A novel stereoselective synthesis of *N*-heterocycles by intramolecular hydrovinylation †

Ulrich Bothe, Hans Christian Rudbeck, David Tanner and Mogens Johannsen *

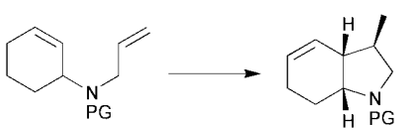
Department of Chemistry, Building 201, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Received (in Cambridge, UK) 13th September 2001, Accepted 5th November 2001
First published as an Advance Article on the web 28th November 2001

A novel method for the synthesis of bicyclic amines has been developed. Cyclisation of 1,6-dienes by intramolecular hydrovinylation in the presence of catalytic amounts of allylpalladium chloride dimer afforded bicyclic amines in one step. Added phosphines, silver salts, as well as the nature of the *N*-protecting group influenced the yield and selectivity of the reactions. Most strikingly, intramolecular hydrovinylation allowed the preparation of diastereomerically pure bicyclic amines as *e.g.* hexahydroindoles **2a**–**2d**.

Introduction

A great deal of attention has been paid to the synthesis of cyclopentanes and cyclopentenes by intramolecular hydrovinylation of 1,6-dienes catalysed by Ru,[1] Pd,[2] Ni,[2a] Ti[3] as well as Rh[4] complexes. Quite surprisingly, the preparation of cyclic amines of potential pharmacological interest by intramolecular hydrovinylation is not that well established, although the groups of Yamamoto[1] and RajanBabu[2a] have described the cyclisation of *N*-acyl and *p*-tolylsulfonyl derivatives of diallylamine. During an investigation on the scope of the intramolecular hydrovinylation reaction we recently discovered a class of unsymmetrical diallylamines which could be transformed in the presence of a catalytic amount of a palladium catalyst into bicyclic amines. To the best of our knowledge, the present paper describes the first selective intramolecular hydrovinylation of 1,6-dienes in which one double bond is situated in a ring system. Contrary to existing methods for the preparation of similar structures,[5] our procedure is very short and moreover atom-economic.[6] The scope of our new protocol is outlined by the example in Scheme 1.



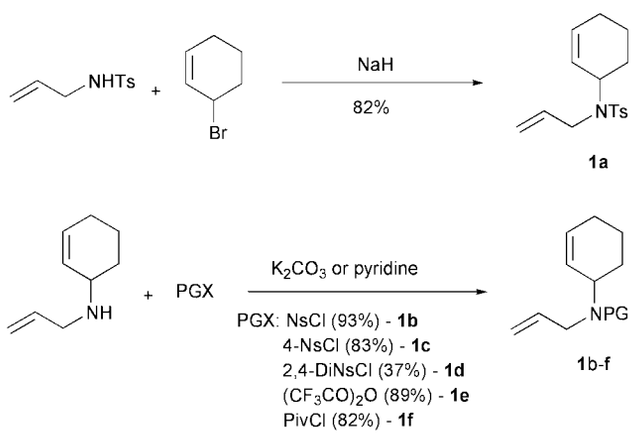
1 **2**

Scheme 1

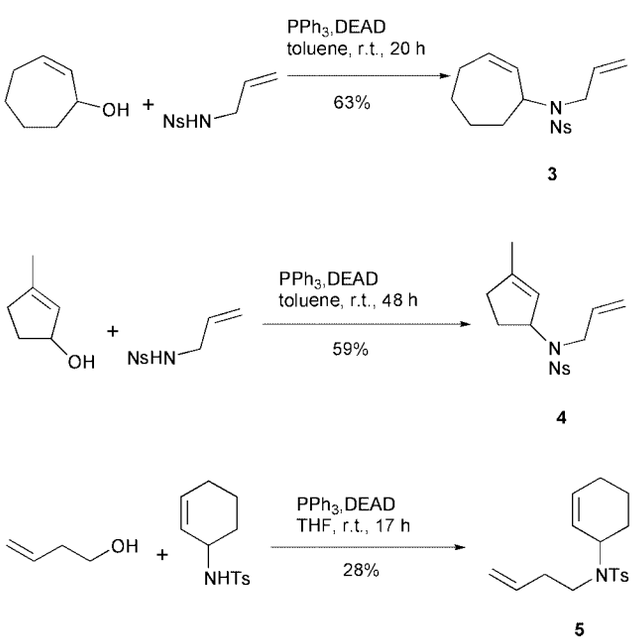
Results

The synthesis of the diene substrates used in the present work is simple, and is shown in Schemes 2 and 3. The precursor **1a** was made by *N*-alkylation of *N*-allyltoluenesulfonamide using cyclohex-2-enyl bromide and sodium hydride as base in 82% yield. However, the rest of the compounds **1b**–**f** were more adequately made by acylation of *N*-allyl-*N*-cyclohex-2-enylamine in yields ranging from 37–93% (Scheme 2).

For the synthesis of the diene substrates **3**, **4** and **5** an approach based on the Mitsunobu reaction was chosen. Using standard Mitsunobu chemistry the compounds could be obtained in yields ranging from 28–63% (Scheme 3).



Scheme 2



Scheme 3

Only a few cases of *selective* cyclisations by intramolecular hydrovinylation of disubstituted olefins have been published, *e.g.* the cyclisation of malonate derivatives.[1,2a] Therefore

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compounds **1a**–**f**, **2a**–**d**, **3**–**5**, **8**–**10**. See http://www.rsc.org/suppdata/p1/b1/b108310d/

DOI: 10.1039/b108310d

This journal is © The Royal Society of Chemistry 2001

we were pleased that in our exploratory experiments the unsymmetrical diene **1a**, having an endocyclic double bond, could be transformed to the diastereomerically pure hexahydroindole **2a** in 29% yield in the presence of 7 mol% of the Pd-dimer, AgOTf and PPh_3 in dichloromethane (Table 1, entry 1).[7] The relative stereochemistry of the product was determined by 2D-NOESY and COSY experiments. As this is a novel and short access to a hydroindole moiety, we then optimised the reaction conditions by varying the added silver salt and phosphine. First we used $AgSbF_6$ instead of AgOTf, because it was shown that application of the former gives superior yields in the *inter*molecular hydrovinylation (addition of ethylene to styrenes).[8,9] This observation was also made for the cyclisation of **1a**: the desired product **2a** was formed in 38% yield (entry 2). Switching from PPh_3 to the more electron rich tri(2-furyl)-phosphine had little effect on the yield of the transformation (entry 3). Remarkably, a combination of the Pd-dimer with the sterically hindered dicyclohexyl(biphenyl-2-yl)phosphine, which was for example successfully applied in Pd-catalysed aminations,[9] did not catalyse the reaction (entry 4).

It had been demonstrated earlier that the protecting group on the nitrogen atom had a remarkable influence on the yield and selectivity of the Pd-catalysed cycloisomerisation of diallylamine[2a] and that substrates lacking an electron-withdrawing group on nitrogen did not react in the cycloisomerisation using allylpalladium chloride dimer as catalyst. Therefore allyl(cyclohexenyl)amine[5f] was protected with the 2-nitrophenylsulfonyl (Ns), 4-nitrophenylsulfonyl (4-Ns), 2,4-dinitrophenylsulfonyl (2,4-DiNs), trifluoroacetyl and the pivaloyl (Piv) group, respectively, to afford protected amines **1b**–**1f**. The results of the cycloisomerisation experiments are shown in Table 2. Interestingly, when **1b** having a more electron-withdrawing 2-nitrophenylsulfonyl group was cycloisomerised in the presence of PPh_3 and $AgSbF_6$ (Table 2, entry 1), the yield was significantly increased to 53%. A similar yield of hexahydroindole **2c** was obtained when substrate **1c** having a 4-nitrophenylsulfonyl group was used as starting material (entry 2). However, a further increase of the electron-withdrawing ability of the protecting group by applying the 2,4-dinitrophenylsulfonyl-protecting group (substrate **1d**) did not further increase the yield of the cyclised product **2d** (entry 3).

