Communication

Gold-Catalyzed Synthesis of 2-Sulfenylspiroindolenines via Spirocyclizations

Valentin Magné, Pascal Retailleau, Angela Marinetti, Arnaud Voituriez and Xavier Guinchard *

Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1 av. de la Terrasse, 91198 Gif-sur-Yvette cedex, France; valentin.magne@gmail.com (V.M.);
pascal.retailleau@cnrs.fr (P.R.); angela.marinetti@cnrs.fr (A.M.); arnaud.voituriez@cnrs.fr (A.V.)
* Correspondence: xavier.guinchard@cnrs.fr; Tel.: +33-1-6982-4582

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Abstract: 2-Phenylsulfenyl-N-propargyl tryptamines have been prepared by electrophilic sulfuration of the corresponding tryptamines. These compounds undergo gold-catalyzed spirocyclizations to the corresponding 2-phenylthiospiroindolenines in good yields. The compounds were analyzed by NMR experiments, infrared, mass spectra and X-ray diffraction. This method provides a new efficient entry to the synthesis of 2-sulfenyl spiroindolic compounds.

Keywords: gold catalysis; indoles; alkynes; spiro compounds; sulfenyl group

1. Introduction

Gold complexes are highly effective catalysts to trigger the addition of nucleophiles to alkynes [1–6]. Over the last few years, the functionalization of indoles using gold catalysis has stimulated very active research in the fields of catalysis and organic synthesis. It is now well established that indoles can react with alkynes in an intramolecular fashion, upon exposure to Au(I) or Au(III) catalysts, via either their positions 2 or 3 [1,3,6]. When the alkyne is tethered to the 3-position of the indole and if position 2 is substituted, the compound will undergo dearomatizing cyclization [7–9], as illustrated by the conversion of the 2-methyltryptamine derivative 1 (X = Me) into the spiro-compound 2 [10] (Scheme 1). In this field, we have introduced the use of 2-bromotryptamines that led to spirooxindoles 3 after acidic hydrolysis of the spirobromoindolenine resulting from the protodeauration of the intermediate [11–13]. We reasoned that the scope of these spirocyclization reactions might expand to tryptamines with other substituents on their 2-positions and hypothesized that tryptamines substituted by a SPh group should lead to 2-sulfenylspiroindolenines 4. Few members of this general class of compounds were previously studied for their structural resemblance with biologically active spirooxindoles, spiroindolenines or spiroindolines [12]. Their synthetic routes were reported mainly via Pummerer reaction [14–16], thio-Claisen rearrangement [17], isocyanate trapping [18] or electrophilic activation upon silver catalysis [19]. In this paper we report on the use of novel 2-thiophenyltryptamines in gold(I) promoted cyclization reactions for the synthesis of original 2-thiophenylspiroindolenines.
was obtained as an inseparable 88/12 mixture of diastereomers. NOESY experiments allowed the facile determination of the relative configurations of the major diastereoisomer: major-4b displays an (S)-configuration at the quaternary carbon at the ring junction.

We have investigated the cyclization reactions with tryptamine and tryptophane derived substrates. Starting from N-nosyltryptamine 5a (R = H) and N-nosyltryptophane ethyl ester 5b (R = CO₂Et), we have envisaged to functionalize them using the metal-free electrophilic sulfonylation reported by Cossy [20,21], because of its simplicity and efficiency. We first exposed tryptamines 5 to propargyl bromide and successfully set up the propargyl group in good yields (Scheme 2). Tryptamines 6 were next engaged in the sulfonylation reaction using N-(thiophenyl)succinimide [22] in the presence of trifluoroacetic acid. These conditions gave totally regioselective sulfonylation of the C-2 position, leading to the required tryptamine derivatives 7 in good yields.

