JOC Article

Synthesis of Octahydroquinolines through the Lewis Acid Catalyzed Reaction of Vinyl Allenes and Imines

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Received April 15, 2003

The reaction of vinyl allenes with imines under Lewis acid catalysis has been explored. Vinyl allenes in which the allenic portion of the molecule is tri- or tetrasubstituted gave octahydroquinoline derivatives as single isomers together with a minor compound formed by an ene reaction of the imine with the allene. Compounds in which the allene is 1,3-disubstituted do not react under the conditions assayed.

Introduction

Vinyl allenes have been described as taking part in different types of pericyclic reactions, and it has been observed that in several of those reactions the presence of the allene moiety facilitates the reaction when compared with similar dienic systems. For instance, in [1,5] hydrogen sigmatropic shifts, the energy of activation for the reaction is 8−12 kcal/mol lower in vinyl allenes than in similar dienes.[1] In $4e^-$ electrocyclizations, the presence of the allene shifts the equilibrium position from the open form in dienes[2] to an almost equimolecular mixture of the open and closed form in vinyl allenes.[3] In diallenes, the closed form (3,4-bis(alkylidene)cyclobutene) predominates.[4] In cycloaddition chemistry, vinyl allenes have been used in the intra- and intermolecular versions of the Diels−Alder reactions. The intramolecular reaction allows for the preparation of polycyclic compounds with high selectivity,[5] and in the intermolecular case, the Diels−Alder reaction has been studied with carbon dienophiles,[6] the conclusion of those studies being that both facial and endo/exo selectivity are largely governed by steric interactions between the incoming dienophile and the out-of-plane substituents on the vinyl allene. Also, Krause and co-workers concluded,[6c] based on semiempirical calculations on the parent 1,2,4-pentatriene, that the regioselectivity is controlled by steric factors, since the HOMO coefficients for the carbon atoms at the extreme of the dienic portion of the molecule are similar in size. Theoretical calculations at the ab initio level have also been carried out for the Diels−Alder reaction of vinyl allenes and acrolein,[7] showing that when the parent system is considered, no regioselectivity is expected. However, in the methyl-substituted vinyl allene (3-methyl-1,2,4-hexatriene), the electron-donating ability of the methyl groups results in one of the regioisomers being favored. The same study concluded that the reaction is a concerted asynchronous process. Recently,[8] we have found that 1-cyclohexenyl allenes, which were shown to display high selectivity in Diels−Alder reactions by Krause and co-workers,[6c] can also act as dienes in hetero-Diels−Alder reactions with aldehydes under Lewis acid catalysis, showing reactivity similar to that displayed by dienes activated by one silyloxy group,[9] that is, good facial and regioselectivity and moderate endo/exo selectivity, the yields being good for this reaction (36−70%).

Interest in the stereoselective preparation of nitrogen-containing heterocyclic compounds prompted us to investigate the feasibility of using the equivalent reaction with imines as heterodienophiles,[10] which should allow for the preparation of substituted octahydroquinoline derivatives.

(1) (a) Barrack, S. A.; Okamura, W. H. *J. Org. Chem.* **1986**, *51*, 3201. (b) Skattebøl, L. *Tetrahedron* **1969**, *25*, 4933. (c) Heimgartner, H.; Zsindely, J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2924. (d) Jensen, F. *J. Am. Chem. Soc.* **1995**, *117*, 7487.

(2) Durst, T.; Breau, L. *Cyclobutene Ring Opening Reactions in Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, pp 675−697.

(3) (a) Gil-Av, E.; Herling, J. *Tetrahedron Lett.* **1967**, 1. (b) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1989**, *54*, 4028. (c) Murakami, M.; Amii, H.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1476.

(4) (a) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1989**, *54*, 3544. (b) Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 732. (c) Hopf, H.; Lenich, F. T. *Chem. Ber.* **1973**, *106*, 3461.

(5) (a) Okamura, W. H.; Curtin, M. L. *Synlett* **1990**, 1. (b) Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062. (c) Gibbs, R. A.; Bartels, K.; Lee, R. W. K.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 3717. (d) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282. (e) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791. (f) Deutsch, E. A.; Snider, B. B. *Tetrahedron Lett.* **1983**, *24*, 3701. (g) Deutsch, E. A.; Snider, B. B. *J. Org. Chem.* **1982**, *47*, 2682.

(6) (a) Reich, H. J.; Eisenhart, E. K.; Whipple, W. L.; Kelly, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6432. (b) Spino, C.; Thibault, C.; Gingras, S. *J. Org. Chem.* **1998**, *63*, 5283. (c) Koop, U.; Handke, G.; Krause, N. *Liebigs Ann.* **1996,** 1487.

(7) Wright, J. B.; Pranata, J. *THEOCHEM* **1999**, *460*, 67.

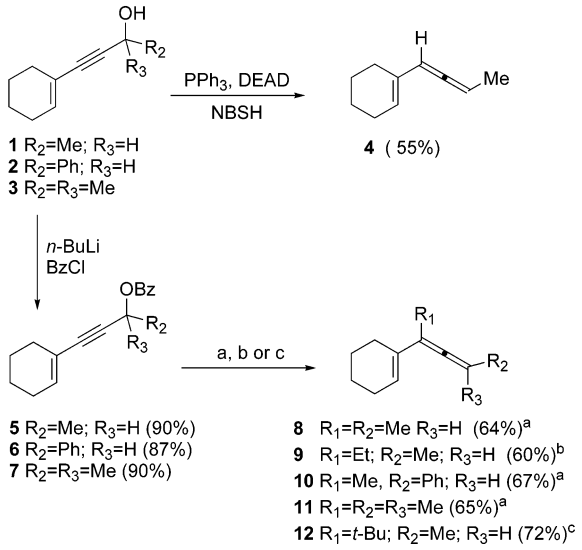
(8) Regás, D.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A. *Tetrahedron Lett.* **2000**, *41*, 6781.

(9) Mujica, M. T.; Afonso, M. M.; Galindo, A.; Palenzuela, J. A. *J. Org. Chem.* **1998**, *63*, 9728.

(10) Imines have been used as heterodienophiles in inter- and intramolecular Diels−Alder reactions. The reaction conditions depend on the nature of the substituents on the imine. Simple, neutral imines need the presence of Lewis acids to react with electron-rich dienes. For leading references, see: Weinreb, S. M. *Heterodienophile Additions to Dienes in Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, pp 401−449.

10.1021/jo034480z CCC: $25.00
Published on Web 09/12/2003

SCHEME 1[a]



[a] Key: (a) MeMgBr, CuI, LiBr, 0 °C; (b) EtMgBr, CuBr·Me_2S, −60 °C; (c) *t*-BuLi, CuCN, −78 °C.

Octahydroquinolines have been prepared through hetero-Diels−Alder reactions between acetylcyclohexene trimethylsilyl enol ethers and imines,[11] the proportion of endo/exo isomers depending on the reaction conditions. Thus, under kinetic control an almost 1:1 ratio of the two isomers is formed, whereas under thermodynamic conditions the exo is favored. This has been explained as a Diels−Alder−retro-Diels−Alder equilibrium process.

In this paper, we present the results of our studies on the selectivity of the hetero-Diels−Alder reaction of vinyl allenes with imines leading to octahydroquinolines.

Results and Discussion

For this work, six vinyl allenes (**4**, **8**−**12**) were prepared in racemic form using literature procedures for allene formation starting from the corresponding propargyl alcohols.[12] Thus, vinyl allene **4**[13] was prepared in a 55% yield following Myers's procedure[14] using *o*-nitrobenzenesulfonylhydrazine (NBSH) and starting from propargyl alcohol **1**. Compounds **8**−**12**[15] were obtained in good yields (60−75%) by S_N2' displacement reactions of benzoates **5**−**7** obtained from the corresponding propargyl alcohols **1**−**3** (Scheme 1).[16]

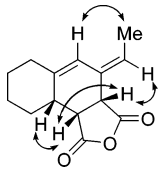
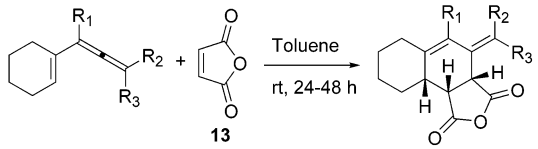


FIGURE 1. Observed NOEs for compound **14**.

