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# A Series of Novel *N*,*N*-Donor Ligands with Binaphthyl Backbones

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Chiral ligands with the 1,1′-binaphthyl unit as the backbone play an important role in enantioselective catalysis. In this paper we present the synthesis and characterization of three novel azole-functionalized 1,1-binaphthyl derivatives. These systems are accessible from commercially available starting materials in not more than four steps.


## Introduction

The 1,1′-binaphthyl backbone is one of the central ligand motifs in enantioselective catalysis. Inspired by the work of Noyori et al.[1] a variety of differently substituted 1,1′-binaphthyl systems with phosphorus donor sites have been developed during the last two decades.[2] The main application of such ligands is in catalysis with late transition metal centres for reactions such as hydrogenation,[3] hydrosilylation,[4] hydroformylation,[5] coupling reactions[6] and many more. The archetype of this class of ligands is 2,2′-bisdiphenylphosphanyl-1,1′-binaphthyl (BINAP), which has gained industrial application in the so-called Takasago menthol process.[7]

1,1′-Binaphthyl systems with nitrogen donor sites, however, are much less widespread, although such ligands should be of interest both for the electron-rich late transition metal sites and for the harder Lewis acids on the left-hand side of the transition metal section. Nitrogen additionally opens up the opportunity to be directly embedded in the 2,2′-positions of the 1,1′-biaryl motif, as in 2,2′-biquinoline. The *N*,*N*′-dioxides of this compound and of 1,1′-biisoquinoline were used as catalysts for the asymmetric allylation of aldehydes with allyltrichlorosilane.[8]

Introduction of the nitrogen donors at the 2,2′-positions of the 1,1′-binaphthyl backbone – similarly to the case of phosphorus derivatives – leads to quite simple chiral bidentate nitrogen donors such as 2,2′-diamino-1,1′-binaphthyl (DABN) and its alkylated congeners. The application of such ligands in homogeneous catalysis has previously given promising enantiomeric excesses, especially in combination with lanthanides and in organocatalysis.[9] However, DABN is also the starting material for 1,1′-binaphthyl systems functionalized with *N*-heterocyclic carbenes. A doubly benzimidazolylidene-functionalized 1,1′-binaphthyl ligand reported by Shi et al. gave enantiomeric excesses of up to 98% in the rhodium-catalysed asymmetric hydrosilylation of ketones.[10] Hoveyda et al. published asymmetrically functionalized 2-hydroxy-2′-imidazolium-1,1′-binaphthyl salts that have found applications in asymmetric ROMP[11] and copper-catalysed asymmetric allylic substitution.[12] Further similar NHC ligands have been reported by Crabtree et al.[13]

As demonstrated by the success of the NHC ligands discussed above, it seems to be beneficial to introduce nitrogen donors not directly at the 2,2′-positions of the 1,1′-binaphthyl system, but with one (carbon) atom in between. Interestingly, this approach has previously been used only a few times: the 1,1′-binaphthyl backbone was functionalized with a series of different (chiral) oxazolines, synthesized by condensing 1,1′-binaphthyl-2,2′-dicarboxylic acid with the appropriate amino alcohols. Such systems give excellent enantiomeric excesses in palladium-catalysed Wacker-type cyclizations,[14] as well as in copper-catalysed cyclopropanation of styrene with 1-menthyl diazoacetate.[15] It turned out that the substituents at the oxazoline units influence the stereoselectivities of these reactions in a matched/mismatched sense.

We have been interested in pyrazole as a central motif for ligands for potential applications in catalysis for quite some time.[16] This was largely a consequence of the fact that these five-membered heterocycles are simple to synthesize and to modify in terms of their steric and electronic features. To the best of our knowledge, there is no report on symmetrically 2,2′-pyrazolyl-functionalized 1,1′-binaphthyls. In this paper we report the synthesis of such chiral ligands and one analogous 2,2′-ditriazolyl derivative.

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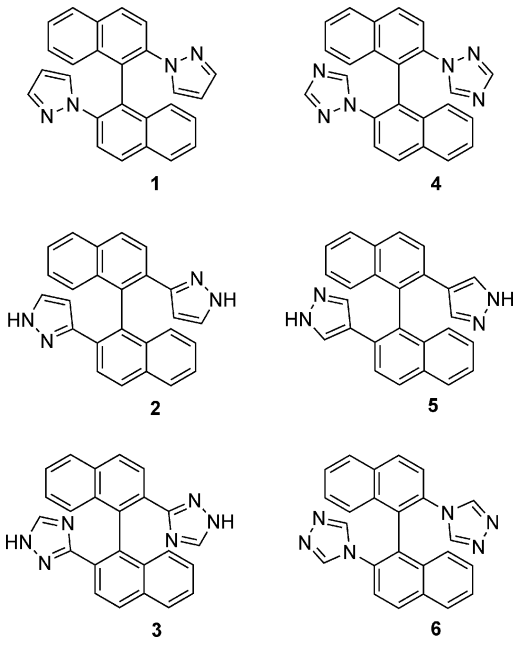
## Results and Discussion

There are three isomers both for the pyrazole and for the triazole systems, as shown in Scheme 1. We have found synthetic routes to compounds **1**–**3**, whereas compound **4** is currently under investigation. The isomers **5** and **6** would not be expected to undergo chelating coordination to a metal site, due to the positioning of the nitrogen donor atoms. However, such donors may be of interest for the synthesis of chiral metal-organic frameworks (MOFs).[17]

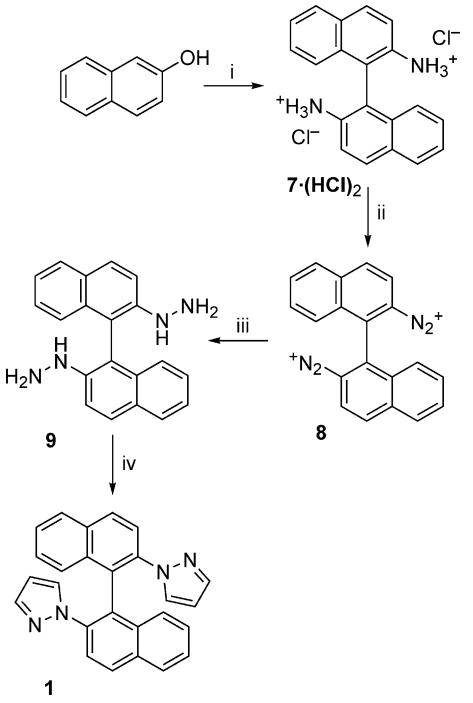



Scheme 1. Azole-functionalized binaphthyls.

