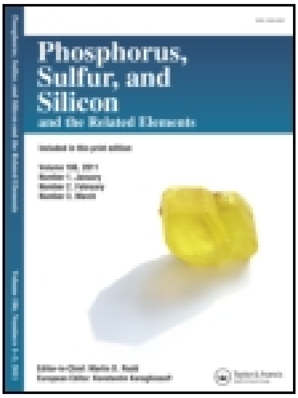

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Application of Secondary Amines in the Synthesis of Some New Spiro Heterocyclic Compounds

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APPLICATION OF SECONDARY AMINES IN THE SYNTHESIS OF SOME NEW SPIRO HETEROCYCLIC COMPOUNDS

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1-Anilinocycloalkanecarbonitriles 1a–c were prepared and reacted with active methylene reagents to give compounds 5a–c through 10a–c and reacted with different other reagents such as benzaldehyde, ethyl aminoacetate, ethyl mercaptoacetate, or hydrazine carbothioamide, which afforded the desired spiro heterocycles compounds 11a–c through 14a–c.

Keywords Anilinocycloalkane; halocompounds; malononitrile; spirocycloalkanyl

INTRODUCTION

The synthesis of new spiro heterocyclic systems was one of the targets of research work done in our laboratory. Recently, and in accordance with the considerable importance of ketoketen,[1] or cyanoketen S,S-acetals,[2] as well as heterocyclic keten N,N—,[3–8] N,S—,[9–11] or N,O—,[12] acetals we have reported the synthesis of some new spiro heterocyclic systems.[13–15] Photochromic organic molecules (including spiro pyrans and spirooxazines) have been under intense study in the last few years because they can be used in optical systems for recording and displaying information, as well as in sensors, optobio- and optoelectronics, transport systems, and catalysis.[16–19]

RESULTS AND DISCUSSION

In order to find out new and efficient routes for the synthesis of a new class of spiro heterocycles we used 1-anilinocycloalkanecarbonitriles **1a–c**, which proved to be excellent precursors. This class of compounds was prepared either by reaction of N-cycloalkylidinoanilines, prepared[20–21] by treatment of aniline with the corresponding cyclic ketone, along with hydrocyanic acid, or directly[22] by treatment with a cold solution of the cyclic ketone in glacial acetic acid successively with aniline and sodium cyanide.

We report herein also the reaction of cyclopentanone, cyclohexanone, or cycloheptanone with 1,2-diaminobenzene, 2-aminophenol, or 2-(methylthio)aniline following the same procedure, where we were able to obtain the corresponding 1-substituted phenylaminocycloalkanecarbonitriles, namely, 1-[(2-aminophenyl)amino]

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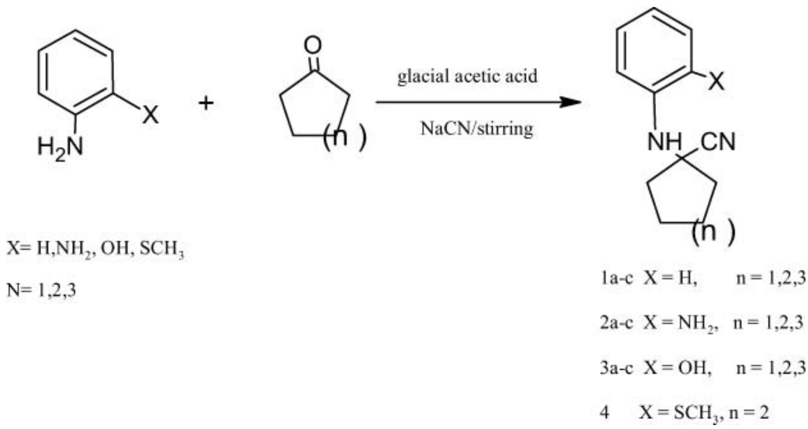
cycloalkanecarbonitrile **2a–c**, 1-[(2-hydroxyphenyl)amino]cycloalkanecarbonitriles **3a–c**, or 1-[(2-methylthiopheyl)amino]cycloalkane carbonitriles **4**, respectively. These compounds were also used as important substrates for the synthesis of some new spiro heterocycles.

The synthesis of compounds **1–4** was assumed to go through a nucleophlic addition of the $-NH_2$ group in the starting materials at the carbonyl group of the cyclic ketones, followed by another nucleophilic attack of the cyanide ion −CN at the C−OH linkage with elimination of the OH ion (see Scheme 1, Tables I and II).

