Cobalt-Catalyzed Asymmetric Hydrovinylation of 1,3-Dienes
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General methods

Synthesis of complexes

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X₂Co(L)-Catalyzed Hydrovinylation of 1,3-Dienes

Hydrovinylation of (E)-nona-1,3-diene (12a) using [DPPB]CoCl₂ (Table 1, Entry 9, Typical procedure for ligand screening).
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Iron-catalyzed hydrovinylation of (E)-nona-1,3-diene using[DPPE]FeCl₃ (Equation 11):
Unsuccessful hydrovinylation of substrate \((E)\)-ethyl-2-methylpenta-2,4-dienoate using \([dppm]CoCl_2\).

Unsuccessful attempt to dimerize \((E)\)-1,3-nonadiene and propylene using \([dppe]CoCl_2\) (Equation 10).

**Cobalt-Catalyzed Hydrovinylation of 1,3-Dienes. Scope of Substrates (Tables 3 and 5)**

\((E)\)\-nona-1,3-diene (12a)

Typical procedure for asymmetric Co-catalyzed hydrovinylation reactions of \((E)\)\-nona-1,3-diene (12a) for ligand screening (Table 4, Entries 1-20).

Asymmetric Co-catalyzed hydrovinylation reactions \((E)\)-1,3-nonadiene (12a) by using \((S,S,R,R)\)-Tangphos \([L14]CoCl_2\) (Table 5, Entry 3).

Asymmetric Co-catalyzed hydrovinylation reaction \((E)\)-1,3-nonadiene by using 1 mol \% Josiphos 2 \([L18]CoCl_2\) (Table 5, Entry 4).

\((E)\)-Deca-1,3-diene (12b)

Hydrovinylation of \((E)\)-deca-1,3-diene using \((R,R)\)[DIOP]CoCl_2 (Table 5, Entry 5).

\((E)\)-Undeca-1,3-diene (12c)

Hydrovinylation of \((E)\)-undeca-1,3-diene using 1 mol \% \([L18] Josiphos-2\)CoCl_2 Loading (Table 5, Entry 7).

\((E)\)-Dodeca-1,3-diene (12d)

Hydrovinylation of \((E/Z)\)-dodeca-1,3-diene using \([DPPB]CoCl_2\) (Table 3, Entry 5).

Hydrovinylation of \((E/Z)\)-dodeca-1,3-diene using \((S,S)\)[DIOP]CoCl_2 (Table 5, Entry 10)

1-Cyclohexyl-1,3-butadiene (12e)

Hydrovinylation of \((E/Z)\)-1-cyclohexyl-1,3-butadiene using \([DPPB]CoCl_2\) (Table 3, Entry 6):

Unsuccessful hydrovinylation of (only Z)-1-cyclohexyl-1,3-butadiene using \((S,S)\)[DIOP]CoCl_2 and TMA (Table 3, Entry 6, but only Z-isomer).

\((E)\)-1,3-pentadiene (12f)

Hydrovinylation of \((E)\)-1,3-pentadiene using \([DPPB]CoCl_2/Me_3Al\) at – 10 °C (Table 3, Entry 7).

Hydrovinylation of \((E)\)-1,3-pentadiene using \((R,R)\)-[DIOP]CoCl_2/Me_3Al at – 45 °C (Table 5, Entry 12).

\((E)\)-1-phenyl-1,3-butadiene (12g)

Hydrovinylation of \((E)\)-1-phenyl-1,3-butadiene using \([dppp]CoCl_2\) (Table 3, Entry 8)

Hydrovinylation of \((E)\)-1-phenyl-1,3-butadiene using \([dppm]CoCl_2\) (Table 3, Entry 10)

Hydrovinylation of \((E)\)-1-phenyl-1,3-butadiene using \((S,S)\)[DIOP]CoCl_2 (Table 5, Entry 13)

\((E)\)-ethyl hexa-3,5-dienoate (12h)
Hydrovinylation of (E)-ethyl hexa-3,5-dienoate using [DPPM]CoCl₂ (Table 3, Entry 14)

(E)-6-benzyloxy-1,3-hexadiene (12i)
Hydrovinylation of (E)-6-benzyloxy-1,3-hexadiene using [dppb]CoCl₂ (Table 3, Entry 15)
Asymmetric hydrovinylation of (E)-6-benzyloxy-1,3-hexadiene using (S,S)-[DIOP]CoCl₂ (Table 5, Entry 17)

(E/Z)-hexa-3,5-dienylbenzene (12j)
Hydrovinylation of (E/Z)-hexa-3,5-dienylbenzene using [dppb]CoCl₂ (Table 3, Entry 16)

(E)-4-(buta-1,3-dienyl)-N,N-dimethylaniline (12k)
Hydrovinylation of (E)-4-(buta-1,3-dienyl)-N,N-dimethylaniline using DPPBCoCl₂ (Table 3, Entry 17)

(E)-1-phenyl-2-methyl-1,3-butadiene (12l)
Hydrovinylation of (E)-1-phenyl-2-methyl-1,3-butadiene using [dppm]CoCl₂ (Table 3, Entry 18 and 19).

7-Methyl-3-methylene-octa-1,6-diene (β-myrcene) (12m)
Hydrovinylation of 7-methyl-3-methylene-octa-1,6-diene (β-myrcene) using [dppp]CoCl₂ (Table 3, Entry 21)

Isoprene (12n)
Hydrovinylation of Isoprene using [dppp]CoCl₂ (Table 3, Entry 22)

References
SUPPORTING INFORMATION

Cobalt-Catalyzed Hydrovinylation of 1,3-Dienes

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General methods. Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen or argon by using Schlenk techniques or a Vacuum Atmospheres glovebox. Ethylene (99.5%) was purchased from Matheson Inc., and passed through a column of Drierite® before use. All chemicals obtained from commercial sources were used as received unless otherwise mentioned. All dienes, unless otherwise mentioned, were prepared via Wittig reaction of the corresponding aldehydes with the Wittig reagent generated from methyl triphenylphosphonium bromide and n-BuLi in THF. Tetrahydrofuran and diethyl ether were distilled under nitrogen over sodium/benzophenone. Dichloromethane and toluene were purified by distillation from calcium hydride, and subsequently storing over 4 Å molecular sieve. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Absence of polymeric impurities was ascertained by NMR of the crude materials. Except for the volatile materials, the isolated yields of the products were not significantly different from the conversions. The percentage compositions for isomeric products was determined by uncalibrated analysis of the areas. This is possible since the response of volatile isomeric hydrocarbons are essentially same in flame ionization detection as determined by comparison of GC-derived compositions with that obtained from 1H NMR in several cases. Gas chromatographic analyses were performed on Agilent gas chromatographs using a HP-1 Methylsilicone column [30 m x 0.250 mm, 0.25 µm film thickness, achiral stationary phase (or ASP) GC column] and an FID detector. Enantiomeric excesses of chiral compounds were determined by chiral stationary phase gas chromatographic (CSP GC) analyses, which were performed on a Hewlett-Packard 5890 with Cyclodex-B capillary GC column (60 m x 0.25 mm, 0.25 µm film thickness) or on an Agilent 7820A using a Cyclosil-B capillary GC column (25 m x 0.25 mm, 0.25 µm film thickness) using helium or hydrogen as a carrier gas. The columns containing Chiral Stationary Phase (CSP) materials were also used for analysis of some of the geometric isomers because they gave better separation. These are indicated under appropriate chromatograms. Where ever appropriate, %ee’s were determined from chromatograms where base-line separation of the enantiomers was achieved for an authentic racemic mixture. Limits of detection of the minor enantiomer were established by analyzing mixtures of both enantiomers of known compositions. Optical rotations were recorded on a Rudolph Research Analytical AUTOPOL VI polarimeter in the solvents mentioned. Unless otherwise mentioned, the measurements were done on a filtered (45 micron filter) solution at the sodium line at room temperature. 1H and 13C NMR spectra were recorded either on a spectrometer operating at 500 MHz for 1H and 125 MHz for 13C, or a machine operating at 400 MHz for 1H and 162.02 MHz for 31P. Proton chemical shifts were internally referenced to the residual solvent proton resonance (e.g., CHCl3 at δ 7.26). In several instances where there is a minor deviation, position of a reference peak is included in the data to facilitate assignments. Coupling constants are
reported in Hz. Phosphorous ($^{31}$P NMR) are reported as $\delta$ in units of parts per million (ppm) relative to external H$_3$PO$_4$ ($\delta$ 0.0).

**Synthesis of Cobalt Complexes**

Literature methods$^1$ were used for preparation of complexes Co(dppm)Cl$_2$ and Co(dppp)Cl$_2$. For the preparation of Co(dppb)Cl$_2$, [(RR)-(-)(DIOP)CoCl$_2$], [(SS)-(+)-(DIOP)CoCl$_2$] and [(SS)-(-)-(BDPP)CoCl$_2$] modified procedures (see below) were used. Solid-state structures of these two complexes have been reported in our previous publication.$^2$

**Typical modified procedure for synthesis of cobalt complexes:** [(R,R)-DIOP]CoCl$_2$. A 25-mL dry round bottom flask loaded with anhydrous CoCl$_2$ (10.9 mg, 0.0839 mmol) was charged with THF (5 mL). On stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of (R,R)-DIOP (41.8 mg, 0.0839 mmol) in dry and degassed ether (5 mL) was added dropwise to yield a blue turbid solution. After stirring at room temperature for 6 h, 20 mL deoxygenated hexane was added in one portion to get a blue solid. The resulting solid was washed with diethyl ether and hexane (1:1) mixture (3 X 5 mL) to remove any unreacted DIOP. Further purification was accomplished by crystallization of the Co(II)-complex from a saturated CHCl$_3$ solution by slow vapor diffusion of pentane at room temperature. The solid state structure determined by X-ray crystallography has been reported.$^2$

[(R,R)-BDPP]CoCl$_2$. Cobalt chloride (50.5 mg, 0.390 mmol) was added to a previously flame-dried 50-mL round two-necked bottom flask fitted with a flow control gas inlet and magnetic stir-bar loaded in a glove box under nitrogen. Outside the box, the nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (5 mL) was added, and upon stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of (S,S)-BDPP (181 mg, 0.410 mmol) in freshly distilled, degassed ether (5 mL) was added dropwise to yield a blue turbid solution. After stirring at room temperature for 12 h, 20 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 X 5 mL) to remove any unreacted (S,S)-BDPP, resulting in quantitative yield of a light blue solid, which was used with no further purification. A sample was recrystallized from saturated CHCl$_3$ solution by slow vapor diffusion of pentane at room temperature. The solid-state structure determined by X-ray crystallography has been reported.$^2$

[(2S,4S)-(--)••-2,4-Bis(diphenylphosphino)-pentane dichlorocobalt(II): (++)[(SS)-(--)-(BDPP)CoCl$_2$]. Yield 96%. Elemental analysis calculated for C$_{29}$H$_{30}$Cl$_2$CoP$_2$: C, 61.07; H, 5.30. Found C, 60.69; H, 5.28.

\[\text{Co}^{2+} + 2\text{Cl}^{-} + 2\text{Ph}_{2}\text{P}(\text{O})(\text{CH}_{2})_{3}\text{P(Ph)}_{2} \rightarrow \text{Co}^{2+} \cdot \text{Cl}_{2} \cdot 2\text{Ph}_{2}\text{P}(\text{O})(\text{CH}_{2})_{3}\text{P(Ph)}_{2} \]
Cobalt(II)-complexes of ligands listed in Table 1 and Figure 5 were similarly prepared and used for hydrovinylation under conditions listed in various tables.

