Dimethylzinc-Promoted Vinylation of Nitrones with Vinylboronic Esters of Pinacol: A New Route to *N*-Allylic Hydroxylamines

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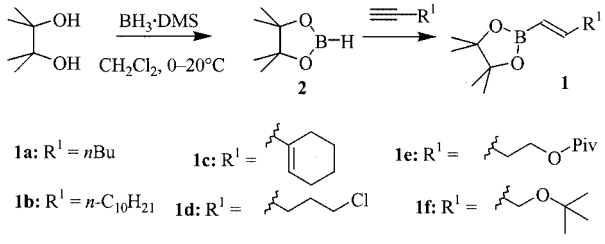
Activation of vinylboronic esters of pinacol (alkenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes) with dimethylzinc allows nucleophilic addition of the vinyl group onto nitrones, producing *N*-allylic hydroxylamines in excellent yields.

Introduction

In the course of the preparation of some allylic amines, we recently showed[1] that the vinylic organometallic species 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 the hydrozirconation was replaced by hydroboration would be advantageous.

The question of the addition of a vinylborane onto a carbonyl group was first addressed by Brown et al,[2] who proposed direct reactions between 9-BBN derivatives and aldehydes. Trialkylboranes react directly with nitrones, with medium efficiency.[3,4] Srebnik[5,6] and Oppolzer[7] found that vinylboranes can be transmetallated to vinylzinc species by the action of diethylzinc, addition onto aldehydes then being achievable 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] while the important studies on the transmetallation of alkylboranes by Knochel's group[10–12] should also 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 could be extended to other aldehydes, provided that they present a vicinal OH or NH group.[14–18] The activation of esters of vinylboronic acids by KOH[19] or MeLi[20] also allows the transfer of vinyl groups in Rh- (or Ni-) catalysed reactions.

Our attempts to adapt Oppolzer's and Srebnik's methods [from dicyclohexyl(vinyl)borane and trivinylborane, respectively] to nitrones were disappointing, producing complex mixtures of products. We therefore considered the use of the vinylboronic ester **1**, derived from pinacol (Scheme 1). Such compounds are easily available from boronic ester **2**.[21–23] This latter compound readily hydroborates 1-alkynes, and the reaction is compatible with the presence of various functional groups.[21] Its major advantage, however, is that the vinylboronate can be handled in air and purified by silica chromatography, avoiding the difficulties inherent in the use of a mixture of borane products present in solution after a hydroboration (unchanged starting materials, differently substituted boron atoms).



Scheme 1. Preparation of the vinylboronic esters

Results and Discussion

Six vinylboronic esters **1** were prepared by a modified[24] procedure and chromatographed, in yields from **2** ranging in our hands from 42 to 57% (Scheme 1).

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

Another important point is that nitrones react very sluggishly with diethylzinc[1] (and trialkylboranes[3,4]). The vinylboronate can therefore be treated with dialkylzinc in the presence of the nitrone electrophile (Barbier-like con-

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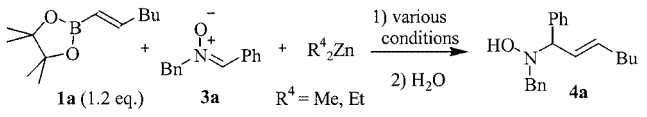
ditions). This trapping in situ avoids problems arising from possible instability of the new species.

Dialkylzinc-Promoted Reaction between the Vinylboronate and a Nitrone

The model reaction between the benzyl benzylidene nitrone (**3a**) (easily available from oxidation of dibenzylamine), the vinylboronic ester **1a** (1.2 equiv.) and diethyl- or dimethylzinc was examined in various solvents (Table 1).



Scheme 2. Model reaction

We found that the expected reaction does take place, although slowly, at room temperature in diethyl ether and DMF as solvents. The use of diethylzinc gave a mixture of vinyl and ethyl adducts, but the side-product was suppressed by replacement with dimethylzinc. This reagent did not give a detectable adduct, even when present in excess, traces of methyl adduct being observed only in a control run in the absence of vinylboronate (Entry 16, Table 1). A rather large excess (see Entries 11−13, Table 1) of dimethylzinc is necessary for complete conversion. As standard conditions for further study, we selected 2.5 equiv. of dimethylzinc in DMF at 60 °C. Note that vinyl addition was not observed in the absence of dimethylzinc (Entry 15, Table 1). The replacement of dialkylzinc with 2 equiv. of $ZnCl_2$ (NMP, 60 °C, 4 h) did not produce any vinyl adduct. No 1,3-dipolar cycloaddition[26] was ever observed.

The model reaction was repeated in deuterated DMF at 50 °C, and its progress was monitored by ^{11}B and ^{1}H NMR spectroscopy. The ^{11}B signal of the initial vinylboronic ester (δ = 29.6 ppm, 140 Hz wide) slowly disappeared over 3.5 h, with the simultaneous appearance of a new signal (δ = 33.5 ppm, 61 Hz wide). In the ^{1}H NMR spectra, the disappearance of the signals of dimethylzinc (δ = −0.71 ppm) and vinylboronic ester was synchronous with the appearance of two new lines (δ = 0.22 ppm, broad singlet for B−Me, and δ = 0.95 ppm, singlet for pinacol). These new lines are consistent 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 a zinc salt were broad and unreadable.

