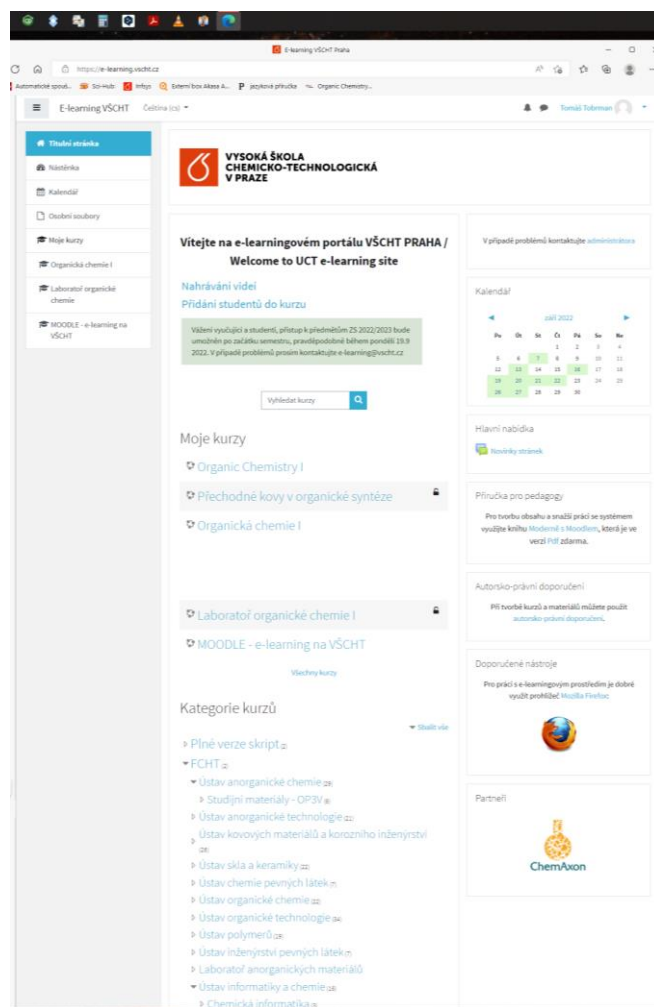
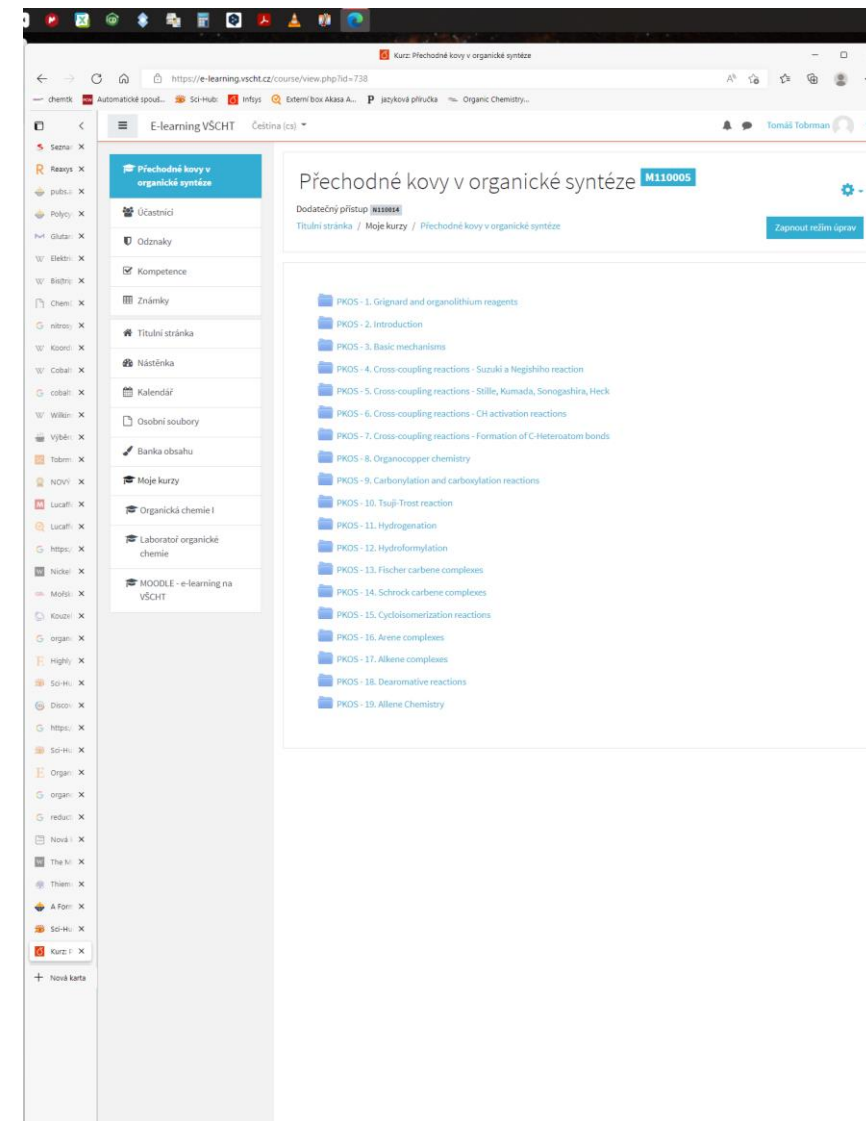


- <https://e-learning.vscht.cz/course/view.php?id=738>
- Požadavky – 2 testy (Minimálně 60 % z každého testu), ústní zkouška



The screenshot shows the homepage of the VŠCHT Prague e-learning portal. The header includes the VŠCHT logo and the text "VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE". The main content area is titled "Vítejte na e-learningovém portálu VŠCHT PRAHA / Welcome to UCT e-learning site". It features a navigation menu on the left with options like "Hlavní stránka", "Kalendář", "Osobní soubory", "Moje kurzy", "Organická chemie I", "Laboratorní organická chemie", and "MOODLE - e-learning na VŠCHT". The main content includes a "Nahrávání videí" section, a "Moje kurzy" section listing "Organic Chemistry I" and "Přechodné kovy v organické syntéze", and a "Kategorie kurzů" section listing various courses and departments.



The screenshot shows the course page for "Přechodné kovy v organické syntéze" (Transition Metals in Organic Synthesis) on the VŠCHT e-learning portal. The page title is "Přechodné kovy v organické syntéze M110005". The left sidebar contains a navigation menu with options like "Účastníci", "Oznamenání", "Kompetence", "Známky", "Titulní stránka", "Nástěnka", "Kalendář", "Osobní soubory", "Banka obsahu", "Moje kurzy", "Organická chemie I", "Laboratorní organická chemie", and "MOODLE - e-learning na VŠCHT". The main content area displays a list of course topics, including "PKOS - 1. Grignard and organolithium reagents", "PKOS - 2. Introduction", "PKOS - 3. Basic mechanisms", "PKOS - 4. Cross-coupling reactions - Suzuki a Negishiho reaction", "PKOS - 5. Cross-coupling reactions - Stille, Kumada, Sonogashira, Heck", "PKOS - 6. Cross-coupling reactions - C-H activation reactions", "PKOS - 7. Cross-coupling reactions - Formation of C-Heteroatom bonds", "PKOS - 8. Organocopper chemistry", "PKOS - 9. Carbonylation and carboxylation reactions", "PKOS - 10. Tsuji-Trost reaction", "PKOS - 11. Hydrogenation", "PKOS - 12. Hydroformylation", "PKOS - 13. Fischer carbene complexes", "PKOS - 14. Schrock carbene complexes", "PKOS - 15. Cycloisomerization reactions", "PKOS - 16. Arene complexes", "PKOS - 17. Alkene complexes", "PKOS - 18. Dearomative reactions", and "PKOS - 19. Alkene Chemistry".

## Periodic table of the elements

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Lanthanoidy	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Aktinoidy	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



= Alkalické kovy



= Kovy



= Polokovy



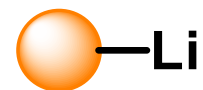
= Kovy alkalických zemin



= Přechnodné kovy

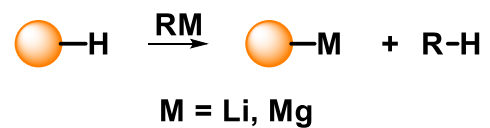


= Nekovy

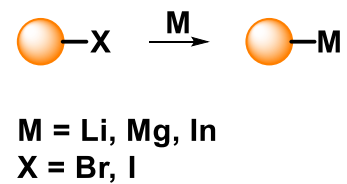


## ➤ General procedures for their synthesis

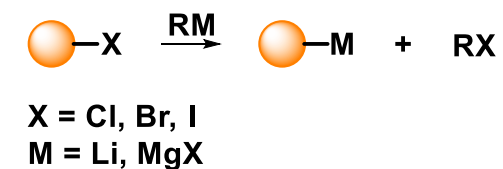
- Acid-base reactions

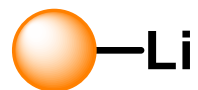


- Reaction with metals



- Halogen–metal exchange reactions



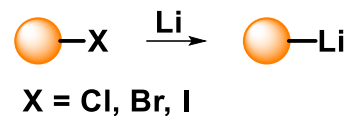


➤ General procedures for the synthesis of organolithium reagents

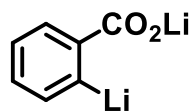
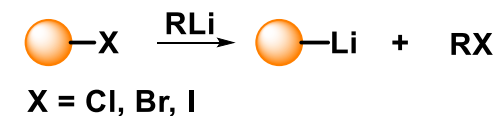
- Acid-base reactions



