Conjunctive Reagents

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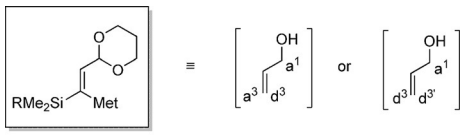
# Polyfunctional Lithium, Magnesium, and Zinc Alkenyl Reagents as Building Blocks for the Synthesis of Complex Heterocycles

*Zhi-Liang Shen[+], Vasudevan Dhayalan[+], Andreas D. Benischke[+], Robert Greiner, Konstantin Karaghiosoff, Peter Mayer, and Paul Knochel**

*Dedicated to Professor Manfred Heuschmann*

***Abstract:*** *New conjunctive β-silylated organometallic reagents of Li, Mg, and Zn have been prepared and used for an expeditive construction of various polyfunctionalized 5-, 6-, and 7-membered heterocycles, such as furans, pyrroles, quinolines, benzo[b]thieno-[2,3-b]pyridine, naphthyridines, fused pyrazoles, and 2,3-dihydro-benzo[c]azepines. The latent silyl group has been converted into various carbon–carbon bonds in most heterocycle types.*

Main-group polyfunctional organometallic reagents[1] of lithium,[2] magnesium,[3] and zinc[4] have found many synthetic applications. The presence of electrophilic functional groups in close proximity to a reactive carbon–metal bond opens numerous synthetic opportunities to perform cyclizations and therefore to construct new heterocyclic scaffolds of high interest for the pharmaceutical and agrochemical industry.[5] Herein, we wish to report the synthesis of the conjunctive reagents **1**–**3** (Met = Li, MgCl, ZnCl).[6] These β-silylated[7] β-metalated unsaturated acetals provide an entry to important functionalized 5-, 6-, and 7-membered heterocycles and are synthetic equivalents of the two allylic conjunctive synthons[8] **4** and **5** (Scheme 1). These reagents combine an electrophilic



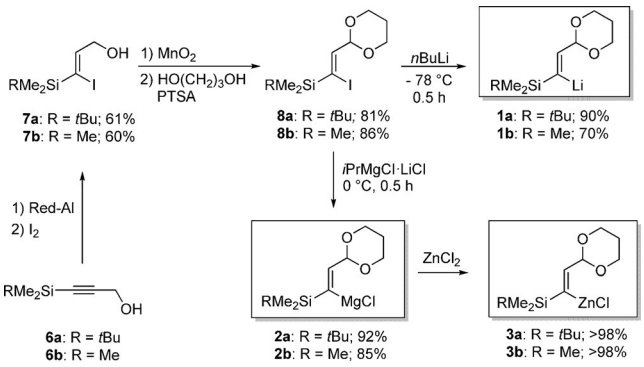

**1a-b**: Met = Li
**2a-b**: Met = MgCl
**3a-b**: Met = ZnCl
**a**: R = *t*Bu; **b**: R = Me

**4** **5**

***Scheme 1.*** The conjunctive reagents **1**–**3** (Met = Li, MgCl, and ZnCl).

acetal function with two 1,1-bimetallic[9] nucleophilic entities of well-differentiated reactivity. Furthermore, the silyl group may be converted into various carbon–carbon bonds.

Thus, the trialkylsilyl-substituted[10] propargyl alcohols (**6a**–**b**) were hydroaluminated with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al)[11] followed by iodolysis, providing the *Z*-allylic alcohols **7a**–**b** in 60–61% overall yield (Scheme 2). After $MnO_2$ oxidation[12] and standard acetal




***Scheme 2.*** Preparation of acetal-containing organometallic reagents **1**–**3** from trialkylsilyl-substituted propargylic alcohols **6a**–**b**.

formation,[13] the *Z*-alkenyl iodides **8a**–**b** were obtained in 81–86% yield. Treatment of **8a**–**b** with *n*BuLi[14] (1.1 equiv, THF, −78 °C, 0.5 h) furnished the expected lithium reagents **1a**–**b** in 70–90%. The reactions of **8a**–**b** with *i*PrMgCl·LiCl[14] (1.2 equiv, THF, 0 °C, 0.5 h) gave the corresponding magnesium reagents (**2a**–**b**) in 85–92% yield. Further transmetalation of **2a**–**b** with $ZnCl_2$ led to the corresponding alkenylzinc reagents **3a**–**b** in >98% yield.[15] With these six alkenylmetallic reagents **1a/b**–**3a/b** in hand, we have prepared a range of valuable heterocycles.

