

Supporting Information

Expeditious Synthesis of a Common Intermediate of L-1-Deoxyallonojirimycin and L-1-Deoxymannojirimycin

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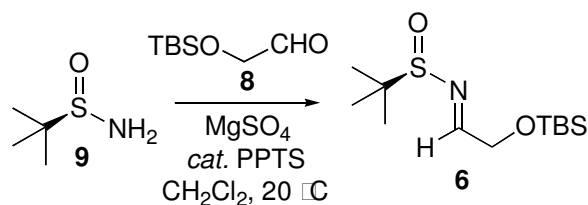
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I. General information

Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry N₂. Liquid nitrogen was used as a cryoscopic fluid. A four-necked, round-bottomed flask equipped with an internal thermometer, a septum cap, a nitrogen inlet, and a mechanical stirrer was used. Anhydrous solvents were distilled to remove stabilizers and dried with a double column purification system. Zinc bromide (98%) was melted under dry N₂ and, immediately after cooling to room temperature, was dissolved in anhydrous Et₂O. All other reagents and solvents were of commercial quality and were used without further purification. For ¹H NMR and ¹³C NMR spectra, chemical shifts are reported in δ relative to an internal standard of residual chloroform (δ = 7.27 for ¹H NMR and 77.1 for ¹³C NMR).

II. Synthesis of (–)-(R_S,E)-N-[2-(*tert*-Butyldimethylsiloxy)ethylidene]-2-methylpropane-2-sulfinamide (6).



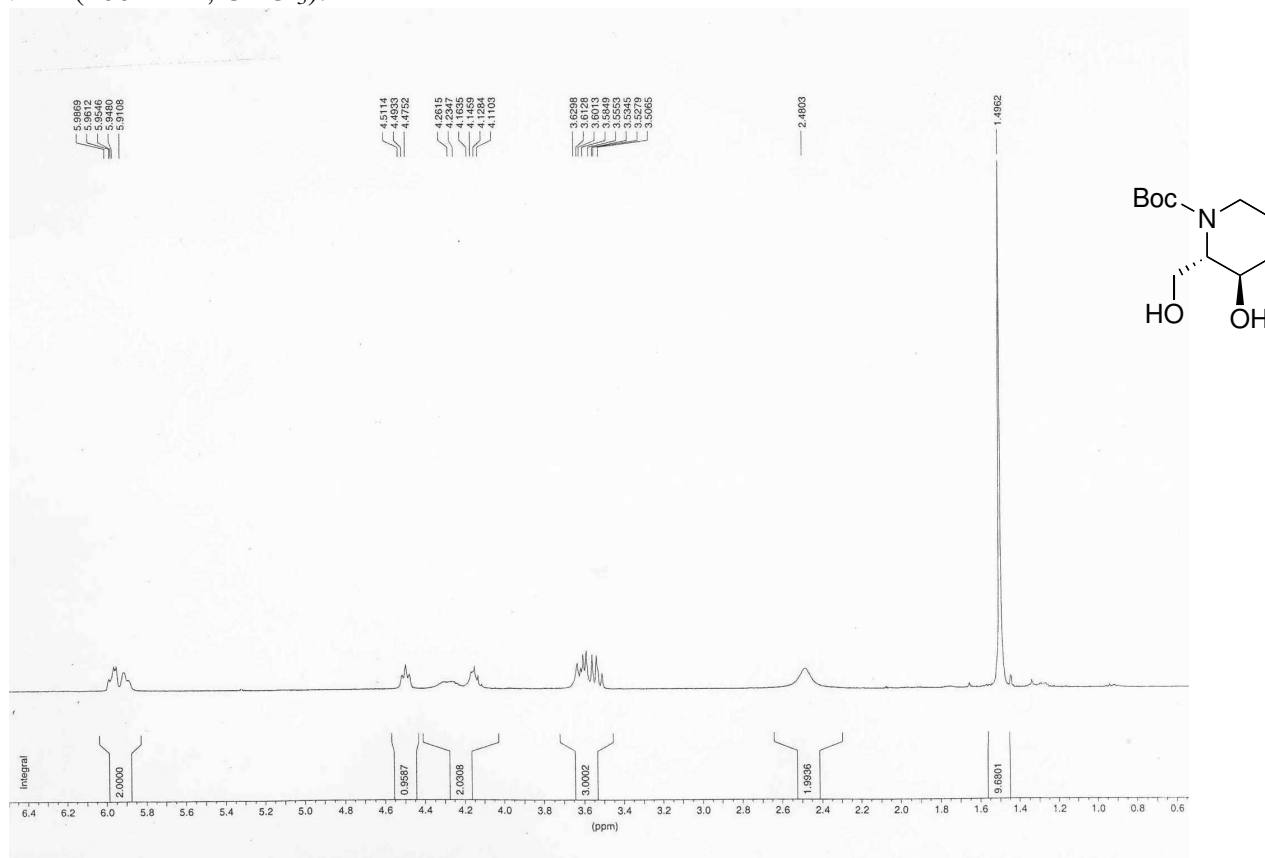
Under a nitrogen atmosphere, to a stirred solution of commercially available (*R_S*)-*tert*-butylsulfinamide (**9**) (1.69 g, 14.00 mmol), PPTS (175 mg, 0.70 mmol) and anhydrous MgSO₄ (8.40 g, 70.00 mmol) in anhydrous CH₂Cl₂ (20 mL) was added dropwise, at 20 °C, (*tert*-butyldimethylsilyloxy)acetaldehyde (**8**)¹ (4.97 g, 28.00 mmol) in anhydrous CH₂Cl₂ (10 mL). The resulting suspension was stirred for 24 h at 20 °C, filtered and the solvent was removed in vacuo. The residual oil was purified by flash silica gel chromatography (10% EtOAc/cyclohexane) to give the title compound **6** (3.44 g, 83%) as a pale yellow oil : ¹H NMR (400 MHz, CDCl₃) δ 8.08 (t, *J* = 3 Hz, 1H), 4.57 (d, *J* = 3 Hz, 2H), 1.23 (s, 9H), 0.94 (s, 9H), 0.12 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 65.5, 56.7, 25.7, 22.3, 18.3, −5.4; HRMS (ESI) Calcd. For C₁₂H₂₈NO₂SSi [M+H]⁺: 278.1605. Found: 278.1604; [α]_D²⁰ = −164.9 (*c* 0.77, CHCl₃).

