Spiro-heterocycles from Substituted Pyridines, Pyrans and Thiopyrans

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A new class of spiro-pyrimidines, pyrazoles and isoxazoles are prepared by nucleophilic reaction of 3,5-diaroyl-2,6-diaryl-piperidine-4,4-dicarbonitrile (1), 3,5-diaroyl-2,6-diaryl-tetrahydropyran-4,4-dicarbonitrile (2) and 3,5-diaroyl-2,6-diaryl-tetrahydrothiopyran-4,4-dicarbonitrile (3) with urea, *N*,*N*'-dimethyl urea, thiourea, hydrazine hydrate and hydroxylamine hydrochloride.

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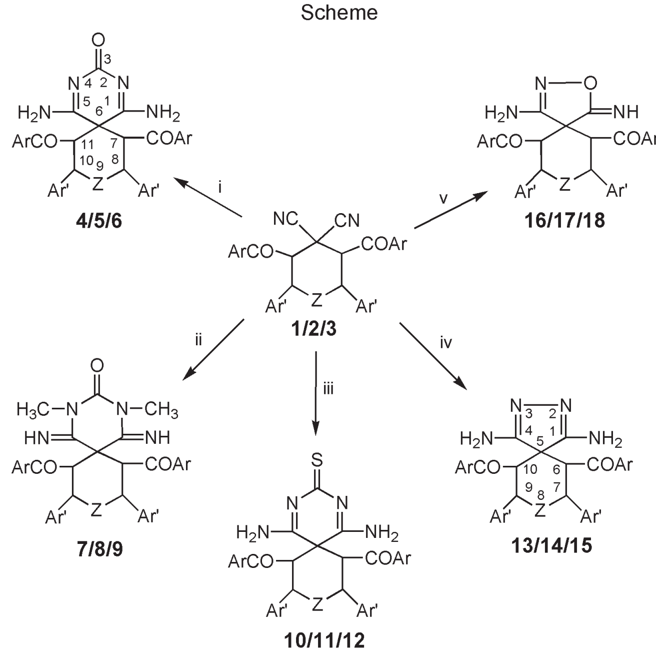
In recent years we have been actively involved in the synthesis of spiro-heterocycles by the reaction of carbocycle- or heterocycle-1,1-dicarboxylic esters with various nucleophiles [1-6]. Prompted by the successful results on this front, we present in this article the utilization of compounds having *gem*-dicyano functionality in the synthesis of spiro-heterocycles by the cyclocondensation of former with various nucleophiles *viz*, urea, *N*,*N'*-dimethyl urea, thiourea, hydrazine hydrate and hydroxylamine hydrochloride.

