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THE USE OF FORMALDEHYDE IN THE RHODIUM-CATALYZED *LINEAR*-SELECTIVE HYDROFORMYLATION OF VINYLHETEROARENES

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Abstract – An accessible protocol for the *linear*-selective hydroformylation of vinylheteroarenes using formaldehyde as a substitute for syngas is reported. The simultaneous use of BIPHEP and Nixantphos ligands permitted a high regioselectivity (*linear*/*branched* = up to 93/7) and moderate yield of isolated product (up to 84%) to be obtained. Under such catalytic conditions, vinylheteroarenes containing a vinyl group at the 2-position in the heterocycle ring reacted more *linear*-selectively with formaldehyde than at the 3-position.

INTRODUCTION

Hydroformylation is a simple, convenient synthetic method for preparing aldehydes from alkenes.[1] The reaction involves the addition of carbon monoxide (CO) and hydrogen (H_2) to a double bond in an alkene C=C in the presence of a transition metal-catalyst, mainly such as Co, Rh, and Pt.[2] The *linear*-selective hydroformylation of vinylarenes to give *linear*-aldehydes is quite difficult, because the regioselectivity is mainly directed to the formation of branched aldehydes due to the thermodynamic stability of the η^3-benzylic metal intermediate that is involved in the reaction.[3] The use of calixarenes diphosphine,[3a,4] tetraphosphorus ligands,[3b] and SUPRAPhos,[3c] was reported to lead to the formation of highly *linear*-selective hydroformylation of vinylarenes.

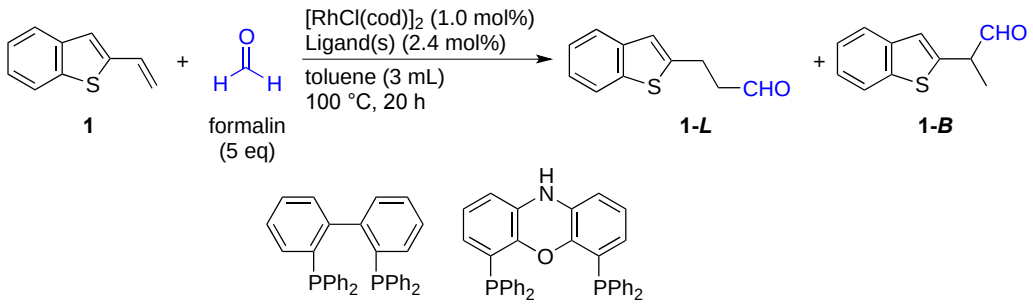
On the other hand, from the point of view that the elemental composition of formaldehyde (HCHO) is equal to that of a mixture of CO and H_2 (1C, 1O, and 2H), so-called syngas, the use of formaldehyde instead of syngas is clearly a recent advance in hydroformylation reactions.[5] The use of formaldehyde in hydroformylation reactions has been reported.[6] The reaction consists of the decarbonylative degradation of formaldehyde to a carbonyl moiety and hydrogen, followed by the hydroformylation of a C=C double

bond with the resulting CO and H_2. Our group recently reported on the Rh(I)-catalyzed, highly linear-selective hydroformylation of 1-alkenes in which formaldehyde was used as a substitute for syngas.[6d] The key to the success of the reaction is the simultaneous use of BIPHEP and Nixantphos, which are responsible for the decarbonylation of formaldehyde and the *linear*-selective hydroformylation of 1-alkenes, respectively.

Herein we report on the *linear*-selective hydroformylation of vinylheteroarenes using formaldehyde as a substitute for syngas. To the best of our knowledge, the use of formaldehyde in analogous transformations of vinylheteroarenes has not been previously reported. Heteroaryl-substituted aldehydes are important precursors to drugs and bioactive molecules, such as porphobilinogen,[7] and 5-hydroxytryptamine.[8] Therefore, the method described here represents a new and accessible protocol for producing such compounds.

RESULTS AND DISCUSSION

After the previous report on the use of formaldehyde in *linear*-selective hydroformylation reactions,[6d] we examined the rhodium-catalyzed hydroformylation reaction of 2-vinylbenzothiophene (**1**) with formaldehyde under catalytic conditions consisting of $[RhCl(cod)]_2$, BIPHEP, and Nixantphos: **1** (1 formalin (0.37 mL of a 37 wt% aqueous solution, 5 equivalents to formaldehyde), $[RhCl(cod)]_2$ (0.01 mmol), BIPHEP (0.012 mmol), and Nixantphos (0.012 mmol) in toluene (3 mL) at 100 °C for 20 h in a mL closed vessel. 2-Vinylbenzothiophene (**1**) reacted with formaldehyde to give a mixture of *linear* and *branched* aldehydes (**1-*L*** and **1-*B***) in 57% yield in a ratio of **1-*L***/**1-*B*** = 65/35 (Scheme 1(a)).[9] The use of only BIPHEP gave the branched aldehyde **1-*B*** predominantly with a high *branched*-selectivity (**1-*L***/**1-*B*** = 10/90) (b). In contrast, when only Nixantphos was present, no reaction of **1** with formaldehyde was observed (c). Thus, the synergic cooperation of the BIPHEP and Nixantphos ligands resulted in a higher *linear*-aldehyde selectivity.