SCHEME 2



4 R_1=H; R_2=Me; R_3=H
10 R_1=Me; R_2=Ph; R_3=H
11 R_1=R_2=R_3=Me
12 R_1=*t*-Bu; R_2=Me; R_3=H

14 R_1=H; R_2=Me; R_3=H (94%)
15 R_1=Me; R_2=Ph; R_3=H (93%)
16 R_1=R_2=R_3=Me (83%)
17 R_1=*t*-Bu; R_2=Me; R_3=H (75%)

The reactivity of several of the vinyl allenes prepared was compared with the literature data for similar compounds[6c] using maleic anhydride as dienophile. Four vinyl allenes (**4**, **10**, **11**, and **12**) with diverse substituents on the allene were chosen to check whether electronic or steric factors preclude those molecules from acting as dienes.

The reactions were carried out in dry toluene at room temperature using 1 equiv of maleic anhydride. After 24−48 h and removal of solvent, a white solid, which was identified as a single cycloadduct to the limits of detection of the NMR, was obtained in each case in high yield (Scheme 2). The structure of the cycloadducts was established on the basis of spectroscopic data,[17] and the relative stereochemistry was deduced from NOE experiments (NOESY or GOESY[18]) as shown in Figure 1 for one representative example.

For the reaction of **4**, **10**, and **12**, the structure and relative stereochemistry of the products obtained indicate a highly selective process in which the dienophile approaches the diene through the less hindered face, that is, the one opposite to the substituent at the terminus of the allene, as deduced from the geometry of the exocyclic double bond in the cycloadduct. For compound **17**, the lower yield obtained may be the result of the increased difficulty encountered by the vinyl allene in attaining the required s-cis conformation needed for the reaction to proceed. The cis disposition of the hydrogen atoms at the ring junctions in all cycloadducts is indicative of an endo approach of the maleic anhydride to the vinyl allene. These results indicate that the vinyl allenes prepared in this work are at least as reactive as the similar ones described previously in the literature.[6c]

Once the pericyclic reactivity of the vinyl allenes was checked, we turned our attention to their reaction with imines. We first explored the reactivity of **9** since it gave good results in our previous work with aldehydes.[8] Using imine **18** and different Lewis acids in CH_2Cl_2 at room temperature (Table 1), we found that only one cycloadduct was formed (**19**), together in some cases with a

(11) (a) Veyrat, C.; Wartski, L.; Seyden-Penne, J. *Tetrahedron Lett.* **1986**, *27*, 2981. (b) Le Coz, L.; Veyrat-Martin, C.; Wartski, L.; Seyden-Penne, J.; Bois, C.; Philoche-Levisalles, M. *J. Org. Chem.* **1990**, *55*, 4870. (c) Paugam, R.; Valenciennes, E.; Le Coz-Bardol, L.; Garde, J.-C.; Wartski, L.; Lance, M.; Nierlich, M. *Tetrahedron*: *Asymmetry* **2000**, *11*, 2509.

(12) The propargyl alcohols were prepared by the addition of the lithium acetylide of 1-ethynylcyclohexene to the corresponding aldehyde or ketone in tetrahydrofuran at low temperature.

(13) The preparation of this vinyl allene by other methods has been reported: (a) Konoike, T.; Araki, Y. *Tetrahedron Lett.* **1992**, *33*, 5093. (b) Bardouy, R.; Delbecq, F.; Gore, J. *Tetrahedron Lett.* **1979**, 937.

(14) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.

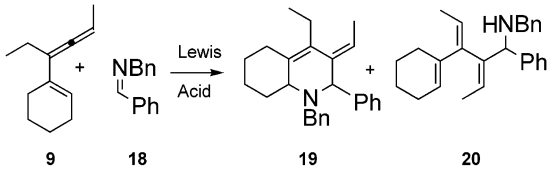
(15) The preparation of vinyl allene **8** has been reported previously: Baudouy, R.; Delbecq, F.; Gore, J. *Tetrahedron* **1980**, *36*, 189. Also see ref 13b.

(16) (a) Erdik, E. *Tetrahedron* **1984**, *40*, 641. (b) Westmijze, H.; Meijer, J.; Bos, H. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 299. (c) Lipshutz, B. H. *Synthesis* **1987**, 325. (d) Lipshutz, B. H.; Sengupta, S. *Org. React. N.Y.* **1992**, *41*, 135.

(17) The spectroscopic data recorded for most of the new compounds prepared in this work include mono- (^1H, ^{13}C) and bidimensional (COSY, HSQC, HMBC) NMR experiments.

(18) Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 6037.

TABLE 1



9 18 19 20

Lewis acid	time (d)	**19** (%)	**20** (%)
$BF_3{\cdot}Et_2O$	4	67	–
$AlCl_3$	1.5	55	–
$TiCl_4$	3	49	8
Et_2AlCl	5	48	9

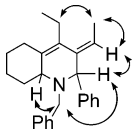


FIGURE 2. Observed NOEs for compound **19**.

minor compound (**20**) resulting from an ene reaction between the allene and the imine. The best results were obtained using $BF_3{\cdot}Et_2O$, since only the cycloadduct **19** was obtained in 67% yield. $AlCl_3$ also gave exclusively compound **19**, although in lower yield. The use of diethyl ether as solvent also gave similar results, but the reaction was considerably slower. Other Lewis acids ($SnCl_4$ or $ZnCl_2$) resulted in no reaction.

The structure of **19** was established on the basis of its spectroscopic data.[17] The geometry of the exocyclic double bond, deduced from NOE experiments (Figure 2), indicates that the approach of the imine takes place exclusively through the face of the diene opposite to the methyl group on the terminus of the allene, in a manner similar to that found for the reaction with maleic anhydride or with aldehydes.[8]

The regiochemistry is also consistent with that exhibited in the reaction of aldehydes with this vinyl allene, in which the carbon atom of the imine double bond attaches to the central carbon of the allene.

The relationship between the two hydrogens at the positions adjacent to the nitrogen atom could not be established at this point, although the absence of NOE between them led us to think at first that they were disposed in trans. However, the observed NOE between both methine hydrogens and the benzylic methylene protons and the fact that the lack of NOE is not valid evidence of a stereochemical relationship cast some doubts on the relative configuration of those two centers.[19]

The structure of **20** was difficult to establish at this point because the ^1H NMR spectrum at room temperature showed a complex mixture of conformers, which could be partially clarified by heating at 75 °C in C_6D_6.[20] Thus, **20** was assigned the structure shown by comparison with the minor compounds obtained in the other similar reactions described later in this work.[21]

Once the reactivity of **9** was established, we carried out the reaction with the remainder of the vinyl allenes using imines **18**, **21**, and **22** as dienophiles and $BF_3{\cdot}Et_2O$ as Lewis acid in CH_2Cl_2 as solvent. Vinyl allene **4**, the only one in which R_1 is a hydrogen atom, did not react under those conditions or any others assayed, yielding only decomposition products under forced reaction conditions. The results obtained with the other vinyl allenes and imines prepared in this work are summarized in Table 2.

It was observed that vinyl allenes **8**−**12** reacted to yield cyclization compounds as the main product, alone or as a mixture with the compounds derived from the ene reaction. The structure of all bicyclic compounds follows the same pattern found for **19**, and the structure of the minor ones was deduced from the spectroscopic analysis of several of the compounds obtained in these reactions. We still needed to unambiguously establish the relative configuration of the chiral centers adjacent to the nitrogen atom (H-2 and H-8a) in the bicyclic compounds, and thus, a great effort was made in order to crystallize any of the octahydroquinolines obtained in order to confirm the structure by X-ray diffraction methods. Finally, we were successful in obtaining suitable crystals of compound **29**. Figure 3 shows a computer-generated perspective view[22] of the final X-ray model of **29**,[23] clearly indicating a cis relationship between the methine hydrogens.

