Molbank **2013**, M795

Support Information

1. ^{1}H- and ^{13}C-NMR spectra of product 3

📖 6,6'-(1*E*,1'*E*)-((1*R*,2*R*)-1,2-Diphenylethane-1,2-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-((trimethylsilyl)ethynyl)phenol) (**3**)

Chemical Formula: $C_{46}H_{56}N_2O_2Si_2$

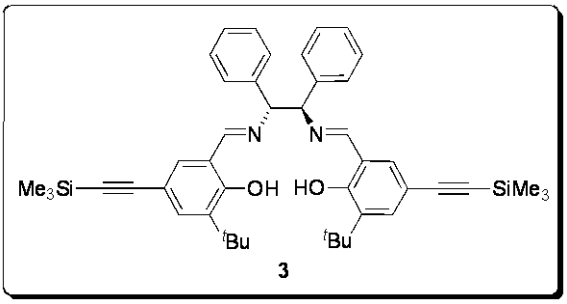


Figure S1. ^{1}H-NMR spectrum of **3** (300 MHz, $CDCl_3$).

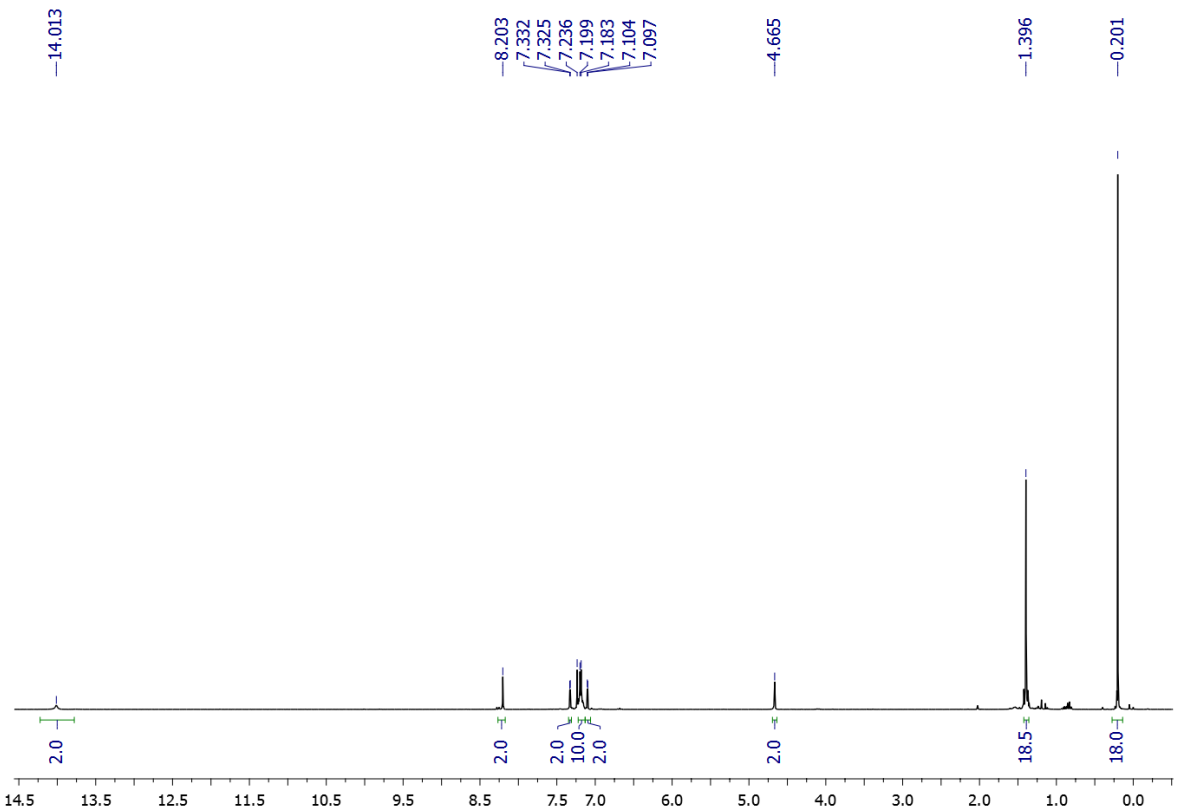
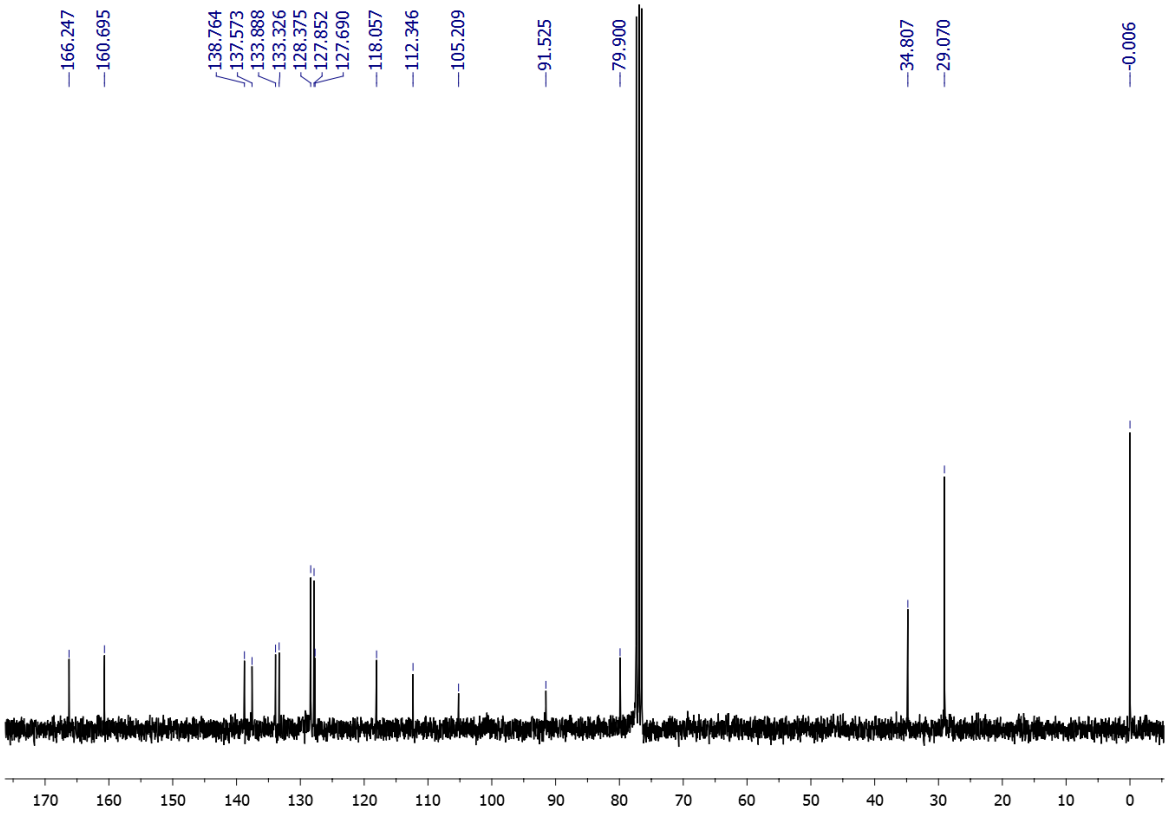


