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Dimethylzinc-Promoted Vinylation of Nitrones with Pinacol Vinylboronates: a New Access to Allylic *N*-Hydroxyl Amines.

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Activation of the vinylboronic esters of pinacol (alkenyl-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolanes) with dimethylzinc, allows the nucleophilic addition of the vinyl group onto nitrones, producing allylic *N*-hydroxy-amines in excellent yields.

Introduction

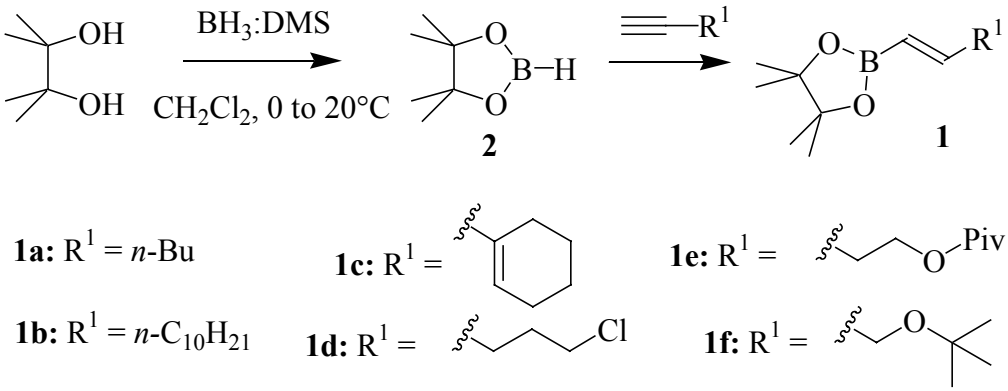
In the course of the preparation of some allylic amines, we recently showed[1] that the vinylic organometallic specie obtained by the hydrozirconation of a terminal alkyne followed by its transmetallation with dialkylzinc, readily adds onto nitrones to produce allylic hydroxylamines. Nevertheless, we thought that an analogous sequence in which hydroboration would replace hydrozirconation, would be advantageous.

The question of the addition of a vinylborane onto a carbonyl group has been first addressed by Brown et al,[2] who proposed the direct reaction of 9-BBN derivatives with aldehydes. The direct reaction of trialkylboranes with nitrones has also been proposed, with medium efficiency.[3,4] Srebnik[5,6] and Oppolzer[7] found than vinylboranes can be transmetallated to vinylzinc species by action of diethylzinc. Then, addition onto aldehydes can be achieved in the presence of various amino-alcohol catalysts.[8] This result could be related to the aryl transfer from a "Ph_3BEt_2Zn" entity proposed by Tamaru.[9] The important studies on the transmetallation of alkylboranes by Knochel's group[10-12] must be mentioned. Another important breakthrough was initiated by Petasis, who proposed[13] a three-component reaction between an amine, formaldehyde, and a vinylboronic acid, to produce an allylic amine. This reaction was extended to other aldehydes, provided that they present a vicinal OH or NH.[14-18]. Activation of esters of vinylboronic acids by KOH[19] or MeLi[20] also allows the transfer of vinyl groups in Rh (resp. Ni)-catalysed reactions.

Our attempts to transpose Oppolzer and Srebnik's methods (resp. from dicyclohexyl-vinylborane and trivinylborane) to nitrones were disappointing, leading to complex mixtures of products. Thus, we considered the use of the vinylboronic ester **1** derived from pinacol (Scheme 1). Such compounds are easily available from pinacolborane **2**.[21-23] **2** hydroborates 1-alkynes readily, and the reaction is compatible with various functional groups.[21] But its major advantage is that the vinylboronate can be handled in air and purified by quick silica chromatography. This avoids the difficulties inherent to the use of a mixture of borane products present in solution after a hydroboration (unreacted starting materials, differently substituted boron atoms).

Results and Discussion

Five vinylboronic esters **1** were prepared using a modified[24] protocol, and chromatographied in yields ranging in our hands from 42 to 57% from **2** (Scheme **1**).



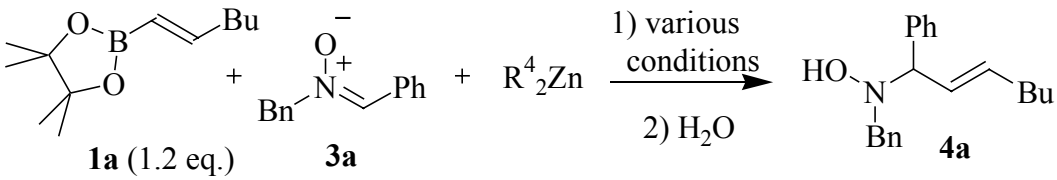
Scheme **1**. Preparation of the vinylboronic esters.

Transmetallation of these reagents with dialkylzinc was not described to the best of our knowledge, although positive results have been obtained from alkylcatecholboranes.[25]

Another important point is that nitrones react very sluggishly with diethylzinc[1] (and trialkylboranes[3,4]). Thus, the vinylboronate can be treated with dialkylzinc with the nitrone electrophile being present (Barbier-like conditions). This trapping in situ avoids problems arising from a possible instability of the new specie.

Reaction of the vinylboronate and a nitrone, promoted by dialkylzinc.

The model reaction of benzyl benzylidene nitrone **3a** (easily available from oxidation of dibenzylamine), vinylboronic ester **1a** (1.2 eq.), and diethyl or dimethylzinc was then checked in various solvents: Table **1**.



Scheme 2. Model reaction.

Table 1. Reaction of vinylboronate **1**, nitrone **3a** and dialkylzinc in various conditions.

Run	Solvent	Temperature	Time	Dialkylzinc (amount, mol/mol nitrone)	Vinyl adduct	Alkyl adduct
1	CH_2Cl_2	r.t.	24h	Et_2Zn(1)	0	0
2	Toluene	r.t	24h	Et_2Zn(1)	traces	7
3	Diethyl ether	r.t	24h	Et_2Zn(1)	11	12
4	THF	r.t.	48h	Et_2Zn(1)	29	29
5	THF	60°C	24h	Me_2Zn(2.5)	66	0
6	Diethyl ether	r.t	48h	Me_2Zn(1)	29	0
7	Diethyl ether	r.t	96h	Me_2Zn(1)	60	0
8	DMF	r.t	48h	Me_2Zn(1.2)	40	0
9	DMF	r.t	48h	Me_2Zn(3)	80	0
10	DMF[(a)]	r.t.	24h	Me_2Zn(3)	86	0
11	DMF	60°C	3.5h	Me_2Zn(1.5)	56	0
12	DMF	60°C	3.5h	Me_2Zn(2)	88	0
13	DMF	60°C	3.5h	Me_2Zn(3)	>95	0
14	DMF	60°C	3.5h	Et_2Zn(3)	60	40
15	DMF	60°C	3.5h	none	no reaction	0
16	DMF	60°C	3.5h	Me_2Zn(1.2)(b)	0[(b)]	4

