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Synthesis of Functionalised Furans and Pyrroles through Annulation Reactions of 4-Pentynones.

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Abstract: A new approach to 4-pentynones through palladium-catalysed coupling reaction of the ready available 2-propynyl ketones with aryl iodides and/or vinyl triflates is proposed. Annulation reactions of both 2-propynyl ketones and 4-pentynones gave functionalised furans using potassium *tert*-butoxide in DMF and functionalised pyrroles in the presence of benzylamine or ammonia, respectively in good to high yields. The methodology has been extended to the preparation of 17β-hydroxyandrost-4-en[3,2-*b*](5-methyl)furan and to 17β-hydroxyandrost-4-en[3,2-*b*](1-benzyl-5-methyl)pyrrole. A different reaction pattern was observed when the 4-pentynones were treated with sodium methoxide in MeOH. The influence of the reaction medium on the outcome of the annulation reaction in the case of one 2-pentyn-1,6-dione (heteroannulation *vs.* carbocyclization) is also shown.

INTRODUCTION

Compounds containing a furan or pyrrole ring can be found in many naturally occurring compounds. Polysubstituted furans and pyrroles provide unabated interest in terms of pharmacology, synthesis and reactivity.[1] For example, strategies for the total synthesis of pseudopterolide and allied pseudopterans and furanocembranolides based on the elaboration of suitable 2,3,5-trisubstituted furans have been presented.[2] A short and highly efficient synthesis of calicogorgin A and C, 3-ketosphinganine derivatives isolated from marine invertebrates which show lethal and repellent activities against the gastropod D. *fragum*, has been accomplished.[3] 2,5-Bis-(4-amidinophenyl)furan was recently reported to be effective in vivo at submicromolar dosage against *Pneumocystis carinii* in the immunosuppressed rat model; its strong DNA affinity and effective antimicrobial activity led us to consider other modifications of this structure with the goal of improved efficacy and reduced toxicity.[4] Success with three HMG-CoA reductase (HMGR) inhibitors for treating hypercholesterolemia, lovastatin, pravastatin, and simvastatin, led to a surge in novel HMGR inhibithors that are more potent and synthesised by simple chemical processes.[5] Dual inhibitors of cyclooxygenase and 5-lipoxygenase of the arachidonic acid cascade as agents for the treatment of arthritis have been efficiently

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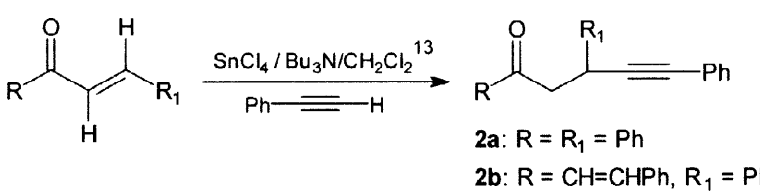
synthesised as well.[6] For this reason the syntheses of polysubstituted furans and pyrroles continue to attract the interest of many synthetic chemists. The construction of ring systems by intramolecular addition of anionic centre to a carbon π-bond of alkynes has attracted considerable attention in recent years.[7] The synthesis of many different substituted five-membered heteroaromatic rings has been achieved through the intramolecular attack of a suitable nucleophile on an alkyne functionality.[3,8]

In the course of our investigations devoted to the development of new synthetic strategies for the construction of heterocyclic rings involving alkyne derivatives,[9] we have previously reported that the regioselective intramolecular *exo-dig* cyclization of 4-pentynones could represent a general procedure for the synthesis of functionalised furans. Moreover the sequential addition/elimination/cycloamination of 4-pentynones in the presence of benzylamine or ammonia produced 1,2,3,5-substituted and 2,3,5-substituted pyrroles and fused pyrrole systems.[10] With the purpose of developing the title heterocyclic ring structures from α-propynyl ketones as starting building blocks, we now wish to report the full details of the results we have obtained as well as the scope and limitations of this synthetic methodology.

RESULTS AND DISCUSSION

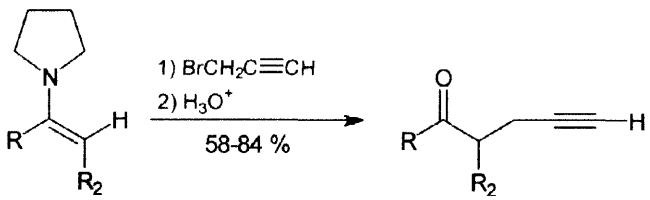
The conjugate addition of an alkynyl group to an α,β-unsaturated ketone to give 4-pentynones **2** has been a formidable synthetic challenge. Alternatively 4-pentynones **2** may be synthesised by multistep procedures such as that involving addition of hydrogen bromide to α,β-enones, ketalization, alkylation of lithium salt of 1-alkyne and deketalization.[11] Acetylenic alanes and trialkynylboron derivatives add their alkynyl units to α,β-enones but only under certain circumstances.[12] Recently, it was found that a Sn(IV) reagent system, $SnCl_4$-Bu_3N, can be used to alkynylate enones under considerably milder reaction conditions[13] (scheme 1) and the substrates **2a-b** were prepared by alkynylation of the corresponding α,β-unsaturated-β-substituted ketones.



SCHEME 1

However the alkynylation of α,β-unsaturated-β-unsubstituted ketones failed to give the target compounds **2**. To overcome this severe limitation, we attempted to develop a new and more versatile procedure to 4-pentynones **2** based on the utilization of the easily available 2-propynyl ketones **1** (terminal 4-pentynones) as suitable starting building blocks. 2-Propynyl ketones are valuable substrates in organic chemistry and a variety of methods exist for their preparation. The selective alkylation of carbonyl compounds has been a long

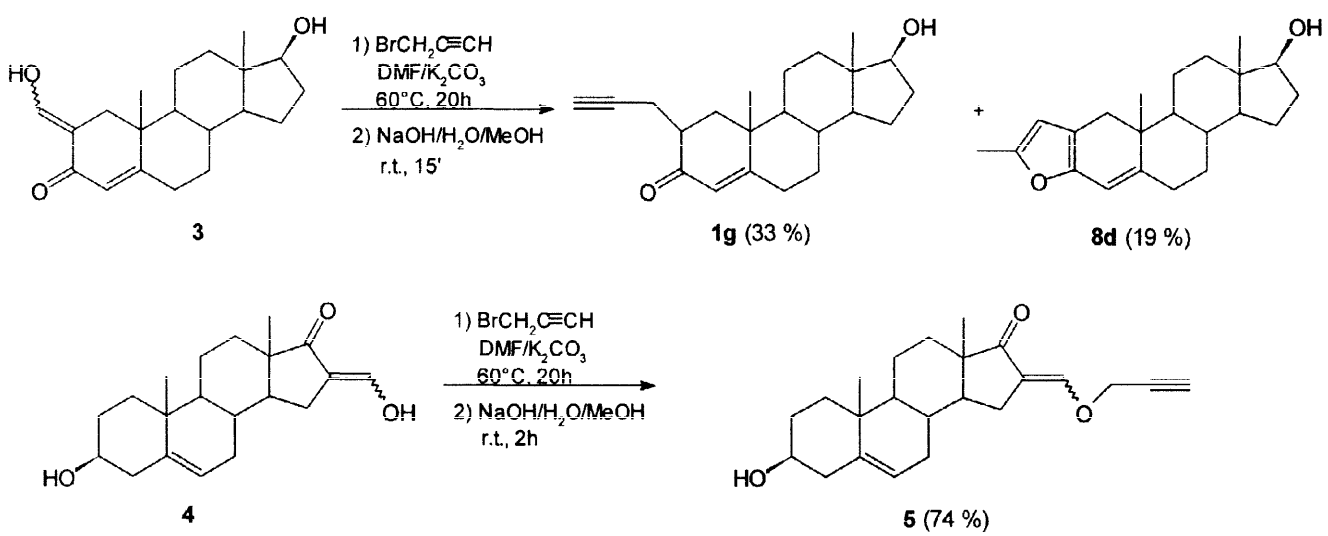
sought goal in organic synthesis. Accordingly, several approaches to this have been developed, with varying success, to overcome the frequently encountered problems of polyalkylation, competing aldol condensation, and lack of regio- and stereoselectivity. On the other hand, very useful alkylation procedures are known which combine the ketone directly as its enol derivative with a suitable alkylating agent.[14] Examples of this latter type include the enamine alkylation.[15] By employing this strategy we obtained the starting building blocks 2-propynyl ketones **1a-f**, by the Stork enamine reaction with propargyl bromide[16] (Scheme 2, Table 1)



1a-f

SCHEME 2

Although the preparation of the enamine derivatives of steroidal carbonyl compounds[17] may be carried out under the usual reactions conditions, we failed to obtain the target 2-propynyl steroidal ketones by this route. As part of a program devoted to the synthesis of analogs of furanosteroids[18] and related steroid-fused isoxazoles[19] and pyrazoles[20] with the aim to evaluate their ability as modulators of androgen biosynthesis and as potential agents for the treatment of prostatic cancer and hypertension we accomplished the synthesis of the 17 β-hydroxy-2-propargyl-4-androsten-3-one **1g** by the following alternative two-step sequence (Scheme 3): a) selective formylation[21] of the 17β-hydroxyandrost-4-en-3-one to give its 2-hydroxymethylene derivative; b) subsequent propargylation and deformylation to afford the 2α-propargyl derivative **1g**. Moreover furan derivative **8d** was isolated as by-product at the end of the second hydrolytic step in 19 % yield. The yield of **8d** can be improved to 32% if prolonged reaction time was used (24 h).



