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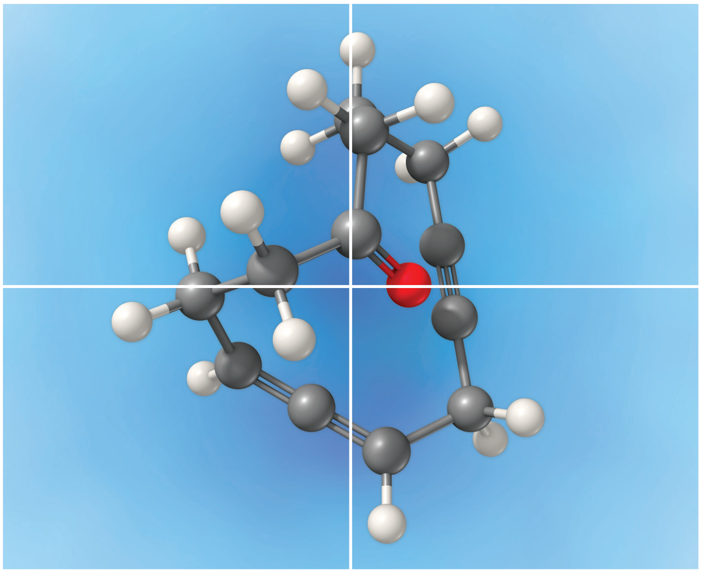

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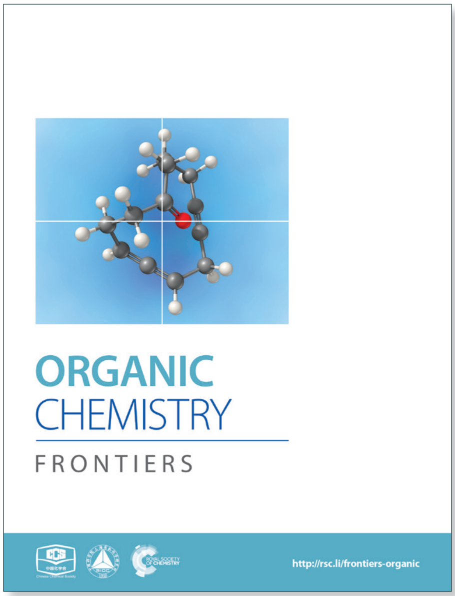

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Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis and Application of a New Triphosphorus Ligand for Regioselective Linear Hydroformylation: A Potential Way for the Stepwise Replacement of PPh_3 for Industrial Use

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A new triphosphorus ligand Tribi was developed for regioselective linear hydroformylation of terminal and internal olefins with excellent catalytic activity and regioselectivities. More importantly, the synthesis of the new triphosphorus ligand was scaled-up (> 140 g scale) for the practical industrial use. An effective method was also developed for the stepwise replacement of PPh_3 for potential industrial use.

Discovered by Otto Roelen in 1938,[1] hydroformylation now is the world largest industrial homogeneous reaction, converting the readily available inexpensive chemical feedstock into aldehydes which are served as versatile intermediates and building blocks for the generation of numerous chemical products.[2] Oxo products produced annually *via* the hydroformylation process are estimated at over 10 million tons worldwide and this number is still steadily increasing.[3] Among all commercial hydroformylation processes, the most important one is the production of *n*-butyraldehyde with the worldwide consumption of over 50% of all aldehydes by weight.[3] Largely produced by the big companies like BASF, Dow Chemical, Shell, Oxea, Evonick, Eastman and others, *n*-butyraldehyde is mainly used to manufacture the standard plasticizer[4] used in polyvinyl chloride (PVC) bis(2-ethylhexyl) phthalate (DEHP) with an annually production of over 3 million tons (Figure 1). However, DEHP has a potential disadvantage of leakage leading to toxicity. To overcome this inherent problem, isomeric mixture of butenes was employed as the substrate,[5] thus a higher molecular weight plasticizer was produced which has a less risk of leakage and lower toxicity (Figure 1). But for the latter process, it is particularly challenging to ensure high regioselectivity when isomeric mixture of butenes is subjected to hydroformylation.

