2,3-Disubstituted indoles from olefins and hydrazines *via* tandem hydroformylation–Fischer indole synthesis and skeletal rearrangement

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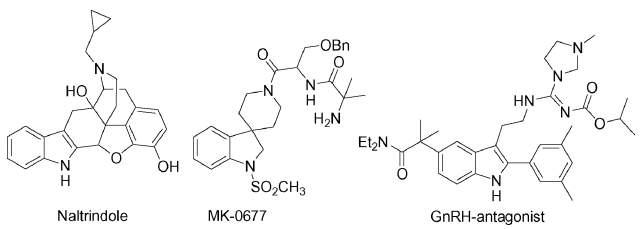
The tandem hydroformylation–Fischer indolisation protocol is used in the synthesis of 2,3-disubstituted indoles. After hydroformylation of selected olefins to form α-branched aldehydes in a one-pot procedure these are condensed with phenylhydrazine to give hydrazones. Upon acid-promoted [3,3]-sigmatropic rearrangement indolenine intermediates with quaternary centres in the 3-position are formed, which, after selective Wagner–Meerwein-type rearrangement of one of the substituents from the 3- to the 2-position, lead to 2,3-disubstituted indoles. Several olefins, bearing substituents with various functional groups, as well as cyclic olefinic systems are investigated.

Introduction

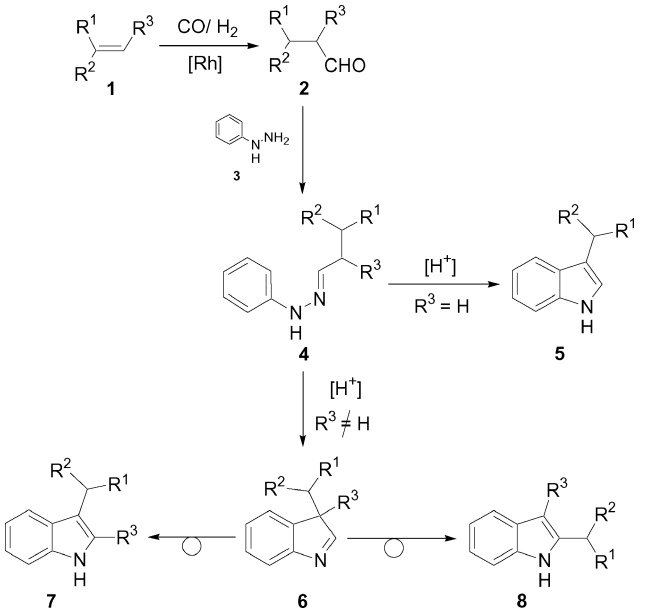
The indole core is a substructure of numerous natural products and pharmaceuticals possessing anti-inflammatory, antimalaria, antidepressant, antitumor or various other activities.[1] Their structures often include annelated and spirocyclic carbo- or heterocycles. In Scheme 1 some of the more complex examples of indoles are shown. Among these, naltrindole is an efficient selective δ-opioid receptor ligand, the spiro-piperidine-indane MK-0677 is a growth hormone secretagogue and the third compound is active as a GnRH-antagonist.[2–4]



Scheme 1 Some examples of biologically active indoles.

Due to the large structural varieties there is a strong interest in developing new efficient synthetic strategies towards highly substituted and polycyclic indoles. On the other hand well established methods like the Fischer indole synthesis even today remain important reactions to form the indole systems and are further optimised.[5] If using Fischer indolisation, aldehydes or ketones are condensed with aryl hydrazines to give hydrazones, which then undergo an acid-promoted [3,3]-sigmatropic rearrangement to form the indole system.

The use of aldehydes in the Fischer indole synthesis is rather limited due to their tendency to undergo side reactions under the harsh reaction conditions that are often required. In order to avoid these unwanted side reactions, acetals or aminals can be used, which liberate the aldehydes *in situ*.[5c,d] As an alternative, aldehydes can also be generated from olefins under the conditions of Fischer indole synthesis if hydroformylation is used, an industrially important method for the generation of aldehydes.[6] Using this concept, we recently have reported sequential hydroformylation and Fischer indole synthesis as a novel approach to 3-substituted indole systems.[7] Upon regioselective hydroformylation of terminal olefins **1** (R^3 = H) the *in situ* generated aldehyde **2** is trapped and protected as a hydrazone **4** (Scheme 2). If the reaction is performed in the presence of acids, tautomerisation and [3,3]-sigmatropic rearrangement takes place to give the 3-substituted indoles **5**. With this method, indoles are synthesised in a one-pot procedure directly from olefins with good to excellent yields. Various functional groups are tolerated in the side chain, *e.g.* to give tryptamine and tryptophol derivatives from allylic amines and alcohols.[7]



Scheme 2 Mechanism of the indole formation.

While indoles with linear side chains are obtained if monosubstituted olefins are used, 1,1-disubstituted terminal olefins lead to indoles with branched side chains. If the hydroformylation of terminal olefins is not fully regioselective a mixture of an

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n- and an isoaldehyde is obtained, leading to different indole products. Normally the selectivity towards the *n*-aldehyde can be effectively controlled by using sterically demanding ligands such as BIPHEPHOS or XANTPHOS.[8] In some cases, however the iso-hydroformylation of terminal olefins cannot be suppressed, especially when styrenes or functionalised olefins are used. These isoaldehydes, as well as aldehydes obtained from internal olefins, are likewise synthetically useful α-branched aldehydes[9] of type **2** ($R^3 \neq H$) if selectively formed. α-Branched aldehydes, however, in Fischer indole synthesis cannot directly form the aromatic system. Instead, indolenines of type **6** are formed, bearing a quaternary centre in the 3-position. Only after rearrangement of one of the blocking groups is the indole core obtained, with substituents both in the 2- and 3-position.

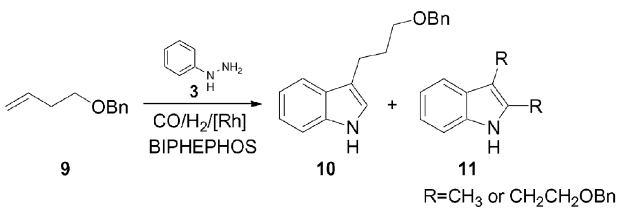
Thus, in principle, olefins giving branched aldehydes could facilitate a new synthetic route for 2,3-disubstituted indoles. This however not only requires regioselective hydroformylation but also selective migration if two different groups are present at the quaternary centre of the indolenine **6**. As known from other Wagner–Meerwein-type rearrangements, migration tendency is controlled by formation of the most stable cation as the decisive factor.[10] This appears also to be valid in the above mentioned rearrangements of indolenines to indoles.[11] To the best of our knowledge only a few examples of Fischer indole synthesis with α-branched aldehydes have been reported.[12] The investigations presented here therefore had the goal to exploit the hydroformylation–Fischer indolisation sequence for the synthesis of 2,3-disubstituted indoles. These are obtained in combination with selective conversions of the indolenine intermediates formed from α-branched aldehydes including a rearrangement.

Results and discussion

As discussed above, formation of 2,3-disubstituted indoles from olefins requires selective formation of α-branched aldehydes and selective rearrangement of one group from the quaternary centre at C-3 to C-2. This cannot be expected in all cases.

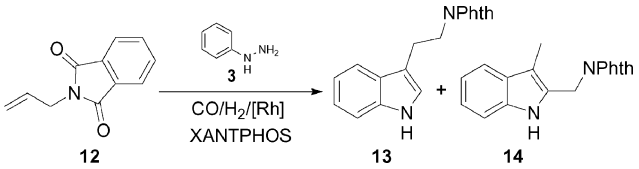
Branched aldehydes from terminal olefins

If the benzyl protected homoallylic alcohol **9** is reacted in the presence of BIPHEPHOS, two different indoles are detected in the crude reaction mixture by NMR spectroscopy (Scheme 3). While the major product **10** is an indole derived from the linear aldehyde, the minor product **11** (<10%, not isolated) results from the branched aldehyde. Although the amount of this product could be increased if the reaction is carried out without a ligand, this does not allow selective formation of the 2,3-disubstituted product.



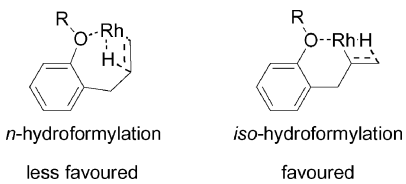
Scheme 3 Tandem reaction of an homoallylic alcohol.

Similar indole side products derived from the isoaldehyde after rearrangement are observed if nitrogen-containing monosubstituted olefins are used. Thus reaction of *N*-allylphthalimide (**12**) leads to a 3-substituted indole **13** from the *n*-aldehyde and a 2,3-disubstituted indole **14** from the isoaldehyde (Scheme 4). Again the conversion could not be shifted completely towards the 2,3-disubstituted rearrangement product due to the low tendency to form the branched isoaldehyde.



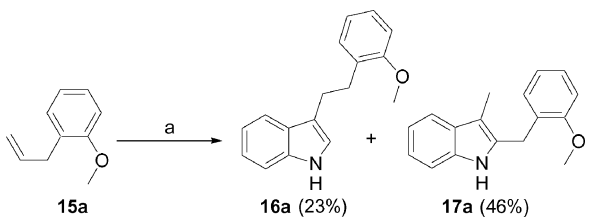
Scheme 4 Tandem reaction of an allylic amine.

Earlier investigations had shown that the hydroformylation of allylic phenols as well as of their O-protected analogues leads to increased amounts of the isoaldehyde.[13] Due to a precoordination of the Rh-catalyst by the oxygen atom different transition states are possible (Scheme 5). The hydrometallation of the Rh-hydride species in the *n*-position requires the less favoured seven-membered ring transition state whereas the corresponding six-membered ring leads to the iso-product.



Scheme 5 Possible transition states.

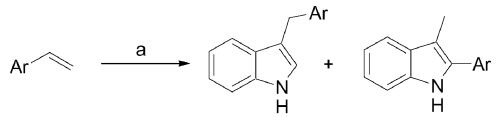
Consequently tandem reaction of 1-allyl-2-methoxybenzene (**15a**) leads to 23% of the 3-substituted indole **16a** and 46% of the 2,3-disubstituted indole **17a**, with a clear preference of the benzyl group over the methyl group to migrate (Scheme 6).



Scheme 6 Tandem reaction of an allylic benzene with O-function: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 1 d.

Styrenes

Styrene-type olefins are known to give predominantly the iso-products upon hydroformylation.[14] If the tandem reaction including indolisation is carried out with styrene (**15b**) two indoles are formed (Scheme 7). The 3-substituted indole **16b** of the *n*-aldehyde can be isolated in 8% yield whereas the isoaldehyde, upon cationic rearrangement, forms the 2,3-disubstituted indole **17b** in 31% yield

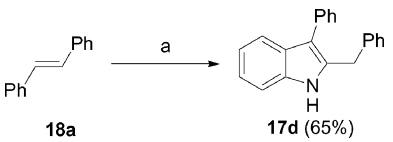


15b (Ar = Ph) **16b** (8%) **17b** (31%)
15c (Ar = 2-Naphthyl) **17c** (45%)

Scheme 7 Tandem reaction of monosubstituted styrenes: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 2 d.

as the major product. Even more selectively, 2-vinylnaphthalene (**15c**) yields 3-methyl-2-naphthylindole (**17c**) as the only product albeit in medium yields.

As to be expected here the aryl migration is preferred in both cases. This, however, must not necessarily be true in other cases. Thus hydroformylation–Fischer indole synthesis with stilbene (**18a**) leads to 2-benzyl-3-phenylindole (**17d**) in 65% yield (Scheme 8). Here migration of the benzyl unit outruns the phenyl group.

