

●Supporting Information●

Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias*

*Christoph Schnabel and Martin Hiersemann**

Fakultät Chemie, Technische Universität Dortmund, 44227 Dortmund, Germany

martin.hiersemann@tu-dortmund.de

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GENERAL EXPERIMENTAL METHODS

Methods and Materials: Unless otherwise stated, commercially available reagents were used as purchased. Solvents were dried by passage through activated alumina columns of a solvent purification system: tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), diethylether (Et_2O), *N,N*-dimethylformamide (DMF), and toluene (PhMe). Diisopropylamine and pyridine were distilled from CaH_2 and stored over activated 3 Å molecular sieves. Methanol was distilled from magnesium and stored over activated 3 Å molecular sieves. Dimethyl sulfoxide (DMSO, $\geq 99.5\%$, stored over molecular sieves) was used as purchased.

2-Iodoxybenzoic acid (IBX) was prepared according to the literature¹ and was stored in the refrigerator. The concentrations of *n*-BuLi, MeLi, and *t*-BuLi were determined employing 4-biphenylmethanol as indicator.²

The aqueous pH7 buffer was prepared according to Sørensen ($0.45 \text{ g Na}_2\text{HPO}_4 + 0.57 \text{ g NaH}_2\text{PO}_4$ in 100 mL H_2O).³

All moisture-sensitive reactions were performed in flame-dried septum-sealed glassware under an argon atmosphere. Reagents were transferred by means of syringe or cannula. For the cross-coupling reactions, commercially available glass pressure tubes with a screw-cap (Ace pressure tube, 35 mL, PTFE bushing FETFE O-ring, type A) were used. Analytical TLC was performed using pre-coated silica gel foils (4 cm). Visualization was achieved using 365 nm ultraviolet irradiation followed by staining with the K \ddot{a} gi-Miescher reagent⁴ (*p*-anisaldehyde 2.53 vol%, acetic acid 0.96 vol%, ethanol

¹ (a) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287. (b) Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019–8022.

² Juaristi, E.; Martinez-Richa, A.; Garcia-Rivera, A.; Cruz-Sanchez, J. S. *J. Org. Chem.* **1983**, *48*, 2603–2606.

³ Romeis, B. *Mikroskopische Technik* R. Oldenbourg Verlag, München, **1989**, 17th edition, p 657.

⁴ (a) Miescher, K. *Helv. Chim. Acta* **1946**, *29*, 743–752. (b) Stahl, E., Kaltenbach. U. *J. Chromatog.* **1961**, *5*, 351–355.

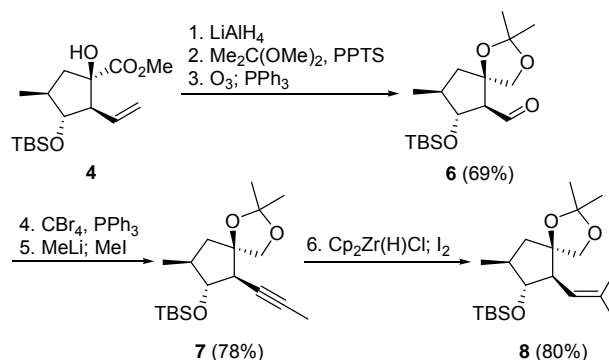
93.06 vol%, conc. H₂SO₄ 3.45 vol%). Flash chromatography⁵ was performed using silica gel (particle size 0.040-0.063 mm) and mixtures of cyclohexane and ethyl acetate as eluent. A commercially available ozonizer with oxygen as source was employed with an amperage of 1 A.

¹H NMR spectra were recorded at 400 MHz, 500 MHz, or 600 MHz. Chemical shifts are reported in ppm relative to chloroform (δ 7.26 ppm).⁶ Signal splitting patterns are labeled by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non equivalent resonances. ¹³C NMR spectra were recorded at 101 MHz. Chemical shifts are reported in ppm relative to CDCl₃ (77.1 ppm).⁶ The assignment of CH₂ is based on APT (attached proton test).

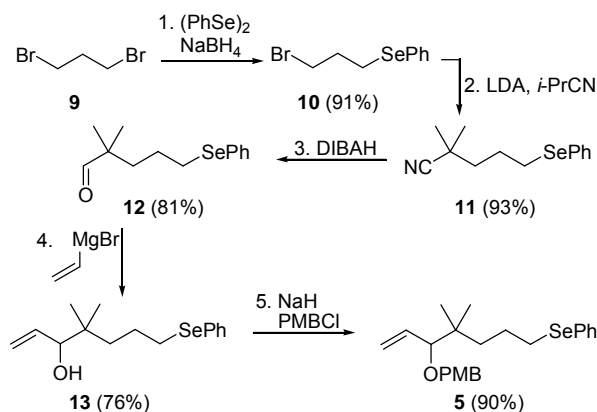
Infrared spectra were recorded as a thin film on a KBr disk (“film on KBr”). Molecular formula assignment was confirmed by combustion elemental analysis. Melting points were measured with a capillary melting point device. For water determinations of solvents a coulometer according to Karl Fischer was applied.

⁵ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

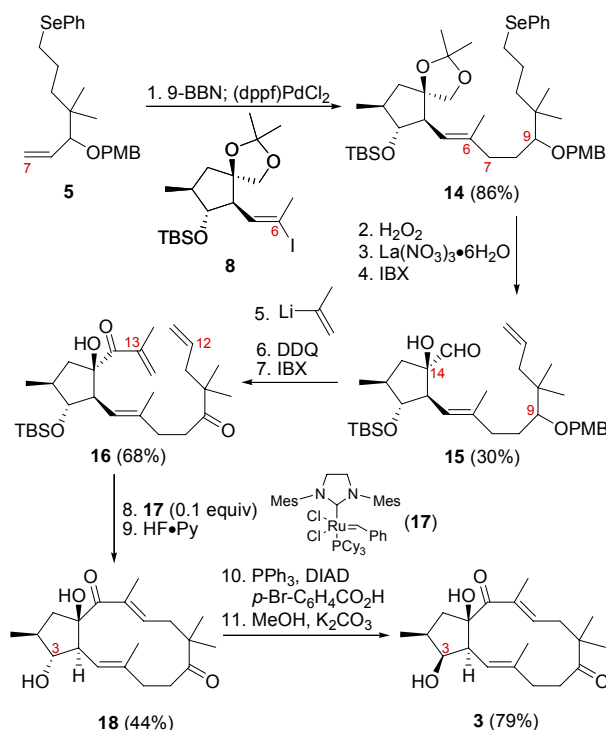
⁶ Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.

Scheme 1^a

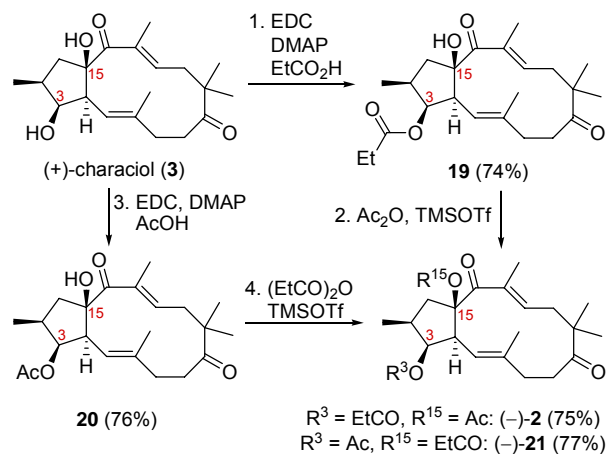
^a key: Synthesis of the vinyl iodide **8** from the known cyclopentanoid **4** in 6 steps and 43% yield; **1.** LiAlH₄ (3 equiv), THF, 23 °C, 75 min, 90%; **2.** Me₂C(OMe)₂ (1.5 equiv), PPTS (0.15 equiv), CH₂Cl₂, 23 °C, 18.5 h, 85%; **3.** O₃, Sudan Red B (cat.), CH₂Cl₂, MeOH (2/1), –78 °C, then PPh₃ (3.1 equiv) –78 °C → 23 °C, 90%; **4.** CBr₄ (1.8 equiv), PPh₃ (3.6 equiv), CH₂Cl₂, –78 °C, 75 min; **5.** MeLi (3.6 equiv), THF, –78 °C, 30 min, then MeI (5.1 equiv), THF, –78 °C to 23 °C, 78%, for the 2 steps; **6.** (Cp)₂Zr(H)Cl (3 equiv), THF, 40 °C, 1.5 h, then I₂ (saturated) in CH₂Cl₂, 0 °C, 10 min, 80%.

Scheme 2^a

^a key: **1.** (PhSe)₂ (1 equiv), NaBH₄ (2.5 equiv), MeOH, 0 °C, 30 min, then **9** (20 equiv), 0 °C to 23 °C, 91%; **2.** LDA (1.7 equiv), *i*-PrCN (1.6 equiv), Et₂O, 0 °C, 1 h, then **10**, 0 °C to 23 °C, 93%; **3.** DIBAH (1.1 equiv), toluene, –78 °C, 1 h, 81%; **4.** H₂C=CHMgBr (1.3 equiv), THF, –78 °C, 45 min, 76%; **5.** NaH (1.3 equiv), PMBCl (1.1 equiv), TBAI (0.05 equiv), THF, DMSO (2/1), 0 °C to 23 °C, 17 h, 90%. TBAI = *tetra-n*-butylammonium iodide.

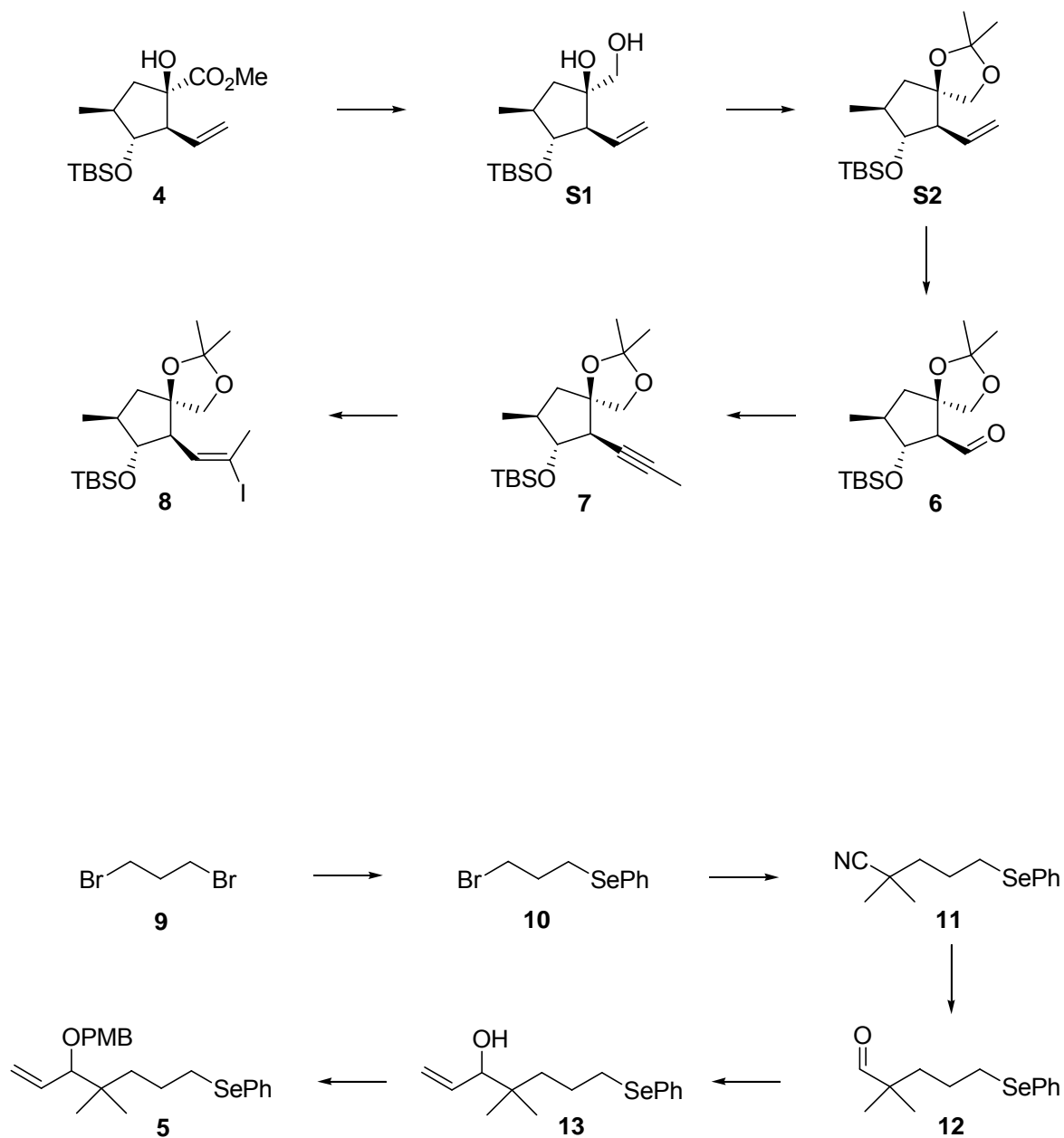
Scheme 3 ^a

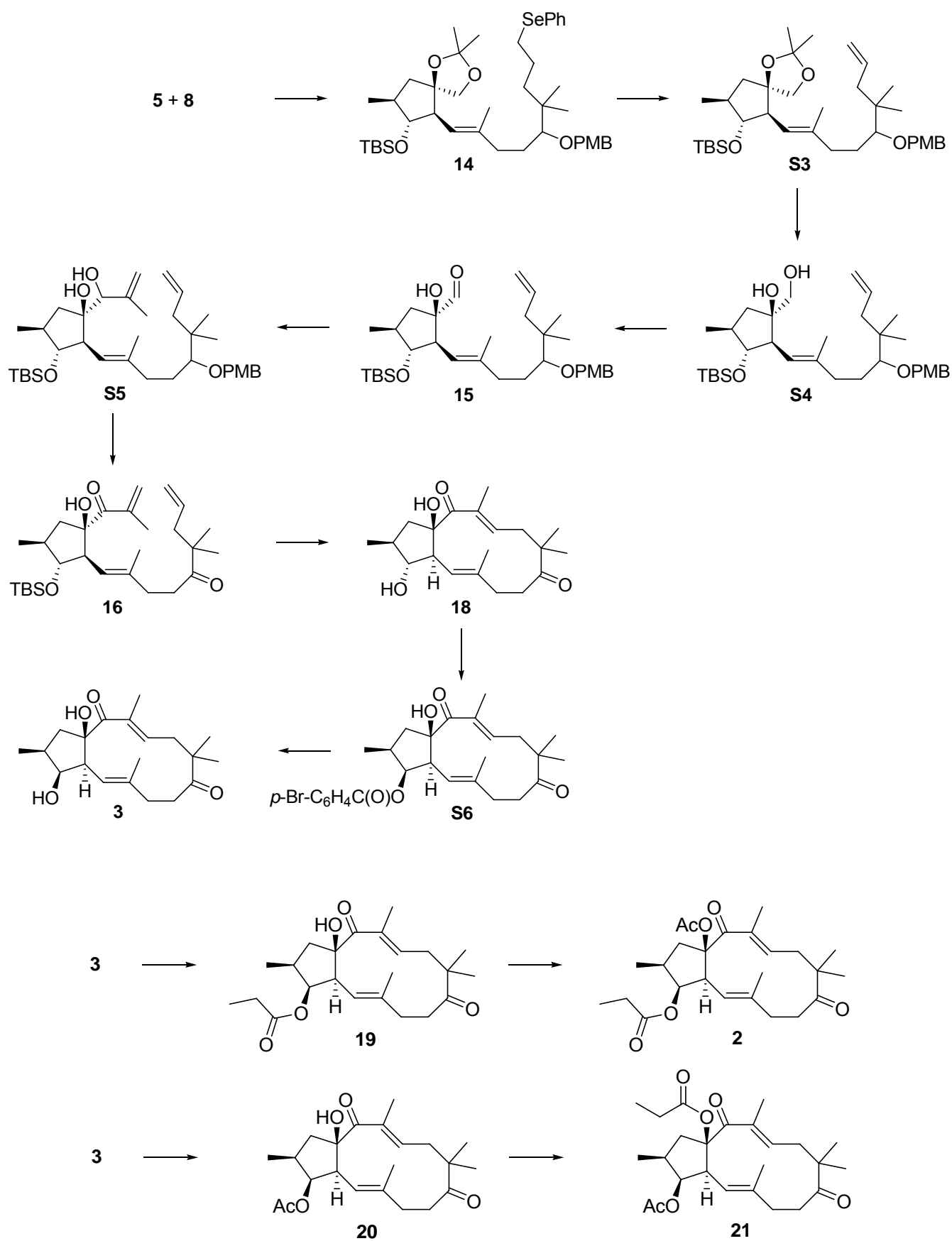
^a key: Synthesis of (+)-characiol (**3**) from the building blocks **5** and **8** in 11 steps and 6% yield; **1. 5** (2.1 equiv), 9-BBN (6.5 equiv), THF, 40 °C, 24 h; **8** (1 equiv), (dppf)PdCl₂·CH₂Cl₂ (0.07 equiv), Ph₃As (0.2 equiv), Cs₂CO₃ (2.7 equiv), THF, DMF, H₂O (14/2/1), 80 °C, 8 h, 86%; **2. 30%** H₂O₂ in H₂O (2.1 equiv), NaHCO₃ (4.2 equiv), THF, 0 °C, 1.5 h; 23 °C, 22.5 h, 68%; **3. La**(NO₃)₃·6H₂O (5.2 equiv), MeCN, 50 °C, 25 h, 54%; **4. IBX** (3 equiv), CH₂Cl₂/DMSO (1:1), 23 °C, 6 h, 81%; **5. H₂C=C(Me)Br** (4 equiv), *t*-BuLi (7.7 equiv), THF, −78 °C, 15 min, then **15** (1 equiv), THF, −78 °C, 30 min, 91%; **6. DDQ** (1.5 equiv), pH = 7 phosphate buffer, 23 °C, 2.5 h; **7. IBX** (6 equiv), CH₂Cl₂, DMSO (1/1), 23 °C, 6 h, 75% for the two steps; **8. 17** (0.1 equiv), toluene (c = 1.3×10^{−3} mol/L), 110 °C, 2 h; **9. HF·Py**, THF, 0 °C, 10 min; 23 °C, 75 min, 44% for the two steps; **10. DIAD** (2.7 equiv), PPh₃ (2.1 equiv), *p*-BrC₆H₄CO₂H (2.1 equiv), THF, 0 °C, 3 h, 87%; **11. K₂CO₃** (27 equiv), MeOH, 23 °C, 5 h, 91%. DPPF = diphenyl(ferrocenyl)phosphane, IBX = *o*-iodoxybenzoic acid, DIAD = diisopropyl azodicarboxylate

Scheme 4 ^a

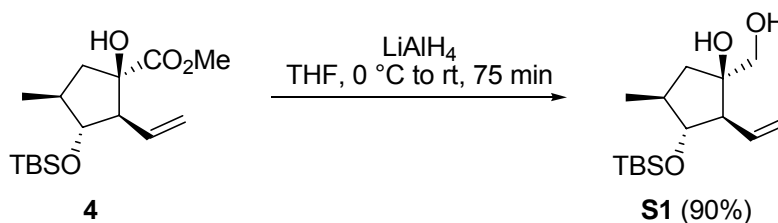
^a key: **1.** EDC•HCl (10 equiv), DMAP (0.7 equiv), EtCO₂H (8 equiv), CH₂Cl₂, 0 °C to 23 °C, 74%; **2.** Ac₂O (41 equiv), TMSOTf (cat.), CH₂Cl₂, 23 °C, 10 min, 75%; **3.** EDC•HCl (10 equiv), DMAP (0.4 equiv), AcOH (10 equiv), CH₂Cl₂, 0 °C to 23 °C, 76%; **4.** (EtCO)₂O (37 equiv), TMSOTf (cat.), CH₂Cl₂, 23 °C, 10 min, 77%. EDC = 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide.

CHART OF ALL SYNTHESIZED COMPOUNDS (S1-S6, 5-21, 3, AND 2) IN ORDER OF THEIR APPEARANCE

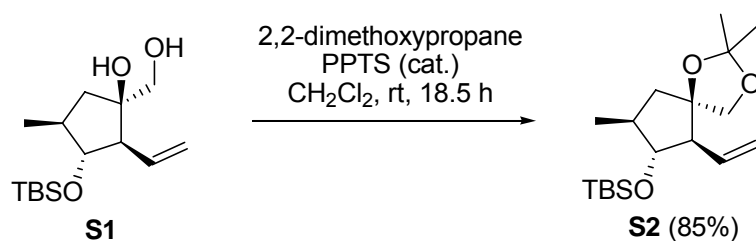




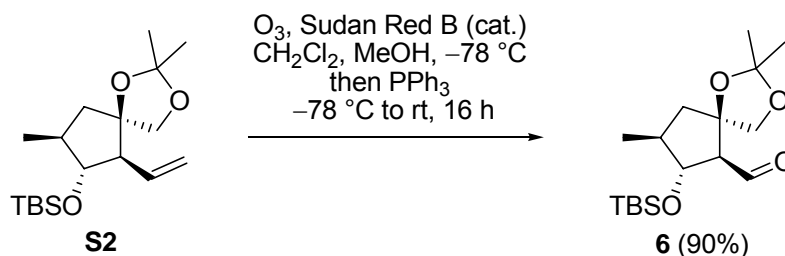
EXPERIMENTAL PROCEDURES AND ANALYTICAL DATA FOR COMPOUND S1-S6, 5-21, 3, AND 2



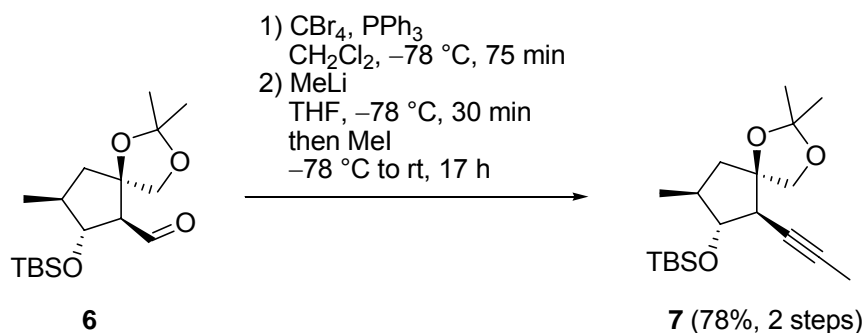
Diol S1: LiAlH₄ (989 mg, 26.06 mmol, 3 eq) was carefully added to a stirred solution of the ester **4** (2.73 g, 8.69 mmol, 1 equiv) in THF (42 mL, 4.8 mL/mmol **4**) at 0 °C. After being stirred for 75 minutes at room temperature, the reaction mixture was diluted at 0 °C by the careful addition of saturated aqueous NH₄Cl solution. The phases were then separated, the aqueous layer was extracted with CH₂Cl₂ (5×), the combined organic phases were dried (MgSO₄) and concentrated at reduced pressure. Purification by chromatography (cyclohexane/ethyl acetate 10/1 to 2/1) provided the diol **S1** (2.25 g, 7.82 mmol, 90%) as a white solid (mp: 57 °C): *R_f* 0.56 (cyclohexane/ethyl acetate 1/1); ¹H NMR (400 MHz, CDCl₃) δ 0.00 (s, 3H), 0.05 (s, 3H), 0.86 (s, 9H), 1.08 (d, ³*J* = 7.0 Hz, 3H), 1.29 (dd, ³*J* = 9.7 Hz, ²*J* = 13.9 Hz, 1H), 1.63 (s, br, 2OH), 1.71–1.83 (m, 1H), 2.13 (dd, ³*J* = 9.0 Hz, ²*J* = 13.9 Hz, 1H), 2.20 (dd, ³*J*₁ = ³*J*₂ = 9.2 Hz, 1H), 3.43 (d^{AB}, ²*J* = 11.0 Hz, 1H), 3.53 (d^{AB}, ²*J* = 11.0 Hz, 1H), 3.70 (dd, ³*J*₁ = ³*J*₂ = 8.8 Hz, 1H), 5.17 (dd, ²*J* = 1.5 Hz, ³*J* = 17.3 Hz, 1H), 5.24 (dd, ²*J* = 1.5 Hz, ³*J* = 10.3 Hz, 1H), 5.87 (ddd, ³*J*₁ = 9.2 Hz, ³*J*₂ = 10.3 Hz, ³*J*₃ = 17.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ −4.0 (CH₃), −3.4 (CH₃), 18.1 (C), 18.5 (CH₃), 26.0 (3 × CH₃), 39.9 (CH), 41.7 (CH₂), 60.1 (CH), 70.3 (CH₂), 78.9 (C), 83.1 (CH), 119.5 (CH₂), 136.9 (CH); IR (film on KBr) ν 3310, 2955, 2930, 2860, 1125, 1045, 775 cm^{−1}; Anal. Calcd for C₁₅H₃₀SiO₃: C, 62.89; H, 10.55. Found: C, 62.8; H, 10.7; [α]²⁵_D +16.6 (c 0.308, CHCl₃).



Acetal S2: 2,2-Dimethoxypropane (2.8 mL, 22.58 mmol, 1.5 equiv) and PPTS (545 mg, 2.17 mmol, 0.15 equiv) were added at 0 °C to a solution of the diol **S1** (4.2 g, 14.66 mmol, 1 equiv) in CH₂Cl₂ (15 mL, 1 mL/mmol **S1**). The reaction mixture was stirred for 18.5 hours at room temperature and then diluted with saturated aqueous NaHCO₃ solution. The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3×). The combined organic phases were dried (MgSO₄) and concentrated at reduced pressure. Purification by chromatography (cyclohexane/ethyl acetate 100/1) provided the acetal **S2** (4.06 g, 12.46 mmol, 85%) as a colorless oil: *R_f* 0.74 (cyclohexane/ethyl acetate 5/1); ¹H NMR (400 MHz, CDCl₃) δ 0.00 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 1.06 (d, ³*J* = 6.5 Hz, 3H), 1.28 (s, 3H), 1.38 (s, 3H), 1.53 (dd, ³*J* = 9.8 Hz, ²*J* = 13.6 Hz, 1H), 1.65–1.77 (m, 1H), 2.12–2.18 (m, 2H), 3.60 (dd, ³*J*₁ = ³*J*₂ = 8.3 Hz, 1H), 3.74 (d^{AB}, ²*J* = 8.3 Hz, 1H), 3.82 (d^{AB}, ²*J* = 8.3 Hz, 1H), 5.04 (dd, ²*J* = 1.5 Hz, ³*J* = 17.1 Hz, 1H), 5.13 (dd, ²*J* = 1.5 Hz, ³*J* = 10.3 Hz, 1H), 5.80 (ddd, ³*J*₁ = 7.5 Hz, ³*J*₂ = 10.3 Hz, ³*J*₃ = 17.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ –4.0 (CH₃), –3.4 (CH₃), 18.1 (C), 18.6 (CH₃), 26.0 (3 × CH₃ + 1 × CH₃), 27.5 (CH₃), 40.2 (CH), 45.3 (CH₂), 60.2 (CH), 73.9 (CH₂), 83.0 (CH), 86.1 (C), 109.6 (C), 118.3 (CH₂), 136.4 (CH); IR (film on KBr) ν 2955, 2930, 2860, 1370, 1255, 1120, 890, 835, 775 cm^{–1}; Anal. Calcd for C₁₈H₃₄SiO₃: C, 66.21; H, 10.49. Found: C, 66.2; H, 10.6; [α]_D²⁵ –12.9 (c 1.085, CHCl₃).



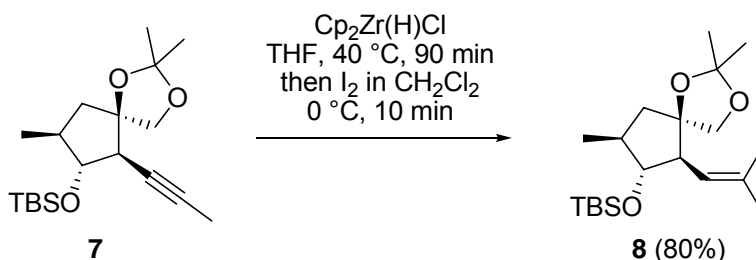
Aldehyde 6: a catalytic amount of Sudan Red B was added to a solution of the alkene **S2** (579 mg, 1.77 mmol, 1 equiv) in CH_2Cl_2 (3 mL, 1.7 mL/mmol **S2**) and methanol (1.5 mL, 0.85 mL/mmol **S2**). The raspberry red solution was cooled to $-78\text{ }^\circ\text{C}$ and an ozone/oxygen-mixture was passed through the solution until the red color had disappeared. The flask was purged with argon for five minutes. After adding PPh_3 (1.42 g, 5.41 mmol, 3.1 equiv), the solution was allowed to warm to room temperature and stirred for 16 hours. The solvents were then removed under reduced pressure. Chromatography (cyclohexane to cyclohexane/ethyl acetate 100/1) afforded the aldehyde **6** (524 mg, 1.59 mmol, 90%) as a clear oil: R_f 0.76 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ -0.02 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 1.08 (d, $^3J = 7.0$ Hz, 3H), 1.30 (s, 3H), 1.36 (s, 3H), 1.55 (dd, $^2J = ^3J = 12.5$ Hz, 1H), 1.67 – 1.79 (m, 1H), 2.05 (dd, $^3J = 7.2$ Hz, $^2J = 12.5$ Hz, 1H), 2.58 (dd, $^3J_1 = 3.1$ Hz, $^3J_2 = 6.8$ Hz, 1H), 3.94 (d^{AB} , $^2J = 8.5$ Hz, 1H), 3.97 (d^{AB} , $^2J = 8.5$ Hz, 1H), 4.17 (dd, $^3J_1 = ^3J_2 = 7.2$ Hz, 1H), 9.71 (d, $^3J = 3.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ -4.5 (CH_3), -4.4 (CH_3), 17.4 (CH_3), 17.9 (C), 25.8 ($3 \times \text{CH}_3$), 25.8 (CH_3), 27.1 (CH_3), 40.7 (CH), 45.0 (CH_2), 66.2 (CH), 75.6 (CH_2), 77.8 (CH), 86.4 (C), 110.1 (C), 201.5 (CH); IR (film on KBr) ν 3445, 3020, 2960, 1715, 1365, 1220, 755 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{SiO}_4$: C, 62.15; H, 9.82; Found: C, 62.1; H, 9.6; $[\alpha]_{\text{D}}^{25} +38.4$ (c 1.13, CHCl_3).



Alkyne 7: PPh_3 (9.27 g, 35.34 mmol, 3.6 equiv) was added to a solution of CBr_4 (5.86 g, 17.67 mmol, 1.8 equiv) in CH_2Cl_2 (35 mL, 3.6 mL/mmol **6**) at $0\text{ }^\circ\text{C}$. After cooling the reaction mixture to $-78\text{ }^\circ\text{C}$, a solution of the aldehyde **6** (3.22 g, 9.81 mmol, 1 equiv) in CH_2Cl_2 (30 mL, 3.1 mL/mmol **6**) was added. The reaction mixture was stirred for 75 minutes at $-78\text{ }^\circ\text{C}$, and then diluted with saturated aqueous NH_4Cl solution. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 (~ 2 mL) and cyclohexane (~ 100 mL), filtered through a plug of Celite and the filtrate was concentrated under reduced pressure. This procedure was repeated two times. Purification of the crude product by chromatography (cyclohexane to cyclohexane/ethyl acetate 100/1) afforded the dibromide (3.82 g, 7.85 mmol, 80%, R_f 0.78 cyclohexane/ethyl acetate 5/1) as a pale yellow oil.

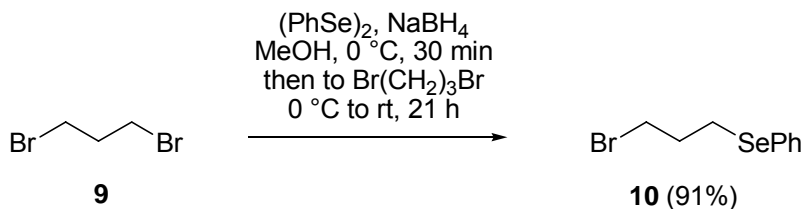
MeLi (18 mL, 1.6 M in Et_2O , 28.8 mmol, 3.6 equiv) was added dropwise to a cooled ($-78\text{ }^\circ\text{C}$) solution of the dibromide (3.82 g, 7.85 mmol, 1 equiv) in THF (25 mL, 3.2 mL/mmol **6**). After being stirred for 30 minutes at $-78\text{ }^\circ\text{C}$, MeI (2.5 mL, 40.32 mmol, 5.1 equiv) was added. The solution was slowly warmed to room temperature over a period of 17 hours. Saturated aqueous NH_4Cl solution was added, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 100/1 to 50/1) provided the alkyne **7** (2.59 g, 7.61 mmol, 97%) as a clear oil: R_f 0.69 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ

0.09 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 1.03 (d, $^3J = 6.5$ Hz, 3H), 1.41 (s, 3H), 1.42 (s, 3H), 1.56 (dd, $^3J = 10.0$ Hz, $^2J = 12.9$ Hz, 1H), 1.61–1.68 (m, 1H), 1.81 (d, $^5J = 2.5$ Hz, 3H), 2.08 (dd, $^3J = 7.7$ Hz, $^2J = 12.9$ Hz, 1H), 2.47 (dd, $^5J = 2.5$ Hz, $^3J = 8.1$ Hz, 1H), 3.70 (dd, $^3J_1 = ^3J_2 = 8.1$ Hz, 1H), 3.83 (d^{AB}, $^2J = 8.3$ Hz, 1H), 3.90 (d^{AB}, $^2J = 8.3$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ –4.5 (CH_3), –3.9 (CH_3), 3.8 (CH or CH_3), 18.1 (C), 18.4 (CH_3), 25.9 ($3 \times \text{CH}_3$), 26.0 (CH_3), 27.4 (CH_3), 40.0 (CH), 44.5 (CH_2), 48.2 (CH or CH_3), 74.5 (CH_2), 77.3 (C), 80.0 (C), 84.0 (CH), 85.4 (C), 110.1 (C); IR (film on KBr) ν 2960, 2860, 1465, 1380, 1255, 1115, 1065, 885, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{34}\text{SiO}_3$: C, 67.40; H, 10.12; Found: C, 67.2; H, 10.2; $[\alpha]_D^{25}$ –4.4 (c 0.945, CHCl_3).



Vinyl Iodide 8: To a solution of alkyne **7** (2.18 g, 6.44 mmol, 1 equiv) in THF (45 mL, 7 mL/mmol **7**) was added $\text{Cp}_2\text{Zr(H)Cl}$ (5 g, 19.39 mmol, 3 eq) at room temperature. After the gas evolution had ceased, the solution was stirred for 90 minutes at 40 °C and a solution of iodine (saturated) in CH_2Cl_2 (78 mL, 12 mL/mmol **7**) was subsequently added to the brownish-yellow reaction mixture at 0 °C. A change of color from brown to yellow to dark purple was observed. After stirring for ten minutes at 0 °C, the reaction mixture was diluted with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution and with water. The phases were subsequently separated, and the aqueous layer was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification of the residue (cyclohexane to cyclohexane/ethyl acetate 100/1) afforded the vinyl iodide **8** (2.41 g, 5.15 mmol, 80%) as a light yellow oil: R_f 0.72 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.87 (s, 9H), 1.04 (d, $^3J = 6.5$ Hz, 3H), 1.31 (s, 3H), 1.39 (s, 3H), 1.54 (dd, $^3J = 9.5$ Hz, $^2J = 13.8$ Hz, 1H), 1.67–1.79 (m, 1H), 2.17 (dd, $^3J = 9.1$ Hz, $^2J = 13.8$ Hz, 1H), 2.39 (d, $^5J = 1.0$ Hz, 3H), 2.48 (dd, $^3J_1 = ^3J_2 = 9.9$ Hz, 1H), 3.58 (dd, $^3J_1 = ^3J_2 = 8.8$ Hz, 1H), 3.71 (d^{AB},

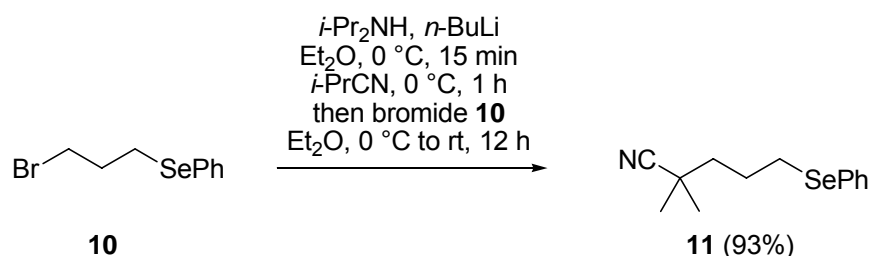
$^2J = 8.4$ Hz, 1H), 3.84 (d^{AB}, $^2J = 8.4$ Hz, 1H), 6.24 (d, $^3J = 10.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ –4.2 (CH_3), –3.9 (CH_3), 17.9 (C), 18.4 (CH_3), 25.9 ($3 \times \text{CH}_3$), 25.9 (CH_3), 27.4 (CH_3), 28.2 (CH_3), 40.0 (CH), 45.3 (CH_2), 56.3 (CH), 74.0 (CH_2), 82.9 (CH), 86.0 (C), 96.9 (C), 110.0 (C), 139.7 (CH); IR (film on KBr) ν 2955, 2930, 2855, 1255, 1120, 1060, 900, 835, 775 cm^{-1} ; Anal. Calcd for C, 48.92; H, 7.56; Found: C, 48.9; H, 7.3; $[\alpha]_{\text{D}}^{25} -36.8$ (c 1.285, CHCl_3).



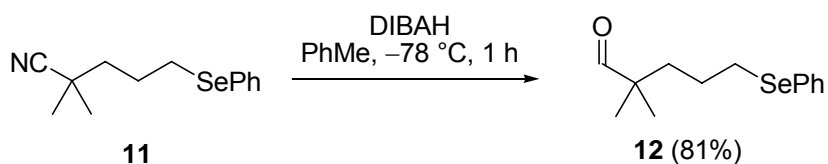
Bromide 10⁷: NaBH_4 (1.48 g, 39.13 mmol, 2.5 equiv) was carefully added at 0 °C (intense gas evolution) to a suspension of $(\text{PhSe})_2$ (4.98 g, 15.95 mmol, 1 equiv) in MeOH (30 mL, 1.9 mL/mmol $(\text{PhSe})_2$). This solution was stirred for 30 minutes at 0 °C, and then transferred to a second flask containing a solution of 1,3-dibromopropane (**9**) (32.5 mL, 320 mmol, 20 equiv) in MeOH (30 mL, 1.9 mL/mmol $(\text{PhSe})_2$) at 0 °C. After stirring the reaction mixture for 21 hours at room temperature, the MeOH was removed under reduced pressure. The residue was dissolved in a saturated aqueous NaHCO_3 solution and diluted with Et_2O . The phases were separated, and the aqueous layer was extracted with Et_2O (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. The crude product was subjected to Kugelrohr distillation (65 °C, 8 mbar) to remove the remaining 1,3-dibromopropane (**9**) (44.8 g, 69% reisolated); the residue was then further purified by chromatography (cyclohexane to cyclohexane/ethyl acetate 100/1) to provide the bromide **10** (8.07 g, 29.03 mmol, 91%) as a yellow oil: R_f 0.69 (cyclohexane/ethyl acetate 20/1); ^1H NMR (400 MHz, CDCl_3) δ 2.19 (tt, $^3J_1 = ^3J_2 = 6.5$ Hz, 2H), 3.03 (t, $^3J = 6.5$ Hz, 2H), 3.51 (t, $^3J = 6.5$ Hz, 2H), 7.26–7.30

⁷ Middleton, D. S.; Simpkins, N. S.; Begley, M. J.; Terrett, N. K. *Tetrahedron* **1990**, *46*, 545–564.

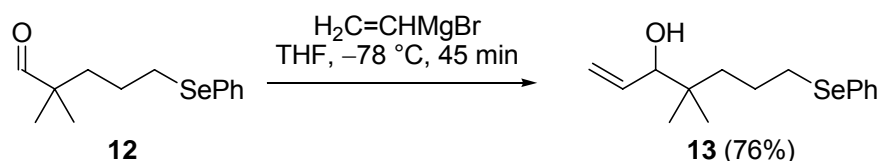
(m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 25.8 (CH_2), 32.7 (CH_2), 33.1 (CH_2), 127.2 (CH), 129.2 ($2 \times \text{CH}$), 129.5 (C), 133.0 ($2 \times \text{CH}$); IR (film on KBr) ν 3070, 2960, 1580, 1480, 1435, 1385, 1235, 735, 690 cm^{-1} .



Nitrile 11: *n*-BuLi (22 mL, 2.2 M in *n*-hexane, 48.4 mmol, 1.7 equiv) was added to a solution of *i*-Pr₂NH (7.2 mL, 51.2 mmol, 1.8 equiv) in Et₂O (16 mL, 0.5 mL/mmol **10**) at 0 °C. After stirring for 15 minutes at 0 °C, isobutyronitrile (4.1 mL, 45.1 mmol, 1.6 equiv) was added. The reaction mixture was stirred for one hour at 0 °C; a color change to yellow-green was observed. A solution of the bromide **10** (8.07 g, 29.02 mmol, 1 equiv) in Et₂O (25 mL, 0.9 mL/mmol **10**) was subsequently added dropwise over a period of ten minutes. The solution was stirred for 12 hours at room temperature; the color changed via yellow to orange. After diluting the reaction mixture with saturated aqueous NH₄Cl solution, the phases were separated. The aqueous layer was extracted with CH₂Cl₂ (3×), the combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. Chromatographic purification (cyclohexane to cyclohexane/ethyl acetate 50/1) afforded the nitrile **11** (7.22 g, 26.99 mmol, 93%) as a clear oil: *R*_f 0.45 (cyclohexane/ethyl acetate 10/1); ^1H NMR (400 MHz, CDCl_3) δ 1.31 (s, 6H), 1.63–1.68 (m, 2H), 1.83–1.91 (m, 2H), 2.93 (t, $^3J = 7.0\text{ Hz}$, 2H), 7.23–7.30 (m, 3H), 7.50 (dd, $^3J_1 = 1.5\text{ Hz}$, $^3J_2 = 7.0\text{ Hz}$, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 25.8 (CH_2), 26.7 ($2 \times \text{CH}_3$), 27.6 (CH_2), 32.1 (C), 40.9 (CH_2), 124.9 (C), 127.1 (CH), 129.2 ($2 \times \text{CH}$), 129.8 (C), 133.0 ($2 \times \text{CH}$); IR (film on KBr) ν 2975, 2940, 2230, 1580 1480 , 1440, 1385, 1265, 1020, 735, 690, 670 cm^{-1} ; Anal. Calcd for C₁₃H₁₇NSe: C, 58.65; H, 6.44; N, 5.26; Found: C, 58.5; H, 6.2; N, 5.0.

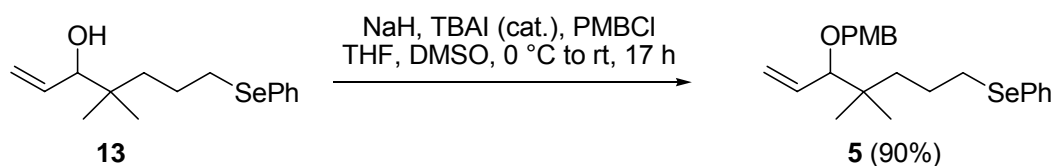


Aldehyde 12: DIBAH (30 mL, 1 M in CH_2Cl_2 , 30 mmol, 1.1 equiv) was dropwise added to a cooled ($-78\text{ }^{\circ}\text{C}$) solution of the nitrile **11** (7.22 g, 27.12 mmol, 1 equiv) in toluene (27 mL, 1 mL/mmol **11**) over a period of ten minutes. The reaction mixture was stirred for one hour at $-78\text{ }^{\circ}\text{C}$ and then carefully diluted by the addition saturated aqueous NH_4Cl solution. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification by chromatography (cyclohexane/ethyl acetate 100/1 to 50/1) provided the aldehyde **12** (5.91 g, 21.97 mmol, 81%) as a clear oil: R_f 0.57 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ 1.03 (s, 6H), 1.58–1.63 (m, 4H), 2.88 (t, $^3J = 6.0\text{ Hz}$, 2H), 7.22–7.28 (m, 3H), 7.47 (dd, $^3J_1 = 1.5\text{ Hz}$, $^3J_2 = 7.0\text{ Hz}$, 2H), 9.42 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 21.4 (2 \times CH_3), 24.9 (CH_2), 28.3 (CH_2), 37.1 (CH_2), 45.7 (C), 127.0 (CH), 129.1 (2 \times CH), 130.1 (C), 132.7 (2 \times CH), 206.0 (CH); IR (film on KBr) ν 2965, 2930, 1730, 1580, 1480, 1440, 1385, 1020, 735, 690 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{OSe}$: C, 57.99; H, 6.74; Found: C, 57.8; H, 6.9.



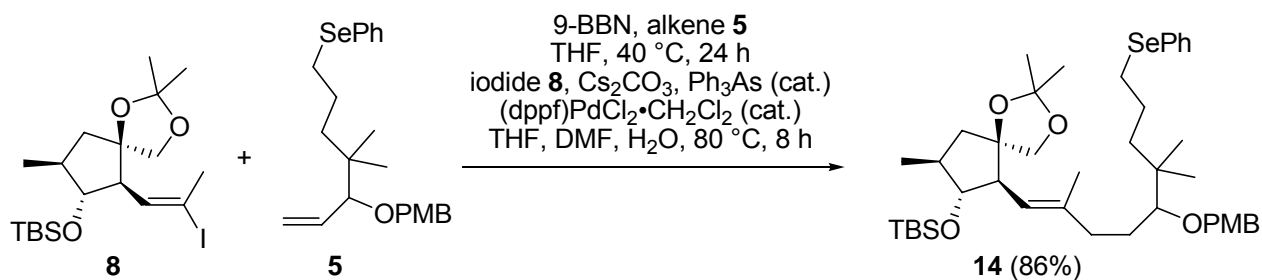
Alcohol 13: Vinylmagnesium bromide (41 mL, 0.7 M in THF, 28.7 mmol, 1.3 equiv) was added to a cooled ($-78\text{ }^{\circ}\text{C}$) solution of the aldehyde **12** (5.91 g, 21.96 mmol, 1 equiv) in THF (80 mL, 3.6 mL/mmol **12**). After stirring the reaction mixture for 45 minutes at $-78\text{ }^{\circ}\text{C}$, saturated aqueous NH_4Cl solution was added. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 \times). The combined organic phases were dried (MgSO_4), concentrated under reduced pressure, and the residue was purified by chromatography (cyclohexane/ethyl acetate 50/1 to 20/1) to deliver the

alcohol **13** (4.98 g, 16.74 mmol, 76%) as a colorless oil: R_f 0.39 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ 0.84 (s, 3H), 0.87 (s, 3H), 1.34 (td, $^2J = 12.0$ Hz, $^3J = 5.0$ Hz, 1H), 1.45 (td, $^2J = 12.0$ Hz, $^3J = 6.0$ Hz, 1H), 1.47 (s, br, 1OH), 1.71 (tdd, $^3J_1 = 5.0$ Hz, $^3J_2 = 6.0$ Hz, $^3J_3 = 7.0$ Hz, 2H), 2.89 (t, $^3J = 7.0$ Hz, 2H), 3.79 (d, $^3J = 6.0$ Hz, 1H), 5.15–5.23 (m, 2H), 5.91 (ddd, $^3J_1 = 6.5$ Hz, $^3J_2 = 10.5$ Hz, $^3J_3 = 17.0$ Hz, 1H), 7.21–7.28 (m, 3H), 7.48 (dd, $^3J_1 = 1.5$ Hz, $^3J_2 = 8.0$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 22.8 (CH_3), 22.9 (CH_3), 24.6 (CH_2), 28.8 (CH_2), 37.2 (C), 39.0 (CH_2), 79.9 (CH), 116.7 (CH_2), 126.7 (CH), 129.0 ($2 \times \text{CH}$), 130.6 (C), 132.4 ($2 \times \text{CH}$), 137.8 (CH); IR (film on KBr) ν 3445, 3070, 2960, 2870, 1580, 1480, 1440, 1385, 1365, 1025, 1000, 925, 735, 690 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{OSe}$: C, 60.60; H, 7.46; Found: C, 60.8; H, 7.2.



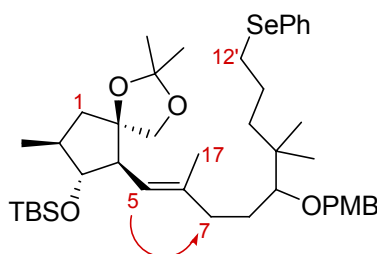
PMB-ether 5: NaH (868 mg, 60% dispersion in mineral oil, 21.7 mmol, 1.3 equiv) was added at 0 °C to a solution of the alcohol **13** (4.97 g, 16.72 mmol, 1 equiv) in THF (20 mL, 1.2 mL/mmol **13**) and DMSO (10 mL, 0.6 mL/mmol **13**). After being stirred for 10 minutes at 0 °C, TBAI (293 mg, 0.79 mmol, 0.05 equiv) and PMBCl (2.5 mL, 18.36 mmol, 1.1 equiv) were added. The solution was stirred for 17 hours at room temperature and then diluted by the addition of saturated aqueous NH_4Cl solution. The phases were separated, the aqueous layer was extracted with CH_2Cl_2 (3 \times), the combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification of the residue (cyclohexane to cyclohexane/ethyl acetate 100/1) afforded the PMB-ether **5** (6.29 g, 15.05 mmol, 90%) as a clear oil: R_f 0.61 (cyclohexane/ethyl acetate 10/1); ^1H NMR (400 MHz, CDCl_3) δ 0.84 (s, 3H), 0.89 (s, 3H), 1.30–1.37 (m, 1H), 1.46–1.53 (m, 1H), 1.63 (tt, $^3J_1 = ^3J_2 = 7.5$ Hz, 2H), 2.86 (t, $^3J = 7.5$ Hz, 2H), 3.35 (d, $^3J = 8.0$ Hz, 1H), 3.82 (s, 3H), 4.19 (d^{AB} , $^2J = 11.5$ Hz, 1H), 4.52 (d^{AB} , $^2J = 11.5$ Hz, 1H), 5.17 (dd, $^3J = 17.1$ Hz, 1H), 5.32 (dd, $^3J = 10.5$ Hz, 1H), 5.77 (ddd, $^3J_1 =$

8.0 Hz, $^3J_2 = 10.5$ Hz, $^3J_3 = 17.1$ Hz, 1H), 6.89 (d, $^3J = 8.5$ Hz, 2H), 7.21–7.28 (m, 5H), 7.48 (dd, $^3J_1 = 1.5$ Hz, $^3J_2 = 7.0$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 23.4 (CH_3), 23.4 (CH_3), 24.7 (CH_2), 28.8 (CH_2), 37.1 (C), 39.4 (CH_2), 55.3 (CH_3), 69.9 (CH_2), 86.8 (CH), 113.6 ($2 \times \text{CH}$), 118.9 (CH_2), 126.6 (CH), 129.0 ($2 \times \text{CH}$), 129.2 ($2 \times \text{CH}$), 130.8 (C), 131.1 (C), 132.3 ($2 \times \text{CH}$), 135.7 (CH), 158.9 (C); IR (film on KBr) ν 2960, 2870, 2835, 1610, 1580, 1515, 1475, 1300, 1250, 1175, 1075, 1035, 735, 690 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Se}$: C, 66.18; H, 7.24; Found: C, 66.2; H, 7.2.

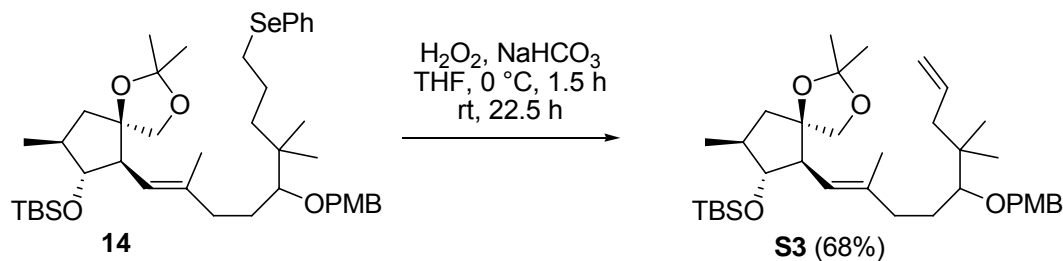


Alkene 14: 9-BBN (13 mL, 0.5 M in THF, 6.5 mmol, 6.5 equiv) was added to a solution of the alkene **5** (881 mg, 2.11 mmol, 2.1 equiv) in THF (0.6 mL, 0.6 mL/mmol **8**) in a glass pressure tube at room temperature. The tube was sealed with a Teflon screw-cap, heated in an oil bath (40 °C) for 24 hours, and then cooled to room temperature. The iodide **8** (445 mg, 0.997 mmol, 1 equiv) in DMF (1.6 mL, 1.6 mL/mmol **8**), Cs_2CO_3 (889 mg, 2.73 mmol, 2.7 equiv), Ph_3As (58 mg, 0.189 mmol, 0.2 equiv) and degassed H_2O (1 mL, 1 mL/mmol **8**) were successively added. The resulting heterogeneous solution was streamed with argon for five minutes, (dppf) $\text{PdCl}_2 \cdot \text{CH}_2\text{Cl}_2$ (55 mg, 0.067 mmol, 0.07 equiv) was added, the tube was sealed, heated at 80 °C for eight hours, and then saturated aqueous NH_4Cl solution was added. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by chromatography (cyclohexane to cyclohexane/ethyl acetate 100/1 to 50/1) provided the alkene **14** (637 mg, 0.857 mmol, 86%) as a pale yellow oil. Alkene **14** was obtained as a 1:1 mixture of C9 epimers: R_f 0.46 (cyclohexane/ethyl acetate 5/1); COSY and NOESY methods were used to confirm the NMR peak assignments on the basis of the jatrophone

numbering; ^1H NMR (400 MHz, CDCl_3) δ -0.03 (s, TBS- CH_3 , 3 + 3H), 0.04 (s, TBS- CH_3 , 3 + 3H), 0.86 (s, $3 \times$ TBS- CH_3 , 9 + 9H, 18- or 19- CH_3 , 3 + 3H), 0.88 (s, 18- or 19- CH_3 , 3 + 3H), 1.06 (d, $^3J = 6.8$ Hz, 16- CH_3 , 3 + 3H), 1.26 (s, acetal- CH_3 , 3 + 3H), 1.40 (s, acetal- CH_3 , 3 + 3H), 1.32–1.57 (m, 1- CH_2 , 1H^{Re} , 8- CH_2 , 1H, 11- CH_2), 1.63 (s, 17- CH_3 , 3 + 3H), 1.60–1.79 (m, 2- CH , 8- CH_2 , 1H, 12- CH_2), 1.95–2.06 (m, 7- CH_2 , 1 + 1H), 2.18 (dd, $^3J = 9.0$ Hz, $^2J = 13.8$ Hz, 1- CH_2 , 1 + 1H^{Si}), 2.24–2.35 (m, 7- CH_2 , 1 + 1H), 2.51 (dd, $^3J_1 = ^3J_2 = 9.8$ Hz, 4- CH , 1 + 1H), 2.86 (t, $^3J = 7.3$ Hz, 12'- CH_2 , 2 + 2H), 3.01 (d, $^3J = 6.3$ Hz, 9- CH , 1 + 1H), 3.55 (dd, $^3J_1 = ^3J_2 = 8.5$ Hz, 3- CH , 1 + 1H), 3.66 (d^{AB} , $^2J = 8.3$ Hz, 14- CH_2 , 1 + 1H), 3.80 (s, PMB- OCH_3 , 3 + 3H), 3.82 (d^{AB} , $^2J = 8.3$ Hz, 14- CH_2 , 1 + 1H), 4.43–4.54 (m, PMB- OCH_2Ar , 2 + 2H), 5.24 (d, $^3J = 10.0$ Hz, 5- CH , 1 + 1H), 6.87 (d, $^3J = 8.5$ Hz, $2 \times$ Ar- CH , 2 + 2H), 7.21–7.28 (m, $5 \times$ Ar- CH , 5 + 5H), 7.46–7.48 (m, $2 \times$ Ar- CH , 2 + 2H); ^{13}C NMR (101 MHz, CDCl_3) δ -4.2 (1 + 1 CH_3), -4.0 (1 + 1 CH_3), 17.1 (1 + 1 CH_3), 18.0 (1 + 1C), 18.6 (1 + 1 CH_3), 23.6 (1 + 1 CH_3), 23.8 (1 + 1 CH_3), 24.9 (1 + 1 CH_2), 25.9 (3 + 3 CH_3), 25.9 (1 + 1 CH_3), 27.6 (1 + 1 CH_3), 28.8 (1 + 1 CH_2), 29.6 (1 + 1 CH_2), 38.3 (1 + 1 CH_2), 38.7 (1 + 1C), 39.4 (1 + 1 CH_2), 40.1 (1 + 1CH), 45.6 (1 + 1 CH_2), 53.1 (1 + 1CH), 55.3 (1 + 1 CH_3), 73.8 (1 + 1 CH_2), 74.4 (1 + 1 CH_2), 84.0 (1 + 1CH), 86.9 (1 + 1C), 87.1 (1 + 1CH), 109.5 (1 + 1C), 113.7 (2 + 2CH), 122.4 (1 + 1CH), 126.6 (1 + 1CH), 129.0 (2 + 2CH), 129.2 (2 + 2CH), 130.8 (1 + 1C), 131.4 (1 + 1C), 132.3 (2 + 2CH), 138.2 (1 + 1C), 159.0 (1 + 1C); IR (film on KBr) ν 2930, 2855, 1515, 1250, 1120, 1040, 835, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{42}\text{H}_{66}\text{O}_5\text{SeSi}$: C, 66.55; H, 8.78; Found: C, 66.5; H, 8.4.

