Supporting Information

Rationally Designed Chiral Synthons Enabling Asymmetric *Z*- and *E*-Selective Vinylogous Aldol Reactions of Aldehydes

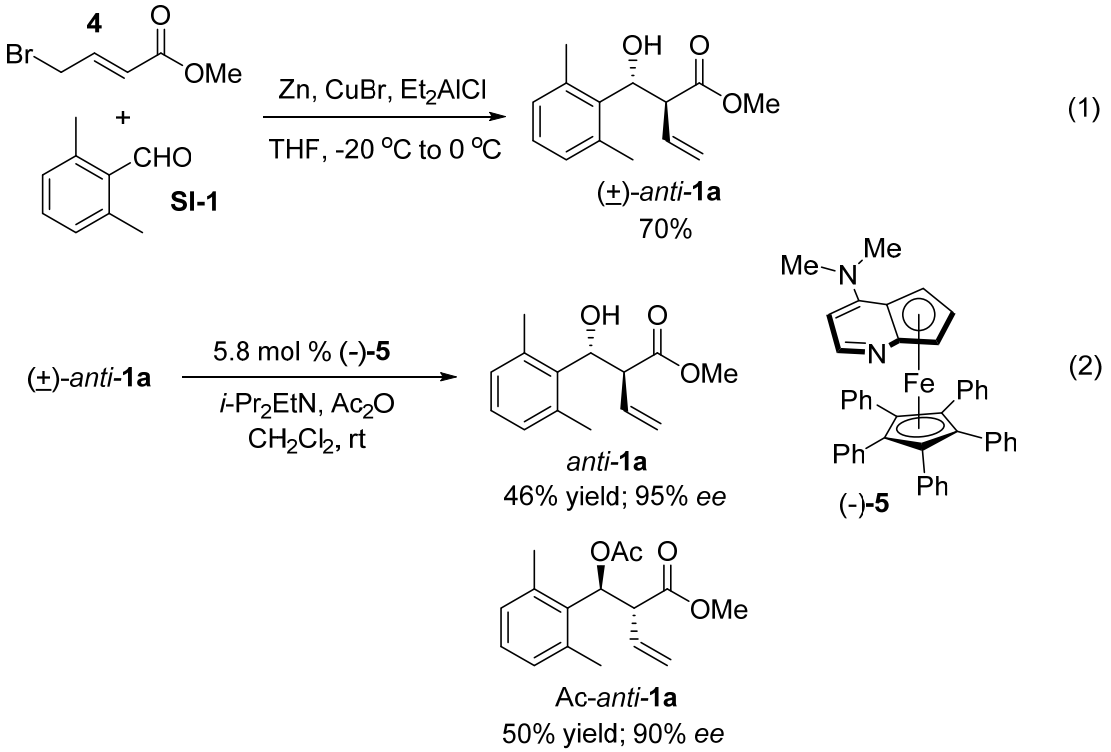
Akhil Padarti and Hyunsoo Han*

Department of Chemistry, University of Texas at San Antonio,
One UTSA Circle, San Antonio, TX, 78249-0698, USA.

Contents:

1. General Information. All reagents, otherwise mentioned, were purchased from commercial sources and used as received. Dichloromethane (DCM) and tetrahydrofuran (THF) were purified by passing through columns of activated alumina, and all other solvents were purchased as anhydrous grade, and used without further purification. All reactions were carried out in oven-dried glassware under an atmosphere of helium unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography on silica gel (Silicycle, 40-63 μm). Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates, and spots were visualized with UV and/or by staining with $KMnO_4$ or phosphomolybdic acid. ^{1}H- & ^{13}C-NMR Spectra were recorded on Varian-300 (300 MHz) or Varian-500 (500 MHz) instruments using residual protio solvent signals as internal standards. The following abbreviations were used to indicate signal multiplicity: s= singlet; d= doublet; t= triplet; q= quartet; m= multiplet; br= broad, and coupling constants were described in hertz (Hz). Optical rotations were measured by AP-100 with a 10 cm cell (concentration *c* given in g/100 mL). High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and reported as m/z (relative intensity), and exact masses were reported for the molecular ion $(M+Na)^+$, M^+ or a suitable fragment ion. Enantiomeric excesses were determined by Shimadzu HPLC LC-8A using Diode array detector SPD-10A, Chiracel OD-H (250 x 4.6 mm) or Chiracel OD (250 x 4.6 mm) columns, and *n*-hexane-isopropyl alcohol as mobile phase.

2. Preparations of Vinylogous Aldolation Synthons 1a-d (Scheme 3)

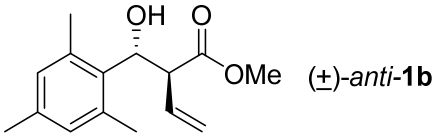


Eq 1: Diethylaluminum chloride solution (1M in hexane, 24 mL) was slowly added to a mixture of zinc dust (2.1399 g, 32.73 mmol) and a catalytic amount of cuprous bromide (0.1565 g, 1.091 mmol) in dry THF (75 mL) with stirring under argon atmosphere at rt. The resulting mixture was cooled to -20 °C, and a solution of **4** (4.5953 g, 21.82 mmol) and **SI-1** (3.2206 g, 24.00 mmol) in dry THF (total volume 20 mL) was added dropwise over 40 min by using a syringe pump at the rate of 30 mL/hour at -20 °C. The temperature was raised to 0 °C, and the reaction mixture was stirred until most (±)-*syn*-1a formed initially converted to (±)-*anti*-1a as judged on TLC. The reaction mixture was quenched by the addition of pyridine (7.5 mL) followed by the slow addition of 2N HCl solution (100 mL) at -20 °C (vigorous bubbling took place). The product was extracted with ethyl ether three times, and the ether extracts were washed with brine and dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/15) to give racemic (±)-*anti*-**1a** as a yellowish solid (3.5798 g, 70%).

Eq 2: To a mixture of (±)-*anti*-**1a** (1.2202 g, 5.21 mmol), (-)-**5** (0.2000 g, 0.303 mmol), and *i*-Pr_2EtN (2.0188 g, 15.62 mmol) in DCM (55 mL) at rt was slowly added Ac_2O (1.5959 g, 15.62

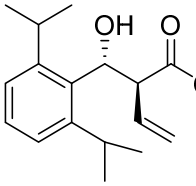
mmol). After stirring for 51 hours at rt, all solvents were removed below 30 °C, and the residue was purified by chromatography (ethyl acetate/hexane 1/9) to give *anti*-**1a** as a yellowish solid (m.p. = 45 °C, 0.5613 g, 46%) and Ac-*anti*-**1a** as an oil (0.7195 g, 50%). The *ee's* of *anti*-**1a** and Ac-*anti*-**1a** were determined to be >95% and 90% respectively by chiral HPLC (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 15.112 min and 23.780 min): $[\alpha]_D^{26}$ = -62.83 (c = 2.87, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 5.52-5.61 (m, 1H), 5.53 (d, *J* = 10.6 Hz, 1H), 4.91-4.97 (m, 2H), 3.88 (dd, *J* = 10.5, 8.6 Hz, 1H), 3.80 (s, 3H), 2.46 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.8, 136.9, 135.9, 131.5, 129.4 (br), 127.7, 118.9, 71.4, 55.5, 52.1, 21.1; **HRMS** (ESI^+): *m/z*: calcd for $C_{14}H_{18}O_3$ $[M + Na]^+$: 257.1148, found: 257.1146.

The recovery of the catalyst (-)-5: After eluting *anti*-**1a** and then washing the column with 100% AcOEt, the catalyst was eluted with a 1:1 mixture of AcOEt and Et_3N. The fractions with purple color were collected, concentrated, and dried under high vacuum to give (-)-**5**. The recovery yields typically ranged from 95% to 100%, and the recovered catalysts could be reused without any notable differences.



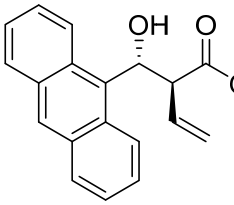
(±)-*anti*-**1b**

This compound was prepared according to eq 3 (see below) by using mesitaldehyde instead of 2,6-dimethylbenzaldehyde (**SI-1**): Yellowish solid (m.p. = 51 °C); Yield 27% [along with the corresponding *syn*-isomer (40%)]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.81 (s, 2H), 5.51-5.60 (m, 1H), 5.49 (d, *J*= 10.5 Hz, 1H), 4.96 (dd, *J*= 13.7, 3.2 Hz, 2H), 3.87 (t, *J*= 9.5, 1H), 3.81 (s, 3H), 2.43 (S, 6H), 2.25 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.90, 137.19, 136.77, 132.93, 131.61, 130.13, 118.85, 71.35, 55.47, 52.17, 20.94, 20.78; **HRMS** (ESI^+): *m/z*: calcd for $C_{15}H_{20}O_3$ $[M + Na]^+$: 271.1305, found: 271.1304.