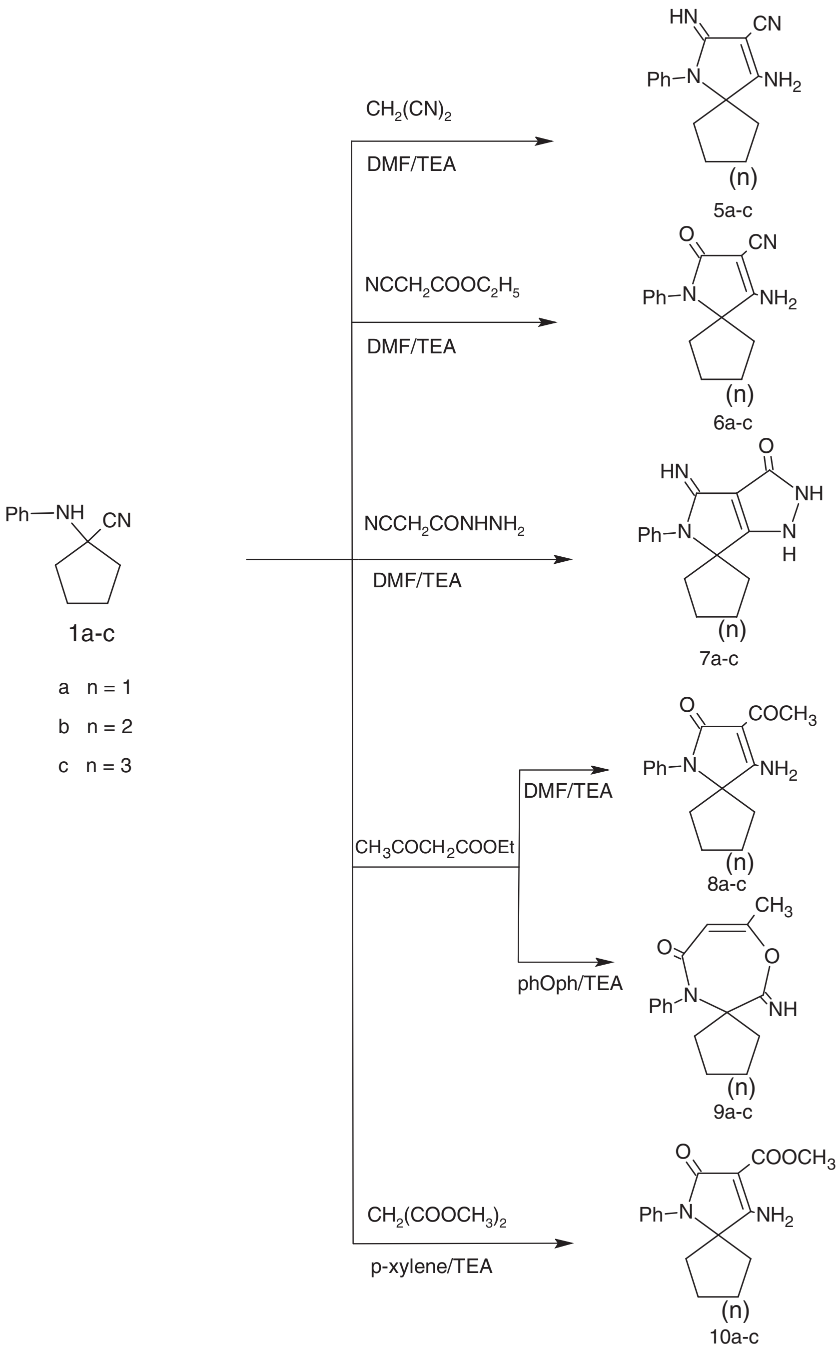


Scheme 1

Compounds **1a–c** were allowed to react with malononitrile in DMF containing TEA as a catalyst, where the corresponding spiro[cycloalkanyl-1,2-(3-amino-4-cyano-5-amino-1-phenyl)pyrroles] **5a–c** were obtained. The reaction pathway was assumed to follow a nucleophilic addition of the NH group at the CN function of malononitrile, followed by another nucleophilic addition of the active methylene group of $-CH_2CN$ at the cyano function of the substrate and cyclization.

In analogy with malononitrile, the reaction of compounds **1a–c** with a variety of active methylene reagents including ethylcyanoacetate, cyanoacetohydrazide (ethylacetoacetate), or diethylmalonate was achieved following the stated experimental conditions to give desired spiro heterocycles. The reaction of **1a–c** with ethylcyanoacetate was assumed to go through a nucleophilic attack of the −NH group at the carbonyl ester with subsequent elimination of the ethanol molecule followed by another nucleophilic attack of the CH_2 group of the reagent at the cyano function and cyclization to give compounds **6a–c**.

The reaction of compounds **1a–c** with cyanoacetohydrazide underwent a nucleophilic attack of the –NH group in the substrate at the cyano function of the reagent, followed by another nucleophilic attack of the $-CH_2$ group in the reagent at the cyano group and cyclization, elimination of NH_3 molecule and cyclization afforded the desired spiro heterocycles **7a–c**. In addition, the reaction of compounds **1a–c** with ethyl acetoacetate was carried out in the same previous experimental conditions that gave compounds **9a–c**. (**8a–c**) and by using diphenylether as a solvent, it gave compounds **9a–c**. Dimethyl malonate ester was allowed to react with **1a–c** in the same reaction conditions mentioned before and gave the compounds **10a–c** (see Scheme 2, Tables I and II).



Scheme 2

Compounds **1a–c** were allowed to react with other reagents, such as benzaldehyde, ethyl aminoacetate, ethyl mercaptoacetate, or hydrazine carbothioamide, which afforded the desired spiro heterocycles **11a–c**, **12a–c**, **13a–c**, or **14a–c**, respectively.

Table I Analytical and experimental data of the new compounds

Product No.	Time of Reaction	Yield %	Mp°C	Molecular Formula	Analysis (calc./found) C%	H%	N%
1a	1 h	90	59	$C_{12}H_{14}N_2$	77.38	7.58	15.04
				186.25	77.47	7.44	15.19
1b	1 h	90	76	$C_{13}H_{16}N_2$	77.96	8.05	13.99
				200.28	77.82	8.16	14.10
1c	1 h	90	85	$C_{14}H_{18}N_2$	78.46	8.47	13.07
				214.31	78.36	8.58	13.12
2a	1 h	80	147	$C_{12}H_{15}N_3$	71.62	7.51	20.88
				201.26	71.50	7.62	20.74
2b	1 h	85	150	$C_{13}H_{17}N_3$	72.52	7.96	19.52
				215.29	72.40	7.82	19.39
2c	1 h	80	115	$C_{14}H_{19}N_3$	73.33	8.35	18.32
				229.32	73.21	8.49	18.19
3a	1 h	90	65	$C_{12}H_{14}N_2O$	71.27	6.97	13.85
				202.25	71.40	6.85	13.96
3b	1 h	90	70	$C_{13}H_{16}N_2O$	72.20	7.45	12.95
				216.28	72.32	7.33	12.81
3c	1 h	90	81	$C_{14}H_{18}N_2O$	73.01	7.87	12.16
				230.30	73.13	7.70	12.32
4	1 h	60	67	$C_{14}H_{18}N_2S$	68.25	7.36	11.37
				246.37	68.36	7.47	11.25
5a	3 h	65	140	$C_{15}H_{16}N_4$	71.41	6.39	22.21
				252.31	71.52	6.25	22.38
5b	3 h	75	160	$C_{16}H_{18}N_4$	72.16	6.81	21.04
				266.33	72.34	6.70	21.24
5c	3 h	60	150	$C_{17}H_{20}N_4$	72.83	7.19	19.98
				280.37	72.70	6.90	19.84
6a	3 h	60	180	$C_{15}H_{15}N_3O$	71.13	5.96	16.58
				253.30	71.00	6.11	16.43
6b	3 h	65	200	$C_{16}H_{17}N_3O$	71.89	6.41	15.72
				267.32	71.73	6.55	15.61
6c	3 h	70	210	$C_{17}H_{19}N_3O$	72.57	6.80	14.93
				281.35	72.40	6.95	14.80
7a	3 h	60	140	$C_{15}H_{16}N_4O$	67.15	6.00	20.88
				268.31	67.30	6.11	20.65
7b	3 h	70	170	$C_{16}H_{18}N_4O$	68.07	6.42	19.84
				282.33	68.26	6.35	19.70
7c	3 h	62	193	$C_{17}H_{20}N_4O$	68.89	6.80	18.90
				296.37	68.77	6.90	18.72
8a	3 h	60	100	$C_{16}H_{18}N_2O_2$	71.09	6.70	10.36
				270.32	71.22	6.55	10.21
8b	3 h	50	95	$C_{17}H_{20}N_2O_2$	71.81	7.08	9.85
				284.35	71.68	7.28	9.96
8c	3 h	55	150	$C_{18}H_{22}N_2O_2$	72.46	7.43	9.39
				(298.38)	72.60	7.55	9.51
9a	3 h	90	240	$C_{16}H_{18}N_2O_2$	71.09	6.70	10.36
				(270.32)	71.32	6.56	10.48
9b	3 h	85	270	$C_{17}H_{20}N_2O_2$	71.81	7.08	9.85
				(284.35)	71.69	7.19	9.96
9c	3 h	87	225	$C_{18}H_{22}N_2O_2$	72.46	7.43	9.39
				(298.37)	72.57	7.32	9.51
10a	3 h	40	270	$C_{16}H_{18}N_2O_3$	67.12	6.33	9.78
				(286.32)	67.00	6.46	9.50