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

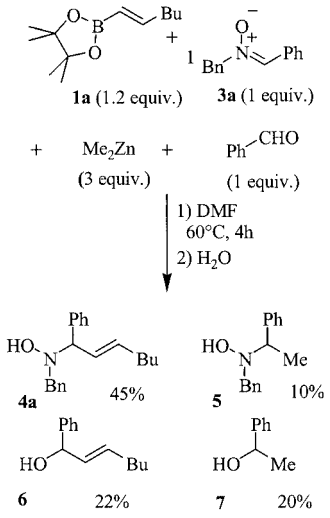
Reactions with Other Carbonyl Compounds

The above conditions did not afford any product when applied to simple imines (DMF, 60 °C, 24 h). As far as aldehydes are concerned, the reaction between **1a**, dimethylzinc and benzaldehyde was more sluggish than with nitrones (DMF, 60 °C, 7−20 h) and afforded the expected allylic alcohol **6**. The addition of methyl residues (product **7**, Scheme 3) competed with the desired process, and we had to use a larger excess of **1a** (2 equiv.) to suppress this methyl adduct. Even so, no complete conversion of the aldehyde into pure vinyl adduct could be achieved.

Table 1. Reaction between vinylboronate **1**, nitrone **3a** and dialkylzinc under various conditions

Entry	Solvent	Temp.	Time [h]	Dialkylzinc (amount [mol/mol nitrone])	Vinyl adduct	Alkyl adduct
1	CH_2Cl_2	room temp.	24	Et_2Zn (1)	0	0
2	Toluene	room temp.	24	Et_2Zn (1)	traces	7
3	Et_2O	room temp.	24	Et_2Zn (1)	11	12
4	THF	room temp.	48	Et_2Zn (1)	29	29
5	THF	60 °C	24	Me_2Zn (2.5)	66	0
6	Et_2O	room temp.	48	Me_2Zn (1)	29	0
7	Et_2O	room temp.	96	Me_2Zn (1)	60	0
8	DMF	room temp.	48	Me_2Zn (1.2)	40	0
9	DMF	room temp.	48	Me_2Zn (3)	80	0
10	DMF[a]	room temp.	24	Me_2Zn (3)	86	0
11	DMF	60 °C	3.5	Me_2Zn (1.5)	56	0
12	DMF	60 °C	3.5	Me_2Zn (2)	88	0
13	DMF	60 °C	3.5	Me_2Zn (3)	> 95	0
14	DMF	60 °C	3.5	Et_2Zn (3)	60	40
15	DMF	60 °C	3.5	none	0	0
16	DMF	60 °C	3.5	Me_2Zn (1.2)[b]	0[b]	4

[a] Commercial, undried DMF. [b] Run in the absence of vinylboronate.

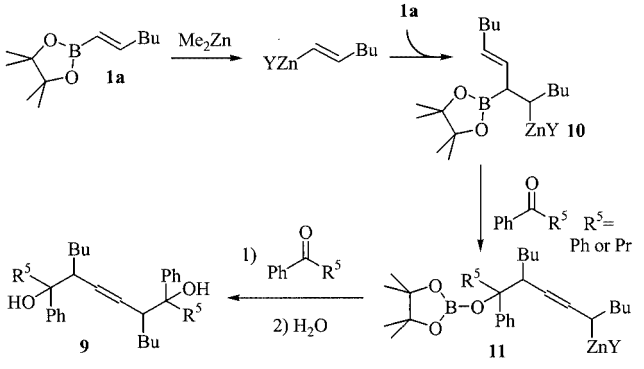


Scheme 3. Competition between aldehyde and nitrone

Other aldehydes gave poor isolated yields of vinyl adducts [**6b** from cinnamaldehyde: 29%; **6c** from 2-phenylpropanal: 28% (30% *de*)]. Note that the results did not change in the presence of 5% of Chirald®, a catalyst for the addition of diethylzinc to aldehydes.[28]

In an attempt to compare the reactivities of the nitrone and the aldehyde electrophiles, we designed the competition experiment described in Scheme 3. All four possible adducts were recovered, together with unchanged electrophiles. Clearly, the nitrone reacted more rapidly with the vinylic organometallic compound than the aldehyde. In this run, with the vinylboronic ester in deficit, methyl addition onto the nitrone (product **5**) was evident in small proportions. It is likely that the formation of **5** took place after all the vinylic species had been consumed.

