Supporting Information

Chiral [16]-aneP_4N_2 macrocycles: stereoselective synthesis and unexpected intermolecular exchange of endocyclic fragments.

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Experimental part

Equilibration of 1*R* in the acidic or basic media.

In a typical experiment, compound **1*R*** was accurately weighed into an NMR tube and dissolved in benzene–d_6 (0.5 mL). $^{31}P\{^1H\}$ NMR spectrum of sample was immediately registered. Then 0.1 ml of corresponding acetic acid solution (0.1 % or 10 %) or 0.05 ml of NEt_3 or 0.05 ml of NaOH in ethanol was accurately added to sample by microsyringe. The solution was monitored by ^{31}P NMR spectroscopy up to the equilibrium achievement (the amount of peaks and integral intensity ratio retained unchanged).
The experimental spectra are presented in figs. S1 – S4

Equilibration of 1*RS* and mixture of 1*R* and 1*S*.

Compound **1*RS*** (0.01 g) was accurately weighed into an NMR tube and dissolved in benzene–d_6 (0.5 mL). $^{31}P\{^1H\}$ NMR spectrum of sample was immediately registered. The solution was monitored by ^{31}P NMR spectroscopy up to the equilibrium achievement (the amount of peaks and integral intensity ratio retained unchanged) (Figures S5, S6).
Macrocycles **1*R***[1] (0.01 g) and **1*S***[1] (0.01 g) were weighed into an NMR tube and dissolved in benzene–d_6 (0.5 mL). The solution was monitored by ^{31}P NMR spectroscopy up to the equilibrium achievement (the amount of peaks and integral intensity ratio retained unchanged) (Figure S6).

^{31}P spectra illustrating interconversions of chiral 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes in acidic media