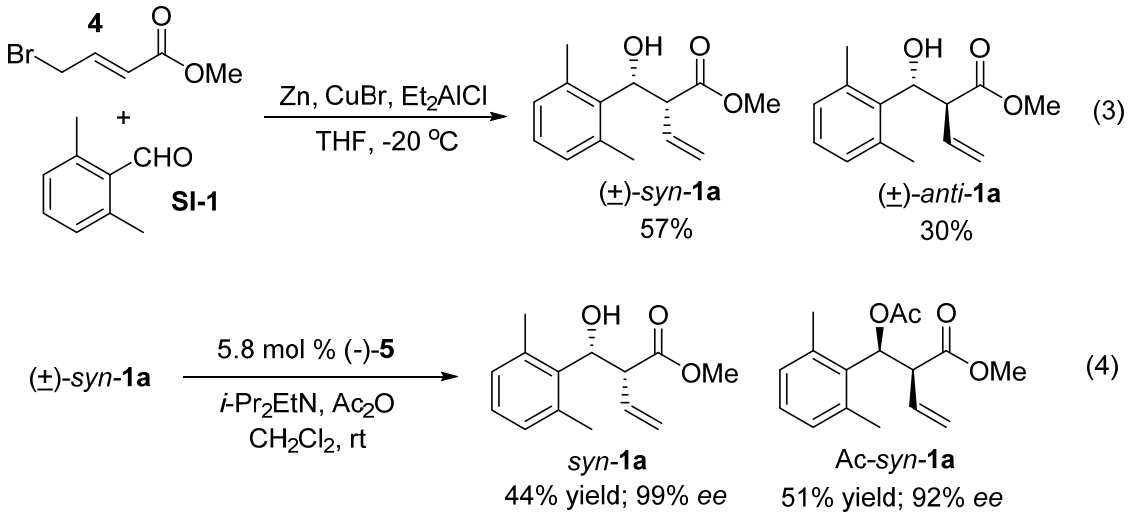
(±)-*anti*-**1c**

This compound was prepared according to eq 3 (see below) by using 2,6-diisopropylbenzaldehyde instead of **SI-1**: Yellowish solid (m.p. = 60 ^{o}C); Yield 28% [along with the corresponding *syn*-isomer (35%)]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J*= 7.3 Hz, 1H), 7.21 (br s, 1H), 7.10 (br s, 1H), 5.70 (d, *J*= 10.7 Hz, 1H), 5.51-5.62 (m, 1H), 4.88-5.01 (m, 2H), 3.83 (s, 3H), 3.24 (br s, 1H), 2.46 (br s, 1H), 1.26 (br s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.77, 133.20, 132.13, 128.26, 125.24 (multiple signals), 122.64 (multiple signals), 119.03, 70.48, 57.18, 52.18, 29.15, 25.68 (25.31, 24.49, 22.92, 22.74); **HRMS** (ESI^+): *m/z*: calcd for $C_{18}H_{26}O_3$ $[M + Na]^+$: 313.1774, found: 313.1774.



(±)-*anti*-**1d**

This compound was prepared according to eq 3 (see below) by using anthracene-9-carbaldehyde instead of **SI-1**: Yellowish solid (m.p. = 72 ^{o}C); Yield 25% [along with the corresponding *syn*-isomer (34%)]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10-9.30 (br s, 2H), 8.42 (s, 1H), 8.01 (d, *J*= 8.3 Hz, 2H), 7.53 (t, I= 8.3 Hz, 2H), 7.47 (t, I= 7.8 Hz, 2H), 6.65 (d, I= 10.5 Hz, 1H), 5.41-5.50 (m, 1H), 4.58-4.68 (m, 2H), 4.40 (t, I= 9.7 Hz, 1H), 3.89 (S, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.00, 131.41, 130.75, 130.07, 129.38, 128.84, 125.89 (multiple signals), 124.76, 119.03, 70.98, 57.18, 52.32); **HRMS** (ESI^+): *m/z*: calcd for $C_{20}H_{18}O_3$ $[M + Na]^+$: 329.1148, found: 329.1148.

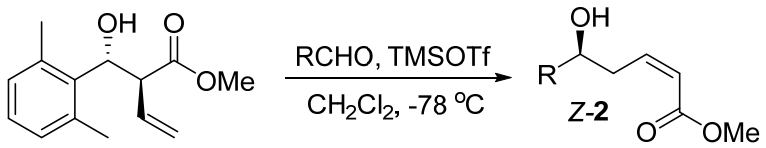


Eq 3: Diethylaluminum chloride solution (1M in hexane, 24 mL) was slowly added to a mixture of zinc dust (2.1399 g, 32.73 mmol) and a catalytic amount of cuprous bromide (0.1565 g, 1.091 mmol) in dry THF (75 mL) with stirring under argon atmosphere at rt. The resulting mixture was cooled to -20 °C, and a solution of **4** (4.5953 g, 21.82 mmol) and **SI-1** (3.2206 g, 24.00 mmol) in dry THF (total volume 20 mL) was added dropwise over 40 min by using a syringe pump at the rate of 30 mL/hour at -20 °C. After 30 min at -20 °C, the reaction mixture was quenched by the addition of pyridine (7.5 mL) followed by the slow addition of 2N HCl solution (100 mL) at -20 °C (vigorous bubbling took place). The product was extracted with ethyl ether three times, and the ether extracts were washed with brine and dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/15) to give racemic (±)-*syn*-**1a** as an oil (3.009 g, 57%) along with (±)-*anti*-**1a** (1.5342 g, 30%).

Eq 4: To a mixture of (±)-*syn*-**1a** (1.2202 g, 5.21 mmol), (-)-**5** (0.2000 g, 0.303 mmol), and *i*-Pr_2EtN (2.0188 g, 15.62 mmol) in CH_2Cl_2 (55 mL) at rt was slowly added Ac_2O (1.5959 g, 15.62 mmol). After stirring for 22 hours at rt, all solvents were removed below 30 °C, and the residue was purified by chromatography (ethyl acetate/hexane 1/9) to give *syn*-**1a** as an oil (0.5330 g, 44%) and Ac-*syn*-**1a** as an oil (0.7287 g, 51%). The *ee's* of *syn*-**1a** and Ac-*syn*-**1a** were determined to be 99% and 92% respectively by chiral HPLC (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 14.060 min and 17.172 min): $\mathbf{[\alpha]_D^{26}}$ = +76.67 (c = 2.03, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* =

7.5 Hz, 2H), 6.10 (m, 1H), 5.31-5.40 (m, 3H), 3.81 (t, J = 9.2 Hz, 1H), 3.41 (s, 3H), 2.49 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 137.1, 135.7, 134.1, 129.5, 127.8, 120.3, 71.1, 56.2, 51.7, 20.9; **HRMS** (ESI^+): *m/z*: calcd for $C_{14}H_{18}O_3$ $[M + Na]^+$: 257.1148, found: 257.1142.

3. Enantio- and *Z*-selective Vinylogous Aldol Reactions of Aldehydes by *anti*-1a (Table 1)



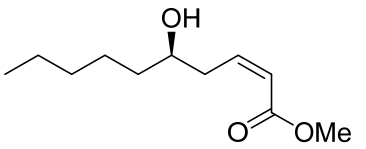
anti-**1a**: 95% *ee*

The allyl transfer reagent *anti*-**1a** (95% *ee*; 0.213 mmol) and an aldehyde (2.00 equiv relative to *anti*-**1a**) were dissolved in CH_2Cl_2 (4 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (1.50 equiv relative *anti*-**1a**) was added at once. The resulting mixture was stirred at -78 °C for 60 min. The reaction mixture was quenched with saturated $NaHCO_3$ (1.5 mL) -78 ^oC. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product *Z*-**2**.

Reaction between *anti*-1a and cyclohexanecarboxaldehyde at 1 mmol scale (entry 4): *anti*-**1a** (95% *ee*; 0.2343 g, 1.00 mmol) and cyclohexanecarboxaldehyde (0.2243 g, 2.00 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (0.3334 g, 1.50 mmol) was added dropwise. The resulting mixture was stirred at -78 °C for 60 min. The reaction mixture was quenched with saturated $NaHCO_3$ (15 mL) -78 ^oC. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product *Z*-**2d** (0.2059 g, 97%)

Note: All *Z*-**2** products were further characterized by converting into the corresponding 5,6-dihydropyran-2-ones (see the following section 4).

Table 1, entry 1

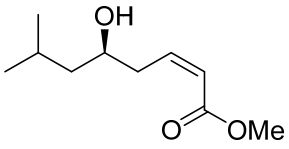


Z-**2a**

Methyl (R,Z)-5-hydroxydec-2-enoate, *Z*-2a

Oil, 37.1 mg, 87% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.35-6.44 (m, 1H), 5.92 (d, *J* = 11.6 Hz, 1H), 3.75 (m, **1H**), 3.71 (s, 3H), 2.80 (dd, *J* = 7.0, 7.0, 2H), 2.10 (br s, 1H), 1.15-1.58 (m, 8H), 0.89 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.3, 146.6, 121.3, 71.4, 51.2, 37.5, 36.6, 31.8, 25.3, 22.6, 14.0; **HPLC:** The *ee* value was determined to be 94% by measuring that of the corresponding 5,6-dihydropyran-2-one by chiral HPLC analysis (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 23.980 min and 25.944 min).