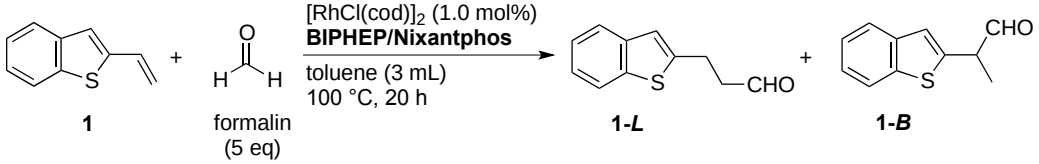


	BIPHEP	Nixantphos	
(a)	1.2 mol%	1.2 mol%	57% (**1-*L***/**1-*B*** = 65/35)
(b)	2.4 mol%	–	42% (**1-*L***/**1-*B*** = 10/90)
(c)	–	2.4 mol%	0%

Scheme 1. Rh(I)-Catalyzed Reactions of 2-Vinylbenzothiophene (**1**) with Formaldehyde

We next investigated the influence of the ratio of BIPHEP and Nixantphos in the reaction on *linear*-selectivity and the results are summarized in Table 1. When the ratio of BIPHEP and Nixantphos was changed from 1/1 to 1/4 (1.2/1.2 mol% to 0.48/1.92 mol%) (Table 1, Entries 1-4), the best result was obtained when a ratio of BIPHEP/Nixantphos = 1/3 was used (Entry 3). The simultaneous use of BINAP and Xantphos in the same ratio, instead of BIPHEP and Xantphos alone, respectively, gave a *linear*-selectivity similar to that for Entry 3 (Entry 5) but the yield was somewhat lower.

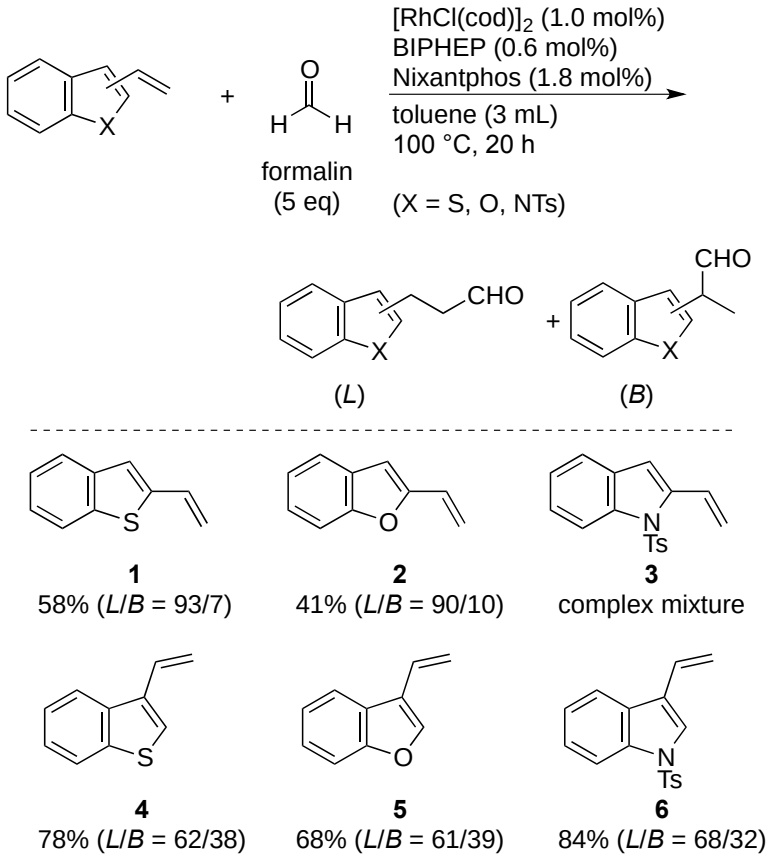
Table 1. Influence of the Ratio of BIPHEP and Nixantphos on Linear-selectivity[a]



Entry	BIPHEP	Nixantphos	Yield[b]	Ratio(*L*/*B*)[b]
1	1.2 mol%	1.2 mol%	57%	65/35
2	0.8 mol%	1.6 mol%	58%	85/15
3	0.6 mol%	1.8 mol%	58%	93/7
4	0.48 mol%	1.92 mol%	57%	83/17
5[c]	0.6 mol%	1.8 mol%	49%	94/6

[a] Conditions: **1** (1 mmol), formalin (37%; 0.37 mL, 5 mmol), $[RhCl(cod)]_2$ (0.01 mmol), ligands (0.024 mmol), toluene (3 mL), 100 °C, 20 h.
[b] Yields of isolated product are the sum of **1-*L*** and **1-*B***, and ratios (*L*/*B*) were determined by ^{1}H NMR of the crude reaction mixture.
[c] (*R*)-BINAP and Xantphos were used instead of BIPHEP and Nixantphos, respectively.

With the standard catalytic conditions consisting of 1.0 mol% $[RhCl(cod)]_2$, 0.6 mol% BIPHEP, and 1.8 mol% Nixantphos in hand, we examined hydroformylative reactions of various substrates with formaldehyde. Benzothiophenes, benzofurans, and indoles containing a vinyl group at the 2- or 3-position were used as reactants (Scheme 2). Reactions of substrates **1**, **2**, and **4**-**6** proceeded with moderate to high yields, to afford mixtures of the corresponding *linear* and *branched* aldehydes. In each case, the *linear*-aldehyde was the predominant product. When vinyl-benzothiophenes (**1** and **4**) and -benzofurans (**2** and **5**) were used as a substrate, the reactions of substrates having a vinyl group at the 2-position gave a higher *L*/*B* ratio than that at the 3-position.