(1) Paterson, I.; Delgado, O.; Florence, G. J.; Lyothier, I.; O'Brien, M.; Scott, J. P.; Sereinig, N. *J. Org. Chem.* **2005**, *70*, 150–160.

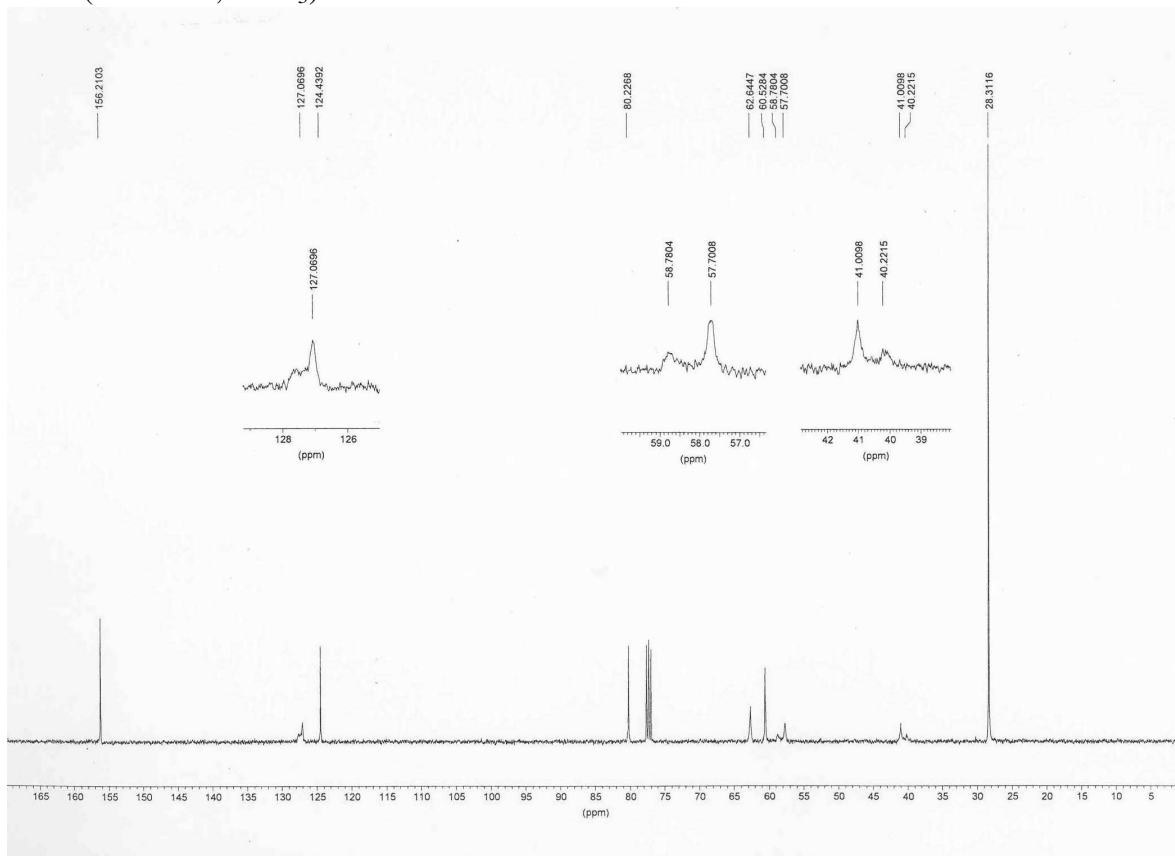
III. ^1H and ^{13}C NMR Spectra