The 3,5-diaroyl-2,6-diaryl-piperidine-4,4-dicarbonitrile (**1**), 3,5-diaroyl-2,6-diaryl-tetrahydropyran-4,4-dicarbonitrile (**2**) and 3,5-diaroyl-2,6-diaryl-tetrahydrothiopyran-4,4-dicarbonitrile (**3**) are prepared by the reaction of 2,2-bis(1-benzoyl-2-phenyl-vinyl)-malononitrile with NH_4OAc, P_2O_5 and P_2S_5 [7]. The cyclocondensation of **1**, **2** and **3** with urea in the presence of NaOMe gave 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-2,4,9-triazaspiro[5.5]undeca-1,4-dien-3-one (**4**) 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]-undeca-1,4-dien-3-one (**5**) and 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]undeca-1,4-dien-3-one (**6**). Similar reaction of **1, 2** and **3** with *N*,*N'*-dimethyl urea and thiourea afforded 7,11-dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-2,4,9-triazaspiro[5.5]undecan-3-one (**7**), 7,11-dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]-undecan-3-one (**8**), 7,11-dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]undecan-3-one (**9**) and 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-2,4,9-triazaspiro[5.5]undeca-1,4-dien-3-thione (**10**), 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]undeca-1,4-dien-3-thione (**11**), 1,5-diamino-7,11-dibenzoyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]-undeca-1,4-dien-3-thione (**12**), respectively. Likewise, five membered spiro heterocycles, 1,4-diamino-6,10-dibenzoyl-7,9-diphenyl-2,3,8-triazaspiro[4.5]deca-1,3-diene (**13**), 1,4-diamino-6,10-dibenzoyl-7,9-diphenyl-8-oxa-2,3-diazaspiro[4.5]deca-1,3-diene (**14**), 1,4-diamino-6,10-dibenzoyl-7,9-diphenyl-8-thia-2,3-diazaspiro[4.5]deca-1,3-diene (**15**) and 4-amino-6,10-dibenzoyl-7,9-diphenyl-1-imino-2-oxa-3,8-diazaspiro[4.5]deca-3-ene (**16**), 4-amino-6,10-dibenzoyl-7,9-diphenyl-1-imino-2,8-dioxa-3-azaspiro[4.5]deca-3-ene (**17**), 4-amino-6,10-dibenzoyl-7,9-diphenyl-1-imino-2-oxa-8-thia-3-azaspiro[4.5]deca-3-ene (**18**) were prepared by refluxing **1**, **2** and **3** with hydrazine hydrate and hydroxylamine hydrochloride, respectively (Scheme & Table 1). Though there is a possibility of diastereoisomers particularly in compounds **16-18** we were able to isolate one isomer under the conditions adopted. The IR spectra of **4-18** displayed an absorption band at 3210-3340 cm^{-1} for NH_2 and/or NH. Apart from these compounds **4-9** exhibited an absorption band at 1665-1680 cm^{-1} (C=O of pyrimidine ring) while **10-12** at 1480-1520 cm^{-1} (C=S). In the ^1H NMR spectra of these compounds the methine protons displayed doublets at δ 4.30-5.47 (C*H*Ar) and 3.76-4.35 (C*H*COAr). The coupling constants $J \sim 9.0$ Hz indicates that they possess *trans* geometry. Thus the ^1H NMR spectra of **4-18** can be rationalized by

Scheme



		Ar	Ar'
1,4,7,10,13,16; Z=NH	a	Ph	Ph
2,5,8,11,14,17; Z=O	b	Ph	4-OMe•Ph
3,6,9,12,15,18; Z=S	c	4-Cl•Ph	Ph

i) NH_2CONH_2/NaOMe ii) $CH_3NHCONHCH_3$/NaOMe
iii) NH_2CSNH_2/NaOMe iv) NH_2NH_2•H_2O/NaOMe v) NH_2OH•HCl/NaOMe

