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Synthesis, Structure and Emission Properties of Spirocyclic Benzofuranones and Dihydroindolones: A Domino Insertion–Coupling–Isomerization–Diels–Alder Approach to Rigid Fluorophores

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Dedicated to Professor Peter Hofmann on the occasion of his 60th birthday

Abstract: An alkynoyl *ortho*-iodo phenolester or alkynoyl *ortho*-iodo anilides and propargyl allyl ethers react under Sonogashira coupling conditions in the sense of an insertion–coupling–isomerization–Diels–Alder hetero domino reaction to furnish (tetrahydroisobenzofuran)-spirobenzofuranones and -spirodihydroindolones in good yields. Many representatives can be crystallized and single crystal structure analyses display steric and electronic substituent effects on the torsional angles of the terminal (hetero)aryl groups and the central *cis*,-*trans*-butadiene fragment. DFT computations reveal that in the final pericyclic step the Diels–Alder termination is by far thermodynamically and kinetically favored over a possible Claisen rearrangement. Compounds of this new class of spirocyclic compounds possess large Stokes shifts and fluoresce intensively with blue over green to orange colors. As a consequence of the spirocyclic rigidity fluorescence lifetimes and quantum yields are rather high in some cases.

Keywords: C–C coupling · cycloaddition · domino reactions · fluorescence · spiro compounds

Introduction

In the past decade the productive concepts of multicomponent processes, domino reactions and sequential transformations have considerably stimulated the scientific community in search for economical and ecological access to biologically active scaffolds and lead structures.[1,2] In particular, these diversity oriented syntheses[3] address the fundamental issues of preparative efficiency and reaction design. Mastering various combinations of elementary organic and organometallic transformations under similar conditions is the major conceptual challenge in engineering novel types of uni-, bi- and multimolecular sequences. From a practical point of view the expansion of diversity oriented synthesis into combinatorial chemistry[4] and solid-phase syntheses[2d,5] promises manifold opportunities for developing novel lead structures of pharmaceuticals, catalysts and even novel molecule based materials.

Generally, domino reactions[6] are regarded as sequences of uni- or bimolecular elementary reactions that proceed without isolation of intermediates or workup. The reactive functionality of the preceding step has been formed in the previous transformation. Although, quite remarkable syntheses of natural products with polycyclic frameworks have successfully been achieved by the application of domino reactions as key steps, a domino approach to functional materials, such as chromophores, fluorophores and redox active molecules, is still in its infancy.[7] Nevertheless, the prospect to simultaneously accessing new scaffolds and a large structural space sets the stage for new innovative synthetic concepts in search for fluorescent materials. In addition, the ongoing quest for high-performance fluorophores in OLED with peculiar properties is a stimulating challenge.[8] As part

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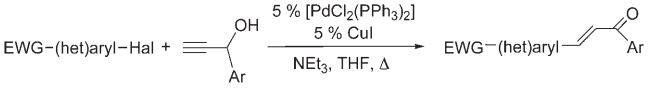
of our program to develop new multicomponent methodologies for the synthesis of chromophores and fluorophores, we have recently communicated a domino synthesis of fluorescent butadienes that are structurally rigidified by a spirocyclic framework.[9] Here, we report on the synthetic expansion to diversely substituted representatives, computional studies on the concluding pericyclic step, and photophysical investigations of this new class of rigidified fluorophores.

Results and Discussion

Domino synthesis of spirobenzofuranones and spirodihydroindolones: In recent years we have developed consecutive multicomponent syntheses of pharmaceutically relevant heterocycles[10,11] initiated by a coupling–isomerization reaction[10,12] (CIR) (Scheme 1).

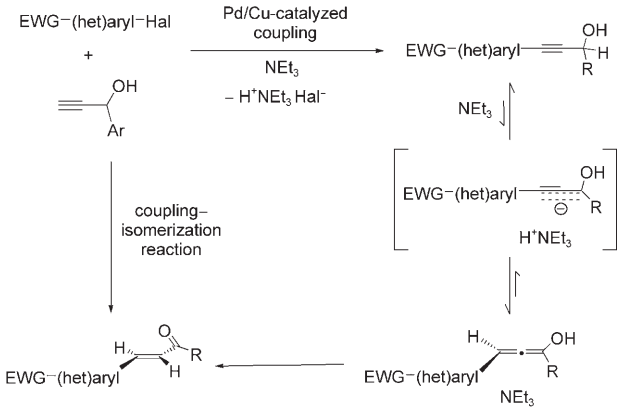


EWG: electron-withdrawing group

Scheme 1. Coupling–isomerization reaction (CIR), a novel synthesis of chalcones and enones.

The CIR of electron deficient (hetero)aryl halides and (hetero)aryl propargyl alcohols occurs under the conditions of the Sonogashira coupling[13] and represents a mild and efficient access to enones. Mechanistically, the CIR can be rationalized as a rapid palladium-copper catalyzed alkynylation reaction followed by a slow base catalyzed propargyl alcohol to enone isomerization (Scheme 2).

Abstract in German: *Alkinoyl* ortho-*iodphenolester oder Alkinoyl* ortho-*iodanilide und Propargylallylether reagieren unter den Bedingungen der Sonogashira-Kupplung im Sinne einer Insertions–Kupplungs–Diels–Alder-Hetero-Domino-Reaktion zu (Tetrahydroisobenzofuran)-spirobenzofuranonen bzw. -spirodihydroindolonen in guten Ausbeuten, von denen viele kristallisiert werden konnten. Die Einkristallstrukturanalysen offenbaren sterische und elektronische Substituenteneffekte auf die Torsionswinkel der terminalen (Hetero)arylgruppen und des zentralen* cis,trans-*Butadienfragments. DFT-Rechnungen zeigen, dass im letzten pericyclischen Schritt die Diels–Alder-Reaktion gegenüber einer möglichen Claisen-Umlagerung bei weitem thermodynamisch und kinetisch begünstigt ist. Viele Verbindungen dieser neuen Spirocyclenklasse besitzen große Stokes-Verschiebungen und fluoreszieren intensive mit blauer, grüner oder oranger Farbe. Als Folge der spirocyclischen Rigidität sind in einigen Fällen die Fluoreszenzlebensdauern und Quantenausbeuten relative hoch.*

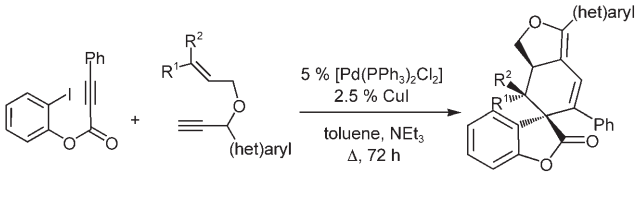


Scheme 2. Mechanistic rationale of the CIR.

Although, the proposed allenol intermediate remains an elusive and highly reactive intermediate, the major potential of the CIR clearly lies in selectively addressing allenol derivative intermediates by thermodynamically and kinetically favored intramolecular trapping reactions. Furthermore, the installation of the required conjugation of an electron-withdrawing functionality by an organometallic elementary step such as an insertion of an alkyne into a carbon–palladium bond[14] followed by a CIR would not only represent a methodological extension, but could also provide new access to hetero domino reactions.[6,15] As a consequence of an insertion–CIR an electron deficient diene can be readily established. Assuming a highly reactive allenol intermediate of the CIR (see above) in this particular case the transient should be a vinyl allene, that is, a reactive diene in Diels–Alder reactions. Hence, we set out to conduct the insertion–CIR with a propargyl allyl ether, not only shutting off the irreversible allenol–enone tautomerism but also implementing a tethered dienophile functionality as a trap for an intramolecular [4+2] cycloaddition with inverse electron demand.

Indeed, reaction of alkynoyl *ortho*-iodo phenolester **1** and propargyl allyl ethers **2** in presence of catalytic amounts of $[Pd(PPh_3)_2Cl_2]$ and CuI in a boiling mixture of toluene and triethylamine gives rise to the formation of the class of (tetrahydroisobenzofuran)spirobenzofuranones **3** in moderate to excellent yields (Scheme 3, Table 1).

Likewise, upon reacting alkynoyl *ortho*-iodo anilides **4** and propargyl allyl ethers **2** under Sonogashira conditions in a boiling mixture of butyronitrile and triethylamine (tetrahydroisobenzofuran)spiroindolones **5** can be isolated in moderate to excellent yields (Scheme 4, Table 2).

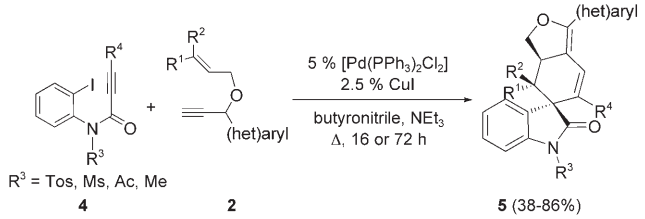


Scheme 3. Insertion–coupling–isomerization–Diels–Alder domino reaction to spirobenzofuranones **3**.

Table 1. Insertion–coupling–isomerization–Diels–Alder domino reaction to spirobenzofuranones **3**.[a]

Entry[a]	Propargyl allyl ether **2**	Spirobenzofuranones **3** (yield [%])[b]
1	**2a**: $R^2=R^3=H$, (het)aryl = *p*-NCC_6H_4	**3a**: $R^2=R^3=H$, (het)aryl = *p*-NCC_6H_4 (51)
2	**2b**: $R^2=R^3=H$, (het)aryl = *o*-FC_6H_4	**3b**: $R^2=R^3=H$, (het)aryl = *o*-FC_6H_4 (50)
3	**2c**: $R^2=R^3=H$, (het)aryl = *p*-$MeOC_6H_4$	**3c**: $R^2=R^3=H$, (het)aryl = *p*-$MeOC_6H_4$ (66)
4	**2d**: $R^2=R^3=H$, (het)aryl = *p*-$EtOC_6H_4$	**3d**: $R^2=R^3=H$, (het)aryl = *p*-$EtOC_6H_4$ (46)
5	**2e**: $R^2=R^3=H$, (het)aryl = *p*-$Me_2NC_6H_4$	**3e**: $R^2=R^3=H$, (het)aryl = *p*-$Me_2NC_6H_4$ (32)
6	**2f**: $R^2=CH_3$, $R^3=H$, (het)aryl = *p*-$EtOC_6H_4$	**3f**: $R^2=CH_3$, $R^3=H$, (het)aryl = *p*-$EtOC_6H_4$ (29)
7	**2g**: $R^2=CH_3$, $R^3=H$, (het)aryl = 2-thienyl	**3g**: $R^2=CH_3$, $R^3=H$, (het)aryl = 2-thienyl (49)
8	**2h**: $R^2=R^3=CH_3$, (het)aryl = *p*-$MeOC_6H_4$	**3h**: $R^2=R^3=CH_3$, (het)aryl = *p*-$MeOC_6H_4$ (33)

[a] Reaction conditions: 1.0 equiv aryl iodide **1**, 1.1 equiv propargyl allyl ether **2** (0.1 M in toluene/triethylamine 1:1), 0.05 equiv $[Pd(PPh_3)_2Cl_2]$ and 0.05 equiv CuI were heated to reflux temperature for 72 h. [b] Yields refer to isolated yields of compounds **3** after flash chromatography on silica gel and recrystallization to be $\geq 95\%$ pure as determined by NMR spectroscopy and elemental analysis.



Scheme 4. Insertion–coupling–isomerization–Diels–Alder domino reaction to spiroindolones **5**.

The structures of spirocycles **3** and **5** were unambiguously supported by spectroscopic (^1H, ^{13}C and DEPT, COSY, NOESY, HETCOR and HMBC NMR experiments, IR, UV/Vis, mass spectrometry) and combustion analyses. Most distinctly, the spirocyclic juncture causes a considerable conformational fixation and, therefore, the relative configuration of both series of spirocycles **3** and **5** can be characteristically assigned by examining the NOE contacts of the C^{7a} methine multiplet resonances appearing between δ 3.52 and 4.02 ppm in the NOESY spectra (Figure 1).

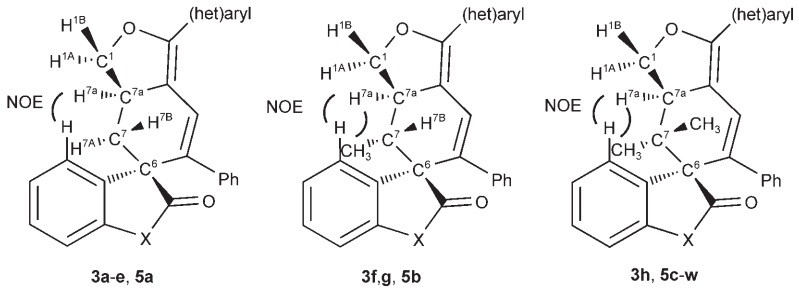


Figure 1. Assignment of selected ^1H NMR resonances of **3** and **5**.

These methine resonances not only show distinct cross-peaks in the $^1H,^1H$-COSY spectra to the methylene protons H^{1A} but also to the methylene protons H^{7A}. The methyl group bound to carbon C^7, which points in the same hemisphere, can be identified in the NOESY spectra. In some cases the splitting patterns of the methine and methylene protons are well resolved and the dihedral angles as derived from the Karplus curve are in good agreement with the data obtained from X-ray structure analyses (see below). In the ^{13}C NMR spectra the characteristic sp^3-hybrized quaternary spiro carbon resonances of C^6 are found between δ 53.1 and 62.4 ppm depending on the lactone or lactam nature of the benzoannelated ring. Likewise, the carbonyl resonances, indicative for lactams and lactones, range from δ 174.6 and 178.5 ppm.

Additionally, the molecular structure of the spirocyclic systems **3** and **5** was corroborated by X-ray structure analyses of the benzofuranones **3a–c**, **e**, **h**, and the dihydroindolones **5d**, **f–h**, **l**, **p–q** (Figures 2–13).[16]

Besides the unambiguous structural assignment of the spirocyclic scaffold the single crystal data disclose more detailed insight into conformational biases exerted by substitution patterns. Since the central butadiene chromophore is rigidified by its bicyclic nature the appending substituents, which are predominantly (hetero)aromatic moieties, can adopt preferred conformations (Figure 14). The mutual orientations of these planar substituents are best described by the interplanar angles between the (hetero)aromatic substituents at C^3 (plane 1) and the butadiene unit (plane 2) and between plane 2 and the (hetero)aromatic fragment at C^5 (plane 3) (Table 3).

For the benzofuranones **3** the interplanar angles between planes 1 and 2 lie within the small range of 31.0 and 40.5°, independent both of the electronic nature of the (hetero)aromatic substituents at C^3 and the methyl substitution at C^7. Likewise, the interplanar angles between planes 2 and 3 are also found in a narrow margin between 42.7 and 50.7°. For the dihydroindolones the substituent variation is broader and encompasses electronically variable substitution at both C^3 and C^5, and at the indolone nitrogen substituent. The interplanar angles between planes 1 and 2 vary from 7.5 to 43.1°, a range that reflects the electronic and steric impact of the (hetero)aromatic substituents at C^3. Expectedly, with an angle of 15.8° the thienyl substituent (**5f**)[17] is arranged almost coplanarily with respect to the conformationally fixed butadienyl system, however, highest planarization is observed for the *p*-chlorophenyl substituted derivative **5d** (7.5°) and the *p*-formylphenyl substituted representative **5q** (8.2°). In the latter case the push–pull character of the substitution pattern is apparently even responsible for the rather small interplanar angle between planes 2 and 3 (30.2°).

