

# Preparation and structural characterization of bis(acetylacetonato)ruthenium(II)–BINAP: an efficient route to an effective asymmetric hydrogenation catalyst precursor

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## Abstract

A simple one-pot synthesis of Ru(acac)<sub>2</sub>(*S*-BINAP) in near quantitative yield was achieved by the reduction of Ru(acac)<sub>3</sub> (acac=acetylacetonate) with activated Zn in the presence of *S*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*S*-BINAP). The X-ray diffraction study revealed the presence of two independent molecules of Ru(acac)<sub>2</sub>(*S*-BINAP) as well as three acetone molecules (solvent of crystallization) in the unit cell (monoclinic, space group *P*2<sub>1</sub> with *a* = 15.681(5), *b* = 12.765(4), *c* = 25.607(9) Å, β = 98.16(3)°, *V* = 5074(3) Å<sup>3</sup>, *Z* = 2, *R* = 0.059 and *R*<sub>w</sub> = 0.067). Each ruthenium(II) complex has a distorted octahedral geometry involving two phosphorus atoms of BINAP and four atoms of oxygen from two η<sup>2</sup>-acac ligands. Although the conformation of the BINAP-containing seven-membered ring is δ in each molecule, both Λ and Δ metal configurations are observed. The molecular structure has been compared with Ru(OCOR)<sub>2</sub>(BINAP) (OCOR = pivalate, tiglate) structures. Ru(acac)<sub>2</sub>(*S*-BINAP) was used to catalyze the asymmetric hydrogenation of 2-(6'-methoxy-2'-naphthyl)acrylic acid to yield *S*-naxproren in high optical purity.

**Keywords:** Crystal structures; Hydrogenation; Catalysis; Ruthenium complexes; Acetylacetonato complexes; BINAP complexes

## 1. Introduction

The homogeneous asymmetric hydrogenation reactions involving Ru(BINAP) type catalysts have attracted much attention in recent years [1]. While Ru(OAc)<sub>2</sub>(BINAP) has been most extensively studied in these reactions, it has recently been noted that different anionic ligands on the catalyst may change the property of the catalyst substantially [2]. Recently Manimaran et al. reported an in situ synthesis of Ru(acac)<sub>2</sub>(BINAP) from the reaction of Ru(acac)<sub>3</sub> with BINAP under H<sub>2</sub> in the presence of an organic base (e.g. NEt<sub>3</sub>) [3]. In our attempt to explore the effect of the anionic ligands on the Ru(BINAP) catalysts, we developed a convenient method for the synthesis of this complex in high yields and high purity. With proper treatment, this complex exhibited extremely high catalytic activity and high enantioselectivity in the hydrogenation of 2-arylacrylic acids including 2-(6-methoxy-

2-naphthyl)acrylic acid [4]. In this paper we report the synthesis and the structural characterization of this species.

## 2. Experimental

Except as noted, all operations were carried out in a nitrogen atmosphere glovebox. All solvents were obtained from Fisher Scientific Company and were degassed by nitrogen sparge before use. Ampuled deuterated solvents were purchased from Aldrich and were used as received. 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), Ru(acac)<sub>3</sub> (acac = acetylacetonato) and zinc powder were purchased from Aldrich. The zinc powder was activated with concentrated HCl, washed with water and acetone, and dried under vacuum before use.

NMR spectra were recorded on a Varian VXR-400 (<sup>31</sup>P NMR (161 MHz), <sup>1</sup>H NMR (400 MHz)) spectrometer. IR spectra were recorded on a Nicolet

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IR/42 spectrometer. Elemental analyses were performed by Oneida Research Services and the X-ray diffraction analysis was performed by Crystallitics Co.