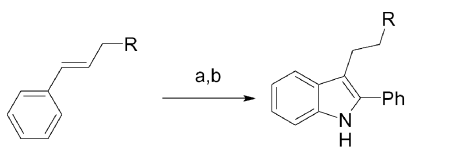


18a **17d** (65%)

Scheme 8 Tandem reaction of a symmetric styrene: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 3 d.

Unsymmetrical styrene-type internal olefins

As in the case of styrene-type olefins the formation of isoaldehydes is favoured and furthermore the migration of aryl as well as benzyl substituents is preferred over normal alkyl substituents, we can take advantage of this fact in the hydroformylation of unsymmetrical internal aryl olefins. Tandem reaction of a cinnamyl alcohol derivative **18b** under hydroformylation conditions in the presence of BIPHEPHOS as ligand, enabling the use of mild conditions upon hydroformylation, with high selectivity introduces the aldehyde function in the benzyl position (Scheme 9). After condensation with phenylhydrazine (**3**) and indolisation *via* rearrangement, the indole **17e**, with the preferably migrating phenyl group in the 2-position, is obtained. Similarly cinnamyl piperidine **18c** is converted to product **17f** in 60% yield.



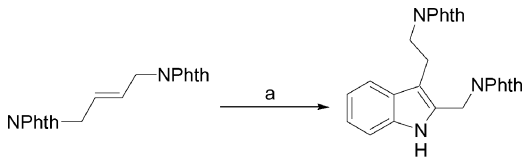
18b (R=OBz) **17e** (R=OBz; 54%)
18c (R=NC_5H_{10}) **17f** (R=NC_5H_{10}; 60%)

Scheme 9 Tandem reaction with unsymmetrical styrenes: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 10 mol% BIPHEPHOS, 10 bar CO, 10 bar H_2, 100 °C, 3 d; b) 4 wt% H_2SO_4 in THF, reflux (Rf), 3 h.

The substitution patterns thus obtained consist of a heterofunctionalised side chain in the 3-position and an aryl group in the 2-position. This pattern is present in various natural products and bioactive pharmaceuticals such as the GnRH-antagonist mentioned above.

Internal olefins with two functionalised side chains

As observed in the examples described above, migration of aryl and benzyl groups is preferred over normal carbon aliphatic side chains. For further elucidations of migration tendencies we investigated the hydroformylation of internal olefins not containing aryl substituents. Thus under the reaction conditions described above conversion of symmetrical 1,4-diphthalimidobut-2-ene (**18d**) leads to 95% of **17g** (Scheme 10). Here competition of an aminomethyl group and a 2-aminoethyl group is clearly decided in favour of the former due to the fact that here the rearrangement that takes place can be considered as a retro-Mannich reaction.



18d **17g** (95%)

Scheme 10 Olefin with two functionalised side chains: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 3 d.

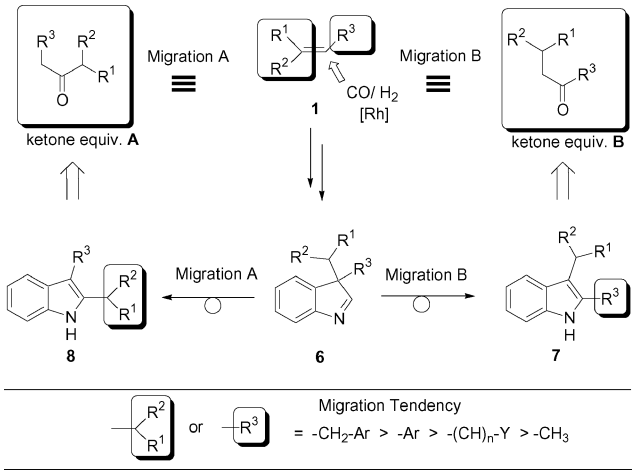
Indoles bearing an aminomethyl group are normally prepared *via* Mannich reaction from the preformed indole or even less conveniently from the corresponding methyl derivatives *via* bromination and substitution at the bromomethyl group. As the 3-position is the most reactive for electrophilic substitution, the substituents are introduced first into this position. Indoles with longer amino chains cannot be obtained *via* Mannich reactions.

In conclusion, the sequence of hydroformylation of acyclic olefins, hydrazone formation, Fischer indolisation and final rearrangement works with good to excellent yields if hydroformylation regioselectivity as well as group migration is selective. For both clear tendencies are observed. Thus the hydroformylated olefins including the rearrangements serve as synthetic equivalents for unsymmetrical ketones **A** or **B** (depending on the migration tendencies) as starting materials in the Fischer indole synthesis (Scheme 11).

If, however, using such unsymmetrical ketones different regioselectivities can be observed *e.g.* for methyl ketones where the methyl group normally ends up in the 2-position whereas in the hydroformylation route the methyl group mostly has the lower tendency to migrate, therefore the other group will preferably be found in the 2-position.[15] In other cases the conventional route from unsymmetrically substituted ketones may be hard to achieve since control of regioselectivity in one specific direction could be critical. Here the hydroformylation–rearrangement approach is more convenient and serves as a complementary method for 2,3-disubstituted indoles.

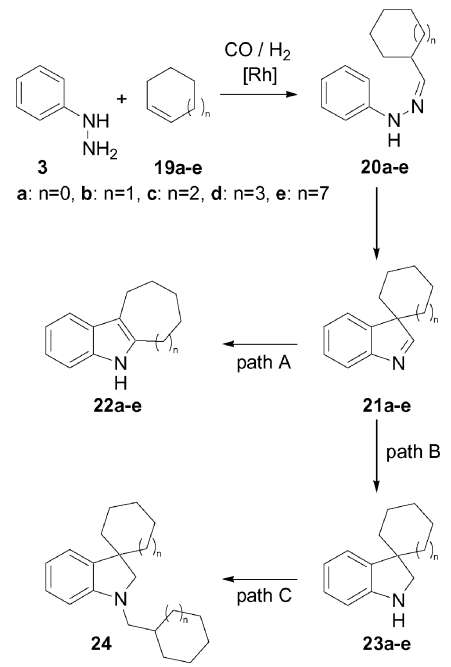
Cyclic olefins

For further applications of our protocol cyclic olefins were subjected to the hydroformylation–indolisation conditions. Here, depending on the substrate and/or the reaction conditions at



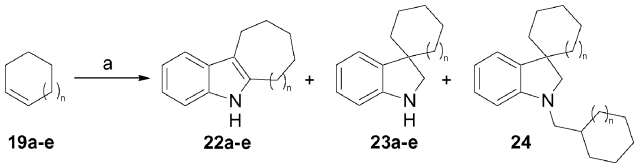
Scheme 11 Branched aldehydes as substitutes for ketones.

least four different product types are obtainable from symmetrical carbocyclic olefins. Hydroformylation of symmetric ring systems **19** leads to a single aldehyde which condenses with phenylhydrazine (**3**) to form the expected hydrazone **20** (Scheme 12). [3,3]-Sigmatropic rearrangement results in a spirocyclic indolenine intermediate **21**, with a quaternary centre in the 3-position and an imine group. In principle, under hydroformylation conditions in the presence of acids, these intermediates cannot only rearrange to form the ring annelated indoles **22** (path A). The imine group can also be hydrogenated to form the spirocyclic saturated indoline **23** (path B). These latter products may then further react as a nucleophile in a hydroaminomethylation reaction with another equivalent of aldehyde to form product **24** (path C). Substances of this type had not been observed with acyclic olefins, presumably due to rapid rearrangements of the substituents at the quaternary centre. With cyclic substrates the rearrangement may also be influenced by the ring size and be suppressed in certain cases.



Scheme 12 Tandem reaction of cyclic olefins.

Table 1 Tandem reaction with cyclic olefins



n	CO (bar)	H_2 (bar)	**22** (%)	**23** (%)	**24** (%)
			22a		
0	50	20	98	—	—
0	20	50	95	—	—
			22b	**23b**	**24b**
1	60	10	36	15	—
1	20	50	—	43[a]	—
1	20	50	—	—	44[b]
			22c	**23c**	
2	50	20	60	11	—
2	20	50	—	59[a]	—
			22d	**23d**	
3	50	20	70	8	—
3	20	50	—	90[a]	—
			22e	**23e**	
7	50	20	89	—	—
7	20	50	38	47[a]	—

[a] 1.5 eq. phenylhydrazine. [b] 0.5 eq. phenylhydrazine, (a) 0.5 mol% $Rh(acac)(CO)_2$, 1.0 eq. phenylhydrazine, 1.0 eq. PTSA, 100 °C, 1 d.

As there are various interesting biologically active substances with 2,3-annelated rings or 3-spirocyclic structures[16] we studied the product distribution for different ring sizes and reaction conditions. As can be seen from the results compiled in Table 1 here indeed products from paths B and C (Scheme 12) are obtainable.

As to be expected, the hydrogenation of the C=N double bond for path B is enhanced with a higher partial pressure of hydrogen. On the other hand decrease of the hydrogen pressure favours the rearrangement to the 2,3-annelated indoles (path A). In addition this is supported by a higher partial pressure of carbon monoxide.

If the reaction sequence is performed with cyclohexene (**19b**) ($n = 1$) under a higher partial pressure of hydrogen the expected 3-spiro-indoline **23b** ($n = 1$) can be isolated (path B). In contrast to the indole nitrogen function which does not have to be protected during the reaction, the nitrogen of the indoline can react as a nucleophile (path C) and undergo another tandem reaction by condensing with a second molecule of the aldehyde to form an imine or enamine. Hydrogenation leads to the tertiary amine **24** (path C). The whole reaction sequence is known as hydroaminomethylation.[17] This extended tandem procedure of hydroformylation–indolisation followed by indolenine hydrogenation and hydroaminomethylation is successfully achieved if two equivalents of cyclohexene (**19b**) are used, giving 44% of **24b** ($n = 1$). While it is possible to conduct the reaction to form the indoline **23b** as the sole product, it is not possible to control the exclusive formation of the 2,3-disubstituted indole **22b** ($n = 1$). Even with a higher partial pressure of carbon monoxide a two to one mixture of the indole **22b** and the indoline **23b** is obtained. Obviously due to the stability of the six-membered ring the rearrangement appears to be slow enough for a hydrogenation of the C=N double bond.

With cyclopentene (**19a**) ($n = 0$), however, even under more forcing hydrogenation conditions the rearranged 2,3-annelated indole **22a** ($n = 0$) is formed in nearly quantitative yield.

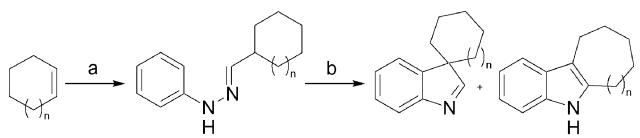
The stability of the six-membered ring leads to a much faster rearrangement as compared to the hydrogenation of the C=N double bond.

If using cycloheptene (**19c**) ($n = 2$) and cyclooctene (**19d**) ($n = 3$) the product distribution can selectively be controlled in either direction. Under hydrogenating conditions the indolines **23c** ($n = 2$) and **23d** ($n = 3$) are obtained in up to 90% yield. A higher pressure of carbon monoxide leads to the expected indoles **22c** ($n = 2$) and **22d** ($n = 3$) along with small amounts of the indolines. With larger cycles such as cyclododecene (**19e**) ($n = 7$) only the indole **22e** ($n = 7$) is formed under higher carbon monoxide pressure, whereas with a higher hydrogen pressure a close to one to one mixture of indole **22e** and indoline **23e** ($n = 7$) is obtainable. Here the rearrangement seems to be so fast that the indole formation cannot be suppressed.