(a): commercial, undried DMF

(b): run in the absence of vinylboronate

We found that the expected reaction does take place in ether solvents and DMF, slowly at room temperature. Use of diethylzinc led to a mixture of ethyl and vinyl adduct, but this side-reaction could easily be suppressed by replacement with dimethylzinc. The latter did not give detectable adduct, even when present in excess. Traces of methyl adduct could be observed only in a control run in the absence of vinylboronate (run 16). A rather large excess (see runs 11-13) of dimethylzinc is necessary for complete conversion. We selected 2.5 eq. of dimethylzinc in DMF at 60°C as standard conditions for further study. It should be noted that vinyl addition was not observed in the absence of dimethylzinc (run 15). Replacement of dialkylzinc with 2 equivalents of $ZnCl_2$ (NMP, 60°C, 4h) did not produce any vinyl adduct. The 1,3-dipolar cycloaddition[26] was never observed.

The model reaction was repeated in deuterated DMF at 50°C, and evolution was observed by ^{11}B and ^{1}H NMR. The ^{11}B signal (29.6 ppm, 140 Hz wide) of the initial vinylboronic ester slowly disappeared over 3.5h, with simultaneous raise of a new signal (33.5 ppm, 61 Hz wide). In the ^{1}H NMR spectra, the decrease of the signals of dimethylzinc (-0.71 ppm) and vinylboronic ester was synchronous with the increase of two new lines (0.22 ppm, broad singlet for B-Me, and 0.95 ppm,

singlet from pinacol). These new lines are in agreement with literature[27] data for the methylboronic ester (2,4,4,5,5-pentamethyl-[1,3,2]dioxaborolane). The nitrone disappeared at the same rate. Unfortunately, the signals of the adduct in its form of zinc salt were too broad and unreadable.

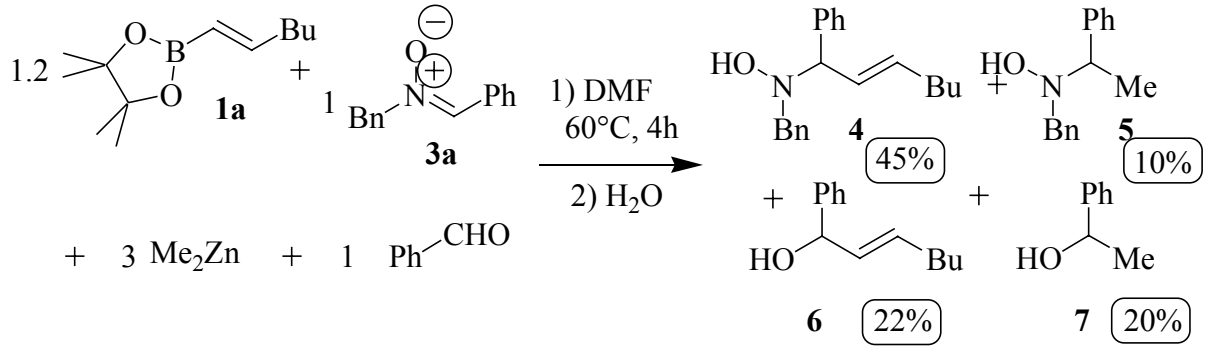
According to these observations, the simplest hypothesis is that the rate-limiting step would be a methyl-vinyl exchange producing Me-Zn-Vinyl, followed by a nucleophilic addition onto the nitrone. Alternatively, there could be a methyl transfer from zinc to boron to produce a "$MeZn^+$ $VinylMe(OR)_2B^-$" complex that would be the reactive intermediate. We are currently investigating this point. Obviously, a globally radical process cannot be ruled out. If it was the case, a good initiation step could be the reaction of dimethylzinc and small amounts of oxygen. Nevertheless, we observed that opening the reaction vessel to room atmosphere after mixing the reagents under nitrogen did not change the rate of the global process.

Reactions with other carbonyl compounds

The above conditions did not lead to any product when applied to simple imines (DMF, 60°C, 24h). As far as aldehydes are concerned, the reaction of **1a**, dimethylzinc and benzaldehyde was more sluggish than with nitrones (DMF, 60°C, 7 to 20h) and led to the expected allylic alcohol. The addition of methyl rests (product **7,** scheme **3**) was observed, in competition with the desired process. We had to use a larger excess of **1a** (2 eq.) to suppress this competing methyl addition. Even so, a complete conversion of the aldehyde into pure vinyl adduct could not be achieved.

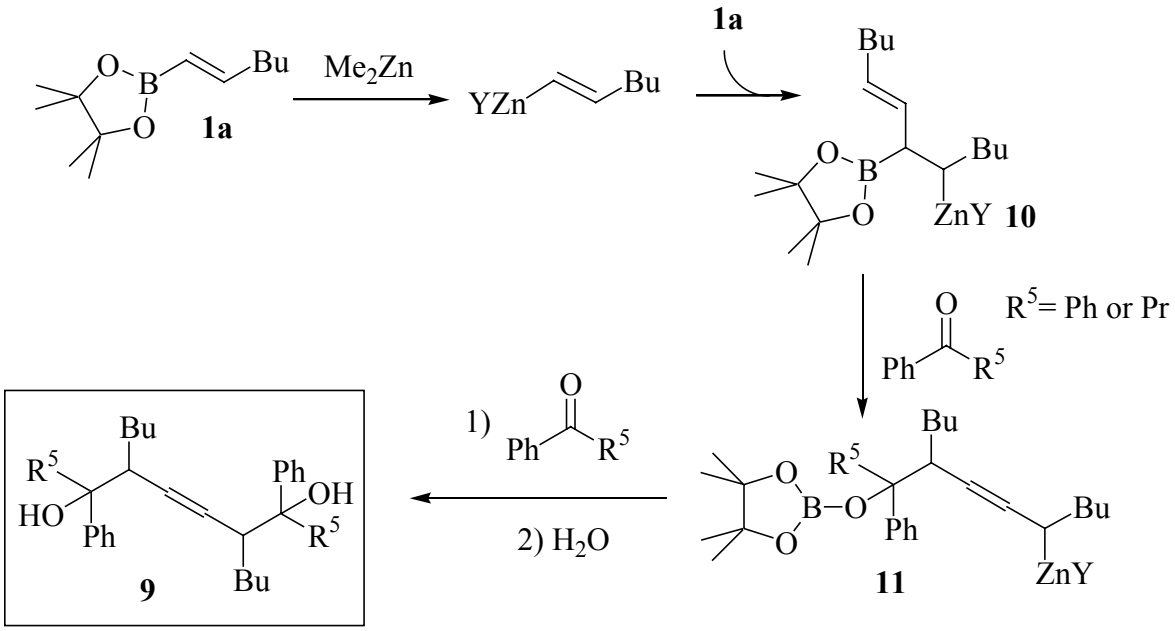
Other aldehydes led to poor isolated yields in vinyl adducts (cinnamaldehyde: 29%, 2-phenylpropanal 28% (d.e. 30%)). It should also be noted that the results did not change in the presence of 5% of Chirald®, a catalyst of the addition of diethylzinc on aldehydes.[28]

