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Synthesis of Functionalized Spiro[cycloalkanono-2,3′-thiophenes] *via* Tandem Conjugate Addition-Cyclization of 3-Oxoacid Thioanilides to Nitroalkenes

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Summary. A convenient method is described for the synthesis of functionalized spiro[cycloalkanono-2,3′-thiophenes] by treatment of cyclic 3-oxoacid thioanilides with β-nitrostyrenes. Reaction of the obtained products with acetic anhydride yielded the corresponding oxime acetates.

Keywords. 3-Oxoacid thioanilides; β-Nitrostyrene; *Michael* addition; Spiro[cycloalkanono-2,3′-thiophenes].

Introduction

Michael addition is one of the most important strategies for forming C–C bonds. This is mainly due to the broad spectrum of donors and acceptors that can be employed in these syntheses. Nitroalkenes have found wide application as acceptors in these reactions because the nitro group may be converted into diverse functionalities, such as amines, aldehydes or ketones, oximes, amides, and nitriles [1, 2]. Conjugate addition of CH acids, *e.g.* 1,3-dicarbonyl compounds to nitroalkenes catalysed by potassium fluoride afforded furan derivatives [3]. *Barton et al.* [4, 5], *Ono et al.* [6], and *Lash et al.* [7] have successfully applied reactions of nitroalkenes with alkyl isocyanoacetates in the synthesis of pyrrole derivatives, which were in turn used for the construction of porphyrins and related compounds. *Pätzel et al.* [8] have demonstrated the synthesis of optically active β-amino acids *via* conjugate addition and transformation of optically active nitroalkenes to vinylmagnesium bromide.

Recently, we have reported an efficient synthesis of functionalized thiophenes as well as their conversion into nitrogen heterocycles. The synthesis consists of the

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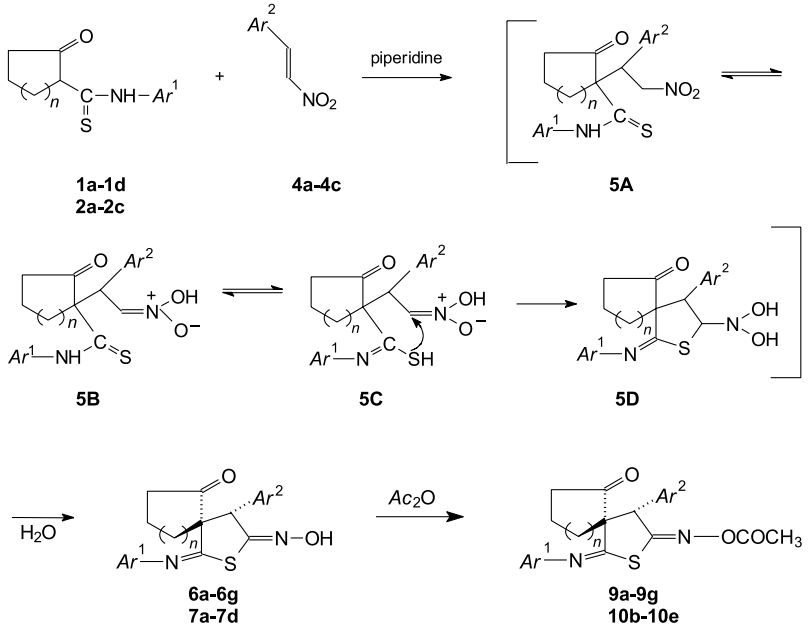
reaction of (*E*)-β-nitrostyrenes with 3-oxoacid thioanilides, *e.g.* 3-(benzoyl)-thioacetanilides [9], 1-oxo-1,2,3,4-tetrahydro-2-carbothioic acid arylamides [10], and 3-(2-thienylcarbonyl)thioacetanilides [11]. To establish utility and scope of this method, we studied herein the reactions of cyclic 3-oxoacid thioanilides containing five and six membered cycloakanone rings with β-nitrostyrenes and the behaviour of the obtained products under basic and acidic conditions.

Results and Discussion

The starting materials in our experiments were the easily available 2-oxocyclopentano- (**1a**–**1d**), 2-oxocyclohexano-1-carbothioic acid anilides (**2a**–**2c**), 1-oxoindano-2-carbothioic acid anilides (**3a**–**3d**), and *p*-substituted (*E*)-β-nitrostyrenes (**4a**–**4c**). The aim of our studies was to determine the influence of the size of cycloalkanone rings and the substituents in the aryl groups of the thioanilide moiety on the yields and stabilities of the products as well as on the reaction rates.



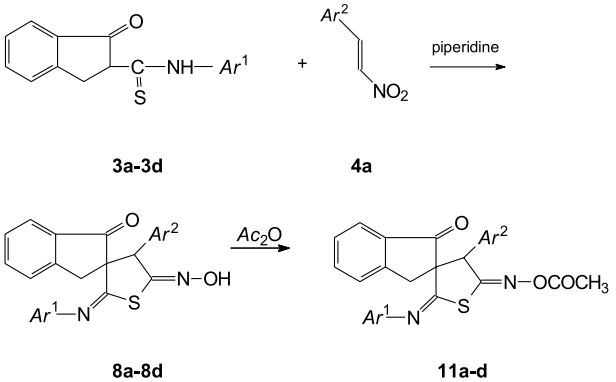
				n	Ar^1	Ar^2
1a	**4a**	**6a**	**9a**	1	C_6H_5	C_6H_5
1a	**4b**	**6b**	**9b**	1	C_6H_5	4-Cl-C_6H_4
1b	**4a**	**6c**	**9c**	1	4-Cl-C_6H_4	C_6H_5
1c	**4a**	**6d**	**9d**	1	4-CH_3-C_6H_4	C_6H_5
1d	**4a**	**6e**		1	4-CH_3O-C_6H_4	C_6H_5
1b	**4b**	**6f**	**9f**	1	4-Cl-C_6H_4	4-Cl-C_6H_4
1c	**4c**	**6g**	**9g**	1	4-CH_3-C_6H_4	4-CH_3-C_6H_4
2a	**4a**	**7a**		2	C_6H_5	C_6H_5
2a	**4b**	**7b**	**10b**	2	C_6H_5	4-Cl-C_6H_4
2b	**4a**	**7c**	**10c**	2	4-Cl-C_6H_4	C_6H_5
2c	**4a**	**7d**	**10d**	2	4-CH_3-C_6H_4	C_6H_5
2a	**4c**	**7e**	**10e**	2	C_6H_5	4-CH_3-C_6H_4

