

Electronic Supporting Information

Dendron-anchored organocatalysts: The asymmetric reduction of imines with trichlorosilane, catalysed by an amino acid-derived formamide appended to a dendron

Marek Figlus,^a Stuart T. Caldwell,^a Dawid Walas,^a Gulen Yesilbag,^b Graeme Cooke,^{*a} Pavel Kočovský^{*a} Andrei V. Malkov,^{*a,c} and Amitav Sanyal,^{*b}

^a WestCHEM, Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, U.K.

^b Department of Chemistry, Bogazici University, Bebek, Istanbul 34342, Turkey.

^c Current address: Department of Chemistry, Loughborough University, Loughborough LE11 3TU, UK

E-mail: A.Malkov@lboro.ac.uk, graemec@chem.gla.ac.uk, pavelk@chem.gla.ac.uk, amitav.sanyal@boun.edu.tr

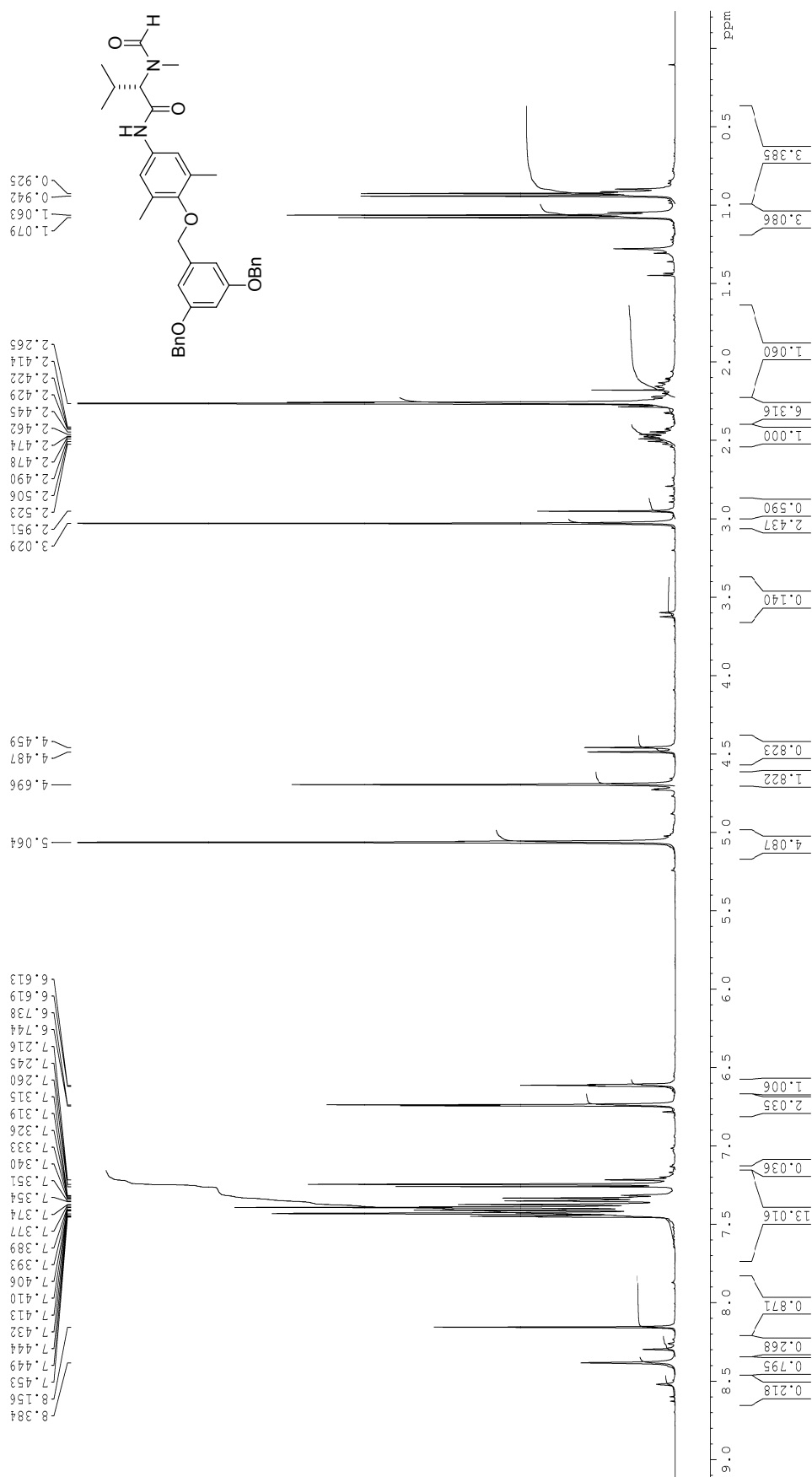
Table of Contents

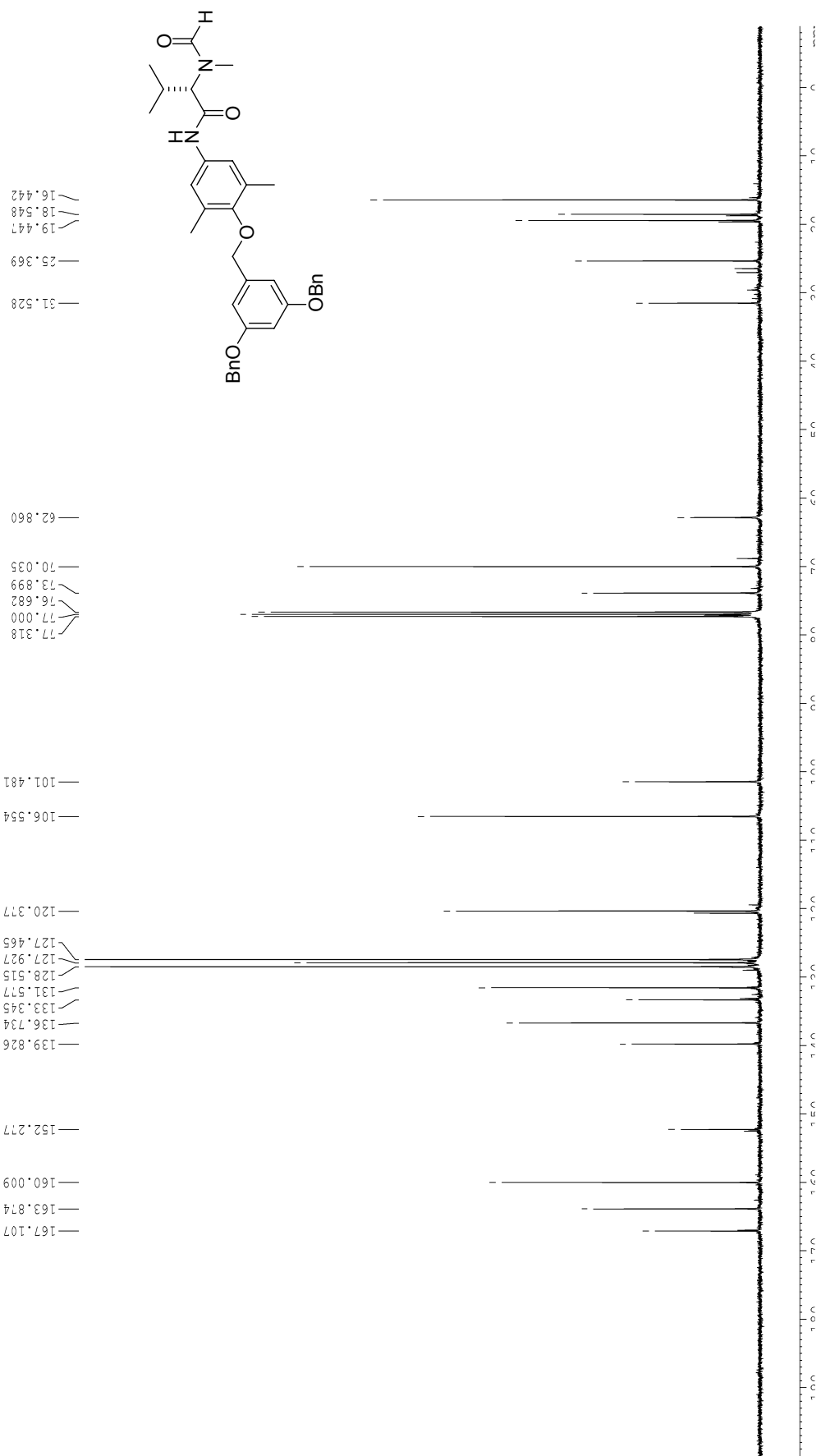
General Methods	S2
¹ H and ¹³ C NMR spectra of the dendron-anchored catalysts 11a-c	S3 – S8