III.1. (-)-(2*S*,3*R*)-3-Hydroxy-2-hydroxymethyl-3,6-dihydro-2*H*-pyridine-1-carboxylic *tert*-butyl ester (**3**).

^1H NMR (400 MHz, CDCl_3):

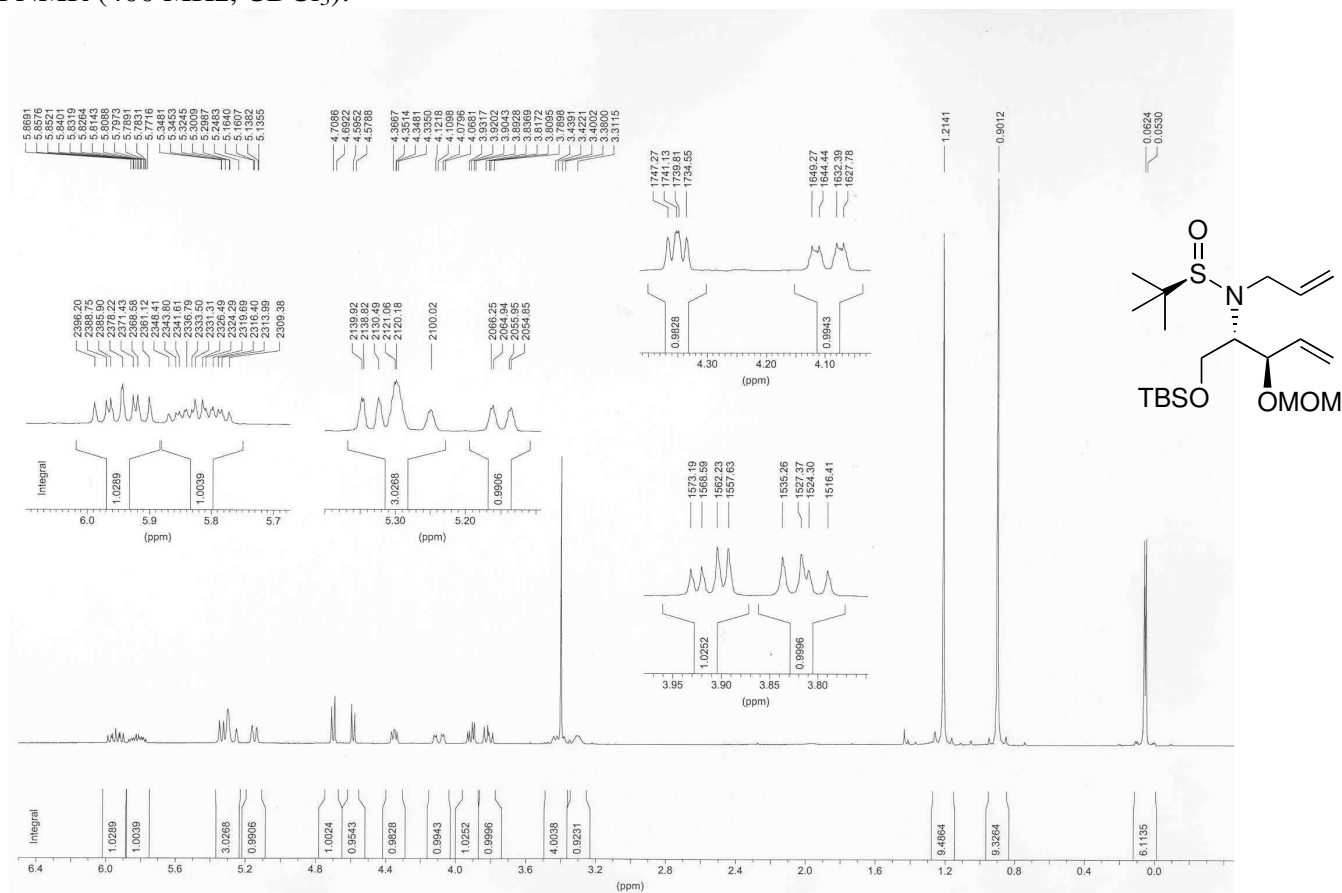


^{13}C NMR (100 MHz, CDCl_3):

