Selective hydroformylation of alkyl acrylates using [2,2’-bis(dipyrrolylphosphinooxy)-1,1’-(±)-binaphthyl]/Rh catalyst: reversal of regioselectivity

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1. General information

All reactions involving air-sensitive chemicals were carried out under an argon atmosphere with standard schlenk techniques. All glasswares were oven-dried before use. Toluene was distilled over sodium under argon atmosphere prior to use. GC analysis was conducted on a GC-Agilent 7890B equipped with a capillary column (25 m × 0.53 mm) and a FID detector. NMR spectra were recorded at a Bruker ARX400 NMR instrument. 1H and 31P NMR spectra were obtained for samples in CDCl$_3$ or C$_6$D$_6$ solutions at 25 °C. 1H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for CDCl$_3$ and δ 7.16 ppm for C$_6$D$_6$. Splitting patterns are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants are reported in Hz.

2. Preparation of ligands L1-L5

Ligands (L1-L5) were prepared based on references and confirmed by 1H and 31P NMR measurements.1-4

Synthesis of Ligand L1.1 Under argon atmosphere, a solution of 2, 2'-dihydroxy-1,1'- (±)-binaphthyl (1.4 g, 4.6 mmol) and triethylamine (1.6 ml, 12.0 mmol) in 30 ml THF was added dropwise to a solution of chlorodipyrrolylphosphine (2.3 g, 11.4 mmol) in 20 ml THF at 0 °C. The Et$_3$N·HCl salt was filtered off after 12 h of stirring at room temperature and the solvent was
removed under vacuum to get yellow oily product. The crude product was recrystallized by ethyl alcohol to get white solid 1.28g and the yield was 45.7%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, J = 8.8Hz, 2H), 7.36 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.23 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.07 (d, J = 8.9 Hz, 1H), 6.38 (dtt, J = 7.6, 4.1, 2.2 Hz, 3.9H), 6.16-5.39 (m, 3.9H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 108.15 (s).

**Synthesis of Ligand L2.** Under Ar atmosphere, a solution of 2, 2′-dihydroxy-1,1′-biphenyl (1.7 g, 9.0 mmol) in 25 mL of THF was added dropwise to a solution of chlorodipyrrolylphosphine (3 mL, 18.0 mmol) and triethylamine (6.0 ml, 43.0 mmol) in 30 mL of THF at 0 ℃. The Et$_3$N·HCl salt was filtered off after 12 h of stirring at room temperature and the solvent was removed under vacuum to get yellow oily product. The crude product was recrystallized by ethyl alcohol to get white solid 1.94 g and the yield was 42.4%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.25 (m, 1.9H), 7.17 (t, J=7.4 Hz, 1H), 6.85 (t, J=8.5 Hz, 1H), 6.71 (s, 3.7H), 6.33-6.19 (m, 3.7H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 108.30 (s).

**Synthesis of Ligand L3.** Under Ar atmosphere, a solution of 2, 2′ -dihydroxy-1, 1′ - (±)-binaphthyl (1.4 g, 4.6 mmol) and triethylamine (1.6 ml, 12.0 mmol) in 30 ml THF was added dropwise to a solution of chlorodiphenylphosphane (2.3 g, 11.4 mmol) in 20 ml THF at 0 ℃. The Et$_3$N·HCl salt was filtered off after 12 h of stirring at room temperature and the solvent was removed under vacuum to get yellow oily product. The crude product was recrystallized by CH$_2$Cl$_2$/EtOH (4/10 ml), to afford white solid products 1.05 g and the yield was 34.9%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (t, J = 7.9 Hz, 2H), 7.47-7.42 (m, 1H), 7.32 (ddd, J = 6.5, 5.5, 1.5 Hz, 1H), 7.28-7.22 (m, 2H), 7.17 (dddt, J = 14.2, 13.0, 4.8, 2.4 Hz, 2H), 7.12-7.01 (m, 5H), 7.01-6.92 (m, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 110.40 (s).
Synthesis of Ligand L4. Under Ar atmosphere, to a solution of 2, 2'-dihydroxy-1, 1'-biphenyl (1.7 g, 9.0 mmol) chlorodiphenylphosphane (3.3 mL, 18.0 mmol) in THF (25 mL) was added dropwise a solution of triethylamine (6.0 ml, 43 mmol) in THF (30 mL) at -15 °C in 30 minutes. The Et₃N·HCl salt was formed immediately after the addition. The reaction mixture was stirred overnight at room temperature. The Et₃N·HCl salt was then filtered off, and the solvent was removed under vacuum. The crude product was extracted by n-hexane (10 ml), to afford white oil products 1.85 g and the yield was 37.1%; ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, J = 16.9 Hz, 16H), 7.24-7.13 (m, 9.7H), 7.09 (s, 1H), 7.08 (d, J = 1.3 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃): δ 111.74 (s).