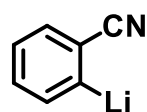
- Reaction with metals



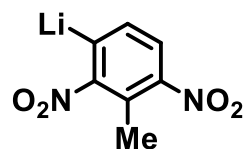
- Halogen–Lithium exchange reactions



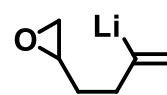
-100 °C



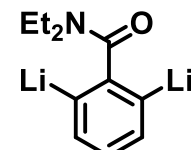
-100 °C



-100 °C

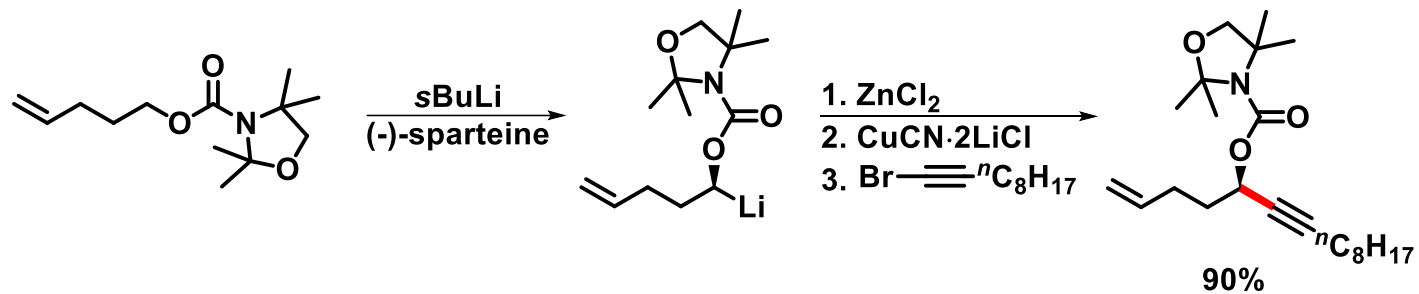


-110 °C

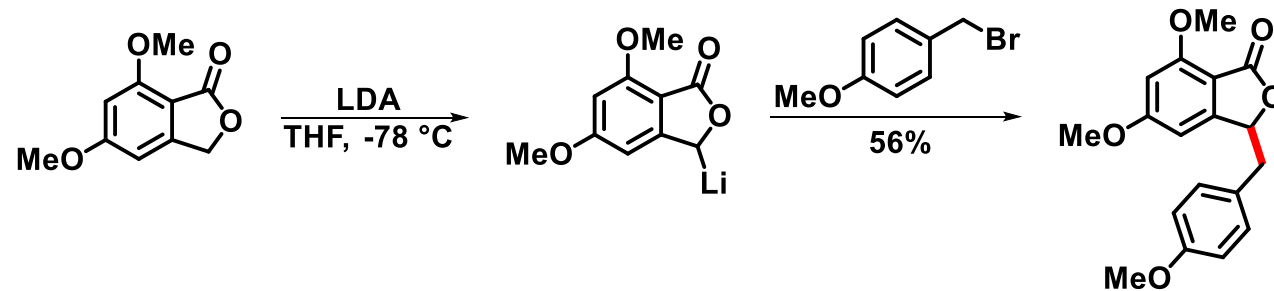


-78 °C

- Acid-base reactions



*Org. Lett.* **2002**, *4*, 119

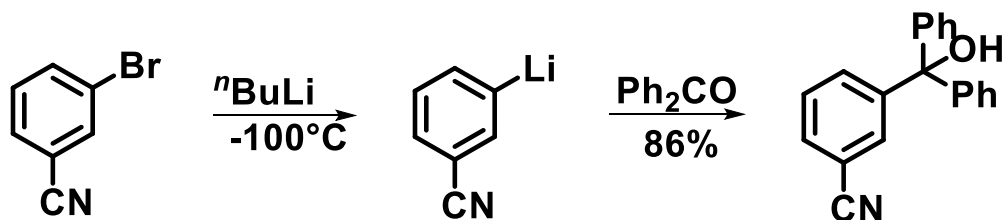


*J. Chem. Soc., Perkin Trans. 1* **2001**, 3017.

- Halogen–metal exchange reactions



X = Cl, Br, I

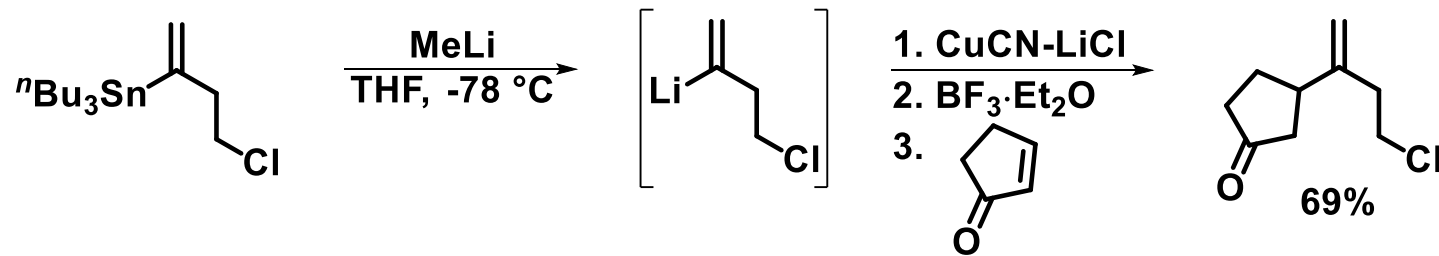


*J. Org. Chem.* 1976, 41, 1187

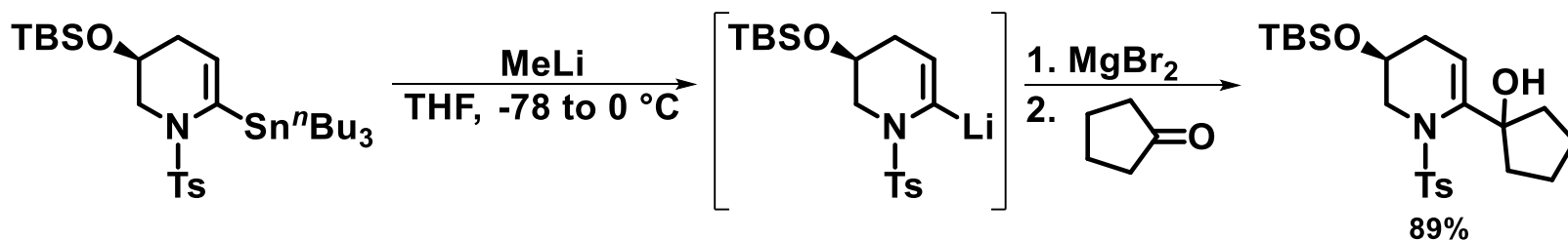
- Metal–metal exchange reactions



X = <sup>n</sup>Bu<sub>3</sub>Sn or <sup>n</sup>Me<sub>3</sub>Sn

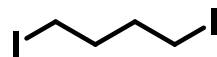
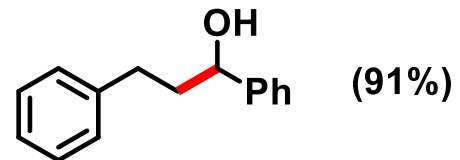
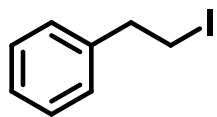
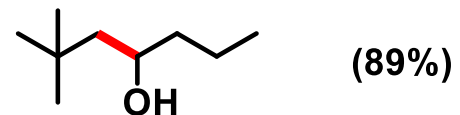
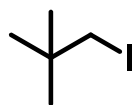
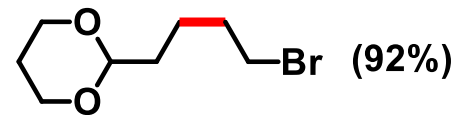
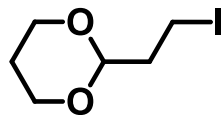
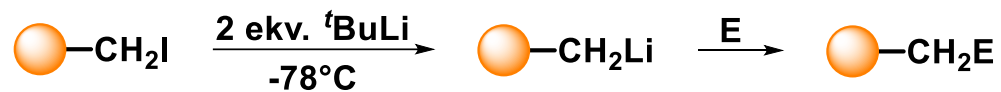


*Synthesis* 2001, 2138



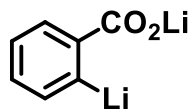
*Org. Lett.* 2003, 5, 4313.