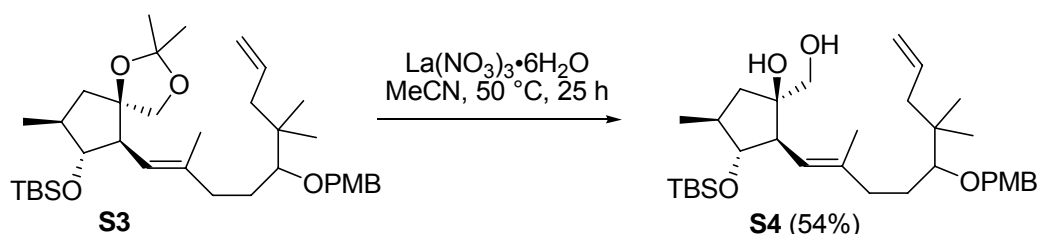
Table SI-1. 1D NOE experiment, irradiation at 5.24 ppm (**5-CH**).

entry	NOE observed to	supported conclusion
1	1.95–2.06 ppm 7-CH₂ , 1H (strong)	(5E)
2	2.24–2.35 ppm 7-CH₂ , 1H (strong)	(5E)
3	1.63 ppm 17-CH₃ (weak)	(5E)



Diene S3: NaHCO₃ (299 mg, 3.56 mmol, 4.2 equiv) and H₂O₂ (0.18 mL, 30% in H₂O, 1.77 mmol, 2.1 equiv) were added at 0 °C to a solution of the alkene **14** (637 mg, 0.84 mmol, 1 equiv) in THF (7 mL, 8.3 mL/mmol **14**). The reaction mixture was stirred for 1.5 hours at 0 °C, 22.5 hours at room temperature and then diluted with saturated Na₂S₂O₃ solution. The phases were separated, the aqueous layer was extracted with CH₂Cl₂ (3×), the combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. Chromatographic purification (cyclohexane to cyclohexane/ethyl acetate 100/1) afforded the diene **S3** (244 mg, 0.57 mmol, 68%) as a clear oil. Diene **S3** was obtained as a 1:1 mixture of C9 epimers: *R_f* 0.51 (cyclohexane/ethyl acetate 5/1); ¹H NMR (400 MHz, CDCl₃) δ –0.03 (s, 3 + 3H), 0.04 (s, 3 + 3H), 0.85 (s, 9 + 9H), 0.88 (s, 3 + 3H), 0.93 (s, 3 + 3H), 1.06 (d,

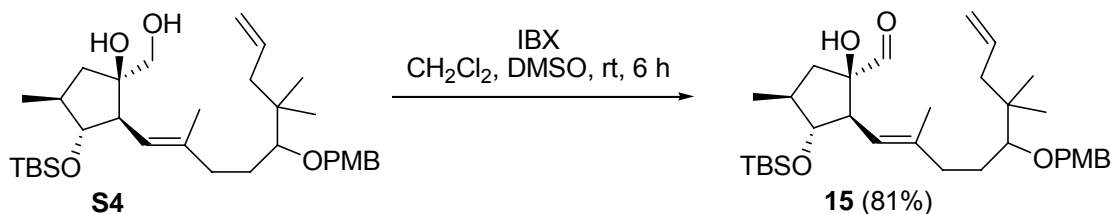
$^3J = 6.5$ Hz, 3 + 3H), 1.26 (s, 3 + 3H), 1.40 (s, 3 + 3H), 1.50–1.57 (m, 1 + 1H), 1.64 (s, 3 + 3H), 1.59–1.79 (m, 3 + 3H), 1.96–2.06 (m, 2 + 2H), 2.10–2.14 (m, 1 + 1H), 2.17 (dd, $^3J = 9.1$ Hz, $^2J = 13.7$ Hz, 1 + 1H), 2.25–2.36 (m, 1 + 1H), 2.51 (dd, $^3J_1 = ^3J_2 = 9.6$ Hz, 1 + 1H), 3.05 (d, $^3J = 8.8$ Hz, 1 + 1H), 3.55 (dd, $^3J_1 = ^3J_2 = 8.1$ Hz, 1 + 1H), 3.66 (d^{AB}, $^2J = 8.3$ Hz, 1 + 1H), 3.80 (s, 3 + 3H), 3.82 (d^{AB}, $^2J = 8.3$ Hz, 1 + 1H), 4.47–4.56 (m, 2 + 2H), 4.99–5.04 (m, 2 + 2H), 5.24 (d, $^3J = 10.0$ Hz, 1 + 1H), 5.79–5.89 (m, 1 + 1H), 6.87 (d, $^3J = 8.5$ Hz, 2 + 2H), 7.28 (d, $^3J = 8.8$ Hz, 2 + 2H); ^{13}C NMR (101 MHz, CDCl_3) δ -4.1 (1 + 1CH₃), -3.9 (1 + 1CH₃), 17.2 (1 + 1CH₃), 18.0 (1 + 1C), 18.7 (1 + 1CH₃), 23.5 (1 + 1CH₃), 23.6 (1 + 1CH₃), 25.9 (3 + 3CH₃), 26.0 (1 + 1CH₃), 27.6 (1 + 1CH₃), 29.6 (1 + 1CH₂), 38.3 (1 + 1CH₂), 39.1 (1 + 1C), 40.2 (1 + 1CH), 43.8 (1 + 1CH₂), 45.6 (1 + 1CH₂), 53.2 (1 + 1CH), 55.3 (1 + 1CH₃), 73.9 (1 + 1CH₂), 74.3 (1 + 1CH₂), 84.0 (1 + 1CH), 86.9 (1 + 1C), 87.0 (1 + 1CH), 109.5 (1 + 1C), 113.7 (2 + 2CH), 117.0 (1 + 1CH₂), 122.4 (1 + 1CH), 129.0 (2 + 2CH), 131.5 (1 + 1C), 135.6 (1 + 1CH), 138.2 (1 + 1C), 159.0 (1 + 1C); IR (film on KBr) ν 2955, 2930, 2855, 1515, 1250, 1120, 1060, 895, 835, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{O}_5\text{Si}$: C, 71.95; H, 10.06; Found: C, 71.8; H, 10.2.



Diol S4: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (535 mg, 1.236 mmol, 5.2 equiv) was added at room temperature to a solution of the diene **S3** (142 mg, 0.236 mmol, 1 equiv) in acetonitrile⁸ (4 mL, 17 mL/mmol **S3**). After being stirred for 25 hours at 50 °C, water and CH_2Cl_2 were added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (5×). The combined organic phases were dried (MgSO_4) and

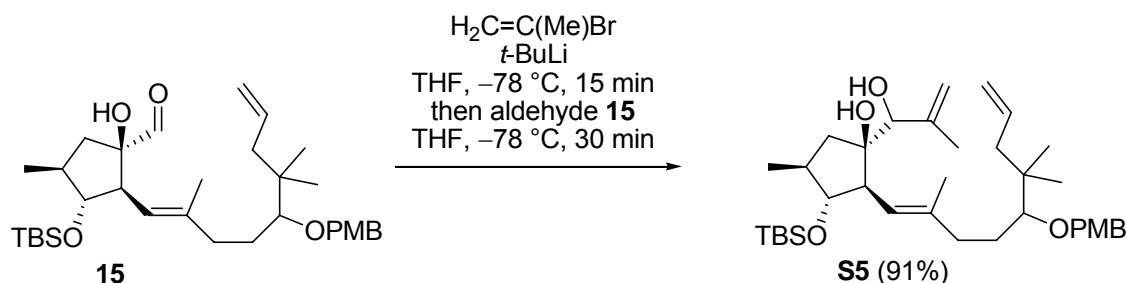
⁸ The acetonitrile (water content 56 ppm) was used as purchased (HPLC grade).

concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 50/1 to 5/1) of the residue afforded the diol **S4** (71 mg, 0.127 mmol, 54%) as a clear oil. Diol **S4** was obtained as a 1:1 mixture of C9 epimers: R_f 0.54 (cyclohexane/ethyl acetate 1/1); ^1H NMR (400 MHz, CDCl_3) δ -0.03 (s, 3 + 3H), 0.04 (s, 3 + 3H), 0.85 (s, 9 + 9H), 0.90 (s, 3 + 3H), 0.94 (s, 3 + 3H), 1.06 (d, $^3J = 6.8$ Hz, 3 + 3H), 1.24–1.30 (m, 2 + 2H), 1.58–1.71 (m, 1 + 1H), 1.65 (s, 3 + 3H), 1.73–1.83 (m, 1 + 1H), 2.00–2.10 (m, 3 + 3H), 2.11–2.18 (m, 2 + 2H), 2.28–2.37 (m, 2 + 2H), 2.46 (dd, $^3J_1 = ^3J_2 = 8.8$ Hz, 1 + 1H), 3.04–3.07 (m, 1 + 1H), 3.38 (d^{AB}, $^2J = 10.9$ Hz, 1 + 1H), 3.44 (d^{AB}, $^2J = 10.9$ Hz, 1 + 1H), 3.61 (dd, $^3J_1 = ^3J_2 = 8.4$ Hz, 1 + 1H), 3.80 (s, 3 + 3H), 4.51–4.53 (m, 2 + 2H), 5.00–5.06 (m, 2 + 2H), 5.18 (d, $^3J = 10.0$ Hz, 1 + 1H), 5.79–5.90 (m, 1 + 1H), 6.87 (d, $^3J = 8.8$ Hz, 2 + 2H), 7.28 (d, $^3J = 8.8$ Hz, 2 + 2H); ^{13}C NMR (101 MHz, CDCl_3) δ -4.1 (1 + 1CH₃), -3.9 (1 + 1CH₃), 17.1 (1 + 1CH₃), 18.0 (1 + 1C), 18.5 (1 + 1CH₃), 23.6 (1 + 1CH₃), 23.6 (1 + 1CH₃), 25.9 (3 + 3CH₃), 29.7 (1 + 1CH₂), 38.3 (1 + 1C), 39.1 (1 + 1CH₂), 39.9 (1 + 1CH), 41.5 (1 + 1CH₂), 43.8 (1 + 1CH₂), 53.5 (1 + 1CH), 55.3 (1 + 1CH₃), 70.2 (1 + 1CH₂), 74.7 (1 + 1CH₂), 79.5 (1 + 1C), 84.3 (1 + 1CH), 86.8 (1 + 1CH), 113.7 (2 + 2CH), 117.1 (1 + 1CH₂), 122.2 (1 + 1CH), 129.1 (2 + 2CH), 131.3 (1 + 1C), 135.5 (1 + 1CH), 140.8 (1 + 1C), 159.0 (1 + 1C); IR (film on KBr) ν 3420, 2955, 2857, 1615, 1515, 1250, 1115, 1040, 835, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{33}\text{H}_{56}\text{O}_5\text{Si}$: C, 70.67; H, 10.06; Found: C, 70.5; H, 9.7.

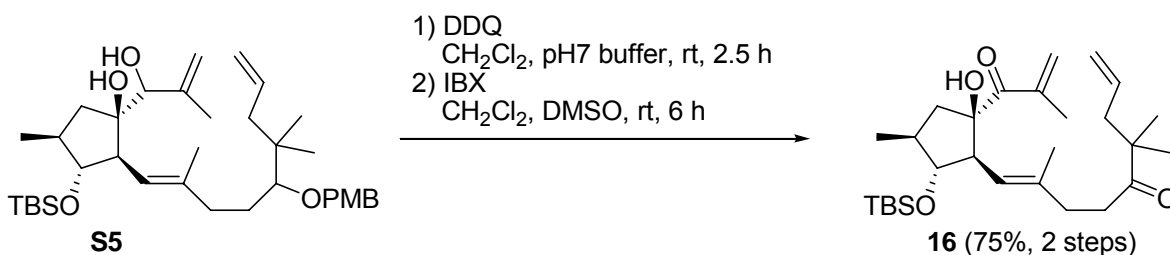


Aldehyde 15: IBX (1067 mg, 3.81 mmol, 3 equiv) was added at room temperature to a solution of the diol **S4** (709 mg, 1.264 mmol, 1 equiv) in CH₂Cl₂ (5 mL, 4 mL/mmol **S4**) and DMSO⁹ (5 mL, 4 mL/mmol **S4**). After stirring for six hours at room temperature, the reaction mixture was diluted with water. The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (4×). The combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 10/1) of the crude product provided the aldehyde **15** (572 mg, 1.024 mmol, 81%) as a clear oil. Aldehyde **15** was obtained as a 1:1 mixture of C9 epimers: *R_f* 0.74 (cyclohexane/ethyl acetate 2/1); ¹H NMR (400 MHz, CDCl₃) δ −0.02 (s, 3 + 3H), 0.06 (s, 3 + 3H), 0.86 (s, 9 + 9H), 0.88 (s, 3 + 3H), 0.92 (s, 3 + 3H), 1.14 (d, ³*J* = 6.8 Hz, 3 + 3H), 1.36 (dd, ³*J* = 8.5 Hz, ²*J* = 14.5 Hz, 1 + 1H), 1.55 (s, 3 + 3H), 1.58–1.69 (m, 2 + 2H), 1.91–2.05 (m, 3 + 3H), 2.13 (dd, *J*₁ = 7.6 Hz, *J*₂ = 13.5 Hz, 1 + 1H), 2.21–2.30 (m, 1 + 1H), 2.47 (dd, ³*J* = 9.9 Hz, ²*J* = 14.5 Hz, 1 + 1H), 2.86 (dd, ³*J*₁ = ³*J*₂ = 9.4 Hz, 1 + 1H), 2.98–3.05 (m, 1 + 1H), 3.11 (s, br, 1 + 1H), 3.75 (dd, ³*J*₁ = ³*J*₂ = 8.6 Hz, 1 + 1H), 3.80 (s, 3 + 3H), 4.47–4.52 (m, 2 + 2H), 5.00–5.05 (m, 2 + 2H), 5.09 (d, ³*J* = 9.5 Hz, 1 + 1H), 5.79–5.90 (m, 1 + 1H), 6.87 (d, ³*J* = 8.5 Hz, 2 + 2H), 7.29 (d, ³*J* = 8.5 Hz, 2 + 2H), 9.39 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ −4.1 (1 + 1CH₃), −3.9 (1 + 1CH₃), 17.2 (1 + 1CH₃), 18.0 (1 + 1C), 18.7 (1 + 1CH₃), 23.6 (1 + 1CH₃), 25.9 (3 + 3CH₃), 27.0 (1 + 1CH₃), 29.1 (1 + 1CH₂), 38.0 (1 + 1CH₂), 39.1 (1 + 1C), 39.6 (1 + 1CH₂), 40.5 (1 + 1CH), 43.8 (1 + 1CH₂), 52.0 (1 + 1CH), 55.4 (1 + 1CH₃), 74.6 (1 + 1CH₂), 83.9 (1 + 1CH), 84.6 (1 + 1C), 86.8 (1 + 1CH), 113.8 (2 + 2CH), 117.1 (1 + 1CH₂), 119.3 (1 + 1CH), 129.1 (2 + 2CH), 131.4 (1 + 1C), 135.6 (1 + 1CH), 141.0 (1 + 1C), 159.1 (1 + 1C), 201.1 (1 + 1CH); IR (film on KBr) ν 3500, 2955, 2930, 2855, 1720, 1515, 1250, 1110, 835, 775 cm^{−1}; Anal. Calcd for C₃₃H₅₄O₅Si: C, 70.92; H, 9.74; Found: C, 70.8; H, 9.4.

⁹ CH₂Cl₂ (water content 55 ppm) and DMSO (water content 246 ppm) were used as purchased (HPLC grade).



Diol S5: *t*-BuLi (4.4 mL, 1.8 M in pentane, 7.92 mmol, 7.7 equiv) was added to a cooled ($-78\text{ }^\circ\text{C}$) solution of 2-bromopropene (0.36 mL, 4.074 mmol, 4 equiv) in THF (5 mL, 4.9 mL/mmol **15**). After stirring for 15 minutes at $-78\text{ }^\circ\text{C}$, a solution of the aldehyde **15** (572 mg, 1.024 mmol, 1 equiv) in THF (10 mL, 9.8 mL/mmol **15**) was added. The solution was stirred for 30 minutes at $-78\text{ }^\circ\text{C}$ and saturated aqueous NH_4Cl solution was then added: The phases were separated, the aqueous layer was extracted with CH_2Cl_2 (4 \times), the combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification by chromatography (cyclohexane/ethyl acetate 20/1 to 10/1) afforded the diol **S5** (562 mg, 0.935 mmol, 91%) as a clear oil. Diol **S5** was obtained as a mixture of C9/C14 epimers: R_f 0.71 (cyclohexane/ethyl acetate 2/1); ^1H NMR (400 MHz, CDCl_3) δ -0.03 (s, 3H), 0.04 (s, 3H), 0.86 (s, 9H), 0.90 (s, 3H), 0.94 (s, 3H), 1.08 (d, $^3J = 6.5$ Hz, 3H), 1.18 – 1.28 (m, 1H), 1.51 – 1.69 (m, 4H), 1.72 (s, 3H), 1.80 (s, 3H), 2.00 – 2.07 (m, 2H), 2.12 – 2.20 (m, 2H), 2.28 – 2.41 (m, 2H), 2.60 – 2.78 (m, 1H), 2.97 – 3.08 (m, 1H), 3.53 – 3.66 (m, 1H), 3.80 (s, 3H), 4.04 (s, 1OH), 4.40 – 4.58 (m, 2H), 4.91 – 4.96 (m, 2H), 5.00 – 5.11 (m, 2H), 5.15 – 5.30 (m, 1H), 5.80 – 5.90 (m, 1H), 6.88 (d, $^3J = 8.3$ Hz, 2H), 7.29 (d, $^3J = 8.3$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ -4.1 (CH_3), -4.0 (CH_3), 17.3 (CH_3), 18.0 (C), 19.2 (CH_3), 19.4 (CH_3), 23.6 (CH_3), 23.6 (CH_3), 25.9 ($3 \times \text{CH}_3$), 29.6 (CH_2), 38.4 (CH_2), 39.1 (C), 39.8 (CH), 41.1 (CH_2), 43.8 (CH_2), 55.3 (CH_3), 56.4 (CH), 74.7 (CH_2), 81.4 (C), 82.7 (CH), 84.5 (CH), 87.0 (CH), 113.8 ($2 \times \text{CH}$), 115.3 (CH_2), 117.1 (CH_2), 123.1 (CH), 129.1 ($2 \times \text{CH}$), 131.3 (C), 135.5 (CH), 140.8 (C), 144.2 (C), 159.1 (C); IR (film on KBr) ν 3475, 2955, 2930, 2855, 1615, 1515, 1250, 1110, 1040, 835, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{O}_5\text{Si}$: C, 71.95; H, 10.06; Found: C, 71.7; H, 10.4.

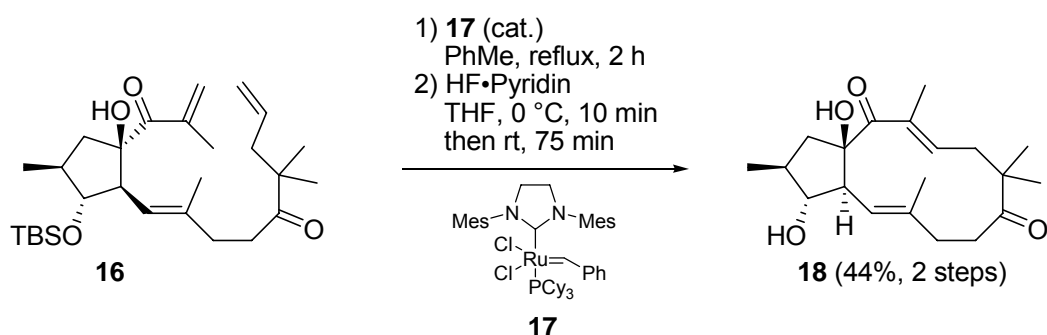


Diketone 16: DDQ (317 mg, 1.396 mmol, 1.5 equiv) was added at room temperature to a solution of the diol **S5** (562 mg, 0.935 mmol, 1 equiv) in CH_2Cl_2 (5 mL, 5.3 mL/mmol **S5**) and aqueous pH7 buffer (1 mL, 1.1 mL/mmol **S5**). After being stirred for 2.5 hours in the dark, the reaction mixture was diluted with saturated aqueous NH_4Cl solution. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 10/1 to 2/1) of the residue provided the triol (424 mg, 0.882 mmol, 94%, R_f 0.48 cyclohexane/ethyl acetate 2/1) as a pale yellow oil.

IBX (1471 mg, 5.253 mmol, 6 equiv) was added at room temperature to a solution of the triol (424 mg, 0.882 mmol, 1 equiv) in CH_2Cl_2 (7 mL, 7.9 mL/mmol triol) and DMSO^{10} (7 mL, 7.9 mL/mmol triol). The reaction mixture was stirred for 6 hours at room temperature and then diluted with water. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 20/1) of the residue furnished the diketone **16** (335 mg, 0.706 mmol, 80%) as a clear oil: R_f 0.63 (cyclohexane/ethyl acetate 5/1); ^1H NMR (400 MHz, CDCl_3) δ -0.04 (s, 3H), 0.05 (s, 3H), 0.85 (s, 9H), 1.11 (s, 6H), 1.12 (d, $^3J = 6.8$ Hz, 3H), 1.47 (s, 3H), 1.54 (dd, $^3J = 9.8$ Hz, $^2J = 14.8$ Hz, 1H), 1.91 (s, 3H), 1.99–2.12 (m, 1H), 2.14–2.21 (m, 2H), 2.24 (d, $^3J = 7.3$ Hz, 2H), 2.49–2.53 (m, 2H), 2.73 (dd, $^3J = 10.0$ Hz, $^2J = 14.8$ Hz, 1H), 3.13 (dd,

¹⁰ CH_2Cl_2 (water content 55 ppm) and DMSO (water content 246 ppm) were used as purchased (HPLC grade).

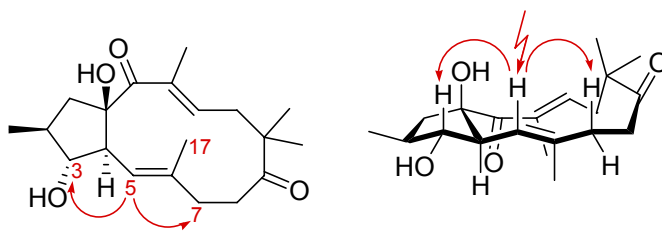
$^3J_1 = ^3J_2 = 9.8$ Hz, 1H), 3.74 (dd, $^3J_1 = ^3J_2 = 9.2$ Hz, 1H), 3.89 (s, 1H, OH), 5.01–5.05 (m, 2H), 5.10 (d, $^3J = 9.5$ Hz, 1H), 5.61–5.71 (m, 1H), 5.88 (s, 1H), 6.07 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ –4.0 (CH_3), –3.8 (CH_3), 17.1 (CH_3), 18.0 (C), 18.4 (CH_3), 20.1 (CH_3), 24.2 ($2 \times \text{CH}_3$), 25.9 ($3 \times \text{CH}_3$), 33.7 (CH_2), 35.6 (CH_2), 40.4 (CH), 44.1 (CH_2), 44.7 (CH_2), 47.6 (C), 56.8 (CH), 83.8 (CH), 84.6 (C), 118.0 (CH_2), 121.1 (CH), 125.7 (CH_2), 134.2 (CH), 139.2 (C), 140.0 (C), 204.3 (C), 214.6 (C); IR (film on KBr) ν 3470, 2960, 2930, 2855, 1705, 1660, 1385, 1255, 1120, 870, 835, 775 cm^{-1} ; Anal. Calcd for $\text{C}_{28}\text{H}_{48}\text{O}_4\text{Si}$: C, 70.54; H, 10.15; Found: C, 70.5; H, 10.0; $[\alpha]_D^{25} -10.7$ (c 1.31, CHCl_3).



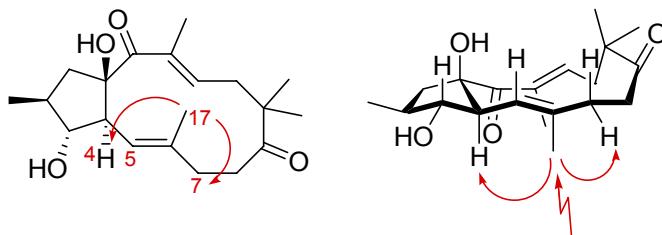
3-*epi*-Characiol (18): $(\text{PCy}_3)(\text{C}_3\text{H}_4\text{N}_2\text{Mes}_2)\text{Cl}_2\text{Ru}=\text{CHPh}$ (**17**) (9 mg, 0.011 mmol, 0.1 equiv) was added as a solid to a solution of the diketone **16** (49 mg, 0.103 mmol, 1 equiv) in toluene (80 mL, 8.2 mL/mmol **16**, $c = 1.3 \times 10^{-3}$ mol/L). The reaction mixture was refluxed while a constant stream of argon was maintained. After tlc indicated the complete consumption of the starting material (about 2 h), the solvent was removed at reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 20/1 to 10/1) of the residue provided the crude product (35 mg, R_f 0.36 cyclohexane/ethyl acetate 5/1) as a yellow oil.

HF·pyridine (0.4 mL, 65–70%, 4 mL/mmol **16**) was added at 0 °C to a solution of the crude product (35 mg) in THF (2 mL, 19 mL/mmol **16**). The reaction mixture was stirred for ten minutes at 0 °C, for 75 minutes at room temperature and then diluted with saturated aqueous NaHCO_3 solution at 0 °C. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by

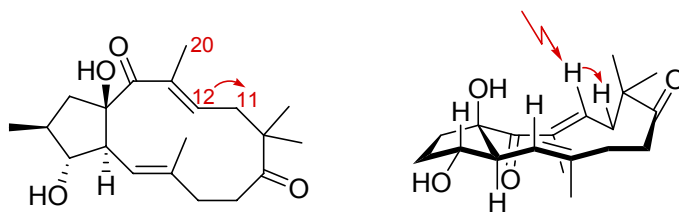
chromatography (cyclohexane/ethyl acetate 5/1 to 2/1) afforded 3-*epi*-characiol (**18**) (15 mg, 0.046 mmol, 44% from **16**) as a white solid (mp: 179 °C–184 °C decomposition): R_f 0.15 (cyclohexane/ethyl acetate 2/1); COSY, HSQC, and NOESY methods were used to confirm the NMR peak assignments on the basis of the jatrophone numbering; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (s, 18- or 19- CH_3), 1.11 (d, 16- CH_3), 1.10–1.15 (m, 1- CH_2 , 1H^{Re}), 1.20 (s, 18- or 19- CH_3), 1.42 (s, 17- CH_3), 1.70 (s, 20- CH_3), 1.79–1.89 (m, 2- CH + OH), 2.02–2.14 (m, 8- CH_2), 2.24 (s, br, OH), 2.27 (dd, $^3J_1 = ^3J_2 = 10.1$ Hz, 4- CH), 2.39 (dd, $^3J = 5.7$ Hz, $^2J = 18.2$ Hz, 11- CH_2 , 1H), 2.47 (dd, $^3J = 5.7$ Hz, $^2J = 18.2$ Hz, 11- CH_2 , 1H), 2.91–2.98 (m, 7- CH_2), 3.24 (dd, $^3J = 8.9$ Hz, $^2J = 13.9$ Hz, 1- CH_2 , 1H^{Si}), 3.67 (dd, $^3J_1 = ^3J_2 = 9.4$ Hz, 3- CH), 5.42 (d, $^3J = 10.5$ Hz, 5- CH), 6.97 (dd, $^3J_1 = ^3J_2 = 5.7$ Hz, 12- CH); ^{13}C NMR (101 MHz, CDCl_3) δ 12.7 (20- CH_3), 16.4 (17- CH_3), 17.9 (16- CH_3), 24.0 (18- or 19- CH_3), 25.2 (18- or 19- CH_3), 34.1 (7- CH_2), 35.0 (8- CH_2), 39.6 (2- CH), 40.4 (11- CH_2), 45.8 (1- CH_2), 48.1 (10- C), 56.3 (4- CH), 83.4 (3- CH), 87.2 (15- C), 126.4 (5- CH), 135.9 (6- or 13- C), 139.9 (6- or 13- C), 143.4 (12- CH), 201.5 (14- C), 215.5 (9- C); IR (film on KBr) ν 3470, 2965, 2925, 1700, 1635, 1385, 1075, 732 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$: C, 71.82; H, 9.04; Found: C, 71.5; H, 9.0; $[\alpha]_D^{25} +69.9$ (c 0.51, CHCl_3).

Table SI-2. 1D-NOE experiment, irradiation at 5.42 ppm (**5-CH**).

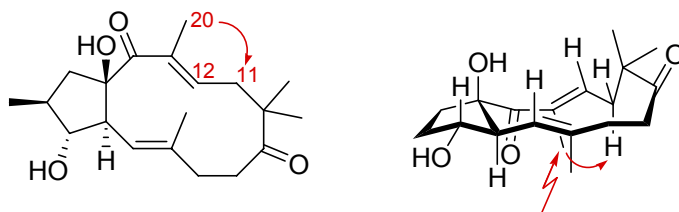
entry	observable NOE	supported conclusion
1	3.67 ppm 3-CH (strong)	—
2	2.91–2.98 ppm 7-CH₂ (strong)	(5 <i>E</i>)
3	1.42 ppm 17-CH₃ (weak)	(5 <i>E</i>)

Table SI-3. 1D-NOE experiment, irradiation at 1.42 ppm (**17-CH₃**).

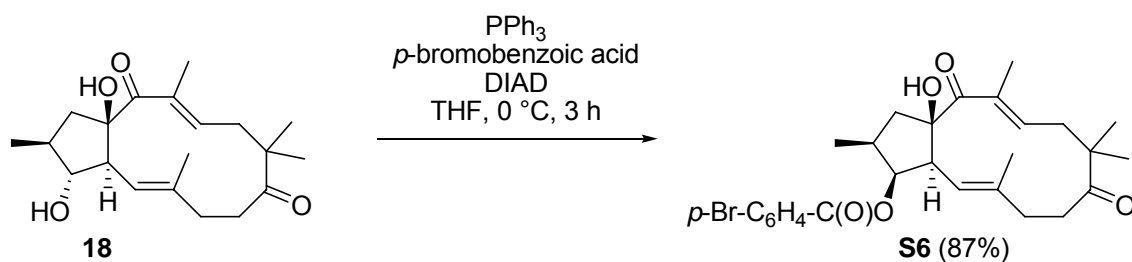
entry	observable NOE	supported conclusion
1	2.27 ppm 4-CH (strong)	(5 <i>E</i>)
2	2.91–2.98 ppm 7-CH₂ (strong)	—
3	5.42 ppm 5-CH (weak)	(5 <i>E</i>)

Table SI-4. 1D-NOE experiment, irradiation at 6.97 ppm (**12-CH**).

entry	NOE observed to	supported conclusion
1	2.39 and 2.47 ppm 11-CH₂ (strong)	—
2	1.70 ppm 20-CH₃ (weak)	—

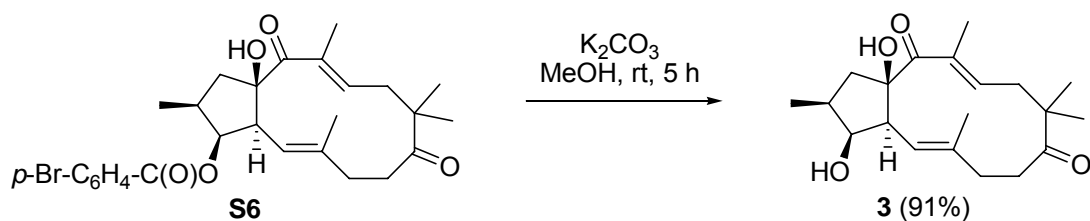
Table SI-5. 1D-NOE experiment, irradiation at 1.70 ppm (**20-CH₃**).

entry	NOE observed to	supported conclusion
1	2.39 and 2.47 ppm 11-CH₂ (strong)	(12 <i>E</i>)
2	6.97 ppm 12-CH (weak)	(12 <i>E</i>)

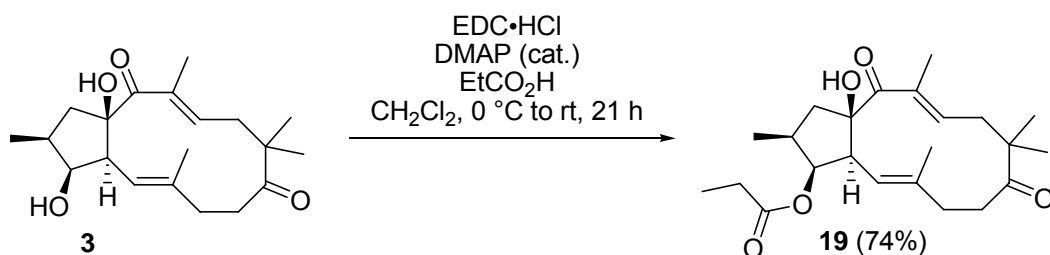


3-*O*-*p*-Bromobenzoylcharaciol (S6): PPh_3 (21 mg, 0.08 mmol, 2.1 equiv), *p*-bromobenzoic acid (16 mg, 0.08 mmol, 2.1 equiv) and DIAD (0.02 mL, 0.101 mmol, 2.7 equiv) were added at 0 °C to a solution of 3-*epi*-characiol (**18**) (13 mg, 0.038 mmol, 1 equiv) in THF (1.4 mL, 37 mL/mmol **18**). After being stirred for three hours at 0 °C, the reaction mixture was diluted with saturated aqueous NH_4Cl solution. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (4×). The combined organic phases were dried (MgSO_4), concentrated under reduced pressure and the residue was purified by chromatography (cyclohexane/ethyl acetate 20/1 to 10/1) to deliver 3-*O*-*p*-bromobenzoylcharaciol (**S6**) (17 mg, 0.033 mmol, 87%) as a white solid (mp: 126 °C): R_f 0.62 (cyclohexane/ethyl acetate 2/1); the ^1H NMR peak assignments were deduced from ^1H - ^1H COSY spectra and are listed on the basis of the jatrophone numbering; ^1H NMR (400 MHz, CDCl_3) δ 0.99 (d, $^3J = 6.8$ Hz, 16- CH_3), 1.10 (s, 18- or 19- CH_3), 1.18 (s, 18- or 19- CH_3), 1.40 (s, 17- CH_3), 1.55 (dd, $^3J = 11.9$ Hz, $^2J = 13.5$ Hz, 1- CH_2 , 1H^{Re}), 1.72 (s, 20- CH_3), 1.97–2.08 (m, 8- CH_2), 2.20–2.32 (m, 2- CH + OH), 2.38–2.50 (m, 11- CH_2), 2.60 (dd, $^3J_1 = 3.5$ Hz, $^3J_2 = 10.5$ Hz, 4- CH), 2.78 (dd, $J_1 = J_2 = 12.1$ Hz, 11- CH_2 , 1H), 2.92 (dd, $J_1 = J_2 = 13.3$ Hz, 11- CH_2 , 1H), 3.24 (dd, $^3J = 8.3$ Hz, $^2J = 13.5$ Hz, 1- CH_2 , 1H^{Si}), 5.33 (d, $^3J = 10.5$ Hz, 5- CH), 5.49 (dd, $^3J_1 = ^3J_2 = 3.5$ Hz, 3- CH), 7.01 (dd, $^3J_1 = ^3J_2 = 6.0$ Hz, 12- CH), 7.64 (d, $^3J = 8.5$ Hz, $2 \times \text{CH}_{\text{ar}}$), 7.89 (d, $^3J = 8.5$ Hz, $2 \times \text{CH}_{\text{ar}}$); ^{13}C NMR (101 MHz, CDCl_3) δ 12.6 (CH_3), 14.3 (CH_3), 16.4 (CH_3), 24.1 (CH_3), 25.0 (CH_3), 33.9 (CH_2), 35.1 (CH_2), 38.7 (CH), 40.3 (CH_2), 48.1 (C or CH_2), 48.3 (C or CH_2), 52.7 (CH), 83.2 (CH), 90.4 (C), 120.3 (CH), 128.4 (C), 128.9 (C), 131.2 ($2 \times \text{CH}$), 132.1 ($2 \times \text{CH}$), 135.8 (C), 139.1 (C), 144.3 (CH), 165.5 (C), 201.1 (C), 215.2 (C); IR (film on KBr) ν 3485, 2965, 2930, 1705, 1650, 1385, 1270,

1115, 1010, 735 cm^{-1} ; Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{BrO}_5$: C, 62.67; H, 6.43; Found: C, 62.5; H, 6.5; $[\alpha]_{\text{D}}^{25} +153.5$ (c 0.34, CHCl_3).

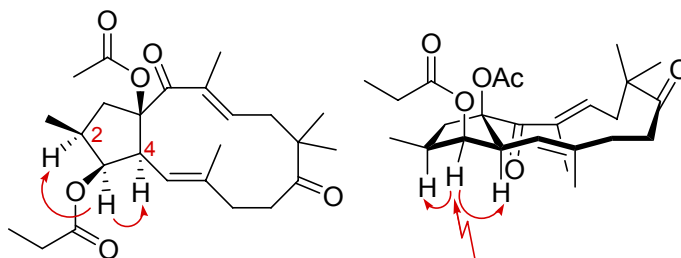


Characiol (3): Solid K_2CO_3 (157 mg, 1.136 mmol, 27 equiv) was added at room temperature to a solution of 3-*O*-*p*-bromobenzoylcharaciol (**S6**) (22 mg, 0.043 mmol, 1 equiv) in methanol (2 mL, 48 mL/mmol **S6**). The reaction mixture was stirred for 5 hours at room temperature and then diluted with saturated aqueous NH_4Cl solution and CH_2Cl_2 . The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by chromatography (cyclohexane/ethyl acetate 10/1 to 5/1) provided characiol (**3**) (13 mg, 0.039 mmol, 91%) as a white solid (mp: 103 $^\circ\text{C}$): R_f 0.25 (cyclohexane/ethyl acetate 2/1); the ^1H NMR peak assignments were deduced from ^1H - ^1H COSY spectra and are listed on the basis of the jatrophone numbering; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (d, $^3J = 6.8$ Hz, 16- CH_3), 1.15 (s, 18- or 19- CH_3), 1.19 (s, 18- or 19- CH_3), 1.32 (s, 17- CH_3), 1.49 (dd, $^3J = 10.5$ Hz, $^2J = 14.1$ Hz, 1- CH_2 , 1H^{Re}), 1.70 (s, 20- CH_3), 1.98–2.02 (m, 8- CH_2 , 1H), 2.05–2.19 (m, 2- CH , 8- CH_2 , 1H, OH), 2.37 (dd, $^3J_1 = 2.9$ Hz, $^3J_2 = 10.3$ Hz, 4- CH), 2.38–2.43 (m, 11- CH_2 , 1H), 2.52 (dd, $^3J = 5.8$ Hz, $^2J = 18.7$ Hz, 11- CH_2 , 1H), 2.85–2.99 (m, 7- CH_2), 3.21 (dd, $^3J = 9.8$ Hz, $^2J = 14.1$ Hz, 1- CH_2 , 1H^{Si}), 3.37 (s, OH), 3.97 (dd, $^3J_1 = ^3J_2 = 2.9$ Hz, 3- CH), 5.63 (d, $^3J = 10.3$ Hz, 5- CH), 7.19 (dd, $^3J_1 = ^3J_2 = 5.8$ Hz, 12- CH); ^{13}C NMR (101 MHz, CDCl_3) δ 12.7 (CH_3), 14.4 (CH_3), 16.5 (CH_3), 24.0 (CH_3), 25.4 (CH_3), 34.1 (CH_2), 34.6 (CH_2), 38.9 (CH), 40.6 (CH_2), 47.8 (C or CH_2), 48.0 (C or CH_2), 54.5 (CH), 81.4 (CH), 92.6 (C), 121.9 (CH), 136.7 (C), 138.4 (C), 145.1 (CH), 201.0 (C), 215.4 (C); IR (film on KBr) ν 3465, 2965, 2930, 1705, 1645, 1385, 1245, 1140, 1075 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$: C, 71.82; H, 9.04; Found: C, 71.6; H, 9.1; $[\alpha]_{\text{D}}^{25} +54.8$ (c 0.605, CHCl_3).

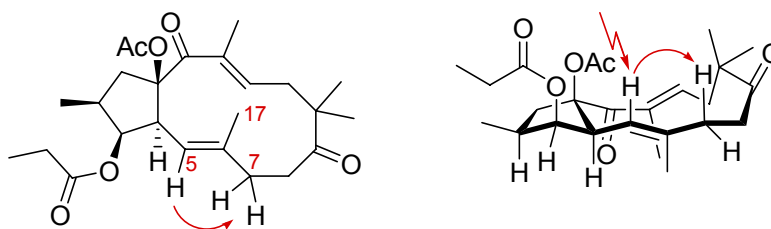


3-*O*-Propionylcharaciol (19): Propionic acid (0.02 mL, 0.267 mmol, 8 equiv) was added at 0 °C to a solution of EDC·HCl (63 mg, 0.329 mmol, 10 equiv) and DMAP (3 mg, 0.025 mmol, 0.7 equiv) in CH₂Cl₂ (1 mL, 30 mL/mmol **3**). After stirring the mixture for 5 minutes at 0 °C, a solution of characiol (**3**) (11 mg, 0.033 mmol, 1 equiv) in CH₂Cl₂ (2 mL, 60 mL/mmol **3**) was added. The reaction mixture was allowed to warm to room temperature, then stirred for 21 hours and finally diluted with saturated aqueous NH₄Cl solution. The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (4×). The combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by chromatography (cyclohexane/ethyl acetate 10/1) delivered 3-*O*-propionylcharaciol (**19**) (9.5 mg, 0.024 mmol, 74%) as a colorless oil: *R*_f 0.51 (cyclohexane/ethyl acetate 2/1); the ¹H NMR peak assignments were deduced from ¹H-¹H COSY spectra and are listed on the basis of the jatrophone numbering; ¹H NMR (400 MHz, CDCl₃) δ 0.95 (d, ³*J* = 7.0 Hz, 16-CH₃), 1.12 (s, 18- or 19-CH₃), 1.19 (s, 18- or 19-CH₃), 1.22 (t, ³*J* = 7.6 Hz, propionic acid ester-CH₃), 1.34 (s, 17-CH₃), 1.40 (dd, ³*J* = 11.4 Hz, ²*J* = 13.9 Hz, 1-CH₂, 1H^{*Re*}), 1.71 (s, 20-CH₃), 1.97–2.02 (m, 8-CH₂, 1H), 2.05–2.10 (m, 8-CH₂, 1H), 2.13–2.23 (m, 2-CH), 2.37 (s, OH), 2.42–2.51 (m, 4-CH, 11-CH₂, propionic acid ester-CH₂), 2.82–2.94 (m, 7-CH₂), 3.23 (dd, ³*J* = 9.1 Hz, ²*J* = 13.9 Hz, 1-CH₂, 1H^{*Si*}), 5.26 (d, ³*J* = 10.5 Hz, 5-CH), 5.30 (dd, ³*J*₁ = ³*J*₂ = 3.5 Hz, 3-CH), 7.09 (dd, ³*J*₁ = ³*J*₂ = 5.8 Hz, 12-CH); ¹³C NMR (101 MHz, CDCl₃) δ 9.6 (CH₃), 12.6 (CH₃), 14.4 (CH₃), 16.4 (CH₃), 24.0 (CH₃), 25.2 (CH₃), 27.8 (CH₂), 33.9 (CH₂), 35.0 (CH₂), 38.3 (CH), 40.4 (CH₂), 48.1 (C or CH₂), 48.5 (C or CH₂), 52.9 (CH), 82.5 (CH), 91.3 (C), 120.5 (CH), 136.1 (C), 138.9 (C), 145.0 (CH), 173.7 (C), 200.5 (C), 215.2 (C); IR (film on KBr) ν 3480, 2970, 2930, 1730, 1710, 1650, 1385 cm⁻¹; HRMS (ESI) Calcd for C₂₃H₃₄O₅Na ([M+Na]⁺): 413.2299; Found: 413.2302; [α]_D²⁵ +101.4 (c 0.45, CHCl₃).

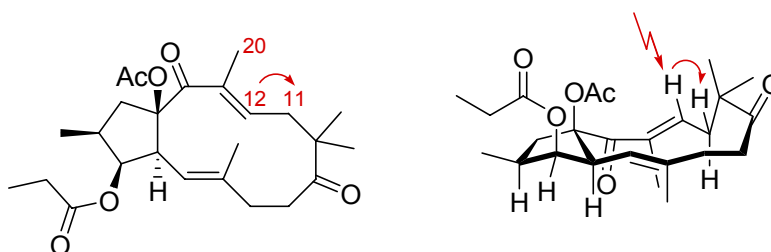
33

Table SI-6. 1D-NOE experiment, irradiation at 5.24 ppm (**3-CH**).

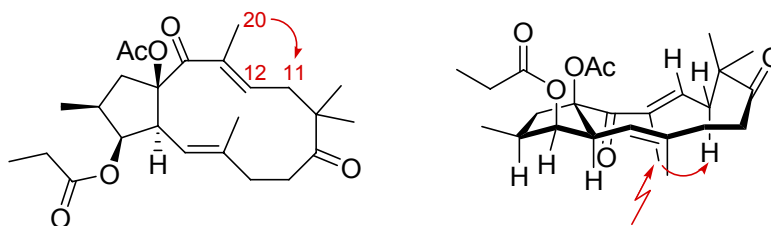
entry	NOE observed to	supported conclusion
1	2.13–2.23 ppm 2-CH (strong)	3-CH and 2-CH are <i>cis</i>
2	2.55 ppm 4-CH (strong)	3-CH and 4-CH are <i>cis</i>

Table SI-7. 1D-NOE experiment, irradiation at 5.42 ppm (**5-CH**).

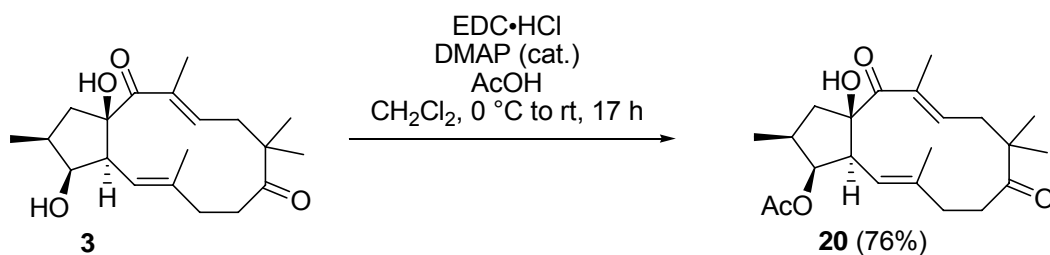
entry	NOE observed to	supported conclusion
1	2.88 ppm 7-CH₂ (strong)	(5 <i>E</i>)
2	1.39 ppm 17-CH₃ (weak)	(5 <i>E</i>)

Table SI-8. 1D-NOE experiment, irradiation at 6.37 ppm (**12-CH**).

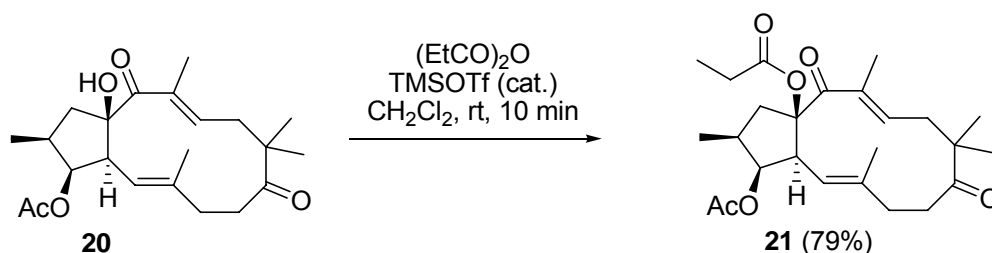
entry	NOE observed to	supported conclusion
1	2.32–2.45 ppm 11-CH₂ (strong)	—
2	1.69 ppm 20-CH₃ (weak)	—

Table SI-9. 1D-NOE experiment, irradiation at 1.69 ppm (**20-CH₃**).

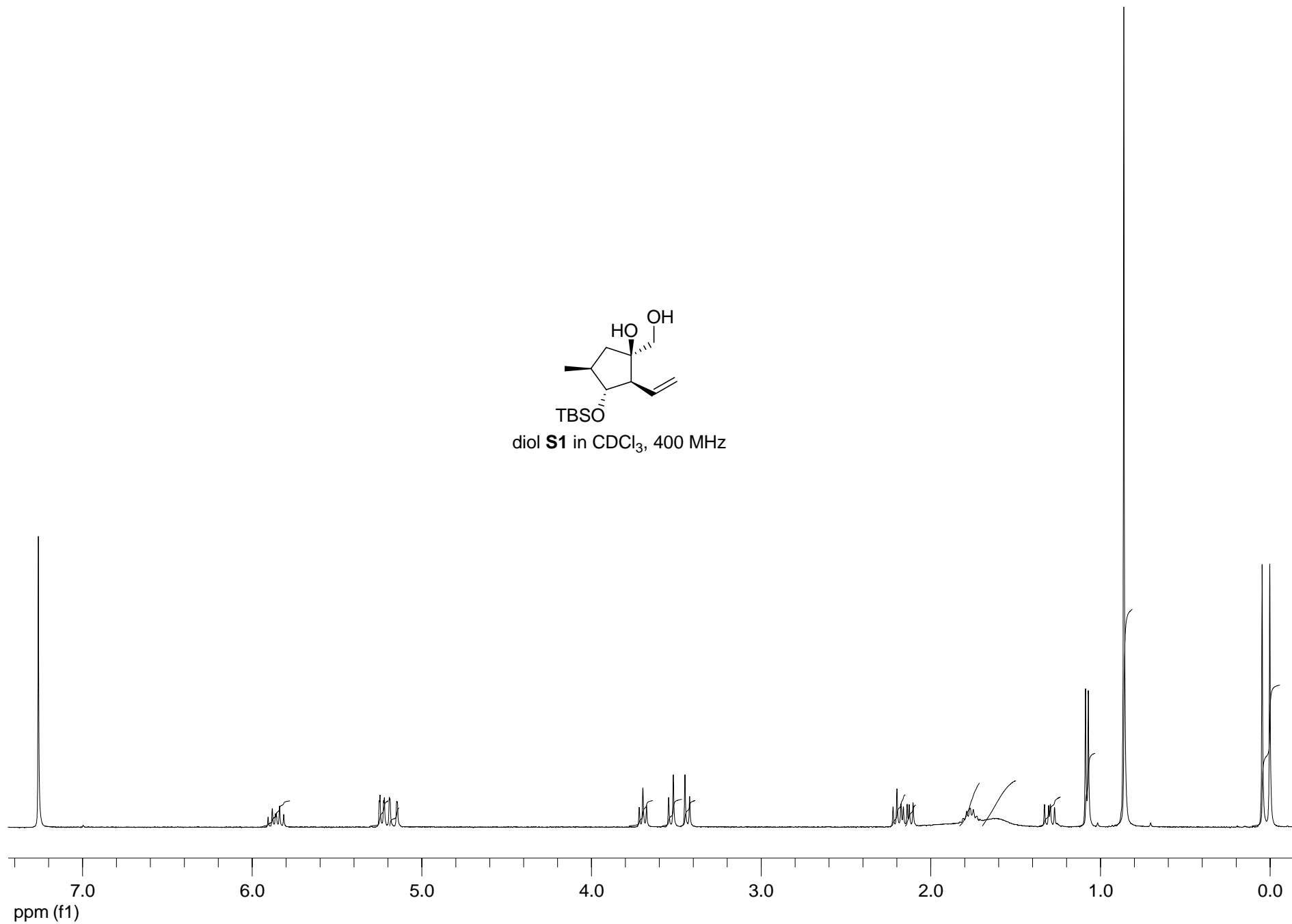
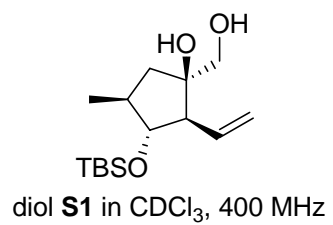
entry	NOE observed to	supported conclusion
1	2.32–2.45 ppm 11-CH₂ (strong)	(12 <i>E</i>)
2	6.37 ppm 12-CH (weak)	(12 <i>E</i>)



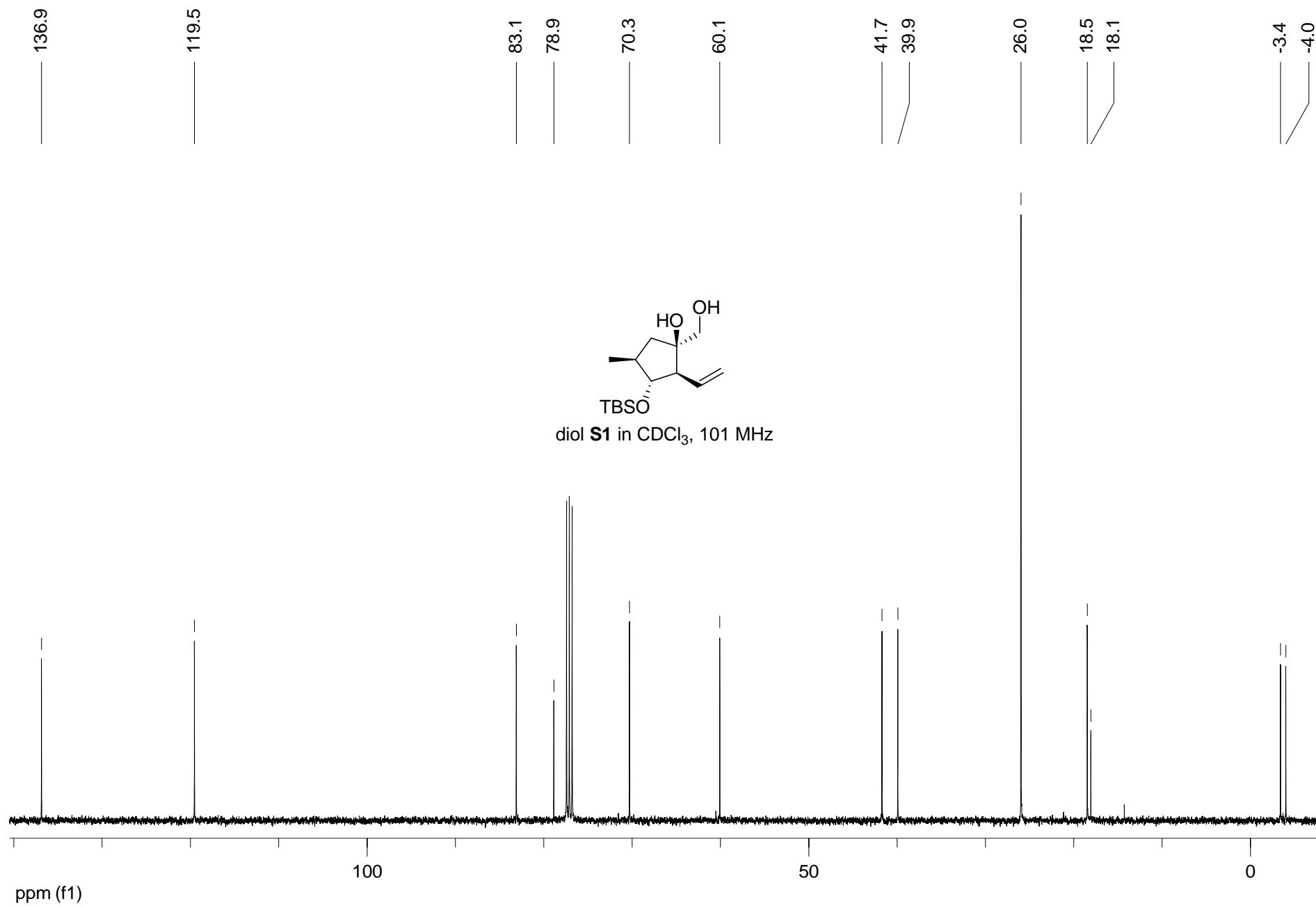
3-*O*-Acetylcharaciol (20): Acetic acid (0.05 mL, 0.873 mmol, 10 equiv) was added at 0 °C to a solution of EDC·HCl (164 mg, 0.856 mmol, 10 equiv) and DMAP (4 mg, 0.033 mmol, 0.4 equiv) in CH₂Cl₂ (1 mL, 12 mL/mmol **3**). After stirring the reaction mixture for 5 minutes at 0 °C, a solution of characiol (**3**) (28 mg, 0.084 mmol, 1 equiv) in CH₂Cl₂ (2 mL, 24 mL/mmol **3**) was added. The reaction mixture was allowed to warm to room temperature and then stirred for 17 hours. Saturated aqueous NH₄Cl solution was added, the phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (4×). The combined organic phases were dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by chromatography (cyclohexane/ethyl acetate 10/1) to furnish 3-*O*-acetylcharaciol (**20**) (24 mg, 0.064 mmol, 76%) as a colorless oil: *R*_f 0.47 (cyclohexane/ethyl acetate 2/1); the ¹H NMR peak assignments were deduced from ¹H-¹H COSY spectra and are listed on the basis of the jatrophone numbering; ¹H NMR (400 MHz, CDCl₃) δ 0.96 (d, ³*J* = 6.8 Hz, 16-CH₃), 1.13 (s, 18- or 19-CH₃), 1.20 (s, 18- or 19-CH₃), 1.34 (s, 17-CH₃), 1.40 (dd, ³*J* = 11.5 Hz, ²*J* = 13.8 Hz, 1-CH₂, 1H^{*Re*}), 1.71 (s, 20-CH₃), 1.98–2.11 (m, 8-CH₂), 2.13–2.23 (m, 2-CH), 2.17 (s, acetate-CH₃), 2.33 (s, br, OH), 2.38–2.52 (m, 4-CH, 11-CH₂), 2.84–2.95 (m, 7-CH₂), 3.22 (dd, ³*J* = 9.2 Hz, ²*J* = 13.8 Hz, 1-CH₂, 1H^{*Si*}), 5.26–5.29 (m, 3-CH, 5-CH), 7.08 (dd, ³*J*₁ = ³*J*₂ = 5.8 Hz, 12-CH); ¹³C NMR (101 MHz, CDCl₃) δ 12.6 (CH₃), 14.4 (CH₃), 16.4 (CH₃), 21.2 (CH₃), 24.0 (CH₃), 25.1 (CH₃), 33.9 (CH₂), 35.0 (CH₂), 38.3 (CH), 40.4 (CH₂), 48.1 (C or CH₂), 48.4 (C or CH₂), 52.8 (CH), 82.7 (CH), 91.2 (C), 120.4 (CH), 136.1 (C), 139.0 (C), 145.0 (CH), 170.3 (C), 200.5 (C), 215.2 (C); IR (film on KBr) ν 3480, 2970, 2930, 1735, 1650, 1385, 1245, 1145, 1075, 1020, 730 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₃₃O₅ ([M+H]⁺): 377.2323; Found: 377.2324; [α]_D²⁵ +76.8 (c 1.15, CHCl₃).