Table 1, entry 2

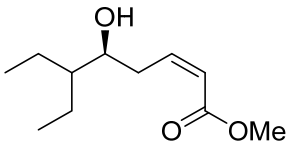


Z-**2b**

Methyl (R,Z)-5-hydroxy-7-methyloct-2-enoate, *Z*-2b

Oil, 35.7 mg, 90% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.35-6.43 (m, 1H), 5.92 (dt, *J* = 11.5, 1.4 Hz, 1H), 3.79-3.87 (m, 1H), 3.71 (s, 3H), 2.73-2.84 (m, 2H), 1.71-1.85 (m, 1H), 1.40-1.51 (m, 1H), 1.22-1.32 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J*= 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.2, 146.6, 121.5, 69.6, 51.2, 46.7, 37.1, 24.7, 23.3, 22.2; **HPLC:** The *ee* value was determined to be 93% by measuring that of the corresponding 5,6-dihydropyran-2-one by chiral HPLC analysis (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 27.040 min and 36.236 min).

Table 1, entry 3



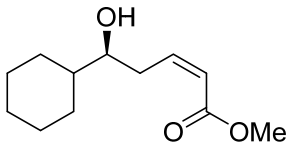
Z-**2c**

Methyl (S,Z)-6-ethyl-5-hydroxyoct-2-enoate, *Z*-2c

Oil, 38.8 mg, 91%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.44 (dt, *J* = 11.5, 7.9 Hz, 1H), 5.96 (ddd, *J* = 11.5, 2.4, 1.4 Hz, 1H), 3.73-3.80 (m, 1H), 3.74 (s, 3H), 2.83-2.94 (m, 1H), 2.68-2.78 (m, 1H), 1.15-1.64 (m, 5H), 0.94 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.5, 147.5, 121.2, 72.8, 51.3, 47.2, 33.7, 21.9, 21.2, 11.7, 11.7; **HPLC:** The *ee* value was determined to be 95% by measuring that of the corresponding 5,6-dihydropyran-2-one by chiral HPLC analysis (Chiralcel

OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 20.792 min and 24.028 min).

Table 1, entry 4

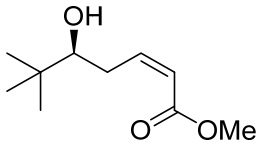


Z-**2d**

Methyl (S,Z)-5-cyclohexyl-5-hydroxypent-2-enoate, *Z*-2d

Oil, 0.2059 g, 97% yield at 1 mmol scale; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.41 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.91 (dt, *J* = 11.5, 1.4 Hz, 1H), 3.71 (s, 3H), 3.45-3.51 (m, 1H), 2.73-2.85 (m, 2H), 1.55-1.99 (m, 5H), 0.91-1.52 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 147.4, 121.1, 75.6, 51.3, 43.9, 33.7, 29.0, 28.1, 26.4, 26.2, 26.1; **HPLC:** The *ee* value was determined to be 96% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 13.524 min and 28.176 min).

Table 1, entry 5

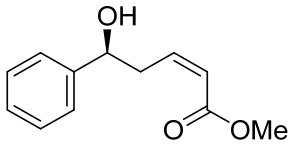


Z-**2e**

Methyl (S,Z)-5-hydroxy-6,6-dimethylhept-2-enoate, *Z*-2e

Oil, 34.9 mg, 88%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.43 (dt, *J* = 11.5, 7.7 Hz, 1H), 5.92 (dt, *J* = 11.5, 1.3 Hz, 1H), 3.70 (s, 3H), 3.31 (dd, *J* = 9.4, 3.8 Hz, 1H), 2.68-2.80 (m, 2H), 0.92 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.7, 148.1, 121.0, 79.3, 51.2, 35.1, 31.5, 25.6; **HPLC:** The *ee* value was determined to be 95% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 9.028 min and 27.060 min).

Table 1, entry 6

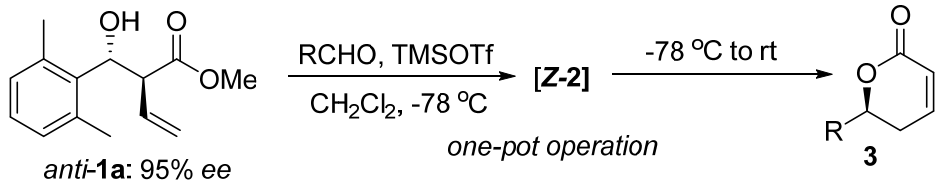


Z-**2f**

Methyl (S,Z)-5-hydroxy-5-phenylpent-2-enoate, *Z*-2f

Oil, 27.7 mg, 63% (along with 26% of the corresponding 5,6-dihydropyran-2-one **3f**); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.49 (m, 5H), 6.36 (dt, *J* = 11.6, 7.8 Hz, 1H), 5.97 (dt, *J* = 11.5, 1.3 Hz, 1H), 4.90 (dd, *J* = 7.6, 5.0, 1H), 3.74 (s, 3H), 3.05-3.17 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 145.7, 143.9, 128.4, 127.6, 125.7, 121.8, 73.4, 51.4, 38.5; **HPLC:** The *ee* value was determined to be >92% by measuring that of the corresponding 5,6-dihydropyran-2-one by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 41.368 min and 48.984 min).

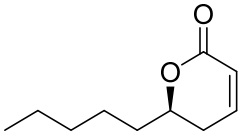
4. Enantioselective One-Pot Synthesis of 5,6-Dihydro-pyran-2-ones via the 2-OCR Reaction of anti-1a (Table 2)



The allyl transfer reagent *anti*-**1a** (95% *ee*; 0.213 mmol) and an aldehyde (2.00 equiv relative to *anti*-**1a**) were dissolved in CH_2Cl_2 (4 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (1.5 equiv relative to *anti*-**1a**) was added at once. The resulting mixture was stirred at -78 °C until *anti*-**1a** disappeared on TLC, and then the temperature was naturally raised to rt for the condition A or -30 °C for the condition B until the intermediate *Z*-**2** disappeared on TLC (total 5 h for the condition A; total 90 min for the condition B). The reaction mixture was quenched with saturated $NaHCO_3$ (1.5 mL). The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product **3**.

Reaction between *anti*-1a and cyclohexanecarboxaldehyde at 1 mmol scale (entry 4): *anti*-**1a** (95% *ee*; 0.2343 g, 1.00 mmol) and cyclohexanecarboxaldehyde (0.2243 g, 1.20 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (0.3334 g, 1.50 mmol) was added dropwise. The resulting mixture was stirred at -78 °C until *anti*-**1a** disappeared on TLC, and then the temperature was naturally raised to rt until the intermediate *Z*-**2d** disappeared on TLC (total 5 h). The reaction mixture was quenched with saturated $NaHCO_3$ (15 mL) -78 °C. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product **3d** (0.1388 g, 77%)

Table 2, entry 1



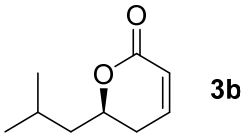
3a

(R)-6-pentyl-5,6-dihydro-2H-pyran-2-one, 3a[1]

Oil, 25.4 mg, 71% yield; $[\alpha]_D^{26}$ = -95.2 (c = 0.88, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.87 (ddd, *J* = 9.9, 5.5, 2.9 Hz, 1H), 6.01 (ddd, *J* = 9.9, 2.43, 1.2 Hz, 1H), 4.37-4.45 (m, 1H), 2.25-2.39 (m, 2H), 1.09-1.95 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.7, 145.2, 121.5, 78.0, 34.8, 31.6, 29.4, 24.5, 22.7, 14.0; **HRMS** (ESI^+): *m/z*: calcd for $C_{10}H_{16}O_2$ $[M + H]^+$: 169.1223, found: 169.1220; **HPLC:** The *ee* value was determined to be 94% by chiral HPLC analysis (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 23.980 min and 25.944 min)

[1]Asaoka, M.; Hayashibe, S.; Sonoda, S.; Takei, H. *Tetrahedron Lett.* **1990**, *31*, 4761-4764: $[\alpha]_D^{19}$ = -96.3 (c = 1.26, $CHCl_3$)

Table 2, entry 2

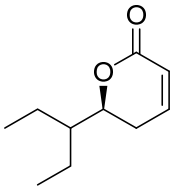


3b

(R)-6-isobutyl-5,6-dihydro-2H-pyran-2-one, 3b

Oil, 24.6 mg, 75% yield; $[\alpha]_D^{26}$ = -92.2 (c = 0.735, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.88 (ddd, *J* = 9.7, 5.8, 2.8 Hz, 1H), 6.02 (ddd, *J* = 9.8, 2.7, 1.0 Hz, 1H), 4.45-4.54 (m, 1H), 2.23-2.40 (m, 2H), 1.85-1.99 (m, 1H), 1.73-1.84 (m, 1H), 1.34-1.46 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.7, 145.2, 121.5, 76.3, 43.9, 30.0, 24.0, 23.1, 22.1; **HRMS** (ESI^+): *m/z*: calcd for $C_9H_{14}O_2$ $[M + H]^+$: 155.1067, found: 155.1069.; **HPLC:** The *ee* value was determined to be 93% by chiral HPLC analysis (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 27.040 min and 36.236 min).