- Halogen–metal exchange reactions

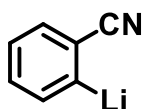


*J. Org. Chem.* **1990**, *55*, 5404; *J. Org. Chem.* **1990**, *55*, 5406

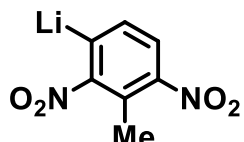
➤ Advanced functionalized organolithium reagents formation in a flow microreactor



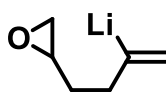
-100 °C



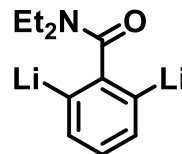
-100 °C



-100 °C



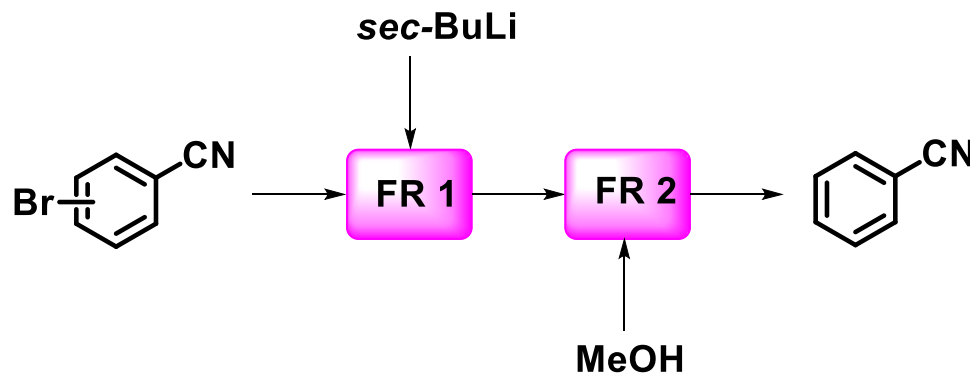
-110 °C



-78 °C



<https://www.mersen.com/products/graphite-specialties/boostecr-silicon-carbide-sic/continuous-flow-reactors-chemical-industry>



*o*-bromobenzonitrile 90%, residence time = 0.01 s (20 °C)

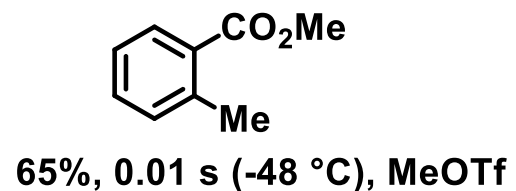
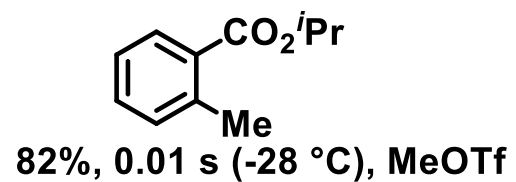
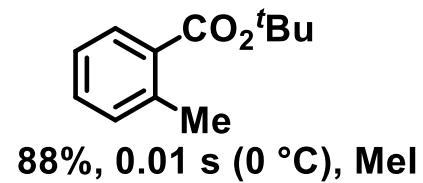
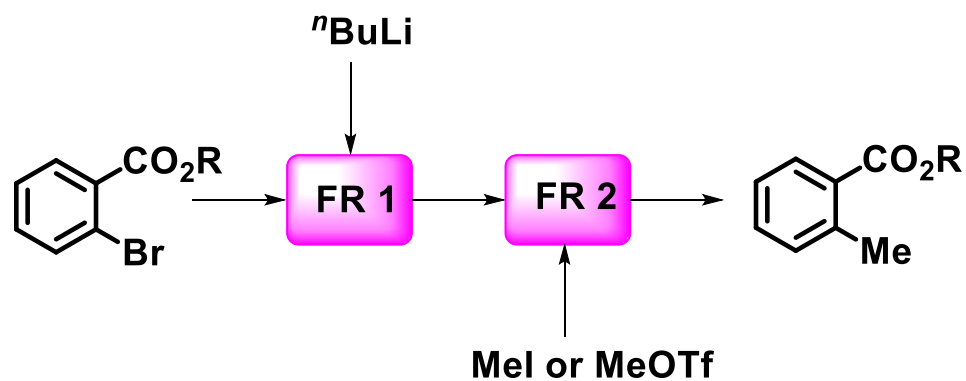
*m*-bromobenzonitrile 82% residence time = 0.01 s (0 °C)

*p*-bromobenzonitrile 88% residence time = 0.01 s (0 °C)

*Org. Biomol. Chem.* 2010, 8, 1212–1217



- Advanced functionalized organolithium reagents formation in a flow microreactor



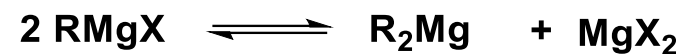
<https://www.mersen.com/products/graphite-specialties/boostecr-silicon-carbide-sic/continuous-flow-reactors-chemical-industry>

*Angew. Chem. Int. Ed.* **2008**, *47*, 7833–7836.

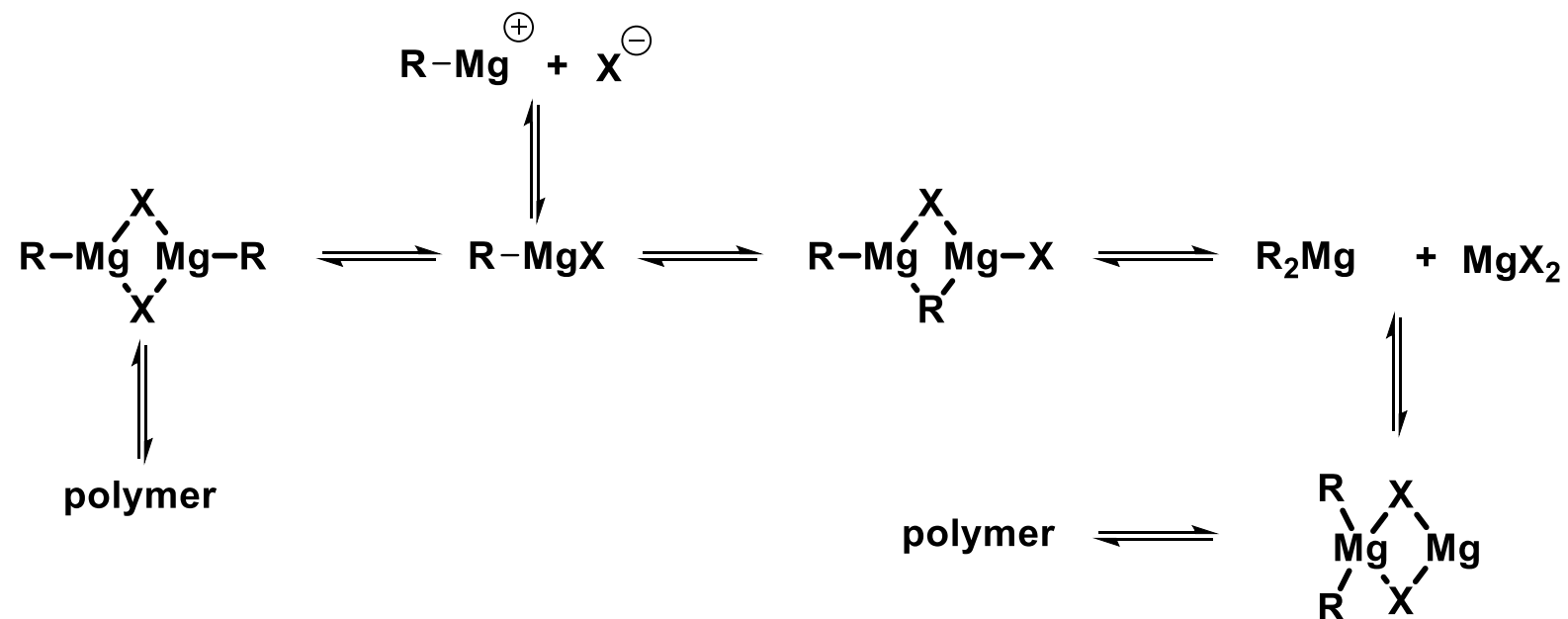
➤ Structure of Grignard reagents in solution



- Basic Schlenk equilibrium

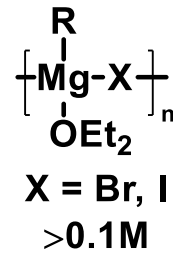
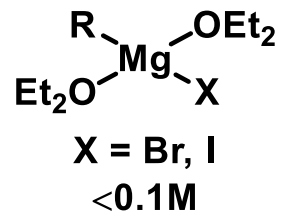
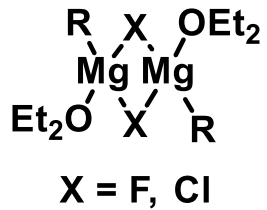


- Extended Schlenk equilibrium

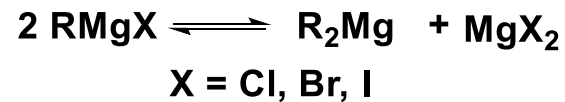
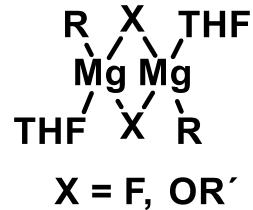