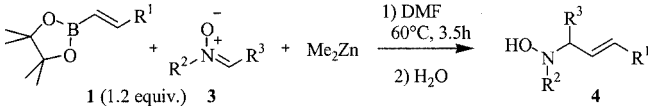
The same reaction was repeated with benzophenone and propiophenone as trapping reagents. In each case, none of the expected allyl alcohol was present in the crude product. Instead, we recovered (chromatography in 50 and 77% yields from ketones, respectively) two products of the general formula **9** in Scheme 4 (as mixtures of isomers; the structure of **9** was ascertained by extensive NMR studies



Scheme 4. Reaction with ketones

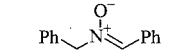
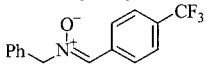
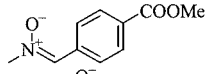
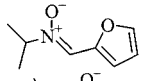
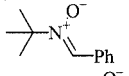
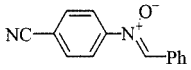
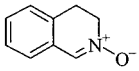
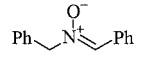
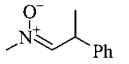
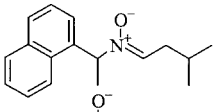
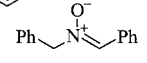
and mass spectroscopy). Analogous structures have already been isolated in transmetallation reactions with cerium.[29,30] We tentatively explain their formation in terms of Scheme 4: after transmetallation, the first vinylzinc species, unreactive towards a ketone, would carbometallate a second vinylborane to give **10**. The allylic species **10** could add onto a ketone with allylic transposition to give **11**. This is also an allylic organometallic compound, and is therefore also able to add onto a second molecule of ketone, producing **9** on hydrolysis.

These results raise an observation. In studies directed towards new preparations of mildly reactive organometallic species, such as dialkylzinc compounds, one generally needs a simple transformation to verify the presence of the ex-



Scheme 5. Examples of additions to nitrones (R^2,R^3: see Table 2)

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

Entry	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		**4e**: 37[b]
24	*n*Bu		**4f**: 92
25	$CH_2CH_2CH_2Cl$	"	**4g**: 91
26	Cyclohexen-1-yl	"	**4h**: 66
27	CH_2CH_2OPiv	"	**4i**: 90[c]
28	*n*Bu		**4j**: 63 (*de* 43%)
29	*n*Bu		**4k**: 56 (*de* 50%)
30	CH_2OtBu		**4l**: < 14

[a] Fast reaction, product decomposes. [b] Me adduct is present: 40% yield. [c] 2 mol-equiv. of **1e**, 1h.

pected species. This has to be a robust, simple and efficient reaction, and, preferably, one that results in a new C−C bond. In dialkylzinc chemistry, uncatalysed additions to carbonyl groups do not fulfil these conditions.[31] The comparison of nitrones with aldehydes in the current work prompts us to suggest that the addition to nitrones may be a useful tool for such purposes.

Other Nitrones and Vinylboronic Esters

We thus studied the extension of the reaction to different nitrones and vinylboronates (Table 2). The reaction proceeds readily with *N*-aryl- and *N*-alkyl-substituted nitrones, and several functional groups, both on the nitrone and on the vinylic reagents, are tolerated. Poor yields in hydroxylamine in Entries 20−22 (Table 2) are due to subsequent side-reactions already observed by us.[1] The very reactive cyclic nitrone of Entry 23 (Table 2) gave a mixture of methyl (40% yield) and vinyl (37%) adducts. The most disappointing results are summarized in Entry 30 (Table 2): All attempts to obtain adducts from vinylboronic esters derived from propargylic alcohol derivatives gave very poor yields. When Entry 31 (Table 2) was repeated in a ^{1}H NMR tube in [D$_7$]DMF, we observed the rapid formation of a new vinylic species that does not react further with the nitrones.

Conclusion

We have thus found that the reaction between a vinylboronic ester of pinacol and a nitrone in the presence of dimethylzinc efficiently provides various *N*-allylic hydroxylamines in good yields. The boronic esters of pinacol, easily available from the corresponding borane, are interesting derivatives because of their stability to air and moisture.[21] This work is the first example of successful transmetallation of members of this family with dialkylzinc.

Experimental Section

General: All reactions were performed by use of conventional Schlenk techniques, under dry nitrogen in oven-dried glassware, with magnetic stirring. All reagents were purchased from Aldrich, Acros or Fluka and were 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*-methylpyrrolidin-2-one (NMP) were distilled and stored over 4 Å molecular sieves. The reactions were monitored by thin layer chromatography (TLC) on commercial aluminium-backed silica gel plates (Merck, Kieselgel 60 F_{254}). Forced-flow column chromatography was performed on Macherey−Nagel Silica Gel 60, 230−400 mesh. Infrared (IR) spectra were obtained either from neat films or sintered KBr discs. All IR spectra were recorded with a Nicolet Impact-400 FTIR apparatus. ^{1}H NMR (200 or 300 MHz), and ^{13}C NMR (50 or 75 MHz) spectra were recorded either with a Bruker AC 200 or with an Advance 300 spectrometer. All chemical shifts for ^{1}H spectra (reference tetramethylsilane) are listed according to: chemical shift (ppm), multiplicity, integration, and coupling constants (Hz). Mass spectra were recorded with a ThermoFinnigan PolarisQ ion-trap spectrometer by chemical ionisation (ammonia/isobutane = 63:37). HRMS and elemental analyses were performed at the Service Central d'Analyse du CNRS, Vernaison, France.

