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SYNTHESIS OF β-ENAMINOESTERS AND LACTAMS BY MICHAEL ADDITION OF *N*-BENZYLANILINE TO NEW ALLENIC ESTERS AND LACTAMS

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Abstract : The synthesis of original allenic lactams **2** and allenic esters **5** is presented and their Michael condensation with *N*-benzylaniline described.

Enaminones are useful intermediates for the synthesis of carbocyclic and polyheterocyclic compounds (*e.g.* quinoline, acridine, benzoxazine, hexahydrocarbazolones...).[1] Recently, we have reported an efficient and stereospecifical synthesis of spiroindoline lactones **7** by photocyclisation of enaminolactones **3** which are easily obtained by condensation of *N*-benzylaniline with allenic lactones **1**.[2] As an extension of this work, we became interested in preparation of enaminolactams **4** and esters **6**[3], precursors of spiroindoline lactams **8** which could be further transformed into dihydroindolic pentacyclic *Aspidosperma* alkaloids (figure 1).

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Enaminones are usually prepared by condensation of a primary or a secondary amine on a 1,3-diketone under acidic conditions.[1] Enaminoesters derived from primary amines could be prepared in the same way by condensation on a 1,3-ketoester. Nevertheless, when secondary amines were used the reaction did not lead to the desired enaminoester but to the β-ketoamide (figure 1). New methods have been developed to allow the formation of the enaminoester and to improve the chemical yield of enamino compounds among which are BF_3 catalysis[4], heterogeneous media[5], microwave irradiation[6], high pressure and lanthanide catalysis.[7] But none of them is general. Therefore, we have extended our methodology[2] to the synthesis of substituted β-enaminoesters **6** and β-enaminolactams **4**.

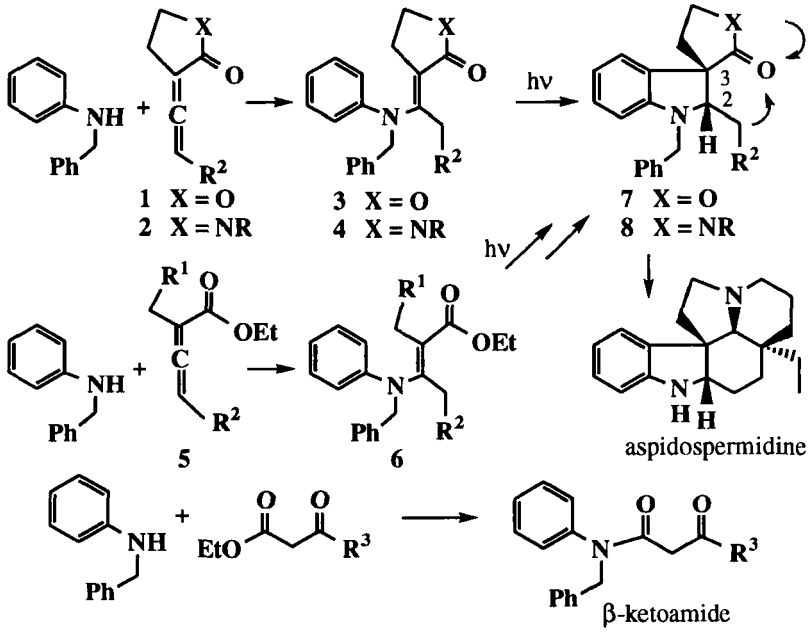


FIG. 1

We report herein the synthesis of **4** and **6** by Michael addition of *N*-benzylaniline with allenic lactams **2** and esters **5**. Allenic compounds **2** and **5** were prepared by a Wittig reaction[8] between the acid choride **9**, **10** or **11** and the phosphorane **15** or **17**.

Preparation of allenic lactams 2 and esters 5

3-Benzyloxypropionyl chloride (**9**)[9] was obtained in two steps with 56% overall yield starting from β-propiolactone. 3,3-Ethylenedioxybutanoyl chloride (**10**) and 4-carbomethoxy-3,3-ethylenedioxybutanoyl chloride (**11**) were prepared in three steps with respectively 42% and 54% overall yield from ethyl acetoacetate and methyl 1,3-acetonedicarboxylate by a procedure already reported in the literature.[10] Allenic lactams **2** were conveniently synthesized by a Wittig reaction between the acid chloride **9** and the phosphorane **15** with a good yield (figure 2, table 1). The phosphonium salts **15a,b** were easily prepared in four steps with 54% and 46% overall yield, respectively. Thus, 2,4-dibromobutanoyl chloride (**12**) obtained from γ-butyrolactone in 62% yield using a Hell-Vollhardt-Zelinski reaction[11] was condensed with benzylamine or *n*-butylamine and led to the amide **13a,b** in 95.5% and 91% yield, respectively. The cyclization of **13a,b** was effected in basic medium using sodium hydride in THF instead of sodium ethoxide in EtOH as previously described[11] and afforded the 3-bromopyrrolidone **14a,b** in 95.5% yield. Finally, **14a,b** were converted to their phosphonium salts **15a,b** by heating in anhydrous toluene with triphenylphosphine in 96% and 85% yield, respectively.

The structures of allenic lactams **2** were confirmed on the basis of their IR, ^1H and ^{13}C NMR spectroscopic data.

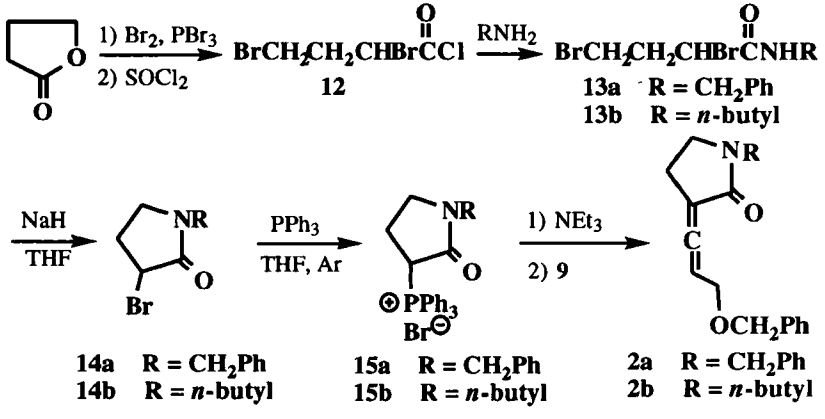
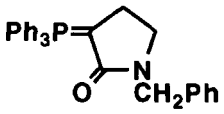
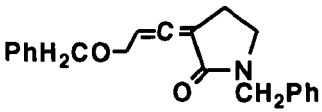
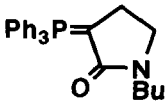
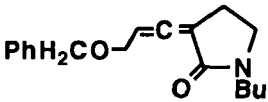
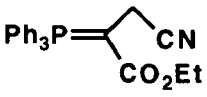
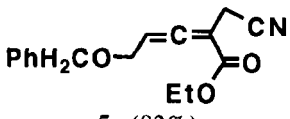
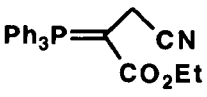
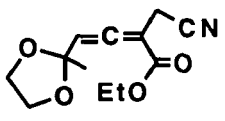
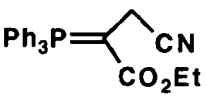
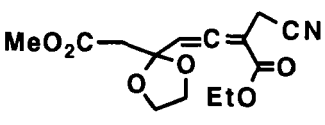
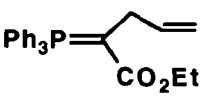
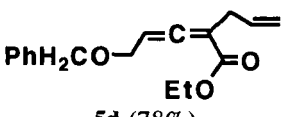
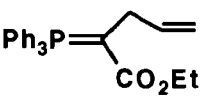
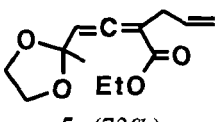


FIG. 2

Table 1. Synthesis of allenic lactams **2** and esters **5**.

Phosphorane	RCOCl	Allenic Compounds (yield %)	ν_{allene} (cm^{-1})	δ (Cβ) ppm
 **15a**	9	 **2a** (79 %)	1970	203.9
 **15b**	9	 **2b** (62%)	1970	202.8
 **17a**	9	 **5a** (83%)	1965	210.2
 **17a**	10	 **5b** (88%)	1970	207.8
 **17a**	11	 **5c** (82%)	1970	208.3
 **17b**	9	 **5d** (78%)	1975	210.6
 **17b**	10	 **5e** (73%)	1965	213.4

Condensation[8] of the acid chloride **9**, **10** or **11** in the presence of triethylamine with the phosphoranes **17**[12] readily obtained by alkylation of commercially available carboethoxymethylenetriphenylphosphorane (**16**) with bromoacetonitrile or allyl bromide, led in good yield to the allenic esters **5**, which were fully characterized (figure 3 and table 1).

