A Unique Approach to Catalyst-Free, One-Pot Synthesis of Spirooxindole-Pyrazolines

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Abstract: A pseudo-five-component synthesis of spirooxindole-pyrazolines via a one-pot and catalyst-free reaction under mild conditions is reported. The 1,1-bishydrazino-2-nitroethylene intermediate generated in situ from the addition of aqueous hydrazine to 1,1-bis(methylthio)-2-nitroethylene is trapped by two equivalents of isatin derivatives to obtain the title compounds.

Key words: spirooxindole, isatin, spiropyrazole, pyrazoline, 1,1-bis(methylthio)-2-nitroethylene, one-pot reaction

The biological activity and structural complexity found in nature has stimulated generations of synthetic chemists to design strategies for assembling challenging structures found in natural products.[1]

Spirooxindole heterocycles, in which the indole ring is linked to the other heterocyclic system through the spiro carbon atom at C-3, show an increased spectrum of biological activities.[2] In addition they are commonly found in pharmaceuticals and a number of natural spirooxindole alkaloids.[3] For example, coerulescine, the simplest spirooxindole found in nature, displays a local anesthetic effect. Figure 1 shows some of the naturally occurring and biologically active spirooxindoles.[4]

Although spirooxindole-pyrazolines are an interesting class of spirooxindoles, they have been less studied than spirooxindole-pyrrolidines. To the best of our knowledge there are only three[5–7] procedures for the synthesis of spirooxindole-pyrazolines, and all of them require at least two steps starting from the condensation of isatine and a reactive methylene nucleophile (Scheme 1).

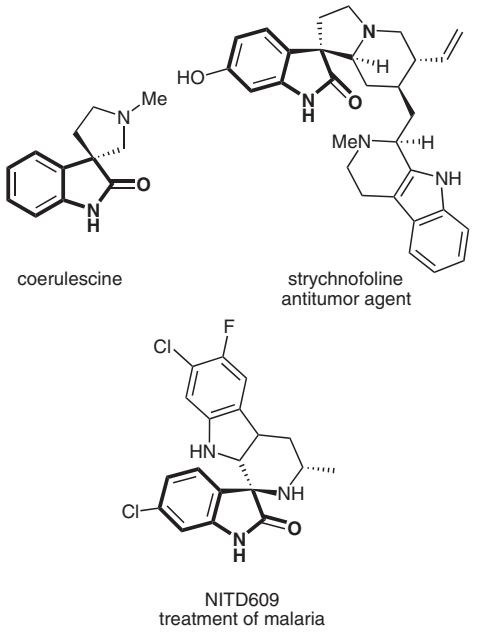
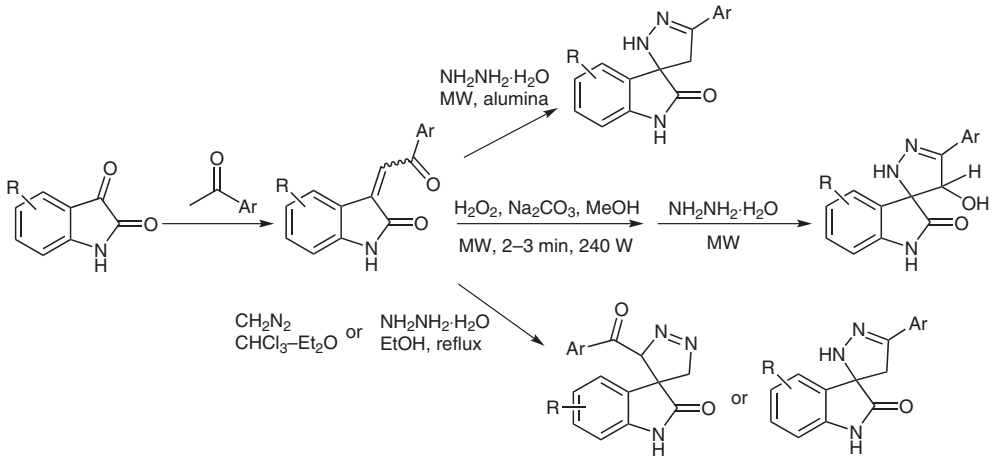


Figure 1 Examples of naturally occurring and biologically active spirooxindoles



Scheme 1 Reported synthesis of spirooxindole-pyrazolines under various conditions requiring at least two steps

