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INSTITUTE OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF CATALYTIC ACTIVITY OF FERROCENE BASED BIS(PHOSPHINITE) Ru(II) BENZENE COMPLEXES IN ASYMMETRIC REDUCTION OF KETONES

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M.Sc. Thesis

DEPARTMENT OF CHEMISTRY

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ABSTRACT

INVESTIGATION OF CATALYTIC ACTIVITY OF BIS(PHOSPHINITE) FERROCENE BASED Ru (II) BENZENE COMPLEXES IN ASYMMETRIC REDUCTION OF KETONES

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2016

Chiral substances are very important in industry and academic works. The most elegant approach for the synthesis of such compounds is via asymmetric catalytic process. Asymmetric catalysis has been developed very rapidly in the past three decades. Chiral bidentate phosphinite ligands easily coordinate to a metal through unpaired electron pairs on both phosphorus atoms and they have different binding properties (monodentate, bidentate and bridged), and thus they are attracting considerable attention.

Transition metal complexes of ferrocene have been active catalysts in various asymmetric transformations. Among these reactions, hydrogenation, hydrosilylation, cross-coupling reactions and aldol condensation are commonly used in organic synthesis. Use of ferrocenyl containing chiral ligands in transfer hydrogenation catalyzed by ruthenium(II) complexes is not so extensive.

In the present study, the chiral C_2-symmetric ferrocenylaminoalcohols were synthesized from the chiral compounds having different R-groups. The new C_2-symmetric bis (phosphinite) ligands were prepared from these aminoalcohols and Ph_2PCl or $^{i}Pr_2PCl$. Then bis(phosphinite)-Ru(II) benzene complexes were synthesized. Finally, catalytic activity of Ru(II) benzene complexes in asymmetric transfer hydrogenation reactions of ketones was studied.

Keywords: Amino alcohol, Ferrocene, Phosphinite, Ru(II), P-Ligands,Asymmetric Catalysis

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SYMBOLS and ABBREVIATIONS

Ar	Aryl
ATH	Asymmetric Transfer Hydrogenation
$CDCl_3$	Chloroform-d_1
CH_2Cl_2	Dichloromethane
Cod	1,5-cyclooctadiene
min	Minute
DEPT	Distortionless Enhancement by Polarization Transfer
DMF	N,N'-Dimetylformamide
DMSO-d_6	Dimethyl sulfoxide-d_6
Con.	Conversion
ee	Enantiomeric excess
Et_3N	Triethylamine
GC	Gas Chromatography
HETCOR	Heteronuclear correlation (^{13}C-^{1}H)
IR	Infra Red
J	Coupling constant
NMR	Nuclear Magnetic Resonance
Ph_2PCl	Monochlorodiphenylphosphine
$^{i}P_2PCl$	Monochlorodiisopropylphosphine
ppm	Part Per Million
R	Alkyl
TH	Transfer Hydrogenation
THF	Tetrahydrofuran
h	Hour
υ	Frequency (cm^{-1})
δ	Chemical shift

1. INTRODUCTION

In chemical synthesis, catalysis plays a significant role in organometallic chemistry. Even though selectivity is a main problem in organic synthesis, productivity as well as reactivity is also important to carry out effective reactions (Ohkuma et al. 2001).

Since the need for enantiomerically pure compounds increases, asymmetric catalysis grows. Due to the specificity required for effective drugs, main demand for these compounds comes from drug industry. In asymmetric catalysis, a chiral catalyst should be employed so that it transfers chirality from catalyst to the substrate. An efficient asymmetric catalyst is expected to form a chiral product in good yield and in high enantioselectivity (Ghent et al. 2007).

Although there are many reducing agent employed in a variety of processes, hydrogen is the cleanest one. Furthermore, hydrogenation is known as the most important catalytic method in synthetic chemistry. Catalytic hydrogenation is employed for several important purposes, such as, chiral reductions (Blaser et al. 2003).

The notion of C_2-symmetry in ligands was first presented by Kagan who synthesized DIOP. Presence of a C_2-symmetrical axis in ligands leads to a decrease in the number of possible competing, diastereomeric transition states (Whitesell et al.1989).

1. INTRODUCTION

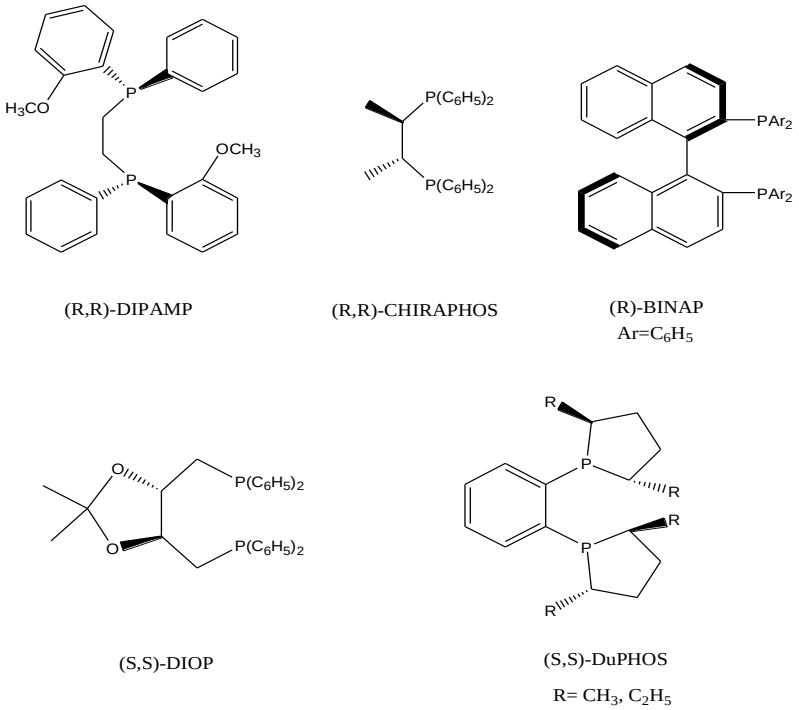


Figure 1. Chiral chelate ligands having C_2-symmetry plane

Design of enantiopure substituted ferrocenes by Ugi inspired Kumada and Hayashi, who discovered ferrocene containing diphosphines (Hayashi et al. 1976). In recent years, chiral metallocene ligands, particularly chiral ferrocenylphosphine ones have attracted considerable interest, because these catalysts have various applications (Ghent et al. 2007).

Chiral ferrocenyl ligands in particular have shown over the years a high modularity and a very broad applicability in catalysis including important industrial applications and were first included in the family of the privileged ligands by Blaser in 2002 (Dai et al. 2004). After the development of Josiphos, many other ferrocenyl derivatives, especially diphosphines have emerged as very useful giving high enantioselectivities for a variety of organic transformations. The possibility of having the most successful ones collected in a commercially available kit for ligand screening helps researchers around the world to find further applications of such ligands (Ursini et al. 2006). Chiral ferrocenes have been attracted considerable attention particularly in asymmetric catalysis. Ferrocenylphosphines are efficient ligands in asymmetric reactions, and they usually yield high enantioselectivity (Fukuzawa et al. 2007).

Phosphines and phosphinites are important phosphorous-containing ligands in organometallic chemistry since they have various electronic and steric features.

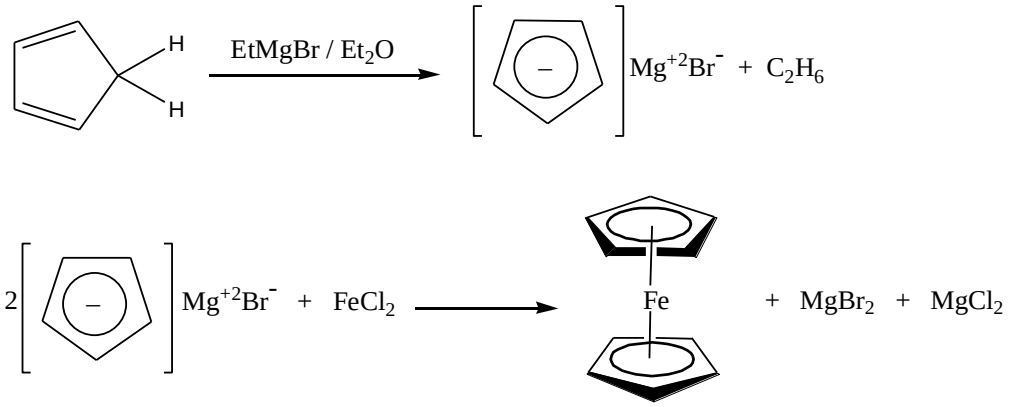
Therefore, they have widespread applications in asymmetric conversions catalyzed by transition metals. Because they possess a variety of structural, electronic and chemical advantages in comparison with other phosphorous-containing ligands, phosphinites have widely investigated in catalysis. One important advantage of these ligands is strength of metal-phosphorous bond owing to the existence of the electron-withdrawing P-OR group. Furthermore, valence σ*-orbital of the $P(OR)R_2$ is a better acceptor. Hence, they introduce lots of prospects to develop better ligands for asymmetric studies (Galka et al. 2003).

1. INTRODUCTION

2. LITERATURE SURVEY

2.1. Ferrocene

When ferrocene was first synthesized is unknown, however it was recorded as a ‘yellow sludge’ in the late 1940s by process technicians (P. L. Pauson, 2001). However it was first reported in the literature by two different groups in December 1951 (T. J. Kealy and P. L. Pauson, 1951)” and February 1952 (S.A. Miller, J. A. Tebboth, J. F. Tremaine, 1952).



Scheme 1. Synthesis of ferrocene

Ferrocenyl derivatives are among the most noticeable classes out of chiral compounds, because their structure introduces different types of chirality. Ferrocenyl containing phosphines have been employed in asymmetric hydrogenation conversions catalyzed with Rh. Due to their high efficiency and versatility; Josiphos-type ligands (Fig. 4) are the most significant ones, which were involved in the choice of advantaged ligands (Almassy et al. 2007)

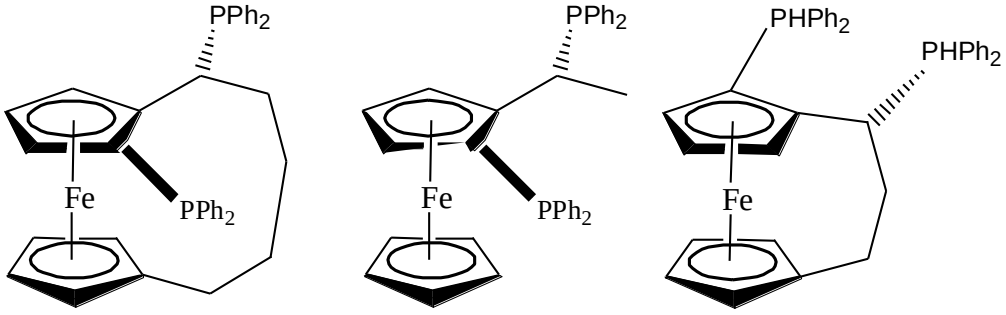


Figure 2. Josiphos-type diphosphines

These ligands were continued to tuning by changing of the substituents at the phosphorus atoms systematically (Almassy et al. 2007).

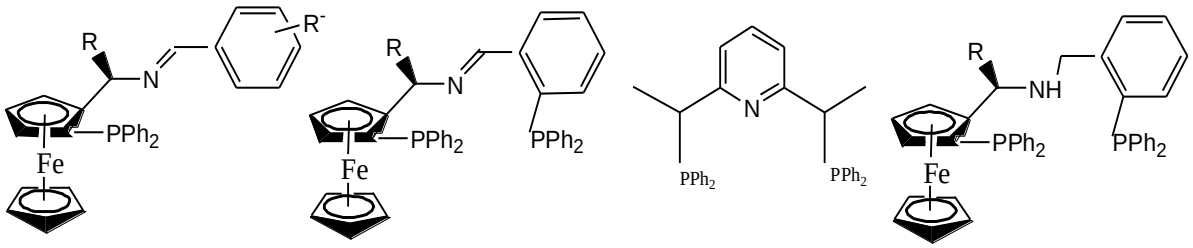


Figure 3. Important chiral ferrocenyldiphosphine ligands

After the development of Josiphos, many other ferrocenyl derivatives, especially diphosphines, have emerged as very useful giving high enantioselectivities for a variety of organic transformations. The possibility of having the most successful ones collected in a commercially available kit for ligand screening helps researchers around the world to find further applications of such ligands (Ursini et al. 2006).

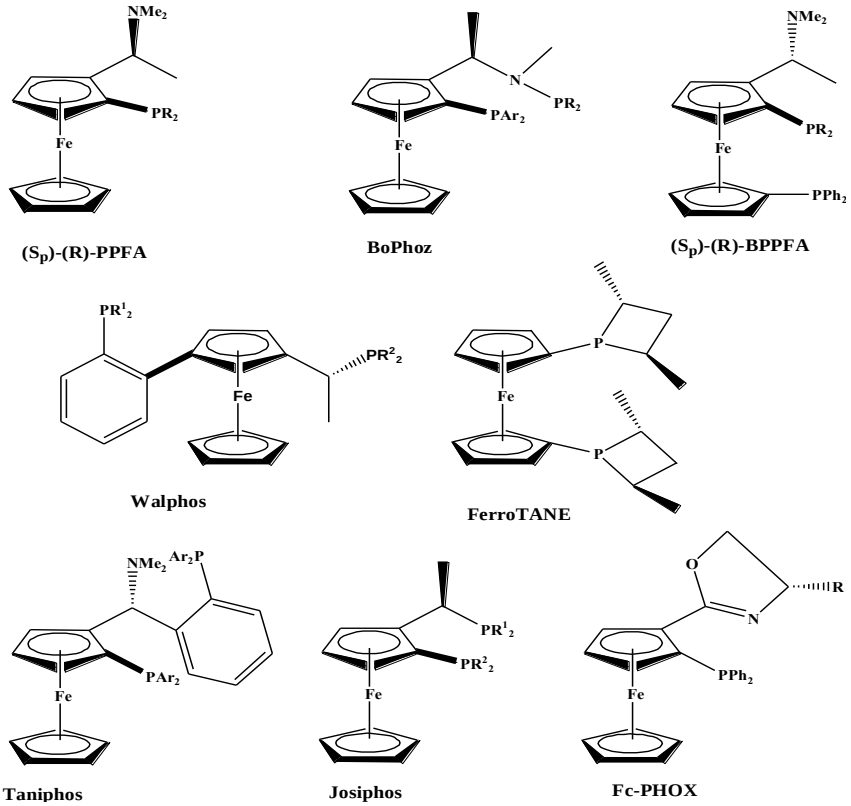


Figure 4. **Several representative chiral ferrocenyl ligands**

2.2. Organophosphorus Ligands

Phosphine complexes have been widely employed in homogeneous catalysis since Wilkinson's well-known study on the use of $Rh(PPh_3)_3Cl$ as catalyst in

hydrogenation reactions. In recent years, chiral phosphine complexes have been attracting significant interest in asymmetric reactions (Appleby and Woollins, 2002).

2.3. Catalytic studies of organophosphorus ligands

Ligands containing phosphorus atoms especially chiral ones have been attracting considerable attention since they have been widely applied in organometallic chemistry. So far, more than 1000 chiral diphosphine ligands have been developed for asymmetric catalysis. Among them, DIPAMP, DIOP, Chiraphos, BINAP, and Duphos have become very successful (Longmire et al. 1997).

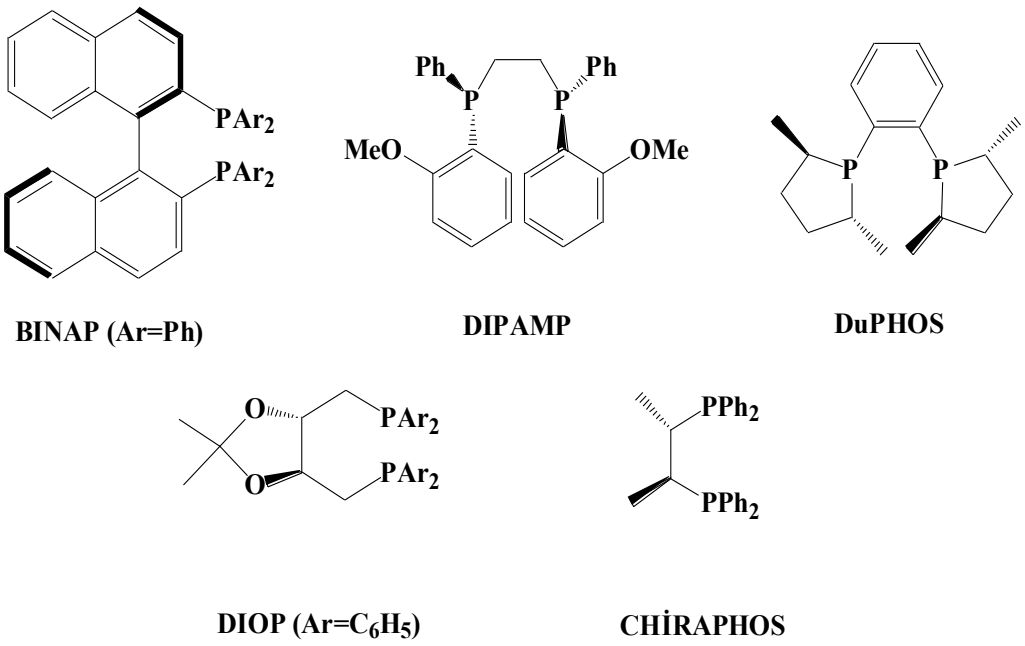
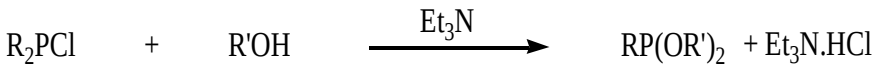


Figure 5. Chiral phosphorus ligands

2.4 Phosphinites and their catalytic use



Scheme 2. Synthesis of phosphinites

Because they introduce many prospects for designing novel effective ligands to be used in asymmetric catalysis, phosphinites have widely been investigated as ligand in catalysis (Galka ve Kraatz, 2003).