In summary complete control of the product distribution of the tandem reaction under the conditions used is not always achieved. In order to avoid purification problems we considered a modification of the one-pot protocol. Here, first the hydrazones are formed under hydroformylation conditions in one step from commercially available olefins. As known from earlier investigations the C=N double bond of the aryl hydrazones is stable under these conditions. Then, without isolation, in a one-pot procedure the hydrazones are converted under acidic conditions. This avoids hydrogenation of the indolenines if indoles shall be obtained. Choosing among several methods for the Fischer indolisation we decided to run the reaction in 4 wt% sulfuric acid in tetrahydrofuran. This modification of the reaction sequence was investigated with cyclopentene (**19a**), cyclohexene (**19b**) and cycloheptene (**19c**). The results are compiled in Table 2.

According to these investigations the hydrazones **20a–c** are formed in quantitative yields starting from the cycloalkenes. If the indolisation is carried out with the cyclopentene-derived hydrazone **20a** at room temperature after 18 h the rearranged indole **22a** is obtained in 98% yield. Even shorter reaction times (45, 30 and 15 min) at room temperature only lead to a maximum yield of 36% of indolenine **21a**. After 15 min already 60% of the hydrazone is converted to the indole **22a** and indolenine **21a** in a ratio of 1:1.5. So even under these conditions it is not possible to obtain the spiro-compound **21a** with the five-membered ring as the only product due to rapid rearrangement that takes place more or less directly after **21a** is formed.

Table 2 Stepwise reaction of cyclic olefins



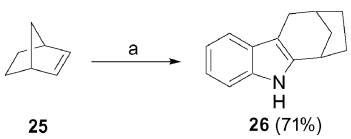
n	t	**20**[a]	**21**	**22**	Conversion[a]
		20a	**21a**	**22a**	
0	18 h	0%	—	98%	100%
0	45 min	6%	31%	63%[a]	94%
0	30 min	18%	36%	46%[a]	82%
0	15 min	40%	36%	24%[a]	60%
		20b	**21b**	**22b**	
1	18 h	0%	99%	—	100%
1	3 h[b]	0%	—	49%	100%
		20c	**21c**	**22c**	
2	18 h	0%	93%	—	100%[a]
2	18 h[c]	0%	—	43%	100%[a]

[a] Detected *via* ^{1}H-NMR spectroscopy. [b] Rf (dioxane). [c] Rf, (a) 1.0 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 50 bar CO, 20 bar H_2, 100 °C, 3 d; (b) after pressure release addition of 4 wt% H_2SO_4 in THF, RT.

Indolisation of cyclohexene-derived hydrazone **20b** at room temperature gives 99% of the indolenine **21b**. Hydrogenation of the C=N double bond yields 84% of the indoline **23b**. So the indoline **23b** can be obtained with an overall yield of 83%. As the rearrangement of the six-membered ring is slower, due to its stability, harsher reaction conditions are required for the formation of indole **22b**. After three hours at reflux temperature in dioxane 49% of the desired indole **22b** are obtained as the only product. Similarly, conversion of the cycloheptene-derived hydrazone **20c** at room temperature leads to 93% of the indolenine **21c**, while indolisation with a longer reaction time yields 43% of the expected indole **22c**.

Thus with this modified protocol the product distribution can be controlled towards either of the desired products in good to very good yields. Cyclic alkenes thus give a diversity of substances by simple variation of the reaction conditions. In 1985 Rodríguez *et al*. similarly had investigated the indolisation of hydrazones obtained from cycloalkyl carbaldehydes.[12] Here, however, the latter were prepared in a rather lengthy five-step procedure from the corresponding cycloalkanones. Similar to the results described above, only with hydrazones derived from cyclohexyl-, cycloheptyl- and cyclooctylcarbaldehyde could both indolenine or rearranged indoles be obtained with varying selectivities depending on the conditions and acids used. Here too, cyclopentylcarbaldehyde gave no spiro-indolenines due to rapid rearrangement. Indolines were not obtained since no reductive conditions were applied.

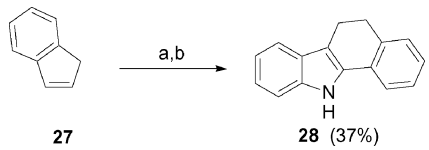
Next the tandem hydroformylation–Fischer indole protocol was applied to the bicyclic system norbornene (**25**) (Scheme 13). Since norbornene (**25**) consists of a five- and a six-membered cycle the formation of different products *via* variation of the reaction conditions should be possible. A higher pressure of hydrogen could lead to the formation of a spirocyclic compound, while performing the reaction with a higher carbon monoxide pressure could yield a rearranged 2,3-annelated indole. In both cases, however, only one product, the 2,3-disubstituted indole **26**, was formed smoothly in up to 71% yield. The tendency of the five-membered ring to form the rearranged six-membered ring is dominating. Even under an increased pressure of hydrogen the rearrangement is faster than the hydrogenation of the C=N double bond to form a spirocyclic compound.



Scheme 13 Tandem reaction of a bicyclic olefin: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 1 d.

Although the hydroformylation may give both isomeric aldehydes with an unsymmetrically substituted internal olefin, such as indene (**27**), the aldehyde in the benzylic position is exclusively

formed due to the styrene-type double bond. After condensation with phenylhydrazine (**3**) and [3,3]-sigmatropic rearrangement, product **28**, with the aromatic substituent in the 2-position, can be isolated (Scheme 14).

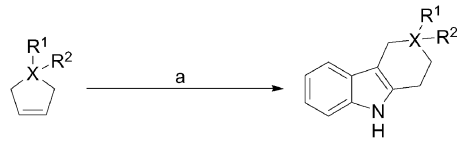


27 **28** (37%)

Scheme 14 Reaction of an unsymmetrical cyclic olefin: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 10 mol% BIPHEPHOS, 10 bar CO, 10 bar H_2, 100 °C, 3 d; b) 4 wt% H_2SO_4 in THF, Rf, 3 h.

Thus it is possible to use even unsymmetrical cyclic olefins for the tandem hydroformylation–Fischer indole synthesis. Considering biologically active indoles with 2,3-annelated cycles, functional groups or heterocycles are important. Conversions starting from cyclic olefins can likewise be applied to form products of this type. Since the conversion of cyclopentene (**19a**) to the indole **22a** worked very well, other five-membered ring systems should also serve as substrates.

As shown in Scheme 15 cyclopentene derivatives **29a,b**, which can easily be prepared *via* ring closing metathesis of the corresponding bis-homoallylic alcohols,[18] give the corresponding indoles **30a,b** with a free hydroxy function in up to 36% yield. Although the yields need further improvement it is shown that in this manner substructures of more complex alkaloid systems can be directly synthesised regioselectively.

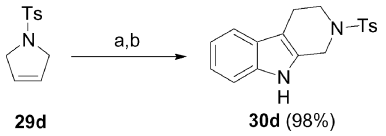


29a (X=C; R^1=OH, R^2=CH_2OBn) **30a** (28%)
29b (X=C; R^1=OH, R^2=*tert*-Bu) **30b** (36%)
29c (X=Si; R^1, R^2=Ph) **30c** (39%)

Scheme 15 Functionalised cyclic olefins: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 1 eq. PTSA, 50 bar CO, 20 bar H_2, 100 °C, 3 d.

Similarly the heterocyclic system **29c**, containing silicon, forms the expected indole **30c** in 39% yield. Due to the β-silicon effect cations in a β-position to the silicon are stabilised and therefore the longer chain rearranges to the 2-position of the indole system. Prior to deprotonation to form the aromatic system and after the rearrangement a second cation is formed in the 3-position. As this cation is also in a β-position to the silicon it is also stabilised. Some related oxygen-containing heterocycles tested did not lead to selective product formation under the conditions used as they seem to be unstable.

Among the indoles with an annelated heterocycle a very large and interesting group of biologically active compounds are the β-carbolines, which possess an additional nitrogen atom in the third ring.[1,12] Therefore the nitrogen-containing cyclopentene derivative **29d**, again obtained *via* ring closing metathesis, was converted following the stepwise protocol. The desired hydrazone was formed in



29d **30d** (98%)

Scheme 16 Preparation of a β-carboline derivative: a) 1 eq. phenylhydrazine, 0.5 mol% $Rh(acac)(CO)_2$, 50 bar CO, 20 bar H_2, 100 °C, 3 d; b) 4 wt% H_2SO_4 in THF, 3 h, Rf.

a nearly quantitative yield. After the acid-catalysed rearrangement the expected indole **30d** was isolated in 98% yield (Scheme 16). This rearrangement, with the opposite regioselectivity as compared to the silicon heterocycle **30c**, proceeds *via* a retro-Mannich reaction to form selectively only one indole system.

Conclusion

The tandem hydroformylation–Fischer indole synthesis can be used to build up 2,3-disubstituted indoles from olefins in good to very good yields. The reaction sequence depends on two factors, the regioselective hydroformylation to form α-branched aldehydes and the selective migration of one of the two substituents. For both factors clear tendencies were observed. According to Wagner–Meerwein-type rearrangements in all examples presented, one substituent migrated selectively into the 2-position of the indole scaffold. The use of cyclic olefins permits the formation of 2,3-annelated indoles in up to 98% yield and 3-spiro-indolines in up to 90% yield depending on the reaction conditions. According to the nucleophilic character of the indoline nitrogen an extended tandem reaction consisting of hydroformylation–Fischer indole synthesis and hydroaminomethylation can be performed. As it is not necessary to isolate any intermediate this method gratifyingly saves time and avoids waste material.

Experimental section

General

All reactions with air sensitive compounds were carried out in dry reaction vessels under an atmosphere of dry argon. Solvents were purified with standard procedures.[19] Column chromatography was conducted with silica gel 60, cyclohexane and MTBE or EA. ^{1}H-NMR spectra were recorded at 400 MHz, 500 MHz or 600 MHz in $CDCl_3$ with $CHCl_3$ as internal standard (δ = 7.26 ppm). ^{13}C-NMR spectra were recorded at 100 MHz or 125 MHz in $CDCl_3$ with $CDCl_3$ as internal standard (δ = 77.0 ppm). Different carbon groups were analysed by APT experiments. IR spectra were recorded as films on NaCl or KBr plates or for solids pressed with KBr. The peak intensities are defined as very strong (vs), strong (s), middle (m) or weak (w). Mass spectra were obtained at 70 eV. 4-Benzyloxybutene **9**,[20] *N*-allylphthalimide **12**,[21] 2-allylanisole **15a**,[22] benzoic acid 3-phenylallyl ester **18b**,[23] 1-(3-phenylbut-3-enyl)piperidine **18c**,[24] 1,4-di(2-isoindole-1,3-dion)but-2-ene **18d**,[25] 1-benzyloxymethylcyclopent-3-ene-1-ol **29a**,[18] 1-*tert*-butylcyclopent-3-ene-1-ol **29b**[18] and 1,1-diphenyl-1-silylcyclopent-3-ene **29c**[18] were prepared according to previously reported procedures.

General procedure A for the preparation of indoles

1 eq. olefin, 1 eq. phenylhydrazine (**3**), 1 eq. *p*-toluenesulfonic acid and (0.5 mol%) $Rh(acac)(CO)_2$ are diluted in anhydrous THF or dioxane, transferred to an autoclave and pressurised with 50 bar CO and 20 bar H_2. After stirring at 100 °C the mixture is washed with aqueous ammonia and dried over $MgSO_4$. The solvent is evaporated and the residue is purified by flash chromatography on silica.

