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Synthesis and Conformation of Chiral Biheteroaryls

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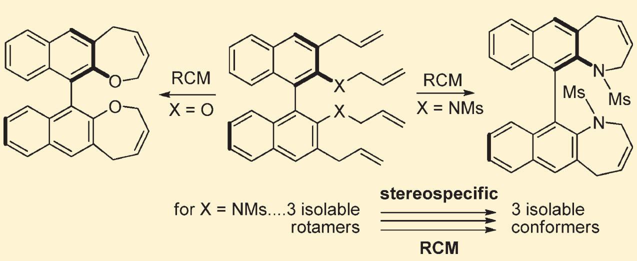
Ⓢ *Supporting Information*

ABSTRACT: Bridging 2,3 and 2′,3′ positions in 2,2′-dihydroxy-1,1′-binaphthyl and 2,2′-diamino-1,1′-binaphthyl, respectively, resulted in formation of chiral O- and N-bis-tricyclic compounds accessible in 4 steps from known 3,3′-diiodo precursors. In both cases, 2-fold ring closing metathesis of tetraallyl intermediates proceeded regioselectively to give tetrahydrobinaphtho[2,3-*b*]oxepine and -azepine, respectively. In case of the *N*-mesyl-*N*-allyl precursor, three, at room temperature separable, rotamers were isolated and characterized by NMR spectroscopy and X-ray structure determination. Their interconversion (process I) was followed by NMR, yielding rate constants and thermodynamic parameters. The rotamers with either C_1 or C_2 symmetry were stereospecifically cyclized to conformatively moderately stable bis-sulfonamides. Also in this case, the kinetics of their interconversion (process II) was investigated and from two of them the crystal structure was determined. Processes I and II were investigated by a DFT method, M06-2X, to gain insight into electronic and steric peculiarities responsible for the remarkable conformative stabilities. Transition state geometries and energies were calculated and compared with empirical data.



INTRODUCTION

Among atropisomeric biaryl structures, 2,2′-substituted 1,1′-binaphthyls deserve special attention due to their broad applicability as chiral ligands in transition metal-catalyzed transformations or as auxiliaries in asymmetric organo catalysis.[1] In cases where a high substrate specificity is desired, a tailored cavity is required, and its shape should be complementary in terms of steric as well as electronic interaction with the guest. An optimal fit will demand the introduction of rigid and conformationally mobile subunits.

With the aid of calculations a deeper understanding for the preferred conformations of host structures will enable a rational design of a chirally enveloped catalytic center. For synthetic access a modular approach with gradual variation of the three-dimensional structure is desired.

In a first step, we intended to extend the original binaphthyl structures with coordination sites at substituents in positions 2 and 2′ by introducing heterocyclic elements through bridging of positions 2 and 3, as well as 2′ and 3′ (Figure 1).[2] In the present paper, we describe a straightforward strategy to obtain seven-membered biheteroaryls with O and N heteroatoms via ortho-substitution of 2,2′-dihydroxy- and 2,2′-diamino-1,1′-binaphthyl and 2-fold ring closing metathesis (RCM) reaction as the key steps. Investigation of the mutual interaction of biaryl-halves concerning conformative stabilities and interconversions should be helpful to characterize the flexibility of novel heteroaromatic systems and evaluate their appropriateness for modeling a chiral sphere.

RESULTS AND DISCUSSION

Synthesis. The synthesis of O- or N-containing target structures bis(azaheteroaryls) and bis(oxaheteroaryls), respectively (Figure 1), can be performed from 2,2′-dihydroxy-1,1′-binaphthyl and 2,2′-diamino-1,1′-binaphthyl according to Schemes 1 and 2. (with $n = m = 1$, yielding compounds **6** and **12**, respectively). Strategies for synthesizing bicyclic oxa- and aza-compounds, consisting of a benzene ring, an annealed 5- to 8-membered heterocycle with varying degree of unsaturation, and the heteroatom adjacent to the benzene nucleus, are numerous.[3] Many syntheses start with thermic or Lewis acid-catalyzed Claisen rearrangements,[4] followed by *O*- or *N*-allylation or vinylation. Eventually, double bond shift precedes the concluding RCM step.[5] In this way, indole-, quinoline-, benzofurane-, chromene-, and azepine-type compounds were obtained.[6] An alternative

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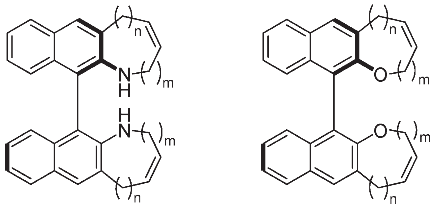
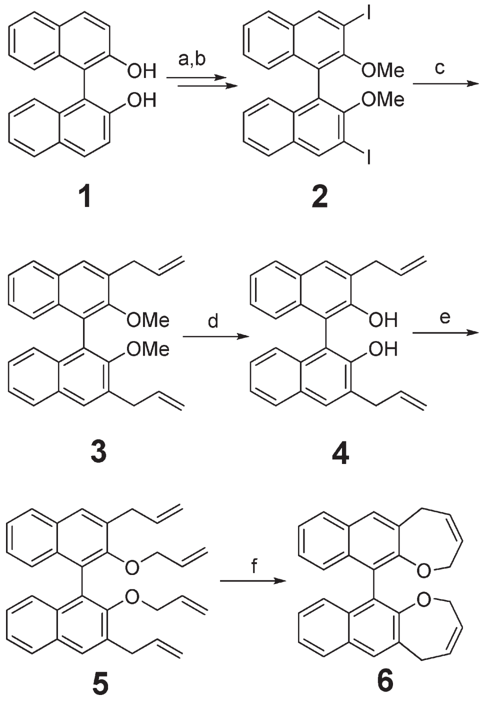


Figure 1. Chiral *N*- and *O*-bis-tricyclic compounds.

Scheme 1[a]

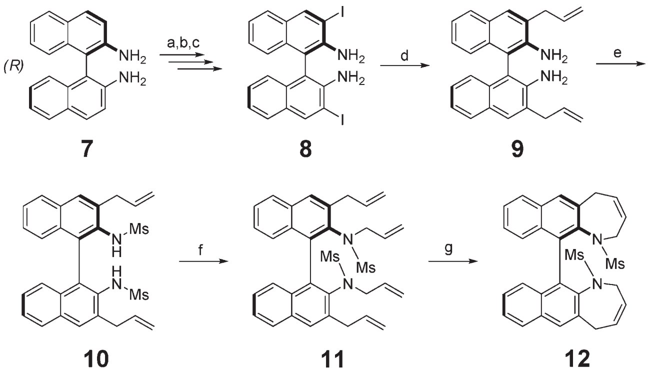


[a] Reagents and conditions: (a) MeI, K_2CO_3, acetone, reflux; (b) (i) *n*-BuLi/TMEDA, Et_2O, rt; (ii) I_2, −78 °C → rt; (c) allyltributylstannane, $Pd(PPh_3)_4$, reflux; (d) BBr_3, DCM, −78 °C; (e) allyl bromide, K_2CO_3, acetone, reflux; (f) Grubbs I (20 mol %), DCM, rt.

approach starts from *o*-halo phenol or *o*-halo amino aryl precursors which were cross-coupled with allyl or vinyl reagents (allyl-$B(OR)_2$, Bu_3Sn(allyl), Bu_3Sn(vinyl), etc.) by using a Suzuki or Stille protocol. Moreover, *o*-halo-substituted *N*-allyl arenes undergo an intramolecular Heck reaction affording cyclic products with an exocyclic double bond.[7] Since Claisen rearrangement of allylphenols requires harsh reaction conditions, not compatible with atropisomeric species, preference was given to a Stille coupling protocol[8] to access **3** from **2**. *O*-Protected binaphthol **1** was ortho-metalated and reacted with iodine following a known procedure to give **2** (79% from **1**).[9] Subsequent Stille-type coupling[8a,b,10] yielded the 3,3′-allylated intermediate **3** (41%).[6c,11] After demethylation with BBr_3 and *O*-allylation, the 2-fold RCM afforded **6** in 87% yield.

