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Efficient Preparation of (*Z*)-Alkenyl Derivatives from (*Z*)-Vinyl (*N,N*-Diisopropyl)Carbamate via Ni-Catalyzed Coupling Reactions

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Abstract— A (*Z*)-vinyl (*N,N*-diisopropyl)carbamate treated with Grignard reagents, under Wenkert Nickel-catalyzed conditions, gave an access to several substituted (*Z*)-alkenyl derivatives. These Nickel-catalyzed reactions, carried out with vinyl-, phenyl-, *p*-methoxyphenyl-, trimethylsilylmethylmagnesium bromide and benzylmagnesium chloride, led to the corresponding (*Z*)-alkenyl derivatives in good yields and high stereoselectivities. © 2021 Elsevier Science. All rights reserved

The aldehyde allylation reaction described by Hoppe¹ was advantageously used in total synthesis.² Under original conditions, crotyl carbamate **1** treated with *n*-BuLi/(-)-sparteine in pentane/cyclohexane at -78°C, followed by transmetalation with Ti(O*i*-Pr)₄, led to an optically pure crotyltitane intermediate *via* a second order asymmetric induction. Reaction of this latter with an aldehyde gave the (*Z*)-*anti* homoallylic alcohol **2** in an enantioselective way (Scheme 1, a).

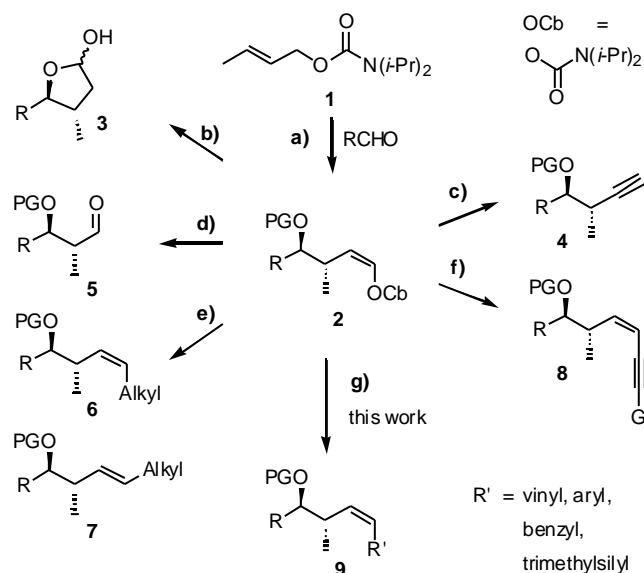
The synthetic utility of a vinyl (*N,N*-diisopropyl)carbamate group was found by its transformation into lactol **3** (b),^{2d,3} acetylenic **4** (c)^{2b-c,4} or aldehyde **5** (d) function.^{1,2} Preparation of (*Z*)- or (*E*)-alkyl compound **6** or **7** (e)⁵ and enyne derivative **8** (f),⁶ from (*Z*)-vinyl carbamates was also described.

For synthetic reasons we were interested to get an access, from carbamate **2**, to (*Z*)-vinyl products **9** (g) in which R' could be, a vinyl, an aryl, a benzyl, or a trimethylsilylmethyl group. A direct access could be planned, *via* a metal insertion into the C-O bond of the carbamate moiety, in a coupling reaction as described by Kocienski^{5a} for preparation of alkyl derivatives **6** and **7**. So we turned our efforts to the Wenkert method⁷ to develop the preparation of **9**.

Scheme 1. Reactivity of vinyl carbamate function.

Generally Nickel-catalyzed coupling reactions were effected and optimised in presence of catalytic amount of Ni(acac)₂

in Et₂O at room temperature,⁸ or NiCl₂(tpp)₂⁹ and NiCl₂(dppe)⁵ in boiling benzene using an excess of the



Grignard reagent.

The (*Z*)-*anti* vinyl carbamate **10**³ was prepared *via* a Hoppe allylation of isobutyraldehyde in a racemic way. Reaction between butyldimethylsilyl ether **11**, derived from **10**,¹⁰ and vinylmagnesium bromide **12** in excess (Scheme 2), in

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presence of a catalytic amount of Ni(acac)₂ (10 mol %), at -5°C for 12 h in Et₂O, gave the expected dienylyl derivative (**Z**)-**13** and the reduced compound **14** in a 80:20 ratio and 72% yield (Table 1, entry 1).¹¹ Employment of NiCl₂(dppe), at 0°C for 2h, led to a 91:9 mixture of compounds (**Z**)-**13** and **14** in 65% yield (Entry 2). In the last attempt, treatment with NiCl₂(dppp) in boiling toluene (3 h) resulted in formation of compound (**Z**)-**13** and homocoupling product **15** in a 70:30 ratio and a 89% yield (Entry 3), the significant change was the formation of **15** and the disappearance of the reduced derivative **14**.