General procedure B for the preparation of indolines

1 eq. olefin, 1.5 eq. phenylhydrazine (**3**), 1 eq. *p*-toluenesulfonic acid and (0.5 mol%) $Rh(acac)(CO)_2$ are diluted in anhydrous THF or dioxane, transferred to an autoclave and pressurised with 20 bar CO and 50 bar H_2. After stirring at 100 °C the mixture is washed with aqueous ammonia and dried over $MgSO_4$. The solvent is evaporated and the residue is purified by flash chromatography on silica.

General procedure C for the preparation of hydrazones

1 eq. olefin, 1. eq. phenylhydrazine (**3**) and (0.5 mol%) $Rh(acac)(CO)_2$ are diluted in anhydrous THF, transferred to an autoclave and pressurised with 50 bar CO and 20 bar H_2. After stirring for 3 d at 100 °C the solvent is evaporated.

General procedure D for the preparation of indoles or indolenines *via* hydrazones

The hydrazone prepared according to procedure C is dissolved in 4 wt% H_2SO_4 in anhydrous THF. After stirring the reaction mixture is washed with aqueous ammonia and dried over $MgSO_4$. The solvent is evaporated and the residue is purified by flash chromatography on silica.

3-(3-Benzyloxypropyl)indole (10). Following general procedure A, 0.17 g (1.0 mmol) 4-benzyloxybutene (**9**) and 0.08 g (10 mol%) BIPHEPHOS were stirred in anhydrous THF for 3 d to yield 0.27 g crude product, which was analysed by NMR spectroscopy (indoles: *n*:iso ≈ 19:1). 3-(3-Benzyloxypropyl)indole (**10**): **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.04 (tt, ^3J = 6.5; 7.5 Hz, 2 H, CH_2), 2.86 (t, ^3J = 7.5 Hz, 2 H, CH_2), 3.55 (t, ^3J = 6.5 Hz, 2 H, CH_2), 4.52 (s, 2 H, CH_2), 6.92 (s, 1 H, C*H*), 7.10 (dd, ^3J = 7.0; 8.0 Hz, 1 H, C*H*), 7.18 (dd, ^3J = 7.0; 8.0 Hz, 1 H, C*H*), 7.30–7.38 (6 H, 6 × C*H*), 7.62 (d, ^3J = 8.0 Hz, 1 H, C*H*), 7.91 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 21.6 (*C*H_2), 30.1 (*C*H_2), 69.9 (*C*H_2), 72.9 (*C*H_2), 111.0 (*C*H), 116.1 (C_q), 118.9 (*C*H), 119.1 (*C*H), 121.3 (*C*H), 121.8 (*C*H), 125.8 (C_q), 127.5 (*C*H), 127.7 (2 × *C*H), 128.4 (2 × *C*H), 136.3 (C_q), 138.6 (C_q). Characteristic data for the isomer **11**: **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.00 (t, ^3J = 6.5 Hz, 2 H, CH_2), 4.67 (s, 2 H, CH_2), 7.67 (d, ^3J = 7.8 Hz, 1 H, C*H*), 8.13 (bs, 1 H, N*H*). **MS** (FAB): *m*/*z* (%) = 266 (M + H$^+$, 18), 265 (M$^+$, 29), 130 (36), 91 (100). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3420 (m), 3058 (m), 2937 (s), 1455 (s), 1101 (s), 741 (vs). **HR-MS** (FAB): calculated for $C_{18}H_{19}NO$ 265.1467 g mol^{-1}; found: 265.1484 g mol^{-1}.

2-[2-(1*H*-Indol-3-yl)ethyl]isoindole-1,3-dione (13). Following general procedure A, 0.32 g (1.7 mmol) 2-allylisoindole-1,3-dione (**12**), 0.1 mg (0.3 mol%) $Rh(acac)(CO)_2$ and 29.9 mg (3.0 mol%) XANTPHOS were stirred in anhydrous THF. After purification 0.26 g (51%) of **13** and **14** as a mixture of *n*- and iso-isomers is isolated. Analytical data was obtained from the mixture. *n*-Regioisomer: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 3.17 (dd, 2 H, ^3J = 7.5; 8.1 Hz, CH_2), 4.02 (dd, 2 H, ^3J = 7.5; 8.1 Hz, CH_2), 7.08 (s, 1 H, C*H*), 7.13 (dd, 1 H, ^3J = 7.3; 8.1 Hz, C*H*), 7.19 (dd, 1 H, ^3J = 7.3; 8.1 Hz, C*H*), 7.34 (d, 1 H, ^3J = 8.1 Hz, C*H*), 7.50 (d, 1 H, ^3J = 7.0 Hz, C*H*), 7.75 (d, 1 H, ^3J = 7.3 Hz, C*H*), 7.86 (d, 2 H, ^3J = 5.5 Hz, 2 × C*H*), 8.11 (s, 1 H, N*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 24.4 (*C*H_2), 38.5 (*C*H_2), 111.1 (*C*H), 112.9 (C_q), 118.8 (*C*H), 119.4 (*C*H), 122.0 (*C*H), 123.1 (2 × *C*H), 127.3 (2 × C_q), 132.4 (C_q), 133.6 (2 × *C*H), 136.2 (2 × C_q), 168.3 (2 × C_q). Characteristic data for the iso-regioisomer (**14**): **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 2.44 (s, 3 H, CH_3), 4.97 (s, 2 H, CH_2), 7.07 (dd, 1 H, ^3J = 7.0; 7.0 Hz, C*H*), 7.15 (dd, 1 H, ^3J = 7.0; 7.0 Hz, C*H*), 7.28 (d, 1 H, ^3J = 7.0 Hz, C*H*), 7.50 (d, 1 H, ^3J = 7.0 Hz, C*H*), 7.66 (d, 2 H, ^3J = 5.5 Hz, 2 × C*H*), 7.80 (d, 2 H, ^3J = 5.5 Hz, 2 × C*H*), 8.56 (s, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 8.3 (*C*H_3), 32.6 (*C*H_2), 110.1 (C_q), 110.8 (*C*H), 119.0 (*C*H), 119.2 (*C*H), 122.5 (*C*H), 123.4 (2 × *C*H), 128.2 (C_q), 128.9 (C_q), 131.9 (2 × C_q), 134.1 (2 × *C*H), 135.6 (C_q), 168.4 (2 × C_q). **HRMS**: calculated for $C_{18}H_{14}N_2O_2$ 290.1055 g mol^{-1}; found: 290.1068 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

2-(2-Methoxybenzyl)-3-methylindole (17a). Following general procedure A, 0.45 g (3.0 mmol) 2-allylanisole (**15a**) were stirred in anhydrous dioxane for 1 d. After purification 0.35 g (46%) 2-(2-methoxybenzyl)-3-methylindole (**17a**) were isolated along with 0.18 g (23%) 3-[2-(2-methoxyphenyl)ethyl]indole (**16a**). 2-(2-Methoxybenzyl)-3-methylindole (**17a**): **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.40 (s, 3 H, CH_3), 3.96 (s, 3 H, CH_3), 4.11 (s, 2 H, CH_2), 6.92–6.96 (2 H, 2 × C*H*), 7.14–7.18 (3 H, 3 × C*H*), 7.25–7.29 (2 H, 2 × C*H*), 7.57 (d, ^3J = 8.0 Hz, 1 H, C*H*), 8.01 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 8.5 (*C*H_3), 26.7 (*C*H_2), 55.5 (*C*H_3), 107.1 (C_q), 110.2 (*C*H), 110.6 (*C*H), 118.1 (*C*H), 118.8 (*C*H), 120.9 (*C*H), 120.9 (*C*H), 127.7 (C_q), 127.8 (*C*H), 129.2 (C_q), 130.0 (*C*H), 133.6 (C_q), 135.2 (C_q), 157.0 (C_q). **GC-MS** (EI): *m*/*z* (%) = 251 (M$^+$, 100), 236 (12), 220 (9), 204 (9), 144 (54), 130 (43), 91 (9), 77 (12). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3411 (s), 3056 (m), 2924 (s), 2836 (m), 1600 (s), 1464 (vs), 1037 (s), 751 (vs). **HR-MS** (EI): calculated for $C_{17}H_{17}NO$ 251.1310 g mol^{-1}; found: 251.1286 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

3-[2-(2-Methoxyphenyl)ethyl]indole (16a). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.11 (s, 4 H, 2 × CH_2), 3.90 (s, 3 H, CH_3), 6.94–6.98 (3 H, 3 × C*H*), 7.18–7.29 (4 H, 4 × C*H*), 7.37 (d, ^3J = 8.0 Hz, 1 H, C*H*), 7.75 (d, ^3J = 7.8 Hz, 1 H, C*H*), 7.86 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 25.6 (*C*H_2), 31.1 (*C*H_2), 55.2 (*C*H_3), 110.2 (*C*H), 111.0 (*C*H), 116.7 (C_q), 119.0 (*C*H), 119.0 (*C*H), 120.3 (*C*H), 121.1 (*C*H), 121.7 (*C*H), 127.0 (*C*H), 127.5 (C_q), 129.8 (*C*H), 130.8 (C_q), 136.2 (C_q), 157.5 (C_q). **GC-MS** (EI): *m*/*z* (%) = 251 (M$^+$, 53), 131 (46), 130 (100), 103 (8), 91 (8), 77 (11). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3420 (vs), 3056 (m), 2935 (s), 2835 (m), 1600 (s), 1493 (vs), 1031 (s), 750 (vs). **HR-MS** (EI): calculated for $C_{17}H_{17}NO$ 251.1310 g mol^{-1}; found: 251.1306 g mol^{-1}.

3-Methyl-2-phenylindole (17b). Following general procedure A, 0.32 g (3.1 mmol) styrene (**15b**) were stirred in anhydrous THF for 2 d. After purification 0.19 g (31%) 3-methyl-2-phenylindole

(**17b**) were isolated, along with 0.05 g (8%) 3-benzylindole (**16b**). The spectroscopic data fits with the literature.[26–27]

3-Methyl-2-naphthylindole (17c). Following general procedure A, 0.46 g (3.0 mmol) 2-vinylnaphthalene (**15c**) were stirred in anhydrous THF for 2 d. After purification 0.35 g (45%) 3-methyl-2-naphthylindole (**17c**) were isolated: **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.56 (s, 3 H, CH_3), 7.21 (dd, ^3J = 7.0; 8.0 Hz, 1 H, CH), 7.27 (dd, ^3J = 7.0; 8.0 Hz, 1 H, CH), 7.38 (d, ^3J = 7.8 Hz, 1 H, CH), 7.50–7.58 (2 H, 2 × CH), 7.67 (d, ^3J = 7.8 Hz, 1 H, CH), 7.71 (d, ^3J = 8.5 Hz, 1 H, CH), 7.87–7.95 (3 H, 3 × CH), 7.99 (s, 1 H, CH), 8.07 (bs, 1 H, NH). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 9.8 (CH_3), 109.1 (C_q), 110.7 (CH), 119.0 (CH), 119.6 (CH), 122.4 (CH), 125.7 (CH), 126.1 (CH), 126.4 (CH), 126.5 (CH), 127.8 (CH), 128.0 (CH), 128.4 (CH), 130.1 (C_q), 130.7 (C_q), 132.4 (C_q), 133.5 (C_q), 134.0 (C_q), 136.0 (C_q). **MS** (FAB): m/z (%) = 257 (M^+, 100), 155 (7), 141 (10). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3394 (s), 3049 (m), 2919 (m), 1599 (m), 1455 (m), 1241 (m), 820 (s), 748 (vs). **HR-MS** (FAB): calculated for $C_{19}H_{15}N$ 257.1204 g mol^{-1}; found: 257.1219 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

