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Rhodium Catalyzed [2π + 2π + 2π]-Cycloaddition of Alkynyl-Ynamides and Carbon Disulfide to Indolo-Thiopyrane Thiones

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Abstract

The synthesis of new indoloannulated thiopyranethiones is reported. The key-step is a rhodium-catalyzed [2 + 2 + 2]-cycloaddition of alkynyl-ynamides with carbon disulfide to close the pyrrole and the thiopyranethione rings simultaneously. A violet idolothiopyrane thione or a mixture of the violet and a red isomer result from $[RhCl(C_8H_{14})_2]_2$/3BINAP catalyzed cycloadditions, the regiochemistry is controlled by the substitution pattern on the alkynyl-ynamide.

Keywords

Cycloaddition, Heterocycles, Rhodium, Sulfur, Alkyne

1. Introduction

Heteroannulated indoles like carbolines (1,2, **Figure 1**) form the core of a large group of alkaloids [1] [2] [3] [4] [5]. Many of these alkaloids possess pharmacological properties, ranging from antitumor to anxiolytic and anti-HIV activity [6]-[11]. Therefore, compounds based on these heterocyclic cores remain important targets for organic syntheses [12]-[17]. Classical methods for the synthesis of (hetero) annulated indoles are condensation reactions, e.g. Pictet-Spengler and Bischler-Napieralski. In recent times, highly successful Pd-catalyzed methods have been developed for the formation of the biaryl bond or closure of the pyrrole ring [18]-[26]. The comparably mild reaction conditions and the tolerance of a large scope of functional groups are advantages of this approach. The [2 + 2 + 2]-cycloaddition, found by Berthelot, has become a powerful tool for the synthesis of aromatics since the introduction of nickel catalysts by Reppe [27] [28] [29]. Transition-metal catalyzed [2 + 2 + 2]-cycloadditions receive continuously

growing attention, with topical focusses like polycyclic systems and stereoselective arene formation [27]-[39]. The similar cocyclization of alkynes and nitriles is a highly effective route for the synthesis of pyridines [40]-[50]. Even annulated pyridines are accessible, either from tethered diynes or cyanoalkynes [51]-[67]. Modern catalytic systems for [2 + 2 + 2]-cycloadditions are typically based on cobalt, ruthenium and rhodium, other transition metals are emerging [68]-[75]. In some cases, Lewis acid catalysis effectively initiates cycloaddition [61] [76]. As part of a project focusing on condensed heterocycles, we used rhodium and ruthenium-based catalysts for the addition of nitriles to alkynyl-ynamides [77]-[86]. These metals catalyze the simultaneous construction of the pyrrole and the pyridine ring, thus forming β- and γ-carbolines **1**,**2** (**Figure 1**). The β/γ-ratio is strongly depending on the catalyst. This strategy has been successfully applied to the synthesis of alkaloids like lavendamycin [87] [88] [89].

The [2 + 2 + 2]-co-cycloaddition methodology is not limited to alkynes with nitriles, cyclizations of alkynes with hetero-substituted nitriles, allenes, and even heterocumulenes have been performed [90]-[102]. Wakatzuki [103] reported the cobalt-catalyzed cocyclization of tolane and carbon disulfide to thiopyranthione **3** (**Figure 1**) already in 1973. This cycloaddition was followed by rare examples; Yamamoto applied Cp*RuCl(COD) as a catalyst for the cocyclization of 1,6-diynes **4** with CS_2 and Tanaka introduced $[RhCl(COD)]_2$/BINAP (**Scheme 1**) as a very efficient catalytic system for this route to thiopyranethiones **5** [104] [105] [106].

[2 + 2 + 2]-Cocyclizations of tethered diynes and heterocumulenes to form annulated heterocycles appear only occasionally in the literature [101] [102] [104] [105] [106] [107]. Recently, we could show that rhodium catalyzes the addition of CS_2 to an alkynyl-ynamide to form an indolothiopyrane thione, an unprecedented route to an almost unknown heterocyclic system [108] [109]. The intention of this communication is to extend the applicability of the [2 + 2 + 2]-cycloaddition approach with alkynyl-ynamides to the synthesis of indolo-annulated thiopyranethiones.

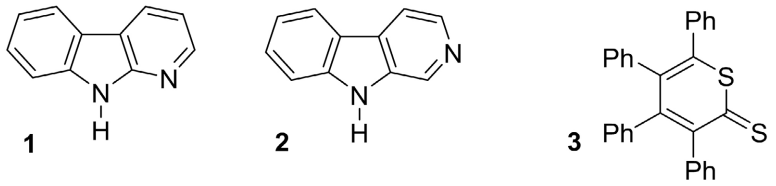
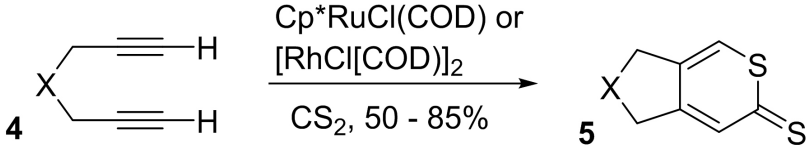


Figure 1. Heteroannulated indoles **1**,**2** and thiopyran-2-thione **3**.

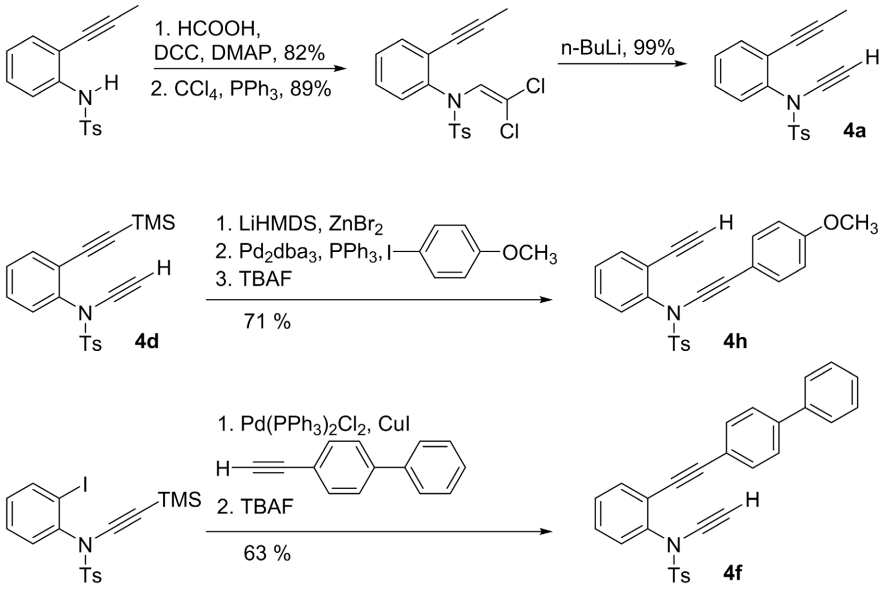


Scheme 1. [2 + 2 + 2]-cycloaddition of diynes **4** and CS_2 to annulated thiopyranethiones **5**.

2. Results and Discussion

2.1. Synthesis of *o*,*N*-Dialkynyl-*N*-Tosylanilides

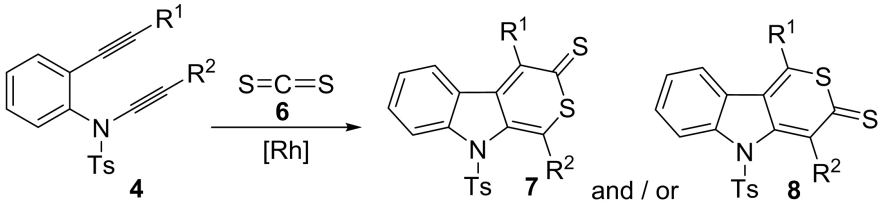
The literature gives four independent routes to ynamides, direct oxidative alkyne-amide coupling, transfer of an activated alkyne to the amide, and stepwise construction of the ynamide [108]-[115]. While the alkynyliodonium routeoffers excellent yield, it is limited to certain substituents [111] [112]. The lengthy Brückner route [115] converts a formamide via dichlorovinyl-amide to a lithioynamide—beneficial for a one-pot Negishi coupling [111]. Most alkynylynamides **4b** - **4e**, **4g** in this study were prepared via alkynyliodonium salts [116] according to the literature [84] [89] [117]. The new syntheses of alkynyl ynamides via Brückner route (**4a**, **4e**), via Negishi coupling (**4h**, **4i**), and the Sonogashira coupling to **4f** are exemplified in Scheme 2.



