Remarkable Diastereoselectivity in the Addition of Allylic and Unsaturated Diorganozinc Reagents to *β*-(*N*,*N*-Dialkylamino)-aldehydes

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1,3-Anti amino alcohols **5**[a]−**18**[a] are obtained with high diastereoselectivity by use of diorganozinc reagents in additions to amino aldehydes **2a** and **2b**. The corresponding Grignard reagents exhibit low to modest diastereoselectivity. The highly diastereoselective zinc-based method makes available a wide range of 4,4-disubstituted cyclohexenone derivatives containing contiguous stereocenters.

Introduction

Stereoselective carbon−carbon single-bond formation by substrate-controlled addition of an organometallic reagent to an aldehyde or ketone is an important process in organic synthesis.[1] Chelation in the presence of neighboring Lewis basic functionalities can reverse the sense of stereoinduction[2] from the classic Cram[3]/Felkin[4]−Ahn[5]-type additions. While much work has been reported concerning the addition of organometallics to α- and *β*-alkoxy ketones[6] and aldehydes[7] and carbamate-protected α-amino aldehydes,[8] there are no apparent examples of chelation-controlled additions to *β*-dialkylamino aldehydes or ketones.

In the course of exploring synthetic strategies to access a common skeletal motif found in the viridin,[9] samaderine,[10] and quassinoid[11] classes of natural products, we identified substructures of type **1** (Figure 1) as versatile synthetic intermediates. Access to such substructures was envisioned through the use of a chelation-controlled addition of an organometallic reagent to *β*-amino aldehyde **2** to set the two contiguous stereocenters. It was predicted that an appropriate organometallic reagent would approach from the convex face of a cup-shaped chelate. Aldehyde **2** is readily accessed by Diels−Alder reaction of methacrolein (**3**) with 1-amino-3-siloxybutadiene (**4**) as previously reported by Rawal and coworkers.[12]

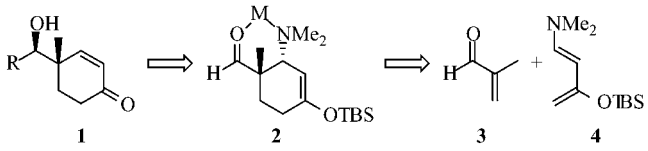

Figure 1. Retrosynthesis of common substructure **1**.

Herein, we report our observations concerning the addition of various Grignard and diorganozinc reagents to *β*-(*N*,*N*-dialkylamino)-aldehydes. Of particular interest are the high diastereoselectivities obtained with allylic and unsaturated diorganozinc reagents.

Results and Discussion

In an initial experiment, the addition of vinyl Grignard reagent to **2a** gave a 97% yield of secondary allylic alcohols **5**[a] (anti isomer) and **5**[s] (syn isomer) as a separable 1:3 mixture of diastereomers (Table 1, entry 1). The relative stereochemistry of the minor diastereomer **5**[a] proved to be the desired one and was assigned by conversion to ketone **6** as shown in Scheme 1. The relative configuration was determined by NOE experiments on the cis-6,5-fused system of **6**. To rationalize the stereochemical outcome of the reaction, it is proposed that

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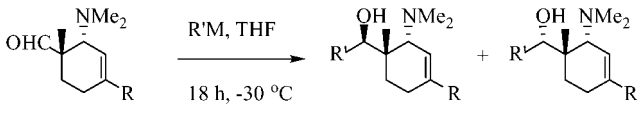
Table 1. Organometallic Additions to 2a and 2b



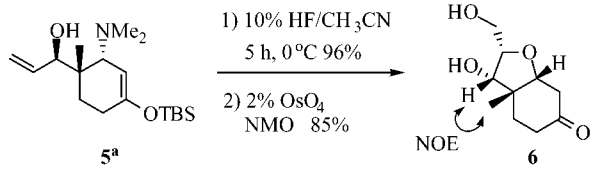
2a : R = OTBS
2b : R = H

1,3-*anti* **1,3-*syn***

entry	substrate	R′M	anti ([a]): syn ([s])[a]	yield[b]
1	**2a**	vinylMgBr	**5[a]:5[s]** 1:3	97%
2	**2a**	vinyl$_2$Zn	**5[a]** only[c]	97%
3	**2a**	allyl$_2$Zn	**7[a]** only[c]	87%
4	**2a**	allylMgBr	**7[a]:7[s]** 1:2	94%
5	**2a**	Ph$_{2Zn}$	**9[a]** only[c]	86%
6	**2a**	PhMgBr	**9[a]** only[c]	99%
7	**2b**	vinyl$_2$Zn	**10[a]** only[c]	93%
8	**2b**	vinylMgBr	**10[a]:10[s]** 1:3	96%
9	**2b**	allyl$_2$Zn	**11[a]** only[c]	85%
10	**2b**	allylMgBr	**11[a]:11[s]** 1:2	90%
11	**2b**	Et$_2$Zn	**12[a]:12[s]** 3.5:1[d]	70%
12	**2b**	EtMgBr	**12[a]:12[s]** 2:1	65%
13	**2b**	Cyhex$_2$Zn	**11[a]:11[s]** 3.7:1	55%
14	**2b**	CyhexMgBr	**11[a]:11[s]** 2.7:1	53%

[a] Ratios determined by ^{1}H NMR at 400 MHz. [b] Isolated yields. [c] No minor diastereomer detected by ^{1}H NMR. [d] Configurations determined by hydrogenation of **10[a]/10[s]**.