Scheme 1

The reactions of **1** and **2** with **4** carried out in boiling anhydrous ethanol in presence of catalytic amounts of piperidine afford the colorless products **6** and **7** in moderate to good yields (41–86%). Reaction of **1c** with **4a** yielding **6d** (Scheme 1) was representative and allowed us to establish the structure of all obtained products as spiro[cycloalkanono-2,3′-thiophene] derivatives. The molecular mass of **6d** ($m/z = 364$) showed that the addition of **1c** to **4a** was followed by elimination of a water molecule. The IR spectrum of **6d** exhibits a broad band at $\bar{\nu} = 3188\,\mathrm{cm}^{-1}$, characteristic for OH stretching vibration, and the intensive band at $1601\,\mathrm{cm}^{-1}$ of the C=N group. The ^{1}H NMR spectrum of **6d** shows a methyl group singlet at $\delta = 2.35$ ppm and five multiplets in the region of $\delta = 1.43$–3.04 ppm assigned to CH_2 protons of the cyclopentanone ring, and two singlets at $\delta = 4.13$ and 7.83 ppm. The first was assigned to the 4′-H proton of the formed thiophene ring, whereas the second one to the hydroxyl group. Aromatic protons resonate at $\delta = 6.83$–7.34 ppm. The spectral features of **6** and **7** were similar to those of **6d**. Since **6** and **7** were formed as single diastereoisomers, the reaction between the two reagents at prostereogenic centers with formation of two new stereogenic centers proceeded in a diastereoselective way. The proposed mechanism of their synthesis is outlined in Scheme 1.

The key step of this reaction is the *Michael* addition of **1** to **4** giving the saturated nitroalkane **5A**, which may exist in two tautomeric forms **5B** and **5C**. In the second step the nucleophilic attack of a sulfur atom on the α-carbon atom of **5C** gives rise to ring closure furnishing **5D**. Elimination of a water molecule from intermediate **5D** yields spiro[cycloalkanone-2,3′-thiophene] systems **6** and **7**. Similarly, reaction of thioanilides **3** with **4** afforded compounds **8** (Scheme 2). Their spectral features were consistent with the proposed structure.

It was found that the presence of methyl or chlorine substituents in the thioanilide fragments of **1** and **2** or **3** strongly increased the yields of products. In



				Ar^1	Ar^2
3a	**4a**	**8a**	**11a**	C_6H_5	C_6H_5
3b	**4a**	**8b**	**11b**	4-Cl-C_6H_4	C_6H_5
3c	**4a**	**8c**	**11c**	4-CH_3-C_6H_4	C_6H_5
3d	**4a**	**8d**	**11d**	4-Br-C_6H_4	C_6H_5

Scheme 2

addition, it facilitated their isolation and purification. Moreover, the reaction with thioanilides **1** and **3** containing five membered rings, occurred faster than with **2** yielding the products in higher yields. They easily crystallized from the reaction mixture.

The presence of two C=N bonds in the oxime and arylimine groups of **6**, **7**, and **8** suggested the possibility of their transformation into nitrogen heterocycles, according to *Dimroth* or *Beckmann* rearrangements. These processes are catalysed by acids. When compounds **6** were heated in ethanol solution with diluted hydrochloric acid or in a mixture of acetic acid and acetic anhydride, as well as in *PPA* medium, they underwent decomposition. Similarly, all attempts of ring transformation of **7** and **8** under acidic condition were also unsuccessful. However, **6**, **7**, and **8** were stable and soluble in ethanol solution of sodium hydroxide, but did not undergo any ring transformation. Neutralization of the alkaline solution recovered unchanged material. Heating of **6** in acetic anhydride led to their dissolution and to change of colour of a reaction mixture from pale yellow to intensive yellow. Work-up of the mixture with ice and water followed by chromatographic purification and crystallization afforded colourless crystalline products **9**, which were oxime acetates. In a similar way compounds **7** and **8** yielded the corresponding esters **10** (Scheme 1) and **11** (Scheme 2). The structures of **9**, **10**, and **11** were consistent with their analytical and spectral data.

In summary we present here an efficient one-pot synthesis of polyfunctionalized thiophenes. The failure of their transformation to nitrogen heterocycles is probably due to the low stability of the products under acidic conditions. Efforts to use these and related reactions in the synthesis of other heterocyclic systems are ongoing in our laboratory.

Experimental

Melting points were determined on a *Boetius* hot stage apparatus. IR spectra: Bruker IFS 48 in KBr pellets. NMR spectra: Bruker AMX 500 (^{1}H: 500.14 MHz, ^{13}C: 125.76 MHz) in *DMSO*-d_6 *or* $CDCl_3$ with *TMS* as internal standard. Mass spectra: Finningan Mat 95 (EI, 70 eV). Microanalyses were performed with Euro EA 3000 Elemental Analyzer; their results agreed satisfactorily with the calculated values. 3-Oxoacid thioanilides **1**, **2**, and **3** were obtained according to Refs. [12–14]. Silica gel 60,063-0.2 mm, was used for column chromatography.

*General Procedure for the Synthesis of Compounds **6–8***

A solution of thioanilide **1**, **2**, or **3** (**1a**: 1.09 g; **2a**: 1.16 g; **3a**: 1.33 g, 5 mmol) and the appropriate (*E*)-β-nitrostyrene **4** (**4a** 0.75 g, 5 mmol) in 50 cm^3 of anhydrous ethanol was refluxed with a few drops of piperidine for 3 h. The precipitate was filtered off and washed with 10 cm^3 of ethanol. Products were purified by column chromatography on silica gel using $CHCl_3$ as eluent and crystallized from methanol.