Our first idea for the synthesis of ligand **1** was to use C–N coupling reactions. For this purpose, 2,2′-dibromo-1,1′-binaphthyl[18] and the bistriflate of 2,2′-dihydroxy-1,1′-binaphthyl[19] were first tested in palladium-catalysed C–N coupling reactions[20] with 1*H*-pyrazole. None of these experiments gave the desired product. Such C–N couplings generally prefer electron-rich amines, which is not the case with the electronic situation of 1*H*-pyrazole. There are some examples of palladium-catalysed pyrazolylations in the literature, although only with electron poor aryl halides.[21] 2,2′-Dibromo-1,1′-binaphthyl did not react at all, whereas for the bistriflate of 2,2′-dihydroxy-1,1′-binaphthyl a small amount of dinaphthofuran was detected.

With copper as the catalytically active species[22] the situation is different: with the CuI/TMEDA/$Cs_2CO_3$ or CuI/*trans*-*N*,*N*′-dimethyl-1,2-cyclohexanediamine/$Cs_2CO_3$ catalyst systems, DMF as the solvent and 2,2′-dibromo- or 2,2′-diiodo-1,1′-binaphthyl as the substrates, about 10–15% yields (by NMR) of mono- and dipyrazolylated 1,1′-binapththyls could be obtained. A second copper-based catalyst system – [CuO/$Fe(acac)_3$/$Cs_2CO_3$] – with DMF or NMP as the solvent, recently reported by Taillefer et al.,[23] led to slightly better yields: with 2,2′-dibromo-1,1′-binaphthyl about a 25% yield of the desired ligand **1** was obtained after 48 h at 160 °C. The yield is poorer and the reaction time much longer than for the published synthesis of 1-(2-naphthyl)pyrazole, probably due to the steric demand of the bulky 1,1′-binaphthyl moiety.

However, ligand **1** was finally obtained by a reaction sequence starting from the oxidative coupling of 2-naphthol in the presence of hydrazine at 180 °C. This reaction gives 2,2′-diamino-1,1′-binaphthyl (**7**; Scheme 2) in 42% yield,[24] and this compound can be separated from side products of the reaction as the dihydrochloride by a simple procedure.




Scheme 2. Synthesis of 2,2′-(dipyrazol-1-yl)-1,1′-binaphthyl (**1**). i) $N_2H_4$, 180 °C, HCl; ii) $NaNO_2$, HCl; iii) $SnCl_2$, HCl; iv) $(MeO)_2CHCH_2CH(OMe)_2$, EtOH, reflux.

A suspension of **7** in concd. HCl was then treated with $NaNO_2$ to give the intermediate 2,2′-bisdiazo-1,1′-binaphthyl (**8**), which can be reduced in situ to 2,2′-dihydrazinyl-1,1′-binaphthyl (**9**) with $SnCl_2$. Compound **9** precipitates from the solution. According to its $^1H$ and $^{13}C$ NMR spectroscopic data, the dihydrazinyl derivative **9** is not obtained in a protonated form although the reaction takes place in a strongly acidic solution. Compound **9** was used directly without further purification for a double ring-closure reaction with 1,1,3,3-tetramethoxypropane, resulting in the formation of **1** in about 30% overall yield (from 2-naphthol; 81% from compound **7**).[25] The $^1H$ NMR spectrum of **1** shows the typical resonances of a pyrazole substituted at the 1-position, with small $^3J_{H,H}$ coupling constants (1.6 and 2.3 Hz) accompanied by resonances for a symmetrically functionalized 1,1′-binaphthyl system. Additionally, a signal in the $^{13}C\{^1H\}$ NMR spectrum at $\delta$ = 106.4 ppm can be assigned to the carbon atom in the 4-position of the pyrazole ring.

Recrystallization of **1** from ethyl acetate gave bright yellow prismatic single crystals suitable for X-ray structure analysis. Compound **1** crystallizes in the orthorhombic

space group *Pbcn*. Figure 1 presents the molecular structure of **1** in the solid state and characteristic structural parameters.

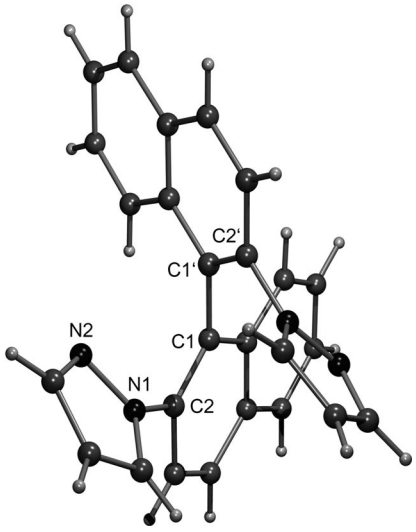
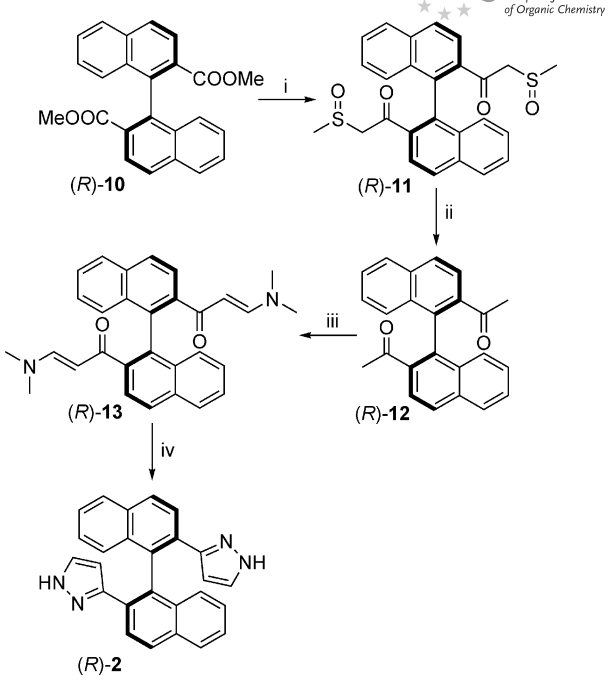



Figure 1. Molecular structure of racemic **1** in the solid state. Selected dihedral angles [°]: C2–C1–C1′–C2′ 69.32(15), N2–N1–C2–C1 52.99(16).