To test our concept, we have prepared 1,2-disubstituted furans and pyrroles. Thus, after treating the alkenylmagnesium reagents (**2a**–**b**) with various aryl and heteroaryl aldehydes bearing either electron-donating or -withdrawing substituents followed by an acid-mediated deacetalization, we observed a spontaneous cyclization, leading to a variety of 1,2-di-substituted furans[16] **9a**–**f** in 68–92% overall yield (Scheme 3).

Importantly, the TMS group (TMS = $SiMe_3$) present in **9d** can be readily converted into an iodide with ICl, affording the 3-iodo-furan (**10**) in 71% yield. After an I/Mg-exchange with *i*PrMgCl·LiCl[14] leading to an intermediate Grignard reagent, the addition of a second aldehyde provides the hydroxyarylated product **11** in 94% yield (Scheme 4).

[*] Dr. Z.-L. Shen,[+] Dr. V. Dhayalan,[+] M. Sc. A. D. Benischke,[+] M. Sc. R. Greiner, Prof. Dr. K. Karaghiosoff, Dr. P. Mayer, Prof. Dr. P. Knochel
Department Chemie, Ludwig-Maximilians-Universität München
Butenandtstrasse 5–13, Haus F, 81377 München (Germany)
E-mail: paul.knochel@cup.uni-muenchen.de
[+] These authors contributed equally to this work.

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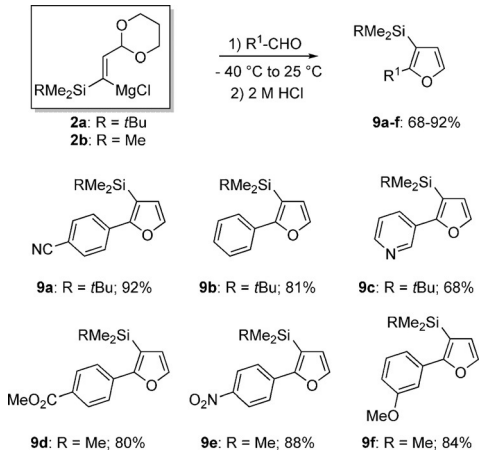
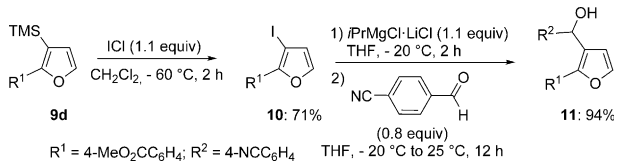
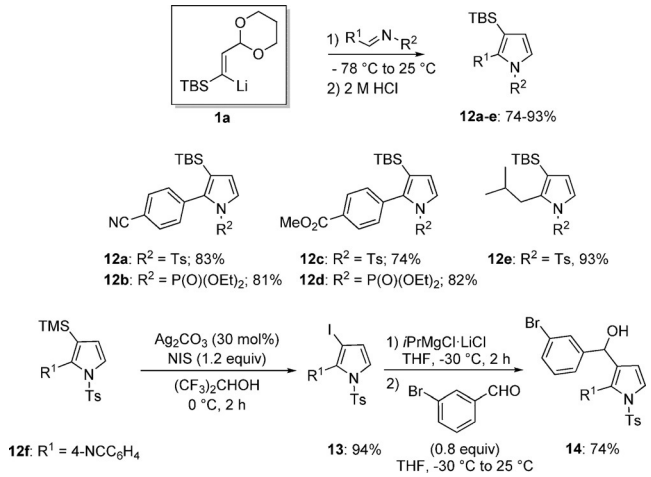



