Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Biomimetic regioselective and high-yielding Cu(I)-catalyzed dimerization of sinapate esters in green solvent Cyrene™: towards sustainable antioxidant and anti-UV ingredients

Matthieu M. Mention,[a] Amandine L. Flourat,[a] Cédric Peyrot [a] and Florent Allais[a]*

[a] URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 51110 Pomacle, France

* Corresponding author: florent.allais@agroparistech.fr

Table of Contents

1. General Information

Syringaldehyde, copper(I) bromide, aniline, pyridine, malonic acid, heptan-1-ol, *tert*-butanol, *iso*-propanol, gaïacol, sodium carbonate, methyl iodine, acetic anhydride, DIBAl-H, palladium on carbon (10wt. % loading), potassium persulfate, Laccase from *Trametes versicolor* and Horseradish peroxidase (type II and IV) were purchased from Sigma Aldrich. Meldrum's acid, ABTS and 2-ethylhexan-1-ol were purchased from TCI. HCl_{conc} and solvents were purchased from Fisher scientific and used as received. Cyrene was kindly offered by Circa Group (Australia). All chemicals were used directly without purification.

Chromatographic purifications of products were accomplished using a flash-prep LC system puriFlash® 4100 from Interchim with prepacked silica column (30 µm, Interchim PF-Si30-HP), dual wavelength collection (λ = 254 and 320 nm) and a mixture of cyclohexane/ethyl acetate as eluant. ^{1}H NMR spectra were recorded on a Brucker Fourier 300 (300 MHz) and were calibrated with residual Acetone-*d6*, DMSO-*d6* or $CDCl_3$ protons signals at δ 2.05, 2.50 or 7.26 ppm respectively. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = doublet of doublets, td = triplet of doublets and m = multiplet), integration, coupling constant (Hz) and assignment. ^{13}C NMR spectra were recorded on a Brucker Fourier 300 (75 MHz) and were calibrated with Acetone-*d6*, DMSO-*d6* or $CDCl_3$ signals at δ 29.84, 39.52 or 77.16 ppm respectively. Data are reported as follows: chemical shift (δ ppm) and attribution. All NMR assignments were made using COSY, HMBC and HSQC spectrum. Solvents were dried on a MBRAUN-SPS-800. IR spectra were recorded on an Agilent Cary 630 FTIR Spectrometer and are reported in frequency of absorption (cm^{-1}). UV/Vis spectra were recorded in ethanol (C = 10^{-5} mol/L) on an Agilent Cary 60 UV-Vis with 1 cm cuvette made of quartz and are reported in wavelength (nm). Melting points were recorded on a Mettler Toledo MP50 Melting Point System ($T_{initial}$: 40 °C; Heating: 2 °C/min until 170 °C) with ME-18552 sample tubes. HPLC analysis were carried out on a Dionex UltiMate 3000 equipped with a Zorbax Eclipse Plus C18 column (2.1*50 mm*1.8 µm), a DAD and a Corona ultra RS both at λ = 320 nm (flow rate set at 0.6 $mL.min^{-1}$, oven temperature at 30 °C, and gradient applied: H_2O/CH_3CN from 75/25 to 70/30 in 18 min). High resolution mass spectrometries were performed by the PlAneT platform at URCA on a Micromass GC-TOF. Modde v.12.0 software (Umetrics AB, Sweden) was used to generate the design of experiments and analyze the experimental data by Response Surface Methodology (RSM), based on a 4 factors and 3 central points cubic centered face (CCF) design.

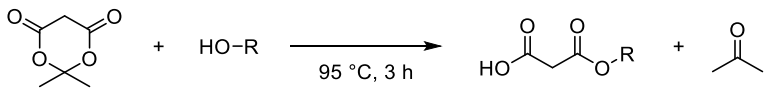
ABTS assays were adapted from Re et al.[1]. In summary, $ABTS^{\bullet+}$ solution was prepared in water with ABTS (C = 7 $mmol.L^{-1}$) and potassium persulfate (final concentration 2.45 $mmol.L^{-1}$). Mixture was left to agitate in the dark for 16h and diluted by 50 with ethanol to reach around 0.7 of absorbance at 734 nm and 37 °C. In a 96 wells microplate, a mixture containing 10 µL of antiradical solution (final concentration in microwell were 2 to 60 $\mu mol.L^{-1}$) and 190 µL of ABTS solution incubated at 37 °C. Absorbance was recorded at 734 nm until stabilization of the signal (6 min). To determine the exact value of inhibition, a reference (190 µL of ABTS solution with 10 µL of Ethanol) and a blank (200 µL of ethanol) were performed at the same time as each experiment. All experiments were carried out on an Epoch 2 from Biotek using 96-wells microplate.

2. Synthesis

2.1. Synthesis of malonate mono-esters

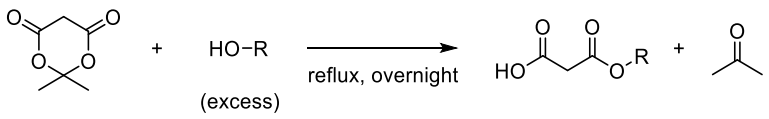
Malonate mono-esters were synthesized following methods described in the literature[2,3]. All malonate mono-esters were used without further purification for the synthesis of corresponding sinapate esters.

2.1.1. General Procedure (GP1)



Meldrum's acid (5.0 g, 35 mmol) and the corresponding alcohol (35 mmol, 1 eq) were melted at 95 °C and agitated for 3 h. After cooling at r.t., the reaction mixture was partitioned between ethyl acetate and saturated $NaHCO_3$. The aqueous layer was acidified until pH = 1 with concentrated HCl and extracted with ethyl acetate. The resulting organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated.

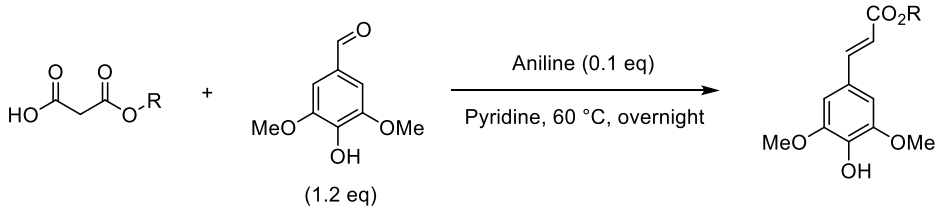
2.1.2. General Procedure (GP2)



Meldrum's acid (4.0 g, 27.8 mmol) and an excess of alcohol were heated at reflux overnight. After cooling at r.t., the excess of alcohol was evaporated under reduced pressure.

2.2. Synthesis of sinapate esters

2.2.1. General Procedure (GP3)



The corresponding malonate mono-esters (8.6 mmol, 1.5 M), syringaldehyde (1.89 g, 10.4 mmol) and aniline (79 µL, 0.86 mmol) were mixed in pyridine (5.7 mL). The reaction mixture was stirred at 60 °C overnight. After cooling at r.t., the reaction was partitioned between ethyl acetate and 1M aqueous HCl. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated before being purified by flash chromatography using cyclohexane/ethyl acetate.

2.2.2. Ethyl sinapate

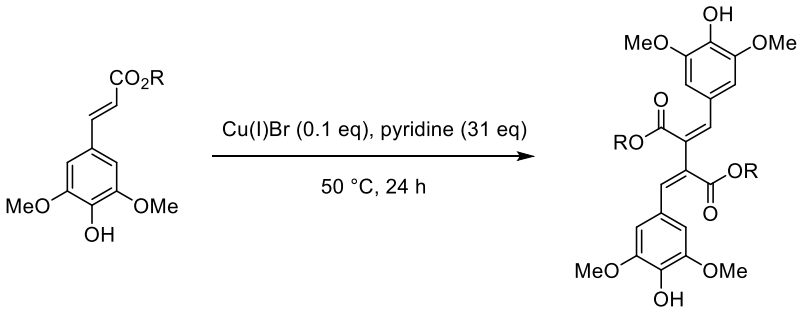
Ethyl sinapate was synthesized following method described by Jaufurally et al.[4]

2.2.3. Sinapoyl di-*tert*-butyl malate

Sinapoyl di-*tert*-butyl malate was synthesized following method described by Allais et al.[5]

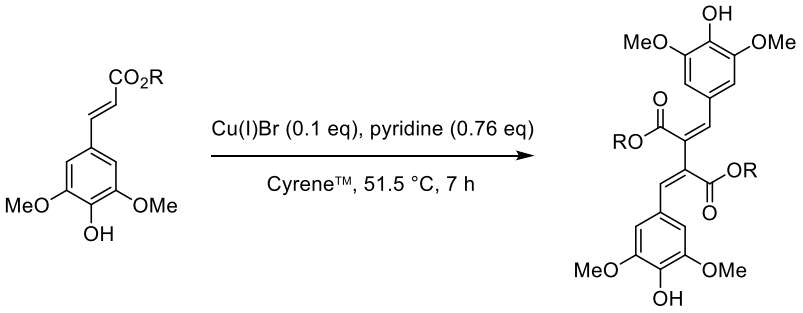
2.3. Synthesis of sinapate esters β-β' dehydrodimers

2.3.1. Initial Procedure



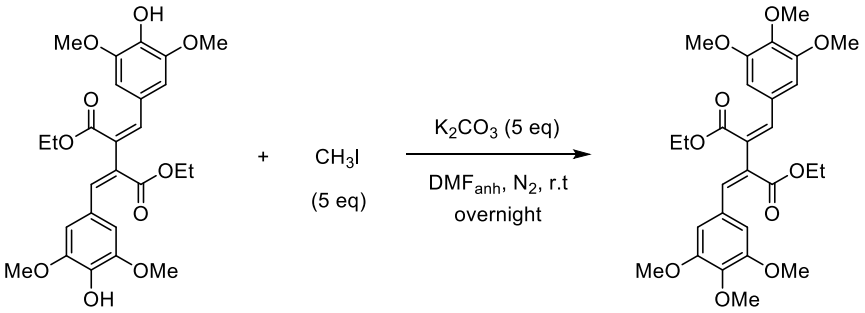
The corresponding sinapate ester (32 mmol) and Cu(I)Br (0.459 g, 3.2 mmol) were dissolved in pyridine (80 mL, 993 mmol) and warmed up at 50 °C. The reaction was stirred for 24 h in an opened flask. After cooling at r.t., the reaction mixture was diluted with ethyl acetate and washed with 1M aqueous HCl. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated before being purified by flash chromatography using cyclohexane/ethyl acetate.

2.3.2. Optimized Procedure



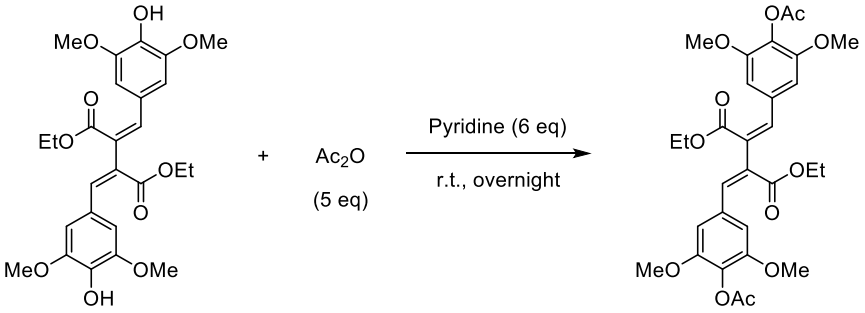
The corresponding sinapate ester (1 mmol, 1.81 M), Cu(I)Br (14.3 mg, 0.1 mmol) and pyridine (61 µL, 0.76 mmol) were mixed in Cyrene™ (552 µL). The reaction was stirred at 51.5 °C for 7 h in an opened flask. After cooling at r.t., the reaction mixture was diluted with ethyl acetate and washed with 1M aqueous HCl and water. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to afford the corresponding β-β' dimer.

2.4. Methylation of ethyl sinapate β-β' dehydrodimer



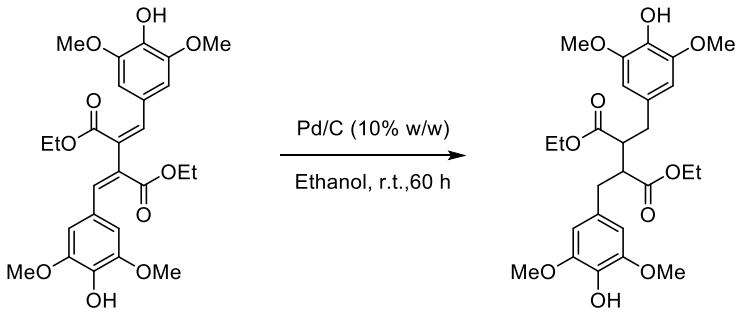
Ethyl sinapate β-β' dehydrodimer (201 mg, 0.40 mmol, 0.5 M) was dissolved in anhydrous DMF (800 µL) and placed under N_2. After 10 min of stirring, K_2CO_3 (276 mg, 2 mmol) and methyl iodide (125 µL, 2 mmol) were added and the reaction was kept agitating under N_2 at r.t. overnight. The mixture was then diluted in 1M aqueous HCl and partitioned between ethyl acetate and H_2O. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated.

2.5. Acetylation of ethyl sinapate β-β' dehydrodimer



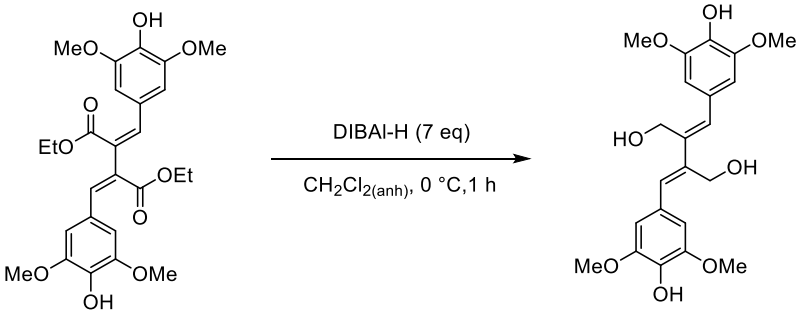
Ethyl sinapate β-β' dehydrodimer (201 mg, 0.40 mmol) was dissolved in acetic anhydride (189 µL, 2 mmol) and pyridine (193 µL, 2.4 mmol) and stirred at r.t. overnight. The resulting precipitate was filtered and washed with 0.1M aqueous HCl and water, before being dried under vacuum.

2.6. Hydrogenation of ethyl sinapate β-β' dehydrodimer



Ethyl sinapate β-β' dehydrodimer (1 g, 2 mmol) was dissolved in ethanol and stirred under N_2 for 10 min. Palladium on carbon (100 mg, 10% w/w) was added and the mixture was stirred 10 more minutes before being placed under H_2 for 60 h. The reaction was flushed with N_2 and filtered over a pad of Celite® prior concentration under reduced pressure.

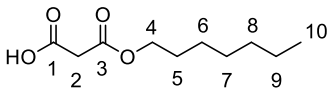
2.7. Ester reduction of ethyl sinapate β-β' dehydrodimer



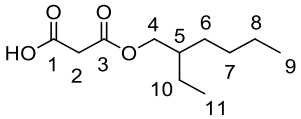
Ethyl sinapate β-β' dehydrodimer (2 g, 4 mmol, 0.1 M) was dissolved in anhydrous dichloromethane under N_2. A solution of DIBAl-H (27.7 mL, 27.7 mmol, 1 M in CH_2Cl_2) was added dropwise at 0 °C over 15 min. After 1 h, reaction was stopped by adding 15 mL of ethanol before being concentrated. The crude oil was partitioned between water and ethyl acetate. Organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated before being purified by flash chromatography using cyclohexane/ethyl acetate.

3. Compounds Characterizations

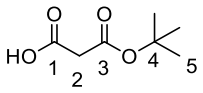
3.1. Malonate mono-ester



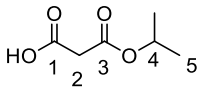
GP1 was followed with heptan-1-ol to obtain **monoheptyl malonate** as a colorless oil (77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6 Hz, H_{10}), 1.29 (m, 8H, $H_{6,7,8,9}$), 1.65 (m, 2H, H_5), 3.44 (s, 2H, H_2), 4.17 (t, 2H, J = 6.7 Hz, H_4); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 14.2 (C_{10}), 22.7 (C_9), 25.8 (C_8), 28.5 (C_5), 29.0 (C_7), 31.8 (C_6), 40.7 (C_2), 66.4 (C_4), 167.5 (C_3), 171.11 (C_1); **IR** (FTIR): 2926, 2856, 1714, 1463, 1410, 1318, 1150 cm^{-1}; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{10}H_{18}O_4Na$, 225.1103; found, 225.1103.



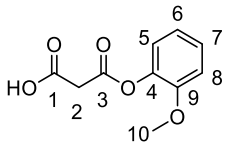
GP1 was followed with 2-ethylhexan-1-ol to obtain **mono-2-ethylhexyl malonate** as a light-yellow oil (83% yield). **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 0.85 (m, 6H, $H_{9,11}$), 1.29 (m, 8H, $H_{6,7,8,10}$), 1.54 (m, 1H, H_5), 3.36 (s, 2H, H_2), 3.97 (s, 2H, H_4), 12.76 (s, 1H, H_{COOH}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 10.8 (C_9), 14.0 (C_{11}), 22.4 (C_8), 23.1 (C_{10}), 28.3 (C_7), 29.7 (C_6), 38.1 (C_5), 41.7 (C_4), 66.6 (C_2), 167.0 (C_3), 168.1 (C_1); **IR** (FTIR): 2958, 2928, 2861, 1717, 1461, 1410, 1382, 1318, 1267, 1149 cm^{-1}; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{11}H_{20}O_4Na$, 239.1259; found, 239.1262.



GP2 was followed with *tert*-butanol to obtain **mono-*tert*-butyl malonate** as a pale-yellow oil (97% yield). Characterization data were identical with those already described[6].

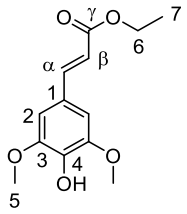


GP2 was followed with *iso*-propanol to obtain **mono-*iso*-propyl malonate** as a pale-yellow oil (76% yield). Characterization date were identical with those already described[7].

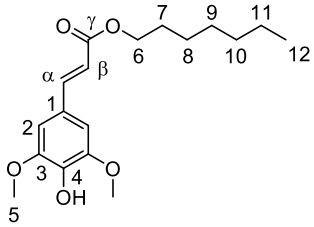


GP1 was followed with gaïacol to obtain **monogaïacol malonate** as a white crystal (60% yield). Characterization data were identical with those already described[8].

3.2. Sinapate esters

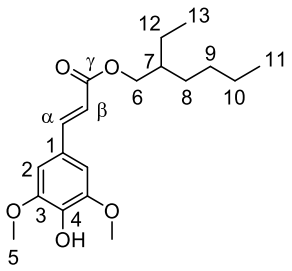


Ethyl sinapate was synthesized in two steps following methods from Jaufurally et al.[4] (80% global yield). Characterization data were identical with those already described[4].

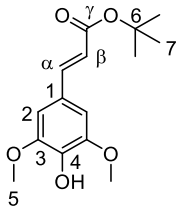


GP3 was followed with monoheptyl malonate to obtain **heptyl sinapate** as a brown oil (72% yield). **^{1}H NMR** (300 MHz, Acetone-*d6*): δ 0.77 (t, 3H, J = 6.8 Hz, H_{12}), 1.23 (m, 8H, $H_{8,9,10,11}$), 1.58 (m, 2H, H_7), 3.79 (s, 6H, H_5), 4.08 (t, 2H, J = 6.7 Hz, H_6), 6.19 (d, 1H, J = 15.9 Hz, H_β), 6.65 (s, 2H, H_2), 7.47 (d, 1H, J = 15.9 Hz, H_α); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 14.1 (C_{12}), 22.6 (C_{11}), 26.0 (C_{10}), 28.8 (C_7), 29.0(C_9), 31.8 (C_8), 56.3 (C_5), 64.7 (C_6), 105.0 (C_2), 116.0 (C_β), 125.9 (C_1), 137.1 (C_4), 144.9 (C_α), 147.2 (C_3), 167.3 (C_γ); **IR** (FTIR): 3406, 2925, 2853, 1700, 1631, 1601, 1511, 1455, 1424, 1375, 1337, 1279, 1252, 1214,

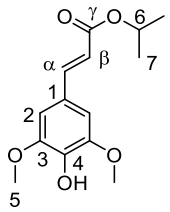
1149, 1109 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 241, 330 nm; **HRMS** (*m/z*) $[M+H]^+$ calcd for $C_{18}H_{27}O_5$, 323.1858; found, 323.1855.



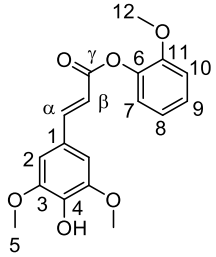
GP3 was followed with mono-2-ethylhexyl malonate to obtain **2-ethylhexyl sinapate** as a yellow-orange oil (66% yield). **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 0.88 (t, 6H, J = 7.4 Hz, $H_{11,13}$), 1.34 (m, 8H, $H_{8,9,10,12}$), 1.59 (m, 1H, H_7), 3.80 (s, 6H, H_5), 4.05 (dd, 2H, *J* = 5.7, 2.0 Hz, H_6), 6.53 (d, 1H, J = 15.9 Hz, H_β), 7.03 (s, 1H, H_2), 7.54 (d, 1H, J = 15.9 Hz, H_α), 9.00 (s, 1H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 10.9 (C_{11}), 14.0 (C_{13}), 22.5 (C_{10}), 23.2 (C_{12}), 28.4 (C_9), 29.8 (C_8), 38.4 (C_7), 56.1 (C_5), 65.7 (C_6), 106.2 (C_2), 114.9 (C_β), 124.4 (C_1), 138.2 (C_4), 145.4 (C_α), 148.0 (C_3), 168.9 (C_γ); **IR** (FTIR): 3407, 2928, 2858, 1699, 1631, 1598, 1511, 1455, 1424, 1377, 1337, 1278, 1252, 1214, 1148, 1109 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 240, 332 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{19}H_{28}O_5Na$, 359.1834; found, 359.1835.



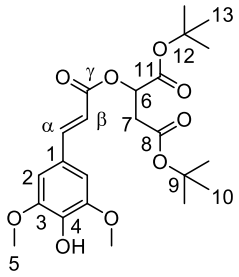
GP3 was followed with mono-*tert*-butyl malonate to obtain ***tert*-butyl sinapate** as a pale-yellow powder (56% yield). **mp**: 68 – 71 °C; **^{1}H NMR** (300 MHz, Acetone-*d6*): δ 1.46 (s, 9H, H_7), 3.85 (s, 6H, H_5), 6.29 (d, 1H, J = 15.9 Hz, H_β), 6.95 (s, 2H, H_2), 7.46 (d, 1H, J = 15.9 Hz, H_α); **^{13}C NMR** (75 MHz, Acetone-*d6*): δ 28.4 (C_7), 56.6 (C_5), 80.1 (C_6), 106.5 (C_2), 118.0 (C_β), 126.2 (C_1), 139.1 (C_4), 145.0 (C_α), 148.8 (C_3), 166.9 5 (C_γ); **IR** (FTIR): 3388, 2970, 2933, 1706, 1631, 1598, 1511, 1463, 1424, 1367, 1333, 1308, 1248, 1222, 1133, 1096 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 204, 238, 327 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$, 303.1208; found, 303.1207.



GP3 was followed with mono-*iso*-propyl malonate to obtain ***iso*-propyl sinapate** as a pale-yellow oil (73% yield). Characterization data were identical to those already described[9].

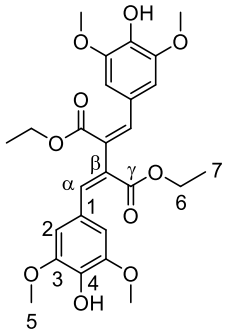


GP3 was followed with monogaïacol malonate to obtain **gaïacol sinapate** as a yellow-orange solid (55% yield). **mp**: 158 – 160 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 3.77 (s, 3H, H_{12}), 3.82 (s, 6H, H_5), 6.78 (d, 1H, *J* = 15.9 Hz, H_β), 6.97 (td, 1H, *J* = 7.7, 1.5 Hz, H_7), 7.14 (m, 4H, $H_{2,8,9}$), 7.25 (td, 1H, *J* = 7.7, 1.5 Hz, H_{10}), 7.73 (d, 1H, *J* = 15.9 Hz, H_α), 9.08 (s, 1H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 55.7 (C_{12}), 56.1 (C_5), 106.6 (C_2), 112.8 (C_8), 113.7 (C_β), 120.6 (C_7), 123.0 (C_9), 124.3 (C_1), 126.8 (C_{10}), 138.7 (C_4), 139.5 (C_6), 147.3 (C_α), 148.1 (C_3), 151.1 (C_{11}), 164.8 (C_γ); **IR** (FTIR): 3377, 3062, 3021, 2936, 2842, 1716, 1603, 1496, 1458, 1426, 1380, 1338, 1307, 1286, 1248, 1213, 1154, 1106 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 201, 220, 242, 337 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{18}H_{18}O_6Na$, 353.1001; found, 353.1002.

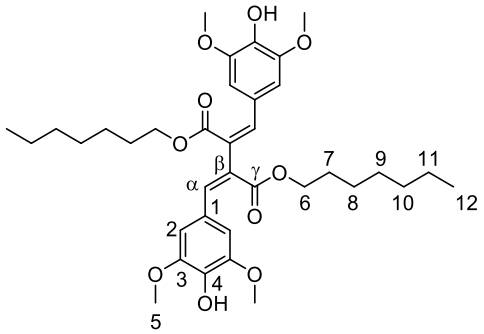


Sinapoyl di*tert*-butyl malate was synthesized as a yellow oil in 5 steps following methods from Allais et al.[5] (33% global yield). **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 1.41 (s, 18H, $H_{10,13}$), 2.79 (m, 2H, H_7), 3.81 (s, 6H, H_2), 5.25 (m, 1H, H_6), 6.60 (d, 1H, J = 15.8 Hz, H_β), 7.06 (s, 2H, H_2), 7.61 (d, 1H, J = 15.8 Hz, H_α), 9.04 (s, 1H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*) δ 27.5 (C_{10}), 27.7 (C_{13}), 37.0 (C_7), 68.7 (C_6), 80.9 (C_9), 81.9 (C_{12}), 106.4 (C_2), 113.7 (C_β), 124.2 (C_1), 138.6 (C_4), 146.7 (C_α), 148.1 (C_3), 165.8 (C_γ), 167.7 (C_8), 168.2 (C_{11}); **IR** (FTIR): 3421, 2976, 2935, 1711, 1631, 1599, 1512, 1456, 1367, 1218, 1138, 1109; **UV/Vis** (Ethanol): λ_{max} 242, 334 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{23}H_{32}O_9Na$, 475.1944; found, 475.1950.

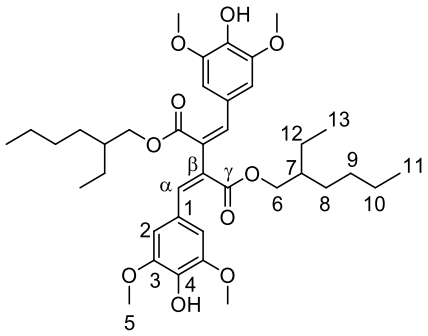
3.3. Sinapate esters β-β' dimers



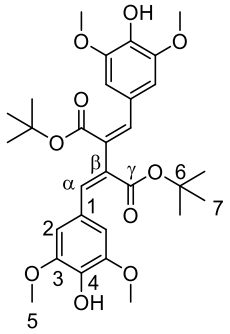
Dimerization of ethyl sinapate led to **ethyl sinapate β-β' dehydrodimer (8)** as a yellow powder (62% non-optimized yield / 89% optimized yield). **mp**: 98 – 101 °C; **^{1}H NMR** (300 MHz, Acetone-*d6*): δ 1.12 (t, 6H, *J* = 7.1 Hz, H_7), 3.76 (s, 12H, H_5), 4.14 (q, 4H, *J* = 7.0 Hz, H_6), 6.96 (s, 4H, H_2), 7.82 (s, 2H, H_α); **^{13}C NMR** (75 MHz, Acetone-*d6*): δ 14.6 (C_7), 56.6 (C_5), 61.3 (C_6), 108.8 (C_2), 126.2 (C_β), 126.6 (C_1), 139.0 (C_4), 142.7 (C_α), 148.6 (C_3), 167.6 (C_γ); **IR** (FTIR): 3525, 3263, 2956, 1693, 1580, 1510, 1452, 1329, 1212, 1152, 1102, 1028 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 203, 243, 331 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{26}H_{30}O_{10}Na$, 525.1737; found, 525.1740.



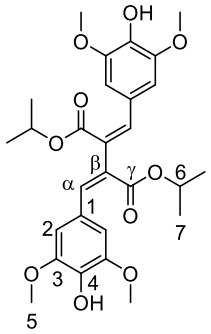
Dimerization of heptyl sinapate led to **heptyl sinapate β-β' dehydrodimer (9)** as a yellow-brown oil (64% non-optimized yield / 90% optimized yield). **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 0.82 (t, 6H, J = 6.9 Hz, H_{12}), 1.16 (m, 16H, $H_{8,9,10,11}$), 1.42 (m, 4H, H_7), 3.66 (s, 12H, H_5), 3.98 (m, 2H, H_6), 4.10 (m, 2H, H_6), 6.93 (s, 4H, H_2), 7.78 (s, 2H, H_α), 9.04 (s, 2H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 13.9 (C_{12}), 22.0 (C_{11}), 25.3 (C_{10}), 28.2 (C_9), 28.3 (C_7), 31.2 (C_8), 55.8 (C_5), 64.5 (C_6), 107.8 (C_2), 124.0 (C_β), 124.6 (C_1), 138.0 (C_4), 141.6 (C_α), 147.7 (C_3), 166.7 (C_γ); **IR** (FTIR): 3464, 3168, 2924, 1707, 1582, 1513, 1453, 1329, 1214, 1107 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 201, 244, 333 nm; **HRMS** (*m/z*) $[M+H]^+$ calcd for $C_{36}H_{51}O_{10}$, 643.3482; found, 643.3473.



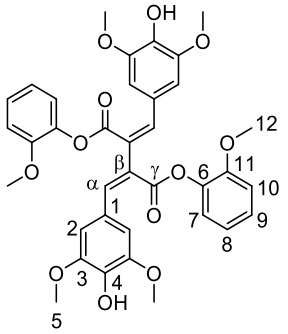
Dimerization of 2-ethylhexyl sinapate led to **2-ethylhexyl sinapate β-β' dehydrodimer (10)** as a yellow-brown oil (55% non-optimized yield / 88% optimized yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.77 (m, 12H, $H_{11,13}$), 1.15 (m, 16H, $H_{8,9,10,12}$), 1.42 (m, 2H, H_7), 3.79 (s, 12H, H_5), 3.95 (m, 2H, H_6), 4.03 (m, 2H, H_6), 5.71 (s, 2H, H_{phenol}), 6.84 (s, 4H, H_2), 7.81 (s, 2H, H_α); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 11.0 (C_{11}), 14.2 (C_{13}), 23.0 (C_{10}), 23.8 (C_{12}), 29.0 (C_9), 30.4 (C_8), 38.9 (C_7), 56.30 (C_5), 67.3 (C_6), 107.1 (C_2), 125.5 (C_β), 126.3 (C_1), 136.7 (C_4), 142.1 (C_α), 147.0 (C_3), 167.6 (C_γ); **IR** (FTIR): 3407, 2927, 1698, 1588, 1510, 1454, 1329, 1213, 1152, 1104 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 244, 333 nm; **HRMS** (*m/z*) $[M+H]^+$ calcd for $C_{38}H_{55}O_{10}$, 671.3795; found, 671.3800.



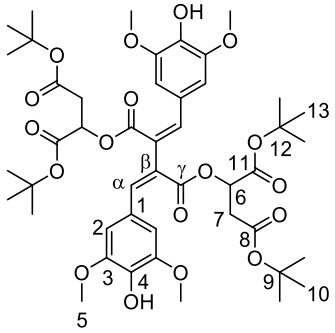
Dimerization of *tert*-butyl sinapate led to ***tert*-butyl sinapate β-β' dehydrodimer (11)** as a yellow powder (58% non-optimized yield / 89% optimized yield). **mp**: 75 – 77 °C; **^{1}H NMR** (300 MHz, Acetone-d*6*): δ 1.36 (s, 18H, H_7), 3.77 (s, 12H, H_5), 6.92 (s, 4H, H_2), 7.67 (s, 2H, H_α); **^{13}C NMR** (75 MHz, Acetone-*d6*): δ 28.0 (C_7), 56.2 (C_5), 80.4 (C_6), 107.9 (C_2), 108.3 (C_2), 126.8 (C_β), 128.1 (C_1), 138.1 (C_4), 141.3 (C_α), 148.3 (C_3), 166.9 (C_γ); **IR** (FTIR): 3394, 2933, 1689, 1588, 1510, 1452, 1331, 1245, 1145, 1105 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 204, 244, 328 nm; **HRMS** (m/z) $[M+Na]^+$ calcd for $C_{30}H_{38}O_{10}Na$, 581.2363; found, 581.2358.



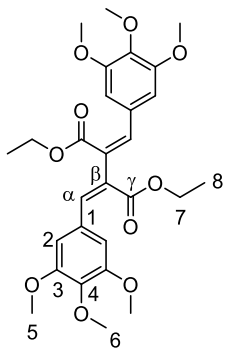
Dimerization of *iso*-butyl sinapate led to ***iso*-butyl sinapate β-β' dehydrodimer (12)** as a yellow powder (58% non-optimized yield / 91% optimized yield). **mp**: 48 – 51 °C; **^{1}H NMR** (300 MHz, Acetone-d6): δ 1.04 (d, 2H, *J* = 6.2 Hz, H_7), 1.18 (d, 2H, *J* = 6.2 Hz, $H_{7'}$), 3.76 (s, 12H, H_5), 4.98 (sept, 2H, *J* = 6.3 Hz, H_6), 6.94 (s, 4H, H_2), 7.78 (s, 2H, H_α); **^{13}C NMR** (75 MHz, Acetone-d6): δ 21.9 (C_7), 22.1 ($C_{7'}$), 56.6 (C_5), 68.6 (C_6), 108.6 (C_2), 126.8 (C_β), 126.9 (C_1), 138.8 (C_4), 142.4 (C_α), 148.6 (C_3), 167.2 (C_γ); **IR** (FTIR): 3384, 2935, 1688, 1587, 1509, 1451, 1370, 1325, 1214, 1154, 1092 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 201, 244, 333 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{28}H_{34}O_{10}Na$, 553.2050; found, 553.2049.



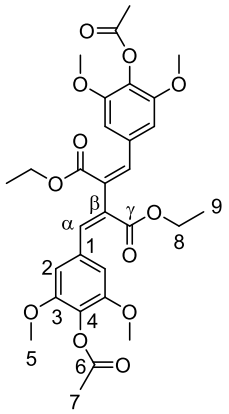
Dimerization of gaïacol sinapate led to **gaïacol sinapate β-β' dehydrodimer (13)** as a yellow powder (42% non-optimized yield / 87% optimized yield). **mp**: 128 – 131 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 3.58 (s, 6H, H_{12}), 3.72 (s, 12H, H_5), 6.87 (dd, 2H, *J* = 7.9, 1.7 Hz, H_7), 6.95 (td, 2H, J = 7.6, 1.4 Hz, H_8), 7.11 (dd, 2H, *J* = 7.9, 1.7 Hz, H_{10}), 7.15 (s, 4H, H_2), 7.23 (m, 2H, H_9), 8.04 (s, 2H, H_α), 9.20 (s, 2H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 55.6 (C_{12}), 55.9 (C_5), 108.3 (C_2), 113.1 (C_{10}), 120.7 (C_8), 122.5 (C_7), 122.6 (C_β), 124.4 (C_1), 127.0 (C_9), 138.5 (C_4), 139.6 (C_6), 143.9 (C_α), 147.7 (C_3), 151.1 (C_{11}), 164.9 (C_γ); **IR** (FTIR): 3398, 2935, 1712, 1585, 1498, 1453, 1329, 1211, 1148, 1105, 1021 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 246, 338 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{36}H_{34}O_{12}Na$, 681.1948; found, 681.1953.



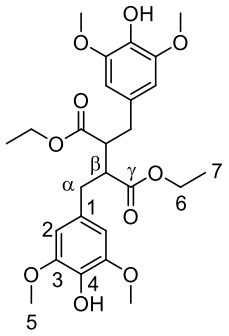
Dimerization of sinapoyl di*tert*-butyl malate led to **sinapoyl di*tert*-butyl malate β-β' dehydrodimer (14)** as a yellow powder (42% non-optimized yield / 88% optimized yield). **mp**: 72 – 74 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 1.33 (m, 18H, H_{10}), 1.37 (m, 18H, H_{13}), 2.74 (m, 4H, H_7), 3.66 (s, 12H, H_5), 5.19 (m, 2H, H_6), 6.88 (m, 4H, H_2), 7.77 (s, 2H, H_α), 9.05 's, 2H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 27.5 ($C_{10,13}$), 36.8 (C_7), 55.8 (C_5), 69.2 (C_6), 80.7 (C_9), 81.7 (C_{12}), 108.0 (C_2), 122.3 (C_β), 124.1 (C_1), 138.2 (C_4), 142.6 (C_α), 147.6 (C_3), 165.5 (C_γ), 167.4 (C_{11}), 168.0 (C_8); **IR** (FTIR): 3421, 2975, 1709, 1590, 1510, 1454, 1366, 1212, 1143, 1101 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 204, 243, 329 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{46}H_{62}O_{18}Na$, 925.3834; found, 925.3835.



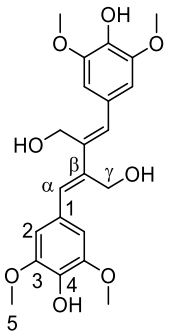
Methylation of ethyl sinapate β-β' dehydrodimer (8) led to **methylated ethyl sinapate β-β' dehydrodimer (15)** as an orange solid (93% yield). **mp**: 130 – 132 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 1.10 (t, 6H, *J* = 7.1 Hz, H_8), 3.77 (s, 12H, H_5), 3.84 (s, 6H, H_6), 4.15 (m, 4H, H_7), 6.78 (s, 4H, H_2), 7.83 (s, 2H, H_α); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 14.2 (C_8), 56.1 (C_5), 61.1 (C_6), 61.4 (C_7), 107.1 (C_2), 126.9 (C_β), 130.4 (C_1), 139.5 (C_4), 142.3 (C_α), 153.2 (C_3), 167.0 (C_γ); **IR** (FTIR): 2936, 1695, 1573, 1500, 1459, 1415, 1333, 1230, 1115, 1029 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 202, 230, 310 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{28}H_{34}O_{10}Na$, 553.2050; found, 553.2051.



Acetylation of ethyl sinapate β-β' dehydrodimer (8) let to **acetylated ethyl sinapate β-β' dehydrodimer (16)** as a light-yellow solid (99% yield). **mp**: 99 – 101 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 1.10 (t, 6H, J = 7.1 Hz, H_9), 2.31 (s, 6H, H_7), 3.73 (s, 12H, H_5), 4.15 (m, 4H, H_8), 6.72 (s, 4H, H_2), 7.81 (s, 2H, H_α); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 14.2 (C_9), 20.6 (C_7), 56.2 (C_5), 61.5 (C_8), 106.4 (C_2), 128.0 (C_β), 129.8 (C_4), 133.2 (C_1), 142.4 (C_α), 152.2 (C_3), 166.7 (C_γ), 168.6 (C_6); **IR** (FTIR): 2939, 1767, 1695, 1584, 1502, 1460, 1416, 1227, 1192, 1125, 1010 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 205, 222, 299 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{30}H_{34}O_{12}Na$, 609.1948; found, 609.1946.



Hydrogenation of ethyl sinapate β-β' dehydrodimer (8) led to **ethyl sinapate β-β' dihydrodimer (17)** as a light-yellow solid (95% yield). **mp**: 73 – 76 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ 1.08 (t, 6H, *J* = 7.2 Hz, H_7), 2.79 (m, 4H, H_α), 2.89 (m, 2H, H_β), 3.68 (s, 12H, H_5), 3.96 (q, 4H, *J* = 7.2 Hz, H_6), 6.34 (s, 4H, H_2), 8.16 (s, 2H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 14.0 (C_7), 35.5 (C_α), 48.6 (C_β), 55.8 (C_5), 59.9 (C_6), 106.3 (C_2), 128.4 (C_1), 134.0 (C_4), 147.7 (C_3), 173.0 (C_γ); **IR** (FTIR): 3443, 2937, 1720, 1609, 1515, 1457, 1369, 1323, 1207, 1105, 1031 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 207, 273 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{26}H_{34}O_{10}Na$, 529.2050; found, 529.2048.



DIBAl-H reduction of ethyl sinapate β-β' dehydrodimer (8) led to **sinapic alcohol β-β' dehydrodimer (18)** as a yellow powder (46% yield). **mp**: 84 – 86 °C; **^{1}H NMR** (300 MHz, DMSO-*d6*): δ **δ_H** 3.63 (s, 12H, H_5), 3.92 (dd, 4H, *J* = 14.4, 3.9 Hz, H_γ), 5.10 (t, 2H, *J* = 5.1 Hz, $H_{alcohol}$), 6.56 (s, 2H, H_α), 6.81 (s, 4H, H_2), 8.38 (s, 2H, H_{phenol}); **^{13}C NMR** (75 MHz, DMSO-*d6*): δ 55.7 (C_5), 63.6 (C_γ), 105.3 (C_2), 124.1 (C_α), 127.2 (C_1), 134.7 (C_4), 139.0 (C_β), 147.7 (C_3); **IR** (FTIR): 3352, 2935, 1595, 1511, 1451, 1320, 1210, 1108, 1018 cm^{-1}; **UV/Vis** (Ethanol): λ_{max} 210, 274 nm; **HRMS** (*m/z*) $[M+Na]^+$ calcd for $C_{22}H_{26}O_8Na$, 441.1525; found, 441.1519

4. Enzymatic dimerization of ethyl sinapate

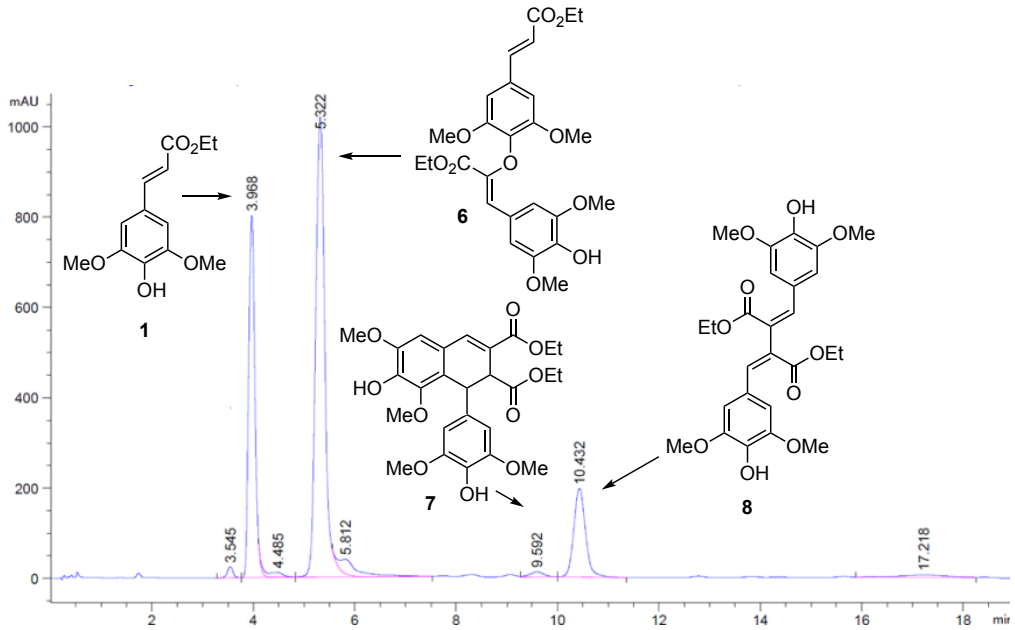


Figure S1. HPLC chromatogram for the dimerization of ethyl sinapate with laccase from *Trametes versicolor* (Zorbax Eclipse Plus C18 (2.1 mm*50 mm*1.8 µm), λ = 320 nm, flow rate set at 0.6 mL.min^{-1}, oven temperature at 30 °C, and gradient applied: H_2O/CH_3CN from 75/25 to 70/30 in 18 min).

5. Optimization of the sinapate ester β-β' dimerization

5.1. Screening of solvents

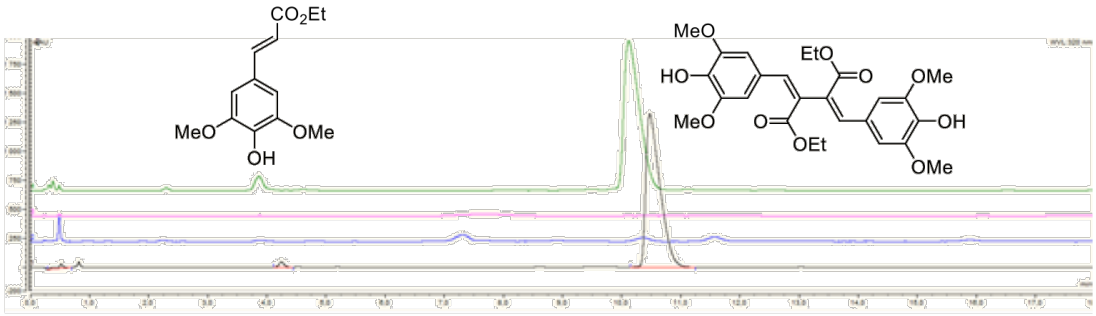


Figure S2. HPLC chromatograms of the dimerization of ethyl sinapate in pyridine (black), ethanol (pink), ethyl acetate (blue) and Cyrene™ (green) (Zorbax Eclipse Plus C18 (2.1 mm*50 mm*1.8 µm), λ = 320 nm, flow rate set at 0.6 mL.min^{-1}, oven temperature at 30 °C, and gradient applied: H_2O/CH_3CN from 75/25 to 70/30 in 18 min).

5.2. Design of experiments (D.O.E.)

The effect of the four independent variables X_1 (Temperature), X_2 (ratio Catalyst/Substrate), X_3 (Ratio Amine/Catalyst) and X_4 (Concentration) on responses Y_1 (yield) and Y_2 (conversion) was modelled using a polynomial response:

$$Yi = \beta 0 + \sum_{i=13} \beta kixi + \sum_{i=13} \beta kiixi^2 + \sum_{i=12} \sum_{j=i+13} \beta kijxixj$$

where Y_i represents the response i, x_i are the coded independent variables, β_0 is a constant coefficient, and β_{ki}, β_{kii}, and β_{kij} are the linear, quadratic, and interaction coefficients, respectively.

The variable levels X_i were scaled and centered (coded) according to the equation below such that X_0 corresponded to the central value:

$$xi = Xi - X0\Delta Xi \;\; where \;\; i = 1,2,3, \dots, k$$

where x_i is the dimensionless value of an independent variable, X_i is the real value of an independent variable, X_0 is the real value of an independent variable at the centre point, and ΔX_i is the step change.