Table 2. Insertion–coupling–isomerization–Diels–Alder domino reaction to spiroindolones **5**.[a]

Entry	Alkynoyl iodo anilide **4**	Propargyl allyl ether **2**	Spiroindolones **5** (yield [%])[b]
1	**4a**: R^3 = Ts, R^4 = Ph	**2c**	**5a**: R^2 = R^3 = H, (het)aryl = *p*-$MeOC_6H_4$, R^3 = Ts, R^4 = Ph (81)
2	**4a**	**2g**	**5b**: R^2 = CH_3, R^3 = H, (het)aryl = 2-thienyl, R^3 = Ts, R^4 = Ph (72)
3	**4a**	**2i**: R^2 = R^3 = CH_3, (het)aryl = *p*-$OHCC_6H_4$	**5c**: R^2 = R^3 = CH_3, (het)aryl = *p*-$OHCC_6H_4$, R^3 = Ts, R^4 = Ph (71)
4	**4a**	**2j**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4	**5d**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ts, R^4 = Ph (86)
5	**4a**	**2k**: R^2 = R^3 = CH_3, (het)aryl = Ph	**5e**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ts, R^4 = Ph (86)
6	**4a**	**2l**: R^2 = R^3 = CH_3, (het)aryl = 2-thienyl	**5f**: R^2 = R^3 = CH_3, (het)aryl = 2-thienyl, R^3 = Ts, R^4 = Ph (72)
7	**4a**	**2h**	**5g**: R^2 = R^3 = CH_3, (het)aryl = *p*-$MeOC_6H_4$, R^3 = Ts, R^4 = Ph (79)
8	**4b**: R^3 = Ts, R^4 = *n*Bu	**2j**	**5h**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ts, R^4 = *n*Bu (81)
9	**4b**	**2k**	**5i**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ts, R^4 = *n*Bu (79)
10	**4b**	**2h**	**5j**: R^2 = R^3 = CH_3, (het)aryl = *p*-$MeOC_6H_4$, R^3 = Ts, R^4 = *n*Bu (77)
11	**4c**: R^3 = Ts, R^4 = *i*Pr_3Si	**2j**	**5k**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ts, R^4 = *i*Pr_3Si (79)
12	**4c**	**2k**	**5l**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ts, R^4 = *i*Pr_3Si (85)
13	**4c**	**2h**	**5m**: R^2 = R^3 = CH_3, (het)aryl = *p*-$MeOC_6H_4$, R^3 = Ts, R^4 = *i*Pr_3Si (77)
14	**4d**: R^3 = Ms, R^4 = *p*-$MeOC_6H_4$	**2j**	**5n**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ms, R^4 = *p*-$MeOC_6H_4$ (53)
15	**4d**	**2k**	**5o**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ms, R^4 = *p*-$MeOC_6H_4$ (63)
16	**4d**	**2h**	**5p**: R^2 = R^3 = CH_3, (het)aryl = *p*-$MeOC_6H_4$, R^3 = Ms, R^4 = *p*-$MeOC_6H_4$ (63)
17	**4e**: R^3 = Ts, R^4 = *p*-$MeOC_6H_4$	**2i**	**5q**: R^2 = R^3 = CH_3, (het)aryl = *p*-$OHCC_6H_4$, R^3 = Ts, R^4 = *p*-$MeOC_6H_4$ (66)
18	**4e**	**2j**	**5r**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ts, R^4 = *p*-$MeOC_6H_4$ (87)
19	**4e**	**2k**	**5s**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ts, R^4 = *p*-$MeOC_6H_4$ (88)
20	**4f**: R^3 = Ts, R^4 = 10-methyl-phenothiazin-3-yl	**2j**	**5t**: R^2 = R^3 = CH_3, (het)aryl = *p*-ClC_6H_4, R^3 = Ts, R^4 = 10-methylphenothiazin-3-yl (58)
21	**4g**: R^3 = *p*-($AcOCH_2CH_2OC_6H_4SO_2$, R^4 = Ph	**2k**	**5u**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = *p*-($AcOCH_2CH_2OC_6H_4SO_2$, R^4 = Ph (73)
22	**4h**: R^3 = Ac, R^4 = Ph	**2k**	**5v**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Ac, R^4 = Ph (46)
23	**4i**: R^3 = Me, R^4 = Ph	**2k**	**5w**: R^2 = R^3 = CH_3, (het)aryl = Ph, R^3 = Me, R^4 = Ph (38)

[a] Reaction conditions: 1.0 equiv aryl iodide **4**, 1.1 equiv propargyl allyl ether **2** (0.1 M in butyronitrile/triethylamine 1:1), 0.05 equiv $[Pd(PPh_3)_2Cl_2]$ and 0.05 equiv CuI were heated to reflux temperature for 48–36 h. [b] Yields refer to isolated yields of compounds **5** after flash chromatography on silica gel and recrystallization to be ≥95% pure as determined by NMR spectroscopy and elemental analysis.

Most significantly, two anisyl substituents cause the inverse effect and lead to torsions of 32.9° (interplanar angle plane 1 vs 2) and 56.0° (interplanar angle plane 2 vs 3) in compound **5p**.

Based upon the product analysis the hetero domino sequence can be interpreted as a combination of a transition-metal-catalyzed insertion cascade that concludes in a pericyclic final step. Intramolecular Heck reactions[18] have been developed to a broad methodology and have culminated in impressive domino sequences like Negishi's zippers,[14] however, the termination of insertion cascades by Sonogashira alkynylation[13] has received only little attention.[19] Hence, the hetero domino sequence can be rationalized as follows (Scheme 5): as an insertion alkynylation followed by a base-catalyzed isomerization of an electron poor vinyl propargyl allyl ether to give an electron poor vinyl allene that reacts in an intramolecular [4+2] cycloaddition through an *anti–exo* transition state to conclude the sequence by formation of spirocycles **3** or **5** (Table 1, entries 6 and 7, Table 2, entry 2). Methodologically, upon formation of four new carbon–carbon bonds with concomitant generation of a complex tetracyclic framework in high efficiency this insertion–CI–Diels–Alder domino reaction furnishes spirocyclic benzofuranones **3** and dihydroindolones **5** in moderate to excellent yields.

Computational studies on the concluding pericyclic steps of the domino sequence: In comparison with the CIR and most distinctly, the tautomerism of the elusive allenol can be shut off by etherification of the propargylic alcohol. Hence, the allenyl intermediate should react in an intramolecular pericyclic fashion under the applied reaction conditions. The insertion establishes a conjugated electron-withdrawing vinyl carbonyl group that readily activates the propargylic position. Now, the isomerization of a coupled vinyl propargyl allyl ether to a vinyl allenyl allyl

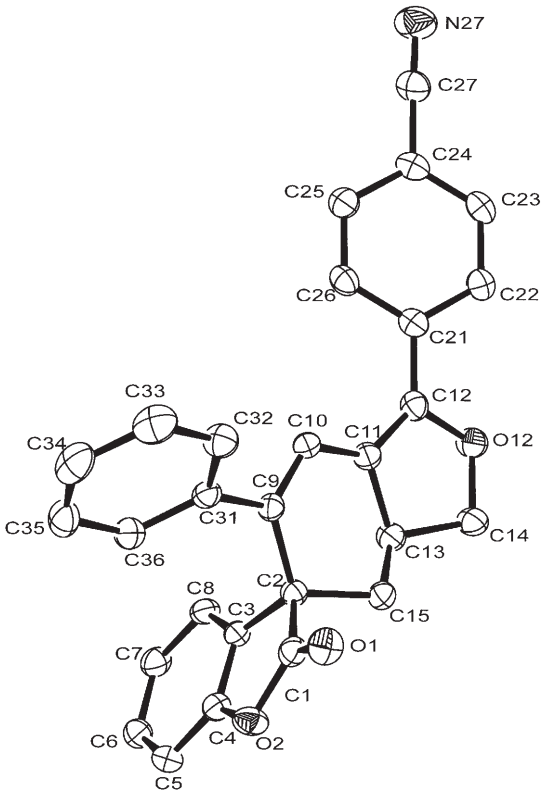


Figure 2. Molecular structure of **3a** (hydrogen atoms are omitted for clarity).

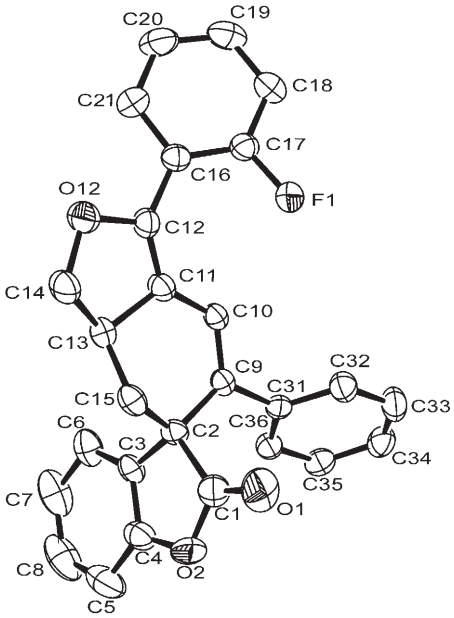


Figure 3. Molecular structure of **3b** (hydrogen atoms are omitted for clarity).

ether opens in principle two reaction pathways: either a [3,3]-sigmatropic rearrangement in the sense of a allyl–vinyl Claisen rearrangement or a [4+2] cycloaddition, that is, an intramolecular Diels–Alder (IMDA) reaction with inverse

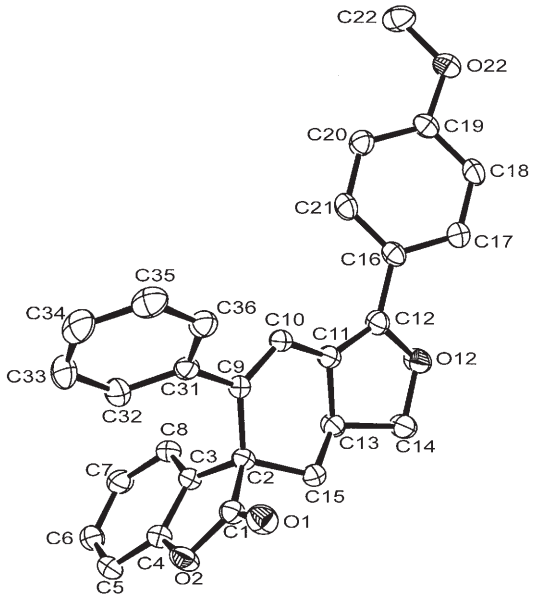


Figure 4. Molecular structure of **3c** (hydrogen atoms are omitted for clarity).

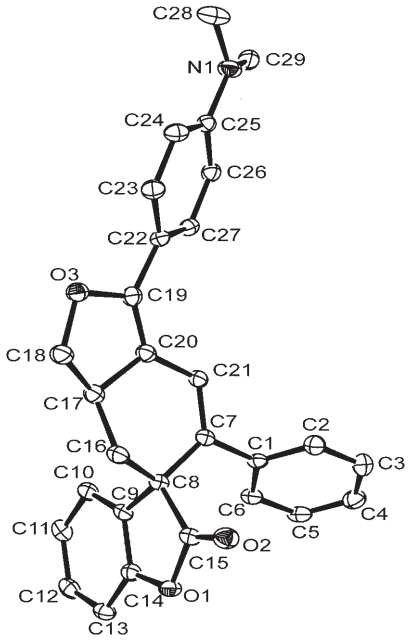


Figure 5. Molecular structure of **3e** (hydrogen atoms are omitted for clarity).

electron demand[20] of the vinyl allene with the tethered allyl dienophile. Experimentally, only the IMDA can be observed (see above). Hence, the question arises whether the observed cycloaddition is the thermodynamically or kinetically favored process. As both pathways proceed intramolecularly, thus, a direct comparison by computational studies lies at hand.

Therefore, a model system, based upon a reduction on the required functional features, was designed for quantum chemical calculations (Scheme 6 and Table 4). Thus, starting

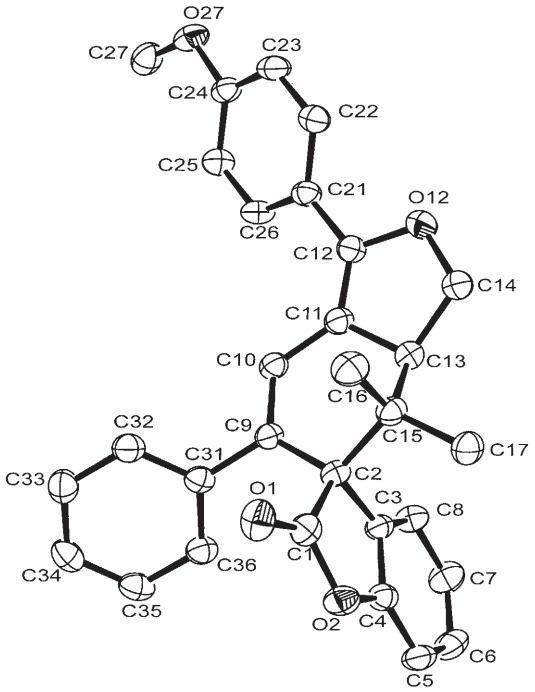


Figure 6. Molecular structure of **3h** (hydrogen atoms are omitted for clarity).

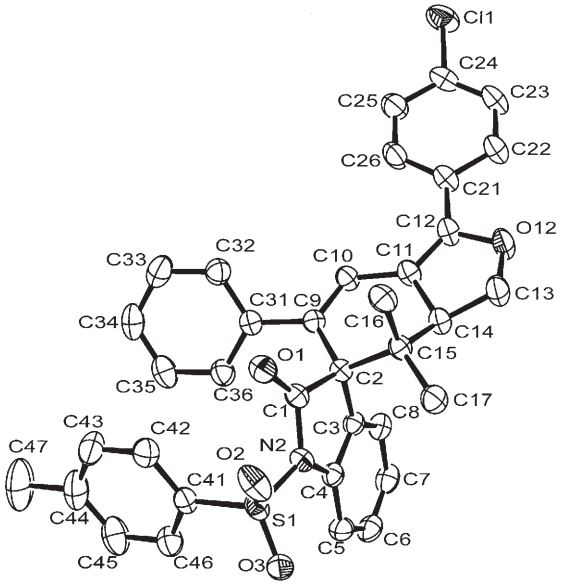


Figure 7. Molecular structure of **5d** (hydrogen atoms are omitted for clarity).

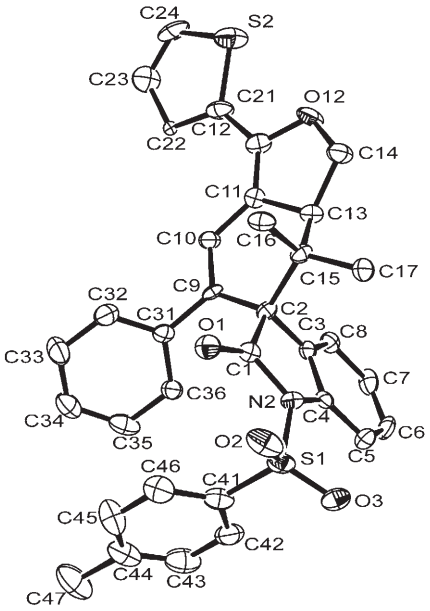


Figure 8. Molecular structure of **5f** (hydrogen atoms are omitted for clarity).

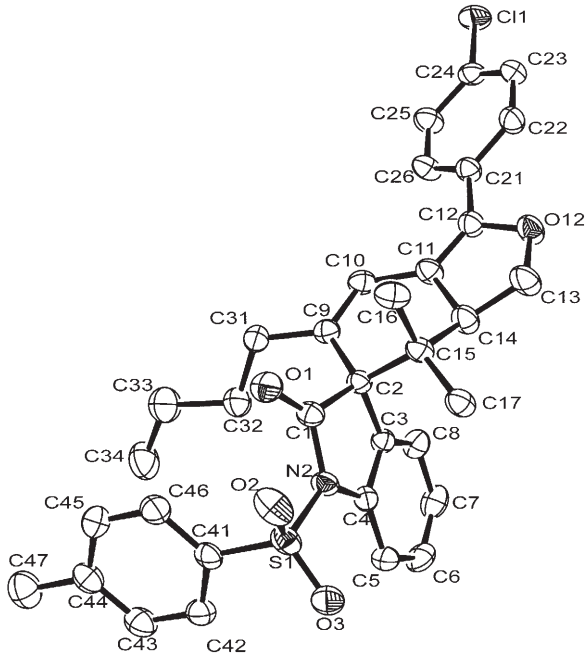


Figure 9. Molecular structure of **5h** (hydrogen atoms are omitted for clarity).

points of [3,3]-sigmatropic rearrangement or [4+2]-cycloaddition pathways are the allyloxy enallenes **6** giving rise either to the allyl substituted oxo dienes **8** or the tetrahydrobenzofurans **10**.

The structure optimizations of starting, end and transition-state geometries were performed by DFT calculations using the [RB3LYP/6-31+G(d,p)] functional.[21] Then, for energy calculations the optimized geometries were entered to post-HF single point energy calculations on the MP2 level of theory [RMP2/6-311++G(2d,2p)//RB3LYP/6-31+G-(d,p)] (Table 4).[21] The results obtained not only support the observed exclusive preference of the intramolecular [4+2] cycloaddition over the Claisen rearrangement but also clearly indicate that the cycloaddition is the favored process both thermodynamically and kinetically. This result also reproduces with slightly more expanded systems that emphasize the actual steric bias at the termini of vinyl allene moieties, still leading to spirocyclization, that is, the formation of benzo-

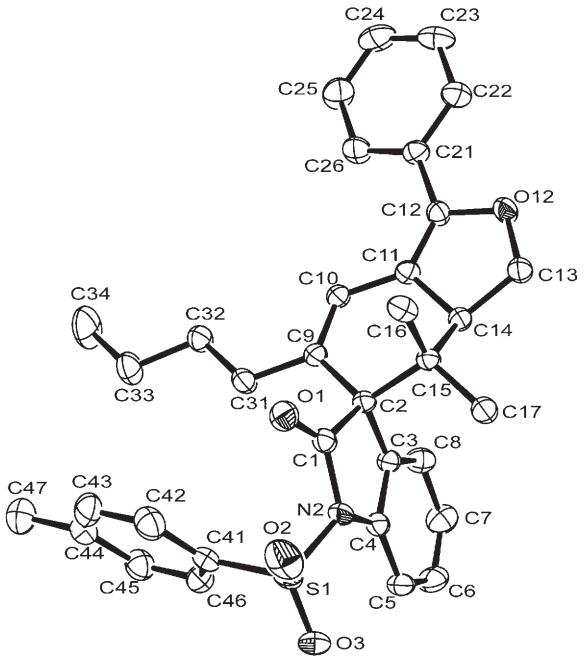


Figure 10. Molecular structure of **5i** (hydrogen atoms are omitted for clarity).

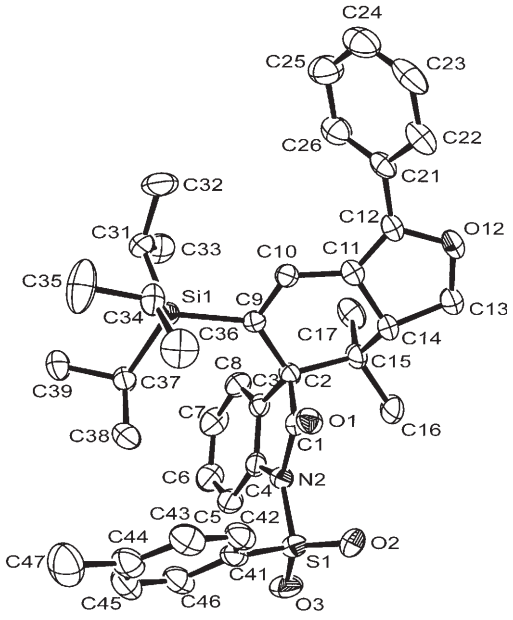


Figure 11. Molecular structure of **5l** (hydrogen atoms are omitted for clarity).

furanones and dihydroindolones (Scheme 7 and Table 4). Only if the vinyl allyloxyallene is truncated to an allyloxyallene Claisen rearrangements become the relevant process.[22]

UV/Vis absorption and emission properties of spirocyclic benzofuranones 3 and dihydroindolones 5: Most interestingly, upon irradiation with UV light all members of this new class of pale yellow to yellow absorbing spirocycles display a pronounced and intense blue over green to yellow orange

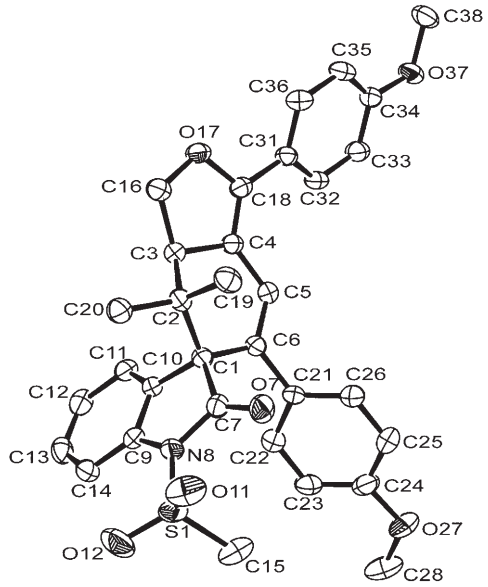


Figure 12. Molecular structure of **5p** (hydrogen atoms are omitted for clarity).

