Supporting Information

DIVERGENT SYNTHESIS OF 2,6-DISUBSTITUTED PIPERIDINE ALKALOID, (+)-SPECTALINE BY PALLADIUM-CATALYZED CYCLIZATION

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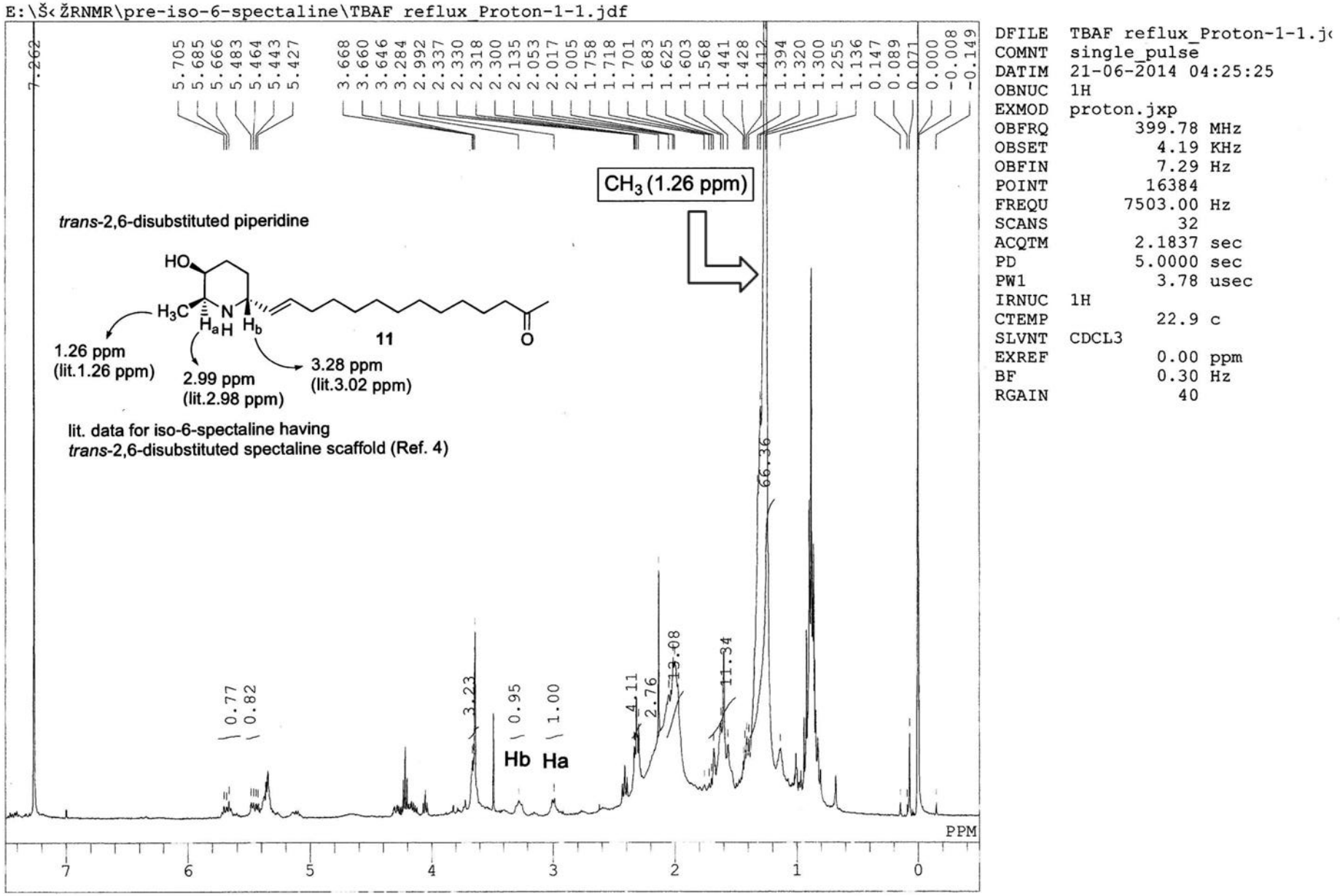
EXPERIMENTAL

General Methods. ^{1}H NMR spectra were recorded in $CDCl_3$ on agilent UNITY INOVA 400 NB spectrometer. Chemical shifts are expressed in ppm relative to tetramethylsilane (0.00 ppm). The coupling constants are given in Hz.