The absence of NOE can be explained by the conformation adopted by **29**, in which both hydrogens H-2 and H-8a are quite apart, assuming a similar conformation in solution. The remainder of the bicyclic compounds are also assumed to be cis because of the similarity of their spectroscopical data with those of **29**. This result indicates an endo approach of the dienophile to the dienic portion of the vinyl allene with the benzyl group on the nitrogen occupying the exo position in the transition state, assuming that the imine is in the *E* configuration, as depicted in Scheme 3 for a pericyclic mechanism.

In most entries in Table 2, some vinyl allene was recovered unaltered and the application of heat resulted in the decomposition of several of the examples shown.

From Table 2, it can be observed that the qualitative rate of the reactions is influenced by the size of the substituents on the allene. Thus, for trisubstituted systems, the change of a methyl group in **8** to an ethyl group in **9** results in a longer reaction time, but the reaction proceeds at room temperature. When the ethyl group is replaced by a *tert*-butyl (**12**), the reaction is slower and requires heating to yield the cycloadduct. This is likely due to the increased difficulty in the diene attaining the s-cis conformation required for the reaction to take place, as observed in the reaction of this vinyl allene with maleic anhydride. Comparing vinyl allene **8** (R_2 = Me) with **10** (R_2 = Ph), it can be observed that the change of substituent on the extreme of the allene also results in slower reactions, whereas when the allene is tetrasubstituted (**11**), the reaction is even slower since

(19) We thank one of the reviewers for helpful discussions in regard to this problem.

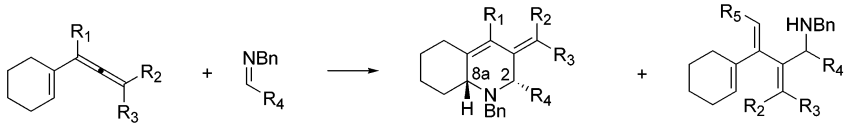
(20) The conformational behavior of this compound also precluded obtaining a satisfactory ^{13}C NMR spectrum. See the Supporting Information for copies of the NMR spectra.

(21) The geometry of the double bonds in the ene compounds was assigned on the basis of the ROESY spectra of compounds **33**−**36**.

(22) Spek, A. L. PLATON92, University of Utrecht, The Netherlands, 1992.

(23) See the Supporting Information for the X-ray data.

TABLE 2. Reaction of Vinyl Allenes and Imines under Lewis Acid Catalysis[a,b]



8 R_1=R_2=Me; R_3=H
9 R_1=Et; R_2=Me; R_3=H
10 R_1=Me; R_2=Ph; R_3=H
11 R_1=R_2=R_3=Me
12 R_1=*t*-Bu; R_2=Me; R_3=H

18 R_4=Ph
21 R_4=*i*-Pr
22 R_4=*n*-Hex

23 R_1=R_2=Me; R_3=H; R_4=Ph
24 R_1=R_2=Me; R_3=H; R_4=*i*-Pr
25 R_1=Et; R_2=Me; R_3=H; R_4=*i*-Pr
26 R_1=Me; R_2=Ph; R_3=H; R_4=Ph
27 R_1=Me; R_2=Ph; R_3=H; R_4=*i*-Pr
28 R_1=Me; R_2=Ph; R_3=H; R_4=*n*-Hex
29 R_1=R_2=R_3=Me; R_4=Ph
30 R_1=R_2=R_3=Me; R_4=*i*-Pr
31 R_1=R_2=R_3=Me; R_4=*n*-Hex
32 R_1=*t*-Bu; R_2=Me; R_3=H; R_4=Ph

33 R_2=Me; R_3=H; R_4=Ph; R_5=H
34 R_2=Me; R_3=H; R_4=*i*-Pr; R_5=H
35 R_2=Me; R_3=H; R_4=*i*-Pr; R_5=Me
36 R_2=Ph; R_3=H; R_4=Ph; R_5=H
37 R_2=Ph; R_3=H; R_4=*i*-Pr; R_5=H
38 R_2=Ph; R_3=H; R_4=*n*-Hex; R_5=H
39 R_2=R_3=Me; R_4=Ph; R_5=H
40 R_2=R_3=Me; R_4=*i*-Pr; R_5=H
41 R_2=R_3=Me; R_4=*n*-Hex; R_5=H

entry	vinyl allene	imine	*T* (°C)	time (d)	**23**−**32** (%)	**33**−**41** (%)	% recovered allene[c]
1	**8**	**18**	rt	1.5	**23** (54)	**33** (11)	−
2	**8**	**21**	rt	1.5	**24** (43)	**34** (7)	20
3	**9**	**21**	rt	3	**25** (39)	**35** (4)	24
4	**10**	**18**	rt	4	**26** (71)	**36** (5)	13
5	**10**	**21**	rt	4	**27** (61)	**37** (12)	15
6	**10**	**22**	rt	3	**28** (57)	**38** (3)	5
7	**11**	**18**	40	3	**29** (67)	**39** (6)	−
8	**11**	**21**	40	5	**30** (37)	**40** (2)	15
9	**11**	**22**	40	5	**31** (41)	**41** (7)	23
10	**12**	**18**	40	5	**32** (34)	−	25

[a] Only one enantiomer shown. [b] All reactions were carried out using BF_3·Et_2O in CH_2Cl_2. [c] A dash indicates no recovered vinyl allene. The rest of the mass balance results from decomposition.

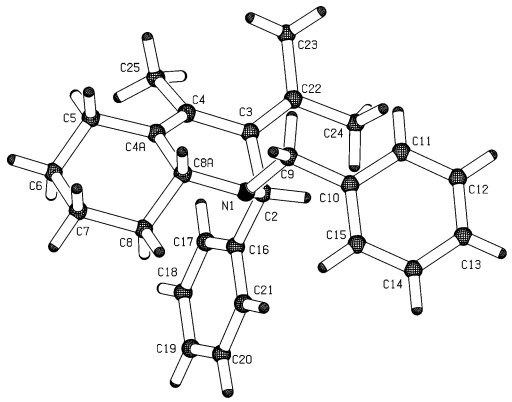
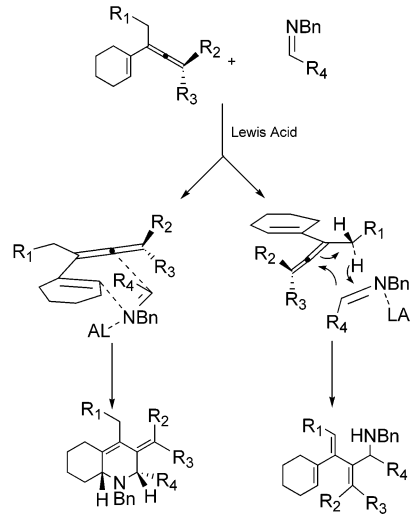


FIGURE 3. Computer-generated view of the X-ray structure of **29**.

heating is again required to obtain reaction products. These results, especially the latter, can be explained by the increased difficulty of the imine to approach the dienic portion of the vinyl allene.

The experimental data obtained did not allow us to confirm the mechanism of the reaction, which may be either an asynchronous concerted reaction or a cationic stepwise process. Thus, the fact that vinyl allene **4** (R_1 = H) did not react, whereas with an alkyl group at the R_1 position cyclization products were obtained, may indicate that an electron-donating group is needed at that position to activate the reaction by raising the energy of the HOMO of the diene. This activation may also be responsible for the regiochemistry shown by the reaction, as described for the reaction of vinyl allenes and acroleine.[7] An alternative explanation could be that the group at R_1 stabilizes the positive charge formed at that position in a stepwise mechanism and that the regiochemistry is due to steric reasons as proposed in the previously cited works. However, the high selectivity shown by the reaction, in which only one cyclization product was obtained, and especially the geometry of the exocyclic double bond seem to point to a pericyclic mechanism.

SCHEME 3



In conclusion, we have found that vinyl allenes in which the allene portion of the molecule is tri- or tetrasubstituted react with imines in the presence of Lewis acids to afford octahydroquinoline derivatives with high facial, regio-, and endo selectivities. This results in compounds with cis stereochemistry at the two positions adjacent to the nitrogen atom as the major products. Depending on the Lewis acid used, minor compounds resulting from an ene reaction are also obtained.