In an attempt to compare the reactivity of the nitrone and the aldehyde electrophiles, we designed the competition experiment described in Scheme **3** below. All four possible adducts were recovered, together with unreacted electrophiles. Clearly, the nitrone reacted faster with the vinylic organometallic than the aldehyde. In this run, with the vinylboronic ester in default, methyl addition onto the nitrone (product **5**) was observed in small proportion. It is likely that the formation of **5** took place after all the vinylic specie was consumed.



Scheme 3. Competition between aldehyde and nitrone.

The same reaction was repeated with benzophenone and propiophenone as trapping reagents. In both cases, the expected allyl alcohol was not present in the crude. Instead, we recovered (chromatography, in resp. 50 and 77% yields from ketones) two products of the general formula **9** in Scheme **4** below (as mixtures of isomers; the structure of **9** was ascertaineded by extensive NMR studies and mass spectroscopy). Analogous structures have already been isolated in transmetallation reactions to Cerium.[29,30] We tentatively explain their formation according to the scheme below: after transmetallation, the first vinylzinc specie, unreactive towards a ketone, would carbometallate a second vinylborane to give **10**. The allylic specie **10** could add onto a ketone with allylic transposition to give **11**. The latter is also an allylic organometallic, thus is also able to add onto a second molecule of ketone, leading to **9** on hydrolysis.



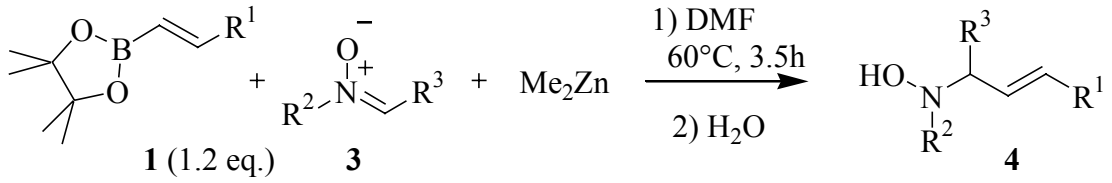
Scheme 4. Reaction with ketones.

These results raise an observation. In studies directed to new preparations of mildly reactive organometallics, *e.g.* dialkylzincs, one generally needs a quenching reaction to prove the presence of the expected specie. It has to be a robust, simple and efficient reaction, rather leading to a new C-C bond. In the dialkylzinc chemistry, uncatalyzed additions to carbonyl groups do not fulfil these conditions.[31] The comparison of nitrones with aldehydes in the present work prompts us to suggest that the addition to nitrones can be a useful tool for such purposes.

Other nitrones and vinylboronic esters.

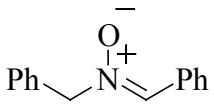
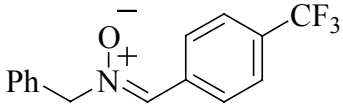
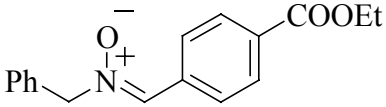
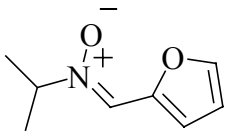
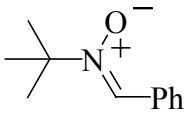
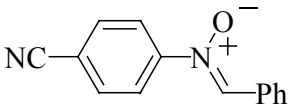
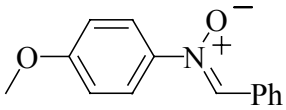
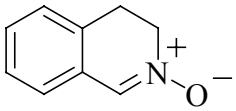
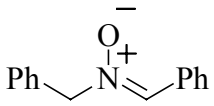
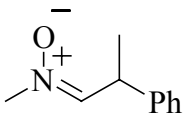
Then, extension to different nitrones and vinylboronates was studied (Table **2**). The reaction proceeds readily with *N*-aryl and *N*-alkyl substituted nitrones, and several functional groups are tolerated on both the nitrone and the vinylic reagents. Poor yields in hydroxylamine in runs 20-23

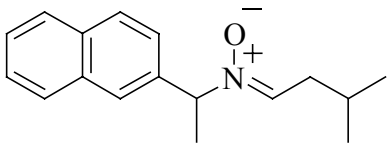
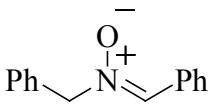
are due to subsequent side-reactions already observed by us.[1] The cyclic nitrone of run 24 led to a mixture of methyl (40% yield) and vinyl (37%) adducts. This is best explained assuming that this nitrone is more reactive towards all organozinc reagents, and thus more prone to non–selective trapping of dimethylzinc.



Scheme 5. Examples of additions to nitrones

Table 2. Addition of vinylboronates onto nitrones in the presence of Me_2Zn

Run	Alkyne: R^1 in **1**	Nitrone **3**	Yield in **4** (%)
17	*n*-Bu		**4a:** 90
18	*n*-Bu		**4b:** 92
19	*n*-Bu		**4c:** 85
20	*n*-Bu		**4d**: 18
21	*n*-Bu		0(a)
22	*n*-Bu		0(a)
23	*n*-Bu		0[a]
24	*n*-Bu		**4e:** 37[b]
25	Oct		**4f:** 92
26	$CH_2CH_2CH_2Cl$	"	**4g:** 91
27	Cyclohexen-1-yl	"	**4h:** 66
38	CH_2CH_2OPiv	"	**4i:** 90[c]
29	*n*-Bu		**4j:** 63 (d.e. 43%)

30	*n*-Bu		**4k:** 56 (d.e. 50%)
31	$CH_2O^{tert}Bu$		**4l:** <14

a) fast reaction, product decomposes

b) Me adduct is present: 40% yield

c) 2 mol. eq. of **1e**, 1hr.

