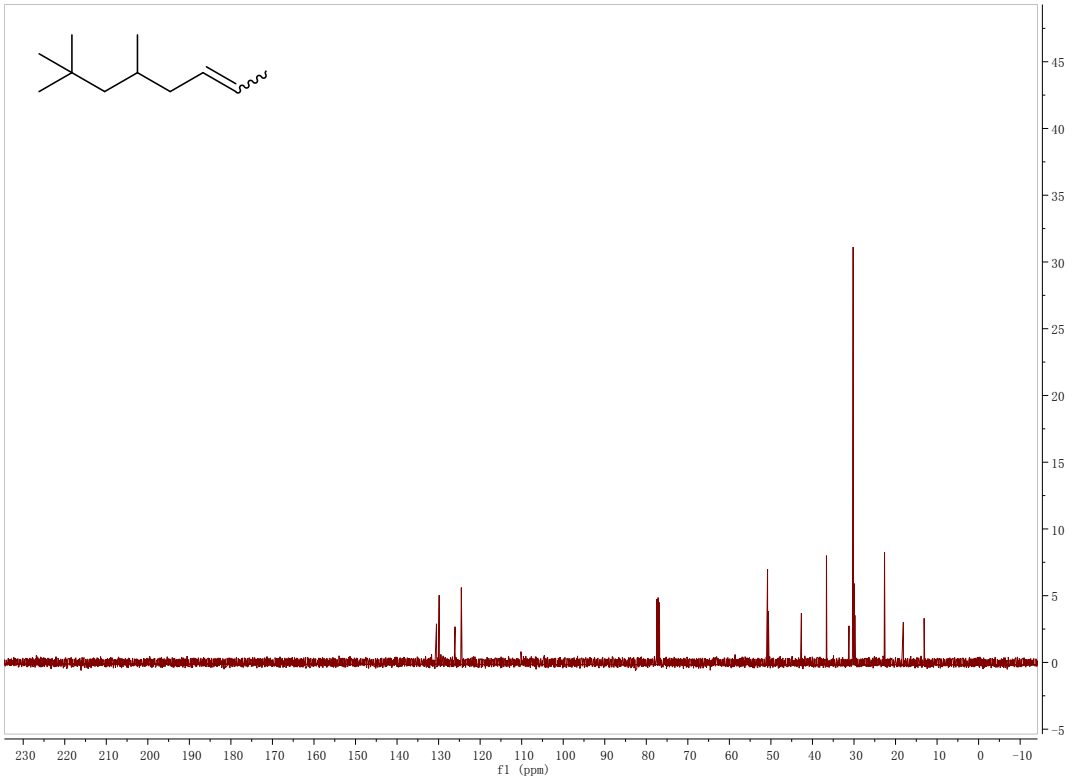
^{1}H NMR (400 MHz, CD_3Cl) for **4**



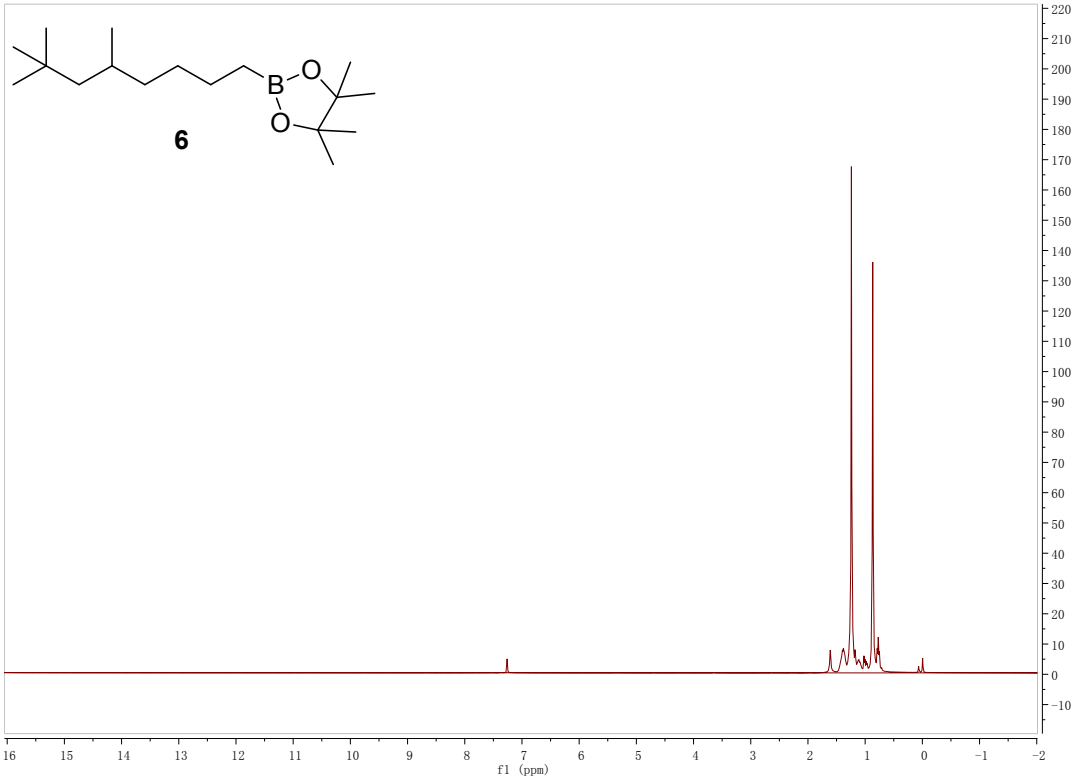