## ➤ Structure of Grignard reagents in solution

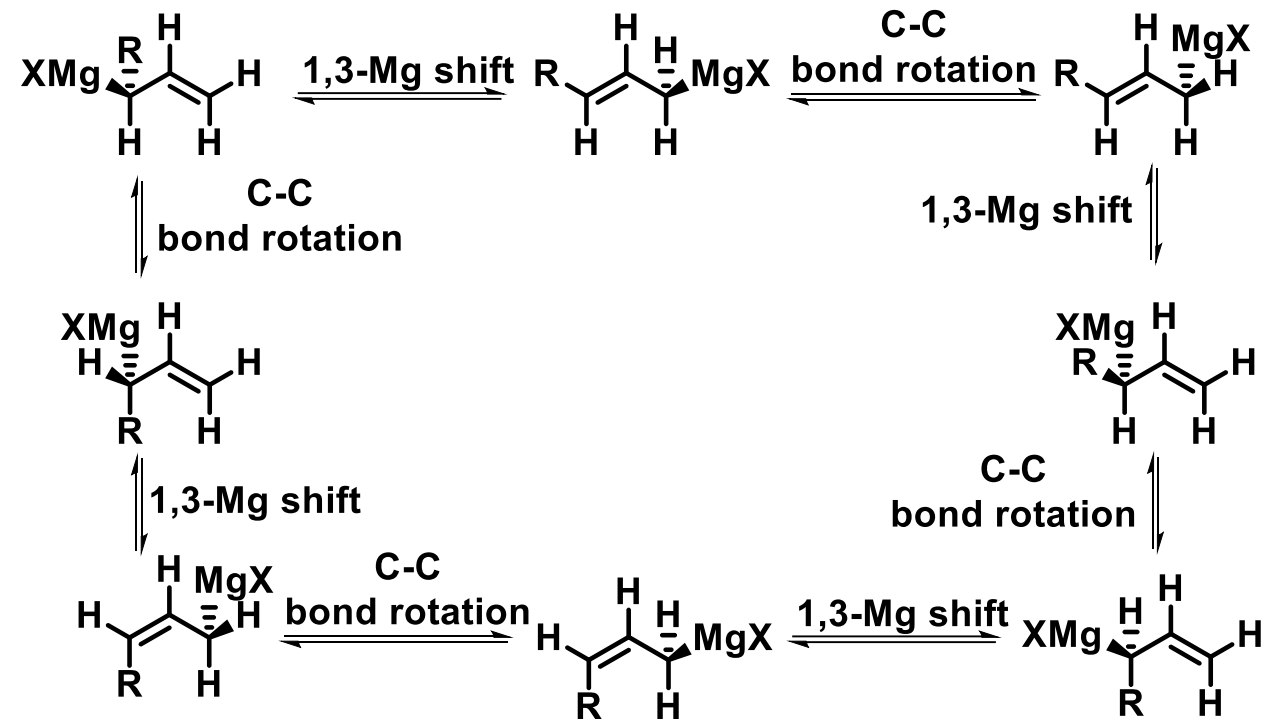
### • Et<sub>2</sub>O



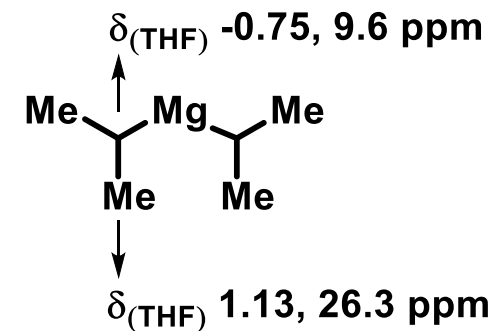
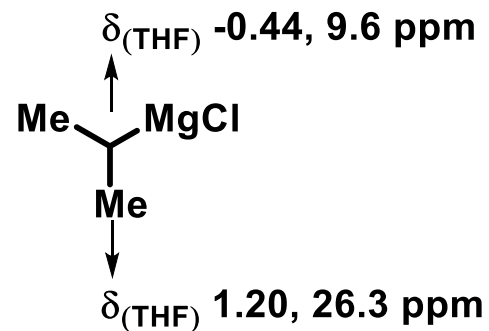
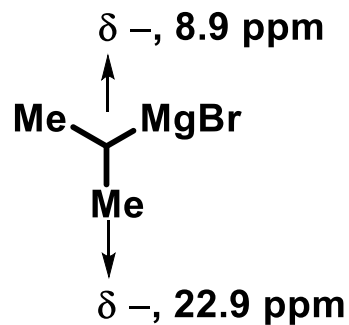
### • THF



### • Dynamic equilibria in allyl Grignard reagents



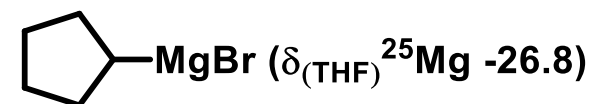
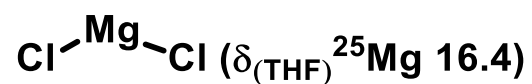
➤  $^1\text{H}$  and  $^{13}\text{C}$  NMR of selected organomagnesium compounds



➤  $^{25}\text{Mg}$  NMR parameters:

spin 5/2

Natural abundance 10.13%

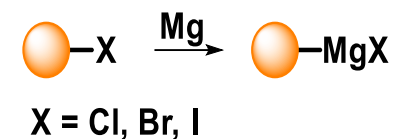


➤ General procedures for the synthesis of organomagnesium reagents

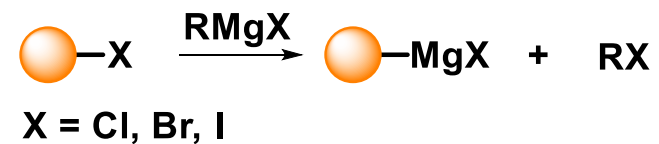
- Acid–base reaction



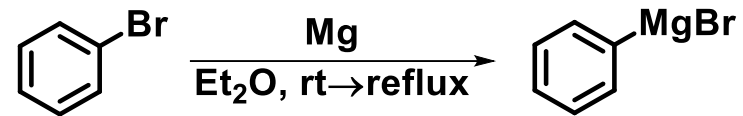
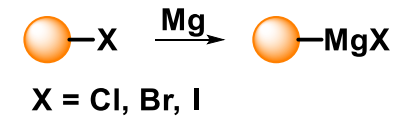
- Reaction with metal



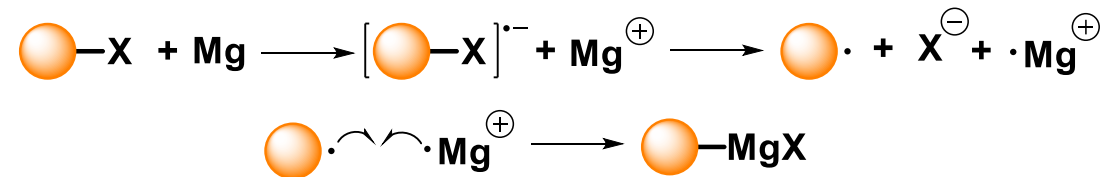
- Halogen–Magnesium exchange reaction



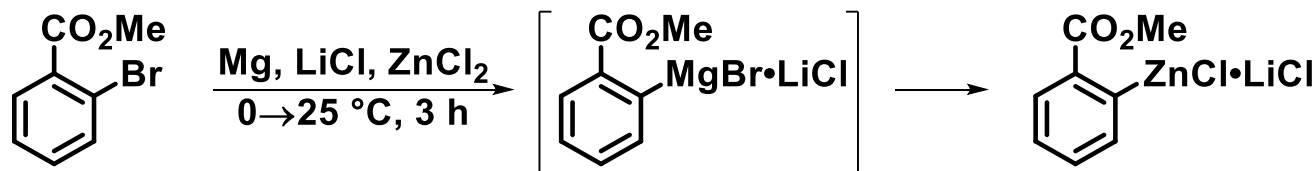
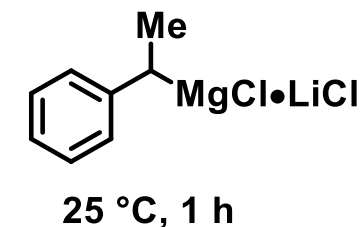
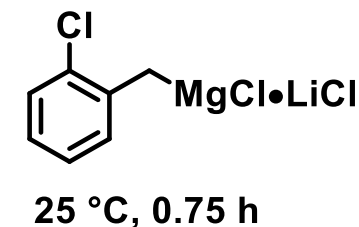
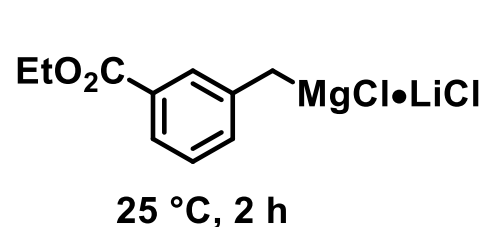
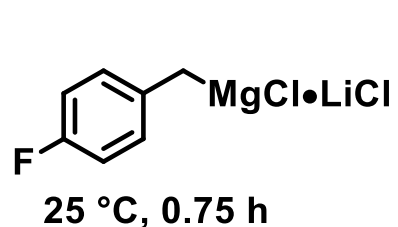
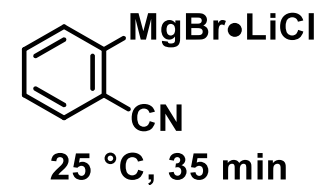
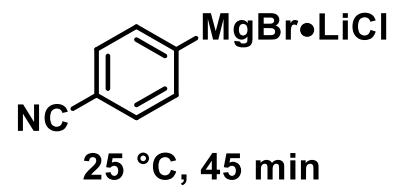
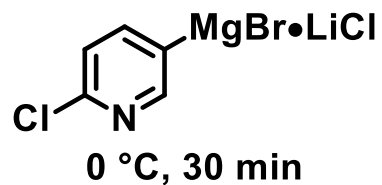
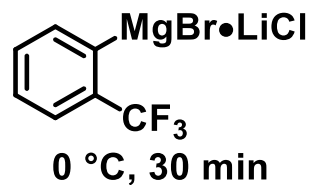
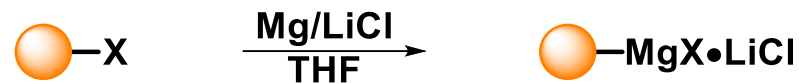
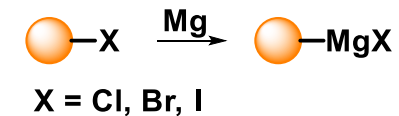
- Formation of Grignard reagents by insertion of Mg into C–halogen bond



