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Stereoselective migration of sterically hindered organoboranes in cyclic and acyclic systems. A stereoselective allylic C–H activation reaction

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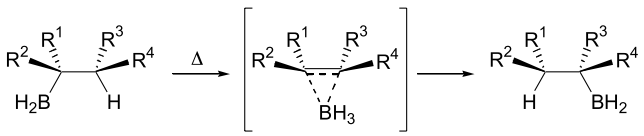
Abstract—The thermal migration of cyclic and acyclic organoboranes were studied. In most cases, a stereoselective 1,2-dyotropic migration was observed, allowing the stereocontrol of three contiguous chiral centers. Scope and limitations of this thermal migration are presented.

1. Introduction

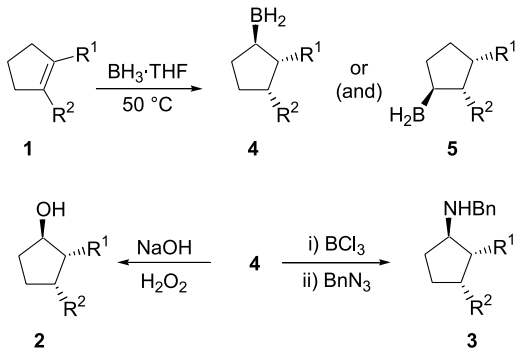
The diastereoselective synthesis of organic molecules is an important research field and numerous important synthetic contributions have been made in recent years.[1] It was known that organoboranes derived from disubstituted olefins by hydroboration undergo a thermal isomerization at elevated temperatures (100–160°C).[2,3] We have shown that cyclic[3,4] and acyclic[5] tetrasubstituted olefins undergo a 1,2-thermal migration under milder conditions. Furthermore, these rearrangements occur with a good or excellent transfer of the stereochemical information, allowing the control of up to three stereogenic centers. Herein, we wish to report the scope and the limitations of thermal rearrangements of organoboranes according to the general Scheme 1.



Scheme 1.

2. Results and discussion

The driving force for the rearrangement of organoboranes is the release of steric strain. Organoboranes attached at a tertiary carbon atom such as H_2B-C(R^1)(R^2)(R^3), obtained by the hydroboration of tetrasubstituted alkenes, are especially prone to undergo a thermal rearrangement as first shown by Rickborn and Field in the case of 1,2-dimethylcyclopentene.[3] We have examined a range of tetrasubstituted cyclopentene derivatives of type **1** (see Scheme 2 and Table 1).[6]



Scheme 2.

Thus, the hydroboration of 1,2-diphenylcyclopentene (**1a**) with BH_3·THF (THF, 50°C, 3 h) leads to a rearranged organoborane, which after oxidation with NaOH (2 M in H_2O) and H_2O_2 (30% in H_2O) furnishes 2,3-diphenylcyclopentanol (**2a**) as a single diastereoisomer in 82% yield (entry 1 of Table 1). We have always observed the migration in the direction of the ring system and not in the direction of the side-chain. This is due to the higher conformational rigidity and better coplanarity of the adjacent C–H bond with the C–B bond facilitating the dehydroboration step.

Similarly, 1,2-dialkylcyclopentenes (**1b–1d**) produce after NaOH/H_2O_2-oxidation the cyclopentanols **2b–d** in 51–71% yields with d.r.≥98% (entries 2–4). 1,2-Dibenzylcyclopentene (**1e**) reacts with an excellent yield leading only to the expected cyclopentanol **2e** (entry 5). By reacting the intermediate organoborane with BCl_3 (25°C, 3 h)

Keywords: stereoselective synthesis; 1,2-migration; organoboranes; C–H-activation; amination.
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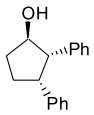
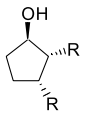
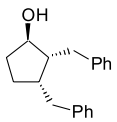
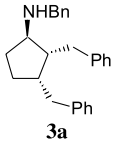
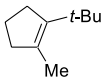
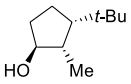
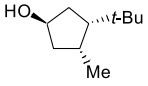
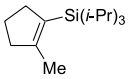
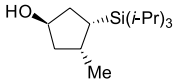
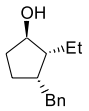
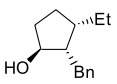
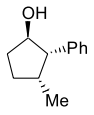
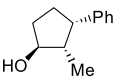
Table 1. Products of type **2** and **3** obtained by thermal rearrangement of organoboranes (3 h, 50°C), resulting from the hydroboration of tetrasubstituted cyclopentene derivatives of type **1**

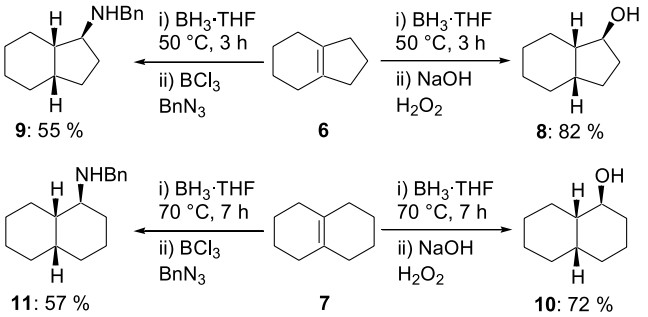
Entry	Olefin of type **1**	Products of type **2** or **3**	Yield (%)[a]
1	 **1a**	 **2a**	82
2	 **1b**: R = Et	 **2b**: R = Et	71
3	**1c**: R=Pr	**2c**: R=Pr	62
4	**1d**: R=Bu	**2d**: R=Bu	51
5	 **1e**	 **2e**	80
6	**1e**	 **3a**	62
7	 **1f**	 **2f**	70
8	**1f**	 **2g**	64[b]
9	 **1g**	 **2h**	60[c]
10	 **1h**	 **2i** : 58 %	 **2j** : 12 %
11	 **1i**	 **2k** : 40 %	 **2l** : 30 %

[a] Isolated yield of analytically pure compound.
[b] The reaction mixture was stirred at 65°C for 96 h.
[c] The reaction mixture was stirred at 50°C for 24 h.

followed by the addition of benzyl azide (25°C, 1 h),[7] benzylamine **3a** is isolated in 62% yield (entry 6). Both products (**2e** and **3a**) are formed in high diasteroselectivity (d.r.≥98%). In the case of unsymmetrical disubstituted cyclopentenes of type **1** ($R^1 \neq R^2$), two intermediate regioisomeric organoboranes **4** and **5** can be obtained. If the difference of the steric hindrance between the two substituents is large, the migration occurs preferentially on the side of the least bulky substituent. Thus, 1-*tert*-butyl-2-methylcyclopentene (**1f**) produces only 3-*tert*-butyl-2-methylcyclopentanol (**2f**) after oxidation in 70% yield (d.r.≥98%; entry 7).

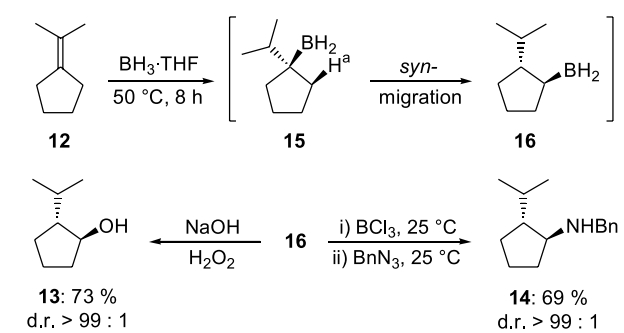
Interestingly, by performing the reaction at 65°C instead of 50°C and with 96 h reaction time, a further migration of the boron atom occurs producing 3-*tert*-butyl-4-methylcyclopentanol (**2g**) in 64% yield as one diastereoisomer (d.r.≥98%) showing the importance of the temperature control for performing these rearrangements (entry 8). The relative stereochemistry of **2g** confirms also the suprafacial nature of the boron migration. Similarly, alkenylsilane **1g** affords after 24 h of heating at 50°C the double migration product **2h** in 60% yield (entry 9). In the case of unsymmetrical cyclopentenes like **1h** and **1i**, a mixture of migration products in both directions was observed. This low regioselectivity could not be improved despite numerous experiments involving a change of the reaction conditions or the substrate of type **1** were carried out (entries 10 and 11).

As reported earlier,[4a] bicyclic alkenes like **6** and **7** undergo stereoselective migrations. The bicyclic olefin **6** reacts similarly to the substituted cyclopentenes at 50°C within 3 h affording alcohol **8** in 82% yield after oxidative workup, and amine **9** in 55% yield after amination (d.r.≥98:2) (Scheme 3). The six-membered bicyclic system **7** reacts much slower and requires 7 h reaction time at 70°C. After oxidation with $NaOH/H_2O_2$ and amination according to the procotol described above, the expected products **10** and **11** are obtained as one diastereoisomer (d.r.≥98%) and in 72 and 57% yield (Scheme 3).



Scheme 3.

The hydroboration of *exo*-alkylidene cyclopentane derivatives like **12** proceeds also smoothly (BH_3·THF, 50°C, 8 h) leading only to the migration product in the cyclopentane ring, affording the *trans*-products **13** and **14**, respectively, after oxidation and amination. The *trans*-stereochemistry is

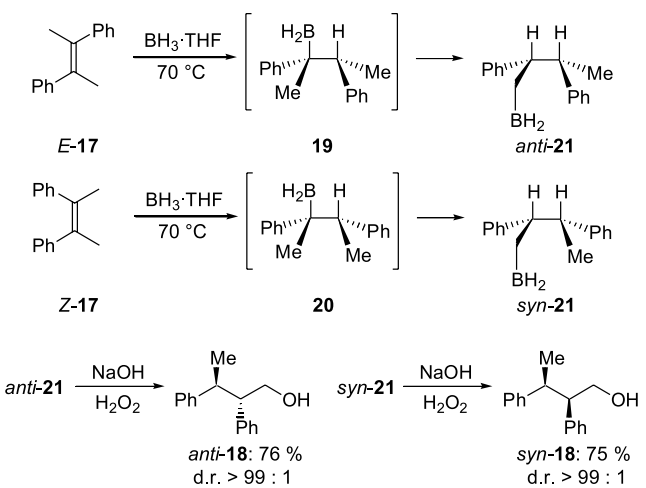


Scheme 4.

readily explained by a *syn*-migration[8] of the intermediate tertiary organoborane **15** leading to the *trans*-organoborane **16** (Scheme 4).[5a]

The regioselectivity of the migration inside the cyclopentane ring is best explained by the favored arrangement of the BH_2 group and the *syn*-hydrogen atom H^a of **15**, facilitating the 1,2-migration step.