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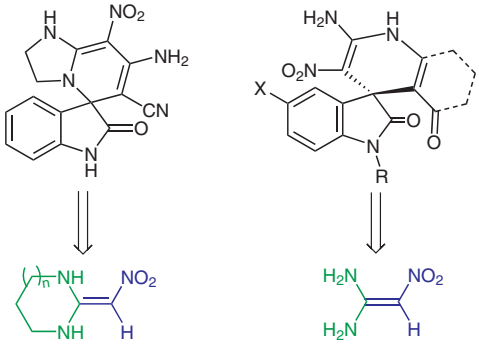
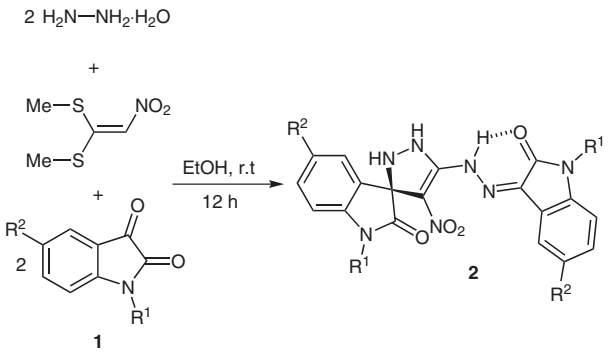
The importance of spirooxindoles has led to a demand for a synthetic methodology; particularly to access those that are fused to a pyrazole ring. Recently, we became interested in the application of ketene aminal intermediates resulting from the reaction of 1,1-bis(methylthio)-2-nitroethylene and nitrogen nucleophiles such as diamines or ammonia for the synthesis of interesting heterocycles in one-pot processes[8] (Scheme 2). Following this lead and in the context of our ongoing investigations on the construction of two-nitrogen heterocycles,[9] we decided to evaluate the reaction of hydrazine hydrate and 1,1-bis(methylthio)-2-nitroethylene in the presence of isatin for the synthesis of spirooxindole-pyrazolines. Initial investigation of the NMR spectrum of the product showed that two equivalents of isatin have been consumed in the reaction. Thus we then optimized the amount of reagents as well as reaction conditions such as solvent, temperature, and time.



Scheme 2 Synthesis of spirooxindoles using ketene aminal intermediates

As shown in Scheme 3, the reaction of two equivalents of hydrazine hydrate, one equivalent of 1,1-bis(methylthio)-2-nitroethylene, and two equivalents of isatin **1** proceeds smoothly in EtOH at room temperature in eight hours to produce spirooxindole-pyrazolines **2** in 60–70% yields.



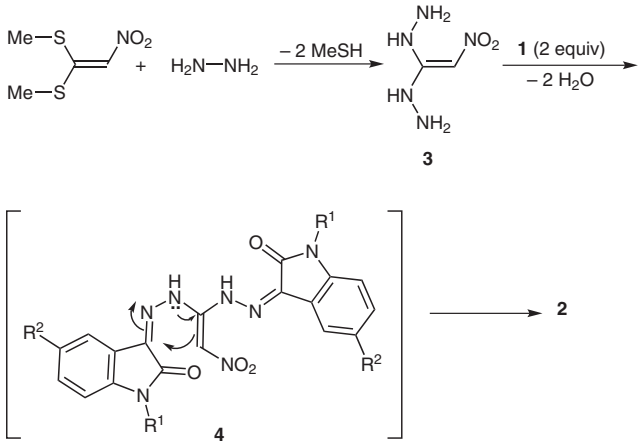
Scheme 3 General one-pot reaction for the synthesis of spirooxindole-pyrazolines

Different types of isatin such as 5-bromo, 5-nitro, and *N*-alkyl isatins were used under the same conditions to investigate the reaction scope and limitations. As depicted in Table 1, the reaction is general with regard to the isatin component (Table 1).

The molecular structure of all spiro compounds **2a–h** was elucidated from their mass spectrometric analyses, IR, and high-field ^{1}H NMR and ^{13}C NMR spectra as described for **2a**.[10] The mass spectrum of **2a** displayed the molecular ion peak at *m/z* = 319 with low intensity. In the IR spectrum, stretching frequencies of five NH groups appear as two broad bands in the region of 3100–3500 cm^{-1}. Absorption bands at 1715, 1616, 1558, and 1340 cm^{-1} are related to NC=O, C=N, C=C, and NO_2 groups, respectively, and indicate the most important functional groups of the product.

