DOI: 10.1002/ejoc.201301244

A Copper-Catalyzed One-Pot, Three-Component Diastereoselective Synthesis of 3-Spiroazetidinimine-2-oxindoles and Their Synthetic Transformation into Fluorescent Conjugated Indolones

Somasundharam Periyaraja,[a] Ponnusamy Shanmugam,*[a] and Asit Baran Mandal[b]

Keywords: Synthetic methods / Multicomponent reactions / Nitrogen heterocycles / Spiro compounds / Copper / Click chemistry

A facile and efficient copper(I)-catalyzed one-pot, three-component diastereoselective synthesis that provides new 3-spiroazetidinimine-2-oxindoles in excellent yield has been accomplished. The 3-spiroazetidinimine-2-oxindoles underwent a facile ring-opening reaction of the spiroazetidinimine unit by treatment with KOH/MeOH and *p*-thiocresol under basic conditions to afford two new classes of fluorescent conjugated indolones. This method has general applications with regard to the imines that are derived from 9-fluorenone, 1,2-diketones, and 1,2,3-triketones.

Introduction

Spirocyclic compounds are an important class of naturally occurring substances because of their pronounced biological properties.[1–3] Among them, spiro-β-lactams are important because of their antiviral[4] and antibacterial properties.[5] Several syntheses of spiro-β-lactams have been described in the literature.[6] The copper(I)[7]-catalyzed multicomponent reaction[8] between sulfonyl azides and alkynes has drawn special interest because its products are synthetically and biologically important.[9] The synthesis of *N*-sulfonylazetidin-2-imines[9a] through a copper-catalyzed cascade reaction of an alkyne and azide with an imine has been reported. However, copper-catalyzed alkyne–azide cycloaddition reactions (CuAAC) with imines that are derived from 1,2-diketones and 1,2,3-triketones have not been explored. To the best of our knowledge, there have been no reports for the synthesis of 3-spiroazetidinimine-2-oxindoles. Therefore, in continuation of our work on the synthesis of spirooxindoles,[10] we, herein, report the results for the synthesis of various ketone-derived spiroazetidin-2-imines by using a copper-catalyzed in situ generated ketenimine and imine in a formal [2+2] cycloaddition reaction. Ring-opening reactions of azetidines are very efficient methods to synthesize biologically important nitrogen heterocycles.[11] Thus, in addition, we, herein, report two efficient methods for the ring-opening reaction of 3-spiroazetidinimines by using methanolic KOH and *p*-thiocresol under mild basic conditions to afford two new classes of merocyanine dye analogues. One of the ring-opened conjugated indolones shows emission in the violet region.

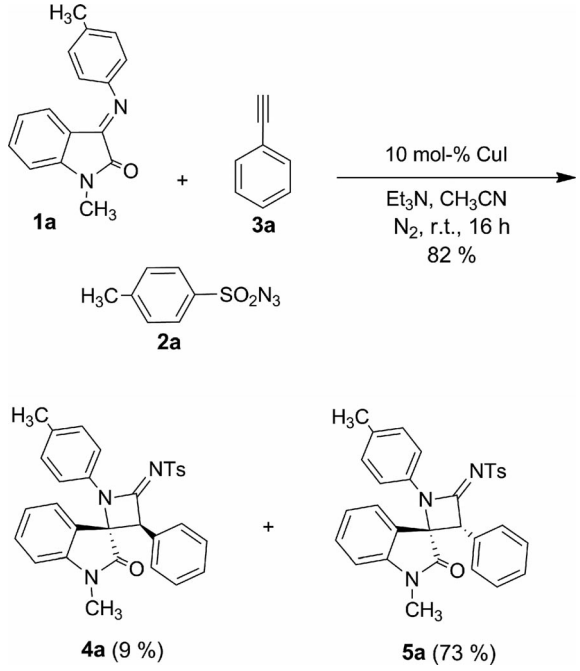
Results and Discussion

Initially, to a mixture of *N*-methylisatinimine **1a** (1.0 equiv.), *p*-toluenesulfonyl azide (**2a**, 1.1 equiv.), and 10 mol-% of CuI in CH_3CN were added phenyl acetylene (**3a**, 1.1 equiv.) and Et_3N (2 equiv.), and the resulting mixture was stirred at room temperature for 16 h under nitrogen. The reaction afforded a mixture of the separable diastereomeric 3-spiroazetidinimine-2-oxindoles **4a** and **5a** in 9 and 73% yield, respectively (see Scheme 1). The structure of compounds **4a** and **5a** were assigned on the basis of spectroscopic analysis (FTIR, ^1H and ^{13}C NMR, and HRMS), and the relative stereochemistry of compounds **4a** and **5a** were derived from single-crystal X-ray analysis (see Figure 1).[12]

To optimize the reaction conditions, different parameters were studied that include changing the molar ratio of the catalyst as well as varying the solvent and base. Using 10 mol-% of CuI and 2 equiv. of Et_3N in CH_3CN were determined as the optimum conditions to afford the maximum yield of products (see Table 1, Entry 1). A prolonged reaction time of 24 h or the use of 2 equiv. of pyridine as the base did not improve the yield. In addition to CH_3CN, a number of other solvents such as CH_2Cl_2, $CHCl_3$, and tetrahydrofuran (THF) were examined under the basic conditions, but no obvious improvement in the yield was observed (see Table 1, Entries 4–6). A change to the molar ratio of the catalyst also proved to be unsuccessful (see

[a] Organic Chemistry Division, Council of Scientific and Industrial Research (CSIR) – Central Leather Research Institute (CLRI),
Adyar, Chennai 600020, India
E-mail: shanmu196@rediffmail.com
http://www.clri.org/WriteReadData/Biodata/PShanmugam.html
[b] Chemical Laboratory, Council of Scientific and Industrial Research (CSIR) – Central Leather Research Institute (CLRI), Adyar, Chennai 600020, India

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301244.



Scheme 1. Synthesis of 3-spiroazetidinimine-2-oxindoles **4a** and **5a**.

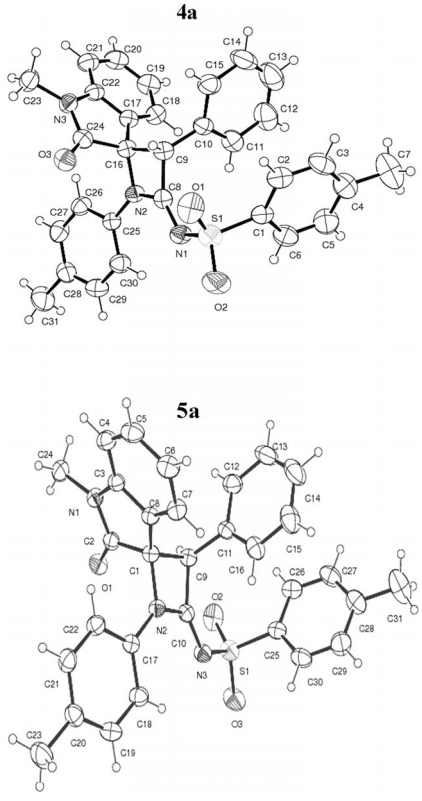


Figure 1. ORTEP diagrams of compounds **4a** and **5a**.

Table 1, Entries 7 and 8). The diastereomeric ratio of the products was determined by ^{1}H NMR spectroscopic analysis of the crude samples.

Table 1. Optimization of the synthesis of 3-spiroazetidinimine-2-oxindoles **4a** and **5a**.

Entry	Catalyst [mol-%]	Solvent	Base	% Yield **4a**/**5a**[a,b]	Diastereomeric ratio **4a**/**5a**[c]
1	10	CH_3CN	Et_3N	9/73	15:85
2	10	CH_3CN	Et_3N	6:71[d]	10:90
3	10	CH_3CN	pyridine	8:68	12:88
4	10	CH_2Cl_2	Et_3N	7:62	14:86
5	10	$CHCl_3$	Et_3N	6:69	8:92
6	10	THF	Et_3N	4:58	7:93
7	20	CH_3CN	Et_3N	7:72	9:91
8	5	CH_3CN	Et_3N	2:64	12:88

[a] Isolated yield. [b] All reactions were performed for 16 h. [c] Determined by the ^{1}H NMR spectroscopic analysis of the crude product. [d] Reaction was performed for 24 h.

Having optimized reaction conditions in hand, the methodology was extended to isatinimines **1a**–**1j** (see Supporting Information, Figure S1) with phenylacetylene (**3a**) and 4-ethynyl-α,α,α-trifluorotoluene (**3b**). All the reactions proceeded smoothly and provided the corresponding 3-spiroazetidinimine-2-oxindoles in good to excellent combined yields (see Figure 2). Imines that were derived from *N*-methylisatin and anilines that contained an electron-releasing group afforded the products in a very good combined yield. Imine **1b**, which was derived from *p*-bromoaniline and *N*-methylisatin, afforded the single diastereomer **5b** in 70% yield. Imine **1c**, which was derived from isatin and *p*-toluidine afforded the single diastereomer **5c** in 66% yield, which is a lower yield than that of the products from imine **1a**. Imine **1d**, which was derived from *p*-anisidine and *N*-methylisatin, resulted in the single diastereomer **5d** in 74% yield. The reaction of imine **1e** that was derived from 1-naphthylamine and *N*-methylisatin gave the single isomer **5e** in 62% yield, which was probably lower than the others because of steric factors. Imine **1f**, which is derived from aniline and *N*-methylisatin, afforded diastereomers **4f** and **5f** in 79% combined yield with a diastereomeric ratio of 11:89. Imine **1g** that was derived from aniline and 5-nitro-1-methylisatin resulted in product **5g** in 72% yield. Imine **1h**, which was derived from aniline and 5-bromo-1-methylisatin, afforded diastereomers **4h** and **5h** in 82% combined yield with a diastereomeric ratio of 13:87. Imine **1i**, from aniline and 5-fluoro-1-methylisatin, afforded diastereomers **4i** and **5i** in a combined yield of 86% with a diastereomeric ratio of 29:71. Imine **1j**, which was derived from aniline and 5-(trifluoromethoxy)-1-methylisatin, afforded diastereomers **4j** and **5j** in 82% combined yield with a diastereomeric ratio of 14:86. The reaction of **1a** and the alkyne substrate **3b** afforded diastereomers **4k** and **5k** in a combined yield of 82% with a diastereomeric ratio of 15:85. Thus, the substitution of the aniline moiety altered the product yield considerably more than that from the substitution of the *N*-methylisatin unit or phenyl acetylene.