Scheme 2. Synthesis of alkynyl-ynamides **4a**, **4h**, **4f**.

2.2. [2 + 2 + 2]-Cycloadditions with Carbon Disulfide

Like the formation of carbazoles or carbolines in [2 + 2 + 2]-cycloadditions of *o*,*N*-dialkynyl-*N*-tosylanilides and alkynes or nitriles, a cycloaddition of carbon disulfide to the alkynyl-ynamide results in the synchronous formation of a pyrrole ring and an additional heterocycle, here, a thiopyranethione (Scheme 3).



Scheme 3. Isomeric indolothiopyrane thiones **7**, **8** from [2 + 2 + 2]-cycloaddition of alkynyl-ynamides 4 and carbon disulfide **5**.

As the orientation of the nitrile to the initially formed metallacyclopentadiene [104] [105] is decisive for the formation of *β*- and *γ*-carbolines, two different indolo-thiopyranthiones **7**, **8** can result from the CS_2 addition. Depending on the orientation of carbon disulfide in the addition step to the rhodacyclopentadiene, the thiopyrano[3,4-*b*]indole-3-thione **7** or its [4,3-*b*]-annulated isomer **8** results. We used *o*-propynyl-*N*-ethynyl-*N*-tosylanilide **4a** ($R^1 = CH_3$, $R^2 = H$) as a model system for the anticipated addition of CS_2 to form indolothiopyrane thiones **7a** and **8a** and [Rh(COD)2]$^+$ BF_4^- /BINAP, and Cp*RuCl(COD) as catalytic systems. These had been successfully applied in the synthesis of *β*- and *γ*-carbolines from alkynyl-ynamides [87] [88] [89] and of heterocumulenes with 1,6-diynes [104] [105]. Unfortunately, these catalysts gave no conversion (Table 1, entry 1, 2).

Recently, $Rh(COD)Cl]_2$/2BINAP, a neutral complex, had been rewardingly applied by Tanaka [20] in cycloadditions of 1,6-diynes to give bicyclic dithiopyrones. Inspired by this work, we choose $[RhCl(C_8H_{14})_2]_2$ with BINAP as ligand. The precatalyst was activated by hydrogenation and revealed a high activity: with 3.5 mol-% of $[RhCl(C_8H_{14})_2]_2$ and 10 mol-% BINAP, cycloadduct **7a** was formed in 84% yield within 3 h at 40˚C. Lowering the reaction temperature to 25˚C reduced the yield to 56%—even after a five-fold reaction time. A 95% yield of **8a** was obtained when the addition was performed at 80 °C, but further increase of the temperature initiated side reactions. Lower yields were obtained upon reduction of the catalyst loading or use of other ligands, e.g. Xantphos (Table 1, entry 6 - 8).

The first successful experiment in this series (Table 1, entry 3) led to an apparently regiospecific formation the violet *β*-thio-*γ*-thione derivative **7a** ($R^1 = CH_3$, $R^2 = H$). The structure was confirmed by spectroscopic data and X-ray scattering [108]. However, in further experiments we observed a second product: according

Table 1. Study of the [2 + 2 + 2]-cycloaddition of diyne 4a with CS_2 in dichloroethane.

Entry	Catalytic System [a]	T	time	Yield [b]
1	[Rh(COD)2]$^+$ BF_4^- /BINAP5 mol%/6 mol%	80˚C	6 h	0% [c]
2	Cp*RuCl(COD) 10 mol%	80˚C	6 h	0%
3	$[RhCl(C_8H_{14})_2]_2$/3BINAP3.5 mol%/10 mol%	40˚C	3 h	84%
4	$[RhCl(C_8H_{14})_2]_2$/3BINAP3.5 mol%/10 mol%	25˚C	15 h	56%
5	$[RhCl(C_8H_{14})_2]_2$/3BINAP3.5 mol%/10 mol%	80˚C	3 h	95%
6	$[RhCl(C_8H_{14})_2]_2$/3BINAP2 mol%/6 mol%	80˚C	6 h	67%
7	$[RhCl(C_8H_{14})_2]_2$/Xantphos3.5 mol%/10 mol%	80˚C	6 h	0%
8	$[RhCl(C_8H_{14})_2]_2$/dppf3.5 mol%/10 mol%	80˚C	6 h	0%

As all reaction performed with 10 equiv. CS_2 [a] activation of the Rh-precatalyst by hydrogenation [b] isolated yield of both isomers; [c] decomposition of starting material.

to ^{1}H-NMR, this red component was formed in up to 3% but all attempts to isolate this side product failed due to decomposition. The successful cycloaddition to **7a** prompted us to investigate the reaction more in detail; results are collected in Table 2. Variation of the substituent R^1 on the alkynyl-ynamides has a strong impact on yield and regiochemistry. The violet compounds **7** are accompanied by **8**, their red isomers (vide infra). Surprisingly, exchanging $R^1 = CH_3$ with the small hydrogen (entry 2) or with larger groups (entry 3 - 5) reduces the regioselectivity. The reaction with the non-substituted diyne led to both substituent-free thiopyranothiones **7b**/**8b** (entry 2), as indicated by the violet and red spots observed on the TLC and the ^{1}H NMR of the crude product. However, isolation of **7b** failed due to decomposition during chromatography. Furthermore, while phenyl and butyl give almost equimolar amounts of both isomers, the voluminous TMS group hampers the reaction, inverts the **7**/**8** ratio to 1:2 and is split off to yield **7b**/**8b**. Finally, the reactions with diynes having a substituted ynamide moiety **4g** - **4i** proceed with a surprisingly excellent regioselectivity, as only the violet thiopyranothiones **7g** - **7i** are obtained. This perfect selectivity resembles the regiochemistry of aminonitrile addition to diynes which was explained by sterical crowding [100]. This approach does not hold for alkynyl ynamides substituted on the phenylacetylene segment. Nearly all of these cycloadditions result in an excess of adduct **7**—with the thiocarbonyl vicinal to the substituent!

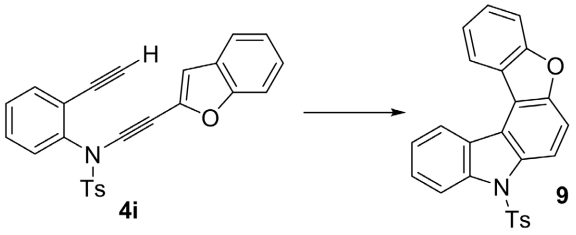
Table 2. [2 + 2 + 2]-cycloaddition of various diynes with CS_2.

Entry	Diyne	R1	R^2	Isolated Yield [a]	Ratio [b] 7/8
1	**4a**	CH_3	H	95%	33/1
2	**4b**	H	H	84% [c]	3/1
3	**4c**	n-Bu	H	71%	10/11
4	**4d**	TMS	H	31% [c]	1/2[d]
5	**4e**	Ph	H	92%	5/4
6	**4f**	4-Ph-Ph	H	34%	2/1
7	**4g**	H	Ph	68% [e]	>99/1
8	**4h**	H	4-MeO-Ph	36% [e]	>99/1
9	**4i**	H	Benzofuranyl-2	21% [e]	>99/1

[a] reactions performed with 10 equiv. CS_2, 3.5 mol%/10 mol% of $[RhCl(C_8H_{14})_2]_2$/3BINAP in DCE at 80˚C; activation of the Rh-precatalysts by hydrogenation; [b] determined by 1H-NMR of the crude product [c] 84% of product was isolated but was partially decomposed [d] proto-desilylation during reaction; [e] catalyst loading of 2.5 mol%/6 mol%.