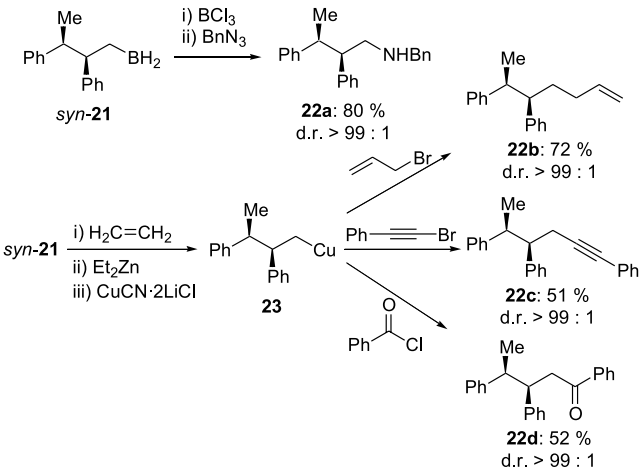
Stereoselective boron-migrations are also observed in open-chain systems. The two isomeric stilbenes *E*- and *Z*-1,2-dimethyl-1,2-diphenylethylenes (*E*- and *Z*-**17**) provide, after hydroboration, thermal rearrangement at 70°C (14 h reaction time) and $NaOH/H_2O_2$-oxidation, the *anti*- and *syn*-alcohols (*anti*-**18** and *syn*-**18**), respectively, in 76 and 75% yield. The observed stereoselectivity is readily explained by assuming as usually a *syn*-dyotropic rearrangement[9] via the boranes **19**, **20** and *syn*- and *anti*-**21** (Scheme 5).



Scheme 5.

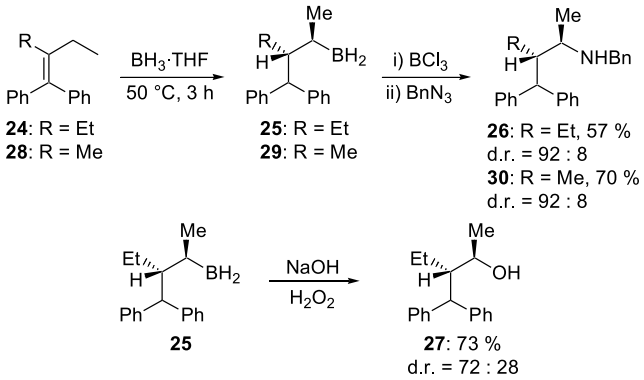
The intermediate organoborane *syn*-**21** was further converted in a range of derivatives. By using the amination procedure (BCl_3 followed by BnN_3),[7] the benzylamine **22a** is obtained in 80% yield. The treatment of the organoborane *syn*-**21** with ethylene produces a diethylborane derivative, which undergoes a boron–zinc exchange[10] with Et_2Zn leading to an organozinc derivative, which after transmetalation with the THF soluble copper-salt, CuCN·2LiCl[11] gives the copper intermediate **23**. The reaction of **23** with allyl bromide leads to the allylated product **22b** in 72% yield. The reaction with 2-bromo-1-phenylacetylene furnishes the cross-coupling product **22c** in 51% yield.[12] The addition of benzoyl chloride to **23** leads to the aromatic ketone **22d** in 52% yield (Scheme 6).

Tetrasubstituted double bonds bearing ethyl substituents undergo also the boron migration at 50–65°C. Although we claimed to have complete control of the relative stereochemistry of the newly chiral center generated from the ethyl group,[5] a closer look to the crude reaction mixtures showed that the diastereoselectivity is less selective as previously reported. Thus, heating 2-ethyl-1,1-diphenylbut-1-ene (**24**) with BH_3·THF (3 equiv.) for 4 h at 50°C produces the organoborane **25**. Its conversion to the corresponding benzylamine was performed as described



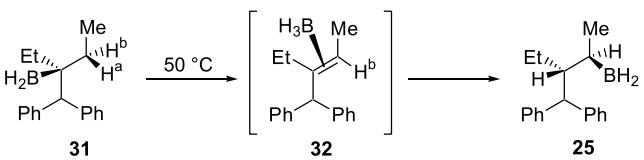
Scheme 6.

(BCl_3, 25°C, 4 h; then BnN_3, 0–25°C, overnight), leading to the amine **26** in 57% yield as a mixture of two diastereoisomers in a ratio of 92:8 as indicated by GC–MS-analysis (see Section 4). The oxidation of **25** with $NaOH/H_2O_2$ affords a 72:28 mixture of the secondary alcohol **27** in 73% yield. A similar result was obtained starting with 2-methyl-1,1-diphenylbut-1-ene (**28**), which provides after amination of the intermediate organoborane (**29**) the expected benzylic amine **30** in 70% yield (d.r.=92:8, Scheme 7).



Scheme 7.

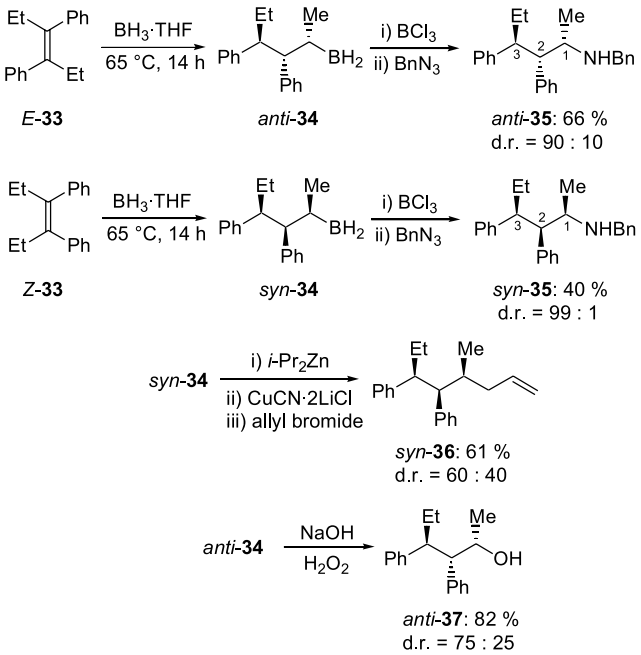
The relative stereochemistry has been established by performing an X-ray analysis of the 3,5-dinitrobenzoate derived from the alcohol **27**.[5b,c] This relative stereochemistry is best explained by the thermal dehydroboration of the primary intermediate of **24** (or **28**) (e.g. **31**). It will proceed preferentially with the adjacent hydrogen H^a (and not H^b), since this dehydroboration would result in the formation of the least bulky alkene–borane complex (**32**) having the bulky benzhydryl group (Ph_2CH) and the methyl substituent in a *trans*-arrangement (Scheme 8).



Scheme 8.

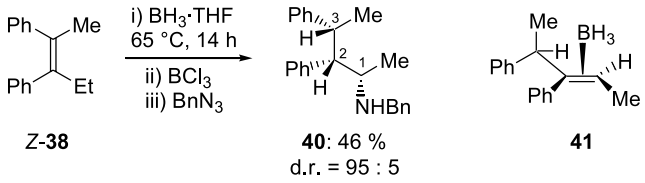
The rehydroboration of **32** will lead to organoborane **25**. The moderate diastereoselectivity of **27** obtained after $NaOH/H_2O_2$ oxidation of **25** may be explained by epimerization during the oxidation step, in contrast to the amination reaction leading to products **26** and **30** with a diastereoselectivity of 92:8 (Scheme 7).

This reaction proceeds also well with other various-substituted stilbene derivatives. Thus, the *E*- and *Z*-stilbenes *E*- and *Z*-**33** undergo the thermal boron migration with excellent diastereoselectivities leading to the *anti*- and *syn*-organoboranes *anti*- and *syn*-**34**. After amination of **34** (BCl_3, 25°C, 4 h; then BnN_3, 0–25°C, overnight), the corresponding benzylic amines (*anti*- and *syn*-**35**) were obtained in 66 and 40% yield and with a diastereoselectivity better than 90:10 between C(1) and C(2) (Scheme 9). The relative stereochemistry of *syn*-**34** was established by X-ray analysis of the corresponding alcohol.[5b,d]



Scheme 9.

Interestingly, the transmetalation of *syn*-**34** to the corresponding zinc–copper compound by reaction with *i*-Pr_2Zn (4 equiv., 25°C, 3 h) followed by the addition of CuCN·2LiCl (1 equiv., −78°C, 30 min) and subsequent allylation occurred with good overall yield (61%) but led to a partial epimerization of the intermediate organometallic reagent, producing the allylated product *syn*-**36** as a 60:40 mixture of epimers at C(1) (Scheme 9). Also the $NaOH/H_2O_2$-oxidation of *anti*-**34** was not stereoselective furnishing the alcohol *anti*-**37** as a 75:25 mixture of epimers at C(1) in 82% yield (Scheme 9). Remarkable regioselectivities have been observed in the thermal migration of several tetrasubstituted alkenes such as *Z*-**38** and **39**. Thus, the hydroboration of *Z*-**38** furnishes only the migration product in the direction of the ethyl group. Furthermore, the migration was stereoselective providing after the standard amination sequence the benzylic amine **40** in 46% yield (Scheme 10). The diastereoselectivity between C(1) and C(2) was 95:5 and >99:1 between C(2) and C(3). The relative stereochemistry, which was established by X-ray analysis of the corresponding alcohol obtained by oxidative workup ($NaOH/H_2O_2$),[5b,e] can be best explained by assuming as previously (see Scheme 8) that the most stable alkene–borane complex (**41**) is formed.



Scheme 10.

3. Conclusion

In summary, we have described that the migration of organoboranes attached to a tertiary carbon atom proceeds with good stereoselectivity in cyclic systems, the fastest rearrangements occurring in cyclopentane rings. In unsymmetrically substituted cyclopentenes, the migration was not regioselective and complicated by multiple migration products. Tetrasubstituted acyclic alkenes provide the migration products under comparable reaction conditions. The stereoselectivity of the migration is predictable but strongly depends on the structure of the alkene and on the reaction conditions. The diastereoselectivity was established by ^1H NMR and (or) GC–MS analysis, the relative stereoselectivity was in several cases secured by X-ray analysis. Attempts to use functionalized cyclic or acyclic alkenes were complicated by various side-reactions and found not to be synthetically useful under our reaction conditions, limiting the scope of the reaction.

