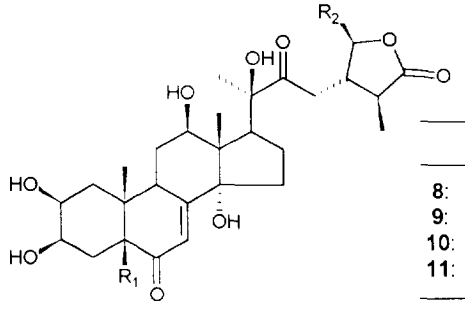
structure and the absence (or very low proportion) of the γ-lactonic compounds **4-7**. Two of these compounds had retention times between those of cyasterone and ajugalactone suggesting some possible structural relationship with these phytoecdysteroids whereas the other two compounds appeared at much higher retention times.

Table I. Ecdysteroid retention times (min.) and relative contents (%) of aerial part of: A) *Ajuga reptans* (green variety) greenhouse fast growing; B) *Ajuga reptans* (red variety) greenhouse fast growing and C) *Ajuga reptans* (red variety) autumn collected analyzed by RP-HPLC (see conditions in experimental part). nd means not detected and -- indicate a non resolved peak shoulder that elute in the base of the next compound.

Compound	7	6	3	5	2	4	11	10	1	9	8
Ret. time (min)	11.5	13.5	14.5	16.0	17.2	19.1	23.1	29.3	32.4	51.5	60.0
A content (%)	35	36	nd	5	4	4	nd	nd	15	nd	nd
B content (%)	6	4	2	--	56	7	nd	nd	25	nd	nd
C content (%)	nd	nd	nd	2	47	nd	8	3	12	9	7

Unequivocal structural assignments for these new compounds were carried out from ^{1}H and ^{13}C (BB and DEPT) NMR spectra, COSY and HETCOR correlations and comparison with the corresponding spectral data of the parent compounds. It is worth mentioning that COSY and HETCOR correlations were also established for those reference phytoecdysteroids, namely **1**, **5** and **6**, to complete (or secure dubious) previously reported data[10,12,13]. According to the spectral data summarized in Tables II and III, these new compounds were identified as 22-dehydro-12β-hydroxy analogs of phytoecdysteroids **4-7** as shown in Figure 2.



Compound	R1	R2
8: 22-Dehydro-12-hydroxycyasterone	H	CH_3
9: 22-Dehydro-12-hydroxysengosterone	OH	CH_3
10: 22-Dehydro-12-hydroxy-29-*nor*-cyasterone	H	H
11: 22-Dehydro-12-hydroxy-29-*nor*-sengosterone	OH	H

Figure 2.- Structure of the new family of ecdysteroids isolated from aerial part of *Ajuga reptans* var. *atropurpurea* harvested at the begining of autumn.

An initial inspection of ^{1}H-NMR spectra shows a high similarity between the absorptions corresponding to compounds **8-9** and **10-11** with the exception that in **9** and **11** the characteristic signal assignable to H-5 does not appear. As this change is concurrent with the appearance of one quaternary C-O and the absence of

one C-H in the ^{13}C-NMR spectra and changes in the ^{1}H-NMR spectra derived from the hydroxylation of C-5, probably compounds **8-9** and **10-11** will have similar structures with the only difference of the hydroxy substitution at C-5. On the other hand, the ^{1}H NMR spectra revealed the presence of four methyls, one of them doublet, in compounds **10** and **11**, or five methyl groups, two of them doublets, in **8** and **9**, with chemical shifts and coupling constants similar to those characteristic ones of phytoecdysteroids with γ-lactone side chain as **4-7**. Furthermore, a high field signal at 0.84-0.76 ppm., attributable to the 18-Me, agrees with the spectral data recorded for non-hydroxylated ecdysteroids at C-20, whereas the singlet at δ 1.56-1.58 of the 21-Me appears at a normal position for 20-OH derivatives. This apparent anomaly should be originated by some structural changes in the vicinity of the 18-Me group. Finally, the apparition of a new signal around 5.0 ppm in the ^{1}H-NMR spectrum and the change of one CH_2 by a CH-O in the ^{13}C-NMR spectrum suggest that C-12 could be another oxidation site which would explain the above abnormal chemical shift of C-18 methyl group.

