

A REVIEW ARTICLE ORGANOZINC REAGENT PREPARATION METHOD**Ramesh Gawade*¹, Arvind Burungale¹, Ashok Pise¹, Santosh Devkate¹ and Sunil Jadhav²**¹Department of Chemistry, S. M. Joshi College Hadapsar Dist Pune 411028 (M. S.) India.²Department of Chemistry D. P. Bhosale College Koregaon Dist Satara 415501 (M.S.) India.

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India.**ABSTRACT**

Organozinc reagents have unique ability to tolerate high functional group, valuable in many organic transformations via nucleophilic addition and cross coupling. The synthetic utilities of available organozinc reagents lead to development of various method of their generation. Now day pyrophoric and moisture sensitive organozinc reagent is replaced by solid air stable organozinc reagent.

KEYWORD: Organozinc reagent, zinc, insertion.**INTRODUCTION**

Organometallic reagents should have some desirable properties like an excellent selectivity and reactivity combined with low costs, environmental friendliness and a high functional group tolerance, the transformation of organic molecules should occur in an atom-economic fashion. Organometallic chemistry has the potential to fulfill all these requirements so the last decades, a large range of metals were applied in synthetic organic chemistry to solve ongoing problems. The reactivity of organometallic reagents is increases with the ionic character of the carbon-metal bond. Through the use of highly reactive organometallic species, such as organolithium and organomagnesium reagents, selectivity is often compromised. Furthermore, reduced tolerance toward sensitive functional groups, such as esters, nitriles, ketones and aldehydes, is always observed. However, the less reactive organometallic species, such as organozinc, organoboron, organoindium and organotin reagents, display only moderate reactivity towards most organic electrophiles and thus tolerate many functional groups but they need transition metal catalyst for efficient reaction. Organoborane reagents are air stable but they need harsh condition for preparation and difficulty lies in their transmetallation. Indium metal is expensive and tin not absolutely environmental friendly, so both metal organometallic reagent avoid in synthesis.

Recent 25 years organozinc reagents are concentrate the attention of synthetic organic chemist because of easy preparation and facile transmetallation compare to other organometallic reagent. Today, these reagents are more valuable in organometallic chemistry due to some

desirable properties like an excellent selectivity and reactivity, low cost, environmental friendliness and high functional group tolerance. In comprise with other organometallic reagent organozinc reagents are more convenient in their preparation and handling also. They are important tool to build up polyfunctional molecules without the use of multiple protections and deprotections steps. Generally, every synthesis of natural product has at least one step which involves use of this kind of reagent. Many organometallic reagents are available in the market. But among that highest position is occupied by Organozinc reagent. Overall this is indication of superiority of Organozinc reagent in the synthetic utility.

First Organozinc reagent was synthesized by Frankland in 1849 and laid down milestone for the modern organometallic chemistry.^[1-2] The potential of Organozinc reagent and its synthetic utility was ignored for more than 100 years after their discovery. Exceptional, few Organozinc reagents were reported such as zinc enolate^[3] Iodomethylzinc iodide^[4] their synthetic potential has only been recognized by reformatsky, Simon-Smith, Furukawa Sawada reagents recently.^[5-14] The Organozinc reagents were ignored because of their low reactivity and lack general method of synthesis. Remarkable advantage of these reagents is high functional group tolerance which lack in other organometallic reagent viz, organomagnesium and organolithium. Unique feature of Organozinc reagent is large number of functional group tolerance because of similar electronegativity of zinc and carbon, metal carbon bond acquire high covalent character.^[14-15] The carbon-zinc bond is therefore inert to moderately polar electrophile such as aldehyde, ketone, ester or nitrile. High covalent character of zinc carbon bond makes

organozinc configurationally stable at the same temperature organomagnesium and organolithium undergo racemisation or decomposition this property leads to development chiral organometallic.^[16-17]

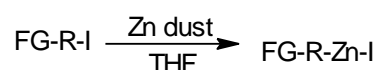
The Organozinc reagents have availability of empty low lying p orbital at the zinc centre readily interact with the d orbital of transition metal allows transmetallation with a number of transition metal complexes.^[18] Reactivity of these reagents drastically tremendous changes after transmetallation they form highly reactive intermediate, d-orbital at the transition metal centre that makes number of new reaction pathways that were not accessible to the zinc-carbon bond. Organozinc and organocopper are an indispensable part of organometallic chemistry. Organocopper Complexes are undergo major pathway for carbon-carbon bond formation as conjugate addition to α , β unsaturated carbonyl compounds, cross coupling,^[19] addition to acetylene and nucleophilic displacement of halides, sulphonates, allylic acetates.^[20] The organozinc halides are undergo transmetallation by number of transition metal salt or complex such as copper, cobalt, iron, manganese, titanium zirconium, palladium and nickel etc.

A variety of organozinc reagents are prepared from organic halide by oxidative insertion of zinc metal or transmetallation. Recently, pyrophoric and moisture sensitive organozinc reagents are replaced by air stable organozinc pivalate prepared by transmetallation followed by zinc pivalate.

PREPARATION METHOD

The most common method for preparation of organozinc compound is oxidative addition of activated zinc dust into functionalized organic halide. This method is useful

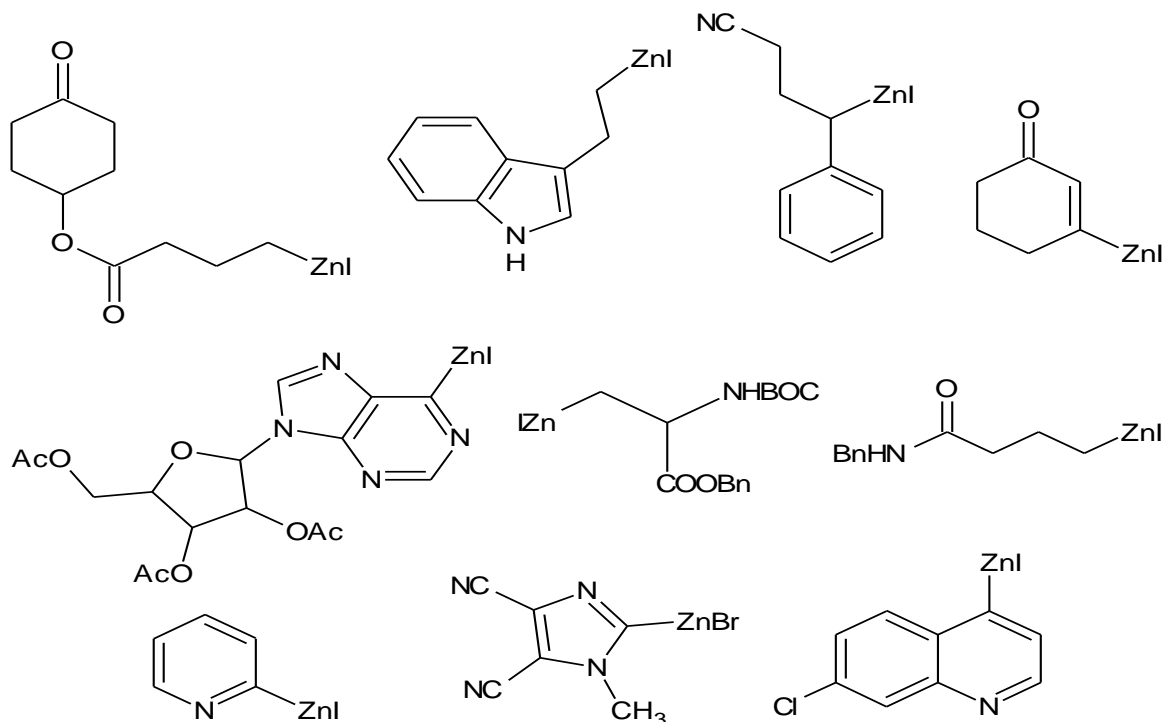
for preparation of organozinc iodides bearing almost all functionalities. Tetrahydrofuran is the best solvent proved for insertion reaction.^[21] The primary alkyl iodide is undergoes zinc metal insertion at $\sim 40^{\circ}\text{C}$, secondary alkyl iodide undergoes zinc insertion at $\sim 25^{\circ}\text{C}$, similarly the benzylic and allylic bromide undergoes optimal zinc insertion at $\sim 0^{\circ}\text{C}$ in solvent THF. Alternatively, highly active zinc is prepared by reduction of zinc chloride in lithium naphthalenide used for insertion reaction with less reactive aryl bromide and iodide. The oxidative insertion of zinc metal into organic halide is very sensitive reaction it influenced by solvent, concentration temperature, nature of halide and method of zinc activation. Some functional group such as nitro, azide and hydroxy are retard the insertion of zinc into organic halide. The nitro and azide inhibit the electron transfer reaction and hydroxy form zinc alkoxide coat zinc surface. The insertion of zinc dust into aromatic iodide is require higher temperature or polar cosolvent,^[22] longer reaction time.