4. Experimental

4.1. General methods

Unless otherwise indicated, all reactions were carried out under argon. Solvents were dried and freshly distilled. Reactions were monitored by gas chromatography (GC and GC–MS) or thin layer chromatography (TLC). The ratios between diastereoisomers were determined by ^1H NMR spectroscopy and/or GC–MS analysis; GC–MS: column HP-5MS (15 m×250 μm×0.25 μm); method A: 1 min at 110°C, ramp of 50°C/min to 250°C, 10 min at 250°C, method B: 1 min at 90°C, ramp of 50°C/min to 250°C, 8 min at 250°C, method C: 1 min at 70°C, ramp of 50°C/min to 250°C, 8 min at 250°C.

Starting materials. Preparation of starting materials not known in the literature.

Disubstituted cyclopentenes **1b–d**, **1g** and **1h** were prepared from 1-bromo-2-alkyl(benzyl)cyclopentenes (general procedure II), prepared from 1,2-dibromocyclopentene[13] (general procedure I).

4.2. General procedure I. Preparation of 1-bromo-2-alkyl(benzyl)-cyclopentenes

A solution of 1,2-dibromocyclopentene[13] (3.39 g, 15 mmol) in THF (30 mL) was cooled down to −78°C and treated slowly with *t*-BuLi (20 mL, 30 mmol, 1.5 M in pentane). The mixture was stirred at −78°C for 15 min before the corresponding alkyl iodide (18 mmol) or benzyl bromide (15 mmol) was added. After warming up to room temperature, the reaction mixture was quenched with water (50 mL). The aqueous phase was extracted with pentane (2×20 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (pentane) or by distillation to give the desired 1-bromo-2-alkyl(benzyl)cyclopentene.

4.2.1. 1-Bromo-2-methylcyclopentene. According to general procedure I, 1,2-dibromocyclopentene[13] was reacted with *t*-BuLi and methyl iodide (2.56 g, 18 mmol) to give the corresponding cyclopentenyl bromide (1.50 g, 62%) as a colourless oil, bp 61–63°C/30 mbar. IR (film): 2916, 2855, 1711, 1443, 1025, 977 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.66–2.57 (m, 2H), 2.33–2.26 (m, 2H), 1.97–1.87 (m, 2H), 1.73–1.71 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=137.1, 115.6, 39.9, 36.1, 21.7, 15.6; MS (EI): 162 (25), 160 (26, M^+), 81 (100); HRMS calcd for C_6H_9Br: 159.9888, found: 159.9855.

4.2.2. 1-Bromo-2-ethylcyclopentene. According to general procedure I, 1,2-dibromocyclopentene[13] was reacted with *t*-BuLi and ethyl iodide (2.81 g, 18 mmol) to give the corresponding cyclopentenyl bromide (1.89 g, 72%) as a colourless oil. IR (film): 2967, 2936, 2876, 2853, 1709, 1460, 895 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.65–2.58 (m, 2H), 2.34–2.27 (m, 2H), 2.21–2.14 (m, 2H), 1.97–1.87 (m, 2H), 0.99 (t, *J*=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.2, 114.5, 39.9, 33.2, 23.1, 21.7, 11.7; MS (EI): 174 (24, M^+), 95 (100); HRMS calcd for $C_7H_{11}Br$: 174.0044, found: 174.0028.

4.2.3. 1-Bromo-2-propylcyclopentene. According to general procedure I, 1,2-dibromocyclopentene[13] was reacted with *t*-BuLi and *n*-propyl iodide (3.06 g, 18 mmol) to give the corresponding cyclopentenyl bromide (1.25 g, 44%) as a colourless oil. IR (film): 2959, 2933, 2870, 2847, 1710, 1655, 1463, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.66–2.57 (m, 2H), 2.32–2.26 (m, 2H), 2.16–2.11 (m, 2H), 1.96–1.86 (m, 2H), 1.50–1.38 (m, 2H), 0.91 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.0, 115.6, 39.9, 33.7, 31.8, 21.8, 20.4, 13.9; MS (EI): 190 (48), 188 (47, M^+), 109 (100), 79 (62), 67 (48); HRMS calcd for $C_8H_{13}Br$: 188.0201, found: 188.0204.

4.2.4. 1-Bromo-2-butylcyclopentene. According to general procedure I, 1,2-dibromocyclopentene[13] was reacted with *t*-BuLi and *n*-butyl iodide (3.31 g, 18 mmol) to give the corresponding cyclopentenyl bromide (2.41 g, 79%) as a colourless oil. IR (film): 2958, 2931, 2858, 1710, 1656, 1466, 1067 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.64–2.58 (m, 2H), 2.31–2.26 (m, 2H), 2.18–2.13 (m, 2H), 1.96–1.86 (m, 2H), 1.44–1.25 (m, 4H), 0.92 (t, *J*=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.1, 115.3, 39.9, 33.7, 29.6, 29.3, 22.5, 21.7, 13.9; MS (EI): 204 (18), 202 (18, M^+), 123 (16), 81 (100), 67 (29); HRMS calcd for $C_9H_{15}Br$: 202.0357, found: 202.0337.

4.2.5. 1-Bromo-2-benzylcyclopentene. According to general procedure I, 1,2-dibromocyclopentene[13] was reacted with *t*-BuLi and benzyl bromide (2.57 g, 15 mmol) to give the corresponding cyclopentenyl bromide (3.13 g, 88%) as a colourless oil. IR (film): 3085, 3062, 3027, 2953, 2849, 1494, 1453, 761, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.32–7.26 (m, 2H), 7.23–7.18 (m, 3H), 3.50 (s, 2H), 2.71–2.64 (m, 2H), 2.24–2.18 (m, 2H), 1.95–1.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=139.8, 138.7, 128.6, 128.4, 126.2, 116.7, 39.9, 36.4, 33.6, 21.6; MS (EI): 238 (16), 236 (16, M^+), 157 (100), 129 (63), 91 (47); HRMS calcd for $C_{12}H_{13}Br$: 236.0201, found: 236.0182.

4.3. General procedure II. Preparation of 1,2-disubstituted cyclopentenes

1-Bromo-2-alkyl(benzyl)cyclopentene (10 mmol) was dissolved in THF (20 mL). The solution was cooled down to −78°C and treated slowly with *t*-BuLi (13.3 mL, 20 mmol, 1.5 M in pentane). The mixture was stirred at −78°C for 15 min before the corresponding alkyl iodide (12 mmol) or TIPS-chloride (10 mmol, 1.93 g) was added. After warming up to room temperature the reaction mixture was quenched with water (30 mL). The aqueous phase was extracted with pentane (2×20 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After the solvents were removed under reduced pressure, the crude product was purified by column chromatography (pentane) and (or) by distillation to give the desired 1,2-disubstituted cyclopentene.

4.3.1. 1,2-Diethylcyclopentene (1b). According to general procedure II, 1-bromo-2-ethylcyclopentene (1.75 g, 10 mmol) was reacted with *t*-BuLi and ethyl iodide (1.87 g, 12 mmol). Purification by column chromatography (pentane) gave the corresponding alkene **1b** (0.91 g, 73%) as a colourless oil. IR (film): 2965, 2876, 2851, 1477, 1463, 1370 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.30 (t, *J*=7.5 Hz, 4H), 2.06 (q, *J*=7.7 Hz, 4H), 1.81–1.70 (m, 2H), 0.96 (t, *J*=7.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=136.1, 35.4, 21.6, 21.3, 13.2; MS (EI): 124 (26, M^+), 95 (100); HRMS calcd for C_9H_{16}: 124.1252, found: 124.1233.

4.3.2. 1,2-Dipropylcyclopentene (1c). According to general procedure II, 1-bromo-2-propylcyclopentene (1.13 g, 6 mmol) was reacted with *t*-BuLi (8 mL, 12 mmol) and *n*-propyl iodide (1.22 g, 7.2 mmol). Purification by column chromatography (pentane) gave the corresponding alkene **1c** (0.64 g, 70%) as a colourless oil. IR (film): 2956, 2931, 2870, 2841, 1464 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.28 (t, *J*=7.3 Hz, 4H), 2.02 (t, *J*=7.7 Hz, 4H), 1.79–1.70 (m, 2H), 1.44–1.32 (m, 4H), 0.87 (t, *J*=7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=135.4, 35.8, 30.4, 21.8, 21.4, 14.1; MS (EI): 152 (75, M^+), 123 (42), 109 (71), 81 (100), 67 (48); HRMS calcd for $C_{11}H_{20}$: 152.1565, found: 152.1551.

4.3.3. 1,2-Dibutylcyclopentene (1d). According to general procedure II, 1-bromo-2-butylcyclopentene (1.23 g, 11 mmol)

was reacted with *t*-BuLi (14.7 mL, 22 mmol) and *n*-butyl iodide (2.43 g, 13.2 mmol). Purification by column chromatography (pentane) gave the corresponding alkene **1d** (1.52 g, 77%) as a colourless oil. IR (film): 2956, 2929, 2872, 2858, 2841, 1466 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.27 (t, J=7.3 Hz, 4H), 2.04 (t, J=7.1 Hz, 4H), 1.79–1.68 (m, 2H), 1.45–1.21 (m, 8H), 0.89 (t, J=7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=135.4, 35.8, 30.5, 28.1, 22.7, 21.8, 14.0; MS (EI): 180 (21, M^+), 123 (29), 95 (71), 81 (100), 67 (40); HRMS calcd for $C_{13}H_{24}$: 180.1878, found: 180.1888.

4.3.4. 1,2-Dibenzylcyclopentene (1e). A solution of benzylzinc bromide, prepared from benzyl bromide (5.13 g, 30 mmol) and zinc (2.42 g, 37 mmol) in THF (20 mL),[14] was transferred via cannula to a solution of $Pd(dba)_2$ (0.574 g, 1 mmol), PPh_3 (0.524 g, 2 mmol) and 1,2-dibromocyclopentene[13] (2.26 g, 10 mmol) in THF (20 mL). The mixture was stirred at 60°C for 36 h. After the mixture was cooled to 0°C, NH_4Cl solution (30 mL, 2 M in H_2O) was added. The aqueous phase was extracted with pentane (2×20 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. Solvents were removed under reduced pressure and the crude product was purified by column chromatography (pentane) to give the desired alkene **1e** (1.76 g, 71%) as a colourless oil. IR (film): 3084, 3062, 3026, 3002, 2922, 2867, 2842, 1602, 1494, 1452, 1030, 720, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.33–7.28 (m, 4H), 7.24–7.19 (m, 6H), 3.56 (s, 4H), 2.29 (t, J=7.3 Hz, 4H), 1.80–1.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=140.3, 135.4, 128.6, 128.3, 125.8, 35.9, 34.9, 21.5; MS (EI): 248 (15, M^+), 157 (100), 129 (31), 91 (32); HRMS calcd for $C_{19}H_{20}$: 248.1565, found: 248.1587.