5′-Hydroxyimino-4′-phenyl-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6a**, $C_{20}H_{18}N_2O_2S$)

Colourless prisms; mp 207–208°C; yield 52%; IR (KBr): $\bar{\nu} = 3264$ (OH), 2922–3030 (C–H), 1735 (C=O), 1630 (C=N), 947 (N–O oxime) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.41$–1.50 (m, 1H, CH_2), 1.68–

1.75 (m, 1H, CH_2), 1.99–2.07 (m, 1H, CH_2), 2.21–2.32 (m, CH_2), 2.98–3.03 (m, 1H, CH_2), 4.14 (s, 4′-CH), 6.91–6.93 (m, 2H arom), 7.15–7.37 (m, 8H arom), 7.86 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.22$ (C-3), 32.57 (C-4), 39.31 (C-5), 57.77 (C-4′), 67.67 (C-2,3′ spiro), 119.82, 125.36, 128.52, 128.72, 129.28, 130.56, 133.48, 150.36 (12C arom), 156.10, 166.94 (C=N), 210.34 (C=O) ppm; MS: m/z (%) = 350 (100, $[M]^{+\bullet}$), 333 (15), 295 (76).

4′-(4-Chlorophenyl)-5′-hydroxyimino-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6b**, $C_{20}H_{17}ClN_2O_2S$)

Colourless prisms; mp 182–183°C; yield 86%; IR (KBr): $\bar{\nu} = 3214$ (OH), 2964–3035 (C–H), 1744 (C=O), 1606 (C=N), 961 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.68$–1.73 (m, 1H, CH_2), 1.77–1.82 (m, 1H, CH_2), 2.00–2.10 (m, 1H, CH_2), 2.27–2.32 (m, 1H, CH_2), 2.41–2.48 (m, CH_2), 4.58 (s, 4′-CH), 6.87–6.92 (m, 2H arom), 7.18–7.46 (m, 7H arom), 11.49 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.32$ (C-3), 30.87 (C-4), 36.75 (C-5), 51.57 (C-4′), 67.21 (C-2,3′ spiro), 119.30, 125.11, 128.59, 129.29, 139.83, 132.22, 136.88, 150.45 (12C arom), 153.15, 168.21 (C=N), 212.89 (C=O) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 367 (12), 329 (93).

2′-(4-Chlorophenylimino)-5′-hydroxyimino-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6c**, $C_{20}H_{17}ClN_2O_2S$)

Colourless prisms; mp 224–225°C; yield 58%; IR (KBr): $\bar{\nu} = 3160$ (OH), 2964–3038 (C–H), 1741 (C=O), 1611 (C=N), 951 (N–O oxime) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.31$–1.36 (m, 1H, CH_2), 1.59–1.66 (m, 1H, CH_2), 1.86–1.92 (m, 1H, CH_2), 2.23–2.31 (m, CH_2), 2.84–2.90 (m, 1H, CH_2), 4.58 (s, 4′-CH), 6.90–6.96 (m, 2H arom), 7.24–7.49 (m, 7H arom), 11.52 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.56$ (C-3), 32.14 (C-4), 39.21 (C-5), 55.94 (C-4′), 67.47 (C-2,3′ spiro), 121.29, 128.04, 129.11, 129.28, 130.32, 134.36, 148.85, 149.32 (12C arom), 152.15, 169.17 (C=N), 213.51 (C=O) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 367 (13), 329 (95).

5′-Hydroxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6d**, $C_{21}H_{20}N_2O_2S$)

Colourless prisms; mp 218–219°C; yield 83%; IR (KBr): $\bar{\nu} = 3188$ (OH), 2962–3059 (C–H), 1746 (C=O), 1601 (C=N), 957 (N–O oxime) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.43$–1.50 (m, 1H, CH_2), 1.68–1.75 (m, 1H, CH_2), 2.00–2.08 (m, 1H, CH_2), 2.20–2.32 (m, CH_2), 2.35 (s, CH_3), 2.98–3.04 (m, 1H, CH_2), 4.13 (s, 4′-CH), 6.83–6.85 (m, 2H arom), 7.16–7.34 (m, 7H arom), 7.83 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.20$ (CH_3), 20.93 (C-3), 32.57 (C-4), 39.32 (C-5), 57.69 (C-4′), 67.66 (C-2,3′ spiro), 119.83, 128.47, 128.69, 129.82, 130.58, 133.58, 135.06, 147.83 (12C arom), 156.29, 166.24 (C=N), 213.37 (C=O) ppm; MS: m/z (%) = 364 (100, $[M]^{+\bullet}$), 347 (10), 309 (75).

5′-Hydroxyimino-2′-(4-methoxyphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6e**, $C_{21}H_{20}N_2O_3S$)

Colourless prisms; mp 215–216°C; yield 41%; IR (KBr): $\bar{\nu} = 3135$ (OH), 2962–3034 (C–H), 1741 (C=O), 1605 (C=N), 950 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.29$–1.38 (m, 1H, CH_2), 1.59–1.66 (m, 1H, CH_2), 1.85–1.95 (m, 1H, CH_2), 2.22–2.29 (m, CH_2), 2.86–2.92 (m, 1H, CH_2), 3.77 (s, CH_3), 4.52 (s, 4′-CH), 6.86–6.89 (m, 2H arom), 6.97–7.36 (m, 7H arom), 11.44 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.56$ (CH_3), 32.19 (C-3), 38.92 (C-4), 55.12 (C-5), 55.72 (C-4′), 67.32 (C-2,3′ spiro), 114.38, 120.98, 127.67, 127.97, 130.33, 134.56, 143.07, 152.69 (12C arom), 156.69, 166.52 (C=N), 213.68 (C=O) ppm; MS: m/z (%) = 380 (46, $[M]^{+\bullet}$), 363 (3), 325 (42), 84 (100).