Scheme 1: Preparation of organozinc reagent.

R = alkyl, aryl, benzyl, allyl.
 F. G. = Ester,^[23-49] Ether,^[25-26, 41] Acetate^[25-32, 34-35, 38-39, 43], Ketone^[23-24], Cyano^[23-32, 38, 39-41], Halide,^[22-23, 32, 39, 42, 48] Amino^[50-51], Amide & Pthalimide^[52-54], Sulfoxide^[55], Sulfide^[56], Sulfone,^[55-56] Thioester^[56], Boronic ester.^[36-37, 39, 42, 57-59] Enone,^[29, 60-62] and Phosphate.^[63]

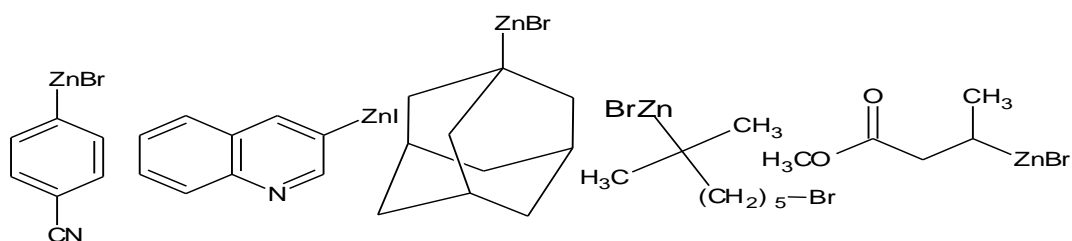
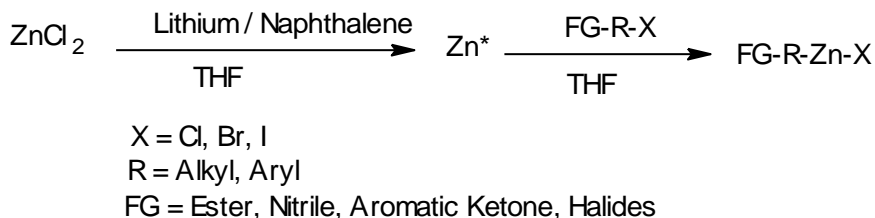
Many heterocyclic organozinc halide are prepared by directly using zinc dust and heteroaryl halide.^[64]



Scheme: 2 Functionalized organozinc compound prepared by oxidative addition.

An especially active zinc powder can be generated by reducing zinc chloride with lithium metal and naphthalene in THF. Some less reactive organic halide

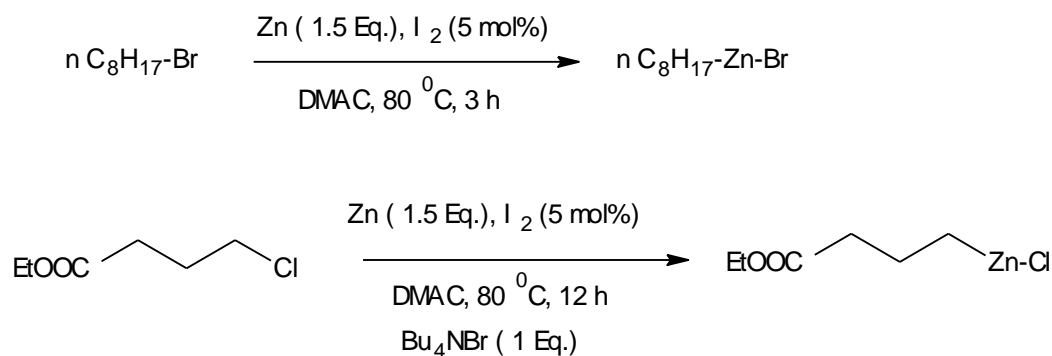
inert to above zinc insertion method such as aryl iodide, secondary and tertiary alkylbromide they are undergoing zinc insertion prepared by rieke method. This active zinc is inserted into alkyl bromide at room temperature and inserted into aryl bromide at reflux.^[65-73]



Scheme: 3 Organozinc halides prepared by oxidative insertion of Rieke zinc

Alkylzinc halides were prepared by direct insertion of zinc dust into alkyl bromide and chloride in presence of

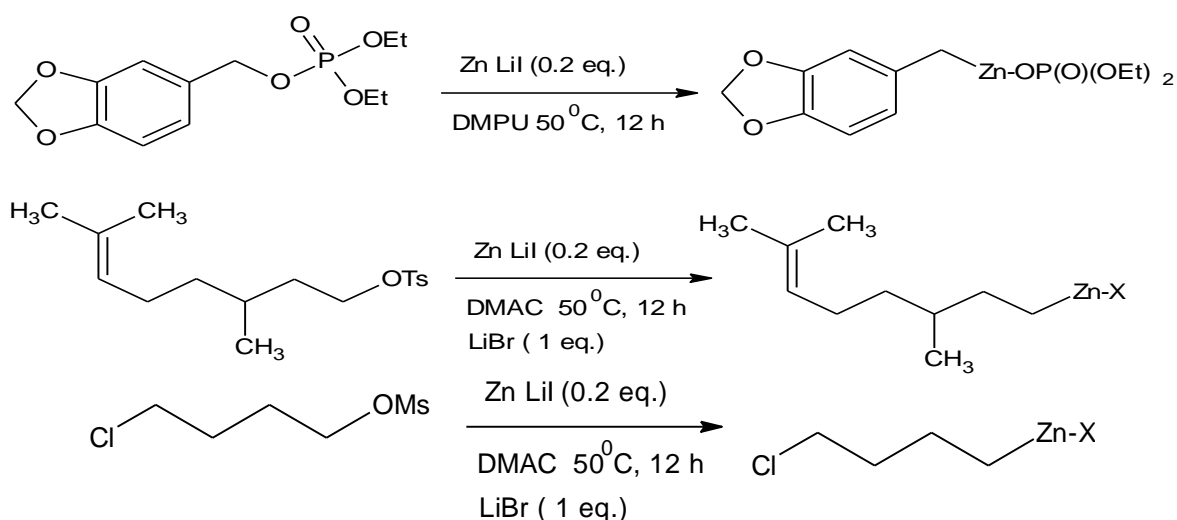
iodine (5 mol %) in a polar solvent such as DMAC. The best result was obtained in presence of tetrabutyl ammonium bromide (1 Equivalent.).^[74]



Scheme: 4 Iodine catalyzed formation of organozinc halides

The leaving group in nucleophilic substitution reaction such as phosphonate, tosylates and mesylates were