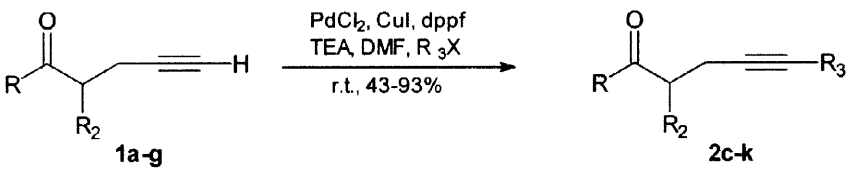
3 **1g** (33 %) **8d** (19 %)

4 **5** (74 %)

SCHEME 3

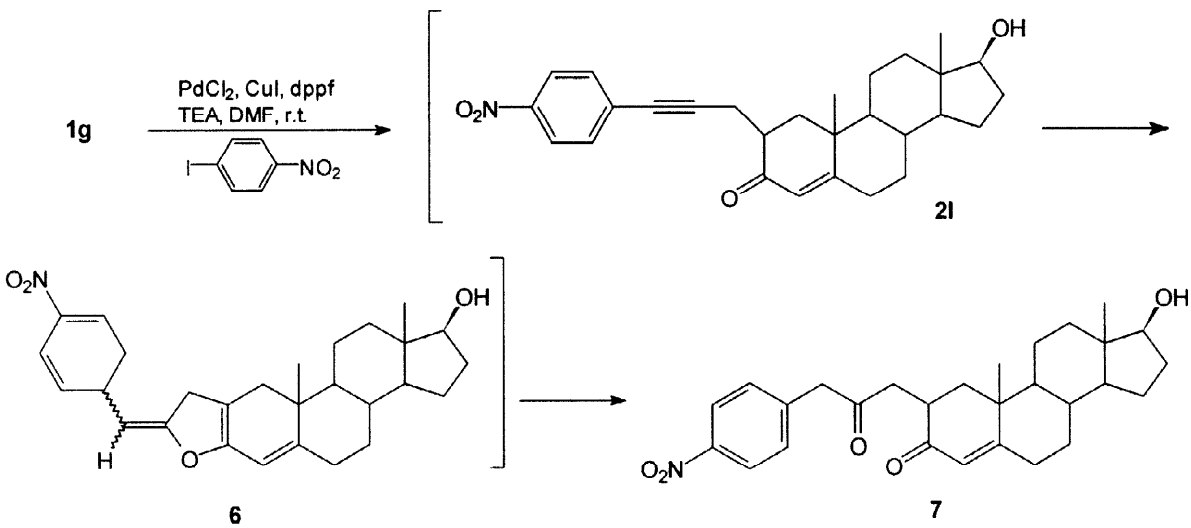
By contrast, the alkylation of the 16-formyl derivative **4** with propargyl bromide gave the O-propargylated[22] product **5** (Scheme 3).

The palladium-catalysed coupling reactions[23] of **1** with aryl iodides and vinyl triflates at r.t., in the presence of $PdCl_2$/dppf/CuI catalytic system (Scheme 5, Table 1) represents a very useful and versatile procedure for the synthesis of functionalized 4-pentynones **2** in moderate to high yields. Moreover it allows us in fact to channel the metal-mediated synthetic approach to this class of compounds by means of the conjugate addition of alkynes to α,β-enones, usually requiring strong conditions, into a mild procedure that can accommodate a variety of functional groups. This method, also, avoids the use of a specific acetylenic compound for each 4-pentynone. Indeed several 4-pentynones **2** could be synthesised from the same acetylenic building block.



SCHEME 4

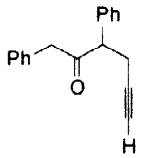
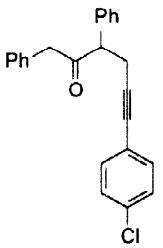
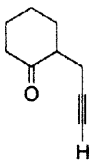
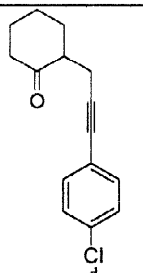
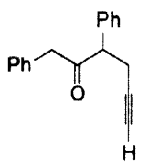
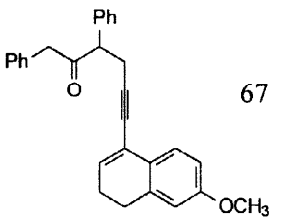
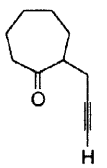
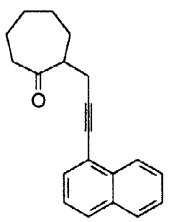
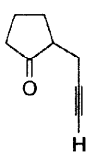
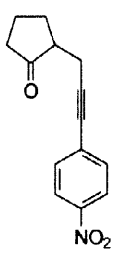
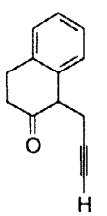
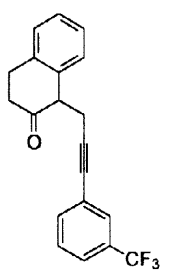
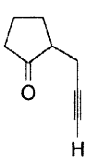
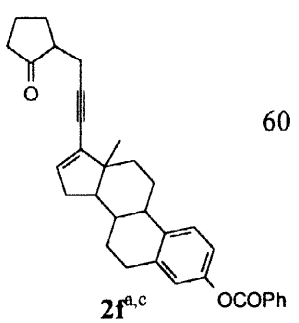
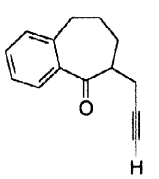
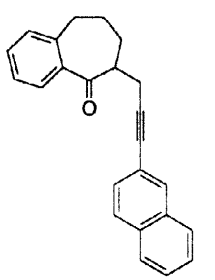
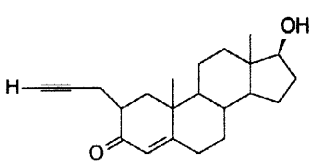
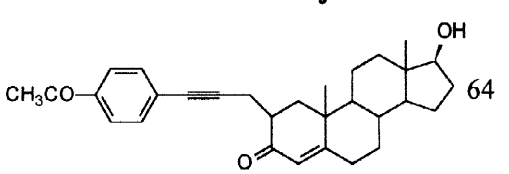
It is worthwhile pointing out that the simultaneous presence[24] of an easily enolizable carbonyl functionality and an electron deficient alkyne in the intermediate 4-pentynone **2l**, derived from the palladium-catalysed coupling of **1g** with 4-iodonitrobenzene, yields (90%) (Scheme 6) the β-dicarbonyl derivative 7.



SCHEME 5

Very likely **7** is formed through a tandem palladium-catalysed coupling/regioselective base promoted *exo-dig* annulation reaction to give the trienol ether **6**. The facile hydrolysis of this exocyclic trienol ether[25] gives **7**. Although we have not thoroughly investigated this point, because of the presence of a large excess of Et_3N under reactions conditions, which usually is added to avoid the hydrolysis of exocyclic enol ethers, the formation of **7** most probably occurs during the work-up of the reaction mixture. It is worthwhile emphasising

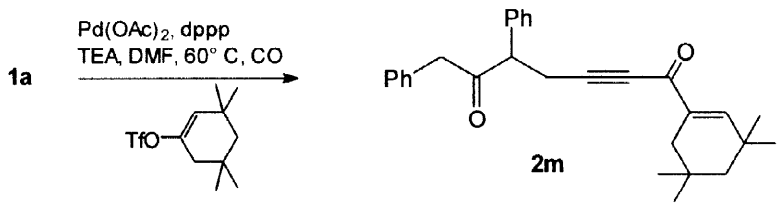
Table 1. Synthesis of 4-Pentynones 2.

Products 1	Products 2	Yield (%)	Time (h)	Products 1	Products 2	Yield (%)	Time (h)
		93	24			81	2
1a	**2c**[a,b]			**1c**	**2g**[d]		
		67	17			86	48
1a	**2d**[a,c]			**1d**	**2h**[a,b]		
		66	8			43	3
1b	**2e**[a,b]			**1e**	**2i**[e]		
		60	12			98	24
1b	**2f**[a,c]			**1f**	**2j**[a,c]		
						64	6
1g				**2k**[a,b]			

[a]The reaction was carried out in DMF at r.t. under N_2 atmosphere using the following molar ratios RX : TEA : $PdCl_2$: dppf : CuI = 1.2 : 5 : 0.02 : 0.04 : 0.04. [b]At 60°C, RX : K_2CO_3 : $Pd(OAc)_2$: $P(o\text{-}tol)_3$=1.2 : 5: 0.05 : 0.2. [c]In DMF/TEA 1 : 4, 60°C, RX : $Pd(OAc)_2$: PPh_3 = 1.2 : 0.02 : 0.04.

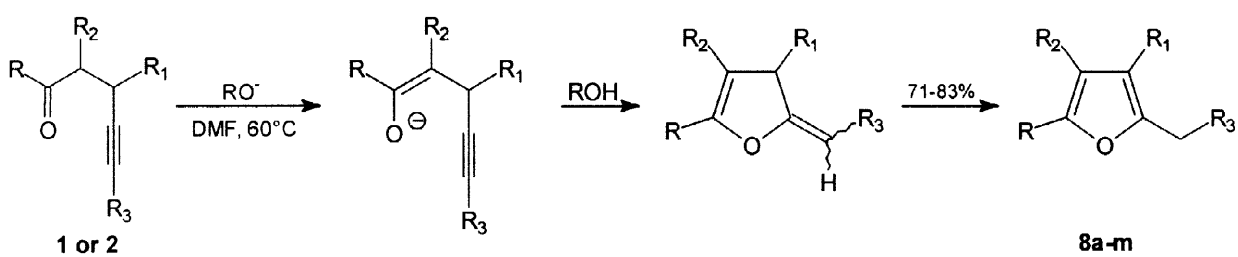
the completely different reactivity of **4-pentynone 2** compared to the reactivity of the very easy enolizable 1,3-dicarbonyl-2-propynyl derivatives and 1,3-dicarbonyl-4-propynyl derivatives which undergo, in the presence of K_2CO_3, Pd(0) and aryl iodides and/or vinyl triflates, palladium-catalysed domino reactions to give heterocyclic derivatives through a mechanism which rules out the cleavage of the C_{sp}-H bond.[26]

Furthermore, the carbonylative palladium-catalyzed reaction[27] could be an alternative methodology for the synthesis (Scheme 8) of the functionalized 2-pentyn-1,6-diones **2m**.