***Scheme 3.*** Preparation of furans **9a–f** using alkenylmetallic reagents **2a–b**.



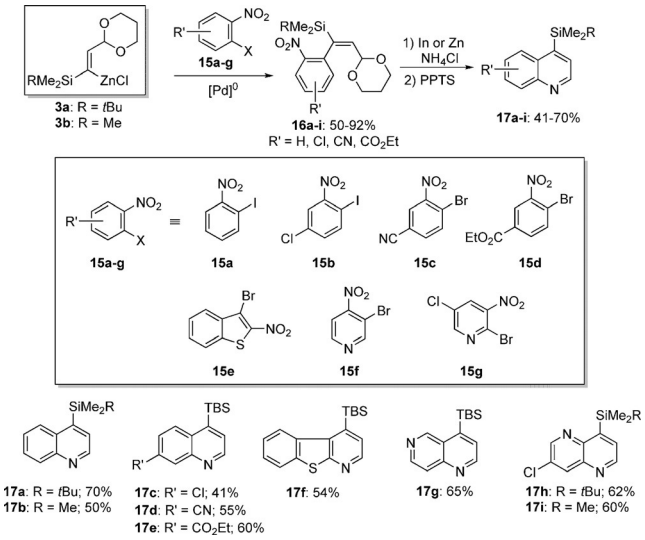

***Scheme 4.*** Conversion of the 3-TMS-furan (**9d**) to 3-iodo-furan (**10**) followed by an I/Mg-exchange.

Our method was extended to a pyrrole synthesis by using the Li-conjunctive reagent **1a** instead of **2a–b**.[17] Thus, the alkenyllithium (**1a**) adds to various *N*-sulfonylaldimines or *N*-(diethoxyphosphoryl)aldimines at −78 °C, providing after an acidic deacetalization and spontaneous cyclization various 1,2-disubstituted pyrroles (**12a–e**) in 74–93 % yield. Similarly, the 3-TMS-pyrrole **12f** (which was prepared from **1b** in 52 % yield)[10] was converted into an iodide using *N*-iodosuccinimide (NIS) and $Ag_2CO_3$ ($(CF_3)_2CHOH$, 0 °C, 2 h).[18] After an I/Mg-exchange and addition to 3-bromo-benzaldehyde, the pyrrole **14** is obtained in 74 % yield (Scheme 5). The versatile




***Scheme 5.*** Preparation of pyrroles **12a–f** using alkenylmetallic reagents **1a–b** and further functionalization.

reagents **1–3** prove also their utility in the synthesis of annelated 6-membered heterocycles such as quinolines, benzo[*b*]thieno-[2,3-*b*]pyridine, and naphthyridines,[19] which are relevant heterocycles for pharmaceutical applications.[20] Thus, the alkenylzincs (**3a–b**) underwent Pd-catalyzed Negishi[21] cross-couplings with various 1-halo-2-nitroarenes (**15a–g**), providing alkenylated nitroarenes of type **16**, which after indium- or zinc-mediated reduction[22] and acidic acetal cleavage gave the annelated pyridines **17a–i** in 41–70 % yield (Scheme 6).



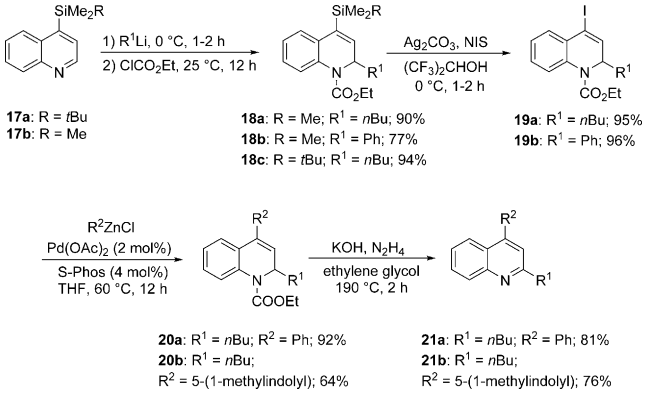

***Scheme 6.*** Pd-catalyzed cross-couplings of alkenylzinc reagents **3a–b** with 1-halo-2-nitroarenes **15a–g** for the preparation of annelated pyridines **17a–i**.