Scheme 1. Structure Proof for 5[a]

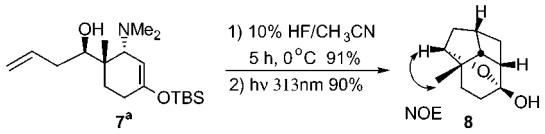


5[a] **6**

the highly reactive Grignard reagent adds preferentially through the Cram/Felkin−Ahn-type open transition state and not through a closed chelate or perhaps only through partial chelation. Steric inhibition of chelation in the presence of the intervening quaternary center may be the reason for this. This result raised the question whether other organometallic species could be used to overcome this steric barrier to chelation, allowing access to the desired relative configuration **5[a]**.

Further investigations led to the exploration of diorganozinc reagents as a means of enhancing the diastereoselectivity. The addition of diorganozincs to aldehydes has been well studied.[13] Typically dialkylzincs require the use of Lewis acid and/or ligand-accelerated catalysis for reaction with aldehydes and ketones. In contrast, unsaturated zinc reagents exhibit greater reactivity and do not necessarily require catalytic additives. Even so, it was projected that the zinc-based reagents would be less reactive than the corresponding Grignard

Scheme 2. Structure Proof for 7[a]



7[a] **8**

reagent, and that could impact the ability to efficiently chelate amino aldehyde **2a**. *Gratifyingly, it was found that when aldehyde **2a** was treated with 2 equiv of divinylzinc at −30 °C for 18 h, a 97% yield of **5[a]** was obtained, and there was no detectable trace of the undesired diastereomer **5[s]** by ^{1}H NMR.* (Table 1, entry 2) Interestingly, the addition of 1 equiv of divinylzinc under similar conditions gave only 5% conversion to the desired product **5[a]** with the remainder of the mass being unreacted starting material **2a**.

A number of diorganozincs and their corresponding Grignard reagents were screened, and the results are summarized in Table 1. Addition of diallylzinc to **2a** (entry 3) gave an 87% yield of **7[a]**, favoring reaction with stereoselectivity identical to that of the divinylzinc reagent. The allyl Grignard reagent (entry 4), on the other hand, gave a 1:2 ratio of **7[a]:7[s]**, similar to the result with the vinyl Grignard reagent. Confirmation of the relative stereochemistry for the allylation with the zinc reagent was accomplished by conversion to cage compound **8** as shown in Scheme 2.

Diphenylzinc (entry 5) gave 86% yield of adduct **9[a]** as the only detectable diastereomer by ^{1}H NMR. Phenyl adduct **9[a]** was highly crystalline, and an X-ray crystal structure confirmed the assignment of the relative configuration. The corresponding phenyl Grignard reagent (entry 6) exhibited selectivity identical to that of the corresponding zinc reagent. The disparity in the behavior of the phenyl Grignard reagent relative to that of the other Grignard reagents has yet to be reconciled.

Substrate **2b** lacking the siloxy group was also prepared[14] and screened in the addition reaction. The diorganozinc additions (entries 7 and 9) were also found to be superior to the corresponding Grignard reagents (entries 8 and 10). Interest in these adducts stems from the utility of 1,3-dialkylamino alcohols as chiral ligands for asymmetric catalysis.[15]

Interestingly, saturated dialkylzinc reagents do not react with high diastereoselectivity with amino aldehyde substrate **2b**. Diethylzinc and dicyclohexyl zinc react (entries 11 and 13) with modest diastereoselectivity, as do the corresponding Grignard reagents (entries 12 and 14). It was also found that only 1 equiv of the saturated dialkylzinc reagent is required for reaction in these cases. With substrate **2a**, the dialkylzincs proved to be poor coupling partners, causing premature unraveling of the amino silyl enol ether functionality. Despite the poor performance of the saturated diorganozinc reagents,

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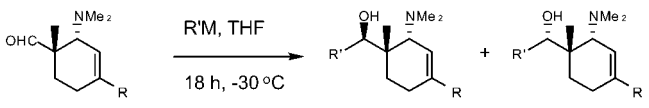
Table 2. Substituted Zinc Additions to 2a and 2b



2a : R = OTBS
2b : R = H

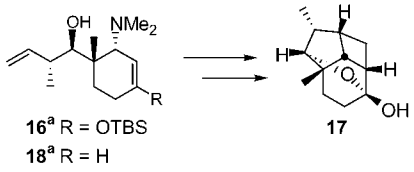
1,3-*anti* **1,3-*syn***

Entry	Substrate	R'M	*anti* (ª): *syn* (ˢ) [a]	Yield [b]
1	**2b**		**14ª** only	79%
2	**2b**		**14ª** : **14ˢ** 8.4:1	71%
3	**2b**		**15ª** : **15ˢ** 8.1:1	67%
4	**2b**		**15ª** : **15ˢ** 3.6:1	84%
5	**2a**		**16ª** only	82%
6	**2a**		1:1.6:2.2[d]	68%[c]
7	**2b**		**18ª** only	82%

[a] Ratios determined by ^{1}H NMR at 400 MHz. [b] Isolated yields. [c] No minor diastereomer detected by ^{1}H NMR. [d] Mixtures not separated. [e] Two-step yield after deprotecting amino silyl enol ether.

access to the alkyl-substituted products is readily accomplished by hydrogenation of the vinyl- or allyl-substituted precursor. In fact, assignments of the diethylzinc diastereomers **12ª** and **10ˢ** were made by correlation with the hydrogenation products of **10ª** and **10ˢ**, respectively.