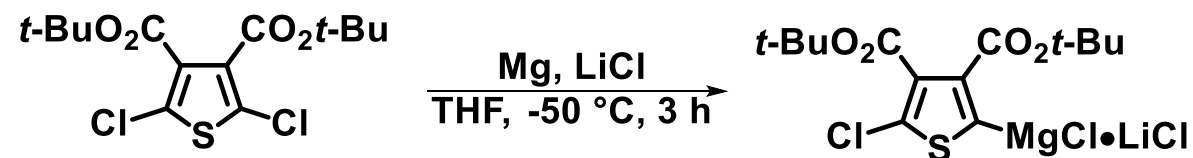
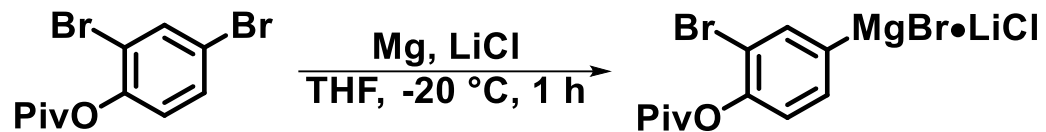
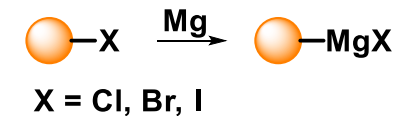
- Mechanism of Mg insertion into C–halogen bond



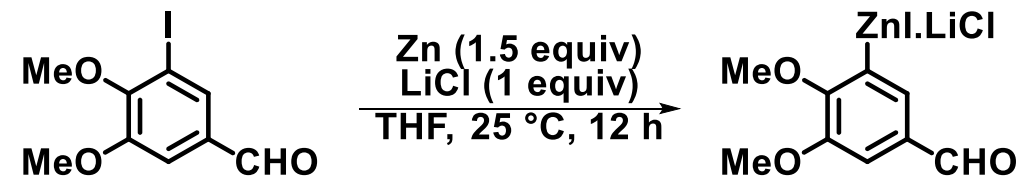
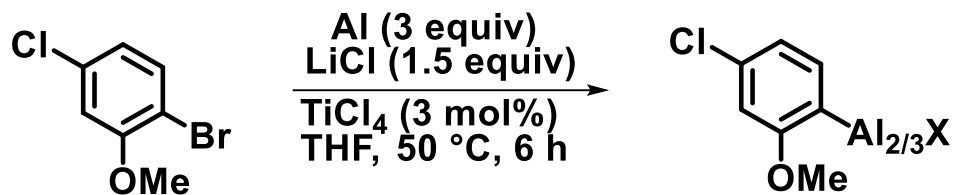
➤ Functionalized Grignard reagents by insertion of Mg into C–halogen bond



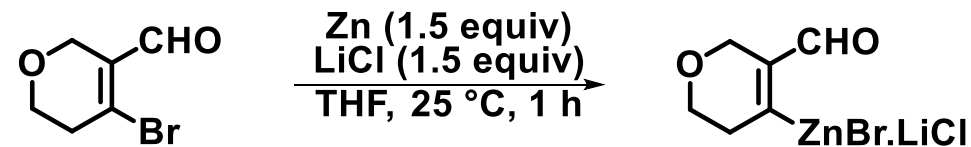
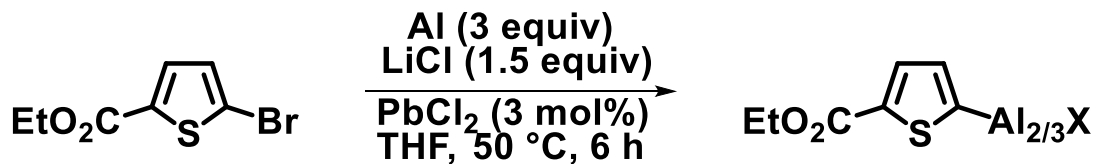
➤ Functionalized Grignard reagents by insertion of Mg into C–halogen bond



*Angew. Chem. Int. Ed.* 2008, 47, 6802



*Angew. Chem. Int. Ed.* 2006, 45, 6040

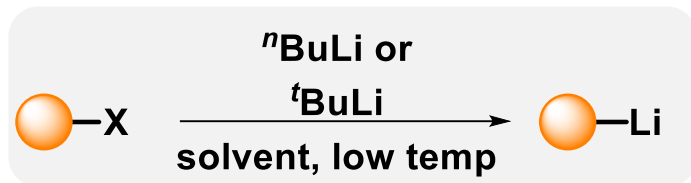


*Nat. Chem.* 2010, 3, 6802

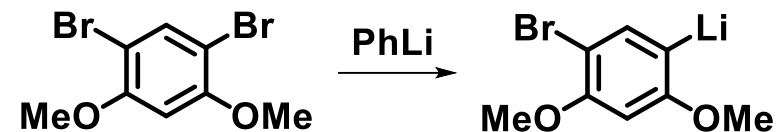
*Angew. Chem. Int. Ed.* 2013, 52, 9495



➤ Formation of Grignard reagents by halogen–Mg exchange reaction



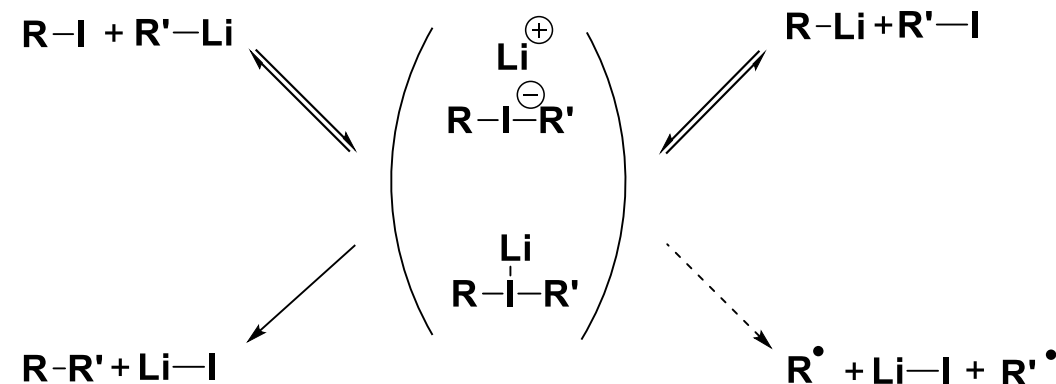
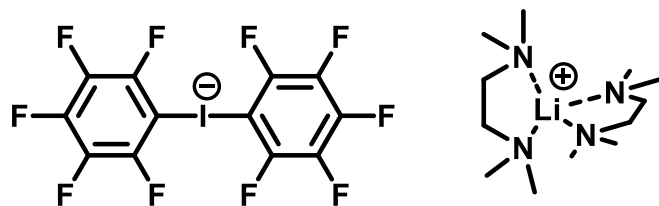
Gilman 1938



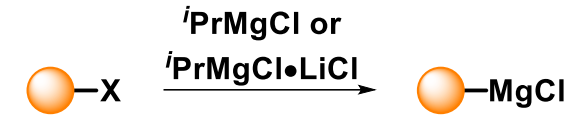
Wittig 1939

• Proposed mechanism

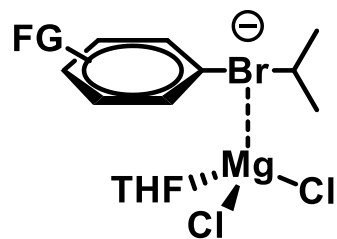
• X-ray structure



➤ Formation of Grignard reagents by halogen–Mg exchange reaction



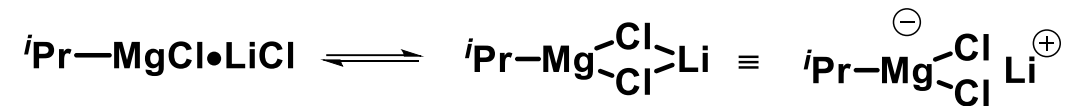
• Proposed transition state



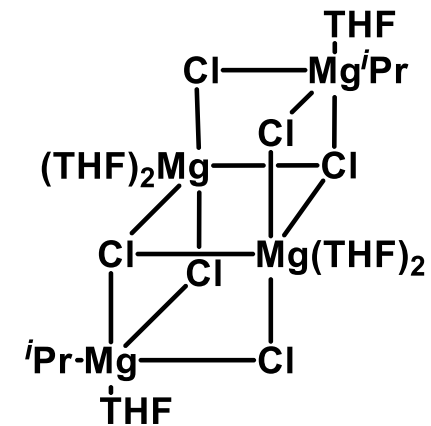
EWG–Ar >>> EDG–Ar

Ar–I > Ar–Br >> Ar–Cl

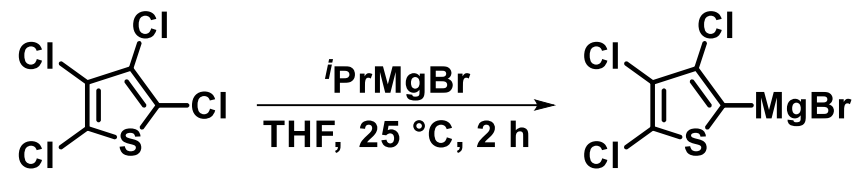
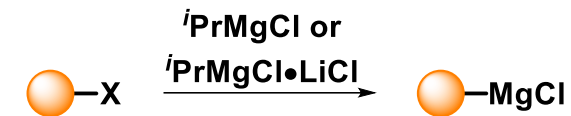
• Proposed structure of *i*-PrMgCl•LiCl in solution