^{1}H NMR (400 MHz, CD_3Cl) for **5**



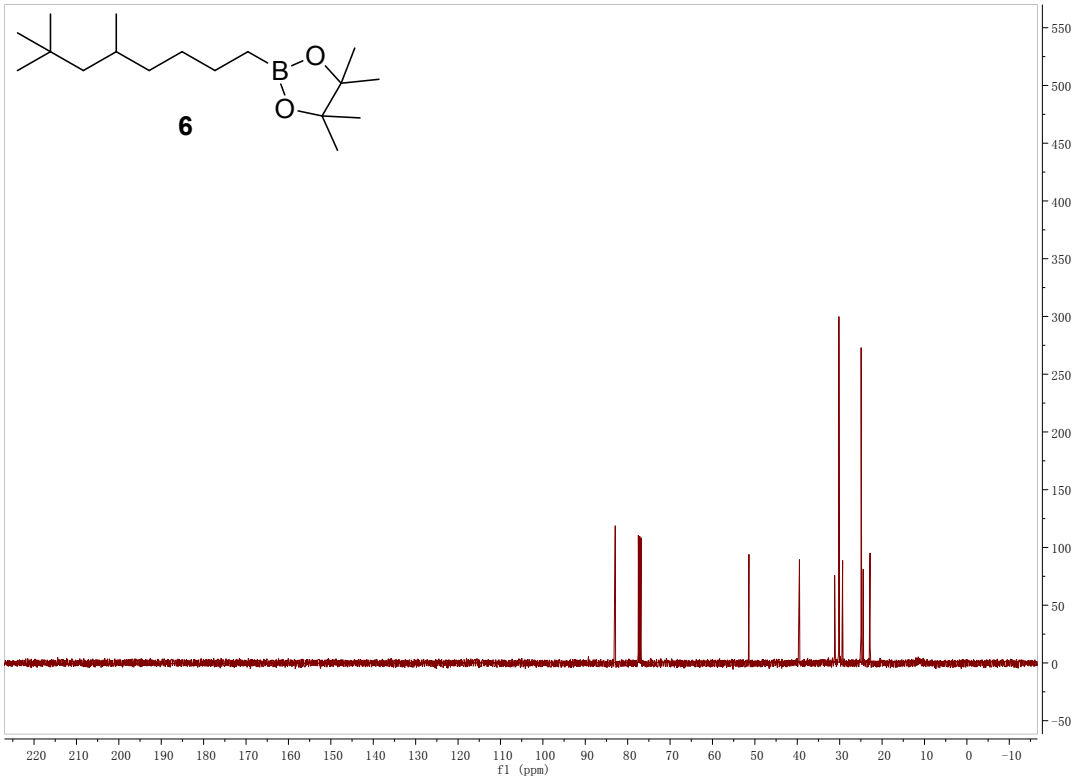
^{1}H NMR (400 MHz, CD_3Cl) for 5,7,7-trimethyloct-2-ene