Several of the cycloadditions above are accompanied by formation of small amounts of side products, FD-MS and some ^{1}H-NMR signals indicate dimers formed via [2 + 2 + 2]-cycloaddition of diynes. On the other hand, benzofuranyl diyne **4i** underwent an intramolecular cyclization to carbazole **9** (Scheme 4), probably via a dehydro Diels-Alder addition followed by a 1,5-H-shift. The mechanism follows Saá *et al.* who developed this route to new and successful access to benzo-annulated carbazoles [118] [119].

Unfortunately, some of the thiopyranethiones, especially the violet isomers, are highly sensitive towards light and air, in several cases impeding the complete analytical and spectral characterization; aromatic substituents appear to be beneficial for stability.



Scheme 4. Intramolecular cyclization of 4i to carbazole 9.

2.3. Optical properties

Indolothiopyranethiones are deeply colored in solution and in the solid state; β-(**8**) and γ-thiono (**7**) derivatives are clearly distinguishable by their violet or red color. The absorption spectra of **7b** and **8d** without additional substituents on the thiopyrane ring are depicted in Figure 2. The intense color of these compound results from their absorption in the blue or green region of the visible spectrum. These maxima (535 nm resp. 474 nm) probably correspond to n $\rightarrow \pi^*$ transition of the thiocarbonyl group. Interestingly, the long-wavelength absorption maximum of related indolopyrones appear at λ_{max} = 370 nm ("**oxa-7**") and λ_{max} = 309 nm ("**oxa-8**"), both about $\Delta\lambda$ = 160 nm at shorter wavelengths [120] [121]. The length of the conjugation path from indole-N to carbonyl-O/-S appears

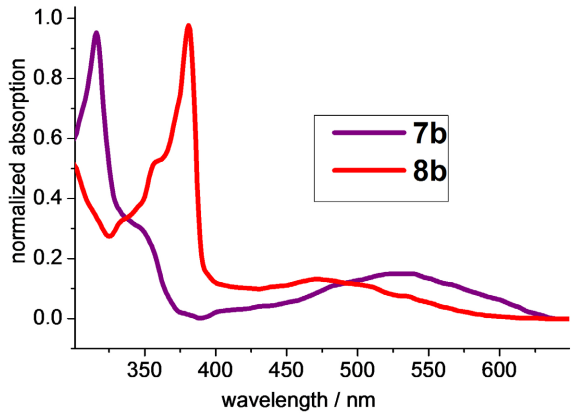


Figure 2. Electronic spectra of isomeric indolothiopyrane thione.

to be decisive for the red shift. Separated by huge energy differences ($\Delta\tilde{\nu}$ = 12,954 cm^{-1} (**7b**); 5535 cm^{-1} (**8b**), the $\pi^* \rightarrow \pi^*$ transitions occur in the UV (316 nm, 378 nm), with extinction coefficients about 6 - 7 times higher than of the $n \rightarrow \pi^*$ transitions. Donor-substitution on thiopyranethiones **7** shifts both transitions to lower energies (e.g. **7i**: λ_{max} = 391, 547 nm), the effect of substituents vicinal to the thiocarbonyl group are less pronounced than those in the α-position (**7e**: λ_{ma}x = 313 nm, 535 nm, but **7g**: λ_{max} = 322 nm, 527 nm). Solvatochromism of both transitions of **7** and **8** is weak ($\Delta\lambda \leq 10$ nm), but typically inverted, e.g. **7e**: λ_{max} in cyclohexane: 535 nm, 307 nm; in dichloromethane: 540 nm, 317 nm and in ethanol 535 nm, 313 nm.

3. Conclusion

The [2 + 2 + 2]-cycloaddition of alkynyl-ynamide to carbon disulfide catalyzed by Rhodium/Binap complexes is a short access to the unprecedented indolothiopyrane thione. Depending on the relative orientation, two different regioisomers are formed, a red β- and a violet γ-isomer. The formation of the violet isomers **7** is generally preferred, if the ynamide is substituted, nearly exclusively formation of the violet **7** occurs. The UV-vis spectra of the isomers differ not only in the long-wavelength absorption, even the $\pi - \pi^*$ transitions are separated by more than 6000 cm^{-1}.

4. Experimental Part

General Information

All reactions were carried out under dry argon or nitrogen unless otherwise indicated. Commercially available reagents were used without further purification unless otherwise indicated; solvents and gases were dried by standard procedures. Yields refer to chromato-graphically and spectroscopically pure compounds unless otherwise stated. ^{1}H and ^{13}C NMR spectra: Bruker AC 300 (300 MHz), Bruker AV 400 (400 MHz), and Bruker ARX 400 (400 MHz), in $CDCl_3$, CD_3OD, and DMSO-d_6. H and C signals were assigned on the basis of DEPT, COSY 45, HMQC, and HMBC experiments. Chemical shifts as δ values in ppm, coupling constants are given in Hz. Melting points: Büchi HWS SG 200; IR: JASCO 4100 FT-IR (ATR); FD-MS: Mat 95 (Finnigan); HR-ESI: Q-TOF-ULTIMA 3 with Lock Spray device (Waters-Micromass), NaICsI Standard as reference. UV-vis: Perkin-Elmer Lambda 16. Elemental analyses were carried out by using a Vario EL.

Starting materials: 4-methyl-*N*-(2(prop-1-ynyl)phenyl)benzenesulfonamide, *N*-(2-iodophenyl)-4-methyl-*N*-(trimethylsilylethynyl)-benzenesulfonamide, 4-methyl-*N*-(2(phenylethynyl)phenyl)-benzene-sulfonamide, and diynes **4b** - **4d**, **4g**, **4h** were prepared according to the literature. [14f, 15c, 27]

Negishi coupling on TMS-diynes: A freshly prepared LiHMDS solution (6.0 mL, 0.5M in THF, 1.5 equiv.) was added slowly to a cooled solution (−78˚C) of the diyne (2 mmol) in dry THF (10 mL) After stirring for 1 h, a solution of $ZnBr_2$

(1.5 M in THF, 1.5 mL, 1.1 equiv.) was added via syringe and stirred for 20 min at 25˚C. The mixture was transferred via cannula to a solution of $Pd_2(dba)_3$*$CHCl_3$ (103.5 mg, 0.1 mmol), PPh_3 (104.9 mg, 0.4 mmol) and the haloarene in dry THF (4 mL) and stirred for 15 h. The solvent was removed, the residue portioned between CH_2Cl_2 and water (30 mL each) and the aqueous layer extracted with CH_2Cl_2 (3*20 mL). The combined organic layers were washed with 50 mL brine, dried ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography.

Desilylation of ynamides with TBAF to a solution of the silylated ynamide (1.0 mmol) in THF (20 mL) and two drops of water was added dropwise at 0˚C TBAF in THF (1M, 1.2 mL, 1.2 mmol). The solution was stirred at 0˚C. After completion of the reaction (TLC), EtOAc (20 mL) and brine (20 mL) were added. The aqueous layer was extracted twice with 20 mL of EtOAc. The combined organic layers were dried (MgSO4), filtered and concentrated. The crude product was purified by a column chromatography.