Vinylboronic Ester 1f:[24] Colourless oil. TLC: R_f = 0.85 (cyclohexane/ethyl acetate, 85:15). ^{11}B NMR (96.3 MHz, $CDCl_3/BF_3{\cdot}Et_2O$): δ = 29.5 (288 Hz width at half heights) ppm. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.13 (s, 9 H), 1.16 (s, 12 H), 3.91 (dd, *J* = 1.8, 3.5 Hz, 2 H), 5.64 (dt, *J* = 1.8, 8.0 Hz, 1 H), 6.60 (dt, *J* = 3.5, 6.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 24.75, 27.53, 63.73, 73.23, 83.12, 118.3 (br.), 150.97 ppm. IR (KBr disc): $\tilde{\nu}$ = 2976, 2931, 2873, 1644, 1388, 1345, 1321, 973, 849 cm^{-1}. LRMS (CI): *m*/*z* (%) = 259 (16), 258 (100), 257 (44). HRMS (CI): calcd. for $C_{13}H_{29}BNO_3$ 258.2240; found 258.22300.

General Procedure A. Reaction of Nitrones in DMF: Dimethylzinc (2 M solution in toluene, 0.625 mL, 1.25 mmol, 2.5 equiv.) was added under nitrogen to a mixture of nitrone (0.5 mmol) and vinylborane (0.6 mmol) in anhydrous DMF (0.50 mL). The mixture was stirred at 60 °C for 3.5 h. Hydrolysis was performed at 20 °C by addition of a saturated solution of $NaHCO_3$ (2 mL) and the mixture was extracted with DCM (3 × 5 mL). The collected organic phases were filtered through a pad of silica gel, dried with sodium sulfate and concentrated under reduced pressure. The crude material was chromatographed on silica gel (pentane/DCM, 90:10) 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: Dimethylzinc (2 M solution in toluene, 0.625 mL, 1.25 mmol, 2.5 equiv.) was added under nitrogen to a mixture of nitrone (0.5 mmol) and vinylborane (0.6 mmol) in anhydrous NMP (0.25 mL). The mixture was stirred at 60 °C for 2 h. Hydrolysis was performed at 20 °C by addition of a saturated solution of $NaHCO_3$ (2 mL) and the mixture was extracted with DCM (3 × 5 mL). The combined organic phases were dried with sodium sulfate and concentrated under reduced pressure. The crude material was purified by double chromatography on silica gel. The first (cyclohexane/ethyl acetate, 50:50) eliminated the NMP. The second (cyclohexane/ethyl acetate, 90:10) yielded the pure hydroxylamine (colourless oil).

General Procedure C. Reaction of Aldehydes or Ketones in DMF: Dimethylzinc (2 M solution in toluene, 0.750 mL; 1.5 mmol; 3 equiv.) was added under nitrogen to a mixture of aldehyde (0.5 mmol) and vinylborane (1 mmol) in anhydrous DMF (0.5 mL). The mixture was stirred at 60 °C for 7−20 h. Hydrolysis was performed at 20 °C by addition of a saturated solution of $NaHCO_3$ (2 mL) and the mixture was extracted with DCM (3 × 5 mL). The combined organic phases were dried with sodium sulfate and concentrated under reduced pressure. Chromatography (cyclohexane/ethyl acetate, 90:10) furnished the pure allylic alcohol.

***N*-Benzyl-*N*-(1-phenylhept-2-enyl)hydroxylamine (4a):**[1] This compound was prepared by General Procedure A from benzyl(benzylidene)azane oxide (**3a**, 0.5 mmol, 105 mg) and dioxaborolane **1a** (0.6 mmol, 126 mg), in 90% yield (133 mg). Colourless oil. TLC: R_f = 0.52 (cyclohexane/ethyl acetate, 50:50). ^{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 (q, *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) ppm. ^{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 ppm. IR (KBr

disc): $\tilde{\nu}$ = 3553, 3240, 3086, 3061, 2955, 2922, 1591, 1502, 1380, 971, 702 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 295 (2) [M^+], 213 (7), 212 (9), 173 (30), 91 (100). $C_{20}H_{25}NO$ (295.4): calcd. C 81.31, H 8.53, N 4.74; found C 81.60, H 8.53, N 4.74.

***N*-Benzyl-*N*-(1-phenylethyl)hydroxylamine (5):**[33] This compound was identified as a side product. Colourless oil. TLC: R_f = 0.64 (cyclohexane/ethyl acetate, 85:15). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.44 (d, *J* = 6.5 Hz, 3 H), 3.69 (br. d, *J* = 13.4 Hz, 1 H), 3.72 (d, *J* = 13.4 Hz, 1 H), 3.80 (q, *J* = 6.6 Hz, 1 H), 4.56 (s, OH), 7.15−7.35 (m, 10 H) ppm.

***N*-Benzyl-*N*-(1-phenylpropyl)hydroxylamine (5′):**[1] This compound was identified as a side product. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.65 (t, *J* = 7.4 Hz, 3 H), 1.64 (ddt, *J* = 13.5, 9.5, 7.5 Hz, 1 H), 2.05 (ddt, *J* = 13.5, 9.5, 5.0 Hz, 1 H), 3.45 (dd, *J* = 5.0, 9.5 Hz, 1 H), 3.45 (d, 13.1 Hz, 1 H), 3.60 (d, *J* = 13.1 Hz, 1 H), 3.64 (d, *J* = 13.4 Hz, 1 H), 3.77 (br. d, *J* = 13.4 Hz,1 H), 7.15−7.30 (m, 10 H) ppm.

