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ARTICLE

A step towards hydroformylation under sustainable conditions: platinum-catalysed enantioselective hydroformylation of styrene in gamma-valerolactone

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Platinum-catalysed enantioselective hydroformylation of styrene was performed in γ -valerolactone (GVL) as a proposed environmentally benign reaction media. Optically active bidentate ligands, possessing various types of chirality elements *e.g.* central (BDPP), axial (BINAP, SEGPHOS, DM-SEGPHOS, DTBM-SEGPHOS) and planar/central (JOSIPHOS) elements, were applied in *in situ* generated Pt-diphosphine-tin(II)chloride catalyst systems. In general, slightly higher activities and regioselectivities towards branched aldehyde (2-phenylpropanal) were obtained in toluene as a reference conventional solvent. However, higher chemoselectivities towards aldehydes (up to 98%) in GVL were obtained at lower temperatures. The application of GVL proved to be also advantageous regarding enantioselectivity: although moderate enantioselectivities were obtained in both solvents, in most cases higher *ee* values were detected in GVL. From mechanistic point of view, the formation of different catalytic intermediates and/or different kinetics can be envisaged from the different temperature dependence of *ee* in GVL and toluene. The ³¹P-NMR characterization of catalyst species in GVL was also provided.

Introduction

Solvents are intrinsic part of many chemical reactions and the “solvent friendly chemical thinking” has evolved due to many advantages in both industrial and laboratory operations.¹ Thus, the industrial activities involving solvents are resulting in the release of 10–15 million tons of solvents into the atmosphere annually, some of which are leading to serious environmental concerns and economic issues. Consequently, the replacement of conventional organic solvents with green alternatives having low vapour pressure even at high temperature, low or no toxicity, low flammability and limited negative impacts on the environment is a crucial part in the development of greener and cleaner chemical technologies.² Although, “solvent free” transformation could offer environmental friendly solutions, many thousands if not millions of reactions can only be operated in the presence of solvents. According to FDA guidelines³ the use of several common organic solvents has to be avoided such as benzene and chlorinated hydrocarbons or

limited including toluene, hexane *etc.* just to name a few. However, if a solvent is crucial to perform the target transformation, an alternative that has no or limited impact on the environment and health has to be selected. Several alternative solvents such as water,⁴ ‘fluorous’ solvents⁵ and ionic liquids,⁶ supercritical carbon-dioxide⁷ have been proposed for better solutions and some of them have industrial importance, *e.g.* Ruhrchemie/Rhone-Poulenc aqueous biphasic hydroformylation process.⁸ Moreover, the application on a non-toxic reaction media is fundamentally important in pharmaceutical industry, where the residual solvent traces could result in serious health issues.

The intensive research activity on biomass conversion, as the most preferred alternative, has led to the identification of several platform molecules such as γ -valerolactone (GVL)⁹ which could replace the currently used fossil-based chemicals including solvents. Due to the environmentally friendly chemical and physical properties, GVL has been considered as a sustainable liquid.^{9,10} It is renewable and can efficiently be produced by hydrogenation of levulinic acid (LA).¹¹ GVL has already been used for the production of alkanes,^{11e} transportation fuels,¹² ionic liquids,¹³ 1,4-pentanediol,^{11d,e} adipic acid,¹⁴ polymers,¹⁵ illuminating liquid and lighter fluid¹⁶ *etc.* Since it was firstly suggested by Horváth, only a few studies have been published concerning for utilization of GVL as a solvent. It was shown that GVL could be used as reaction media for acid catalysed dehydration of various carbohydrates and wastes.¹⁷ We demonstrated that the selective

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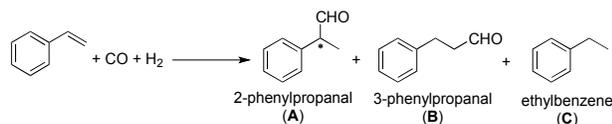
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hydrogenation of LA could be performed in GVL and/or GVL-water mixture.^{11a-c} Very recently, heterogeneous Sonogashira,¹⁸ Heck¹⁹ and Hiyama²⁰ cross-coupling reactions were performed in GVL as well.