**Synthesis of cobalt complexes of N-heterocyclic carbene ligand (Figure 3).** In a typical procedure the bromide salt of a carbene precursor (195 mg, 0.46 mmol, 1 equiv.) and potassium tert-butoxide (306 mg, 2.73 mmol, 6 equiv.) were added to a previously oven-dried 20-mL round bottom flask with magnetic stir-bar loaded in a glove box under nitrogen. Freshly distilled THF (5 mL) was added and stirred at room temperature for 36 hours under nitrogen in glove box. The reaction solution was passed through a pad of celite in dry box and the solvent was evaporated under vacuum to get free carbene. Anhydrous CoCl₂ (48 mg, 0.37 mmol, 0.95 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet and magnetic stir-bar loaded in a glove box under nitrogen. The flask was removed from the drybox and the nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (4 mL) was added, and upon stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of free carbene (104 mg, 0.39 mmol, 1 equiv.) in freshly distilled degassed THF (2 mL) was added dropwise to yield a blue solution. After stirring at room temperature for 32 h, 10 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 10 mL) to remove any unreacted carbene, resulting in quantitative yield of a light blue solid, which was used in hydrovinylation with no further purification.

**Synthesis of CoCl₂[tert-butyl bis-oxazoline] complex.** Similar procedure was used for synthesis of cobalt complexes from dinitrogen based chelating ligands (–)-sparteine and the bis-oxazoline complexes (Figure 3). As a typical procedure, anhydrous CoCl₂ (23 mg, 0.18 mmol, 1 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet under nitrogen. The nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (3 mL) was added, and upon stirring at room temperature for 20 min, a clear deep blue solution formed. A solution of the tert-butyl bis-oxazoline ligand (51 mg, 0.19 mmol, 1.05 equiv.) in freshly distilled degassed THF (3 mL) was added dropwise to yield a blue solution. After stirring at room temperature for 36 h, 15 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 15 mL) to remove any unreacted ligand, resulting in quantitative yield of a light blue solid, which was used for hydrovinylation of 1,3-dienes with no further purification.

**Synthesis of [dppe]FeCl₃ complex.** As a typical procedure, anhydrous FeCl₃ (45 mg, 0.28 mmol, 1 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet under nitrogen. Freshly distilled, degassed THF (2 mL) was added, and upon stirring at room temperature for 20 min, a black-brown solution formed. A solution of DPPE (47 mg, 0.29 mmol, 1.05 equiv.) in freshly distilled degassed THF (3 mL) was added dropwise to yield a light pink solution. After stirring at room temperature for 24 h, 15 mL
freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 15 mL) to remove any unreacted dppe, resulting in good yield of a light blue solid (130 mg, 84%), which was used for hydrovinylation of 1,3-dienes with no further purification.

**Synthesis of Methylaluminoxane.** A flame-dried 250 mL three-necked round-bottom flask equipped with a septum, flow control gas inlet, temperature probe, and magnetic stir-bar was purged with argon and charged with 3.85 g Al₂(SO₄)₃.16 H₂O, 15 mL dry, distilled toluene and chilled to −10 °C using a salt/ice bath. To this slurry was added 20 mL 2 M trimethylaluminum solution in toluene stored at 0 °C dropwise via syringe with vigorous stirring. The ice bath was removed and the solution allowed to warm to room temperature slowly, and then heated to 30 °C for 4 hrs. After the first heating period, the mixture was then slowly brought to 50 °C and stirred for 8 hrs overnight. A Schlenk filter (12” column fitted with two male ground glass joints and a microporous fret in the center) and a 250 mL single-necked round-bottom were flame dried and attached to the 250 mL three-necked flask. The solution was filtered to remove the solids and the resulting toluene filtrate was distilled to remove the toluene to give a white glassy solid that was harvested in an inert atmosphere glovebox to get the product as a white solid 0.610 g (26% yield).

**Synthesis of Substrates**

**Synthesis of (E)-6-benzyloxy-1,3-hexadiene (12i).** A 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with methyltriphenylphosphonium bromide (6.31 g, 17.66 mmol, 1.1 equiv.) and anhydrous THF (25.0 mL). n-BuLi (2.5 M in hexane, 7.1 mL, 17.66 mmol, 1.1 equiv.) was added dropwise via syringe at 0 °C and the reaction mixture was allowed to stir at 0 °C for 2 h. A solution of (E)-5-(benzyloxy)pent-2-enal (3.0 g, 15.77 mmol) dissolved in anhydrous THF was added dropwise and the reaction mixture was allowed to stir at ambient temperature for 12 h. The reaction mixture was diluted with pentane, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (pentane-ether, 20:1) to yield the 1,3 diene (2.04 g, 69%) as a E-1,3-diene. ¹H NMR and ¹³C NMR agreed with published data. ¹H NMR (CDCl₃, 400 MHz): 2.48 (q, J = 4 Hz, 2 H), 3.59 (t, J = 8 Hz, 2 H), 4.58 (s, 2 H), 5.05 (d, J = 8 Hz, 1 H), 5.17 (d, J = 16 Hz, 1 H), 5.75 – 5.82 (m, 1 H), 6.15 – 6.22 (m, 1 H), 6.33 – 6.43 (m, 1 H), 7.31 – 7.43 (m, 5 H, aromatic). Gas Chromatography: CSP GC (Cyclosil, OT 150 °C/ isothermal) Rₜ for diene = 12.357 min. Methyl silicone SP GC (OT 150 °C/ isothermal) Rₜ for diene product = 10.492 min.

All the (E)-1,3-dienes as well as like 12a, 12b, 12c, 12d, and 12e were prepared by the literature methods of Wittig olefination using the corresponding aldehyde. Dienes like β-myrcene (12m), isoprene (12n) and (E)-1,3-pentadiene (12f) were purchased directly and used after proper distillation.

**Synthesis of (E)-ethyl-2-methyl-penta-2,4-dienoate.** A 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with (1-ethoxycarbonylethyl)triphenylphosphonium bromide (5.0 g, 11.28 mmol, 1.0 equiv.) and anhydrous CH₂Cl₂ (20.0 mL). Potassium
hydroxide (KOH) (0.8 gm, 13.54 mmol, 1.2 equiv.) as aqueous solution was added dropwise and stirred for 3 hrs at room temperature. A solution of acrolein (0.8 g, 13.54 mmol) dissolved in anhydrous CH2Cl2 was added dropwise and the reaction mixture was refluxed for 3 hrs and stirred 24 hrs at room temperature. The reaction mixture was diluted with petroleum ether, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (Hex-EtOAc, 7:1) to yield the 1,3 diene (0.6 g, 38%) as a E-1,3-diene. 1H NMR and 13C NMR agreed with published data.5-7 1H NMR (CDCl3, 400 MHz): 1.29 (t, J = 7.2 Hz, 3 H), 1.93 (s, 3 H), 4.20 (q, J = 7.2 Hz, 2 H), 5.42 (d, J = 8 Hz, 1 H), 5.53 (d, J = 16 Hz, 1 H), 6.59 – 6.68 (m, 1 H), 7.13 (d, J = 12 Hz, 1 H). CSP GC (OT 80 °C/ isothermal, H2 carrier gas) Conditions: Rf for diene product = 14.28 min.

Synthesis of (E)-ethyl-hexa-3,5-dienoate and (E)-t-Bu-hexa-3,5-dienoate. A 250 mL flask with condenser equipped with a magnetic stirring bar, purged with nitrogen, was charged with hexa-2,4-dienoic acid (12.0 g, 107 mmol, 1.0 equiv.) and 5 drops of DMF and 3 boiling chips were added. Thionyl chloride (19 g, 161 mmol, 1.5 mmol) was added from the top of the condenser dropwise and refluxed 30 minutes. HCl and SO2 gas were trapped by dil. NaOH solution throughout the reflux period and the reaction was stopped when there was no more evolution of HCl and SO2 gas through the NaOH solution. Hexa-2,4-dienoyl chloride (10 g, 71%) was distilled out from the same round bottom flask and directly used for the next setup reaction for diene synthesis. Freshly distilled ethyl alcohol (5.6 g, 123 mmol, 2 equiv.) and freshly distilled triethyl amine (12.4 g, 122.54 mmol, 2 equiv.) were mixed in 120 mL CH2Cl2 and chilled under dry ice/acetone. Hexa-2,4-dienoyl chloride (8 g, 61.27 mmol, 1 equiv.) was added dropwise via syringe. After 1 hr, a thick white precipitate appeared and the reaction was allowed to warm to room temperature and left overnight. Around 200 mL water was added and partitioned between water and DCM. The organic layer was washed (2 X 10% H2SO4, 1 X saturated NaHCO3, 1 x H2O, 1 X brine) and dried with MgSO4 and solvent was evaporated to get crude diene. A few crystals of BHT were added to the crude product which was then distilled to afford ethyl-3,5-hexadienoate (5.1 g, 59%). 1H NMR and 13C NMR agreed with published data.8-9

Same procedure was applied to synthesize (E)-t-Bu-hexa-3,5-hexadienoate by using t-butyl alcohol instead of ethyl alcohol.

1H NMR (CDCl3, 400 MHz): 1.21 (t, J = 7.2 Hz, 3 H), 3.07 (d, J = 6.4 Hz, 2 H), 4.12 (q, J = 4 Hz, 2 H), 5.02 (d, J = 10.4 Hz, 1 H), 5.12 (d, J = 16.4 Hz, 1 H), 5.71 – 5.78 (m, 1 H), 6.06 – 6.13 (m, 1 H), 6.25 – 6.34 (m, 1 H). CSP GC (OT 90 °C/ isothermal, cyclodex-B, He carrier gas) Rf for diene product = 38.27 min.

1H NMR (CDCl3, 400 MHz): 1.59 (s, 9 H), 3.16 (d, J = 8 Hz, 2 H), 5.18 (d, J = 10.4 Hz, 1 H), 5.28 (d, J = 17.2 Hz, 1 H), 5.87 – 5.94 (m, 1 H), 6.22 – 6.28 (m, 1 H), 6.42 – 6.51 (m, 1 H). 13C NMR (CDCl3, 125.02 MHz): 28.30, 39.45, 80.99, 116.76, 126.63, 134.16, 136.79, 171.04. CSP GC (OT 100 °C/ isothermal, cyclosil, H2 carrier gas) Rf for diene product = 12.09 min.
Synthesis of (Z/E)-1-cyclohexyl-1,3-butadiene and other related dienes. As a typical procedure to make (E/Z)-mixture of 1-cyclohexyl-1,3-butadiene, a 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with allyltriphenylphosphonium bromide (7.0 g, 18.0 mmol, 1.5 equiv.) and anhydrous THF (30.0 mL). Base n-BuLi (2.5 M in hexane, 6.5 mL, 16.2 mmol, 0.9 equiv.) was added dropwise via syringe at 0 °C and the reaction mixture was allowed to stir at 0 °C for 1 h. A solution of cyclohexanecarboxaldehyde (1.82 g, 16.2 mmol) dissolved in anhydrous THF was added dropwise and the reaction mixture was allowed to stir at ambient temperature for 12 h. The reaction mixture was diluted with pentane, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (pentane-ether, 20:1) to yield the 1,3 diene (1.30 g, 59%) as a mixture of Z- and E-isomers (53:47, by GC). 1H NMR and 13C NMR agreed with published data.10-11 1H NMR (CDCl3, 400 MHz): δ 1.05-1.30 (m, 11 H, both E and Z), 1.61-1.72 (m, 9 H, both E and Z), 1.96 – 1.98 (m, 1 H, E only), 2.41 – 2.44 (m, 1 H, Z only), 4.93 (d, J = 9 Hz, 1 H, E only), 5.03 – 5.17 (m, 3 H, overlapped E and Z), 5.29 (t, J = 10 Hz, 1 H, Z only), 5.64 (dd, J = 5, 16 Hz, 1 H, E only), 5.86 (t, J = 11 Hz, 1 H, Z only), 5.96 – 6.02 (m, 1 H, E only), 6.23 – 6.33 (m, 1 H, E only), 6.58 – 6.68 (m, 1 H, Z only). 13C NMR (CDCl3, 125.72 MHz): 26.07, 26.22, 26.38, 32.97, 33.45, 37.07, 40.84, (both E and Z overlapped), 114.90 (E), 116.88 (Z), 127.47 (Z), 128.53 (E), 132.81 (Z), 137.88 (E), 139.15 (Z), 141.51 (E).