***N*-Benzyl-*N*-[1-(4-trifluoromethylphenyl)hept-2-enyl]hydroxylamine (4b):** This compound was prepared by General Procedure B from benzyl(4-trifluoromethylbenzylidene)azane oxide (138 mg, 0.5 mmol) and dioxaborolane **1a** (0.6 mmol, 126 mg) in 92% yield (166 mg).Colourless oil. TLC: R_f = 0.63 (cyclohexane/ethyl acetate, 50:50). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.20−1.45 (m, 4 H), 2.12 (td, *J* = 7.6, 6.4 Hz, 2 H), 3.70 (d, *J* = 13.4 Hz, 1 H), 3.99 (d, *J* = 13.4 Hz, 1 H), 4.27 (d, *J* = 7.7 Hz, 1 H), 4.66 (br. s, OH), 5.65−5.80 (m, 2 H), 7.2−7.4 (m, 5 H), 7.5−7.7 (m, 4 H) ppm. ^{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) ppm. IR (film): $\tilde{\nu}$ = 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). $C_{21}H_{24}F_3NO$ (363.42): calcd. C 69.40, H 6.66, N 3.85; found C 69.66, H 6.65, N 3.86.

Methyl 4-{1-[Hydroxy(methyl)amino]hept-2-enyl}benzoate (4c): This compound was prepared by General Procedure B from 4-{(*Z*)-[methyl(oxido)imino]methyl}benzoate (97 mg, 0.5 mmol) and dioxaborolane **1a** (0.6 mmol, 126 mg) in 85% yield (118 mg). Colourless oil. TLC: R_f = 0.46 (cyclohexane/ethyl acetate, 50:50). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.86 (t, *J* = 7.0 Hz, 3 H), 1.15−1.40 (m, 5 H), 2.12 (td, *J* = 6.9, 6.3 Hz, 2 H), 2.58 (s, 3 H), 3.90 (s, 3 H), 4.03 (d, *J* = 7.9 Hz, 1 H), 5.55−5.80 (m, 2 H), 7.41 (d, *J* = 8.2 Hz), 7.99 (d, *J* = 8.2 Hz, 2 H) ppm. ^{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) ppm. IR (film): $\tilde{\nu}$ = 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 (38) [MH^+], 360 (24), 231 (100). $C_{16}H_{23}NO_3$ (277.36): calcd. C 69.29, H 8.36, N 5.05; found C 69.38, H 8.34, N 5.04.

***O*-(1-Butyl-3-furan-2-ylallyl)-*N*-isopropylhydroxylamine (from 4d):** This compound was prepared by General Procedure B from (2-furylmethylene)isopropylazane oxide (77 mg, 0.5 mmol) and dioxaborolane **1a** (0.6 mmol, 126 mg). Conventional workup produced a crude material that, by ^1H NMR, was a mixture of *N*-(1-furan-2-ylhept-2-enyl)-*N*-(isopropyl)hydroxylamine (**4d**) and its rearrangement product *O*-[1-butyl-3-(furan-2-yl)allyl]-*N*-isopropylhydroxylamine. Silica gel column chromatography (cyclohexane/ethyl acetate, 75:25) furnished solely the rearranged *O*-alkylated product in 18% yield (21 mg), colourless oil. TLC: R_f = 0.46 (cyclohexane/ethyl acetate, 50:50). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.81 (t, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.3 Hz, 3 H), 1.07 (d, *J* = 6.3 Hz, 3 H), 1.15−1.30 (m, 4 H + OH), 1.40−1.55 (m, 1 H), 1.70−1.85 (m, 1 H), 3.02 (sept, *J* = 6.3 Hz, 1 H), 3.26 (dt, *J* = 4.5, 9.0 Hz, 1 H), 6.10 (dd, *J* = 9.1, 16.0 Hz, 1 H), 6.07 (d, *J* = 3.3 Hz, 1 H), 6.22 (d, *J* = 16.0 Hz, 1 H), 6.29 (dd, *J* = 1.9, 3.3 Hz, 1 H), 7.26 (d, *J* = 1.8 Hz, 1 H) ppm. ^{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 ppm. LRMS (CI): *m*/*z* (%) = 236 (100), 220 (30), 177 (29), 163 (80), 124 (14), 110 (8).

1-Hex-1-enyl-3,4-dihydro-1*H*-isoquinolin-2-ol (4e):[34] This compound was prepared by General Procedure B from 3,4-dihydroisoquinoline *N*-oxide (74 mg, 0.5 mmol) and dioxaborolane **1a** (0.6 mmol, 126 mg) for only 1 h at 60 °C. On TLC (cyclohexane/ethyl acetate, 50:50) the reaction was complete in 30 min. Chromatography produced allylic hydroxylamine (28 mg, 37% yield) and methyl adduct (33 mg, 40% yield). Colourless oils. TLC: R_f = 0.57 and 0.26, respectively (cyclohexane/ethyl acetate, 50:50),