The very low toxicity of GVL⁹ makes it a particularly attractive reaction media in the synthesis of pharmaceuticals. Since chiral aldehydes are potential precursors of non-steroidal anti-inflammatory drugs (NSAI), such as ibuprofen, naproxen or suprofen,^{21,22} the enantioselective hydroformylation of vinyl aromatics to 2-arylpropanals in the presence of rhodium and platinum catalysts is of the utmost importance. Soon after the recognition of the hydroformylation activity of *in situ* generated platinum-monophosphine-tin(II)halide systems,²³ the corresponding 'preformed' PtCl(SnCl₃)(chiral diphosphine) catalysts and PtCl₂(chiral diphosphine) + tin(II) halide systems were tested in enantioselective oxo-synthesis.^{24,25a} In addition, to the most widely used vinyl aromatics, 1,1-disubstituted olefins were also used as model substrates in highly enantioselective hydroformylation.²⁵ During the past three decades, various types of chiral mono- and bidentate phosphorus ligands were tested in platinum-based hydroformylation with the aim of increasing activity, chemo-, regio- and enantioselectivity.²⁶ Since the industrial hydroformylation was carried out in alternative solvents to facilitate catalyst recycling,²⁷ even the enantioselective hydroformylation was performed in water,²⁸ in ionic liquids,²⁹ as well as fluorinated/scCO₂ media.³⁰

We report here the investigation of asymmetric hydroformylation of styrene (Scheme 1) in the presence of platinum–chiral diphosphine–tin(II)chloride *in situ* generated catalyst systems comparing their activity and selectivities in toluene as a conventional and in γ -valerolactone as a non-toxic



Scheme 1 Hydroformylation of styrene

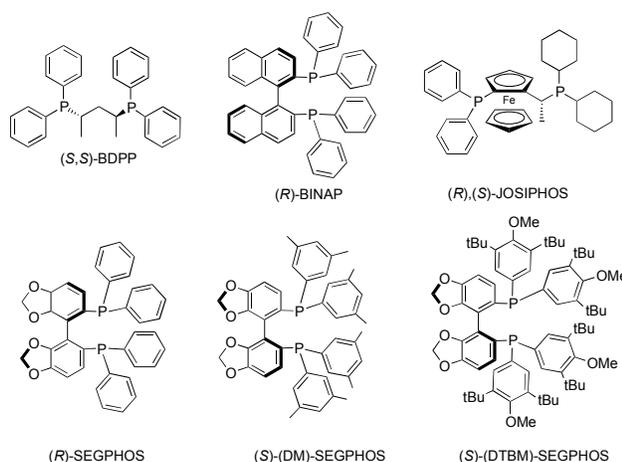


Fig. 1 Ligands used in Pt-catalysed hydroformylation

and environmentally benign solvent. It has to be also emphasized that to the best of our knowledge, some of the diphosphines (the SEGPHOS family) were not tested in hydroformylation at all.

Results and discussion

Initially, the formation of the corresponding platinum complexes of the applied ligands in gamma-valerolactone was investigated. The ³¹P-NMR measurement clearly established the *in situ* formation of PtCl₂(diphosphine) complexes from PtCl₂(PhCN)₂ (0.005 mmol) and 0.005 mmol ligands (*S,S*)-BDPP, (*R*)-SEGPHOS, (*R*),(*S*)-JOSIPHOS and (*R*)-BINAP (Fig. 1.) representing square-planar geometry in GVL (0.6 mL). The ¹J(³¹P,¹⁹⁵Pt) coupling constants of diagnostic value show that phosphorus donor atoms are coordinated *trans* to the chloro ligands (Table 1). Similarly, the excellent solubility of the PtCl₂(diphosphine) complexes and SnCl₂ in GVL allows us to study the structure of the PtCl(SnCl₃)(diphosphine) complexes formed in the 'carbene-like' insertion of tin(II)-chloride into the Pt-Cl bond. The formation of the trichlorostannato ligand was undoubtedly proved by increasing the chemical shift and decreasing the ¹J(³¹P,¹⁹⁵Pt) coupling constants of the phosphorus *trans* to SnCl₃. The 2:1 mixture of two isomers (I and II) were formed when JOSIPHOS possessing two chemically different phosphorus was used. It is worth mentioning that the NMR characteristics were found to be almost identical to those obtained in CDCl₃.^{26c} It should be emphasized, that the characterization of bidentate phosphine modified Pt- and even Pt/SnCl₃-complexes in GVL has not yet been described. Accordingly, it can be proposed that GVL could also be a good solvent for characterization of transition metal complexes, as well.