Table 2, entry 3

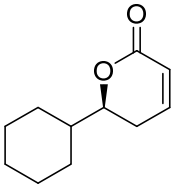


3c

(S)-6-(pentan-3-yl)-5,6-dihydro-2H-pyran-2-one, 3c

Oil, 25.8 mg, 72% yield; $[\alpha]_D^{26}$ = -87.3 (c = 0.74, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (ddd, *J* = 9.7, 6.3, 2.1 Hz, 1H), 6.02 (ddd, *J* = 9.8, 2.8, 0.7 Hz, 1H), 4.44 (dt, *J* = 12.5, 4.1 Hz, 1H), 2.34-2.45 (m, 2H), 2.21-2.31 (m, 1H), 1.15-1.70 (m, 5H), 0.94 (d, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.9, 145.4, 121.3, 79.5, 44.6, 26.3, 21.5, 21.3, 11.4, 11.3; **HRMS** (ESI^+): *m/z*: calcd for $C_{10}H_{16}O_2$ $[M + H]^+$: 169.1223, found: 169.1225; **HPLC:** The *ee* value was determined to be 95% by chiral HPLC analysis (Chiralcel OB-H; 5% isopropyl alcohol in hexane; 0.6 mL/min flow rate; retention times: 20.792 min and 24.028 min).

Table 2, entry 4



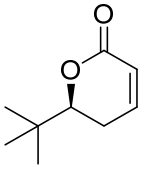
3d

(S)-6-cyclohexyl-5,6-dihydro-2H-pyran-2-one, 3d[2]

Oil, 138.8 mg 77% at 1 mmol scale; $[\alpha]_D^{26}$ = -103.6 (c = 1.00, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.89 (ddd, *J* = 9.8, 6.0, 2.5 Hz, 1H), 6.00 (ddd, *J* = 9.7, 2.5, 1.0 Hz, 1H), 4.18 (ddd, *J* = 11.9, 6.2, 4.3 Hz, 1H), 2.24-2.41 (m, 2H), 1.90-2.01 (m, 1H), 1.57-1.85 (m, 5H), 0.97-1.35 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8, 145.3, 121.2, 81.8, 41.7, 28.22, 28.21, 26.6, 26.2, 25.9, 25.8; **HRMS** (ESI^+): *m/z*: calcd for $C_{11}H_{16}O_2$ $[M + H]^+$: 181.1223, found: 181.1221; **HPLC:** The *ee* value was determined to be 96% by measuring that of the corresponding alcohol **SI-11d** by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 13.524 min and 28.176 min).

[2]Park, Y. S.; Grove, C. I.; Gonzalez-Lopez, M.; Urgaonkar, S.; Fettinger, J. C.; Shaw, J. T. *Angew. Chem. Int. Ed.* **2011**, *50*, 3730-3733: $[\alpha]_D^{22}$ = -71.7 (c = 0.57, EtOH)

Table 2, entry 5



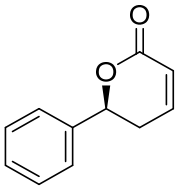
3e

(S)-6-(tert-butyl)-5,6-dihydro-2H-pyran-2-one, 3e[3]

Oil, 22.3 mg, 68%; $[\alpha]_D^{26}$ = -102 (c = 0.595, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (ddd, *J* = 9.7, 6.1, 2.4 Hz, 1H), 6.01 (ddd, *J* = 9.7, 2.7, 0.9 Hz, 1H), 4.07 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.24-2.40 (m, 2H), 1.00 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8, 145.5, 121.0, 85.4, 33.7, 25.3, 24.7; **HRMS** (ESI^+): *m/z*: calcd for $C_9H_{14}O_2$ $[M + H]^+$: 155.1067, found: 155.1070; **HPLC:** The *ee* value was determined to be 95% by measuring that of the corresponding alcohol **SI-11e** by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 9.028 min and 27.060 min).

[3](a) Chen, J.; Forsyth, C. J. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 12067-12072: $[\alpha]_D^{25}$ = -97.8 (c= 2.21, $CHCl_3$). (b) Ma, D.; Zou, B.; Cai, G.; Hu, X.; Liu, J. O. *Chem. Eur. J.* **2006**, *12*, 7615-7626: $[\alpha]_D^{20}$ = -129 (c = 0.51, $CHCl_3$)

Table 2, entry 6



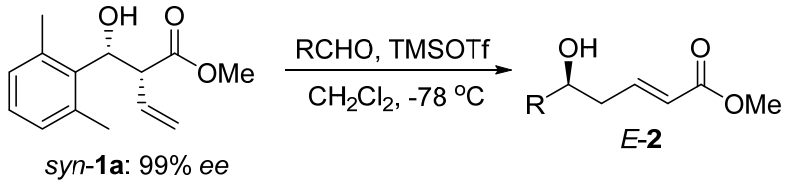
3f

(S)-6-phenyl-5,6-dihydro-2H-pyran-2-one, 3f[4]

Oil, 26.0 mg, 70%; $[\alpha]_D^{26}$ = -210 (c = 0.755, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.46 (m, 5H), 6.97 (ddd, *J* = 9.8, 5.6, 2.8 Hz, 1H), 6.14 (ddd, *J* = 9.8, 2.7, 1.0 Hz, 1H), 5.46 (dd, *J* = 11.1, 4.9 Hz, 1H), 2.57-2.73 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.2, 145.0, 138.5, 128.8, 128.7, 126.2, 121.7, 79.4, 31.6; **HRMS** (ESI^+): *m/z*: calcd for $C_{11}H_{10}O_2$ $[M + H]^+$: 175.0754, found: 175.0755; **HPLC:** The *ee* value was determined to be >92% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 41.368 min and 48.984 min).

[4](a) Devasagayaraj, A.; Schwink, L.; Knochel, P. *J. Org. Chem.* **1995**, *60*, 3311-3317: $[\alpha]_D^{25}$ = -210 (c = 3.50, $CHCl_3$, >96% *ee*). (b) Bazan-Tejeda, B.; Bluet, G.; Broustal, G.; Campagne, J.-M. *Chem. Eur. J.* **2006**, *12*, 8358-8366: $[\alpha]_D^{20}$ = -188 (c = 1.5, $CHCl_3$, 85% *ee*)

5. Enantio- and *E*-selective Vinylogous Aldol Reactions of Aldehydes by *syn*-1a (Table 3)

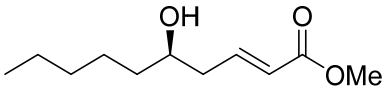


syn-**1a**: 99% *ee*

The allyl transfer reagent *syn*-**1a** (99% *ee*; 0.213 mmol) and an aldehyde (2.00 equiv relative to *syn*-**1a**) were dissolved in CH_2Cl_2 (4 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (1.50 equiv relative to *syn*-**1a**) was added at once. The resulting mixture was stirred at -78 °C for 60 min. The reaction mixture was quenched with saturated $NaHCO_3$ (1.5 mL) -78 °C. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product *E*-**2**.

Reaction between *syn*-1a and cyclohexanecarboxaldehyde at 1 mmol scale (entry 4): *syn*-**1a** (95% *ee*; 0.2343 g, 1.00 mmol) and cyclohexanecarboxaldehyde (0.2243 g, 2.00 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction mixture was cooled down to -78 °C in a dry ice-acetone bath, and then neat TMSOTf (0.3334 g, 1.50 mmol) was added dropwise. The resulting mixture was stirred at -78 °C for 60 min. The reaction mixture was quenched with saturated $NaHCO_3$ (15 mL) -78 °C. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give the desired product *E*-**2d** (0.2059 g, 97%)

Table 3, entry 1



E-**2a**

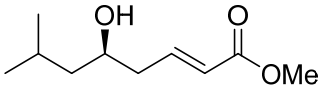
Methyl (R,E)-5-hydroxydec-2-enoate, *E*-2a[5]

Oil, 38.4 mg, 90%; $[\alpha]_D^{26}$ = -11.3 (c = 0.885, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.98 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.89 (dt, *J* = 15.7, 1.3 Hz, 1H), 3.68-78 (m, 1H), 3.72 (s, 3H), 2.27-2.43 (m, 2H), 1.13-1.58 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 145.8, 123.3, 70.4, 51.6, 40.1, 37.1, 31.5, 25.1, 22.6, 14.9; **HRMS** (ESI^+): *m/z*: calcd for $C_{11}H_{20}O_3$ [M +

H]$^+$: 201.1485, found: 201.1483; **HPLC:** The *ee* value was determined to be >99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 16.688 min and 19.048 min).

[5](a) Fu, K.; Zheng, J.; Lin, L.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 3106-3108: $[\alpha]_D^{25.1}$ = -6.25 (c = 0.40, $CHCl_3$). (b) Mineeva, I. V. *Russian J. Org. Chem.* **2013**, *49*, 979-985: $[\alpha]_D$ = -5.4 (c = 2.3, $CHCl_3$)

Table 3, entry 2

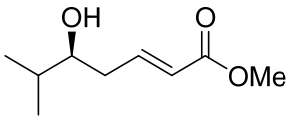


E-**2b**

Methyl (R,E)-5-hydroxy-7-methyloct-2-enoate, *E*-2b

Oil, 35.7 mg, 90%; $[\alpha]_D^{26}$ = -3.9 (c = 0.76, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (dt, *J* = 15.7, 7.5 Hz, 1H), 5.90 (dt, *J* = 11.5, 1.4 Hz, 1H), 3.79-3.87 (m, 1H), 3.72 (s, 3H), 2.27-2.42 (m, 2H), 1.71-1.81 (m, 1H), 1.36-1.47 (m, 1H), 1.19-1.30 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 145.5, 123.5, 68.6, 51.2, 46.2, 40.6, 24.4, 23.3, 21.9; **HRMS** (ESI$^+$): *m/z*: calcd for $C_{10}H_{18}O_3$ [M + H]$^+$: 187.1329, found: 187.1328; **HPLC:** The *ee* value was determined to be >99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 14.540 min and 16.684 min).