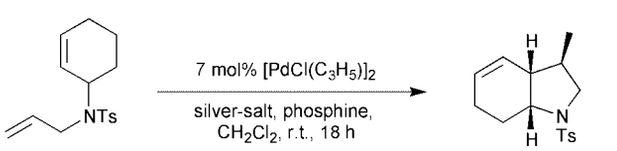
Contrary to the results described above, the cyclisation of **1e** protected with the trifluoroacetyl group gave a complex mixture of isomers (entry 4), and starting material was recovered when pivaloyl-protected **1f** was used as starting material (entry 5).

Addition of a coordinating co-solvent was shown to improve the yield of the intermolecular Pd-catalysed hydrovinylation reaction.[7] However, cycloisomerisation of 2-nitrophenylsulfonyl-protected allyl(cyclohexenyl)amine **1b** in the presence of THF as co-solvent (entry 6) gave the cyclised product in a yield similar to that obtained in pure dichloromethane (see entry 1). The use of the more sterically hindered tri-*o*-tolylphosphine did not improve the yield of the cyclisation (entry 7). Recently, we developed a synthesis of novel aryl-MOno-PhosphinoFerrocenyl ligands (MOPF), which we applied in enantioselective hydrosilylation reactions.[10] When the simple phenyl-MOPF ligand (Ph-MOPF) was applied to the cyclisation of 4-nitrophenylsulfonyl-protected allyl(cyclohexenyl)amine **1c**, the yield of the cyclised product **2c** was not improved in comparison to the experiment with triphenylphosphine (entry 8 in Table 2).

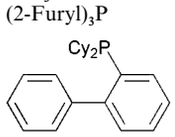
However, using Ph-MOPF in the intramolecular hydrovinylation of a simple diallylic substrate **6** selectively gave the 5-membered cycloadduct **7** (Scheme 4). In comparison the same reaction has been reported to give a mixture of 5- and 6-membered products upon cyclisations using triphenylphosphine as ligand.[2a]

Remarkably, the Ru-catalyst $[(COD)RuCl_2]_n$ which was successfully applied for the cyclisation of acetyl-protected

Table 1 Preliminary cyclisations of diene **1a** using various combinations of phosphines and silver salts

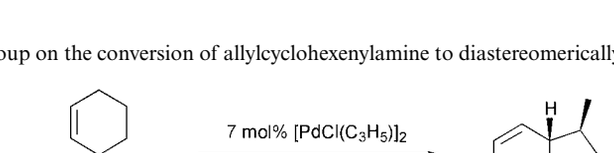


1a **2a**

Entry	Phosphine[a]	Silver salt[a]	Yield (%)[b]
1	PPh_3	AgOTf	29
2	PPh_3	$AgSbF_6$	38
3	$(2\text{-Furyl})_3P$	$AgSbF_6$	37
4		$AgSbF_6$	No reaction

[a] A 2 : 1 ratio of phosphine as well as silver salt to Pd-dimer was used. [b] In all cases the amount of other isomers was <5%.

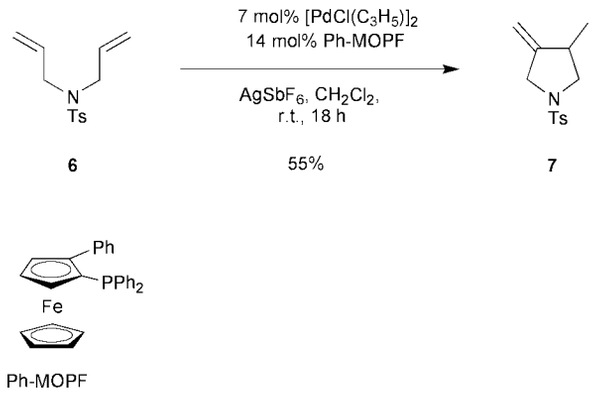
Table 2 Influence of the protecting group on the conversion of allylcyclohexenylamine to diastereomerically pure hexahydroindole[a,b,c]



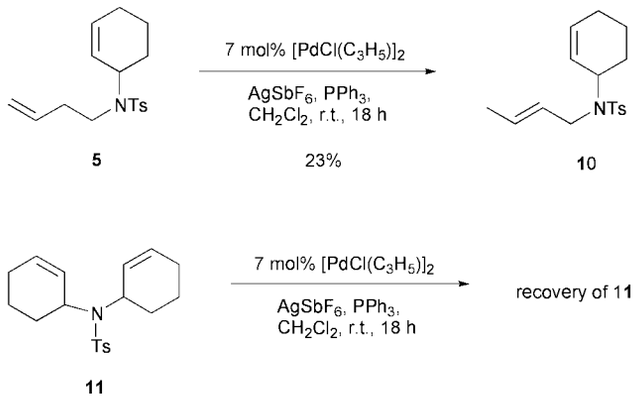
1b-f **2b-d**

	Entry	Substrate	PG	Product(s)	Yield (%)[d]	Remarks
	1	**1b**	Ns	**2b**	53	
	2	**1c**	4-Ns	**2c**	52	
	3	**1d**	2,4-DiNs	**2d**	51	
	4	**1e**	CF_3CO	Complex mixture	(58)	Combined yield of all isomers
	5	**1f**	Piv	—	No reaction	
	6	**1b**	Ns	**2b**	53	4% THF as co-solvent
	7[e]	**1c**	4-Ns	**2c**	37	$(2\text{-Me-}C_6H_4)_3P$ as ligand
	8[f]	**1c**	4-Ns	**2c**	45	Ph-MOPF as ligand

[a] The reactions were performed on a 0.9–1.1 mmolar scale. [b] Substrates **1b**–**1f** were synthesised from allyl(cyclohexenyl)amine[5f] (see Experimental section). [c] A 2 : 1 ratio of phosphine as well as silver salt to Pd-dimer was used. [d] In all cases yield of other isomers <5%. [e] 10 mol% of the Pd-dimer were used. [f] Experiment was performed on a 0.1 mmolar scale.



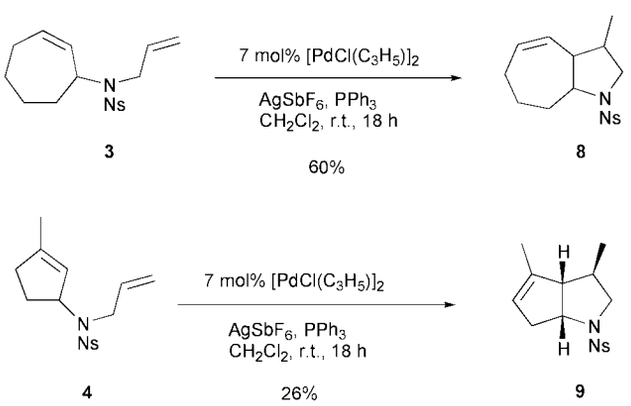
Scheme 4



Scheme 6 Attempted cyclisations of **5** and **11**.

diallylamine[1] was not capable of catalysing the cycloisomerisation of 2-nitrophenylsulfonyl-protected amine **1b**. After heating a mixture of **1b** in isopropyl alcohol in the presence of 3 mol% of the catalyst for 18 h, only starting material was recovered.