Using 3-bromo-2-nitrobenzo[*b*]thiophene or bromo-nitro-pyridines as coupling reagents provides a short access to the valuable benzo[*b*]thieno[2,3-*b*]pyridine (**17f**, 54 % yield) and the 1,5- and 1,6-naphthyridines (**17g–i**, 60–65 % yield).[23]

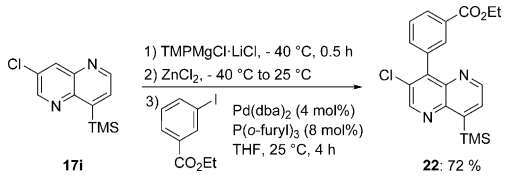
Performance of an I/Si-exchange on the quinolines **17a–b** proved difficult both with 4-TMS- or 4-TBS-substituted quinolines owing to the electron-deficient nature of this heterocyclic ring. However, dearomatization of the *N*-heterocycles (**17a–b**) by performing a 1,2-addition of an organolithium (*n*BuLi or PhLi) provides after a treatment with $ClCO_2Et$ the alkenylsilanes (**18a–c**) in 77–94 % yield. Iodination of **18a–c** using NIS and $Ag_2CO_3$[18] furnishes the 4-iodo derivatives (**19a–b**) in 95–96 % yield.[10] Negishi cross-coupling with phenylzinc chloride or 1-methyl-1*H*-indol-5-ylzinc bromide gives the desired coupling products **20a–b** (64–92 % yield). Rearomatization of **20a–b** using $KOH/N_2H_4$ in ethylene glycol (190 °C, 2 h) provides the 2,4-difunctionalized quinolines **21a–b** in 76–81 % yield (Scheme 7). Furthermore, the naphthyridine **17i** was readily magnesiated with TMPMgCl·LiCl (−40 °C, 0.5 h).[24] Negishi cross-coupling with ethyl 3-iodo-benzoate provides the 4-substituted naphthyridine **22** in 72 % yield (Scheme 8).

Novel heterocycles were prepared using the conjunctive reagent **3a**. Thus, the cross-coupling of **3a** with the 2-

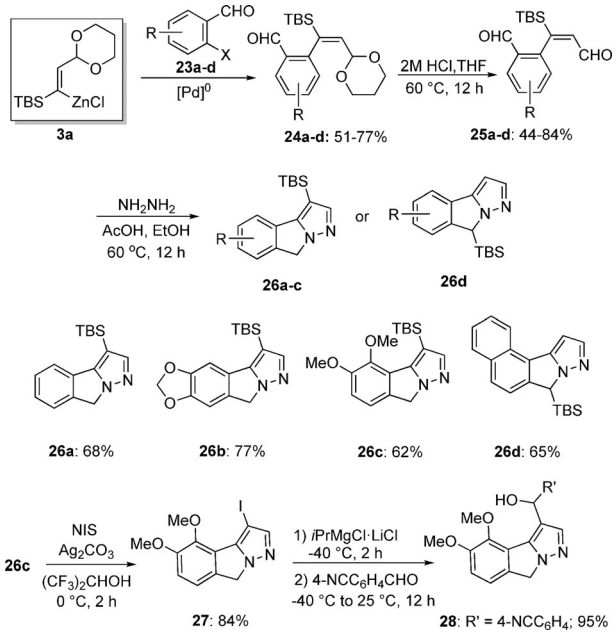



***Scheme 7.*** I/Si-exchange of the quinolines **17a–b**, Negishi cross-coupling, and rearomatization leading to functionalized quinolones **21a–b**.