Tryptamine 7a was exposed to several Au(I) catalysts at different temperature and we finally found that the Gagosz catalyst Ph₃PAuNTf₂ [23] provided the best catalytic activity, leading to the desired spiroindolenine 4a in 97% isolated yield (Scheme 3). This compound showed good chemical stability and could be isolated and characterized without any trouble. Crystals of 4a suitable for X-ray diffraction experiments were grown by slow evaporation of dichloromethane and X-ray data confirmed the structural assignment. An ORTEP (Oak Ridge Thermal Ellipsoid Plot Program) drawing of 4a is displayed in Figure 1 hereafter. We pursued this study with the tryptophane derivative 7b, that led, under similar conditions, to the analogous 2-sulfonylspiroindolenine 4b in 95% yield. This compound was obtained as an inseparable 88/12 mixture of diastereomers. NOESY experiments allowed the facile determination of the relative configurations of the major diastereoisomer: major-4b displays an (S)-configuration at the quaternary carbon at the ring junction.
Transition metal-catalyzed spirocyclizations of N-propargyl or N-allenyl tryptamines have been carried out so far on only a few substrates bearing substituents at the position 2 of the indole. In most of the reported examples, the indole unit is substituted by a methyl or a bromide group [10–13]. The method described herein introduces the sulfenyl group as substituent at C2 of the indole and we demonstrated its compatibility with Au(I)-catalyzed cyclization processes. This route could be applied to both tryptamine and tryptophane derivatives and provides an entry to new members of the 2-sulfenylspiroindoles series. Starting from the chiral tryptophane type substrate, gold(I)-catalyzed cyclization allowed a highly diastereoselective (dr 88/12) synthesis of the corresponding spiroindolenine. It is noteworthy that the cyclization proceeded in excellent yields for both series. Extension of the synthetic approach to spiroindolenines with 2-sulfenyl moieties has also the major advantage to allow post-functionalization of this skeleton of interest, thanks to the known reactivity of the sulfenyl group [14–16].
4. Materials and Methods

Reactions were performed using oven-dried glasswares under an atmosphere of argon. All separations were carried out under flash-chromatographic conditions on silica gel (Redi Sep prepacked column, 230–400 mesh) at medium pressure (20 psi) with use of a CombiFlash Companion. Reactions were monitored by thin-layer chromatography on Merck silica gel plates (Merck, Darmstadt, Germany) (60 F254 aluminum sheets) which were rendered visible by ultraviolet and spraying with vanillin (15%) + sulfuric acid (2.5%) in EtOH followed by heating. CH₂Cl₂, DMF and toluene were purchased at the highest commercial quality and used without further purification. Reagent-grade chemicals were obtained from diverse commercial suppliers and used as received. ¹H-NMR (500 or 300 MHz) and ¹³C-NMR (125 or 75 MHz) spectra were recorded on Bruker Avance spectrometers (Bruker, Wiessembourg, France) at 298 K unless otherwise stated. Chemical shifts are given in ppm (δ) and are referenced to the internal solvent signal or to TMS used as an internal standard. Coupling constants J are given in Hz. Carbon multiplicities were determined by DEPT135 experiments. Diagnostic correlations were obtained by two-dimensional COSY, HSQC and NOESY experiments. Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system (Waltham, MA, USA) using diamond window Dura SamplIR II and the data are reported in reciprocal centimeters (cm⁻¹). Optical rotations were measured on an Anton Paar MCP 300 polarimeter (Anton-Paar, Courtaboeuf, France) at 589 nm.

N-[2-(1H-Indol-3-yl)ethyl]-4-nitro-N-(prop-2-yn-1-yl)benzenesulfonamide (6a)

N-[2-(1H-Indol-3-yl)ethyl]-4-nitrobenzenesulfonamide (5a) (1.0 g, 2.9 mmol, 1 equiv.) was solubilized in dry dimethylformamide (30 mL) under argon, and K₂CO₃ (483 mg, 3.5 mmol, 1.2 equiv.) and propargyl bromide solution (0.31 mL, 80% w/w solution, 3.5 mmol, 1.2 equiv.) were added sequentially. The reaction mixture was stirred for 4 h at room temperature. Then a saturated aqueous solution of NH₄Cl was added before pouring the reaction media in a separatory funnel containing ethyl acetate. After separation of the phases the aqueous phase was extracted twice with ethyl acetate, then dried over MgSO₄ before removing the solvent under reduced pressure. Finally the crude mixture was purified over silica gel column chromatography (eluent 10 to 50% EtOAc/Heptane), furnishing the pure product 6a as an orange foam (1.04 g, 2.71 mmol, 94%).
Ethyl-N-[(4-nitrophenyl)sulfonyl]-N-(prop-2-yn-1-yl)-L-tryptophanate (6b)

