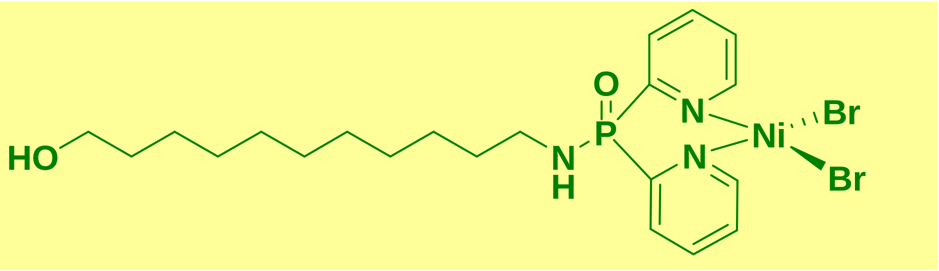
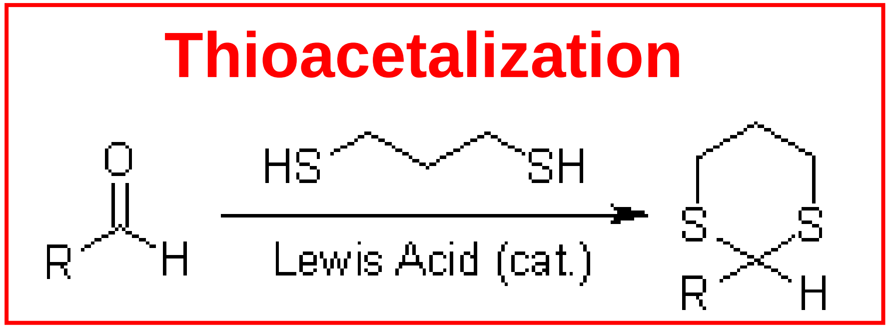
Synthesis and Structural Characterization, of Nickel(II) Complexs Supported by Aminodipyridylphosphine Oxide Ligand. The Catalytic Application to Thioacetalization of Aldehyde

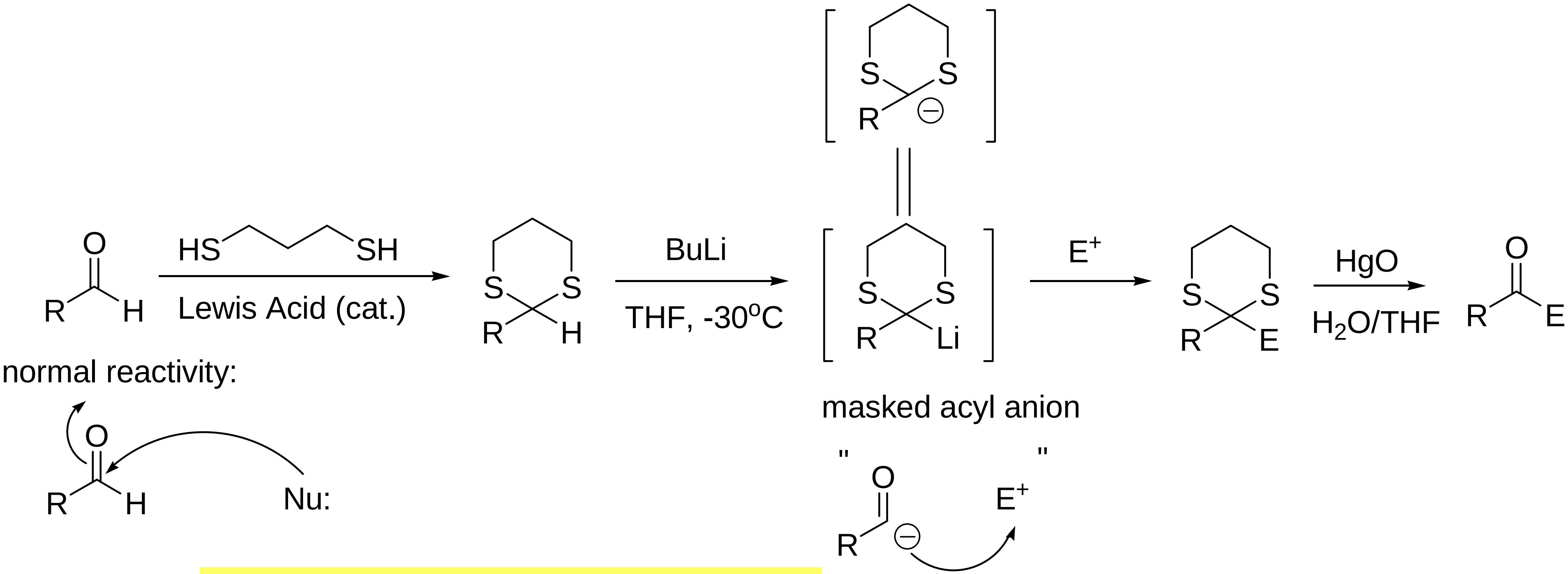
學生：江柏誼

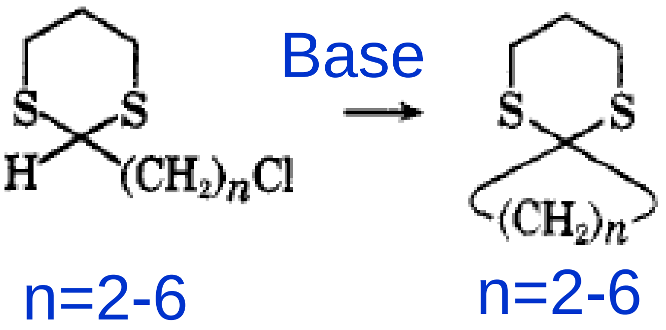
指導教授：于淑君 博士




Thioacetalization

Corey-Seebach Reaction

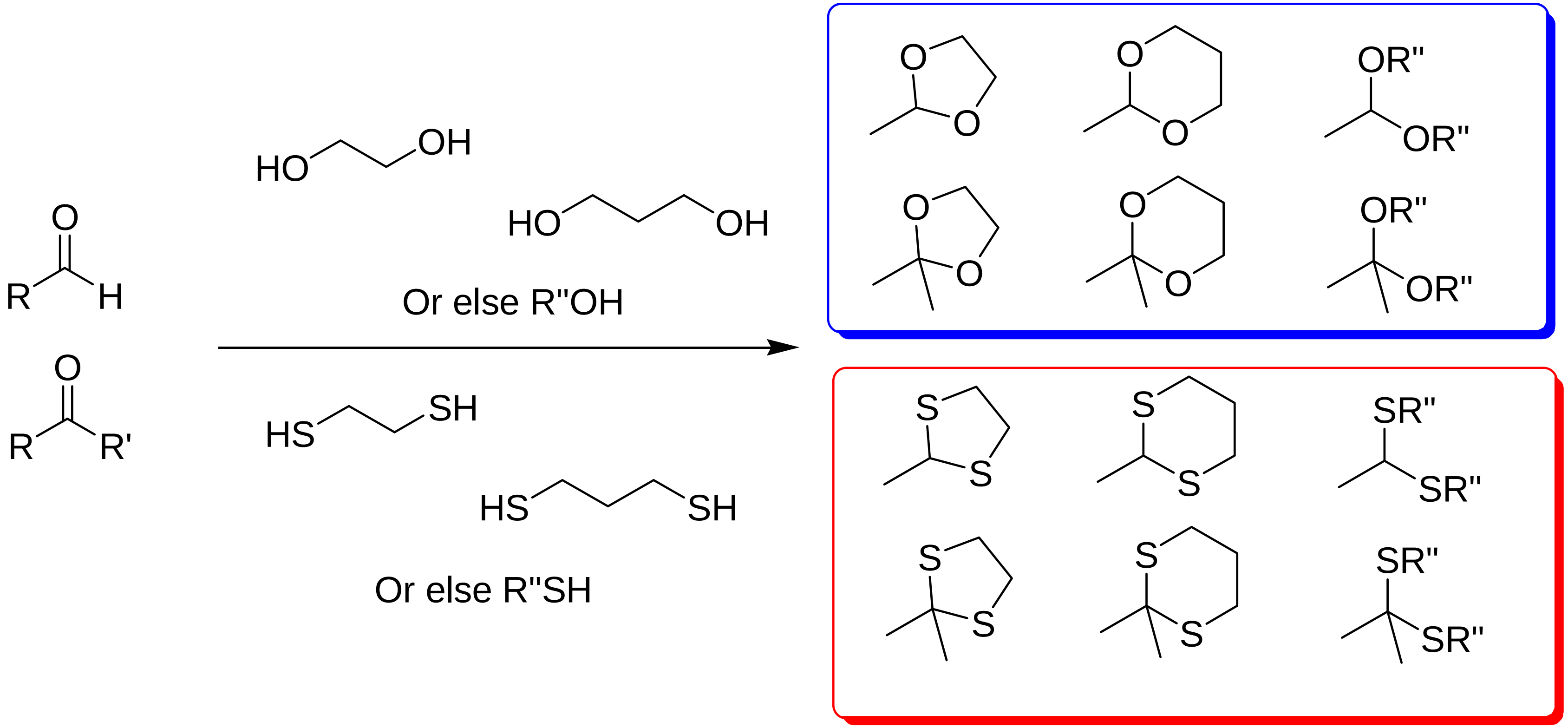




Seebach, D.; Jones, N. R.; Corey, E. J. *J. Org. Chem.* **1968**, *33*, 300-105.

Acetalization and Thioacetalization of Carbonyl Compounds

Acetalization

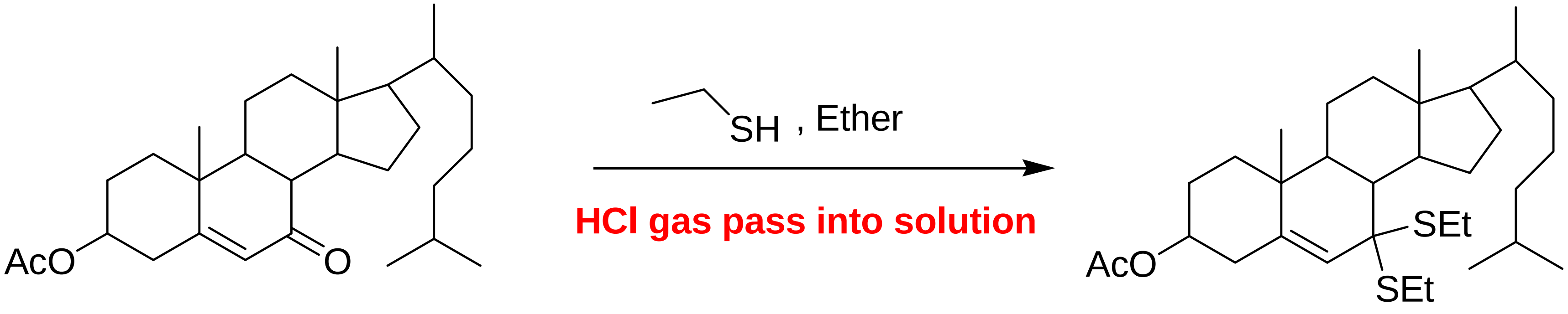


Or else R''OH

Or else R''SH

Thioacetalization

The Earlier Catalyst for Thioacetalization

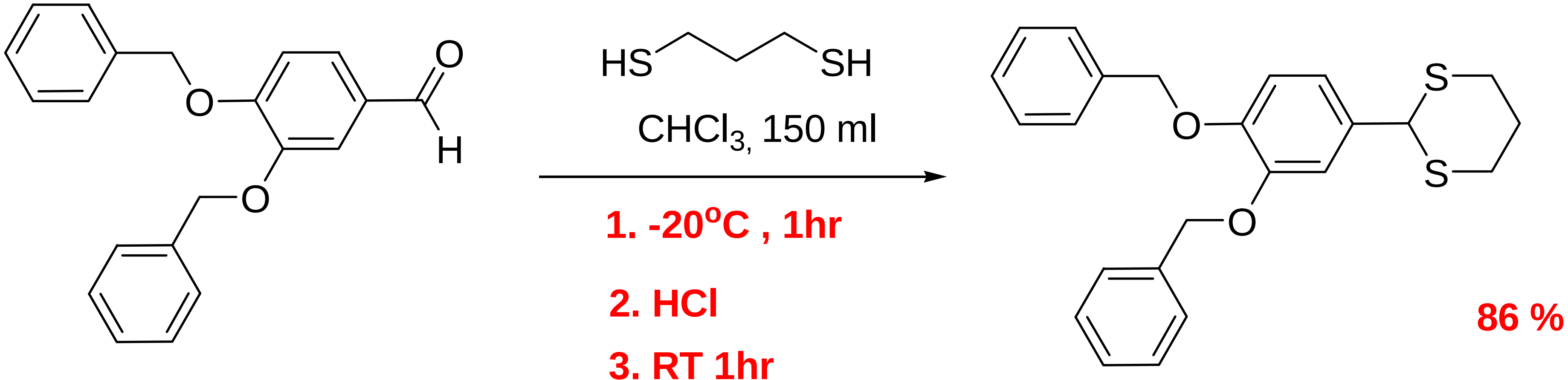


HCl gas pass into solution

1hour
40 %

J.W. Ralls, et. al., *J. Am.Chem. Soc.* **1949**, *71*, 3320-3325

HCl Catalyzed Thioacetalization



3,4-dibenzyloxybenzaldehyde

$CHCl_3$, 150 ml

1. -20°C , 1hr

2. HCl

3. RT 1hr

86 %

quench HCl with 10 % KOH 75 ml

Robert Ramage, et. al., *J. Chem. Soc., Perkin Trans. 1* **1984**, *71*, 1547-1553.