4′-(4-Chlorophenyl)-2′-(4-chlorophenylimino)-5′-hydroxyimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6f**, $C_{20}H_{16}Cl_2N_2O_2S$)

Colourless prisms; mp 227–228°C; yield 72%; IR (KBr): $\bar{\nu} = 3241$ (OH), 2966–3052 (C–H), 1739 (C=O), 1608 (C=N), 946 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 1.35$–1.44 (m, 1H, CH_2), 1.69–1.76 (m, 1H, CH_2), 1.89–1.98 (m, 1H, CH_2), 2.23–2.36 (m, CH_2), 2.83–2.89 (m, 1H, CH_2), 4.64 (s, 4′-CH), 6.84–6.92 (m, 2H arom), 7.32–7.45 (m, 6H arom), 11.57 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.63$ (C-3), 32.11 (C-4), 38.94 (C-5), 54.82 (C-4′), 67.36 (C-2,3′ spiro), 121.26, 128.08, 129.16, 129.27, 132.12, 132.56, 133.39, 148.93 (12C arom), 151.90, 168.77 (C=N), 213.39 (C=O) ppm; MS: m/z (%) = 419 (21, $[M]^{+\bullet}$), 402 (15), 363 (100).

5′-Hydroxyimino-4′-(4-methylphenyl)-2′-(4-methylphenylimino)-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**6g**, $C_{22}H_{22}N_2O_2S$)

Colourless prisms; mp 200–202°C; yield 66%; IR (KBr): $\bar{\nu} = 3208$ (OH), 2950–3027 (C–H), 1747 (C=O), 1614 (C=N), 953 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 1.61$–1.79 (m, CH_2), 1.86–1.92 (m, 1H, CH_2), 1.99–2.05 (m, 1H, CH_2), 2.28 (s, CH_3), 2.38–2.48 (m, CH_2), 4.44 (s, 4′-CH), 6.77–6.82 (m, 2H arom), 7.11–7.23 (m, 6H arom), 11.36 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.30$, 2.35 (CH_3), 20.48 (C-3), 30.90 (C-4), 36.81 (C-5), 52.02 (C-4′), 67.36 (C-2,3′ spiro), 119.31, 127.85, 129.08, 129.69, 134.24, 134.92, 136.71, 148.04 (12C arom), 153.75, 168.13 (C=N), 213.16 (C=O) ppm; MS: m/z (%) = 378 (100, $[M]^{+\bullet}$), 361 (17), 323 (76).

5′-Hydroxyimino-4′-phenyl-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**7a**, $C_{21}H_{20}N_2O_2S$)

Colourless prisms; mp 192–193°C; yield 45%; IR (KBr): $\bar{\nu} = 3266$ (OH), 2937–3060 (C–H), 1714 (C=O), 1620 (C=N), 951 (N–O oxime) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.74$–1.77 (m, CH_2), 1.82–1.99 (m, CH_2), 2.16–2.20 (m, CH_2), 2.52–2.64 (m, CH_2), 4.17 (s, 4′-CH), 6.93–6.98 (m, 2H arom), 7.17–7.39 (m, 8H arom), 7.88 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.42$ (C-3), 24.90 (C-4), 37.47 (C-5), 40.07 (C-6), 58.85 (C-4′), 67.88 (C-2,3′ spiro), 119.50, 125.35, 128.21, 128.54, 129.33, 130.25, 135.34, 150.76 (12C arom), 156.77, 168.36 (C=N), 205.74 (C=O) ppm; MS: m/z (%) = 364 (97, $[M]^{+\bullet}$), 347 (80), 281 (90), 77 (100).

4′-(4-Chlorophenyl)-5′-hydroxyimino-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**7b**, $C_{21}H_{19}ClN_2O_2S$)

Colourless prisms; mp 202–203°C; yield 45%; IR (KBr): $\bar{\nu} = 3171$ (OH), 2944–2959 (C–H), 1719 (C=O), 1614 (C=N), 940 (N–O oxime) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.59$–1.62 (m, 1H, CH_2), 1.71–1.78 (m, 1H, CH_2), 1.87–1.93 (m, 1H, CH_2), 2.03–2.08 (m, 1H, CH_2), 2.10–2.16 (m, 1H, CH_2), 2.23–2.30 (m, 1H, CH_2), 2.58–2.68 (m, CH_2), 4.08 (s, 4′-CH), 6.94–6.96 (m, 2H arom), 7.18–7.40 (m, 7H arom), 7.78 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.42$ (C-3), 24.93 (C-4), 36.71 (C-5), 40.85 (C-6), 58.02 (C-4′), 67.89 (C-2,3′ spiro), 119.49, 125.51, 128.67, 129.37, 131.82, 133.64, 134.18, 150.52 (12C arom), 156.42, 167.59 (C=N), 205.59 (C=O) ppm; MS: m/z (%) = 398 (80, $[M]^{+\bullet}$), 381 (83), 315 (73), 77 (100).

2′-(4-Chlorophenylimino)-5′-hydroxyimino-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**7c**, $C_{21}H_{19}ClN_2O_2S$)

Colourless prisms; mp 234–236°C; yield 48%; IR (KBr): $\bar{\nu} = 3168$ (OH), 2947–3034 (C–H), 1701 (C=O), 1605 (C=N), 955 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d6): $\delta = 1.59$–1.61 (m, 1H, CH_2),

1.68–1.78 (m, 1H, CH_2), 1.79–1.89 (m, CH_2), 1.97–2.02 (m, 1H, CH_2), 2.17–2.21 (m, 1H, CH_2), 2.34–2.40 (m, 1H, CH_2), 2.46–2.49 (m, 1H, CH_2), 4.58 (s, 4′-CH), 6.96–7.01 (m, 2H arom), 7.27–7.51 (m, 7H arom), 11.45 (s, OH) ppm; ^{13}C NMR (*DMSO*-d6): $\delta = 20.60$ (C-3), 24.41 (C-4), 36.57 (C-5), 40.74 (C-6), 56.73 (C-4′), 67.40 (C-2,3′ spiro), 120.92, 127.48, 127.96, 129.02, 129.29, 129.84, 136.37, 149.51 (12C arom), 152.56, 170.31 (C=N), 205.20 (C=O) ppm; MS: m/z (%) = 398 (71, $[M]^{+\bullet}$), 381 (42), 315 (55), 169 (100).