![Image of Ethyl-N-[(4-nitrophenyl)sulfonyl]-N-(prop-2-yn-1-yl)-L-tryptophanate (6b)]

Ethyl [(4-nitrophenyl)sulfonyl]-L-tryptophanate (5b) (415 mg, 1.0 mmol, 1 equiv.) was solubilized in dry dimethylformamide (10 mL) under argon, and K$_2$CO$_3$ (152 mg, 1.2 mmol, 1.2 equiv.) and propargyl bromide solution (0.12 mL, 80% w/v solution, 1.1 mmol, 1.1 equiv.) were added sequentially. The reaction mixture was stirred for 4 h at room temperature. Then a saturated aqueous solution of NH$_4$Cl was added before to pour the reaction media in a separatory funnel containing ethyl acetate. After separation of the phases the aqueous phase was extracted twice with ethyl acetate, then the combined organic phases were washed twice with water and with brine. The organic phase was then dried over MgSO$_4$ before removing the solvent under reduced pressure. Finally the crude mixture was purified over silica gel column chromatography (eluent 20 to 50% EtOAc/Heptane), furnishing the pure product 6b as an orange foam (385 mg, 0.845 mmol, 85%).

IR (neat) $\nu_{\text{max}}$: 3370, 3285, 3105, 3070, 1715, 1531, 1353, 1166, 1150, 887, 856, 748 cm$^{-1}$. $^1$H-NMR (CDCl$_3$, 300 MHz): 7.96 (brs, 1H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.66 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.25–7.22 (m, 1H), 7.17 (td, $J = 7.2$ and 1.5 Hz, 1H), 7.1 (ddd, $J = 7.7$, 6.8 and 1.5 Hz, 1H), 6.99 (d, $J = 2.5$ Hz, 1H), 4.81 (dd, $J = 9.6$ and 5.3 Hz, 1H), 4.55 (dd, $J = 18.8$ and 2.5 Hz, 1H), 4.29 (dd, $J = 19.8$ and 2.6 Hz, 1H), 4.17 (qd, $J = 7.2$ and 1.7 Hz, 2H), 3.51–3.44 (m, 1H), 3.18 (dd, $J = 15.0$ and 9.6 Hz, 1H), 2.30 (t, $J = 2.4$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$, 75 MHz): 170.4 (C$_q$), 149.5 (C$_q$), 145.2 (C$_q$), 136.2 (C$_q$), 128.3 (C$_q$), 126.7 (C$_q$), 124.0 (CH), 123.2 (2CH), 122.5 (CH), 120.0 (CH), 118.3 (CH), 111.4 (CH), 110.0 (C$_q$), 79.2 (C$_q$), 73.4 (CH), 62.0 (CH$_2$), 60.6 (CH), 34.2 (CH$_2$), 26.5 (CH$_2$), 14.2 (CH$_3$). HRMS (ESI): calcd. for C$_{19}$H$_{18}$N$_3$O$_4$S$_2$ [M + H]$^+$ 492.1046, found 492.1053. 

$\left\uparrow$-Nitro-N-[2-(phenylthio)-1H-indol-3-yl]ethyl-N-(prop-2-yn-1-yl)benzenesulfonamide (7a)

To a solution of N-[2-(1H-indol-3-yl)ethyl]-N-(prop-2-yn-1-yl)benzenesulfonamide (6a) (383 mg, 1.0 mmol, 1 equiv.) in dry DCM (2 mL) was added 1-(phenylthio)pyrrolidine-2,5-dione (207 mg, 1.0 mmol, 1.0 equiv.) and trifluoroacetic acid (1.15 mL, 15.0 mmol, 15 equiv.). The solution was stirred for 18 h, and the crude media was quenched by a careful addition of NaHCO$_3$ aqueous saturated solution. The aqueous phase was then extracted two times with DCM. The combined organic phases were dried over MgSO$_4$ before removing the solvent under reduced pressure. Finally the crude mixture was purified over silica gel column chromatography (elucent 10 to 50% EtOAc/Heptane), furnishing the pure desired product 7a as a yellow amorphous solid (455 mg, 0.93 mmol, 93%).