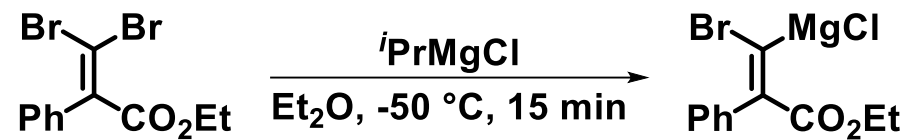
• Crystallographic structure of *i*-PrMgCl•LiCl



➤ *i*-PrMgCl for the halogen–Mg exchange reaction

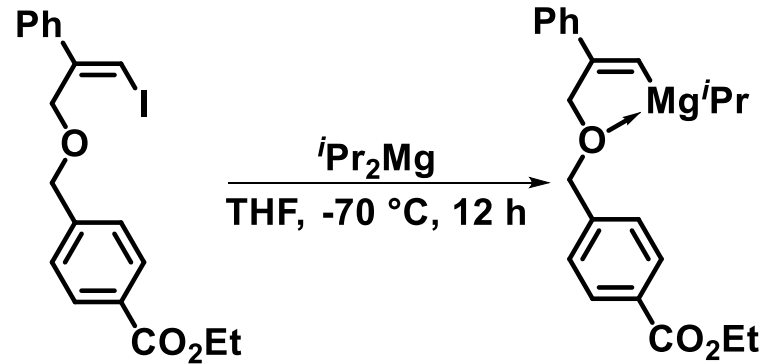
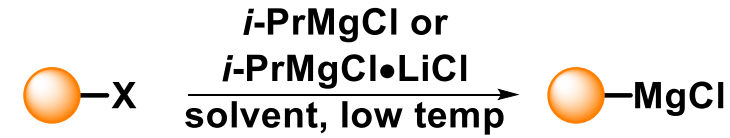


*J. Org. Chem.* **2000**, *65*, 4618

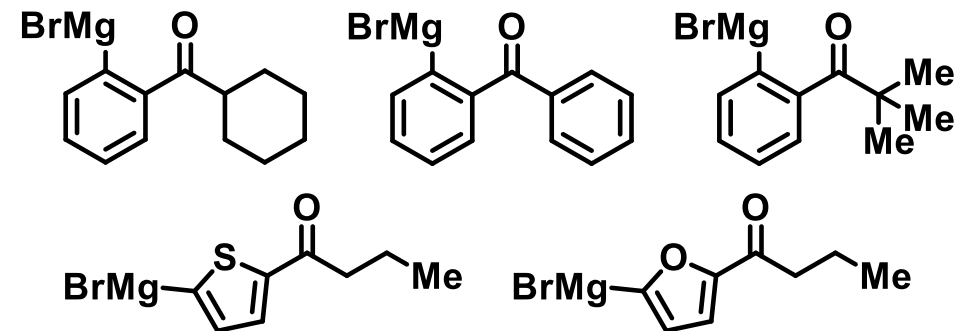
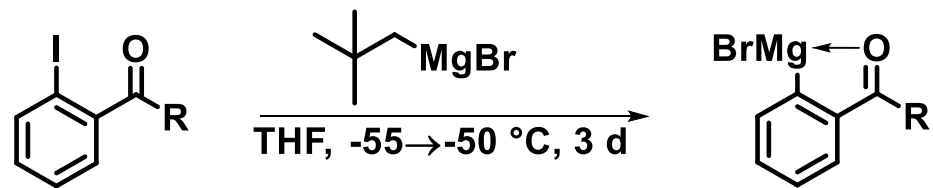


*Synthesis* **2003**, 1797

➤ *i*-PrMgCl for the halogen–Mg exchange reaction

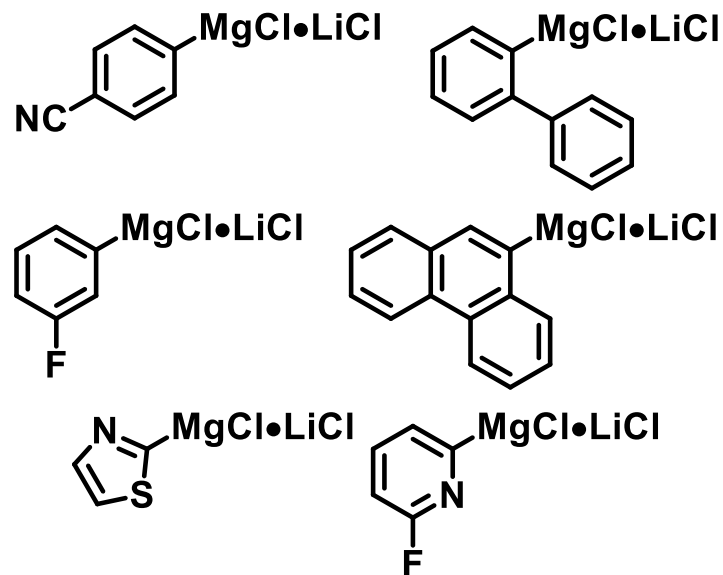
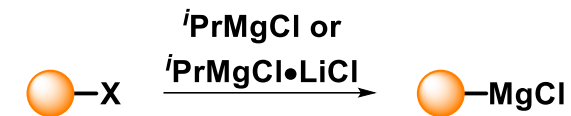


*J. Org. Chem.* 1999, 64, 1080

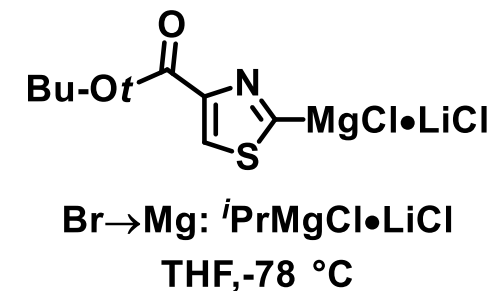
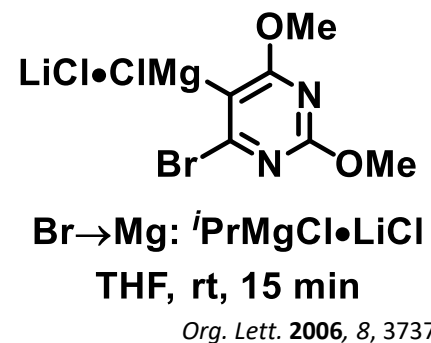


*Synlett* 2002, 11, 1799

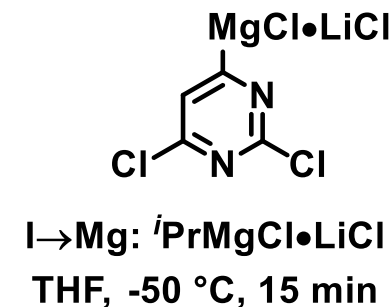
➤  $i\text{PrMgCl}\cdot\text{LiCl}$  for the halogen–Mg exchange reaction



*Angew. Chem., Int. Ed.* **2004**, *43*, 3333

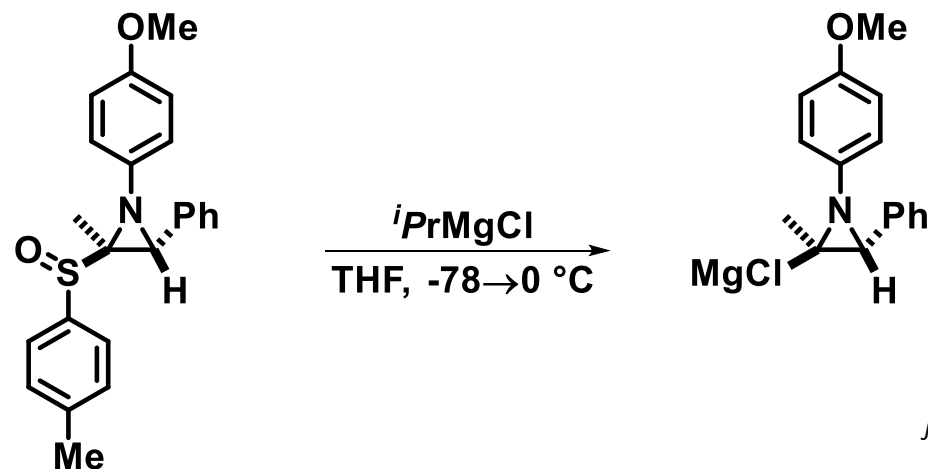
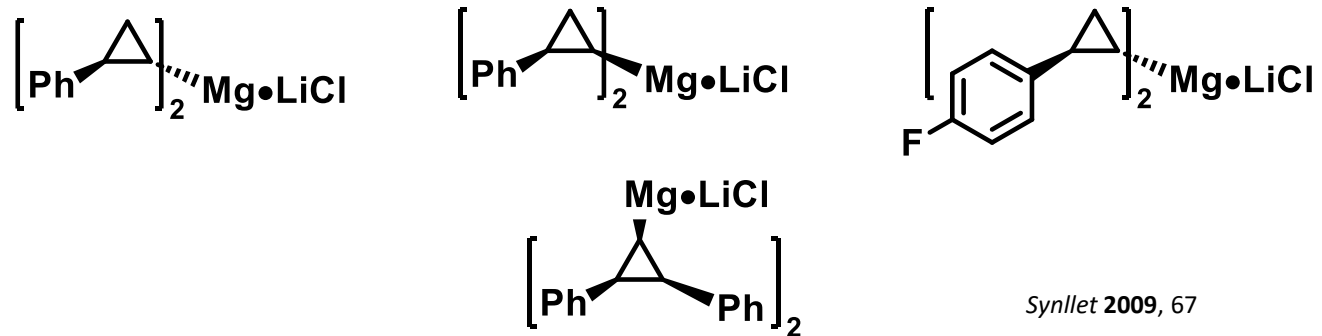
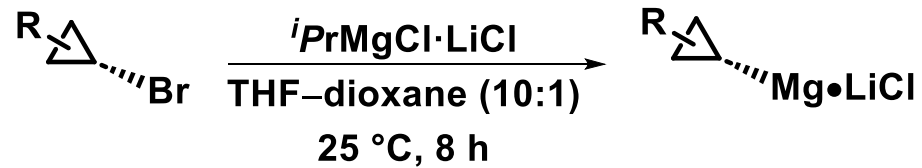
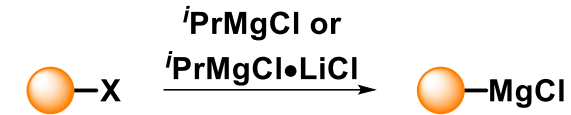