To demonstrate the scope of the reaction, imines derived from various ketones were also employed (see Supporting Information, Figure S1). Imine **1k**, which was derived from aniline and 9-fluorenone, afforded the single isomer **5k** in 90% yield. Similarly, imine **1l** that was derived from aniline

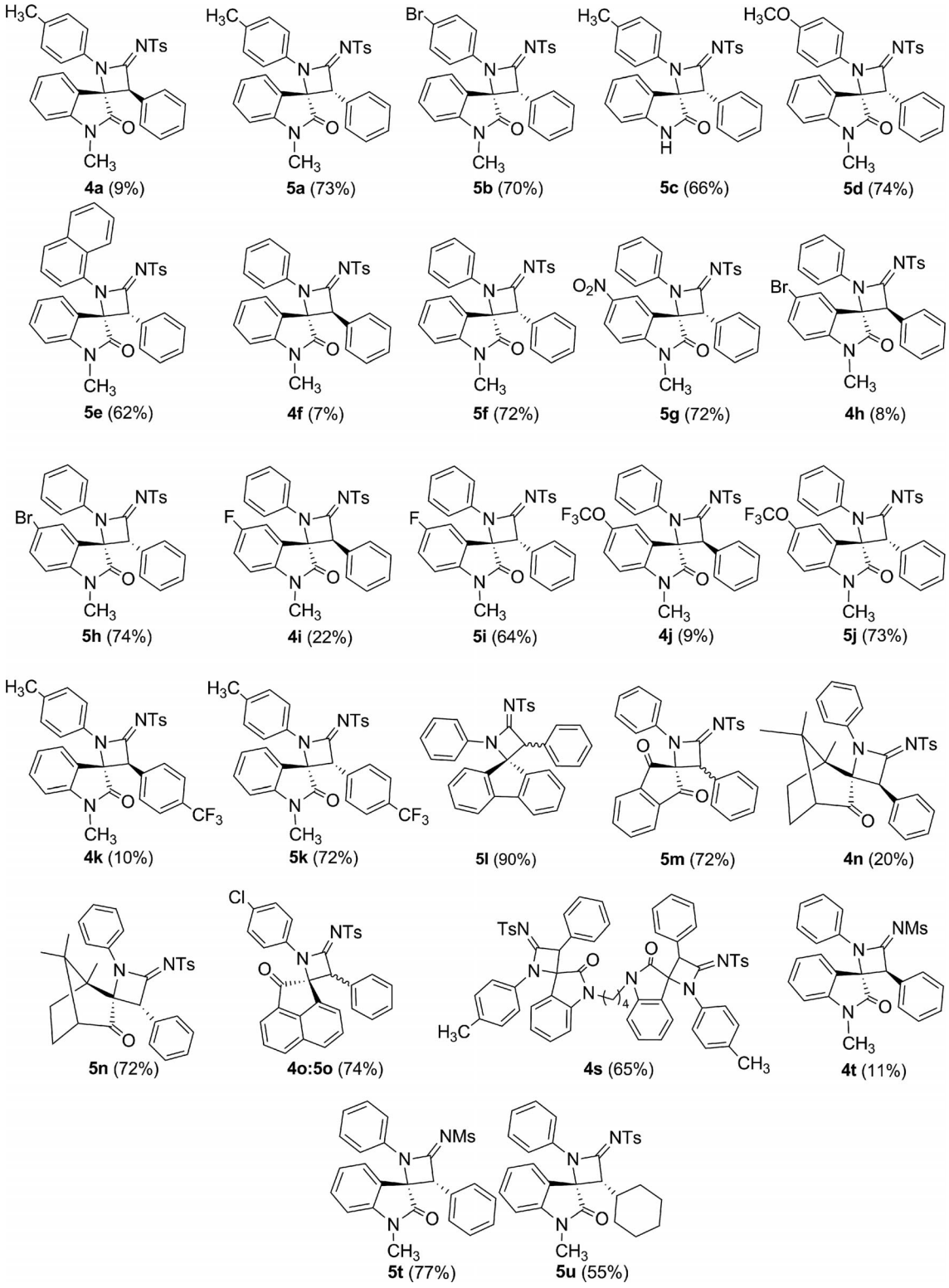
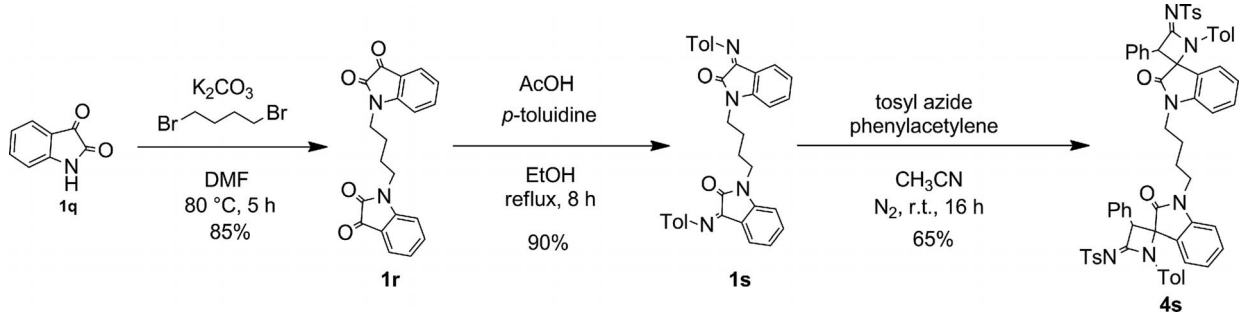


Figure 2. Synthesized spiroazetidinimines (Ts = *p*-tolylsulfonyl, Ms = methylsulfonyl).

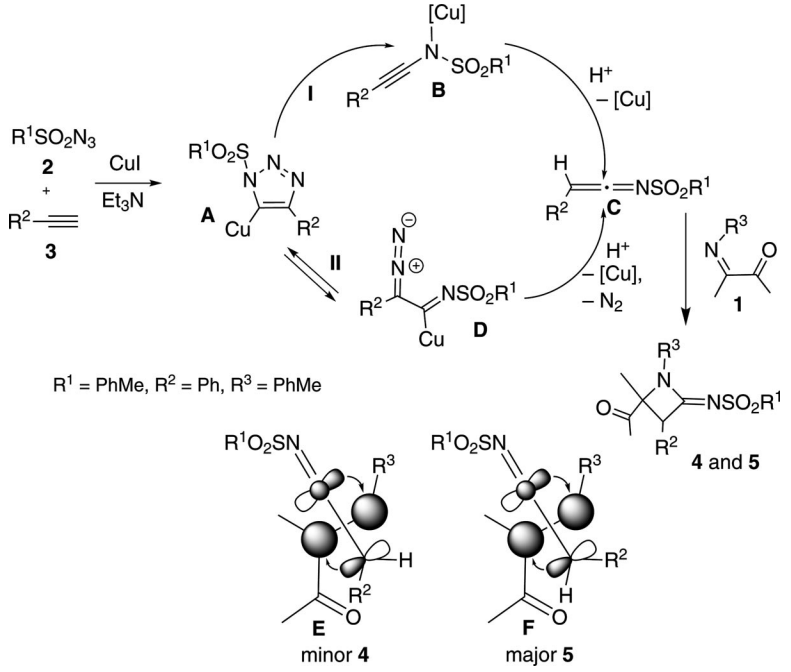
and ninhydrin afforded the single isomer **5l** in 72% yield. Imine **1m**, from aniline and camphoroquinone, afforded diastereomers **4m** and **5m** in a combined yield of 92% with a diastereomeric ratio of 26:74. Imine **1n**, which was derived from 4-chloroaniline and acenaphthoquinone, afforded an inseparable diastereomeric mixture of spiroazetidinimines **4n** and **5n** in 74% combined yield with a diastereomeric ratio of 20:80. However, the imines of 9,10-phenanthroquinone **1o** and **1p** that are derived from 2,4,6-trimethylaniline and 2,6-diisopropylaniline, respectively, decomposed to 9,10-phenanthrenequinone in the reaction to form the azetidinimine. An aliphatic sulfonyl azide such as mesyl az-

ide **2b** with imine **1a** and alkyne **3a** afforded diastereomers **4t** and **5t** in 88% combined yield with a diastereomeric ratio of 17:83. An aliphatic acetylene such as cyclohexylacetylene (**3c**) with imine **1a** and *p*-toluenesulfonyl azide (**2a**) afforded only the single isomer **5u** in 55% yield.

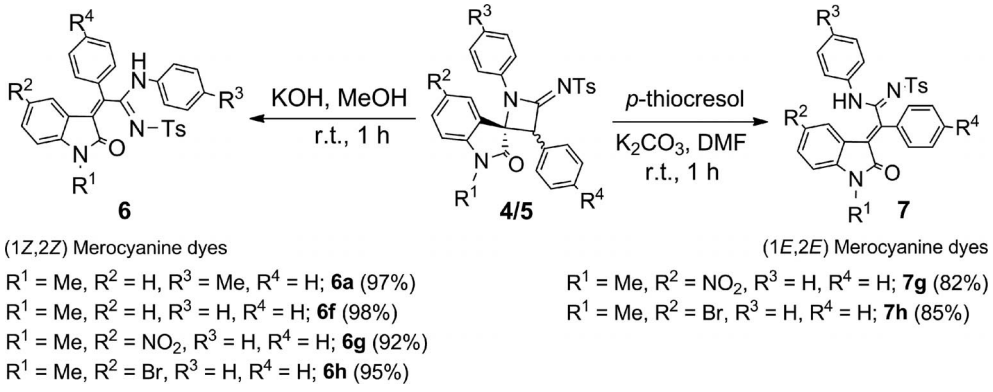
To further demonstrate this method, isatin **1q** and 1,3-dibromopropane under basic conditions afforded the highly functionalized *N*-bridged isatin **1r** in 85% yield. Bis(imine) **1s** was prepared in 90% yield by treating *N*-bridged bis-(isatin) **1r** in ethanol with 2.1 equiv. of *p*-toluidine and a catalytic amount of glacial acetic acid followed by heating the reaction mixture to reflux. To our delight, imine **1s** in CH_3CN with tosyl azide (**2a**), phenyl acetylene (**3a**), CuI, and triethylamine was stirred for 16 h to afford a single iso-



Scheme 2. Synthesis of bis(3-spiroazetidinimine-3-oxindole) **4s**.



Scheme 3. A plausible mechanism of the reaction.



Scheme 4. Synthetic transformations of 3-spiroazetidinimine-2-oxindoles **4** and **5**.

mer of *N*-bridged bis(3-spiroazetidinimine-2-oxindole) **4s** in 65% yield (see Scheme 2).

A plausible reaction mechanism for the formation of **4** and **5** is shown in Scheme 3. Initially, alkyne **3** undergoes a reaction with sulfonyl azide **2** in the presence of triethylamine and CuI to form the (1-sulfonyl-4-phenyltriazol-5-yl) copper intermediate **A**. By following pathways **I** and **II**, intermediate **A** could give the two possible intermediates **B** and **D**, respectively, which could lead to the formation of ketenimine intermediate **C** along with the regeneration of the Cu catalyst. The mechanism of ketenimine formation is well established from the literature.[9a] Then, intermediate **C** could undergo a reaction with imine **1**, which is derived from a ketone. This reaction could proceed through a [2+2] cycloaddition reaction to afford the observed products **4** and **5**. The selectivity of the product formation can be explained from the well-established polarization of the ketenimine and the imine p and p* orbitals.[9f] Thus, orientation **E** gives the minor product **4**, whereas orientation **F** affords the major product **5**.

To demonstrate the synthetic use of the 3-spiroazetidinimine-2-oxindoles, we conducted the reaction of **5h** with KOH in methanol to afford the ring-opened product **6h** in excellent yield. However, both the product and the starting material had the same R_f value, as the reaction was monitored by TLC (see Scheme 4). On the other hand, the attempt to detosylate **5g** by using *p*-thiocresol and K_2CO_3 in *N*,*N*-dimethylformamide (DMF) gave the spiroazetidinimine ring-opened product **7g** in excellent yield (with a lower R_f value than the starting material). The relative stereochemistry of compounds **6h** (1*Z*,2*Z*) and **7g** (1*E*,2*E*) were derived from single-crystal X-ray analysis (see Figure 3).[12] Experiments involving both reactions pathways and starting with mixtures of diastereomers **4** and **5** also afforded single isomers of the ring-opened product. Thus, this method is an efficient route to the synthesis of synthetically important conjugated imine analogues.[13] Azetidinimine **5l** from 9-fluorenone was treated with methanolic KOH to afford ring-opened product **6l** in 97% yield. Upon treatment with methanolic KOH, the inseparable mixture of the diastereomeric spiroazetidinimines **4o** and **5o** afforded the single ring-opened product **6o** in 94% yield.