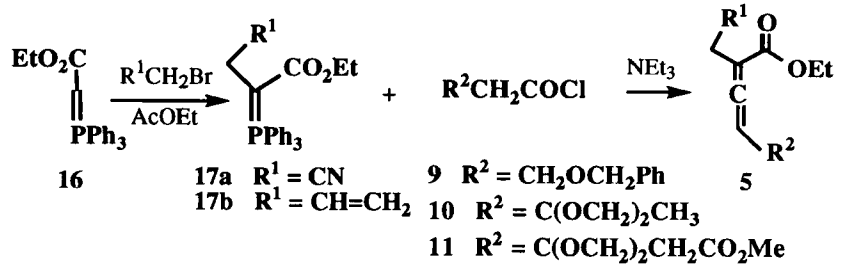


FIG. 3

For all compounds **2** and **5** an absorption band near 1950 cm^{-1} assignable to the allenic function is observed in the IR spectra; the signal due to the central carbon atom of the allene (Cβ) appears near 205 ppm in the ^{13}C NMR spectra.[13]

Preparation of β-enaminoesters 6

Condensation of *N*-benzylaniline with allenic esters **5** in refluxing benzene[14] furnished the enaminoesters **6**. In addition, in the case of **5a,d** the enaminoesters **18a,d** resulting from benzylic alcohol elimination were isolated (figure 4, table 2). Compounds **6** and **18** were fully characterized by IR, ^1H and ^{13}C NMR, mass spectroscopy or combustion analysis and present an E[14] stereochemistry as demonstrated by NOE experiments. Indeed, the irradiation of the signal due to the two diastereotopic protons of the CH_2R^1 chain resulted in an enhancement of the signal area of the *ortho* and the *meta* protons of the aromatic moiety.

Preparation of β-enaminolactams 4

In contrast, condensation of *N*-benzylaniline with allenic lactams **2a,b** following the same procedure afforded the enaminolactams in a poor yield (**4a** : 10% ; **4b** : 15% ; **19a** : 20% ; **19b** : 5%). The major products were the cyclobutanes **20** and **21** resulting from dimerisation of the allenes **2**[15] (figure 5). All attempts to improve the formation of enaminolactams **4** failed.

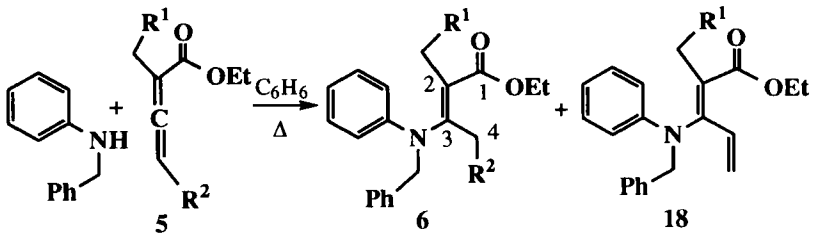


FIG. 4

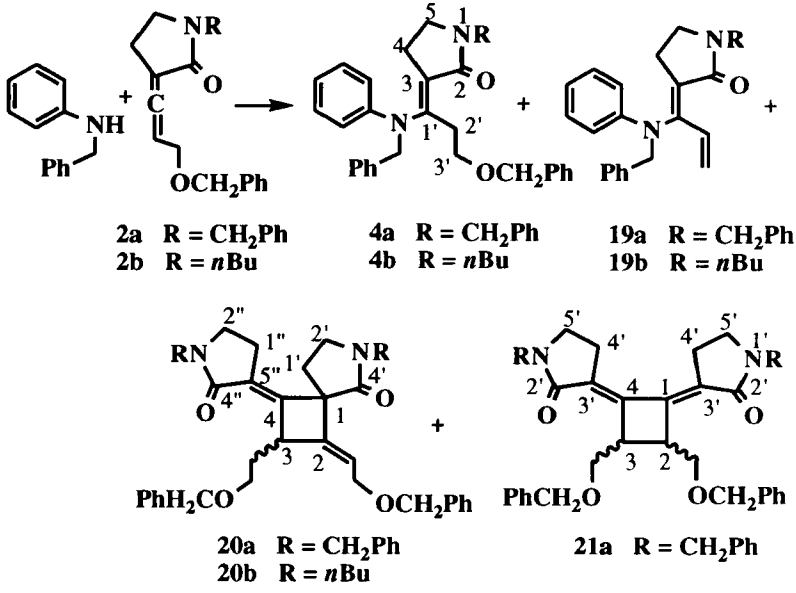
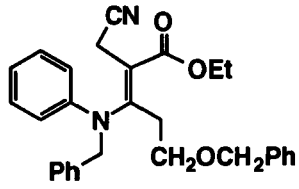
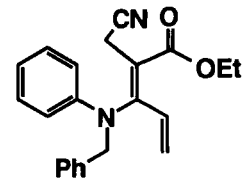
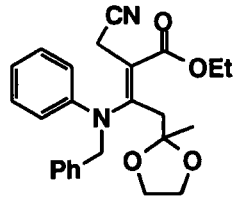
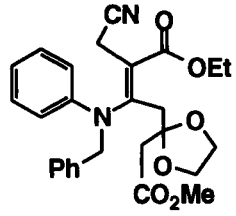
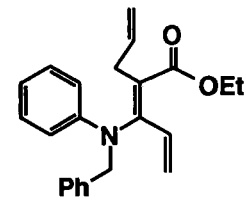
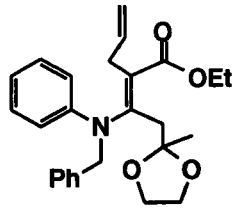


FIG. 5

The structures of **4**, **19**, **20** and **21** were determined on the basis of their spectral and analytical data. We observed only one compound in the ^{1}H NMR spectra of **4**, **19**, **20** and **21**. The stereochemistry of **4** and **19** is E; the stereochemistry of **20** and **21** has not been determined.

Table 2. Condensation of *N*-benzylaniline with allenic esters **5**.

allenic ester	Enaminoester **6**	Yield (%)	Enaminoester **18**	Yield (%)
5a	 **6a**	82	 **18a**	5
5b	 **6b**	85	-	-
5c	 **6c**	85	-	-
5d	-	-	 **18d**	43
5e	 **6e**	95	-	-

The IR spectrum of **4** and **19** exhibit an intense band at 1675-1680 cm^{-1} due to the enaminolactam moiety. The ^1H NMR spectra show two triplets at δ 3.52 ppm and 3.82 ppm for **4a** (3.47 ppm and 3.78 ppm for **4b**) corresponding to the two protons H-2' and the two protons H-3'. The ethylenic proton H-2' of **19** appears as a doublet of doublet at δ 8.05 ppm for **19a** with coupling constants of 10.3 Hz and 17.2 Hz (δ 8.00 ppm, *J* 11.2 Hz and 17.6 Hz for **19b**). The two ethylenic protons H-3' are detected as a multiplet centered at δ 4.40 ppm for **19a** and appear as a doublet at δ 5.32 ppm (*J* 11.3 Hz) and 5.37 ppm (*J* 11.3 Hz) for **19b**. In the ^{13}C NMR, the carbon C-1' is detected at δ 148.2 for **4a** (147.3 for **4b**) and at δ 147.0 ppm for **19a** (147.1 ppm for **19b**).

The IR spectra of cyclobutanes **20** show an absorption band at 1690 cm^{-1} for **20a** (1685 cm^{-1} for **20b**) assignable to the lactam moiety. Their ^1H NMR spectra exhibit two characteristics triplets at δ 3.80 ppm (*J* 10Hz) and 5.80 ppm (*J* 7.5 Hz) for **20a** (3.72 ppm and 5.78 ppm for **20b**) corresponding of the proton 3-H and of the ethylenic proton (C_2=C<u>H</u>). In the ^{13}C NMR, the signals due to the α,β-unsaturated lactam carbonyl carbon and to the other lactam carbonyl carbon appear respectively at 167.7 ppm and 175.3 ppm for **20a** (167.8 ppm and 175.2 ppm for **20b**). The molecular formula of **20a** and **20b** are established to be $C_{42}H_{42}N_2O_4$ and $C_{36}H_{46}N_2O_4$ by combustion analysis or mass spectroscopy.