*Tetrahedron: Asymmetry* **2012**, *23*, 474

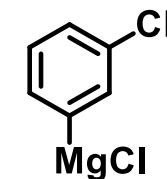
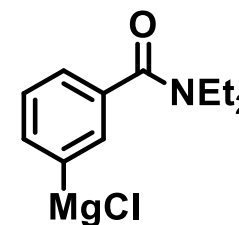
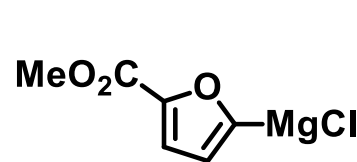
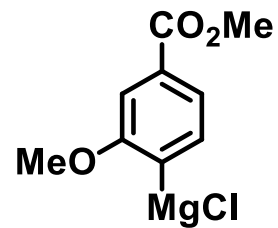
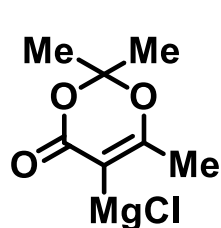
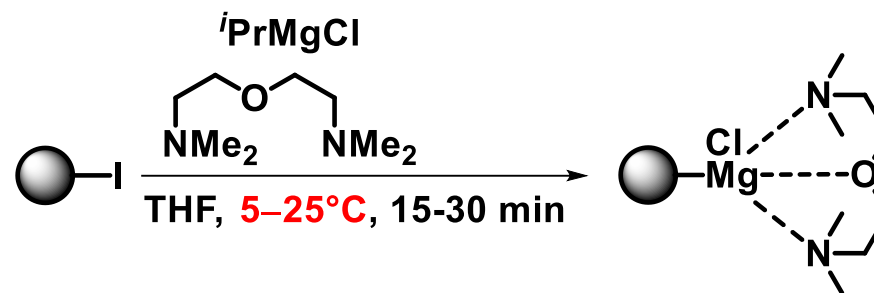
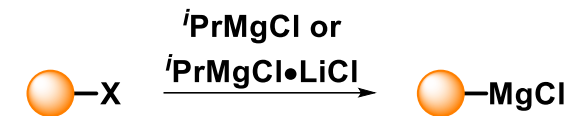


*Tetrahedron Lett.* **2009**, *50*, 5040

➤  $i\text{-PrMgCl}\cdot\text{LiCl}$  for the halogen–Mg exchange reaction

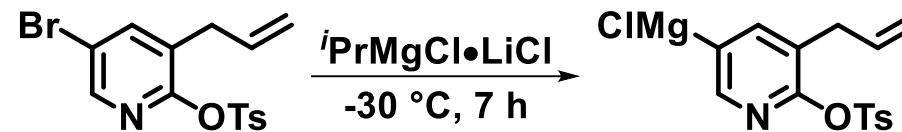
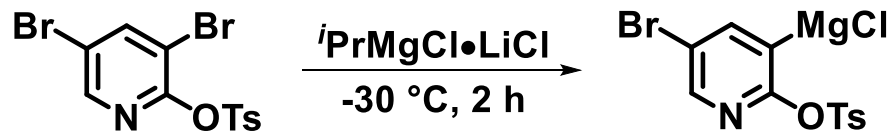
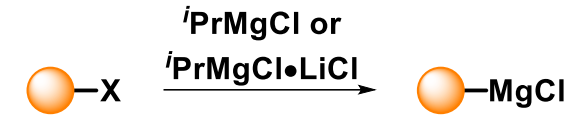


➤ Non-cryogenic conditions for the halogen-magnesium exchange reaction



*Org. Lett.* **2006**, *8*, 305; *Org. Lett.* **2006**, *8*, 3141

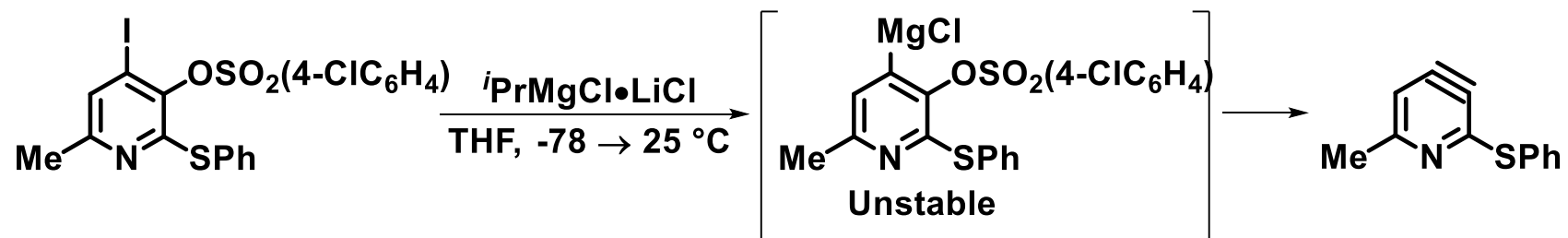
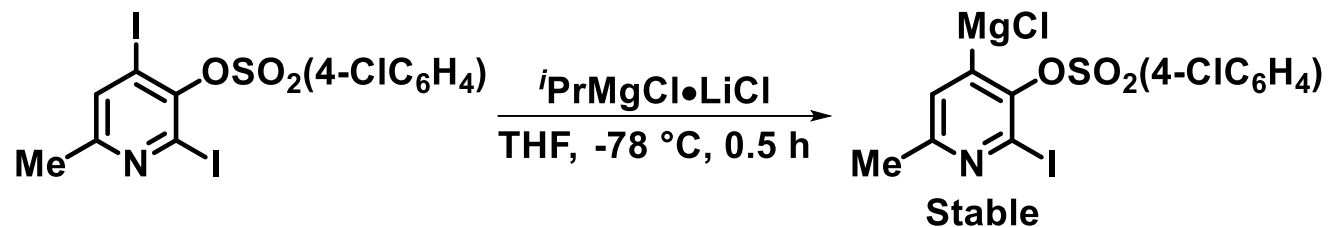
- Halogen–Mg exchange reaction of polyhalogenated heteroaromatics