Lewis Acid Catalyzed Thioacetalization

- **Conventional Lewis Acids**

BF_3-Et_2O、$ZnCl_2$、$AlCl_3$、$SiCl_4$、LiOTf、$InCl_3$

Nakata, T. et. al., *Tetrahedron Lett*. **1985**, *26*, 6461-6464.
Evans, D. V. et. al., *J. Am*. *Chem*. *Soc*. **1977**, *99*, 5009-5017.
Firouzabadi, H. et. al., *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2401-2406.

- **Transition Metal Lewis Acids**

$TiCl_4$、WCl_6、$CoCl_2$、$Sc(OTf)_3$、$MoCl_5$、$NiCl_2$

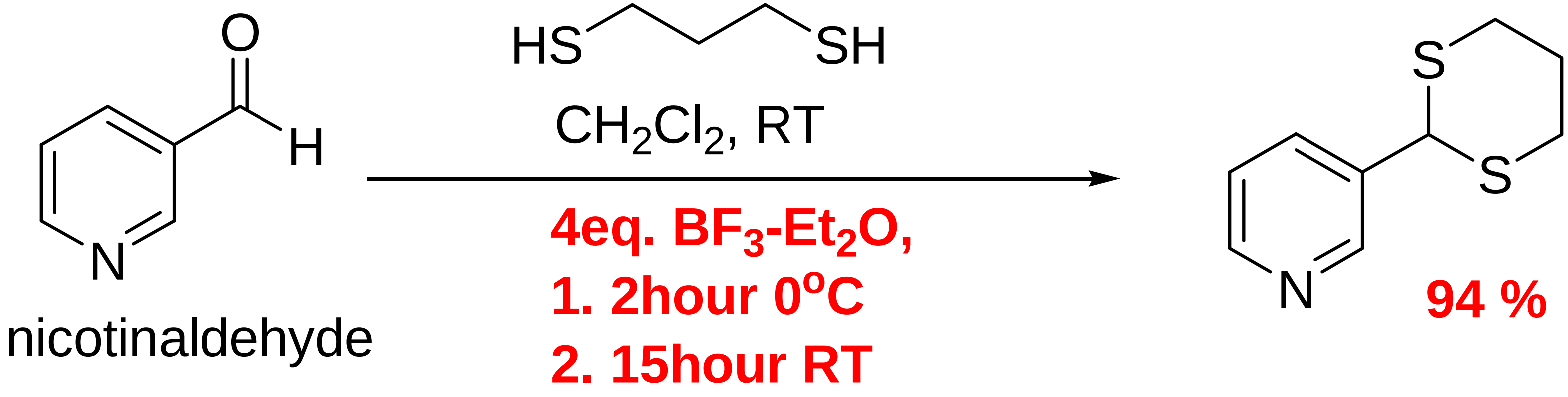
Kumar, V. et. al., *Tetrahedron Lett*. **1983**, *24*, 1289-1292.
Firouzabadi, H. et., al. *Synlett* **1998**, 739-741.
Goswami, S. et. al., *Tetrahedron Lett.* **2008**, *49*, 3092-3096.

- **Lanthanide Metal Lewis Acids**

$Lu(OTf)_3$ 、 $Nd(OTf)_3$

Kanta, D. S. J. Chem. Res. Synop. **2004**,230-231.
Kanta, D. S. Synth. Commun. **2004**, *34*, 230-231.

BF_3-Et_2O Catalyzed Thioacetalization



nicotinaldehyde

CH_2Cl_2, RT

4eq. BF_3-Et_2O,

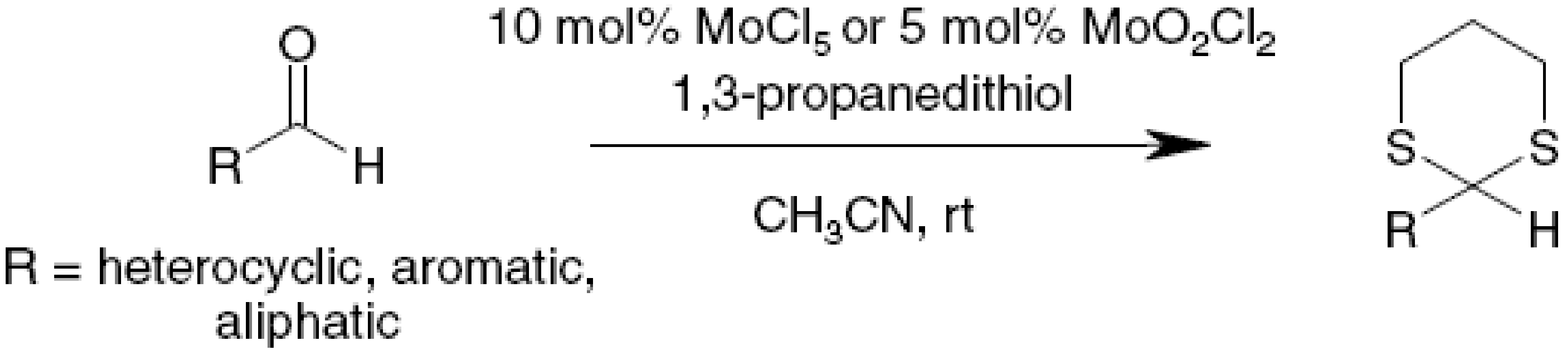
1. 2hour 0^oC

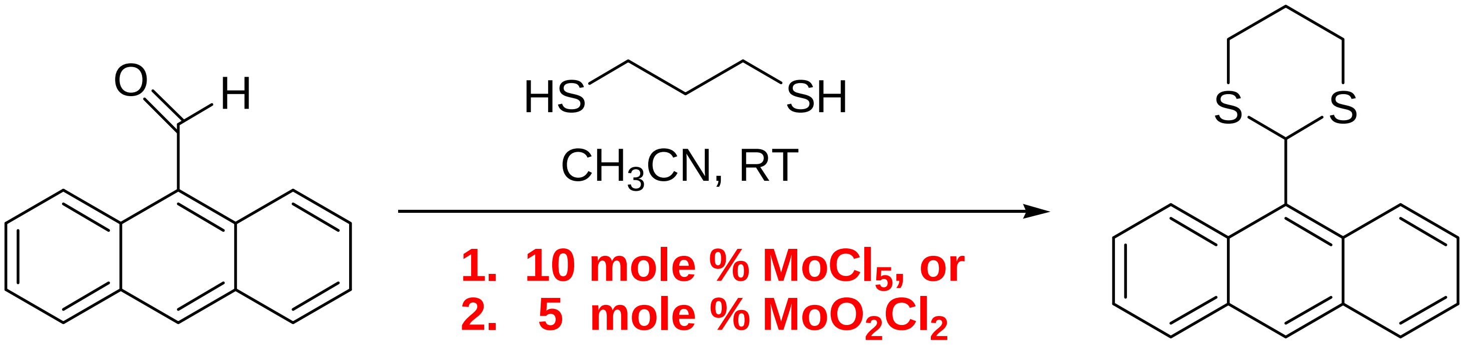
2. 15hour RT

94 %

Paulo J.S. Moran. J. Organomet. Chem. , **2000**, *603*, 220-224

$MoCl_5$ or MoO_2Cl_2 Catalyzed Thioacetalization





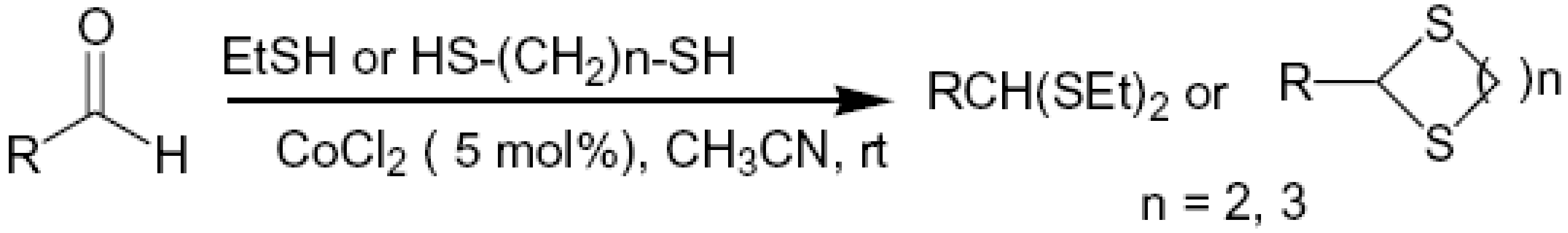
1. 10 mole % $MoCl_5$, or
2. 5 mole % MoO_2Cl_2

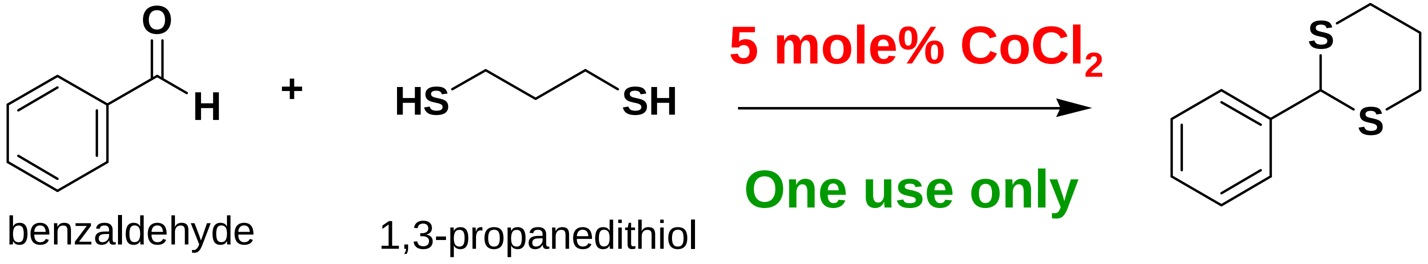
1. 8 min 90 %
2. 25 min 94 %

One use only

S. Goswami, A. C. Maity . Tetrahedron Letters, **2008**, *49*, 3092–3096

$CoCl_2$ Catalyzed Thioacetalization





5 mole% $CoCl_2$

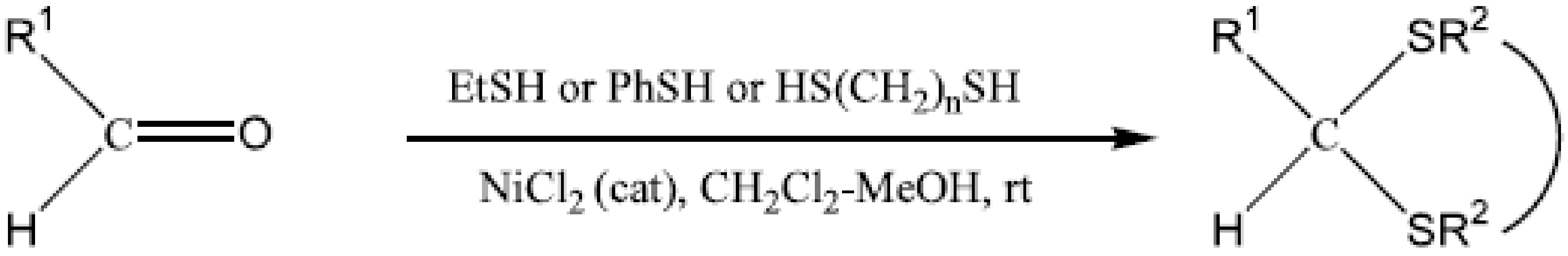
One use only

1hr

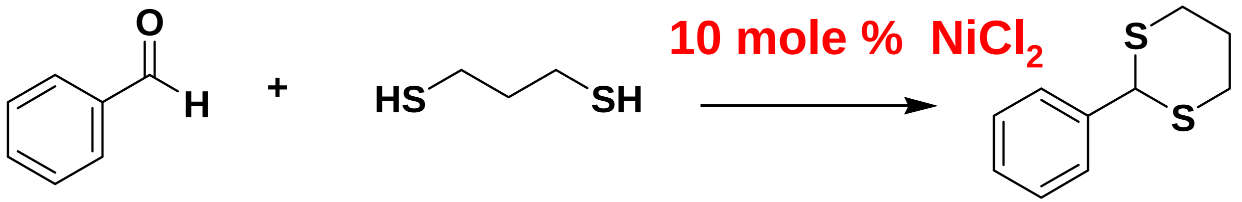
91 %

Surya Kanta De. Tetrahedron Letters, **2004**, *45*, 1035–1036

Nickel(II) Chloride Catalyzed Thioacetalization



R^1 = aryl, alkyl, alkenyl
R^2 = Et, Ph, $-(CH_2)_n-$ n = 2, 3



2.5 hour

96 %

One use only

A. T. Khan et al., *Tetrahedron Lett.* **2003,** *44*, 919–922

Motivation

1. Traditional high valent metal halide Lewis acids are difficult to handle

   ex. MCl_n ,M=Zn、W、Co、Mo…..