The dramatic difference in reactivity between the vinyl-, allyl-, and phenylzinc reagents and the dialkylzinc reagents appears to be a consequence of differing Lewis acidities of these reagents. The scope of vinylic and allylic zinc reagents that participate in this reaction was next examined, and the results are summarized in Table 2 below. Substitution in the β-position of the vinyl zinc reagent is tolerated (entry 1). Remarkably, the corresponding Grignard reagent (entry 2) led to the same diastereomer, but with lower selectivity. Erosion of selectivity occurred upon substitution in the α-position of the vinylic zinc and Grignard reagents (entries 3 and 4), though clearly better selectivities are obtained with the zinc-based reagent. Substitution on the olefin of the allylic system is also tolerated (entries 5−8). Dicrotylzinc[16] (entries 5 and 7) led to a single diastereomeric product of four possible products. The corresponding Grignard reagent (entries 6 and 8) gave inseparable mixtures of three and four possible diastereomers, respectively. It is important to note that crotylation with the zinc reagent occurs with transposition of the double bond (Figure 2) analogous to the reactivity of the crotyl Grignard reagent as characterized by Young and Roberts.[17] The structure of **16ª** was confirmed by X-ray crystallography of derivative **17**, prepared by the same method as **8**. While the exclusive formation of **16ª** and



16ª R = OTBS
18ª R = H

17

Figure 2. Structure proof of **16**ª.

18ª certainly arises from a highly ordered transition state, further mechanistic work will be necessary to shed light on the reaction path for these diorganozinc reactions.

Conclusion

Allylic, vinylic, and phenyl diorganozincs were found to be superior reagents for effecting the directed addition to β-amino aldehydes **2a** and **2b**. By this methodology, 4,4-disubstituted cyclohexenone building blocks in diastereomerically pure form are now available. Further work includes mechanistic studies to clarify the course of the reaction as well as extend these results to other β-dialkylamino aldehyde and ketone systems. Currently, we are applying this methodology to the synthesis of the viridin class of natural products.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Common solvents were purified before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium-benzophenone ketyl. Dichloromethane (CH_2Cl_2) and benzene were distilled from calcium hydride. All reagents used were reagent grade and purified where necessary. Reactions were monitored by thin-layer chromatography (TLC) using 250 μm Baker precoated silica gel plates. Flash column chromatography was performed over EM Science Laboratories silica gel (230−400 mesh). Carbon and proton NMR spectra were recorded on Bruker AC-250, Avance400, and Avance500 spectrometers. ^{1}H NMR chemical shifts are reported as δ values (ppm) relative to internal timethylsilane or residual $CHCl_3$ (7.26) in $CDCl_3$. Infrared spectra were recorded with a Nicolet 205 FT-IR spectrometer and a Nicolet Avatar 320 FT-IR instrument. Recorded data are reported in reciprocal centimeters (cm^{-1}). Mass spectra were obtained on a Finnigan Mat 95 apparatus. Data for compounds **9ª** and **17** were collected on a Bruker CCD SMART system, equipped with graphite monochromated Mo Kα radiation ($l = 0.71073 \approx$) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS and difference Fourier maps and refined by using full matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions and allowed to ride on the attached carbon atoms [d(C−H) = 0.95 Å]. Refinement of positional and anisotropic thermal parameters led to convergence.

Drying and Preparing Zinc Chloride Solutions. Zinc chloride was dried by fusing under vacuum at 0.3 mmHg. A 0.5 M solution in dry ether was prepared directly with the exclusion of water.

General Procedure for all Diorganozinc Additions Except Entry 11; Compounds 12ª and 12ˢ. Vinyl Adduct 5ª. To 1.47 mL of a 1.0 M solution of vinylmagnesium bromide in THF was added 0.61 mL of THF. The solution was cooled to −30 °C, and 1.47 mL of a 0.5 M solution of dry zinc chloride in ether was added dropwise. The white suspension was stirred for 30 min. To the newly formed divinylzinc reagent was added a solution of **2a** (0.108 g, 0.367 mmol) in 0.61 mL of THF at −30 °C. The reaction was stirred at −25 °C for 18 h and was then quenched at −30 °C with 3 mL of saturated NH_4Cl. After

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warming to room temperature, the reaction mixture was diluted with ether and washed three times with water, and the water layer was back-extracted once. The organics were dried with anhydrous Na_2SO_4, filtered, and then concentrated in vacuo to afford the allylic alcohol **5a**. Purification via flash chromatography (10% TEA/hexanes) yielded 0.115 g (97%) of pure **5a** as a light yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$, δ) 6.45 (s, 1H), 5.98 (m, 1H), 5.23 (m, 2H), 4.85 (d, J = 5.2 Hz, 1H), 3.92 (d, J = 6.3 Hz, 1H), 2.28 (s, 6H), 1.92−2.01 (m, 3H), 1.31 (m, 1H), 0.925 (s, 9H), 0.874 (s, 3H), 0.152 (s, 6H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 153.9, 136.8, 125.5, 116.1, 98.9, 80.2, 69.7, 38.7, 30.3, 26.5, 25.9, 25.7, 25.6, 22.6, 21.7, 17.9, −3.5, −4.1; IR (neat film) 3200−2900, 2813, 2794, 1656, 1478, 1384, 1201, 1006, 634, 597 cm^{-1}; HRMS-EI m/z [M$^+$] calcd for $C_{18}H_{35}NO_2Si$ 325.243708, found 325.243696.