5′-Hydroxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**7d**, $C_{22}H_{22}N_2O_2S$)

Colourless prisms; mp 221–222°C; yield 52%; IR (KBr): $\bar{\nu} = 3154$ (OH), 2941–3027 (C–H), 1702 (C=O), 1602 (C=N), 933 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.57$–1.59 (m, 1H, CH_2), 1.71–1.82 (m, CH_2), 1.84–1.90 (m, 1H, CH_2), 1.97–2.03 (m, 1H, CH_2), 2.15–2.20 (m, 1H, CH_2), 2.32 (s, CH_3), 2.37–2.43 (m, 1H, CH_2), 2.46–2.49 (m, 1H, CH_2), 4.52 (s, 4′-CH), 6.82–6.84 (m, 2H arom), 7.22–7.37 (m, 7H arom), 11.37 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 20.33$ (CH_3), 20.63 (C-3), 24.45 (C-4), 36.61 (C-5), 40.72 (C-6), 56.70 (C-4′), 67.26 (C-2,3′ spiro), 118.95, 127.37, 127.90, 129.69, 129.84, 134.03, 136.49, 148.27 (12C arom), 152.98, 168.56 (C=N), 205.32 (C=O) ppm; MS: m/z (%) = 378 (100, $[M]^{+\bullet}$), 361 (50), 295 (61), 91 (100).

5′-Hydroxyimino-4′-(4-methylphenyl)-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**7e**, $C_{22}H_{22}N_2O_2S$)

Colourless prisms; mp 215–216°C; yield 49%; IR (KBr): $\bar{\nu} = 3289$ (OH), 2949–3078 (C–H), 1695 (C=O), 1632 (C=N), 921 (N–O oxime) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.62$–1.68 (m, 1H, CH_2), 1.72–1.88 (m, CH_2), 1.95–2.01 (m, 1H, CH_2), 2.14–2.23 (m, CH_2), 2.32 (s, CH_3), 2.51–2.64 (m, CH_2), 4.15 (s, 4′-CH), 6.95–6.97 (m, 2H arom), 7.12–7.38 (m, 7H arom), 7.40 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.08$ (CH_3), 21.44 (C-3), 24.87 (C-4), 36.96 (C-5), 41.10 (C-6), 58.67 (C-4′), 67.85 (C-2,3′ spiro), 119.52, 125.31, 129.29, 129.46, 130.17, 132.23, 137.99, 150.82 (12C arom), 157.07, 168.49 (C=N), 205.85 (C=O) ppm; MS: m/z (%) = 378 (100, $[M]^{+\bullet}$), 361 (70), 295 (77).

5′-Hydroxyimino-4′-phenyl-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**8a**, $C_{24}H_{18}N_2O_2S$)

Colourless prisms; mp 166–167°C; yield 48%; IR (KBr): $\bar{\nu} = 3288$ (OH), 2920–3066 (C–H), 1711 (C=O), 1620 (C=N), 942 (N–O oxime) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 3.32$ (d, $J = 18$ Hz, 3-CH), 4.22 (d, $J = 18$ Hz, 3-CH), 4.38 (s, 4′-CH), 6.89–6.90 (m, 1H arom), 7.13–7.60 (m, 13H arom), 7.92 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 35.96$ (C-3), 57.20 (C-4′), 68.36 (C-2,3′ spiro), 119.94, 124.71, 125.39, 125.91, 127.66, 128.44, 129.22, 130.48, 132.49, 134.47, 135.49, 150.16, 152.58 (18C arom), 155.99, 165.97 (C=N), 200.32 (C=O) ppm; MS: m/z (%) = 398 (100, $[M]^{+\bullet}$), 381 (31), 264 (57).

2′-(4-Chlorophenylimino)-5′-hydroxyimino-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**8b**, $C_{24}H_{17}ClN_2O_2S$)

Colourless prisms; mp 210–211°C; yield 61%; IR (KBr): $\bar{\nu} = 3288$ (OH), 2919–3064 (C–H), 1714 (C=O), 1617 (C=N), 947 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 3.44$ (d, $J = 18$ Hz, 3-CH), 4.10 (d, $J = 18$ Hz, 3-CH), 4.88 (s, 4′-CH), 6.85–6.87 (m, 1H arom), 7.11–7.60 (m, 12H arom), 11.65 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 35.62$ (C-3), 54.96 (C-4′), 68.02 (C-2,3′ spiro), 121.36, 123.78, 126.13, 127.59, 127.70, 129.20, 129.26, 130.38, 133.27, 133.63, 135.69, 148.70, 151.98 (18C arom), 152.77, 168.43 (C=N), 200.55 (C=O) ppm; MS: m/z (%) = 432 (100, $[M]^{+\bullet}$), 415 (20), 306 (43).

5′-Hydroxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**8c**, $C_{25}H_{20}N_2O_2S$)

Colourless prisms; mp 207–209°C; yield 81%; IR (KBr): $\bar{\nu} = 3284$ (OH), 2924–3062 (C–H), 1714 (C=O), 1618 (C=N), 952 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 2.28$ (s, CH_3), 3.43 (d, $J = 18$ Hz, 3-CH), 4.11 (d, $J = 18$ Hz, 3-CH), 4.84 (s, 4′-CH), 6.75–6.77 (m, 1H arom), 7.10–7.60 (m, 12H arom), 11.62 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 20.33$ (CH_3), 35.64 (C-3), 54.83 (C-4′), 67.92 (C-2,3′ spiro), 119.43, 123.74, 126.13, 127.54, 127.67, 127.71, 129.68, 130.42, 133.45, 134.29, 135.63, 147.36, 152.44 (18C arom), 152.82, 166.55 (C=N), 200.75 (C=O) ppm; MS: m/z (%) = 412 (100, $[M]^{+\bullet}$), 395 (16), 246 (23).