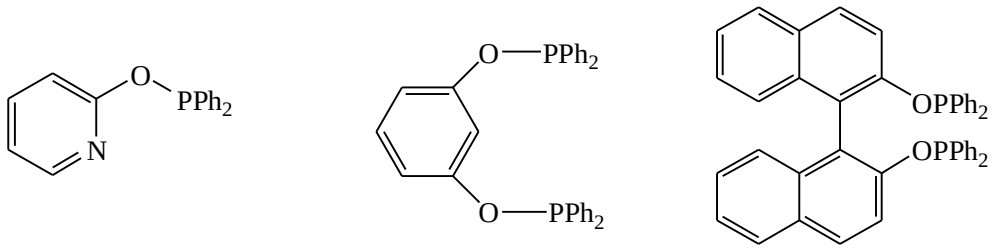


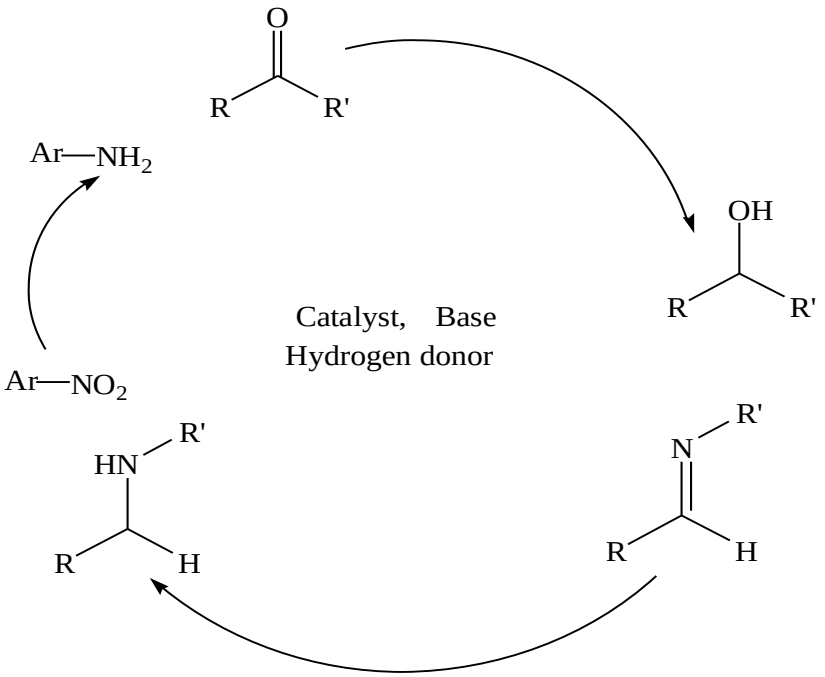
Figure 6. Several representative phosphinites

2.4. Transfer Hydrogenation

Traditionally, main source of hydrogen in catalytic hydrogenations is the molecular hydrogen. Yet, this conversion can also be carried out via transfer hydrogen reaction. In transfer hydrogenation, hydrogen is transferred from a donor molecule (DH_2) to the substrate to give reduced substrate and the oxidized donor D. This process does not require hydrogen gas and pressure equipment, which may result in safety problems (Blaser et al. 2003).

$$DH_2 + A \rightleftharpoons D + AH_2$$

Scheme 3. Hydride transfer from hydrogen donor DH_2 to substrate A, DH_2:Hydrogendonor; A: hydrogen acceptor



Scheme 4. Reduction of multiple bonds by transfer hydrogenation

Catalyst: metal complex; Base: K_2CO_3, NaOH, KOH, ^{t}BuOK, Hydrogen donor: 2-Propanol, HCO_2H/NEt_3 (Çetinkaya et al. 2010)

2.5. Hydrogen Sources in Transfer Hydrogenation

Two important hydrogen sources used in transfer hydrogenation are isopropanol and formic acid. The former needs existence of a strong base, and the reaction should be performed in dilute, usually in 0.1 M substrate concentration, since the reaction is reversible. The latter usually consists of an azeotropic 5:2 mixture of HCOOH and NEt_3. It has several advantages such as giving high substrate concentrations, being irreversible and allowing high conversions without back-reaction and racemization. However, important drawback of the method that it should be run in an open system, since CO_2 gas is released.

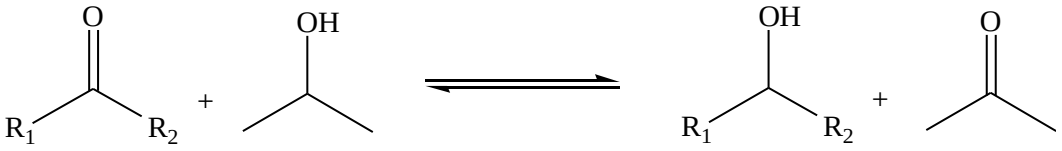


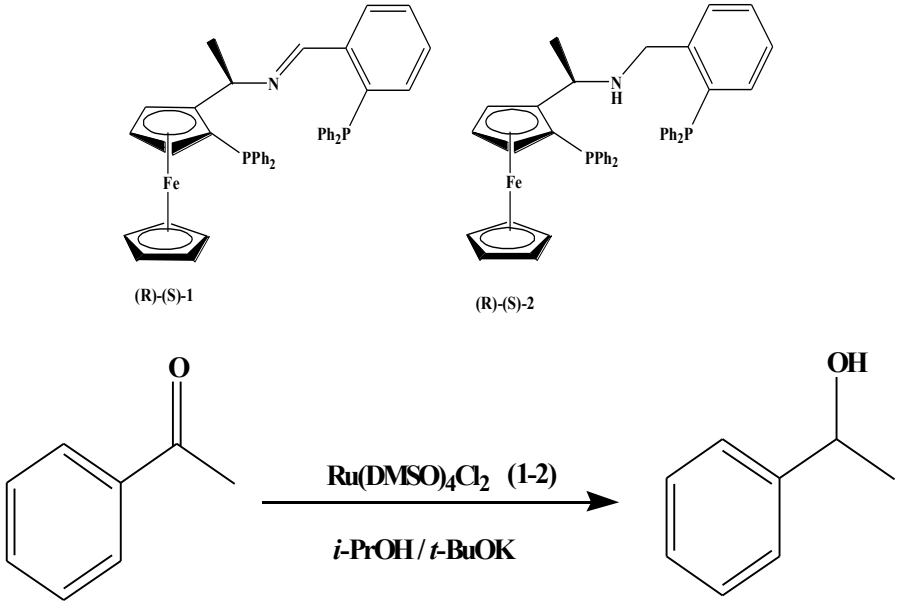
Figure 7. Use of 2-propanol as a hydrogen source

2-Propanol is the commonly used hydrogen source in transfer hydrogenation, because it has several advantages such as, being stable, facile to use (bp 82 °C), environmentally friendly, nontoxic, inexpensive and dissolving a lot of organic compounds. Furthermore, the acetone product is readily removable, since its boiling point is low (Noyori et al. 2001).

2. LITERATURE SURVEY

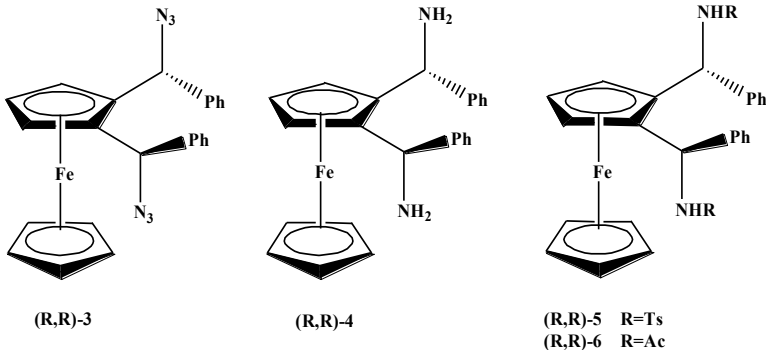
3. PREVIOUS STUDIES

Dai et al. (2004) prepared new chiral ferrocenyldiphosphine ligands and employed them in Ru(II) catalyzed asymmetric transfer hydrogenation of ketones to afford corresponding secondary alcohols. They obtained up to 99% conversion and 90% e.e. by using $Ru(DMSO)_4Cl_2$/**2** in transfer hydrogenation of acetophenones in propan-2-ol.



Scheme 5. Reduction of acetophenone

Fukuzawa et al. (2006) proposed "that the retentive substitution of both acetoxy groups in (*R*,*R*)-**1** by the azide ion could be" performed with azidotrimethylsilane ($TMSN_3$). However, they did not obtained anticipated diazide and they recovered almost the entire starting complex after 24 h at room temperature.



3. PREVIOUS STUDIES

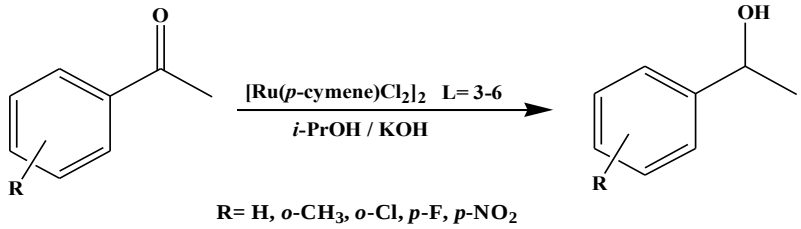
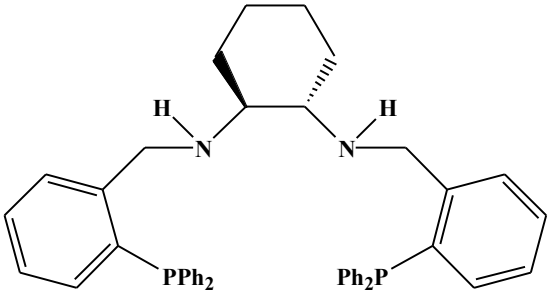


Figure 8. Reduction of substituted acetophenones

Xing et al. (2006) applied chiral PNNP ligand (**7**) and $[IrHCl_2(COD)]_2$ in the asymmetric transfer hydrogenation of aromatic ketones, affording the alcohols in high yield and excellent enantioselectivity (up to 99% ee).



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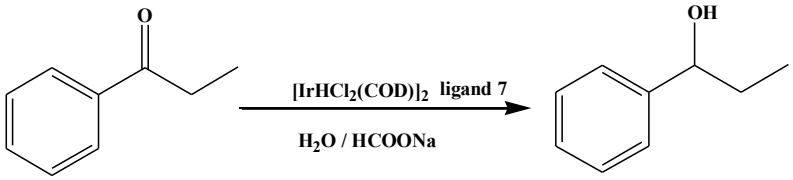


Figure 9. Reduction of propiophenone

Cabou et al. (2005) use (*R*)-(+)-N,N-dimethylaminoethylferrocene to synthesize novel ferrocenyl diphosphines enantioselectively. Then, they synthesized dissymmetric ferrocenyl diphosphines as well, and investigated catalytic activity of their Ru complexes in asymmetric transfer hydrogenation of acetophenone.

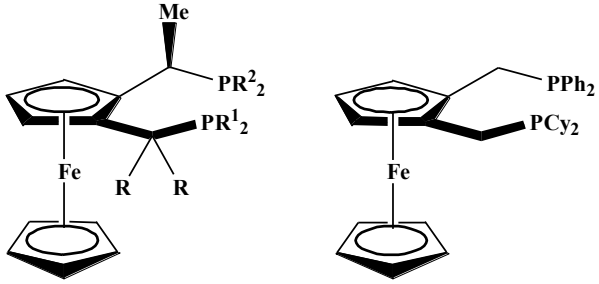


Figure 10. New optically pure ferrocenyl diphosphines as ligands in asymmetric transfer hydrogenation of acetophenone

Elma et al. (2013) synthesized enantioselective C_2-symmetric bis(phosphinite) ligands. They prepared their Ru(II) complexes in situ and used these complexes as catalyst for the asymmetric transfer reactions.

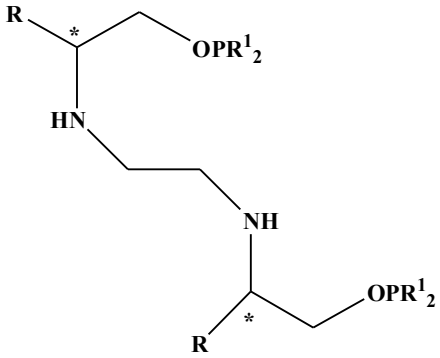


Figure 11. Enantioselective C_2- symmetric bis(phosphinites)

Ak et al. (2013) prepared a new and versatile class of unsymmetrical ferrocenyl-phosphinite ligands possessing a stereogenic center from commercially available, inexpensive aminoacids such as, *D*-, *L*-phenylglycine and D-, L-phenylalanine, through a concise synthetic procedure. These ligands were not very sensitive to air and moisture, and display good enantioselectivities in the asymmetric transfer hydrogenation of acetophenone derivatives, in which up to 91% *ee* was obtained.

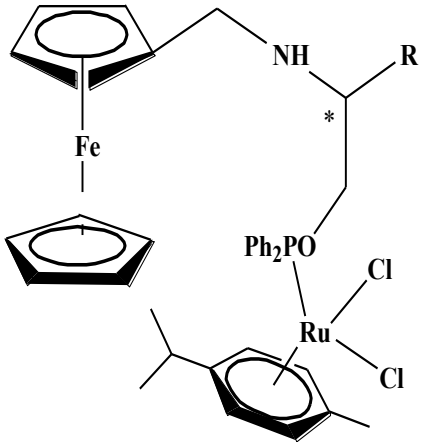


Figure 12. Unsymmetrical ferrocenyl-phosphinite ligands .

Işık et al. (2013) reported new examples of enantiomerically pure monodendate phosphinite ligands containing both a ferrocene moiety and NH bridging moiety adjacent to the stereocenter, as well as their ruthenium(II) dichloro complexes, and employed them in transfer hydrogenation of aromatic ketones. They obtained up to 99% conversion with 97% *ee*.

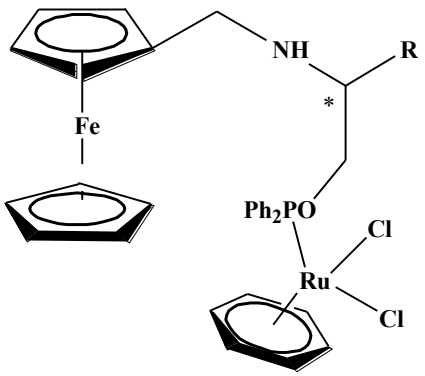
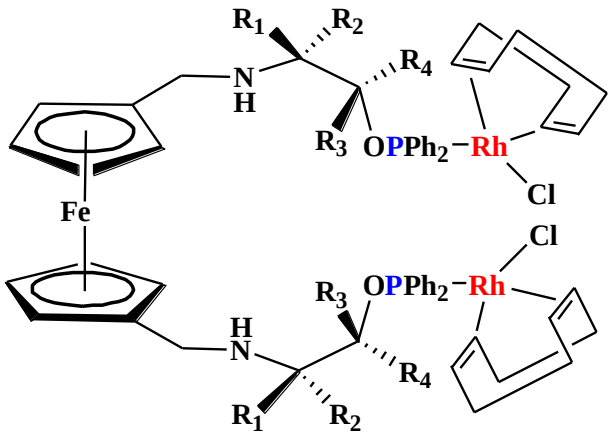


Figure 13. Ruthenium(II) dichloro complexes of enantiomerically pure monodendate phosphinite ligands

Ak et al. (2015) prepared a new class of chiral modular C_2-symmetric ferrocenyl-phosphinite ligands in good yields by using 1,1'-ferrocenedicarboxyaldehyde and various ferrocene based-amino alcohols as starting materials, and applied rhodium(I) complexes of ferrocene based-phosphinites in the asymmetric transfer hydrogenation (ATH) of aromatic ketones using *iso*PrOH as the hydrogen source. They found that when the chiral center was near rhodium center, the ee% was higher. They also showed aryl moiety was more responsible for higher activity than alkyl moiety. They proposed that this different behavior in enantioselectivities can be explained on the basis of aromatic moiety (phenyl) near chiral carbon center in the ligand backbone responsible for the optimization molecular rigidity.

R_1: benzyl,	**R_2**: H,	**R_3:** H,	**R_4**: H,	;	**R_1:** H,	**R_2**: H,	**R_3:** CH_3,	**R_4**: H,
R_1: phenyl,	**R_2**: H,	**R_3:** H,	**R_4**: H,	;	**R_1:** H,	**R_2**: H,	**R_3:** phenyl,	**R_4**: H,
R_1: *iso*butyl,	**R_2**: H,	**R_3:** H,	**R_4**: H,	;	**R_1:** ethyl,	**R_2**: H,	**R_3:** H,	**R_4**: H,
R_1: *sec*butyl,	**R_2**: H,	**R_3:** H,	**R_4**: H,	;	**R_1:** phenyl,	**R_2**: H,	**R_3:** phenyl,	**R_4**: H,



Scheme 6. Synthesis of rhodium complexes

Reagents and conditions (i) n-buthyllithium, TMEDA, - 78 °C, THF, DMF; *(ii)* L-phenyl alaninol, L-phenyl glycinol, L-leucinol, L-isoleucinol, (*S*)-(+)-1-amino-2-propanol, (*R*)-(-)-2-amino-1-phenylethanol, (*R*)-(-)-2-amino-1-butanol or (1S,2*R*)-(+)-2-amino-1,2-diphenylethanol; *(iii)* 2 equiv. Ph_2PCl, 2 equiv. Et_3N; *(iv)* 1 equiv. $[Rh(\mu\text{-}Cl)(cod)]_2$.

3. PREVIOUS STUDIES

4. MATERIALS and METHODS

4.1.Chemicals

1.	Ferrocene	**19.**	Benzophenone
2.	Tetramethylethylenediamine	**20.**	Sodium
3.	L-phenyl glycinol	**21.**	Toluene
4.	L-isoleucinol	**22**.	Dichloromethane
5.	*n*-Butyllithium	**23**.	n-Hexane
6.	Tetrahydrofuran	**24.**	Diethylether
7.	Methanol	**25.**	Triethylamine
8.	*N*,*N*-Dimethylformamide	**26.**	Monochlorodiphenylphosphine
9.	Ethyl acetate	**27.**	Monochlorodiisopropylphosphine
10.	Magnesium sulfate	**28.**	$[Ru(\eta^6\text{-benzene})Cl_2]_2$
11.	Sodium sulfate	**29.**	Potassium hydroxide
12.	Sodium borohydride	**30.**	2-Propanol
13.	Ammonium chloride	**31.**	Acetophenone
14.	Chloroform	**32.**	4-Fluoroacetophenone
15.	Acetonitrile	**33.**	4-Chloroacetophenone
16.	Chloroform-*d*	**34.**	4-Bromoacetophenone
17.	Calcium hydride	**35.**	4-Methoxyacetophenone
18.	*di*-phosphoruspentaoxide	**36.**	2-Methoxyacetophenone

These reagents and solvents were purchased from Merck, Fluka and Aldrich.