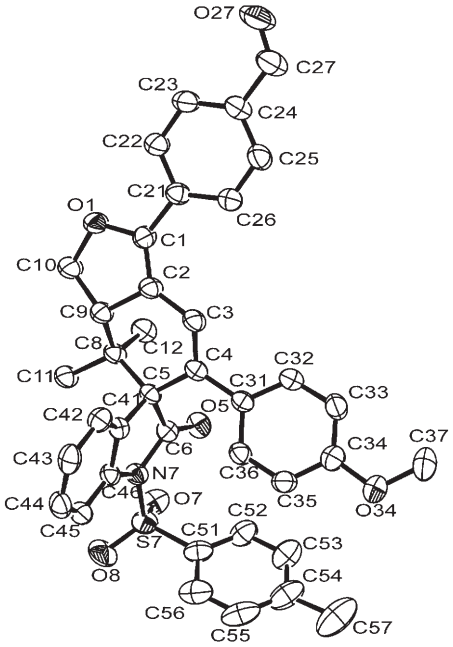


Figure 13. Molecular structure of **5q** (hydrogen atoms are omitted for clarity).

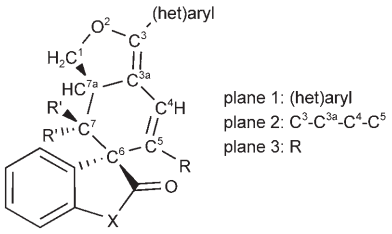
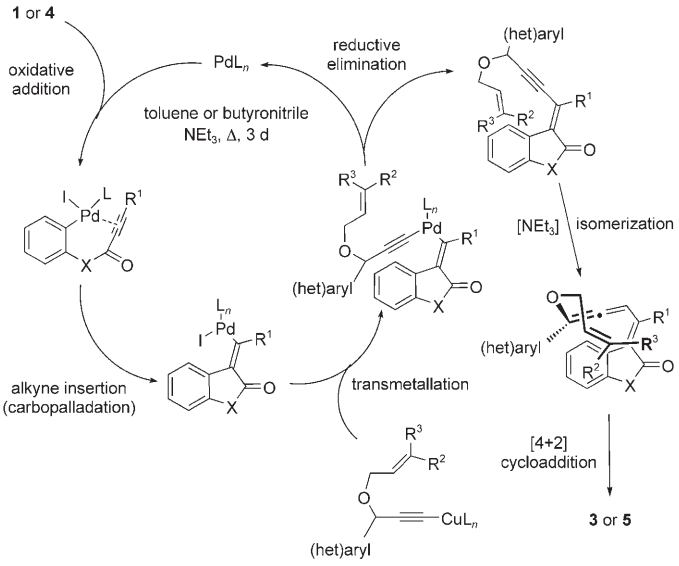


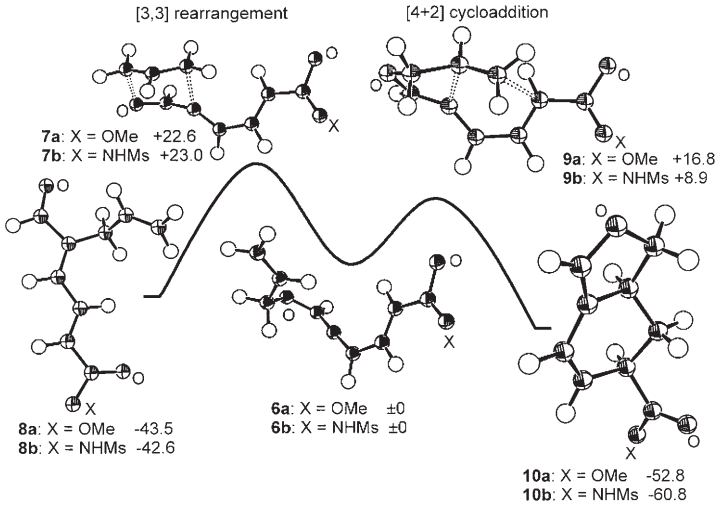
Figure 14. Numbering of the tetrahydrobenzofuran and assignment of planes of **3** and **5**.

Table 3. Selected interplanar angles [°] of spirocyclic benzofuranones **3** to spiroindolones **5**.

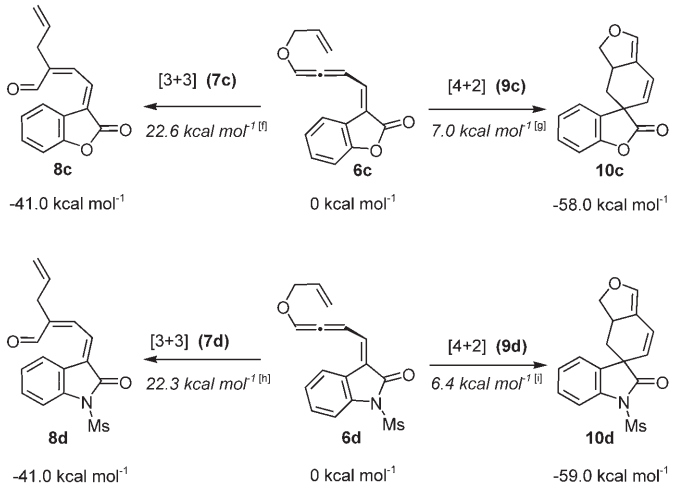
Compound	Interplanar angle planes 1 vs 2	Interplanar angle planes 2 vs 3
3a	35.1	49.8
3b	31.0	52.3
3c	40.5	42.7
3e	39.3	50.7
3h	35.3	44.9
5d	7.5	43.7
5f	15.8	48.5
5h	25.8	–
5i	17.1	–
5l	43.1	–
5p	32.9	56.0
5q	8.2	30.2



Scheme 5. Mechanistic rationale for the domino sequence to spirobenzofurans **3** and spirodihydroindolones **5**.



Scheme 6. Energy profile of the modeled pericyclic reactions (energies are given in kcal mol^{-1}).



Scheme 7. Expanded models for the gas-phase computations of concluding pericyclic step (transition-state energies in italics).[21]

fluorescence with large Stokes shifts in solution (4300 to 9600 cm^{-1}) and in the solid state (Figure 15, Table 5). All spirocyclic benzofuranones **3** and dihydroindolones **5** were studied by UV/Vis and fluorescence spectroscopy, and besides absorption and emission also the fluorescence quantum yields and lifetimes of the excited states were determined for all members of the series. Albeit the structural relations between spirocyclic benzofuranones and dihydroindolones are striking, both absorption and emission properties are strongly effected by minute substituent variations or conformational biases.

All chromophores show absorptions between near UV and the edge to visible where the longest wavelength absorption maxima are between 327 to 398 nm with molar extinction coefficients ε ranging from 12700 to 35000 mol^{-1} dm^3 cm^{-1}. Position and magnitude of these longest wavelength absorption bands can be therefore assigned to π–π^* transitions, also reflecting S_0–S_1 excitation.

Table 4. Relative single point energies of the structures **6**, **8** and **10** and the corresponding transititon states **7** and **9** calculated on the MP2 level of theory [RMP2/6-311++G(2d,2p)//RB3LYP/6-31+G(d,p)] (energies are given in kcal mol^{-1}).[21]

Allyloxy enallene **6**	Claisen product **8**	TS[3,3] **7**	Diels–Alder product **10**	TS[4+2] **9**	Δ[[TS[4+2] (**7**) −TS[3,3] (**9**)]
0[a] (**6a**)	−43.50 (**8a**)	22.60 (**7a**)[b]	−52.10 (**10a**)	16.80 (**9a**)[c]	−5.80 [(**7a**)−(**9a**)]
0[a] (**6b**)	−42.60 (**8b**)	23.00 (**7b**)[d]	−60.00 (**10b**)	8.90 (**9b**)[e]	−14.10 [(**7b**)−(**9b**)]
0[a] (**6c**)	−41.00 (**8c**)	22.60 (**7c**)[f]	−58.00 (**10c**)	7.00 (**9c**)[g]	−15.60 [(**7c**)−(**9c**)]
0[a] (**6d**)	−41.00 (**8d**)	22.30 (**7d**)[h]	−59.00 (**10d**)	6.40 (**9d**)[i]	−15.90 [(**7d**)−(**9d**)]

[a] Energies are set to 0 kcal mol^{-1}. Imaginary frequencies from the DFT geometry optimizations that verify transition states: [b] i508.05 cm^{-1}. [c] i463.57 cm^{-1}. [d] i508.78 cm^{-1}. [e] i456.06 cm^{-1}. [f] i505.64 cm^{-1}. [g] i456.88 cm^{-1}. [h] i503.87 cm^{-1}. [i] i455.57 cm^{-1}.

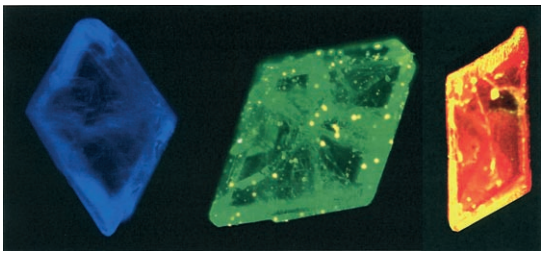


Figure 15. Blue (**5e**), green (**5f**) and orange (**5q**) fluorescent single crystals (excitation at 370 nm).

Table 5. Selected absorption and emission data, fluorescence quantum yields, Stokes shifts and fluorescence lifetimes of spirocycles **3** and **5** (recorded in CH_2Cl_2, $T=298$ K).

Compound	Absorption[a] $\lambda_{max,abs}$ [nm] (ε)	Emission[b] $\lambda_{max,em}$ [nm] (Φ_f)[c]	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}][c]	Fluorescence lifetimes $\tau_{1/2}$ [ns][e]
3a	368 (12700) 282 (500), 242 (11000)	500 (0.58)	7200	1.50 (0.10) 4.30 (0.90)
3b	335 (23200) 282 (7900)	487 (0.29)	9300	1.20 (0.15) 2.70 (0.85)
3c	350 (26700) 255 (17500)	515 (0.06)	9200	0.81
3d	347 (23400) 254 (15600)	517 (0.07)	9500	2.00 (0.65) 2.70 (0.35)
3e	372 (21200) 284 (11400)	522 (0.12)	7700	2.78 (0.03) 1.00 (0.97)
3f	345 (23000) 255 (15100)	512 (0.07)	9500	2.00 (0.06) 0.82 (0.94)
3g	359 (21100) 257 (13900)	525 (0.08)	8800	0.90 (0.64) 1.8 (0.36)
3h	350 (35000) 254 (17000)	502 (0.25)	8700	2.3 (0.93) 0.98 (0.07)
5a	345 (24900) 242 (20000)	502 (0.18)	9100	1.77
5b	360 (20500) 254 sh (20000)	528 (0.09)	8800	1.90 (0.41) 0.95 (0.59)
5c	391 (15900) 250 (23800)	532 (0.39)	6800	4.97 (0.93) 1.55 (0.07)
5d	353 (22900) 243 sh (27000)	485 (0.50)	7700	3.62 (0.96) 1.44 (0.04)
5e	348 (24900) 244 sh (27600)	487 (0.44)	8200	3.40
5f	367 (18600) 253 (19600)	515 (0.22)	7800	1.77 (0.31) 2.90 (0.69)
5g	353 (20900) 250 (25500)	503 (0.25)	8400	2.20
5h	327 (22000) 242 sh (20300)	436 (0.04)	7600	0.09 (0.99) 2.22 (0.01)
5i	362 (18900) 246 (16900)	433 (0.05)	4500	0.30 (0.98) 1.85 (0.02)
5j	333 (20600) 246 (19600)	440 (0.21)	7300	1.05 (0.79) 1.65 (0.21)
5k	346 (17700)	466 (0.45)	7400	1.20 (0.06) 3.00 (0.94)
5l	388 (14900) 254 (14000)	466 (0.15)	4300	1.36 (0.41) 0.88 (0.59)
5m	343 (11800) 242 sh (16500)	475 (0.04)	8100	0.26 (0.98) 0.80 (0.02)
5n	353 (24200) 338 (21200) 247 sh (19200)	480 (0.62)	7500	3.66
5o	347 (21800) 270 (10300) 242 sh	520 (0.58)	9600	3.64 (0.90) 1.49 (0.10)
5p	351 (27400) 256 (21200)	488 (0.37)	8000	2.74
5q	398 (20100) 288 sh (12800) 249 (24200)	545 (0.36)	6800	1.78 (0.10) 4.50 (0.90)
5r	356 (28500) 242 sh (30100)	477 (0.53)	7100	1.00 (0.26) 3.50 (0.74)
5s	349 (26600) 246 (26600)	475 (0.42)	7600	2.60 (0.93) 1.04 (0.07)
5t	377 (20300) 338 (35500) 225	545 (0.20)	8200	4.07 (0.89) 1.67 (0.11)
5u	347 (29300) 245 (40200)	488 (0.43)	8300	3.37
5v	348 (21300) 235 sh (24800)	485 (0.46)	8100	0.70 (0.04) 3.54 (0.96)

[a] Recorded at $c=10^{-4}$ M. [b] Recorded at $c=10^{-7}$ M. [c] Determined with DPA and with quinine in 0.1 M sulfuric acid as standards. [d] $\Delta\tilde{\nu}=\lambda_{max,abs}-\lambda_{max,em}$ [cm^{-1}]. [e] Determined by time-correlated single-photon counting (TCSPC) at an excitation wavelength of 370 nm.

Expectedly, aldehyde substitution (compounds **5c**, **q**) leads to the most pronounced bathochromic shift of absorption and emission maxima. In the fluorescence spectra, the shortest wavelength emission maxima range from 433 to 545 nm and are always accompanied by either a blue- or red-shifted shoulder. The large Stokes shift can not be explained by polar solvent relaxation alone but indicates further photochemical mechanisms leading to the formation of the emissive state. The (hetero)aromatic substituents at C^3 can be accounted for twisted intramolecular charge transfer (TICT), most probably going along with a distortion of the molecular framework as reported for coumarin derivates.[23] The latter notion arises because the model *trans,cis*-1,4-diphenyl butadiene does not fluoresce at all upon photo excitation, but rather undergoes a conformational twisting and an efficient internal conversion back to the ground state.[24] This deviating peculiar behavior of the spirocyclic 1-(hetero)aryl-4-(hetero)aryl butadienes **3** and **5** can be unequivocally attributed to structurally fixed conformations in the excited state.

Time-correlated single-photon counting (TCSPC) measurements have revealed luminescence lifetimes for spirocycles **3** and **5** that lie between 0.26 and 4.97 ns with exception of compound **5h** (0.09 ns). Therefore, the emission from the excited state can be attributed to fluorescence from an excited singlet state. In most cases a single exponential is not sufficient to model the measured decay curves, thus two, and in some cases even three exponentials have been used to describe the data, indicating multiple concurring pathways for non-radiative de-excitation.

Further indication of the concomitant distortion of the heterocyclic framework is reflected by steric substituent effects. Thus, dimethyl substitution at C^7 obviously leads to a more rigid and hence stabilized emissive state, thereby lowering the Stokes shift by 1000 cm^{-1} and increasing excited state lifetimes. Further photochemical studies of differences due to solvent polarity and in rigid matrices accompanied by theoretical quantum mechanical modeling are necessary to support this interpretation, and are currently under investigation.

Electronically, acceptor substitution at C^3 leads to higher fluorescence quantum yields with exception of series **5h–j**. On the other hand the structural nature of the spirocyclic framework by going from benzofuranones (compounds **3c**, **h**) to dihydroindolones (compounds **5a**, **g**) only affects absorption maxima to a minor extent. However, dimethyl sub-

stitution increases the fluorescence quantum yield considerably for benzofuranones **3** and only to a minor extent for dihydroindolones **5**. But dimethyl substitution has no influence on the emission wavelength of dihydroindolones.

Arylsubstituted *p*-chlorophenyl butadienes (compounds **5d**, **n**, **r**) are very similar with respect to absorption and emission maxima, absorbance and fluorescence quantum yield, phenothiazine as a substituent (compound **5r**) causes a red-shift of absorption and emission maxima, however, with a decrease in fluorescence quantum yield. Upon alkyl and silyl substitution (compounds **5h**, **k**) both absorption and emission maxima are blue-shifted. Remarkably, silyl substituents display comparably high fluorescence quantum yields, whereas the butyl chain causes a dramatic decrease.

Interestingly, variation of the nitrogen substituent in a consanguineous series of dihydroindolones (compounds **5e**, **u**, **v**, **w**) with a diphenyl substituted butadiene chromophore neither affects the absorption and emission maxima nor the fluorescence quantum yields.