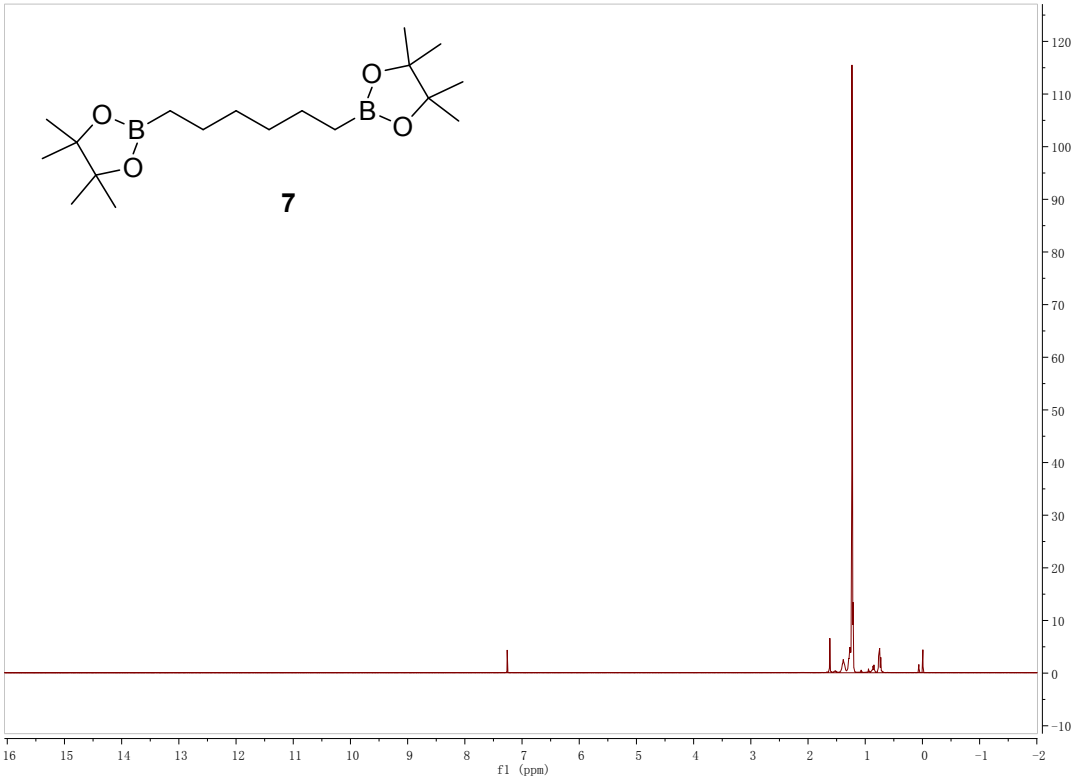
^{13}C NMR (100 MHz, CD_3Cl) for 5,7,7-trimethyloct-2-ene