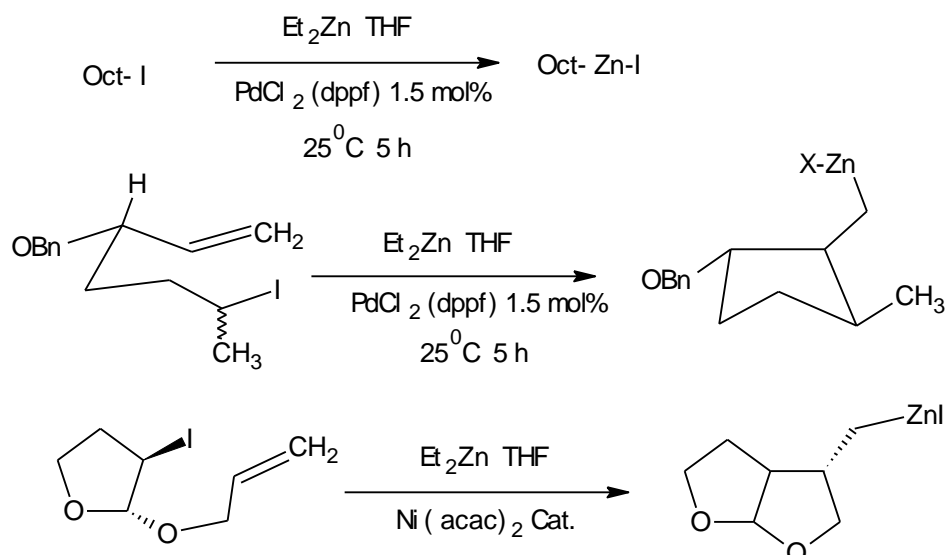
readily converted into organozinc compound by direct insertion of zinc metal. This reaction was performed in presence of catalytic amount of lithium iodide in polar solvent dimethyltetrahydropyrimidinone or N, N dimethylacetamide. The addition of lithium bromide is necessary to enhancement of reaction rate.^[75-76]

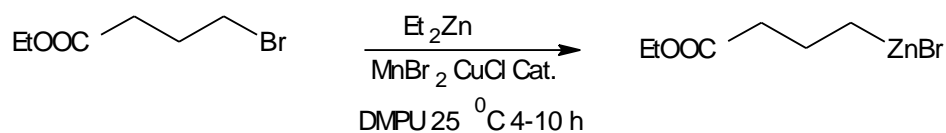


Scheme: 5 Preparation of organozinc derivatives starting from phosphonate tosylates mesylates.

The reaction of organic iodides with diethyl zinc in the presence of nickel manganese or palladium involves

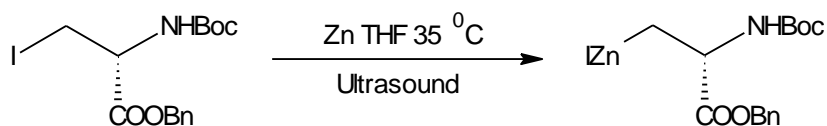
radical reaction leading to an organometallic product at 25°C, 5h.^[77-82] Natural product methylenolactonin and cis-methyl jasmone synthesis has been accomplished by this method.





Scheme: 6 Preparations of zinc organometallics by palladium, manganese and nickel catalysed radical cyclisation.

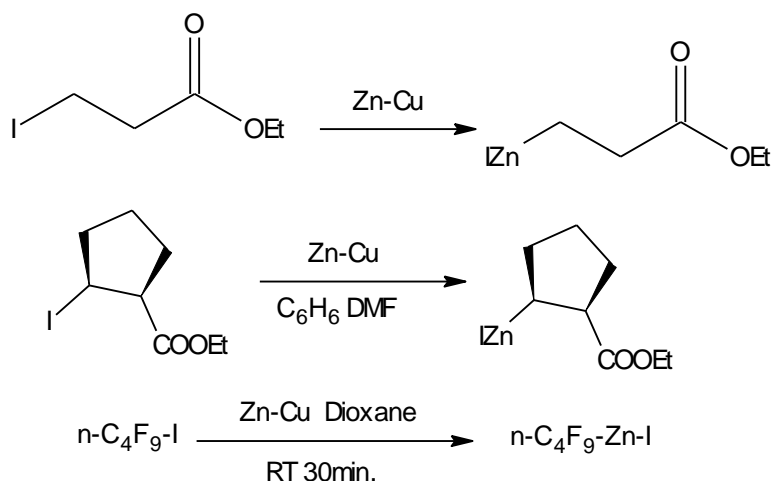
The zinc insertion was accomplished with help of ultrasound especially useful for the formation of the Jackson reagent derived from serine. This is valuable reagent in synthesis of enantiomerically pure amino acids.^[83-85]



Scheme: 7 Ultrasound mediated preparation of zinc organometallic.

dust and copper (I) chloride in ether.^[86] Number of polyfluorinated organometallics are prepared by this method.^[87-98]

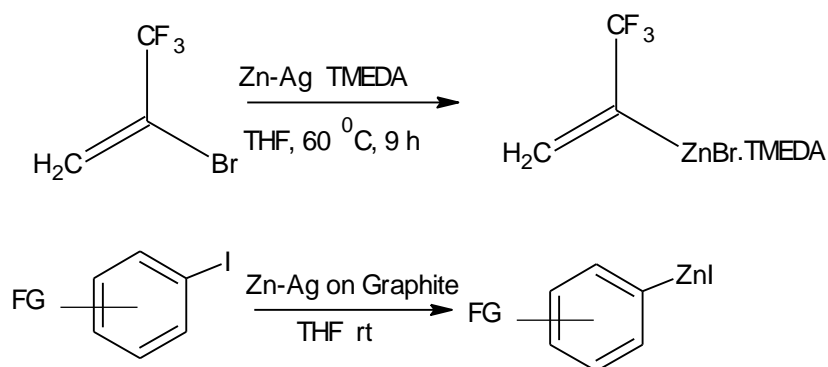
For insertion of zinc metal into organic iodide Zn-Cu couple has been prepared by refluxing a mixture of zinc



Scheme: 8 Zinc-copper coupled mediated preparation of zinc organometallics.

This couple is useful for preparation of fluorinated zinc organometallics in the presence of TMEDA.^[100-102] The insertion of zinc caused by zinc silver couple deposited on graphite which is react with functionalized aromatic and hetero aromatic iodides at rt.^[103]

Zinc silver couple is prepared by adding granular zinc to a stirred hot solution of silver acetate in acetic acid.^[99]

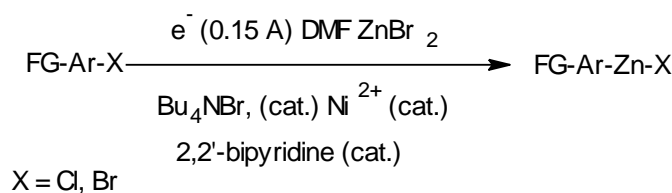


Scheme: 9 Zinc-silver coupled mediated preparation of zinc organometallics.

Electrochemical method for preparation of arylzinc halides is also the best method, it accomplished with

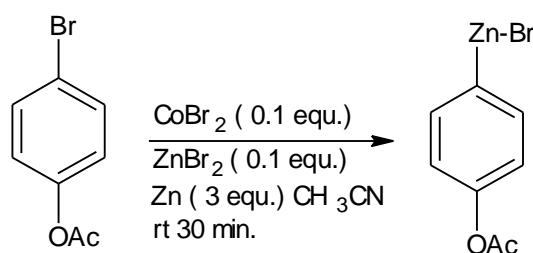
sacrificial zinc anode and in presence nickel, 2,2 bipyridyl. This method is useful for preparation of heterocyclic α -bromoesters, allylic and benzylic organozinc compound.^[104-109] Electrochemical method

can also be achieved by a cobalt catalyst in DMF and pyridine mixture.^[110-112] The detail mechanism of this reaction has been carefully studied involves electro reduction of zinc halides.^[113]



Scheme: 10 Electrochemical preparation of functional organic halides.