2. Nickel is less expensive than other transition metal

   $NiCl_2$ 50g $ 29.2 WCl_6 100g $ 152.5 $PdCl_2$ 25g $ 849

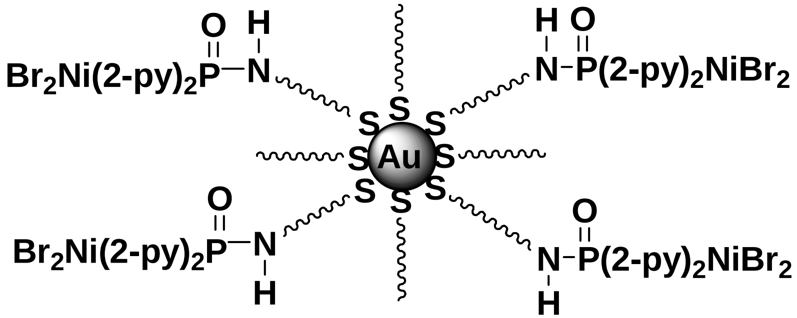
   $NIBr_2$ 50g $ 72.2 $W(CO)_6$ 50g $ 176

3. $(DME)NiBr_2$ as preferable precursor not $(DME)NiCl_2$

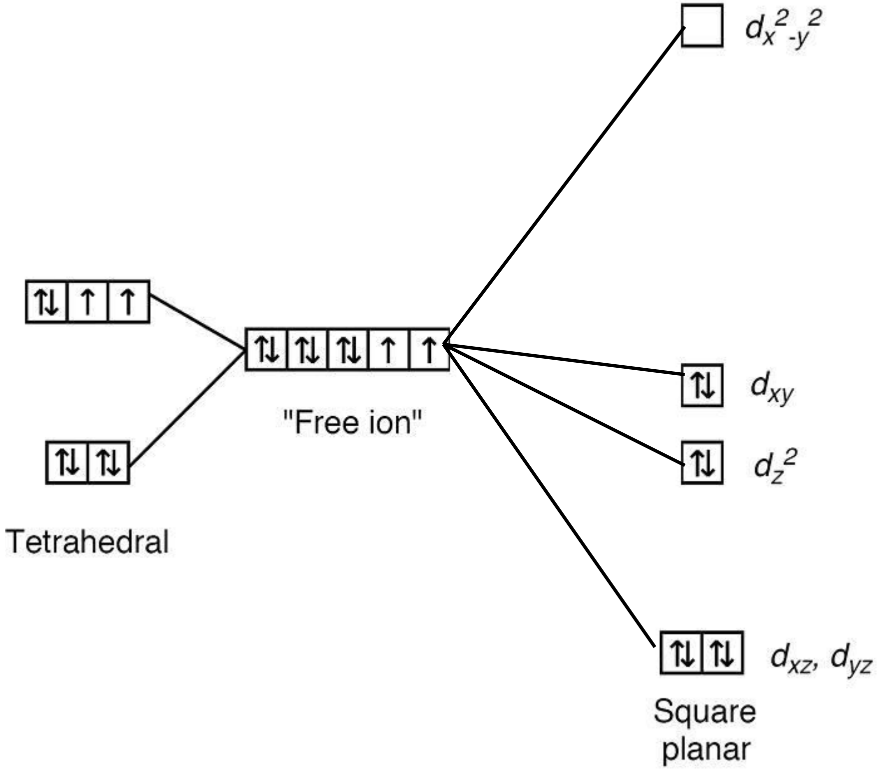
   $[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$ & $[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiCl_2$

4. Use $HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2$ as chelate ligand

$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$



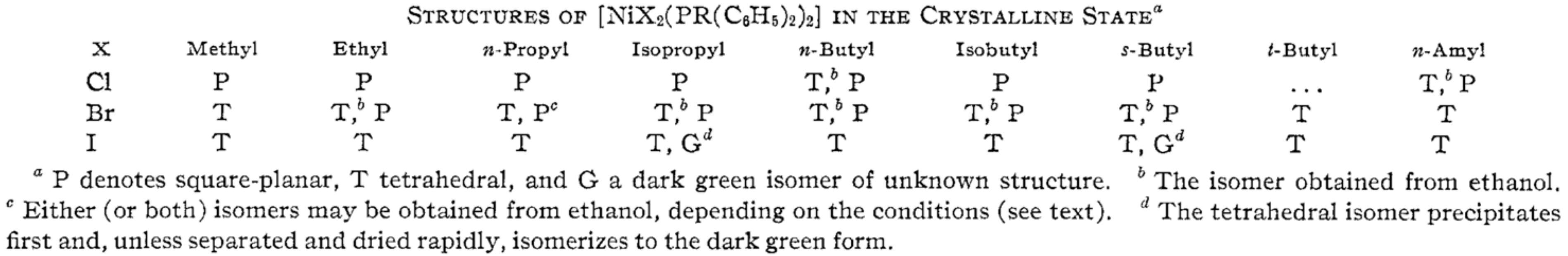
Comparison of M^{2+}(d^8 species) Square Planar vs. Tetrahedral Complexes



- Ni => small Δ_o => tetrahedral & square planar
  Pd & Pt => large Δ_o => square planar

- Ligands => large , weak-field => tetrahedral
  Ligands => small, strong-field => square planar

Square Planar - Tetrahedral Isomerism of Nickel Halide Complexes of Ni(PPh$_2$R)$_2$X$_2$



Structures of [NiX$_2$(PR(C$_6$H$_5$)$_2$)$_2$] in the Crystalline State[a]

X	Methyl	Ethyl	*n*-Propyl	Isopropyl	*n*-Butyl	Isobutyl	*s*-Butyl	*t*-Butyl	*n*-Amyl
Cl	P	P	P	P	T,[b] P	P	P	. . .	T,[b] P
Br	T	T,[b] P	T, P[c]	T,[b] P	T,[b] P	T,[b] P	T,[b] P	T	T
I	T	T	T	T, G[d]	T	T	T, G[d]	T	T

[a] P denotes square-planar, T tetrahedral, and G a dark green isomer of unknown structure. [b] The isomer obtained from ethanol. [c] Either (or both) isomers may be obtained from ethanol, depending on the conditions (see text). [d] The tetrahedral isomer precipitates first and, unless separated and dried rapidly, isomerizes to the dark green form.

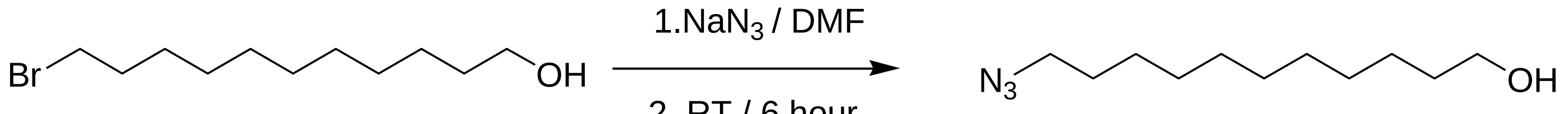
The tetrahedral structure is *increasingly* favored in the orders

PPh$_2$R ：P(C$_2$H$_5$)$_3$ < P(C$_2$H$_5$)$_2$C$_6$H$_5$ < PC$_2$H$_5$(C$_6$H$_5$)$_2$ < P(C$_6$H$_5$)$_3$

X ：Cl < Br < I

R. G. Hayter, F. S. Humiec. *Inorg. Chem*. **1965**, *12,* 1701-1706.

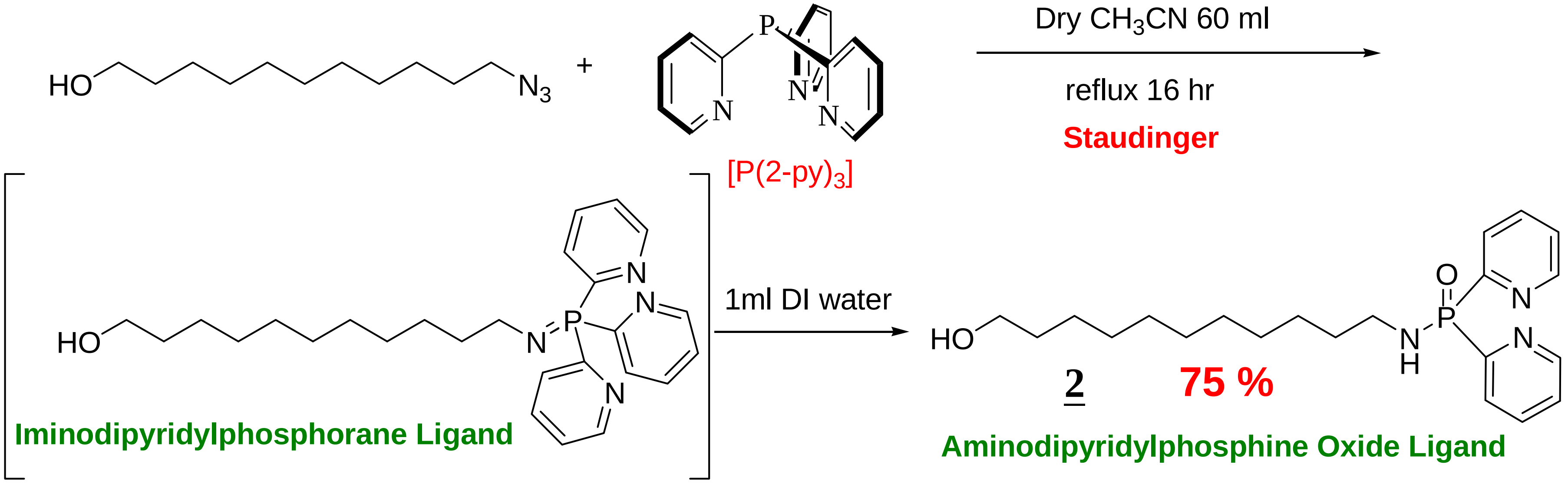
Preparation of Aminodipyridylphosphine Oxide Ligand



1.NaN_3 / DMF

2. RT / 6 hour

1 **93 %**



[$P(2\text{-}py)_3$]

Dry CH_3CN 60 ml

reflux 16 hr

Staudinger

1ml DI water

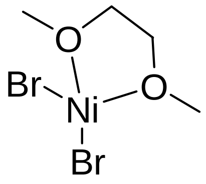
Iminodipyridylphosphorane Ligand

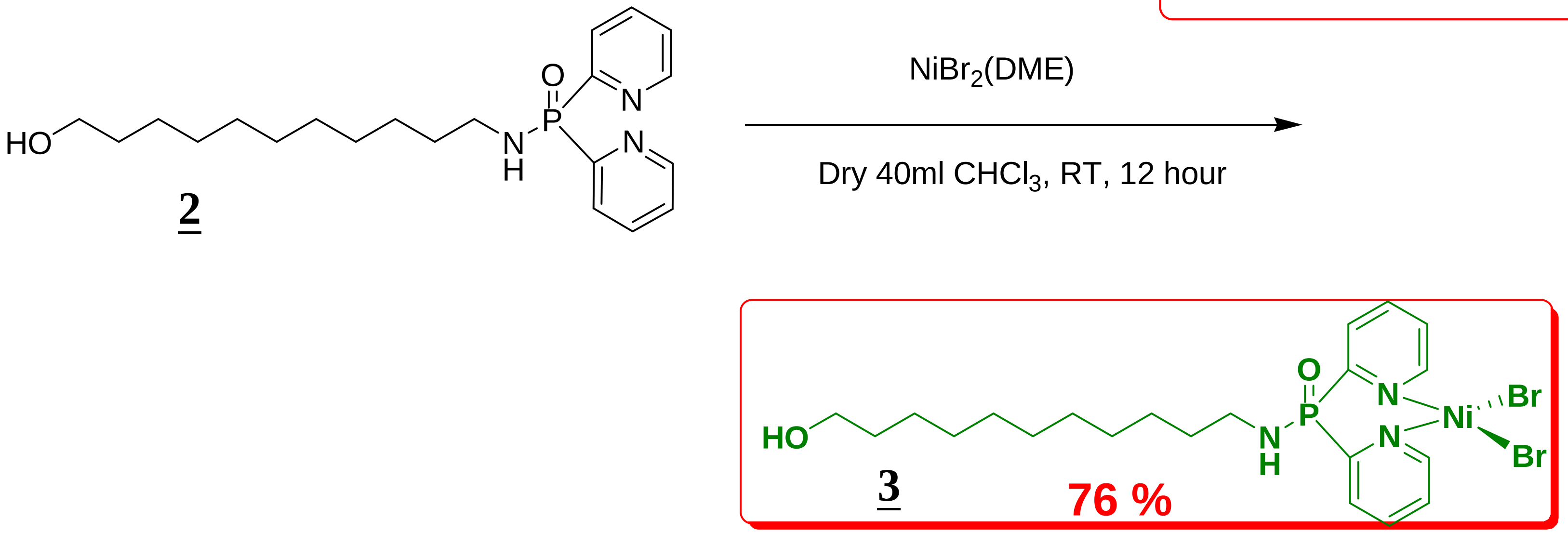
2 **75 %**

Aminodipyridylphosphine Oxide Ligand

Preparation of Nickel(II) Complex Catalyst

NiBr$_2$(DME) =





2

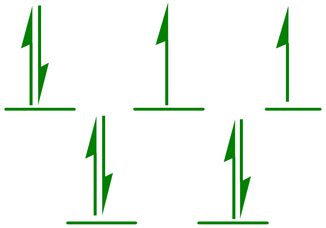
NiBr$_2$(DME)

Dry 40ml CHCl$_3$, RT, 12 hour

3

76 %

Cat.