### 2.1. Preparation of $Ru(acac)_2(S-BINAP) \cdot CH_3COCH_3$

$Ru(acac)_3$  (1.007 g, 2.530 mmol), *S*-BINAP (1.575 g, 2.530 mmol) and activated Zn dust (3.28 g) were weighed in a glove box and placed in a Fischer-Porter bottle along with 40 ml of EtOH and 6 ml of  $H_2O$ . The mixture was heated to reflux for 15 h (overnight) during which time the mixture became a yellow slurry. The solvent was stripped from the slurry, leaving a brownish yellow solid.  $^{31}P$  NMR of the solid indicated that the reaction had proceeded to virtual completion (> 98%) to  $Ru(acac)_2(S-BINAP)$ . The residue was extracted with  $CH_2Cl_2$ , suction filtered and washed with  $CH_2Cl_2$  until there was no color in the washing (~70 ml dichloromethane was used). Removal of the solvent from the clear red filtrate in vacuo gave an orange-red solid. About 70 ml of acetone were added to dissolve the solid. The flask was capped with a septum and the solution was allowed to stand overnight during which time an orange solid crystallized. The solids were isolated by filtration and 0.851 g of pure crystals were obtained. Reducing the volume of the filtrate produced an additional 1.35 g of product which contained some  $Zn(acac)_2$ . The product was extracted by petroleum ether and the insoluble zinc compound was removed by filtration. Concentration of the filtrate gave another 1.154 g of pure product. The overall isolated yield was 86%.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  1.31 (s,  $CH_3COCH-$ ), 1.62 (s,  $CH_3COCH-$ ), 1.93 (s,  $CH_3COCH-$ ), 2.12 (s,  $CH_3COCH-$ ), 4.87 (s,  $CH_3COCH-$ ), 5.12 (s,  $CH_3COCH-$ ), 6.45–7.92 (m, aromatic protons).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ ):  $\delta$  52.3 (s), d 52.7 (s). IR (KBr): 1480, 1586  $cm^{-1}$  (acac). *Anal. Calc.* for  $C_{117}H_{110}O_{11}P_4Ru_2$ : C, 69.63; H, 5.49. Found: C, 68.73; H, 5.21%.

### 2.2. X-ray data collection on $[Ru(acac)_2(S-BINAP)]_2 \cdot 3OC_3H_6$

Orange crystals of the complex were grown from a saturated acetone solution by slowly evaporating the solvent in a glovebox. A suitable single crystal measuring  $0.43 \times 0.55 \times 0.70$  mm was sealed inside a thin-walled glass capillary. Diffraction data were collected on a computer-controlled four-circle Nicolet (Siemens) auto-diffractometer using graphite-monochromated Mo  $K\alpha$  radiation at 20 °C. Details of the crystallographic data are summarized in Table 1. Automatic centering of 15 reflections of  $2\theta > 20^\circ$  and least-squares refinements gave the following cell dimensions: monoclinic, space group  $P2_1$ , with  $a = 15.681(5)$ ,  $b = 12.765(4)$ ,  $c = 25.607(9)$  Å,  $\beta = 98.16(3)^\circ$ ,  $V = 5074(3)$  Å<sup>3</sup>, and  $Z = 2$  formula units ( $D_{calc} = 1.321$  g  $cm^{-3}$ ;  $\mu_a(Mo K\alpha) = 0.41$  mm<sup>-1</sup>). A total

Table 1

Crystallographic data and data collection parameters of  $2[Ru(O_2C_3H_7)_2(C_{44}H_{32}P_2)] \cdot 3OC_3H_6^a$

Formula	$C_{117}H_{110}O_{11}P_4Ru_2$
Formula weight	2018.2
Crystal system	monoclinic
Space group	$P2_1$ (No. 4)
$a$ (Å)	15.681(5)
$b$ (Å)	12.765(4)
$c$ (Å)	25.607(9)
$\beta$ (°)	98.16(3)
$V$ (Å <sup>3</sup> )	5074(3)
$Z$	2
$D_{calc}$ (g $cm^{-3}$ )	1.321
$\lambda$ (Å)	0.71073
Temperature (°C)	20
Crystal size (mm)	$0.43 \times 0.55 \times 0.70$
Crystal shape	rectangular parallelepiped
Linear absorption coefficient (mm <sup>-1</sup> )	0.41
Scan type	$\Omega$
Scan speed (°/min)	2–6
$2\theta$ Limits (°)	3–51
Total reflections collected	9755
Independent reflections used	5555 ( $I > 3\sigma(I)$ )
$R$	0.059
$R_w$	0.067
$GOF$	1.216
Largest shift/e.s.d. final cycle	0.26