Ketone 6. Compound **5a** (43.6 mg, 0.135 mmol) was transferred to a plastic centrifuge tube with 0.3 mL of CH_3CN. The solution was cooled to 0 °C, and 0.1 mL of 10% of HF/CH_3CN was added; the solution was allowed to warm to room temperature over 5 h. The reaction mixture was diluted with 3 mL of ether and washed twice with saturated $NaHCO_3$ and then once with water. The water layer was back-extracted with ether, and the organic layers were combined, dried with anhydrous Na_2SO_4, and concentrated in vacuo. Purification by flash column chromatography (50% ether/hexanes) afforded 21.3 mg (0.129 mmol, 96%) of an enone as a light yellow oil that was carried on immediately: ^{1}H NMR (250 MHz, $CDCl_3$, δ) 6.80 (d, J = 10.3 Hz, 1H), 5.8 (m, 2H), 5.2 (m, 2H), 3.9 (d, J = 6.0 Hz, 1H), 2.4 (m, 2H), 2.2−1.9 (m, 1H), 1.8−1.5 (m, 1H), 0.78 (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 199.6, 155.9, 136.6, 128.3, 117.6, 78.8, 40.0, 33.8, 30.8, 19.9; IR (neat film) 3750−3100, 2964, 2873, 2103, 1652, 1558, 1539, 1506, 1457, 1418, 1373, 1329, 1201, 1232, 1117, 1043, 928, 805 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{10}H_{14}O_2$ 166.099380, found 166.099658. The enone (27.8 mg, 0.204 mmol) was dissolved in 0.4 mL of acetone, and to this was added a solution of 0.1 mL of 10% OsO_4 in t-BuOH, NMO (25.3 mg, 0.216 mmol), 0.04 mL of acetone, and 0.1 mL of water while the solution cooled in a 10 °C water bath. The reaction proceeded at room temperature for 14 h, after which the solvent was removed and the crude product was purified via flash chromatography (5% MeOH/CH_2Cl_2). Compound **6** (26.9 mg, 0.158 mmol, 78%) was recovered as a colorless oil that crystallized upon standing: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 4.05 (m, 1H), 3.87 (m, 2H), 3.75 (m, 1H), 3.62 (m, 1H), 2.60 (m, 2H), 2.50−2.25 (m, 2H), 1.90 (m, 1H), 1.65 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 210.4, 84.3, 83.4, 77.9, 62.3, 42.4, 41.8, 35.8, 32.3, 18.5; IR (neat film) 3700−3150, 2961, 2932, 2877, 1708, 1651, 1461, 1408, 1385, 1337, 1259, 1122, 921, 887 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{10}H_{16}O_4$ 200.104859, found 200.104600. NOE confirmation can be found in Supporting Information.

Allyl Adduct 7a: Light yellow oil (87% yield); ^{1}H NMR (250 MHz, $CDCl_3$ δ) 0.11 (s, 6H), 0.78 (s, 3H), 0.89 (s, 9H), 1.31 (m, 1H), 1.70 (m, 1H), 1.89−2.35 (m, 1H), 2.87 (d, J = 5.6 Hz, 1H), 3.45 (dd, J = 2.92, 2.98 Hz, 1H), 4.82 (d, J = 4.87 Hz, 1H), 5.07 (m, 2H), 5.92 (m, 1H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 153.7, 137.5, 155.6, 97.4, 77.1, 66.0, 39.1, 35.7, 28.5, 26.5, 25.6, 19.8, 17.9, −4.3, −4.4; IR (neat film) 3700−3110, 3095, 2925, 2898, 2850, 2830, 2790, 1676, 1632, 1478, 1389, 1310, 1254, 1205, 1162, 1060, 1023, 1004, 910, 880, 779 cm^{-1}; HRMS-EI m/z [M$^+$] calcd for $C_{19}H_{37}NO_2Si$ 340.261986, found 340.261746.

Compound 8. Compound **7a** was deprotected and purified using the same procedure as in the synthesis of **6**. The enone was isolated as a yellow oil (90% yield) and taken on directly: ^{1}H NMR (250 MHz, $CDCl_3$, δ) 6.95 (d, J = 15.7 Hz, 1H), 6.05 (d, J = 14.0 Hz, 1H), 5.83 (m, 1H), 5.19 (m, 2H), 3.45 (dd, J = 2.2, 10.6 Hz, 1H), 2.53 (m, 2H), 2.41−1.73 (m, 4H), 0.85 (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 199.5, 156.1, 134.9, 128.0, 118.9, 76.1, 39.9, 36.5, 33.9 30.3, 20.0; IR (neat film) 3700−3100, 2962, 2874, 2089, 1665, 1458, 1418, 1391, 1327, 1262, 1228, 1121, 1059, 992, 915, 806, 668 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{11}H_{16}O_2$ 180.115030, found 180.115200. The enone (51.5 mg) was irradiated for 30 min at 313 nm in 5 mL of a 5% solution of methanol in hexanes. Concentration in vacuo and chromatography of the product afforded 90% of hemiacetal **8** as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 4.11 (s, 1H), 3.32 (s, 1H), 2.75 (m, 1H), 2.63 (m, 1H), 2.42 (m, 2H), 2.10−1.82 (m, 4H), 1.86−1.61 (m, 3H), 0.65 (s, 3H); IR (neat film) 3500−3110, 2936, 2860, 1461, 1375, 1334, 1202, 1085, 1055, 967, 890 cm^{-1}; ^{13}C NMR (500 MHz, $CDCl_3$, δ) 95.7, 86.9, 46.5, 41.0, 39.4, 38.5, 35.4, 32.7, 29.3, 27.4, 21.5; HRMS-EI (m/z) [M$^+$] calcd for $C_{11}H_{16}O_2$ 180.115030, found 180.114861. NOE confirmation can be found in Supporting Information.