Paramagnetic

Chemical Shift of Paramagnetic Compounds for NMR

$$\delta_{\text{observed}} = \delta_{\text{diamagnetic}} + \delta_{\text{hyperfine}}$$

due to the paramagnetic center presence

$\delta_{\text{diamagnetic}}$ = diamagnetic shift corresponds to the values for the free ligand.

$$\delta_{\text{hyperfine}} = \delta_{\text{contact}} + \delta_{\text{dipolar}}$$

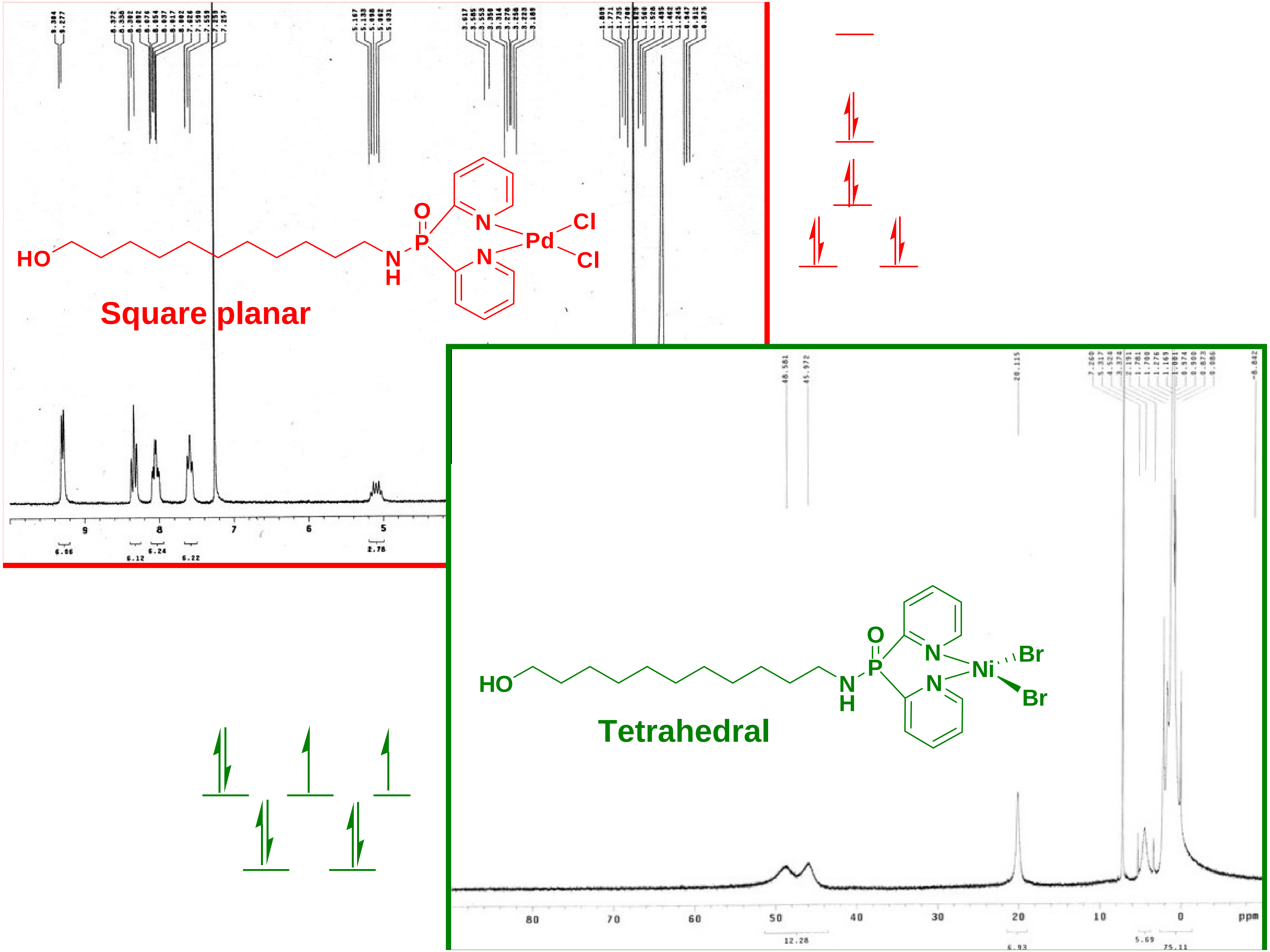
Major

δ_{contact} = contact shifts are caused by spin delocalization of the unpaired electrons through chemical bonds (through bond)

δ_{dipolar}= dipolar shifts, between the paramagnetic center and the nucleus of interaction (through space)

→ **Broad signal**

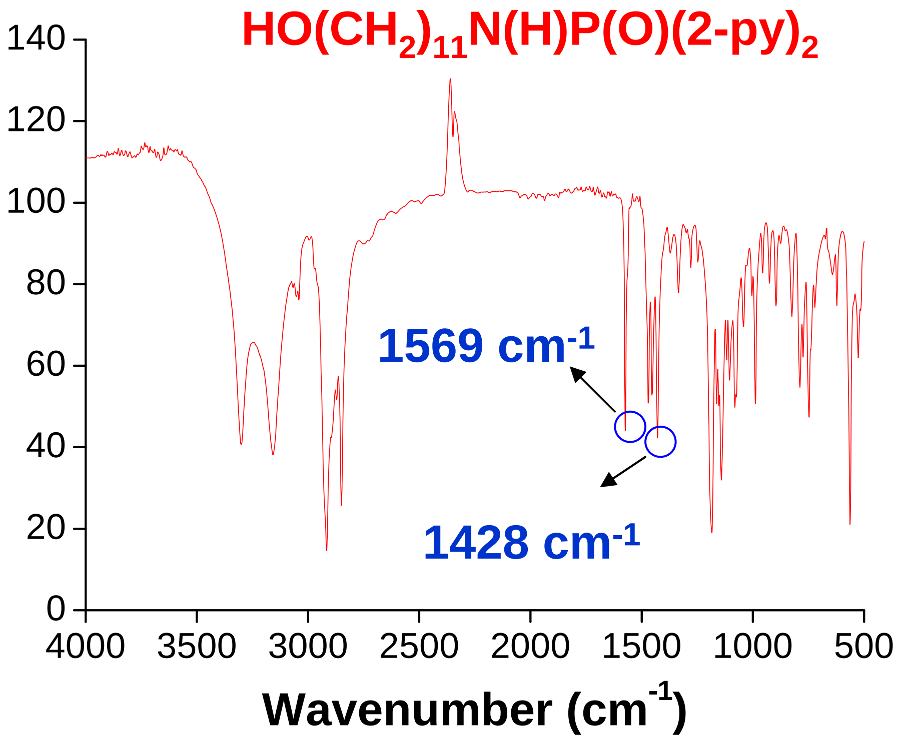
J. Phys. Chem. A, **2003**, *107*, 5821-5825

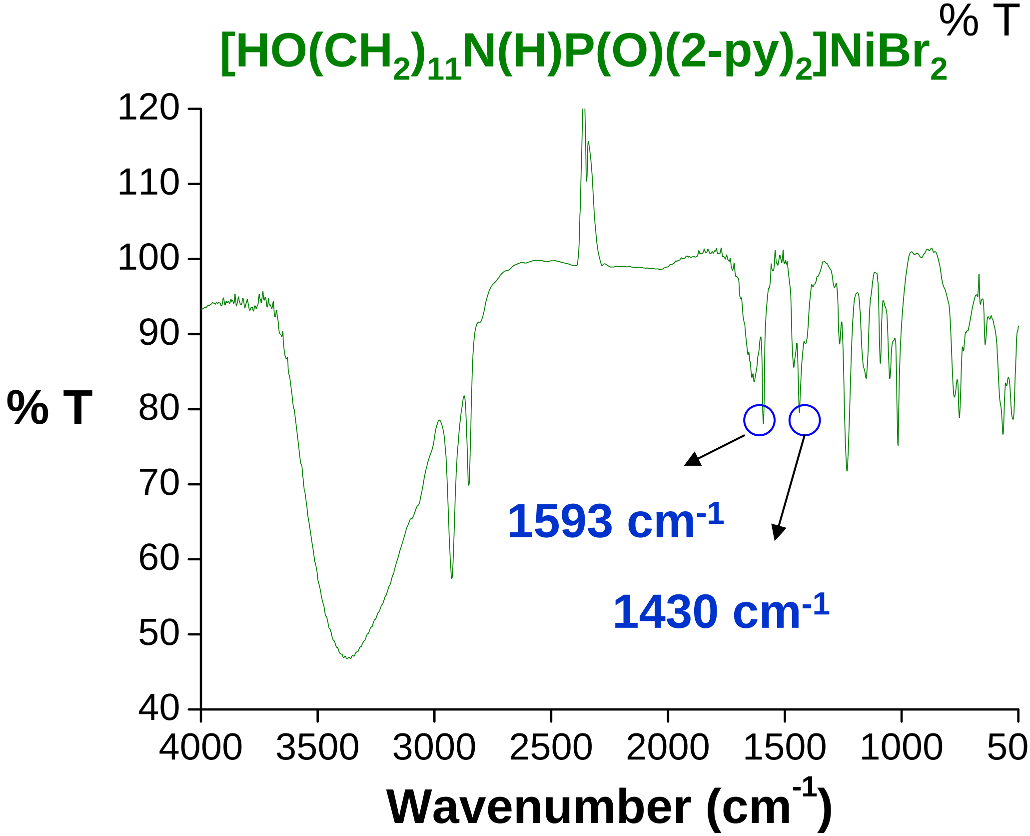


Square planar

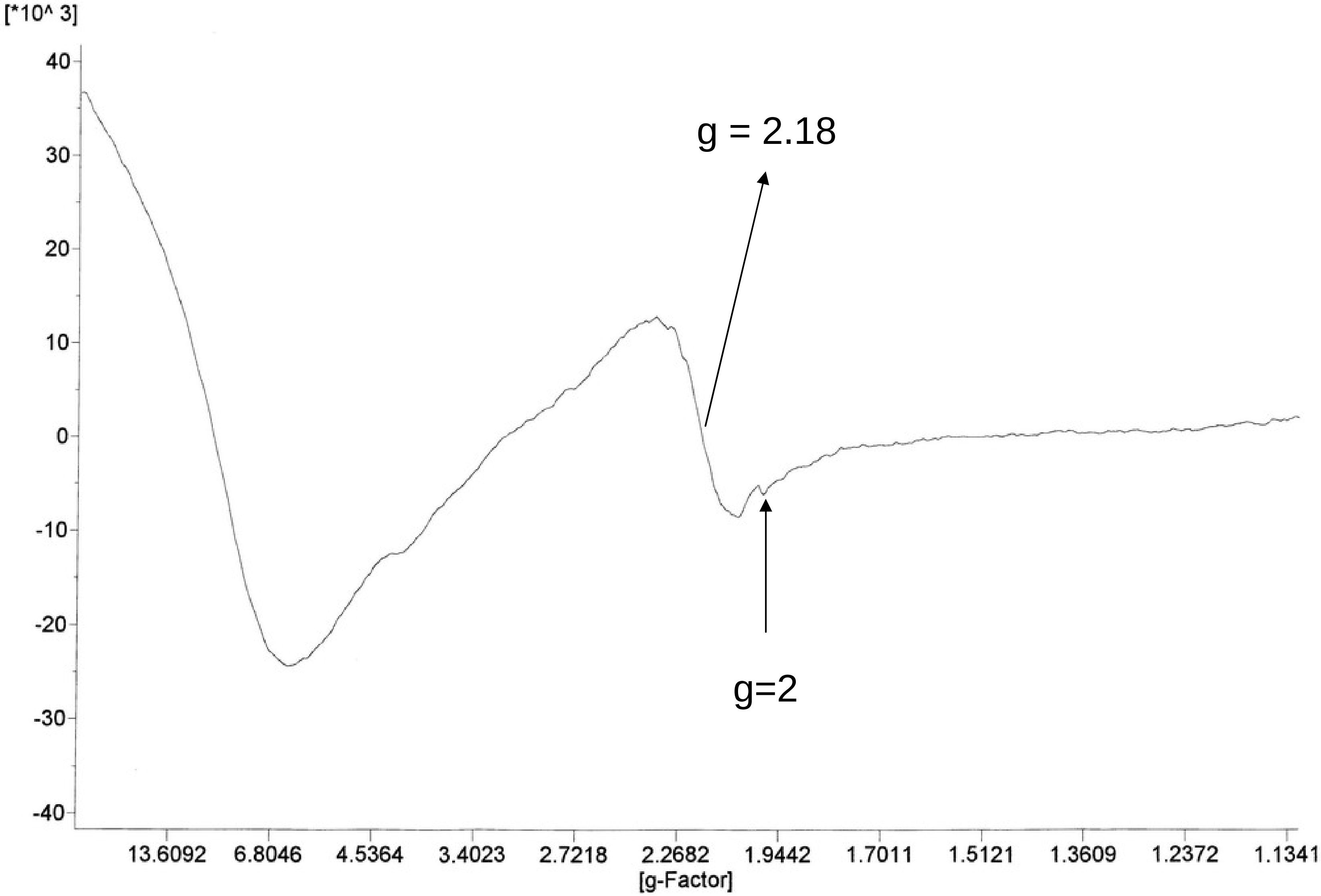
Tetrahedral

IR of $[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$





EPR of $HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$



g = 2.18

g=2

SUQID of HO(CH$_2$)$_{11}$N(H)P(O)(2-py)$_2$]NiBr$_2$

χ = m / H

χ_m = (χ / W) × M

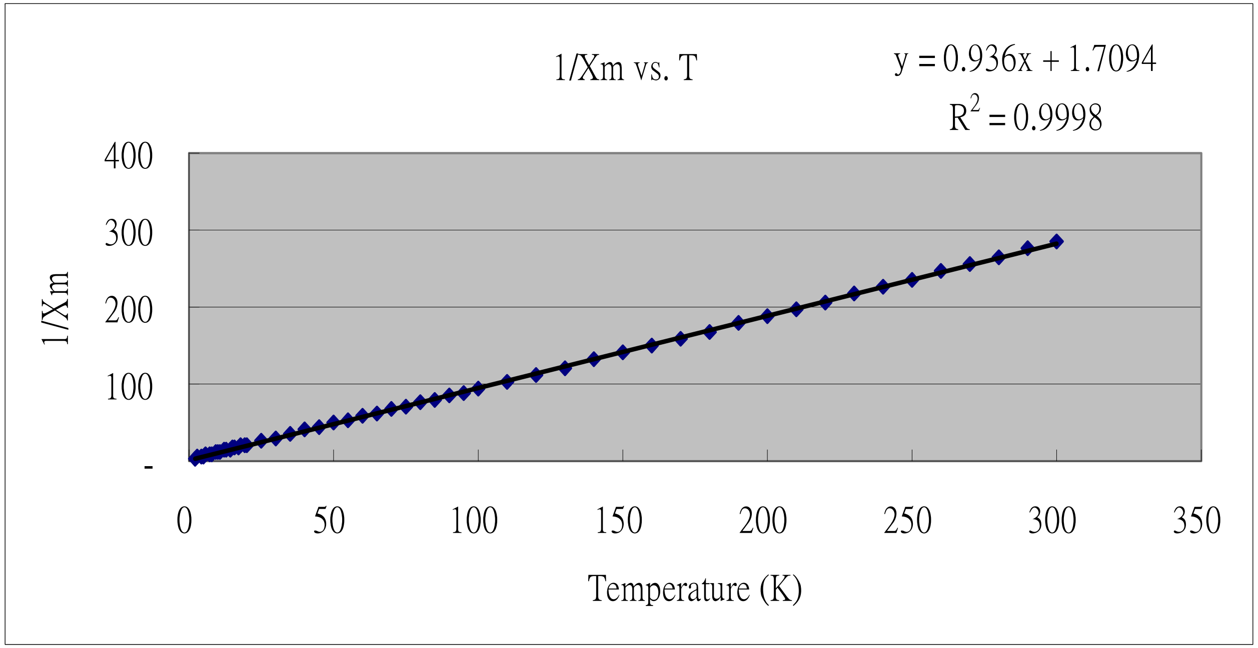
μ_{eff} = (3k / Nβ 2)1/2(χ mT)1/2 = 2.828(χ_mT)$^{1/2}$