Gas Chromatography: (Cyclosil, temp. 80 °C / isothermal, H2 carrier gas) starting material RT = 18.63 min for Z-diene and 26.243 min for E diene.

Similar procedure was used for the synthesis of (E/Z)-mixture of 1,3-dienes like (E/Z) dodeca-1,3-diene (12d), (E/Z)1-phenyl-1,3-butadiene (12g) and (E/Z) hexa-3,5-dinylbenzene (12j) using corresponding aldehyde and allyltriphenylphosphonium bromide.

X2Co(L)-Catalyzed Hydrovinylation of 1,3-Dienes

Hydrovinylation of (E)-nona-1,3-diene using [DPPB]CoCl2 (Table 1, Entry 9, Typical procedure for ligand screening). To an oven dried round bottom flask with a sidearm, was added [DPPB]CoCl2 (35 mg, 0.063 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.17 mL, 0.32 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept at 0 °C temperature and (E)-nona-1,3-diene (78 mg, 0.63 mmol) in dichloromethane (0.5 mL) solution added under ethylene and the mixture was stirred for 0.5 h. The ethylene balloon was removed and 0.1 mL of methanol was added to the flask. The reaction solution was diluted with pentane (3 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil (96% 1,4-Z (13a) and 1,4-linear (16a) by GC and NMR analysis.

All the reactions in Table 1 were performed in similar fashion using the conditions described in the Table 1 using Co(II)-complexes prepared as described before. Some typical procedures are described below after details of the identification of the isomeric products from 12a.
Identification of Products of Hydrovinylation of (E)-nona-1,3-diene (12a)

[The following data extracted from ref. 2, which also contains details of gas chromatographic analysis including chiral stationary phase separations of various isomers. The reported ee’s were determined from these gas chromatograms.]

**Hydrovinylation of (E)-nona-1,3-diene (13a) using [dppb]CoCl₂/Me₃Al at -10 °C (Entry 9, Table 1), or using [DIOP]CoCl₂ at -45 °C (Entry 8, Table 4)**

(Z)-4-Vinynon-2-ene (13a):

\[ \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta \text{ 0.869 (t, J = 7 Hz, 3 H, H}^9), 1.21-1.35 (m, 7 H), 1.38-1.45 (m, 1 H) 1.21-1.45 total 8 H, 1.622 (dd, J = 6.5 Hz, 2 Hz, 3 H, H}^1), 3.011 (m, 1 H, H}^4), 4.929 (ddd, J = 10 Hz, 1.5 Hz, 1.5 Hz, 1 H, H}^{11}), 5.216 (ddq, 10 Hz, 10 Hz, 1.5 Hz, H}^3), 5.495 (dq, 10.5 Hz, 6.5 Hz, 1 Hz, H}^2), 5.709 (ddd, 17 Hz, 10 Hz, 7 Hz, 1H, H}^{10}). \]

Assignments and coupling confirmed by COSY and NOESY (C\text{H}_1 \rightarrow C\text{H}_4).

\[ \text{13C NMR (CDCl}_3\text{): } \delta \text{ 13.02, 14.07 22.63, 26.79, 31.90, 35.24, 41.26, 112.87, 123.78, 133.23, 141.87. } \]

The peak at \( \delta \) 14.07 (due to the vinyl methyl carbon is at a higher field compared to the corresponding peak in the corresponding (E)-isomer, which appears at \( \delta \) 17.96, see below). IR (neat cm⁻¹): 3079 (w), 3111 (m), 2959 (s), 2927 (s), 2858 (s), 1636 (m), 992 (w), 909 (m), 724 cm⁻¹ is characteristic of a (Z)-alkene. Absence of peaks ~ 960-970 cm⁻¹ indicates absence of the (E)-isomer, 14a.

ESI-MS; m/z 191.1 [M+K]; mass calculated for C\text{11H}_{20}K, 191.1.

Product from (RR)-(−)-DIOP [\( \alpha\text{]}^2_\text{D} = −20.9 \) (hexane, c 1.15)

Gas Chromatography: (Polymethylsiloxane column): 80 °C \( R_T \) 13a: 21.169 min.; 14a: 21.93min.; 15a 22.77 min.; CSP GC (Cyclodex B) 60 °C 13a: \( R_T \) = 26.07 min. (S), 27.25 (R); 16a 44.79 min.

**Isomeric hydrovinylation products obtained from (E)-nona-1,3-diene (13a) using [dppm]CoCl₂/Me₃Al (Entries 12 and 13, Table 1)**

(E)-4-vinynon-2-ene (14a):

\[ \text{1H NMR (CDCl}_3\text{): } \delta \text{ 0.85-0.91 (m, 3 H, H}^9), 1.21-1.41 (m, H}^5, H}^6, H}^7, H}^8), 1.669 (dd, J = 6 Hz, 0.5 Hz, 3 H, H}^1), 2.619 (pent, J = 7.5 Hz, 1 H, H}^4), 4.931 (dm, J = 10 Hz, 1 H, H}^{11}), 4.977 (dm, J = 17.5 Hz, 1 H, H}^{12}), 5.29-5.45 (m, 2H, H}^2, H}^3), 5.706 (dd, J = 17.5, 10, 7.5 Hz, 1 H, H}^{10}). \]

Chemical shifts and coupling constants assigned by COSY and double irradiation experiments.

\[ \text{13C NMR (CDCl}_3\text{): } \delta \text{ 14.07, 17.96 (vinyl Me), 22.63, 26.84, 31.88, 34.86, 46.88, 113.24, 124.53, 134.17, 142.35. } \]

The peak at \( \delta \) 17.96 (due to vinyl methyl carbon is at a lower field compared to the corresponding peak in the (Z)-isomer 13a, which appears at \( \delta \) 17.07, see under 13a, the previous compound.)

Gas chromatography: (polydimethylsiloxane column): see previous experiment.

(E)-3-methyldeca-1,4-diene (15a). \[ \text{1H NMR (CDCl}_3\text{): 0.85-0.91 (m, 3 H, H}^{10}), 1.075 (d, J = 6.5 Hz, 1 H, H}^{11}), 1.20-1.40 (m, H}^7, \]
H$^8$, H$^9$), 1.990 (ddd, J = 6.5, 6.5, 6.5 Hz, 2 H, H$^6$), 2.807 (ddq, J = 6.0, 6.0, 6.0 Hz, H$^3$), 4.931 (dm, J = 10 Hz, 1 H, H$^1c$), 4.977 (dm, J = 17.5 Hz, 1 H, H$^1t$), 5.352 (dd, J = 15.5, 6.5 Hz, 1 H, H$^4$), 5.416 (dt, J = 15.5, 6.5, 1 H, H$^5$), 5.791 (ddd, J = 17, 10.5, 6.5 Hz, 1 H, H$^2$). Chemical shifts and coupling constants assigned by COSY and double irradiation experiments.

$^{13}$C NMR (CDCl$_3$): 14.04, 20.00, 22.54, 29.23, 31.41, 32.55, 40.31, 112.37, 129.44, 133.86, 143.40.

Gas chromatography: (polydimethylsiloxane column) : see under 13a.

**Procedure for Co-catalyzed hydrovinylation of (E)-nona-1,3-diene using [dppb]CoBr$_2$ (Table 1, Ligand Screening, Entry 10).**

To an oven dried round-bottom-flask with a sidearm, was added [dppb]CoBr$_2$ (16 mg, 0.025 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.12 mL, 0.24 mmol) was added dropwise and the color of the solution changed from blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 °C and (E)-nona-1,3-diene (30 mg, 0.24 mmol) in a dichloromethane (1 mL) added under ethylene and the mixture was stirred for 20 h. The progress of the reaction was monitored via gas chromatography until completion. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil as 94% (Z)-1,4 HV product (13a) and 5% (Z)-1,4-linear dimerized HV product (16a).

**Hydrovinylation of (E)-nona-1,3-diene using[dppp]CoCl$_2$ at room temperature (Ligand screening, Table 1, Entry 7).**

To an oven-dried round-bottom flask with a sidearm, was added [dppp]CoCl$_2$ (11 mg, 0.020 mmol) under argon and it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.03 mL, 0.060 mmol) was added dropwise as color of the solution quickly changed from deep blue to brown with the formation of white fumes over the solution. When all the fumes disappeared in about 5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, (E)-nona-1,3-diene (25 mg, 0.20 mmol) was added under ethylene at room temperature and the mixture was stirred for 1 h until the completion of reaction monitored via gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of solvent yielded the product as a colorless oil and isomeric compositions were determined by gas chromatography and NMR spectroscopy. The ratios of products are indicated in the table.

**Hydrovinylation of (E)-nona-1,3-diene using[dppm]CoCl$_2$ at room temperature (Ligand screening, Table 1, Entry 12).**

To an oven-dried round-bottom flask with a sidearm, was added [dpmm]CoCl$_2$ (42 mg, 0.082 mmol) under argon and it was dissolved in dichloromethane (1.5 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.13 mL, 0.25 mmol) was added dropwise as color of the solution quickly changed from bluish brown to red brown with the formation of white fumes over the solution. When all the fumes disappeared in around
5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, \((E)\)-nona-1,3-diene (102 mg, 0.82 mmol) in dichloromethane (1 mL) was added under ethylene at room temperature and the mixture was stirred for 2 h. The progress of the reaction was monitored via gas chromatography intermittently. After 2 hours, the ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil and isomeric compositions were determined by gas chromatography and NMR spectroscopy (Table 1, entry 12).

**Hydrovinylation of \((E)\)-nona-1,3-diene using[BISBI]CoCl\(_2\) (Ligand Screening, Table 1, Entry 14).** To an oven-dried round-bottom flask with a sidearm, was added [BISBI]CoCl\(_2\) (20 mg, 0.029 mmol) under argon and it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.15 mL, 0.29 mmol) was added dropwise as color of the solution quickly changed from blue to red brown with the formation of white fumes over the solution. When all the fumes disappeared in around 5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, \((E)\)-nona-1,3-diene (36 mg, 0.29 mmol) in dichloromethane (1 mL) was added under ethylene at -12 °C temperature and the mixture was stirred for 6 h. The progress of the reaction was monitored via gas chromatography intermittently. After 6 hours, the ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of solvent yielded the product as a colorless oil and isomeric compositions \([13a], 1,4-Z \text{HV} (65\%) \text{ and } [15a], 1,2-E \text{HV} (34\%)] were determined by gas chromatography and NMR spectroscopy.

