Ⅰ.Studies of Molecular Pd(II) and Cu(I) Complex Catalysts and Ionic Liquid Catalysts in Homogeneous and Inter-face Systems.

Ⅱ.Coordination Chemistry of Ag(I) with Tripodal Pyridylphosphite and Pyridylphosphine Oxide Ligands.

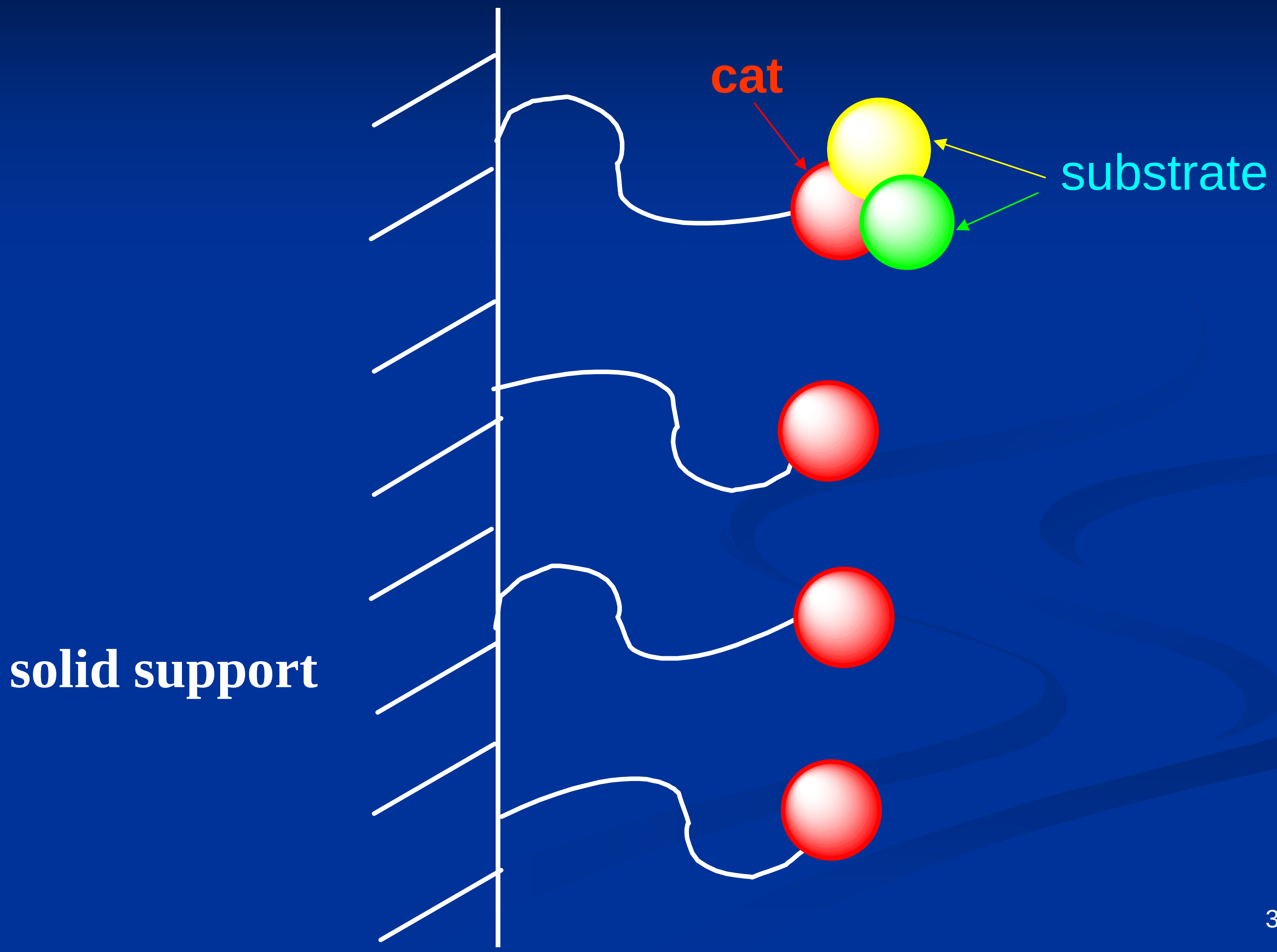
Lin Yu-Yun

2008 / 06 / 17

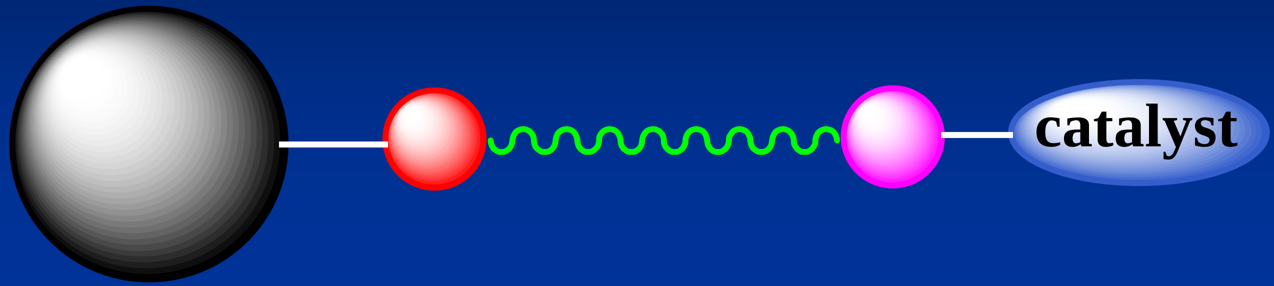
Types of Catalysts

Characteristics of catalysts	Homogenous	Heterogeneous	Hybrid
Cat. structure	Known	Unknown	Known
Catalyst modification	Easy	Difficult	Easy
Activity	High	Low	High
Selectivity	High	Low	High
Conditions of catalysis	Mild	Harsh	Mild
Poisoning of cat.	High risk	Low risk	Low risk
Mechanical strength	Low	High	High
Cat. stabilities	Low	High	High
Separation & recycle of cat.	Difficult	Easy	Easy
Industrialization	Difficult	Accessible	Accessible

Hybrid Catalyst

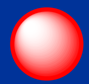


Catalyst Design

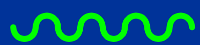


nanoparticles
with controllable solubility

soluble metal complex

 functional groups

 coordinationl ligands

 space linker

Green Chemistry

01. Prevention
02. Less Hazardous Chemical Syntheses
03. Design for Degradation
04 Design Safer Chemicals
05. Safer Solvents and Auxiliaries
06. Atom Economy
07. Design for Energy Efficiency
08. Use Renewable Feedstocks
09. Reduce Derivatives
10. Catalysis
11. Real-Time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Anastas, P. T.; Warner, J. C. *Green Chemistry : Theory and Practice*, Oxford University Press, oxford, 1998.

Motivation

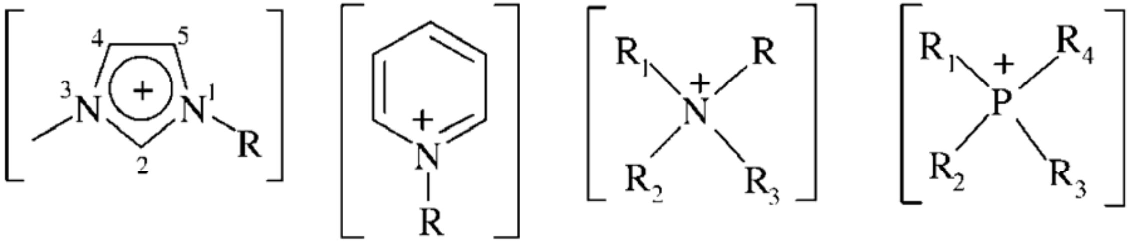
- **Recyclable Catalysts and Their Applications in both Homogeneous and Hybrid Systems**

- **Greener Solvents**
  r. t. ionic liquids

- **Energy Saving**
  catalysis under microwave flash heating to replace conventional thermal heating

Green Solvent Alternatives - Ionic Liquids

Most commonly used cations:



1-alkyl-3-methyl-imidazolium	*N*-alkyl-pyridinium	Tetraalkyl-ammonium	Tetraalkyl-phosphonium

($R_{1,2,3,4}$ = alkyl)

Some possible anions:

water-insoluble	⟶	water-soluble
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[(CF_3SO_2)_2N]^-$	$[CF_3SO_3]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$		Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains:

ethyl, butyl, hexyl, octyl, decyl

Seddon, K. R.; Stark A., Torres M. J. *Pure Appl. Chem.*, **2000,** *72*, 2275-2287.

Coordinative Characteristics and acidity of Various Anions

basic/ strongly coordinating	neutral/ weakly coordinating	acidic/ coordination	acidic/non-coordinating
AcO^-	SbF_6^-		$Al_2Cl_7^-$
NO_3^-	BF_4^-		
	PF_6^-	$AlCl_4^-$	$Al_3Cl_{10}^-$
SO_4^{2-}		$CuCl_2^-$	$Cu_2Cl_3^-$
Cl^-			$Cu_3Cl_4^-$
			HSO_4^-

Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000,** *39, 3772*-3789.

Ionic Liquids Can Be Used as

(1) Solvent

(2) Stabilizer for metal nanoparticles

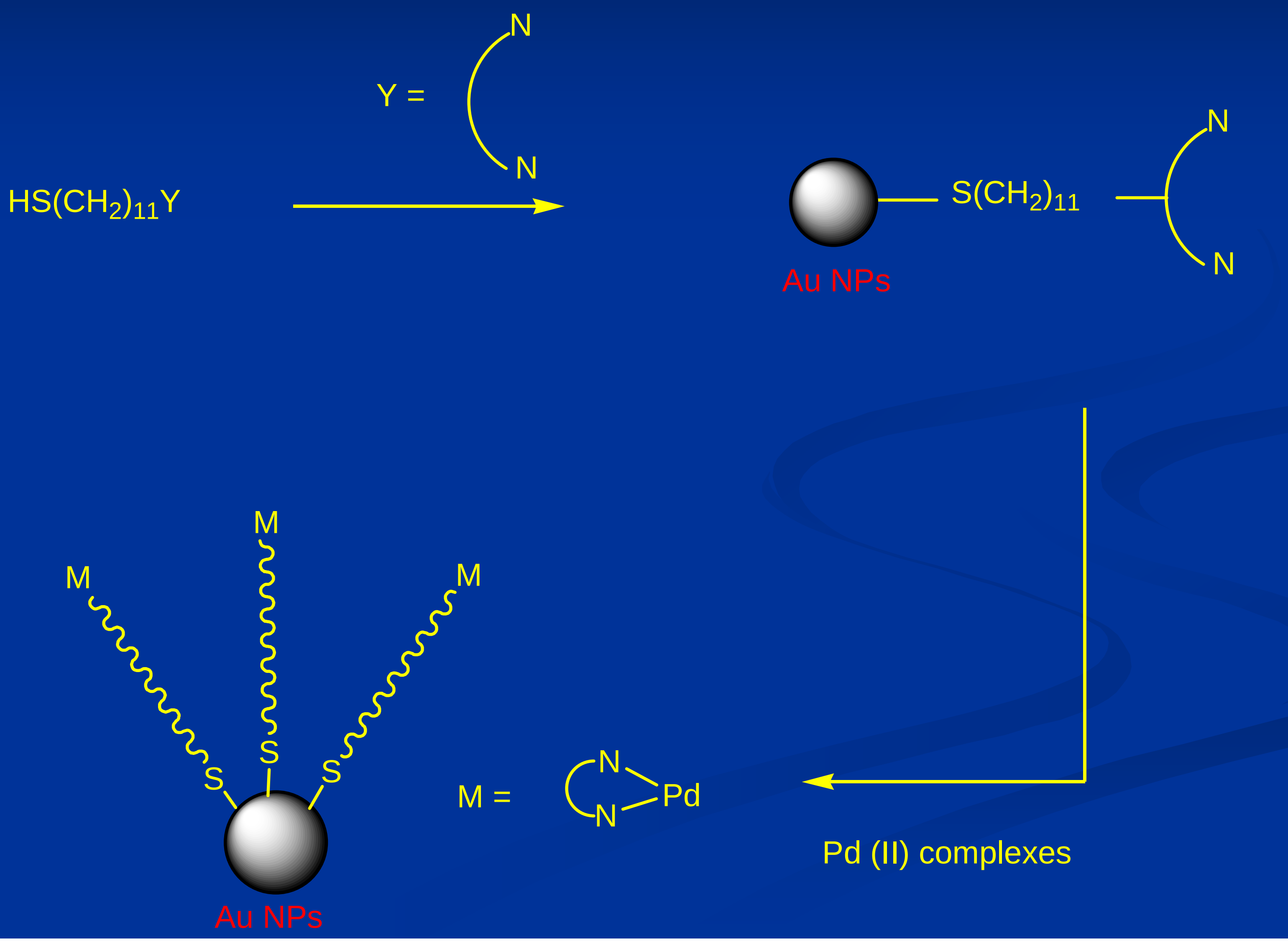
(3) Catalyst

(4) Ligand

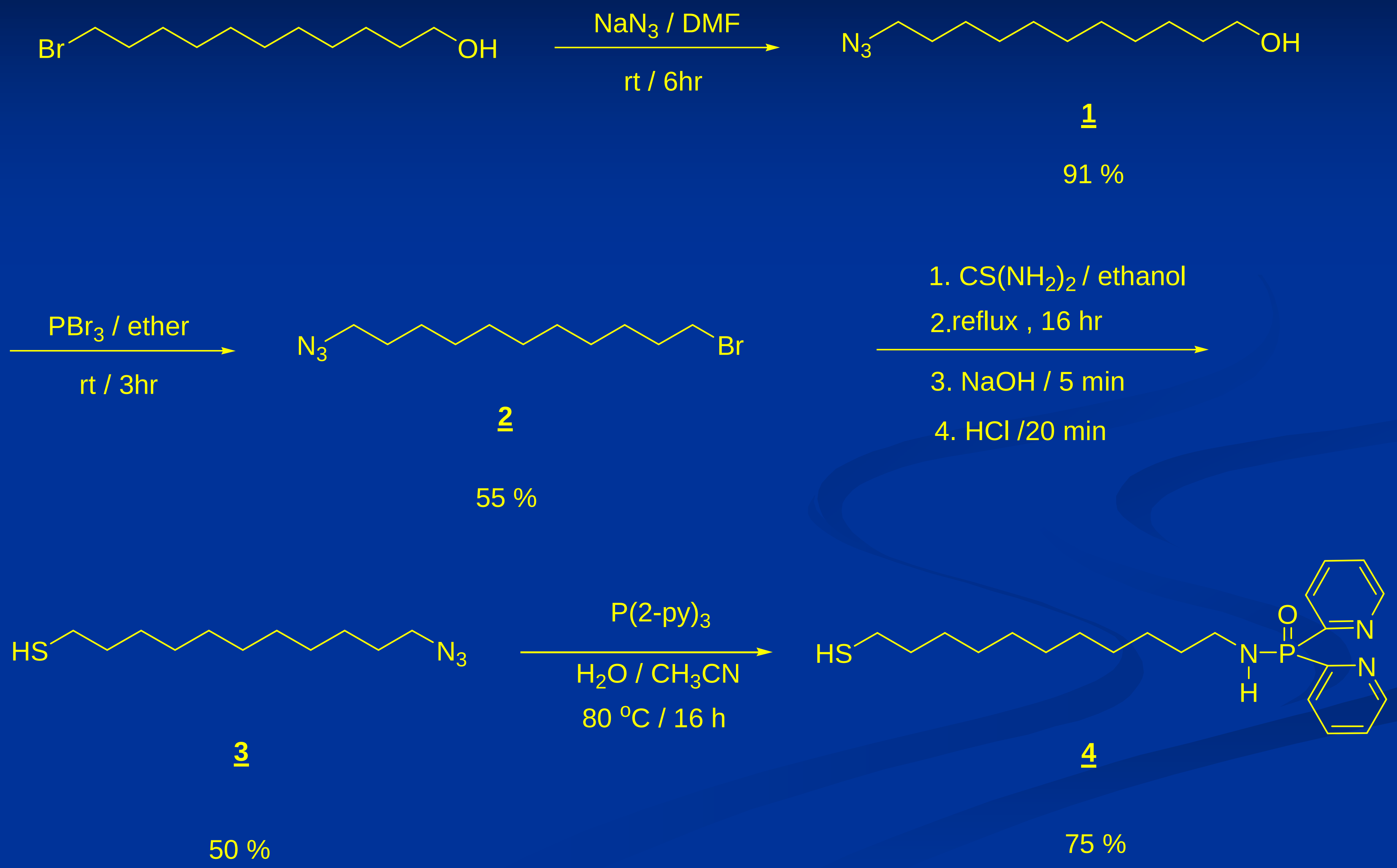
I . Studies of Molecular Pd(II) and Cu(I) Complex Catalysts and Ionic Liquid Catalysts in Homogeneous and Inter-face Systems.

Synthesis of Hybrid Pd(II) and Ionic Liquid Catalysts and Their Catalytic Applications

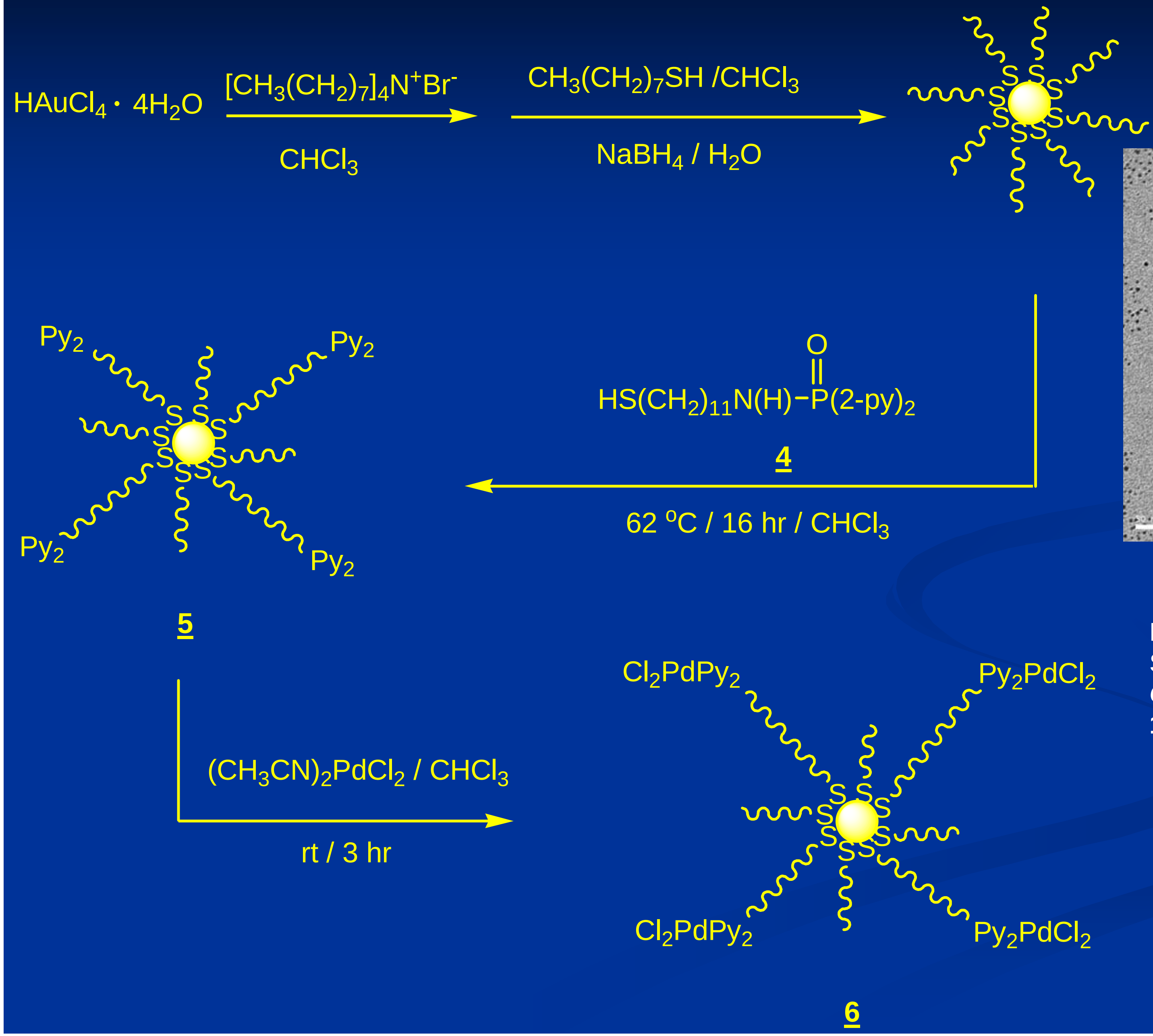
Nano-Gold Surface-Immobilized Pd(II) Complex

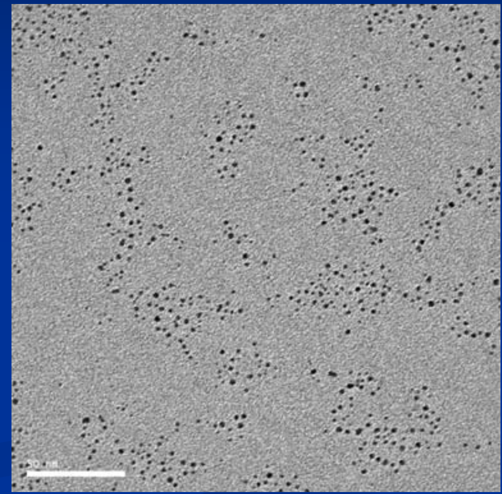


Synthesis of the Linker (4)



Synthesis of the Au-L-Pd NPs (6)

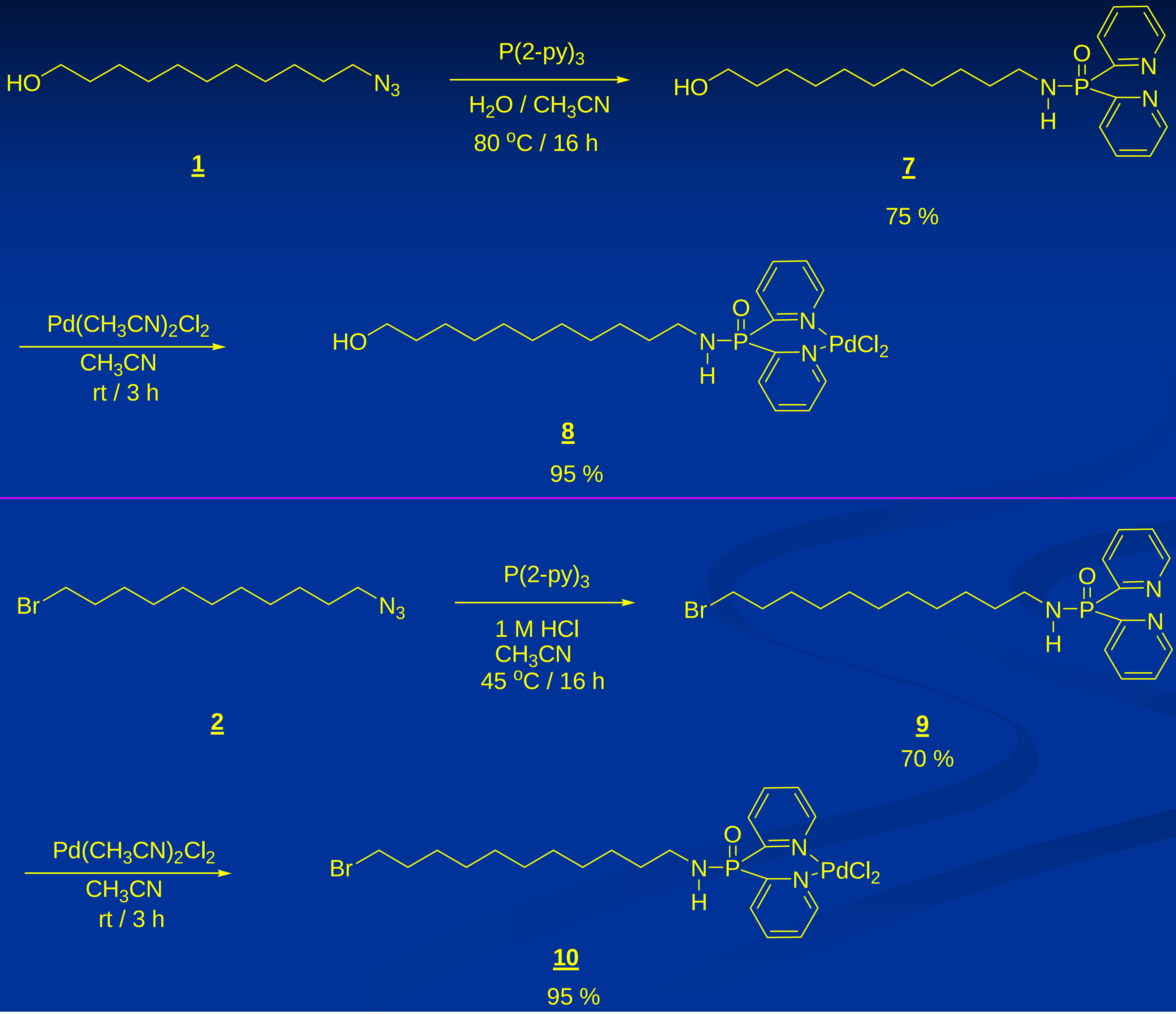




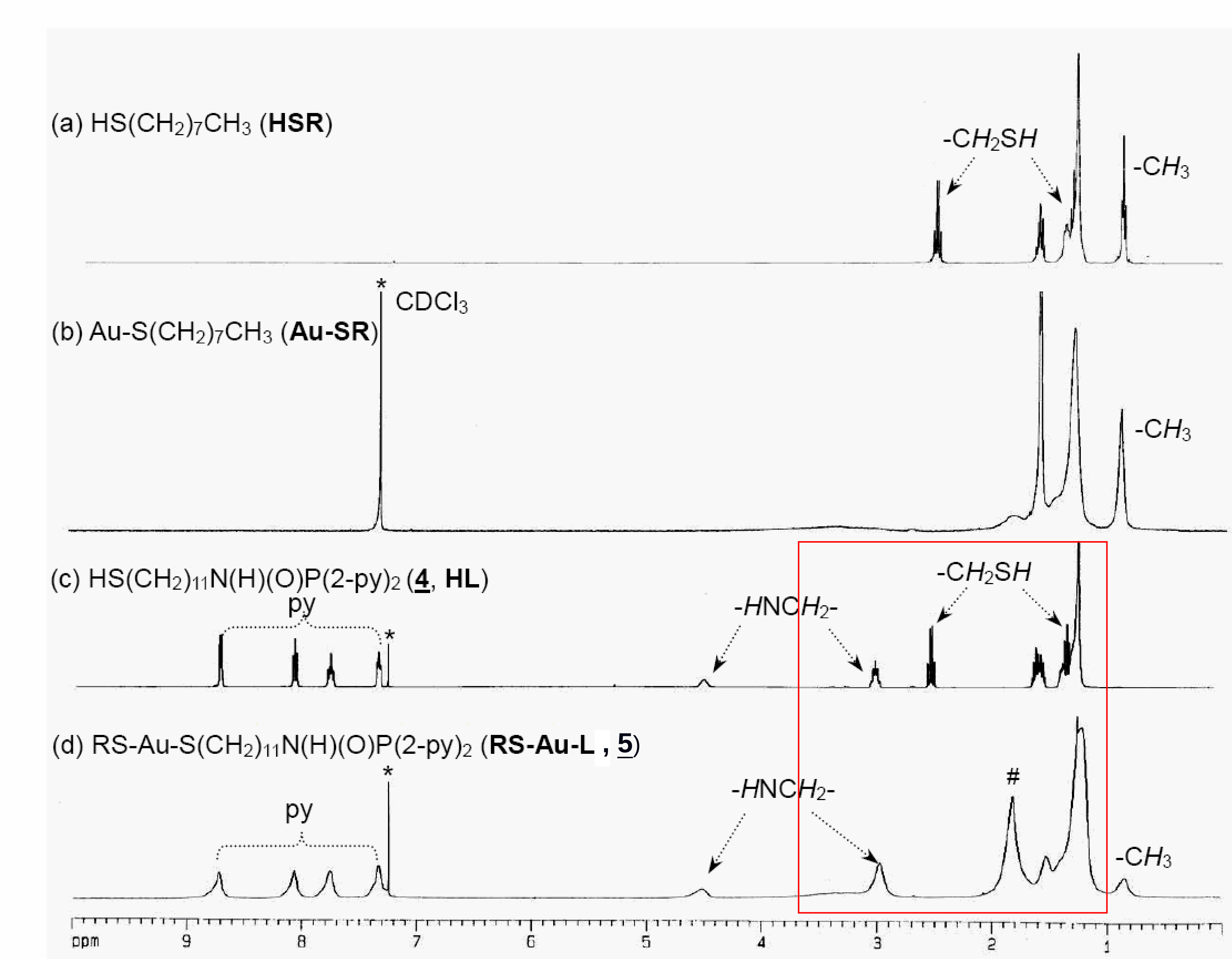
2.3 nm ± 0.1

Brust, M,; Walker, M.; Bethell, D,; Schiffrin, D, J.; Whyman, R.*J. Chem. Soc. Chem. Commun*. **1994**, 801-802.

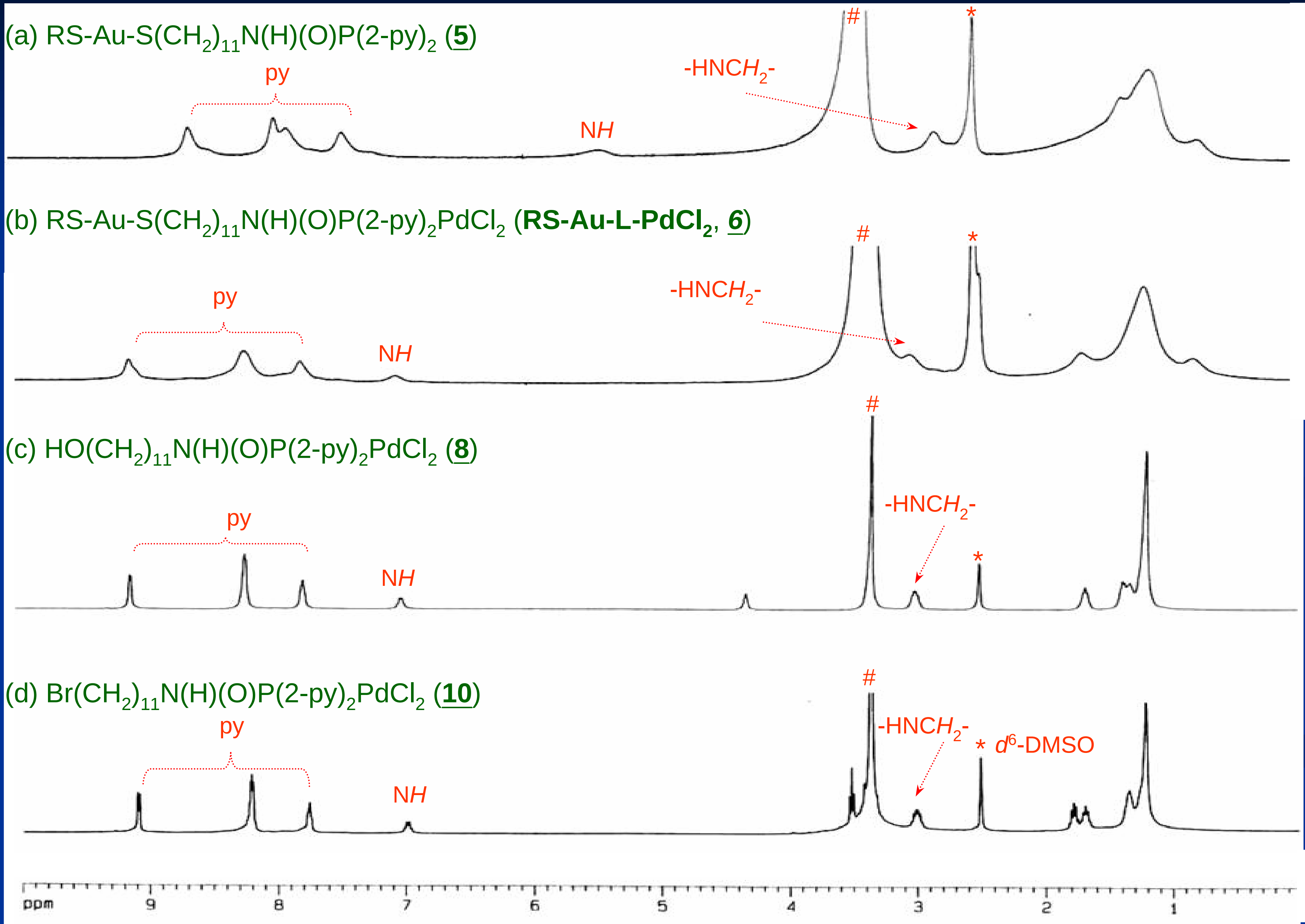
Synthesis of Pd(II) Compounds(8, 10)



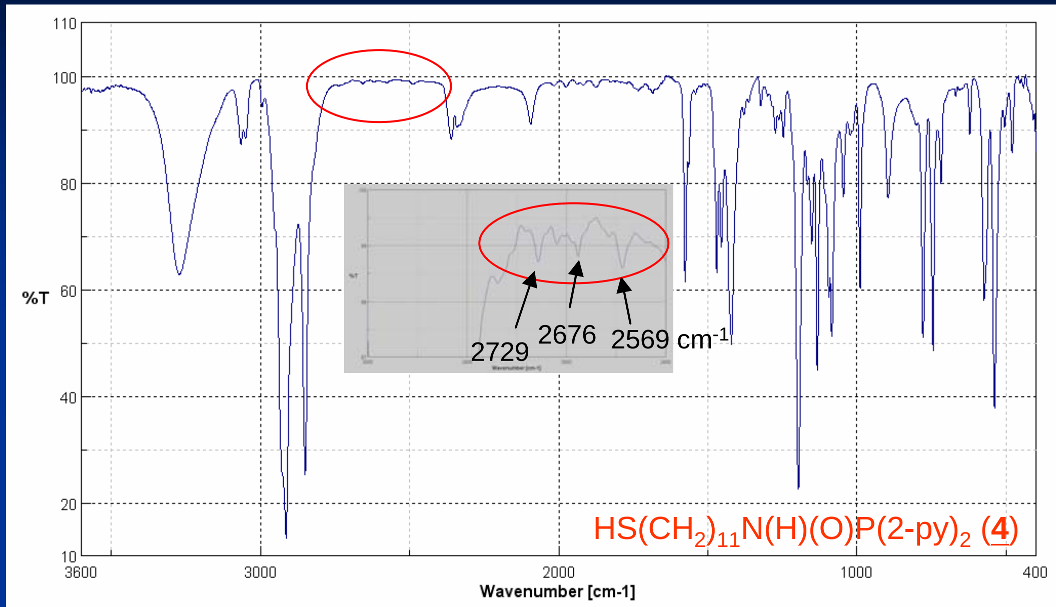
^1H NMR Spectra



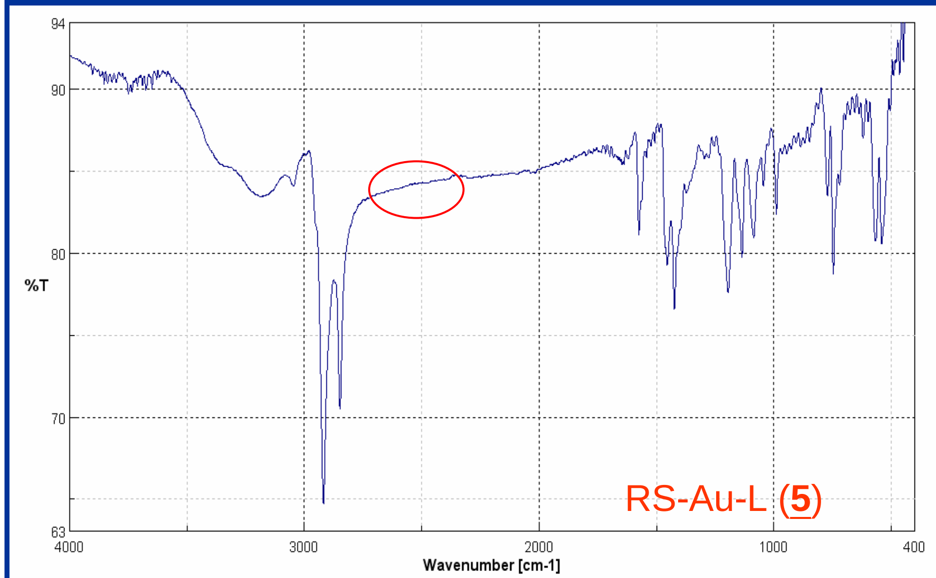
^1H NMR Spectra



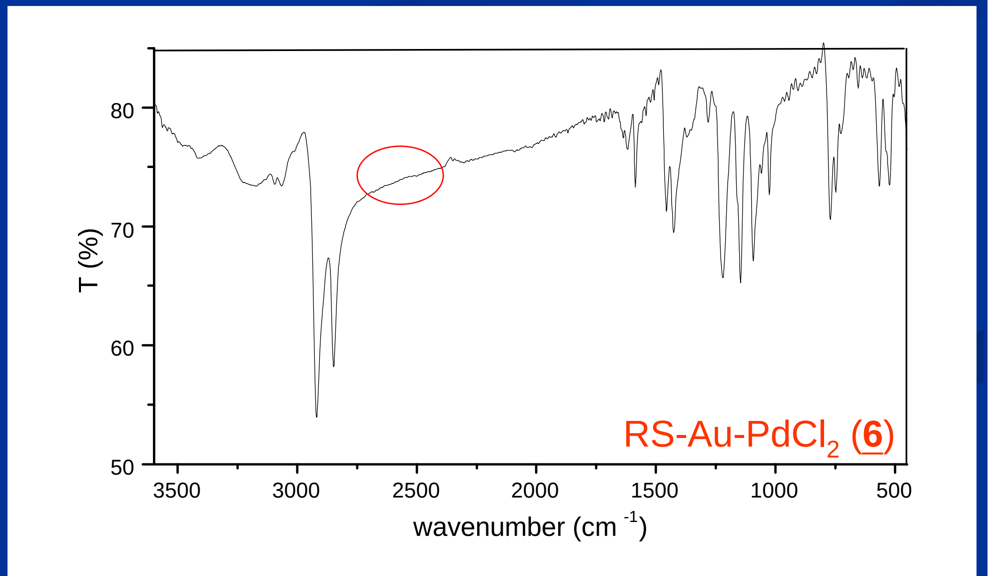
IR Spectrum



%T
Wavenumber [cm-1]
2729
2676
2569 cm-1
HS(CH2)11N(H)(O)P(2-py)2 (4)

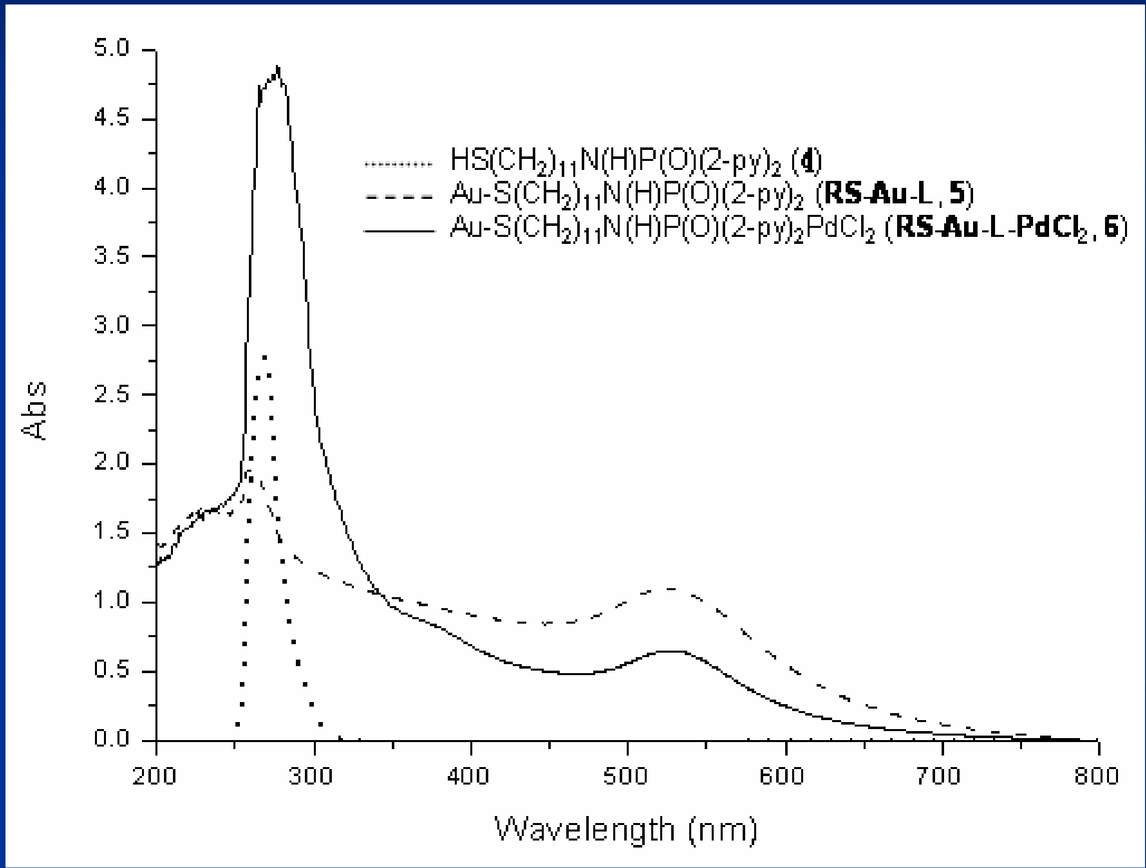


%T
Wavenumber [cm-1]
RS-Au-L (5)

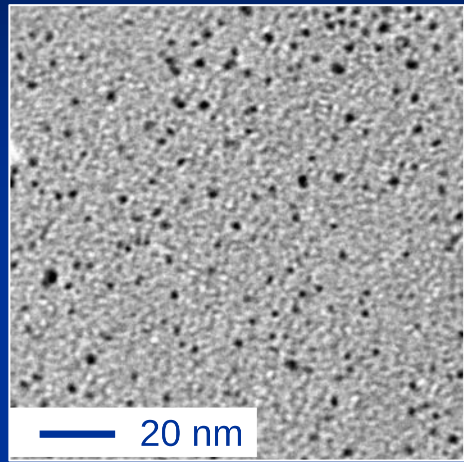


T (%)
wavenumber (cm -1)
RS-Au-PdCl2 (6)

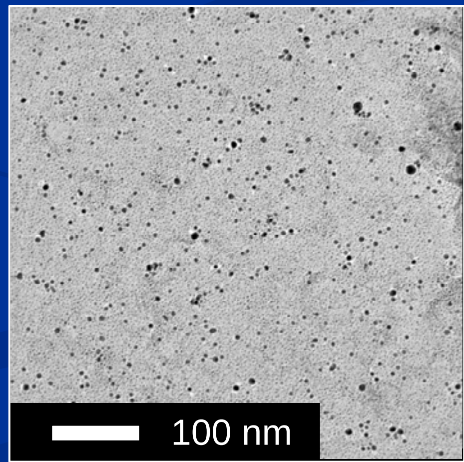
Uv-vis Spectra and TEM Images



UV spectra of the bipyridyl-substituted spacer ligand **4**, RS-Au-L **5** and RS-Au-L-PdCl$_2$ **6** particles in DMSO.

