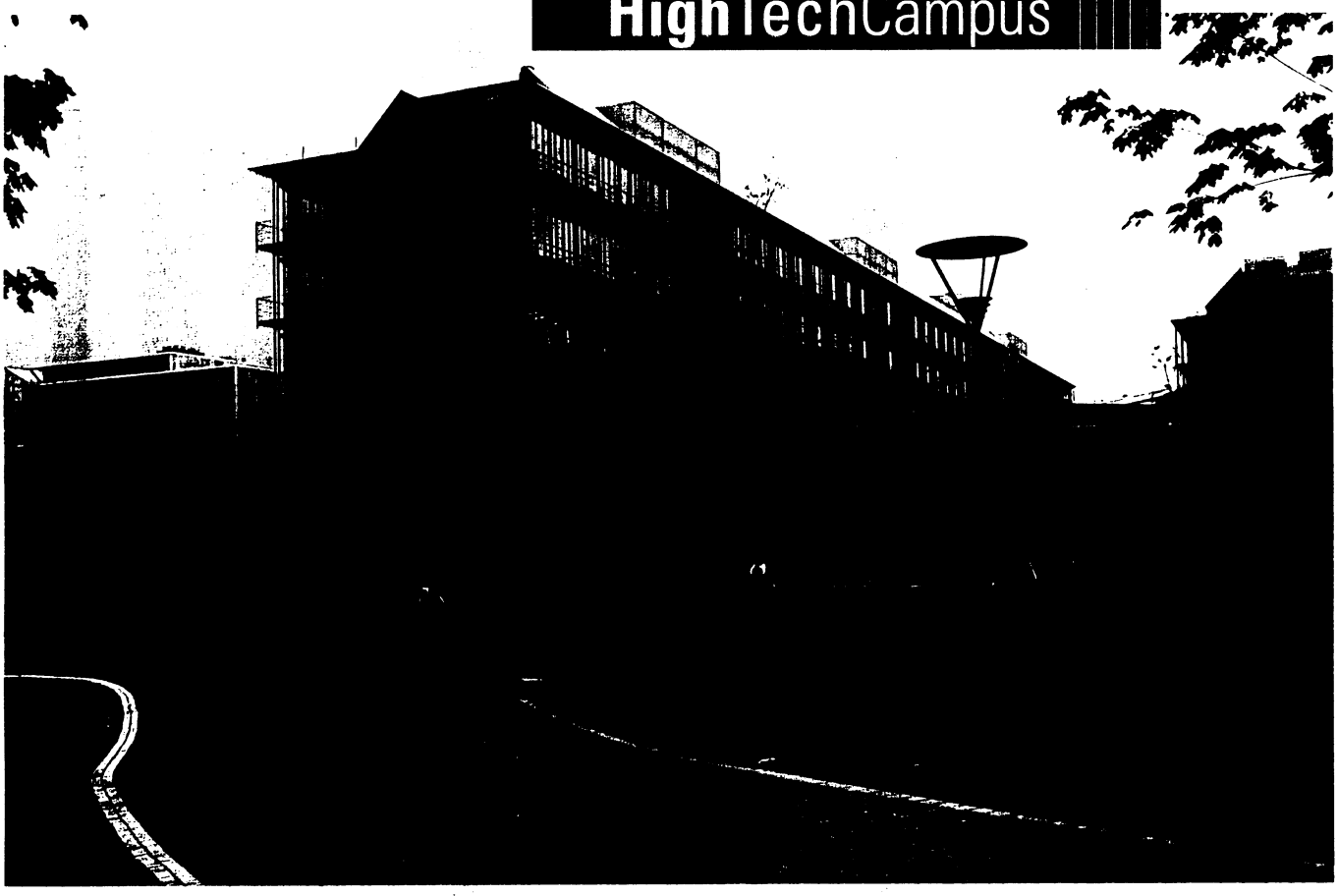
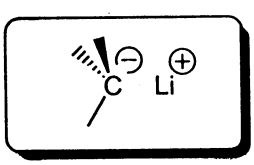
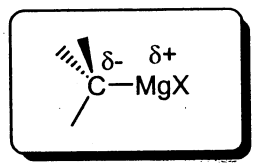
HighTechCampus LMU

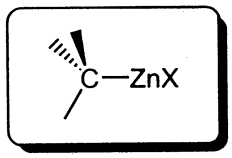


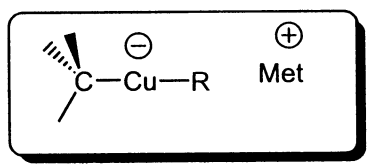
FUNCTIONALIZED ORGANOMETALLICS in ORGANIC SYNTHESIS

Prof. Paul Knochel, LMU-University Munich (Germany)







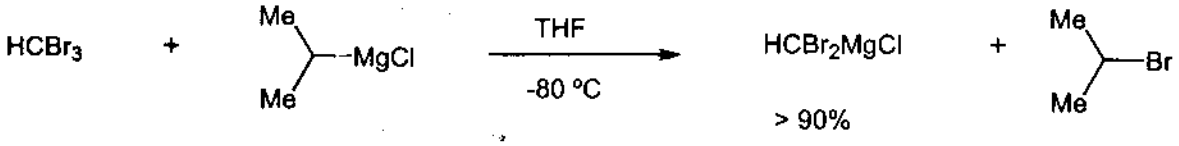


Problems : - Preparation

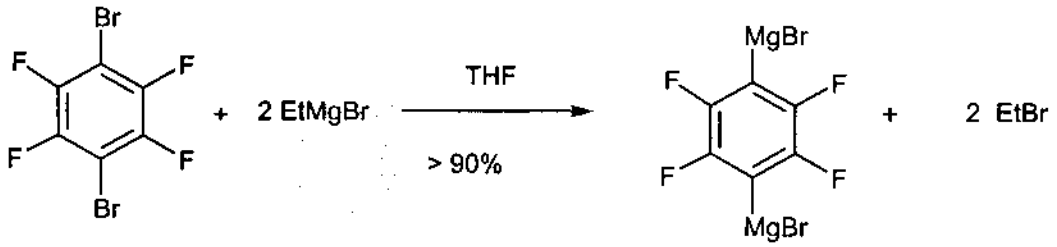
- Functional group tolerance

- Reactivity with electrophiles

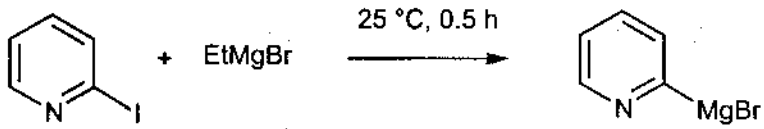
Halogen-magnesium exchange



J. Villieras, *Bull. Soc. Chim. Fr.* **1967**, 1520

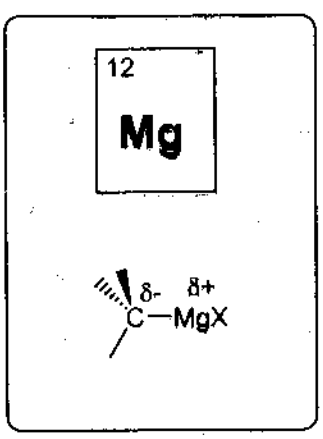


C. Tamborski *J. Organomet. Chem.* **1971**, *26*, 153



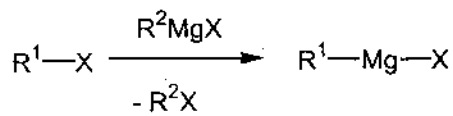
N. Furukawa *Tetrahedron Lett.* **1987**, *28*, 5848

1) General Preparation of Functionalized Organomagnesium Reagents

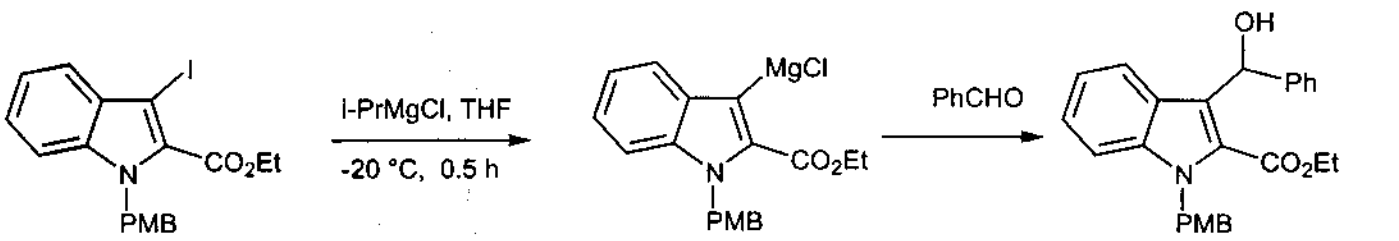


Grignard : 1900

Halogen-Magnesium Exchange

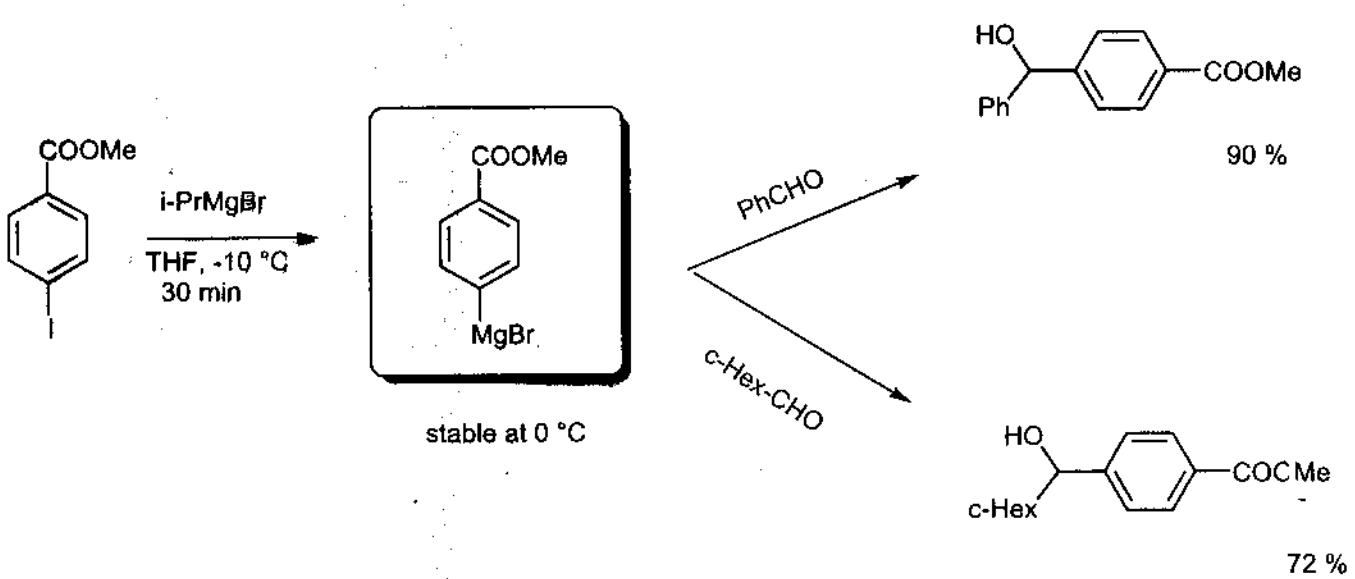


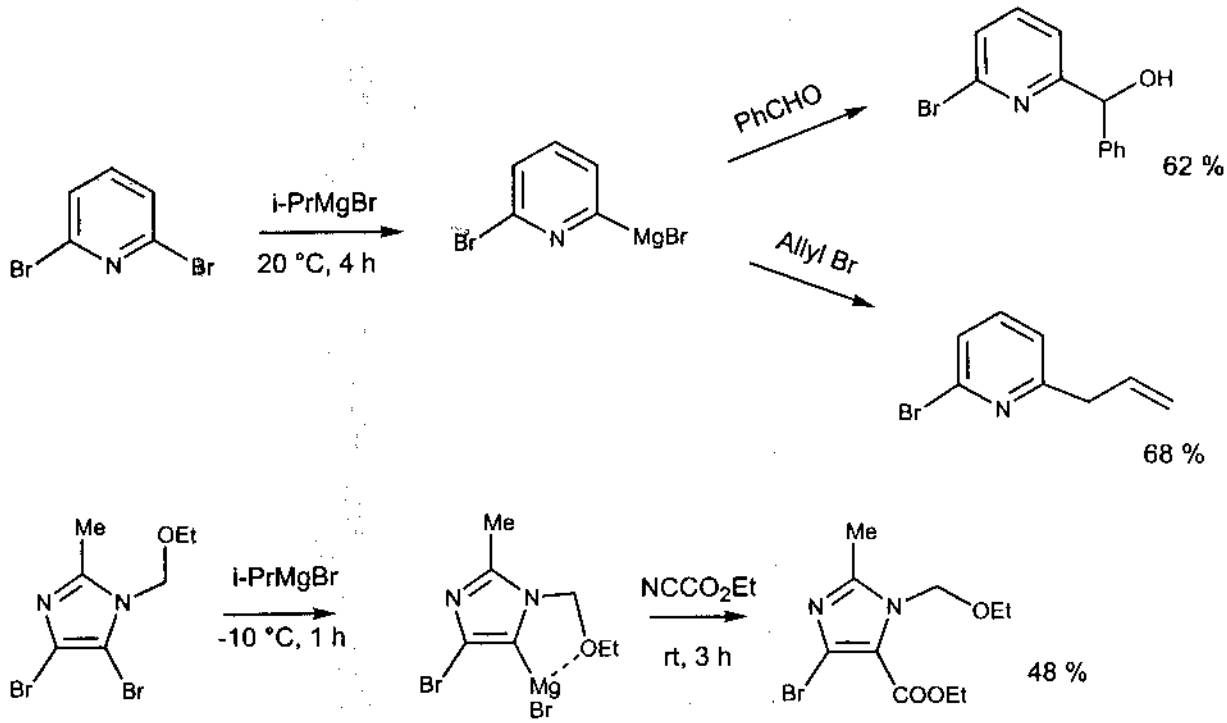
Synthesis of Functionalized Indolylmagnesium Compounds