For the synthesis of the aza-analogue **12** the required 2,2′-diamino-3,3′-diiodo-1,1′-binaphthyl **8** was accessible from nonracemic diamino precursor (*R*)-**7** in 3 steps following published procedures[12] (overall yield 60%). Stille coupling of **8** with allyltributylstannane/$Pd(PPh_3)_4$ in toluene yielded **9** (67%), which was mesylated (**10**; 79%) and *N*-allylated to yield a mixture of separable atropisomers of **11** (69%, m.d., see below) which were separately cyclized to afford slowly interconverting conformers of **12** (50−60%).

Scheme 2[a]



[a] Reagents and conditions: (a) Raney-Ni, 2-PrOH/H_2O, reflux; (b) $BnMe_3N^+ICl_2^-$, DCM, rt; (c) DDQ, benzene, reflux; (d) allyltributylstannane, $Pd(PPh_3)_4$, reflux; (e) MsCl, DCM/py, 0 °C → rt; (f) allyl bromide, K_2CO_3, CH_3CN, reflux; (g) Grubbs I, DCM, rt.

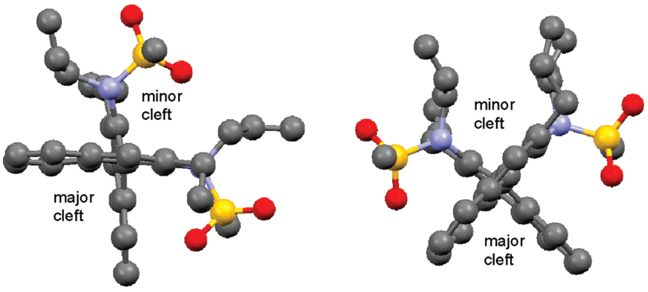


Figure 2. X-ray structures of **11A** (left) and **11B** (right).

Stereochemistry, Solid State Structure, and Conformational Stability of 11A/11B/11C. Since we expected that the presence of two stable precursors for the RCM should have consequences on the geometry of the hetero rings in **12**, a more detailed investigation of the tetraallyl compounds **11** was performed. When refluxing **10** with an excess of allyl bromide/K_2CO_3 in acetonitrile for 48 h under Ar, TLC indicated complete consumption of starting material and the formation of comparable amounts of two (main) products. After standard workup, chromatographic separation yielded two crystalline compounds **11A** and **11B**. MS showed nearly identical spectra (ESI), while NMR spectra displayed C_1 symmetry for **11A**, but C_2 symmetry for **11B**. Their ratio as obtained from the reaction was approximately 2:1.

Crystal structure analyses of both species were performed showing two atropisomers which differ in the relative orientation of *N*-allyl groups (Figure 2). While in **11A** one *N*-allyl substituent is directed toward the opposite mesyl group in the "minor cleft" and the second one is directed to the rear side of the binaphthyl, in **11B** both *N*-allyl groups point likewise into the minor cleft thus corresponding to the observed C_2 symmetry.

Careful repetition of the synthesis on a larger scale showed that from the reaction mixture also a third conformer can be isolated in 2−4%, which also displayed C_2 symmetry in NMR and which is most likely the missing conformer **11C** with both mesyl substituents located in the minor cleft. If the reaction was stopped

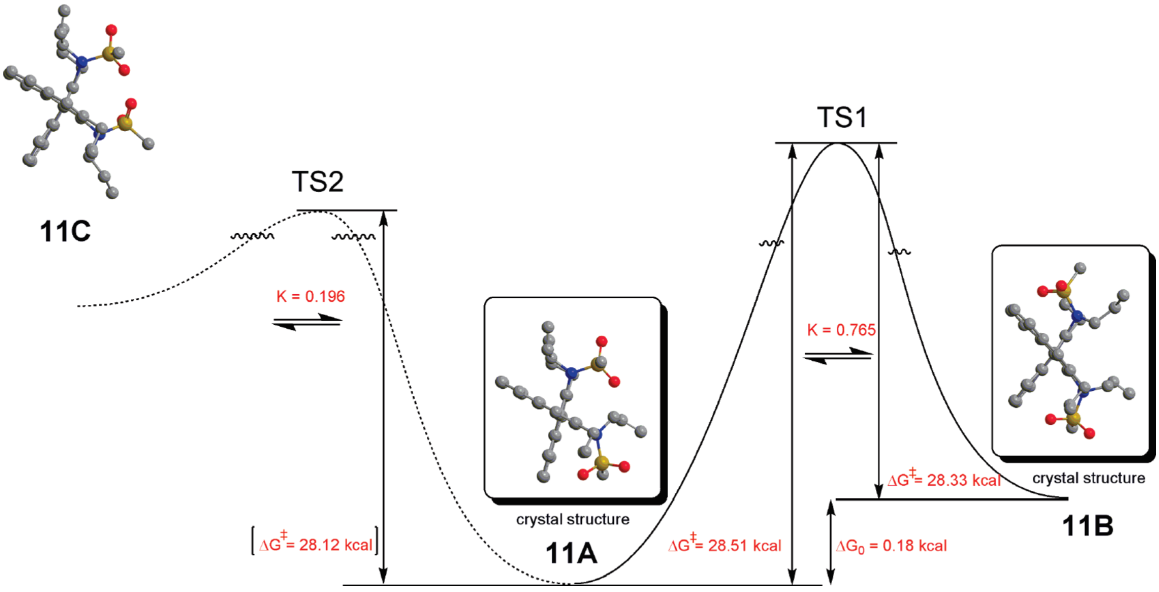


Figure 3. Interconversion of conformers of **11** based on kinetics at 333 K in toluene.