Table S1 | Design of experiments for the β-β' dimerization of ethyl sinapate (experimental values obtained by HPLC)

Exp No	Exp Name	Run Order	Incl/Excl	Temperature (°C)	Ratio Cat/Substrate	Ratio amine/cat	Concentration (mol.L^{-1})	Yield (%)	Conversion (%)
1	N1	3	Incl	25	2.01	1	0.249	0.01	0.01
2	N2	14	Incl	70	2.03	1	0.247	0.01	7.58
3	N3	15	Incl	25	10.1	1	0.249	0.01	0.01
4	N4	27	Incl	70	10	1	0.25	0.01	0.01
5	N5	17	Incl	25	2.01	10	0.249	0.01	0.01
6	N6	4	Incl	70	2.01	10.1	0.246	1.63	3.26
7	N7	7	Incl	25	9.95	10.02	0.251	2.84	5.68
8	N8	23	Incl	70	10.2	10	0.246	16.83	20.71
9	N9	9	Incl	25	1.99	1.01	2.49	0.01[a]	33.31
10	N10	10	Incl	70	2.01	1.02	2.447	3.41	59.34
11	N11	1	Incl	25	10.1	1	2.49	12.27	81.05
12	N12	11	Incl	70	10.2	1	2.447	4.22	83.89
13	N13	24	Incl	25	2.02	10	2.48	3.88	27.71
14	N14	5	Incl	70	2	10.07	2.487	34.49	97.08
15	N15	12	Incl	25	9.91	10.02	2.52	35.49	94.8
16	N16	20	Incl	70	10.3	9.99	2.428	26.23	99.99
17	N17	13	Incl	25	6.02	5.5	1.358	34.99	56.7
18	N18	26	Incl	70	6.06	5.49	1.358	40.78	98.37
19	N19	21	Incl	47.5	1.99	5.51	1.374	55.79	64.59
20	N20	16	Incl	47.5	10.47	5.3	1.358	69.77	99.99
21	N21	25	Incl	47.5	5.99	1	1.368	7.32	88.61
22	N22	22	Incl	47.5	6.02	10.02	1.363	53.29	79.64
23	N23	8	Incl	47.5	6.06	5.5	0.248	5.41	11.18
24	N24	6	Incl	47.5	6	5.51	2.497	49.87	98.69
25	N25	18	Incl	47.5	5.98	5.51	1.374	89.05	98.02
26	N26	19	Incl	47.5	6.02	5.51	1.363	83.3	95.4
27	N27	2	Incl	47.5	6.03	5.51	1.363	81.46	97.01
28	N28	28	Incl	70	2.01	10.1	0.246	0.01	28.68
29	N29	29	Incl	70	2	10.07	2.487	35.7	88.56
30	N30	30	Incl	25	9.91	10.02	2.52	61.11	95
31	N31	31	Incl	25	6.02	5.5	1.358	57.5	75.11
32	N32	32	Incl	47.5	6.02	10.02	1.363	53.02	60.59

[a] abnormal value excluded of the D.O.E for the yield optimization

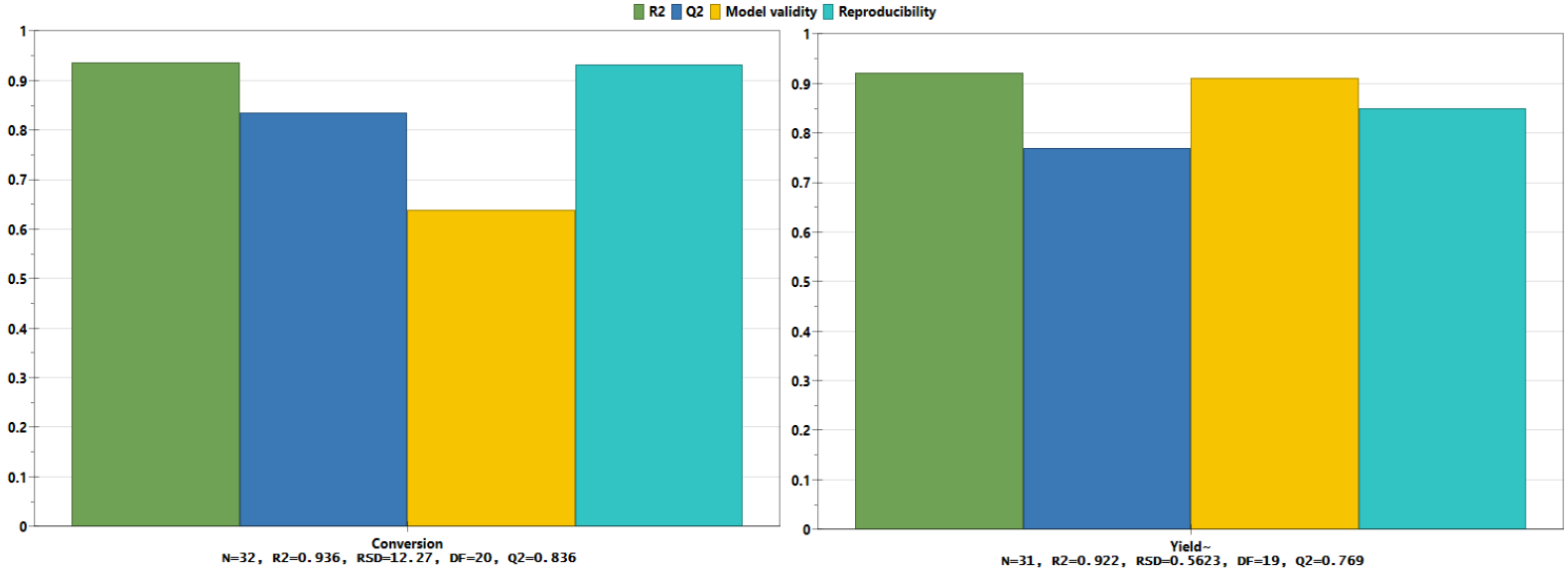


Figure S3 | Summary of fit for conversion (left) and yield (right)

Table S2 | Analysis of the variance (ANOVA) for the logit model of the conversion

Source of variation	Degrees of freedom	Sum of squares	Mean square	Standard deviation	Significance
Regression	11	44155	40414	63.357	0[a]
Residual	19	3012	150.6	12.272	
Lack of Fit	12	2298	176.8	13.298	0.237[b]
Pure error	7	713.25	101.89	10.094	
R^2/R^2adj^c	0.933/0.876				
Q^2	0.839				

[a] Significance at the 95 % level; [b] lack of fit; [c] R^2 adjusted for degree of freedom

Table S3 | Analysis of the variance (ANOVA) for the logit model of the yield

Source of variation	Degrees of freedom	Sum of squares	Mean square	Standard deviation	Significance
Regression	11	70.675	6.425	2.5348	0[a]
Residual	19	6.0076	0.3162	0.5623	
Lack of Fit	12	3.3232	0.2769	0.5262	0.704[b]
Pure error	7	2.6844	0.3839	0.6193	
R^2/R^2adj^c	0.933/0.876				
Q^2	0.769				

[a] Significance at the 95 % level; [b] lack of fit; [c] R^2 adjusted for degree of freedom

6. Antiradical properties

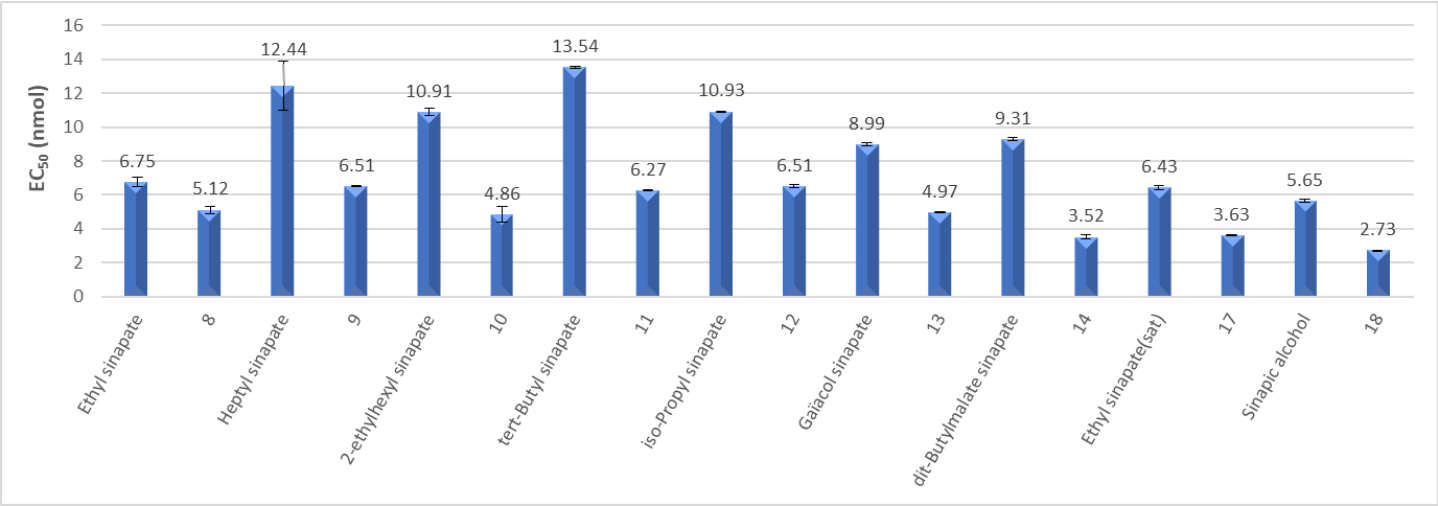
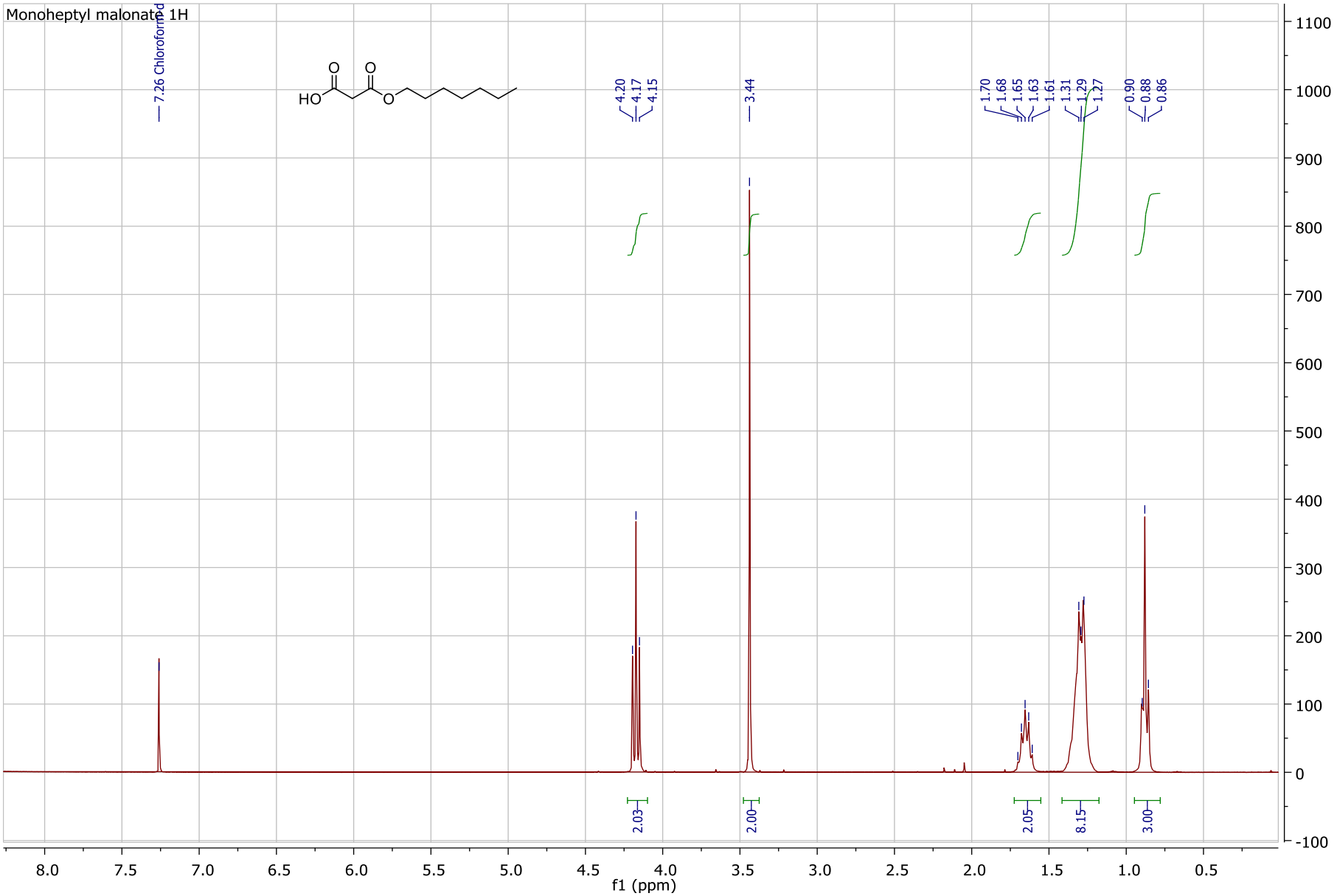
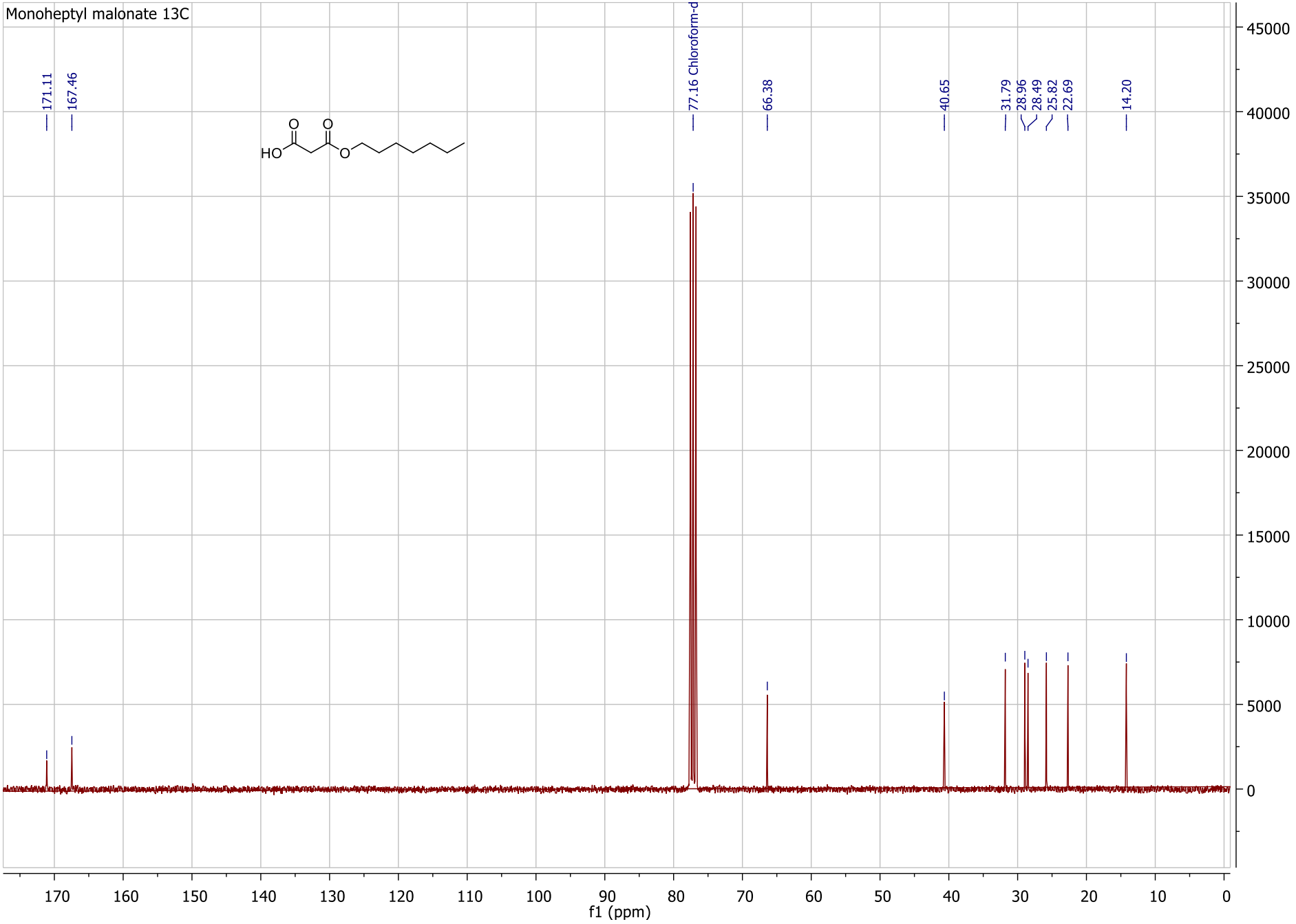


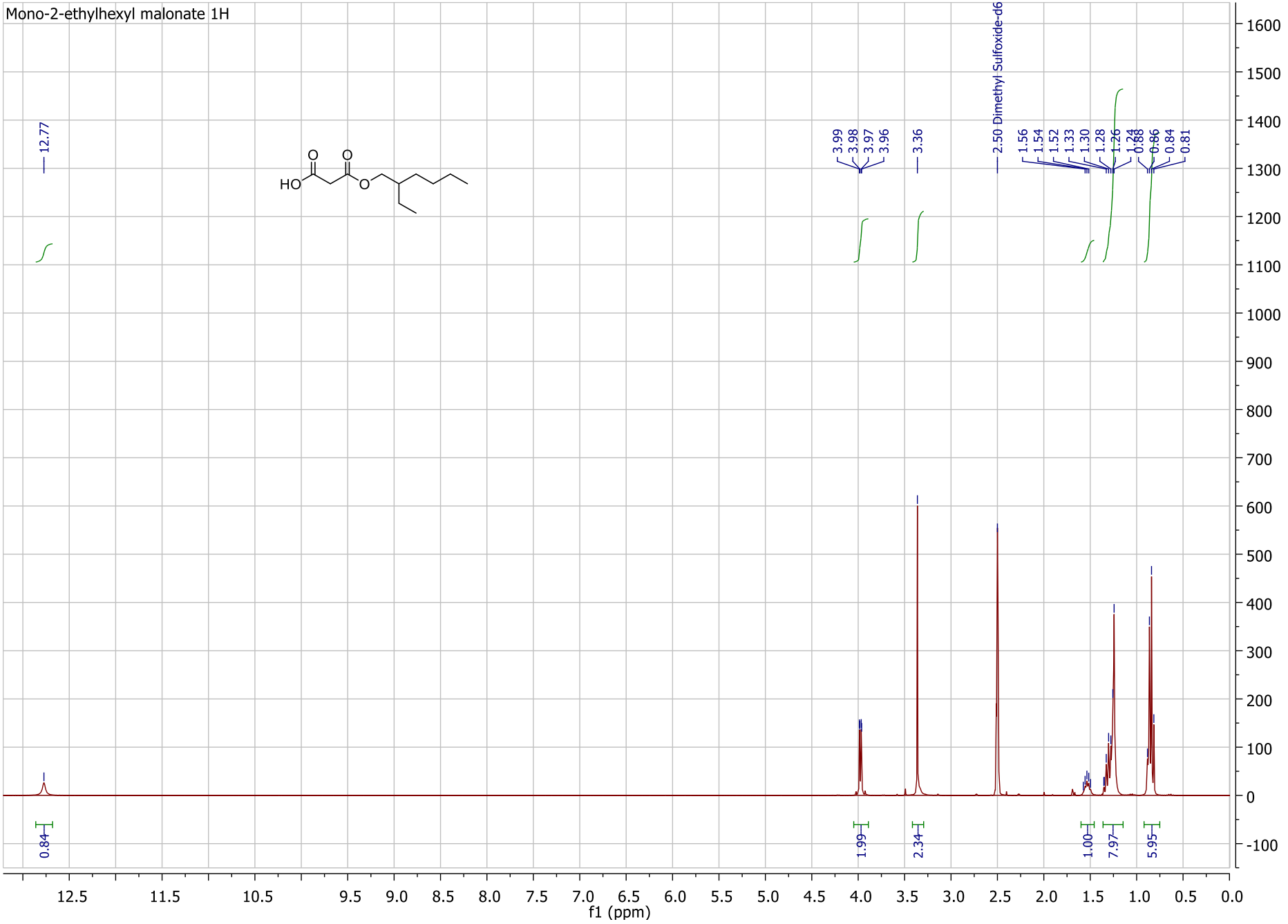
Figure S4 | Antiradical properties from the $ABTS^{\bullet+}$ assay: comparison of EC_{50} between sinapate esters and their β-β' dimers.

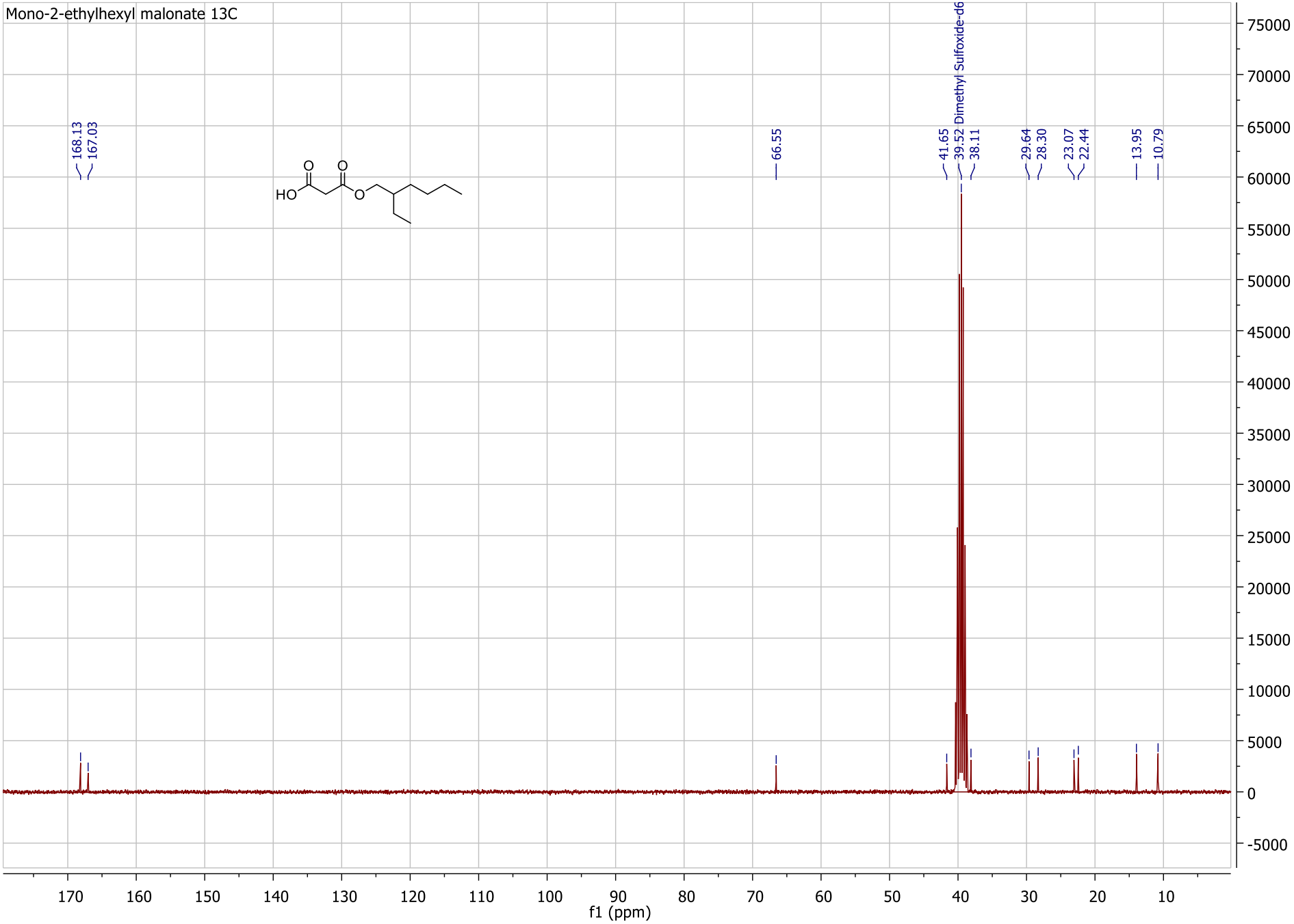
7. Characterization Data

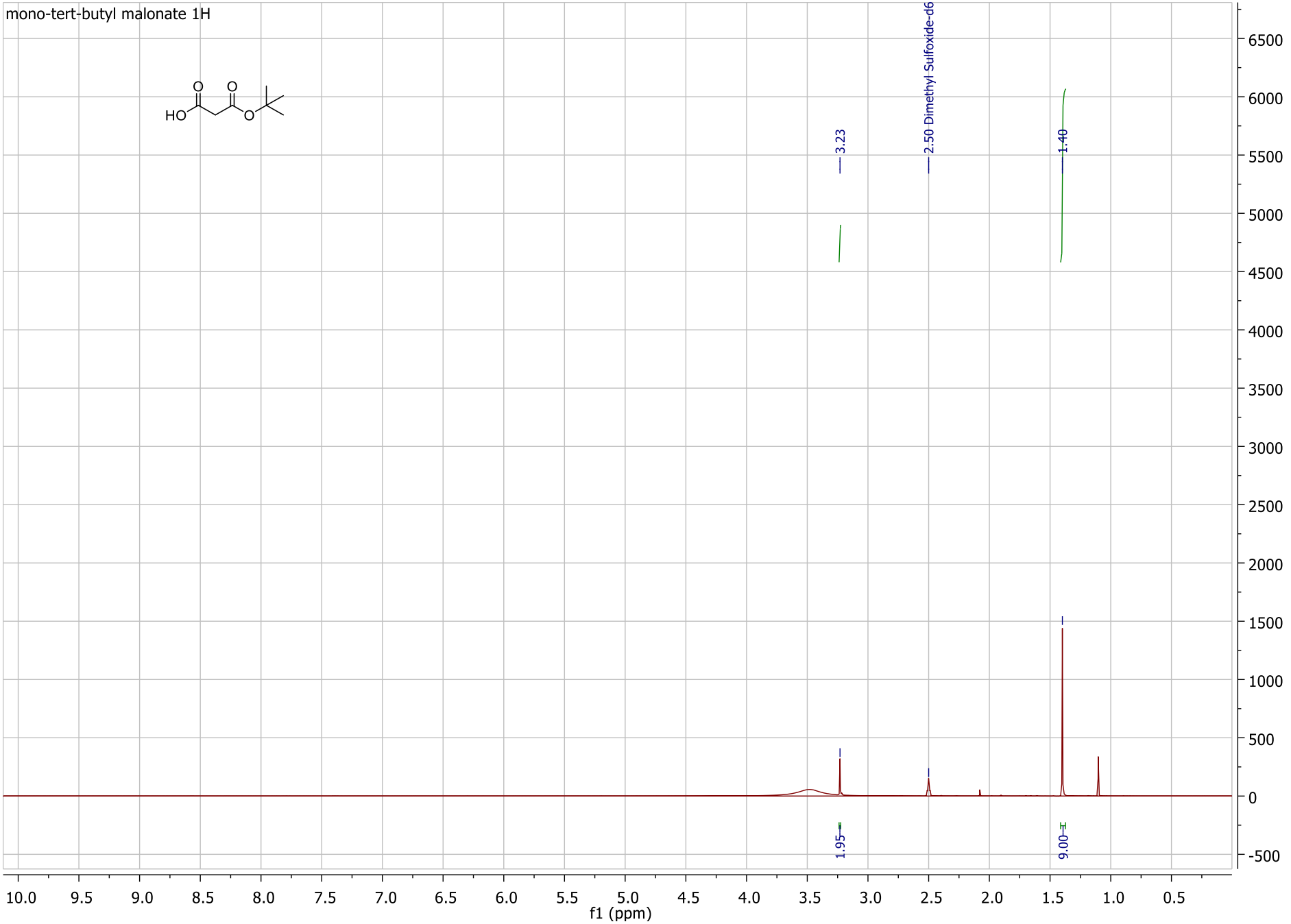
7.1. ^{1}H & ^{13}C NMR spectra

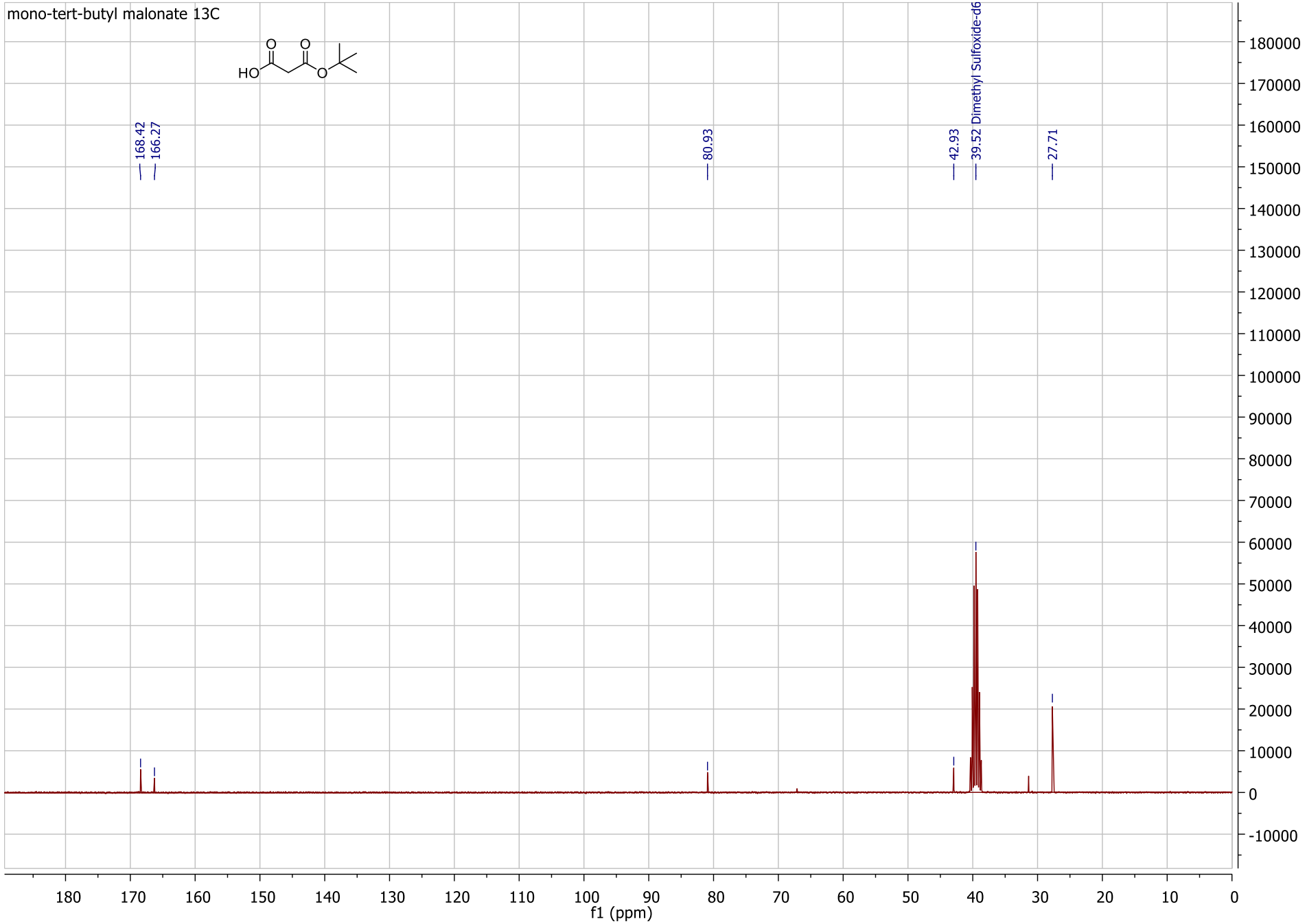


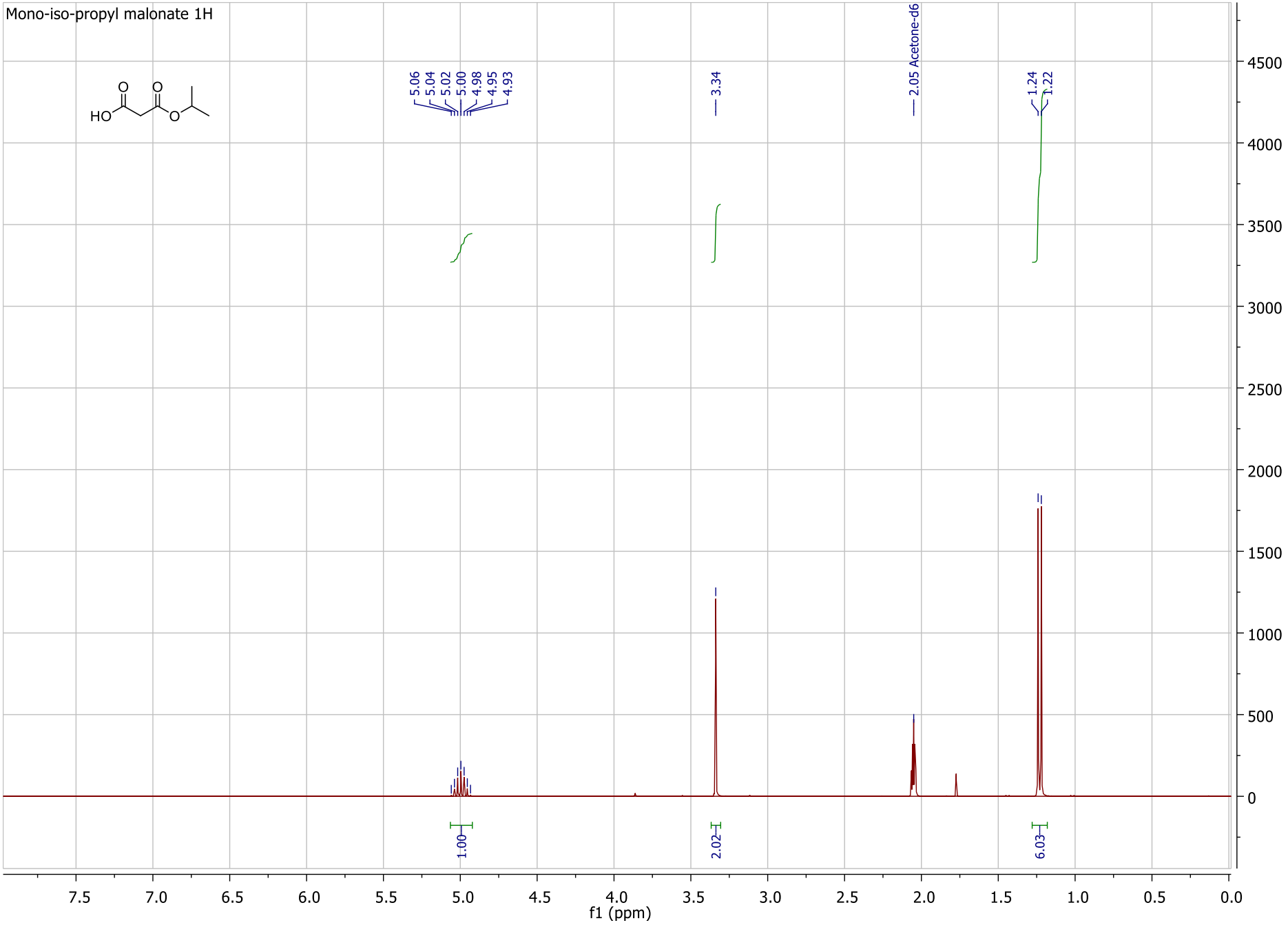

Monoheptyl malonate 13C
171.11
167.46
77.16 Chloroform-d
66.38
40.65
31.79
28.96
28.49
25.82
22.69
14.20
HO
O
O
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

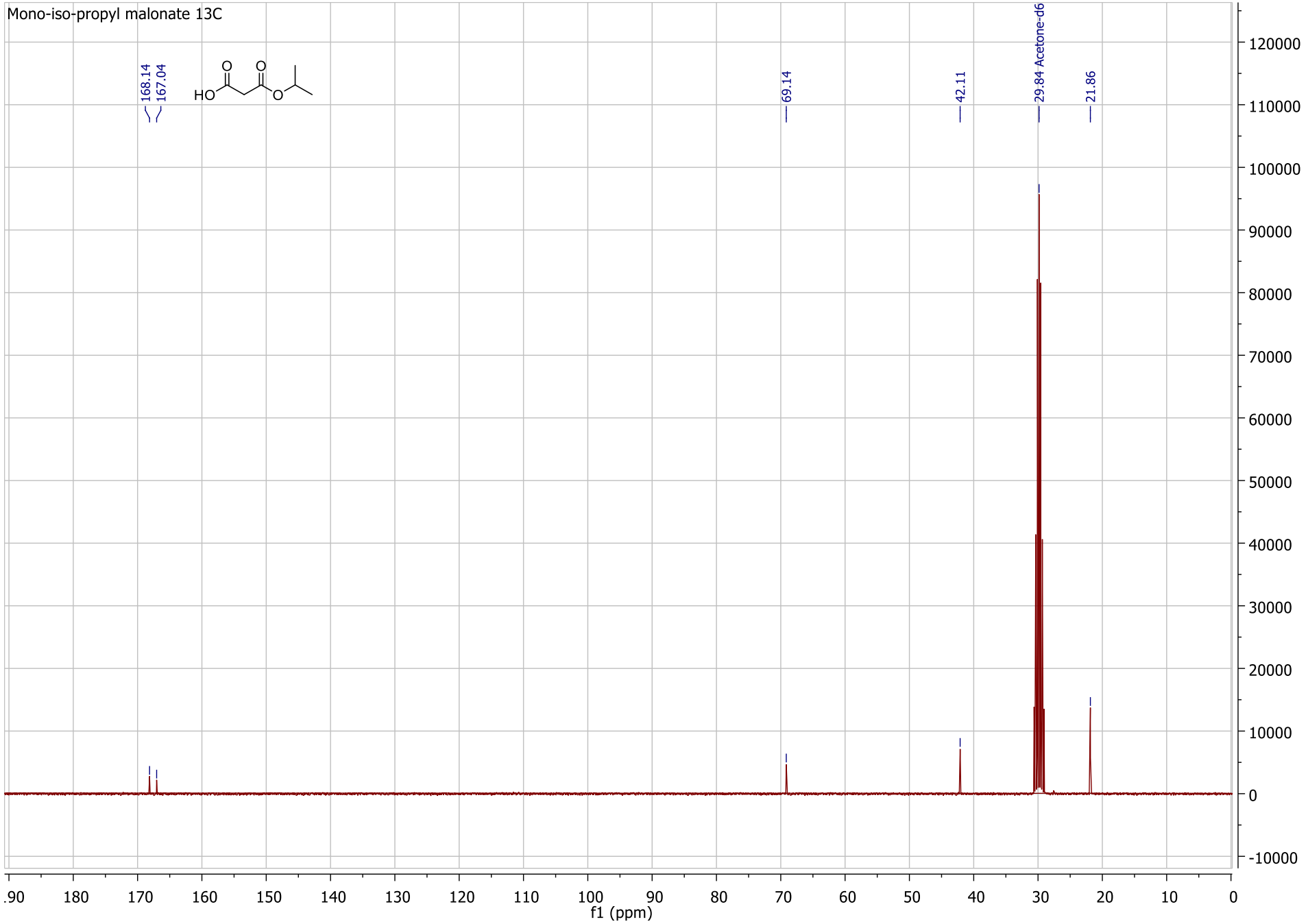

Mono-2-ethylhexyl malonate 1H
12.77
3.99
3.98
3.97
3.96
3.36
2.50 Dimethyl Sulfoxide-d6
1.56
1.54
1.52
1.33
1.30
1.28
1.26
0.88
0.86
0.84
0.81
HO
O
O
O
0.84
1.99
2.34
1.00
7.97
5.95
f1 (ppm)

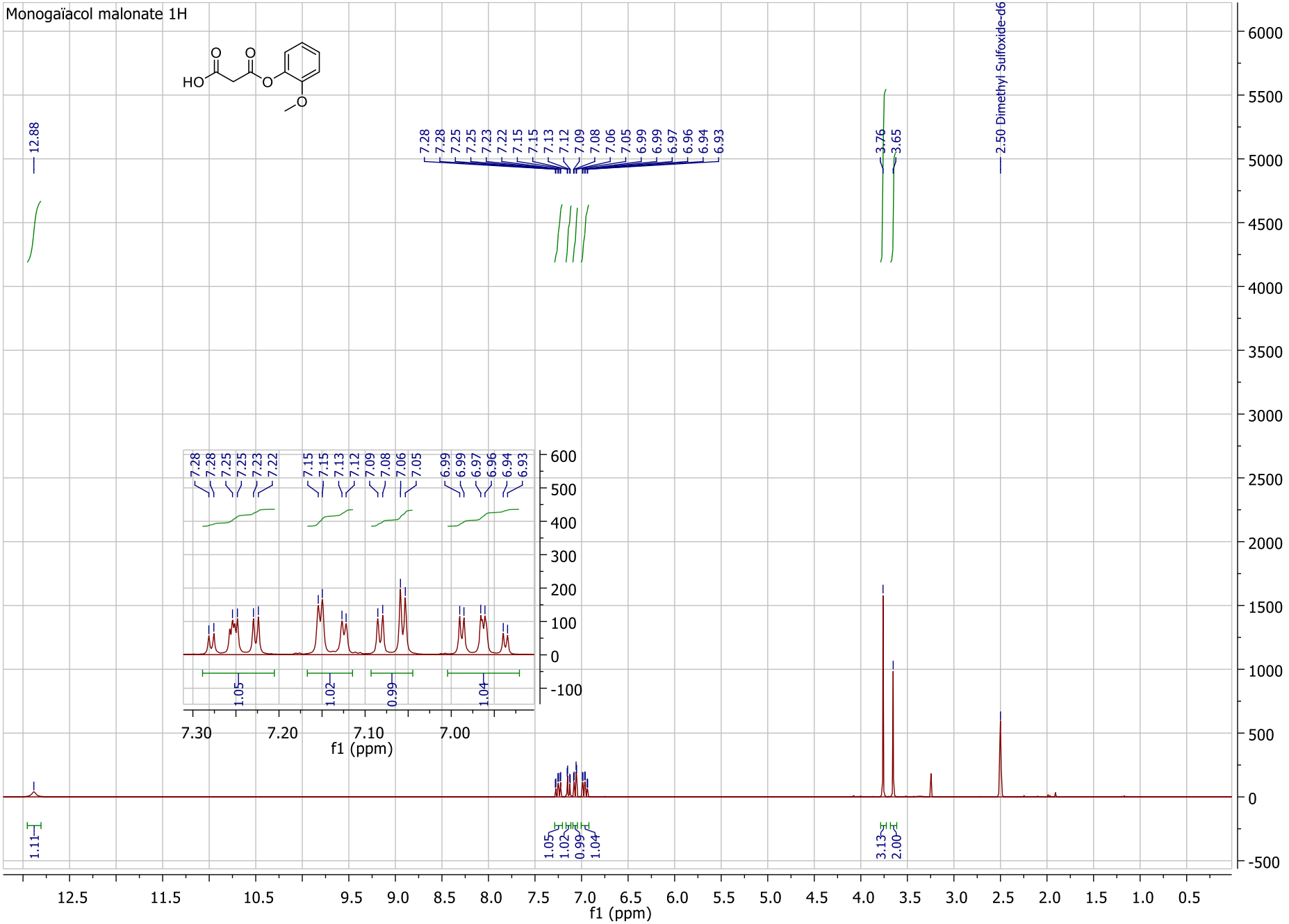

Mono-2-ethylhexyl malonate 13C
168.13
167.03
66.55
41.65
39.52
Dimethyl Sulfoxide-d6
38.11
29.64
28.30
23.07
22.44
13.95
10.79
HO
O
O
O
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

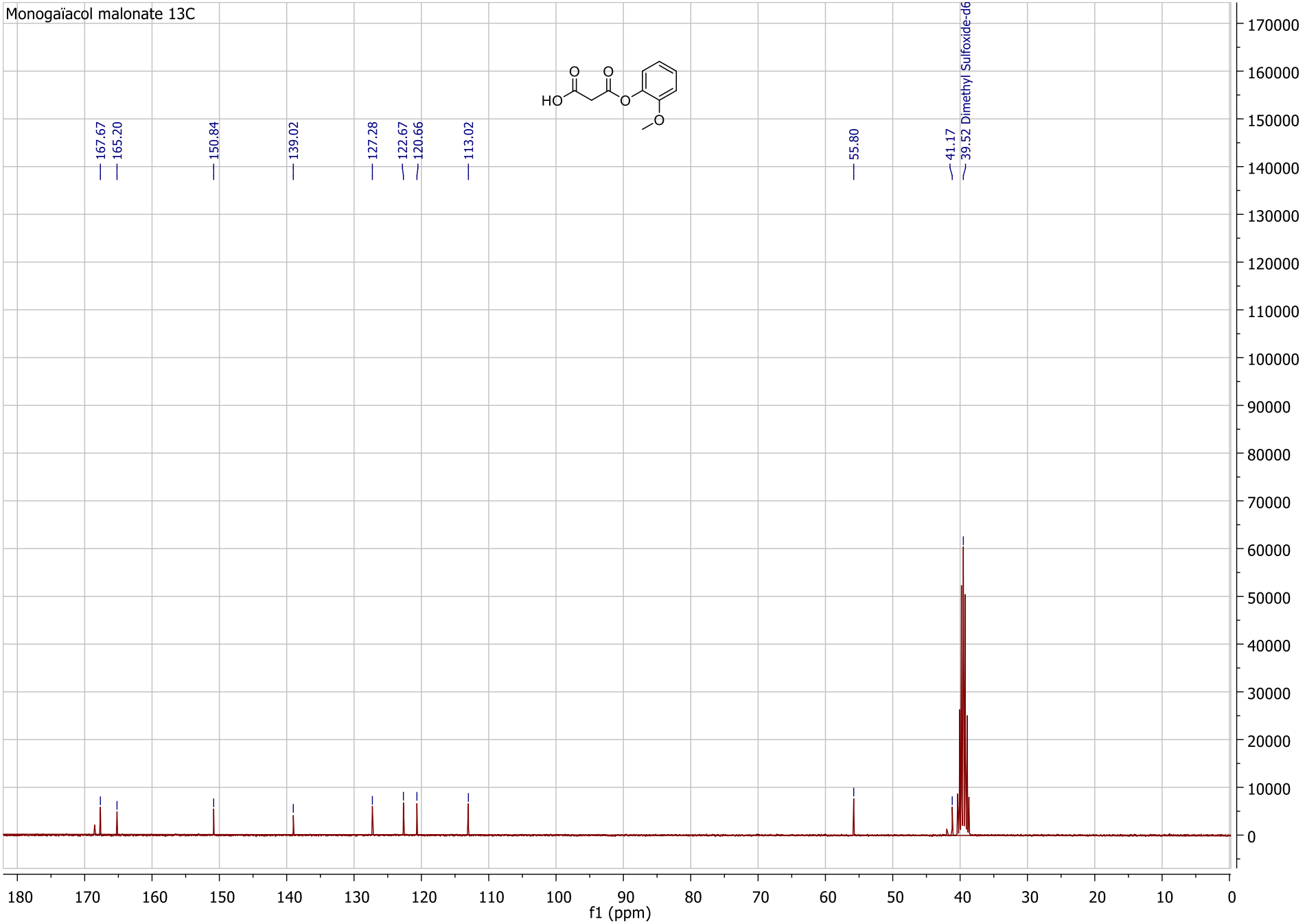

mono-tert-butyl malonate 1H
HO
O
O
O
3.23
2.50 Dimethyl Sulfoxide-d6
1.40
1.95
9.00
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

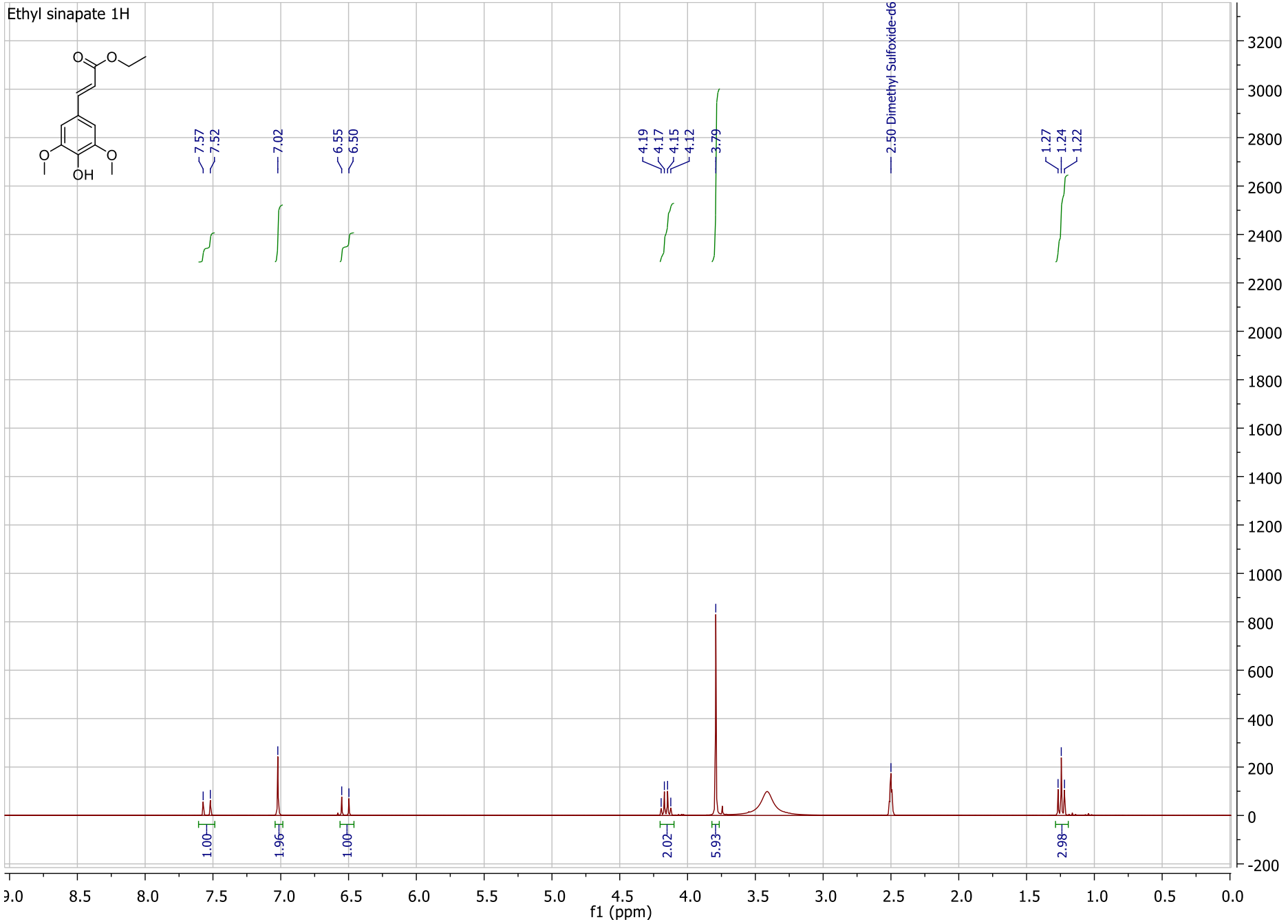

mono-tert-butyl malonate 13C
HO
O
O
O
168.42
166.27
80.93
42.93
39.52 Dimethyl Sulfoxide-d6
27.71
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

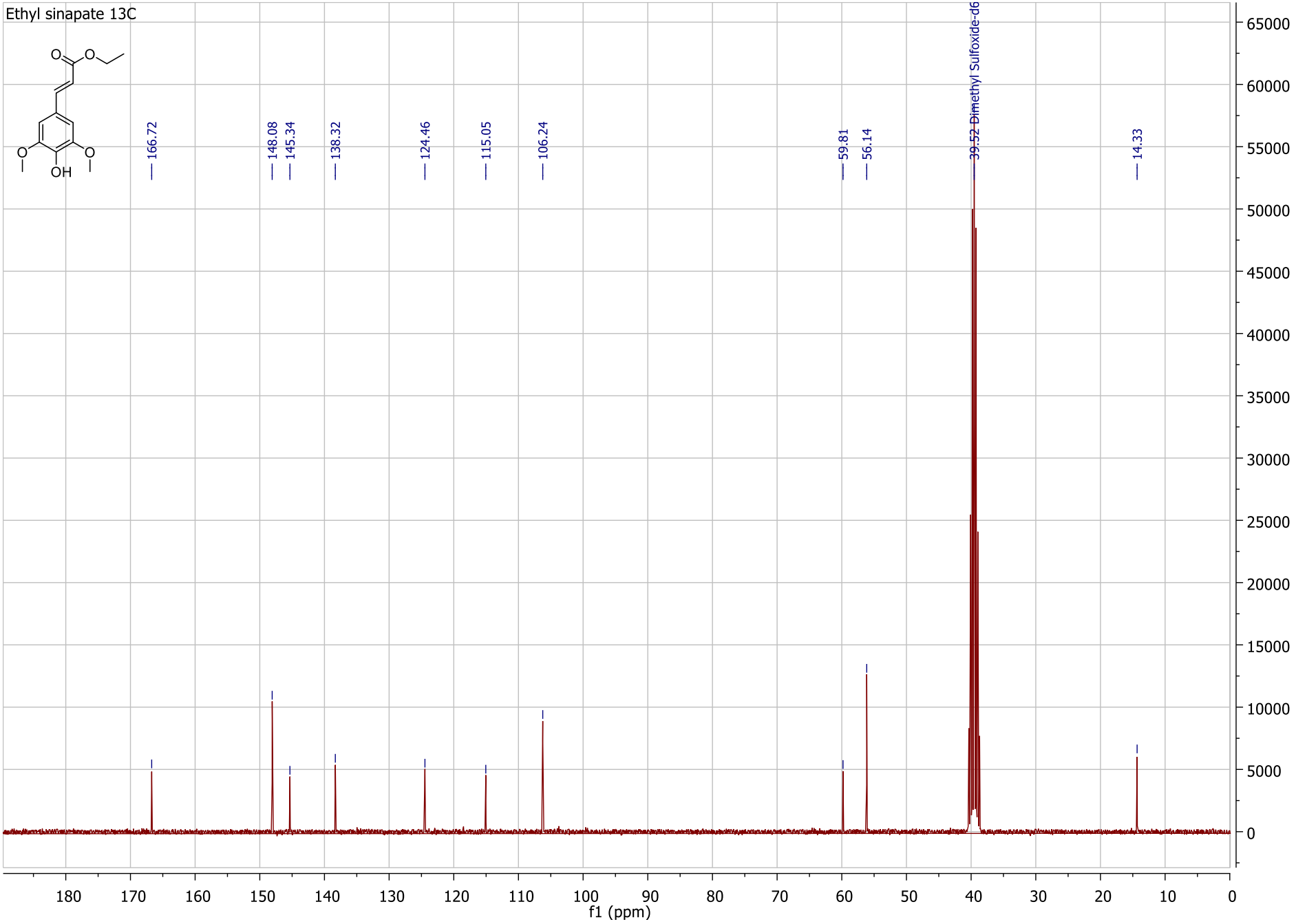

Mono-iso-propyl malonate 1H
HO
O
O
O
5.06
5.04
5.02
5.00
4.98
4.95
4.93
3.34
2.05 Acetone-d6
1.24
1.22
1.00
2.02
6.03
f1 (ppm)