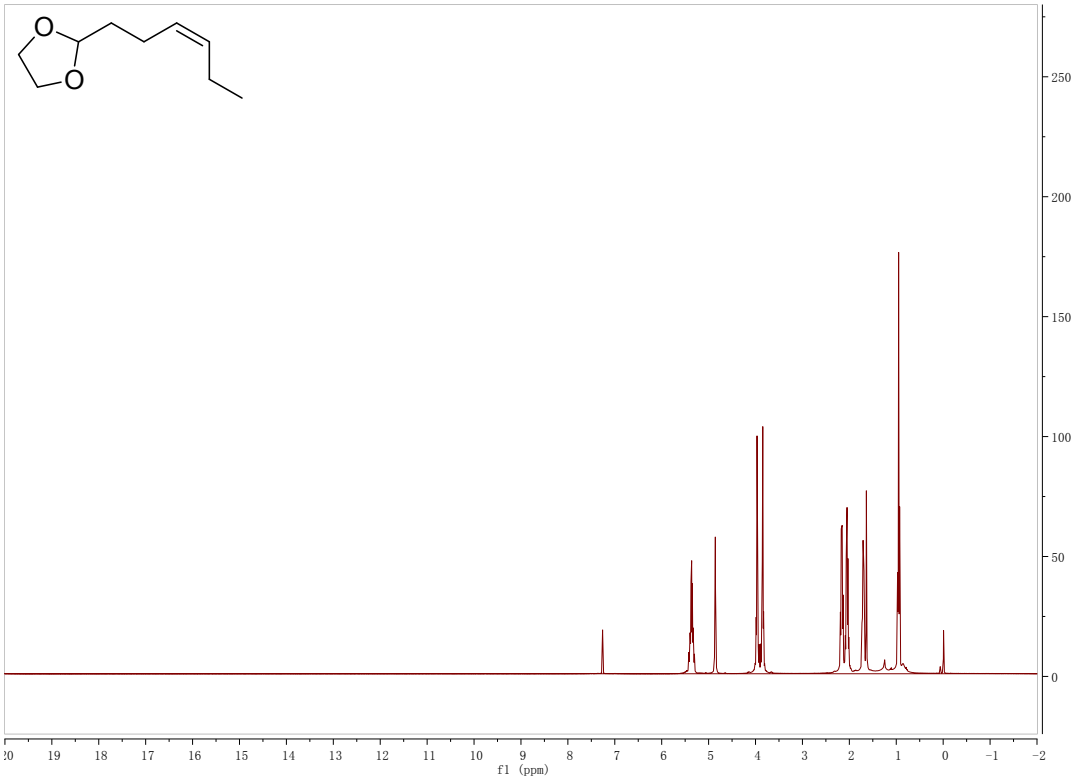
^{1}H NMR (400 MHz, CD_3Cl) for **6**



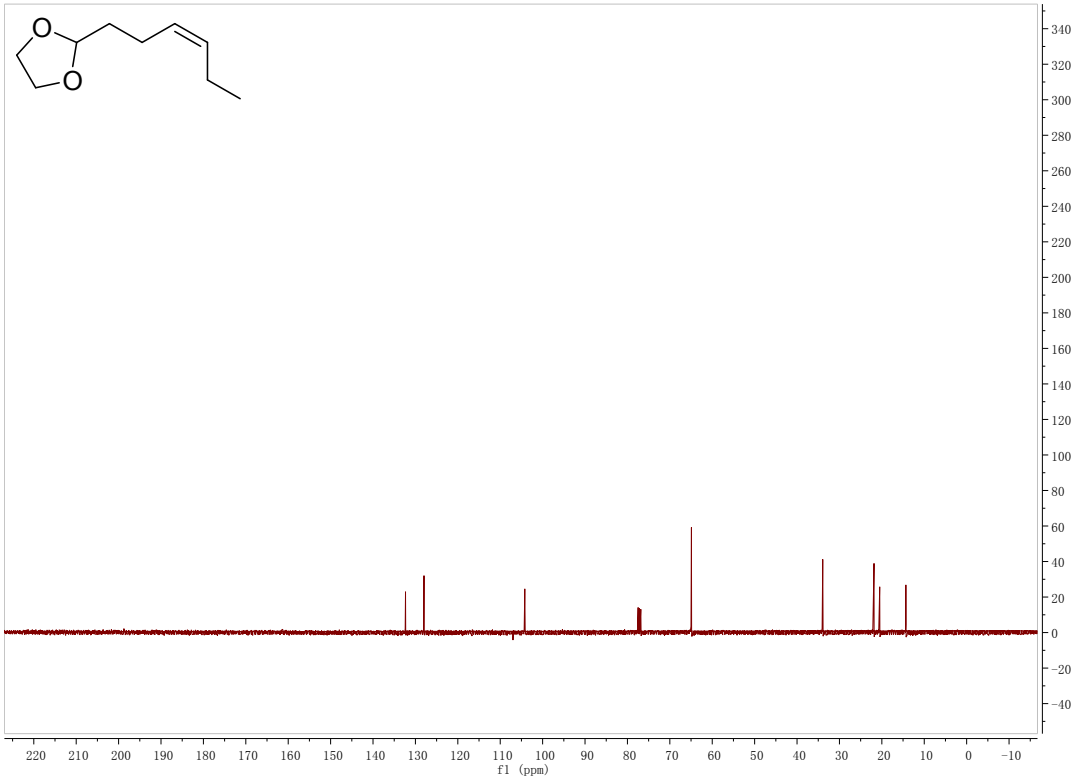
^{13}C NMR (100 MHz, CD_3Cl) for **6**



