Electronic supplementary materials *Mendeleev Commun.*, 2018, **28**, 27–28

Enhanced enantiostability of BINOL dimethyl ether under moderate acidic conditions

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Experimental

Materials and equipment

Racemic BINOL (1,1'-bi-2-naphthol, **1**), (*S*)-BINOL ((*S*)-**1**), (−)-isopulegol, quinine and europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] ($Eu(hfc)_3$) were purchased from chemical suppliers and used as received.

The ^{13}C and ^{1}H NMR spectra were recorded in the Chemical Service Center of Joint Use of SB RAS (N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry) using Bruker AV-600 spectrometer. The chemical shifts were measured relative to the residual proton and carbon signals of $CDCl_3$ (δ_H 7.24 ppm, δ_C 76.9 ppm) or CD_2Cl_2 (δ_H 5.33 ppm, δ_C 53.6 ppm). The experimental uncertainty in the optical purity measurements on the basis of the ^{13}C and ^{1}H NMR chiral discrimination did not exceed 2% and 0.5%, respectively.

Preparation of (*S*)-BINOL dimethyl ether (*S*)-5

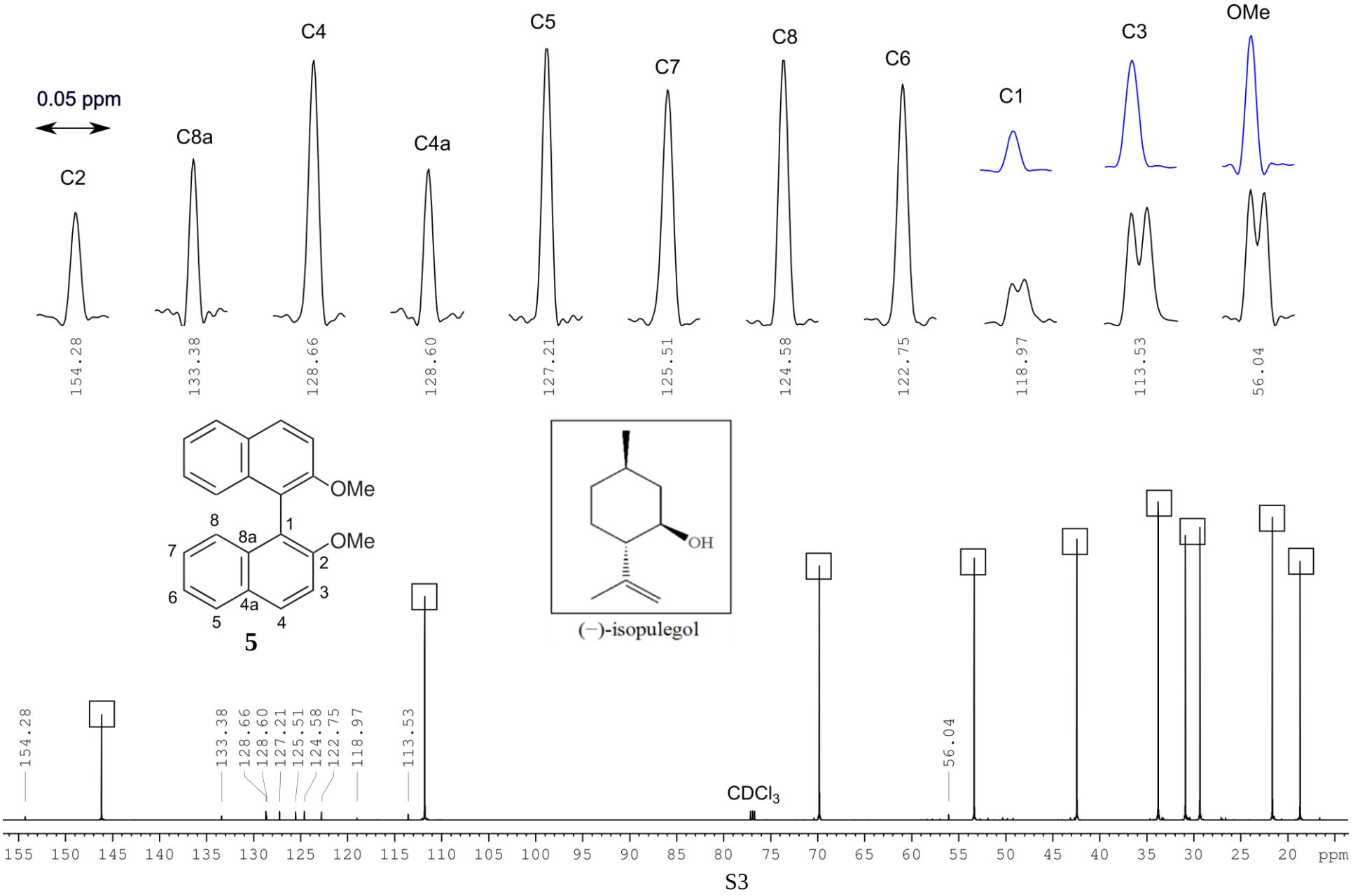
Iodomethane (0.85 g, 6 mmol) was added to a stirred mixture of (*S*)-**1** (0.5 g, 1.6 mmol) and powdered K_2CO_3 (0.79 g, 5.7 mmol) in 10 ml of DMF. The mixture was stirred at 25 °C for 100 h, and then poured into water (50 ml). The precipitate was filtered off, washed with water, then washed with cold acetone and dried to obtain (*S*)-**5** as a white powder (0.49 g, 89%), mp 224-226 °C. Lit. mp 224-225 °C.[1] ^{1}H NMR ($CDCl_3$) δ: 3.77 (s, 6H), 7.11 (d, 2H, *J* 8.8 Hz), 7.21 (m, 2H), 7.31 (m, 2H), 7.46 (d, 2H, *J* 8.8 Hz), 7.86 (d, 2H, *J* 8.3 Hz), 7.97 (d, 2H, *J* 8.8 Hz). At that, no impurity of (*R*)-**5** was observed by ^{13}C NMR and ^{1}H chiral discrimination, which is in accordance with the literature.[2]

References

1 D. S. Lingenfelter, R. C. Helgeson and D. J. Cram, *J. Org. Chem*., 1981, **46**, 393.

2 L. Đorđević, T. Marangoni, T. Miletić, J. Rubio-Magnieto, J. Mohanraj, H. Amenitsch, D. Pasini, N. Liaros, S. Couris, N. Armaroli, M. Surin and D. Bonifazi, *J. Am. Chem. Soc*., 2015, **137**, 8150.

^{13}C NMR spectrum (151 MHz) of (*R*,*S*)-BINOL dimethyl ether (racemic compound **5**, 3 mg) in (−)-isopulegol (0.3 ml) and $CDCl_3$ (0.3 ml) at 26 °C. The blue colored signals belong to (*S*)-BINOL dimethyl ether (compound (*S*)-**5**) after treatment with H_2SO_4-H_2O/1,4-dioxane at 100 °C for 40 h.



^{1}H NMR spectrum (600.3 MHz) of (*R*,*S*)-BINOL dimethyl ether (racemic compound **5**, 2 mg) in CCl_4 (0.4 ml) and CD_2Cl_2 (0.1 ml) at 26 °C (a). The same after addition of 0.5 mg of Eu(hfc)$_3$ (b). The blue colored spectrum refers to (*S*)-**5** after treatment with H_2SO_4-H_2O/1,4-dioxane at 100 °C for 40 h (solution in CCl_4/CD_2Cl_2/ Eu(hfc)$_3$).