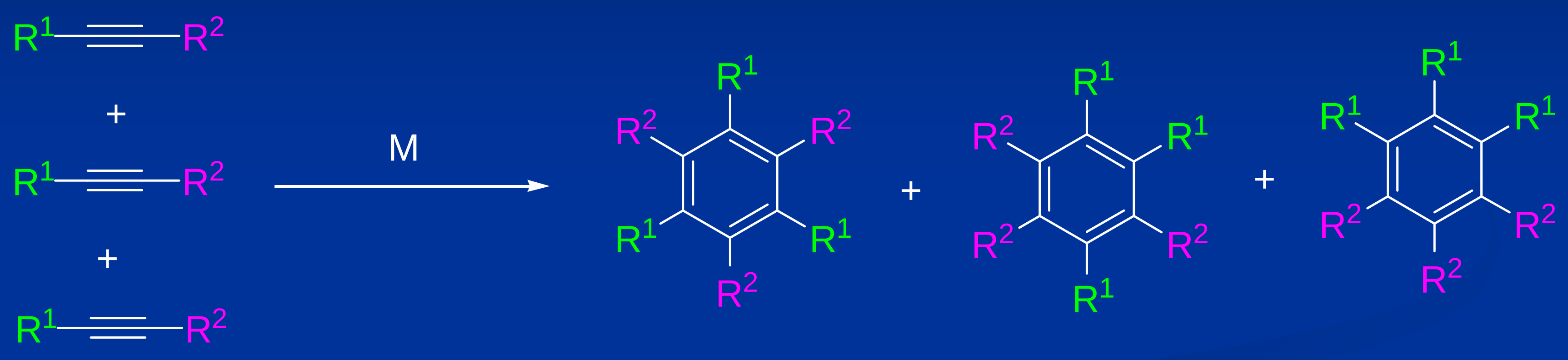


Au-L **(5),** D = 3.9 ± 0.4 nm



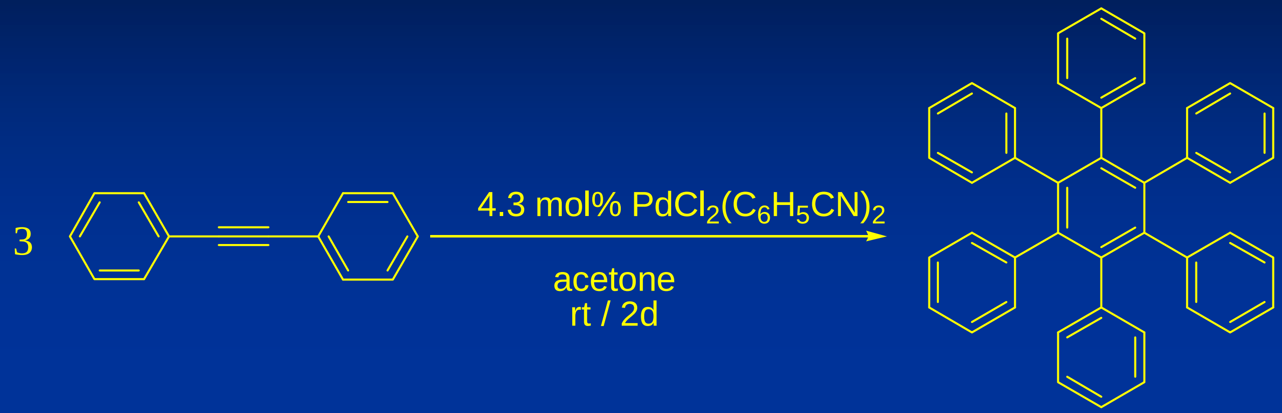
Au-L-Pd **(6),** D = 4.8 ± 0.1 nm

[2 + 2 + 2] Alkyne Cyclotrimerization



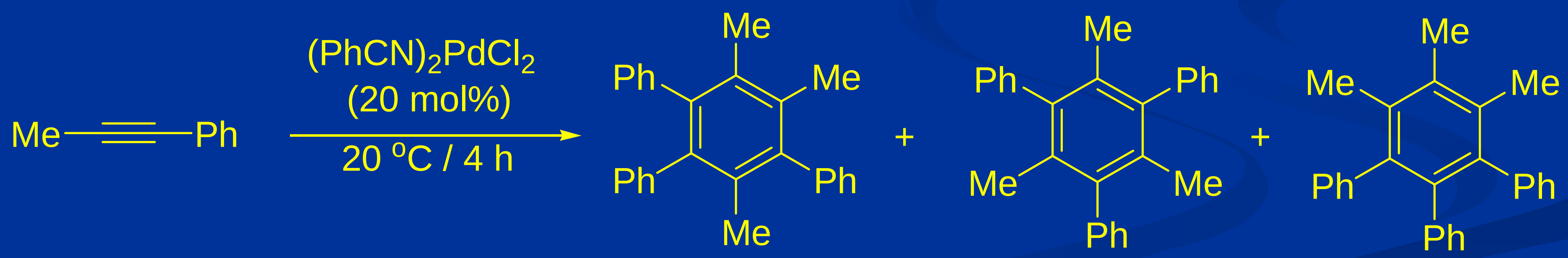
Reppe, W.; Scjweclemdiek, W. J. *Justus Liebigs*. *Ann*. *Chem*. **1948**, *560*, 104-116.

$(PhCN)_2PdCl_2$ Catalyzed [2 + 2 + 2] Alkyne Cyclotrimerization



85 %

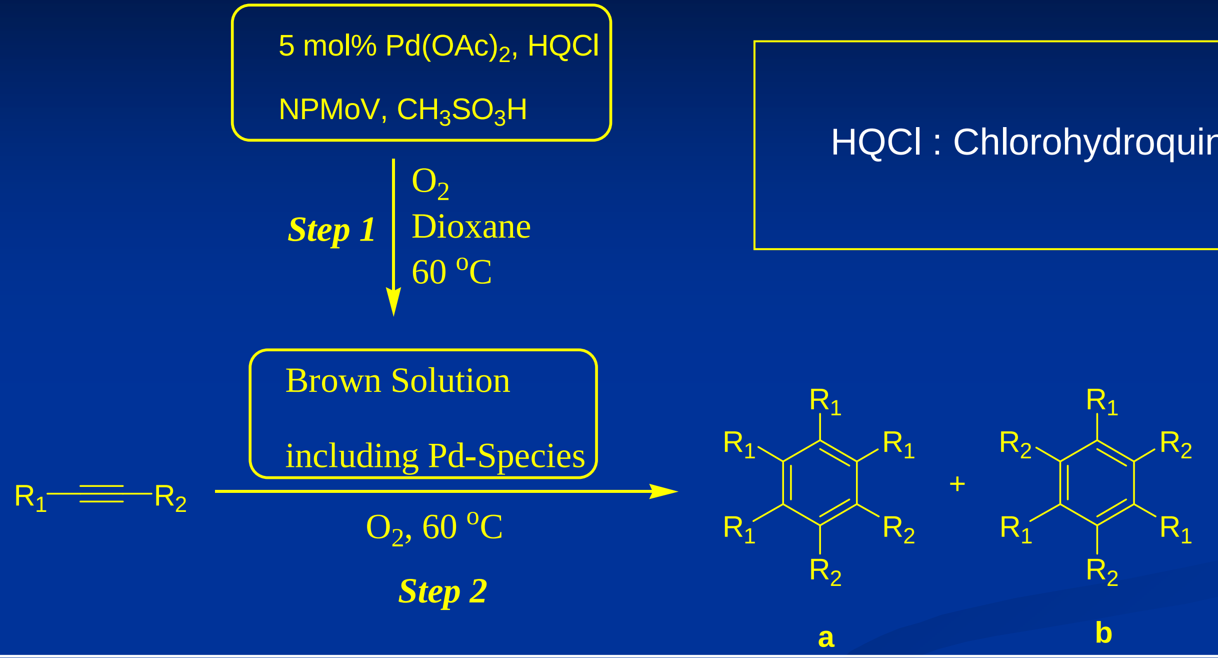
Blomquist, A. T.; Maitlis, P. M. *J. Am. Chem. Soc*. **1962**, *84*, 2329-2334.



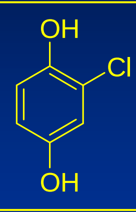
58 % 39 % 3 %

Dietl, H.; Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc*. **1970**, *92*, 2276-2285.

Pd(OAc)$_2$ / HQCl / NPMoV / O$_2$ Catalyzed [2 + 2 + 2] Alkyne Cyclotrimerization



HQCl : Chlorohydroquinone

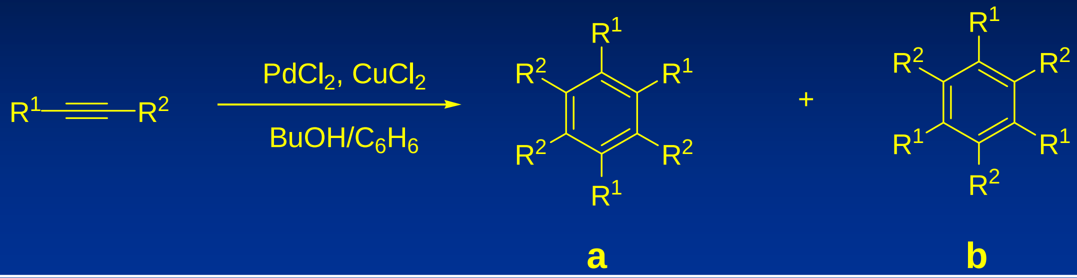


Run	Alkyne	Temp. / °C	Time / h	Product (Yield %)
1	$R_1 = R_2 = C_2H_5$	60	1	100
2	$R_1 = R_2 = C_6H_5$	60	5	54
3	$R_1 = n\text{-}C_4H_9$, $R_2 = C_2H_5$	60	1	72 (**a**), 8 (**b**)
4	$R_1 = C_2H_5$, $R_2 = CH_3$	60	2	50 (**a** + **b**)
5	$R_1 = t\text{-}C_4H_9$, $R_2 = H$	60	1	0 (**a**), 63 (**b**)
6	$R_1 = n\text{-}C_6H_{13}$, $R_2 = H$	60	1	complex mixture

Alkyne (2 mmol) was added to preactivated Pd(II) obtained by a mixture of Pd(OAc)$_2$ (5 mol%), HQ-Cl (20 mol%), NPMoV (35 mg), CH_3SO_3H (20 mg) in dioxane (10 mL) under O_2 at 60°C for 2 h and stirred at 60°C for 1-5 h

Yotota, T,; Sakurai, Y,; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett*. **1997**, *38*, 3923-3926.

$PdCl_2$ / $CuCl_2$ Catalyzed [2 + 2 + 2] Alkyne Cyclotrimerization

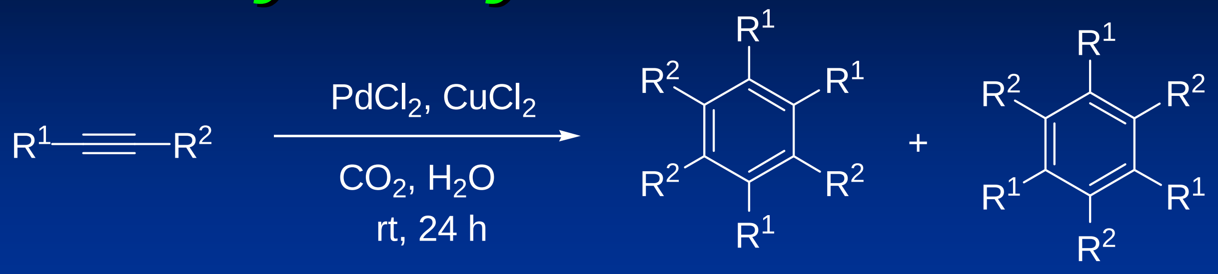


run	R^1	R^2	time (h)	temp. (°C)	Yield (%)[b]	
1	Ph	Ph	34	60	*c*	
2[d]	Ph	Ph	34	60	*c*	
3[d]	C_5H_{11}	H	12	40	0	← No $CuCl_2$ was added
4	C_5H_{11}	H	12	40	78 (**b**)	
5[e]	C_5H_{11}	H	12	40	41 (**b**)	← No BuOH was added
6[f]	C_5H_{11}	H	12	40	35 (**b**)	← Only BuOH was used as solvent
7	C_6H_{13}	H	12	40	70 (**b**)	
8	*t*-Bu	H	12	40	100 (**b**)	
9[d]	Ph	H	12	40	*c*	
10	Ph	H	12	40	*c*	
11	*p*-MePh	H	15	40	95 (**b**)	
12	*p*-ClPh	H	15	40	90 (**b**)	
13	Ph	Me	12	40	80 (**a**)	

[a] Reaction conditions: Alkyne (1 mmol), $PdCl_2$ (10 mg), $CuCl_2$ (2 mmol), and BuOH/benzene (0.6/10, 10.6 mL). [b] Isolated yields.
[c] The products are red oils and unidentified. [d] No $CuCl_2$ was added.[e] No BuOH was added. [f] Only BuOH was used as solvent.

Li, J.; Jiang, H.-F.; Chen, M. *J. Org. Chem.* **2001,** *66,* 3627-3629.

$PdCl_2$ / $CuCl_2$ / CO_2 Catalyzed [2 + 2 + 2] Alkyne Cyclotrimerization in Water

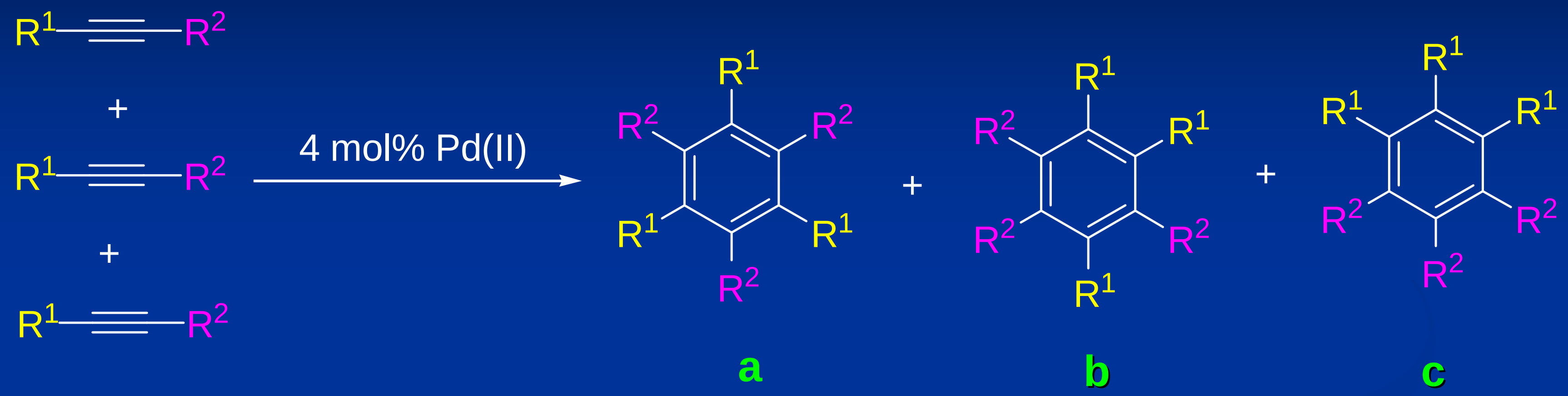


Entry	R^1	R^2	Isolated yield (%)	
1[b]	Ph	H	7(**b**) + *c*	← absence of $CuCl_2$ and CO_2
2[c,d]	Ph	H	31(**b**) + *c*	← absence of CO_2
3	Ph	H	90 (**b**)	
4	*p*-MeC_6H_4	H	95 (**b**)	
5	Ph	Me	91 (**a**)	
6	C_5H_{11}	H	87 (**b**)	
7[e]	C_5H_{11}	H	*c*	← absence of $CuCl_2$
8	C_3H_7	C_3H_7	99 (**b**)	

[a]Reaction conditions: Alkyne 1 (1 mmol), $PdCl_2$ (5 mol%),$CuCl_2$ (2 mmol), CO_2 (1.0 MPa), and H_2O (5 mL) at room temperature for 24 hr. [b]In the absence of $CuCl_2$ and CO_2.[c]The products were red oils and unidentified. [d]In the absence of CO_2. [e]In the absence of $CuCl_2$.

Li, J.-H.; Xie, Y.-X. *Synth. Commun*. **2004**, *34*, 1737-1743.

Au NPs-Supported Pd(II) Catalyzed [2 + 2 + 2] Alkyne Cyclotrimerization Reactions[a]



Substrates :

R1	**R2**
Me	Me
Et	Et
n-Pr	*n*-Pr
Ph	Ph
Me	Et
Me	*n*-Pr
H	Pr

Catalysts : Au-L-$PdCl_2$ (**6**)
$HO(CH_2)_{11}PdCl_2$ (**8**)
$Br(CH_2)_{11}PdCl_2$ (**10**)
$Pd(CH_3CN)_2Cl_2$
$Pd(PhCN)_2Cl_2$
SiO_2-$PdCl_2$

Solvent **:** $CDCl_3$, THF, [bmim]PF_6

Energy Source **:** Thermal, MW

entry	*alkyne*		*catalyst*	*solvent*	*T* (ºC)	*time* (hr)	*conversion*[c] (%)	*product ratio*[e] *a*:*b*:*c*
	R^1	R^2						
1	Me	Me	**6**	$CDCl_3$	27	3.0	99	
2	Et	Et	**6**	$CDCl_3$ $CDCl_3$ THF	27 62 62	0.5 0.167 0.25	99 99 99	
3	^{n}*Pr*	^{n}*Pr*	**6**	$CDCl_3$ $CDCl_3$ THF	27 62 62	0.667 0.5 0.5	99 99 99	
4	Ph	Ph	**6**	$CDCl_3$	62	24	60	
5	Me	Et	**6**	$CDCl_3$	27 50	3.0 1.0	99 99	33:67:0 33:67:0 (35:65:0)
6	Me	^{n}*Pr*	**6**	$CDCl_3$	27 62	1.5 1.0	99 99	18:63:19 18:60:22 (17:61:22)
7	H	Ph	**6**	$CDCl_3$	27 62	5.5 3.0	99 99	22:78:0 19:81:0

[a]*Reaction conditions: alkyne (0.075 mmol) in $CDCl_3$* (1 mL), catalyst loading = 4 mol%. [b]*Reaction conditions: alkyne (0.56 mmol) in $CDCl_3$* (3 mL), catalyst loading = 4 mol%. [c]*Conversions were determined by* ^{1}H-NMR spectroscopy. [d]*Products were purified and isolated by flash chromatography on SiO_2* with hexane/ethyl acetate. [e]*Isomers ratios were determined by GC.*

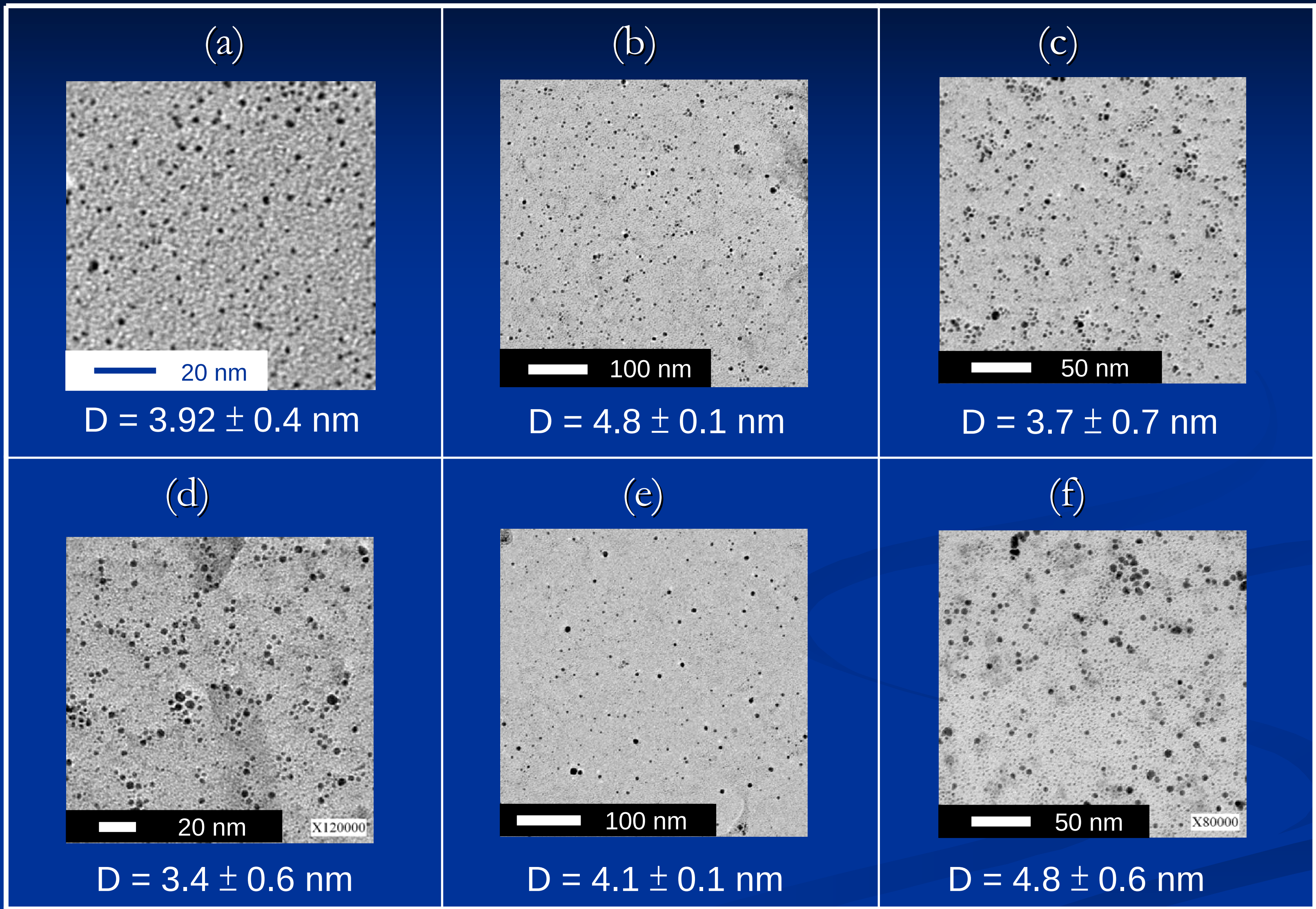
8	Et	Et	SiO_2-$PdCl_2$ [b]	$CHCl_3$	27 62 27 62	0.5 0.5 36 16	6 23 88 [d] 91 [d]	
9	Et	Et	**<u>8</u>**	$CDCl_3$	27 62	0.5 0.167	NR NR	
10	Et	Et	**<u>10</u>**	$CDCl_3$	27 62	0.5 0.17	NR NR	
11	Et	Et	$Pd(PhCN)_2Cl_2$	$CDCl_3$	27 62	0.5 0.167	99 99	
12	Et	Et	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	27 62	0.5 0.5	95 99	
13	Ph	Ph	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	62	24	56	
14	${}^{n}Pr$	${}^{n}Pr$	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	27	0.67	50	
15	Me	Et	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	27	3.0	47	35:65:0
16	Me	${}^{n}Pr$	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	27 62	1.5 1.0	40 70	19:62:19 18:63:19
17	H	Ph	$Pd(CH_3CN)_2Cl_2$	$CDCl_3$	27	5.5	75	17:83:0

[2 + 2 + 2] Alkyne Cyclotrimerization Under MW

entry	alkyne R¹	alkyne R²	catalyst	solvent	time (min)	conversion[d] (%)	product ratio[e] **a**:**b**:**c**
1	Et	Et	**6**	$bmimPF_6$	1.5	>99	
2	^{n}Pr	^{n}Pr	**6**	$bmimPF_6$	2.0	>99	
3	Ph	Ph	**6**	$bmimPF_6$	10	32	
4	Me	Et	**6**	$bmimPF_6$	2.0	>99	29:71:0
5	Me	^{n}Pr	**6**	$bmimPF_6$	3.0	>99	22:75:3
6	H	Ph	**6**	$bmimPF_6$	5.0	>99	21:79:0
7	Et	Et	$Pd(CH_3CN)_2Cl_2$	$bmimPF_6$	1.5	53	
8	^{n}Pr	^{n}Pr	$Pd(CH_3CN)_2Cl_2$	$bmimPF_6$	2.0	65	
9	Me	Et	$Pd(CH_3CN)_2Cl_2$	$bmimPF_6$	2.0	40	35:65:0
10	Me	^{n}Pr	$Pd(CH_3CN)_2Cl_2$	$bmimPF_6$	3.0	68	25:73:2
11	H	Ph	$Pd(CH_3CN)_2Cl_2$	$bmimPF_6$	5.0	75	20:80:0
12	Et	Et	**6**	THF[b]	5.0	98	
13	^{n}Pr	^{n}Pr	**6**	THF[b]	7.0	99	
14	Me	Et	**6**	THF[c]	8.5	99	29:71:0
15	Me	^{n}Pr	**6**	THF[b]	10	99	55:45:0

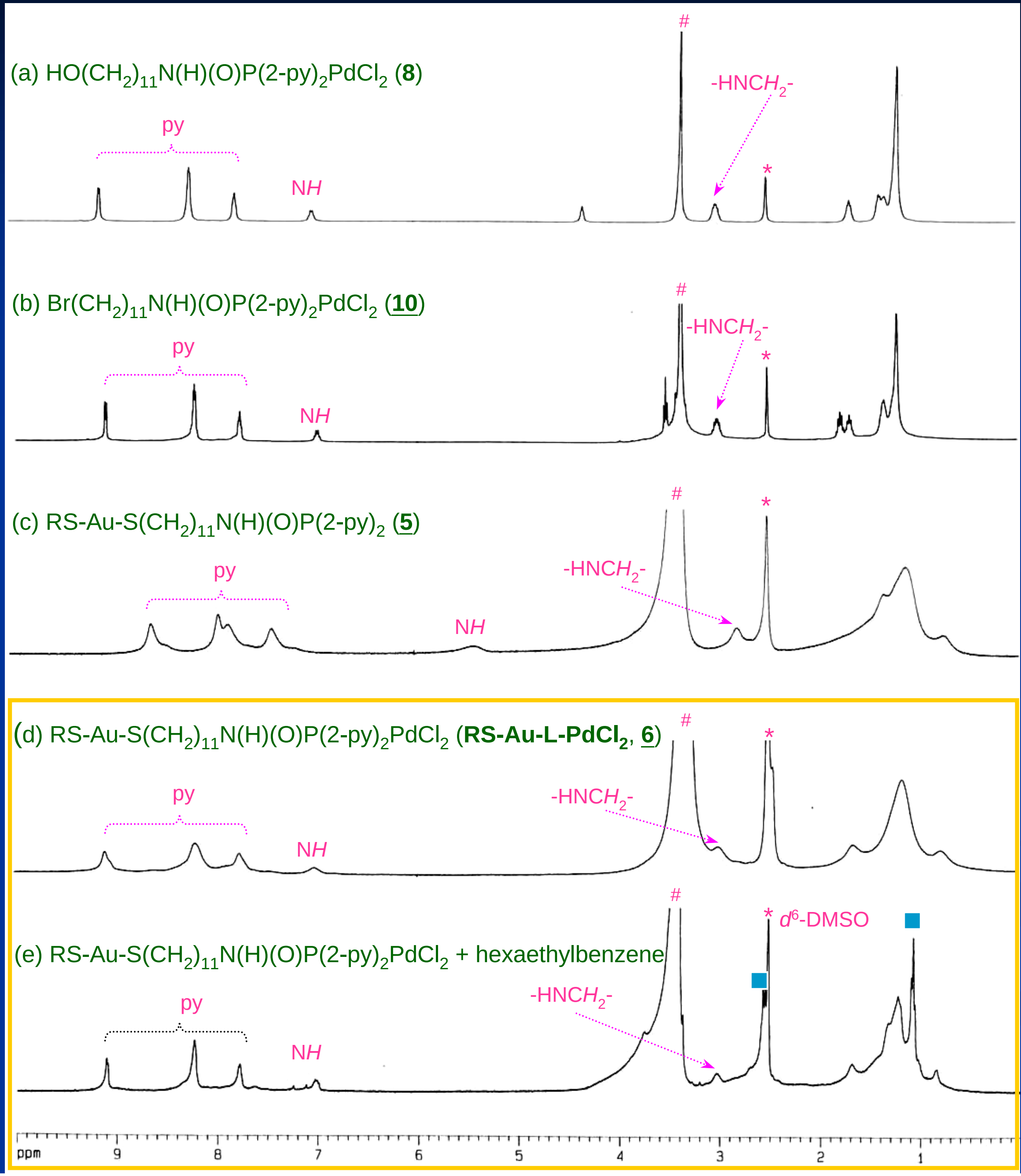
[a]reaction conditions: alkyne (0.075 mmol) in $bmimPF_6$ or THF (1 mL), catalyst loading = 4 mol% under 300 W MW irradiation. [b]under MW irradiation (max. 300 W) and a preset temperature of 62 °C. [c]under MW irradiation (max. 300 W) and a preset temperature of 50 °C. [d]Conversions were determined by 1H-NMR spectroscopy. [e]Products were purified and isolated by flash chromatography on SiO2 with hexane/ethyl acetate (10/1) as eluent and isomers ratios were determined by GC-MS.

TEM Images

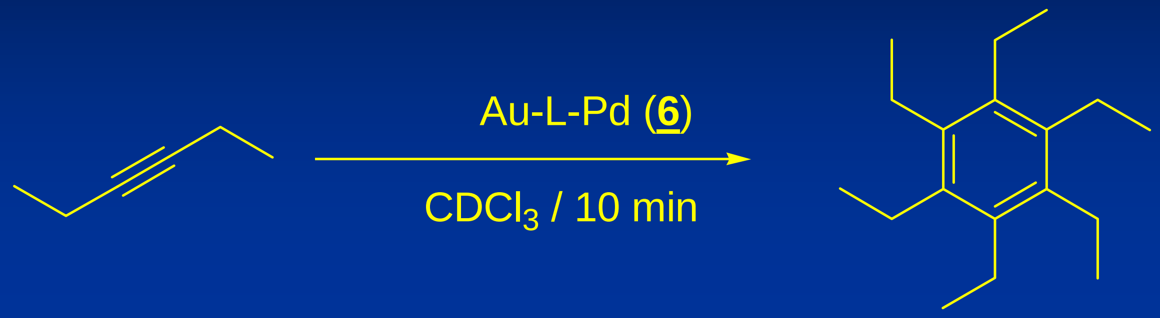


(a) RS-Au-L NPs **5**; (b) RS-Au-L-PdCl2 NPs **6**; (c) Au NPs **6** after catalysis at rt for 30 min; (d) Au NPs **6** after catalysis at 62 ^{o}C for 10 min; (e) Au NPs **6** after catalysis under 300 W microwave conditions for 5 min, where RS = $S(CH_2)_7CH_3$; L = $SCH_2(CH_2)_9CH_2NHP(O)(2\text{-}py)_2$. (f) Au NPs **6** after reused at rt . [28]

^{1}H NMR Spectra



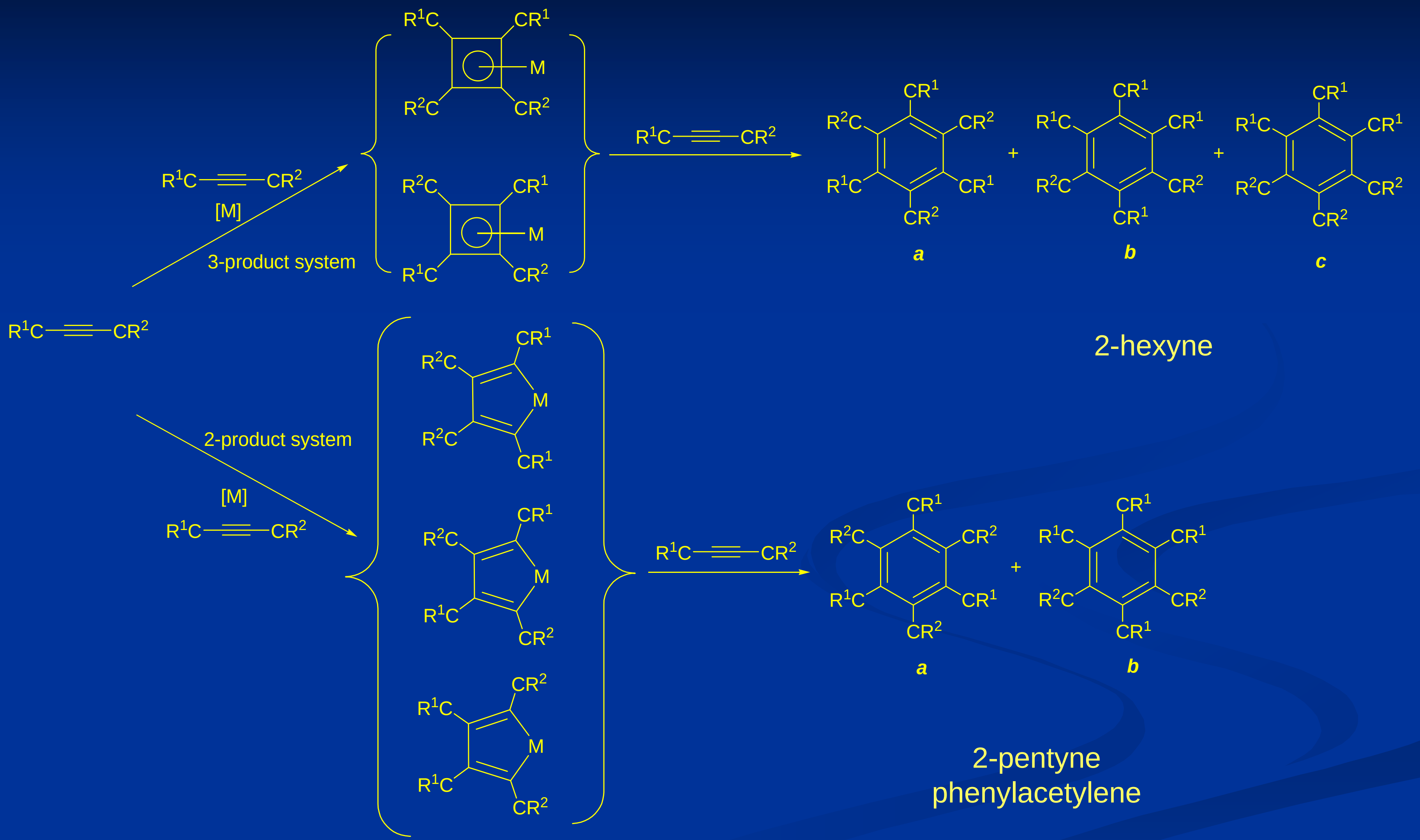
Reuse of Cat. 6 toward [2+2+2] Alkyne Cyclotrimerization Reactions



catalyst	cycle (% conv.[b])								
	1	2	3	4	5	6	7	8	9
6	>99	>99	>99	>99	90	82	75	68	57
$Pd(CH_3CN)_2Cl_2$	>99	82	44	20	—	—	—	—	—

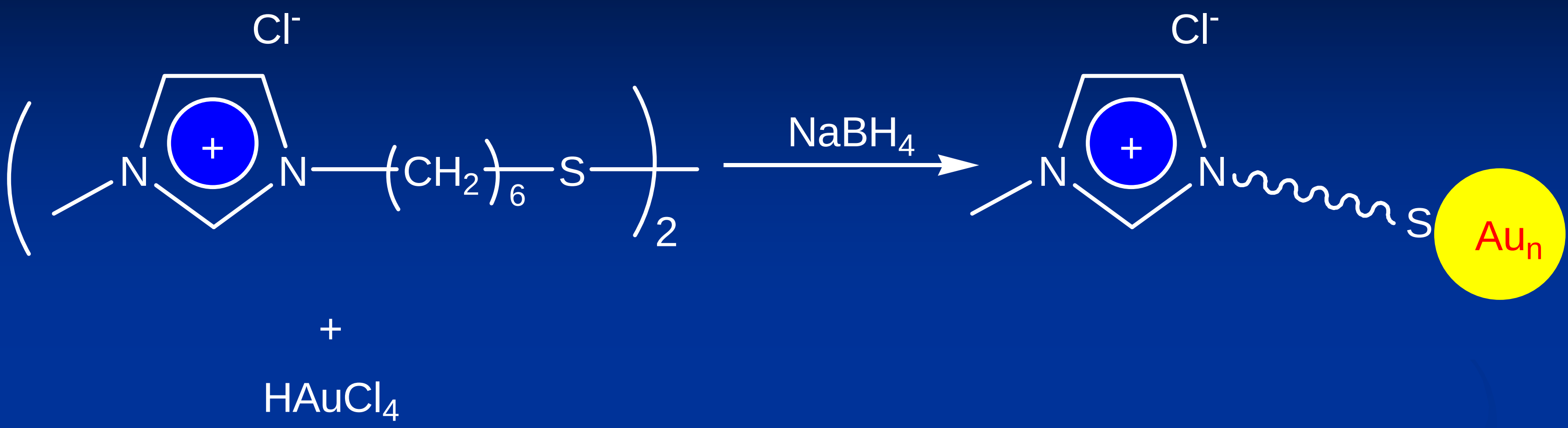
[a]*Reaction conditions: alkyne (0.0375 mmol) in* $CDCl_3$(0.5 mL) at 34 ^oC, catalyst loading = 16 mol%, reaction time = 10 min for each cycle. [b]*Determined by* ^1H NMR spectroscopy analysis.