The simplicity of the ^1H and ^{13}C NMR spectra of **21** is in good agreement with the proposed symmetrical structure. In particular, in the ^1H NMR spectrum, the signals corresponding of the four NCH_2Ph and the four OCH_2Ph protons appear respectively as a singlet at δ 4.5 ppm and as an AB spectrum centered at δ 4.60 ppm. The ^{13}C NMR spectrum show one tertiary carbon atom at δ 46.6 ppm (C-2 and C-3) and three quaternary carbon atoms at respectively 125.4 ppm (C-3'), 146.0 ppm (C-1 and C-4) and 167.9 ppm (C-2') (figure 5). Elemental analysis of **21** give expected H, N and C values.

Molecular Modelling Study

It is noteworthy that nucleophilic addition on allenic derivatives lead to a single E stereoisomer but it is not the general case.[16] Therefore, we undertook molecular modelling study to determine the relative stabilities of both E and Z isomers of *N*-methyl lactams **4c** (R = CH_3, R^2 = H) and esters **6f** (R^2 = *t*-Bu) as simplified

models of lactams **4** and esters **6**. This study was performed by way of the molecular modelling software SYBYL 6.2[17] as described in experimental section. All the generated geometries were minimized using the Tripos force field and then optimized using AM1[18] calculations. In the case of ester model **6f** the free rotation around the two bonds of the *N*-CH_2Ph group generates a multiplicity of conformers among which a minimum was found. The single product of Michael addition of *N*-benzylaniline to allenes **5** is, in fact, the less stable isomer E **6**.Results obtained for enaminolactam **4c** showed that beside the most stable isomer E exist the isomer Z with the relative enthalpy of 7.6 kJ.mol^{-1} although only the E isomer was experimentaly obtained. The results are summarized in figure 6.

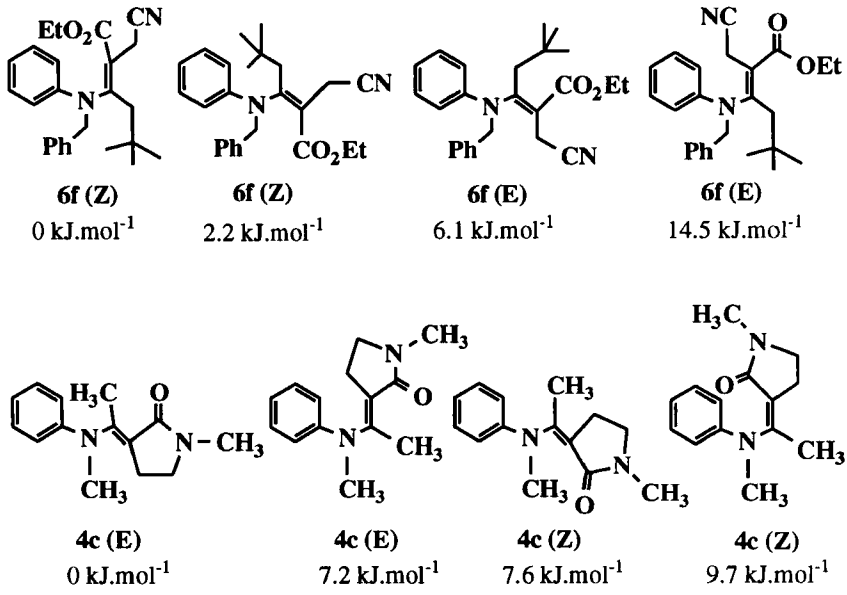


FIG. 6

In conclusion, we have prepared new and original allenic esters and lactams by a Wittig condensation between a phosphorane and an acid chloride. Michael addition of *N*-benzylaniline to these conjugated allenic compounds led to (E)-β-enaminoesters and (E)-β-enaminolactams with a moderate to good yield. These experimental and molecular modelling results clearly show that Michael addition of

amines on allenic esters **5** and lactams **2** will probably be kinetically controlled. The use of β-enaminoesters and β-enaminolactams in the synthesis of spiranic indolines precursors of *Aspidosperma* alkaloids is in progress.

EXPERIMENTAL

General : Infrared spectra were recorded with a Perkin-Elmer 815 spectrophotometer. NMR spectra were performed on a Bruker AC at 400MHz for ^{1}H and 100 MHz for ^{13}C NMR in $CDCl_3$ as solvent with chemical shifts referenced to $SiMe_4$ ($\delta = 0$). EIMS, HRMS and microanalyses were determined at the Service Central d'Analyse of Vernaison (France). Flash chromatography was carried out on Merck silica gel 60 (40-63 μm).

Molecular Modelling Study

Molecular Modelling study of described molecules was performed using the SYBYL 6.2 software package on a Silicon Graphics Indigo2 R8000 workstation. Structures were built within SYBYL and minimized by MAXIMIN 2 with the Tripos force field, in vacuo conditions, to provide reasonnable standard geometries. Molecules were deemed to be minimized by conjugated gradient method when there was a minimum energy change of less than 0.021 $kJ.mol^{-1}$ for one iteration. The conformational spaces of **4c** and **6f** were explored using the SYBYL search facility. Torsion angles were defined and a grid search was performed allowing choosen bonds to rotate with a 360° or 180° revolution by 15° increments. The lowest energy conformers thus obtained were submitted to AM1 calculations (MOPAC version 5.0) to optimize their geometry. The energies were calculated after optimization of all molecule parameters and compared.

N-benzyl-2,4-dibromobutyramide 13a

To a solution of *N*-benzylamine (1.88 ml, 17.2 mmol) in anhydrous ether (V = 40 ml) was added, under argon, triethylamine (2.84 ml, 20.4 mmol) followed by a solution of 2,4-dibromobutanoyl chloride (**12**) (5 g, 18.9 mmol) in anhydrous ether (V = 10 ml). After 2 hours at room temperature, the solution was filtered and the filtrate dried over $MgSO_4$. The solvent was evaporated and the crude residue purified on silica gel eluting with AcOEt/hexane (1/1) to give **13a** (5.5 g, 95.5%).
13a : oil, IR (CCl_4) 3425, 1675 . ^{1}H NMR : δ 1.35-1.40 (m, 2H, H-3), 3.36 (t, 2H, J = 6.3 Hz, H-4), 4.30 (2H, AB spectrum, J = 6.3 Hz, $\Delta\nu$ = 11 Hz,

NCH2Ph), 4.52-4.62 (m, 1H, H-2), 7.10-7.55 (m, 5H, H aromatic), 7.90-8.10 (se, 1H, NH). ^{13}C NMR ($CDCl_3$) : δ 30.0 (C-3), 36.9 (C-4), 43.3 (NCH2Ph), 46.9 (C-2), 127.7, 127.8, 128.8, 137.3 (C-*ipso*), 168.2 (C-1).

***N*-*n*-butyl-2,4-dibromobutyramide 13b**

Compound **13b** was prepared as **13a** from **12** (8 g, 30.2 mmol) and *n*-butylamine (2.72 ml, 27.4 mmol). After chromatography on silica gel with AcOEt/hexane (3/7) as eluent **13b** was obtained (7.5 g, 91%).

13b : oil, IR (CCl_4) 3435, 1680. ^{1}H NMR : δ 0.92 (t, 3H, *J* = 7.2 Hz, CH3), 1.35 (t, 2H, *J* = 7.2 Hz, CH2CH3), 1.50 (qt, 2H, *J* = 7.2 Hz, CH2CH2CH3), 2.40-2.50 (m, 1H, CH2CH2CH2CH3), 2.60-2.70 (m, 1H, CH2CH2CH2CH3), 3.28 (q, 2H, *J* = 7.2 Hz, H-3), 3.50-3.57 (m, 2H, H-4), 4.50-4.55 (m, 1H, H-2), 6.50-6.55 (se, 1H, NH). ^{13}C NMR : δ 13.7 (CH3), 20.0 (CH2CH3), 30.5 (C-3)*, 31.3 (CH2CH2CH3)*, 37.8 (C-4), 40.0 (CH2CH2CH2CH3), 48.5 (C-2), 167.8 (C-1).