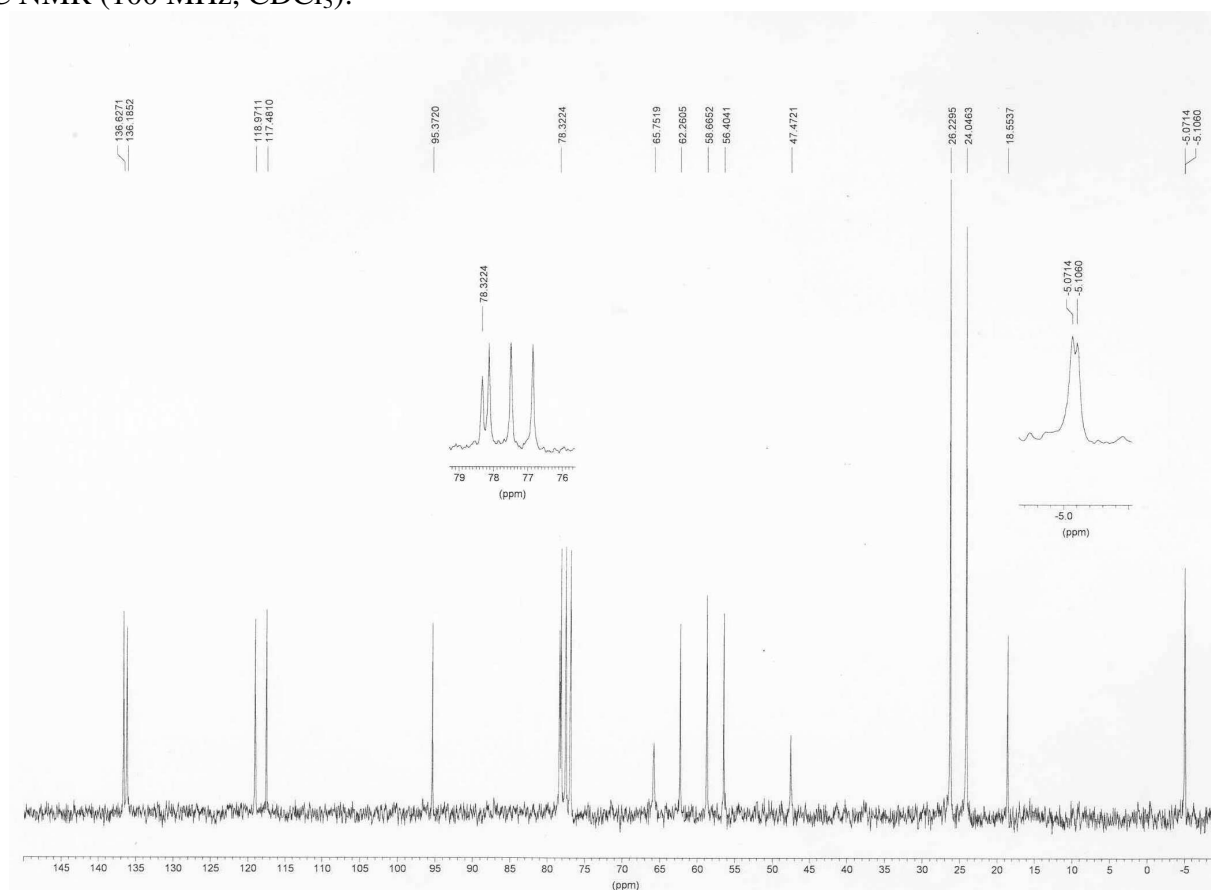


III.2. (+)-(R_S)-N-Allyl-N-{(1S,2R)-1-[(*tert*-butyldimethylsiloxy)methyl]-2-(methoxymethoxy)but-3-enyl}-2-methylpropane-2-sulfinamide (4).