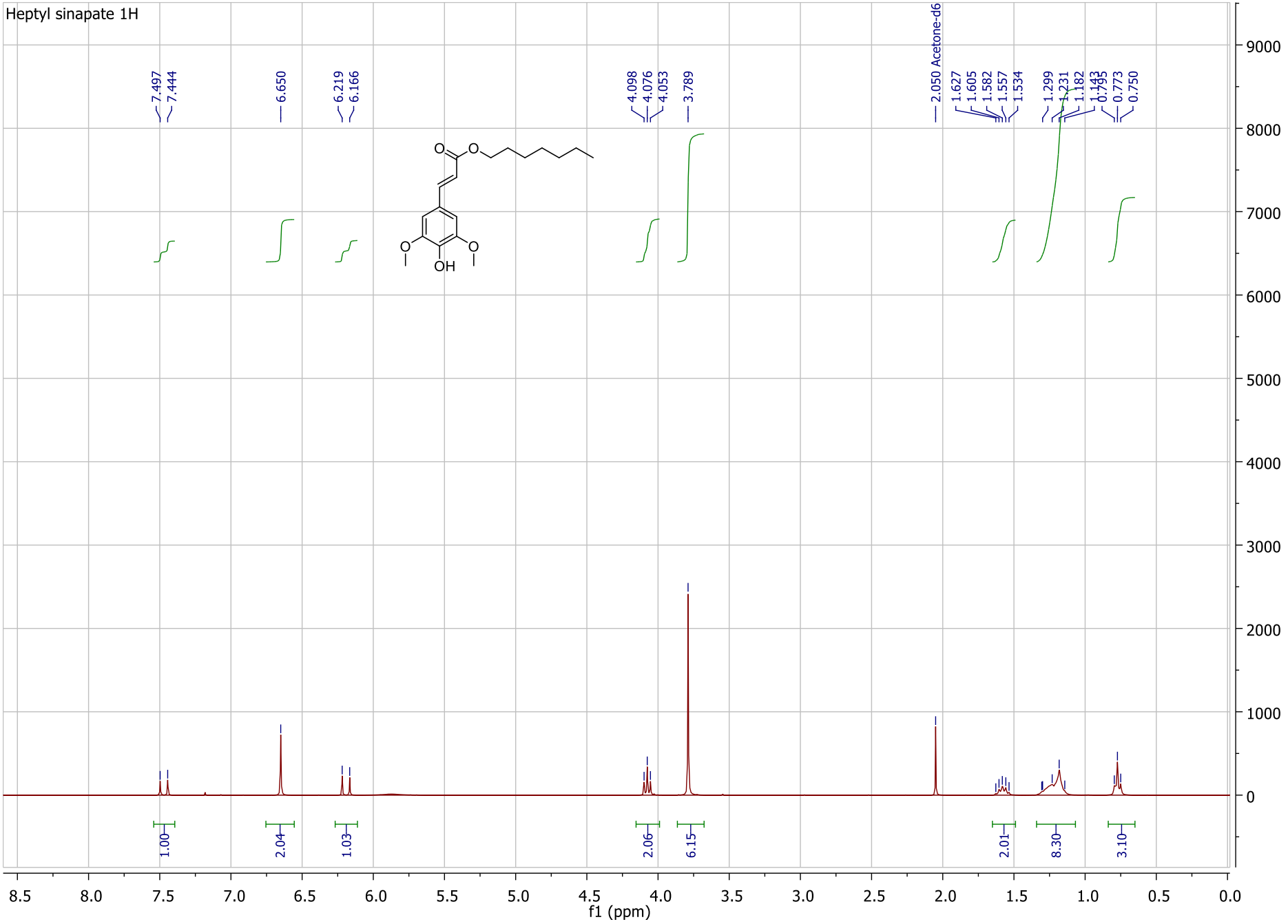

Mono-iso-propyl malonate 13C
168.14
167.04
69.14
42.11
29.84 Acetone-d6
21.86
HO
O
O
O
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
.90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

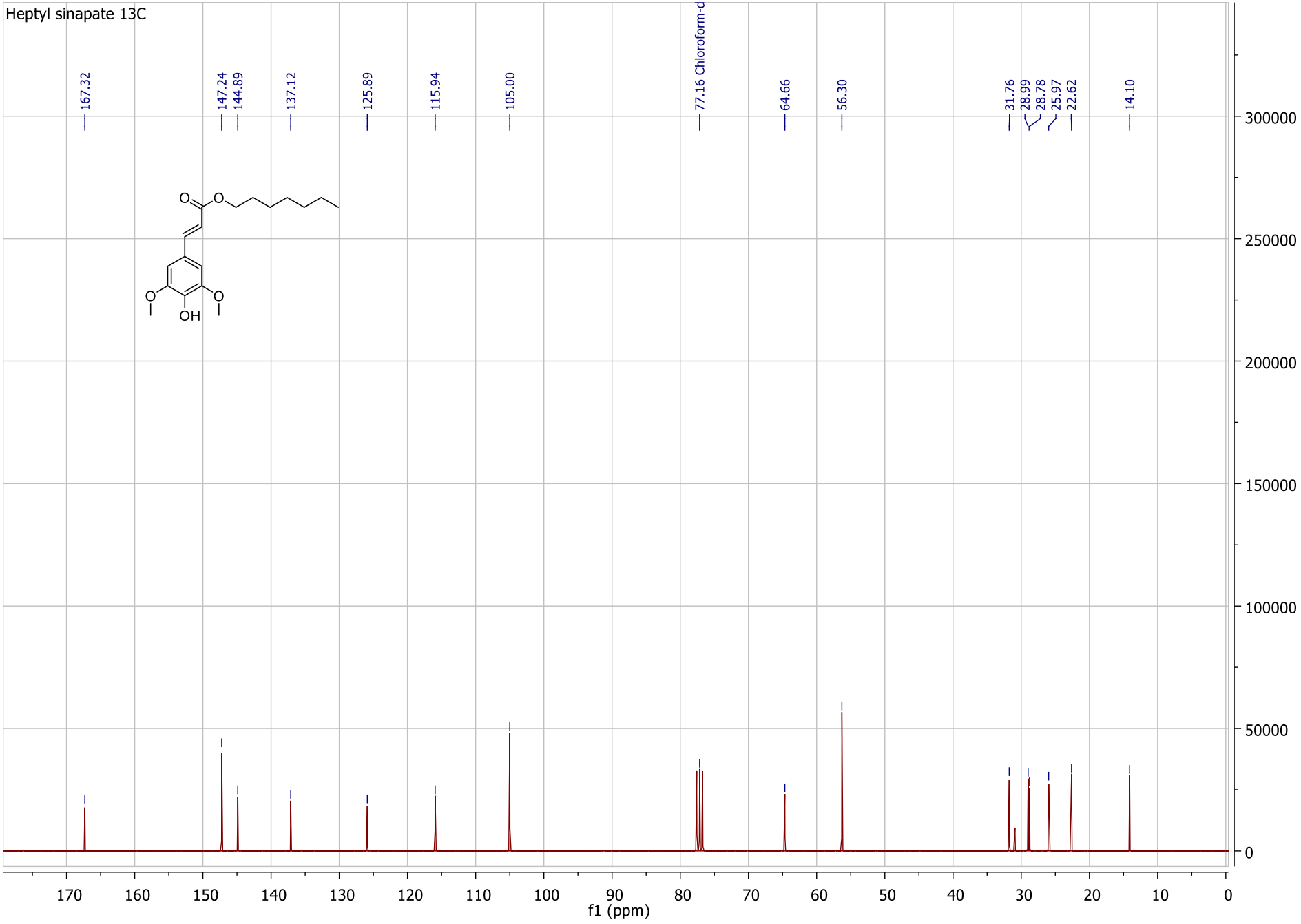

Monogaïacol malonate 1H
HO
O
O
O
O
12.88
7.28
7.28
7.25
7.25
7.23
7.22
7.15
7.15
7.13
7.12
7.09
7.08
7.06
7.05
6.99
6.99
6.97
6.96
6.94
6.93
3.76
3.65
2.50 Dimethyl Sulfoxide-d6
1.05
1.02
0.99
1.04
7.30
7.20
7.10
7.00
f1 (ppm)
1.11
1.05
1.02
0.99
1.04
3.13
2.00
f1 (ppm)

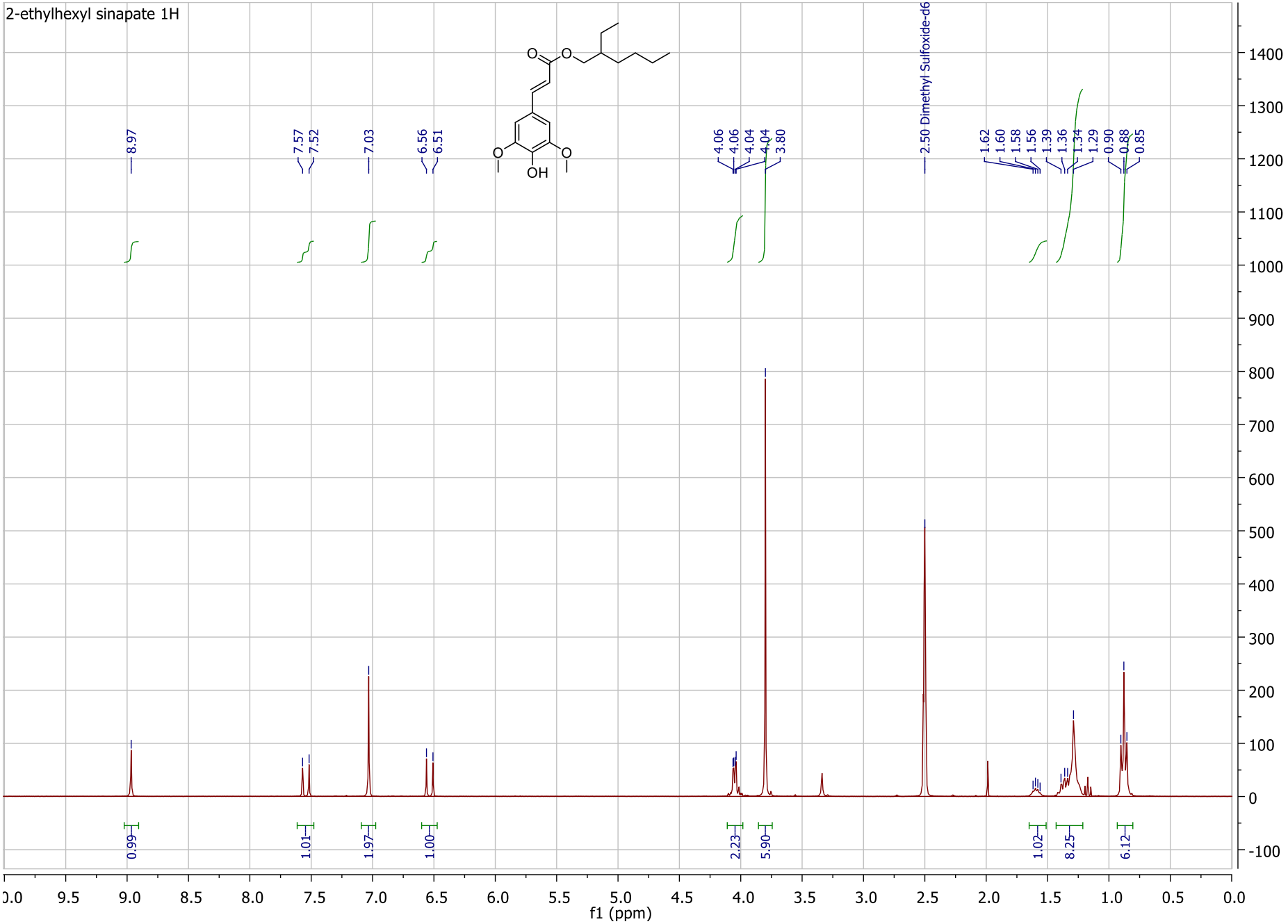

Monogaïacol malonate 13C
HO
O
O
O
O
167.67
165.20
150.84
139.02
127.28
122.67
120.66
113.02
55.80
41.17
39.52 Dimethyl Sulfoxide-d6
f1 (ppm)

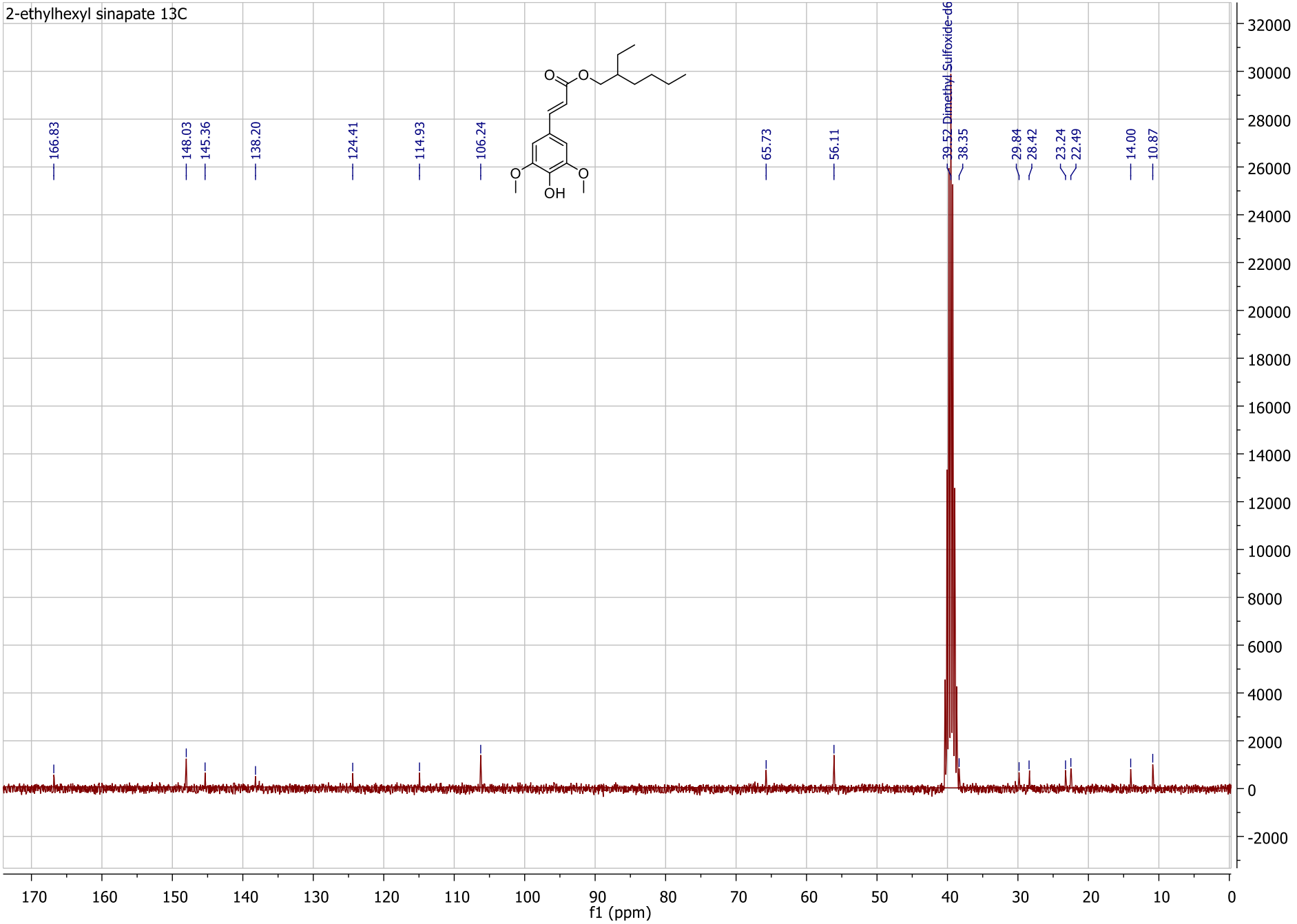

Ethyl sinapate 1H
7.57
7.52
7.02
6.55
6.50
4.19
4.17
4.15
4.12
3.79
2.50 Dimethyl Sulfoxide-d6
1.27
1.24
1.22
1.00
1.96
1.00
2.02
5.93
2.98
f1 (ppm)

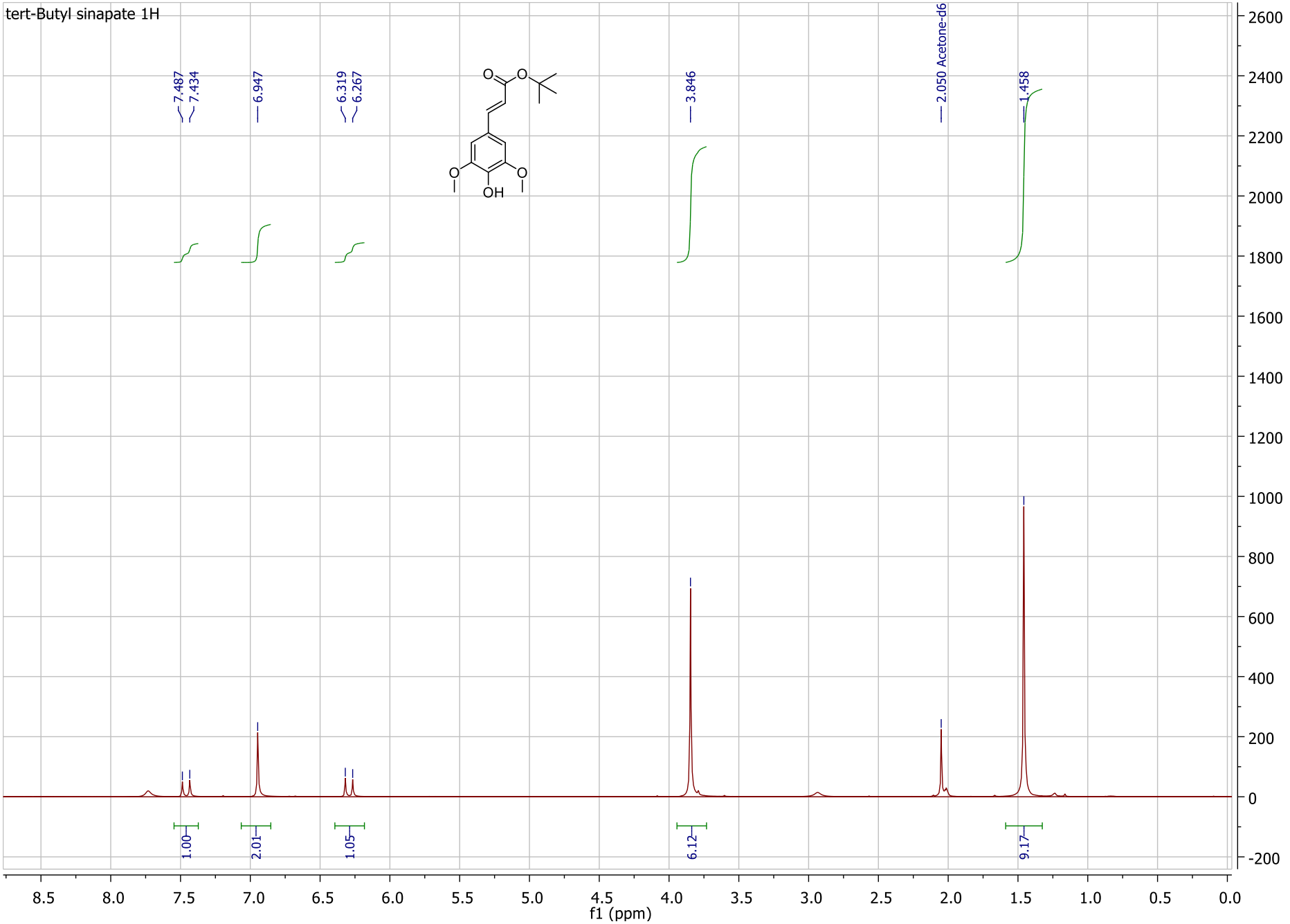

Ethyl sinapate 13C
166.72
148.08
145.34
138.32
124.46
115.05
106.24
59.81
56.14
39.52 Dimethyl Sulfoxide-d6
14.33
f1 (ppm)

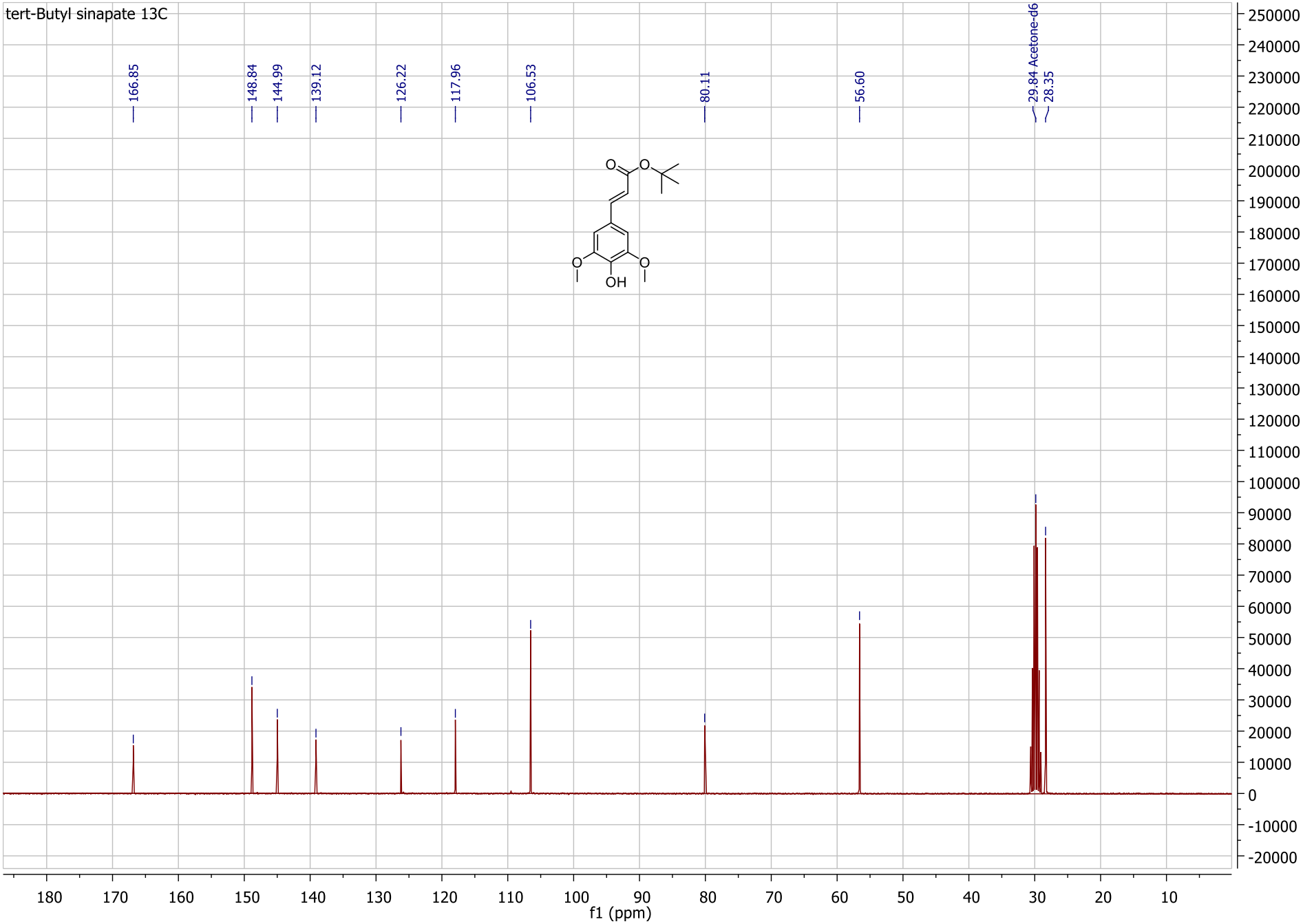

Heptyl sinapate 1H
7.497
7.444
6.650
6.219
6.166
4.098
4.076
4.053
3.789
2.050 Acetone-d6
1.627
1.605
1.582
1.557
1.534
1.299
1.231
1.182
1.143
0.795
0.773
0.750
O
O
O
O
OH
1.00
2.04
1.03
2.06
6.15
2.01
8.30
3.10
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

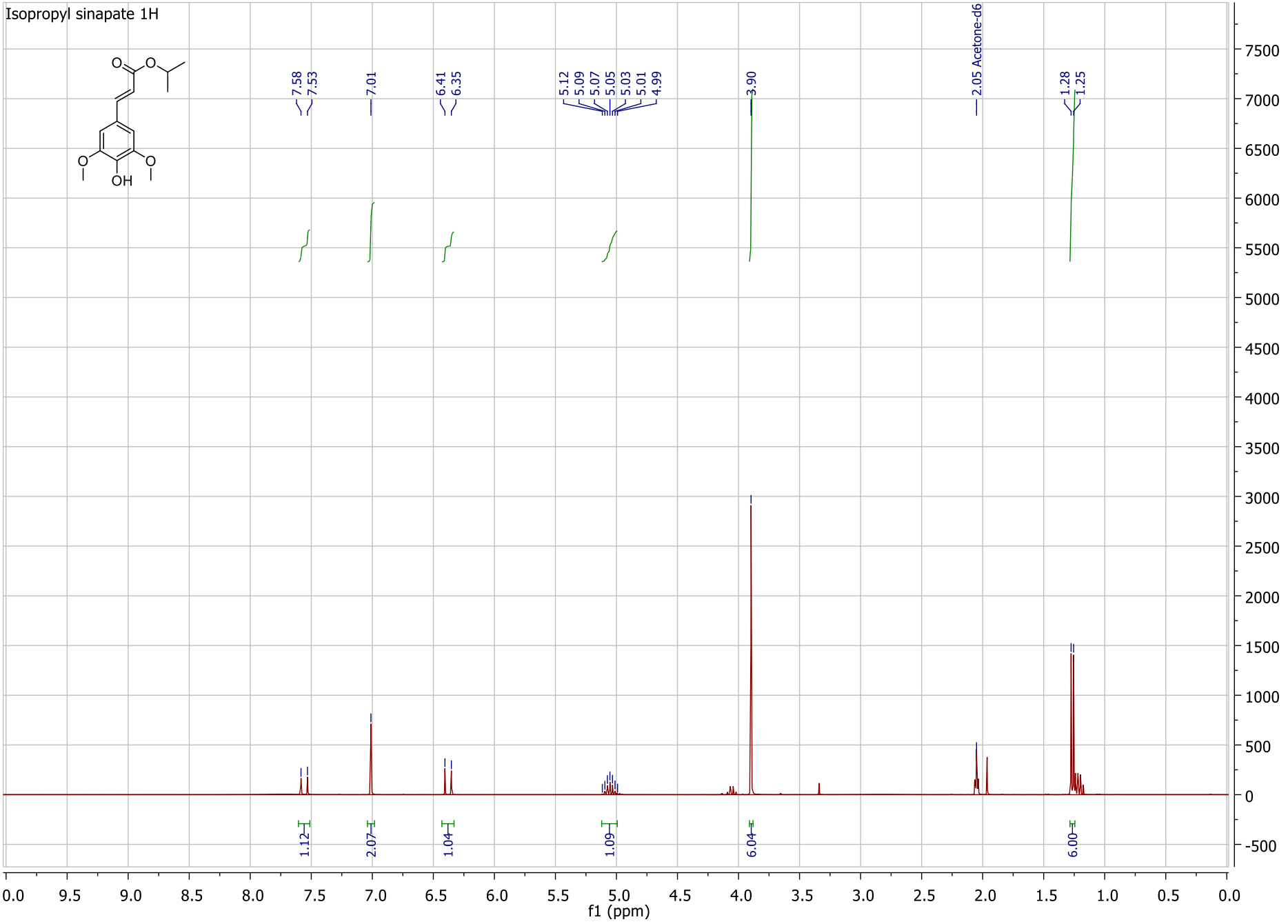

Heptyl sinapate 13C
167.32
147.24
144.89
137.12
125.89
115.94
105.00
77.16 Chloroform-d
64.66
56.30
31.76
28.99
28.78
25.97
22.62
14.10
O
O
O
O
OH
300000
250000
200000
150000
100000
50000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

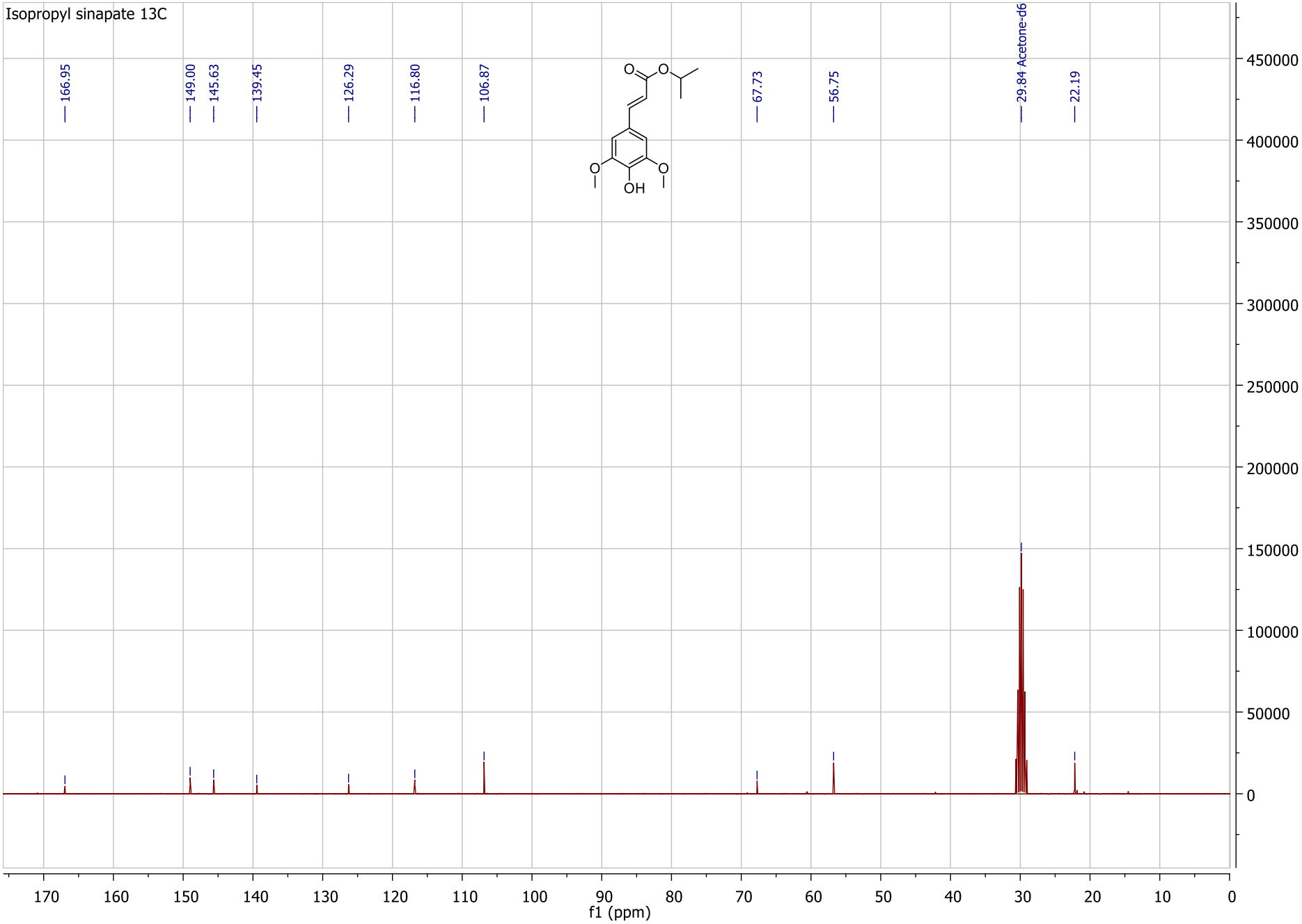

2-ethylhexyl sinapate 1H
2.50 Dimethyl Sulfoxide-d6
8.97
7.57
7.52
7.03
6.56
6.51
4.06
4.06
4.04
4.04
3.80
1.62
1.60
1.58
1.56
1.39
1.36
1.34
1.29
0.90
0.88
0.85
OH
0.99
1.01
1.97
1.00
2.23
5.90
1.02
8.25
6.12
f1 (ppm)

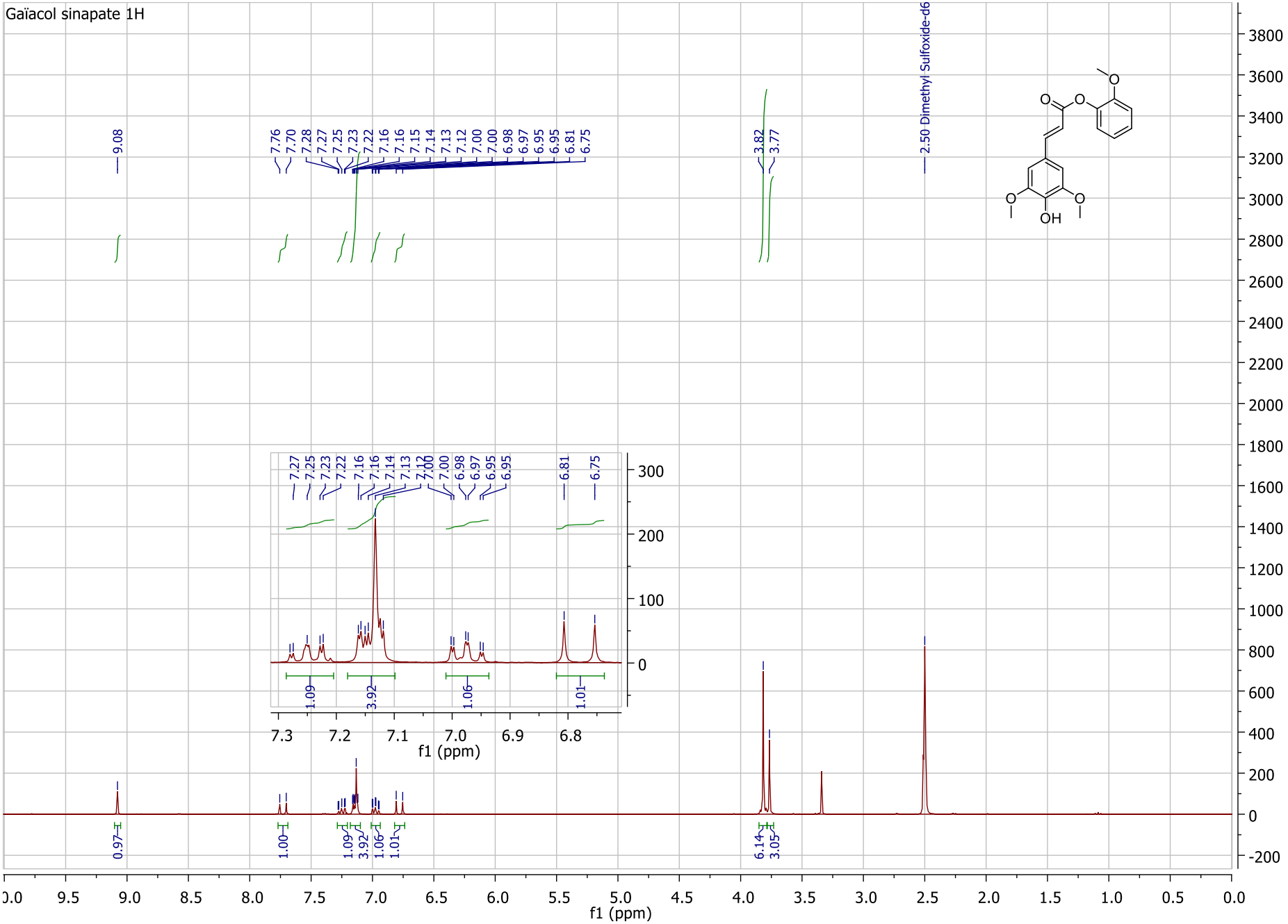

2-ethylhexyl sinapate 13C
166.83
148.03
145.36
138.20
124.41
114.93
106.24
65.73
56.11
39.52 Dimethyl Sulfoxide-d6
38.35
29.84
28.42
23.24
22.49
14.00
10.87
O
O
O
O
OH
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

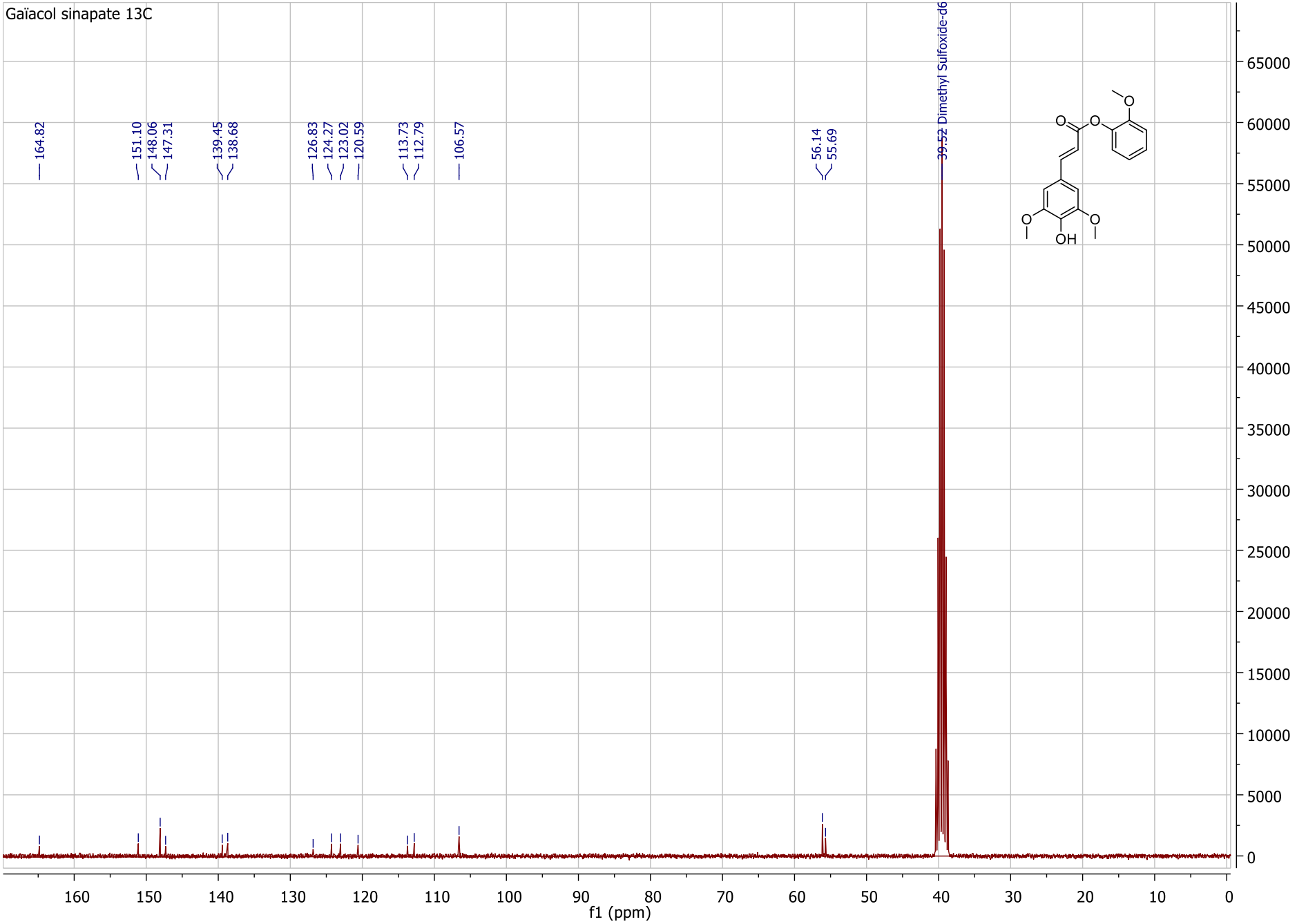

tert-Butyl sinapate 1H
7.487
7.434
6.947
6.319
6.267
3.846
2.050 Acetone-d6
1.458
OH
1.00
2.01
1.05
6.12
9.17
f1 (ppm)

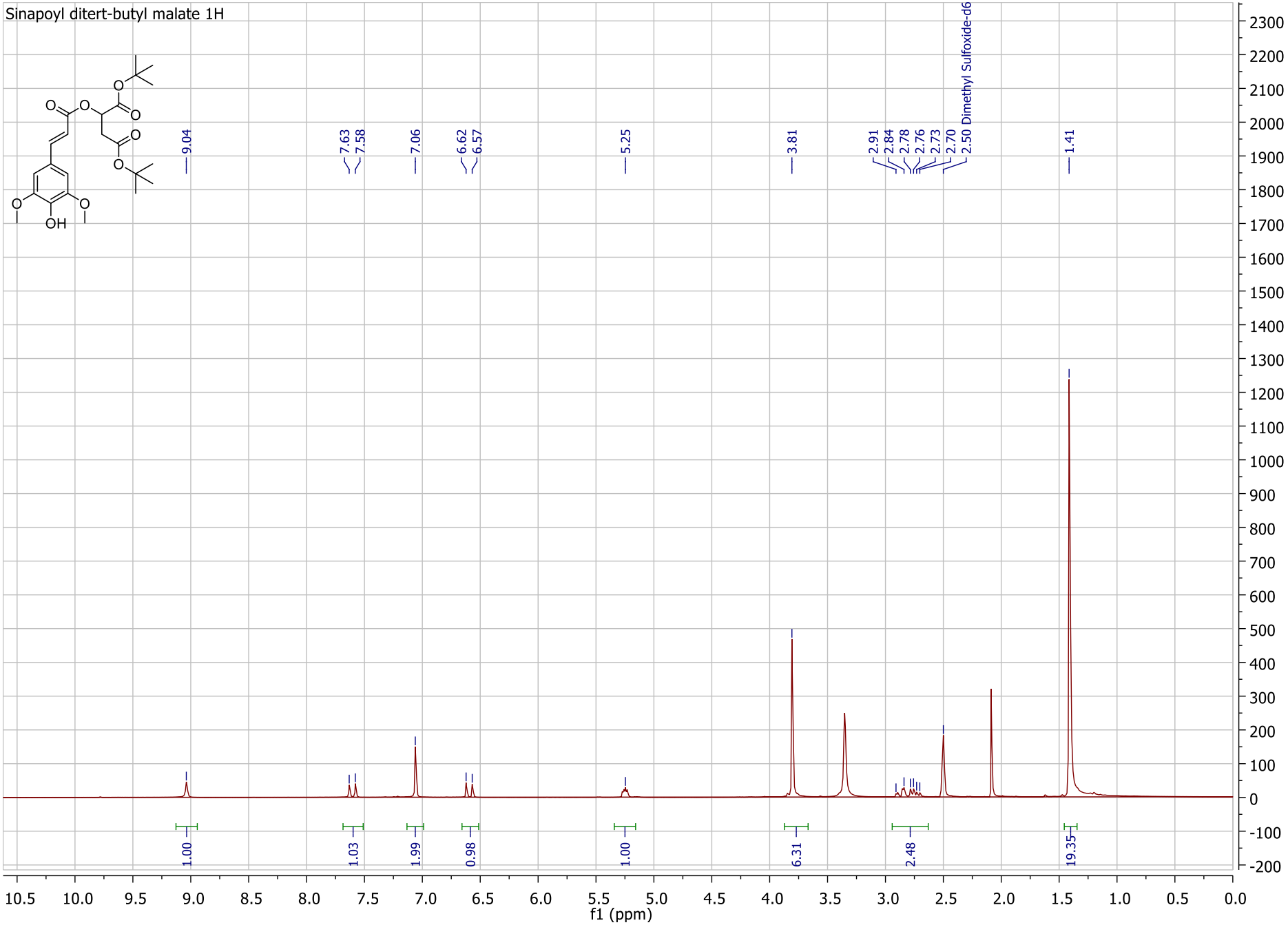

tert-Butyl sinapate 13C
166.85
148.84
144.99
139.12
126.22
117.96
106.53
80.11
56.60
29.84 Acetone-d6
28.35
O
O
O
O
OH
250000
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

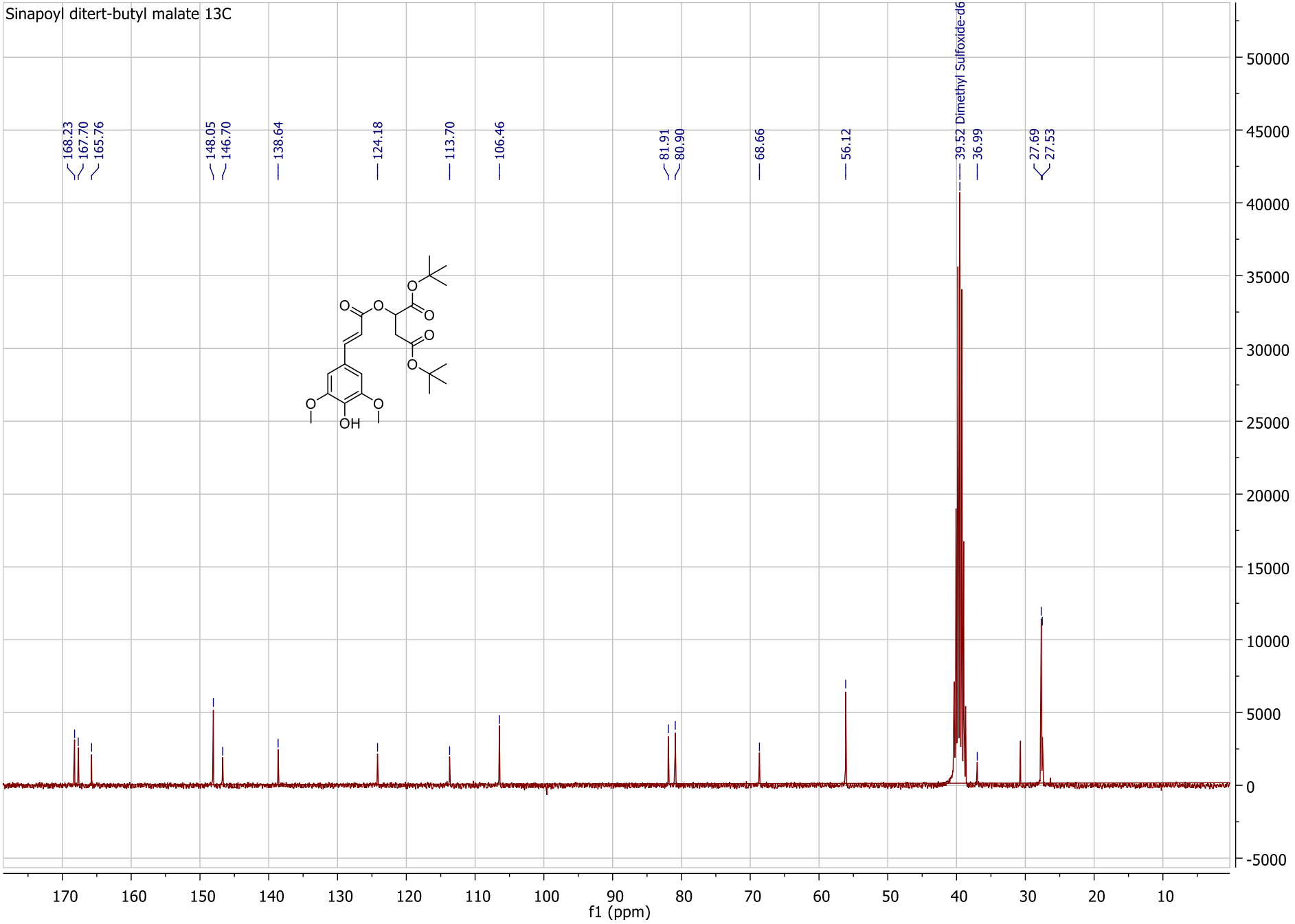

Isopropyl sinapate 1H
7.58
7.53
7.01
6.41
6.35
5.12
5.09
5.07
5.05
5.03
5.01
4.99
3.90
2.05 Acetone-d6
1.28
1.25
1.12
2.07
1.04
1.09
6.04
6.00
f1 (ppm)

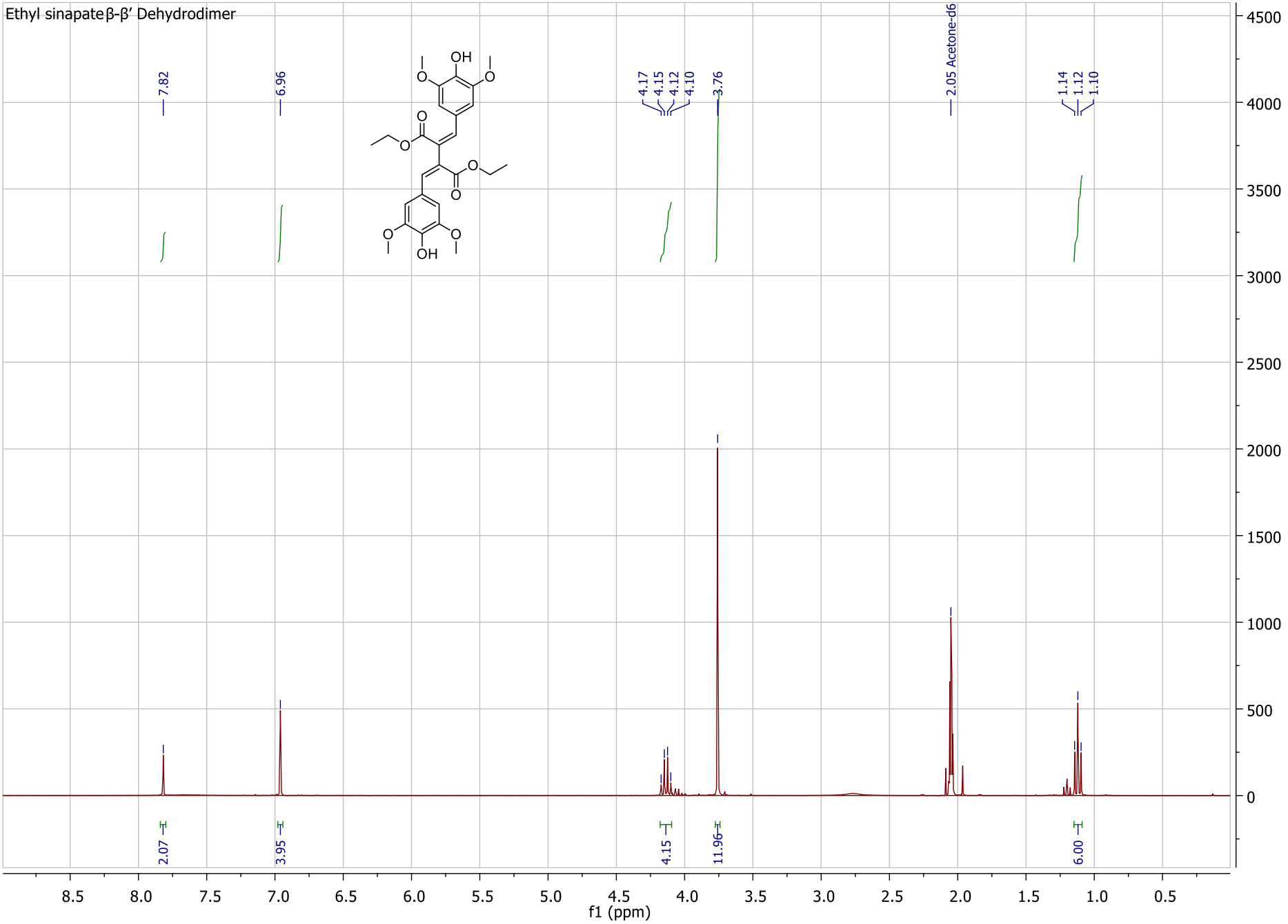

Isopropyl sinapate 13C
166.95
149.00
145.63
139.45
126.29
116.80
106.87
67.73
56.75
29.84 Acetone-d6
22.19
O
O
O
O
OH
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

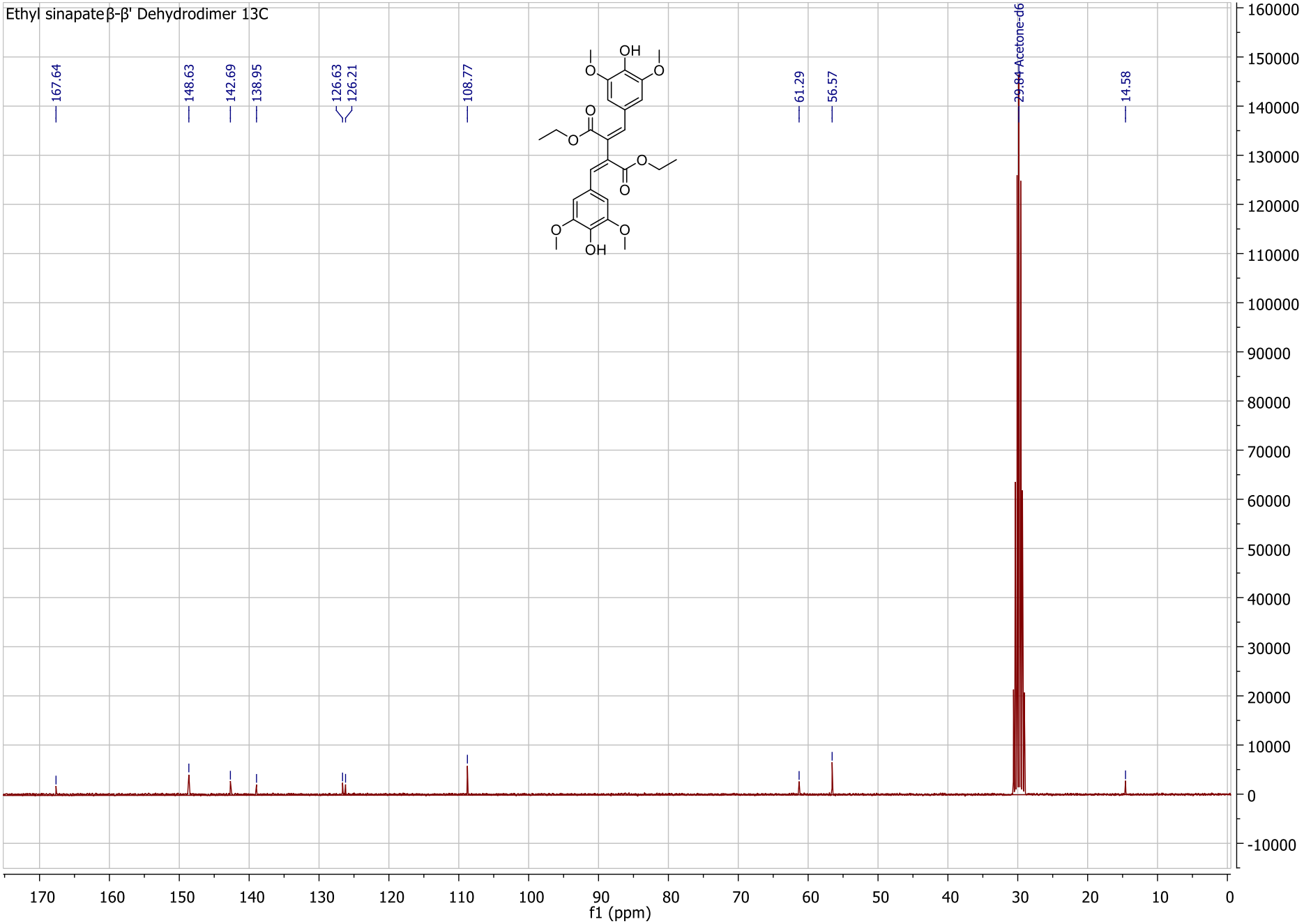

Gaïacol sinapate 1H
2.50 Dimethyl Sulfoxide-d6
9.08
7.76
7.70
7.28
7.27
7.25
7.23
7.22
7.16
7.16
7.15
7.14
7.13
7.12
7.00
7.00
6.98
6.97
6.95
6.95
6.81
6.75
3.82
3.77
OH
f1 (ppm)