IR (neat) $\nu_{\text{max}}$: 3346, 3272, 3100, 3063, 1603, 1581, 1524, 1444, 1344, 1160, 1090, 855 cm$^{-1}$. $^1$H-NMR (CDCl$_3$, 300 MHz): 8.14 (d, $J = 9.2$ Hz, 2H), 8.08 (brs, 1H), 7.84 (d, $J = 9.2$ Hz, 2H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.29–7.27 (m, 1H), 7.25–7.14 (m, 5H), 7.06–7.03 (m, 2H), 4.26 (d, $J = 2.5$ Hz, 2H), 3.49 (ddd, $J = 9.0$ and 6.3 Hz, 2H), 3.17 (dd, $J = 9.1$ and 6.8 Hz, 2H), 2.05 (t, $J = 2.5$ Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 75 MHz): 147.2 (C$_q$), 144.9 (C$_q$), 137.1 (C$_q$), 136.8 (C$_q$), 129.4 (2CH), 128.8 (2CH), 127.5 (C$_q$), 126.9 (2CH), 126.3 (CH), 124.0 (CH), 124.0 (2CH), 123.0 (C$_q$), 120.4 (CH), 119.4 (C$_q$), 119.2 (CH), 111.3 (CH), 76.4 (C$_q$), 416.0916, found 416.0908. [a]$_D$ $-$ 15.5 (c 1.0, CHCl$_3$).
74.5 (CH), 46.9 (CH2), 36.8 (CH2), 24.0 (Cq). HRMS (ESI): calcd. for C25H22N3O4S2 [M + H]+ 492.1046, found 492.1053.

**Ethyl-(S)-2-[(4-nitro-N-(prop-2-yn-1-yl)phenyl)sulfonamido)-3-[2-(phenylthio)-1H-indol-3-yl]propanoate (7b)**

To solution of ethyl N-[(4-nitrophenyl)sulfonyl]-N-(prop-2-yn-1-yl)-L-tryptophanate (6b) (385 mg, 0.85 mmol, 1 equiv.) in dry DCM (2 mL) was added 1-(phenylthio)pyrroli dine-2,5-dione (184 mg, 0.89 mmol, 1.05 equiv.), and trifluoroacetic acid (0.98 mL, 12.75 mmol, 15 equiv.). The solution was stirred for 18 h, and the crude media was quenched by a careful addition of NaHCO3 aqueous saturated solution. The aqueous phase was then extracted two times with DCM. The combined organic phases were dried over MgSO4 and the volatiles were removed under vacuum. The crude mixture was then purified over silica gel column chromatography (eluent 20 to 50% EtOAc/Heptane), furnishing the pure desired product 7b as a yellow amorphous solid (269 mg, 0.477 mmol, 56%).

**3′-Methylene-1′-[4-nitrophenyl]sulfonyl]-2-(phenylthio)spiro[indole-3,4′-piperidine] (4a)**

4-Nitro-N-[2-[2-(phenylthio)-1H-indol-3-yl]ethyl]-N-(prop-2-yn-1-yl)benzenesulfonamide (7a) (116 mg, 0.236 mmol, 1 equiv.) was poured in a shlenck tube filled with argon, dry toluene (2.4 mL) and PPh3AuNTf2 (8.7 mg, 0.012 mmol, 5 mol %) were added, and the solution was stirred at 70 °C for 15 h. Then the solvent was evaporated and the crude mixture was then purified over silica gel column chromatography (10 to 30% EtOAc:Heptane), furnishing the pure product 4a as a yellowish solid (113 mg, 0.229 mmol, 97%).