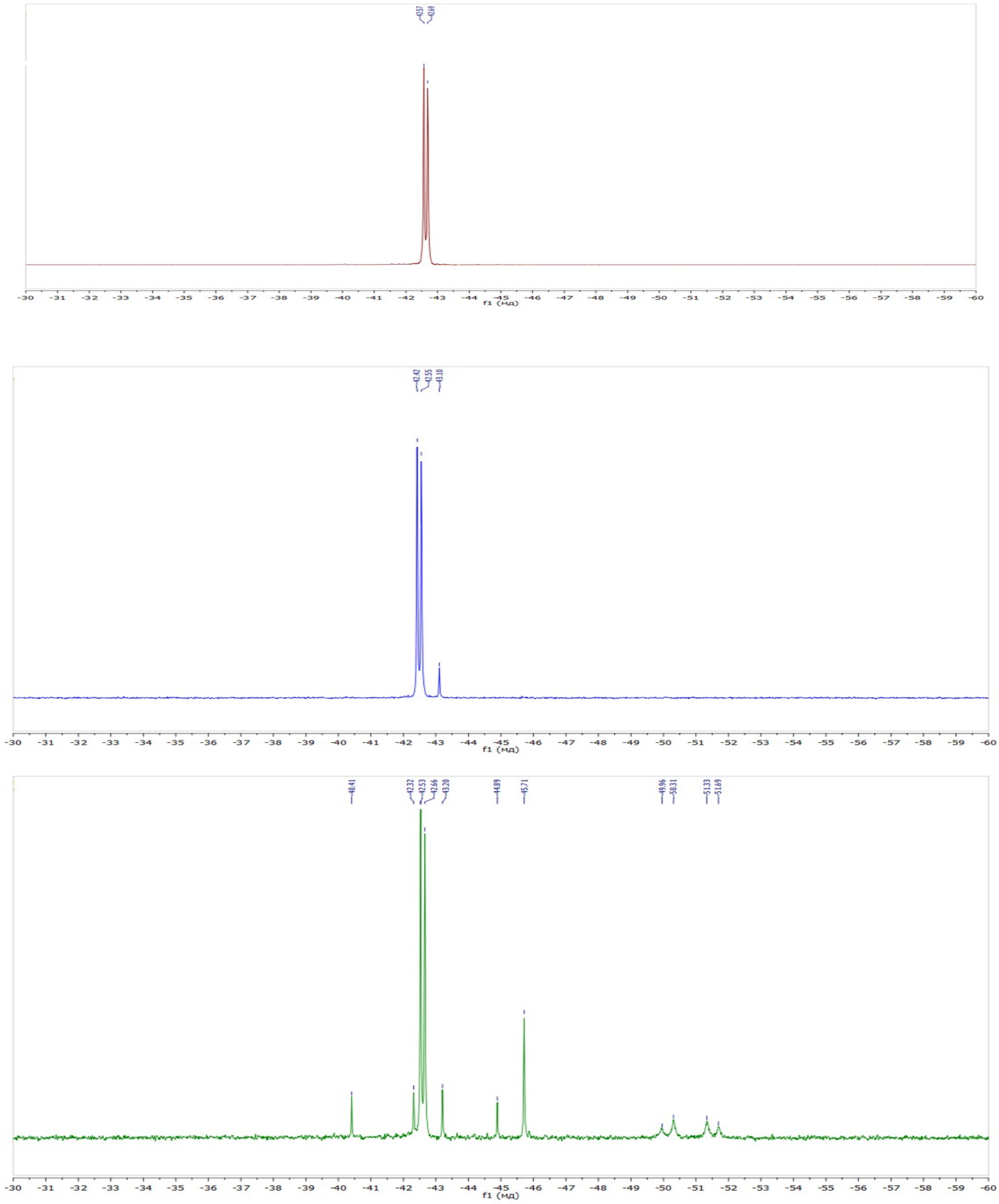

Figure S1. Evolution of **1*R*** after addition of 0.1 mL of a **0.1 %** acetic acid in benzene (solvent: C_6D_6, *V*=0.5 mL, c = 0.01 g/mL). ^{31}P{^{1}H} NMR spectra without acetic acid (red); measured 40 minutes after preparing of the sample (blue); measured 44 hours after prerparing of the sample (green).