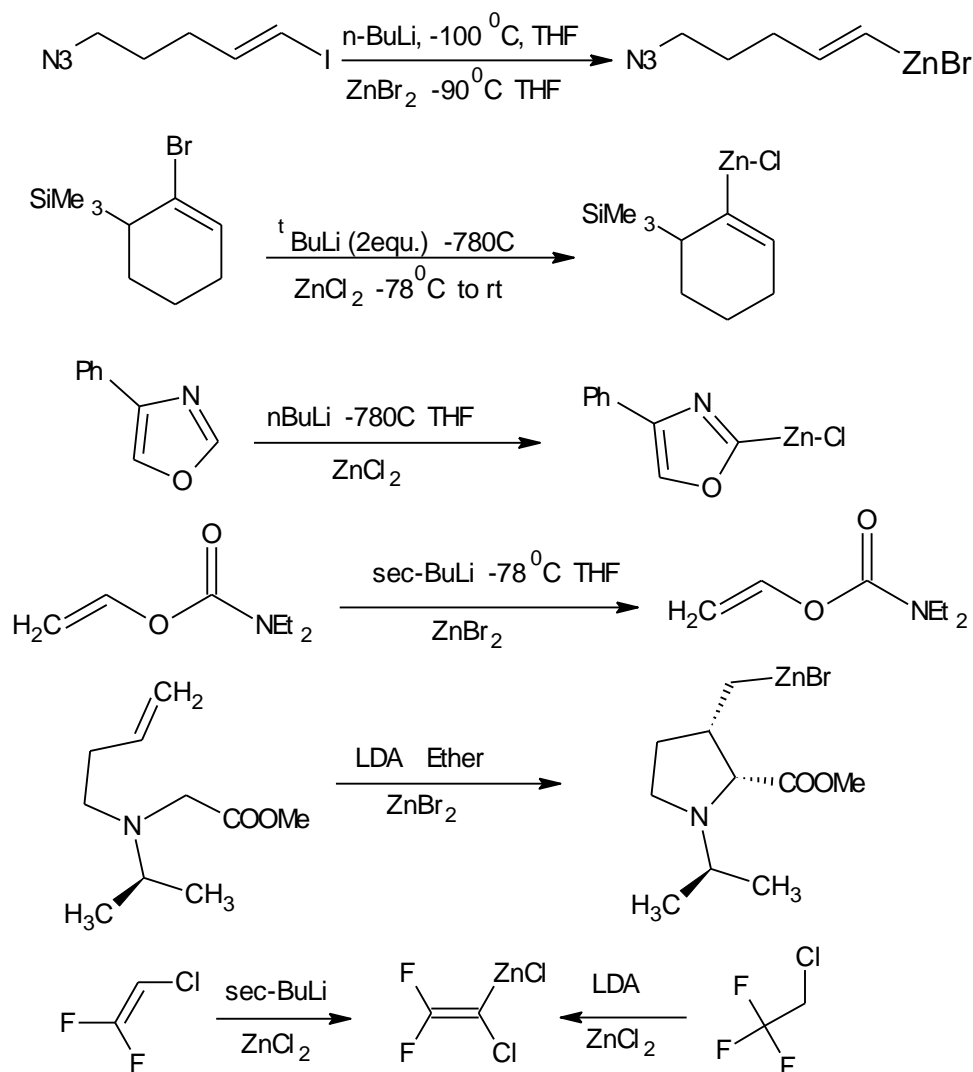
The low-valent cobalt species assist the zinc insertion reaction into less reactive aryl bromide in presence of zinc dust. This reaction is useful for preparation of functional aryl zinc bromide.^[114-118]



Scheme: 11 Cobalt mediated insertion of zinc into functionalized aryl bromide.

A number of transmetalation protocols leading to zinc organometallics, generally, reactive more polar metal-carbon bond is readily transmetalate by the reaction of zinc salt to the less polar more covalent zinc-carbon bond. Remarkable, advantage offered by this method is preparation of nitro and azide functionalized zinc organometallics.^[119-121] Organolithium compound are highly reactive organometallic species prepared by halogen-lithium exchange reaction followed by transmetalation with zinc halide. The reaction of the azide alkenyl iodide with n-butyl lithium at -100°C leads to organolithium followed by the transmetalation with zinc bromide in THF gives the expected organozinc

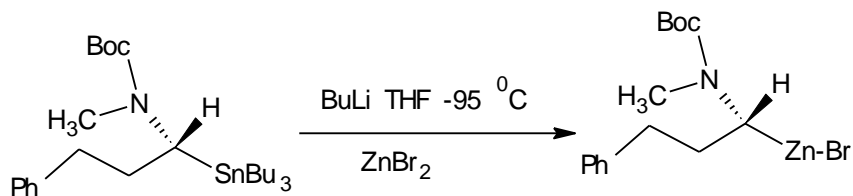
halides 85% yields. Silicon Zinc bimetallic reactive species is prepared by bromine-lithium exchange reaction followed by transmetalation with zinc chloride.^[122] 2-lithiated oxazoles are unstable compounds, stability induced by transmetalation to corresponding 2-zincated oxazole.^[123] The lithiation of O-vinyl carbamate with sec. butyl lithium followed by transmetalation with zinc bromide, the deprotonation of aminoester with lithium diisopropyl amide followed by transmetalation with zinc bromide in ether furnishes corresponding vinylic organozinc and zinc enolate respectively.^[124-128] 1-Chloro-2,2-difluorovinylzinc chloride have been prepared by the deprotonation of 1-chloro-2,2-difluoroethane and transmetalation.^[129-130]



Scheme: 12 Zinc organometallics prepared by transmetalation of lithium.

The organotin compound have been converted to organozinc by treating with butyl lithium in THF and followed by zinc halide, overall this reaction involved

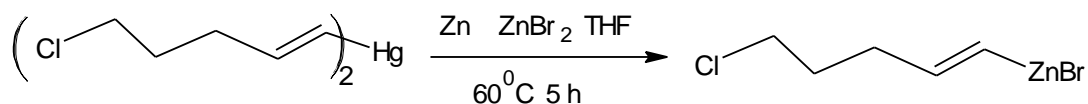
double transmetalation reaction. A chiral α -aminostannanes compound was undergo low temperature tin-lithium exchange reaction with BuLi in THF followed by transmetalation with zinc bromide, retention of configuration.^[131]



Scheme: 13 Preparation of zinc organometallic starting from organotin reagent.

The weak carbon-mercury bond favors transmetalations, the reaction of functionalized organomercury with zinc

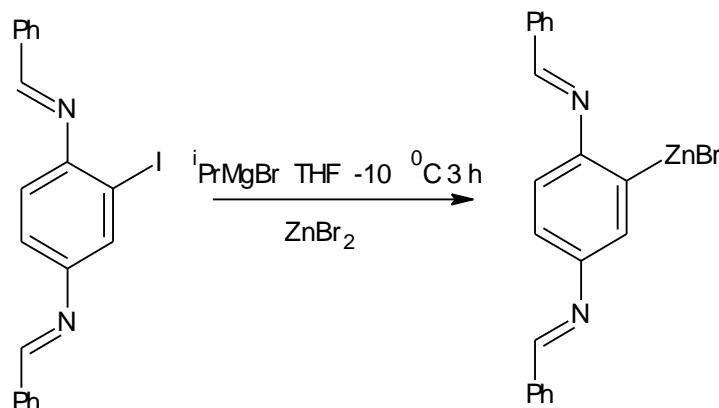
in the presence of zinc bromide leads to corresponding organozinc reagent in high yields, excellent stereoisomeric purity.^[132,133]



Scheme: 14 Zinc organometallic derived from organomercury.

A few polyfunctional organomagnesium compound are prepared by oxidative insertion of magnesium to organic halide. The carbon magnesium bond is less polar than carbon lithium bond therefore considerably more