4.3.5. 1-*tert*-Butyl-2-methylcyclopentene (1f). A solution of 2-*tert*-butylcyclopentanone[15] (10.5 g, 75 mmol) in Et_2O (50 mL) was added dropwise to a solution of MeLi (50 mL, 80 mmol, 1.6 M in Et_2O) in Et_2O (50 mL) at −78°C. The mixture was allowed to warm up to 0°C and then added to cold aqueous hydrochloric acid (200 mL, 20% in water) and stirred for 2 h at room temperature. The aqueous phase was extracted with pentane (2×50 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. Distillation gave 6.73 g (65%) of a mixture, containing 67% of 1-*tert*-butyl-2-methylcyclopentene, 15% of 1-methyl-5-*tert*-butylcyclopentene and 18% of 2-*tert*-butylcyclopentanone. This mixture was then reacted with diethylborane, prepared from $BH_3{\cdot}Me_2S$ (0.46 g, 6 mmol) and Et_3B (1.18 g, 12 mmol), in THF (40 mL) at room temperature for 24 h in order to remove undesired alkene and starting ketone. After the solution was cooled to 0°C, NaOH (10 mL, 2 M in H_2O) and H_2O_2 (10 mL, 30% in H_2O) were added carefully and the mixture was stirred for 30 min at room temperature. Usual workup, followed by purification on a short column (pentane) and distillation, gave 3.7 g (36% based on 2-*tert*-butylcyclopentanone) of desired alkene **1f** as a colourless oil, bp 54–56°C/20 mbar. IR (film): 2953, 2868, 2841, 1463, 1362 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.42–2.36 (m, 2H), 2.33–2.26 (m, 2H), 1.77–1.75 (m, 3H), 1.70–1.60 (m, 2H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.5, 129.2, 41.5, 35.5, 33.3, 30.3, 21.4, 16.0; MS (EI): 138 (34, M^+), 123 (100), 81 (64); HRMS calcd for $C_{10}H_{18}$: 138.1409, found: 138.1407.

4.3.6. 1-(Triisopropylsilyl)-2-methylcyclopentene (1g). According to general procedure II, 1-bromo-2-methylcyclopentene (1.61 g, 10 mmol) was reacted with *t*-BuLi (13.3 mL, 20 mmol) and TIPS-chloride (1.92 g, 10 mmol). Distillation gave the desired alkene **1g** (1.31 g, 55%) as a colourless oil, bp 71–72°C/0.8 mbar. IR (film): 2944, 2890, 2865, 1607, 1464, 883, 674 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=2.47–2.40 (m, 2H), 2.38–2.31 (m, 2H), 1.82–1.80 (m, 3H), 1.80–1.70 (m, 2H), 1.28–1.16 (m, 3H), 1.06 (d, J=7.1 Hz, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=151.6, 129.6, 41.5, 40.3, 24.2, 18.9, 18.3, 12.4; MS (EI): 238 (1, M^+), 195 (100), 153 (100), 125 (42), 111 (32); HRMS calcd for $C_{15}H_{30}Si$: 238.2117, found: 238.2107.

4.3.7. 1-Benzyl-2-ethylcyclopentene (1h). According to general procedure II, 1-bromo-2-benzylcyclopentene (2.84 g, 12 mmol) was reacted with *t*-BuLi (16 mL, 24 mmol) and ethyl iodide (2.25 g, 14.4 mmol). Purification by column chromatography (pentane) gave the corresponding alkene **1h** (2.19 g, 98%) as a colourless oil. IR (film): 3084, 3062, 3027, 2963, 2932, 2842, 1602, 1494, 1453, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.34–7.29 (m, 2H), 7.24–7.17 (m, 3H), 3.43 (s, 2H), 2.43–2.38 (m, 2H), 2.30–2.22 (m, 4H), 1.84–1.74 (m, 2H), 1.08 (t, J=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=140.7, 138.5, 132.9, 128.5, 128.2, 125.6, 36.9, 35.3, 34.7, 21.6, 13.1; MS (EI): 186 (100, M^+), 157 (87), 129 (43), 91 (53); HRMS calcd for $C_{14}H_{18}$: 186.1409, found: 186.1404.

4.3.8. 2-Ethyl-1,1-diphenylbut-1-ene (24). To a solution of Ti(IV)-chloride (40.98 g, 216 mmol) in Et_2O (300 mL) at 0°C was added Zn-dust (26.15 g, 400 mmol) and pyridine (16 mL). After addition of benzophenone (18.22 g, 100 mmol) and 3-pentanone (8.61 g, 100 mmol), the solution was refluxed for 24 h. The resulting solution was carefully quenched by slowly adding to an aqueous solution of Na_2CO_3 (800 mL, 5%) and then filtered through celite, which was washed with Et_2O (400 mL). The phases were separated and the organic phase washed with aqueous HCl (2 M) and brine. After evaporation of the solvent, the crude product was purified by column chromatography (pentane), yielding **24** (21.38 g, 90%) as a colourless oil. IR (film): 3077, 3056, 2967, 2873, 1945, 1875, 1598, 1491, 758, 701, 625, 568 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ=7.58–7.13 (m, 10H), 2.16 (q, J=7.6 Hz, 4H), 1.00 (t, J=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=143.4, 142.2, 137.2, 129.3, 128.0, 126.0, 24.4, 13.3; MS (EI): 236 (28, M^+), 207 (41), 179 (37), 129 (100), 91 (62). Anal. calcd for $C_{18}H_{20}$: C 91.47, H 8.53; found: C 91.28, H 8.66.

4.4. General procedure III. Formation of the alcohols

To a solution of the corresponding olefin (1 mmol) in THF (4 mL) was slowly added $BH_3{\cdot}THF$ (3 mL, 3 mmol, 1 M in THF) at 0°C. The resulting solution was stirred for the time and at the temperature stated. After the solution was cooled to 0°C, NaOH (4 mL, 2 M in H_2O) and H_2O_2 (4 mL, 30% in H_2O) were slowly added. The resulting solution was stirred for 2 h at 25°C. After usual workup, the crude alcohols were purified by column chromatography (pentane/Et_2O).

4.4.1. 2,3-Diphenylcyclopentanol (2a). According to general procedure III, 1,2-diphenylcyclopentene **1a**[16] (0.220 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2a** was obtained as one diastereoisomer (0.195 g, 82%, column chromatography with pentane/Et_2O=1:1). IR (film): 3351, 3028, 2956, 1603, 1497, 1451, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.13–7.02 (m, 6H), 6.84–6.76 (m, 4H), 4.70–4.63 (m, 1H), 3.75–3.67 (m, 1H), 3.35 (dd, J=8.0, 6.2 Hz, 1H), 2.58–2.47 (m, 1H), 2.38–2.26 (m, 1H), 2.18–2.05 (m, 1H), 1.96–1.84 (m, 1H), 1.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.9, 139.4, 128.7, 128.4, 127.7, 127.6, 126.1, 125.8, 77.2, 59.6, 48.5, 33.6, 28.3; MS (EI): 238 (17, M^+), 220 (100), 147 (38), 129 (47), 91 (44); HRMS calcd for $C_{17}H_{18}O$: 238.1358, found: 238.1362.

4.4.2. 2,3-Diethylcyclopentanol (2b). According to general procedure III, 1,2-diethylcyclopentene **1b** (0.186 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **2b** was obtained as one diastereoisomer (0.151 g, 71%, column chromatography with pentane/Et_2O=3:1). IR (film): 3342, 2959, 2934, 2874, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=4.00–3.98 (m, 1H), 2.04–1.98 (m, 2H), 1.86–1.80 (m, 1H), 1.63–1.58 (m, 1H), 1.50–1.45 (m, 1H), 1.42–1.32 (m, 2H), 1.27–1.19 (m, 1H), 1.14–1.02 (m, 2H), 0.92 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=77.5, 52.8, 42.0, 33.0, 27.7, 22.6, 19.6, 13.0, 12.7; MS (EI): 142 (1, M^+), 124 (7), 98 (45), 95 (100); HRMS calcd for $C_9H_{18}O$: 142.1358, found: 142.1369.

4.4.3. 2,3-Dipropylcyclopentanol (2c). According to general procedure III, 1,2-propylcyclopentene **1c** (0.152 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2c** was obtained as one diastereoisomer (0.105 g, 62%, column chromatography with pentane/Et_2O=3:1). IR (film): 3340, 2956, 2929, 2871, 1466, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=4.02–4.00 (m, 1H), 2.17–2.11 (m, 1H), 2.08–2.02 (m, 1H), 1.88–1.82 (m, 1H), 1.73–1.69 (m, 1H), 1.52–1.47 (m, 2H), 1.44–1.21 (m, 6H), 1.16–1.02 (m, 2H), 0.95–0.91 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=77.9, 50.9, 39.8, 33.0, 32.2, 29.2, 28.1, 21.7, 21.4, 14.5, 14.4; MS (EI): 169 (1, $[M-H]^+$), 109 (100), 84 (96), 56 (89), 41 (50); HRMS calcd for $C_{11}H_{21}O$: 169.1592, found: 169.1607.

4.4.4. 2,3-Dibutylcyclopentanol (2d). According to general procedure III, 1,2-dibutylcyclopentene **1d** (0.180 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2d** was obtained as one diastereoisomer (0.101 g, 51%, column chromatography with pentane/Et_2O=3:1). IR (film): 3338, 2956, 2927, 2859, 1466, 1022 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=4.02–3.97 (m, 1H), 2.15–1.97 (m, 2H), 1.89–1.77 (m, 1H), 1.71–1.63 (m, 1H), 1.53–1.42 (m, 2H), 1.39–1.02 (m, 12H), 0.92–0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=77.9, 51.1, 40.1, 33.0, 30.8, 30.5, 29.6, 28.1, 26.6, 23.1, 23.0, 14.1, 14.1; MS (EI): 197 (0.3, $[M-H]^+$), 180 (4), 123 (100), 81 (59), 56 (68), 41 (57); HRMS calcd for $C_{13}H_{25}O$: 197.1905, found: 197.1931.