Table 1. Experimental Data for the Interconversion of Conformers of 11

$$\mathbf{11C} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathbf{11A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{11B}$$

equilibrium (rel%): 10 51 39

equilibrium constants: $K_{CA} = 0.196 = k_4/k_3$ $K_{BA} = 0.765 = k_1/k_2$

rate constants (at 335K): $k_1 = 1.74\ (\pm 0.1) \times 10^{-6}\ s^{-1}$
$k_2 = 2.29\ (\pm 0.1) \times 10^{-6}\ s^{-1}$
$k_3 = 1.6\ (\pm 0.4) \times 10^{-5}\ s^{-1}$
$k_4 = 3.0\ (\pm 0.5) \times 10^{-6}\ s^{-1}$

	$\Delta G^{\ddagger}$, kcal·mol^{-1} (kJ·mol^{-1})	$\Delta H^{\ddagger}$, kcal·mol^{-1} (kJ·mol^{-1})	$\Delta S^{\ddagger}$, cal·mol^{-1}·T^{-1} (J·mol^{-1}·T^{-1})	E_a,[a] kcal·mol^{-1} (kJ·mol^{-1})
11A → 11B	28.51 (119.4)	30.81 (129.0)	6.9 (29)	31.48 (131.8)
11B → 11A	28.33 (118.6)	30.69 (128.5)	7.0 (29)	31.75 (132.9)

[a] Based on Arrhenius plots for T = 335−345 K, with R^2 = 0.992.

after 24 h, up to 11% of **11C** were isolated. This isomer (70−80% purity) as obtained by chromatography did not crystallize, and due to its observed sensitivity to heating, no further purification attempts have been made. Its structure was confirmed (i) by its appearance in the equilibrated mixture from kinetic experiments and (ii) crystal structure of **12C** derived therefrom by RCM (see below).

While at room temperature in solution no interconversion of sulfonamides was observed, the equilibration processes at elevated temperature could be conveniently followed by ^{1}H NMR. Keeping separate samples of **11A** and **11B** in toluene-d_8 for 24 h at 363 K resulted in the same equilibrium mixture of **11A**:**11B**:**11C** = 51:39:10 (Figure 3). Kinetic measurements starting from samples of the main rotamers were performed at T = 335−345 K and rate constants k_1−k_4 for reversible reactions **11B** ⇄ **11A** ⇄ **11C** were determined by using the iteration facility "solver" provided within the program Excel (Microsoft). Results are summarized in Table 1.

Stereochemistry, Solid State Structure, and Conformational Stability of 12A/12B/12C. With separate fractions of all conformers in hand, it was obvious to investigate the stereo/regioselectivity of a (2-fold) RCM reaction. Samples of **11A**, **11B**, and **11C** were treated with Grubbs I catalyst in DCM at room temperature yielding stereospecifically either **12A** (52%) with C_1 symmetry from **11A**, or **12B** (62%) as well as **12C** (60%) both with C_2 symmetry from **11B** and **11C**, respectively. It is noteworthy that all steroisomers could be purified by chromatography at rt without interconversion as evidenced by TLC and ^{1}H NMR. The crystal structures of **12A** and **12C** were determined showing envelope-type geometry of seven-membered *N*-cycles with both *N*-mesyl groups in *pseudo-axial* position, but with different orientation in **12A** and **12C** (Figure 4).

A projection along the biaryl axis shows a surprisingly high degree of conformative similarity between substrate **11A** and product **12A** (see Figures 2 and 4). This explains reasonably the ease and selectivity of RCM requiring only minimal

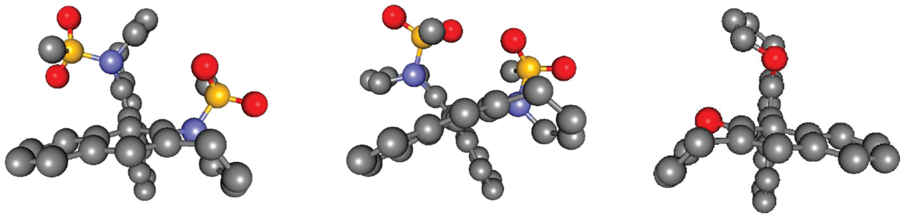


Figure 4. X-ray structures of **12A** (left), **12C** (center), and **6** (right).

Table 2. Experimental Data for the Interconversion of Conformers of 12

$$\mathbf{12A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{12B}$$

equilibrium (rel%): 60.5 39.5

equilibrium constants: $K_{BA} = 0.653 = k_1/k_2$

rate constants (at 334 K): $k_1 = 1.32\ (\pm 0.3) \times 10^{-5}\ s^{-1}$
$k_2 = 2.02\ (\pm 0.3) \times 10^{-5}\ s^{-1}$

	$\Delta G^{\ddagger}$, kcal·mol^{-1} (kJ·mol^{-1})	$\Delta H^{\ddagger}$, kcal·mol^{-1} (kJ·mol^{-1})	$\Delta S^{\ddagger}$, cal·mol^{-1}·T^{-1} (J·mol^{-1}·T^{-1})	E_a,[a] kcal·mol^{-1} (kJ·mol^{-1})
12A → **12B**	27.05 (113.3)	25.05 (104.9)	−6 (25)	25.71 (107.6)
12B → **12A**	26.77 (112.1)	25.08 (105.0)	−5 (21)	25.74 (107.8)

[a] Based on Arrhenius plots for T = 328−341 K, with R^2 = 0.986.

conformational changes to proceed. For comparison, also the crystal structure of the corresponding oxa-analogue **6** was determined (Figure 4). In contrast, in the case of the oxa-cycle no further conformers could be detected. Since **6** displays C_2 symmetry in the ^{1}H NMR spectrum but crystallizes in C_1 symmetrical conformation, it is concluded that the benzooxepine moiety is highly flexible (no line broading in NMR at 320 K). It may be speculated that the C_1-symmetrical species is also in this case slightly more stable (see below). Apart from different biaryl angles in **12A** (99°) and **6** (87°) which may be attributed to steric repulsion of the *N*-mesyl substituent in the minor cleft with the opposite aza-cycle, a largely similar geometry is observed in the solid state.

Similar to **11A**/**11B** also isomers **12A**/**12B** showed slow interconversion, which also could be followed by ^{1}H NMR in a temperature range of 328−341 K. Equilibration in toluene (48 h at 360 K) gave a **12A**/**12B** ratio of 60.5:39.5. No signals due to isomer **12C** were detected. Results are summarized in Table 2.

When comparing the two transformations **11A**−**11B** vs **12A**−**12B**, the process of rotation converting **11A** into **11B** required ca. 1.5 kcal more energy than a combined ring-flip/*N*-mesyl-interconversion of **12A**/**12B**. A positive activation entropy was found in the former (7 cal·mol^{-1}·T^{-1}), a negative one in the latter case (ca. −6 cal·mol^{-1}·T^{-1}).

NMR Assignment and Solution Geometry of 11A/11B and 12A/12B. 11A: Solvent-dependent shift differences are pronounced (see the Supporting Information). While in toluene-d_8 the MeSO$_2$ groups are nearly isochronous, a shift difference of >0.1 ppm is observed in CDCl$_3$. A complete assignment of the ^{13}C shifts from HSQC and HMBC was hampered by small shift differences for corresponding signals of the *exo*- and *endo*-mesyl unit in the ^{13}C NMR, typically less than 0.3 ppm. Their partial assignment (Figure 5) was, therefore, only possible based on COSY and NOESY spectra. The labeling of selected NOE's between the ^{1}H NMR signals is indicated by green arrows in Figure 6, with different colors for the *exo*- and *endo*-mesyl units. All four allyl groups could be identified by shift correlation. The link of C-allyl fragments to aromatic protons H-4′ and H-4 is evidenced through $^4J_{H-H}$ coupling with H-12′a and H-12a, respectively, as well as by several NOE's, which are indicated in Figure 6. Protons H-4′ and H-4 show further scalar $^4J_{H-H}$ couplings and dipolar interactions with the aromatic protons H-5′ and H-5, respectively. These couplings are clearly detectable in spite of very similar chemical shifts. Hence, they allow the identification of the linkages to the according aromatic moieties.