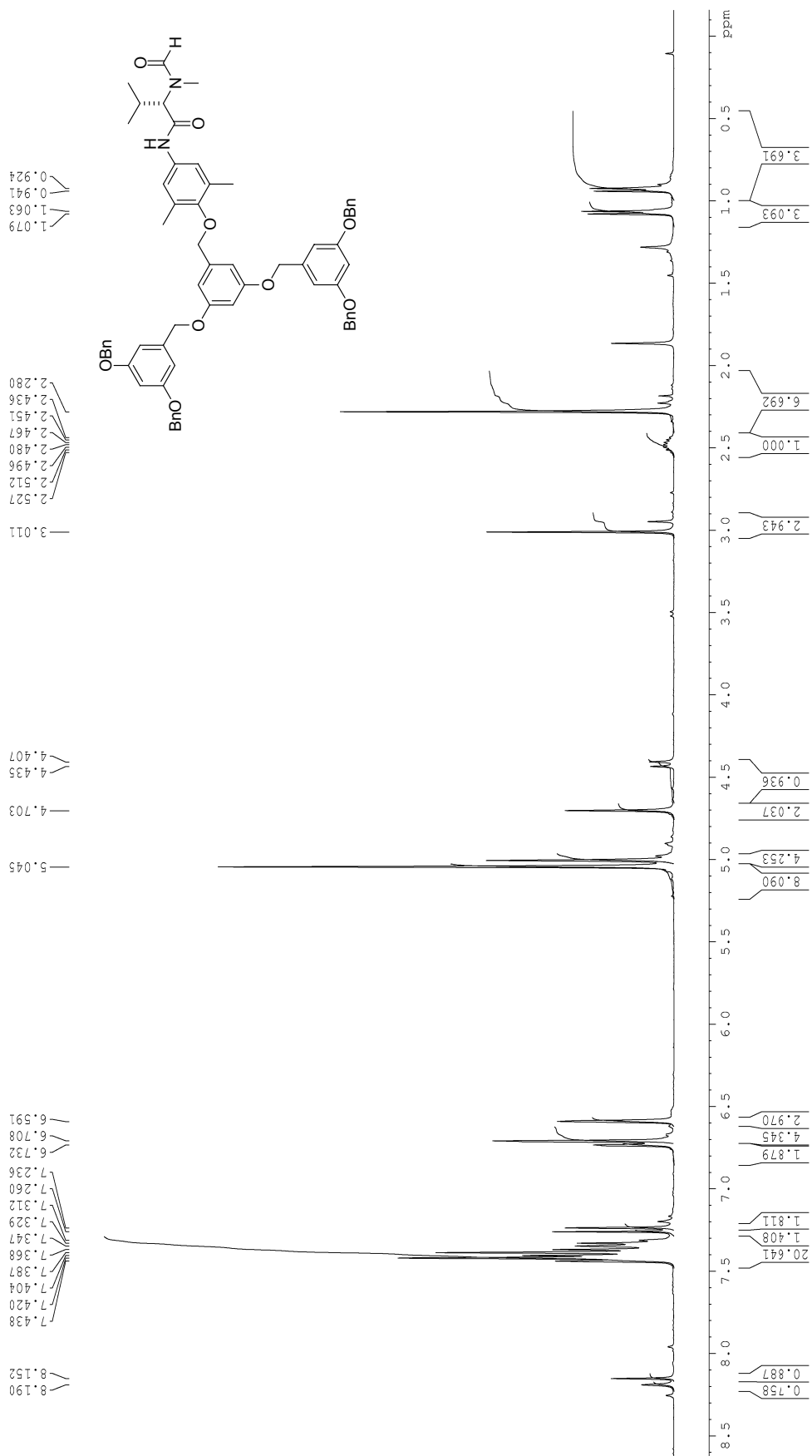
General Methods. Melting points were determined on a Kofler block and are uncorrected. The NMR spectra were recorded for CDCl₃ solutions, ¹H at 400 MHz and ¹³C at 100.6 MHz with chloroform-*d*₁ (δ 7.26, ¹H; δ 77.0, ¹³C) or TMS as internal standard unless otherwise indicated. Various 2D-techniques and DEPT experiments were used to establish the structures and to assign the signals. The IR spectra were recorded for a thin film of CHCl₃ solutions between NaCl plates. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. Some reactions, when needed, were performed under an atmosphere of dry, oxygen-free argon in oven-dried glassware twice evacuated and filled with argon. Solvents and solutions were transferred by syringe-septum technique. Solvents for the reactions were of reagent grade and were dried as follows: THF, toluene, and dichloromethane were obtained from Pure-Solv™ Solvent Purification System (Innovative Technology). Aniline and *p*-anisidine were distilled prior to use. Petroleum ether refers to the fraction boiling in the range of 40-60 °C. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior. The chiral GC and HPLC methods were calibrated with the corresponding racemates. Imines **1a-f** and amines **2a-f** are known compounds, previously prepared in this Laboratory; ^{S1} synthesis of the phenolic derivative **6** was reported by us recently.^{S1c,e} Dendrons **12 a-12c** were prepared using the previously reported methodology.^{S2} For the chiral HPLC traces of the reduction products, see the adjacent paper.^{S1g}