A plausible mechanism for the formation **6** and **7** has been proposed in Scheme 5. The highly strained spiroazetidinimine ring system is vulnerable to undergo a ring-opening reaction with nucleophiles. Thus, the first step to form product **6** is the nucleophilic attack of the alkoxide ion (RO^-) at the spiro carbon. The subsequent cleavage of the C–N bond gives ring-opened intermediate **I**, which can be drawn as its resonance structure intermediate **J**. Deprotonation followed by elimination of ROH affords the final product **6**. Similarly, the first step to form product **7** is the nucleophilic attack of ArS^- at the spiro carbon to give ring-opened intermediate **K**. Intermediate **K** can also be drawn as its resonance structure intermediate **L**. Deprotonation followed by elimination of ArSH affords the final product **7**. There is steric hindrance between the nucleophile ArS^- and the tosyl group. Thus, the reaction between azetidine **4/5** and the nucleophile ArS^- exclusively affords product **7**, whereas the reaction with the less sterically hindered RO^- nucleophile affords product **6**.

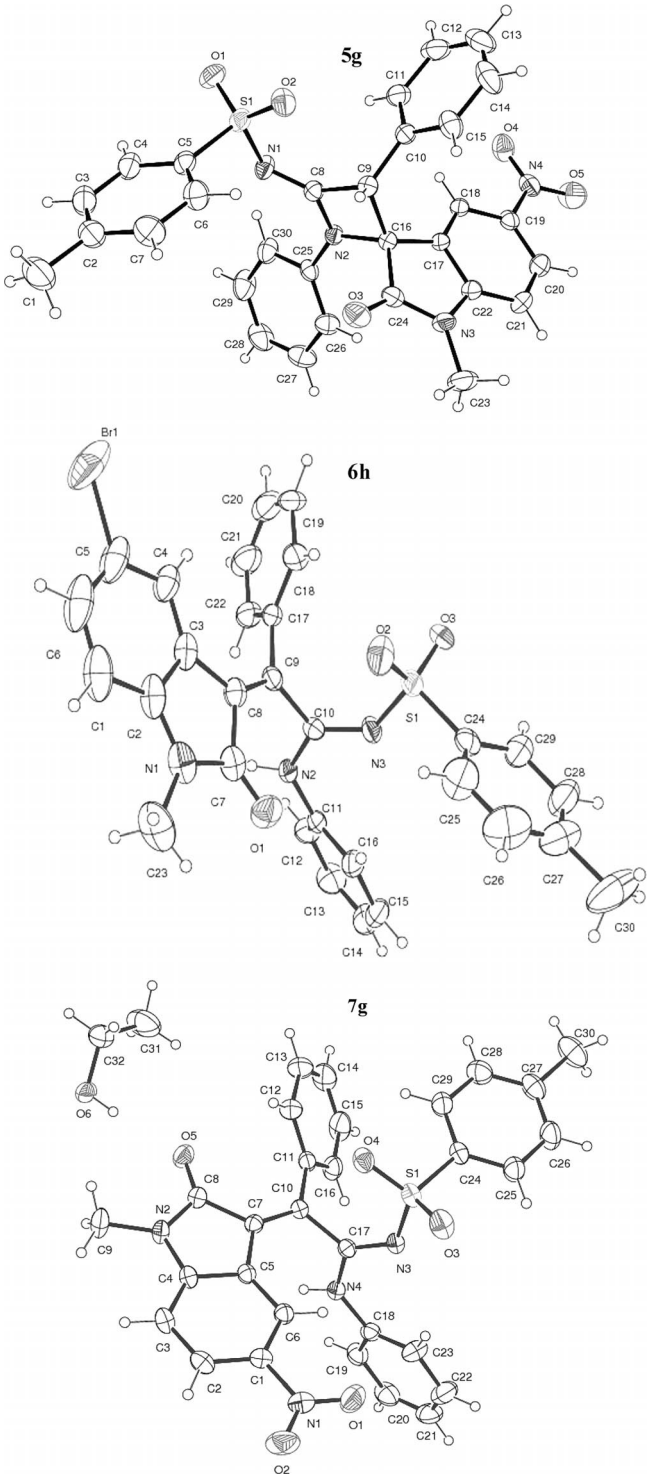
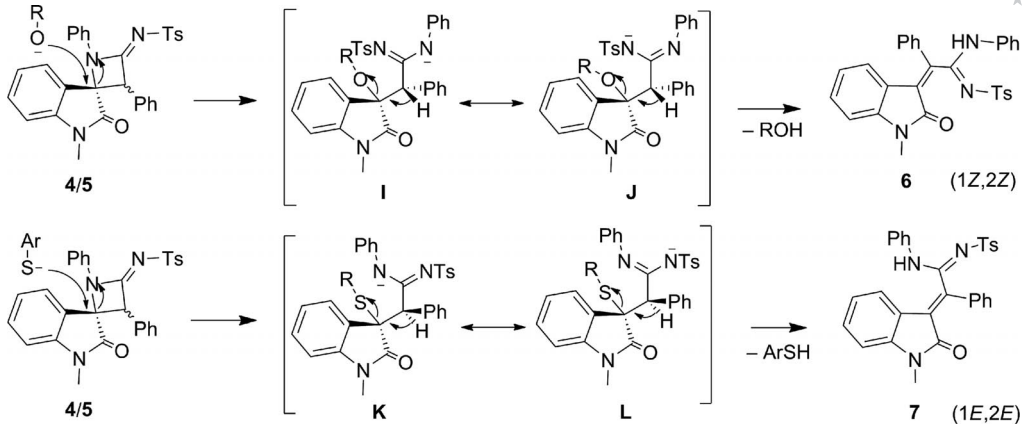


Figure 3. ORTEP diagrams of compounds **5g**, **6h**, and **7g**.

To confirm the fluorescent properties of conjugated indolones **6** and **7**, absorption and emission spectra of these compounds were recorded. Compounds **6f**, **6g**, **6h**, **6l**, and



Scheme 5. Plausible mechanism for the formation of **6** and **7**.

6o showed UV absorption maxima in a range from 312 to 322 nm (see Figure 4 and Table 2) and emission in a range from 408 to 424 nm (see Figure 5 and Table 2). Compounds **7g** and **7h** showed UV absorption at 317 and 320 nm, respectively, however, they did not show any emission.

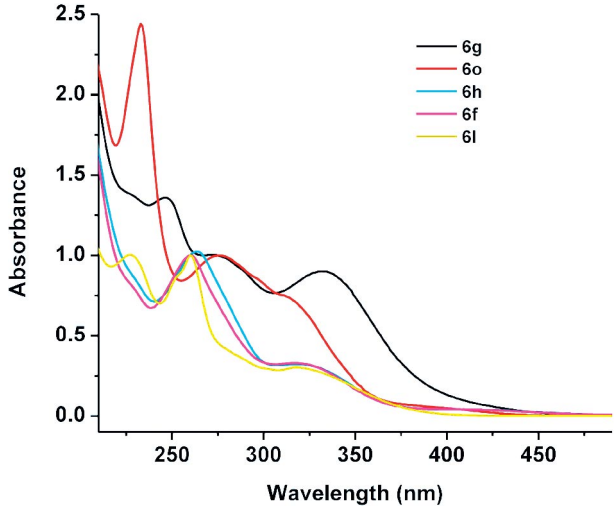


Figure 4. Absorption spectrum of compounds **6g**, **6o**, **6h**, **6f**, and **6l**.

Table 2. Absorption and emission data of compounds **6f**, **6g**, **6h**, **6l**, and **6o**.

Entry	Product	Absorption[a] $\lambda_{max,abs}$ [nm]	Emission[a,b] $\lambda_{max,em}$ [nm]	Stokes shift [cm^{-1}]
1	**6f**	322	415	6959
2	**6g**	333	409	5580
3	**6h**	322	424	7471
4	**6l**	320	408	6741
5	**6o**	312	414	7897

[a] Recorded in CH_3CN at 25 °C. [b] Excited at the longest wavelength of the absorption maxima.

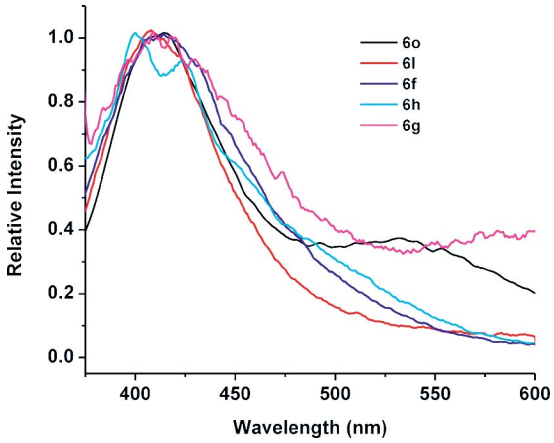


Figure 5. Emission spectrum of compounds **6g**, **6o**, **6h**, **6f**, and **6l**.

Conclusions

In summary, we have demonstrated a one-pot, three-component synthesis that provides new 3-spiroazitidinimine-2-oxindoles in excellent yields. The approach has been successfully extended to synthetically and biologically important mono-, di-, and triketones. Both diastereomeric 3-spiroazetidinimine-2-oxindoles underwent a facile ring-opening reaction of the spiroazetidinimine unit by treatment with methanolic KOH and *p*-thiocresol under mild basic conditions to afford two new classes of synthetically important conjugated indolones.

Experimental Section

General Methods: All reactions were carried out in oven-dried glassware. The progress of the reactions was monitored by thin layer chromatography (TLC), and purification of crude compounds was carried out by column chromatography with neutral alumina. The NMR spectroscopic data were recorded with Jeol-500 MHz and Bruker-400 MHz spectrometers. Chemical shifts are reported

in δ (ppm) relative to TMS (for ^{1}H NMR) or $CDCl_3$ (for ^{13}C NMR) as internal standards. The signal integrations are in accordance with the assignments, and coupling constants are given in Hz. All the ^{13}C NMR spectra are proton decoupled. Multiplicity is indicated according to s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), and br. s (broad singlet). HRMS analyses were recorded with a Waters® Micromass® Q-TOF Micro TM spectrometer, yields refer to the quantities that were obtained after chromatography. All solvents were purified prior to use by following literature procedures.

Typical Experimental Procedure for the Synthesis of Diastereomeric 3-Spiroazetidinimine-2-oxindoles 4a and 5a: A mixture of *N*-methylisatin (161 mg, 1 mmol, 1 equiv.), *p*-toluidine, (0.128 mg, 1.0 mmol, 1.2 equiv.), and acetic acid (catalytic amount) in ethanol was heated at reflux for 2 h. After the completion of the reaction (monitored by TLC, the R_f values of the imines were similar to their corresponding isatin), ethanol and acetic acid were removed by using a rotary evaporator at 70 °C under vacuum. The resulting residue was purified by column chromatography on silica gel (ethyl acetate/hexane, 30:70) to afford imine **1a** as a yellow solid (212 mg, 85% yield). To imine **1a** (125 mg, 0.5 mmol, 1.0 equiv.) in acetonitrile (3 mL) were added tosyl azide (**2a**, 0.086 mL, 1.1 equiv.), copper iodide (9.5 mg, 10 mol-%), phenylacetylene (**3a**, 0.06 mL, 1.1 equiv.), and triethylamine (0.13 mL, 2 equiv.), and the resulting mixture was stirred at room temperature for 16 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was passed through a pad of neutral alumina (ethyl acetate), and the solvent was evaporated in vacuo. The residue was treated with dichloromethane (25 mL) and washed successively with dilute HCl (10 mL) and brine solution (10 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Chromatography on silica gel (gradient of ethyl acetate/hexane) yielded compounds **4a** (23.5 mg, 9% yield) and **5a** (190.5 mg, 73% yield).