Since the *in situ* formation of precursors of catalytically active species from PtCl₂(PhCN)₂, optically active bidentate phosphine, and tin(II)chloride in GVL was established, they were applied for the hydroformylation of styrene. Various types of chiral ligands possessing stereogenic centres (BDPP,

Table 1 ³¹P-NMR data of the platinum complexes formed *in situ* in GVL^a

Complex	$\delta(P_A)$ (ppm)	¹ J(Pt,P _A) (Hz)	$\delta(P_B)$ (ppm)	¹ J(Pt,P _B) (Hz)
PtCl ₂ (BDPP)	6.8	3394	-	-
PtCl ₂ (SEGPHOS)	7.5	3662	-	-
PtCl ₂ (JOSIPHOS) ^c	-0.7	3570	44.4	3537
PtCl ₂ (BINAP)	9.7	3665	-	-
PtCl(SnCl ₃)(BDPP)	7.8	3302	13.1	2780
PtCl(SnCl ₃)(SEGPHOS)	6.8	3512	17.2	3110
PtCl(SnCl ₃)(JOSIPHOS) (I)	1.3	3450	59.5	3072
PtCl(SnCl ₃)(JOSIPHOS) (II) ^b	11.7	3048	58.9	3496
PtCl(SnCl ₃)(BINAP)	8.4	3515	18.8	3070

^aPtCl₂(PhCN)₂/SnCl₂ = 1/2, P_A: *trans* to Cl; P_B: *trans* to SnCl₃; ^bP_A *trans* to SnCl₃, P_B *trans* to Cl. ^cchemically different phosphorus atoms; Solvent: GVL; for spectra see (ESI Fig. S1-9).

Table 2 Hydroformylation of styrene in the presence of Pt-L-SnCl₂ catalysts in toluene and GVL^a

Entry	Ligand (L)	Solvent	T (°C)	Time (h)	Conv. (%)	R _c ^b (%)	R _{br} ^c (%)	e.e. ^d (%)
1	(S,S)-BDPP	toluene	100	3	99	81	33	7 (R)
2	(S,S)-BDPP	toluene	80	20	99	86	36	14 (R)
3	(S,S)-BDPP	GVL	100	20	91	85	23	2 (S)
4	(S,S)-BDPP	GVL	80	96	99	93	26	18 (S)
5 ^e	(R)-BINAP	toluene	120	20	99	78	48	16 (S)
6	(R)-BINAP	toluene	100	20	99	88	44	28 (S)
7 ^f	(R)-BINAP	toluene	100	20	96	82	48	30 (S)
8	(R)-BINAP	toluene	80	70	99	92	45	2 (S)
9	(R)-BINAP	toluene	60	144	99	94	36	19 (R)
10	(R)-BINAP	toluene	40	120	16	91	31	32 (R)
11 ^g	(R)-BINAP	GVL	130	20	99	59	20	5 (S)
12	(R)-BINAP	GVL	100	20	83	86	19	26 (S)
13 ^f	(R)-BINAP	GVL	100	20	58	84	22	16 (S)
14 ^h	(R)-BINAP	GVL	100	20	94	84	21	15 (S)
15 ⁱ	(R)-BINAP	GVL	100	20	98	72	21	25 (S)
16	(R)-BINAP	GVL	80	72	99	94	21	10 (S)
17	(R)-BINAP	GVL	60	240	70	90	26	28 (S)
18	(R)-BINAP	GVL	40	336	46	95	23	49 (S)
19	(R)-SEGPPOS	toluene	100	24	99	82	48	21 (S)
20	(R)-SEGPPOS	GVL	100	20	14	80	23	45 (S)
21	(S)-DM-SEGPPOS	toluene	120	5	83	77	36	1 (S)
22	(S)-DM-SEGPPOS	toluene	100	20	99	83	39	10 (S)
23	(S)-DM-SEGPPOS	toluene	80	72	99	90	46	21 (S)
24	(S)-DM-SEGPPOS	GVL	120	20	30	55	25	24 (S)
25	(S)-DM-SEGPPOS	GVL	100	20	45	86	24	14 (S)
26	(S)-DM-SEGPPOS	GVL	80	71	10	92	32	36 (S)
27	(S)-DTBM-SEGPPOS	toluene	100	24	2	73	23	n.d.
28	(S)-DTBM-SEGPPOS	toluene	100	48	11	74	42	40 (S)
29	(S)-DTBM-SEGPPOS	GVL	100	24	17	82	16	46 (S)
30 ⁱ	(S)-DTBM-SEGPPOS	GVL	100	24	20	93	24	56 (S)
31	(S)-DTBM-SEGPPOS	GVL	80	48	20	98	12	57 (S)
32	(R)-(S)-JOSIPHOS	toluene	100	24	99	82	28	13 (S)
33	(R)-(S)-JOSIPHOS	toluene	60	48	99	88	34	6 (S)
34	(R)-(S)-JOSIPHOS	GVL	100	24	52	80	22	31 (S)
35	(R)-(S)-JOSIPHOS	GVL	60	72	6	97	30	70 (S)
36 ⁱ	(R)-(S)-JOSIPHOS	GVL	60	240	13	94	28	36 (S)