From the NOESY spectrum the orientation of the out-of-plane mesyl groups was also unambiguously elucidated. The *exo*-mesyl group (A) gives a cross peak with H-8′, while the *endo*-mesylate displays NOE's with multiplets of H-11′a, H-11′b, and H-9′a (Figure 6). Moreover, the signal of H-9′ shows a NOE on H-8, thus confirming the above assignment. Pronounced NOE's of proton in both C-3 and C-3′ bound allyl fragments (H-12a, H-12b, H-13 and H-12′a, H-12′b, H-13′) can be detected to H-4 and H-4′, respectively (Figure 6). They point to similar out-of-plane conformations.

11B: All proton signals could be assigned unequivocally (see the Supporting Information). Not unexpectedly the ^{1}H NMR is very similar to the *exo*-mesyl unit of **11A** ($\Delta\delta$ = 0.0−0.1 ppm), merely H-8 (7.45, +0.27 ppm) and H-9 (3.71, −0.30 ppm) are affected through the changed orientation of the MeSO$_2$ in the opposite naphthyl fragment. But this effect for H-8 is significantly smaller than in the *endo*-mesyl unit of **11A** (7.61 ppm), which might be explained by a decreased biaryl angle in **11B**.

12A: For the C_1-symmetrical bis-heteroaryl **12A** all ^{1}H and by far all ^{13}C resonances could be assigned by using the standard 2D

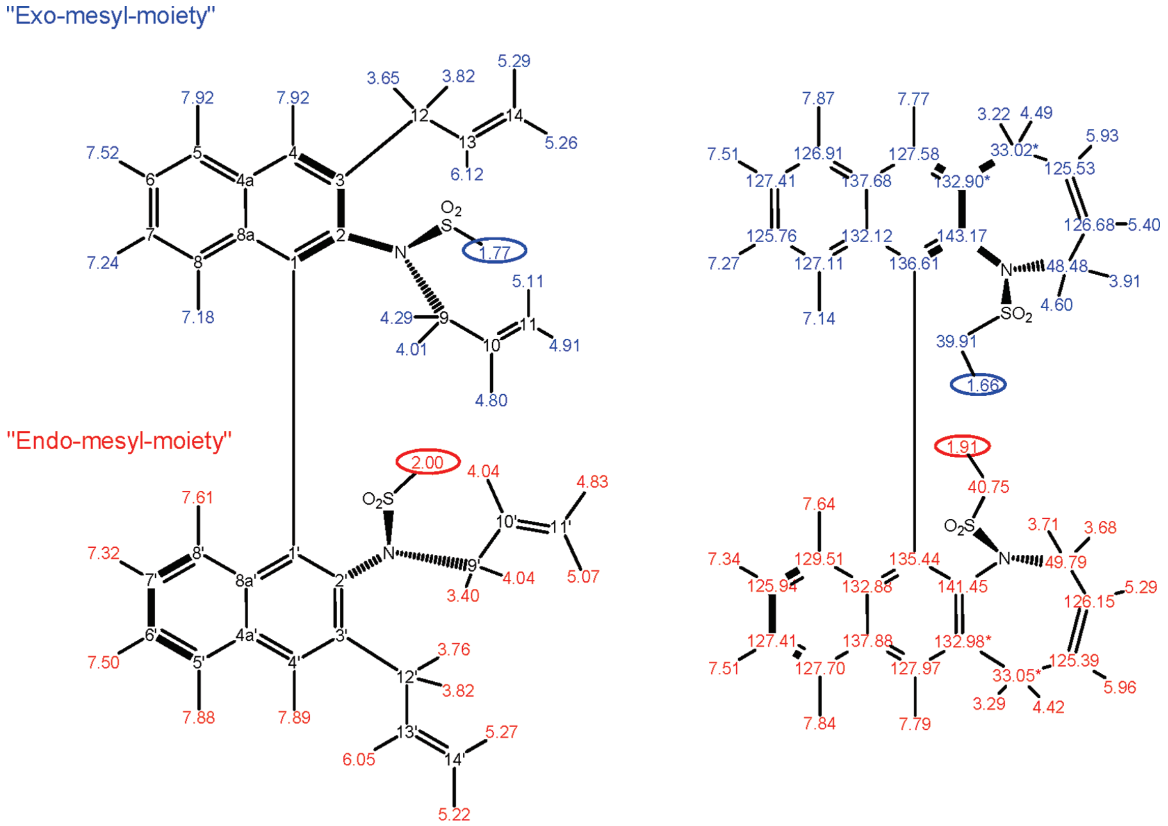


Figure 5. Shift values from ^{1}H and ^{13}C NMR spectra in CDCl$_3$ of **11A** (left) and **12A** (right).

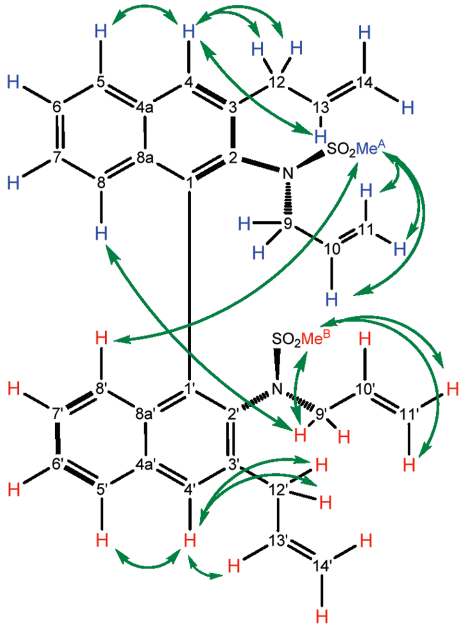


Figure 6. ^{1}H NMR shift assignment of **11A** in CDCl$_3$ (blue labels for the *exo*-mesyl moiety, red ones for the *endo*-mesyl moiety) as well as selected NOE's (green arrows).

NMR techniques. While shift differences of aromatic protons in **11A** and **12A** are negligible, the conformationally rigid fragment N−C9−C10−C11−C12 in **12A** differs significantly from that of the tetraallyl precursor **11A**.

12B: Similarly, for the C_2-symmetrical isomer **12B**, complete assignment of signals was possible (see the Supporting Information). A NOE of the MeSO$_2$ with H-8 confirmed the *exo*-mesyl geometry.

Calculations. For molecular calculations the density functional, M06-2X,[13] as implemented in the GAUSSIAN09 suite of programs,[14] has been used, because this method is well-suited for the description of molecules in which intramolecular dispersion contributions play an important role. Throughout, the 6-31G(d, p) basis set was used.