m ：磁矩, H ：外加磁場 (10000 guess), χ ：磁化率

χ_m ：莫耳磁化率, W：樣品重量, M：樣品分子量

μ_{eff} ：有效磁矩, T ： 溫度, β ：波耳磁元

K ：波茲曼常數, N：6.02 x 1023



slope = 1/(χ_mT) = 0.936

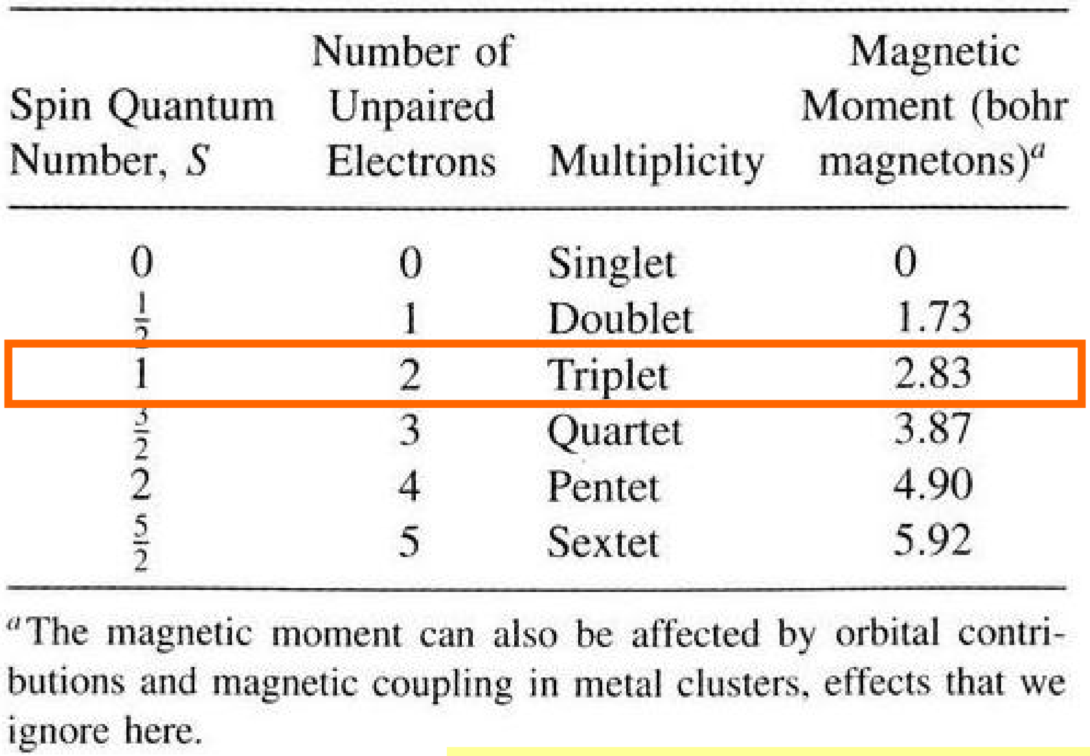
χ_mT = 1/0.936

μ_{eff} = 2.828 (χ_mT)$^{1/2}$

μ_{eff} = 2.92

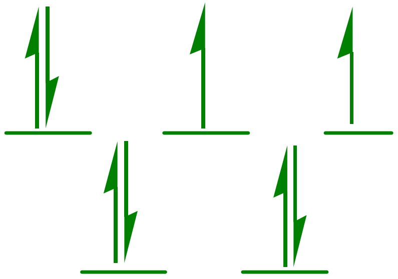
$HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$

$\mu_{eff} = 2.92$



Spin Quantum Number, S	Number of Unpaired Electrons	Multiplicity	Magnetic Moment (bohr magnetons)[a]
0	0	Singlet	0
$\frac{1}{2}$	1	Doublet	1.73
1	2	Triplet	2.83
$\frac{3}{2}$	3	Quartet	3.87
2	4	Pentet	4.90
$\frac{5}{2}$	5	Sextet	5.92

[a] The magnetic moment can also be affected by orbital contributions and magnetic coupling in metal clusters, effects that we ignore here.

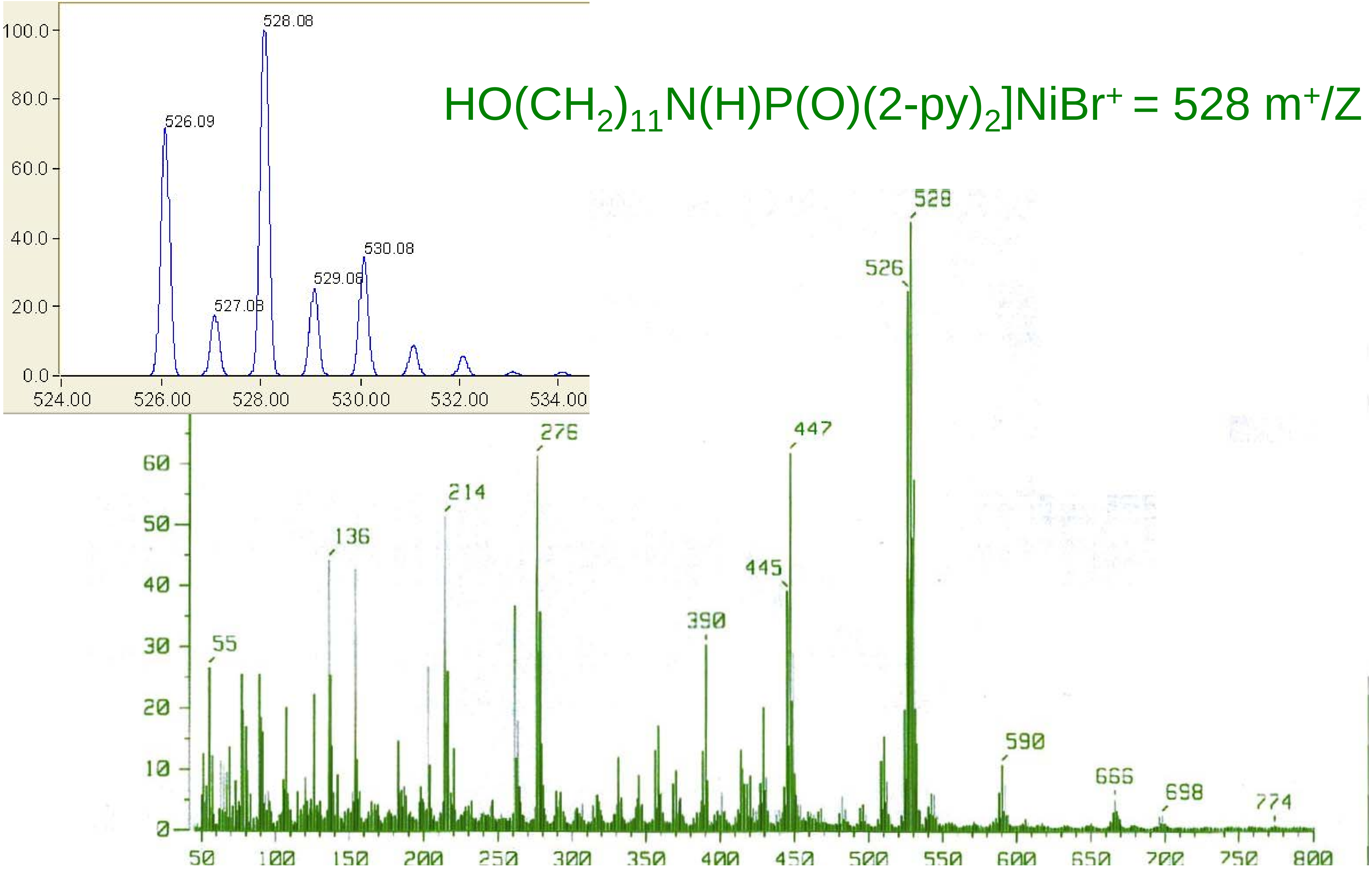


Tetrahedral

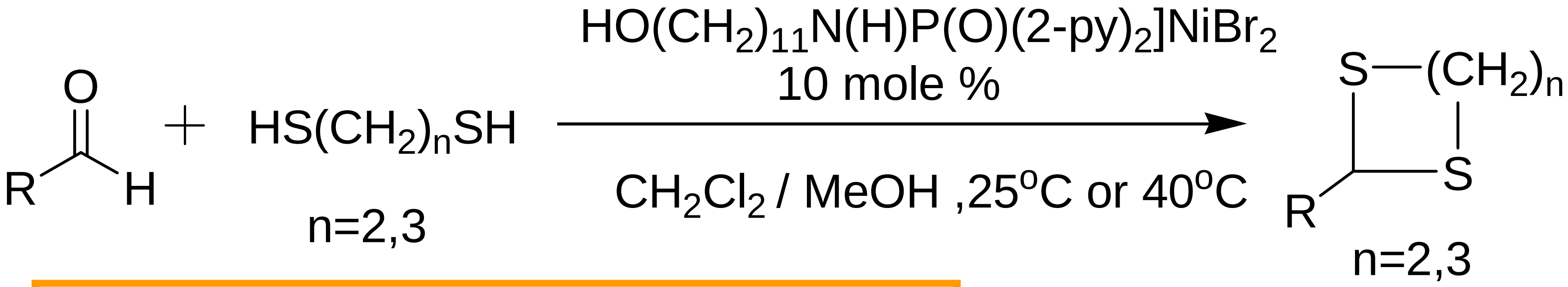
The Organometallic Chemistry of The Transition Metals. **2005**

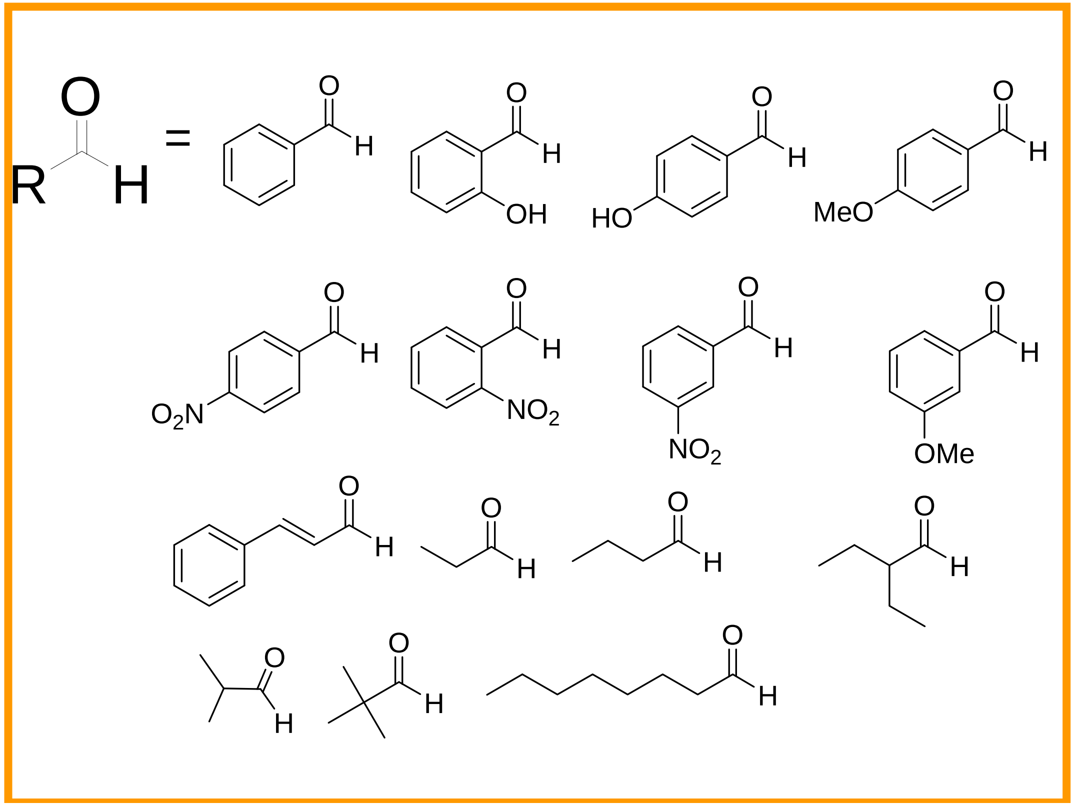
FAB-MS of $HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$