Scheme 3. Synthesis of (*R*)-2,2′-bis[3,(5)-pyrazolyl]-1,1′-binaphthyl [(*R*)-**2**]. i) NaH, DMSO, 0°→ room temp.; ii) $HOOCCH_3$, EtOH, Zn; iii) DMFDMA, reflux; iv) $N_2H_4$, EtOH, reflux.

The shape of the molecule is determined by the dihedral angles between the two 1,1′-binaphthyl units (69.32°) and between the pyrazole ring and the naphthyl ring (52.99°). An almost parallel orientation of the two pyrazolyl rings with an interplanar distance of about 3.40 Å provides evidence in support of an intramolecular π–π stacking of these units.

For the synthesis of 2,2′-bis(1,2-pyrazol-3-yl)-1,1′-binaphthyl (**2**) a different strategy had to be applied. Pyrazoles bound to an aromatic ring at their 3-positions are obtained in high yields through ring-closure reactions between hydrazine and 1-aryl-3-(dimethylamino)prop-2-en-1-ones.[26] To follow this route (Scheme 3), enantiomerically pure dimethyl (*R*)-1,1′-binaphthyl-2,2′-dicarboxylate [(*R*)-**10**][27] was treated with NaH/DMSO[28] to give (*R*)-2,2′-bis(methylsulfinylacetyl)-1,1′-binaphthyl [(*R*)-**11**]. The $^1H$ NMR spectrum of (*R*)-**11** shows four methyl signals with almost identical intensities at 2.6–2.5 ppm, for the chiral methylsulfinyl units, and eight doublets with typical geminal coupling constants for the diastereotopic methylene protons. This indicates a 1:2:1 mixture of the (*R*,*R*,*R*), (*R*,*R*,*S*) [= (*S*,*R*,*R*)] and (*S*,*R*,*S*) diastereomers, additionally confirmed by a fourfold set of resonances in the $^{13}C\{^1H\}$ NMR spectrum. The IR spectrum of (*R*)-**11** shows two dominant absorptions at 1681 ($\nu_{CO}$) and 1031 ($\nu_{SO}$) $cm^{-1}$.

Compound (*R*)-**11** was reduced to the diketone (*R*)-2,2′-diacetyl-1,1′-binaphthyl [(*R*)-**12**] by treatment with Zn in acetic acid/ethanol.[29] The acetyl group of (*R*)-**12** gives typical resonances in the $^1H$ NMR ($\delta$ =2.09 ppm) and $^{13}C\{^1H\}$ NMR spectrum (201.4, 29.4 ppm), as well as a characteristic absorption in the IR spectrum ($\nu_{CO}$ = 1689 $cm^{-1}$). Treatment of compound (*R*)-**12** with dimethylformamide dimethyl acetal (DMFDMA)[26] generates (*R*)-2,2′-bis[3-(dimethylamino)prop-2-enoyl]-1,1′-binaphthyl [(*R*)-**13**], which makes the target molecule **2** accessible by ring closure with hydrazine. Compound (*R*)-**13** can be identified spectroscopically by the typical resonances of the 3-(dimethylamino)-prop-2-enoyl units: because of the hindered rotation around the CH–N bond[26] two broad resonances are found for the terminal methyl groups both in the $^1H$ (2.83, 2.15 ppm) and in the $^{13}C\{^1H\}$ NMR spectrum (44.5, 36.4 ppm). The inclusion of the nitrogen lone pair in the π system of the side chain increases the electron density at the carbonyl C atom and leads to low-field shifting of the CO resonance in the $^{13}C\{^1H\}$ NMR spectrum. Consistently with this, the IR absorption of the carbonyl group is found at quite low energies ($\nu_{CO}$ = 1637 $cm^{-1}$). The $^1H$ NMR spectrum of the target compound **2** recorded in $CDCl_3$ shows the typical pattern for the naphthyl units in the aromatic region, although the resonances of the three different pyrazolyl protons are shifted to quite unusual values: the signal of the NH proton appears at $\delta$ = 14.4 ppm, indicating that this proton is involved in a strong hydrogen bond. Even in $[D_6]$-DMSO, which is known for its strong proton-accepting properties, the chemical shift for the NH proton is only 12.7 ppm. The CH protons can be assigned to two sharp resonances at $\delta$ = 4.77 ppm (H4; in $[D_6]$DMSO: 5.00 ppm) and 6.26 ppm (H5; $[D_6]$DMSO: 7.19 ppm!). The strong shielding of H5 in particular in the poorly proton-accepting solvent $CDCl_3$ indicates the presence of a supramolecular structure, which is broken in DMSO. This is corroborated by the strongly solvent-dependent optical rotation of (*R*)-**2**: $[\alpha]_{589}^{21}$ = –46 in DMSO (0.25 g in 100 mL) and $[\alpha]_{589}^{21}$ = +365 in $CHCl_3$ (0.10 g in 100 mL).

Enantiomerically pure (*R*)-**2** crystallizes from chloroform in the chiral hexagonal space group *R*3 as colourless prismatic single crystals. Figure 2 presents the molecular structure of (*R*)-**2** in the solid state with characteristic structural parameters.

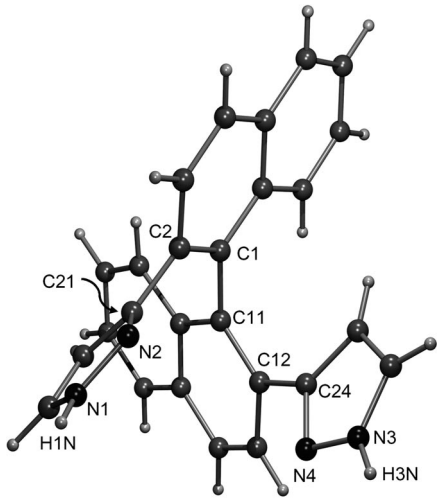



Figure 2. Molecular structure of (*R*)-**2** in the solid state. Selected dihedral angles [°] and hydrogen bond parameters [Å,°]: C2–C1–C11–C12 –75.6(3), C1–C2–C21–N2 138.6(2), C11–C12–C24–N4 137.0(2); N1–H1N 0.88, H1N···N2 2.02, N1···N2 2.854(4), N1–H1N···N2 158.00, N3–H3N 0.88, H3N···N4 2.02, N3···N4 2.857(4), N3–H3N···N4 159.00.