Table I Analytical and experimental data of the new compounds *(Continued)*

Product No.	Time of Reaction	Yield %	Mp°C	Molecular Formula	Analysis (calc./found)		
					C%	H%	N%
10b	3 h	50	275	$C_{17}H_{20}N_2O_3$	67.98	6.70	9.33
				(300.35)	67.81	6.51	9.45
10c	3 h	45	250	$C_{18}H_{22}N_2O_3$	68.77	7.05	8.91
				(314.38)	68.55	7.19	9.25
11a	3 h	60	95	$C_{19}H_{20}N_2O$	78.05	6.89	9.58
				(292.37)	78.22	7.07	9.45
11b	3 h	65	120	$C_{20}H_{22}N_2O$	78.41	7.23	9.14
				(306.40)	78.55	7.11	9.28
11c	3 h	60	132	$C_{21}H_{24}N_2O$	78.72	7.54	8.74
				(320.42)	78.86	7.41	8.85
12a	3 h	60	135	$C_{14}H_{17}N_3O$	69.11	7.04	17.27
				(243.30)	69.00	7.19	17.12
12b	3 h	70	140	$C_{15}H_{19}N_3O$	70.01	7.44	16.32
				(257.32)	70.13	7.55	16.43
12c	3 h	70	105	$C_{16}H_{21}N_3O$	70.82	7.79	15.48
				(271.35)	70.67	7.65	15.61
13a	3 h	50	120	$C_{14}H_{16}N_2OS$	64.58	6.19	10.76
				(260.35)	64.41	6.33	10.87
13b	3 h	60	180	$C_{15}H_{18}N_2OS$	65.66	6, 61	10.21
				(274.38)	65.80	6.49	10.02
13c	3 h	45	130	$C_{16}H_{20}N_2OS$	66.64	6.98	9.71
				(288.40)	66.49	6.72	9.93
14a	3 h	60	200	$C_{13}H_{16}N_4S$	59.97	6.19	21.52
				(260.35)	59.79	6.01	21.67
14b	3 h	65	185	$C_{14}H_{18}N_4S$	61.28	6.61	20.41
				(274.38)	61.06	6.77	20.22
14c	3 h	50	220	$C_{15}H_{20}N_4S$	62.47	6.98	19.42
				(288.40)	62.61	6.72	19.50
15a	3 h	60	127	$C_{20}H_{20}N_2O$	78.92	6.62	9.20
				(304.38)	78.71	6.51	9.07
15b	3 h	65	240	$C_{21}H_{22}N_2O$	79.22	6.96	8.79
				(318.41)	79.36	7.12	8.90
15c	3 h	70	145	$C_{22}H_{24}N_2O$	79.49	7.27	8.42
				(332.43)	79.31	7.45	8.56
16a	3 h	60	110	$C_{14}H_{18}N_2O$	73.01	7.88	12.16
				(230.31)	73.16	7.72	12.01
16b	3 h	50	137	$C_{15}H_{20}N_2O$	73.74	8.25	11.46
				(244.32)	73.85	8.03	1160
16c	3 h	50	130	$C_{16}H_{22}N_2O$	74.38	8.57	10.84
		70		(258.35)	74.21	8.42	10.62
17a	2 h		180	$C_{14}H_{19}N_3$	73.33	8.35	18.32
		70		(229.31)	73.45	8.45	18.11
17b	2 h		175	$C_{15}H_{21}N_3$	74.04	8.69	17.27
		65		(243.34)	74.91	8.86	17.00
17c	2 h		205	$C_{16}H_{23}N_3$	74.67	9.00	16.32
				(257.36)	74.52	8.87	16, 03
18a	3 h	70	190	$C_{12}H_{15}N_3$	71.61	7.51	20.87
				(201.26)	71.45	7.39	20.73
18b	3 h	80	135	$C_{13}H_{17}N_3$	72.52	7.95	19.52
				(215.29)	72.69	8.20	19.67

(Continued on next page)

Table I Analytical and experimental data of the new compounds *(Continued)*

Product No.	Time of Reaction	Yield %	Mp°C	Molecular Formula	Analysis (calc./found) C%	H%	N%
18c	3 h	85	140	$C_{14}H_{19}N_3$	73.33	8.34	18.32
				(229.31)	73.15	8.11	18.43
19a	3 h	90	210	$C_{12}H_{14}N_2O$	71.26	6.97	13.85
				(202.25)	71.48	6.80	13.70
19b	3 h	85	220	$C_{13}H_{16}N_2O$	72.19	7.45	12.95
				(216.27)	72.02	7.66	13.16
19c	3 h	70	197	$C_{14}H_{18}N_2O$	73.01	7.87	12.16
				(230.30)	73.20	7.61	12.03
20	2 h	70	85	$C_{14}H_{18}N_2O_2S$	60.41	6.51	10.03
				(278.36)	60.53	6.67	10.22
21	7 h	50	140	$C_{13}H_{18}N_4$	67.80	7.88	24.33
				(230.31)	75.66	7.60	24.63

The reaction of compounds **1a–c** with halo compounds including 2-bromo-1-phenylethanone, 2-chloroethanol, or 2-aminoethanol in $POCl_3$ was carried out, where we were able to isolate the corresponding spiro products **15a–c**, **16a–c**, or **17a–c**, respectively (see Scheme 3, Tables I and II).

The prepared substrates 1-(2-aminophenyl)aminocyclohexane-1-carboniles **2a–c** or 1-(2-hydroxyphenyl)aminocycloalkane-1-carbonitriles **3a–c** were allowed to undergo an intramoleculare nucleophilic addition with subsequent cyclization by boiling in p-xylene or dioxan in the presence of TEA as catalyst where the corresponding spiro derivatives, namely, spiro[cycloalkanyl-1′,2-(3-amino)(1H)-quinoxaline] **18a–c** or spiro[cycloalkanyl-1′,3-(2-imino)-(4H)-benzoxazine **19a–c**, respectively, were obtained in fair yields.

The intramolecular cyclization of 1-(2-methylthiopheyl)aminocyclohexane-1-carbonitriles **4** was achieved in a two-step reaction. In the first step, compound **4** was oxidized by using H_2O_2 in acetic acid to give 1-(2-methylsulphonephenyl)-aminocyclohexane-1-carbonitrile **20**, which was allowed in the second step to react with hydrazine hydrate in absolute ethanol, where spiro ([cycloalkanyl-1′,2-(3-amino)-(1H,5H)-1,4,5-benzotriazepine)] **21** was obtained (see Scheme 4, Tables I and II).

EXPERIMENTAL

All melting points were obtained on Melt-Temp II melting point apparatus and were uncorrected. IR spectra were obtained on a Nicolet 710 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Varian EM 360 A at 60 MHz using TMS as an internal standard. Elemental analyses were performed on a Perkin-Elmer CHN-2400C analyzer model.