The ^{1}H NMR spectrum of **2a** exhibited four singlets at δ = 6.13, 10.79, 11.21, and 13.37 ppm and were assigned as NH protons, as all were exchangeable with D_2O. The first signal is due to the two NH protons of the pyrazoline ring. The second and third signals are attributed to the two NH groups of isatins and are not present when *N*-alkyl isatins are used. The latter is related to the NHN=C which resonates downfield due to intramolecular hydrogen bonding with the NO_2 group, in addition of conjugation with C=CNO_2. Observation of 18 distinct signals in the ^{1}H-decoupled ^{13}C NMR spectrum of **2a** is in agreement with the proposed structure. In the aliphatic region there is one characteristic signal at δ = 74.33 ppm corresponding to the C-3 spiro carbon. Signals of two amidic carbonyls appear at δ = 162.46 and 164.24 ppm. It is proposed that intramolecular hydrogen bonding results in the formation of the *Z*-isomer around the C=N bond in the products **2**.

Although no detailed mechanistic studies have been carried out at this point, our postulated reaction pathway is shown in Scheme 4. Based on the established chemistry of isatin in the presence of compounds containing two nucleophilic centers,[11] 1,1-bishydrazino-2-nitroethylene (**3**) apparently results from the addition of two equivalents of hydrazine to 1,1-bis(methylthio)-2-nitroethylene followed by the loss of two equivalents of methanethiol. Nucleophilic addition via the NH_2 of ketene aminal **3** to the reactive ketonic carbonyl of isatin followed by loss of two equivalents of H_2O affords intermediate **4** which is a bishydrazone. Finally, intermediate **4** undergoes an intramolecular cyclization to form spirooxindole-pyrazoline **2**.



Scheme 4 Proposed mechanism for the one-pot synthesis of spirooxindole-pyrazoline **2**

Table 1 Synthetic Spirooxindole-pyrazolines from the One-Pot Reaction of Hydrazine Hydrate, 1,1-Bis(methylthio)-2-nitroethylene, and Various Isatins

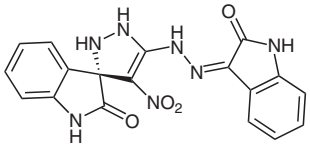
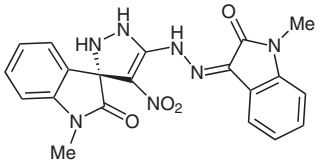
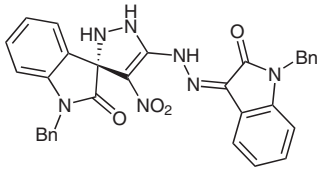
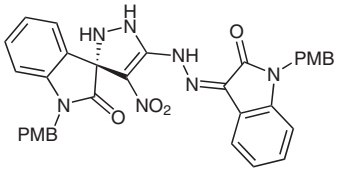
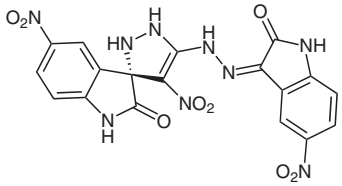
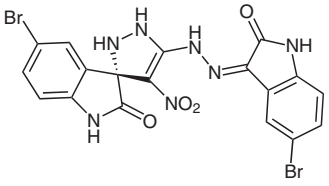
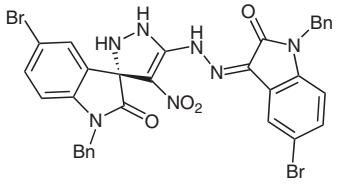
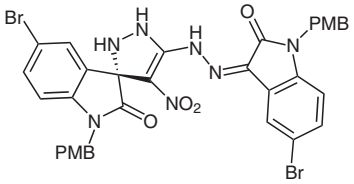
Entry	R^1	R^2	Product	Yield (%)
1	H	H	 **2a**	76
2	Me	H	 **2b**	70
3	Bn	H	 **2c**	65
4	PMB	H	 **2d**	65
5	H	NO_2	 **2e**	64
6	H	Br	 **2f**	68
7	Bn	Br	 **2g**	60