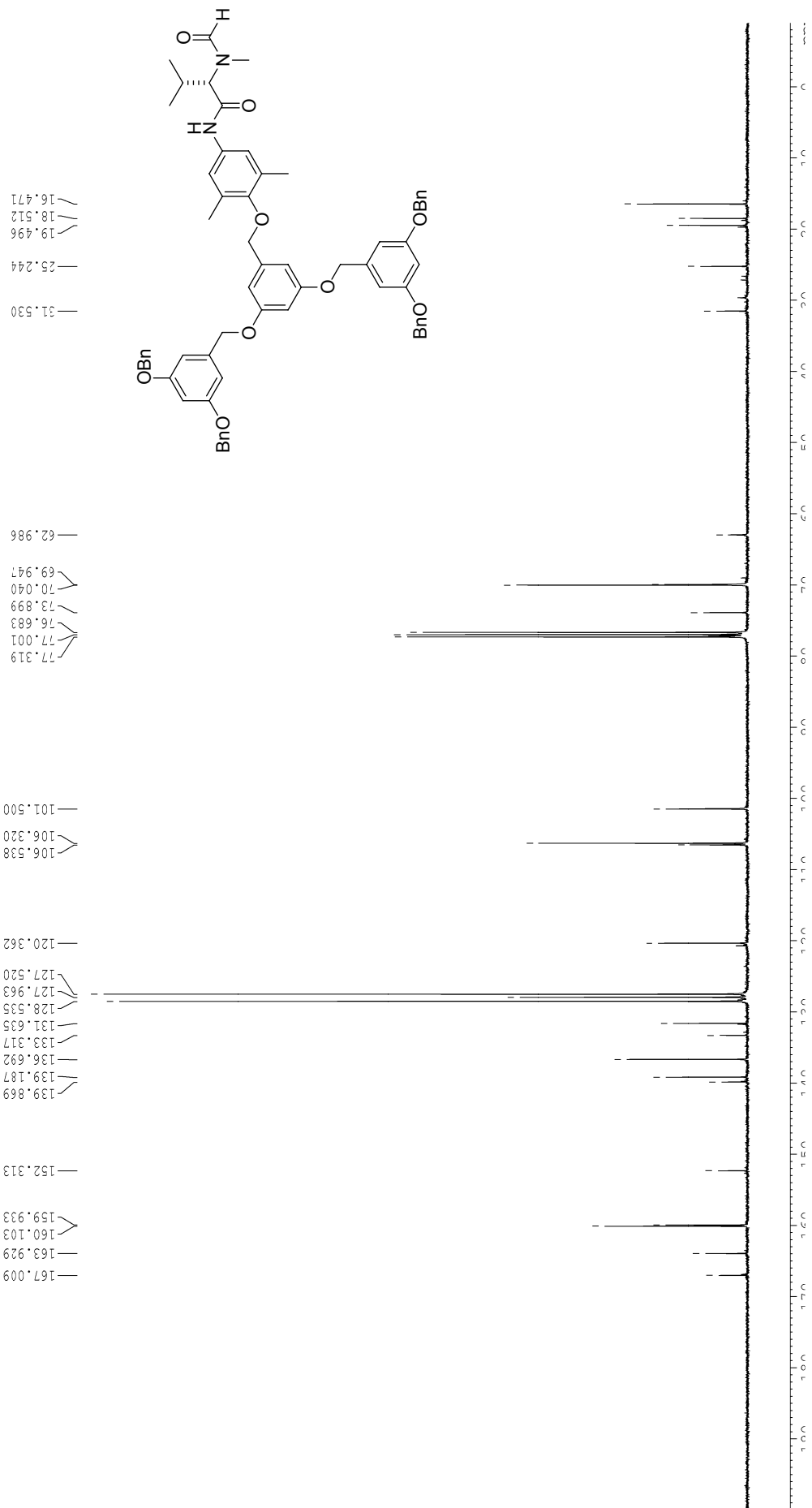
(S1) (a) Malkov, A. V.; Mariani, A.; MacDougall, K. N.; Kočovský, P. *Org. Lett.* **2004**, *6*, 2253. (b) Malkov, A. V.; Stončius, S.; MacDougall, K. N.; Mariani, A.; McGeoch, G. D.; Kočovský, P. *Tetrahedron* **2006**, *62*, 264. (c) Malkov, A. V.; Figlus, M.; Stončius, S.; Kočovský, P. *J. Org. Chem.* **2007**, *72*, 1315. (d) Malkov, A. V.; Stončius, S.; Kočovský, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 3722. (e) Malkov, A. V.; Figlus, M.; Kočovský, P. *J. Org. Chem.* **2008**, *73*, 3985. (f) Malkov, A. V.; Stončius, S.; Vranková, K.; Arndt, M.; Kočovský, P. *Chem. Eur. J.* **2008**, *14*, 8082. (g) Malkov, A. V.; Vranková, K.; Stončius, S.; Kočovský, P. *J. Org. Chem.* **2009**, *74*, [in press](#). (h) Malkov, A. V.; Vranková, K.; Sigerson, R.; Stončius, S.; Kočovský, P. [manuscript in preparation](#). (i) Malkov, A. V.; Figlus, M.; Cooke, G.; Caldwell, S. T.; Rabani, G.; Prestly, M. R.; Kočovský, P. *Org. Biomol. Chem.* **2009**, 1878. (j) Malkov, A. V.; Figlus, M.; Prestly, M. R.; Rabani, G.; Cooke, G.; Kočovský, P. [manuscript in preparation](#).