11A/11B/11C: Three global minima were found for each of the atropisomers **11A**, **11B**, and **11C**. The overall global minimum was found for **11A**. The deepest energy minimum of rotamer **11B** was estimated with 0.97 kcal·mol^{-1} higher than **11A**, that for **11C** was found to be 3.4 kcal·mol^{-1} higher with respect to **11A**. In addition to these energy minima, several local minima were found with slightly different orientations of the allyl groups. In Figure 7, the superposition of several sampled local minima and the global minimum is depicted. Comparison with experimental data showed that relative stabilities are fairly reproduced but energy differences are by trend too high (**11A**:**11B**:**11C**, exptl 51:39:10, calcd 81:18:1). We attribute this discrepancy to the coexistence of several "allyl-conformers" within each rotamer.

As can be seen, the position of the binaphthyl ring system as well as the position of the sulfonamide groups are the same in all conformations, whereas various orientations of the allyl groups are observed. Due to the presence of several energy minima for the conformers **11A**, **11B**, and **11C**, many individual transition states could be found by estimating the rotational barriers of the rotatable single bonds, and on average a transition energy range of 25−30 kcal·mol^{-1} was calculated.

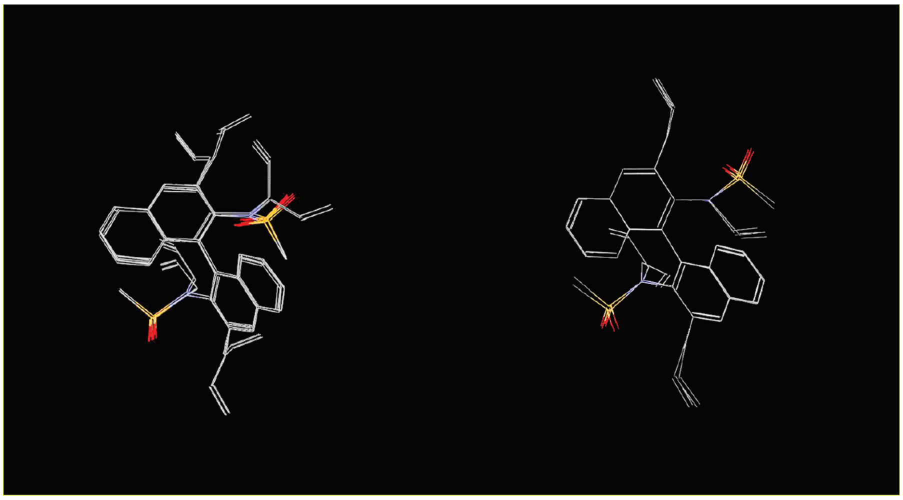


Figure 7. Superposition of minimum energy conformers of **11A** (left) and **11B** (right).

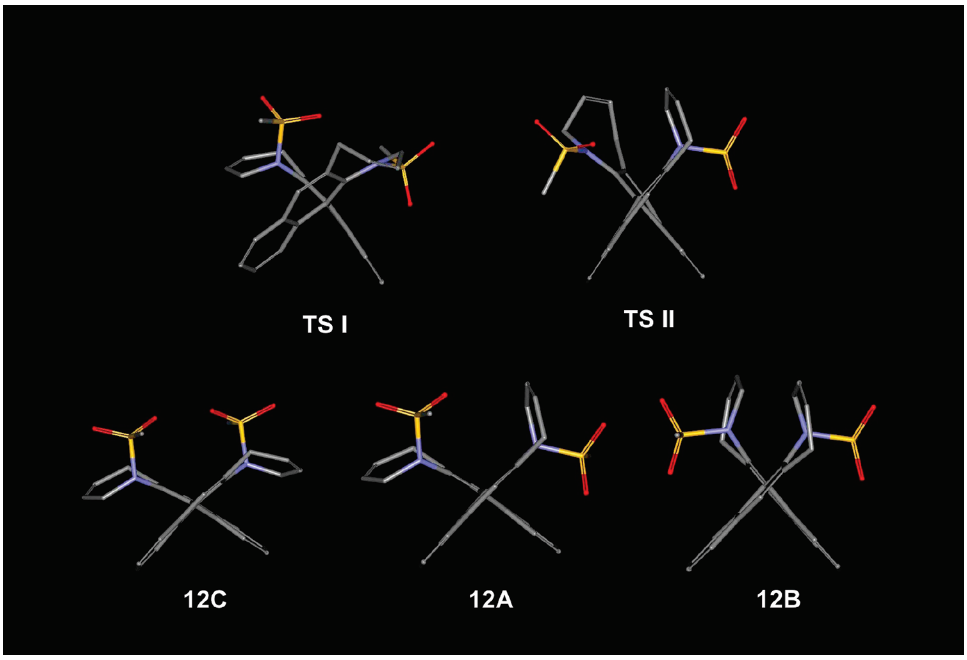


Figure 8. Minimum energy conformers of **12A**–**12C** (bottom) and corresponding transition state geometries (top).

The relative stabilities of heterocycles **12A**/**12B**/**12C** (Figure 8) largely parallel those of their precursors. As before, the C_1-symmetrical species **12A** is the most stable one. On the basis of calculated energy differences $\Delta E = 0.34$ kcal·mol^{-1} for **12B** and $\Delta E = 2.01$ kcal·mol^{-1} for **12C** relative equilibrium concentrations can be estimated which are in fair agreement with the experimental data (**12A**:**12B**:**12C**, exptl 60.5:39.5:0, calcd 61:36:3).

For these interconversions, formally two synchronous processes are assumed to agree with the observed geometry/symmetry of conformers. To transform **12A**, for which *pseudo-axial* mesyl substituents were established by X-ray analysis, into **12B**, the inversion of the *exo*-boat into the *endo*-boat conformation would move the mesyl group in an equatorial position. Since this hypothetic intermediate has C_1 symmetry, this must be accompanied by a *N*-inversion ending up with the C_2-symmetrical species **12B**. Consequently, transition state geometries display nearly planar nitrogen. While for the process **12A** → **12B** via TS II $\Delta E^{\ddagger} \approx 30$ kcal·mol^{-1} was calculated, a significantly higher energy is required to reach **12C** from **12A** via TS I ($\Delta E^{\ddagger} \approx 38$ kcal·mol^{-1}). The apparent bending of the biaryl axis in TS I may be responsible for the higher activation energy and reasonably explains the fact that no trace of **12C** was detected in equilibrium mixtures originating from heating **12A** or **12B** (48 h, 360 K).

■ CONCLUSIONS

In summary, a stereospecific 2-fold RCM of conformationally stable C_{ar}–N rotamers led to conformers of bis(azaheteroaryls). From both, substrates and products, all interconverting species could be isolated and characterized at room temperature and the kinetics of interconversion at elevated temperature was followed by NMR. Activation energies of 28.51 and 28.33 kcal·mol^{-1} were found for the rotational barriers **11A** and **11B**, respectively, while the process of a boat–boat interconversion accompanied by *N*-inversion, as expected for the mutual transformation of **12A**/**12B**, required 27.05 and 26.77 kcal·mol^{-1}, respectively. Solid state structures of **11A**, **11B**, **12A**, and **12C** confirmed the configurational assignment, and 2D NMR investigations indicated that a largely similar geometry is maintained in solution. A positive reaction entropy, calculated for the first process, can be rationalized through the coexistence of several species subdividing each C–N rotamer with a different geometry of allyl substituents and comprising a broad range of transition states, while the negative reaction entropy calculated in the second process is in agreement with the higher rigidity of the seven-membered *N*-heterocycles **12** and a higher degree of order in the corresponding transition state.