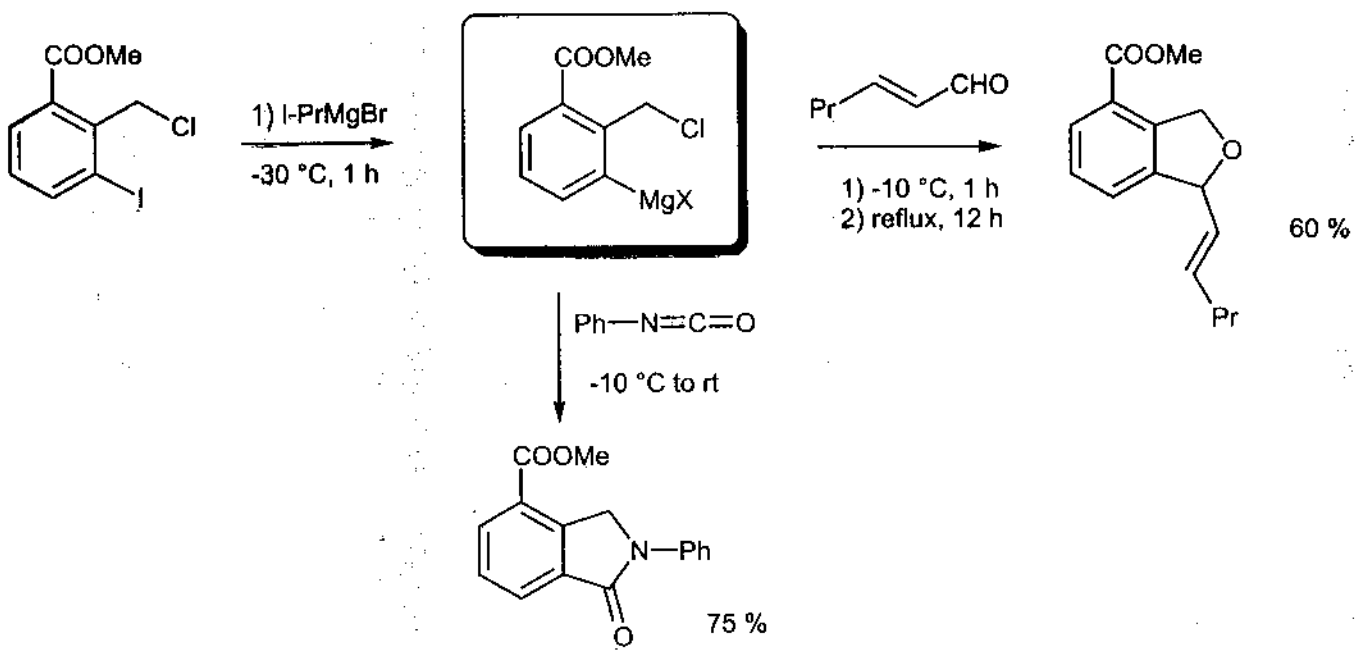
84 %

I. SAPOUNTZIS



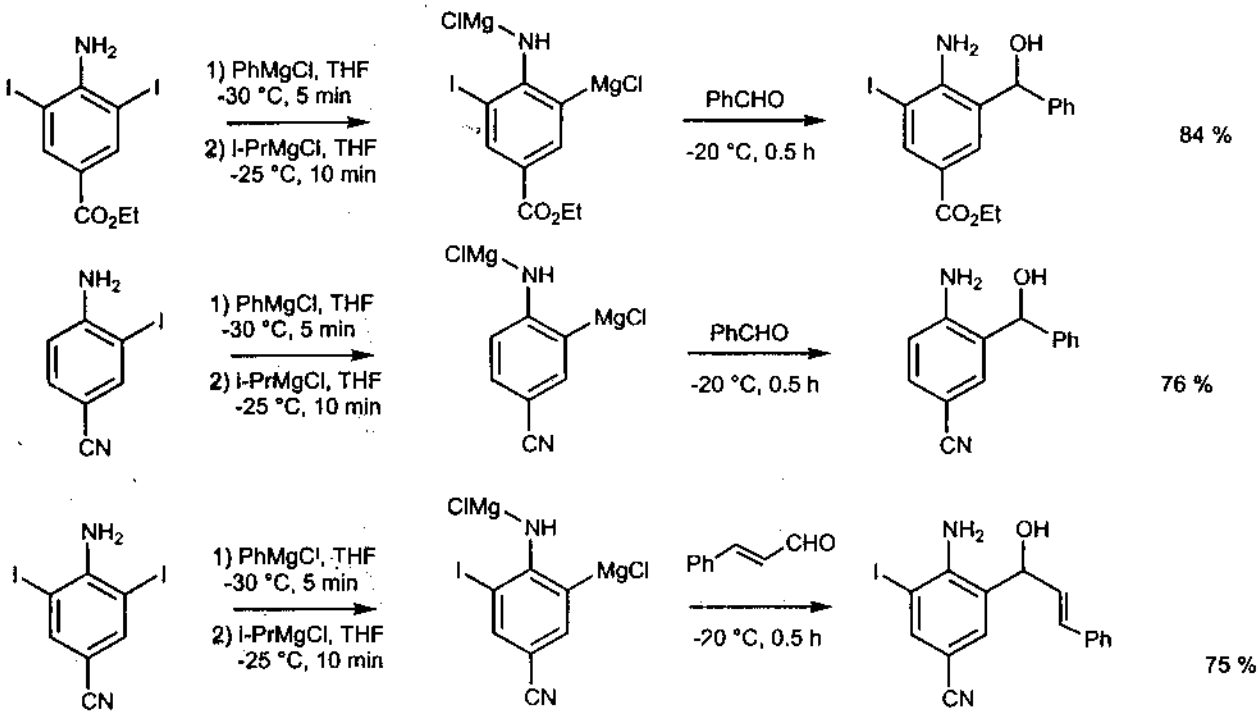


M. ABARBRI, F. DEHMEL, P. K. *J. Org. Chem.* **2000**, *65*, 4618

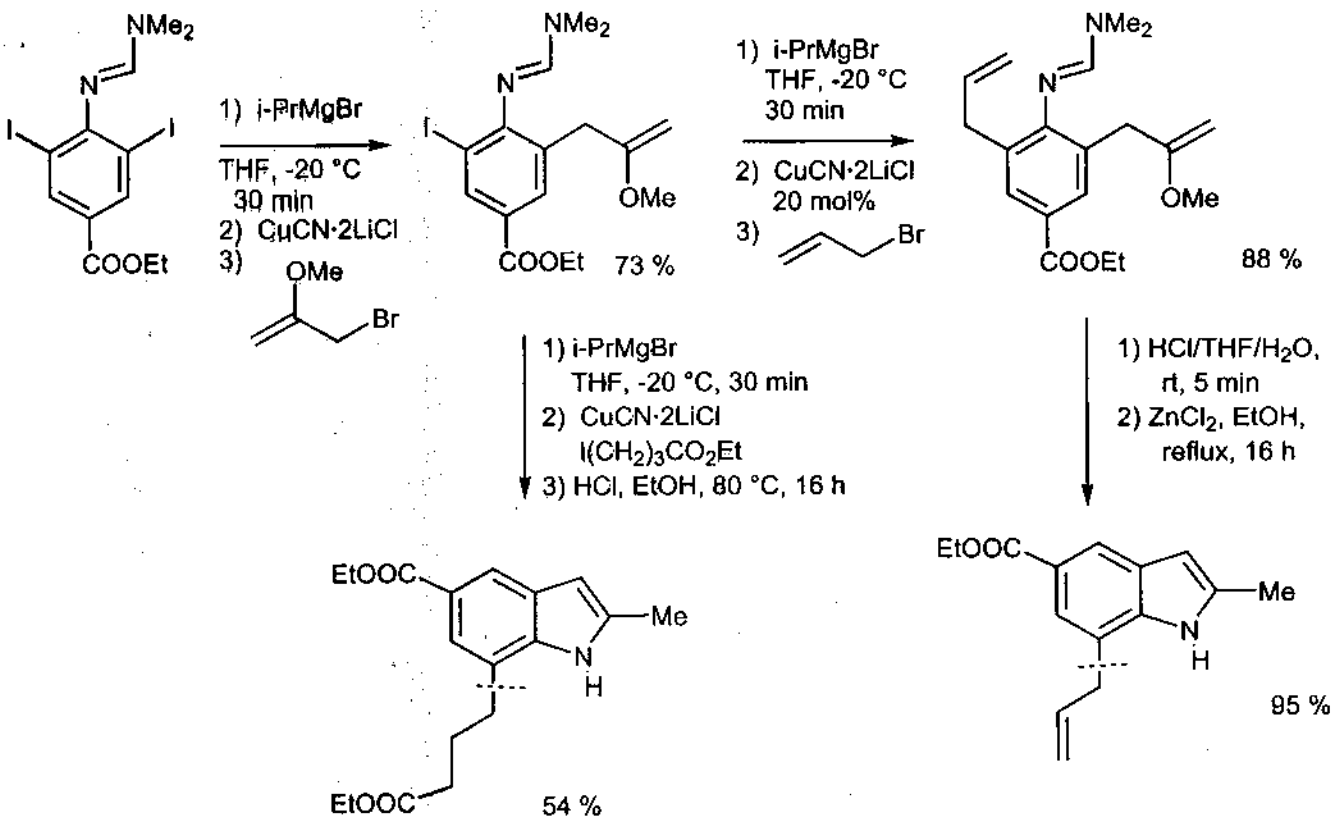


T. DELACROIX, L. BERILLON, J. THIBONNET, P. KNOCHEL, *J. Org. Chem.* **2000**, *65*, 8108

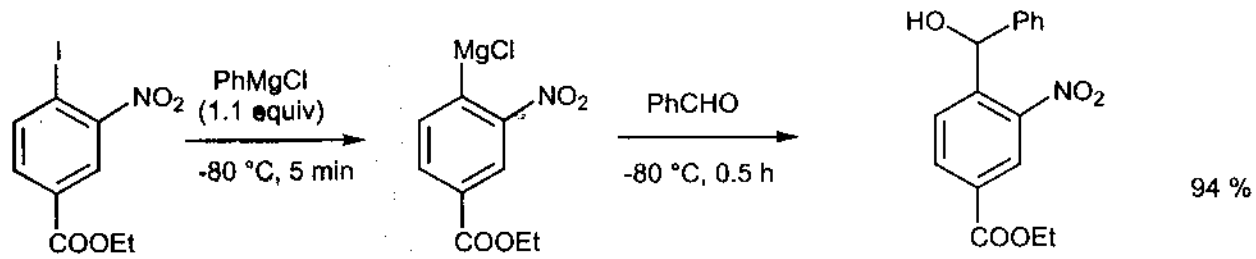
Unprotected Amino-Substituted Arylmagnesium Reagents

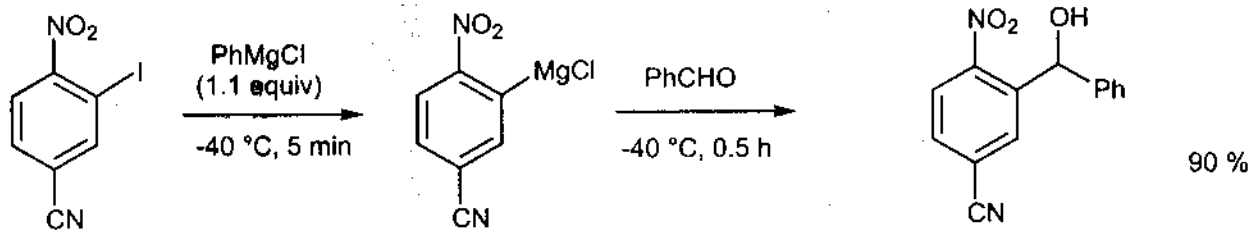


C. KOFINK, G. VARCHI, D.W. LINDSAY



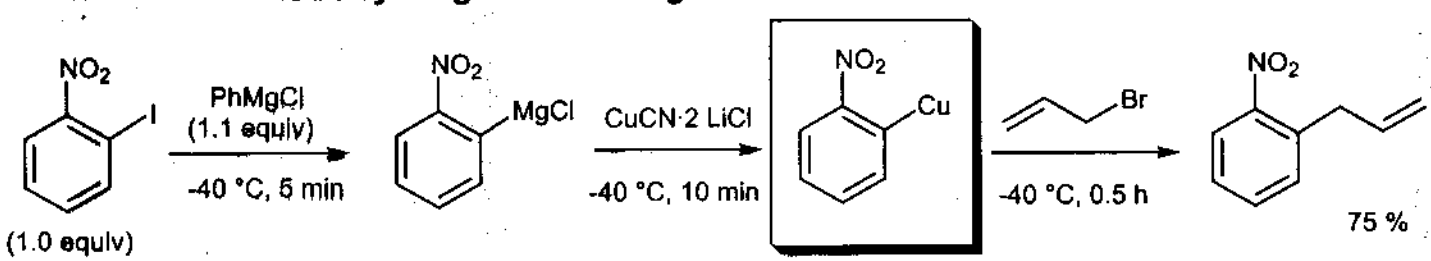
Nitro-Substituted Arylmagnesium Reagents