*Chem. Chemunn. 2006, 726*

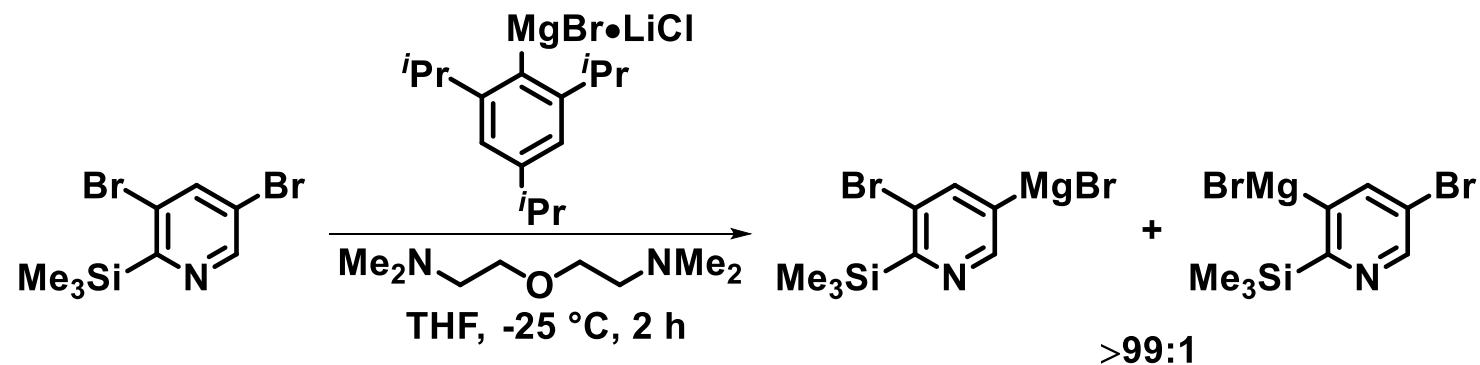
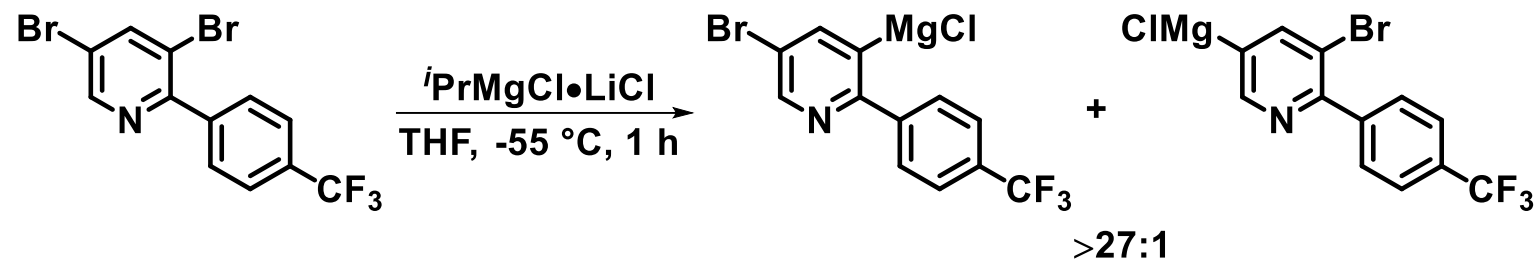


- Halogen–Mg exchange reaction of polyhalogenated heteroaromatics



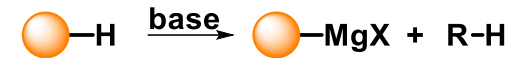
*Tetrahedron* **2007**, 63, 2787

➤ Halogen–Mg exchange reaction of polyhalogenated aromates

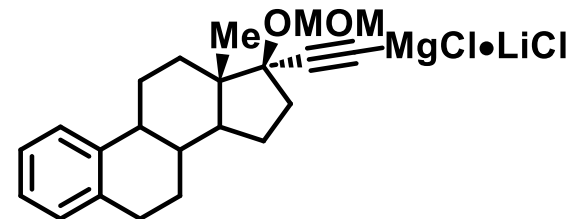
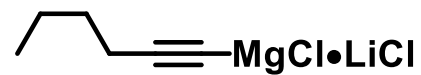
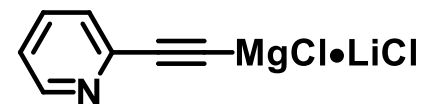
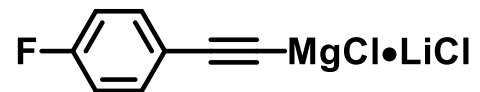
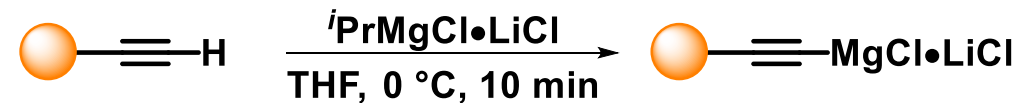


Chem. Eur. J. 2012, 18, 16145

➤ The synthesis of Grignard reagents by an acid–base reaction

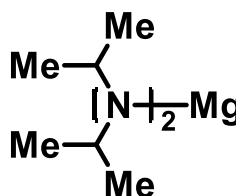
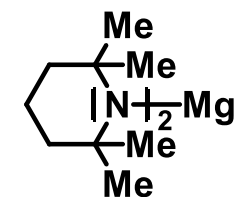
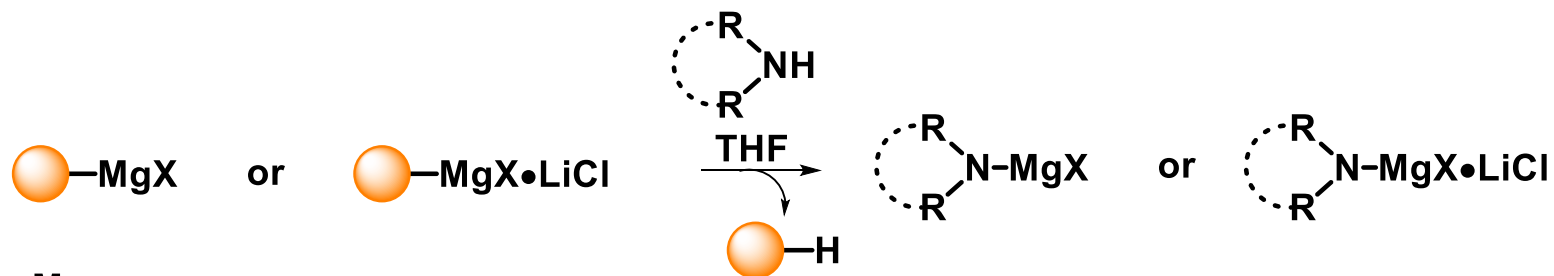
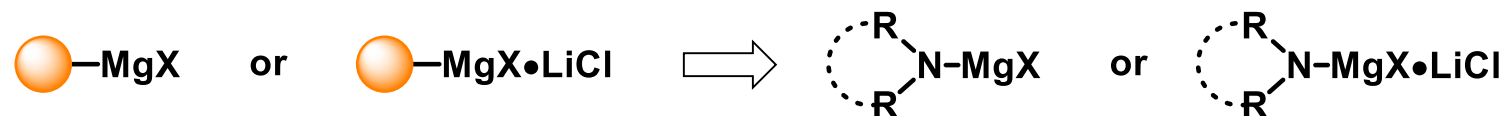


- Acid–base reaction



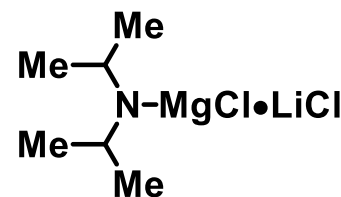
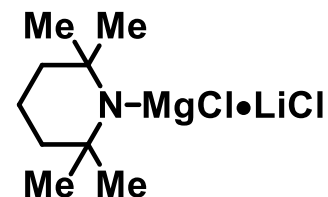
*Synthesis* **2010**, 2085; *Chem. Eur. J.* **2011**, *17*, 2948

➤ The synthesis of Grignard reagents by an acid–base reaction  $\text{R-H} \xrightarrow{\text{base}} \text{R-MgX} + \text{H}_2$

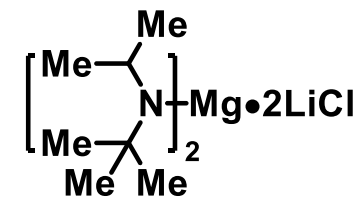
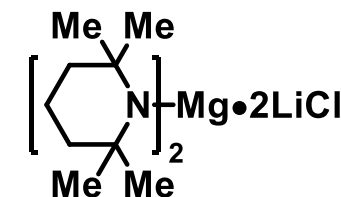


Hauser bases

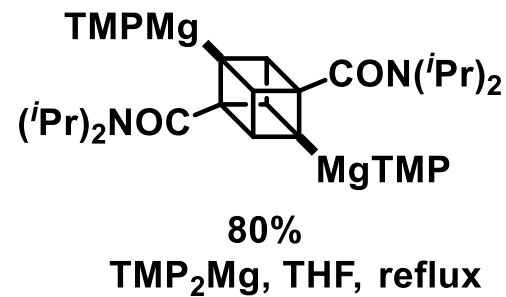
Low solubility in THF



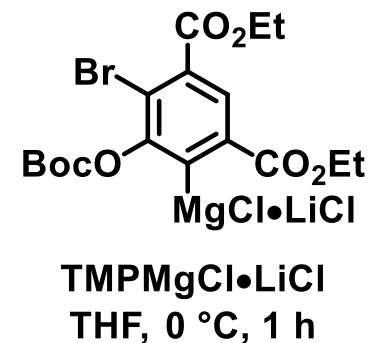
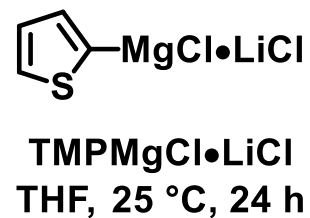
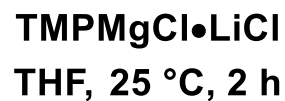
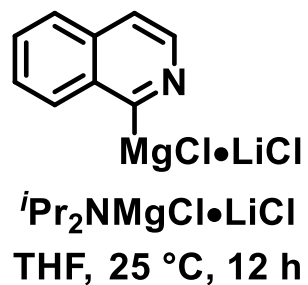
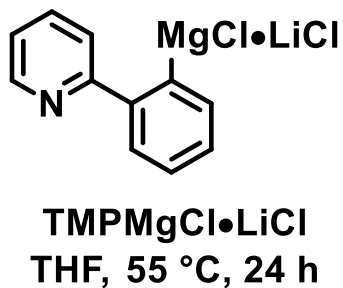
Turbo-Hauser bases



➤ The synthesis of Grignard reagents by an acid–base reaction



*J. Am. Chem. Soc.* **1989**, *111*, 8018



*Org. Lett.* **2006**, 5673  
*Angew. Chem. Int. Ed.* **2006**, *45*, 2958