2′-(4-Bromophenylimino)-5′-hydroxyimino-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**8d**, $C_{24}H_{17}BrN_2O_2S$)

Colourless prisms; mp 207–208°C; yield 57%; IR (KBr): $\bar{\nu} = 3365$ (OH), 2920–3060 (C–H), 1710 (C=O), 1624 (C=N), 944 (N–O oxime) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.34$ (d, $J = 18$ Hz, 3-CH), 4.24 (d, $J = 18$ Hz, 3-CH), 4.38 (s, 4′-CH), 6.88–6.91 (m, 1H arom), 7.32–7.59 (m, 12H arom), 7.81 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 35.96$ (C-3), 57.22 (C-4′), 68.36 (C-2,3′ spiro), 119.94, 121.79, 124.70, 125.38, 125.91, 127.66, 128.43, 129.21, 130.47, 132.30, 135.39, 149.90, 152.32 (18C arom), 155.73, 165.70 (C=N), 200.05 (C=O) ppm; MS: m/z (%) = 478 (13, $[M]^{+\bullet}$), 476 (12, $[M]^{+\bullet}$), 461 (5), 398 (100), 264 (45).

*General Procedure for the Synthesis of Compounds **9–11***

Compound **6**, **7**, **8** (**6b**: 0.38 g; **7b**: 0.40 g; **8b**: 0.43 g, 1 mmol) was treated with 5 cm^3 of acetic anhydride. The mixture was refluxed for 2 h. The deep yellow solution was poured into ice/H_2O. The precipitate was separated and washed with H_2O. Products were purified by column chromatography on silica gel using $CHCl_3$ as eluent and crystallized from methanol.

5′-Acetoxyimino-4′-phenyl-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9a**, $C_{22}H_{20}N_2O_3S$)

Colourless prisms; mp 168–169°C; yield 63%; IR (KBr): $\bar{\nu} = 2965$–3058 (C–H), 1781, 1737 (C=O), 1653 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.49$–1.56 (m, 1H, CH_2), 1.68–1.75 (m, 1H, CH_2), 2.02–2.08 (m, 1H, CH_2), 2.09 (s, CH_3), 2.27–2.33 (m, CH_2), 2.98–3.04 (m, 1H, CH_2), 4.29 (s, 4′-CH), 6.91–6.93 (m, 2H arom), 7.45–7.41 (m, 8H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.19$ (CH_3), 19.25 (C-3), 32.54 (C-4), 39.15 (C-5), 57.79 (C-4′), 67.98 (C-2,3′ spiro), 119.70, 125.66, 128.56, 128.69, 129.40, 130.62, 132.61, 150.11 (12C arom), 164.85 (C-5′), 165.43 (C-2′), 167.24, 212.80 (C=O) ppm; MS: m/z (%) = 392 (100, $[M]^{+\bullet}$), 333 (39), 277 (74).

5′-Acetoxyimino-4′-(4-chlorophenyl)-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9b**, $C_{22}H_{19}ClN_2O_3S$)

Colourless prisms; mp 184–185°C; yield 68%; IR (KBr): $\bar{\nu} = 2926$–3068 (C–H), 1770, 1738 (C=O), 1654 (C=N) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 1.39$–1.46 (m, 1H, CH_2), 1.73–1.79 (m, 1H, CH_2), 1.93–2.04 (m, 1H, CH_2), 2.07 (s, CH_3), 2.25–2.39 (m, CH_2), 2.87–2.91 (m, 1H, CH_2), 4.97 (s, 4′-CH), 6.89–6.91 (m, 2H arom), 7.22–7.48 (m, 7H arom) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.62$ (CH_3), 18.72 (C-3), 31.63 (C-4), 36.58 (C-5), 54.74 (C-4′), 67.49 (C-2,3′ spiro), 119.17, 125.51, 128.35, 129.50, 132.09, 132.16, 133.01, 149.68 (12C arom), 164.30, 164.84 (C=N), 165.57, 213.15 (C=O) ppm; MS: m/z (%) = 426 (95, $[M]^{+\bullet}$), 383 (10), 371 (32), 169 (74), 69 (100).

5′-Acetoxyimino-2′-(4-chlorophenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9c**, $C_{22}H_{19}ClN_2O_3S$)

Colourless prisms; mp 175–176°C; yield 58%; IR (KBr): $\bar{\nu} = 2923–3066$ (C–H), 1772, 1733 (C=O), 1650 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.48–1.55$ (m, 1H, CH_2), 1.68–1.75 (m, 1H, CH_2), 2.00–2.07 (m, 1H, CH_2), 2.11 (s, CH_3), 2.25–2.33 (m, CH_2), 2.96–3.01 (m, 1H, CH_2), 4.29 (s, 4′-CH), 6.85–6.87 (m, 2H arom), 7.26–7.37 (m, 7H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.18$ (CH_3), (C-3), 32.5 (C-4), 39.15 (C-5), 57.83 (C-4′), 68.09 (C-2,3′ spiro), 121.18, 128.64, 128.73, 129.54, 130.58, 131.14, 132.44, 148.52 (12C arom), 164.40, 166.56 (C=N), 167.09, 212.58 (C=O) ppm; MS: m/z (%) = 426 (100, $[M]^{+\bullet}$), 383 (10), 371 (37).

5′-Acetoxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9d**, $C_{23}H_{22}N_2O_3S$)

Colourless prisms; mp 194–195°C; yield 88%; IR (KBr): $\bar{\nu} = 2921–3056$ (C–H), 1773, 1733 (C=O), 1643 (C=N) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 1.48–1.55$ (m, 1H, CH_2), 1.68–1.75 (m, 1H, CH_2), 2.02–2.07 (m, 1H, CH_2), 2.09 (s, CH_3), 2.26–2.32 (m, CH_2), 2.36 (s, CH_3), 2.97–3.03 (m, 1H, CH_2), 4.27 (s, 4′-CH), 6.82–6.84 (m, 2H arom), 7.18–7.34 (m, 7H arom) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 19.17$ (CH_3), 20.96 (C-3), 32.52 (C-4), 39.16 (C-5), 57.68 (C-4′), 67.96 (C-2,3′ spiro), 119.70, 128.51, 128.66, 129.93, 130.62, 132.68, 135.43, 147.54 (12C arom), 164.65, 165.04 (C=N), 167.25, 212.73 (C=O) ppm; MS: m/z (%) = 406 (100, $[M]^{+\bullet}$), 364 (6), 351 (33), 348 (11), 291 (55).