Vinyl Adduct 4e: ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.92 (t, *J* = 7.03 Hz, 3 H), 1.2−1.5 (m, 4 H + OH), 2.15 (q, *J* = 6.5 Hz, 2 H), 2.81−2.95 (m, 1 H), 2.95−3.15 (m, 2 H), 3.40−3.55 (m, 1 H), 4.28 (br. d, *J* = 8.2 Hz, 1 H), 5.51 (dd, *J* = 8.2, 15.1 Hz, 1 H), 5.78 (dt, *J* = 15.3, 6.7 Hz), 7.05−7.20 (m, 4 H) ppm. ^{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−*C*H=), 133.26, 135.85, 136.98 (=*C*H−Bu) ppm. IR (film): $\tilde{\nu}$ = 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: ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.50 (d, *J* = 6.7 Hz,3 H), 2.75−3.10(m, 3 H), 3.30−3.45 (m, 1 H), 3.90 (br., 1 H), 6.95−7.10 (m, 4 H) ppm. ^{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 ppm. IR (film): $\tilde{\nu}$ = 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-phenyltridec-2-enyl)hydroxylamine (4f):** This compound was prepared by General Procedure A from benzyl(benzylidene)azane oxide (211 mg, 1 mmol) and dioxaborolane **1b** (1.2 mmol, 319 mg), in 91% isolated yield (346 mg). Colourless oil. TLC: R_f = 0.33 (diethyl ether/pentane, 90:10). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.79 (t, *J* = 6.5 Hz, 3 H), 1.05−1.35 (m, 16 H), 1.97 (q, *J* = 6.9 Hz, 2 H), 3.61(d, *J* = 13.4 Hz, 1 H), 3.77 (br. d, *J* = 13.3 Hz, 1 H), 4.10(d, *J* = 8.2 Hz, 1 H), 4.93 (br. s, 1 H), 5.58(dt, *J* = 6.3, 15.5 Hz, 1 H), 5.67 (dd, *J* = 8.1, 15.8 Hz, 1 H), 7.10−7.35 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$/TMS): δ = 14.27, 22.85, 29.32, 29.37, 29.51, 29.62, 29.78(2 C), 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 ppm. IR (KBr disc): $\tilde{\nu}$ = 3543, 3249, 3025, 2917, 2840, 1461, 1069, 1037, 960, 914, 743 cm^{-1}. LRMS (CI): *m*/*z* (%) = 380 (100) [MH^+], 362 [M − OH]$^+$ (18), 257 (51). HRMS (CI) calcd. for $C_{26}H_{38}NO$: 380.2953; found 380.2975.

***N*-Benzyl-*N*-(6-chloro-1-phenylhex-2-enyl)hydroxylamine (4g):** This compound was prepared by General Procedure A from benzyl(benzylidene)azane oxide (211 mg, 1 mmol) and dioxaborolane **1d** (1.2 mmol, 242 mg) in 90% isolated yield (284 mg). Colourless oil. TLC: R_f = 0.75 (cyclohexane/ethyl acetate, 50:50). ^1H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.73 (quint, *J* = 6.9 Hz, 2 H), 2.11

(q, 7.1 Hz, 2 H), 3.36 (t, J = 6.6 Hz, 2 H), 3.59 (d, J = 13.3 Hz, 1 H), 3.68 (br. d, J = 13.3 Hz, 1 H), 4.08 (d, J = 8.6 Hz, 1 H), 5.11 (s, OH), 5.51 (dt, J = 6.4, 15.4 Hz, 1 H), 5.77 (dd, J = 8.6, 15.4 Hz, 1 H), 7.10−7.30 (m, 10 H) ppm. ^{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 ppm. IR (KBr disc): ṽ = 3535, 3453, 3232, 3060, 3030, 2930, 1950, 1595, 1495, 1455, 1305, 970 cm^{-1}. LRMS (CI): m/z (%) = 319 (8), 318 (30), 317 (24), 316 (88), 196 (4), 195 (32), 194 (14), 193 (100). $C_{19}H_{22}ClNO$ (315.8): calcd. C 72.25, H 7.02, N 4.43; found C 72.51, H 7.03, N 4.45.

***N*-Benzyl-*N*-[3-(cyclohex-1-enyl)-1-phenylallyl]hydroxylamine (4h):** This compound was prepared by General Procedure A from benzyl(benzylidene)azane oxide (211 mg, 1 mmol) and dioxaborolane **1c** (282 mg, 1.2 mmol) in 66% yield (209 mg). Colourless oil. TLC: R_f = 0.60 (cyclohexane/ethyl acetate, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.45−1.55 (m, 4 H), 1.95−2.15 (m, 4 H), 3.6 (d, J = 13.8 Hz, 1 H), 3.86 (d, J = 13.8 Hz, 1 H), 4.22 (d, J = 8.7 Hz, 1 H), 4.49 (s, OH), 5.65−5.80 (m, 2 H), 6.17 (d, J = 15.8 Hz, 1 H), 7.10−7.40 (m, 10 H) ppm. ^{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 ppm. IR (KBr disc): ṽ = 3518, 3437, 3216, 3055, 3025, 2922, 2863, 2238, 1957, 1498, 1453, 1022, 971, 905 cm^{-1}. LRMS (CI): m/z (%) = 320 (3) [MH$^+$], 302 [M − OH]$^+$ (7), 214 (8), 197 (100). HRMS (CI) calcd. for $C_{22}H_{26}NO$: 320.2014; found 320.2070.