***N*-benzyl-3-bromopyrrolidin-2-one 14a**

To a solution of **13a** (3 g, 8.95 mmol) in anhydrous THF (V = 50 ml) was added, under argon, small amounts of NaH (0.39 g, 9.85 mmol). The reaction mixture was stirred 12 hours at room temperature and then quenched with water. The organic layer was filtered and dried over $MgSO_4$. The solvent was evaporated and the crude residue purified by flash chromatography eluting with AcOEt/hexane (1/1) to afford **14a** (2.0 g, 95.5%).

14a : mp 30-31°C (AcOEt), IR (CCl_4) 1700. ^{1}H NMR : δ 2.20-2.25 (m, 1H, H-4), 2.45-2.55 (m, 1H, H-4), 3.10-3.20 (m, 1H, H-5), 3.30-3.40 (m, 1H, H-5), 4.44 (2H, AB spectrum, *J* = 15 Hz, Δν = 50.5 Hz, NCH2Ph), 4.42 (dd, 1H, *J* = 7 Hz and 3 Hz, H-3), 7.20-7.35 (m, 5H, H aromatic). ^{13}C NMR : δ 29.9 (C-4), 44.3 (C-5), 44.4 (C-3), 46.8 (CH2Ph), 127.6, 127.8, 128.6, 135.4 (C-*ipso*), 170.5 (C-2). HRMS : calc. for $C_{11}H_{12}NBrO$: 253.0102, found : 253.0102.

***N*-*n*-butyl-3-bromopyrrolidin-2-one 14b**

Compound **14b** was prepared as **14a** from **13b** (3 g, 9.96 mmol) and NaH (0.44 g, 11 mmol) in THF (V = 50 ml). Column chromatography with AcOEt/hexane (1/1) as eluent gave **14b** (2 g, 92%).

14b : oil, IR (CCl_4) 1710. ^{1}H NMR : δ 0.82 (t, 3H, *J* = 7.2 Hz, CH3), 1.20-1.30 (m, 2H, CH2CH3), 1.40-1.50 (m, 2H, CH2CH2CH3), 2.20-2.30 (m, 1H, H-5),

2.45-2.55 (m, 1H, H-4), 3.10-3.20 (m, 1H, H-4), 3.20-3.35 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 3.40-3.50 (m, 1H, H-5), 4.32 (dd, 1H, J = 7 Hz and 4 Hz, H-3). ^{13}C NMR : δ 13.5 ($\underline{C}H_3$), 19.7 ($NCH_2CH_2\underline{C}H_2CH_3$), 28.9 ($NCH_2\text{-}\underline{C}H_2CH_2CH_3$), 30.1 (C-4), 42.7 ($N\underline{C}H_2CH_2CH_2CH_3$)*, 44.7 (C-3), 45.0 (C-5)*, 170.3 (C-2). EIMS m/z (%) 221 (M+1, 1), 219 (1), 176 (2), 141 (20), 140 (100), 132 (5), 125 (1), 95 (28), 97 (3), 69 (12), 68 (10), 55 (19), 42 (40), 41 (80), 39 (62), 29 (80), 28 (32), 26 (21).

Preparation of phosphoranes 15a and 15b

Phosphoranes **15a,b** were prepared quantitatively by heating **14a,b** (7 mmol) in THF (V = 50 ml) under argon during 24 hours. The salts thus obtained were filtered under argon and used in the next step without purification.

3-(3'-Benzyloxy-1'-propenylidene)-*N*-benzylpyrrolidin-2-one 2a

To a solution of **15a** (3.05 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 60 ml) was added drop to drop and under argon a solution of **9** (1.40 g, 7 mmol) in anhydrous CH_2Cl_2 (V = 20 ml). The resulting solution was stirred at room temperature during 6 hours. After evaporation of the solvent, the residue was purified by column chromatography using AcOEt/hexane (1/1) as eluent and gave **2a** (1.76 g, 79%).

2a : oil, IR (CCl_4) 1970, 1690. ^1H NMR : δ 2.85 (td, 2H, J = 6.3 and 3 Hz, H-4), 3.30 (t, J = 6.3 Hz, 2H, H-5), 4.20-4.30 (m, 2H, H-3'), 4.55 (s, 2H, $NC\underline{H}_2Ph$)*, 4.65 (s, 2H, $OC\underline{H}_2Ph$)*, 5.80-5.90 (m, 1H, H-2'), 7.25-7.45 (m, 10H, H aromatic). ^{13}C NMR : δ 22.6 (C-4), 44.0 (C-5), 47.6 ($N\underline{C}H_2Ph$), 67.0 (C-3'), 71.8 ($O\underline{C}H_2Ph$), 95.5 (C-2'), 100.1 (C-3), 127.7, 127.8, 128.1, 128.4, 128.8, 128.9, 136.4 (C-*ipso*), 138.1 (C-*ipso*), 167.2 (C-2), 203.9 (C-1'). EIMS m/z (%) 320 (M+1, 2), 319 (M^+, 14), 305 (18), 291 (6), 277 (6), 229 (2), 213 (2), 201 (2), 191 (3), 178 (2), 174 (13), 123 (34), 122 (26), 108 (11), 107 (16), 105 (30), 92 (11), 91 (100), 79 (19), 77 (31), 65 (12), 51 (10). HRMS : calc. for $C_{21}H_{21}NO_2$ 319.1572, found : 319.1556

3-(3'-Benzyloxy-1'-propenylidene)-*N*-butylpyrrolidin-2-one 2b

Compound **2b** was prepared as **2a** from **15b** (2.8 g, 7 mmol), **9** (1.4 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 100 ml). After

purification with AcOEt/hexane (1/1) as eluent, **2b** was obtained (1.25 g, 62%).
2b : oil, IR (CCl_4) 1970, 1690. ^1H NMR : δ 0.92 (t, 3H, J = 7 Hz, CH_3), 1.30-2.40 (st, 2H, J = 7 Hz, CH_2CH_3), 1.55 (qt, 2H, J = 6.5 Hz, $CH_2CH_2CH_3$), 2.80-2.90 (m, 2H, H-4), 3.82 (t, 2H, J = 6.2 Hz, H-5)*, 3.92 (t, 2H, J = 6.2 Hz, $NCH_2CH_2CH_2CH_3$)*, 4.10-4.20 (m, 2H, H-3'), 4.60 (s, 2H, O-CH_2Ph), 5.75-5.80 (m, 1H, H-2'), 7.25-7.40 (m, 5H, H aromatic). ^{13}C NMR : δ 13.8 (CH_3), 20.1 (CH_2CH_3), 22.7 (CH_2CH_2-CH_3), 29.3 (C-4), 43.2 (C-5)*, 44.5 (NCH_2-$CH_2CH_2CH_3$)*, 67.1 (C-3'), 71.7 (O-CH_2Ph), 95.3 (C-2'), 100.3 (C-3), 127.6, 127.7, 128.0, 138.1 (C-*ipso*), 167.0 (C-2), 202.8 (C-1'). EIMS m/z (%) 286 (M+1, 1), 285 (M^+, 1), 250 (3), 236 (35), 181 (2), 167 (2), 158 (1), 144 (20), 129 (98), 122 (2), 114 (24), 100 (75), 107 (5), 91 (100), 86 (5), 77 (14), 72 (32), 65 (15), 58 (62). HRMS : calc. for $C_{18}H_{23}NO_2$ 285.1729, found : 285.1730.

Ethyl 2-cyanomethyl-5-benzyloxy-penta-2,3-dienoate 5a
To a solution of **17a** (2.7 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 20 ml) was added, drop to drop and under argon, a solution of **9** (1.4 g, 7 mmol) in anhydrous CH_2Cl_2 (V = 20 ml). The resulting mixture was stirred at room temperature until the reaction was complete. The solvent was evaporated and the crude residue chromatographed over silica gel with AcOEt/hexane (1/1) as eluent to give **5a** (1.55 g, 83%).
5a : oil, IR (CCl_4) 2260, 1965, 1715. ^1H NMR : δ 1.32 (t, 3H, J = 7 Hz, CH_3), 3.40 (s, 2H, CH_2CN), 4.25-4.35 (m, 4H, O-CH_2Ph et O-CH_2), 4.55-4.65 (m, 2H, H-5), 5.95-6.00 (m, 1H, H-4), 7.35 (s, 5H, H aromatic). ^{13}C NMR : δ 13.9 (CH_3), 18.1 (CH_2CN), 61.9 (CH_2-CH_3), 65.7 (C-5), 71.8 (O-CH_2Ph), 93.9 (C-4), 97.2 (C-2), 116.9 (CN), 127.5, 128.1, 128.8, 138.0 (C-*ipso*), 165.3 (C-1), 210.2 (C-3). EIMS m/z (%) m/z (%) 272 (4), 271 (4), 258 (6), 245 (1), 182 (10), 181 (4), 154 (4), 134 (4), 107 (20), 106 (10), 105 (9), 92 (19), 91 (17), 77 (14), 55 (10), 45 (2). HRMS : calc. for $C_{16}H_{17}NO_3$: 271.1208, found : 271.1208.