Table 1

Physical Properties of Compounds **4-18**

Compd. No.	M.P. (°C)	Yield (%)	Mol. Formula (Mol.Wt)	Calcd. (Found) (%) C	H	N
4a	276-278	56	$C_{34}H_{29}N_5O_3$ (555.64)	73.50 (73.12)	5.26 (5.21)	12.60 (12.69)
4b	290-292	60	$C_{36}H_{33}N_5O_5$ (615.69)	70.23 (70.30)	5.40 (5.36)	11.37 (11.46)
4c	>300	63	$C_{34}H_{27}Cl_2N_5O_3$ (624.52)	65.39 (65.45)	4.36 (4.39)	11.21 (11.27)
5a	293-295	62	$C_{34}H_{28}N_4O_4$ (556.63)	73.37 (73.27)	5.07 (5.10)	10.07 (10.19)
5b	260-262	58	$C_{36}H_{32}N_4O_6$ (616.68)	70.12 (70.02)	5.23 (5.27)	9.08 (9.00)
5c	285-287	65	$C_{34}H_{26}Cl_2N_4O_4$ (625.52)	65.28 (65.35)	4.19 (4.16)	8.96 (9.05)
6a	269-271	57	$C_{34}H_{28}N_4O_3S$ (572.69)	71.31 (71.22)	4.93 (4.98)	9.78 (9.84)
6b	276-277	61	$C_{36}H_{32}N_4O_5S$ (632.75)	68.34 (68.28)	5.09 (5.13)	8.85 (8.80)
6c	280-281	65	$C_{34}H_{26}Cl_2N_4O_3S$ (641.59)	63.65 (63.57)	4.08 (5.00)	8.73 (8.79)
7a	288-290	60	$C_{36}H_{33}N_5O_3$ (583.70)	74.08 (73.94)	5.70 (5.75)	12.00 (12.11)
7b	273-275	58	$C_{38}H_{37}N_5O_5$ (643.74)	70.90 (70.99)	5.79 (5.74)	10.88 (10.96)
7c	282-284	66	$C_{36}H_{31}Cl_2N_5O_3$ (625.58)	69.12 (69.18)	4.99 (5.04)	11.19 (11.12)
8a	268-270	62	$C_{36}H_{32}N_4O_4$ (584.68)	73.96 (74.02)	5.52 (5.56)	9.58 (9.63)
8b	293-295	56	$C_{38}H_{36}N_4O_6$ (644.73)	70.79 (70.85)	5.63 (5.60)	8.69 (8.78)
8c	>300	65	$C_{36}H_{30}Cl_2N_4O_4$ (653.58)	66.16 (66.07)	4.63 (4.67)	8.57 (8.50)
9a	272-274	60	$C_{36}H_{32}N_4O_3S$ (600.75)	71.98 (71.91)	5.37 (5.34)	9.33 (9.41)
9b	283-285	67	$C_{38}H_{36}N_4O_5S$ (660.80)	69.07 (69.14)	5.49 (5.51)	8.48 (8.42)
9c	295-297	62	$C_{36}H_{30}Cl_2N_4O_3S$ (669.65)	64.57 (64.52)	4.51 (4.55)	8.37 (8.42)
10a	272-275	59	$C_{34}H_{29}N_5O_2S$ (571.71)	71.43 (71.48)	5.11 (5.04)	12.25 (12.29)
10b	240-242	61	$C_{36}H_{33}N_5O_4S$ (631.76)	68.44 (68.50)	5.26 (5.30)	11.08 (11.00)
10c	>300	65	$C_{34}H_{27}Cl_2N_5O_2S$ (640.59)	63.75 (63.81)	4.25 (4.23)	10.93 (10.99)
11a	296-298	57	$C_{34}H_{28}N_4O_3S$ (572.69)	71.31 (71.38)	4.93 (4.98)	9.78 (9.85)
11b	288-290	66	$C_{36}H_{32}N_4O_5S$ (632.75)	68.34 (68.43)	5.09 (5.06)	8.85 (8.94)
11c	279-281	64	$C_{34}H_{26}Cl_2N_4O_3S$ (641.59)	63.65 (63.58)	4.08 (4.00)	8.73 (8.79)
12a	258-259	58	$C_{34}H_{28}N_4O_2S_2$ (588.76)	69.36 (69.45)	4.79 (4.73)	9.52 (9.64)
12b	278-279	63	$C_{36}H_{32}N_4O_4S_2$ (648.81)	66.64 (66.54)	4.97 (4.92)	8.63 (8.55)
12c	284-286	65	$C_{34}H_{26}Cl_2N_4O_2S_2$ (657.65)	62.09 (62.17)	3.98 (3.92)	8.52 (8.60)
13a	275-277	56	$C_{33}H_{29}N_5O_2$ (527.63)	75.12 (75.05)	5.54 (5.58)	13.27 (13.36)
13b	289-291	61	$C_{35}H_{33}N_5O_4$ (587.68)	71.53 (71.63)	5.66 (5.68)	11.92 (12.00)
13c	297-299	67	$C_{33}H_{27}Cl_2\ N_5O_2$ (596.51)	66.45 (66.39)	4.56 (4.52)	11.74 (11.80)
14a	273-275	59	$C_{33}H_{28}N_4O_3$ (528.62)	74.98 (74.88)	5.34 (5.31)	10.60 (10.68)
14b	279-280	65	$C_{35}H_{32}N_4O_5$ (588.67)	71.41 (71.52)	5.48 (5.51)	9.52 (9.46)
14c	>300	62	$C_{33}H_{26}Cl_2N_4O_3$ (597.51)	66.33 (66.40)	4.39 (4.35)	9.38 (9.46)
15a	248-250	57	$C_{33}H_{28}N_4O_2S$ (544.68)	72.77 (72.83)	5.18 (5.09)	10.29 (10.36)
15b	234-236	66	$C_{35}H_{32}N_4O_4S$ (604.74)	69.51 (69.57)	5.33 (5.37)	9.26 (9.20)
15c	269-271	59	$C_{33}H_{26}Cl_2N_4O_2S$ (613.58)	64.59 (64.65)	4.27 (4.32)	9.13 (9.23)
16a	264-266	58	$C_{33}H_{28}N_4O_3$ (528.62)	74.98 (75.03)	5.34 (5.38)	10.60 (10.66)
16b	258-259	60	$C_{35}H_{32}N_4O_5$ (588.67)	71.41 (71.32)	5.48 (5.45)	9.52 (9.60)
16c	268-270	64	$C_{33}H_{26}Cl_2N_4O_3$ (597.51)	66.33 (66.39)	4.39 (4.37)	9.38 (9.32)
17a	246-248	56	$C_{33}H_{27}N_3O_4$ (529.60)	74.84 (74.81)	5.14 (5.19)	7.93 (7.98)
17b	235-237	61	$C_{35}H_{31}N_3O_6$ (589.65)	71.29 (71.24)	5.29 (5.32)	7.13 (7.23)
17c	256-258	64	$C_{33}H_{25}Cl_2N_3O_4$ (598.49)	66.23 (66.29)	4.21 (4.25)	7.02 (7.09)
18a	232-233	57	$C_{33}H_{27}N_3O_3S$ (545.67)	72.64 (72.69)	4.99 (5.05)	7.70 (7.78)
18b	244-246	63	$C_{35}H_{31}N_3O_5S$ (605.72)	69.40 (69.47)	5.16 (5.11)	6.94 (6.90)
18c	271-272	65	$C_{33}H_{25}Cl_2N_3O_3S$ (614.56)	64.49 (64.43)	4.10 (4.06)	6.84 (6.93)