The most disappointing results are summarized in run 31: all attempts to obtain adducts from vinylboronic esters derived from propargylic alcohol derivatives resulted in very poor yields. When run 31 was repeated in a ^{1}H NMR tube in D_7-DMF, we observed the rapid formation of a new vinylic specie that does not react further with the nitrones.

Conclusion

Thus, we found that the reaction of a pinacol vinylboronic ester and a nitrone in the presence of dimethylzinc, leads efficiently to various *N*-allylic hydroxylamines, in good yields. The pinacol esters of boronic acids are an interesting family of boranes because of their stability to air and moisture, easily available from pinacolborane.[21] The present work is the first example of successful transmetallation of members of this family with dialkylzinc.

Experimental Section

Generalities:

All reactions were performed under conventional Schlenk techniques, under dry nitrogen in oven-dried glassware, with magnetic stirring. All reagents were purchased from Aldrich, Acros or Fluka and used as received. Dichloromethane (DCM) was distilled from CaH_2. Diethyl ether and THF were distilled from sodium/benzophenone. Toluene was distilled from sodium. Dimethylformamide (DMF) and *N*-methyl-pyrrolidin-2-one were distillated and stored on 4Å molecular sieves. The reactions were monitored by thin layer chromatography (TLC) using commercial aluminium-

backed silica gel plates (Merck, Kieselgel 60 F_{254}). Forced-flow column chromatography was performed using Macherey-Nagel Silica Gel 60, 230-400 mesh. Infrared (IR) spectra were obtained either as neat films, or as sintered KBr discs. All IR spectra were recorded on a Nicolet Impact-400 FTIR apparatus. ^{1}H NMR (200 or 300 MHz), and ^{13}C NMR (50 or 75 MHz) spectra were run on either a Bruker AC200 or Advance300 spectrometer. All chemical shifts for ^{1}H spectra (ref. tetramethylsilane) are listed according to: chemical shift (ppm), multiplicity, integration, and coupling constants (Hz). Mass spectra were recorded on a ThermoFinnigan PolarisQ ion-trap spectrometer using Chemical Ionisation (ammonia/isobutane 63/37). HRMS and elemental analyses were performed at the Service Central d'Analyse du CNRS, Vernaison, France.

Vinylboronic ester 1e:[24]

Colourless oil. TLC*: Rf* 0.85 (85/15-cyclohexane/ethyl acetate); ^{11}B NMR (96.3 MHz, $CDCl_3$-BF_3-Et_2O) 29.5 ppm, 288 Hz width at half heights); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 1.13 (s, 3H), 1.16 (s, 3H), 3.91 (dd, J=1.8, 3.5 Hz, 2H), 5.64 (dt, 1.8, 8.0 Hz, 1H), 6.60 (dt, J= 3.5, 6.6 Hz, 1H).

General procedure A: reaction of nitrones in DMF

To a mixture of nitrone **(** 0.5 mmol) and vinylborane (0.6 mmol) in 0.50 mL of anhydrous dimethylformamide (DMF), under nitrogen atmosphere, was added dimethylzinc (2 M solution in toluene, 0.625 mL; 1.25 mmol; 2.5 eq.). The mixture was stirred at 60°C for 3.5 hr. Hydrolysis was performed at 20°C by addition of a saturated solution of $NaHCO_3$ (2 mL) and extracted with DCM (3x5 mL). The gathered organic phases were filtered through a pad of silica gel, dried over sodium sulfate and concentrated under reduced pressure. The crude material was chromatographied on silica gel (eluent 90/10 pentane/DCM) to yield the hydroxylamine as a colourless oil. The reaction of the *N,N*-dialkylhydroxylamine with triphenyltetrazolium chloride on the TLC plate[32] provided an efficient diagnosis (strong red colour on gentle heating).

General procedure B: reaction of nitrones in NMP

To a mixture of nitrone **(** 0.5 mmol) and vinylborane (0.6 mmol) in 0.25 mL of anhydrous *N*-methyl-pyrollidinone (NMP), under nitrogen atmosphere, was added dimethylzinc (2 M solution in toluene, 0.625 mL; 1.25 mmol; 2.5 eq.). The mixture was stirred at 60°C for 2h. Hydrolysis was performed at 20°C by addition of a saturated solution of $NaHCO_3$ (2 mL) and extracted with DCM (3x5 mL). The gathered organic phases were dried over sodium sulfate and concentrated under reduced pressure. The crude material was purified by two chromatographies on silica gel. The first one (50/50-cyclohexane/ethyl acetate) eliminated the NMP. The second (90/10 cyclohexane/ethyl acetate) yielded the pure hydroxylamine (colourless oil).

General procedure C: reaction of aldehydes or ketones in DMF

To a mixture of aldehyde **(**0.5 mmol) and vinylborane (1 mmol) in 0.5 mL of anhydrous DMF, under nitrogen atmosphere, was added dimethylzinc (2 M solution in toluene, 0.750 mL; 1.5 mmol; 3 eq.). The mixture was stirred at 60°C for 7 to 20h. Hydrolysis was performed at 20°C by addition of a saturated solution of $NaHCO_3$ (2 mL) and extracted with DCM (3x5 mL). The gathered organic phases were dried over sodium sulfate and concentrated under reduced pressure. Chromatography (90/10 cyclohexane/ethyl acetate) furnished the pure allylic alcool.

N-Benzyl-N-(1-phenyl-hept-2-enyl)-hydroxylamine [1]

Prepared according to procedure A from benzyl-benzylidene-amine *N*-oxide **3a (**0.5 mmol, 105mg) and dioxaborolane **1a** (0.6 mmol, 126mg) in 90% yield (133mg, M=295.4). Colourless oil. TLC*: Rf* 0.52 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$-TMS) δ 0.87 (t, J = 6.8 Hz, 3 H); 1.20-1.45 (m, 4 H); 2.05 (q4, J = 6.7 Hz, 2 H); 3.68 (d, J = 13.7 Hz, 1 H); 3.83 (d, J = 13.4 Hz, 1 H); 4.17 (d, J = 7.9 Hz, 1 H); 5.19 (s, 1 H); 5.64 (dd, J = 6.2, 15.4 Hz, 1 H); 5.80 (dd, J = 7.5, 15.8 Hz, 1 H); 7.15-7.40 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 14.36, 22.71, 29.32, 31.76, 61.50, 75.05, 127.52, 127.60, 128.44, 128.64, 128.91, 129.47 (br),129.82, 135.23, 138.68, 142.36; IR (KBr) 3553, 3240, 3086, 3061, 2955, 2922, 1591, 1502, 1380, 971, 702 cm^{-1}; LRMS (EI, 70eV) *m/z* (%) 295($M^{+\cdot}$, 2),213 (7), 212 (9), 173 (30), 91 (100).