In order to achieve high regioselectivities, several generations of catalysts have been developed for industrial use.[6] Due to superior reactivity, chemo- and regioselectivity compared with the corresponding cobalt catalysts, rhodium precursor with new bisphosphorus ligands have been used as the third generation catalyst playing a dominant role in industry and gained intensive attention since its first discovery by Wilkinson in 1965.[7] For the rhodium-catalyzed hydroformylation processes, numerous new bisphosphorus ligands have been developed and patented [8-15] As an elegant example, Bisbi ligand (Figure 2) has been developed and used in industry for more than 20 years since its first discovery by Eastman in 1987.[8] Recently, our group successfully developed conceptually new tetraphosphorus ligands and unprecedented regioselectivities have been achieved.[16] Even though bisphosphorus ligands and tetraphosphorus ligands have been intensively investigated for industrial use, it seems that very rare examples of triphosphorus ligands have been reported for highly regioselective linear hydroformylation.[17] Further development of triphosphorus ligands for practical industrial use is highly desirable. Herein, we report the scale-up synthesis (> 140 g scale) and application of a new triphosphorus ligand which we name Tribi (Figure 2) for potential industrial use. We envision that two identical coordination modes can ensure higher local phosphine concentration of rhodium center and provide better chelating ability (Figure 2), which may form more selective catalytic species compared with the corresponding Bisbi ligand. As a result, better regioselectivities will be highly expected.

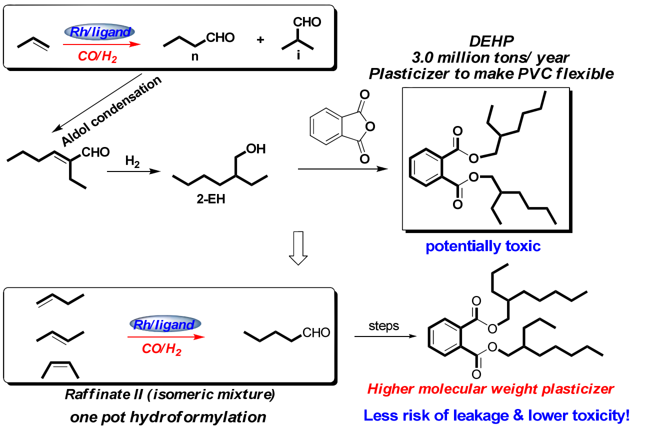


Figure 1. Industrial production of the plasticizer DEHP and the further improvement process

One of the key factors of a ligand for practical use in industry is that the ligand synthesis has to be efficient and can be scaled-up, which remains a challenging problem for many widely used ligands. Herein we developed a very efficient route for the scale-up synthesis of the

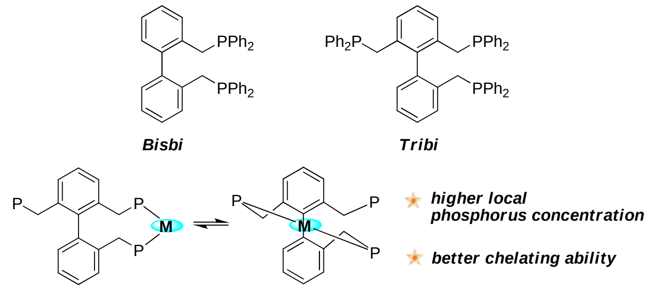


Figure 2. Bisbi and Tribi ligands and the two identical coordination modes of Tribi

new Tribi ligand from readily available staring materials (Figure 3). Ligand skeleton **3** was easily obtained by utilizing a simple Suzuki coupling method.[18] The following new developed method smoothly converted **3** to acid **4**, which is very challenging and unprecedented for the oxidation of three methyl groups in two different aryl rings in single one step utilizing the traditional oxidant $KMnO_4$. The key to the success was the addition of the surfactant $C_{16}H_{33}NMe_3Br$. Acid **4** was subsequently esterified and reduced with lithium aluminium hydride to give alcohol **6** in high yield. The desired Tribi ligand **8** was obtained by chlorination of alcohol **6** followed by treating with lithium diphenylphosphine generated *in situ* in very high overall yield (50%). For comparison, Bisbi ligand (Figure 2) was synthesized simultaneously following known procedures.[8a]