We were then eager to find out if our optimised conditions for the Pd-catalysed hydrovinylation were also suitable for the construction of bicyclic ring systems with other ring sizes. Therefore, we tested 2-nitrophenylsulfonyl-protected allyl(cycloheptenyl)amine **3** in the hydrovinylation reaction. Fortunately, cyclisation applying 7 mol% Pd-dimer, PPh_3 as well as $AgSbF_6$ afforded the cyclised product **8** in 60% yield, however as a 1 : 1 : 1 mixture of 3 diastereoisomers according to ^1H NMR (Scheme 5).



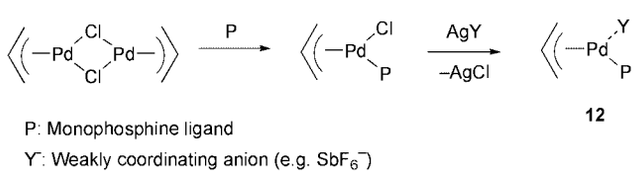
Scheme 5 Cyclisation of cyclic 1,6-dienes with larger and smaller ring sizes.

To the best of our knowledge a cyclisation of a diene having one *triply* substituted double bond by hydrovinylation-catalysis has not been reported in the literature. Quite remarkably, substrate **4** reacted in the hydrovinylation reaction affording the single diastereomer **9** in 26% yield after column chromatography and subsequent recrystallisation. As previously, the relative stereochemistry of the cyclised product was assigned on the basis of extensive NMR experiments. It should be noted that the simpler analogue of **4** lacking the methyl group on the alkene also cyclised smoothly to give the product in 50–60% yield, but with lower diastereoselectivity.[11]

Next the cyclisation of *p*-tolylsulfonyl-protected but-3-enyl-(cyclohexenyl)amine **5**, having a 1,7-diene structure, was investigated. However, instead of a bicyclic product only the diene **10** derived from an isomerisation of the external double bond to the internal position could be isolated in low yield (Scheme 6). Moreover, protected dicyclohexenylamine **11** having two disubstituted double bonds could not be cyclised to a tricyclic ring system in the presence of the Pd-dimer. Only starting material could be recovered in this case.

We also tested a variety of analogous structures having an allyl ether structure, but these afforded complex product mixtures in the Pd- as well as in the Ru-catalysed hydrovinylation.[12]

The mechanism and selectivity of the present hydrovinylation can be rationalised on the basis of the following discussion. The monoallylpalladium complex **12** which serves as the catalyst precursor is prepared prior to reaction by addition of two equivalents of phosphine ligand and an appropriate silver salt to the palladium allyl dimer (Scheme 7).

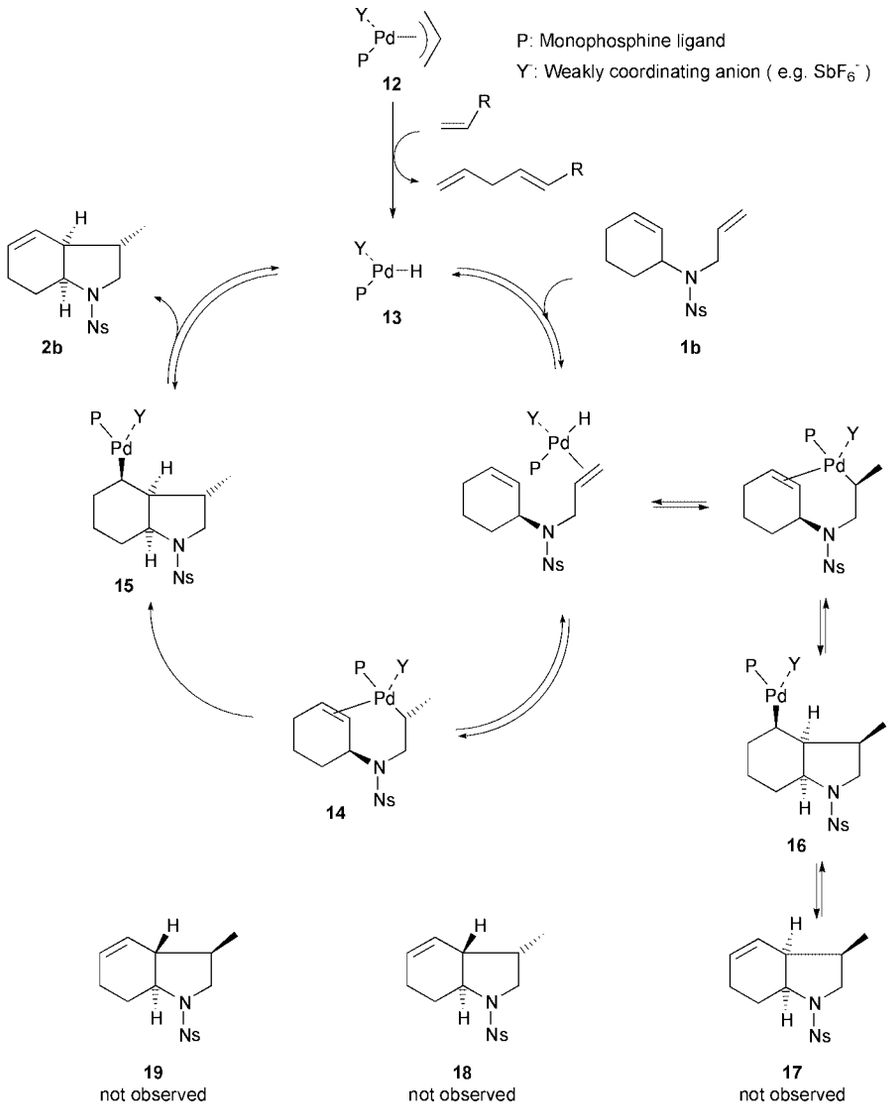


Scheme 7

The catalytically active palladium hydride complex **13** (Scheme 8) is thereafter formed *in situ* by 1,2-insertion of the palladium monoallylic complex into a double bond of the starting material, *e.g.* **1b**, followed by a β-elimination. The catalytic cycle now proceeds through coordination of the least hindered double bond of the diene substrate to the palladium complex followed by a hydropalladation giving **14**. An insertion into the second double bond *cis* to the amine substituent gives the intermediate **15** which on β-elimination releases the product **2b** and regenerates the catalyst **13**. The predominant formation of the diastereoisomer shown can be rationalized on the basis of a comparison with the more sterically congested intermediate **16** on the path to the epimer **17**. Note that both the palladium and the methyl group point into the concave part of the *cis*-fused bicyclic indoline skeleton. The two other possible isomers **18** and **19** could have arisen through an energetically more demanding hydropalladation *trans* to the amine substituent on the cyclohexenyl ring giving a *trans* fused indoline skeleton, but its formation was not observed.

Although the net result of our reaction is similar to that described[5e] by Uesaka *et al.* (who used a zirconium catalysed cyclisation of analogous substrates in the presence of an excess of Grignard reagent) the present method is more straightforward and proceeds with higher diastereoselectivity.

In summary, we have developed a new atom-economic and simple synthesis of bicyclic *N*-heterocycles, which may serve especially in the case of the hexahydroindoles **2a**–**2d** as valuable building blocks for the construction of more complex molecules. Currently, we are further investigating the scope of the intramolecular hydrovinylation reaction in asymmetric synthesis and for the preparation of cyclic amino acids.