5′-Acetoxyimino-4′-(4-chlorophenyl)-2′-(4-chlorolphenylimino)-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9f**, $C_{22}H_{18}Cl_2N_2O_3S$)

Colourless prisms; mp 201–202°C; yield 62%; IR (KBr): $\bar{\nu} = 2922–3060$ (C–H), 1781, 1735 (C=O), 1651 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.54–1.61$ (m, 1H, CH_2), 1.73–1.79 (m, 1H, CH_2), 2.05–2.10 (m, 1H, CH_2), 2.11 (s, CH_3), 2.22–2.36 (m, CH_2), 2.95–3.01 (m, 1H, CH_2), 4.26 (s, 4′-CH), 6.84–6.87 (m, 2H arom), 7.25–7.37 (m, 6H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.22$ (CH_3), 29.66 (C-3), 32.41 (C-4), 39.10 (C-5), 56.90 (C-4′), 68.02 (C-2,3′ spiro), 121.15, 128.97, 129.57, 130.98, 131.26, 132.00, 134.81, 148.38 (12C arom), 164.04, 165.98 (C=N), 166.90, 212.34 (C=O) ppm; MS: m/z (%) = 460 (100, $[M]^{+\bullet}$), 401 (24), 418 (14), 169 (64).

5′-Acetoxyimino-4′-(4-methylphenyl)-2′-(4-methylphenylimino)-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclopentane-2,3′-thiophene] (**9g**, $C_{24}H_{24}N_2O_3S$)

Colourless prisms; mp 165–166°C; yield 88%; IR (KBr): $\bar{\nu} = 2921–3035$ (C–H), 1784, 1737 (C=O), 1648 (C=N) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 1.32–1.41$ (m, 1H, CH_2), 1.64–1.71 (m, 1H, CH_2), 1.89–1.96 (m, 1H, CH_2), 2.07 (s, CH_3), 2.25–2.29 (m, CH_2), 2.31 (s, CH_3), 2.86–2.91 (m, 1H, CH_2), 4.82 (s, 4′-CH), 6.79–6.81 (m, 2H arom), 7.18–7.25 (m, 6H arom) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.56$, 18.75, 20.33 (CH_3), 20.52 (C-3), 31.64 (C-4), 36.57 (C-5), 55.47 (C-4′), 67.46 (C-2,3′ spiro), 119.17, 125.51, 128.35, 129.50, 132.09, 132.16, 133.01, 149.68 (12C arom), 164.30, 164.84 (C=N), 165.57, 213.15 (C=O) ppm; MS: m/z (%) = 420 (100, $[M]^{+\bullet}$), 360 (34), 230 (68).

5′-Acetoxyimino-4′-(4-chlorophenyl)-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**10b**, $C_{23}H_{21}ClN_2O_3S$)

Colourless prisms; mp 130–131°C; yield 62%; IR (KBr): $\bar{\nu} = 1771$, 1707 (C=O), 1649 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.66–1.72$ (m, 1H, CH_2), 1.78–1.84 (m, 1H, CH_2), 1.88–1.93 (m, 1H, CH_2), 2.07 (s, CH_3), 2.09–2.12 (m, 1H, CH_2), 2.16–2.26 (m, CH_2), 2.55–2.59 (m, 1H, CH_2), 2.65–2.71

(m, 1H, CH_2), 4.30 (s, 4′-CH), 6.95–6.97 (m, 2H arom), 7.21–7.43 (m, 7H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.08$ (CH_3), 21.46 (C-3), 25.28 (C-4), 37.29 (C-5), 41.04 (C-6), 57.73 (C-4′), 68.02 (C-2,3′ spiro), 119.31, 125.81, 128.77, 129.51, 131.42, 133.13, 134.39, 150.33 (12C arom), 164.69, 166.09 (C=N), 167.04, 204.61 (C=O) ppm; MS: m/z (%) = 440 (32, $[M]^{+\bullet}$), 381 (100), 357 (14), 202 (93).

5′-Acetoxyimino-2′-(4-chlorophenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**10c**, $C_{23}H_{21}ClN_2O_3S$)

Colourless prisms; mp 136–137°C; yield 82%; IR (KBr): $\bar{\nu} = 2933$–3028 (C–H), 1769, 1715 (C=O), 1660 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.72$–1.81 (m, 1H, CH_2), 1.83–1.87 (m, CH_2), 1.96–2.02 (m, 1H, CH_2), 2.075 (s, CH_3), 2.09–2.16 (m, 1H, CH_2), 2.23–2.28 (m, 1H, CH_2), 2.49–2.56 (m, CH_2), 4.45 (s, 4′-CH), 6.89–6.94 (m, 2H arom), 7.29–7.39 (m, 7H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.08$ (CH_3), 21.54 (C-3), 25.29 (C-4), 37.83 (C-5), 41.39 (C-6), 58.32 (C-4′), 68.09 (C-2,3′ spiro), 120.81, 128.49, 128.69, 129.63, 129.73, 131.13, 134.77, 149.05 (12C arom), 164.80, 167.01 (C=N), 167.97, 204.43 (C=O) ppm; MS: m/z (%) = 440 (28, $[M]^{+\bullet}$), 382 (93), 169 (99), 111 (100).

5′-Acetoxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**10d**, $C_{24}H_{24}N_2O_3S$)

Colourless prisms; mp 130–131°C; yield 94%; IR (KBr): $\bar{\nu} = 2943$–3029 (C–H), 1772, 1695 (C=O), 1645 (C=N) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.49$–1.53 (m, 1H, CH_2), 1.74–1.82 (m, CH_2), 1.92–1.98 (m, 1H, CH_2), 2.04 (s, CH_3), 2.05–2.10 (m, 1H, CH_2), 2.14–2.19 (m, 1H, CH_2), 2.33 (s, CH_3), 2.42–2.48 (m, 1H, CH_2), 2.52–2.56 (m, 1H, CH_2), 4.79 (s, 4′-CH), 6.85–6.87 (m, 2H arom), 7.25–7.42 (m, 7H arom) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 18.70$, 20.34 (CH_3), 20.52 (C-3), 24.22 (C-4), 35.64 (C-5), 40.26 (C-6), 56.74 (C-4′), 67.49 (C-2,3′ spiro), 118.85, 127.86, 128.12, 129.89, 130.22, 134.65, 134.71, 147.76 (12C arom), 164.95, 165.83 (C=N), 166.53, 204.89 (C=O) ppm; MS: m/z (%) = 420 (67, $[M]^{+\bullet}$), 361 (100), 337 (17), 91 (74).