IR (neat) νmax: 3372, 3287, 3105, 3070, 2926, 1734, 1717, 1530, 1349, 1144, 1093, 855, 739 cm⁻¹. 1H-NMR (CDCl3, 300 MHz): 8.07 (brs, 1H), 8.00 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.9 Hz, 2H), 7.56 (dd, J = 7.9 and 0.9 Hz, 1H), 7.25–7.10 (m, 6H), 7.03–7.00 (m, 2H), 4.91 (t, J = 7.8 Hz, 1H), 4.46 (t, J = 2.2 Hz, 2H), 3.99 (q, J = 7.2 Hz, 2H), 3.37 (dd, J = 14.5 and 7.5 Hz, 1H), 3.31 (dd, J = 14.5 and 8.1 Hz, 1H), 2.21 (t, J = 2.5 Hz, 1H), 1.04 (t, J = 7.1 Hz, 3H). 13C-NMR (CDCl3, 75 MHz): 170.1 (Cq), 149.8 (Cq), 145.6 (Cq), 137.0 (Cq), 136.3 (Cq), 129.5 (2CH), 128.7 (2CH), 127.4 (Cq), 127.0 (2CH), 126.4 (CH), 124.1 (CH), 123.6 (2CH + Cq), 120.5 (CH), 119.2 (CH), 117.5 (Cq), 111.3 (CH), 78.7 (Cq), 73.7 (CH), 61.9 (CH2), 59.7 (CH2), 34.4 (CH2), 26.1 (CH2), 13.9 (CH3). HRMS (ESI): calcd. for C28H26N3O6S2 [M + H]+ 564.1258, found 564.1268. [α]D 50 = 50.4 (c 1.0 CHCl3).

**Ethyl-(S)-2-[(4-nitro-N-(prop-2-yn-1-yl)phenyl)sulfonamido)-3-[2-(phenylthio)-1H-indol-3-yl]propanoate (7b)**

4-Nitro-N-[2-[2-(phenylthio)-1H-indol-3-yl]ethyl]-N-(prop-2-yn-1-yl)benzenesulfonamide (7a) (116 mg, 0.236 mmol, 1 equiv.) was poured in a shlenck tube filled with argon, dry toluene (2.4 mL) and PPh3AuNTf2 (8.7 mg, 0.012 mmol, 5 mol %) were added, and the solution was stirred at 70 °C for 15 h. Then the solvent was evaporated and the crude media was quenched by a careful addition of NaHCO3 aqueous saturated solution. The aqueous phase was then extracted two times with DCM. The combined organic phases were dried over MgSO4 and the volatiles were removed under vacuum. The crude mixture was then purified over silica gel column chromatography (eluent 20 to 50% EtOAc/Heptane), furnishing the pure product 7b as a yellow amorphous solid (269 mg, 0.477 mmol, 56%).

IR (neat) νmax: 3372, 3287, 3105, 3070, 2926, 1734, 1717, 1530, 1349, 1144, 1093, 855, 739 cm⁻¹. 1H-NMR (CDCl3, 300 MHz): 8.07 (brs, 1H), 8.00 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.9 Hz, 2H), 7.56 (dd, J = 7.9 and 0.9 Hz, 1H), 7.25–7.10 (m, 6H), 7.03–7.00 (m, 2H), 4.91 (t, J = 7.8 Hz, 1H), 4.46 (t, J = 2.2 Hz, 2H), 3.99 (q, J = 7.2 Hz, 2H), 3.37 (dd, J = 14.5 and 7.5 Hz, 1H), 3.31 (dd, J = 14.5 and 8.1 Hz, 1H), 2.21 (t, J = 2.5 Hz, 1H), 1.04 (t, J = 7.1 Hz, 3H). 13C-NMR (CDCl3, 75 MHz): 170.1 (Cq), 149.8 (Cq), 145.6 (Cq), 137.0 (Cq), 136.3 (Cq), 129.5 (2CH), 128.7 (2CH), 127.4 (Cq), 127.0 (2CH), 126.4 (CH), 124.1 (CH), 123.6 (2CH + Cq), 120.5 (CH), 119.2 (CH), 117.5 (Cq), 111.3 (CH), 78.7 (Cq), 73.7 (CH), 61.9 (CH2), 59.7 (CH2), 34.4 (CH2), 26.1 (CH2), 13.9 (CH3). HRMS (ESI): calcd. for C28H26N3O6S2 [M + H]+ 564.1258, found 464.1268. [α]D 50 = 50.4 (c 1.0 CHCl3).
Ethyl-(2'S,3S)-5'-methylene-1'-[(4-nitrophenyl)sulfonyl]-2-(phenylthio)spiro[indole-3,4'-piperidine]-2'-carboxylate (4b)