***N*-(2-(Prop-1-ynyl)phenyl)-*N*-tosylformamide** Under N_2 in a Schlenk tube, 4-methyl-*N*-(2(prop-1-inyl)phenyl)benzenesulfonamide (1.54 g, 5.4 mmol), formic acid (549 mg, 0.45 mL) and *N*,*N*-dimethylaminopyridine (7.3 mg, 0.11 mmol) in 10 mL toluene was stirred at 0˚C and *N*,*N*'-dicyclohexylcarbodiimide (DCC) (2.80 g, 13.6 mmol) was added. After 24 h at 25˚C, filtration through celite and chromatography (SiO_2; petroleum ether: ethyl acetate = 2:1, R_f: 0.49) yielded 1.34 g (82%) of a colorless solid with m.p. = 103˚C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.69 (s, 3H'), 2.41 (s, 3H); 7.19 (t, 1 H, J = 5.2 Hz); 7.37 - 7.23 (m, 5H); 7.59 (d, 2H, J = 6.0 Hz); 9.23 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 4.35, 21.68, 75.20, 128.33, 128.45, 129.71, 129.77, 130.85, 132.45, 133.16, 134.95, 145.36, 160.31; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3263, 2917, 2091, 1707, 1595, 1595, 1485, 1364, 1170, 1080, 992, 812, 757; FD-MS: m/z (%) = 313.3 (100) [M^+].

***N*-(2,2-Dichlorovinyl)-4-methyl-*N*-(2-(prop-1-ynyl)phenyl)benzenesulfonamide** Tetrachloromethane (0.35 mL, 3.2 mmol) was added to a solution of *N*-(2-(prop-1-ynyl)phenyl)-*N*-tosylformamide (100 mg, 0.32 mmol) and triphenylphosphine (250 mg, 0.94 mmol) in dry toluene (1.5 mL). After 24 h at 110˚C, the solvent was removed and the residue purified via chromatography (SiO_2; petroleum ether: ethyl acetate = 4:1, R_f: 0.39) to yield 108 mg (89%) of a yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.74 (s, 3H), 2.41 (s, 3H), 7.02 (s, 1H), 7.15 (d, 1H, J = 7.8 Hz), 7.32 - 7.20 (m, 4H, 7.43 (d, 1H, J = 7.7 Hz); 7.51 (d, 2H, J = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.60, 29.68, 75.98, 91.96, 113.21, 126.07, 126.72, 127.90, 128.03, 128.34, 129.54, 131.92, 133.01, 135.29, 144.33; IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 2920, 2155, 1484, 1362, 1246, 1089, 1009, 840, 754; FD-MS: m/z (%) = 379.0 (100%, M^+).

***N*-Ethinyl-4-methyl-*N*-(2-(prop-1-ynyl)phenyl)benzenesulfonamide 4a** To *N*-(2,2-dichlorovinyl)-4-methyl-*N*-(2-(prop-1-inyl)phenyl)benzenesulfonamide (68 mg, 0.18 mmol) in 1 mL dry THF at −78˚C was added butyl lithium (0.16 mL, 2.5M). Upon warming to −30˚C methanol (50 µL) was added, at 25˚C, pe-

troleum ether (3 mL) and sat. $NaHCO_3$ were added, the solvent stripped off to yield 55 mg (99%) of **4a**. Analytical data were identical to the literature. [15a]

***N*-(2-(Phenylethinyl)phenyl)-*N*-tosylformamide** Under N_2 in a Schlenk tube, 4-methyl-*N*-(2(phenylethynyl)phenyl)-benzenesulfonamide (1.81 g, 5.4 mmol), formic acid (549 mg, 0.45 mL) and *N*,*N*-dimethylaminopyridine (7.3 mg, 0.11 mmol) in 10 mL toluene were stirred at 0˚C and *N*,*N*'-dicyclohexylcarbodiimide (2.80 g) was added. After 24 h at 25˚C, filtration through celite and chromatography (SiO_2; petroleum ether: ethyl acetate = 2:1, R_f: 0.44) yielded 1.78 g (90%) of a colorless solid, m.p. = 109˚C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.23 (s, 3H), 7.07 (d, 2H, J = 8.0 Hz), 7.17 - 7.61 (m, 11H), 9.28 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 21.55, 75.65, 84.83, 113.78, 124.17, 128.15, 128.68, 129.17, 129.87, 131.13, 131.50, 131.52, 132.96, 133.01, 134.66, 145.45, 160.29, IR (ATR): (cm^{-1}) = 3232, 2988, 1708, 1496, 1364, 1284, 1171, 1122, 1076, 1019, 906, 865, 756, 667; FD-MS: m/z (%) = 375.3 (100) [M^+].

***N*-(2,2-Dichlorovinyl)-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide** Tetrachloromethane (0.5 mL, 3.2 mmol) was added to a solution of *N*-(2-(phenylethynyl)phenyl)-*N*-tosylformamide (395 mg, 5 mmol) and triphenylphosphine (395 mg, 1.51 mmol) in dry toluene (3 mL). After 24 h at 110˚C, the solvent was removed and the residue purified via chromatography (SiO_2; petroleum ether: ethyl acetate = 4:1, R_f: 0.34) to yield 95 mg (45 %) of a yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.24 (s, 3H), 7.07 (d, 2H, J = 8.6 Hz), 7.15 (s, 1H), 7.25 (d, 2H, J = 8.4 Hz), 7.35 – 7.31 (m, 4H), 7.45 - 7.39 (m, 2H), 7.50 (d, 2H, J = 8.3 Hz, 7.57 (dd, 1H, J = 7.8, 1.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 21.47, 85.37, 94.84, 115.03, 122.22, 122.50, 126.16, 127.72, 128.22, 128.32, 128.64, 128.79, 129.78, 131.30, 132.2, 132.98, 134.72, 138.66, 144.50; IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3062, 2885, 2201, 1493, 1443, 1366, 1170, 1088, 912, 754; FD-MS: m/z (%) = 441.2 (100) [M^+].

***N*-Ethynyl-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide4e** To *N*-(2,2-Dichlorovinyl)-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (80 mg, 0.18 mmol) in 1 mL dry THF at −78˚C was added butyl lithium (0.16 mL, 2.5M). Upon warming to −30˚C, methanol (50 µL) was added, at 25˚C, petroleum ether (3 mL) and sat. $NaHCO_3$ were added, the solvent stripped off to yield 62 mg (92%) of **4a**. Analytical data were identical to the literature [14f].

***N*-(2-(Biphenylyl-4-ethynyl)phenyl)-*N*-ethynyl-4-methylbenzenesulfonamide4f**: $Pd(PPh_3)_2Cl_2$ (5 mol-%) and CuI (10 mol-%) were dissolved in THF/NEt_3 (1:2, v:v) under N_2 in a Schlenk tube, *N*-(2-iodophenyl)-4-methyl-*N*-(trimethylsilylethynyl)benzolsulfonamide (265 mg, 0.57 mmol) added and a solution of 4-biphenylylacetylene (131 mg, 0.734 mmol) in THF added dropwise. After stirring for 24 h at 80˚C, the solvent was evaporated and the crude product 4f-TMS was directly desilylated to yield 154 mg (0.35 mmol, 63%) **4f** after chromatography. R_f = 0.28 (PE/EtOAc 40/10). ^{1}H NMR (300 MHz, $CDCl_3$, 25˚C): δ = 7.73 (d, J = 8.2 Hz, 2H, 2-H, 6-H Ts), 7.62 (d, J = 7.5 Hz, 2H), 7.37 - 7.57 (m,

11H), 7.13 (d, J = 8.1 Hz, 2H), 2.95 (s, CCH), 2.20 (s, 3H, CH3 Ts). ^{13}C NMR (75 MHz, $CDCl_3$, 25˚C): δ = 144.9 (C-4 Ts), 141.1 (Cq), 140.4 (Cq), 138.2 (Cq), 134.6 (Cq), 134.5 (Cq), 133.3 (CH), 132.0 (CH), 130.6 (CH), 129.9 (CH), 129.6 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 127.7 (CH), 127.0 (CH), 124.4 (CH), 122.8 (Cq), 121.7 (Cq), 95.3 (Cq), 88.4 (Cq), 85.5 (Cq), 59.1 (Cq), 21.5 (CH_3). IR (neat, ATR) $\tilde{\nu}$ = 3297, 3034, 2130, 1489, 1392, 1169, 1089, 912, 763 cm^{-1}. FD-MS: m/z (%) = 447.3 (100) [M^+], 894.4 (22) [M^{2+}].