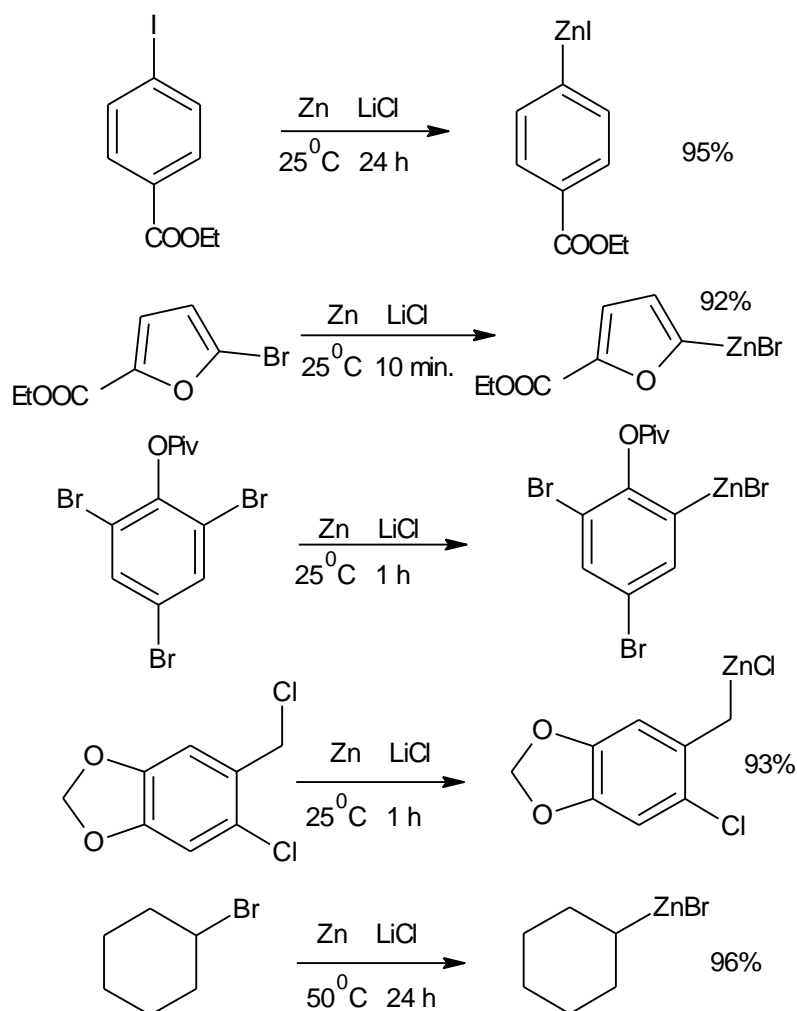
functional group are tolerated.^[134] The reaction of aryl iodide with grignard reagent at -10°C for 3 h provide an intermediate magnesium reagent followed by transmetallation with zinc bromide furnishes the zinc organometallics.^[135]



Scheme: 15 Preparation of arylzinc halide by transmetallation of magnesium.

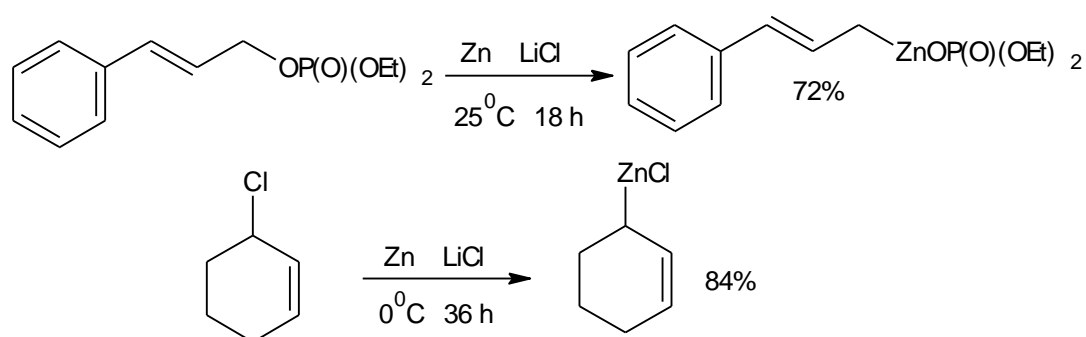
The preparation of zinc organometallics generally needs organic iodides and zinc insertion take place at elevated temperature in polar solvent. This harsh condition could be mild by using LiCl and expensive organoiodo starting compound replaced by organic bromide or organic chloride. The reaction of ethyl 4-iodobenzoate with zinc dust at reflux THF for 24 h not gave expected aryl zinc iodide. Alternatively, same reaction in presence of stoichiometric amount of LiCl leads to desire aryl zinc compound at 24 h rt stirring.^[136] Similarly, the bromo substituted aryl halide, alkyl halide functionalized benzyl

chloride were converted to corresponding organozinc reagents in THF solvent.^[136-138]



Scheme -: 16 Preparation of functionalized zinc organometallics using zinc dust in the presence of LiCl. A LiCl mediated direct insertion of zinc powder to cyclic allylic chloride or phosphonates leads to the

corresponding allylic zinc organometallics. this procedure was successfully extended to many allylic zinc reagents from allylic chloride or allylic phosphonates.^[139-141]



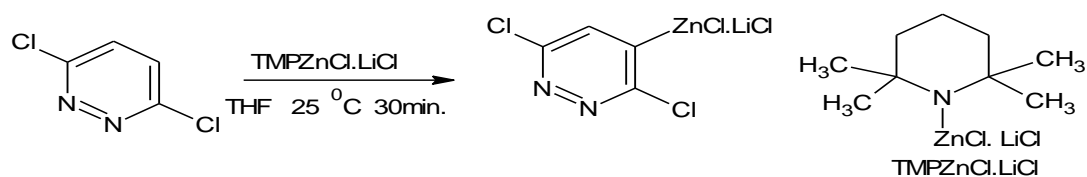
Scheme-: 17 LiCl mediated zinc insertion to allylic position.

Knochel and Co-worker could demonstrate that the presence of LiCl makes the synthesis of zinc organometallic from corresponding alkyl, aryl, heteroaryl bromides and iodides, as well as benzyl chlorides using commercially available zinc dust in good yield.^[136-139] The LiCl not only assist the zinc insertion but also

solubilize the organozinc halides. Therefore the organozinc halides are easily release from zinc metal surface result rapid reaction as well as high yield with short reaction time, this remarkable advantage offered by LiCl.

The mild base $\text{TMPZnCl}\cdot\text{LiCl}$ was developed by Knochel *et al.* which show chemoselectivity in metallation of heterocyclic compound at ambient temperature.^[142-143]

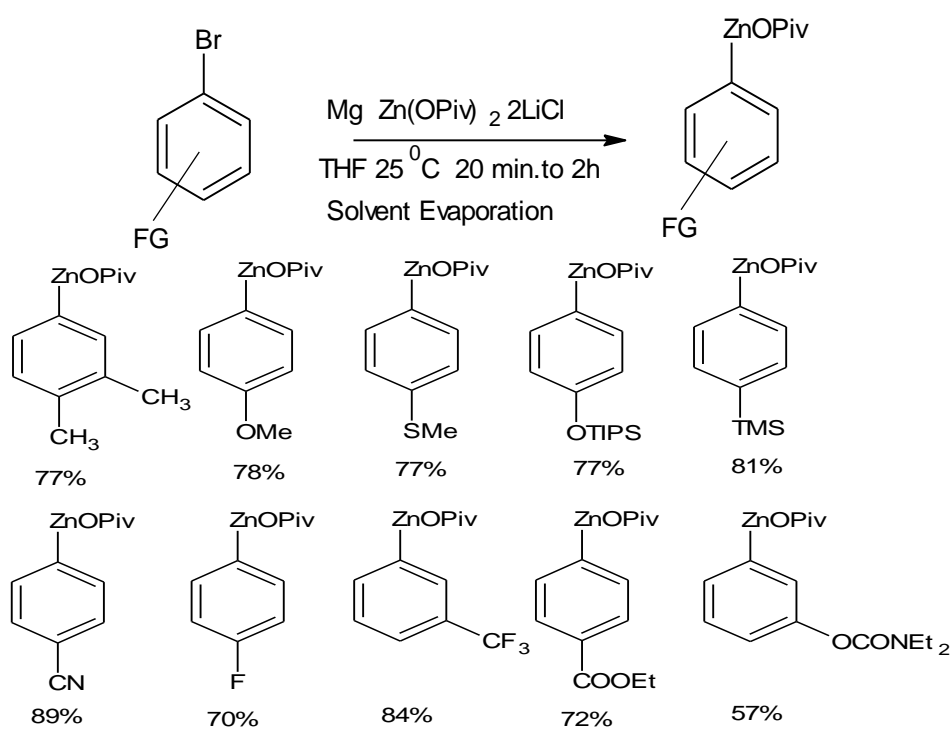
The advantage offered by base is direct way for the preparation of functionalized aryl and heteroaryl zinc halides.



Scheme:- 18 Direct Zinc metallation of 3,6 dichloropyridazine using the mild base.