Synthesis of Ligand L5. Under Ar atmosphere, triphenylphosphine (5.2 g, 19.8 mmol), THF (30 ml) and lithium (0.45 g, 64.8 mmol) were mixed in a 100 ml three-necked flask. Then the mixture was stirred overnight at room temperature and the lithium was gradually dissolved. The mixture was cooled to 10 °C and tertiary butyl chloride (2.0 ml, 18.4 mmol) was added over 1 h while the temperature was held below 30 °C with a water bath. After the addition was finished, the reaction mixture was heated to 40 °C for 0.5 h and then cooled to -10 °C. Then 2, 2'-bis(chloromethy)-1, 1'-biphenyl (3.0 g, 8.8 mmol) in THF (15 ml) was added dropwise and heated to reflux for 0.5 h after the addition. The solvent was removed under vacuum and then dichloromethane (20 ml) and deionized water (20 ml) were added. The organic layer was separated and dried by MgSO₄. After MgSO₄ was filtrated, the filtrate was distilled under vacuum and recrystallized by CH₂Cl₂/EtOH to afford BISBI (3.9 g) with a yield of 70.0%. ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.25 (m, 6H), 7.20 (dd, J = 17.3, 10.0 Hz, 2H), 7.15-7.05 (m, 4H), 7.05-6.98 (m, 1H), 6.94-6.83 (m, 1H), 3.25 (d, J = 13.5 Hz, 1H), 3.13 (d, J = 13.5 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃): δ -10.53 (s).
3. Hydroformylation of ethyl acrylate in different ratio of H\textsubscript{2}/CO

Table S1. Hydroformylation of alkyl acrylates with \textbf{L1} under 90 °C

| entry | \( \text{P}_{\text{H}_2}/\text{P}_{\text{CO}} \) (MPa) | Conv. (%) | Hydro. (%) | Aldehydes(%) | L/B |
|-------|-----------------|------------|------------|--------------|-----|
| 1     | 0.5/1.5         | 99.5       | 32.4       | 67.6         | 1.0 |
| 2     | 1/1             | 99.9       | 14.4       | 85.6         | 2.0 |
| 3     | 1.5/0.5         | 93.6       | 7.5        | 92.5         | 2.9 |
| 4     | 1.75/0.25       | 65.9       | 3.9        | 96.1         | 4.7 |

Conditions: \( \text{S/C} = 10000, \ T = 90 \ ^\circ \text{C}, \ \text{P} = 2 \text{ MPa},\ t = 2 \text{ h}, \ [\text{Rh}] = 1.7 \times 10^{-4} \text{ mol/L}, \text{ toluene as the solvent} \\

Table S2. Hydroformylation of alkyl acrylates with \textbf{L1} under 20 °C

| entry | \( \text{P}_{\text{H}_2}/\text{P}_{\text{CO}} \) (MPa) | Conv. (%) | Hydro. (%) | Aldehydes(%) | B/L |
|-------|-----------------|------------|------------|--------------|-----|
| 1     | 0.5/1.5         | 100        | 7.2        | 92.8         | 70.4|
| 2     | 1/1             | 96.3       | 2.5        | 97.5         | >99 |
| 3     | 1.5/0.5         | 77.1       | 1.3        | 98.7         | 94.1|
| 4     | 1.75/0.25       | 51.9       | 1.0        | 99.0         | >99 |

Conditions: \( \text{S/C} = 10000, \ T = 20 \ ^\circ \text{C}, \ \text{P} = 2 \text{ MPa},\ t = 12 \text{ h}, \ [\text{Rh}] = 1.7 \times 10^{-4} \text{ mol/L}, \text{ toluene as the solvent} \\

4. Hydroformylation product analysis

Except for aldehyde and hydrogenation products, no polymetric product was detected by GC analysis, whatever under high or low temperatures. Considering that GC was unable to determine the polymetric product, the residue after hydroformylation under 20 °C and 90 °C was collected for \textsuperscript{1}H NMR analysis, the characteristic shift of the terminal vinylidene (ca. 5.5 and 6.2 ppm) was not observed (see Fig. S11 and Fig. S12 in the supporting information),\textsuperscript{5} which confirmed that no polymetric product was generated in \textbf{L1}/Rh catalyzed hydroformylation of ethyl acrylate. \textsuperscript{1}H
NMR also proved that branched product was dominant at 20 °C, since the characteristic chemical shifts of branched aldehyde (9.45 ppm, CHO, 1H), its keto-enol isomer (11.75 ppm, OH, 1.48H) and trace amount of hydrogenation product (2.18 ppm, -CH₂CO-, 0.14H) were observed, which hinted that the molar ratio of enol to branched aldehyde was around 1.48 (Fig. S11).