Table 3, entry 3



E-**2c**

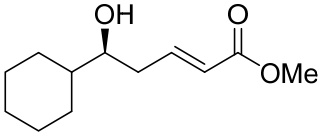
Methyl (S,E)-5-hydroxy-6-methylhept-2-enoate, *E*-2c[6]

Oil, 31.3 mg, 85%; $[\alpha]_D^{26}$ = -28.7 (c = 0.78, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.01 (dt, *J* = 15.7, 7.3 Hz, 1H), 5.91 (dt, *J* = 15.7, 1.4 Hz, 1H), 3.71 (s, 3H), 3.51 (ddd, *J* = 8.5, 5.5, 3.9 Hz, 1H), 2.26-2.44 (m, 2H), 1.63-1.74 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 146.2, 123.0, 75.3, 51.5, 37.1, 33.4, 18.6, 17.2; **HRMS** (ESI$^+$): *m/z*: calcd for $C_9H_{16}O_3$ [M + H]$^+$: 173.1172, found: 173.1171; **HPLC:** The *ee* value was

determined to be >99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 15.520 min and 24.840 min).

[6](a) Fu, K.; Zheng, J.; Lin, L.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 3106-3108: $[\alpha]_D^{29.1}$ = -13.89 (c = 0.18, $CHCl_3$). (b) Simsek, S.; Horzella, M.; Kalesse, M. *Org. Lett.* **2007**, *9*, 5637-5639: $[\alpha]_D^{20}$ = 17.7 (c = 1.3, $CHCl_3$) for *ent-E-***2c**.

Table 4, entry 4



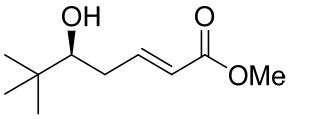
*E-***2d**

Methyl (S,E)-5-cyclohexyl-5-hydroxypent-2-enoate, *E*-2d[7]

Oil, 205.9 mg, 97% at 1 mmol scale; $[\alpha]_D^{26}$ = -18.2 (c = 1.05, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.01 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.91 (dt, *J* = 15.7, 1.4 Hz, 1H), 3.72 (s, 3H), 3.46-3.53 (m, 1H), 2.21-2.53 (m, 2H), 1.58-1.87 (m, 5H), 0.95-1.41 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 146.2, 123.0, 74.8, 51.4, 43.3, 37.1, 29.1, 27.8, 26.4, 26.1, 26.0; **HRMS** (ESI^+): *m/z*: calcd for $C_{12}H_{20}O_3$ $[M + H]^+$: 213.1485, found: 213.1482; **HPLC:** The *ee* value was determined to be >99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 16.256 min and 18.316 min).

[7]Simsek, S.; Horzella, M.; Kalesse, M. *Org. Lett.* **2007**, *9*, 5637-5639: $[\alpha]_D^{20}$ = 43.3 (c = 1.0, $CHCl_3$) for *ent-E-***2d**.

Table 3, entry 5



*E-***2e**

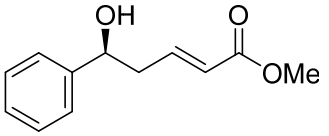
Methyl (S,E)-5-hydroxy-6,6-dimethylhept-2-enoate, *E*-2e[8]

Oil, 32.9 mg, 83%; $[\alpha]_D^{26}$ = -43.9 (c = 0.825, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (ddd, *J* = 15.7, 7.7, 6.7 Hz, 1H), 5.91 (dt, *J* = 15.7, 1.3 Hz, 1H), 3.72 (s, 3H), 3.35 (dd, *J* = 10.4, 2.2 Hz, 1H), 2.39-2.47 (m, 1H), 2.13-2.23 (m, 1H), 0.92 (s, 9H); **HRMS** (ESI^+): *m/z*: calcd for

$C_{10}H_{18}O_3$ $[M + H]^+$: 187.1329, found: 187.1326; **HPLC:** The *ee* value was determined to be >99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 12.280 min and 19.620 min).

[8](a) Fu, K.; Zheng, J.; Lin, L.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 3106-3108: $[\alpha]_D^{23.9}$ = -10.00 (c = 0.08, $CHCl_3$). (b) Simsek, S.; Horzella, M.; Kalesse, M. *Org. Lett.* **2007**, *9*, 5637-5639: $[\alpha]_D^{20}$ = 34.3 (c = 1.1, $CHCl_3$) for *ent-E*-**2e**.

Table 3, entry 6



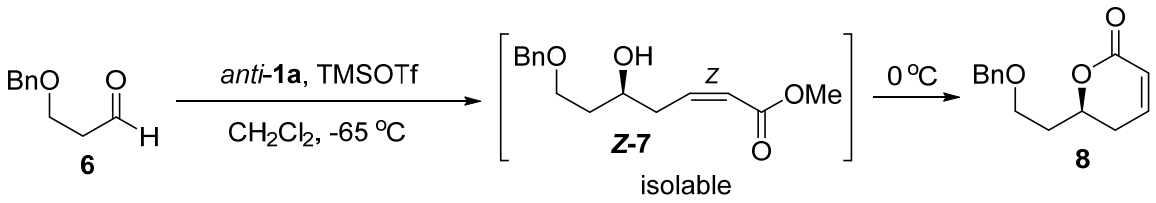
E-**2f**

Methyl (S,E)-5-hydroxy-5-phenylpent-2-enoate, *E*-2f[9]

Oil, 36.5 mg, 83%; $[\alpha]_D^{26}$ = -44.9 (c = 0.69, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.40 (m, 5H), 6.97 (dt, *J* = 15.7, 7.2 Hz, 1H), 5.90 (dt, *J* = 11.5, 1.3 Hz, 1H), 4.81 (dd, *J* = 7.7, 5.2, 1H), 3.71 (s, 3H), 3.57-3.71 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 145.0, 143.4, 128.6, 127.9, 125.7, 123.5, 72.9, 51.4, 41.9; **HRMS** (ESI^+): *m/z*: calcd for $C_{12}H_{14}O_3$ $[M + Na]^+$: 229.0835, found: 229.0834; **HPLC:** The *ee* value was determined to be 99% by chiral HPLC analysis (Chiralcel OD-H; 2% isopropyl alcohol in hexane; 1.0 mL/min flow rate; retention times: 53.388 min and 62.260 min).

[9](a) Fu, K.; Zheng, J.; Lin, L.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 3106-3108: $[\alpha]_D^{21.6}$ = -41.32 (c = 0.48, $CHCl_3$). (b) Simsek, S.; Horzella, M.; Kalesse, M. *Org. Lett.* **2007**, *9*, 5637-5639: $[\alpha]_D^{20}$ = 28.2 (c = 1.2, $CHCl_3$) for *ent-E*-**2e** (82% *ee*)

6. Synthetic Applications [Scheme 4(a)]

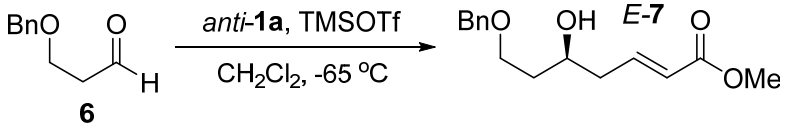


To a solution of **6** (0.0532 g, 0.324 mmol) and *anti*-**1a** (0.0380 g, 0.162 mmol) in CH_2Cl_2 (4 mL) at -65 °C was added neat TMSOTf (44 μL, 0.243 mmol) at once.

(a) For ***Z*-7**: After stirring for 120 min at -65 °C, the reaction mixture was quenched with saturated $NaHCO_3$. Ethyl ether was added up to ~total 14 ml. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over $MgSO_4$. After concentrating to ~100 μL below 30 °C, the residue was purified by column chromatography (ethyl acetate/hexane 2/3) to give ***Z*-7** (0.0305 g, 71%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.37 (m, 5H), 6.41 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.90 (dt, *J* = 11.5, 1.6 Hz, 1H), 4.52 (s, 2H), 3.978 (m, 1H), 3.63-3.77 (m, 2H), 3.70 (s, 3H), 3.20 (br s, 1H), 2.86 (m, 2H), 1.81 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 146.6, 137.9, 128.4, 127.7, 127.7, 121.0, 73.3, 70.7, 68.9, 51.1, 36.6, 36.3.