Scheme 2. Cross coupling reaction between vinyl carbamate **11** and vinylmagnesium bromide.


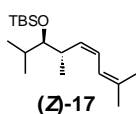
Table 1. Cross coupling reaction between vinyl carbamate **11** and vinylmagnesium bromide.


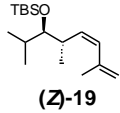

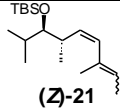
Entry	[Ni] ^a	Yield ^b	(Z)- 13/14/15 ^c
1	Ni(acac) ₂ /Et ₂ O -5°C, 12 h	72%	80:20:0
2	NiCl ₂ (dppe)/Et ₂ O 0°C, 2 h	65%	91:9:0
3	NiCl ₂ (dppp)/toluene Reflux, 3 h	89%	70:0:30

^a [Ni] = 10 mol%. ^b Isolated Yield. ^c GC/MS analysis.

Application of these conditions into preparation of substituted dienes was performed with Grignard reagents **16**, **18** and **20**. In the case of isobutenylmagnesium bromide **16**, method A [Ni(acac)₂ 10 mol%, Et₂O, 0-5°C, 12 h], gave access to the pure compound (**Z**)-**17** in 57% yield (Table 2, entry 1). Under **B** [NiCl₂(dppp) 10 mol%, toluene, reflux, 3 h] or **C** [Ni(acac)₂ 10 mol%, toluene, reflux, 3 h] conditions, yield did not increase, and a non-identified isomer was detected, probably the (**E**)-**17** isomer (Entries 2 and 3). Treatment of **11** with the Grignard reagent **18** applying **A** protocol, conducted to the (**Z**)-**19** derivative in good yield, together with a few amount of the reduced product **14** and also a non identified isomer (Entry 4, 70% yield, (**Z**)-**19/14/15/isomer** 90:3:0:7). When the Grignard reagent **20** was used, application of method **A** give also the best result and the expected (**Z**)-**21** isomer was obtained in 73% yield as the only product (Entry 5).

Table 2. Cross coupling of vinyl carbamate **11** with substituted vinylmagnesium bromides.

Entry	Grignard Reagent	Method ^a	Coupling Product	Yield ^b Selectivity ^c
1		A ^d		(Z)- 17/14/15/isomer 57% 100:0:0
2		B ^d		(Z)- 17/14/15/isomer 56% 89:4:0:7
3		C		(Z)- 17/14/15/isomer 63% 89:0:6:5
4				

		A		(Z)- 19/14/15/isomer 70% 90:3:0:7
		A		(Z)- 21/14/15/isomer 73% 100:0:0:0

^a Method A: Ni(acac)₂ 10 mol%, Et₂O, 0°C, 12 h, Grignard Reagent 10 equiv. Method B: NiCl₂(dppp) 10 mol%, toluene, reflux, 3 h, Grignard Reagent 10 equiv. Method C: Ni(acac)₂ 10 mol%, toluene, reflux, 3 h, Grignard Reagent 5 equiv. ^b Isolated Yield. ^c GC/MS analysis.

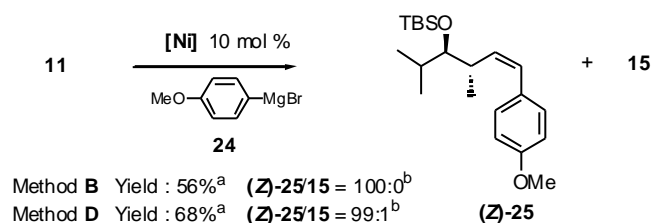
In continuation of our study, an investigation with phenylmagnesium bromide **22** was undertaken (Scheme 3). Reaction of **11** with PhMgBr **22** under method **B** conditions, afforded the expected coupling product (**Z**)-**23** with the corresponding identified (**E**)-**23** isomer, and the homocoupling product **15** in a 68:12:20 ratio and a 95% yield.