Synthesis of 1-Anilinocycloalkanecarbonitrile 1a–c, 1-[(2-Aminophenyl) amino]cyclopentanecarbonitrile 2a–c, 1-[(2-Hydroxyphenyl)amino]cyclopentanecarbonitrile 3a–c, and 1-{[2-(Methyl thio)phenyl]amino}cyclohexanecarbonitrile 4: General Procedure

An equimolar mixture (0.05 mol) of cycloketones (e.g., cyclopentanone, cyclohexanone, or cycloheptanone) and proper amines [aniline, benzene-1,2-diamine, 2-aminophenol, or 2-(methylthio)aniline] in cold glacial acetic acid (70 mL) was treated

Table II Spectral data (IR, ^{1}H NMR) of the new compounds

Comp. No.	IR (KBr) v cm^{-1}	^{1}H-NMR (DMSO-d_6) δ ppm
1a	3366 (NH), 3082 (CH-arom.), 2921 (CH-aliph.), 2235 (CN).	7.5–6.8 (m, 5H, CH-arom.), 3.7 (s, 1H, NH), 2.6–1.2 (m, 8H, cyclic CH_2).
1b	3350 (NH), 3044 (CH-arom.), 2932 (CH-aliph.), 2266 (CN).	7.5–6.9 (m, 5H, CH-arom.), 3.75 (s, 1H, NH), 2.6–1.2 (m, 10H, cyclic CH_2).
1c	3362 (NH), 3036 (CH-arom.), 2926 (CH-aliph.), 2235 (CN).	7.6–6.9 (m, 5H, CH-arom.), 3.4 (s, 1H, NH), 2.4–1.5 (m, 12H, cyclic CH_2).
2a	3439, 3377, 3310 (NH_2, NH), 3053 (CH-arom.), 2926 (CH- aliph.), 2224 (CN)	7.7–7.0 (m, 4H, CH-arom.), 4.8 (br, 2H, NH_2), 3.5 (s, 1H, NH), 2.4–1.3 (m, 8H, cyclic CH_2).
2b	3446, 3382.3306 (NH_2, NH), 3036 (CH-arom.), 2920 (CH-aliph.), 2232 (CN).	7.8–7.1 (m.4H, CH-arom.), 4.8 (br, 2H, NH_2), 3.65 (s, 1H, NH), 2.5–1.5 (m, 10H, cyclic CH_2).
2c	3440, 3372, 3316 (NH, NH_2), 3053 (CH-arom.), 2932 (CH-aliph.), 2216 (CN).	7.7–7.0 (m, 4H, CH-arom.), 4.9 (br, 2H, NH_2), 3.75 (s, 1H, NH), 2.4–1.2 (m, 12H, cyclic CH_2).
3a	3300 (OH), 3134 (NH), 3048 (CH-arom.), 2950 (CH-aliph.), 2230 (CN).	7.2–6.6 (m, 4H, CH-arom.), 4.5 (br, 1H, OH), 3.7 (s, 1H, NH), 2.5–1.6 (m, 8H, cyclic CH_2).
3b	3312 (OH), 3171 (NH), (CH-arom.), 2939 (CH-aliph.), 2235 (CN).	7.2–6.5 (m, 4H, CH-arom.), 4.55 (br, 1H, OH), 3.7 (s, 1H, NH), 2.3–1.3 (m, 10H, cyclic CH_2).
3c	3316 (OH), 3193 (NH), 3043 (CH-arom.), 2946 (CH-aliph.), 2225 (CN).	7.1–6.4 (m, 4H, CH-arom.), 4.7 (br, 1H, OH), 3.75 (s, 1H, NH), 2.4–1.2 (m, 12H, cyclic CH_2).
4	3346 (NH), 3057 (CH-arom.), 2932 (CH-aliph.), 2233 (CN).	7.6–6.8 (m, 4H, CH-arom.), 5.1 (s, 1H, NH), 2.3 (s, 3H, SCH_3)2.1–1.3 (m, 10H, cyclic CH_2).
5a	3410, 3352, 3220 (NH, NH_2), 3052 (CH-arom.), 2953 (CH-aliph.), 2197 (CN).	9.2 (s, 1H, NH), 7.6–6.8 (m, 5H, CH-arom.), 4.3 (br, 2H, NH_2), 2.2–1.4 (m, 8H, cyclic CH_2).
5b	3435, 3361, 3208 (NH, NH_2), 3053 (CH-arom.), 2937 (CH-aliph.), 2197 (CN).	9.1 (s, 1H, NH), 7.8–7.1 (m, 5H, CH-arom.), 5.9 (br, 2H, NH_2), 2.2–1.3 (m, 10H, cyclic CH_2).
5c	3426, 3335, 3230 (NH, NH_2), 3061 (CH-arom.), 2928 (CH-aliph.), 2204 (CN).	9.2 (s, 1H, NH), 7.5–6.8 (m, 5H, CH-arom.), 5.3 (br, 2H, NH_2), 2.4–1.2 (m, 12H, cyclic CH_2).
6a	3274, 3207 (NH_2), 3056 (CH-arom.), 2958 (CH-aliph), 2260 (CN), 1669 (C=O).	7.8–7.2 (m, 5H, CH, arom.), 3.9 (br, 2H, NH_2), 1.8–1.2 (m, 8H, cyclic CH_2).
6b	3273, 3197 (NH_2), 3065 (CH-arom.), 2959 (CH-aliph.), 2260 (CN), 1670 (C=O).	7.7–7.1 (m, 5H, CH, arom.), 4.2 (br, 2H, NH_2), 1.9–1.2 (m, 10H, cyclic CH_2).
6c	3277, 3195 (NH_2), 3062 (CH-arom.), 2956 (CH-aliph.), 2260 (CN), 1670 (C=O).	7.9–7.2 (m, 5H, CH, arom.), 4.5 (br, 2H, NH_2), 1.8–1.1 (m, 12H, cyclic CH_2).
7a	3406, 3318, 3182 (3NH), 3049 (CH-arom.), 2932 (CH-aliph.), 1666 (C=O).	9.4–9.1 (br, 3H, 3NH), 7.8–7.2 (m, 5H, CH-arom.), 2.1–1.2 (m, 8H, cyclic CH_2).
7b	3418, 3326, 3205 (3NH), 3063 (CH-arom.), 2942 (CH-aliph.), 1666 (C=O).	9.5–9.2 (br, 3H, 3NH), 7.7–7.1 (m, 5H, CH-arom.), 2.2–1.2 (m, 10H, cyclic CH_2).
7c	3412, 3321, 3214 (3NH), 3058 (CH-arom.), 2924 (CH-aliph), 1668 (C=O).	9.3–9.0 (br, 3H, 3NH), 7.7–7.2 (m, 5H, CH-arom.), 2.4–1.2 (m, 12H, cyclic CH_2).
8a	3314, 3215 (NH_2), 3065 (CH-arom.), 2945 (CH-aliph.), 1678, 1664 (2C=O).	7.8–7.2 (m, 5H, CH-arom.), 5.5 (br, 2H, NH_2), 2.2–1.6 (br, 11H, cyclic CH_2+$COCH_3$).
8b	3302, 3205 (NH_2), 3055 (CH-arom.), 2926 (CH-aliph.), 1672, 1668 (2C=O).	7.8–7.4 (m, 5H, CH-arom.), 5.3 (br, 2H, NH_2), 2.4–1.8 (br, 13H, cyclic CH_2+$COCH_3$).
8c	3306, 3209 (NH_2), 3056 (CH-arom.), 2930 (CH-aliph.), 1670, 1666 (2C=O).	7.8–7.4 (m, 5H, CH-arom.), 5.6 (br, 2H, NH_2), 2.2–1, 6 (br, 15H, cyclic $\mathbf{CH_2}$+$COC\mathbf{H_3}$).