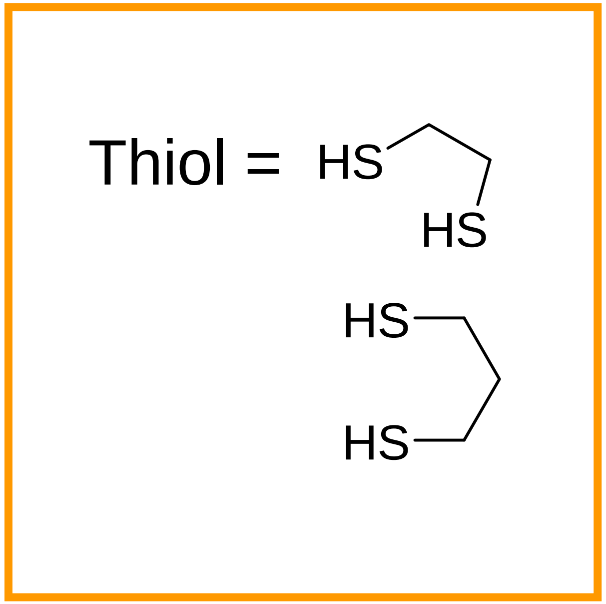
$HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr^+ = 528\ m^+/Z$

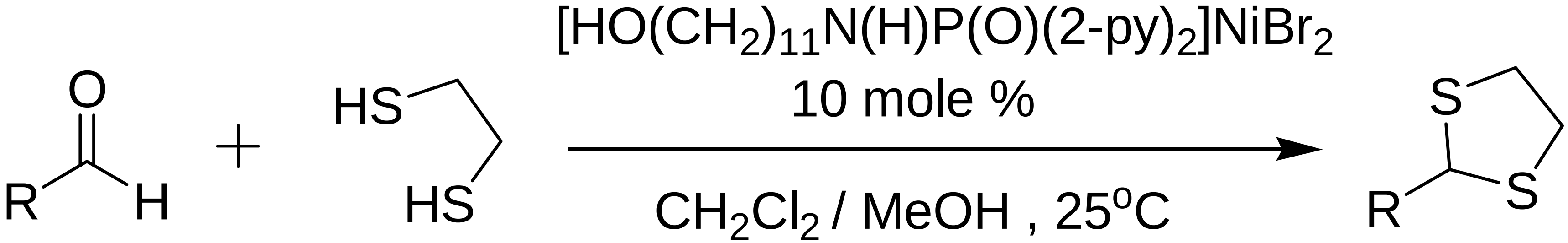


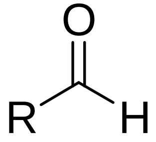
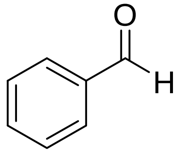
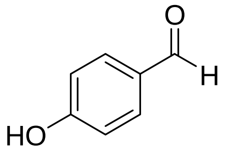
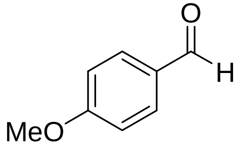
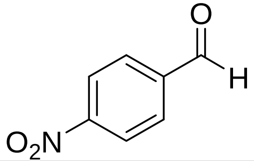
Nickel Lewis Acids Complex Catalyzed Thioacetalization

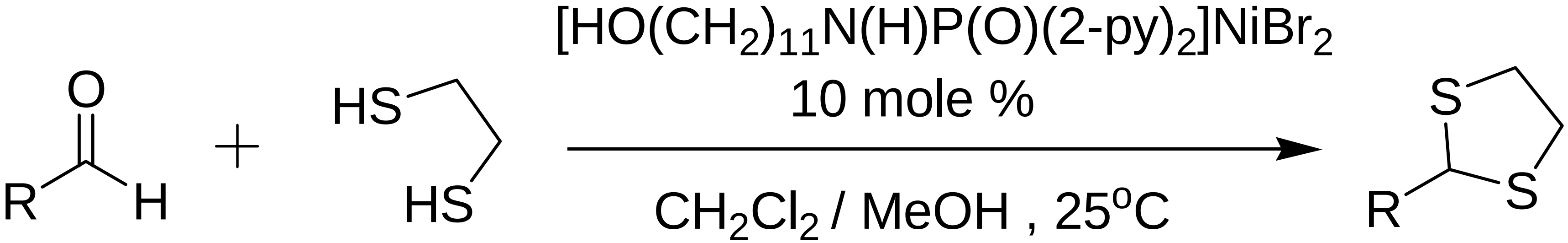


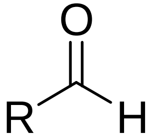
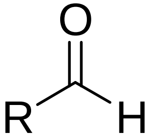
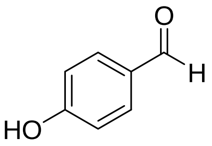
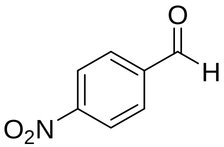
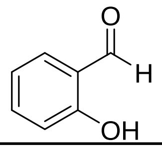
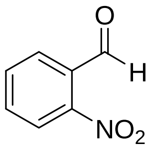
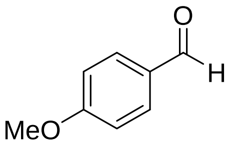
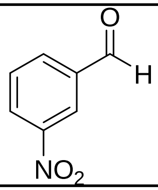
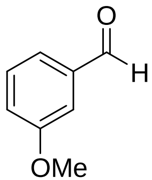


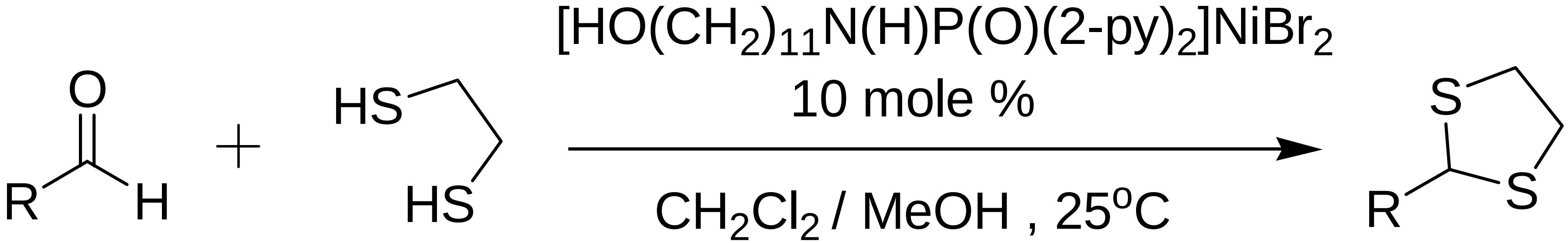




Entry		*Time*	*Yield (%)*	*Paper Reported cat. ($NiCl_2$)*	
				Time	*Yield (%)*
1		**1.5 hr**	**92**	**2.75 hr**	**96**
2		**2 min**	**>99**	**8 min**	**96**
4		**10 min**	**99**	**45 min**	**90**
6		**5 hr**	**92**	**20 hr**	**82**



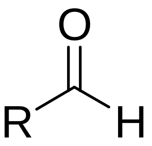
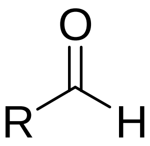
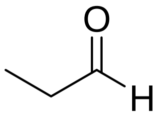
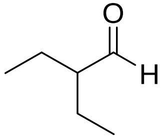
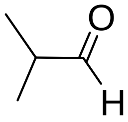
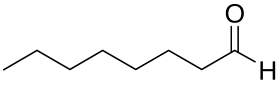
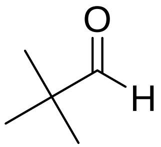
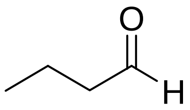
Entry		*Time*	*Yield (%)*	*Entry*		*Time*	*Yield (%)*
2		**2 min**	**>99**	**6**		**5 hr**	**92**
3		**40 min**	**90**	**7**		**15 hr**	**80**
4		**10 min**	**99**	**8**		**3 hr**	**92**
5		**2 hr**	**90**				

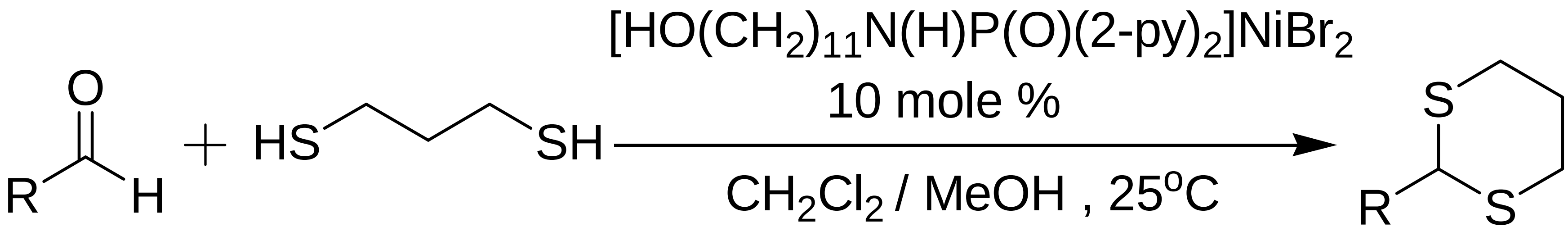


$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$

10 mole %

CH_2Cl_2 / MeOH , 25^{o}C

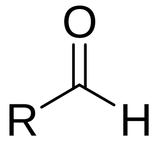
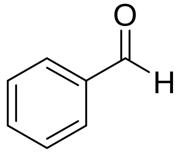
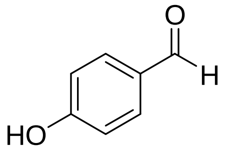
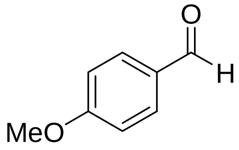
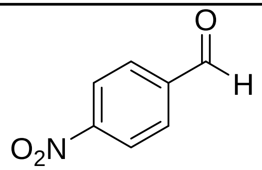
Entry		***Time***	***Yield (%)***	***Entry***		***Time***	***Yield (%)***
10		**2 hr**	**91**	**14**		**60 min/** **4.5 hr**	**79 /** **70**
11		**60 min**	**95**			**60 min**	**94**
12		**4.5 hr**	**87**				
13		**60 min**	**92**				

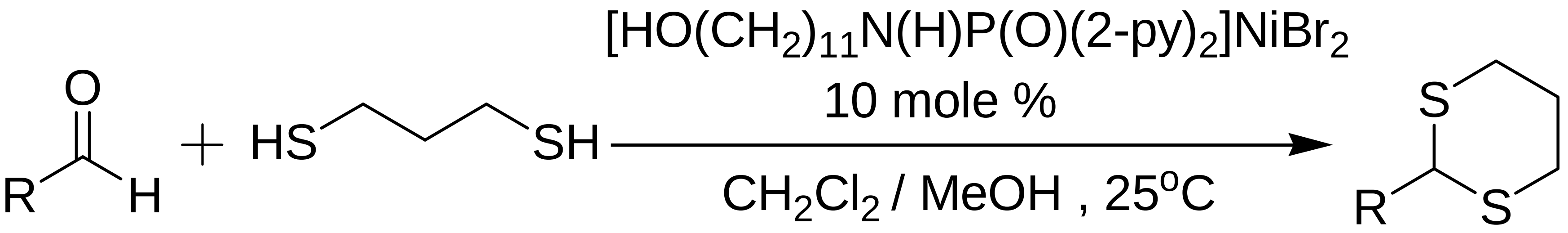


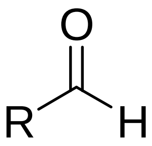
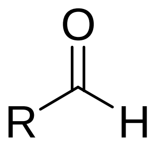
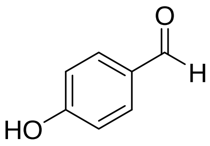
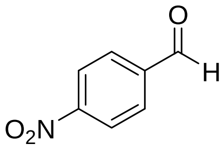
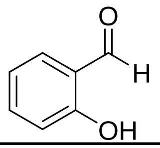
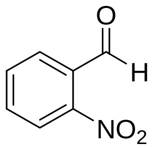
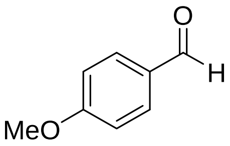
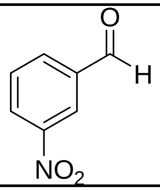
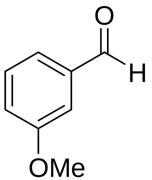
$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$