Conclusion

In conclusion, we have developed a new insertion–coupling–isomerization–Diels–Alder domino reaction that furnishes spirocyclic benzofuranones **3** and dihydroindolones **5** in moderate to excellent yields. DFT and MP2 calculations show that in the product forming step the Diels–Alder reaction is thermodynamically and kinetically favored over a Claisen rearrangement. The solid-state structure of these poly(hetero)cyclic frameworks reveals considerable substituent effects on the torsional angles between the central butadiene chromophore and the terminal (hetero)aryl substituents. In addition, these new poly(hetero)cyclic entities establish a new class of fluorophores with tuneable absorption and emission properties. As the fluorescence colors can range from blue over green to orange and as emission shows a high Stokes shift both in solution and in solid state they are promising candidates for solution and solid state applications both in biolabeling (e.g. with side chain functionalized representatives such as compound **5u**) and OLED devices. Furthermore, the complex structural framework in conjunction with a diversity oriented domino approach opens new opportunities towards multifluorophore systems.

Experimental Section

General considerations: All reactions involving palladium/copper catalysis were performed in degassed oxygen free solvents under a nitrogen atmosphere using Schlenk and syringe techniques. The catalysts [Pd(Ph_3P)$_2$$Cl_2$], and CuI were purchased reagent grade from ACROS, Aldrich, Fluka or Merck and used without further purification. Triethylamine, toluene and butyronitrile were dried and distilled according to standard procedures.[25] Detailed preparative procedures including full analytics and ^{1}H, ^{13}C and 135DEPT NMR spectra of *ortho*-iodo phenolester **1**, propargyl allyl ethers **2** and *ortho*-iodo phenolamides **4** can be found in the Supporting Information. Column chromatography: silica gel 60 mesh 230–400 (Macherey-Nagel, Düren). TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Büchi Melting Point B-540. ^{1}H and ^{13}C NMR spectra in $CDCl_3$: Bruker DRX 300, Bruker DRX 500 and Bruker AC 300.The assignments of quaternary C CH, CH_2 and CH_3 have been made by using DEPT spectra. IR: Bruker Vector 22 FT-IR. UV/Vis: Perkin Elmer Models Lambda 16 and Hewlett Packard HP8452A. Fluorescence: Perkin Elmer LS-55. MS: Jeol JMS-700 and Finnigan TSQ 700. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg (Germany).

X-ray structure determination of compounds 3a–c, e, h, 5d, f, h, i, l, p, and q: Program SADABS V2.03 for absorption correction as well as software package SHELXTL V6.12 for structure solution and refinement:[26] The data of the X-ray structure analyses of the compounds are summarized in Tables 6 and 7.

Spectroscopy: Absorption spectra were taken on a Cary 500 UV-Vis-NIR spectrometer (Varian, Darmstadt, Germany). All spectra were taken in standard quartz cuvettes (Hellma, Mülheim, Germany) with a path length of 0.3 cm in CH_2Cl_2.

Steady-state fluorescence spectra were measured on a Cary Eclipse fluorescence spectrometer (Varian, Darmstadt, Germany) by excitation of the respective absorption maxima. To avoid re-absorption and re-emission effects the concentrations were strictly kept below 1 μM.

Ensemble fluorescence lifetime measurements were performed on a FluoTime 100 (PicoQuant, Berlin, Germany) using time-correlated single-photon counting (TCSPC). For excitation we used a pulsed LED emitting at 370 nm with a pulse width <600 ps (fwhm) operated at 20 MHz. The measurements were done in standard quartz cuvettes ($d=$ 0.3 cm). To exclude polarization effects fluorescence was observed under magic angle conditions (54.7°). Typically 10000 photons were collected in the maximum channel of a total of 4096 channels. The lifetime was determined by least-squares deconvolution and their quality judged by the reduced χ^2 values and the randomness of the weighted residuals.

We estimated the quantum yields of our compounds by comparison with the known quantum yields of 9,10-diphenylanthracence and quinine sulfate at an excitation wavelength of 366 nm. According to Equation (1) the fluorescence emission I_i of standards R and samples S at five different optical densities OD_i, that is, concentrations, were determined and corrected for the refractive index n_i of the respective solutions i. The presented quantum yields Q were obtained in each case by averaging of five measurements yielding a respective standard deviation $<0.1\,\%$.[27]

$$Q_S = Q_R \frac{I_S}{I_R}\frac{OD_R}{OD_S}\frac{{n_S}^2}{{n_R}^2} \quad (1)$$

General procedure for the insertion–coupling–isomerization–cycloaddition sequence to spirobenzofuranones 3: In a heat gun dried and nitrogen filled Schlenk crew cap vessel phenylpropynoic acid 2-iodophenyl ester (**1**) (348 mg, 1.00 mmol) and propargyl allyl ether **2** (1.10 mmol) were dissolved in toluene (3 mL) and triethylamine (3 mL) (for experimental details see Table 8). The solution was deaerated with a weak stream of nitrogen through a cannula for 5 min. Then, [$PdCl_2(PPh_3)_2$] (35 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added and the mixture was stirred for 1 h at RT. The vessel was placed in the reactor[28] and the reaction mixture was heated to reflux temperature for 72 h. Then, the reaction mixture was cooled to room temp, the solvents were removed in vacuo and the residue was purified by chromatography on silica gel (hexanes/ethyl acetate). Further purification was achieved by recrystallization from pentane/ether and the spirobenzofuranones **3** were obtained as analytically pure crystalline solids.

***3H*-Benzofuran-2-one-3-spiro-5′-4′-(6′-phenyl-3′,3a′,4′,5′-tetrahydroisobenzofuran-1′-yl)-benzonitrile (3a)**: According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3a** was obtained as intensively yellow-blue fluorescent crystals. M.p. 241 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=2.19$ (dd, $J=12.2$ Hz, 1H), 2.37 (t, $J=12.3$ Hz, 1H), 3.93 (m, 1H), 4.01 (dd, $J=8.1$, 13.0 Hz, 1H), 4.78 (t, $J=8.3$ Hz, 1H), 6.85–6.87 (m, 2H), 7.11 (s, 1H), 7.15–7.20 (m, 4H), 7.33 (dd, $J=0.8$,

Table 6. Crystal data and structure refinements for **3a–c**, **e**, and **h**.

Compound	**3a**	**3b**	**3c**	**3e**	**3h**
Empirical formula	$C_{28}H_{19}NO_3$	$C_{27}H_{19}FO_3$	$C_{28}H_{22}O_4$	$C_{29}H_{25}NO_3$	$C_{30}H_{26}O_4$
F_w	417.44	410.42	422.46	435.50	450.51
T [K]	200(2)	200(2)	200(2)	100(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	4	4	2
unit cell dimensions					
a [Å]	12.1661(8)	11.9124(2)	12.5638(3)	12.2819(15)	7.1775(1)
b [Å]	11.5630(7)	14.3534(2)	11.8966(2)	12.2233(15)	8.0619(1)
c [Å]	14.5855(10)	12.6520(2)	14.2975(3)	15.0269(19)	20.0116(1)
α [°]	90	90	90	90	81.414(1)
β [°]	92.381(1)	112.350(1)	92.121(1)	92.821(2)	84.705(1)
γ [°]	90	90	90	90	81.149(1)
V [Å^3]	050.1(2)	2000.77(5)	2135.53(8)	2253.2(5)	1128.49(2)
ρ_{calcd} [g cm^{-3}]	1.35	1.36	1.31	1.28	1.33
μ [mm^{-1}]	0.09	0.09	0.09	0.08	0.09
crystal size [mm^3]	0.40×0.34×0.29	0.32×0.26×0.23	0.40×0.30×0.26	0.30×0.30×0.16	0.50×0.24×0.22
θ range for data collection [°]	2.1 to 27.5	2.0 to 27.5	2.2 to 27.5	2.1 to 28.3	1.0 to 27.5
index ranges	$-11\le h\le 15$ $-11\le k\le 13$ $-14\le l\le 18$	$-15\le h\le 25$ $-18\le k\le 18$ $-16\le l\le 16$	$-16\le h\le 16$ $-15\le k\le 15$ $-18\le l\le 18$	$-16\le h\le 13$ $-14\le k\le 16$ $-19\le l\le 20$	$-9\le h\le 9$ $-10\le k\le 10$ $-25\le l\le 25$
reflections collected	6776	20352	21703	16528	10926
independent reflections	4418 (R-(int) = 0.0192)	4585 (R-(int) = 0.0330)	4877 (R-(int) = 0.0264)	5596 (R-(int) = 0.0316)	5115 (R-(int) = 0.0203)
obsd reflections	3200 ($I>2\sigma(I)$)	3304 ($I>2\sigma(I)$)	4012 ($I>2\sigma(I)$)	4548 ($I>2\sigma(I)$)	4140 ($I>2\sigma(I)$)
absorption correction	semiempirical from equivalents				
max. and min. transmission	0.97 and 0.97	0.98 and 0.97	0.98 and 0.97	0.99 and 0.98	0.98 and 0.96
refinement method	full-matrix least-squares on F^2				
data/restraints/parameters	4418/0/289	4585/3/289	4877/0/290	5596/0/398	5115/0/310
GoF on F^2	1.03	1.02	1.02	1.03	1.01
final R indices ($I>2\sigma(I)$)					
$R1$	0.040	0.043	0.037	0.041	0.040
$wR2$	0.090	0.098	0.088	0.108	0.096

7.6 Hz, 1H), 7.40–7.43 (m, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.78 ppm (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 38.3 (CH), 38.6 (CH_2), 53.3 (C_{quat}), 74.6 (CH_2), 111.4 (CH), 112.1 (C_{quat}), 113.7 (C_{quat}), 118.6 (C_{quat}), 122.6 (CH), 124.6 (CH), 124.7 (CH), 126.6 (CH), 127.5 (CH), 127.9 (CH), 128.6 (CH), 129.5 (CH), 132.3 (CH), 132.3 (C_{quat}), 134.8 (C_{quat}), 135.2 (C_{quat}), 139.7 (C_{quat}), 149.8 (C_{quat}), 152.4 (C_{quat}), 177.8 ppm (C_{quat}); EI MS (70 eV): m/z (%): 417 (100) [M^+], 388 (9), 312 (10), 296 (9), 259 (7), 162 (7), 130 (11); HRMS: m/z: calcd for $C_{28}H_{19}NO_3$: 417.1365; found: 417.1351; IR (KBr): $\tilde{\nu}$ = 3056 (w), 2934 (w), 2877 (w), 2226 (s), 1805 (s), 1607 (s), 1520 (m), 1474 (s), 1230 (m), 1078 (s), 1051 (s), 762 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (11000), 282 (500), 368 nm (12700 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{28}H_{19}NO_3 \cdot 0.2\,C_4H_9O$ (417.5 + 14.8): C 80.02, H 4.90, N 3.24; found: C 79.96, H 4.56, N 3.50.

3*H*-Benzofuran-2-one-3-spiro-6′-3′-(2′-fluorophenyl)-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3b): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3b** was obtained as intensively yellow fluorescent crystals. M.p. 189 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.18 (dd, J = 4.4, 12.0 Hz, 1H), 2.38 (t, J = 12.4 Hz, 1H), 3.92 (m, 1H), 4.04 (dd, J = 8.4, 12.8 Hz, 1H), 4.77 (t, J = 8.5 Hz, 1H), 6.83–6.85 (m, 2H), 6.94 (d, J = 2.4 Hz, 1H), 7.13–7.17 (m, 4H), 7.20 (dt, J = 1.0, 7.6 Hz, 2H), 7.24 (dd, J = 1.0, 5.7 Hz, 1H), 7.40 (dq, J = 1.3, 7.8 Hz, 2H), 7.44 (dd, J = 1.1, 7.6 Hz, 1H), 7.61 ppm (dt, J = 1.8, 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 37.9 (CH), 39.1 (CH_2), 53.3 (C_{quat}), 74.9 (CH_2), 111.2 (CH), 113.0 (C_{quat}), 116.2 (CH), 116.4 (CH), 118.4 (C_{quat}), 118.5 (C_{quat}), 123.4 (CH), 123.4 (CH), 124.2 (CH), 124.5 (CH), 124.9 (CH), 126.5 (CH), 126.7 (CH), 127.5 (CH), 128.1 (C_{quat}), 128.5 (CH), 129.3 (CH), 130.2 (CH), 130.2 (CH), 130.9 (CH), 131.0 (CH), 132.4 (CH), 132.8 (C_{quat}), 140.0 (C_{quat}), 147.4 (C_{quat}), 152.4 (C_{quat}), 158.4 (C_{quat}), 160.4 (C_{quat}), 178.2 ppm (C_{quat}); EI MS (70 eV): m/z (%): 410 (100) [M^+], 381 (12), 305 (12), 289 (14), 259 (6), 123 (22); HRMS: m/z: calcd for $C_{27}H_{19}FO_3$: 410.1318; found: 410.1326; IR (KBr): $\tilde{\nu}$ = 3058 (w), 2989 (w), 2935 (w), 2876 (w), 1902 (s), 1615 (m), 1596 (w), 1492 (m), 1461 (m), 1230 (m), 1051 (s), 758 (s), 590 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 282 (7900), 334 nm (23200 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{19}FO_3$ (422.5): C 79.01, H 4.67; found: C 78.86, H 4.74.

3*H*-Benzofuran-2-one-3-spiro-6′-3′-(4′-methoxyphenyl)-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3c): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3c** was obtained as intensively yellow-blue fluorescent crystals. M.p. 208 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.16 (dd, J = 4.4, 12.0 Hz, 1H), 2.32 (t, J = 12.2 Hz, 1H), 3.86 (s, 3H), 3.89 (m, 1H), 3.97 (dd, J = 8.1, 12.8 Hz, 1H), 4.73 (t, J = 8.3 Hz, 1H), 6.85–6.87 (m, 2H), 6.95 (d, J = 8.9 Hz, 2H), 7.15–7.16 (m, 4H), 7.20 (d, J = 8.0 Hz, 1H), 7.24 (dt, J = 0.6, 7.6 Hz, 1H), 7.39 (dd, J = 1.3, 7.9 Hz, Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.64 ppm (d, = 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 38.0 (CH), 38.8 (CH_2), 53.2 (C_{quat}), 55.3 (CH_3), 74.5 (CH_2), 108.9 (C_{quat}), 111.2 (CH), 114.0 (CH), 123.2 (C_{quat}), 123.7 (CH), 124.4 (CH), 124.8 (CH), 126.4 (CH), 127.3 (CH), 128.5 (CH), 128.8 (CH), 129.2 (CH), 131.5 (C_{quat}), 133.1 (C_{quat}), 140.3 (C_{quat}), 150.4 (C_{quat}), 152.4 (C_{quat}), 160.3 (C_{quat}), 178.3 ppm (C_{quat}); EI MS (70 eV): m/z (%): 422 (100) [M^+], 393 (29), 369 (6), 301 (31), 267 (26), 162 (32), 113 (52); HRMS: m/z: calcd for $C_{28}H_{22}O_4$: 422.1518;

Table 7. Crystal data and structure refinements for **5d**, **f**, **h**, **i**, **l**, **p**, and **q**.

Compound	**5d**	**5f**	**5h**	**5i**	**5l**	**5p**	**5q**
empirical formula	$C_{36}H_{30}ClNO_4S$	$C_{34}H_{29}NO_4S_2$	$C_{34}H_{34}ClNO_4S$	$C_{34}H_{35}NO_4S$	$C_{39}H_{47}NO_4SSi$	$C_{32}H_{31}NO_6S$	$C_{38}H_{33}NO_6S$
F_w	608.12	579.70	588.13	553.69	653.93	557.64	631.71
T [K]	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	2	2	4	4	2
unit cell dimensions							
a [Å]	11.2088(2)	11.424(1)	9.1393(3)	9.8926(3)	10.7040(3)	10.1932(3)	9.170(1)
b [Å]	19.9746(3)	18.584(2)	11.7505(4)	10.5896(3)	11.8527(4)	10.4287(3)	12.481(2)
c [Å]	13.8293(2)	13.719(1)	14.4395(4)	14.8590(4)	27.9972(9)	25.6579(8)	14.435(2)
α [°]	90	90	104.341(1)	70.728(1)	90	90	103.203(3)
β [°]	99.168(1)	101.869(3)	94.156(1)	79.595(1)	95.053(1)	95.436(1)	93.917(3)
γ [°]	90	90	94.205(1)	73.190(1)	90	90	98.107(3)
V [Å^3]	3056.71(8)	2850.1	1491.71(8)	1400.33(7)	3538.24(19)	2715.22(14)	1583.7(5)
ρ_{calcd} [g cm^{-3}]	1.32	1.35	1.31	1.31	1.23	1.36	1.33
μ [mm^{-1}]	0.23	0.23	0.24	0.16	0.17	0.17	0.15
crystal size [mm^3]	0.32×0.30×0.20	0.14×0.12×0.08	0.24×0.18×0.14	0.30×0.16×0.10	0.24×0.16×0.10	0.22×0.18×0.12	0.31×0.15×0.12
θ range for data collection [°]	1.8 to 27.5	1.9 to 23.3	1.8 to 27.5	2.1 to 27.5	1.5 to 24.4	1.6 to 25.4	1.5 to 24.1
index ranges	$-14\le h\le 14$	$-12\le h\le 12$	$-11\le h\le 11$	$-12\le h\le 12$	$-12\le h$ 12	$-12\le h\le 12$	$-10\le h\le 10$
	$-25\le k\le 25$	$-20\le k\le 20$	$-15\le k\le 15$	$-13\le k\le 13$	$-13\le k\le 13$	$-12\le k\le 12$	$-14\le k\le 14$
	$-17\le l\le 17$	$-15\le l\le 15$	$-18\le l\le 18$	$-19\le l\le 19$	$-32\le l\le 32$	$-30\le l\le 30$	$-16\le l\le 16$
reflns collected	31600	19052	15673	14660	28571	23583	11956
independent reflns	7008 (R-(int) = 0.0379)	4057 (R-(int) = 0.0807)	6786 (R-(int) = 0.0406)	6372 (R-(int) = 0.0336)	5842 (R-(int) = 0.0638)	4979 (R-(int) = 0.0560)	5038 (R-(int) = 0.0246)
obsd reflns	2138 ($I>2\sigma(I)$)	3697 ($I>2\sigma(I)$)	4376 ($I>2\sigma(I)$)	4392 ($I>2\sigma(I)$)	3955 ($I>2\sigma(I)$)	3401 ($I>2\sigma(I)$)	3861 ($I>2\sigma(I)$)
absorption correction	semiempirical from equivalents						
max. and min. transmission	0.95 and 0.93	0.98 and 0.97	0.97 and 0.95	0.98 and 0.95	0.98 and 0.96	0.98 and 0.96	0.98 and 0.95
refinement method	full-matrix least-squares on F^2						
data/restraints/parameters	7008/0/391	4057/0/368	6786/2/383	6372/0/365	5842/0/424	4979/0/367	5038/0/419
GoF on F^2	1.01	1.34	1.00	1.01	1.01	1.01	1.03
final R indices ($I>2\sigma(I)$)							
$R1$	0.038	0.112	0.044	0.042	0.041	0.039	0.040
$wR2$	0.094	0.199	0.094	0.093	0.093	0.082	0.097
largest diff. peak and hole [e Å^{-3}]	0.25 and −0.38	0.68 and −0.50	0.35 and −0.36	0.24 and −0.42	0.25 and −0.36	0.22 and −0.27	0.22 and −0.23

Table 8. Experimental details of the synthesis of spirobenzofuranones **3**.