Ethyl 2-cyanomethyl-5,5-ethylenedioxy-hexa-2,3-dienoate 5b
Compound **5b** was prepared as **5a** from **17a** (2.7 g, 7 mmol), **10** (1.15 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 50 ml). After purification (AcOEt/hexane (1/1) as eluent), **5b** was isolated (1.46 g, 88%).
5b : oil, IR (CCl_4) 2875, 2265, 1970, 1715. ^1H NMR : δ 1.28 (t, 3H, J = 7 Hz,

CH_3-CH_2), 1.60 (s, 3H, H-6), 3.35 (s, 2H, CH_2CN), 4.00 (s, 4H, O-CH_2-CH_2-O), 4.10-4.30 (m, 2H, O-CH_2), 5.80 (s, 1H, H-4). ^{13}C NMR : δ 14.1 (CH_3-CH_2), 18.9 (CH_2CN), 25.9 (CH_3), 61.9 (CH_2-CH_3), 64.8 (O-CH_2-CH_2-O), 64.9 (O-CH_2-CH_2-O), 85.3 (C-4), 102.4 (C-2), 105.9 (C-5), 116.4 (CN), 164.6 (C-1), 207.8 (C-3). EIMS m/z (%) 238 (50), 222 (28), 208 (12), 192 (38), 178 (18), 166 (14), 152 (25), 145 (15), 129 (38), 113 (32), 105 (20), 95 (18), 87 (100), 77 (3), 51 (3), 43 (30).

Ethyl 6-carbomethoxy-2-cyanomethyl-5,5-ethylenedioxy-hexa-2,3-dienoate 5c

Compound **5c** was prepared as **5a** from **17a** (2.7 g, 7 mmol), **11** (1.55 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 60 ml). After purification (AcOEt/hexane (1/1) as eluent) **5c** was obtained (1.7 g, 82%).

5c : oil, IR (CCl_4) 2900, 2265, 1970, 1745, 1715. ^1H NMR : δ 1.27 (t, 3H, J = 7 Hz, CH_3-CH_2), 2.85 (s, 2H, H-6), 3.35-3.38 (m, 2H, CH_2CN), 3.70 (s, 3 H, OCH_3), 3.98-4.08 (m, 4H, O-CH_2-CH_2-O), 4.16-4.28 (m, 2H, CH_3-CH_2), 6.03 (t, 1H, J = 3 Hz, H-4). ^{13}C NMR : δ 14.1 (CH_3-CH_2), 18.3 (CH_2CN), 44.0 (C-6), 52.0 (OCH_3), 62.0 (CH_3-CH_2), 65.2 and 65.3 (O-CH_2-CH_2-O), 95.7 (C-4), 101.2 (C-2), 105.1 (C-5), 116.4 (CN), 164.4 (C-1)*, 168.8 (CO_2CH_3)*, 208.3 (C-3). EIMS m/z (%) 296 (M+1), 266 (1), 250 (1), 236 (1), 222 (10), 210 (1), 194 (2), 178 (2), 164 (1), 145 (100), 132 (1), 123 (2), 113 (5), 103 (43), 93 (1), 86 (4), 77 (6), 69 (3); 59 (17).

Ethyl 2-allyl-5-benzyloxy-penta-2,3-dienoate 5d

Compound **5d** was prepared as **5a** from **17b** (2.7 g, 7 mmol), **9** (1.4 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 50 ml). After purification by flash column chromatography with AcOEt/hexane (1/9) as eluent, **5d** was isolated (1.5 g, 78%).

5d : oil, IR (CCl_4) 1975, 1725. ^1H NMR : δ 1.28 (t, 3H, J = 7 Hz, CH_3), 3.02-3.07 (m, 2H, CH_2-CH=CH_2), 4.10-4.25 (m, 4H, H-5 et O-CH_2), 4.60 (2H, AB spectrum, J = 11.5 Hz, Δν = 21.9 Hz, O-CH_2Ph), 5.08 (dd, 1H, J = 10 and 1.5 Hz, CH_2-CH=CH_2), 5.12 (dd, 1H, J = 17 and 1.5 Hz, CH_2-CH=CH_2), 5.65-5.72 (m, 1H, H-4), 5.78-5.90 (m, 1H, J = 10 and 17 Hz, CH_2-CH=CH_2), 7.35 (s, 5H, H aromatic). ^{13}C NMR : δ 14.3 (CH_3), 33.0 (CH_2-CH=CH_2), 61.2

($\underline{C}H_2CH_3$), 66.7 (C-5), 71.5 (O-$\underline{C}H_2Ph$), 92.9 (C-4), 100.2 (C-2), 116.5 (CH_2-$CH=\underline{C}H_2$), 127.8, 127.9, 128.6, 134.9 (CH_2-$\underline{C}H=CH_2$), 137.9 (C-*ipso*), 166.7 (C-1), 210.6 (C-1').

Ethyl 2-allyl-5,5-ethylenedioxy-hexa-2,3-dienoate 5e

Compound **5e** was prepared as **5a** from **17b** (2.7 g, 7 mmol), **10** (1.16 g, 7 mmol) and NEt_3 (0.97 ml, 7 mmol) in anhydrous CH_2Cl_2 (V = 50 ml). The resulting oil was purified by flash column chromatography eluting with AcOEt/hexane (1/9) and afford **5e** (1.22 g, 73%).

5e : oil, IR (CCl_4) 2900, 1965, 1710. ^1H NMR : δ 1.27 (t, 3H, *J* = 7 Hz, $C\underline{H}_3$-CH_2), 1.57 (s, 3H, H-6), 3.00-3.05 (m, 2H, $C\underline{H}_2$-$CH=CH_2$), 3.95-4.04 (m, 4H, O-$C\underline{H}_2$-$C\underline{H}_2$-O), 4.12-4.28 (q, 2H, *J* = 7Hz, CH_3-$C\underline{H}_2$), 5.06 (ddd, 1H, *J* = 1, 2.9 and 10 Hz, CH_2-$CH=C\underline{H}_2$), 5.13 (ddd, 1H, *J* = 1.7, 3 and 17 Hz, CH_2-$CH=C\underline{H}_2$), 5.55 (t, 1H, *J* = 3 Hz, H-4), 5.75-5.88 (m, 1H, CH_2-$\underline{C}H=CH_2$). ^{13}C NMR : δ 14.3 (C-6), 25.5 ($\underline{C}H_3$-CH_2), 32.9 ($\underline{C}H_2$-$CH=CH_2$), 61.1 ($\underline{C}H_2$-CH_3), 64.5 and 64.8 (O-$\underline{C}H_2$-CH_2-O), 99.1 (C-4), 102.1 (C-2), 106.5 (C-5), 116.6 (CH_2-$CH=\underline{C}H_2$), 134.7 (CH_2-$\underline{C}H=CH_2$), 166.7 (C-1), 213.4 (C-3).

Condensation of *N*-benzylaniline with allene 5a

To a solution of **5a** (1.5 g, 5.53 mmol) in anhydrous benzene (V = 40 ml), under argon, was added a solution of *N*-benzylaniline (0.91 g, 4.98 mmol) in anhydrous benzene (V = 40 ml). The resulting mixture was heated at reflux during 24 hours. After cooling the solvent was evaporated and the crude mixture purified by chromatography on silica gel eluting with AcOEt/hexane (5/95) to give **6a** (2.05 g, 82%) and **18a** (0.04g, 5%).