■ EXPERIMENTAL SECTION

General. Melting points: Kofler melting point apparatus, uncorrected. NMR: recorded at 400.27 MHz (^{1}H) and 100.66 MHz (^{13}C), respectively. Chemical shifts δ are reported in ppm; for ^{1}H relative to residuals nondeuterated solvent signals (chloroform-*d*: 7.24, toluene-d_8: 2.08 ppm), for ^{13}C to CDCl$_3$ at 77.00 ppm, or CD$_3$C$_6$D$_5$ at 21.40 ppm, respectively. Coupling patterns are designated as s (singlett), d (doublett), t (triplett), q (quartet), m (multiplet), p (pseudo), and br (broad). ^{13}C{^{1}H} NMR spectra are recorded in a *J*-modulated mode; signals are assigned as C, CH$_2$, and CH$_3$; undesignated signals refer to CH-resonances. MS: ESI or EI (70 eV).

n-Hexane, dichloromethane (DCM), and ethyl acetate (EtOAc) were distilled, absolute THF from sodium benzophenone ketyl, Et$_2$O from LiAlH$_4$; toluene, DCM abs., and acetonitrile from CaH$_2$; *n*-BuLi was used as a 1.6 M solution in *n*-hexane. All the other chemicals were analytical grade and were used without further purification. Column chromatography was performed on SiO$_2$, 40–63 μm. Reported procedures have been followed to obtain 3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthyl[9] and 2,2′-diamino-3,3′-diiodo-1,1′-binaphthyl.[12]

***rac*-3,3′-Diallyl-2,2′-dimethoxy-1,1′-binaphthyl, 3.** To a degassed solution of diiodide **2** (283 mg, 0.5 mmol) in toluene (3 mL) was added Pd(PPh$_3$)$_4$ (58 mg, 10 mol %) and allyltributylstannane (433 μL, 1.5 mmol) and the solution was refluxed for 24 h. After cooling in an ice bath the reaction was quenched with water. The aqueous layer was extracted with toluene (4 × 2 mL) and the combined extracts were dried (MgSO$_4$). The solvents were evaporated and the residue was dissolved in MeOH (2 mL). To this solution was added KF (40 mg) and the precipitate formed was separated. The procedure was repeated and the crude product was purified by chromatography (SiO$_2$, *n*-hexane/EtOAc, 95:5) to give 132 mg (67%) of **3** as an oil: ^{1}H NMR (CDCl$_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.78 (s, 2H), 7.35 (ddd, *J* = 8.1, 5.6, 1.4 Hz, 2H), 7.18 (ddd, *J* = 7.9, 5.6, 1.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.16 (m, 2H), 5.15–5.20 (m, 4H), 3.67 (br d, *J* = 6.7 Hz, 4H), 3.26 (s, 6H) ppm; ^{13}C NMR (CDCl$_3$) δ 155.2 (C), 137.1, 133.6 (C), 133.3 (C), 130.7 (C), 129.2, 127.5, 125.7, 125.7, 124.7 (C), 124.6, 116.2 (CH$_2$), 60.7 (CH$_3$), 34.8 (CH$_2$) ppm; HRMS (EI, 30 °C) calcd for C$_{28}$H$_{26}$O$_2$: 394.1933, found 394.1935.

***rac*-3,3′-Diallyl-1,1′-binaphthyl-2,2′-diol, 4.** Dimethoxy compound **3** (128 mg, 0.324 mmol) was dissolved in DCM (5 mL) and the mixture was cooled to −78 °C. At the same temperature BBr$_3$ (112 μL, 1.17 mmol, 3.6 equiv) was added dropwise and stirring was continued for 30 min. The reaction was slowly warmed to rt and stirred for 4 h. After quenching with water at 0 °C the mixture was extracted with DCM (3 × 5 mL) and the organic phase was washed with brine and dried (MgSO$_4$). Chromatographic purification (SiO$_2$, *n*-hexane/DCM, 50:50) afforded 75 mg (61%) of **4** as a pale yellow foam: ^{1}H NMR (CDCl$_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.80 (s, 2H), 7.33 (m, 2H), 7.24 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.16 (ddpt, *J* = 17.0, 10.2, 6.6 Hz, 2H), 5.19 (dm, *J* = 17.0 Hz, 2H), 5.17 (dm, *J* = 10.1 Hz, 2H), 5.12 (m, 2H), 3.64 (br d, *J* = 6.6 Hz, 4H) ppm; ^{13}C NMR (CDCl$_3$) δ 151.5 (C), 136.2, 132.3 (C), 130.2, 129.5 (C), 129.0 (C), 127.9, 126.7, 124.0 (2× CH), 116.4 (CH$_2$), 111.0 (C), 34.9 (CH$_2$) ppm; HRMS (ESI) calcd for C$_{26}$H$_{21}$O$_2$ 365.1542 ([M + H]$^{+}$), found 365.1538 ([M + H]$^{+}$).

***rac*-3,3′-Diallyl-2,2′-bis(allyloxy)-1,1′-binaphthyl, 5.** Diol **4** (75 mg, 0.21 mmol) was dissolved in acetone p.a. (10 mL), K$_2$CO$_3$ (113 mg, 0.84 mmol, 4 equiv) was added, and the mixture was degassed. After adding dropwise allyl bromide (54 mg, 0.63 mmol, 3 equiv) the reaction was refluxed for 20 h and the bulk of the solvent was evaporated. Workup with water/EtOAc was followed by chromatographic purification (SiO$_2$, *n*-hexane/DCM, 30:70) to yield 66 mg (72%) of **5** as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 2H), 7.35 (ddd, *J* = 8.0, 6.6, 1.5 Hz, 2H), 7.18 (ddd, *J* = 8.6, 6.6, 1.3 Hz, 2H), 7.13 (bd, *J* = 8.5 Hz, 2H), 6.15 (m, 2H), 5.47 (ddpt, *J* = 17.1, 10.5, 5.6 Hz, 2H), 5.18 (m, 2H), 5.15 (m, 2H), 4.82 (m, 2H), 4.79 (m, 2H), 4.05 (ddpt, *J* = 12.2, 5.7, 1.3 Hz, 2H), 3.80 (ddpt, *J* = 12.3, 5.5, 1.4 Hz, 2H), 3.66 (m, 4H) ppm; ^{13}C NMR (CDCl$_3$) δ 154.6 (C), 137.2, 133.9, 133.8 (C), 133.3 (C), 130.7 (C), 129.1, 127.5, 125.8, 125.7, 125.1 (C), 124.6, 116.6 (CH$_2$), 116.2 (CH$_2$), 74.1 (CH$_2$), 34.9 (CH$_2$) ppm; HRMS (EI, 30 °C) calcd for C$_{32}$H$_{30}$O$_2$ 446.2246, found 446.2247.