Scheme 8 The catalytic cycle.

Experimental

General information

All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. All solvents were distilled prior to use. THF was distilled from sodium–benzophenone, dichloromethane from calcium hydride. Allylpalladium chloride dimer was purchased from Aldrich and used as obtained. Column chromatography was performed using Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh). Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates. IR spectra were measured on a Perkin Elmer 1720 Infrared Fourier Transform Spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Gemini 300 NMR spectrometer at ambient temperature. Chemical shifts are reported in ppm. Multiplicity is given as follows: br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Electron Impact (EI) Mass Spectra were recorded on a VG Trio-2 single quadrupole instrument. FAB and EI HRMS spectra were recorded on a JEOL JMS-HX/HX 110A (FAB and EI) and a Micromass QTOF-1 (ES).

Synthesis of protected allylcyclohexenylamines 1a–1f

***N*-Allyl-*N*-(cyclohex-2-enyl)toluene-*p*-sulfonamide 1a.** Sodium hydride (723 mg, 55%–65% in oil) was added to *N*-allyltoluene-*p*-sulfonamide (2.32g, 10.9 mmol) in DMF (30 mL) and the mixture was stirred for 35 min at rt. After slow addition of 3-bromocyclohexene (1.5 mL, 13 mmol) *via* syringe, the mixture was stirred for 17 h at ambient temperature and was then carefully poured into ice-cold water (50 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL) and the combined organics were washed with water (30 mL), brine (30 mL) and dried over sodium sulfate. Purification by column chromatography on silica gel (pentane–Et_2O 2 : 1) afforded diene **1a** (2.60 g, 82%) as a white solid. Mp 62–63 °C; ν_{max}(KBr)/cm^{-1} 2944, 1649, 1596, 1433, 1333, 1308, 1160, 1096 and 817; ^{1}H NMR (300 MHz, $CDCl_3$): 1.53–1.94 (6H, m, CH_2CH_2CH_2CH), 2.42 (3H, s, Ts-Me), 3.58–3.66 (1H, m, NCH_aH$_b$CH=CH_2), 3.81–3.90 (1H, m, NCH$_a$$H_b$CH=C$H_2$), 4.49–4.53 (1H, m, NC*H*), 5.07–5.12 (2H, m, olefin), 5.17–5.24 (1H, m, olefin), 5.76–5.93 (2H, m, olefin), 7.26–7.30 (2H, m, aromat), 7.70–7.74 (2H, m, aromat); ^{13}C NMR (75 MHz, $CDCl_3$): 21.7, 21.9, 24.7, 29.1, 46.7, 55.7, 116.7, 127.3, 127.7, 129.8, 132.6, 136.7, 138.6, 143.2; MS (EI): *m*/*z* 291 (M^+, 5%), 155 (70, Ts), 136 (61, M − Ts$^+$), 135 (68, M − Ts − H), 91 (100, Bzl). HRMS (ES, *m*/*z*) calcd. for $C_{16}H_{22}NO_2S$ ((M + 1)$^+$) 292.1371 found 292,1373.

***N*-Allyl-*N*-(cyclohex-2-enyl)-2-nitrobenzenesulfonamide 1b.** Allyl(cyclohex-2-enyl)amine[5f] (1.71 g, 12.5 mmol) was added within 10 min *via* syringe to a stirred suspension of 2-nitrobenzenesulfonyl chloride (3.12 g, 14.1 mmol, 1.1 eq.) and potassium carbonate (1.98 g, 14.3 mmol, 1.1 eq.) in dichloromethane (30 mL). The reaction mixture was stirred for 75 min at rt and

was then hydrolysed by water (20 mL) and aqueous HCl solution (10%, 20 mL). The organic layer was separated, washed with aqueous HCl solution (10%, 20 mL), sat. $NaHCO_3$ solution, brine and dried with sodium sulfate. Removal of the solvent and recrystallisation from toluene–pentane 1 : 1 at 5 °C afforded **1b** (3.75 g, 93%) as a white solid. Mp 72–73 °C; ν_{max}(KBr)/cm^{-1} 2939, 1646, 1589, 1547, 1381, 1342, 1166, 1152 and 781; ^{1}H NMR (300 MHz, $CDCl_3$): 1.58–1.83 (3H, m), 1.93–1.97 (3H, m), 3.77–3.85 (1H, m), 3.93–4.02 (1H, m), 4.53–4.58 (1H, m), 5.02–5.06 (1H, m), 5.14–5.20 (1H, m), 5.35–5.40 (1H, m), 5.72–5.91 (2H, m), 7.59–8.27 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 21.7, 24.4, 28.7, 46.9, 55.9, 117.3, 124.1, 127.4, 131.3, 131.5, 132.8, 133.3, 134.3, 135.7, 136.5; MS (EI): *m*/*z* 322 (M^+, 2%), 186 (35, Ns), 136 (52, M − Ns), 81 (100, cyclohexene). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{18}N_2O_4S$ (M^+) 322.0987, found 322.0979.

***N*-Allyl-*N*-(cyclohex-2-enyl)-4-nitrobenzenesulfonamide 1c.** Reaction as described for **1b** of allyl(cyclohex-2-enyl)amine (373 mg, 2.72 mmol), 4-nitrobenzenesulfonyl chloride (720 mg, 3.25 mmol, 1.2 eq.) and potassium carbonate (449 mg, 3.25 mmol, 1.2 eq.) in dichloromethane (10 mL) at 0 °C with warming up to rt over night afforded after column chromatography on silica (pentane–ethyl acetate 4 : 1) amine **1c** (724 mg, 83%) as a slightly reddish solid. Mp 86–87 °C; ν_{max}(KBr)/cm^{-1}2932, 1649, 1605, 1528, 1345, 1306, 1166 and 856; ^{1}H NMR (300 MHz, $CDCl_3$): 1.57–1.64 (2H, m), 1.68–1.89 (2H, m), 1.94–1.99 (2H, m), 3.71 (1H, dddd, *J* = 16.5, 6.3, 1.4, 1.4 Hz, C*H*$_a$H$_b$CH=CH$_2$), 3.89 (1H, dddd, *J* = 16.6, 5.7, 1.4, 1.4 Hz, CH$_a$*H*$_b$CH=CH$_2$), 4.53–4.59 (1H, m, CHN), 5.08–5.30 (3H, m), 5.74–5.87 (2H, m), 8.00–8.04 (2H, m, aromat), 8.32–8.36 (2H, m, aromat); ^{13}C NMR (75 MHz, $CDCl_3$): 21.6, 24.3, 28.8, 46.7, 55.9, 117.7, 124.3, 126.7, 128.3, 133.3, 135.4, 147.2, 149.8; MS (EI): *m*/*z* 322 (M^+1), 186 (4, *p*-nitrobenzenesulfonyl), 136 (21, M − *p*-nitrobenzenesulfonyl), 136 (34, M − *p*-nitrobenzenesulfonyl − 1), 81 (98, cyclohexene). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{18}N_2O_4S$ (M^+) 322.0987, found 322.0991.