(Continued on next page)

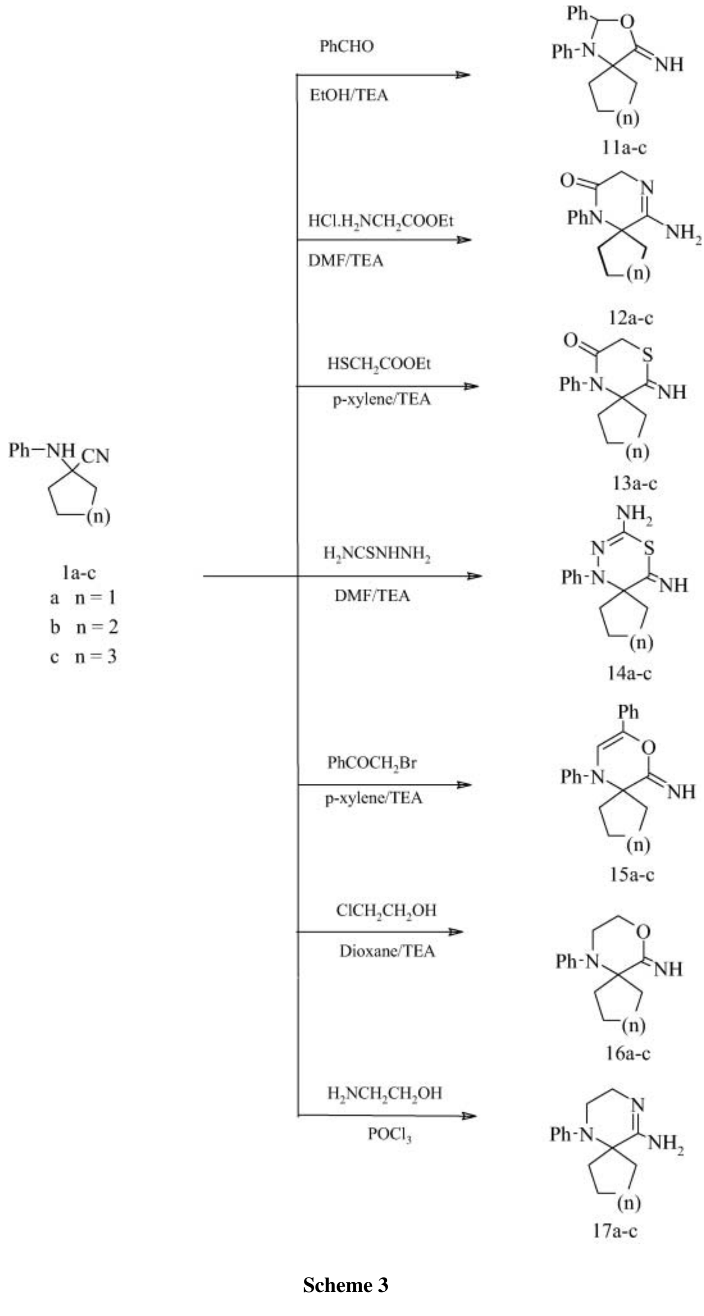
Table II Spectral data (IR, ^{1}H NMR) of the new compounds *(Continued)*

Comp. No.	IR (KBr) v cm^{-1}	^{1}H-NMR (DMSO-d$_6$) δ ppm
9a	3418 (NH), 3013 (CH-arom.), 2930 (CH-aliph.), 1650 (C=O).	10.1 (br, 1H, NH), 8.2–7.6 (m, 5H, CH-arom.), 6.5 (s, 1H, =CH), 2.2–1.8 (br, 11H, cyclic CH_2+CH_3).
9b	3416 (NH), 3042 (CH-arom.), 2930 (CH-aliph.), 1666 (C=O).	9.8 (br, 1H, NH), 7.7–7.2 (m, 5H, CH-arom.), 6.2 (s, 1H, =CH), 2.4–1.3 (br, 13H, cyclicCH_2+CH_3).
9c	3439 (NH), 3035 (CH-arom.), 2924 (CH-aliph.), 1649 (C=O).	9.6 (br, 1H, NH), 7.7–7.1 (m, 5H, CH-arom.), 6.3 (s, 1H, =CH), 2.6–1.4 (br, 15H, cyclic CH_2+CH_3).
10a	3416, 3320 (NH_2), 3057 (CH-arom.), 2926 (CH-aliph.), 1732, 1660 (2CO).	7.8–7.3 (m, 5H, CH-arom.), 5.5 (br, 2H, NH_2), 2.4–18 (br, 11H, cyclic CH_2+CH_3 ester).
10b	3427, 3332 (NH_2), 3055 (CH-arom.), 2937 (CH-aliph.), 1732, 1660 (2CO).	7.8–7.3 (m, 5H, CH-arom.), 5.6 (br, 2H, NH_2), 2.2–1.6 (br, 13H, cyclic CH_2+CH_3ester).
10c	3417, 3330 (NH_2), 3065 (CH-arom.), 2934 (CH-aliph.), 1724, 1666 (2CO).	7.7–7.2 (m, 5H, CH-arom.), 5.4 (br, 2H, NH_2), 2.1–1.4 (br, 15H, cyclic CH_2+CH_3 ester).
11a	3391 (NH), 3036 (CH-arom.), 2920 (CH-aliph.).	10.2 (br, 1H, NH), 7.7–7.1 (m, 10H, CH-arom.), 4.8 (s, 1H, CH-ph), 2.2–1.4 (m, 8H, cyclic CH_2).
11b	3337 (NH), 3049 (CH-arom.), 2936 (CH-aliph.).	10.1 (br, 1H, NH), 7.8–7.2 (m, 10H, CH-arom.), 4.6 (s, 1H, CH-ph), 2.2–1.6 (m, 10H, cyclic CH_2).
11c	3342 (NH), 3055 (CH-arom.), 2936 (CH-aliph.).	9.8 (br, 1H, NH), 7.6–7, 0 (m, 10H, CH-arom.), 4.8 (s, 1H, CH-ph), 2.4–1.6 (m, 12H, cyclic CH_2).
12a	3402, 3300 (NH_2), 3055 (CH-arom.), 2920 (CH-aliph.), 1676 (CO).	7.8–7.2 (m, 5H, CH-arom), 4.7 (br, 2H, NH_2), 4.2 (s, 2H, CH_2 pyrazine), 1.9–1.2 (m, 8H, cyclic CH_2).
12b	3258, 3175 (NH_2), 3049 (CH-arom.), 2926 (CH_aliph.), 1682 (CO).	8.0–7.2 (m, 5H, CH-arom), 4.4 (br, 2H, NH_2), 4.0 (s, 2H, CH_2 pyrazine), 2.2–1.4 (m, 10H, cyclic CH_2).
12c	3381, 3269 (NH_2), 3060 (CH-arom.), 2939 (CH-aliph.), 1682 (CO).	7.7–7.1 (m, 5H, CH-arom), 4.4 (br, 2H, NH_2), 3.9 (s, 2H, CH_2 pyrazine), 2.1–1.6 (m, 12H, cyclic CH_2).
13a	3364 (NH), 3056 (CH-arom.), 2953 (CH-aliph.), 1668 (CO).	9.8 (br, 1H, NH), 7.7–7.1 (m, 5H, CH-arom.), 4.2 (s, 2H, CH_2 thiazine), 1.9–1.1 (m, 8H, cyclic CH_2).
13b	3414 (NH), 3055 (CH-arom.), 2930 (CH-aliph.), 1678 (CO).	9.6 (br, 1H, NH), 7.6–7.1 (m, 5H, CH-arom.), 4.0 (s, 2H, CH_2 thiazine), 2.1–1.2 (m, 10H, cyclicCH_2).
13c	3416 (NH), 3049 (CH-arom.), 2928 (CH-aliph.), 1665 (CO).	9.8 (br, 1H, NH), 7.6–7.2 (m, 5H, CH-arom.), 4.1 (s, 2H, CH_2 thiazine), 2.1–1.3 (m, 12H, cyclic CH_2).
14a	3435, 3306, 3181 (NH, NH_2), 3055 (CH-arom.), 2951 (aliph.).	9.9 (br, 1H, NH), 7.6–7.1 (m, 5H, CH-arom.), 5.9 (br, 2H, NH_2), 2.6–1.5 (m, 8H, cyclic CH_2).
14b	3418, 3258, 3165 (NH, NH_2), 3056 (CH-arom.), 2924 (CH-aliph.).	9.8 (br, 1H, NH), 7.8–7.0 (m, 5H, CH-arom.), 6.1 (br, 2H, NH_2), 2.5–1.5 (m, 10H, cyclic CH_2).
14c	3410, 3320, 3230 (NH, NH_2), 3046 (CH-arom.), 2936 (CH-aliph.).	10.1 (br, 1H, NH), 8.0–7.3 (m, 5H, CH-arom.), 5.4 (br, 2H, NH_2), 2.3–1.6 (m, 12H, cyclic CH_2).
15a	3430 (NH), 3049 (CH-arom.), 2910 (CH-aliph.).	9.5 (br, 1H, NH), 7.6–7.2 (m, 11H, CH-arom., =CH), 2.2–1.6 (m, 8H, cyclicCH_2).