(b) For **8**: After complete disappearance of *anti*-**1a** on TLC, the temperature was naturally raised to -0 °C over 90 min. The reaction mixture was quenched with saturated $NaHCO_3$. Ethyl ether was added up to ~total 14 mL. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 2/3) to give **8** (0.0318 g, 85%) as an oil. The *ee* of **8** was determined to be >99% by chiral HPLC analysis [Chiralcel OB-H; 5% isopropyl alcohol in hexane; 1.5 mL/min flow rate; retention times: 100.152 min and 114.376 min (major)]. The analytical data of **8** (optical rotation and ^{1}H and ^{13}C-NMR) were consistent with those of the literature:[10] **$[\alpha]_D^{26}$** = -33.1 (c = 1.50, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21-7.42 (m, 5H), 6.87 (dt, *J* = 9.8, 4.2 Hz, 1H), 6.02 (dt, *J* = 9.9, 1.7 Hz, 1H), 4.64 (m, 1H), 4.53 (d, *J* = 11.8, 1H), 4.48 (d, *J* = 11.8, 1H), 3.60-3.74 (m, 2H), 2.37 (m, 2H), 1.90-2.13 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.3, 145.1, 138.1, 128.4, 127.69, 127,67, 121.4, 75.3, 73.2, 65.6, 35.1, 29.5.

[10]Shinde, D. B.; Kanth, B. S.; Satyakumar, A.; Kamble, V. T.; Das, B. *Lett. in Org. Chem.* **2013**, *10*, 317-323: $[\alpha]_D^{32}$ = -32.6 (c = 1.0, CHCl3); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.38-7.20 (5H, m), 6.83 (1H, m), 5.99 (1H, d, *J* = 9.0 Hz), 4.51 (1H, d, *J* = 12.0 Hz), 4.43 (1H, d, *J* = 12.0 Hz), 3.72-3.55 (2H, m), 2.60-2.27 (2H, m), 2.10-1.83 (2H, m); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ163.6, 144.3, 128.2, 127.5, 123.9, 121.8, 74.9, 72.8, 65.3, 35.2, 29.8.

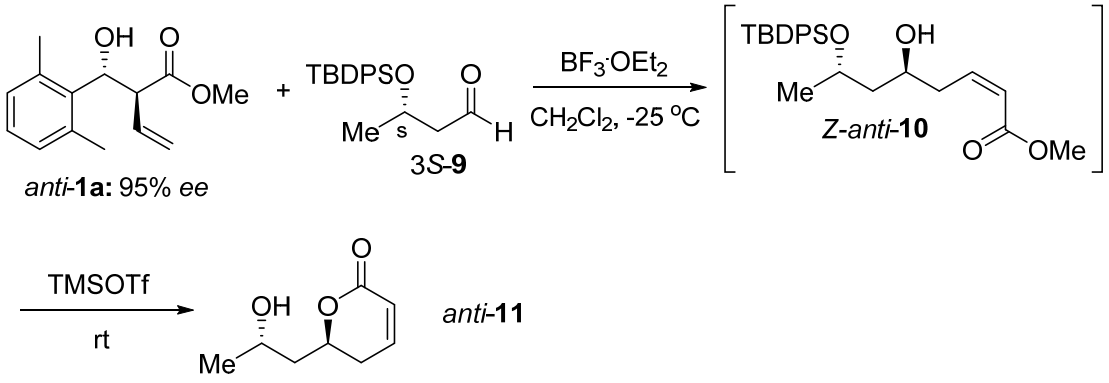


To a solution of *anti*-**1a** (0.0564 g, 0.241 mmol) and **6**[11] (0.0791 g, 0.482 mmol) in CH_2Cl_2 (4 mL) at -65 °C was added neat TMSOTf (65 μL, 0.362 mmol) at once. After stirring for 30 min at -65 °C, the reaction mixture was quenched with saturated $NaHCO_3$. Ethyl ether was added up to ~total 14 mL. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over $MgSO_4$. After concentrating to ~100 μL below 30 °C, the residue was purified by column chromatography (ethyl acetate/hexane 2/3) to give *E*-**7** (0.0542 g, 85%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (m, 5H), 6.99 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.89 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.51 (s, 2H), 3.97 (m, 1H), 3.71 (m, 1H), 3.71 (s, 3H), 3.64 (m, 1H), 2.37 (m, 2H), 1.76 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 145.5, 137.7, 128.5, 127.8, 127.7, 123.2, 73.4, 70.1, 68.8, 51.4, 40.1, 36.0. The *ee* of *E*-**7** was determined to be 98% by chiral HPLC analysis [Chiralcel OB-H; 5% isopropyl alcohol in hexane; 1.5 mL/min flow rate; retention times: 42.140 min and 62.288 min (major)]. The analytical data of *E*-**7** (^{1}H and ^{13}C-NMR) were consistent with those of *ent*-*E*-**7** in the literature.[12]

[11]Ren, H.; Wulff, W. D. *Org. Lett.* **2013**, *15*, 242-245.

[12]Sawant, P.; Maier, M. E. *Eur. J. Org. Chem.* **2012**, 6576-6585: **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.68–1.83 (m, 2 H, 6-H), 2.30–2.44 (m, 2 H, 4-H), 3.64 (ddd, *J* = 9.3, 7.6, 5.0 Hz, 1 H, 7-H), 3.68–3.74 (m, 1 H, 7-H), 3.71 (s, 3 H, OCH3), 3.92–4.01 (m, 1 H, 5-H), 4.51 (s, 2 H, CH_2Ph), 5.88 (ddd, *J* = 15.7, 1.5, 1.3 Hz, 1 H, 2-H), 6.98 (ddd, *J* = 15.7, 7.6, 7.3 Hz, 1 H, 3-H), 7.25–7.37 (m, 5 H, Ar-H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 35.9 (C-6), 40.5 (C-4), 51.4 (OCH_3), 68.9 (C-7), 70.2 (C-5), 73.4 (CH_2Ph), 123.2 (C-2), 127.7 (2CH, phenyl), 127.8 (CH, phenyl), 128.5 (2CH, phenyl), 137.7 (C, phenyl), 145.5 (C-3), 166.7 (C-1).

7. Synthetic Applications [Scheme 4(b)]



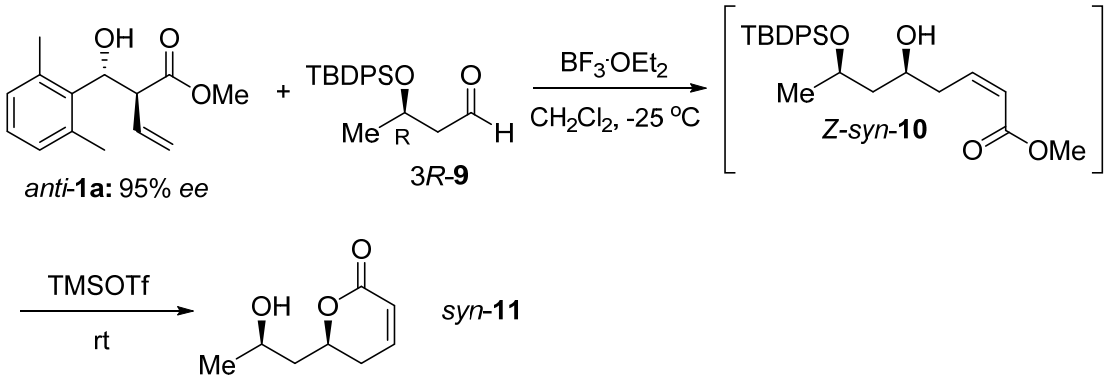
To a solution of *anti*-**1a** (0.0385 g, 0.164 mmol) and 3*S*-**9**[11] (0.1054 g, 0.329 mmol) in CH_2Cl_2 (4 mL) at -25 °C was added neat $BF_3{\cdot}OEt_2$ (61 μL, 0.492 mmol) at once.

(a) For *Z*-*anti*-**10**: After stirring for 60 min at between -25 °C and -20 °C, the reaction mixture was quenched with saturated $NaHCO_3$. Ethyl ether was added up to ~total 14 mL. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over $MgSO_4$. After concentrating to ~100 μL below 30 °C, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give *Z*-*anti*-**10** (0.0646 g, 92%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.43 (m, 6H), 6.40 (dt, *J* = 11.6, 7.4 Hz, 1H), 5.89 (d, *J* = 11.6 Hz, 1H), 4.18 (m, 2H), 3.71 (s, 3H), 2.81 (m, 2H), 1.76 (ddd, *J* = 14.4, 9.9, 3.9 Hz, 1H), 1.52 (ddd, *J* = 14.4, 5.2, 2.1, 1H), 1.12 (d, *J* = 6.3, 3H), 1.07 (s, 9H).

(b) For *anti*-**11**: After complete disappearance of *anti*-**1a** on TLC, TMSOTf (1.5 equiv to *anti*-**1a**) was added to the reaction mixture. The temperature was naturally raised to rt over five hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/1) to give *anti*-**11** (0.0195 g, 75%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.90 (m, 1H), 6.03 (m, 1H), 4.74 (m, 1H), 4.21 (m, 1H), 2.37 (m, 2H), 1.91 (m, 1H), 1.84 (br s, 1H), 1.67 (m, 1H), 1.25 (d, *J* = 6.2, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 145.3, 121.3,

75.1, 63.5, 43.9, 29.9, 24.2. The analytical data of *anti*-**11** (^{1}H and ^{13}C-NMR) were consistent with those of *ent-anti*-**11** in the literature.[13]

[13]Huang, S.; Liu, D.; Tang, L.; Huang, F.; Yang, W.; Wang, X. *Synlett* **2015**, *26*, 2019-2023: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92-6.87 (m, 1H), 6.01 (d, *J* = 9.6 Hz, 1H), 4.73-4.69 (m, 1H), 4.21-4.18 (m, 1H), 2.37-2.34 (m, 2H), 2.12 (brs, 1H), 1.92-1.82 (m, 1H), 1.69-1.62 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5, 145.5, 121.2, 75.0, 63.3, 43.8, 29.8, 24.1.