SCHEME 6

The construction of heterocyclic derivatives based upon the concept of palladium-catalysed coupling/cyclization of alkynes bearing a proximate (pro)nucleophile proved to be a versatile and efficient synthetic methodology,[28] prompted us to investigate the base promoted intramolecular cyclization of 2-propynyl ketones **1** and 4-pentynones **2** which present both the enolizable carbonyl functionality and the alkyne framework. Indeed the easily available derivatives **1** and **2** containing a potential nucleophilic centre, under appropriate reactions conditions can undergo regioselective intramolecular *exo-dig* heteroannulation reactions to give functionalised furans **8** and pyrroles **12**. The expected furan derivatives **8a-k** were obtained in good yields by reacting the corresponding derivatives **1** and **2** with t-BuOK in dry DMF (Scheme 7, Table 2).

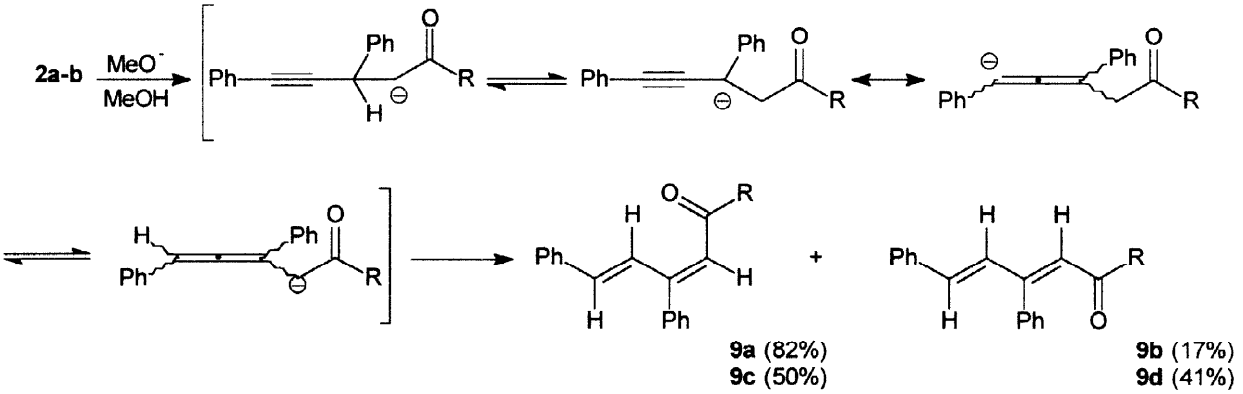


2a-b: R_1 = Ph
1a, 1e, 1f, 2c, 2g-i: R_1 = H

SCHEME 7

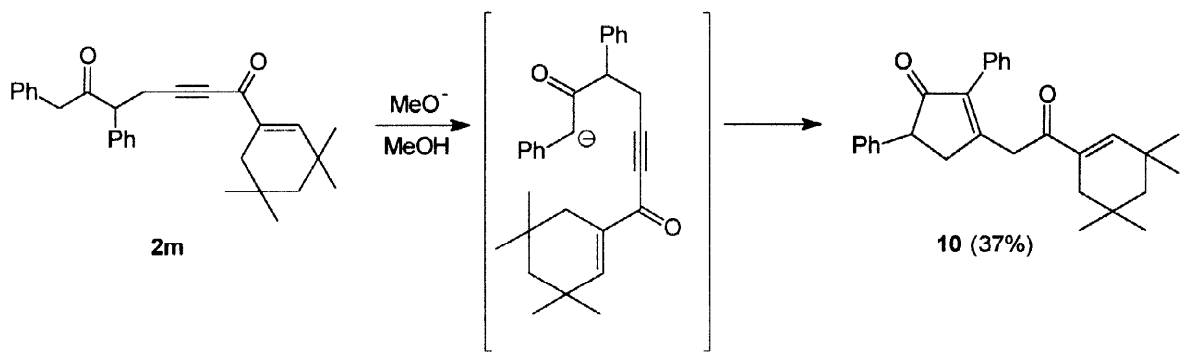
When the compounds **2a,b,c,g,i,m** were reacted with MeONa (1.2 mol. equiv.) in MeOH at 60 °C a different reaction pattern was observed. Compounds **2a** and **2b** gave respectively the (E,E) and (Z,E)-1,3,5-triphenyl-penta-2,4-dien-1-ones **9a** and **9b** and the (E,E,E) and (E,Z,E)-1,5,7-triphenyl-hepta-1,4,6-trien-3-ones **9c** and **9d** (Scheme 8). The structure of **9a-d** was assigned on the basis of ^{1}H-NMR analysis.[29] Moreover, whereas compounds **2c,g,i** were recovered unreacted even after prolonged reaction time, compound **2m** gave the 2-cyclopentenone **10**. These results can be rationalized taking into account the relative stability and the

equilibrium existing between the propargyl enolate and the cumulenyl enolate generated by the base-catalysed rearrangement, which, when the reactions are performed in methanol, is switched towards the synthesis of α,β,γ,δ-dienones **9a-d** (Scheme 8).



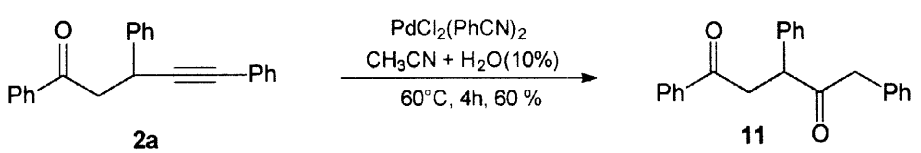
SCHEME 8

Instead a different behaviour was showed by the carbanion of **2m** which carbocyclizes through a conjugated addition over the activated triple bond giving rise mainly to the 2-cyclopentenone **10** (Scheme 9).



SCHEME 9

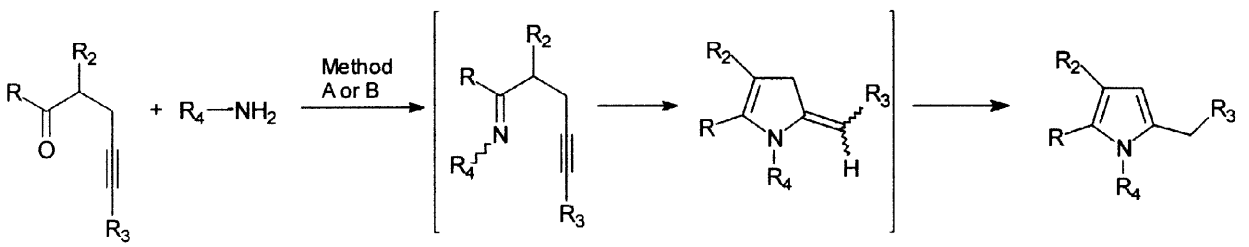
The influence of the reaction medium is supported by the results obtained when compounds **2a** and **2m** were treated with sodium methoxide (1.2 mol. equiv.) in a non-protic solvent such DMF. Under these conditions the furans **8e** and **8m** were obtained as the sole reaction products (Table 2). Moreover the diketone **11** is, also, regioselectively obtained from **2a** by palladium catalysis[30] (Scheme 10).



SCHEME 10

The reaction mechanism for the synthesis of furans probably involves a regioselective 5-*exo-dig* cyclization of the enolate (Scheme 7) onto the carbon-carbon triple bond followed by tautomerization to give furans **8a-m**. Polycyclic cyclohexa[*b*]furan and cyclohepta[*b*]furan can also be efficiently synthesised, but the described procedure failed to give cyclopenta[*b*]furan. The only steroidal derivative **2k** represents a different kind of isomerization to give the conjugated trienone **8l** (Table 2).

The synthesis of functionalised pyrroles **12a-o** can be carried out in good to high yields by the reaction of **1** and **2** with benzylamine or ammonia (Scheme 11, method A or B, Table 2). The reaction mechanism probably involves the formation of an imine that undergoes a 5-*exo-dig* cyclization followed by isomerization to give pyrroles.



1a-d, 1g: R_3=H
2c-e, g, i, j: $R_3 \neq H$

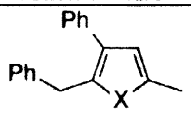
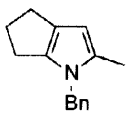
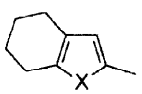
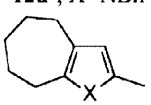
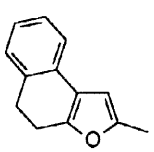
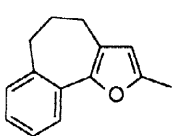
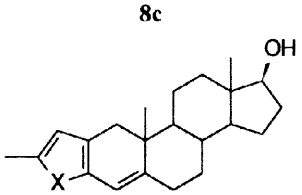
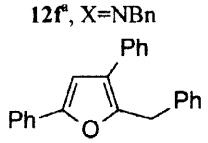
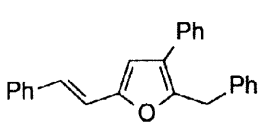
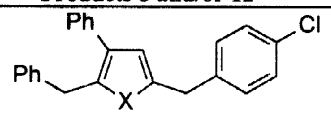
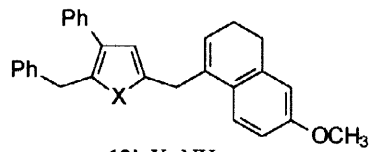
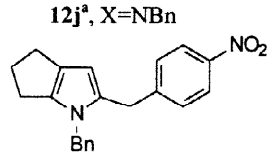
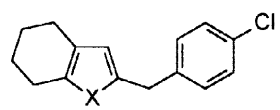
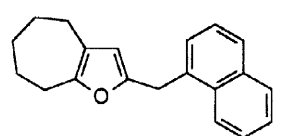
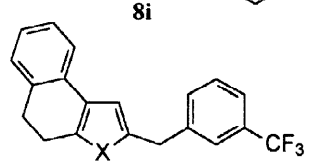
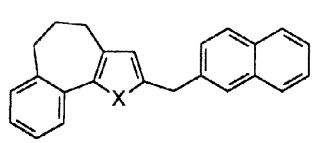
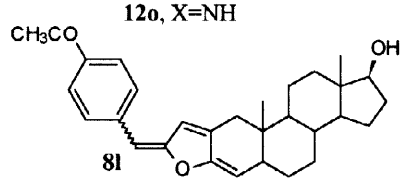
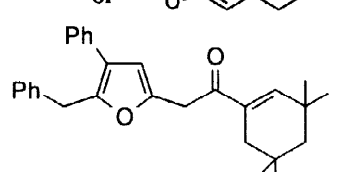
method A: R_4 = Bn, toluene or xylene/pTSA, ΔT, 2-23h, 76-97%
method B: R_4 = H, 2M in MeOH, 120°C, 9-24 h, 50-89%