2-(2-Trimethylsilylethynyl)-*N*-(2-(4-methoxyphenyl)ethynyl)-*N*-tosylbenzenamine4h-TMS: Prepared according to the Negishi procedure from **4d** and 4-iodoanisole, yield = 83%, yellow oil, purified by column chromatography (SiO_2, PE/EtOAc 95/5) R_f = 0.33 (PE/EtOAc 90/10). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.75 (d, ^{3}J = 8.3 Hz, 2H, 2-H, 6-H, Ts), 7.52 (d, ^{3}J = 5.7 Hz, 1H, 3-H), 7.32 (m, 7H, 3-H, 5-H Ts, 4-H, 5-H, 6-H An, 2-H, 6-H Ph), 6.80 (d, ^{3}J = 8.9 Hz, 2H, 3-H, 5-H Ph), 3.78 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3 Ts), 0.14 (9H, CH_3 TMS). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 159.2 (Cq, C-4 Ph), 144.6 (Cq, C-4 Ts), 139.5 (Cq, C-1 An), 134.6 (Cq, C-1 Ts), 134.0 (CH, C-3), 133.0 (CH, C-2, C-6 Ph), 129.5 (CH, C-3, C-5 Ts), 129.1, 128.9, 128.6 (CH, C-4, C-5, C-6), 128.4 (CH, C-2, C-6 Ts), 122.8 (Cq, C-2), 114.9 (Cq, C-1 Ph), 113.7 (CH, C-3, C-5 Ph), 101.1 (Cq, C-C-TMS), 100.0 (Cq, C-C-TMS), 81.0 (Cq, C-C-Ph), 70.0 (Cq, C-C-Ph), 55.2 (OCH_3), 21.6 (CH_3, Ts), -0.4 (CH_3, TMS). IR (neat, ATR) $\tilde{\nu}$ = 2958, 2837, 2238, 2157, 1600, 1567, 1508, 1486, 1444, 1366, 1291, 1245, 1173, 1089, 1032, 923, 830, 764, 706, 658 cm^{-1}. FD-MS: m/z (%) = 473.4 (100) [M^+].

***N*-(2-Ethynylphenyl)-*N*-((4-methoxyphenyl)ethynyl)-4-methylbenzenesulfonamide4h**: According to the general procedure for desilylation of TMS-diynes, 440 mg, 0.95 mmol) of **4h-TMS** gave 310 mg (0.80 mmol, 86 %) of **6h** as colorless solid. R_f= 0.39 (PE/EtOAc 40/10). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.71 (d, ^{3}J = 8.1 Hz, 2H, 2-H, 6-H, Ts), 7.49 (d, ^{3}J = 9.3 Hz, 1H, H-6 An), 7.23 - 7.34 (m, 7H), 6.77 (d, 2H, ^{3}J = 8.7 Hz, 3-H, 5-H Ts), 3.75 (s, 3H, OCH_3), 3.05 (s, 1H, CCH), 2.42 (s, 3H, CH_3 Ts). IR (neat) $\tilde{\nu}$ = 2958, 2837, 2234, 2159, 1603, 1569, 1511, 1491, 1447, 1372, 1291, 1249, 1172, 1081, 1032, 923, 830, 764, 706, 658 cm^{-1}.

2-(2-Trimethylsilylethynyl)-*N*-(2-(benzofuran-2-yl)ethynyl)-*N*-tosylbenzenamine4i-TMS: Prepared according to the Negishi procedure from **4d** and 2-iodobenzofurane [115], yield = 85%, yellow oil, purified by column chromatography (SiO_2, PE/EtOAc 95/5), R_f = 0.58 (PE/EtOAc, 80/20). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.71 (d, ^{3}J = 8.2 Hz, 2H, 2-H, 6-H Ts), 7.47 (m, 2H, 5-H Bf, 3-H An), 7.34 (m, 7H, 3-H, 5-H Ts, 4-H, 5-H, 6-H An, 6-H or 7-H, 8-H Bf), 7.23 (t, ^{3}J = 6.9 Hz, 1H, 6-H or 7-H Bf), 6.91 (s, 1H, 3-H Bf), 2.46 (s, 3H, CH_3 Ts), 0.19 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 154.9 (Cq, C-9 Bf), 145.0 (Cq, C-4 Ts), 138.7, 138.6 (Cq, C-1 An and C-2 Bf), 134.6 (C, C-1 Ts), 134.5 (CH, C-3), 130.2 (CH, C-3, C-5 Ts), 129.6 (CH, C-2, C-6 Ts), 129.5, 128.9 (CH, C-4, C-5, C-6 sup.), 127.7 (Cq, C-4 Bf), 125.9 (CH, C-7 Bf), 123.4 (CH, C-6 Bf), 122.9 (Cq, C-2), 121.5 (CH, C-5 Bf), 113.0 (CH, C-8 Bf), 111.5 (CH, C-3Bf),

102.3 (Cq, C-C-TMS), 99.9 (Cq, C-C-TMS), 87.8 (Cq, C-C-Bf), 62.1 (Cq, C-C-Bf), 22.25 (CH_3, Ts), 0.1 (CH_3, TMS). IR (neat) $\tilde{\nu}$ = 3070, 2960, 2227, 2160, 1601, 1478, 1442, 1372, 1247, 1173, 1092, 844, 812, 753 cm^{-1}. FD-MS: m/z (%) = 482.8 (100) $[M]^+$.

2-Ethynyl-N-(2-(benzofuran-2-yl)ethynyl)-*N*-tosylbenzenamine4i Desilylation according to the general procedure from **4i-TMS**, yield= 79%, white solid, m.p.: 127˚C, purified by column chromatography (SiO_2, PE/EtOAc 90/10) R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.76 (d, ^3J = 8.3 Hz, 2H, 2-H, 6-H Ts), 7.54 (m, 3H), 7.36 (m, 7H), 7.23 (t, ^3J = 7.2 Hz, 1H, Bf), 6.94 (s, 1H, Bf), 3.10 (s, 1H, CCH), 2.48 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 154.9 (Cq, Bf), 145.3 (Cq, C-4 Ts), 139.2 (Cq, C-1 An), 138.6 (C-2, Bf), 134.2 (CH, C-3 An), 134.0 (C, C-1 Ts), 129.8 (CH, C-3, C-5 Ts), 129.7, 129.3, 129.2 (CH, C-4, C-5, C-6 An), 128.6 (CH, C-2, C-6 Ts), 127.7 (Cq, Bf), 125.6 (CH, Bf), 123.1 (CH, Bf), 122.2 (Cq, C-2 An), 121.1 (CH, Bf), 113.0 (CH, Bf), 111.2 (CH, Bf), 87.6 (Cq, N-CC), 83.4 (CH, CCH), 78.5 (Cq, CCH), 61.6 (Cq, N-CC), 21.77 (CH_3 Ts). IR (neat) $\tilde{\nu}$ = 3262, 2233, 1600, 1474, 1447, 1366, 1258, 1170, 1062, 923, 818, 754, 689 cm^{-1}. FD-MS: m/z (%) = 411.1 (100) $[M]^+$.

General procedure for [2 + 2 + 2]-cycloaddition of diynes with CS_2

A degassed solution of BINAP (15.6 mg, 0.025 mmol, 10 mol%) and $[RhCl(C_8H_{14})_2]_2$ (6.1 mg, 0.0087 mmol, 3.5 mol%) in CH_2Cl_2 (3.0 mL) was stirred in a Schlenk tube at 25˚C for 5 min under Ar and connected to a H_2 reservoir for 30 min. The solvent was evaporated and the residue dissolved in dichloroethane (3.0 mL). A solution of the diyne (0.25 mmol) and CS_2 (150 µL, 2.5 mmol) in DCE (7 mL) was added dropwise via syringe and the mixture was stirred at 80˚C. After completion of the reaction (TLC), the solvent was removed and the residue was purified by column chromatography.