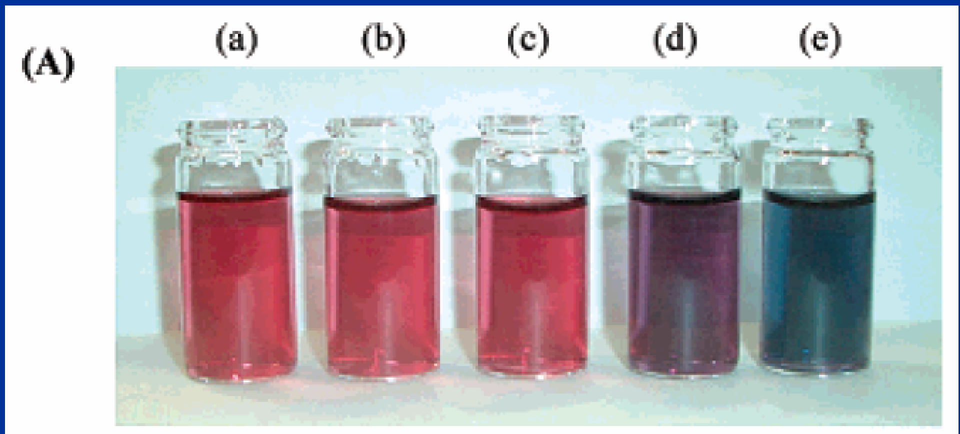
Mechanism of [2+2+2] Alkyne Cyclotrimerization

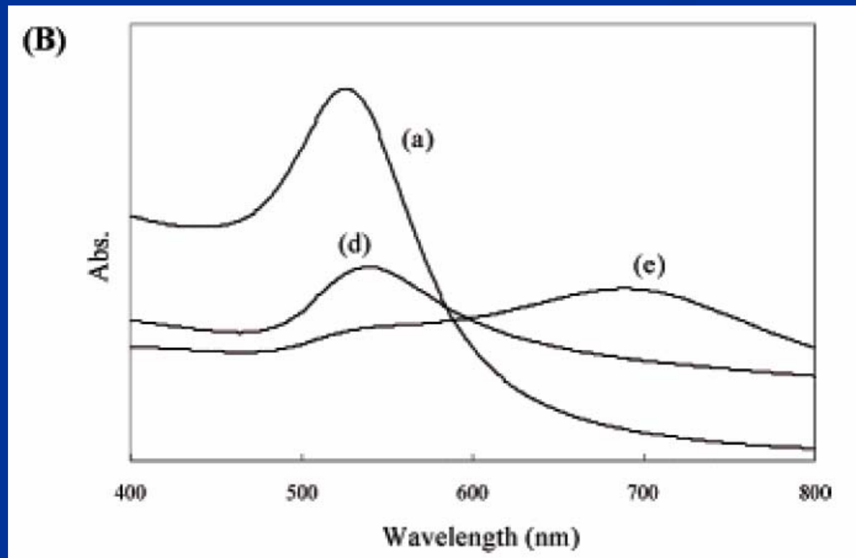


Ehmann, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 3800-3807.

Ionic Liquids As Stabilizing Agents for NPs



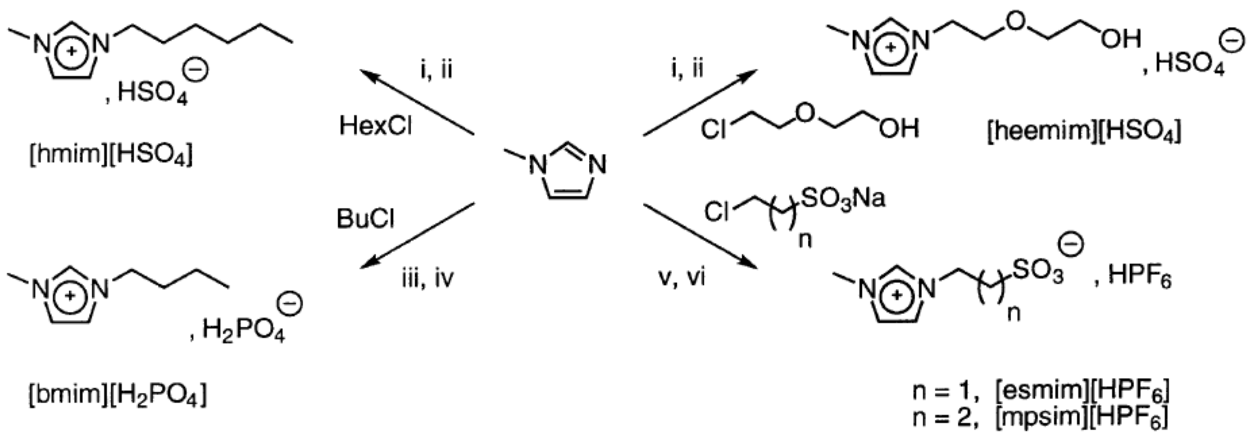




(A) Addition of (**a**) HCl, (**b**) HBr, (**c**) HBF_4, (**d**) HI,and (**e**) HPF_6.
(B) UV-vis absorption spectra corresponding to (**a**), (**d**), and (**e**) in photograph A.

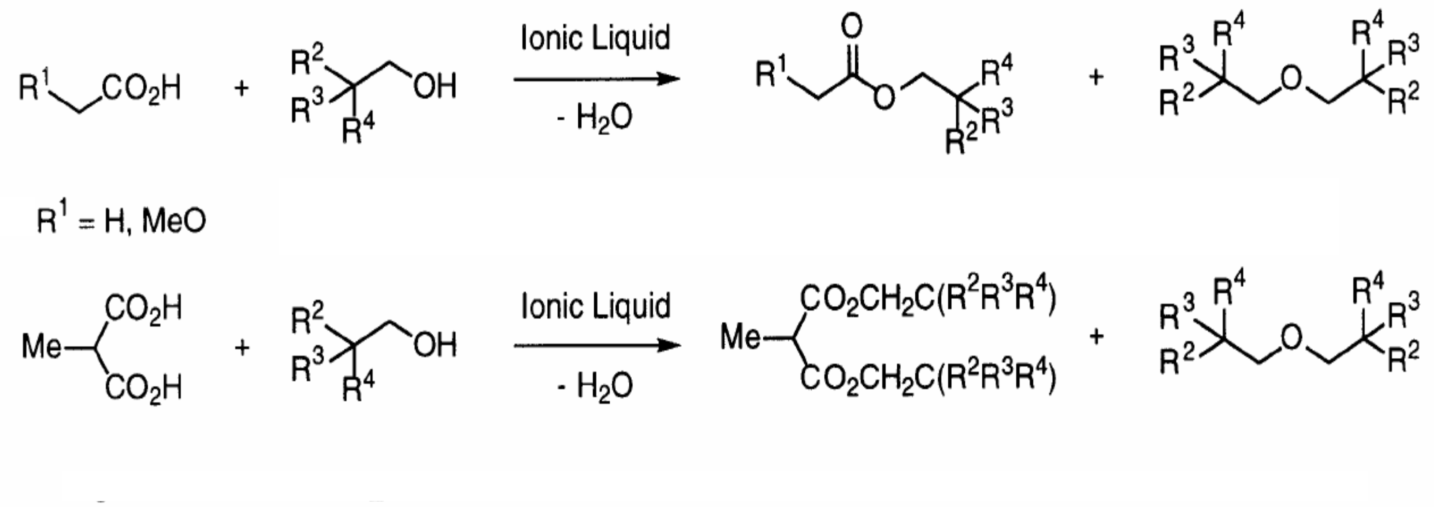
Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc*. **2004**, *126*, 3026-3027.

Brønsted Acidic Ionic Liquids



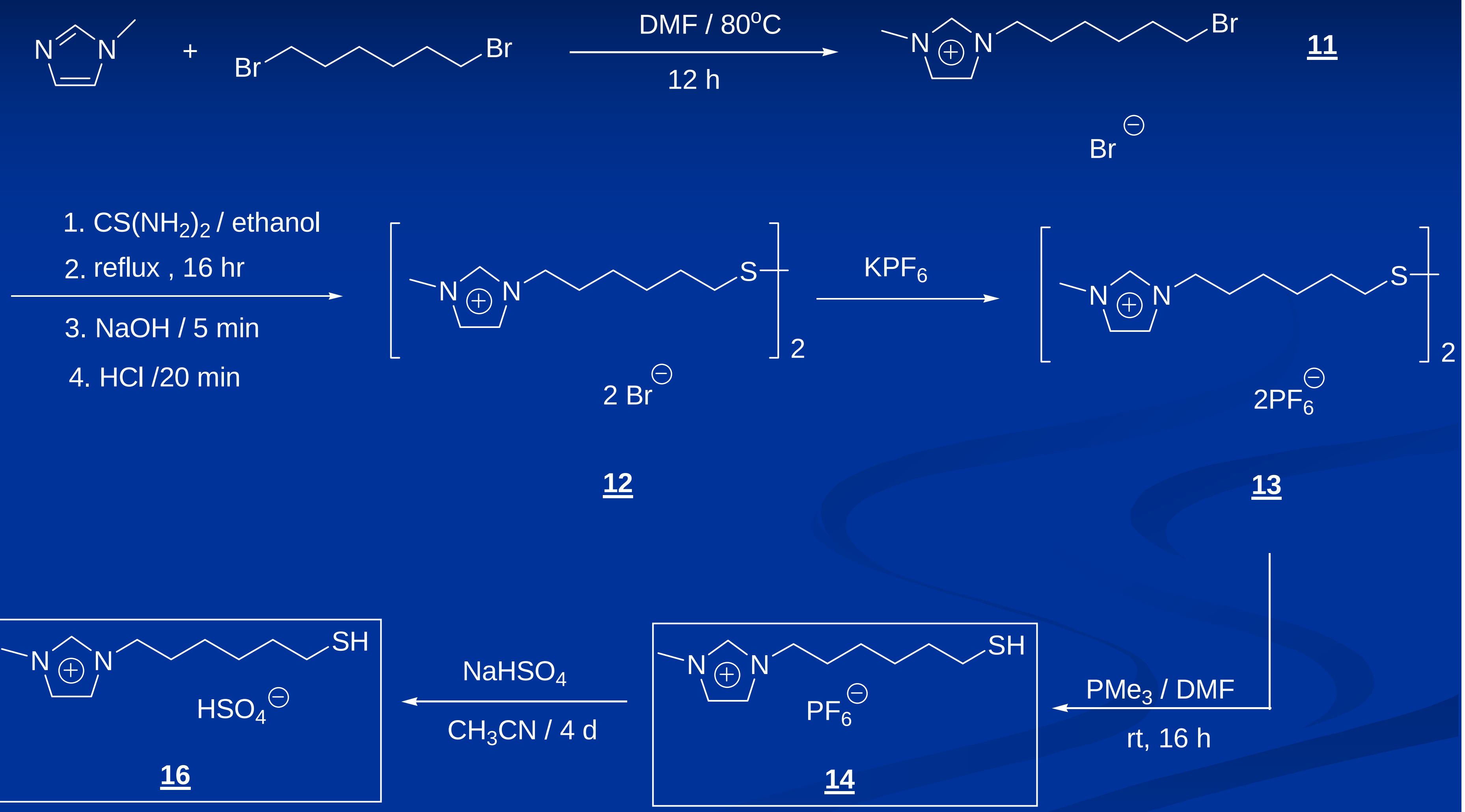
Scheme 1. *Reagents and reaction conditions*: (i) RCI (1 equivalent), $\mu\omega$, 120 °C, 30 min. (ii) H_2SO_4 97% (1 equivalent), CH_2Cl_2 0 °C then reflux, 48 h. (iii) BUCL (1.5 equivalent), $\mu\omega$, 150 °C, 30 min. (iv) H_3PO_4 85% (1 equivalent) CH_2Cl_2, 0 → reflux, 5 h then 25 °C, 48 h. (v) RC1 (1 equivalent), deionized H_2O, reflux, 48 h, then recryst. from Etoh. (vi) HPF_6 60% (1 equivalent), 0 → 25 °C, 48 h.

Esterification

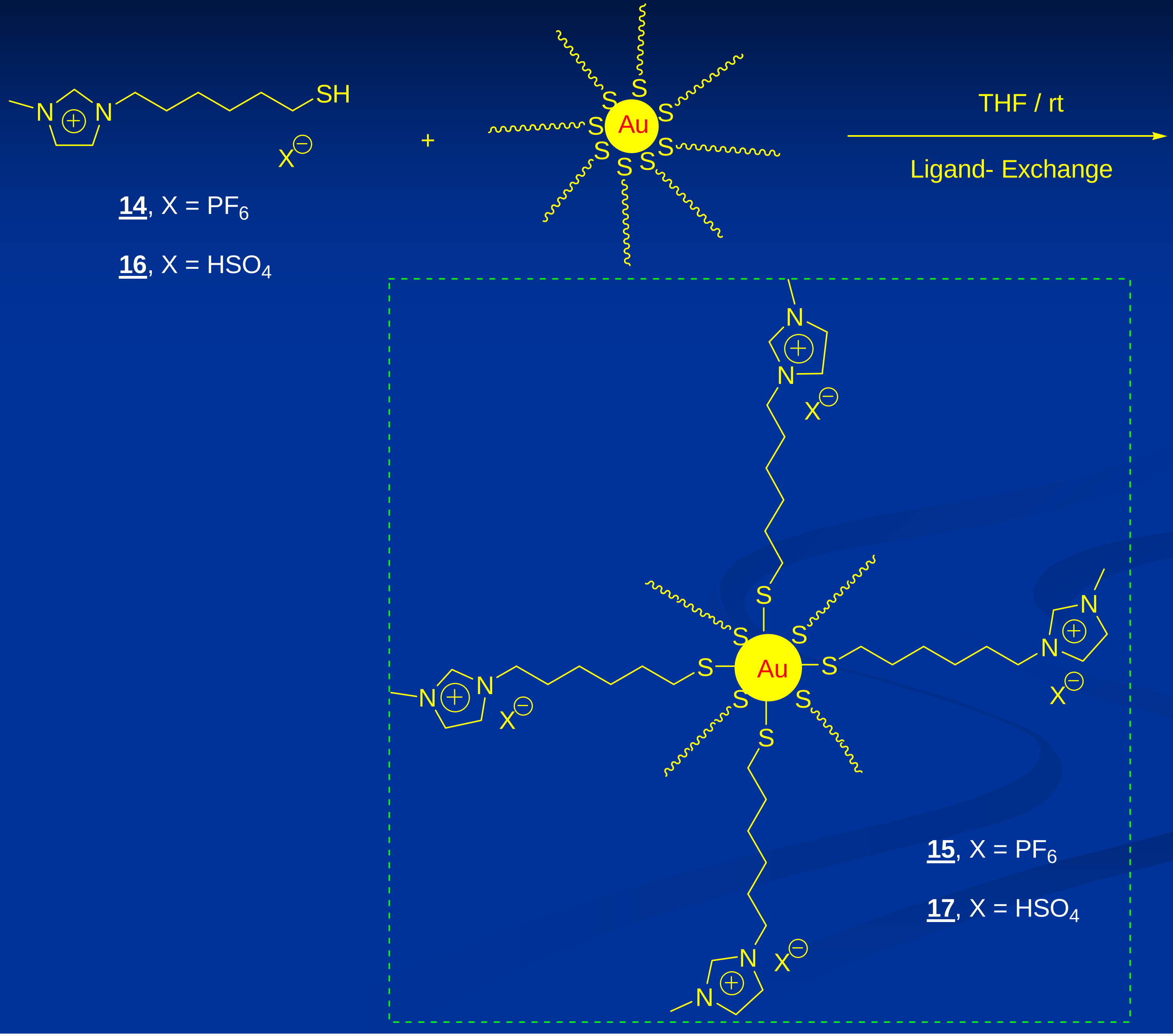


Fraga-Dubreuil, J.; Bourahla, K.; Rahmouni, M.; Bazureau. J. P.; Hamelin, J.; *Catal. Commun*. **2002**, *3*, 185-190.

Synthetic Strategy



Nano-Gold Surface-Immobilized ILs



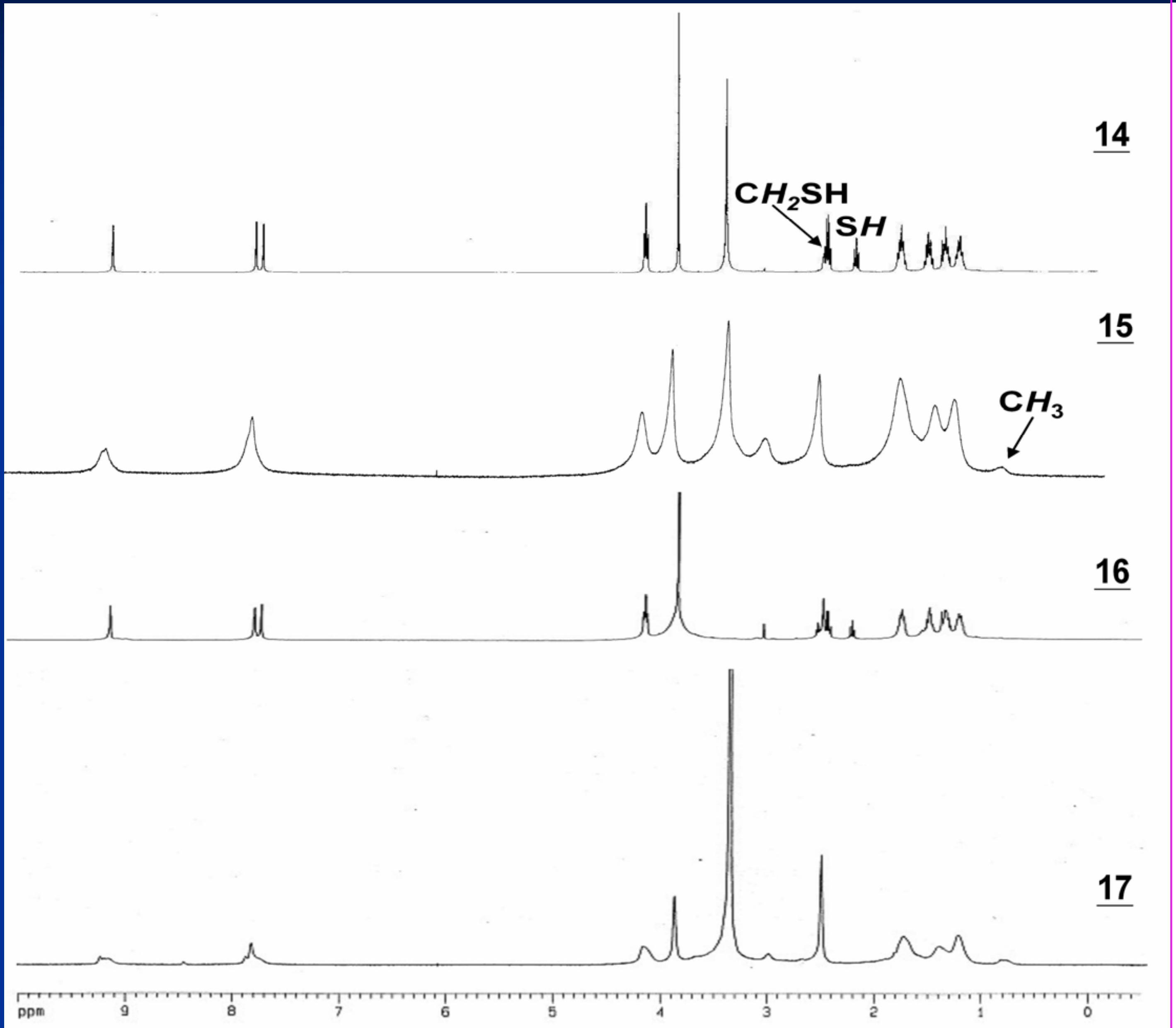
14, X = PF_6

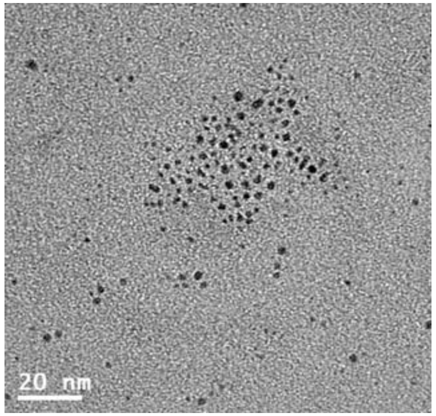
16, X = HSO_4

15, X = PF_6

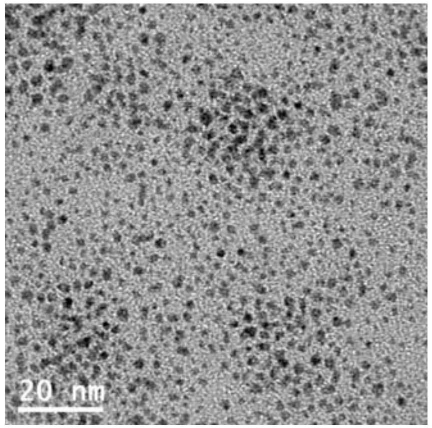
17, X = HSO_4

NMR Spectra and TEM images



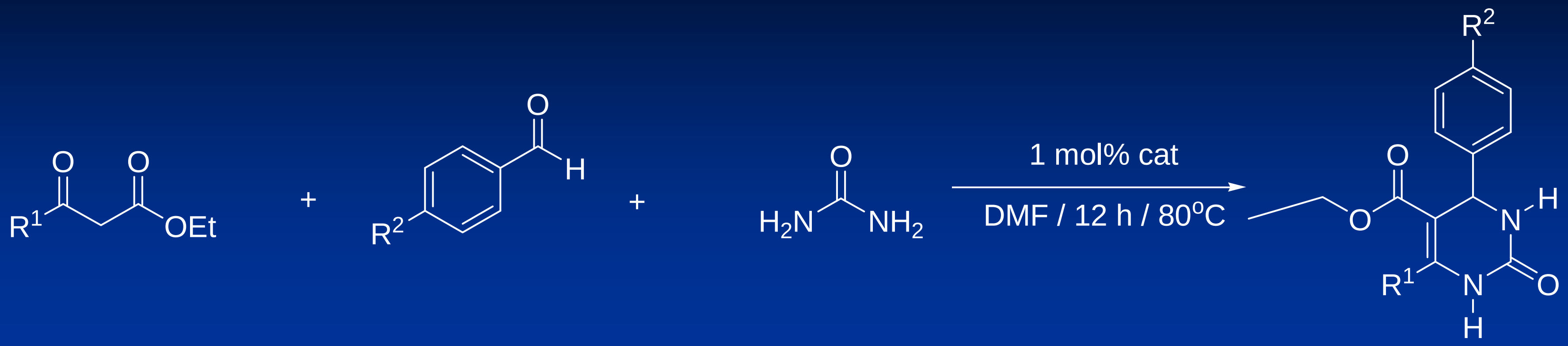


15, D = 2.4 ± 0.1 nm



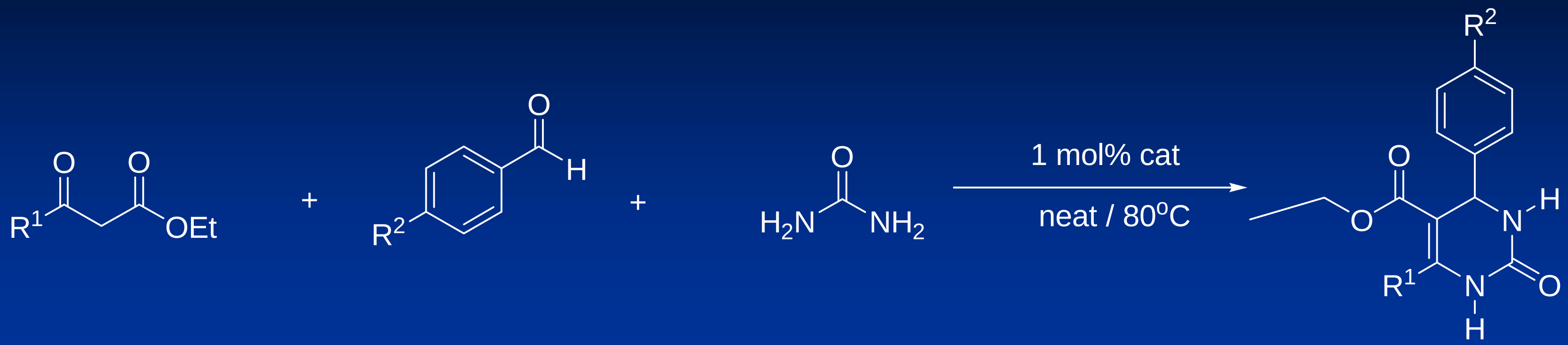
17, D = 2.2 ± 0.1 nm

Biginelli Condensation Reactions (1)



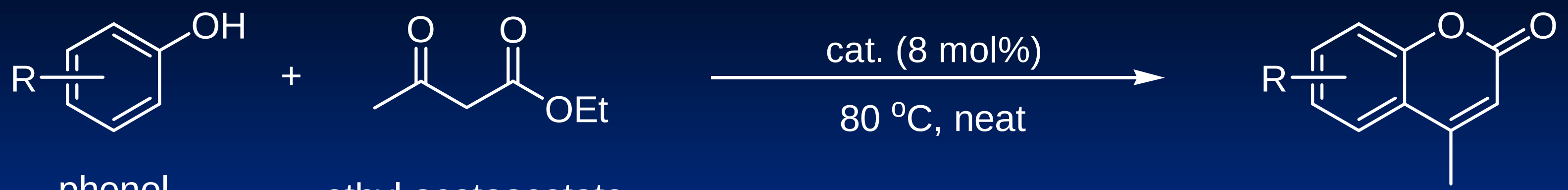
Entry	R^1	R^2	Yield (%)		
			Au-(hmim)PF_6 (**15**)	(hmim)PF_6	Au-(hmim)HSO_4 (**17**)
1	CH_2Cl	OH	91	90	92
2	CH_2Cl	Cl	77	75	87
3	CH_2Cl	H	94	92	93
4	CH_2Cl	F	82	81	91
5	Me	OH	47	8	91
6	Me	Cl	46	N.D.	75
7	Me	H	70	42	87
8	Me	F	37	32	93

Biginelli Condensation Reactions (2)

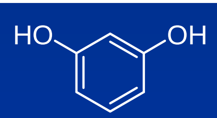
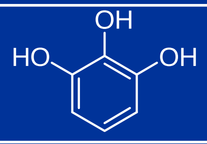
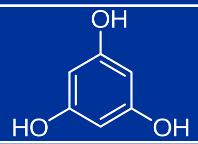
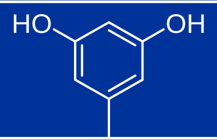
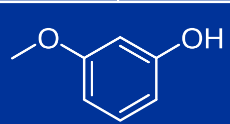
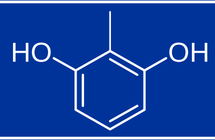
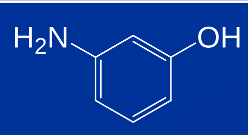


entry	R^1	R^2	time (h)	Yield (%)		time (h)	Yield (%)
				Au-(hmim)PF_6 (**15**)	(hmim)PF_6		Au-(hmim)HSO_4 (**17**)
1	CH_2Cl	H	3	68	67	-	-
2	CH_2Cl	F	3	76	58	-	-
3	CH_2Cl	OH	2	93	93	0.5	10
4	CH_2Cl	Cl	4	55	32	-	-
5	Me	H	6	93	91	0.5	10
6	Me	F	6	95	73	0.5	5
7	Me	OH	7	95	80	-	-
8	Me	Cl	0.5	80	79	0.5	5

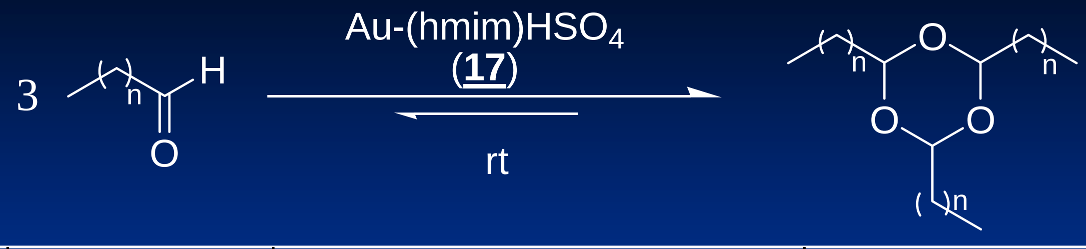
Pechmann Condensation Reactions



phenol ethyl acetoacetate

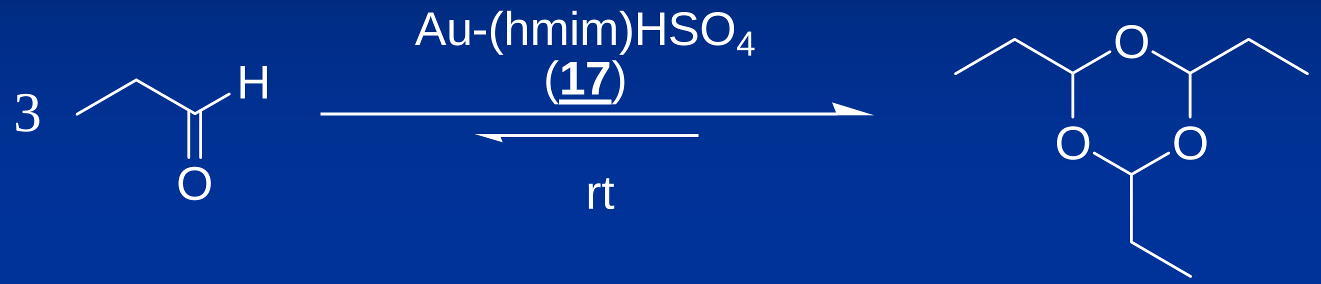
Entry	Phenol	Cat. (16) Time (h)	Cat. (16) Yield (%)	Cat. (17) Time (h)	Cat. (17) Yield (%)
1		24	78	24	34
2		2	70	4.5	75
3		1	40	3	64
4		48	8	48	13
5		48	3	48	13
6		48	74	48	35
7		48	37	48	38

Aldehyde Cyclotrimerization



entry	n	mol %	solvent	Time (h)	conversion (%)
1	1	1	neat	24	60
2	1	3	neat	24	81
3	1	1	$CDCl_3$ (0.3 mL)	24	45
4	1	1	$CDCl_3$ (0.1 mL)	24	77
5	1	1	$CDCl_3$ (0.1 mL)	12	99
6	1	1	$CDCl_3$ (0.1 mL)	6	75
7	1	10	$CDCl_3$ (0.1 mL)	1	99
8	2	1	neat	24	16
9	2	1	$CDCl_3$ (0.1 mL)	24	43
10	2	3	$CDCl_3$ (0.1 mL)	24	62
11	2	10	$CDCl_3$ (0.1 mL)	1	45
12	3	1	$CDCl_3$ (0.1 mL)	24	5
13	3	1	$CDCl_3$ (0.1 mL)	12	5
14	5	1	neat	24	36
15	7	1	neat	24	20

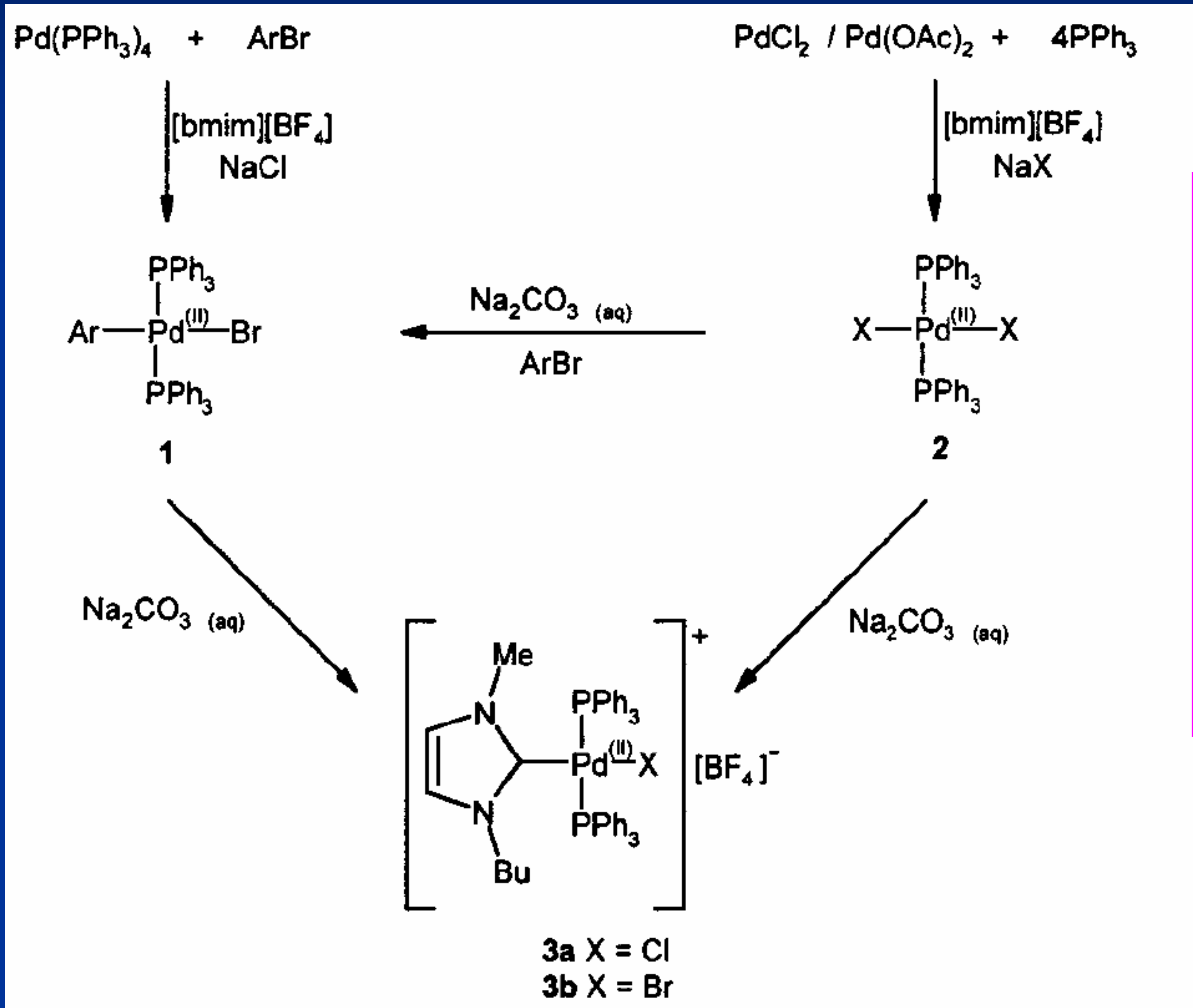
Reuse of Cat. 17 toward
Aldehyde *Cyclotrimerization Reactions*

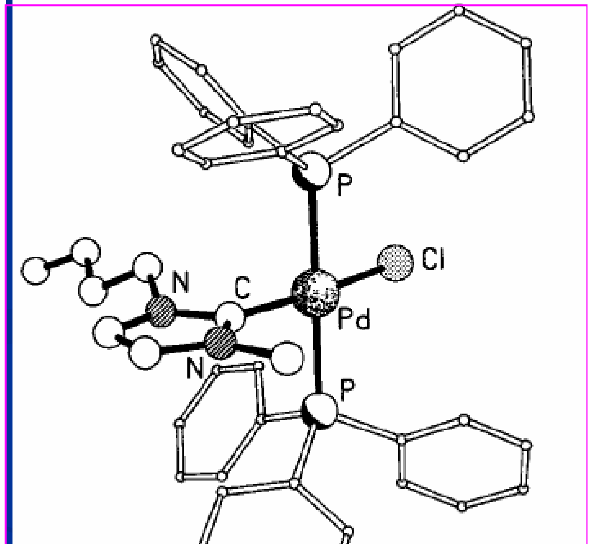


catalyst	cycle (% conversion)						
	1	2	3	4	5	6	7
17	96	93	92	91	90	88	85

[a]Reaction conditions: aldehyde (0.5 mmol) in CDCl3(0.5 mL) at 27 °C, catalyst loading = 6 mol%, reaction time = 3 h for each cycle. [b]Determined by ^{1}H NMR spectroscopy analysis.