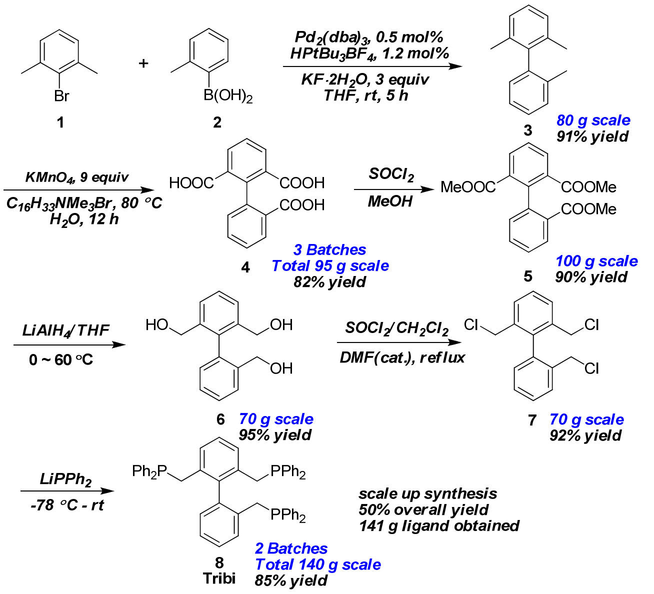
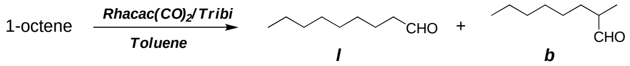


Figure 3. Scale-up synthesis of the Tribi ligand

Hydroformylation using the two ligands was then examined. Screening of the reaction conditions for the Tribi ligand was initiated using 1-octene as the substrate. Ligand/metal ratio played a substantial role in determining the regioselectivity. The l/b ratio was dramatically increased from 3.7 to 40.6 with the increase of ligand/Rh ratio (Table 1, entries 1-5). The ligand/Rh ratio was fixed at 4 and the catalyst loading was investigated. When lowering the catalyst loading from S/C = 2, 000 to 10, 000, the regioselectivity maintained and the percentage of the isomerized alkene slightly decreased (Table 1, entry 6). Longer reaction time (4 h) was required to increase the TON value (Table 1, entry 7). The reaction temperature was then examined. To our surprise, the regioselectivity increased when increasing the temperature from 100 to 120 °C while further increasing the reaction temperature to 140 °C led to a decreased regioselectivity (Table 1, entries 8-9). The syngas pressure was found important in determining the regioselectivity and 5:5 bar gave the best results (Table 1, entries 10-11).

Table 1. Screening of the reaction conditions[a]



entry	L/Rh	S/C	Temp. (°C)[b]	CO/H_2 (bar)	Time (h)	Iso. (%)[c]	l/b (%)[d]	linear (%)[e]	TON[f]
1	1:1	2 000	100	10:10	1	5.2	3.7	78.5	2.0 x 10^3
2	2:1	2 000	100	10:10	1	5.1	36.4	97.3	1.8 x 10^3
3	3:1	2 000	100	10:10	1	5.0	38.3	97.5	1.7 x 10^3
4	**4:1**	**2 000**	**100**	**10:10**	**1**	**5.0**	**39.3**	**97.5**	**1.7 x 10^3**
5	6:1	2 000	100	10:10	1	4.7	40.6	97.6	1.6 x 10^3
6	4:1	10 000	100	10:10	1	3.4	41.1	97.6	4.6 x 10^3
7	**4:1**	**10 000**	**100**	**10:10**	**4**	**6.3**	**35.8**	**97.3**	**9.9 x 10^3**
8	**4:1**	**10 000**	**120**	**10:10**	**4**	**6.9**	**42.5**	**97.7**	**9.9 x 10^3**
9	4:1	10 000	140	10:10	4	6.4	34.4	97.2	9.9 x 10^3
10	4:1	10 000	120	20:20	4	5.5	22.9	95.8	9.4 x 10^3
11	***4:1***	***10 000***	***120***	***5:5***	***4***	***8.7***	***67.8***	***98.6***	***9.9 x 10^3***

[a] Tribi as ligand, toluene as solvent, decane as internal standard, all results were repeated three times. [b] Oil bath temperature. [c] Percentage of the isomerized alkene. [d] Linear/branched ratio, determined by GC analysis. [e] Percentage of linear aldehyde. [f] Turn over number, determined on the basis of the alkene conversion by GC analysis.