SCHEME 11

It is worth noting that the regioselective outcome of the annulation reaction (6-*endo-dig* cyclization *vs.* 5-*exo-dig* cyclization) can be determined by suitable choice of the starting γ-ketoalkyne derivative (scheme 6): the presence of the γ-ketoalkyne moiety in an aromatic framework is responsible for the 6-*endo-dig* cyclization.[31] Moreover this methodology has been also extended to the preparation of cyclopenta[*b*]pyrroles.[32]

In conclusion, the results reported here show that the internal 4-pentynones can be easily obtained through the palladium-catalysed coupling reaction of 2-propynyl ketones with aryl iodides and/or vinyl triflates. The *t*-BuOK promoted reaction of both terminal and internal 4-pentynones in DMF is a synthetically useful reaction that affords regioselectively functionalised furans. Different substituted pyrroles are synthesised by cyclization of the same 4-pentynones in the presence of benzylamine or ammonia. The methodology has been extended to the preparation of 17β-hydoxyandrost-4-en[3,2-b]furan and 17β-hydoxyandrost-4-en[3,2-b]pyrrole derivatives. A different reaction pattern can be observed when 4-pentynones were treated with sodium methoxide in MeOH to give, in some cases, conjugated dienones. The influence of the reaction medium on the outcome of the annulation reaction in the case of one 2-pentyn-1,6-dione(heteroannulation *vs.* carbocyclization) is also shown.

Table 2. Synthesis of furans **8** and pyrroles **12** by annulation reaction of 4-pentynones **1** and **2**.

1/2	Products 8 and/or 12	Yield, %	Time, h
1a			
	8a, X = O	61	1
	12a, X = NH	50	24
1b			
	12b[a]	59	24
1c			
	12c, X=NH	69	9
	12d[b], X=NBn	97	2
1d			
	12e[b], X=NBn	78	16
1e			
	8b	62	1
1f			
	8c	68	5
1g			
	8d, X=O	32	24
	12f[a], X=NBn	77	2
2a			
	8e	90	3
2b			
	8f	79	2
2c			
	8g, X=O	70	4
	12g, X=NH	89	24
	12h[a], X=NBn	92	23
2d			
	12i, X=NH	65	22
	12j[a], X=NBn	76	7
2e			
	12k[a], X =NBn	55	7
2g			
	8h, X=O	70	4
	12l, X=NH	84	22
	12m[b], X=NBn	94	7
2h			
	8i	61	2
2i			
	8j, X=O	76	1
	12n[b], X=NBn	92	18
2j			
	8k, X=O		
	12o, X=NH		
2k			
	8l	70	1
			
	8m	75	3

[a] The reaction was performed in xylene with a catalityc amount of pTSA. [b] Performed in toluene.

EXPERIMENTAL

Mps are uncorrected and were measured with a Buchi apparatus. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50.3 MHz) spectra were recorded in $CDCl_3$ with a Bruker AC 200 E or with a Varian Gemini 200 spectrometer. EI (70eV) mass spectra were recorded with a TSQ 700 Finnigan/Mat instrument. I. R. were recorded with a Perkin-Elmer 683 spectrometer. All starting materials, catalysts, ligands, bases, and solvents (anhydrous solvents included) if not already stated, are commercially available and were used as purchased, without further purification. Vinyl triflates were prepared according to ref 33 and were purified by chromatography on silica gel eluting with *n*-hexane/EtOAc mixtures. 2-Propynyl ketones **1b, c, f** [16] and **1g**[21] are known compounds, 4-pentynones **1a, d, e,** are new and were prepared according to described method[15,16].

1,3-Diphenyl-4-hexyn-2-one 1a: purified by flash chromatography (PE/EtOAc 95:5); white solid; mp 49-51 °C; yield 72 % (from 1,3-diphenylacetone); ^{1}H NMR ($CDCl_3$) δ 1.85 (t, 1 H, J = 2.6 Hz), 2.52 (ddd, 1 H, J = 17.4, 7.6, 2.6), 2.84 (ddd, 1 H, J = 17.4, 7.2, 2.6), 3.63 (s, 2 H), 3.95 (t, 1 H, J = 7.4), 7.05 (m, 2 H); 7.15-7.47 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 21.85, 48.45, 56.48, 69.85, 81.84, 126.87, 127.76, 128.33, 128.46, 128.96, 129.48, 139.79, 137.02, 203.43; I. R. (melt) (cm^{-1}) 3278, 2080, 1710, 1592; elem. anal., found (calcd for $C_{18}H_{16}O$): C 87.24 (87.05); H 6.52 (6.49).

2-Propynylcycloheptanone 1d: purified by distillation; bp 80-82 °C (30 mm Hg); pale yellow oil; yield 42% (from cycloheptanone); ^{1}H NMR ($CDCl_3$) δ 1.24-1.77 (m, 4 H), 1.81-2.04 (m, 4 H), 1.95 (t, 1 H, J = 2.6), 2.27 (ddd, 1H, J = 16.9, 8.4, 2.6), 2.38-2.61 (m, 3 H), 2.67-2.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.27, 24.30, 29.29, 29.78, 30.73, 43.71, 51.13, 69.72, 83.05, 214.01; EI MS *m/z* (relative intensity) 150 (M^+, 18), 149 (15), 135 (19), 121 (18), 107 (100), 98 (36); 94 (93); I. R. (neat) (cm^{-1}) 3288, 2118, 1700.

1-Propynyl-2-tetralone 1e: purified by flash chromatography (PE/EtOAc 95:5); pale yellow oil; yield 84 % (from pyrrolidino enamine of 2-tetralone); ^{1}H NMR ($CDCl_3$) δ 1.95 (m, 1 H), 2.45-3.14 (m, 6 H), 3.64 (dd, 1 H, J = 6.4, 5.4), 7.23-7.39 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.08, 27.75, 37.54, 51.33, 70.33, 81.63, 126.90, 126.98, 127.05, 127.62, 135.09, 137.16, 209.68; I. R. (neat) (cm^{-1}) 3272, 2108, 1682, 1608.

16-Propargyloxymethylene-5,6-dehydro-epiandrosterone 5.

To a well stirred solution of 16-formyl-5,6-dehydro-epiandrosterone **4**[21] (1 g, 3.16 mmol) in dry DMF (25 ml) K_2CO_3 (436 mg, 3.16 mmol) and propargyl bromide (1.50 g, 12.65 mmol) were added. The mixture was stirred at 60°C for 24h, then poured in HCl 0.1M (200ml) ed extracted twice with ethylacetate. The organic, dried over Na_2SO_4, was evaporated to dryness and the crude purified by flash chromatography over silica gel eluting with hexane/ethylacetate 1:1 yielding pure **5** (0.83 g, 74 %).

16-Formyl-5,6-dehydro-epiandrosterone 4: white solid; m.p 251-253 °C; yield 99 %; ^{1}H NMR (DMSO) δ 0.88 and 0.97 (s, 3 H); 0.86-2.45 (17 H, aliphatyc pattern), 3.26 (m, 1 H), 4.50 (bs, 1 H); 5.29 (m, 1 H); 7.36(s, 1 H), 10.60 (bs, 1 H); ^{13}C NMR (DMSO) δ 13.96, 19.07, 19.95, 24.27, 30.20, 30.46, 31.20, 31.34, 36.20, 36.77,

42.17, 47.21, 49.42, 49,79, 69.89, 113.00, 119.96, 141.37, 150.06, 208.45; I. R. (KBr) (cm^{-1}) 3222, 1708, 1626, 1244, 1054; elem. anal., found (calcd for $C_{20}H_{28}O_3$): C 75.86 (75.90); H 8.85 (8.92).

16-Propargyloxymethylene-5,6-dehydro-epiandrosterone 5: white solid; m.p. 105-107 °C; yield 74 %; ^1H NMR (DMSO) δ 0.82 and 0.99 (s, 3 H), 0.93-3.29 (17 H, aliphatic pattern), 3.27 (m, 1 H); 3.71 (t, 1 H, J = 2.3), 4.63 (bs, 1 H), 4.80 (d, 2 H, J = 2.3), 5.32 (m, 1 H), 7.30 (s, 1 H); ^{13}C NMR (DMSO) δ 14.21, 19.40, 20.27, 24.84, 30.47, 30.84, 31.45, 31.67, 36.56, 37.14, 42.49, 47.76, 49.47, 50.12, 60.98, 70.28, 79.04, 79.56, 115.86, 120.29, 142.01, 152.22, 208.43; I. R. (KBr) (cm^{-1}) 3496, 3280, 2122, 1702, 1670, 1654, 1618, 1282, 1168; elem. anal., found (calcd for $C_{23}H_{30}O_3$): C 77.53 (77.92); H 8.27 (8.53).

4-Pentynones 2c-k.

The reactions performed as reported in Ref. 23 and Table 1 gave after flash chromatography (silica gel, hexane/ethylacetate mixtures) 4-pentinones **2c-k**.

2c: white solid; mp 73-74 °C; ^1H NMR ($CDCl_3$) δ 2.70 (dd, 1 H, J = 16.9, 7.4), 3.04 (dd, 1H, J = 16.9, 7.4), 3.64 (s, 2 H), 4.03 (t, 1 H, J = 7.4), 7.03-7.34 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 22.92, 48.71, 56.62, 81.23, 88.68, 122.46, 127.02, 127.87, 128.41 (2C), 128.64, 129.06, 129.49, 132.70, 133.53, 133.84, 137.16, 205.78; I. R. (KBr) 1700, 1600, 745, 725; elem. anal., found (calcd for $C_{24}H_{19}OCl$): C 80.48 (80.32); H 5.45 (5.33).