4.4.5. 2,3-Dibenzylcyclopentanol (2e). According to general procedure III, 1,2-dibenzylcyclopentene **1e** (0.248 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2e** was obtained as one diastereoisomer (0.213 g, 80%, column chromatography with pentane/Et_2O=1:1). IR (film): 3360, 3350, 3025, 2934, 1602, 1495, 1454, 738, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=7.32–7.28 (m, 4H), 7.23–7.19 (m, 6H), 4.06–4.04 (m, 1H), 2.92–2.86 (m, 2H), 2.63–2.57 (m, 1H), 2.52 (dd, J=13.5, 9.8 Hz, 1H), 2.41 (dd, J=14.1, 10.6 Hz, 1H), 2.21–2.13 (m, 2H), 1.84–1.78 (m, 1H), 1.57–1.51 (m, 1H), 1.46–1.40 (m, 1H), 1.23 (brs, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.6, 141.0, 128.8, 128.7, 128.5, 128.3, 126.0, 125.8, 76.9, 52.5, 42.0, 36.4, 33.6, 32.4, 27.8; MS (EI): 266 (1, M^+), 248 (9), 157 (100), 117 (43); HRMS calcd for $C_{19}H_{22}O$: 266.1671, found: 266.1690.

4.4.6. 3-*tert*-Butyl-2-methylcyclopentanol (2f). According to general procedure III, 1-*tert*-butyl-2-methylcyclopentene **1f** (0.207 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **2f** was obtained as one diastereoisomer (0.164 g, 70%, column chromatography with pentane/Et_2O=3:1). IR (film): 3326, 2958, 2903, 2877, 1471, 1364, 1023 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=3.83–3.82 (m, 1H), 2.06–1.95 (m, 4H), 1.70–1.64 (m, 1H), 1.51–1.44 (m, 2H), 0.92 (s, 9H), 0.78 (d, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=80.8, 50.2, 44.9, 31.9, 31.7, 29.3, 21.8, 14.4; MS (EI): 154 (0.3, $[M-2H]^+$), 139 (2), 123 (59), 99 (36), 81 (100); HRMS calcd for $C_{10}H_{18}O$: 154.1358, found: 154.1360.

4.4.7. 3-*tert*-Butyl-4-methylcyclopentanol (2g). According to general procedure III, 1-*tert*-butyl-2-methylcyclopentene **1f** (0.207 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 65°C for 96 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **2g** was obtained as one diastereoisomer (0.150 g, 64%, column chromatography with pentane/Et_2O=3:1). IR (film): 3340, 2956, 2870, 1476, 1365 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=3.73–3.71 (m, 1H), 1.76–1.70 (m, 1H), 1.64–1.55 (m, 3H), 1.54–1.49 (m, 1H), 1.42 (brs, 1H), 1.32–1.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=81.2, 56.5, 43.7, 33.9, 32.7, 27.9, 25.2, 21.4; MS (EI): 124 (7, $[M-CH_3OH]^+$), 123 (93), 99 (70), 83 (100); HRMS calcd for C_9H_{16}: 124.1252, found: 124.1206.

4.4.8. 3-Methyl-4-(triisopropylsilyl)cyclopentanol (2h). According to general procedure III, 1-(triisopropylsilyl)-2-methylcyclopentene **1g** (0.238 g, 1 mmol) was reacted with BH_3·THF at 50°C for 24 h. After oxidative workup, the desired alcohol **2h** was obtained as one diastereoisomer (0.154 g, 60%, column chromatography with pentane/Et_2O=3:1). IR (film): 3328, 2945, 2867, 1464, 1028, 883, 833, 663 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=4.47–4.42 (m, 1H), 2.55–2.47 (m, 1H), 2.06–1.95 (m, 1H), 1.79–1.70 (m, 3H), 1.67–1.58 (m, 1H), 1.47 (s, 1H), 1.16–1.05 (m, 21H), 0.92 (d, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=73.2, 46.2, 37.7, 35.5, 26.3, 20.7, 19.5, 19.4, 12.2; MS (EI): 213 (41, $[M-C_3H_7]^+$), 131 (22), 81 (100); HRMS calcd for $C_{12}H_{25}OSi$: 213.1675, found: 213.1649.

4.4.9. 3-Benzyl-2-ethylcyclopentanol (2i). According to general procedure III, 1-benzyl-2-ethylcyclopentene **1h** (0.186 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2i** was obtained as one diastereoisomer (0.118 g, 58%, column chromatography with pentane/Et_2O=1:1). IR (film): 3342, 3026, 2958, 2933, 2873, 1603, 1496, 1454, 1030, 737, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=7.36–7.33 (m, 2H), 7.26–7.23 (m, 3H), 4.17–4.14 (m, 1H), 2.85 (dd, J=13.4, 5.3 Hz, 1H), 2.60–2.54 (m, 1H), 2.40 (dd, J=13.4, 10.7 Hz, 1H), 2.20–2.14 (m, 1H), 1.82–1.75 (m, 2H), 1.63–1.54 (m, 2H), 1.46–1.37 (m, 2H), 1.36–1.29 (m, 1H), 1.07 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.9, 128.7, 128.2, 125.6, 77.5, 53.3, 41.9, 36.0, 33.0, 27.7, 20.1, 12.7; MS (EI): 204 (55, M^+), 157 (71), 117 (100), 113 (82), 104 (27); HRMS calcd for $C_{14}H_{20}O$: 204.1514, found: 204.1515.

4.4.10. 2-Benzyl-3-ethylcyclopentanol (2j). According to general procedure III, 1-benzyl-2-ethylcyclopentene **1h** (0.186 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. After oxidative workup, the desired alcohol **2j** was obtained as one diastereoisomer (0.024 g, 12%, column chromatography with pentane/Et_2O=1:1). IR (film): 3351, 3026, 2957, 2933, 2872, 1603, 1495, 1454, 1017, 740, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=7.30–7.28 (m, 2H), 7.20–7.18 (m, 3H), 3.99–3.97 (m, 1H), 2.77 (dd, J=13.9, 4.8 Hz, 1H), 2.24 (J=13.9, 10.1 Hz, 1H), 2.17–2.07 (m, 3H), 1.96–1.90 (m, 1H), 1.56–1.49 (m, 2H), 1.38–1.33 (m, 1H), 1.32–1.26 (m, 1H), 1.17 (brs, 1H), 0.95 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.3, 128.8, 128.4, 125.9, 77.0, 52.3, 42.3, 33.3, 32.5, 27.9, 23.1, 13.0; MS (EI): 204 (20, M^+), 186 (56), 157 (61), 117 (75), 113 (100); HRMS calcd for $C_{14}H_{20}O$: 204.1514, found: 204.1514.

4.4.11. 3-Methyl-2-phenylcyclopentanol (2k). According to general procedure III, 1-phenyl-2-methylcyclopentene **1i**[17] (0.237 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **2k** was obtained as one diastereoisomer (0.106 g, 40%, column chromatography with pentane/Et_2O=1:1). IR (film): 3341, 3028, 2871, 1602, 1495, 1454, 834, 747, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=7.31 (t, J=7.6 Hz, 2H), 7.24–7.20 (m, 1H), 7.18–7.16 (m, 2H), 4.58–4.55 (m, 1H), 3.04 (t, J=7.6 Hz, 1H), 2.50–2.43 (m, 1H), 2.30–2.25 (m, 1H), 2.13–2.07 (m, 1H), 1.76 (brs, 1H), 1.72–1.66 (m, 1H), 1.43–1.37 (m, 1H), 0.63 (d, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=140.4, 128.7, 128.2, 126.1, 76.6, 58.1, 36.6, 33.4, 31.1, 17.4; MS (EI): 176 (67, M^+), 132 (74), 117 (100); HRMS calcd for $C_{12}H_{16}O$: 176.1201, found: 176.1187.

4.4.12. 2-Methyl-3-phenylcyclopentanol (2l). According to general procedure III, 1-phenyl-2-methylcyclopentene **1i**[17] (0.237 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **2l** was obtained as one diastereoisomer (0.079 g, 30%, column chromatography with pentane/Et_2O=1:1). IR (film): 3344, 3028, 2876, 1602, 1497, 1452, 834, 746, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=7.31–7.28 (m, 2H), 7.20–7.18 (m, 3H), 4.08–4.06 (m, 1H), 3.57–3.53 (m, 1H), 2.30–2.26 (m, 1H), 2.22–2.17 (m, 1H), 2.16–2.10 (m, 1H), 2.01–1.94 (m, 1H), 1.71–1.65 (m, 2H), 0.58 (d, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.5, 128.3, 128.0, 125.8, 79.7, 47.1, 46.0, 33.2, 26.4, 13.2; MS (EI): 176 (1, M^+), 158 (61), 143 (100), 117 (44); HRMS calcd for $C_{12}H_{16}O$: 176.1201, found: 176.1198.

4.5. General procedure IV. Formation of the amines

To a solution of the corresponding olefin (1 mmol) in THF (4 mL) was slowly added BH_3·THF (3 mL, 3 mmol, 1 M in THF) at 0°C. The resulting solution was stirred for the time and at the temperature stated. The solvent and the excess of borane were removed under reduced pressure (0.1 mm Hg, 1 h). The residue was dissolved in CH_2Cl_2 (2 mL) and BCl_3 (5 mL, 5 mmol, 1 M in CH_2Cl_2) was added at 0°C. After stirring for 4 h at 25°C, the solvent and an excess of BCl_3 were removed under reduced pressure (0.1 mm Hg, 1 h). The residue was dissolved in CH_2Cl_2 (2 mL) and benzyl azide (0.399 g, 3 mmol) was added at 0°C. The solution was allowed to warm up to 25°C overnight. The reaction mixture was then quenched with NaOH (2 M in H_2O) and worked up as usual. The crude amines were purified by column chromatography (pentane/Et_2O).

4.5.1. *N*-2,3-Tribenzylcyclopentanamine (3a). According to general procedure IV, 1,2-dibenzylcyclopentene **1e** (0.248 g, 1 mmol) was reacted with BH_3·THF at 50°C for 3 h. The desired amine **3a** was obtained as one diastereoisomer (0.220 g, 62%, column chromatography with pentane/Et_2O=1:3). IR (film): 3025, 2933, 2864, 1602, 1495, 1454, 738, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.35–7.18 (m, 13H), 7.05–7.02 (m, 2H), 3.54–3.43 (m, 2H), 3.00–2.86 (m, 3H), 2.56–2.43 (m, 3H), 2.23–2.07 (m, 2H), 1.80–1.69 (m, 1H), 1.51–1.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.8, 141.2, 140.4, 129.0, 128.7, 128.4, 128.2, 128.2, 128.0, 126.6, 125.9, 125.7, 62.5, 52.1, 50.0, 43.0, 36.3, 34.9, 31.1, 28.8; MS (EI): 356 (22), 355 (22, M^+), 264 (43), 146 (96), 91 (100); HRMS calcd for $C_{26}H_{29}N$: 355.2300, found: 355.2296.