Phenyl Adduct 9a: White needle crystals, mp 78−80 °C (86% yield); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 7.33 (m, 5H), 4.91 (d, J = 4.88 Hz, 1H), 4.64 (s, 1H), 3.0 (d, J = 4.83 Hz, 1H), 2.39 (s, 6H), 1.89 (m, 3H), 1.25 (m, 1H), 0.93 (s, 9H), 0.70 (s, 3H), 0.15 (s, 6H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 154.1, 140.9, 128.2, 127.3, 126.8, 97.4, 79.6, 65.8, 10.1, 29.1, 26.5, 25.7, 20.2, 18.0, −4.2, −4.3; IR (neat film) 3500−3000, 1700, 1663, 1653, 1559, 1471, 1370, 1250, 1198, 1184, 909, 881, 851, 830, 777, 702, 668 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{22}H_{37}NO_2Si$ 375.259358, found 375.258719. Crystallographic data can be found in Supporting Information.

Divinylzinc Adduct 10a: Light yellow oil (93% yield); ^{1}H NMR (250 MHz, $CDCl_3$ δ) 5.93 (m, 2H), 5.65 (m, 1H), 5.25 (d, J = 16.0 Hz, 1H), 5.15 (d, J = 9.89 Hz, 1H), 4.19 (d, J = 6.11 Hz, 1H), 2.77 (d, J = 5.35 Hz, 1H), 2.36 (s, 6H), 2.2−1.5 (m, 2H), 1.32 (m, 2H), 0.79 (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 136.5, 131.2, 128.3, 121.4, 116.1, 80.6, 68.4, 38.9, 30.3, 22.4, 22.2, 21.0; IR (neat film) 3700−2800, 2943, 2090, 1654, 1637, 1560, 1459, 1430, 1244, 1056, 1012, 919, 714 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{12}H_{21}NO$ 195.162314, found 195.162137.

Diallylzinc Adduct 11a: Light yellow oil (85% yield); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 5.99 (m, 2H), 5.73 (m, 1H), 5.10 (m, 2 H), 3.54 (dd, J = 2.67, 2.68 Hz, 1H), 2.78 (s, 1H), 2.5−1.9 (m, 9H), 1.71−1.1 (m, 3H), 0.84 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$, δ) 137.4, 132.6, 120.9. 115.9, 65.1, 39.7, 35.6, 29.4, 27.8, 22.7, 22.0, 19.6, 14.1; IR (neat film) 3600−3100, 3018, 2935, 2834, 2788, 2359, 1639, 1463, 1378, 1285, 1097, 1060, 907, 841, 701 cm^{-1}; HRMS-EI (m/z) [M$^+$] calcd for $C_{13}H_{23}NO$ 209.177964, found 209.177669.

Ethyl Adduct 12a and 12s. To 0.67 mL of a freshly prepared 0.5 M solution $ZnCl_2$ was added 0.22 mL (0.67 mmol) of EtMgBr; this was stirred for 2 h at room temperature. Dry dioxane (0.5 mL) was then added, and the mixture was stirred for an additional 1 h before cooling to −30 °C. The aldehyde **2b** (0.022 g, 0.134 mmol) in 0.3 mL of dry ether was then added, at −30 °C, and was maintained at that temperature for 19 h. The reaction was worked-up according to **5a** and subjected to flash chromatography (50% ether/hexanes). A 17 mg quantity of the two diastereomers was isolated, yielding a yellow oil (70%) in a 3.5:1 mixture of **12a** to **12s**: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.99 (m, 1H **s**), 5.97 (m, 1H **a**), 5.66 (m, 1H **s**), 5.65 (m, 1H **a**), 3.48 (d, J = 10.3 Hz, 1H **s**), 3.31 (d, J = 8.42 Hz, 1H **a**), 2.65 (bs, 1H **s**), 2.75 (bs, 1H **a**), 2.31 (s, 6H **s**), 2.30 (s, 6H **a**), 2.00 (m, 2H **s**, 2H **a**), 1.51 (m, 2H **s**, 2H **a**), 1.30 (m, 2H **s**, 2H **a**), 1.03 (m, 3H **s**, 3H **a**), 0.78 (s, 3H **s**), 0.73 (s, 3H **s**); HRMS-CI (m/z) [M + H] calcd for $C_{12}H_{24}NO$ 198.185789, found 198.185773.

Cyclohexyl Adduct 13a and 13s: Light yellow oil (55% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.99 (m, 1H **a**), 5.91 (m, 1H **s**), 5.67 (m, 1H **a**), 5.60 (m, 1H **s**), 3.38 (d, J = 1.78 Hz, 1H **s**), 3.24 (d, J = 2.35 Hz, 1H **a**), 2.80 (m, 1H **a**), 2.59 (d, J = 4.43 Hz, 1H **s**), 2.30 (bs, 6H **a**, 6H **s**), 2.15−1.08 (m, 30H, **a** + **s**), 0.85 (s, 3H **a**), 0.79 (s, 3H **s**); HRMS-CI (m/z) [M + H] calcd for $C_{16}H_{30}NO$ 252.232740, found 252.233033.