4.2. Instrument Used For Characterization

1. FT-IR Spectrometer (Mattson 1000 ATI UNICAM)

2. Elemental analysis (Fisons EA 1108 CHNS-O)

3. NMR Spectrometer (Bruker AV400)

4. Gas chromatograph (Shimadzu GC 2010 Plus)

5. Melting points (Gallenkamp MPD 350 BM 2.5)

6. Polarimeter (Perkin Elmer 341)

4.3. Method

The study can be outlined with three main titles:

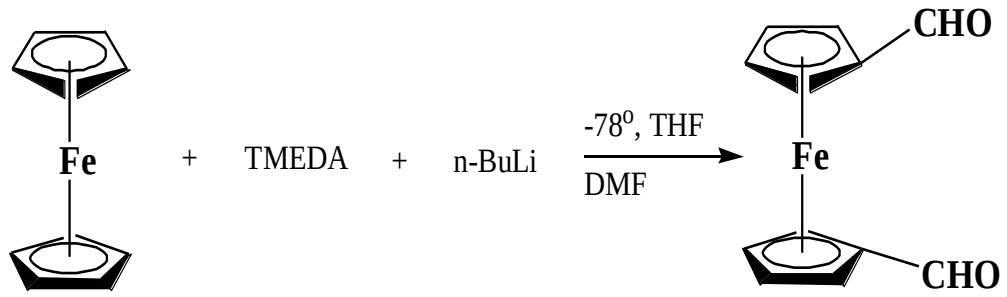
i. Synthesis of ferocene based C_2-symmetric bis(phosphinite) ligands,

ii. Synthesis of bis(phosphinite) Ru(II)-benzene complxes,

iii. Application of bis(phosphinite)-Ru(II)-benzene complexes as catalyst in transfer hydrogenation reactions and determining their catalytic activity.

All experimental studies, i.e. synthesis of *iso*-propyl based C_2-symmetric bıs(phosphinites) and their Ru(II) benzene complexes, and use of them in catalytic investigations were accomplished according to the literature (Ak et al. 2015).

4.3.1 Synthesis of 1,1'-ferrocenedicarboxyaldehyde (Bastin, S. et al. 2001)

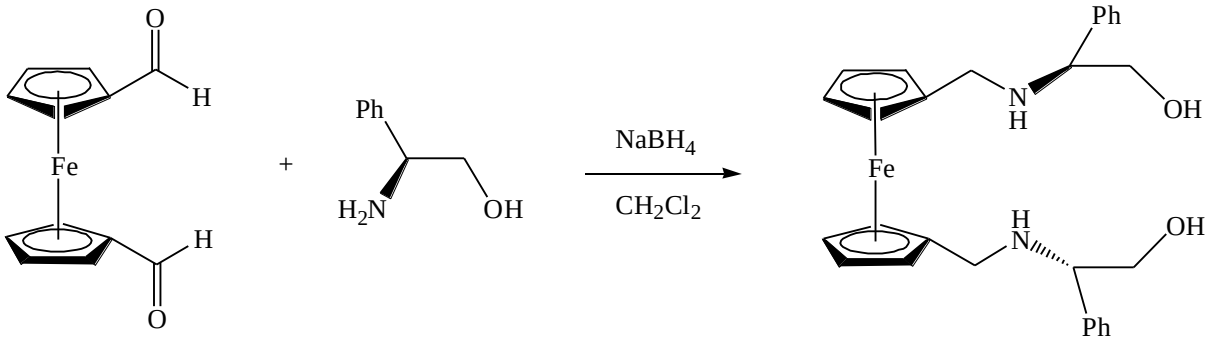


Tetramethylethylenediamine (TMEDA) (5.32 ml, 35.4 mmol) was added to a solution of ferrocene (3.00 g, 16.2 mmol) in dry *n*-hexane (60 ml) and the suspension was stirred for 5 min under argon. *n*-BuLi (22 ml, 35.4 mmol, 1.7 M in hexane) was added dropwise with a syringe. The mixture was left to stirr at room temperature overnight. After stirring at -78 ºC for 15 min, THF (30 ml) followed by anhydrous DMF (2.7 ml) were added to the reaction mixture. The solution was quenched with brine (20 ml) and CH_2Cl_2 (10 ml). The phases were separated and the aqueous phase was extracted with (3 x 30ml). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified through column chromatography (SiO_2, hexane: diethylether: ethylacetate; 4: 1: 0.1) giving the ferrocene-1,1'-dicarboxaldehyde, as bright red crystalline solid in third fraction. Color: Bright. Yield: 2.70 g. (70%). ^{1}H NMR ($CDCl_3$) δ(ppm): “9.94 (s, 2H, CHO), 4.88 (s, 4H, Cp-C<u>H</u>), 4.67 (s, 4H, Cp-C<u>H</u>).” ^{13}C NMR ($CDCl_3$) δ(ppm): 192.82 (CHO), 80.30 (*i*-Cp-C), 74.84 (Cp-<u>C</u>), 70.87 (Cp-<u>C</u>). Anal.Calcd. For $C_{22}H_{10}O_2Fe$ (362.17 g/mol): “C, 59.54; H, 4.17. Found: C, 59.48; 4.10.”

4.3.2 General procedures "for the synthesis of" C_2-symmetric "ferrocenyl amino alcohols"

A mixture of ferrocenedicarboxaldehyde (4.13 mmol) and the amino alcohol (12.4 mmol) in previously dried CH_2Cl_2 (250 ml) containing molecular sieves (4Å, 5.00 g.) was refluxed under argon for 10 h. The mixture was filtered through Celite 545. The solvent was removed under reduced pressure and the residue was re-dissolved in dry methanol (150 ml). Solid $NaBH_4$ (20.8 mmol) was added in small portions at 0 ºC. After stirring for 1h., the reaction was quenched by addition of a saturated solution of NH_4Cl (250 ml) and extracted with CH_2Cl_2 (3 x 30ml). The combined organic extracts was dried over Na_2SO_4 and evaporated. The subsequent purification by column chromatography (SiO_2, eluent:$CHCl_3$ /CH_3CN: 7/3) yielded the desired yellow crystals of the amino acohols.

"4.3.2.1 (*S*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,1'-ferrocenylmethyl diamine, (1)"

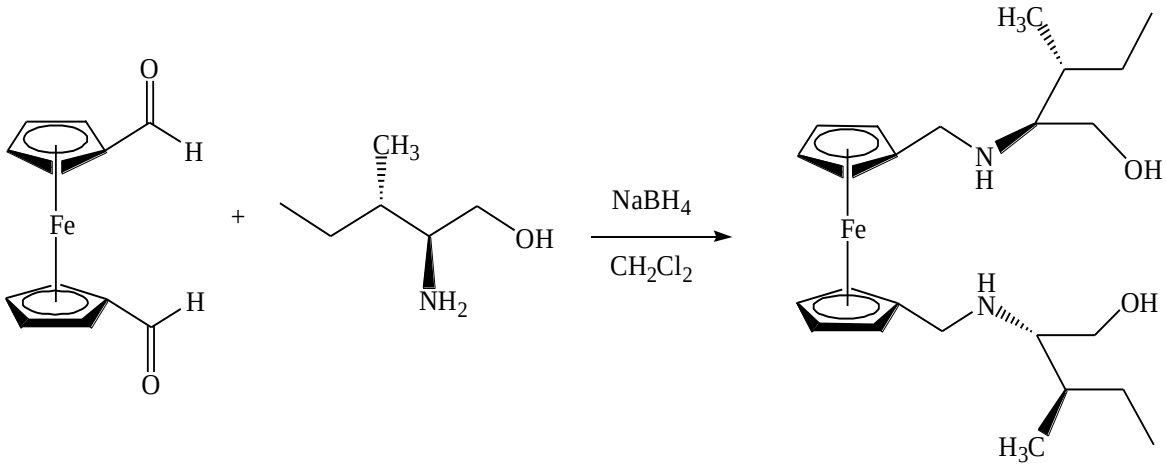


(1)

Color: Yellow. Yield: 1.40 g, yellow crystals (70%). Mp: 130-132 ºC. "$[\alpha]_D^{20}$ +31.6 (c 1.2, MeOH)]; ^{1}H NMR" ($CDCl_3$, ppm) δ:7.28-7.40 (m, 10H, $C_6\underline{\mathbf{H}}_5$), 3.98-4.33 (m, 8H, $C_5\underline{\mathbf{H}}_4$), 3.96 (m, 2H, C**H**N), 3.78-3.82 (m, 2H, C$\underline{\mathbf{H}}_2$OH (a)), 3.66-3.71 (m, 2H, C$\underline{\mathbf{H}}_2$OH (b)), "3.42 (d, *J*=12.7 Hz, 2H, C$\underline{\mathbf{H}}_2$NH (a)), 3.16 (d, *J*=12.7 Hz, 2H, C$\underline{\mathbf{H}}_2$NH (b)), 2.98 (br, 4H, N**H** and O**H**). ^{13}C NMR" ($CDCl_3$, ppm): δ 139.73 (*i*-C_6H_5), 128.71, 127.75, 127.48 ($\underline{\mathbf{C}}_6H_5$), 87.96 (*i*-$C_5H_4$), 68.86, 68.16, 67.90 ($\underline{\mathbf{C}}_5H_4$), 67.01 ($\underline{\mathbf{C}}H_2OH$), 65.13 ($\underline{\mathbf{C}}HN$), 46.08 ($\underline{\mathbf{C}}H_2NH$). "IR (KBr pellet in cm^{-1})" υ(O-H): 3420, (N-H): 3283, (C=C-Cp): 1451, (C-H): 3081, 3027, 2915, 2839. Anal. Calcd. for

$C_{28}H_{32}N_2O_2Fe$ (484.42 g/mol): C, 69.41; H, 6.67; N, 5.78, found: C, 69.12; H, 6.48; N, 5.63 %.

4.3.2.2 (*S*)-bis[*N*-(2-hydroxy-1-*sec*-butyl)ethyl]-1,1'-ferrocenylmethyldi amine, (2)



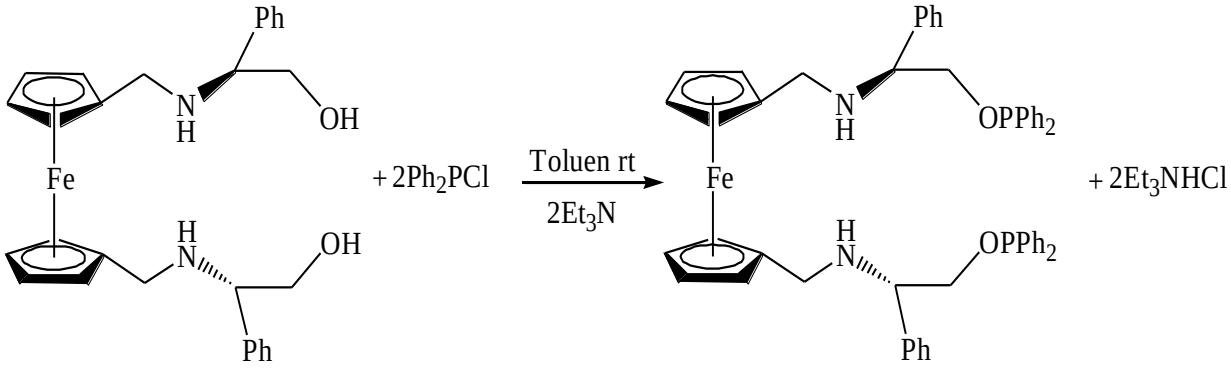
(2)

Color: Yellow. Yield: 1.25 g, (68%). "Mp: 64-66 ºC. $[\alpha]_D^{20}$ +53.9 (c 1.2, MeOH)]; ^{1}H NMR ($CDCl_3$, ppm): δ 4.11-4.21" (m, 8H, $C_5\underline{\mathbf{H}}_4$), 3.63 (dd, 2H, *J*= 4.0 and 10.7 Hz, $C\underline{\mathbf{H}}_2OH$ (a)), 3.55 (d, 2H, *J*=12.8 Hz, $C\underline{H}_2NH$ (a)), 3.36-3.41 (m, 2H, $C\underline{\mathbf{H}}_2OH$ (b) and 2H, $C\underline{\mathbf{H}}_2NH$ (b)), 2.62 (m, 2H, C**H**N), 2.48 (br, 4H, N**H** and O**H**), 1.61-1.67 (m, 2H, $C\underline{\mathbf{H}}CH_3$), 1.44-1.50 (m, 2H, $C\underline{\mathbf{H}}_2CH_3$ (a)), 1.18-1.27 (m, 2H, $C\underline{\mathbf{H}}_2CH_3$ (b)), 0.95 (t, 6H, *J*=7.4 Hz, $CH_2C\underline{\mathbf{H}}_3$), 0.89 (d, 6H, *J* = 6.9 Hz, $CHC\underline{\mathbf{H}}_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 87.84 (*i*-$C_5H_4$), 68.49, 68.42, 68.29, 68.06 ($\underline{\mathbf{C}}_5H_4$), 62.56 (**C**HN), 60.34 ($\underline{\mathbf{C}}H_2OH$), 46.20 ($\underline{\mathbf{C}}H_2NH$), 35.33 ($\underline{\mathbf{C}}HCH_3$), 26.45 ($\underline{\mathbf{C}}H_2CH_3$), 14.39 ($CH\underline{\mathbf{C}}H_3$), 11.87 ($CH_2\underline{\mathbf{C}}H_3$). "IR (KBr pellet in cm^{-1}) υ" (O-H): 3416, (N-H): 3279, (C=C-Cp): 1456, (C-H): 2958, 2929, 2871, 2830. Anal. Calcd. for $C_{24}H_{40}N_2O_2Fe$ (444.44 g/mol): "C, 64.85; H, 9.09; N, 6.30, found: C, 64.79; H, 8.96; N, 6.24 %."

"4.3.3 General procedure for synthesis of ferrocene based" C_2-symmetric bis(phosphinite) Ligands, 3-6.

To a solution of the amino alcohol (0.15 mmol) in dry toluene (20 ml) was added triethylamine (0.30 mmol) and the mixture was stirred for 10 min under argon atmosphere. To this solution was added dropwise monochlorodiphenylphosphine, PPh2Cl (0.30 mmol). The mixture was then stirred at room temperature until all the reactions were completed. A white precipitate of triethylamine hydrochloride was removed by filtration under argon and remaining organic phase was evaporated under reduced pressure to produce a yellow viscous oily product.

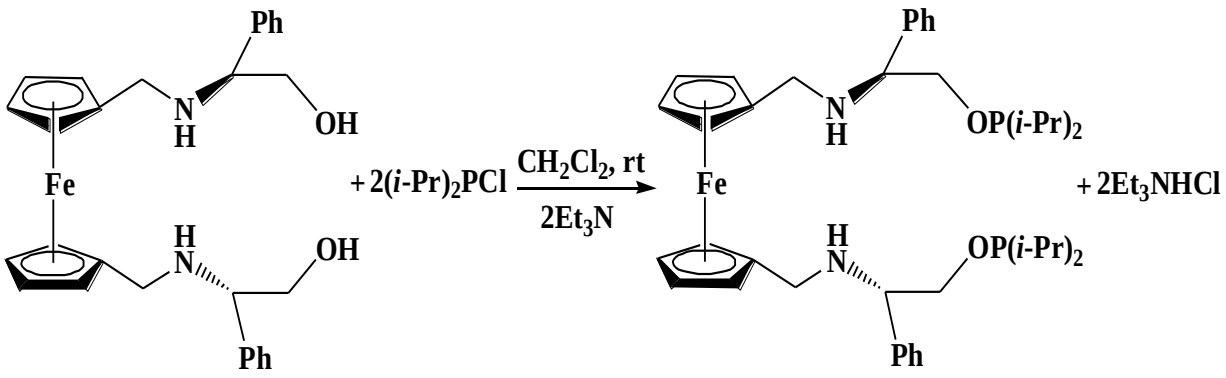
"4.3.1.(*S*)-bis[*N*-2-diphenylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiamine, (3)"



(3)

Color: Yellow. Yield: 0.098 g, (76.6 %). $[\alpha]_D^{20}$ +56.1° "(c 1.2, MeOH)]; ^{1}H NMR ($CDCl_3$, ppm)" δ 7.28-7.65 (m, 30 H, $C_6\underline{\mathbf{H}}_5PO$ and $C_6\underline{\mathbf{H}}_5$), 4.02-4.07 (m, 8H, $C_5\underline{\mathbf{H}}_4$ and 2H, C**H**N), 3.93 (m, 4H, C$\underline{\mathbf{H}}_2$OP), 3.41 (d, 2H, *J*=13.1 Hz, C$\underline{\mathbf{H}}_2$NH (a)), 3.22 (d, 2H, *J*=13.1 Hz, C$\underline{\mathbf{H}}_2$NH (b)), 2.42 (br, 2H, N$\underline{H}$). ^{13}C NMR ($CDCl_3$, ppm): δ 141.76 (d, *J*=18.6 Hz, *i*-$\underline{\mathbf{C}}_6H_5PO$), 140.11 (*i*-$\underline{\mathbf{C}}_6H_5$), 130.61, 130.47, 130.39, 129.44, 128.51, 128.45, 128.38, 127.92, (*o*-$\underline{\mathbf{C}}_6H_5PO$, *p*-$\underline{\mathbf{C}}_6H_5PO$, *m*-$\underline{\mathbf{C}}_6H_5PO$, *o*-, *p*-, *m*-$\underline{\mathbf{C}}_6H_5$), 87.06 (*i*-$\underline{\mathbf{C}}_5H_4$), 74.74 (d, *J*=18.1 Hz, ($\underline{\mathbf{C}}H_2OP$), 68.68, 68.49, 68.42, 68.18 ($\underline{\mathbf{C}}_5H_4$), 63.39 (d, *J*=8.0 Hz, **C**HN), 46.18 (($\underline{\mathbf{C}}H_2NH$). "^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ" 116.76 (s, O$\underline{\mathbf{P}}Ph_2$). "IR (KBr pellet in cm^{-1})" υ(N-H): 3331, (C=C-Cp): 1436, (O-P): 1020, (C-H): 3068, 3028, 2922, 2862. Anal. Calcd. for $C_{52}H_{50}N_2O_2P_2Fe$ (852.77 g/mol): C, 73.23; H, 5.92; N, 3.29, found: C, 73.11; H, 5.82; N, 3.18 %.