4.5.2. Octahydro-1*H*-inden-1-ol (8). According to general procedure III, 2,3,4,5,6,7-hexahydro-1*H*-indene **6**[18] (0.183 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **8** was obtained as one diastereoisomer (0.172 g, 82%, column chromatography with pentane/Et_2O=3:1). IR (film): 3339, 2923, 2853, 1448, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ=4.04–4.02 (m, 1H), 2.21–2.11 (m, 2H), 1.79–1.72 (m, 2H), 1.59 (s, 1H), 1.54–1.41 (m, 6H), 1.38–1.19 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=77.0, 48.1, 36.5, 32.9, 27.7, 26.9, 25.0, 23.6, 22.7; MS (EI): 140 (2, M^+), 122 (53), 96 (66), 81 (100); HRMS calcd for $C_9H_{16}O$: 140.1201, found: 140.1173.

4.5.3. *N*-Benzyloctahydro-1*H*-inden-1-amine (9). According to general procedure IV, 2,3,4,5,6,7-hexahydro-1*H*-indene **6**[18] (0.183 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. The residue was further reacted with BCl_3 (7.5 mL,

7.5 mmol, 1 M in CH_2Cl_2) in CH_2Cl_2 (4 mL) and benzyl azide (0.599 g, 4.5 mmol) in CH_2Cl_2 (6 mL). Evaporation of solvents after treatment with BCl_3 was performed at 50 mbar vacuum. The desired amine **9** was obtained as one diastereoisomer (0.189 g, 55%, column chromatography with pentane/Et_2O=1:3). IR (film): 3027, 2922, 2853, 1495, 1453, 732, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ= 7.33–7.21 (m, 5H), 3.83–3.71 (m, 2H), 2.98–2.92 (m, 1H), 2.16–2.03 (m, 2H), 1.80–1.66 (m, 2H), 1.56–1.25 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=140.8, 128.3, 128.1, 126.7, 61.6, 52.6, 45.3, 37.7, 31.0, 28.1, 28.0, 26.3, 23.5, 23.4; MS (EI): 229 (14, M^+), 200 (17), 146 (100), 91 (61); HRMS calcd for $C_{16}H_{23}N$: 229.1830, found: 229.1819.

4.5.4. Decahydro-1-naphthalenol (10). According to general procedure III, 1,2,3,4,5,6,7,8-octahydronaphthalene **7**[19](0.204 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (6 mL 2 M NaOH, 6 mL 30% H_2O_2), the desired alcohol **10** was obtained as one diastereoisomer (0.147 g, 72%, column chromatography with pentane/Et_2O=3:1). IR (film): 3350, 2924, 2859, 1448, 1045 cm^{-1}; ^1H NMR (toluene-d_8, 400 MHz, T=373 K): δ=3.53–3.48 (m, 1H), 1.80–1.73 (m, 2H), 1.66–1.60 (m, 1H), 1.54–1.11 (m, 13H), 0.67 (brs, 1H); ^{13}C NMR (toluene-d_8, 100 MHz, T=373 K): δ=69.0, 44.6, 35.2, 33.9, 29.9, 29.8, 26.6, 25.2, 23.8, 21.1; MS (EI): 153 (0.4, $[M-H]^+$), 136 (100), 121 (45), 94 (58); HRMS calcd for $C_{10}H_{17}O$: 153.1279, found: 153.1265.

4.5.5. *N*-Benzyldecahydro-1-naphthalenamine (11). According to general procedure IV, 1,2,3,4,5,6,7,8-octahydronaphthalene **7**[19] (0.204 g, 1.5 mmol) in THF (6 mL) was reacted with BH_3·THF (4.5 mL, 4.5 mmol, 1 M in THF) at 50°C for 3 h. The residue was further reacted with BCl_3 (7.5 mL, 7.5 mmol, 1 M in CH_2Cl_2) in CH_2Cl_2 (4 mL) and benzyl azide (0.599 g, 4.5 mmol) in CH_2Cl_2 (6 mL). Evaporation of solvents after treatment with BCl_3 was performed at 50 mbar vacuum. The desired amine **11** was obtained as one diastereoisomer (0.208 g, 57%, column chromatography with pentane/Et_2O=1:3). IR (film): 3028, 2923, 2857, 1495, 1448, 746, 698 cm^{-1}; ^1H NMR (toluene-d_8, 400 MHz, T=373 K): δ=7.28–7.26 (m, 3H), 7.14 (t, J=7.6 Hz, 2H), 3.74–3.61 (m, 2H), 2.57–2.53 (m, 1H), 1.87–1.10 (m, 16H); ^{13}C NMR (toluene-d_8, 100 MHz, T=373 K): δ=139.1, 128.5, 128.5, 127.0, 56.0, 51.9, 42.7, 34.7, 30.4, 30.2, 29.6, 27.5, 27.7, 27.7, 21.5; MS (EI): 243 (9, M^+), 200 (55), 146 (86), 91 (100); HRMS calcd for $C_{17}H_{25}N$: 243.1987, found: 243.2005.

4.5.6. 2-Isopropyl-cyclopentanol (13). According to general procedure III, (1-methylethylidene)cyclopentane **12**[20] (0.331 g, 3 mmol) in THF (23 mL) was reacted with BH_3·THF (9 mL, 9 mmol, 1 M in THF) at 50°C for 8 h. After oxidative workup (25 mL 2 M NaOH, 10 mL 30% H_2O_2), the desired alcohol **13** was obtained as one diastereoisomer (0.280 g, 73%; column chromatography with pentane/Et_2O=3:1). IR (film): 3307, 3076, 3061, 3029, 2872, 1632, 733, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=3.91 (m, 1H), 1.82–1.39 (m, 7H), 1.22–1.09 (m, 1H), 0.92 (d, J=6.8 Hz, 3H), 0.83 (d, J=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=76.7, 55.2, 35.7, 30.5, 27.9, 22.6, 21.4, 19.9; MS (EI): 128 (3, M^+), 110 (11), 95 (53), 82 (100), 57 (29). Anal. calcd for $C_8H_{16}O$: C 74.94, H 12.58; found: C 75.12, H 12.67.

4.5.7. 2-Isopropyl-1-(*N*-benzylamino)-cyclopentane (14). According to general procedure IV, (1-methylethylidene)-cyclopentane **12**[20] (0.331 g, 3 mmol) in THF (23 mL) was reacted with BH_3·THF (9 mL, 9 mmol, 1 M in THF) at 50°C for 12 h. The residue was further reacted with BCl_3 (12 mL, 12 mmol, 1 M in CH_2Cl_2) in CH_2Cl_2 (25 mL) and benzyl azide (0.479 g, 3.6 mmol) in CH_2Cl_2 (20 mL). The desired amine **14** was obtained as one diastereoisomer (0.449 g, 69%; column chromatography with pentane/Et_2O=2:1). IR (film): 3086, 3063, 3027, 2870, 1603, 1453, 1343, 1066, 975, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.40–7.23 (m, 5H), 3.88 (d, J=12.9 Hz, 1H), 3.81 (d, J=12.9 Hz, 1H), 2.85 (q, J=6.9 Hz, 1H), 1.88–1.24 (m, 8H), 0.94 (d, J=7.1 Hz, 3H), 0.89 (d, J=6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=140.9, 128.3, 128.2, 126.7, 62.0, 53.4, 52.8, 33.1, 30.8, 28.1, 23.8, 21.7, 19.5; MS (EI): 217 (10, M^+), 146 (100), 91 (94). Anal. calcd for $C_{15}H_{23}N$: C 82.89, H 10.67, N 6.44; found: C 82.68, H 10.85, N 6.70.

4.5.8. 2,3-Diphenylbutan-1-ol (*syn*-18). According to general procedure III, *Z*-1,2-dimethyl-1,2-diphenylethylene *Z*-**17**[21,22] (0.208 g, 1 mmol) was reacted with BH_3·THF under reflux for 16 h. After oxidative workup, the desired alcohol *syn*-**18** was obtained as one diastereoisomer (0.170 g, 75%; column chromatography with pentane/Et_2O=2:1). IR (KBr): 3480, 3080, 3024, 2960, 2924, 1342, 1055, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ= 7.34–7.21 (m, 10H), 3.59–3.44 (m, 2H), 2.95–2.88 (m, 2H), 1.02 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.5, 141.5, 128.7, 128.6, 128.5, 127.2, 126.8, 126.3, 65.7, 55.5, 42.2, 20.8; MS (EI): 226 (3, M^+), 121 (24), 105 (100), 91 (23); anal. calcd for $C_{16}H_{18}O$: C 84.91, H 8.02, O 7.07; found: C 84.43, H 7.58, O 6.89.

4.5.9. 2,3-Diphenylbutan-1-ol (*anti*-18). According to general procedure III, *E*-1,2-dimethyl-1,2-diphenylethylene *E*-**17**[21,22] (0.208 g, 1 mmol) was reacted with BH_3·THF under reflux for 16 h. After oxidative workup, the desired alcohol *anti*-**18** was obtained as one diastereoisomer (0.172 g, 76%; column chromatography with pentane/Et_2O=2:1). IR (film): 3558, 3375, 3084, 3061, 3028, 2964, 2930, 1494, 1452, 1047, 763 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.31–6.93 (m, 10H), 4.03–3.85 (m, 2H), 3.20–3.00 (m, 2H), 1.36 (d, J=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.7, 140.4, 128.9, 128.1, 127.9, 127.8, 126.6, 125.9, 64.7, 54.8, 41.9, 19.7; MS (EI): 226 (51, M^+), 105 (100), 91 (19), 28 (31); HRMS calcd for $C_{16}H_{18}O$: 226.1358, found: 226.1354.

4.5.10. *N*-Benzyl-2,3-diphenylbutan-1-amine (22a). According to general procedure IV, *Z*-1,2-dimethyl-1,2-diphenylethylene *Z*-**17**[21,22] (0.208 g, 1 mmol) was reacted with BH_3·THF under reflux for 16 h. The desired amine **22a** was obtained as one diastereoisomer (0.251 g, 80%; column chromatography with pentane/Et_2O=3:1). IR (film): 3308, 3084, 3026, 2966, 2026, 1494, 1452, 775, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.33–6.92 (m, 15H), 3.62 (d, J=13.4 Hz, 1H), 3.42 (d, J=13.4 Hz, 1H), 3.00 (dt, J=10.1, 4.3 Hz, 1H), 2.91–2.80 (m, 1H), 2.70 (dd, J=11.7, 9.9 Hz, 1H), 2.59 (dd, J=11.7, 4.3 Hz, 1H), 0.98 (d, J=7.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.9, 142.4, 139.8, 128.6, 128.5, 128.4, 128.2, 127.9, 127.4, 126.8, 126.7, 126.3, 53.5, 53.0, 52.9, 44.5, 21.0; MS (EI): 313 (3), 195 (3), 121 (18), 120 (100), 105 (20), 91 (97), 43 (9); HRMS calcd for $C_{23}H_{23}N$: 313.1830, found: 313.1829.