**Screening of activators in the Co-Catalyzed hydrovinylation of 1,3-dienes (Table 2)**

The typical procedure described above (Hydrovinylation of \((E)\)-nona-1,3-diene using[DPPB]CoCl\(_2\) (Table 1, Entry 9) was used in screening various promoters for the reaction (Table 2).

The solid activators like Mn, InI\(_3\), and Zn/ZnI\(_2\) were added at the same time with cobalt complexes in the round bottom flask with side-arm in the nitrogen atmosphere glove box. Liquid activators like Me\(_3\)B, Et\(_3\)B, Ph\(_3\)B, i-BuAlH, LiEt\(_3\)BH (in THF), Et\(_2\)AlOEt, Et\(_2\)AlCl, EtAlCl\(_2\), PhMgBr, were added in the same way as trimethylaluminium (TMA solution in toluene) to the solution of cobalt complexes via syringe.

Typical experiments are described below:

**Unsuccessful hydrovinylation of nona-1,3-diene using [dppe]CoCl\(_2\) and Mn as promoter (Promoters screening, Table 2, Entry 9).** As a typical procedure, to an oven dried round-bottom-flask with a sidearm, was added DPPECoCl\(_2\) (21 mg, 0.040 mmol) and Mn (22 mg, 0.40 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. After 30 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept in room temperature and the nona-1,3-diene (50 mg, 0.40
mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 14 h at room temperature intermittently monitoring the progress of reaction by gas chromatography. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 X 6 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.

**Hydrovinylation of (E)-dodeca-1,3-diene using [DPPP]COBr₂ and Zn/ZnI₂. (Promoters screening, Table 2, Entry 20)** To an oven dried round-bottom-flask with a sidearm, was added [DPPP]CoBr₂ (20 mg, 0.032 mmol), Zn dust (4.2 mg, 0.064 mmol) and ZnI₂ (20 mg, 0.064 mmol) under argon and was dissolved in dichloromethane (2 mL) at room temperature. The solution was stirred for at least 30 minutes at room temperature, and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 °C and (E)-dodeca-1,3-diene (53 mg, 0.32 mmol) was added under ethylene. After 1 hour, first aliquot of the reaction mixture was taken out via syringe and flush through a small pad of silica and was analyzed by GC. Reaction was monitored by GC analysis until completion. Finally after stirring the reaction mixture for 4 h at ambient temperature, the ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (3 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as a mixture of hydrovinylation product (13d, 1,4-Z, 79%) and linear hydrovinylation product (16d, 1,4-Z-linear, 21%) from GC and NMR analysis. All the reactions in Table 2 using Zn and ZnI₂ were performed exactly the same way using the conditions described therein.

**Unsuccessful hydrovinylation of (E)-dodeca-1,3-diene using DPPBCoCl₂ and diethyl aluminum chloride (Et₂AlCl) as a promoter (Table 2, Entry 13).** To an oven dried round-bottom-flask with a sidearm, was added DPPBCoCl₂ (35 mg, 0.063 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Diethylaluminium chloride (Et₂AlCl) as a 2M solution in toluene (0.16 mL, 0.32 mmol) was added dropwise and the color of the solution remain unchanged from its blue color. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -10 °C and (E)-dodeca-1,3-diene (105 mg, 0.63 mmol) in a dichloromethane (1 mL) added under ethylene and the mixture was stirred for 5 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Removal of solvent and analysis by GC and NMR gave none of the expected hydrovinylation products.

**Unsuccessful hydrovinylation of nona-1,3-diene using [DPPM]CoCl₂ and MeMgBr and AgOTf as promoters (Promoters screening, Table 2, Entry 12).** As a typical procedure, to an oven dried round-bottom-flask with a sidearm, was added [DPPM]CoCl₂ (19 mg, 0.037 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Methylmagnesium bromide (MeMgBr) as a 3M solution in ether (0.01 mL, 0.037 mmol) was added via syringe and the color of the solution changed from deep blue to black with the formation of white fumes over the solution. Subsequently, AgOTf (9.3 mg, 0.037 mmol) was added to the solution. After 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 °C and the nona-1,3-
diene (46 mg, 0.37 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 4 h at 0 °C to rt. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (3 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 6 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.

Iron-catalyzed hydrovinylation of (E)-nona-1,3-diene using [DPPE]FeCl$_3$ (Equation 11): To an oven dried round-bottom-flask with a sidearm, was added [DPPE]FeCl$_3$ (56 mg, 0.099 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.24 mL, 0.49 mmol) was added dropwise and the color of the solution changed from light pink to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -10 °C and (E)-nona-1,3-diene (61 mg, 0.49 mmol) as a dichloromethane solution (0.5 mL) was added under ethylene and the mixture was stirred for 3 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 7 mL). Removal of solvent yielded the product as a colorless oil as a mixture of (Z)-1,4-product (30%), 1,4-linear dimerized product (10%) and starting material (60%) by GC and NMR analysis.

Unsuccessful hydrovinylation of substrate (E)-ethyl-2-methylpenta-2,4-dienoate using [dppm]CoCl$_2$. To an oven dried round-bottom-flask with a sidearm, was added [dppm]CoCl$_2$ (30 mg, 0.058 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.6 mL, 1.16 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 °C and (E)-ethyl-2-methylpenta-2,4-dienoate (81 mg, 0.58 mmol) as a dichloromethane solution (0.5 mL) was added under ethylene and the mixture was stirred for 15 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 5 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.

Unsuccessful attempt to dimerize (E)-1,3-nonadiene and propylene using [dppe]CoCl$_2$ (Equation 10). To an oven dried round-bottom-flask with a sidearm, was added (dppe)CoCl$_2$ (30 mg, 0.056 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.08 mL, 0.17 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with propylene from a balloon. The reaction vessel was cooled to -20 °C and (E)-1,3-nonadiene (70 mg, 0.56 mmol) as a dichloromethane solution (0.5 mL) was added under propylene and the mixture was stirred
for 14 h. The propylene balloon was removed and 0.1 mL of methanol was added to the flask. The solution was diluted with pentane (4 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 7 mL). Removal of solvent showed no codimerization reaction as all the (E)-1,3-nonadiene starting material was recovered as judged by GC and $^1$H NMR.
Cobalt-Catalyzed Hydrovinylation of 1,3-Dienes. Scope of Substrates (Tables 3 and 5)

Hydrovinylation of different dienes and the major products obtained from them are listed below:

Hydrovinylation of (E)-nona-1,3-diene (12a)

The exploratory studies of effects of ligands and additives were conducted using this substrate. Rigorous identifications of all products from this substrate were described in our original communication. For hydrovinylation procedure for (E)-nona-1,3-diene using [DPPB]CoCl₂ (Table 1, Entry 9, see under Ligand Screening). Details of the identification of various products were also listed earlier.

Typical procedure for asymmetric Co-catalyzed hydrovinylation reactions of (E)-nona-1,3-diene for ligand screening (Table 4, Entry 1-20). To an oven-dried round-bottom flask with a sidearm, was added (RR)-[DIOP]CoCl₂ (12.6 mg, 0.0201 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (2.0 mL) and toluene (0.5 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (4.3 mg, 30 µl, 0.0604 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared (typically in 5-10 min depending on complex), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3-5 min. The reaction vessel was cooled to – 45 °C (or whatever is the prescribed temperature with other ligands and substrates) and (E)-nona-1,3-diene (50.0 mg, 0.403 mmol) was added under ethylene and the mixture was stirred for 6 h (color of the reaction solution turned blue again at the end of the reaction). The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil (58.2 mg, 95%). Analysis by GC and NMR showed that the product was essentially pure. Isomeric compositions were determined by gas chromatography and NMR spectroscopy.

Details of the identification of the individual components of the mixture and chromatographic separation of these compounds including those of the enantiomers have been reported before. The enantioselectivities obtained with various other chiral ligands under different conditions are listed in Table 4. Typical examples are described below:

Asymmetric Co-catalyzed Hydrovinylation Reactions (E)-1,3-nonadiene by using (S,S,R,R)-Tangphos [(L14)CoCl₂] (Table 5, Entry 3). To an oven-dried round-bottom flask with a sidearm, was added (S,S,R,R)-[Tangphos]CoCl₂ (19 mg, 0.046 mmol) under argon and it was dissolved in a degassed dichloromethane (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.07 mL, 0.14 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution.
When all the fumes disappeared (typically in 5 min), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3 minute. The reaction vessel was cooled to – 10 °C and (E)-nona-1,3-diene (57 mg, 0.46 mmol) in dichloromethane (1 mL) was added under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil. Analysis by GC and NMR showed that the product was essentially pure with two major isomers (13a product with 39% yield and 95% ee and the linear product 16a product in 40% yield). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (See attached chromatograms and Spectra).

Asymmetric Co-catalyzed hydrovinylation reaction (E)-1,3-nonadiene by using 1 mol % Josiphos 2 [(18)CoCl2] (Table 5, Entry 4). To an oven-dried round-bottom flask with a sidearm, was added [Josiphos]CoCl2 (4 mg, 0.0038 mmol) under argon and it was dissolved in a degassed dichloromethane (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.0057 mL, 0.0114 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared (typically in 5 min), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3 minute. The reaction vessel was cooled to – 20 °C and (E)-nona-1,3-diene (47 mg, 0.38 mmol) in dichloromethane (1 mL) was added under ethylene and the mixture was stirred for 14 h until the completion of reaction monitored by gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil. Analysis by GC and NMR showed that the product was essentially pure with major isomer (13a product with 95% yield and 87% ee). Isomeric compositions were determined by gas chromatography and NMR spectroscopy.

Highest ee for this substrate was obtained using (R,R)-DIOP (>95% ee, >95% yield) or (S,S)-BDPP (>97% ee, >95% yield) at -45 °C.2
13a using Cl2Co(dppb) Entry 1, Table 3

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13a using (S,S)-(BDPP) Entry 2, Table 5

(Cyclohexyl)bis(2,6-dimethyl-4-hydroxyphenyl)cyclohexane-1,3-dione

(S,S)-(BDPP)
GC (Cyclodex-B, 70 degree) of Compound 13a (HV using Cl2Co(Josiphos Ligand L18, Entry 4, Table 5)
Hydrovinylation of \((E)-\text{deca-1,3-diene (12b)}\)

**Hydrovinylation of \((E)-\text{deca-1,3-diene using (R,R)\[DIOP\]CoCl}_2\) (Table 5, Entry 5).** To an oven dried round bottom flask with a sidearm, was added \((RR)\[DIOP\]CoCl\(_2\) (3 mg, 0.0028 mmol) and dichloromethane (0.5 mL) was added. Trimethylaluminium solution (2 M) (0.05 mL, 0.008 mmol) was added to the solution and the color changed from deep blue to red brown with the formation of white fumes. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -45 °C and \((E)-\text{deca-1,3-diene (43 mg, 0.28 mmol), was added via syringe under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 6 mL). Removal of the solvent yielded the product as colorless oil. GC showed 97% \((Z)-1,4\)-product and 3% \(1,4\)-linear dimerized product.

An authentic sample of the racemic compound was prepared by similar procedure (Table 3, Entry 2) using corresponding achiral complex [(dppb)CoCl\(_2\)] at the prescribed temperature.