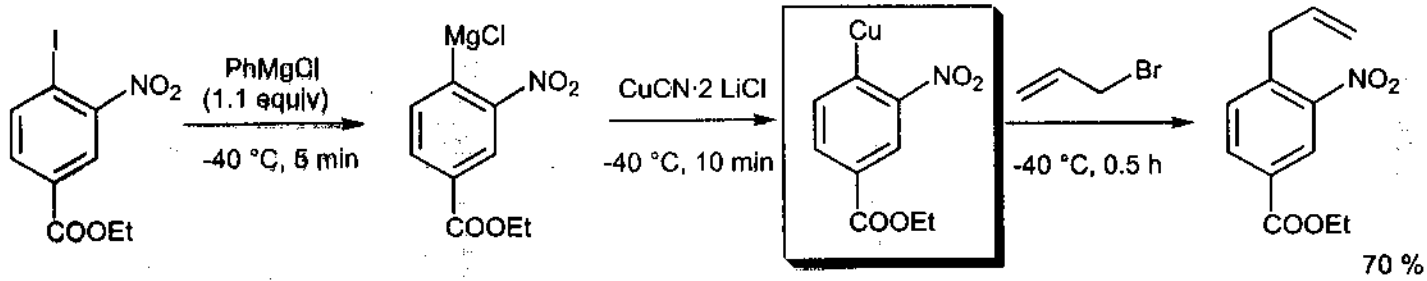


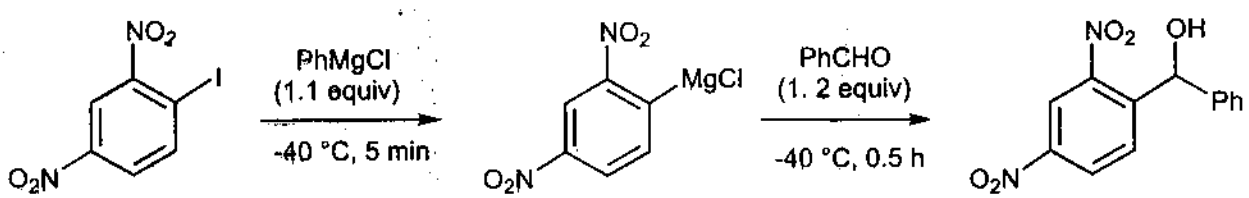


I.SAPOUNTZIS

· Nitro-Substituted Arylmagnesium Reagents

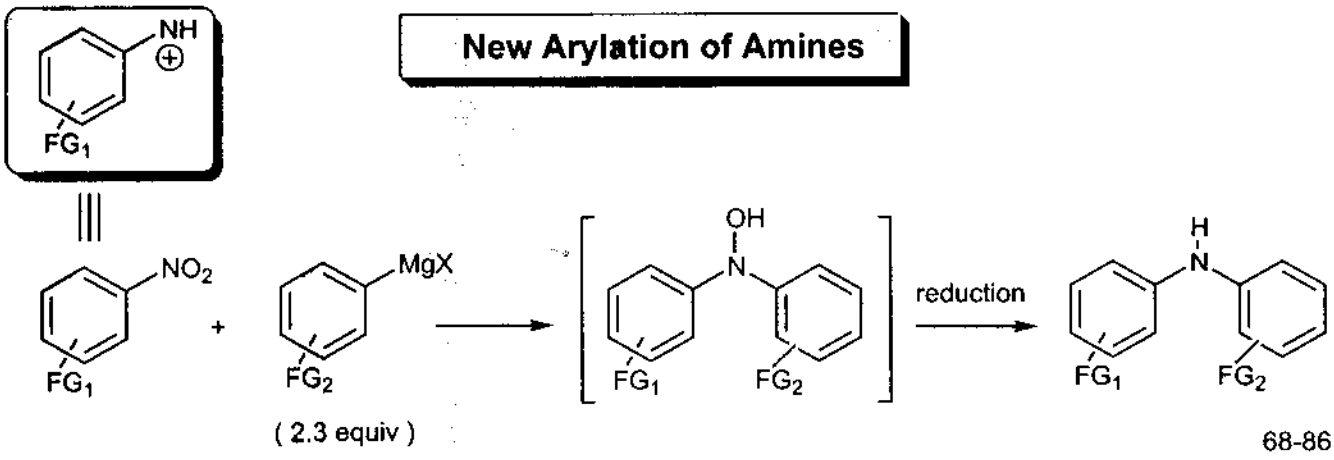




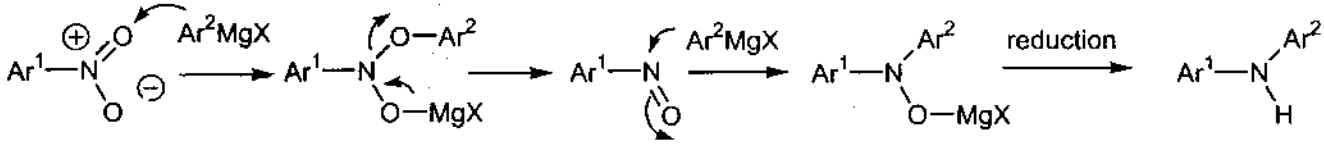


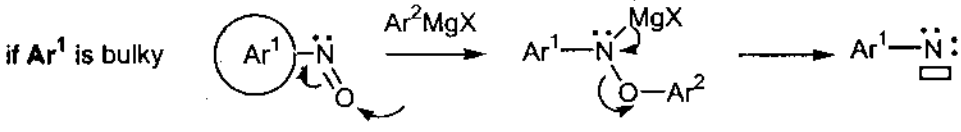
I.SAPOUNTZIS

New Arylation of Amines



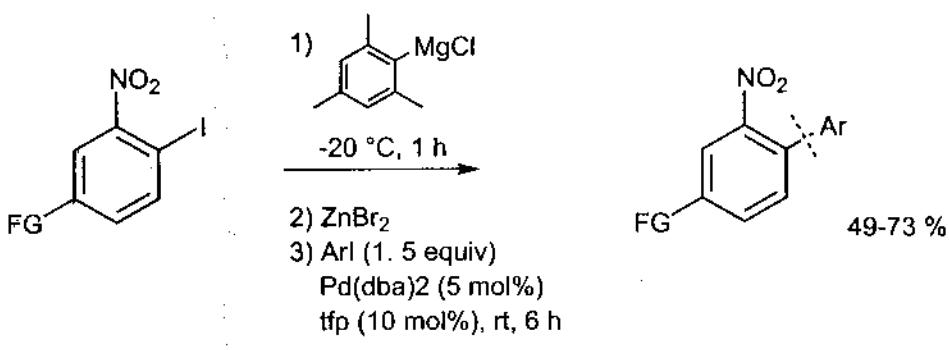
Mechanism

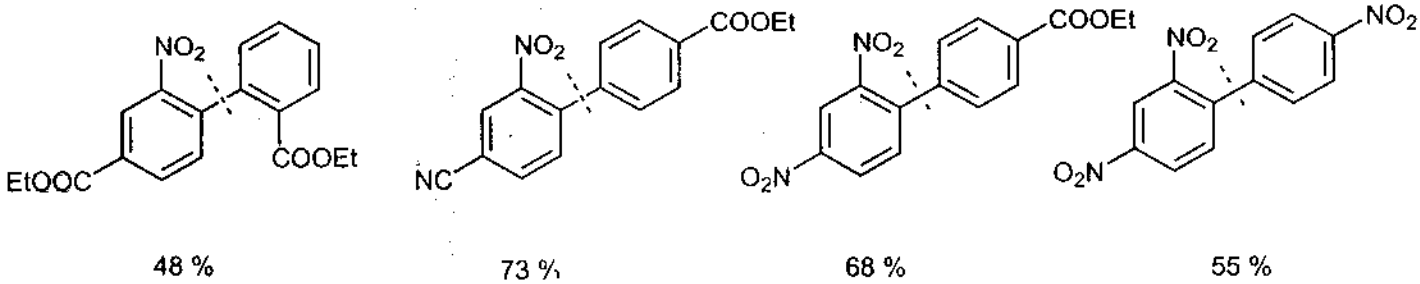




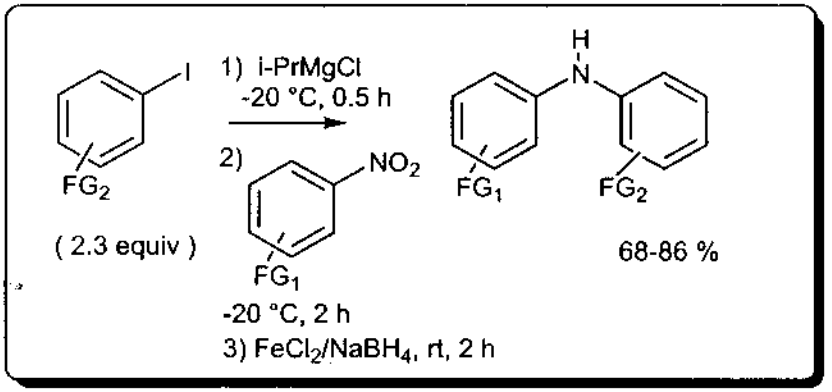
I. SAPOUNTZIS

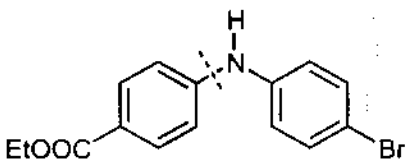
Negishi-Cross-Coupling Reactions





New Arylation of Amines

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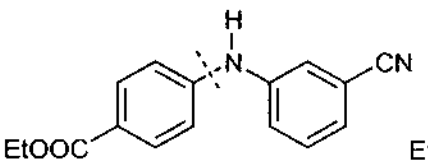
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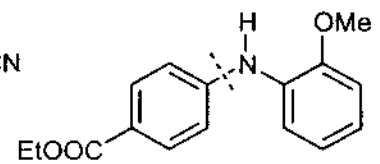
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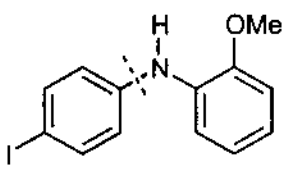
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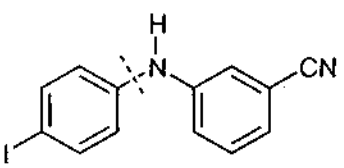
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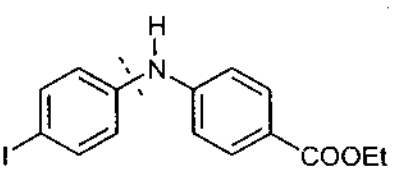
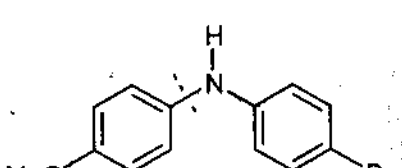