***N*-Allyl-*N*-(cyclohex-2-enyl)-2,4-dinitrobenzenesulfonamide 1d.** Reaction of allyl(cyclohex-2-enyl)amine (980 mg, 7.15 mmol), 2,4-dinitrobenzenesulfonyl chloride (2.11 g, 7.91 mmol, 1.1 eq.), potassium carbonate (1.15 g, 8.32 mmol, 1.2 eq.) and DMAP (50 mg) at rt for 14 h as described for **1b** afforded after recrystallisation from toluene–pentane at 5 °C amine **1d** (800 mg, 37%) as a yellowish solid. Mp 88–89 °C; ν_{max}(KBr)/cm^{-1} 2944, 1641, 1605, 1547, 1537, 1370, 1348, 1303, 1167, 1143, 745 and 736; R_f (pentane–Et$_2$O 2 : 1) = 0.37; ^{1}H NMR (300 MHz, $CDCl_3$): 1.50–2.10 (6H, m), 3.81–3.89 (1H, m, C*H*$_a$H$_b$CH=CH$_2$), 3.95–4.02 (1H, m, CH$_a$*H*$_b$CH=CH$_2$), 4.56–4.61 (1H, m, CHN), 5.06–5.09 (1H, m), 5.17–5.23 (1H, m), 5.35–5.39 (1H, m), 5.69–5.80 (1H, m), 5.90–5.95 (1H, m), 8.25–8.30 (1H, m), 8.42–8.45 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 21.8, 24.5, 29.1, 47.4, 56.8, 118.4, 119.8, 126.1, 127.0, 133.3, 133.8, 135.1, 140.1, 148.5, 149.8; MS (EI): *m*/*z* = 367 (M^+, 2%), 231 (10, dinitrobenzenesulfonyl), 136 (17, M − dinitrobenzenesulfonyl), 81 (100, cyclohexene). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{18}N_3O_6S$ ($(M + H)^+$) 368.0916, found 368.0911.

***N*-Allyl-*N*-(cyclohex-2-enyl)trifluoroacetamide 1e.** Freshly distilled trifluoroacetic anhydride (1.0 mL, 7.1 mmol) was added within 20 min to an ice-cold solution of the amine (479 mg, 3.49 mmol) in dichloromethane (20 mL) and pyridine (5 mL). The solution was warmed up to rt and stirring was continued for 20 h. After pouring of the reaction mixture into water (50 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL). Washing of the combined organic layers with aqueous HCl solution (1 M, 2 × 20 mL), sat. sodium bicarbonate solution, brine and drying with sodium sulfate gave after evaporation of the solvent and purification by column chromatography on silica gel (pentane–Et$_2$O 4 : 1) protected amine **1e** (698 mg, 89%) as a colourless liquid. ν_{max}($CHCl_3$)/cm^{-1} 3027, 2947, 1683, 1650, 1466, 1450, 1433, 1219, 1148, 877 and 931; ^{1}H NMR (300 MHz, $CDCl_3$, broadening of signals due to rotamers): 1.5–2.1 (6H, m), 3.7–4.0 (2H, m, C*H*$_2$N), 4.5–4.6 (0.7H, m, C*H*N) and 4.9–5.0 (0.3H, m, C*H*N), 5.1–5.2 (2H, m, olefin), 5.4–5.5 (1H, m, olefin), 5.7–6.0 (2H, m, olefin); ^{13}C NMR (75 MHz, $CDCl_3$): complex, due to amide rotamers; MS (EI): *m*/*z* 233 (M^+, 5), 192 (98, M − allyl), 81 (92, cyclohexenyl), 41 (100, allyl). HRMS (ES, *m*/*z*) calcd. for $C_{14}H_{24}NO$ ($(M + H)^+$) 222.1858, found 222.1850.

***N*-Allyl-*N*-(cyclohex-2-enyl)trimethylacetamide 1f.** Reaction as described for **1b** of allyl(cyclohex-2-enyl)amine (530 mg, 3.87 mmol), pivaloyl chloride (572 mg, 4.74 mmol, 1.2 eq.) and potassium carbonate (656 mg, 4.75 mmol, 1.2 eq.) in dichloromethane (10 mL) at 0 °C with warming up to rt gave after purification by column chromatography (pentane–ethyl acetate 5 : 1) title compound **1f** (698 mg, 82%) as a colourless liquid. ν_{max}($CHCl_3$)/cm^{-1} 3005, 2942, 1613, 1478, 1407, 1191, 982 and 923; ^{1}H NMR (300 MHz, $CDCl_3$): 1.29 (9H, s, *t*-butyl), 1.58–1.74 (2H, m), 1.83–1.89 (2H, m), 2.00–2.06 (2H, m), 3.57–3.64 (1H, m, C*H*$_a$H$_b$CH=CH$_2$), 3.93–4.01 (1H, m, CH$_a$*H*$_b$CH=CH$_2$), 4.73–4.77 (1H, m, CHN), 5.02–5.11 (2H, m), 5.46–5.51 (1H, m), 5.77–5.91 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): 22.0, 24.8, 28.7, 28.8, 39.3, 46.6, 55.0, 115.1, 129.1, 131.8, 136.3, 177.5; MS (EI): *m*/*z* 221 (M^+, 1%), 180 (43, M − allyl), 81 (85, cyclohexene); 57 (100, C_4H_9). HRMS (ES, *m*/*z*) calcd. for $C_{11}H_{15}NOF_3$ ($(M + H)^+$) 234.1106, found 234.1097

Preparation of dienes 3, 4 and 5 by Mitsunobu reaction [13]

***N*-Allyl-*N*-(cyclohept-2-enyl)-2-nitrobenzenesulfonamide 3.** A solution of *N*-allyl-*o*-nitrobenzenesulfonamide [14] (1.00 g, 4.13 mmol), cyclohept-2-en-1-ol [15] (708 mg, 5.80 mmol) and PPh_3 (1.56 g, 5.95 mmol) in toluene (12 mL) was cooled in an ice-bath and diethyl azodicarboxylate (867 mg, 5.89 mmol) was added dropwise. Then the ice-bath was removed and the solution was stirred for 19.5 h at rt. Water (50 mL) was added and the aqueous layer was extracted by Et_2O (30 mL). After drying over sodium sulfate and column chromatography on silica (pentane–ethyl acetate 3.5 : 1) title compound **3** was obtained as a white solid (871 mg, 63%). Mp 90–91 °C; ν_{max}(KBr)/cm^{-1} 2933, 1640, 1588, 1540, 1437, 1373, 1342, 1162, 1128 and 782; ^{1}H NMR (500 MHz, $CDCl_3$): 1.29–1.38 (1H, m), 1.54–1.63 (1H, m), 1.69–1.78 (2H, m), 1.88–1.94 (2H, m), 2.03–2.10 (1H, m), 2.17–2.22 (1H, m), 3.86–3.90 (1H, m, C*H*$_a$H$_b$N), 4.02–4.07 (1H, m, CH$_a$*H*$_b$N), 4.61–4.63 (1H, m, C*H*N), 5.07–5.09 (1H, m, olefin), 5.19–5.23 (1H, m, olefin), 5.49–5.51 (1H, m, olefin), 5.74–5.89 (2H, m, olefin), 7.60–7.69 (3H, m, aromat), 8.04–8.05 (1H, m, aromat); ^{13}C NMR (125 MHz, $CDCl_3$): 26.1, 27.2, 28.0, 34.0, 47.6, 60.1, 117.5, 123.9, 131.1, 131.4, 132.4, 133.0, 133.1, 134.1, 135.5, 168.1; MS (EI): *m*/*z* 336 (M^+, <1%), 186 (26, Ns), 150 (18, M − Ns), 81 (22, cyclohexene), 41 (100, allyl). HRMS (ES, *m*/*z*) calcd. for $C_{16}H_{21}N_2O_4S$ ($(M + H)^+$) 337.1222, found 337.1214.