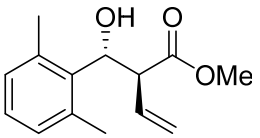
To a solution of *anti*-**1a** (0.0364 g, 0.155 mmol) and 3*R*-**9** (0.1054 g, 0.329 mmol) in CH_2Cl_2 (4 mL) at -25 °C was added neat $BF_3{\cdot}OEt_2$ (61 μL, 0.492 mmol) at once.

(a) For *Z-syn*-**10**: After stirring for 60 min at between -25 °C and -20 °C, the reaction mixture was quenched with saturated $NaHCO_3$. Ethyl ether was added up to ~total 14 mL. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over $MgSO_4$. After concentrating to ~100 μL below 30 °C, the residue was purified by column chromatography (ethyl acetate/hexane 1/4) to give *Z-syn*-**10** (0.0653 g, 99%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (m, 4H), 7.42 (m, 6H), 6.38 (dt, *J* = 11.6, 7.5 Hz, 1H), 5.90 (d, *J* = 11.6 Hz, 1H), 4.14 (m, 1H), 3.98 (m, 1H), 3.71 (s, 3H), 2.80 (m, 2H), 1.77 (m, 1H), 1.59 (m, 1H), 1.05 (s, 9H), 1.01 (d, *J* = 6.2, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 146.5, 135.8, 135.8, 134.3, 133.5, 129.8, 129.6, 127.7, 127.5, 121.0, 70.3, 70.1, 51.1, 46.1, 36.8, 26.9, 24.0, 19.1.

(b) For *syn*-**11**: After complete disappearance of *anti*-**1a** on TLC, TMSOTf (1.5 equiv to *anti*-**1a**) was added to the reaction mixture. The temperature was naturally raised to rt over six hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$. After evaporating all solvents, the residue was purified by column chromatography (ethyl acetate/hexane 1/1) to give *syn*-**11** (0.0187 g, 76%) as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (m, 1H), 6.04 (m, 1H), 4.65 (m, 1H), 4.11 (m, 1H), 2.41 (m, 2H), 2.02 (m, 1H), 1.72 (br s, 1H), 1.77 (m, 1H), 1.28 (d, *J* = 6.2, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.9, 145.1, 121.3, 76.9, 63.4, 43.6, 29.5, 23.8. The ^{1}H NMR data of *syn*-**11** were consistent with those of *syn*-**11** in the literature.[14]

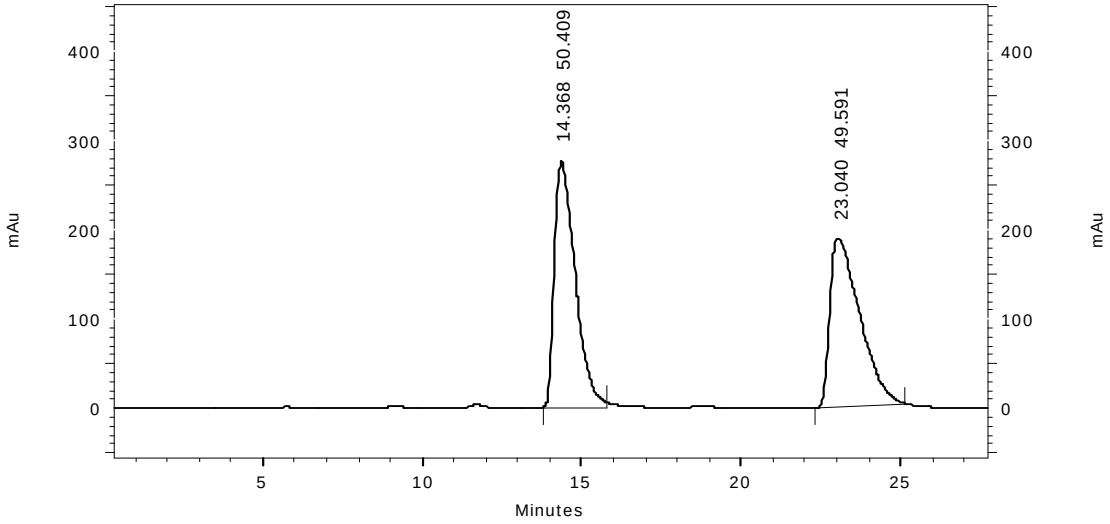
[14]Lee, H.-Y.; Sampath, Y.; Yoon, Y. *Synlett* **2009**, 249-252: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89–6.84 (ddd, *J* = 13.9, 6.7, 4.6 Hz, 1 H), 6.01–5.97 (dt, *J* = 9.7, 1.7 Hz, 1 H), 4.65–4.58 (m, 1 H), 4.08–4.03 (m, 2 H), 2.40–2.36.