The solid-state structure of (*R*)-**2** is quite unique. It is well known that pyrazoles, which combine proton-donating and -accepting sites in one molecule, form hydrogen-bonded trimers or tetramers in the solid state.[30] Here, each of the two pyrazolyl groups of **2** is included in an almost planar hydrogen-bonded pyrazole trimer, which leads to a pelton wheel-like structure generated by three molecules of (*R*)-**2** (Figure 3). These trimers pile up into columns along the crystallographic *c*-axis. Looking at [(*R*)-**2**]$_3$ makes it clear that the H4 pyrazolyl protons of the top pyrazole trimer are located directly in the shielding cone of the bottom pyrazole trimer and vice versa. This situation is responsible for the pronounced shift of the resonance of this proton to higher field in $CDCl_3$ solution. We found seven hydrogen-bonded and structurally characterized pyrazole trimers in the CCDC.[31] The N···N distances are in a range between 2.82 and 3.02 Å, which confirms the presence of a rather strong N···H–N interaction (2.85 Å) in [(*R*)-**2**]$_3$ as already revealed by the chemical shift of the NH proton.

The 2,2′-ditriazolyl derivatives **3** and (*R*)-**3** were obtained from the corresponding starting 1,1′-binaphthyl-2,2′-dicarboxamides [**14** or (*R*)-**14**; Scheme 4].[32] When these compounds are treated with dimethylformamide dimethylacetal, the bis[(dimethylamino)methylene]diamides **15** or (*R*)-**15** are accessible in high yields, and then undergo ring closure by condensation with hydrazine.[33]

The resonance of the methine proton of compound **15** is found at $\delta$ = 8.21 ppm in the $^1$H NMR spectrum. Because of the π-donation of the $NMe_2$ group, the rotation around the C–$NMe_2$ bond is hindered, leading to two chemically

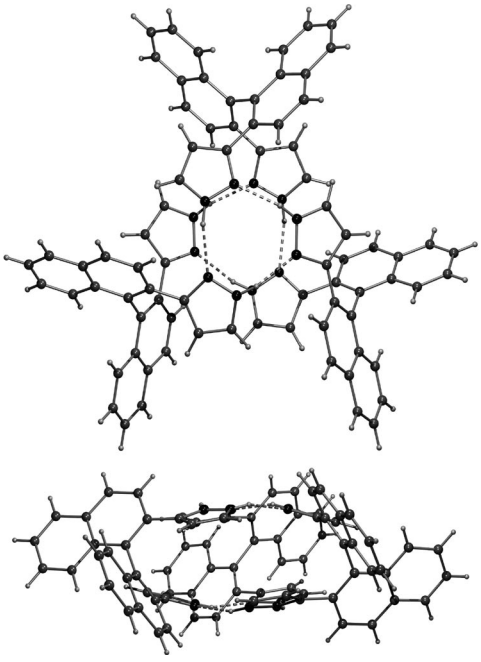
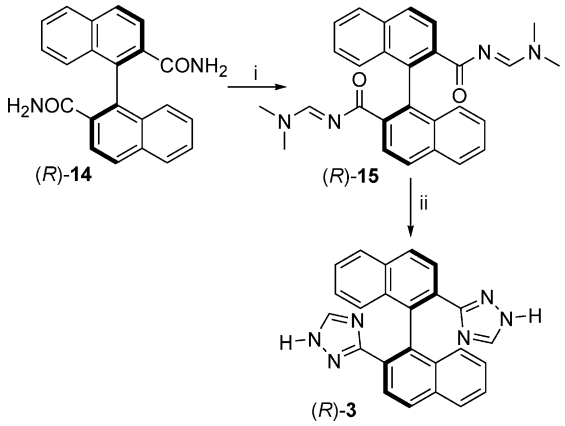


Figure 3. Top and side view of a trimer of (*R*)-**2** formed by intermolecular hydrogen bonds.




Scheme 4. i) DMFDMA, reflux.; ii) $HOOCCH_3$, $N_2H_4$, 90 °C.

different methyl groups on the timescale of $^1$H (2.78, 2.14 ppm) and $^{13}$C{$^1$H} NMR (40.8, 34.3 ppm) and the carbonyl group becomes electron enriched ($\nu_{CO}$ = 1632 cm$^{-1}$). Compound **3** is only poorly soluble in the nonpolar $CDCl_3$, probably due to the formation of oligomers in solution (see solid-state structure below). In its $^1$H NMR spectrum it shows a broad signal at $\delta$ = 11.69 ppm for the NH proton, which is involved in hydrogen bonding, whereas the resonance of the triazolyl proton is observed as one sharp signal at $\delta$ = 7.86 ppm. In the proton-accepting [$D_6$]DMSO, the spectrum changes: one of the naphthyl protons, most probably the one in the 3-position, is shifted, giving a broad resonance at $\delta$ = 8.23 ppm, indicating a change in the chemical environment due to the binding of DMSO.