Ionic Liquids As Ligands of *N*HC Complexes

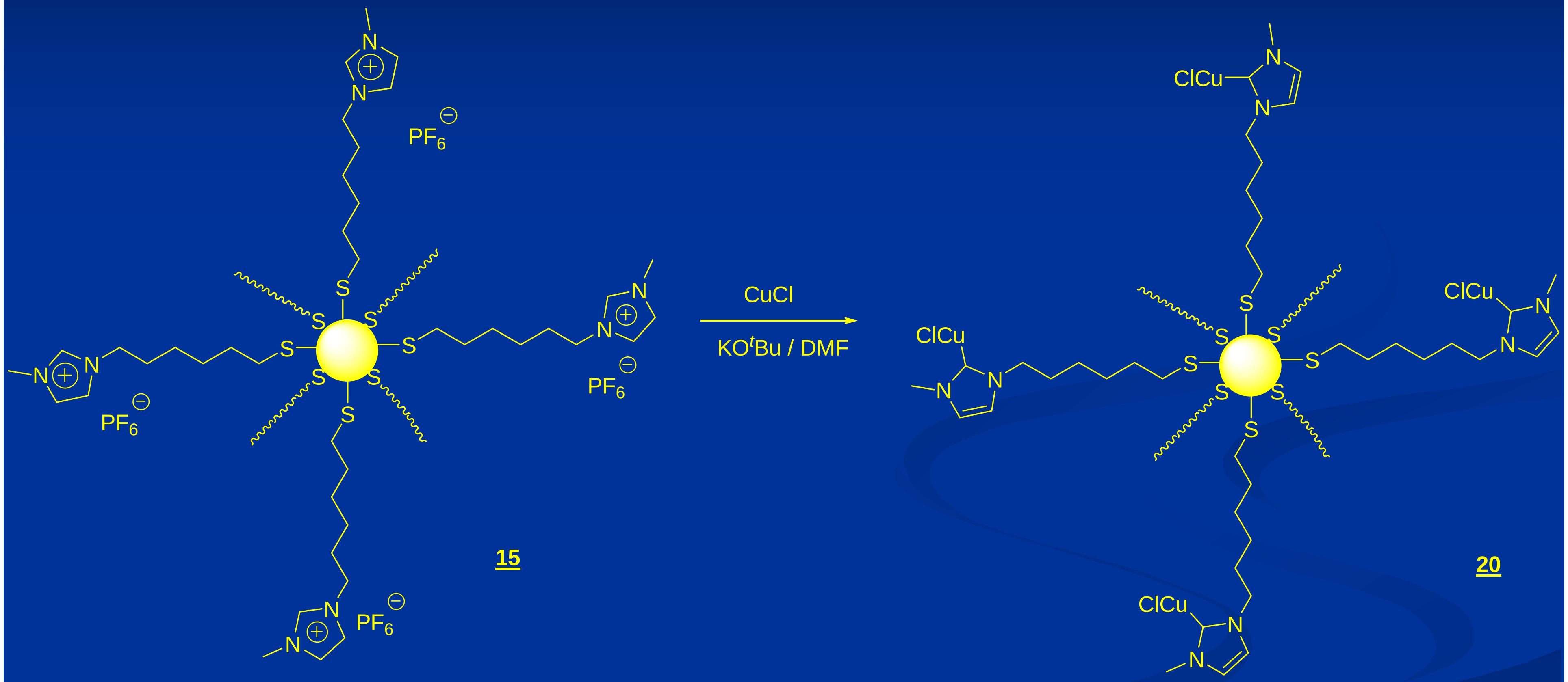




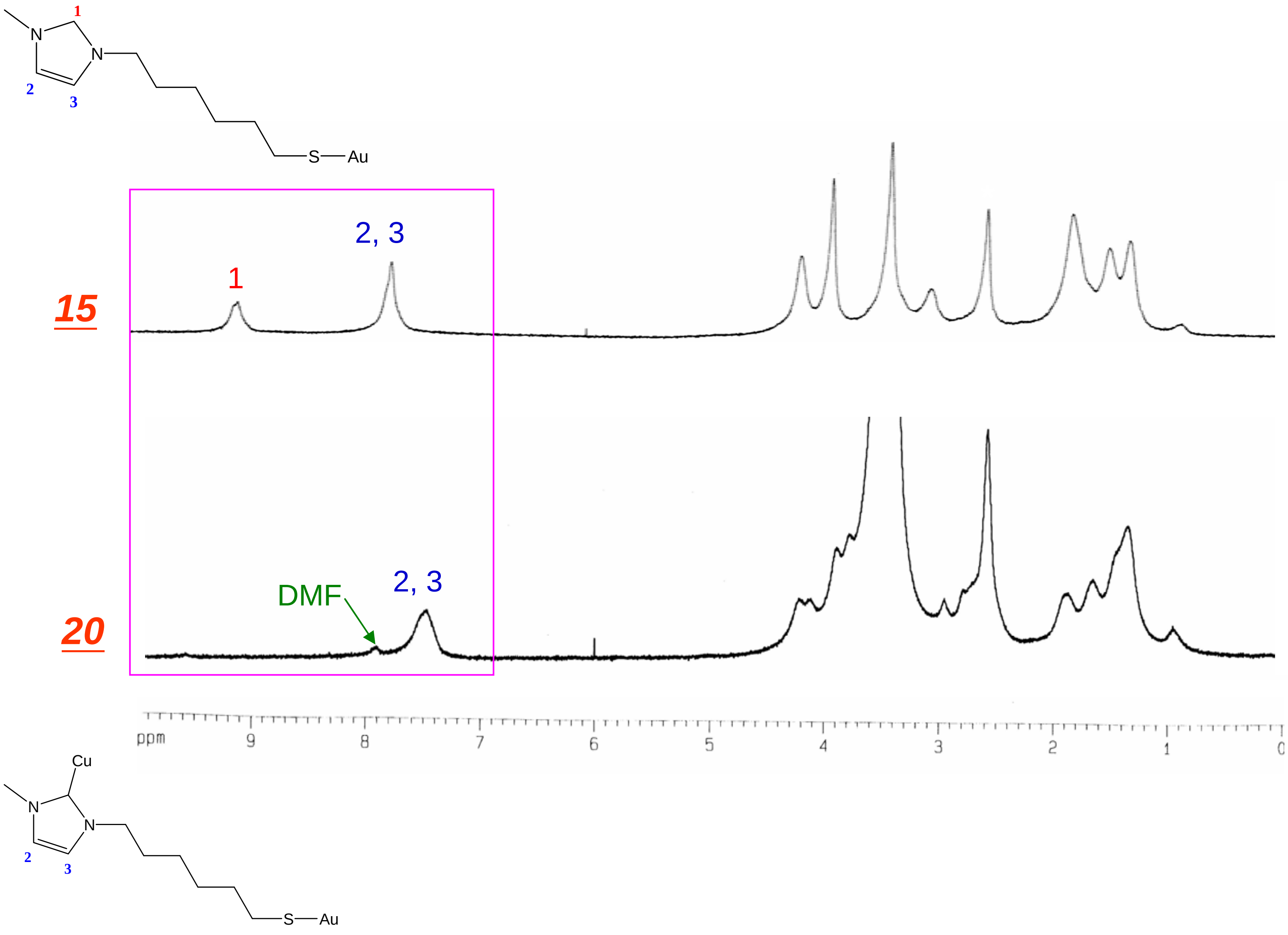
3a

Organometallics **2001,** *20, 3848-3850*.

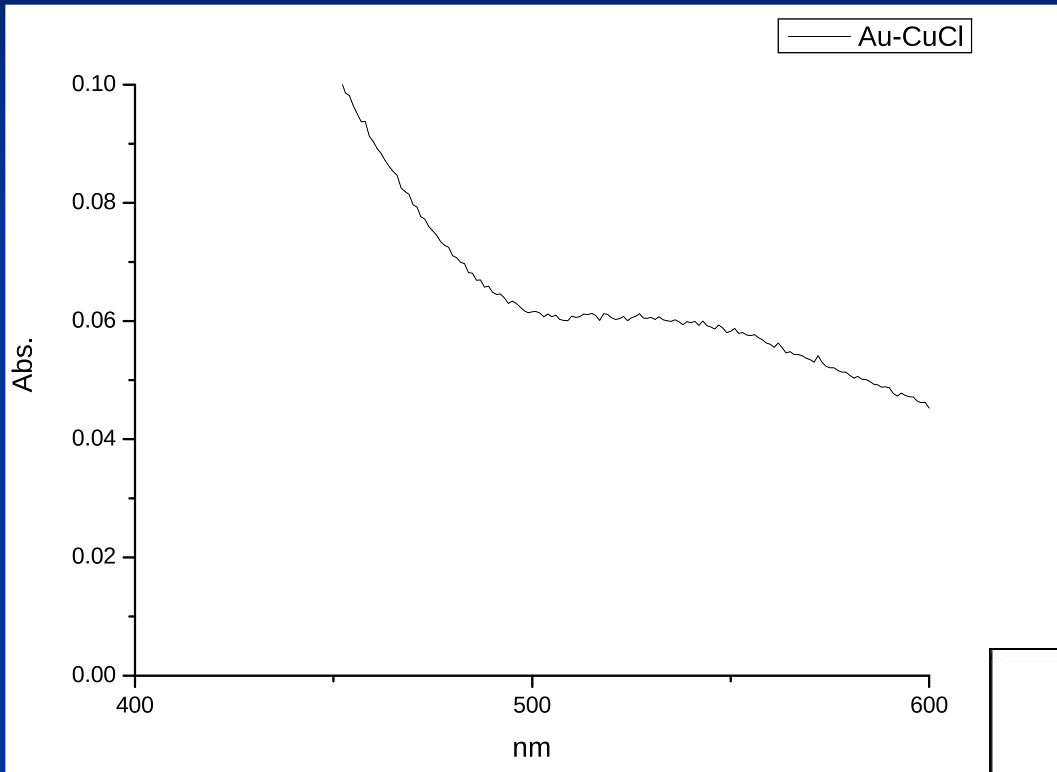
Au NPs-Supported Cu(I) Complexes via Thiolated NHC Carbene Ligatior

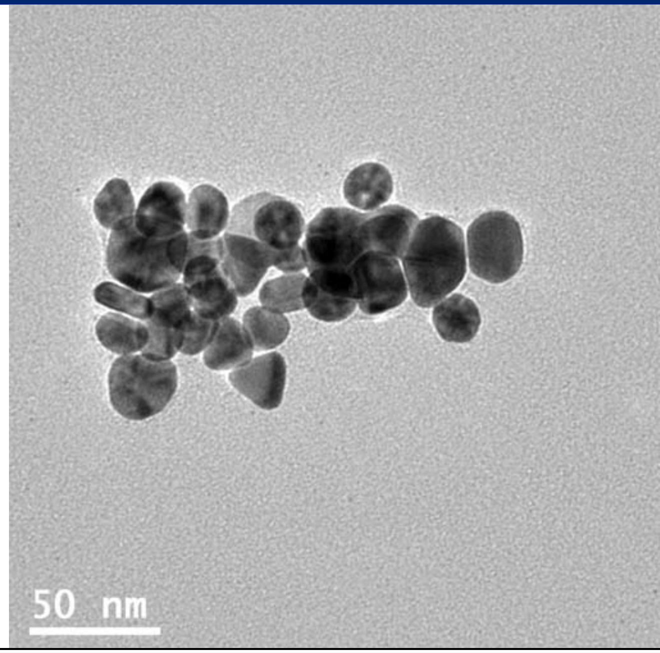


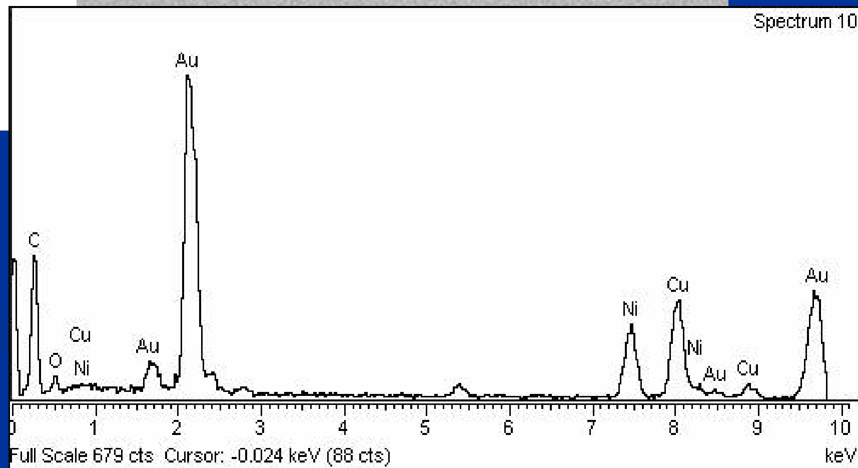
NMR Spectra of 15 and 20



The Character of compound 20







Conclusions

1. We have developed a method to successfully immobilize molecular Pd(II) complexes and ionic liquid catalysts onto surfaces of Au NPs.

2. Since the Au NPs-Pd(II) and Au NPs-ILs hybrid catalysts are highly soluble in organic solvents, their structures and reactions could be easily studied by simple solution NMR technique.

3. The Au NPs-Pd(II) complexes were proven to be highly effective catalysts for a series of [2+2+2] alkyne cyclotrimerizations reactions.

4. The Au NPs-Pd(II) hybrid catalysts can be easily recovered and reused many times without significant loss of reactivity.

5. A series of the Au NPs-ILs hybrid catalysts were catalysts for Biginelli、Pechmann Condensation and Aldehyde Cyclotrimerization Reactions.

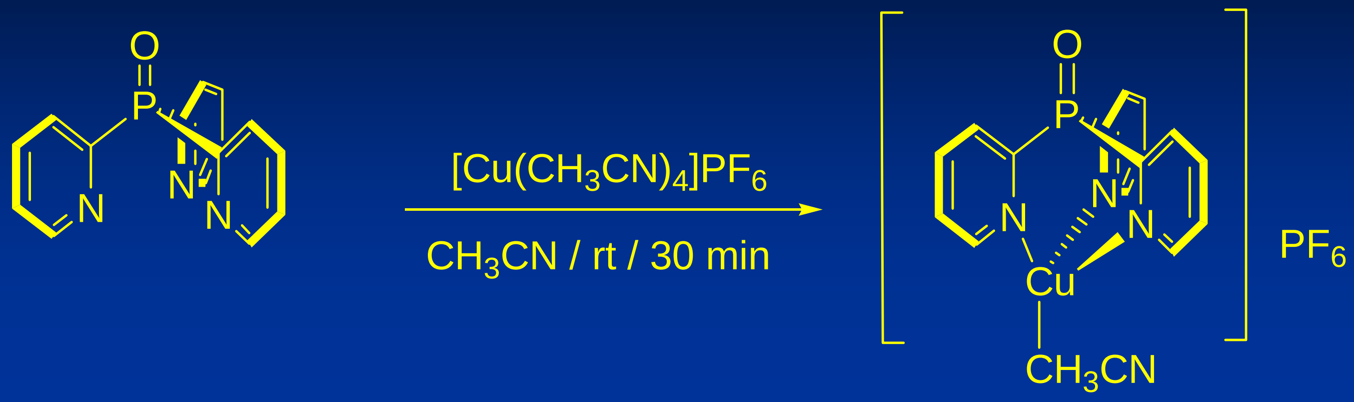
6. We have developed a method to successfully immobilize (*N*HC)CuCl onto surfaces of Au NPs.

I . Studies of Molecular Pd(II) and Cu(I) Complex Catalysts and Ionic Liquid Catalysts in Homogeneous and Inter-face Systems.

Syntheses of Homogenous Cu(I) Catalysts and Their Catalytic Applications

- *Inexpensive Cu to replace Pd as catalyst for multi- C–X coupling rxns (X = C, S, O).*

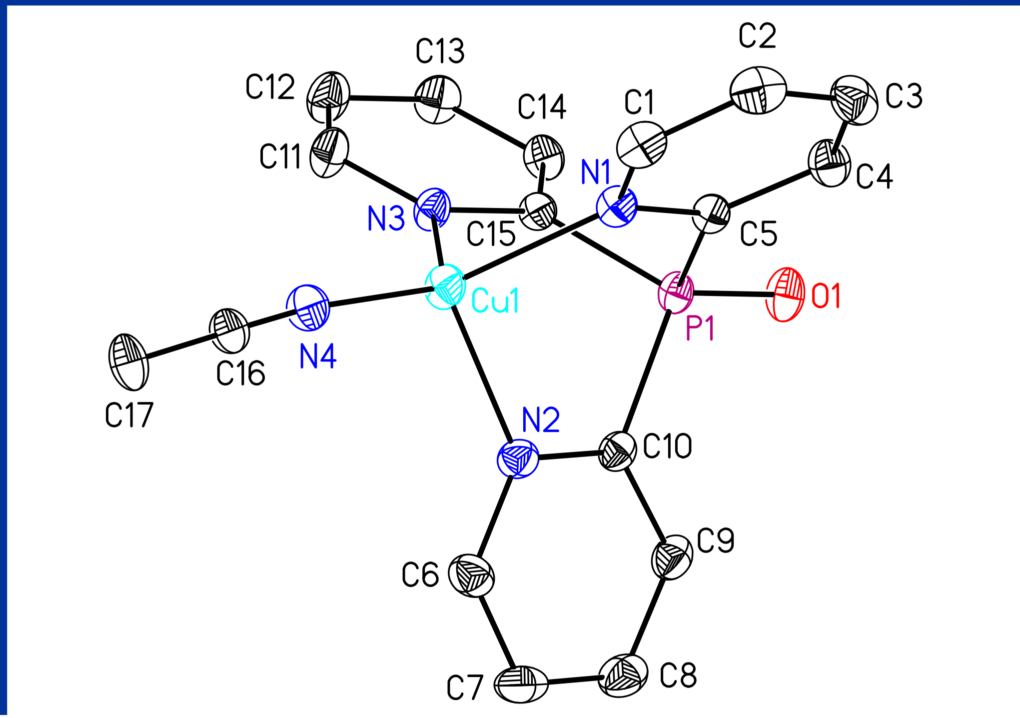
Synthesis of Cu(I) Compound (18)



80 %

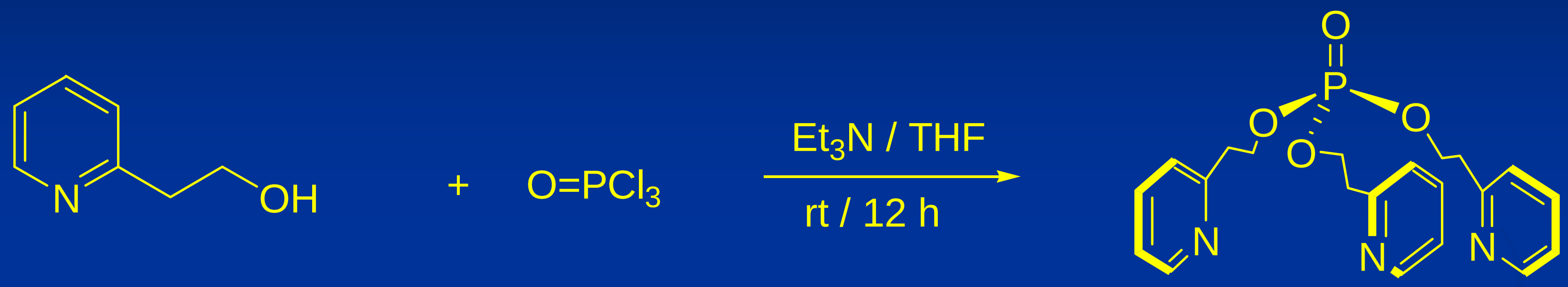
L_1

18



Cu(1)-N(1) 2.057(4)
Cu(1)-N(2) 2.093(4)
Cu(1)-N(3) 2.063(4)
Cu(1)-N(4) 1.906(4)

Synthesis of Cu(I) Compound (<u>19</u>)



L_2

58 %

$\xrightarrow[CH_3CN\ /\ rt\ /\ 30\ min]{[Cu(CH_3CN)_4]PF_6}$ $\{(OP([CH_2)_2(2\text{-}py)]_3Cu(CH_3CN))(PF_6)$

<u>19</u>

75 %

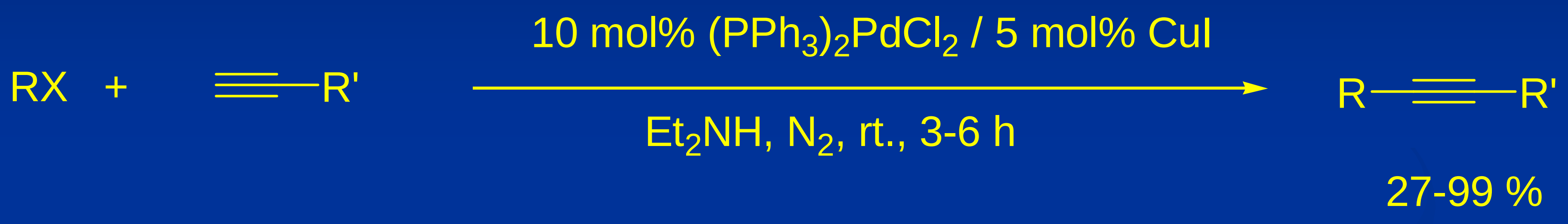
The Catalytic Applications of Cu(I) Compounds

1. Sonogashira Coupling Reactions

2. C-S Bond Coupling Reactions

3. Allylic Oxidations of Olefins

Sonogashira Reactions

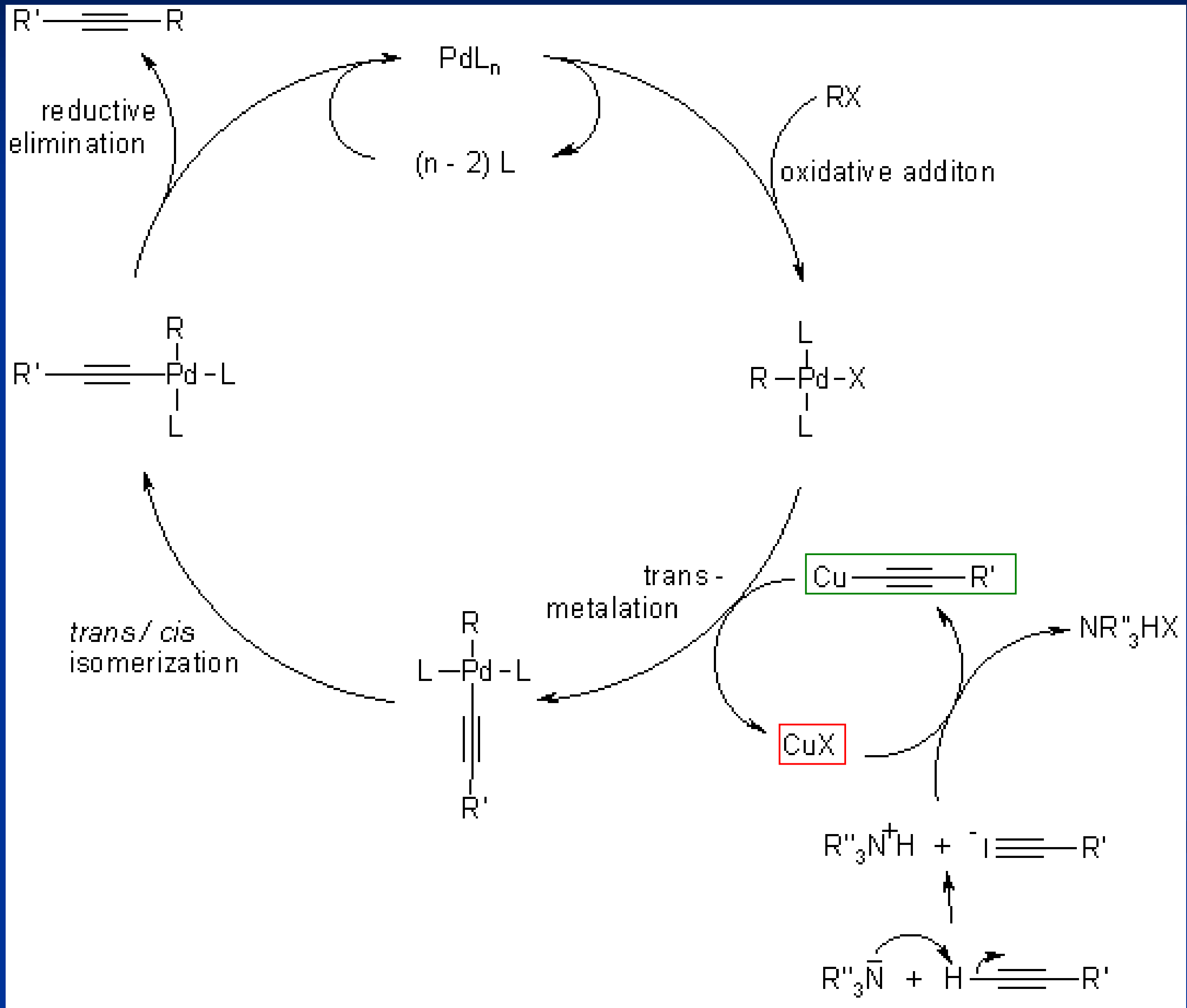


RX = iodoarenes, bromoalkenes,
bromopyridines

R' = H, Ph, CH_2OH

Sonogashira, K.; Tohda, Y.; Hagihara. N. *Tetrahedron Lett*. **1975**, *50*, 4467-4470.

Mechanism of Traditional Sonogashira Rxns



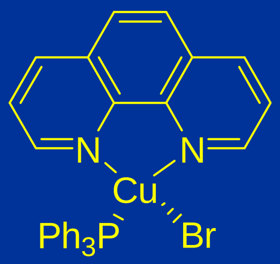
The First Copper Catalyzed Sonogashira Rxns

$$R^1X + HC\equiv CR^2 \xrightarrow[\text{DMF or DMSO, 80-120}^{o}\text{C / 10-40 h}]{\text{5 mol\% CuI / 10 mol\% PPh}_3\text{ / K}_2\text{CO}_3} R^1C\equiv CR^2 \quad \text{8-98 \%}$$

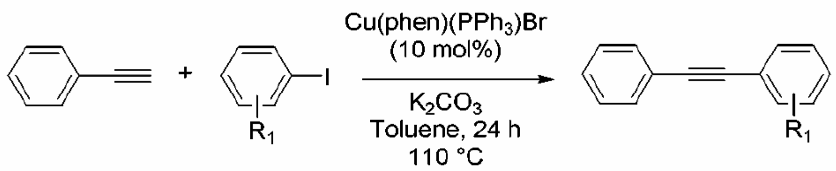
R^1 = aryl, vinyl; X= Br, I; R^2 = Ph, n-pentyl

Okuro, K.; Furuune, M.; Miura, M.; Nomura, M. *Tetrahedron Lett*. **1992**, *33*, 5363–5364.

Cu(phen)(PPh$_3$)Br Catalyzed Sonogashira Rxns



Cu(phen)(PPh$_3$)Br

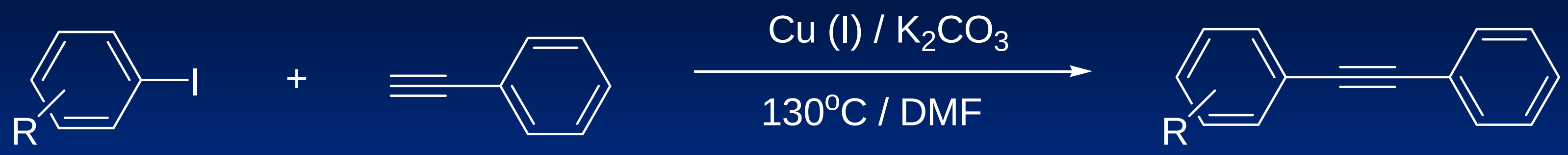


entry	R_1	yield[a] (%)
1	H	80
2	*p*-CH_3	74
3	*o*-CH_3	71
4	*p*-OCH_3	97
5	*o*-OCH_3	70
6	*p*-$COOCH_3$	89
7	*o*-$COOCH_3$	76
8	*p*-$COCH_3$	85

[a] Isolated yields.

Venkataraman, D. *Org. Lett*. **2001**, *3*, 4315-4317.

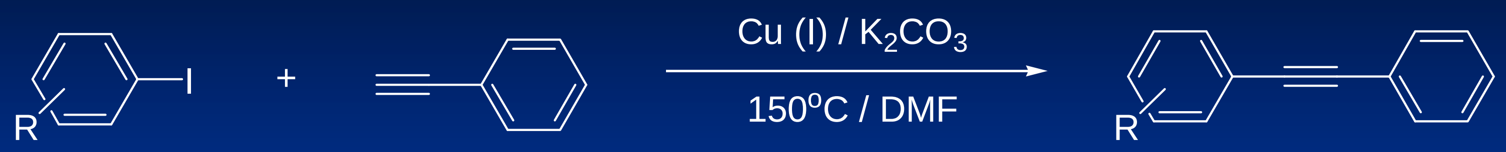
Cu(I)-Catalyzed Sonogashira Rxns



Entry	R	Cat.	Conversion (%)			
			24 h	18 h	12 h	6 h
1	H	**18**	99	99	99	46
2	H	**19**	99	99	87	27
3	*p*-CH_3	**18**	99	99	99	37
4	*p*-CH_3	**19**	99	99	99	23
5	*p*-OCH_3	**18**	99	99	88	20
6	*p*-OCH_3	**19**	99	99	89	93
7	*p*-$COCH_3$	**18**	99	99	91	67
8	*p*-$COCH_3$	**19**	99	99	60	31
9	*o*-COCl	**18**	99	80	75	60
10	*o*-COCl	**19**	99	99	76	72

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Phenylacetylene, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

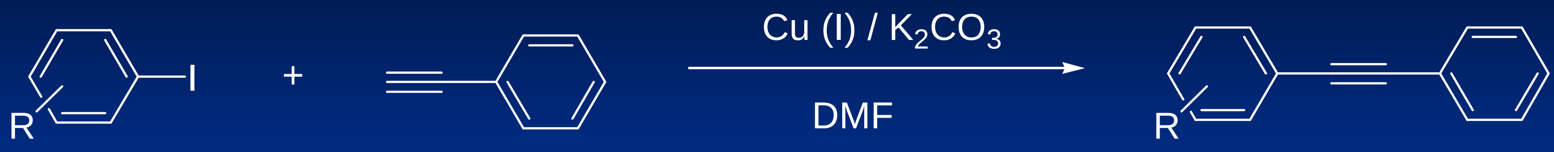
Cu(I)-Catalyzed Sonogashira Rxns at 150 ^oC



Entry	R	Cat. (10 mol%)	Time (h)	Conversion (%) 150 ^oC	Conversion (%) 130 ^oC
1	H	**18**	6	23	46
2	H	**19**	6	20	27
3	*p*-CH_3	**18**	6	99	37
4	*p*-CH_3	**19**	6	99	23
5	*p*-OCH_3	**18**	6	35	20
6	*p*-OCH_3	**19**	6	22	93
7	*p*-$COCH_3$	**18**	6	52	67
8	*p*-$COCH_3$	**19**	6	80	31
9	*o*-COCl	**18**	6	90	60
10	*o*-COCl	**19**	6	90	72

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Phenylacetylene, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

Optimized Reactions Conditions Under Thermal Heating



Entry	R	Cat. (10 mol%)	Temp. (°C)	Time (h)	Conversion (%)
1	H	**18**	130	12	99
2	H	**19**	130	18	99
3	*p*-CH_3	**18**	130	12	99
4	*p*-CH_3	**19**	130	12	99
5	*p*-CH_3	**18**	150	6	99
6	*p*-CH_3	**19**	150	6	99
7	*p*-OCH_3	**18**	130	18	99
8	*p*-OCH_3	**19**	130	12	99
9	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	130	24	40
10	*p*-$COCH_3$	**18**	130	18	99
11	*p*-$COCH_3$	**19**	130	18	99
12	*o*-COCl	**18**	130	24	99
13	*o*-COCl	**19**	130	18	99

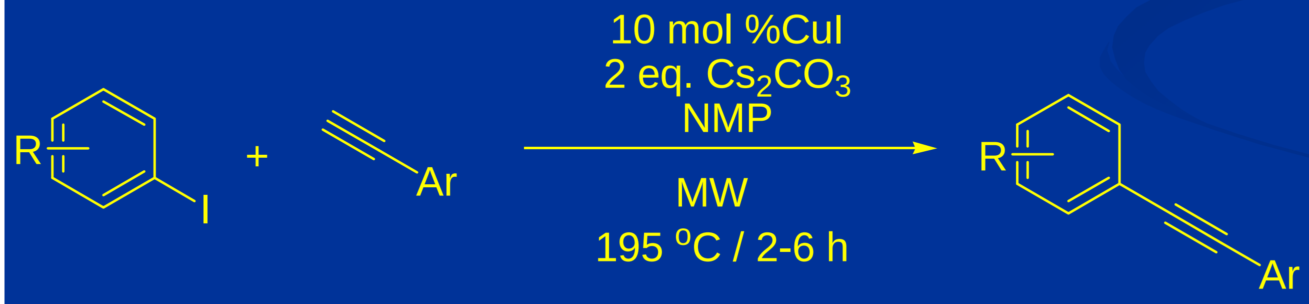
Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Phenylacetylene, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

CuI-Catalyzed Sonogashira Rxns Using Microwave Heating

$$R^1C\equiv CH \; + \; R_2I \xrightarrow[\text{375 W / 10 min / DMF}]{\text{10 mol\% CuI / 20 mol\% PPh}_3\text{ / K}_2\text{CO}_3} R^1C\equiv CR^2$$

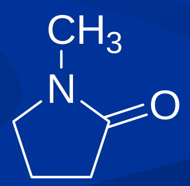
80-92%

Wang, J.-X.; Liu, Z.; Hu, Y.; Wei, B.; Kang, L. *Synth. Commun*. **2002**, 32, 1937–1945.



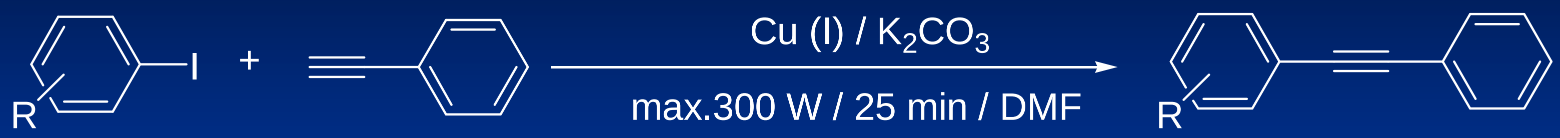
43- 87 %

NMP = N-Methylpyrrolidone



He, H.; Wu. Y.-J. *Tetrahedron Lett* **2004**, *45*, 3237–3239.

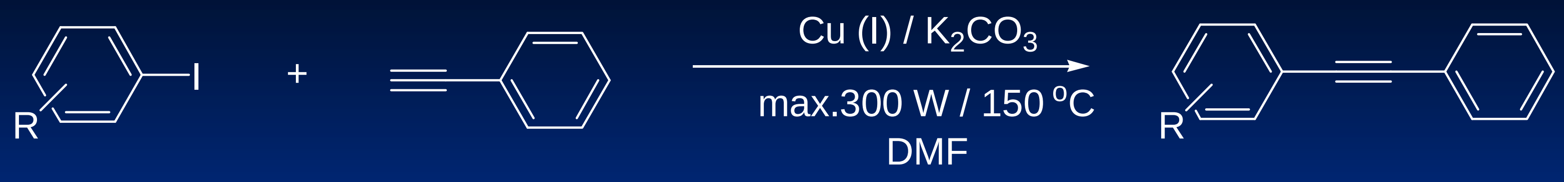
Microwave Assisted Sonogashira Rxns by Cu(I) Catalysts



Entry	R	Cat.	Conversion (%)	
			130 °C	150 °C
1	H	**18**	23	99
2	H	**19**	43	99
3	*p*-CH_3	**18**	-	99
4	*p*-CH_3	**19**	-	99
5	*p*-OCH_3	**18**	8	99
6	*p*-OCH_3	**19**	13	99
7	*p*-$COCH_3$	**18**	-	99
8	*p*-$COCH_3$	**19**	-	99
9	*o*-COCl	**18**	-	99
10	*o*-COCl	**19**	-	99

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Phenylacetylene, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

Optimized Catalytic Conditions Using MW



Entry	R	Cat. (10 mol%)	Time (min)	Conversion (%)
1	H	**18**	15	99
2	H	**19**	15	99
3	*p*-CH_3	**18**	15	99
4	*p*-CH_3	**19**	15	99
5	*p*-CH_3	**18**	10	90
6	*p*-CH_3	**19**	10	90
7	*p*-OCH_3	**18**	15	99
8	*p*-OCH_3	**19**	15	99
9	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	15	11
10	*p*-$COCH_3$	**18**	15	99
11	*p*-$COCH_3$	**19**	15	99
12	*o*-COCl	**18**	25	99
13	*o*-COCl	**19**	25	99

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Phenylacetylene, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

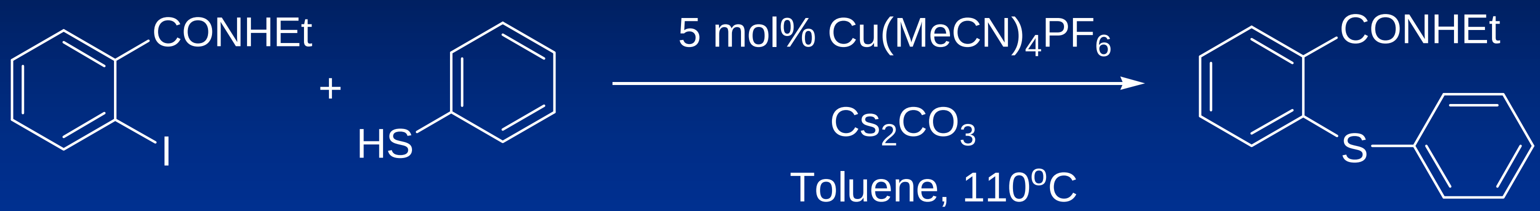
The First Example of Metal Mediated for C-S Bond Formation

PhBr + EtSH $\xrightarrow[\text{DMSO, } t\text{-BuONa, } 100^{o}\text{C, 18 h}]{Pd(PPh_3)_4}$ PtSEt

98 %

(a) Migital, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kasugi, M. *Bull. Chem. Soc. Jpn*. **1980**, *53*, 1385-1389.
(b) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett*. **1978**, 13-14.