6a : oil, IR (CCl_4) 2250, 1705. ^1H NMR : δ 1.32 (t, 3H, *J* = 7 Hz, CH_3), 3.15 (s, 2H, $C\underline{H}_2CN$), 3.22 (t, 2H, *J* = 7 Hz, H-4), 3.78 (t, 2H, *J* = 7 Hz, H-5), 4.25 (q, 2H, *J* = 7Hz, $C\underline{H}_2CH_3$), 4.50 (s, 2H, $OC\underline{H}_2Ph$), 4.95 (s, 2H, $NC\underline{H}_2Ph$), 6.95-7.00 (m, 3H, H aromatic), 7.20-7.40 (m, 12H, H aromatic). ^{13}C NMR : δ 14.2 (CH_3), 19.0 ($\underline{C}H_2CN$), 32.8 (C-4), 54.4 ($NC\underline{H}_2Ph$), 61.1 ($\underline{C}H_2CH_3$), 69.0 (C-5), 73.1 ($O\underline{C}H_2Ph$), 119.5 (CN), 122.2 (C-2), 126.7, 127.4, 127.7, 128.4, 128.9, 129.9, 138.0 (C-*ipso*), 138.3 (C-*ipso*), 148.0 (C-*ipso*), 160.0 (C-3), 166.6 (C-1). EIMS m/z (%) 454 (M^+, 18), 437 (4), 414 (5), 409 (2), 381 (3), 363 (25), 346 (8), 333 (2), 306 (5), 292 (2), 273 (6), 260 (3), 246 (4), 229 (5), 209

(2), 195 (2), 183 (8), 167 (2), 156 (4), 130 (12), 107 (8), 91 (100), 77 (14), 65 (9). HRMS : calc. for $C_{29}H_{30}N_2O_3$ 454.2335, found : 454.2354. UV (EtOH, λ) 329 nm (10200).

18a : oil, IR (CCl_4) 2250, 1720. ^1H NMR : δ 1.40 (t, 3H, *J* = 7 Hz, CH_3), 3.18 (s, 2H, $\underline{C}H_2CN$); 4.35 (q, 2H, *J* = 7 Hz, $C\underline{H}_2CH_3$), 4.60 (s, 2H, $NC\underline{H}_2Ph$), 5.58 (dd, 1H, *J* = 10 and 1 Hz, H-5), 5.62 (dd, 1H, *J* = 10 and 1 Hz, H-5), 6.90-6.95 (m, 3H, H-4 and H aromatic), 7.25-7.40 (m, 8H, H aromatic). ^{13}C NMR : δ 14.1 (CH_3); 18.9 ($\underline{C}H_2CN$), 55.0 ($N\underline{C}H_2Ph$), 61.5 ($\underline{C}H_2CH_3$), 115.6 (C-5), 120.5 (CN), 124.1 (C-4), 127.6 127.7, 128.5, 128;9, 129.7, 129.8, 131.8 (C-2), 138.0 (C-*ipso*), 147.3 (C-*ipso*), 154.7 (C-3), 166.0 (C-1). EIMS m/z (%) 446 (4), 196 (12), 182 (6), 181 (2), 179 (2), 106 (6), 91 (100), 89 (5), 77 (25), 65 (28), 54 (19), 51 (18), 50 (8), 45 (2), 38 (15), 29 (80), 27 (40), 26 (8). UV (EtOH, λ) 251 (17500).

Condensation of *N*-benzylaniline with allene 5b

Condensation of **5b** (1.0 g, 4.22 mmol) and *N*-benzylaniline (0.69 g, 3.78 mmol) in refluxing anhydrous benzene (V = 50 ml) led after column chromatography using AcOEt/hexane (1/9) as eluent to **6b** (1.5 g, 85%).

6b : oil, IR (CCl_4) 2885, 2260, 1730. ^1H NMR : δ 1.38 (t, 3H, *J* = 7 Hz, $CH_2C\underline{H}_3$), 1.42 (s, 3H, H-6), 3.18 (s, 2H, $C\underline{H}_2CN$), 3.52 (s, 2H, H-4), 3.80-3.95 (m, 4H, O-$C\underline{H}_2$-$C\underline{H}_2$-O), 4.30 (q, 2H, *J* = 7 Hz, $C\underline{H}_2CH_3$), 5.05 (s, 2H, N-$C\underline{H}_2Ph$), 6.90-7.45 (m, 10H, H aromatic). ^{13}C NMR : δ 14.2 ($CH_2\underline{C}H_3$), 19.5 ($\underline{C}H_2CN$), 25.5 (C-6), 38.8 (C-4), 53.8 (N-$\underline{C}H_2Ph$), 61.0 ($\underline{C}H_2CH_3$), 64.6 (O-$\underline{C}H_2$-$\underline{C}H_2$-O), 109.6 (C-5), 119.7 (CN), 121.8 (C-2), 126.6, 127.1, 128.8, 129.6, 138.5 (C-*ipso*), 146.8 (C-*ipso*), 155.2 (C-3), 167.5 (C-1). EIMS m/z (%) 420 (M^+, 45), 405 (5), 375 (12), 359 (5), 333 (18), 319 (4), 306 (3), 290 (5), 278 (3), 260 (4), 245 (3), 229 (18), 218 (9), 202 (3), 183 (23), 169 (5), 144 (4), 130 (5), 118 (3), 105 (12), 91 (100), 77 (3). HRMS : calc. for $C_{25}H_{28}N_2O_4$ 420.2049, found : 420.2047. UV (EtOH, λ) 330 (11480).

Condensation of *N*-benzylaniline with allene 5c

Condensation of **5c** (1.0 g, 3.39 mmol) and *N*-benzylaniline (0.69 g, 3.78 mmol) in refluxing anhydrous benzene (V = 80 ml) gave after purification using AcOEt/hexane (3/7) as eluent **6c** (1.5 g, 95%).

6c : oil, IR (CCl_4) 2900, 2250, 1745, 1700. ^1H NMR : δ 1.35 (t, 3H, J = 7 Hz, $C\underline{H}_3CH_2$), 2.72 (s, 2H, H-6), 3.12 (s, 2H, $C\underline{H}_2CN$), 3.59 (s, 3H, $C\underline{H}_3$), 3.75 (s, 2H, H-4), 3.86-4.06 (m, 4H, $O\text{-}C\underline{H}_2\text{-}C\underline{H}_2\text{-}O$), 4.25 (q, 2H, J = 7 Hz, $C\underline{H}_2CH_3$), 5.05 (s, 2H, $N\text{-}C\underline{H}_2Ph$), 7.10-7.40 (m, 9H, H aromatic). ^{13}C NMR : δ 14.2 ($CH_2\underline{C}H_3$), 19.5 ($\underline{C}H_2CN$), 37.2 (C-4), 43.8 (C-6), 51.8 ($N\text{-}\underline{C}H_2Ph$), 61.0 ($\underline{C}H_2CH_3$), 65.0 ($O\text{-}\underline{C}H_2\text{-}\underline{C}H_2\text{-}O$), 108.6 (C-5), 119.8 (CN),122.0 (C-2), 126.7, 128.9, 129.7, 138.6 (C-*ipso*), 146.8 (C-*ipso*), 154.1 (C-3), 167.6 (C-1)*, 169.6 ($\underline{C}O_2CH_3$)*. EIMS m/z (%) 479 (3), 478 (7), 447 (1), 433 (2), 417 (1), 405 (6), 333 (13), 319 (2), 288 (1), 276 (2), 229 (4), 218 (1), 202 (1), 183 (2), 169 (2), 146 (7), 145 (100), 130 (2), 103 (30), 91 (60), 77 (9), 59 (10). HRMS : calc. for $C_{27}H_{30}N_2O_6$ 478.2100, found : 478.2104. UV (EtOH, λ) 329 (10860).

Condensation of *N*-benzylaniline with allene 5d

Condensation of **5d** (1.5 g, 5.5 mmol) and *N*-benzylaniline (0.91 g, 4.95 mmol) in refluxing anhydrous benzene (V = 60 ml) led after purification using AcOEt/hexane (5/95) as eluent to **18d** (0.74 g, 43%).