Table 2. Comparison of Tribi and Bisbi under different temperature. [a]

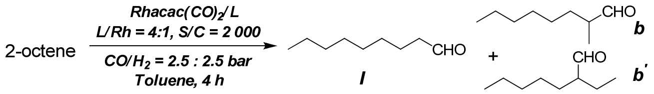
$$\text{1-octene/1-hexene} \xrightarrow[\substack{CO/H_2 = 5:5\ \text{bar} \\ \text{Toluene, 4 h}}]{\substack{Rhacac(CO)_2/L \\ L/Rh = 4:1,\ S/C = 10\,000}} \underset{l}{\text{nonanal/heptanal}} + \underset{b}{\text{2-methyloctanal/2-methylhexanal}}$$

entry	Substrate	L	T (°C)[b]	Iso. (%)[c]	l/b[d]	linear (%)[e]	TON[f]
1	1-octene	Tribi	120	8.7	67.8	98.6	9.9 x 10^3
2	1-octene	Bisbi	120	11.1	43.7	97.8	9.9 x 10^3
3	1-octene	Tribi	140	8.9	51.2	98.1	9.9 x 10^3
4	1-octene	Bisbi	140	14.8	34.1	97.2	9.9 x 10^3
5	1-hexene	Tribi	120	6.9	66.8	98.5	9.9 x 10^3
6	1-hexene	Bisbi	120	8.1	47.5	97.9	9.9 x 10^3
7	1-hexene	Tribi	140	7.1	44.1	97.8	9.9 x 10^3
8	1-hexene	Bisbi	140	14.2	30.9	96.9	9.9 x 10^3

[a] S/C = 10, 000, [Rh] = 0.2 mM, toluene as solvent, decane as internal standard, ligand/metal ratio = 4, CO/H_2 = 5:5 bar, reaction time = 4 h, all results were repeated three times. [b] Oil bath temperature. [c] Percentage of the isomerized alkene. [d] Linear/branched ratio, determined by GC analysis. [e] Percentage of linear aldehyde. [f] Turn over number, determined on the basis of the alkene conversion by GC analysis.

In order to compare the regioselectivities of the two ligands (Figure 2), Bisbi was also employed in the hydroformylation of 1-octene and 1-hexene under different reaction temperature. As summarized in Table 2, it is clear that in all cases Tribi afforded better regioselectivities than Bisbi. These results correspond to the hypothesis we made that two identical coordination modes of Tribi can ensure higher local phosphine concentration of rhodium center and afford better chelating ability, forming more selective catalytic species. Lower reaction temperature gave better regioselectivities for both ligands (Table 2, entries 1-2, 5-6). Increasing the reaction temperature resulted in the decreased regioselectivities (Table 2, entries 3-4, 7-8). It should be noted that, at high temperature the regioselectivities of Tribi ligand remained high (Table 2, entries 3, 7), whereas for the Bisbi ligand, high temperature led to a distinct drop of the regioselectivities (Table 2, entries 4, 8). These results indicated that when the two ligands are employed in the hydroformylation process at high temperature, Tribi ligand afford better results than the Bisbi ligand, which is very important for practical use and provides a convenient way for the separation of the aldehyde products by distillation at high temperature.

Table 3. Hydroformylation results of 2-octene with Tribi and Bisbi under different temperature. [a]

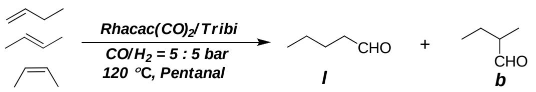


entry	L	T (°C)[b]	l/b/b' [c]	linear (%)[d]	TON[e]
1	Tribi	120	10.1 : 1 : 0.45	87.4	1.4×10^3
2	Bisbi	120	8.2 : 1 : 0.50	84.5	1.4×10^3
3	Tribi	140	9.7 : 1 : 0.46	86.9	1.7×10^3
4	Bisbi	140	7.1 : 1 : 0.46	82.9	1.6×10^3

[a] S/C = 2, 000, [Rh] = 1.0 mM, toluene as solvent, decane as internal standard, ligand/metal ratio = 4, CO/H_2 =2.5:2.5 bar, reaction time = 4 h, all results were repeated three times. [b] Oil bath temperature. [c] Linear/branched ratio, determined by GC analysis. [d] Percentage of linear aldehyde of all the aldehydes determined. [e] Turn over number, determined on the basis of the alkene conversion by GC analysis.