Typical Experimental Procedure for the Synthesis of Merocyanine 6: A mixture of 3-spiroazetidinimine-2-oxindole **4a/5a** (156 mg, 0.3 mmol, 1 equiv.) and potassium hydroxide (56 mg, 0.3 mmol, 3 equiv.) in ethanol (5 mL) was stirred at room temperature for 1 h. After the completion of the reaction (monitored by TLC, product had same R_f value as the corresponding spiroazetidine), the ethanol was removed in vacuo. The residue was treated with dichloromethane (25 mL) and washed successively with dilute HCl (10 mL) and brine solution (10 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Chromatography on silica gel (gradient of hexane/ethyl acetate) yielded compound **6a** (151 mg, 97% yield) as a yellow solid.

Typical Experimental Procedure for the Synthesis of Merocyanine 7: A mixture of 3-spiroazetidinimine-2-oxindole **4h/5h** (175 mg, 0.3 mmol, 1 equiv.), *p*-thiocresol (55.8 mg, 0.3 mmol, 1.5 equiv.), and potassium carbonate (124.3 mg, 0.3 mmol, 3 equiv.) in DMF was stirred at room temperature for 1 h. After the completion of the reaction (monitored by TLC, product had lower R_f value than the corresponding spiroazetidine), the reaction mixture was treated with dichloromethane (25 mL) and washed successively with dilute HCl (10 mL) and brine solution (10 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Chromatography on silica gel (gradient of hexane/ethyl acetate) yielded compound **7h** (148 mg, 85% yield) as a yellow solid.

4-Methyl-*N*-[(2*S*,3*S*)-1′-methyl-2′-oxo-3-phenyl-1-*p*-tolylspiro-(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (4a): White powder (23.5 mg, 9% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3427, 2924, 1730, 1640, 1515, 1491, 1415, 1154, 1092, 817, 759 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.23 (s, 3 H), 2.40 (s, 3 H), 3.09 (s, 3 H), 5.24 (s, 1 H), 6.91 (d, J = 7.5 Hz, 1 H), 7.01 (d, J = 8 Hz, 2 H), 7.11–7.18 (m, 9 H), 7.24–7.28 (m, 1 H), 7.42–7.45 (m, 1 H), 7.47 (d, J = 7 Hz, 1 H), 7.52 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.1, 21.6, 64.6, 71.4, 109.2, 118.5, 123.6, 123.8, 124.3, 127.0, 127.1, 127.9, 128.0, 128.5, 129.0, 129.1, 129.2, 129.6, 129.8, 130.3, 131.2, 133.9, 135.7, 138.9, 142.9, 143.4, 163.2, 169.7 ppm. HRMS: calcd. for $C_{31}H_{27}N_3O_3S$ [M + H]$^+$ 522.1851; found 522.1849.

4-Methyl-*N*-[(2*S*,3*R*)-1′-methyl-2′-oxo-3-phenyl-1-*p*-tolylspiro-(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5a): White powder (190.5 mg, 73% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3438, 3062, 2925, 1745, 1616, 1515, 1470, 1402, 1371, 1315, 1250, 1155, 1091, 1016, 915, 812, 737, 700, 670, 548 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.19 (s, 3 H), 2.39 (s, 3 H), 3.30 (s, 3 H), 5.31 (s, 1 H), 6.13–6.66 (m, 2 H), 6.85 (d, J = 8 Hz, 1 H), 6.96 (d, J = 8 Hz, 2 H), 7.05–7.09 (m, 4 H), 7.19–7.24 (m, 6 H), 7.75 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 20.9, 21.6, 62.2, 71.0, 118.3, 118.4, 120.6, 122.8, 126.0, 126.9, 127.0, 128.1, 128.5, 128.6, 129.2, 129.3, 129.7, 129.8, 131.0, 134.3, 135.5, 139.2, 142.8, 143.6, 163.3, 173.3 ppm. HRMS: calcd. for $C_{31}H_{27}N_3O_3S$ [M + H]$^+$ 522.1851; found 522.1832.

***N*-[(2*S*,3*R*)-1-(4-Bromophenyl)-1′-methyl-2′-oxo-3-phenylspiro-(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (5b):** White powder (205 mg, 70% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3441, 3061, 2928, 1730, 1623, 1489, 1394, 1372, 1315, 1251, 1156, 1090, 1010, 857, 820, 669, 546 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 3.32 (s, 3 H), 5.32 (s, 1 H), 6.61 (d, J = 7.5 Hz, 1 H), 6.68 (t, J = 8 Hz, 1 H), 6.87 (d, J = 7.5 Hz, 1 H), 7.03–7.08 (m, 4 H), 7.20–7.29 (m, 8 H), 7.74 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.1, 62.5, 71.1, 109.1, 118.7, 119.9, 120.3, 123.0, 127.1, 128.3, 128.5, 128.7, 129.4, 131.3, 132.3, 132.4, 135.9, 138.9, 143.2, 143.6, 163.5, 172.8 ppm. HRMS (FAB): calcd. for $C_{30}H_{25}BrN_3O_3S$ [M + H]$^+$ 585.0799; found 585.0797.

4-Methyl-*N*-[(2*S*,3*R*)-2′-oxo-3-phenyl-1-*p*-tolylspiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5c): White powder (167.5 mg, 66% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3365, 3310, 2960, 2923, 1739, 1616, 1469, 1403, 1307, 1188, 1152, 921, 813, 762, 669, 542 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.21 (s, 3 H), 2.40 (s, 3 H), 5.40 (s, 1 H), 6.56–6.64 (m, 2 H), 6.89 (d, J = 7.5 Hz, 1 H), 6.99 (d, J = 8.5 Hz, 2 H), 7.10–7.23 (m, 10 H), 7.74 (d, J = 8.5 Hz, 2 H), 9.24 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.0, 21.6, 62.1, 71.5, 111.3, 115.4, 118.4, 120.5, 120.9, 122.8, 126.2, 127.1, 128.3, 128.7, 129.3, 129.7, 129.9, 131.0, 132.3, 134.4, 135.7, 139.1, 140.9, 142.9, 163.5, 175.4 ppm. HRMS: calcd. for $C_{30}H_{26}N_3O_3S$ [M + H]$^+$ 508.1695; found 508.1688.

***N*-[(2*S*,3*R*)-1-(4-Methoxyphenyl)-1′-methyl-2′-oxo-3-phenylspiro-(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (5d):** White powder (198.6 mg, 74% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3436, 3032, 3006, 2936, 2836, 1728, 1615, 1511, 1469, 1370, 1309, 1251, 1154, 1091, 1021, 914, 880, 738, 701 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 3.30 (s, 3 H), 3.67 (s, 3 H), 5.50 (s, 1 H), 6.63 (d, J = 7.5 Hz, 1 H), 6.67–6.61 (m, 3 H), 6.85 (d, J = 8.5 Hz, 1 H), 7.09–7.13 (m, 4 H), 7.19–7.26 (m, 6 H), 7.75 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.6, 27.0, 55.5, 62.3, 71.3, 108.9, 114.5, 120.3, 120.7, 122.9, 126.1, 126.9, 128.2, 128.6, 128.7, 129.3, 130.1, 131.1, 132.6, 142.9, 143.8, 157.4, 163.2, 173.1 ppm. HRMS: calcd. for $C_{31}H_{28}N_3O_4S$ [M + H]$^+$ 538.1800; found 538.4416.

4-Methyl-*N*-[(2*S*,3*R*)-1′-methyl-1-(naphthalen-1-yl)-2′-oxo-3-phenylspiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5e): White powder (173 mg, 62% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3360, 3262, 2923, 2852, 1732, 1629, 1529, 1492, 1306, 1160, 1087, 907, 817, 703, 535 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.41 (s, 3 H), 3.16 (s, 3 H), 5.54 (s, 1 H), 6.68 (t, J = 7 Hz, 2 H), 6.79 (d, J = 7.5 Hz, 1 H), 7.14 (t, J = 8 Hz, 1 H), 7.21 (d, J = 7.5 Hz, 3 H), 7.24–7.31 (m, 6 H), 7.40–7.47 (m, 2 H), 7.70 (d, J = 8.5 Hz, 2 H), 7.75 (t, J = 7.5 Hz, 2 H), 8.17 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.6, 62.8, 74.9, 108.8, 120.8, 122.7, 124.1, 124.3, 125.1, 126.4, 126.7, 126.8, 126.9, 128.1, 128.2, 128.7, 128.9, 129.2, 129.4, 129.9, 131.0, 131.8, 133.0, 134.3, 139.5, 142.7, 144.5, 167.1, 173.6 ppm. HRMS: calcd. for $C_{34}H_{28}N_3O_3S$ [M + H]$^+$ 558.1851; found 558.1832.

4-Methyl-*N*-[(2*S*,3*S*)-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (4f): White powder (17 mg, 7% yield). FTIR (KBr. FTIR (KBr): $\tilde{\nu}_{max}$ = 3439, 3056, 2961, 2930, 2872, 1729, 1641, 1495, 1471, 1415, 1314, 1248, 1154, 1091, 916, 819, 760, 704, 541 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 3.05 (s, 3 H), 5.26 (s, 1 H), 6.92 (d, J = 8 Hz, 1 H), 7.07–7.1 (m, 1 H), 7.13 (d, J = 7 Hz, 2 H), 7.16–7.19 (m, 5 H), 7.21–7.24 (m, 4 H), 7.26 (d, J = 5.5 Hz, 1 H), 7.44 (t, J = 7.5 Hz, 1 H), 7.49 (d, J = 7.5 Hz, 1 H), 7.52 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 26.8, 64.6, 71.4, 109.2, 118.4, 123.6, 123.8, 124.2, 125.0, 127.0, 128.0, 128.5, 129.2, 129.3, 130.2, 131.3, 136.3, 138.7, 142.9,143.3, 163.4, 169.6 ppm. HRMS: calcd. for $C_{30}H_{26}N_3O_3S$ [M + H]$^+$ 508.1695; found 508.1697.

4-Methyl-*N*-[(2*S*,3*R*)-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5f): White powder (182.5 mg, 72% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3433, 3061, 2931, 1726, 1624, 1407, 1408, 1370, 1317, 1251, 1016, 917, 754, 674, 546 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 3.32 (s, 3 H), 5.32 (s, 1 H), 6.62 (d, J = 6.5 Hz, 1 H), 6.67 (t, J = 7.5 Hz, 1 H), 6.87 (d, J = 8 Hz, 1 H), 7.02–7.06 (m, 2 H), 7.08–7.11 (m, 2 H), 7.15–7.20 (m, 7 H), 7.24 (d, J = 9 Hz, 2 H), 7.76 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.1, 62.3, 71.1, 109.0, 118.4, 120.6, 122.9, 125.7, 126.1, 127.1, 128.2, 128.6, 128.7, 129.3, 129.4, 131.1, 136.9, 139.2, 143.0, 143.7, 163.6, 173.0 ppm. HRMS: calcd. for $C_{30}H_{26}N_3O_3S$ [M + H]$^+$ 508.1695; found 508.1688.