18d : oil, IR (CCl_4) 1710. ^1H NMR : δ 1.40 (t, 3H, J = 6.5 Hz, CH_3); 3.10 (d, 2H, J = 6.5 Hz, $C\underline{H}_2\text{-}CH{=}CH_2$); 4.34 (q, 2H, J = 6.5 Hz, $C\underline{H}_2CH_3$); 4.74 (s, 2H, $NC\underline{H}_2Ph$); 4.90-4.98 (m, 2H, $CH_2\text{-}CH{=}C\underline{H}_2$); 5.35 (dd, 1H, J = 1 and 10.5 Hz, H-5); 5.38 (dd, 1H, J = 1 and 17 Hz, H-5); 5.47-5.60 (m, 1H, $CH_2\text{-}C\underline{H}{=}CH_2$); 6.95 (dd, 1H, J = 10.5 and 17 Hz, H-4); 7.20-7.50 (m, 10H, H aromatic). ^{13}C NMR : δ 14.3 (CH_3), 34.6 ($\underline{C}H_2\text{-}CH{=}CH_2$), 55.3 ($N\text{-}\underline{C}H_2Ph$), 60.9 ($\underline{C}H_2CH_3$), 117.0 (C-5), 118.2 (C-4), 120.2 ($CH_2\text{-}CH{=}\underline{C}H_2$), 131.0 ($CH_2\text{-}\underline{C}H{=}CH_2$), 132.5 (C-*ipso*)*, 133.7 (C-2)*, 138.7 (C-*ipso*), 146.6 (C-3), 168.8 (C-1). HRMS : calc. for $C_{23}H_{25}NO_2$ 347.4620, found : 347.4621.

Condensation of *N*-benzylaniline with allene 5e

Condensation of **5e** (1.0 g, 4.20 mmol) and *N*-benzylaniline (0.69 g, 3.78 mmol) in refluxing anhydrous benzene (V = 60 ml) gave after purification using AcOEt/hexane (5/95) as eluent **6e** (2.5 g, 85%).

6e : oil, IR (CCl_4) 2890, 1715. ^1H NMR : δ 1.34 (t, 3H, J = 7 Hz, $CH_2C\underline{H}_3$), 1.38 (s, 3H, H-6), 3.02-3.08 (m, 2H, $C\underline{H}_2\text{-}CH{=}CH_2$), 3.15 (s, 2H, H-4), 3.62-3.73 (m, 2H, $O\text{-}C\underline{H}_2\text{-}CH_2\text{-}O$), 3.78-3.88 (m, 2H, $O\text{-}C\underline{H}_2\text{-}CH_2\text{-}O$), 4.25 (q, 2H, J = 7Hz, $C\underline{H}_2CH_3$), 4.80 (s, 2H, $N\text{-}C\underline{H}_2Ph$), 4.86-4.93 (m, 1H, $CH_2\text{-}$

CH=C<u>H</u>2), 4.89-4.94 (m, 1H, CH2-CH=C<u>H</u>2), 5.57-5.68 (m, 1H, CH2-C<u>H</u>=CH2), 6.70-6.80 (m, 4H, H aromatic), 7.10-7.40 (m, 6H, H aromatic). ^{13}C NMR : δ 14.3 (C-6), 25.0 (C-6), 34.7 (<u>C</u>H2-CH=CH2), 38.9 (C-4), 54.6 (N-<u>C</u>H2Ph), 60.0 (<u>C</u>H2CH3), 64.5 (O-<u>C</u>H2-<u>C</u>H2-O), 109.8 (C-5), 116.4 (CH2-CH=<u>C</u>H2), 129.8 (C-2), 134.7 (CH2-<u>C</u>H=CH2), 138.8 (C-*ipso*), 146.0 (C-*ipso*)*, 146.8 (C-3)*, 169.5 (C-1). EIMS m/z (%) 422 (M+1, 8), 334 (5), 188 (2), 91 (26), 87 (100), 77 (6), 65 (4), 43 (29). UV (EtOH, λ) 395 (15160). HRMS : calc. for C26H31NO4 421.5419, found : 421.5417.

Condensation of *N*-benzylaniline with allene 2a

Condensation of *N*-benzylaniline (0.77 g, 4.23 mmol) with **2a** (1.5 g, 4.70 mmol) in refluxing anhydrous benzene (V = 80 ml) led, after column chromatography using AcOEt/hexane (5/95) as eluent to **4a** (0.235 g, 10 %), **19a** (0.370 g, 20 %), **20a** (0.750 g, 25 %) and **21a** (0.750 g, 25 %).

4a : oil, IR (CCl4) 1680. ^{1}H NMR : δ 2.22 (t, 2H, *J* = 6.2 Hz, H-4), 3.07 (t, 2H, *J* = 6.2 Hz, H-5), 3.52 (t, 2H, *J* = 6.5 Hz, H-2'), 3.82 (t, 2H, *J* = 6.5 Hz, H-3'), 4.50 (s, 2H, OC<u>H</u>2Ph), 4.55 (s, 2H, NC<u>H</u>2Ph), 4.85 (s, 2H, NC<u>H</u>2Ph), 7.15-7.50 (m, 15 H, H aromatic). ^{13}C NMR : δ 25.7 (C-4), 28.6 (C-2'), 43.4 (C-5), 47.2 (NbC<u>H</u>2Ph), 53.6 (NaC<u>H</u>2Ph), 69.4 (C-3'), 72.7 (O<u>C</u>H2Ph), 120.4 (C-3), 126.6, 126.9, 127.4, 127.5, 127.8, 128.1, 128.3, 128.5, 129.1, 136.9 (C -*ipso*), 138.7 (C-*ipso*), 139.5 (C-*ipso*), 147.0 (C-*ipso*), 148.2 (C-1'), 169.3 (C-2). Anal calc. for C34H34N2O2 : C, 81.27, H, 6.77, N, 5.57; found C, 81.54, H, 6.96, N, 4.83. UV (EtOH, λ) 325.5 (11000)

19a : oil, IR (CCl4) 1680. ^{1}H NMR : δ 2.38 (t, 2H, *J* = 6.5 Hz, H-4), 3.07 (t, 2H, *J* = 6.5 Hz, H-5), 4.55 (s, 2H, NC<u>H</u>2Ph), 4.70 (s, 2H, NC<u>H</u>2Ph), 4.35-4.45 (m, 2H, H-3'), 6.65-7.40 (m, 15 H, H aromatic), 8.05 (dd, 1H, *J* = 10.3 and 17.2 Hz, H-2'). ^{13}C NMR : δ 25.1 (C-4), 43.4 (C-5), 47.4 (NbC<u>H</u>2Ph), 54.4 (NaC<u>H</u>2Ph), 114.0, 118.4 (C-3), 122.3 (C-3'), 126.6, 127.9, 128.3, 128.4, 128.5, 128.6, 128.8, 129.4, 129.7, 133.4 (CH2=<u>C</u>H), 136.5 (C-*ipso*), 138.9 (C-*ipso*), 138.9 (C-2'), 146.8 (C-*ipso*)*, 147.0 (C-1'), 168.4 (C-2). UV (EtOH, λ) 314 (11700). Anal calc. for C27H26N2O : C, 82.20, H, 6.64, N, 7.10; found C, 82.67, H, 6.54, N, 6.87.

20a : oil, IR (CCl4) 1690. ^{1}H NMR : δ 2.00-2.10 (m, 1H, H-1"), 2.45-2.55 (m, 1H, H-1"), 2.65-2.85 (m, 2H, H-1'), 2.90-3.00 (m, 1H, H-2"), 3.15-3.30 (m,

1H, H-2"), 3.30-3.35 (m, 2H, H-2'), 3.80 (t, 1H, J = 10 Hz, H-3), 3.92 (d, 2H, J = 7.5 Hz, CH_2-CH=), 4.00-4.10 (m, 1H, CH_2-C-3), 4.30-4.70 (m, 9H, O-CH_2Ph, N-CH_2Ph and CH_2-C-3), 5.80 (t, 1H, J = 7.5 Hz, CH=C-2). ^{13}C NMR : δ 24.4 (C-1'), 25.3 (C-1"), 44.1 (C-2")*, 44.3 (C-2')*, 46.9 (N-CH_2Ph), 48.6 (C-3), 55.1 (C-1), 66.0 (CH_2-OCH_2Ph), 68.5 (CH_2-OCH_2Ph), 72.7 (OCH_2Ph), 72.8 (OCH_2Ph), 124.6 (CH=C-2), 125.3 (C-2), 127.1, 127.7, 127.8, 128.2, 128.4, 128.7, 136.4 (C-*ipso*), 136.5 (C-5"), 137.9 (C-*ipso*), 138.6 (C-*ipso*), 140.2 (C-*ipso*), 146.2 (C-4), 167.7 (C-4"), 175.3 (C-4'). Anal calc. for $C_{42}H_{42}N_2O_4$: C, 78.99, H, 6.58, N, 4.38; found C, 78.78, H, 6.74, N, 4.45.