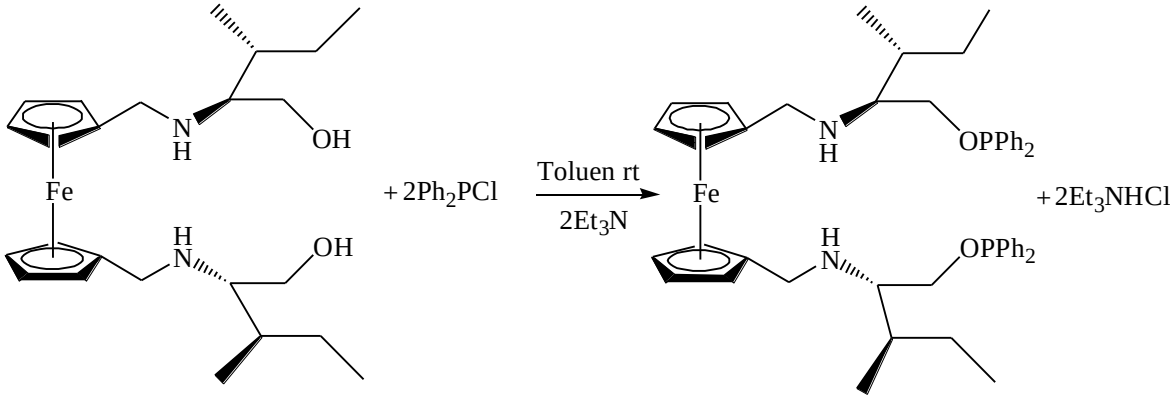
4.3.2. (*S*)-bis[*N*-2- diisopropylphosphinite -1-phenyl)ethyl]-1,1'-ferrocenylmethyl diamine, (4)



(4)

Color: Yellow. Yield: 0.09 g, (83.7 %). $[\alpha]_D^{20}$ +27.7 “(c 1.0, CH_2Cl_2]; ^{1}H NMR ($CDCl_3$, ppm): δ 7.29-7.42 (m, 10 H, $C_6\underline{\mathbf{H}}_5$), 4.09 (d, 4H, *J*=5.8 Hz, $C_5\underline{\mathbf{H}}_4$), 4.03” (s, 4H, $C_5\underline{\mathbf{H}}_4$), 3.92 (m, 2H, C**H**N), 3.74 (m, 4H, C$\underline{\mathbf{H}}_2$OP), 3.40 (d, 2H, *J*=13.1 Hz, C$\underline{\mathbf{H}}_2$NH (a)), 3.24 (d, 2H, *J*=13.2 Hz, C$\underline{\mathbf{H}}_2$NH (b)), 1.69-1.75 (m, 4H, PC$\underline{\mathbf{H}}$(CH)$_3$), 0.96-1.12 (m, 24H, PCH(C$\underline{\mathbf{H}}$)$_3$); ^{13}C NMR ($CDCl_3$, ppm): δ 140.33 (*i*-$\underline{\mathbf{C}}_6H_5$), 128.39, 127.82, 127.47 (*o*-, *p*-, *m*-$\mathbf{C}_6H_5$), 87.38 (*i*-$\underline{\mathbf{C}}_5H_4$), 77.22 ($\underline{\mathbf{C}}H_2$OP), 68.49, 68.43, 68.34, 68.08, 67.98 ($\underline{\mathbf{C}}_5H_4$), 63.75 (d, $^3J_{P\text{-}C}$ =7.0 Hz, $\underline{\mathbf{C}}$HN), 46.20 (($\underline{\mathbf{C}}H_2$NH), 28.04 (dd, $^1J_{P\text{-}C}$= 17.1 Hz, $^1J_{P\text{-}C}$= 36.2 Hz, P$\underline{\mathbf{C}}$H(CH)$_3$, 17.98 (s, PCH($\underline{\mathbf{C}}$H)$_3$, 17.78 (s, PCH($\underline{\mathbf{C}}$H)$_3$, 17.08 (d, $^2J_{P\text{-}C}$= 2.6 Hz, PCH($\underline{\mathbf{C}}$H)$_3$, 16.99 (d, $^2J_{P\text{-}C}$= 2.2 Hz, PCH($\underline{\mathbf{C}}$H)$_3$; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 154.69 (s, O$\underline{\mathbf{P}}$CH(CH$_3$)$_2$). “IR (KBr pellet in cm^{-1}) υ” (N-H): 3233, (P-CH(CH$_3$): 1454, (O-P): 1039, (C-H): 2963, 2870. Anal.Calcd. for $C_{40}H_{58}N_2O_2P_2Fe$ (716.71 g/mol): C, 67.04; “H, 8.16; N, 3.91, found: C, 66.87; H, 7.94; N, 3.68.”

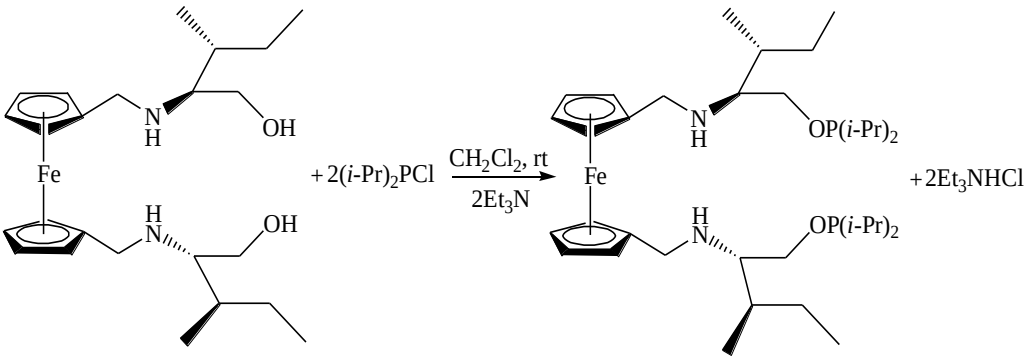
"4.3.3.(*S*)-bis[*N*-2-diphenylphosphinite-1-*sec*-butyl)ethyl]-1,1'-ferrocenylmethyldiamine, (5)" (Ak. B. et al. 2015)



(5)

Color: Yellow. Yield: 0.099 g, (81.2 %). $[\alpha]_D^{20}$ +66.2 (c 1.2, MeOH)]; ^{1}H "NMR ($CDCl_3$, ppm): δ 7.53 (m, 8H, *o*-$C_6\underline{\mathbf{H}}_5P$), 7.38-7.46 (m, 12H, *m*- and *p*-$C_6\underline{\mathbf{H}}_5P$), 4.02-4.18 (m, 8H, $C_5\mathbf{H}_4$), 3.92" (m, 4H, $C\underline{\mathbf{H}}_2OP$), 3.52 (br, 4H, $C\underline{\mathbf{H}}_2NH$), 2.81 (br, 2H, $C\underline{\mathbf{H}}N$), 1.68 (br, 2H, $C\underline{\mathbf{H}}CH_3$), "1.53 (m, 2H, $C\underline{\mathbf{H}}_2CH_3$ (a)), 1.24 (m, 2H, $C\underline{\mathbf{H}}_2CH_3$" (b)), 0.88-0.95 (m, 12H, $CHC\underline{\mathbf{H}}_3$, (a) and $CH_2C\underline{\mathbf{H}}_3$, (b)). ^{13}C NMR ($CDCl_3$, ppm): δ 142.00 (d, *J*=17.1 Hz, *i*-$\underline{\mathbf{C}}_6H_5PO$), 130.41 (d, $^2J_{P\text{-}C}$=21.5Hz, *o*-$\underline{\mathbf{C}}_6H_5PO$), 129.36 (s, *p*-$\underline{\mathbf{C}}_6H_5PO$), 128.39 (s, $^3J_{P\text{-}C}$ =5.1 Hz, *m*-$\underline{\mathbf{C}}_6H_5PO$), 87.06 (*i*-$\underline{\mathbf{C}}_5H_4$), 69.67, 69.49, 68.97, 68.88, 68.40 ($\underline{\mathbf{C}}H_2OP$, $\underline{\mathbf{C}}_5H_4$), 61.83 ($\underline{\mathbf{C}}HN$), 46.70 ($\underline{\mathbf{C}}H_2NH$), 35.79 ($\underline{\mathbf{C}}HCH_3$), 26.07 ($\underline{\mathbf{C}}H_2CH_3$), 14.82 ($CH\underline{\mathbf{C}}H_3$, (a), 12.14 ($CH_2\underline{\mathbf{C}}H_3$, (a). ^{31}P-{^{1}H} "NMR ($CDCl_3$, ppm): δ 115.66 (s, O$\underline{\mathbf{P}}Ph_2$). IR (KBr pellet in cm^{-1}) υ" (N-H): 3332, (C=C-Cp): 1437, (O-P): 1026, (C-H): 3069, 2960, 2926, 2873. Anal. Calcd. for $C_{48}H_{58}N_2O_2P_2Fe$ (812.79 g/mol): C, 70.92; H, 7.21; N, 3.45, found: C, 70.75; H, 7.06; N, 3.30 %.

4.3.4.(*S*)-bis[*N*-2-diisopropylphosphinite-1-*sec*-butyl)ethyl]-1,1'ferrocenylmethyl diamine, (6)



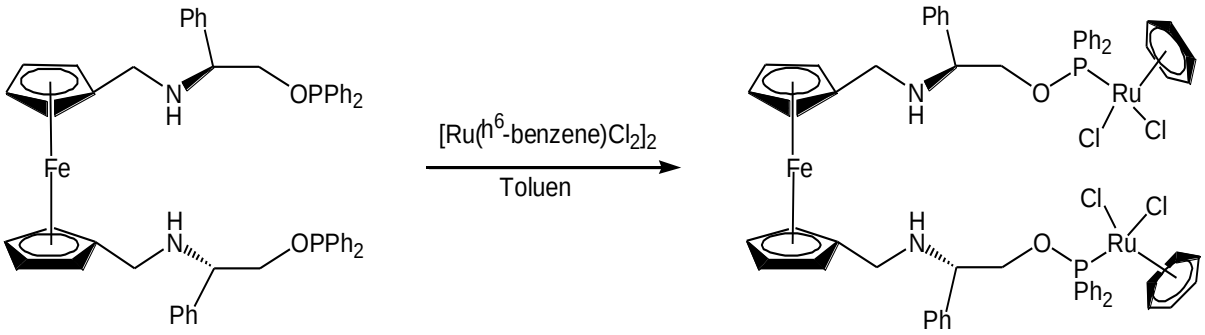
(6)

Color: Yellow. Yield: 0.085 g, (83.7 %). $[\alpha]_D^{20}$ +66.2 (c 1.2, MeOH)]; ^{1}H NMR ($CDCl_3$, ppm): δ 4.18 (s, 2H, $C_5\underline{\mathbf{H}}_4$), 4.15 (s, 2H, $C_5\underline{\mathbf{H}}_4$), 4.06-4.07 (m, 4H, $C_5\underline{\mathbf{H}}_4$), 3.67-3.75 (m, 4H, C$\underline{\mathbf{H}}_2$OP), 3.53 (br, 4H, C$\underline{\mathbf{H}}_2$N), 2.67 (br, 2H, C$\underline{\mathbf{H}}$N), 1.69-1.75 (m, 4H, PC$\underline{\mathbf{H}}(CH)_3$), 1.62 (br, 2H, C$\underline{\mathbf{H}}CH_3$), "1.48 (m, 2H, C$\underline{\mathbf{H}}_2CH_3$ (a)), 1.23 (m, 2H, C$\underline{\mathbf{H}}_2$CH$_3$ (b)), 1.01-1.13" (m, 24H, PCH(C$\underline{\mathbf{H}}$)$_3$), 0.88-0.93 (m, 6H, CHC$\underline{\mathbf{H}}_3$ and 6H, CH$_2$C$\underline{\mathbf{H}}_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 87.76 (*i*-$\underline{\mathbf{C}}_5$H$_4$), 71.82, 68.91, 68.67, 68.32, 67.66 ($\underline{\mathbf{C}}_5$H$_4$+$\underline{\mathbf{C}}$H$_2$OP), 62.30 (*J*= 8.1 Hz, $\underline{\mathbf{C}}$HN), 46.63 ($\underline{\mathbf{C}}$H$_2$NH), 35.36 ($\underline{\mathbf{C}}$HCH$_3$), 28.01 (dd, $^1J_{P\text{-}C}$= 12.8 Hz, $^1J_{P\text{-}C}$= = 16.6 Hz, P$\underline{\mathbf{C}}$H(CH$_3$)$_2$), 26.03 ($\underline{\mathbf{C}}$H$_2$CH$_3$), 18.09 (s, PCH($\underline{\mathbf{C}}$H$_3$)$_2$), 17.89 (s, PCH($\underline{\mathbf{C}}$H$_3$)$_2$), 17.14 (d, $^2J_{P\text{-}C}$=2.0 Hz, PCH($\underline{\mathbf{C}}$H$_3$)$_2$), 17.06 (d, $^2J_{P\text{-}C}$= 2.0 Hz, PCH($\underline{\mathbf{C}}$H$_3$)$_2$),14.61 (CH$\underline{\mathbf{C}}$H$_3$), 12.17 (CH$_2\underline{\mathbf{C}}$H$_3$). ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 152.51 (s, O$\underline{\mathbf{P}}$CH(CH$_3$)$_2$). "IR (KBr pellet in cm^{-1}) υ" (N-H): 3212, (P-CH(CH$_3$)$_2$): 1459, (O-P): 1039, (C-H): 2864. Anal.Calcd. for $C_{36}H_{66}N_2O_2P_2Fe$ (676.73 g/mol): "C, 63.90; H, 9.83; N, 4.14, found: C, 63.75; H, 9.66; N, 3.91."

4.4. Synthesis of the ferrocene based C_2-symmetric bis(phosphinites)-Ruthenium (II) complexes, 3a-6a.

At first, [Ru(η6-benzene)(μ-Cl)Cl]2 (0.15 mmol) and the phosphinite ligand (0.15 mmol) were dissolved in 30 mL of toluen under an argon atmosphere and stirred for 4 h at room temperature. The resulting red solution was concentrated to 2 ml under reduced pressure, and addition of petroleum ether (30 ml) caused the precipitation of a dark red solid. The supernatant solution was decanted, the solid was washed with hexane : diethylether (1:1) and dried by vacuum, yielding the corresponding Ruthenium complex.

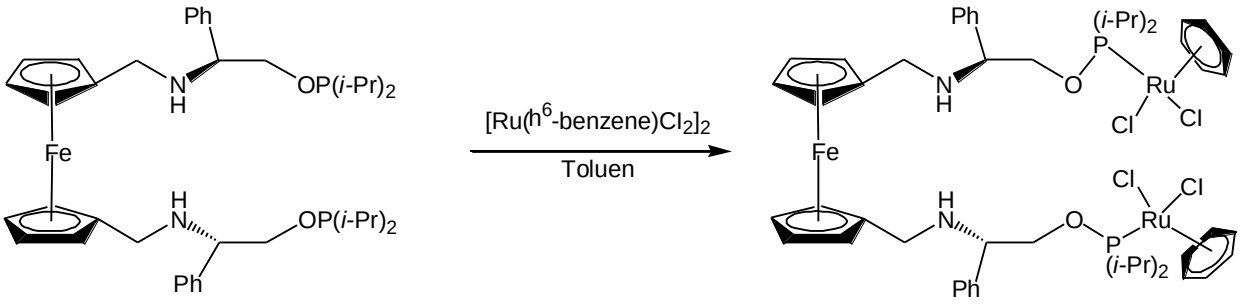
"4.4.1. (*S*)-bis[[*N*-2-diphenylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenyl methyldiamine bis(dichloro η^6-benzene ruthenium(II))], (3a)



(3a)

Yield: 0.018 g, 88.7 %, m.p. >240 ^{o}C. (dec.) $[\alpha]_D^{20}$ = +17^o "(c: 0.1, CH_2Cl_2)]; ^{1}H NMR ($CDCl_3$, ppm): δ 7.77-7.85" (m, 8 H, *o*-$C_6\underline{\mathbf{H}}_5PO$), 7.33-7.43 (m, 12H, *m*-, *p*-$C_6\underline{\mathbf{H}}_5PO$ and 10H, $C_6\underline{\mathbf{H}}_5$), 5.37 (s, 12H, Ru-$C_6\underline{\mathbf{H}}_6$), 3.97-4.21 (m, 8H, $C_5\underline{\mathbf{H}}_4$+2H, C**H**N and 4H, C$\underline{\mathbf{H}}_2$OP), 3.50 (br, 2H, C$\underline{\mathbf{H}}_2$NH (a)), 3.30 (d, 2H, *J*=12.1 Hz, C$\underline{\mathbf{H}}_2$NH (b)). ^{13}C NMR ($CDCl_3$, ppm): δ 142.69, 141.66 (*i*-$\underline{\mathbf{C}}_6H_5PO$ and *i*-$\underline{\mathbf{C}}_6H_5$), 132.82 (d, $^2J_{P\text{-}C}$ =14.1 Hz, *o*-$\underline{\mathbf{C}}_6H_5PO$), 131.76 (d, $^3J_{P\text{-}C}$ =11.1 Hz, *m*-$\underline{\mathbf{C}}_6H_5PO$), 131.18 (s, *p*-$\underline{\mathbf{C}}_6H_5PO$), 128.71, 128.29, 128.19 (*o*-, *p*-, *m*-$\mathbf{C}_6H_5$), 90.09 (d, $^2J_{P\text{-}C}$ =3.0 Hz, Ru-$\underline{\mathbf{C}}_6H_6$), (not observed *i*-$\underline{\mathbf{C}}_5H_4$), 77.26 ($\underline{\mathbf{C}}H_2OP$), 70.93, 69.43, 68.96, 68.60 ($\underline{\mathbf{C}}_5H_4$), 61.92 (d, *J* =9.1 Hz, $\underline{\mathbf{C}}HN$), 45.93 ($\underline{\mathbf{C}}H_2NH$). ^{31}P-{^{1}H} "NMR ($CDCl_3$, ppm): δ 111.77 (s, O$\underline{\mathbf{P}}Ph_2$). IR (KBr pellet in cm^{-1}): υ" (N-H): 3313, (CH): 3054, 3015, 2907, 2855, (C-C-Cp): 1426, (O-P): 1008; Anal. Calc. for [$C_{64}H_{62}N_2O_2P_2FeRu_2Cl_4$] (1352.95 g/mol): C 56.82, N 2.07, H 4.62; found: C 56.69, N 1.99, H 4.45 %.