A: 2-phenylpropanal, **B:** 3-phenylpropanal, **C:** ethylbenzene.

^a Reaction conditions: Pt/styrene = 1/100, Pt/SnCl₂ = 1/2; p(CO) = p(H₂) = 40 bar, 1 mmol of styrene, solvent: 5 mL of toluene (or GVL).

^b Chemoselectivity towards aldehydes (**A**, **B**). [(moles of **A** + moles of **B**)/(moles of **A** + moles of **B** + moles of **C**) × 100].

^c Regioselectivity towards branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) × 100].

^d Enantioselectivities were determined by chiral GC.

^e ca. 8% alcohols as side-products

^f p(CO)=p(H₂)=20 bar; ^g ca. 5% alcohols as side-products; ^h p(CO)=20 bar, p(H₂)=60 bar; ⁱ p(CO)=40 bar, p(H₂)=80 bar

entries 1-4), perpendicular dissymmetric planes due to restricted rotation (BINAP, entries 5-18; SEGPPOS, entries 19-20; DM-SEGPPOS, entries 21-26; DTBM-SEGPPOS, entries 27-31) and both stereogenic center and planar element of chirality (JOSIPHOS, entries 32-36) were used (Figure 1, Table 1). As a major aim of this paper, the applicability of GVL in hydroformylation was tested and the most important issues such as activity, chemo-, regio- and enantioselectivity were investigated. As a comparison, toluene as generally used solvent in platinum-catalysed hydroformylation was also

investigated in all cases. It has to be added that the SEGPPOS family were not tested in hydroformylation, even using GVL as a solvent.

All catalysts show remarkable catalytic activity in GVL under standard 'oxo-conditions' (p(CO) = p(H₂) = 40 bar, 60-100 °C). As generally observed in the hydroformylation of styrene (Scheme 1), in addition to the branched and linear formyl regioisomers (2-phenylpropanal (**A**) and 3-phenylpropanal (**B**), respectively) the hydrogenation by-product ethylbenzene (**C**) was also formed.

The catalytic activity of the above systems in GVL was comparable to those observed in toluene. However, in general lower activities were obtained in GVL when experiments were carried out under identical conditions (compare for instance entries 1 and 3 (BDPP), entries 6 and 12 (BINAP), entries 19 and 20 (SEGPPOS), entries 22 and 25 (DM-SEGPPOS), entries 32 and 34 (JOSIPHOS). The only exception is DTBM-SEGPPOS which formed more active catalysts in GVL (entries 27 and 29). It has to be added that the activities obtained with Pt-DTBM-SEGPPOS catalyst in both solvents fall far behind those ones generally observed in platinum-catalysed hydroformylation of styrene.²⁴⁻²⁶ It should be noted, that the hydroformylations carried out above 120°C resulted in the formation of some alcohols as side-products, *i.e.*, the hydrogenation products of the aldehydes (**A** and **B**) (entries 5 and 11).