Hydroformylation of internal olefins was also conducted using 2-octene as a representative substrate employing Tribi and Bisbi for further comparison. As internal alkenes are relatively less reactive for hydroformylation, S/C ratio was changed to 2 000. In order to ensure relatively high regioselectivities, syngas pressure was fixed at 2.5:2.5 bar. As shown in Table 3, apart from the linear aldehyde and the normal branched aldehyde **b**, 2-ethylheptanal also formed as the third major aldehyde product **b'**. In all cases, the Tribi ligand showed better regioselectivities (Table 3, entries 1, 3) than the Bisbi ligand (Table 3, entries 2, 4).

Table 4. Hydroformylation results of 1-butene, *cis/trans*-2-butene and butene mixture. [a]

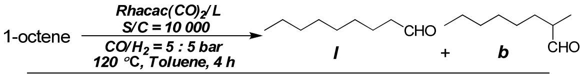


entry	substrate	Time (h)	Conv. (%)[c]	l/b[d]	linear (%)[e]	TOF (h^{-1})[f]
1	1-butene	3.5	81	29.9	96.8	3.0×10^3
2	*cis*-2-butene	4.5	80	15.2	93.8	2.3×10^3
3	*trans*-2-butene	5	79	19.3	95.1	1.2×10^3
4	butene mixture [b]	4.5	81	21.2	95.5	1.9×10^3

[a] S/C = 4, 000, pentanal as solvent, ligand/metal ratio = 5, CO/H_2 =5:5 bar, temperature = 120 °C, substrates were employed in 150 g scale. [b] *Trans*-2-butene/*cis*-2-butene/1-butene = 0.35 : 0.4 : 0.25. [c] Conversion of butenes, determined by the consumption of CO volume. [d] Linear/branched ratio, determined by GC analysis. [e] Percentage of linear aldehyde of all the aldehydes determined. [f] Turn over frequency, determined by the largest CO consumption rate.

Butene mixture is cheap available C4 feedstock usually generated from Crack-C4 from naphtha steam cracking.[19] As mentioned in Figure 1, hydroformylation of the so called Raffinate II which contains 1-butene, *cis/trans*-2-butene, and the isomeric butanes can afford the highly desired pentanal which upon further transformation gives the new low toxic plasticizer. However, hydroformylation of butenes is rarely reported academically probably due to the problems in operation and the challenges in ensuring high regioselectivities.[20] Herein, we report the hydroformylation of butenes utilizing Tribi ligand for practical industrial use. 1-Butene, *cis/trans*-2-butene and butene mixture were independently hydroformylated in 150 g scale (Table 4). In order to mimic industrial hydroformylation conditions, syngas pressure was fixed at 5:5 bar and the S/C ratio was set as 4000 using pentanal as solvent. High regioselectivities and TOFs were obtained in all cases. Unsurprisingly, 1-butene showed a much higher TOF than 2-butenes and the regioselectivity obtained was the highest (Table 4, entry 1). *Cis*-2-butene exhibited a larger reaction rate while the regioselectivity obtained was slightly lower compared with *trans*-2-butene (Table 4, entries 2-3). Butene mixture was also employed for the direct conversion to the highly desired pentanal. Good regioselectivity together with high TOF was obtained (Table 4, entry 4) which showed great practical usage of the new Tribi ligand in industry.