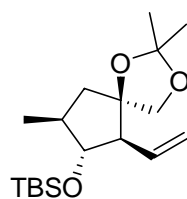


3-*O*-Acetyl-15-*O*-propionylcharaciol (21**):** Propanoic anhydride (0.12 mL, 0.936 mmol, 19 eq) and TMSOTf (one drop, cat.) were added at room temperature to a solution of 3-*O*-acetylcharaciol (**20**) (19 mg, 0.05 mmol, 1 equiv) in CH_2Cl_2 (2 mL, 40 mL/mmol **20**); the initially colorless solution changed color to pink. After being stirred for 10 minutes at room temperature, the reaction mixture was diluted with methanol and saturated aqueous NH_4Cl solution. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 \times). The combined organic phases were dried (MgSO_4) and concentrated under reduced pressure. Chromatographic purification (cyclohexane/ethyl acetate 10/1) of the residue provided 3-*O*-acetyl-15-*O*-propionylcharaciol (**21**) (17 mg, 0.039 mmol, 79%) as a white solid (mp: 134 °C): R_f 0.53 (cyclohexane/ethyl acetate 2/1); the ^1H NMR peak assignments were deduced from ^1H - ^1H COSY spectra and are listed on the basis of the jatrophone numbering; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (d, $^3J = 6.8$ Hz, 16- CH_3), 1.01 (s, 18- or 19- CH_3), 1.16 (t, $^3J = 7.5$ Hz, propionic acid ester- CH_3), 1.18 (s, 18- or 19- CH_3), 1.40 (s, 17- CH_3), 1.42 (dd, $^3J = ^2J = 13.3$ Hz, 1- CH_2 , 1H^{Re}), 1.69 (s, 20- CH_3), 2.02–2.09 (m, 8- CH_2), 2.12 (s, acetate- CH_3), 2.14–2.23 (m, 2- CH), 2.30–2.45 (m, 11- CH_2), 2.41 (q, $^3J = 7.5$ Hz, propionic acid ester- CH_2), 2.55 (dd, $^3J_1 = 3.8$ Hz, $^3J_2 = 10.3$ Hz, 4- CH), 2.84–3.02 (m, 7- CH_2), 3.30 (dd, $^3J = 7.8$ Hz, $^2J = 13.3$ Hz, 1- CH_2 , 1H^{Si}), 5.22 (dd, $^3J_1 = ^3J_2 = 3.8$ Hz, 3- CH), 5.43 (d, $^3J = 10.3$ Hz, 5- CH), 6.35 (dd, $^3J_1 = ^3J_2 = 6.2$ Hz, 12- CH); ^{13}C NMR (101 MHz, CDCl_3) δ 8.8 (CH_3), 12.1 (CH_3), 13.7 (CH_3), 16.2 (CH_3), 21.0 (CH_3), 24.1 (CH_3), 24.9 (CH_3), 28.1 (CH_2), 33.7 (CH_2), 35.4 (CH_2), 38.5 (CH), 40.0 (CH_2), 46.2 (C or CH_2), 47.8 (C or CH_2), 51.5 (CH), 80.9 (CH), 92.7 (C), 120.8 (CH), 135.6 (C), 138.8 (C), 139.3 (CH), 170.7 (C), 173.6 (C), 198.5 (C), 215.1 (C); IR (film on KBr) ν 2970, 2935, 1735, 1705, 1660, 1385, 1240, 1220, 1110, 1020 cm^{-1} ; Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{O}_6$: C, 69.42; H, 8.39; Found: C, 69.3; H, 8.2; $[\alpha]_D^{25}$ -14.5 (c 0.43, CHCl_3).

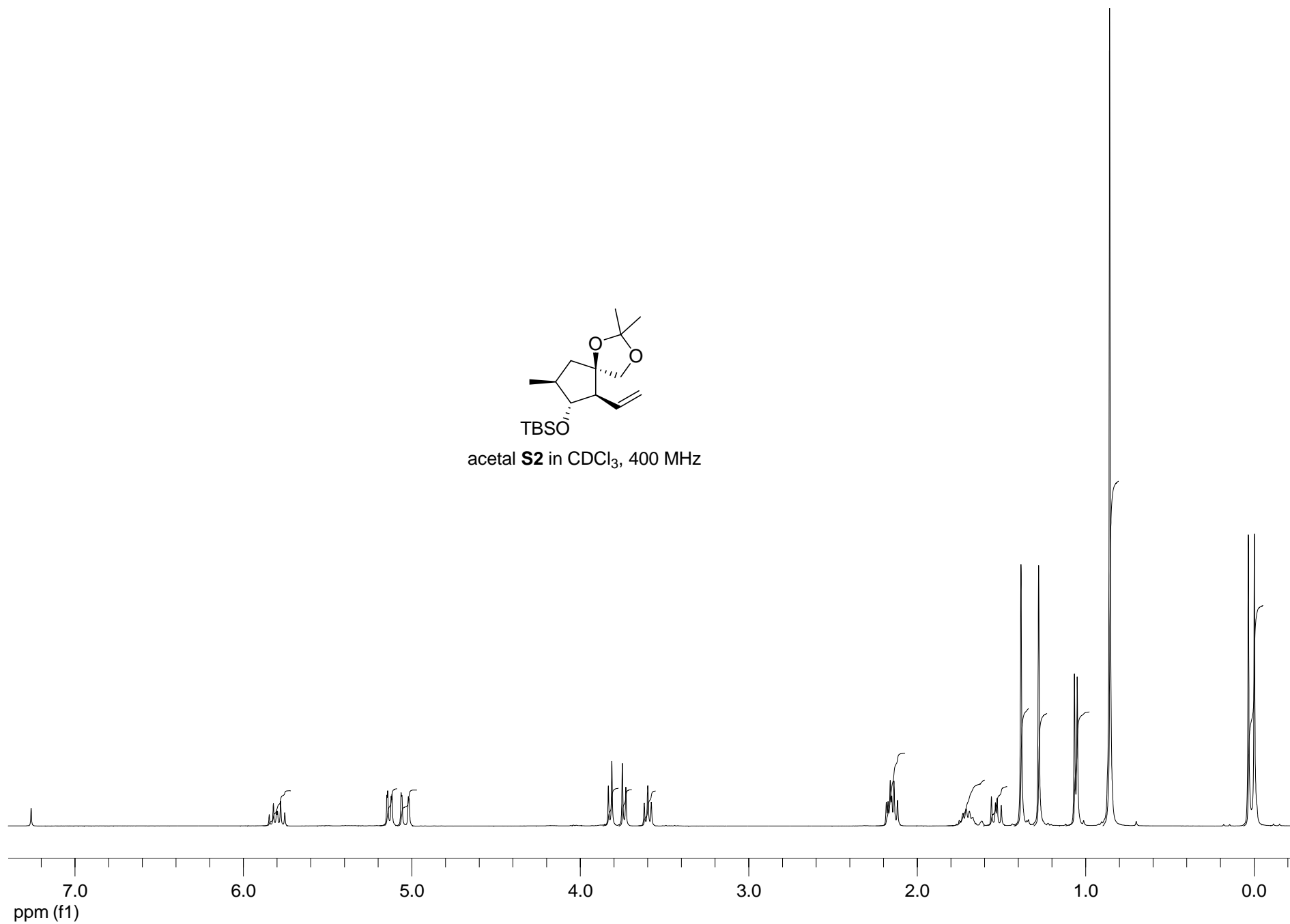


Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

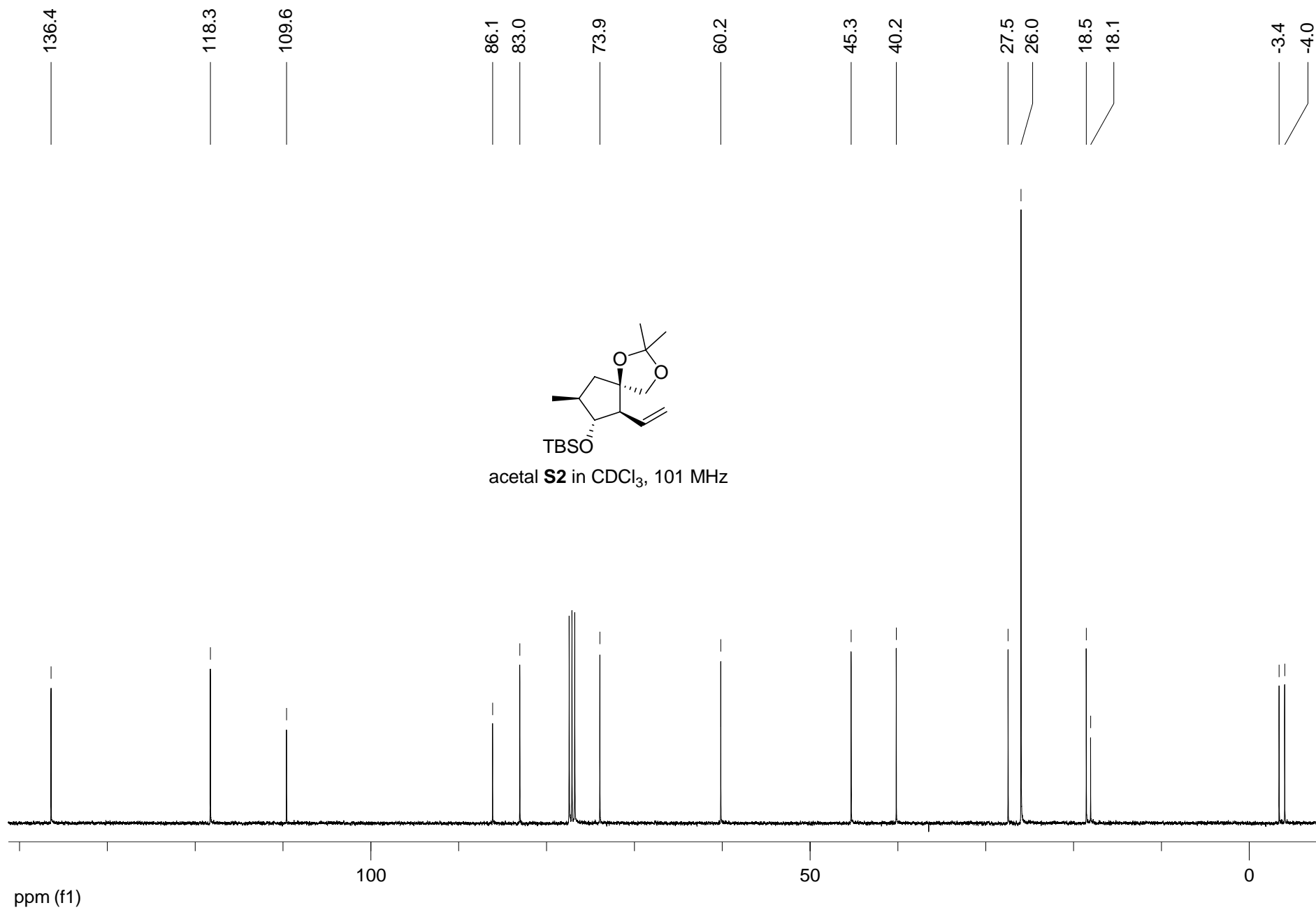


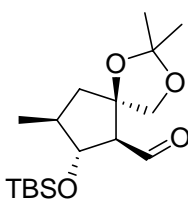


acetal **S2** in CDCl₃, 400 MHz

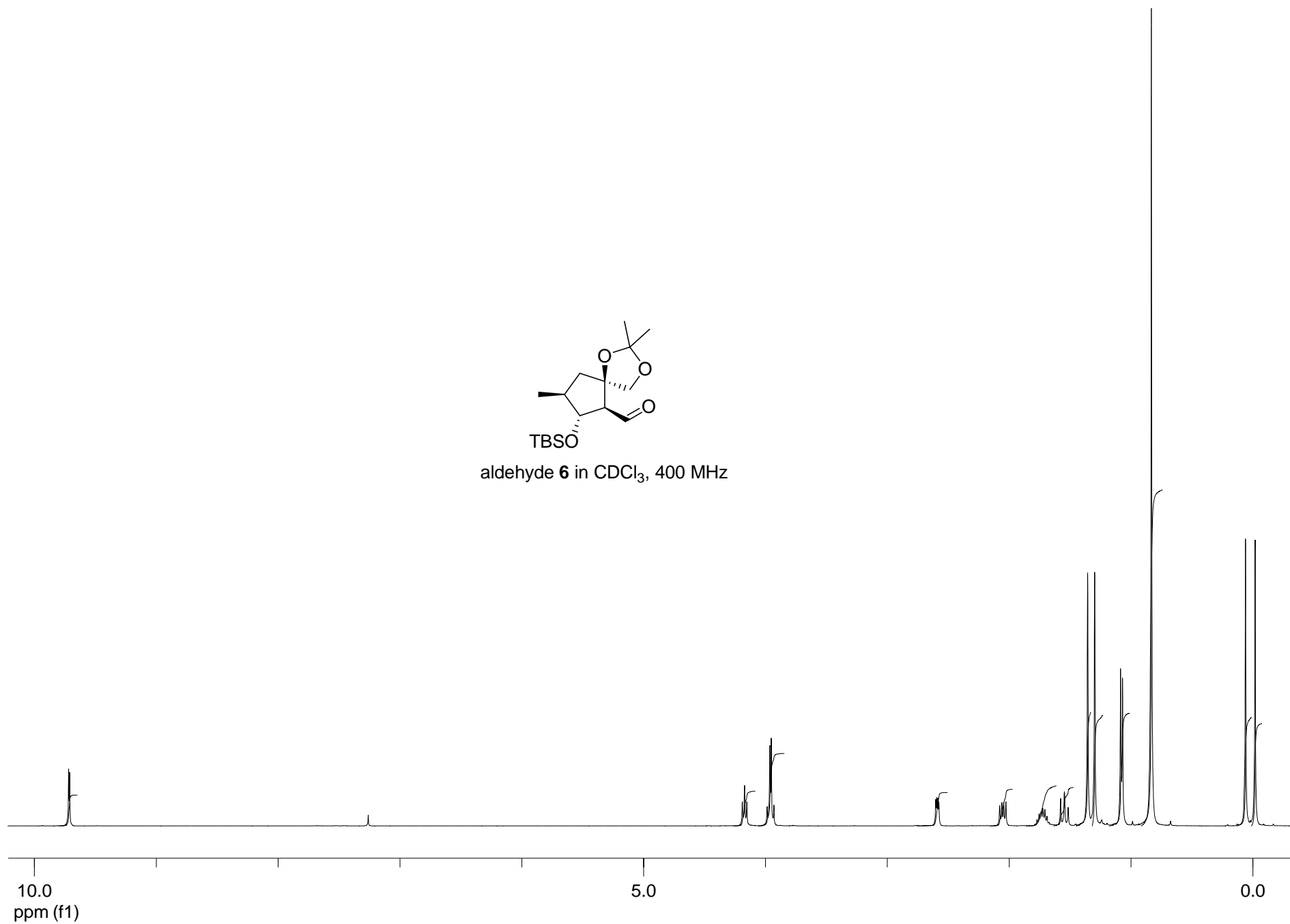


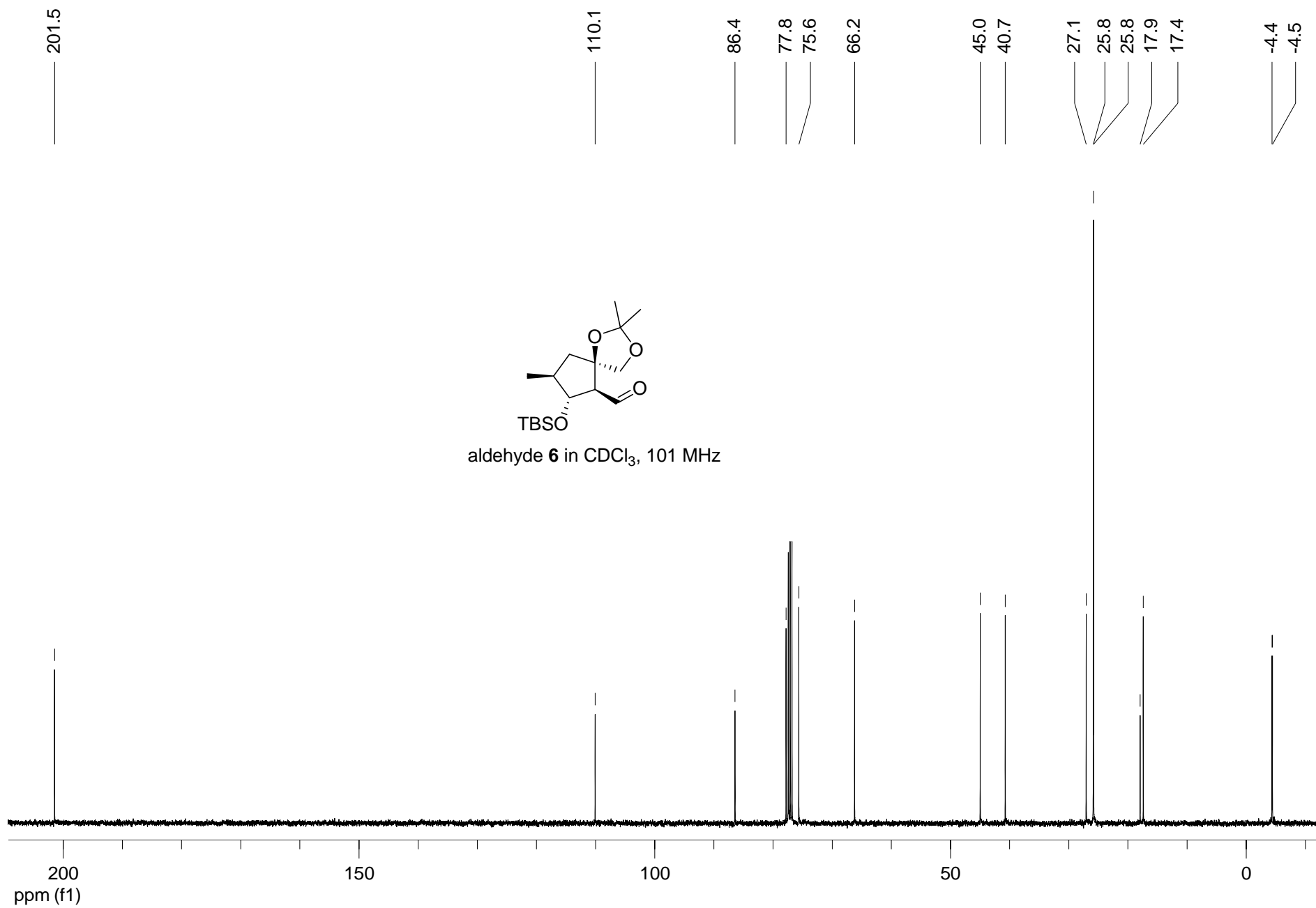
Total Synthesis of Jatropha Diterpenes from *Euphorbia characias* – Supporting Information

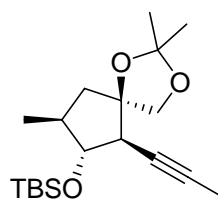




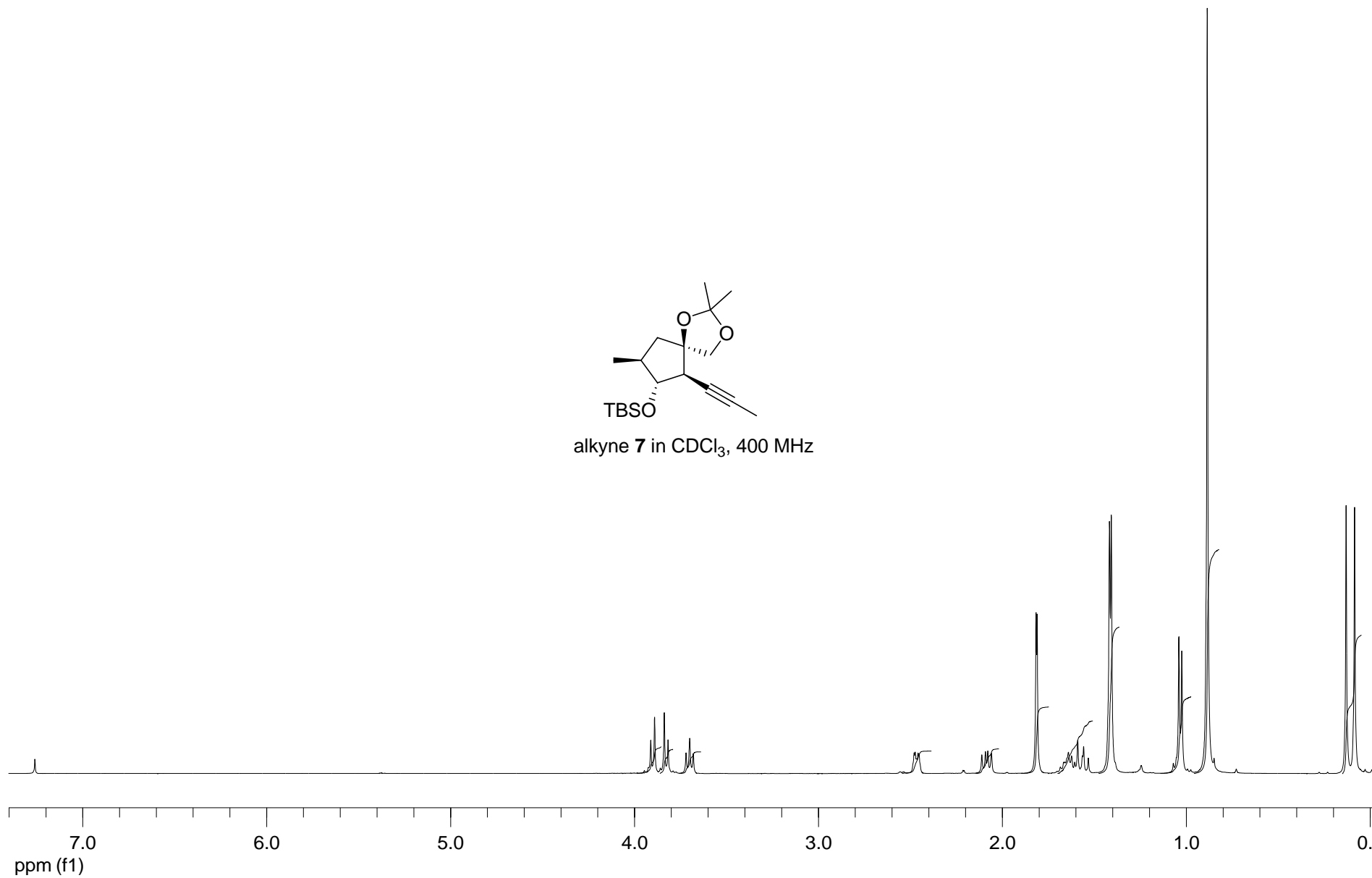
aldehyde **6** in CDCl₃, 400 MHz



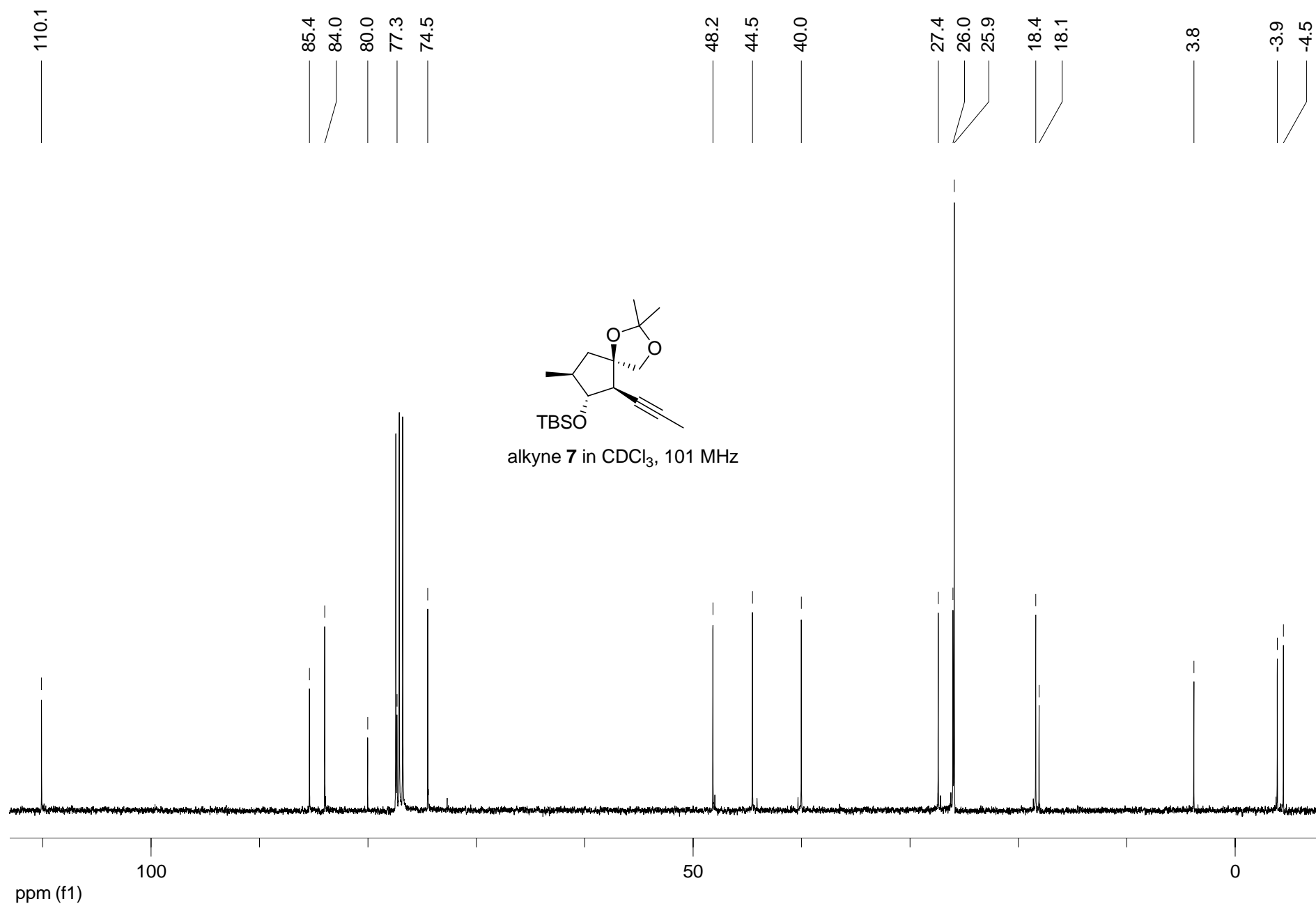


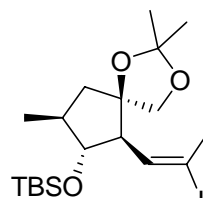


alkyne **7** in CDCl₃, 400 MHz

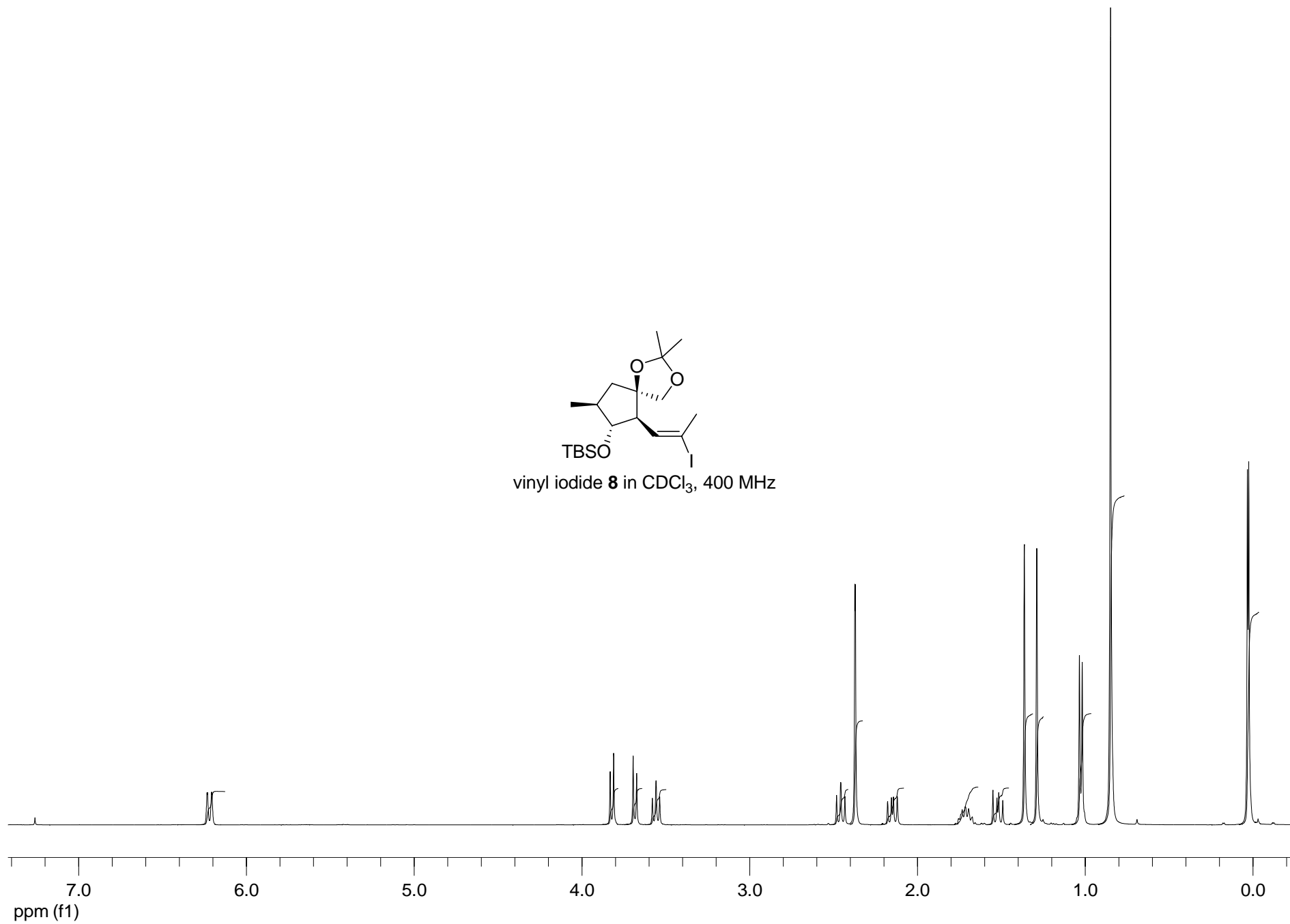


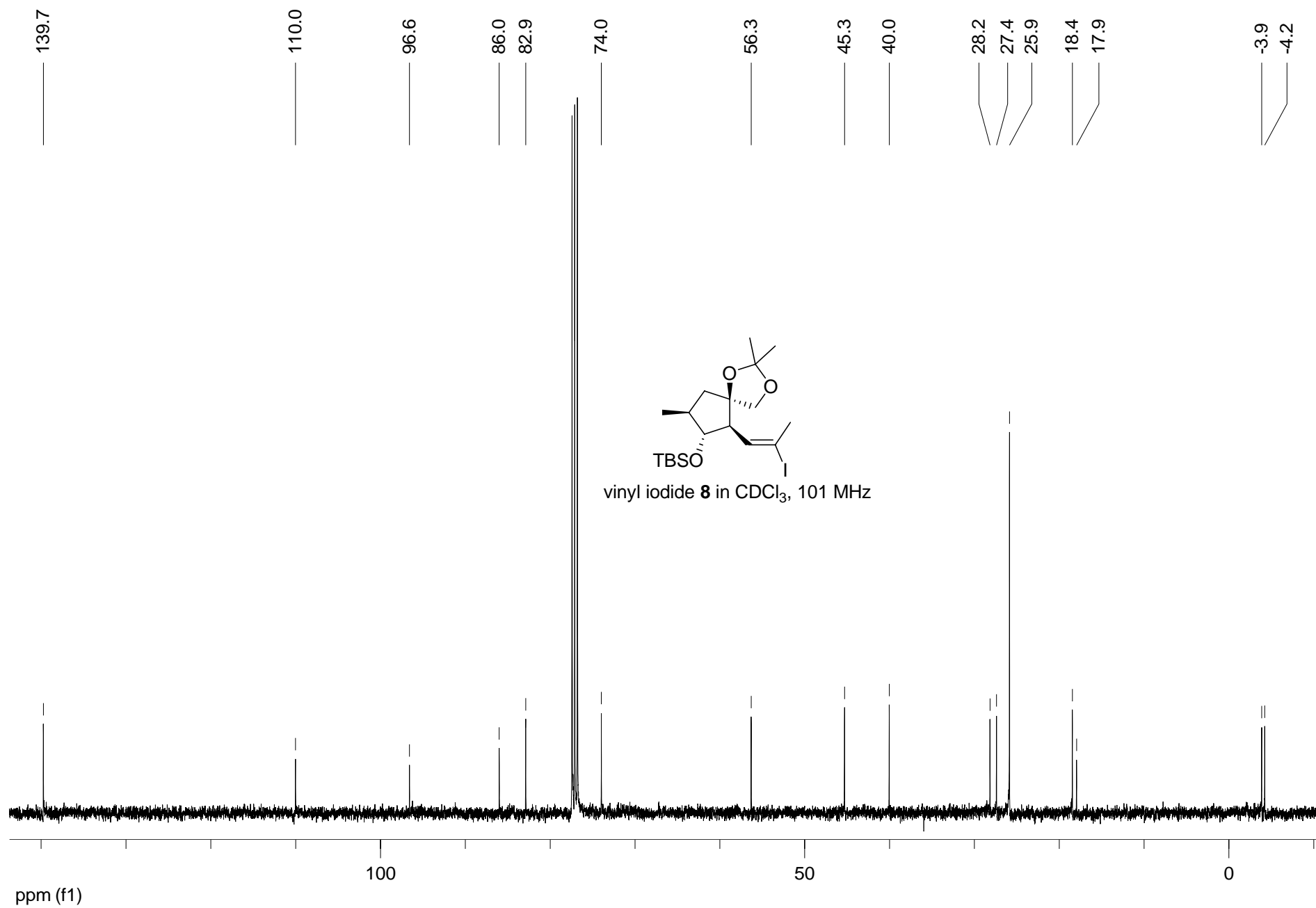
Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

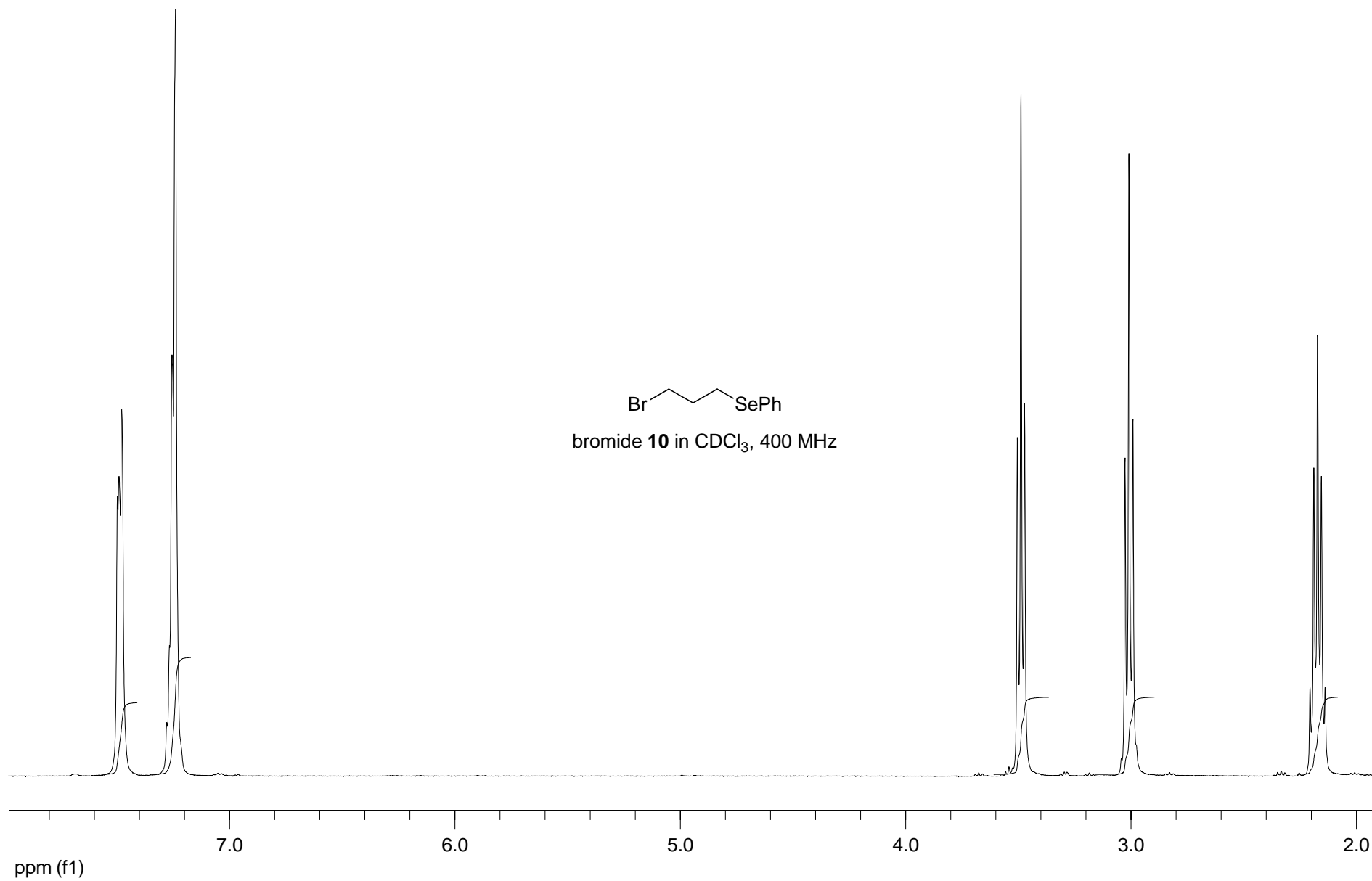


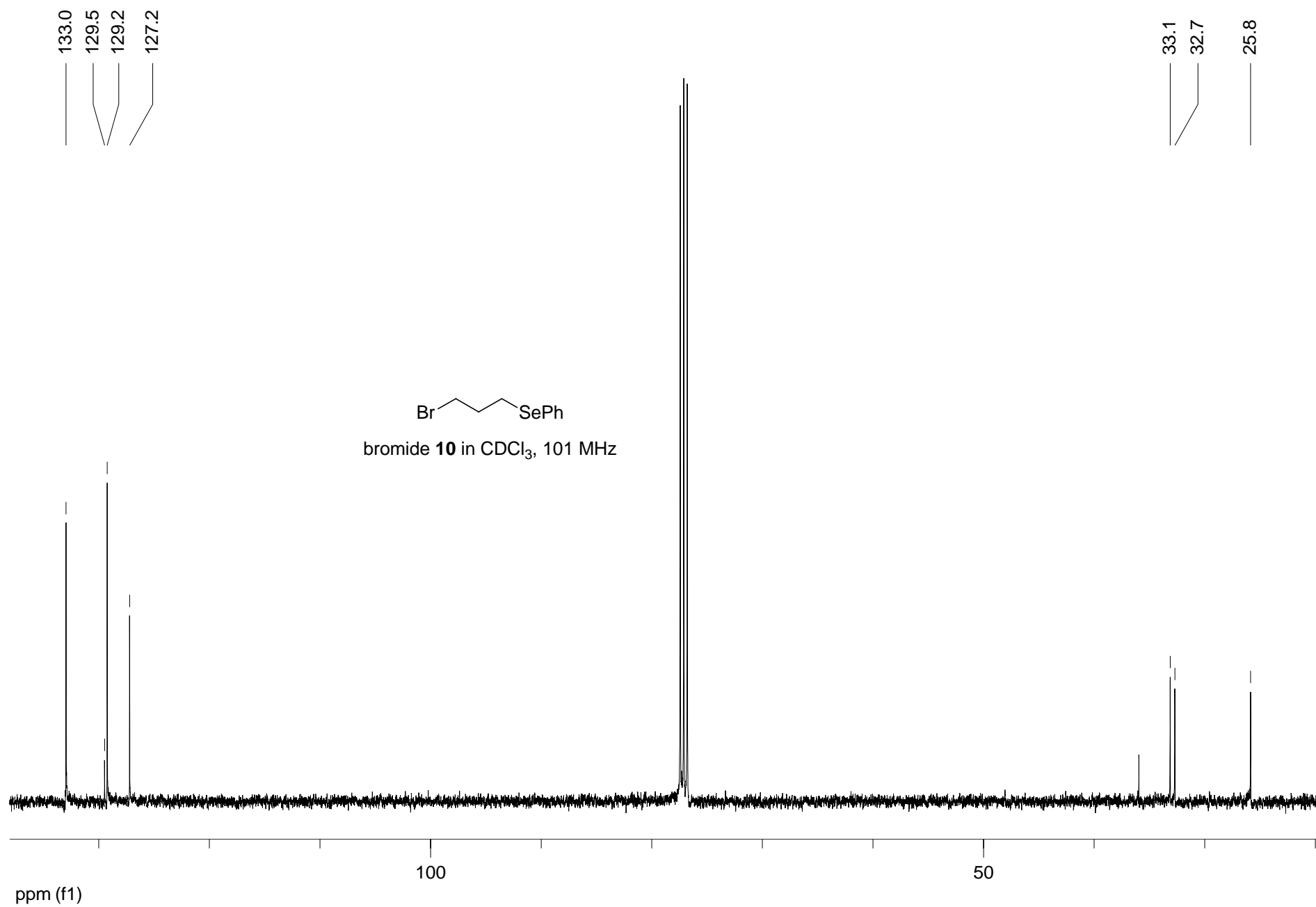


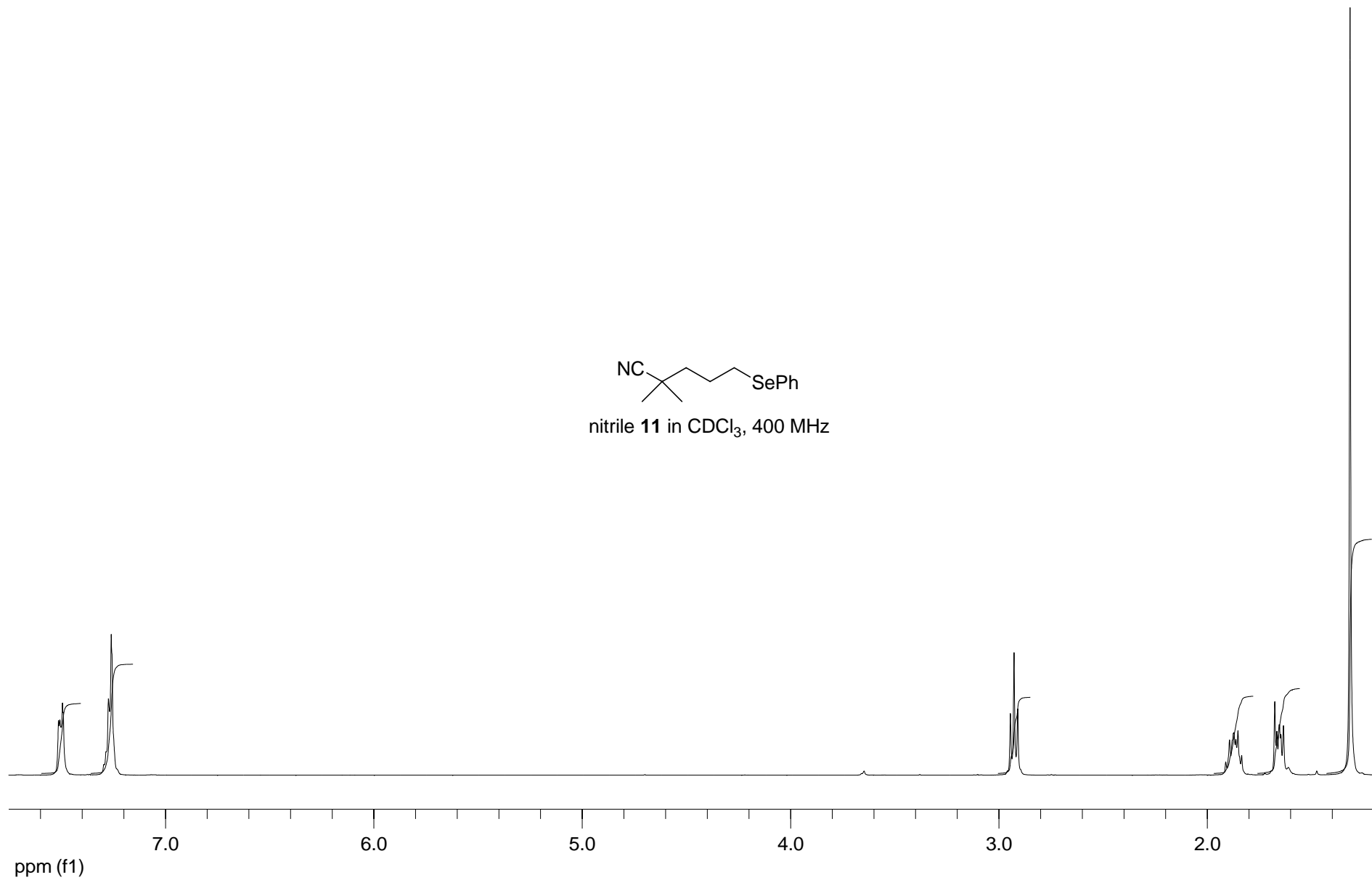
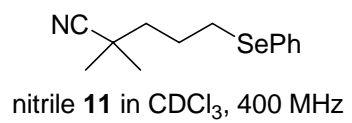
vinyl iodide **8** in CDCl₃, 400 MHz