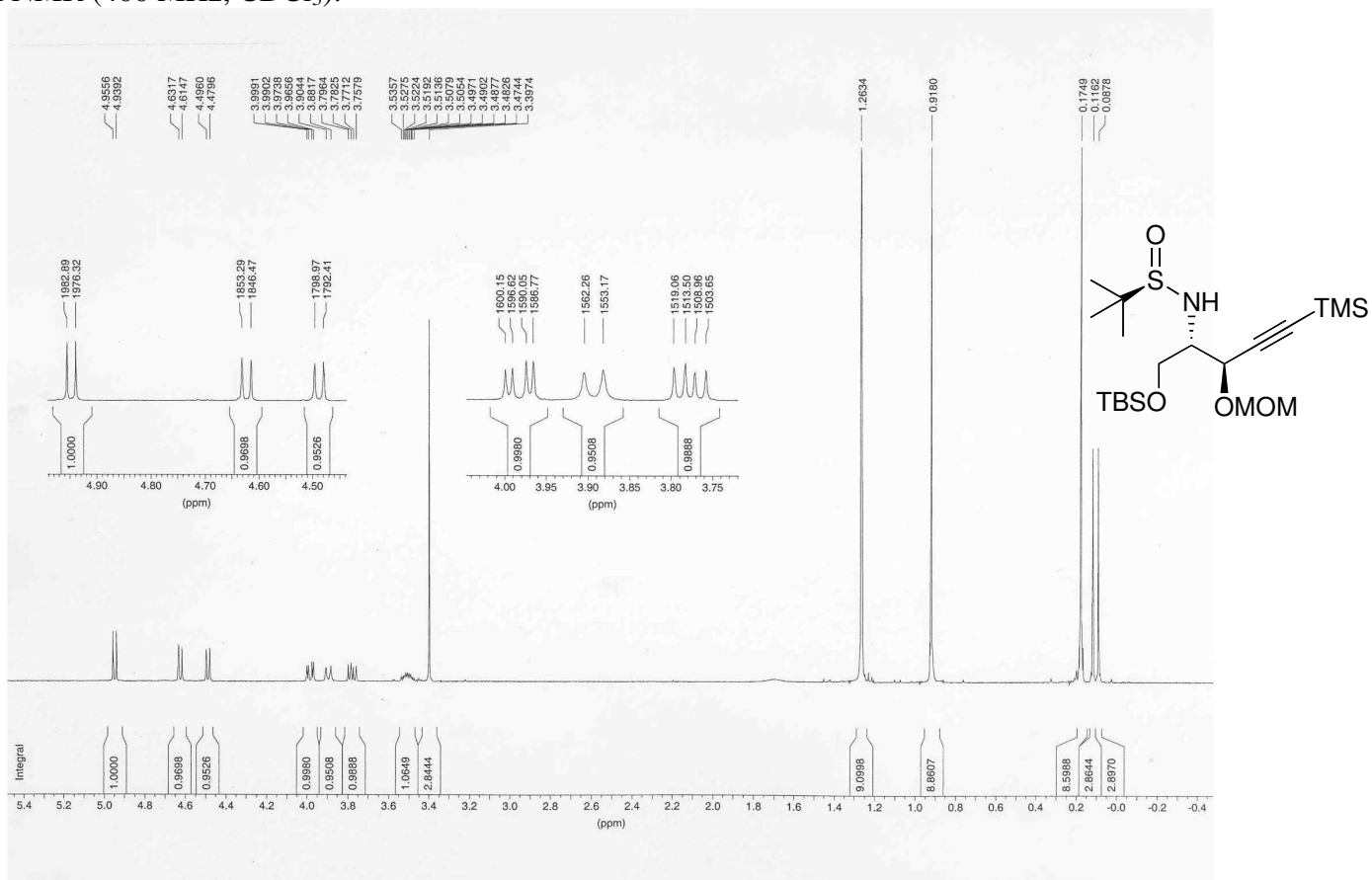
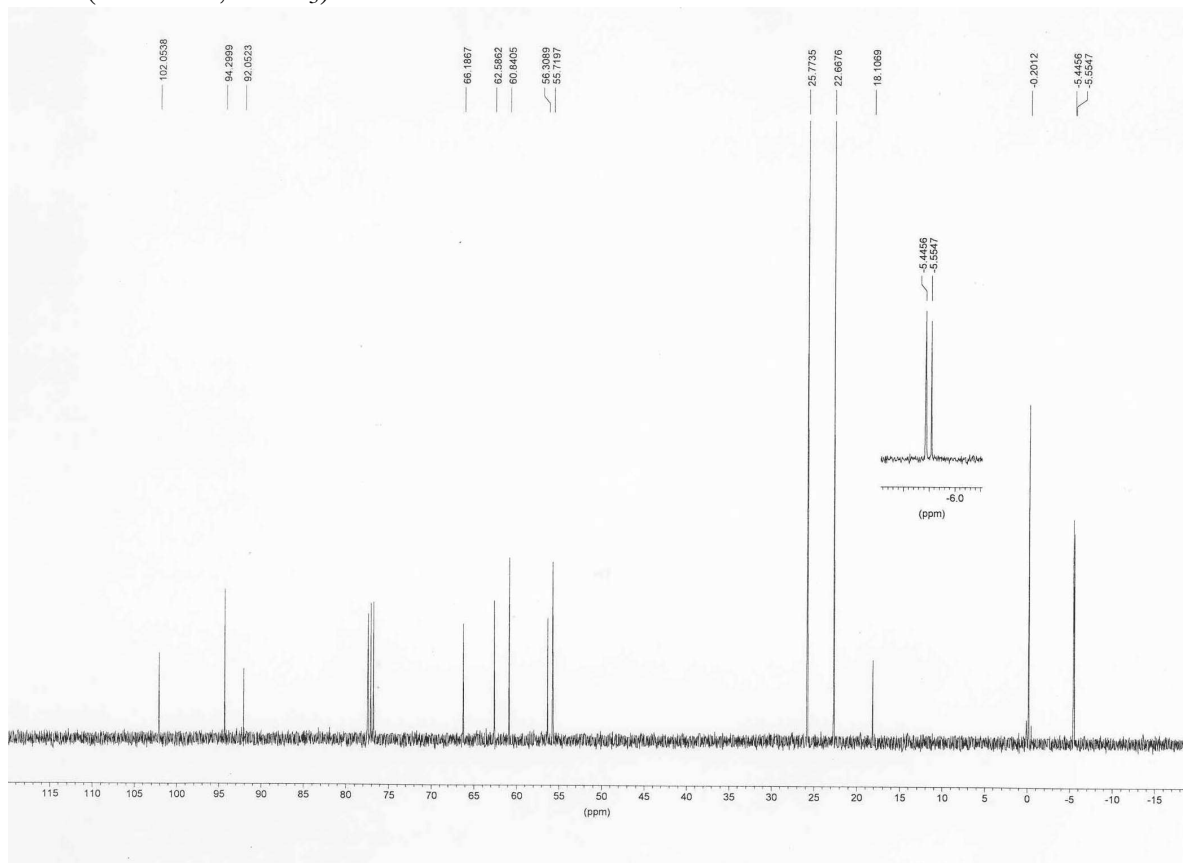
¹H NMR (400 MHz, CDCl₃):