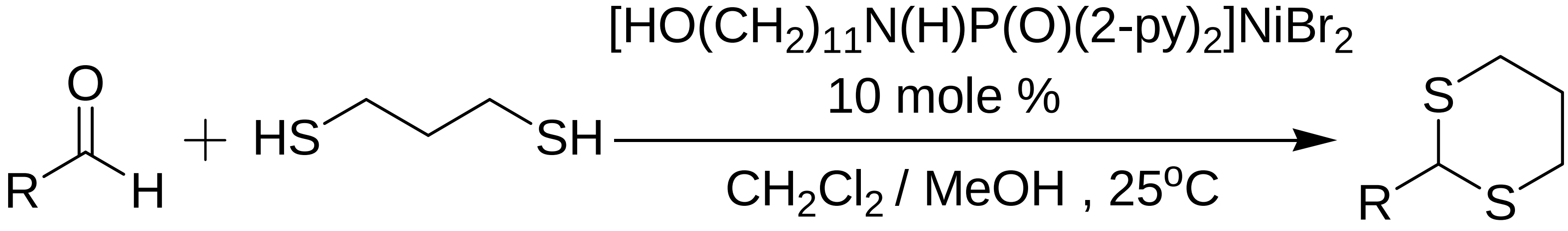
10 mole %

CH_2Cl_2 / MeOH , 25°C

Entry		***Time***	***Yield (%)***	***Paper Reported cat. ($NiCl_2$)*** ***Time***	 ***Yield (%)***
15		**2.5 hr**	**89**	**2.5 hr**	**94**
16		**5 min**	**>99**	**30 min**	**93**
18		**30 min**	**94**	**1.15 hr**	**89**
20		**18 hr**	**93**		



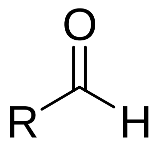
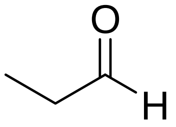
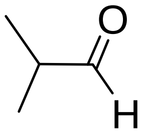
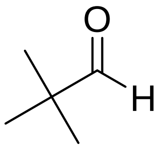
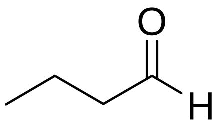
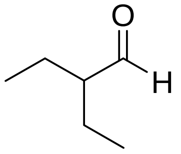
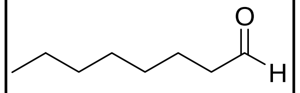
Entry		***Time***	***Yield (%)***	***Entry***		***Time***	***Yield (%)***
16		**5 min**	**>99**	**20**		**18 hr**	**93**
17		**2.5 hr**	**91**	**21**		**18 hr**	**61**
18		**30 min**	**94**	**22**		**6.5 hr**	**82**
19		**4.5 hr**	**92**				

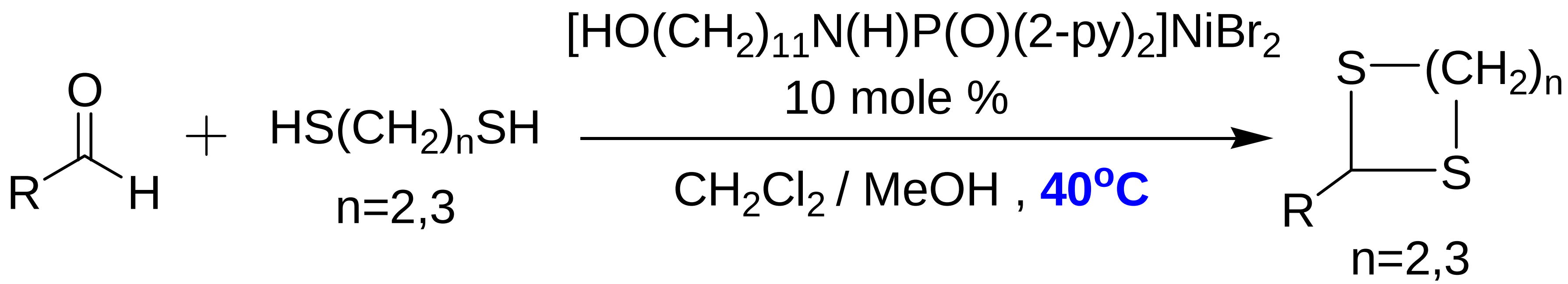


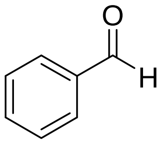
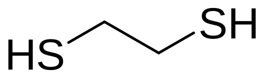
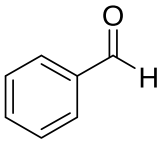
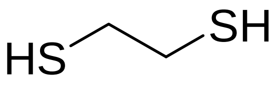
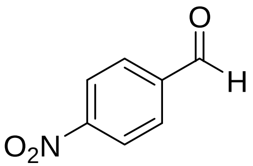
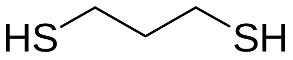
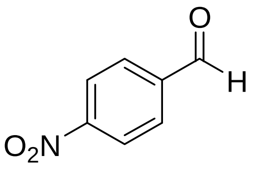
$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$

10 mole %

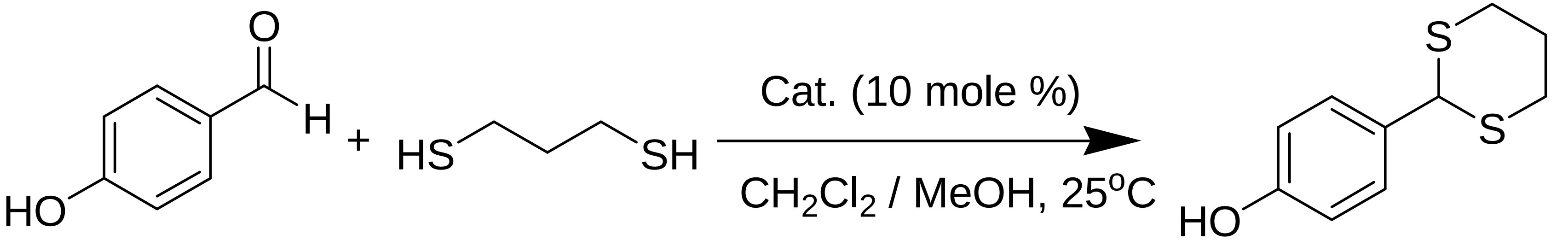
CH_2Cl_2 / MeOH , 25°C

Entry		*Time*	*Yield (%)*
24		**2 hr**	**91**
25		**30 min**	**91**
26		**5.5 hr**	**79**
27		**50 min**	**97**
28		**30 min/** **5.5 hr**	**75/** **82**
		**30 min**	**93**



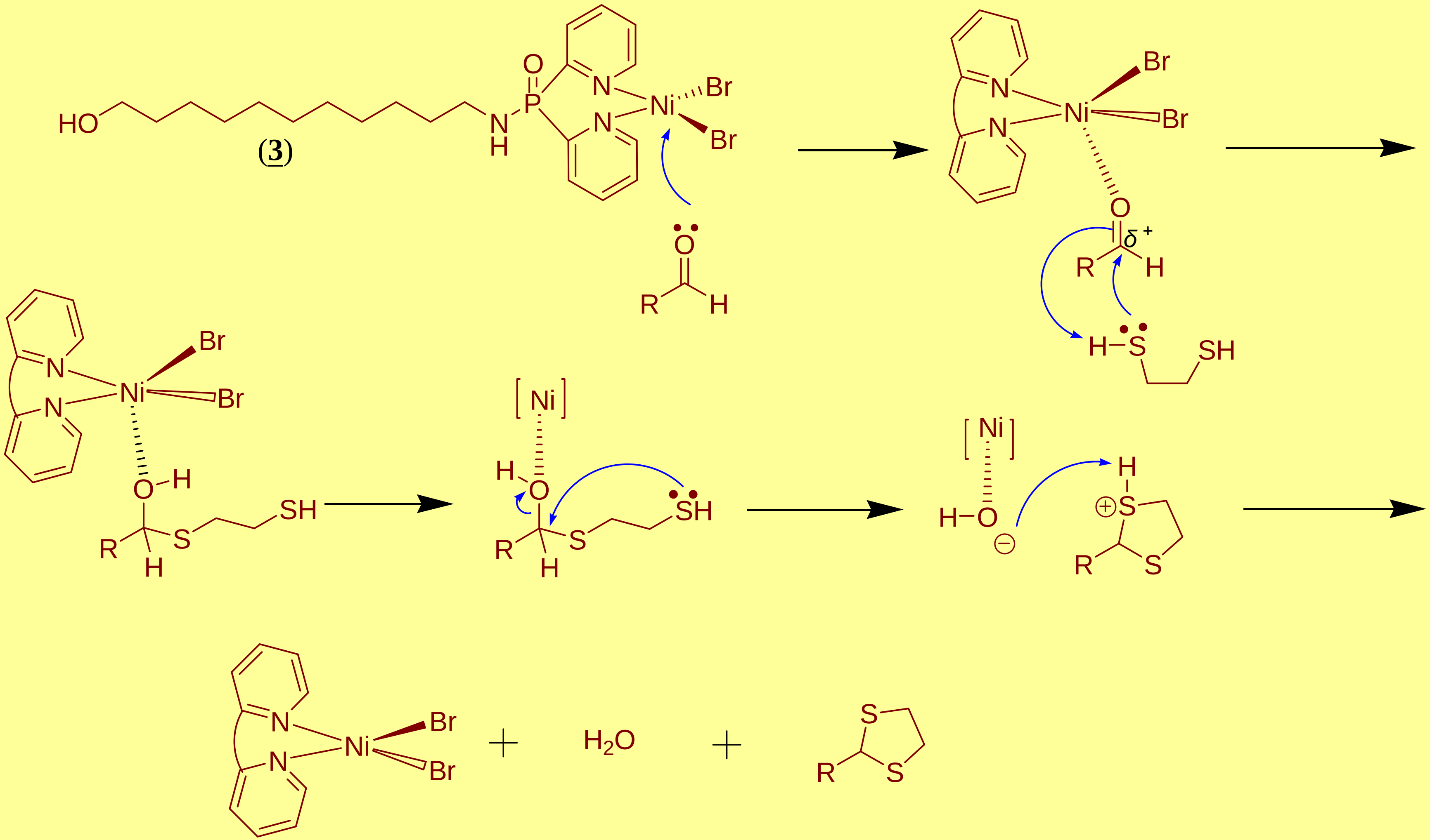
Entry	***R***	***Thiol***	**40°C**		**25°C**	
			Time	***Yield (%)***	***Time***	***Yield(%)***
29			**10 min**	**88**	**1.5 hr (1)**	**92**
30			**15 min**	**87**	**2.5 hr (15)**	**89**
31			**1.5 hr**	**86**	**5 hr (6)**	**92**
32			**3 hr**	**90**	**18 hr (20)**	**93**

Comparison of Catalytic Activity Amoung Various Different Catalyst

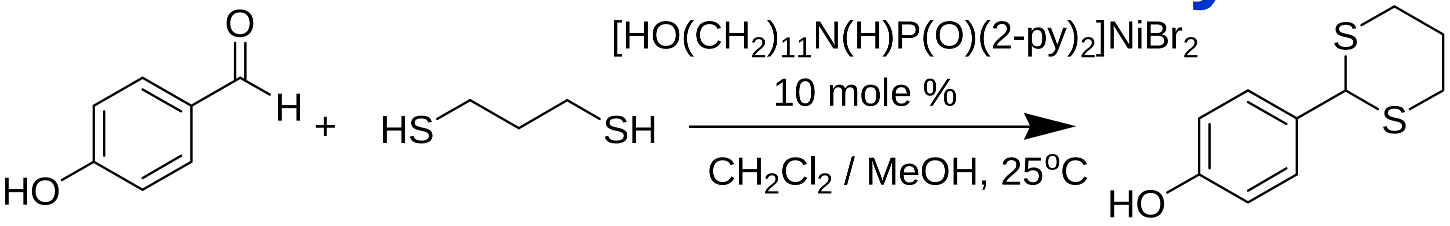


Entry	*Cat.*	*Time*	*Yield (%)*
A	Paper ($NiCl_2$ anhydrous)	30 min	93
B	NONE	24 hour	96
C	$HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2$	190 hour	34
D	$(DME)NiCl_2$	5 min	90
E	$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiCl_2$	35 min	93
F	$(DME)NiBr_2$	5 min	95
G	$[HO(CH_2)_{11}N(H)P(O)(2\text{-}py)_2]NiBr_2$	5 min	>99