4-Methyl-*N*-[(2*S*,3*R*)-1′-methyl-5′-nitro-2′-oxo-1,3-diphenylspiro-(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5g): White powder (198 mg, 72% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3460, 3066, 2927, 1741, 1631, 1523, 1457, 1494, 1405, 1336, 1157, 1090, 933, 824, 675, 547 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.43 (s, 3 H), 3.41 (s, 3 H), 5.39 (s, 1 H), 6.98 (d, J = 8.5 Hz, 1 H), 7.08–7.14 (m, 5 H), 7.19–7.26 (m, 7 H), 7.52 (d, J = 2.5 Hz, 1 H), 7.71 (d, J = 8.5 Hz, 2 H), 8.17 (dd, J = 9.25, 2.5 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.6, 62.8, 70.1, 108.8, 118.2, 121.7, 126.1, 127.2, 127.8, 128.3, 128.9, 129.1, 129.4, 129.6, 131.5, 136.4, 138.6, 143.4, 148.8, 162.8, 173.2 ppm. HRMS: calcd. for $C_{30}H_{25}N_4O_5S$ [M + H]$^+$ 553.1545; found 553.1546.

***N*-[(2*S*,3*S*)-5′-Bromo-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (4h):** White powder (23 mg, 8% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3440, 3062, 2979, 2927, 1732, 1631, 1494, 1411, 1310, 1245, 1152, 1093, 927, 820, 739, 691, 543 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.41 (s, 3 H), 3.03 (s, 3 H), 5.25 (d, J = 8.5 Hz, 1 H), 7.10–7.14 (m, 3 H), 7.17–7.21 (m, 6 H), 7.23 (d, J = 7.5 Hz, 2 H), 7.27–7.30 (m, 1 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.57 (dd, J = 8, 2.5 Hz, 1 H), 7.6 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 26.9, 64.8, 70.0, 110.8, 116.5, 118.3, 118.4, 125.9, 126.2, 126.7, 127.1, 128.1, 128.7, 128.9, 129.2, 129.3, 129.4, 129.5, 129.9, 134.2, 136.1, 138.6, 142.2, 143.1, 163.0, 169.0 ppm. HRMS: calcd. for $C_{30}H_{24}BrN_3O_3S$ [M]$^+$ 588.0779; found 588.0796.

***N*-[(2*S*,3*R*)-5′-Bromo-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (5h):** White powder (216 mg, 74% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3443, 3062, 2924, 1731, 1632, 1493, 1461, 1407, 1319, 1251, 1156, 1094, 926, 813, 742, 675, 547 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.39 (s, 3 H), 3.29 (s, 3 H), 5.33 (s, 1 H), 6.70 (d, J = 1.5 Hz, 1 H), 6.75 (d, J = 8.5 Hz, 1 H), 7.07 (t, J = 6.5 Hz, 2 H), 7.14–7.24 (m, 10 H), 7.31 (d, J = 8.5 Hz, 1 H), 7.73 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.3, 62.4, 70.7, 110.5, 115.6, 118.2, 122.5, 125.9, 127.1, 128.5, 128.6, 128.9, 129.1, 129.4, 129.5, 132.1, 133.9, 136.6, 138.9, 142.6, 143.2, 163.2, 172.4 ppm. HRMS: calcd. for $C_{30}H_{24}BrN_3O_3S$ [M]$^+$ 588.0779; found 588.0789.

***N*-[(2*S*,3*S*)-5′-Fluoro-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (4i):** White powder (57 mg, 22% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3437, 3069, 2924, 2855, 1728, 1628, 1495, 1456, 1320, 1159, 1093, 975, 882, 812, 756, 672, 548 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.41 (s, 3 H), 3.33 (s, 3 H), 5.35 (s, 1 H), 6.38 (d, J = 8 Hz, 1 H), 6.81 (dd, J = 4, 4.5 Hz, 1 H), 6.94 (dt, J = 8.5 Hz, 1 H), 7.06–7.09 (m, 3 H), 7.15 (d, J = 8 Hz, 2 H), 7.19 (d, J = 7.5 Hz, 2 H), 7.25–7.28 (m, 5 H), 7.76 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.3, 63.35, 70.81, 109.6, 114.1, 114.3, 117.4, 117.6, 118.3, 122.4, 125.8, 127.1, 128.4, 128.6, 129.4, 132.1, 136.7, 138.9, 139.6, 143.2, 157.9, 159.8, 163.2, 172.8 ppm. HRMS: calcd. for $C_{30}H_{25}FN_3O_3S$ [M + H]$^+$ 526.1600; found 526.1592.

***N*-[(2*S*,3*R*)-5′-Fluoro-1′-methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (5i):** White powder (168 mg, 64% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3361, 3262, 2925, 2855, 1732, 1627, 1550, 1304, 1259, 1217, 1156, 1093, 1019, 815, 693, 548 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.43 (s, 3 H), 3.05 (s, 3 H), 5.23 (s, 1 H), 6.91–6.94 (dd, J = 9.15, 4 Hz), 7.12 (d, J = 7.5 Hz, 3 H), 7.19–7.22 (m, 7 H), 7.24–7.28 (q, J = 8.5, 7.5 Hz, 3 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 27.3, 62.4, 70.8, 109.5, 109.6, 114.1, 114.3, 117.4, 117.6, 118.3, 122.4, 122.5, 125.8, 127.1, 128.4, 128.6, 128.9, 129.2, 129.3, 129.4, 132.1, 136.7, 139.5, 143.1, 157.9, 159.8, 163.2, 172.8 ppm. HRMS: calcd. for $C_{30}H_{25}FN_3O_3S$ [M + H]$^+$ 526.1601; found 526.1584.

4-Methyl-*N*-[(2*S*,3*S*)-1′-methyl-2′-oxo-1,3-diphenyl-5′-(trifluoromethoxy)spiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (4j): White powder (27 mg, 9% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3445, 3065, 2927, 1733, 1632, 1496, 1459, 1406, 1319, 1363, 1632, 1496, 1459, 1406, 1319, 1363, 1319, 1254, 1220, 1158, 1092, 919, 862, 814, 755, 737, 692, 547 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.39 (s, 3 H), 3.31 (s, 3 H), 5.35 (s,1 H), 6.53 (s, 1 H), 6.88 (d, J = 8.5 Hz, 1 H), 7.04–7.10 (m, 4 H), 7.14–7.23 (m, 9 H), 7.73 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (500.1 MHz, $CDCl_3$/TMS): δ = 21.6, 27.3, 62.4, 70.8, 109.9, 118.3, 119.2, 119.9, 121.2, 122.1, 124.5, 125.5, 127.1, 128.3, 128.6, 128.9, 129.4, 129.5, 131.9, 136.6, 138.9, 142.3, 143.3, 144.6, 163.3, 173.9 ppm. HRMS: calcd. for $C_{31}H_{25}F_3N_3O_4S$ [M + H]$^+$ 592.1518; found 592.1536.

4-Methyl-*N*-[(2*S*,3*R*)-1′-methyl-2′-oxo-1,3-diphenyl-5′-(trifluoromethoxy)spiro(azetidine-2,3′-indoline)-4-ylidene]benzenesulfonamide (5j): White powder (215 mg, 73% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3443, 3065, 3035, 2927, 1732, 1632, 1599, 1498, 1406, 1364, 1458, 1406, 1316, 1256, 1220, 1157, 919, 862, 814, 756, 693, 611, 546 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.41 (s, 3 H), 3.05 (s, 3 H), 5.25 (s, 1 H), 6.93 (d, J = 8.5 Hz, 1 H), 7.09–7.15 (m, 3 H), 7.19–7.24 (m, 8 H), 7.29 (t, 1 H), 7.33 (d, J = 8.5 Hz, 1 H), 7.38 (s, 1

H), 7.55 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.6, 27.3, 62.5, 70.7, 109.7, 110.2, 117.5, 118.3, 119.2, 119.9, 121.2, 122.2, 124.2, 124.4, 125.9, 127.0, 127.1, 128.1, 128.3, 128.6, 128.9, 129.3, 129.4, 129.5, 129.9, 136.6, 138.9, 142.2, 143.2, 144.6, 163.2, 172.9 ppm. HRMS: calcd. for $C_{31}H_{25}F_3N_3O_4S$ [M + H]$^+$ 592.1518; found 592.1521.

4-Methyl-*N*-{(2*S*,3*S*)-1′-methyl-2′-oxo-1-*p*-tolyl-3-[4-(trifluoromethyl)phenyl]spiro(azetidine-2,3′-indoline)-4-ylidene}benzenesulfonamide (4k): White powder (29 mg, 10% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3439, 3063, 2987, 2927, 1730, 1632, 1515, 1471, 1324, 1247, 1155, 1121, 1091, 1069, 922, 861, 815, 754, 685, 661, 540 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.25 (s, 3 H), 2.40 (s, 3 H), 3.06 (s, 3 H), 5.28 (s, 1 H), 6.9 (d, J = 8 Hz, 1 H), 7.03 (d, J = 8.5 Hz, 2 H), 7.13 (t, J = 8.5 Hz, 4 H), 7.18 (t, J = 8 Hz, 1 H), 7.24 (d, J = 8.5 Hz, 2 H), 7.37 (d, J = 8 Hz, 2 H), 7.45 (d, J = 8 Hz, 3 H), 7.50 (d, J = 7 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.0, 21.5, 26.9, 63.6, 71.2, 109.4, 118.4, 122.9, 123.7, 123.8, 123.9, 124.8, 124.9, 125.1, 125.1, 126.6, 129.2, 129.9, 130.1, 130.2, 130.5, 131.6, 133.6, 133.9, 136.0, 138.7, 143.1, 143.2, 162.6, 169.4 ppm. HRMS: calcd. for $C_{31}H_{27}F_3N_3O_3S$ [M + H]$^+$ 590.1725; found 590.1734.

4-Methyl-*N*-{(2*S*,3*R*)-1′-methyl-2′-oxo-1-*p*-tolyl-3-[4-(trifluoromethyl)phenyl]spiro(azetidine-2,3′-indoline)-4-ylidene}benzenesulfonamide (5k): White powder (212 mg, 72% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3435, 3063, 2925, 1731, 1633, 1614, 1517, 1406, 1371, 1251, 1158, 1115, 1091, 1068, 1018, 918, 834, 812, 754, 731, 709, 662, 550, 537 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.21 (s, 3 H), 2.41 (s, 3 H), 3.34 (s, 3 H), 5.37 (s, 1 H), 6.59 (d, J = 7.5 Hz, 1 H), 6.71 (t, J = 7.5 Hz, 1 H), 6.89 (d, J = 7.5 Hz, 1 H), 6.98 (d, J = 8.5 Hz, 2 H), 7.05 (d, J = 7.05 Hz, 2 H), 7.22–7.28 (m, 5 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.75 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.0, 21.6, 27.2, 61.5, 70.9, 109.2, 118.4, 120.3, 122.8, 123.1, 125.0, 125.6, 125.7, 125.9, 126.7, 126.9, 129.0, 129.2, 129.4, 130.2, 131.4, 134.1, 135.9, 136.7, 139.1, 143.2, 143.7, 143.7, 162.4, 172.7 ppm. HRMS: calcd. for $C_{31}H_{27}F_3N_3O_3S$ [M + H]$^+$ 590.1725; found 590.1731.