Ethyl-(S)-2-[(4-nitro-N-(prop-2-yn-1-yl)phenyl)sulphonamide]-3-[2-(phenylthio)-1H-indol-3-yl]propanoate (7b) (56.4 mg, 0.1 mmol, 1 equiv.) was poured in a shlenck tube filled with argon, dry toluene (1 mL) and PPh₃AuNTf₂ (3.7 mg, 0.005 mmol, 5 mol %) were added, and the solution was stirred at 70 °C for 15 h. Then the solvent was evaporated and the crude mixture was purified over silica gel column chromatography (10 to 30% EtOAc:Heptane), furnishing the pure product 4b as a yellowish solid (53.7 mg, 0.95 mmol, 95%). A 88/12 mixture of diastereoisomers was obtained and characterized without further separation. For 1H-NMR only the most abundant diastereomer is described.

IR (neat) νmax: 3105, 3065, 2983, 1740, 1606, 1529, 1454, 1348, 1310, 1164, 1023, 909, 732 cm⁻¹. Mp 82–83 °C. 1H-NMR of major diastereoisomer (CDCl₃, 500 MHz): 8.41 (d, J = 8.9 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H), 7.62–7.60 (m, 2H), 7.45–7.41 (m, 4H), 7.29 (td, J = 7.5 and 1.2 Hz, 1H), 7.18–7.16 (m, 1H), 7.09 (td, J = 7.4 and 0.8 Hz, 1H), 5.12 (s, 1H), 4.83 (dd, J = 11.1 and 5.9 Hz, 1H), 4.60 (s, 1H), 4.47 (d, J = 15.3 Hz, 1H), 4.28 (dt, J = 15.2 and 1.8 Hz, 1H), 4.19-4.07 (m, 2H), 2.63 (dd, J = 14.2 and 11.0 Hz, 1H), 2.08 (dd, J = 14.2 and 6.0 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H). 13C-NMR of major diastereoisomer (CDCl₃, 125 MHz): 183.6 (Cq), 171.0 (Cq), 154.4 (Cq), 150.3 (Cq), 145.6 (Cq), 144.0 (Cq), 138.9 (Cq), 134.4 (2CH), 129.6 (CH), 129.6 (2CH), 129.1 (2CH), 128.8 (CH), 127.7 (Cq), 125.4 (CH), 124.4 (2CH), 122.4 (CH), 120.3 (CH), 115.7 (CH₂), 62.3 (CH₂), 61.3 (Cq), 53.9 (CH), 47.6 (CH₂), 35.1 (CH₂), 14.2 (CH₃). 13C-NMR of minor diastereoisomer (CDCl₃, 125 MHz): 183.3 (Cq), 170.8 (Cq), 153.5 (Cq), 145.6 (Cq), 143.5 (Cq), 137.3 (Cq), 134.7 (Cq), 134.4 (2CH), 129.0 (2CH), 128.7 (CH), 127.9 (Cq), 124.7 (CH), 124.4 (2CH), 121.9 (CH), 111.5 (CH₂), 62.3 (CH₂), 61.9 (Cq), 53.7 (CH), 47.5 (CH₂), 35.9 (CH₂), 14.0 (CH₃). HRMS (ESI): calcd. for C₂₈H₂₆N₃O₈S₂ [M + H]+ 564.1258, found 564.1254.

5. Conclusions

In conclusion, we have reported a new efficient route to 2-sulfenylspiroindolenines using a gold-catalyzed spirocyclization as the key reaction. The key point in this field is often the nature of the substituent at position 2 of the indole, allowing either the synthesis of spiro compounds, or achiral compounds if position 2 is unsubstituted. The synthetic strategy developed features the use of a thiophenyl substituting group at the position 2 of the indole that serves as a directing group to ensure a full regioselectivity at position 3 of the indole during the cyclization. The spiranic derivatives were obtained in excellent yields (>95%) and diastereoselectivity (88/12 dr) when an N-propargyl tryptophane was used. With the ease and excellent regioselectivity of the sulfonylation of the indole and efficiency of spirocyclization, this method might pave the way to the design of new spirocyclizations of indole derivatives.
Supplementary Materials: The following are available online, NMR spectra for all new compounds, cif file for 4a.

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Author Contributions: V.M. performed the experiments and analyzed the IR, MS, and NMR spectral data. P.R. performed the XRay analyses. A.M., A.V. and X.G. conceived and designed the project. X.G. wrote the paper.

References