Supporting Information

Convenient One-Pot Synthesis of Spirooxindole Derivatives Containing 1,3,4-Thiadiazine Scaffold

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**Experimental Section**

**General remarks:**
Melting points measured on an Electrothermal 9100 apparatus. IR spectra were recorded as KBr pellets on a NICOLET FT-IR 100 spectrometer. $^1$H NMR (300 MHz, 500 MHz) and $^{13}$C NMR (75 MHz) spectra were obtained using Bruker DRX-300 AVANCE and Bruker DRX-500 AVANCE spectrometers. All NMR spectra at room temperature were recorded in DMSO-$d_6$. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants ($J$ values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Elemental analyses for C, H and N performed using a Heraeus CHN–O–Rapid analyzer. All chemicals were purchased from Merck or Aldrich and were used without further purification.

**General Procedure for the preparation of compounds 4a-g**
A mixture of isatin derivatives 1 (1 mmol), 1-aryl-2-thiocyanatoethanone 2 (1 mmol) and Et$_3$N (1 mmol) in EtOAc (3 mL) was stirred at room temperature for 8 h. Then hydrazonoyl chloride 3 (1 mmol) was added to the above mixture and the reaction was stirred at reflux temperature for 10 min. After completion of the reaction, the reaction mixture was filtered, EtOAc was evaporated and the residue was purified by recrystallization from ethanol to afford the pure product 4 in high yield. The two diastereoisomers of products 4a-c were separated by washing the precipitate with n-Hexane/EtOAc (10/1).

**Characteristic data for compounds 4c-g**

6′-(4-Methoxybenzoyl)-2′,4′-diphenyl-4′,6′-dihydrospiro[indoline-3,5′-[1,3,4]thiadiazin]-2-one (4c) major diastereoisomer

Yellow powder; yield: 0.24 g (48%); mp 165-166 °C. IR (KBr): 3428 (NH), 1716 (C=O, NC=O), 1599 and 1495 (Ar) cm$^{-1}$. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta_H = 3.75$ (3H, s, OCH$_3$), 5.61 (1H, s, CH), 6.79 (2H, d, $^3J_{HH} = 7.7$ Hz, 2×CH of Ar), 6.86 (1H, t, $^3J_{HH} = 7.7$ Hz, CH$_{para}$ of Ph), 6.94 (2H, d, $^3J_{HH} = 6.4$ Hz, 2×CH$_{ortho}$ of Ph), 7.11 (1H, t, $^3J_{HH} = 7.5$ Hz, CH of Ar), 7.28-7.31 (5H, m, 5×CH), 7.40-7.42 (3H, m, 3×CH), 7.50-7.52 (2H, m, 2×CH), 7.86 (2H, d, $^3J_{HH} = 7.0$ Hz, 2×CH of Ar), 10.65 (1H, s, NH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta_C = 52.9$ (CH), 55.6 (OCH$_3$), 87.0 (C$_{spiro}$), 109.1 (CH of Ar), 113.9 (2×CH of Ar), 115.4 (2×CH$_{ortho}$ of Ph), 120.9 (CH of Ar), 121.5 (CH$_{para}$ of ph), 124.0 (CH of Ar), 125.6 (CH of Ar), 126.3 (2×CH$_{ortho}$ of Ph), 128.5 (C$_{ipso}$-C$_{spiro}$), 128.9 (2×CH$_{meta}$ of Ph), 129.1 (2×CH$_{meta}$ of Ph), 129.3 (CH$_{para}$ of ph), 129.6 (2×CH of Ar), 131.1 (C$_{ipso}$-C=N), 131.5 (C$_{ipso}$-C=O), 141.1 (C$_{ipso}$-NHCO), 142.7 (C=N), 143.7 (C$_{ipso}$-N), 163.6 (C$_{ipso}$-OMe),
6'-{(4-Methoxybenzoyl)-2',4'-diphenyl-4',6'-dihydrospiro[indoline-3,5'-[1,3,4]thiadiazin]-2-one (4c) minor diastereoisomer