(*R*)-*N*-(1,3-Diphenylspiro[azetidine-2,9′-fluorene]-4-ylidene)-4-methylbenzenesulfonamide (5l): White powder (236 mg, 90% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3427, 3060, 2924, 2856, 1621, 1496, 1458, 1408, 1311, 1241, 1155, 1091, 910, 808, 748, 686, 544 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 5.44 (s, 1 H), 6.77 (d, J = 3.5 Hz, 2 H), 6.91–6.96 (m, 3 H), 7.02 (t, J = 7.5 Hz, 2 H), 7.06–7.10 (m, 3 H), 7.14 (d, J = 8.5 Hz, 2 H), 7.17–7.21 (m, 1 H), 7.26 (d, J = 7.5 Hz, 2 H), 7.28–7.31 (m, 1 H), 7.43 (t, J = 7.5 Hz, 1 H), 7.52 (d, J = 7.0 Hz, 1 H), 7.61 (d, J = 7.5 Hz, 1 H), 7.72 (d, J = 6.5 Hz, 1 H), 7.81 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 63.6, 76.7, 118.8, 120.5, 120.9, 122.9, 125.3, 126.0, 127.1, 127.3, 127.8, 128.4, 128.5, 128.7, 129.1, 129.4, 129.9, 130.3, 133.6, 136.8, 138.0, 139.5, 139.9, 140.5, 142.9, 143.1, 163.8 ppm. HRMS: calcd. for $C_{34}H_{25}N_2O_2S$ [M + H]$^+$ 527.1793; found 527.1793.

(*R*)-*N*-(1,3-Diphenylspiro[azetidine-2,9′-fluorene]-4-ylidene)-4-methylbenzenesulfonamide (5l): White powder (236 mg, 90% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3427, 3060, 2924, 2856, 1621, 1496, 1458, 1408, 1311, 1241, 1155, 1091, 910, 808, 748, 686, 544 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 5.44 (s, 1 H), 6.77 (d, J = 3.5 Hz, 2 H), 6.91–6.96 (m, 3 H), 7.02 (t, J = 7.5 Hz, 2 H), 7.06–7.10 (m, 3 H), 7.14 (d, J = 8.5 Hz, 2 H), 7.17–7.21 (m, 1 H), 7.26 (d, J = 7.5 Hz, 2 H), 7.28–7.31 (m, 1 H), 7.43 (t, J = 7.5 Hz, 1 H), 7.52 (d, J = 7.0 Hz, 1 H), 7.61 (d, J = 7.5 Hz, 1 H), 7.72 (d, J = 6.5 Hz, 1 H), 7.81 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 63.6, 76.7, 118.8, 120.5, 120.9, 122.9, 125.3, 126.0, 127.1, 127.3, 127.8, 128.4, 128.5, 128.7, 129.1, 129.4, 129.9, 130.3, 133.6, 136.8, 138.0, 139.5, 139.9, 140.5, 142.9, 143.1, 163.8 ppm. HRMS: calcd. for $C_{34}H_{25}N_2O_2S$ [M + H]$^+$ 527.1793; found 527.1793.

(*R*)-*N*-(1′,3′-Dioxo-1,3-diphenyl-1′,3′-dihydrospiro[azetidine-2,2′-indene]-4-ylidene)-4-methylbenzenesulfonamide (5m): White powder (182 mg, 72% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3450, 3.61, 2924, 1751, 1718, 1632, 1595, 1498, 1458, 1410, 1314, 1226, 1154, 1090, 882, 755, 728, 694, 554, 530 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 5.26 (s, 1 H), 7.06 (d, J = 7.5 Hz, 1 H), 7.11–7.14 (m, 1 H), 7.17–7.29 (m, 10 H), 7.54 (d, J = 7.5 Hz, 2 H), 7.75 (d, J = 7.5 Hz, 1 H), 7.90 (t, J = 7.5 Hz, 1 H), 7.98 (t, J = 7.5 Hz, 1 H), 8.14 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.6, 62.7, 74.1, 118.1, 124.2, 124.4, 126.1, 127.0, 128.6, 128.9, 129.1, 129.7, 129.2, 129.3, 129.4, 129.9, 136.2, 137.2, 137.6, 138.6, 139.7, 140.4, 143.1, 162.1, 191.6, 193.6 ppm. HRMS: calcd. for $C_{30}H_{23}N_2O_4S$ [M + H]$^+$ 507.1378; found 507.1374.

4-Methyl-*N*-[(1′*S*,2*R*,3*S*,4′*R*)-1′,7′,7′-trimethyl-3′-oxo-1,3-diphenylspiro(azetidine-2,2′-bicyclo[2.2.1]heptane)-4-ylidene]benzenesulfonamide (4n): White powder (51 mg, 20% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3430, 3063, 3035, 2965, 2934, 2875, 1744, 1627, 1593, 1454, 1408, 1310, 1154, 1091, 1008, 915, 881, 827, 768, 734, 684, 553 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 0.79 (s, 3 H), 0.84 (s, 3 H), 0.95 (s, 3 H), 1.22–1.28 (m, 1 H), 1.29–1.34 (m, 1 H), 1.54–1.59 (m, 1 H), 1.61–1.67 (m, 1 H), 2.27 (s, 3 H), 2.61 (d, J = 4.5 Hz, 1 H), 4.94 (s, 1 H), 6.89 (s, 4 H), 7.28 (t, J = 6.5 Hz, 3 H), 7.33–7.37 (m, 5 H), 7.45 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 9.6, 18.9, 20.9, 21.5, 22.3, 31.3, 45.0, 55.5, 60.2, 65.2, 81.7, 124.5, 126.5, 127.9, 128.1, 128.3, 128.6, 128.8, 129.5, 130.8, 137.2, 138.5, 142.2, 166.8, 213.1 ppm. HRMS: calcd. for $C_{31}H_{33}N_2O_3S$ [M + H]$^+$ 513.2212; found 513.2226.

4-Methyl-*N*-[(1′*S*,2*R*,3*R*,4′*R*)-1′,7′,7′-trimethyl-3′-oxo-1,3-diphenylspiro(azetidine-2,2′-bicyclo[2.2.1]heptane)-4-ylidene]benzenesulfonamide (5n): White powder (184 mg, 72% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3469, 3092, 3004, 3034, 2875, 1748, 1632, 1592, 1495, 1453, 1420, 1305, 1152, 1090, 1003, 914, 880, 833, 768, 686, 539 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 0.07 (s, 3 H), 0.61 (s, 3 H), 0.83 (s, 3 H), 0.85–0.89 (m, 1 H), 1.38–1.40 (m, 1 H), 2.06–2.12 (m, 1 H), 2.29 (s, 3 H), 2.53 (d, J = 4 Hz, 1 H), 5.23 (s, 1 H), 6.97 (d, J = 8.5 Hz, 2 H), 7.14–7.18 (m, 5 H), 7.22 (d, J = 7 Hz, 1 H), 7.26–7.28 (m, 4 H), 7.32–7.36 (m, 3 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 9.3, 19.9, 21.5, 21.6, 25.4, 26.6, 46.2, 51.6, 57.5, 60.7, 82.3, 126.6, 128.0, 128.1, 128.8, 129.3, 129.5, 129.8, 129.9, 131.3, 135.2, 139.3, 143.1, 168.8, 211.1 ppm. HRMS: calcd. for $C_{31}H_{33}N_2O_3S$ [M + H]$^+$ 513.2212; found 513.2196.

(*S*)-*N*-[1′-(4-Chlorophenyl)-2-oxo-3′-phenyl-2*H*-spiro(acenaphthylene-1,2′-azetidine)-4′-ylidene]-4-methylbenzenesulfonamide (4o): White powder (207 mg, 74% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3434, 3057, 2924, 1730, 1634, 1494, 1401, 1313, 1153, 1014, 931, 857, 834, 733, 691, 552 cm^{-1}. ^{1}H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.43 (s, 2 H), 2.44 (s, 3 H), 5.32 (s, 1 H), 5.40 (s, 1 H), 7.04 (s, 2 H), 7.08–7.17 (m, 8 H), 7.19 (d, J = 8.5 Hz, 2 H), 7.23 (t, J = 8 Hz, 1 H), 7.28–7.30 (m, 2 H), 7.54 (d, J = 7.5 Hz, 2 H), 7.43–7.79 (m, 5 H), 7.82–7.86 (m, 1 H), 8.04 (t, J = 4.5 Hz, 1 H), 8.14 (d, J = 7.0 Hz, 1 H), 8.19–8.23 (m, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 22.6, 62.5, 65.5, 75.6, 75.7, 119.6, 119.7, 120.4, 122.9, 123.3, 123.4, 126.5, 126.9, 127.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 129.2, 129.3, 129.5, 130.5, 130.6, 130.7, 130.8, 130.9, 132.7, 132.8, 133.5, 134.9, 135.5, 140.9, 141.8, 143.2, 143.3, 163.7, 163.8, 195.9, 199.3 ppm. HRMS: calcd. for $C_{33}H_{24}ClN_2O_3S$ [M + H]$^+$ 563.1196; found 563.1210.

Bis(spiroazetidine-3-oxindole) (4s): White powder (347 mg, 65% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3435, 3033, 2927, 2865, 1725, 1629, 1515, 1466, 1316, 1156, 1091, 917, 812, 745, 698, 672 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 1.82 (s, 4 H), 1.97 (s, 4 H), 2.09 (s, 2 H), 2.38–2.40 (br. d, 6 H), 3.83–3.98 (m, 4 H), 5.30 (d, J = 4.5 Hz, 2 H), 6.57 (d, J = 7.5 Hz, 1 H), 6.62–6.68 (m, 3 H), 6.78–6.81 (m, 4 H), 6.85–6.89 (m, 2 H), 6.93 (d, J = 8.5 Hz, 3 H), 6.98–7.04 (m, 4 H), 7.09 (t, J = 7.5 Hz, 3 H), 7.13–7.18 (m, 6 H), 7.23 (d, J = 7.5 Hz, 4 H), 7.74–7.76 (m, 4 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 20.8, 20.9, 21.6, 24.9, 25.1, 40.1, 62.2, 62.3, 70.8, 70.9, 109.1, 109.2, 117.8, 118.1, 120.6, 120.7, 126.3, 127.0, 128.2, 128.3, 128.4, 128.7, 128.8, 129.2, 129.3, 129.7, 129.8, 131.2, 132.4, 132.5, 133.9, 134.3, 135.6, 135.7, 139.2, 139.3, 142.5, 142.6, 142.9, 163.1, 163.2, 173.3 ppm. HRMS: calcd. for $C_{64}H_{57}N_6O_6S_2$ $[M + H]^+$ 1069.3781; found 1069.3765.

***N*-[(2*S*,3*S*)-1′-Methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]methanesulfonamide (4t):** White powder (24 mg, 11% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3437, 3229, 1726, 1632, 1499, 14561, 1415, 1308, 1149, 1113, 972, 793, 761, 734, 704, 530, 513 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 2.97 (s, 3 H), 3.08 (s, 3 H), 5.23 (s, 1 H), 6.94 (d, J = 7.6 Hz, 1 H), 7.12 (q, J = 8.6, 4.4 Hz, 1 H), 7.17 (t, J = 7.6 Hz, 1 H), 7.22–7.27 (m, 4 H), 7.30–7.35 (m, 5 H), 7.40–7.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 26.8, 42.3, 64.4, 71.5, 109.2, 118.4, 123.6, 123.9, 125.8, 127.9, 128.2, 128.8, 129.2, 136.2, 143.2, 164.5, 169.5 ppm. HRMS: calcd. for $C_{24}H_{21}N_3O_3NaS$ $[M + Na]^+$ 454.1202; found 454.1199.