The First Cu-Catalyzed C-S Coupling Rxn



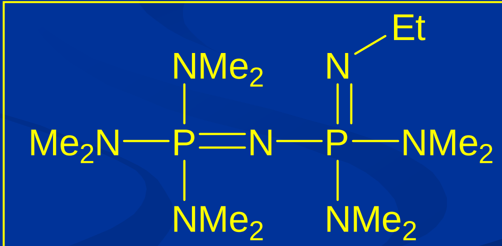
97 %

Kalinin, A. V.; Bower, J. F.; Riebel, P.; Snieckus, V. *J. Org. Chem.* **1999**, *64*, 2986-2987.

CuBr-Catalyzed C-S Coupling Rxns

Ar-I + Ar'-SH $\xrightarrow[\text{toluene, 110 }^{o}\text{C; 4-6 h}]{P_2\text{-Et (2 eq), CuBr (10 mol\%)}}$ Ar-S-Ar'

Yield : 60-100 %

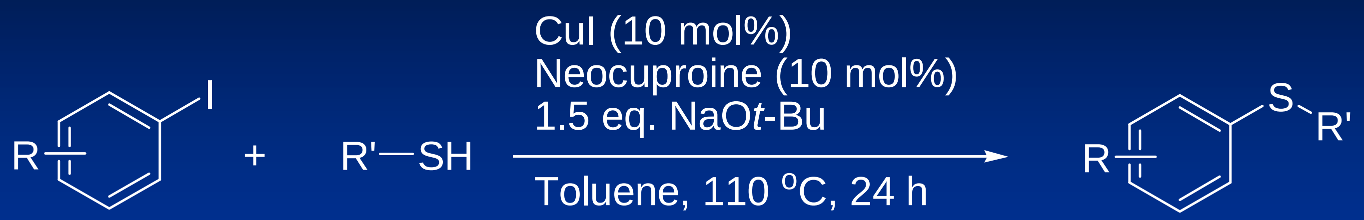


P_2-Et :

NT 13000 / 5 mL (Aldrich)

Palomo, C.; Oiarbide, M.; Lopez, R.; Gomez-Bengoa, E. *Tetrahedron, Lett.* **2000**, *41*, 1283-1286.

CuI-Catalyzed C-S Coupling



Yield = 77%-98%

Neocuproine

Bates, C. G.; Gujadhur, R. K.; Venkataraman, D. *Org. Lett.* **2002,** 4, 2803-2806.

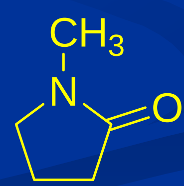
Cu-Catalyzed C-S Bonds Coupling Using Microwave Heating

R-SH + Ar-X → R-S-Ar

Conditions: CuI (10 mol%), Cs_2CO_3 (2 equiv.), NMP, microwave heating, 195 °C, 2-6 h

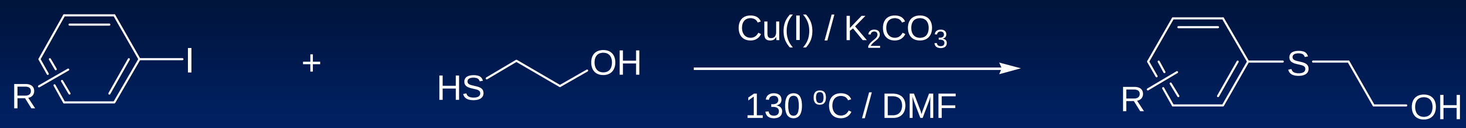
64-89 %

NMP = N-Methylpyrrolidone



Wu, Y.-J.; He, H. *Synlett* **2003**, *12*, 1789-1780.

Cu(I) Ctalyzed C-S Coupling Rxns[a]

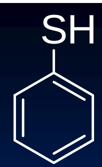


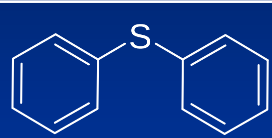
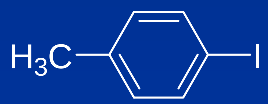
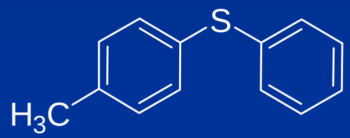
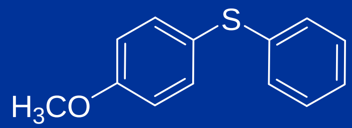
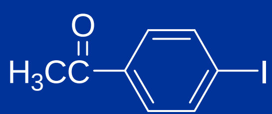
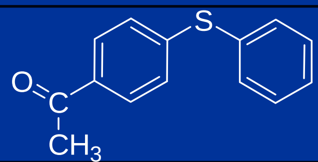
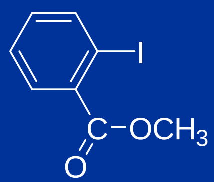
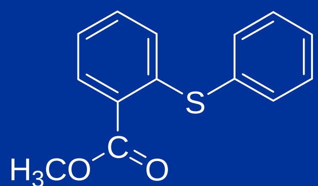
Entry	R	Cat.	Isolated Yield (%)[b]			
			48 h	24 h	18 h	12 h
1	H	<u>**18**</u>	-	98	92	85
2	H	<u>**19**</u>	-	95	95	87
3	*p*-CH_3	<u>**18**</u>	-	98	85	-
4	*p*-CH_3	<u>**19**</u>	-	95	92	-
5	*p*-OCH_3	<u>**18**</u>	-	87	64	-
6	*p*-OCH_3	<u>**19**</u>	-	88	64	-
7	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	-	70	-	-
8	*p*-$COCH_3$	<u>**18**</u>	85	68	37	-
9	*p*-$COCH_3$	<u>**19**</u>	88	60	32	-
10	*o*-$COOCH_3$	<u>**18**</u>	72	70	65	-
11	*o*-$COOCH_3$	<u>**19**</u>	65	65	60	-

[a] Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol 2-Mercaptoethanol ,1.2 mmol K_2CO_3 , 1.0 mL DMF.[b] Products were purified and isolated by flash chromatography on SiO_2..

Entry	R	Cat.	Isolated Yield (%)	
			24 h	18 h
1	H	**18**	98	95
2	H	**19**	96	95
3	*p*-CH_3	**18**	90	85
4	*p*-CH_3	**19**	95	92
5	*p*-OCH_3	**18**	96	93
6	*p*-OCH_3	**19**	95	84
7	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	72	-
8	*p*-$COCH_3$	**18**	95	93
9	*p*-$COCH_3$	**19**	98	87
10	*o*-$COOCH_3$	**18**	98	90
11	*o*-$COOCH_3$	**19**	95	95

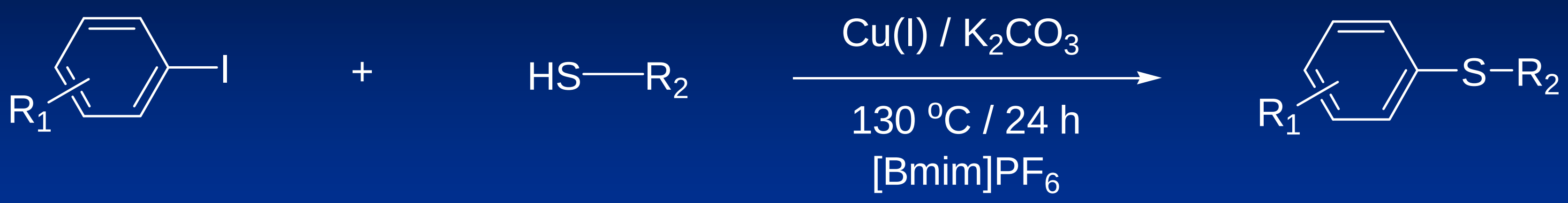
Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol 1-Octanethiol, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

Substrate +  —[Cu (I) / K_2CO_3 ; 130 ^oC / 24 h / DMF]→ Product

Entry	Substrate	Product	Cat. (10 mol%)	Isolated Yield (%)
1			**18**	98
2			**19**	98
3			**18**	98
4			**19**	95
5			**18**	91
6			**19**	94
7			**18**	90
8			**19**	92
9			**18**	61
10			**19**	66
11			**18**	98
12			**19**	93

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol Thiophenol, 1.2 mmol K_2CO_3 , 1.0 mL DMF.

Cu(I) Ctalyzed C-S Coupling in [Bmim]PF_6



Entry	R_1	R_2	Cat. (10 mol%)	Yield (%)
1 2	H	$-(CH_2)_2OH$	**18** **19**	60 70
3 4	*p*-OCH_3	$-(CH_2)_2OH$	**18** **19**	65 72
5 6	H	$-(CH_2)_7CH_3$	**18** **19**	75 80
7 8	*p*-OCH_3	$-(CH_2)_7CH_3$	**18** **19**	72 80

Cu(I) Catalyzed C-S Coupling Under MW

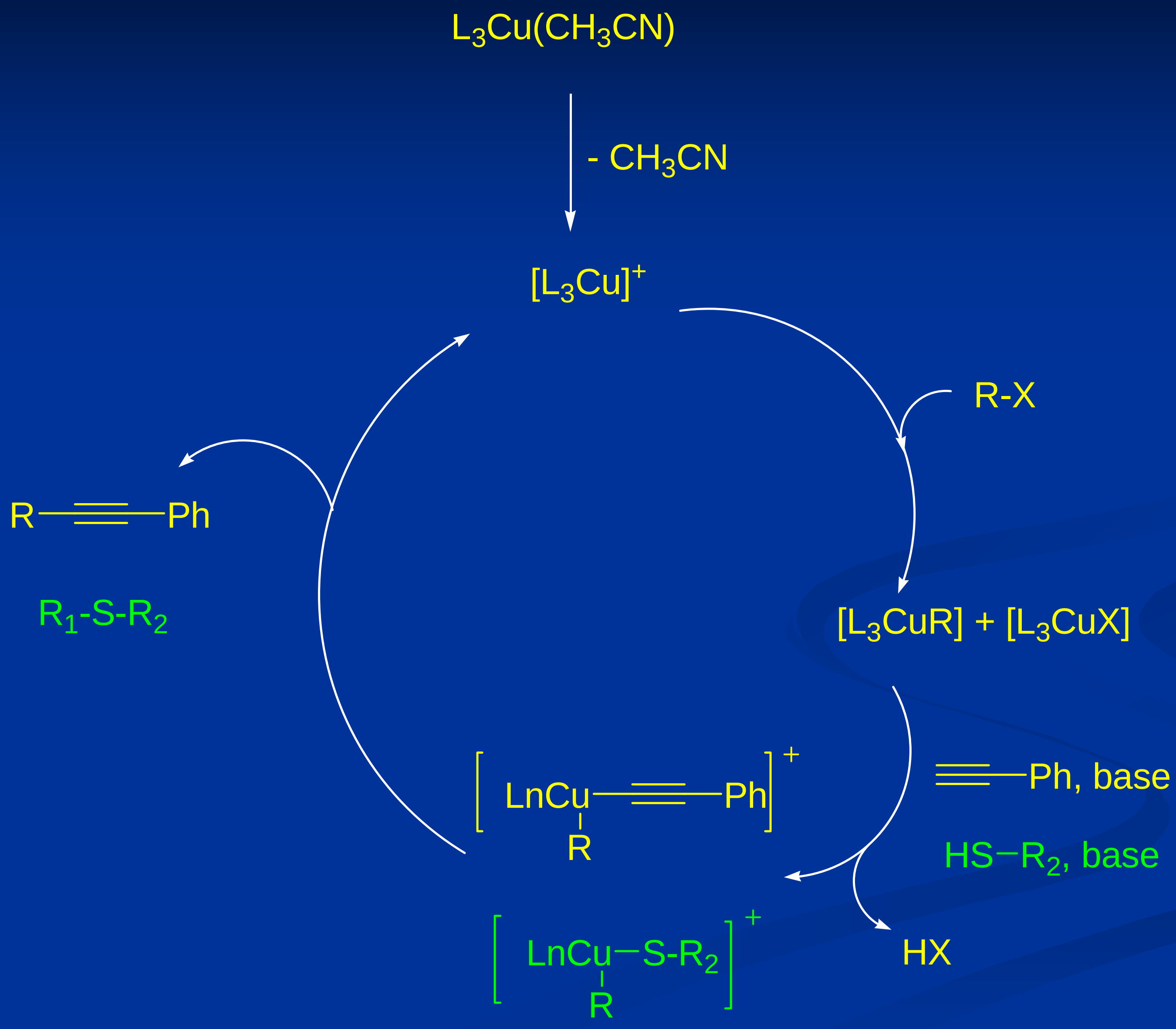
Entry	R	Cat.	Conversion (%)			
			35 min	30 min	25 mim	20 min
1	H	**18**	-	99	40	-
2	H	**19**	-	99	27	-
3	*p*-CH_3	**18**	-	99	99	90
4	*p*-CH_3	**19**	-	99	98	-
5	*p*-OCH_3	**18**	-	99	99	40
6	*p*-OCH_3	**19**	-	99	80	-
7	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	-	70	-	-
8	*p*-$COCH_3$	**18**	-	99	80	-
9	*p*-$COCH_3$	**19**	99	67	99	-
10	*o*-$COOCH_3$	**18**	-	99	20	-
11	*o*-$COOCH_3$	**19**	90	70	90	

Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol 2-Mercaptoethanol ,
1.2 mmol K_2CO_3 , 1.0 mL DMF.

Entry	R	Cat.	Conversion (%)			
			35 min	30 min	25 mim	20 min
1	H	**18**	-	99	65	
2	H	**19**	99	60	-	
3	*p*-CH_3	**18**	-	99	85	
4	*p*-CH_3	**19**	-	99	40	
5	*p*-OCH_3	**18**	-	99	99	10
6	*p*-OCH_3	**19**	-	99	99	70
7	*p*-OCH_3	**$Cu(CH_3CN)_4PF_6$**	-	-	60	-
8	*p*-$COCH_3$	**18**	-	99	99	60
9	*p*-$COCH_3$	**19**	80	73	-	-
10	*o*-$COOCH_3$	**18**	80	75	-	-
11	*o*-$COOCH_3$	**19**	90	85	-	-

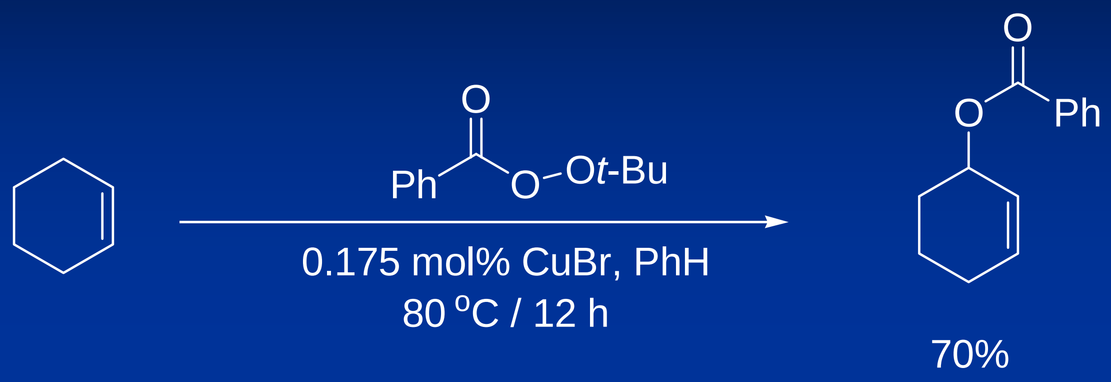
Conditions : 10 mol % Cat.,1.0 mmol Aryl Iodides, 1.2 mmol 1-Octanethiol,
1.2 mmol K_2CO_3 , 1.0 mL DMF.

Mechanism of C-C or C-S Coupling Reactions

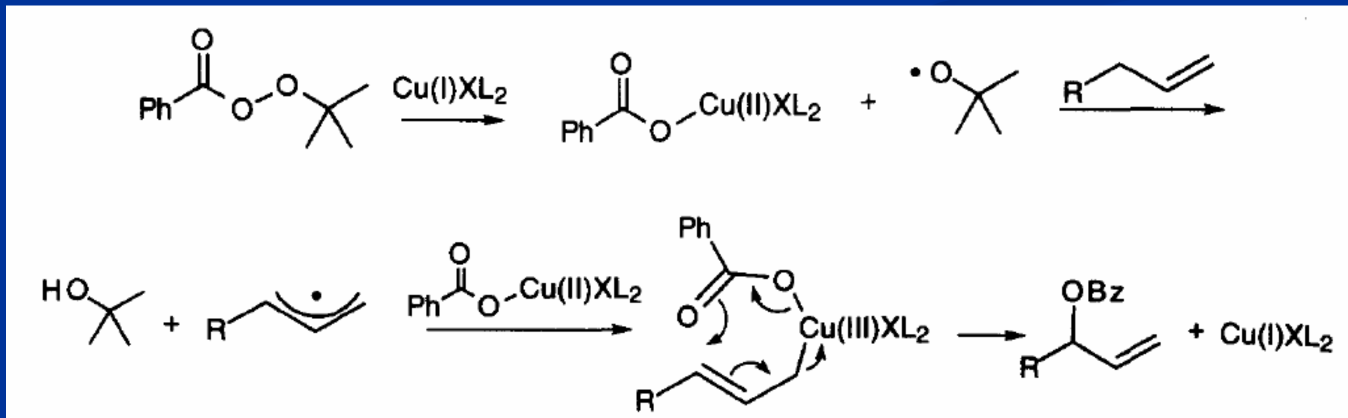


Chem. Rev. **2007**, *107*, 874-922

Allylic Oxidation of Olefin (Kharasch-Sosnovsky Reaction)



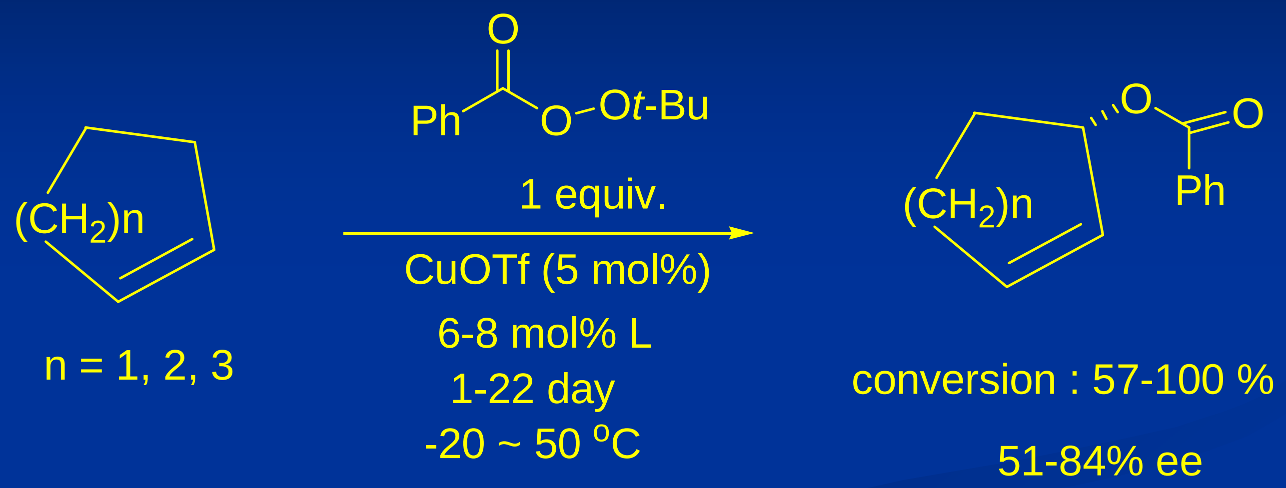
Mechanism



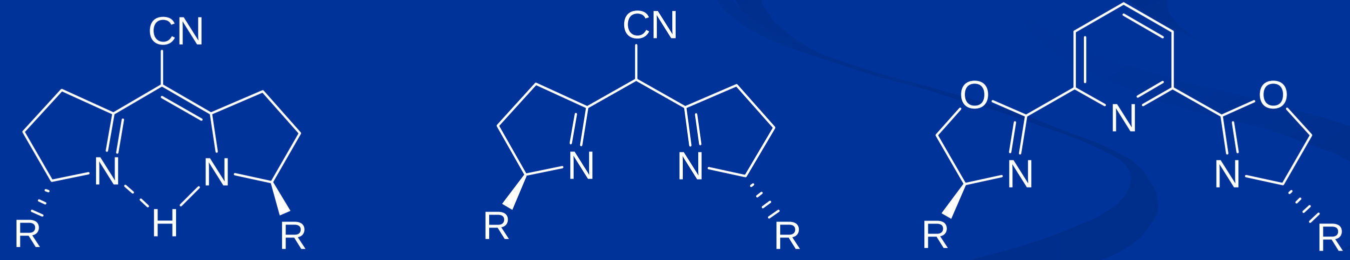
70

Kharasch, M. S.; Sosnovsky, G.; Yang, N. C. *J. Am. Soc. Chem*. **1959,** *81*, 5819-5824.

Enantioselective Allylic Oxidation Catalyzed by Chiral Bisoxazoline –Copper Complexes



L =



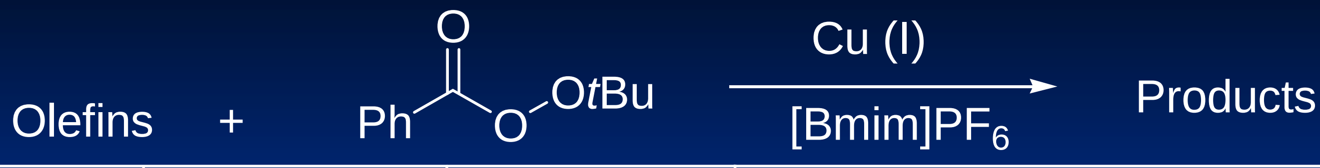
R = CH_2OSiMe_2*t*-Bu

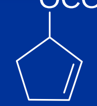
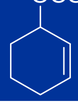
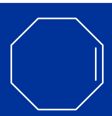
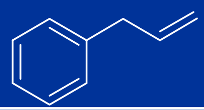
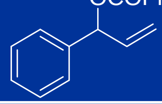
R = *i*-Pr
R = *t*-Bu
R = Ph

R = *i*-Pr

Gokhale, A.S.; Minidis, A. B. E.; Pfaltz, A. *Tetrahedron Lett*. **1995**, *36*, 1831-1834.

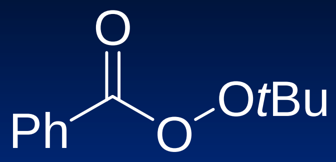
Cu(I) Catalyzed C-O Coupling Rxns in IL



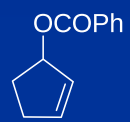
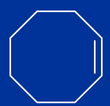
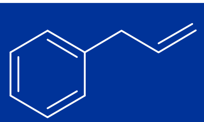
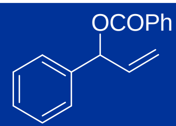
Entry	Olefin	Product	Cat.	27°C		70 °C	
				Time (d)	Conv.[a] (%)	Time (h)	Conv.[a] (%)
1			**18**	1	99	3	99
2			**19**	1	99	3	99
3			**$Cu(CH_3CN)_4PF_6$**	-	-	3	0
5			**18**	-	-	3	32[b]
6			**19**	-	-	3	55[b]
7			**18**	1	99	3	99
8			**19**	2	99	5	99
9			**18**	2	99	3	85
10			**19**	2	99	3	76
11			**18**	3	99	4	99
12			**19**	3	99	4	99
13			**18**	2	70	3	99
14			**19**	2	53	4	99

[a] Conditions : 5 mol % Cat.,1.0 mmol *t*-Butyl perbenzoate, 5.0 mmol Olefins in 1.0 mL $[Bmim]PF_6$.
[b] in 1.0 mL CH_3CN.

Cu(I) Catalyzed C-O Coupling Rxns under MW

Olefins + 

$\xrightarrow[\text{max.300 W / [Bmim]PF}_6]{\text{Cu (I)}}$ Products

Entry	Olefin	Product	Cat.	70 ºC	
				Time (min)	Conversion (%)
1			**18**	25	99
2			**19**	30	99
3			**$Cu(CH_3CN)_4PF_6$**	30	30
4			**18**	10	99
5			**19**	20	99
6			**18**	40	99
7			**19**	40	99
8			**18**	30	99
9			**19**	25	99
10			**18**	25	99
11			**19**	25	99

Conditions : 5 mol % Cat.,1.0 mmol *t*-Butyl perbenzoate, 5.0 mmol Olefins,1.0 mL [Bmim]PF_6.[73]

Conclusions

1. In comparison to palladium chemistry, Cu chemistry is simple and mild without the use of air sensitive and expensive phosphine ligands or additives.

2. We have successfully demonstrated the catalytic activity of the Cu complexes (18 and 19) for Sonogashira、C-S bond coupling and Allylic Oxidations of olefins reactions.

3. The successful use of microwave irradiation in Sonogashira、C-S bond coupling and Allylic Oxidations of olefin to further accelerate rxn rates and increase conversions.

II .Coordination Chemistry of Ag(I) with Tripodal Pyridylphosphite and Pyidylphosphine Oxide Ligands.

Applications of Metal-Organic Framework

1. Molecular sieves

2. Sensors

3. Ion-exchangers

4. Catalysts

Effects of the Metal-Organic Framework

1. The Coordination Mode of the Metal Center

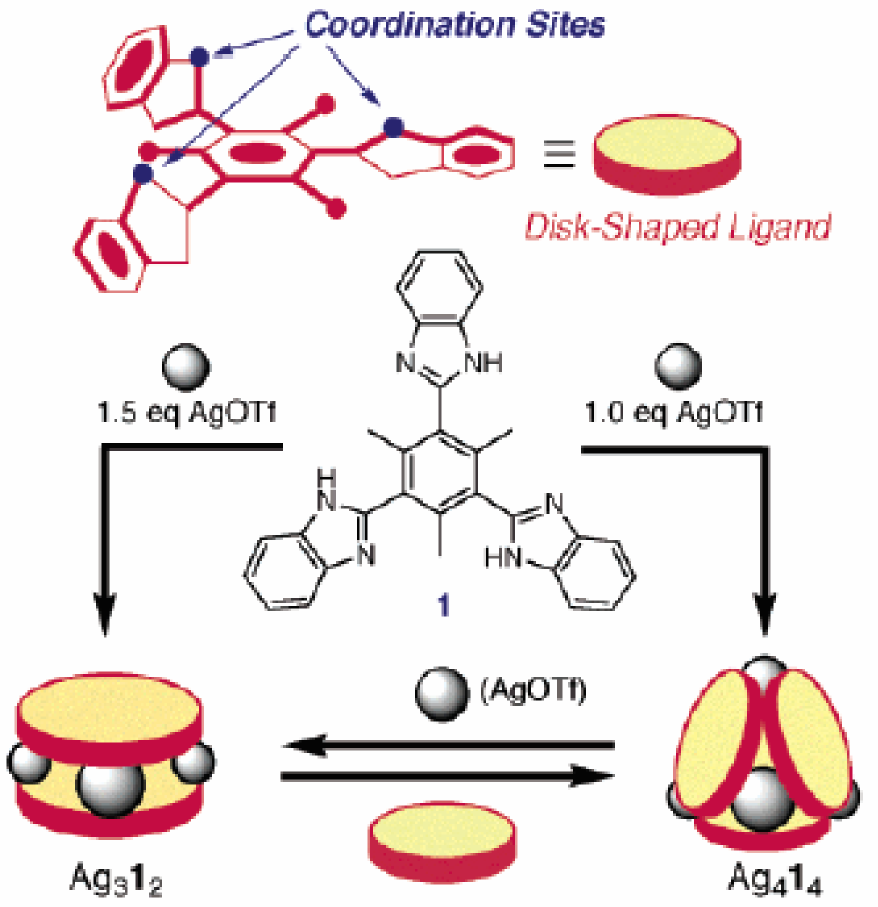
2. The structure of the ligand

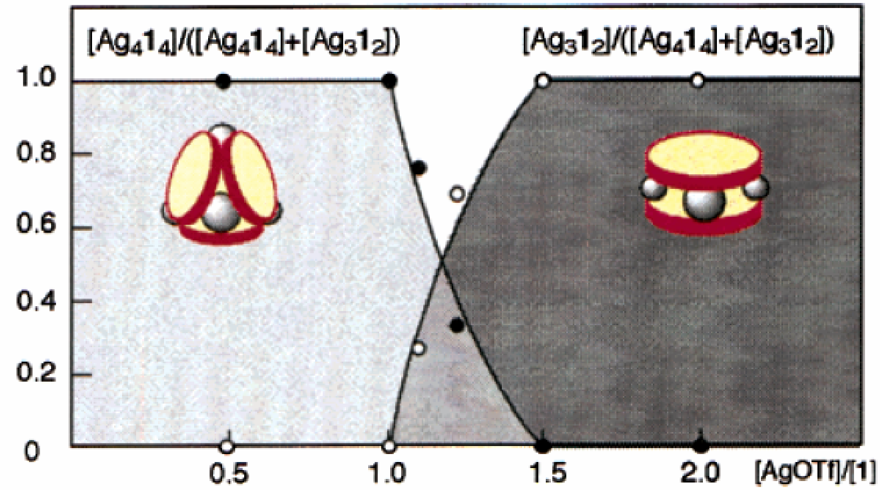
3. Solvent Systems

4. Counter Ions

5. The Ratio of Ligand and Metal

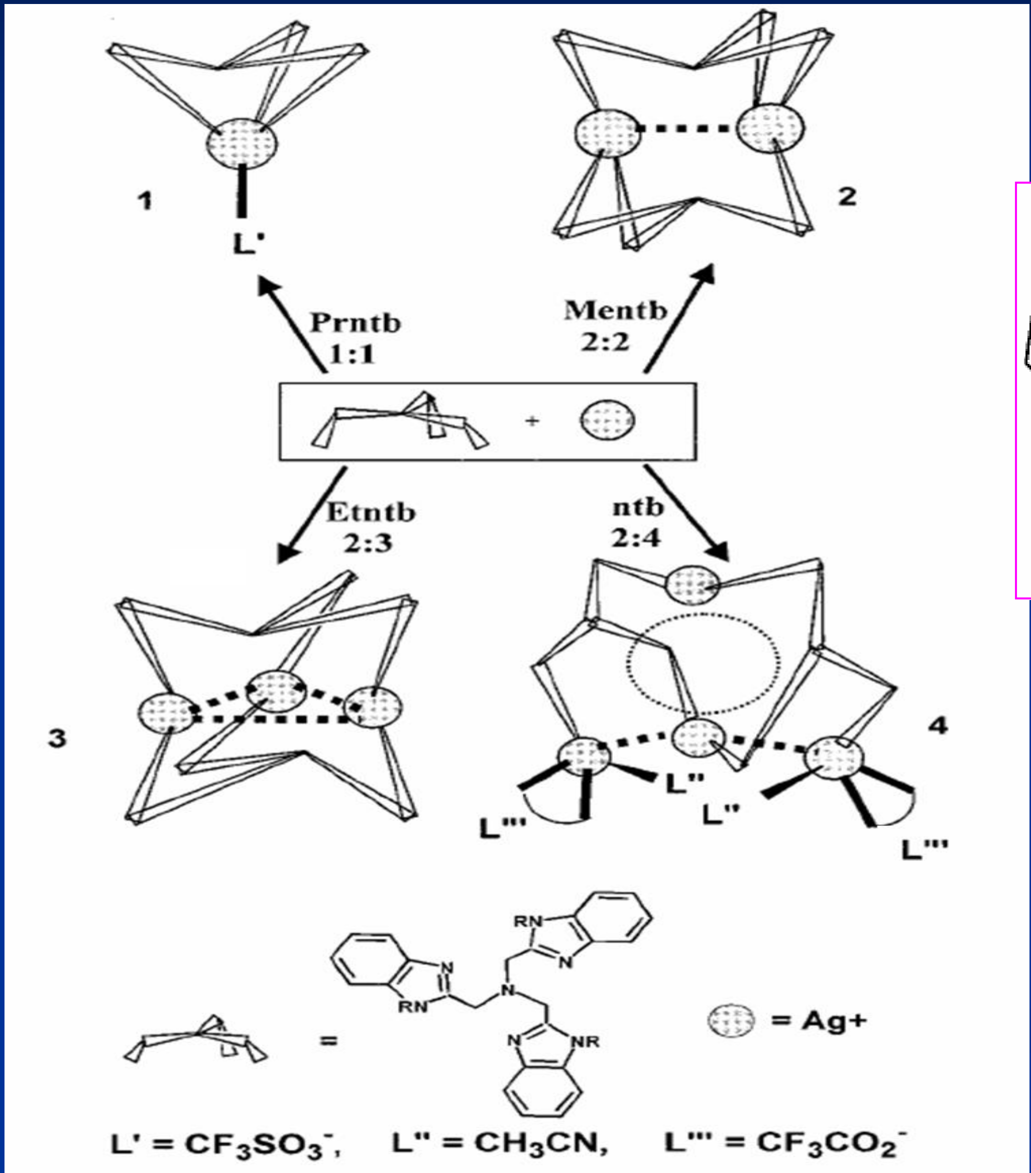
Ag(I) Cpds Dependent on the Metal-Ligand Ratio

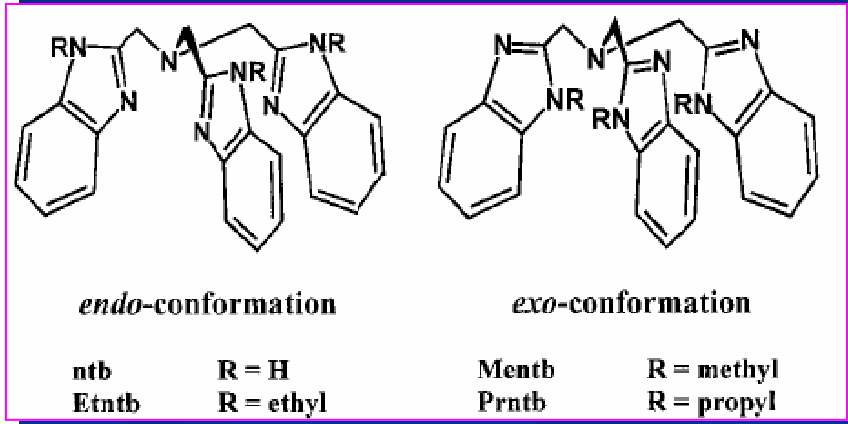




Shuichi, H.; Tao, Y.; Motoo, S.; Mitsuhiko, S. *J. Am. Chem. Soc.* **2002**, *124*, 14510-14511.