Yellow powder; yield: 0.20 g (40%); mp 167-169 °C. IR (KBr): 3428 (NH), 1716 (C=O, NC=O), 1599 and 1495 (Ar) cm\(^{-1}\). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta_H = 3.73\) (3H, s, OCH\(_3\)), 4.99 (1H, s, CH), 6.75 (2H, d, \(J_{HH} = 7.7\) Hz, 2×CH of Ar), 6.82 (1H, t, \(3J_{HH} = 7.0\) Hz, CH\(_{para}\) of Ph), 6.91 (2H, d, \(3J_{HH} = 6.4\) Hz, 2×CH\(_{ortho}\) of Ph), 7.20-7.28 (5H, m, 5×CH), 7.39-7.55 (6H, m, 6×CH), 7.97 (2H, d, \(3J_{HH} = 7.7\) Hz, 2×CH of Ar), 10.54 (1H, s, NH). \(13C\) NMR (75 MHz, DMSO-d\(_6\)): \(\delta_C = 52.9\) (CH), 55.6 (OCH\(_3\)), 90.1 (C\(_{spiro}\)), 109.3 (CH of Ar), 113.8 (2×CH of Ar), 115.3 (2×CH\(_{ortho}\) of Ph), 120.7 (CH of Ar), 121.7 (CH\(_{para}\) of ph), 124.1 (CH of Ar), 125.7 (CH of Ar), 126.1 (2×CH\(_{ortho}\) of Ph), 128.6 (C\(_{ipso-C_{spiro}}\)), 128.9 (2×CH\(_{meta}\) of Ph), 129.1 (2×CH\(_{meta}\) of Ph), 129.3 (CH\(_{para}\) of ph), 129.9 (2×CH of Ar), 131.1 (C\(_{ipso-C=N}\)), 131.5 (C\(_{ipso-C=O}\)), 141.1 (C\(_{ipso-NHCO}\)), 142.7 (C=N), 143.5 (C\(_{ipso-N}\)), 163.2 (C\(_{ipso-OMe}\)), 173.2 (NCO), 189.7 (C=O). Anal. Calcd for C\(_{30}H_{23}N_3O_3S\) (505.59): C, 71.27; H, 4.59; N, 8.31%. Found: C, 71.35; H, 4.55; N, 8.25%.

6'-Benzoyl-5-bromo-2',4'-diphenyl-4',6'-dihydrospiro[indoline-3,5'-[1,3,4]thiadiazin]-2-one (4d)