\(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.891 (t, J = 7 Hz, 3 H, H\(_{10}\)), 1.23-1.40 (m, 9 H), 1.38-1.47 (m, 1 H), 1.23-1.47 total 10 H, 1.628 (dd, J = 7, 2 Hz, 3 H, H\(_1\)), 3.027 (m, 1 H, H\(_4\)), 4.935 (dm, J = 10 Hz, H\(_{12}\)), 4.987 (ddd, J = 17.5 Hz, m, 1 H, H\(_{13}\)), 5.222 (app t m, 10.5 Hz, H\(_3\)), 5.502 (dq m, 11.5 Hz, 6.5 Hz, 1 Hz, H\(_2\)), 5.714 (dd, 17 Hz, 10 Hz, 7 Hz, 1H, H\(_{11}\)). [toluene @ 2.364]. Also seen: (t, J = 6.5 Hz) 0.221 up-field from C\(_{\text{sp3}}\)-CH (3.027) ~ 2% (bis-allylic CH\(_2\)).

\(^13\)C (CDCl\(_3\)) 13.01, 14.07, 22.66, 27.10, 29.34, 31.87, 35.30, 41.26, 112.86, 123.77, 133.23, 141.86.

Mass spectrum: m/z = 167.1 (calculated for [M+H]\(^{+}\), M= C\(_{12}\)H\(_{23}\) 167.1)

Product from \((RR)-(\text{--})-\text{DIOP [\(\alpha\)}^{25}_D = -18.6 (hexane, c 1.25)

Gas chromatography: (Polydimethylsiloxane) conditions: 90 °C isotherm, retention time (min): \(R_T = 27.40\). CSP GC (Cyclodex) conditions: 60 °C isotherm, \(R_T = 35.94\) min. (S, 97.7%), 38.07 (R, 2.3%).
13b using (RR)-DIOP -45 degree methylsilicone column
90 degree isotherm, Entry 5, Table 5
13b using (RR)-DIOP -45 degree cyclodex-B, 60 degree isoterm, column 90 degree isotherm, Entry 5, Table 5

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RUN# 3963 JUN 27, 2009 22:45:12

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Hydrovinylation of \((E)\)-undeca-1,3-diene (12c)

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\end{array}
\]

Hydrovinylation of \((E)\)-undeca-1,3-diene using 1 mol \% \([\text{L18 Josiphos-2}]\text{CoCl}_2\) Loading (Table 5, Entry 7). To an oven dried round bottom flask with a sidearm, was added \([\text{L18CoCl}_2]\) (3 mg, 0.0028 mmol) and dichloromethane (0.5 mL) was added. Trimethylaluminium solution (2 M) (0.05 mL, 0.008 mmol) was added to the solution and the color changed from deep blue to red brown with the formation of white fumes. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -20 °C and \((E)\)-undeca-1,3-diene (43 mg, 0.28 mmol), was added via syringe under ethylene and the mixture was stirred for 7 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 6 mL). Removal of the solvent yielded the product as colorless oil. GC showed 97% \((Z)\)-1,4-product and 3% 1,4-linear dimerized product. Gas Chromatography (13c): CSP GC (Cyclodex-B, OT 100 °C/ isothermal, H₂ carrier gas). Rₜ for product = 50.0 min and 51.2 min (enantioselectivity 87 %ee).

\([\text{(R,R)-DIOP}]\text{CoCl}_2\) at -45 °C (6 h) gave the highest selectivity for this substrate (>95 %ee).
13c using (dppb)CoCl₂ (Table 3, entry 3)
methylsilicone column Oven temp 110 degrees
Racemic 13c using (dppb)CoCl$_2$ (Table 3, entry 3) cyclodex-B column oven temp 70 degrees/30 min, increase to 85 degree at 0.7 degree per minute
13c using (RR)-DIOPCoCl2 at -45 degree (entry 6, Table 5) cyclodex-B column oven temp 70 degrees/30 min, increase to 85 degree at 0.7 degree per minute

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RUN# 3956 JUN 26, 2009 23:38:42

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GC (Cyclodex-B, 100 degree) of Compound 13c (HV using Josiphos ligand L18) (entry 7, Table 5) 87% ee
GC (Cyclodex-B, 100 degree) of Compound 13c Using Josiphos Ligand L17
Hydrovinylation of (E/Z)-dodeca-1,3-diene (12d)

**Hydrovinylation of (E/Z)-dodeca-1,3-diene using [DPPB]CoCl₂ (Table 3, Entry 5).** To an oven dried round bottom flask with a sidearm, was added DPPBCoCl₂ (21 mg, 0.038 mmol) and methylaluminoxane (44 mg, 0.76 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 °C and (E/Z)-dodeca-1,3-diene (63 mg, 0.38 mmol), mixture of E:Z in the ratio of 54:46 via GC, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (61 mg, 82%). GC and NMR analysis showed that the product was essentially pure. 

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz): 0.836 (t, J = 7 Hz, 3 H), 1.25 – 1.43 (m, 14 H), 1.60 (dd, J = 7, 2 Hz, 3 H), 2.96 – 3.03 (m, 1 H), 4.89 - 4.99 (m, 2 H), 5.16 – 5.23 (m, 1 H), 5.43 - 5.51 (m, 1 H), 5.69 (ddd, J = 17, 10, 7 Hz, 1 H).} \]

\[ ^{13}C \text{ NMR (CDCl}_3, 125.02 \text{ MHz): 13.26, 14.33, 22.91, 27.37, 29.56, 29.83, 29.92, 32.14, 35.52, 41.49, 113.10, 124.01, 133.46, 142.10.} \]

Gas Chromatography (13d): CSP GC (Cyclosil, OT 90 °C/ isothermal, H₂ carrier gas): starting material Rₜ = 31.19 min. for E-diene and 31.81 for Z diene. Rₜ for product = 51.74 min and 54.82 min (racemic). Cycodex-B 65 °C/30 min increase 2 °C per min to 80 °C (He): Rₜ for product = 96.65 min and 99.14 min (racemic).

Hydrovinylation of (E/Z)-dodeca-1,3-diene using (S,S)[DIOP]CoCl₂ (Table 5, Entry 10): To an oven-dried round-bottom flask with a sidearm, was added (SS)-[DIOP]CoCl₂ (20 mg, 0.032 mmol) under argon and it was dissolved in a degassed dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.08 mL, 0.16 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 4 minutes. The reaction vessel was cooled to – 45 °C and (E/Z)-dodeca-1,3-diene (53 mg, 0.32 mmol, E:Z = 54:46) was added under ethylene and the mixture was stirred for 1 h until the completion of the reaction monitored by gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 X 10 mL). Pentane was removed and product was separated as a colorless oil as a major product 1,4-Z hydrovinylation product, 13d (53% yield) with 74% ee. Isomeric compositions were determined by gas chromatography and NMR spectroscopy. 

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz): 0.836 (t, J = 7 Hz, 3 H), 1.25 – 1.43 (m, 14 H), 1.60 (dd, J = 7, 2 Hz, 3 H), 2.96 – 3.03 (m, 1 H), 4.89 - 4.99 (m, 2 H), 5.16 – 5.23 (m, 1 H), 5.43 - 5.51 (m, 1 H), 5.69 (ddd, J = 17, 10, 7 Hz, 1 H).} \]

\[ ^{13}C \text{ NMR (CDCl}_3, 125.02 \text{ MHz): 13.26, 14.33, 22.91, 27.37, 29.56, 29.83, 29.92, 32.14, 35.52, 41.49, 113.10, 124.01, 133.46, 142.10.} \]

Hydrovinylation of (E)-dodeca-1,3-diene using (S,S)[DIOP]CoCl₂ at -45 °C (6 h) gave the highest ee for this substrate (>96 %ee, Table 5, Entry 8).
13d using (dppb)CoCl₂ (entry 4, Table 3) methylsilicone 130 degree isotherm

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\text{(Cyclopentadiene, B. 85 °C/30 min/0.2 g)}
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(Entry 8, Table 5)

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$3\% (-)\text{DIOPCoCl}_2/-45^\circ\text{C}$
Hydrovinylation of (E/Z)-1-cyclohexyl-1,3-butadiene using [DPPB]CoCl₂ (Table 3, Entry 6): To an oven dried round bottom flask with a sidearm, was added DPPBCoCl₂ (30 mg, 0.053 mmol) and methylaluminoxane (62 mg, 1.06 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 °C and (E/Z)-1-cyclohexyl-1,3-butadiene (72 mg, 0.53 mmol), mixture of E/Z in the ratio of 45:55, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (78 mg, 90%). GC and NMR analysis showed that the product (13e) was essentially pure. ¹H NMR (CDCl₃, 400 MHz): 1.07 - 1.26 (m, 6 H), 1.58 (dd, J = 1.6, 7 Hz, 3 H), 1.62 - 1.73 (m, 5 H), 2.79 (q, J = 8 Hz, 1 H), 4.91 - 4.91 (m, 1 H), 4.94 - 4.96 (m, 1 H), 5.24 - 5.30 (m, 1 H), 5.45 - 5.53 (m, 1 H), 5.62 - 5.71 (m, 1 H). ¹³C NMR (CDCl₃, 125.02 MHz): 13.11, 26.48, 26.54, 26.64, 30.29, 30.95, 42.16, 47.75, 113.82, 124.02, 131.75, 140.55. Gas Chromatography: Methyl silicone SP GC (OT 90 °C/ isothermal) Rₜ for product = 17.05 min. CSP GC (Cyclodex, OT 100 °C/ isothermal, He carrier gas): starting material Rₜ= 25.28 min. for Z-diene and 29.84 for E diene. Rₜ for product = 45.19 min and 46.35 min (enantiomers, racemic). CSP GC (Cyclosil, OT 80 °C/ isothermal) Rₜ for product = 34.52 min and 37.04 min (enantiomers, racemic).

An enantioselectivity of 84 %ee was obtained with (S,S)-[DIOP]CoCl₂ (at -10 °C, 8 h) with only the E-diene undergoing the conversion. With this ligand, when both E and Z are converted, maximum enantioselectivity is only 15%. With (R,R)-[BDPP]CoCl₂ and E and Z full conversion, maximum enantioselectivity is 35% [determined by CSP GC].

The following table shows the detail of HV reactions using (E/Z)-mixture of 1-cyclohexyl-1,3-diene using various ligands.