4-Methyl-9-tosylthiopyrano[3,4-b]indole-3(9*H*)-thione7a: According to the general procedure 77.3 mg (0.25 mmol) of **4a** gave 91.6 mg (0.237 mmol, 95%) of **7a** as a violet solid with m. p. = 175˚C - 176˚C. Rf = 0.46 (Al_2O_3, PE/EtOAc 90/10). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H, 1-H), 8.28 (d, ^3J = 8.3 Hz, 1H, 8-H), 8.14 (d, ^3J = 8.0, 1H, 5-H), 7.67 (“t”, ^3J = 7.9 Hz, 1H, 7-H), 7.59 (d, ^3J = 8.5 Hz, 2H, 2-H, 6-H Ts), 7.42 (“t”, ^3J = 7.5 Hz, 1H, 6-H), 7.18 (d, ^3J = 8.4 Hz, 2H, 3-H, 5-H Ts), 2.94 (s, 3H, 4-CH_3 Ts), 2.33 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 197.6 (Cq, C=S), 146.0 (Cq, C-4 Ts), 142.2 (Cq, C-8a), 141.2 (Cq, C-9a), 134.3 (Cq, C-4), 134.2 (Cq, C-4a), 133.4 (Cq, C-1 Ts), 132.3 (CH, C-7), 130.1 (CH, C-3, C-5 Ts), 126.7 (CH, C-2, C-6 Ts), 126.6 (CH, C-5), 125.3 (CH, C-6), 125.3 (Cq, C-4b), 125.0 (CH, C-1), 115.3 (CH, C-8), 21.6 (CH3, Ts), 18.4 (4-CH_3 Tp). IR (neat, ATR) $\tilde{\nu}$ = 2925, 1600, 1508, 1456, 1369, 1345, 1269, 1188, 1155, 1089, 1028, 936, 788, 743, 703, 668 cm^{-1}. FD-MS: m/z (%) = 385.2 (100.0) [M]+. $C_{19}H_{15}NO_2S_3$ (385.52): calcd.: C 59.19, H 3.92, N 3.63, S 24.95; found: C 59.35, H 3.94, N 3.58, S 24.43. UV-Vis (CH_2Cl_2): $\lambda_{max,1}$ = 529 nm, ε_1 = 3927 cm^2/mmol, $\lambda_{max,2}$ = 312 nm, ε_2 = 19,974 cm^2/mmol.

Cycloaddition of CS_2 to 4b (R^1 = R^2 = H) According to the general proce-

dure, addition of CS_2 to $_{4b}$ (74.2 mg, 0.25 mmol) gave 15.9 mg (partially dec., 0.043 mmol, 17%) of **8b** as a red solid together with 62.3 mg (partially dec., 0.168 mmol, 67%) of **7b** as a violet solid.

8b: **5-Tosyl-thiopyrano[4,3-*b*]indole-3(5*H*)-thione**, red solid with m.p.: 172˚C - 173˚C (dec.) R_f = 0.43 (SiO_2, PE/CH_2 Cl_2/EtOAc 6/3/1). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.58 (s, 1H, 4-H), 8.22 (d, ^{3}J = 8.4 Hz, 1H, 6-H), 8.15 (s, 1H, 1-H), 7.81 (d, ^{3}J = 8.3 Hz, 2-H, 6-H Ts), 7.68 (d, ^{3}J = 7.7 Hz, 1H, 9-H), 7.54 ("t", ^{3}J = 7.5 Hz, 1H, 7-H), 7.36 ("t", ^{3}J = 7.5 Hz, 1H, 8-H), 7.27 (d, ^{3}J = 8.5 Hz, 3-H, 5-H Ts), 2.37 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 199.1 (Cq, C=S), 146.3 (Cq, C-4 Ts), 144.9 (Cq, C-4a), 139.8 (Cq, C-5a), 134.6 (CH, C-1), 134.0 (Cq, C-1 Ts), 130.4 (CH, C-7), 130.3 (CH, C-3, C-5 Ts), 127.0 (Cq, C-9b), 127.0 (CH, C-2, C-6 Ts), 125.3 (CH, C-8), 123.0 (CH, C-9), 122.9 (Cq, C-9a), 120.3 (CH, C-4), 115.3 (CH, C-6), 21.5 (CH_3 Ts). IR (neat, ATR) $\tilde{\nu}$ = 1586, 1510, 1453, 1402, 1372, 1224, 1170, 1092, 987, 944, 866, 806, 752, 668 cm^{-1}. FD-MS: m/z (%) = 371.2 (100) $[M]^+$. HR-MS: $[M + H]^+$ calcd: 372.0181; found 372.0189. UV-Vis (CH_2Cl_2): $\lambda_{max,1}$ = 474 nm, ε_1 = 3562 cm^2/mmol, $\lambda_{max,2}$ = 378 nm, ε_2 = 27,770 cm^2/mmol.

7b: **9-Tosyl-thiopyrano[3,4-*b*]indole-3(5*H*)-thione** Violet solid, R_f = 0.43 (SiO_2, PE/EtOAc 80/20). ^{1}H NMR (300 MHz, $CDCl_3$, 25˚C): δ = 8.49 (s, 1H, 1-H), 8.16 (d, J = 8.5 Hz, 1H, 8-H), 8.02 (s, 1H, 4-H), 7.80 (d, 1H, J = 7.7 Hz, 5-H), 7.69 (t, 1H, 7-H), 7.64 (d, 2H, J = 8.4 Hz, 2-H, 6-H Ts), 7.39 (t, J = 7.2 Hz, 6-H), 7.21 (d, J = 8.1 Hz, 2H, 3-H, 5-H Ts), 2.35 (s, 3H, CH_3Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 197.9 (C=S), 146.3 (C-4 Ts), 142.5 (C-8a), 137.0 (C-4), 134.4 (C-9a), 133.7 (C-4a), 133.5 (C-1 Ts), 130.9 (C-7), 130.2 (C-3, C-5 Ts), 127.0 (C-2, C-6 Ts), 126.7 (C-6), 125.6 (C-4b), 122.9 (C-1), 115.5 (C-8), 21.67 (CH_3 Ts). IR (neat, ATR) $\tilde{\nu}$ = 1589, 1515, 1451, 1372, 1224, 1171, 992, 957, 816, 767, 668 cm^{-1}. FD-MS: m/z (%) = 371.2 (100) $[M^+]$; UV-Vis (CH_2Cl_2): $\lambda_{max,1}$ = 535 nm, ε_1 = 5678 cm^2/mmol, $\lambda_{max,2}$ = 316 nm, ε^2 = 33456 cm^2/mmol.

Cycloaddition of the diyne 4c (R^1 = n-Bu, R^2 = H, 84 mg 0.24 mmol) and CS_2 according to the general procedure gave 72.8 mg (0.17 mmol, 71%) of a mixture of **7c** and **8c**.