Experimental Section

(±)-1-Buta-1,2-dienylcyclohexene (4). To a suspension of PPh_3 (5.6 g, 21.3 mmol) and DEAD (3.2 mL, 20.3 mmol) in THF (43 mL) at −15 °C was slowly added a solution of propargyl alcohol **1** (2.65 g, 17.7 mmol) in THF (7 mL). After 10 min, 2-nitrobenzenesulfonylhydrazine (4.6 g, 21.2 mmol) in THF (25 mL) was added via cannula. The reaction mixture was allowed to warm to rt and was stirred for 7 h. Then it was poured over pentane (50 mL), and the organic layer was washed with cold water (5 × 150 mL), dried (Na_2SO_4), and concentrated. Flash column chromatography (hexanes) afforded vinyl allene **4** (1.3 g, 55%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.63 (s, 1H), 5.32 (m, 1H), 2.09 (m, 2H), 2.02 (m, 2H), 1.68 (dd, J = 3.2, 7.0 Hz, 3H), 1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 132.4, 125.3, 97.0, 88.5, 25.7, 25.6, 22.5, 22.4, 14.6.

(±)-1-(1-Methylbuta-1,2-dienyl)cyclohexene (8). To a stirred suspension of LiBr (1.2 g, 13.9 mmol) and CuI (2.6 g, 13.9 mmol) in THF (25 mL) at 0 °C was slowly added a solution of MeMgBr 2.8 M in diethyl ether (4.95 mL, 13.9 mmol). After the mixture was stirred for 15 min, a solution of benzoate **5** (585 mg, 2.3 mmol) in THF (40 mL) was added via cannula. The reaction mixture was allowed to warm to rt overnight, and then a saturated solution of NH_4Cl (50 mL) was added and the reaction was extracted with diethyl ether (4 × 50 mL). After drying (Na_2SO_4), concentration, and flash column chromatography (hexanes), vinyl allene **8** was obtained (218 mg, 64%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.21 (bs, 1H), 2.10 (m, 4H), 1.82 (s, 3H), 1.65 (d, J = 7.0 Hz, 3H), 1.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 134.0, 122.1, 101.9, 86.4, 27.0, 25.9, 22.9, 22.4, 16.3, 14.9; IR ($CHCl_3$) 2900, 1935, 1680, 1640 cm^{-1}; MS(EI) m/z 148 (M^+, 27), 133 (50), 119 (29), 105 (100); HRMS (EI) m/z calcd for $C_{11}H_{16}$ 148.1252, found 148.1295.

(±)-1-(1-Ethylbuta-1,2-dienyl)cyclohexene (9). To a stirred suspension of CuBr·Me_2S (9.1 g, 44.3 mmol) in THF (150 mL) at −60 °C was added a solution of EtMgBr 3 M in diethyl ether (14.8 mL, 44.3 mmol). After the mixture was stirred for 1 h, a solution of benzoate **5** (1.87 g, 7.39 mmol) in THF (50 mL) was added via cannula. The reaction mixture was allowed to warm to rt overnight, and then a saturated solution of NH_4Cl (150 mL) was added and the reaction extracted with diethyl ether (3 × 200 mL). After drying (Na_2SO_4), concentration, and flash column chromatography (hexanes), vinyl allene **9** was obtained (720 mg, 60%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 5.25 (bs, 1H), 2.15 (m, 6H), 1.68 (d, J = 7 Hz, 3H), 1.61 (m 4H), 1.02 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 133.3, 121.5, 108.9, 88.8, 27.3, 25.7, 22.5, 21.6, 20.1, 14.7, 12.5; IR ($CHCl_3$) 2880, 1930, 1700 cm^{-1}; MS(EI) m/z 162 (M^+,45), 147 (33), 133 (41), 119 (40), 103 (93), 91 (100); HRMS (EI) m/z calcd for $C_{12}H_{18}$ 162.1408, found 162.1433.

(±)-(3-Cyclohex-1-enylbuta-1,2-dienyl)benzene (10). Following the same procedure used for the preparation of **8**, and starting with benzoate **6** (923 mg, 2.92 mmol), vinyl allene **10** was obtained (411 mg, 67%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 3H), 7.20 (m, 2H), 6.30 (s, 1H), 5.82 (m, 1H), 2.19 (m, 3H), 2.11 (m, 1H), 1.98 (s, 3H), 1.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 135.4, 133.2, 128.5, 127.7, 123.3, 106.5, 95.6, 26.9, 25.9, 22.8, 22.3, 15.9; IR ($CHCl_3$) 2875, 1920, 1590 cm^{-1}; MS(EI) m/z 210 (M^+, 100), 195 (21), 181 (20), 167 (54); HRMS (EI) m/z calcd for $C_{16}H_{18}$ 210.1408, found 210.1397.

1-(1,3-Dimethylbuta-1,2-dienyl)cyclohexene (11). Following the same procedure used for the preparation of **8**, and starting with benzoate **7** (2.24 g, 8.34 mmol), vinyl allene **11** was obtained (879 mg, 65%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (bs, 1H), 2.14 (m, 2H), 2.04 (m, 2H), 1.79 (s, 3H), 1.69 (s, 6H), 1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 134.9, 121.5, 100.2, 95.5, 26.9, 25.9, 23.0, 22.5, 20.7, 16.4; IR ($CHCl_3$) 2945, 1950, 1450 cm^{-1}; MS(EI) m/z 162 (M^+, 44), 147 (88), 133 (14), 119 (100); HRMS (EI) m/z calcd for $C_{12}H_{18}$ 162.1408, found 162.1394.

(±)-1-(1-*tert*-Butylbuta-1,2-dienyl)cyclohexene (12). To a stirred solution of CuCN (354 mg, 3.95 mmol) in diethyl ether (20 mL) at −78 °C was slowly added a solution of *t*-BuLi 1.7 M in pentane (4.6 mL, 7.9 mmol). After 5 min, the reaction mixture was warmed to 0 °C, and after 15 min it was cooled again to −78 °C and a solution of benzoate **5** (500 mg, 1.97 mmol) in diethyl ether (10 mL) was then slowly added. The reaction mixture was stirred for 1 h and allowed to warm to 0 °C. After 1 h, water (50 mL) was added, and the mixture was extracted with diethyl ether (3 × 30 mL). After drying and concentration of the organic layer, the crude reaction mixture was purified by flash column chromatography (hexanes) yielding vinyl allene **12** (269 mg, 72%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (s, 1H), 5.06 (q, J = 6.8 Hz, 1H), 2.08 (m, 4H), 1.66 (d, J = 6.8 Hz, 3H), 1.58 (m, 4H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 134.1, 124.6, 116.6, 85.5, 33.8, 30.7, 30.2, 25.5, 23.1, 22.0, 14.9; IR ($CHCl_3$) 2850, 1940 cm^{-1}; MS(EI) m/z 190 (M^+, 20), 175 (60), 147 (14), 133 (31); HRMS (EI) m/z calcd for $C_{14}H_{22}$ 190.1721, found 190.1709.

General Experimental Procedure for the Reaction of Vinyl Allenes with Maleic Anhydride. To a stirred solution of the vinyl allene in toluene (0.3 M) at rt under argon atmosphere was added maleic anhydride (1 equiv). After 24−36 h, the solvent was removed, and after filtration through a short pad of silica gel the product was obtained as a white solid.

(3a*R,9a*S**,9b*R**)-4(*E*)-Ethylidene-3a,4,6,7,8,9,9a,9b-octahydronaphtho[1,2-*c*]furan-1,3-dione (14).** Following the general procedure, vinyl allene **4** (150 mg, 1.12 mmol) furnished, after 6 h, cycloadduct **14** (244 mg, 94%): white solid; mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 1H), 5.57 (q, J = 7.1 Hz, 1H), 3.73 (d, J = 8.6 Hz, 1H), 3.47 (t, J = 8.6 Hz, 1H), 2.58 (m, 1H), 2.39 (d, J = 13.2 Hz, 1H), 2.09 (m, 1H), 1.94−1.84 (m, 2H), 1.83 (d, J = 7.1 Hz, 3H), 1.47−1.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 171.3, 141.4, 126.2, 122.7, 115.7, 45.0, 43.9, 36.6, 36.1, 31.2, 28.3, 26.7, 13.0; IR ($CHCl_3$) 2880, 1855, 1770, 1700, 1435 cm^{-1}; MS (EI) m/z 232 (M^+, 54), 204 (22), 159 (100); HRMS (EI) m/z calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1102.