Scheme 2. Scope of Substrates

Consistent with our previous report,[6d] we found that two kinds of *in situ*-generated rhodium complexes are responsible for the *linear*-selectivity in the present catalytic system. A mixture of $[RhCl(cod)]_2$, (*R*)-BINAP and Xantphos[10] (in a molar of 1/0.6/1.8) in toluene-d_8 at room temperature showed two NMR signals at δ = 49.5 ppm (d, $J_{P\text{-}Rh}$ = 195.4 Hz) and 2.4 ppm (d, $J_{P\text{-}Rh}$ = 90.7 Hz). These two signals were assigned to $[RhCl((R)\text{-BINAP})]_2$[11] and RhCl(cod)(Xantphos),[6d] respectively. When the mixture was treated with a large excess (100 eq) of formaldehyde (formalin), new signals appeared at 45.7 ppm (dd, $J_{p\text{-}p}$ = 44.1 Hz, $J_{P\text{-}Rh}$ = 115.6 Hz) and 25.3 ppm (dd, $J_{p,p}$ = 44.1 Hz, $J_{P\text{-}Rh}$ = 129.2 Hz) as a pair, and 20.7 ppm (d, $J_{P\text{-}Rh}$ = 133.2 Hz), which are assigned to RhCl(CO)((*R*)-BINAP)[11b] and $RhH(CO)_2$(Xantphos),[12] respectively. It is noteworthy that no simultaneous coordination of these phosphines to one rhodium center was observed during these reactions. It therefore appears that RhCl(CO)((*R*)-BINAP) and $RhH(CO)_2$(xantphos) are both involved in the present *linear*-selective hydroformylation using formaldehyde. The simultaneous use of BIPHEP and Nixantphos also has a similar role in the catalysis.

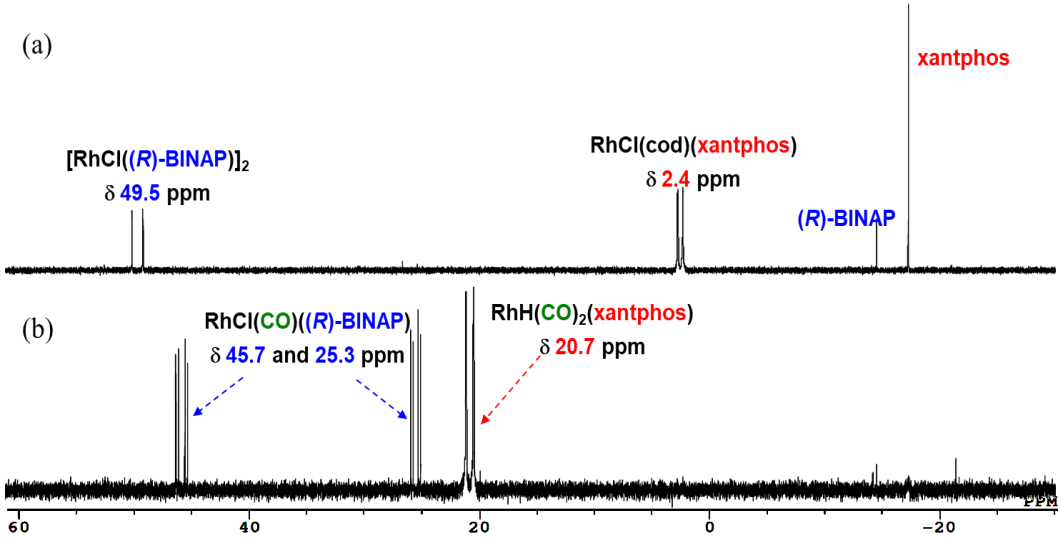
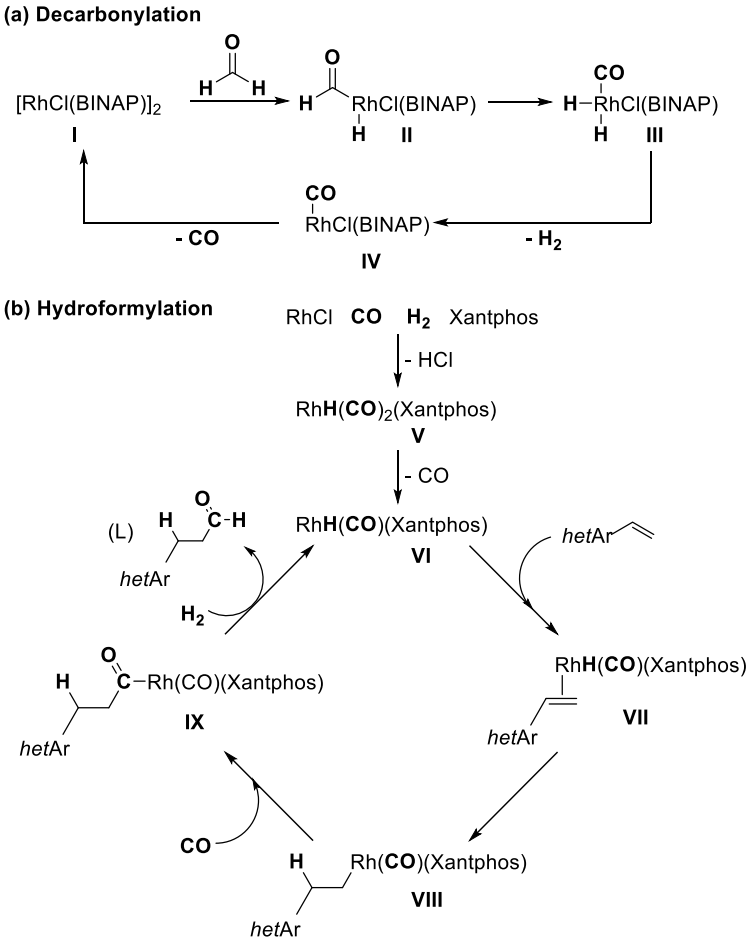