Entry	Propargyl allyl ether **2** [mg] ([mmol])	Spirobenzofuranones **3** (Yield [%])
1	217 (1.10) of **2a**	213 (51) of **3a**
2	209 (1.10) of **2b**	211 (50) of **3b**
3	222 (1.10) of **2c**	279 (66) of **3c**
4	194 (1.10) of **2d**	201 (46) of **3d**
5	237 (1.10) of **2e**	139 (32) of **3e**
6	253 (1.10) of **2f**	131 (29) of **3f**
7	212 (1.10) of **2g**	202 (49) of **3g**
8	253 (1.10) of **2h**	149 (33) of **3h**

found: 422.1532; IR (KBr): $\tilde{\nu}$ = 3053 (w), 2933 (w), 2872 (w), 1803 (s), 1612 (s), 1510 (m), 1474 (m), 1254 (m), 1078 (w), 1050 (s), 755 (m), 600 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (17500), 348 nm (26700 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{28}H_{22}O_4$ (422.5): C 79.60, H 5.25; found: C 79.28, H 5.23.

3*H*-Benzofuran-2-one-3-spiro-6′-3′-(4′-ethoxyphenyl)-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3d): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3d** was obtained as intensively yellow fluorescent crystals. M.p. 198 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.44 (t, J = 7.9 Hz, 3H), 2.15 (dd, J = 4.3, 12.0 Hz, 1H), 2.32 (t, J = 12.1 Hz, 1H), 3.87 (m, 1H), 3.96 (dd, J = 8.2, 12.8 Hz, 1H), 4.08 (q, J = 6.9 Hz, 2H), 4.72 (t, J = 8.2 Hz, 1H), 6.85–6.87 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 7.15–7.16 (m, 4H), 7.20 (d, J = 8.0 Hz, 1H), 7.24 (dt, J = 0.7, 7.6 Hz, 1H), 7.39 (dd, J = 1.1, 7.8 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.63 ppm (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.8 (CH_3), 38.0 (CH), 38.8 (CH_2), 53.2 (C_{quat}), 63.5 (CH_2), 74.4 (CH_2), 108.9 (C_{quat}), 111.2 (CH), 114.6 (CH), 123.0 (C_{quat}), 123.8 (CH), 124.4 (CH), 124.9 (CH), 162.4 (CH), 127.3 (CH), 128.5 (CH), 128.8 (CH), 129.2 (CH), 131.4 (C_{quat}), 133.1 (C_{quat}), 140.3 (C_{quat}), 152.3 (C_{quat}), 152.5 (C_{quat}), 159.7 (C_{quat}), 178.3 ppm (C_{quat}); EI MS (70 eV): m/z (%): 436 (100) [M^+], 408 (8), 407 (18), 311 (11), 315 (17), 287 (8), 149(13); HRMS: m/z: calcd for $C_{29}H_{24}O_4$: 436.1675; found: 436.1660; IR (KBr): $\tilde{\nu}$ = 3053 (w), 2981 (w), 2934 (w), 2873 (w), 1803 (s), 1610 (s), 1509 (m), 1474 (m), 1252 (m), 1231 (w), 1078 (w), 1049 (s), 756 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (15600), 348 nm (23400 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{29}H_{24}O_4$ (436.5): C 79.80, H 5.54; found: C 79.76, H 5.55.

3*H*-Benzofuran-2-one-3-spiro-5′-dimethyl-[4′-(6′-phenyl-3′,3a′,4′,5′-tetrahydroisobenzofuran-1′-yl)phenyl]amine (3e): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3e** was obtained as intensive yellow crystals. M.p. 205 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.14 (dd, J = 12.0 Hz, 1H), 2.30 (t, J = 12.1 Hz, 1H), 3.03 (s, 6H), 3.68 (m, J = 4.4 Hz, 1H), 3.94 (dd, J = 8.0, 12.7 Hz, 1H), 4.70 (t,

J=8.1 Hz, 1H), 6.74 (d, J=8.4 Hz, 2H), 6.82–6.88 (m, 2H), 7.13–7.16 (m, 3H), 7.19–7.21 (m, 2H), 7.23 (dt, J=1.0, 7.6 Hz, J=1.0 Hz, 1H), 7.40 (dt, J=1.4, 7.8 Hz, 2H), 7.43 ppm (dd, J=1.0, 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=37.9 (CH_3), 38.9 (CH_2), 40.2 (CH), 53.1 (C_{quat}), 74.3 (CH_2), 107.5 (C_{quat}), 111.1 (CH), 111.8 (CH), 124.3 (CH), 124.4 (CH), 124.9 (CH), 126.3 (CH), 127.1 (CH), 128.5 (CH), 128.5 (CH), 129.1 (CH), 130.0 (C_{quat}), 133.4 (C_{quat}), 140.6 (C_{quat}), 150.8 (C_{quat}), 152.3 (C_{quat}), 153.4 (C_{quat}), 178.5 ppm (C_{quat}); EI MS (70 eV): m/z (%): 435 (100) [M^+], 407 (11), 406 (32), 330 (7), 314 (9), 267 (8), 236 (8), 217 (10), 162 (21), 113 (15); HRMS: m/z: calcd for $C_{29}H_{25}NO_3$: 435.1834; found: 435.1830; IR (KBr): $\tilde{\nu}$=3054 (w), 2985 (w), 2931 (w), 2875 (w), 1803 (s), 1610 (s), 1512 (m), 1475 (m), 1373 (m), 1230 (w), 1053 (m), 760 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε)=286 (11400), 374 nm (21200 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{29}H_{25}NO_3 \cdot 0.2\,C_4H_9O$ (435.5 + 14.9): C 79.48, H 6.04, N 3.11; found: C 79.18, H 5.73, N 3.34.

3*H*-Benzofuran-2-one-3-spiro-6′-3′-(4′-ethoxyphenyl)-7′-methyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3f): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3f** was obtained as yellow fluorescent crystals. M.p. 206 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.68 (d, J=6.6 Hz, 3H), 1.44 (t, J=7.1 Hz, 3H), 2.49 (dq, J=6.9, 12.5 Hz, 1H), 3.57 (dt, J=8.9, 12.4 Hz, 1H), 3.97 (dd, J=8.4, 12.5 Hz, 1H), 4.07 (q, J=6.8 Hz, 2H), 4.70 (t, J=8.5 Hz, 1H), 6.82–6.86 (m, 2H), 6.93 (d, J=8.8 Hz, 2H), 7.15–7.22 (m, 5H), 7.25–7.28 (m, 1H), 7.35–7.44 (m, 2H), 7.61 pppm (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.0 (CH_3), 14.7 (CH_3), 42.5 (CH), 44.1 (CH), 58.6 (C_{quat}), 63.5 (CH_2), 74.0 (CH_2), 109.1 (C_{quat}), 110.8 (CH), 114.5 (CH), 114.5 (CH), 123.1 (C_{quat}), 123.4 (CH), 124.5 (CH), 125.5 (CH), 126.8 (CH), 127.3 (CH), 128.4 (CH), 128.7 (CH), 129.3 (CH), 130.0 (C_{quat}), 133.4 (C_{quat}), 140.7 (C_{quat}), 152.3 (C_{quat}), 153.1 (C_{quat}), 159.6 (C_{quat}), 178.1 ppm (C_{quat}); EI MS (70 eV): m/z (%): 450 (100) [M^+], 407 (9), 301 (17), 194 (8), 149 (21), 121 (21); IR (KBr): $\tilde{\nu}$=3053 (w), 2981 (w), 2934 (w), 2872 (w), 1803 (s), 1610 (s), 1596 (w), 1509 (m), 1475 (m), 1252 (m), 1231 (m), 1078 (m), 1049 (s), 755 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε)=256 (15100), 348 nm (23000 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{30}H_{26}O_4$ (450.5): C 79.98, H 5.82; found: C 79.80, H 5.54.

3*H*-Benzofuran-2-one-3-spiro-6′-7′-methyl-5′-phenyl-3′-thien-2′-yl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3g): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3g** was obtained as deep yellow fluorescent crystals. M.p. 204 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ=0.68 (d, J=6.7 Hz, 1H), 2.52 (dq, J=6.9, 12.3 Hz, 1H), 3.56 (dt, J=8.7, 12.4 Hz, 1H), 3.99 (dd, J=8.5, 12.6 Hz, 1H), 4.71 (t, J=8.5 Hz, 1H), 6.85–6.87 (m, 2H), 7.10 (dd, J=3.7, 5.0 Hz, 1H), 7.14–7.17 (m, 5H), 7.24 (dd, J=0.8, 7.6 Hz, 1H), 7.33 (dd, J=1.1, 7.5 Hz, 1H), 7.39–7.41 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=14.0 (CH), 42.6 (CH), 44.0 (CH), 58.7 (C_{quat}), 74.4 (CH_2), 110.3 (C_{quat}), 110.9 (CH), 122.7 (CH), 124.6 (CH), 125.4 (CH), 126.4 (CH), 126.7 (CH), 126.8 (CH), 127.5 (CH), 127.5 (CH), 128.5 (CH), 129.5 (CH), 129.7 (C_{quat}), 132.6 (C_{quat}), 134.6 (C_{quat}), 140.4 (C_{quat}), 146.8 (C_{quat}), 153.1 (C_{quat}), 177.9 ppm (C_{quat}); EI MS (70 eV): m/z (%): 412 (100) [M^+], 369 (7), 317 (5), 301 (16), 291 (5), 194 (7), 150 (11), 113 (10), 111 (23); HRMS: m/z: calcd for $C_{26}H_{20}O_3S$: 412.1133; found: 412.1119; IR (KBr): $\tilde{\nu}$=2963 (w), 2871 (w), 1803 (s), 1617 (s), 1460 (m), 1229 (w), 1054 (m), 1031 (w), 759 (m), 704 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε)=260 (13900), 358 nm (21100 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{26}H_{20}O_3S$ (412.5): C 75.70, H 4.89, S 7.77; found: C 75.77, H 4.91, S 7.74.

3*H*-Benzofuran-2-one-3-spiro-6′-3′-(4′-methoxyphenyl)-7′,7′-dimethyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (3h): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 5:1) and recrystallization from diethyl ether/pentane spirobenzofuranone **3h** was obtained as yellow-blue fluorescent crystals. M.p. 199 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ=0.72 (s, 3H), 1.28 (s, 3H), 3.86 (s, 3H), 3.94 (dd, J=8.7, 12.4 Hz, 1H), 4.23 (dd, J=8.7, 12.4 Hz, 1H), 4.51 (dd, J=8.9, 9.6 Hz, 1H), 6.83–6.85 (m, 2H), 6.96 (d, J=9.0 Hz, 2H), 7.05 (s, 1H), 7.16–7.19 (m, 4H), 7.23 (dt, J=1.0, 7.6 Hz, 1H), 7.34 (dd, J=1.3, 7.6 Hz, 1H), 7.40 (dt, J=1.3, 7.6 Hz, 1H), 7.66 ppm (d, J=8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=16.6 (CH_3), 22.5 (CH_3), 39.4 (C_{quat}), 47.7 (CH), 55.3 (CH_3), 61.8 (C_{quat}), 70.1 (CH_2), 108.1 (C_{quat}), 110.5 (CH), 114.0 (CH), 122.6 (CH), 123.3 (C_{quat}), 124.1 (CH), 126.0 (CH), 126.2 (CH), 127.2 (CH), 128.5 (CH), 128.8 (CH), 129.2 (CH), 131.7 (C_{quat}), 132.9 (C_{quat}), 141.2 (C_{quat}), 153.0 (C_{quat}), 160.3 (C_{quat}), 175.6 ppm (C_{quat}); EI MS (70 eV): m/z (%): 450 (100) [M^+], 381 (5), 369 (5), 315 (11), 267 (6), 247 (10), 162 (11), 135 (24), 113 (10); HRMS: m/z: calcd for $C_{30}H_{26}O_4$: 450.1831; found: 450.1824. IR (KBr): $\tilde{\nu}$=3053 (w), 2954 (w), 2894 (w), 2837 (w), 1803 (s), 1609 (s), 1595 (w), 1511 (m), 1474 (m), 1255 (s), 1080 (m), 1046 (s), 757 (m), 699 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε)=256 (17000), 350 nm (35000 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{30}H_{26}O_4$ (450.5): C 79.98, H 5.82; found: C 79.70, H 5.72.

General procedure for the insertion–coupling–isomerization–cycloaddition sequence to spiroindolones 5: In an heat gun dried and nitrogen filled Schlenk crew cap vessel alkynyoyl iodo anilide **4** (1.50 mmol) and propargyl allyl ether **2** (1.65 mmol) were dissolved in butyronitrile (6 mL) and triethylamine (6 mL) (for experimental details see Table 9). The solution was deaerated with a weak stream of nitrogen through a cannula for 5 min. Then, [$PdCl_2(PPh_3)_2$] (53 mg, 0.08 mmol) and CuI (8 mg, 0.04 mmol) were added and the mixture was stirred for 1 h at RT. The vessel was placed in the reactor[28] and the reaction mixture was heated to reflux temperature for 16 or 72 h. Then, the reaction mixture was cooled to RT, the solvents were removed in vacuo and the residue was purified by chromatography on silica gel (hexanes/ethyl acetate). Further purification was achieved by recrystallization from pentane/ether

Table 9. Experimental details of the synthesis of spiroindolones **5**.

Entry	Alkynoyl iodo anilide **4** [mg] ([mmol])	Propargyl allyl ether **2** [mg] ([mmol])	Spiroindolones **5** [mg] (Yield [%])[b]
1[a]	752 (1.50) of **4a**	334 (1.65) of **2c**	698 (81%) of **5a**
2[a]	752 (1.50) of **4a**	317 (1.65) of **2g**	612 (72) of **5b**
3[b]	752 (1.50) of **4a**	499 (1.65) of **2i**	641 (71) of **5c**
4[a]	752 (1.50) of **4a**	387 (1.65) of **2j**	785 (86) of **5d**
5[a]	752 (1.50) of **4a**	330 (1.65) of **2k**	740 (86) of **5e**
6[a]	752 (1.50) of **4a**	340 (1.65) of **2l**	627 (72) of **5f**
7[a]	752 (1.50) of **4a**	380 (1.65) of **2h**	712 (79) of **5g**
8[a]	722 (1.50) of **4b**	387 (1.65) of **2j**	715 (81) of **5h**
9[a]	722 (1.50) of **4b**	330 (1.65) of **2k**	658 (79) of **5i**
10[a]	722 (1.50) of **4b**	380 (1.65) of **2h**	673 (77) of **5j**
11[a]	872 (1.50) of **4c**	387 (1.65) of **2j**	811 (79) of **5k**
12[a]	872 (1.50) of **4c**	330 (1.65) of **2k**	831 (85) of **5l**
13[a]	872 (1.50) of **4c**	380 (1.65) of **2h**	789 (77) of **5m**
14[b]	683 (1.50) of **4d**	387 (1.65) of **2j**	450 (53) of **5n**
15[b]	683 (1.50) of **4d**	330 (1.65) of **2k**	500 (63) of **5o**
16[b]	683 (1.50) of **4d**	380 (1.65) of **2h**	510 (63) of **5p**
17[b]	797 (1.50) of **4e**	499 (1.65) of **2i**	625 (66) of **5q**
18[b]	797 (1.50) of **4e**	387 (1.65) of **2j**	833 (87) of **5r**
19[b]	797 (1.50) of **4e**	330 (1.65) of **2k**	797 (88) of **5s**
20[b]	955 (1.50) of **4f**	387 (1.65) of **2j**	647 (58) of **5t**
21[b]	884 (1.50) of **4g**	330 (1.65) of **2k**	725 (73) of **5u**
22[a]	584 (1.50) of **4h**	330 (1.65) of **2k**	318 (46) of **5v**
23[a]	542 (1.50) of **4i**	330 (1.65) of **2k**	247 (38) of **5w**

[a] Heating for 72 h. [b]Heating for 16 h.