Table 5. Hydroformylation results of 1-octene with Tribi in the presence of PPh_3. [a]



entry	PPh_3/Tribi/Rh	Iso. (%)[b]	l/b[c]	linear (%)[d]	TON[e]
1	10 : 0 : 1	1.7	1.9	66.1	9.7×10^3
2	10 : 1 : 1	1.7	3.0	75.0	9.6×10^3
3	10 : 2 : 1	7.1	17.5	94.6	9.5×10^3
4	10 : 4 : 1	15.1	38.0	97.4	9.5×10^3
5	10 : 8 : 1	20.9	52.9	98.1	9.5×10^3
6	10 : 10 : 1	22.0	56.5	98.3	9.5×10^3
7	0 : 4 : 1	8.7	67.8	98.6	9.9×10^3

[a] S/C = 10, 000, [Rh] = 0.2 mM, toluene as solvent, decane as internal standard, CO/H_2 = 5:5 bar, temperature = 120 ºC (oil bath), reaction time = 4 h, all results were repeated three times. [b] Percentage of the isomerized alkene. [c] Linear/branched ratio, determined by GC analysis. [d] Percentage of linear aldehyde. [e] Turn over number, determined on the basis of the alkene conversion by GC analysis.

In fact, many industrial hydroformylation processes are still using PPh_3 as the ligand which gives rather poor regioselectivity. As shown in Table 5, very low l/b ratio of 1.9 was obtained with PPh_3 as the only ligand (Table 5, entry 1). Considering the high price of Rhacac$(CO)_2$ which should not be removed from the reaction system, it will benefit a lot if PPh_3 can be stepwise replaced by adding a more efficient ligand which can highly improve the regioselectivity into the Rhacac$(CO)_2$-PPh_3 catalytic system. According to this hypothesis, tribi ligand was added with different equivalents relative to rhodium in order to improve the regioselectivities stepwise in the hydroformylation of 1-octene. To our delight, the addition of Tribi ligand effectively improved the regioselectivity from 1.9 to 56.5 (l/b ratio, Table 5, entries 1, 6). Increasing of the Tribi/Rh ratio led to a steadily improvement of the regioselectivity (Table 5, entries 2-6). The trend of the improvement of the regioselectivities is clearly depicted in Figure 4 (see supporting information). The highest l/b ratio was 56.5 utilizing the Tribi/Rh ratio of 10 (Table 5, entry 6), and this l/b ratio was close to that when only Tribi was employed as the ligand (Table 5, entry 7). These results indicate that Tribi ligand can form much more stable coordinating complex with rhodium compared with PPh_3. As a result, Tribi ligand can effectively replace PPh_3 from rhodium forming much more selective catalytic species which afford much better regioselectivities. The results shown in Table 5 are very useful to the practical industrial use for the stepwise replacement of PPh_3.

Conclusions

In conclusion, a new triphosphorus ligand was developed for regioselective linear hydroformylation of terminal and internal olefins. Importantly, the synthesis of the Tribi ligand was very efficient and can be scaled-up for the potential practical industrial use. The newly developed Tribi ligand exhibited better regioselectivities than the Bisbi ligand. Moreover, butene mixture was also smoothly hydroformylated with high regioselectivity and TOF which showed great practical usage of the new Tribi ligand in industry. At last, an effective method was developed for the stepwise replacement of PPh_3 for potential industrial use.

We are grateful for the financial support by the grant from Wuhan University (203273463), “111” Project of the Ministry of Education of China and the National Natural Science Foundation of China (Grant No. 21372179).

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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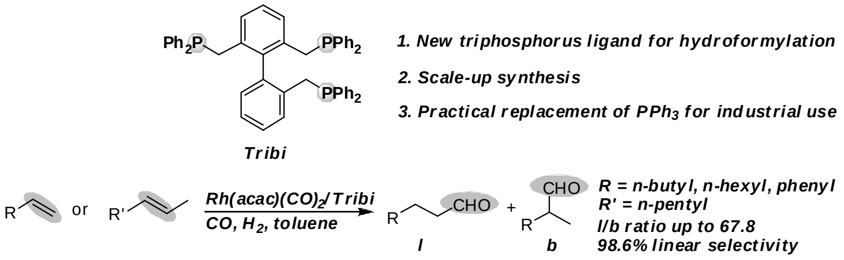

A new triphosphorus ligand Tribi was developed for regioselective linear hydroformylation of terminal and internal olefins with excellent catalytic activity and regioselectivities. More importantly, the synthesis of the new triphosphorus ligand was scaled-up (> 140 g scale) for the practical industrial use. An effective method was also developed for the stepwise replacement of PPh_3 for potential industrial use.