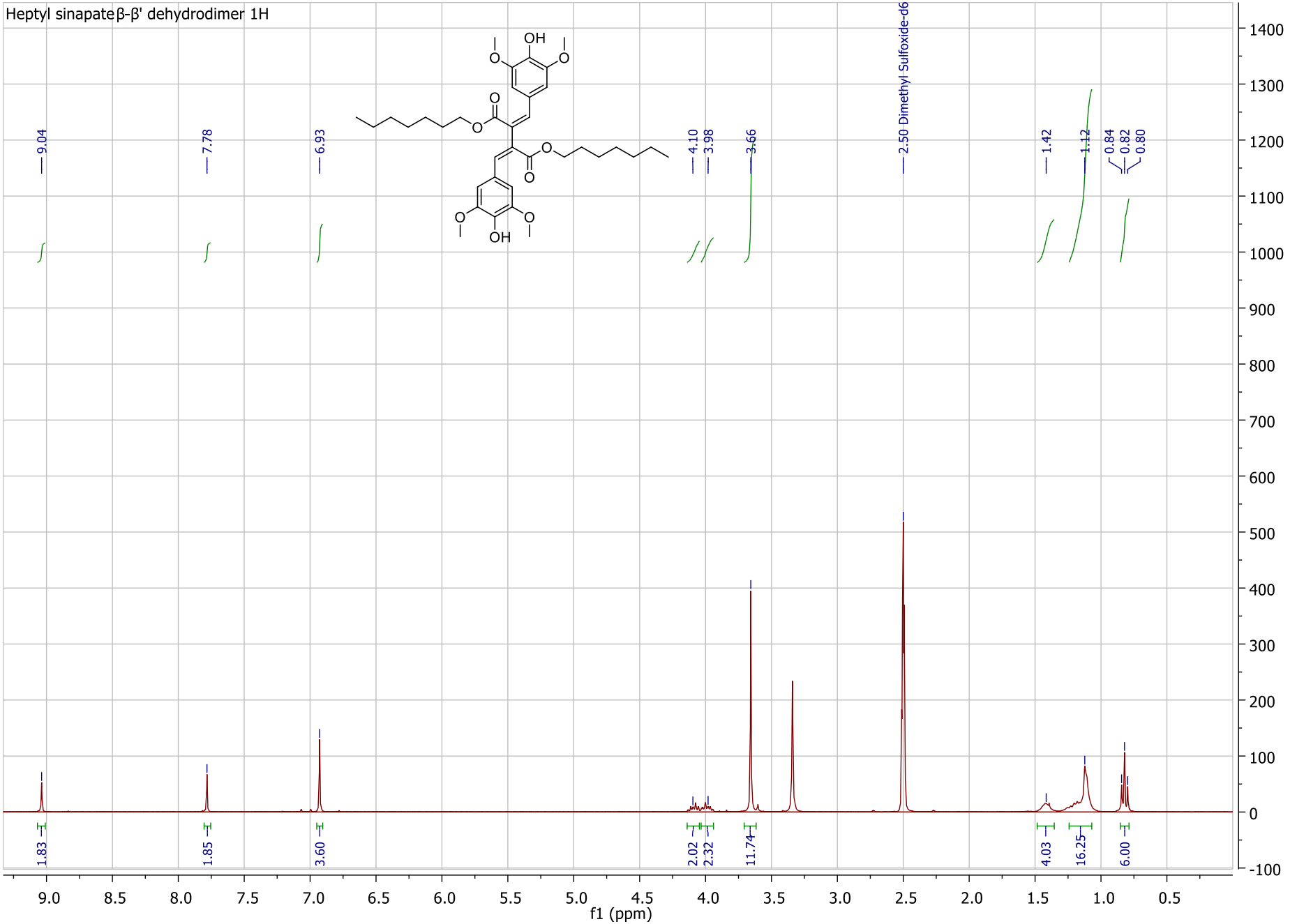

Gaïacol sinapate 13C
164.82
151.10
148.06
147.31
139.45
138.68
126.83
124.27
123.02
120.59
113.73
112.79
106.57
56.14
55.69
39.52 Dimethyl Sulfoxide-d6
OH
f1 (ppm)

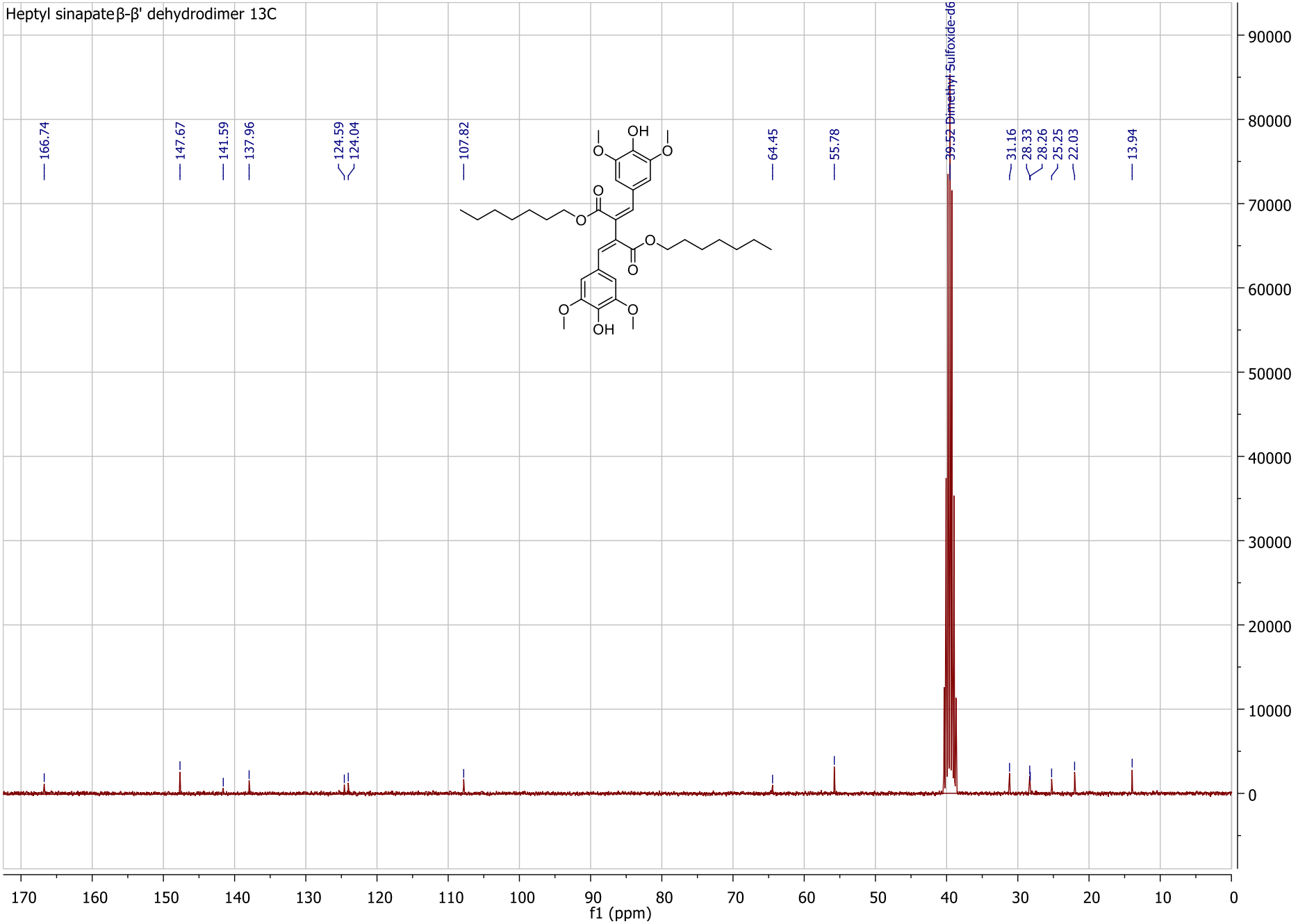

Sinapoyl ditert-butyl malate 1H
9.04
7.63
7.58
7.06
6.62
6.57
5.25
3.81
2.91
2.84
2.78
2.76
2.73
2.70
2.50 Dimethyl Sulfoxide-d6
1.41
1.00
1.03
1.99
0.98
1.00
6.31
2.48
19.35
f1 (ppm)

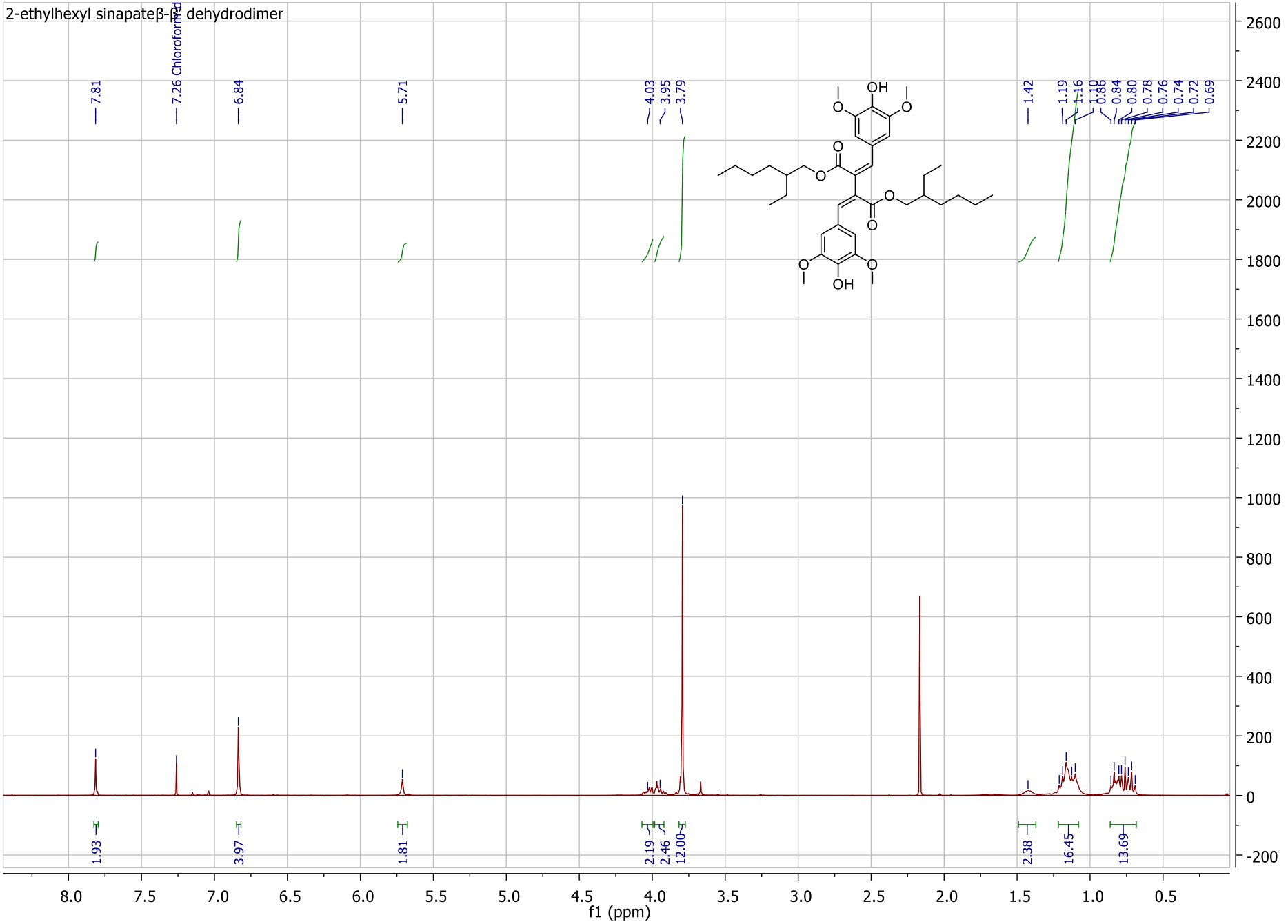

Sinapoyl ditert-butyl malate 13C
168.23
167.70
165.76
148.05
146.70
138.64
124.18
113.70
106.46
81.91
80.90
68.66
56.12
39.52 Dimethyl Sulfoxide-d6
36.99
27.69
27.53
OH
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

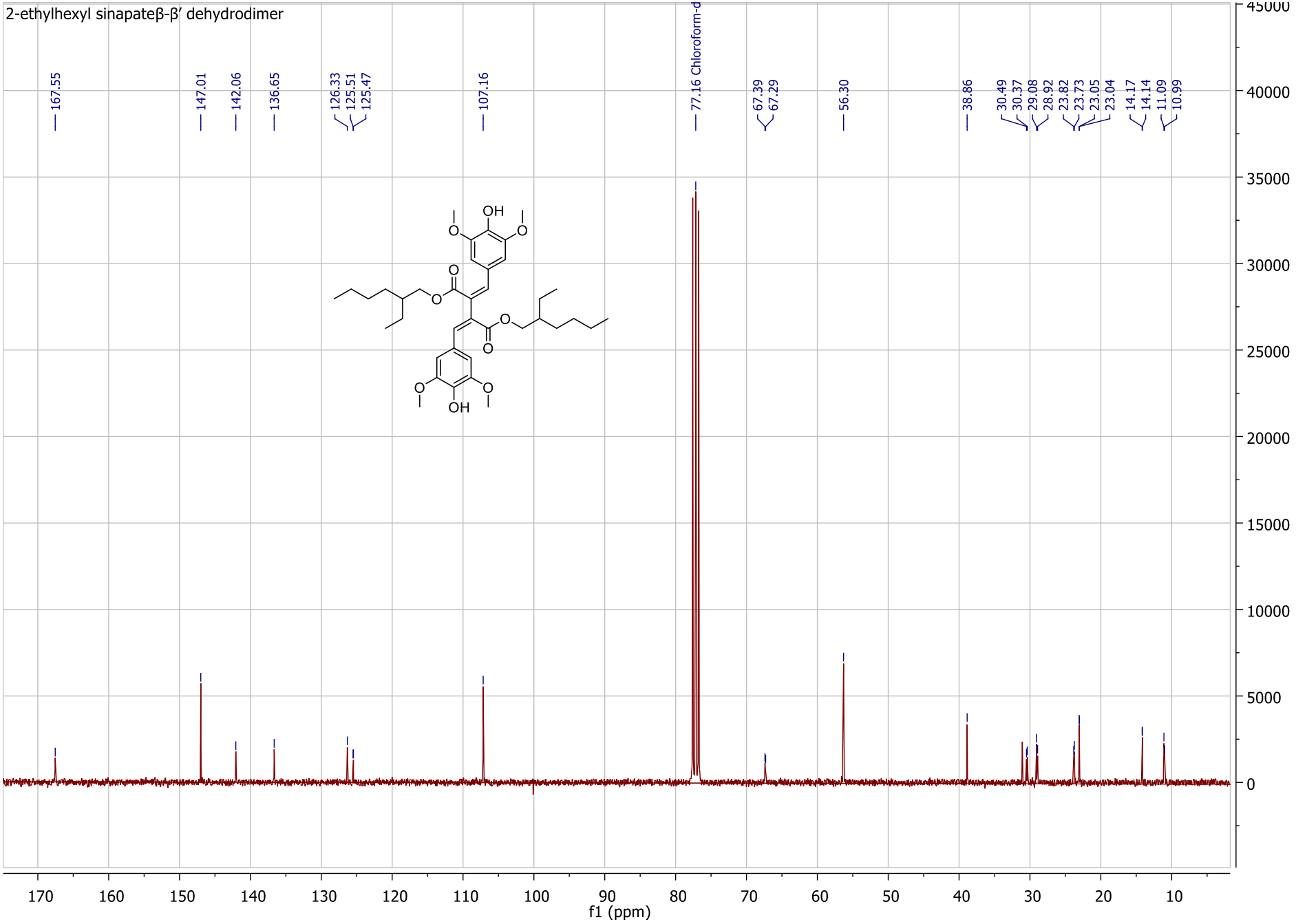

Ethyl sinapate β-β′ Dehydrodimer
7.82
6.96
4.17
4.15
4.12
4.10
3.76
2.05 Acetone-d6
1.14
1.12
1.10
OH
O
OH
2.07
3.95
4.15
11.96
6.00
f1 (ppm)

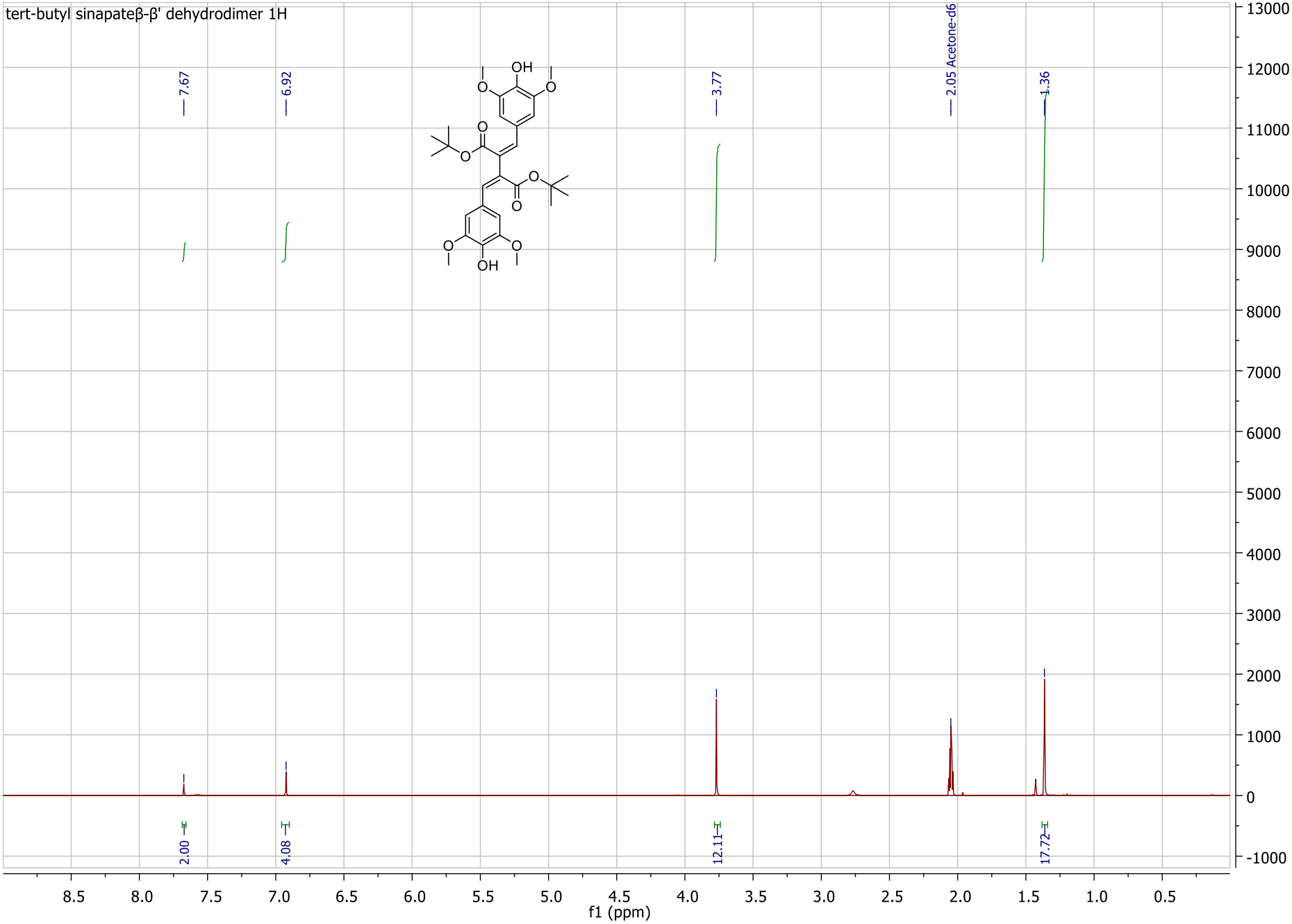

Ethyl sinapate β-β' Dehydrodimer 13C
167.64
148.63
142.69
138.95
126.63
126.21
108.77
61.29
56.57
29.84 Acetone-d6
14.58
OH
O
O
O
O
O
O
O
O
OH
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

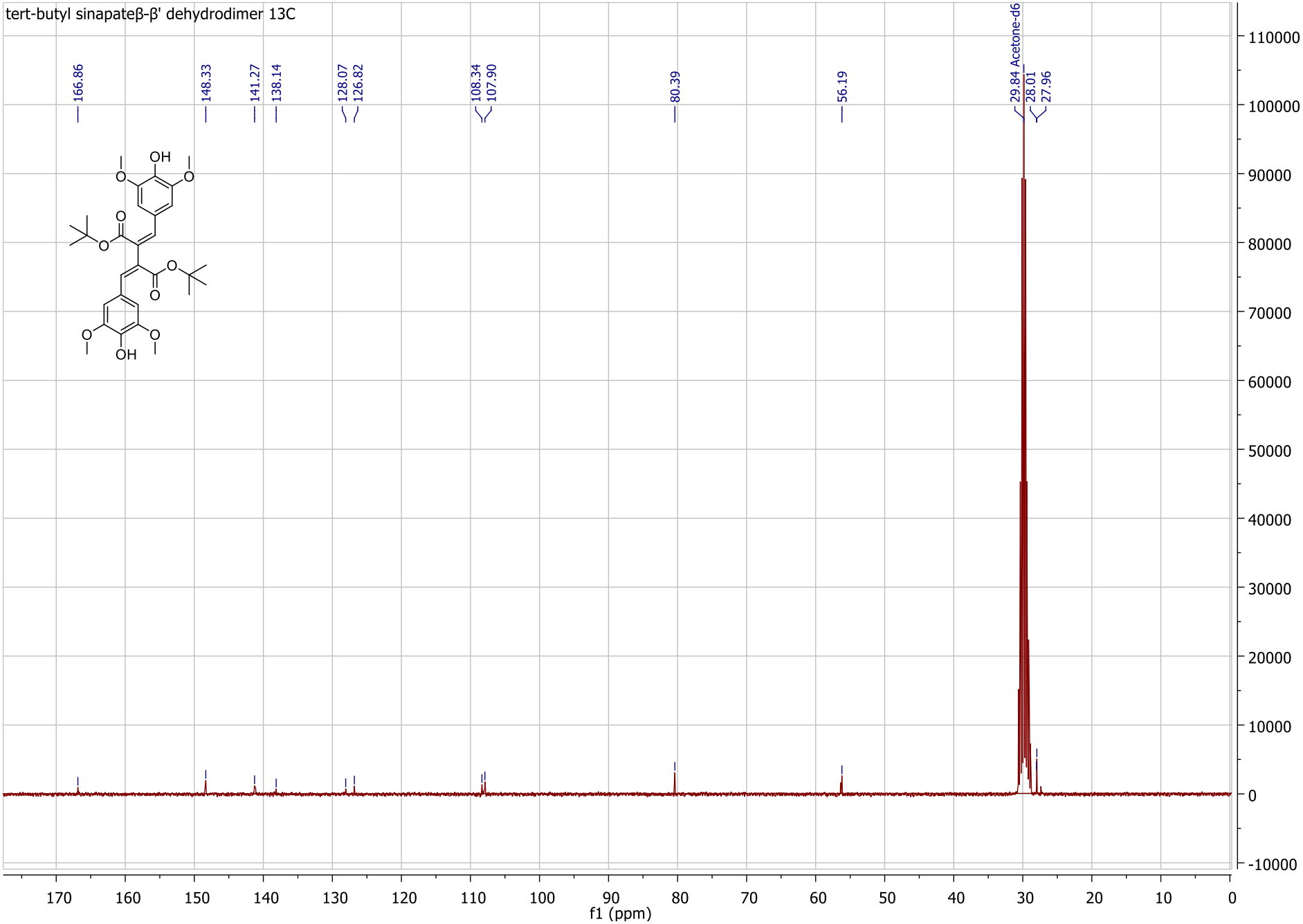

Heptyl sinapate β-β' dehydrodimer 1H
9.04
7.78
6.93
4.10
3.98
3.66
2.50 Dimethyl Sulfoxide-d6
1.42
1.12
0.84
0.82
0.80
1.83
1.85
3.60
2.02
2.32
11.74
4.03
16.25
6.00
f1 (ppm)

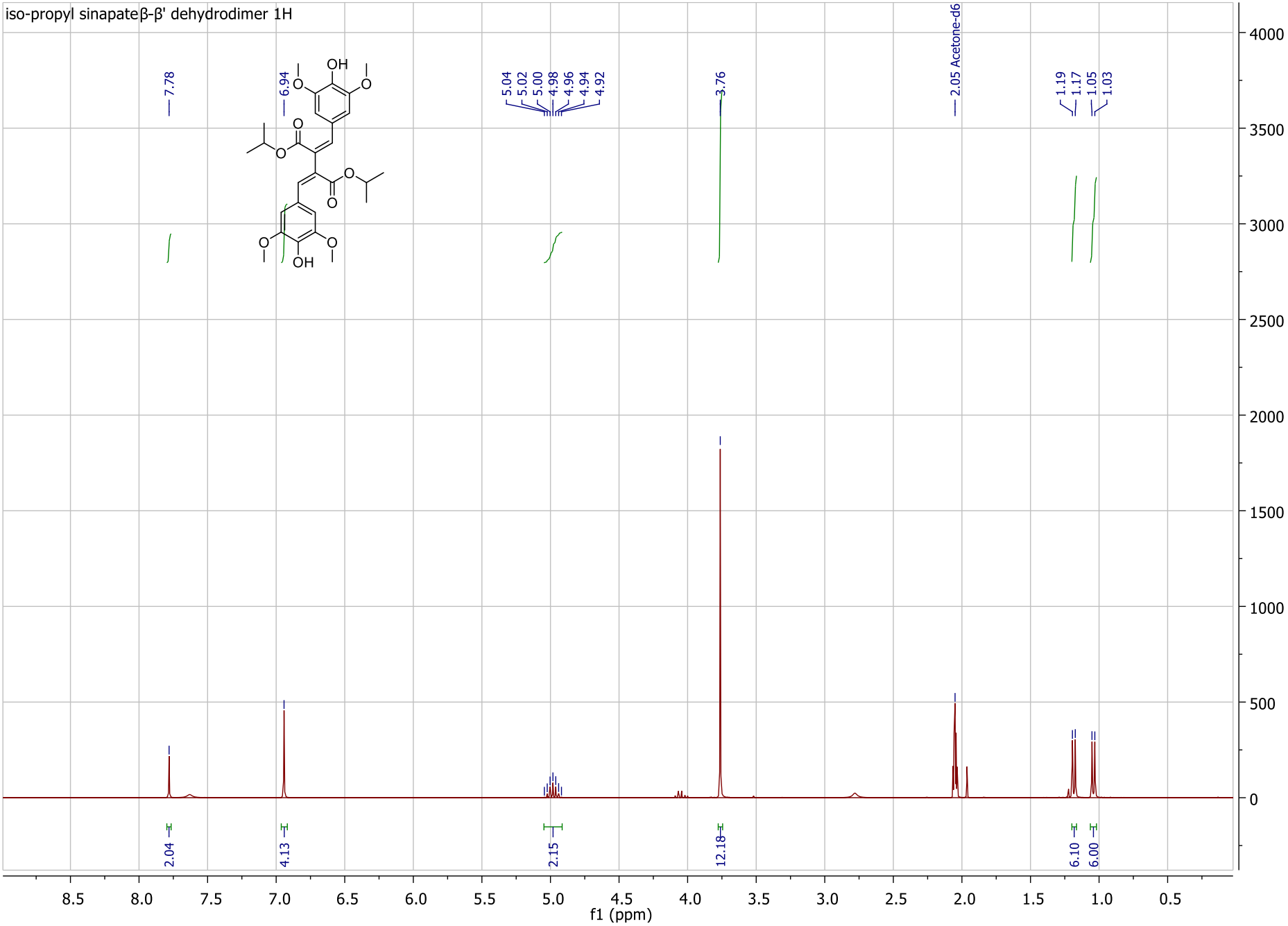

Heptyl sinapate β-β' dehydrodimer 13C
166.74
147.67
141.59
137.96
124.59
124.04
107.82
64.45
55.78
39.52 Dimethyl Sulfoxide-d6
31.16
28.33
28.26
25.25
22.03
13.94
OH
O
O
O
O
O
O
O
O
OH
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

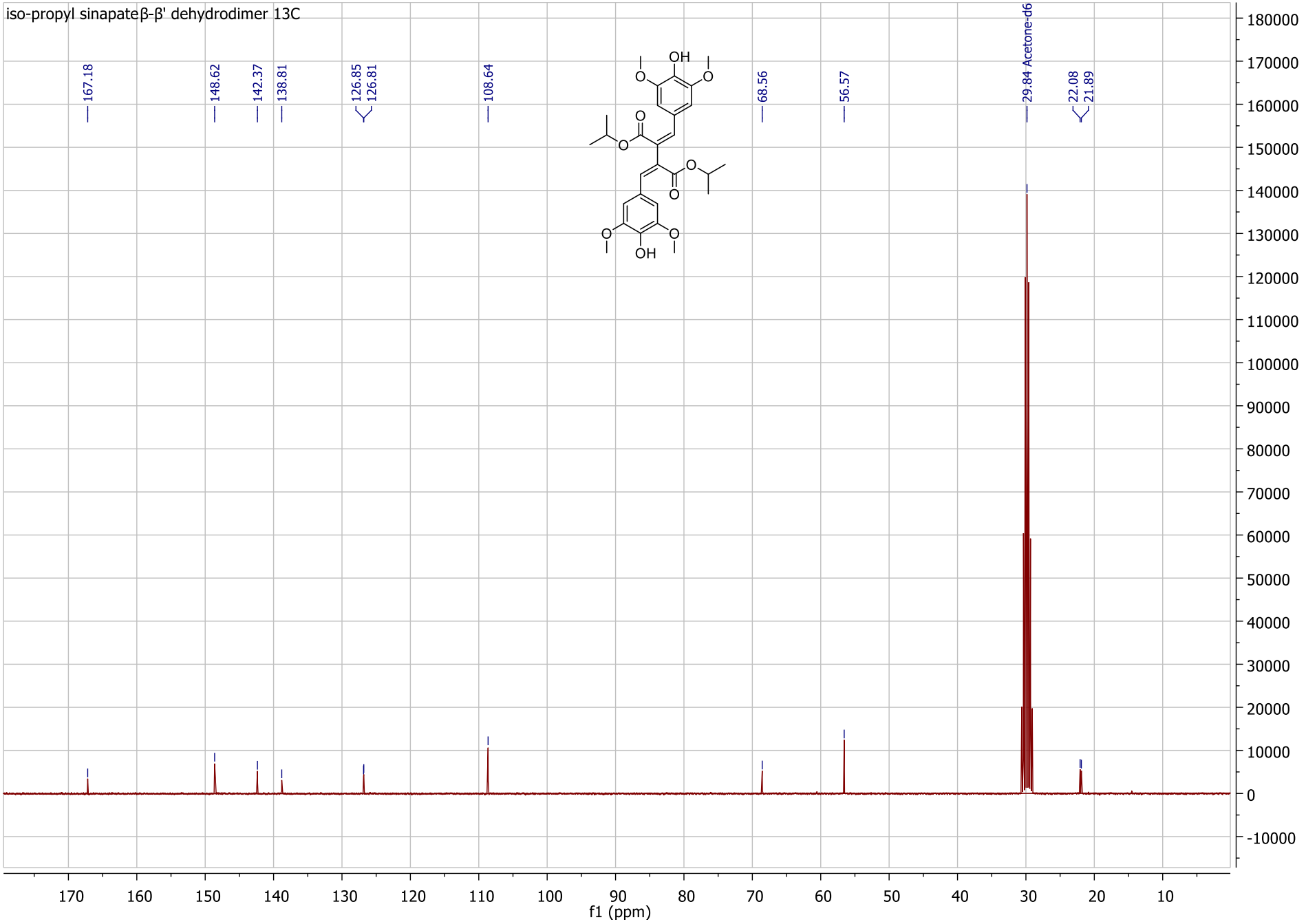

2-ethylhexyl sinapateβ-β dehydrodimer
7.81
7.26 Chloroform-d
6.84
5.71
4.03
3.95
3.79
1.42
1.19
1.16
1.10
0.86
0.84
0.80
0.78
0.76
0.74
0.72
0.69
OH
OH
1.93
3.97
1.81
2.19
2.46
12.00
2.38
16.45
13.69
f1 (ppm)

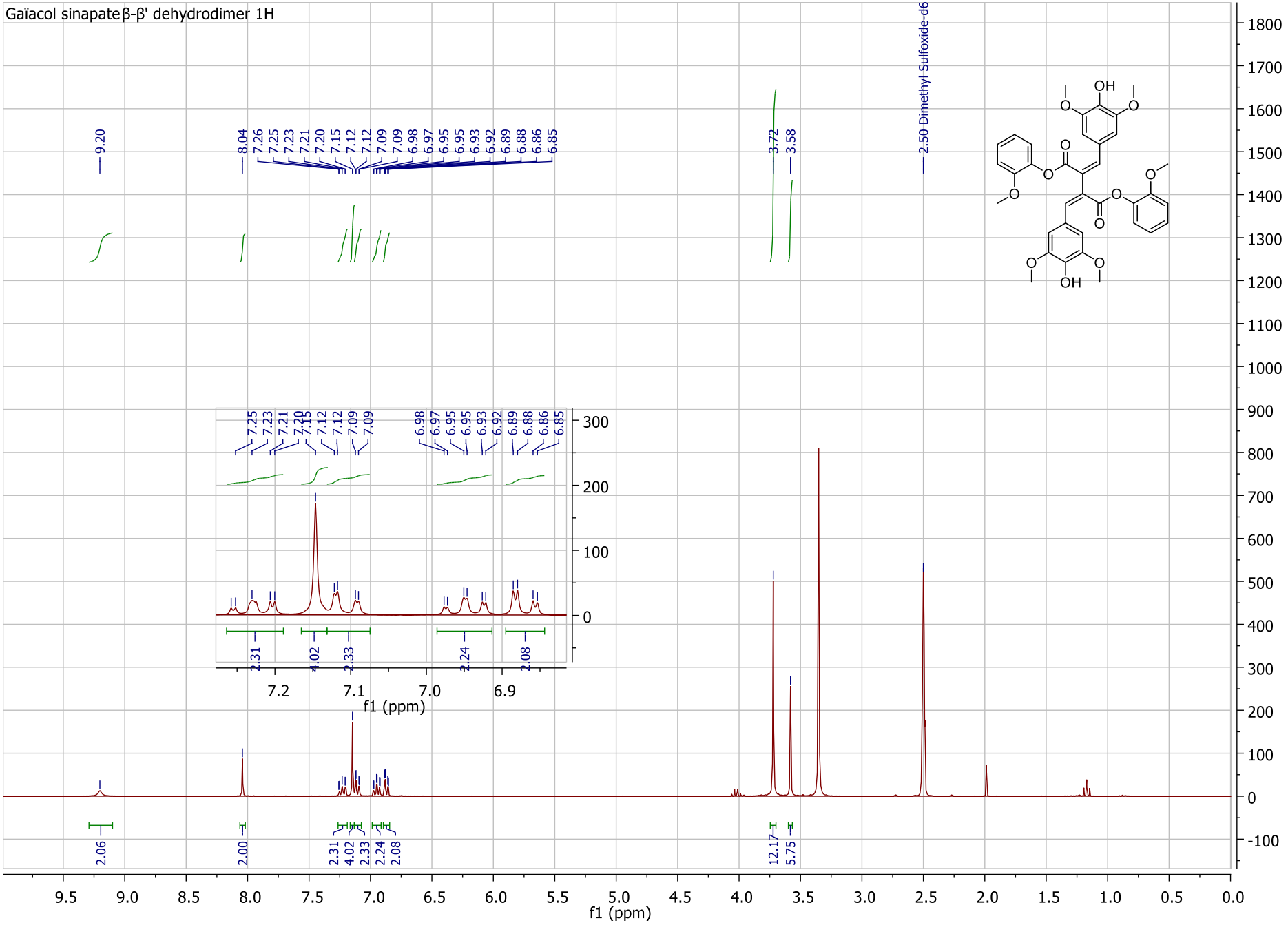

2-ethylhexyl sinapateβ-β′ dehydrodimer
167.55
147.01
142.06
136.65
126.33
125.51
125.47
107.16
77.16 Chloroform-d
67.39
67.29
56.30
38.86
30.49
30.37
29.08
28.92
23.82
23.73
23.05
23.04
14.17
14.14
11.09
10.99
OH
O
O
O
O
O
O
O
O
OH
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

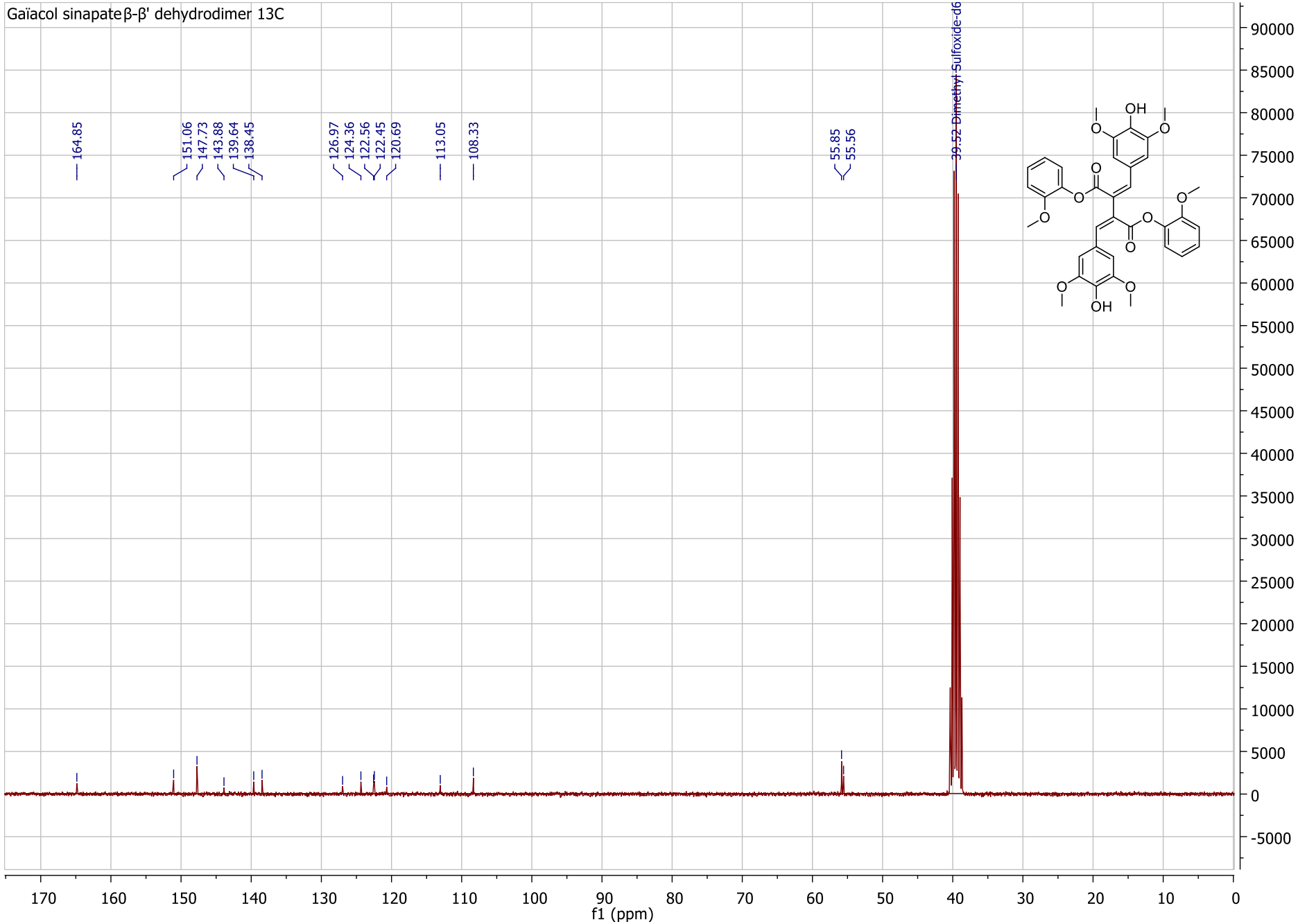

tert-butyl sinapateβ-β' dehydrodimer 1H
7.67
6.92
3.77
2.05 Acetone-d6
1.36
2.00
4.08
12.11
17.72
f1 (ppm)

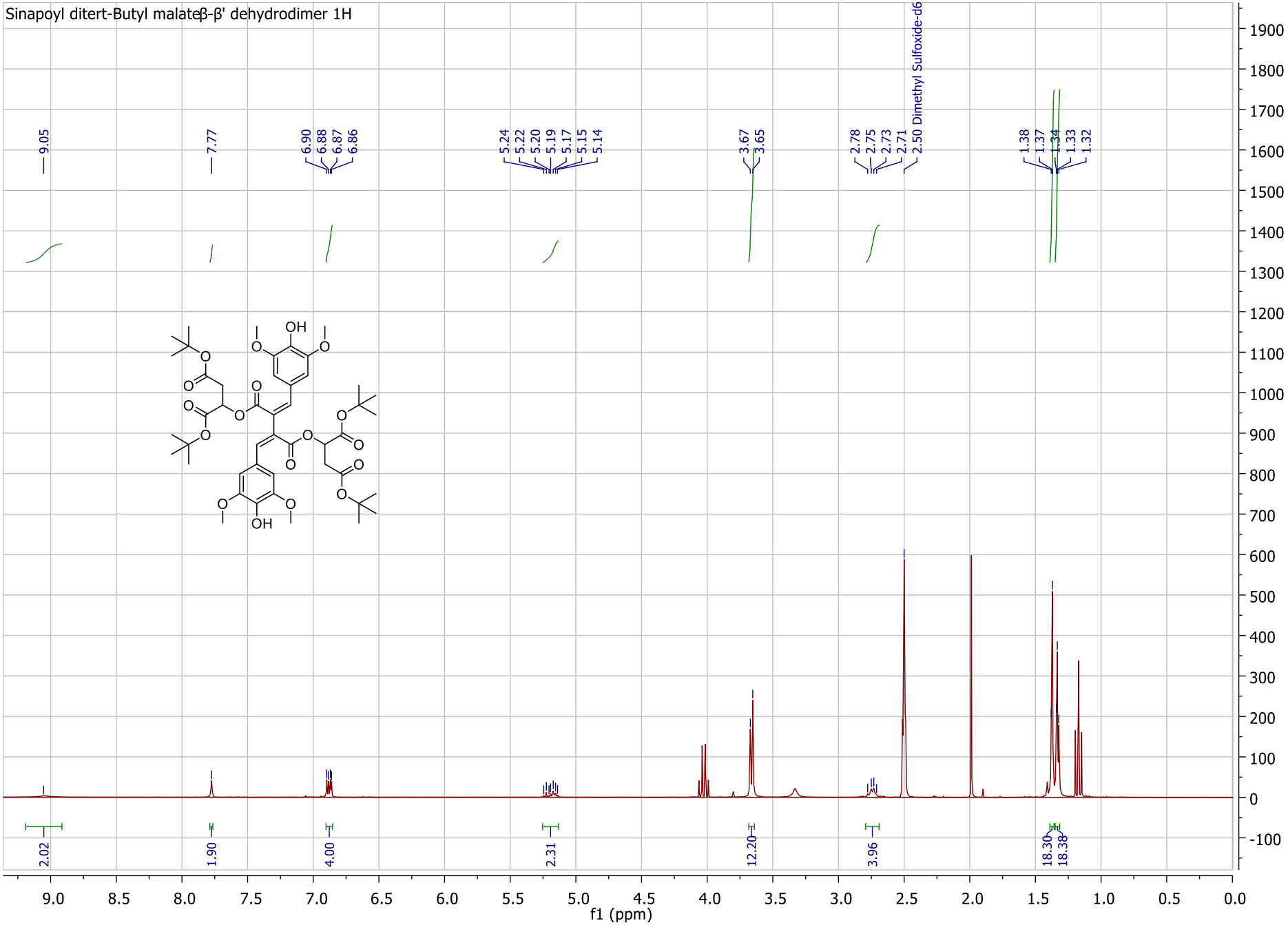

tert-butyl sinapateβ-β' dehydrodimer 13C
166.86
148.33
141.27
138.14
128.07
126.82
108.34
107.90
80.39
56.19
29.84 Acetone-d6
28.01
27.96
OH
O
O
O
O
O
O
O
OH
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

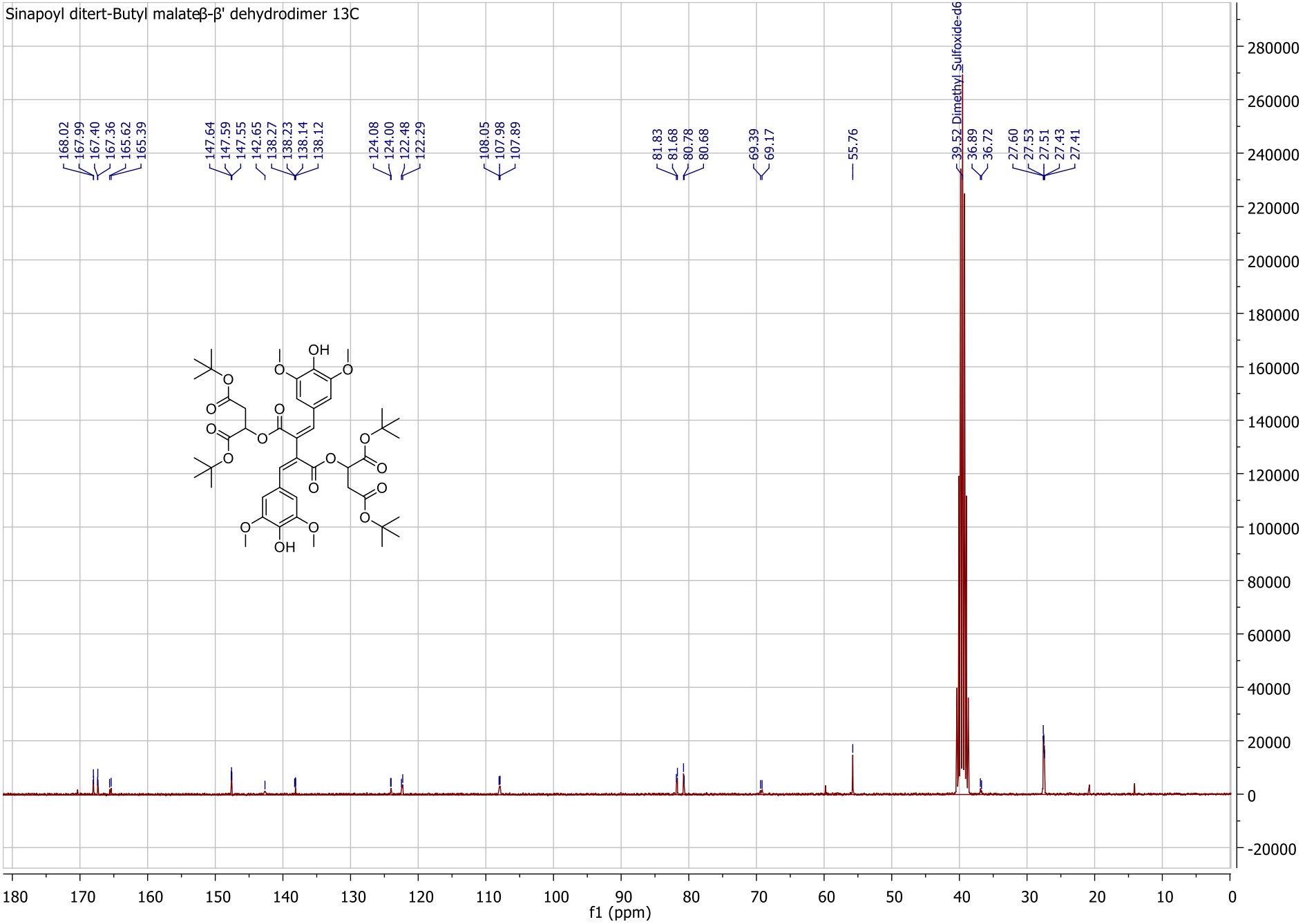

iso-propyl sinapateβ-β' dehydrodimer 1H
7.78
6.94
5.04
5.02
5.00
4.98
4.96
4.94
4.92
3.76
2.05 Acetone-d6
1.19
1.17
1.05
1.03
2.04
4.13
2.15
12.18
6.10
6.00
f1 (ppm)