21a : oil, IR (CCl_4) 1690. ^{1}H NMR : δ 2.75-2.95 (m, 4H, H-4'), 3.20-3.30 (m, 4H, H-5'), 3.80-3.90 (m, 4H, CH_2-OCH_2Ph), 4.15-4.20 (m, 2H, H-2 and H-3), 4.50 (s, 4H, N-CH_2Ph)*, 4.60 (4 H, AB spectrum, J = 11.5 Hz, Δν = 51.5 Hz, O-CH_2Ph)*, 7.20-7.40 (m, 20 H, H aromatic). ^{13}C NMR : δ 25.0 (C-4'), 44.0 (C-5'), 46.6 (C-2 and C-3), 47.1 (NCH_2Ph), 71.6 (CH_2-OCH_2Ph), 72.6 (OCH_2Ph), 125.4 (C-3'), 127.1, 127.5, 127.7, 128.2, 128.4, 128.8, 128.8, 136.5 (C-*ipso*), 139.3 (C-*ipso*), 146.0 (C-1 and C-4), 167.9 (C-2'). Anal calc. for $C_{42}H_{42}N_2O_4$: C, 78.99, H, 6.58, N, 4.38; found C, 78.67, H, 6.81, N, 4.51.

Condensation of *N*-benzylaniline with allene 2b

Condensation of *N*-benzylaniline (0.77 g, 4.23 mmol) with **2b** (1.0 g, 3.51 mmol) in refluxing anhydrous benzene (V = 80 ml) led, after purification with AcOEt/hexane (5/95) as eluent, to **4b** (0.240 g, 15 %), **19b** (0.063 g, 5 %) and **20b** (1.0 g, 50 %).

4b : oil, IR (CCl_4) 1675. ^{1}H NMR : δ 0.95 (t, 3H, J = 6.9 Hz, CH_3), 1.30 (st, 2H, CH_2CH_3), 1.48 (qt, 2H, $CH_2CH_2CH_3$), 2.25 (t, 2H, J = 6.5 Hz, H-4), 3.18 (t, 2H, J = 6.5 Hz, H-5)*, 3.32 (t, 2H, J = 6.6 Hz, CH_2-N)*, 3.47 (t, 2H, J = 6.6 Hz, H-2'), 3.78 (t, 2H, J = 6.7 Hz, H-3'), 4.55 (s, 2H, O-CH_2Ph), 4.82 (s, 2H, N-CH_2Ph), 6.80-6.90 (m, 3H, H aromatic), 7.15-7.40 (m, 12H, H aromatic). ^{13}C NMR : δ 13.9 (CH_3), 20.3 (CH_2CH_3), 25.8 (CH_2-CH_2CH_3), 28.6 (C-2'), 29.5 (C-4), 42.8 (N-CH_2)*, 42.9 (C-5)*, 53.4 (N-CH_2Ph), 69.4 (C-3'), 72.7 (O-CH_2Ph), 119.7, 121.6 (C-3), 126.6, 127.3, 127.5, 127.6, 127.7, 128.4, 128.6, 128.7, 138.8 (C-*ipso*), 139.5 (C-*ipso*), 147.0 (C-*ipso* N-Ph)*, 147.3 (C-1'), 169.1 (C-2). UV (EtOH, λ) 323 (23800). EIMS m/z (%) 469 (M+1, 14), 468 (M^+, 33), 440 (1), 425 (1), 407 (1), 391 (1), 377 (14), 360 (28),

347 (25), 333 (18), 319 (2), 304 (1), 271 (13), 269 (15), 262 (10), 252 (6), 234 (7), 222 (5), 208 (3), 195 (5), 182 (51), 182 (22), 179 (9), 156 (4), 141 (7), 130 (8), 117 (7), 104 (4), 91 (100), 77 (14), 65 (10), 57 (4). HRMS : calc. for $C_{31}H_{36}N_2O_2$ 468.2776, found : 468.2775.

19b : oil, IR (CCl_4) 1675. ^1H NMR : δ 0.95 (t, 3H, *J* = 7 Hz, CH_3), 1.35 (st, 2H, *J* = 7 Hz, CH_2CH_3), 1.55 (qt, 2H, $CH_2CH_2CH_3$), 2.38 (t, 2H, *J* = 6.8 Hz, H-4), 3.20 (t, 2H, *J* = 6.8 Hz, H-5)*, 3.35 (t, 2H, *J* = 6.8 Hz, CH_2-N)*, 4.70 (s, 2H, N-CH_2Ph), 5.32 (d, 1H, *J* = 11.3 Hz, H-3'), 5.37 (d, 1H, *J* = 11.3 Hz, H-3'), 6.60-6.80 (m, 3H, H aromatic), 7.20-7.40 (m, 7H, H aromatic), 8.00 (dd, 1H, *J* = 11.2 and 17.6 Hz, H-2'). ^{13}C NMR : δ 13.9 (CH_3), 20.2 (CH_2CH_3), 25.1 (CH_2-CH_2CH_3), 29.5 (C-4), 43.1 (N-CH_2)*, 43.8 (C-5)*, 54.3 (N-CH_2Ph), 113.0 (C-3), 113.9, 118.1 (C-3'), 127.1, 129.7, 129.8 (C-2'), 139.2 (C-*ipso*), 145.9 (C-*ipso*), 147.1 (C-1'), 168.0 (C-2). UV (EtOH, λ) 296 (12400). EIMS m/z (%) 361 (M+1, 26), 360 (M^+, 81), 359 (M-1, 13), 345 (6), 331 (19), 317 (3), 303 (3), 288 (5), 269 (16), 262 (27), 247 (10), 246 (14), 220 (6), 196 (9), 183 (12), 182 (51), 170 (34), 156 (4); 144 (5), 130 (23), 106 (7), 92 (9), 91 (100), 77 (40), 69 (11), 65(13), 57 (18), 51 (7), 43 (13). HRMS : calc. for $C_{25}H_{28}N_2O_2$ 360.2201, found : 360.2200.

20b : oil, IR (CCl_4) 1685. ^1H NMR : δ 0.87 (t, 3H, *J* = 7.5 Hz, CH_3), 0.92 (t, 3H, *J* = 7.5 Hz, CH_3), 1.20-1.60 (m, 8H, CH_2CH_3 and $CH_2CH_2CH_3$), 2.00-2.10 (m, 1H, H-1")*, 2.45-2.55 (m, 1H, H-1")*, 2.65-2.85 (m, 2H, H-1'), 2.95-3.05 (m, 1H, CH_2-N), 3.10-3.50 (m, 7H, CH_2-N, H-2' and H-2"), 3.72 (t, 1H, *J* = 10 Hz, H-3), 3.85-4.00 (m, 3H, CH_2-CH= and CH_2-C-3), 4.35-4.60 (m, 5H, O-CH_2Ph and CH_2-C-3), 5.78 (t, 1H, *J* = 7.5 Hz, CH=C-2). ^{13}C NMR : δ 13.9 (CH_3), 20.0 (CH_2CH_3), 20.1 (CH_2-CH_3), 24.7 (C-1'), 25.7 (C-1"), 29.2 ($CH_2CH_2CH_3$), 42.5 (C-2')*, 42.8 (C-2")*, 44.7 (NCH_2-$CH_2CH_2CH_3$); 47.1 (C-3), 53.4 (C-1), 66.1 (CH_2-OCH_2Ph), 68.7 (CH_2-OCH_2Ph), 72.8 (OCH_2Ph), 124.2 (CH=C-2), 125.8 (C-2), 127.4, 127.7, 127.8, 128.0, 128.2, 128.5, 138.1 (C-*ipso*)*, 138.8 (C-*ipso*)*, 139.5 (C-4)*, 146.6 (C-4), 167.8 (C-4"), 175.2 (C-4'). UV (EtOH, λ) 296 (12400). EIMS m/z (%) 570 (M^+, 7), 555 (1), 540 (1), 527 (1), 511 (2), 495 (8), 479 (15), 465 (7), 463 (7), 449 (3), 433 (2), 419 (2), 403 (3), 387 (9), 371 (18), 354 (19), 341 (10), 327 (4), 302 (3), 285 (4), 287 (2), 272 (3), 258 (3), 232 (4), 316 (5), 182 (3), 156 (3), 141 (9), 122 (4), 108 (17), 107 (13), 105 (19), 91 (100), 77 (20), 65 (11), 57 (9), 43 (5). HRMS : calc. for $C_{36}H_{46}N_2O_4$ 570.7812, found : 570.7820.

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