Yellow powder; yield: 0.48 g (85%). IR (KBr): 3424 (NH), 1711 (C=O, NCO), 1596 and 1488 (Ar) cm\(^{-1}\). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta_H = 5.12\) (1H, s, CH of minor diastereoisomer), 5.74 (1H, s, CH of major diastereoisomer), 6.75 (2H, d, \(3J_{HH} = 8.2\) Hz, 2×CH\(_{ortho}\) of Ph), 6.85 (1H, t, \(3J_{HH} = 7.5\) Hz, CH of Ph), 6.90-7.01 (2H, m, 2×CH), 7.16-7.20 (5H, m, 5×CH), 7.26-7.32 (4H, m, 4×CH), 7.40-7.44 (12H, m, 12×CH), 7.49-7.52 (3H, m, 3×CH), 7.55-7.59 (3H, m, 3×CH), 7.79 (2H, d, \(3J_{HH} = 8.0\) Hz, 2×CH\(_{meta}\) of Ph), 7.97 (2H, d, \(3J_{HH} = 7.7\) Hz, 2×CH\(_{ortho}\) of Ph), 10.70 (1H, s, NH of minor diastereoisomer), 10.84 (1H, s, NH of major diastereoisomer). \(13C\) NMR of major diastereoisomer (75 MHz, DMSO-d\(_6\)): \(\delta_C = 53.1\) (CH), 87.4 (C\(_{spiro}\)), 111.3 (CH of Ar), 113.1 (C\(_{ipso-Br}\)), 115.8 (2×CH\(_{ortho}\) of Ph), 122.3 (CH\(_{para}\) of ph), 122.7 (CH of Ar), 126.3 (2×CH\(_{ortho}\) of Ph), 127.3 (CH of Ar), 128.4 (2×CH\(_{meta}\) of Ph), 128.6 (2×CH\(_{meta}\) of Ph), 128.8 (CH\(_{para}\) of ph), 129.2 (2×CH\(_{meta}\) of Ph), 129.4 (2×CH\(_{ortho}\) of Ph), 129.7 (C\(_{ipso-C_{spiro}}\)), 130.4 (CH\(_{para}\) of ph), 131.7 (C\(_{ipso-C=N}\)), 133.5 (C\(_{ipso-C=O}\)), 133.9 (C\(_{ipso-NHCO}\)), 142.5 (C=N), 142.7 (C\(_{ipso-N}\)), 174.6 (NCO), 190.5 (C=O). \(13C\) NMR of minor diastereoisomer (75 MHz, DMSO-d\(_6\)): \(\delta_C = 54.1\) (CH), 87.4 (C\(_{spiro}\)), 111.2 (CH of Ar), 113.0 (C\(_{ipso-Br}\)), 115.8 (2×CH\(_{ortho}\) of Ph), 122.6 (CH\(_{para}\) of ph), 122.7 (CH of Ar), 126.4 (2×CH\(_{ortho}\) of Ph), 127.3 (CH of Ar), 128.4 (2×CH\(_{meta}\) of Ph), 128.6 (2×CH\(_{meta}\) of Ph), 128.8 (CH\(_{para}\) of ph), 129.0 (2×CH\(_{meta}\) of Ph), 129.4 (2×CH\(_{ortho}\) of Ph), 129.7 (C\(_{ipso-C_{spiro}}\)), 130.4 (CH\(_{para}\) of ph), 131.2 (C\(_{ipso-C=N}\)), 133.4 (C\(_{ipso-C=O}\)), 133.9 (C\(_{ipso-NHCO}\)), 142.5 (C=N), 142.7 (C\(_{ipso-N}\)), 175.1 (NCO), 186.2
6'-Benzoyl-2'-(4-chlorophenyl)-1-methyl-4'-phenyl-4',6'-dihydrospiro[indoline-3,5'-[1,3,4]thiadiazin]-2-one (4e)

Orange powder; yield: 0.42 g (80%). IR (KBr): 1712 (C=O, NCO), 1595, 1495 (Ar) cm⁻¹. ¹H NMR (300.13 MHz, DMSO-dma): δH = 2.85 (3H, s, Me of major diastereoisomer), 3.04 (3H, s, Me of minor diastereoisomer), 5.21 (1H, s, CH major diastereoisomer), 5.75 (1H, s, CH of minor diastereoisomer), 6.61 (1H, d, 3JHH = 7.9 Hz, CH of Ar), 6.88 (2H, d, 3JHH = 7.9 Hz, 2×CHortho of Ph), 6.94-6.98 (3H, m, 3×CH), 7.01-7.11 (5H, m, 5×CH), 7.19-7.32 (7H, m, 7×CH), 7.37-7.57 (14, m, 14×CH), 7.78 (2H, d, 3JHH = 8.1 Hz, 2×CH of Ar), 7.97-8.06 (2H, m, 2×CH). ¹³C NMR of major diastereoisomer (75 MHz, DMSO-dma): δC = 26.2 (Me), 52.8 (CH), 88.5 (Cspiro), 108.4 (CH of Ar), 116.1 (2×CHortho of Ph), 122.2 (CH of Ar), 122.4 (CHpara of ph), 123.2 (CH of Ar), 123.5 (CH of Ar), 123.7 (2×CHmeta of Ph), 128.3 (2×CH of Ar), 128.7 (2×CH of Ar), 128.8 (Cipso-Cspiro), 129.2 (2×CHortho of Ph), 129.5 (2×CHortho of Ph), 130.3 (CHpara of ph), 133.3 (Cipso-C=N), 133.6 (Cipso-Cl), 134.1 (Cipso-C=O), 141.6 (Cipso-NMeCO), 142.4 (C=N), 143.1 (Cipso-N), 173.4 (NCO), 192.1 (C=O). ¹³C NMR of minor diastereoisomer (75 MHz, DMSO-dma): δC = 26.1 (Me), 53.1 (CH), 88.6 (Cspiro), 108.4 (CH of Ar), 116.1 (2×CHortho of Ph), 122.3 (CH of Ar), 122.4 (CHpara of ph), 123.2 (CH of Ar), 123.5 (CH of Ar), 127.7 (2×CHmeta of Ph), 128.3 (2×CH of Ar), 128.7 (2×CH of Ar), 128.8 (Cipso-Cspiro), 129.3 (2×CHmeta of Ph), 129.5 (2×CHortho of Ph), 130.4 (CHpara of ph), 133.3 (Cipso-C=N), 133.7 (Cipso-Cl), 134.0 (Cipso-C=O), 141.3 (Cipso-NMeCO), 142.4 (C=N), 143.3 (Cipso-N), 173.3 (NCO), 192.1 (C=O). Anal. Calcd for C₃₀H₂₂ClN₃O₂S (524.03): C, 68.76; H, 4.23; N, 8.02%. Found: C, 68.81; H, 4.27; N, 7.95%

