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Table S1: ^1H chemical shifts δ [ppm] for **6a** and **6b** in CDCl_3 solution at 300 K reported relative to TMS.^{a)}

Proton ^{b)}	δ [ppm] 6a	δ [ppm] 6b
H1	4.96	4.90
H2a	3.30	2.79
H2e	2.80	3.08
H3	3.10	3.05
H4	3.97	4.24
H5a	3.00	3.03
H5e	2.47	2.56
H6	7.02	7.00
H7	7.17	7.15
H8	7.21	7.17
H9	7.12	7.08
H10a	4.43	4.42
H10e	4.65	4.75
H11	7.82	7.85
H12	7.65	7.61
H13	7.57	7.56
H14	7.48	7.48
H15	7.43	7.42
H16	2.75	2.57

a) a: axial; e: equatorial.

b) see figure 1 for C/H assignment

Table S2: Experimental and backcalculated homonuclear $^3J(\text{H,H})$ coupling constants for **6a** and **6b** from 600 MHz 2D-DQF COSY and 1D spectra at 300 K in CDCl_3 solution.**6a:**

Proton	Proton	$^3J_{\text{exp}}$	NMR ^{a)}	$^3J_{\text{NMR}}^{\text{c)}$	Xray ^{b)}	$^3J_{\text{Xray}}^{\text{c)}$
H1	H2a	9.0	-12.1	9.31	-7.1	9.56
H1	H2e	7.1	-170.1	12.59	-171.5	12.67
H2a	H3	1.0	-90.2	1.80	-112.6	3.82
H2e	H3	7.6	31.9	7.29	56.9	3.75
H3	H4	10.2	-178.2	12.89	-178.0	12.89
H4	H5a	2.0	66.3	2.69	87.7	1.75
H4	H5e	5.8	-62.4	3.09	-58.3	3.58

6b:

Proton	Proton	$^3J_{\text{exp}}$	NMR ^{a)}	$^3J_{\text{NMR}}^{\text{c)}$	Xray ^{b)}	$^3J_{\text{Xray}}^{\text{c)}$
H1	H2a	9.0	-31.7	7.32	-11.8	9.33
H1	H2e	4.5	89.3	1.78	108.8	3.30
H4	H5e	6.0	-55.4	3.95	-64.4	2.88

a) Dihedral angle obtained using the best NMR derived structure.

b) Dihedral angle obtained using the solid state structure.

c) Computed coupling constants using Karplus' equation (¹³) and the following parameters:
A=9.5, B=-1.6, C=1.8.

Table S3: NOE Analysis for most acceptable 20 conformers for **6a** with RSS configuration.

ATOM1	ATOM2	LOWER	UPPER	AV_DIST	AV_VIOL	RMS_VIOL
H1	H4	2.43	2.97	2.42	0.01	0.01
H1	H2a	1.80	5.00	2.53	0.00	0.00
H1	H3	1.80	5.00	3.86	0.00	0.00
H1	H2e	2.88	3.52	3.08	0.00	0.00
H1	H11	3.60	6.40	3.58	0.02	0.02
H2a	H11a	3.60	4.40	4.15	0.01	0.02
H2a	H4	2.43	2.97	2.86	0.00	0.00
H2a	H10e	3.96	4.84	4.18	0.00	0.00
H2a	H3	1.80	5.00	2.78	0.00	0.00
H2a	H10a	2.79	3.41	3.02	0.00	0.00
H2e	H3	2.16	2.64	2.37	0.00	0.00
H2e	H10a	3.60	4.40	3.57	0.03	0.03
H3	H10a	2.43	2.97	2.47	0.00	0.00
H3	H10e	3.87	4.73	3.87	0.00	0.00
H3	H4	2.61	3.19	3.07	0.00	0.00
H3	QC16	2.07	3.53	2.80	0.00	0.00
H4	H11	2.25	4.75	3.18	0.00	0.00
H4	H5a	2.34	2.86	2.48	0.00	0.00
H4	H5e	2.16	2.64	2.51	0.00	0.00
H4	QC16	3.33	5.07	4.29	0.00	0.00
H5a	H6	2.34	2.86	2.48	0.00	0.00
H5a	H10a	3.60	4.40	4.49	0.09	0.09
H5e	H6	2.88	3.52	3.19	0.00	0.00
H5e	H10e	2.97	3.63	3.72	0.09	0.09
H5e	H11	2.70	5.30	4.79	0.00	0.00
H6	QC16	3.42	5.18	4.01	0.00	0.00
H9	H10e	2.52	3.08	2.65	0.00	0.00
H9	H10a	2.61	3.19	2.76	0.00	0.00
H10e	H11a	2.43	2.97	2.80	0.01	0.03
H10a	H11a	3.51	4.29	3.48	0.03	0.03
H12	H13	1.80	2.20	2.31	0.11	0.11

Average Restraint Violation: 0.013

Average RMS Restr Violation: 0.017

Table S4: NOE Analysis for most acceptable 28 conformers for **6b** with RSR configuration.