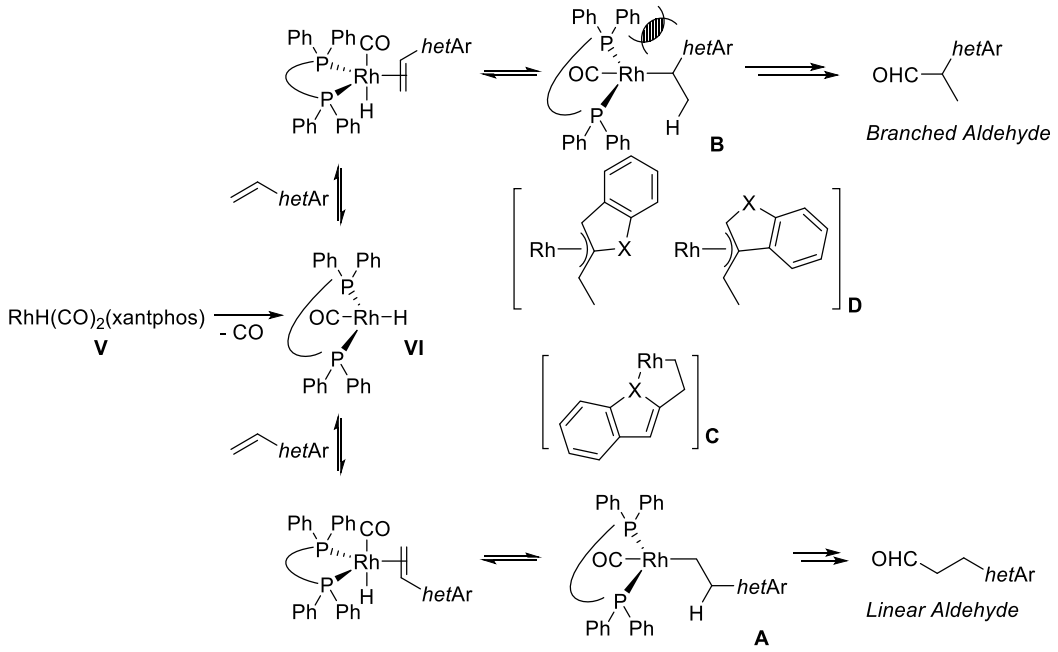
Figure 1. ^{31}P NMR spectra of (a) a mixture of $[RhCl(cod)]_2$, (R)-BINAP, and xantphos (molar ratio 1/0.6/1.8) in toluene-d_8 solution and (b) the addition of excess formaldehyde into the reaction mixture (a)

Based on the above results, an acceptable catalytic cycle is as follows. There are two processes involved in the reaction: the decarbonylation of formaldehyde and the subsequent hydroformylation of the vinylheteroarene derivative. The decarbonylation of formaldehyde begins with the oxidative addition of the aldehydic C-H bond of formaldehyde to a rhodium(I) complex **I**, followed by the migratory extrusion of the carbonyl group on the rhodium(III) center **III** and the subsequent reductive elimination of hydrogen to generate a carbonyl moiety and H_2 (Scheme 3(a)). On the other hand, the vinylheteroarene derivative is hydrorhodated by the Rh(I)-H species **VI**, which is generated *in situ* from the reaction of a Rh(I)-Cl and H_2, to give the heteroarylalkyl-Rh species **VII**. *Linear*- and *branched*-aldehydes are produced when the formed carbonyl is inserted into the Rh(I)-C bond in the heteroarylalkyl-Rh(I) complex **VIII**, followed by hydrogenolysis by the formed H_2, accompanied by the regeneration of the Rh-H species **VI** (b). Madsen *et al*. reported that a Rh(I) complex ligated by BINAP has a higher catalytic activity to decarbonylate aldehydes than Xantphos.[13] In addition, our previous results show that Xantphos is effective for the reactivity and *linear*-selectivity in the hydroformylation of 1-alkenes with formaldehyde.[6d] These knowledges mean that Rh-BINAP and Rh-Xantphos species which were observed in the above ^{31}P NMR experiments are responsible for the former decarbonylation process of formaldehyde and the latter hydroformylation process, respectively. A similar role-sharing (decarbonylation and hydroformylation) would also function well under catalytic conditions in the presence of BIPHEP and Nixantphos.



Scheme 3. Possible Reaction Pathway of Hydroformylation Controled by BIPHEP and Nixantphos

The origin of the selectivity can be rationalized as shown in Scheme 4. First, the *in situ*-generated Rh-H species **VI** adds to a vinylheteroarene to give two types of alkyl-rhodium intermediates **A** and **B**. **A** gives rise to the linear aldehyde via the insertion of a carbonyl followed by hydrogenolysis, while **B** gives the branched aldehyde. It is likely that the addition of Rh-H that gives rise to intermediate **B** takes place predominantly due to the contribution of the η^3-benzyl-like form in **D**.[3] On the other hand, steric hindrance between the Ph group on the phosphorous atom of the (Ni)xantphos and the heteroaryl group (*het*Ar) led to the preferential formation of intermediate **A**. In the present catalysis, the steric effects conferred by (Ni)xantphos are superior to the contribution of the η^3-benzyl-like intermediate, resulting in the predominant formation of the *linear* aldehyde in all of the reactions. In addition, in reactions of 2-vinylheteroarenes, when the heteroatom is at a position amenable for ligation to the rhodium center, cyclometalation would be promoted, giving rise to the formation of a stable five-membered metallacycle **C**. As a result, reactions of 2-vinylheteroarenes showed a higher regioselectivity (*linear*-selectivity) than the corresponding reactions of 3-vinylheteroarenes.