¹³C NMR (100 MHz, CDCl₃):

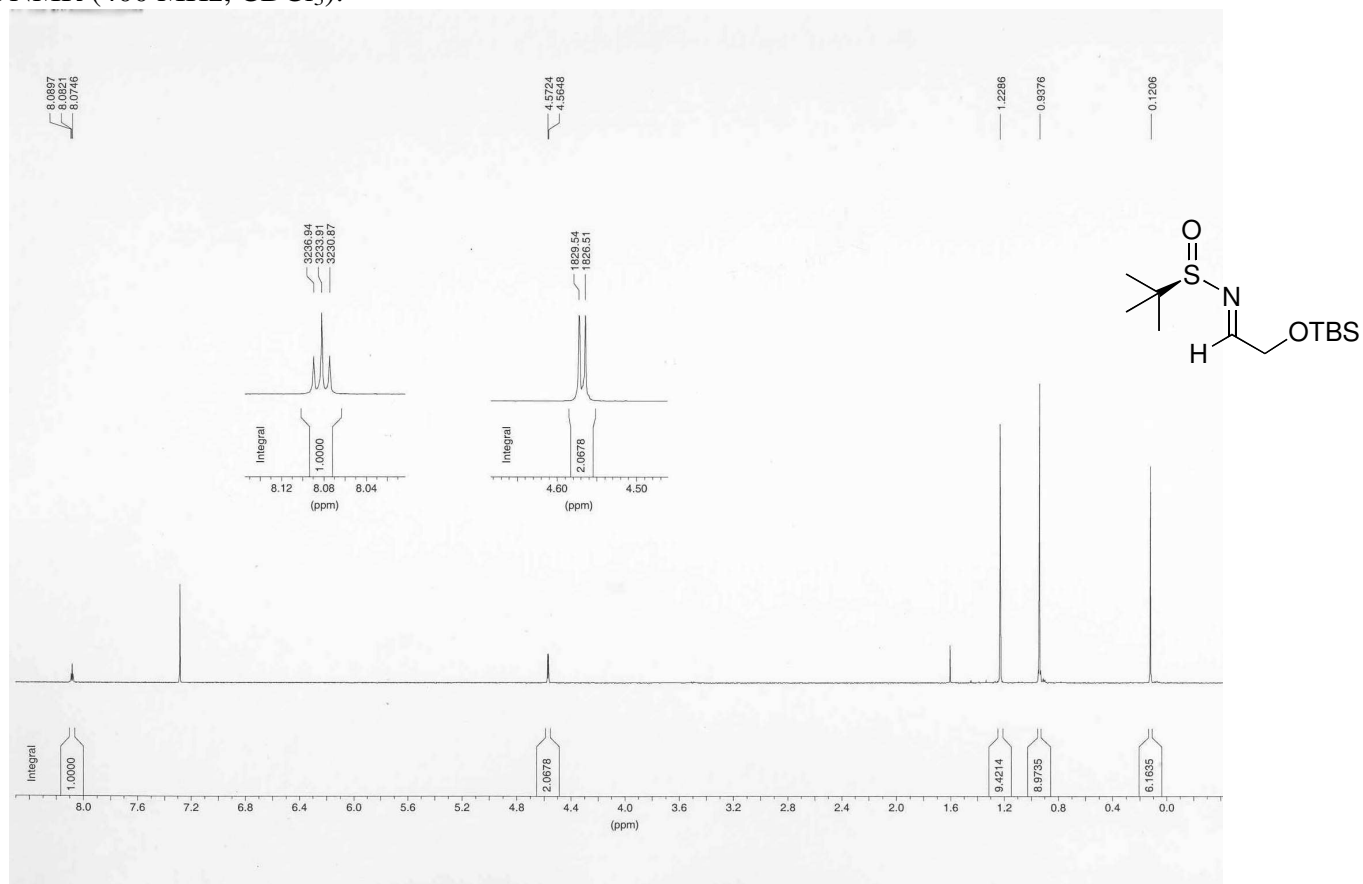


III.3. (-)-(R_S)-N-{(1*S*,2*R*)-1-[(*tert*-Butyldimethylsiloxy)methyl]-2-(methoxymethoxy)-4-