Table 1 Synthetic Spirooxindole-pyrazolines from the One-Pot Reaction of Hydrazine Hydrate, 1,1-Bis(methylthio)-2-nitroethylene, and Various Isatins (continued)

Entry	R^1	R^2	Product	Yield (%)
8	PMB	Br	 **2h**	63

Overall, we have succeeded in developing a novel synthetic method for spirooxindole-pyrazolines of potential synthetic and pharmacological interest from the reaction of hydrazine hydrate, 1,1-(bismethylthio)-2-nitroethylene, and isatin derivatives. Our work presents a very simple one-pot reaction performed under neutral conditions and in the absence of catalyst. From a structural viewpoint, the products are polynitrogen compounds that will be suitable for further elaboration. The products are strongly colored with high heat resistance. High yields and simple reaction and purification procedures are advantages of this approach.

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(10) **Synthesis of Compound 2**

To a magnetically stirred 10 mL flask containing 1,1-bis(thiomethyl)-2-nitroethylene (0.17 g, 1 mmol) in EtOH (4 mL) was added $NH_2NH_2{\cdot}H_2O$ (80% aq, 0.12g, 2 mmol). After 5 h, isatin (0.30 g, 2 mmol) was added to the reaction mixture, and stirring was allowed to continue for 3 h. After the completion of the reaction, the precipitated product was filtered and washed with cold EtOH. Product **2a** was obtained as an orange powder.

Analytical Data for Compounds 2

Compound **2a**: yield 0.30 g (76%); mp >300 °C (dec.). IR (KBr): 3100–3500 (2 br bands, 5 NH), 1715 (2 NC=O), 1616 (C=N, C=C), 1558 and 1340 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.13 (2 H, s, 2 NH), 6.87–7.07 (4 H, m, 4 CH of Ar), 7.36 (3 H, br, 3 CH of Ar), 8.17 (1 H, br, CH of Ar), 10.79 (1 H, s, NH), 11.21 (1 H, s, NH), 13.37 (1 H, s, NH). ^1H NMR (500 MHz, DMSO-d_6–D_2O): δ = 6.84 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH of Ar), 6.88 (1 H, d, $^3J_{HH}$ = 7.6 Hz, CH of Ar), 6.96 (1 H, t, $^3J_{HH}$ = 8.1 Hz, CH of Ar), 7.02 (1 H, t, $^3J_{HH}$ = 7.5 Hz, CH of Ar), 7.29–7.34 (3 H, m, 3 CH of Ar), 8.11 (1 H, d, $^3J_{HH}$ = 7.4 Hz, CH of Ar). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 74.3 (C_{spiro}), 110.6 (CH), 111.2 (CH), 116.6 (C), 119.4 (C), 120.3 (CH), 122.0 (CH), 122.4 (CH), 129.1 (CH), 131.6 (CH), 133.8 (CH), 135.4 (C), 142.4 (C), 145.0 (C), 150.3 (C), 151.0 (C), 162.5 (C=O), 164.2 (C=O). MS: *m/z* (%) = 391 (4) [M^+], 368 (10), 313 (7), 239 (13), 147 (30), 132 (25), 118 (55), 104 (49), 91 (37), 77 (78), 67 (30), 57 (100), 56 (85).

Compound **2b**: yield 0.29 g (70%); orange powder; mp 280 °C (dec). IR (KBr): 3440 (br, 3 NH), 1715 (2 NC=O), 1613 (C=N, C=C), 1561 and 1360 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.21 (3 H, s, Me), 3.33 (3 H, s, Me), 6.15 (2 H, s, 2 NH), 7.06–7.15 (4 H, m, 4 CH of Ar), 7.38–7.49 (3 H, m, 3 CH of Ar), 8.20 (1 H, d, $^3J_{HH}$ = 7.4 Hz, CH of Ar), 13.36 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.7 (Me), 26.0 (Me), 74.3 (C_{spiro}), 109.3 (CH), 110.0 (CH), 116.0 (C), 118.7 (C), 120.0 (CH), 122.6 (CH), 123.0 (CH), 128.8 (CH), 131.6 (CH), 133.8 (CH), 134.8 (C), 143.6 (C), 146.1 (C), 149.7 (C), 151.1 (C), 160.8 (C=O), 162.7 (C=O). MS: *m/z* (%) = 419 (9) [M^+], 373 (10), 232 (12), 214 (13), 200(7), 187 (30), 186 (30), 185 (31), 173 (21), 160 (59), 146 (45),131 (100), 117 (95), 104 (63), 90 (86), 77 (55), 63 (17), 51 (22).