Recrystallization of racemic **3** obtained by diffusion of pentane into a solution of **3** in ethyl acetate gave colourless single crystals suitable for X-ray structure analysis. The so-

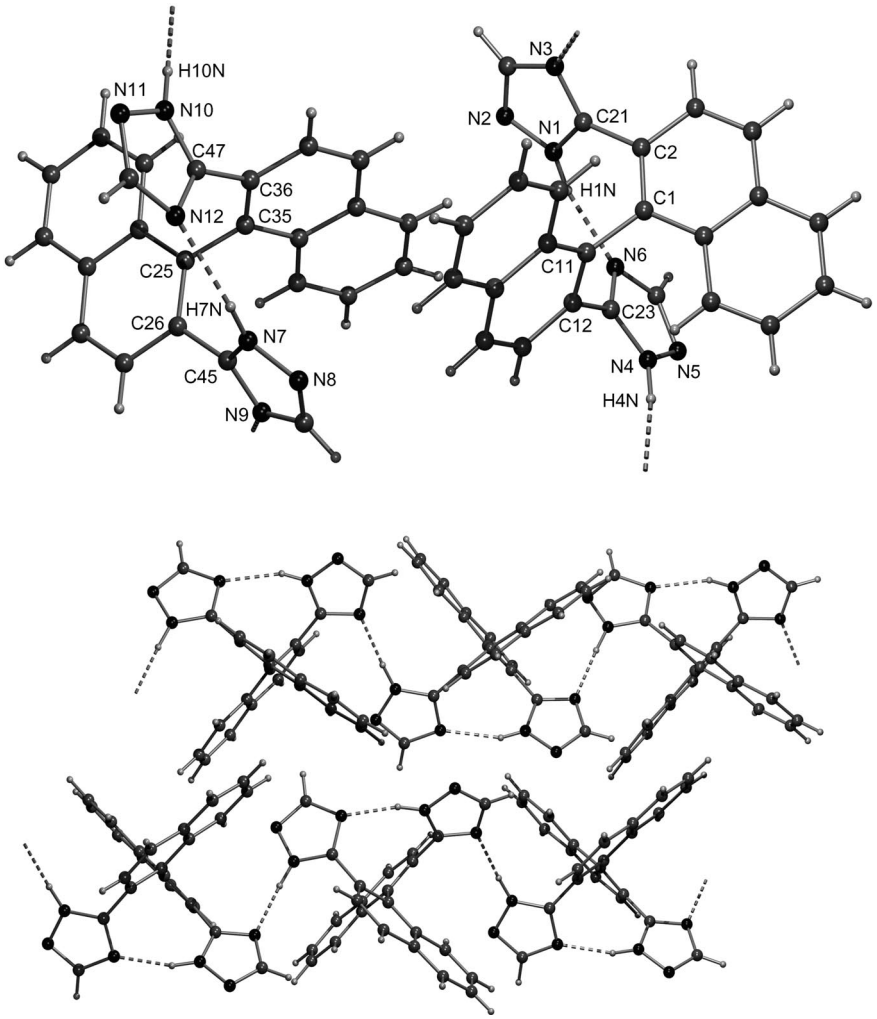



Figure 4. Top: molecular structure of racemic **3** in the solid state. Selected dihedral angles [°] and hydrogen bond parameters [Å,°]: C2–C1–C11–C12 101.35(17), C1–C2–C21–N3 123.77(17), C11–C12–C23–N4 111.70(17), C26–C25–C35–C36 –100.31(16), C35–C36–C47–N10 –116.97(16), C25–C26–C45–N7 60.7(2); N1–H1N 0.943(13), H1N···N6 1.947(13), N1···N6 2.8512(18), N1–H1N···N6 160.1(13), N4–H4N 0.951(13), H4N···N3 1.916(14), N4···N3 2.8607(19), N4–H4N···N3 171.9(14), N7–H7N 0.896(13), H7N···N12 2.111(13), N7···N12 2.9590(16), N7–H7N···N12 157.7(14), N10–H10N 0.967(14), H10N···N9 1.910(13), N10···N9 2.8752(18), N10–H10N···N9 176.2(13). Bottom: formation of one-dimensional chains through hydrogen bonds.

lid-state structure of **3** is shown in Figure 4. There are two independent molecules in the unit cell. Only the 2,2′-bis(2*H*-1,2,4-triazol-3-yl)-1,1′-binaphthyl tautomer is found in the crystal structure. This allows the formation of a strong intramolecular hydrogen bond and opens the dihedral angle between the naphthyl units to about 100°. Further hydrogen bonds give rise to the formation of parallel chains along the crystallographic *c*-axis.

Up to now it has not been possible to obtain single crystals from the enantiomerically pure compound (*R*)-**3**. The $[a]_{589}^{21}$ value for the optical rotation, measured in chloroform solution is +18.5, which does not corroborate the formation of a supramolecular structure in solution as in the case of (*R*)-**2**. The presence of a third electronegative nitrogen atom in the azole ring decreases the basicity of the nitrogen sites and gives rise to a competitive situation for the two proton-accepting sites.

## Conclusion

We have been able to show that 2,2′-azole-functionalized 1,1′-binaphthyl ligands can be obtained in just a few steps from versatile starting materials. Although compound **1** was synthesized from a racemic precursor, the procedure that leads to this ligand is mild enough to rule out racemisation during the synthetic processes. It is therefore very likely that enantiomerically pure **1** should be obtainable by the same methodology. We are at the moment in the process of synthesizing this ligand in its enantiomerically pure form and of investigating the use of all azole-functionalized binaphthyls in enantioselective catalysis.

## Experimental Section

**General Remarks:** All commercially available starting materials were used without further purification. The starting compounds

**7**·$(HCl)_2$,[24] (*R*)-**10**[27] and **14**[32] were synthesized by published procedures. All NMR spectra were recorded at room temperature.

**2,2′-Dihydrazinyl-1,1′-binaphthyl (9):** Compound **7**·$(HCl)_2$ (4.12 g, 11.5 mmol) was suspended in concd. HCl (75 mL). After the mixture had been cooled to –5 °C, a precooled solution of $NaNO_2$ (1.60 g, 23.2 mmol) in water (6 mL) was added dropwise. The mixture was stirred at a temperature below 0 °C for a further 45 min. After filtration of the mixture, the filtrate was poured into a solution of $SnCl_2·2H_2O$ (32.22 g, 142.8 mmol) in concd. aqueous HCl (130 mL). Stirring at room temperature for 1 h resulted in the formation of a white precipitate, which was filtered off, washed with water and some ethanol and dried in vacuo. This crude product was used for the following synthesis without further purification. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 10.19 (br. s, 6 H, N*H*N$H_2$), 8.16 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, $H_{naph}$), 7.98 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.72 (d, $^3J_{H,H}$ = 9.4 Hz, 2 H, $H_{naph}$), 7.38 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $H_{naph}$), 7.26 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, $H_{naph}$), 6.78 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{naph}$) ppm. $^{13}$C NMR (150.92 MHz, [D$_6$]DMSO): $\delta$ = 141.4, 132.6, 130.1, 129.6, 128.3, 127.3, 124.3, 124.1, 116.0, 114.7 ppm. IR (KBr): $\tilde{\nu}$ = 3226 (s, $\nu_{NH}$), 2926 (vs), 1621 (s), 1598 (s), 1516 (vs), 1489 (m), 1139 (w), 1024 (w), 811 (s), 754 (m), 701 (w), 606 (m), 435 (w) cm$^{-1}$.