presuming that the substituents in piperidine, tetrahydropyran and tetrahydrothiopyran rings are in true *cis*-1,3-diequatorial arrangement in their preferred rigid chair conformation [8]. The pyrimidine/pyrazole/isoxazole rings which are nearly planar would be perpendicular to the average plane of the rings. All the compounds displayed a broad singlet at δ 6.68-10.15 (NH_2/NH), which disappeared on deuteration. The compounds **7-9** showed a singlet at δ 2.70-2.74 (N-CH_3) (Table 2).

A new class of amino spiro-pyrimidines, pyrazoles and isoxazoles are prepared by simple and well-versed methodology.

EXPERIMENTAL

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate/hexane, 3:1). The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, model 337 in KBr pellets. The ^{1}H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a Varian EM-360 spectrometer (300 MHz) with TMS as an internal standard. The elemental analyses were performed at Punjab University, Chandigarh, India. The compounds 3,5-diaroyl-2,6-diaryl-piperidine-4,4-dicarbonitrile (**1**), 3,5-diaroyl-2,6-diaryl-tetrahydropyran-4,4-dicarbonitrile (**2**) and 3,5-diaroyl-2,6-diaryl-tetrahydrothiopyran 4,4-dicarbonitrile (**3**) were prepared according to the literature procedure [7].