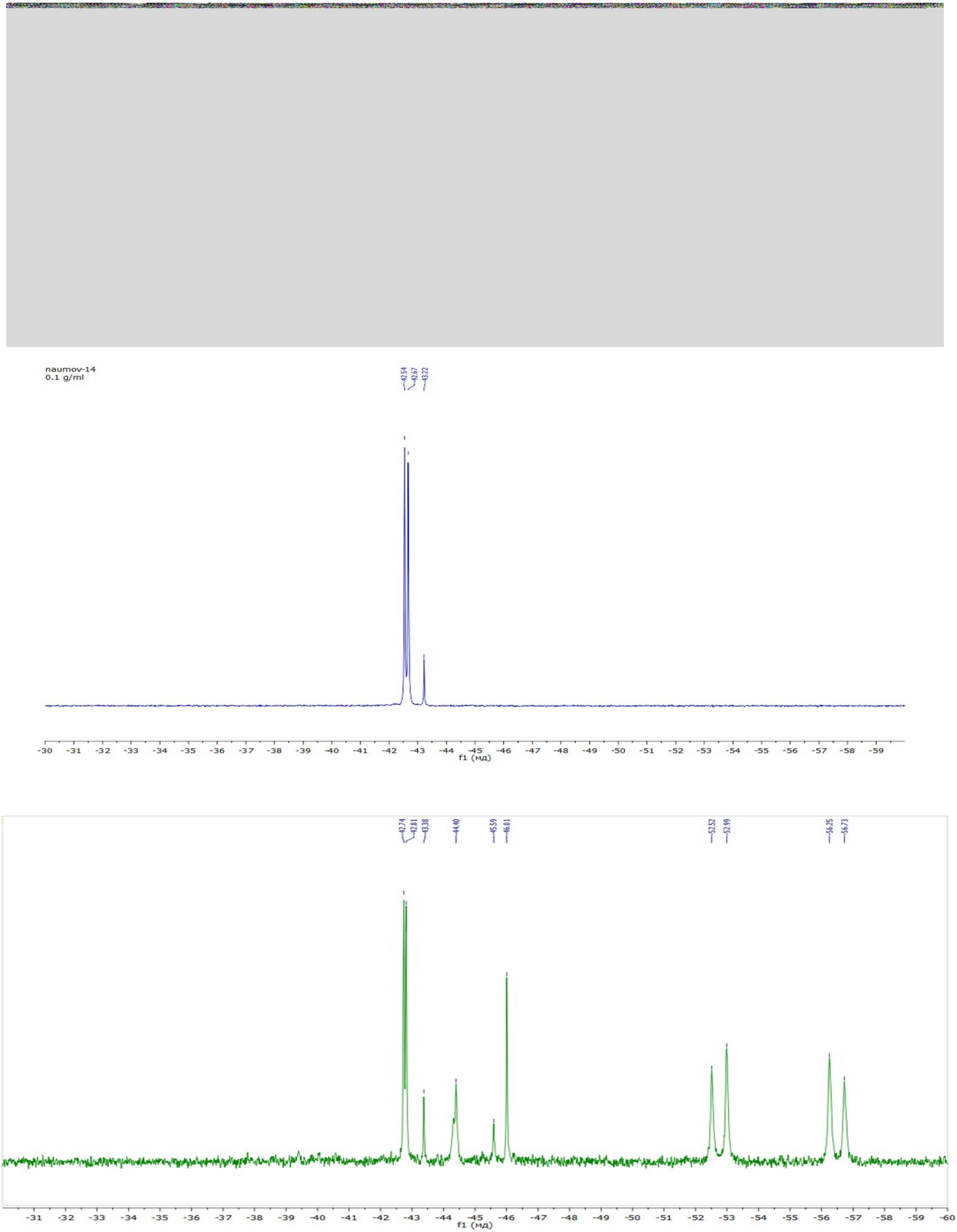

Figure S2. Evolution of **1*R*** after addition of 0.1 mL of a **10%** acetic acid in benzene (solvent: C_6D_6, *V*=0.5 mL, c = 0.01 g/mL). $^{31}P\{^1H\}$ NMR spectra without acetic acid (red); measured 5 minutes after preparing of the sample (blue); measured 23 minutes after preparing of the sample (green).

^{31}P spectra illustrating stability of chiral 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes in basic media