(trimethylsilyl)but-3-ynyl}-2-methylpropane-2-sulfinamide (5).

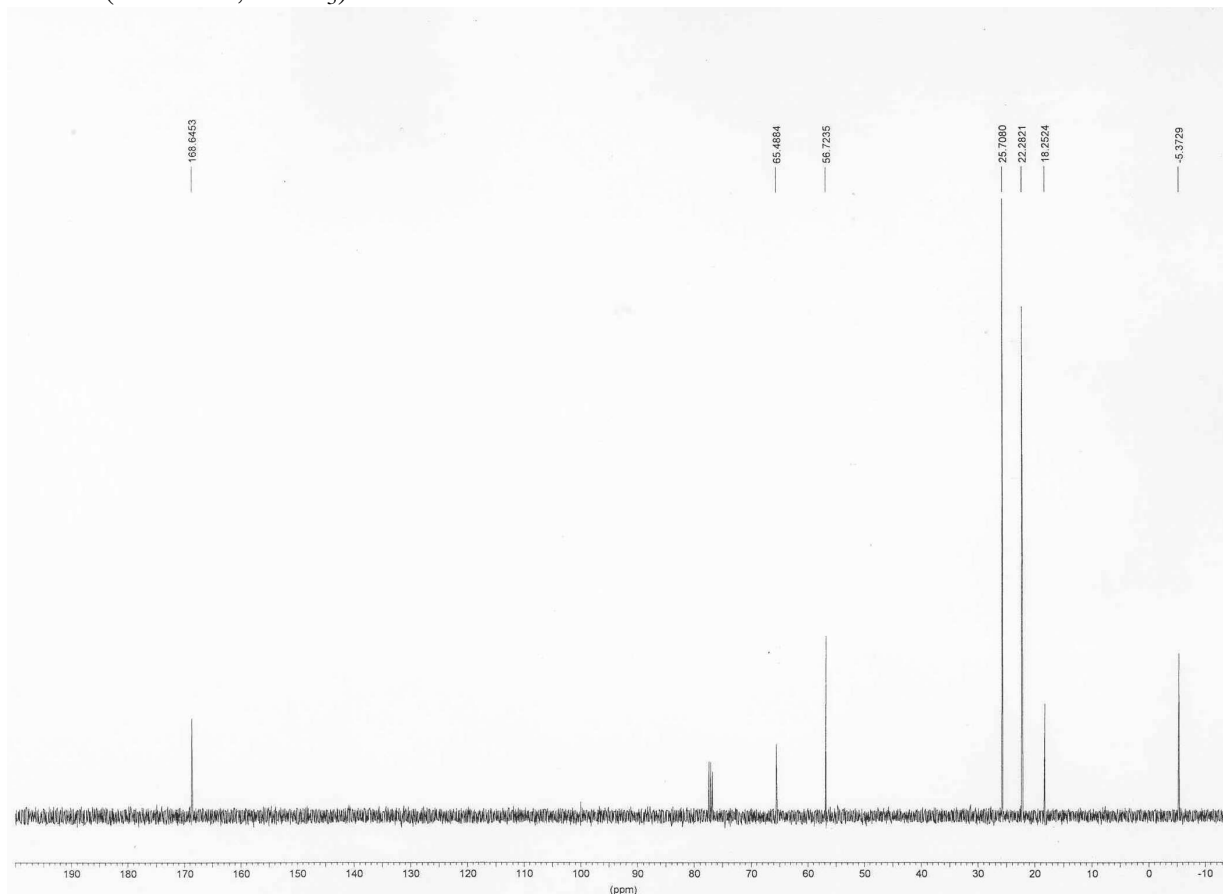
¹H NMR (400 MHz, CDCl₃): ^{13}C NMR (100 MHz, CDCl_3):