Table II. ^{1}H-NMR chemical shifts for reference compounds **1**, **5**, **6** and for the new isolated ecdysteroids (**8-11**) obtained from ^{1}H-NMR, COSY and HETCOR spectrum. # denotate corrected values and * indicate additional data to those previously reported in the literature[10,12,13].

	1	**6**	**5**	**8**	**9**	**10**	**11**
1-H	1.96 *	2.14, 1.98 *	2.22, 2.08 *	2.11, 2.02	2.22, 2.05	2.13, 1.98	2.25, 2.10
2-H	4.00	4.17	4.25	4.16	4.25	4.15	4.25
3-H	4.20	4.22	4.16	4.22	4.17	4.23	4.19
4-H	2.02, 1.62 *	2.03, 1.78 *	2.06, 1.95 *	2.02, 1.74	1.98	2.01, 1.74	2.00
5-H	3.09	3.03	-	3.04	-	3.05	-
7-H	6.40	6.28	6.31	6.30	6.33	6.30	6.33
9-H	4.00 #	3.60	3.65	3.78	3.81	3.75	3.82
11-H	2.86 *	1.91, 1.77 *	1.93, 1.80 *	2.45, 1.92	2.50, 2.00	2.46, 1.92	2.49, 1.99
12-H	-	2.64;2.04 *	2.64;2.05 *	5.08	5.02	5.04	5.02
15-H	2.46, 2.04 *	2.21, 1.95 *	2.21, 1.97 *	2.19, 1.95	2.13, 1.96	2.16, 1.94	2.11, 1.94
16-H	2.62, 2.08 *	2.46, 2.06 *	2.47, 2.05 *	2.83, 2.25	2.81, 2.25	2.81, 2.25	2.81, 2.25
17-H	3.50 #	2.87 *	2.85 *	3.42	3.39	3.39	3.37
22-H	4.46	3.89	3.94	-	-	-	-
23-H	2.42, 2.23 *	1.95, 1.57 *	1.70 *	3.57;3.31	3.56;3.32	3.63;3.30	3.64;3.30
24-H	-	2.39 *	2.22 *	2.40	2.41	2.65	2.64
25-H	-	2.23 *	2.36 *	2.53	2.54	2.33	2.34
28-H	1.87	4.65, 3.96	4.02	4.24	4.25	4.78;3.84	4.78;3.85
18-Me	1.54	1.23	1.24	0.84	0.83	0.77	0.76
19-Me	1.16	1.07	1.17	1.08	1.18	1.10	1.20
21-Me	1.70	1.57	1.57	1.58	1.57	1.56	1.56
27-Me	1.87	1.16	1.36	1.31	1.31	1.18	1.19
29-Me	0.68	-	1.31	1.41	1.41	-	-

A close examination of the data depicted in Table II revealed the disappearance of the 22-H signals at ~3.9 ppm in the proton spectra of compounds **8-11** suggesting the quaternization of C-22 probably by oxidation, which could be confirmed by the appearance of a new ketone carbon absorption in the carbon

spectra (see Table III) with a chemical shift in the region of α-hydroxy ketones. Moreover, in the range of 3.2 to 3.7 ppm appeared new signals of two diastereotopic hydrogens coupled with only one other hydrogen, which is compatible with the above C-22 oxidation. All the above data taken together indicate that the new compounds were structurally related to the γ-lactone phytoecdysteroids **4-7** with the differences of a new hydroxy group at C-12 and the oxidation of C-22 alcohol to the corresponding ketone. These structural modifications could be completely confirmed by analysis of the ^{13}C-NMR signals depicted in Table III. The spectra of all four new compounds exhibit, in the 160-220 ppm carbonyl region, the presence of two ketone signals at 200-220 ppm and one ester signal around 179 ppm, together with one double bond as expected and confirmed by absorptions at 120-122 and 163-167 ppm.

Table III. ^{13}C-NMR chemical shifts for reference compounds **1**, **5**, **6** and new phytoecdysteroids **8-11**. Data obtained from ^{13}C, DEPT and HETCOR spectra.