2-Methyl-1-propenyl Adduct 14a: Light yellow oil (79% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.97 (m, 1H), 5.68 (m, 1H), 5.31 (d, J = 9.44 Hz, 1H), 4.17 (d, J = 9.48 Hz, 1H), 2.81 (s, 1H), 2.35 (m, 6H), 2.15 (m, 2H), 1.73 (s, 3H), 1.67 (s, 3H), 1.21 (m, 2H), 0.78 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$, δ) 134.6, 131.7, 127.2, 121.7, 75.7, 64.6, 40.4, 30.8, 27.8, 26.2, 22.3, 20.4, 18.6; IR (neat film) 3630−3100, 2965, 2832, 1675, 1450, 1374, 1037, 1021, 842 cm^{-1}; HRMS-CI (m/z) [M$^+$H] calcd for $C_{14}H_{26}$-NO 224.201739, found 224.201235.

Isopropenyl Adduct 15a and 15s: Yellow oil (67% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.95 (m, 1H **a**, 1H **s**), 5.82−5.65 (m, 1H **a**, 1H **s**), 4.97 (m, 1H **a**, 1H **s**), 4.84 (m, 1H **a**, 1H **s**), 4.13 (s, 1H **s**), 4.09 (s, 1H **a**), 2.86 (m, 1H **a**), 2.73 (d, J = 5.40

Hz, 1H **s**), 2.37 (bs, 6H **a**, 6H **s**), 2.26−1.97 (m, 2H **a**, 2H **s**), 1.89 (s, 3H **a**), 1.45 (m, 1H **a**, 1H **s**), 1.27 (m, 1H **a**, 1H **s**), 0.84 (s, 3H **a**), 0.82 (s, 3H s); HRMS-CI (*m*/*z*) [M$^+$H] calcd for $C_{13}H_{24}NO$, 210.185670 found 210.185789.

Crotyl Adduct 16^a: Yellow oil (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.09 (s, 1H), 4.99 (m, 1H), 4.82 (d, J = 5.28 Hz, 1H), 3.36 (s, 1H), 3.05 (d, J = 5.12 Hz, 1H), 2.53 (m, 1H), 2.25 (M, 6H), 1.98 (m, 3H), 1.34 (m, 1H), 1.14 (d, J = 6.96 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$, δ) 154.0, 142.7, 113.7, 98.1, 82.4, 66.5, 40.5, 39.9, 30.1, 27.0, 26.1, 22.4, 21.7, 18.4, −3.9, −4.1; IR (neat film) 3500−3010, 2957, 2929, 2859, 2784, 1666, 1472, 1468, 1388, 1257, 1204, 1013 cm^{-1}; HRMS-CI (*m*/*z*) [M$^+$H] calcd for $C_{20}H_{40}NO_2Si$ 354.28283, found 354.28274. Compound **16^a** was unraveled by the same procedure used in the generation of **6** and **8**: yellow oil (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.91 (d, J = 9.44 Hz, 1H), 5.88 (m, 2H), 5.13 (m, 2H), 3.36 (m, 1H), 2.50 (m, 3H), 2.14 (m, 1H), 1.85 (m, 2H), 1.20 (s, 3H), 1.11 (d, J = 9.44 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$, δ) 199.9, 1.56, 139.9, 128.2, 117.1, 81.4, 40.5, 39.9, 34.6, 31.7, 22.4, 20.5; IR (neat film) 3670−3100, 2963, 2930, 2869, 1668, 1225, 1109, 1011, 910, 803 cm^{-1}; HRMS-CI (*m*/*z*) [M$^+$H] calcd for $C_{12}H_{19}O_2$ 195.13850, found 195.13856.

Hemiacetal 17. The enone above was irradiated for 6 h at 366 nm in 5.0 mL of a 5% solution of methanol in hexanes. A 1.5 mL quantity of the reaction mixture was removed and concentrated in vacuo. The resulting oil was chromatographed using 50% ether/hexane. The starting material **16^a** was recovered in the first few fractions, and the product **17** was isolated as white needle crystals after slow evaporation of the solvent upon standing: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.76 (s, 1H), 2.61 (m, 2H), 2.37 (s, 2H), 2.26−1.67 (m, 7H), 1.11 (d, J = 6.84 Hz, 3H), 0.75 (s, 3H); HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{12}H_{18}O_2$ 194.130680, found 194.130763. Crystallographic data can be found in Supporting Information.

Crotyl Adduct 18^a: Yellow oil (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.56 (s, 1H), 6.13 (m, 1H), 6.07 (m, 1H), 5.65 (m, 1H), 5.02 (m, 2H), 3.36 (s, 1H), 2.93 (s, 1H), 2.55 (M, 1H), 2.30 (s, 3H), 2.08 (m, 2H), 1.93 (m, 1H), 1.36 (m, 1H), 1.15 (d, J = 10 Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$, δ) 142.4, 130.7, 128.6, 120.7, 113.2, 82.3, 65.2, 40.0, 39.9, 29.1, 22.2, 21.9, 21.1; IR (neat film) 3675−3150, 2964, 2931, 2868, 2832, 1635, 1461, 1377, 1017, 903, 842 cm^{-1}; HRMS-CI (*m*/*z*) [M$^+$H] calcd for $C_{14}H_{26}NO$ 224.201439, found 224.201490.