71 %

I. SAPOUNTZIS

New Arylation of Amines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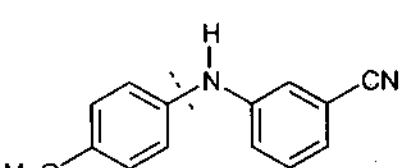
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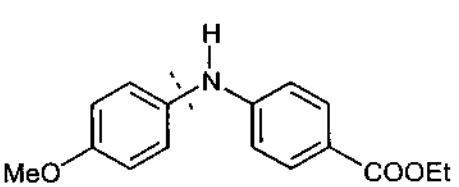
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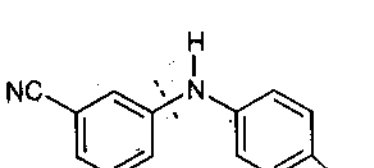
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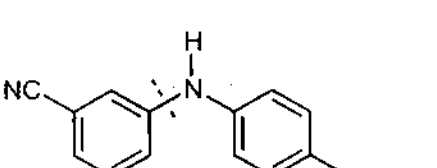
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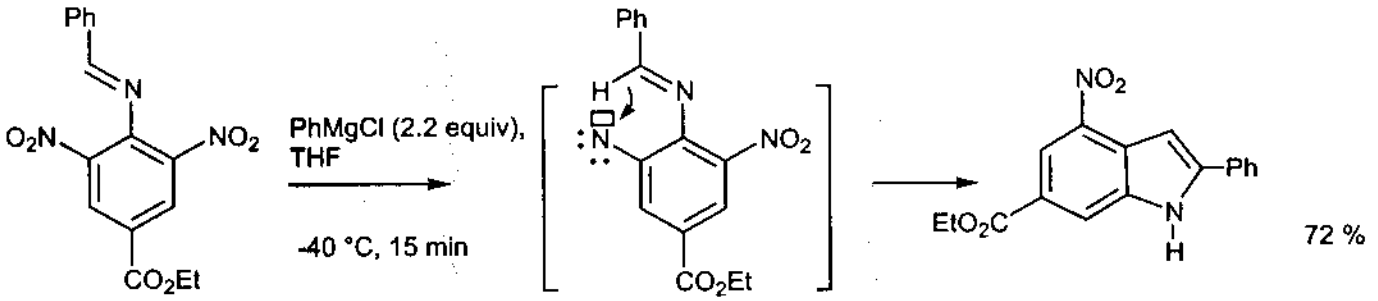
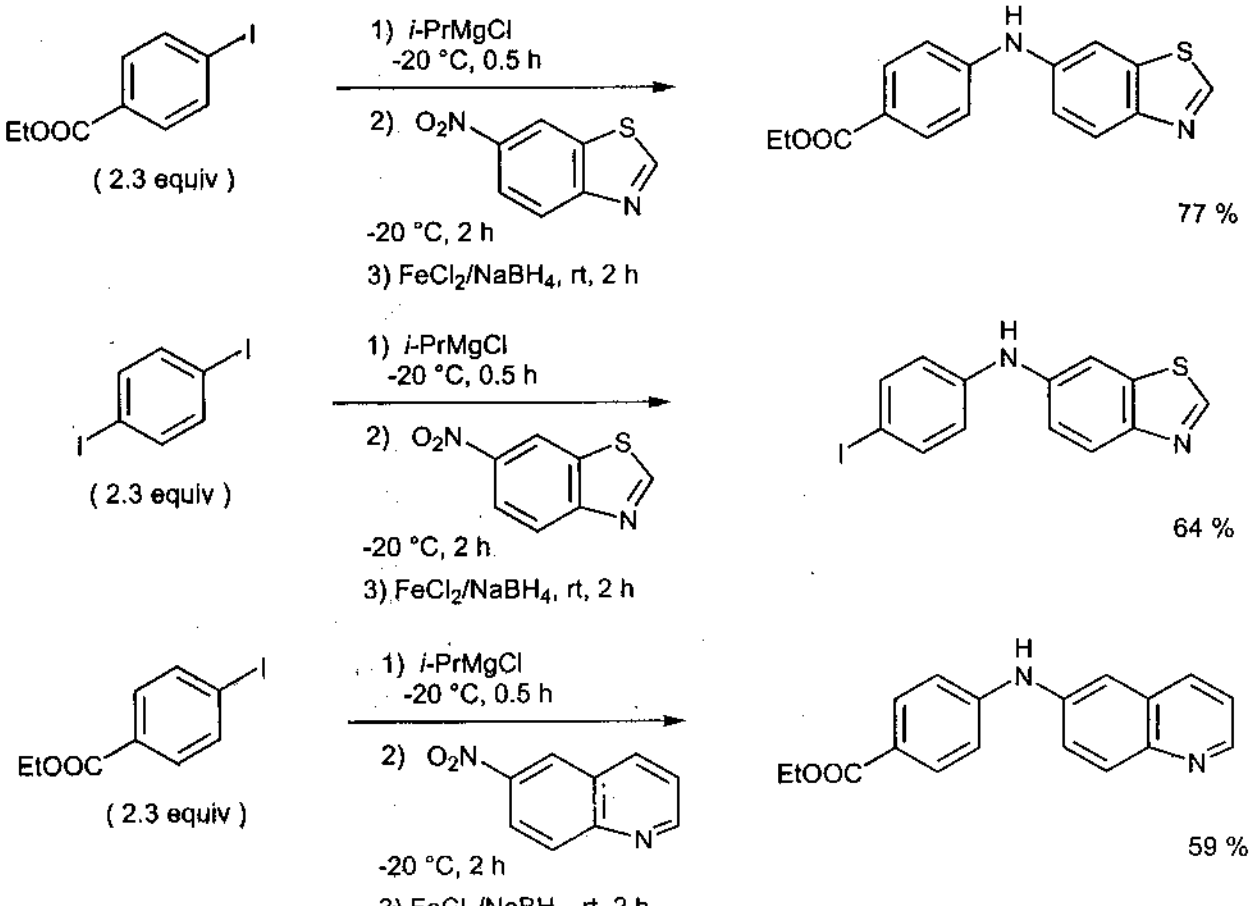
One-pot Synthesis of Indoles

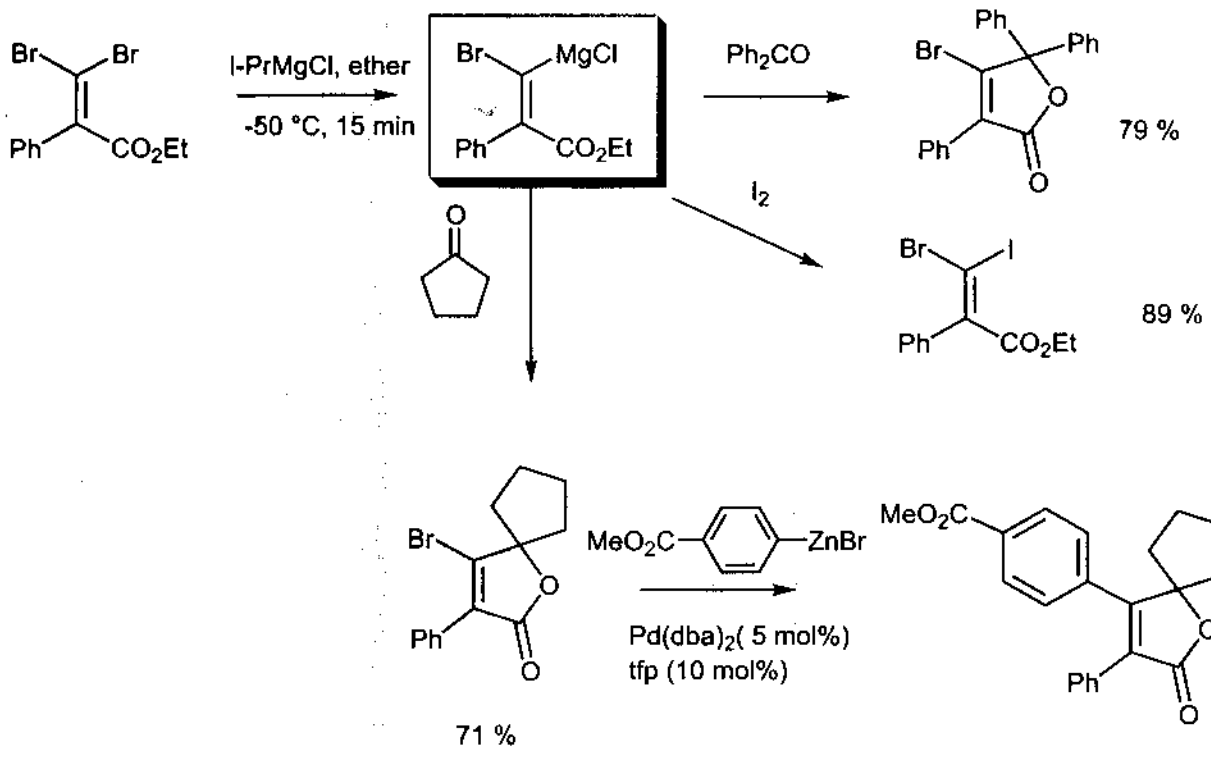


W. DOHLE



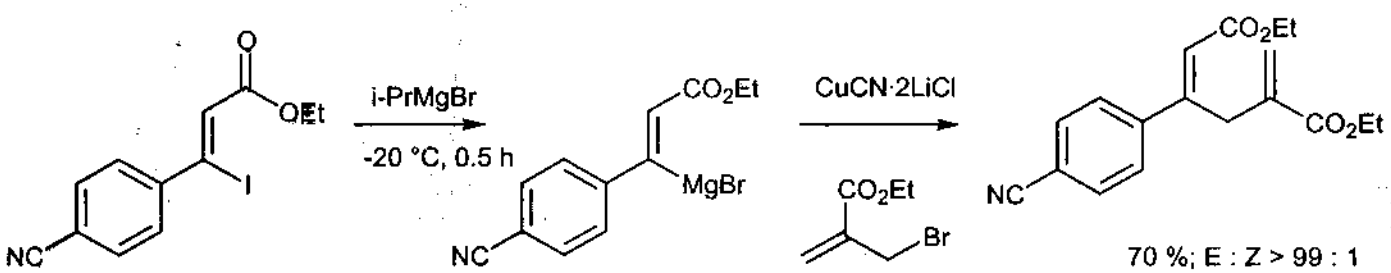
I. SAPOUNTZIS

Functionalized Alkenyl-Magnesium Carbenoids

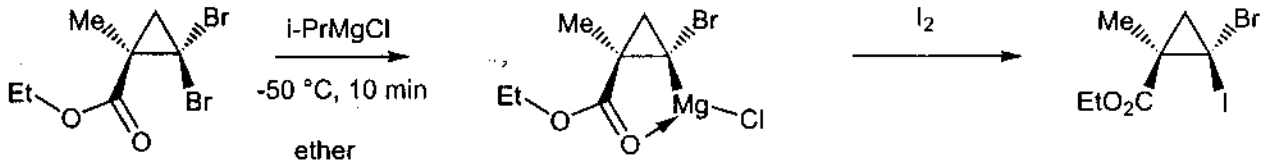


VIET ANH VU

Functionalized Ester-Substituted Alkenylmagnesium Reagents



Ester-Substituted Magnesium Carbenoids



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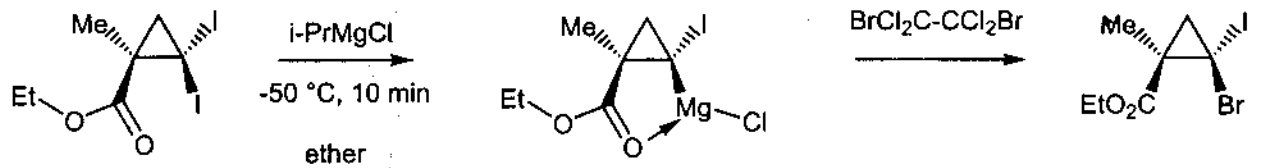
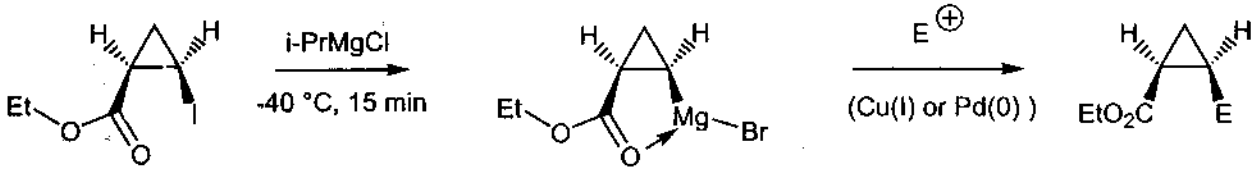
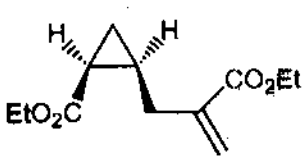


80 %; dr > 99:1

VIET-ANH VU

Ester-Substituted Alkylmagnesium Reagents





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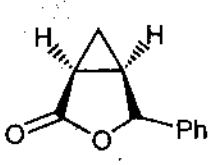

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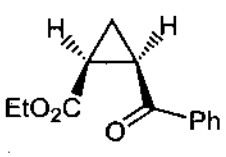

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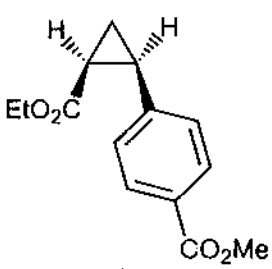
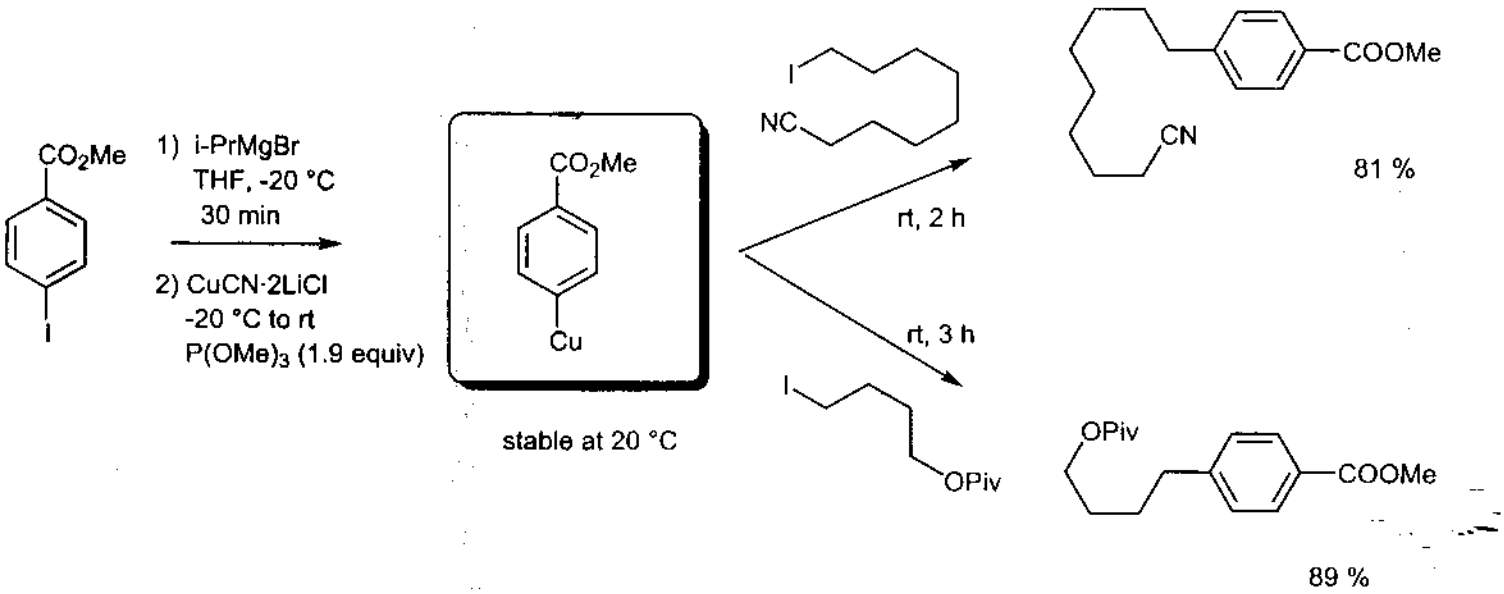
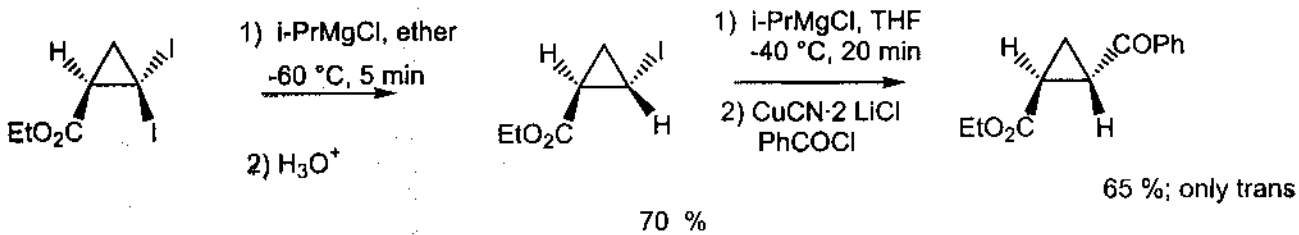