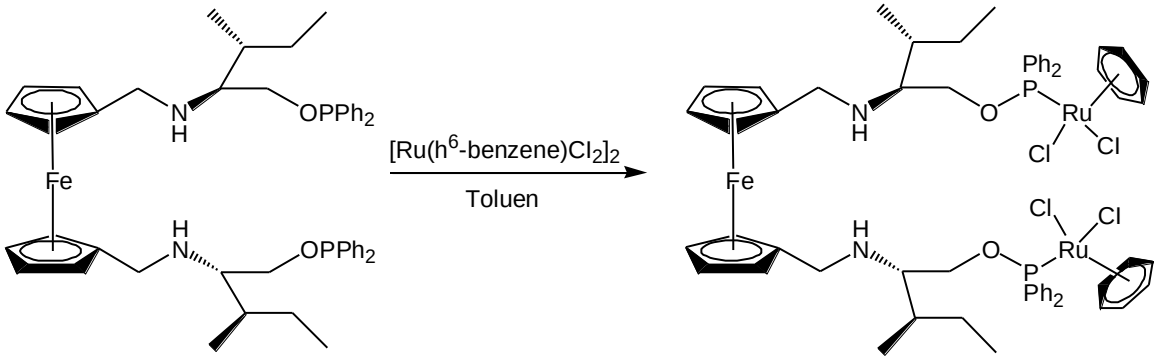
"4.4.2. (*S*)-bis[[*N*-2-diisopropylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenyl methyldiamine bis(dichloro η^6-benzene ruthenium(II))], (4a)



(4a)

Yield: 0.159 g, 87.1 %, m.p: 150-152 ^{o}C. $[\alpha]_D^{20}$ = +4^{o} "(c:0.1, CH_2Cl_2)]; ^{1}H NMR ($CDCl_3$, ppm): δ 7.28-7.43" (m, 10 H, $C_6\underline{\mathbf{H}}_5$), 5.62 (s, 12H, Ru-$C_6\underline{\mathbf{H}}_6$), 3.93-4.17 (m, 8H, $C_5\underline{\mathbf{H}}_4$+2H, C**H**N and 4H, C$\underline{\mathbf{H}}_2$OP), 3.53 (br, 2H, C$\underline{\mathbf{H}}_2$NH (a)), 3.35 (br, 2H, C$\underline{\mathbf{H}}_2$NH (b)), "2.84 (m, 4H, PC**H**$(CH_3)_2$), 1.24-1.28 (m, 24H, PCH(C$\underline{\mathbf{H}}_3)_2$). ^{13}C NMR" ($CDCl_3$, ppm): δ 142.47 (*i*-$\underline{\mathbf{C}}_6H_5$), 128.75, 128.19, 127.55 (*o*-, *p*-, *m*-$\mathbf{C}_6H_5$), 88.61 (br, Ru-$\underline{\mathbf{C}}_6H_6$), 87.21 (*i*-$\underline{\mathbf{C}}_5H_4$), 74.01 ($\underline{\mathbf{C}}H_2OP$), 69.31, 69.15, 68.92, 68.61 ($\underline{\mathbf{C}}_5H_4$), 62.12 (d, *J* =7.0 Hz, $\underline{\mathbf{C}}$HN), 46.01 ($\underline{\mathbf{C}}H_2NH$), 31.59-31.02 (m, P$\underline{\mathbf{C}}H(CH_3)_2$, 18.23 (d, $^2J_{P\text{-}C}$ =8.1 Hz, PCH($\underline{\mathbf{C}}H_3)_2$). ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 150.54 (s, O$\underline{\mathbf{P}}CH(CH_3)_2$). "IR (KBr pellet in cm^{-1}): υ" (N-H): 3313, (CH): 3054, 3015, 2907, 2855, (C-C-Cp): 1426, (O-P): 1008; Anal. Calc. for [$C_{52}H_{70}N_2O_2P_2FeRu_2Cl_4$] (1216.88 g/mol): C 51.33, N 2.30, H 5.80; found: C 51.12, N 2.11, H 5.52 %.

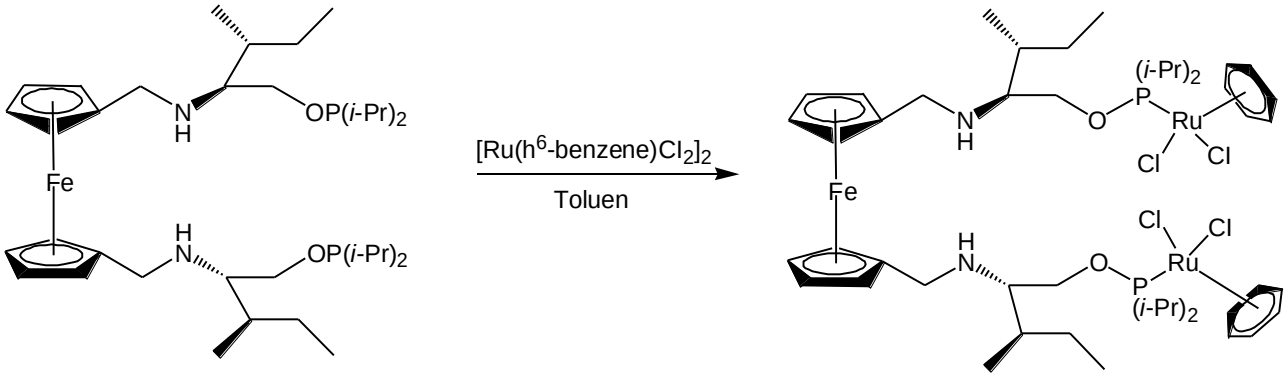
"4.4.3. (*S*)-bis[[*N*-2-diphenylphosphinite-1-*sec*-butyl)ethyl]-1,1'-ferrocenyl methyldiamine bis(dichloro η^6-benzene ruthenium(II))], (5a)



(5a)

Yield: 0.175 g, 88.8 %, m.p. 210^{o}C (dec. $[\alpha]_D^{20}$ = +3^o "(c: 0.1, CH_2Cl_2)]; ^{1}H NMR ($CDCl_3$, ppm): δ 7.78-7.92" (m, 8H, *o*-$C_6\underline{\mathbf{H}}_5P$), 7.47 (br, 12H, *m*-, *p*- $C_6\underline{\mathbf{H}}_5P$), 5.53 (s, 12H, Ru-$C_6\underline{\mathbf{H}}_6$), 3.90-4.33 (m, 8H, $C_5\mathbf{H}_4$,+ 4H, $C\underline{\mathbf{H}}_2OP$ and 4H, $C\underline{\mathbf{H}}_2NH$), 2.79 (br, 2H, $C\underline{\mathbf{H}}N$), 1.65 (br, 2H, $C\underline{\mathbf{H}}CH_3$), 0.68-1.26 (m, 4H, $C\underline{\mathbf{H}}_2CH_3$ +6H, $CHC\underline{\mathbf{H}}_3$ and 6H, $CH_2C\underline{\mathbf{H}}_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 135.33 (br, *i*-$\underline{\mathbf{C}}_6H_5PO$), 132.54 (d, $^2J_{P\text{-}C}$ =25.2 Hz, *o*-$\underline{\mathbf{C}}_6H_5PO$), 131.43 (d, $^3J_{P\text{-}C}$ =14.2 Hz, *m*-$\underline{\mathbf{C}}_6H_5PO$), 128.34 (s, *p*-$\underline{\mathbf{C}}_6H_5PO$), 90.34 (Ru-$\underline{\mathbf{C}}_6H_6$), 87.10 (*i*-$\underline{\mathbf{C}}_5H_4$), 70.49, 69.82, 69.67, 69.55, 69.04 ($\underline{\mathbf{C}}_5H_4$+$\underline{\mathbf{C}}H_2OP$), 60.21 (br, $\underline{\mathbf{C}}HN$), 46.45 ($\underline{\mathbf{C}}H_2NH$), 33.71 ($\underline{\mathbf{C}}HCH_3$), 25.97 ($\underline{\mathbf{C}}H_2CH_3$), 14.81 ($CH\underline{\mathbf{C}}H_3$), 11.59, 11.45 ($CH_2\underline{\mathbf{C}}H_3$). ^{31}P-{^{1}H} "NMR ($CDCl_3$, ppm):δ 114.28 (s, O$\underline{\mathbf{P}}Ph_2$). IR (KBr pellet in cm^{-1}): υ" (N-H): 3215, (CH): 3073, 3053, 2960, 2823, (PPh): 1436, "(O-P): 1024; Anal. Calc. for" $[C_{60}H_{70}N_2O_2P_2FeRu_2Cl_4]$ (1312.97 g/mol): C 54.89, N 2.13, "H 5.37; found: C 54.61, N 1.97, H 5.19 %."

"4.4.4.(*S*)-bis[[*N*-2-diisopropylphosphinite-1-*sec*-butyl)ethyl]-1,1'-ferrocenylmethyl diamine bis(dichloro η^6-benzene ruthenium(II))], (6a)



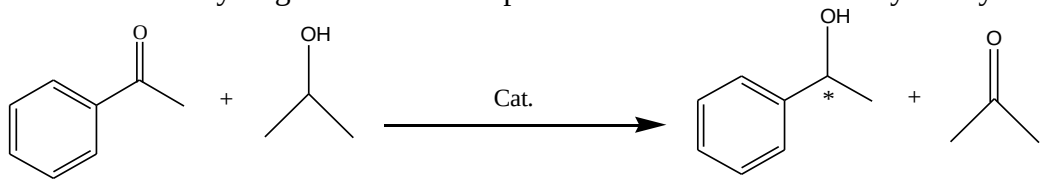
(6a)

Yield: 0.148 g, 83.9 %, m.p: 157-158 ^{o}C. $[\alpha]_D^{20}$ = +14^{o} (c: 0.1, CH_2Cl_2)]; ^{1}H NMR ($CDCl_3$, ppm): δ 5.79 (s, 12H, Ru-$C_6\underline{\mathbf{H}}_6$), "4.28 (s, 4H, $C_5\mathbf{H}_4$) 4.12 (br, 4H, $C_5\mathbf{H}_4$+2H, $C\underline{\mathbf{H}}_2OP$ (a)), 3.80" (br, 2H, $C\underline{\mathbf{H}}_2OP$ (b)+ 4H, $C\underline{\mathbf{H}}_2NH$), 2.91 (br, 2H, $C\underline{\mathbf{H}}N$ and 4H, $PC\underline{\mathbf{H}}(CH_3)_2$), 1.69 (br, 2H, $C\underline{\mathbf{H}}CH_3$), 1.17-1.38 (m, 4H, $C\underline{\mathbf{H}}_2CH_3$+24H, $PCH(C\underline{\mathbf{H}}_3)_2$), 0.90 (m, 6H, $CHC\underline{\mathbf{H}}_3$ and 6H, $CH_2C\underline{\mathbf{H}}_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 88.80 (Ru-$\underline{\mathbf{C}}_6H_6$), 86.87 (*i*-$\underline{\mathbf{C}}_5H_4$), 70.16, 69.31, 69.20, 67.96, 67.23 ($\underline{\mathbf{C}}H_2OP$**,** $\underline{\mathbf{C}}_5H_4$), 60.63 ($\underline{\mathbf{C}}HN$), 46.80 ($\underline{\mathbf{C}}H_2NH$), 35.14 ($\underline{\mathbf{C}}HCH_3$), 32.00 (br, $P\underline{\mathbf{C}}H(CH_3)_2$), 31.56 (s, $P\underline{\mathbf{C}}H(CH_3)_2$), 26.10 ($\underline{\mathbf{C}}H_2CH_3$), 18.42 (s, $PCH(\underline{\mathbf{C}}H_3)_2$), 14.76 ($CH\underline{\mathbf{C}}H_3$), 12.04 ($CH_2\underline{\mathbf{C}}H_3$). ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): 152.58 (s, $O\underline{\mathbf{P}}CH(CH_3)_2$). "IR (KBr pellet in cm^{-1}): υ" (N-H): 3292, (CH): 2961, 2925, (P-$CH(CH_3)_2$): 1441, (O-P): 1054; Anal. Calc. for [$C_{48}H_{78}N_2O_2P_2FeRu_2Cl_4$] (1176.90 g/mol): C 48.99, "N 2.38, H 6.68; found: C 48.78, N 2.16, H" 6.43 %.

4.5. Catalytic Studies

Within the scope of this thesis, "catalytic activities of" ruthenium complexes **3a**-**6a** in asymmetric transfer hydrogenation reactions of acetophenone and its derivatives were investigated and the results are shown in Tables 1 and 2.

"Table 1. Transfer hydrogenation of acetophenone with *iso-P*rOH catalyzed by **3a-6a"**

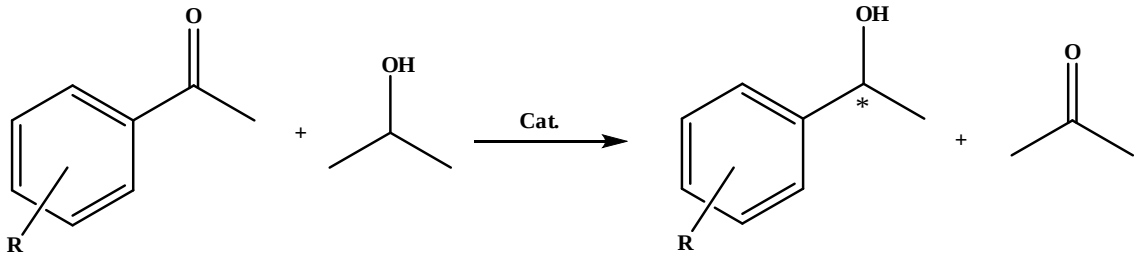


"Entry	Catalyst	S/C/KOH	Time"	Conversion(%)[e]	%*ee*[f]	Configuration	TOF(h^{-1}) [g]
1	**3a**[a]	"100:1:5"	24 h	"trace"	---		---
2	**4a**[a]	"100:1:5"	24 h	"trace"	---		---
3	**5a**[a]	"100:1:5"	24 h	"trace"	---		---
4	**6a**[a]	"100:1:5"	24 h	"trace"	---		---
5	**3a**[b]	"100:1"	5 h	<5	---		---
6	**4a**[b]	"100:1"	5 h	<5	---		---
7	**5a**[b]	"100:1"	5 h	<5	---		---
8	**6a**[b]	"100:1"	5 h	<5	---		---
9	**3a**[c]	100:1:5	45 min	97(95)	56(54)	S	129(127)
10	**4a**[c]	100:1:5	90 min	98(97)	35(35)	S	65(65)
11	**5a**[c]	100:1:5	45 min	98(95)	52(50)	S	131(127)
12	**6a**[c]	100:1:5	90 min	96(93)	35(33)	S	64(62)
13	**3a**[d]	500:1:5	120 min	93	41	S	233
14	**4a**[d]	500:1:5	210 min	91	22	S	130
15	**5a**[d]	500:1:5	120 min	94	39	S	235
16	**6a**[d]	500:1:5	210 min	90	23	S	129

Reaction conditions:

[a] At room temperature; acetophenone/Cat./KOH, 100:1:5, [b] Refluxing in *iso*-PrOH; acetophenone/Cat, 100:1, in the absence of base, [c] Refluxing in *iso*-PrOH;acetophenone/Cat/KOH, 100:1:5, in parenthesis; acetophenone/Cat/NaOH, 100:1:5, [d] Refluxing in *iso*-PrOH;acetophenone/Cat/KOH, [e] Determined by GC (three independent catalytic experiments), [f] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values. [g] TOF = (mol product/mol Cat.) × h^{-1}.

"Table 2. Transfer hydrogenation results for substituted acetophenones by" **3a-6a**. [a]



Entry	R	Time	Conversion(%)[b]	*ee*[c]	TOF(h^{-1})[d]
			***Cat:*3a**		
1	4-F	1/4 h	98	55	392
2	4-Cl	1/2 h	99	53	198
3	4-Br	3/4 h	96	52	128
4	2-MeO	2 h	99	66	50
5	4-MeO	3 h	99	48	33
			***Cat:*4a**		
6	4-F	1/2 h	99	36	198
7	4-Cl	1 h	98	32	98
8	4-Br	3/2 h	97	30	65
9	2-MeO	3 h	99	48	33
10	4-MeO	4 h	99	28	25
			***Cat:*5a**		
11	4-F	1/4 h	98	53	392
12	4-Cl	1/2 h	96	50	192
13	4-Br	3/4 h	95	47	127
14	2-MeO	2 h	98	67	49
15	4-MeO	3 h	95	50	32
			***Cat:*6a**		
16	4-F	1/2 h	99	38	198
17	4-Cl	1 h	97	37	97
18	4-Br	3/2 h	98	34	65
19	2-MeO	3 h	99	50	33
20	4-MeO	4 h	96	33	24

Reaction conditions:

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), KOH (0.025 mmol %), 82 °C, respectively, the concentration of acetophenone derivatives is 0.1 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone; [c] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values. [d] TOF = (mol product/mol Cat.) × h^{-1}

"5. RESULTS and DISCUSSION"

"5.1. Synthesis of Ferrocene Based C_2-symmetric bis(phosphinite) Ligands, (3-6)"

In this study, initially, "(*S*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,1'-ferrocenyl methyldiamine, **(1)** and (*S*)-bis[*N*-(2-hydroxy-1-*sec*-butyl)ethyl]-1,1'-ferrocenylmethyl diamine, **(2)"** were synthesized according to the modified literature procedures as precursors for bis(phosphinite) ligands (Ak. et al. 2015). Then, ferrocene based C_2-symmetric bis(phosphinite) ligands, **3-6** were prepared by the reaction of these diols with one equivalents of Ph_2PCl or $(i\text{-}Pr)_2PCl$ in the presence of a base (Et_3N) in anhydrous toluene under argon atmosphere (Figure 14). In the $^{31}P–\{^1H\}$ NMR spectra of compounds, disappearance of the signal for the starting material PPh_2Cl at δ 81.0 ppm or $(i\text{-}Pr)_2PCl$ at δ 133.8 ppm and appearance of new singlets at δ 116.76 (s, O**P**Ph_2), 154.69 (s, O**P**$CH(CH_3)_2$), 115.66 ppm (s, O**P**Ph_2), 152.51 (s, O**P**$CH(CH_3)_2$), for ligands, **3-6**, respectively, due to the ferrocene based bis(phosphinite) ligands clearly demonstrated formation of the ligands as for similar compounds (see spectra section) [Durap et al. 2013, Ak. 2015, Elma et al. 2013, Aydemir et al. 2005]. Furthermore, ^1H- NMR, ^{13}C-NMR, FT-IR spectra and C, H, N elemental analysis results are in accord with the expected structures for ferrocene based C_2-symmetric bis(phosphinite) ligands.