General Procedure for Grignard Additions: Detailed Example Procedure Given for Compound 6^s. Vinyl Adduct 5^s: Light yellow oil (97% yield of **5^a** and **5^s**); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 6.45 (s, 1H), 5.99 (m, 1H), 5.23 (m, 2H), 4.85 (d, J = 5.24 Hz, 1H), 3.92 (d, J = 6.3 Hz, 1H), 2.28 (s, 6H), 1.92−2.01 (m, 3H), 1.31 (m, 1H), 0.925 (s, 9H), 0.874 (s, 3H), 0.152 (s, 6H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 155.7, 137.7, 116.0, 97.9, 65.9, 39.0, 28.4, 26.6, 25.7, 16.7, −3.2, −4.3; IR (neat film) 3450−3120, 2965, 2858, 2830, 2767,1664, 1483, 1369, 1252, 1195, 1164, 1169, 929, 900, 852, 838, 802, 779 cm^{-1}; HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{18}H_{35}NO_2Si$ 325.243708, found 325.243696. See section on **5a** for its spectral data.

Allyl Adduct 7^s: (94% yield of **7^a** and **7^s**). Aldehyde **2a** (0.19 g, 0.64 mmol) was dissolved in 2.1 mL of THF. The mixture was cooled to −78 °C, and 1.28 mL of a 1.0 M solution of allylmagnesium bromide in ether was added dropwise. The reaction mixture was kept at a low temperature until the reaction was judged to be complete by NMR (usually 4−5 h). The reaction mixture was diluted with 5 mL of ether and 3 mL of saturated NH_4Cl at a low temperature. After warming to room temperature, the reaction mixture was diluted with ether and washed three times with water. The organics were dried with anhydrous Na_2SO_4 and concentrated in vacuo to afford the homoallylic alcohol. Purification via flash chromatography (10% TEA/hexanes) yielded 0.2037 g (94%) of pure **7^s** as a light yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$, δ) 5.92 (m, 1H), 5.11 (m, 2H), 4.82 (d, J = 5.94 Hz, 1H), 3.67 (dd, J = 2.56, 2.59 Hz, 1H), 2.80 (d, J = 5.42 Hz, 1H), 1.93−2.45 (m, 1H), 1.40 (m, 1H), 0.92 (s, 9H), 0.78 (s, 3H), 0.14 (s, 6H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 153.7, 137.5, 115.7, 98.7, 78.6, 69.8, 38.9, 35.8, 28.6, 26.5, 25.36, 22.5, 21.7, 17.9, −4.2, −4.4; IR (neat film) 3500−3110, 3095, 2954,2895, 2862, 2858, 2834, 2710, 1664, 1472, 1463, 1366, 1258, 1184, 1060, 996, 906, 883, 852, 800, 778 cm^{-1}; HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{19}H_{37}NO_2Si$ 340.261986, found 340.261746. See section on **7^a** for its pure and complete spectral information.

Phenyl Adduct 9^a: White needle crystals; mp 78−70 °C (99% yield); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 7.33 (m, 5H), 4.91 (d, J = 4.88 Hz, 1H), 4.64 (s, 1H), 3.0 (d, J = 4.83 Hz, 1H), 2.39 (s, 6H), 1.89 (m, 3H), 1.25 (m, 1H), 0.93 (s, 9H), 0.70 (s, 3H), 0.15 (s, 6H); ^{13}C NMR (250 MHz, $CDCl_3$, δ) 154.1, 140.9, 128.2, 127.3, 126.8, 97.4, 79.6, 65.8, 10.1, 29.1, 26.5, 25.7, 20.2, 18.0, −4.2, −4.3; IR (neat film) 3500−3000, 1700, 1663, 1653, 1559, 1471, 1370, 1250, 1198, 1184, 909, 881, 851, 830, 777, 702, 668 cm^{-1}; HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{22}H_{37}NO_2Si$ 375.259358, found 375.258719. Crystallographic data can be found in Supporting Information.

Vinyl Adduct 10^a and 10^s: Light yellow oil (96% yield of a diastereomeric mixture); the major isomer was not separated; ^{1}H NMR (250 MHz, $CDCl_3$ δ) 5.93 (m, 2H **a**, 2H **s**), 5.65 (m, 1H **a**, 1H **s**), 5.25 (d, J = 16.0 Hz, 1H **a,** 1H **s**), 5.15 (d, J = 9.89 Hz, 1H **a**, 1H **s**), 4.19 (d, J = 6.11 Hz, 1H **a**), 3.92 (d, J = 6.31 Hz, 1H **s**), 2.77 (d, J = 5.35 Hz, 1H **a**), 2.65 (d, J = 5.25 Hz, 1H **s**), 2.45 (s, 6H **s**), 2.36 (s, 6H **a**), 2.2−1.5 (m, 2H **a**, 2H **s**), 1.32 (m, 2H **a**, 2H **s**), 0.79 (s, 3H **a,** 3H **s**); HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{12}H_{21}NO$ 195.162314, found 195.162137. See section on **10^a** for its pure and complete spectral information.

Allyl Adduct 11^a and 11^s: Light yellow oil (90% yield of a diastereomeric mixture); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 5.99 (m, 2H **a**, 2H **s**), 5.73 (m, 1H **a**, 1H **s**), 5.10 (m, 2H **a**, 2H **s**), 3.76 (dd, J = 2.72, 2.75 Hz, 1H **s**), 3.54 (dd, J = 2.67, 2.68 Hz, 1H **a**), 2.81 (s, 1H **s**), 2.78 (bs, 1H **a**), 2.5−1.9 (m, 9H **a**, 9H **s**), 1.71−1.10 (m, 3H **a**, 3H **s**), 0.84 (s, 3H **a**, 3H **s**); HRMS-EI (*m*/*z*) [M$^+$] calcd for $C_{13}H_{23}NO$ 209.177964, found 209.177669. See section on **11^a** for its pure and complete spectral information.