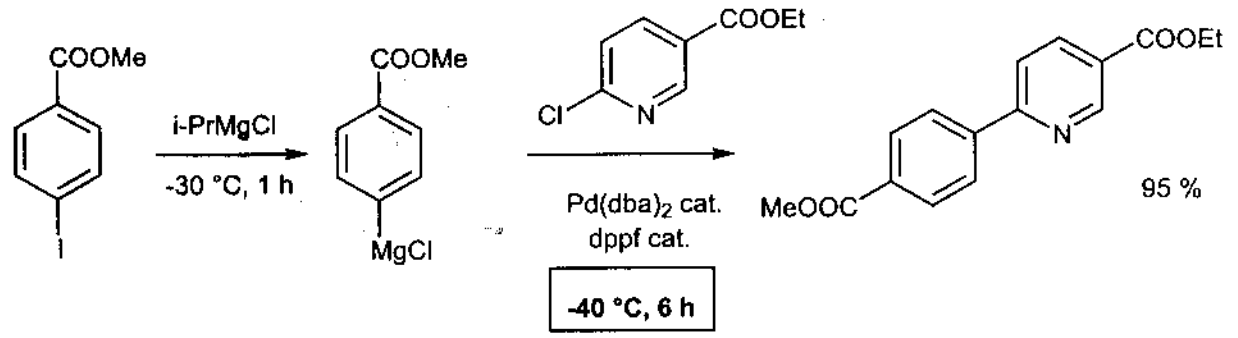
92 %

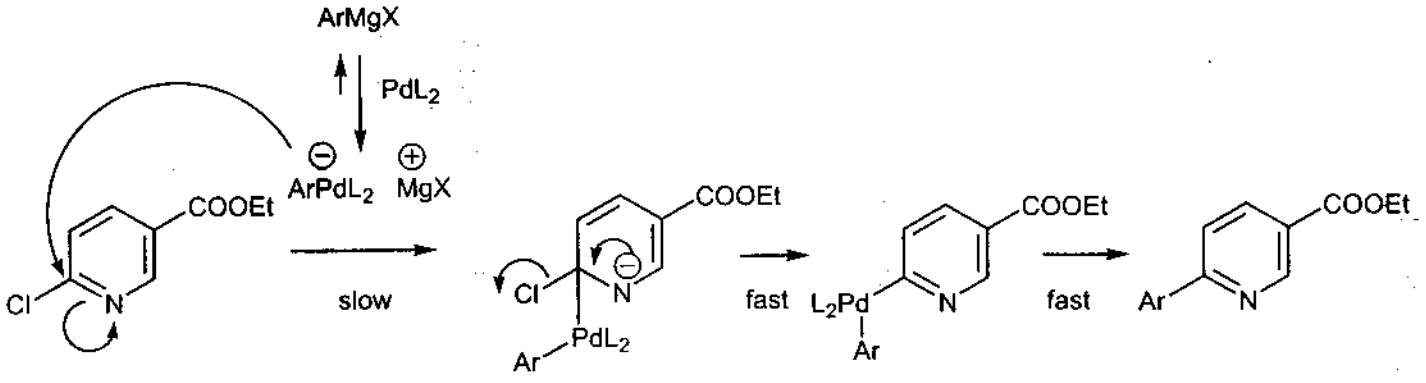


D. LINDSAY

New preparation of functionalized cyclopropyl-magnesium compounds

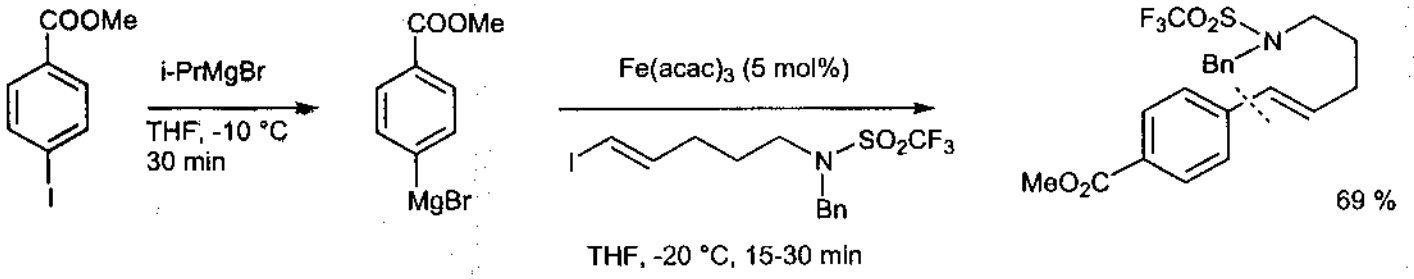


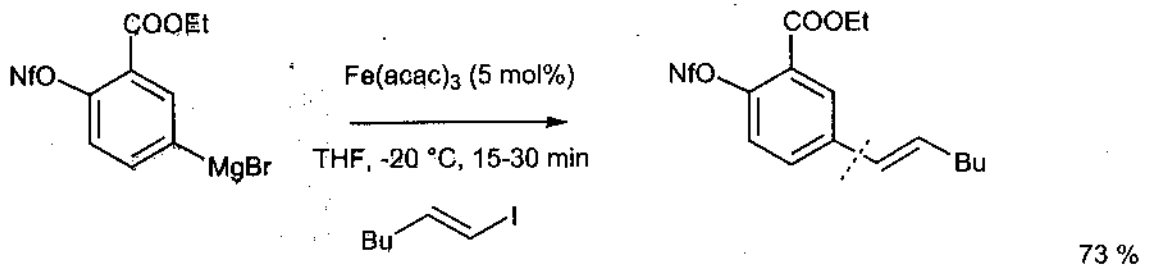




V. BONNET, G. QUEGUINER

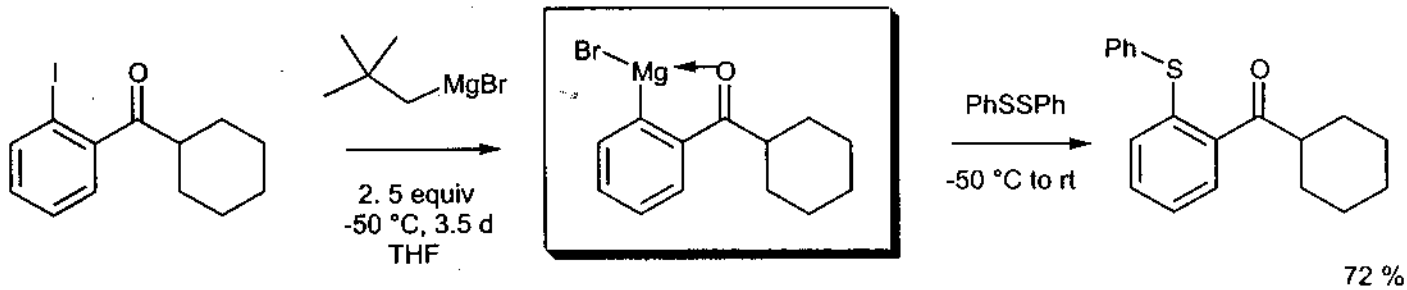
Fe(III)-catalyzed Cross-Coupling between Csp^2-centers

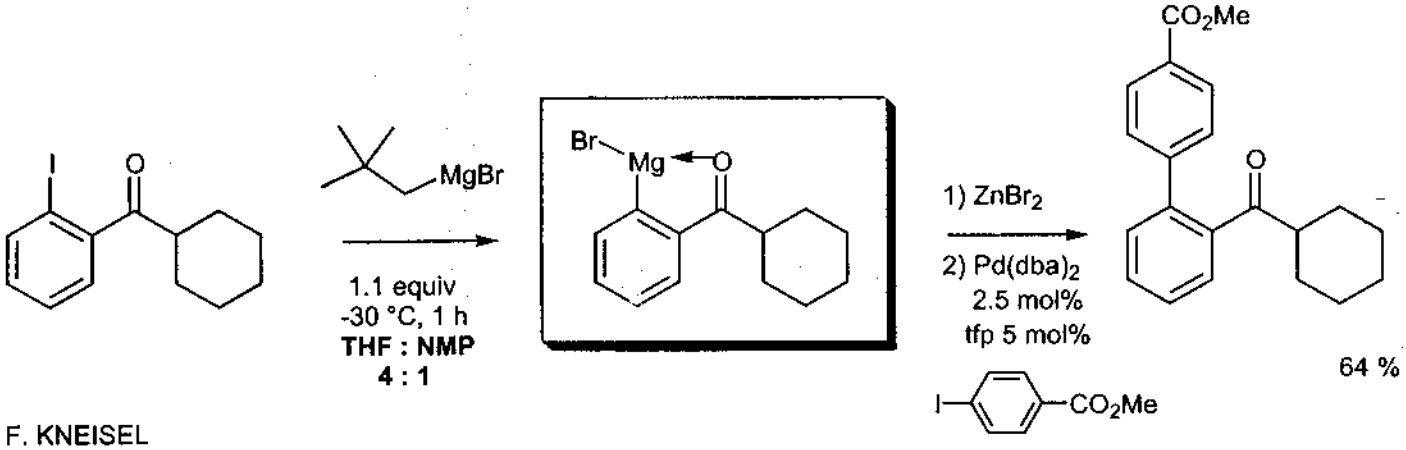




W. DOHLE

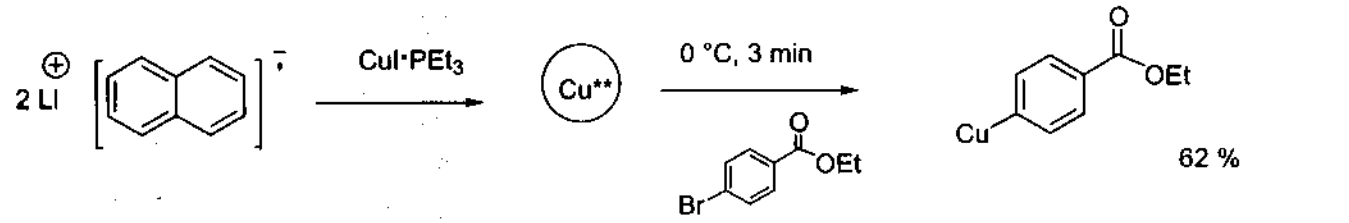
Keto-Substituted Arylmagnesium Reagents

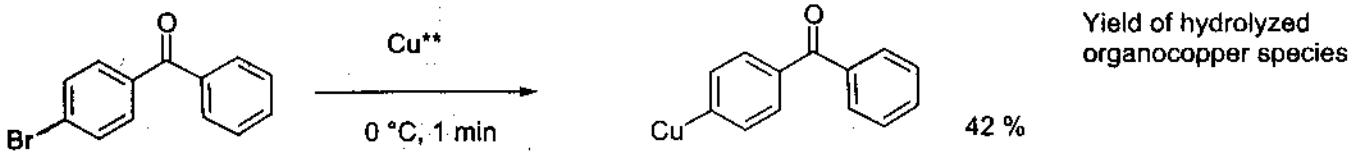




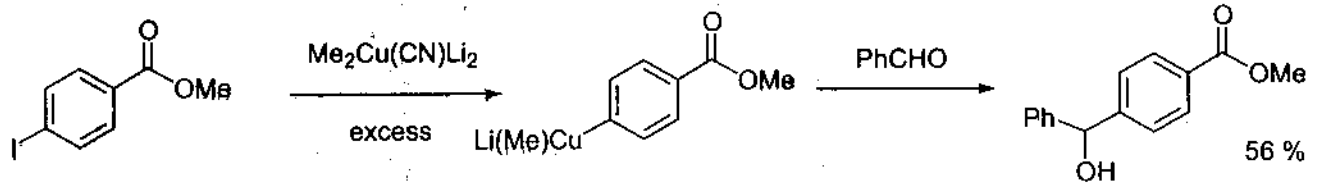
F. KNEISEL

Synthesis of Functionalized Organocoppers



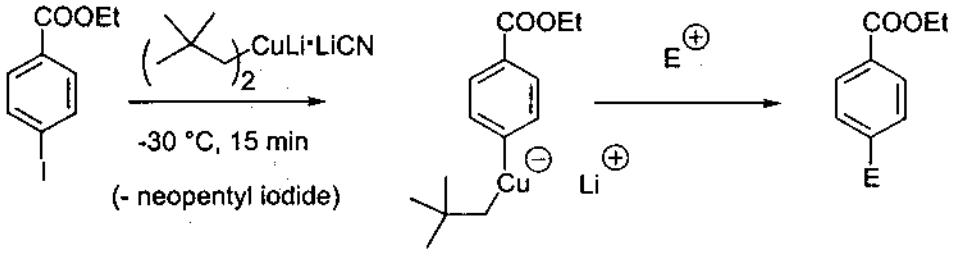


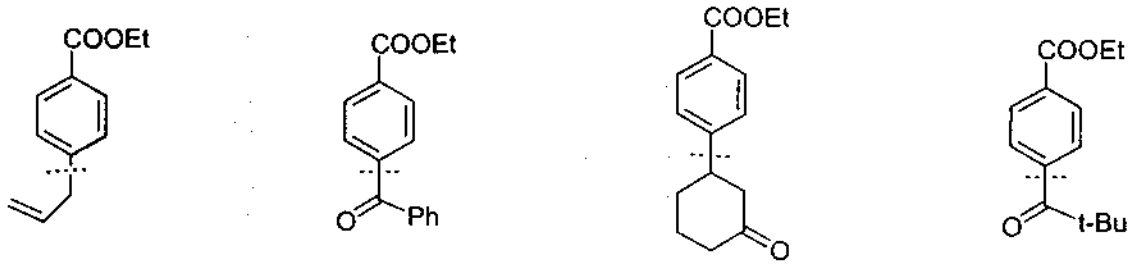
G. W. Ebert, R. D. Rieke *J. Org. Chem.* **1988**, *53*, 4482