	1	**6**	**5**	**8**	**9**	**10**	**11**
C-1	37.8	38.0	34.8	37.9	34.8	37.9	34.8
C-2	67.9	68.1	67.8	68.0	67.8	67.9	67.7
C-3	67.6	68.0	69.8	67.9	69.7	67.8	69.7
C-4	32.1	32.4	35.9	32.4	35.8	32.3	35.8
C-5	50.8	51.4	79.8	51.2	79.8	51.2	79.8
C-6	202.7	203.6	200.9	203.3	200.7	203.3	200.7
C-7	123.3	121.8	120.1	122.3	120.8	122.3	120.8
C-8	166.8	165.9	166.4	163.1	163.6	163.1	163.6
C-9	36.8	34.4	38.2	34.5	38.1	34.5	38.1
C-10	39.8	38.7	44.8	38.8	45.1	38.8	45.2
C-11	36.8	21.0	22.0	29.7	30.7	29.7	30.7
C-12	210.2	32.0	32.2	71.0	70.8	70.9	70.8
C-13	61.5	48.2	48.2	51.8	51.9	51.9	51.9
C-14	89.1	84.1	83.9	85.9	85.8	85.9	85.7
C-15	31.9	31.8	31.9	31.6	31.6	31.6	31.6
C-16	21.0	21.4	21.2	23.0	23.0	22.9	22.9
C-17	43.8	50.1	49.8	59.3	59.2	59.3	59.2
C-18	17.4	17.8	17.8	12.1	12.1	12.2	12.3
C-19	23.7	24.5	17.1	24.3	17.2	24.3	17.2
C-20	74.9	76.7	76.7	79.0	79.0	78.9	78.9
C-21	22.1	21.2	20.9	28.8	28.9	28.7	28.8
C-22	83.1	76.0	73.9	218.4	218.5	219.0	219.0
C-23	30.1	34.7	34.4	42.0	42.0	42.8	42.8
C-24	154.2	43.3	48.6	45.8	45.8	39.7	39.7
C-25	121.2	40.7	42.4	42.2	42.2	39.2	39.2
C-26	162.1	179.8	179.2	178.6	178.7	179.4	179.4
C-27	12.2	14.4	15.8	14.7	14.7	13.8	13.8
C-28	27.0	72.9	79.8	79.8	79.8	71.4	71.4
C-29	11.5	-	19.3	20.2	20.3	-	-

Further examination of the C-OH moieties absorption region at 60-85 ppm revealed the occurrence of six signals in the spectra of **8** and **10** and seven in those of **9** and **11**, respectively. Likewise, a comparison of

the absorptions of A and B rings showed a great similarity in the signals of **8** and **10** and of **9** and **11** with those of **6** and **5**, respectively, in agreement with the above mentioned differences of functionalization at C-5. Likewise, the absence of the signals attributable to 29-Me in compounds **10** and **11** and the concomitant appearance of absorptions in agreement with a CH_2O moiety, in the corresponding ^{13}C-NMR spectra, suggest 29-nor structures for these compounds.

At this stage, one could easily accept that the structures depicted in Figure 2, assigned to the new compounds, were soundly established. However, in order to further substantiate the proposed structures from first principles, we tried to assign the greatest number possible of ^{1}H and ^{13}C signals through the data from COSY and HETCOR spectra. From the COSY data one could obtain the coupling profile corresponding to side chain and the rings A, C and D which confirm the proposed structures. With the aid of these data and the HETCOR spectra the assignments of carbon resonances were straightforward. At this stage, comparison of the data for the new compounds with those of the reference ones led us to obtain a series of $\Delta\delta$ ^{13}C for the different carbons which could be fully explained by the structural differences. Furthermore, the configuration of the hydroxyl group in these compounds could be assigned from the ^{13}C NMR data for sterols reported by C. Djerassi and coworkers[14] who compared the chemical shifts of a broad set of sterols with the related non-hydroxylated compounds. The chemical shifts differences observed for the C-9, C-11, C-12, C-13, C-14 and C-18 signals between compounds **9** and **5** (similarly between **11** and **5**, **8** and **6** and **10** and **6**) -0.1, 8.7, 38.6, 3.7, 1.9 and -5.7 ppm respectively (see Table III), are in agreement with those found for a β-hydroxyl configuration at C-12 in the work of Djerassi. Only the increase of 9.4 ppm for the C-17 signal was higher than expected. However, this apparent anomaly can also be explained by the anisotropic effect of the C-22 carbonyl group in the α-hydroxy ketone moiety in the new compounds which also produces a similar effect (8.0 ppm) on the positionally related C-21.