N-Benzyl-N-(1-phenyl-ethyl)-hydroxylamine [33]

Identified as side-product. Colourless oil. TLC*: Rf* 0.64 (85/15-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 1.44 (d, J=6.5 Hz, 3H), 3.69 (bd, J= 13.4 Hz, 1H), 3.72 (d, J= 13.4 Hz, 1H), 3.80 (q, J= 6.6 Hz, 1H), 4.56 (s, OH), 7.15-7.35 (m, 10H).

N-Benzyl-N-(1-phenyl-propyl)-hydroxylamine[1]

Identified as side-product. ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.65 (t, J=7.4 Hz, 3H), 1.64 (ddt, J= 13.5, 9.5, 7.5 Hz, 1H), 2.05 (ddt, J= 13.5, 9.5, 5.0 Hz, 1H), 3.45 (dd, J= 5.0, 9.5 Hz, 1H), 3.45 (d, 13.1 Hz, 1H), 3.60 (d, J=13.1 Hz, 1H), 3.64 (d, J=13.4 Hz, 1H), 3.77 (bd, J=13.4 Hz,1H), 7.15-7.30 (m, 10H).

N-Benzyl-N-[1-(4-trifluoromethyl-phenyl)-hept-2-enyl]-hydroxylamine

Prepared according to procedure B from 138mg (0.5mmol) of benzyl-(4-trifluoromethyl-benzylidene)-amine-*N*-oxide and dioxaborolane **1a** (0.6 mmol, 126mg) in 92 % yield (166 mg). M=363.42. Colourless oil. TLC: R_f 0.63 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.88 (t, J=7.0 Hz, 3H), 1.20-1.45 (m, 4H), 2.12 (td, J=7.6, 6.4 Hz, 2H), 3.70 (d, J=13.4 Hz, 1H), 3.99 (d, J=13.4 Hz, 1H), 4.27 (d, J=7.7 Hz, 1H), 4.66 (bs, OH), 5.65-5.80 (m, 2H),

7.2-7.4 (m, 5H), 7.5-7.7 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 13.85 (CH_3), 22.24 (CH_2), 31.21 (CH_2), 32.17 (CH_2), 61.37 (CH_2), 74.37 (CH), 125.39 (CH), 127.26 (CH), 127.82 (CF_3), 128.12 (CH), 128.18 (CH), 128.30 (CH), 129.09 (CH), 129.26 (CH), 135.74 (CH), 138.05 (C), 146.19 (C); IR (film) 3543, 3445, 3071, 3035, 2964, 2932, 2878, 2857, 1621, 1453, 1421, 1325, 1168, 1129, 1069, 1019, 973, 834, 808, 745, 698 cm^{-1}; LRMS (CI) *m/z* (%) 364 (82), 346 (34), 241 (48), 185 (17), 177 (18), 136 (28), 124 (20), 122 (23), 91 (64), 81, 60 (100). Anal. Calcd. for $C_{21}H_{24}F_3NO$ C: 69.40, H: 6.66, N: 3.85; Fnd. C: 69.66, H: 6.65, N: 3.86.

4-[1-(hydroxy-methyl-amino)-hept-2-enyl]-benzoic acid methyl ester

Prepared according to procedure B from 97 mg (0.5 mmol) of 4-methyliminomethyl-benzoic acid methyl ester *N*-oxide and dioxaborolane **1a** (0.6 mmol, 126mg) in 85 % yield (118 mg) ; M=277.36. Colourless oil. TLC: R_f 0.46 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.86 (t, J=7.0 Hz, 3H), 1.15-1.40 (m, 5H), 2.12 (td, J=6.9, 6.3 Hz, 2H), 2.58 (s, 3H), 3.90 (s, 3H), 4.03 (d, J=7.9 Hz, 1H), 5.55-5.80 (m, 2H), 7.41 (d, J=8.2 Hz), 7.99 (d, J=8.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 13.82 (CH_3), 22.15 (CH_2), 31.11 (CH_2), 32.08 (CH_2), 45.85 (CH_3), 52.01 (CH_3), 77.28 (CH), 127.80 (CH), 128.71 (C), 129.03 (C), 128.85 (CH), 135.25 (CH), 147.15 (C), 166.92 (C); IR (film) 3465, 3189, 3039, 2999, 2960, 2931, 2876, 2861, 1721, 1669, 1615, 1460, 1434, 1417, 1284, 1185, 1116, 1022, 976, 772, 714 cm^{-1}; LRMS (CI) *m/z* (%) 278 (MH^+ (38), 360 (24), 231 (100); Anal. Calcd. For $C_{16}H_{23}NO_3$ C: 69.29, H: 8.36, N: 5.05; Fnd. C: 69.38, H: 8.34, N: 5.04.

***N*-(1-Butyl-3-furan-2-yl-allyl)-*N*-isopropyl-hydroxylamine**

Prepared according to procedure B from 77 mg (0.5 mmol) of isopropyl-2-furylidene-amine-*N*-oxyde and dioxaborolane **1a** (0.6 mmol, 126mg). Usual work-up produced a crude material that, on ^{1}H-NMR, was a mixture of *N*-(1-furan-2-yl-hept-2-enyl)-*N*-isopropyl-hydroxylamine and *N*-(1-butyl-3-furan-2-yl-allyl)-*N*-isopropyl-hydroxylamine **4g**. Silica gel column chromatography (75/25 cyclohexane/ethyl acetate) furnished solely the rearranged *O*-alkylated product **4g** in 18 % yield (21 mg); Colourless oil. TLC: R_f 0.46 (50:50-cyclohexane:ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ compound **4g**, 0.81 (t, J=6.8 Hz, 3H), 0.95 (d, J=6.3 Hz, 3H), 1.07 (d, J=6.3 Hz, 3H), 1.15-1.30 (m, 4H+OH), 1.40-1.55 (m, 1H), 1.70-1.85 (m, 1H), 3.02 (h7, J=6.3 Hz, 1H), 3.26 (dt, J=4.5, 9.0 Hz, 1H), 6.10 (dd, J= 9.1, 16.0 Hz, 1H), 6.07 (d, J=3.3 Hz, 1H), 6.22 (d, J=16.0 Hz, 1H), 6.29 (dd, J=1.9, 3.3Hz, 1H), 7.26 (d, J=1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 13.84, 20.33, 20.38, 22.65, 28.41, 32.57, 53.78, 66.15, 107.19, 111.16, 120.74, 127.56, 141.69, 152.57; LRMS (CI) *m/z* (%) 236 (100), 220 (30), 177 (29), 163 (80), 124 (14), 110 (8).