Compound **2c**: yield 0.37 g (65%); orange powder; mp 238–240 °C. IR (KBr): 3447 and 3201 (br, 3 NH), 1722 (2 NC=O), 1610 (C=N, C=C), 1559 and 1353 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.97 (4 H, d, $^3J_{HH}$ = 15.7 Hz, 2 CH_2), 6.20 (2 H, s, 2 NH), 6.97–7.11 (6 H, m, 5 CH of Ar), 7.27–7.374 (12 H, m, 10 CH of Ar), 8.29 (1 H, d, $^3J_{HH}$ = 6.9 Hz, CH of Ar), 13.42 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 42.6 (CH_2), 42.8 (CH_2), 74.3 (C_{spiro}), 109.9 (CH), 110.5 (CH), 116.1 (C), 118.9 (C), 119.5 (C), 120.2 (CH), 122.8 (CH), 123.1 (CH),127.2 (2 CH), 127.3 (2 CH), 127.5 (CH), 127.5 (CH), 128.7 (4 CH), 129.0 (CH), 131.5 (CH), 133.7 (CH), 134.7 (C), 135.6 (C), 136.0 (C), 145.08 (C), 149.54 (C),151. 51 (C), 160.81 (C=O), 163.0 (C=O). MS: *m/z* (%) = 368 (20), 353 (5), 339 (3), 313 (14), 299 (12), 285 (8), 255 (16), 236 (48), 222 (10), 208 (12), 194 (22), 152 (24), 125 (19), 111 (36), 97 (67), 83 (76), 69 (90), 57 (100).

Compound **2d**: yield 0.38 g (65%); orange powder; mp 249 °C. IR (KBr): 3440 (br, 3 NH), 1722 (2 NC=O), 1607 (C=N and C=C), 1561 and 1352 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.25 (6 H, s, 2 Me), 4.93 (4 H, d, $^3J_{HH}$ = 15.2 Hz, 2 CH_2), 6.18 (2 H, s, 2 NH), 6.96–7.04 (4 H, m, 4 CH of Ar), 7.14 (2 H, d, $^3J_{HH}$ = 5.8 Hz, 4 CH of Ar), 7.26 (2 H, d, $^3J_{HH}$ = 6.5 Hz, 4 CH of Ar), 7.35–7.42 (4 H, m, 4 CH of Ar), 8.25 (1 H, d, $^3J_{HH}$ = 6.4 Hz, CH of Ar), 13.41 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.6 (2 Me), 42.3 (CH_2), 42.5 (CH_2), 74.3 (C_{spiro}), 109.9 (CH), 110.6 (CH), 116.1 (C), 118.9 (C), 119.6 (C), 120.2 (CH), 122.7 (CH), 123.1 (CH),127.3 (2 CH), 127.3 (2 CH), 129.2 (4 CH), 131.4 (C), 131.5 (C), 132.2 (CH), 132.5 (CH), 133.7 (CH), 136.7 (C), 136.8 (C), 145.1 (C), 149.6 (C), 151.5 (C), 160.8 (C=O), 163.1 (C=O). MS: *m/z* (%) = 551 (5), 523 (7), 368 (26), 353 (8), 313 (11), 285 (6), 255 (14), 236 (45), 221 (11), 194 (13), 152 (17), 123 (21), 105 (72), 83 (65), 77 (81), 57 (100).