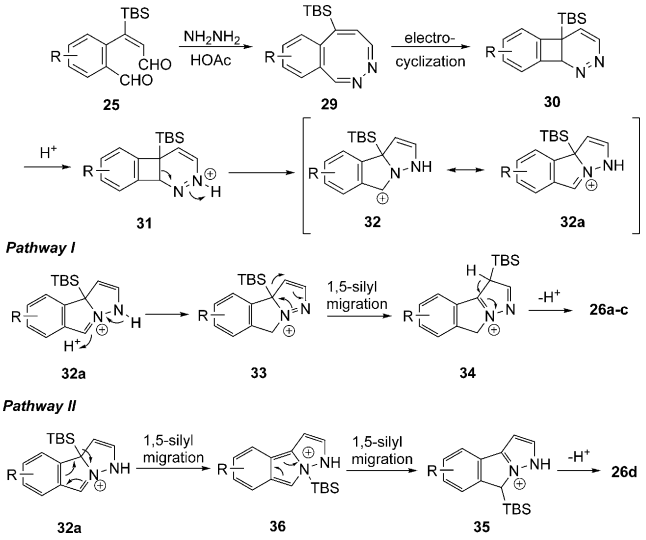



***Scheme 8.*** Directed metalation of 1,5-naphthyridine (**17i**) followed by Negishi cross-coupling.

halogeno-benzaldehydes (**23a–d**) provides the polyfunctionalized arenes **24a–d** in 51–77% yield. After acid hydrolysis, the 1,6-dialdehydes (**25a–d**) were obtained in 44–84% yield (Scheme 9). Remarkably, the 1,6-dialdehydes (**25a–c**) readily underwent a cyclization after treatment with hydrazine monohydrate in a 1:4 mixture of acetic acid and ethanol, leading to the tricyclic fused pyrazoles **26a–c** in 62–77% yield, instead of the expected 8-membered ring system of type **29**




***Scheme 9.*** Preparation of fused pyrazoles of type **26** using the conjunctive reagent **3a** and further functionalization.




***Scheme 10.*** Proposed mechanism for the formation of heterocycles **26**.

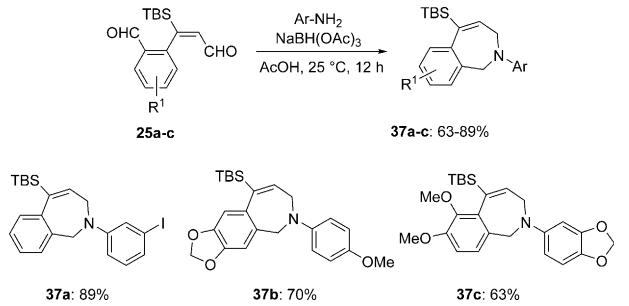
(Scheme 10). Interestingly, performing this reaction using 1,6-dialdehyde **25d** gives a similar fused pyrazole **26d** (65% yield), in which the TBS-group has migrated formerly from the pyrazole ring to a benzylic position. The structures of **26c–d** were unambiguously confirmed by X-ray diffraction analysis.[23] The C–Si bond of these fused pyrazoles can be readily converted in two steps into a new C–C bond. Thus, an I/Si-exchange of **26c** using NIS and $Ag_2CO_3$ provides the iodide **27** in 84% yield.[18] An I/Mg-exchange with *i*PrMgCl·LiCl[14] and subsequent quenching with 4-cyano-benzaldehyde leads to the pyrazole derivative **28** in 95% yield (Scheme 9).

A tentative mechanism for the formation of compounds **26** may involve the formation of an 8-membered ring of type **29,** which undergoes an electrocyclization, leading to the tricyclic ring system **30**. Acidic rearrangement of **30** provides the iminium intermediate **32a**, which leads to the formation of products **26a–c** or **26d** (Scheme 10). Thus, the iminium **32a** may undergo a proton migration, leading to **33**, which undergoes a 1,5-silyl migration,[25] affording the intermediate **34**, which after aromatization furnishes **26a–c**. On another hand, if a bulky substituent (annelated ring) is present in the intermediate **32a**, the steric hindrance favors a double 1,5-silyl migration, affording intermediate **35** via the silylammonium ion **36**. After proton loss, the desired silyl derivative **26d** is obtained.

Furthermore, the 1,6-dialdehydes of type **25** were also converted into benzo[*c*]azepine derivatives of type **37** via a double reductive amination[26] using $NaBH(OAc)_3$ and an aniline derivative, affording the corresponding 2,3-dihydro-benzo[*c*]-azepines[27] **37a–c** in 63–89% yield (Scheme 11).

In conclusion, we have described the preparation of new conjunctive alkenyl-Li, -Mg, and -Zn reagents (**1**–**3**), bearing a latent aldehyde function and a silyl group facilitating further functionalizations. These versatile building blocks allow the synthesis of various classes of important heterocycles (including furans, pyrroles, quinolines, a benzo[*b*]thieno[2,3-*b*]pyridine, a 1,5-naphthyridine, and a 1,6-naphthyridine), as well as




***Scheme 11.*** Reductive amination of the 1,6-dialdehydes (**25a–c**) leading to 7-membered *N*-heterocycles **37a–c**.

2,3-dihydro-benzo[*c*]azepines and fused pyrazoles. We have demonstrated the utility of the silyl group performing further functionalization in several cases. Further extensions for the preparation of other complex heterocycles are currently underway in our laboratories.

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