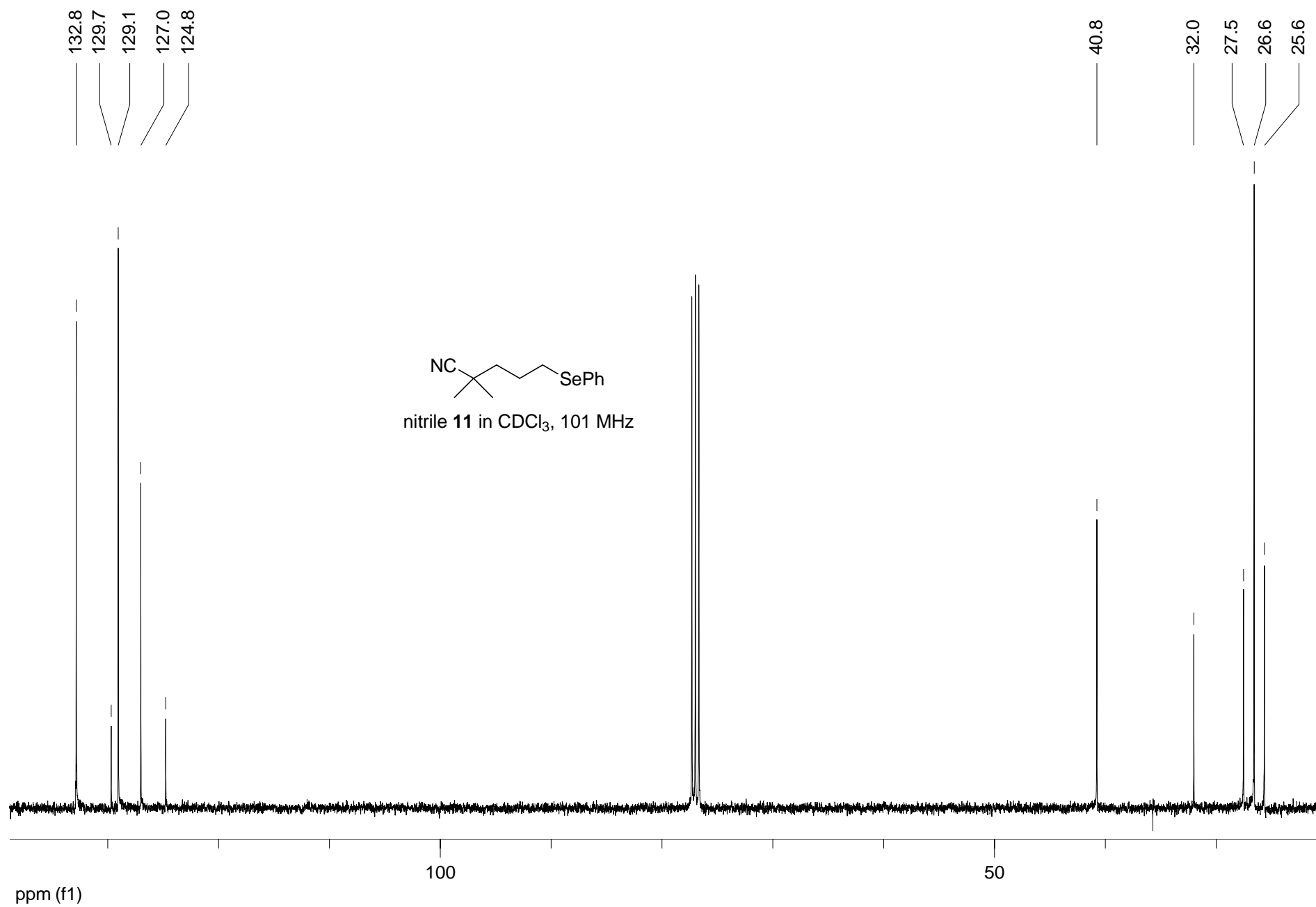


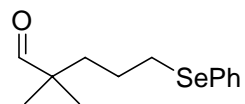




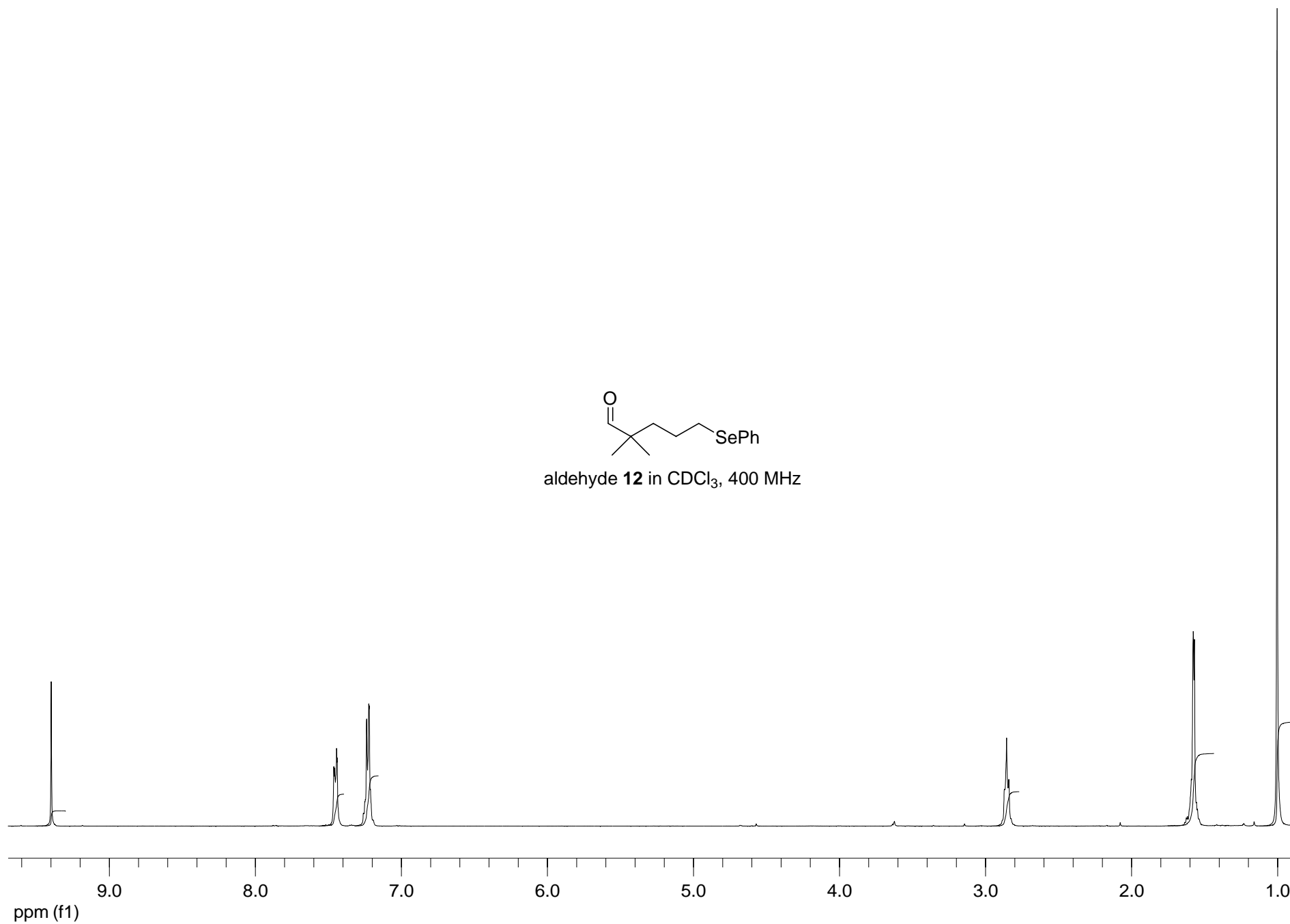


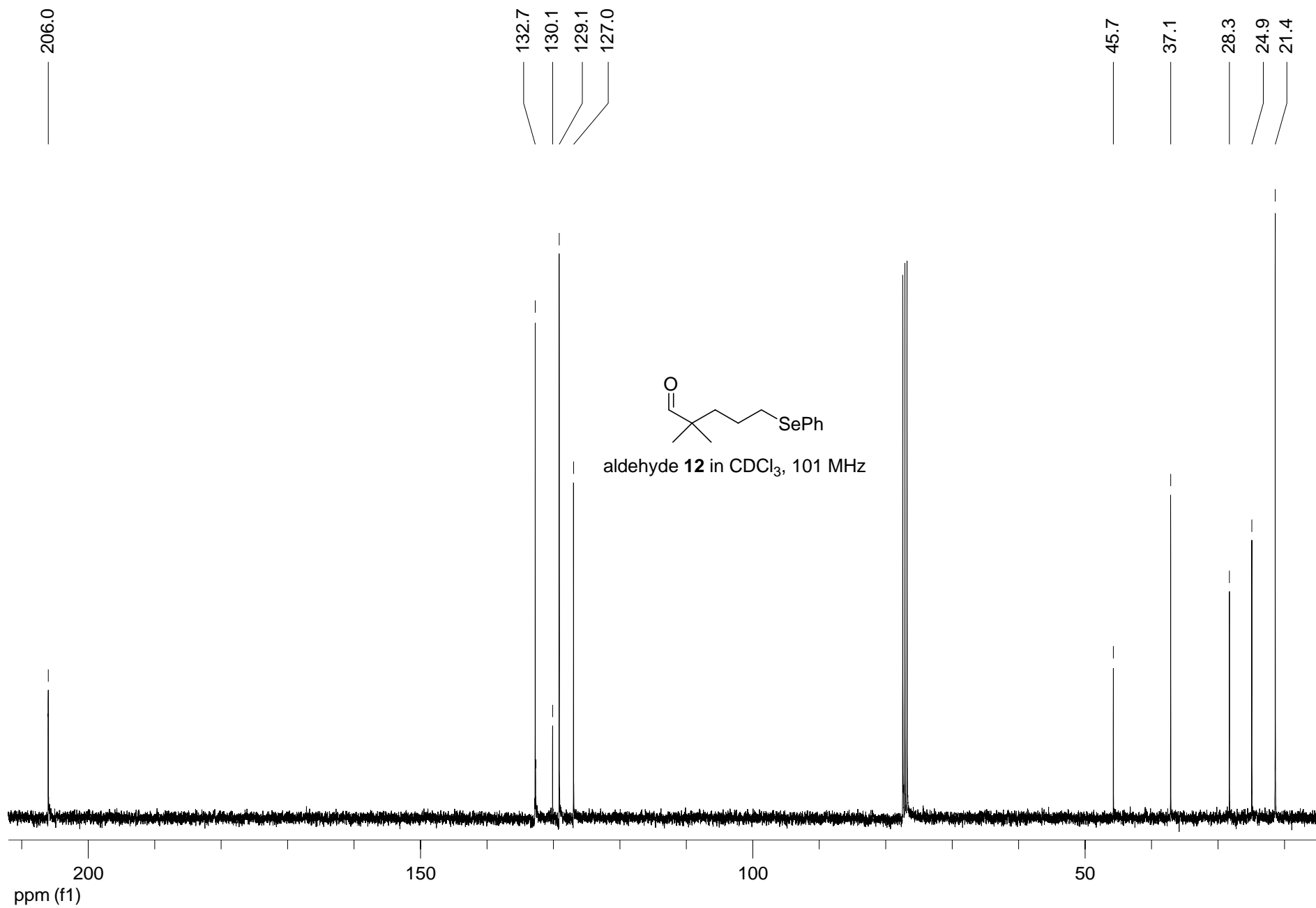


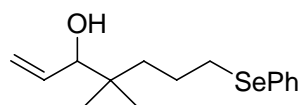




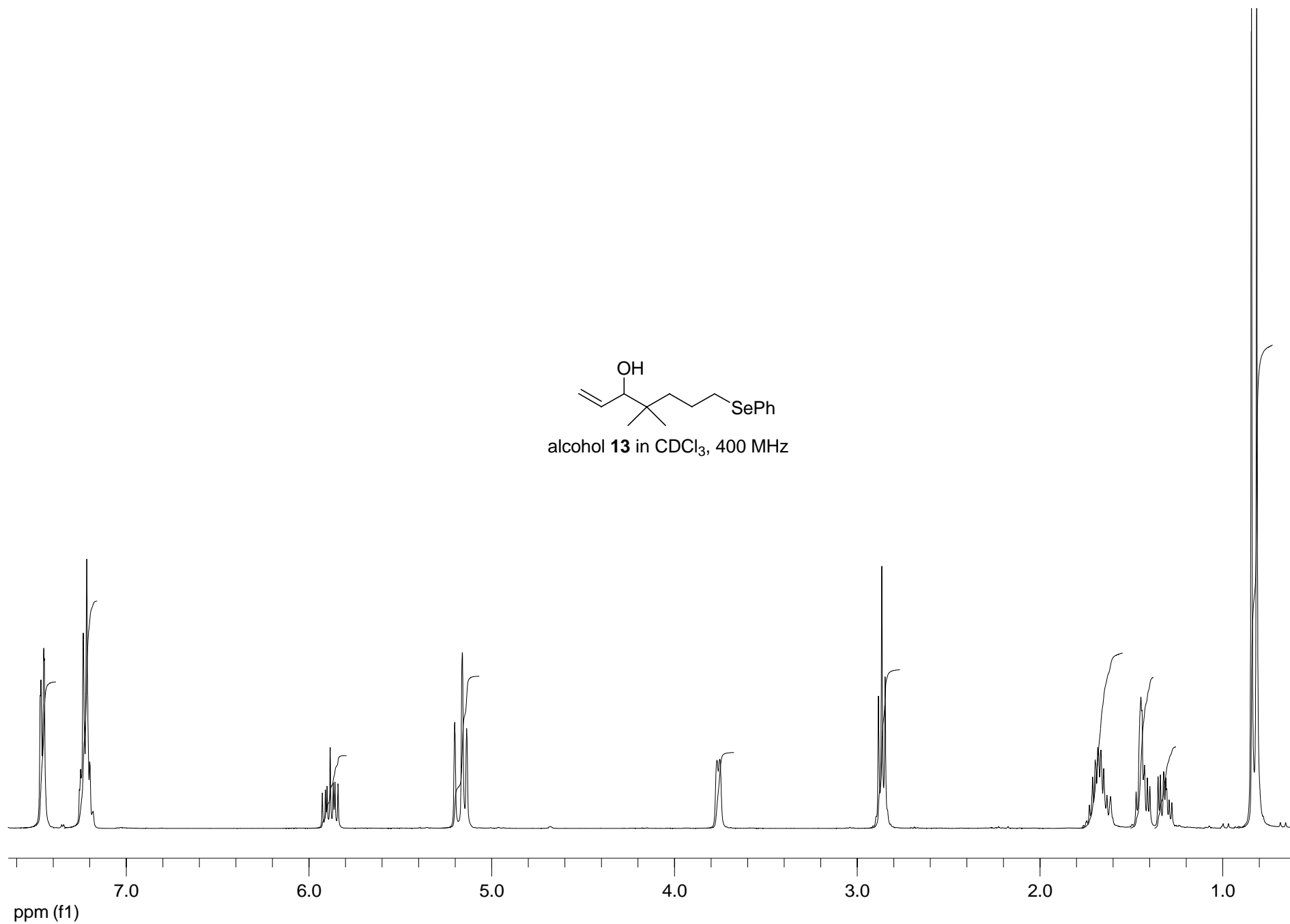
aldehyde **12** in CDCl₃, 400 MHz

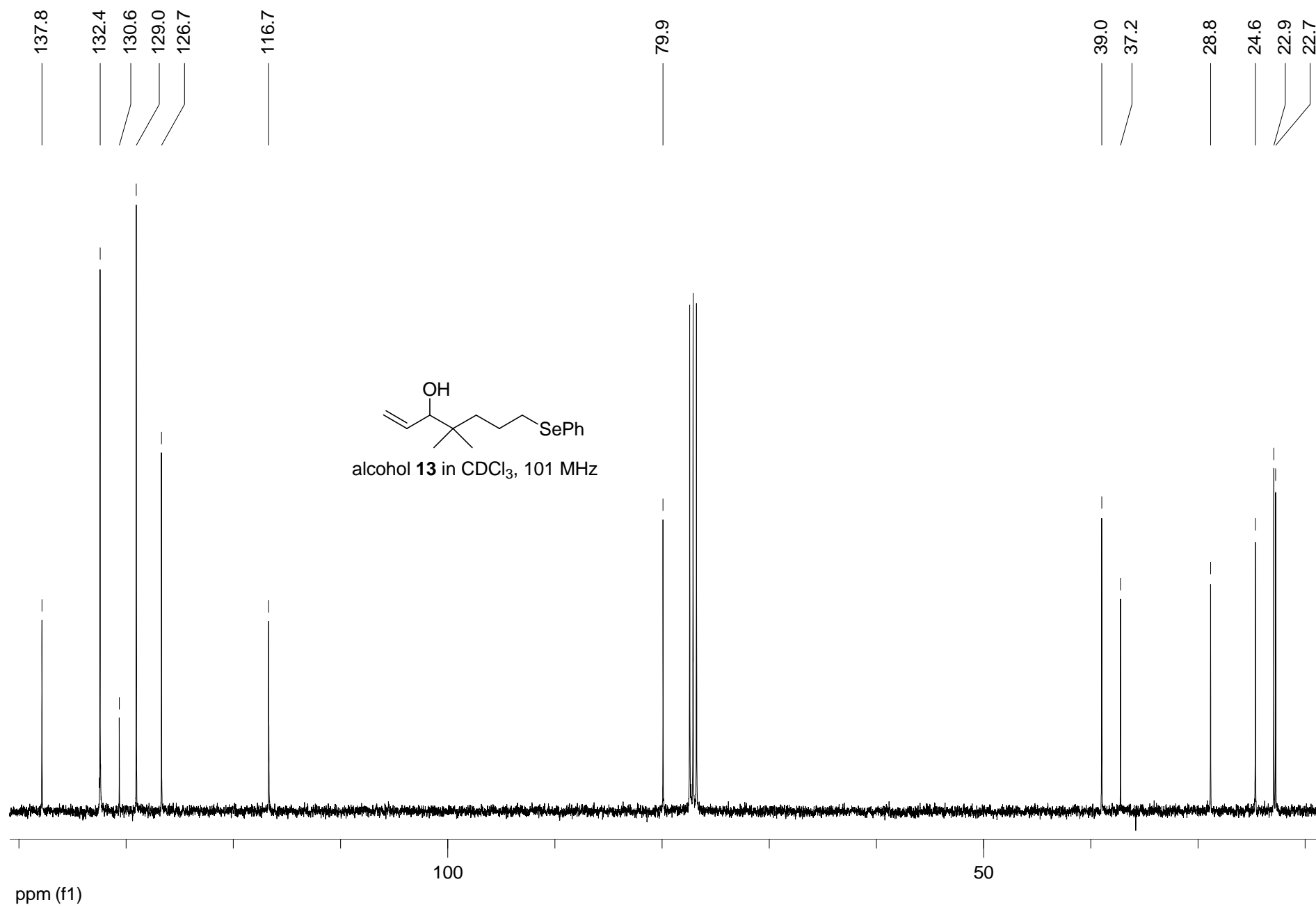


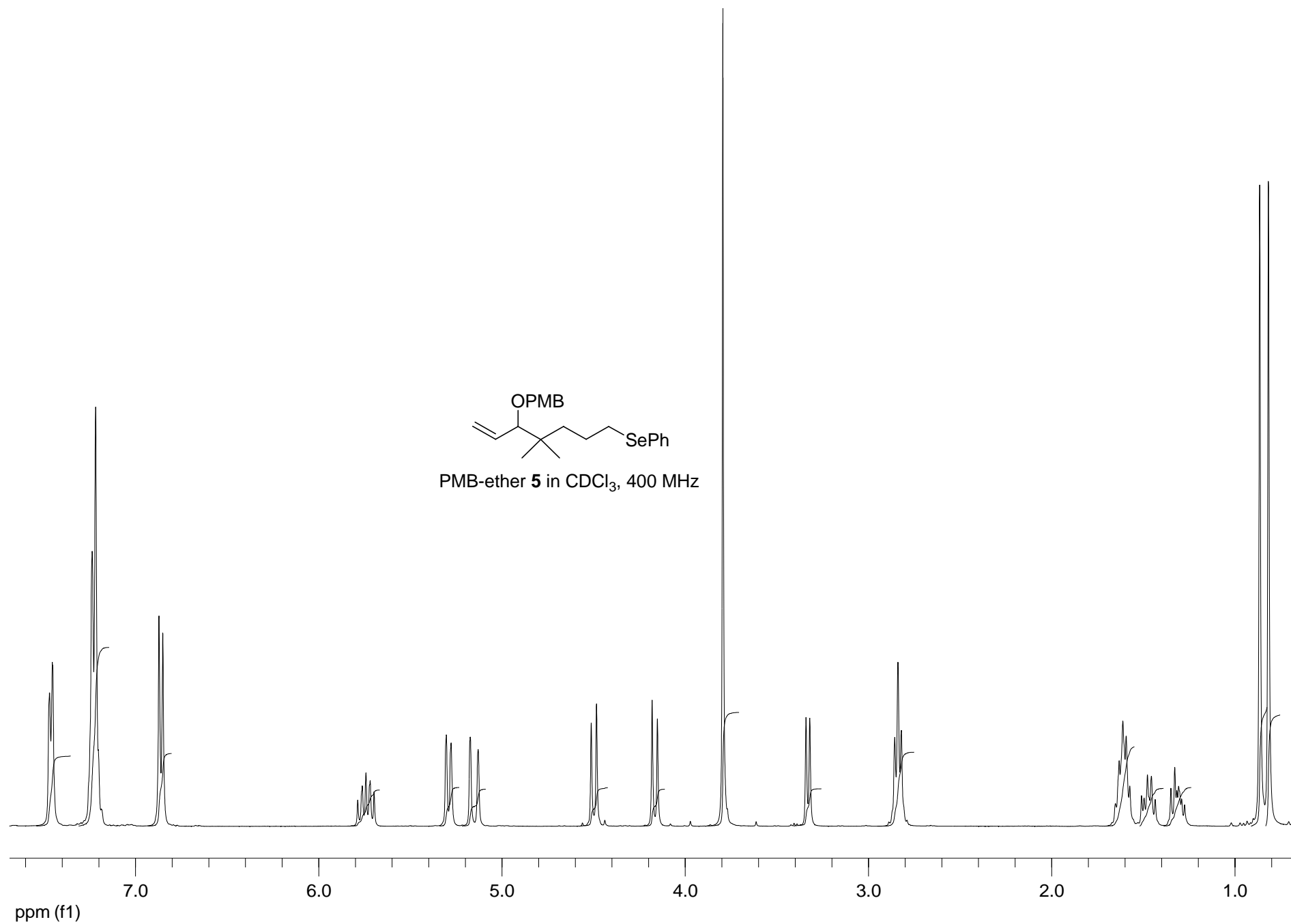




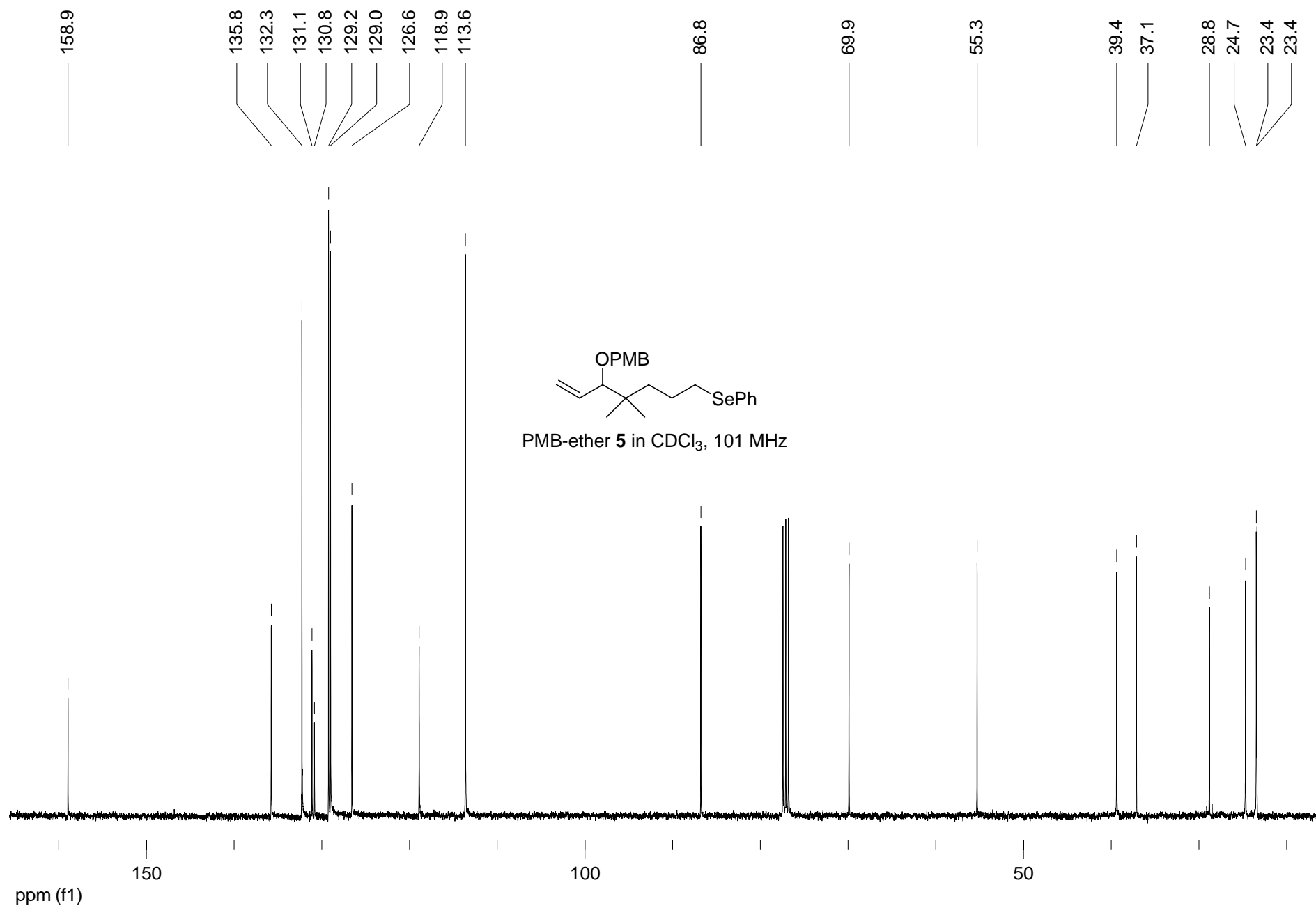
alcohol **13** in CDCl₃, 400 MHz

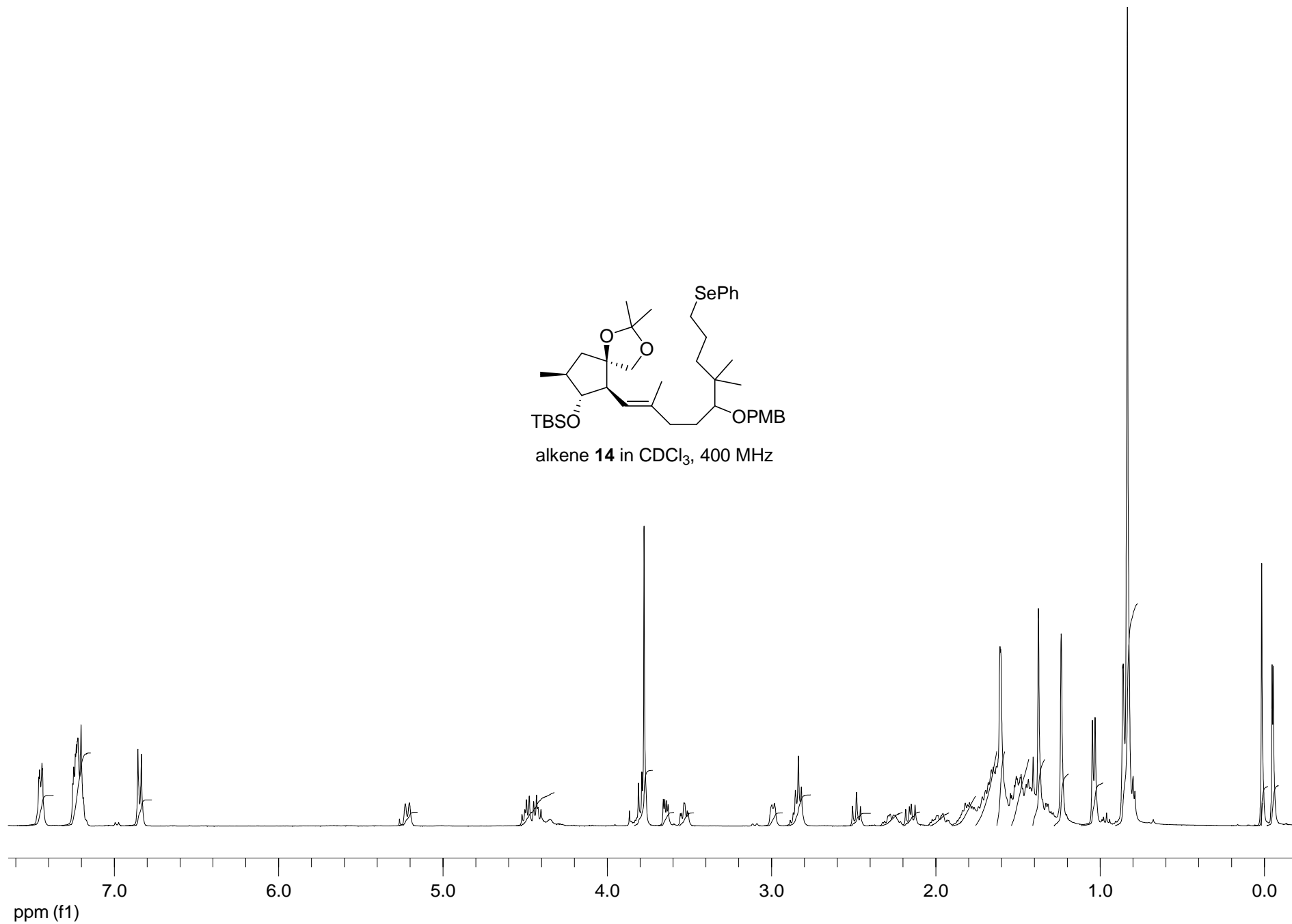
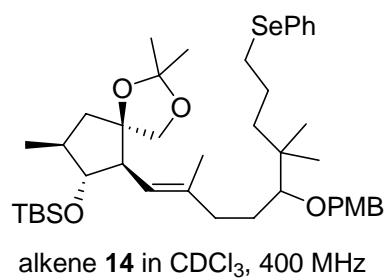




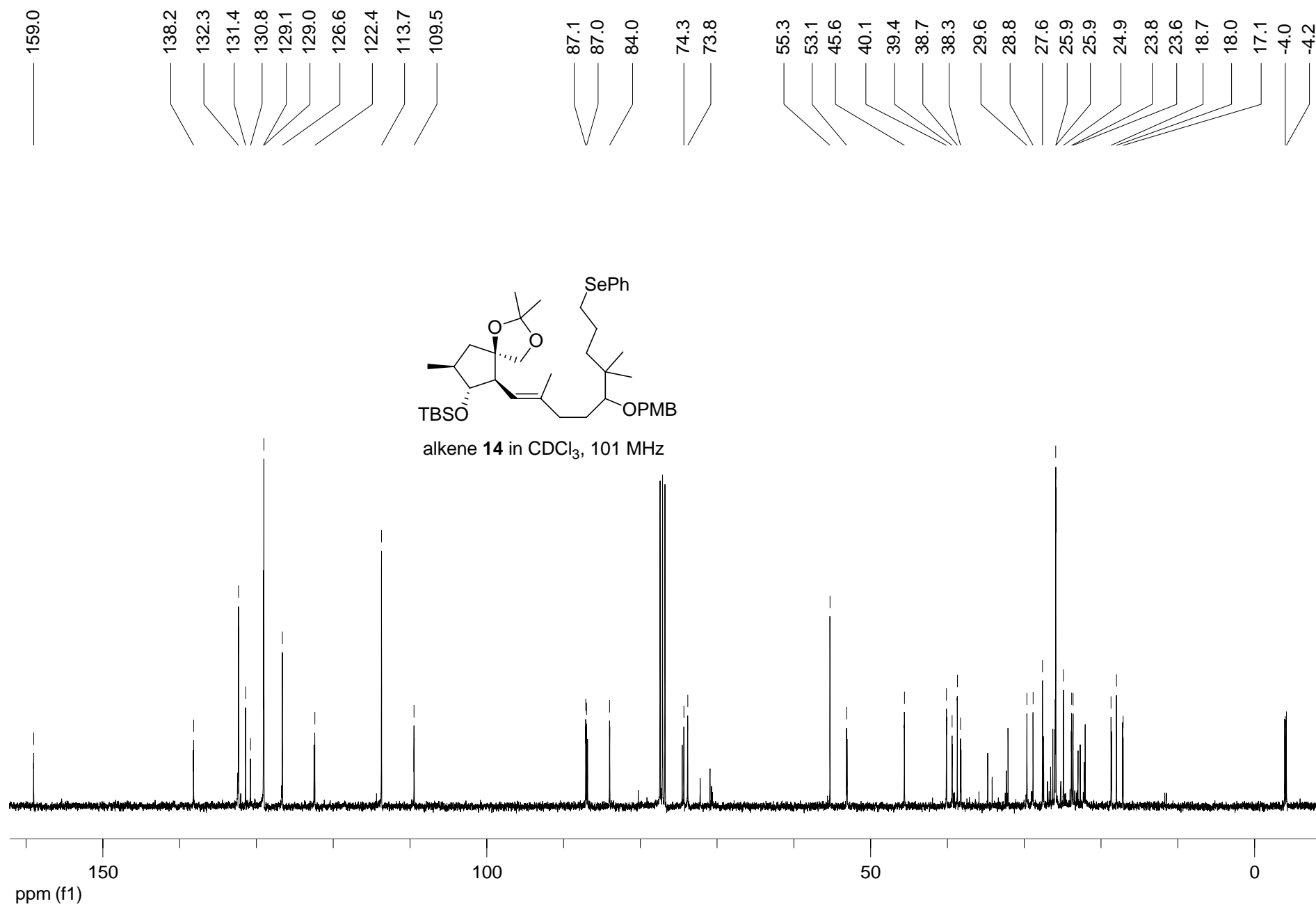


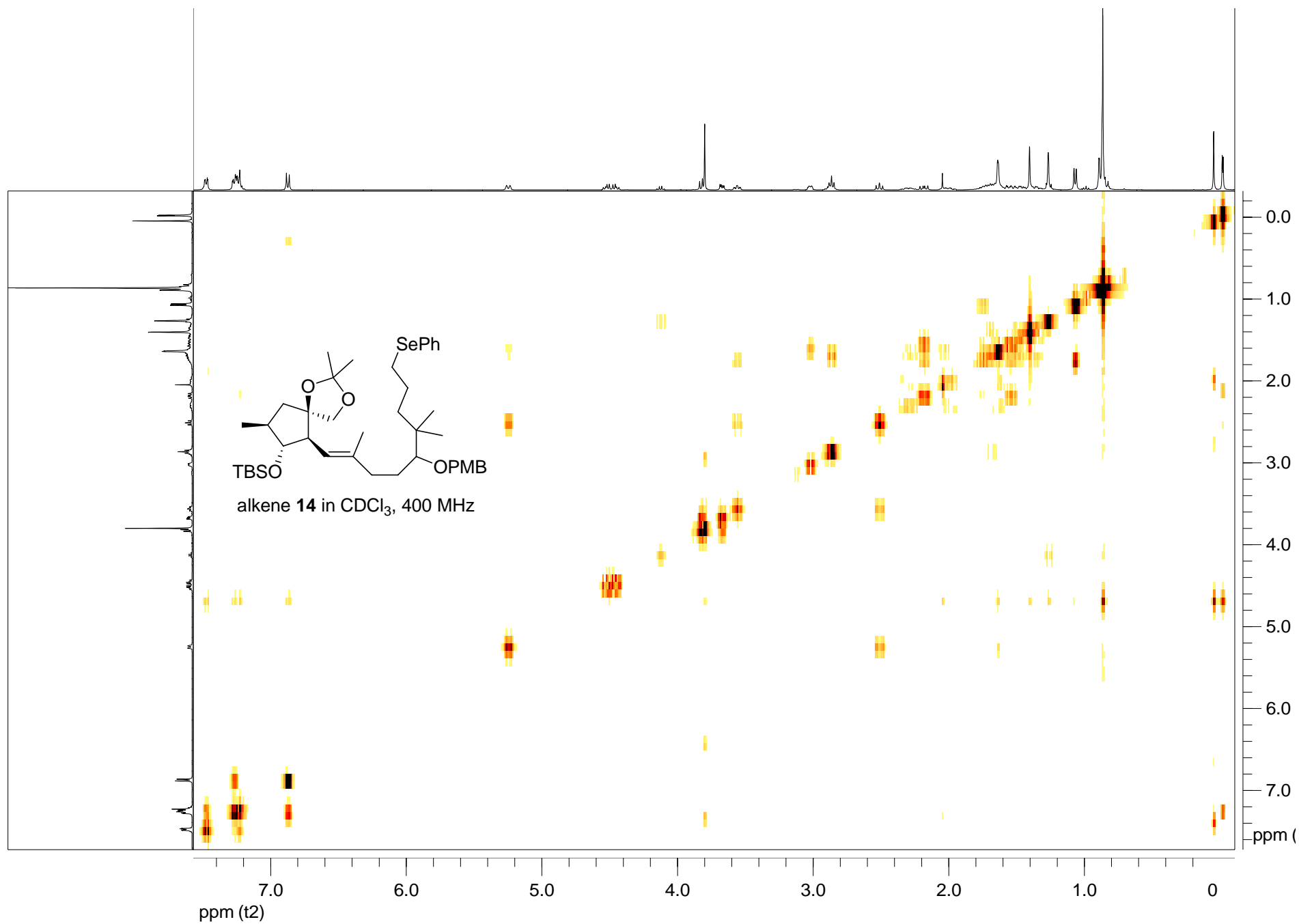
Total Synthesis of Jatropha Diterpenes from *Euphorbia characias* – Supporting Information

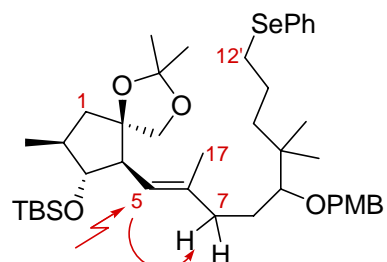




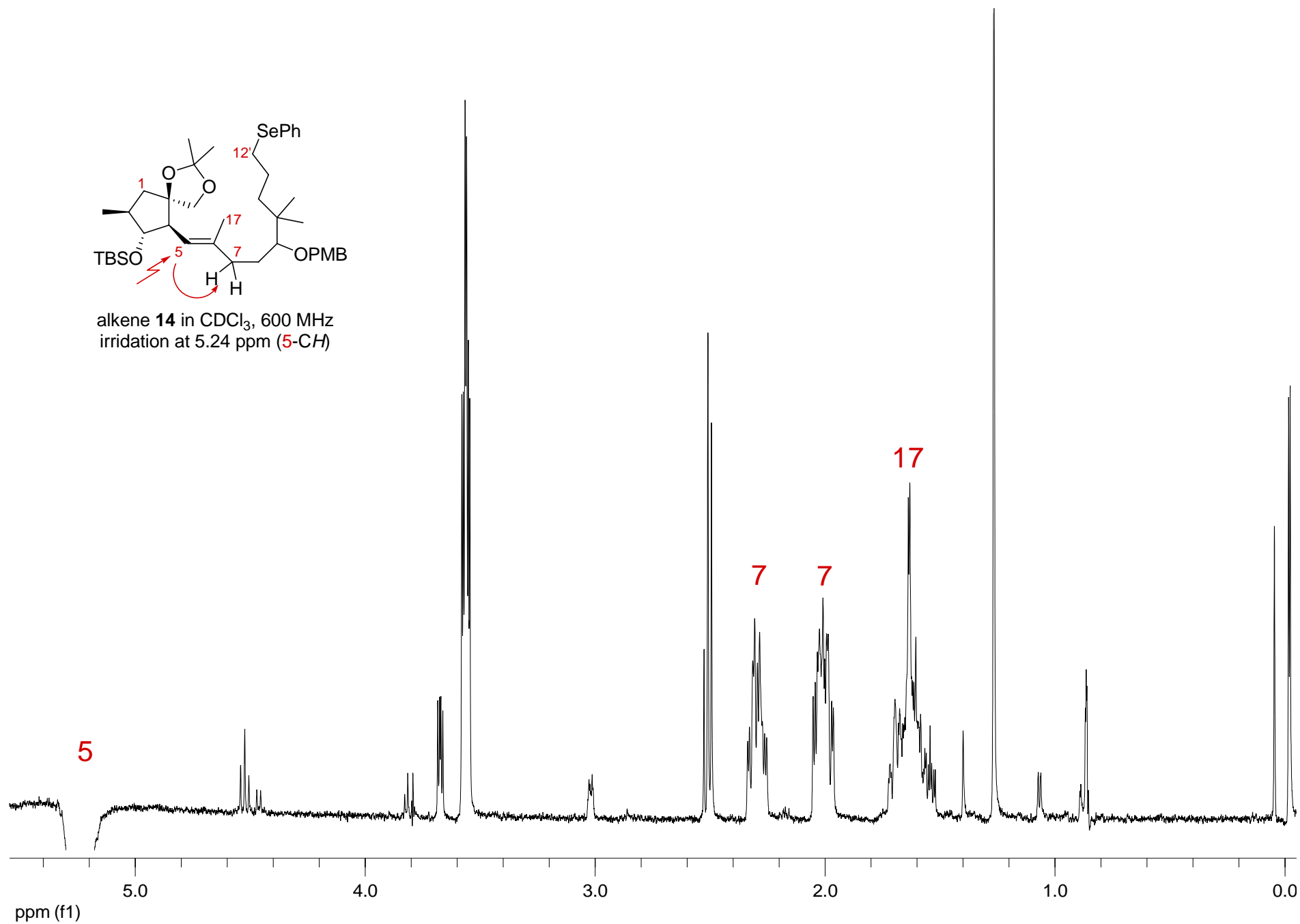
Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

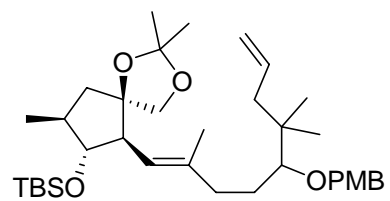




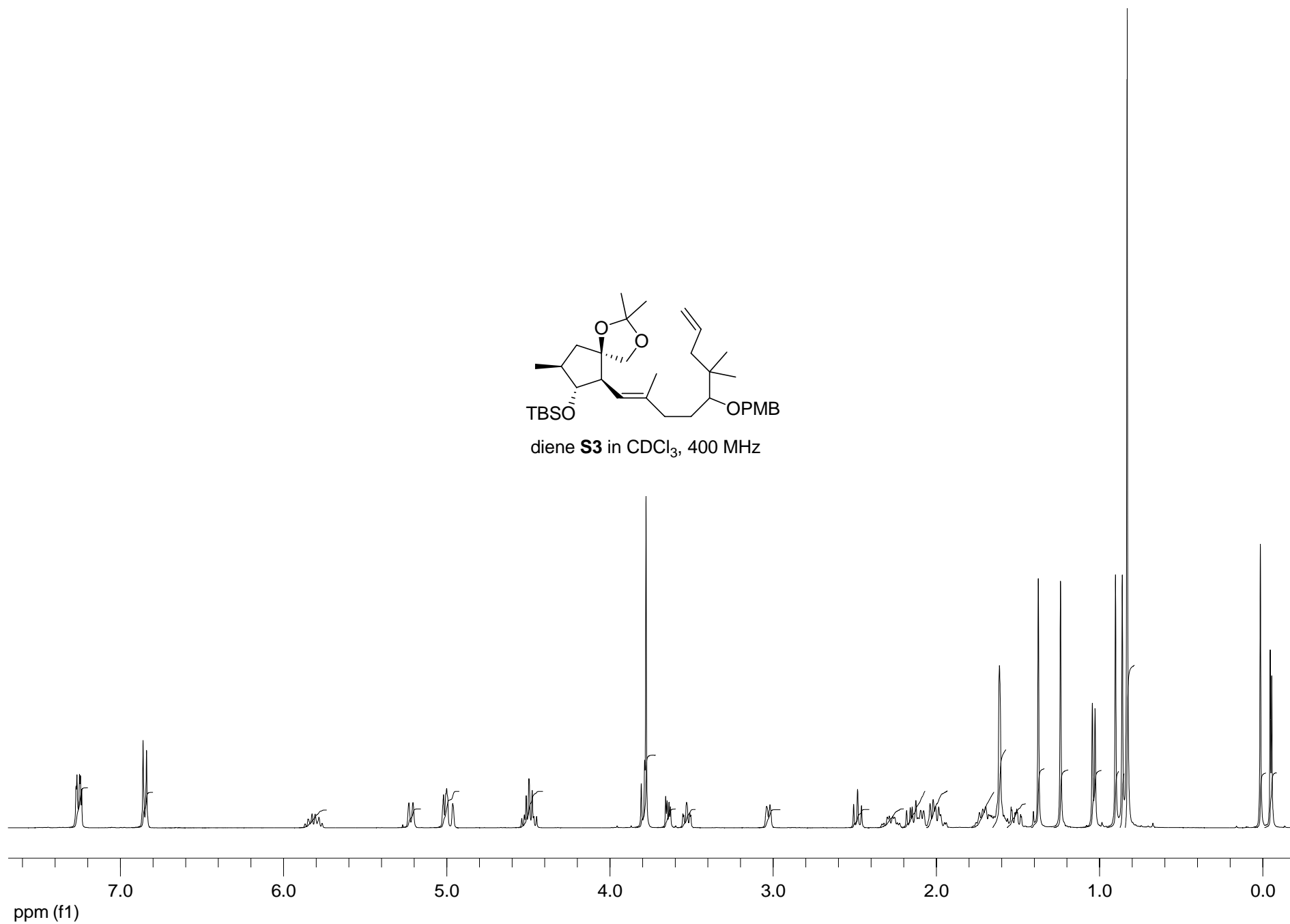


alkene **14** in CDCl₃, 600 MHz
irradiation at 5.24 ppm (5-CH)

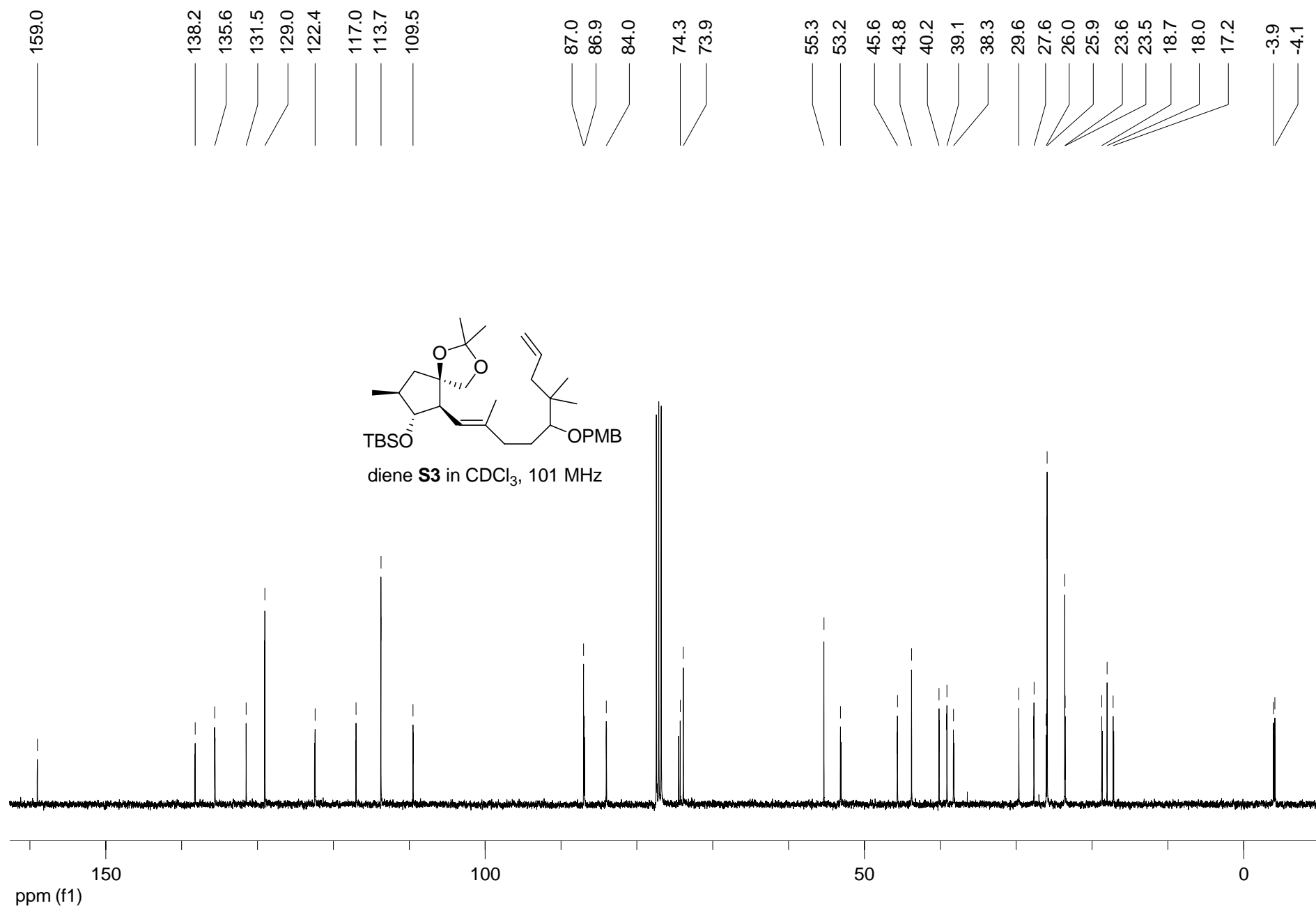


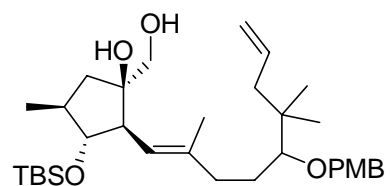


diene **S3** in CDCl₃, 400 MHz

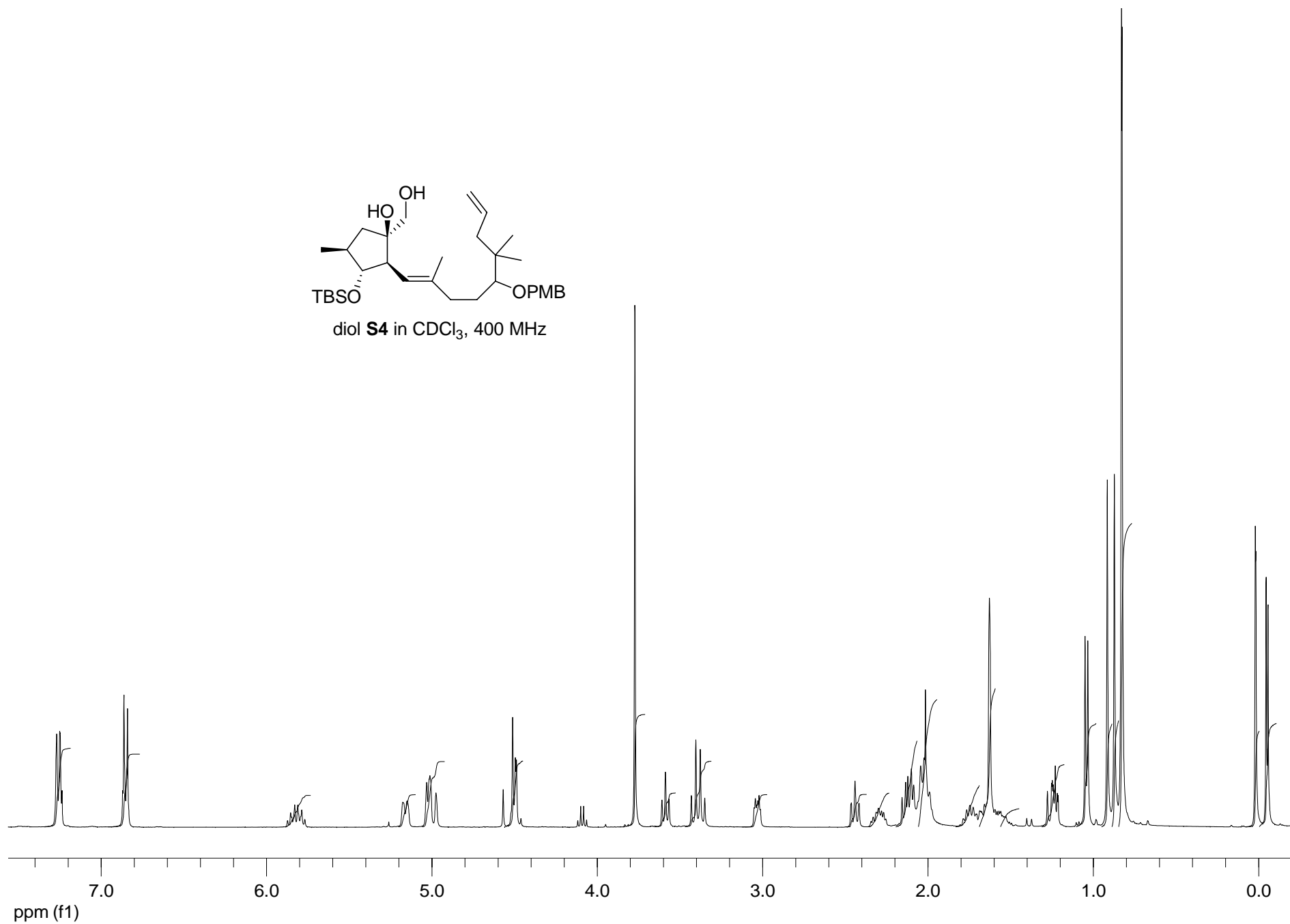


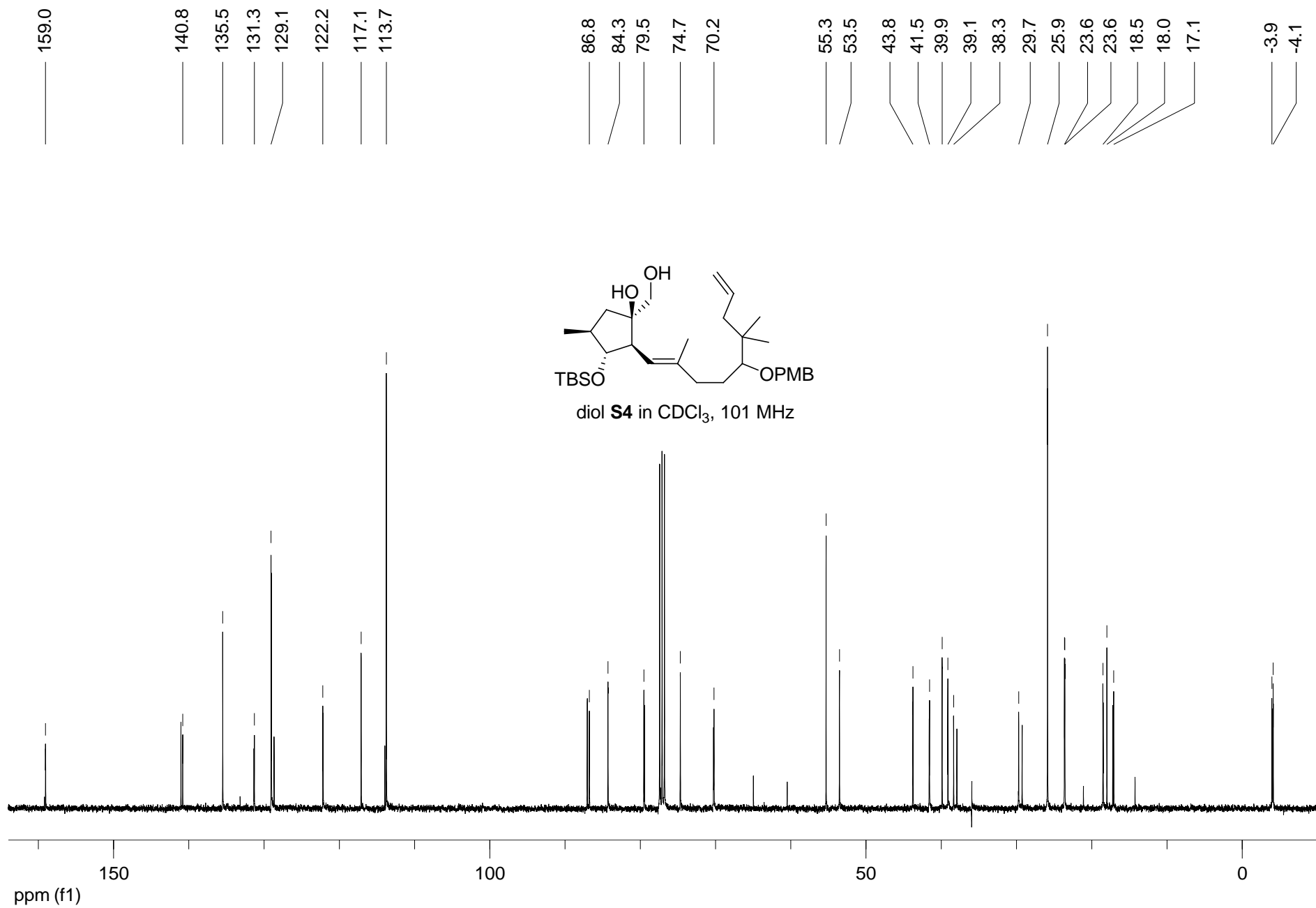
Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

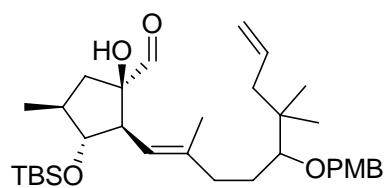




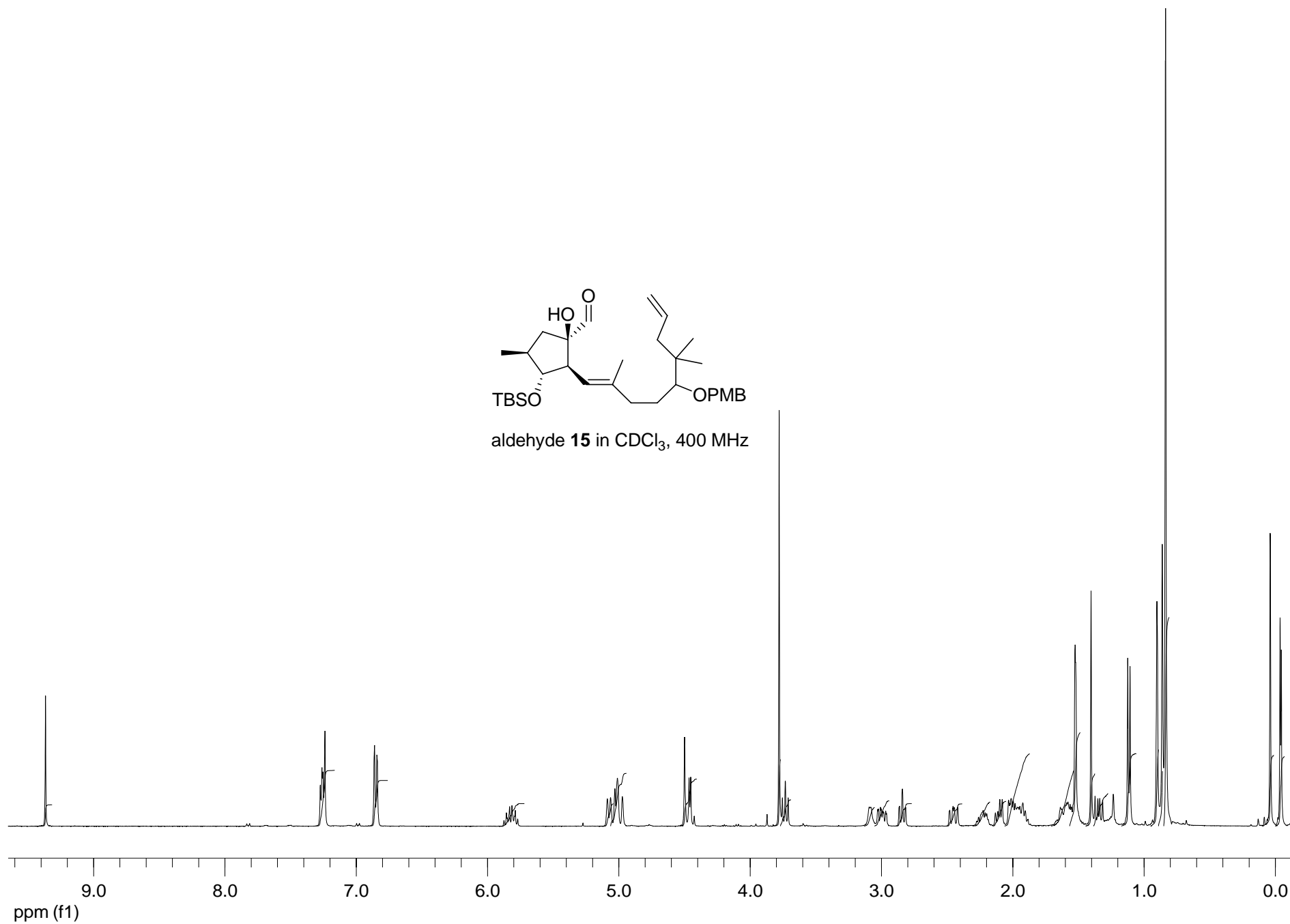
diol **S4** in CDCl₃, 400 MHz

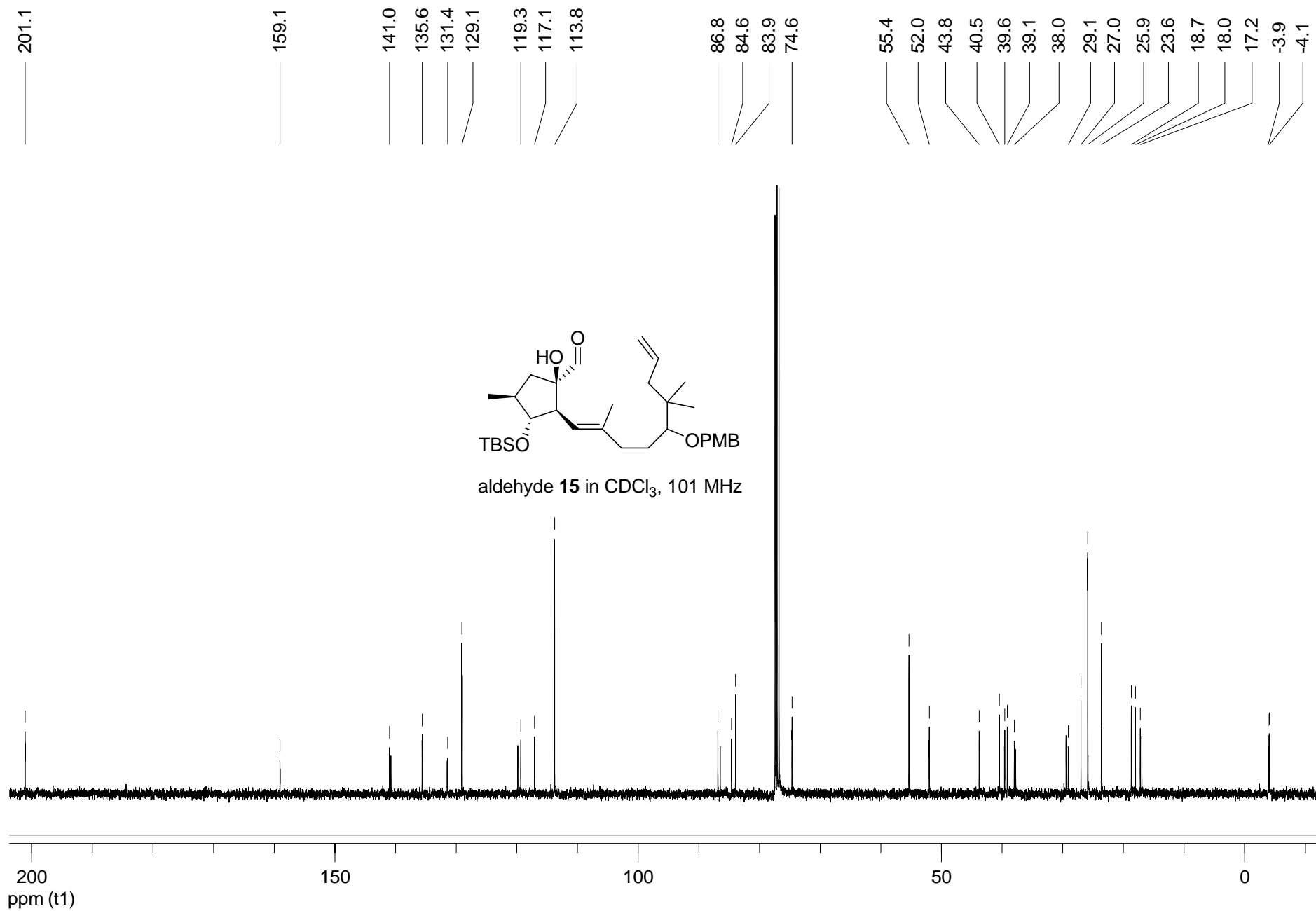


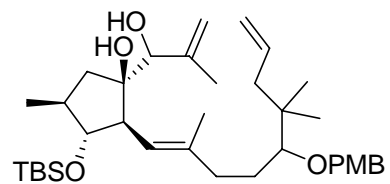
Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information