4-*n*-Butyl-9-tosyl-thiopyrano[3,4-*b*]indole-3(9*H*)-thione7c Violet solid, isolated by column chromatography (Al_2O_3, PE/EtOAc 90/10), R_f = 0.65 (SiO_2, PE/EtOAc 80/20). Decomposition above 110˚C. ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.54 (s, 1H, 1-H), 8.30 (d, ^{3}J = 8.4 Hz, 1H, 8-H), 7.99 (d, ^{3}J = 7.8 Hz, 1H, 5-H), 7.67 (t, ^{3}J = 8.4 Hz, 1H, 7-H), 7.60 (d, ^{3}J = 8.4 Hz, 2H, 2-H, 6-H Ts), 7.43 (t, ^{3}J = 8.2 Hz, 1H, 6-H), 7.19 (d, ^{3}J = 8.2 Hz, 2H, 3-H, 5-H Ts), 2.34 (s, 3H, CH_3 Ts), 1.69 (m, 2H, α-CH_2), 1.57 (m, 2H, β-CH_2), 1.25 (m, 2H, γ-CH_2), 1.00 (t, ^{3}J = 6.9 Hz, 3H, CH_3 Bu). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 197.8 (C=S), 146.1 (C-4), 146.0 (C-4 Ts), 142.3 (C8a), 134.7 (C-9a), 133.8 (C-4a), 133.5 (C-1 Ts), 132.2 (C-7), 130.1 (C-3, C-5 Ts), 126.7 (C-2, C-6 Ts), 126.2 (C-5), 125.5 (C-6), 125.0 (C-4b), 124.6 (C-1), 115.5 (C-8), 30.4 (α-CH_2 Bu), 27.5 (CH_2 Bu), 23.1 (CH_2 Bu), 21.7 (CH_3 Ts), 13.9 (CH_3 Bu). FD-MS: m/z (%) = 427.1 (100) $[M^+]$.

The product **8c** was decomposed before all analyses were performed.

1-*n*-Butyl-5-tosyl-thiopyrano[4,3-*b*]indole-3(5*H*)-thione8c, red solid, decomposition above 100˚C. Isolated by column chromatography (Al_2O_3, PE/EtOAc 90/10), R_f= 0.48 (SiO_2, PE/EtOAc 80/20). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.59 (s, 1H, 4-H), 8.32 (d, ^{3}J = 8.4 Hz, 1H, 6-H), 7.80 (d, ^{3}J = 8.6 Hz, 2H, 2-H, 6-H Ts), 7.73 (d, ^{3}J = 8.0 Hz, 1H, 9-H), 7.54 (t, ^{3}J = 8.4 Hz, 1H, 7-H), 7.39 (m, 1H, 8-H), 7.27 (d, ^{3}J = 8.4 Hz, 2H, 3-H, 5-H Ts), 3.05 (t, ^{3}J = 7.8 Hz, 2H, α-CH_2), 2.37 (s, 3H, CH_3 Ts), 1.74 (m, 2H, β-CH_2), 1.50 (m, 2H, γ-CH_2), 0.98 (t, ^{3}J = 7.3 Hz, 3H, CH_3 Bu). FD-MS: m/z (%) = 427.3 (100) $[M]^+$. The product 9c was decomposed before all analyses were performed.

Cycloaddition of CS_2 to4e (R^1 = Ph, R^2= H, 0.25 mmol) according to the general procedure, gave 103 mg (92 %) of a 5 /4 mixture of **7e** and **8e**. Separation by column chromatography (Al_2O_3, PE/$CHCl_3$/EtOAc 7/2/1).

4-Phenyl-9-tosyl-thiopyrano[3,4-*b*]indole-3(9*H*)-thione7e: violet solid, m.p. = 167˚C - 168˚C, R_f= 0.54 (PE/EtOAc 80/20). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.61 (s, 1H, H-1), 8.16 (d, ^{3}J = 8.5 Hz, 1H, H-8), 7.66 (d, ^{3}J = 8.4 Hz, 2H, 2-H, 6-H Ts), 7.54 (m, 4H, 7-H Bz, 3-H, 5-H Ph), 7.24 (d, ^{3}J = 8.5 Hz, 2H, 3-H, 5-H Ts), 7.14 (d, 3J = 7.7 Hz, 2H, 2-H, 6-H Ph), 6.94 (“t”, ^{3}J = 8.7 Hz, 1H, 6-H), 6.11 (d, ^{3}J = 8.2 Hz, 1H, 5-H), 2.38 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 197.8 (Cq, C-3), 146.1 (Cq, C-4 Ts), 143.6 (Cq, C-9a), 142.4 (Cq, C-8a), 136.6 (Cq, C-1 Ph), 134.8 (Cq, C-4), 134.6 (Cq, C-4a), 133.5 (Cq, C-1 Ts), 132.6 (CH, C-7), 130.1 (CH, C-3, C-5 Ts), 129.8 (CH, C-3, C-5 Ph), 128.8 (CH, C-4 Ph), 128.5 (CH, C-2, C-6 Ph), 126.7 (CH, C-2, C-6 Ts), 126.6 (CH, C-1), 126.2 (CH, C-5), 124.9 (CH, C-6), 124.2 (Cq, C-4b), 114.8 (CH, C-8), 21.6 (CH_3 Ts). IR (neat, ATR): $\tilde{\nu}$ = 3084, 2988, 1594, 1513, 1447, 1375, 1342, 1282, 1251, 1167, 1159, 1092, 1041, 953, 899, 839, 809, 749, 695, 665 cm^{-1}. FD-MS: m/z (%) = 447.2 (100) $[M]^+$. HR-MS: $[M + H]^+$ calcd.: 448.0494; found 448.0495. UV-Vis: (CH_2Cl_2): $\lambda_{max,1}$ = 535 nm, ε_1 = 4240 cm^2/mmol, λ_2 = 313 nm, ε_2 = 21,099 cm^2/mmol.

1-Phenyl-5-tosyl-thiopyrano[4,3-*b*]indole-3(5*H*)-thione8e: red solid, m.p. = 146˚C - 147˚C, R_f= 0.48 (Al_2O_3, PE/EtOAc 80/20). ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.66 (s, 1H, 4-H), 8.26 (d, ^{3}J = 8.4 Hz, 1H, 6-H), 7.86 (d, ^{3}J = 8.4 Hz, 2H, 2-H, 6-H Ts), 7.56 (m, 3H, 3-H, 4-H, 5-H Ph), 7.42 (m, 3H, 7-H In, 2-H, 6-H Ph), 7.31 (d, ^{3}J = 8.0 Hz, 2H, 3-H, 5-H Ts), 7.01 (t, ^{3}J = 8.0 Hz, 1H, 8-H), 6.78 (d, ^{3}J = 8.0 Hz, 1H, 9-H), 2.40 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 198.9 (Cq, C=S), 154.5 Cq, C-1), 146.3 (Cq, C-4 Ts), 145.9 (Cq, C-4a), 139.9 (Cq, C-5a), 134.0 (C, C-1 Ts), 133.2 (Cq, C-1 Ph), 130.8 (CH, C-4 Ph), 130.3 (CH, C-3, C-5 Ts), 129.93 (CH, C-7), 129.5 (CH, C-3, C-5 Ph), 128.5 (CH, C-2, C-6 Ph), 127.0 (CH, C-2, C-6 Ts), 124.8 (CH, C-8), 123.9 (Cq, C-9b), 122.8 (Cq, C-9a), 122.38 (CH, C-9), 121.4 (CH, C-4), 115.0 (CH, C-6), 21.7 (CH_3 Ts). IR (neat, ATR): $\tilde{\nu}$ = 2973, 1583, 1519, 1456, 1363, 1176, 1155, 1086, 984, 942, 809, 746, 695, 671 cm^{-1}. FD-MS: m/z (%) = 447.2 (100) $[M]^+$. HR-MS: $[M + H]^+$ calcd.: 448.0494; found 448.0513. UV-Vis: (CH_2Cl_2): $\lambda_{max,1}$ = 497 nm, ε_1 = 46,310

cm^2/mmol, $\lambda_{max,2}$ = 378 nm, ε_2 = 23,841 cm^2/mmol.

Cycloaddition of diyne4f (R^1 = 4-biphenylyl, R^2 = H) (134 mg, 0.3 mmol and CS_2 according to the general procedure, gave 50 mg (34%) of a 2/1 mixture of 4-(biphenyl-4-yl)-9-tosylthiopyrano[3,4-b]indol-3(9*H*)-thione **7f** and 1-(biphenyl4-yl)-5-tosylthiopyrano[4,3-b]indol-3(5*H*)-thione **8f**. The violet isomer 7f decomposed very fast.