5′-Acetoxyimino-4′-(4-methylphenyl)-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[cyclohexane-2,3′-thiophene] (**10e**, $C_{24}H_{24}N_2O_3S$)

Colourless prisms; mp 122–123°C; yield 83%; IR (KBr): $\bar{\nu} = 2935$–3058 (C–H), 1777, 1718 (C=O), 1649 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.73$–1.79 (m, 1H, CH_2), 1.81–1.89 (m, CH_2), 2.00–2.03 (m, 1H, CH_2), 2.05 (s, CH_3), 2.09–2.16 (m, 1H, CH_2), 2.21–2.26 (m, 1H, CH_2), 2.31 (s, CH_3), 2.51–2.59 (m, CH_2), 4.41 (s, 4′-CH), 6.96–6.98 (m, 2H arom), 7.12–7.43 (m, 7H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.11$, 21.07 (CH_3), 21.56 (C-3), 25.44 (C-4), 37.88 (C-5), 41.42 (C-6), 57.95 (C-4′), 67.94 (C-2,3′ spiro), 119.32, 125.59, 129.36, 129.45, 129.55, 131.88, 138.16, 150.66 (12C arom), 165.39, 166.90 (C=N), 167.15, 204.57 (C=O) ppm; MS: m/z (%) = 420 (42, $[M]^{+\bullet}$), 361 (100), 337 (18), 202 (84).

5′-Acetoxyimino-4′-phenyl-2′-phenylimino-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**11a**, $C_{26}H_{20}N_2O_3S$)

Colourless prisms; mp 196–198°C; yield 82%; IR (KBr): $\bar{\nu} = 2920$–3063 (C–H), 1770, 1707 (C=O), 1653 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.12$ (s, CH_3), 3.40 (d, $J = 17$ Hz, 3-CH), 4.25 (d, $J = 17$ Hz, 3-CH), 4.54 (s, 4′-CH), 6.88–6.91 (m, 2H arom), 7.12–7.57 (m, 12H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.26$ (CH_3), 35.90 (C-3), 57.33 (C-4′), 68.65 (C-2,3′ spiro), 119.79, 124.76, 125.67, 125.90, 127.76, 128.39, 129.33, 130.47, 131.58, 134.18, 135.57, 149.88, 152.37 (18C arom), 164.54, 164.76 (C=N), 167.32, 199.83 (C=O) ppm; MS: m/z (%) = 440 (85, $[M]^{+\bullet}$), 398 (21), 381 (63), 264 (100).

5′-Acetoxyimino-2′-(4-chlorophenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**11b**, $C_{26}H_{19}ClN_2O_3S$)

Colourless prisms; mp 153–155°C; yield 76%; IR (KBr): $\bar{\nu} = 2921–3070$ (C–H), 1766, 1720 (C=O), 1643 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.14$ (s, CH_3), 3.40 (d, $J = 17$ Hz, 3-CH), 4.22 (d, $J = 17$ Hz, 3-CH), 4.50 (s, 4′-CH), 6.83–6.86 (m, 2H arom), 7.12–7.57 (m, 11H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.24$ (CH_3), 35.86 (C-3), 57.37 (C-4′), 68.75 (C-2,3′ spiro), 121.29, 124.81, 125.89, 127.85, 128.43, 129.48, 129.33, 130.44, 131.41, 134.09, 135.67, 148.32, 152.30 (18C arom), 164.31, 165.69 (C=N), 167.18, 199.68 (C=O) ppm; MS: m/z (%) = 474 (93, $[M]^{+\bullet}$), 415 (78), 169 (100).

5′-Acetoxyimino-2′-(4-methylphenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**11c**, $C_{27}H_{22}N_2O_3S$)

Colourless prisms; mp 169–171°C; yield 85%; IR (KBr): $\bar{\nu} = 2923–3032$ (C–H), 1770, 1715 (C=O), 1649 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.13$ (s, CH_3), 3.39 (d, $J = 17$ Hz, 3-CH), 4.32 (d, $J = 17$ Hz, 3-CH), 4.48 (s, 4′-CH), 6.80–6.81 (m, 2H arom), 7.12–7.57 (m, 11H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.27, 20.96$ (CH_3), 35.89 (C-3), 57.26 (C-4′), 68.64 (C-2,3′ spiro), 119.81, 124.74, 125.90, 127.73, 128.37, 129.87, 130.47, 131.66, 134.24, 135.45, 135.53, 147.33, 152.39 (18C arom), 163.79, 164.97 (C=N), 167.34, 199.91 (C=O) ppm; MS: m/z (%) = 454 (100, $[M]^{+\bullet}$), 395 (54), 246 (63).

5′-Acetoxyimino-2′-(4-bromophenylimino)-4′-phenyl-1-oxo-2′,3′,4′,5′-tetrahydrospiro[indane-2,3′-thiophene] (**11d**, $C_{26}H_{19}BrN_2O_3S$)

Colourless prisms; mp 177–179°C; yield 61%; IR (KBr): $\bar{\nu} = 2921–3064$ (C–H), 1770, 1707 (C=O), 1653 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.15$ (s, CH_3), 3.41 (d, $J = 17$ Hz, 3-CH), 4.26 (d, $J = 17$ Hz, 3-CH), 4.52 (s, 4′-CH), 6.89–6.91 (m, 2H arom), 7.14–7.59 (m, 11H arom) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.27$ (CH_3), 35.91 (C-3), 57.34 (C-4′), 68.67 (C-2,3′ spiro), 119.81, 124.77, 125.68, 125.89, 127.77, 128.39, 129.34, 130.48, 131.59, 134.19, 135.78, 149.89, 152.38 (18C arom), 164.55, 164.76 (C=N), 167.32, 199.83 (C=O) ppm; MS: m/z (%) = 518 (5, $[M]^{+\bullet}$), 520 (4, $[M]^{+\bullet}$), 440 (91), 381 (65), 264 (100).

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