EXPERIMENTAL SECTION

Plants

Ajuga reptans, green and atropurpurea varieties were obtained by propagation from wild plants in the greenhouse and cultured under optimal conditions. Mature plants were obtained in the area of Cabrils (Catalunya, Spain) and harvested at the end of September 1993. Plant samples were water cleaned and air dried, after that aerial part was separated and used in analytical and preparative work.

HPLC analysis

The HPLC analyses were carried out under reversed-phase conditions, controlled temperature and isocratic conditions (column: LiChroCART 125 x 4 mm, packed with LiChrospher 100 RP-18, 5 μm, protected with a guard column, Waters, 24 x 4 mm, packed with Bondapak C-18, 10 μm, at 55 °C; mobile phase: *i*-PrOH:H_2O 1:14.7 at 1.2 mL/min.). Samples of 200 mg of dry vegetable material were extracted with

methanol and the residue obtained after solvent removal was treated and the phytoecdysteroid content was quantified according to previously described procedures[15].

Extraction and isolation of phytoecdysteroids

The vegetable material (4x200 g) was washed with hexane (3x2L during 48 h), dichloromethane (2x2L, 48 h) and the residue extracted with methanol (3x2L, 48 h). The joined extracts were dried and treated as described previously[7]. The final purification of ecdysteroids was carried out by semipreparative HPLC (System 3: Spherisorb ODS-2, 10 μm; 300 x 7.8 mm, at 23°C; *i*-PrOH:H_2O 1:5.6 at 3 mL/min) monitored by TLC (eluting with 4:1, $CHCl_3$:MeOH) and by HPLC.

NMR spectroscopy

^{1}H-NMR (300 MHz), ^{13}C-NMR (75 MHz), H,H-COSY and H,C-HETCOR were recorded on a Varian Unity 300 spectrometer under standard conditions. Chemical shifts are given in ppm, the coupling constants and width at half height ($w_{1/2}$) are given in Hz. and the ^{13}C-NMR multiplicities were determined by DEPT experiments. For small samples, spectra were recorded by dissolving in 250 μL (sample concentration *ca.* 25 mM) of dry deuteropyridine and using special low volume NMR tubes with reduction and antivortex glass plugs (Shigemi Inc., BMS-05 microtube).

Mass spectrometry

Spectra were obtained by HPLC-MS using thermospray ion source in a HP-5988A quadrupole instrument with the following conditions: direct flow injection of the sample dissolved in acetonitrile, mobile phase of buffered water (ammonium formate 50 mM pH=6) : acetonitrile (50:50) at 1 ml/min. TSP temperatures: tip=180°C, stem=96°C and ion source=260°C.

Analytical data of isolated new compounds of aerial part.

2β,3β,12β,14α,20R-Pentahydroxy-6,22-dioxo-5β-stigmast-7-ene-26,24^1-lactone (22-Dehydro-12-hydroxy-cyasterone **8**). From the starting material and following the described isolation procedure 3.5 mg of the pure compound were obtained. IR ν: 3405, 1757, 1708, 1658 cm^{-1}. MS (TSP) m/z(negative ions): 579 [M+HCOO], 561 [M+HCOO-H_2O]. ^{1}H-NMR δ: 6.30 (d 2 Hz,1H,H-6), 5.08 (H-12), 4.24 (dq 8.5, 6 Hz,1H,H-28), 4.22 (H-3), 4.16 ($w_{1/2}$ 24 Hz,1H,H-2), 3.78 ($w_{1/2}$ 26 Hz,1H,H-9), 3.57 (dd 19, 6 Hz,1H,H-23a), 3.42 (t 9.5 Hz,1H,H-17), 3.31 (dd 19, 6 Hz,1H,H-23b), 3.04 (dd 13, 3.5 Hz,1H,H-5), 2.83 (m,1H,H-16a), 2.53 (dq 11, 7 Hz,1H,H-25), 2.50-2.34 (ca,2H,H-24 H-11a), 2.34-1.86 (ca,7H,H-1 H-4a H-11b H-16b H-15), 1.74 (t 14 Hz, 1H,H-4b), 1.58 (s,3H,H-21), 1.41 (d 6.5 Hz,3H,H-29), 1.31 (d 7 Hz,3H,H-27), 1.08 (s,3H,H-19), 0.84 (s,3H,H-18) ppm.