Scheme 4. Rational Explanation on the Selectivity

In summary, we report on the use of formaldehyde in the highly *linear*-selective hydroformylation of vinylheteroarenes. In this work, the high regioselectivity (up to *L*/*B* = 93/7) can be attributed to the simultaneous use of two types of phosphines (BIPHEP and Nixantphos) as ligands to $[RhCl(cod)]_2$ as a catalyst. The Rh/BIPHEP species appears to be responsible for decarbonylation process, while the Rh/Nixantphos species catalyzes the hydroformylation process to yield *linear* aldehydes with a high degree of *linear*-selectivity. Under such catalytic conditions, vinylheteroarenes having a vinyl group at the 2-position in the heterocycles were found to react more *linear*-selectively with formaldehyde than at the 3-position.

EXPERIMENTAL

General considerations

Nuclear magnetic resonance spectra were recorded on a 500 MHz spectrometer. Chemical shifts of ^1H NMR spectra are given in ppm using the solvent signal as the internal standard ($CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm). Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant in Hz, and integration. ^{13}C NMR chemical shifts are given in ppm using the solvent signal ($CDCl_3$, 77.0 ppm; DMSO-d_6, 39.5 ppm) as the internal standard. Infrared spectra (IR) were collected on a JASCO FT/IR-4200 spectrometer; absorption peaks are reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained with ionization voltages of 70 eV. Column chromatography was performed

using a SiO_2 (MERCK Silica gel 60).

Materials

All commercial reagents were used as supplied or purified by standard techniques when necessary. $[RhCl(cod)]_2$,[14] vinylhetroarenes **1**,[15] **2**,[15] **3**,[16] **4**,[17] and **6**,[18] were prepared using a previously reported method. Formalin, 2,2'-Bis(diphenylphosphino)-1,1'-biphenyl (BIPHEP), Bis(diphenylphosphino)-phenoxazine (Nixantphos), (*R*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene ((*R*)-BINAP), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry Co. Toluene (dehydrated) was purchased from Kanto Chemical Co.

Typical procedure for the preparation of vinylhetroarenes 1, 2, 3, 4, and 6 by Wittig olefination

To a suspension of methyltriphenylphosphonium bromide (1.2 equiv.) in dry THF (2 mL per mmol) was added *n*-BuLi (1.6 M in hexane, 1.2 equiv.) dropwise at –78 °C. The resulting solution was then allowed to warm up to 0 °C over a period of 1 h. The solution was then cooled to –30 °C and treated with a mixture of the corresponding aldehyde (1.00 equiv.) with stirring at room temperature (rt) until the starting material had disappeared, as evidenced by TLC. The reaction mixture was quenched by adding H_2O (10 mL per mmol), the phases were separated, the aqueous phase was extracted with Et_2O, and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The product was obtained by column chromatography.

Preparation of 3-vinylbenzofuran

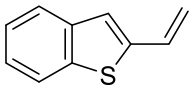
To a stirred solution of 3-bromobenzofuran (197.03 mg, 1 mmol) and potassium vinyltrifluoroborate (267.90 mg, 2 mmol) in EtOH (10 mL) was added TEA (0.42 mL, 3 mmol) and resulting mixture was degassed with nitrogen for 30 min. $PdCl_2(dppf)Cl_2 \cdot CH_2Cl_2$ (40.80 mg, 0.05 mmol) was then added and the resulting mixture was sealed and heated at 85 °C for 12 h. The reaction mixture was cooled to rt, filtered through a pad of cellite and washed with AcOEt (10×3 mL) and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (hexane) to afford the product as colorless oil (64%).

Typical procedure for the hydroformylation of vinylheteroarenes using formalin

A 10 mL J-young tube containing a stirring bar was charged with $[RhCl(cod)]_2$ (4.93 mg, 0.01 mmol), Nixantphos (9.93 mg, 0.018 mmol), BIPHEP (3.14 mg, 0.006 mmol), substrate (1.0 mmol), formalin (37%, 0.37 mL, 5.0 mmol), and toluene (3 mL) under nitrogen. The mixture was degassed and purged with nitrogen (three freeze-pump-thaw cycles). The J-young tube containing the mixture was placed in a

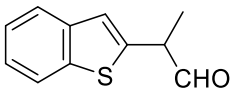
100 °C oil bath and stirred for 20 h. After the reaction was completed, the solvent was removed under reduced pressure. The product was obtained by column chromatography.

Spectral data of vinylheteroarenes 1, 2, 3, 4, 5, 6 and the branched/linear products



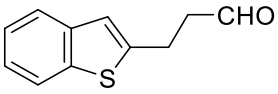
1

2-Vinylbenzo[b]thiophene.[15] White solid; R_f 0.88 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (1H, d, *J* = 10.9 Hz), 5.66 (1H, d, *J* = 17.2 Hz), 6.92 (1H, dd, *J* = 17.2, 8.6 Hz), 7.17 (1H, s), 7.28-7.33 (2H, m), 7.68-7.70 (1H, m), 7.75-7.77 (1H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.92, 115.94, 122.2, 123.1, 124.4, 124.8, 130.6, 138.8, 140.0, 143.1; MS (GC-MS): *m/z* (%) = 160 ($[M]^+$, 100), 128 (15), 116 (18), 115 (53).