Table II Spectral data (IR, ^{1}H NMR) of the new compounds *(Continued)*

Comp. No.	IR (KBr) v cm^{-1}	^{1}H-NMR (DMSO-d_6) δ ppm
15b	3400 (NH), 3061 (CH-arom.), 2930 (CH-aliph.).	9.8 (br, 1H, NH), 7.7–7.1 (m, 11H, CH-arom., =CH), 2.0–1.4 (m, 10H, cyclic CH_2).
15c	3397 (NH), 3062 (CH-arom.), 2926 (CH-aliph.).	9.6 (br, 1H, NH), 7.8–7.2 (m, 11H, CH-arom., =CH), 2.9–1.4 (m, 12H, cyclic CH_2).
16a	3329 (NH), 3054 (CH-arom.), 2937 (CH-aliph.).	8.8 (br, 1H, NH), 7.6–6.9 (m, 5H, CH-arom.), 3.8 (br, 4H, $2CH_2$), 1.9–1.1 (m, 8H, cyclic CH_2).
16b	3410 (NH), 3053 (CH-arom.), 2930 (CH-aliph).	9.1 (br, 1H, NH), 7.8–7.2 (m, 5H, CH-arom.), 4.0 (br, 4H, $2CH_2$), 2.1–1.4 (m, 10H, cyclic CH_2).
16c	3418 (NH), 3056 (CH-arom.), 2943 (CH-aliph.).	9.3 (br, 1H, NH), 7.8–7.1 (m, 5H, CH-arom.), 4.0 (br, 4H, $2CH_2$), 2.2–1.6 (m, 12H, cyclic CH_2).
17a	3418, 3309 (NH_2), 3055 (CH-arom.), 2937 (CH-aliph.).	7.8–7.2 (m, 5H, CH, arom.), 4.5 (br, 2H, NH_2), 3.8 (br, 4H, $2CH_2$), 2.6–1.8 (m, 8H, cyclic CH_2).
17b	3418, 3316 (NH_2), 3061 (CH-arom.), 2926 (CH-aliph.).	7.7–7.2 (m, 5H, CH-arom.), 4.6 (br, 2H, NH_2), 3.9 (br, 4H, $2CH_2$), 2.5–1.6 (m, 10H, cyclic CH_2).
17c	3416, 3308 (NH_2), 3041 (CH-arom.), 2941 (CH-aliph.).	8.0–7.2 (m, 5H, CH-arom.), 5.1 (br, 2H, NH_2), 4.0 (br, 4H, $2CH_2$), 2.6–1.6 (m, 12H, cyclic CH_2).
18a	3450, 3335, 3312 (NH, NH_2), 3050 (CH-arom.), 2930 (CH-aliph.).	8.6 (s, 1H, NH), 7.8–7.2 (m, 4H, CH-arom.), 5.2 (s, 2H, NH_2), 1.9–1.5 (m, 8H, cyclic CH_2).
18b	3450, 3352, 3265 (NH, NH_2), 3044 (CH-arom.), 2926 (CH-aliph.)	8.7 (s, 1H, NH), 7.8–7.3 (m, 4H, CH-arom.), 5.0 (s, 2H, NH_2), 2.0–1.6 (m, 10H, cyclic CH_2).
18c	3460, 3337, 3250 (NH, NH_2), 3057 (CH-arom.), 2953 (CH-aliph.).	8.6 (s, 1H, NH), 7.6–6.9 (m, 4H, CH-arom.), 4.8 (s, 2H, NH_2), 2.1–1.6 (m, 12H, cyclic CH_2).
19a	3397, 3150 (2NH), 3061 (CH-arom.), 2955 (CH-aliph.).	7.8–6.8 (m, 4H, CH-arom.), 5.0 (br, 1H, NH), 3.5 (br, 1H, NH), 2.3–1.6 (m, 8Hcyclic CH_2)
19b	3327, 3246 (2NH), 3061 (CH-arom.), 2939 (CH-aliph.).	7.0–6.4 (m, 4H, CH-arom.), 4.6 (br, 1H, NH), 3.4 (br, 1H, NH), 2.0–1.5 (m, 10H, cyclic CH_2)
19c	3337, 3255 (2NH), 3059 (CH-arom.), 2946 (CH-aliph.).	7.8–7.0 (m, 4H, CH-arom.), 4.7 (br, 1H, NH), 3.7 (br, 1H, NH), 1.9–1.5 (m, 12H, cyclic CH_2)
20	3354 (NH), 3060 (CH-arom.), 2936 (CH-aliph.), 2224 (CN), 1313, 1128 (SO_2).	7.6–7.0 (m, 4H, CH-arom.), 5.1 (br, 1H, NH), 2.9 (s, 3H, CH_3), 2.0–1.3 (m, 10H, cyclic CH_2).
21	3450, 3416, 3352, 3256 (2NH, NH_2), 3046 (CH-arom.), 2946 (CH-aliph.).	9.7 (br, 2H, 2NH), 7.8–7.0 (m, 4H, CH-arom), 5.4 (s, 2H, NH_2), 2.1–1.5 (m, 10H, cyclic CH_2).