***N*-Allyl-*N*-(3-methylcyclopent-2-enyl)-2-nitrobenzenesulfonamide 4.** A solution of *N*-allyl-*o*-nitrobenzenesulfonamide (1.01 g, 4.17 mmol), 3-methylcyclopent-2-en-1-ol (805 mg, 8.20 mmol) and PPh_3 (2.19 g, 8.35 mmol) in toluene (12 mL) was cooled in an ice-bath and diethyl azodicarboxylate (1.19 g, 8.09 mmol) was added dropwise. Then the ice-bath was removed and the solution was stirred for 48 h at rt. Workup as described for **3** gave after column chromatography on silica (pentane–ethyl acetate 3.5 : 1) title compound **4** as a yellow oil (791 mg, 59%). ν_{max}($CHCl_3$)/cm^{-1} 3029, 2916, 1659, 1592, 1545, 1371, 1349 and 1160; ^{1}H NMR (500 MHz, $CDCl_3$): 1.74 (3H, s, Me), 1.74–1.78 (1H, m), 2.24–2.28 (3H, m), 3.77–3.79 (2H, m, C*H*$_2$N), 5.01–5.09 (3H, m, C*H*N, olefin), 5.77–5.80 (2H, m, olefin), 7.60–7.68

(3H, m, aromat), 8.04–8.06 (1H, m, aromat); ^{13}C NMR (125 MHz, $CDCl_3$): 17.3, 30.0, 36.3, 47.3, 65.9, 117.5, 123.8, 123.9, 124.7, 131.9, 132.1, 133.9, 136.5, 147.5, 168.2; MS (EI): *m*/*z* 322 (M^+, <1%), 186 (23, Ns), 81 (100, methylcyclopentene), 41 (27, allyl). HRMS (ES, *m*/*z*) calcd. for $C_{15}H_{19}N_2O_4S$ (($M + H)^+$) 323.1066, found 323.1074.

***N*-But-3-enyl-*N*-(cyclohex-2-enyl)toluene-*p*-sulfonamide 5.** A solution of *N*-cyclohex-2-enyltoluene-*p*-sulfonamide (1.00 g, 3.98 mmol), but-3-en-1-ol (567 mg, 7.86 mmol) and PPh_3 (2.25 g, 8.58 mmol) in THF (24 mL) was cooled in an ice-bath and diethyl azodicarboxylate (1.00 mL, 7.52 mmol) was added dropwise. The solution was then stirred at rt for 17 h. Then the solvent was evaporated and the residue purified by column chromatography on silica (pentane–Et_2O 5 : 1) to afford **5** (340 mg, 28%) as a white solid. Mp 58–59 °C; ν_{max}(KBr)/cm^{-1} 3027, 2935, 1643, 1599, 1446, 1336, 1165, 1142, 999 and 817; ^{1}H NMR (300 MHz, $CDCl_3$): 1.43–1.99 (5H, m), 2.31–2.59 (2H, m), 2.42 (3H, s, Me), 2.95–3.22 (2H, m,), 4.43–4.49 (1H, m, C*H*N), 5.00–5.12 (3H, m, olefin), 5.68–5.82 (2H, m, olefin), 7.26–7.30 (2H, m, aromat), 7.70–7.76 (2H, m, aromat); ^{13}C NMR (300 MHz, $CDCl_3$): 21.7, 21.9, 24.6, 29.6, 36.6, 44.0, 55.5, 116.8, 127.3, 128.0, 129.8, 132.4, 135.4, 139.4, 143.2; MS (EI): *m*/*z* 305 (M^+, <1%), 155 (42, Ts), 81 (100, cyclohexene). HRMS (ES, *m*/*z*) calcd. for $C_{17}H_{24}NO_2S$ (($M + H)^+$) 306.1533, found 306.1538.

General procedure for intramolecular hydrovinylation of 1,6-dienes using Pd-dimer

Dichloromethane was added through a septum to a Schlenk flask containing the allylpalladium chloride dimer (7 mol%) and the phosphine (14 mol%) and the resulting yellowish solution was stirred under an argon atmosphere for 30 min at rt. Then $AgSbF_6$ (14 mol%) was added in one portion and after a further 15 min the diene. The resulting mixture was stirred at rt for 18 h and was then filtered. Removal of the solvent *in vacuo* and purification of the residue by column chromatography on silica afforded the cyclised products. The products derived from the cyclisations had in all cases slightly lower R_f-values than the 1,6-dienes used as substrates.

1-(*p*-Tolylsulfonyl)-3-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole 2a. *p*-Tolylsulfonyl-protected diene **1a** (273 mg, 0.94 mmol) was cyclised within 14.5 h according to the general procedure by Pd-dimer (23 mg, 0.063 mmol, 7 mol%), PPh_3 (38 mg, 0.14 mmol) and $AgSbF_6$ (45 mg, 0.13 mmol) and dichloromethane (5 mL) as solvent. Purification by column chromatography on silica (pentane–Et_2O 4 : 1) gave first a small fraction consisting of a complex mixture of isomers (7 mg) and with higher polarity hexahydroindole **2a** (105 mg, 38%) as a yellowish solid. Mp 96 °C; ν_{max}(KBr)/cm^{-1} 2920, 1598, 1341, 1176, 1159, 1128, 1093, 1041 and 822; ^{1}H NMR (500 MHz, $CDCl_3$): 0.90 (3H, d,*J* = 6.4 Hz, Me), 1.58–1.65 (1H, m), 1.70–1.80 (1H, m, 3a-H), 1.98–2.14 (4H, m, includes 3-H), 2.43 (3H, s, Ts-Me), 2.67 (1H, dd, *J* = 9.6, 9.6, 2-H_a), 3.57 (1H, dd, *J* = 8.9, 6.8, 2-H_b), 3.73 (1H, ddd, *J* = 11.1, 7.7, 4.3, 7a-H), 5.56–5.59 (1H, m, 4-H), 5.76–5.79 (1H, m, 5-H), 7.30–7.33 (2H, m, Ts-H), 7.71–7.72 (2H, m, Ts-H). The configuration of **2a** was determined by NOESY and COSY experiments; ^{13}C NMR (75 MHz, $CDCl_3$): 15.38, 21.51, 23.54, 27.88, 38.34, 45.73, 55.09, 58.80, 125.3, 127.5, 128.6, 129.5, 134.8, 143.1; MS (EI): *m*/*z* 291 (M^+, 51%), 155 (24, Ts), 136 (100, M − Ts), 91 (85, Bzl). HRMS (ES, *m*/*z*) calcd. for $C_{15}H_{19}N_2O_4S$ (M^+) 291.1293, found 291.1294.

1-(*o*-Nitrophenylsulfonyl)-3-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole 2b. 2-Nitrophenylsulfonyl-protected diene **1b** (327 mg, 1.01 mmol) was cyclised within 15 h according to the general procedure using PPh_3 (35 mg, 0.13 mmol), Pd-dimer (25 mg, 0.068 mmol, 7 mol%), and $AgSbF_6$ (49 mg, 0.14 mmol) and dichloromethane (4 mL) as solvent. Purification by column chromatography (pentane–ethyl acetate 2 : 1) afforded **2b** (167 mg, 51%) as slightly yellow solid. Mp 91–96 °C; ν_{max}(KBr)/cm^{-1} 2957, 1589, 1544, 1373, 1350, 1184, 1163 and 745; ^{1}H NMR (300 MHz, $CDCl_3$): 1.02 (3H, d, *J* = 6.3 Hz, Me), 1.55–2.17 (6H, m), 2.93 (1H, dd, *J* = 9.4, 9.4 Hz, 2-H_a), 3.61–3.67 (1H, m, 2-H_b), 4.02–4.10 (1H, m, 7a-H), 5.62–5.66 (1H, m, 4-H), 5.73–5.81 (1H, m, 5-H), 7.57–8.20 (4H, m, aromat); ^{13}C NMR (75 MHz, $CDCl_3$): 15.5, 23.4, 27.2, 38.5, 45.9, 54.8, 59.3, 123.9, 125.3, 128.5, 130.7, 131.3, 132.3, 133.4; MS (EI): *m*/*z* 322 (M^+, 4%), 186 (82, Ns), 136 (100, M − Ns). HRMS (ES, *m*/*z*) calcd. for $C_{16}H_{21}NO_2S$ (($M + H)^+$) 323.1066, found 323.1067.