5-(Benzylhydroxyamino)-5-phenylpent-3-enyl 2,2-Dimethylpropionate (4i): This compound was prepared by General Procedure B from benzyl(benzylidene)azane oxide (42 mg, 0.2 mmol) and dioxaborolane **1e** (0.4 mmol, 68 mg) in 90% yield (66 mg). Colourless oil. TLC: R_f = 0.61 (cyclohexane/ethyl acetate, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.11 (s, 9 H), 2.38 (q, J = 6.6 Hz, 2 H), 3.71 (d, J = 13.6 Hz, 1 H), 3.87 (d, J = 13.6 Hz, 2 H), 4.09 (t, J = 6.4 Hz, 1 H), 4.22 (d, J = 8.4 Hz, 1 H), 4.93 (s, OH), 5.65 (dt, J = 6.7, 15.6 Hz, 1 H), 5.87 (dd, J = 8.3.15.6 Hz, 1 H), 7.20−7.40 (m, 10 H) ppm. ^{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 ppm. IR (film): ṽ = 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-phenylethyl)hept-2-enyl]hydroxylamine (4j):** This compound was prepared by General Procedure A from methyl(2-phenylpropylidene)azane oxide (163 mg, 1 mmol) and dioxaborolane **1a** (250 mg, 1.2 mmol) in 50% isolated yield (120 mg). Colourless oil. TLC: R_f = 0.78 (cyclohexane/ethyl acetate, 50:50 ; diastereoisomers unresolved). The diastereoisomeric excess (43%) was measured by NMR spectroscopy. **Major Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.80 (t, J = 7.2 Hz, 3 H), 1.05−1.40 (m, 4 H), 1.33 (d, 7.1 Hz, 3 H), 1.85−1.95 (m, 2 H), 2.58 (s, 3 H), 2.98 (t, J = 8.4 Hz, 1 H), 3.14 (quint, J = 6.0 Hz, 1 H), 5.16 (dd, J = 9.0, 15.4 Hz, 1 H), 5.30 (dt, J = 15.6, 6.7 Hz), 7.0−7.3 (m, 5 H) ppm. ^{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 ppm. **Minor Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.88 (t, J = 7.0 Hz, 3 H), 1.05−1.40 (m, 4 H), 1.20 (d, J = 7.0 Hz, 3 H), 2.0−2.10 (m, 2 H), 2.51 (s, 3 H), 3.04 (t, J = 8.0 Hz, 1 H), 3.14 (quint, J = 6.0 Hz, 1 H), 5.38−5.45 (m, 2 H), 7.0−7.3 (m, 5 H) ppm. ^{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 ppm.

(1-Isobutylhept-2-enyl)[1-(naphthalen-1-yl)ethyl]amine (4k): This compound was obtained by General Procedure A from nitrone (255 mg, 1.0 mmol) and dioxaborolane **1a** (250 mg, 1.2 mmol) in 56% yield (188 mg). Colourless oil. TLC: R_f = 0.50 (cyclohexane/ethyl acetate, 50:50).The product was dissolved in a 4:1 acetic acid/water mixture and stirred with zinc dust (721 mg) overnight at room temp. The suspension was filtered, concentrated, taken up in ethyl acetate, and washed with 2 × 1 mL of a saturated $NaHCO_3$ solution. Measurement of the *de* was accomplished by HPLC: column Kromasil C18, 250 × 4.6 mm, UV detection 218 nm, eluent acetonitrile/water (95:5), 2 mL/min, major peak 11.7 min, minor peak 13.7min. NMR of major isomer: ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.72 (J = 6.5 Hz, 3 H), 0.77 (d, J = 6.6 Hz, 3 H), 0.98 (m, 3 H), 1.2−1.4 (m, 4 H), 1.49 (d, J = 6.8 Hz, 3 H), 1.9−2.0 (m, 2 H), 2.8−2.95 (m, 1 H),; 4.84 (q, J = 6.6 Hz, 1 H), 5.03 (dt, J = 15.4, 6.6 Hz, 1 H), 5.22 (br. dd, J = 15.2, 8.8 Hz, 1 H), 7.4−8.85 (m, 7 H) ppm. ^{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 ppm. LRMS (CI): m/z (%) = 338 (14), 325 (21), 324 (100), 323 (8), 322 (21), 266 (12), 186 (22), 155 (27) (3) [MH$^+$], 302 (7) [M − OH]$^+$, 214 (8), 197 (100). HRMS (CI) calcd. for $C_{23}H_{34}N$ 324.2691; found 324.256.

Reactions with Aldehydes

1-Phenylethanol: This compound was isolated as a side product. TLC: R_f = 0.19 (cyclohexane/ethyl acetate, 50:50). ^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.42 (d, J = 6.5 Hz, 3 H), 1.7 (OH), 4.83 (q, J = 6.5 Hz, 1 H), 7.1−7.3 (m, 5 H) ppm.