2d: pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.22 (m, 2 H), 2.66 (t, 2 H, J = 8.0), 2.81 (dd, 1 H, J = 16.9, 8.2), 3.02 (dd, 1 H, J = 16.9, 6.8), 3.64 (s, 2 H), 3.72 (s, 3 H), 4.02 (dd, 1 H, J = 8.2, 6.8), 6.09 (t, 1 H, J = 4.8), 6.58 (m, 2 H), 6.98 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 22.68, 23.22, 27.48, 48.42, 54.98, 56.76, 79.89, 87.86, 111.01, 112.99, 120.98, 125.82, 126.17, 126.76, 127.60, 128.40 (2C), 128.91, 129.35, 131.58, 133.66, 136.49, 137.18, 158.74, 205.75; I. R. (neat) (cm^{-1}) 2270, 2108, 1710, 1595.

2e: yellow solid; mp 54-55 °C; ^1H NMR ($CDCl_3$) δ 1.84-1.89 (m, 2 H), 2.09-2.16 (m, 2 H), 2.35-2.43 (m, 3 H), 2.63 (dd, 1 H, J = 13.2, 6.7), 2.83 (dd, 1 H, J = 13.2, 4.1), 7.50 and 8.14 (AA'-BB' system, 4 H, J = 6.9); ^{13}C NMR ($CDCl_3$) δ 19.60, 20.49, 28.89, 37.95, 47.72, 80.23, 93.67, 123.46, 130.59, 132.35, 146.69, 218.53; EI MS *m/z* (relative intensity) 243 (M^+, 9), 242 (12), 215 (100), 139 (10), 115 (20); I. R. (KBr) 2200, 1730, 1585; elem. anal., found (calcd for $C_{14}H_{13}NO_3$): C 69.35 (69.11); H 5.47 (5.38); N 5.81 (5.75).

2f: white solid; mp 60-62 °C; ^1H NMR ($CDCl_3$) δ 0.85 (s, 3 H), 1.25-2.95 (m, 22 H), 5.94 (m, 1 H); 6.93 (m, 2 H), 7.32 (d, 1 H, J = 8.5), 7.45-7.62 (m, 3 H), 8.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.19, 19.75, 20.54, 26.34, 27.55, 28.75, 29.44, 31.62, 34.57, 37.14, 38.22, 44.50, 48.00 (2C), 55.30, 77.08, 90.63, 118.65, 121.59, 126.15, 128.28, 128.50, 129.57, 130.10, 133.47, 134.25, 137.42, 138.16, 148.65, 165.43, 219.12; EI MS *m/z* (relative intensity) 478 (M^+, 3), 105 (100), 77 (19); I. R. (KBr) (cm^{-1}) 1740, 1595, 1250, 690; elem. anal., found (calcd for $C_{33}H_{34}O_3$): C 82.68 (82.80); H 7.02 (7.16).

2g: pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.35-2.65 (m, 10 H), 2.83 (dd, 1 H, J = 16.6, 3.9), 7.10-7.55 (m, 4 H), ^{13}C NMR ($CDCl_3$) δ 19.75, 25.10, 27.82, 33.41, 41.89, 49.62, 80.64, 89.99, 122.34, 128.43, 132.79, 133.47, 210.87; I. R. (neat) (cm^{-1}) 1710, 1585, 730.

2h: pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.24-1.84 (m, 8 H), 2.42-2.90 (m, 5 H), 7.30-7.79 (m, 6 H), 8.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 22.20, 23.75, 29.20, 29.26, 30.38, 43.30, 50.94, 79.60, 93.33, 121.34, 125.15, 126.22, 126.38, 126.54, 128.07, 128.19, 130.09, 133.11, 133.42, 214.01; EI MS *m/z* (relative intensity) 276 (M^+, 77), 233 (100); 165 (54); I. R. (neat) (cm^{-1}) 2183, 1695, 1578, 1248.

2i: pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.58 (m, 2 H), 3.08 (m, 4 H), 3.70 (dd, 1 H, J = 6.9, 5.3), 7.21-7.53 (m, 8 H); ^{13}C NMR ($CDCl_3$, C-F coupled) δ 20.55, 27.83, 37.77, 51.61, 81.13, 89.29, 121.25, 124.33, 124.41, 127.04, 127.24, 127.30, 127.78, 128.19, 128.26, 128.34, 128.41, 128.74, 130.62, 131.06, 134.68, 135.35, 137.22, 209.99; I. R. (neat) (cm^{-1}) 2190, 1720, 1600.

2j: pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.66 (m, 2 H), 2.45 (m, 2 H), 2.65-3.30 (m, 5 H), 7.13-7.43 (m, 6 H), 7.66-7.76 (m, 4 H), 7.86 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.57, 25.36, 29.26, 33.39, 49.00, 81.93, 88.61, 120.99, 126.28, 126.34, 126.43, 127.49, 127.62, 127.75, 128.47, 128.60, 129.88, 131.09, 131.62, 132.42, 132.90, 139.08, 141.97, 205.22; EI MS *m/z* (relative intensity) 324 (M^+, 100); 323 (31); 295 (13); 267 (21); 165 (87); 152 (30); 91 (21); I. R. (neat) (cm^{-1}) 2185, 1670, 1593, 1235.

2k: white solid; mp 85-87 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 3 H), 0.89-2.56 (m, 20 H), 1.34 (s, 3 H), 2.59 (s, 3 H), 3.04 (dd, 1 H, J = 2.8), 3.65 (t, 1 H, J = 8.4), 5.75 (s, 1 H), 7.45 and 7.88 (AA'BB' system, 4 H, J = 6.6); ^{13}C NMR ($CDCl_3$) δ 11.06, 17.70, 19.82, 20.55, 23.31, 26.60, 30.31, 31.41, 32.49, 35.49, 36.34, 39.40, 41.56, 41.78, 42.78, 50.40, 54.25, 81.36, 81.58, 92.08, 123.20, 128.17, 128.85, 131.75, 135.75, 171.05, 175.09, 198.72; EI MS *m/z* (relative intensity) 444 (M^+, 100); 443 (33), 429(11), 329 (9), 277 (15), 263 (24), 252 (9), 235 (13), 147 (25), 121 (28), 105 (25), 91 (38); I. R. (KBr) (cm^{-1}) 3410, 2108, 1703, 1660, 1595, 1250; elem. anal., found (calcd for $C_{30}H_{36}O_3$): C 80.91 (81.03), H 8.08 (8.16).

2-(4-nitrobenzoyl)-methyl-17β-hydroxyandrost-4-en-3-one 7.

The reaction performed as reported in Ref. 24 gave after flash chromatography (silica gel, hexane/ethylacetate 1:1) compound 7 as a pale yellow solid (90 %). M.p. 75-79 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 and 1.26 (s, 3 H), 0.78-2.54 (19 H, aliphatic pattern), 3.05 (m, 2 H), 3.65 (t, 1 H, J= 7.6), 3.88 and 4.06 (d, 1 H, J= 15.2), 5.73 (bs, 1H), 7.40 and 8.20 (AA'BB' system, 4 H, J= 10.9); ^{13}C NMR ($CDCl_3$) δ 11.42, 17.85, 20.89, 22.71, 22.88, 23.69, 30.81, 31.84, 32.89, 35.05, 36.29, 39.31, 40.11, 42.95, 43.16, 50.22, 50.85, 54.72, 81.95, 123.13, 124.05, 131.07, 142.17, 171.41, 199.99, 205.69; EI MS *m/z* (relative intensity) 465 (M^+, 2), 329 (100); I. R. (KBr) (cm^{-1}) 3640, 1720, 1670, 1515; elem. anal., found (calcd for $C_{28}H_{35}NO_5$): C 72.35 (72.22); H 7.89 (7.57).

4-Pentynone 2m[27].

Pale yellow oil; yield 50 %; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 6 H); 1.03 (s, 3 H); 1.05 (s, 3 H); 1.32 (s, 2 H); 1.95 (s, 2 H); 2.84 (dd, 1 H, J = 18, 8.5); 3.17 (dd, 1 H, J = 18, 6.5); 3.64 (s, 2 H); 4.37 (dd, 1 H, J = 6.5, 8.5); 7.18 (s, 1H); 7.19 (m, 2 H); 7.22-7.35 (m, 8 H);); ^{13}C NMR ($CDCl_3$) δ 22.33, 29.49 (2C), 29.98, 30.36, 30.43, 33.88, 35.37, 48.22, 49.38, 55.72, 79.81, 90.95, 127.02, 128.09, 128.37, 128.59, 129.22, 129.37, 133.49, 136.47, 136.56, 154.94, 179.95, 205.19; I. R. (neat) (cm^{-1}) 2080, 1720, 1680, 1590.

1, 2, 4-Trisubstituted-Furans 8a-m. General procedures:

To a well stirred suspension of potassium *tert*-butoxide (1.2 mmol, 135 mg) in dry DMF (1 ml) a solution of the appropriate 4-pentynone **1** or **2** (1 mmol) in dry DMF (2 ml), was added. The mixture was stirred at 60°C for 1-5 h and then poured in HCl 0.1 N (50 ml)/EtOAc (50 ml). The organic layer was separated and the aqueous phase extracted twice with EtOAc. The combined organic phases, dried over Na_2SO_4, were evaporated to dryness and the crude **8** purified by flash chromatography over silica gel eluting with hexane/EtOAc mixture.

8a: pale yellow oil; yield 61 %; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 4.07 (s, 2 H), 6.13 (s, 1 H), 6.99-7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.50, 32.77, 107.18, 123.03, 126.24, 126.38, 127.98, 128.10, 128.24, 128.50, 134.21, 138.86, 147.30, 150.71. I. R. (neat) (cm^{-1}) 1600, 1580, 750, 710, 680.

8b: pale yellow oil; yield 62 %; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 2.84 (t, 2 H, J = 8), 3.03 (t, 2 H, J = 8), 6.23 (s, 1 H), 6.86-7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.69, 21.95, 29.16, 107.19, 122.07, 124.13, 124.53, 125.38, 126,26, 128.42, 131.54, 133.08, 151.88; I. R. (neat) (cm^{-1}) 1590, 1570, 780, 740, 710.