2β,3β,5β,12β,14α,20R-Hexahydroxy-6,22-dioxo-stigmast-7-ene-26,24^1-lactone (22-Dehydro-12-hydroxy-sengosterone **9**) 15 mg. IR ν: 3405, 1755, 1706, 1674 cm^{-1}. MS (TSP) m/z(positive ions): 551 [M+1], 533 [M+1-H_2O], 515 [M+1-2 H_2O], 497 [M+1-3 H_2O], 479 [M+1-4 H_2O], 461 [M+1-5 H_2O]. ^{1}H-NMR δ: 6.33 (d 2.5 Hz,1H,H-6), 5.02 (H-12), 4.25 (dq 8.5, 6 Hz,1H,H-28), 4.25 (H-2), 4.17 ($w_{1/2}$ 12 Hz,1H,H-3), 3.81 ($w_{1/2}$ 24 Hz,1H,H-9), 3.56 (dd 19, 5 Hz,1H,H-23a), 3.39 (t 10 Hz,1H,H-17), 3.32 (dd 19, 6 Hz,1H,H-23b), 2.81 (m,1H,H-16a), 2.54 (dq 11, 7 Hz,1H,H-25), 2.50-2.34 (ca,2H,H-24 H-11a), 2.30-1.90 (ca,8H,H-1 H-4 H-11b H-16b H-15), 1.56 (s,3H,H-21), 1.41 (d 6.0 Hz,3H,H-29), 1.31 (d 7 Hz,3H,H-27), 1.18 (s,3H,H-19), 0.83 (s,3H,H-18) ppm.

2β,3β,12β,14α,20R-Pentahydroxy-6,22-dioxo-5β-campest-7-ene-26,24^1-lactone (22-Dehydro-12-hydroxy-29-*nor*-cyasterone **10**) 1 mg. IR ν: 3394, 1754, 1705, 1652 cm^{-1}. MS (TSP) m/z(negative ions): 565 [M+HCOO],

547 [M+HCOO-H_2O]. ^{1}H-NMR δ: 6.30 (d 2.0 Hz,1H,H-6), 5.04 (H-12), 4.78 (t 8.5Hz,1H,H-28a), 4.23 ($w_{1/2}$ 12 Hz,1H,H-3), 4.15 ($w_{1/2}$ 26 Hz,1H,H-2), 3.84 (t 8.5 Hz,1H,H-28b), 3.75 ($w_{1/2}$ 16 Hz,1H,H-9), 3.63 (dd 19, 3.5 Hz,1H,H-23a), 3.39 (t 9.5 Hz,1H,H-17), 3.30 (dd 19, 10 Hz,1H,H-23b), 3.05 (dd 13, 3.5 Hz,1H,H-5), 2.81 (m,1H,H-16a), 2.65 (m,1H,H-24), 2.46 (m,1H,H-11a), 2.33 (dq 11, 7 Hz,1H,H-25), 2.30-1.85 (ca,7H,H-1 H-4a H-11b H-16b H-15), 1.74 (t 15 Hz,H-4b), 1.56 (s,3H,H-21), 1.18 (d 7 Hz,3H,H-27), 1.10 (s,3H,H-19), 0.77 (s,3H,H-18) ppm.