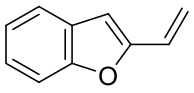
1*B*

2-(Benzo[b]thiophen-2-yl)propanal. Colorless oil; R_f 0.67 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (3H, d, *J* = 6.9 Hz), 3.93-3.95 (1H, m), 7.17 (1H, s), 7.32-7.36 (2H, m), 7.74 (1H, d, *J* = 3.4 Hz), 7.81 (1H, d, *J* = 4.6 Hz), 9.73 (1H, d, *J* = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.0, 45.5, 122.2, 122.3, 123.3, 124.3, 124.5, 139.5, 139.8, 141.0, 196.6; IR (neat) 3056 w, 2976 w, 2931 w, 1727 s, 1666 w, 1457 m, 1435 m, 1067 w, 830 w, 746 s, 726 m; MS (GC-MS): *m/z* (%) = 190 ($[M]^+$, 34), 161 (100), 128 (62), 115 (21); Exact mass (EI) calcd for $C_{11}H_{10}OS$ 190.0452, found 190.0430.



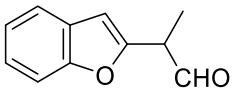
1*L*

3-(Benzo[b]thiophen-2-yl)propanal. Colorless oil; R_f 0.56 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.94 (2H, t, *J* = 7.4 Hz), 3.26 (2H, t, *J* = 7.4 Hz), 7.05 (1H, s), 7.27-7.34 (2H, m), 7.68 (1H, d, *J* = 8.0 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 9.87 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.2, 44.7, 121.3, 122.1, 122.9, 123.8, 124.2, 139.3, 140.0, 143.8, 200.6; IR (neat) 3126 w, 3056 w, 2920 w, 2823 w, 2722 w, 1722 s, 1435 m, 820 w, 746 m, 726 m, 528 w, 512 m; MS (GC-MS): *m/z* (%) = 190 ($[M]^+$, 51), 161 (26), 148 (41), 147 (100), 134 (51), 128 (22), 115 (21); Exact mass (EI) calcd for $C_{11}H_{10}OS$ 190.0452, found 190.0430.



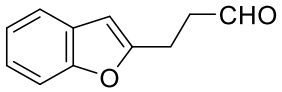
2

2-Vinylbenzofuran.[15] Colorless oil; R_f 0.69 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) 5.39 (1H, dd, *J* = 11.5, 1.1 Hz), 5.96 (1H, dd, *J* = 17.2, 1.1 Hz), 6.60-6.67 (2H, m), 7.20 (1H, t, *J* = 7.4 Hz), 7.27-7.28 (1H, m), 7.45 (1H, d, *J* = 9.2 Hz), 7.53 (1H, d, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 104.7, 111.0, 115.7, 121.0, 122.8, 124.6, 125.2, 126.8, 154.7, 154.8; MS (GC-MS): *m/z* (%) = 144 ($[M]^+$, 100), 115 (78), 63 (13).



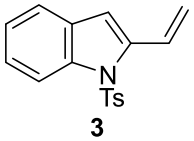
2B

2-(Benzofuran-2-yl)propanal. Colorless oil; R_f 0.59 (hexane/AcOEt = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (3H, d, *J* = 6.9 Hz), 3.84-3.87 (1H, m), 6.61 (1H, s), 7.22-7.24 (1H, m), 7.26-7.30 (1H, m), 7.46 (1H, d, *J* = 8.0 Hz), 7.55 (1H, d, *J* = 6.9 Hz), 9.79 (1H, d, *J* = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.1, 47.0, 104.2, 111.3, 120.8, 122.9, 124.2, 128.2, 128.3, 154.5 155.1; IR (neat) 2917 w, 2830 w, 2727 w, 1718 s, 1676 m, 1627 m, 1603 m, 1455 s, 1252 m, 1105 m, 946 w, 798 w, 749 s; MS (GC-MS): *m/z* (%) = 174 ($[M]^+$, 41), 145 (21), 132 (19), 131 (100), 118 (46), 115 (19), 77 (22); Exact mass (EI) calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0670.



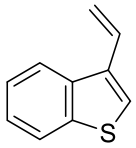
2L

3-(Benzofuran-2-yl)propanal.[19] Colorless oil; R_f 0.48 (hexane/AcOEt = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.91-2.94 (2H, m), 3.13 (2H, t, *J* = 7.2 Hz), 6.43 (1H, d, *J* = 1.1 Hz), 7.19-7.23 (2H, m), 7.41 (1H, d, *J* = 7.4 Hz), 7.49 (1H, dd, *J* = 7.2, 1.4 Hz), 9.87 (1H, t, *J* = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 41.6, 102.7, 110.8, 120.4, 122.6, 123.5, 126.6, 156.9, 200.6; IR (neat) 2900 w, 2831 w, 2730 w, 1721 s, 1603 w, 1455 s, 1252 m, 1166 w, 944 w, 797 w, 750 s; MS (GC-MS): *m/z* (%) = 174 ($[M]^+$, 43), 145 (21), 131 (100), 118 (51), 115 (21),77 (24); Exact mass (EI) calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0670.