E. J. Corey, G. H. Posner, *J. Am. Chem. Soc.* **1968**, *90*, 5615
Y. Kondo, T. Sakamoto, *Angew. Chem.* **1996**, *108*, 818

The Halogen- Copper Exchange for the Synthesis of Functionalized Organocoppers

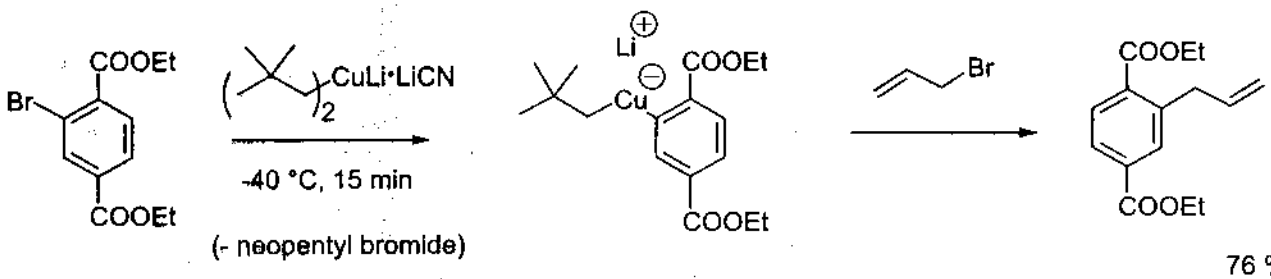




95 % 87 % 70 % 83 %

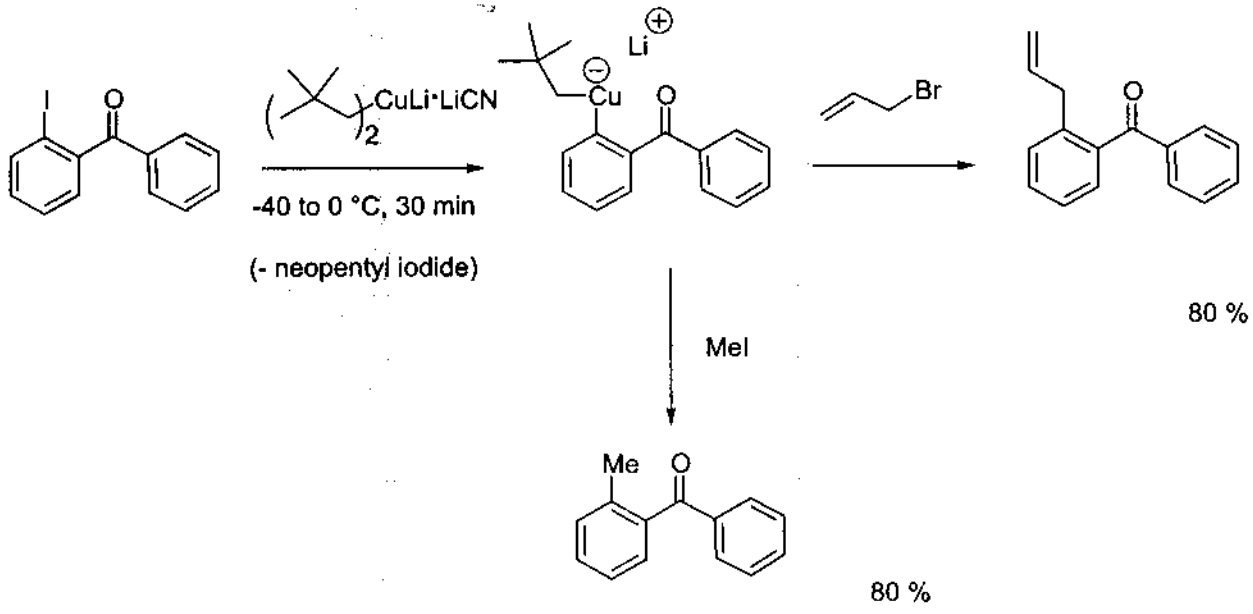
C. PIAZZA

The Bromine- Copper Exchange for the Synthesis of Functionalized Organocoppers



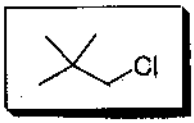
76 %

The Halogen- Copper Exchange for the Synthesis of Functionalized Organocoppers



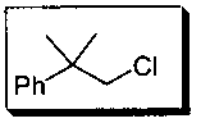
C. PIAZZA

Convenient preparation of functionalized cuprates via Dineophyl Lithium Cuprate



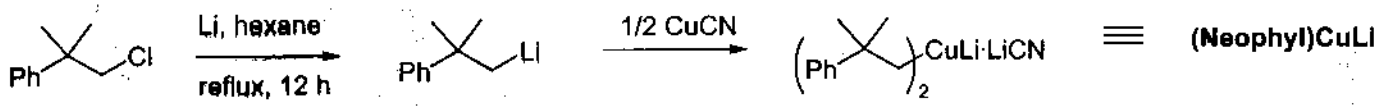
1 mol : 830 Euros

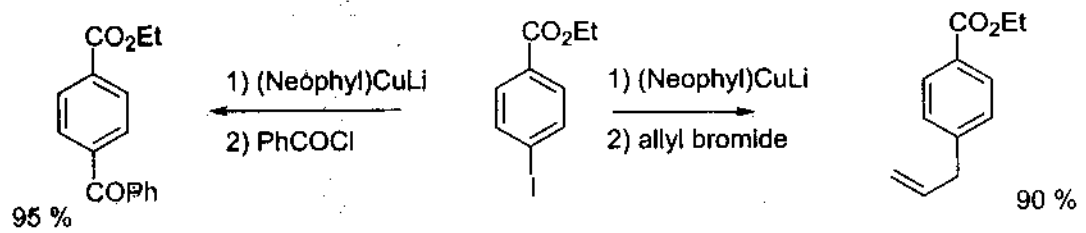
Neopentyl chloride



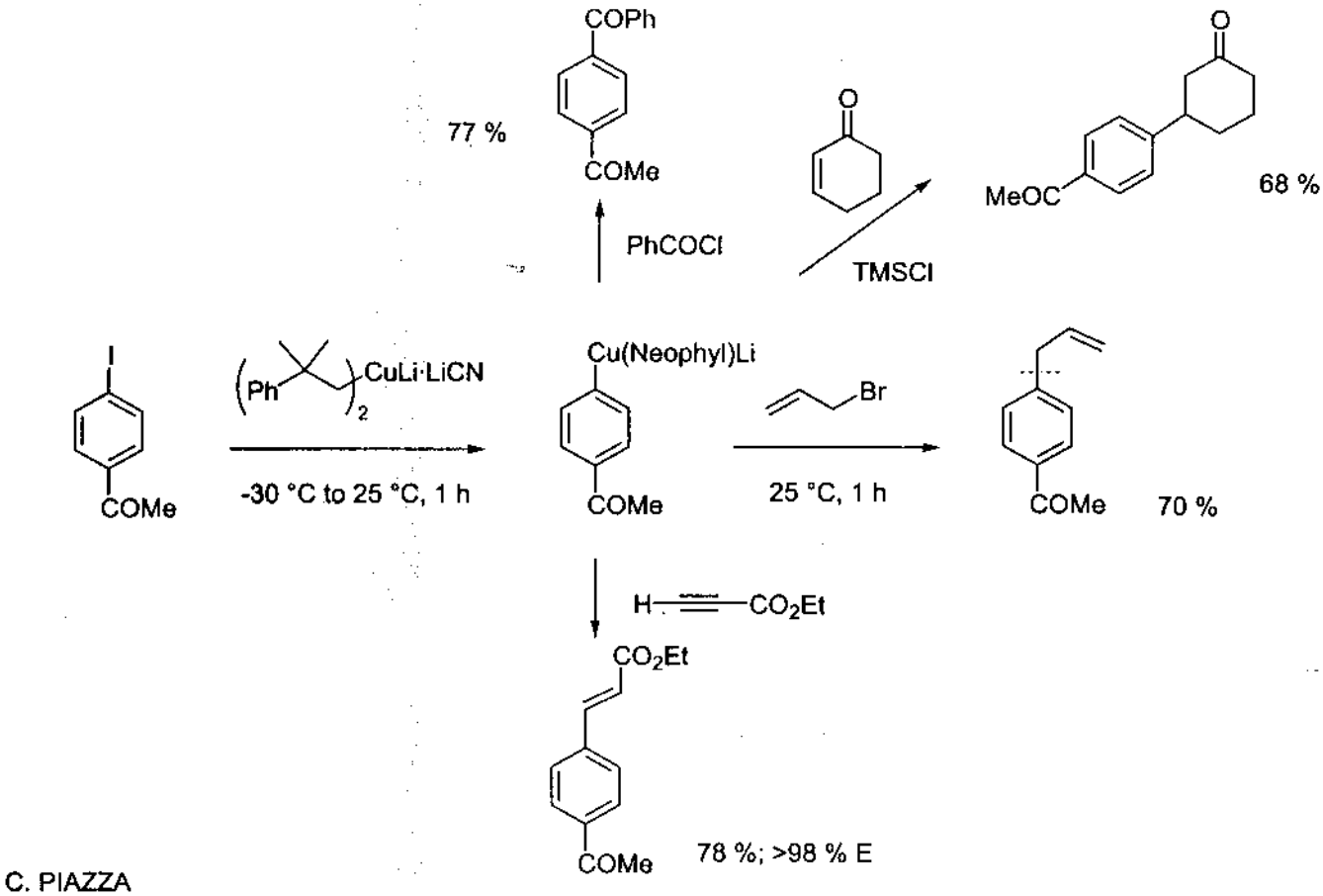
1 mol : 11 Euros

Neophyl chloride

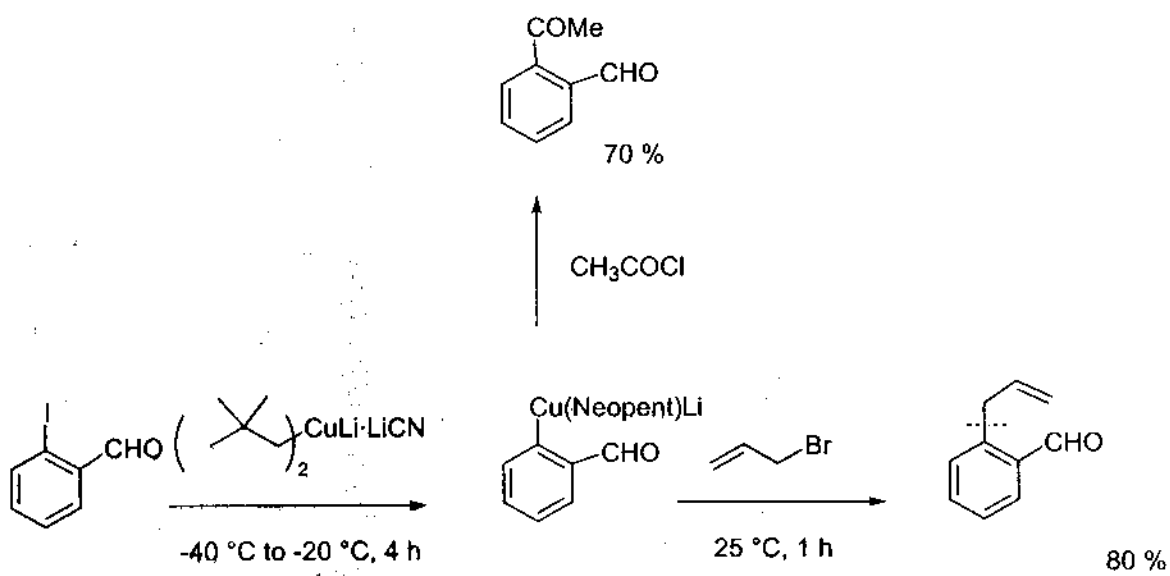




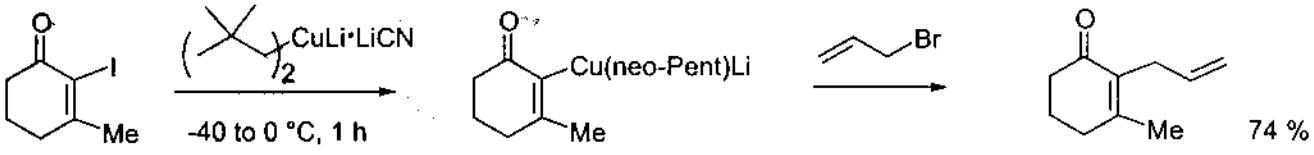
C. PIAZZA, I. CALAZA

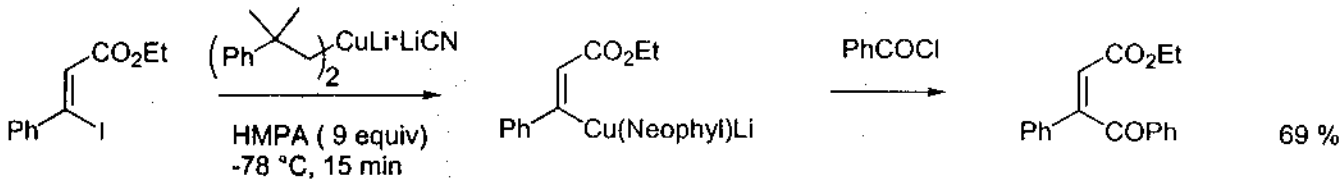

77 %
COPh
COMe
PhCOCl
TMSCl
MeOC
68 %
CuLi·LiCN
-30 °C to 25 °C, 1 h
Cu(Neophyl)Li
Br
25 °C, 1 h
COMe
70 %
H
CO2Et
78 %; >98 % E