2β,3β,5β,12β,14α,20R-Hexahydroxy-6,22-dioxo-campest-7-ene-26,24^1-lactone (22-Dehydro-12-hydroxy-29-*nor*-sengosterone **11**) 5 mg. IR ν: 3416, 1759, 1709, 1674 cm^{-1}. MS (TSP) m/z(positive ions: 537 [M+1], 519 [M+1-H_2O], 501 [M+1-2 H_2O], 483 [M+1-3 H_2O], 465 [M+1-4 H_2O]. ^{1}H-NMR δ: 6.33 (d 3.5 Hz,1H,H-6), 5.02 (H-12), 4.78 (t 8.5Hz,1H,H-28a), 4.25 ($w_{1/2}$ 25 Hz,1H,H-2), 4.19 ($w_{1/2}$ 16 Hz,1H,H-3), 3.85 (t 8.5 Hz,1H,H-28b), 3.82 ($w_{1/2}$ 16 Hz,1H,H-9), 3.64 (dd 19, 3.5 Hz,1H,H-23a), 3.38 (t 9.5 Hz,1H,H-17), 3.30 (dd 19, 10 Hz,1H,H-23b), 2.81 (m,1H,H-16a), 2.65 (m, 1H,H-24), 2.49 (m,1H,H-11a), 2.34 (dq 11, 7 Hz,1H,H-25), 2.30-1.85 (ca,8H,H-1 H-4 H-11b H-16b H-15), 1.56 (s,3H,H-21), 1.20 (s,3H,H-19), 1.19 (d 7 Hz,3H,H-27), 0.76 (s,3H,H-18) ppm.

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Iminophosphorane-mediated Bispyrido Annulation onto Five-membered Rings. X-Ray Crystal Structure of 6,7-Dibenzylamino-13-methoxymethyl-13H-diquino[4,3-*b*:3',4'-*d*]pyrrole . Acetonitrile Complex.

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Abstract: Bispyrido annulation reaction onto a preformed five-membered heterocycle is achieved by the tandem aza Wittig/electrocyclic ring closure methodology. The method allows the one-step formation of diquinopyrroles, dipyridopyrroles, furodipyridines and thienodipyridines. The crystal and molecular structure of the 6,7-dibenzylamino-13-methoxymethyl-13H-diquino[4,3-*b*:3',4'-*d*]pyrrole . acetonitrile complex has been solved by X-ray analysis.

Pyrido annulation reaction based on the aza Wittig reaction of β-aryl(heteroaryl)vinyliminophosphoranes with iso(thio)cyanates or ketenes is a well-documented process.[1] Normally, the heterocyclization reaction takes place by electrocyclic ring-closure of the resulting heterocumulene (aza Wittig product) to give a *c*-fused pyridine.

Continuing our interest in the preparation and synthetic applications of C,C-bis(iminophosphoranes), we wish to report now a new one-flask bispyrido annulation reaction starting from appropriate C,C-bis(iminophosphoranes) in which both iminophosphorane groups are directly linked to different aromatic rings which are connected by a heteroaromatic ring.