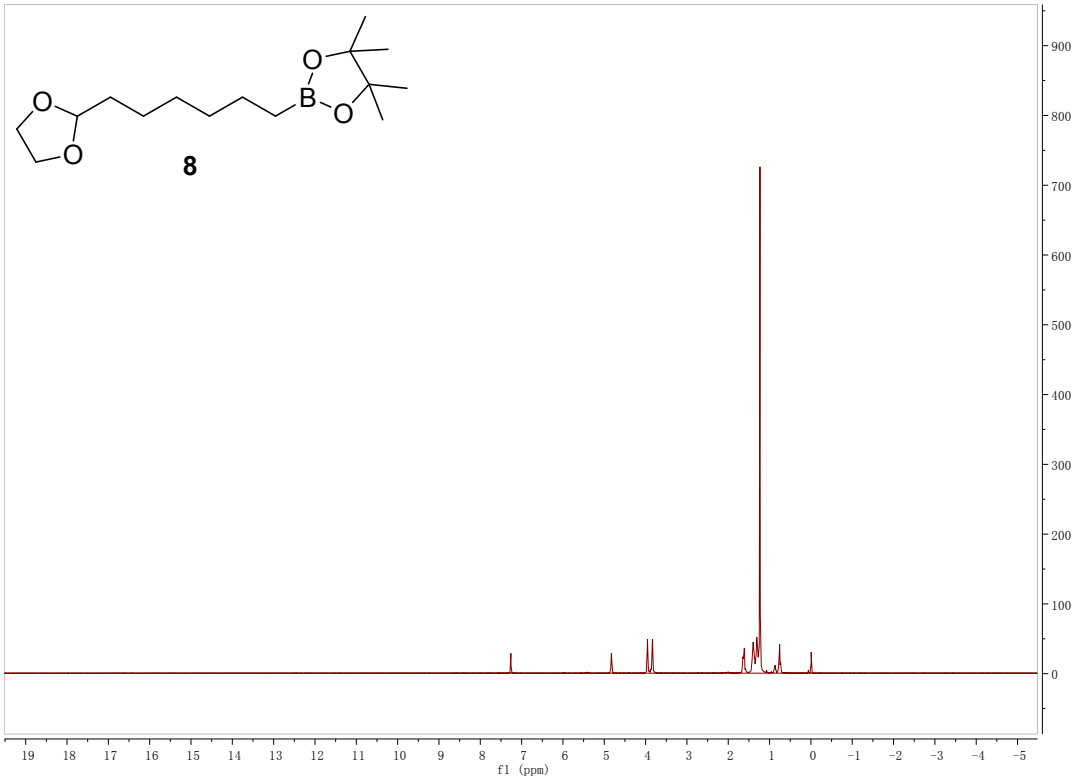
^{1}H NMR (400 MHz, CD_3Cl) for **7**



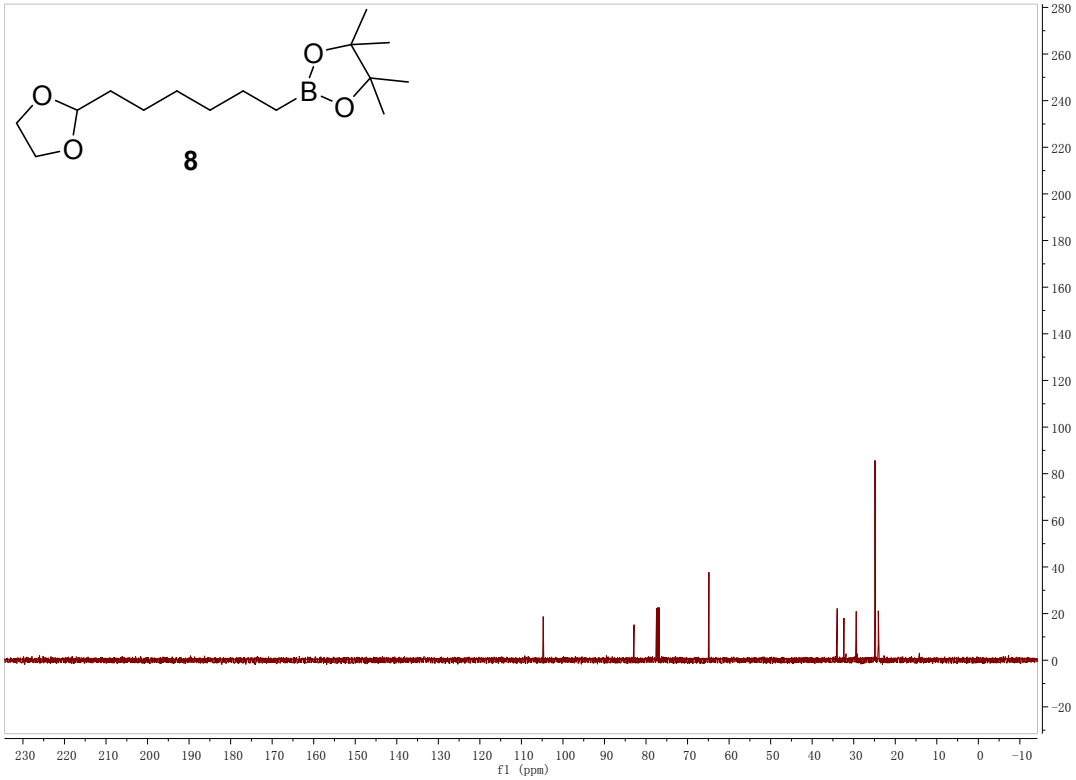
^{1}H NMR (400 MHz, CD_3Cl) for (Z)-2-(hex-3-en-1-yl)-1,3-dioxolane