2-Benzyl-3-phenylindole (17d). Following general procedure A, 0.54 g (3.0 mmol) stilbene (**18a**) were stirred in anhydrous dioxane for 3 d. After purification 0.55 g (65%) 2-benzyl-3-phenylindole (**17d**) were isolated. The spectroscopic data fits with the literature.[28]

3-(2-Benzyloxyethyl)-2-phenylindole (17e). 0.72 g (3.0 mmol) benzoic acid 3-phenylallyl ester (**18b**), 0.33 g (3.1 mmol) phenylhydrazine (**3**), 4 mg (0.5 mol%) $Rh(acac)(CO)_2$ and 0.23 g (9.9 mol%) BIPHEPHOS were diluted in 12 ml anhydrous THF, transferred to an autoclave and pressurised with 10 bar CO and 10 bar H_2. After stirring for 3 d at 100 °C the solvent was evaporated. The crude hydrazone was dissolved in 12 g, 4 wt% H_2SO_4 in anhydrous THF. After stirring under reflux for 3 h, the reaction mixture was washed with aqueous ammonia and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica to yield 0.55 g (54%) 3-(2-benzyloxyethyl)-2-phenylindole (**17e**): **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 3.40 (t, ^3J = 7.3 Hz, 2 H, CH_2), 4.61 (t, ^3J = 7.3 Hz, 2 H, CH_2), 7.18 (dd, ^3J = 8.0; 8.0 Hz, 1 H, CH), 7.24 (dd, ^3J = 8.0; 8.0 Hz, 1 H, CH), 7.37–7.42 (4 H, 4 × CH), 7.49 (dd, ^3J = 7.5; 8.0 Hz, 2 H, 2 × CH), 7.54 (dd, ^3J = 7.2; 7.5 Hz, 1 H, CH), 7.63 (d, ^3J = 8.0 Hz, 2 H, 2 × CH), 7.76 (d, ^3J = 8.0 Hz, 1 H, CH), 7.96 (d, ^3J = 7.2 Hz, 2 H, 2 × CH), 8.13 (bs, 1 H, NH). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 24.3 (CH_2), 65.0 (CH_2), 108.6 (C_q), 110.9 (CH), 119.1 (CH), 119.9 (CH), 122.5 (CH), 127.9 (CH), 128.0 (2 × CH), 128.2 (2 × CH), 129.0 (2 × CH), 129.2 (C_q), 129.6 (2 × CH), 130.3 (C_q), 132.8 (CH), 132.9 (C_q), 135.6 (C_q), 135.8 (C_q), 166.7 (C_q). **MS** (FAB): m/z (%) = 341 (M^+, 71), 220 (100), 206 (29), 105 (33), 77 (24). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3365 (s), 3056 (w), 2974 (w), 2896 (w), 1705 (vs), 1601 (m), 1450 (m), 1280 (s), 1114 (m), 739 (s). **HR-MS** (FAB): calculated for $C_{23}H_{19}NO_2$ 341.1416 g mol^{-1}; found: 341.1398 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

2-Phenyl-3-[2-(piperidin-1-yl)ethyl]-1*H*-indole (17f). Following the procedure for product **17e**, 0.31 g (1.6 mmol) 1-(3-phenylbut-3-enyl)piperidine (**18c**), 0.17 g (1.6 mmol) phenylhydrazine (**3**), 2 mg (0.5 mol%) $Rh(acac)(CO)_2$ and 0.12 g (10.0 mol%) BIPHEPHOS were reacted to give 0.30 g (60%) 2-phenyl-3-[2-(piperidin-1-yl)ethyl]-1*H*-indole (**17f**): **^{1}H-NMR**: ($CDCl_3$, 500 MHz) δ [ppm] = 1.46 (bs, 2 H, CH_2), 1.63 (bs, 4 H, 2 × CH_2), 2.52 (bs, 4 H, 2 × CH_2), 2.68 (t, 2 H, J = 8.5 Hz, CH_2), 3.12 (t, 2 H, J = 8.5 Hz, CH_2), 7.14 (dd, 1 H, J = 7.1; 7.0 Hz, CH), 7.20 (dd, 1 H, J = 7.1; 7.7 Hz, CH), 7.34–7.37 (2 H, 2 × CH), 7.44 (dd, 2 H, J = 8.0; 8.0 Hz, 2 × CH), 7.56 (d, 2 H, J = 8.0 Hz, 2 × CH), 7.65 (d, 1 H, J = 8.0 Hz, CH), 8.31 (s, 1 H, NH). **^{13}C-NMR**: ($CDCl_3$, 125 MHz) δ [ppm] = 22.1 (CH_2), 24.4 (CH_2), 25.9 (2 × CH_2), 54.6 (2 × CH_2), 60.0 (CH_2), 110.8 (CH), 111.2 (C_q), 119.1 (CH), 119.5 (CH), 122.2 (CH), 127.5 (CH), 127.9 (2 × CH), 128.8 (2 × CH), 129.2 (C_q), 133.2 (C_q), 134.7 (C_q), 135.9 (C_q). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3405 (m), 2931 (s), 1602 (s), 1456 (s), 1261 (s), 1101 (s), 739 (vs), 696 (vs). HRMS found $[M + H]^+$ 305.1991 $C_{21}H_{27}N_2$ requires $[M + H]^+$, 305.1974. Structure was clarified by 1D-NOESY experiments.

2-(Methyl-2-isoindole-1,3-dion)-3-[2-(2-isoindole-1,3-dion)ethyl]-indole (17g). Following general procedure A, 0.35 g (1.0 mmol) 1,4-di(2-isoindole-1,3-dion)but-2-ene (**18d**) were stirred in anhydrous THF for 3 d. After purification 0.43 g (95%) 2-(methyl-2-isoindole-1,3-dion)-3-[2-(2-isoindole-1,3-dion)ethyl]indole (**17g**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 3.30 (t, ^3J = 7.8 Hz, 2 H, CH_2), 4.00 (t, ^3J = 7.8 Hz, 2 H, CH_2), 5.05 (s, 2 H, CH_2), 7.03 (dd, ^3J = 7.0; 8.2 Hz, 1 H, CH), 7.13 (dd, ^3J = 7.0; 8.2 Hz, 1 H, CH), 7.28 (d, ^3J = 8.2 Hz, 1 H, CH), 7.66–7.70 (5 H, 5 × CH), 7.80–7.84 (4 H, 4 × CH), 8.68 (bs, 1 H, NH). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 23.2 (CH_2), 32.6 (CH_2), 38.7 (CH_2), 110.7 (C_q), 110.9 (CH), 119.1 (CH), 119.7 (CH), 122.7 (CH), 123.1 (2 × CH), 123.5 (2 × CH), 127.4 (C_q), 129.9 (C_q), 131.9 (2 × C_q), 132.2 (2 × C_q), 133.7 (2 × CH), 134.2 (2 × CH), 135.6 (C_q), 168.3 (2 × C_q), 168.4 (2 × C_q). **MS** (EI): m/z (%) = 449 (M^+, 13), 155 (46), 137 (100), 77 (23). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3400 (m), 3061 (w), 2930 (w), 1769 (m), 1708 (vs), 1394 (s), 1083 (m), 715 (s). **HR-MS** (EI): calculated for $C_{27}H_{19}N_3O_4$ 449.1376 g mol^{-1}; found: 449.1372 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

1,2,3,4-Tetrahydrocarbazole (22a). (a) Following general procedure A, 0.21 g (3.1 mmol) cyclopentene (**19a**) were stirred in anhydrous dioxane for 1 d. After purification 0.52 g (98%) 1,2,3,4-tetrahydrocarbazole (**22a**) were isolated. The spectroscopic data fits with the literature.[29]

(b) Following general procedure B, 0.23 g (3.1 mmol) cyclopentene (**19a**) were stirred in anhydrous dioxane for 1 d. After purification 0.50 g (95%) 1,2,3,4-tetrahydrocarbazole (**22a**) were isolated.

5,6,7,8,9,10-Hexahydrocyclohepta[b]indole (22b). Following general procedure A, 0.26 g (3.2 mmol) cyclohexene (**19b**) were stirred in anhydrous dioxane for 1 d (60 bar CO and 10 bar H_2). After purification 0.20 g (36%) 5,6,7,8,9,10-hexahydrocyclohepta[b]indole (**22b**) were isolated along with 0.09 g (15%) spiro[cyclohexan-1,3′-indoline] (**23b**). 5,6,7,8,9,10-Hexahydrocyclohepta[b]indole (**22b**): the spectroscopic data fits with the literature.[12]

5,6,7,8,9,10,11-Heptahydrocycloocta[b]indole (22c). Following general procedure A, 0.29 g (3.1 mmol) cycloheptene (**19c**) were stirred in anhydrous dioxane for 1 d. After purification 0.36 g (60%) 5,6,7,8,9,10,11-heptahydrocycloocta[b]indole (**22c**) were isolated along with 0.07 g (11%) spiro[cycloheptane-1,3′-indoline] (**23c**).

5,6,7,8,9,10,11-Heptahydrocycloocta[b]indole (**22c**): the spectroscopic data fits with the literature.[12]

5,6,7,8,9,10,11,12-Octahydrocyclononan[b]indole (22d). Following general procedure A, 0.33 g (3.0 mmol) cyclooctene (**19d**) were stirred in anhydrous dioxane for 1 d. After purification 0.45 g (70%) 5,6,7,8,9,10,11,12-octahydrocyclononan[b]indole (**22d**) were isolated along with 0.05 g (8%) spiro[cyclooctane-1,3′-indoline] (**23d**). 5,6,7,8,9,10,11,12-Octahydrocyclononan[b]indole (**22d**): **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.36–1.53 (6 H, 3 × CH_2), 1.70–1.80 (4 H, 2 × CH_2), 2.84 (t, ^3J = 6.2 Hz, 2 H, CH_2), 2.88 (t, ^3J = 6.2 Hz, 2 H, CH_2), 7.07–7.14 (2 H, 2 × C*H*), 7.29 (d, ^3J = 7.5 Hz, 1 H, C*H*), 7.51 (d, ^3J = 7.5 Hz, 1 H, C*H*), 7.64 (bs, 1 H, N*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 22.5 (*C*H_2), 24.8 (*C*H_2), 25.2 (*C*H_2), 25.6 (*C*H_2), 25.9 (*C*H_2), 26.9 (*C*H_2), 27.3(*C*H_2), 110.1 (*C*H), 112.2 (C_q), 117.9 (*C*H), 118.8 (*C*H), 120.8 (*C*H), 128.8 (C_q), 135.3 (C_q), 135.8 (C_q). **MS** (FAB): *m/z* (%) = 213 (M^+, 100), 214 (31), 171 (20), 143 (20), 130 (24), 117 (20). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3406 (vs), 3054 (s), 2922 (vs), 1682 (s), 1602 (s), 1456 (s), 1337 (s), 1169 (m), 739 (s). **HR-MS** (FAB): calculated for $C_{15}H_{19}N$ 213.1517 g mol^{-1}; found: 213.1535 g mol^{-1}.