(1'*EZ*,2*S*,3*S*,6*R*)-3-Hydroxy-2-methyl-6-(13'-oxotetradec-1'-en-1'-yl)piperidine (11): To a solution of **4** (11 mg, 0.023 mmol) and tetradec-13-en-2-one (29 mg, 0.14 mmol) in CH_2Cl_2 (2.0 mL) was added Grubbs 2nd catalyst (3.9 mg, 0.0046 mmol). After stirring for 1 day under reflux, an additional solution of Grubbs 2nd catalyst in CH_2Cl_2, (3.9 mg, 0.0046 mmol) was added. After stirring for 1 day under reflux, the solvent was removed and the residue was roughly purified by silica gel column chromatography (hexane/EtOAc = 20:1). The product was used for next step without further purification. The product was dissolved in MeOH (2 mL) and 12 mol/L HCl (0.2 mL) was added. After stirring for 12 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was roughly purified by silica gel column chromatography (hexane/EtOAc = 1:1). The product was used for next step without further purification. The product was dissolved in THF (1 mL) and TBAF (1.0 mol/L in THF, 0.2 mL, 0.2 mmol) was added. After stirring for 12 h under reflux, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative TLC ($CHCl_3$/MeOH = 5:1) to give **11** as a yellowish oil and it's epimer **10** (**11**:**10** = 1:3). ^{1}H NMR (400 MHz) δ: 1.26-1.44 (13H, m), 1.56-1.76 (9H, m), 2.02-2.05 (3H, m), 2.05 (3H, s), 2.32 (2H, t, *J* = 7.4 Hz), 2.99 (1H, m), 3.28 (1H, m), 3.66-3.67 (1H, m), 5.43-5.48 (1H, m), 5.67-5.71 (1H, m).

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FREQU        7503.00 Hz
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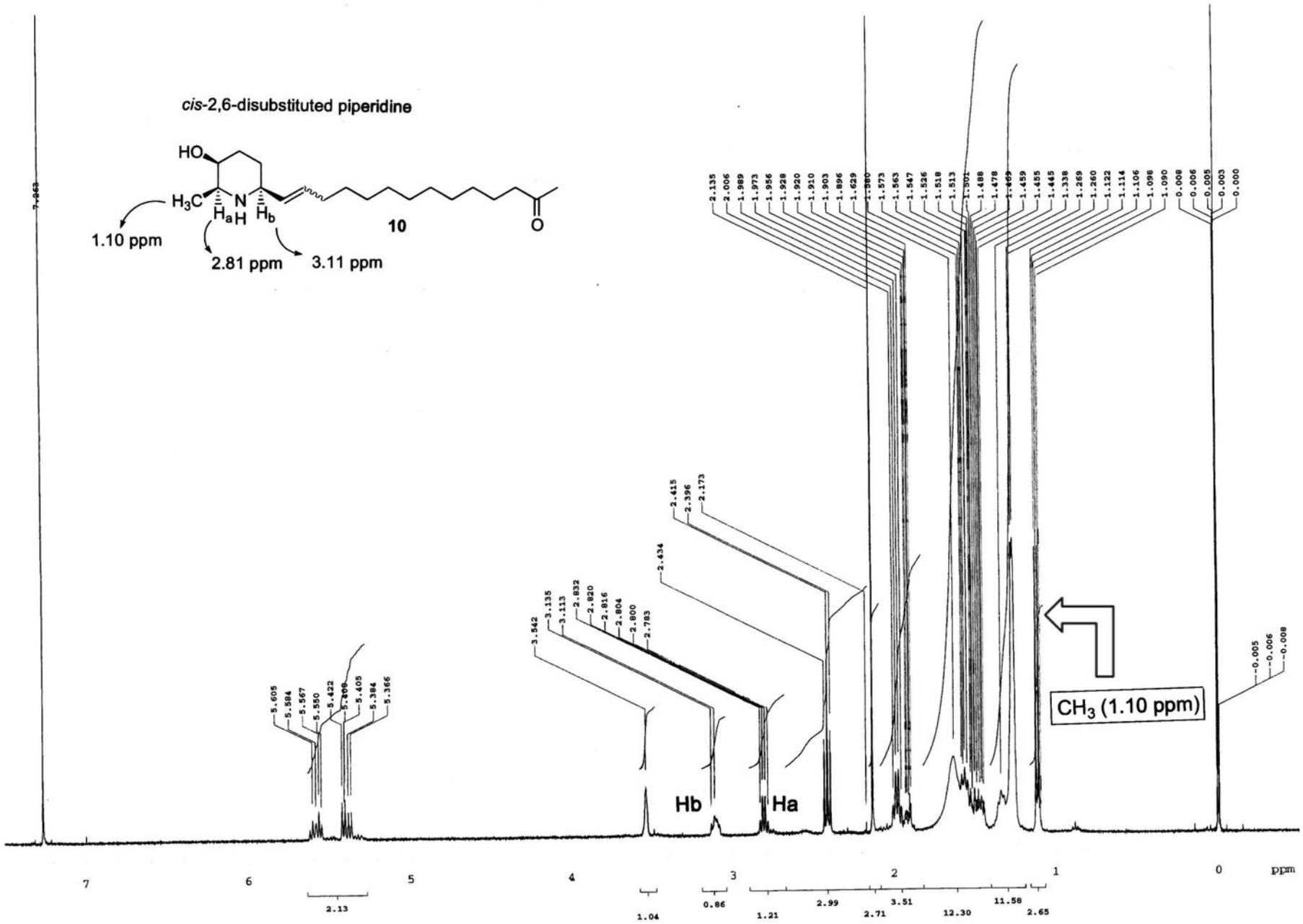
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Ha H
Hb
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O
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2.81 ppm
3.11 ppm
CH3 (1.10 ppm)
Hb
Ha
ppm
2.13
1.04
0.86
1.21
2.99
2.71
3.51
12.30
11.58
2.65