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<td>1,4- (Z)- HV(78%), 35% ee, linear(21%)</td>
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Unsuccessful hydrovinylation of (only Z)-1-cyclohexyl-1,3-butadiene using (S,S)\[DIOP\]CoCl$_2$ and TMA (Table 5, Entry 11, but only Z-isomer). To an oven dried round bottom flask with a side-arm, was added (S,S)\[DIOP\]CoCl$_2$ (15 mg, 0.024 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.03 mL, 0.072 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from balloon. The reaction vessel was cooled to -12 °C and (Z)-1-cyclohexyl-1,3-butadiene (32 mg, 0.23 mmol) added under ethylene and the mixture was stirred for 12 h at -12 °C. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug very quickly. The plug was washed with pentane (3 x 6 mL). Removal of solvent was difficult so GC and NMR analysis showed that the product was complex mixture of many unidentified different compounds along with starting material.
GC (HP-5, methyl silicone, 90 degree) of Compound 13e (HV using Cl2Co(DPPB) (entry 6, Table 3)
GC (Cyclosil-B, 80 degree) of Racemic Compound 13e Using DPPB (Entry 6, Table 3)
GC (HP-5, methyl silicone, 90 degree) of mixture of 13e and Z-12e
(Entry 11, Table 5)
GC (Cyclosil-B, 80 degree) of Mixture of Z-12e (st. mat.) and 13e (Entry 11, Table 5)

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Use Multiplier & Dilution Factor with ISTDs

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Proton NMR (400 MHz, D-chloroform) spectrum of Compound 13e (HV using DPPB) (entry 6, Table 3)
Proton NMR (400 MHz, D-chloroform) spectrum of compound 13e (HV using DPPB, Alkene Region Expansion)
Carbon NMR (100 MHz, D-chloroform) spectrum of Compound 13e

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+ unreacted Z-12e

(Entry 11, Table 5)
Hydrovinylation of (E)-1,3-pentadiene (12f)²

Hydrovinylation of (E)-1,3-pentadiene using [DPPB]CoCl₂/Me₃Al at – 10 °C (Table 3, Entry 7). [Extracted from ref. 2] To an oven-dried round-bottom flask with a sidearm, was added [dppb]CoCl₂ (20.4 mg, 0.037 mmol) under argon and it was dissolved in a mixture of dichloromethane and toluene (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.06 mL 0.11 mmol) was added dropwise as color of the solution changed from deep blue to brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon and a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 5 min and the reaction vessel was cooled to – 10 °C and (E)-1,3-pentadiene (50.0 mg, 0.74 mmol) was added under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.1 mL of water was introduced into the flask and stirring was continued for five minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL) and pentane was removed under vacuum in acetonitrile bath (-20 °C). Concentration yielded the product as a colorless oil (product + toluene; 501 mg). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (see attached chromatograms and spectra).

¹H NMR (500 MHz, CDCl₃): 1.072 (d, 7 Hz, 3 H), 1.570 (dd, 6.5, 1.5, Hz, 1 H), 3.167 (m, 1 H), 4.975 (ddd, 10, 1.5, 1.5, 1 H), 5.055 (ddd, 17, 1.5, 1.5, 1 H), 5.301 (ddq, 10, 10, 1.5 Hz, 1 H), 5.451 (ddq, 10, 1, 6.5, 1 H), 5.783 (ddd, 17.5, 11.0, 6.5, 1 H), [toluene @  2.183]
In addition, the following minor peaks are seen in the ¹H NMR: a doublet at  0.009 ppm up-field from the Csp³-CH₃; a triplet of multiplet at 0.417 upfield from the bis-allylic CH at 3.167. These minor peak might correspond to isomeric byproduct(s).

¹³C NMR (CDCl₃): 12.85, 20.42, 35.20, 112.14, 123.18, 134.30, 142.89. Isomeric purity by GC (Polydimethylsiloxane): (R₁ = 6.289 min.)
CSP GC (Cyclodex-B, 28 °C ): R₁ = 7.36 min (R), 7.47 min (S). (E)-1,3-pentadiene R₁ = 3.20 min., (Z)-1,3-pentadiene R₁ = 3.47 min.
Asymmetric hydrovinylation of (E)-penta-1,3-diene using(R,R)[DIOP]CoCl₂ at -45 °C (6 h) gave the highest ee for this substrate (>90 %ee, Table 5, Entry 12).²

Hydrovinylation of (E)-1,3-pentadiene using (R,R)-[DIOP]CoCl₂ /Me₃Al at – 45 °C (Table 5, Entry 12). To an oven-dried round-bottom flask with a sidearm, was added (RR)-[DIOP]CoCl₂ (138 mg, 0.220 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (6 mL) and toluene (1.5 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (47.6 mg, 330 μl, 0.6604 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 3-5 min. The reaction vessel was cooled to – 45 °C and (E)-1,3-pentadiene (300 mg, 440 μl, 4.404 mmol, E:Z = 99:1) was added under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.2 mL of water was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 20 mL). Pentane was removed by evacuation from a cold bath (-20 °C). Product
was distilled bulb to bulb at room temperature as a colorless oil (product + toluene; 668 mg). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (see attached chromatograms and spectra).

The product from (dppb)CoCl₂ (Entry 7, Table 3) reaction has, the following signals in addition to the ones due to the major product: a $CH_3$ (?)-doublet ($J = 7$ Hz) $\delta$ 0.008 down-field from the $C_{sp^3}$-$CH_3$; a $CH_3$ doublet of multiplet ($J = 5$ Hz, 3 H) at $\delta$ 0.035 down-field from the major $C_{sp^2}$-$CH_3$ signal; a CH or CH₂ a multiplet $\delta$ 0.384 up-field from the bis-allylic CH proton. These peaks correspond to isomeric byproduct as determined by GC (see GC traces: isomeric purity of major product determined by GC 94.5%).

Product 13f from hydrovinylation using [(R,R)-(-)-DIOP]CoCl₂ at –45 °C; $[\alpha]_{24}^{20} = -25.6$ (toluene, $c$ 11.4); lit.⁴ $[\alpha]_{20}^{20}$ (CH₂Cl₂, $c$ 10); – 34.8 for 13f of %ee 37% (S); Because of the volatility of the product, there is some uncertainty in these optical rotation measurements. However, the enantioselectivity measured by CSP GC (Cyclodex-B, 28 °C ) is unambiguous (see the attached chromatograms). Enantioselectivity determined by CSP GC: 90.1 % ee (S)

Product 13f from hydrovinylation using [(S,S)-(+)-DIOP]CoCl₂ at – 45 °C: $[\alpha]_{24}^{20} = +29.1$ (toluene, $c$ 0.39). Enantioselectivity determined by CSP GC (Cyclodex-B, 28 °C ); 89.1 % ee (R).
13f from (dppb)CoCl2 (Entry 7, Table 3)

H₃C
[CoCl₂(DPPB)]⁻¹⁰°C

Polydimethylsiloxane (35°C)
(with pentane and toluene)
13f from (dppb)CoCl$_2$
(entry 7, Table 3)

(Cyclohexyl-B, 28 $^\circ$C)

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13f from (-)-DIOP)CoCl₂
(entry 12, Table 5)

(Cyclodex-B 28 °C)

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TOTAL AREA= 20289
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Hydrovinylation of (E)-1-phenyl-1,3-butadiene

Hydrovinylation of (E)-1-phenyl-1,3-butadiene using [dppp]CoCl₂ (Table 3, Entry 8): To an oven dried round-bottom-flask with a sidearm, was added DPPPCoCl₂ (45 mg, 0.083 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.13 mL, 0.25 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 °C and (E)-1-phenyl-1,3-butadiene (108 mg, 0.83 mmol) as a dichloromethane solution (0.5 mL) was added under ethylene and the mixture was stirred for 4 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as a colorless oil (113 mg, 86%). GC and NMR analysis showed that the product was essentially pure linear adduct (16g). ¹H NMR (CDCl₃, 500 MHz): 2.95-2.98 (m, 2 H), 3.45 (d, J = 7.5 Hz, 2 H), 5.06 (dq, J = 10, 1.5 Hz, 1 H), 5.13 (dq, J= 17, 1.5 Hz, 1 H), 5.56 - 5.62 (m, 1 H), 5.67 - 5.72 (m, 1 H), 5.89 (ddd, J = 6, 10, 17 Hz, 1 H), 7.21 - 7.23 (m, 3 H, aromatic ), 7.31 - 7.34 (m, 2 H, aromatic). ¹³C NMR (CDCl₃, 125.02 MHz): 31.74, 33.66, 115.14, 126.12, 127.86, 128.58, 128.64, 129.53, 136.91, 141.07. Gas Chromatography: CSP GC (Cyclosil, OT 100 °C/ isothermal, H₂ carrier gas). Starting material Rₜ = 17.68 min. Rₜ for achiral linear product = 32.58 min.

This following table shows the additional experiments conducted with this diene, 1-phenyl-1,3-butadiene, employing 10 mol % catalyst (see Table 3 in the paper for details).

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GC (Cyclosil-B, 100 degree) of Compound 16g
(Entry 8, Table 3)

---

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Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals : 730.55345 41.96559

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*** End of Report ***
Proton NMR (500 MHz, D-Chloroform) spectrum of compound 16g (HV using Cl2Co(DPPP)) (Entry 8, Table 3)
Proton NMR (500 MHz, D-Chloroform) spectrum of compound 16g (HV using Cl2Co(DPPP)) (Alkene Expansion)
Carbon NMR (500 MHz, D-Chloroform) spectrum of compound 16g (HV using Cl_2Co(DPPP))

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EXPNRO: 5
PROCNG: 1

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FIDRES: 0.4598222 Hz
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MG: 2298.6
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DE: 6.00 usec
TE: 300.2 K
DI: 2.00000000 sec
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MCREST: 0 sec
MCWRR: 0.01500000 sec

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F1: 14.00 usec
PL1: -1.00 dB
SFQ1: 125.7376725 MHz

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NUC2: 1H
FRED2: 68.00 usec
PL2: -1.00 dB
PL12: 10.87 dB
PL13: 22.50 dB
SFQ2: 500.0000000 MHz

F2 - Processing parameters
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LB: 1.00 Hz
GB: 0
PC: 1.40
Hydrovinylation of \((E)-1\text{-phenyl-1,3-butadiene using [dppm]CoCl}_2\) (Table 3, Entry 10): To an oven dried round-bottom-flask with a sidearm, was added DPPMCoCl\(_2\) (34 mg, 0.066 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.1 ml, 0.20 mmol) was added dropwise and the color of the solution changed from bluish brown to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 °C and \((E)-1\text{-phenyl-1,3-butadiene} (86 mg, 0.66 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 7 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 5 mL). Removal of solvent yielded the product as colorless oil (83 mg, 80%). GC and NMR analysis showed that the product was essentially pure 1,2 hydrovinylation product (15g). \(^1\)H NMR (CDCl\(_3\), 500 MHz): 1.19 (d, J = 7 Hz, 3 H), 2.99 – 3.05 (m, 1 H), 4.99 – 5.08 (m, 2 H), 5.87 (ddd, J = 6.5, 10, 17 Hz, 1 H), 6.17 (dd, J = 7, 16 Hz, 1 H), 6.37 (d, J = 16 Hz, 1 H), 7.18 – 7.36 (m, aromatic, 5 H). \(^{13}\)C NMR (CDCl\(_3\), 125.02 MHz): 20.00, 40.85, 113.54, 126.28, 127.20, 128.69, 128.86, 134.47, 137.86, 142.64. Gas Chromatography: CSP GC (Cyclosil, OT 120 °C/ isothermal, H\(_2\) carrier gas) \(R_T\) for chiral 1,2 product = 14.34 and 14.58 min (enantiomers, racemic), (SS)-DIOP gave 52% ee with 43% yield. Methylsilicone SP GC (OT 120 °C/ isothermal, He carrier gas) \(R_T\) for chiral 1,2 product = 10.56 min.