5,6,7,8,9,10,11,12,13,14,15,16-Dodecahydrocyclotridecan[b]indole (22e). Following general procedure A, 0.51 g (3.0 mmol) cyclododecene (**19e**) were stirred in anhydrous dioxane for 1 d. After purification 0.72 g (89%) 5,6,7,8,9,10,11,12,13,14,15,16-dodecahydrocyclotridecan[b]indole (**22e**) were isolated: **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 1.10–1.35 (14 H, 7 × CH_2), 1.64–1.75 (4 H, 2 × CH_2), 2.66 (t, ^3J = 7.2 Hz, 2 H, CH_2), 2.70 (t, ^3J = 7.2 Hz, 2 H, CH_2), 7.03–7.10 (2 H, 2 × C*H*), 7.24 (dd, ^3J = 7.3; 7.5 Hz, 1 H, C*H*), 7.51 (d, ^3J = 7.3 Hz, 1 H, C*H*), 7.74 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 22.7 (*C*H_2), 24.2 (*C*H_2), 24.5 (*C*H_2), 25.7 (*C*H_2), 25.8 (*C*H_2), 26.1 (*C*H_2), 26.2 (*C*H_2), 26.3 (*C*H_2), 26.8 (*C*H_2), 27.2 (*C*H_2), 28.1 (*C*H_2), 110.1 (*C*H), 112.2 (C_q), 118.3 (*C*H), 118.8 (*C*H), 120.6 (*C*H), 129.2 (C_q), 135.0 (C_q), 135.2 (C_q). **GC-MS** (EI): *m/z* (%) = 269 (M^+, 100), 156 (25), 144 (67), 131 (34). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3384 (s), 2941 (vs), 2854 (s), 1655 (w), 1465 (m), 1241 (w), 749 (m). **HR-MS** (EI): calculated for $C_{19}H_{27}N$ 269.2143 g mol^{-1}; found: 269.2151 g mol^{-1}.

Spiro[cyclohexane-1,3′-indoline] (23b). Following general procedure B, 0.25 g (3.1 mmol) cyclohexene (**19b**) were stirred in anhydrous dioxane for 1 d. After purification 0.25 g (43%) spiro[cyclohexane-1,3′-indoline] (**23b**) were isolated. The spectroscopic data fits with the literature.[30]

Spiro[cycloheptane-1,3′-indoline] (23c). Following general procedure B, 0.29 g (3.1 mmol) cycloheptene (**19c**) were stirred in anhydrous dioxane for 1 d. After purification 0.36 g (59%) spiro[cycloheptane-1,3′-indoline] (**23c**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.57–1.89 (12 H, 6 × CH_2), 3.36 (s, 2 H, CH_2), 3.71 (bs, 1 H, N*H*), 6.67 (d, ^3J = 7.5 Hz, 1 H, C*H*), 6.77 (dd, ^3J = 7.2; 7.5 Hz, 1 H, C*H*), 7.06 (dd, ^3J = 7.2; 7.5 Hz, 1 H, C*H*), 7.17 (d, ^3J = 7.2 Hz, 1 H, C*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 23.9 (*C*H_2), 23.9 (*C*H_2), 29.9 (*C*H_2), 29.9 (*C*H_2), 39.3 (*C*H_2), 39.3 (*C*H_2), 48.7 (C_q), 59.2 (*C*H_2), 109.7 (*C*H), 118.8 (*C*H), 122.3 (*C*H), 127.1 (*C*H), 140.0 (C_q), 149.8 (C_q). **GC-MS** (EI): *m/z* (%) = 201 (M^+, 44), 144 (15), 131 (35), 130 (100), 117 (10), 77 (6). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3379 (m), 3028 (w), 2926 (vs), 2851 (s), 1606 (s), 1485 (s), 1261 (m), 740 (s). **HR-MS** (EI): calculated for $C_{14}H_{19}N$ 201.1517 g mol^{-1}; found: 201.1503 g mol^{-1}. **Elementary analysis** calculated for $C_{14}H_{19}N$: C: 83.53%, H: 9.51%, N: 6.96%; found: C: 83.61%, H: 9.43%, N: 6.94%.

Spiro[cyclooctane-1,3′-indoline] (23d). Following general procedure B, 0.33 g (3.0 mmol) cyclooctene (**19d**) were stirred in anhydrous dioxane for 1 d. After purification 0.58 g (90%) spiro[cyclooctane-1,3′-indoline] (**23d**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.50–1.78 (10 H, 5 × CH_2), 1.82 (dd, ^3J = 9.2 Hz, ^2J = 14.5 Hz, 2 H, CH_2), 1.97 (dd, ^3J = 9.0 Hz, ^2J = 14.5 Hz, 2 H, CH_2), 3.35 (s, 2 H, CH_2), 3.59 (bs, 1 H, N*H*), 6.66 (d, ^3J = 7.7 Hz, 1 H, C*H*), 6.75 (dd, ^3J = 7.5; 7.5 Hz, 1 H, C*H*), 7.05 (dd, ^3J = 7.5; 7.7 Hz, 1 H, C*H*), 7.13 (d, ^3J = 7.5 Hz, 1 H, C*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 23.3 (2 × *C*H_2), 25.0 (*C*H_2), 28.6 (2 × *C*H_2), 34.3 (2 × *C*H_2), 48.7 (C_q), 61.0 (*C*H_2), 109.8 (*C*H), 118.4 (*C*H), 123.1 (*C*H), 127.2 (*C*H), 138.4 (C_q), 150.2 (C_q). **MS** (FAB): *m/z* (%) = 215 (M^+, 100), 214 (36), 130 (37). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3381 (m), 3028 (w), 2918 (vs), 1606 (m), 1486 (s), 1234 (m), 1032 (m), 740 (s). **HR-MS** (FAB): calculated for $C_{15}H_{21}N$ 215.1674 g mol^{-1}; found: 215.1693 g mol^{-1}. **Elementary analysis** calculated for $C_{15}H_{21}N$: C: 83.67%, H: 9.83%, N: 6.50%; found: C: 83.71%, H: 9.72%, N: 6.52%.

Spiro[cyclododecane-1,3′-indoline] (23e). Following general procedure B, 0.51 g (3.1 mmol) cyclododecene (**19e**) were stirred in anhydrous dioxane for 1 d. After purification 0.38 g (47%) spiro[cyclododecane-1,3′-indoline] (**23e**) were isolated along with 0.30 g (38%) (**22e**). Spiro[cyclododecane-1,3′-indoline] (**23e**): **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 1.30–1.60 (20 H, 10 × CH_2), 1.86–1.93 (2 H, CH_2), 3.31 (s, 2 H, CH_2), 3.53 (bs, 1 H, N*H*), 6.67 (d, ^3J = 7.5 Hz, 1 H, C*H*), 6.72 (dd, ^3J = 7.5; 7.5 Hz, 1 H, C*H*), 7.03–7.07 (2 H, 2 × C*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 19.3 (*C*H_2), 19.3 (*C*H_2), 22.1 (*C*H_2), 22.1 (*C*H_2), 22.5 (*C*H_2), 22.5 (*C*H_2), 26.1 (*C*H_2), 26.5 (*C*H_2), 26.5 (*C*H_2), 31.5 (*C*H_2), 31.5 (*C*H_2), 47.7 (C_q), 60.0 (*C*H_2), 109.6 (*C*H), 118.1 (*C*H), 123.8 (*C*H), 127.1 (*C*H), 136.9 (C_q), 150.4 (C_q). **GC-MS** (EI): *m/z* (%) = 271 (M^+, 41), 144 (11), 131 (42), 130 (100). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3368 (vs), 3046 (w), 2933 (vs), 2846 (vs), 1606 (m), 1486 (vs), 1206 (m), 751 (vs). **HR-MS** (EI): calculated for $C_{19}H_{29}N$ 271.2300 g mol^{-1}; found: 271.2303 g mol^{-1}.

1′-Cyclohexylmethyl-spiro[cyclohexane-1,3′-indoline] (24b). Following general procedure B, (but with 2 eq. of the olefin) 0.58 g (7.1 mmol) cyclohexene (**19b**) were stirred in anhydrous dioxane for 1 d. After purification 0.37 g (44%) 1′-cyclohexylmethyl-spiro[cyclohexane-1,3′-indoline] (**24b**) were isolated: **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 0.90–1.05 (2 H, CH_2), 1.10–1.47 (6 H, 3 × CH_2), 1.50–1.90 (13 H, 6 × CH_2, C*H*), 2.85 (d, ^3J = 7.3 Hz, 2 H, CH_2), 3.23 (s, 2 H, CH_2), 6.42 (d, ^3J = 7.8 Hz, 1 H, C*H*), 6.64 (dd, ^3J = 7.0; 7.8 Hz, 1 H, C*H*), 7.02 (d, ^3J = 7.0 Hz, 1 H, C*H*), 7.08 (dd, ^3J = 7.0; 7.8 Hz, 1 H, C*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 23.1 (2 × *C*H_2), 25.8 (*C*H_2), 26.0 (2 × *C*H_2), 26.7 (*C*H_2), 31.4 (2 × *C*H_2), 36.5 (2 × *C*H_2), 37.1 (*C*H), 44.5 (C_q), 55.6 (*C*H_2), 63.8 (*C*H_2), 105.9 (*C*H), 116.3 (*C*H), 122.1 (*C*H), 127.5 (*C*H), 138.4 (C_q), 151.9 (C_q). **GC-MS** (EI): *m/z* (%) = 283 (M^+, 26), 201 (15), 200 (100), 144 (9), 77 (4), 55 (23). **IR**: $\tilde{\nu}$ [cm^{-1}] = 2924 (vs), 2851 (s), 1605 (s), 1491 (s), 1454 (m), 1368 (w), 1259 (m), 1021 (w), 741 (s). **Elementary analysis** calculated for $C_{20}H_{29}N$: C: 84.75%, H: 10.31%, N: 4.94%; found: C: 84.64%, H: 10.51%, N: 4.84%.

***N*-Cyclopentylmethylene-*N*′-phenylhydrazine (20a).** Following general procedure C, 0.14 g (2.0 mmol) cyclopentene (**19a**) were stirred in anhydrous THF. After evaporation 0.37 g (99%) *N*-cyclopentylmethylene-*N*′-phenylhydrazine (**20a**) as *E*/*Z*-isomers were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.53–1.79 (6 H, 3 × CH_2), 1.87–1.95 (2 H, CH_2), 2.79 (m, 1 H, C*H*), 6.84 (dd, ^3J = 7.5; 8.4 Hz, 1 H, C*H*), 7.01 (d, ^3J = 8.4 Hz, 2 H, 2 × C*H*), 7.03 (d, ^3J = 6.5 Hz, 1 H, C*H*=N), 7.14 (bs, 1 H, N*H*), 7.26 (dd, ^3J = 7.5; 8.4 Hz, 2 H, 2 × C*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 25.3 (2 × *C*H_2), 30.9 (2 × *C*H_2), 42.4 (*C*H), 112.5 (2 × *C*H), 119.4 (*C*H), 129.2 (2 × *C*H), 145.4 (*C*H=N), 145.5 (C_q). **MS** (FAB): *m*/*z* (%) = 189 (M + H$^+$, 80), 188 (M$^+$, 100), 92 (22), 77 (24). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3317 (m), 3053 (m), 2954 (s), 2867 (s), 1601 (vs), 1505 (s), 1445 (m), 1256 (s), 1116 (m), 749 (vs). **HR-MS** (FAB): calculated for $C_{12}H_{16}N_2$ 188.1313 g mol^{-1}; found: 188.1331 g mol^{-1}. Characteristic data for the isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 2.00–2.09 (2 H, CH_2), 2.88 (m, 1 H, C*H*), 6.53 (d, ^3J = 6.5 Hz, 1 H, C*H*=N), 7.07 (d, ^3J = 8.5 Hz, 2 H, 2 × C*H*).