(3a*R,9a*S**,9b*R**)-4(*Z*)-Benzylidene-5-methyl-3a,4,6,7,8,9,9a,9b-octahydronaphtho[1,2-*c*]furan-1,3-dione (15).** Following the general procedure, vinyl allene **10** (69.4 mg, 0.33 mmol) furnished, after 48 h, cycloadduct **15** (94.6 mg, 93%): white solid; mp 111−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.19 (m, 5H), 6.49 (s, 1H), 3.96 (d, J = 9.1 Hz, 1H), 3.41 (dd, J = 6.1, 9.1 Hz, 1H), 2.47 (bs, 1H), 2.38−2.17 (m, 3H), 1.87 (m, 2H), 1.66 (m, 2H), 1.55 (s, 3H), 1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.8, 139.2, 136.5, 132.4, 129.7, 128.8, 128.6, 128.1, 127.5, 52.0, 45.4, 36.9, 25.0, 24.3, 21.7, 21.3, 16.5; IR ($CHCl_3$) 1850, 1765, 1440 cm^{-1}; MS (EI) m/z 308 (M^+, 100), 262 (96), 247 (26), 235 (36), 221 (86); HRMS (EI) m/z calcd for $C_{20}H_{20}O_3$ 308.1412, found 308.1398.

(3a*R,9a*S**,9b*R**)-4-Isopropylidene-5-methyl-3a,4,6,7,8,9,9a,9b-octahydronaphtho[1,2-*c*]furan-1,3-dione (16).** Following the general procedure, vinyl allene **11** (150 mg, 0.92 mmol) furnished, after 48 h, cycloadduct **16** (200 mg, 83%): white solid; mp 123−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (d, J = 9.0 Hz, 1H), 3.27 (dd, J = 5.1, 9.0 Hz, 1H), 2.12−2.26 (m, 4H), 1.89 (s, 3H), 1.77 (s, 3H), 1.75 (s, 3H), 1.73 (m, 2H), 1.65 (m, 1H), 1.56 (m, 1H), 1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 172.3, 137.0, 131.8, 128.8, 126.4, 46.6, 46.0, 36.2, 24.5, 24.0, 23.0, 21.5, 21.1, 20.9, 18.2; IR ($CHCl_3$) 2950, 2855, 1860, 1780 cm^{-1}; MS (EI) m/z 260 (M^+, 57), 232 (55), 217 (19), 199 (9), 187 (65), 173 (100); HRMS (EI) m/z calcd for $C_{16}H_{20}O_3$ (M^+) 260.1412, found 260.1387.

(3a*R,9a*S**,9b*R**)-5-*tert*-Butyl-4(*Z*)-ethylidene-3a,4,6,7,8,9,9a,9b-octahydronaphtho[1,2-*c*]furan-1,3-dione (17).** Following the general procedure, vinyl allene **12** (52 mg, 0.27 mmol) furnished, after 72 h, cycloadduct **17** (59 mg, 75%): white solid; mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46

(q, J = 6.9 Hz, 1H), 3.78 (d, J = 9.0 Hz, 1H), 3.20 (dd, J = 5.1, 9.0 Hz, 1H), 2.70 (dd, J = 3.9, 9.3 Hz, 1H), 2.19 (m, 1H), 2.09 (m, 1H), 1.96 (m, 1H), 1.85 (m, 2H), 1.67 (d, J = 6.9 Hz, 3H), 1.64 (m, 1H), 1.40 (m, 2H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.9, 140.3, 139.6, 125.9, 53.3, 45.3, 39.9, 33.8, 30.5, 25.0, 25.0, 22.3, 19.7, 17.2; IR ($CHCl_3$) 2900, 2825, 1845, 1760, 1455 cm^{-1}; MS (EI) m/z 288 (M^+, 38), 260 (19), 245 (33), 159 (100); HRMS (EI) m/z calcd for $C_{18}H_{24}O_3$ (M^+) 288.1725, found 288.1736.

General Experimental Procedure for the Reaction of Vinyl Allenes with Imines. Vinyl allene (1.0 equiv) was added to a stirred solution of the imine (1−2 equiv) and boron trifluoride etherate (1.1−1.2 equiv) in CH_2Cl_2 (0.1 M) at 0 °C. The reaction mixture was stirred at room temperature or refluxed for 36 h to 5 days, and then TEA (2.4 equiv) and water (10 mL) were added and the reaction mixture was extracted with CH_2Cl_2. Drying ($MgSO_4$) and concentration afforded crude products. Flash column chromatography on silica gel (hexanes/EtOAc) gave the products in the yields indicated.

Reaction of Vinyl Allene 9 with Imine 18. Following the general procedure, vinyl allene **9** (133 mg, 0.82 mmol), imine **18** (240 mg, 1.23 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 4 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **19** (196 mg, 67%). When $TiCl_4$ was used as Lewis acid, **19** was obtained in a 49% yield together with triene **20** (8%).

(2*R,8a*S**)-1-Benzyl-4-ethyl-3(*E*)-ethylidene-2-phenyl-1,2,3,5,6,7,8,8a-octahydroquinoline (19):** oily; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.42−7.33 (m, 4H), 7.27−7.14 (m, 4H), 5.18 (q, J = 7.39 Hz, 1H), 4.06 (s, 1H), 3.85 (d, J = 13.4 Hz, 1H), 3.74 (d, J = 13.4 Hz, 1H), 2.82−2.76 (m, 2H), 2.66−2.55 (m, 2H), 1.99 (d, J = 7.38 Hz, 3H), 1.66−1.53 (m, 2H), 1.43−1.42 (m, 1H), 1.20 (t, J = 7.47 Hz, 3H), 1.10−1.07 (m, 1H), 0.90−0.80 (m, 2H), 0.64−0.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.2, 137.8, 132.2, 129.4, 129.1, 128.5, 128.4, 127.6, 127.2, 126.4, 122.9, 68.6, 64.2, 62.1, 36.0, 30.3, 27.5, 27.2, 23.0, 15.7, 15.3; IR ($CHCl_3$) 2900, 1590, 1485, 1440 cm^{-1}; MS (EI) m/z 357 (M^+, 27), 328 (100), 280 (21), 91 (60); HRMS (EI) m/z calcd for $C_{26}H_{31}N$ 357.2456, found 357.2402.

(±)-Benzyl-(3-cyclohex-1-enyl-2(*E*)-ethylidene-1-phenylpent-3(*E*)-enyl)amine (20): colorless oil; ^{1}H NMR (400 MHz, C_6D_6, 348 K) δ 7.48−7.16 (m, 10H), 6.05 (bs, 1H), 5.77 (bs, 1H), 5.64 (bs, 1H), 4.33 (s, 1H), 3.80 (d, J = 13.5 Hz, 1H), 3.68 (d, J = 13.5 Hz, 1H), 2.17 (bs, 2H), 2.05 (bs, 2H), 1.75−1.36 (m, 5H), 1.58 (bs, 6H); IR ($CHCl_3$) 2900, 1600, 1485, 1440 cm^{-1}; MS (EI) m/z 357 (M^+, 45), 307 (38), 251 (31), 196 (62), 154 (79); HRMS (EI) m/z calcd for $C_{26}H_{31}N$ 357.2456, found 357.2550.

Reaction of Vinyl Allene 8 with Imine 18. Following the general procedure, vinyl allene **8** (150 mg, 1.01 mmol), imine **18** (300 mg, 1.52 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 1.5 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **23** (187 mg, 54%) and triene **33** (32 mg, 11%).