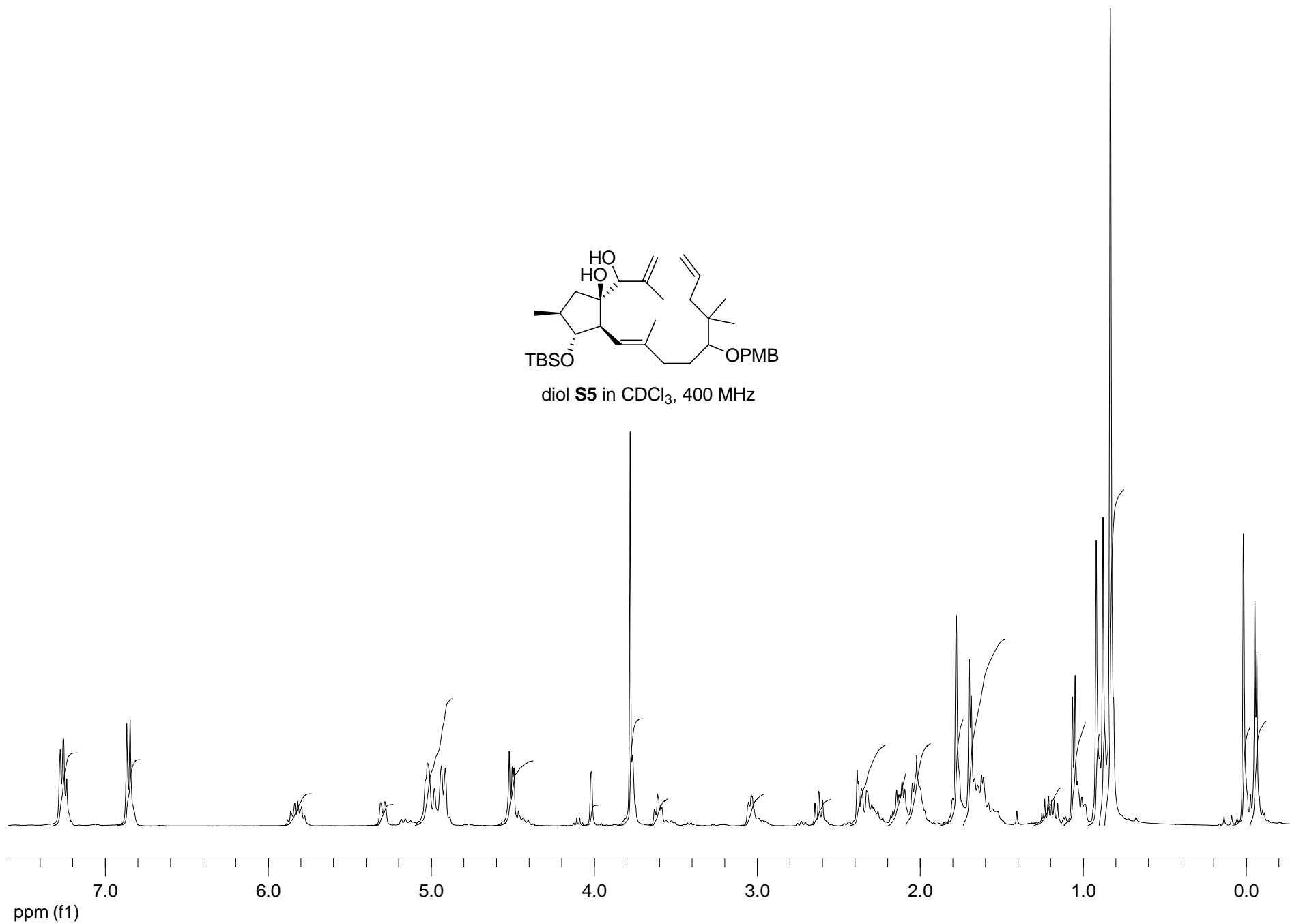
aldehyde **15** in CDCl₃, 400 MHz



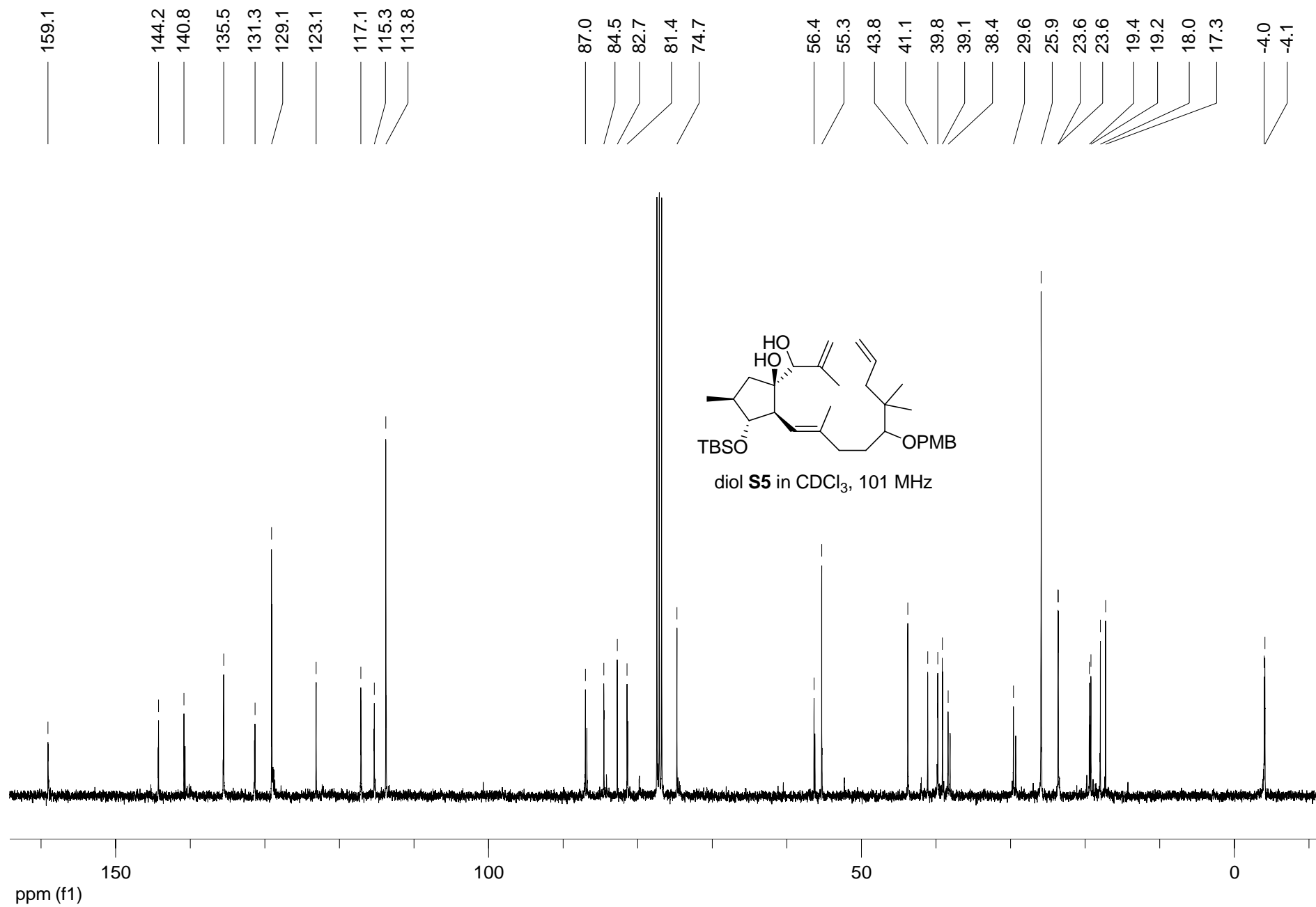


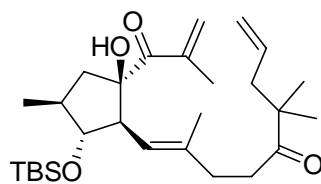


diol **S5** in CDCl₃, 400 MHz

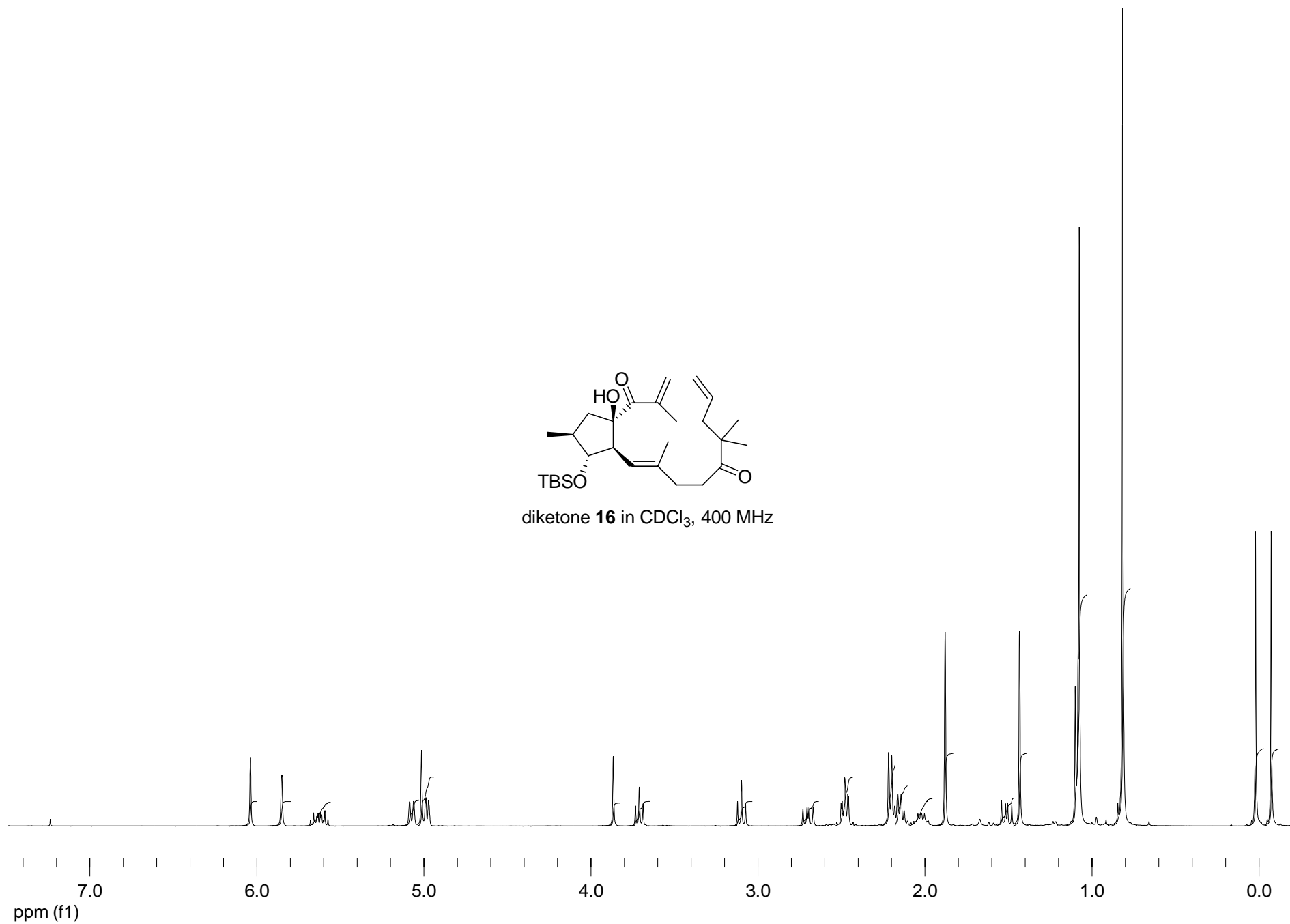


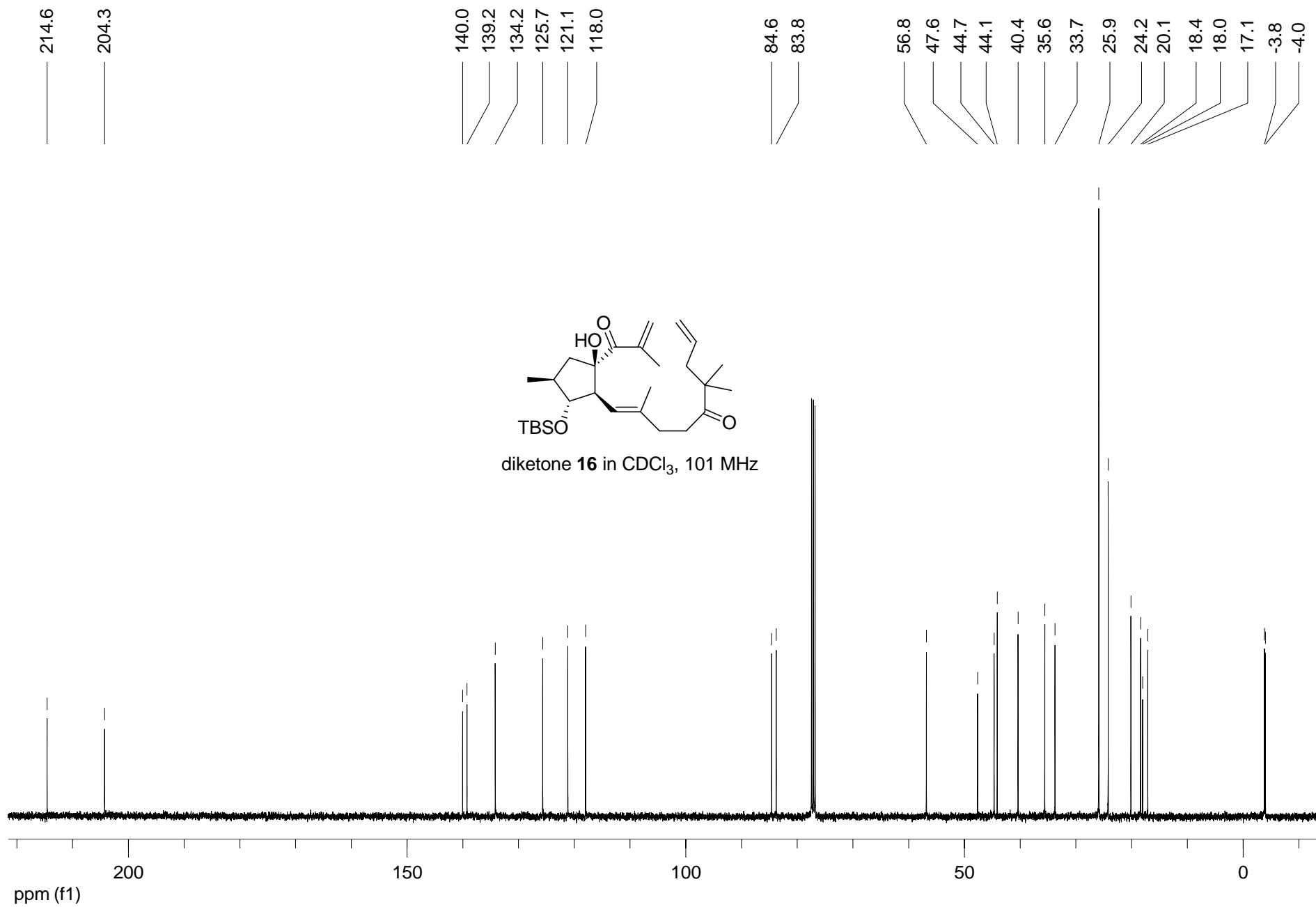
Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

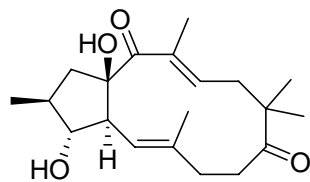
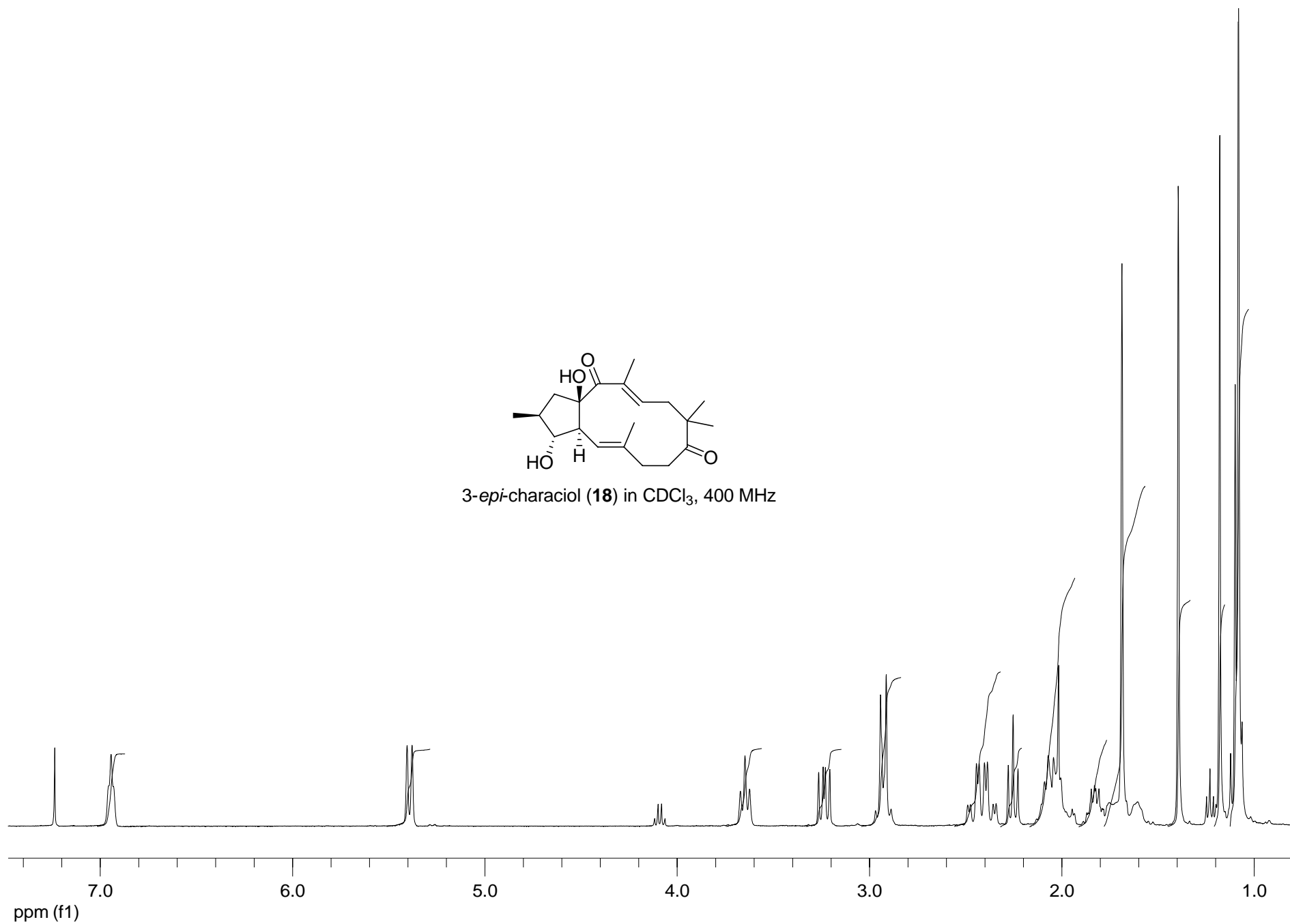


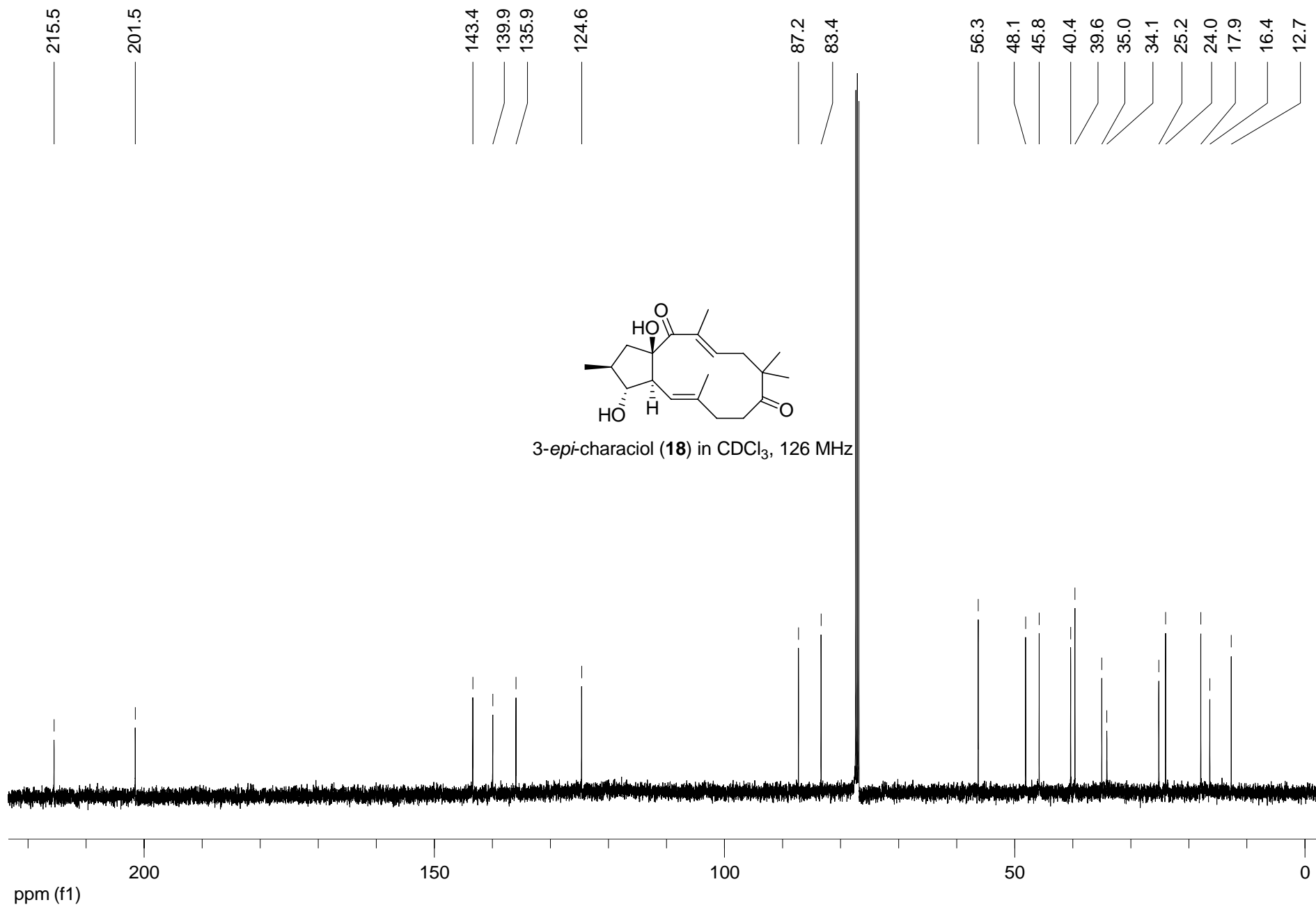


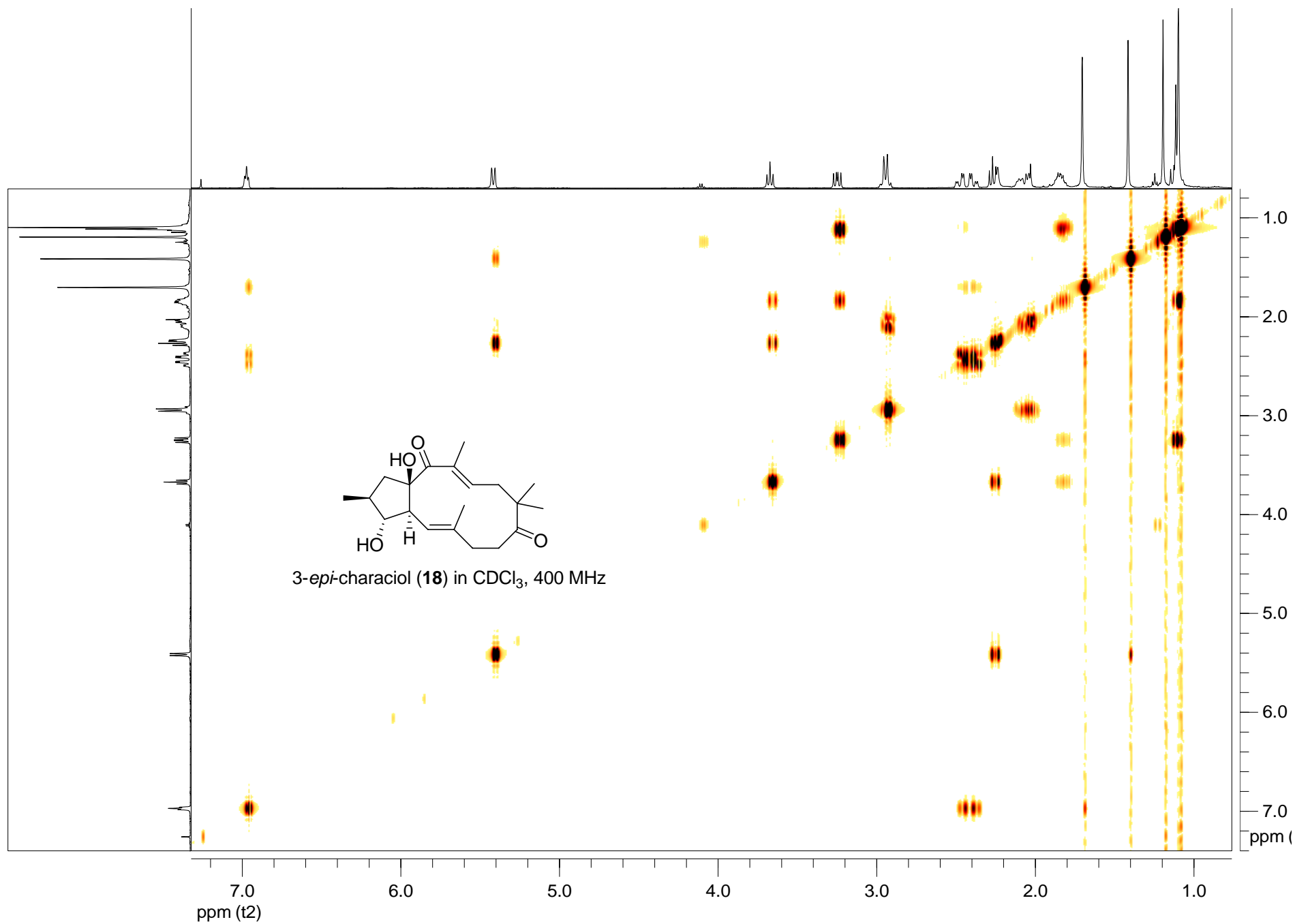
diketone **16** in CDCl₃, 400 MHz

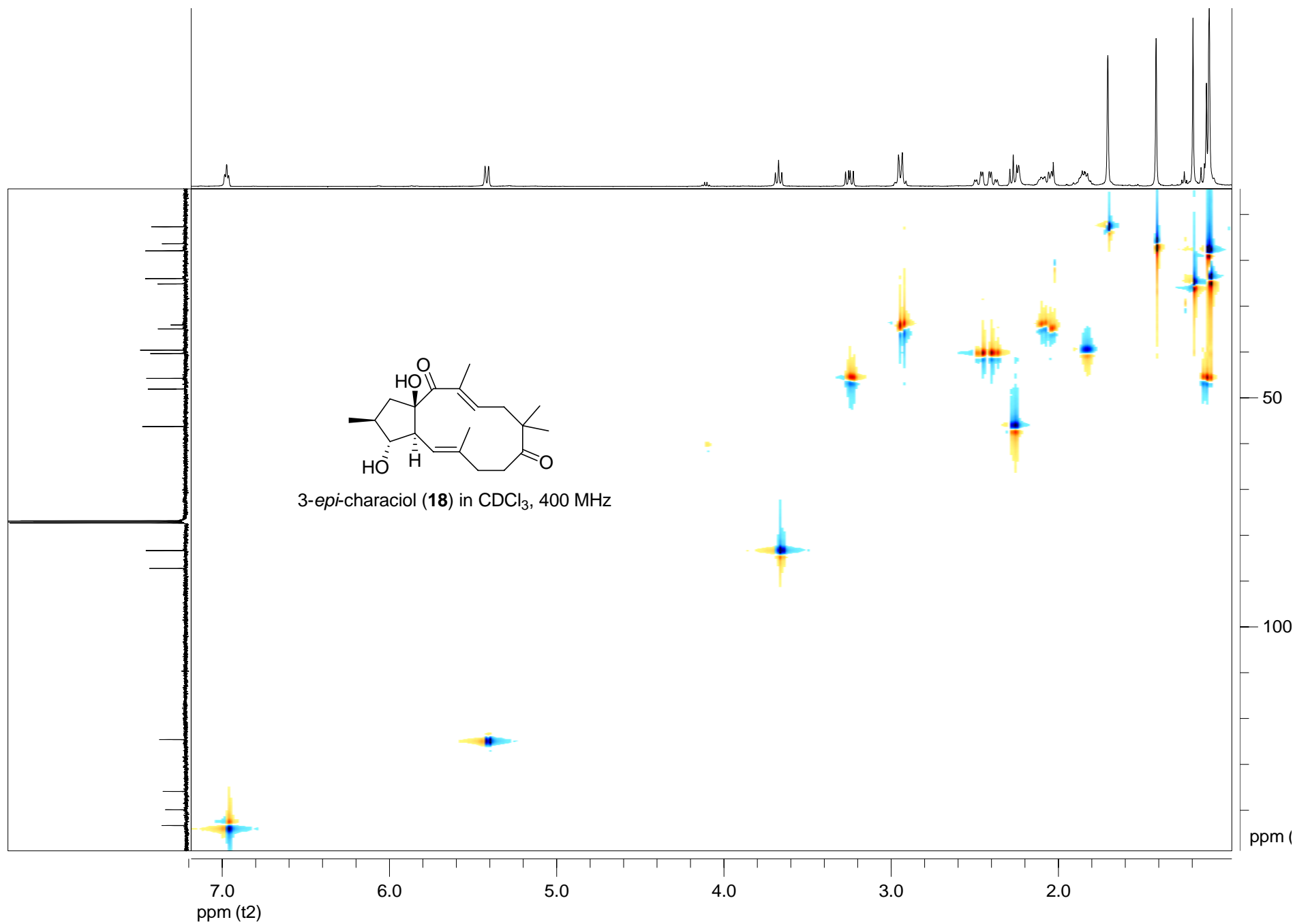


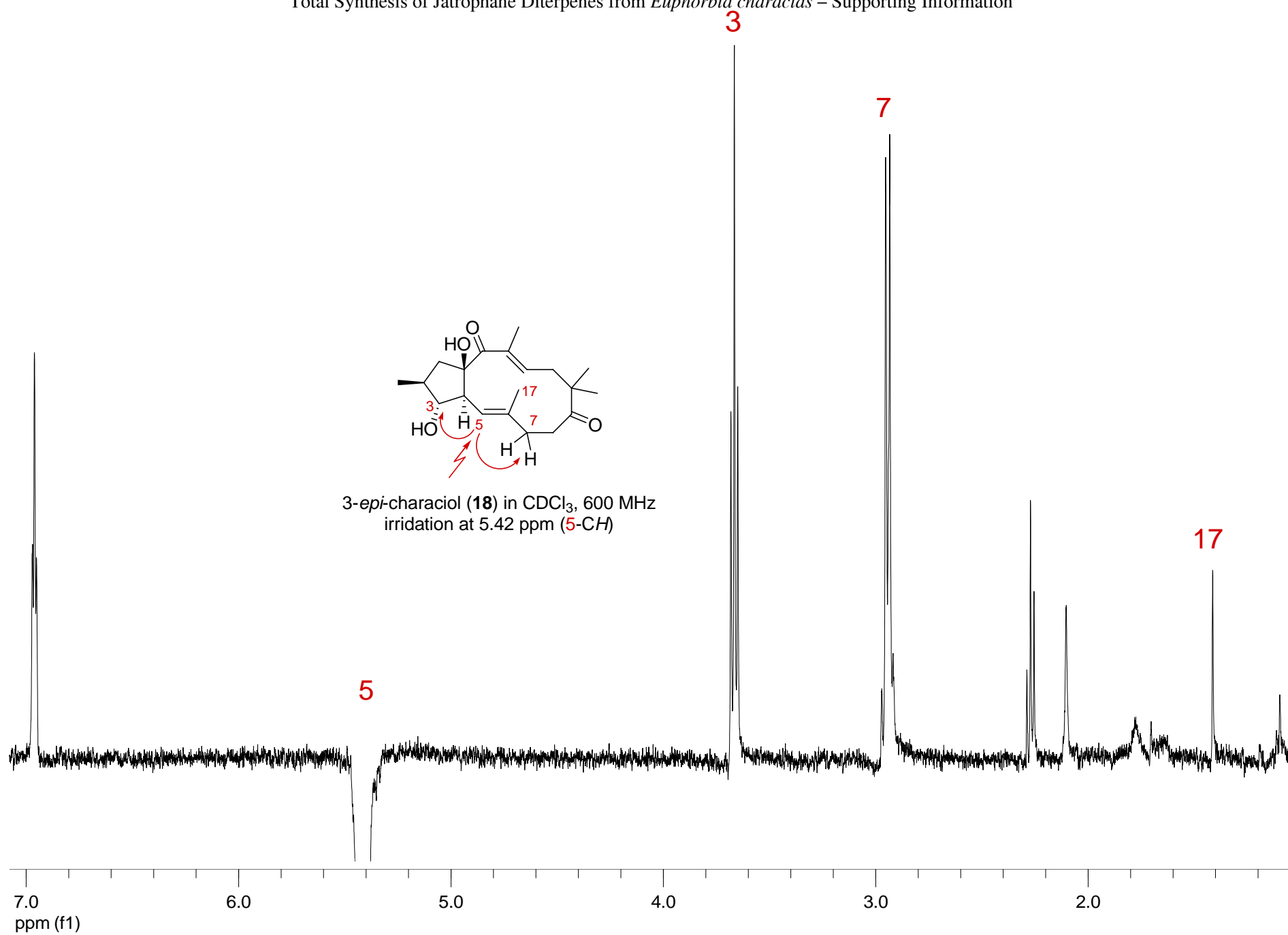


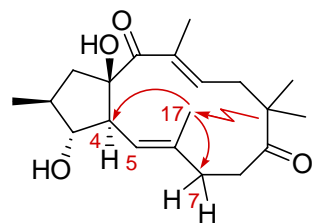
3-*epi*-characiol (**18**) in CDCl₃, 400 MHz



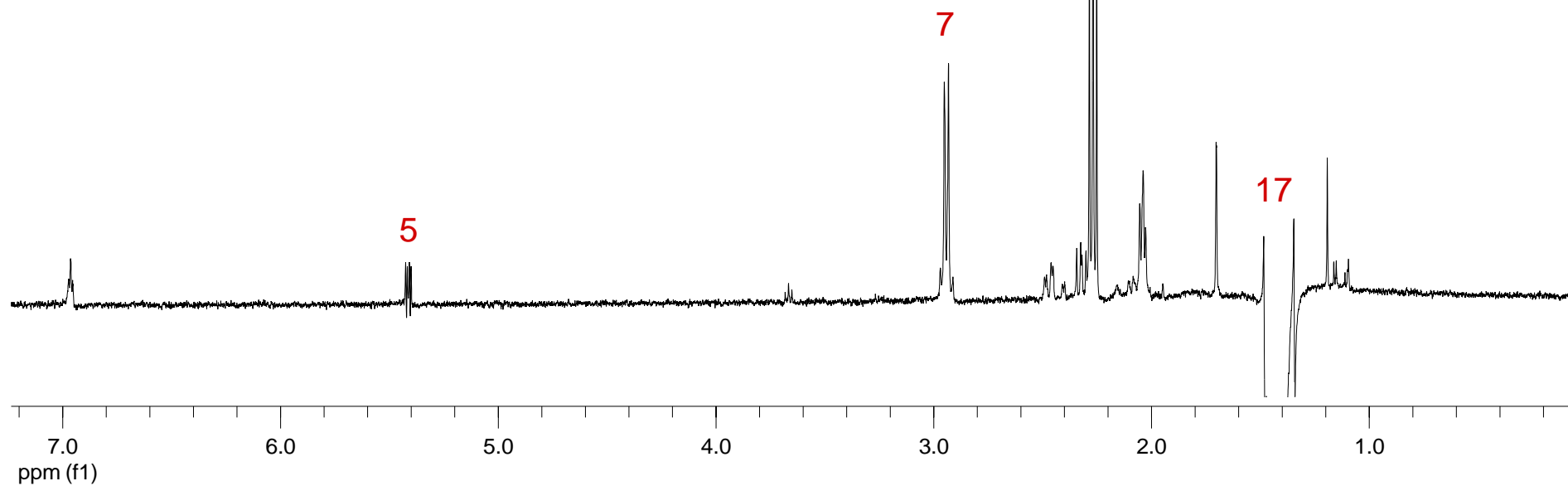


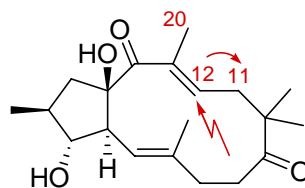




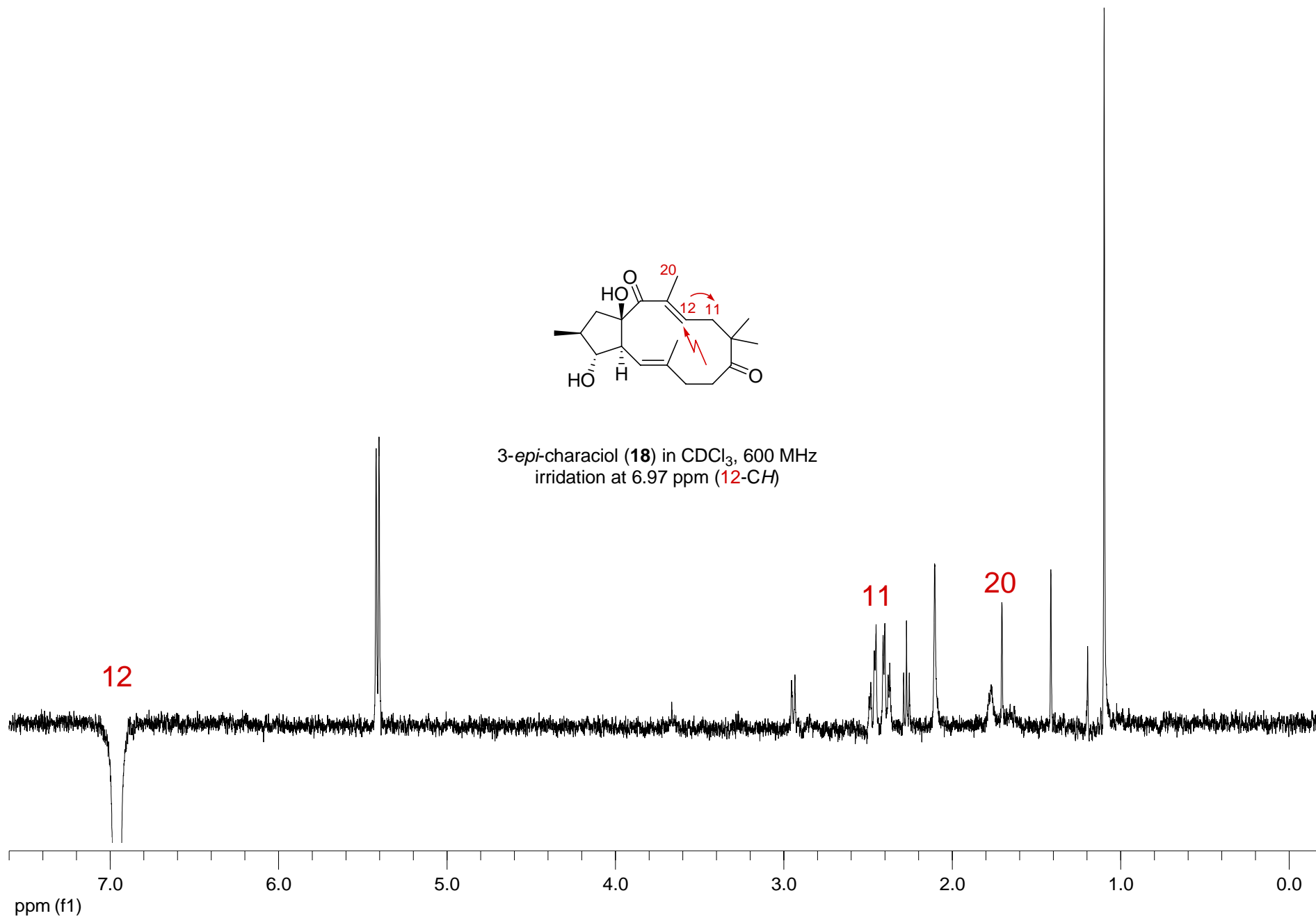


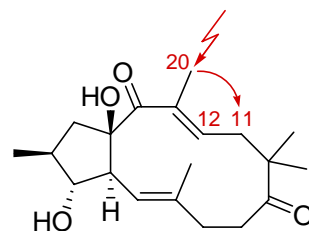
3-*epi*-characiol (**18**) in CDCl₃, 600 MHz
irradiation at 1.42 ppm (**17**-CH₃)



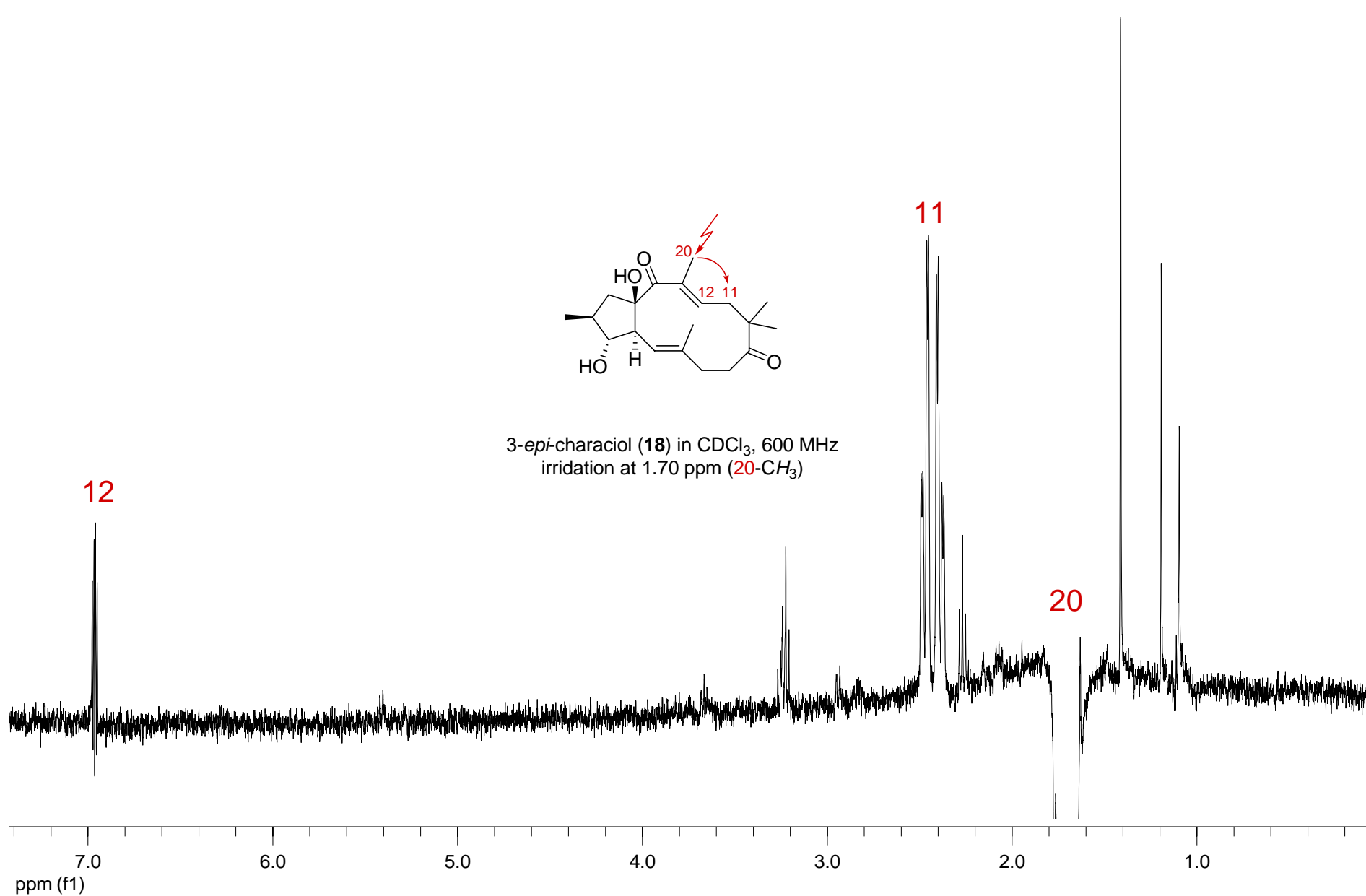


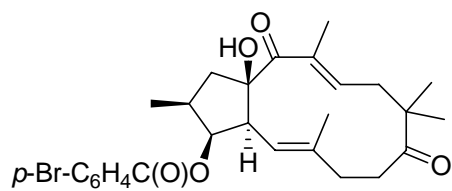
3-*epi*-characiol (**18**) in CDCl₃, 600 MHz
irradiation at 6.97 ppm (**12-CH**)



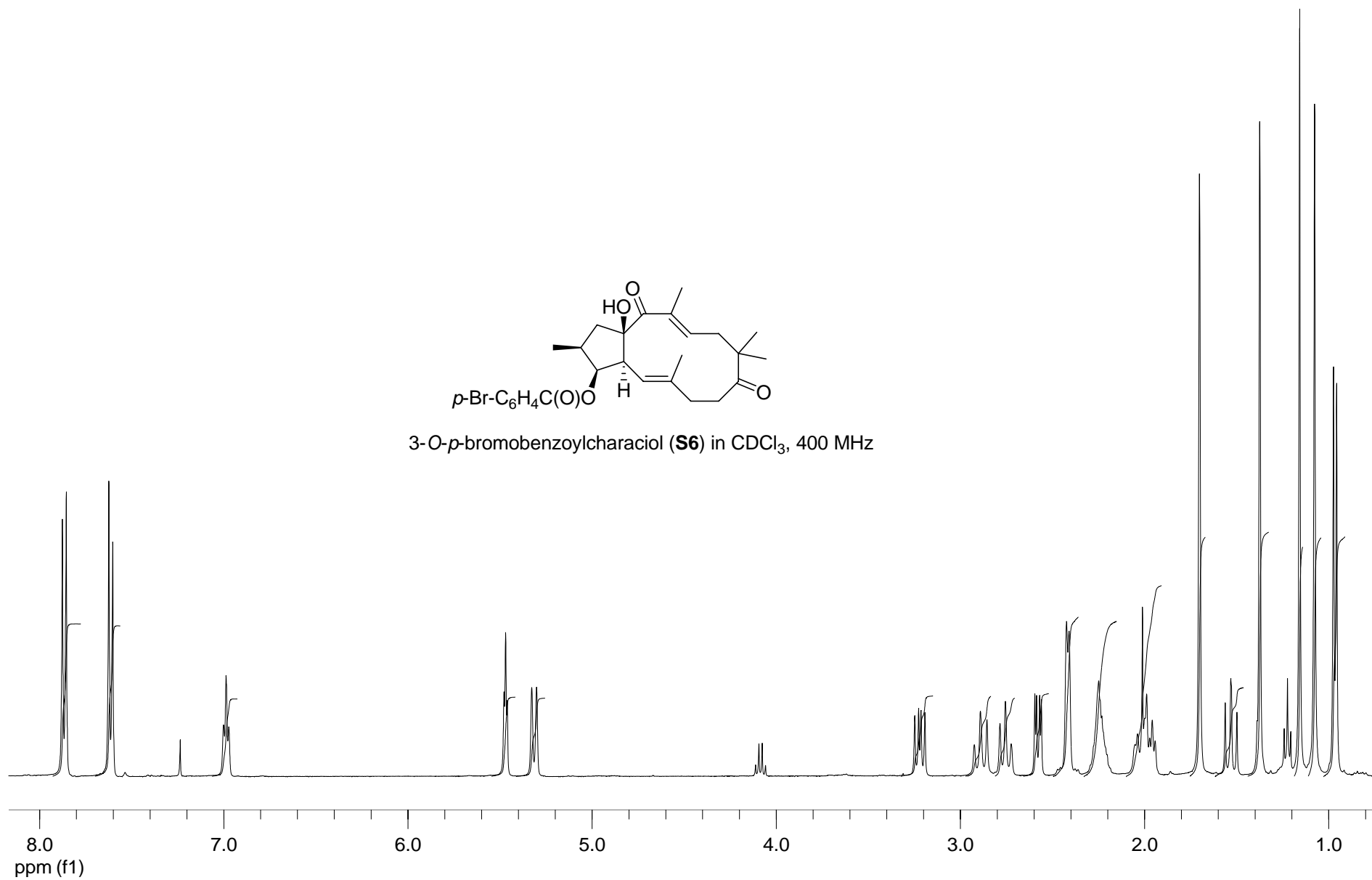


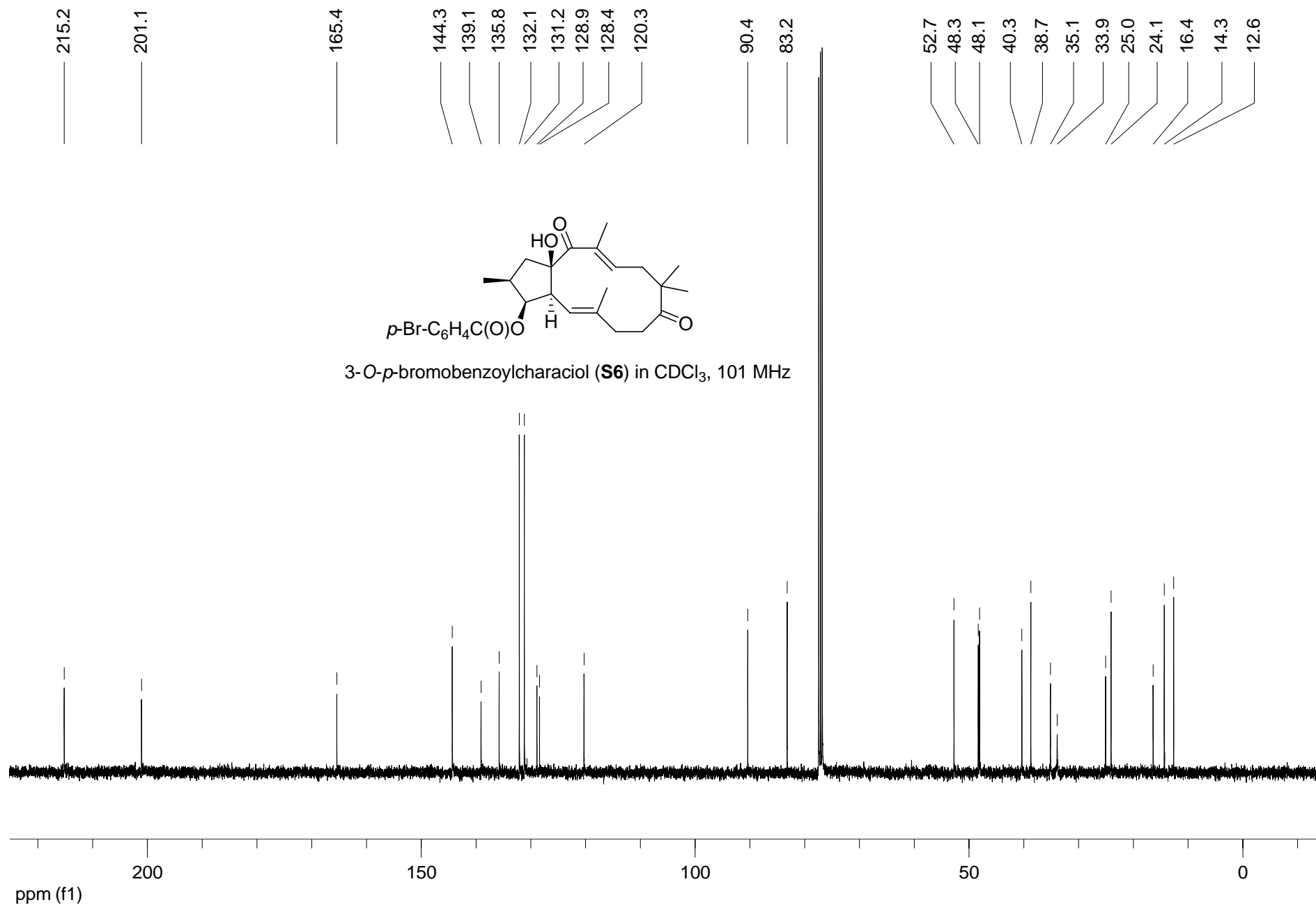
3-*epi*-characiol (**18**) in CDCl₃, 600 MHz
irradiation at 1.70 ppm (**20**-CH₃)