^a Isolated yield. ^b GC/MS analysis. ^c Method D: Ni(acac)₂ 10 mol%, DIBAL-H 20 mol%, PPh₃ 20 mol%, Et₂O, 0°C, 12 h, Grignard Reagent 5 equiv. ^d The reduced compound **14** was isolated in 3% yield.

Scheme 3. Cross coupling reaction with phenylmagnesium bromide.

Using [Ni(acac)₂ 10 mol%, DIBAL-H 20 mol%, PPh₃ 20 mol%, Et₂O, 0°C, 12 h, RMgX 5 equiv.] conditions (method **D**),¹² the reaction proceeded in 72% yield, and compound

(*Z*)-**23** was isolated together with its (*E*)-**23** isomer and a few amount of the reduced derivative **14** in a (*Z*)-**23**/*(E)*-**23**/**14** = 72:25:0:3 selectivity. Formation of homocoupling product **15** was totally avoided in this case. Interestingly, the coupling reaction of **11** and *p*-methoxyphenylmagnesium bromide **24** (Scheme 4), in presence of Ni(acac)₂ (**A** or **C** protocol) gave access to the (*Z*)-**25** derivative as a mixture with the homocoupling product **15**. Surprisingly method **B** conducted to compound (*Z*)-**25** in 56% yield and total stereocontrol. The best result was obtained with **D** conditions, compound (*Z*)-**25** was isolated in 68% yield, the homocoupling product **15** being produced in less than 1% yield (Entry 4).



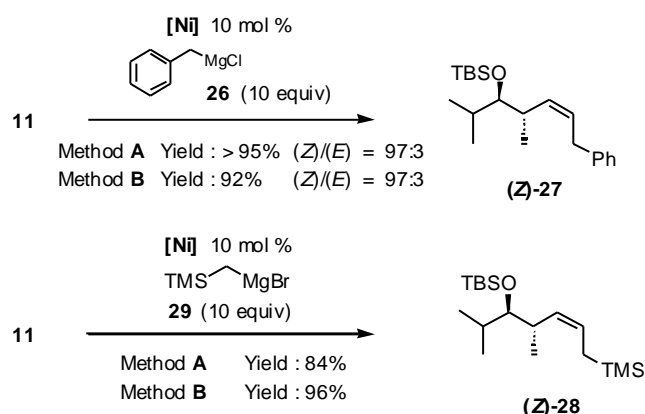
^a Isolated yield. ^b GC/MS analysis.

Scheme 4. Cross coupling reaction with *p*-methoxyphenylmagnesium bromide.

Another application of this Ni-catalyzed reaction was also performed with benzylmagnesium chloride **26** (Scheme 5). Under **A** conditions, reaction proceeded in an excellent 95% yield and the vinyl adduct (*Z*)-**27** was cleanly produced with a high selectivity [(*Z*)/(*E*) = 97:3]. Employing **B** conditions, comparable yield and selectivity were observed [92% yield, (*Z*)/(*E*) = 97:3].

An interesting synthetic point of view was the transformation of the vinyl carbamate **11** into the allylsilane (*Z*)-**28** (Scheme 5) to promote a subsequent aldehyde allylation either in preparation of the extended chain or furan derivative.¹³ As a satisfying result, coupling reaction between vinyl carbamate **11** and the trimethylsilylmethylmagnesium bromide **29**, either applying **A** or **B** conditions, gave the pure allylsilane (*Z*)-**28** in 84% and 96% yield respectively.¹⁴ Production of the two possible by-products, reduced compound **14** and homocoupling product **15**, was not observed in these cases.

In conclusion it was shown that a direct Ni-catalyzed coupling reaction between the (*Z*)-vinyl (*N,N*-diisopropyl)carbamate **11**, and vinyl-, aryl-, benzyl- and trimethylsilylmethyl Grignard reagents led to the corresponding substituted (*Z*)-alkenyl derivatives in good yields and high stereoselectivities. These coupling reactions could be considered as a useful tool in organic synthesis¹⁵ and applications are underway.



Scheme 5. Cross coupling reaction with benzylmagnesium chloride and trimethylsilylmethylmagnesium bromide.