4.6. General procedure V. Formation of the zinc-reagents

To a solution of *Z*-1,2-dimethyl-1,2-diphenylethylene *Z*-**17**[21,22] (0.416 g, 2 mmol) in THF (10 mL) was slowly added BH_3·THF (4 mL, 4 mmol, 1 M in THF). The resulting solution was heated to reflux for 16 h. The solvent and the excess of borane were removed under reduced pressure (0.1 mm Hg, 1 h). The residue was dissolved in THF (10 mL) and treated with ethylene for 0.5 h. After the solvent was removed under reduced pressure (0.1 mm Hg, 1 h), Et_2Zn (2.1 mL, 20 mmol) was added at 0°C and stirring was continued for 3 h at this temperature. The excess of Et_2Zn and the solvent were removed under reduced pressure (0.1 mm Hg, 1 h) and the residue was diluted with THF (10 mL). The resulting mixture was cooled to −78°C and a solution of CuCN·2LiCl (0.4 mL, 0.4 mmol, 1 M in THF) was slowly added. The mixture was allowed to warm to −60°C and the corresponding electrophile (10 mmol) was added. The solution was allowed to warm up to 25°C and stirred at this temperature for 1 h. After usual workup, the crude products were purified by column chromatography (pentane/Et_2O).

4.6.1. 5,6-Diphenyl-1-heptene (22b). According to general procedure V, **22b** was obtained after reaction with allyl bromide (10 mmol, 1.21 g) as one diastereoisomer (0.361 g, 72%; column chromatography with pentane). IR (KBr): 3063, 3026, 2972, 2926, 1639, 1494, 1452, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.36–7.12 (m, 10H), 5.64–5.47 (m, 1H), 4.86–4.71 (m, 2H), 2.92–2.76 (m, 1H), 2.73–2.58 (m, 1H), 1.80–1.41 (m, 4H), 0.96 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.6, 143.9, 138.6, 128.4, 128.2, 127.6, 126.1, 126.0, 114.3, 52.4, 46.4, 33.5, 31.7, 21.1; MS (EI): 250 (2, M^+), 145 (34), 105 (56), 91 (100); HRMS calcd for $C_{19}H_{22}$: 250.1722, found: 250.1716.

4.6.2. 1,4,5-Triphenyl-1-hexyne (22c). According to general procedure V, **22c** was obtained after reaction with (bromoethynyl)benzene (10 mmol, 1.81 g) as one diastereoisomer (0.316 g, 51%; column chromatography with pentane). IR (film): 3082, 3061, 3028, 2962, 2926, 1491, 1452, 756, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.42–7.14 (m, 15H), 3.24–3.10 (m, 1H), 3.33–2.89 (m, 1H), 2.52–2.35 (m, 2H), 1.06 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.8, 143.0, 131.4, 131.4, 128.5, 128.4, 128.2, 128.1, 127.6, 127.4, 126.6, 126.4, 88.7, 82.4, 52.1, 44.2, 25.6, 20.7; MS (EI):310 (19, M^+), 205 (100), 105 (90), 91 (75), 77 (22); HRMS calcd for $C_{24}H_{22}$: 310.1721, found: 310.1721.

4.6.3. 1,3,4-Triphenylpentan-1-one (22d). According to general procedure V, **22d** was obtained after reaction with benzoyl chloride (10 mmol, 1.41 g) as one diastereoisomer (0.327 g, 52%; column chromatography with pentane/Et_2O=9:1). IR (KBr): 3057, 3026, 2953, 2922, 1676, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.67–7.61 (m, 2H), 7.46–7.12 (m, 13H), 3.51 (td, *J*=10.2, 3.6 Hz, 1H), 3.24 (dd, *J*=16.4, 10.1 Hz, 1H), 3.04–2.91 (m, 2H), 1.03 (d, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=199.1, 145.8, 143.3, 137.3, 132.6, 128.6, 128.3, 127.7, 127.3, 126.5, 126.4, 48.4, 45.9, 44.1, 20.9; MS (EI): 210 (6), 194 (29), 105 (100), 77 (24); HRMS calcd for $C_{15}H_{14}$: 194.1096, found: 194.1092.

4.6.4. *N*-Benzyl-*N*-[1-methyl-2-ethyl-3,3-diphenylpropyl]-amine (26). According to general procedure IV, 2-ethyl-1,1-diphenylbut-1-ene **24** (0.708 g, 3 mmol) in THF (25 mL) was reacted with BH_3·THF (9 mL, 9 mmol, 1 M in THF) at 50°C for 3 h. The residue was further reacted with BCl_3 (12 mL, 12 mmol, 1 M in CH_2Cl_2) in CH_2Cl_2 (25 mL) and benzyl azide (0.479 g, 3.6 mmol) in CH_2Cl_2 (15 mL). The desired amine **26** was obtained as a diastereomeric mixture of 92:8 (GC–MS, method B, 6.74 min and 6.89 min) (0.587 g, 57%; column chromatography with pentane/Et_2O=2:1). IR (film): 3061, 2961, 1597, 1493, 1451, 1380, 1029, 744, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.26–6.98 (m, 15H), 3.63 (m, 3H), 2.68 (m, 1H), 2.38 (m, 1H), 1.49 (m, 1H), 1.25–0.79 (m, 2H), 0.86 (m, 3H), 0.63 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.6, 144.3, 128.5, 128.3, 128.3, 128.3, 128.0, 127.8, 126.7, 126.0, 125.9, 56.1, 53.5, 51.5, 46.2, 20.7, 15.2, 14.5; MS (EI): 343 (1, M^+), 134 (100), 91 (51); HRMS calcd for $C_{25}H_{30}N$: 344.2378, found: 344.2365.

4.6.5. 3-Benzhydrylpentan-2-ol (27). According to general procedure III, 2-ethyl-1,1-diphenylbut-1-ene **24** (0.708 g, 3 mmol) in THF (23 mL) was reacted with BH_3·THF (9 mL, 9 mmol, 1 M in THF) at 50°C for 3 h. After oxidative workup (25 mL 2 M NaOH, 10 mL 30% H_2O_2), the desired alcohol **27** was obtained as a diastereomeric mixture of 72:28 (GC–MS, method B, 4.19 and 4.22 min) (0.556 g, 73%; column chromatography with pentane/Et_2O=3:1). IR (film): 3321, 3067, 2922, 1939, 1860, 1557, 1490, 1377, 1352, 986, 772, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.26–7.06 (m, 10H), 3.79 (m, 1H), 3.65 (d, *J*=10.8 Hz, 1H), 2.36 (m, 1H), 1.54–1.13 (m, 3H), 1.02 (d, *J*=6.4 Hz, 3H), 0.72 (t, *J*=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.0, 144.0, 128.3, 128.2, 128.0, 127.8, 126.1, 126.0, 69.1, 55.0, 49.4, 21.0, 18.3, 13.5; MS (EI): 254 (71, M^+), 195 (59), 174 (66), 91 (100), 28 (37). Anal. calcd for $C_{18}H_{22}O$: C 84.99, H 8.72; found: C 84.78, H 8.55.

4.6.6. *N*-Benzyl-*N*-[1,2-dimethyl-3,3-diphenylpropyl]-amine (30). According to general procedure IV, 2-methyl-1,1-diphenylbut-1-ene **28**[21,23] (0.667 g, 3 mmol) in THF (25 mL) was reacted with BH_3·THF (9 mL, 9 mmol, 1 M in THF) at 50°C for 3 h. The residue was further reacted with BCl_3 (12 mL, 12 mmol, 1 M in CH_2Cl_2) in CH_2Cl_2 (25 mL) and benzyl azide (0.479 g, 3.6 mmol) in CH_2Cl_2 (15 mL). The desired amine **30** was obtained as a diastereomeric mixture of 92:8 (GC–MS, method B, 6.00 and 6.19 min) (0.691 g, 70%; column chromatography with pentane/Et_2O=2:1). IR (film): 3096, 3051, 3020, 2870, 1944, 1746, 1495, 1384, 1123, 973, 914, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.22–7.00 (m, 15H), 3.62 (m, 2H), 3.50 (d, *J*=11.5 Hz, 1H), 2.61 (m, 2H), 0.85 (d, *J*=6.1 Hz, 3H), 0.70 (d, *J*=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.6, 143.8, 140.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 126.7, 126.0, 56.6, 52.4, 51.3, 39.3, 13.9, 11.4; MS

(EI): 329 (20, M^+), 258 (44), 251 (61), 91 (100). Anal. calcd for $C_{24}H_{27}N$: C 87.49, H 8.26, N 4.25; found: C 87.37, H 8.40, N 4.04.

4.6.7. *N*-Benzyl-3,4-diphenyl-2-hexanamine (*syn*-35). According to general procedure IV, *Z*-3,4-diphenylhex-3-ene *Z*-**33**[21,22c] (0.236 g, 1 mmol) was reacted with BH_3·THF under reflux for 14 h. The desired amine *syn*-**35** was obtained as one diastereoisomer (0.137 g, 40%; column chromatography with pentane/Et_2O=1:1). IR (film): 3025, 2964, 1494, 1451, 1377, 751, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.43–7.18 (m, 15H), 3.79 (d, J=13.2 Hz, 1H), 3.66 (d, J=13.2 Hz, 1H), 3.28 (m, 1H), 2.95 (m, 1H), 2.63 (m, 1H), 1.52 (m, 1H), 1.33 (m, 1H), 0.90 (d, J=6.6 Hz, 3H), 0.60 (t, J=7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=143.7, 140.9, 139.9, 129.9, 128.4, 128.2, 128.1, 127.9, 126.6, 126.4, 126.1, 54.8, 53.0, 50.8, 49.4, 27.9, 15.9, 12.0; MS (CI): 344 (100, $[M+H]^+$), 119 (40), 105 (36), 91 (28). Anal. calcd for $C_{25}H_{29}N$: C 87.41, H 8.51, N 4.08; found: C 87.36, H 8.73, N 4.24.