***rac*-2,2′,5,5′-Tetrahydro-11,11′-binaphtho[2,3-b]oxepine, 6.** The tetraallyl compound **5** (45 mg, 0.1 mmol) was dissolved in DCM (3 mL) under argon. A solution of Grubbs I catalyst (16.5 mg, 20 mol %) in DCM (2 mL) was added with a syringe pump during 10 h. After removal of solvent the crude mixture was chromatographed (SiO$_2$, *n*-hexane/EtOAc, 95:5) to give 34 mg (87%) of **6**: mp 197–199 °C; ^{1}H NMR (CDCl$_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.69 (s, 2H), 7.35 (ddd, *J* = 7.9, 6.6, 1.1 Hz, 2H), 7.17 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.11 (d, *J* = 8.4 Hz), 5.91 (m, 2H), 5.34 (dm, *J* = 11.6 Hz, 2H), 4.44 (dm, *J* = 17.3 Hz, 2H), 4.11 (dm, *J* = 17.2 Hz, 2H), 3.92 (dm, *J* = 16.2 Hz), 3.52 (dd, *J* = 16.2, 6.6 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$) δ 154.6 (C), 136.9 (C), 133.3 (C), 130.8 (C), 127.6, 127.4, 126.7, 125.7, 125.5, 125.3, 125.0 (C), 124.8, 71.3 (CH$_2$), 32.1 (CH$_2$) ppm; HRMS (EI, 30 °C) calcd for C$_{28}$H$_{22}$O$_2$ 390.1620 (M^{+}), found 390.1614.

(*R*)-3,3′-Diallyl-1,1′-binaphthyl-2,2′-diamine, 9. To a degassed solution of 3,3′-diiodo-2,2′-diamino-1,1′-binaphthyl (107 mg, 0.2 mmol) in dry toluene (10 mL) were added under argon atmosphere Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol) and allyltributylstannane (184 μL, 0.6 mmol). The reaction was heated at reflux for 24 h. The cooled reaction mixture was diluted with water and repeatedly extracted with DCM. The combined organic layers were washed with brine, dried (Na$_2$SO$_4$), and concentrated, and the residue was purified by column chromatography (SiO$_2$, *n*-hexane/EtOAc, 9:1) to afford 49 mg (67%) of **9**: mp 127–129 °C; ^{1}H NMR (CDCl$_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.68 (s, 2H), 7.13–7.23 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.06–6.15 (m, 2H), 5.14–5.28 (m, 4H), 3.74 (br s, 4H), 3.56 (d, *J* = 5.9 Hz, 4H) ppm; ^{13}C NMR (CDCl$_3$) δ 142.2 (C), 135.8, 132.6 (C), 129.0, 128.4 (C), 127.6, 126.9 (C), 126.2, 123.8, 122.5, 116.9 (C), 113.6 (C), 37.0 (CH$_2$) ppm; HRMS (ESI) calcd for C$_{26}$H$_{25}$N$_2$ 365.2018 ([M + H]$^{+}$), found 365.2015 ([M + H]$^{+}$).

(*R*)-*N*,*N*′-(3,3′-Diallyl-1,1′-binaphthyl-2,2′-diyl)dimethanesulfonamide, 10. To a stirred solution of diamine **9** (46 mg, 0.13 mmol) in DCM (1 mL) and pyridine (250 μL) was slowly added methanesulfonyl chloride (22 μL, 0.28 mmol) in DCM (0.5 mL) at 0 °C. The reaction mixture was stirred at rt for a total of 66 h. A second portion of methanesulfonyl chloride (22 μL, 0.28 mmol) was added after 18 h. The mixture was then quenched with 2 N HCl and extracted with DCM. The combined organic layers were washed subsequently with NaHCO$_3$ and brine, dried (Na$_2$SO$_4$), and concentrated. The residue was purified by column chromatography (SiO$_2$, *n*-hexane/EtOAc, 85:15) to give 53 mg (79%) of bis(sulfonamide) **10**. ^{1}H NMR (CDCl$_3$) δ 7.89 (s, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.47 (pt, *J* = 7.5 Hz, 2H), 7.26 (pt, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.16 (br s, 2H), 6.05−6.16 (m, 2H), 5.23−5.28 (m, 4H), 3.82 (dq, *J* = 16.2, 6.5 Hz, 4H), 2.02 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 137.1 (C), 136.2, 133.6 (C), 133.3 (C), 132.7 (C), 132.1 (C), 129.9, 127.6, 127.1, 126.8, 126.7, 117.6 (CH_2), 42.4 (CH_3), 37.6 (CH_2) ppm; HRMS (ESI) calcd for $C_{28}H_{28}N_2O_4S_2Na$ 543.1388 ($[M + Na]^+$), found 543.1385 ($[M + Na]^+$).

(*R*)-*N*,*N*′-(3,3′-Diallyl-1,1′-binaphthyl-2,2′-diyl)bis(*N*-allylmethane-sulfonamide), 11. To a degassed solution of bis(sulfonamide) **10** (50 mg, 0.096 mmol) in dry CH_3CN (2 mL) were added under argon K_2CO_3 (66 mg, 0.48 mmol, 5 equiv) and allyl bromide (58 μL, 0.672 mmol, 7 equiv). The reaction mixture was stirred at reflux. Additional portions of K_2CO_3 (26.4 mg, 0.192 mmol, 2 equiv) and allyl bromide (24.8 μL, 0.288 mmol, 3 equiv) were added after 22 h and after a total for 45 h the mixture was extracted with DCM. Combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. The crude mixture was subjected to chromatography (SiO_2, *n*-hexane/EtOAc, 85:15) to separate the isomers **11A**, **11B**, and **11C** (49:46:5); total yield 40 mg (69%).

11A: mp 156−8 °C; ^{1}H NMR (toluene-d_8) δ 7.83 (s, 1H), 7.78 (br d, *J* = 8.1 Hz, 1H), 7.71 (s, 1H), 7.54 (br d, *J* = 8.3 Hz, 2H), 7.18 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.02 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 6.96 (m, 1H), 6.85 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 6.18 (dddd, *J* = 17.1, 10.2, 7.3, 6.4 Hz, 1H), 6.05 (ddpt, *J* = 17.0, 10.0, 6.9 Hz, 1H), 5.10−5.28 (m, 6H), 4.95 (m, 1H), 4.78 (m, 1H), 4.62 (m, 1H), 4.48 (m, 1H), 3.93−4.16 (m, 6H), 3.73 (br dd, *J* = 16.3, 7.4 Hz, 1H), 3.14 (m, 1H), 1.67 (2× s, 6H) ppm; ^{13}C NMR (toluene-d_8) δ 142.5 (C), 142.2 (C), 141.8 (C), 140.8 (C), 138.2, 138.0 (C), 137.8 (C), 137.5, 134.2 (C), 134.0 (C), 133.9 (C), 133.7, 133.7 (C), 130.9, 130.8, 130.6, 128.6, 128.3, 128.2, 127.9, 127.3, 127.1, 121.4 (CH_2), 119.3 (CH_2), 118.3 (CH_2), 117.1 (CH_2), 57.3 (CH_2), 57.0 (CH_2), 44.5 (CH_3), 44.3 (CH_3), 38.3 (CH_2), 38.0 (CH_2) ppm; HRMS (ESI) calcd for $C_{34}H_{36}N_2O_4S_2Na$ 623.2009 ($[M + Na]^+$), found 623.2007 ($[M + Na]^+$).