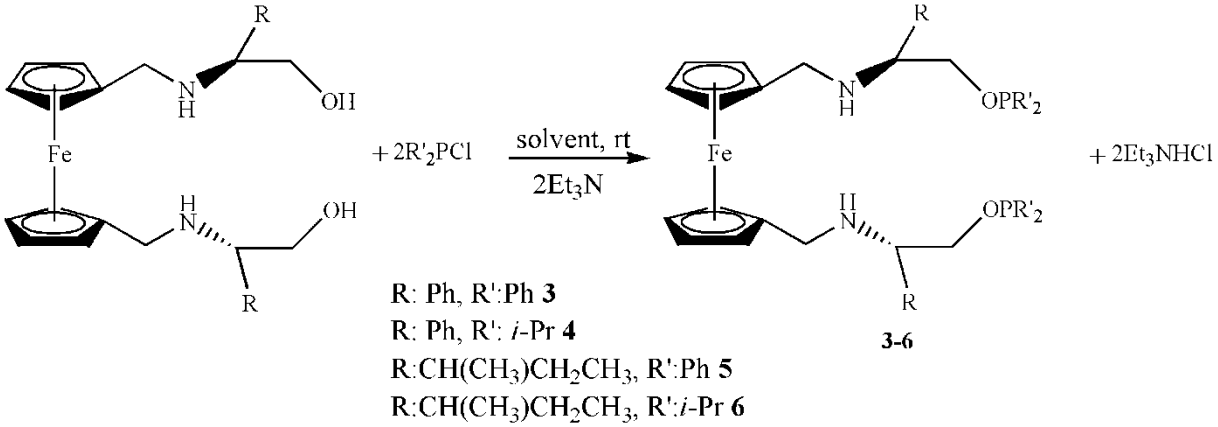


Figure 14. Ferrocene based C_2-symmetric bis(phosphinite) ligands, **3-6**.

5.2. Synthesis of the ferrocene based C_2-symmetric bis(phosphinites)-Ruthenium(II) complexes, 3a-6a.

C_2-symmetric bis(phosphinite) ligands **3-6** were reacted with $[Ru(\eta^6\text{-benzene})Cl_2]_2$ dimers in 1:1 molar ratio at room temperature under inert atmosphere to obtain the corresponding ruthenium(II) complexes, **3a**-6a (Figure 18.). They were obtained as shown by singlet resonances in the $^{31}P\text{-}\{H\}$ NMR spectra at δ 111.77 ppm (s, O**P**Ph_2), 150.54 ppm (s, O**P**$CH(CH_3)_2$), 114.28 (s, O**P**Ph_2) and 152.58 (s, O**P**$CH(CH_3)_2$) ppm for **3a**-**6a,** respectively. In ^1H NMR spectra of **3a**-**6a**, resonances at ca 5-5.5 ppm were assigned to aromatic protons of benzene moiety. Moreover, in ^{13}C NMR spectra of **3a**-**6a**, resonances at ca. 90 ppm were assigned to aromatic carbons of benzene moiety. Furthermore, the ^1H, $^{13}C\text{-}\{^1H\}$ NMR, FT-IR spectroscopic data and the elemental analysis data of the bis(phosphinites)-ruthenium(II) complexes **3a**-**6a** were in agree with the expected compounds.

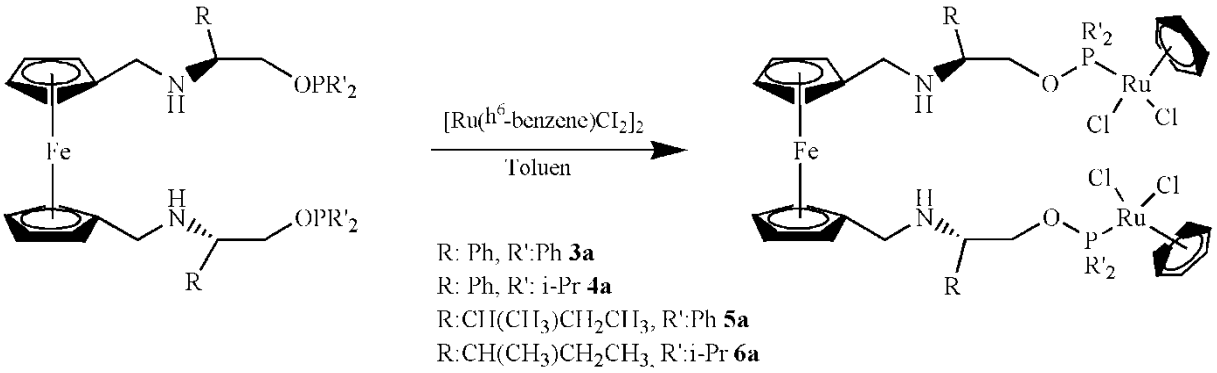


Figure 15. Ferrocene based C_2-symmetric bis(phosphinites)- Ruthenium(II)benzene complexes, **3a-6a**.

"5.3. C_2-symmetric bis(phosphinites)-Ruthenium(II) complexes as catalyst in asymmetric transfer hydrogenation"

In this step, bis(phosphinites)-ruthenium(II) complexes **3a-6a** was tested as catalysts in the transfer hydrogenation of the ketones to evaluate the catalytic effectiveness. We prefer starting with the reduction of acetophenone to corresponding chiral alcohol by *iso*-PrOH/KOH as a reducing system as a standard test reaction. As expected, they promoted the reduction of acetophenone to corresponding alcohol ((*R*), *(S)*-1-phenylethanol). For screening the activity and enantioselectivity for the reaction, the optimal conditions (reaction temperature and molar ratio of substrate to catalyst, base) were investigated.

At room temperature, transfer hydrogenation of acetophenone occurred considerably sluggishly and its conversion was too low (~ 10 % after 24h, Table 1, Entries 1-4) in all the reactions. However, the reaction rate is markedly increased on increasing the reaction temperature from 25 to 82°C and reaction yield became high enough. The range of conversions was between 96 to 98 % after 45-90 min for **3a-6a**. Furthermore, as can be seen inferred from Table 1 (Entry 9-12), the presence of a base is necessary to observe appreciable conversions. The selection of base, such as KOH and NaOH, had little effect on the conversion and enantioselectivity. Although the conversions gradually decreased on increasing the mole ratios of [acetophenone][Ru] from 100/1 to 500/1, except the time lengthened, the enantioselectivities were still moderate (Table 1, Entry 13-16). Among ruthenium(II) complexes, **3a** and **5a** exhibited very high catalytic activity (up to 56% *ee*).

Following investigation of the optimal conditions, we next extended our researchs to involve asymmetric hydrogenation of substituted acetophenone derivatives. The results clearly indicate that all the substituted acetophenones are transformed into the corresponding secondary alcohols in high yields. Complex **3a** showed considerable high activity for the most of the ketones. The results also show that the electronic properties of the substituent on the phenyl ring of the acetophenone change the reduction rate but have only little effect on the enantioselectivity. As expected, we found that the introduction of electron withdrawing substituents (F, Cl and Br) to the *p*- position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was enhanced leading to easier hydrogenation. An electron-withdrawing group such as fluoro group to the *p*-position was useful to achieve excellent conversion and enantioselectivity (up to 59% ee, Table 2), while the introduction of an electron-donating substituent such as methoxy group to the *p*-position caused to lower enantioselectivity while sustaining good activity. The introduction of an electron-donating group such as methoxy group to the *p*-position slows down the reaction, but that to the *o*-position increases the rate and improves the enantioselectivity (Table 2). The best result was acquired in the reduction of *o*-methoxyacetophenone among all selected ketones affording 66% ee (Table 2, Entry 4).

5. RESULTS and DISCUSSION

6. CONCLUSIONS

In conclusion, four ferrocene based C_2-symmetric isopropyl or phenyl moiety bearing bis(phosphinite) ligands **3-6** and their corresponding Ru(II)-benzene complexes **3a-6a** were successfully synthesized and characterized. Ferrocen based C_2-symmetric bis(phosphinite)-Ru(II)-benzene complexes were used in Asymmetric "Transfer Hydrogenation of acetophenone derivatives using 2-propanol in the presence of KOH. Results of the catalytic reactions, high conversion and moderate to good enantioselectivity were gained."

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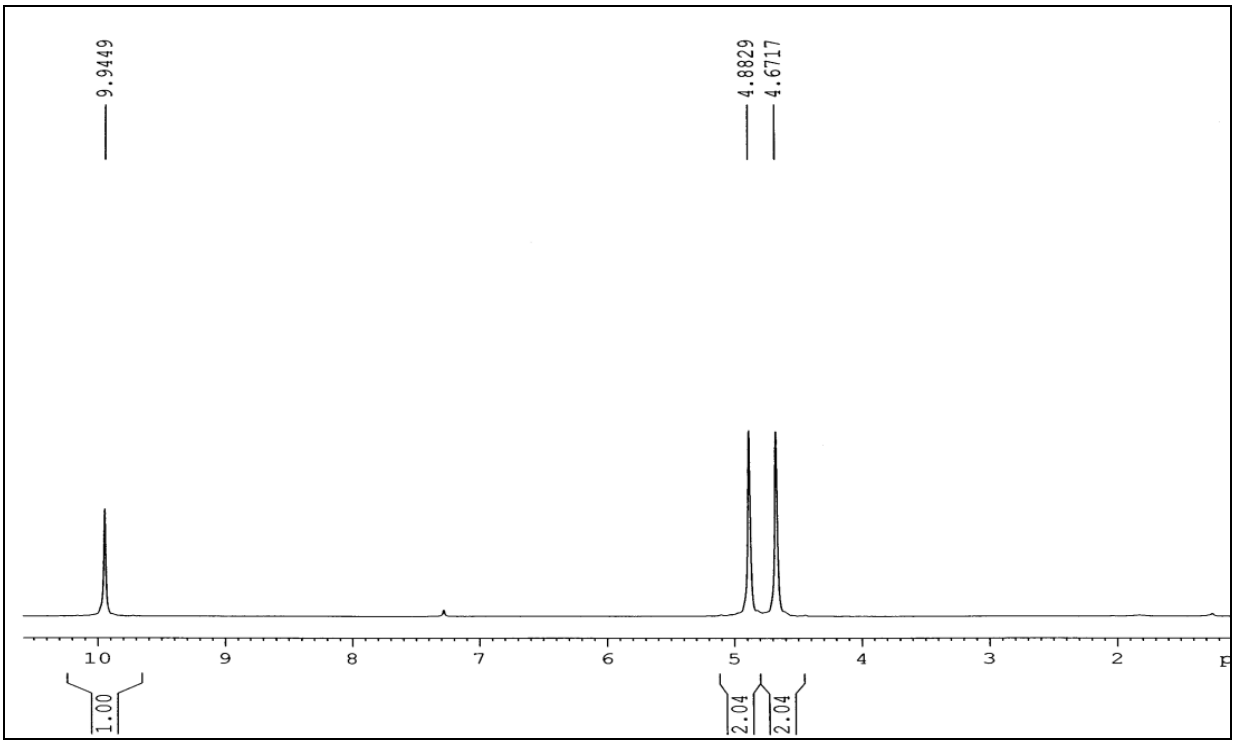
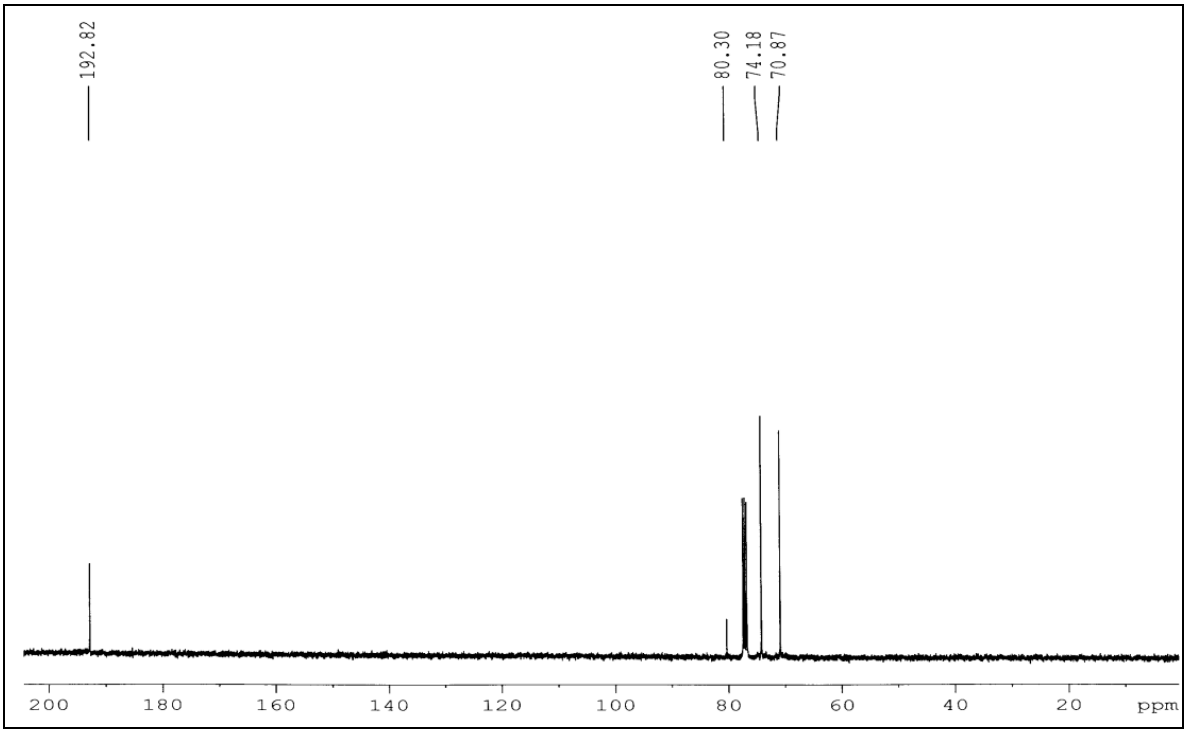
SPECTRA

1. 1,1'-ferrocenedicarboxyaldehyde



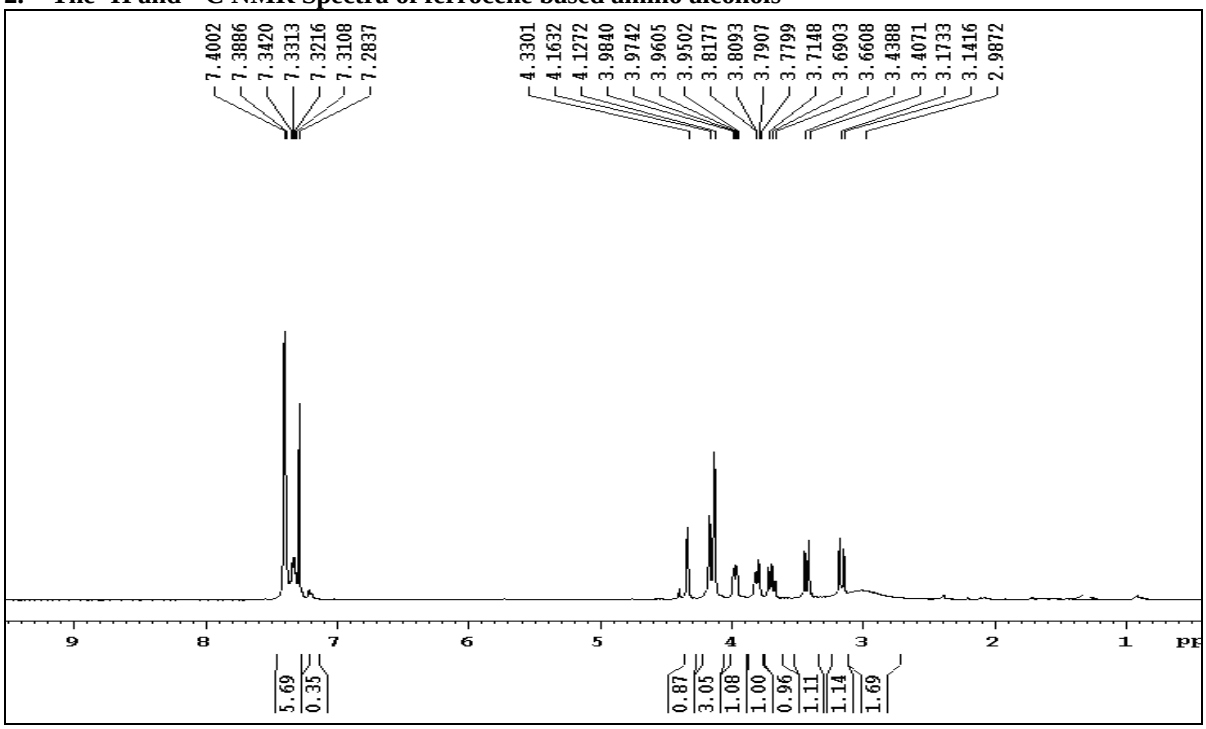
Spectrum 1. ^{1}H NMR Spectrum of 1,1'-ferrocenedicarboxyaldehyde.