**2,2′-Di(pyrazol-1-yl)-1,1′-binaphthyl (1):** The complete amount of crude **9** obtained in the prior synthesis was suspended in a mixture of ethanol (25 mL) and water (10 mL). 1,1,3,3-Tetramethoxypropane (3.76 g, 3.8 mL, 22.9 mmol) was added, and the solution was heated at reflux for 12 h. Neutralization of the resulting brown solution with NaOH (10% in water), extraction of the aqueous phase with dichloromethane, drying of the organic phase over $Na_2SO_4$ and removal of the solvent gave a brown solid, which was dissolved in hot ethyl acetate. On cooling to room temperature, **1** precipitated as bright yellow solid. Yield 3.60 g (9.32 mmol, 81%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.06 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, $H_{naph}$), 7.96 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.83 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, $H_{naph}$), 7.50 (dt, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.5 Hz, 2 H, $H_{naph}$), 7.42 (d, $^3J_{H,H}$ = 1.6 Hz, 2 H, 5-$H_{pz}$), 7.37–7.28 (m, 4 H, $H_{naph}$), 6.98 (d, *J* = 2.3 Hz, 2 H, 3-$H_{Pz}$), 5.97 (dd, 2 H, 4-$H_{Pz}$) ppm. $^{13}$C NMR (150.92 Hz, $CDCl_3$): $\delta$ = 140.4, 137.8, 133.7, 132.4, 130.0, 130.0, 128.3, 127.5, 126.5, 126.3, 126.2, 123.8, 106.4 ppm. IR (KBr): $\tilde{\nu}$ = 1620 (w), 1595 (m), 1518 (s), 1467 (w), 1420 (w), 1395 (vs), 1343 (w), 1193 (w), 1042 (m), 953 (w), 843 (w), 819 (s), 750 (vs), 617 (w), 567 (w) cm$^{-1}$.

**(*R*)-2,2′-Bis(methylsulfinylacetyl)-1,1′-binaphthyl [(*R*)-11]:** NaH (350 mg, 14.6 mmol) was suspended in dry DMSO (30 mL) under dinitrogen and the mixture was stirred for 2 h at 73 °C. The resulting yellow-grey suspension was cooled to 0 °C, diluted with dry THF (15 mL) and treated with the diester (*R*)-**10** (1.0 g 2.66 mmol). After 15 min, the mixture was allowed to warm to room temperature and was stirred for 18 h. Water (40 mL) and chloroform (40 mL) were added, and the mixture was treated with concd. HCl to adjust to a pH of 2–3 in the aqueous phase. Compound **10** was isolated by threefold extraction of the aqueous phase with chloroform (20 mL), washing of the combined organic phases three times with water (15 mL) and drying over $Na_2SO_4$, and removal of the solvent in vacuo. Yield 1.02 g (2.2 mmol, 83%) of a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.15–8.08 (m, 2 H, $H_{naph}$), 8.01–7.90 (m, 4 H, $H_{naph}$), 7.62–7.51 (m, 2 H, $H_{naph}$), 7.37–7.29 (m, 2 H, $H_{naph}$), 7.17–7.05 (m, 2 H, $H_{naph}$), 4.18, 4.18, 4.05, 4.01, 3.85, 3.83, 3.81, 3.81 (8 × d, $^2J_{H,H}$ = ca. 15 Hz, 4 H, $CH_2$), 2.38, 2.37, 2.34, 2.33 (4 × s, 6 H, $CH_3$) ppm. $^{13}$C NMR (150.92 Hz, $CDCl_3$): $\delta$ = 195.4, 195.3, 195.0, 194.9 (4 × CO), 136.7, 136.7, 136.6, 136.4, 135.3, 135.0, 134.9, 134.9, 134.9, 134.8, 134.8, 132.6, 132.6, 132.5, 129.4, 129.3, 129.2, 128.6, 128.6, 128.4, 128.4, 128.3, 127.9, 127.8, 127.8, 127.2, 127.2, 127.1, 127.1, 124.4, 124.3, 124.3, 124.2 (33 × s, 10 C, $C_{naph}$, some of the expected 40 signals are overlapping), 64.6, 64.5, 64.4, 64.4 (4 × $CH_2$), 39.3, 39.2, 39.1, 39.1 (4 × $CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3057 (w), 2919 (w), 1681 (s, $\nu_{CO}$), 1617 (m), 1591 (m), 1459 (m), 1421 (w), 1374 (m), 1319 (m), 1279 (m), 1242 (m), 1192 (m), 1089 (m), 1031 (s, $\nu_{SO}$), 971 (m), 822 (m), 772 (m), 748 (m), 560 (w) cm$^{-1}$.