<sup>a</sup>The standard deviation of the least significant figure is given in parentheses in this and subsequent tables.

of 9755 independent reflections having  $2\theta(Mo K\alpha) < 50.7^\circ$  (the equivalent of 0.8 limiting Cu  $K\alpha$  spheres) was collected using full ( $0.90^\circ$ -wide)  $\omega$  scans. Six standard reflections were monitored over 300 reflections and no correction for absorbance was made. The data were corrected for Lorentz and polarization effects. The structure was solved using direct methods techniques with the Siemens SHELXTL-PLUS software package as modified at Crystallitics Company. The resulting structural parameters were refined to converge ( $R$  (based on  $F$ ) = 0.059 and  $R_w = 0.067$  for 5555 independent reflections having  $2\theta(Mo K\alpha) < 50.7^\circ$  and  $I > 3\sigma(I)$ ) using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the atoms including hydrogen atoms. Three crystallographically-independent acetone solvent molecules of crystallization appear to be present in the lattice; one is ordered and the other two are disordered. Since oxygen atoms could not be distinguished from carbon atoms for either of the disordered solvent molecules, all non-hydrogen atoms for the disordered solvent molecules were included in the structural model with carbon atom scattering factors. The third solvent molecule appears to be statistically disordered with two possible orientations in the lattice: the first orientation is specified by C8s, C9s, C10s and C11s while the second orientation

is specified by C8s, C12s, C13s and C14s. Atoms C9s, C10s, C11s, C12s, C13s and C14s were included in the structural model with occupancy factors of 0.50. The methyl groups of the  $O_2C_5H_7$  ligands and the ordered acetone solvent molecule were refined as rigid rotors with  $sp^3$ -hybridized geometry and a C–H bond length of 0.96 Å. The refined positions for the rigid rotor methyl groups gave C–C–H angles which ranged from 106 to 115°. The remaining hydrogen atoms which were included in the structural model were placed at idealized positions (assuming  $sp^2$ -hybridization of the carbon atoms and a C–H bond length of 0.96 Å) ‘riding’ on their respective carbon atoms. The isotropic thermal parameter of each included hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. Selected bond distances and angles are listed in Tables 2 and 3.

### 3. Results and discussion

In EtOH solution,  $Ru(acac)_3$  was reduced by activated zinc in the presence of *S*-BINAP at 80 °C for 15 h to afford a nearly quantitative yield of  $Ru(acac)_2(S-BINAP)$ . This methodology was applied to other chiral diphosphines (P–P\*) to form  $Ru(acac)_2(P-P^*)$  [5]. The  $Ru(acac)_2(S-BINAP)$  complex thus obtained was further purified by crystallization from acetone and petroleum ether. The stoichiometry of the crystals was confirmed by NMR and by elemental analysis as a combination of two  $Ru(acac)_2(S-BINAP)$  and three molecules of acetone (as solvent of crystallization).

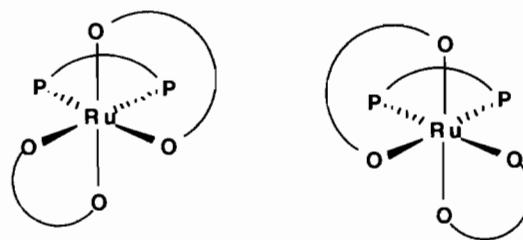
Table 2  
Selective bond distances (Å) of  $\Lambda$ - and  $\Delta$ - $Ru(acac)_2(S-BINAP)$

	$\Lambda$ -Isomer	$\Delta$ -Isomer
Ru–P1	2.277(3)	2.284(4)
Ru–P2	2.289(4)	2.284(3)
Ru–O11	2.057(9)	2.053(11)
Ru–O12	2.116(8)	2.129(11)
Ru–O21	2.097(10)	2.111(10)
Ru–O22	2.080(9)	2.066(12)
O11–C62	1.28(2)	1.28(2)
O12–C64	1.28(2)	1.30(2)
O21–C72	1.27(2)	1.26(2)
O22–C74	1.30(2)	1.26(2)
C61–C62	1.50(2)	1.53(3)
C64–C65	1.56(2)	1.54(2)
C71–C72	1.49(2)	1.52(2)
C74–C75	1.51(2)	1.55(2)
C62–C63	1.44(2)	1.40(3)
C63–C64	1.37(2)	1.31(3)
C72–C73	1.39(2)	1.39(3)
C73–C74	1.37(2)	1.37(3)