1-Hex-1-enyl-3,4-dihydro-*1H*-isoquinolin-2-ol[34]

Prepared according to procedure B from 74 mg (0.5mmol) of 3,4-dihydro-isoquinoline-*N*-oxyde and dioxaborolane **1a** (0.6 mmol, 126mg) at 60°C for only 1h. On TLC (50/50 cyclohexane/ethyl acetate) the reaction was complete in 30 min. Chromatography produced 28mg (37% yield) of allylic hydroxylamine and 33mg of methyl adduct (40 % yield). Colourless oils. TLC: R_f 0.57 resp. 0.26 (50/50-cyclohexane/ethyl acetate);

Vinyl adduct: M= 231. ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.92 (t, J=7.03 Hz, 3H), 1.2-1.5 (m, 4H+OH), 2.15 (q4, J=6.5Hz, 2H), 2.81-2.95 (m, 1H), 2.95-3.15 (m, 2H), 3.40-3.55 (m, 1H), 4.28 (bd, J=8.2 Hz, 1H), 5.51 (dd, J=8.2, 15.1 Hz, 1H), 5.78 (dt, J=15.3, 6.7 Hz), 7.05-7.20 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 13.92, 22.31, 28.28, 31.42, 32.14, 53.45(br, CH_2-N), 71.40 (br, CH-N), 125.87, 126.55, 127.94,128.12, 129.73 (br, N-CH-CH=), 133.26, 135.85, 136.98 (=CH-Bu). IR (film) 3219, 3068, 3026, 2956, 2929, 2863, 1629, 1464, 752 cm^{-1}; LRMS (CI) *m/z* (%) 232 (6), 231 (19), 214 (12), 172 (25), 148 (80), 129 (100).

Methyl adduct M= 163. ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 1.50 (d, J= 6.7 Hz,3H), 2.75-3.10(m, 3H), 3.30-3.45 (m, 1H), 3.90 (br, 1H), 6.95-7.10 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 19.88 (br), 27.79 (br), 53.47 (br), 63.17 (br), 126.13, 126.27, 126.50, 128.20, 133.01, 138.10; IR (film) 3259, 3075, 2966, 2937, 2849, 1650, 1455, 737 cm^{-1}; LRMS (CI) *m/z* (%) 165 (7), 164 (57), 163 (12), 162 (100), 159 (17), 160 (22), 148 (19), 146 (26), 144 (12).

***N*-Benzyl-*N*-(1-phenyl-tridec-2-enyl)-hydroxylamine**

Prepared according to procedure A from benzyl-benzylidene-amine *N*-oxide (211mg, 1mmol) and dioxaborolane **1b** (1.2 mmol, 319 mg) in 91% isolated yield (346mg, M= 379.3). Colourless oil. TLC*: Rf* 0.33 (90/10 ether/pentane); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.79 (t, J=6.5 Hz, 3H), 1.05-1.35 (m, 16H), 1.97 (q, J=6.9 Hz, 2H), 3.61(d, J=13.4 Hz, 1H), 3.77 (br d, J=13.3 Hz, 1H), 4.10(d, J=8.2 Hz, 1H), 4.93 (bs, 1H), 5.58(dt, J=6.3, 15.5 Hz, 1H), 5.67 (dd, J= 8.1, 15.8 Hz, 1H), 7.10-7.35 (m, 10H) ; ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 14.27, 22.85, 29.32, 29.37, 29.51, 29.62, 29.78(2C), 32.08, 32.68, 61.24, 74.76, 127.22, 127.29, 128.17, 128.34, 128.62, 129.23, 129.52, 134.95, 138.52, 142.11; IR (KBr) 3543, 3249, 3025, 2917, 2840, 1461, 1069, 1037, 960, 914, 743 cm^{-1}; LRMS (DCI) *m/z* (%) 380 (MH^+ (100), 362 $(M-OH)^+$ (18), 257 (51). HRMS (DCI) Calcd for $C_{26}H_{38}NO$: 380,2953; Fnd 380.2975

***N*-Benzyl-*N*-(3-cyclohex-1-enyl-1-phenyl-allyl)-hydroxylamine**

Prepared according to procedure A from benzyl-benzylidene-amine *N*-oxide (211mg, 1mmol) and dioxaborolane **1c** (282 mg, 1.2mmol), in 66% yield (209mg, M= 319.4) Colourless oil. TLC*: Rf* 0.60 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 1.45-1.55 (m, 4H), 1.95-2.15 (m, 4H), 3.6 (d, J=13.8 Hz, 1H), 3.86 (d, J= 13.8 Hz, 1H), 4.22 (d, J=8.7Hz, 1H), 4.49 (s, OH), 5.65-5.80 (m, 2H), 6.17 (d, J=15.8 Hz, 1H), 7.10-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$-

TMS) δ 22.53, 22.60, 24.74, 26.01, 61.46, 75.64, 125.17, 127.19, 127.37, 128.01, 128.35, 128.74, 129.32, 130.16, 135.42, 136.66, 138.70, 142.16; IR (KBr) 3518, 3437, 3216, 3055, 3025, 2922, 2863, 2238, 1957, 1498, 1453, 1022, 971, 905 cm^{-1}; LRMS (DCI) *m/z* (%) 320 $(MH^+$ (3), 302 $(M-OH)^+$ (7), 214 (8), 197 (100). HRMS (DCI) Calcd for $C_{22}H_{26}NO$: 320,2014 ; Fnd 320,2070

***N*-Benzyl-*N*-(6-chloro-1-phenyl-hex-2-enyl)-hydroxylamine**

Prepared according to procedure A from benzyl-benzylidene-amine *N*-oxide (211mg, 1mmol) and dioxaborolane **1d** (1.2 mmol, 242 mg) in 90% isolated yield (284mg, M= 315.8).Colourless oil. TLC*: Rf* 0.75 (50/50-cyclohexane/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$-TMS) δ 1.73 (q_5, J= 6.9Hz, 2H), 2.11 (q_4, 7.1Hz, 2H), 3.36 (t, J=6.6 Hz, 2H), 3.59 (d, J=13.3 Hz, 1H), 3.68 (br d, J= 13.3 Hz, 1H), 4.08 (d, J=8.6 Hz, 1H), 5.11 (s, OH), 5.51 (dt, J=6.4, 15.4 Hz, 1H), 5.77 (dd, J=8.6, 15.4 Hz, 1H), 7.10-7.30 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 29.65... 31.91, 44.38, 61.19, 74.42, 127.24, 127.40, 128.13, 128.33, 128.62, 129.44, 130.89, 132.32, 138.23, 141.62; IR (KBr) 3535, 3453, 3232, 3060, 3030, 2930, 1950, 1595, 1495, 1455, 1305, 970 cm^{-1}; LRMS (DCI) *m/z* (%) 319 (8), 318 (30), 317 (24), 316 (88), .196 (4), 195 (32), 194 (14), 193 (100). Anal. Calcd. for $C_{19}H_{22}ClNO$ C: 72.25, H: 7.02, N: 4.43; Fnd. C: 72.51, H: 7.03, N: 4.45.