**III.4. (-)-(R_S,E)-N-[2-(*tert*-Butyldimethylsiloxy)ethylidene]-2-methylpropane-2-sulfonamide
(6).**

¹H NMR (400 MHz, CDCl₃):

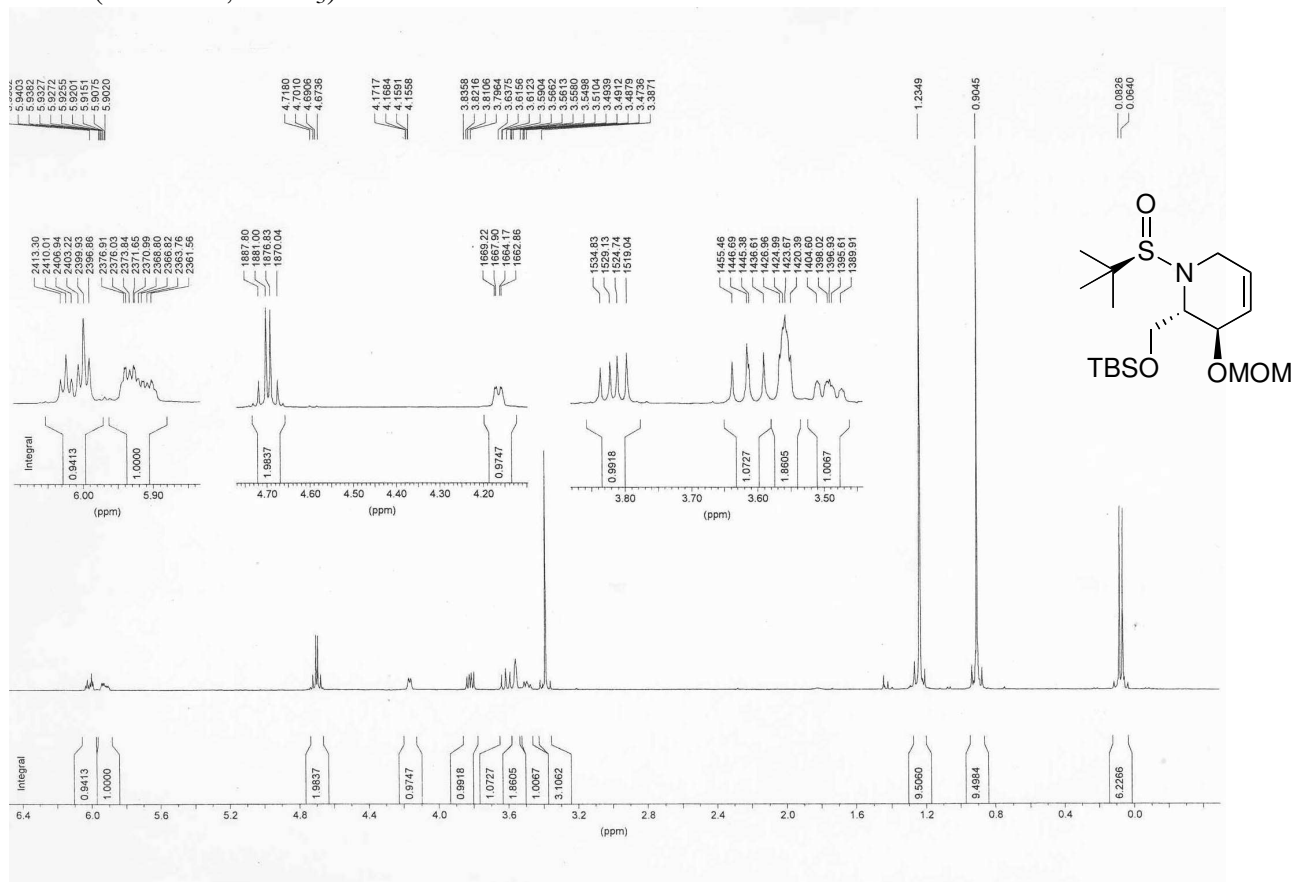


¹³C NMR (100 MHz, CDCl₃):



¹H NMR (400 MHz, CDCl₃):

III.6. (-)-(R_S)-N-{(2*S*,3*R*)-2-[(*tert*-Butyldimethylsiloxy)methyl]-3-(methoxymethoxy)-3,6-dihydro-2*H*-pyridinyl}-2-methylpropane-2-sulfinamide (13).

¹H NMR (400 MHz, CDCl₃): ^{13}C NMR (100 MHz, CDCl_3):