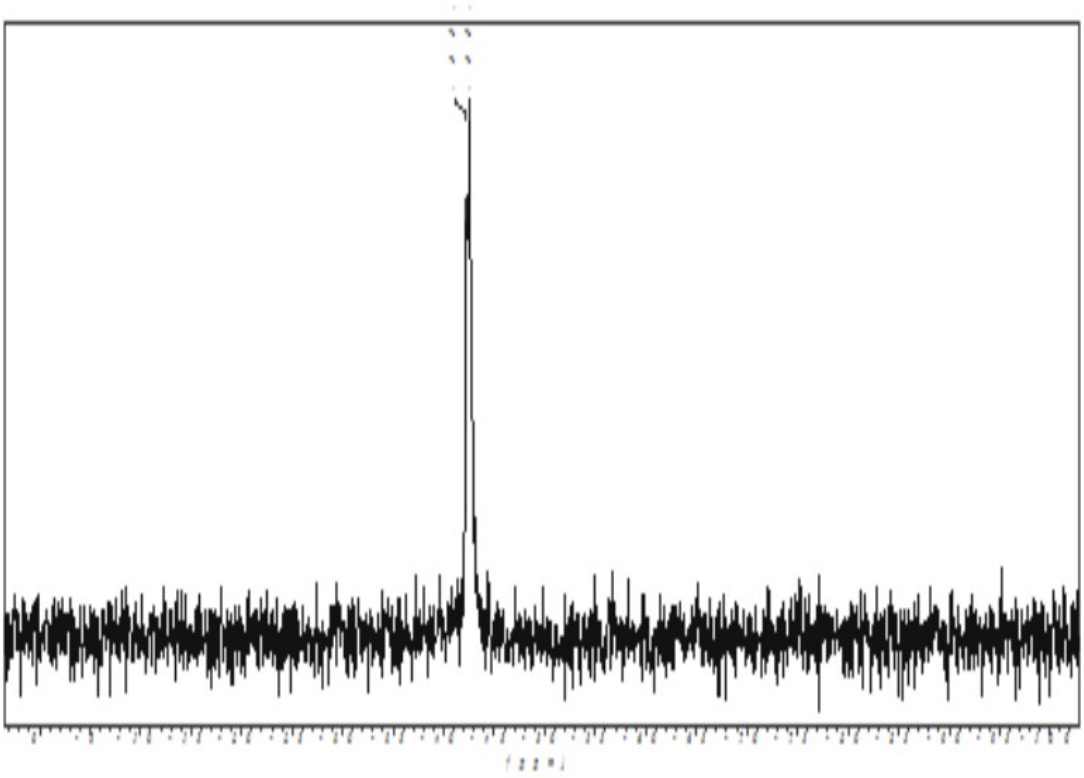

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1*R*** (solvent: C_6H_6, *V*=0.5 mL, c = 0.01 g/mL) and NaOH (solvent: ethanol, *V*=0.05 mL, c = 0.1 g/mL) measured 166 hours after preparing of the sample.

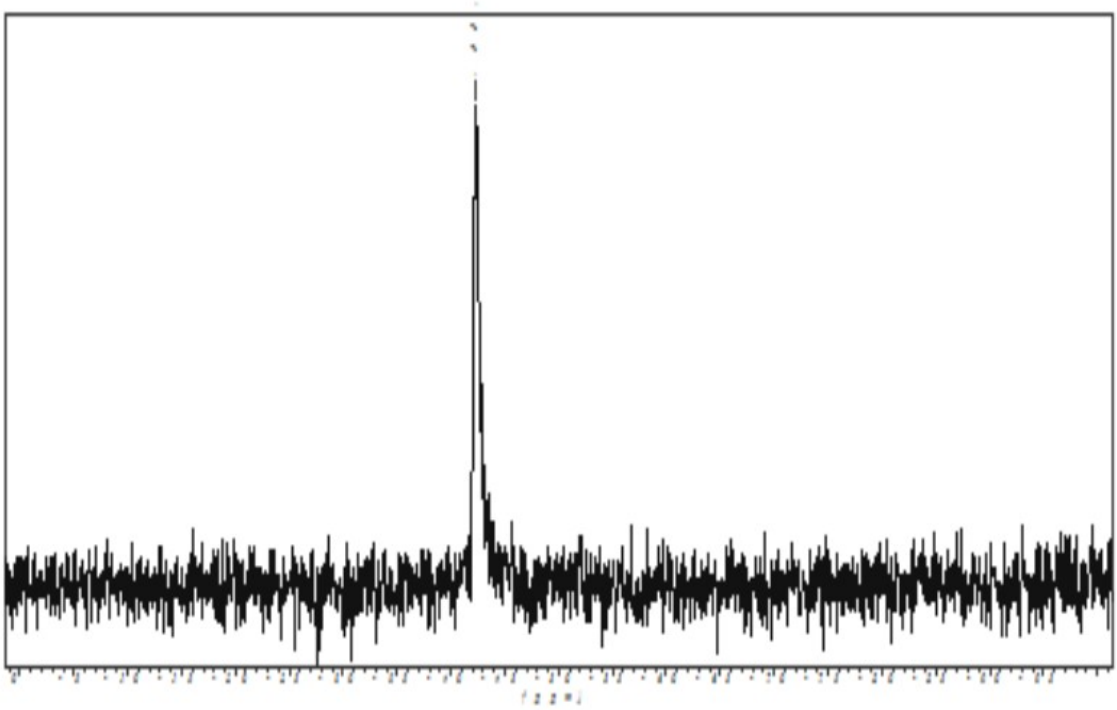

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **1*R*** (solvent: C_6H_6, *V*=0.5 mL, c = 0.01 g/mL) and triethylamine (*V*=0.05 mL) measured 218 hours after preparing of the sample.