1-Phenylhept-2-en-1-ol (6a):[2,35] This compound was prepared by General Procedure C from dioxaborolane **1a** (420 mg, 2 mmol), dimethylzinc in toluene (3 mmol, 1.5 mL) and benzaldehyde (106 mg, 1 mmol) in 89% yield. Colourless oil. TLC: R_f = 0.55 (pentane/CH_2Cl_2, 90:10). ^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 0.88 (t, J = 7.1 Hz, 3 H), 1.2−1.45 (m, 4 H), 1.95−2.15 (m, 2 H), 5.15 (d, J = 6.0 Hz, 1 H), 5.66 (dd, J = 5.5, 14.4 Hz, 1 H), 5.73 (dd, J = 5.7, 14.3 Hz, 1 H), 7.2−7.4 (m, 5 H) ppm.

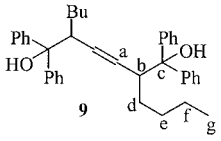
1-Phenylpentadeca-1,4-dien-3-ol (6b): This compound was prepared by General Procedure C from dioxaborolane **1b** (294 mg, 1 mmol), dimethylzinc in toluene (1.6 mmol, 0.8 mL) and cinnamaldehyde (70 mg, 0.5 mmol) in 29% yield. Colourless oil. TLC: R_f = 0.6 (pentane/CH_2Cl_2, 90:10). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.88 (t, J = 6.5 Hz, 3 H), 1.10−1.50 (m, 16 H), 1.47 (br. s, OH), 2.05 (q, J = 6.9 Hz, 2 H), 4.75 (t, J = 6.4 Hz, 1 H), 5.56 (ddt, J = 6.5, 15.4, 1.3 Hz, 1 H), 5.64 (br. dt, J = 15.5, 6.6 Hz, 1 H), 6.25 (dd, J = 6.2, 15.9 Hz, 1 H), 6.58 (d, J = 15.7 Hz, 1 H)7.20−7.40 (m, 5 H) ppm. ^{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 ppm. IR (KBr disc): ṽ = 3354, 3028, 2920, 2849, 1592, 1469 cm^{-1}. LRMS (CI): m/z (%) = 299 (5), 285 (21), 283 (100), 282 (12), 257 (5), 143 (9). $C_{21}H_{32}O$ (300.5): C 83.94, H 10.73; found C 84.04, H 11.11.

2-Phenylnon-4-en-3-ol (6c):[36,37] This compound was prepared by General Procedure C from dioxaborolane **1a** (210 mg, 1 mmol), dimethylzinc in toluene (1.6 mmol, 0.8 mL) and *rac*-2-phenylpropanal (67 mg, 0.5 mmol) in 28% yield (diastereoisomers not separated). Colourless oil. **Major Isomer (*erythro*):**[38] TLC: R_f = 0.52 (cyclohexane/ethyl acetate, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$/

TMS): δ = 0.84 (t, *J* = 7.3 Hz, 3 H), 1.31 (d, *J* = 7.0 Hz, 3 H), 1.15−1.40 (m, 4 H), 1.53 (br. s, OH), 1.97 (br. q, *J* = 6.9 Hz, 2 H), 2.87 (quint, *J* = 6.8 Hz, 1 H), 4.15 (br. t, *J* = 6.2 Hz, 1 H), 5.37 (ddt, *J* = 6.8, 14.1, 2.7 Hz, 1 H), 5.52 (ddt, *J* = 0.9, 15.4, 6.8 Hz), 7.15−7.40 (m, 5 H) ppm. **Minor Isomer**: TLC: R_f = 0.58 (cyclohexane/ethyl acetate, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.89 (t, *J* = 7.5 Hz, 3 H), 1.22 (d, *J* = 7.5 Hz, 3 H), 1.15−1.40 (m, 4 H), 1.45 (br. s, OH), 2.10 (br. q, *J* = 6.7 Hz, 2 H), 2.66 (quint, *J* = 7.3 Hz, 1 H), 4.08 (br. t, *J* = 7.7 Hz, 1 H), 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, 5 H) ppm.

Reactions with Ketones

2,5-Dibutyl-1,1,6,6-tetraphenylhex-3-ene-1,6-diol (9):[30] This compound was prepared by General Procedure C from dioxaborolane **1a** (210 mg, 1 mmol), dimethylzinc in toluene (1 mmol, 0.5 mL) and benzophenone (91 mg, 0.5 mmol). Chromatography yielded 88 mg of a compound that was identified on the basis of its mass spectrum and NMR experiments. Colourless oil. Yield for $C_{38}H_{44}O_2$ (532): 66%. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 0.82 (t, 6 H), 0.8−0.95 (m, 2 H, d), 1.05−1.45 (m, 4 H, e,f), 1.60−1.75 (m, 2 H, d′), 3.58 (br. quint, $J_{ab} \approx 9.0$ Hz; $J_{a'b} \approx -1.0$ Hz, 2 H, b), 4.14 (s, OH), 6.02 (m, $J_{aa'} \approx 15$ Hz, 2 H, a), 7.1−7.4 (m, 20 H) ppm. ^{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 ppm (structure and assignments are in agreement with COSY and H-to-C-correlations). IR (KBr disc): $\tilde{\nu}$ = 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: *m*/*z* (%) = 419 (86), 349(80), 249 (100).



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