ATOM1	ATOM2	LOWER	UPPER	AV_DIST	AV_VIOL	RMS_VIOL
H1	H4	3.60	4.40	3.95	0.00	0.00
H1	H2e	2.70	3.30	2.53	0.17	0.17
H1	H2a	2.16	2.64	2.76	0.12	0.12
H1	QC16	2.43	3.97	4.07	0.10	0.10
H2e	H11a	3.24	3.96	4.03	0.07	0.07
H2a	QC16	1.80	5.00	4.50	0.00	0.00
H2a	H10a	3.33	4.07	4.26	0.19	0.19
H2a	H3	1.80	5.00	2.71	0.00	0.00
H3	H4	1.98	2.42	2.84	0.42	0.42
H3	H10a	2.25	2.75	2.47	0.00	0.00
H3	H9	1.80	5.00	4.27	0.00	0.00
H4	H5e	2.07	2.53	2.45	0.00	0.00
H4	H5a	1.89	2.31	2.40	0.09	0.09
H4	H10e	3.51	4.29	4.00	0.00	0.00
H4	H11	2.25	2.75	2.84	0.09	0.09
H5a	H6	2.25	2.75	2.49	0.00	0.00
H5e	H10e	3.06	3.74	3.49	0.00	0.00
H5e	H6	2.52	3.08	3.13	0.05	0.05
H5e	H12	1.80	5.00	4.26	0.00	0.00
H5e	H11	2.79	3.41	2.87	0.00	0.00
H9	QC16	4.50	6.50	5.78	0.00	0.00
H9	H10e	2.43	2.97	2.95	0.00	0.01
H9	H10a	2.43	2.97	2.69	0.00	0.00
H10e	H11	2.34	2.86	3.08	0.22	0.22
H10a	QC16	3.33	5.07	5.03	0.00	0.01
H12	H13	2.70	3.30	2.91	0.00	0.00

Average Restraint Violation: 0.059

Average RMS Restr Violation: 0.059

Experimental conditions, **2**: 20 g of (*R*)-tetrahydroisoquinoline-carboxylic acid and 2 equiv of potassium carbonate were dissolved in 1.6 L of THF/water (1:1). 4-Biphenyl-sulfonyl chloride (1.2 equiv in 800 mL of THF) was added at room temperature during 30 min. Workup was performed after 4 h by acidification (HCl), extraction with ethyl acetate, and flash chromatography (EtOAc/cyclohexane/1% HOAc); yield, 77%. **3**: 25 g of **2** were dissolved in 300 mL of THF, heated to 50 °C and 1 equiv of neat BMS (borane–dimethyl sulfide complex) was added during 30 min. The reaction mixture was kept at 50 °C until completion. After filtration and evaporation, 150 mL of absolute methanol was added, and the product was repeatedly evaporated after addition of methanol, and then dissolved in dichloromethane, treated with charcoal, and evaporated; yield, 79%. **4**: 17 g of **3** were dissolved in 250 mL of absolute DMSO, 1.5 equiv IBX was added and the mixture stirred overnight. The product was extracted from water/ethyl acetate, dried, evaporated, and directly converted to the nitron. **5**: 2.7 g of **4** were dissolved in 100 mL of THF with 1.5 equiv of each NMM and *N*-methylhydroxylamine hydrochloride. Then 3 equiv of sodium sulfate was added. The reaction was complete after 12 h, the product was isolated by filtration, evaporation, and chromatography (gradient EtOAc/MeOH 40:1 to 10:1); yield, 70%. Cycloaddition: 960 mg of **5** was dissolved in 40 mL of acrylonitrile and heated to 65 °C for 12 h. Both isomers in the crude product after evaporation (1.05 g) were separated by flash chromatography on silica gel using a gradient of ethyl acetate/cyclohexane (from 1:2 to 2:1). Yield of **6a**, 296 mg; **6b**, 280 mg.

Both compounds were crystallized as racemates. Crystals for **6a** were grown from ethanol. Direct methods were used for solving the phase problem, the refinement of structure parameters was done by least-squares methods (minimization of $(F_o^2 - F_c^2)^2$ leading to $R = 0.115$ for all 2375 reflections including most of the hydrogens obtained from a difference Fourier synthesis of the electron density. Crystals for **6b** were made by diffusion of *n*-heptane in the gas phase into a solution of this compound in ethanol. Applying similar methods to solve the structure lead to $R = 0.0672$ for all 3362 reflections including all hydrogens. Full details on both structures and all experimental conditions will be given elsewhere (Paulus, E. F.; Schwab, W.; Knauf, M.; Matter, H. 1998, in preparation.).