Ethyl Adduct 12^a and 12^s: Light yellow oil (65% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.99 (m, 1H **s**), 5.97 (m, 1H **a**), 5.66 (m, 1H **s**), 5.65 (m, 1H **a**), 3.48 (d, J = 10.3 Hz, 1H **s**), 3.31 (d, J = 8.42 Hz, 1H **a**), 2.65 (bs, 1H **s**), 2.75 (bs, 1H **a**), 2.31 (s, 6H **s**), 2.30 (s, 6H **a**), 2.00 (m, 2H **s**, 2H **a**), 1.51 (m, 2H **s**, 2H **a**), 1.30 (m, 2H **s**, 2H **a**), 1.03 (m, 3H **s**, 3H **a**), 0.78 (s, 3H **s**), 0.73 (s, 3H **s**); HRMS-CI (*m*/*z*) [M + H] calcd for $C_{12}H_{24}NO$ 198.185789, found 198.185773.

Cyclohexyl Adduct 13^a and 13^s: Yellow oil (53% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.99 (m, 1H **a**), 5.91 (m, 1H **s**), 5.67 (m, 1H **a**), 5.60 (m, 1H **s**), 3.38 (d, J = 1.78 Hz, 1H **s**), 3.24 (d, J = 2.35 Hz, 1H **a**), 2.80 (m, 1H **a**), 2.59 (d, J = 4.43 Hz, 1H **s**), 2.30 (bs, 6H **a**, 6H **s**), 2.15 (m, 1.08, 15H **a**, 15H **s**), 0.85 (s, 3H **a**), 0.79 (s, 3H **s**); HRMS-CI (*m*/*z*) [M + H] calcd for $C_{16}H_{30}NO$ 252.232740, found 252.233033.

2-Methyl-1-propenyl Adduct 14^a and 14^s: Light yellow oil (71% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.97 (m, 1H **a**), 5.91 (m, 1H **s**), 5.68 (m, 1H **a**), 5.62 (m, 1H **s**), 5.31 (d, J = 9.44 Hz, 1H**a**), 5.29 (d, J = 9.48 Hz, 1H **s**), 4.17 (d, J = 9.48 Hz, 1H**a**), 4.39 (d, J = 9.50 Hz, 1H **s**), 2.81 (s, 1H **a**), 2.71 (s, 1H **s**), 2.35 (m, 3H **a**, 3H **s**), 2.15 (m, 1H **a**, 1H **s**), 1.73 (s, 3H **a**), 1.71 (s, 3H **s**), 1.67 (s, 3H **a**), 1.74 (s, 3H **s**), 1.21 (m, 1H **a**, 1H **s**), 0.78 (s, 3H **a**)**,** 0.66 (s, 3H **s**). See section on **14^a** for its pure and complete spectral information.

Isopropenyl Adduct 15^a and 15^s: Yellow oil (84% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 5.95 (m, 1H **a**. 1H **s**), 5.82−5.65 (m, 1H **a**, 1H **s**), 4.97 (m, 1H **a**, 1H **s**), 4.84 (m, 1H **a**, 1H **s**), 4.13 (s, 1H **s**), 4.09 (s, 1H **a**), 2.86 (m, 1H **a**), 2.73 (d, J = 5.40 Hz, 1H **s**), 2.37 (bs, 6H **a**, 6H **s**), 2.26−1.97 (m, 2H **a**, 2H **s**), 1.89 (s, 3H **a**), 1.45 (m, 1H **a**, 1H **s**), 1.27 (m, 1H **a**, 1H **s**), 0.84 (s, 3H **a**), 0.82 (s, 3H **s**); HRMS-CI (*m*/*z*) [M$^+$H] calcd for $C_{13}H_{24}NO$ 210.185789, found 210.185755.

Crotyl Adduct 16. Three of the above isomers were formed, and the actual assignment was undetermined: yellow oil (68% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.05−5.75 (overlapping m, 4H), 4.89 (overlapping m, 8H), 4.79 (overlapping m, 4H), 3.51−3.35 (overlapping m, 4H), 3.07−2.69 (overlapping m, 4H), 2.58−1.83 (overlapping m, 40H), 1.71−1.15 (overlapping m, 4H) 1.16−1.12 (overlapping

m, 12 H), 0.92 (overlapping m, 18H), 0.83 (overlapping m, 6H), 0.14 (overlapping m, 12H); HRMS-CI *m*/*z* [M^+H] calcd for $C_{12}H_{19}O_2$ 195.13850, found 195.13856.

Crotyl Adduct 18: All four of the isomers were formed, and the actual assignment was undetermined: light yellow oil (81% yield of a diastereomeric mixture); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.13−5.62 (overlapping m,12 H), 4.93 (overlapping m, 8H), 3.60−3.37 (overlapping m, 4H), 2.92−2.51 (overlapping m, 3H), 2.57 (overlapping m, 5H), 2.33 (overlapping m, 24H), 2.06−1.17 (overlapping m, 16H), 1.15 (overlapping m, 12H), 0.84 (overlapping m, 12H). See section on **18a** for its complete spectral information

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Supporting Information Available: NOE data for compounds **6** and **8** and two-dimensional NMR for **8** along with ORTEP diagrams and crystallographic data for compounds **9**[a] and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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