Hydrovinylation of \((E)-1\text{-phenyl-1,3-butadiene using (S,S)[DIOP]CoCl}_2\) (Table 5, Entry 13): To an oven dried round bottom flask with a sidearm, was added (S,S)[DIOP]CoCl\(_2\) (24 mg, 0.038 mmol) and methylaluminoxane (44 mg, 0.76 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1.5 mL) at room temperature. After 2 to 3 minutes when fumes stopped, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to 0 °C and \((E)-1\text{-phenyl-1,3-butadiene} (49 mg, 0.38 mmol) in dichloromethane (1 mL) was added via syringe under ethylene and the mixture was stirred for 5 h in ambient temperature until the completion of reaction monitored via gas chromatography. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 10 mL). Removal of the solvent yielded the product as colorless oil as a mixture of two major isomers 15g (43% with 54% ee) and 16g (55%) (Table 5, Entry 13). GC and NMR analysis showed that the products were essentially pure and the spectra and chromatogram are attached.
GC (HP-5 Methyl silicone, 120 degree) of racemic Compound 15g (HV Using Cl2Co(DPPM) (Entry 10, Table 3)
GC (Cyclosil B, 120 degree) of Racemic Compound 15g (HV using Cl2Co(DPPM) (Entry 10, Table 3)
GC (Cyclosil-B, 100 degree) of Compounds 15g and 16g from the HV reaction of 12g using Cl2Co(SS-DIOP) (Entry 13, Table 5) 52% ee.
Proton NMR (500 MHz, Chloroform) Spectra of Compound 15g Using DPPM
Proton NMR (500 MHz, Chloroform) Spectra of Compound 15g
Carbon NMR (125 MHz, Chloroform) Spectra of Compound 15g

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SPECCD  1

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雖然 CHANNEL f2
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F2 - Processing parameters
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GB  0
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Hydrovinylation of (E)-ethyl hexa-3,5-dienoate (12h)

Hydrovinylation of (E)-ethyl hexa-3,5-dienoate using [DPPM]CoCl₂ (Table 3, Entry 14): To an oven dried round-bottom-flask with a sidearm, was added [DPPM]CoCl₂ (31 mg, 0.060 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.3 mL, 0.60 mmol) was added dropwise and the color of the solution changed from bluish brown to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 °C and (E)-ethyl hexa-3,5-dienoate (84 mg, 0.60 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 15 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Due to low boiling nature of product, toluene solvent was first removed with flash chromatography with neat n-pentane as an eluent and the compound was flushed through diethyl ether to collect the product. Removal of solvent yielded the product as slight yellowish oil (84 mg, 84%). GC and NMR analysis showed that the product (13h) was essentially pure. ¹H NMR (CDCl₃, 400 MHz): 1.22 (t, J = 7.2 Hz, 3 H), 1.62 (d, J = 7 Hz, 3 H), 2.30 (dd, J = 8, 15 Hz, 1 H), 2.42 (dd, J = 7, 15 Hz, 1 H), 3.52 - 3.58 (m, 1 H), 4.09 (q, J = 7 Hz, 2 H), 5.01 (dd, J = 17, 24 Hz, 2 H), 5.20 (t, J = 10 Hz, 1 H), 5.47 - 5.55 (m, 1 H), 5.72 (dd, J = 6.4, 10.4, 17.2 Hz, 1 H). ¹³C NMR (CDCl₃, 125.02 MHz): 13.41, 14.69, 38.23, 40.48, 60.73, 114.54, 125.84, 131.21, 140.02, 172.45. ESI-MS; m/z 191.1061 [M + Na]; mass calculated for C₁₀H₁₆NaO₂, 191.1043.

CSP GC (Cyclosil, OT 80 °C/ isothermal, H₂ carrier gas): Starting material Rᵣ = 19.14 min. Rᵣ for product = 22.84 min and 23.24 min (enantiomers). Enantioselectivity is 92 % with (S,S)-[BDPP]CoCl₂ (Table 5, entry 14). (Josiphos 2)CoCl₂ (5 mol% catalyst) gave no conversion.

This following table shows the additional experiments conducted by using diene (E)-ethyl hexa-3,5-dienoate employing 10 mol % catalyst (see also Table 3 in the paper for details).

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<td>100%</td>
<td>(Z)-1,4HV (92% ee)</td>
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GC (Cyclosil B, 80 degree) of Racemic Compound 13h (HV using Cl2Co(DPPM) (Entry 14, Table 3)

**Area Percent Report**

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals : 1444.60864 121.17726

*** End of Report ***
GC (Cyclosil B, 80 degree) of Chiral Compound 13g [HV using (Cl2Co(S,S-BDPP), Entry 14, Table 5] (84% ee)
Proton NMR (400 MHz, chloroform) spectrum of compound 13h (HV using Cl2Co(DPPM))
Proton NMR (400 MHz, Chloroform) Spectra of Compound 13h Using DPPM (Expanded Alkene Region)
Carbon NMR (125 MHz, Chloroform) Spectra of Compound 13h Using DPPM
Hydrovinylation of (E)-6-benzyloxy-1,3-hexadiene (12i)

Hydrovinylation of (E)-6-benzyloxy-1,3-hexadiene using [dppb]CoCl₂ (Table 3, Entry 15). To an oven dried round bottom flask with a sidearm, was added [dppb]CoCl₂ (26 mg, 0.047 mmol) and methylaluminoxane (55 mg, 0.94 mmol) under argon and dissolved in dichloromethane (1 mL) at room temperature. After addition of dichloromethane, color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -15 °C and (E)-6-benzyloxy-1,3-hexadiene (88 mg, 0.47 mmol) added under ethylene and the mixture was stirred for 14 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (4 mL) and diethyl ether (4 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Flash chromatography (5 % EtOAc in hexane) and removal of solvent yielded the product as slight yellow oil (98 mg, 97%). GC and NMR analysis showed that the product (13i) was essentially pure.

1H NMR (CDCl₃, 400 MHz): 1.54 - 1.59 (m, 1 H), 1.61 (dd, J = 1.6, 6.8 Hz, 3 H), 1.74 - 1.82 (m, 1 H), 3.21 - 3.29 (m, 1 H), 3.40 - 3.51 (m, 2 H), 4.47 (s, 2 H), 4.94 (dd, J = 1.2, 10 Hz, 1H), 4.99 (dt, J = 1.6, 17.2 Hz, 1 H ), 5.19 (td, J = 1.6, 10.8 Hz, 1 H), 5.47 – 5.55 (m, 1 H), 5.71 (dd, J = 6.8, 10.4, 17.2 Hz), 7.25 - 7.33 (m, aromatic, 5H). 13C NMR (CDCl₃, 125.02 MHz): 13.23, 35.17, 38.08, 68.43, 73.21, 113.61, 124.87, 127.69, 127.85, 128.54, 132.49, 138.85, 141.37. ESI-MS; m/z 239.1396 [M + Na]; mass calculated for C₁₅H₂₀ONa, 239.1406.

Gas Chromatography: Methylsilicone SP GC (OT 150 °C/isothermal, He carrier gas) starting material Rₜ = 10.49 min. Rₜ for product = 14.37 min. CSP GC (Cyclosil, OT 150 °C/isothermal, H₂ carrier gas). Starting material Rₜ = 12.36 min. Rₜ for product = 15.08 min. and 15.33 min (enantiomers, racemic from DPPBCoCl₂). (S,S)-DIOPCoCl₂ gave 94% ee. Reaction carried out with [(S,S)-DIOP]CoCl₂ at -20 °C gave 99% ee, albeit in lower (40%) conversion.

Asymmetric hydrovinylation of (E)-6-benzyloxy-1,3-hexadiene using (S,S)-[DIOP]CoCl₂ (Table 5, Entry 17): To an oven dried round bottom flask with a sidearm, was added (SS)-[DIOP]CoCl₂ (10 mg, 0.016 mmol) and methylaluminoxane (18 mg, 0.32 mmol) under argon and dissolved in dichloromethane (0.5 mL) at room temperature. After addition of dichloromethane, color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -15 °C and (E)-6-benzyloxy-1,3-hexadiene (30 mg, 0.16 mmol) added under ethylene and the mixture was stirred for 14 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Flash chromatography (5 % EtOAc in hexane) and removal of solvent yielded the product as slight yellow oil (98 mg, 88%). GC and NMR analysis showed that the product was essentially pure. 1H NMR (CDCl₃, 400 MHz): 1.54 - 1.59 (m, 1 H), 1.61 (dd, J = 1.6, 6.8 Hz, 3 H), 1.74 - 1.82 (m, 1 H), 3.21 - 3.29 (m, 1 H), 3.40 - 3.51 (m, 2 H), 4.47 (s, 2 H), 4.94 (dd, J = 1.2, 10 Hz, 1H), 4.99 (dt, J = 1.6, 17.2 Hz, 1 H ), 5.19 (td, J = 1.6, 10.8 Hz, 1 H), 5.47 – 5.55 (m, 1 H), 5.71 (dd, J = 6.8, 10.4, 17.2 Hz), 7.25 - 7.33 (m, aromatic, 5H).
$^5$H. $^{13}$C NMR (CDCl$_3$, 125.02 MHz): 13.23, 35.17, 38.08, 68.43, 73.21, 113.61, 124.87, 127.69, 127.85, 128.54, 132.49, 138.85, 141.37. ESI-MS; m/z 239.1396 [M + Na]; mass calculated for C$_{15}$H$_{20}$ONa, 239.1406.

[(S,S)-DIOP]CoCl$_2$ gave 94% ee at full conversion.

This following table shows the percent conversion and percent ee’s obtained using other catalysts.

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<td>100</td>
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<td>40</td>
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<td><strong>L18 Joshiphos 2</strong></td>
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<td>92</td>
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$^a$ at -10 °C/6 h, 100%, 94% ee.
GC (HB-5, methyl silicone, 150 degree) of Compound 13i
HV using Cl2Co(DPPB) (Racemic) Entry 15, Table 3)
GC (cyclosil) of racemic Compound 13i (HV using [Cl2Co(DPPB) Entry 15, Table 3])

---

**Area Percent Report**

**Sorted By**: Signal

**Multiplier**: 1.0000

**Dilution**: 1.0000

**Use Multiplier & Dilution Factor with ISTDs**

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**Totals**: 536.94879 81.15174

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***End of Report***
GC (Cyclosil-B, 150 degree) of Compound 13i (from HV reaction using Cl2Co(SS-DIOP) Entry 17, Table 5)

---

Area Percent Report

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Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals: 1403.68178 208.41211

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*** End of Report ***
GC (methyl silicone, 150 degree) of Compound 13i Using SS-BDPP (92% ee)
GC (Cyclosil B, 150 degree) of Compound 13i HV using SS-BDPP Ligand (Entry 18, Table 5 (92%ee))
Proton NMR (400 MHz, D-chloroform) Spectra of Compound 13i
Proton NMR (400 MHz, D-chloroform) spectrum of Compound 13i (HV Using SS-DIOP) (Alkene Region Expansion)
Carbon NMR (400 MHz, D-chloroform) spectrum of Compound 13i (HV Using SS-DIOP)
Hydrovinylation of (E/Z)-hexa-3,5-dienylbenzene (12j)

Hydrovinylation of (E/Z)-hexa-3,5-dienylbenzene using [dppb]CoCl₂ (Table 3, Entry 16). To an oven dried round bottom flask with a sidearm, was added [dppb]CoCl₂ (18 mg, 0.032 mmol) and methylaluminoxane (37 mg, 0.64 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 °C and (E/Z)-hexa-3,5-dienylbenzene (52 mg, 0.32 mmol), mixture of E:Z in the ratio of 53:47, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (51 mg, 84%). GC and NMR analysis showed that the product (13j) was essentially pure. ¹H NMR (CDCl₃, 400 MHz): 1.58 (dd, J = 7, 2 Hz, 3 H), 1.57 – 1.74 (m, 1 H), 1.75 – 1.79 (m, 1 H), 2.54 – 2.63 (m, 2 H ), 3.03 - 3.06 (m, 1 H), 4.94 – 5.02 (m, 2 H), 5.22 - 5.29 (m, 1 H), 5.49 – 5.58 (m, 1 H), 5.72 (ddd, J = 17, 10, 7 Hz, 1 H), 7.14 – 7.27 (m, 5 H, aromatic). ¹³C NMR (CDCl₃, 125.02 MHz): 13.33, 33.64, 37.14, 41.03, 113.65, 124.72, 125.87, 128.49, 128.67, 132.91, 141.56, 142.72.