Table 2

Spectral Data of Compounds of **4-18**

Product	^{1}H NMR (δ, ppm)
4a	3.85 (d, 2H, C_7 & C_{11}-H, *J* = 9.0 Hz), 4.58 (d, 2H, C_8 & C_{10}-H, *J* = 9.0 Hz), 7.05-7.87 (m, 20H, H_{arom}), 6.68 (bs, 4H, NH_2), 10.15 (bs, 1H, NH).
4b	3.72 (s, 6H, Ar-OCH_3), 3.80 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 4.55 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.10-7.92 (m, 18H, H_{arom}), 6.63 (bs, 4H, NH_2), 10.18 (bs, 1H, NH).
4c	3.82 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 4.59 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 7.14-7.83 (m, 18H, H_{arom}), 6.71 (bs, 4H, NH_2), 10.05 (bs, 1H, NH).
5a	3.92 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 5.43 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.22-7.92 (m, 20H, H_{arom}), 6.88 (bs, 4H, NH_2).
5b	3.74 (s, 6H, Ar-OCH_3), 3.90 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 5.41 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.18-7.85 (m, 18H, H_{arom}), 6.78 (bs, 4H, NH_2).
5c	3.88 (d, 2H, C_7 & C_{11}-H, *J* = 9.4 Hz), 5.42 (d, 2H, C_8 & C_{10}-H, *J* = 9.4 Hz), 7.15-7.87 (m, 18H, H_{arom}), 6.72 (bs, 4H, NH_2).
6a	4.02 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 4.29 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 6.69 (bs, 4H, NH_2), 7.04-7.90 (m, 20H, H_{arom}).
6b	3.72 (s, 6H, Ar-OCH_3), 4.06 (d, 2H, C_7 & C_{11}-H, *J* = 9.5 Hz), 4.30 (d, 2H, C_8 & C_{10}-H, *J* = 9.5 Hz), 6.73 (bs, 4H NH_2), 7.09-7.85 (m, 18H, H_{arom}).
6c	4.04 (d, 2H, C_7 & C_{11}-H, *J* = 9.3 Hz), 4.36 (d, 2H, C_8 & C_{10}-H, *J* = 9.3 Hz), 6.75 (bs, 4H NH_2), 7.11-7.86 (m, 18H, H_{arom}).
7a	2.70 (s, 6H, N-CH_3), 3.82 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 4.32 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 7.06-7.92 (m, 20H, H_{arom}), 9.24 (bs, 3H, NH).
7b	2.72 (s, 6H, N-CH_3), 3.70 (s, 6H, Ar-OCH_3), 3.81 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 4.36 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.08-7.95 (m, 18H, H_{arom}), 9.22 (bs, 3H, NH).
7c	2.70 (s, 6H, N-CH_3), 3.84 (d, 2H, C_7 & C_{11}-H, *J* = 9.4 Hz), 4.34 (d, 2H, C_8 & C_{10}-H, *J* = 9.4 Hz), 7.15-7.87 (m, 18H, H_{arom}), 9.28 (bs, 3H, NH).
8a	2.74 (s, 6H, N-CH_3), 3.92 (d, 2H, C_7 & C_{11}-H, *J* = 9.4 Hz), 5.46 (d, 2H, C_8 & C_{10}-H, *J* = 9.4 Hz), 7.18-7.90 (m, 20H, H_{arom}), 9.18 (bs, 2H, NH).
8b	2.71 (s, 6H, N-CH_3), 3.74 (s, 6H, Ar-OCH_3), 3.99 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 5.42 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 7.12-7.85 (m, 18H, H_{arom}), 9.24 (bs, 2H, NH).
8c	2.73 (s, 6H, N-CH_3), 3.94 (d, 2H, C_7 & C_{11}-H, *J* = 9.3 Hz), 5.48 (d, 2H, C_8 & C_{10}-H, *J* = 9.3 Hz), 7.15-7.90 (m, 18H, H_{arom}), 9.24 (bs, 2H, NH).
9a	2.74 (s, 6H, N-CH_3), 3.96 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 4.35 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.15-7.87 (m, 20H, H_{arom}), 9.06 (bs, 2H, NH).
9b	2.72 (s, 6H, N-CH_3), 3.76 (s, 6H, Ar-OCH_3), 4.08 (d, 2H, C_7 & C_{11}-H, *J* = 9.0 Hz), 4.32 (d, 2H, C_8 & C_{10}-H, *J* = 9.0 Hz), 7.04-7.83 (m, 18H, H_{arom}), 9.24 (bs, 2H, NH).
9c	2.70 (s, 6H, N-CH_3), 4.04 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 4.38 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 7.08-7.92 (m, 18H, H_{arom}), 9.24 (bs, 2H, NH).