1-(*p*-Nitrophenylsulfonyl)-3-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole 2c. 4-Nitrophenylsulfonyl-protected diene **1c** (327 mg, 1.01 mmol) was cyclised within 18 h according to the general procedure using Pd-dimer (27 mg, 0.074 mmol, 7 mol%), PPh_3 (39 mg, 0.15 mmol) and $AgSbF_6$ (55 mg, 0.16 mmol) and dichloromethane (3 mL) as solvent. Purification by column chromatography (pentane–ethyl acetate–dichloromethane 9 : 1 : 1) and recrystallisation from toluene at rt afforded the title compound **2c** (178 mg, 53%) as yellow solid. Mp 164–165 °C; ν_{max}(KBr)/cm^{-1} 2939, 1605, 1524, 1350, 1176, 1161, 1043 and 856; ^{1}H NMR (300 MHz, $CDCl_3$): 0.93 (3H, d, *J* = 6.3 Hz, Me), 1.58–1.69 (1H, m), 1.80–1.85 (1H, m), 2.01–2.15 (4H, m), 2.70 (1H, dd, *J* = 9.4, 9.4 Hz, 2-H_a), 3.63 (1H, dd, *J* = 9.4, 6.6 Hz, 2-H_b), 3.77 (1H, ddd, *J* = 11.2, 7.4, 4.0 Hz, 7a-H), 5.55–5.61 (1H, m, 4-H), 5.75–5.81 (1H, m, 5-H), 8.01–8.06 (2H, m, aromat), 8.35–8.40 (2H, m, aromat); ^{13}C NMR (75 MHz, $CDCl_3$): 15.6, 23.6, 27.9, 38.6, 46.0, 55.3, 59.5, 124.5, 125.2, 128.7, 128.9, 144.0, 150.2; MS (EI): *m*/*z* 322 (M, 18%), 186 (10, *p*-nitrophenylsulfonyl), 136 (100, M − *p*-nitrophenylsulfonyl). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{18}N_2O_4S$ (M^+) 322.0987, found 322.0995.

1-(*o*,*p*-Dinitrophenylsulfonyl)-3-methyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole 2d. 2,4-Dinitrophenylsulfonyl-protected diene **1d** (420 mg, 1.14 mmol) was cyclised in 15 h according to the general procedure using PPh_3 (54 mg, 0.21 mmol), Pd-dimer (34 mg, 0.093 mmol, 8 mol%), and $AgSbF_6$ (62 mg, 0.18 mmol) and dichloromethane (4 mL) as solvent. After filtration and evaporation of the dichloromethane a viscous red oil was obtained. Portions of Et_2O were added to the oil and decanted. From the decanted ether-layer **2d** precipitated, and was then carefully washed with ice-cold Et_2O (192 mg of **2d** were obtained). Dissolving the remaining red solid in a little ethyl acetate and purification by column chromatography (ethyl acetate–pentane 2 : 1) gave additional **2d** (24 mg). Overall yield: 216 mg, 51%. Mp 143–148 °C; ν_{max}(KBr)/cm^{-1} 2963, 1604, 1544, 1537, 1354, 1162, 833 and 748; R_f(pentane–Et_2O 2 : 1) = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$): 1.05 (3H, d, *J* = 6.1 Hz, Me), 1.50–1.70 (2H, m), 1.99–2.15 (4H, m), 2.93–2.99 (1H, m, 2-H_a), 3.69 (1H, dd, *J* = 9.4, 6.3 Hz, 2-H_b), 4.04–4.13 (1H, m, 7a-H), 5.63–5.67 (1H, m, 4-H), 5.78–5.83 (1H, m, 5-H), 8.21–8.51 (3H, m, aromat); MS (EI): *m*/*z* 367 (M^+, 7%), 231 (17, 2,4-dinitrophenylsulfonyl), 136 (99, M − 2,4-dinitrophenylsulfonyl). HRMS (EI, *m*/*z*) calcd. for $C_{15}H_{18}N_3O_6S$ (M^+) 367.0838, found 367.0839.

3-Methyl-4-methylene-1-(4-tolylsulfonyl)pyrrolidine 7. *p*-Tolylsulfonyl-protected diene **6** (94 mg, 0.37 mmol) was cyclised within 16 h according to the general procedure by Pd-dimer (5 mg, 0.014 mmol, 3.7 mol%), Ph-MOPF (13 mg, 0.029 mmol, 7.8 mol%) and $AgSbF_6$ (18 mg, 0.052 mmol, 14 mol%) in dichloromethane (3 mL) as solvent. Purification by column chromatography on silica (pentane–Et_2O 6 : 1) gave pyrrolidine **7** (52 mg, 55%) as a yellowish solid. All spectral data were in accordance with published data.[2a]

3-Methyl-1-(*o*-nitrophenylsulfonyl)-1,2,3,3a,6,7,8,8a-octahydrocyclohepta[*b*]pyrrole 8. 2-Nitrophenylsulfonyl-protected diene **3** (375 mg, 1.11 mmol) was cyclised within 18 h according to the general procedure using PPh_3 (43 mg, 0.16 mmol), Pd-dimer (29 mg, 0.079 mmol, 7 mol%), and $AgSbF_6$ (59 mg, 0.16 mmol) and dichloromethane (4 mL) as solvent. Purification by column chromatography (pentane–ethyl acetate 3.5 : 1) afforded **8** (224 mg, 60%) as a viscous yellow oil. $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 2931, 1682, 1546, 1372, 1219, 1213, 1167, 781 and 739; according to ^1H NMR the product consists of three diastereomers. See supporting information for ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra. HRMS (ES, *m*/*z*) calcd. for $C_{16}H_{21}N_2O_4S$ (M^+) 337.1222, found 337.1209.

3-Methyl-1-(*o*-nitrophenylsulfonyl)-1,2,3,3a,6,6a-hexahydrocyclopenta[*b*]pyrrole 9. Diene **4** (280 mg, 0.87 mmol) was cyclised within 18 h according to the general procedure using Pd-dimer (25 mg, 0.068 mmol, 8 mol%), PPh_3 (36 mg, 0.14 mmol), $AgSbF_6$ (50 mg, 0.15 mmol) and dichloromethane (3.5 mL) as solvent. Purification by column chromatography on silica (pentane–ethyl acetate 3.5 : 1) gave a brown solid, which precipitated from toluene–pentane at 5 °C. The title compound **9** was obtained as a slightly brownish solid (72 mg, 26%). The configuration of **9** was determined by NOESY experiments. Mp 93–94 °C; ν_{max}(KBr)/cm^{-1}2918, 1547, 1376, 1356, 1167, 1031 and 770; ^1H NMR (500 MHz, $CDCl_3$): 0.91–0.93 (3H, m, CH_3CH), 1.69 (3H, s, CH_3C=C), 2.21–2.25 (1H, m), 2.44–2.49 (1H, m), 2.60–2.65 (1H, m), 2.78–2.79 (1H, m), 3.24–3.27 (1H, m, 2-H_a), 3.43–3.47 (1H, m, 2-H_b), 4.56–4.59 (1H, m, 6a-H), 5.26–5.27 (1H, m, 5-H), 7.59–7.61 (1H, m, aromat), 7.66–7.70 (2H, m, aromat), 8.01–8.04 (3H, m); MS (EI): *m*/*z* 322 (M^+, 1%), 186 (30, Ns). HRMS (ES, *m*/*z*) calcd. for $C_{15}H_{19}N_2O_4S$ (M^+) 323.1066, found 323.1054.