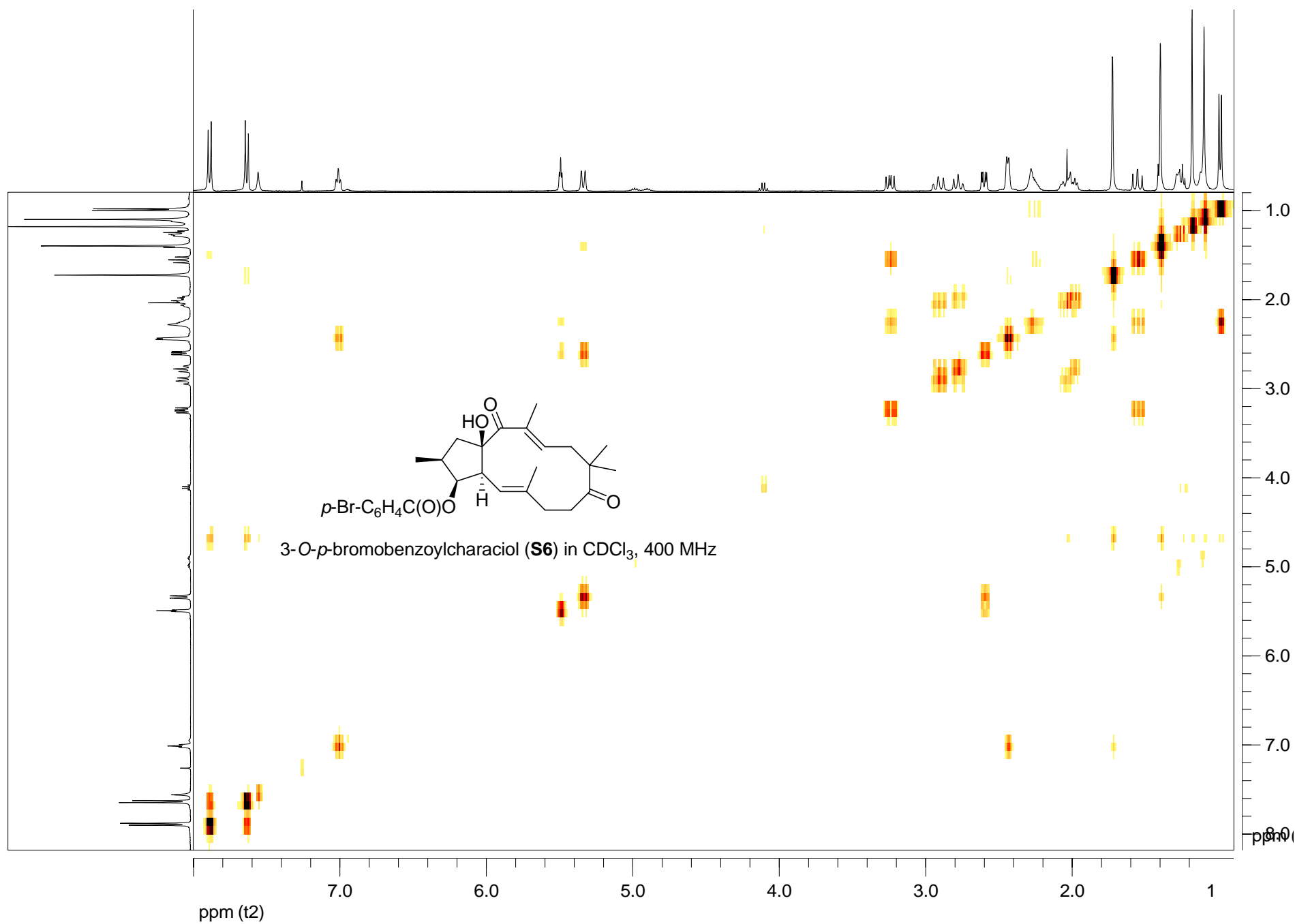


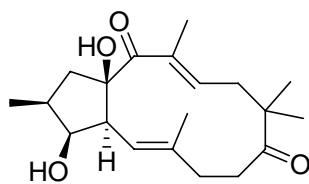


3-*O*-*p*-bromobenzoylcharaciol (**S6**) in CDCl₃, 400 MHz

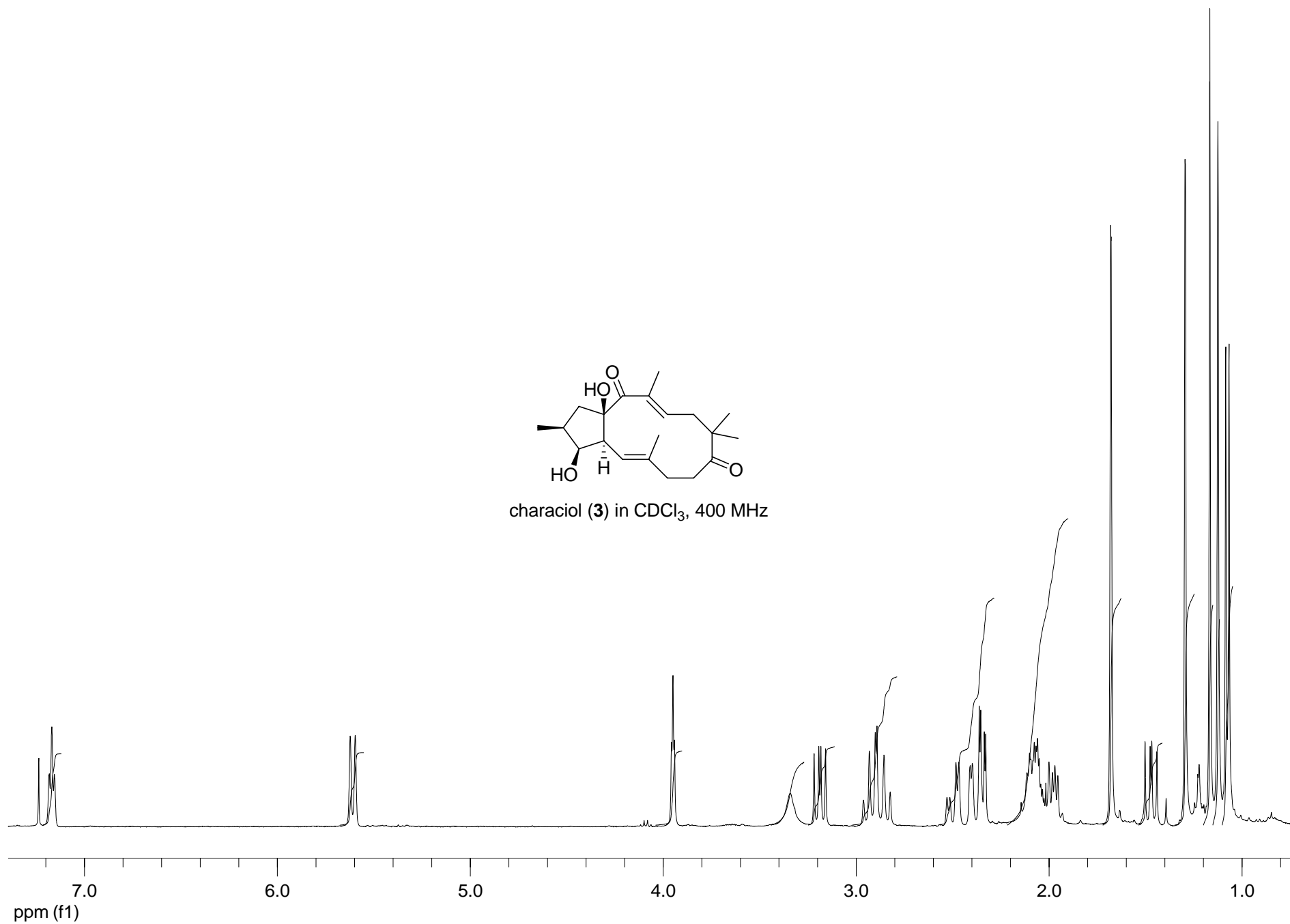


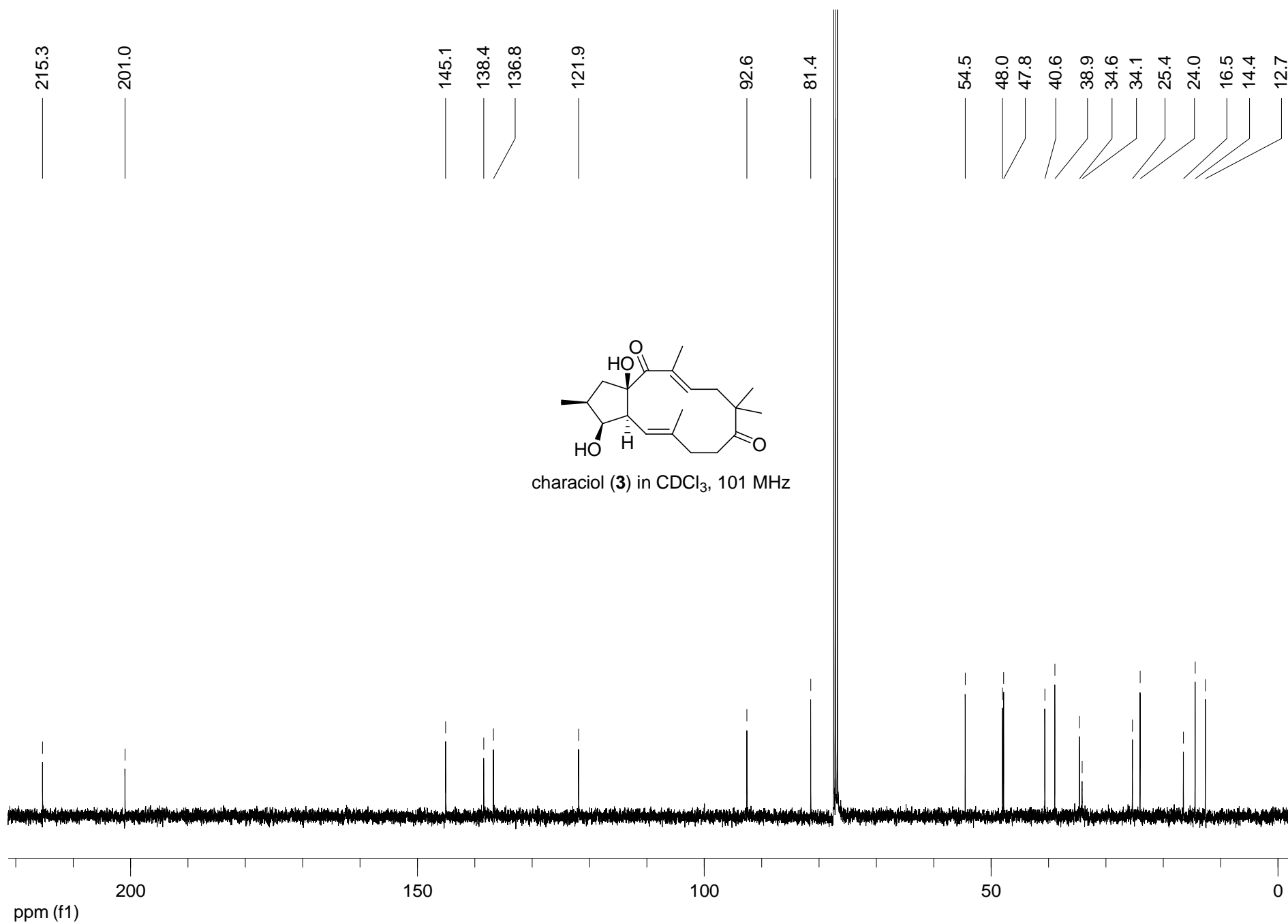


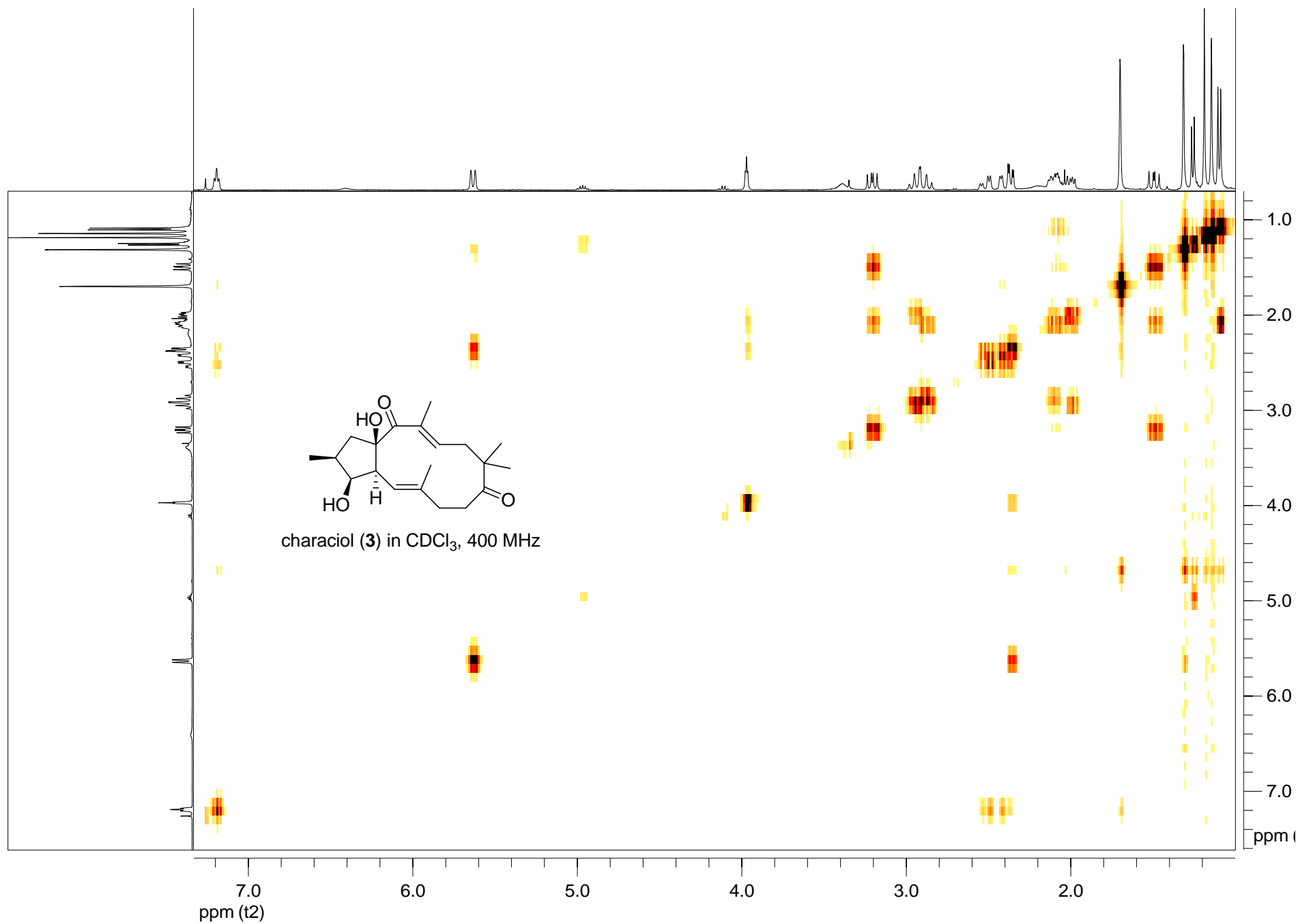


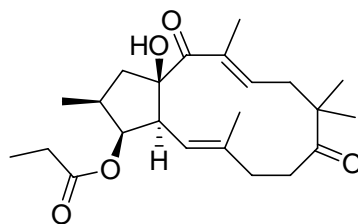


characiol (**3**) in CDCl₃, 400 MHz

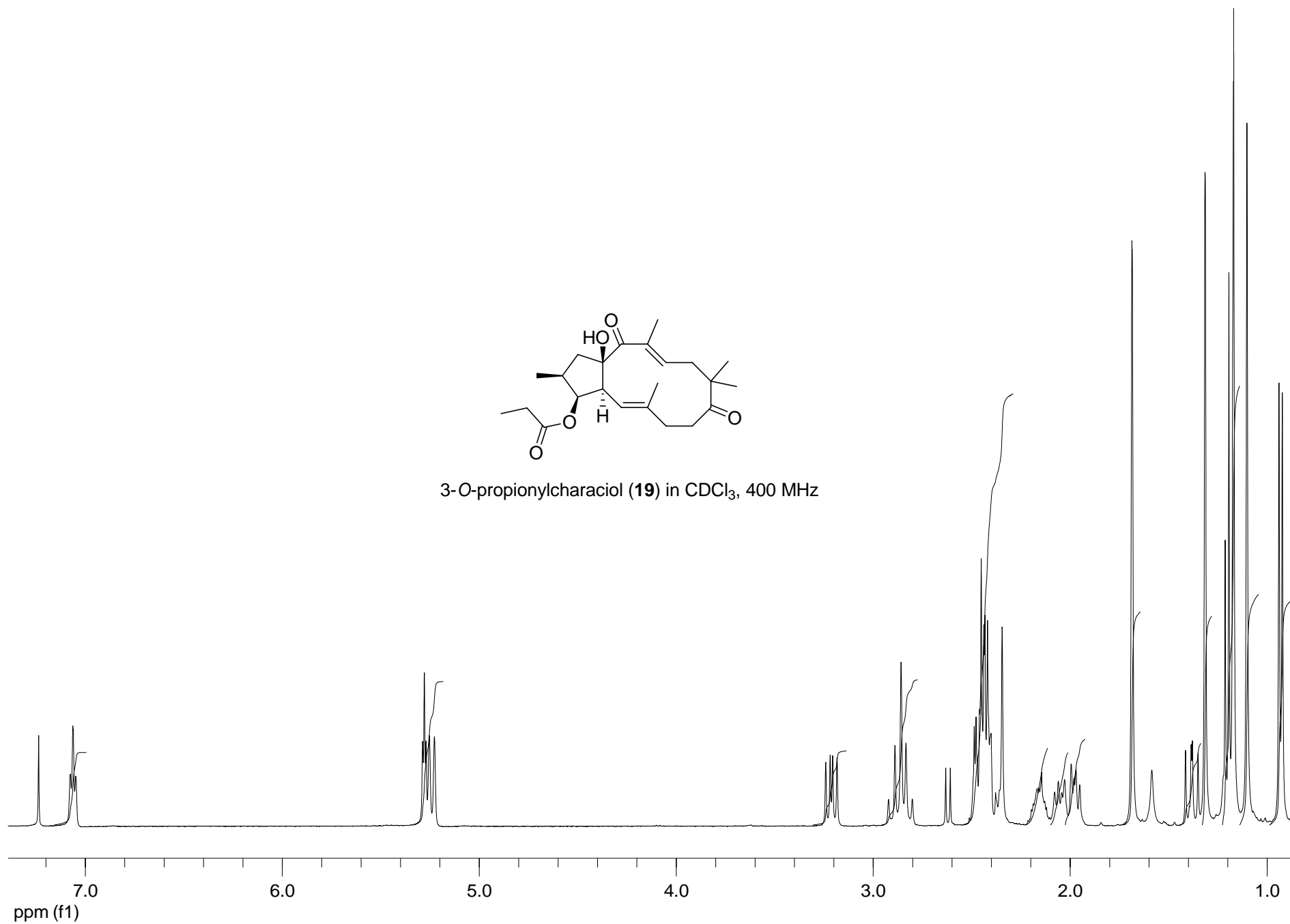


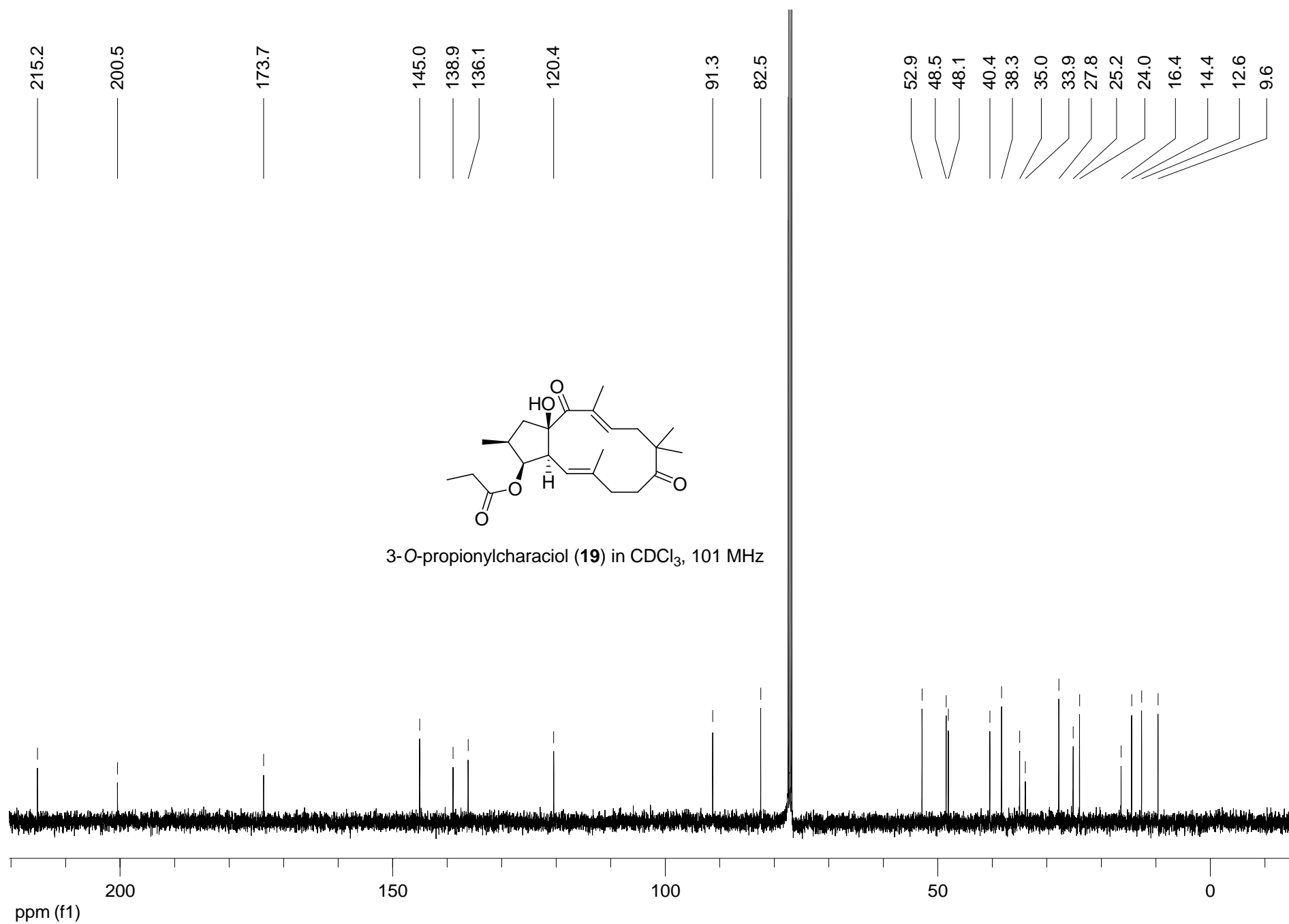


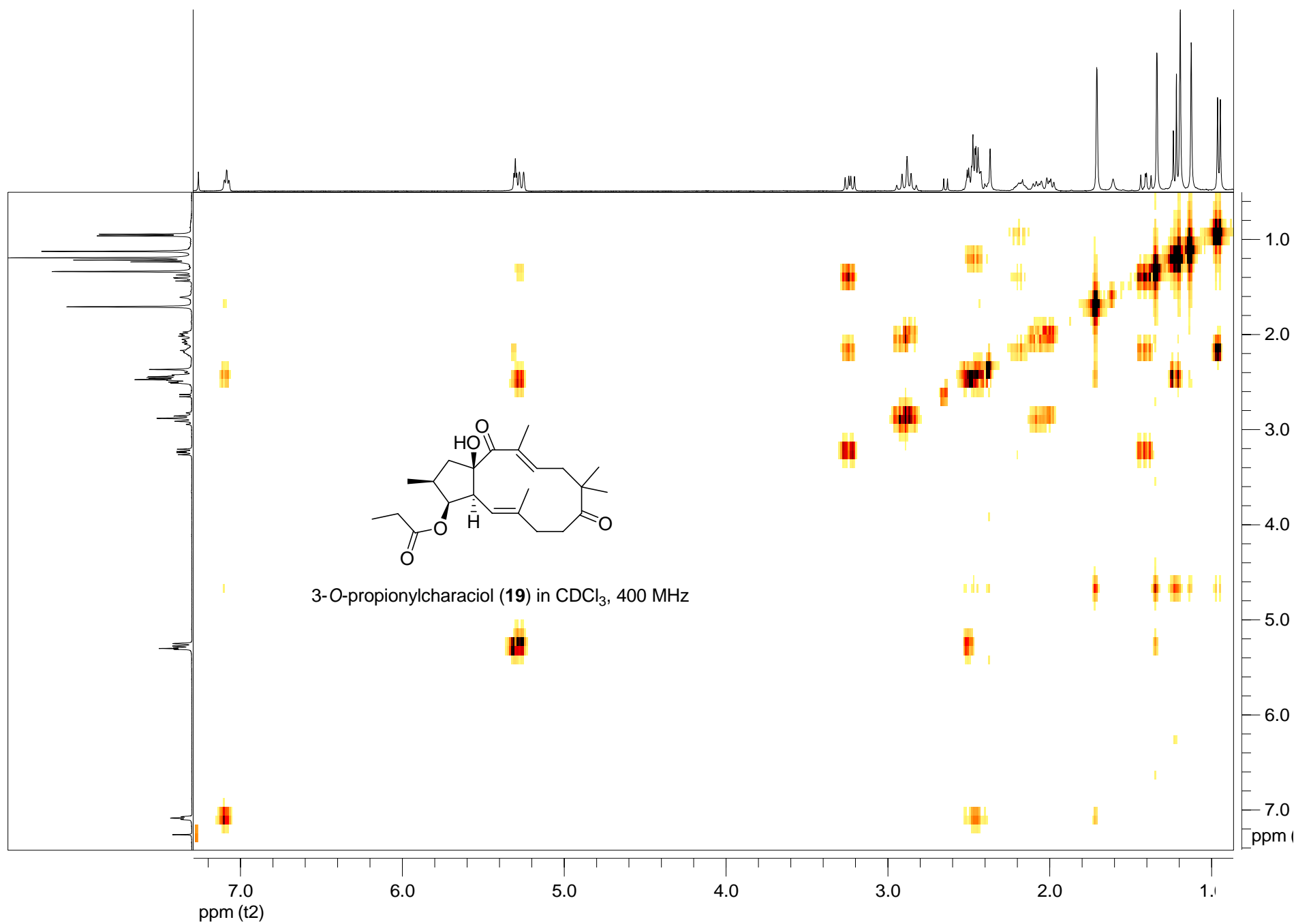




3-O-propionylcharaciol (**19**) in CDCl₃, 400 MHz

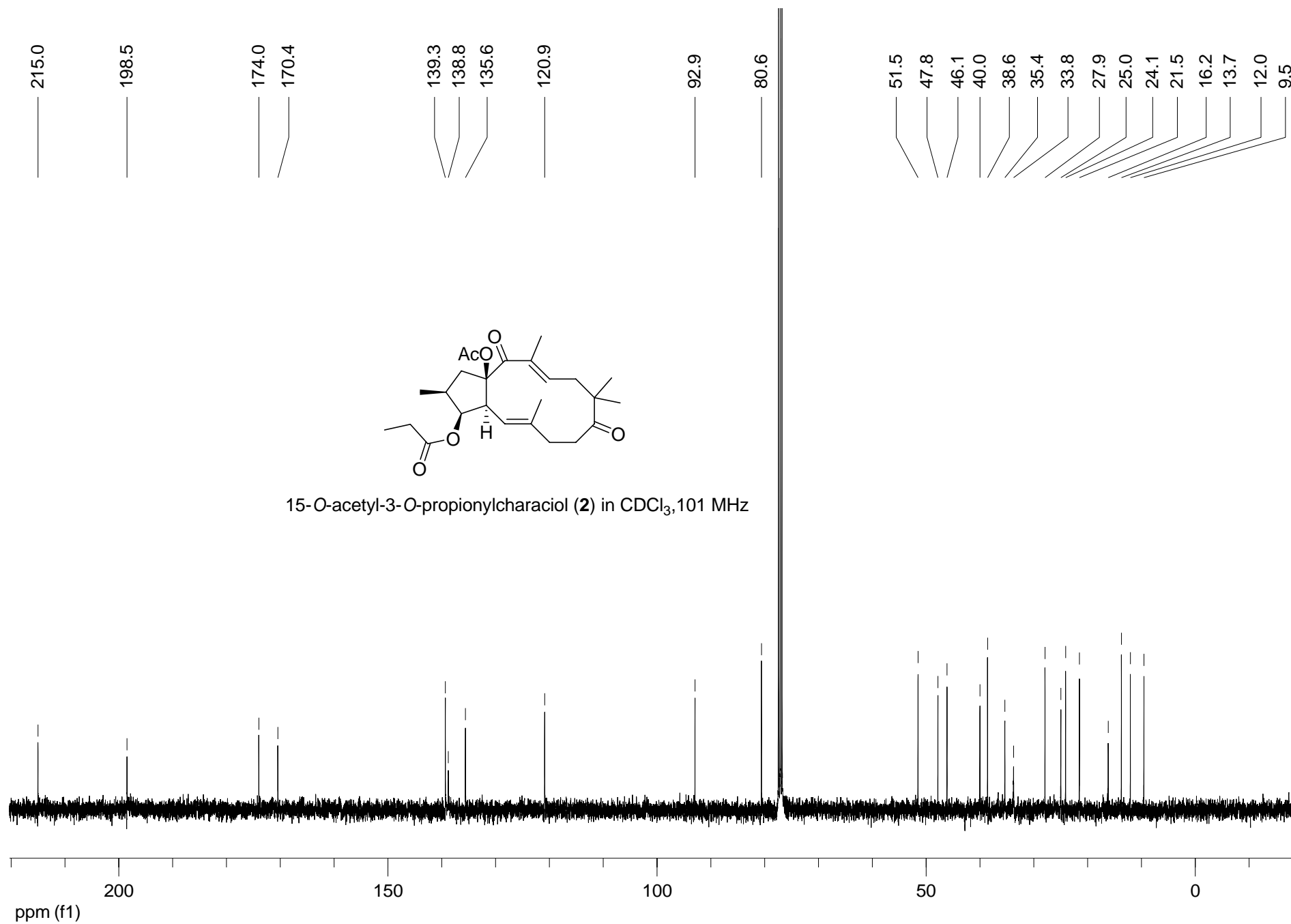


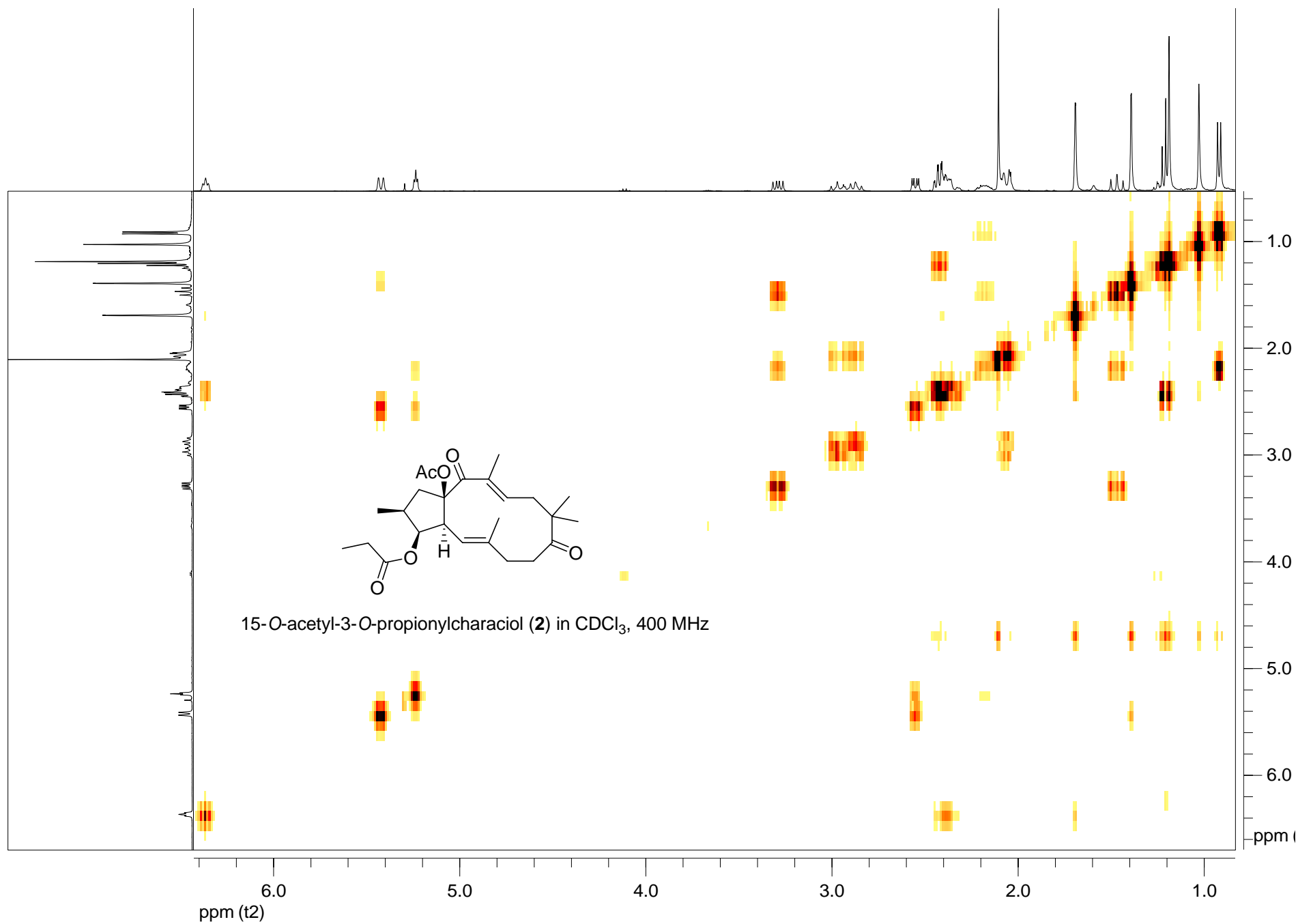


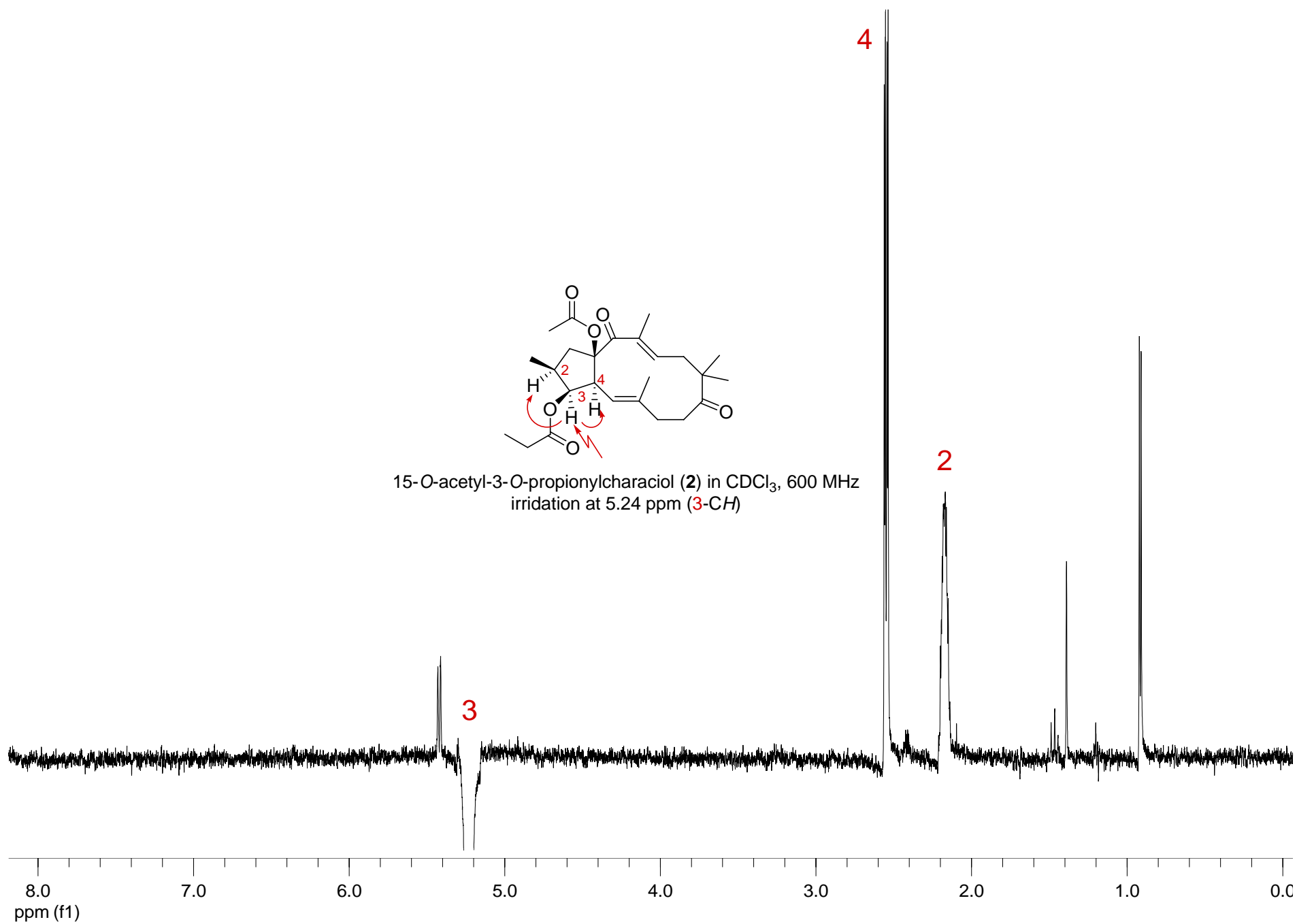


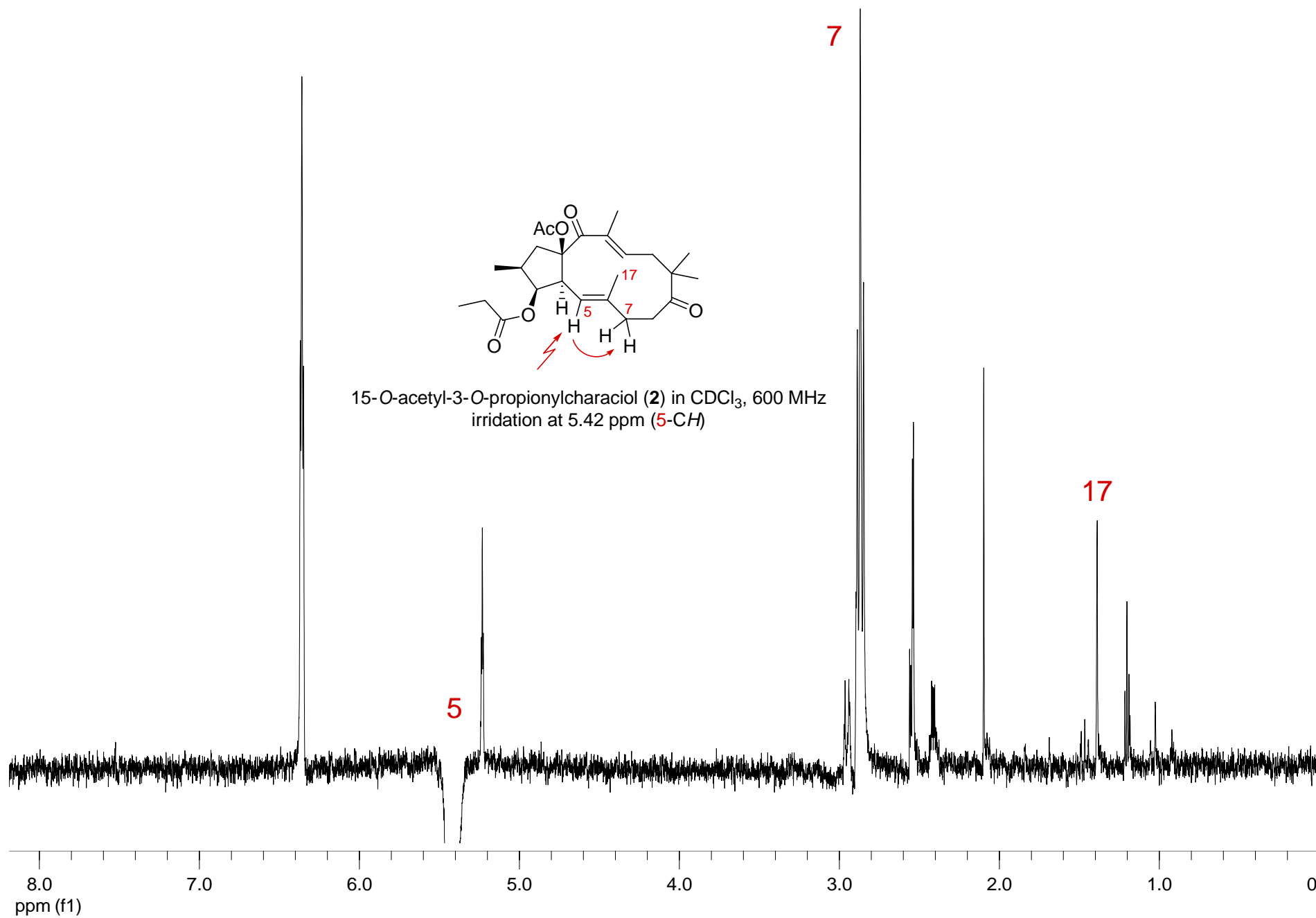
15-O-acetyl-3-O-propionylcharaciol (**2**) in CDCl₃, 400 MHz

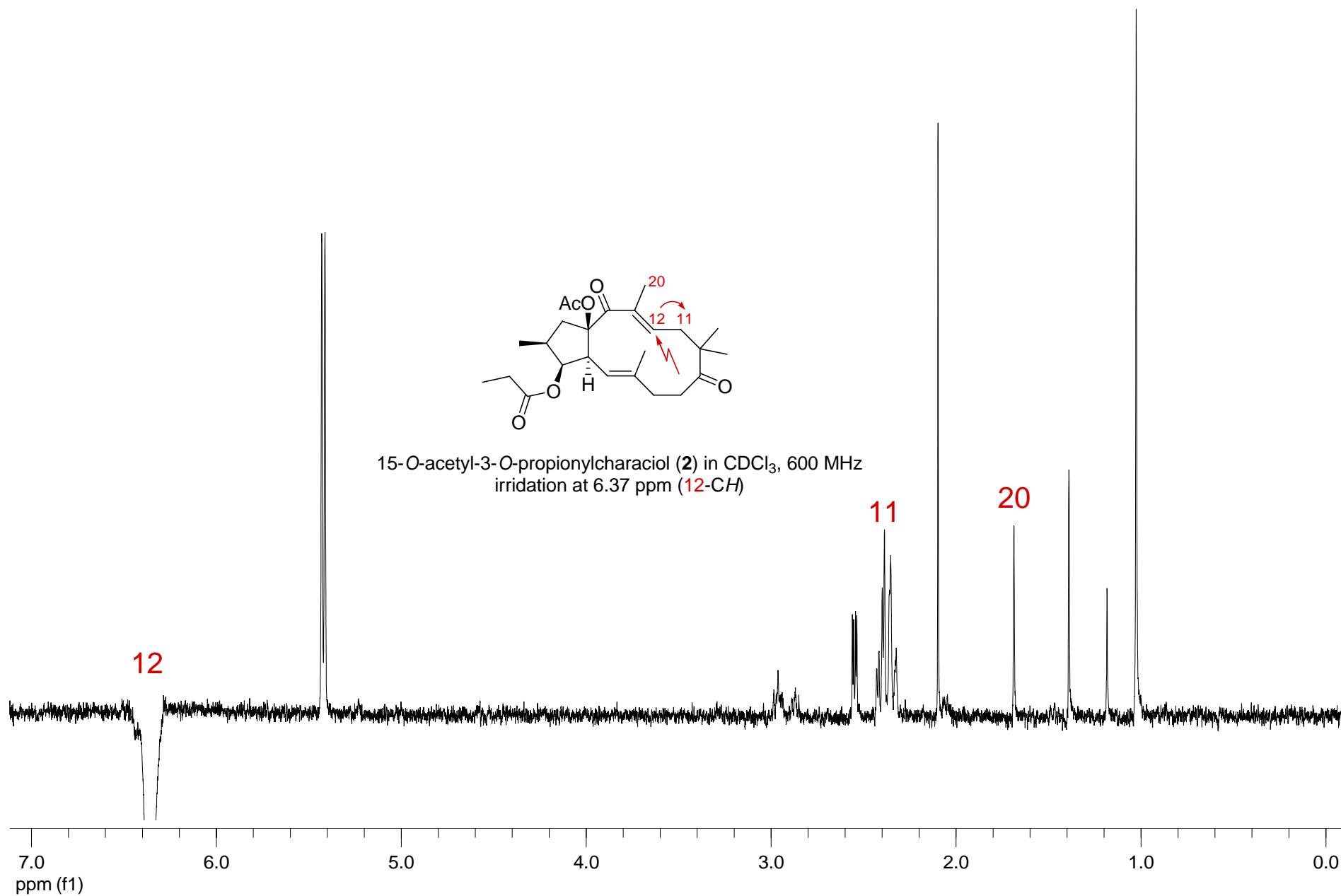
The figure displays the chemical structure of 15-O-acetyl-3-O-propionylcharaciol (**2**) and its corresponding ¹H NMR spectrum. The chemical structure is a complex polycyclic molecule featuring a decalin-like core with various substituents, including an acetoxy group (AcO), a propionyloxy group (PropO), and several methyl groups. The NMR spectrum shows peaks from 0 to 8 ppm, with integration curves overlaid on the baseline.

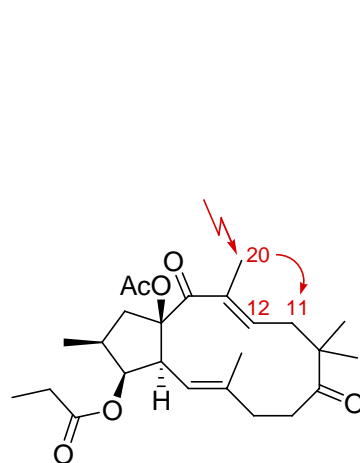




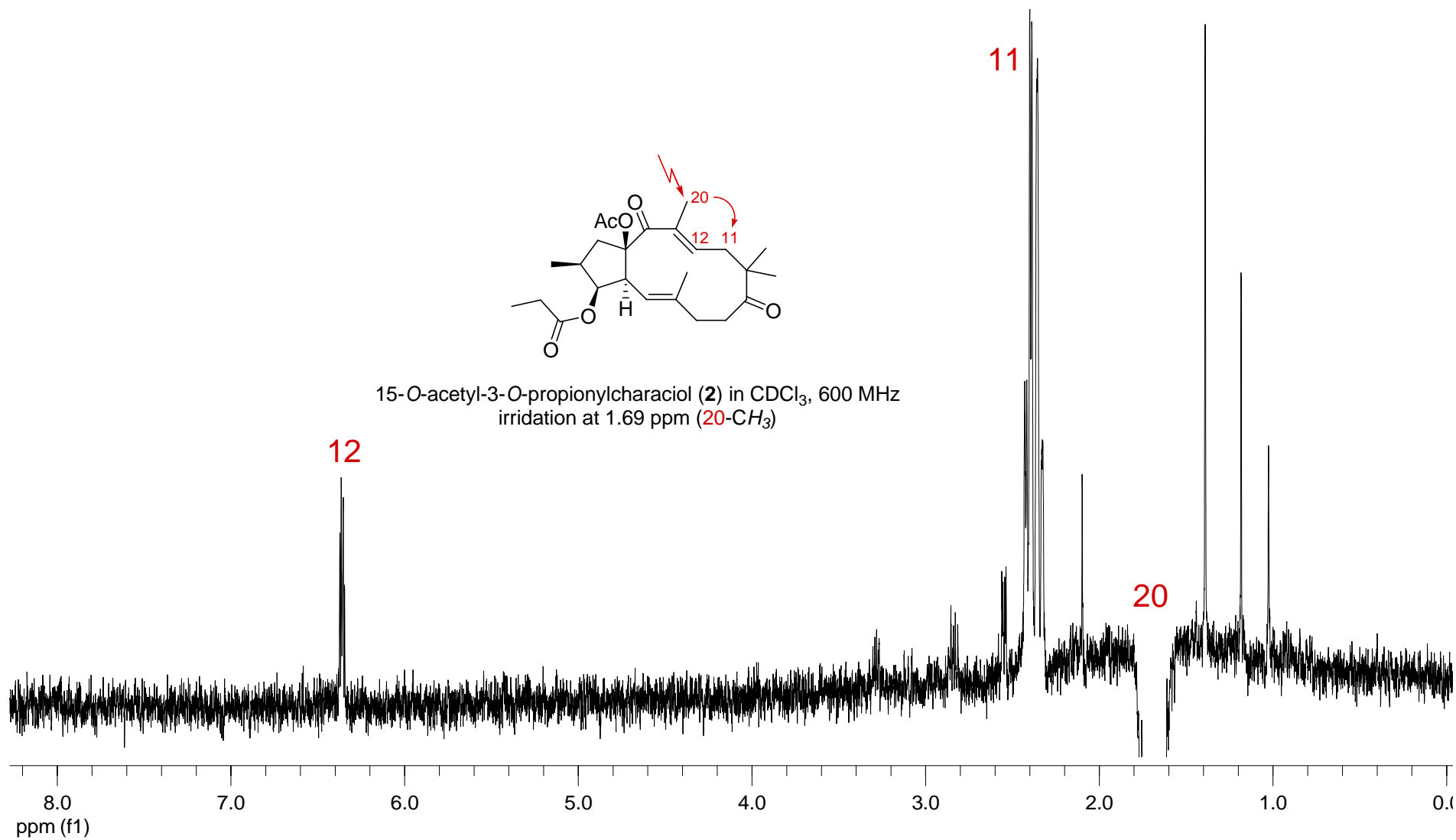


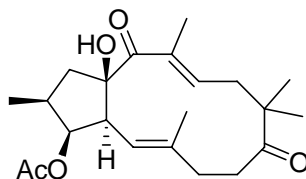




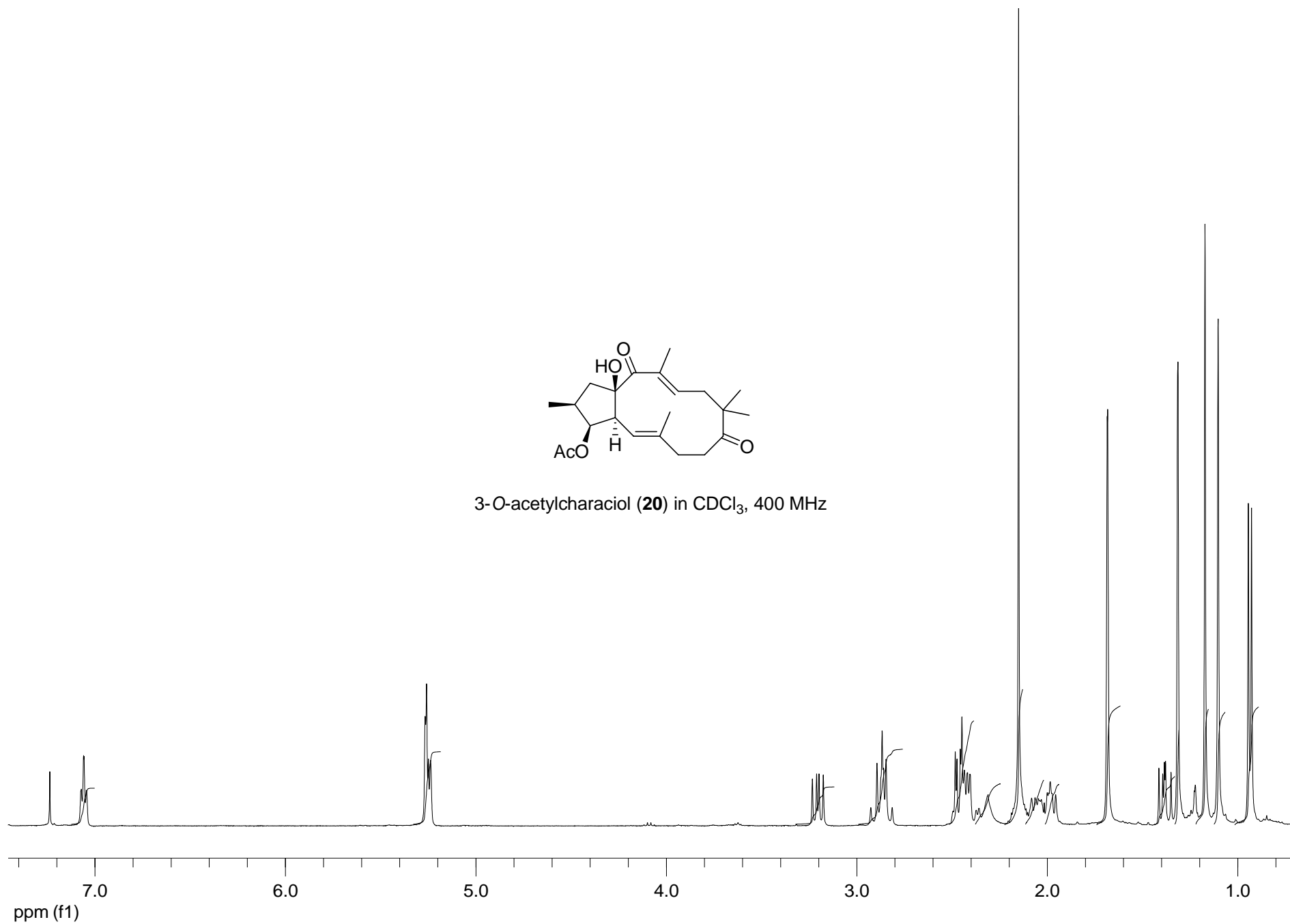


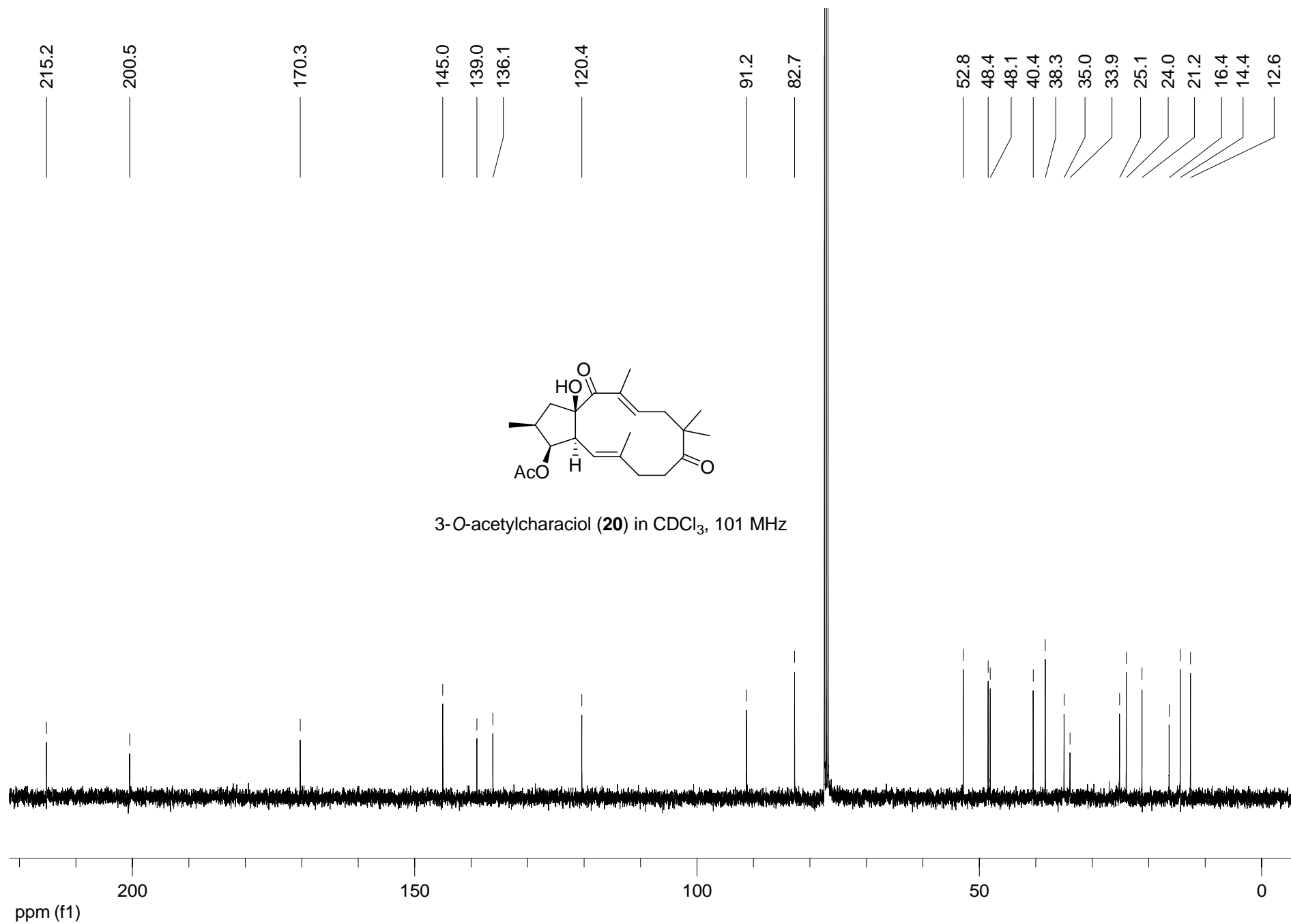
15-O-acetyl-3-O-propionylcharaciol (**2**) in CDCl₃, 600 MHz
irradiation at 1.69 ppm (**20**-CH₃)