Enol: ¹H NMR (400 MHz, C₆D₆) δ 11.75 (d, J = 12.5 Hz, 1.48H, HOCH=CCH₃CO-), 6.75 (dd, J = 12.4 Hz, 1.3Hz, 1.45H, HOCH=CCH₃CO-), 3.95-3.86 (m, 2.9H, OCH₂CH₃), 1.47 (d, J=1.3Hz, 4.45H, HOCH=CCH₃CO-), 0.91 (dt, J =10.1Hz, 7.1Hz, 4.35H, OCH₂CH₃)

Branched aldehyde: ¹H NMR (400 MHz, C₆D₆) δ 9.45 (d, J = 1.2Hz, 1H, CH(OH)CH₃CO-), 3.99-3.80 (m, 2H, OCH₂CH₃), 2.89 (qd, J=7.2Hz, 1.2Hz, 1H, CH(OH)CH₃CO-), 1.07 (d, J = 7.2 Hz, 3H, CHOCH₃CHCO-), 0.91 (dt, J = 10.1 Hz, 7.1 Hz, 3H, OCH₂CH₃)

As for the reaction products under 90 °C, linear aldehyde (9.30 ppm, CHO, 4.4H) indeed predominant accompanied by little hydrogenation product (2.18 ppm, -CH₂CO-, 3.23H), substrate (6.26 ppm, 0.98H; 5.96 ppm, 0.96H; 5.35 ppm, 1H, CH₂=CHCO-) and trace amount of branched product and its enol isomer (Fig. S12), and their molar ratio was at 1/0.11/0.22.

Linear aldehyde: ¹H NMR (400 MHz, C₆D₆) δ 9.30 (s, 1H, CHO), 3.99-3.86 (m, 2H, OCH₂), 2.20-2.16 (m, 2H, CH₂CH₂), 2.12-1.98 (m, 2H, CH₂CH₂), 0.99-0.90 (m, 3H, OCH₂CH₃)

Ethyl propionate: ¹H NMR (400 MHz, C₆D₆) δ 2.03 (q, J = 7.6 Hz, 0.72 H, CH₃CH₂-CO-), 3.99-3.86 (m, 0.72H, -OCH₂CH₃), 0.99-0.90(m, 1.08H, OCH₂CH₃)

Ethyl Acrylate: ¹H NMR (400 MHz, C₆D₆) δ 6.26 (dd, J = 19.0 Hz, 0.22H, CH=CH-CO-), 5.96 (dd, J = 17.3 Hz, 10.4 Hz, 0.22H, CH₂=CH-CO-), 5.35 (dd, J = 12.0 Hz, 1.6 Hz, 0.23H, CH=CH-CO-), 3.99-3.86 (m, 0.44H, OCH₂CH₃), 0.99-0.90 (m, 0.66H, OCH₂CH₃)
5. NMR spectra

**Figure S1.** $^1$H NMR spectrum of ligand L1 in CDCl$_3$.

**Figure S2.** $^{31}$P NMR spectrum of ligand L1 in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of ligand L2 in CDCl$_3$.

Figure S4. $^{31}$P NMR spectrum of ligand L2 in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of ligand L3 in CDCl$_3$.

Figure S6. $^{31}$P NMR spectrum of ligand L3 in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of ligand L4 in CDCl$_3$.

Figure S8. $^{31}$P NMR spectrum of ligand L4 in CDCl$_3$. 
Figure S9. $^1$H NMR spectrum of ligand L5 in CDCl$_3$.

Figure S10. $^{31}$P NMR spectrum of ligand L5 in CDCl$_3$. 
Figure S11. $^1$H NMR spectrum of hydroformylation products at 20 °C in C$_6$D$_6$
Figure S12. $^1$H NMR spectrum of hydroformylation products at 90 °C in C$_6$D$_6$
Figure S13. $^1$H NMR spectrum of deuterioformylation products at 90°C in C$_6$D$_6$
Figure S14. $^1$H NMR spectrum of deuterioformylation products at 20 $^\circ$C in C$_6$D$_6$

6. References

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