2,2-Dimethyl-propionic acid 5-(benzyl-hydroxy-amino)-5-phenyl-pent-3-enyl ester

Prepared according to procedure B from 42 mg (0.2 mmol) of benzyl-benzylidene amine *N*-oxide and dioxaborolane **1e** (0.4 mmol, 68 mg), in 90 % yield (66 mg; M=367.49). Colourless oil. TLC: *Rf* 0.61 (50:50-cyclohexane:ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$-TMS) δ 1.11 (s, 9H), 2.38 (q4, J=6.6Hz, 2H), 3.71 (d, J=13.6 Hz, 1H), 3.87 (d, J=13.6 Hz, 2H), 4.09 (t, J=6.4 Hz, 1H), 4.22 (d, J=8.4 Hz, 1H), 4.93 (s, OH), 5.65 (dt, J=6.7, 15.6Hz, 1H), 5.87 (dd, J=8.3,15.6Hz, 1H), 7.20-7.40 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 27.06, 31.89, 38.60, 61.14, 63.30, 74.54, 127.04, 127.91, 128.15, 128.49, 129.19, 129.44, 132.12, 138.20, 141.43, 178.43; IR (film) 3469, 3108, 3088, 3064, 3030, 2974, 2935, 2906, 2873, 1950, 1884, 1805, 1726, 1601, 1495, 1481, 1456, 1398, 1368, 1286, 1158, 1029, 968, 739, 698 cm^{-1}; LRMS (CI) *m/z* (%) 368 (26), 350 (22), 302 (2), 262 (3), 248 (5), 143 (100).

N-Methyl-N-[1-(1-phenyl-ethyl)-hept-2-enyl]-hydroxylamine

Prepared according to procedure A from methyl-(2-phenyl-propylidene)-amine *N*-oxide (163mg, 1mmol) and dioxaborolane **1a** (250mg, 1.2mmol), in 50% isolated yield (120mg, M= 247). Colourless oil. TLC*: Rf* 0.78 (50/50-cyclohexane/ethyl acetate; diastereoisomers unresolved). The diastereoisomeric excess (43%) was measured by NMR.

Major isomer ^1H NMR (300 MHz, $CDCl_3$-TMS) δ 0.80 (t, J=7.2 Hz, 3H), 1.05-1.40 (m, 4H), 1.33 (d, 7.1 Hz, 3H), 1.85-1.95 (m, 2H), 2.58 (s, 3H), 2.98 (t, J= 8.4 Hz, 1H), 3.14 (q_5, J = 6.0 Hz, 1H), 5.16 (dd, J= 9.0, 15.4 Hz, 1H), 5.30 (dt, J= 15.6, 6.7 Hz), 7.0-7.3 (m, 5H); ^{13}C NMR (75 MHz,

$CDCl_3$-TMS) δ 13.79, 19.43, 21.82, 31.29, 32.00, 41.71, 45.70, 76.57, 124.97, 125.94, 127.93, 128.32, 136.57, 144.55.

Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.88 (t, J= 7.0 Hz, 3H), 1.05-1.40 (m, 4H), 1.20 (d, J= 7.0 Hz, 3H), 2.0-2.10 (m, 2H), 2.51 (s, 3H), 3.04 (t, J= 8.0 Hz, 1H)1H, 3.14 (q_5, J = 6.0 Hz, 1H), 5.38-5.45 (m, 2H), 7.0-7.3 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 13.79, 19.43, 22.15, 31.48, 32.22, 41.48, 45.70, 76.84, 124.85, 125.94, 127.72, 128.11, 136.83, 145.68.

(1-Isobutyl-hept-2-enyl)-(1-naphthalen-1-yl-ethyl)-amine

Obtained according to procedure A from 255mg (1.0mmol) of nitrone and dioxaborolane **1a** (250mg, 1.2mmol), in 56% yield (188 mg, M=339.5). Colourless oil. TLC*: Rf* 0.50 (50/50-cyclohexane/ethyl acetate).The product was dissolved in a 4/1 mixture of acetic acid/water and stirred at r.t. with 721 mg of Zinc dust overnight. The suspension was filtered, concentrated, taken in ethyl acetate, washed with 2x1ml of a saturated $NaHCO_3$ solution. Measurement of the d.e. was accomplished by HPLC: column Kromasil C18, 250x 4.6 mm, UV detection 218nm, eluent acetonitrile/water 95/5, 2ml/mn, major peak 11.7 min, minor 13.7mn. NMR of major isomer: ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.72 (J= 6.5Hz, 3H), 0.77 (d, J= 6.6Hz, 3H), 0.98 (m, 3H), 1.2-1.4 (m, 4H), 1.49 (d, J= 6.8 Hz, 3H), 1.9-2.0 (m, 2H), 2.8-2.95 (m, 1H), ; 4.84 (q, J= 6.6 Hz, 1H), 5.03 (dt, J= 15.4, 6.6 Hz, 1H), 5.22 (bdd, J= 15.2, 8.8 Hz, 1H), 7.4-8.85 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 14.07, 22.35, 22.39, 23.13, 24.26, 24.74, 32.10, 32.16, 45.32, 49.94, 56.68, 122.91, 122.79, 125.68, 125.30, 127.21, 128.88, 131.40, 131.21, 132.63, 132.51, 133.92, 140.23 LRMS (DCI) *m/z* (%) 338 (14), 325 (21), 324 (100), 323 (8), 322 (21), 266 (12), 186 (22), 155 (27) $(MH^+$ (3), 302 $(M\text{-}OH)^+$ (7), 214 (8), 197 (100). HRMS (DCI) Calcd for $C_{23}H_{34}N$ 324.2691; Found 324.256

Reactions with aldehydes

1-phenyl-ethanol

Isolated as side-product. TLC*: Rf* 0.19 (50:50-cyclohexane:ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$-TMS) δ 1.42 (d, J= 6.5 Hz, 3H), 1.7 (OH), 4.83 (q4, J=6.5 Hz, 1H), 7.1-7.3 (m, 5H).