Table 3  
Selected bond angles (°) of  $\Lambda$ - and  $\Delta$ - $Ru(acac)_2(S-BINAP)$

	$\Lambda$ -Isomer	$\Delta$ -Isomer
P1–Ru–P2	91.2(1)	91.2(1)
O11–Ru–O12	90.9(4)	90.5(5)
O21–Ru–O22	90.0(4)	90.7(5)
P1–Ru–O11	89.9(3)	94.9(4)
P1–Ru–O22	94.0(3)	90.1(3)
P1–Ru–O21	95.3(3)	97.7(3)
P1–Ru–O12	178.1(3)	174.6(3)
P2–Ru–O11	97.1(3)	97.6(3)
P2–Ru–O22	87.3(3)	88.1(3)
P2–Ru–O12	90.4(3)	88.5(3)
P2–Ru–O21	173.2(3)	171.1(3)
O11–Ru–O21	85.2(4)	82.9(5)
O11–Ru–O22	174.1(4)	172.3(5)
O12–Ru–O21	83.1(4)	82.6(4)
O12–Ru–O22	85.1(4)	84.4(5)
O11–C62–C61	115.8(14)	113.0(18)
O11–C62–C63	125.1(13)	127.7(19)
C61–C62–C63	119.0(14)	119.2(17)
C62–C63–C64	126.8(14)	127.2(19)
O12–C64–C63	128.9(13)	128.1(18)
O12–C64–C65	112.1(12)	114.0(16)
C63–C64–C65	118.9(14)	117.8(17)
O21–C72–C71	115.9(14)	111.5(18)
O21–C72–C73	122.8(14)	127.0(16)
C71–C72–C73	121.3(13)	121.5(19)
C72–C73–C74	130.7(14)	127.2(18)
O22–C74–C73	126.2(14)	128.6(19)
O22–C74–C75	111.4(13)	115.2(18)
C73–C74–C75	122.3(14)	116.2(17)
Torsional angle	65.3	70.4

These ruthenium(II) complexes had an octahedral geometry defined by the chelating ligands *S*-BINAP and two acac ligands. The presence of two singlets in the  $^{31}P$  NMR at 52.3 and 52.7 ppm indicated that  $Ru(acac)_2(S-BINAP)$  existed as two diastereomers. The two diastereomeric configurations were formed as a result of two possible acac orientations with respect to the chiral diphosphine BINAP around the metal center [3].



The expected structure for  $Ru(acac)_2(S-BINAP)$  was confirmed by a single-crystal X-ray diffraction study (Fig. 1 and Tables 1–3). In fact, the unit cell was found to contain two independent molecules,  $\Lambda$ - and  $\Delta$ - $Ru(acac)_2(S-BINAP)$ , along with three acetone molecules of crystallization.