As for the chemoselectivity towards hydroformylation, in general the GVL-based systems provided higher aldehyde selectivities. When chemoselectivities at higher reaction temperatures (100 °C) are compared, the values fall in the range of 80–88%, with similar chemoselectivities in GVL and toluene. For instance, 81 and 85% (BDPP), 88 and 86% (BINAP), 83 and 86% (DM-SEGPPOS), 82 and 80% (JOSIPHOS) were obtained in toluene and GVL, respectively. However, in some cases more pronounced differences in chemoselectivities obtained in GVL and toluene at lower temperature (80°C) were observed. For instance, 86 and 93% for BDPP was obtained.

When the partial pressure of hydrogen was increased from 40 to 80 bar (while carbon monoxide pressure was kept at 40 bar) decrease in aldehyde selectivity was detected, expectedly (entries 12 and 15). A similar effect was observed when hydrogen partial pressure was increased from 20 to 60 bar (while carbon monoxide partial pressure was kept at 20 bar) (entries 13 and 14). As in case of activity, the DTBM-SEGPPOS-containing systems behave in a different way (entries 29 and 30). As for the regioselectivity, the linear aldehyde (**B**) predominated over the branched one (**A**) in all cases as observed generally when platinum-diphosphine catalysts were used in the hydroformylation of styrene.²⁶ It can be stated that the application of GVL instead of toluene resulted in a drop of *ca.* 10%. While regioselectivities in GVL are in general below 30 %, the corresponding values in toluene fall in the range of 36–48% (BINAP), 36–46% (DM-SEGPPOS). No pronounced effect of the change of the partial pressures on regioselectivities was observed.

Although moderate enantioselectivities were obtained using the above systems, some important phenomena regarding enantioselectivity were observed. The application of GVL instead of toluene resulted in two important features. First, the *ee*-s obtained in GVL were higher in case of all six ligands. Second, the strong dependence of the enantioselectivity on the reaction temperature was not observed neither in case of BDPP nor that of BINAP. As published before, the formation of (*S*)-2-phenylpropanal was found to be favoured at low temperatures while that of the (*R*)-enantiomer at higher temperatures when (*S,S*)-BDPP was used in toluene.^{26c,d} The results were rationalized on the basis of a kinetic phenomenon.³¹ A similar change of the absolute

configuration in the temperature range of 40–100°C was observed with Pt-BINAP system.^{26f}

The GVL-based system differs substantially from the toluene-based one in case of both ligands: neither the application of the Pt-BDPP system nor that of the Pt-BINAP system resulted in the reversal of the enantioselectivity as a function of temperature. The formation of the (*S*)-2-phenylpropanal as predominating enantiomer was observed both with (*S,S*)-BDPP (entries 3, 4) and (*R*)-BINAP (entries 11–18) in the temperature range investigated.

To investigate the effect of the hydrogen partial pressure, a rather complicated picture was obtained. While the increase of the hydrogen pressure from 20 to 60 bar (entries 13, 14), as well as from 40 to 80 bar (entries 12, 15) has no effect on the *ee*-s in case of BINAP, some increase was observed with DTBM-SEGPPOS (entries 29, 30) and substantial decrease with JOSIPHOS (entries 35, 36).

The reproducibility of the catalytic results was confirmed by repeating the experiments performed in the presence of BDPP in GVL (Table 2, entry 4) at 80°C. The parallel experiments resulted practically in the same chemo-, regio- and enantioselectivity. That is, the selectivity values differ by less than 1.5%.

Additionally, efforts were made to separate and re-use the catalyst. Using PtCl₂(PhCN)₂ together with (*S,S*)-BDPP or (*R*)-BINAP ligands, we were able to separate the products as GVL solution from the catalyst by vacuum (10 mmHg) distillation at 80–82 °C. The glue-like residue containing the catalyst, remained in the bottom of the distillation unit, was re-dissolved in GVL and reused in the next catalytic run. The activity and also the regioselectivity of the reaction decreased in those reactions carried out at 100 °C, reflecting to the partial degradation of the catalyst. When recirculation experiments with the Pt-BINAP-tin(II)chloride system were carried out at lower temperature (85 °C) the decrease in the catalytic activity was accompanied by the slight decrease in regioselectivity. Surprisingly, some increase in chemo- and enantioselectivities was observed (Table 3).