^{31}P spectra illustrating the component composition after dissolution of 1*RS* and equimolar mixture of 1*S* + 1*R*

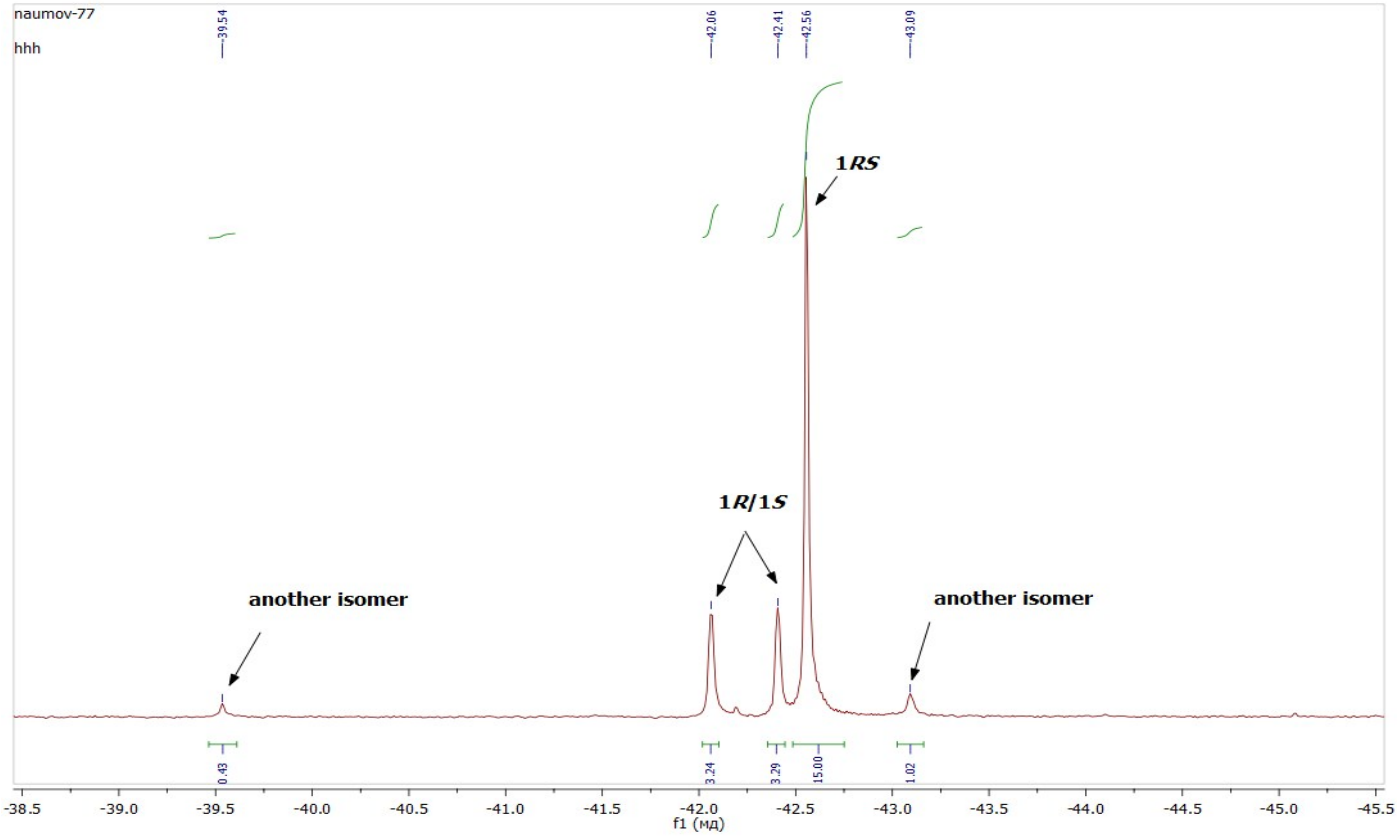

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **1*RS*** in $CDCl_3$ measured **10 minutes** after dissolution of the sample.