(2*R,8a*S**)-1-Benzyl-3(*E*)-ethylidene-4-methyl-2-phenyl-1,2,3,5,6,7,8,8a-octahydroquinoline (23):** oily, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.13 (m, 10H), 5.19 (q, J = 7.26 Hz, 1H), 4.07 (s, 1H), 3.86 (d, J = 13.4 Hz, 1H), 3.75 (d, J = 13.4 Hz, 1H), 2.82−2.74 (m, 2H), 2.17 (s, 3H), 1.98 (d, J = 7.25 Hz, 3H), 1.64−1.42 (m, 4H), 1.11−1.07 (m, 1H), 0.81−0.77 (m, 1H), 0.6−0.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.2, 137.8, 133.9, 129.4, 129.1, 128.6, 127.6, 127.2, 126.5, 122.8, 121.8, 68.3, 64.1, 62.3, 36.0, 30.3, 27.1, 26.8, 18.1, 16.0; IR ($CHCl_3$) 2900, 1595, 1495, 1445 cm^{-1}; MS (EI) m/z 343 (M^+, 39), 328 (95), 314 (16), 266 (77), 91 (100); HRMS (EI) m/z calcd for $C_{25}H_{29}N$ 343.2300, found 343.2265.

(±)-Benzyl[2-(1-cyclohex-1-enylvinyl)-1-phenylbut-2(*E*)-enyl]amine (33): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.20 (m, 10H), 5.69−5.63 (m, 2H), 5.10 (s, 1H), 4.51 (s, 1H), 4.19 (s, 1H), 3.73 (d, J = 13.48 Hz, 1H), 3.64 (d, J = 13.48 Hz, 1H), 2.35 (brs, 1H), 2.10 (brs, 2H), 1.97 (brs, 2H), 1.64−1.47 (m, 4H), 1.54 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.9, 142.9, 141.1, 134.9, 129.1, 128.7, 128.3, 128.3, 128.1, 127.5, 127.2, 123.0, 111.6, 67.0, 52.1, 26.2, 25.8, 23.2, 22.5, 14.9; IR ($CHCl_3$) 2800, 1625, 1585, 1485, 1445; MS (EI) m/z 343 (M^+, 3), 307 (29), 289 (14), 154 (100), 136 (41); HRMS (EI) m/z calcd for $C_{25}H_{29}N$ 343.2300, found 343.2309.

Reaction of Vinyl Allene 8 with Imine 21. Following the general procedure, vinyl allene **8** (150 mg, 1.01 mmol), imine **21** (249 mg, 1.57 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 1.5 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **24** (134 mg, 43%) and triene **34** (22 mg, 7%) together with unreacted **8** (20 mg).

(2*R,8a*S**)-1-Benzyl-3(*E*)-ethylidene-2-isopropyl-4-methyl-1,2,3,5,6,7,8,8a-octahydroquinoline (24):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.21 (m, 5H), 4.97 (q, J = 7.16 Hz, 1H), 3.59 (s, 2H), 2.85−2.81 (m, 1H), 2.71−2.68 (m, 1H), 2.21 (d, J = 10.5 Hz, 1H), 1.99 (s, 3H), 1.93−1.68 (m, 5H), 1.82 (d, J = 7.16 Hz, 3H), 1.53−1.49 (m, 1H), 1.27−1.16 (m, 2H), 0.98 (d, J = 6.5 Hz, 3H), 0.68 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 136.5, 136.0, 129.6, 128.3, 126.9, 122.2, 119.3, 74.6, 62.9, 62.8, 37.1, 29.7, 29.6, 27.0, 26.7, 21.7, 20.5, 18.2, 15.6; IR ($CHCl_3$) 2850, 1585, 1480, 1435 cm^{-1}; MS (EI) m/z 309 (M^+, 0.2), 289 (10), 266 (100), 154 (94), 137 (50); HRMS (EI) m/z calcd for $C_{22}H_{31}N$ 309.2456, found 309.2536.

(±)-Benzyl-[2-(1-cyclohex-1-enylvinyl)-1-isopropylbut-2(*E*)-enyl]amine (34): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.21 (m, 5H), 5.80 (s, 1H), 5.60 (q, J = 6.6 Hz, 1H), 5.18 (s, 1H), 4.65 (s, 1H), 3.87 (d, J = 13.2 Hz, 1H), 3.57 (d, J = 13.2 Hz, 1H), 2.82 (d, J = 4.6 Hz, 1H) 2.21−2.07 (m, 4H), 1.82−1.77 (m, 1H), 1.69−1.52 (m, 5H), 1.63 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 141.9, 141.0, 135.7, 128.6, 127.0, 126.9, 121.9, 111.2, 68.3, 52.0, 29.3, 26.2, 26.1, 23.3, 22.6, 21.2, 17.5, 14.9; MS (EI) m/z 309 (M^+, 8), 307 (28), 289 (19), 266 (21), 154 (100), 136 (66); HRMS (EI) m/z calcd for $C_{22}H_{31}N$ 309.2456, found 309.2547.

Reaction of Vinyl Allene 9 with Imine 21. Following the general procedure, vinyl allene **9** (100 mg, 0.61 mmol), imine **21** (148 mg, 0.92 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 3 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **25** (78 mg, 39%) and triene **35** (8 mg, 4%), together with unreacted **9** (24 mg).

(2*R,8a*S**)-1-Benzyl-4-ethyl-3(*E*)-ethylidene-2-isopropyl-1,2,3,5,6,7,8,8a-octahydroquinoline (25):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.23 (m, 5H), 4.97 (q, J = 7.2 Hz, 1H), 3.58 (s, 2H), 2.85−2.81 (m, 1H), 2.69−2.67 (m, 1H), 2.51−2.39 (m, 2H), 2.20−2.17 (m, 1H), 1.90−1.84 (m, 1H), 1.82 (d, J = 7.2 Hz, 3H), 1.81−1.69 (m, 4H), 1.55−1.51 (m, 1H), 1.28−1.12 (m, 2H), 1.05−0.99 (m, 6H), 0.71 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ141.1, 135.4, 134.5, 129.1, 129.0, 127.8, 126.4, 119.0, 74.6, 62.6, 62.4, 36.7, 29.5, 28.9, 26.9, 26.7, 22.7, 21.1, 20.1, 15.0, 14.7; IR ($CHCl_3$) 2900, 1595, 1485, 1445 cm^{-1}; MS (EI) m/z 323 (M^+, 5.6), 307 (14.6), 280 (100), 154 (28), 136 (22); HRMS (EI) m/z calcd for $C_{23}H_{33}N$ 323.2613, found 323.2651.

(±)-Benzyl(3-cyclohex-1-enyl-2(*E*)-ethylidene-1-isopropylpent-3(*E*)-enyl)amine (35): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 330K): δ 7.38−7.19 (m, 10H), 5.76 (m, 1H), 5.60 (m, 2H), 3.93 (d, J = 13.2 Hz, 1H), 3.61 (d, J = 13.2 Hz, 1H), 2.92 (s, 1H), 2.17 (m, 1H), 2.03 (m, 2H), 1.76, (m, 1H), 1.59 (m, 6H), 0.96 (d, J = 6.8 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H); IR ($CHCl_3$) 2900, 1710, 1595, 1485, 1440 cm^{-1}; MS (EI) m/z 323 (M^+, 12), 307 (23), 280 (81), 154 (100), 136 (44); HRMS (EI) m/z calcd for $C_{23}H_{33}N$ 323.2613, found 323.2676.

Reaction of Vinyl Allene 10 with Imine 18. Following the general procedure, vinyl allene **10** (75 mg, 0.36 mmol), imine **18** (103 mg, 0.53 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 4 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **26** (103 mg, 71%) and triene **36** (7 mg, 5%) together with unreacted **10** (10 mg).