Figure S2. ^{13}C-NMR spectrum of **3** (75 MHz, $CDCl_3$).



2. General procedure for grafting onto 3-mercaptopropyl silica gel

Hydrophilic 3-mercaptopropyl silica gel (c(SH) = 0.43 mmol g^{-1}) was prepared as described in the literature [1]. Reaction of **3** with 3-mercaptopropyl silica gel was performed, upon deprotection of TMS groups, by radical grafting following the general procedure previously described [2].

Procedure:

(i) To a solution of **3** (624 mg, 0.86 mmol) in THF (10 mL), was added TBAF (1.1 mL, from 1 M solution in THF) and HCl (0.9 mL, from a 1 M aqueous solution). The mixture was vigorously stirred at RT for 48 h. After this time, the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic phases were dried over sodium sulfate, filtered and the solvent evaporated to dryness. The obtained residue was used in the next step without further purification.

(ii) 3-Mercaptopropyl silica gel (1 g) and AIBN (149 mg, 0.9 mmol) were subsequently added to a suspension of the above crude in degassed MeOH:$CHCl_3$ (15 mL; 1:1 v/v). The reaction was heated at 70 ℃ for 72 h. After this time, the silica was filtered, washed thoroughly with $CHCl_3$ and the resulting yellow material dried under vacuum. Under these conditions, ca. 73% of SH groups were reacted based on the Ellman's SH test [3]. The loading determined by weight difference was estimated in 0.23 mmol g^{-1}.

References and Notes

1. Heckel, A.; Seebach, D. Preparation and characterization of TADDOLs immobilized on hydrophobic controlled-pore-glass silica gel and their use in enantioselective heterogeneous catalysis. *Chem. Eur. J.* **2002**, *8*, 559–572.
2. Heckel, A.; Seebach, D. Enantioselective heterogeneous epoxidation and hetero-Diels-Alder reaction with Mn- and Cr-salen complexes immobilized on silica gel by radical grafting. *Helv. Chim. Acta* **2002**, *85*, 913–926, and references therein.
3. Ellman, G.L. Tissue sulfhydryl groups. *Arch. Biochem. Biophys.* **1959**, *82*, 70–77.