The reused catalysts were investigated by ³¹P-NMR after removal of volatile compounds from the reaction mixture by. Surprisingly, the characteristic 1/4/1 pattern of the PtCl₂(diphosphine) complex could be seen but no presence of the corresponding trichlorostannato complex (Table 1) was detected. In addition, neither the signals of the uncoordinated diphosphine and its oxide nor that of the hemioxide were

Table 3 Re-use of the Pt-BINAP-tin(II)chloride catalyst in the hydroformylation of styrene at 85°C^a

Cycle	Conv.(%)	R _c (%)	R _{br} (%)	ee (%)
1.	76	94	16	22 (<i>S</i>)
2.	57	96	14	20 (<i>S</i>)
3.	33	97	12	26 (<i>S</i>)
4.	25	97	12	25 (<i>S</i>)

^a Reaction conditions: Pt/styrene = 1/100, Pt/SnCl₂ = 1/2; p(CO) = p(H₂) = 40 bar, 1 mmol of styrene, solvent: 5 mL of GVL, reaction time 24 h. For R_c, R_{br} and *ee* see footnotes to Table 2.

present even after the catalyst was re-circulated three times (ESI Fig. S10-11). It can be assumed that the complete dissociation of the tin(II)chloride in the presence of the rest of the reaction products led to the decreased activity of the catalyst. Presumably, the partial degradation of the catalyst cannot be related to the (partial) oxidation of the diphosphine ligand.

Conclusions

We have demonstrated that γ -valerolactone can be excellent solvent in the enantioselective hydroformylation of styrene in the presence of platinum-diphosphine-tin(II)chloride 'in situ' generated catalysts. Various chiral diphosphines with central, axial and planar elements of chirality were tested. Although more active catalysts were formed in the widely used toluene, the higher chemo- and enantioselectivities, as well as the green properties of GVL would deserve further investigations.

Experimental

Platinum(II)chloride-dibenzonitrile complex was prepared as described before.³² The chiral ligands were purchased from Sigma-Aldrich and were used without further purification. Gamma-valerolactone was purchased from Sigma-Aldrich Kft., Budapest, Hungary and was purified by vacuum distillation (2 Torr, 80-82 °C). The purified GVL was stored under nitrogen.

In a typical hydroformylation experiment, a solution of PtCl₂(PhCN)₂ (2.4 mg, 0.005 mmol), chiral diphosphine (0.005 mmol), and tin(II) chloride (1.9 mg, 0.01 mmol) in 5 mL of GVL containing 0.115 mL (1.0 mmol) of styrene was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure (CO/H₂ = 1/1) and placed in an oil bath of appropriate temperature and the mixture was stirred with a magnetic stirrer. Samples were taken from the mixture and the pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC and chiral GC (on a capillary Cyclodex-column, (*S*)-2-phenylpropanal was eluted before the (*R*) enantiomer). For appropriate determination of enantiomeric excess, 10 mL of hexane was added to a sample of the reaction mixture (2 mL) and washed with water (twice 10 mL). The hexane phase was dried over Na₂SO₄, filtered and concentrated to a colorless oil. The CH₂Cl₂ solution of this GVL free sample was applied for chiral GC.

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A step towards hydroformylation under sustainable conditions: platinum-catalysed enantioselective hydroformylation of styrene in gamma-valerolactone

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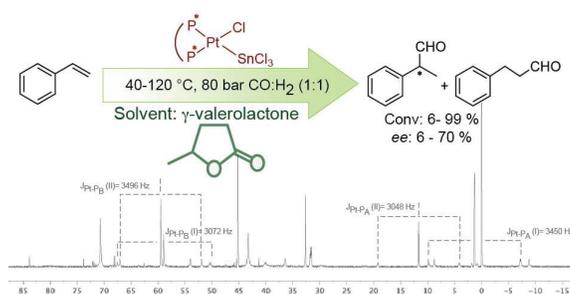
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Platinum-catalysed enantioselective hydroformylation of styrene was investigated in γ-valerolactone as solvent.