C. PIAZZA


COMe
CHO
70 %
CH3COCl
CuLi·LiCN
-40 °C to -20 °C, 4 h
Cu(Neopent)Li
Br
25 °C, 1 h
80 %

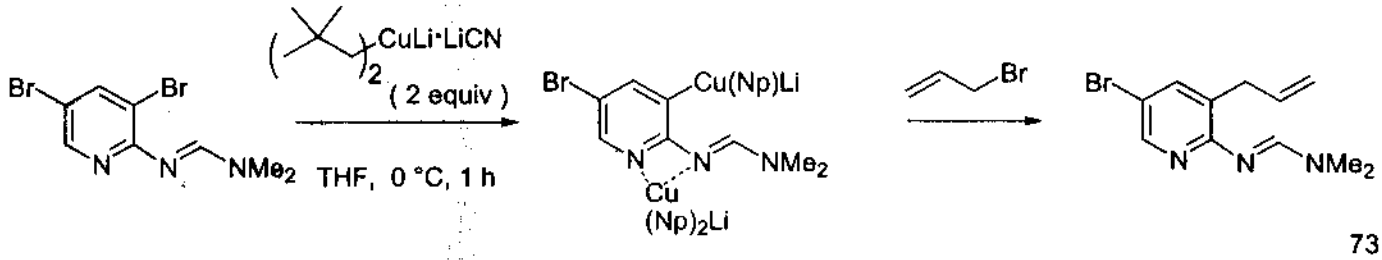
Chemoselective preparation of functionalized cuprates

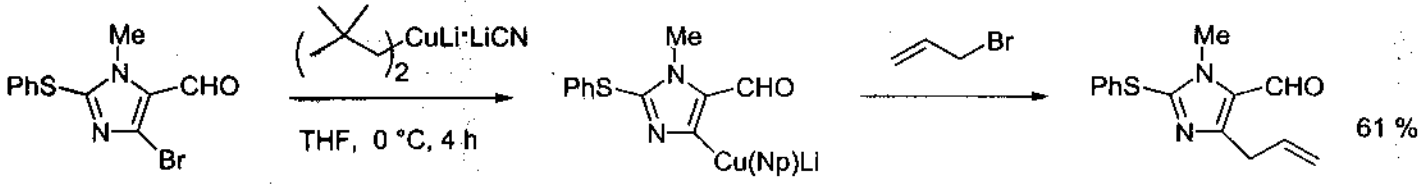


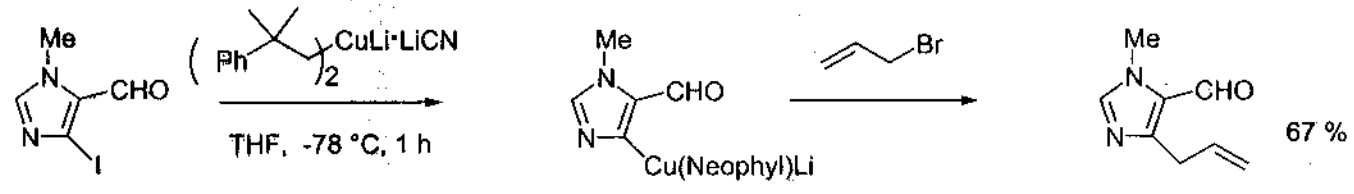


C. PIAZZA

Chemoselective preparation of functionalized cuprates

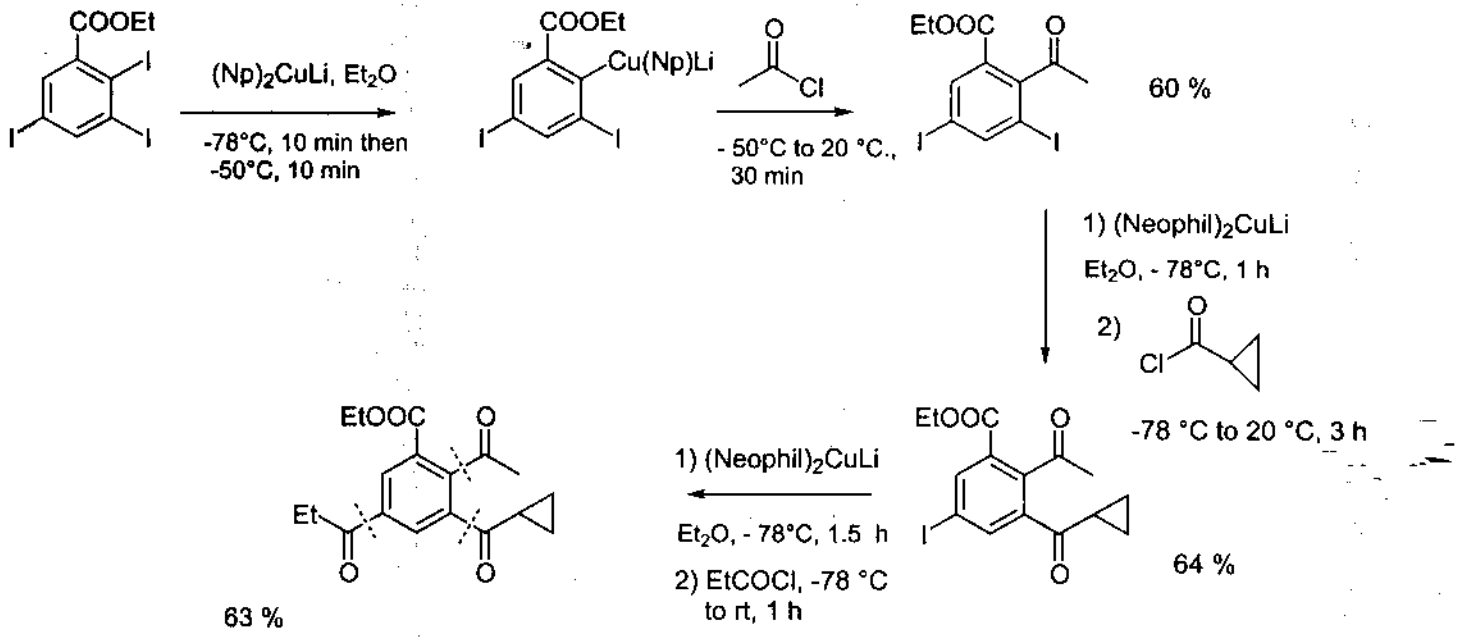






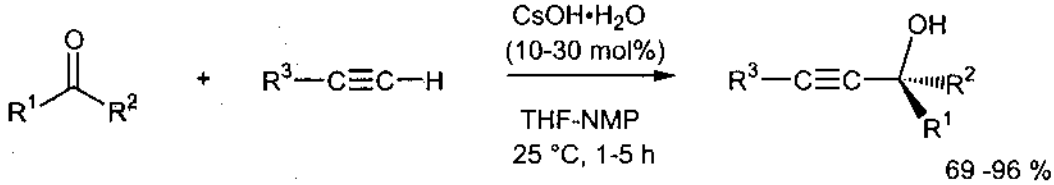
C. PIAZZA

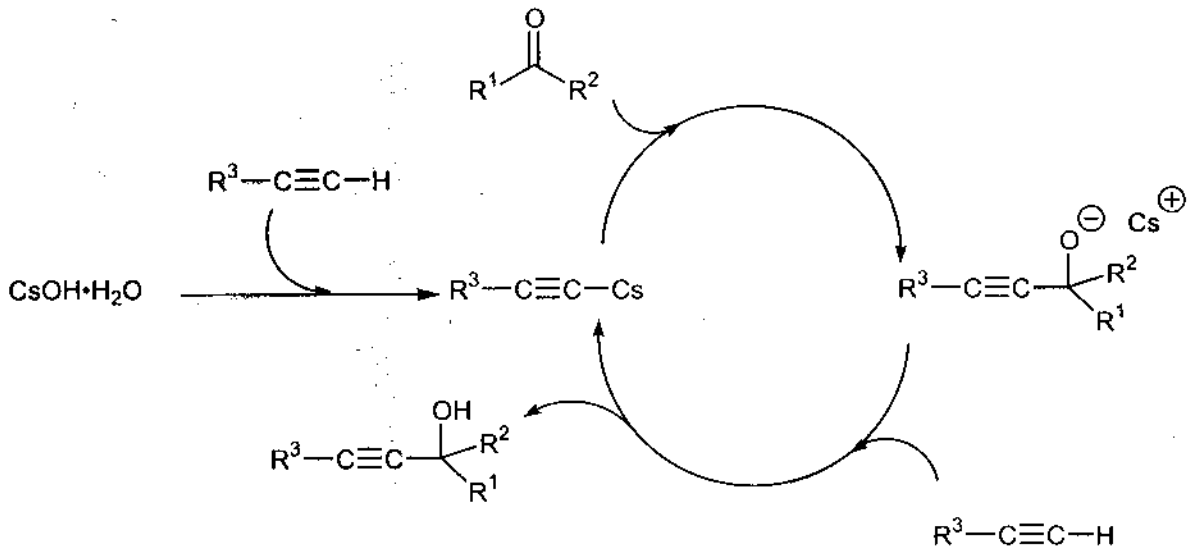
Selective I/Cu-Exchanges of Polyiodo Aromatics



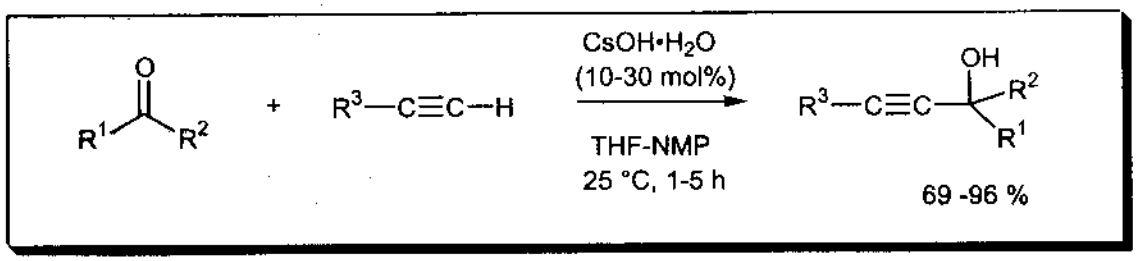
T. ROTTER

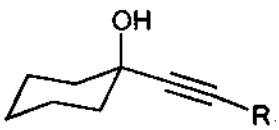
Cesium Hydroxide: A New Catalytic Base



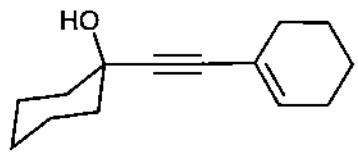


D. Tzalis, P. Knochel *Angew. Chem. Int. Ed.* **1999**, *38*, 1463

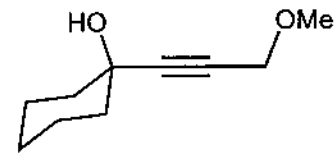




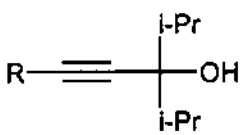
R = Ph : 88 %
R = Bu : 82 %



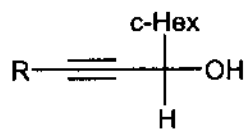
96 %



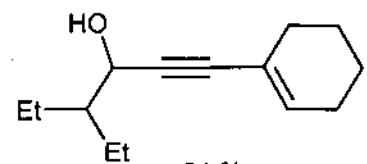
91 %



R = Ph : 91 %
R = Bu : 59 %

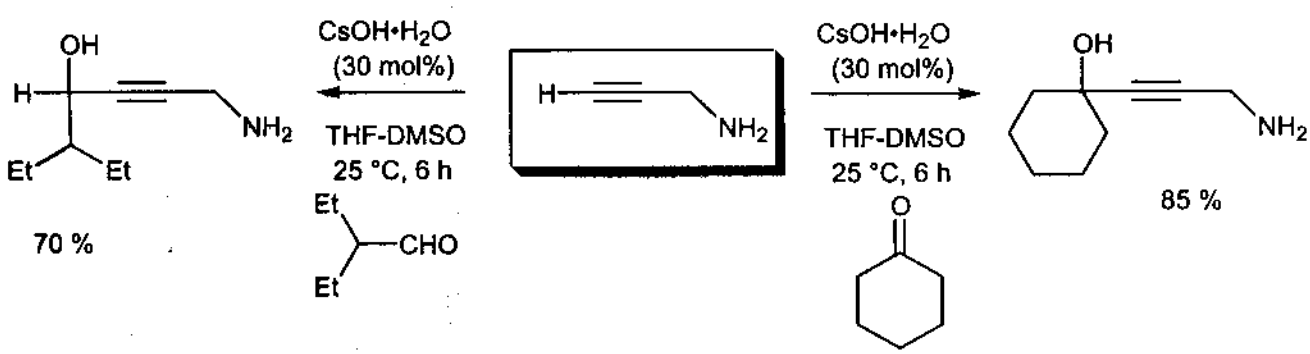


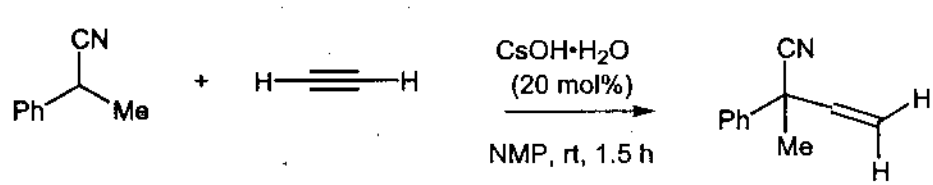
R = Ph : 90 %
R = Bu : 91 %



91 %

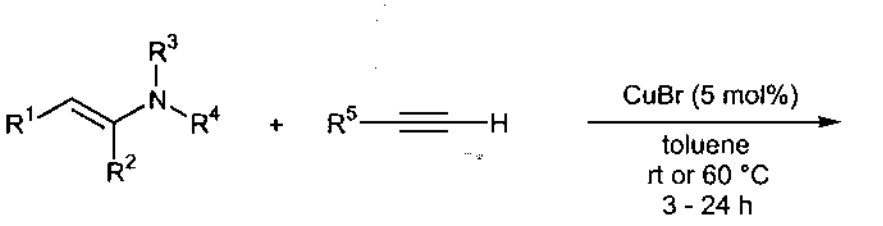
D. TZALIS, *Angew. Chem. Int. Ed.* **1999**, *38*, 1463