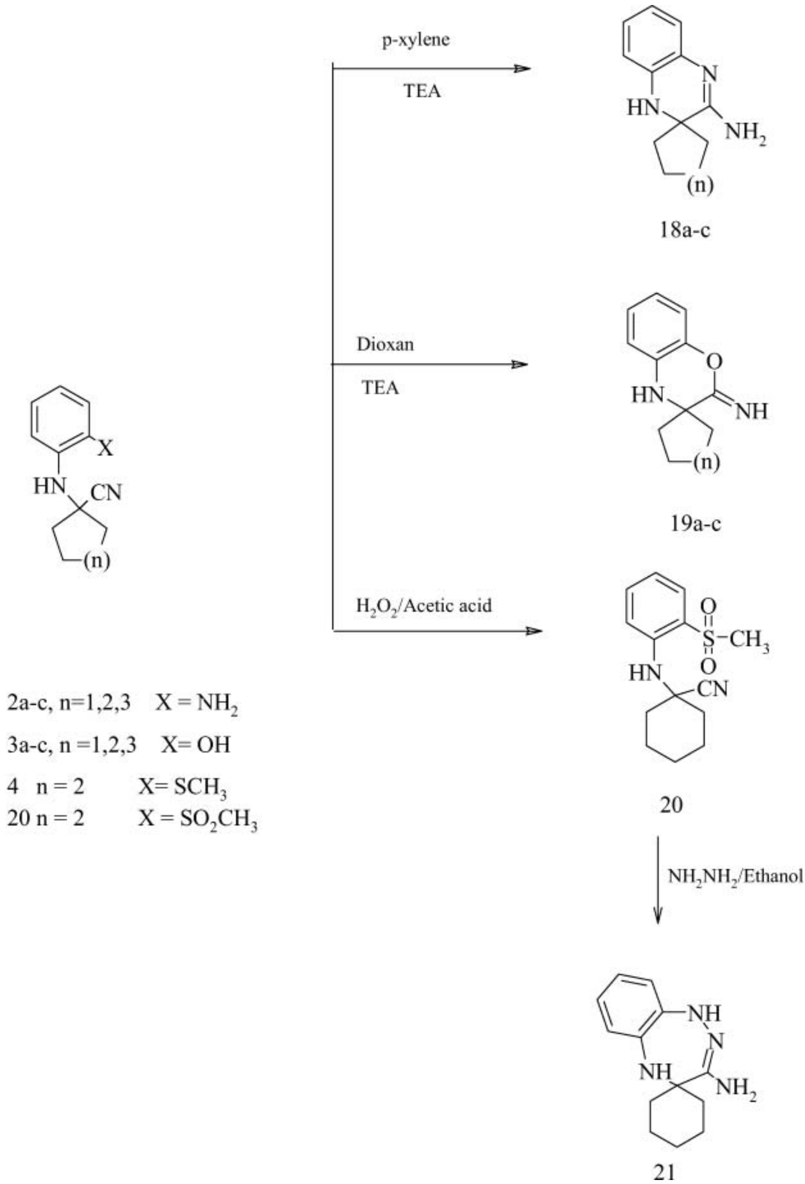
with sodium cyanide (0.05 mol) in small portions under stirring. After addition, the stirring was continued for 1 h at room temperature. The reaction mixture was then poured into ice-cold water. The precipitated solid was filtered off, washed with water, and recrystallized from aqueous ethanol into shining crystals.



Scheme 3

Synthesis of Spiro[cycloalkanyl-1′,2-pyrrole]derivatives 5a–c, 7a-c, 8a–c, 9a–c, Spiro[cycloalkanyl-1′,2-pyrrolo(3,4-c)pyrazole] Derivatives 6a–c, and Spiro[cyclo-alkanyl-1′,4-oxazepine)] Derivatives 10a–c: General Procedure

A mixture of compound **1a**, **1b**, or **1c** (0.01 mol) and triethylamine (TEA) (1 mL) was gradually added to a stirred suspension of the appropriate active methylene reagent (0.01 mol) in DMF, p-xylene, or diphenylether (20 mL) (Scheme II). The reaction mixture



Scheme 4

was refluxed over different periods of time (1–3 h) and was then concentrated. After cooling, the precipitated solid was filtered off and recrystallized from the proper solvent.

Spiro[cyclopentanyl-1′,2-(3-amino-4-cyano-5-imino-1-phenyl)pyrrole] 5a, spiro[cyclohexanyl-1′,2-(3-amino-4-cyano-5-imino-1-phenyl)pyrrole] 5b, and spiro[cyclo-heptanyl-1′,2-(3-amino-4-cyano-5-imino-1-phenyl)pyrrole] 5c. The reaction mixture of compound **1a**, **1b**, or **1c** with malononitrile in DMF (20 mL) was refluxed for 3 h. The solid product was filtered off and recrystallized from petroleum ether (60:80) into colorless crystals.

Spiro[cyclopentanyl-1′,2-(3-amino-4-cyano-1-phenyl)pyrrol-5-one] 6a, spiro[cyclohexanyl-1′,2-(3-amino-4-cyano-1-phenyl)pyrrol-5-one 6b, and Spi rocycloheptanyl-1′,2-(3-amino-4-cyano-1-phenyl)pyrrol-5-one] 6c. The reaction mixture of compound **1a**, **1b**, or **1c** with ethylcyanoacetate in DMF (20 mL) was refluxed for 3 h. The solid product was filtered off and recrystallized from aqueous ethanol into pink crystals.

Spiro[cyclopentanyl-1′,2-(5-imino-1-phenyl)pyrrolo(3,4-c)pyrazol(1H,2H)-5-one]7a, spiro[cyclohexanyl-1′,2-(5-imino-1-phenyl)pyrrolo(3,4-c)pyrazol(1H, 2H)-5-one] 7b, and spirocycloheptanyl-1′,2-(5-imino-1-phenyl)pyrrolo (3, 4-c) pyrazol (1H, 2H)-5-one] 7c. The reaction mixture of compound **1a**, **1b**, or **1c** with cyanoacetohydrazide in DMF (20 mL) was refluxed for 3 h. The solid product was filtered off and recrystallized from aqueous ethanol into yellow crystals.

Spiro[cyclopentanyl-1′,2-(3-amino-4-carbmethoxy-1-phenyl)pyrrol-5-one] 8a, spiro[cyclohexanyl-1′,2-(3-amino-4-carbmethoxy-1-phenyl)pyrrol-5-one 8b, and spiro[cycloheptanyl-1′,2-(3-amino-4-carbmethoxy-1-phenyl) pyrrol-5-one] 8c. The reaction mixture of compound **1a**, **1b**, or **1c** along with ethylacetoacetate in DMF (20 mL) was refluxed for 3 h. The solid product obtained was filtered off and recrystallized from ethanol into white crystals.

Spiro[cyclopentanyl-1′,2-(4-acetyl-3-amino-1-phenyl)pyrrol-5-one] 9a, spiro[cyclohexanyl-1′,2-(4-acetyl-3-amino-1-phenyl)pyrrol-5-one 9b, and spiro[cycloheptanyl-1′,2-(4-acetyl-3-amino-1-phenyl)pyrrol-5-one] 9c. A mixture of compound **1a**, **1b**, or **1c** with ethylacetoacetate in diphenylether (20 mL) was refluxed for 3 h, then the reaction mixture was evaporated in vacuo. Upon cooling, the residual mass was extracted with petroleum ether (40:60) (50 mL), and the ethereal extracted layer was evaporated. The obtained solid was recrystallized from ethanol into brown crystals.

Spiro[cyclopentany-1′,3-(2-imino-4–7-methyl-4-phenyl)-1,4-oxazepin-5-one] 10a, spiro[cyclohexanyl-1′,3-(2-imino-7-methyl-1-phenyl)-1,4-oxazepin-5-one 10b, and spiro[cycloheptanyl-1′,3-(2-imino-7-methyl-1-phenyl)-1,4-oxazepin-5-one] 10c. The reaction mixture of compound **1a**, **1b**, or **1c** with dimethylmalonate in p-xylene (20 mL) was refluxed for 3 h. The solid product was filtered off and recrystallized from ethanol into white crystals.