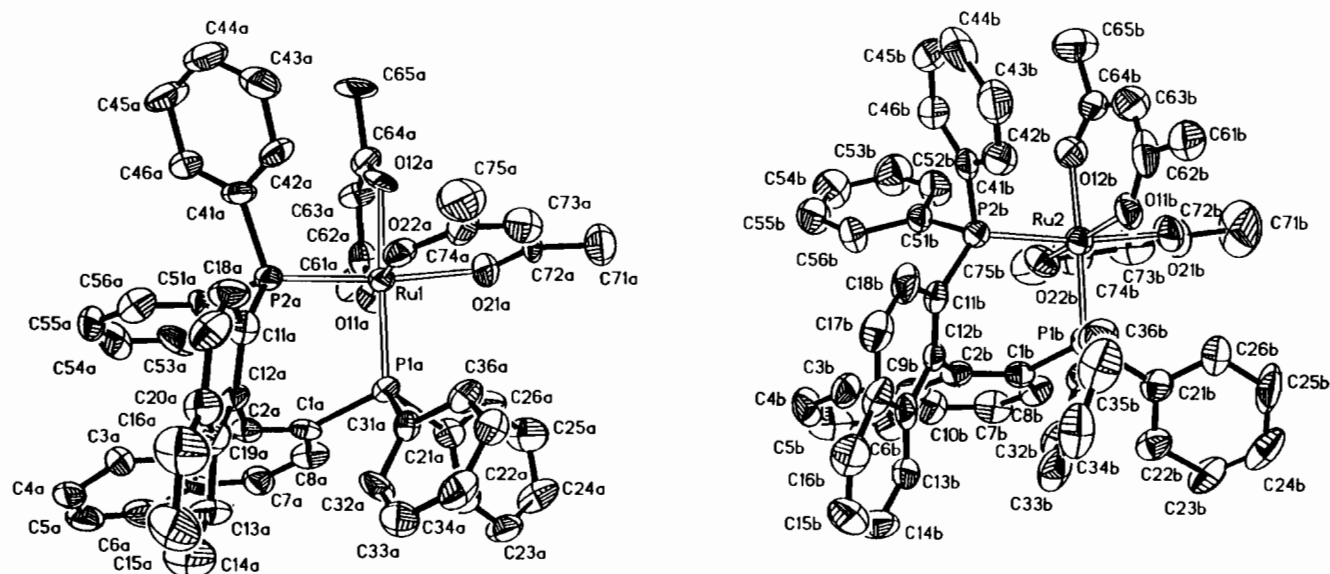


Fig. 1. ORTEP drawing of  $\Lambda$ - $\text{Ru}(\text{acac})_2(\text{S-BINAP})$  (left) and  $\Delta$ - $\text{Ru}(\text{acac})_2(\text{S-BINAP})$  (right). Atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogens have been omitted for clarity.

The structural characteristics of the complexes are as follows. Each central Ru(II) atom has a distorted octahedral coordination geometry and an approximate  $C_2$  symmetry axis. The Ru–P bonds for both complexes range from 2.277(3) to 2.289(4) Å which, when compared to similar Ru(BINAP) complexes, are longer than the Ru–P bonds of 2.241(3) and 2.239(3) Å from  $\Lambda$ -Ru(pivalate) $_2$ (S-BINAP) [1g] and 2.222(2) Å (av.) from  $\Delta$ -Ru(tiglate) $_2$ (R-BINAP) [6].

It has been reported that several ruthenium and rhodium BINAP complexes whose coordination spheres about the metal exhibit approximate  $C_2$  symmetry generally have axial phenyl groups coplanar with the M–P bond, whereas the equatorial phenyl groups are rotated  $\sim 45^\circ$  [6]. It is noted that the rotational orientations of the equatorial and axial phenyl group of  $\Lambda$ - and  $\Delta$ -Ru(acac) $_2$ (S-BINAP) do not comply with this general statement; however, the detailed discussion about the rotational orientations of the phenyl groups in the solid state may not be relevant since their positions are dictated by crystal packing forces. In solution the positions of the phenyl groups are probably fluxional.

An indication of the amount of congestion about the coordination sphere of the metal in  $\Lambda$ - and  $\Delta$ -Ru(acac) $_2$ (S-BINAP) compared to Ru(pivalate) $_2$ (S-BINAP) can be observed in the P–Ru–O (*cis*) interligand angles. The average angles from each P atom are 93.1 and 91.6° for  $\Lambda$ -Ru(acac) $_2$ (S-BINAP) and 94.2 and 91.4° for  $\Delta$ -Ru(acac) $_2$ (S-BINAP), which are smaller as compared to 97.4 and 97.9° in Ru(pivalate) $_2$ (S-BINAP). These results are anticipated since the bite angle of the  $\eta^2$ -carboxylate ligand (60°) is considerably smaller than that of acac (90°).