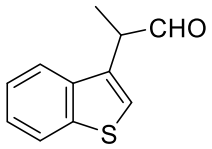
3

1-Tosyl-2-vinyl-1H-indole.[16] Colorless syrup; R_f 0.69 (hexane/AcOEt = 3/1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.29 (3H, s), 7.04 (1H, s), 7.25-7.28 (2H, m), 7.33-7.34 (3H, m), 7.52 (1H, d, J = 7.4 Hz), 7.64 (2H, d, J = 8.6 Hz), 8.08 (1H, d, J = 7.4 Hz); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.0, 109.0, 114.6, 118.9, 121.1, 124.2, 125.0, 126.2, 126.7, 129.5, 130.2, 134.3, 136.4, 139.1, 145.5; MS (GC-MS): *m/z* (%) = 297 ([M]$^+$, 42), 233 (36), 232 (33), 218 (30), 142 (100), 116 (28), 115 (91), 91 (76), 89 (29), 65 (27).



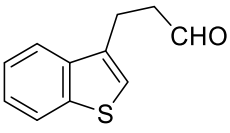
4

3-Vinylbenzo[b]thiophene.[17] Yellowish oil; R_f 0.82 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (1H, dd, J = 11.2, 1.4 Hz), 5.82 (1H, dd, J = 17.2, 1.1 Hz), 6.96-7.02 (1H, m), 7.36-7.39 (1H, m), 7.40-7.44 (1H, m), 7.48 (1H, s), 7.87 (1H, d, J = 8.0 Hz), 7.93 (1H, d, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 115.6, 121.9, 122.2, 122.9, 124.2, 124.4, 129.2, 134.5, 140.4; MS (GC-MS): *m/z* (%) = 160 ([M]$^+$, 100), 159 (21), 116 (32), 115 (90).



4*B*

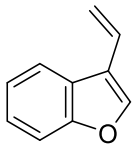
2-(Benzo[b]thiophen-3-yl)propanal.[20] Colorless oil; R_f 0.38 (hexane/CH_2Cl_2= 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (3H, d, J = 6.9 Hz), 4.04-4.07 (1H, m), 7.27 (1H, s), 7.38-7.44 (2H, m), 7.76 (1H, dd, J = 6.6, 2.0 Hz), 7.90 (1H, dd, J = 6.6, 2.0 Hz), 9.67 (1H, d, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.6, 46.7, 121.5, 123.1, 123.7, 124.4, 124.8, 132.2, 136.0, 140.6, 200.0; IR (neat) 3067 w, 2977 w, 2935 w, 1718 s, 1542 w, 1457 w, 1427 m, 1053 w, 846 w, 761 s, 732 s; MS (GC-MS): *m/z* (%) = 190 ([M]$^+$, 33), 161 (100), 128 (63), 115 (24); Exact mass (EI) calcd for $C_{11}H_{10}OS$ 190.0452, found 190.0430.



4*L*

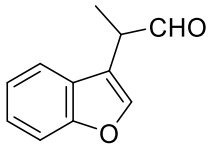
3-(Benzo[b]thiophen-3-yl)propanal. Colorless oil; R_f 0.24 (hexane/CH_2Cl_2= 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.91-2.94 (2H, m), 3.18-3.21 (2H, m), 7.12 (1H, s), 7.35-7.43 (2H, m), 7.74 (1H, dd, J = 7.4, 1.1 Hz), 7.87 (1H, dd, J = 7.7, 1.4 Hz), 9.88 (1H, d, J = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.8,

43.0, 121.4, 121.6, 123.0, 124.0, 124.4, 134.6, 136.5, 140.4, 201.4; IR (neat) 3056 w, 2904 w, 2820 w, 2722 w, 1719 s, 1434 m, 993 w, 821 w, 744 m, 725 m, 568 w, 512 m; MS (GC-MS): *m/z* (%) = 190 ($[M]^+$, 51), 161 (26), 148 (40), 147 (100), 134 (49), 128 (21), 115 (21); Exact mass (EI) calcd for $C_{11}H_{10}OS$ 190.0452, found 190.0430.



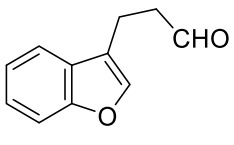
5

3-Vinylbenzofuran.[17] Colorless oil; R_f 0.93 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (1H, d, *J* = 11.5 Hz), 5.85 (1H, d, *J* = 17.8 Hz), 6.79 (1H, dd, *J* = 17.8, 11.5 Hz), 7.30-7.33 (2H, m), 7.50 (1H, d, *J* = 8.0 Hz), 7.66 (1H, s), 7.83 (1H, d, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 111.7, 115.0, 119.6, 120.8, 123.0, 125.8, 126.5, 143.5, 155.8; MS (GC-MS): *m/z* (%) = 144 ($[M]^+$, 97), 116 (18), 115 (100), 89 (14), 63 (14).



5*B*

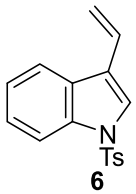
2-(Benzofuran-3-yl)propanal. Colorless oil; R_f 0.57 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56 (3H, d, *J* = 5.4 Hz), 3.83 (1H, q, *J* = 6.9 Hz), 7.27 (1H, t, *J* = 8.0 Hz), 7.33 (1H, t, *J* = 7.7 Hz), 7.52 (2H, t, *J* = 6.9 Hz), 7.56 (1H, s), 9.72 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.3, 43.2, 111.8, 117.2, 119.7, 122.8, 124.8, 126.8, 142.2, 155.5, 200.1; IR (neat) 2981 w, 2808 w, 2714 w, 1725 s, 1453 m, 1185 w, 1104 m, 856 w, 745 s, 519 m; MS (GC-MS): *m/z* (%) = 174 ($[M]^+$, 31), 145 (100), 117 (37), 115 (56), 91 (17); Exact mass (EI) calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0665.