**(*R*)-2,2′-Diacetyl-1,1′-binaphthyl [(*R*)-12]:** Compound (*R*)-**11** (1.00 g, 2.16 mmol) was suspended in a mixture of EtOH (20 mL) and glacial acetic acid (12.5 mL). After the addition of zinc powder (1.62 g, 24.8 mmol), the suspension was stirred for 5 h at room temperature, filtered, diluted with water (30 mL) and neutralized with $Na_2CO_3$. The aqueous phase was extracted once with $CHCl_3$ (30 mL) and three times with $CHCl_3$ (15 mL), and the combined organic phases were extracted three times with saturated aqueous $NaHCO_3$ (15 mL) and dried with $Na_2SO_4$. Removal of the solvent under reduced pressure yielded 636 mg of a pale yellow solid (1.88 mmol, 87%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.04 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, $H_{naph}$), 7.94 (d, $^3J_{H,H}$ = 9.6 Hz, 2 H, $H_{naph}$), 7.92 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, $H_{naph}$), 7.53 (dt, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.0 Hz, 2 H, $H_{naph}$), 7.28 (dt, $^3J_{H,H}$ = 8.6, $^4J_{H,H}$ = 1.5 Hz, 2 H, $H_{naph}$), 7.15 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, $H_{naph}$), 2.09 (s, 6 H, $CH_3$) ppm. $^{13}$C NMR (150.92 Hz, $CDCl_3$): $\delta$ = 201.4 (CO), 137.0, 136.2, 134.5, 132.9, 132.8, 128.6, 128.1, 127.7, 127.2, 124.8, 29.4 ($CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3056 (w), 2995 (w), 2920 (w), 1689 (s, $\nu_{CO}$), 1615 (w), 1590 (m), 1556 (w), 1505 (w), 1458 (m), 1420 (w), 1353 (m), 1316 (m), 1268 (m), 1234 (s), 1123 (m), 977 (w), 861 (w), 817 (s), 747 (s), 704 (m), 552 (w), 535 (w) cm$^{-1}$.

**(*R*)-2,2′-Bis[3-(dimethylamino)prop-2-enoyl]-1,1′-binaphthyl [(*R*)-13]:** Compound (*R*)-**12** (850 mg, 2.51 mmol) was dissolved in DMFDMA (4 mL), and the mixture was heated under reflux conditions for 20 h. Residual DMFDMA was removed in vacuo and the solid residue was washed three times with pentane (20 mL) and dissolved in a small amount of dichloromethane. The solution was transferred to a column for chromatography ($SiO_2$/ethyl acetate). Impurities were eluted first with ethyl acetate, and compound (*R*)-**13** was then eluted with ethanol. Yield 860 mg (1.87 mmol, 75%), yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.94 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{naph}$), 7.87 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, $H_{naph}$), 7.83 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{naph}$), 7.43 (dt, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.3 Hz, 2 H, $H_{naph}$), 7.33 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, $H_{naph}$), 7.30 (d, $^3J_{H,H}$ = 12.7 Hz, 2 H, =*H*CNMe$_2$), 7.26 (dt, $^3J_{H,H}$ = 9.5, $^4J_{H,H}$ = 1.4 Hz, 2 H, $H_{naph}$), 4.87 [d, $^3J_{H,H}$ = 12.7 Hz, 2 H, C(O)CH=], 2.83, 2.15 (2 × s, 12 H, $NMe_2$) ppm. $^{13}$C NMR (150.92 Hz, $CDCl_3$): $\delta$ = 191.5 (CO), 152.7 (=H*C*NMe$_2$), 140.9, 134.1, 133.6, 133.3, 127.8, 127.8, 127.6, 126.4, 126.3, 125.9, 97.1 [C(O)*C*H=], 44.5, 36.4 (2 × $CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (w), 2920 (w), 2803 (w), 1637 (s, $\nu_{CO}$), 1563 (s), 1541 (s), 1432 (m), 1417 (m), 1355 (m), 1276 (m), 1236 (m), 1071 (m), 977 (w), 918 (w), 862 (w), 772 (m), 557 (w) cm$^{-1}$.

**(*R*)-2,2′-Bis[3,(5)-pyrazolyl]-1,1′-binaphthyl [(*R*)-2]:** Compound (*R*)-**13** (700 mg, 1.53 mmol) was dissolved in ethanol (15 mL) and treated with hydrazine hydrate (2 mL). The mixture was heated at reflux for 6 h, all volatiles were stripped off under reduced pressure, and the resulting solid was dissolved in a mixture of water (30 mL) and chloroform (30 mL). The organic phase was separated, and the aqueous phase was extracted three times with chloroform (15 mL). The combined organic phases were washed with water and concd. $Na_2CO_3$ solution and dried with $Na_2SO_4$. Removal of the solvent yielded 484 mg of a pale yellow solid (1.26 mmol, 82%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 14.40 (s, 2 H, NH), 7.93 (d, $^3J_{H,H}$ = 7.7 Hz,

2 H, $H_{naph}$), 7.89 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{naph}$), 7.71 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.57 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.52 (t, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.40 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $H_{naph}$), 6.26 (s, 2 H, $H5_{pz}$), 4.77 (s, 2 H, $H4_{pz}$) ppm. $^{13}$C NMR (150.92 Hz, $CDCl_3$): $\delta$ = 149.2 ($C5_{pz}$), 135.7, 134.4, 132.6, 132.4, 129.5 ($C3_{pz}$), 128.3, 127.9, 127.5, 127.2, 126.8, 125.9, 103.2 ($C4_{pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (m, $\nu_{NH}$), 3159 (s), 2923 (s), 1617 (w), 1507 (w), 1445 (w), 1361 (m), 1331 (m), 1209 (w), 1103 (w), 1051 (m), 1024 (w), 979 (w), 931 (w), 823 (s), 766 (s), 615 (w), 555 (w) cm$^{-1}$. Opt. rotation: $[\alpha]_{589}^{21}$ = –46 in DMSO (0.25 g in 100 mL) and $[\alpha]_{589}^{21}$ = +365 in $CHCl_3$ (0.1 g in 100 mL).

***N*,*N*′-Bis[(dimethylamino)methylene]-1,1′-binaphthyl-2,2′-dicarboxylic Acid Diamide (15):** Compound **14** (620 mg, 1.82 mmol) was suspended in DMFDMA (10 mL) and the system was heated at reflux for 5 h. The mixture was allowed to cool to room temperature, all volatiles were removed in vacuo, and the pale fawn solid was washed with pentane and dried in the air. Yield 820 mg (1.82 mmol, > 99%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.21 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{naph}$), 7.97 (s, 2 H, N=CH–N), 7.90 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{naph}$), 7.85 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, $H_{naph}$), 7.41 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $H_{naph}$), 7.26 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $H_{naph}$), 7.19 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, $H_{naph}$), 2.78, 2.14 (2 × s, 12 H, $NMe_2$) ppm. $^{13}$C NMR (150.92 MHz, $CDCl_3$): $\delta$ = 179.9 (C=O), 158.6 (=H*C*$NMe_2$), 139.5, 134.9, 134.2, 133.7, 128.2, 127.4, 126.9, 126.5, 126.4, 125.9, 40.8, 34.3 (2 × $CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3059 (w), 2923 (w), 1633 (vs., $\nu_{CO}$), 1583 (vs), 1481 (m), 1456 (m), 1426 (s), 1334 (vs), 1275 (m), 1245 (m), 1093 (s), 994 (w), 924 (w), 834 (w), 771 (m) cm$^{-1}$.