Synthesis of spiro[cyclopentanyl-1′,4-(2,3-diphenyl-5-imino)1,3-oxazo lidine] 11a, spiro[cyclohexanyl-1′,4-(2,3-diphenyl-5-imino)-1,3-oxazolidine] 11b, and spiro[cycloheptanyl-1′,4-(2,3-diphenyl-5-imino)-1,3-oxazolidine 11c. The titled products were obtained by adding compound **1a**, **1b**, or **1c** (0.01 mol) to a stirred mixture of benzaldehyde (0.01 mol) and a catalytic amount of TEA in ethanol (30 mL). The reaction mixture was refluxed for 3 h, then concentrated, and the solid product was filtered off and recrystallized from ethanol into brown crystals.

Synthesis of spiro[cyclopentanyl-1′,2-(3-amino-1-phenyl)pyrazinolidin-6-one] 12a, spiro[cyclohexanyl-1′,2-(3-amino-1-phenyl)pyrazinolidin-6-one] 12b, and spiro[cycloheptanyl-1′,2-(3-amino-1-phenyl)pyrazinolidin-6-one] 12c. An equimolar mixture of compound **1a**, **1b**, or **1c** and ethyl glyccinate hydrochloride (0.01 mol) in DMF (30 mL) was treated with TEA (0.012 mol). The reaction mixture was refluxed for 3 h, concentrated to its half volume, and poured into ice-cold water. The crude solid was filtered off and recrystallized from ethanol into reddish brown crystals.

Synthesis of spiro[cyclopentanyl-1′,3-(2-amino)thiazinolidin-5-one] 13a, spiro[cyclohexanyl-1′,3-(2-amino)thiazinolidin-5-one] 13b, and spiro[cycloheptanyl-1′,3-(2-amino)thiazinolidin-5-one] 13c. An equimolar mixture (0.01 mol) of compound **1a**, **1b**, or **1c** and ethyl mercaptoacetate (0.01 mol) in p-xylene (30 mL) was treated with a catalytic amount of TEA. The reaction mixture was refluxed for 3 h and evaporated in vacuo. The residual mass was extracted with petroleum ether (40:60) (50 mL), and the ethereal extracted layer was evaporated. The solid product obtained was recrystallized from ethanol into pink crystals.

Spiro[cyclopentanyl-1′,5-(2-amino-6-imino-4-phenyl)-1,3,4-thiadiazine] 14a, spiro[cyclohexanyl-1′,5-(2-amino-6-imino-4-phenyl)-1,3,4-thiadiazine 14b, and spiro[cycloheptanyl-1′,5-(2-amino-6-imino-4-phenyl) thiadiazine 14c. Compound **1a**, **1b**, or **1c** (0.01 mol) and thiosemicarbazide (0.01 mol) in DMF (30 mL) was treated with a catalytic amount of TEA. The reaction mixture was refluxed for 3h, allowed to cool, and then poured into ice-cold water. The solid so formed was collected by filtration and recrystallized from ethanol into brown crystals.

Synthesis of spiro[cyclopentanyl-1′,3-(4,6-diphenyl-2-imino)-1,4-oxazine] 15a, spiro[cyclohexanyl-1′,3-(4,6-diphenyl-2-imino)-1,4-oxazine] 15b, and spiro[cycloheptanyl-1′,3-(4,6-diphenyl-2-imino)-1,4-oxazine] 15c. A mixture of compound **1a**, **1b**, or 1c (0.01 mol) and phenacyl bromide (0.01 mol) in p-xylene (30 mL) was treated with TEA (0.012 mol) and was refluxed for 3 h. The reaction mixture was concentrated in vacuo, and the obtained solid was filtered off, washed with water, and recrystallized from ethanol into white crystals.

Synthesis of spiro[cyclopentanyl-1′,3-(2-imino-4-phenyl)-5,6dihydro-1,4-oxazine] 16a, spiro[cyclohexanyl-1′,3-(2-imino-4-phynyl)-5,6-dihydro-1, 4-oxazine] 16b, and spiro[cycloheptanyl-1′,3-(-2-imino-4-phenyl)-5,6-dihydro-1,4-oxazine] 16c. An equimolar mixture of compound **1a**, **1b**, or **1c** and 2-chloroethanol (0.01 mol) in dioxane (30 mL) was treated with TEA (0.012 mol). The reaction mixture was refluxed for 3 h and concentrated. The precipitated solid was filtered off, washed with water, and recrystallized from methanol into brown crystals.

Synthesis of spiro[cyclopentanyl-1′,2-(3-amino-1-phenyl)piprazin-3-ene] 17a, spiro[cyclohexanyl-1′,2-(3-amino-1-phynyl)piprazin-3-ene]17b, and spiro[cycloheptanyl-1′,2-(3-amino-1-phenyl)piprazin-3-ene] 17c. The titled products were obtained by reacting an equivalent amounts of compound **1a**, **1b**, or **1c** (0.01 mol) with ethanol amine (0.01 mol) in $POCl_3$ (20 mL). The reaction mixture was refluxed for 2 h. Upon cooling, it was poured into ice-cold water. The precipitated solid was filtered off and recrystallized from ethanol into brown crystals.

Synthesis of spiro[cyclopentanyl-1′,2-(3-amino)(1H)-quinoxaline] 18a, synthesis of spiro[cyclohexanyl-1′,2-(3-amino)(1H)-quinoxaline] 18b, and synthesis of spirocycloheptanyl-1′,2-(3-amino)(1H)-quinoxaline] 18c. Compound **2a**, **2b**, or **2c** (0.01 mol) in p-xylene (30 mL) was allowed to reflux for 3 h. Upon cooling, the precipitated solid was filtered off and recrystallized from ethanol into yellow crystals.

Synthesis of spiro[cyclopentanyl-1′,2-(2-imino)(4H)-bezoxazine] 19a, synthesis of spiro[cyclohexanyl-1′,2-(2-imino)(4H)-benzoxazine] 19b, and synthesis of spiro [cycloheptanyl-1′, 2- (2-imino) (4H)-benzoxazine] 19c. Compound **3a**, **3b**, or **3c** (0.01 mol) in p-xylene (30 mL) was allowed to reflux for 3 h.

Upon cooling, the precipitated solid was filtered off and recrystallized from ethanol into pale yellow crystals.

Synthesis of 1-(2-methylsulphonephenyl)aminocyclohexane-1-carbonitrile 20. Compound **4** (0.02 mol) was dissolved in a mixture of glacial acetic acid (2 mL) and H_2O_2 (15 mL). The reaction mixture was heated at 70–80 °C for 2 h and cooled. The reaction mixture was then poured into crushed ice. The precipitated product was filtered off and recrystallized from aqueous ethanol into colorless crystals.

Synthesis of spiro[cyclohexanyl-1′-2-(3-amino)(1-H,5H)-1,4,5-benzotriazepine] 21. A mixture of compound **20** (0.01 mol) and hydrazine (0.01 mol) in dioxane (30 mL) was refluxed for 7 h. Dioxane was evaporated in vacuo, and the residual mass was extracted with ether (45 mL). The ethereal extracted layer was evaporated, and the solid product was recrystallized from ethanol into brown crystals.

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