Compound **2e**: yield 0.31 g (64%); mustard powder; up 300 °C. IR (KBr): 3000–3500 (2 br bands, 5 NH), 1732 (2 NC=O), 1618 (C=N, C=C), 1545 and 1339 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.28 (2 H, s, 2 NH), 6.98–7.11 (2 H, m, 2 CH of Ar), 8.17–8.30 (3 H, m, 3 CH of Ar), 8.85 (1 H, br, CH of Ar), 11.53 (1 H, s, NH), 11.87 (1 H, s, NH), 13.42 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 74.2 (C_{spiro}), 110.9 (C), 111.5 (CH), 115.6 (CH), 116.3 (C), 120.2 (C), 123.9 (CH), 127.6 (CH), 129.8 (CH), 134.7 (CH), 142.2 (C), 142.7 (C), 147.6 (C), 147.0 (C), 150.5 (C), 153.4 (C), 162.9 (C=O), 164.4 (C=O). MS: *m/z* (%) = 206 (47), 191 (19), 177 (10), 163 (31), 149 (23), 133 (82), 105 (39), 90 (91), 77 (75), 63 (100), 57 (86).

Compound **2f**: yield 0.37 g (68%); dark brown powder; mp up 280 °C. IR (KBr): 3000–3500 (2 br bands, 5 NH), 1718 (2 NC=O), 1600 (C=N, C=C), 1549 and 1367 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.22 (2 H, s, 2 NH), 6.85–6.90 (2 H, m, 2 CH of Ar), 7.39–7.52 (3 H, m, 3 CH of Ar), 8.30 (1 H, br, CH of Ar), 10.95 (1 H, s, NH), 11.35 (1 H, s, NH), 13.36 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 74.1 (C_{spiro}), 112.6 (C), 113.2 (CH), 113.6 (C), 114.1 (CH), 118.1 (C), 121.6 (C), 122.7 (CH), 131.0 (CH), 133.8 (CH), 134.68 (C), 136.07 (CH), 141.54 (C), 144.18 (C), 149.5 (C), 152.2 (C), 162.1 (C=O), 163.8 (C=O). MS: *m/z* (%) = 551 (6) [M^+ + 4], 549 (12), 547 (6), 523 (9), 368 (47), 353 (7), 313 (22), 285 (13), 264 (19), 240 (20), 238 (20), 237 (42), 152 (24), 98 (75), 83 (83), 71 (85), 57 (100).

Compound **2g**: yield 0.44 g (60%); orange powder; mp 220 °C. IR (KBr): 3437 (br, 3 NH), 1721 (2 NC=O), 1600 (C=N, C=C), 1562 and 1342 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.97 (4 H, d, $^3J_{HH}$ = 14.6 Hz, 2 CH_2), 6.27 (2 H, s, 2 NH), 6.93–6.96 (2 H, m, 2 CH of Ar), 7.27–7.34 (10 H, m, 10 CH of Ar), 7.53 (3 H, br, 3 CH of Ar), 8.35 (1 H, br, CH of Ar), 13.41 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 42.7 (CH_2), 42.8 (CH_2), 74.1 (C_{spiro}), 111.9 (C), 112.6 (C), 114.5 (CH), 115.0 (CH), 117.6 (C), 121.1 (C), 122.7 (C), 127.2 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.6 (C), 128.7 (2 CH), 130.9 (CH), 133.7 (C), 133.9 (C), 135.3 (CH), 135.7 (CH), 135.9 (CH), 141.8 (C), 144.2 (C), 148.6 (C), 160.5 (C=O), 162.6 (C=O). MS: *m/z* (%) = 331 (7), 329 (7), 317 (7), 315 (7), 258 (5), 256 (5), 224 (13), 170 (12), 168 (12), 91 (100), 65 (33).

Compound **2h**: yield 0.48 g (63%); dark brown powder; mp 163 °C. IR (KBr): 3308 and 3203 (br, 3 NH), 1719 (2 NC=O), 1604 (C=N, C=C), 1557 and 1348 (NO_2) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.21 (6 H, s, 2 Me), 4.88 (4 H, br, 2 CH_2), 6.23–7.47 (14 H, m, 14 CH of Ar), 8.31 (1 H, s, NH), 10.17 (1 H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): because of insolubility, only some of the resonances are distinguishable including: δ = 20.6 (2 Me), 74.1 (C_{spiro}), 127.2 (2 CH of Ar), 127.3 (2 CH of Ar), 129.2 (4 CH of Ar). MS: *m/z* (%) = 410 (5), 368 (7), 341 (8), 279

(7), 236 (11), 213 (6), 173 (18), 149 (42), 127 (38), 105 (25), 97 (70), 83 (74), 69 (100), 57 (97).

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