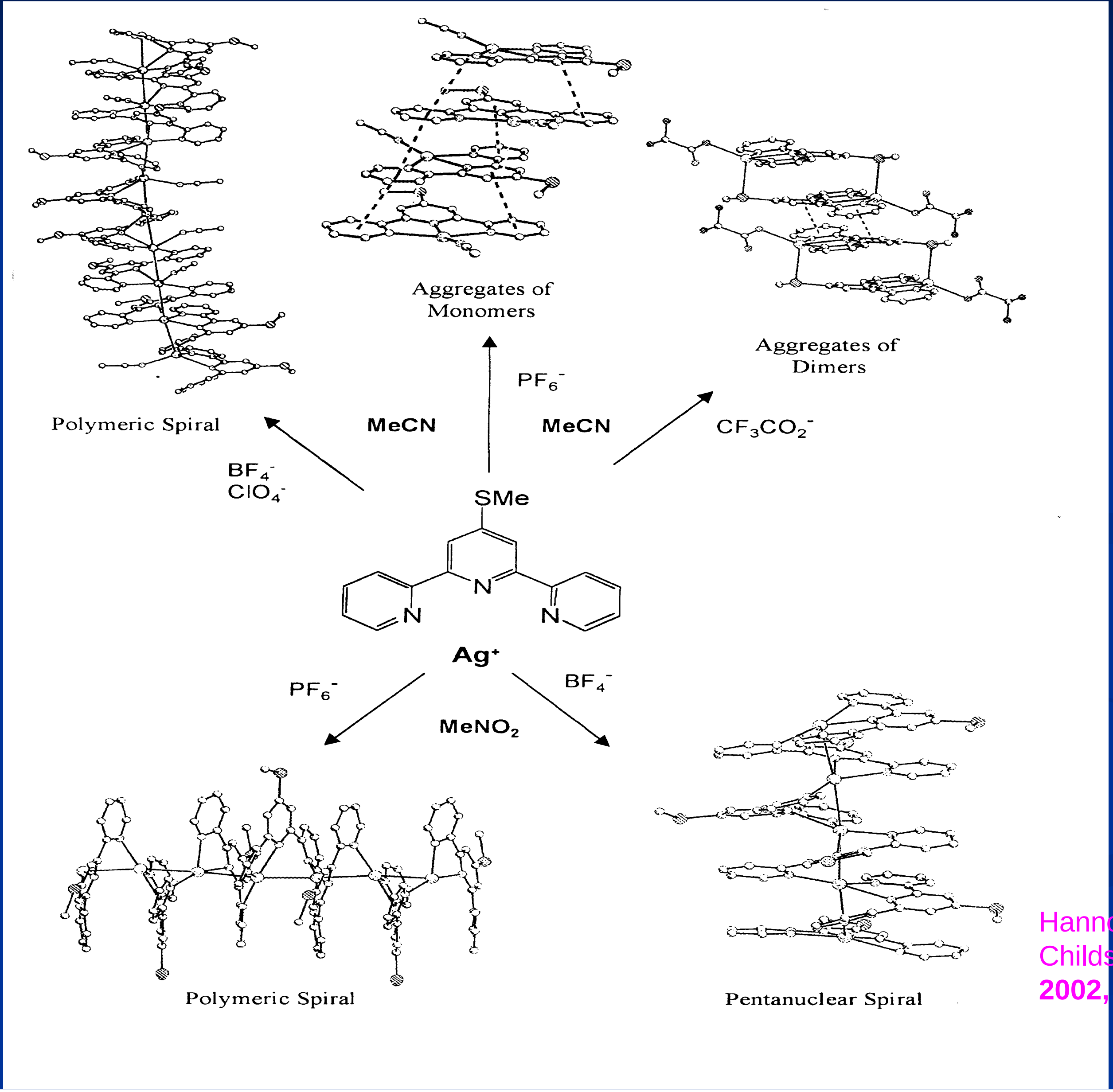
Ag(I) Cpds Dependent on C_3 Ligands and Counter ions





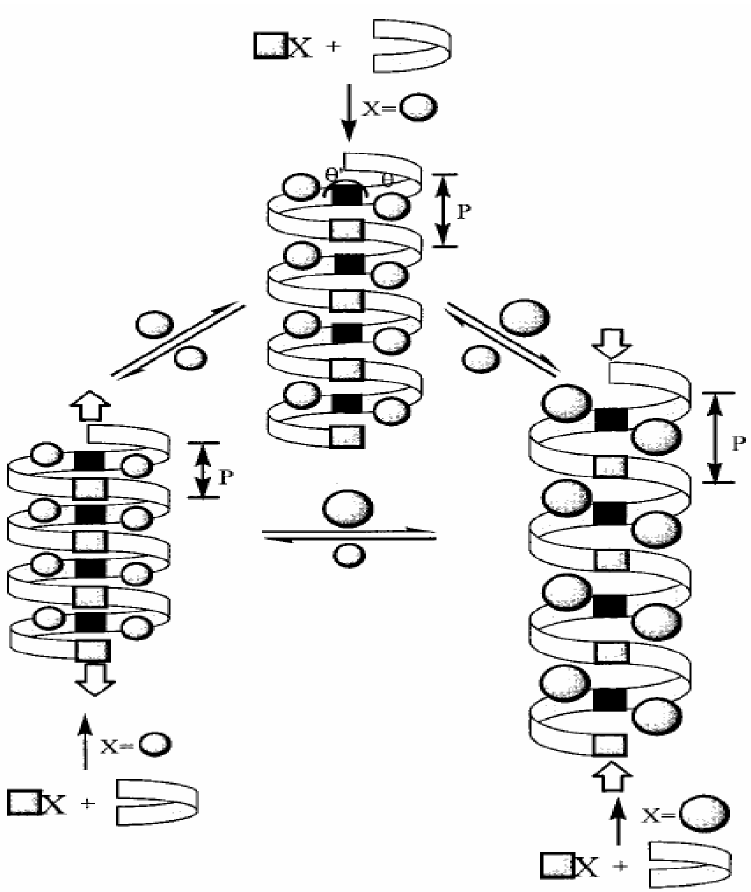
Su, C.-Y.; Kang, B.-S.; Du, C.-X.; Yang, Q.-C.; Mak, T. C. W. *Inorg. Chem.* **2000,** *39, 4843-4849.*

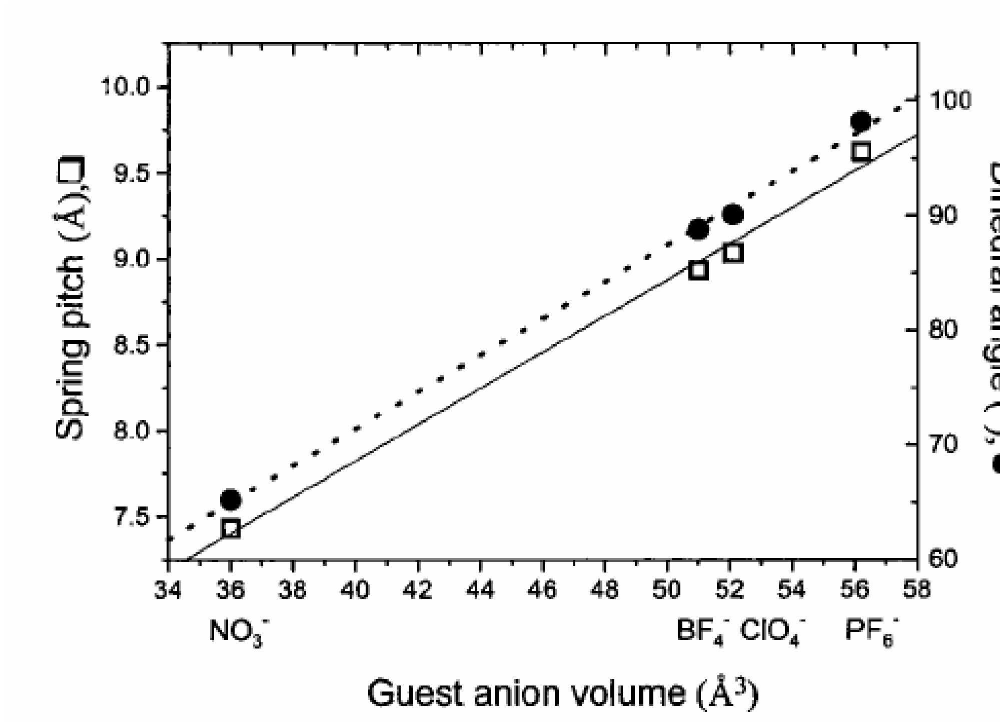
Ag(I) Cpds Dependent on Solvents and Counter ions

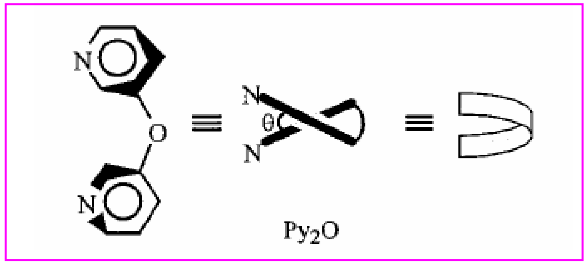


Hannon, M. J.; Painting, C. L.; Plummer, E. A.; Childs, L. J.; Alcock, N. W. *Chem. Eur. J.* **2002**, *8, 2225-2238.*

Molecular Helical Springs as Tunable Receptors







Jung, O. S.; Kim, Y. J. Lee, Y.-A.; Park, J. K. Chae, H. K.
J. Am. Chem. Soc. **2000,** *122, 9921-9925.*

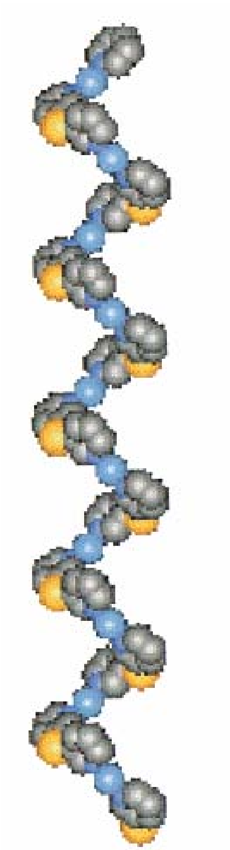
Structures of AgX Bearing 3,3'-Thiobispyridine

3,3'-Py_2S

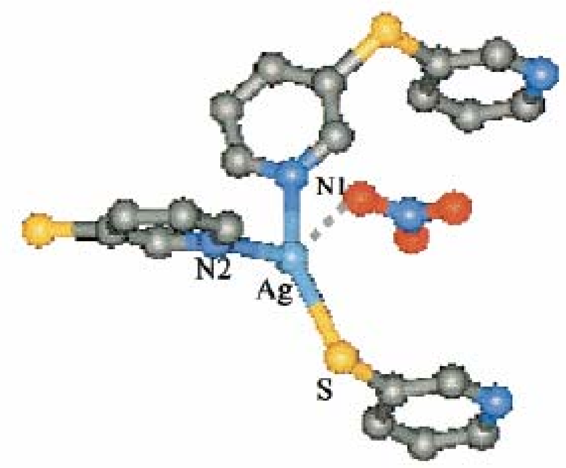
+

AgX

(X = NO_3^-, BF_4^-, ClO_4^-, PF_6^-)



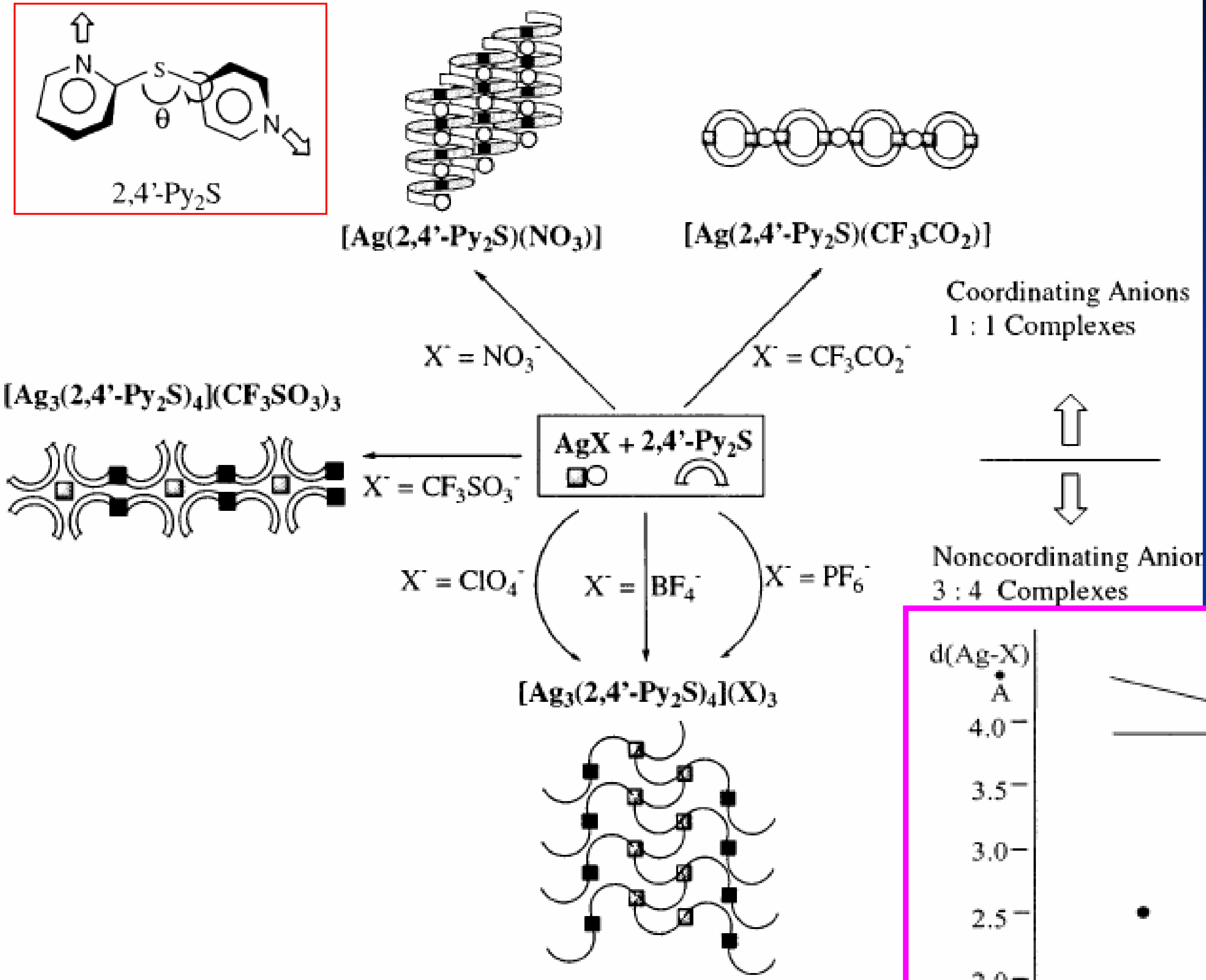
X = BF_4^-, ClO_4^-, PF_6^-

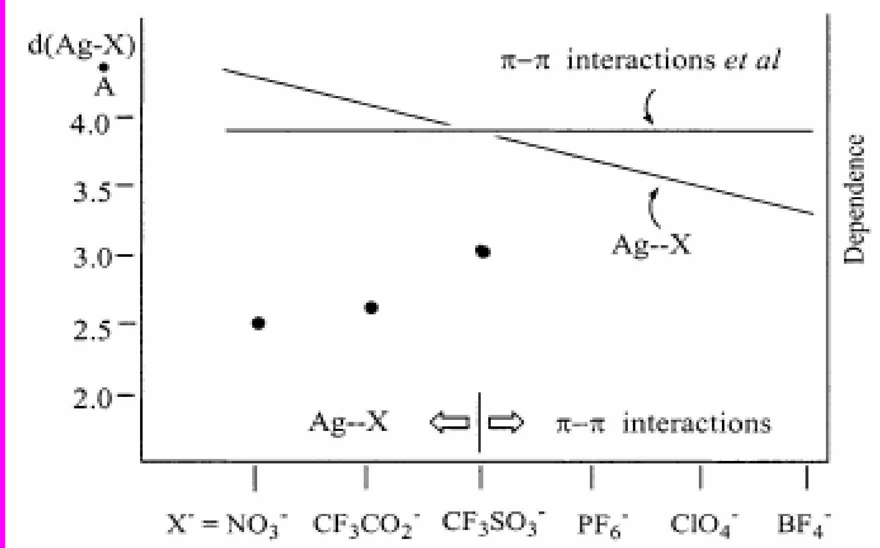


X = NO_3^-

Jung, O.-S. Kim, Y. J.; Lee, Y.-A.; Chae, H. K. Jang, H. G.; Hong, J. *Inorg. Chem.* **2001,** *40, 2105-2110*

Structures of AgX Bearing 2,4'-Thiobispyridine

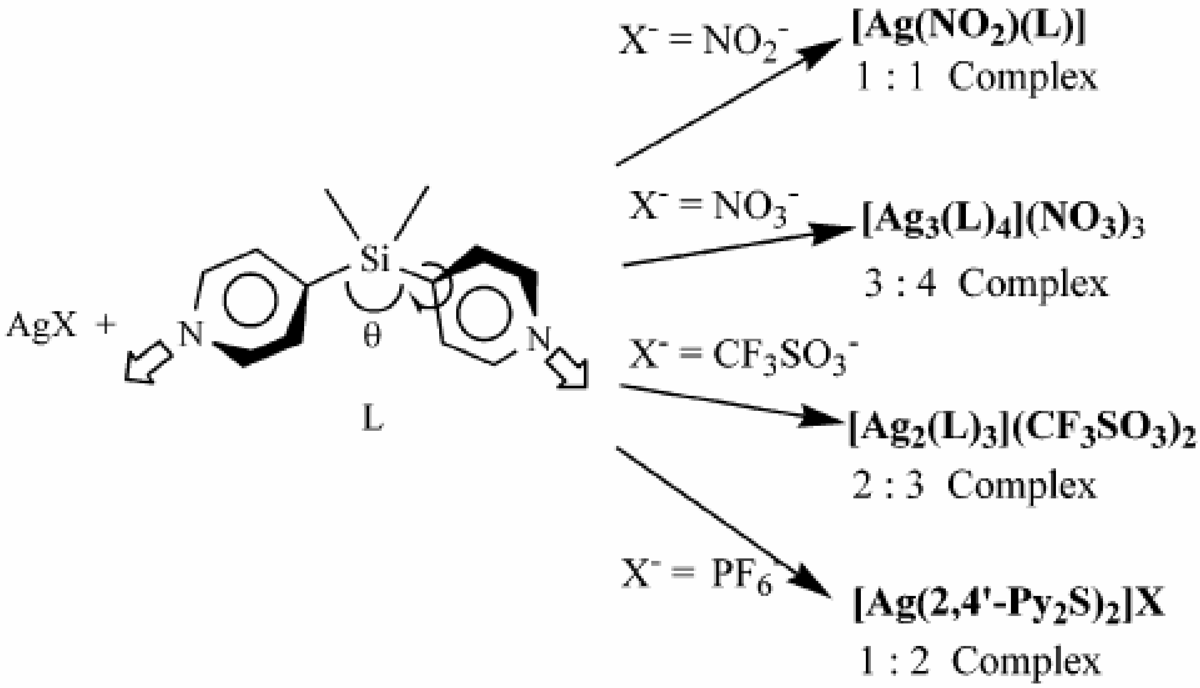


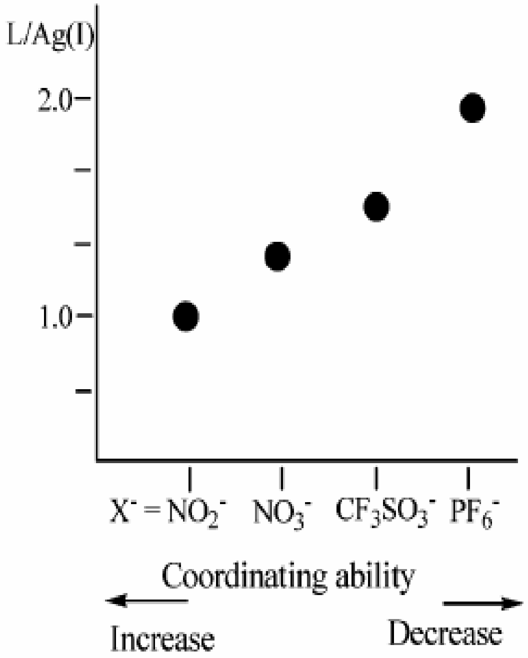


$NO_3^- > CF_3CO_2^- > CF_3SO_3^- > PF_6^- > ClO_4^- > BF_4$

Jung, O.-S.; Kim, Y. J. Lee, Y.-A. Park, K. M.; Lee, S. S. *Inorg. Chem.* **2003,** *42, 844-850.*

Structures of AgX-Bearing Bis(4pyridyl)-dimethylsilane



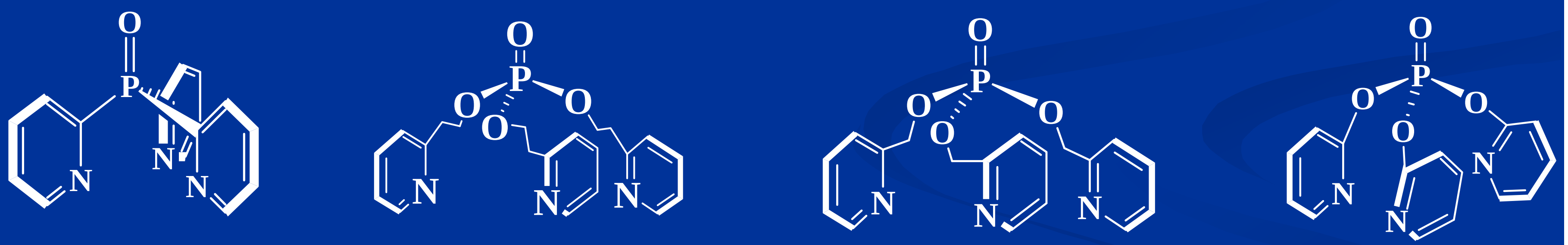


Lee, J. W.; Kim, E. A. Kim, Y. J.; Lee, Y. A.; Pak Y. S.; and Jung O.-S.
Inorg. Chem. **2005,** *44, 3151-3155*

Synthetic Strategy

$$L + AgX \xrightarron[rt,\ 3\ h]{THF} Product \downarrow$$

C_{3v} Ligands



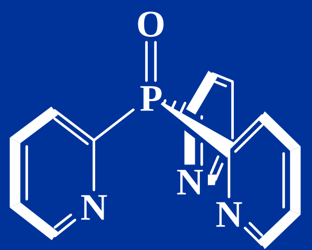
L_1 L_2 L_3 L_4

AgX

$AgBF_4$ *$AgClO_4$*

$AgPF_6$ *$AgSO_3CF_3$*

Structures of AgX Bearing L_1

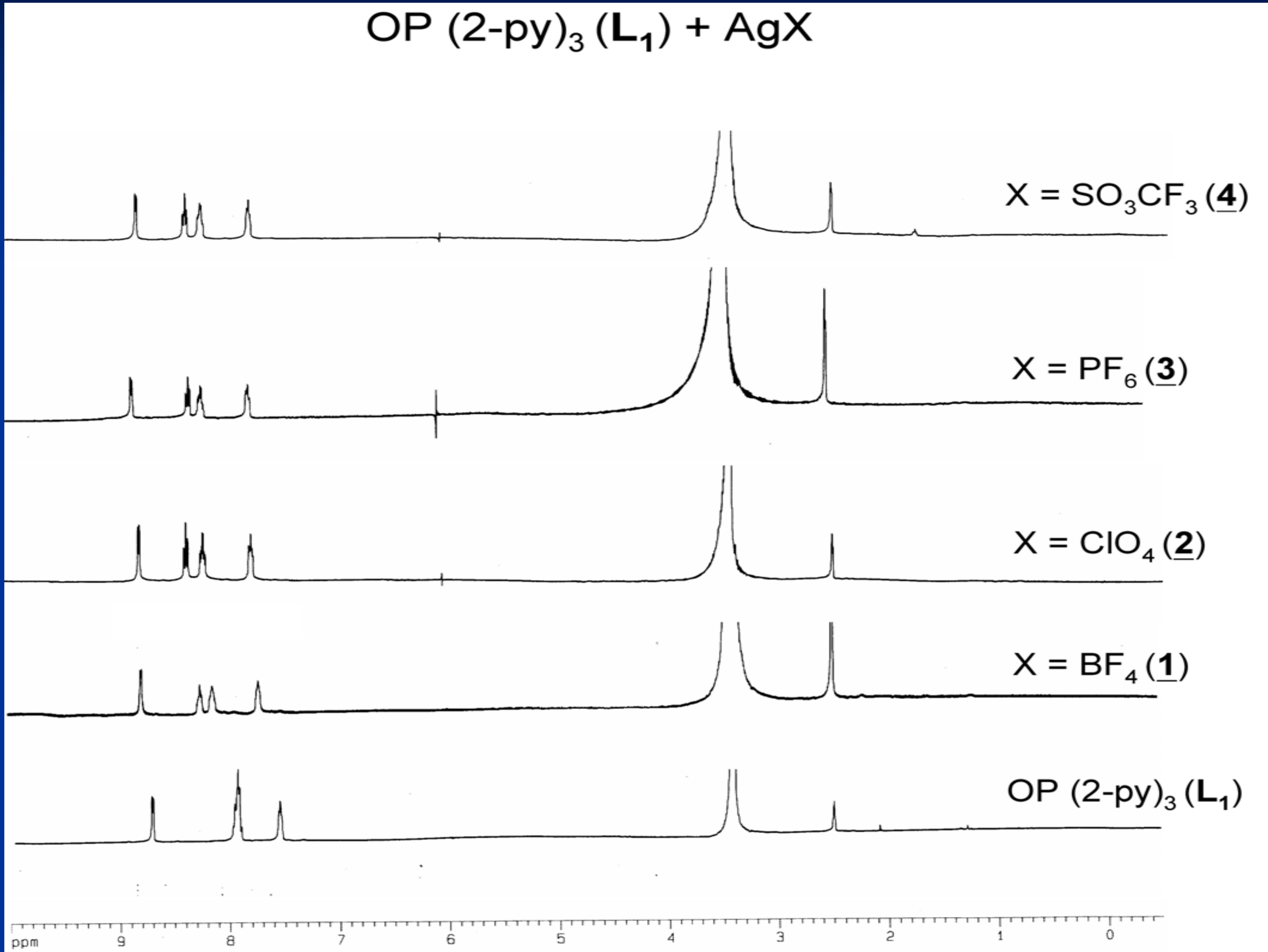


L_1

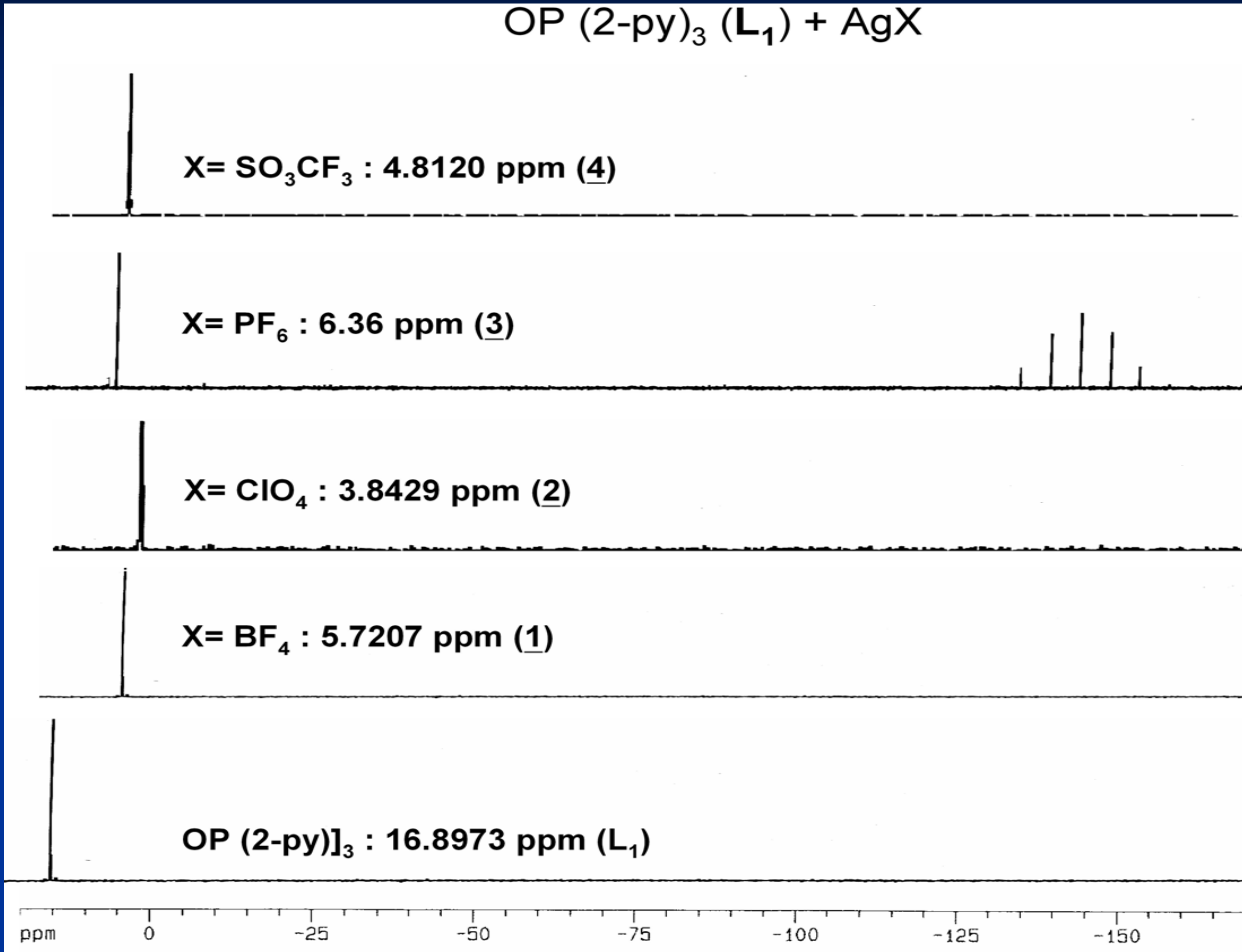
\+

$AgBF_4$	→	$[O{=}P(2\text{-}py)_3]_5(AgBF_4)_5$	**1**
$AgClO_4$	→	$[O{=}P(2\text{-}py)_3]_3(AgClO_4)_5$	**2**
$AgPF_6$	→	$[O{=}P(2\text{-}py)_3]_3(AgPF_6)_5$	**3**
$AgSO_3CF_3$	→	$[O{=}P(2\text{-}py)_3]_2(AgSO_3CF_3)$	**4**

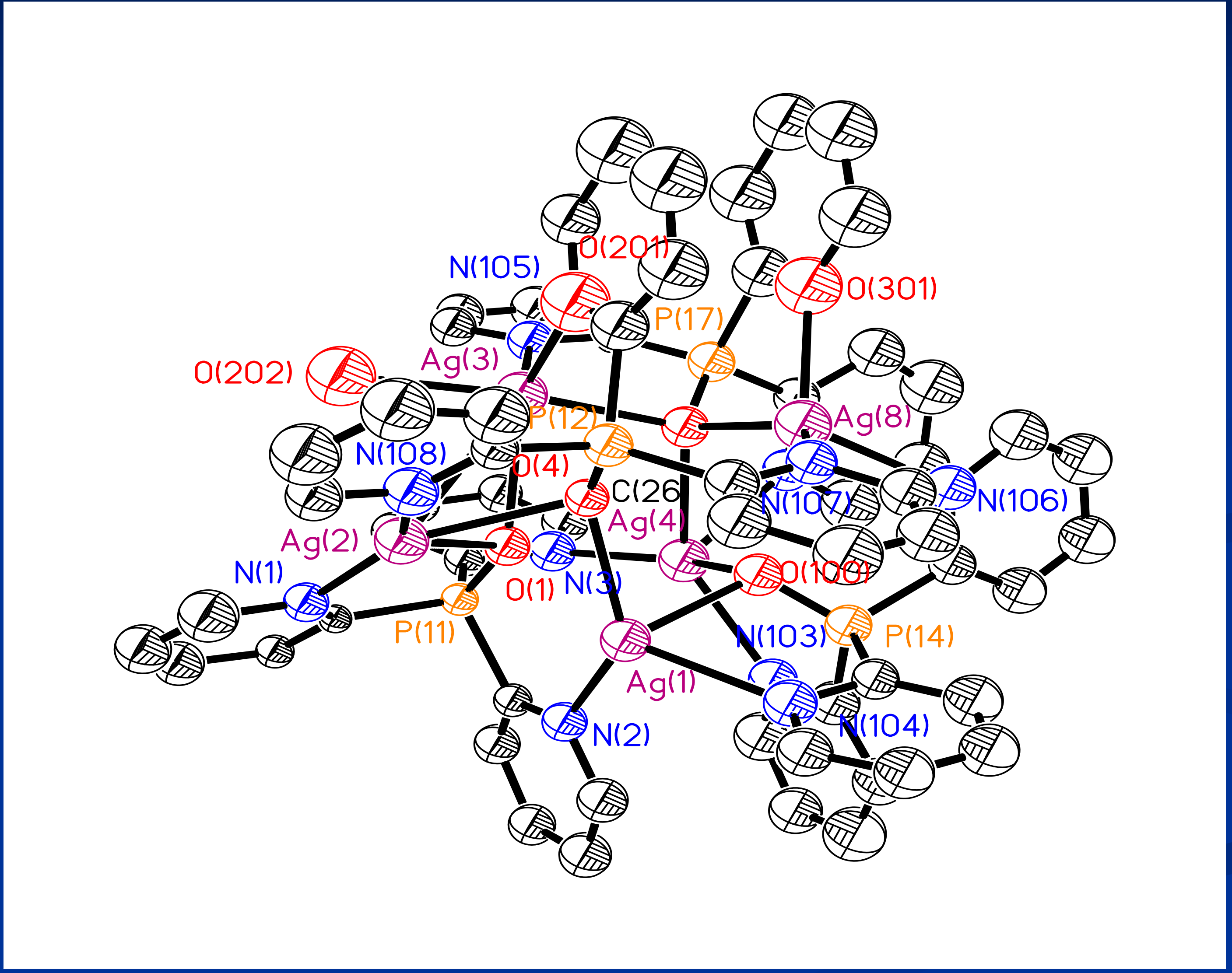
^1H NMR Spectra of L_1 + AgX



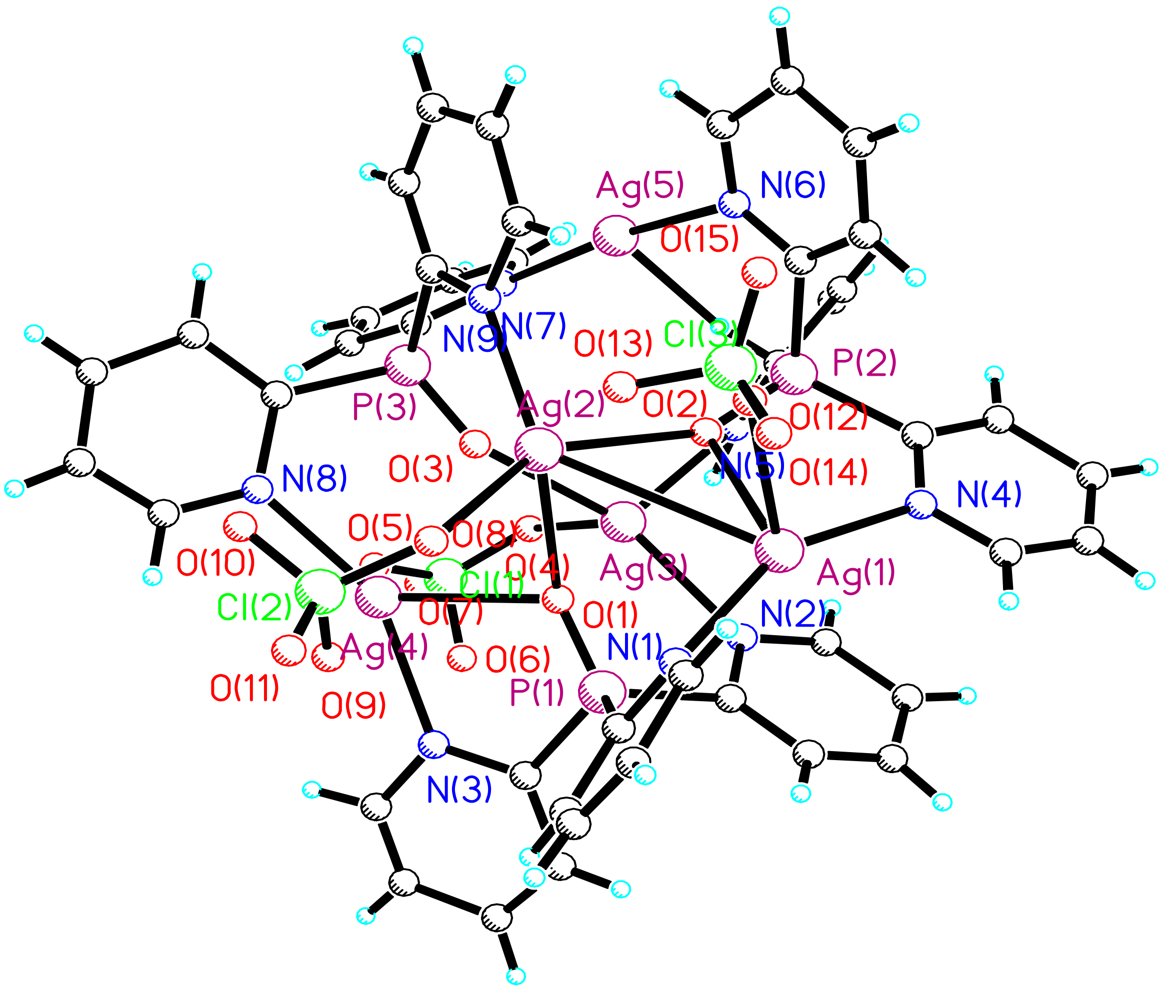
^{31}P NMR Spectra of L_1 + AgX



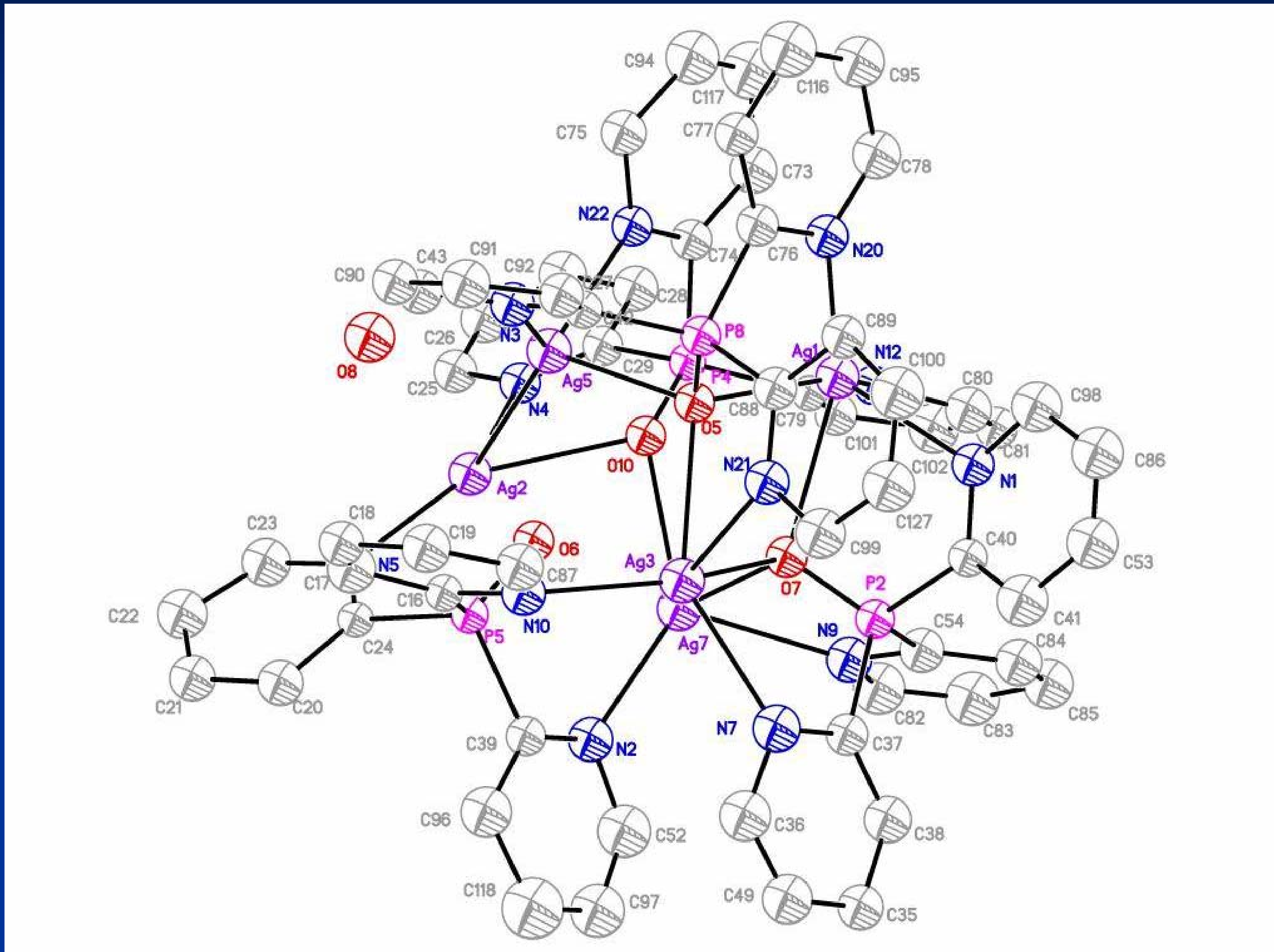
Structure of $[O=P(2\text{-}py)_3]_4(AgBF_4)_5$ (<u>1</u>)