5*L*

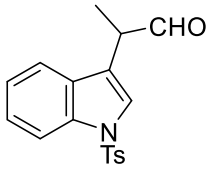
3-(Benzofuran-3-yl)propanal.[21] Colorless oil; R_f 0.43 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.91-2.94 (2H, m), 3.18-3.21 (2H, m), 7.12 (1H, s), 7.35-7.43 (2H, m), 7.74 (1H, dd, *J* = 7.4, 1.1 Hz), 7.87 (1H, dd, *J* = 7.7, 1.4 Hz), 9.88 (1H, d, *J* = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.1, 43.0, 111.6, 118.7, 119.3, 122.4 124.4, 127.6, 141.4, 155.3, 201.3; IR (neat) 2920 w, 2825 w, 2727 w, 1722 s, 1453 s, 1388 w, 1280 w, 1186 m, 1092 m, 1009 w, 857 m, 745 s; MS (GC-MS): *m/z* (%) = 174 ($[M]^+$, 27), 132

(41), 131 (100), 118 (26), 115 (29), 103 (21), 77 (28); Exact mass (EI) calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0665.



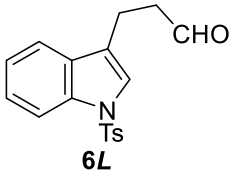
6

1-Tosyl-3-vinyl-1H-indole.[18] White solid; R_f 0.77 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 5.35 (1H, dd, *J* = 11.5, 1.1 Hz), 5.80 (1H, dd, *J* = 17.8, 1.1 Hz), 6.77 (1H, dd, *J* = 17.8, 12.0 Hz), 7.22 (2H, d, *J* = 8.0 Hz), 7.28 (1H, td, *J* = 8.0, 1.1 Hz), 7.34 (1H, td, *J* = 7.9, 1.3 Hz), 7.61 (1H, s), 7.75-7.77 (3H, m), 7.99 (1H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.6, 113.7, 115.3, 120.4, 120.9, 123.5, 124.1, 124.9, 126.8, 127.5, 129.0, 129.9, 135.0, 135.4, 145.0; MS (GC-MS): *m/z* (%) = 297 ([M]$^+$, 23), 142 (100), 115 (97), 91 (37), 89 (18), 65 (24).



6*B*

2-(1-Tosyl-1H-indol-3-yl)propanal.[22] Colorless oil; R_f 0.66 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (3H, d, *J* = 7.4 Hz), 2.35 (3H, s), 3.81 (1H, q, *J* = 6.9 Hz), 7.25 (3H, t, *J* = 7.4 Hz), 7.35 (1H, t, *J* = 7.7 Hz), 7.47 (2H, d, *J* = 8.6 Hz), 7.78 (2H, d, *J* = 8.0 Hz), 7.99 (1H, d, *J* = 8.6 Hz), 9.61 (1H, d, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.4, 21.6, 44.1, 113.8, 118.9, 119.5, 123.4, 123.7, 125.2, 126.8, 129.7, 130.0, 135.0, 135.2, 145.1, 199.9; IR (neat) 1728 m, 1600 w, 1447 m, 1369 m, 1290 w, 1173 s, 1129 m, 1088 m, 964 w, 814 w, 747 m, 668 m, 575 m, 538, m, 512 m; MS (GC-MS): *m/z* (%) = 327 ([M]$^+$, 12), 299 (15), 298 (75), 207 (13), 155 (56), 144 (13), 143 (17), 115 (26), 91 (100), 65 (20); Exact mass (EI) calcd for $C_{18}H_{17}NO_3S$ 327.0929, found 327.0922.



6*L*

3-(1-Tosyl-1H-indol-3-yl)propanal.[23] White solid; R_f 0.54 (hexane/AcOEt = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (3H, s), 2.87 (2H, t, *J* = 7.2 Hz), 3.02 (2H, t, *J* = 7.2 Hz), 7.23-7.25 (3H, m), 7.34 (2H, t, *J* = 6.9 Hz), 7.48 (1H, d, *J* = 7.4 Hz), 7.75 (2H, d, *J* = 8.0 Hz), 7.99 (1H, d, *J* = 8.0 Hz), 9.85 (1H, s); ^{13}C

NMR ($CDCl_3$, 125 MHz) δ 17.3, 21.5, 42.8, 113.8, 119.2, 121.3, 122.9, 123.1, 124.8, 126.7, 129.8, 130.5, 135.1, 135.2, 144.8, 201.1; IR (KBr) 2919 w, 2842 w, 1715 m, 1451 m, 1371 m, 1171 m, 1173 m, 1133 m, 979 w, 754 m, 667 m, 570 w, 537 w; MS (GC-MS): *m/z* (%) = 327 ($[M]^+$, 34), 271 (61), 155 (64), 144 (39), 143 (31), 115 (31), 91 (100), 65 (36), 55 (53); Exact mass (EI) calcd for $C_{18}H_{17}NO_3S$ 327.0929, found 327.0935.

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9. In all the catalytic reactions described here, starting materials were perfectly consumed but no formation of any other products was observed by the detection with GC and TLC. We guess that the consumed starting materials polymerize due to the high reactivity of vinylheteroarenes.
10. (*R*)-BINAP and Xantphos, instead of BIPHEP and Nixantphos respectively, were used for simplifying ^{31}P NMR analyses.
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