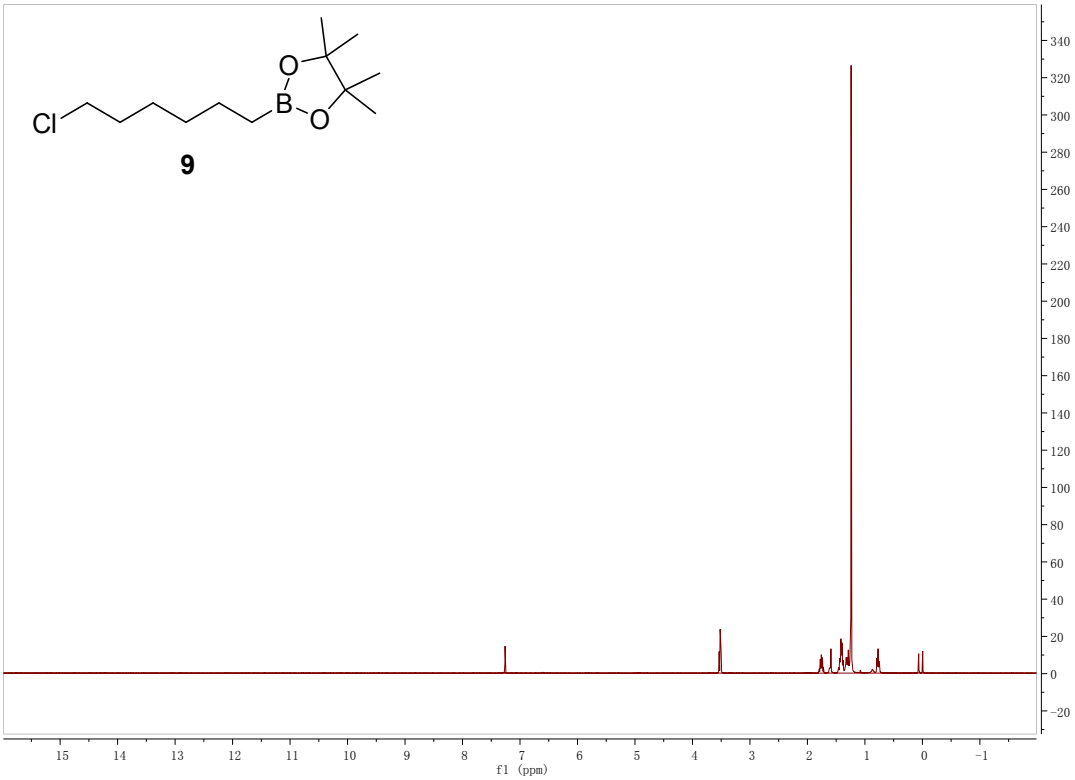
^{13}C NMR (100 MHz, CD_3Cl) for (Z)-2-(hex-3-en-1-yl)-1,3-dioxolane



^{1}H NMR (400 MHz, CD_3Cl) for **8**



^{13}C NMR (100 MHz, CD_3Cl) for **8**



^{1}H NMR (400 MHz, CD_3Cl) for **9**