and the spiroindolones **5** were obtained as analytically pure, yellow fluorescent solids.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-methoxyphenyl)-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5a): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5a** was obtained as a yellow fluorescent solid. M.p. 179 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.00 (dd, J = 4.4, 11.8 Hz, 1H), 2.17 (t, J = 12.1 Hz, 1H), 2.43 (s, 3H), 3.79 (m, 1H), 3.84 (s, 3H), 3.89 (m, 1H), 4.67 (t, J = 8.1 Hz, 1H), 6.51 (d, J = 8.1 Hz, 2H), 6.75 (t, J = 7.4 Hz, 2H), 6.93 (dd, J = 2.2, 8.8 Hz, 3H), 7.10 (s, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 7.7 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.43 (td, J = 0.8, 8.1 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 8.02 ppm (d, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7 (CH_3), 37.9 (CH), 38.8 (CH_2), 54.6 (C_{quat}), 55.3 (CH_3), 74.5 (CH_2), 109.1 (C_{quat}), 113.8 (CH), 114.0 (CH), 123.3 (C_{quat}), 123.9 (CH), 124.6 (CH), 124.9 (CH), 125.7 (CH), 126.2 (CH), 127.5 (CH), 127.9 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 131.8 (C_{quat}), 133.3 (C_{quat}), 135.0 (C_{quat}), 137.9 (C_{quat}), 140.2 (C_{quat}), 145.2 (C_{quat}), 152.3 (C_{quat}), 160.2 (C_{quat}), 177.1 ppm (C_{quat}); EI MS (70 eV): m/z (%): 575 (100) [M^+], 420 (28) [$M^+-SO_2C_6H_4CH_3$], 369 (11), 317 (9); HRMS: m/z: calcd for $C_{35}H_{29}NO_5S$: 575.1766; found: 575.1755; IR (KBr): $\tilde{\nu}$ = 2934 (w), 1763 (s), 1604 (s), 1510 (m), 1376 (m), 1175 (s), 1070 (s), 759 (m), 581 (m), 566 cm^{-1} (w); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (20000), 350 nm (24900 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{35}H_{29}NO_5S{\cdot}0.5H_2O$ (575.7 + 9.0): C 71.90, H 5.17, N 2.40; found: C 72.10, H 5.31, N 2.47.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-methoxyphenyl)-7′-methyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5b): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5b** was obtained as a yellow fluorescent solid. M.p. 184 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.53 (d, J = 6.7 Hz, 3H), 2.42 (s, 3H), 2.40–2.44 (m, 1H), 3.52 (dt, J = 8.7, 12.4 Hz, 1H), 3.93 (dd, J = 8.5, 12.8 Hz, 1H), 4.65 (t, J = 8.5 Hz, 1H), 6.55 (m, 2H), 6.80 (dd, J = 7.7, 8.1 Hz, 2H), 6.96 (m, 1H), 7.04 (s, 1H), 7.07 (dd, J = 3.8, 5.0 Hz, 1H), 7.17 (m, 1H), 7.19 (m, 1H), 7.25 (dd, J = 1.0, 7.4 Hz, 1H), 7.28 (m, 1H), 7.36 (m, 2H), 7.43 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 8.00 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3 (CH_3), 21.7 (CH_3), 43.0 (CH), 43.9 (CH), 59.3 (C_{quat}), 74.5 (CH_2), 110.3 (C_{quat}), 113.4 (CH), 123.0 (CH), 124.9 (CH), 125.8 (CH), 126.3 (CH), 126.6 (CH), 126.6 (CH), 126.7 (CH), 127.4 (CH), 127.8 (CH), 128.1 (CH), 129.2 (CH), 129.6 (CH), 130.0 (C_{quat}), 132.7 (C_{quat}), 134.9 (C_{quat}), 135.2 (C_{quat}), 139.3 (C_{quat}), 140.3 (C_{quat}), 145.2 (C_{quat}), 146. 6 (C_{quat}), 176.7 ppm (C_{quat}); EI MS (70 eV): m/z (%): 565 (100) [M^+], 411 (28) [$M^+-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{33}H_{27}NO_4S_2$: 565.1381; found: 565.1390; IR (KBr): $\tilde{\nu}$ = 3125 (w), 3015 (w), 1758 (s), 1599 (s), 1460 (s), 1377 (s), 1234 (m), 1212 (w), 1190 (w), 1178 (m), 1092 (s), 759 (s), 702 (s), 569 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (20000), 358 nm (20500 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{33}H_{27}NO_4S_2$ (565.7): C 70.06, H 4.81, N 2.48; found: C 69.60, H 4.81, N 2.60.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-formylphenyl)-7′-methyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5c): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5c** was obtained as a yellow fluorescent solid. M.p. 199 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.53 (d, J = 6.7 Hz, 3H), 2.42 (s, 3H), 2.40–2.44 (m, 1H), 3.52 (dt, J = 8.7, 12.4 Hz, 1H), 3.93 (dd, J = 8.5, 12.8 Hz, 1H), 4.65 (t, J = 8.5 Hz, 1H), 6.55 (m, 2H), 6.80 (dd, J = 7.7, 8.1 Hz, 2H), 6.96 (m, 1H), 7.04 (s, 1H), 7.07 (dd, J = 3.8, 5.0 Hz, 1H), 7.17 (m, 1H), 7.19 (m, 1H), 7.25 (dd, J = 1.0, 7.4 Hz, 1H), 7.28 (m, 1H), 7.36 (m, 2H), 7.43 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 8.00 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3 (CH_3), 21.7 (CH_3), 43.0 (CH), 43.9 (CH), 59.3 (C_{quat}), 74.5 (CH_2), 110.3 (C_{quat}), 113.4 (CH), 123.0 (CH), 124.9 (CH), 125.8 (CH), 126.3 (CH), 126.6 (CH), 126.6 (CH), 126.7 (CH), 127.4 (CH), 127.8 (CH), 128.1 (CH), 129.2 (CH), 129.6 (CH), 130.0 (C_{quat}), 132.7 (C_{quat}), 134.9 (C_{quat}), 135.2 (C_{quat}), 139.3 (C_{quat}), 140.3 (C_{quat}), 145.2 (C_{quat}), 146. 6 (C_{quat}), 176.7 ppm (C_{quat}); EI MS (70 eV): m/z (%): 565 (100) [M^+], 411 (28) [$M^+-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{33}H_{27}NO_4S_2$: 565.1381; found: 565.1390; IR (KBr): $\tilde{\nu}$ = 3125 (w), 3015 (w), 1758 (s), 1599 (s), 1460 (s), 1377 (s), 1234 (m), 1212 (w), 1190 (w), 1178 (m), 1092 (s), 759 (s), 702 (s), 569 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (20000), 358 nm (20500 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{33}H_{27}NO_4S_2$ (565.7): C 70.06, H 4.81, N 2.48; found: C 69.60, H 4.81, N 2.60.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-chlorophenyl)-7′,7′-dimethyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5d): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF spiroindolone **5d** was obtained as yellow fluorescent crystals. M.p. 254 °C: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.72 (s, 3H), 1.20 (s, 3H), 2.43 (s, 3H), 3.90 (dd, J = 9.0, 12.4 Hz, 1H), 4.21 (dd, J = 9.0, 12.4 Hz, 1H), 4.52 (m, 1H), 6.43 (m, 2H), 6.68 (dd, J = 7.7, 8.0 Hz, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.94 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.22 (dd, J = 1.0, 7.4 Hz, 1H), 7.26 (m, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.43 (m, 1H), 7.60 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 8.03 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 40.0 (C_{quat}), 47.8 (CH), 62.3 (C_{quat}), 70.2 (CH_2), 110.1 (C_{quat}), 112.9 (CH), 122.4 (CH), 124.5 (CH), 125.9 (CH), 126.2 (CH), 126.3 (CH), 127.9 (CH), 128.1 (CH), 128.5 (CH), 128.8 (CH), 129.2 (CH), 129.6 (CH), 131.5 (C_{quat}), 134.8 (C_{quat}), 134.9 (C_{quat}), 134.9 (C_{quat}), 139.0 (C_{quat}), 141.0 (C_{quat}), 145.2 (C_{quat}), 151.6 (C_{quat}), 174.8 ppm (C_{quat}); EI MS (70 eV): m/z (%): 609 (45) [$M^+-{}^{37}$Cl], 607 (100) [$M^+-{}^{35}$Cl], 454 (11) [$M^+-{}^{37}$Cl$-SO_2C_6H_4CH_3$], 452 (29) [$M^+-{}^{35}$Cl$-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{36}H_{30}{}^{35}ClNO_4S$: 607.1584; found: 607.1552; IR (KBr): $\tilde{\nu}$ = 3048 (w), 2974 (m), 2895 (w), 1759 (s), 1598 (s), 1490 (s), 1460 (s), 1374 (s), 1237 (s), 1190 (m), 1178 (s), 1162 (s), 1093 (s), 1068 (s), 760 (s), 702 (m), 691 (m), 659 (m), 573 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (27000), 350 nm (22900 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{36}H_{30}ClNO_4S$ (608.2): C 71.10, H 4.97, N 2.30, Cl 5.83, S 5.2.7; found: C 71.07, H 5.02, N 2.37, Cl 5.84, S 5.27.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′,5′-diphenyl-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5e): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF spiroindolone **5e** was obtained as yellow fluorescent crystals. M.p. 219 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.73 (s, 3H), 1.21 (s, 3H), 2.44 (s, 3H), 3.91 (dd, J = 10.0, 12.4 Hz, 1H), 4.23 (dd, J = 8.7, 12.4 Hz, 1H), 4.53 (dd, J = 8.7, 9.7 Hz, 1H), 6.44 (dd, J = 1.2, 8.3 Hz, 2H), 6.68 (dd, J = 7.5, 8.2 Hz, 2H), 6.90 (tt, J = 1.1, 7.4 Hz, 2H), 7.01 (s, 1H), 7.19 (m, 2H), 7.23 (dd, J = 1.0, 7.6 Hz, 1H), 7.29 (dd, J = 1.3, 7.6 Hz, 1H), 7.34–7.45 (m, 4H), 7.67 (m, 2H), 7.85 (d, J = 8.4 Hz, 2H), 8.04 ppm (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.6 (CH_3), 21.9 (CH_3), 39.9 (C_{quat}), 47.7 (CH), 62.3 (C_{quat}), 70.2 (CH_2), 109.5 (C_{quat}), 112.8 (CH), 122.8 (CH), 124.4 (CH), 126.1 (CH), 126.2 (CH), 127.2 (CH), 127.9 (CH), 128.0 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 129.5 (CH), 129.6 (CH), 130.7 (C_{quat}), 131.6 (C_{quat}), 134.1 (C_{quat}), 134.9 (C_{quat}), 139.0 (C_{quat}), 141.1 (C_{quat}), 145.1 (C_{quat}), 152.8 (C_{quat}), 174.9 ppm (C_{quat}); EI MS (70 eV): m/z (%): 573 (100) [M^+], 418 (32) [$M^+-SO_2C_6H_4CH_3$], 267 (10), 201 (10); HRMS: m/z: calcd for $C_{36}H_{31}NO_4S$: 573.1974; found: 573.1957; IR (KBr): $\tilde{\nu}$ = 3054 (w), 2974 (w), 1758 (s), 1598 (m), 1492 (w), 1460 (s), 1376 (s), 1190 (m), 1064 (s), 760 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (27600), 348 nm (24900 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{36}H_{31}NO_4S$ (573.7): C 75.37, H 5.45, N 2.44, S 5.59; found: C 75.04, H 5.33, N 2.65, S 5.63.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-7′,7′-dimethyl-5′-phenyl-3′-(2′-thienyl)-1′,6′,7′,7a′-tetrahydroisobenzofuran (5f): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF spiroindolone **5f** was obtained as yellow fluorescent crystals. M.p. 169 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (s, 3H), 1.20 (s, 3H), 2.44 (s, 3H), 3.87 (dd, J = 10.0, 12.0 Hz, 1H), 4.22 (dd, J = 8.7, 12.3 Hz, 1H), 4.51(m, 1H), 6.46 (dd, J = 1.1, 8.3 Hz, 2H), 6.69 (dd, J = 7.5, 8.1 Hz, 2H), 6.90 (t, J = 7.4 Hz, 1H), 7.07 (s, 1H), 7.09 (dd, J = 3.7, 5.0 Hz, 1H), 7.19–7.26 (m, 4H), 7.38 (m, 2H), 7.43 (m, 1H), 7.85 (d, J = 8.4 Hz, 2H), 8.03 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 40.2 (C_{quat}), 47.7 (CH), 62.3 (C_{quat}), 70.6 (CH_2), 109.2 (C_{quat}), 112.8 (CH), 122.3 (CH), 124.5 (CH), 125.8 (CH), 126.3 (CH), 126.3 (CH), 126.4 (CH), 126.6