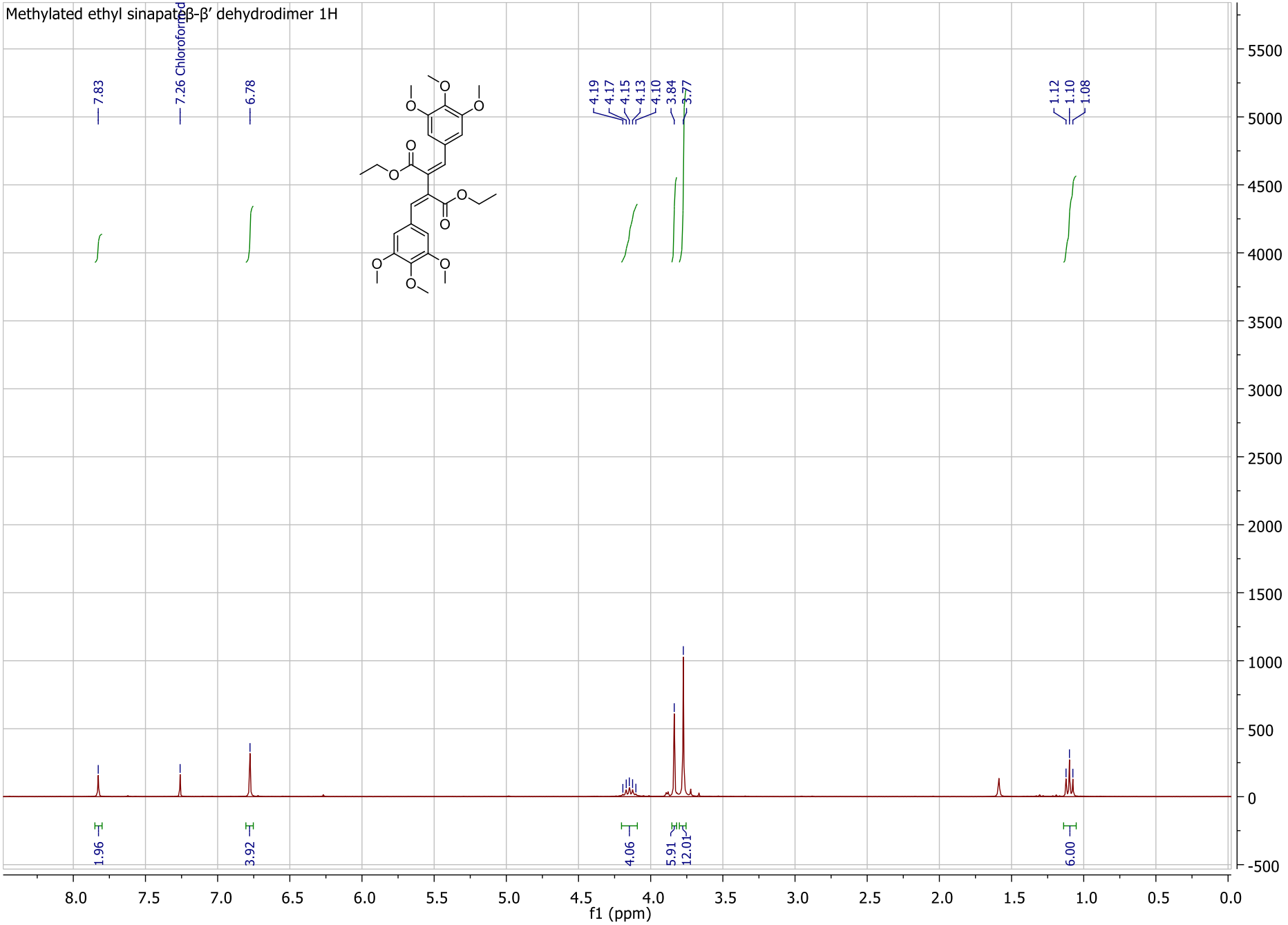

iso-propyl sinapateβ-β' dehydrodimer 13C
167.18
148.62
142.37
138.81
126.85
126.81
108.64
68.56
56.57
29.84 Acetone-d6
22.08
21.89
OH
O
O
O
O
O
O
O
OH
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

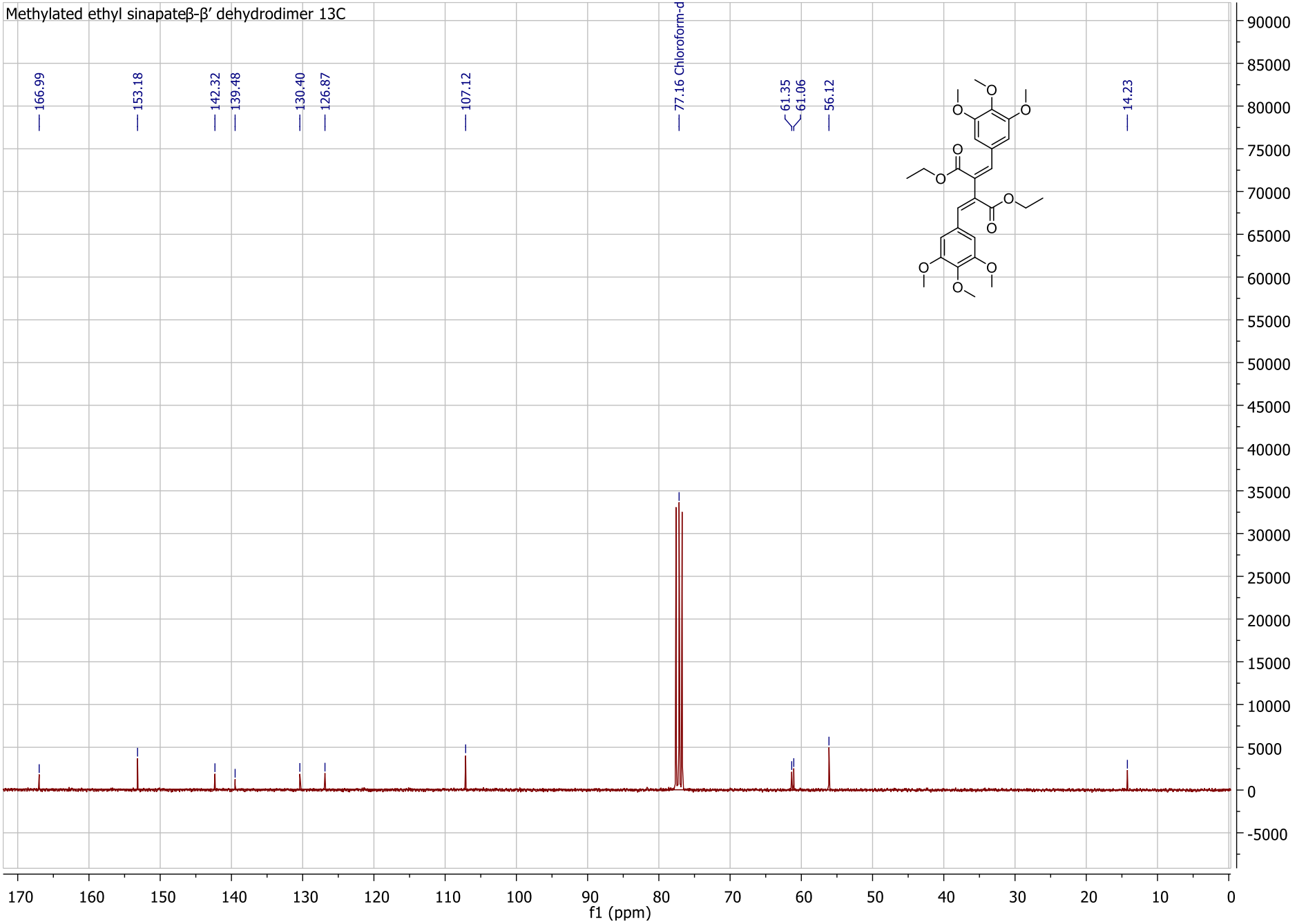

Gaïacol sinapate β-β' dehydrodimer 1H
9.20
8.04
7.26
7.25
7.23
7.21
7.20
7.15
7.12
7.12
7.09
7.09
6.98
6.97
6.95
6.95
6.93
6.92
6.89
6.88
6.86
6.85
3.72
3.58
2.50 Dimethyl Sulfoxide-d6
OH
OH
2.06
2.00
2.31
4.02
2.33
2.24
2.08
12.17
5.75
f1 (ppm)

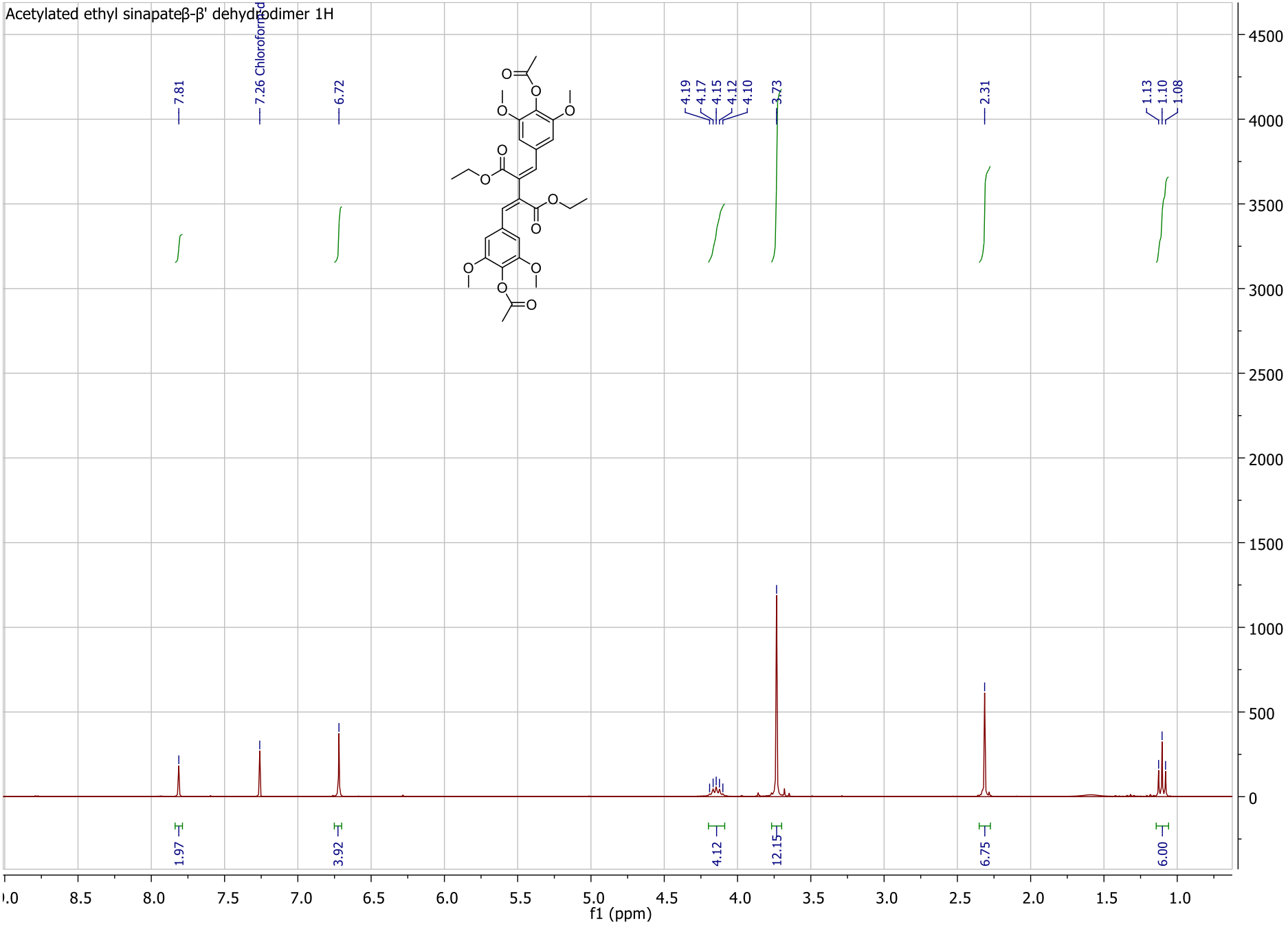

Gaïacol sinapate β-β' dehydrodimer 13C
164.85
151.06
147.73
143.88
139.64
138.45
126.97
124.36
122.56
122.45
120.69
113.05
108.33
55.85
55.56
39.52 Dimethyl Sulfoxide-d6
OH
O
O
O
O
O
O
O
O
O
O
OH
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

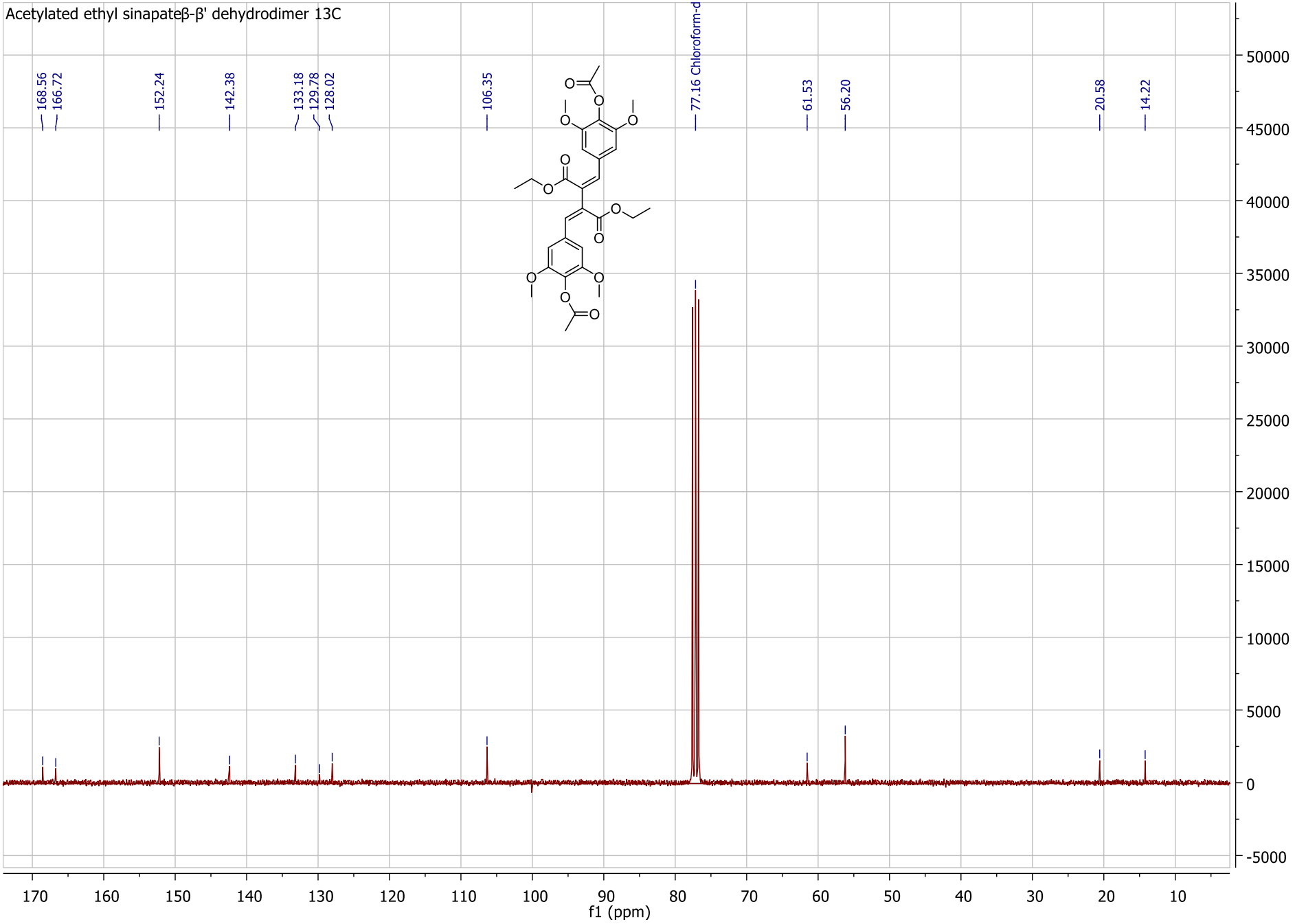

Sinapoyl ditert-Butyl malateβ-β' dehydrodimer 1H
9.05
7.77
6.90
6.88
6.87
6.86
5.24
5.22
5.20
5.19
5.17
5.15
5.14
3.67
3.65
2.78
2.75
2.73
2.71
2.50 Dimethyl Sulfoxide-d6
1.38
1.37
1.34
1.33
1.32
OH
OH
2.02
1.90
4.00
2.31
12.20
3.96
18.30
18.38
f1 (ppm)

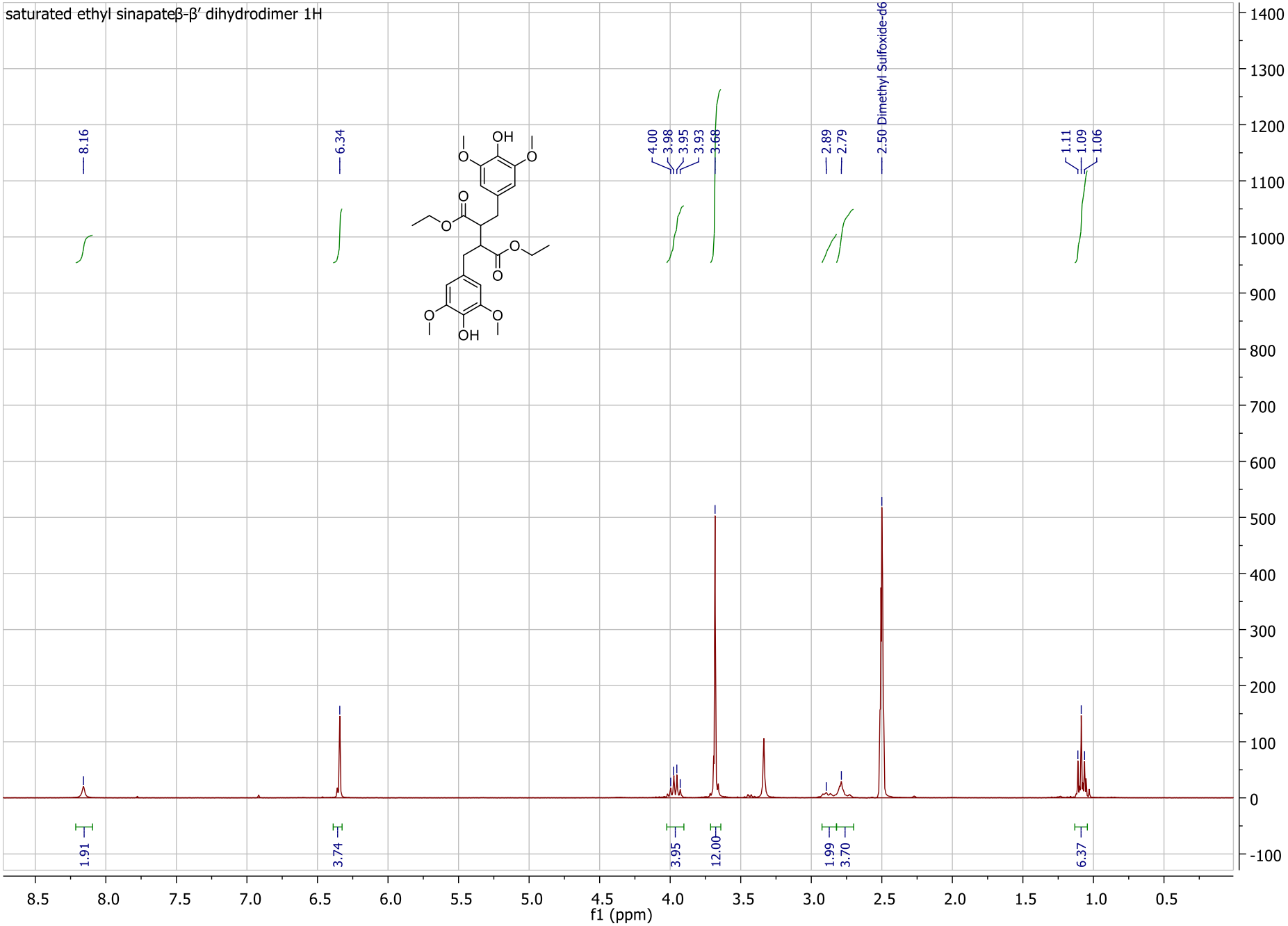

Sinapoyl ditert-Butyl malateβ-β' dehydrodimer 13C
168.02
167.99
167.40
167.36
165.62
165.39
147.64
147.59
147.55
142.65
138.27
138.23
138.14
138.12
124.08
124.00
122.48
122.29
108.05
107.98
107.89
81.83
81.68
80.78
80.68
69.39
69.17
55.76
39.52 Dimethyl Sulfoxide-d6
36.89
36.72
27.60
27.53
27.51
27.43
27.41
OH
OH
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

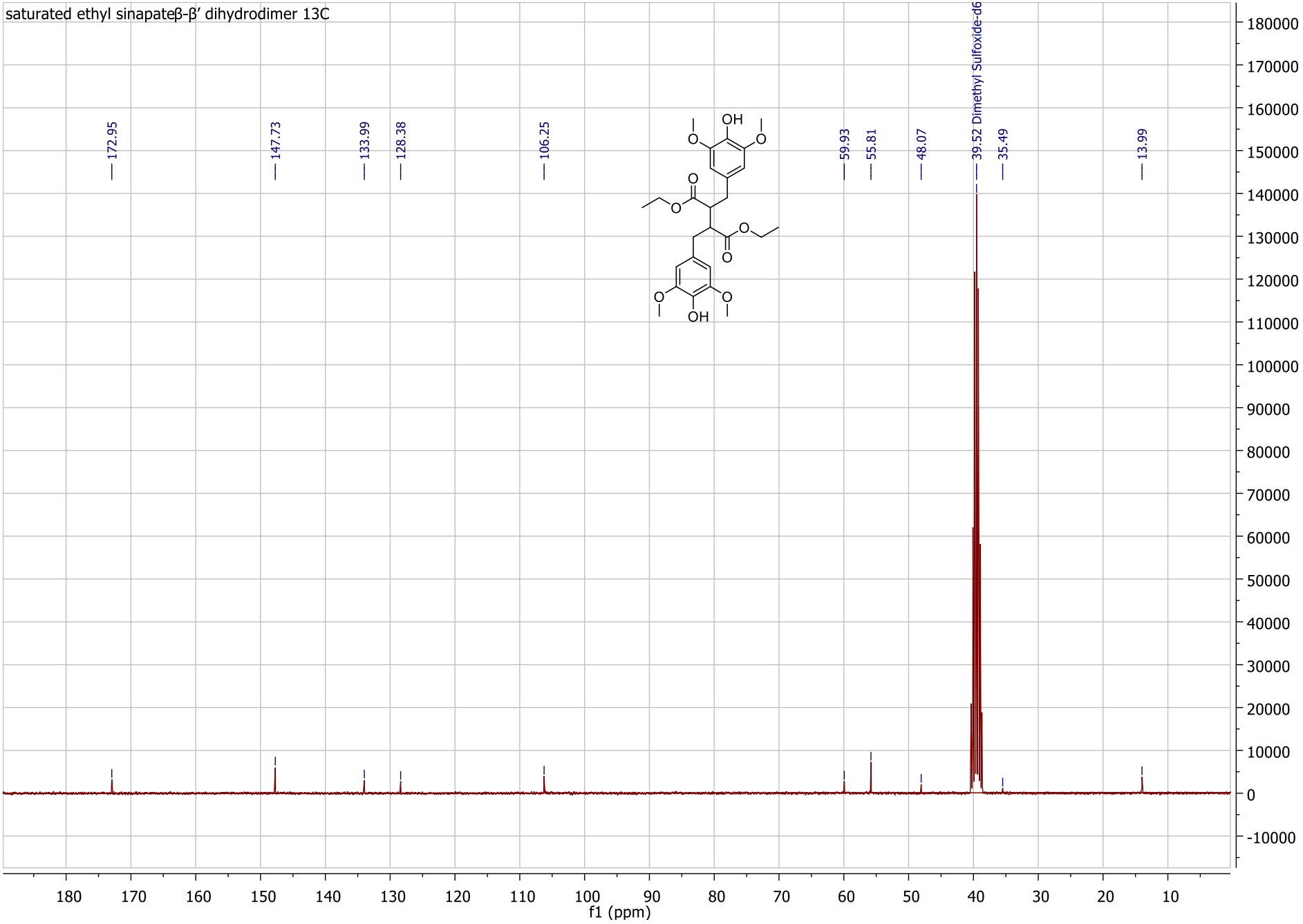

Methylated ethyl sinapate β-β' dehydrodimer 1H
7.83
7.26 Chloroform-d
6.78
4.19
4.17
4.15
4.13
4.10
3.84
3.77
1.12
1.10
1.08
1.96
3.92
4.06
5.91
12.01
6.00
f1 (ppm)

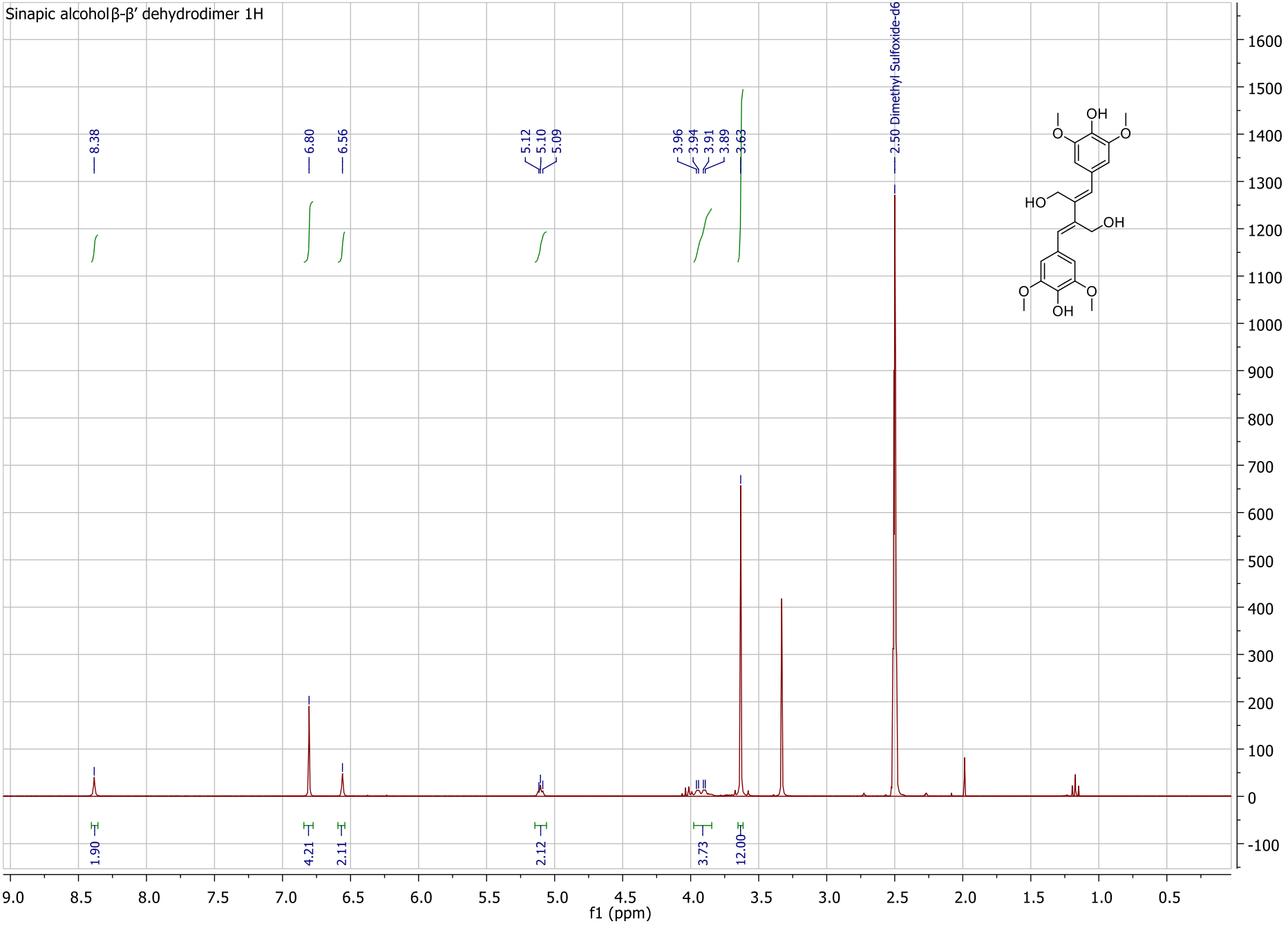

Methylated ethyl sinapateβ-β' dehydrodimer 13C
166.99
153.18
142.32
139.48
130.40
126.87
107.12
77.16 Chloroform-d
61.35
61.06
56.12
14.23
f1 (ppm)

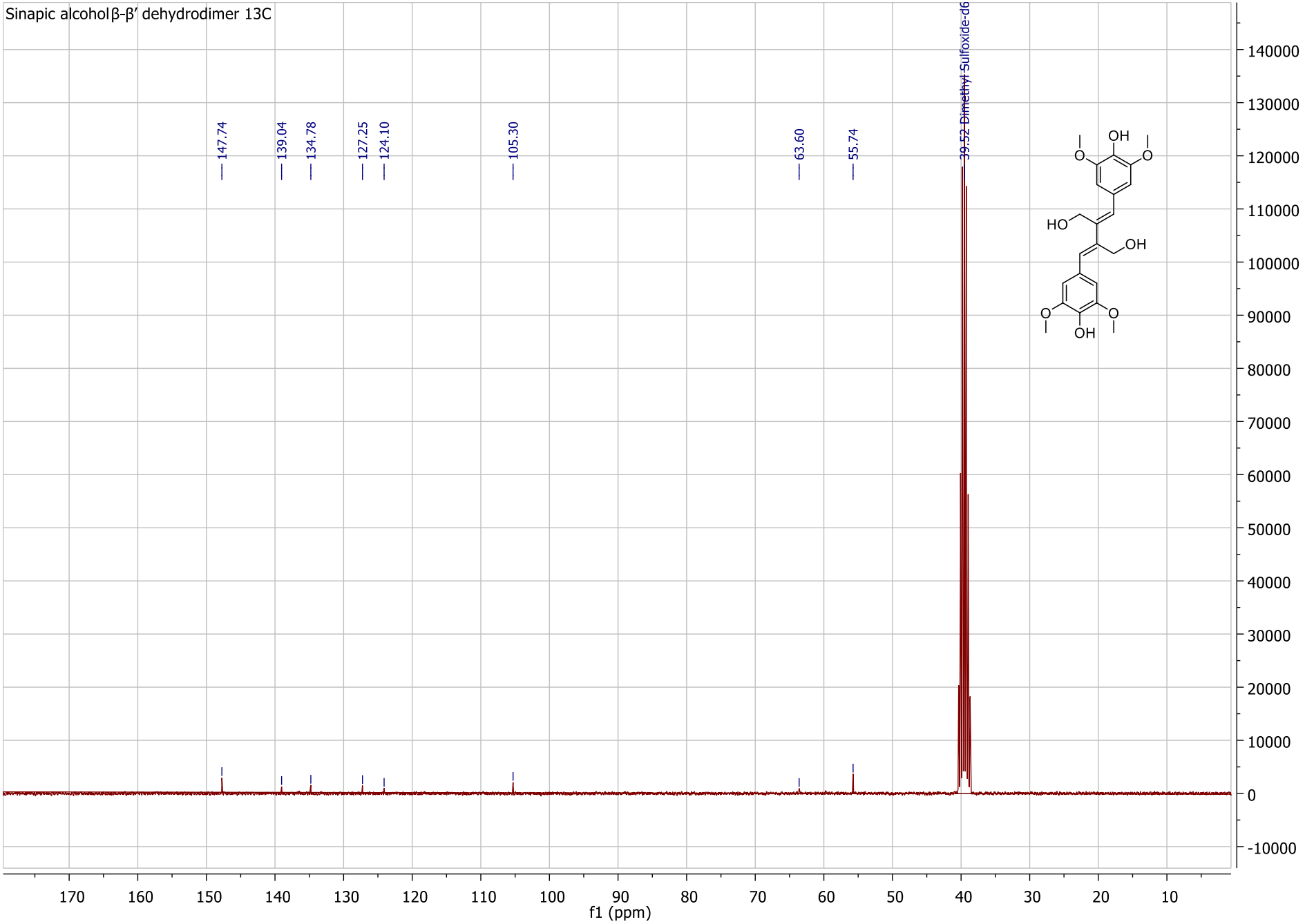

Acetylated ethyl sinapateβ-β' dehydrodimer 1H
7.81
7.26 Chloroform-d
6.72
4.19
4.17
4.15
4.12
4.10
3.73
2.31
1.13
1.10
1.08
1.97
3.92
4.12
12.15
6.75
6.00
f1 (ppm)


Acetylated ethyl sinapateβ-β' dehydrodimer 13C
168.56
166.72
152.24
142.38
133.18
129.78
128.02
106.35
77.16 Chloroform-d
61.53
56.20
20.58
14.22
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

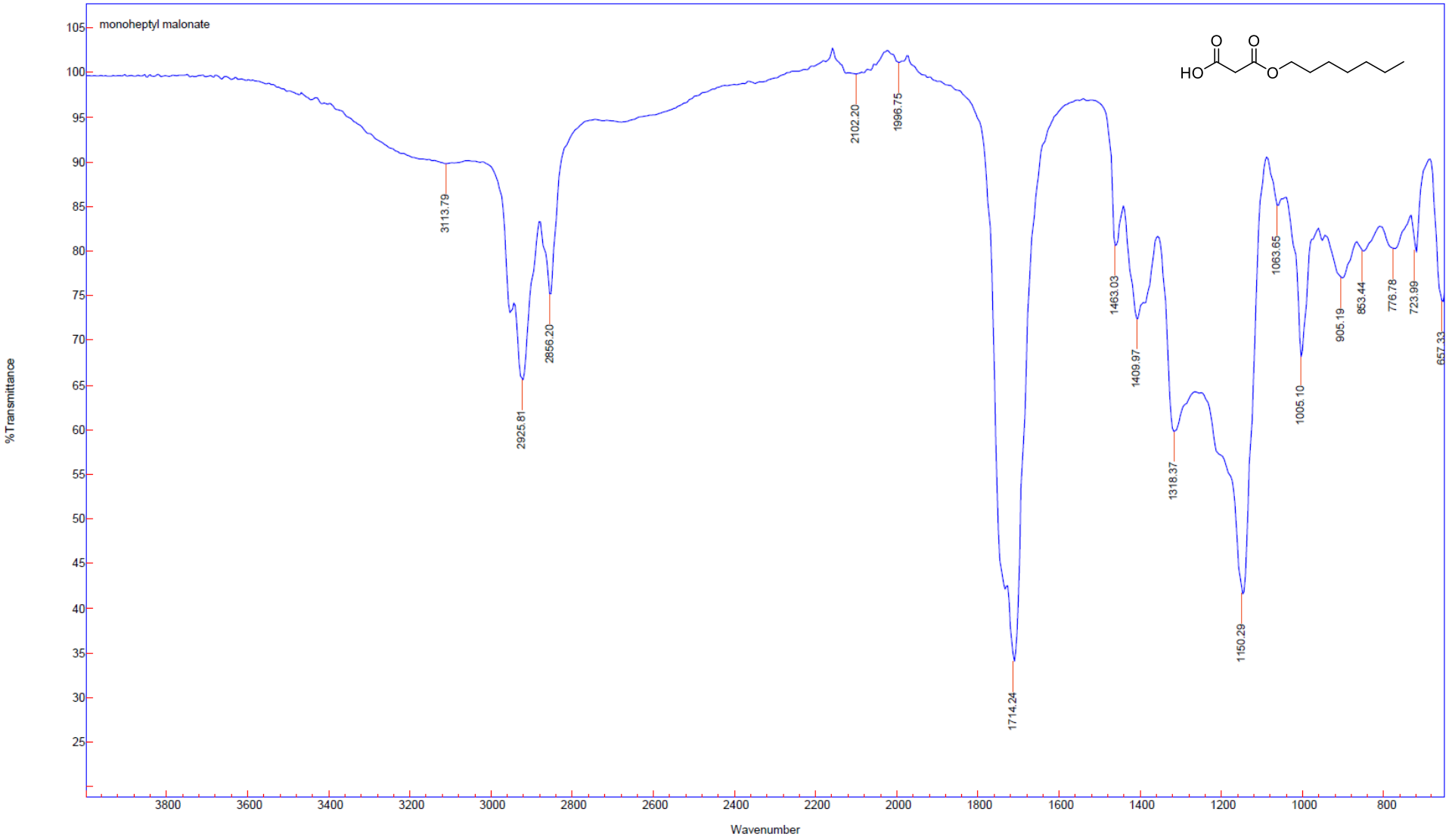

saturated ethyl sinapateβ-β′ dihydrodimer 1H
8.16
6.34
4.00
3.98
3.95
3.93
3.68
2.89
2.79
2.50 Dimethyl Sulfoxide-d6
1.11
1.09
1.06
OH
OH
1.91
3.74
3.95
12.00
1.99
3.70
6.37
f1 (ppm)

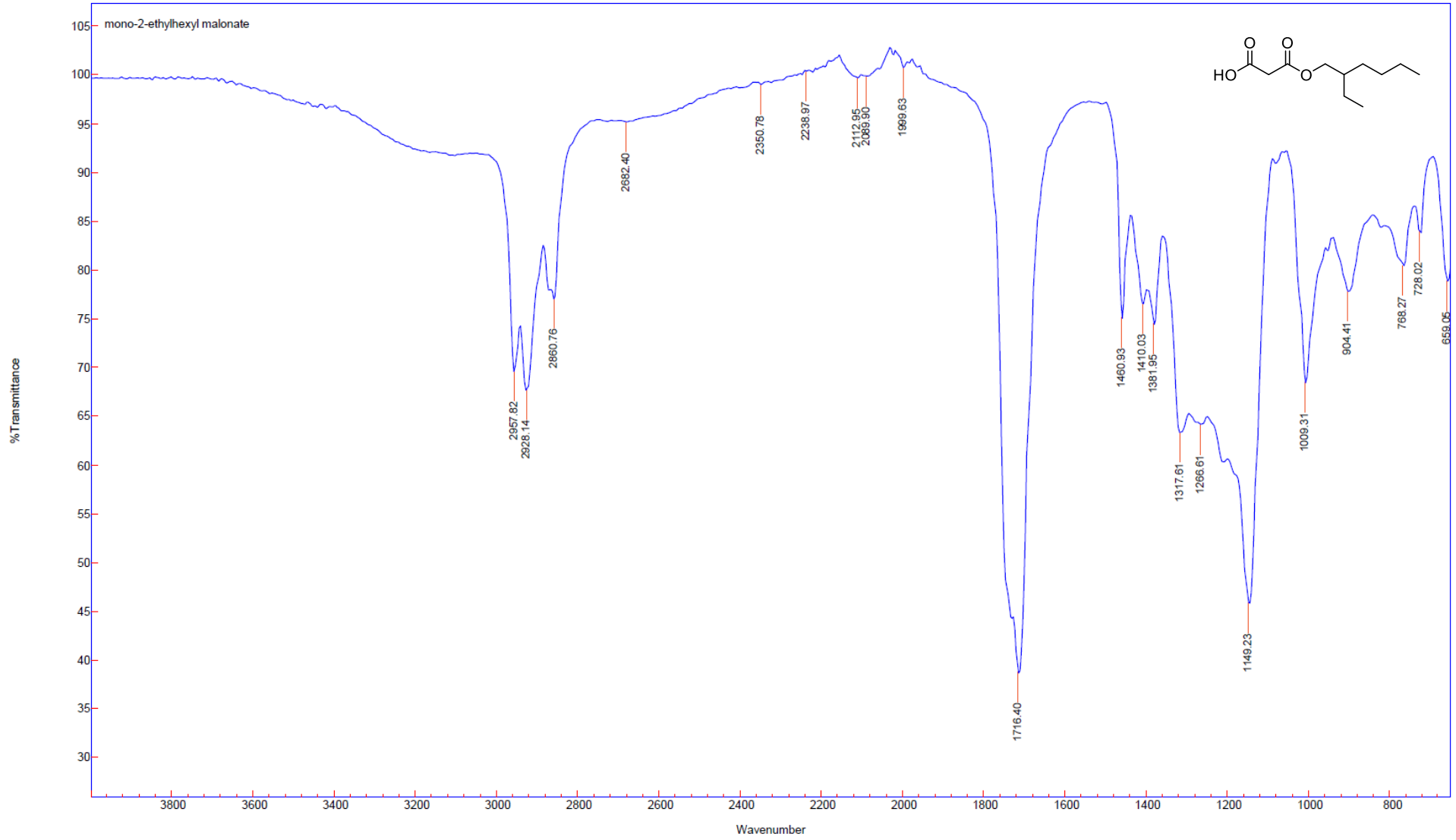

saturated ethyl sinapateβ-β′ dihydrodimer 13C
172.95
147.73
133.99
128.38
106.25
59.93
55.81
48.07
39.52 Dimethyl Sulfoxide-d6
35.49
13.99
OH
O
O
O
O
O
O
O
O
OH
f1 (ppm)


Sinapic alcohol β-β′ dehydrodimer 1H
8.38
6.80
6.56
5.12
5.10
5.09
3.96
3.94
3.91
3.89
3.63
2.50 Dimethyl Sulfoxide-d6
1.90
4.21
2.11
2.12
3.73
12.00
f1 (ppm)


Sinapic alcohol β-β′ dehydrodimer 13C
147.74
139.04
134.78
127.25
124.10
105.30
63.60
55.74
39.52 Dimethyl Sulfoxide-d6
OH
HO
OH
OH
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

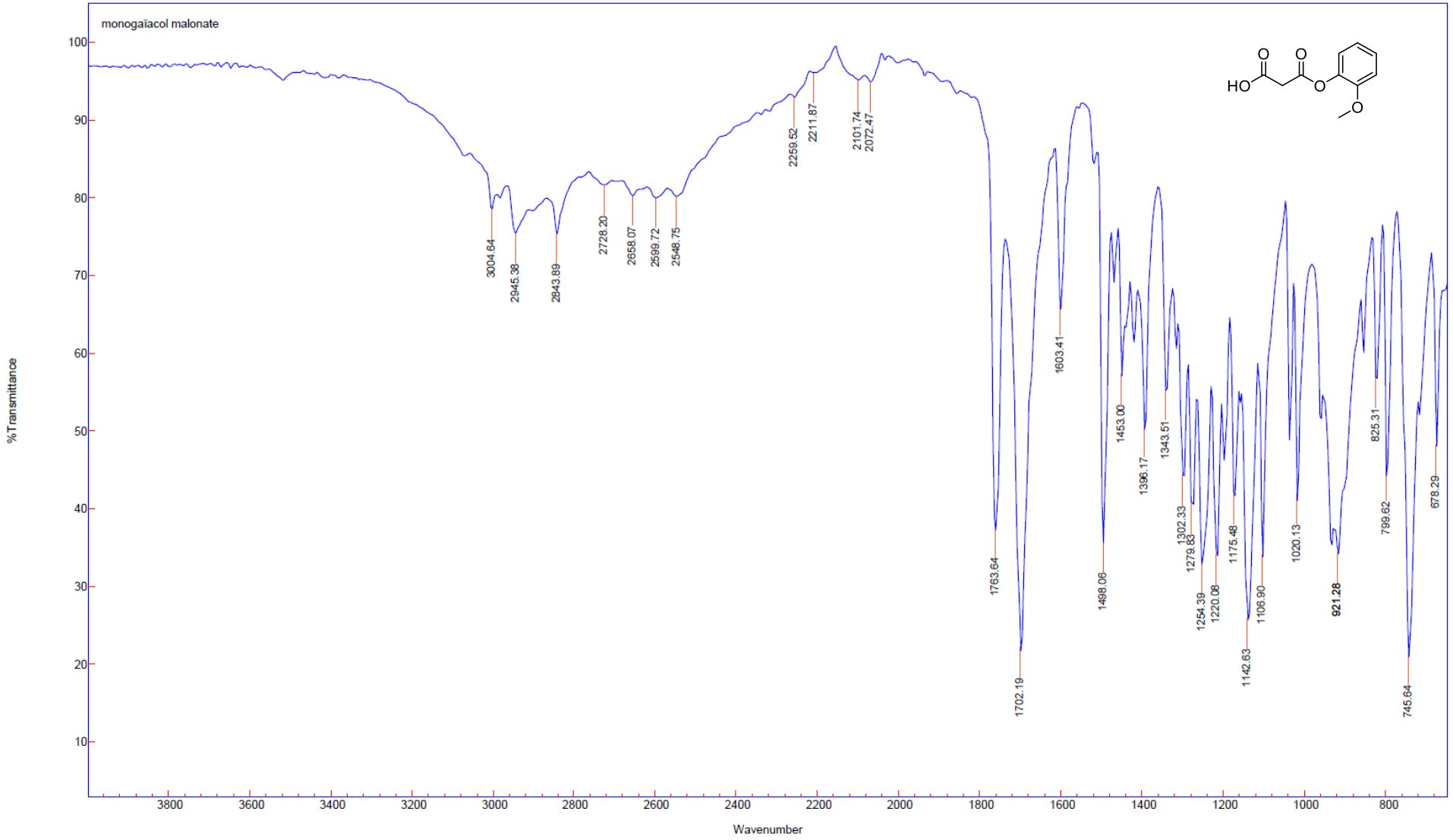
7.2. IR spectra

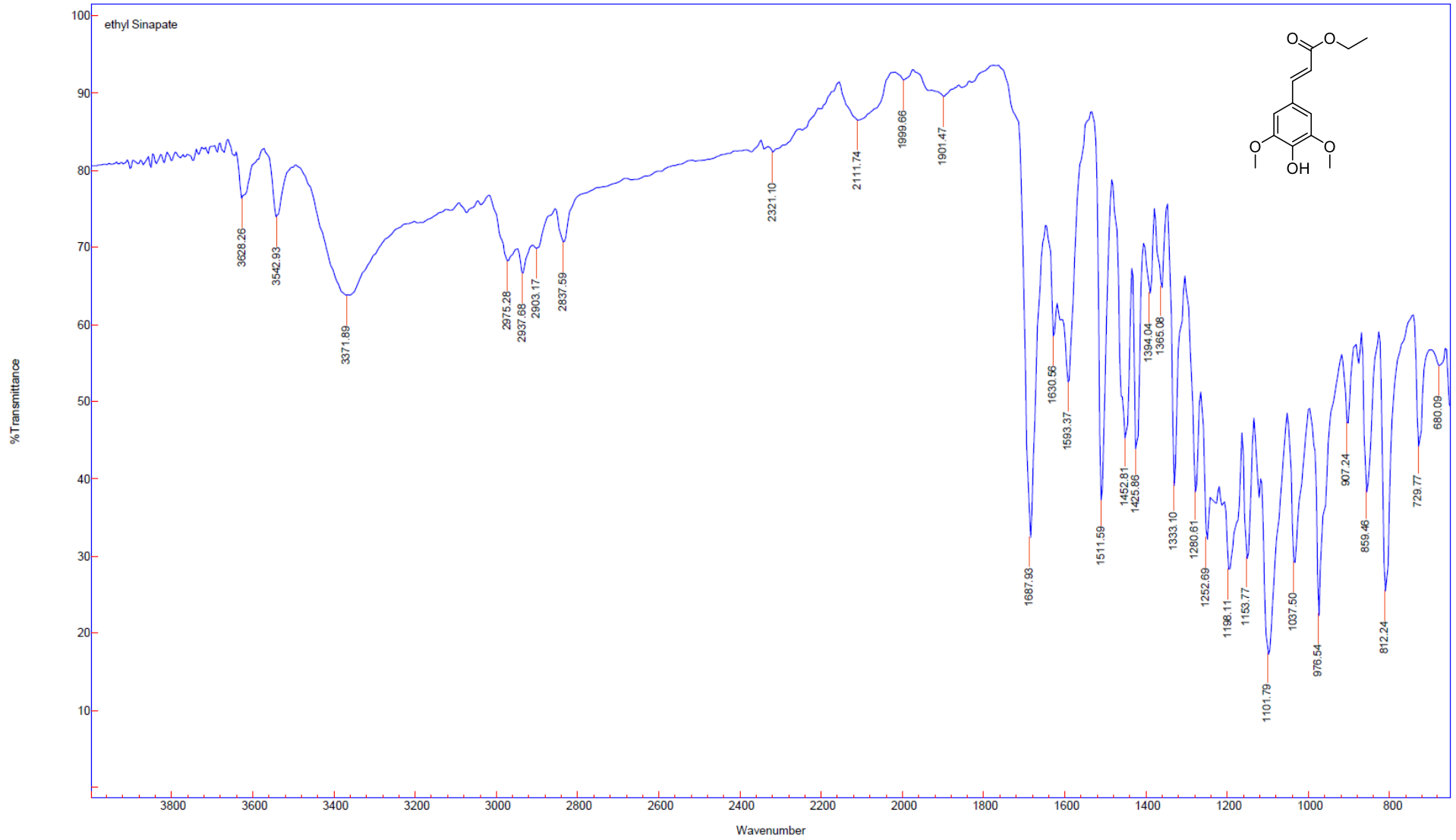



mono-2-ethylhexyl malonate
%Transmittance
Wavenumber
2957.82
2928.14
2860.76
2682.40
2350.78
2238.97
2112.95
2089.90
1999.63
1716.40
1460.93
1410.03
1381.95
1317.61
1266.61
1149.23
1009.31
904.41
768.27
728.02
659.05


mono tBu malonate
%Transmittance
Wavenumber
100
90
80
70
60
50
40
30
20
10
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
2978.81
2935.69
2113.66
2090.86
2000.14
1711.18
1393.33
1368.58
1325.23
1249.71
1217.56
1139.39
1037.56
965.25
902.45
835.06
797.29
747.79
HO
O
O
O

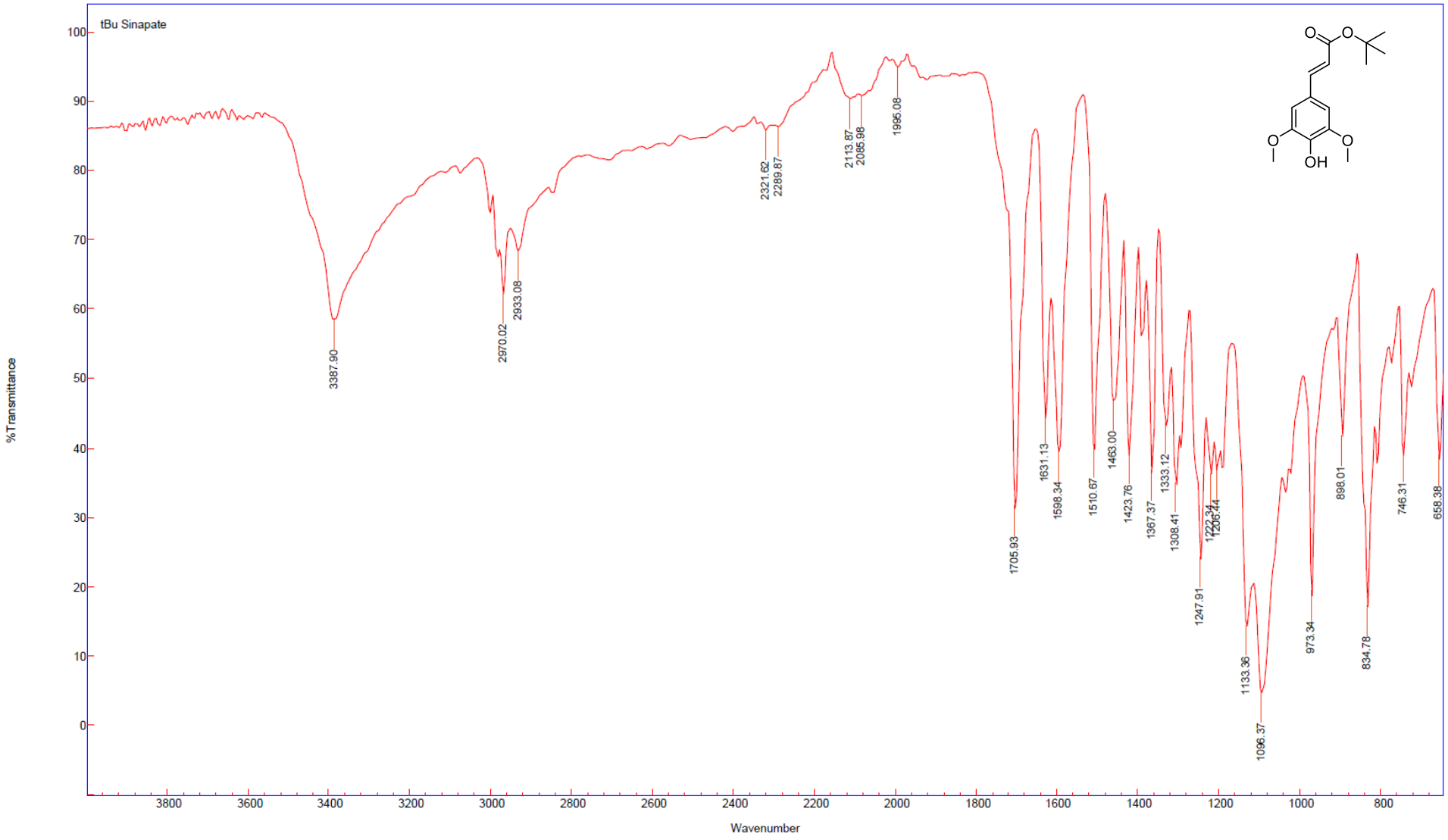

mono iPr malonate
%Transmittance
Wavenumber
3444.29
3177.86
3114.17
2983.67
2940.15
2680.20
2356.49
2116.15
2084.54
1998.45
1709.63
1467.26
1411.05
1374.77
1313.10
1202.09
1146.24
1100.73
975.20
894.89
816.27