1-Phenyl-hept-2-en-1-ol[35] [2]

Prepared according to procedure C from 420 mg (2mmol) of dioxaborolane **1a**, 3 mmol (1.5 ml) of dimethylzinc in toluene, and 106 mg (1 mmol) of benzaldehyde, in 89% yield. Colourless oil. TLC*: Rf* 0.55 (90:10 Pentane:CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$-TMS) δ 0.88 (t, J=7.1 Hz, 3H), 1.2-1.45 (m, 4H), 1.95-2.15 (m, 2H), 5.15 (d, J=6.0Hz, 1H), 5.66 (dd, J=5,5, 14.4 Hz, 1H), 5.73 (dd, J=5.7, 14.3 Hz, 1H), 7.2-7.4 (m, 5H).

1-Phenyl-pentadeca-1,4-dien-3-ol

Prepared according to procedure C from 294 mg (1mmol) of dioxaborolane **1b**, 1.6 mmol (0.8 ml) of dimethylzinc in toluene, and 70 mg (0.5 mmol) of cinnamaldehyde, in 29% yield. Colourless oil. TLC*: Rf* 0.6 (90:10 Pentane:CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.88 (t, J=6.5 Hz, 3H), 1.10-1.50 (m, 16H), 1.47 (bs, OH), 2.05 (q, J= 6.9Hz, 2H), 4.75 (t, J= 6.4Hz, 1H), 5.56 (ddt, J= 6.5, 15.4, 1.3 Hz, 1H), 5.64 (bdt, 15.5, 6.6 Hz, 1H), 6.25 (dd, J= 6.2, 15.9 Hz, 1H), 6.58 (d, J= 15.7 Hz, 1H)7.20-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$-TMS) δ 14.27, 22.85, 29.25, 29.39, 29.51, 29.66, 29.78 (+ unresolved lines), 32.08, 32.44, 73.83, 139.02, 124.71, 136.73, 133.04, 131.15, 130.96, 130.11, 128.49, 127.58, 126.48; IR (KBr): 3354, 3028, 2920, 2849, 1592, 1469 cm^{-1}; LRMS (DCI) *m/z* (%) 299 (5), 285 (21), 283 (100), 282 (12), 257 (5), 143 (9); Anal. Calcd. for $C_{21}H_{32}O$ C: 83,94; H: 10,73; found C:84.04; H: 11.11.

2-Phenyl-non-4-en-3-ol[36,37]

Prepared according to procedure C from 210 mg (1 mmol) of dioxaborolane **1a**, 1.6 mmol (0.8ml) of dimethylzinc in toluene, and 67 mg (0.5 mmol) of (rac.) 2-phenyl-propanal, in 28% yield (diastereoisomers not separated). Colourless oil.

Major isomer (erythro[38]) TLC*: Rf* 0.52 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.84 (t, J= 7.3 Hz, 3H); 1.31 (d, J= 7.0 Hz, 3H), 1.15-1.40 (m, 4H), 1.53 (bs, OH), 1.97 (bq, J= 6.9Hz, 2H), 2.87 (q_5, J= 6.8 Hz, 1H), 4.15 (bt, J= 6.2 Hz, 1H), 5.37 (ddt, J= 6.8, 14.1, 2.7 Hz, 1H), 5.52 (ddt, J=0.9, 15.4, 6.8 Hz), 7.15-7.40 (m, 5H).

Minor Isomer TLC*: Rf* 0.58 (50/50-cyclohexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$-TMS) δ 0.89 (t, J= 7.5 Hz, 3H); 1.22 (d, J= 7.5 Hz, 3H), 1.15-1.40 (m, 4H), 1.45 (bs, OH), 2.10 (bq, J= 6.7 Hz, 2H), 2.66 (q_5, J= 7.3 Hz, 1H), 4.08 (bt, J= 7.7 Hz, 1H), 5.46 (ddt, J= 7.6, 15.4, 1.4 Hz), 5.69 (ddt, J= 0.8, 6.8, 15.4 Hz), 7.15-7.40 (m, 5H).

Reactions with ketones

2,5-dibutyl-1,1,6,6-tetraphenyl-hex-3-ene-1,6-diol [30]

Prepared according to procedure C from 210 mg (1 mmol) of dioxaborolane **1a**, 1 mmol (0.5 ml) of dimethylzinc in toluene, and 91mg (0.5 mmol) of benzophenone. Chromatography yielded 88 mg of a compound that was identified on the basis of mass spectrum and NMR experiments. Colourless oil. Yield for $C_{38}H_{44}O_2$, M =532: 66%. ^{1}H NMR (300 MHz, $CDCl_3$-TMS) d 0.82 (t, 6H), 0.8-.095 (m, 2H, d), 1.05-1.45 (m, 4H, e,f), 1.60-1.75 (m, 2H, d'), 3.58 (bq$_5$; Jab≈9.0 Hz; Ja'b≈-1.0Hz, 2H, b), 4.14 (s, OH), 6.02 (m, Jaa'≈15Hz, 2H, a), 7.1-7.4 (m, 20H). ^{13}C NMR (75.5 MHz, $CDCl_3$-TMS) δ 14.29(g), 23.31(f), 31.12(e), 33.01(d), 46.16(b), 81.22(c), 127.09, 127.32, 127.69, 128.21, 128.58, 129.09, 133.91(a), 143.47, 146.65 (structure and attributions are in agreement with COSY and H-to-C-correlations). IR (KBr): 3358, 3076, 3031, 2960, 2935, 2864, 1494, 1463, 969, 758, 702 cm^{-1};

LRMS (CI) m/z (%) 533 (1), 498 (30), 497 (100, $C_{38}H_{41}^{+}$), 391 (5), 279 (7), 249 (13). MS^2 of ion 497: 419 (86), 349(80), 249 (100).

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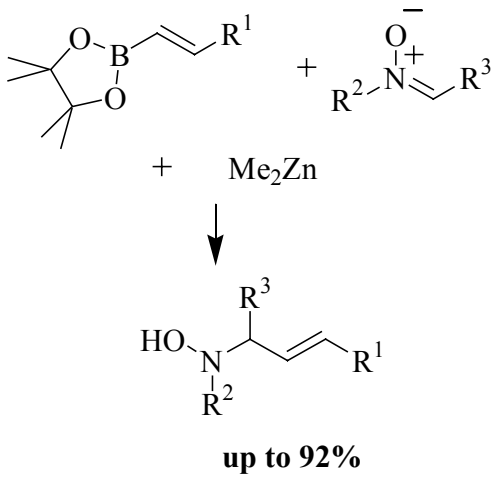
Graphical Abstract



Dimethylzinc activates pinacol vinylboronates for vinyl transfer to C=N and C=O bond.

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