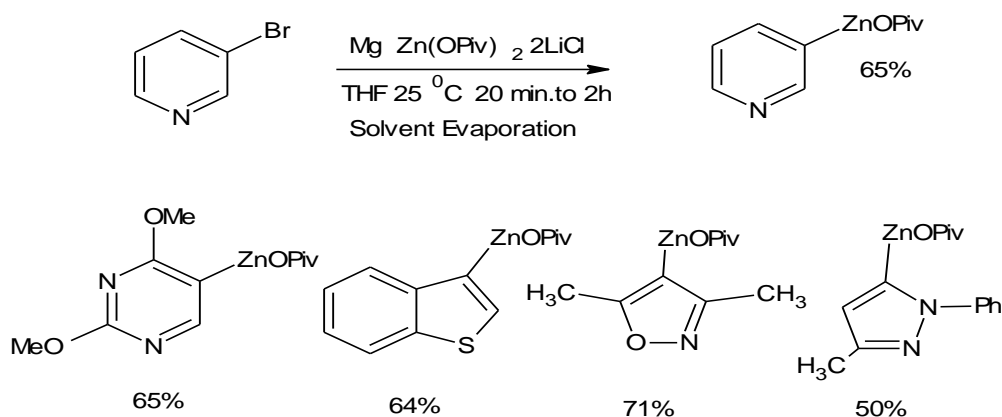
The preparation of solid salt stabilized arylzinc reagents was done by magnesium insertion in the presence of $Zn(OPiv)_2 \cdot 2LiCl$ lead to a fast formation of the zinc reagent at 25°C within 2h. The THF soluble salt

$Zn(OPiv)_2 \cdot 2LiCl$ was stabilize the zinc reagent and accelerate its formation. After formation of organozinc compound evaporate the THF furnishes solid arylzinc reagent were obtained. Using this method functional solid powder arylzinc reagent were prepared, easy to handle.^[144]



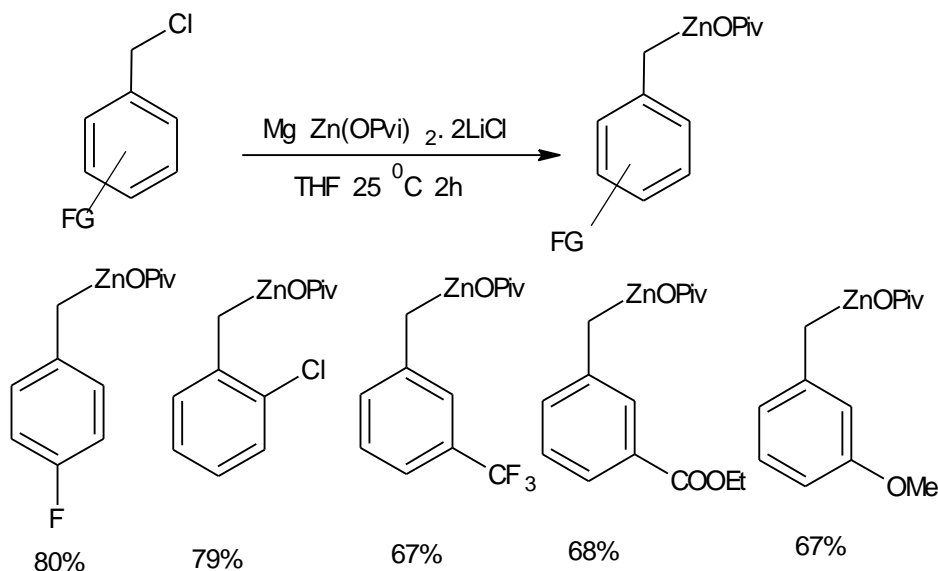
Scheme:- 19 Preparation of solid functionalized aryl zinc pivalates.

The heterocyclic bromides could also be converted to heteroaromatic zinc pivalates. The solid organozinc pivalates were obtained under mild condition.^[145-148]



Scheme:- 20 Preparation of solid functionalized heteroaromatic zinc pivalates.

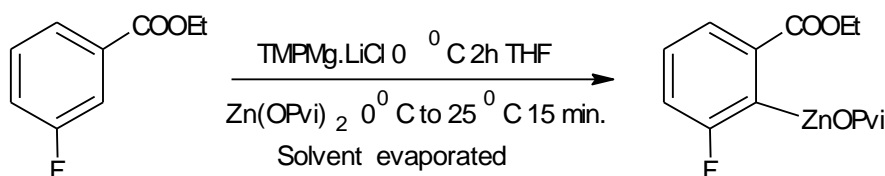
Similarly, benzylic zinc pivalates were prepared by magnesium insertion in the presence of $Zn(OPiv)_2 \cdot 2LiCl$ to functionalized benzylic chloride.^[144]



Scheme:-21 Preparation of functional benzylic organozinc pivalates.

The product obtained above was treated for transmetallation by $Zn(OPiv)_2$ at $0^\circ C$ to $25^\circ C$, 15 min. After evaporation of solvent the solid aryl zinc pivalates was obtained as a yellow fine powder in 92% yield.^[150]

The organozinc pivalates prepared by using $TMPMgCl$. at $0^\circ C$ in THF after 2 h at $0^\circ C$ reaction was completed.



Scheme:- 22 Direct metallation of polyfunctional aryl compound.

CONCLUSION

In this short review, we have summarized various methods for preparation of organozinc reagent. Highly reactive zinc metal was prepared by reduction of zinc chloride using lithium naphthalene readily undergoes oxidative insertion to alkyl, aryl and vinyl halides. In the preparation of maximum number of organozinc reagent zinc or activated zinc metal is used for oxidative insertion of zinc in carbon halide bond. The secondary carbon halogen bond undergoes fast zinc insertion reaction than primary carbon halogen bond. The presence of organic moiety bearing electron withdrawing functional group enhance the rate of zinc insertion reaction. The zinc insertion into sp^2 hybridized carbon halogen bond is more difficult than sp^3 hybridized carbon halogen bond and require zinc or polar solvent or elevated temperature.

REFERENCES

1. Frankland E. Liebigs Ann. Chem, 1848-49: 71, 171.
2. Frankland E. J. Chem. Soc., 1848-49; 2, 263.
3. Reformatsky Chem. Ber. 1887, 20, 1210 & Reformatsky Chem. Ber., 1895; 28: 2842.
4. G. Emschwiller compt. rend., 1929; 188: 1555.
5. Shriner R. L. Org. React., 1942; 1: 1.
6. Simmons H. E., Smith R. D. J. Am. Chem. Soc., 1959; 81: 4256.
7. Blanchard E. P., Simmons H. E., J. Am. Chem. Soc., 1964; 86: 1337, 1347.
8. Furukawa J., Kawabata N., Nishimura J. Tetrahedron Lett., 1966; 3353.
9. Sawada S., Inouye Y. Bull. Chem. Soc. Jpn, 1969, 42, 2669.
10. Simmons H.E., Cairns T. L., Vladuchick A., Hoiness C. M. Org. React., 1972; 20.
11. Furukawa J. Kawabata N. Adv. Organomet. Chem, 1974; 12: 83.
12. Simmons H. E., Smith R. D. J. Am. Chem. Soc., 1985; 80: 5323.