(S2) Hawker, C. J.; Fréchet, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 7638-7647.

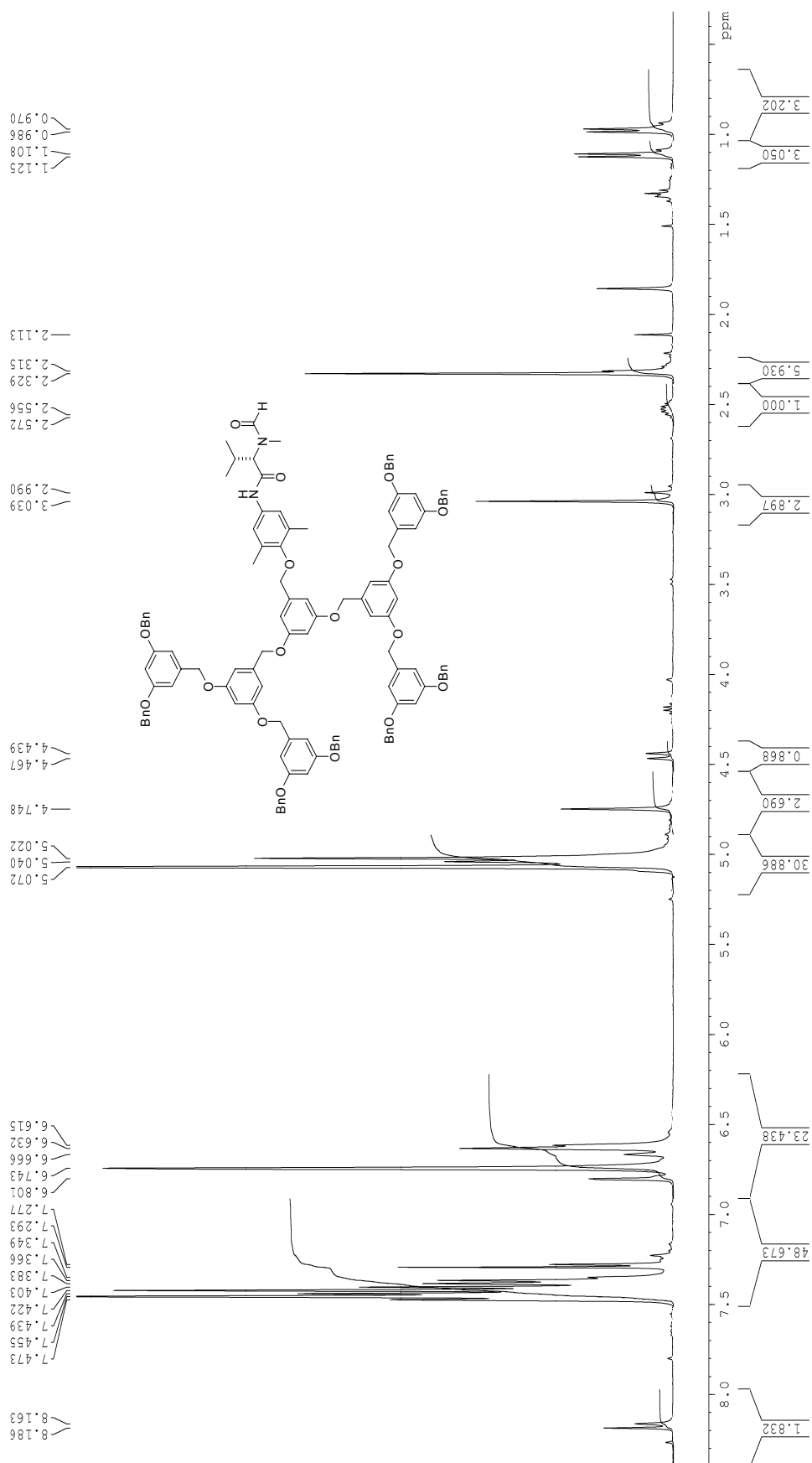








S7



S8