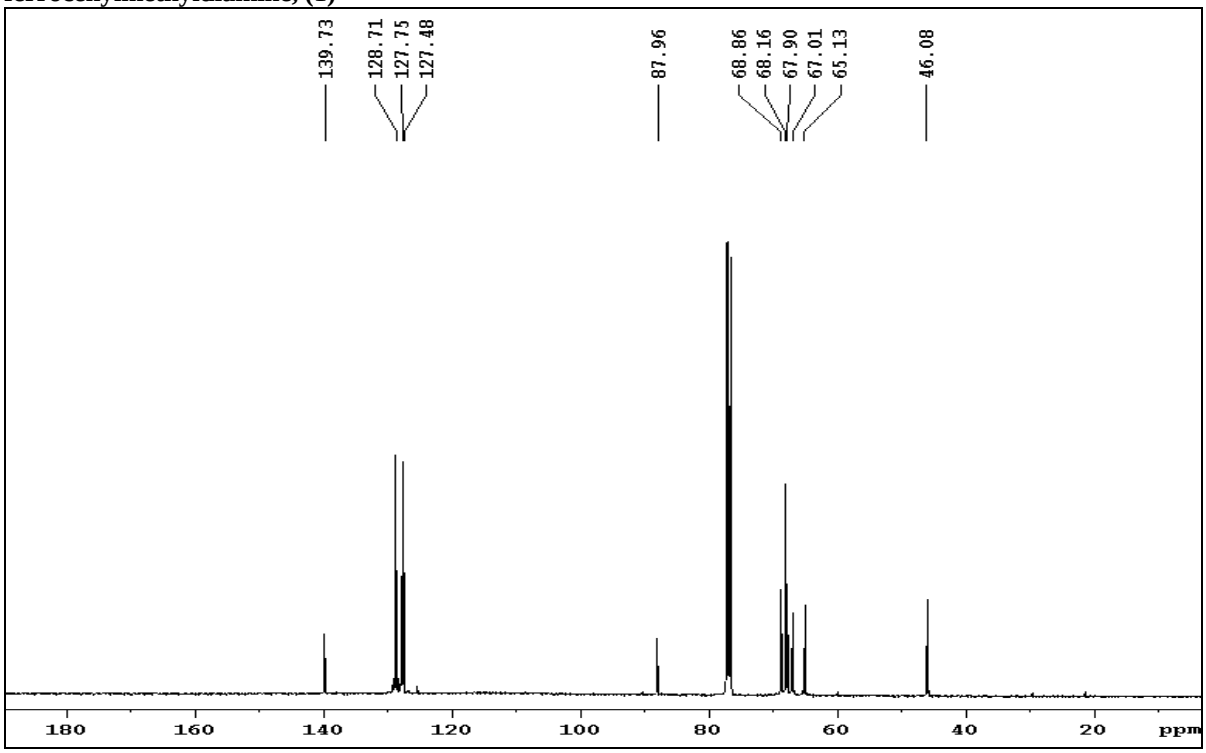
Spectrum 2. ^{13}C NMR Spectrum of 1,1'-ferrocenedicarboxyaldehyde.

SPECTRA

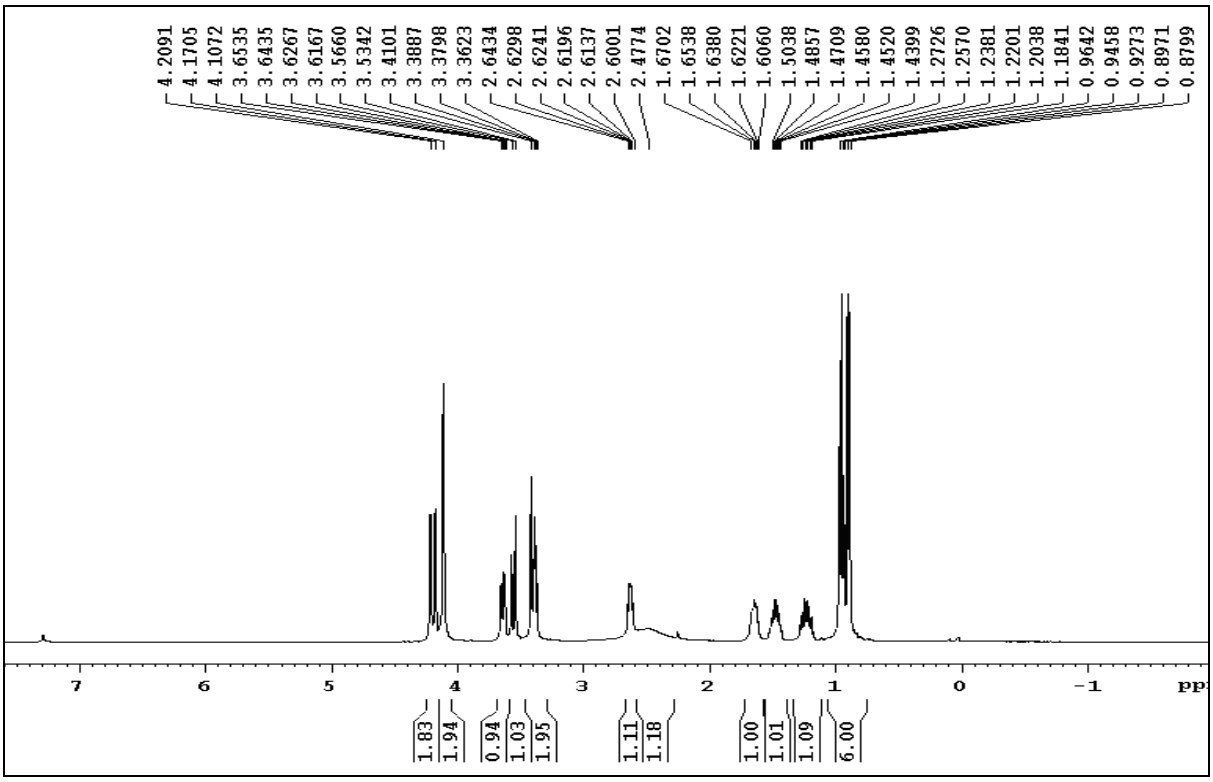
2. The ^{1}H and ^{13}C NMR Spectra of ferrocene based amino alcohols



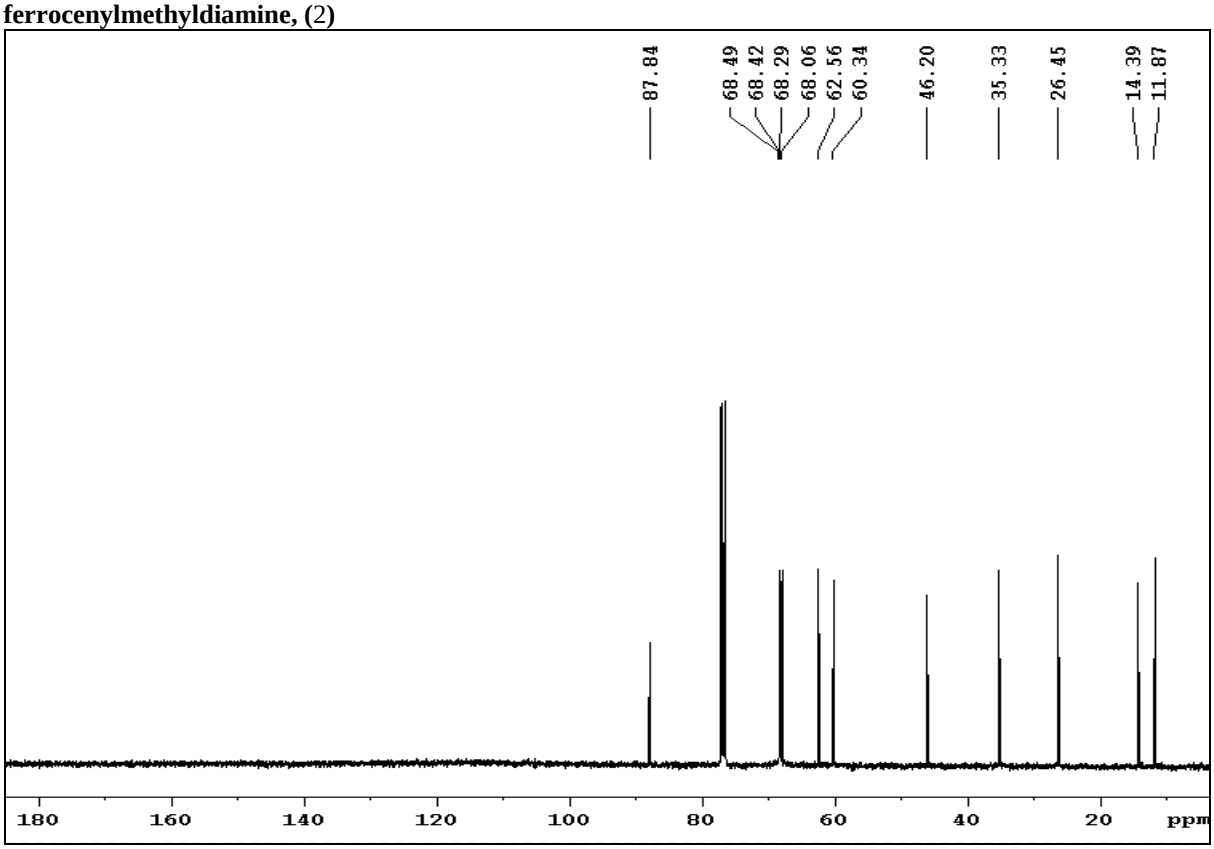
Spectrum 3. ^{1}H NMR Spectrum of (S)-bis[N-(2-hydroxy-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiamine, (1)



Spectrum 4. ^{13}C NMR Spectrum ofS)-bis[N-(2-hydroxy-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiamine, (1)

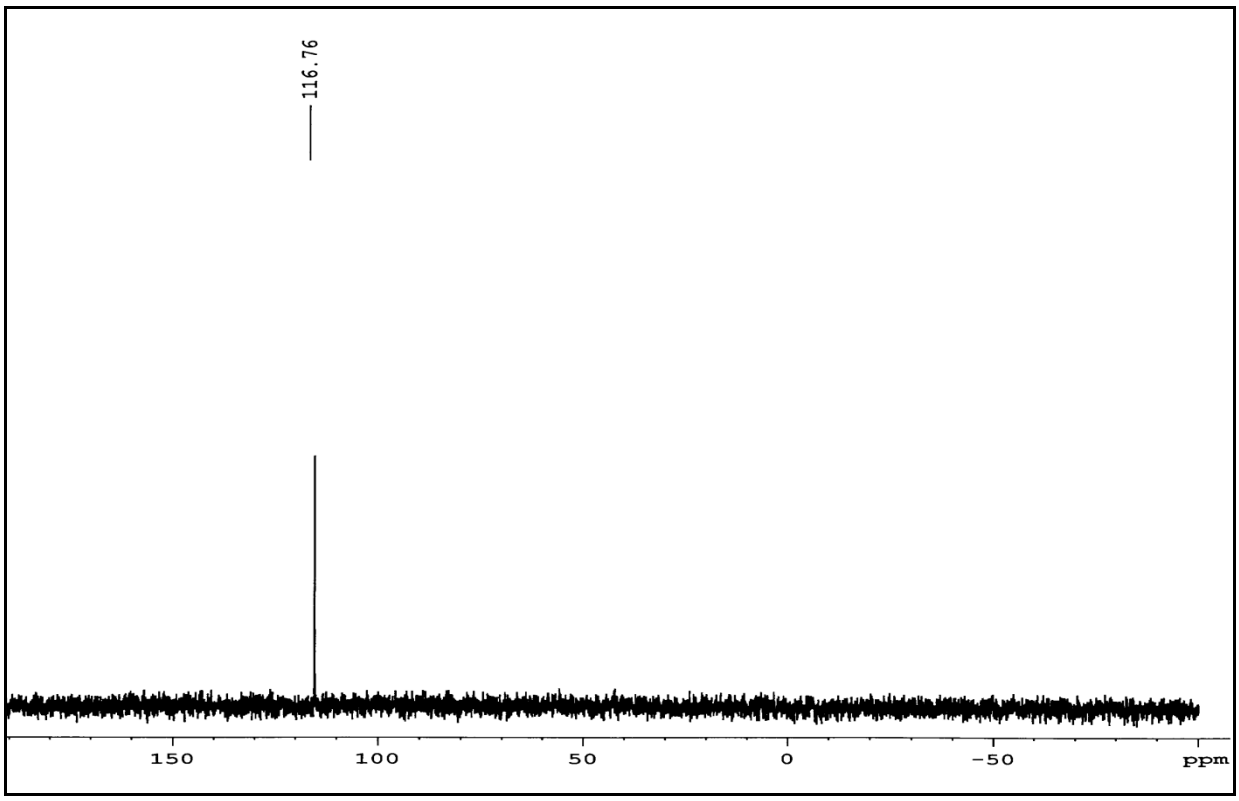


Spectrum 5. ^{1}H NMR Spectrum of (S)-bis[N-(2-hydroxy-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine, (2)

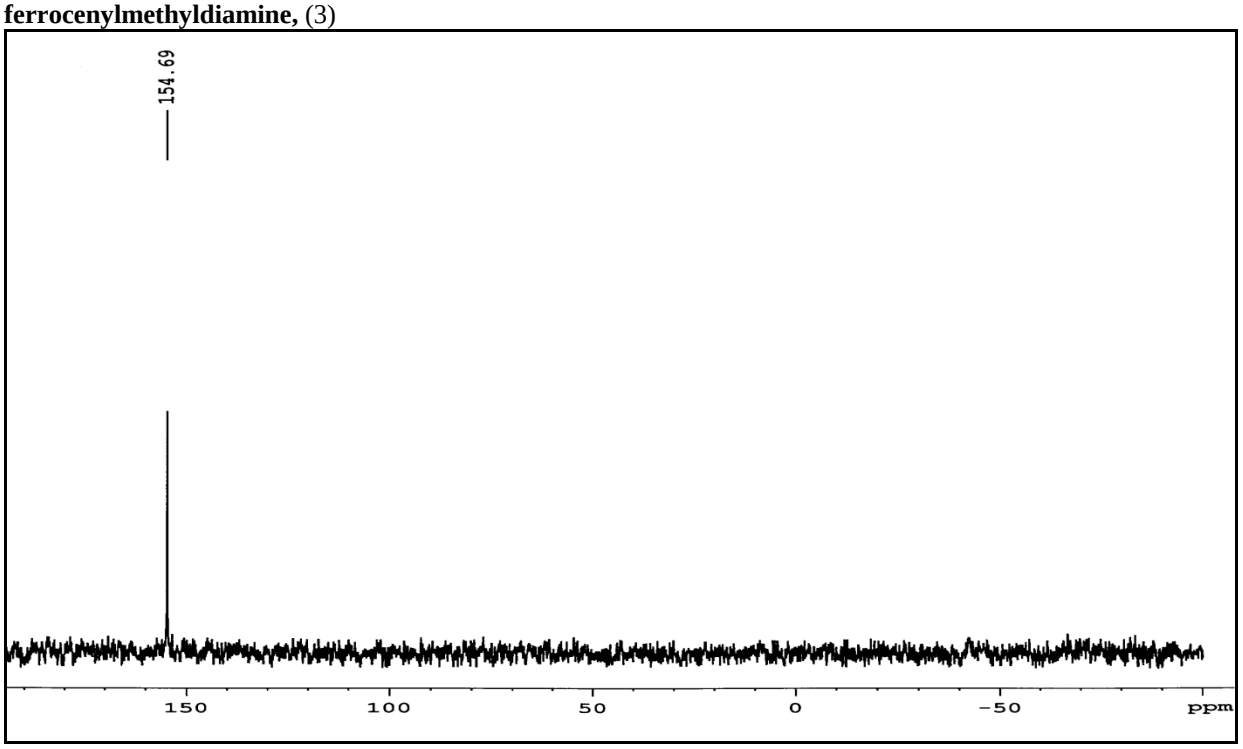


Spectrum 6. ^{13}C NMR Spectrum of (S)-bis[N-(2-hydroxy-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine, (2)

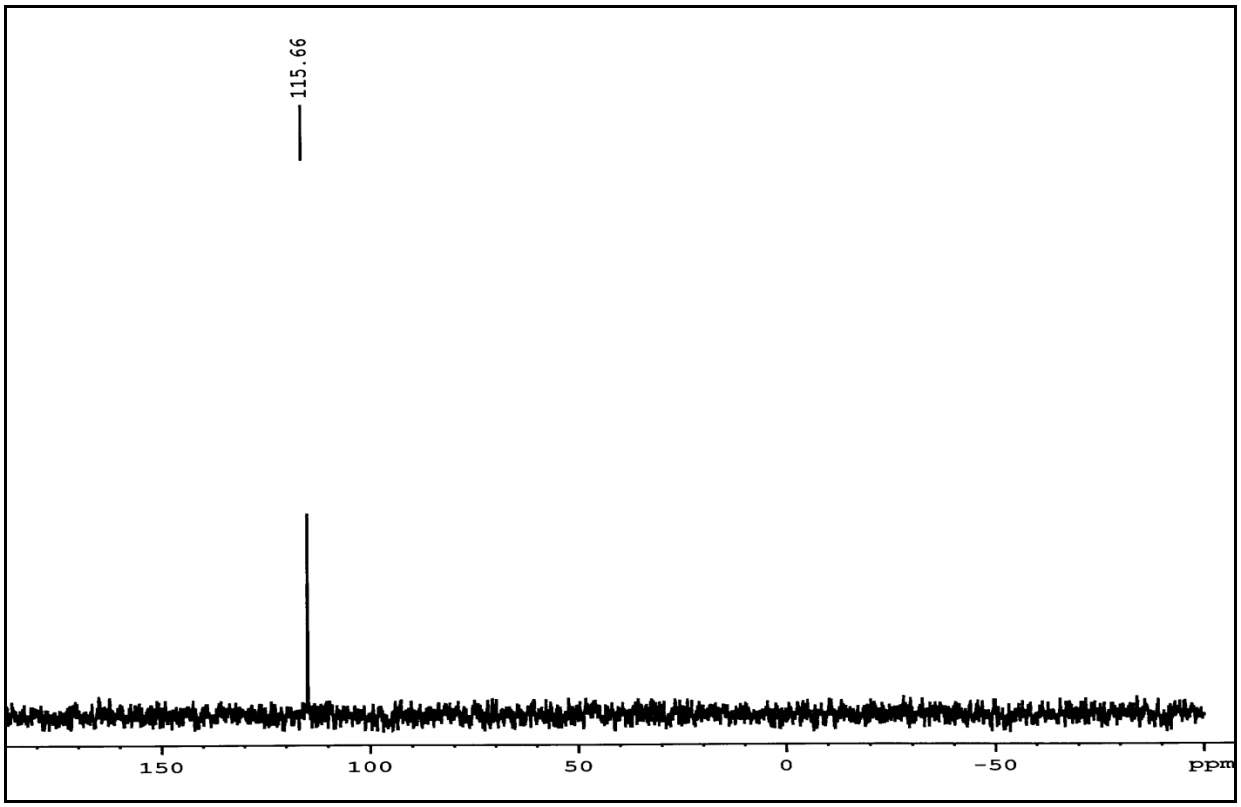
3. The ^{31}P-{^{1}H} NMR Spectra of ferrocene based C_2-symmetric phosphinite ligands