10a	3.83 (d, 2H, C_7 & C_{11}-H, *J* = 9.4 Hz), 4.57 (d, 2H, C_8 & C_{10}-H, *J* = 9.4 Hz), 6.94-7.84 (m, 20H, H_{arom}), 9.22 (bs, 5H, NH, NH_2).
10b	3.70 (s, 6H, Ar-OCH_3), 3.82 (d, 2H, C_7 & C_{11}-H, *J* = 9.3 Hz), 4.56 (d, 2H, C_8 & C_{10}-H, *J* = 9.3 Hz), 6.98-7.87 (m, 18H, H_{arom}), 9.25 (bs, 5H, NH, NH_2).
10c	3.87 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 4.52 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.02-7.85 (m, 18H, H_{arom}), 9.29 (bs, 5H, NH, NH_2).
11a	3.76 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 5.42 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 7.17-7.90 (m, 20H, H_{arom}), 9.45 (bs, 4H, NH_2).
11b	3.68 (s, 6H, Ar-OCH_3), 3.74 (d, 2H, C_7 & C_{11}-H, *J* = 9.4 Hz), 5.42 (d, 2H, C_8 & C_{10}-H, *J* = 9.4 Hz), 7.08-7.84 (m, 18H, H_{arom}), 9.45 (bs, 4H, NH_2).
11c	3.72 (d, 2H, C_7 & C_{11}-H, *J* = 9.1 Hz), 5.47 (d, 2H, C_8 & C_{10}-H, *J* = 9.1 Hz), 7.13-7.59 (m, 18H, H_{arom}), 9.41 (bs, 4H, NH_2).
12a	4.02 (d, 2H, C_7 & C_{11}-H, *J* = 9.3 Hz), 4.35 (d, 2H, C_8 & C_{10}-H, *J* = 9.3 Hz), 7.06-7.84 (m, 20H, H_{arom}), 9.38 (bs, 4H, NH_2).
12b	3.68 (s, 6H, Ar-OCH_3), 4.06 (d, 2H, C_7 & C_{11}-H, *J* = 9.0 Hz), 4.32 (d, 2H, C_8 & C_{10}-H, *J* = 9.0 Hz), 6.89-7.75 (m, 18H, H_{arom}), 9.32 (bs, 4H, NH_2).
12c	4.04 (d, 2H, C_7 & C_{11}-H, *J* = 9.2 Hz), 4.35 (d, 2H, C_8 & C_{10}-H, *J* = 9.2 Hz), 6.92-7.78 (m, 18H, H_{arom}), 9.36 (bs, 4H, NH_2).
13a	3.82 (d, 2H, C_6 & C_{10}-H, *J* = 9.1 Hz), 4.53 (d, 2H, C_7 & C_9-H, *J* = 9.1 Hz), 7.05-7.79 (m, 20H, H_{arom}), 9.26 (bs, 4H, NH_2), 10.18 (bs, 1H, NH).
13b	3.68 (s, 6H, Ar-OCH_3), 3.84 (d, 2H, C_6 & C_{10}-H, *J* = 9.3 Hz), 4.51 (d, 2H, C_7 & C_9-H, *J* = 9.3 Hz), 6.98-7.72 (m, 18H, H_{arom}), 9.30 (bs, 4H, NH_2), 10.18 (bs, 1H, NH).
13c	3.88 (d, 2H, C_6 & C_{10}-H, *J* = 9.4 Hz), 4.58 (d, 2H, C_7 & C_9-H, *J* = 9.4 Hz), 7.08-7.90 (m, 18H, H_{arom}), 9.29 (bs, 4H, NH_2), 10.25 (bs, 1H, NH).
14a	3.91 (d, 2H, C_6 & C_{10}-H, *J* = 9.1 Hz), 5.46 (d, 2H, C_7 & C_9-H, *J* = 9.1 Hz), 7.15-7.94 (m, 20H, H_{arom}), 9.18 (bs, 4H, NH_2).
14b	3.73 (s, 6H, Ar-OCH_3), 3.97 (d, 2H, C_6 & C_{10}-H, *J* = 9.4 Hz), 5.43 (d, 2H, C_7 & C_9-H, *J* = 9.4 Hz), 6.78-7.59 (m, 18H, H_{arom}), 9.21 (bs, 4H, NH_2).
14c	3.99 (d, 2H, C_6 & C_{10}-H, *J* = 9.3 Hz), 5.40 (d, 2H, C_7 & C_9-H, *J* = 9.3 Hz), 6.82-7.65 (m, 18H, H_{arom}), 9.22 (bs, 4H, NH_2).
15a	4.04 (d, 2H, C_6 & C_{10}-H, *J* = 9.2 Hz), 4.32 (d, 2H, C_7 & C_9-H, *J* = 9.2 Hz), 7.10-7.89 (m, 20H, H_{arom}), 9.62 (bs, 4H, NH_2).
15b	3.76 (s, 6H, Ar-OCH_3), 4.08 (d, 2H, C_6 & C_{10}-H, *J* = 9.1 Hz), 4.39 (d, 2H, C_7 & C_9-H, *J* = 9.1 Hz), 7.02-7.82 (m, 18H, H_{arom}), 9.60 (bs, 4H, NH_2).
15c	4.01 (d, 2H, C_6 & C_{10}-H, *J* = 9.0 Hz), 4.30 (d, 2H, C_7 & C_9-H, *J* = 9.0 Hz), 7.15-7.92 (m, 18H, H_{arom}), 9.64 (bs, 4H, NH_2).
16a	3.84 (d, 2H, C_6 & C_{10}-H, *J* = 9.0 Hz), 4.54 (d, 2H, C_7 & C_9-H, *J* = 9.0 Hz), 7.07-7.74 (m, 20H, H_{arom}), 9.82 (bs, 4H, NH, NH_2).
16b	3.70 (s, 6H, Ar-OCH_3), 3.81 (d, 2H, C_6 & C_{10}-H, *J* = 9.1 Hz), 4.58 (d, 2H, C_7 & C_9-H, *J* = 9.1 Hz), 7.02-7.68 (m, 18H, H_{arom}), 9.86 (bs, 4H, NH, NH_2).