***N*-[(2*S*,3*R*)-1′-Methyl-2′-oxo-1,3-diphenylspiro(azetidine-2,3′-indoline)-4-ylidene]methanesulfonamide (5t):** White powder (165 mg, 77% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3439, 2927, 2854, 1730, 1622, 1497, 1468, 1405, 1370, 1309, 1154, 1091, 953, 756, 679, 545 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 3.10 (s, 3 H), 3.35 (s, 3 H), 5.29 (s, 1 H), 6.64–6.72 (m, 2 H), 6.89 (d, J = 8 Hz, 1 H), 7.10 (t, J = 6.8 Hz, 1 H), 7.14–7.18 (m, 2 H), 7.20–7.29 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 27.1, 42.8, 62.1, 71.0, 108.9, 118.32, 120.45, 122.94, 125.74, 126.0, 128.3, 128.4, 128.7, 129.3, 131.1, 132.4, 136.7, 143.5, 164.1, 173.0 ppm. HRMS: calcd. for $C_{24}H_{21}N_3O_3NaS$ $[M + Na]^+$ 454.1202; found 454.1201.

***N*-[(2*S*,3*R*)-3-Cyclohexyl-1′-methyl-2′-oxo-1-phenylspiro(azetidine-2,3′-indoline)-4-ylidene]-4-methylbenzenesulfonamide (5u):** Yellow powder (140.8 mg, 55% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3437, 3031, 1731, 1644, 1498, 1471, 1408, 1298, 1252, 1139, 1115, 971, 915, 858, 786, 763, 691, 505 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$/TMS): δ = 0.92–1.1 (m, 2 H), 1.16–1.37 (m, 1 H), 1.38–1.47 (m, 1 H), 1.48–1.60 (m, 2 H), 1.76–1.80 (m, 1 H), 2.20–2.15 (m, 2 H), 2.40 (s, 3 H), 3.32 (s, 3 H), 3.96 (d, J = 7.6 Hz, 1 H), 6.98–7.01 (m, 4 H), 7.09–7.14 (m, 3 H), 7.29 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 7.44–7.49 (m, 2 H), 7.91 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 21.5, 25.8, 26.2, 26.4, 26.9, 30.2, 31.1, 38.0, 63.5, 69.9, 109.3, 118.5, 121.5, 123.0, 125.3, 126.4, 126.5, 129.1, 131.3, 136.7, 140.1, 142.6, 144.2, 165.2, 174 ppm. HRMS: calcd. for $C_{30}H_{31}N_3O_3NaS$ $[M + Na]^+$ 536.1984; found 536.1989.

(1*E*,2*Z*)-2-(1-Methyl-2-oxoindolin-3-ylidene)-2-phenyl-*N*-*p*-tolyl-*N*′-tosylacetimidamide (6a): Yellow powder (151 mg, 97% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3442, 3283, 3064, 2929, 1742, 1627, 1526, 1492, 1452, 1336, 1294, 1156, 1086, 932, 824, 755, 692, 549 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.26 (s, 3 H), 2.44 (s, 3 H), 3.17 (s, 3 H), 6.59–6.64 (m, 2 H), 6.71 (d, J = 8 Hz, 1 H), 6.84 (d, J = 8.5 Hz, 2 H), 6.93 (d, J = 8.5 Hz, 2 H), 7.05–7.10 (br. s, 2 H), 7.14–7.18 (m, 1 H), 7.23 (t, J = 7.5 Hz, 2 H), 7.31 (d, J = 8 Hz, 2 H), 7.35 (t, J = 7.5 Hz, 1 H), 7.98 (d, J = 8 Hz, 2 H), 9.97 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.1, 21.7, 26.1, 108.2, 120.9, 121.8, 123.2, 126.2, 127.2, 128.5, 128.7, 128.9, 129.2, 129.5, 130.1, 130.6, 133.7, 133.9, 138.1, 138.7, 141.7, 143, 144.7, 164.3, 165.9 ppm. HRMS: calcd. for $C_{31}H_{27}N_3O_3SNa$ $[M + Na]^+$ 544.1671; found 544.1674.

(1*E*,2*Z*)-2-(1-Methyl-2-oxoindolin-3-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (6f): Yellow powder (149 mg, 98% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3439, 3285, 3155, 3118, 3057, 2927, 1711, 1605, 1569, 1521, 1443, 1375, 1341, 1283, 1144, 1085, 1025, 974, 875, 756, 694, 553 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.44 (s, 3 H), 3.17 (s, 3 H), 6.06–6.66 (m, 2 H), 6.96 (d, J = 7.5 Hz, 2 H), 7.06 (s, 2 H), 7.12–7.19 (m, 5 H), 7.22 (t, J = 7 Hz, 2 H), 7.32–7.36 (m, 3 H), 7.98 (d, J = 7.5 Hz, 2 H), 10.07 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 26.1, 108.2, 120.9, 121.8, 123.2, 126.2, 127.2, 128, 128.7, 129, 129.2, 130.1, 130.7, 133.7, 136.3, 138.4, 143.1, 144.7, 164.2, 165.9 ppm. HRMS: calcd. for $C_{30}H_{26}N_3O_3S$ $[M + H]^+$ 508.1695; found 508.1679.

(1*E*,2*Z*)-2-(1-Methyl-5-nitro-2-oxoindolin-3-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (6g): Yellow powder (152 mg, 92% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3438, 3269, 3064, 2926, 1719, 1608, 1569, 1526, 1446, 1337, 1289, 1145, 1085, 1024, 901, 812, 755, 704 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.46 (s, 3 H), 3.27 (s, 3 H), 6.81 (d, J = 8.5 Hz, 1 H), 6.94 (d, J = 6.5 Hz, 2 H), 7.05 (s, 1 H), 7.13–7.17 (m, 2 H), 7.19–7.23 (m, 1 H), 7.28–7.35 (m, 4 H), 7.42–7.48 (m, 1 H), 7.56 (s, 2 H), 7.97 (d, J = 6 Hz, 2 H), 8.14 (d, J = 8.5 Hz, 1 H), 10.09 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$, $[D_6]$DMSO/TMS): δ = 21.5, 26.5, 108.1, 118.6, 121.3, 122.6, 124.8, 125.6, 126.1, 126.3, 126.8, 126.9, 128.7, 129, 129.3, 129.8, 131.1, 133.6, 138.0, 140.2, 142.1, 142.6, 147.2, 149.3, 159.4, 165.9 ppm. HRMS: calcd. for $C_{30}H_{24}N_4O_5NaS$ $[M + Na]^+$ 575.1365; found 575.1381.

(1*E*,2*Z*)-2-(5-Bromo-1-methyl-2-oxoindolin-3-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (6h): Yellow powder (167 mg, 95% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3436, 3250, 3060, 2925, 2856, 1708, 1603, 1563, 1527, 1385, 1280, 1145, 1086, 1025, 988, 884, 810, 763, 702, 542 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.45 (s, 3 H), 3.16 (s, 3 H), 6.59 (d, J = 8.5 Hz, 1 H), 6.73 (s, 1 H), 6.94 (d, J = 8 Hz, 2 H), 7.02 (s, 1 H), 7.13 (t, J = 8 Hz, 3 H), 7.17–7.20 (m, 1 H), 7.23–7.28 (m, 3 H), 7.32 (d, J = 7.5 Hz, 2 H), 7.37 (t, J = 7.5 Hz, 1 H), 7.96 (d, J = 7.5 Hz, 2 H), 10.07 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 26.2, 109.6, 114.4, 125.9, 126.2, 127.2, 128.2, 128.7, 128.8, 129, 129.3, 130.6, 133.1, 133.2, 136.2, 138.4, 143.2, 143.5, 163.6, 165.4 ppm. HRMS: calcd. for $C_{30}H_{24}BrN_3O_3NaS$ $[M + Na]^+$ 608.0620; found 608.0638.

(*Z*)-2-(9*H*-fluoren-9-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (6l): Yellow powder, (153 mg, 97% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3438, 3271, 3058, 2924, 2855, 1599, 1568, 1521, 1442, 1389, 1234, 1146, 1084, 1024, 946, 910, 813, 733, 691, 594, 555, 526 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.46 (s, 3 H), 6.25 (s, 1 H), 6.46 (d, J = 7.5 Hz, 1 H), 6.77 (t, J = 8 Hz, 1 H), 6.88 (d, J = 8 Hz, 2 H), 6.92–6.96 (m, 2 H), 7.10 (t, J = 7.5 Hz, 2 H), 7.14–7.21 (m, 2 H), 7.27–7.35 (m, 4 H), 7.41 (s, 1 H), 7.56 (dd, J = 7.5, 16 Hz, 3 H), 7.65 (d, J = 7.5 Hz, 1 H), 7.90 (d, J = 8 Hz, 2 H), 10.09 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 119.5, 119.8, 121.7, 124.7, 125.1, 125.4, 126.9, 127.4, 125.1, 125.4, 126.9, 127.2, 127.4, 127.7, 127.9, 128.9, 129.1, 129.2, 129.6, 130.9, 133.6, 135.5, 136.2, 137, 137.7, 138.7, 140.9, 141.3, 143.6, 163.7 ppm. HRMS: calcd. for $C_{34}H_{26}N_2O_2NaS$ $[M + Na]^+$ 549.1613; found 549.1590.

(1*Z*,2*E*)-*N*-(4-Chlorophenyl)-2-[2-oxoacenaphthylen-1(2*H*)-ylidene]-2-phenyl-*N*′-tosylacetimidamide (6o): Yellow powder (158 mg, 94% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3410, 3275, 3059, 2924, 1708, 1599, 1566, 1522, 1494, 1433, 1399, 1281, 1148, 1088, 1025,

826, 780, 711, 686, 555, 524 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.45 (s, 3 H), 6.89 (d, J = 8.5 Hz, 2 H), 6.96 (d, J = 7 Hz, 1 H), 7.07 (d, J = 7 Hz, 2 H), 7.19 (s, 2 H), 7.27–7.33 (m, 5 H), 7.42 (t, J = 7.5 Hz, 1 H), 7.71 (t, J = 7.5 Hz, 1 H), 7.78 (d, J = 7 Hz, 1 H), 7.95 (q, J = 4, 7.5 Hz, 3 H), 8.04 (d, J = 7 Hz, 1 H), 10.07 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.8, 120.9, 121.9, 126.8, 127.2, 127.8, 128.1, 128.8, 129.1, 129.3, 130.3, 130.5, 131.7, 131.8, 133.8, 134.9, 135.5, 138.2, 140.9, 143.3, 164.5, 191.3 ppm. HRMS: calcd. for $C_{33}H_{25}ClN_2O_3S$ $[M + H]^+$ 563.1196; found 563.1176.