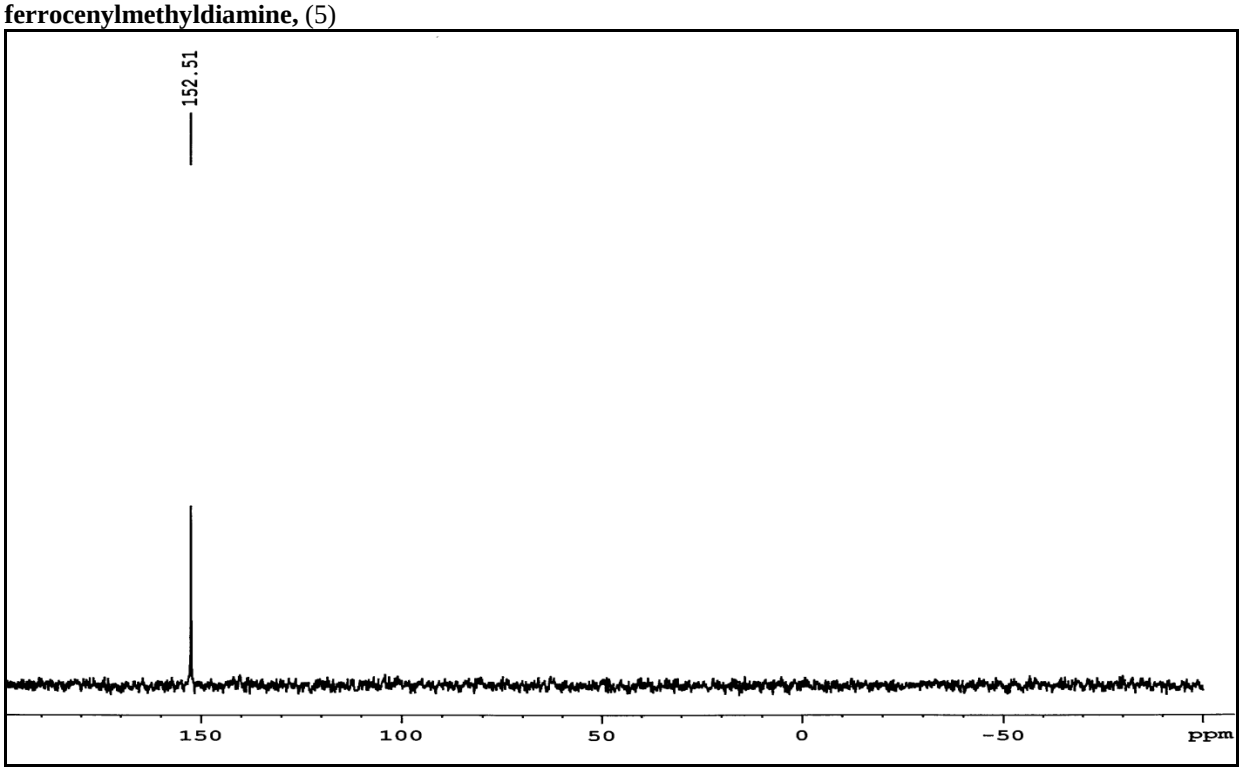
Spectrum 7. ^{31}P-{^{1}H} NMR Spectrum of (S)-bis[N-2-diphenylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiamine, (3)



Spectrum 8. ^{31}P-{^{1}H} NMR Spectrum of (S)-bis[N-2-diisopropylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiamine, **(4)**



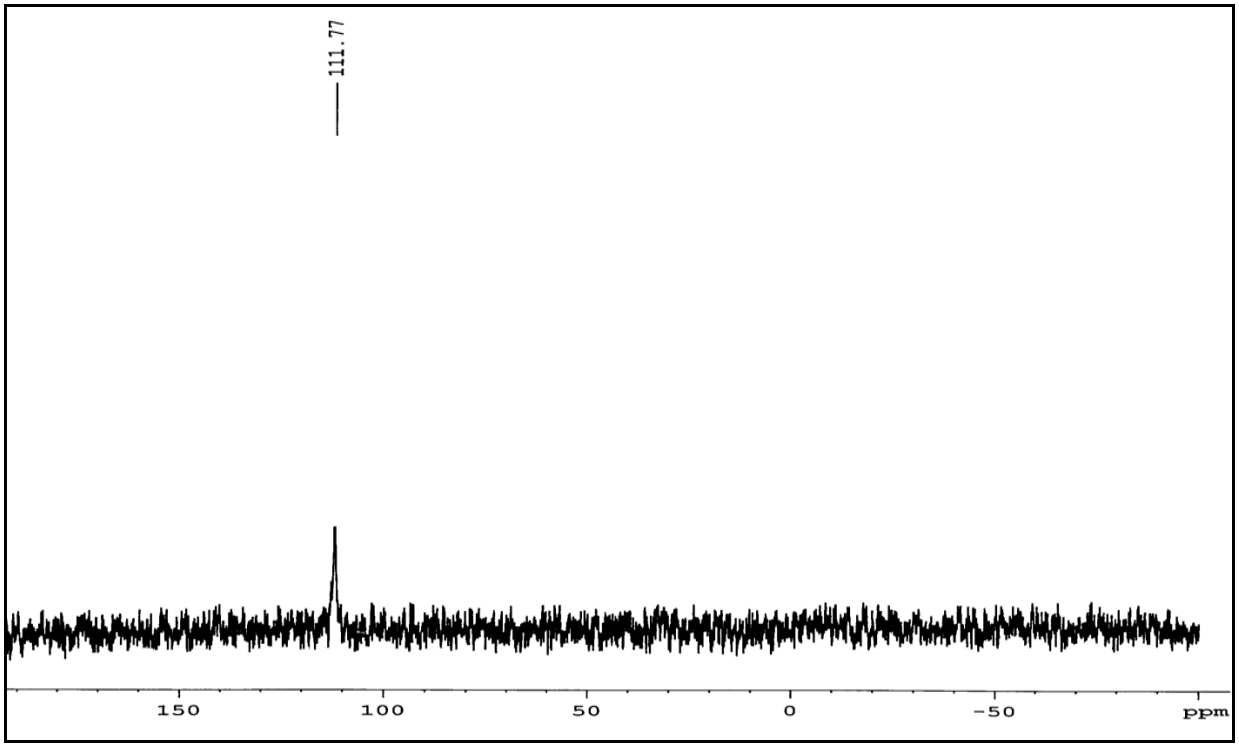
Spectrum 9. ^{31}**P-{**^{1}**H} NMR Spectrum of (S)-bis[N-2-diphenylphosphinite-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine,** (5)



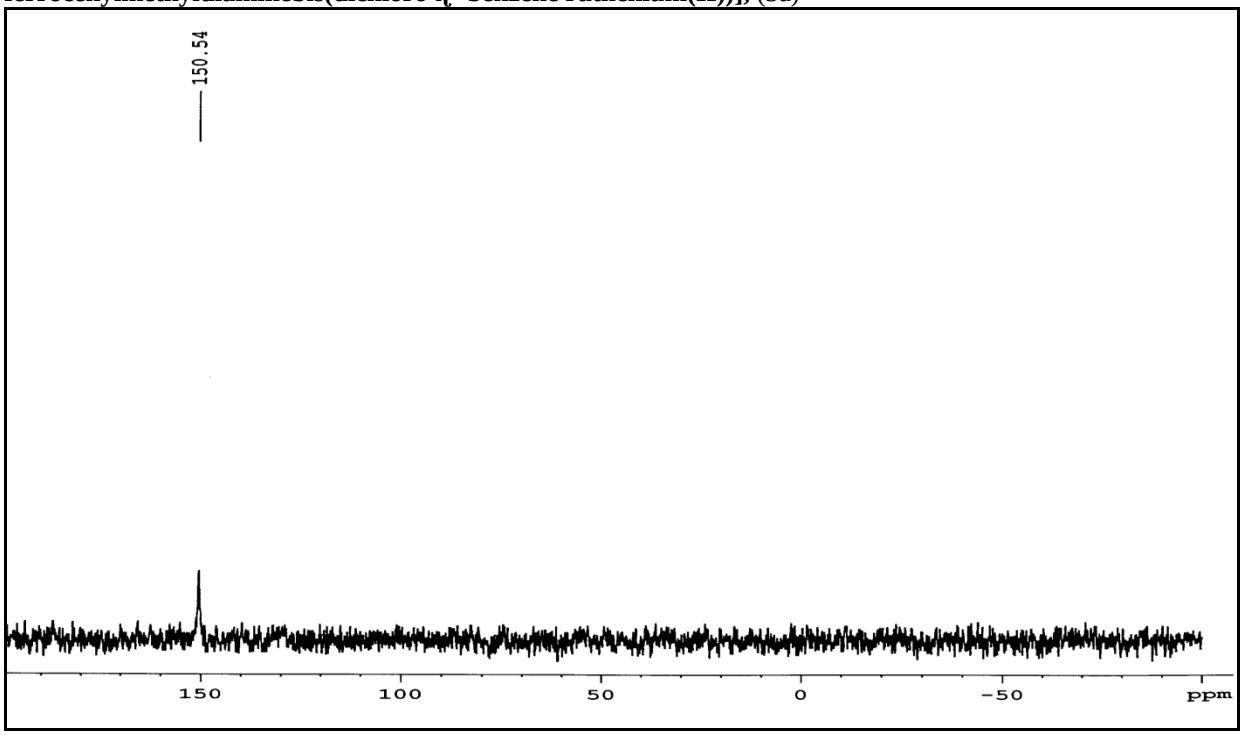
Spectrum 10. ^{31}P-{^{1}H}NMR Spectrum of (S)-bis[N-2-diisopropylphosphinite-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine, **(6)**

SPECTRA

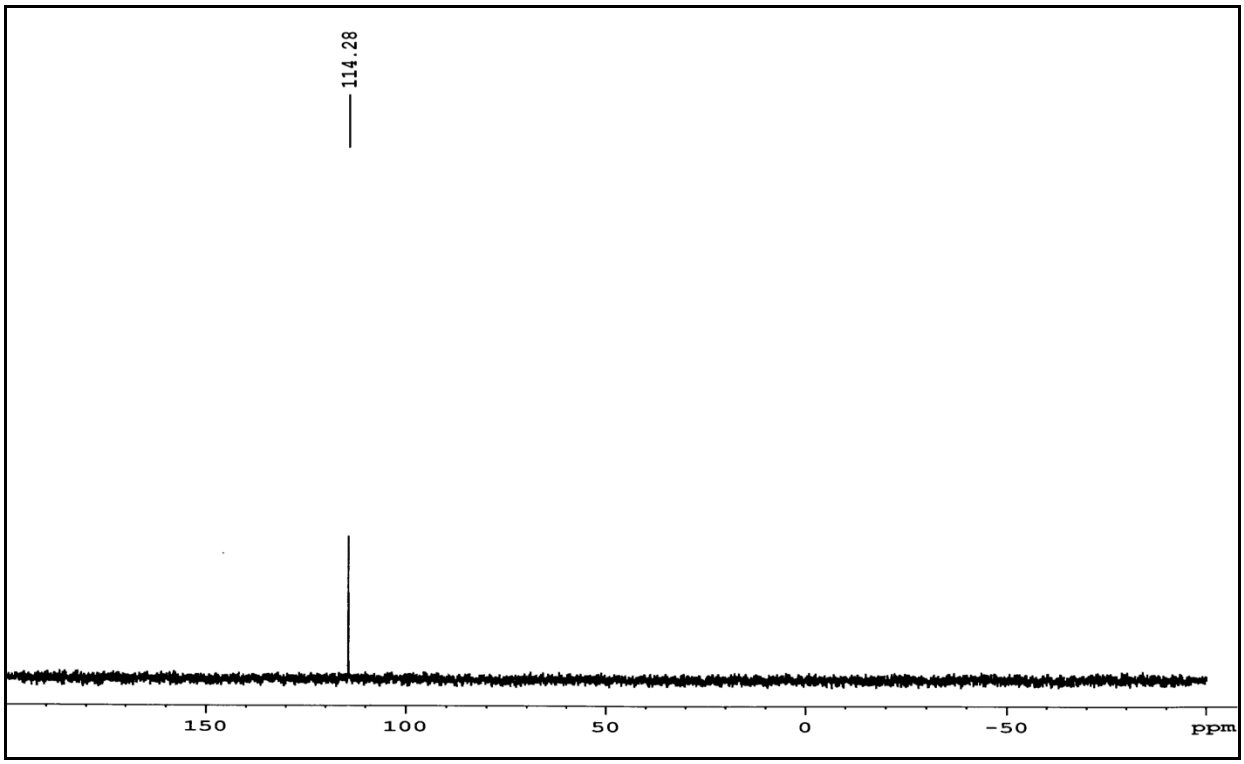
4. ^{31}P-{^{1}H} NMR Spectra of Chiral Ru(II)-C_2-symmetric ferrocenyl Phosphinite Complexes



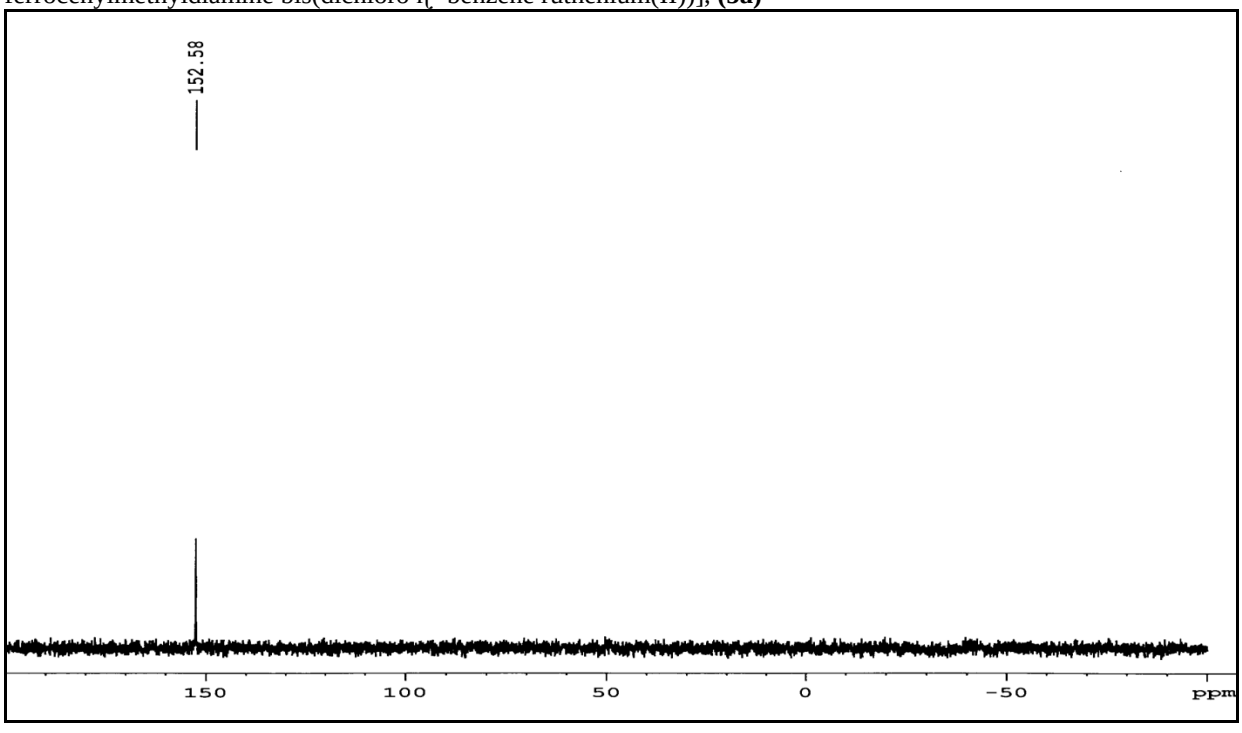
Spectrum 11. ^{31}P NMR Spectrum of (S)-bis[[N-2-diphenylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiaminebis(dichloro η^6-benzene ruthenium(II))], (3a)



Spectrum 12. ^{31}P NMR Spectrum of (S)-bis[[N-2-di<u>iso</u>propylphosphinite-1-phenyl)ethyl]-1,1'-ferrocenylmethyldiaminebis(dichloro η^6-benzene ruthenium(II))], (4a)



Spectrum 13. ^{31}P NMR Spectrum of (S)-bis[[N-2-diphenylphosphinite-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine bis(dichloro η^6-benzene ruthenium(II))], **(5a)**



Spectrum 14.^{31}P NMR Spectrum of (S)-bis[[N-2-diisopropylphosphinite-1-sec-butyl)ethyl]-1,1'-ferrocenylmethyldiamine bis(dichloro η^6-benzene ruthenium(II))], **(6a)**

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:

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