(2*R,8a*S**)-1-Benzyl-3(*E*)-benzylidene-4-methyl-2-phenyl-1,2,3,5,6,7,8,8a-octahydroquinoline (26):** oily, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.20 (m, 15H), 6.26 (s, 1H), 4.33 (s, 1H), 4.04 (d, J = 13.3 Hz, 1H), 3.91 (d, J = 13.3 Hz, 1H), 2.97 (m, 1H), 2.75 (m, 1H), 1.79 (s, 3H), 1.77−0.67 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.8, 139.9, 139.4, 136.2, 129.6, 129.1, 129.1, 128.7, 128.2, 127.8, 127.4, 127.2, 126.8, 126.8, 121.9, 67.8, 64.2, 62.5, 36.0, 30.4, 27.0, 26.5, 18.1; IR ($CHCl_3$) 2850, 1720, 1590, 1480, 1440 cm^{-1}; MS (EI) *m*/*z* 405 (M$^+$, 73), 390 (100), 376 (10), 328 (77), 314 (11); HRMS (EI) *m*/*z* calcd for $C_{30}H_{31}N$ 405.2456, found 405.2452.

(±)-Benzyl(2(*E*)-benzylidene-3-cyclohex-1-enyl-1-phenylbut-3-enyl)amine (36): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.12 (m, 15 H), 6.84 (s, 1H), 5.78 (s, 1H), 5.06 (s, 1H), 4.49 (s, 1H), 4.31 (s, 1H), 3.79 (AB system, J = 13.3 Hz, 2H), 2.16 (m, 2H), 1.94 (m, 2H), 1.63 (m, 2H), 1.5 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.5, 137.5, 134.3, 129.8, 129.2, 128.8, 128.6, 128.4, 128.3, 127.5, 127.3, 127.1, 127.0, 112.0, 68.3, 52.2, 26.2, 25.8, 23.2, 22.5; MS (EI) *m*/*z* 405 (M$^+$, 80), 299 (63), 196 (62), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{30}H_{31}N$ 405.2456, found 405.2495.

Reaction of Vinyl Allene 10 with Imine 21. Following the general procedure, vinyl allene **10** (152 mg, 0.72 mmol), imine **21** (173 mg, 1.07 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 4 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **27** (162 mg, 61%) and triene **37** (32 mg, 12%) together with unreacted **10** (23 mg).

(2*R,8a*S**)-1-Benzyl-3(*E*)-benzylidene-2-isopropyl-4-methyl-1,2,3,5,6,7,8,8a-octahydroquinoline (27):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.18 (m, 10H), 6.00 (s, 1H), 3.71 (m, 2H), 2.82 (m, 2H), 2.45 (d, J = 10.5 Hz, 1H), 2.02 (bs, 1H), 1.75 (m, 2H), 1.71 (m, 2H), 1.64 (s, 3H), 1.54 (dq, J = 3.3, 12.6 Hz, 1H), 1.26 (m, 1H), 1.14 (m, 1H), 1.02 (d, J = 6.4 Hz, 3H), 0.75 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 139.0, 138.5, 137.5, 129.2, 128.9, 127.9, 127.7, 126.6, 125.9, 123.7, 121.9, 73.8, 62.5, 62.3, 36.4, 29.4, 28.9, 26.4, 26.1, 21.0, 19.9, 17.5; IR ($CHCl_3$) 2925, 2850, 1630, 1595 cm^{-1}; MS (EI) *m*/*z* 371 (M$^+$, 1), 329 (27), 328 (100); HRMS (EI) *m*/*z* calcd for $C_{27}H_{33}N$ 371.2613, found 371.2609.

(±)-Benzyl-(2(*E*)-benzylidene-3-cyclohex-1-enyl-1-isopropylbut-3-enyl)amine (37): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.12 (m, 10H), 6.60 (s, 1H), 5.92 (s, 1H), 5.18 (s, 1H), 4.76 (s, 1H), 3.96 (d, J = 13.2 Hz, 1H), 3.64 (d, J = 13.2 Hz, 1H), 3.05 (d, J = 3.7 Hz, 1H), 2.26 (m, 1H), 2.15 (m, 1H), 1.98 (m, 2H), 1.70−1.50 (m, 6H), 1.00 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 138.0, 134.8, 129.1, 128.7, 128.3, 128.1, 127.2, 126.9, 126.7, 124.3, 111.7, 69.1, 52.0, 30.1, 29.7, 26.2, 23.3, 22.5, 21.7, 16.4; IR ($CHCl_3$) 2900, 2850, 1710 cm^{-1}; MS (EI) *m*/*z* 371 (M$^+$, 10), 328 (6), 307 (30), 289 (10), 154 (100); HRMS (EI) *m*/*z* calcd for $C_{27}H_{33}N$ 371.2613, found 371.2541.

Reaction of Vinyl Allene 10 with Imine 22. Following the general procedure, vinyl allene **10** (124 mg, 0.59 mmol), imine **22** (288 mg, 1.42 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 3 days at rt and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **28** (139 mg, 57%) and triene **38** (7 mg, 3%) together with unreacted **10** (6 mg).

(2*R,8a*S**)-1-Benzyl-3(*E*)-benzylidene-2-hexyl-4-methyl-1,2,3,5,6,7,8,8a-octahydroquinoline (28):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.18 (m, 10H), 6.06 (s, 1H), 3.74 (AB system, J = 13.7 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H), 2.84 (m, 1H), 1.96 (m, 1H), 1.76 (m, 3H), 1.61 (s, 3H), 1.25 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.1, 137.3, 129.0, 128.8, 127.7, 126.6, 126.0, 123.6, 121.3, 66.4, 62.1, 61.8, 36.5, 34.2, 31.9, 30.9, 29.6, 29.3, 26.9, 26.5, 26.3, 22.7, 17.7, 14.1; IR ($CHCl_3$) 2800, 1940, 1870, 1790, 1720 cm^{-1}; MS (EI) *m*/*z* 413 (M$^+$, 3), 398 (2), 328 (100); HRMS (EI) *m*/*z* calcd for $C_{30}H_{39}N$ 413.3082, found 413.3076.

(±)-Benzyl[1-(1(*E*)-benzylidene-2-cyclohex-1-enylallyl)-heptyl]amine (38): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.13 (m, 10H), 6.55 (s, 1H), 5.93 (s, 1H), 5.23 (s, 1H), 4.81 (s, 1H), 3.90 (d, J = 13.2 Hz, 1H), 3.70 (d, J = 13.2 Hz, 1H), 3.19 (t, J = 5.7 Hz, 1H), 2.21 (m, 2H), 2.01 (m, 2H), 1.85−1.50 (m, 6H), 1.26 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 142.9, 141.0, 137.3, 134.3, 128.7, 128.3, 128.1, 127.9, 127.9, 126.7, 126.4, 110.7, 64.2, 51.2, 34.2, 31.9, 29.4, 26.2, 25.8, 25.7, 22.9, 22.7, 21.5, 14.1; IR ($CHCl_3$) 3300, 2800, 1930, 1865, 1790, 1725 cm^{-1}; MS (EI) *m*/*z* 413 (M$^+$, 22), 328 (79), 306 (17), 91 (100); HRMS (EI) *m*/*z* calcd for $C_{30}H_{39}N$ 413.3082, found 413.3063.

Reaction of Vinyl Allene 11 with Imine 18. Following the general procedure, vinyl allene **11** (125 mg, 0.77 mmol), imine **18** (225 mg, 1.15 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 3 days at 40 °C and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **29** (184 mg, 67%) and triene **39** (16 mg, 6%).

(2*R,8a*S**)-1-Benzyl-3-isopropylidene-4-methyl-2-phenyl-1,2,3,5,6,7,8,8a-octahydroquinoline (29):** white crystals; mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.14 (m, 10H), 4.60 (s, 1H), 3.77 (m, 2H), 2.77 (d, J = 11.7 Hz, 1H), 2.68 (d, J = 13.9 Hz, 1H), 2.07 (s, 3H), 1.99 (s, 3H), 1.60 (m, 2H), 1.55 (s, 3H), 1.45 (m, 2H), 1.09 (m, 1H), 0.75 (m, 1H), 0.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 141.0, 136.2, 129.1, 128.9, 128.7, 128.1, 127.7, 127.2, 126.7, 126.0, 122.1, 63.1, 62.0, 61.2, 35.8, 29.9, 26.5, 26.0, 23.5, 21.5, 19.4; IR ($CHCl_3$) 3050, 3025, 3000, 2900, 2800, 1940, 1855, 1790, 1730, 1590 cm^{-1}; MS (EI) *m*/*z* 357 (M$^+$, 44), 342 (100), 280 (20); HRMS (EI) *m*/*z* calcd for $C_{26}H_{31}N$ 357.2456, found 357.2458.