4.6.8. *N*-Benzyl-3,4-diphenyl-2-hexanamine (*anti*-35). According to general procedure IV, *E*-3,4-diphenylhex-3-ene *E*-**33**[21,22c] (0.236 g, 1 mmol) was reacted with BH_3·THF under reflux for 14 h. The desired amine *anti*-**35** was obtained as a diastereomeric mixture of 90:10 (GC–MS, method A, 5.41 and 5.61 min) (0.227 g, 66%; column chromatography with pentane/Et_2O=3:2). IR (film): 3083, 3060, 2961, 2928, 1493, 1452, 1147, 753, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.39–7.12 (m, 5H), 7.07–6.93 (m, 6H), 6.83–6.71 (m, 4H), 3.85 (d, J=13.0 Hz, 1H), 3.77 (d, J=12.7 Hz, 1H), 3.27 (m, 1H), 2.99 (m, 2H), 1.68 (m, 1H), 1.47 (m, 1H), 0.90 (d, J=6.1 Hz, 3H), 0.68 (t, J=7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.6, 141.0, 139.6, 130.4, 129.4, 128.4, 128.2, 127.4, 127.2, 126.8, 126.0, 125.6, 56.0, 52.7, 50.9, 47.4, 26.6, 17.4, 12.1; MS (CI): 344 (100, $[M+H]^+$). Anal. calcd for $C_{25}H_{29}N$: C 87.41, H 8.51, N 4.08; found: C 87.30, H 8.36, N 4.45.

4.6.9. (1-Ethyl-3-methyl-2-phenylhex-5-enyl)benzene (*syn*-36). To a solution of *Z*-3,4-diphenylhex-3-ene *Z*-**33**[21,22](0.236 g, 1 mmol) in THF (5 mL) was slowly added BH_3·THF (3 mL, 3 mmol, 1 M in THF). The resulting solution was heated to reflux for 14 h. The solvent and the excess of borane were removed under reduced pressure (0.1 mm Hg, 1 h). The residue was treated with *i*-Pr_2Zn (1 mL, 4 mmol, 4 M in Et_2O) for 3 h at 25°C. After the solvents and the excess of *i*-Pr_2Zn were removed under reduced pressure (0.1 mm Hg, 1 h), the residue was diluted with THF (2 mL). The resulting mixture was cooled to −78°C and a solution of CuCN·2LiCl (1 mL, 1 mmol, 1 M in THF) was slowly added. The mixture was stirred at −78°C for 30 min. Allyl bromide (0.363 g, 3 mmol) in THF (1 mL) was slowly added at this temperature. The solution was allowed to warm up to 25°C overnight. After usual workup, the crude product *syn*-**36** was purified by column chromatography (pentane) and obtained in a 60:40 mixture of diastereoisomers (^1H NMR, e.g. 5.83 and 5.50 ppm) (0.170 g, 61%). IR (film): 3061, 3027, 2962, 2928, 1492, 1452, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.07–6.84 (m, 10H), 5.88–5.78 (m, 1H), 5.06–4.99 (m, 2H), 3.04 (dt, J=9.6, 4.3 Hz, 1H), 2.87 (dd, J=9.2, 5.2 Hz, 1H), 2.19–2.12 (m, 2H), 1.93–1.87 (m, 1H), 1.79–1.74 (m, 1H), 1.59–1.48 (m, 1H), 0.83 (d, J=6.8 Hz, 3H), 0.73 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=143.5, 140.4, 137.8, 130.4, 129.0, 127.5, 127.0, 125.6, 125.5, 116.0, 54.8, 48.5, 40.3, 33.5, 26.8, 15.2, 12.1; MS (EI): 278 (5, M^+), 159 (51), 119 (50), 118 (53), 91 (100). Anal. calcd for $C_{21}H_{26}$: C 90.59, H 9.41; found: C 90.32, H 9.62.

4.6.10. 3,4-Diphenylhexan-2-ol (*anti*-37). According to general procedure III, *E*-3,4-diphenylhex-3-ene *E*-**33**[21,22c] (0.236 g, 1 mmol) was reacted with BH_3·THF under reflux for 14 h. After oxidative workup, the desired alcohol *anti*-**37** was obtained as a diastereomeric mixture of 75:25 (GC–MS, method C, 4.39 and 4.43 min) (0.223 g, 82%; column chromatography with pentane/Et_2O=2:1). IR (KBr): 3367, 3060, 3028, 2962, 2930, 1493, 1453, 1375, 1106, 757, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.22–7.08 (m, 6H), 6.99–6.88 (m, 2H), 6.77–6.71 (m, 2H), 4.07 (m, 1H), 3.37 (m, 1H), 2.92 (m, 1H), 1.79–1.51 (m, 3H), 1.02 (d, J=6.2 Hz, 3H), 0.82 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.4, 138.8, 130.3, 129.7, 127.4, 126.3, 125.9, 67.9, 58.8, 47.0, 26.3, 21.9, 12.2; MS (EI): 236 (4, M^+), 118 (94), 91 (100). Anal. calcd for $C_{18}H_{22}O$: C 84.99, H 8.72; found: C 84.81, H 8.52.

4.6.11. *N*-Benzyl-*N*-[1-methyl-2,3-diphenylbutyl]amine (40). According to general procedure IV, *Z*-2,3-diphenylpent-2-ene *Z*-**38**[24] (0.222 g, 1 mmol) was reacted with BH_3·THF under reflux for 14 h. The desired amine **40** was obtained as a diastereomeric mixture of 95:5 (GC–MS, method A, 5.28 and 5.44 min) (0.151 g, 46%; column chromatography with pentane/Et_2O=2:1). IR (KBr): 3306, 3083, 3026, 2964, 2924, 1493, 1452, 1375, 750, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ=7.28–6.99 (m, 15H), 3.67 (d, J=13.2 Hz, 1H), 3.55 (d, J=13.4 Hz, 1H), 3.07 (m, 2H), 2.56 (m, 1H), 0.96 (d, J=6.6 Hz, 3H), 0.81 (d, J=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.1, 140.8, 139.7, 129.9, 128.5, 128.2, 127.9, 127.9, 127.3, 126.6, 126.4, 126.1, 56.0, 53.0, 50.8, 41.4, 21.5, 16.1; MS (EI): 329 (58, M^+), 134 (100), 91 (80). Anal. calcd for $C_{24}H_{27}N$: C 87.49, H 4.25; found: C 87.30, H 4.09.

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References

1. (a) In *Chemistry for the 21st Century*; Keinan, E., Scheckta, I., Eds.; Wiley-VCH: New York, 2001. (b) Ward, R. S. *Selectivity in Organic Synthesis*; Wiley: New York, 1999. (c) Nogradi, M. *Stereoselective Synthesis*; VCH: New York, 1995. (d) Gawley, R. E.; Aubé, J. *Principles of Asymmetric Synthesis*; Pergamon: Oxford, 1996. (e) Nicolaou, K. C.; Sorensen, E. J. *Classics in Total Synthesis*; VCH: New York, 1996.
2. (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1966**, *88*,

1433. (b) Brown, H. C.; Bhatt, M. V. *J. Am. Chem. Soc.* **1966**, *88*, 1440.
3. (a) Wood, S. E.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 555. (b) Field, L. D.; Gallagher, S. P. *Tetrahedron Lett.* **1985**, *26*, 6125.
4. (a) Lhermitte, F.; Knochel, P. *Angew. Chem.* **1998**, *110*, 2597. *Angew. Chem. Int. Ed.* **1998**, *37*, 2460. (b) Varela, J. A.; Pena, D.; Goldfuss, B.; Polborn, K.; Knochel, P. *Org. Lett.* **2001**, *3*, 2395. (c) X-Ray crystallographic data (excluding structure factors) for the structure of 3,5-dinitrobenzoate of **27** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with refcode GULZUI, NBS Id 734862. (d) X-Ray crystallographic data (excluding structure factors) for the structure of the alcohol, obtained after oxidation of *syn*-**34** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with refcode GUMBAR, NBS Id 734863. (e) X-Ray crystallographic data (excluding structure factors) for the structure of the alcohol, obtained after hydroboration and oxidation of *Z*-**38** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with refcode GUMBEV, NBS Id 734864. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk)
5. (a) Laaziri, H.; Bromm, L. O.; Lhermitte, F.; Gschwind, R. M.; Knochel, P. *J. Am. Chem. Soc.* **1999**, *121*, 6940. (b) Bromm, L. O.; Laaziri, H.; Lhermitte, F.; Harms, K.; Knochel, P. *J. Am. Chem. Soc.* **2000**, *122*, 10218.
6. The diastereoselectivity was determined by NMR analysis of crude reaction mixtures. The precision of this measurement is established to be ±3%.
7. (a) Brown, H. C.; Suzuki, A.; Sonao, S.; Itoh, M.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 4329. (b) Chavant, P.-Y.; Lhermitte, F.; Vaultier, M. *Synlett* **1993**, 519.
8. Goldfuss, B.; Knochel, P.; Bromm, L. O.; Knapp, K. *Angew. Chem.* **2000**, *112*, 4302. *Angew. Chem. Int. Ed.* **2000**, *39*, 4136.
9. Reetz, M. T. *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1977; Vol. 16, pp 1–30.
10. Langer, F.; Schwink, L.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 8229.
11. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.
12. Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1989**, *30*, 4799.
13. Li, J. J.; Anderson, G. D.; Burton, E. G.; Cogburn, J. N.; Collins, J. T.; Garland, D. J.; Gregory, S. A.; Huang, H.-C.; Isakson, P. C. *J. Med. Chem.* **1995**, *38*, 4570.
14. Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* **1988**, *53*, 5789.
15. Chan, T. H.; Paterson, I.; Pinsonnault, J. *Tetrahedron Lett.* **1977**, 4183.
16. Baumstark, A. L.; McCloskey, C. J.; Candice, J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609.
17. Maggio, T. E. *J. Am. Chem. Soc.* **1961**, *83*, 968.
18. Benkeser, R. A.; Kaiser, E. M. *J. Org. Chem.* **1964**, *29*, 955.
19. Kaiser, E. M.; Benkeser, R. A. *Org. Synth.* **1970**, *50*, 88.
20. Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4216.
21. Obtained by Mc-Murry reactions (see synthesis of **24**), compare Leimner, L.; Weyerstahl, P. *Chem. Ber.* **1982**, *115*, 3697.
22. (a) Rele, S.; Talukdar, S.; Banerji, A.; Chattopadhyay, S. *J. Org. Chem.* **2001**, *66*, 2990. (b) Talukdar, S.; Nayak, S.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 4925. (c) Besancon, J.; Szymoniak, J.; Moise, C. *J. Organomet. Chem.* **1992**, *426*(3), 325.
23. Harrison, R. B. *Analyst* **1963**, *88*, 644.
24. Stüdemann, T.; Ibrahim-Ouali, M.; Knochel, P. *Tetrahedron* **1998**, *54*, 1299.