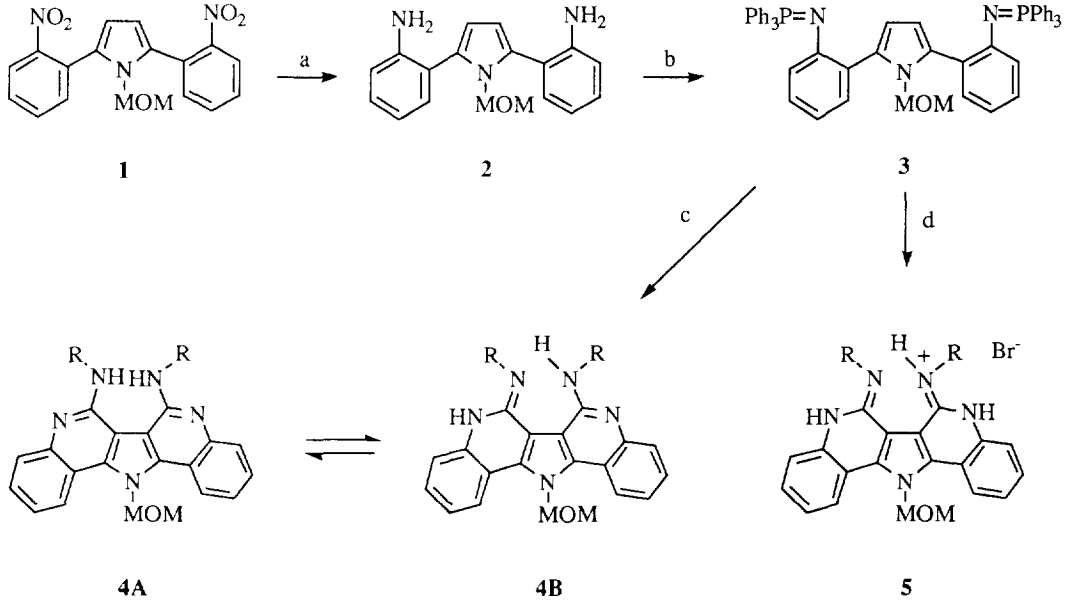
The requisite bis(iminophosphorane) **3** was prepared from 2,5-bis(*o*-nitrophenyl)pyrrole[2] by the three-step sequence: a) protection with the methoxymethyl group (85 %), b) hydrogenation of the *N*-protected pyrrole **1** in the presence of Pd on charcoal to give **2** (81 %), and c) treatment of **2** with dibromotriphenylphosphorane in the presence of triethylamine to afford **3** (76 %). Bis(iminophosphorane) **3** reacted with two equivalents of aromatic or aliphatic iso(thio)cyanates in toluene at reflux temperature to give the previously unreported pentacyclic compounds **4** in moderate to good yields (59-79 %) (Scheme 1). In order to identify unambiguously the structure of compounds **4**, the derivative **4b** (R= $C_6H_5.CH_2$) was recrystallized from different solvents and suitable crystals for X-ray analysis were obtained when acetonitrile was used.

The ^{1}H n.m.r. spectrum of the inclusion complex **4b**.CH_3CN recorded in $CDCl_3$ showed signals due to both the free host **4b** and free CH_3CN in a 1:1 ratio, at the same position as for the separate components. The IR spectrum of the crystalline complex in a nujol emulsion showed the nitrile band at 2247 cm^{-1}. We carried out a thermogravimetric (TG) analysis of the complex **4b**.CH_3CN and we observed an experimental weight loss of

7.33 % at 100-107 °C, in good agreement with that required for the 1:1 complex (7.27 %).

The molecular structure of the acetonitrile complex with the atomic numbering is depicted in Fig. 1. The five-rings system is not planar and the five-membered ring (A) and the fused rings (B and D) makes angles of 1.6(1) and 1.2(1), while the angles between (B, C) and (D, E) are 2.0(1) and 4.3(1)° respectively. Some degree of delocalization has been observed along the N5-C16-N3 and C18-C8-N2 fragments. The acetonitrile molecule presents no significant differences with the averaged values retrieved from the Cambridge Structural Database[3] (April 1995 release). Only 68 structures with R<0.10, no disorder, no metals and with located hydrogen bonds were retained, C-N= 1.123(29), C-C= 1.439(34)Å and NCC= 177(4)°(Table 1).

There is a total of four hydrogen interactions, of them only the N-H...N intramolecular bond could be considered strong when comparing with the result of the statistical analysis carried out for N-H...Nsp^2 interactions and secondary amines as donors (2.871Å and 167°). The N4...N5 distance of 2.766(5)Å is intermediate between the values reported for the neutral fluorene derivatives (2.861(2)-2.783(5)Å when there is no interaction) and those of the corresponding cation (2.588(3)-2.545(4)Å for N-H...N$^+$ bond).[4] The host and guest molecules are joined through weak N-H...N interactions so the whole crystal is built up of these discrete units (Table 1).



R = CH_3, $C_6H_5.CH_2$, 4-$CH_3.C_6H_4$, 4-$CH_3O.C_6H_4$.

R = CH_3, $C_6H_5.CH_2$.

Reagents and Conditions (a) H_2, Pd/C, EtOH, r.t.; (b) Ph_3PBr_2, Et_3N, benzene, reflux;
(c) 2 R-NCO or 2 R-NCS, toluene, reflux; (d) 2 R-NCO or 2 R-NCS, Et_3NHBr, toluene, reflux.

Scheme 1