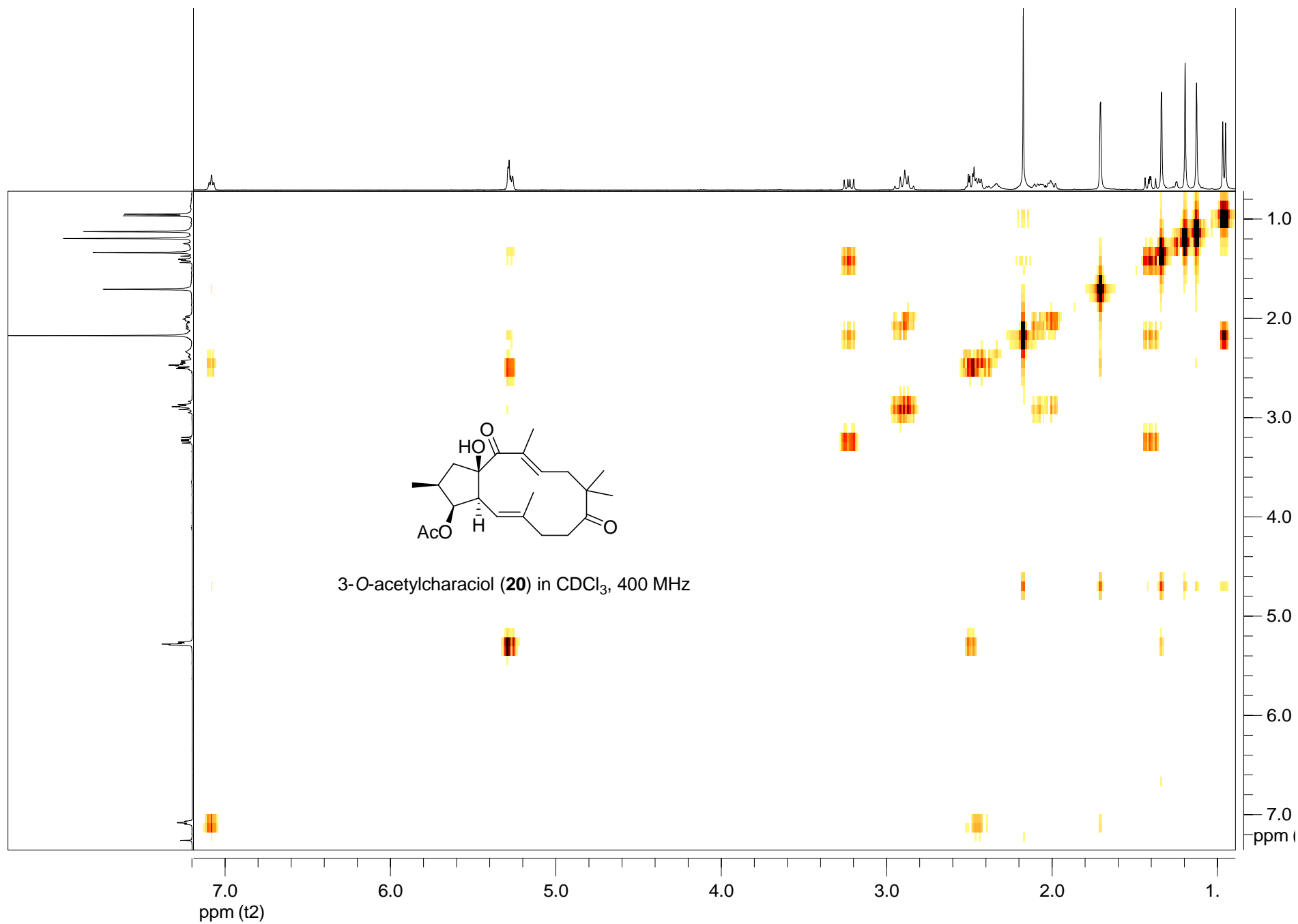


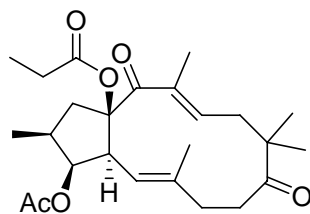


3-O-acetylcharaciol (**20**) in CDCl₃, 400 MHz

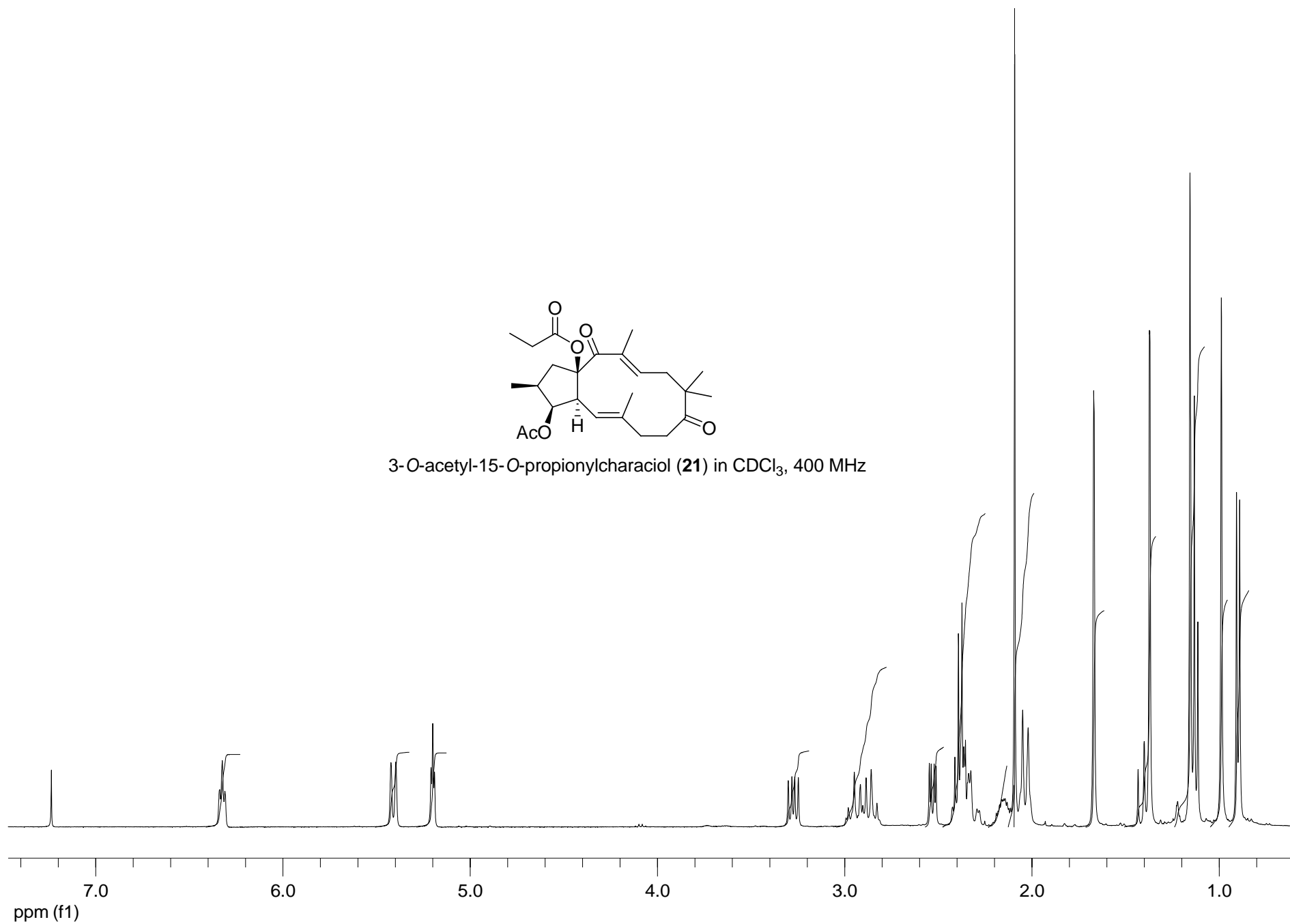




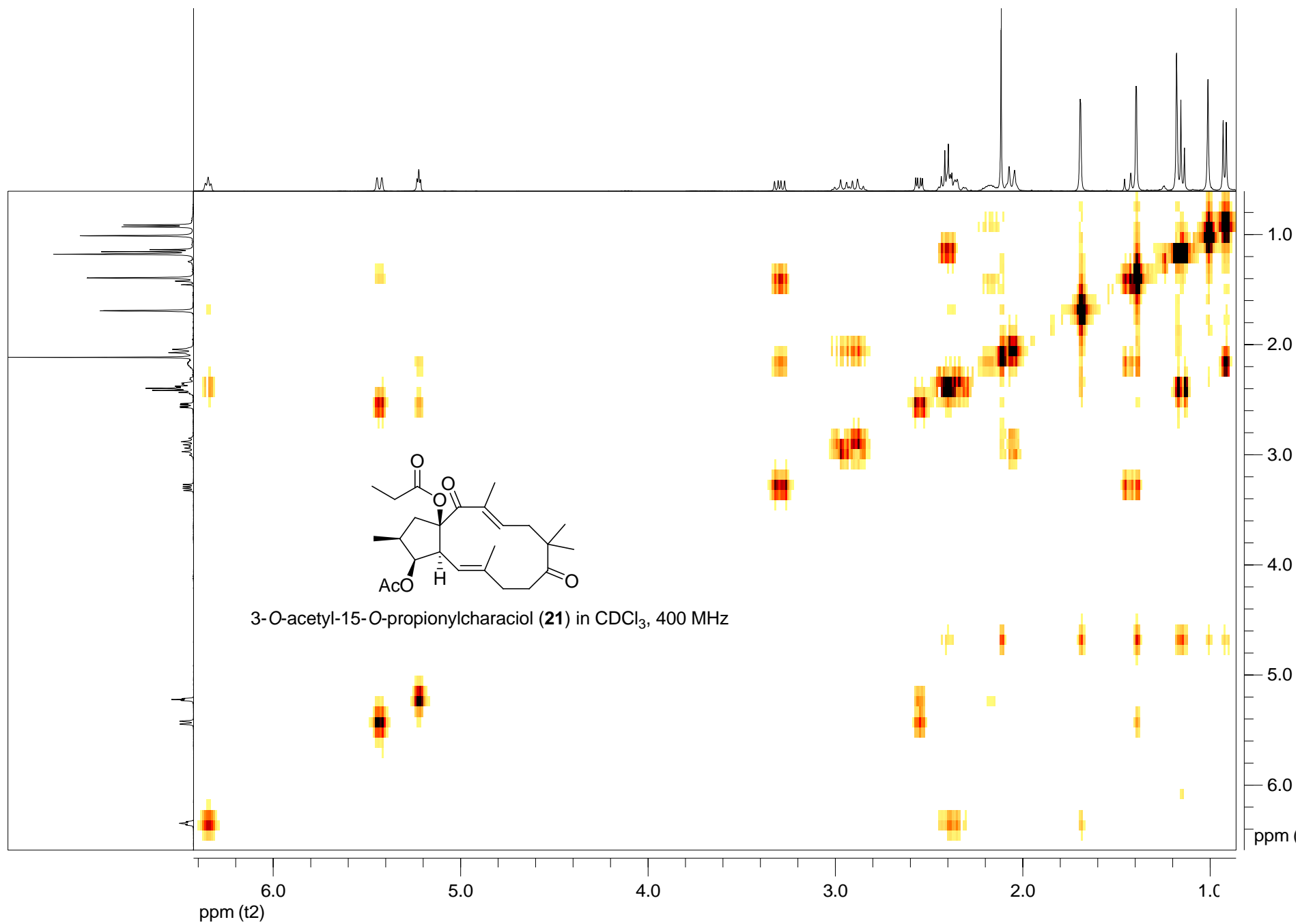


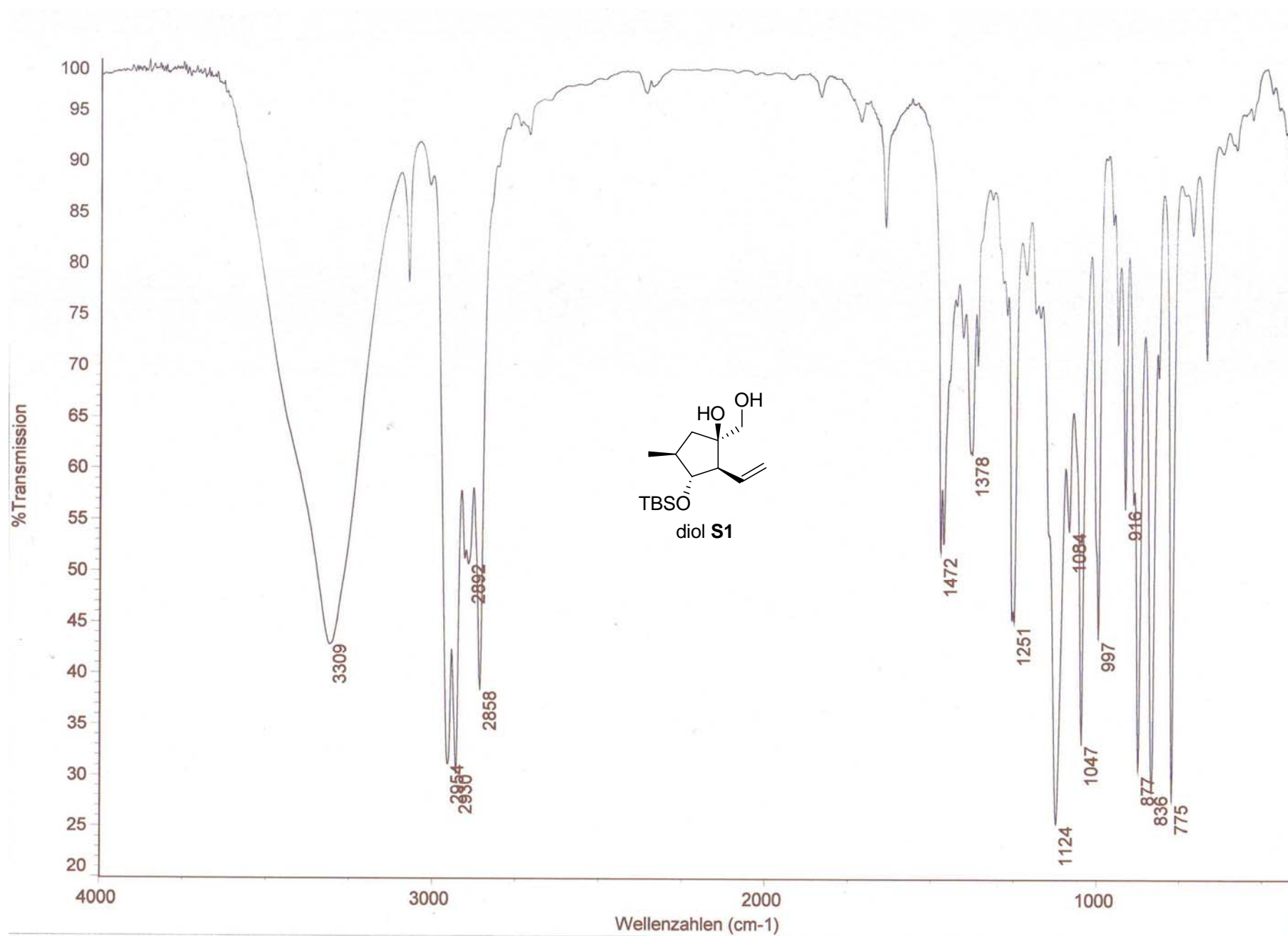


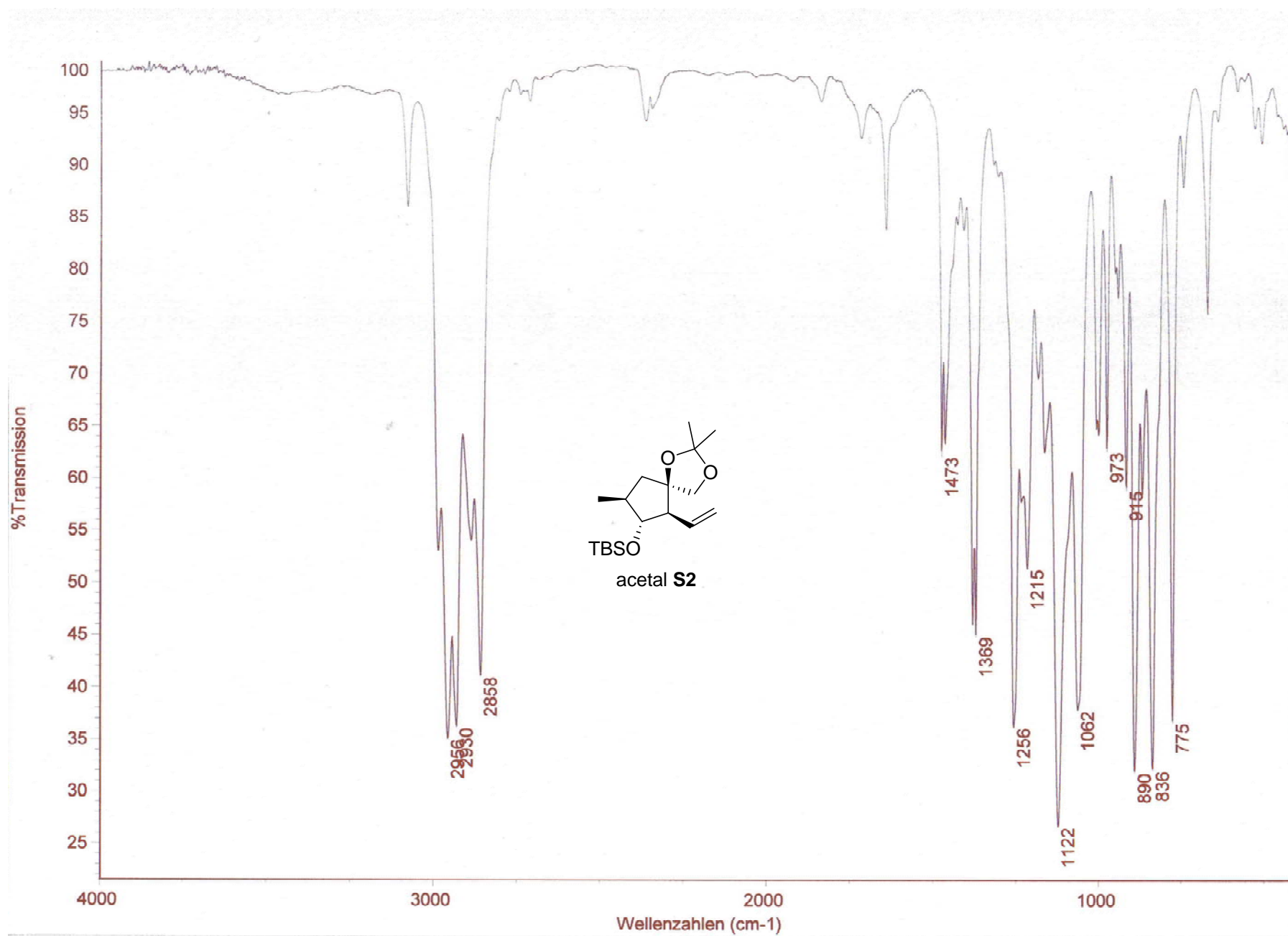
3-O-acetyl-15-O-propionylcharaciol (**21**) in CDCl₃, 400 MHz