***N*-Cyclohexylmethylene-*N*′-phenylhydrazine (20b).** Following general procedure C, 0.17 g (2.1 mmol) cyclohexene (**19b**) were stirred in anhydrous THF. After evaporation 0.42 g (100%) *N*-cyclohexylmethylene-*N*′-phenylhydrazine (**20b**) as *E*/*Z*-isomers were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.20–1.45 (5 H, 2 × CH_2, C*H*H), 1.68–1.94 (5 H, 2 × CH_2, CH*H*), 2.33 (m, 1 H, C*H*), 6.84 (dd, ^3J = 7.5; 8.5 Hz, 1 H, C*H*), 6.98 (d, ^3J = 5.2 Hz, 1 H, C*H*=N), 7.01 (d, ^3J = 7.5 Hz, 2 H, 2 × C*H*), 7.13 (bs, 1 H, N*H*), 7.26 (dd, ^3J = 7.5; 8.5 Hz, 2 H, 2 × C*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 25.6 (2 × *C*H_2), 26.1 (*C*H_2), 30.7 (2 × *C*H_2), 40.4 (*C*H), 112.5 (2 × *C*H), 119.4 (*C*H), 129.2 (2 × *C*H), 145.6 (C_q), 145.8 (*C*H=N). **MS** (FAB): *m*/*z* (%) = 202 (M$^+$, 100), 107 (59), 77 (63). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3305 (m), 3055 (w), 2936 (vs), 2852 (s), 1602 (vs), 1495 (s), 1449 (s), 1258 (s), 1121 (m), 749 (s). **HR-MS** (FAB): calculated for $C_{13}H_{18}N_2$ 202.1470 g mol^{-1}; found: 202.1496 g mol^{-1}. Characteristic data for the isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 2.54 (m, 1 H, C*H*), 6.40 (d, ^3J = 7.3 Hz, 1 H, C*H*=N), 7.07 (d, ^3J = 7.7 Hz, 2 H, 2 × C*H*).

***N*-Cycloheptylmethylene-*N*′-phenylhydrazine (20c).** Following general procedure C, 0.20 g (2.1 mmol) cycloheptene (**19c**) were stirred in anhydrous THF. After evaporation 0.45 g (100%) *N*-cycloheptylmethylene-*N*′-phenylhydrazine (**20c**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.52–1.79 (10 H, 5 × CH_2), 1.92–1.97 (2 H, CH_2), 2.50 (m, 1 H, C*H*), 6.84 (dd, ^3J = 7.3; 7.7 Hz, 1 H, C*H*), 7.01 (d, ^3J = 7.7 Hz, 2 H, 2 × C*H*), 7.03 (d, ^3J = 5.5 Hz, 1 H, C*H*=N), 7.10 (bs, 1 H, N*H*), 7.26 (dd, ^3J = 7.3; 7.7 Hz, 2 H, 2 × C*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 26.2 (2 × *C*H_2), 28.4 (2 × *C*H_2), 32.3 (2 × *C*H_2), 42.2 (*C*H), 112.5 (2 × *C*H), 119.4 (*C*H), 129.2 (2 × *C*H), 145.6 (C_q), 146.5 (*C*H=N). **MS** (FAB): *m*/*z* (%) = 216 (M$^+$, 100), 202 (34), 77 (16). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3398 (s), 3074 (w), 2929 (vs), 2855 (s), 1661 (s), 1602 (vs), 1496 (s), 1456 (m), 1099 (m), 766 (m). **HR-MS** (FAB): calculated for $C_{14}H_{20}N$ 216.1626 g mol^{-1}; found: 216.1634 g mol^{-1}. Characteristic data for the isomer: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.87–1.91 (2 H, CH_2), 2.65 (m, 1 H, C*H*), 6.48 (d, ^3J = 7.5 Hz, 1 H, C*H*=N), 7.07 (d, ^3J = 7.7 Hz, 2 H, 2 × C*H*).

Spiro[1′,3-cyclopentane-3*H*-indole] (21a). a) Following general procedure D, 0.40 g (2.1 mmol) *N*-cyclopentylmethylene-*N*′-phenylhydrazine (**20a**) were stirred in anhydrous THF at room temperature for 15 min. After column chromatography 0.13 g (36%) spiro[1′,3-cyclopentyl-3*H*-indole] (**21a**) were isolated.

b) Following general procedure D, 0.37 g (2.0 mmol) *N*-cyclopentylmethylene-*N*′-phenylhydrazine (**20a**) were stirred in anhydrous THF at room temperature for 30 min. After column chromatography 0.12 g (36%) spiro[1′,3-cyclopentyl-3*H*-indole] (**21a**) were isolated.

c) Following general procedure D, 0.37 g (2.0 mmol) *N*-cyclopentylmethylene-*N*′-phenylhydrazine (**20a**) were stirred in anhydrous THF at room temperature for 45 min. After column chromatography 0.11 g (31%) spiro[1′,3-cyclopentyl-3*H*-indole] (**21a**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.85–1.90 (2 H, CH_2), 2.00–2.15 (6 H, 3 × CH_2), 7.28 (d, ^3J = 8.0 Hz, 1 H, C*H*), 7.33–7.38 (2 H, 2 × C*H*), 7.64 (d, ^3J = 7.7 Hz, 1 H, C*H*), 8.10 (s, 1 H, C*H*=N). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 26.4 (2 × *C*H_2), 33.3 (2 × *C*H_2), 64.3 (C_q), 120.8 (*C*H), 121.3 (*C*H), 126.1 (*C*H), 127.4 (*C*H), 145.5 (C_q), 154.6 (C_q), 178.7 (*C*H=N). **MS** (FAB): *m*/*z* (%) = 172 (M + H$^+$, 74), 171 (M$^+$, 23), 155 (49), 137 (100). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3041 (w), 2944 (m), 2863 (m), 1600 (s), 1475 (s), 1456 (s), 1263 (m), 1162 (m), 735 (vs). **HR-MS** (FAB): calculated for $C_{12}H_{14}N$ 172.1126 g mol^{-1}; found: 172.1128 g mol^{-1}.

Preparation of 1,2,3,4-tetrahydrocarbazole (22a) *via* hydrazone. Following general procedure D, 0.40 g (2.1 mmol) *N*-cyclopentylmethylene-*N*′-phenylhydrazine (**20a**) were stirred in anhydrous THF at room temperature for 18 h. After column chromatography 0.36 g (98%) 1,2,3,4-tetrahydrocarbazole (**22a**) were isolated.

Spiro[1′,3-cyclohexane-3*H*-indole] (21b). Following general procedure D, 0.38 g (1.9 mmol) *N*-cyclohexylmethylene-*N*′-phenylhydrazine (**20b**) were stirred in anhydrous THF at room temperature for 18 h. After column chromatography 0.34 g (99%) spiro[1′,3-cyclohexane-3*H*-indole] (**21b**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.55–1.98 (10 H, 5 × CH_2), 7.27 (dd, ^3J = 7.2; 7.7 Hz, 1 H, C*H*), 7.37 (dd, ^3J = 7.2; 7.7 Hz, 1 H, C*H*), 7.42 (d, ^3J = 7.2 Hz, 1 H, C*H*), 7.67 (d, ^3J = 7.7 Hz, 1 H, C*H*), 8.37 (s, 1 H, C*H*=N). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 24.0 (2 × *C*H_2), 25.6 (*C*H_2), 31.7 (2 × *C*H_2), 58.3 (C_q), 121.2 (*C*H), 122.2 (*C*H), 125.8 (*C*H), 127.7 (*C*H), 144.6 (C_q), 149.3 (C_q), 178.3 (*C*H=N). **MS** (FAB): *m*/*z* (%) = 186 (M + H$^+$, 100), 185 (M$^+$, 53), 130 (21). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3045 (w), 3024 (w), 2930 (m), 1600 (s), 1451 (s), 749 (vs). **HR-MS** (FAB): calculated for $C_{13}H_{16}N$ 185.1283 g mol^{-1}; found: 185.1298 g mol^{-1}.

Preparation of 5,6,7,8,9,10-hexahydrocyclohepta[b]indole (22b) *via* hydrazone. Following general procedure D, 0.30 g (1.5 mmol) *N*-cyclohexylmethylene-*N*′-phenylhydrazine (**20b**) were stirred in anhydrous dioxane at reflux temperature for 3 h. After column chromatography 0.14 g (49%) 5,6,7,8,9,10-hexahydrocyclohepta[b]indole (**22b**) were isolated.

Spiro[1′,3-cycloheptane-3*H*-indole] (21c). Following general procedure D, 0.48 g (2.2 mmol) *N*-cycloheptylmethylene-*N*′-phenylhydrazine (**20c**) were stirred in anhydrous THF at room temperature for 1 d. After column chromatography 0.41 g (93%) spiro[1′,3-cycloheptane-3*H*-indole] (**21c**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.70–1.95 (12 H, 6 × CH_2), 7.25 (dd, ^3J = 7.2; 7.5 Hz, 1 H, C*H*), 7.31 (dd, ^3J = 7.5; 7.8 Hz, 1 H, C*H*), 7.39 (d, ^3J = 7.2 Hz, 1 H, C*H*), 7.60 (d, ^3J = 7.8 Hz, 1 H, C*H*), 8.17

(s, 1 H, C*H*=N). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 25.1 (2 × *C*H_2), 30.4 (2 × *C*H_2), 33.6 (2 × *C*H_2), 60.4 (*C*$_q$), 121.0 (*C*H), 121.6 (*C*H), 126.0 (*C*H), 127.5 (*C*H), 146.2 (*C*$_q$), 154.1 (*C*$_q$), 179.7 (*C*H=N). **MS** (FAB): *m*/*z* (%) = 200 (M + H$^+$, 100), 199 (M$^+$, 24), 130 (37). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3042 (w), 2925 (vs), 2851 (s), 1597 (s), 1474 (vs), 1247 (s), 1163 (m), 738 (s). **HR-MS** (FAB): calculated for $C_{14}H_{18}N$ 200.1439 g mol^{-1}; found: 200.1425 g mol^{-1}.

Preparation of 5,6,7,8,9,10,11-heptahydrocycloocta[b]indole (22c) *via* hydrazone. Following general procedure D, 0.43 g (2.0 mmol) *N*-cycloheptylmethylene-*N*′-phenylhydrazine (**20c**) were stirred in anhydrous THF at room temperature for 18 h. After column chromatography 0.17 g (43%) 5,6,7,8,9,10,11-heptahydrocycloocta[b]indole (**22c**) were isolated.