8c: pale yellow oil; yield 68 %; ^{1}H NMR ($CDCl_3$) δ 1.92-2.04 (m, 2 H), 2.36 (d, 3 H, J = 1), 2.76 (t, 2 H, J = 6.5), 2.88 (m, 2 H), 5.96 (q, 1 H, J = 1), 7.12 (m, 2 H), 7.25 (m, 1 H), 7.82 (d, 1 H, J = 7.6); ^{13}C NMR ($CDCl_3$) δ 14.05, 25.43, 28.26, 36.63, 110.85, 123.85, 125.03, 126.48, 126.70, 129.82, 131.17, 138.95, 146.93, 151.60; EI MS *m/z* (relative intensity) 198 (M^+, 100), 183 (17), 155 (61), 141 (17), 128 (32), 115 (19); I. R. (neat) (cm^{-1}) 1590, 1550, 780, 730, 710.

8e: white solid; yield 90 %; mp 118-123 °C; ^{1}H NMR ($CDCl_3$) δ 4.17 (s, 2 H), 6.80 (s, 1 H), 7.10-7.41 (m, 13 H), 7.65 (dd, 2 H, J = 7,1); ^{13}C NMR ($CDCl_3$) δ 32.92, 106.59, 123.58, 126.34, 126.78, 127.17, 127.85, 128.25, 128.30, 128.54, 128.57, 129.43, 130.69, 133.73, 138.48, 148.91, 152.41; EI MS *m/z* (relative intensity) 310 (M^+, 66), 309 (26), 105 (100), 91 (40); I. R. (KBr) (cm^{-1}) 1640, 1595, 740, 710, 670; elem. anal., found (calcd for $C_{23}H_{18}O$): C 88.65 (88.99); H 5.77 (5.84).

8f: white solid; yield 79 %; mp 121-125 °C; ^{1}H NMR ($CDCl_3$) δ 4.17 (s, 2 H), 6.52 (s, 1 H), 6.84-7.85 (m, 17 H); ^{13}C NMR ($CDCl_3$) δ 31.94, 109.19, 115.29, 125.24, 125.79, 126.49, 127.28, 127.62, 128.01, 128.38, 128.71, 129.28, 129.54, 132.55, 136.02, 137.38, 143.59, 148.16, 150.85; EI MS *m/z* (relative intensity) 336 (M^+, 2), 335 (6), 261 (17), 131 (36), 105 (100), 91 (59); I. R. (KBr) (cm^{-1}) 1654, 1598, 1494, 756, 668; elem. anal., found (calcd for $C_{25}H_{20}O$): C 89.07 (89.24); H 5.75 (5.99).

8g: pale yellow oil; yield 70 %; ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 2 H), 4.09 (s, 2 H), 6.13 (s, 1 H), 7.15-7.34 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 32.82, 33.86, 108.17, 126.33, 126.57, 127.56, 128.27, 128.53, 128.58, 128.80, 128.88, 130.13, 131.21, 133.91, 136.53, 138.67, 148.24, 152.68; EI MS *m/z* (relative intensity) 358 (M^+, 1.5), 357 (2), 248 (5), 233 (4), 191 (5), 175 (10), 165 (5), 139 (38), 125 (20), 105 (48), 91 (100); I. R. (neat) (cm^{-1}) 1655, 1590, 770.

8h: pale yellow oil; yield 70 %; ^{1}H NMR ($CDCl_3$) δ 1.55-1.73 (m, 4 H), 2.34 (t, 2 H, J = 4.4), 2.52 (t, 2 H, J = 4.4), 3.85 (s, 2 H), 5.77 (s, 1 H), 7.16 and 7.25 (AA'BB' system, 4H, J = 8.3); ^{13}C NMR ($CDCl_3$) δ 22.10, 22.70,

23.15 (2 C), 31.64, 107.35, 128.24, 128.56, 129.49, 130.10, 137.07, 149.82, 151.52; EI MS *m/z* (relative intensity): 248 (M+2, 10), 246 (M^+, 37), 245 (100), 139(43), 125 (63); I. R. (KBr) (cm^{-1}) 1655, 1590, 728, 668.

8i: pale yellow oil; yield 61 %; ^1H NMR ($CDCl_3$) δ 1.56-1.80 (m, 6 H), 2.36 (t, 2 H, J = 5.8), 2.74 (t, 2 H, J = 5.8), 4.35 (s, 2 H), 5.64 (s, 1 H), 7.35-7.57 (m, 4 H), 7.76-7.92 (m, 2 H), 8.06-8.12 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.63, 27.19, 29.26, 29.40, 31.18, 32.40, 110.68, 121.77, 124.66, 126.03, 126.08, 126.41, 127.44, 127.77, 129.09, 132.57, 134.41, 135.07, 150.43, 152.26; EI MS *m/z* (relative intensity) 276 (M^+, 100), 222 (14), 205 (14), 191 (24), 165 (34), 141 (55), 135 (45), 115 (41), 107 (26), 91 (20); I. R. (neat) (cm^{-1}) 1575, 780, 750, 710.

8j: pale yellow oil; yield 76 %; ^1H NMR ($CDCl_3$) δ 2.83 (t, 2 H, J = 7.7), 3.03 (t, 2H, J = 7.7), 4.00 (s, 2 H), 6.28 (s, 1 H), 7.05-7.18 (m, 4 H), 7.42-7.53 (m, 4 H); ^{13}C NMR ($CDCl_3$, C-F coupled) δ 21.96, 29.36, 34.48, 103.44, 119.24, 122.02, 123.37, 123.45, 123.52, 125.45, 125.52, 125.67, 126.71, 127.97, 128.97, 131.19, 132.14, 133.05, 139.07, 152.10, 152.78; EI MS *m/z* (relative intensity) 328 (M^+, 100), 309 (7), 285 (7), 215 (9), 181 (13), 169 (28), 159 (28), 141 (56), 115 (42); I. R. (neat) (cm^{-1}) 1630,1590, 790, 740.

8k: pale yellow oil; yield 75 %; ^1H NMR ($CDCl_3$) δ 1.92 (m, 2 H), 2.70 (t, 2 H, J = 6.4), 2.84 (t, 2 H, J = 5.6), 4.14 (s. 2 H), 5.91 (s, 1 H), 7.08 (m, 2 H), 7.21 (m, 1 H), 7.44 (m, 3H), 7.80 (m, 5 H); ^{13}C NMR ($CDCl_3$, 2C overlap in the aromatic pattern) δ 24.73, 27.69, 34.78, 35.98, 111.07, 123.20, 124.64, 125.49, 126.00, 126.10, 126.14, 127.15, 127.36, 127.62, 128.11, 129.27, 130.45, 132.27, 133.57, 135.51, 138.57, 146.99, 153.51; EI MS *m/z* (relative intensity) 324 (M^+, 100), 323 (18), 165 (15), 153 (14), 141 (30), 115 (26); I. R. (neat) (cm^{-1}) 1595, 790, 745, 710.

8l: white solid; yield 70 %; m.p. 85-87 °C; ^1H NMR ($CDCl_3$) δ 0.80, 1.03 and 2.59 (s, 3H), 1.20-2.91 (19 H, aliphatic pattern), 3.67 (t, 1H, J = 8.5), 5.36 (m, 1H), 5.47 (m, 1H), 5.63 (m, 1H), 7.63 and 7.90 (AA'BB' system, 4 H, J = 9); ^{13}C NMR ($CDCl_3$) δ 11.09, 19.97, 21.03, 23.36, 26.52, 30.51, 31.36, 31.72, 33.40, 36.39, 36.52, 36.86, 39.86, 42.82, 48.14, 51.43, 81.82, 99.87, 102.34, 121.46, 127.50, 128.59, 130.34, 139.66, 140.75, 156.35, 156.98, 197.73; EI MS *m/z* (relative intensity) 444 (M^+, 100), 429 (5), 263 (5), 145 (6), 133 (6), 105 (12); ; I. R. (KBr) (cm^{-1}) 3350, 1670, 1590; elem. anal., found (calcd for $C_{30}H_{36}O_3$): C 80.83 (81.03); H 8.03 (8.16).

8m: pale yellow oil; yield 75 %; ^1H NMR ($CDCl_3$) δ 0.92 (s, 6 H), 1.06 (s, 6 H), 1.33 (s, 2 H), 2.01 (s, 2 H), 4.01 (s, 2 H), 4.09 (s, 2 H), 6.34 (s, 1 H), 6.68 (s, 1 H), 7.20-7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 29.59 (2C), 30.16, 30.65 (2C), 32.74, 33.73, 36.30, 37.51, 49.14, 109.41, 123.42, 126.27, 126.54, 127.56, 128.19, 128.53 (2C), 133.89, 134.75, 138.65, 147.89, 148.30, 149.71, 196.63; EI MS *m/z* (relative intensity) 412 (M^+, 2), 411 (3), 165 (39), 137 (16), 105 (54), 95 (51), 91 (100), 81 (30); I. R. (neat) (cm^{-1}) 190, 1620, 1590, 720.

Furan 8d.

Compound **8d** was obtained as by-product during the second hydrolytic step of the propargylation of testosterone performed as described in Ref. 21. Purification of the crude reaction mixture by flash chromatography (silica gel, n-hexane/ethyl acetate 8:2) yields progressively 2-hydroxymethylene-17β-

hydroxyandrost-4-en-3-one **1g** (33%) and **8d** (19%). The yield of **8d** can be improved to 32% if a prolonged reaction time was used (24 h). White solid; m.p. 72-75 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3 H), 1.04 (s, 3 H), 2.31 (s, 3 H), 0.90-1.68 (m, 12 H), 1.70-2.13 (m, 4 H), 2.30-2.42 (m, 2 H), 3.66 (t, 1 H, J = 7.8), 5.78 (s, 1 H), 7.36 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.03, 13.67, 18.06, 20.99, 23.35, 30.25, 30.89, 32.38, 35.71, 36.42, 37.51, 39.91, 42.76, 50.41, 53.21, 81.45, 106.46, 122.88, 123.11, 165.15, 170.33, 189.14; I. R. (KBr) (cm^{-1})3295, 1610; elem. anal., found (calcd for $C_{22}H_{30}O_2$): C 80.74 (80.93); H 9.12 (9.26).