6'-Benzoyl-5-bromo-1-methyl-2',4'-diphenyl-4',6'-dihydrospiro[indoline-3,5'-[1,3,4]thiadiazin]-2-one (4f)

Orange powder; yield: 0.46 g (82%). IR (KBr): 1714 (C=O, NCO), 1594, 1486 (Ar) cm⁻¹. ¹H NMR (300.13 MHz, DMSO-dma): δH = 2.85 (3H, s, Me of major diastereoisomer), 3.04 (3H, s, Me of minor diastereoisomer), 5.21 (1H, s, CH major diastereoisomer), 5.75 (1H, s, CH of minor diastereoisomer), 6.82-6.90 (2H, m, 2×CH), 6.93-6.99 (2H, m, 2×CH), 7.07-7.17 (6H, m, 6×CH), 7.20-7.25 (2H, m, 2×CH), 7.28-7.32 (3H, m, 3×CH), 7.38-7.45 (11H, m, 11×CH), 7.50-7.59 (6H, m, 6×CH), 7.81 (1H, d, 3JHH = 8.1 Hz, CH of Ar), 7.99-8.06 (3H, m, 3×CH). ¹³C NMR of major diastereoisomer (75 MHz, DMSO-dma): δC = 26.3 (Me), 52.8 (CH), 87.6 (Cspiro), 110.3 (CH of Ar), 113.8 (2×CHortho of Ph), 116.0 (Cipso-Br), 122.4 (CH of Ar), 125.8 (CHpara of ph), 126.3 (2×CHortho of Ph), 127.2 (CH of Ar), 128.2 (Cipso-Cspiro), 128.4 (2×CHmeta of Ph), 128.7 (2×CHmeta of Ph), 129.1 (2×CHortho of Ph), 129.4 (CHpara of ph), 129.6 (CHpara of ph), 133.6 (Cipso-C=N), 133.8 (Cipso-C=O), 141.3 (Cipso-NMeCO), 142.4 (C=N), 144.5 (Cipso-N), 172.6 (NCO), 190.5

(C=O). Anal. Calcd for C₂₉H₂₀BrN₃O₂S (554.46): C, 62.82; H, 3.64; N, 7.58%. Found: C, 62.74; H, 3.60; N, 7.53%.
(C=O). $^{13}$C NMR of minor diastereoisomer (75 MHz, DMSO-$d_6$): $\delta_C = 26.0$ (Me), 52.8 (CH), 90.3 ($C_{spiro}$), 110.5 (CH of Ar), 113.8 (2×CH$_{ortho}$ of Ph), 116.0 ($C_{ipso}$-Br), 122.4 (CH of Ar), 125.7 (CH$_{para}$ of Ph), 126.3 (2×CH$_{ortho}$ of Ph), 127.6 (CH of Ar), 128.3 ($C_{ipso}$-$C_{spiro}$), 128.4 (2×CH$_{meta}$ of Ph), 128.7 (2×CH$_{meta}$ of Ph), 128.8 (2CH$_{meta}$ of Ph), 129.0 (2×CH$_{ortho}$ of Ph), 129.4 (CH$_{para}$ of Ph), 129.6 (CH$_{para}$ of Ph), 133.4 ($C_{ipso}$-C=N), 133.8 ($C_{ipso}$-C=O), 141.3 ($C_{ipso}$-NMeCO), 142.4 (C=N), 144.6 ($C_{ipso}$-N), 172.6 (NCO), 190.5 (C=O). Anal. Calcd for C$_{36}$H$_{22}$BrN$_3$O$_2$S (568.48): C, 63.38; H, 3.90; N, 7.39%. Found: C, 63.31; H, 3.94; N, 7.46%.