(±)-Benzyl[2-(1-cyclohex-1-enylvinyl)-3-methyl-1-phenylbut-2-enyl]amine (39): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 328K) δ 7.34−7.12 (m, 10H), 5.36 (bs, 1H), 5.09 (s, 1H), 4.86 (s, 1H), 3.73 (AB system, J = 13.4 Hz, 2H), 2.06 (m, 1H), 1.92 (s, 3H), 1.86 (m, 3H), 1.71 (m, 2H), 1.62 (s, 3H), 1.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 142.7, 140.8, 135.4, 130.0, 128.2, 128.1, 127.5, 127.5, 127.4, 126.7, 126.1, 111.0, 61.3, 51.3, 25.6, 25.1, 22.9, 22.7, 21.9, 19.7; IR ($CHCl_3$) 3000, 2900, 2750, 1725, 1580 cm^{-1}; MS (EI) *m*/*z* 357 (M$^+$, 48), 266 (16), 250 (28), 25 (31), 196 (72), 981 (100); HRMS (EI) *m*/*z* calcd for $C_{26}H_{31}N$ 357.2456, found 357.2445.

Reaction of Vinyl Allene 11 with Imine 21. Following the general procedure, vinyl allene **11** (125 mg, 0.77 mmol), imine **21** (187 mg, 1.16 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 5 days at 40 °C and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **30** (93 mg, 37%) and triene **40** (5 mg, 2%) together with unreacted **11** (19 mg).

(2*R,8a*S**)-1-Benzyl-2-isopropyl-3-isopropylidene-4-methyl-1,2,3,5,6,7,8,8a-octahydroquinoline (30):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.19 (m, 5H), 3.53 (AB system, J = 13.7 Hz, 2H), 2.90 (d, J = 10.5 Hz, 1H), 2.77 (d, J = 13.7 Hz, 1H), 2.66 (d, J = 10.9 Hz, 1H), 1.90−1.62 (m, 5H), 1.92 (s, 3H), 1.82 (s, 3H), 1.62 (s, 3H), 1.45 (m, 1H), 1.16 (m, 2H), 1.00 (d, J = 6.6 Hz, 3 H), 0.66 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 134.4, 132.0, 129.0, 127.7, 126.4, 124.0, 122.8, 66.5, 62.1, 61.9, 36.4, 29.5, 29.3, 26.4, 26.1, 23.1, 21.5, 20.1, 20.1, 19.5; IR ($CHCl_3$) 2850, 1935, 1860, 1795, 1730 cm^{-1}; MS (EI) *m*/*z* 323 (M$^+$, 2), 280 (100), 246 (2); HRMS (EI) *m*/*z* calcd for $C_{23}H_{33}N$ 323.2613, found 323.2596.

(±)-Benzyl[2-(1-cyclohex-1-enylvinyl)-1-isopropyl-3-methylbut-2-enyl]amine (40): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.21 (m, 5H), 5.81 (s, 1H), 5.22 (s, 1H), 4.64 (s, 1H), 3.74 (d, J = 13.1 Hz, 1H), 3.52 (d, J = 13.1 Hz, 1H), 3.07 (d, J = 8.9 Hz, 1H), 2.19 (bs, 2H), 2.06 (bs, 2H), 1.71 (s, 3H), 1.66 (s, 3H), 1.53 (m, 5H), 0.98 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 128.2, 128.0, 127.6, 126.6, 126.0, 114.6, 64.5, 52.4, 31.6, 29.7, 25.8, 23.2, 23.0, 22.2, 20.9, 20.2, 19.9.

Reaction of Vinyl Allene 11 with Imine 22. Following the general procedure, vinyl allene **11** (125 mg, 0.77 mmol), imine **22** (373 mg, 1.84 mmol), and $BF_3{\cdot}Et_2O$ (1.2 equiv), after 5 days at 40 °C and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **31** (115 mg, 41%) and triene **41** (20 mg, 7%) together with unreacted **11** (29 mg).

(2*R,8a*S**)-1-Benzyl-2-hexyl-3-isopropylidene-4-methyl-1,2,3,5,6,7,8,8a-octahydroquinoline (31):** colorless oil; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.40−7.20 (m, 5H), 3.58 (s, 2H), 3.40 (dd, J = 7.0, 7.8 Hz, 1H), 2.80 (d, J = 16.3 Hz, 1H), 2.68 (d, J = 9.9 Hz, 1H), 1.92 (s, 3H), 1.83 (s, 3H), 1.66 (m, 3H), 1.60 (s, 3H), 1.47 (m, 4H), 1.25 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.2, 132.6, 128.7, 127.8, 126.4, 124.1, 122.2, 61.4, 61.4, 59.1, 36.5, 34.2, 31.9, 29.6, 29.5, 26.5, 26.5, 26.3, 23.3, 22.7, 21.4, 19.5, 14.1; IR ($CHCl_3$) 2900, 1720, 1680 cm^{-1}; MS (EI) m/z 365 (M^+, 3), 350 (5), 280 (100); HRMS (EI) m/z calcd for $C_{26}H_{39}N$ 365.3082, found 365.3084.

(±)-Benzyl[1-[1-(1-cyclohex-1-enylvinyl)-2-methylpropenyl]heptyl]amine (41): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.21 (m, 5H), 5.77 (bs, 1H), 5.22 (s, 1H), 4.61 (s, 1H), 3.74 (d, J = 13.3 Hz, 1H), 3.58 (d, J = 13.3 Hz, 1H), 3.51 (t, J = 6.2 Hz, 1H), 2.30−2.23 (m, 4H), 1.71 (s, 3H), 1.64 (s, 3H), 1.65−1.45 (m, 4H), 1.23 (m, 10H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 330 K) δ 148.3, 144.1, 141.3, 136.0, 129.9, 128.6, 128.0, 126.9, 128.5, 110.7, 57.7, 51.5, 35.3, 32.0, 29.5, 27.1, 25.7, 25.6, 23.0, 23.0, 22.7, 22.2, 19.4, 14.1.

Reaction of Vinyl Allene 12 with Imine 18. Following the general procedure, vinyl allene **12** (215 mg 1.1 mmol), imine **18** (330 mg, 1.69 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 5 days at 40 °C and flash chromatography (97:3 hexanes/EtOAc), provided octahydroquinoline **32** (148 mg, 34%) together with unreacted **12** (54 mg).

(2*R,8a*S**)-1-Benzyl-4-*tert*-butyl-3(*E*)-ethylidene-2-phenyl-1,2,3,5,6,7,8,8a-octahydroquinoline (32):** colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 330 K) δ 7.32−7.10 (m, 10H), 5.27 (bs, 1H), 4.19 (s, 1H), 3.84 (d, J = 14.3 Hz, 1H), 3.68 (d, J = 14.3 Hz, 1H), 2.76 (m, 1H), 2.62 (m, 1H), 2.27 (m, 1H), 1.80 (m, 1H), 1.68 (d, J = 6.89 Hz, 3H), 1.64−1.47 (m, 4H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 330 K) δ 145.1, 141.0, 140.1, 138.6, 129.1, 128.6, 128.4, 127.6, 127.0, 126.2, 125.7, 119.3, 72.0, 62.1, 59.8, 34.2, 30.1, 17.2; IR ($CHCl_3$) 2900, 1590, 1485, 1440 cm^{-1}; MS (EI) m/z 385 (M^+, 1.4), 307 (22), 289 (10), 154 (100), 136 (50); HRMS (EI) m/z calcd for $C_{28}H_{35}N$ 385.2769, found 385.2692.

Acknowledgment. This work was supported in part by Grant No. BQU2001-3184 (MCYT, Spain) and Grant No. 1FD97-0747-C04-01 (FEDER, EU). D.R. thanks the MEC (Spain) for a fellowship.

Supporting Information Available: General experimental procedures and NMR spectra for all new compounds and ORTEP drawing and X-ray data for compound **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034480Z