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10. In a first time, attempts conducted on compound 10, with the free secondary hydroxy group, gave any cross coupling product.
11. General procedure for cross-coupling reactions: To a flame-dried flask, under argon, were added vinyl carbamate 11 (200 mg, 0.52 mmol) and Ni(acac)₂ (13 mg, 0.05 mmol, 0.1 equiv.) or [NiCl₂(dppp)] catalyst (28 mg, 0.05 mmol, 0.1 equiv.). Freshly distilled diethyl ether (5 mL) or [toluene (5 mL)] was added, and the solution was degassed and flushing with argon. The mixture was cooled at -5°C and Grignard reagent (1.0M solution in THF, 5 mL, 5.0 mmol, 10 equiv.) was added dropwise and stirred for 12 h at -5°C or [heated to reflux for 3 h]. Then the mixture was quenched by addition of a saturated aqueous NH₄Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. Purification was effected by chromatography on silica gel (cyclohexane).
- (Z)-13: ¹H NMR (270 MHz, CDCl₃) δ 6.55 (ddd, J = 16.8, 11.2, 10.1 Hz, 1H, H-7), 5.91 (dd, J = 11.2, 10.9 Hz, 1H, H-6), 5.52 (dd, J = 10.9, 9.9 Hz, 1H, H-5), 5.13 (dd, J = 16.8, 2.0 Hz, 1H, Ha-8), 5.02 (dd, J = 10.1, 2.0 Hz, 1H, Hb-8), 3.27 (dd, J = 5.6, 3.3 Hz, 1H, H-3), 2.79 (dq, J = 9.9, 6.9, 3.3 Hz, 1H, H-4), 1.66 (heptd, J = 6.9, 5.6 Hz, 1H, H-2), 0.94 (d, J = 6.9 Hz, 3H, CH₃-□), 0.86 [s, 9H, CH₃-□-□Si(CH₃)₃], 0.83 (d, J = 6.9 Hz, 3H, H₃-□ or CH₃-□), 0.81 (d, J = 6.9 Hz, 3H, CH₃-□□ or H₃-□), 0.00 [s, 6H, CH₃-□□Si(CH₃)₂]. ¹³C NMR (67.5 MHz, CDCl₃) δ 135.9 (CH, C-5), 132.8 (CH, C-7), 128.2 (CH, C-6), 116.9 (CH₂, C-8), 81.1 (CH, C-3), 35.7 (CH, C-4), 32.9 (CH, C-2), 26.3 [3CH₃, Si(CH₃)₃], 19.7 (2CH₃, C-1 or CH₃-2 and CH₃-4), 18.9 (CH₃, CH₃-2 or C-1), 18.6 [C, Si(CH₃)₃], -3.6 [2CH₃, Si(CH₃)₂].
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14. (Z)-28: ¹H NMR (270 MHz, CDCl₃) δ 5.33 (dd, J = 10.8, 9.3 Hz, 1H, H-5), 5.29 (ddd, J = 10.8, 8.0, 5.8 Hz, 1H, H-6), 3.27 (dd, J = 5.3, 4.0 Hz, 1H, H-3), 2.59 (dq, J = 9.3, 7.1, 4.0 Hz, 1H, H-4), 1.72 (heptd, J = 6.7, 5.3 Hz, 1H, H-2), 1.52 (dd, J = 13.9, 8.0 Hz, 1H, H-7a), 1.36 (dd, J = 13.9, 5.8 Hz, 1H, H-7b), 0.92 (d, J = 7.1 Hz, 3H, CH₃-4), 0.90 [s, 9H, 3CH₃, Si(CH₃)₃], 0.86 (d, J = 6.7 Hz, 3H, H₃-1 or CH₃-2), 0.85 (d, J = 6.7 Hz, 3H, CH₃-2 or H₃-1), 0.04 [s, 3H, CH₃, Si(CH₃)₂], 0.02 [s, 3H, CH₃, Si(CH₃)₂], 0.00 [s, 9H, 3CH₃, Si(CH₃)₃]. ¹³C NMR (67.5 MHz, CDCl₃) δ 131.0 (CH, C-5), 124.2 (CH, C-6), 81.0 (CH, C-3), 35.2 (CH, C-4), 32.2 (CH, C-2), 26.2 [3CH₃, Si(CH₃)₃], 20.5 (CH₃, C-1 or CH₃-2), 19.0 (2CH₃, CH₃-4 and CH₃-2 or C-1), 18.6 (CH₃, C-1 or CH₃-2), 18.6 (CH₂-7), 18.6 [C, Si(CH₃)₃], -1.5 [3CH₃, Si(CH₃)₃], -3.2 [CH₃, Si(CH₃)₂], -3.6 [CH₃, Si(CH₃)₂].
15. (Z)-vinyl carbamate derivatives could be prepared in good yield and high stereoselectivity from allylic alcohols, see ref 6.