6'-Benzoyl-5-bromo-2'-(4-chlorophenyl)-1-methyl-4'-phenyl-4',6'-dihydrospiro[indoline-3,5']-[1,3,4]thiadiazin]-2-one (4g)

Yellow powder; yield: 0.51 g (85%). IR (KBr): 1716 (C=O, NCO), 1594 and 1486 (Ar) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta_H = 2.84$ (3H, s, Me of major diastereoisomer), 3.04 (3H, s, Me of minor diastereoisomer), 5.21 (1H, s, CH of minor diastereoisomer), 5.75 (1H, s, CH of major diastereoisomer), 5.21-6.88 (2H, m, 2×CH), 6.94-6.98 (2H, m, 2×CH), 7.03-7.05 (1H, t, $^3$$J_{HH} = 7.5$ Hz, CH$_{para}$ of Ph), 7.10-7.13 (3H, m, 3×CH of Ph), 7.25-7.30 (5H, m, 5×CH), 7.38-7.61 (17H, m, 17×CH), 7.80 (2H, d, $^3$$J_{HH} = 7.6$ Hz, 2×CH of Ar), 8.00 (2H, d, $^3$$J_{HH} = 7.5$ Hz, 2×CH of Ar). $^{13}$C NMR of major diastereoisomer (75 MHz, DMSO-$d_6$): $\delta_C = 26.3$ (Me), 52.8 (CH), 88.0 ($C_{spiro}$), 110.3 (CH of Ar), 113.7 (2×CH$_{ortho}$ of Ph), 116.2 ($C_{ipso}$-Br), 122.6 (CH of Ar), 125.7 (CH$_{para}$ of Ph), 127.5 (CH of Ar), 127.9 (2×CH$_{meta}$ of Ph), 128.1 ($C_{ipso}$-$C_{spiro}$), 128.3 (2×CH of Ar), 128.4 (2×CH of Ar), 128.8 (2×CH$_{meta}$ of Ph), 129.2 (2×CH$_{ortho}$ of Ph), 129.6 (CH$_{para}$ of Ph), 133.6 ($C_{ipso}$-Cl), 133.8 ($C_{ipso}$-C=N), 134.9 ($C_{ipso}$-C=O), 140.1 ($C_{ipso}$-NMeCO), 142.2 (C=N), 144.4 ($C_{ipso}$-N), 172.5 (NCO), 190.3 (C=O). $^{13}$C NMR of minor diastereoisomer (75 MHz, DMSO-$d_6$): $\delta_C = 25.9$ (Me), 52.8 (CH), 88.0 ($C_{spiro}$), 110.5 (CH of Ar), 113.7 (2×CH$_{ortho}$ of Ph), 116.2 ($C_{ipso}$-Br), 122.6 (CH of Ar), 125.7 (CH$_{para}$ of Ph), 127.6 (CH of Ar), 127.9 (2×CH$_{meta}$ of Ph), 128.1 ($C_{ipso}$-$C_{spiro}$), 128.2 (2×CH of Ar), 128.5 (2×CH of Ar), 128.7 (2×CH$_{meta}$ of Ph), 129.2 (2×CH$_{ortho}$ of Ph), 129.6 (CH$_{para}$ of Ph), 133.6 ($C_{ipso}$-Cl), 133.9 ($C_{ipso}$-C=N), 134.6 ($C_{ipso}$-C=O), 140.1 ($C_{ipso}$-NMeCO), 142.2 (C=N), 144.4 ($C_{ipso}$-N), 172.5 (NCO), 190.3 (C=O). Anal. Calcd for C$_{30}$H$_{21}$BrClN$_3$O$_2$S (602.93): C, 59.76; H, 3.51; N, 6.97%. Found: C, 59.80; H, 3.49; N, 6.9.