1,3-Ethylene-2,3,4,9-tetrahydro-1*H*-carbazole (26). Following general procedure A, 0.28 g (3.0 mmol) norbornene (**25**) were stirred in anhydrous THF for 1 d. After purification 0.42 g (71%) 1,3-ethylene-2,3,4,9-tetrahydro-1*H*-carbazole (**26**) were isolated. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 1.45 (m, 1 H, C*H*H), 1.75–1.79 (2 H, CH_2), 1.85–1.92 (2 H, CH_2), 2.03 (m, 1 H, CH*H*), 2.49 (d, ^2J = 15.8 Hz, 1 H, C*H*H), 2.67 (m, 1 H, C*H*), 3.06 (d, ^2J = 15.8 Hz, 1 H, CH*H*), 3.31 (m, 1 H, C*H*), 7.05–7.08 (2 H, 2 × C*H*), 7.24 (d, ^3J = 7.7 Hz, 1 H, C*H*), 7.49 (d, ^3J = 8.2 Hz, 1 H, C*H*), 7.63 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ [ppm] = 29.9 (*C*H_2), 32.5 (*C*H), 33.6 (*C*H), 34.1 (*C*H_2), 36.3 (*C*H_2), 37.4 (*C*H_2), 110.4 (*C*H), 117.3 (*C*H), 118.4 (*C*$_q$), 119.0 (*C*H), 120.5 (*C*H), 126.1 (*C*$_q$), 131.4 (*C*$_q$), 136.0 (*C*$_q$). **MS** (FAB): *m*/*z* (%) = 197 (M$^+$, 30), 156 (91), 138 (100), 89 (80). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3404 (m), 3054 (w), 2929 (vs), 1450 (m), 748 (s). **HR-MS** (EI): calculated for $C_{14}H_{15}N$ 197.1204 g mol^{-1}; found: 197.1196 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

5,11-Dihydro-6*H*-benzo[a]carbazole (28). 0.25 g (2.1 mmol) indene (**27**), 0.24 g (2.2 mmol) phenylhydrazine (**3**), 3 mg (0.5 mol%) Rh(acac)(CO)$_2$ and 0.16 g (10.1 mol%) BIPHEPHOS were diluted in 8 ml anhydrous THF, transferred to an autoclave and pressurised with 10 bar CO and 10 bar H_2. After stirring for 3 d at 100 °C the solvent was evaporated. The crude hydrazone was dissolved in 12 g, 4 wt% H_2SO_4 in anhydrous THF. After stirring the reaction mixture was washed with aqueous ammonia and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica to yield 0.16 g (37%) 5,11-dihydro-6*H*-benzo[a]carbazole (**28**). The spectroscopic data fits with the literature.[31]

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (29d). 2.54 g (10 mmol) *N*,*N*-diallyl-4-methylbenzenesulfonamide[32] and 0.40 g (5 mol%) Grubbs I-catalyst were dissolved in 30 ml anhydrous dichloromethane and stirred at room temperature for 1 h. The solvent was evaporated and the residue was recrystallised (CH_2Cl_2–cyclohexane) to yield 2.23 g (100%) 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (**29d**).[33]

3-Hydroxy-3-benzyloxymethyl-1,2,3,4-tetrahydrocarbazole (30a). Following general procedure A, 0.22 g (1.1 mmol) 1-benzyloxymethylcyclopent-3-ene-1-ol (**29a**) were stirred in anhydrous dioxane for 3 d. After purification 0.09 g (28%) 3-hydroxy-3-benzyloxymethyl-1,2,3,4-tetrahydrocarbazole (**30a**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.92 (m, 1 H, C*H*H), 2.05 (m, 1 H, CH*H*), 2.59 (bs, 1 H, O*H*), 2.60 (m, 1 H, C*H*H), 2.83 (s, 2 H, CH_2), 2.85 (m, 1 H, CH*H*), 3.49 (d, ^2J = 12.6 Hz, 1 H, C*H*H), 3.51 (d, ^2J = 12.6 Hz, 1 H, CH*H*), 4.56 (d, ^2J = 12.0 Hz, 1 H, C*H*H), 4.60 (d, ^2J = 12.0 Hz, 1 H, CH*H*), 7.06 (dd, ^3J = 7.5; 7.5 Hz, 1 H, C*H*), 7.10 (dd, ^3J = 7.5; 7.5 Hz, 1 H, C*H*), 7.21 (d, ^3J = 7.5 Hz, 1 H, C*H*), 7.27–7.36 (5 H, 5 × C*H*), 7.41 (d, ^3J = 7.5 Hz, 1 H, C*H*), 7.76 (bs, 1 H, N*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 19.9 (*C*H_2), 31.3 (2 × *C*H_2), 71.7 (*C*$_q$), 73.5 (*C*H_2), 76.5 (*C*H_2), 107.3 (*C*$_q$), 110.5 (*C*H), 117.6 (*C*H), 119.1 (*C*H), 121.2 (*C*H), 127.6 (*C*H), 127.7 (*C*$_q$), 127.8 (2 × *C*H), 128.4 (2 × *C*H), 132.6 (*C*$_q$), 136.3 (*C*$_q$), 138.0 (*C*$_q$). **MS** (FAB): *m*/*z* (%) = 307 (M$^+$, 100), 290 (12), 176 (25), 137 (46), 107 (17), 91 (51), 77 (14). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3520 (vs), 3331 (s), 3048 (w), 2893 (m), 1587 (w), 1452 (m), 1326 (s), 1117 (vs), 740 (vs). **HR-MS** (EI): calculated for $C_{20}H_{21}NO_2$ 307.1572 g mol^{-1}; found: 307.1559 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

3-Hydroxy-3-*tert*-butyl-1,2,3,4-tetrahydrocarbazole (30b). Following general procedure A, 0.28 g (2.0 mmol) 1-*tert*-butylcyclopent-3-ene-1-ol (**29b**) were stirred in anhydrous dioxane for 3 d. After purification 0.18 g (36%) 3-hydroxy-3-*tert*-butyl-1,2,3,4-tetrahydrocarbazole (**30b**) were isolated: **^{1}H-NMR** (400 MHz, DMSO): δ [ppm] = 1.01 (s, 9 H, C(CH_3)$_3$), 1.66 (m, 1 H, CH*H*), 1.93 (m, 1 H, C*H*H), 2.58 (d, ^2J = 16.0 Hz, 1 H, CH*H*), 2.60 (m, 1 H, CH*H*), 2.77 (d, ^2J = 16.0 Hz, 1 H, C*H*H), 2.83 (m, 1 H, C*H*H), 3.85 (bs, 1 H, O*H*), 6.90 (dd, ^3J = 7.5; 8.0 Hz, 1 H, C*H*), 6.97 (dd, ^3J = 7.5; 8.0 Hz, 1 H, C*H*), 7.23 (d, ^3J = 8.0 Hz, 1 H, C*H*), 7.32 (d, ^3J = 7.5 Hz, 1 H, C*H*), 10.58 (bs, 1 H, N*H*). **^{13}C-NMR** (100 MHz, DMSO): δ [ppm] = 19.6 (*C*H_2), 25.4 (3 × *C*H_3), 27.8 (*C*H_2), 28.2 (*C*H_2), 37.8 (*C*$_q$), 73.4 (*C*$_q$), 106.8 (*C*$_q$), 110.5 (*C*H), 116.9 (*C*H), 117.8 (*C*H), 119.8 (*C*H), 128.1 (*C*$_q$), 134.0 (*C*$_q$), 136.1 (*C*$_q$). **MS** (EI): *m*/*z* (%) = 243 (M$^+$, 36), 186 (26), 168 (18), 143 (100), 130 (17), 77 (12). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3538 (vs), 3290 (s), 2964 (m), 1626 (w), 1467 (w), 1384 (m), 1083 (m), 745 (s). **HR-MS** (EI): calculated for $C_{16}H_{21}NO$ 243.1623 g mol^{-1}; found: 243.1640 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

3,3-Diphenyl-1,2,3,4-tetrahydro-3-silylcarbazole (30c). Following general procedure A, 0.16 g (0.7 mmol) 1,1-diphenyl-1-silylcyclopent-3-ene (**29c**) were stirred in anhydrous dioxane for 3 d. After purification 0.09 g (39%) 3,3-diphenyl-1,2,3,4-tetrahydro-3-silylcarbazole (**30c**) were isolated: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.55 (t, ^3J = 6.7 Hz, 2 H, CH_2), 2.46 (s, 2 H, CH_2), 3.03 (t, ^3J = 6.7 Hz, 2 H, CH_2), 7.10–7.18 (2 H, 2 × C*H*), 7.27 (d, ^3J = 8.2 Hz, 1 H, C*H*), 7.33–7.42 (6 H, 6 × C*H*), 7.56–7.62 (5 H, 5 × C*H*), 7.63 (bs, 1 H, N*H*). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 5.0 (*C*H_2), 8.0 (*C*H_2), 21.5 (*C*H_2), 103.4 (*C*$_q$), 110.1 (*C*H), 117.9 (*C*H), 119.1 (*C*H), 121.4 (*C*H), 128.0 (4 × *C*H), 129.5 (2 × *C*H), 130.4 (*C*$_q$), 134.6 (4 × *C*H), 135.3 (*C*$_q$), 135.4 (*C*$_q$), 135.7 (2 × *C*$_q$). **MS** (FAB): *m*/*z* (%) = 339 (M$^+$, 65), 262 (10), 199 (20), 183 (100), 105 (13), 77 (6). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3410 (s), 3067 (w), 2894 (w), 1427 (s), 1326 (w), 1112 (s), 909 (m), 738 (vs). **HR-MS** (EI): calculated for $C_{23}H_{21}NSi$ 339.1443 g mol^{-1}; found: 339.1472 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

2-(Toluene-4-sulfonyl)-2,3,4,9-tetrahydro-1*H*-β-carboline (30d). 0.45 g (2.0 mmol) 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (**29d**), 0.22 g (2.0 mmol) phenylhydrazine (**3**) and 3 mg (0.5 mol%) Rh(acac)(CO)$_2$ were diluted in 8 ml anhydrous THF, transferred to an autoclave and pressurised with 50 bar CO and 20 bar H_2.

After stirring for 3 d at 100 °C the solvent was evaporated. The crude hydrazone was dissolved in 12 g, 4 wt% H_2SO_4 in anhydrous THF. After stirring for 3 h at reflux temperature the reaction mixture was washed with aqueous ammonia and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica to yield 0.64 g (98%) 2-(toluene-4-sulfonyl)-2,3,4,9-tetrahydro-1*H*-β-carboline (**30d**): **^{1}H-NMR** (500 MHz, DMSO): δ [ppm] = 2.34 (s, 3 H, CH_3), 2.65–2.73 (2 H, CH_2), 3.28–3.47 (2 H, CH_2), 4.25 (s, 2 H, CH_2), 6.93 (dd, ^3J = 7.3; 8.0 Hz, 1 H, C*H*), 7.02 (dd, ^3J = 7.3; 7.7 Hz, 1 H, C*H*), 7.27 (d, ^3J = 8.0 Hz, 1 H, C*H*), 7.31 (d, ^3J = 7.7 Hz, 1 H, C*H*), 7.40 (d, ^3J = 8.0 Hz, 2 H, 2 × C*H*), 7.69 (d, ^3J = 8.0 Hz, 2 H, 2 × C*H*), 10.78 (bs, 1 H, N*H*). **^{13}C-NMR** (125 MHz, DMSO): δ [ppm] = 20.9 (*C*H_2), 21.0 (*C*H_3), 43.4 (*C*H_2), 44.1 (*C*H_2), 106.3 (*C*$_q$), 111.2 (*C*H), 117.7 (*C*H), 118.7 (*C*H), 121.1 (*C*H), 126.3 (*C*$_q$), 127.3 (2 × *C*H), 129.3 (*C*$_q$), 130.0 (2 × *C*H), 133.7 (*C*$_q$), 136.0 (*C*$_q$), 143.7 (*C*$_q$). **MS** (FAB): *m*/*z* (%) = 327 (M + H$^+$, 25), 326 (M$^+$, 21), 155 (100). **IR**: $\tilde{\nu}$ [cm^{-1}] = 3390 (m), 3047 (w), 2909 (w), 1596 (m), 1451 (m), 1345 (s), 1165 (vs), 1092 (m), 746 (s). **HR-MS** (EI): calculated for $C_{18}H_{19}NO_2S$ 327.1167 g mol^{-1}; found: 327.1172 g mol^{-1}. Structure was clarified by 1D-NOESY experiments.

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