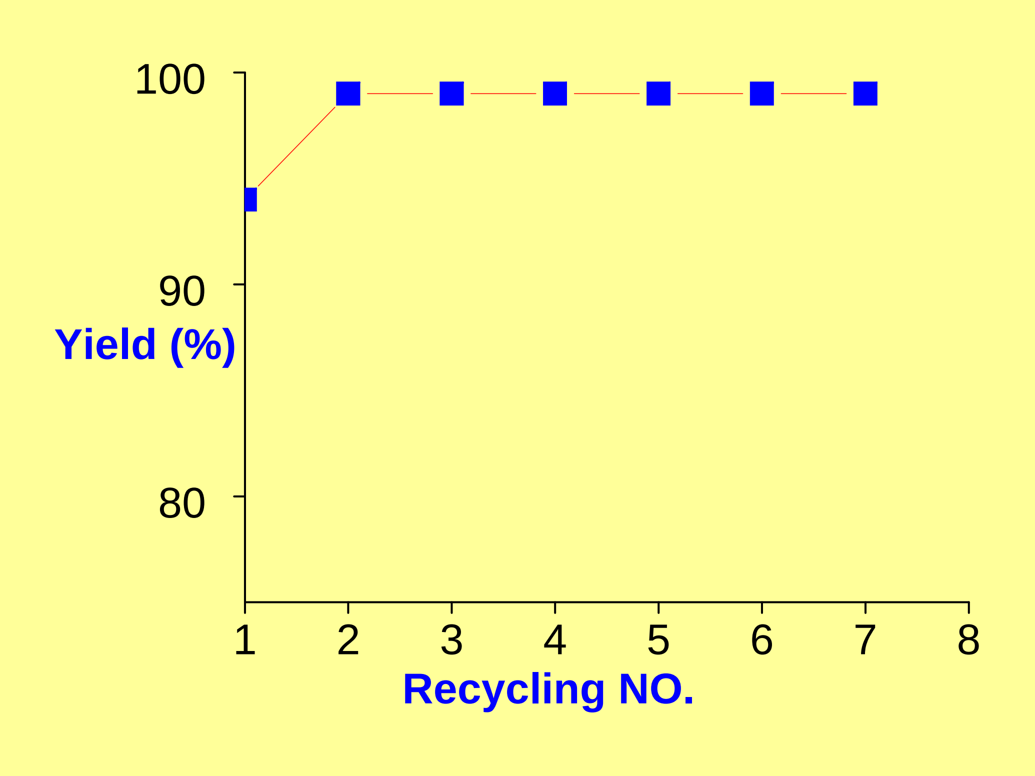
Proposed Mechanism



Recyclable Nickel(II) Complex Catalyst for Thioacetalization of Aldehyde



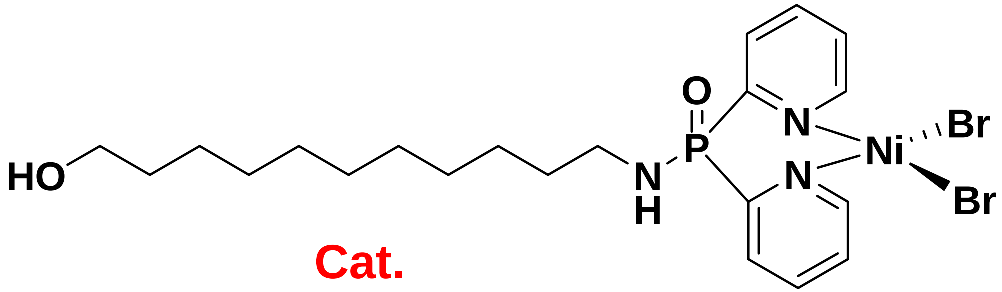
Recycling NO.	Reaction Time	Yield
1	5 min	94 %
2	5 min	99 %
3	5 min	99 %
4	5 min	99 %
5	5 min	99 %
6.	5 min	99%
7.	5 min	99 %
8.	5 min	99 %



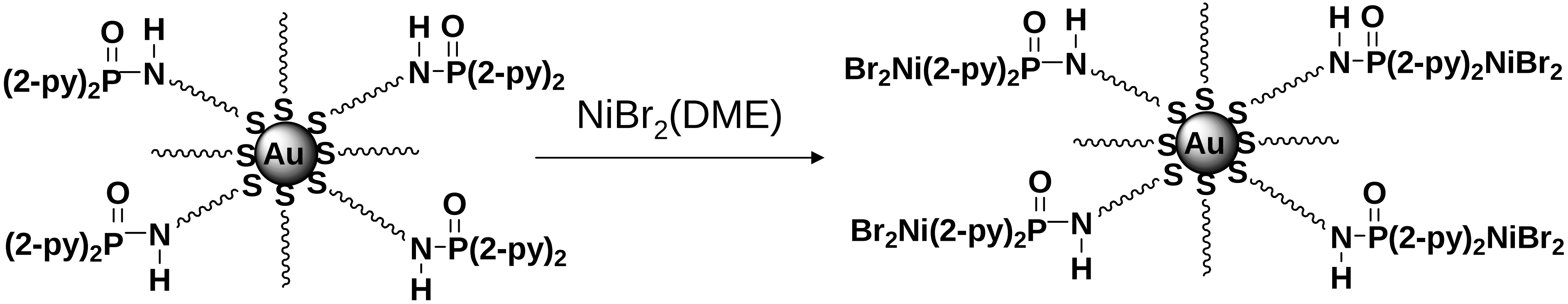
^1H NMR Solvent= $CDCl_3$ (0.01478M 4-Iodoanisole)

Near Future Work for Nickel(II) Complex

- Immobilization onto AuNPs surfaces



Cat.



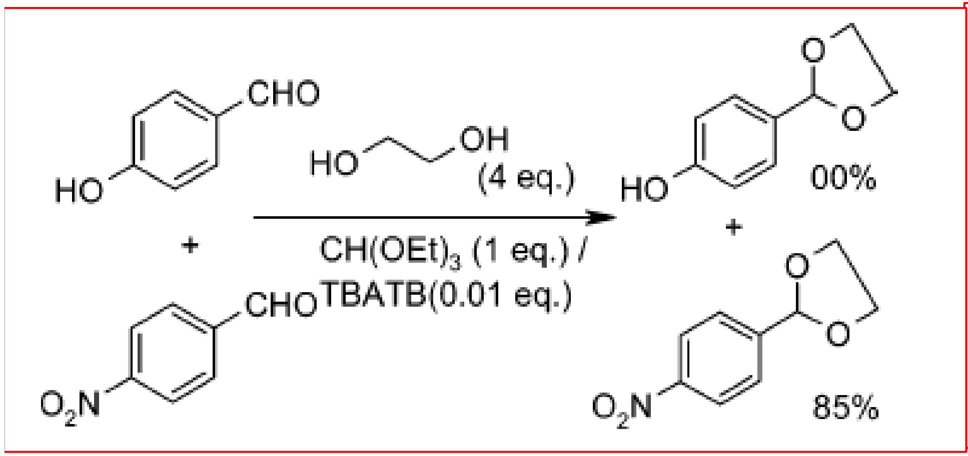
Conclusions

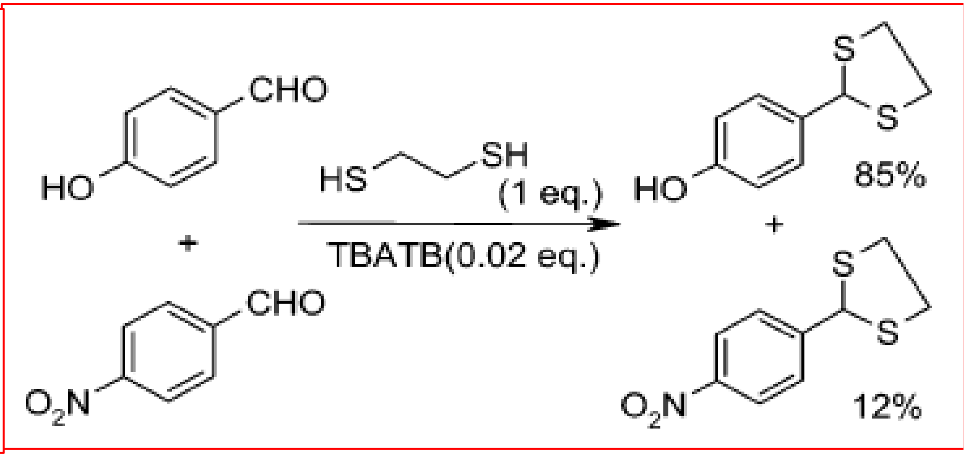
1. We have successfully synthesized an air- and water-stable and efficient catalyst { **$[HO(CH_2)_{11}NHPOpy_2]NiBr_2$** }.

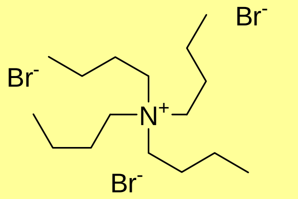
2. We use ^1H NMR、 FT-IR、EPR、SQUID and FAB-MS for structural characterization of Nickel(II) complex, we have proved the compound demonstrated that it is a paramagnetic tetrahedral compound, and we will proceed detection of Elemental Analysis (EA).

3. In Ni-catalyst series, the Nickel(II) complex only can be reused for catalytic of thioacetalization of aldehyde many times without any loss of reactivity.

Chemoselectivities in Acetalization, and Thioacetalization

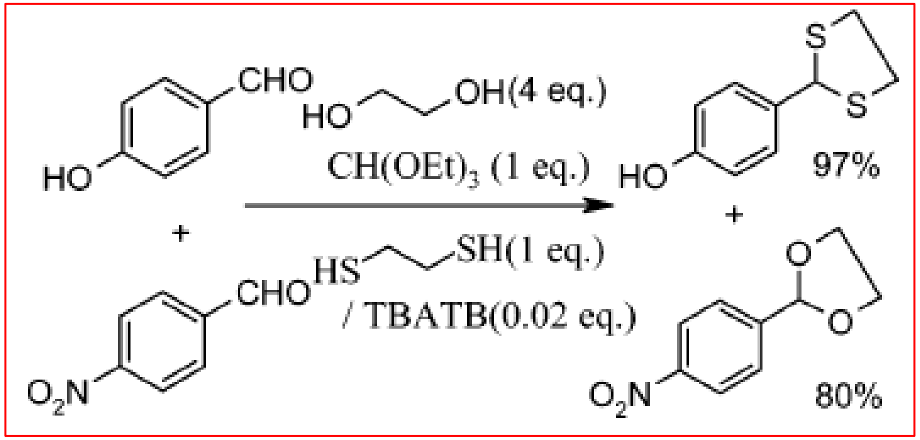






tetrabutylammonium tribromide

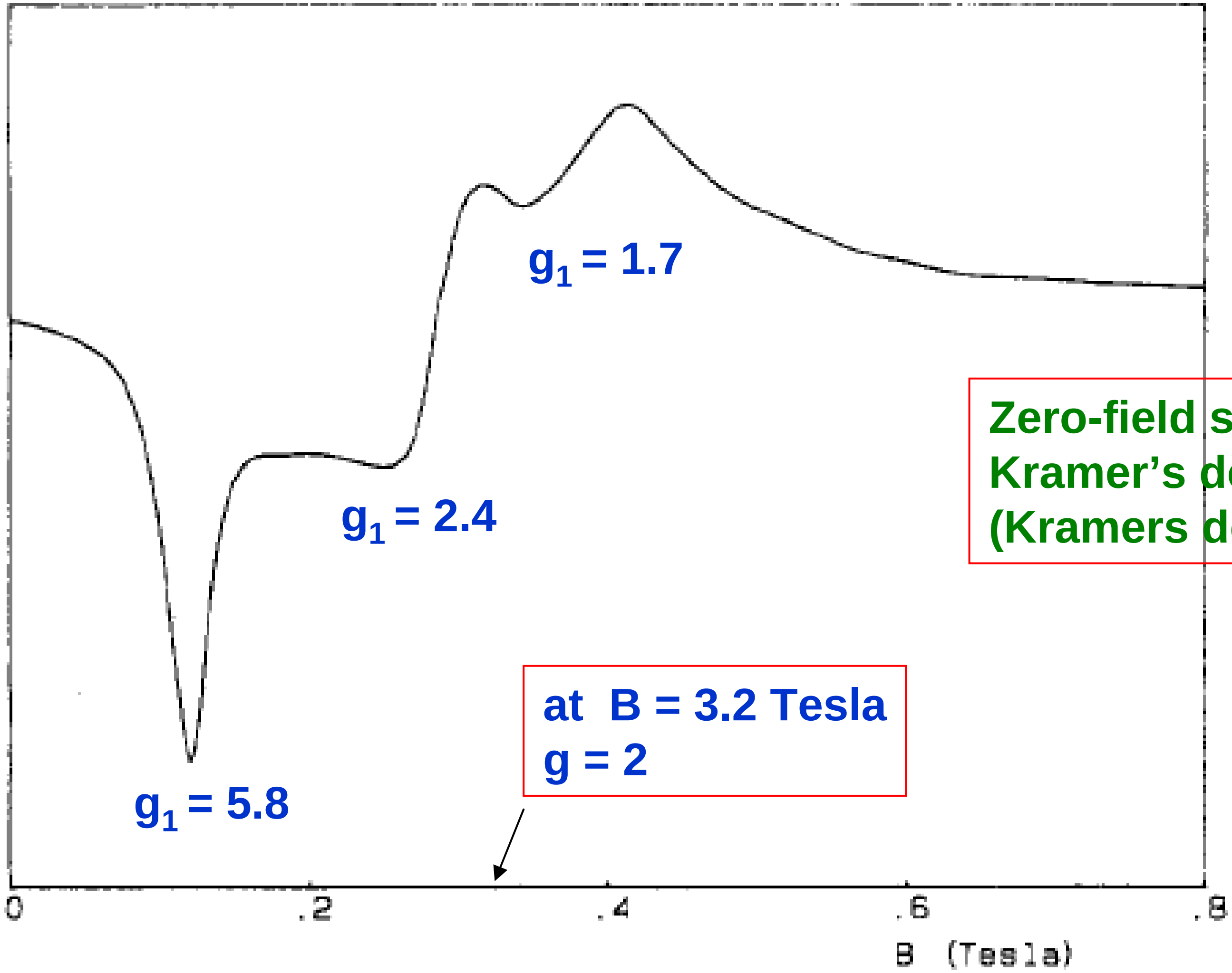
TBATB



J. Phys. Chem. A **2006,** *110,* 2181-2187

- (DME)NiCl$_2$ 5g 3549
- (DME)NiBr$_2$ 5g 4060 $ 77.3
- CoCl$_5$ 100g $ 75
- MoCl$_5$ 100g $ 130 MoO$_2$Cl$_2$ 10g $ 120

EPR of [Ni(CTH)DTBSQ]PF_6



$g_1 = 1.7$

$g_1 = 2.4$

$g_1 = 5.8$

at B = 3.2 Tesla
g = 2

Zero-field spectra and Kramer's degeneracy (Kramers doublet)

Inorganic Chemistry, **1988,** *27*, 2831-2836