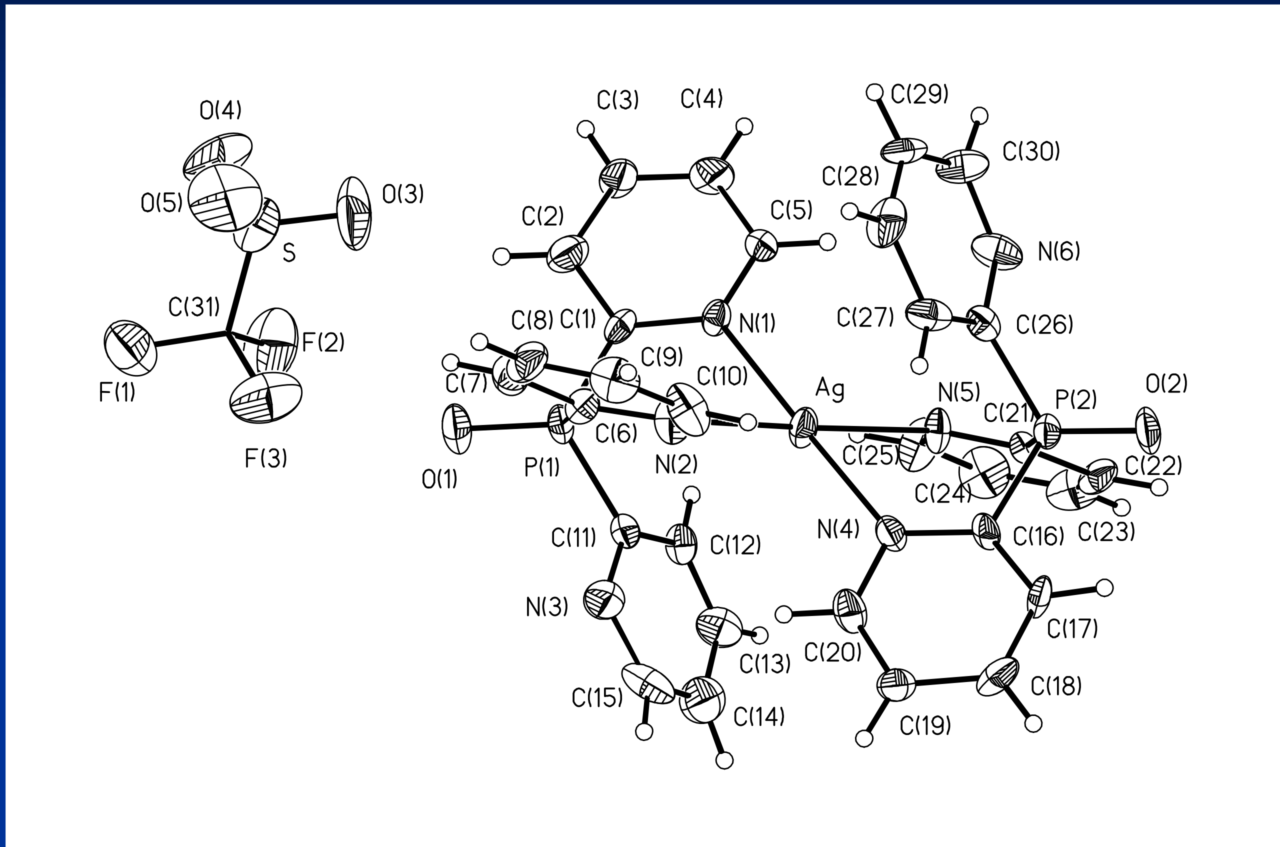
Structure of $[O=P(2\text{-}py)_3]_3(AgClO_4)_5$ (2)



Structure of $[O{=}P(2\text{-}py)_3]_4(AgPF_6)_5$ (<u>3</u>)



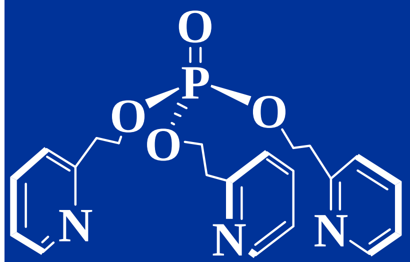
Structure of [O=P(2-py)$_3$]$_2$(AgSO$_3$CF$_3$) (4)



Ag-N(1) : 2.307(7) Å
Ag-N(2) : 2.449(13) Å
Ag-N(4) : 2.281(8) Å
Ag-N(5) : 2.553(10) Å

N(4)-Ag-N(1) : 178.5(5)^o
N(1)-Ag-N(2) : 86.3(3)^o
N(4)-Ag-N(2) : 94.3(4)^o
N(4)-Ag-N(5) : 86.3(4)^o
N(1)-Ag-N(2) : 86.3(3)^o
N(1)-Ag-N(5) : 93.0(3)^o

Structures of AgX Bearing $\underline{L_2}$

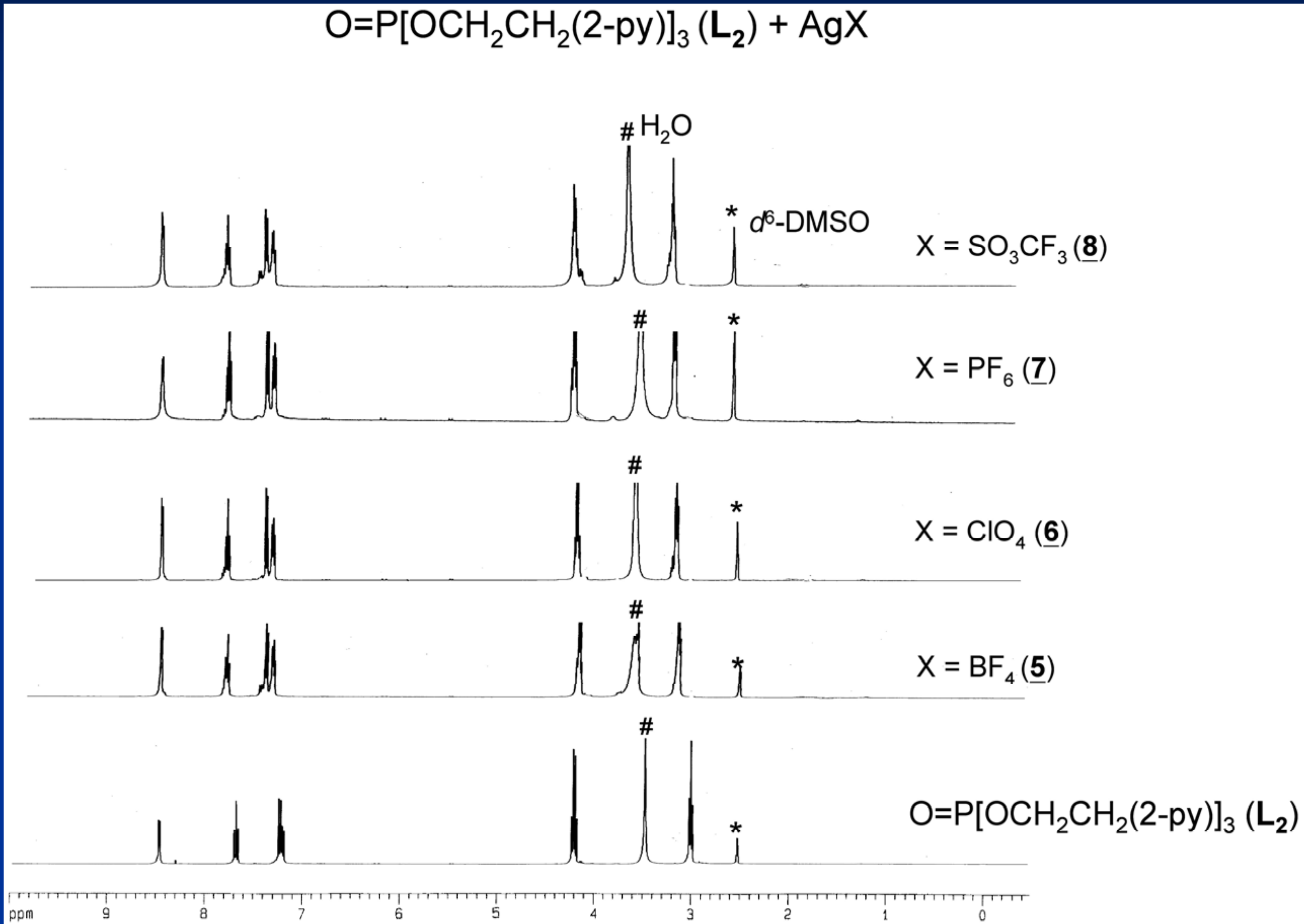


L_2

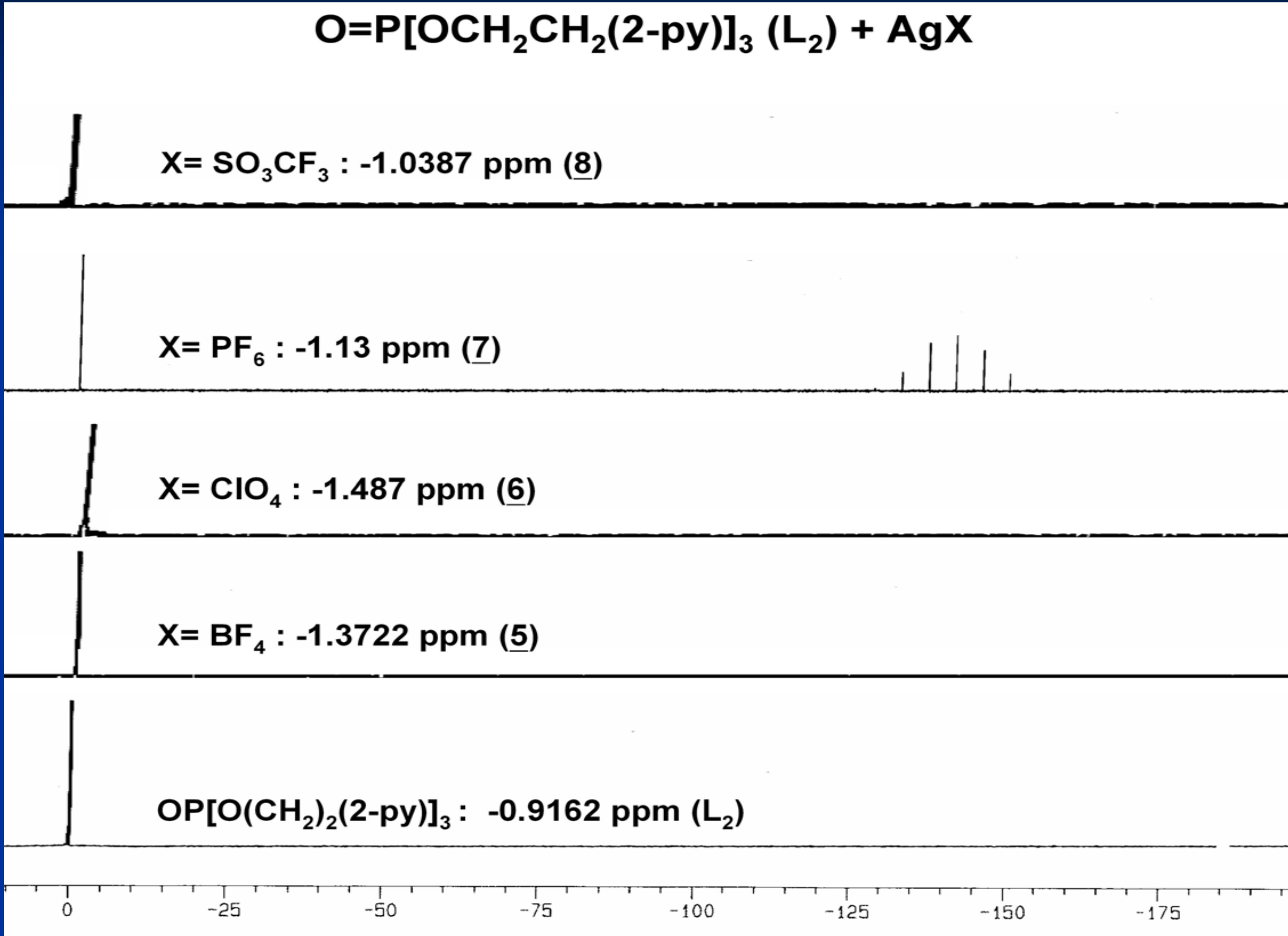
+

$AgBF_4$	→	$\{O{=}P[OCH_2CH_{2(}2\text{-}py)]_3(AgBF_4)\}_\infty$ **<u>5</u>**
$AgClO_4$	→	$\{O{=}P[OCH_2CH_2(2\text{-}py]_3\}_2(AgClO_4)_3$ **<u>6</u>**
$AgPF_6$	→	$\{O{=}P[OCH_2CH_2(2\text{-}py)]_3\}_2(AgPF_6)_3$ **<u>7</u>**
$AgSO_3CF_3$	→	**<u>8</u>**

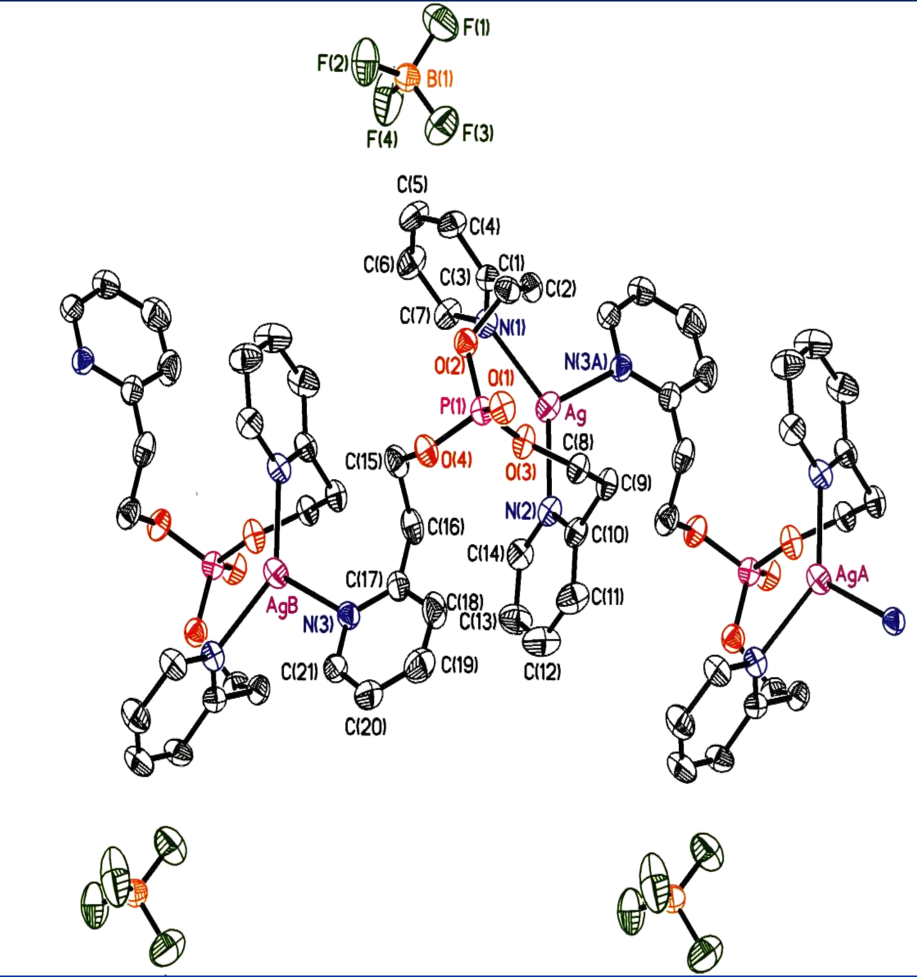
^{1}H NMR Spectra of L$_2$ + AgX

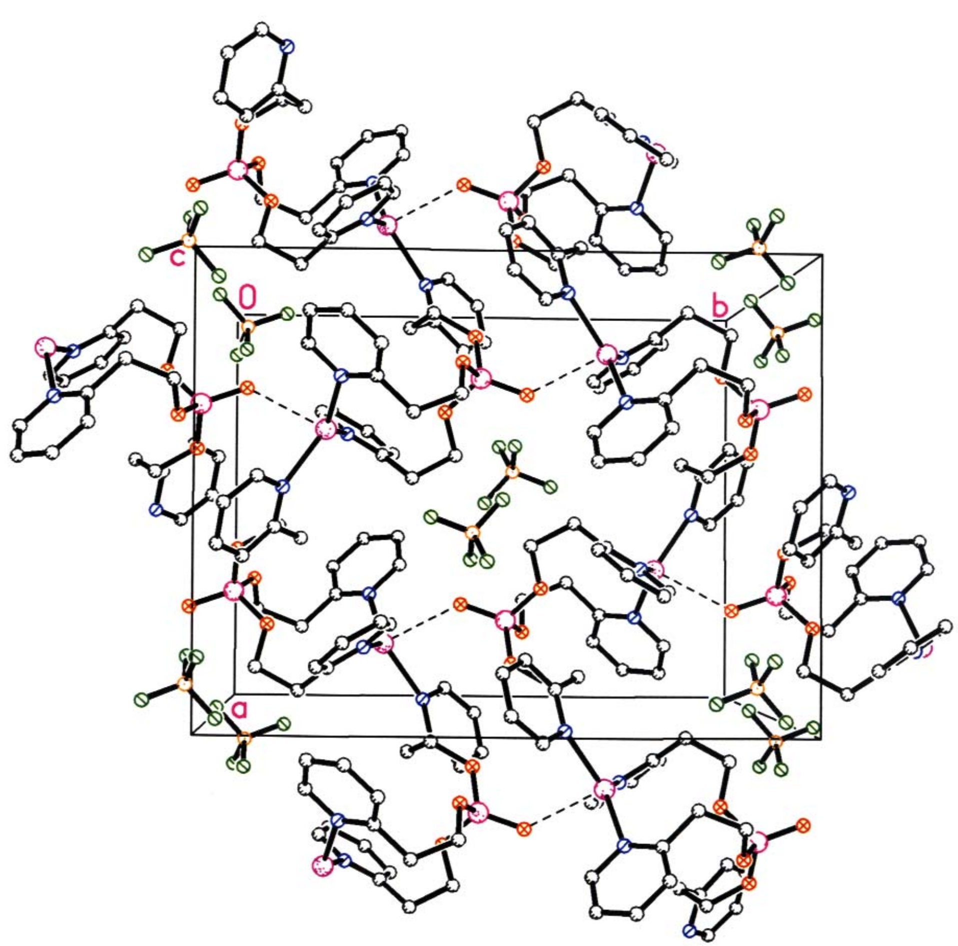


^{31}P NMR Spectra of L_2 + AgX



Structure of $\{O{=}P[OCH_2CH_2(2\text{-}py)]_3(AgBF_4)\}_\infty$ (5)

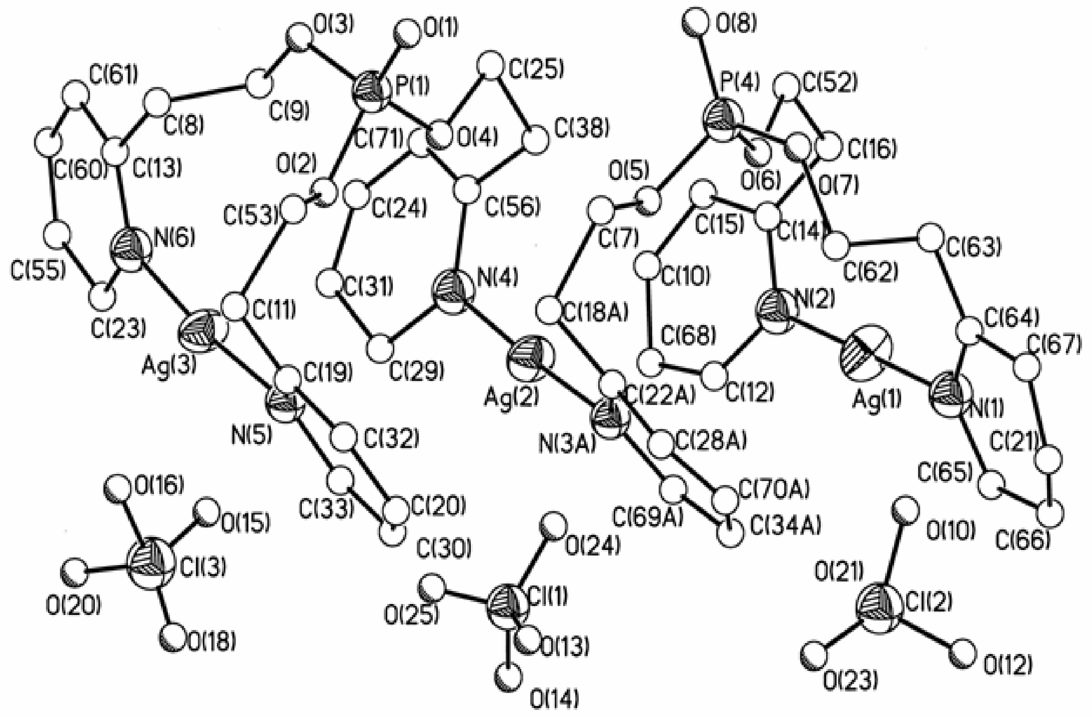




Ag-N(2) : 2.253(4) Å
Ag-N(1) : 2.296(4) Å
Ag-N(3A) : 2.339(4) Å

N(2)-Ag-N(1) : 131.12(12)°
N(2)-Ag-N(3A) : 119.71(12)°
N(1)-Ag-N(3A) :109.12(12)°

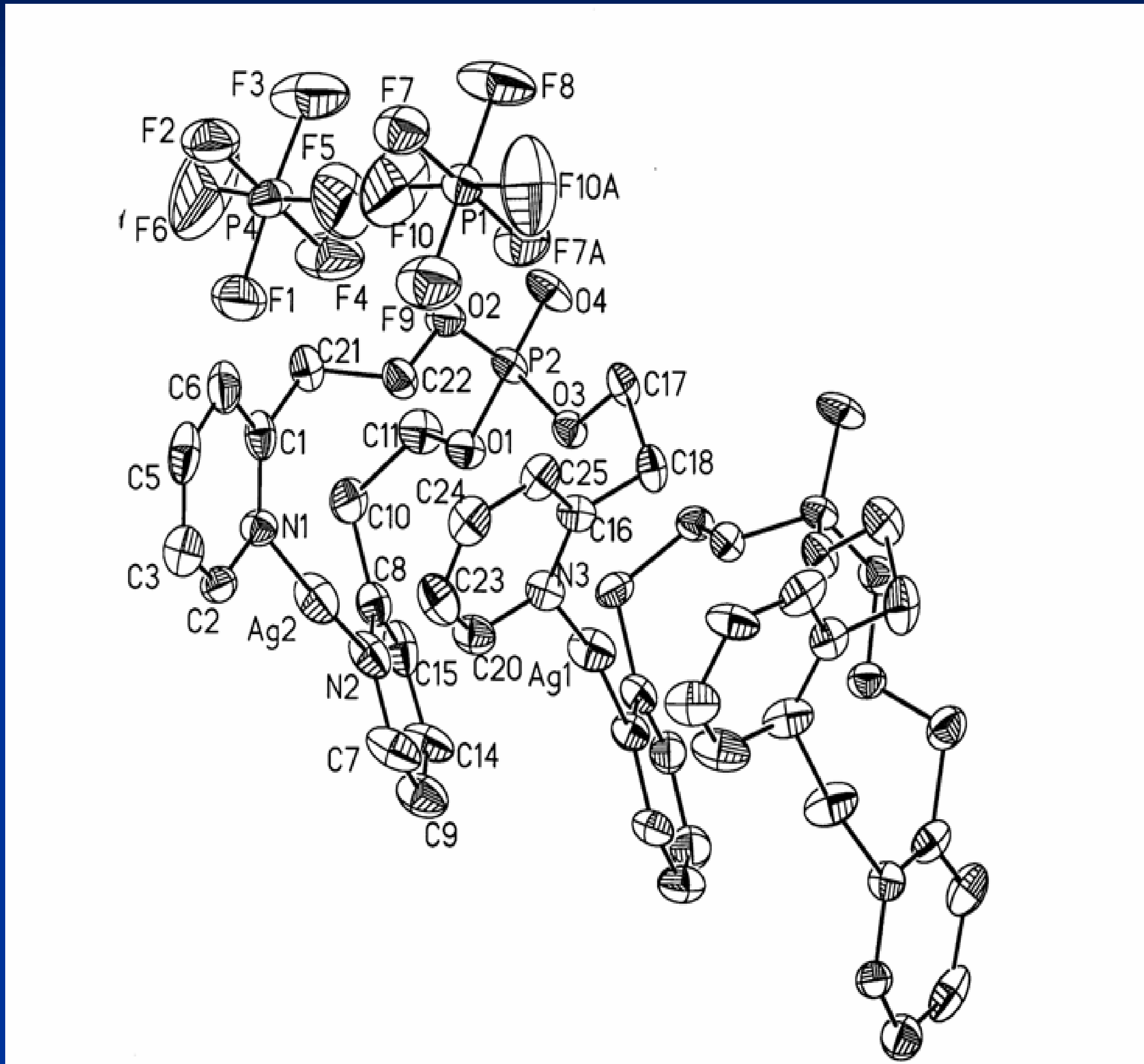
Structure of $\{O{=}P[OCH_2CH_2(2\text{-}py]_3\}_2(AgClO_4)_3$ (6)



Ag(1)-N(1) : 2.113(19)Å
Ag(1)-N(2) : 2.094(19) Å
Ag(2)-N(3) : 2.06(2) Å
Ag(2)-N(4) : 2.082(17) Å
N(5)-Ag(3) : 2.11(2) Å
N(6)-Ag(3) : 2.10(2) Å

N(2)-Ag(1)-N(1) : 174.8(7)^o
N(3)-Ag(2)-N(4) : 175.9(8)^o
N(6)-Ag(3)-N(5) :176.1(8)^o

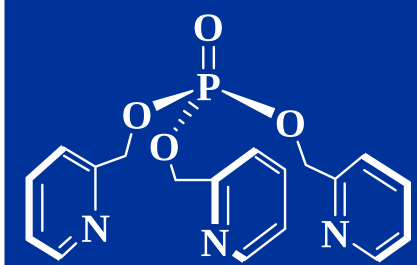
Structure of {O=P[OCH$_2$CH$_2$(2-py]$_3$}$_2$(AgPF$_6$)$_3$ (7)



Ag(2)-N(2)	2.136(6) Å
Ag(2)-N(1)	2.138(7) Å
Ag(1)-N(3)	2.123(6) Å
Ag(2)-N(3A)	2.123(6) Å

N(2)-Ag(2)-N(1)	174.0(3)
N(3)-Ag(1)-N(3A)	170.4(4)

Structures of AgX Bearing L_3

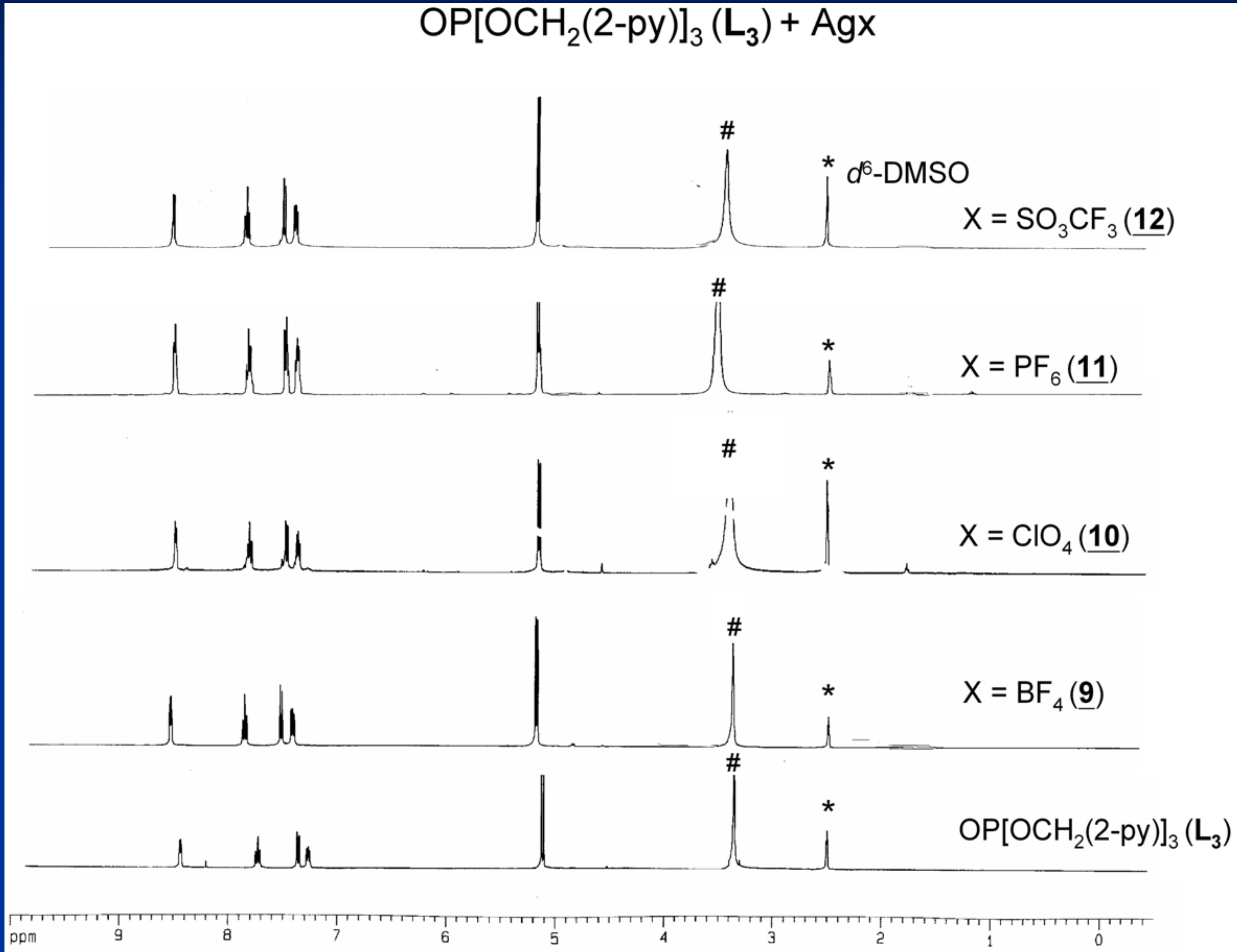


L_3

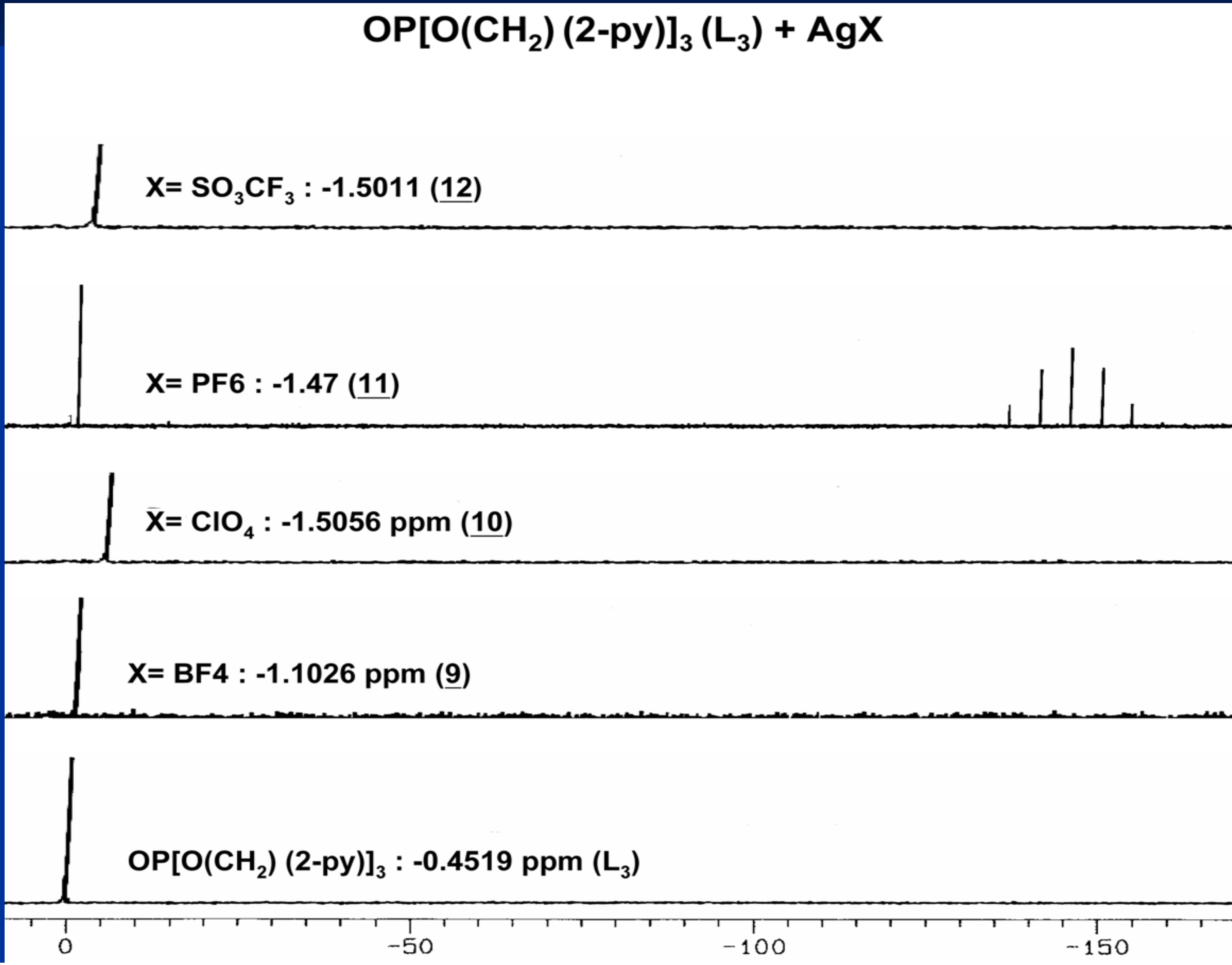
+

$AgBF_4$	→	$\{O{=}P[CH_2\text{-}(2\text{-}py)]_3(AgBF_4)\}_\infty(MeOH)$ <u>**9**</u>
$AgClO_4$	→	$\{O{=}P[CH_2\text{-}(2\text{-}py)]_3\}_2(AgClO_4)_2$ <u>**10**</u>
$AgPF_6$	→	$\{O{=}P[CH_2\text{-}(2\text{-}py)]_3\}_2(AgPF_6)_2$ <u>**11**</u>
$AgSO_3CF_3$	→	$\{O{=}P[CH_2\text{-}(2\text{-}py)]_3\ (AgSO_3CF_3)\}_\infty$ <u>**12**</u>