1-(Biphenyl-4-yl)-5-tosylthiopyrano[4,3-b]indol-3(5*H*)-thione 8f: R_f: 0.43 (petroleum ether/ethyl acetate/dichloromethane = 16/2/1). 1H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 8.67 (s, 1H, H-4), 8.27 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H, Ts), 7.78 (d, J = 7.2 Hz, 2H, Bp), 7.69 (d, J = 7.1 Hz, 2 H Bp), 7.42 - 7.53 (m, 6 H, Bp), 7.31 (d, J = 8.4 Hz, 2 H, Ts), 7.04 (t, J = 7.2 Hz, 1 H), 6.98 (t, J = 7.2 Hz, 1 Bp), 2.40 (s, 3H, CH_3 Ts). ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 205.0 (C=S), 146.4 (C-4, C-1'Bp), 146.1 (C-4 Ts), 140.1 (C-9b), 139.5 (C-5a), 134.2 (C-1 Ts), 130.4 (C-7), 130.0 (C1), 129.1(C-3, C-5 Bp), 128.4 (C-3, C-5 Ts, C-4'Bp), 128.1 (C-2, C-6, C-3', C-5' Bp), 127.2 (C-2, C-6 Ts), 124.8 (C-8), 124.0 (C-9), 123.1 (C-4' Bp), 122.5 (C9a), 121.5 (C-4), 115.1 (C-6), 21.8 (CH_3 Ts), one signal missing due to superposition. IR (neat, ATR) $\tilde{\nu}$ = 3012, 1598, 1505, 1453, 1346, 1172, 1157, 1045, 952, 899, 767 cm^{-1}. FD-MS: m/z (%) = 523.3 (100) [M^+]. The product **7f** decomposed before all analyses were performed.

Cycloaddition of CS_2 to 4g (R^1 = H, R^2 = phenyl, 0.25 mmol) according to the general procedure, catalyst: 2.5 mol-% $[RhCl(COD)]_2$, 5 mol-% 2,2'BINAP (11.2 mg, 0.018 mmol). Purification by column chromatography Rf: 0.46 (Al_2O_3, petroleum ether/ethyl acetate/chloroform = 8:1:1) gave 76 mg (68%) **4-phenyl-9-tosyl-thiopyrano[3,4-b]indole-3(9*H*)-thione** as violet solid with m.p. = 175˚C - 176˚C. ^{1}H NMR ($CDCl_3$) δ ppm: 8.08 (d, J = 8.2 Hz, 1H), 7.75 (m, 2H), 7.70 (s, 1H), 7.63 (m, 2H), 7.54 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 8.3 Hz), 6.97 (d, J = 8.3 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$) δ ppm: 201.0 (Cq), 149.8 (Cq), 145.4 (Cq), 144.8 (Cq), 141.6 (Cq), 135.7 (Cq), 133.6 (Cq), 132.9 (CH), 131.2 (Cq), 130.5 (CH), 129.3 (CH), 129.1 (CH), 128.3 (CH), 127.6 (CH), 127.2 (Cq), 127.1 (CH), 127.0 (CH), 122.4 (CH), 120.1 (CH), 21.6 (CH3); IR (neat, ATR) $\tilde{\nu}$ = 3042, 1600, 1516, 1486, 1453, 1372, 1207, 1167, 1110, 1047, 905, 818, 773, 662 cm^{-1}; FD-MS: m/z (%) = 447.3 (100) [M^+], 448.3 (38), 449.3 (7), 450.3 (3); UV-Vis (CH_2Cl_2): λ_{max1} = 527 nm, ε_1 = 4895 cm^2/mmol, λ_{max2} = 322 nm, ε_2 = 22013 cm^2/mmol.

Cycloaddition of CS_2 to 4h (R^1 = H, R^2 = 4-anisyl, 0.3 mmol) according to the general procedure, catalyst: 3 mol-% $[RhCl(COD)]_2$ (6.5 mg, 0.009 mmol), 6 mol-% 2,2'BINAP (11.2 mg, 0.018 mmol). Purification by column chromatography R_f: 0.22 (petroleum ether/ethyl acetate/DCM = 8:1:1) gave 51 mg (36%). **1-(4-Methoxyphenyl)-9-tosylthiopyrano[3,4-b]indol-3(9*H*)thione7h**. the compound decomposes before melting. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.26 (s, 3H), 3.90 (s, 3H), 6.97 (d, 2H, J = 8.1 Hz), 7.05 (d, 4H), 7.36 (t, 1H, J = 7.2 Hz), 7.59 - 7.65 (m, 2H), 7.66 (s, 1H, H4); 7.74 (d, 2H, H3", J = 8.9 Hz), 8.08 (d, 1H, J = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.59, 55.40, 114.63,

120.27, 122.40, 126.96, 127.03, 127.23, 127.50, 128.19, 129.93, 131.19, 132.72, 133.15, 141.97, 144.90, 145.37, 150.36, 161.50, 200.7; IR ($CDCl_3$, ATR): $\tilde{\nu}$ (cm^{-1}) = 2897, 1495, 1375, 1187, 1084, 925, 827, 827; FD-MS: m/z (%) = 477.2 (100) [M^+]; UV-Vis (CH_2Cl_2): λ_{max1} = 538 nm, ε_1 = 5990 cm^2/mmol, λ_{max2} = 378 nm, ε_2 = 40,456 cm^2/mmol.

Cycloaddition of CS_2 to6i (R^1 = H, R^2 = 2-benzofuranyl, 83 mg, 0.2 mmol) according to the general procedure, catalyst: $[RhCl(COD)]_2$ 3 mol-% (4.3 mg, 0.006 mmol), 6 mol-% 2,2'BINAP (7.5 mg, 0.012 mmol). Purification by column chromatography R_f: 0.25 (petroleum ether/ethyl acetate/DCM = 8:1:1) gave 21 mg (21%) **1-(Benzofuran-2-yl)-9-tosylthiopyrano[3,4-b]indole-3(9*H*)thione7i** together with 7-tosyl-7*H*-benzofuro[2,3-*b*]carbazole **10** as by-product, the compound decomposes before melting. ^{1}H-NMR: (400 MHz, $CDCl_3$): δ (ppm) = 2.27 (s, 3H), 7.00 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 8.4 Hz), 7.29 - 7.37 (m, 2H), 7.41 - 7.47 (m, 1H), 7.51 (s, 1H), 7.57 - 7.65 (m, 4H), 7.71 (d, 1H, J = 7.8 Hz), 8.08 (d, 1H, J = 8.4 Hz); 13C-NMR (100 MHz, CDCl3): δ (ppm) = 21.36, 110.33, 111.67, 119.72, 122.05, 122.20, 123.61, 126.71, 126.76, 126.82, 127.14, 127.55, 127.70, 129.12, 131.22, 132.62, 133.02, 136.41, 141.14, 144.72, 145.24, 148.59, 155.24, 199.59; IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2892, 1608, 1537, 1512, 1368, 1177, 1109, 1046, 971, 890, 812, 755; FD-MS: m/z (%) = 487.2 (100) [M^+]; UV-Vis (CH_2Cl_2): λ_{max1} = 547 nm, ε_1 = 5358 cm^2/mmol, λ_{max2} = 391 nm, ε_2 = 33476 cm^2/mmol.

7-Tosyl-7*H*-benzofuro[2,3-b]carbazole9 R_f: 0.30 (petroleum ether/ethyl acetate/DCM = 8:1:1); ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.23 (s, 3H), 7.07 (d, 2H, J = 8.5 Hz), 7.33 - 7.52 (m, 4H); 7.60 (d, 1H, J = 8.2 Hz), 7.72 (d, 2H, J = 8.4 Hz), 7.98 (t, 2H), 8.35 (d, 2H), 8.54 (s, 1H); IR ($CDCl_3$, ATR): $\tilde{\nu}$ (cm^{-1}) = 3279, 1489, 1370, 1170, 1125, 1124, 998, 809, 741; FD-MS: m/z (%) = 411.3 (100) [M^+].

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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