(CH), 127.4 (CH), 128.0 (CH), 128.1 (CH), 129.2 (CH), 129.6 (CH), 131.5 (C_{quat}), 132.7 (C_{quat}), 134.4 (C_{quat}), 134.9 (C_{quat}), 139.0 (C_{quat}), 140.9 (C_{quat}), 145.2 (C_{quat}), 147.3 (C_{quat}), 174.8 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 579 (100) [M^+], 424 (16) [$M^+-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{34}H_{29}NO_4S_2$: 579.1538; found: 579.1511; IR (KBr): $\tilde{\nu}=3021$ (w), 1758 (s), 1624 (s), 1598 (m), 1460 (s), 1375 (s), 1237 (m), 1190 (s), 1178 (s), 1148 (m), 1092 (m), 1068 (s), 757 (s), 702 (s), 691 (m), 573 (w), 564 (s), 545 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (19600), 362 nm (18600 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{34}H_{29}NO_4S_2$ (579.7): C 70.44, H 5.04, N 2.42, S 11.06; found: C 70.10, H 5.09, N 2.46, S 11.01.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-methoxyphenyl)-7′,7′-dimethyl-5′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5g): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5g** was obtained as a yellow fluorescent solid. M.p. 223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (s, 3H), 1.20 (s, 3H), 2.44 (s, 3H), 3.84 (s, 3H), 3.88 (dd, *J* = 9.9, 11.9 Hz, 1H), 4.20 (dd, *J* = 8.7, 12.3 Hz, 1H), 4.50 (t, *J* = 9.1 Hz, 1H), 6.44 (m, 2H), 6.68 (m, 2H), 6.86–6.94 (m, 2H), 6.98 (s, 1H), 7.20 (m, 2H), 7.27 (m, 3H), 7.43 (m, 1H), 7.62 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 8.04 ppm (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.6 (CH_3), 21.9 (CH_3), 39.8 (C_{quat}), 47.7 (CH), 55.3 (CH_3), 62.2 (C_{quat}), 70.1 (CH_2), 108.0 (C_{quat}), 112.7 (CH), 114.0 (CH), 123.0 (CH), 123.4 (CH), 124.4 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.9 (CH), 128.0 (CH), 128.7 (CH), 129.0 (CH), 129.5 (C_{quat}), 131.8 (C_{quat}), 133.2 (C_{quat}), 135.0 (C_{quat}), 139.0 (C_{quat}), 141.2 (C_{quat}), 145.1 (C_{quat}), 152.9 (C_{quat}), 160.2 (C_{quat}), 175.0 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 603 (100) [M^+], 448 (27) [$M^+-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{37}H_{33}NO_5S$: 603.2079; found: 603.2087; IR (KBr): $\tilde{\nu}$ = 3115 (w), 1757 (s), 1628 (s), 1608 (s), 1511 (m), 1460 (m), 1375 (s), 1253 (s), 1190 (m), 1083 (s), 1068 (s), 758 (m), 585 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (25500), 350 nm (20900 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{37}H_{33}NO_5S$ (603.7): C 73.61, H 5.51, N 2.32, S 5.31; found: C 73.23, H 5.51, N 2.40, S 5.27.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-butyl-3′-(4′-chlorophenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5h): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF/pentane spiroindolone **5h** was obtained as yellow fluorescent crystals. M.p. 222 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.52 (t, *J* = 7.1 Hz, 3H), 0.56 (s, 3H), 0.66-.089 (m, 4H), 1.10 (s, 3H), 1.20–1.27 (m, 1H), 1.52–1.59 (m, 1H), 2.40 (s, 3H), 3.75 (t, *J* = 10.7 Hz, 1H), 4.12 (dd, *J* = 8.8, 11.9 Hz, 1H), 4.41 (m, 1H), 6.54 (s, 1H), 7.10 (m, 1H), 7.14 (dt, *J* = 1.0, 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.36 (m, 3H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.99 ppm (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 17.0 (CH_3), 21.6 (CH_3), 22.0 (CH_3), 22.1 (CH_2), 29.6 (CH_2), 33.5 (CH_2), 39.4 (C_{quat}), 48.1 (CH), 63.0 (C_{quat}), 69.5 (CH_2), 109.8 (C_{quat}), 112.8 (CH), 117.8 (CH), 124.2 (CH), 125.9 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 128.8 (CH), 129.5 (CH), 129.6 (C_{quat}), 131.3 (C_{quat}), 134.1 (C_{quat}), 135.1 (C_{quat}), 136.0 (C_{quat}), 139.2 (C_{quat}), 145.6 (C_{quat}), 148.5 (C_{quat}), 175.6 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 589 (40) [$M^+-{}^{37}Cl$], 587 (100) [$M^+-{}^{35}Cl$], 434 (12) [$M^+-{}^{37}Cl-SO_2C_6H_4CH_3$], 432 (42) [$M^+-{}^{35}Cl-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{34}H_{34}{}^{35}ClNO_4S$: 587.1897; found: 587.1904; IR (KBr): $\tilde{\nu}$ = 2959 (m), 2921 (m), 1752 (s), 1598 (m), 1490 (m), 1460 (s), 1378 (s), 1238 (m), 1190 (m), 1179 (m), 1146 (m), 1093 (m), 1065 (s), 755 (m), 690 (m), 658 (m), 571 (s), 546 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (19600), 252 (16400), 276 (7700), 332 nm (20600 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{34}H_{34}ClNO_4S$ (588.2): C 69.43, H 5.83, N 2.38, Cl 6.03, S 5.45; found: C 69.43, H 5.91, N 2.45, Cl 6.21, S 5.48.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-butyl-7′,7′-dimethyl-3′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5i): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF/pentane spiroindolone **5i** was obtained as yellow fluorescent crystals. M.p. 201 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.52 (t, *J* = 7.1 Hz, 3H), 0.56 (s, 3H), 0.69–0.87 (m, 4H), 1.11 (s, 3H), 1.21–1.26 (m, 1H), 1.56 (m, 1H), 2.40 (s, 3H), 3.76 (m, 1H), 4.13 (dd, *J* = 9.0, 11.8 Hz, 1H), 4.43 (dd, *J* = 9.0, 10.0 Hz, 1H), 6.60 (s, 1H), 7.10–7.16 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.32–7.37 (m, 2H), 7.39 (m, 2H), 7.60 (m, 2H), 7.99 ppm (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (CH_3), 17.0 (CH_3), 21.6 (CH_3), 22.1 (CH_3), 22.2 (CH_2), 29.7 (CH_2), 33.6 (CH_2), 39.5 (C_{quat}), 48.1 (CH), 63.1 (C_{quat}), 69.5 (CH_2), 109.3 (C_{quat}), 112.8 (CH), 118.3 (CH), 124.2 (CH), 125.2 (CH), 126.1 (CH), 126.9 (CH), 128.4 (CH), 128.5 (CH), 128.8 (CH), 129.6 (CH), 131.2 (C_{quat}), 131.6 (C_{quat}), 135.2 (C_{quat}), 135.3 (C_{quat}), 139.2 (C_{quat}), 145.6 (C_{quat}), 149.8 (C_{quat}), 175.8 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 553 (100) [M^+], 298 (31) [$M^+-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{34}H_{35}NO_4S$: 553.2287; found: 553.2288; IR (KBr): $\tilde{\nu}$ = 2956 (m), 2930 (m), 1752 (s), 1598 (m), 1460 (s), 1377 (s), 1237 (m), 1190 (s), 1148 (m), 1090 (s), 1062 (s), 755 (m), 571 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (16900), 362 nm (18900 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{34}H_{35}NO_4S$ (553.7): C 73.75, H 6.37, N 2.53, S 5.79; found: C 73.48, H 6.37, N 2.59, S 5.75.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-butyl-3′-(4′-methoxyphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5j): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5j** was obtained as a yellow fluorescent solid. M.p. 193 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.51 (t, *J* = 7.2 Hz, 3H), 0.55 (s, 3H), 0.69–0.85 (m, 4H), 1.10 (s, 3H), 1.22–1.28 (m, 1H), 1.53–1.59 (m, 1H), 2.34 (s, 3H), 3.74 (t, *J* = 11.0 Hz, 1H), 3.81 (s, 3H), 4.11 (dd, *J* = 8.7, 11.7 Hz, 1H), 4.40 (t, *J* = 9.7 Hz, 1H), 6.58 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.12–7.14 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.32–7.36 (m, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.99 ppm (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 16.9 (CH_3), 21.5 (CH_3), 22.0 (CH_3), 22.1 (CH_2), 29.7 (CH_2), 33.5 (CH_2), 48.0 (CH), 55.2 (CH_3), 62.9 (C_{quat}), 69.4 (CH_2), 107.6 (C_{quat}), 112.6 (CH), 113.8 (CH), 118.3 (CH), 123.8 (C_{quat}), 124.1 (CH), 126.0 (CH), 127.9 (CH), 128.2 (CH), 128.6 (CH), 129.5 (CH), 131.6 (C_{quat}), 134.3 (C_{quat}), 135.1 (C_{quat}), 139.1 (C_{quat}), 145.5 (C_{quat}), 149.6 (C_{quat}), 159.7 (C_{quat}), 175.8 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 583 (100) [M^+], 428 (49) [$M^+-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{35}H_{37}NO_5S$: 583.2392; found: 583.2371; IR (KBr): $\tilde{\nu}$ = 2956 (m), 2932 (w), 1753 (s), 1610 (m), 1599 (m), 1510 (s), 1460 (s), 1376 (s), 1300 (w), 1252 (s), 1190 (m), 1178 (s), 1065 (s), 836 (w), 572 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (20300), 324 nm (22000 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{35}H_{37}NO_5S$ (583.8): C 72.02, H 6.39, N 2.40, S 5.49; found: C 71.98, H 6.45, N 2.47, S 5.72.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-chlorophenyl)-5′-tris(isopropyl)silyl-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5k): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 4:1) and recrystallization from THF/pentane spiroindolone **5k** was obtained as yellow fluorescent crystals. M.p. 203 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (sept, *J* = 7.3 Hz, 3H), 0.56 (s, 3H), 0.67 (d, *J* = 7.3 Hz, 9H), 0.73 (d, *J* = 7.3 Hz, 9H), 0.96 (s, 3H), 2.42 (s, 3H), 4.10–4.19 (m, 2H), 4.51 (dd, *J* = 7.7, 9.5 Hz, 1H), 7.11 (dt, *J* = 1.1, 7.3 Hz, 1H), 7.21 (dd, *J* = 1.1, 7.7 Hz, 1H), 7.27 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.35–7.38 (m, 3H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 8.05 ppm (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.2 (CH), 18.7 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 40.1 (C_{quat}), 45.3 (CH), 61.9 (C_{quat}), 70.3 (CH_2), 110.6 (C_{quat}), 112.4 (CH), 123.5 (CH), 127.6 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 129.5 (CH), 129.5 (C_{quat}), 129.5 (C_{quat}), 130.2 (C_{quat}), 134.5 (C_{quat}), 135.1 (C_{quat}), 136.4 (CH), 140.2 (C_{quat}), 145.6 (C_{quat}), 150.2 (C_{quat}), 175.7 ppm (C_{quat}); EI MS (70 eV): *m/z* (%): 689 (11) [$M^+-{}^{37}Cl$], 687 (21) [$M^+-{}^{35}Cl$], 646 (48) [$M^+-{}^{37}Cl-CH(CH_3)_2$], 644 (100) [$M^+-{}^{35}Cl-CH(CH_3)_2$], 534 (4) [$M^+-{}^{37}Cl-SO_2C_6H_4CH_3$], 532 (6) [$M^+-{}^{35}Cl-SO_2C_6H_4CH_3$]; HRMS: *m/z*: calcd for $C_{34}H_{29}NO_4S_2$: 687.2605; found: 687.2606; IR (KBr): $\tilde{\nu}$ = 2945 (m), 2866 (m), 1747 (s), 1626 (s), 1600 (m), 1489 (m), 1460 (s), 1378 (s), 1238 (m), 1190 (w), 1178 (s), 1093 (m), 1081 (s), 759 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 344 nm (17700 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{34}H_{29}NO_4S_2$ (579.7): C 68.05, H 6.74, N 2.03, S 4.66; found: C 67.98, H 6.78, N 2.11, S 4.88.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-tris(isopropyl)silyl-3′-phenyl-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5l): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 4:1) and recrystallization from THF/pentane spiroindolone **5l** was

obtained as yellow fluorescent crystals. M.p. 179 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (sept, J = 7.3 Hz, 3H), 0.56 (s, 3H), 0.68 (d, J = 7.3 Hz, 9H), 0.74 (d, J = 7.3 Hz, 9H), 0.97 (s, 3H), 2.42 (s, 3H), 4.11–4.21 (m, 2H), 4.53 (dd, J = 8.1, 9.5 Hz, 1H), 7.11 (dt, J = 1.1, 7.7 Hz, 1H), 7.22 (dd, J = 1.1, 7.3 Hz, 1H), 7.31–7.40 (m, 7H), 7.62 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.1 Hz, 1H), 8.06 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.3 (CH), 18.7 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 40.1 (C_{quat}), 45.3 (CH), 61.9 (C_{quat}), 70.3 (CH_2), 110.0 (C_{quat}), 112.8 (CH), 123.3 (CH), 127.1 (CH), 127.6 (CH), 128.4 (CH), 128.4 (CH), 128.7 (CH), 129.0 (CH), 129.3 (C_{quat}), 129.5 (CH), 129.7 (C_{quat}), 131.1 (C_{quat}), 135.1 (C_{quat}), 136.9 (CH), 140.2 (C_{quat}), 145.5 (C_{quat}), 151.4 (C_{quat}), 175.8 ppm (C_{quat}); EI MS (70 eV): m/z (%): 653 (36) [M^+], 610 (100) [M^+−CH(CH_3)$_2$], 498 (7) [M^+−$SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{34}H_{29}NO_4S_2$: 653.2995; found: 653.3019; IR (KBr): $\tilde{\nu}$ = 2944 (m), 2866 (m), 1747 (s), 1626 (m), 1601 (s), 1460 (m), 1377 (s), 1237 (m), 1190 (w), 1178 (m), 1140 (m), 1084 (s), 1069 (s), 758 (m), 703 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 254 (14000), 266 (8400), 274 (6500), 388 nm (14900 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{34}H_{29}NO_4S_2$ (579.7): C 71.63, H 7.24, N 2.14, S 4.90; found: C 71.61, H 7.38, N 2.21, S 5.01.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-tris(isopropyl)silyl-3′-(4′-methoxyphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5m): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 4:1) and recrystallization from diethyl ether/pentane spiroindolone **5m** was obtained as a yellow fluorescent solid. M.p. 188 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (sept, J = 7.4 Hz, 3H), 0.54 (s, 3H), 0.68 (d, J = 7.4 Hz, 9H), 0.74 (d, J = 7.4 Hz, 9H), 0.96 (s, 3H), 2.42 (s, 3H), 3.84 (s, 3H), 4.08–4.17 (m, 2H), 4.50 (dd, J = 7.4, 8.7 Hz, 1H), 6.92 (d, J = 9.0 Hz, 2H), 7.10 (dt, J = 1.0, 7.7 Hz, 1H), 7.22 (dd, J = 7.7, 8.0 Hz, 1H), 7.30–7.32 (m, 3H), 7.35 (m, 1H), 7.56 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 8.05 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.3 (CH), 18.7 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 39.9 (C_{quat}), 45.2 (CH), 55.3 (CH_3), 61.8 (C_{quat}), 70.2 (CH_2), 108.6 (C_{quat}), 112.8 (CH), 113.8 (CH), 123.3 (CH), 123.8 (C_{quat}), 127.6 (CH), 128.0 (C_{quat}), 128.4 (CH), 128.6 (CH), 129.0 (CH), 129.5 (CH), 129.8 (C_{quat}), 135.2 (C_{quat}), 137.2 (CH), 140.2 (C_{quat}), 145.5 (C_{quat}), 151.5 (C_{quat}), 160.0 (C_{quat}), 175.9 ppm (C_{quat}); EI MS (70 eV): m/z (%): 683 (80) [M^+], 640 (100) [M^+−CH(CH_3)$_2$], 528 (12) [M^+−$SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{34}H_{29}NO_4S_2$: 683.3101; found: 683.3087; IR (KBr): $\tilde{\nu}$ = 2945 (m), 2866 (m), 1747 (s), 1626 (m), 1607 (s), 1508 (m), 1460 (m), 1377 (s), 1251 (s), 1190 (w), 1177 (s), 1140 (m), 1081 (s), 607 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 248 (16500), 336 (11800), 486 nm (400 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{34}H_{29}NO_4S_2$ (579.7): C 70.24, H 7.22, N 2.05, S 4.69; found: C 70.40, H 7.50, N 2.05, S 4.68.

1-Mesyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-chlorophenyl)-5′-(4′-methoxyphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5n): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 1:1) and recrystallization from diethyl ether/pentane spiroindolone **5n** was obtained as a yellow fluorescent solid. M.p. 219 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (s, 3H), 1.25 (s, 3H), 3.08 (s, 3H), 3.72 (s, 3H), 3.95 (dd, J = 10.1, 11.8 Hz, 1H), 4.24 (dd, J = 8.7, 12.2 Hz, 1H), 4.54 (dd, J = 8.7, 9.7 Hz, 1H), 6.69 (m, 4H), 6.95 (s, 1H), 7.26 (m, 1H), 7.36–7.41 (m, 4H), 7.62 (d, J = 8.7 Hz, 2H), 7.86 ppm (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_3), 22.1 (CH_3), 40.0 (C_{quat}), 40.9 (CH_3), 47.8 (CH), 55.2 (CH_3), 62.8 (C_{quat}), 70.1 (CH_2), 110.0 (C_{quat}), 113.0 (CH), 113.7 (CH), 121.6 (CH), 124.8 (CH), 126.3 (CH), 127.8 (CH), 128.4 (CH), 128.8 (CH), 129.2 (CH), 129.3 (C_{quat}), 131.4 (C_{quat}), 133.9 (C_{quat}), 134.5 (C_{quat}), 134.7 (C_{quat}), 138.9 (C_{quat}), 151.2 (C_{quat}), 158.9 (C_{quat}), 176.2 ppm (C_{quat}); EI MS (70 eV): m/z (%): 563 (41) [M^+−^{37}Cl], 561 (100) [M^+−^{35}Cl], 484 (16) [M^+−^{37}Cl−SO_2CH_3], (28) [M^+−^{35}Cl−SO_2CH_3]; HRMS: m/z: calcd for $C_{31}H_{28}ClNO_5S$: 561.1377; found: 563.1342; IR (KBr): $\tilde{\nu}$ = 2973 (m), 2836 (m), 1753 (s), 1602 (m), 1510 (m), 1461 (m), 1369 (s), 1246 (s), 1176 (s), 1070 (s), 968 (s), 832 (m), 765 (m), 535 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (19200), 270 (11700), 338 (21200), 352 nm (24200 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{31}H_{28}ClNO_5S$ (562.1): C 66.24, H 5.02, N 2.49, Cl 6.31, S 5.70; found: C 66.32, H 5.05, N 2.47, Cl 6.24, S 5.47.

1-Mesyl-1,3-dihydroindol-2-one-3-spiro-6′-5′-(4′-methoxyphenyl)-7′,7′-dimethyl-3′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5o): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 1:1) and recrystallization from diethyl ether/pentane spiroindolone **5o** was obtained as a yellow fluorescent solid. M.p. 205 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (s, 3H), 1.26 (s, 3H), 3.08 (s, 3H), 3.72 (s, 3H), 3.97 (dd, J = 9.9, 11.8 Hz, 1H), 4.25 (dd, J = 8.8, 12.2 Hz, 1H), 4.55 (dd, J = 8.8, 9.9 Hz, 1H), 6.70 (m, 4H), 7.02 (s, 1H), 7.21–7.29 (m, 1H), 7.38–7.43 (m, 5H), 7.70 (m, 2H), 7.86 ppm (d, J = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_3), 22.1 (CH_3), 40.0 (C_{quat}), 40.9 (CH_3), 47.8 (CH), 55.2 (CH_3), 62.8 (C_{quat}), 70.0 (CH_2), 109.4 (C_{quat}), 112.9 (CH), 113.7 (CH), 122.1 (CH), 124.7 (CH), 126.4 (CH), 127.2 (CH), 127.8 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 130.8 (C_{quat}), 131.6 (C_{quat}), 133.8 (C_{quat}), 134.1 (C_{quat}), 138.8 (C_{quat}), 152.4 (C_{quat}), 158.8 (C_{quat}), 176.3 ppm (C_{quat}); EI MS (70 eV): m/z (%): 527 (100) [M^+], 448 (21) [M^+−SO_2CH_3]; HRMS: m/z: calcd for $C_{31}H_{29}NO_5S$: 527.1766; found: 527.1756; IR (KBr): $\tilde{\nu}$ = 2973 (m), 1750 (s), 1602 (m), 1510 (m), 1460 (m), 1371 (s), 1246 (s), 1176 (s), 962 (m), 767 (m), 535 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (10300), 348 nm (21800 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{31}H_{29}NO_5S$ (527.6): C 70.57, H 5.54, N 2.65, S 6.08; found: C 70.49, H 5.53, N 2.66, S 6.08.