Table 2 (continued)

Product	^{1}H NMR (δ, ppm)
16c	3.82 (d, 2H, C_6 & C_{10}-H, J = 9.3 Hz), 4.55 (d, 2H, C_7 & C_9-H, J = 9.3 Hz), 7.18-7.85 (m, 18H, H_{arom}), 9.89 (bs, 4H, NH, NH_2).
17a	4.26 (d, 2H, C_6 & C_{10}-H, J = 9.2 Hz), 5.35 (d, 2H, C_7 & C_9-H, J = 9.2 Hz), 7.13-7.83 (m, 20H, H_{arom}), 9.30 (bs, 3H, NH, NH_2).
17b	3.69 (s, 6H, Ar-OCH_3), 4.35 (d, 2H, C_6 & C_{10}-H, J = 9.3Hz), 5.43 (d, 2H, C_7 & C_9-H, J = 9.3 Hz), 7.10-7.84 (m, 18H, H_{arom}), 9.32 (bs, 3H, NH, NH_2).
17c	4.33 (d, 2H, C_6 & C_{10}-H, J = 9.1 Hz), 5.40 (d, 2H, C_7 & C_9-H, J = 9.1 Hz), 7.12-7.88 (m, 18H, H_{arom}), 9.34 (bs, 3H, NH, NH_2).
18a	4.02 (d, 2H, C_6 & C_{10}-H, J = 9.4 Hz), 4.35 (d, 2H, C_7 & C_9-H, J = 9.4 Hz), 7.08-7.82 (m, 20H, H_{arom}), 9.30 (bs, 3H, NH, NH_2).
18b	3.78 (s, 6H, Ar-OCH_3), 4.05 (d, 2H, C_6 & C_{10}-H, J = 9.2 Hz), 4.38 (d, 2H, C_7 & C_9-H, J = 9.2 Hz), 6.86-7.75 (m, 18H, H_{arom}), 9.34 (bs, 3H, NH, NH_2).
18c	4.00 (d, 2H, C_6 & C_{10}-H, J = 9.1 Hz), 4.32 (d, 2H, C_7 & C_9-H, J = 9.1 Hz), 7.02-7.80 (m, 18H, H_{arom}), 9.32 (bs, 3H, NH, NH_2).