**2,2′-Di(1,2,4-triazol-3-yl)-1,1′-binaphthyl (3):** Compound **15** (800 mg, 1.77 mmol) was dissolved in glacial acetic acid (20 mL), and the system was treated with hydrazine hydrate (200 mg, 3.99 mmol). The mixture was heated to 90 °C for 12 h and then allowed to cool to room temperature, and the volatiles were removed in vacuo. The resulting precipitate was filtered off and dissolved in $CH_2Cl_2$. This solution was extracted twice with concd. aqueous $NaHCO_3$ (25 mL) and dried with $Na_2SO_4$. After removal of the solvent, 630 mg of compound **3** (1.65 mmol, 92%) was obtained as a colourless solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 11.70 (s, 2 H, NH), 8.04 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $H_{naph}$), 7.99 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, $H_{naph}$), 7.90 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, $H_{naph}$), 7.86 (s, 2 H, $CH_{tz}$), 7.45 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, $H_{naph}$), 7.20 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, $H_{naph}$), 7.05 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, $H_{naph}$) ppm. $^{13}$C NMR (150.92 MHz, $CDCl_3$): $\delta$ = 134.9, 134.8, 134.0, 132.4, 129.3, 128.2, 127.5, 127.4, 127.2, 126.3, 126.2 ppm (one resonance for a quaternary carbon atom was not observed). IR (KBr): $\tilde{\nu}$ = 3429 ($\nu_{NH}$), 3058 (m), 2920 (m), 2841 (m), 2778 (m), 2711 (m), 2371 (w), 1602 (m), 1568 (m), 1552 (m), 1505 (m), 1473 (m), 1456 (m), 1266 (m), 1189 (m), 1084 (m), 1031 (m), 1012 (m), 818 (s), 755 (s) cm$^{-1}$.

**(*R*)-2,2′-Di(1,2,4-triazol-3-yl)-1,1′-binaphthyl [(*R*)-3]:** Compound (*R*)-**3** was synthesized from enantiomerically pure (*R*)-**14** by the same procedure as for the racemic compound. Opt. rotation: $[\alpha]_{589}^{21}$ = +18.5 in $CHCl_3$ (0.1 g in 100 mL).

**X-ray Structure Analyses:** Crystal data and refinement parameters are collected in Table 1. The structures were solved by direct methods (SIR92[34] for compounds **1** and (*R*)-**2** and SHELXS-97[35] for compound **3**), completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures.[35] Semi-empirical absorption corrections from equivalents (Multiscan) were carried out.[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were calculated in ideal positions (riding model) except for the hydrogen atoms bound to nitrogen atoms N1, N4, N7 and N10 in compound **3**, which were located in the difference Fourier synthesis and were refined semi-freely with the help of a distance restraint, while their *U*-values were constrained to 1.2 times the *U*(eq) values of the bonding nitrogen atoms. Due to the presence of severely disordered solvent molecules, the SQUEEZE process implemented in PLATON has been performed for compound (*R*)-**2**. Detailed information on this has been posted in the corresponding CIF file. The large deviation of the Flack-parameter [0.1(5)] prevented the deter-

Table 1. Summary of the crystallographic data and details of data collection and refinement for compounds **1**, (*R*)-**2** and **3**.

| | **1** | (*R*)-**2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{26}H_{18}N_4$ | $C_{26}H_{18}N_4$ | $C_{24}H_{16}N_6$ |
| Formula weight | 386.44 | 386.44 | 388.43 |
| Crystal size [mm] | 0.31 × 0.26 × 0.13 | 0.12 × 0.09 × 0.08 | 0.35 × 0.11 × 0.09 |
| *T* [K] | 150(2) | 150(2) | 150(2) |
| $\lambda$ [Å] | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | orthorhombic | hexagonal | monoclinic |
| Space group | *Pbcn* | *R*3 | $P2_1/c$ |
| *a* [Å] | 9.7419(2) | 28.5064(3) | 16.9153(2) |
| *b* [Å] | 13.4462(3) | 28.5064(3) | 14.45890(10) |
| *c* [Å] | 14.7797(3) | 7.56930(10) | 15.8946(2) |
| $\alpha$ [°] | 90 | 90 | 90 |
| $\beta$ [°] | 90 | 90 | 101.5900(10) |
| $\gamma$ [°] | 90 | 120 | 90 |
| *V* [Å$^3$] | 1936.02(7) | 5326.86(11) | 3808.18(7) |
| *Z* | 4 | 9 | 8 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.326 | 1.084 | 1.355 |
| $\mu$ [mm$^{-1}$] | 0.628 | 0.514 | 0.674 |
| $\theta$-range [°] | 6.36–62.54 | 5.38–62.73 | 4.06–62.63 |
| Reflections collected | 5582 | 17217 | 19403 |
| Indep. reflections | 1527 | 3741 | 5981 |
| Data/restr./parameters | 1527/0/136 | 3741/1/272 | 5981/4/553 |
| Final *R* indices [$I > 2\sigma(I)$][a] | 0.0310, 0.0801 | 0.0371, 0.0976 | 0.0367, 0.0951 |
| *R* indices (all data)[b] | 0.0392, 0.0827 | 0.0415, 0.0997 | 0.0485, 0.1010 |
| *GooF*[c] | 0.984 | 1.019 | 0.954 |
| $\Delta\rho_{max}/_{min}$ [e Å$^{-3}$] | 0.153/–0.152 | 0.294/–0.158 | 0.200/–0.216 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$. [c] $GooF = [\Sigma\omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

mination of the absolute configuration of this compound by the X-ray data. This structural information is only based on the configuration of the starting material and the synthetic sequence applied.

CCDC-713569 (for **1**), -713570 [for (*R*)-**2**] and -713571 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see also the footnote on the first page of this article): Infrared and NMR spectra of new compounds.

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