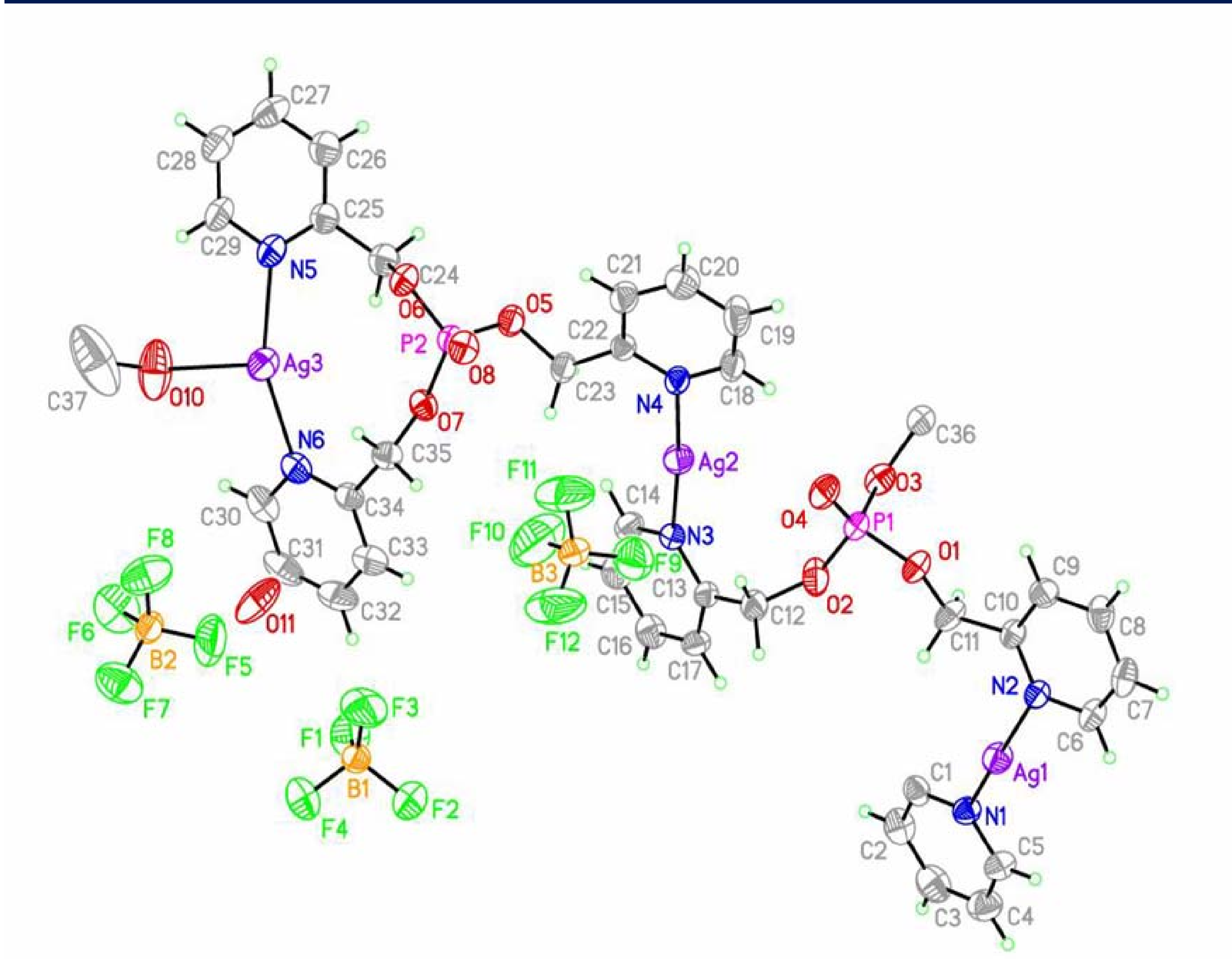
^1H NMR Spectra of L_3 + AgX



^{31}P NMR Spectra of L_3 + AgX



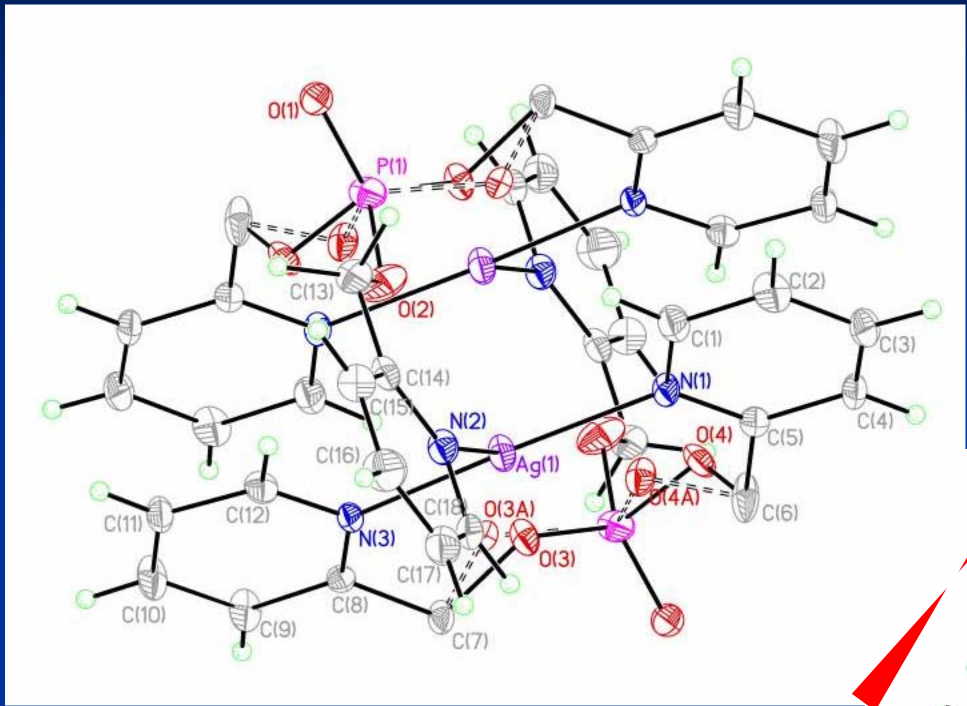
Structure of $\{O{=}P[CH_2\text{-}(2\text{-}py)]_3(AgBF_4)\}_\infty(MeOH)$ (9)

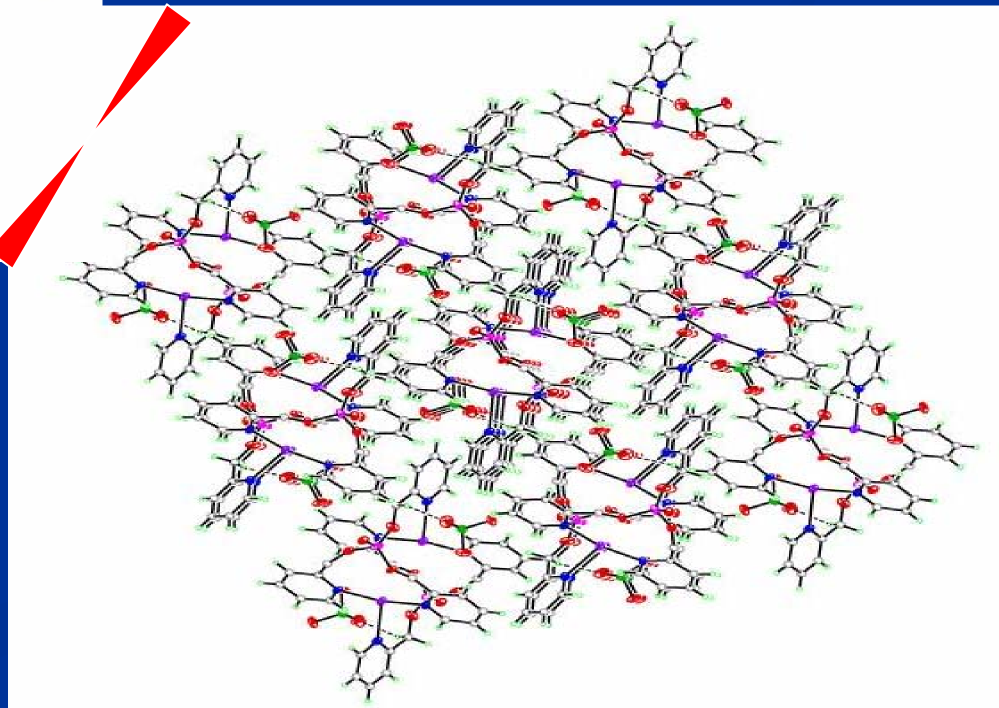


Ag(1)-N(2) : 2.170(5) Å
Ag(1)-N(1) : 2.176(5) Å
Ag(2)-N(3) : 2.138(5) Å
Ag(2)-N(4) : 2.145(5)Å
Ag(3)-N(5) : 2.193(6) Å
Ag(3)-N(6) : 2.224(6) Å
Ag(3)-O(10) : 2.510(5) Å

N(2)-Ag(1)-N(1) : 170.31(2)^{o}
N(3)-Ag(2)-N(4) : 175.58(2)^{o}
N(5)-Ag(3)-N(6) : 152.7(2)^{o}
N(5)-Ag(3)-O(10) :113.11(18)^{o}
N(6)-Ag(3)-O(10) : 90.66(18)^{o}

Structure of {O=P[CH$_2$-(2-py)]$_3$}$_2$(AgClO$_4$)$_2$ (10)



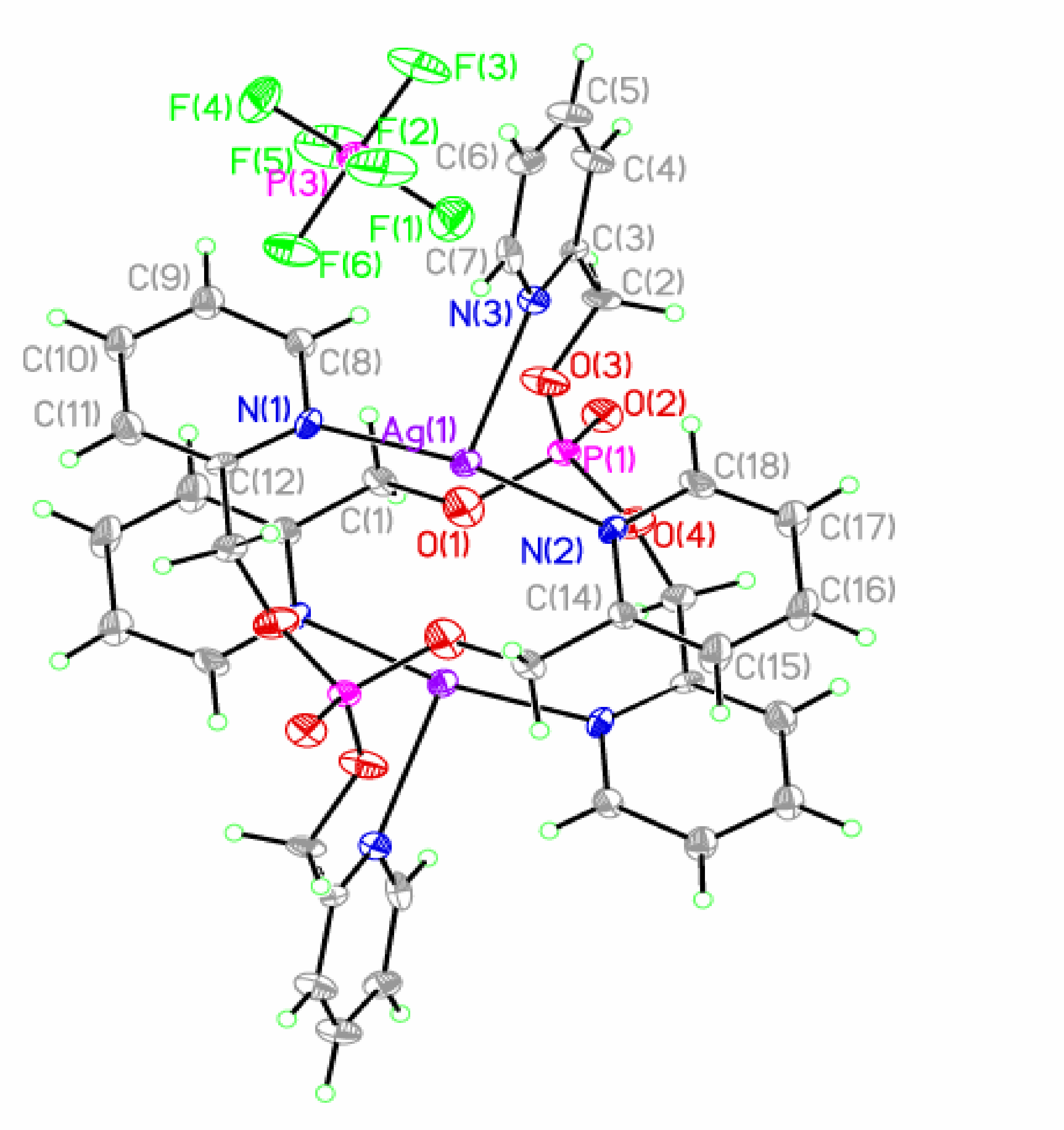


Ag(1)-N(2) : 2.234(4) Å
Ag(1)-N(1) : 2.247(4) Å
Ag(1)-N(3) : 2.537(5) Å

,

N(2)-Ag(1)-N(1) : 167.69(18)^{o}
N(2)-Ag(1)-N(3) : 96.73(17)^{o}
N(1)-Ag(1)-N(3) : 95.58(17)^{o}

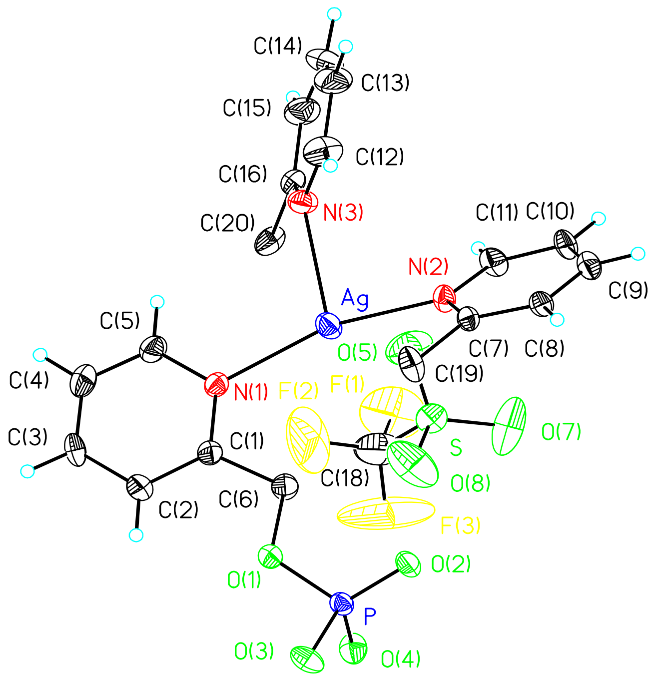
Structure of $\{O=P[CH_2\text{-}(2\text{-py})]_3\}_2(AgPF_6)_2$ (11)

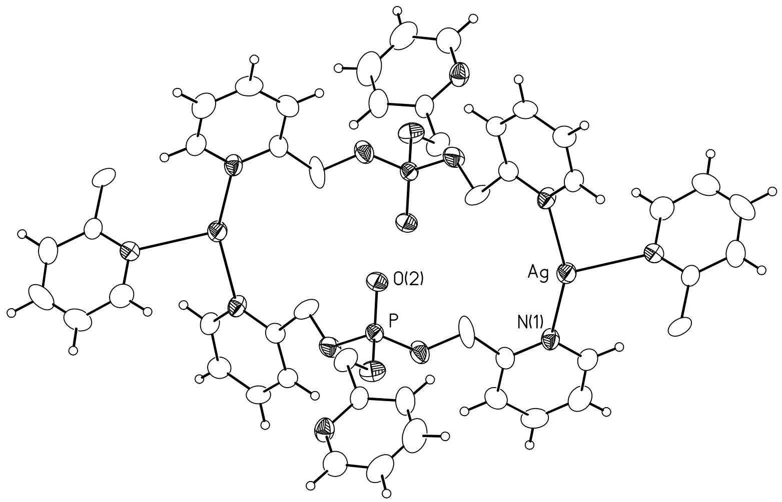


Ag(1)-N(1) : 2.224(7)Å
Ag(1)-N(2) : 2.252(7) Å
Ag(1)-N(3) : 2.539(8) Å
Ag(2)-N(5) : 2.205(8) Å
Ag(2)-N(4) : 2.239(8) Å
Ag(2)-N(6) : 2.603(7) Å

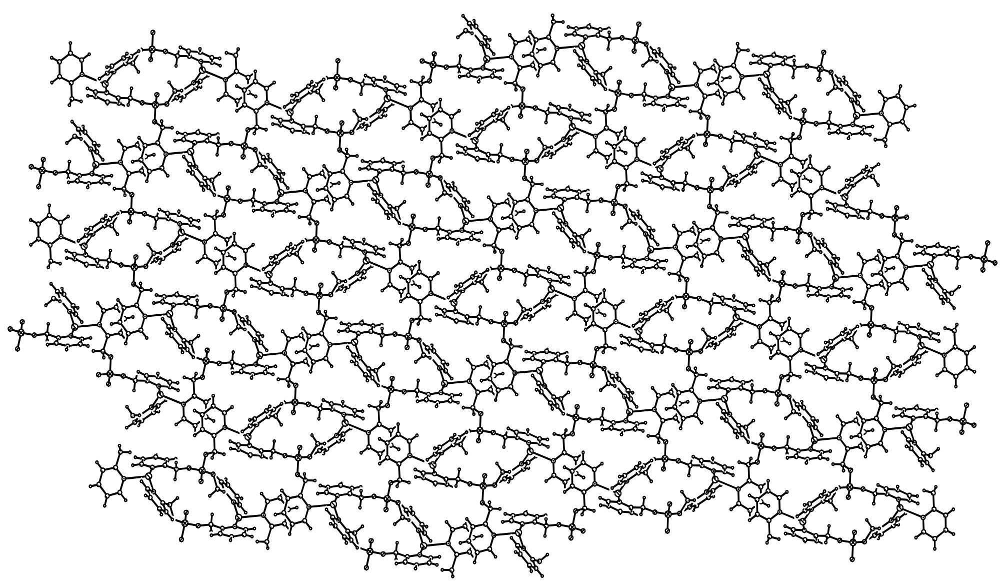
N(1)-Ag(1)-N(2) : 169.1(3)°
N(1)-Ag(1)-N(3) : 95.2(3)°
N(2)-Ag(1)-N(3) : 95.6(3)°
N(5)-Ag(2)-N(4) : 170.0(3)°
N(5)-Ag(2)-N(6) : 101.1(3)°
N(4)-Ag(2)-N(6) : 87.0(3)°

Structure of $\{O{=}P[CH_2\text{-}(2\text{-}py)]_3(AgOTf)\}_\infty$ (12)





Ag-N(1)	2.243(7)
Ag-N(2)	2.267(6)
Ag-N(3)	2.445(7)
N(1)-Ag-N(2)	151.7(2)
N(1)-Ag-N(3)	107.6(2)
N(2)-Ag-N(3)	94.1(2)



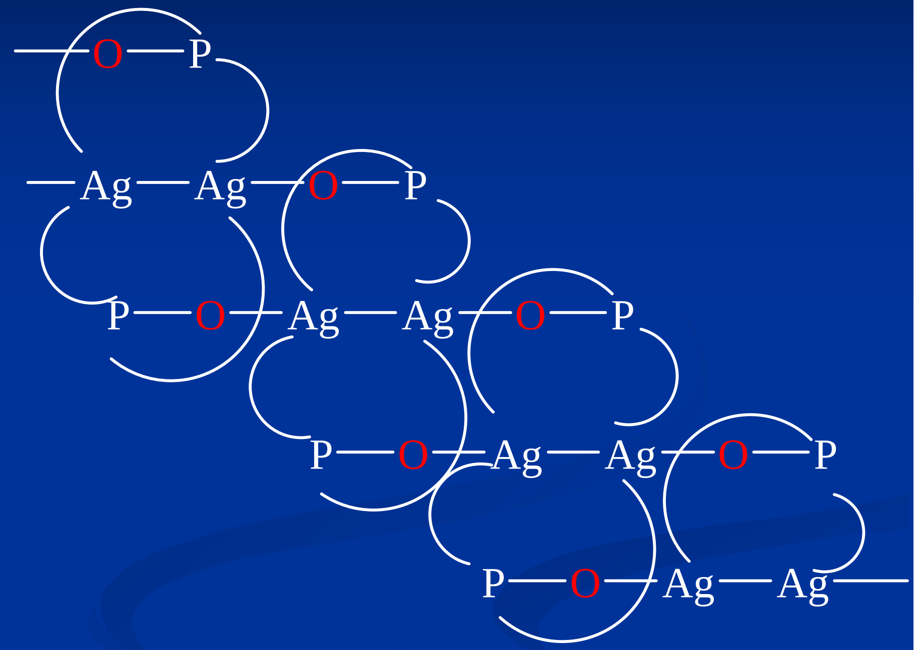
Structures of AgX Bearing L_4

$\underline{L_4}$

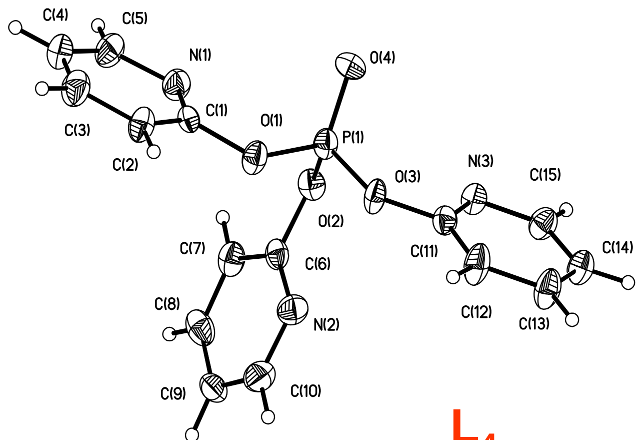
+

$AgPF_6$

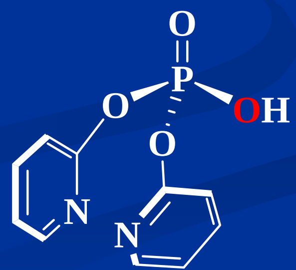
$AgSO_3CF_3$



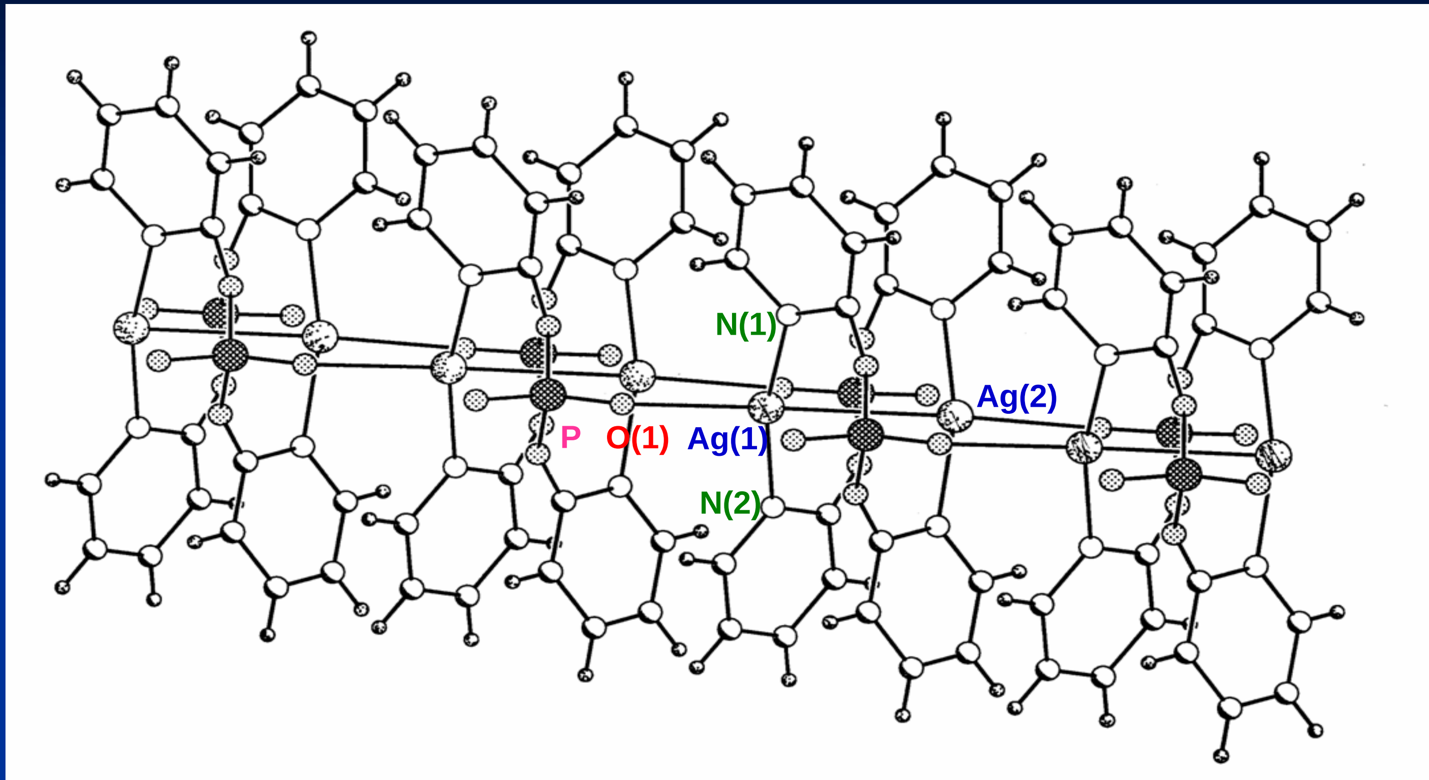
$\underline{13}$



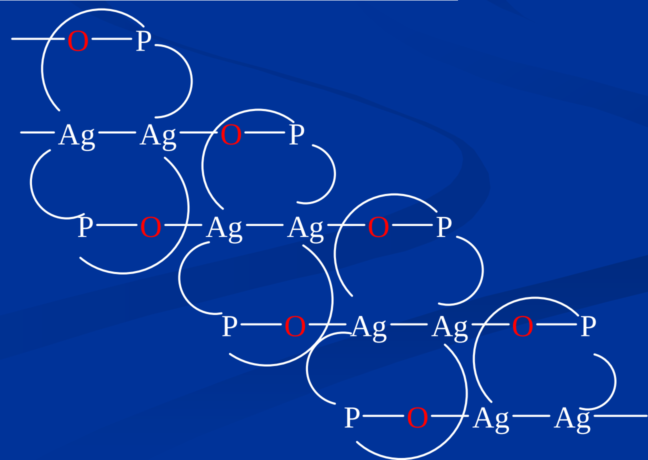
$\underline{L_4}$



Structure of Compound (13)



Ag(1)-N(1)	2.186(3)
Ag(1)-N(2)	2.200(3)
Ag(1)-O(1)	2.474(3)
Ag(1)-Ag(2)	3.1767(6)



Conclusions

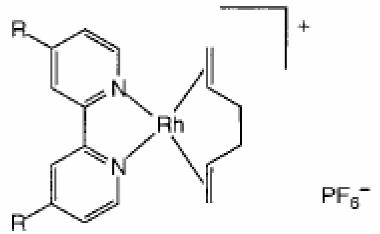
1. A series of Ag complexes with Tripodal Pyridylphosphite and Pyidyl-phosphine Oxide Ligands been synthesized and characterized.

2. The Structures of Ag complexes dependent on Ligand and counter ions.

Impact of Molecular Order in Langmuir-Blodgett Films on Catalysis

Table 1. Hydrogenation of acetone to isopropanol for LB and solution systems. NR, no reaction. Reaction conditions: 72 psi H_2, 48 hours, 25°C, 0.11 mM acetone in water.

Glass type	Catalyst	Turnover
Hydrophilic	None	NR
Hydrophobic	None	NR
–	Suspension of complex **1**	NR
–	Complex **2**, saturated aqueous solution	NR
–	Solution, separated from monolayer after catalysis	No further reaction
Hydrophobic	Monolayer	60,000
Hydrophilic	Quadruple layer	70,000
Hydrophilic	Triple layer	NR
–	Monolayer on water surface	50,000
–	Monolayer on water surface, stirred	NR
–	Complexes **1** or **2** in neat acetone	500



1, R = $CH_3(CH_2)_{16}$
2, R = CH_3

Scheme 1. Catalytic rhodium complexes.

Töllner, K.; Popovitz-Biro, R.; Lahav, M.; Milstein, D. *Science* **1997,** *278, 2100.*

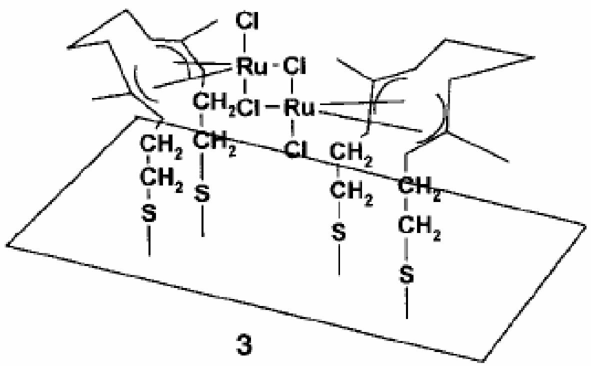
Colloid-Bound Catalysts for Ring-Opening Metathesis Polymerization

Table 1. Ring-opening metathesis polymerization of norbornene with unbound and bound catalysts

Catalyst	Yield[a] [%]	t [min]	$c_{cat.}$ [M]	TOF[b] [h^{-1}]
unbound	30	5	8×10^{-6}	2990
colloid-bound	90	60	9.9×10^{-7}	15000
bound on functionalized glass slide	30	15	2.55×10^{-7}	75000

[a] Yield refers to isolated polymer. [b] TOF = turnover frequency in mol(polynorbornene)/[mol (catalyst) · h].

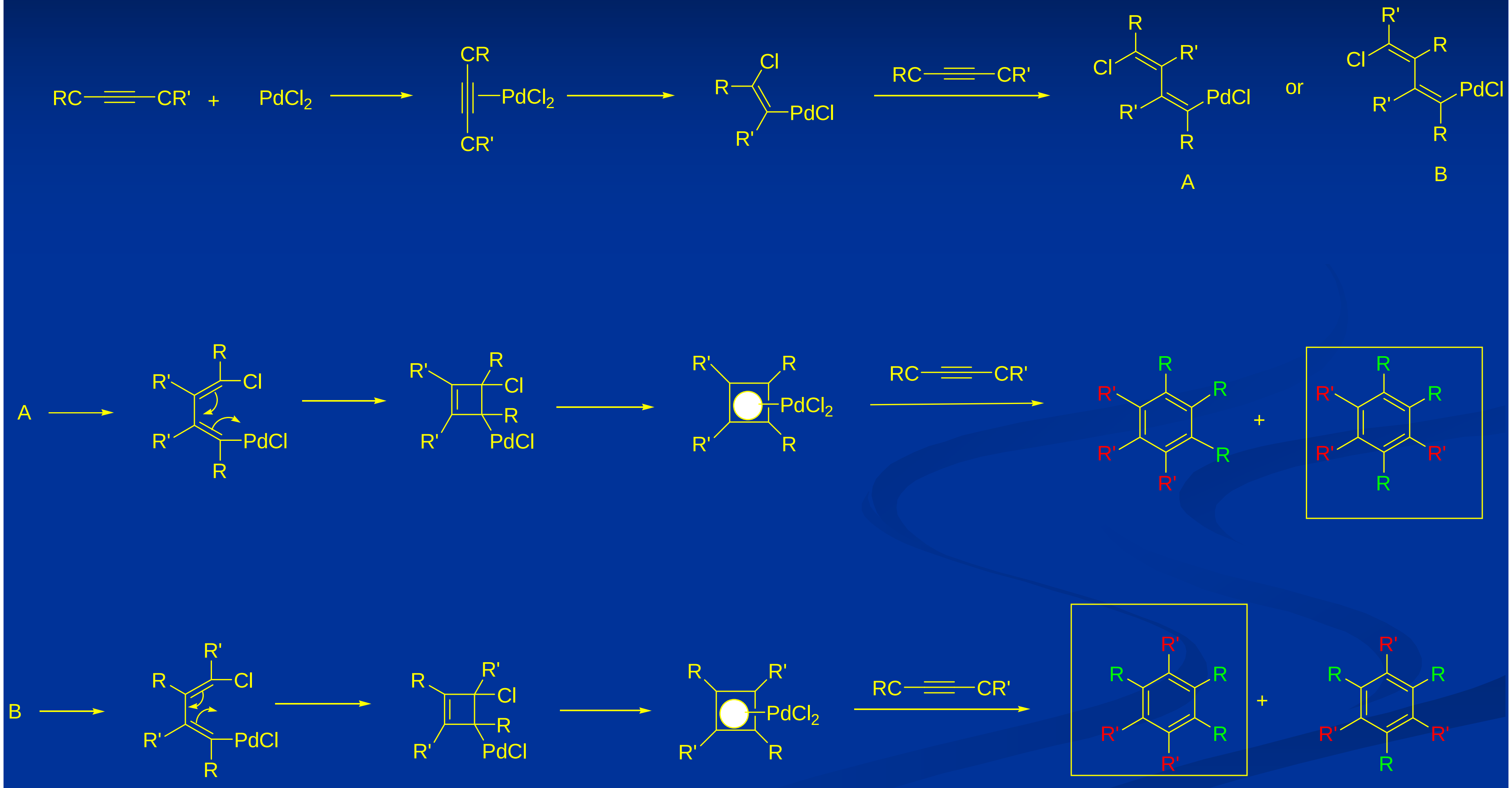
filtration and purified by dissolving in toluene and reprecipitating with methanol.



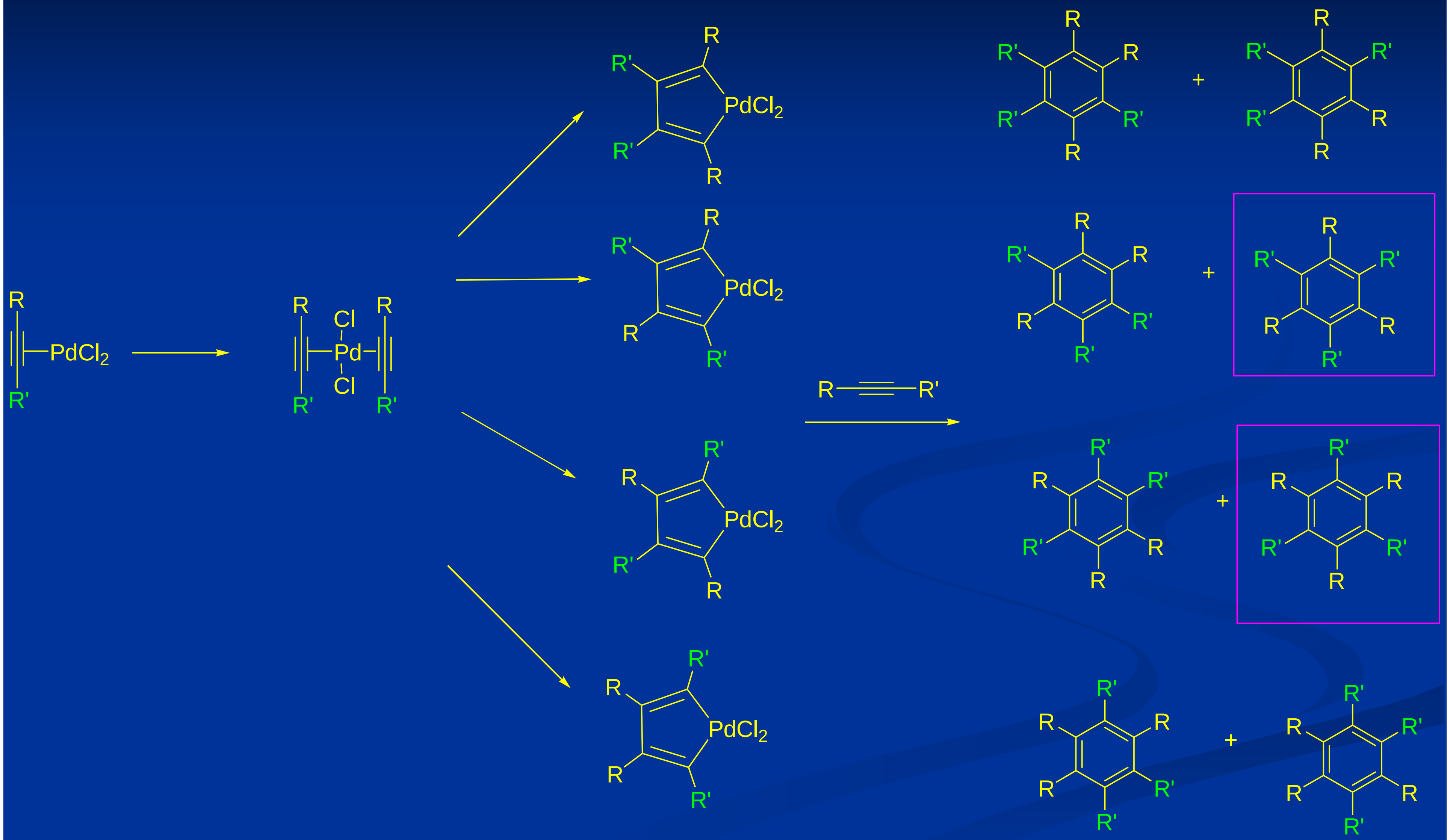
3

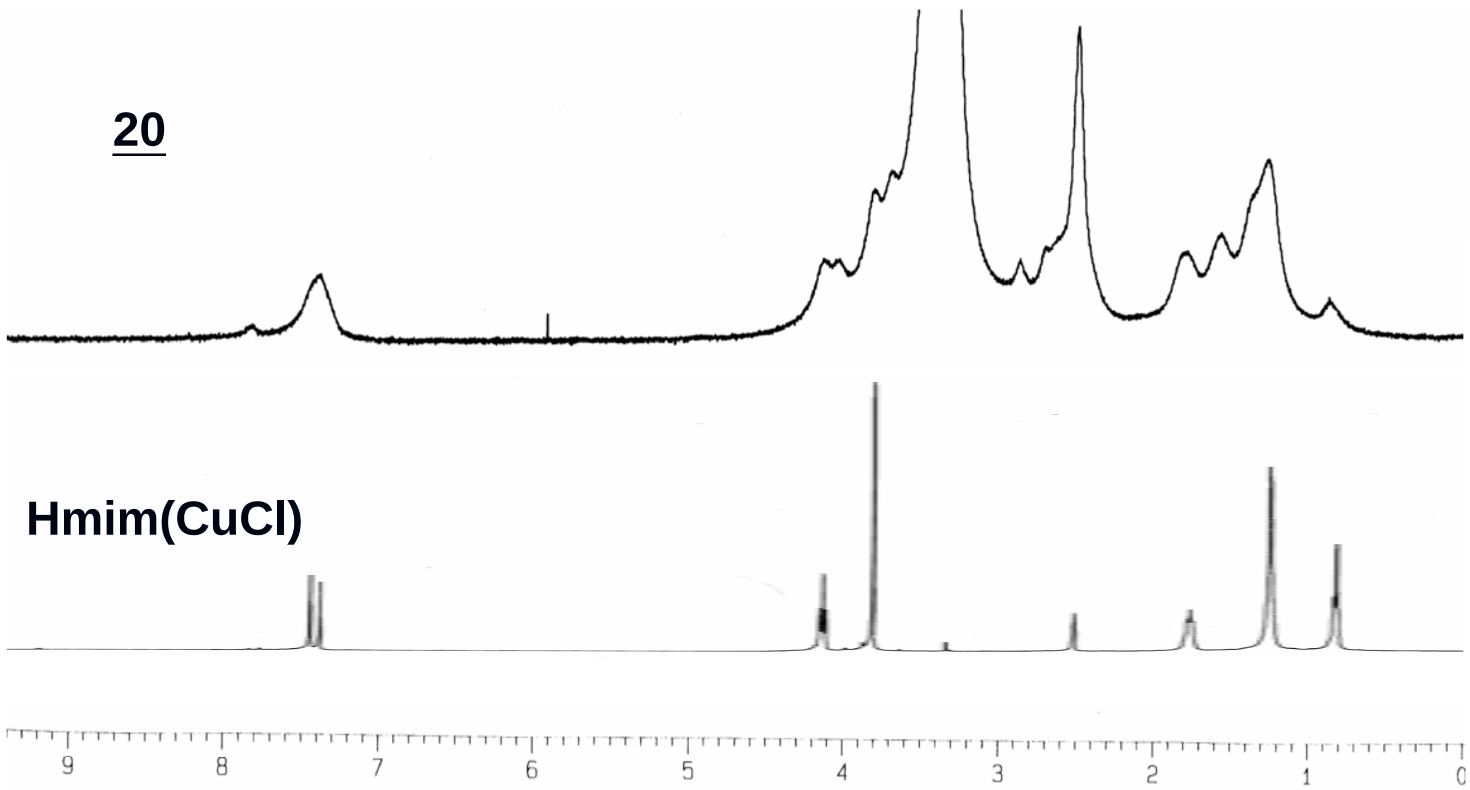
Angew. Chem. Int. Ed. **1998,** *37, 2466-2568*

Mechanism-Path A



Mechanism- Path B




20
Hmim(CuCl)
9
8
7
6
5
4
3
2
1
0