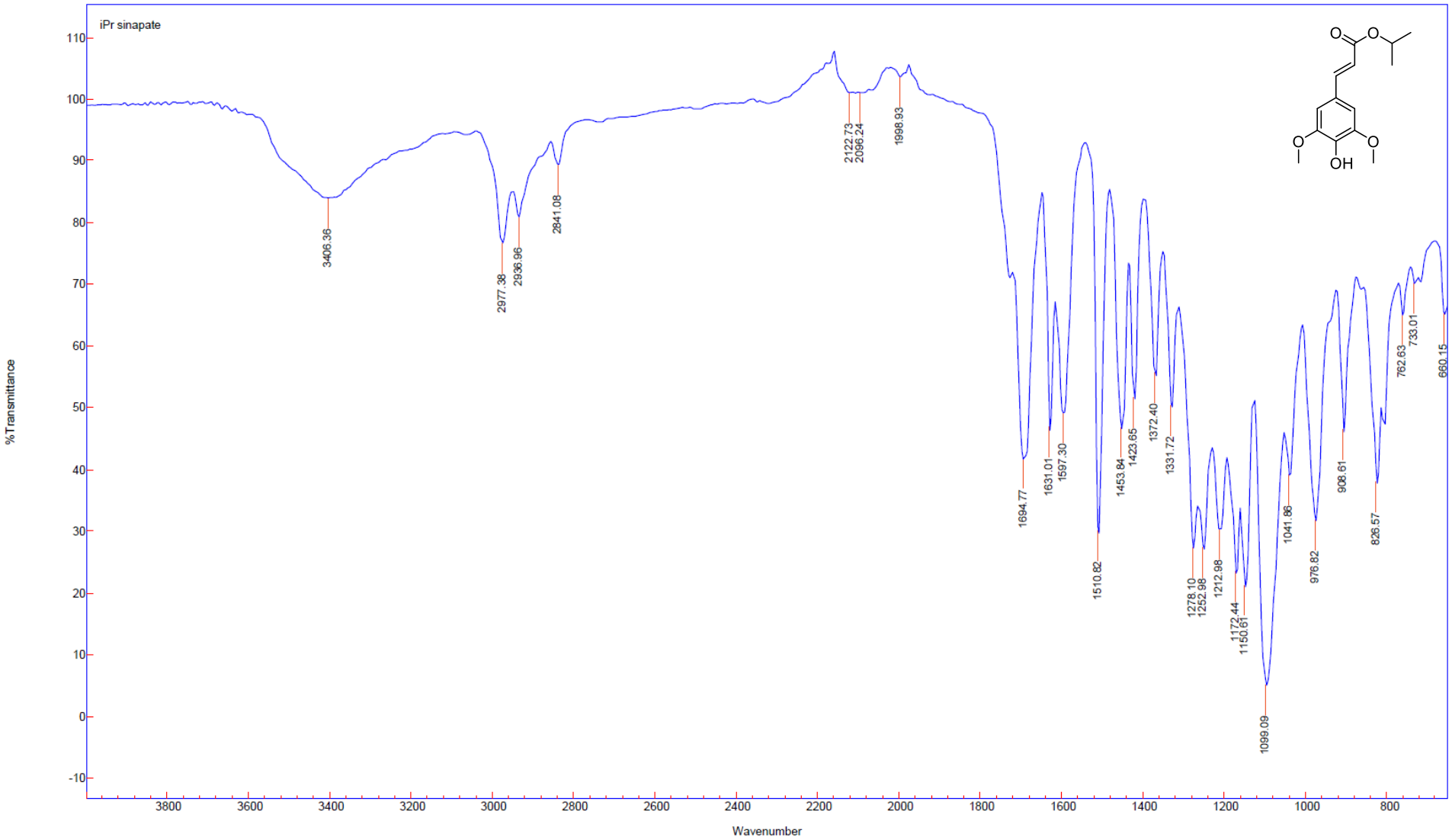

monogaïacol malonate
%Transmittance
Wavenumber
100
90
80
70
60
50
40
30
20
10
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3004.64
2945.38
2843.89
2728.20
2658.07
2599.72
2548.75
2259.52
2211.87
2101.74
2072.47
1763.64
1702.19
1603.41
1498.06
1453.00
1396.17
1343.51
1302.33
1279.83
1254.39
1220.08
1175.48
1142.63
1106.90
1020.13
921.28
825.31
799.62
745.64
678.29
HO
O
O
O
O

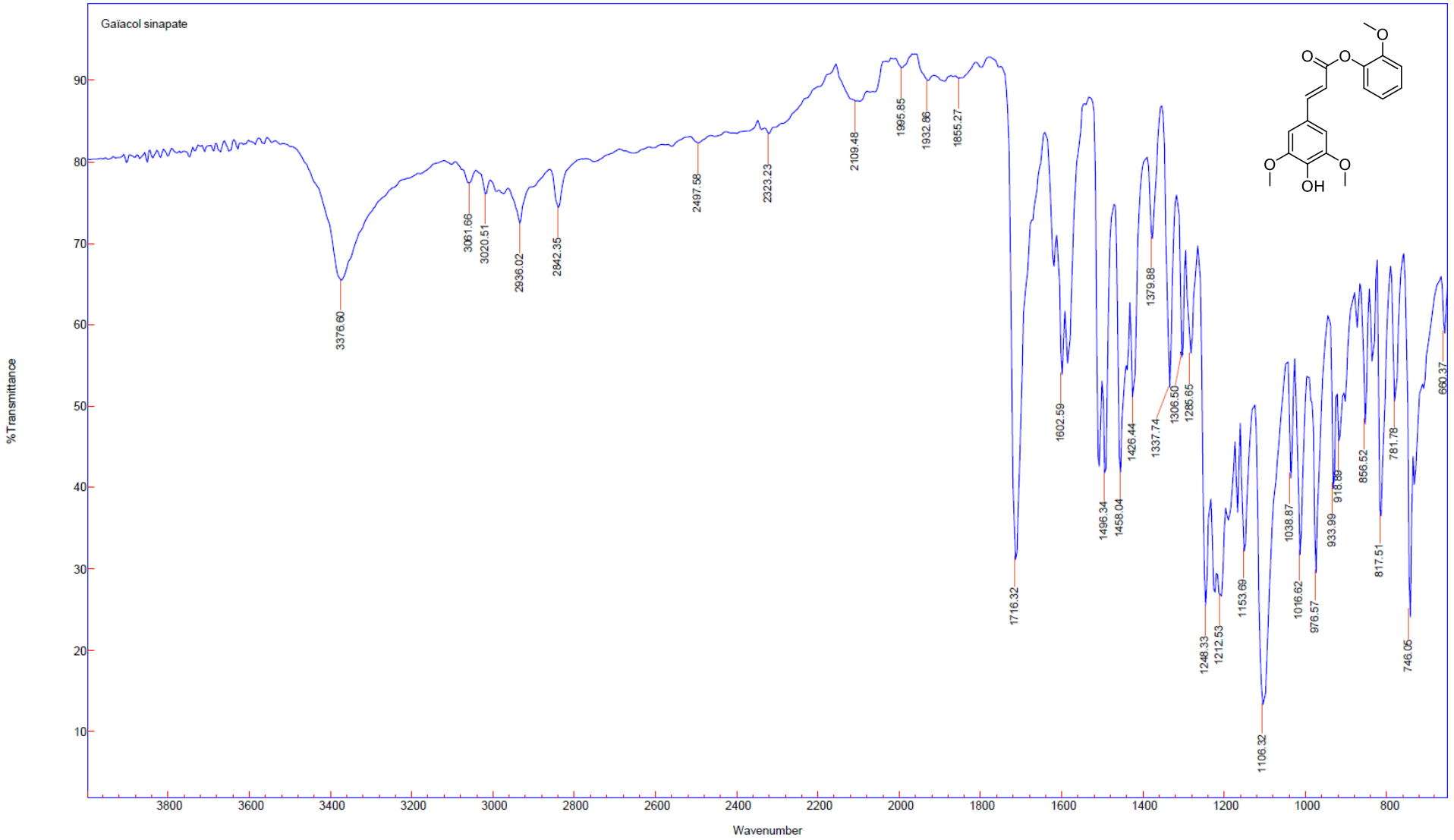

ethyl Sinapate
%Transmittance
Wavenumber
100
90
80
70
60
50
40
30
20
10
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3628.26
3542.93
3371.89
2975.28
2937.68
2903.17
2837.59
2321.10
2111.74
1999.66
1901.47
1687.93
1630.56
1593.37
1511.59
1452.81
1425.86
1394.04
1365.08
1333.10
1280.61
1252.69
1198.11
1153.77
1101.79
1037.50
976.54
907.24
859.46
812.24
729.77
680.09
O
O
O
O
OH

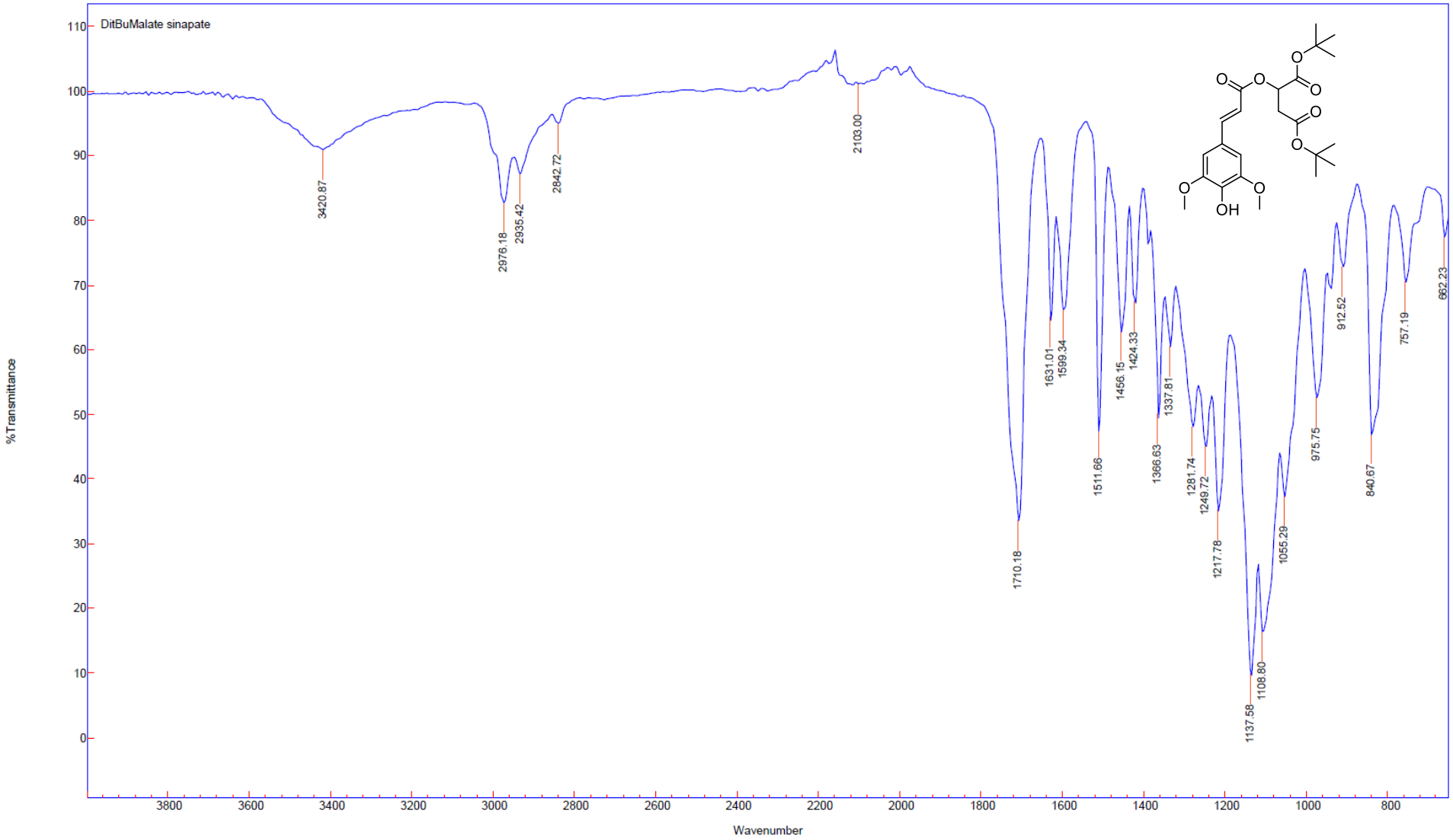

heptyl sinapate
%Transmittance
Wavenumber
3405.84
2925.37
2853.25
2116.80
1996.70
1700.17
1631.10
1600.51
1511.13
1455.20
1423.75
1375.08
1337.31
1278.94
1252.27
1214.13
1148.49
1108.88
1039.92
976.76
911.28
826.75
724.57
660.01
OH

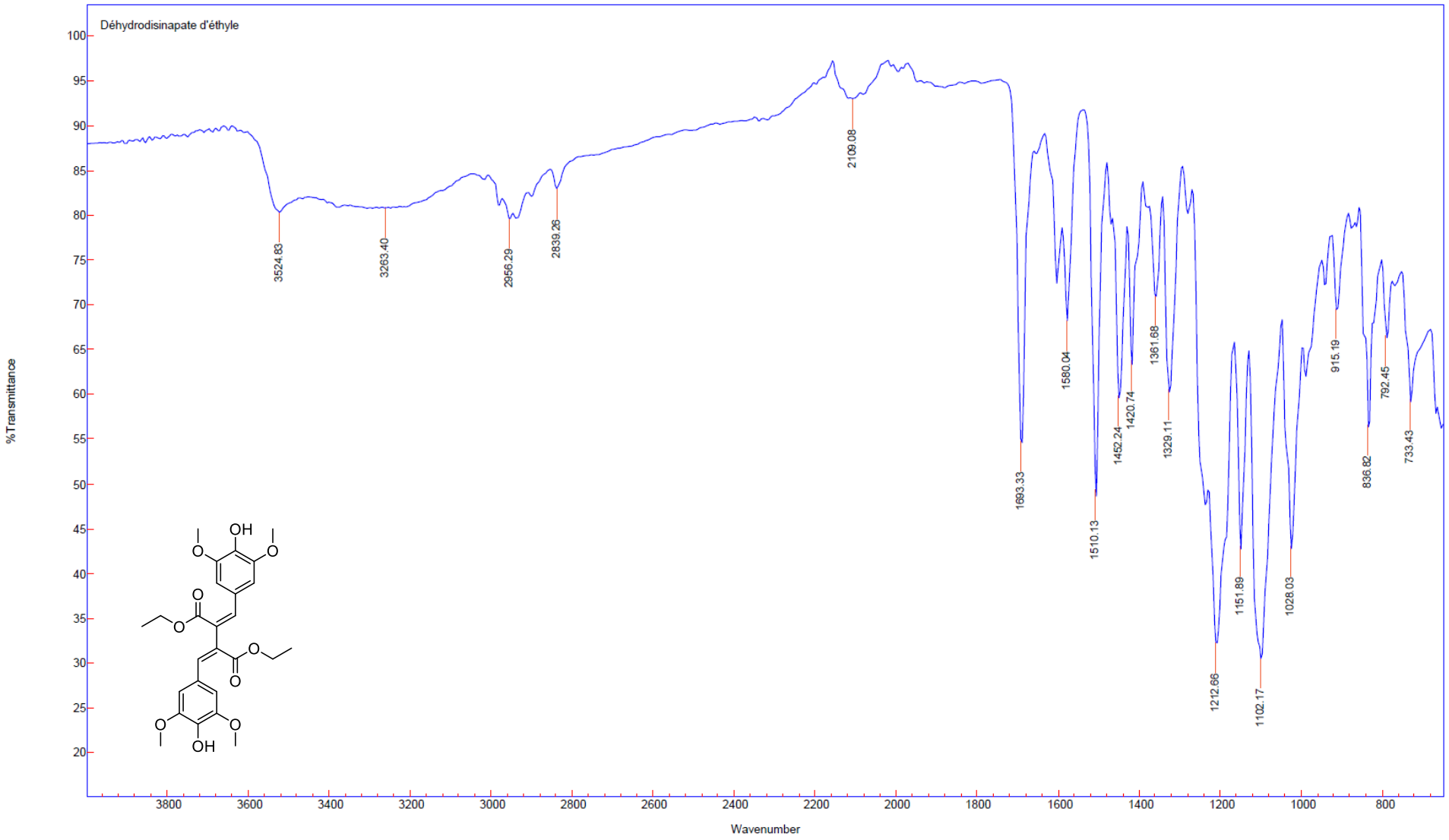

2-ethylhexyl sinapate
%Transmittance
Wavenumber
3407.46
2927.87
2858.06
2121.51
1997.28
1699.08
1630.78
1597.55
1510.93
1455.18
1423.56
1377.10
1336.74
1278.32
1252.18
1214.38
1147.70
1108.75
1030.45
976.07
911.81
826.25
728.28
660.82
OH


tBu Sinapate
%Transmittance
Wavenumber
100
90
80
70
60
50
40
30
20
10
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3387.90
2970.02
2933.08
2321.62
2289.87
2113.87
2085.98
1995.08
1705.93
1631.13
1598.34
1510.67
1463.00
1423.76
1367.37
1333.12
1308.41
1247.91
1222.34
1206.44
1133.36
1096.37
973.34
898.01
834.78
746.31
658.38
O
O
O
O
OH

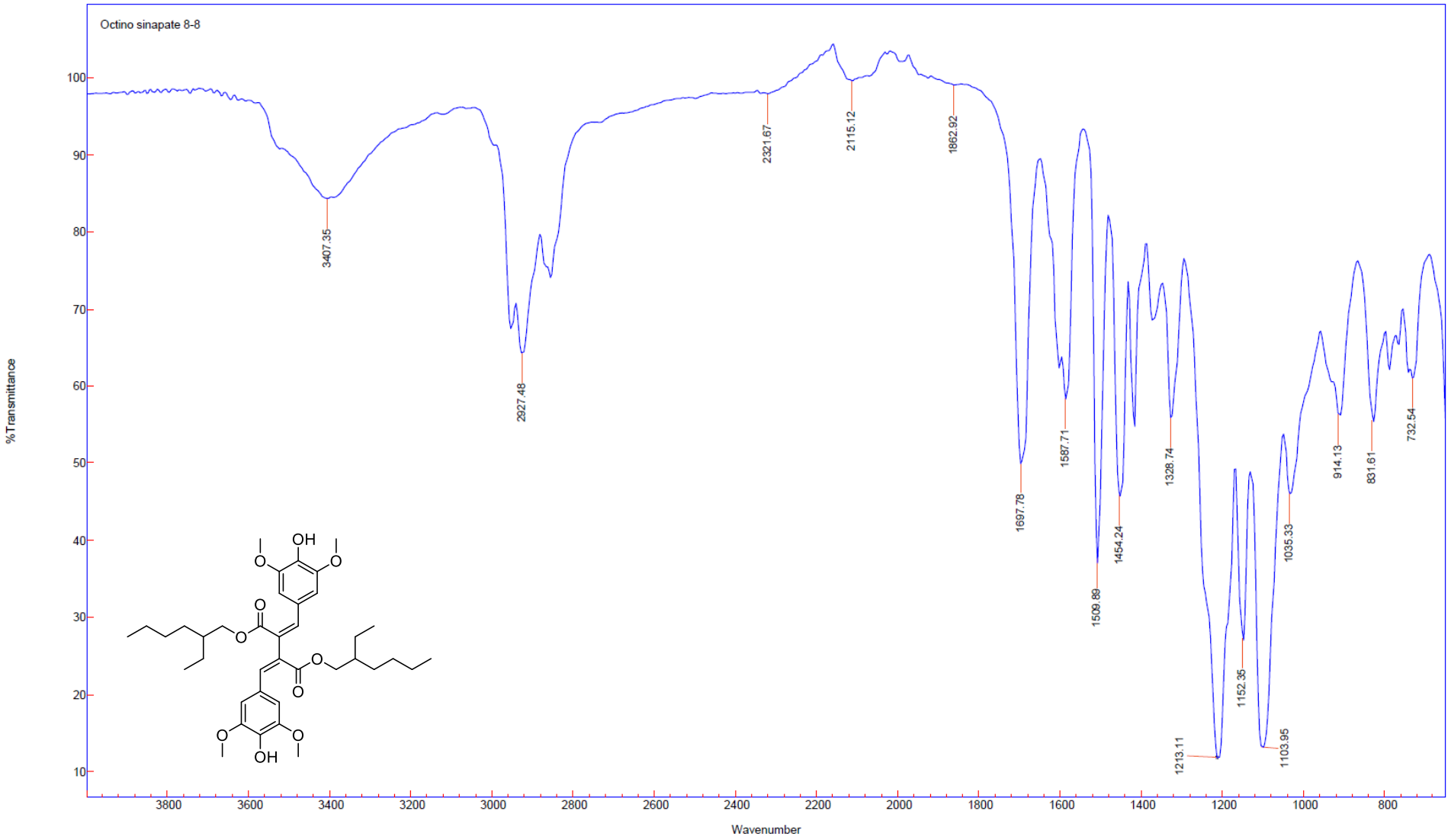

iPr sinapate
% Transmittance
Wavenumber
3406.36
2977.38
2936.96
2841.08
2122.73
2096.24
1998.93
1694.77
1631.01
1597.30
1510.82
1453.84
1423.65
1372.40
1331.72
1278.10
1252.98
1212.98
1172.44
1150.61
1099.09
1041.86
976.82
908.61
826.57
762.63
733.01
680.15
OH

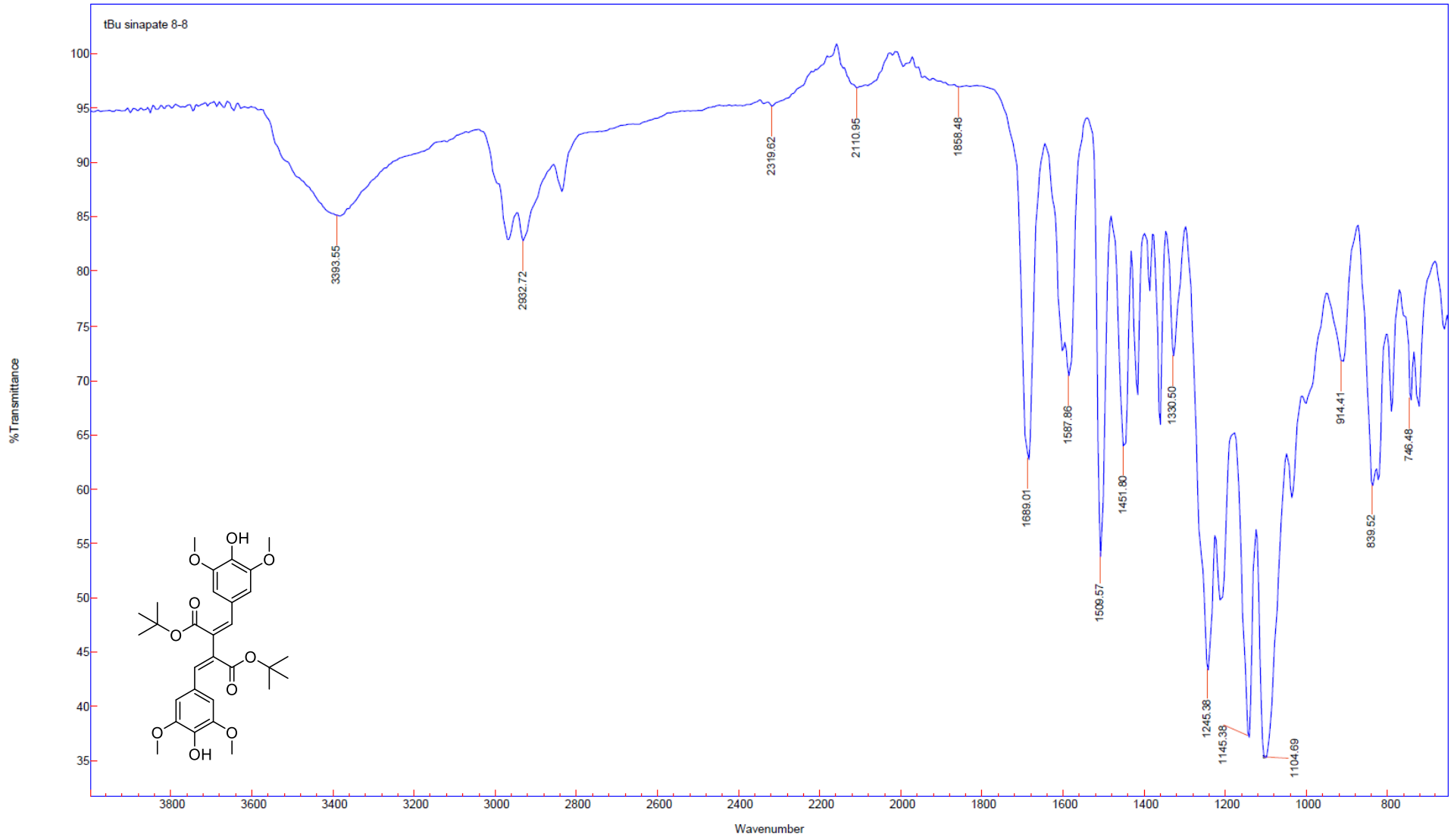

Gaïacol sinapate
%Transmittance
Wavenumber
3376.60
3061.66
3020.51
2936.02
2842.35
2497.58
2323.23
2109.48
1995.85
1932.86
1855.27
1716.32
1602.59
1496.34
1458.04
1426.44
1379.88
1337.74
1306.50
1285.65
1248.33
1212.53
1153.69
1106.32
1038.87
1016.62
976.57
933.99
918.80
856.52
817.51
781.78
746.05
660.37
OH

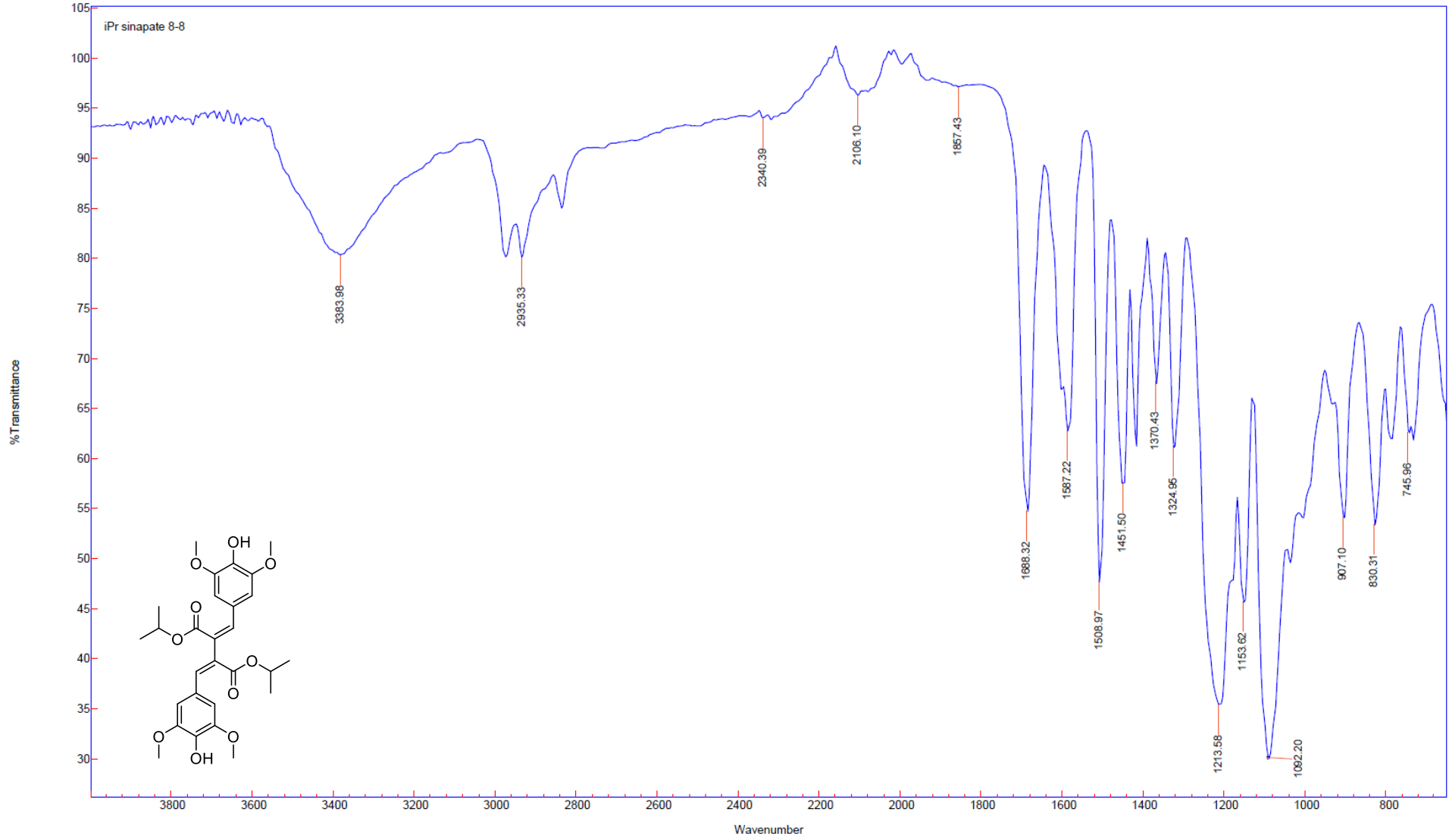

DitBuMalate sinapate
%Transmittance
Wavenumber
3420.87
2976.18
2935.42
2842.72
2103.00
1710.18
1631.01
1599.34
1511.66
1456.15
1424.33
1366.63
1337.81
1281.74
1249.72
1217.78
1137.58
1108.80
1055.29
975.75
912.52
840.67
757.19
662.23
OH

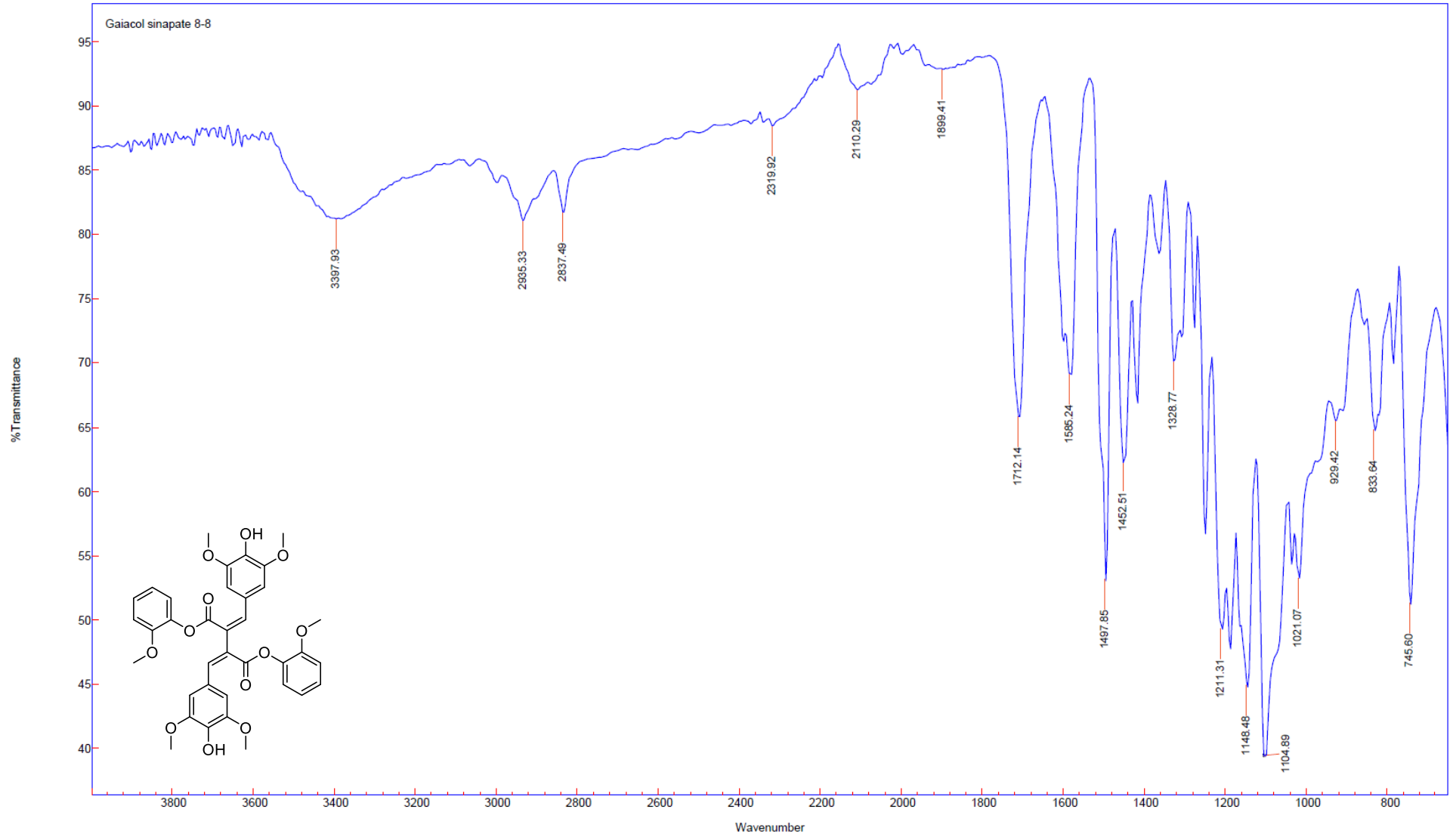

Déhydrodisinapate d'éthyle
%Transmittance
Wavenumber
3524.83
3263.40
2956.29
2839.28
2109.08
1693.33
1580.04
1510.13
1452.24
1420.74
1361.68
1329.11
1212.66
1151.89
1102.17
1028.03
915.19
836.82
792.45
733.43
OH
OH

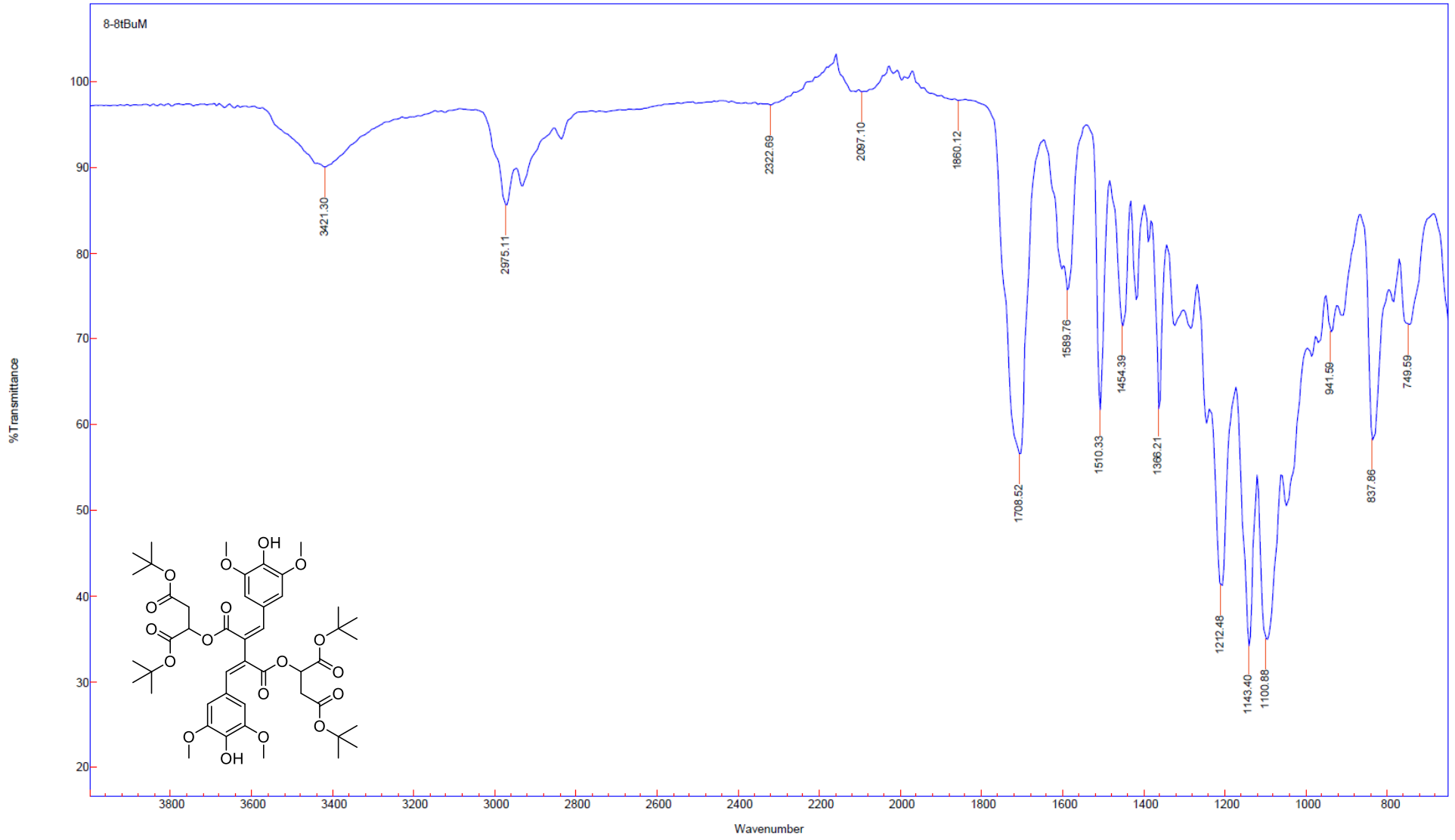

Heptyl sinapate 8-8
%Transmittance
Wavenumber
3464.43
3167.67
2924.30
2849.77
2340.16
2110.82
1854.93
1706.91
1581.49
1512.64
1452.59
1328.91
1214.17
1107.13
930.49
828.47
724.99
OH
OH

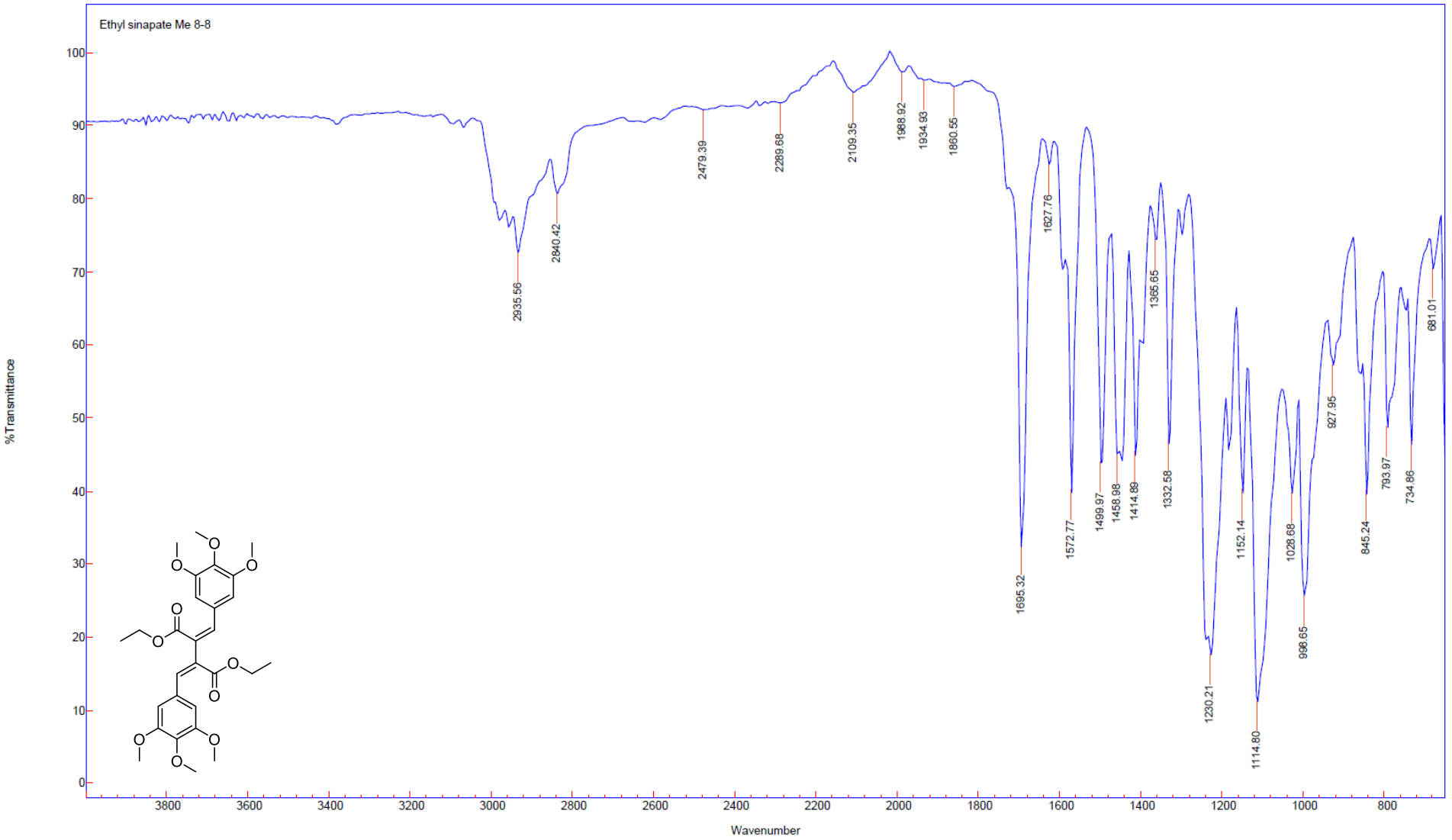

Octino sinapate 8-8
%Transmittance
Wavenumber
3407.35
2927.48
2321.67
2115.12
1862.92
1697.78
1587.71
1509.89
1454.24
1328.74
1213.11
1152.35
1103.95
1035.33
914.13
831.61
732.54
OH
OH

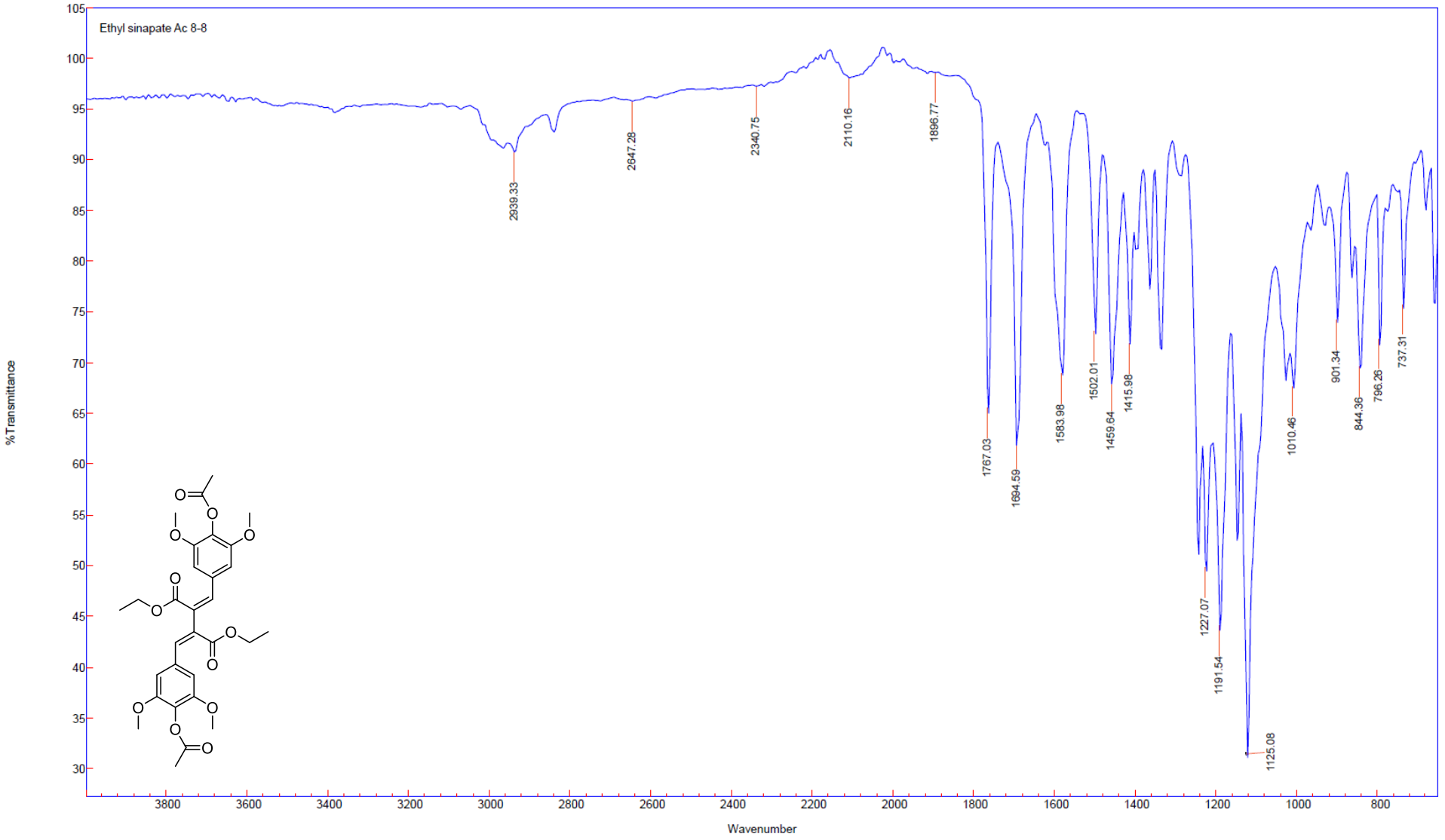

tBu sinapate 8-8
%Transmittance
Wavenumber
3393.55
2932.72
2319.62
2110.95
1858.48
1689.01
1587.86
1509.57
1451.80
1330.50
1245.38
1145.38
1104.69
914.41
839.52
746.48
OH
OH

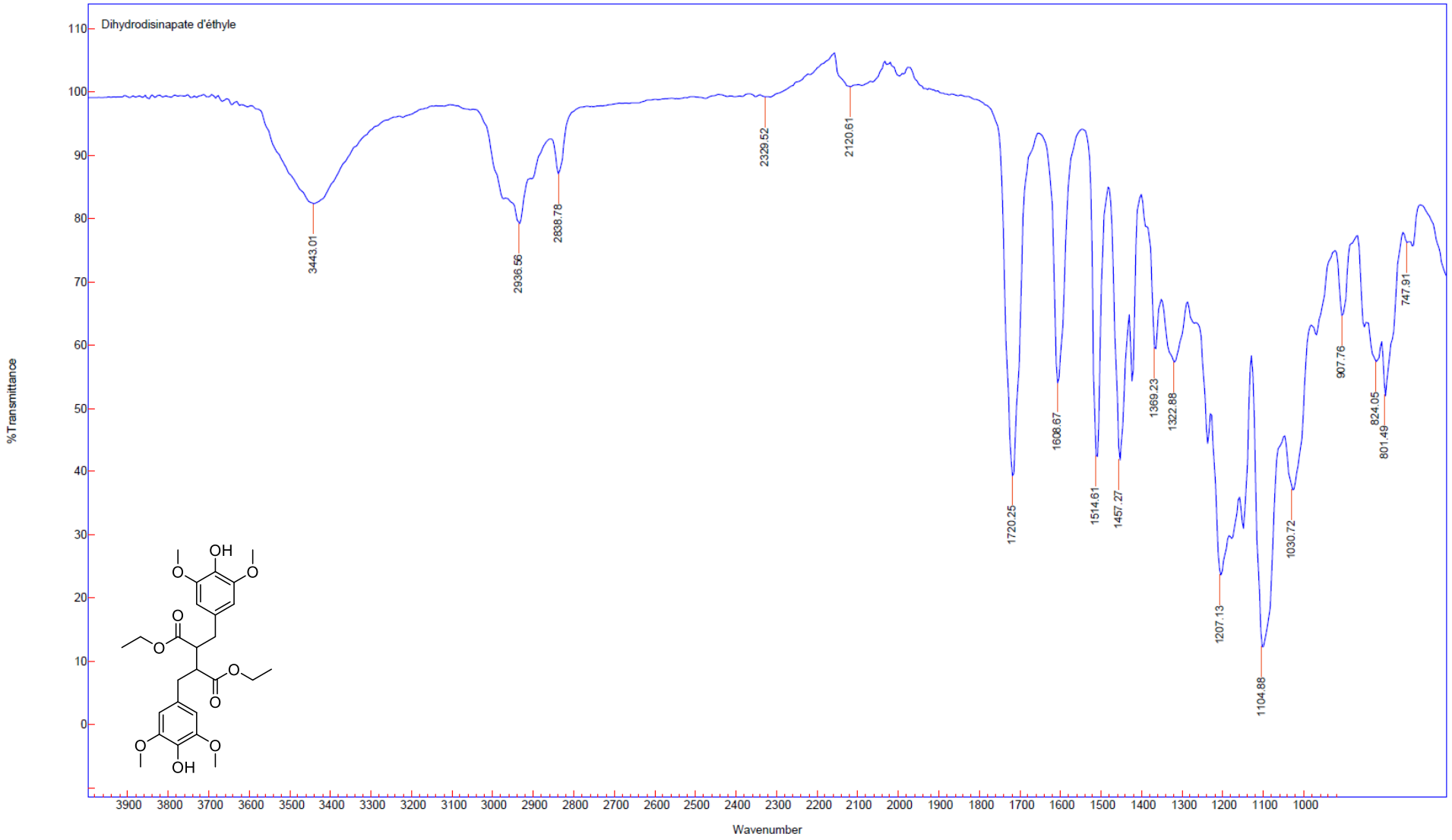

iPr sinapate 8-8
%Transmittance
Wavenumber
3383.98
2935.33
2340.39
2106.10
1857.43
1688.32
1587.22
1508.97
1451.50
1370.43
1324.95
1213.58
1153.62
1092.20
907.10
830.31
745.96
OH
O
OH

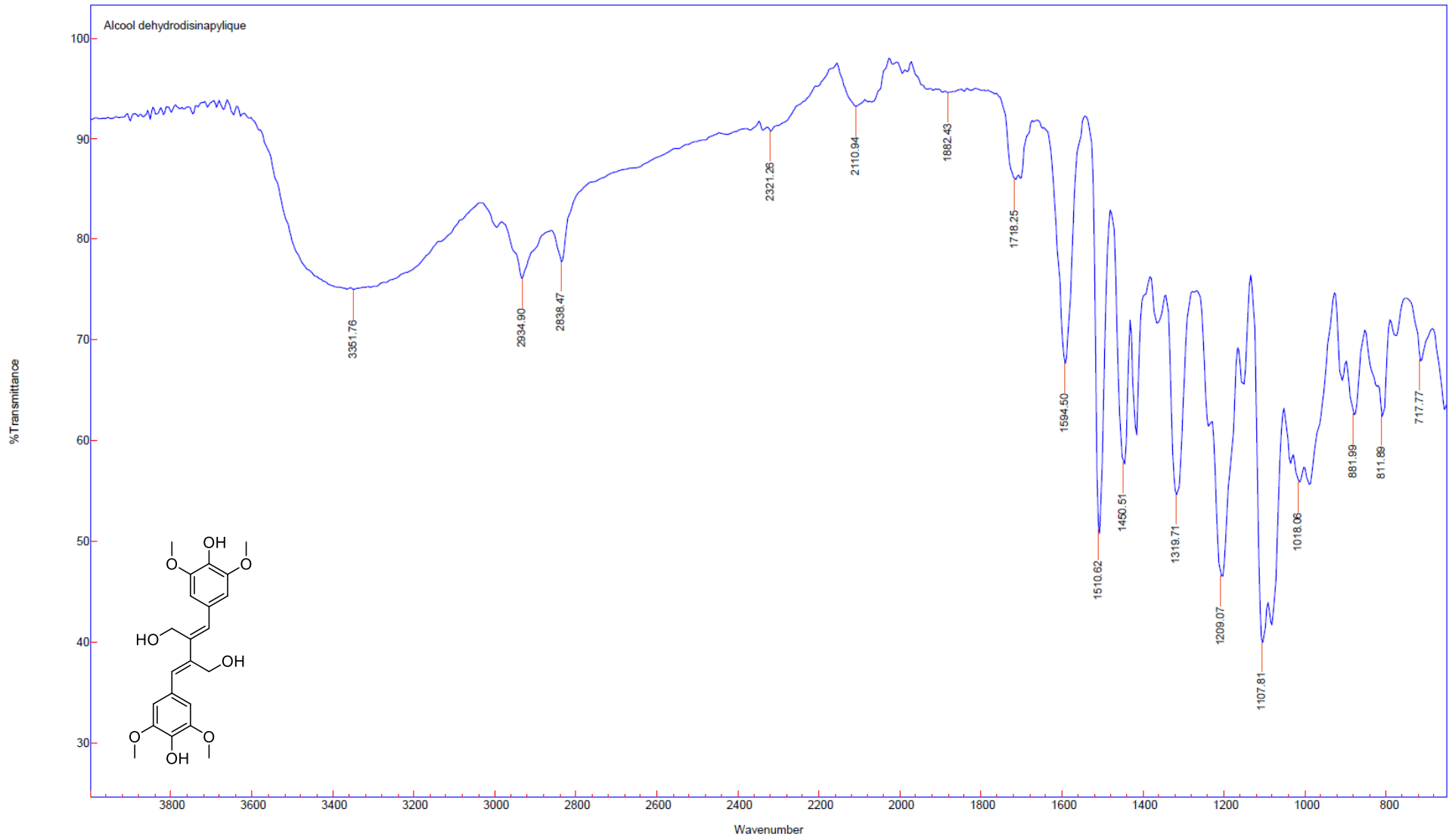

Gaiacol sinapate 8-8
%Transmittance
Wavenumber
3397.93
2935.33
2837.49
2319.92
2110.29
1899.41
1712.14
1585.24
1497.85
1452.51
1328.77
1211.31
1148.48
1104.89
1021.07
929.42
833.64
745.60
OH
OH