(E,E) and (Z,E)-1,3,5-triphenyl-penta-2,4-dien-1-ones 9a and 9b.

To a solution of 1,3,5-triphenyl-4-pentyn-1-one **2a** (176 mg, 0.567 mmol) in dry MeOH (10 ml) a solution of MeONa in MeOH (30 %, 4 ml) was added. The reaction mixture was heated at 60 °C for 1h 30' then diluted with HCl 0.1 M (80 ml) and extracted twice with ethyl acetate (50 ml). The organic layer, dried over anidrous sodium sulphate, was then evaporated to dryness and the crude purified by flash chromatography over silica gel (hexane/EtOAc 99:1) yielding **9a** (87 %) and **9a** (17 %).

(E,E)-1,3,5-triphenyl-penta-2,4-dien-1-one 9a: ^{1}H NMR ($CDCl_3$) δ 6.74 (d, 1 H, J = 16.4), 6.89 (d, 1 H, J = 1), 7.29-7.61 (m, 13 H), 8.02 (dd, 2 H, J = 6.5, 1.7), 8.52 (dd, 1 H, J = 16.2, 1); ^{13}C NMR ($CDCl_3$) δ 122.97, 127.52, 128.10, 128.76, 128.84, 129.03, 129.16 (2C), 129.42, 129.69, 132.98, 137.14, 140.06, 141.05, 141.56, 156.33, 191.45; EI MS *m/z* (relative intensity) 310 (M^+, 76), 309 (37), 233 (58), 205 (34), 105 (63), 77 (100).

(Z,E)-1,3,5-triphenyl-penta-2,4-dien-1-one 9b: ^{1}H NMR ($CDCl_3$) δ 6.50 (d, 1 H, J = 15.8); 7.01 (s, 1 H); 7.14-7.86 (m, 14 H); 7.88 (dd, 2 H, J = 7.8, 1).

(E,E,E) and (E,Z,E)-1,5,7-triphenyl-epta-1,4,6-trien-3-ones 9c and 9d.

To a solution of 1,5,7-triphenyl-epta-1-en-6-yn-3-one **2b** (150 mg, 0.445 mmol) in dry MeOH (10 ml) a solution of MeONa in MeOH (30 %, 3 ml) was added. The reaction mixture was heated at 60 °C for 1h then diluted with HCl 0.1 M (80 ml) and extracted twice with ethyl acetate (50 ml). The organic layer, dried over anydrous sodium sulphate, was then evaporated to dryness and the crude purified by flash chromatography over silica gel (hexane/EtOAc 97:3) yielding **9c** (50 %) and **9d** (41 %).

(E,E,E)-1,5,7-triphenyl-epta-1,4,6-trien-3-ones 9c: ^{1}H NMR ($CDCl_3$) δ 6.42 (d, 1 H, J = 0.7), 6.71 (d, 1 H, J = 14), 6.93 (d, 1 H, J = 16), 7.23-7.57 (m, 15 H), 7.67 (d, 1 H, J = 16), 8.62 (dd, 1H, J = 14, 0.8); ^{13}C NMR ($CDCl_3$) δ 125.13, 127.02, 127.18, 127.66, 128.14, 128.39, 128.73, 128.87, 128.92, 129.17, 129.20, 129.27, 130.34, 134.66, 136.63, 141.15, 142.51, 155.44, 189.44.

(E,Z,E)-1,5,7-triphenyl-epta-1,4,6-trien-3-ones 9d: ^{1}H NMR ($CDCl_3$) δ 6.38 (d, 1 H, J = 15.8), 6.53 (d, 1 H, J = 0.6), 7.15-7.45 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 127.02, 127.17, 127.66, 128.31, 128.40, 128.49, 128.63, 128.68, 128.88, 128.98, 130.03, 130.17, 131.89, 134.93, 136.23, 138.81, 141.50, 152.71, 190.54.

2-Cyclopentenone 10.

To a solution of 4-pentynone **2m** (0.2 g, 0.578 mmol) in dry methanol (15 ml) a solution of a solution of MeONa in MeOH (30 %, 3 ml) was added. The reaction mixture was stirred at room temperature for 1h then

diluted with HCl 0.1 M (80 ml) and extracted twice with ethyl acetate (50 ml). The organic layer, dried over anydrous sodium sulphate, was then evaporated to dryness and the crude purified by flash chromatography over silica gel (hexane/EtOAc, 98:2) yielding pure **10** as a pale yellow oil (37 %).

^{1}H NMR ($CDCl_3$) δ 0.94 (s, 6 H), 1.02 (s, 6 H), 1.35 (s, 2 H), 2.02 (s, 2 H), 2.84 (dd, 1 H, J = 19, 2), 3.16 (dd, 1 H, J = 19, 2), 3.75 (dd, 1 H, J = 7, 2), 3.98 (AB system, 2 H, J = 16), 6.45 (s, 1 H), 7.18-7.43 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 29.51, 29.63, 30.15, 30.58, 30.65, 33.80, 36,26, 39.82, 40.70, 49.05, 51.56, 126.86, 127.59, 128.12, 128.43, 128.77, 129.06, 131.27, 135.11, 139.67, 141.20, 150.03, 167.70, 197.05, 206.09; EI MS *m/z* (relative intensity) 412 (M^+, 5), 411 (3), 165 (100), 137 (18), 105 (18), 95 (27); I. R. (neat) (cm^{-1}) 1700, 1670, 1620, 1595, 720, 680.

1,3,6-Triphenyl-esan-1,4-dione 11.

Compound **11** was prepared according to the procedure described in Ref. 30: Yield 60 %; yellow solid; m.p. 79-80 °C; ^{1}H NMR ($CDCl_3$) δ 3.12 (dd, 1 H, J = 18, 3.7), 3.83 (AB system, 2 H, J = 18.6), 3.98 (dd, 1 H, J = 18, 10), 4.51 (dd, 1 H, J = 10, 3.7), 6.83-7.45 (m, 13 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 42.62, 48.53, 52.78, 126.72, 127.57, 128.02, 128.30, 128.46, 128.48, 129.07, 129.77, 133.15, 134.06, 136.36, 137.65, 197.97, 206.67; EI MS *m/z* (relative intensity) 328 (M^+, 1), 310 (1), 237 (28), 105 (100), 91 (27); I. R. (KBr) (cm^{-1}) 1715, 1685, 1595, 1578; elem. anal., found (calcd for $C_{23}H_{20}O_2$): C 84.27 (84.11); H 6.27 (6.13).

N-Benzylpyrroles 12. General procedure.

A solution of 4-pentynone **1** or **2** (2.03 mmol) and benzylamine (0.325 g, 3.04 mmol) in dry toluene (50 ml) or in xylene (50 ml) with a catalytic amount of pTSA was heated under reflux, in a Dean-Stark apparatus (Aldrich), for 2-24 h. The solvent was then evaporated under reduced pressure. The residue, purified by flash chromatography (silica gel, n-hexane/ethyl acetate mixture), afforded **12**.

12b: dark oil; yield 59 %; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 2.40-2.53 (m, 2 H), 2.64-2.77 (m, 4 H), 5.04 (s, 2 H), 5.86 (s, 1 H), 7.09-7.12 (m, 2 H), 7.33-7.45 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.22, 25.50, 26.41, 29.28, 49.15, 102.48, 125.05, 126.90, 127.66, 129.20, 131.82, 137.85, 139.22; EI MS *m/z* (relative intensity) 211 (M^+, 48), 210 (36), 196 (15), 120 (15), 91 (100).

12d: dark oil; yield 97 %; ^{1}H NMR ($CDCl_3$) δ 1.53-1.69 (m, 4 H), 1.97 (s, 3 H), 2.26 (t, 2 H, J = 4.9), 2.39 (t, 2 H, J = 4.9), 4.75 (s, 2 H), 5.62 (s, 1 H), 6.73-6.77 (m, 2 H), 6.98-7.18 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.76, 22.85, 23.95, 24.33, 24.69, 47.10, 106.15, 117.01, 126.57, 127.59, 127.65, 127.70, 129.36, 139.64; I. R. (neat) (cm^{-1}) 1642, 1606, 1452, 1440, 772.

12e: dark oil; yield 78 %; ^{1}H NMR ($CDCl_3$) δ 1.66-1.94 (m, 6 H), 2.26 (s, 3 H), 2.64-2.74 (m, 4 H), 5.12 (s, 2 H), 5.88 (s, 1 H), 7.01-7.05 (m, 2 H), 7.33-7.46 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.78, 27.36, 28.49, 28.96, 29.77, 32.56, 47.16, 108.06, 122.02, 125.83, 126.24, 127.47, 129.21, 130.89, 139.71; EI MS *m/z* (relative intensity) 239 (M^+, 69), 238 (29), 224 (12), 210 (19), 198 (14), 185 (15), 148 (12), 91 (100).

12f: yellow solid; yield 77 %; mp 79-85 °C; more than one isomer are present in the final product; ^{1}H NMR

($CDCl_3$) δ 0.80 (s, 3 H), 0.98 (s, 3 H), 2.13 (s, 3 H), 0.90-2.45 (m, 17 H), 2.50, 2.73 and 3.05, 3.31 (two couple of d, ratio 4:1, 2 H), 4.96 and 5.00 (two singlets, ratio 4:1, 2 H), 5.74 and 5.76 (two singlets, ratio 4:1, 1 H) 5.81-6.05 (m, 1 H), 6.89-6.98 (m, 2 H), 7.20-7.35 (m, 3 H); ^{13}C NMR ($CDCl_3$) values for the major isomer in parentheses δ 11.48, (11.58), (12.62), (18.69), 20.64, (21.86), 24.01, (24.07), (31.05), (31.86), 32.26, (32.58), 33.30, (37.26), (37.43), (37.98), 38.55, 38.58, (40.66), 43.19, (43.45), (46.75), 47.02, 51.01, (51.26), 51.82, (55.27), (82.38), 105.88, (106.61), (110.53), (114.79), 115.09, 121.77, 124.90, 126.22, (126.43), 126.47, 126.52, (127.47), (127.65), (127.86), 128.02, (129.14), (139.34), 139.80, (141.32); EI MS *m/z* (relative intensity) 415 (M^+, 16), 414 (14), 413 (40), 400 (16), 248 (12), 91 (100); I. R. (KBr) (cm^{-1}) 3422, 1654, 1544, 1496, 1258. Elem. anal., found (calcd for $C_{29}H_{37}NO$): C 83.68 (83.80); H 8.73 (8.97); N 3.28 (3.37).