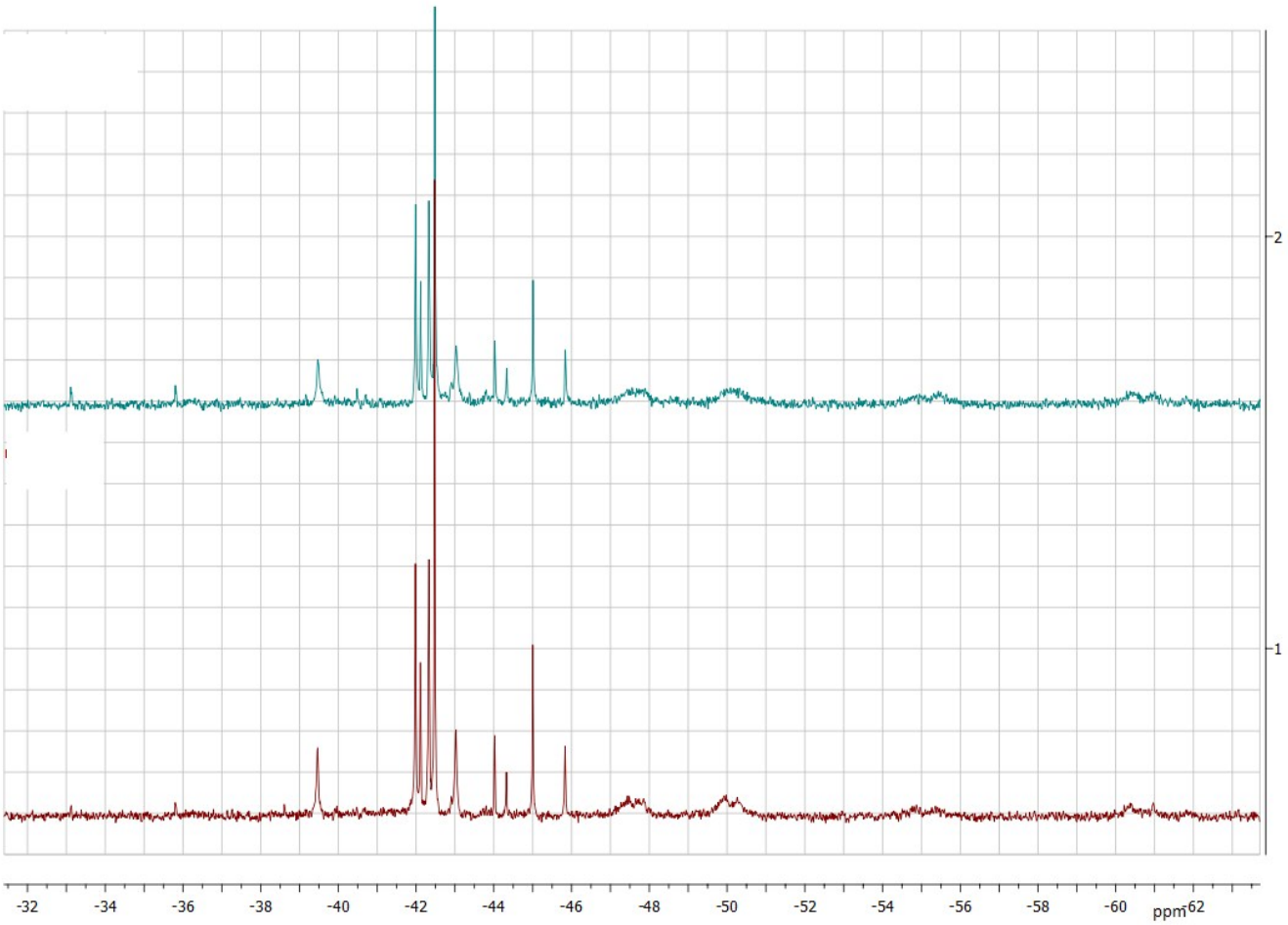

Figure S6. $^{31}P\{^{1}H\}$ NMR stack plot spectra of **1*RS*** in $CDCl_3$ measured **97 hours** after dissolution of the sample (blue) and the mixtuer, consisting the equimolar quantity of **1*S*** and **1*R*** in $CDCl_3$ (measured **67 hours** after dissolution of the sample) (red).

References

1. R.N. Naumov, A.A. Karasik, K.B. Kanunnikov, A.V. Kozlov, Sh.K. Latypov, K.V. Domasevitch, E. Hey-Hawkins, O.G. Sinyashin, *Mendeleev Commun.*, 2008, **18**, 80.