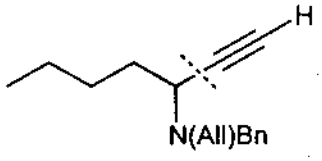




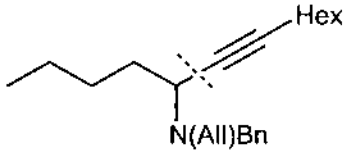
80 %

Synthesis of Propargylamines

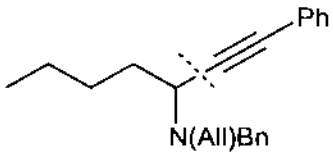




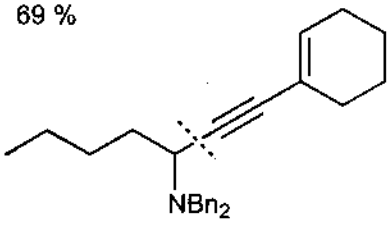
69 %



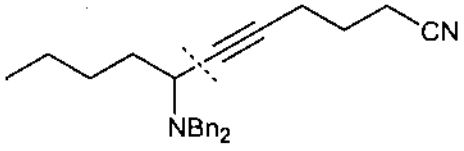
75 %



98 %



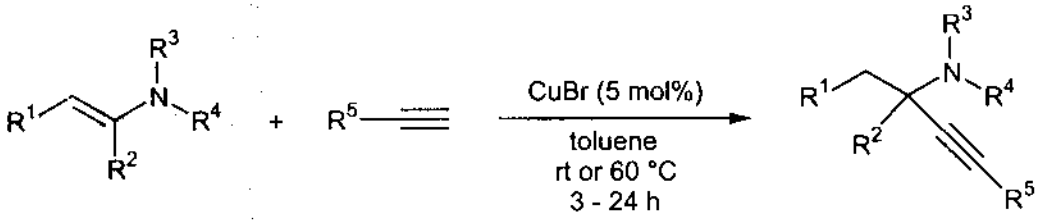
77 %

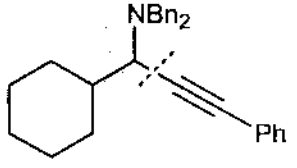


82 %

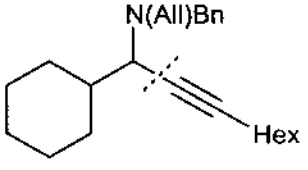
C. Koradin

Synthesis of Propargylamines

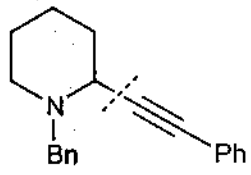




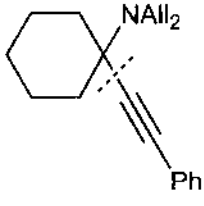
94 %



80 %



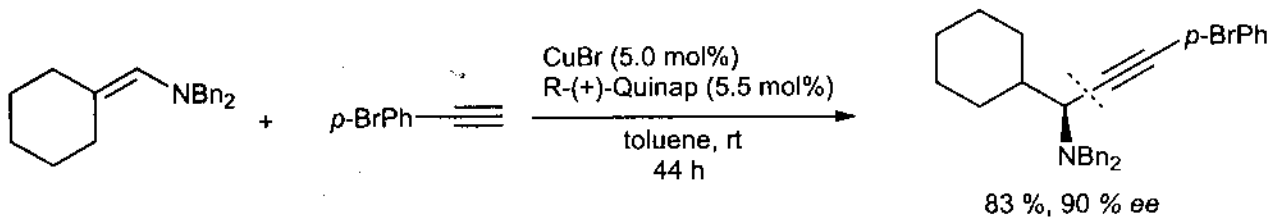
86 %



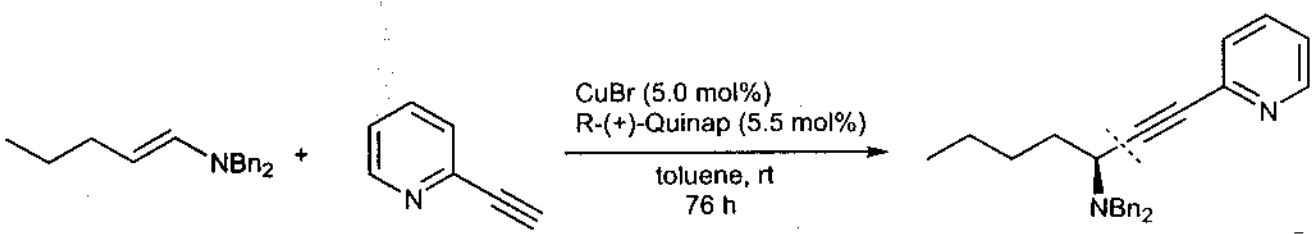
75 %

C. Koradin

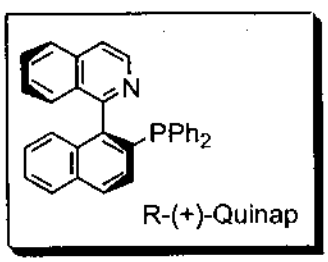
Enantioselective Synthesis of Propargylamines



83 %, 90 % *ee*

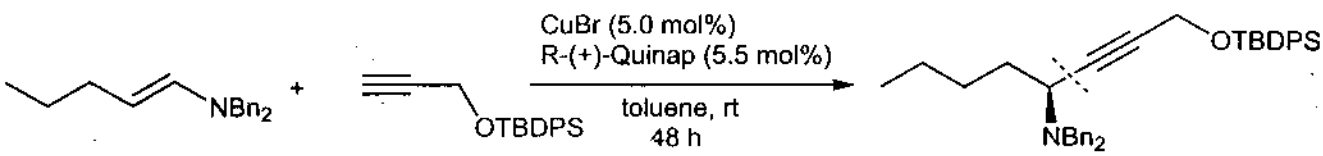


73 %, 70 % *ee*

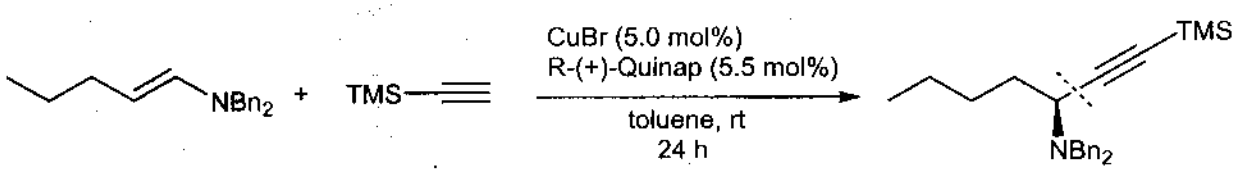


C. Koradin

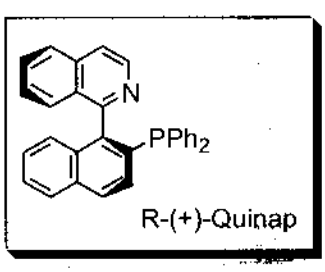
Enantioselective Synthesis of Propargylamines



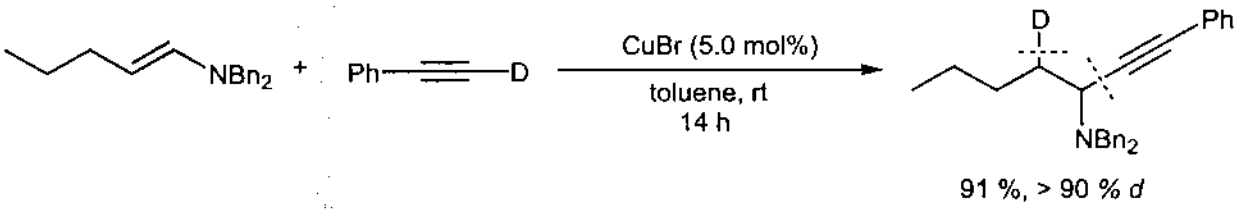
85 %, 72 % *ee*



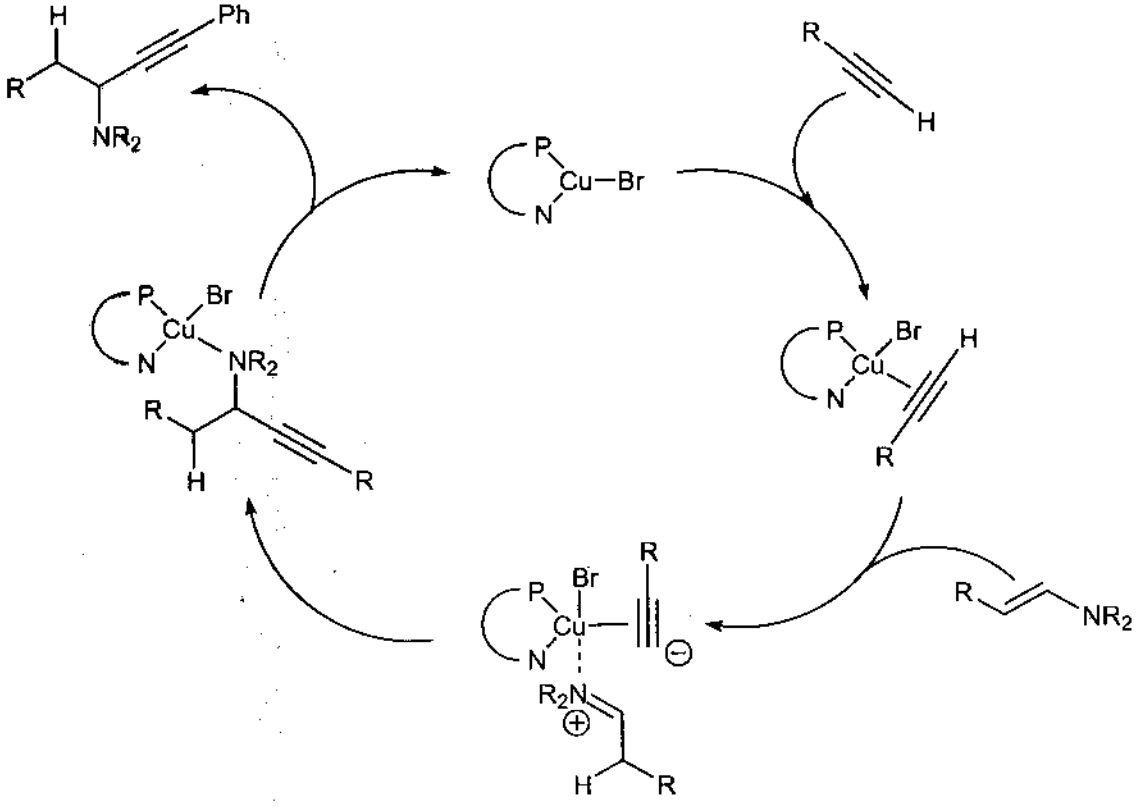
70 %, 86 % *ee*



C. Koradin



Proposed Mechanism



Magnesium-Chemistry

Wolfgang DOHLE
Florian KNEISEL
Ioannis SAPOUNTZIS
Viet Anh VU

Fluorous-Biphasic Catalysis

Dr. Henri HOUTE
Gianna RAGAGNIN

Zinc-Chemistry

Dr. Isabel CALAZA
Dr. Nicole HARRINGTON-FROST
Eike HUPE
Helena LEUSER

C-H-Activation

Dmitri DENISENKO
Kolja KNAPP

Asymmetric Synthesis

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Frederic LIRON
Chistopher KORADIN
Matthias LOTZ
Katja TAPPE
Andrej GAVRYUSHIN
Ralf KLÖTZING
Nina GOMMERMANN

Copper-Chemistry

Claudia PIAZZA
Thomas ROTTER

Collaborations :

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Prof. Ilan MAREK, TECHNION-Haifa, ISRAEL
Prof. Guy QUEGUINER, IRCOF, Universite de ROUEN, FRANCE
Prof. Alfredo RICCI, Universita di BOLOGNA, ITALIA

DFG (Leibniz-program), Fonds der Chemischen Industrie, Alexander von Humboldt-Foundation,

AVENTIS, ZENECA, BASF - BAYER - DEGUSSA-HÜLS - PPG-SIPSY - CHEMETALL