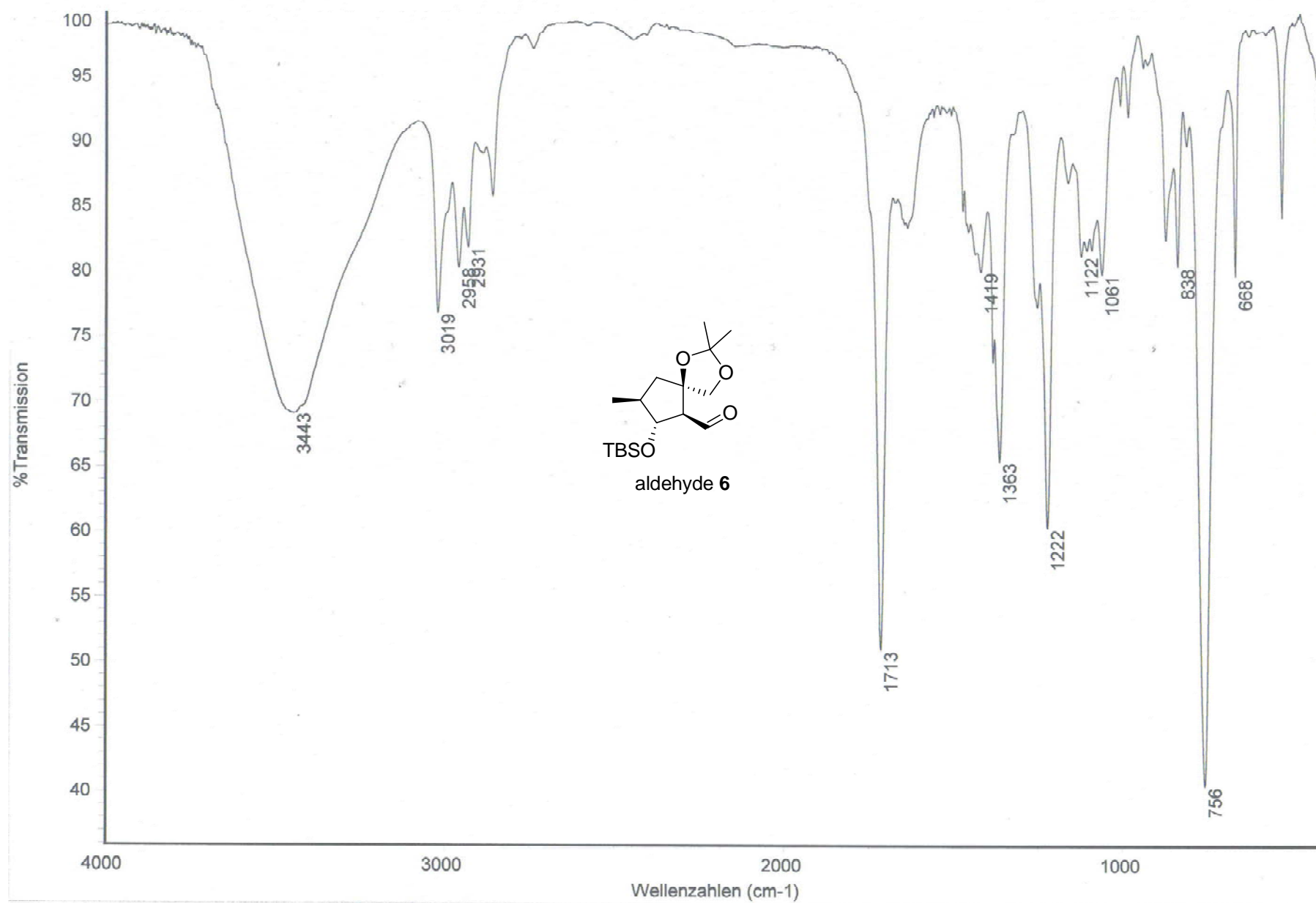


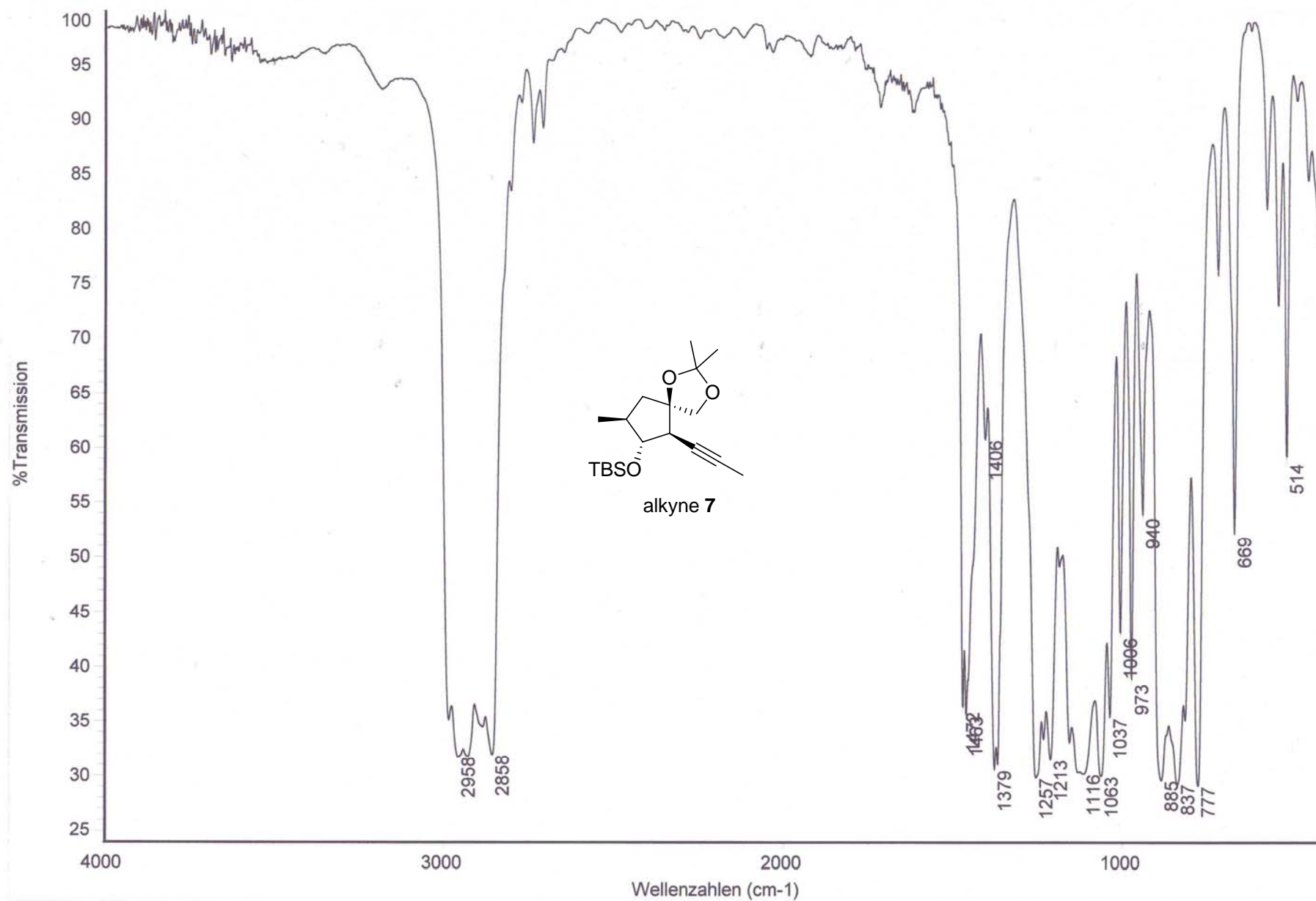


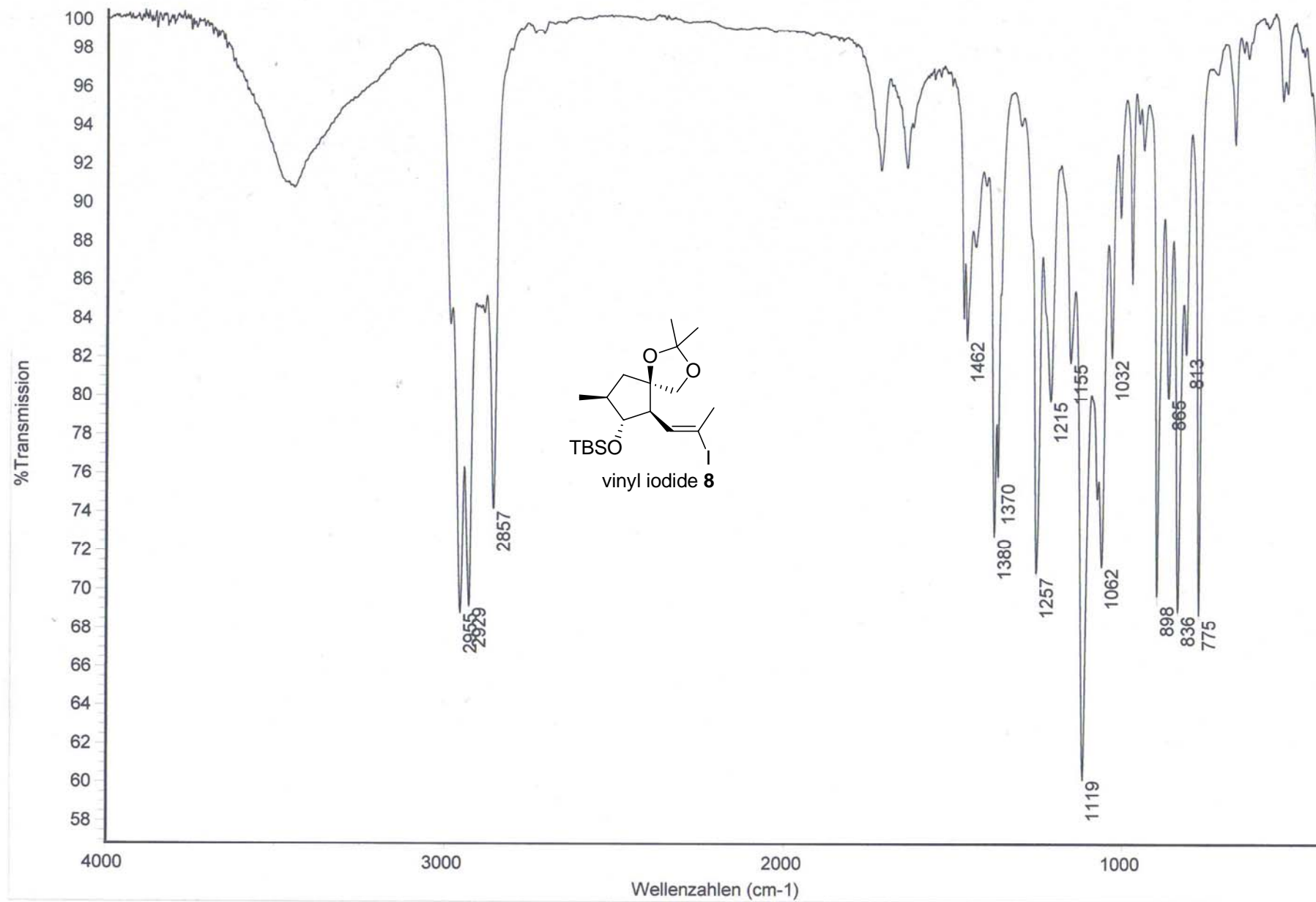


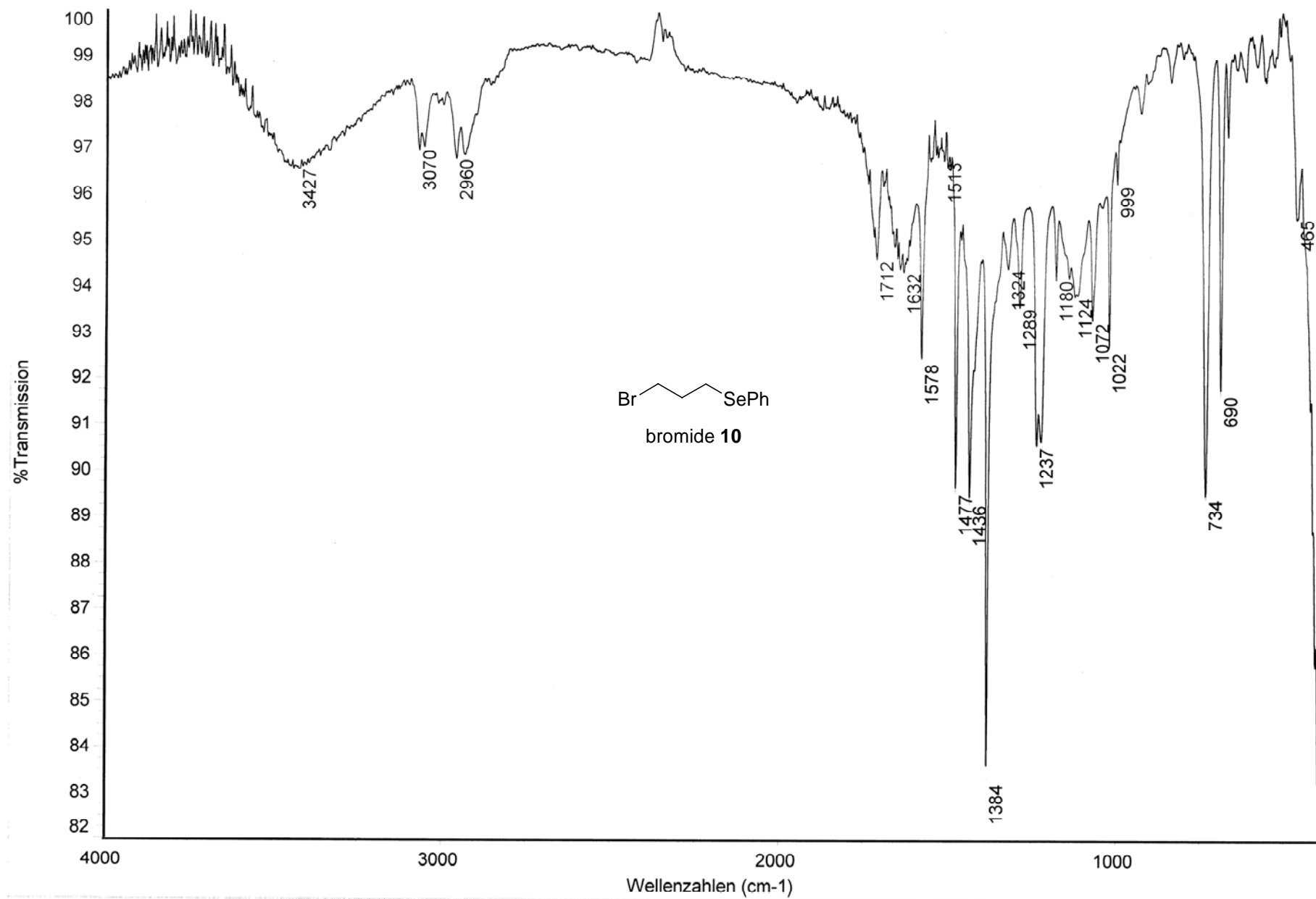


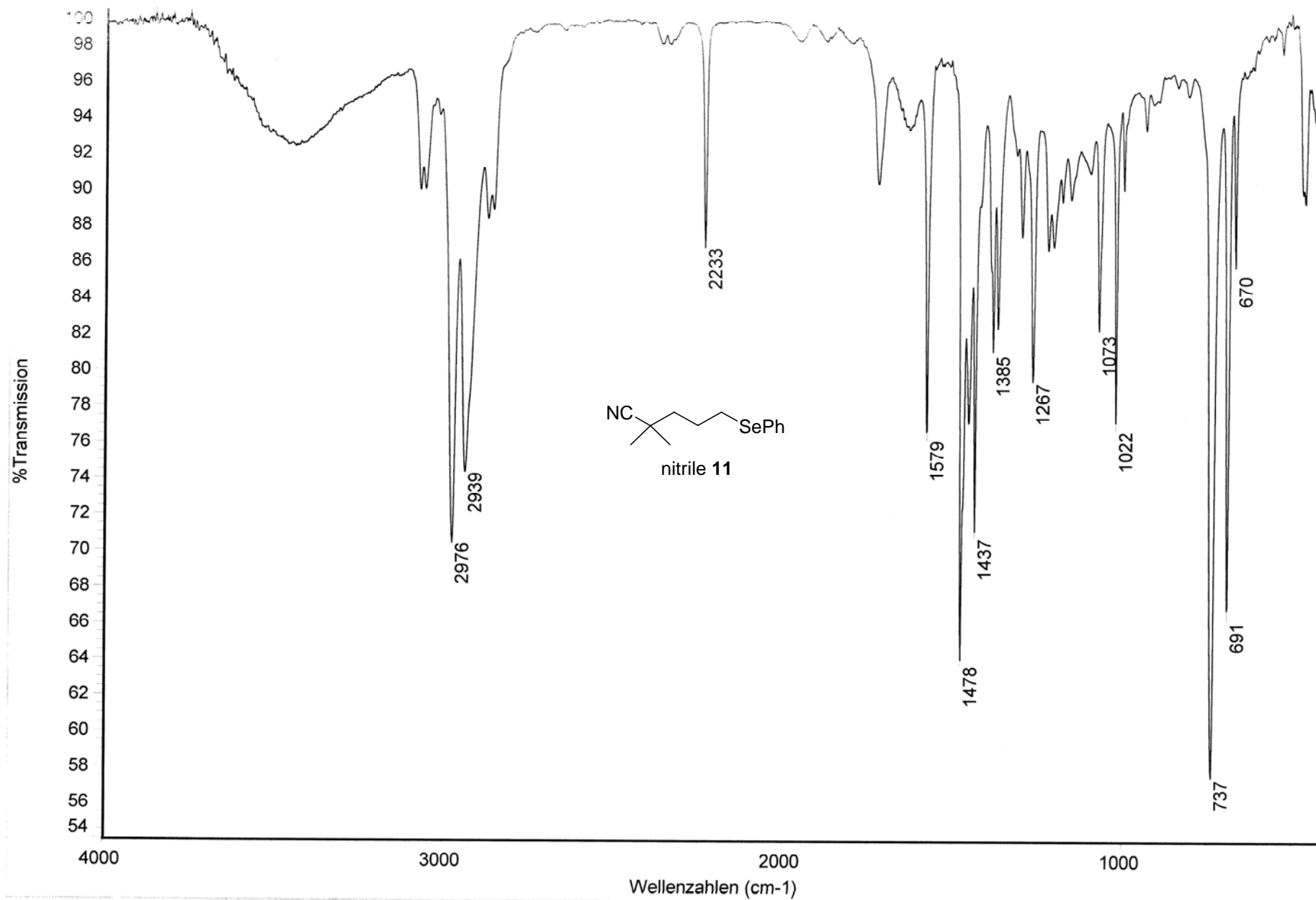


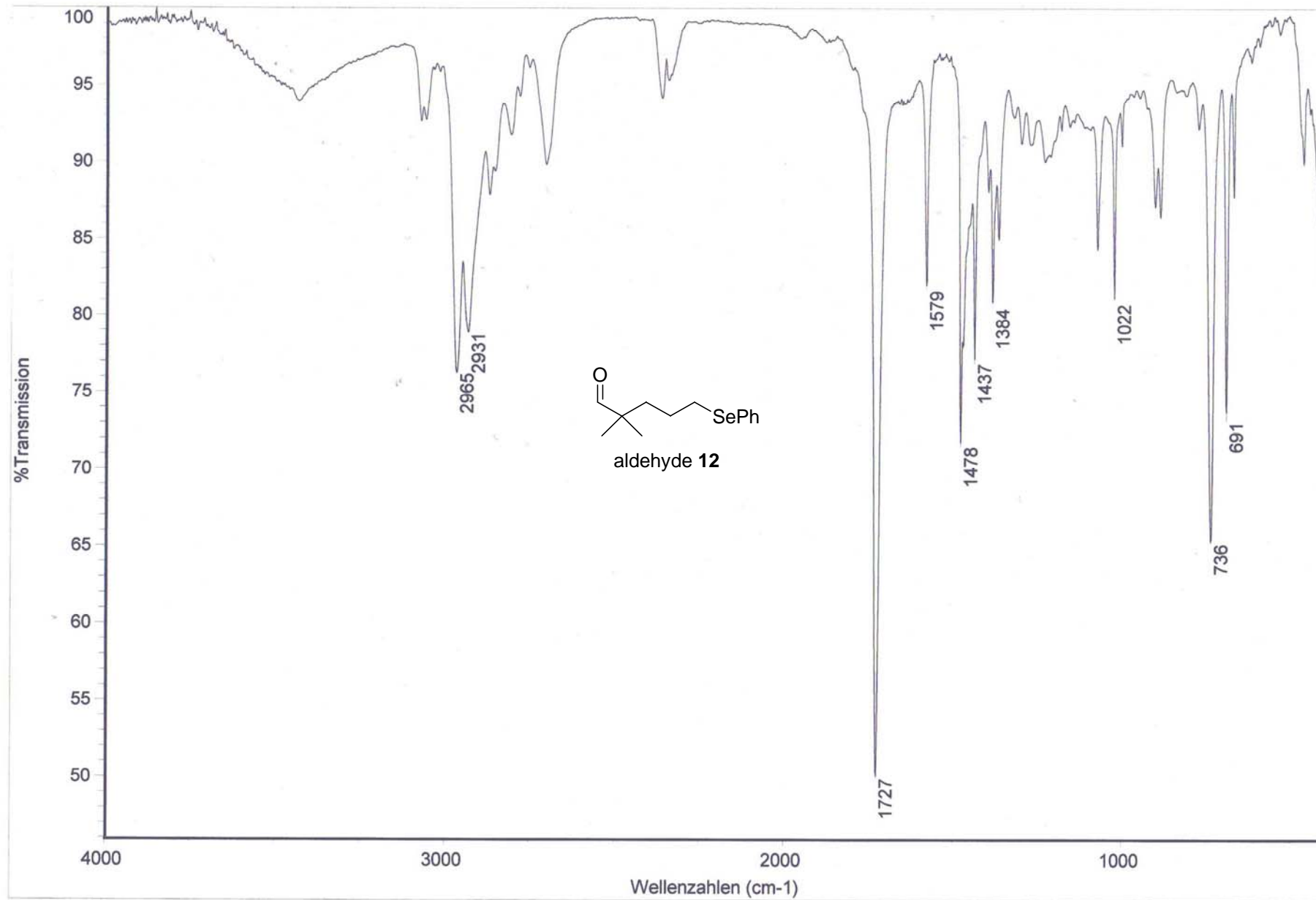


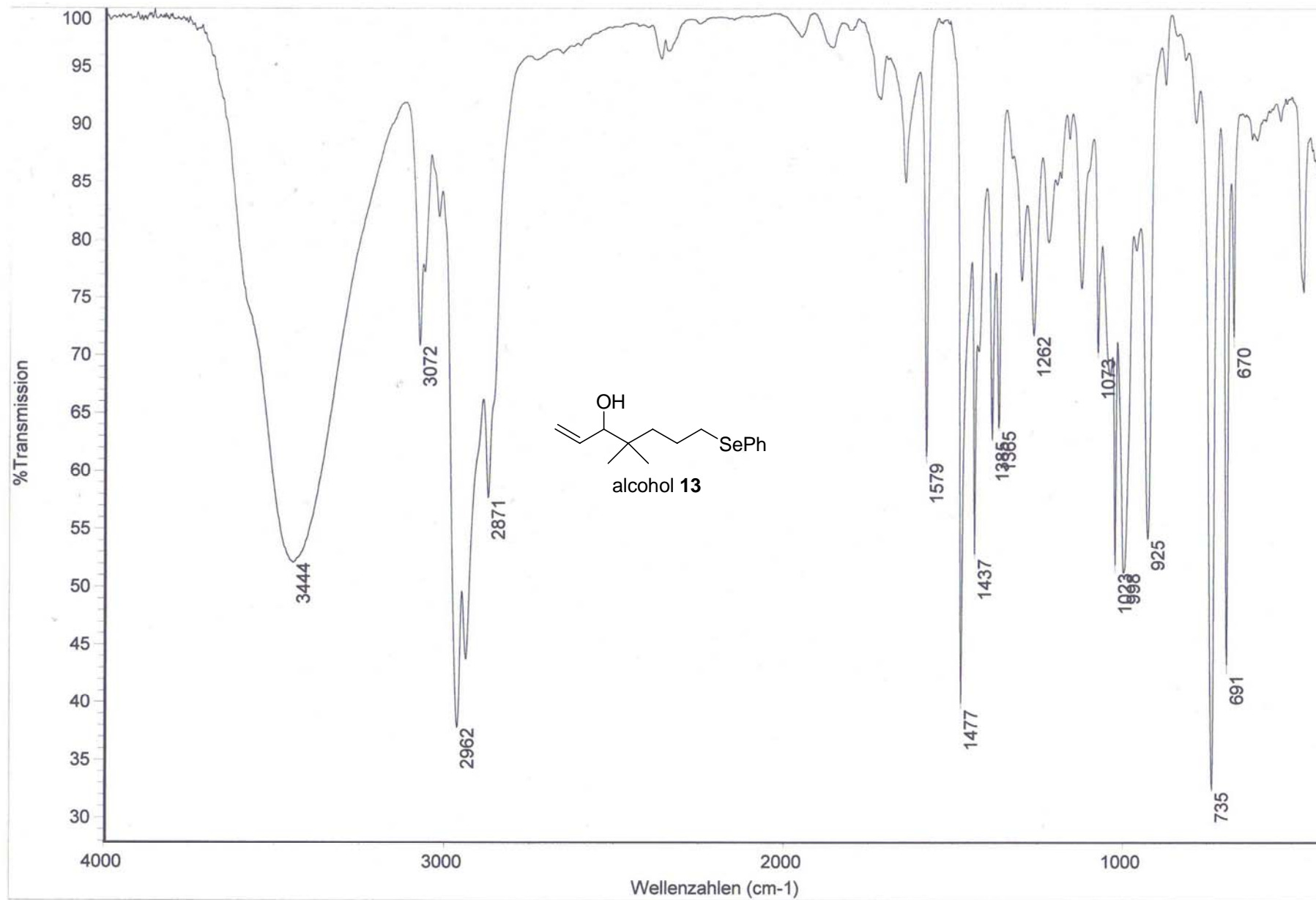


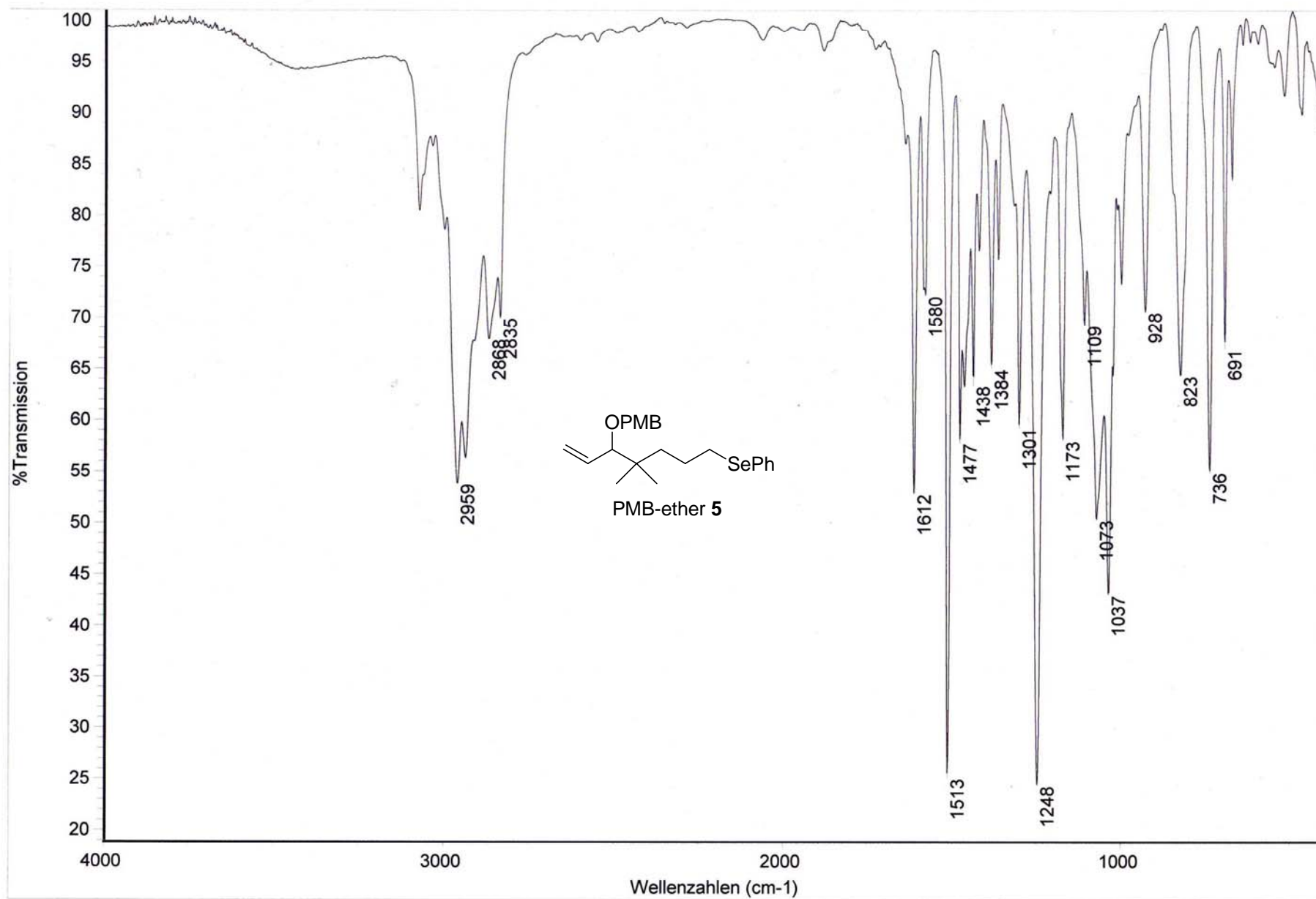


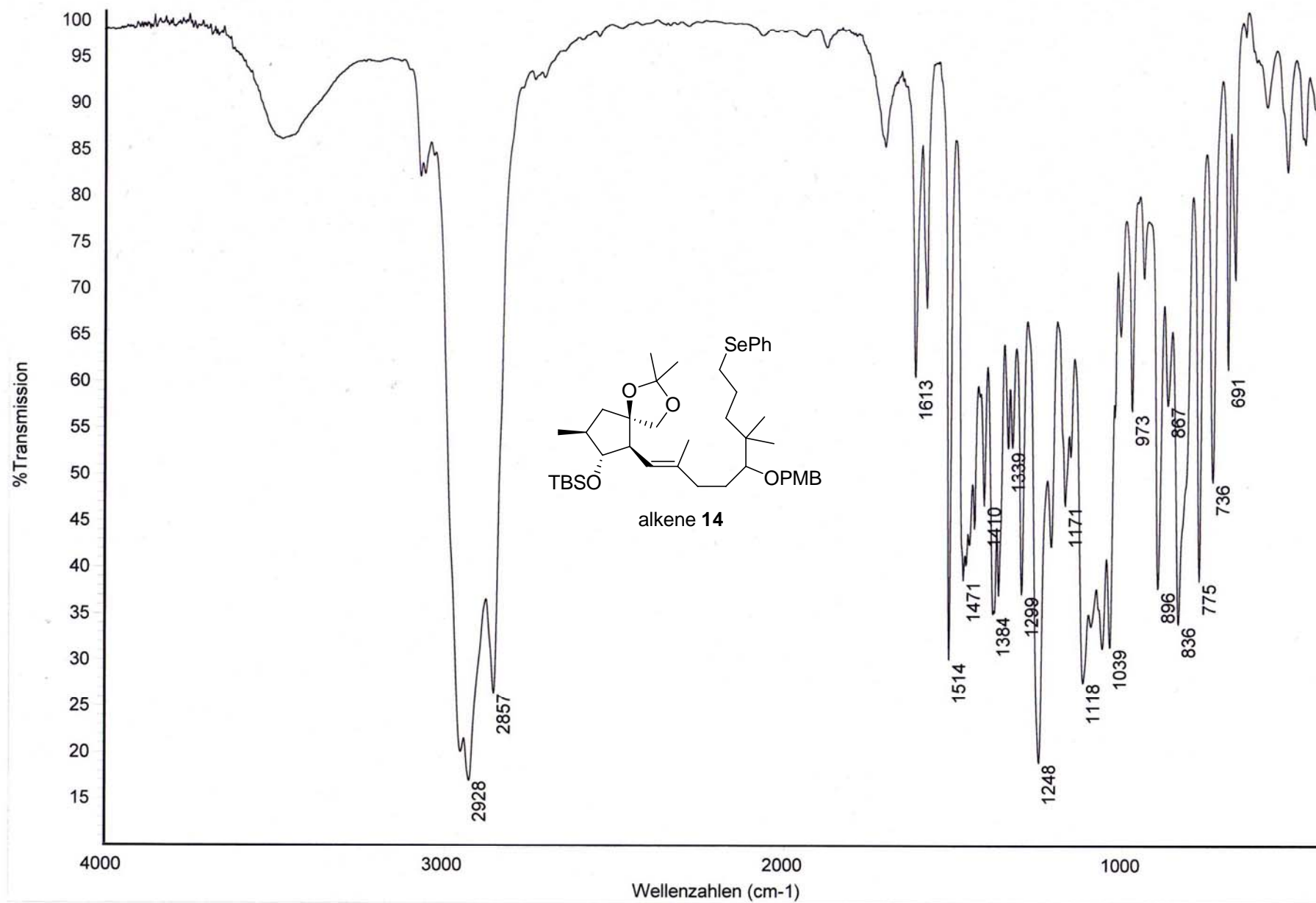


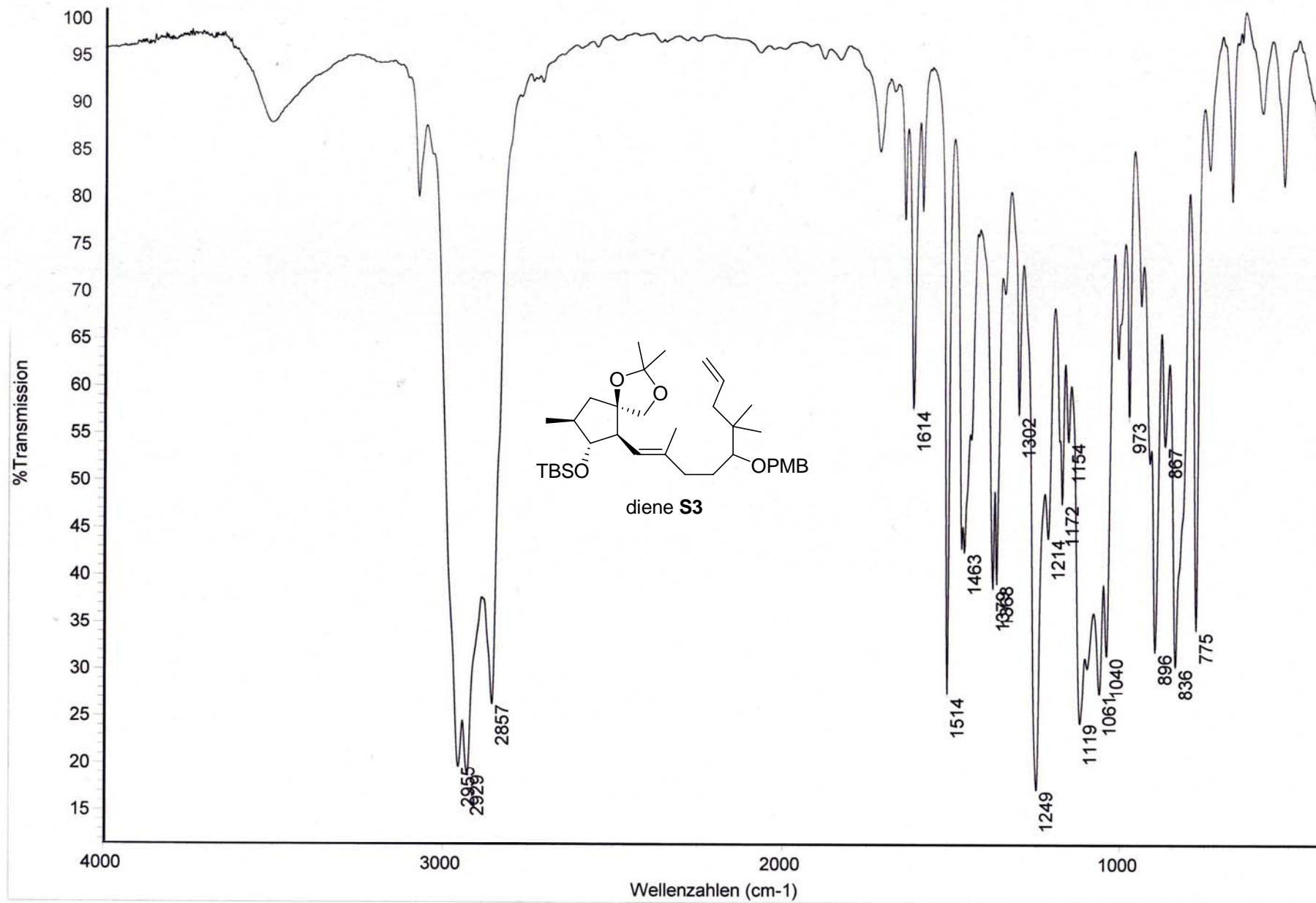


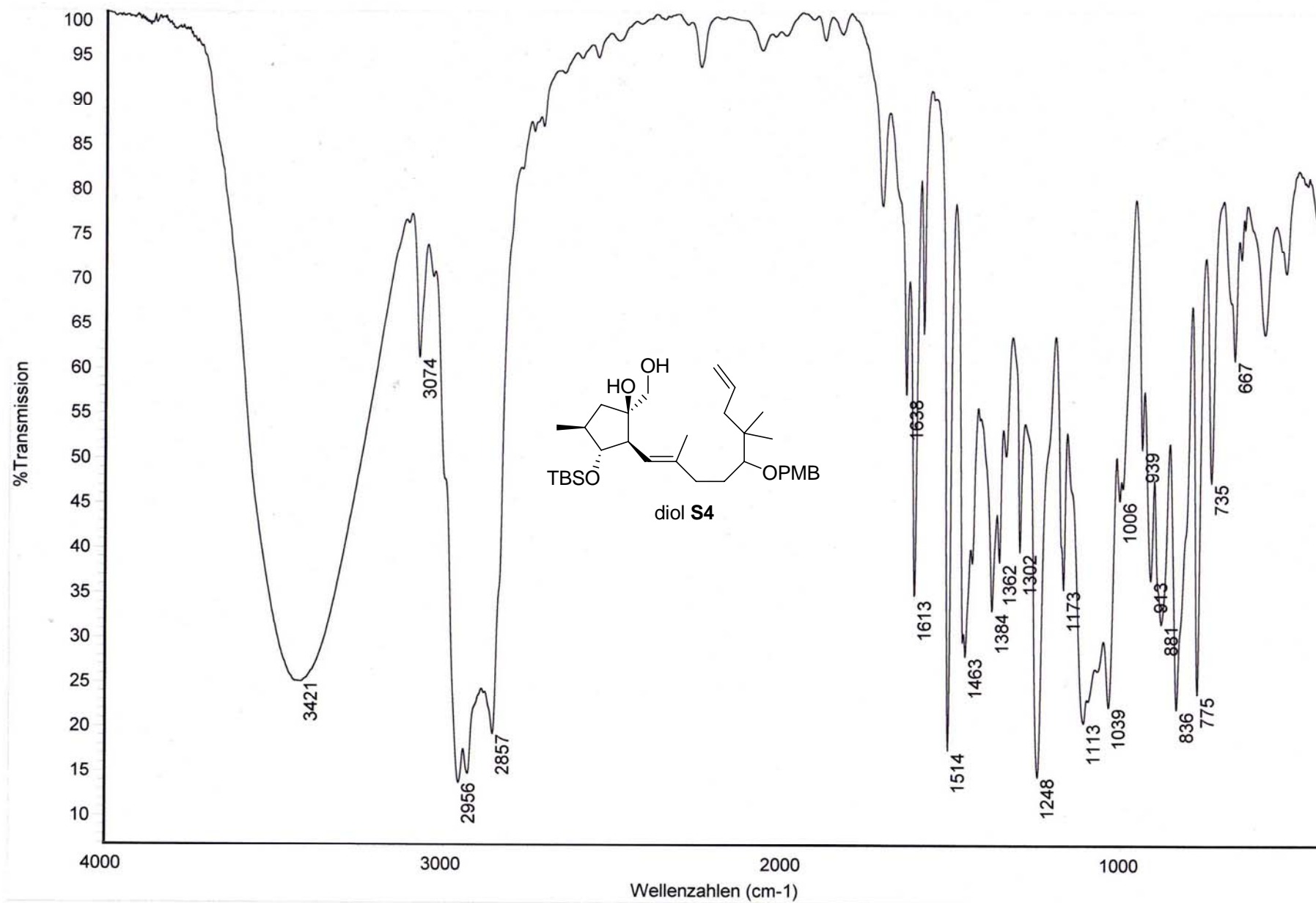


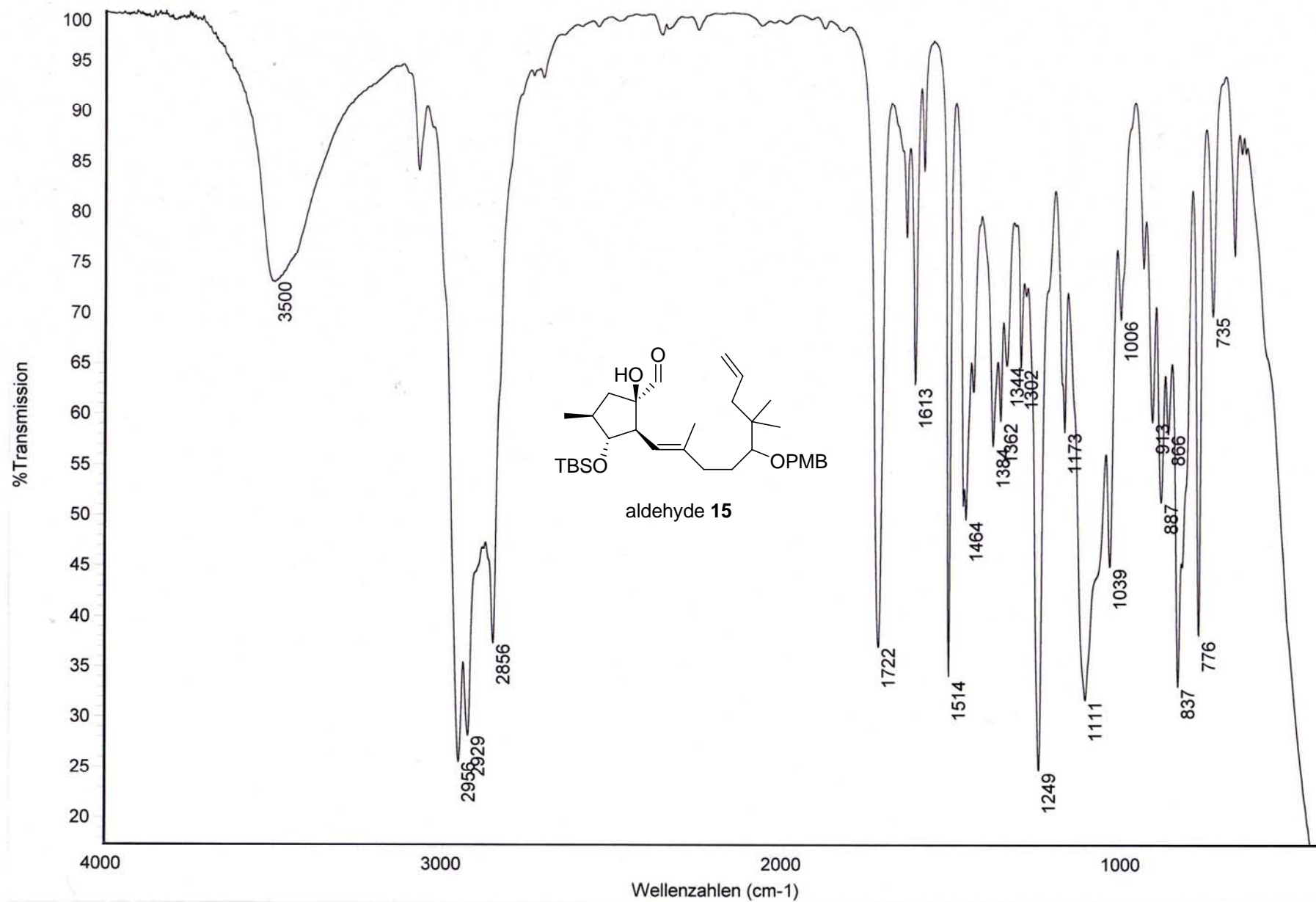


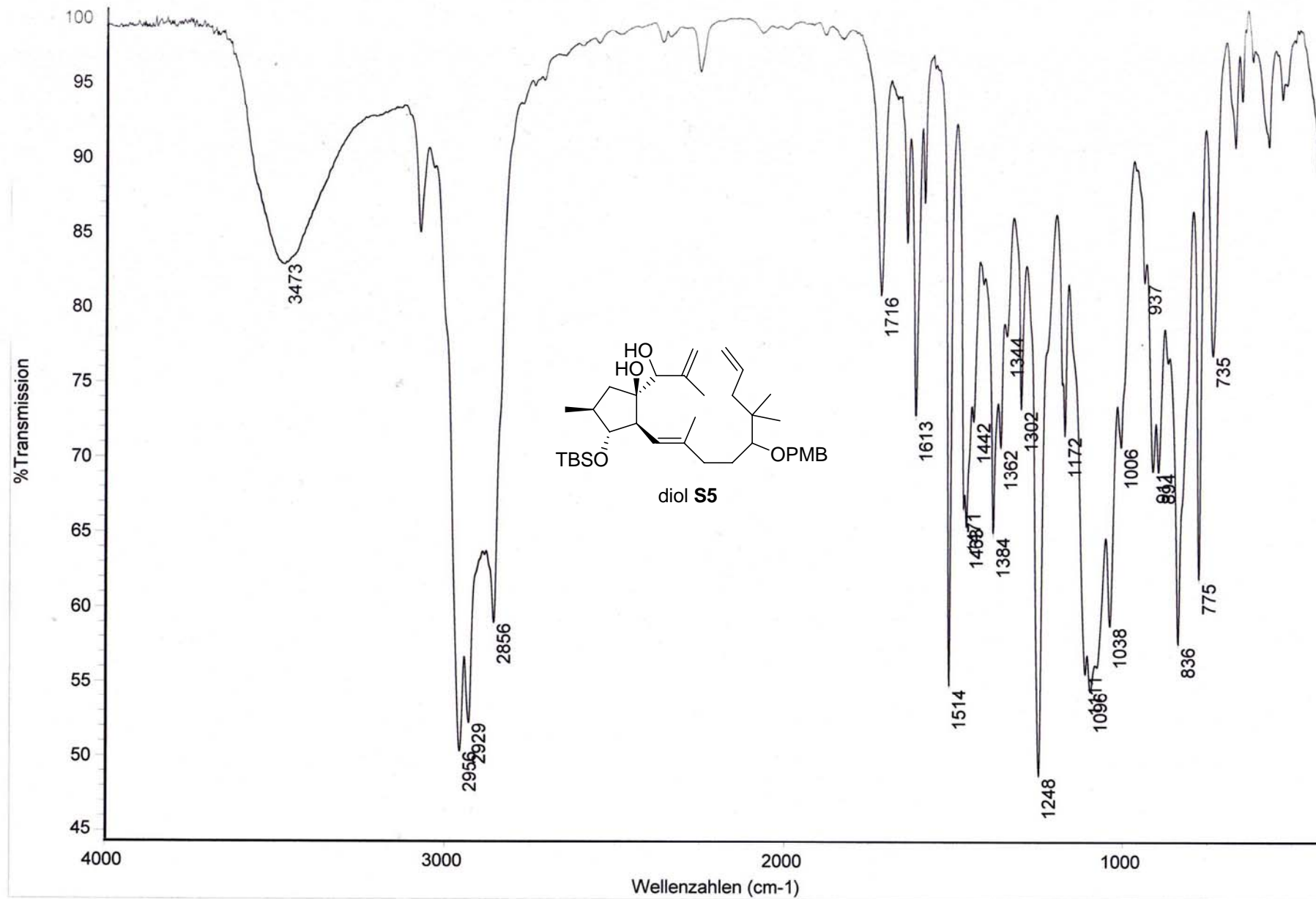


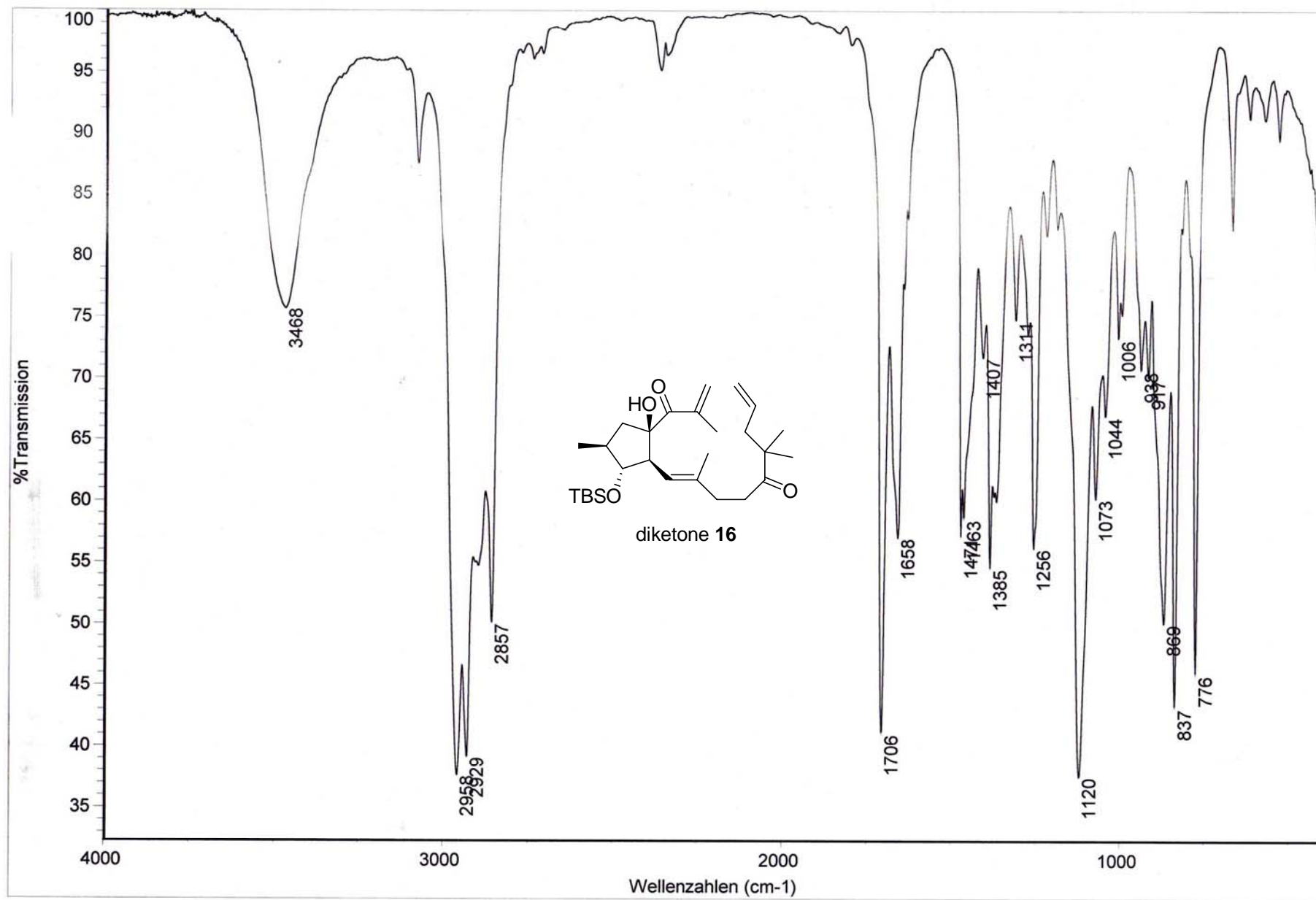


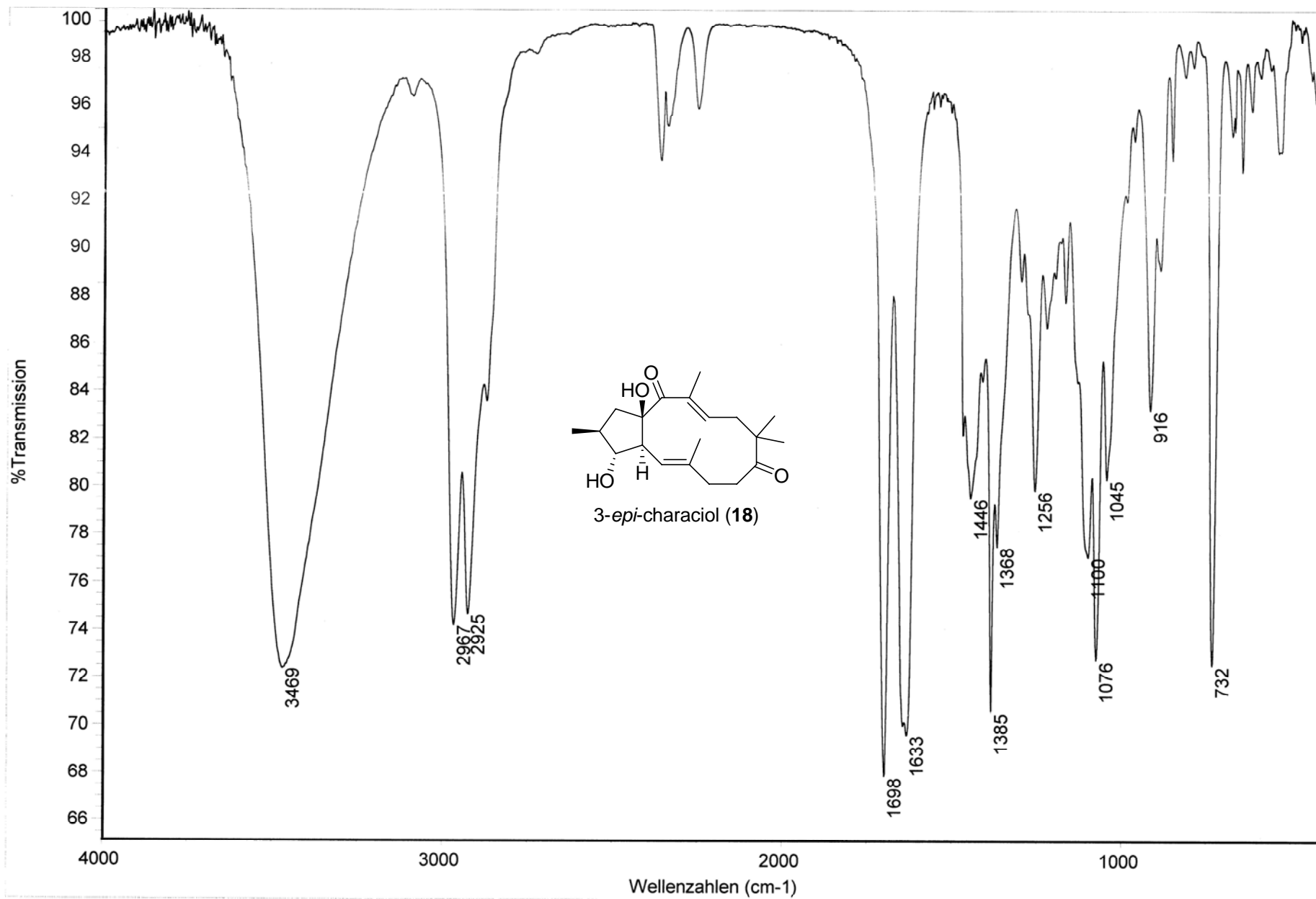


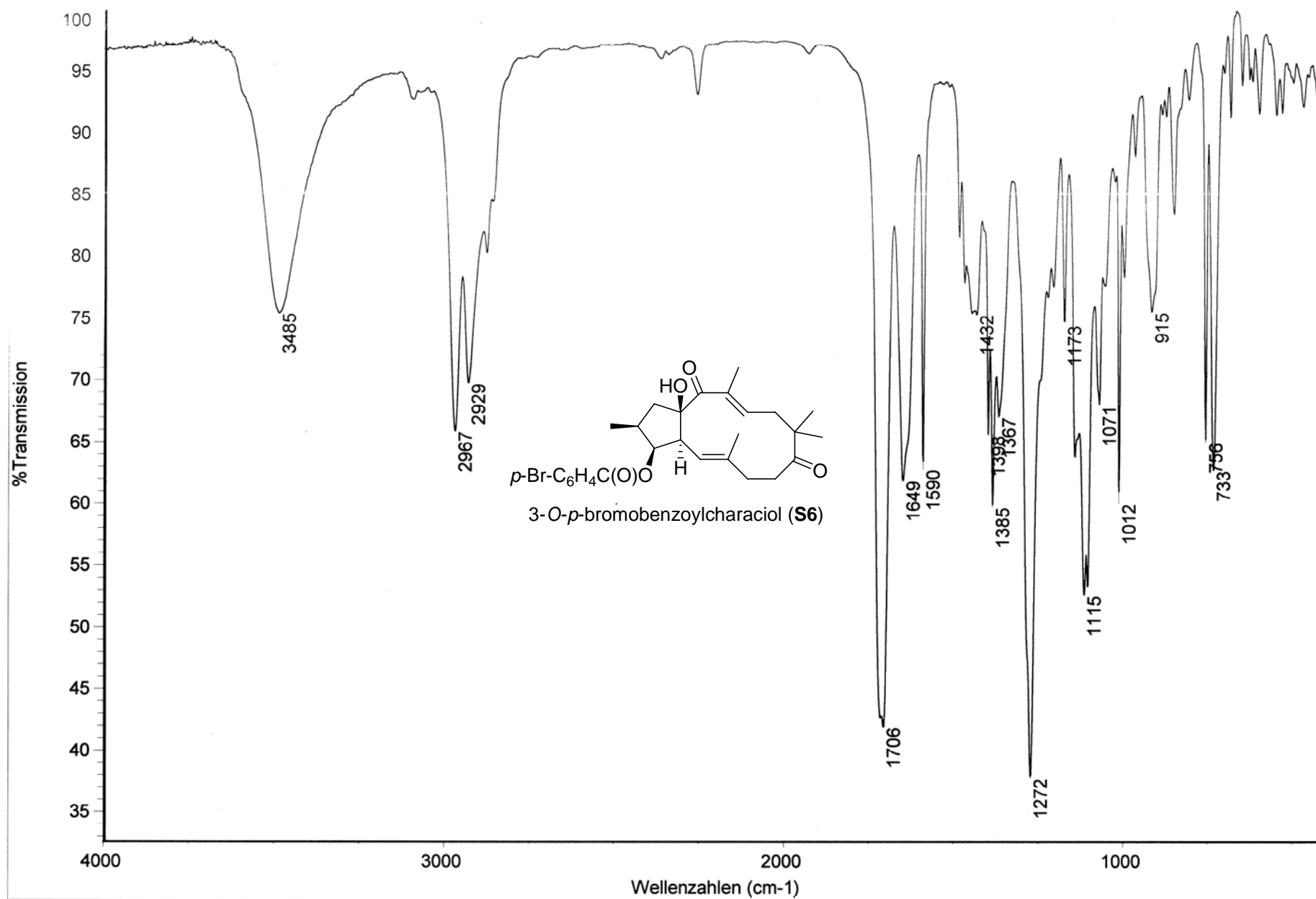




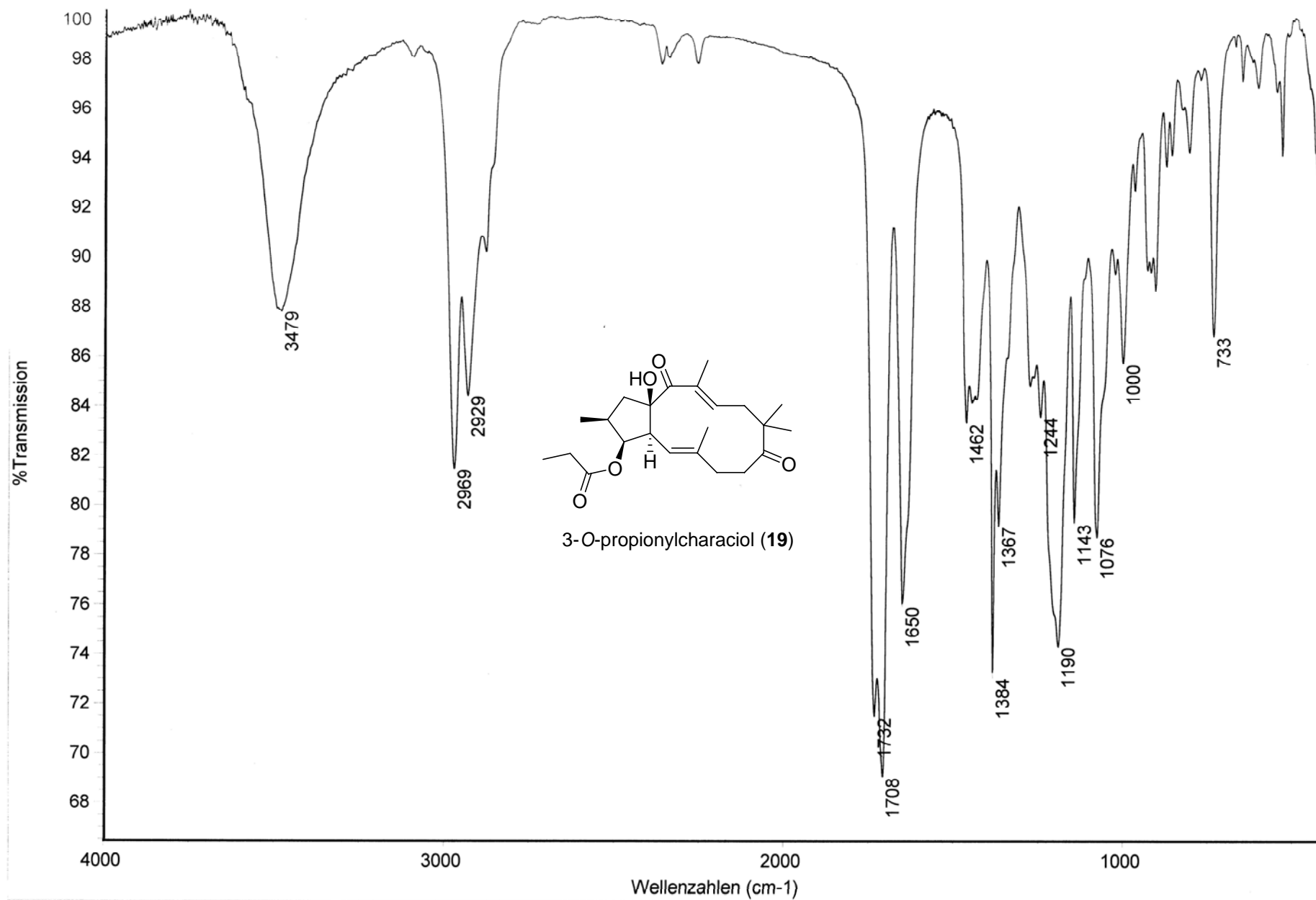


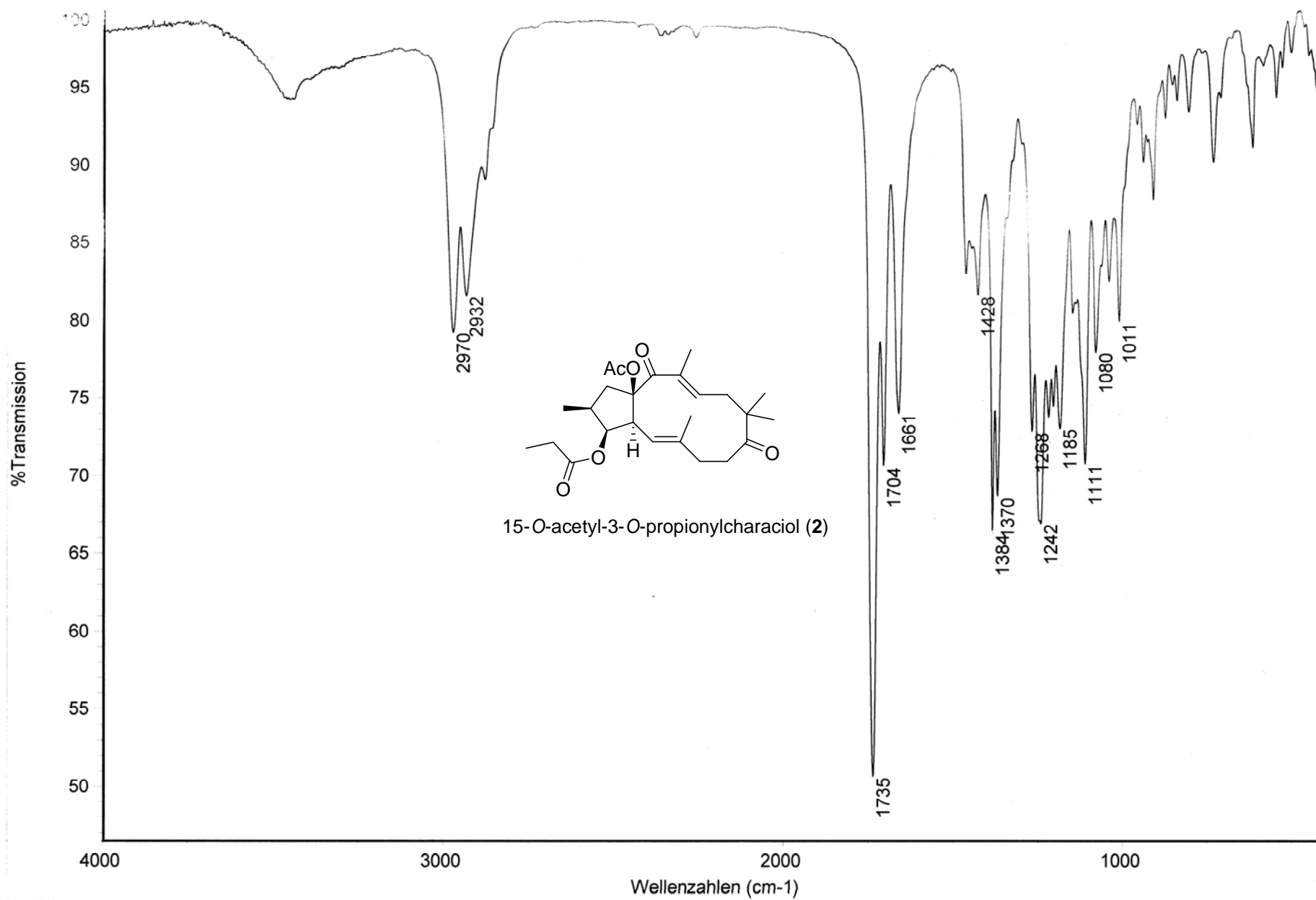


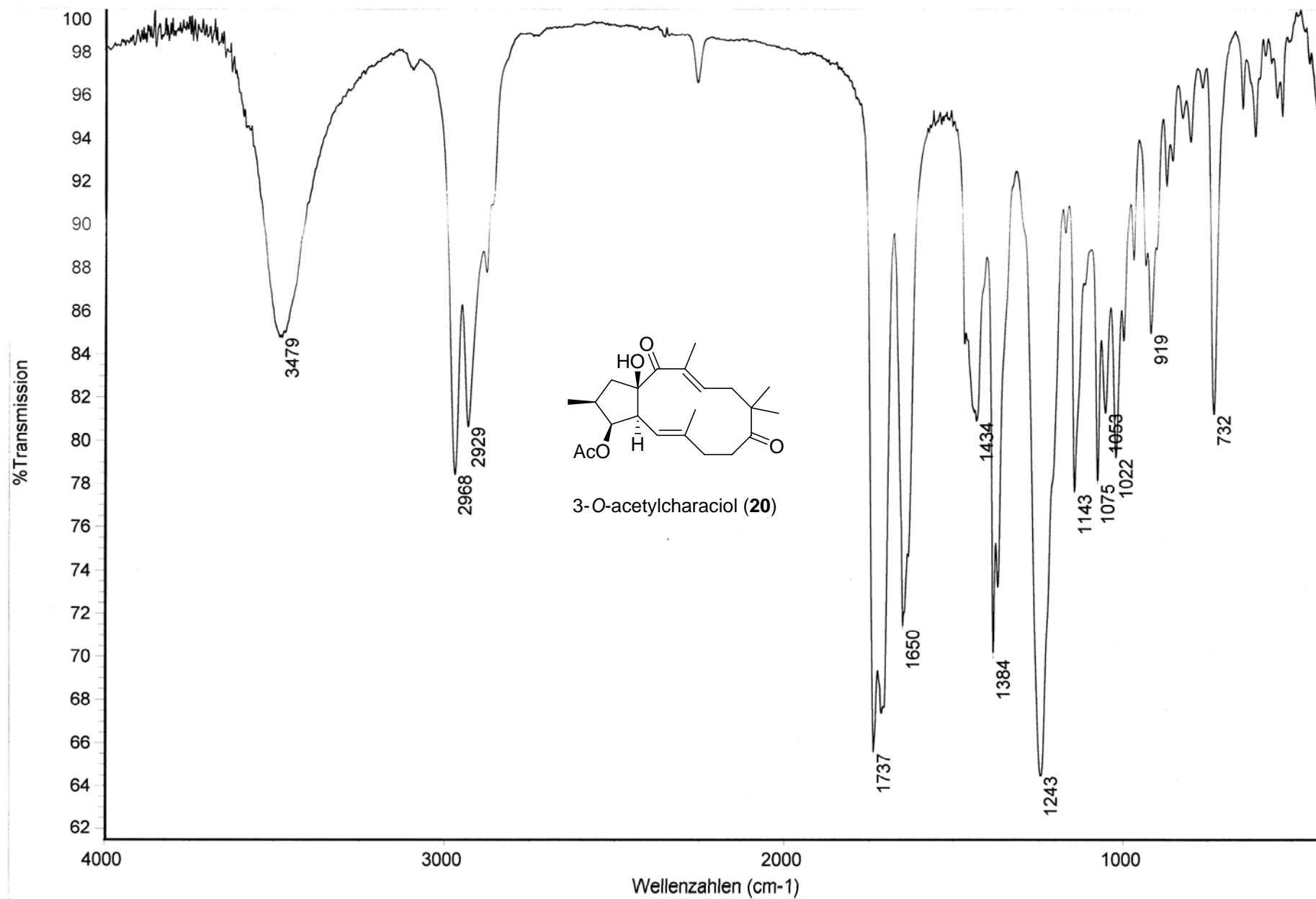


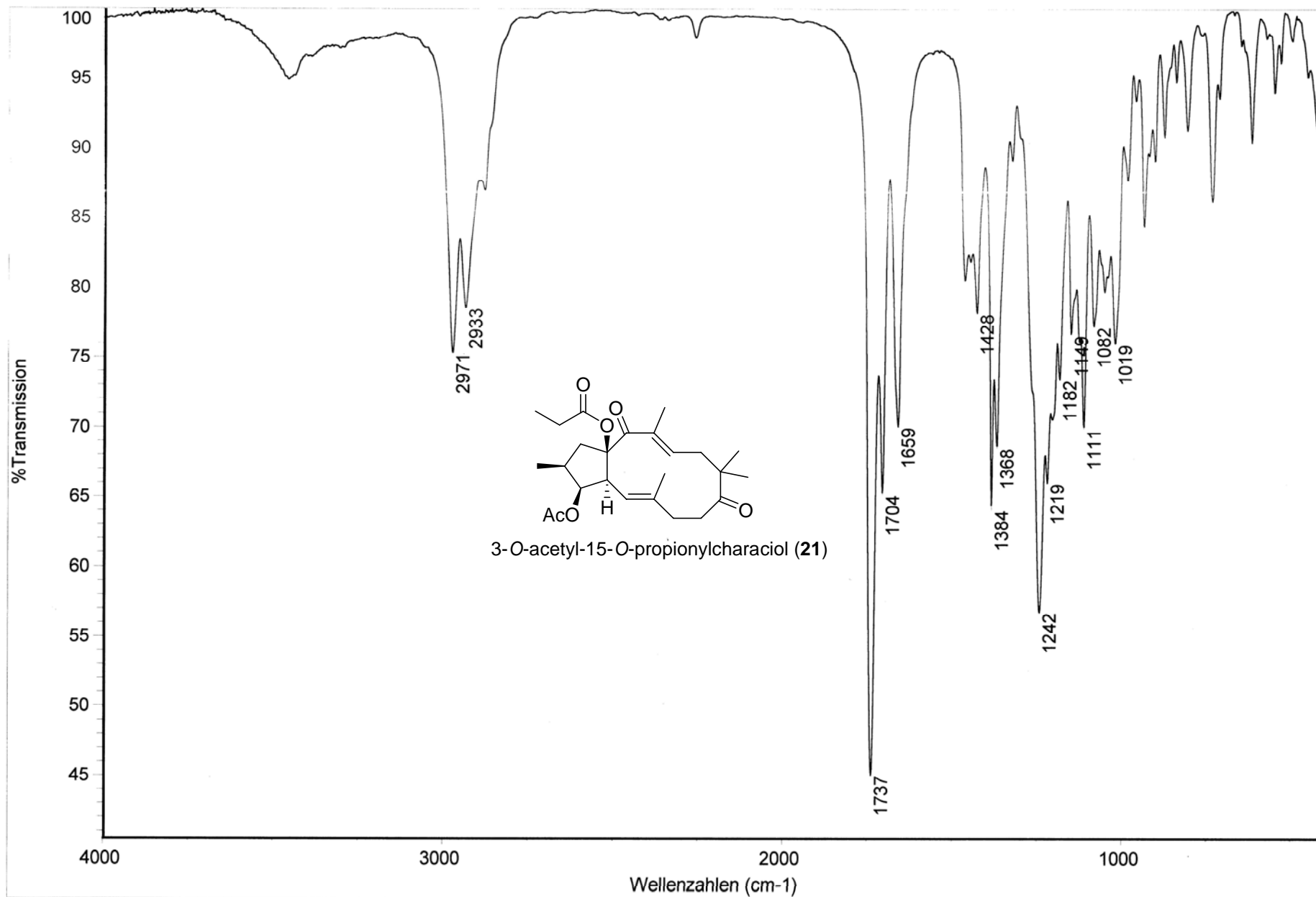












Elementaranalysenauftrag

Schmabel 3895

Auftraggeber

Tel.

12.03.08

Datum

CS346

Probenbezeichnung
(max. 7 Stellen)

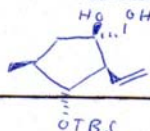
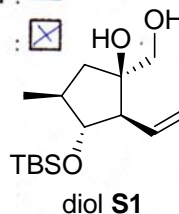
Die Substanz enthält:

 $C_{15}H_{30}O_3Si$ M Smp.: $57^\circ C$

auf Abruf ?

Sdp.: /

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☒

Einwaage:

theor.

prax.

a) 0.955

a

b

b) 1.265

% C: 62.89

62.8

62.7

% H: 10.55

10.7

10.2

% N: /

/

/

Hiesemann

Arbeitskreisleiter

18.3.08 M. Hiesemann

Datum der Ausführung

Elementaranalysenauftrag

Schmabel 3895

Auftraggeber

Tel.

14.03.08

Datum

CS347

Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

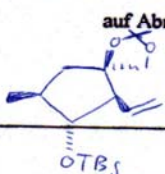
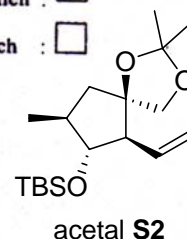
 $C_{18}H_{34}O_3Si$

M Smp.: ?

auf Abruf ?

Sdp.: ?

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☐

Einwaage:

theor.

prax.

a) 1.663

a

b

b) 1.633

% C: 66.21

66.2

66.4

% H: 10.49

10.6

10.4

% N: /

/

/

Hiesemann

Arbeitskreisleiter

17.3.08 M. Hiesemann

Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3835
Auftraggeber Tel.

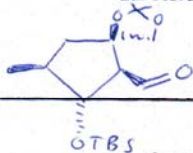
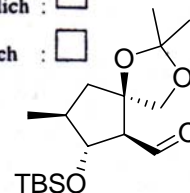
25.04.08
Datum

CS-HS17
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

C₁₇H₃₂O₄SiM Smp.: ?auf Abruf? XSdp.: ?

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☐

aldehyde 6

Einwaage:

theor.

prax.

a) 1.694

a

b

b) 1.711% C: 62.1562.162.1% H: 9.829.69.5% N: ///

Hiersmann
Arbeitskreisleiter

28.4.08 M. Hirs
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3835
Auftraggeber Tel.

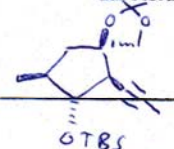
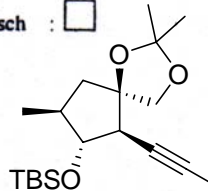
20.03.08
Datum

CS353
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

C₁₉H₃₄O₃SiM Smp.: ?auf Abruf? XSdp.: ?

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☐

alkyne 7

Einwaage:

theor.

prax.

a) 1.795

a

b

b) 1.908% C: 67.4067.167.2% H: 10.1210.110.2% N: ///

Hiersmann
Arbeitskreisleiter

2.4.08 M. Hirs
Datum der Ausführung

Elementaranalysenauftrag

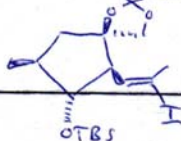
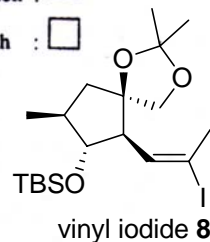
Schubel 3895
Auftraggeber Tel.26.03.08
DatumCS487X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält :

 $C_{13}H_{35}IO_3Si$ M
Smp.: ?auf Abruf ? ☒

Sdp.: ?

Bemerkungen :

Luftempfindlich : ☐Hygroskopisch : ☐

Einwaage :

theor.

prax.

a) 1.623

a

b

b) 1.792

% C : 48.92

48.9

48.8

% H : 7.56

7.3

7.2

% N : /

/

/

Häsemann
Arbeitskreisleiter2.10.08 M. Lüpfm
Datum der Ausführung

Elementaranalysenauftrag

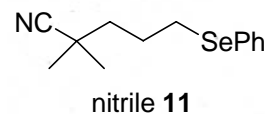
Schubel 3898
Auftraggeber Tel.25.07.07
DatumCS207
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält :

 $C_{13}H_{17}NSe$ M
Smp.: ?auf Abruf ? ☒

Sdp.: ?

Bemerkungen :

Luftempfindlich : ☐Hygroskopisch : ☐

Einwaage :

theor.

prax.

a) 2.140

a

b

b) 2.427

% C : 58.65

58.5

58.5

% H : 6.44

6.2

6.1

% N : 5.26

5.0

5.1

Häsemann
Arbeitskreisleiter3.8.07 M. Lüpfm
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3858
Auftraggeber Tel.

25.07.07
Datum

CS209
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält : $C_{13}H_{18}OSe$

M Smp.: ? auf Abruf ? X

Sdp.: ?

Bemerkungen : 

Luftempfindlich : ☐

Hygroskopisch : ☐

Einwaage :

theor.

prax.

a.) 2.216

a

b

b.) 2.368

% C : 57.99

57.8

57.7

% H : 6.74

6.9

6.9

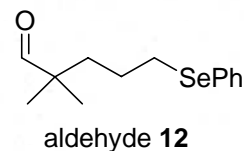
% N : /

/

/

Härsenmann
Arbeitskreisleiter

3.8.07 M. Lippm
Datum der Ausführung



Elementaranalysenauftrag

Schnabel 3858
Auftraggeber Tel.

25.07.07
Datum

CS210
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält : $C_{15}H_{22}OSe$

M Smp.: ? auf Abruf ? X

Sdp.: ?

Bemerkungen : 

Luftempfindlich : ☐

Hygroskopisch : ☐

Einwaage :

theor.

prax.

a.) 1.942

a

b

b.) 2.116

% C : 60.60

60.9

60.8

% H : 7.46

7.3

7.2

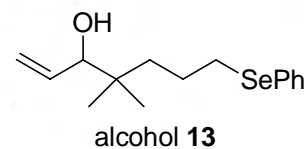
% N : /

/

/

Härsenmann
Arbeitskreisleiter

3.8.07 M. Lippm
Datum der Ausführung



Elementaranalysenauftrag

Schnabel 3838
Auftraggeber Tel.

25.07.07
Datum

CS217

Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

$C_{23}H_{30}O_2Se$

M Smp.: ?

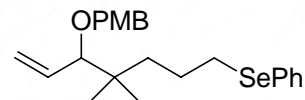
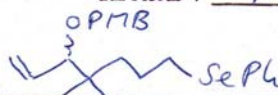
auf Abruf ? ☒

Luftempfindlich: ☐

Sdp.: ?

Hygroskopisch: ☐

Bemerkungen:



PMB-ether 5

Einwaage:

theor.

prax.

a) 1.880

a

b

b) 1.874

% C: 66.18

66.6

66.2

% H: 7.24

7.3

7.2

% N: /

/

/

Hiersmann
Arbeitskreisleiter

3.8.07 M. Diefen
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3835
Auftraggeber Tel.

15.07.08
Datum

CS4346

Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

$C_{42}H_{66}O_5SeSi$

M Smp.: ?

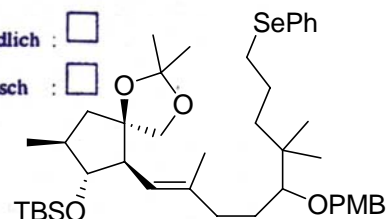
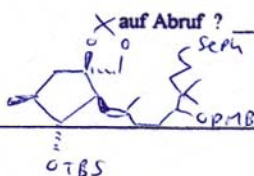
auf Abruf ? ☒

Luftempfindlich: ☐

Sdp.: ?

Hygroskopisch: ☐

Bemerkungen:



alkene 14

Einwaage:

theor.

prax.

a) 2.495

a

b

b) 1.362

% C: 66.55

66.7

66.5

% H: 8.78

9.6
fehlend

8.4

% N: /

/

/

Hiersmann
Arbeitskreisleiter

17.7.08 M. Diefen
Datum der Ausführung

Elementaranalysenauftrag

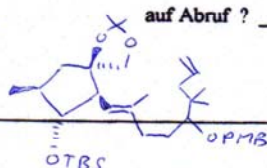
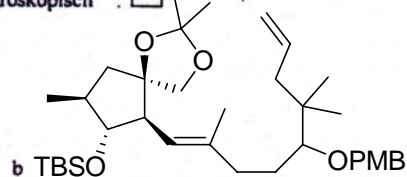
Schnabel 3895
Auftraggeber Tel.03.05.08
DatumC53916
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

 $C_{36}H_{60}O_5Si$ M
Smp.: ?auf Abruf ? ☒

Sdp.: ?

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☐

diene S3

Einwaage:

theor.

prax.

a) 1,445

a

b) 1,557

% C: 71.95

71.8

71.7

% H: 10.06

10.2

10.0

% N: /

/

/

Hiesemann
Arbeitskreisleiter14.5.08 M. Hiesemann
Datum der Ausführung

Elementaranalysenauftrag

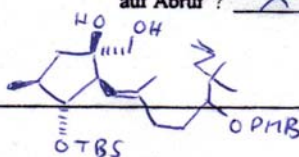
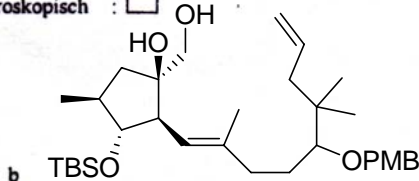
Schnabel 3895
Auftraggeber Tel.12.09.08
DatumC5464X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

 $C_{33}H_{56}O_5Si$ M
Smp.: ?auf Abruf ? ☒

Sdp.: ?

Bemerkungen:

Luftempfindlich: ☐Hygroskopisch: ☐

diol S4

Einwaage:

theor.

prax.

a) 1,684

a

b) 1,455

% C: 70.67

70.3

70.5

% H: 10.06

9.9

9.7

% N: /

/

/

Hiesemann
Arbeitskreisleiter17.9.08 M. Hiesemann
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3895
Auftraggeber Tel.

08.10.08
Datum

C5496X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält: C₃₃H₅₄O₅Si

M Smp.: ?

Sdp.: ?

Bemerkungen:

Einwaage:

a) 1,356

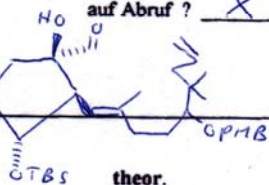
b) 1,194

% C: 70.92

% H: 9.74

% N: /

auf Abruf? X



theor.

prax.

a

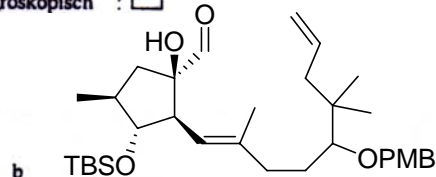
71,2

9,3

/

Luftempfindlich: ☐

Hygroskopisch: ☐



b

aldehyde 15

14.10.08 M. Jipfm
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3895
Auftraggeber Tel.

13.11.08
Datum

C5520X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält: C₃₆H₆₀O₅Si

M Smp.: ?

Sdp.: ?

Bemerkungen:

Einwaage:

a) 1,538

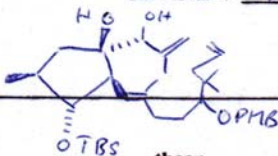
b) 2,259

% C: 71.95

% H: 10.06

% N: /

auf Abruf? X



theor.

prax.

a

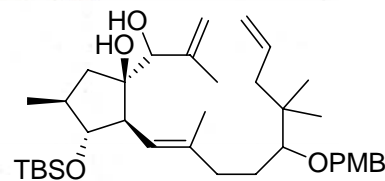
71,6

10,0

/

Luftempfindlich: ☐

Hygroskopisch: ☐



b

diol S5

20.11.08 M. Jipfm
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3895
Auftraggeber Tel.

24.11.08
Datum

C5527X
Probenbezeichnung
(max. 7 Stellen)

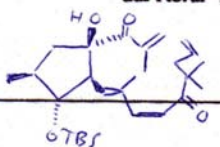
Die Substanz enthält: C₂₈H₄₈O₄Si

M Smp.: ?

auf Abruf? X

Sdp.: ?

Bemerkungen:



Einwaage:

theor.

prax.

a) 1,818

a

b

b) 1,588

% C: 70.54

70.5

70.5

% H: 10.15

10.0

9.8

% N: /

/

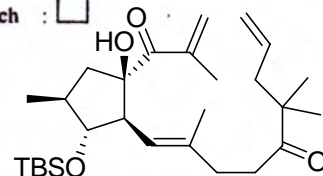
/

Heisenmann
Arbeitskreisleiter

28.11.08 M. K. [Signature]
Datum der Ausführung

Luftempfindlich: ☐

Hygroskopisch: ☐



diketone 16

Elementaranalysenauftrag

Schnabel 3895
Auftraggeber Tel.

10.03.09
Datum

C5538X
Probenbezeichnung
(max. 7 Stellen)

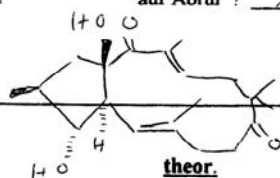
Die Substanz enthält: C₂₆H₃₀O₄

M Smp.: 173°C-184°C

auf Abruf? X

Sdp.: /

Bemerkungen:



Einwaage:

theor.

prax.

a) 1,286

a

b

b.)

% C: 71.82

71.5

% H: 9.04

9.0

% N: /

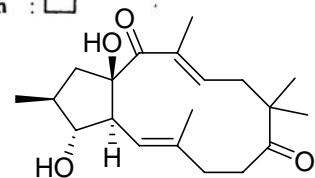
/

Heisenmann
Arbeitskreisleiter

12.3.09 M. K. [Signature]
Datum der Ausführung

Luftempfindlich: ☐

Hygroskopisch: ☐



3-epi-Characiol (18)

Elementaranalysenauftrag

Schnabel 3899
Auftraggeber Tel.

25.07.05
Datum

C5592X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält: $C_{27}H_{33}BrO_5$

M Smp.: 2 auf Abruf? X

Sdp.: 2

Bemerkungen:

Einwaage:

a) 1.782

b) 2.351

% C: 62.67

% H: 6.43

% N: /

theor.

prax.

a

62.5

6.5

/

Luftempfindlich: ☐

Hygroskopisch: ☐

$p\text{-Br-C}_6\text{H}_4\text{C(O)O}$

3-O-*p*-bromobenzoylcharaciol (S6)

b

62.4

6.2

/

Hiesemann
Arbeitskreisleiter

2.3.09 H. Kipfler
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3899
Auftraggeber Tel.

03.03.05
Datum

C5595X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält: $C_{20}H_{30}O_4$

M Smp.: 103 °C auf Abruf? X

Sdp.: /

Bemerkungen:

Einwaage:

a) 2.090

b) 1.788

% C: 71.82

% H: 9.04

% N: /

theor.

prax.

a

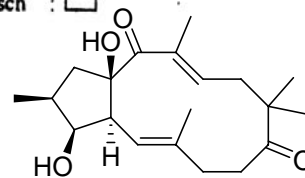
71.6

9.1

/

Luftempfindlich: ☐

Hygroskopisch: ☐



Characiol (3)

b

71.5

8.7

/

Hiesemann
Arbeitskreisleiter

6.3.09 H. Kipfler
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3859
Auftraggeber Tel.

19.02.08
Datum

C5551X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

$C_{25}H_{36}O_6$

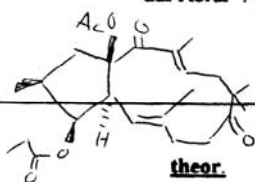
Smp.: 140 °C

auf Abruf? X

Sdp.: /

Bemerkungen:

Einwaage:



theor.

prax.

a) 1,700

a

b

15-O-acetyl-3-O-propionylcharaciol (2)

% C: 69.42

69.4

69.7

b) 2,414

% H: 8.33

8.2

8.8

% N: /

/

/

Heesemann
Arbeitskreisleiter

25.2.09 M. J. / M.
Datum der Ausführung

Elementaranalysenauftrag

Schnabel 3835
Auftraggeber Tel.

10.03.09
Datum

C5606X
Probenbezeichnung
(max. 7 Stellen)

Die Substanz enthält:

$C_{25}H_{36}O_6$

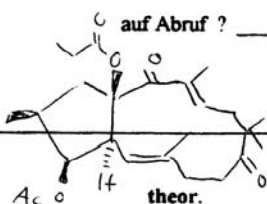
Smp.: 134 °C

auf Abruf? X

Sdp.: /

Bemerkungen:

Einwaage:



theor.

prax.

a) 1,756

a

b

3-O-acetyl-15-O-propionylcharaciol (21)

% C: 69.42

69.3

69.9

b) 2,455

% H: 8.33

8.2

8.5

% N: /

/

/

Heesemann
Arbeitskreisleiter

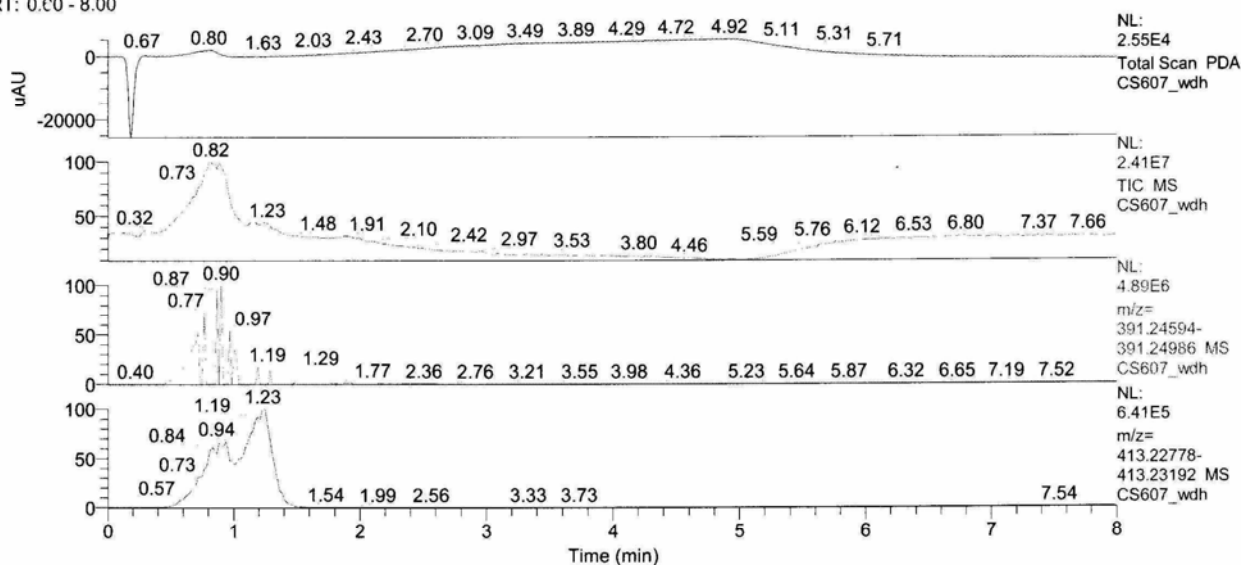
12.3.09 M. J. / M.
Datum der Ausführung

Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

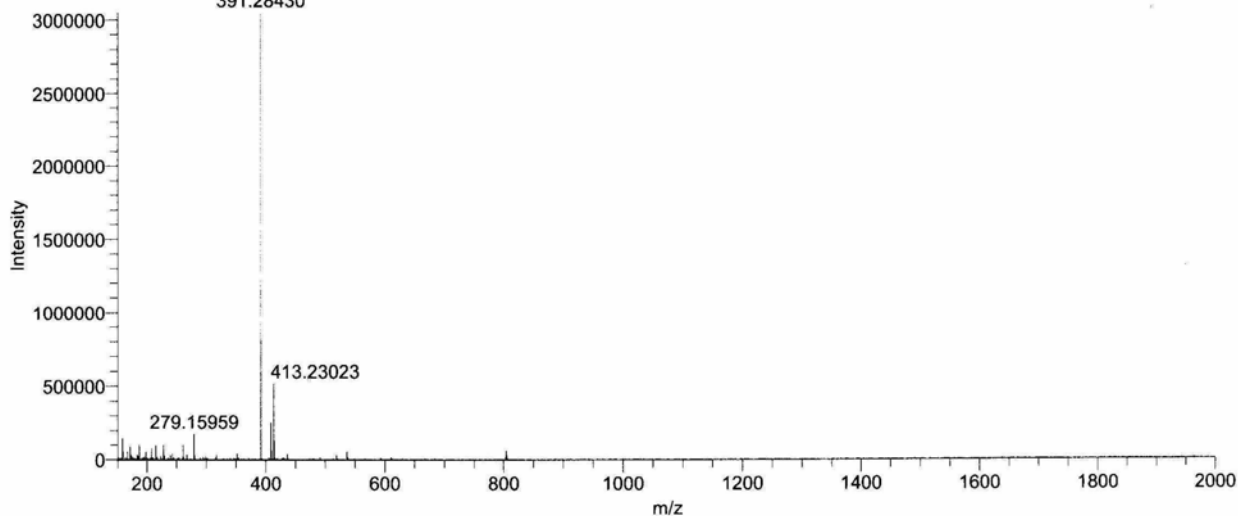
E:\Orbitrapdaten\20090323\CS607_wdh
HPLC-ESI-FTMS / Brockmeyer, Ismail
RT: 0.00 - 8.00

3/28/2009 10:12:07 AM

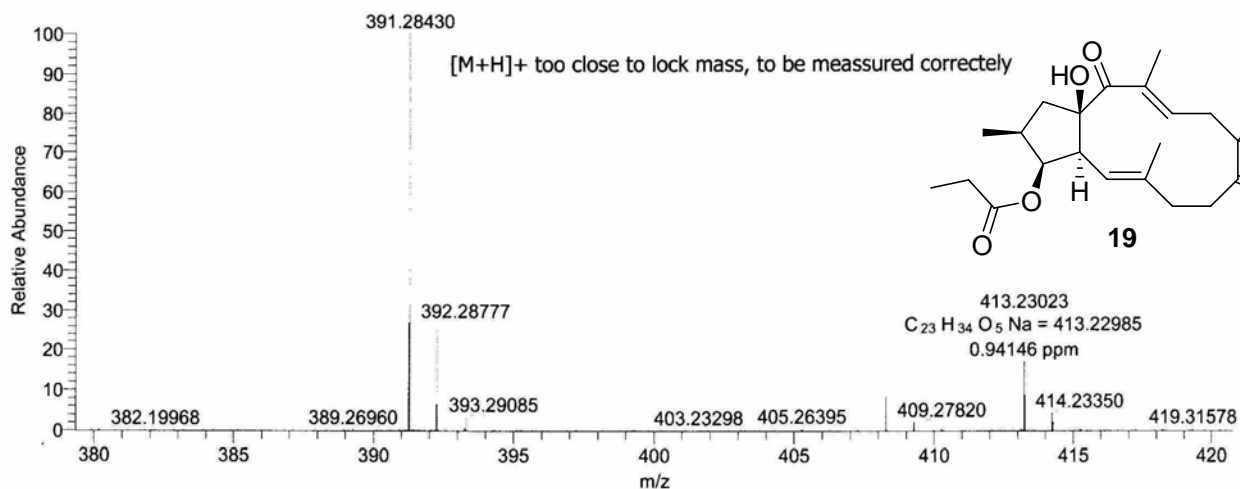
CS607



CS607_wdh #60-71 RT: 1.08-1.29 AV: 12 NL: 3.05E6
T: FTMS + c ESI Full ms [150.00-2000.00]



CS607_wdh #60-71 RT: 1.08-1.29 AV: 12 NL: 3.05E6
T: FTMS + c ESI Full ms [150.00-2000.00]

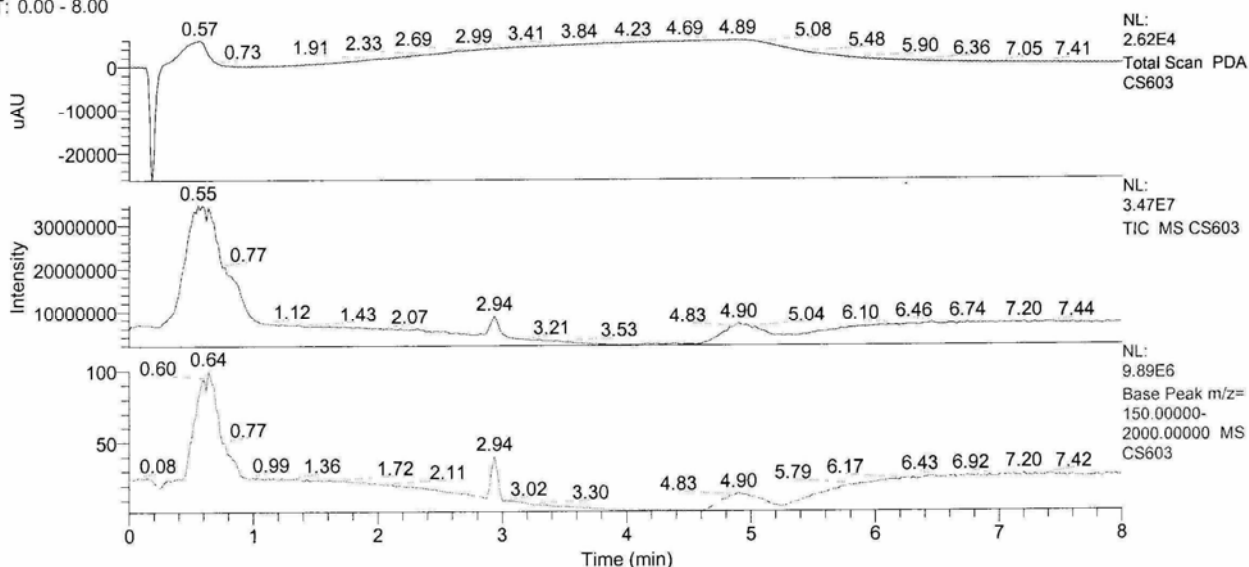


Total Synthesis of Jatrophone Diterpenes from *Euphorbia characias* – Supporting Information

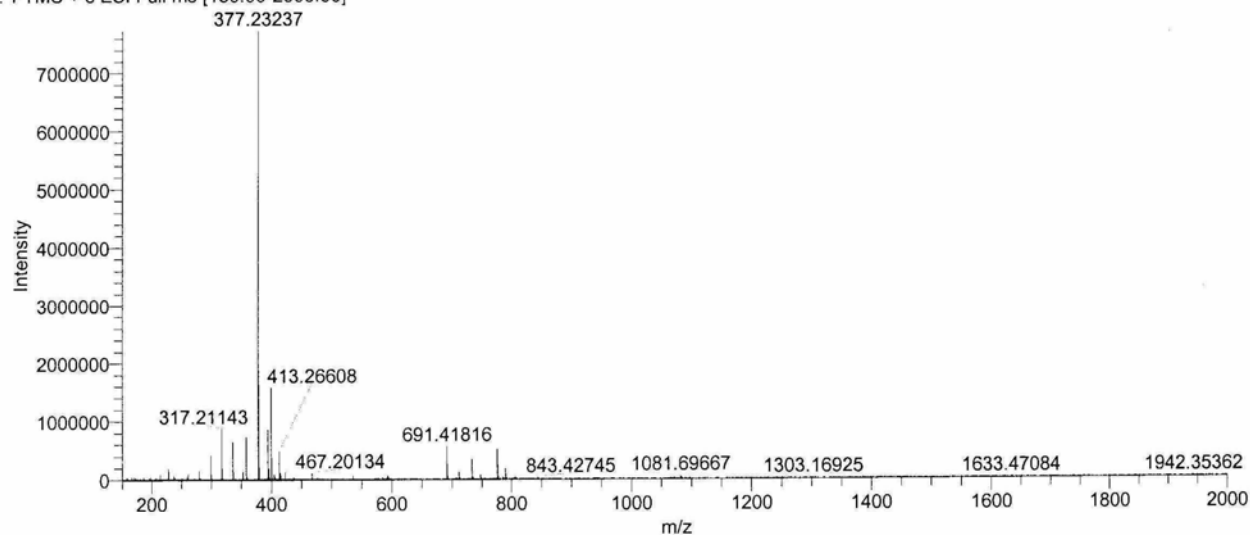
X:\20090323\CS603
HF LC-ESI-FTMS / Brockmeyer, Ismail
RT: 0.00 - 8.00

3/25/2009 8:14:11 PM

CS603 1/10



CS603 #27-42 RT: 0.52-0.77 AV: 16 NL: 7.73E6
T: FTMS + c ESI Full ms [150.00-2000.00]



CS603 #27-42 RT: 0.52-0.77 AV: 16 NL: 7.73E6
T: FTMS + c ESI Full ms [150.00-2000.00]