13. Furstner A. *Synthesis* 1989, 571. b) Furstner A. *Angew. Chem. Int. Ed. Engl.*, 1993; 32: 164.
14. Negishi E *Organometallics in Organic Synthesis*, Vol.1 Wiley New York, 1980.
15. I. Antes, G. Frenking, *Organometallics*, 1995; 14: 4263.
16. E. Hupe, P. Knochel, K. J. Szabo *Organometallics*, 2002; 21: 2203.
17. *Handbook of Grignard Reagents*, G. S. Silverman, P. E. Rakita, Eds., Marcel Dekker, 1996.
18. Skinner H. A. *Adv. Organometal. Chem*, 1964; 2: 49.
19. Giovannini R. Studemann T. Dussin G. Knochel P. *Angew. Chem. Int. Ed.*, 1998; 78: 2387.
20. Review: Wipf P. *Synthesis*, 1993; 537.
21. M. Gaudemar *Bull.Soc.Chim. Fr.*, 1962; 5: 974.
22. Majid T.N. Knochel P. *Tetrahedron Lett.*, 1990; 31: 4413- 4446.
23. Knochel P. Yeh M. C. P. Berk S. C. Talbert J. J. *Org. Chem*, 1988; 53: 2390.
24. Prasad A. S. B. Knochel P. *Tetrahedron*, 1997; 53: 16711.
25. Berk S.C. , Knochel P. Yeh M. C. P. *J. Org. Chem*, 1988; 53: 5798.
26. Berk S.C. Yeh M. C. P., Jeong N, Knochel P. *Organometallics*, 1990; 9: 3053.
27. Yeh M. C. P. , Knochel P. Butler W.M. Berk S. C. *Tetrahedron Lett.* 1988; 29: 6693.
28. Chen H. G. Gage J.L. Barrett S. D. Knochel P. *Tetrahedron Lett.* 1990; 31: 1829.
29. Yeh M. C. P. Knochel P., Sant L. E. *Tetrahedron Lett.*, 1988; 29: 3887.
30. Yeh M. C. P. Knochel P., *Tetrahedron Lett.*, 1989; 30: 4799.
31. Retherford C., Yeh M. C. P., Schipor L. Chen H. G., Knochel P. *J. O. Chem.* 1989; 54: 5200.
32. Tucker C.E., AchyuthaRao S. Knochel P. *J. Org. Chem.*, 1990; 55: 5446.
33. Knochel P. Chou T. S. Chen H. G. Yeh M. C. P. Rozema M. J. *J. Org. Chem.* 1989; 54: 5202.
34. Chou T. S. Knochel P. *J.Org. Chem.*, 1990; 55: 4791.
35. Knochel P., Chou T.S. Jubert C. Rajagopal D. J. *Org. Chem*, 1993; 58: 588.
36. Knochel P., *J. Am. Chem. Soc.*, 1990; 112: 7431.
37. Wass J. R. AchyuthaRao S. Knochel P., *Tetrahedron Lett.*, 1992; 33: 3717.
38. Retherford C. Knochel P., *Tetrahedron Lett.*, 1991; 32: 441.
39. Rozema M.J. AchyuthaRao S. Knochel P., *J. Org. Chem.*, 1992; 57: 1956.
40. Knochel P., Rozema M. J. Tucker C.E. Retherford C. Furlong M. AchyuthaRao S. *Pure Appl. Chem*, 1992; 64: 361.
41. AchyuthaRao S. Knochel P., *J. Org. Chem*, 1991; 56: 4591.
42. Rozema M.J. Rajagopal D. Tucker C.E. Knochel P. *J. Organomet. Chem*, 1992; 438: 11.
43. Yeh M. C. P. Sun M. L. Lin S.K. *Tetrahedron Lett.*, 1991; 32: 113.
44. Yeh M.C.P. Tau S. J. *J. Chem. Soc. Chem. Commun*, 1992; 13.
45. Yeh M.C.P. Tsou C.J. Chuang C. N. Lin H.C. *J.Chem. Soc. Chem. Commun*, 1992; 890.
46. Blankenfeldt W. Liao J. W. Lo L.C. ,Yeh M.C. P. *Tetrahedron Lett.*, 1996; 37: 7361.
47. Yeh M.C.P. Shen B.A. Fu H. W. Tau S. I. Chuang L. W. *J. Am. Chem. Soc.*, 1993; 115: 5941.
48. Yeh M.C.P. Chuang C. N. *J. Chem. Soc. Chem. Commun*, 1994; 703.
49. Jubert C. Knochel P. *J. Org. Chem.*, 1992; 57: 5431.
50. Majid T. N. Yeh M. C. P. Knochel P. *Tetrahedron Lett.*, 1989; 30: 5069.
51. Chen H. C. Hoehstetter C. Knochel P. *Tetrahedron Lett.*, 1989; 30: 4795.
52. Knoess H. P. Furlong M. T. Rozema M. J. Knochel P. *J. Org. Chem.*, 1991; 56: 5974.
53. Yeh M. C. P. Chen H. G. Knochel P. *Org. Synth.*, 1991; 70: 195.
54. Tamaru Y. *InNew Trends in Organometallic Chemistry*, Sakurai H. Ed. Tohoku University Sendai, Japan, 1990; 304.
55. AchyuthaRao S. Tucker C. E. Knochel P. *Tetrahedron Lett.*, 1990; 31: 7575.
56. AchyuthaRao S. Chou T. S. Schipopr I. Knochel P. *Tetrahedron*, 1992; 48: 2025.
57. Kanai G. Miyaura N. Suzuki A. *Chem. Lett.*, 1993; 845.
58. Watanabe T. Miyaura N. Suzuki A. *J. Organomet. Chem*, 1993; 444.
59. Watanabe T. Sakai M. Miyaura N. Suzuki A. *J. Chem. Soc. Chem. Commun*, 1994; 467.
60. JanakiramRao C. Knochel P. *J. Org. Chem*, 1991; 56: 4593.
61. Knochel P. JanakiramRao C. *Tetrahedron*, 1993; 49: 29.
62. Bronk B. S. Lippard S. J. Danheiser R. L. *Organometallics*, 1993; 12: 3340.
63. Retherford C. Chou T. S. Schelkum R. M. Knochel P. *Tetrahedron Lett.*, 1990; 31: 1833.
64. Prasad A. S. B. Stevenson T. M. Citineni J. R. Nyzam V. Knochel P. *Tetrahedron*, 1997; 53: 7237-7254.
65. Zhu L. Wehmeyer R. M. Rieke R. D. *J. Org. Chem.*, 1991; 56: 1445.
66. Rieke R.D., Kim S. H. Wu X. *Org. Chem*, 1997; 62: 6921.
67. Zhu L. Rieke R. D. *Tetrahedron Lett.*, 1991; 32: 2865.
68. Rieke R.D. Soll S.M. Xiong H. *J.Am.Chem.Soc.*, 1995; 117: 5429.
69. Rieke R. D. Uhm S. J. Hudall P.M. *J. Chem.Soc. Chem. Commun*, 1973; 279.
70. Rieke R. D. Li P. T. Burns T. P. Uhm S.T. *J. Org.Chem.*, 1981; 46: 4324.
71. Rieke R. D. Uhm S. J. *Synthesis*, 1975; 452.
72. Rieke R. D. *Science*, 1989; 246: 1260 -1264.
73. Hanson M. V. Rieke R. D. *J. Am. Chem. Soc.*, 1995; 117: 10775-10776.