8-8tBuM
%Transmittance
Wavenumber
3421.30
2975.11
2322.69
2097.10
1860.12
1708.52
1589.76
1510.33
1454.39
1366.21
1212.48
1143.40
1100.88
941.59
837.86
749.59
OH
OH

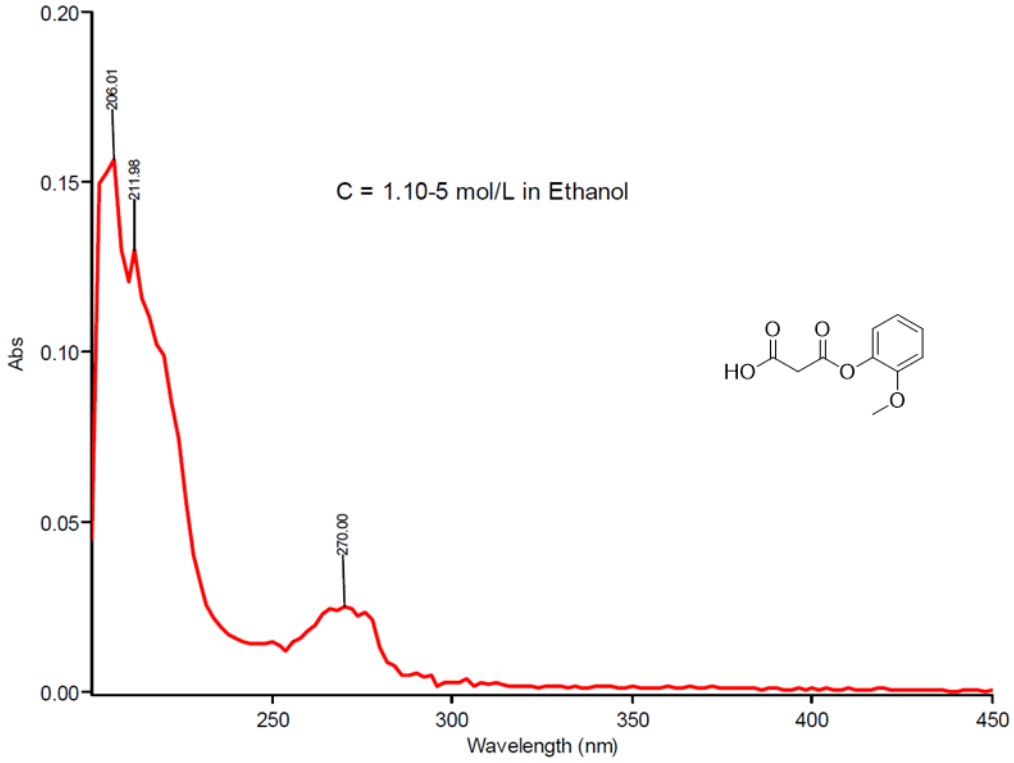

Ethyl sinapate Me 8-8
% Transmittance
Wavenumber
100
90
80
70
60
50
40
30
20
10
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
2935.56
2840.42
2479.39
2289.68
2109.35
1988.92
1934.93
1860.55
1695.32
1627.76
1572.77
1499.97
1458.98
1414.89
1385.65
1332.58
1230.21
1152.14
1114.80
1028.68
998.65
927.95
845.24
793.97
734.86
681.01

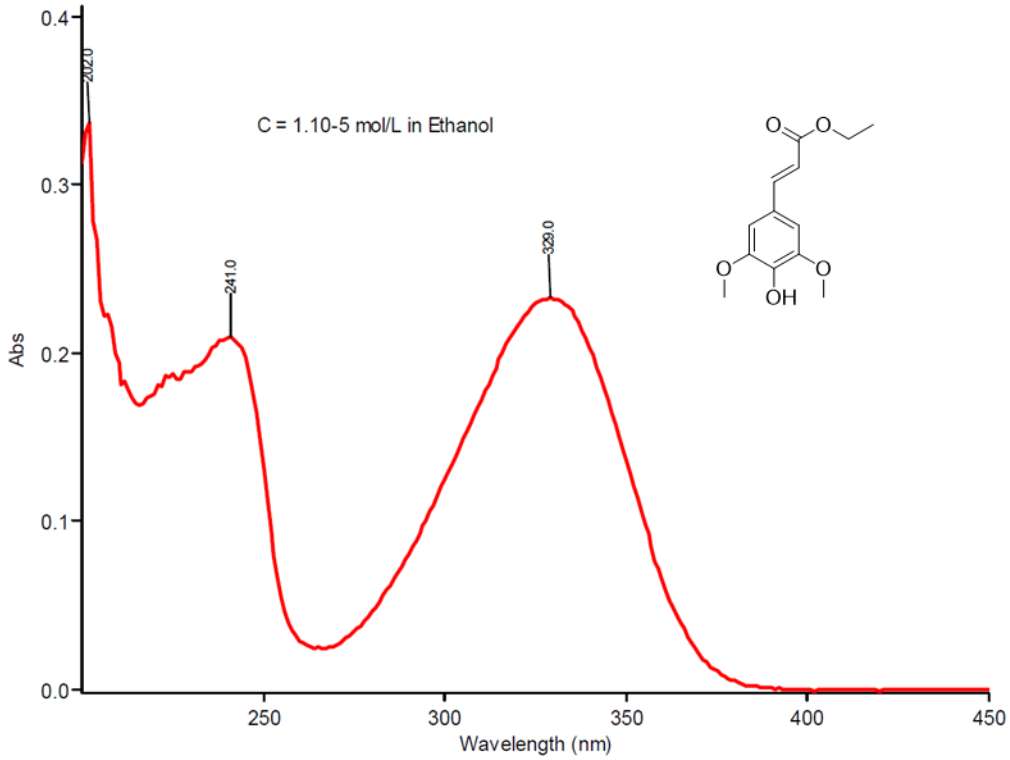

Ethyl sinapate Ac 8-8
%Transmittance
Wavenumber
2939.33
2647.28
2340.75
2110.16
1896.77
1767.03
1694.59
1583.98
1502.01
1459.64
1415.98
1227.07
1191.54
1125.08
1010.46
901.34
844.36
796.26
737.31

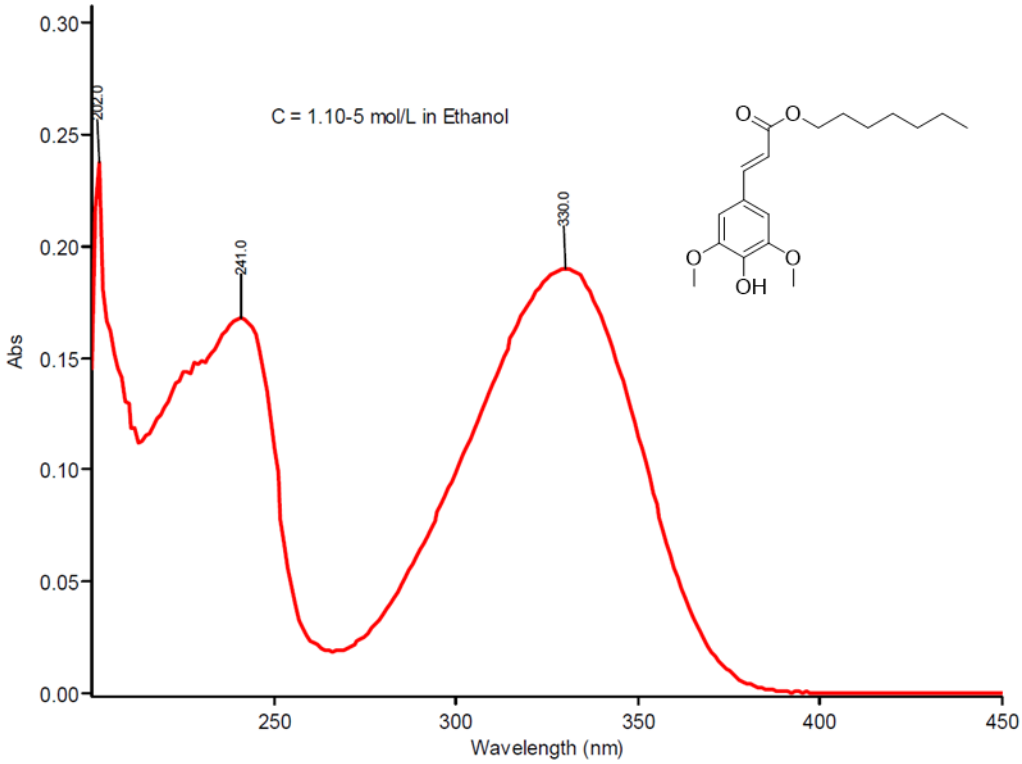

Dihydrodisinapate d'éthyle
%Transmittance
Wavenumber
3443.01
2936.56
2838.78
2329.52
2120.61
1720.25
1608.67
1514.61
1457.27
1369.23
1322.88
1207.13
1104.88
1030.72
907.76
824.05
801.48
747.91
OH
OH

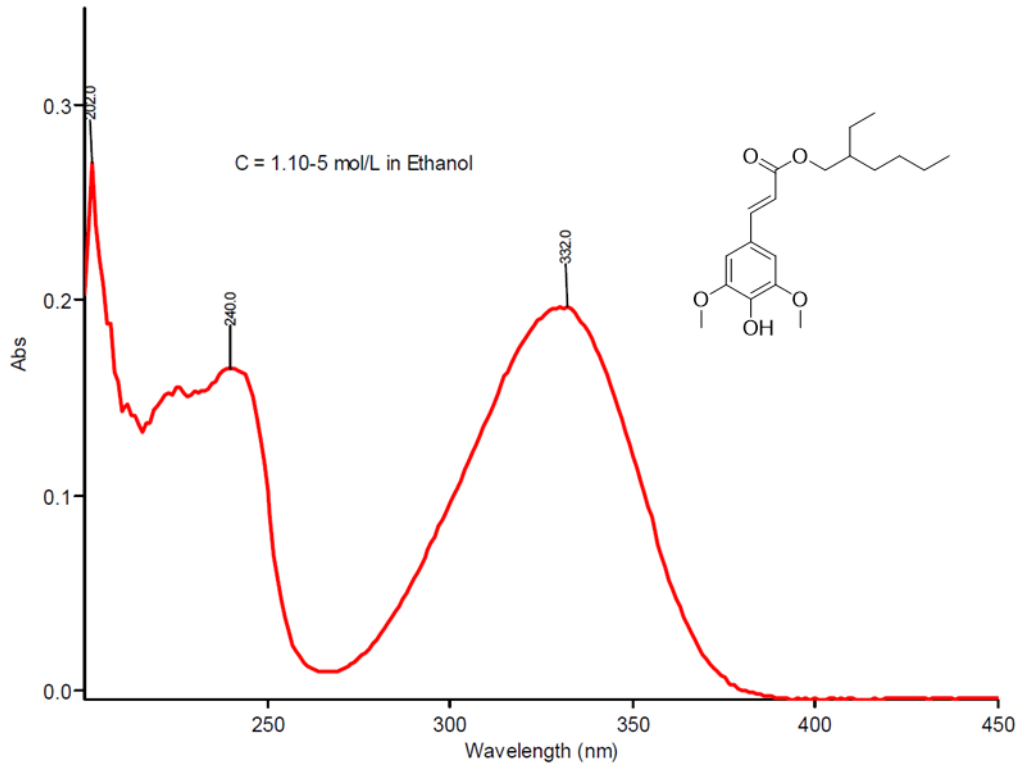

Alcool dehydrodisinapylique
%Transmittance
Wavenumber
100
90
80
70
60
50
40
30
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3351.76
2934.90
2838.47
2321.26
2110.94
1882.43
1718.25
1594.50
1510.62
1450.51
1319.71
1209.07
1107.81
1018.06
881.99
811.89
717.77
HO
OH
OH
O
O
O
O
OH

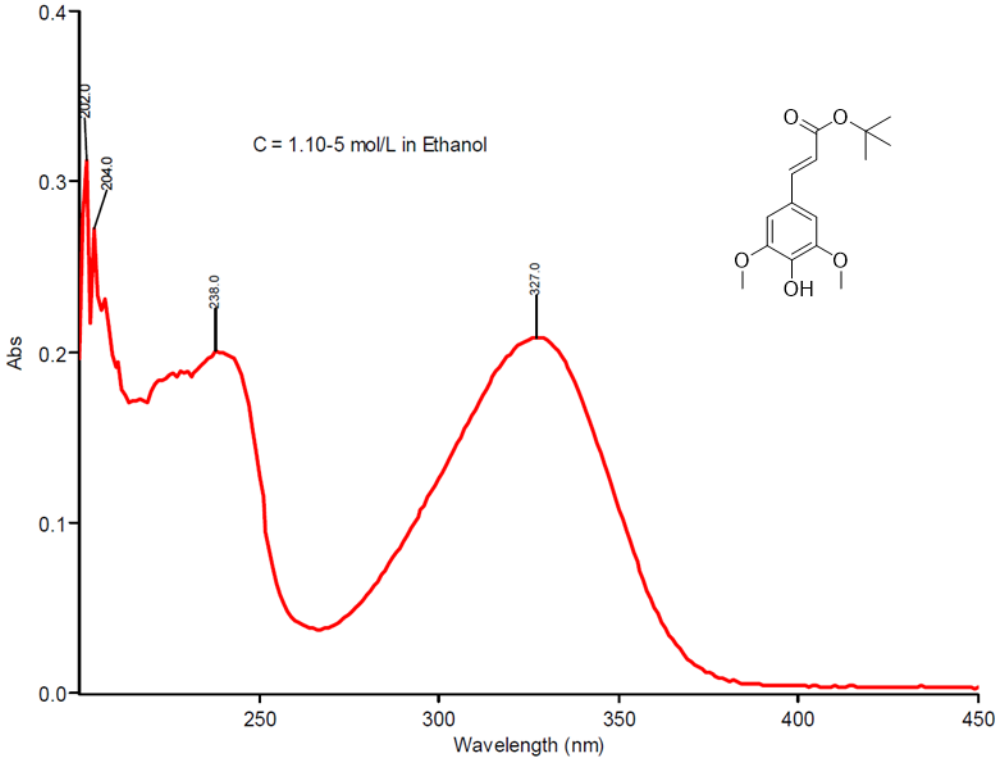
7.3. UV Spectra

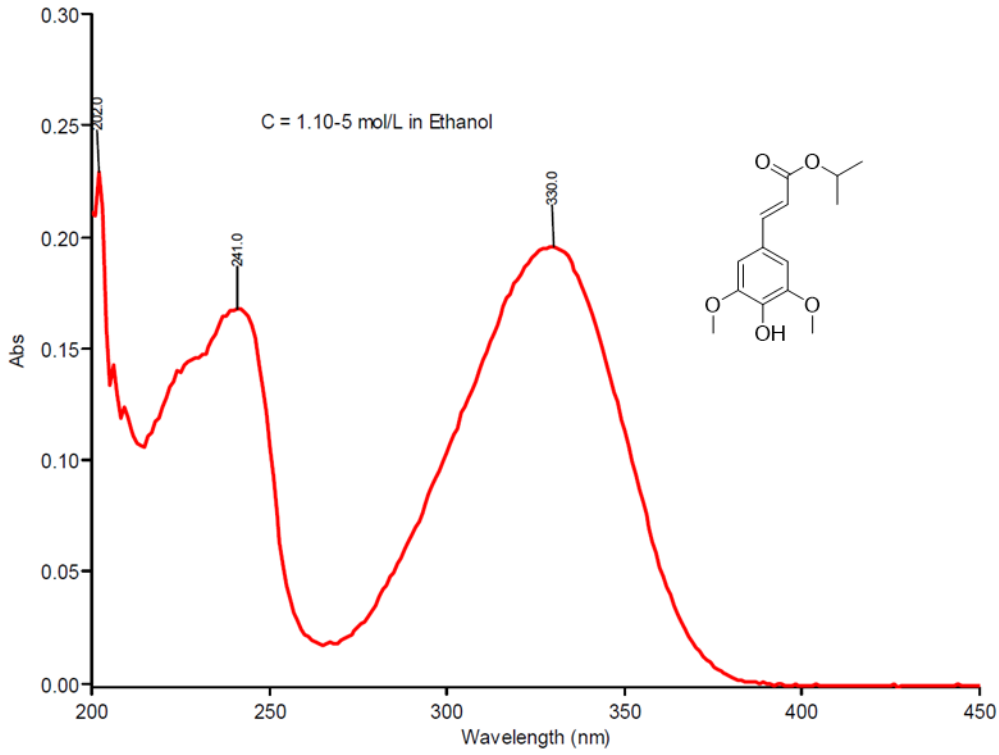


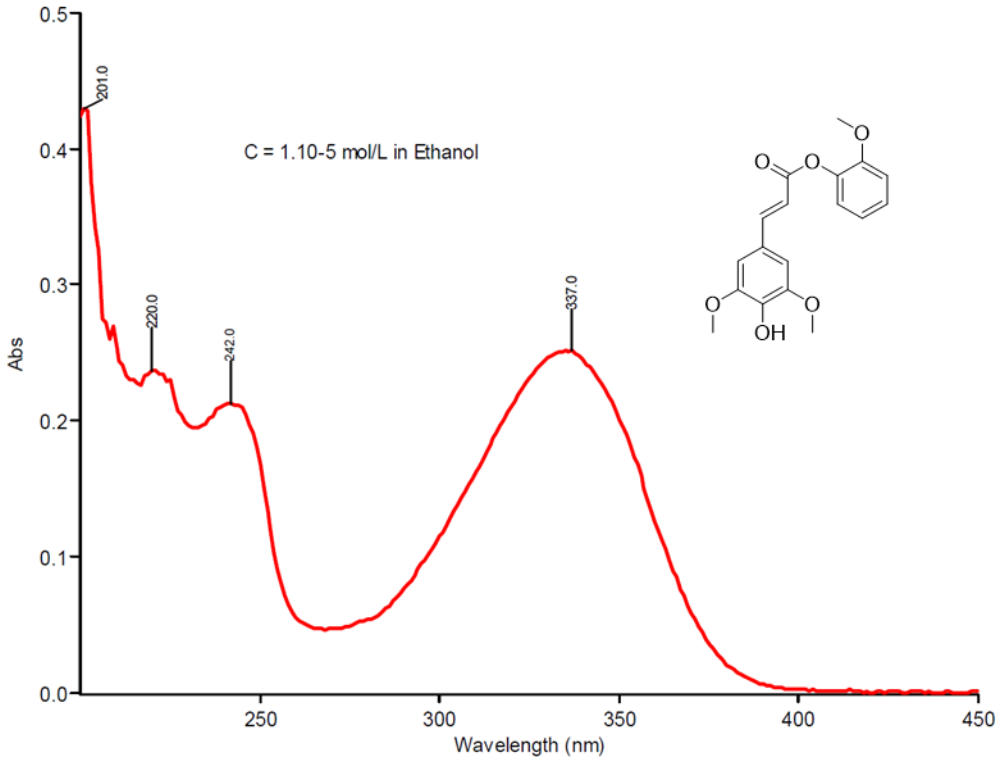


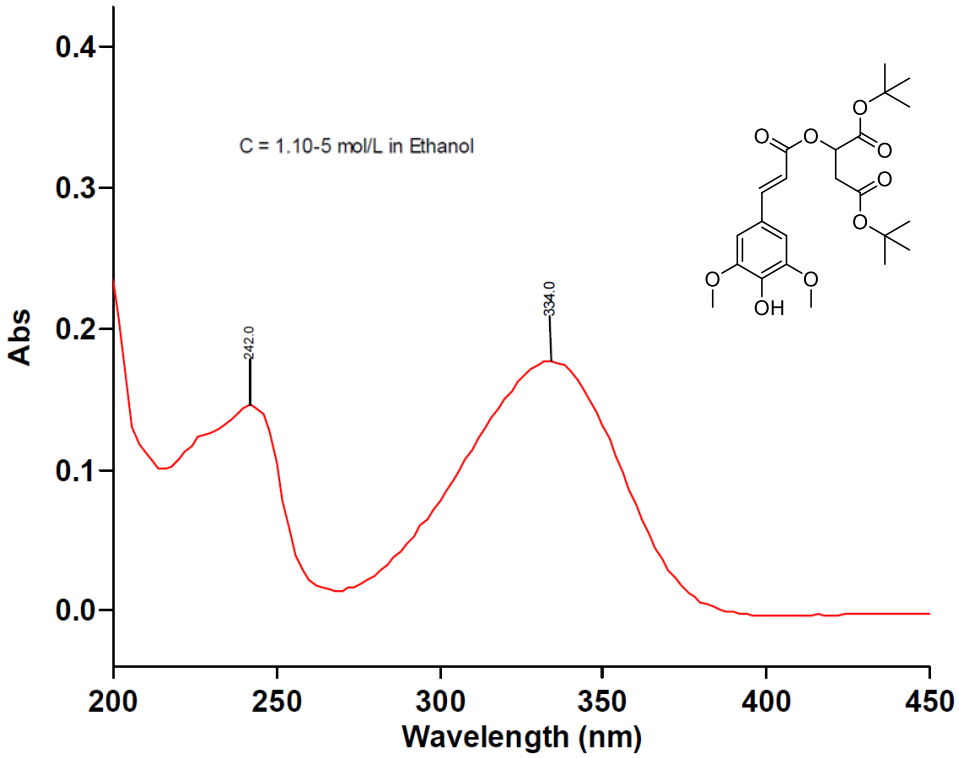

C = 1.10-5 mol/L in Ethanol
202.0
241.0
330.0
Abs
Wavelength (nm)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
250
300
350
400
450
OH

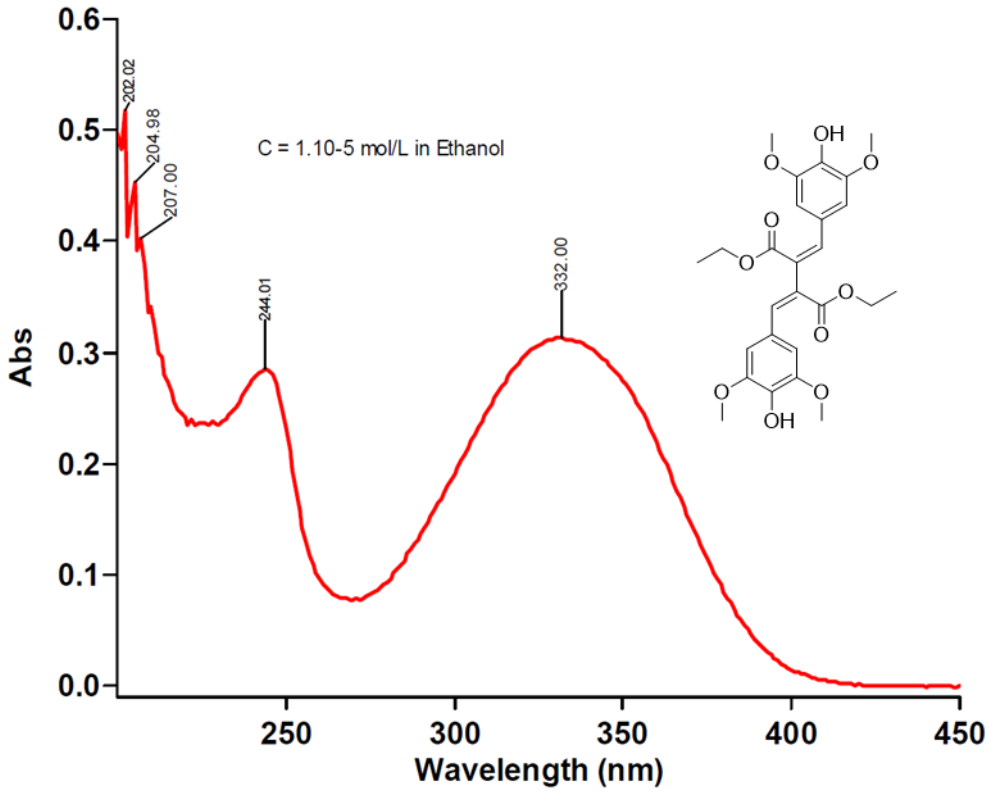

C = 1.10-5 mol/L in Ethanol
202.0
240.0
332.0
Abs
Wavelength (nm)
0.3
0.2
0.1
0.0
250
300
350
400
450
OH

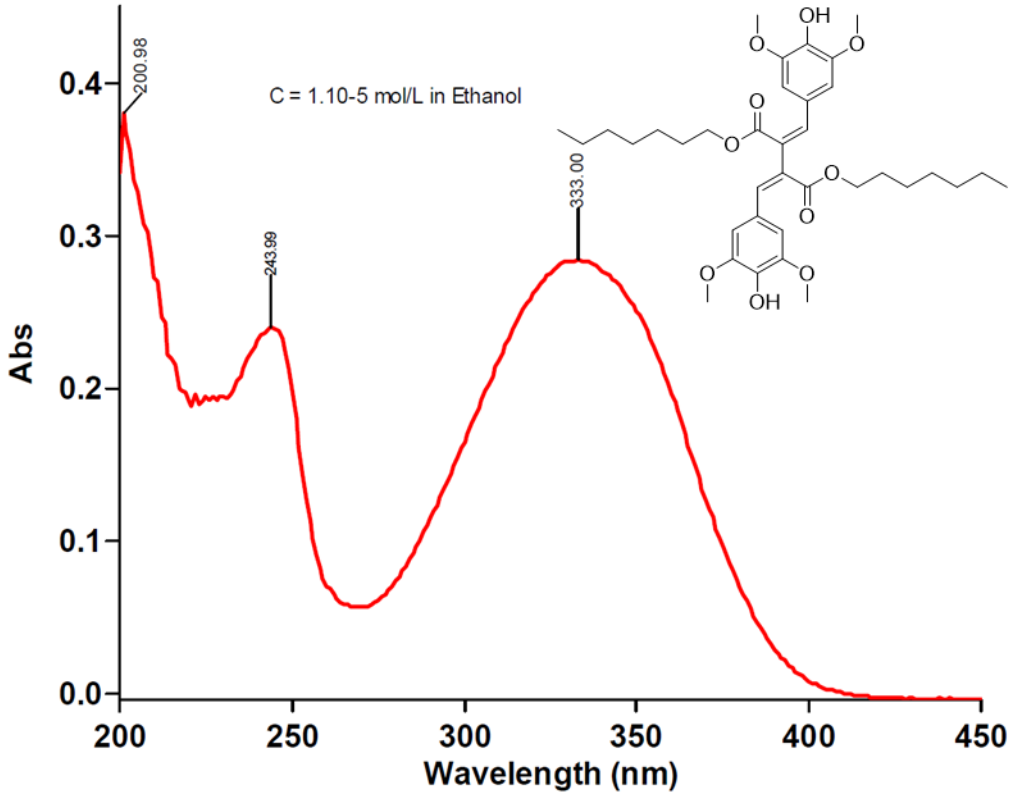

C = 1.10-5 mol/L in Ethanol
202.0
204.0
238.0
327.0
Abs
Wavelength (nm)
OH

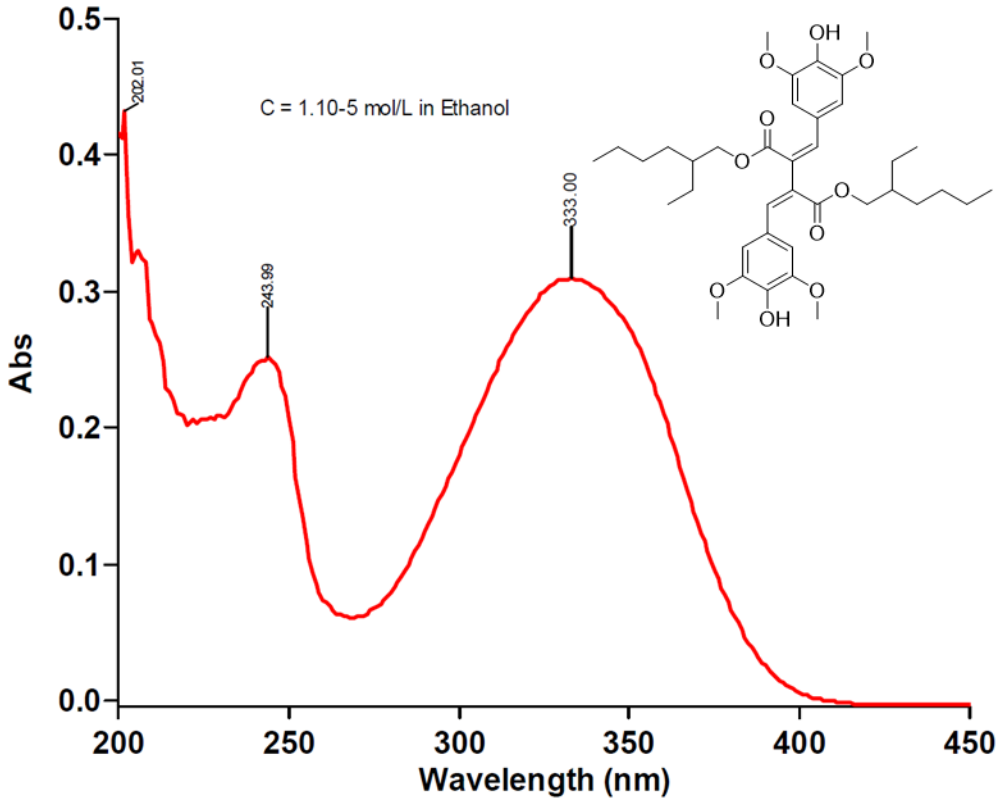

C = 1.10-5 mol/L in Ethanol
202.0
241.0
330.0
Abs
Wavelength (nm)
OH

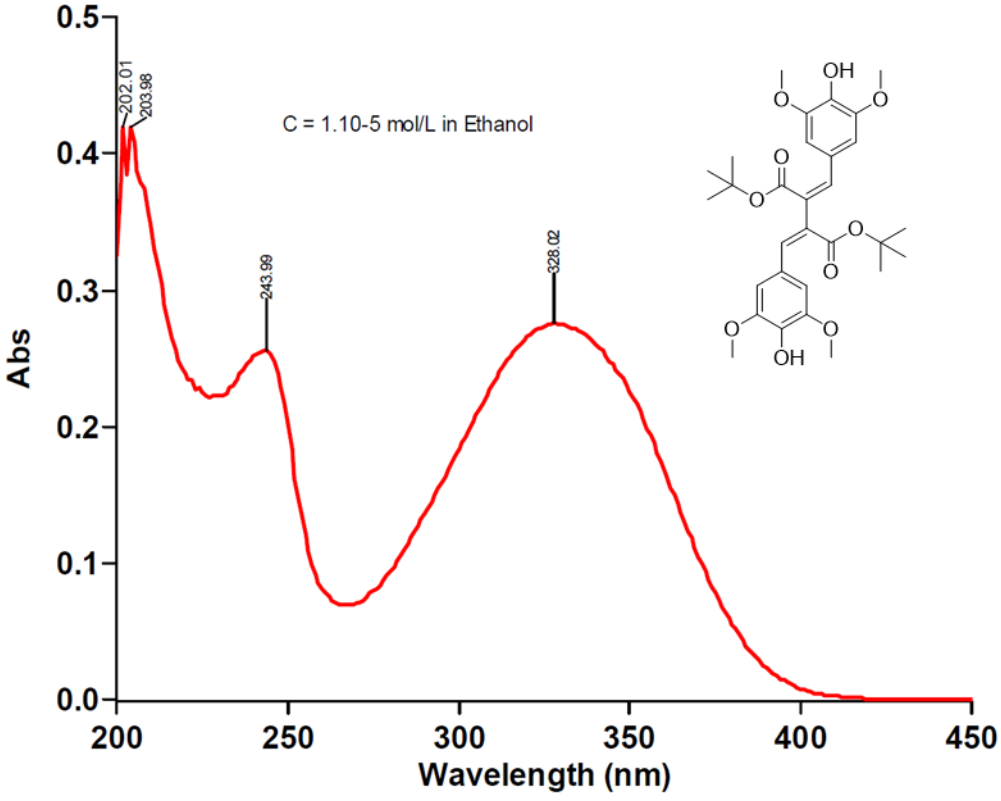

C = 1.10-5 mol/L in Ethanol
Abs
Wavelength (nm)
201.0
220.0
242.0
337.0
OH

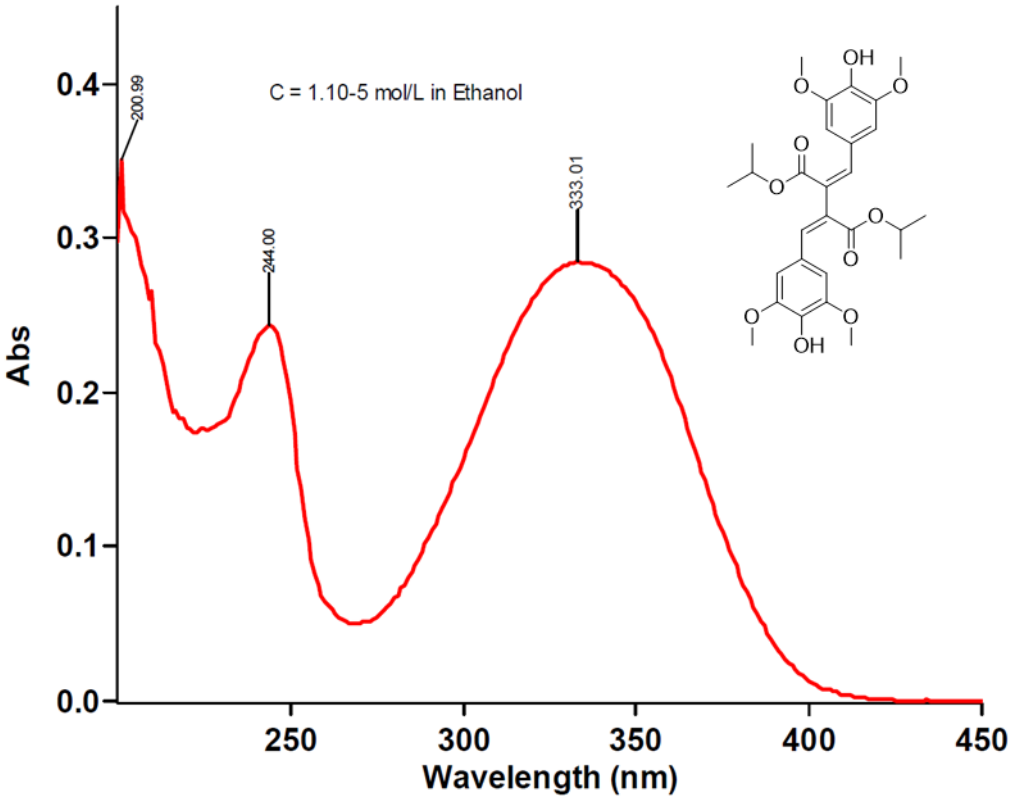

C = 1.10-5 mol/L in Ethanol
Abs
Wavelength (nm)
242.0
334.0
OH

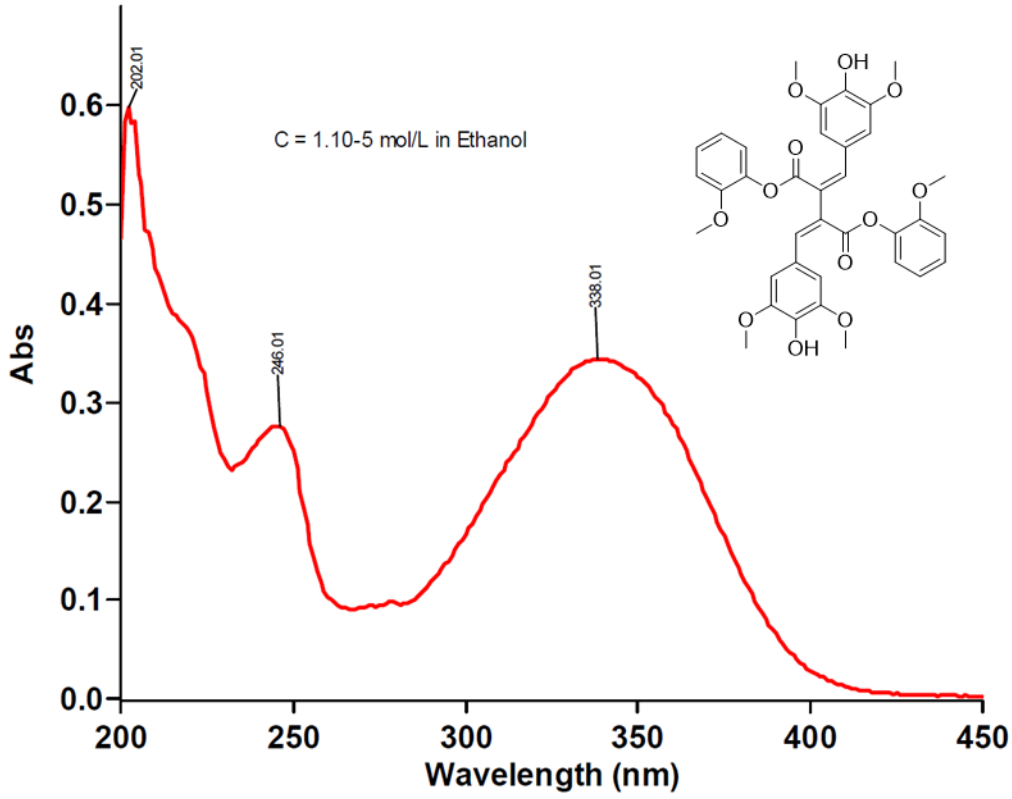

C = 1.10-5 mol/L in Ethanol
202.02
204.98
207.00
244.01
332.00
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
250
300
350
400
450
OH
O
OH

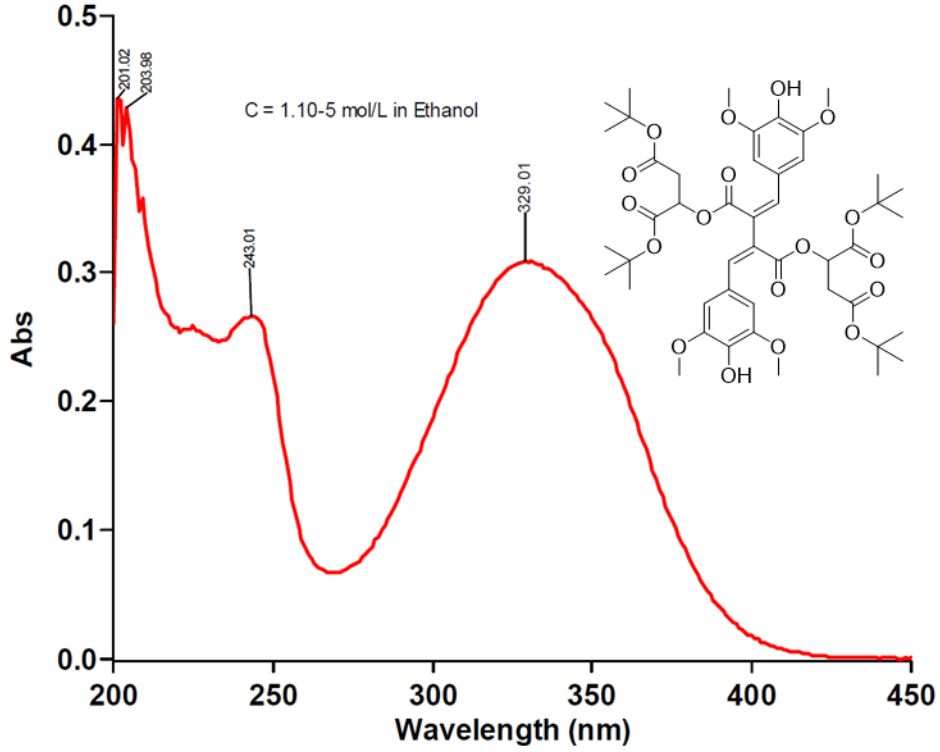

C = 1.10-5 mol/L in Ethanol
200.98
243.99
333.00
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
200
250
300
350
400
450
OH
O
OH

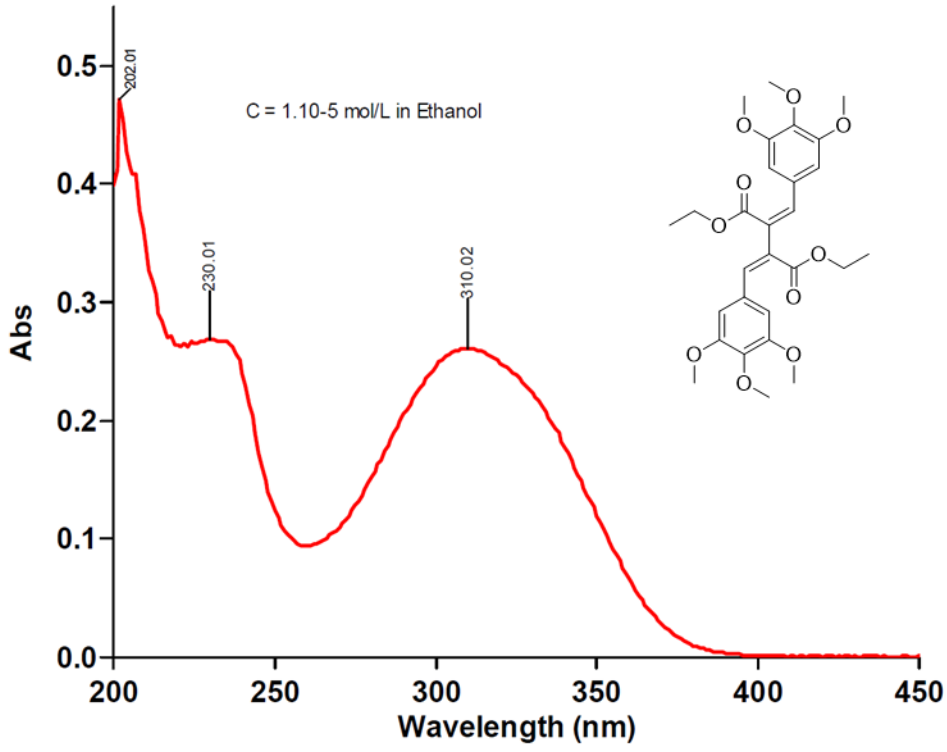

C = 1.10-5 mol/L in Ethanol
202.01
243.99
333.00
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
200
250
300
350
400
450
OH
O
OH

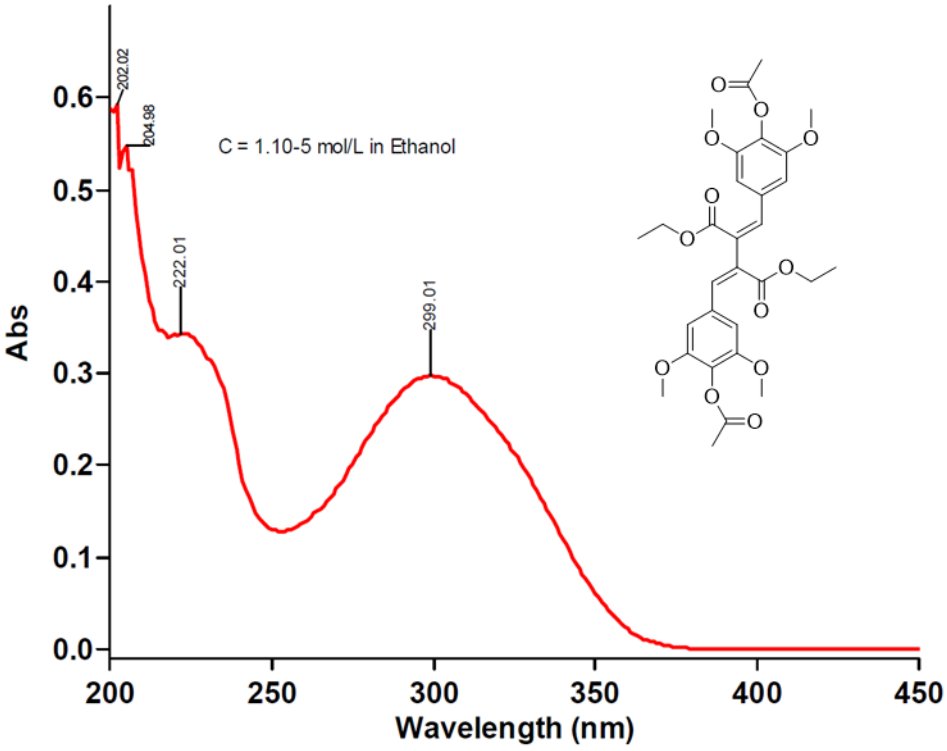

C = 1.10-5 mol/L in Ethanol
202.01
203.98
243.99
328.02
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
200
250
300
350
400
450
OH
O
OH

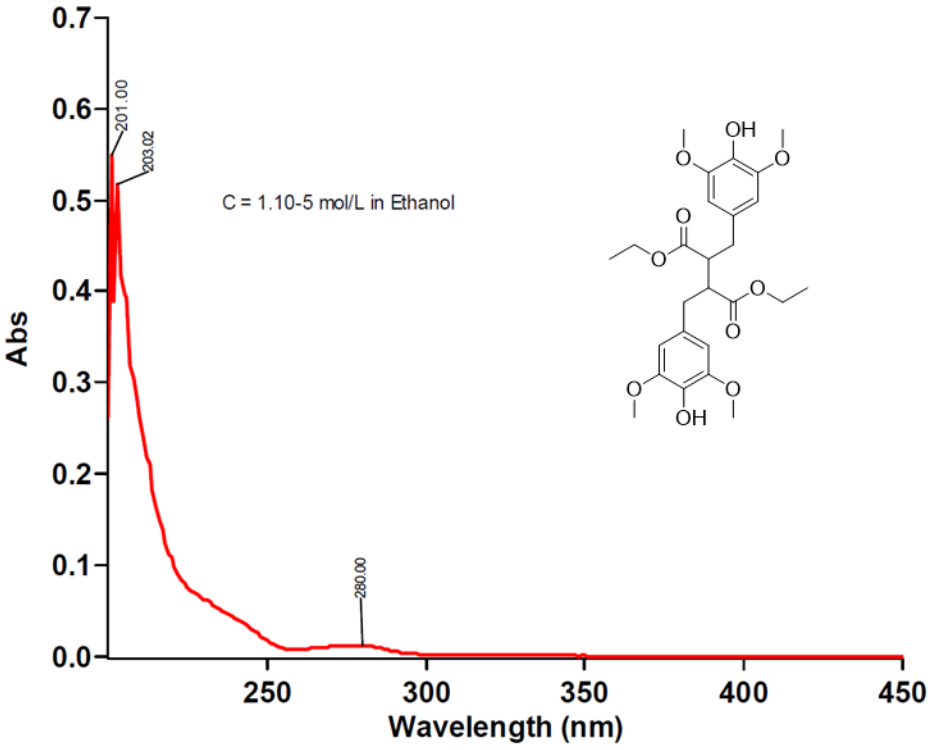

C = 1.10-5 mol/L in Ethanol
200.99
244.00
333.01
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
250
300
350
400
450
OH
O
OH

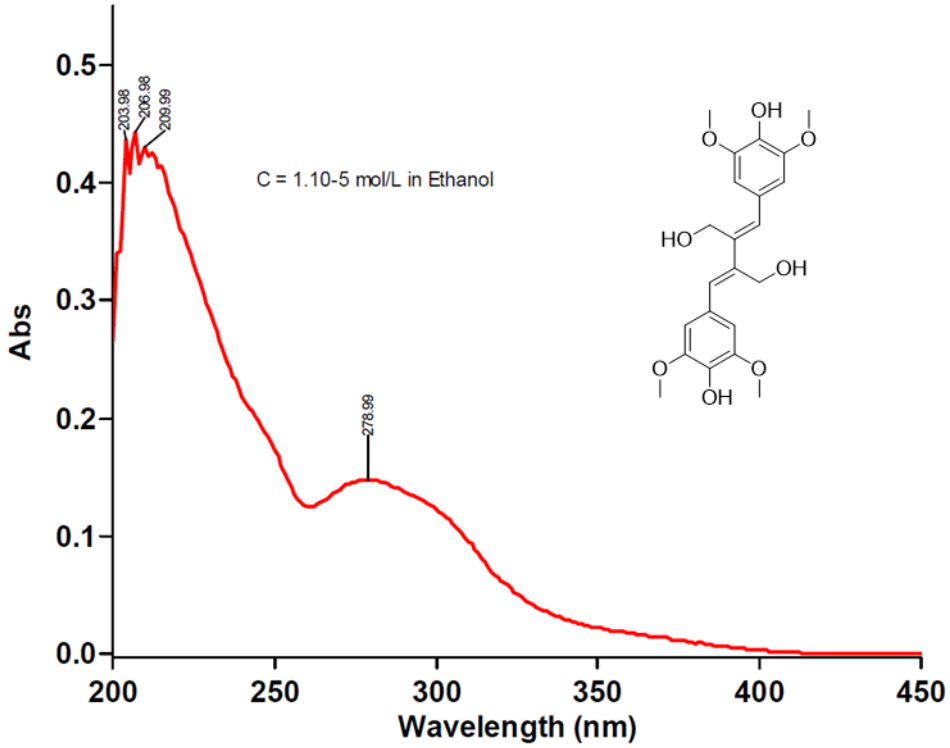

C = 1.10-5 mol/L in Ethanol
202.01
246.01
338.01
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
200
250
300
350
400
450
OH
O
OH


C = 1.10-5 mol/L in Ethanol
201.02
203.98
243.01
329.01
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
200
250
300
350
400
450
OH
OH

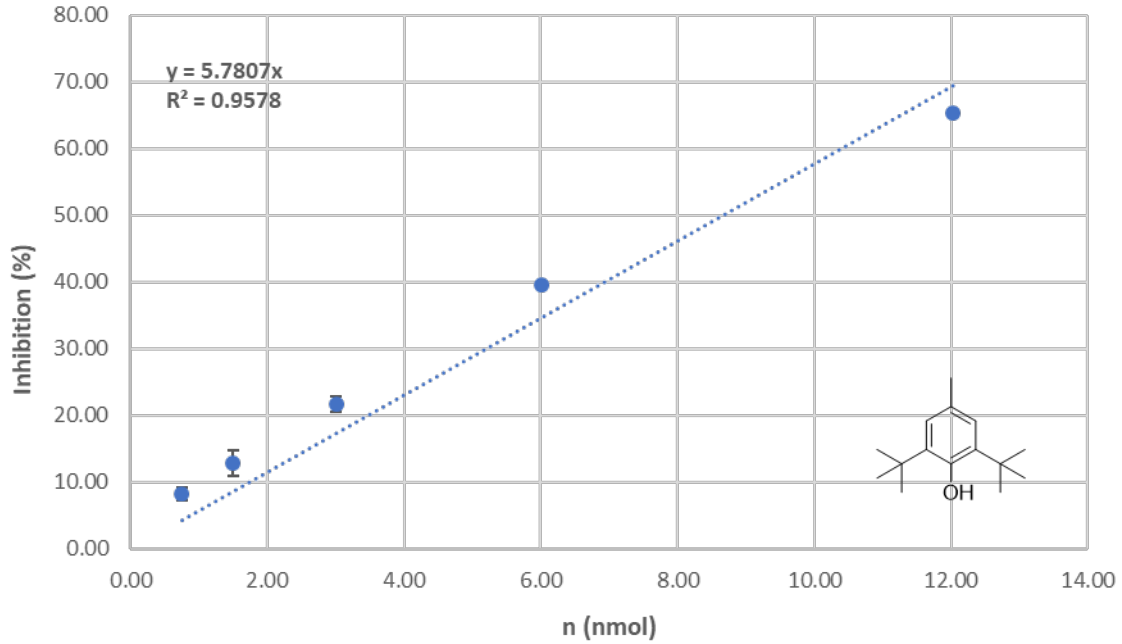

C = 1.10-5 mol/L in Ethanol
202.01
230.01
310.02
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
200
250
300
350
400
450