1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-2,4,9-triazaspiro-[5.5]undeca-1,4-dien-3-one (**4**), 1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]undeca-1,4-dien-3-one (5) and 1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]undeca-1,4-dien-3-one (**6**).

A solution of 10 mmoles of 1, 2 or 3, as appropriate, 15 mmoles of urea, 20 mL of methanol and 5 mL of 10% sodium methoxide was refluxed for 4-6 hours. The solution was cooled and poured onto crushed ice containing HCl. The solid obtained was collected by filtration, dried and recrystallized from methanol.

7,11-Dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-2,4,9-triazaspiro[5.5]undecan-3-one (**7**), 7,11-Dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]undecan-3-one, (**8**) and 7,11-dibenzoyl-1,5-diimino-2,4-dimethyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]undecan-3-one (**9**).

A solution of 10 mmoles of 1, 2 or 3, as appropriate, 10 mmoles of *N*,*N′*-dimethyl urea, 5 mL of 10% sodium methoxide in 20 mL of dry methanol was refluxed for 12-13 hours. Then, it was cooled and poured onto crushed ice containing conc. HCl. The separated solid was collected by filtration, dried and recrystallized from methanol.

1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-2,4,9-triazaspiro[5.5]-undeca-1,4-dien-3-thione (**10**), 1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-9-oxa-2,4-diazaspiro[5.5]undeca-1,4-dien-3-thione (**11**) and 1,5-Diamino-7,11-dibenzoyl-8,10-diphenyl-9-thia-2,4-diazaspiro[5.5]undeca-1,4-dien-3-thione (**12**).

A solution of 10 mmoles of 1, 2 or 3, as appropriate, 10 mmoles of thiourea, 20 mL of methanol and 5 mL of 10% sodium methoxide was added and refluxed for 12-13 hours. The solution was cooled and poured onto crushed ice containing HCl. The solid obtained was collected by filtration, dried and recrystallized from methanol.

1,4-Diamino-6,10-dibenzoyl-7,9-diphenyl-2,3,8-triazaspiro[4.5]-deca-1,3-diene (**13**), 1,4-Diamino-6,10-dibenzoyl-7,9-diphenyl-8-oxa-2,3-diazaspiro[4.5]deca-1,3-diene (**14**) and 1,4-Diamino-6,10-dibenzoyl-7,9-diphenyl-8-thia-2,3-diazaspiro[4.5]deca-1,3-diene (**15**).

To a solution of 10 mmoles of 1, 2 or 3 as appropriate, in 20 mL of methanol, 15 mmoles of 80% hydrazine hydrate and 5 mL of 10% sodium methoxide were added and refluxed for 6-7 hours. The contents were cooled and poured onto crushed ice containing HCl. The separated solid was collected by filtration, dried and recrystallized from 2-propanol.

4-Amino-6,10-dibenzoyl-7,9-diphenyl-1-Imino-2-oxa-3,8-diaza-spiro[4.5]deca-3-ene (**16**), 4-Amino-6,10-dibenzoyl-7,9-diphenyl-2,8-1-Imino-dioxa-3-azaspiro[4.5]deca-3-ene (**17**) and 4-Amino-6,10-dibenzoyl-7,9-diphenyl-1-Imino-2-oxa-8-thia-3-azaspiro[4.5]deca-3-ene (**18**).

A solution of 10 mmoles of **1**, **2** or **3**, as appropriate, 15 mmoles of hydroxylamine hydrochloride, 20 mL of methanol and 5 mL of 10% sodium methoxide was refluxed for 5-6 hours. The mixture was cooled and poured onto crushed ice containing HCl. The solid obtained was collected by filtration, dried and recrystallized from 2-propanol.

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