***N*-(*E*-But-2-enyl)-*N*-(cyclohex-2-enyl)-*p*-toluenesulfonamide 10.** Diene **5** (222 mg, 0.72 mmol) was isomerised according to the general procedure in 18 h using Pd-dimer (19 mg, 0.052 mmol), PPh_3 (29 mg, 0.11 mmol), $AgSbF_6$ (40 mg, 0.12 mmol) and dichloromethane (3 mL) as solvent. Purification by column chromatography (pentane–Et_2O 5 : 1) afforded title compound **10** as a white solid (51 mg, 23%). The *E*-configuration of the double bond was established by comparing the ^1H-NMR data with compound **10** obtained by reaction of *N*-(cyclohex-2-enyl)-*p*-toluenesulfonamide with *E*-but-2-enyl bromide (crotyl bromide) using sodium hydride as a base. Mp 79–84 °C; ν_{max}(KBr)/cm^{-1} 2939, 1598, 1332, 1163, 1090 and 818; ^1H NMR (300 MHz, $CDCl_3$): 1.52–1.64 (6H, m), 1.65–1.94 (3H, m), 2.41 (3H, s, Ts-Me), 3.54–3.62 (1H, m, C$H_a$$H_b$N), 3.74–3.83 (1H, m, C$H_a$$H_b$N), 4.48–4.53 (1H, m, CHN), 5.10–5.16 (1H, m, olefin), 5.40–5.50 (1H, m, olefin), 5.54–5.63 (1H, m, olefin), 5.74–5.81 (1H, m, olefin), 7.24–7.29 (2H, m, aromat), 7.68–7.73 (2H, m, aromat). HRMS (ES, *m*/*z*) calcd. for $C_{17}H_{24}NO_2S$ (M^+) 306.1528, found 306.1517.

Acknowledgements

We thank The Danish Technical Research Council, Leo Pharmaceutical Products, Familien Hede Nielsens Fond, Direktør Ib Henriksens Fond and the Lundbeck Foundation for generous financial support.

References

1 (*a*) Y. Yamamoto, N. Ohkoshi, M. Kameda and K. Itoh, *J. Org. Chem.*, 1999, **64**, 2178; (*b*) Y. Yamamoto, Y. Nakai and K. Itoh, *J. Am. Chem. Soc.*, 2001, **123**, 6372.
2 (*a*) B. Radetich and T. V. RajanBabu, *J. Am. Chem. Soc.*, 1998, **120**, 8007; (*b*) P. Kisanga, L. A. Goj and R. A. Widenhoefer, *J. Org. Chem.*, 2001, **66**, 635; (*c*) T. V. RajanBabu, N. Nomura, J. Jin, B. Radetich, H. Park and M. Nandi, *Chem. Eur. J.*, 1999, **5**, 1963; (*d*) T. V. RajanBabu in *Comprehensive Asymmetric Catalysis*, eds. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer-Verlag, Berlin, Heidelberg, 2000.
3 S. Okamoto and T. Livinghouse, *J. Am. Chem. Soc.*, 2000, **122**, 1223.
4 Directed intramolecular cyclisation of 1,5- and 1,6-dienes by Rh-complexes. N. Fujii, F. Kakiuchi, A. Yamada, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 285.
5 Selected preparations of compounds with a similar hydroindole-structure: Pd-catalysed allylation: (*a*) W. Oppolzer, J.-M. Gaudin, M. Bedoya-Zurita, J. Hueso-Rodriguez, T. M. Raynham and C. Robyr, *Tetrahedron Lett.*, 1988, **29**, 4709–4712; (*b*) R. Grigg, J. M. Sansano, V. Santhakumar, V. Sridharan, R. Thangavelanthum, M. Thornton-Pett and D. Wilson, *Tetrahedron*, 1997, **83**, 11803 Ni-calalysis; (*c*) D. Solé, Y. Cancho, A. Llebaria, J. M. Moretó and A. Delgado, *J. Org. Chem.*, 1996, **61**, 5895; (*d*) D. Solé, Y. Cancho, A. Llebaria, J. M. Moretó and A. Delgado, *J. Am. Chem. Soc.*, 1994, **116**, 12133 Zr-catalysis; (*e*) N. Uesaka, M. Mori, K. Okamura and T. Date, *J. Org. Chem.*, 1994, **59**, 4542; by radical reaction; (*f*) J. E. Brumwell, N. S. Simpkins and N. K. Terrett, *Tetrahedron*, 1994, **50**, 13533; (*g*) V. Gupta, M. Besev and L. Engman, *Tetrahedron Lett.*, 1998, **39**, 2429; metallo-ene-type; (*h*) W. Oppolzer, T. H. Keller, M. Bedoya-Zurita and C. Stones, *Tetrahedron Lett.*, 1989, **30**, 5883.
6 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 259.
7 R. Bayersdörfer, B. Ganter, U. Englert, W. Keim and D. Vogt, *J. Organomet. Chem.*, 1998, **552**, 187.
8 Recent examples of intermolecular hydrovinylation (*a*) G. Hilt, F.-X. du Mesnil and S. Lüers, *Angew. Chem., Int. Ed.*, 2001, **40**, 387; (*b*) U. Englert, R. Haerter, D. Vasen and D. A. Salzer, *Organometallics*, 1998, **18**, 4390; (*c*) J. Jin and T. V. RajanBabu, *Tetrahedron*, 2000, **56**, 2145; (*d*) J. Albert, J. M. Cadena, J. Granell, G. Muller, J. I. Ordinas, D. Panyella, C. Puerta, C. Sañudo and P. Valerga, *Organometallics*, 1999, **18**, 3511; (*e*) A. Wenger and W. Leitner, *Chem. Commun.*, 1999, 1583; (*f*) G. J. P. Britovsek, K. J. Cavell and W. Keim, *J. Mol. Catal: A. Chemical*, 1996, **110**, 77; (*g*) C. S. Yi and D. W. Lee, *Organometallics*, 2001, **20**, 802; see also ref. 2c and 2d.
9 J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 1158.
10 H. L. Pedersen and M. Johannsen, *Chem. Commun.*, 1999, 2517.
11 U. Bothe, unpublished results.
12 Substrates tested using the catalytic system based on allylpalladium chloride dimer, $AgSbF_6$ and PPh_3: allyl cyclohex-2-enyl ether, *cis*-1,4-bis(allyloxy)but-2-ene and *cis*-1,4-bis(cyclohex-2-enyloxy)-but-2-ene.
13 T. Fukuyama, M. Cheung and T. Kan, *Synlett*, 1999, **8**, 1301.
14 A. L. J. Beckwith and C. F. Meijs, *J. Org. Chem.*, 1987, **52**, 1922.
15 S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, 1977, **42**, 1197.