12h: yellow solid; yield 92 %; mp 155-158 °C; ^1H NMR ($CDCl_3$) δ 3.78 (S, 2 H), 4.01 (s, 2 H), 4.69 (s, 2 H), 6.16 (s, 1 H), 6.75-7.40 (m, 19 H); ^{13}C NMR ($CDCl_3$, 2C overlapp in the aromatic pattern) δ 30.73, 32.41, 47.06, 108.41, 123.08, 125.40, 126.21, 126.82, 127.06, 127.48, 127.76, 128.42, 128.46, 128.62, 128.67, 129.82, 130.89, 132.07, 136.96, 137.68, 138.13, 139.90; EI MS *m/z* (relative intensity) 449 (M+2, 3.3), 447 (M^+, 10), 125(10), 91 (100); I. R. (KBr) (cm^{-1}) 1595, 735, 710;elem. anal., found (calcd for $C_{31}H_{26}NCl$): C 82.86 (83.10); H 5.79 (5.85); N 3.02 (3.12).

12j: yellow solid; yield 76 %; mp 157-159 °C; ^1H NMR ($CDCl_3$) δ 2.11-2.22 (m, 2 H), 2.63 (t, 2 H, J = 7.7), 3.57 (s, 2 H), 3.73 (s, 3 H), 4.02 (s, 2 H), 4.81 (s, 2 H), 5.57 (t, 1 H, J = 4.3), 6.24 (s, 1 H), 6.58-7.46 (m, 18 H); ^{13}C NMR ($CDCl_3$, 2 couple of C overlapp in the aromatic pattern) δ 22.05, 27.60, 29.18, 29.70, 45.99, 54.07, 107.12, 109.61, 112.60, 121.85, 122.80, 123.01, 124.14, 124.50 125.10, 125.20, 125.92, 126.41, 126.77, 127.29, 127.55, 129.36, 132.45, 136.15, 137.26, 137.50, 139.12, 157.26; EI MS *m/z* (relative intensity) 495 (M^+, 45), 404 (12), 250 (23), 115 (10), 91 (100); I. R. (KBr) (cm^{-1}) 1595,735,710; elem. anal., found (calcd for $C_{36}H_{33}NO$): C 87.12 (87.22); H 6.65 (6.71); N 2.77 (2.82).

12k: yellow solid; yield 55 %; mp 105-108 °C; ^1H NMR ($CDCl_3$) δ 2.32-2.44 (m, 2 H), 2.56-2.62 (m, 4 H), 3.90 (s, 2 H), 4.84 (s, 2 H), 5.76 (s, 1 H), 6.88-7.08 (m, 2 H), 7.19-7.33 (m, 5 H), 8.07 (d, 2 H, J = 8.6); ^{13}C NMR ($CDCl_3$) δ 25.40, 26.28, 29.09, 34.01, 49.35, 104.58, 124.02, 125.37, 126.62, 127.75, 129.14, 129.77, 132.55, 138.57, 139.45, 147.00, 148.15; EI MS *m/z* (relative intensity) 332 (M^+, 13), 112 (5), 105 (7), 92 (10), 91 (100); elem. anal., found (calcd for $C_{21}H_{20}N_2O_2$): C 75.63 (75.87); H 5.89 (6.06); N 8.16 (8.42).

12m: dark oil; yield 94 %; ^1H NMR ($CDCl_3$) δ 1.61-1.87(m, 4 H), 2.37 (m, 2 H), 2.49 (m, 2 H), 3.70 (s, 2 H), 4.82 (s, 2 H), 5.63 (s, 1 H), 6.79-7.23 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 21.90, 23.06, 23.36, 23.72, 32.37, 46.39, 106.71, 116.34, 125.63, 126.90, 127.99, 128.31, 128.58, 129.45, 129.99, 131.71, 138.07, 138.54; EI MS *m/z* (relative intensity) 337 (M+2, 2.3), 335 (M^+, 107.1), 224 (5.7), 210 (6.4), 180 (6.7), 125 (8.4), 91 (100).

12n: yellow solid; yield 92 %; mp 110-112 °C; ^1H NMR ($CDCl_3$) δ 2.63 (t, 2 H, J = 8.05), 2.94 (t, 2 H, J = 7.88), 3.86 (s, 2 H), 4.89 (s, 2 H), 6.22 (s, 1 H), 6.80-7.40 (m, 13 H); ^{13}C NMR ($CDCl_3$, C-F coupled) δ 20.77, 29.57, 32.87, 46.82, 103.45, 118.02, 121.30, 123.14, 123.22, 124.30, 125.23, 125.30, 125.55, 126.71, 127.25,

127.84, 128.76, 128.84, 130.76, 132.00, 132.66, 133.25, 137.73, 140.25; EI MS *m/z* (relative intensity) 417 (M^+, 5.75), 326 (3.7), 167 (4.9), 159 (5.9), 91 (100); I. R. (KBr) (cm^{-1}) 1600, 1590, 780, 740; elem. anal., found (calcd for $C_{27}H_{22}NF_3$): C 77.48 (77.67); H 5.27 (5.31); N 3.27 (3.35).

N-Unsubstituted Pyrroles 12. General procedure.

A solution of the appropriate 4-pentynone **1** or **2** (1.39 mmol) in dry ammonia and methanol (NH_3/MeOH 2M solution, 10.4 ml) was heated at 120 °C in a steel reactor for 9-24 h. The solvent was then evaporated under reduced pressure. The residue, purified by flash chromatography (silica gel, n-hexane/ethyl acetate mixture), afforded **12**.

12a: dark oil; yield 50 %; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 4.08 (s, 2 H), 6.03 (m, 1 H), 7.14-7.57 (m, 11 H), ^{13}C NMR ($CDCl_3$) δ 12.78, 31.48, 107.07, 123.10, 125.59, 125.86, 126.56, 128.19, 128.39, 128.45, 128.75, 129.01, 137.98, 141.05; I. R. (neat) (cm^{-1}) 3414, 1600, 1494, 760.

12c: dark oil; yield 69 %; ^1H NMR ($CDCl_3$) δ 1.57-1.76 (m, 4 H), 2.13 (s, 3 H), 2.35-2.46 (m, 4 H), 5.56 (m, 1 H), 7.15 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.44, 23.16, 23.35, 23.44, 23.53, 105.53, 117.50, 125.84, 126.17; EI MS *m/z* (relative intensity) 135 (M^+, 51), 134 (50), 133 (38), 132 (44), 117 (32), 107 (100), 91 (25).

12g: dark oil; yield 89 %; ^1H NMR ($CDCl_3$) δ 3.89 (s, 2 H), 4.12 (s, 2 H), 6.10 (m, 1 H), 7.13-7.45 (m, 15 H), ^{13}C NMR ($CDCl_3$) δ 33.11, 33.91, 107.94, 122.79, 125.86, 126.16, 126.97, 128.09, 128.89, 129.01, 129.13, 129.21, 129.71, 130.45, 132.69, 137.26, 138.34, 140.04; EI MS *m/z* (relative intensity) 359 (M+2, 23), 357 (M^+, 69), 356 (19), 280 (23), 266 (31), 232 (100), 202 (28), 167 (31), 154 (60), 125 (72), 105 (29), 91 (67); I. R. (neat) (cm^{-1}) 3408, 1672, 1602, 1490, 1090, 1014, 762.

12i: dark oil; yield 65%; ^1H NMR ($CDCl_3$) 2.19-2.26 (m, 2 H), 2.63-2.71 (m, 2 H), 3.64 (s, 2 H), 3.75 (s, 3 H), 4.05 (s, 2 H), 5.71 (t, 1 H, J = 4.5), 6.14 (m, 1 H), 6.57-6.80 (m, 3 H), 7.05-7.52 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 23.07, 28.73, 31.73, 32.61, 55.16, 108.68, 110.79, 113.81, 124.20, 124.79, 126.03, 126.30, 126.96, 127.48, 127.60, 128.33, 128.47, 128.60, 128.86, 129.08, 129.52, 131.79, 133.62, 138.36, 139.71; I. R. (neat) (cm^{-1}) 3440, 1605, 720.

12l: dark oil; yield 84 %; ^1H NMR ($CDCl_3$) δ 1.64-1.78 (m, 4 H), 2.37-2.52 (m, 4 H), 3.81 (s, 2 H), 5.64 (s, 1 H), 7.10 and 7.22 (AA'BB' system, 4 H, J = 8.2); 7.30 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.60, 22.77, 23.36, 23.74, 33.56, 105.77, 118.82, 126.28, 128.18, 128.52, 130.02, 131.93, 138.21; I. R. (neat) (cm^{-1}) 3450, 1600, 780, 760, 720.

12o: dark oil; yield 80 %; ^1H NMR ($CDCl_3$) δ 1.76 (m, 2 H), 2.76 (t, 2 H), 3.02 (t, 2 H), 4.14 (s. 2 H), 5.90 (s, 1 H), 7.08-7.87 (m, 12 H); ^{13}C NMR ($CDCl_3$, 2C) δ 25.43, 26.43, 34.37, 35.41, 110.19, 123.24, 125.51, 126.10, 126.36, 126.52, 126.94, 127.15, 127.33, 127.56, 128.65, 129.92, 131.15, 132.98, 136.63, 139.17, 140.02; EI MS *m/z* (relative intensity) 324 (M^+, 84), 323 (18), 165 (100), 141 (39), 115 (33); I. R. (neat) (cm^{-1}) 3380,1590, 795, 730.

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