11B: mp 188−9 °C; ^{1}H NMR (toluene-d_8) δ 7.75 (s, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.12 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 2H), 6.98 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 6.14 (ddpt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.23 (dm, *J* = 17.1 Hz, 2H), 5.17 (dm, *J* = 10.1 Hz, 2H), 4.62−4.77 (m, 6H), 4.51 (m, 2H), 3.95 (m, 4H), 3.75 (m, 2H), 1.48 (s, 6H) ppm; ^{13}C NMR (toluene-d_8) δ 141.7 (C), 141.4 (C), 138.4 (C), 135.8, 134.2 (C), 134.0 (C), 130.9, 130.8, 128.3, 127.3, 120.2 (CH_2), 118.0 (CH_2), 55.7 (CH_2), 44.2 (CH_3), 38.2 (CH_2) ppm; HRMS (ESI) calcd for $C_{34}H_{36}N_2O_4S_2Na$ 623.2009 ($[M + Na]^+$), found 623.2010 ($[M + Na]^+$).

11C: 70% purity; ^{1}H NMR ($CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.92 (s, 2H), 7.53 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 2H), 7.25 (m, 2H), 7.20 (br d, *J* = 8.2 Hz, 2H), 6.09 (ddpt, *J* = 16.9, 10.1, 6.8 Hz, 2H), 5.22−5.88 (m, 4H), 5.05 (dm, *J* = 16.7 Hz, 2H), 4.79 (dm, *J* = 9.6 Hz, 2H), 3.95−4.11 (m, 4H), 3.86 (br dd, *J* = 16.4, 6.6 Hz, 2H), 3.68 (br dd, *J* = 16.6, 6.8 Hz, 2H), 3.48 (m, 2H), 2.33 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 140.9 (C), 140.0 (C), 136.8, 137.1 (C), 132.5 (C), 132.3, 132.1 (C), 130.0, 127.7, 127.4, 127.1, 126.0, 120.4 (CH_2), 117.3 (CH_2), 56.3 (CH_2), 43.5 (CH_3), 36.7 (CH_2) ppm.

(*R*)-1,1′-Bis(methylsulfonyl)-2,2′,5,5′-tetrahydro-1*H*,1′*H*-11,11′-binaphtho[2,3-*b*]azepine, 12. A solution of tetraallyl compound **11A** (10 mg, 0.017 mmol) in degassed DCM (1 mL) was stirred with Grubbs I catalyst (3 mg) at rt overnight. Chromatographic purification (*n*-hexane/EtOAc, 15:85) afforded 6 mg (∼50%) of **12A**. Analogous treatment of **11B** and **11C** yielded **12B** (∼60%) and **12C** (∼60%), respectively.

12A: plates, mp 305−8 °C; ^{1}H NMR ($CDCl_3$) δ 7.87 (br d, *J* = 8.2 Hz, 1H), 7.84 (br d, *J* = 8.2 Hz, 1H), 7.79 (s, 1H), 7.77 (s, 1H), 7.64 (dm, *J* = 8.6 Hz, 1H), 7.51 (m, 2H), 7.34 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.27 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.14 (br d, *J* = 8.4 Hz, 1H), 5.94 (m, 2H), 5.40 (dm, *J* = 11.5 Hz, 1H), 5.29 (m, 1H), 4.60 (dm, *J* = 19.6 Hz, 1H), 4.49 (dm, *J* = 16.5 Hz, 1H), 4.42 (dm, *J* = 16.1 Hz, 1H), 3.90 (dm, *J* = 19.8 Hz, 1H), 3.69 (m, 2H), 3.28 (dd, *J* = 16.3, 9.0 Hz, 1H), 3.21 (dd, *J* = 16.4, 9.1 Hz, 1H), 1.96 (s, 3H), 1.71 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) δ 143.2 (C), 141.5 (C), 137.9 (C), 137.7 (C), 136.6 (C), 135.4 (C), 133.0 (C), 132.9 (2 × C), 132.1 (C), 129.5, 128.0, 127.7, 127.6, 127.4 (2 × CH), 127.1, 126.9, 126.7, 126.2, 125.9, 125.8, 125.5, 125.4, 49.8 (CH_2), 48.5 (CH_2), 40.8 (CH_3), 39.9 (CH_3), 33.1 (CH_2), 33.0 (CH_2) ppm; HRMS (ESI) calcd for $C_{30}H_{28}N_2O_4S_2Na$ 567.1383 ($[M + Na]^+$), found 567.1402 ($[M + Na]^+$).

12B: needles, mp 181−6 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.43 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 2H), 7.18 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 6.95 (br d, *J* = 8.8 Hz, 2H), 6.03 (m, 2H), 5.55 (dm, *J* = 11.1 Hz, 2H), 4.42 (dm, *J* = 17.0 Hz, 2H), 4.33 (dm, *J* = 18.3 Hz, 2H), 3.84 (dm, *J* = 18.5 Hz, 2H), 3.37 (dd, *J* = 17.0, 8.8 Hz, 2H), 1.74 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 140.4 (C), 137.4 (C), 135.2 (C), 133.4 (C), 132.8 (C), 129.0, 128.9, 127.4, 126.8, 126.2, 126.1, 125.6, 51.4 (CH_2), 40.9 (CH_3), 33.9 (CH_2) ppm; HRMS (ESI) calcd for $C_{30}H_{28}N_2O_4S_2Na$ 567.1383 ($[M + Na]^+$), found 567.1406 ($[M + Na]^+$).

12C: mp 224−7 °C; ^{1}H NMR ($CDCl_3$) δ 7.89 (bd, *J* = 8.5 Hz, 2H), 7.80 (s, 2H), 7.54 (ddd, *J* = 8.1, 5.9, 2.1 Hz, 2H), 7.34 (m, 4H), 5.90 (m, 2H), 5.35 (dm, *J* = 11.2 Hz, 2H), 4.53 (dm, *J* = 16.4 Hz, 2H), 3.86 (m, 4H), 3.24 (dd, *J* = 16.4, 8.9 Hz, 2H), 2.03 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 142.4 (C), 139.0 (C), 135.5 (C), 133.0 (C), 132.0 (C), 128.2, 127.5, 127.4 (2 × CH), 126.8, 125.5, 124.9, 49.9 (CH_2), 40.8 (CH_3), 33.3 (CH_2) ppm; HRMS (ESI) calcd for $C_{30}H_{28}N_2O_4S_2Na$ 567.1383 ($[M + Na]^+$), found 567.1401 ($[M + Na]^+$).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Spectroscopic data of **3**−**6** and **9**−**12** including assignment of NMR shift data, as well as details of X-ray crystallography and quantum chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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