(1*Z*,2*E*)-2-(1-Methyl-5-nitro-2-oxoindolin-3-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (7g): Yellow powder (141 mg, 82% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3441, 3285, 3066, 2927, 1740, 1629, 1524, 1495, 1452, 1405, 1336, 1294, 1154, 1088, 930, 822, 753, 690, 549 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.40 (s, 3 H), 3.16 (s, 3 H), 6.80 (d, J = 7.5 Hz, 2 H), 6.85 (d, J = 8.5 Hz, 1 H), 7.12 (q, J = 5, 8 Hz, 4 H), 7.19 (t, J = 8 Hz, 3 H), 7.22–7.25 (m, 2 H), 7.32 (t, J = 7.5 Hz, 1 H), 7.87 (d, J = 8.5 Hz, 2 H), 8.23 (dd, J = 2, 6.5 Hz, 1 H), 8.35 (d, J = 2.5 Hz, 1 H), 10.18 (s, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/TMS): δ = 21.7, 26.1, 108.2, 120.9, 121.8, 123.2, 123.9, 125.4, 126.2, 127.1, 127.2, 127.6, 127.6, 128.0, 128.7, 128.8, 129, 129.1, 129.2, 129.7, 130.1, 130.6, 130.7, 131.1, 133.7, 136.3, 138.4, 143.1, 144.7, 164.2, 165.9 ppm. HRMS: calcd. for $C_{30}H_{24}N_4O_5NaS$ $[M + Na]^+$ 575.1365; found 575.1378.

(1*Z*,2*E*)-2-(5-Bromo-1-methyl-2-oxoindolin-3-ylidene)-*N*,2-diphenyl-*N*′-tosylacetimidamide (7h): Yellow powder (149 mg, 85% yield). FTIR (KBr): $\tilde{\nu}_{max}$ = 3439, 3263, 3062, 2926, 1712, 1603, 1483, 1529, 1364, 1332, 1276, 1144, 1067, 1024, 988, 885, 813, 759, 695, 553 cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$/TMS): δ = 2.45 (s, 3 H), 3.15 (s, 3 H), 6.60 (d, J = 8.2 Hz, 1 H), 6.72 (s, 1 H), 6.94 (d, J = 7.24 Hz, 2 H), 7.03 (s, 1 H), 7.14–7.19 (m, 4 H), 7.26–7.29 (m, 3 H), 7.32 (d, J = 7.7 Hz, 2 H), 7.39 (d, J = 7.2 Hz, 1 H), 7.97 (d, J = 7.4 Hz, 2 H), 10.06 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ = 21.7, 26.1, 109.51, 114.3, 118.2, 122.5, 125.8, 126.1, 127.1, 127.5, 128.1, 128.3, 128.6, 128.8, 128.9, 129.2, 129.3, 129.4, 133.1, 133.2, 136.1, 138.3, 143.2, 163.6, 165.3 ppm. HRMS: calcd. for $C_{30}H_{24}BrN_3NaO_3S$ $[M + Na]^+$ 608.0619; found 608.0625.

Supporting Information (see footnote on the first page of this article): Copies of ^1H NMR, ^{13}C NMR and HRMS spectra of all compounds are provided.

Acknowledgments

S. P. thanks the Council of Scientific and Industrial Research (CSIR), New Delhi for the award of Senior Research Fellowship. Funding support from the CSIR-12th five-year plan project CSC-0201 is also acknowledged.

[1] a) C. Marti, E. M. Carreira, *Eur. J. Org. Chem.* **2003**, 2209–2219; b) C. V. Galliford, K. A. Scheidt, *Angew. Chem.* **2007**, *119*, 8902; *Angew. Chem. Int. Ed.* **2007**, *46*, 8748–8758; c) B. M. Trost, M. K. Brennan, *Synthesis* **2009**, 3003–3025; d) H. Waldmann, *Synlett* **1995**, 133–141.

[2] For reviews on spirocycles, see: a) A. P. Krapcho, *Synthesis* **1974**, 383–419; b) M. Sannigrahi, *Tetrahedron* **1999**, *55*, 9007–9071; c) R. Pradhan, M. Patra, A. K. Behera, B. K. Mishra, R. K. Behera, *Tetrahedron* **2006**, *62*, 779–828; d) S. Kotha, A. C. Deb, K. Lahiri, E. Manivannan, *Synthesis* **2009**, 165–193; e) A. Padwa, S. K. Bur, *Tetrahedron* **2007**, *63*, 5341–5378; f) L. F. Tietze, N. Rackelmann, *Pure Appl. Chem.* **2004**, *76*, 1967–1983; g) P. Chiba, W. Holzer, M. Landau, G. Bechmann, K. Lorenz, B. Plagens, M. Hitzler, E. Richter, G. Ecker, *J. Med. Chem.* **1998**, *41*, 4001–4011; h) M. P. Castaldi, D. M. Troast, J. A. Porco, *Org. Lett.* **2009**, *11*, 3362–3365.

[3] For a recent review on spirooxindoles, see: G. S. Singh, Z. Y. Desta, *Chem. Rev.* **2012**, *112*, 6104–6155.

[4] W. Skiles, D. McNeil, *Tetrahedron Lett.* **1990**, *31*, 7277–7280.

[5] a) M. H. Khan, Nizamuddin, *Indian J. Chem. B* **1997**, *36*, 625; b) K. C. Joshi, R. Jain, V. Sharma, *J. Indian Chem. Soc.* **1986**, *63*, 430; c) J. C. Sheehan, E. Chacko, Y. S. Lo, D. R. Ponzi, E. Sato, *J. Org. Chem.* **1978**, *43*, 4856–4859.

[6] For a review on the synthesis and reactivity of spiro-fused β-lactams, see: a) G. S. Singh, M. D'hooghe, N. De Kimpe, *Tetrahedron* **2011**, *67*, 1989–2012; for general papers, see: b) A. Bhalla, P. Venugopalan, K. K. Bhasin, S. S. Bari, *Tetrahedron* **2007**, *63*, 3195–3204; c) C. V. Galliford, J. S. Martenson, C. Stern, K. A. Scheidt, *Chem. Commun.* **2007**, 631–633; d) B. Alcaide, P. Almendros, T. M. del Camop, R. Rodríguez-Acebes, *Adv. Synth. Catal.* **2007**, *349*, 749–758; e) B. V. S. Reddy, G. Karthik, T. Rajasekaran, A. Antony, B. Sridhar, *Tetrahedron Lett.* **2012**, *53*, 2396–2401.

[7] For recent selected papers of Cu-catalyzed multicomponent reactions (MCRs), see: a) N. Chernyak, V. Gevorgyan, *Angew. Chem.* **2010**, *122*, 2803; *Angew. Chem. Int. Ed.* **2010**, *49*, 2743–2746; b) N. Sakai, N. Uchida, T. Konakahara, *Tetrahedron Lett.* **2008**, *49*, 3437–3440; c) K. Namitharan, K. Pitchumani, *Adv. Synth. Catal.* **2013**, *355*, 93–98; d) K. Namitharan, K. Pitchumani, *Org. Lett.* **2012**, *14*, 5728–5731; e) S. U. Dighe, S. Hutait, S. Batra, *ACS Comb. Sci.* **2012**, *14*, 665–672; f) L. Zhang, H. C. Malinakova, *J. Org. Chem.* **2007**, *72*, 1484–1487; g) F. Colombo, M. Benaglia, S. Orlandi, F. Usuelli, *J. Mol. Catal. A: Chem.* **2006**, *260*, 128–134; h) A. Gheorghe, A. Matsuno, O. Reiser, *Adv. Synth. Catal.* **2006**, *348*, 1016–1020.

[8] For reviews, see: a) J. D. Sunderhaus, S. F. Martin, *Chem. Eur. J.* **2009**, *15*, 1300–1308; b) N. Isambert, R. Lavilla, *Chem. Eur. J.* **2008**, *14*, 8444–8454; c) A. Dömling, *Chem. Rev.* **2006**, *106*, 17–89; d) R. V. A. Orru, M. de Greef, *Synthesis* **2003**, 1471–1499; e) H. Bienaymé, C. Hulme, G. Oddon, P. Schmitt, *Chem. Eur. J.* **2000**, *6*, 3321–3329; f) A. Dömling, I. Ugi, *Angew. Chem.* **2000**, *112*, 3300; *Angew. Chem. Int. Ed.* **2000**, *39*, 3168–3210; g) I. Ugi, A. Dömling, B. Werner, *J. Heterocycl. Chem.* **2000**, *37*, 647–658; h) L. Weber, K. Illgen, M. Almstetter, *Synlett* **1999**, 366–374; i) R. W. Armstrong, A. P. Combs, P. A. Tempest, S. D. Brown, T. A. Keating, *Acc. Chem. Res.* **1996**, *29*, 123–131; j) I. Ugi, A. Dömling, W. Hörl, *Endeavour* **1994**, *18*, 115–122.

[9] a) M. Whiting, V. V. Fokin, *Angew. Chem.* **2006**, *118*, 3229; *Angew. Chem. Int. Ed.* **2006**, *45*, 3157–3161; b) M. P. Cassidy, J. Raushel, V. V. Fokin, *Angew. Chem.* **2006**, *118*, 3226; *Angew. Chem. Int. Ed.* **2006**, *45*, 3154–3157; c) E. J. Yoo, I. Bae, S. H. Cho, H. Han, S. Chang, *Org. Lett.* **2006**, *8*, 1347–1350; d) S. L. Cui, X. F. Lin, Y. G. Wang, *Org. Lett.* **2006**, *8*, 4517–4520; e) S. H. Cho, E. J. Yoo, I. Bae, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 16046–16047; f) I. Bae, H. Han, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 2038–2039; g) J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, Oxford, UK, **2001**.

[10] a) P. Shanmugam, V. Vaithiyanathan, V. Baby, *Tetrahedron* **2006**, *62*, 4342–4348; b) P. Shanmugam, B. Viswambharan, M. V. Suchithra, *Org. Lett.* **2007**, *9*, 4095–4098; c) B. Viswambharan, K. Selvakumar, S. Madhavan, P. Shanmugam, *Org. Lett.* **2010**, *12*, 2108–2111; d) S. Periyaraja, P. Shanmugam, A. B. Mandal, T. S. Kumar, P. Ramamurthy, *Tetrahedron* **2013**, *69*, 2891–2899.

[11] a) Y. Dejaegher, N. M. Kuz'menok, A. M. Zvonok, N. De Kimpe, *Chem. Rev.* **2002**, *102*, 29–60; b) Y. Dejaegher, N. De Kimpe, *J. Org. Chem.* **2004**, *69*, 5974–5985; c) K. S. Kenis, M. D'hooghe, G. Verniest, T. A. D. Thi, C. P. The, T. V. Nguyen, N. De Kimpe, *J. Org. Chem.* **2012**, *77*, 5982–5992; d) B. Alcaide, P. Almendros, C. Aragoncillo, *Chem. Commun.* **2000**, 757–758; e) B. Alcaide, P. Almendros, C. Aragoncillo, *Chem. Eur. J.* **2002**, *8*, 3646–3652; f) M. K. Ghorai, A. Kumar,

K. Das, *Org. Lett.* **2007**, *9*, 5441–5444; g) M. K. Ghorai, D. Shukla, A. Bhattacharyya, *J. Org. Chem.* **2012**, *77*, 3740–3753; h) M. K. Ghorai, A. Kumar, D. P. Tiwari, *J. Org. Chem.* **2010**, *75*, 137–151.

[12] CCDC-834010 (for **4a**), -834011 (for **5a**), -916626 (for **5g**), -923623 (for **6h**), and -923622 (for **7g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] a) K. Jiang, B. Tiwari, Y. R. Chi, *Org. Lett.* **2012**, *14*, 2832–2385; b) L. Hao, Y. Du, X. Chen, H. Jiang, Y. Shao, Y. R. Chi, *Org. Lett.* **2012**, *14*, 2154–2157.

Received: August 19, 2013
Published Online: December 2, 2013