74. S. Huo *Org. Lett.*, 2003; 5: 423.
75. C. Jubert P. Knochel *J. Org.Chem*, 1992; 57: 5425.
76. C. Jubert P. Knochel *J. Org.Chem*, 1992; 57: 5431.
77. H. Stadtmuller R. Lentz C. E. Tucker T. Studemann W. Dorner P. Knochel, *J. Am. Chem. Soc.*, 1993; 115: 7027.
78. H. Stadtmuller, A. Vaupel, C. E. Tucker. T. Studemann, P.Knochel *Chem. Eur. J.*, 1996; 2: 1204.
79. A. Vaupel, P.Knochel *J. Org.Chem*, 1996; 61: 5743.
80. H. Stadtmuller .E. Tucker, A. Vaupel, P. Knochel *Tetrahedron Lett.*, 1993; 34: 7911.
81. A. Vaupel P. Knochel *Tetrahedron Lett.*, 1994; 35: 8349.
82. Riguet E. Klement I. Reddy K. C. Cahiez G. Knochel P. *Tetrahedron Lett.*, 1996; 37: 5865-5868.
83. Dunn M. J. Jackson R. F. W. Pietruszka J. Wishart N. Ellis D. Wythes M. J. *Synlett*, 1993; 499-500.
84. Jackson R. F. W. Wishart N. Wythes M.J.*Synlett*, 1993; 219-220.
85. Dunn M. J. Jackson R. F. W. Pietruszka J. Turner D. J *org. chem*, 1995; 60: 2210-2215.
86. R. J. Rawson and I.T. Harrison *J. Org. Chem*, 1970; 35: 2057.
87. Decamp A. E. Kawaguchi A. T. Volante R. P. Shinkai I *Tetrahedron Lett.*, 1991; 32: 1867-70.
88. Sakurai M. Hata T. Yabe Y. *Tetrahedron Lett.*, 1993; 34: 5939.
89. Sakami S. Houkawa T. Asaoka M. Takei H. *J Chem. Soc. Perkin Trans*, 1995; 285.
90. Houkawa T. Ueda T. Sakami S. Takei H. *Tetrahedron Lett.*, 1996; 37: 1045.
91. H. Blancou A. Commeyras *J. Fluorine chem*, 1982; 20: 255.
92. H. Blancou A. Commeyras *J. Fluorine Chem*, 1992; 20: 267.
93. S. Benefice Malouet, H. BlancouA. Commeyras *J. Fluorine Chem*, 1985; 30: 171.
94. R. N. Haszeldine E. G. Walaschewski *J. Chem. Soc.*, 1953; 3607.
95. W. T. Miller E. Bergman A. H. Fainberg *J. Am. Chem. Soc.*, 1957; 79: 4159.
96. R. D. Chambers W. K. R. Musgrave J. Savoy *J. Chem. Soc.*, 1962; 1993.
97. D. J. Burton *Tetrahedron*, 1992; 48: 189.
98. D. J. Burton Z. Y. Yang P. A. Morken *Tetrahedron*, 1994; 50: 2993.
99. J. Denis C. Girard and J. M. Conia *Synthesis*, 1972; 549.
100. B. Jiang Y. Xu *J. Org. Chem.*, 1991; 56: 733.
101. P. A. Morken H. Lu A. Nakamura D. J. Burton *Tetrahedron Lett.*, 1991; 32: 4271.
102. P. A. Morken D. J. Burton *J. Org. Chem*, 1993; 58: 1167.
103. Furstner A. Singer R. Knochel P. *Tetrahedron Lett.*, 1994; 35: 1679.
104. S. Sibille, V. Ratovelomanana, J. Perichon, M. Troupel, *Synthesis*, 1990; 369.
105. M. Durandetti, M. Devaud, J. perichon *New J. Chem*, 1996; 20: 659.
106. S. Sibille, V. Ratovelomanana, J. Y. Nedelec, J. Perichon, *Synlett*, 1993; 425.
107. C. Gosmini J. Y. Nedelec J. Perichon *Tetrahedron Lett.*, 1997; 38: 1941.
108. N. Zylber, J. Zylber, Y. Rollin, E. Dunach J. Perichon *J. Organomet. Chem*, 1993; 444: 1.
109. Y. Rollin S. Derien, E. Dunach, C. Gebehenne, J. Perichon, *Tetrahedron*, 1993; 49: 7723.
110. C. Gosmini Y. Rollin, J. Y. Nedelec, J. Perichon, *J. Org. Chem*. 2000; 65: 6024.
111. P. Gomes C. Gosmini J. Perichon, *Synlett*, 2002; 10: 1673.
112. H. Fillon, E. Le Gall, C. Gosmini, J. Perichon *Tetrahedron Lett.*, 2002; 43: 5941.
113. S. Seka O. Buriez, J. Y. Nedelec, J. Perichon, *Chem. Eur. J.*, 2002; 8: 2534.
114. H. Fillon, C. Gosmini J. Perichon, *J. Am. Chem. Soc.*, 2003; 125: 3867.
115. P. Gomes, C. Gosmini, Perichon *Synthesis*, 2003; 1909.
116. I. Kazmierski, M. Bastienne, C. Gosmini J. M. Paris J. Perichon *J. Org. Chem*, 2004; 69: 936.
117. I. Kazmierski, C. Gosmini, J. M. Paris J. Perichon, *Tetrahedron Lett.*, 2003; 44: 6417.
118. S. Seka O. Buriez, J. Perichon, *Chem. Eur. J.*, 2003; 9: 3597.
119. J. F. Cameron J. M. J. Frechet *J. Am. Chem. Soc.*, 1991; 113: 4303.
120. P. Wiriyachitra S. J. Falcone, M. P. Cava *J.Org.Chem*, 1979; 44: 3957.
121. C. E. Tucker T. N. Majid P. Knochel *J. Am. Chem. Soc.*, 1992; 114: 3983.
122. E.M. E. Viseux, P. J. Parsons, J.B.J. Pavey *Synlett*, 2003; 861.
123. B. A. Anderson, N. K. Harn, *Synthesis*, 1996; 583.
124. S. Superchi N. Sotomayor G. Miao, B. Joseph V. Snieckus *Tetrahedron Lett.*, 1996; 37: 6057.
125. E. Lorthiois, I. Marek, J.F. Normant *Tetrahedron Lett.*, 1997; 38: 89.
126. P. Karoyan G. Chassaing *Tetrahedron Lett.*, 1997; 38: 85.
127. P. Karoyan J. Quancard J. Vaissermann G. Chassaing *J. Org. Chem*, 2003; 68: 2256.
128. Quancard, H. Magella, S. Lavielle, G. Chassaing, P. Karoyan *Tetrahedron Lett.*, 2004; 45: 2185.
129. J. P. Gillet R. Sauvetre J. F. Normant *Synthesis*, 1986; 538.
130. J. F. Normant *J. Organometallic Chemistry*, 1990; 400: 19.
131. R. K. Dieter, R. T. Watson, R. Goswami *Org. Lett.*, 2004; 6: 253.
132. E. Frankland D. Duppa *Liebigs Ann. Chem.*, 1864; 130: 117.
133. M. J. Rozema D. Rajagopal C.E. Tucker P. Knochel *Organomet. Chem*, 1992; 438: 11.
134. P. Knochel W. Dohle, N. Gommermann F. F. Kneisel, F. Kopp, T. Korn I. SApountzis, V. A. Vu *Angew Chem. Int. Ed.*, 2003; 42: 4302.

135. A. E. Jensen P. Knochel J. Organomet. Chem, 2002; 653: 122.
136. A. Krasovskiy V. Malakhov A. Gavryushi P. Knochel Angew Chem. Int. Ed., 2006; 45: 6040.
137. N. Boudet S. Sase P. Sinha, C. Y. Liu A. Krasovskiy, P.Knochel J. Am. Chem. Soc., 2007; 129; 12358.
138. A. Metzger M. A. Schade P. Knochel Org. Lett., 2008; 10: 1107.
139. Ren H. Dunet G. Mayer P. Knochel P. J. Am. Chem. Soc., 2007; 129: 5376.
140. Araki S. Hatano M. Butsugan Y. J. Org. Chem, 1986; 51: 2126.
141. S. Tucker C. E. Jubert J. Org. Chem, 1995; 60: 2762.
142. M. Mosrin P. Knochel Org. Lett., 2009; 11; 1837.
143. M. Mosrin G. Monzon T. Bresser P. Knochel Chem. Commun, 2009; 5615.
144. Sebastian Bernhardt, Georg Manolikakes, Thomas Kunz, and Paul Knochel Angew. Chem. Int. Ed., 2011; 50: 9205 –9209.
145. Christos I. Stathakis, Sebastian Bernhardt, Valentin Quint, and Paul Knochel Angew. Chem. Int. Ed., 2012; 51: 9428 –9432.
146. Mario Ellwart and Paul Knochel Angew. Chem. Int. Ed., 2015; 54: 10662 –10665.
147. Christos I. Stathakis, Sophia M. Manolikakes, and Paul Knochel Org. Lett., 2013; 15(6): 1302-1305.
148. James R. Colombe, Sebastian Bernhardt, Christos Stathakis, Stephen L. Buchwald, and Paul Knochel Org. Lett., 2013; 15(22): 5754-5757.
149. Sophia M. Manolikakes, Mario Ellwart, Christos I. Stathakis, and Paul Knochel Chem. Eur. J., 2014; 20: 12289 – 12297.
150. Mario Ellwart, Yi-Hung Chen, Carl Phillip Tüllmann, Vladimir Malakhov, and Paul Knochel Org. Synth, 2018; 95: 127-141.