The four Ru–O distances are not equivalent in each isomer of Ru(acac) $_2$ (S-BINAP). In  $\Lambda$ -Ru(acac) $_2$ (S-BINAP) the Ru–O bonds that are *trans* to Ru–P are (2.116(8) and 2.097(10) Å), much longer than the Ru–O bonds that are mutually *trans* (2.057(9) and 2.080(9) Å). An identical trend is observed in  $\Delta$ -Ru(acac) $_2$ (S-BINAP) where Ru–O bonds *trans* to Ru–P are found to be 2.129(11) and 2.111(10) Å and the mutually *trans* Ru–O bonds are 2.053(11) and 2.066(12) Å. These observations are consistent with the high *trans* influence of the strongly  $\sigma$ -donating phosphorus atom and have been observed in  $\Lambda$ -Ru(pivalate) $_2$ (S-BINAP) (Ru–O $_{(av.)}$  = 2.201(16) and 2.127(11) Å) and  $\Delta$ -Ru(tiglate) $_2$ (S-BINAP) (Ru–O $_{(av.)}$  = 2.195(6) and 2.121(8) Å). However, the Ru–O bond discrepancies within each subgroup (i.e. Ru–O bonds *trans* to the P atom) of Ru(acac) $_2$ (S-BINAP) may reflect the large congestion about the metal center as the acac ligands attempt to coordinate in the least sterically encumbered orientation. Despite these differences the Ru(acac) $_2$  core in each isomer is nearly identical in which the average O–Ru–O (*cis*) interligand angle is 84.4 and 83.3° for  $\Lambda$ - and  $\Delta$ -Ru(acac) $_2$ (S-BINAP), respectively. Other acac ligand-related parameters are not unusual. The delocalized C–C and C–O bond distances for the acac ligands in  $\Lambda$ - and  $\Delta$ -Ru(acac) $_2$ (S-BINAP) average 1.39(5) and 1.28(2) Å, respectively, and 1.38(7) and 1.28(2) Å, respectively. The C–CH $_3$  bond distances average 1.50(1) and 1.54(2) Å for  $\Lambda$ - and  $\Delta$ -Ru(acac) $_2$ (S-BINAP), respectively. These average internal acac bond distances are in good agreement with bond distances in related Ru(acac) $_2$ (diene) complexes (average delocalized C–C bonds: 1.385(4)–1.93(3) Å; delocalized

C–O bonds: 1.272(2)–1.276(3) Å; C–CH<sub>3</sub> bonds: 1.506(4)–1.510(3) Å [7].

It is notable in the synthesis of Ru(OCOR)<sub>2</sub>(BINAP) (OCOR = carboxylate) that the *S*-isomer of BINAP stereoselectively produces  $\Lambda$ -Ru(OCOR)<sub>2</sub>(*S*-BINAP) and that the *R*-isomer of BINAP produces exclusively  $\Delta$ -Ru(OCOR)<sub>2</sub>(*R*-BINAP). Noyori and co-workers reported that the dissymmetry of the *S*-BINAP ligand fixes a  $\delta$  conformation of the seven-membered Ru–BINAP chelate ring. The chiral disposition of the four phenyl rings on the phosphorus atoms (two equatorial and two axial) exert steric influence and direct the incoming carboxylate to avoid the sterically demanding equatorial phenyl groups yielding the  $\Lambda$  configuration at the metal containing three chelating ligands [1g]. Likewise, *R*-BINAP has a  $\lambda$  conformation, which produces the  $\Delta$  configuration at the metal [6]. Although the conformation of the seven-membered P–Ru–P–C–C–C–C chelate ring is  $\delta$ , both  $\Lambda$  and  $\Delta$  metal configurations are observed when acac is coordinated to ruthenium.

A mixture containing both  $\Lambda$ - and  $\Delta$ -Ru(acac)<sub>2</sub>(*S*-BINAP) has been demonstrated to be a suitable catalyst precursor in the asymmetric hydrogenation of several prochiral acrylic acids. Initial studies have shown that naproxen can be produced in excellent optical purity (96% e.e.) from the hydrogenation of 2-(6-methoxy-2-naphthyl)acrylic acid by using  $\Lambda$ - and  $\Delta$ -Ru(acac)<sub>2</sub>(*S*-BINAP) as the catalyst precursor. The rates of hydrogenation using these catalysts are substantially different from the otherwise identical reactions using the Ru(BINAP)(OAc)<sub>2</sub> catalyst (either much faster or much slower than the Ru(BINAP)(OAc)<sub>2</sub> catalyzed reaction, depending on the pretreatment of the catalysts). Additional hydrogenation results will be reported in a future publication.

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