Gas Chromatography: CSP GC (Cyclosil, OT 100 °C/ isothermal, H₂ carrier gas): starting material Rₜ = 37.70 min. for E-diene and 36.07 min. for Z diene. Rₜ for product = 54.64 min and 57.65 min (racemic).
GC (Cyclosil-B, 100 degree) of Compound 13j

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 B, Back Signal

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Proton NMR (400 MHz, D-Chloroform) spectrum of compound 13j (HV using Cl2Co(DPPB) (Entry 16, Table 3)
Proton NMR (400 MHz, D-Chloroform) spectrum of compound 13j (HV using Cl2Co(DPPB(Alkene Region Expansion))
Carbon NMR (400 MHz, D-chloroform) spectrum of compound 13j (HV using Cl2Co(DPPB))
Hydrovinylation of (E)-4-(buta-1,3-dienyl)-N,N-dimethylaniline (12k)

**Hydrovinylation of (E)-4-(buta-1,3-dienyl)-N,N-dimethylaniline using DPPBCoCl₂ (Table 3, Entry 17):** To an oven dried round bottom flask with a sidearm, was added [DPPB]CoCl₂ (36 mg, 0.065 mmol) and methylaluminoxane (76 mg, 1.30 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at 0 °C and (E)-4-(buta-1,3-dienyl)-N,N-dimethylaniline (113 mg, 0.65 mmol) in dichloromethane (1 mL) added via syringe under ethylene and the mixture was stirred for 13 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature. After this, the reaction solution was subsequently passed through a silica plug. The plug was washed with diethyl ether (3 X 5 mL). Flash column chromatography with (5:1, hexane: ethyl acetate) yielded the product as yellowish oil (104 mg, 79%). GC and NMR analysis showed that the product (16k) was essentially pure. ¹H NMR (CDCl₃, 400 MHz): 2.91 (s, 6 H), 2.91 - 2.95 (overlap with 2.91) (m, 2 H), 3.32 (d, J = 7 Hz, 2 H), 5.01 (dq, J = 10, 1.6 Hz, 1 H), 5.09 (dq, J = 17, 1.6 Hz, 1 H), 5.47 - 5.54 (m, 1 H), 5.59 - 5.67 (m, 1 H), 5.86 (ddt, J = 17, 10, 6 Hz, 1 H ), 6.72 ( d, J = 8 Hz, 2 H, aromatic), 7.07 (d, J = 9 Hz, 2 H, aromatic).

¹³C NMR (CDCl₃, 125.02 MHz): 31.71, 32.60, 41.25, 113.52, 114.99, 127.14, 129.15, 130.32, 137.13.

Gas Chromatography: Methylsilicone SP GC (OT 150 °C/ isothermal, He carrier gas): Rₜ for product = 23.02 min. Rₜ for starting material = 18.68 min. ESI-MS; m/z 202.1593 [M + H]; mass calculated for C₁₄H₂₀N₁, 202.1590.
GC (HP-5 methyl silicone, 150 degree) of Compound 16k
(Entry 17, Table 3)
Proton NMR (400 MHz, D-Chloroform) Spectra of Compound 16k
(Entry 17, Table 3)
Proton NMR (400 MHz, D-chloroform) spectrum of compound 16k
NOESY (500 MHz, D-chloroform) 2D spectrum of compound 16k
Carbon NMR (125 MHz, D-Chloroform) Spectra of Compound 16k
Hydrovinylation of (E)-1-phenyl-2-methyl-1,3-butadiene using [dpdm]CoCl₂ (Table 3, Entry 18 and 19). To an oven-dried 10 mL round-bottom flask with a sidearm, was added [dpdm]CoCl₂ (35.6 mg, 0.0693 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (4.0 mL) and toluene (1 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (15.0 mg, 104 µl, 0.208 mmol) was added dropwise as color of the solution changed from green to brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 5 min. The reaction vessel was cooled to -10 °C and (E)-2-methyl-1-phenyl-1,3-butadiene (100.0 mg, 0.6935 mmol) was added under ethylene and the mixture was stirred for 6 h (color of the reaction solution turned dark green again at the end of the reaction). The ethylene balloon was removed and 0.2 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with hexane (3 X 20 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil (15l, 116.9 mg; 97 %). Isomeric compositions were determined by gas chromatography and NMR spectroscopy. ¹H NMR (CDCl₃, 500 MHz): 1.184 (d, 7 Hz, 3 H), 1.816 (dd, 1.5, 1.5, 3 H), 2.922 (m, 1 H), 5.044 (dm, 17 Hz, 1 H), 5.009 (dm, 12 Hz, 1 H), 6.295 (s, 1H), 5.842 (ddd, 17, 11, 1.5), 6.295 (s, 1 H), 7.10-7.30 (m, aromatic). NOESY: PhCH –> Cₛ𝐩₃-CH₃, bis-allylic CH. ¹³C NMR (CDCl₃): 15.72, 18.16, 46.88, 113.71, 124.61, 125.98, 128.05, 128.98, 138.61, 141.84, 142.31.

Since the HV product itself could not be separated on Cyclodex-B column, further derivatization was employed to prepare an alcohol, which was analyzed as the TMS ether. The hydrocarbon 15l was subjected to hydroboration/oxidation using 9-BBN and the enantiomeric mixture of alcohols were converted into the corresponding –TMS ethers which were analyzed on Cyclodex-B column. The product was ascertained to be nearly racemic. Optical rotation measurements further confirmed these observations.
Proton NMR (400 MHz, D-chloroform) Spectra of compound 15l (HV using Cl2Co(dppp)) (Entry 19, Table 3)
Proton NMR (500 MHz, D-chloroform) Spectra of compound 15I (Alkene Region)
Carbon NMR (125 MHz, D-Chloroform) of compound 15l (Entry 19, Table 3)
Hydrovinylation of 7-methyl-3-methyleneocta-1,6-diene (β-myrccene, 12m)

**Hydrovinylation of (β-myrccene) using [dppp]CoCl₂ (Table 3, Entry 21)**

To an oven dried round bottom flask with a sidearm, was added [DPPP]CoCl₂ (49 mg, 0.090 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.14 mL, 0.27 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept at room temperature and 7-methyl-3-methyleneocta-1,6-diene (0.15 mL, 0.90 mmol) added under ethylene and the mixture was stirred for 1 h. The ethylene balloon was removed and 0.1 mL of methanol was added to the flask. The reaction solution was diluted with pentane (2 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil (123 mg, 83%). GC and NMR analysis showed that the product (16m) was essentially pure. 

**1H NMR (CDCl₃, 400MHz):**
- 1.57 – 1.58 (m, 6 H)
- 1.66 (s, 3 H)
- 1.95 – 2.07 (m, 4 H)
- 2.77 (d, J = 6.4 Hz, 2 H)
- 4.94 - 5.04 (m, 2 H)
- 5.06 - 5.09 (m, 1 H)
- 5.28 (q, J = 7 Hz, 1 H)
- 5.68 - 5.78 (m, 1 H)

**NOESY:**
H₈ ---> H₁₀, H₁; H₉ ---> H₇, H₈, H₁₀; H₇ ---> H₉, H₁₀; H₆ ---> H₁₀, H₉, H₁₁; H₅ → H₁₁, H₁₂, H₁₃

**13C NMR (CDCl₃, 125.02 MHz):**
13.43, 17.90, 25.92, 26.99, 34.81, 37.29, 115.11, 119.85, 124.59, 131.60, 136.38, 137.76

Gas Chromatography: CSP GC (Cyclosil, OT 100 °C/ isothermal, H₂ carrier gas) starting material Rₜ = 6.571 min. Rₜ for product = 9.954 min. The following table shows the additional experiments conducted by using β-myrccene employing 10 mol % catalyst and trimethylaluminium as an activator. The isomeric product has not been identified.

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<tr>
<td>4.</td>
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GC (Cyclosil-B, 100 degree) of Compound 16m
(Entry 21, Table 3)
Proton NMR (400 MHz, D-chloroform) spectra of compound 16m
(Entry 21, Table 3)
Proton NMR (400 MHz, D-chloroform) spectra of compound 16m (Expansion)

Current Data Parameters
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PROCNO: 1

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Time: 16:08
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TD: 6536
SOLVENT: CDC13
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DS: 2
SNR: 8250.825 Hz
FTRES: 0.023898 Hz
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NG: 101.6
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DE: 6.00 usec
TE: 300.2 K
D1: 1.00000000 sec
TDD: 1

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F2 - Processing parameters
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SP: 400.1390179 MHz
MDM: EM
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GC: 1.00

ppm

S111
Carbon NMR (125 MHz, D-chloroform) spectra of compound 16m

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PL2  -1.50 dB
PL12  10.87 dB
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DF02  500.0020000 MHz

F1 - Processing parameters
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NDM  IM
SSB  0
LB  1.00 Hz
GR  0
PC  1.40
NOESY (500 MHz, D-chloroform) 2D spectra of compound 16m
Hydrovinylation of Isoprene using [dppp]CoCl₂ (Table 3, Entry 22):
To an oven dried round bottom flask with a sidearm, was added [dppp]CoCl₂ (50 mg, 0.092 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.14 mL, 0.28 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -20 °C and isoprene (63 mg, 0.92 mmol) added under ethylene and the mixture was stirred for 4 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug very quickly. The plug was washed with pentane (3 x 5 mL). Removal of solvent was difficult due to high volatility of the product so GC and NMR analysis showed that the product was essentially pure (16n).

\[ \text{H NMR (CDCl}_3, 400 MHz): \]
\[ \text{1.64 (d, J = 6.8 Hz, 3 H, H}_a \text{), 1.73 (m, 3 H, H}_c \text{), 2.83 (d, J = 6.4 Hz, 2 H, H}_d \text{?)), 5.02 (dm, J = 10 Hz, 1 H, H}_g \text{), 5.08 (dm, J = 17 Hz, 1 H, H}_f \text{), 5.35 (qm, J = 6.8 Hz, 1 H, H}_b \text{), 5.79 (ddt, J = 6, 10, 17 Hz, 1 H, H}_e \text{).} \]

\[ \text{13C NMR (CDCl}_3, 125.02 MHz): \]
\[ \text{13.31, 23.50, 36.47, 115.09, 120.20, 134.04, 136.16.} \]

GC (Cyclosil-B, 50 degree) of Compound 16n
(Entry 22, Table 3)

Area Percent Report

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Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Totals: 5163.65084 292.32332
Proton NMR (400 MHz, D-chloroform) spectra of compound 16n HV of isoprene using Cl2Co(dppp) (Entry 22, Table 3)
Proton NMR (400 MHz, D-Chloroform) Spectra of Compound 16n (Expansion of Alkene Region)
Carbon NMR (125 MHz, D-chloroform) spectra of 16n Cl2Co(DPPP) complex with solvent toluene and pentane

(*) peaks from 16n, other peaks from pentane and toluene
References