1-Mesyl-1,3-dihydroindol-2-one-3-spiro-6′-3′,5′-bis(4′-methoxyphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5p): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from THF spiroindolone **5p** was obtained as yellow fluorescent crystals. M.p. 187 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (s, 3H), 1.24 (s, 3H), 3.08 (s, 3H), 3.72 (s, 3H), 3.85 (s, 3H), 3.93 (t, J = 11.1 Hz, 1H), 4.22 (dd, J = 8.7, 12.1 Hz, 1H), 4.52 (t, J = 8.7 Hz, 1H), 6.69 (m, 4H), 6.94 (d, J = 8.9 Hz, 2H), 6.98 (s, 1H), 7.26 (dt, J = 0.9, 8.6 Hz, 1H), 7.38 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.85 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_3), 22.1 (CH_3), 39.8 (C_{quat}), 40.9 (CH_3), 47.7 (CH), 55.2 (CH_3), 55.3 (CH_3), 62.7 (C_{quat}), 70.0 (CH_2), 107.9 (C_{quat}), 112.9 (CH), 113.7 (CH), 114.0 (CH), 122.3 (CH), 123.5 (C_{quat}), 124.7 (CH), 126.4 (CH), 127.8 (CH), 128.7 (CH), 129.1 (CH), 131.7 (C_{quat}), 132.9 (C_{quat}), 134.3 (C_{quat}), 138.8 (C_{quat}), 152.5 (C_{quat}), 158.7 (C_{quat}), 160.2 (C_{quat}), 176.4 ppm (C_{quat}); EI MS (70 eV): m/z (%): 557 (100) [M^+], 478 (17) [M^+−SO_2CH_3]; HRMS: m/z: calcd for $C_{32}H_{31}NO_6S$: 557.1872; found: 557.1895; IR (KBr): $\tilde{\nu}$ = 2953 (m), 2837 (m), 1750 (s), 1608 (s), 1508 (s), 1370 (s), 1249 (s), 1175 (s), 969 (s), 833 (m), 536 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (21200), 352 nm (27400 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{32}H_{31}NO_6S$ (557.7): C 68.92, H 5.60, N 2.51, S 5.75; found: C 68.85, H 5.56, N 2.54, S 5.91.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-formylphenyl)-7′-methyl-5′-(4′-methoxyphenyl)-1′,6′,7′,7a′-tetrahydroisobenzofuran (5q): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 3:1) and recrystallization from diethyl ether/pentane spiroindolone **5q** was obtained as a yellow fluorescent solid. M.p. 217 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3H), 1.21 (s, 3H), 2.44 (s, 3H), 3.67 (s, 3H), 3.92 (dd, J = 9.9, 12.1 Hz, 1H), 4.23 (dd, J = 8.9, 12.1 Hz, 1H), 4.54 (t, J = 9.0 Hz, 1H), 6.23 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 8.7 Hz, 2H), 6.96 (s, 1H), 7.22 (m, 1H), 7.27 (m, 1H), 7.44 (m, 1H), 7.80–7.86 (m, 4H), 7.88–7.91 (m, 3H), 8.03 (d, J = 7.6 Hz, 2H), 10.00 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.6 (CH_3), 21.9 (CH_3), 40.1-($C_{quat.}$), 48.0 (CH), 55.0 (CH_3), 62.5 ($C_{quat.}$), 70.1 (CH_2), 112.9 (CH_2), 113.5 (CH_2), 121.0 (CH_2), 124.5 (CH_2), 126.1 (CH_2), 127.0 (CH_2), 127.4 (CH_2), 128.0 (CH_2), 129.3 (CH_2), 129.5 (CH_2), 129.8 (CH_2), 131.1 ($C_{quat.}$), 133.2 ($C_{quat.}$), 134.8 ($C_{quat.}$), 135.8 ($C_{quat.}$), 136.2 ($C_{quat.}$), 136.5 ($C_{quat.}$), 136.6 ($C_{quat.}$), 139.0 ($C_{quat.}$), 145.5 ($C_{quat.}$), 150.4 ($C_{quat.}$), 158.4 ($C_{quat.}$), 174.6 ($C_{quat.}$), 191.5 ppm (CH_2); EI MS (70 eV): m/z (%): 631 (100) [M^+], 476 (17) [M^+−$SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{38}H_{33}NO_5S$: 631.2029; found: 631.2003; IR (KBr): $\tilde{\nu}$ = 2966 (w), 1758 (s), 1699 (s), 1604 (s), 1511 (m), 1460 (s), 1376 (s), 1248 (w), 1245 (s), 1211 (m), 1178 (s), 1082 (s), 832 (m), 575 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 (24200), 292 (12800), 398 nm (20100 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{38}H_{33}NO_5S$ (631.8): C 72.25, H 5.27, N 2.22; found: C 72.32, H 5.10, N 2.40.

1-Tosyl-1,3-dihydroindol-2-one-3-spiro-6′-3′-(4′-chlorophenyl)-5′-(4′-methoxyphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5r): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 1:1) and recrystallization from diethyl ether/pentane spiroindolone **5r** was obtained as a yellow fluorescent solid. M.p. 236 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3H), 1.20 (s, 3H), 2.44 (s, 3H), 3.67 (s, 3H), 3.89 (dd, J = 10.4, 12.2 Hz, 1H), 4.20 (dd, J = 8.6, 12.2 Hz, 1H), 4.50 (dd, J = 9.1, 9.3 Hz, 1H), 6.23 (d, J = 8.7 Hz, 2H), 6.36 (d, J = 8.7 Hz, 2H), 6.87 (s, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.22 (m, 1H), 7.27 (m, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.43 (m, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 8.03 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.6 (CH_3), 22.0 (CH_3), 39.9 ($C_{quat.}$), 47.8 (CH), 55.0 (CH_3), 62.4 ($C_{quat.}$), 70.1 (CH_2), 110.2 ($C_{quat.}$), 112.8 (CH), 113.4 (CH), 121.3 (CH), 124.5 (CH), 126.2 (CH), 127.0 (CH), 128.0 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 129.5 (CH), 131.4 ($C_{quat.}$), 133.5 ($C_{quat.}$), 133.5 ($C_{quat.}$), 134.6 ($C_{quat.}$), 134.7 ($C_{quat.}$), 134.9 ($C_{quat.}$), 139.1 ($C_{quat.}$), 145.4 ($C_{quat.}$), 150.9 ($C_{quat.}$), 158.3 ($C_{quat.}$), 174.8 ppm ($C_{quat.}$); EI MS (70 eV): m/z (%): 639 (61) [$M^+-{}^{37}$Cl], 637 (100) [$M^+-{}^{35}$Cl], 484 (13) [$M^+-{}^{37}$Cl$-SO_2C_6H_4CH_3$], 482 (33) [$M^+-{}^{37}$Cl$-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{37}H_{32}{}^{35}ClNO_5S$: 637.1690; found: 637.1734; IR (KBr): $\tilde{\nu}$ = 2961 (w), 1758 (s), 1626 (s), 1601 (s), 1510 (s), 1490 (m), 1460 (s), 1376 (s), 1245 (s), 1178 (s), 1092 (m), 1069 (m), 833 (m), 660 (m), 574 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (30100), 356 nm (28500 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{37}H_{32}ClNO_5S$ (638.2): C 69.64, H 5.05, N 2.19; found: C 69.49, H 5.05, N 2.24.

1-Tosyl-1,3-dihydroindol-2-on-3-spiro-6′-5′-(4′-methoxyphenyl)-7′,7′-dimethyl-3′-phenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5s): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 2:1) and recrystallization from diethyl ether/pentane spiroindolone **5s** was obtained as a yellow fluorescent solid. M.p. 207 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3H), 1.21 (s, 3H), 2.44 (s, 3H), 3.67 (s, 3H), 3.90 (dd, J = 9.9, 12.2 Hz, 1H), 4.22 (dd, J = 8.7, 12.2 Hz, 1H), 4.52 (dd, J = 8.7, 9.9 Hz, 1H), 6.23 (d, J = 8.8 Hz, 2H), 6.38 (d, J = 8.8 Hz, 2H), 6.95 (s, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.22 (m, 1H), 7.29 (m, 1H), 7.35–7.46 (m, 4H), 7.67 (m, 2H), 7.86 (d, J = 8.4 Hz, 2H), 8.03 ppm (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3), 21.6 (CH_3), 22.0 (CH_3), 39.9 ($C_{quat.}$), 47.8 (CH), 55.0 (CH_3), 62.4 ($C_{quat.}$), 70.1 (CH_2), 109.6 ($C_{quat.}$), 112.8 (CH), 113.4 (CH), 121.7 (CH), 124.4 (CH), 126.3 (CH), 127.1 (CH), 127.2 (CH), 128.0 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 129.5 (CH), 130.9 ($C_{quat.}$), 131.6 ($C_{quat.}$), 133.6 ($C_{quat.}$), 134.0 ($C_{quat.}$), 135.0 ($C_{quat.}$), 139.0 ($C_{quat.}$), 145.3 ($C_{quat.}$), 152.2 ($C_{quat.}$), 158.2 ($C_{quat.}$), 174.9 ppm ($C_{quat.}$); EI MS (70 eV): m/z (%): 603 (100) [M^+], 448 (21) [$M^+-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{37}H_{33}NO_5S$: 603.2079; found: 603.2092; IR (KBr): $\tilde{\nu}$ = 2953 (w), 1758 (s), 1600 (s), 1510 (s), 1493 (s), 1460 (s), 1375 (s), 1285 (m), 1178 (s), 1064 (s), 833 (m), 693 (m), 575 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (26600), 352 nm (26600 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{37}H_{33}NO_5S$ (603.7): C 73.61, H 5.51, N 2.32; found: C 73.43, H 5.50, N 2.34.

1-(Toluol-4-sulfonyl)-1,3-dihydroindol-2-on-3-spiro-6′-3′-[3′-(4′-chlorphenyl)-7′,7′-dimethyl-1′,6′,7′,7a′-tetrahydroisobenzofuran-5′-yl]-10′-methyl-10H′-phenothiazin (5t): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 1:1) and recrystallization from diethyl ether/pentane spiroindolone **5t** was obtained as a green fluorescent solid. M.p. 266 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (s, 3H), 1.17 (s, 3H), 2.31 (s, 3H), 3.19 (s, 3H), 3.87 (dd, J = 12.0 Hz, J = 10.5 Hz, 1H), 4.20 (dd, J = 12.2 Hz, J = 8.7 Hz, 1H), 4.50 (dd, J = 9.5 Hz, J = 9.4 Hz, 1H), 6.08 (m, 2H), 6.55 (m, 1H), 6.73 (d, J = 8.1 Hz, 1H), 6.86 (s, 1H), 6.91 (m, 1H), 7.07 (dd, J = 7.6 Hz, J = 1.4 Hz, 1H), 7.13 (m, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.24 (m, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.43 (m, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 8.00 ppm (d, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 35.1 (CH_3), 40.0 ($C_{quat.}$), 47.8 (CH), 62.3 ($C_{quat.}$), 70.1 (CH_2), 110.0 ($C_{quat.}$), 113.0 (CH), 113.2 (CH), 113.8 (CH), 121.8 (CH), 122.5 (CH), 124.5 (CH), 124.9 (CH), 125.2 (CH), 126.2 (CH), 127.1 (CH), 127.4 (CH), 127.9 (CH), 128.4 (CH), 128.8 (CH), 129.2 (CH), 129.2 ($C_{quat.}$), 129.6 (CH), 131.1 ($C_{quat.}$), 133.8 ($C_{quat.}$), 133.8 ($C_{quat.}$), 134.7 ($C_{quat.}$), 135.3 ($C_{quat.}$), 135.3 ($C_{quat.}$), 139.1 ($C_{quat.}$), 139.1 ($C_{quat.}$), 144.3 ($C_{quat.}$), 145.0 ($C_{quat.}$), 145.2 ($C_{quat.}$), 151.3 ($C_{quat.}$), 174.6 ppm ($C_{quat.}$); FAB MS: m/z (%): 744 (63) [$M^+-{}^{37}$Cl], 742 (100) [$M^+-{}^{35}$Cl], 587 (16) [$M^+-{}^{35}$Cl$-SO_2C_6H_4CH_3$]; HRMS: m/z: calcd for $C_{43}H_{35}{}^{35}ClN_2O_4S_2$: 742.1727; found: 742.1750; IR (KBr): $\tilde{\nu}$ = 2972 (w), 2887 (w), 1758 (s), 1599 (s), 1490 (m), 1464 (s), 1374 (m), 1333 (m), 1259 (m), 1237 (m), 1189 (m), 1177 (s), 1145 (m), 1091 (s), 752 (m), 658 (m), 572 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (35500), 378 nm (20300 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{43}H_{35}ClN_2O_4S_2$ (743.4): C 69.48, H 4.75, N 3.77; found: C 69.53, H 5.04, N 3.78.

7′,7′-Dimethyl-3′,5′-diphenyl-1′,6′,7′,7′-tetrahydroisobenzofuranyl-6′-spiro-3-2-[4-(2-oxo-2,3-dihydroindol-1-sulfonyl)-phenoxy]-ethyl acetate (5u): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 1:1) and recrystallization from diethyl ether/pentane spiroindolone **5u** was obtained as a yellow fluorescent solid. M.p. 237 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (s, 3H), 1.21 (s, 3H), 2.12 (s, 3H), 3.91 (dd, J = 10.0, 12.2 Hz, 1H), 4.22 (m, 3H), 4.47 (m, 2H), 4.53 (t, J = 9.2 Hz, 1H), 6.45 (d, J = 7.5 Hz, 2H), 6.72 (t, J = 7.7 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.89 (m, 1H), 7.00 (s, 1H), 7.22 (m, 1H), 7.29 (m, 1H), 7.40 (m, 4H), 7.67 (m, 2H), 7.90 (d, J = 9.0 Hz, 2H), 8.03 ppm (d, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (CH_3), 20.8 (CH_3), 21.9 (CH_3), 39.9 ($C_{quat.}$), 47.7 (CH), 62.2 (CH_2), 62.3 ($C_{quat.}$), 66.3 (CH_2), 70.2 (CH_2), 109.5 ($C_{quat.}$), 112.8 (CH), 114.6 (CH), 122.9 (CH), 124.5 (CH), 125.9 (CH), 126.2 (CH), 126.3 (CH), 127.3 (CH), 128.1 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 130.3 (CH), 130.7 ($C_{quat.}$), 131.6 ($C_{quat.}$), 134.1 ($C_{quat.}$), 139.0 ($C_{quat.}$), 141.2 ($C_{quat.}$), 152.9 ($C_{quat.}$), 162.9 ($C_{quat.}$), 170.8 ($C_{quat.}$), 175.0 ppm ($C_{quat.}$); EI MS (70 eV): m/z (%): 661 (100) [M^+], 418 (35) [$M^+-SO_2C_6H_4O(CH_2)_2OC(O)CH_3$]; HRMS: m/z: calcd for $C_{39}H_{35}NO_7S$: 661.2134; found: 661.2126; IR (KBr): $\tilde{\nu}$ = 2946 (w), 1753 (s), 1630 (s), 1596 (s), 1495 (m), 1460 (m), 1375 (s), 1234 (s), 1172 (s), 1064 (s), 762 (m), 579 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 248 (40200), 348 nm (29300 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{39}H_{35}NO_7S$ (661.8): C 70.78, H 5.33, N 2.12; found: C 70.89, H 5.39, N 2.18.

1-Acetyl-1,3-dihydroindol-2-one-3-spiro-6′-7′,7′-dimethyl-3′,5′-diphenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5v): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 2:1) and recrystallization from diethyl ether/pentane spiroindolone **5v** was obtained as a yellow fluorescent solid. M.p. 165 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.63 (s, 3H), 1.25 (s, 3H), 2.53 (s, 3H), 3.99 (dd, J = 10.3, 12.2 Hz, 1H), 4.25 (dd, J = 8.7, 12.3 Hz, 1H), 4.54 (t, J = 9.3 Hz, 1H), 6.79 (m, 2H), 7.11 (s, 1H), 7.14–7.15 (m, 3H), 7.29 (d, J = 7.4 Hz, 1H), 7.36 (d, J = 7.0 Hz, 1H), 7.39 (d, J = 7.3 Hz, 1H), 7.41–7.46 (m, 3H), 7.71 (d, J = 7.3 Hz, 2H), 8.33 ppm (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.1 (CH_3), 22.3 (CH_3), 26.7 (CH_3), 40.0 (C_{quat}), 47.7 (CH), 62.7 (C_{quat}), 70.2 (CH_2), 109.7 (C_{quat}), 116.2 (CH), 122.8 (CH), 125.0 (CH), 125.6 (CH), 126.2 (CH), 127.1 (CH), 127.3 (CH), 128.4 (CH), 128.6 (CH), 128.9 (CH), 129.1 (CH), 130.8 (C_{quat}), 131.7 (C_{quat}), 134.7 (C_{quat}), 140.0 (C_{quat}), 141.6 (C_{quat}), 152.8 (C_{quat}), 170.8 (C_{quat}), 176.6 ppm (C_{quat}); EI MS (70 eV): m/z (%): 461 (100) [M^+], 314 (19); HRMS: m/z: calcd for $C_{31}H_{27}NO_3$: 461.1991; found: 461.1993; IR (KBr): $\tilde{\nu}$ = 2951 (w), 1763 (s), 1708 (s), 1629 (s), 1601 (m), 1463 (m), 1372 (m), 1338 (m), 1305 (m), 1278 (s), 1163 (m), 766 (s), 699 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (24800), 348 nm (21300 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{31}H_{27}NO_3$ (461.6): C 78.38, H 6.05, N 2.95; found: C 78.08, H 5.95, N 2.79.

1-Methyl-1,3-dihydroindol-2-one-3-spiro-6′-7′,7′-dimethyl-3′,5′-diphenyl-1′,6′,7′,7a′-tetrahydroisobenzofuran (5w): According to the general procedure after chromatography on silica gel (hexanes/ethyl acetate 4:1) and recrystallization from diethyl ether/pentane spiroindolone **5w** was obtained as a yellow fluorescent solid. M.p. 189 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.60 (s, 3H), 1.32 (s, 3H), 3.14 (s, 3H), 4.02 (dd, J = 9.7, 12.4 Hz, 1H), 4.26 (dd, J = 8.7, 12.4 Hz, 1H), 4.54 (dd, J = 8.7, 9.7 Hz, 1H), 6.77 (m, 2H), 6.89 (d, J = 7.7 Hz, 1H), 7.05 (s, 1H); 7.11–7.13 (m, 4H), 7.33 (d, J = 7.7 Hz, 1H), 7.35–7.39 (m, 2H), 7.42 (m, 2H), 7.72 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7 (CH_3), 22.0 (CH_3), 26.0 (CH_3), 39.0 (C_{quat}), 48.6 (CH), 62.2 (C_{quat}), 70.1 (CH_2), 107.6 (CH), 110.4 (C_{quat}), 122.1 (CH), 122.2 (CH), 125.8 (CH), 126.3 (CH), 126.8 (CH), 127.2 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 128.8 (CH), 131.0 (C_{quat}), 132.9 (C_{quat}), 135.8 (C_{quat}), 141.9 (C_{quat}), 144.0 (C_{quat}), 152.0 (C_{quat}), 176.9 ppm (C_{quat}); EI MS (70 eV): m/z (%): 433 (100) [M^+]; HRMS: m/z:

calcd for $C_{30}H_{27}NO_2$: 433.2042; found: 433.2071; IR (KBr): $\tilde{\nu}$ = 2951 (w), 1714 (s), 1627 (w), 1607 (s), 1490 (m), 1469 (m), 1371 (m), 1344 (m), 1256 (m), 1088 (s), 1067 (s), 1025 (w), 764 (s), 747 cm^{-1} (s); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (18800), 348 nm (22800 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{30}H_{27}NO_2 \cdot H_2O$ (433.6 + 18.0): C 82.43, H 6.32, N 3.20; found: C 82.44, H 6.37, N 3.26.

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