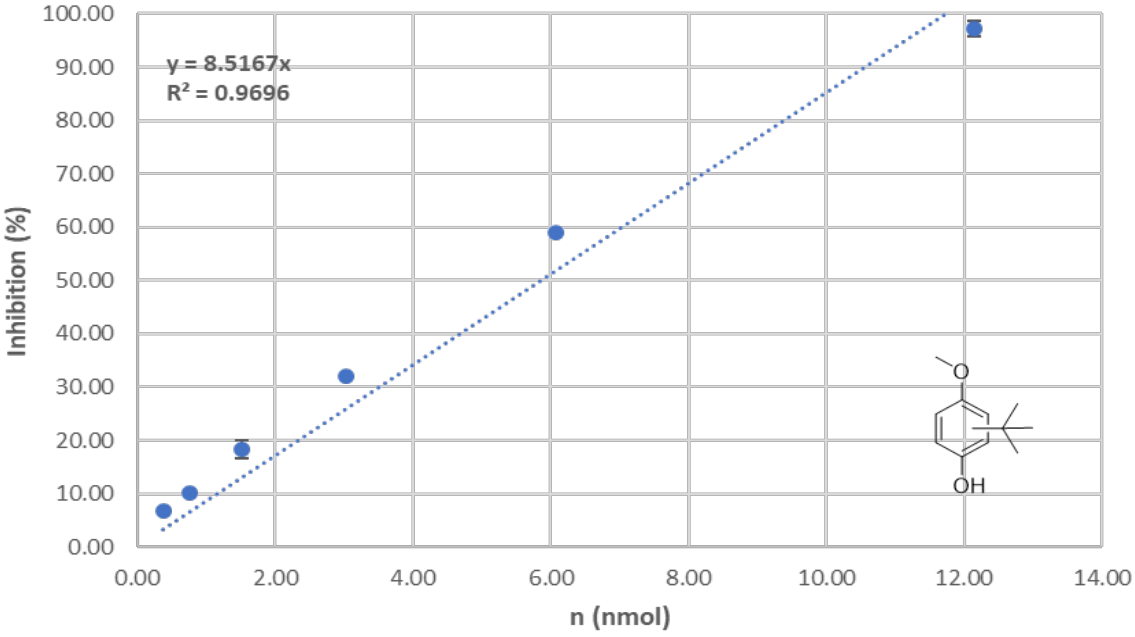

202.02
204.98
222.01
299.01
C = 1.10-5 mol/L in Ethanol
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
200
250
300
350
400
450

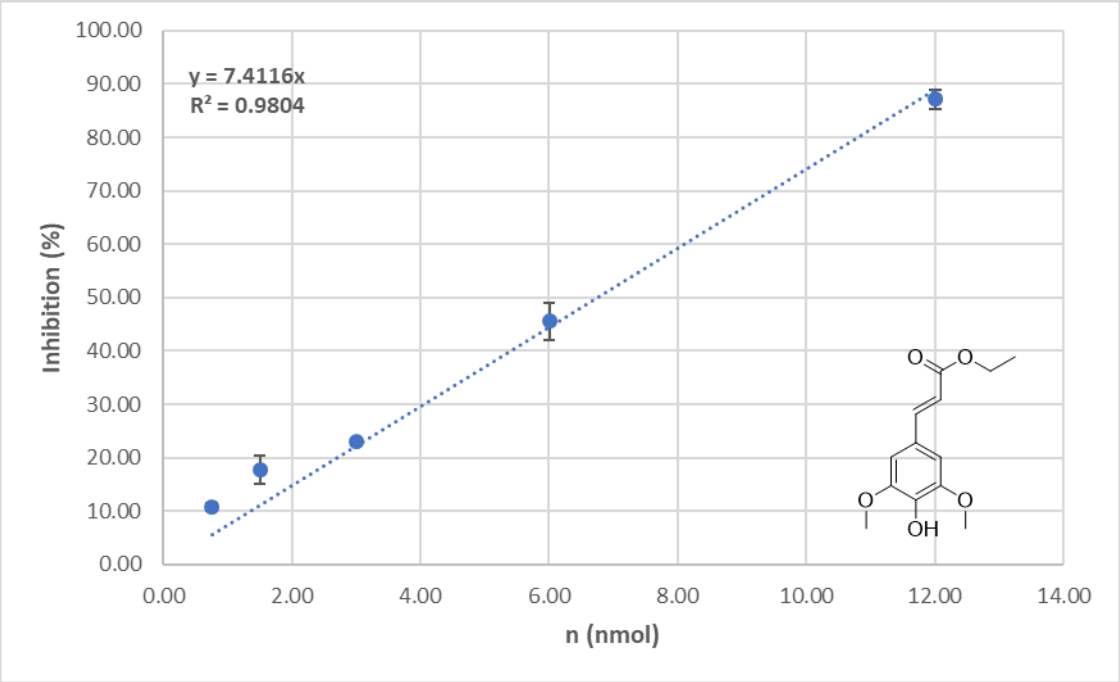

201.00
203.02
280.00
C = 1.10-5 mol/L in Ethanol
OH
OH
Abs
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
250
300
350
400
450

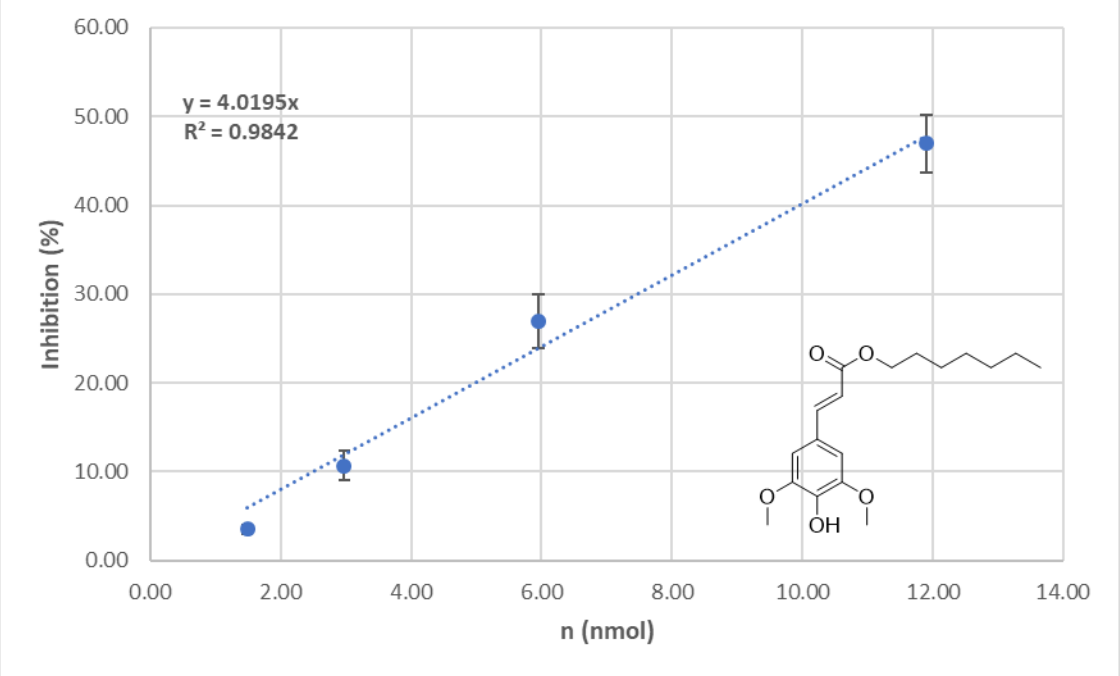

0.5
0.4
0.3
0.2
0.1
0.0
Abs
203.98
206.98
209.99
278.99
C = 1.10-5 mol/L in Ethanol
200
250
300
350
400
450
Wavelength (nm)
OH
O
O
HO
OH
O
O
OH

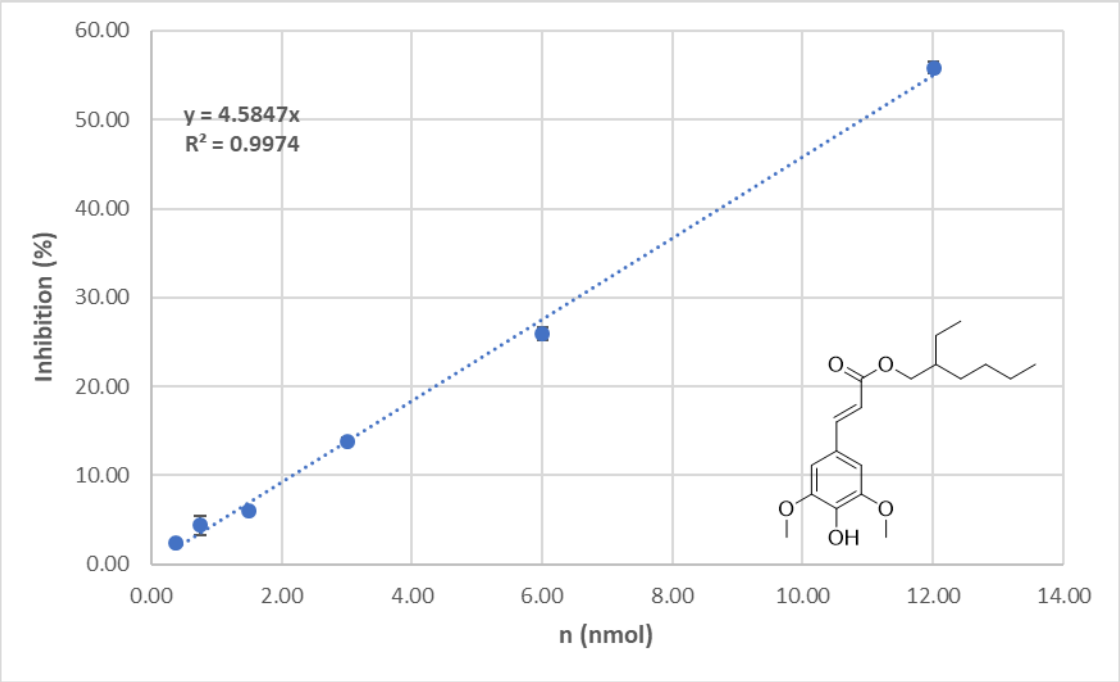
7.4. ABTS inhibition

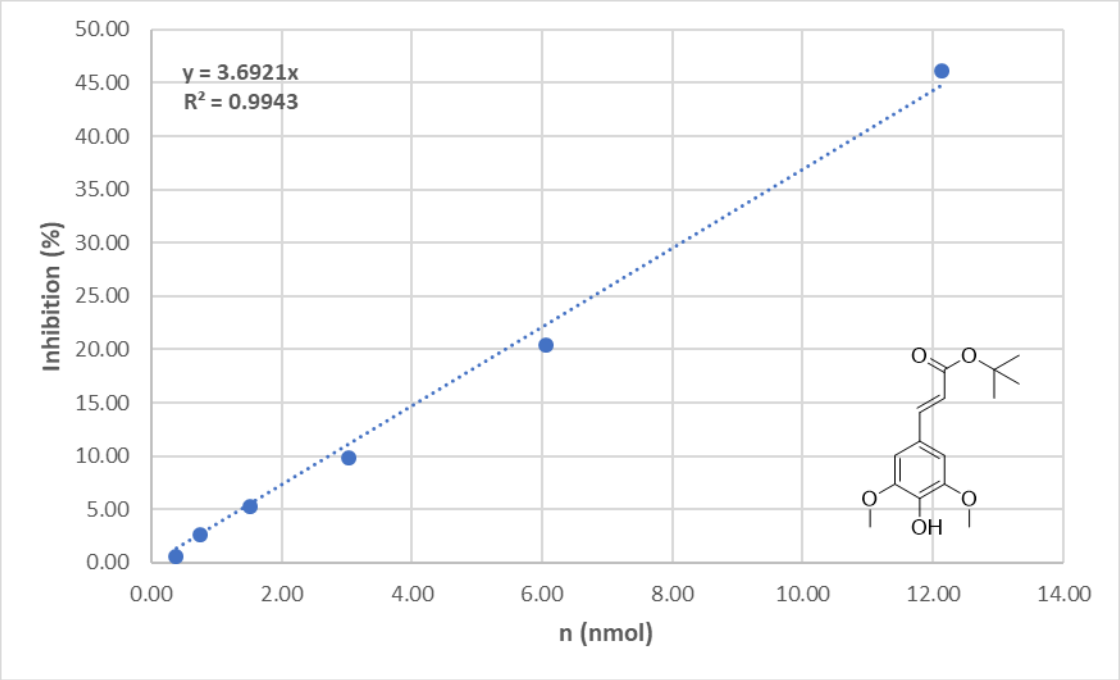


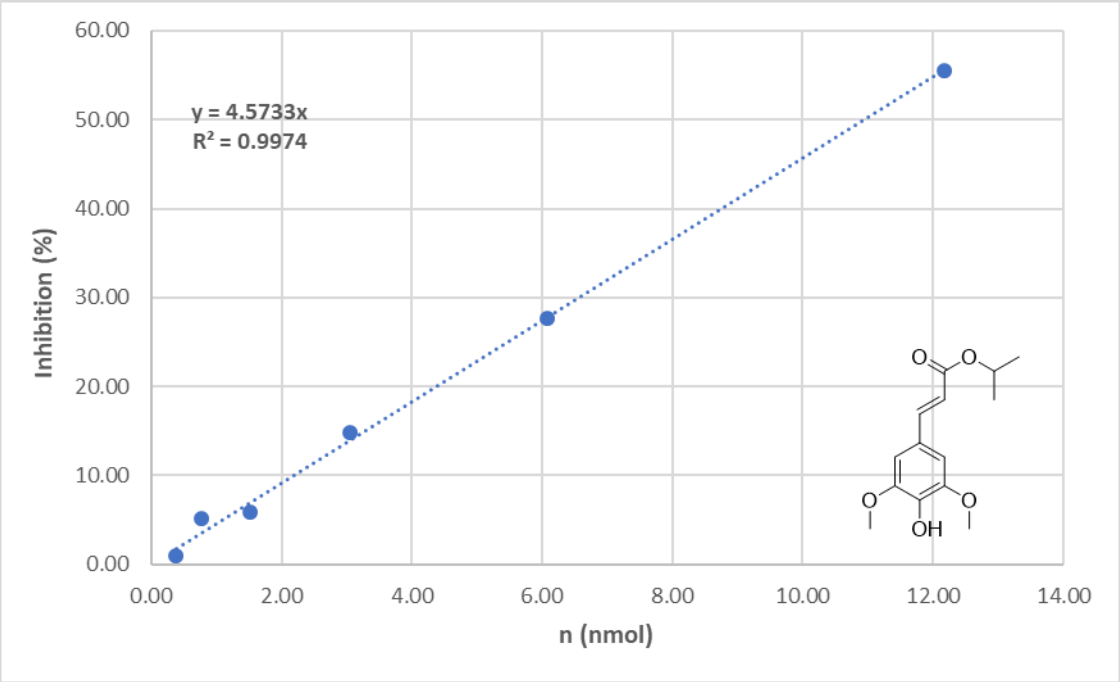


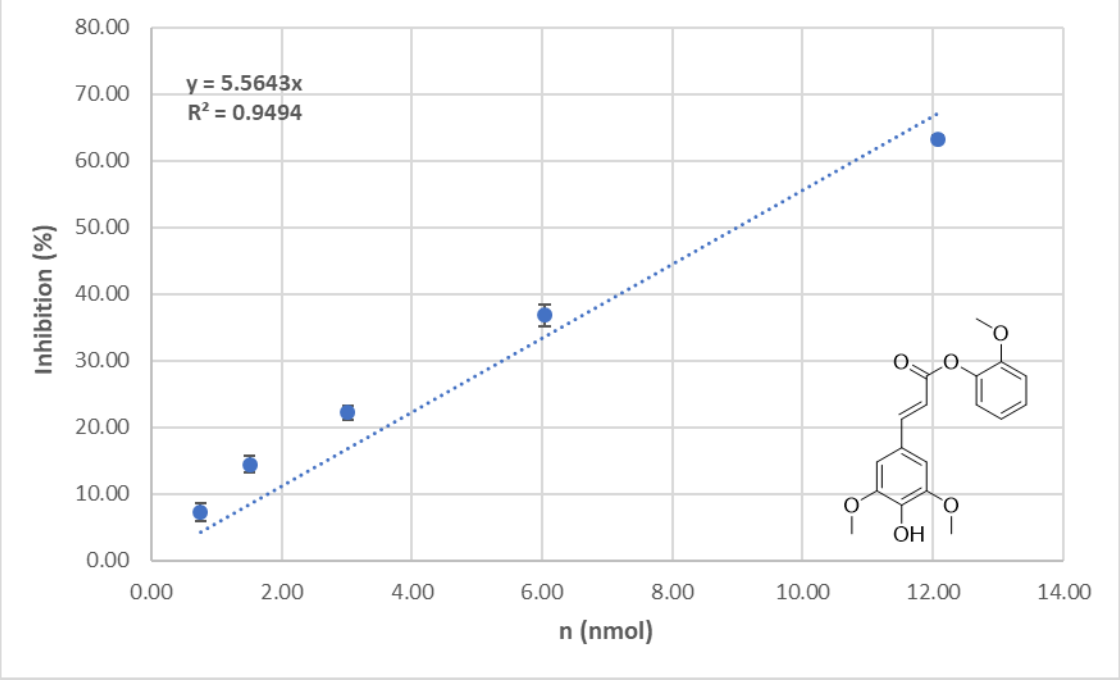

y = 7.4116x
R² = 0.9804
Inhibition (%)
n (nmol)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

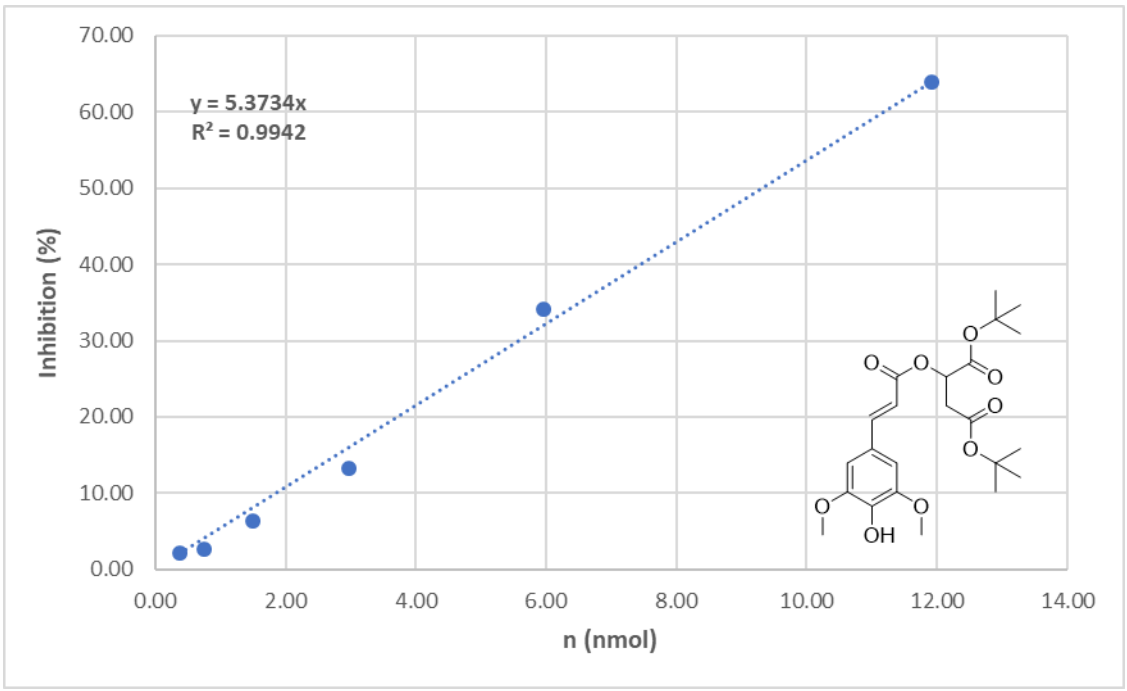

y = 4.0195x
R² = 0.9842
Inhibition (%)
n (nmol)
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

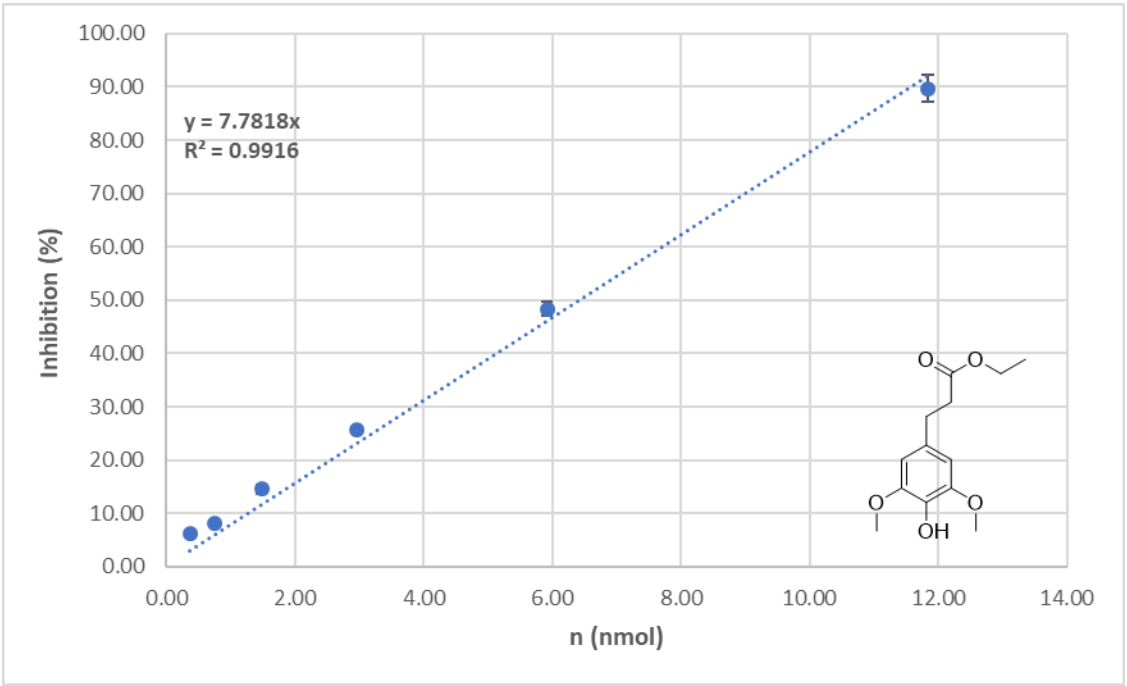

y = 4.5847x
R² = 0.9974
Inhibition (%)
n (nmol)
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

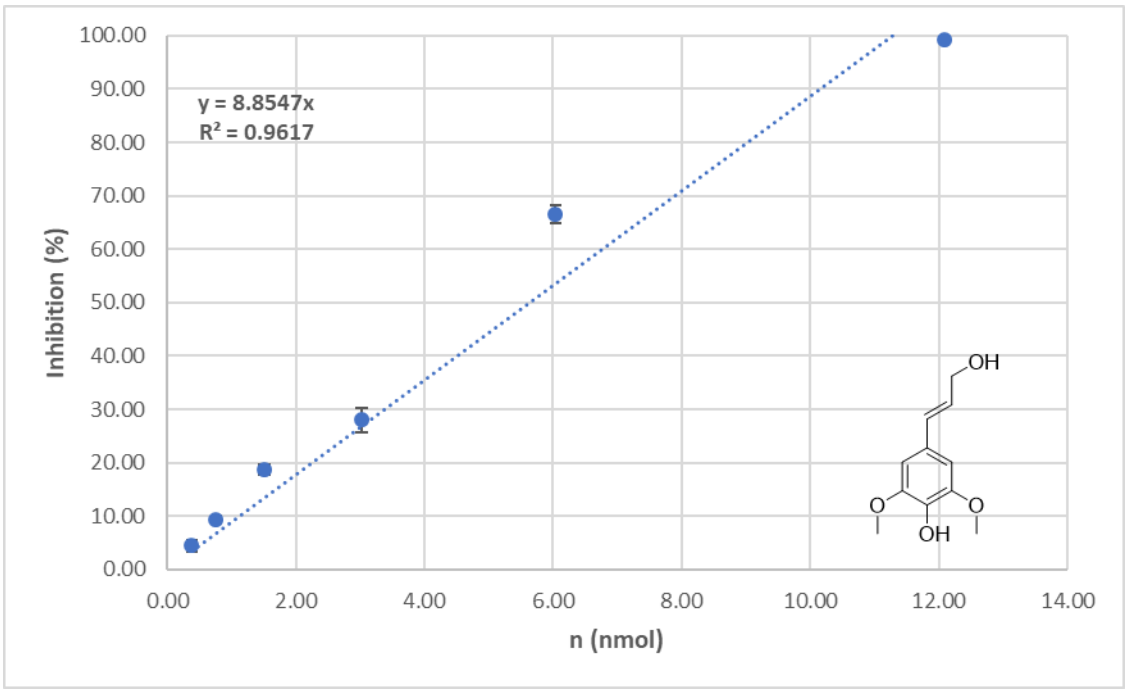

y = 3.6921x
R² = 0.9943
Inhibition (%)
n (nmol)
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

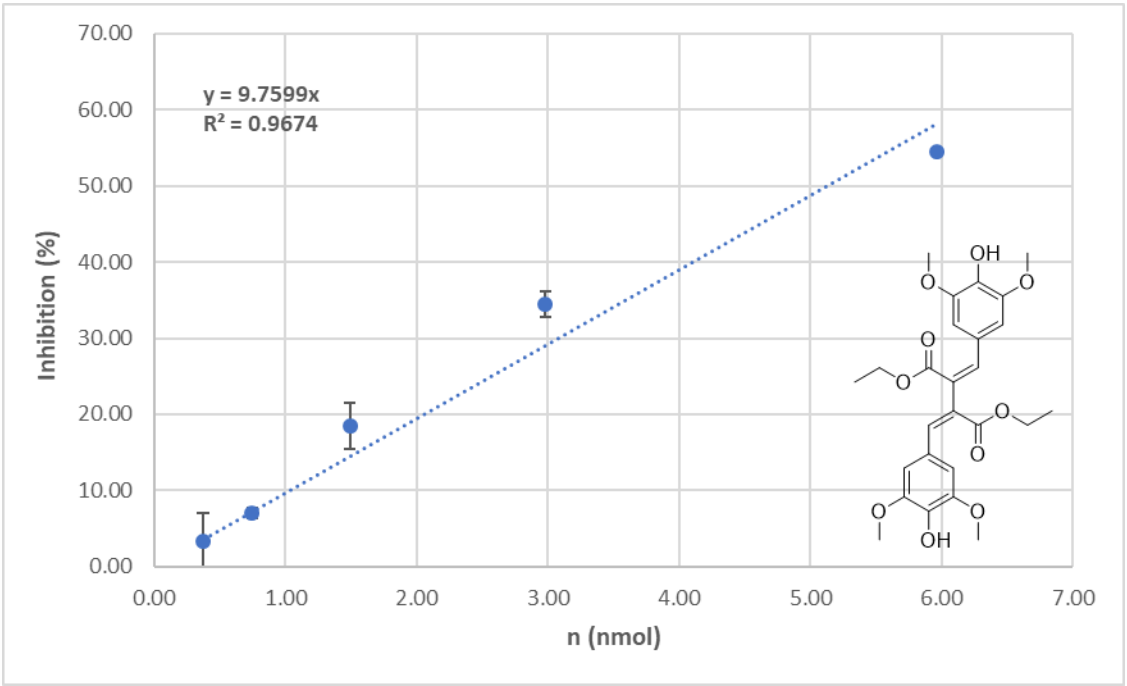

y = 4.5733x
R² = 0.9974
Inhibition (%)
n (nmol)
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

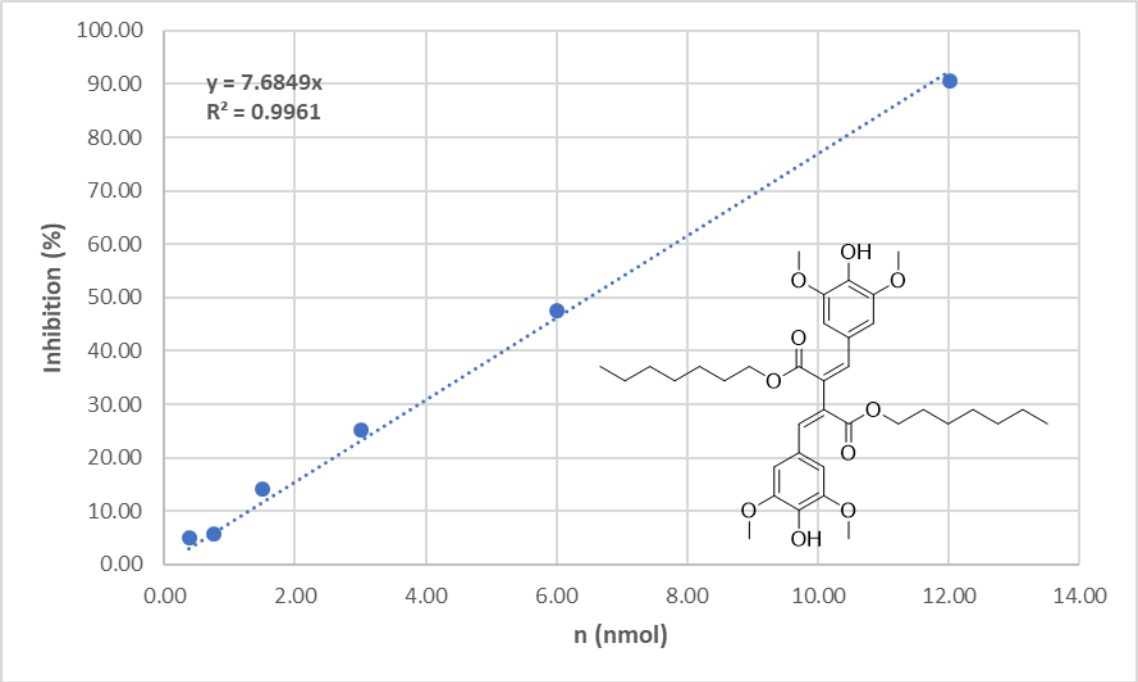

y = 5.5643x
R² = 0.9494
Inhibition (%)
n (nmol)
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
O
OH

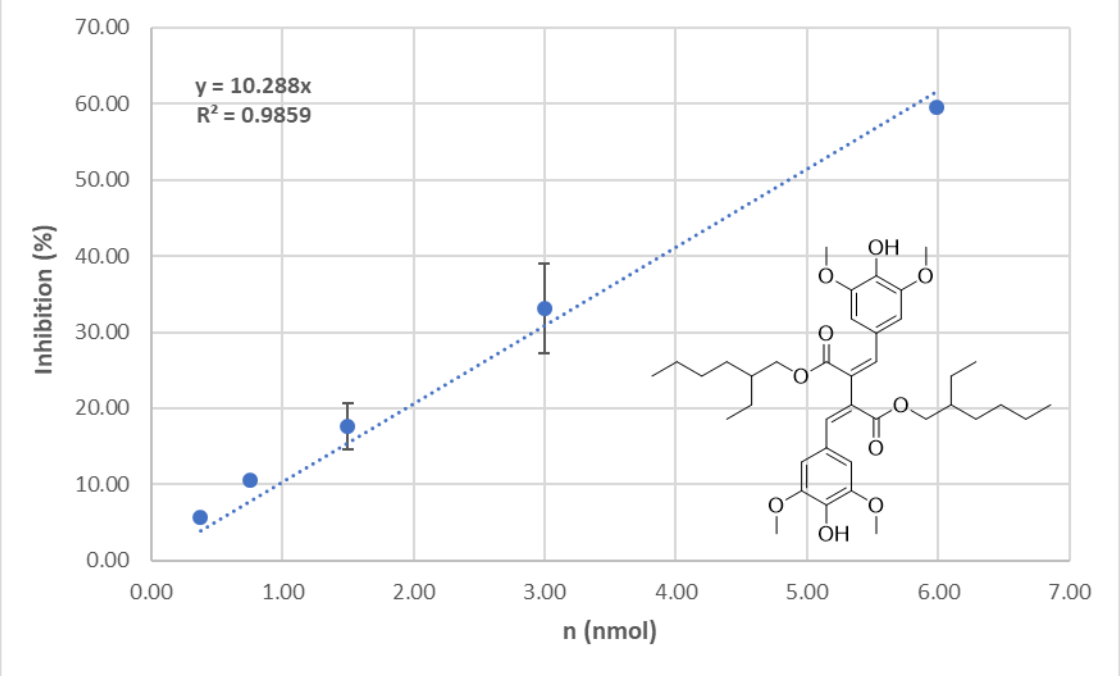

y = 5.3734x
R² = 0.9942
Inhibition (%)
n (nmol)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
O
O
O
O
OH

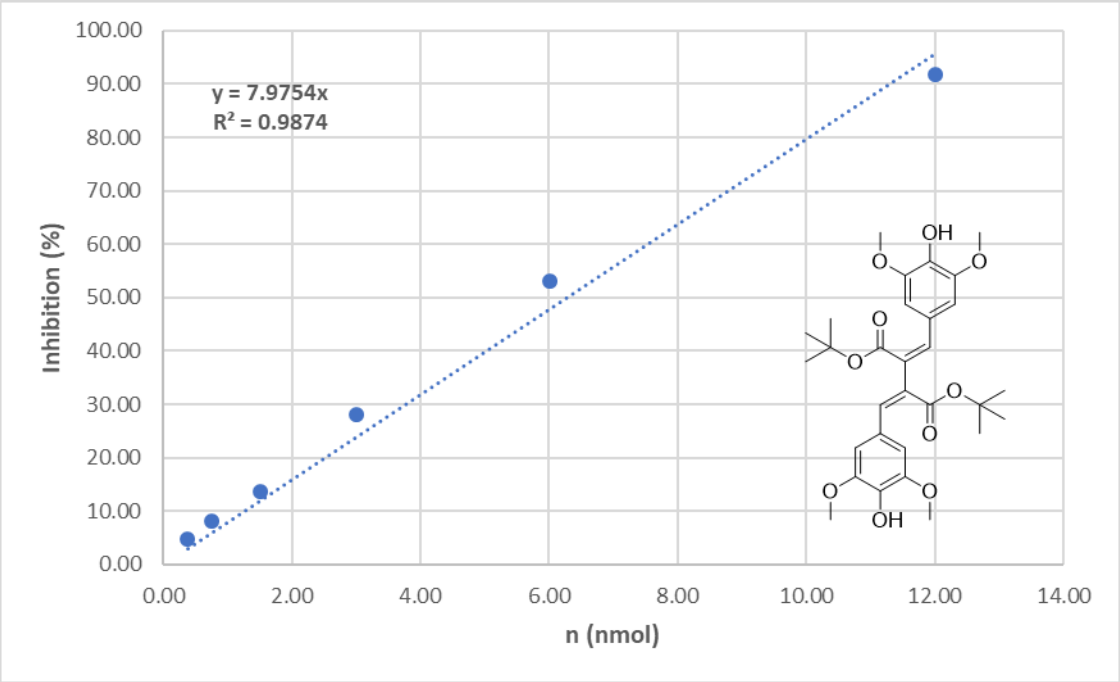

y = 7.7818x
R² = 0.9916
Inhibition (%)
n (nmol)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
O
O
O
O
OH

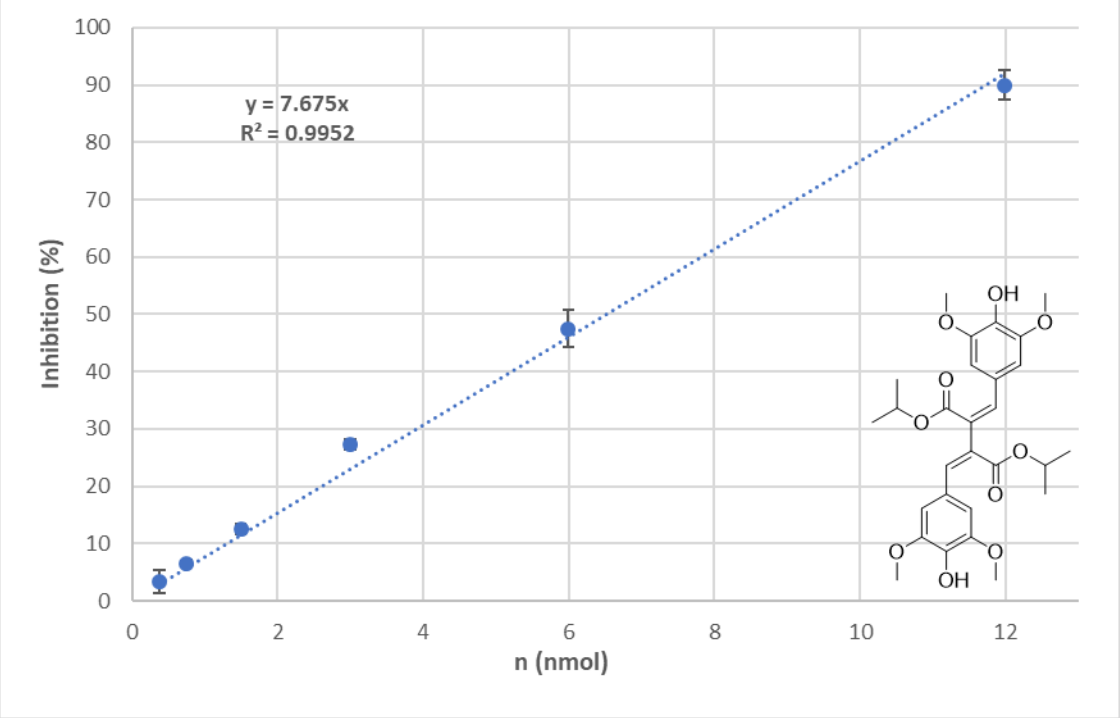

y = 8.8547x
R² = 0.9617
Inhibition (%)
n (nmol)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
OH
O
O
OH

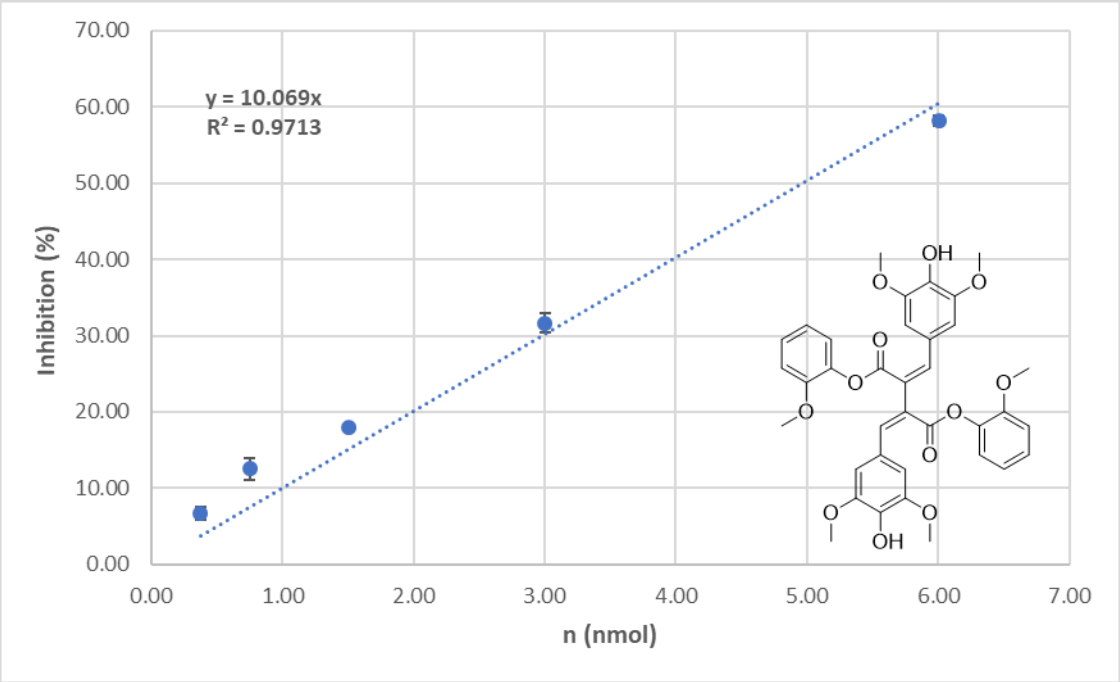

y = 9.7599x
R² = 0.9674
Inhibition (%)
n (nmol)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
OH
O
O
O
O
O
O
O
OH

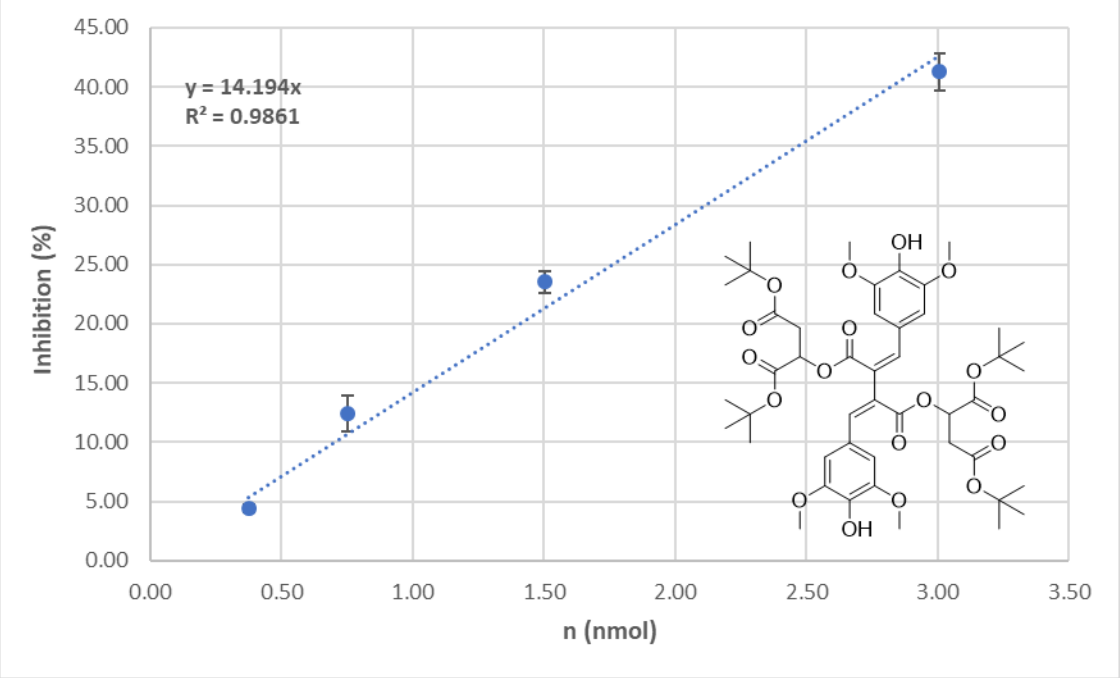

y = 7.6849x
R² = 0.9961
Inhibition (%)
n (nmol)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
OH
O
O
O
O
O
O
O
O
OH

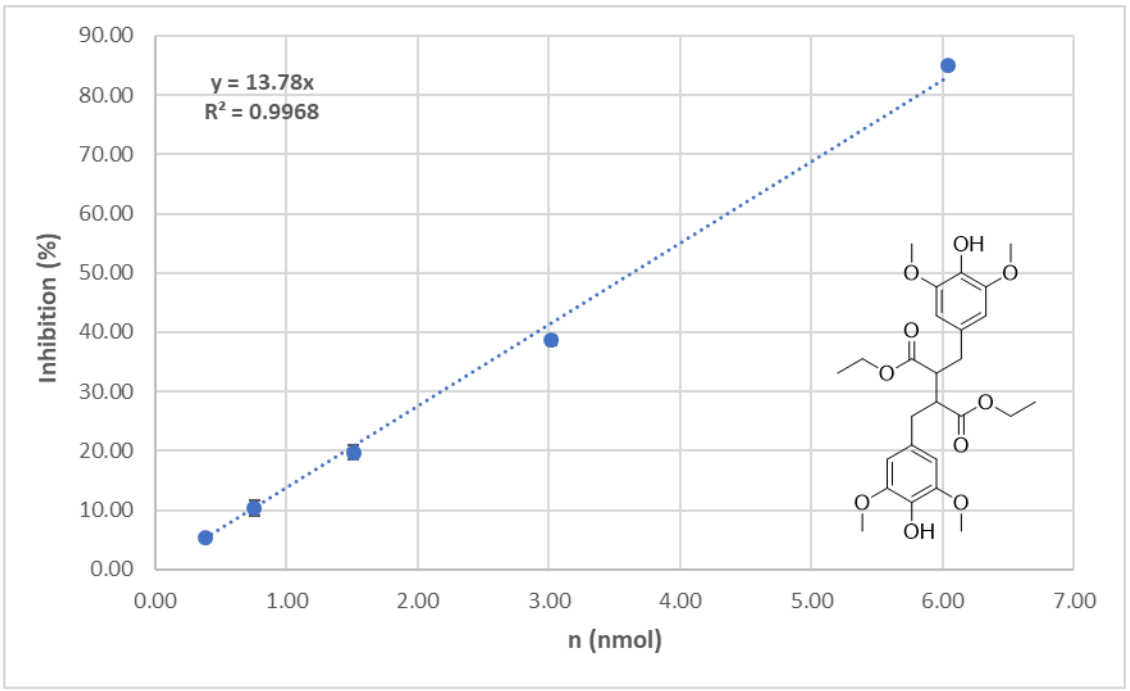

y = 10.288x
R² = 0.9859
Inhibition (%)
n (nmol)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
OH
O
O
O
O
O
O
O
O
OH

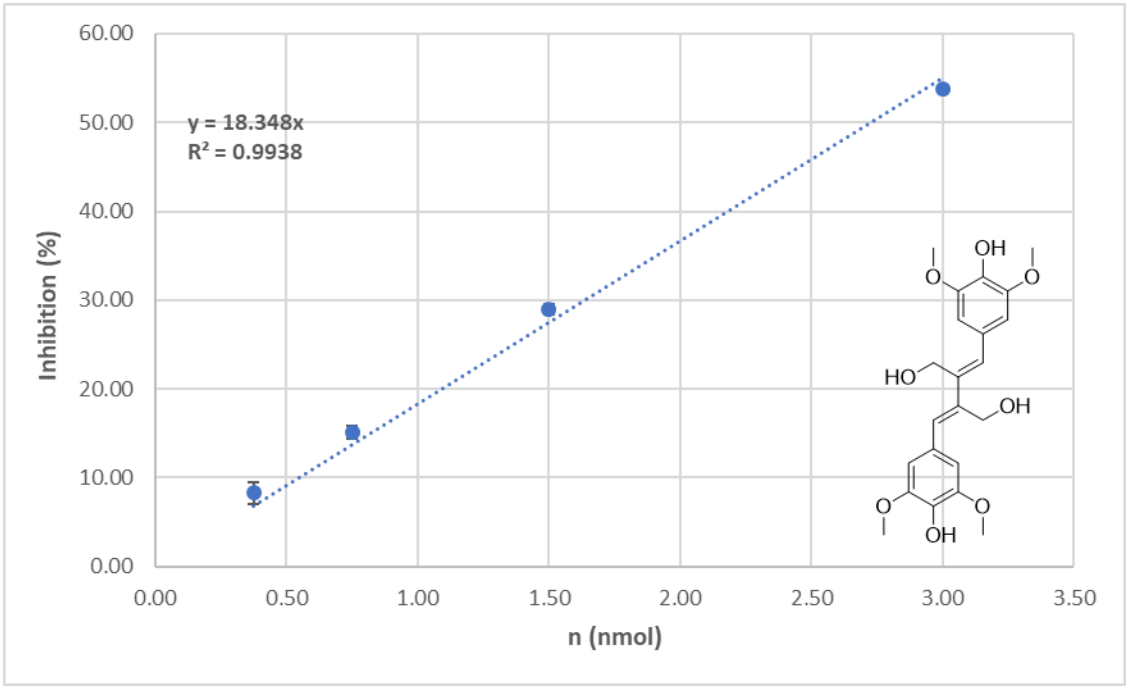

y = 7.9754x
R² = 0.9874
Inhibition (%)
n (nmol)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
OH
O
O
O
O
O
O
O
O
OH


y = 7.675x
R² = 0.9952
Inhibition (%)
n (nmol)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
OH
O
O
O
O
O
O
O
O
OH


y = 10.069x
R² = 0.9713
Inhibition (%)
n (nmol)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
OH
OH


y = 14.194x
R² = 0.9861
Inhibition (%)
n (nmol)
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
OH
OH


y = 13.78x
R² = 0.9968
Inhibition (%)
n (nmol)
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
OH
O
O
O
O
O
O
O
O
OH


y = 18.348x
R² = 0.9938
Inhibition (%)
n (nmol)
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
OH
O
O
HO
OH
O
O
OH

8. References

1. Re R., Pellegrini N., Proteggente A., Pannala A., Yang M., Rice-Evans C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biol. Med.* 1999, **26**(9/10)**:** 1231-1237.

2. Menezes J. C. J. M. D. S., Kamat S. P., Cavaleiro J. A. S., Gaspar A., Garrido J., Borges F. Synthesis and antioxidant activity of long chain alkyl hydroxycinnamates. *Eur. J. Med. Chem.* 2011, **46**(2)**:** 773-777.

3. Padwal J., Lewis W., Moody C. J. Synthesis of the reported structure of crassiflorone, a naturally occurring quinone isolated from the African ebony Diospyros crassiflora, and regioisomeric pentacyclic furocoumarin naphthoquinones. *Org. Biomol. Chem.* 2011, **9**(9)**:** 3484-3493.

4. Jaufurally A. S., Teixeira A. R. S., Hollande L., Allais F., Ducrot P.-H. Optimization of the laccase-catalyzed synthesis of (±)-syringaresinol and study of its thermal and antiradical activities. *ChemistrySelect* 2016, **1**(16)**:** 5165-5171.

5. Allais F., Martinet S., Ducrot P.-H. Straightforward total synthesis of 2-O-feruloyl-L-malate, 2-O-sinapoyl-L-malate and 2-O-5-hydroxyferuloyl-L-malate. *Synthesis* 2009(21)**:** 3571-3578.

6. Kanemitsu T., Furukoshi S., Miyazaki M., Nagata K., Itoh T. Application of asymmetric alkylation of malonic diester with phase-transfer catalysis: synthesis of LFA-1 antagonist BIRT-377. *Tetrahedron: Asymmetry* 2015, **26**(4)**:** 214-218.

7. Page P. C. B., Moore J. P. G., Mansfield I., McKenzie M. J., Bowler W. B., Gallagher J. A. Synthesis of bone-targeted oestrogenic compounds for the inhibition of bone resorption. *Tetrahedron* 2001, **57**(9)**:** 1837-1847.

8. Padilha G., Birmann P. T., Domingues M., Kaufman T. S., Savegnago L., Silveira C. C. Convenient Michael addition/β-elimination approach to the synthesis of 4-benzyl- and 4-aryl-selenyl coumarins using diselenides as selenium sources. *Tetrahedron Lett.* 2017, **58**(10)**:** 985-990.

9. Hayat S., Atta ur R., Choudhary M. I., Khan K. M., Abbaskhan A. Two new cinnamic acid esters from marine brown alga Spatoglossum variabile. *Chem. Pharm. Bull.* 2002, **50**(9)**:** 1297-1299.