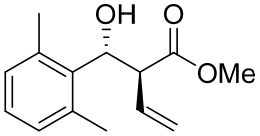
8. HPLC Chromatograms



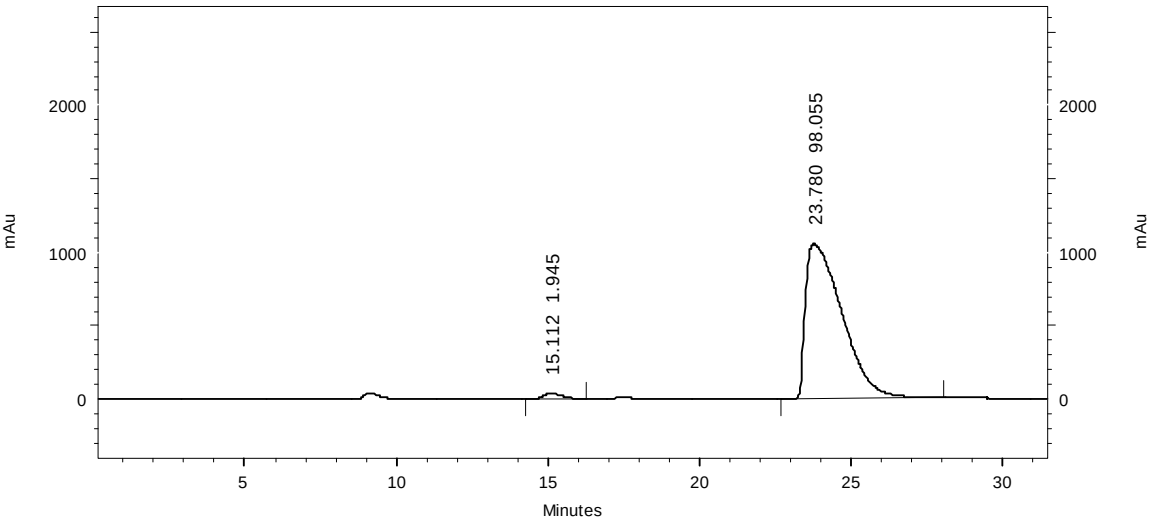
(±)-*anti*-**1a**

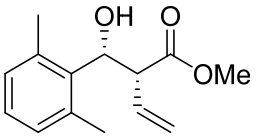
OD-H; 5% IP in Hexane; 0.6 mL/min





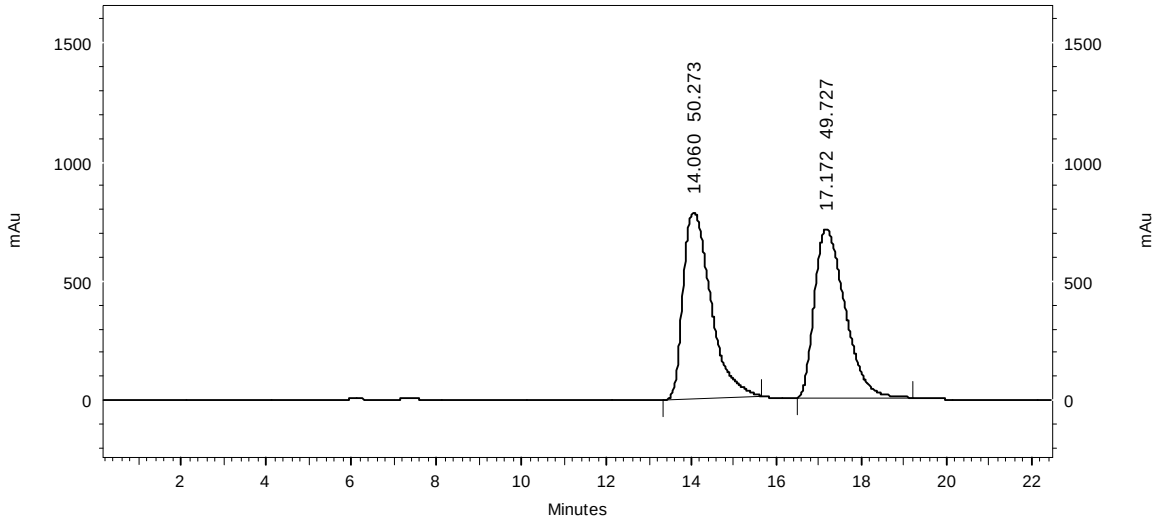
anti-**1a**

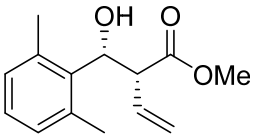




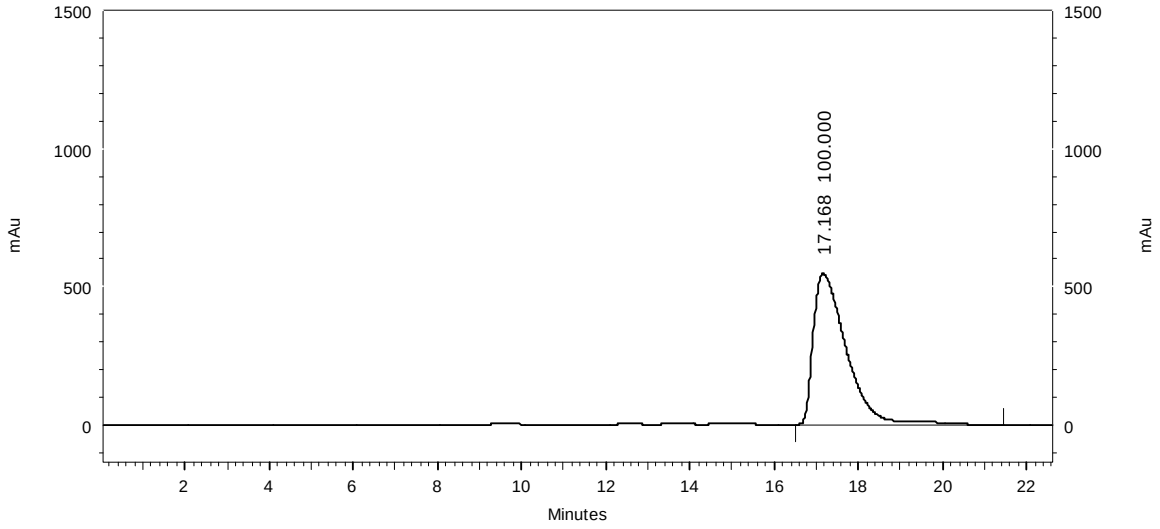
(±)-*syn*-**1a**

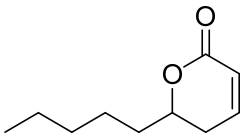
OD-H; 5% IP in Hexane; 0.6 mL/min





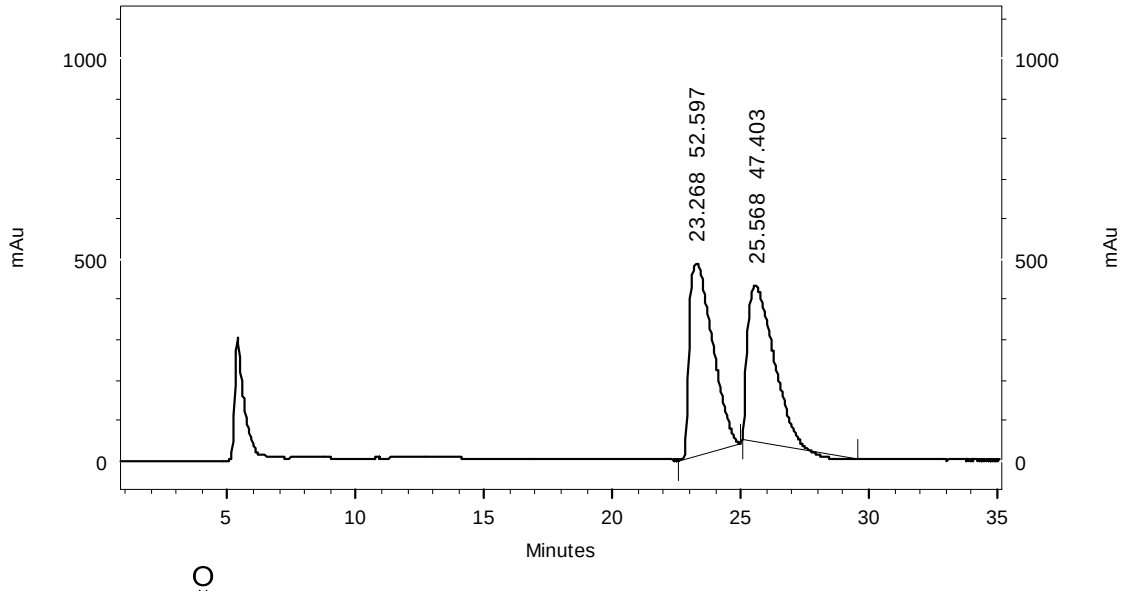
syn-**1a**

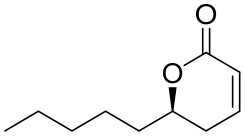




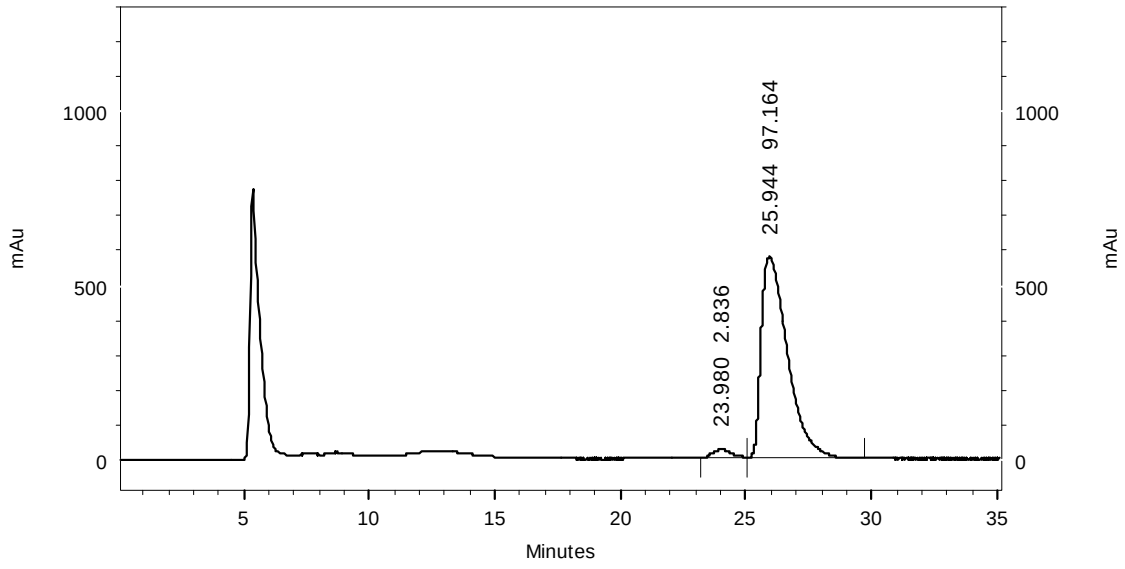
(±)-**3a**

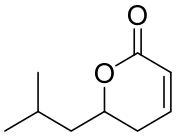
OB-H; 5% IP in Hexane; 0.6 mL/min





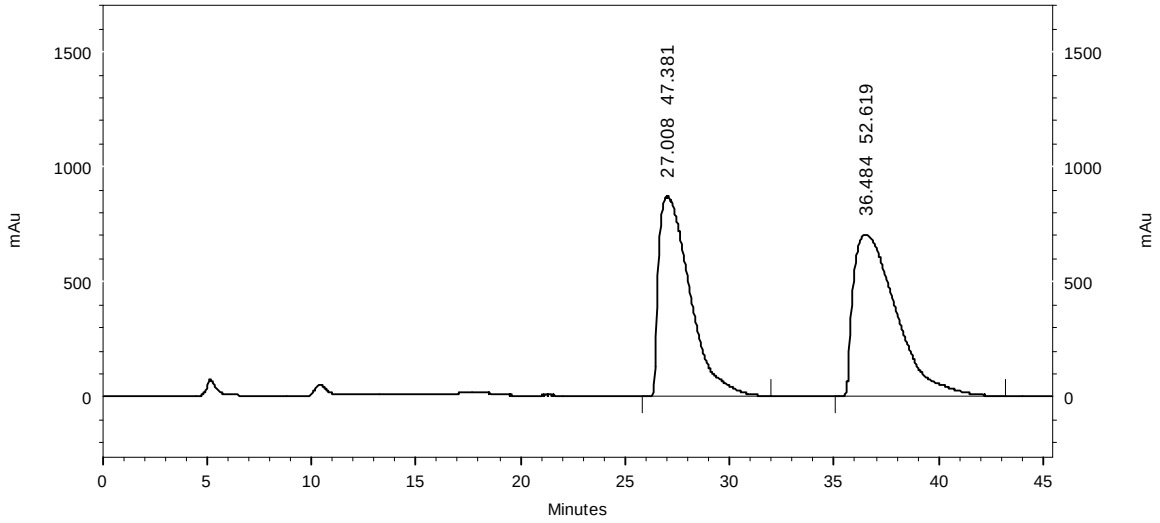
3a

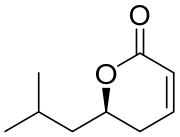




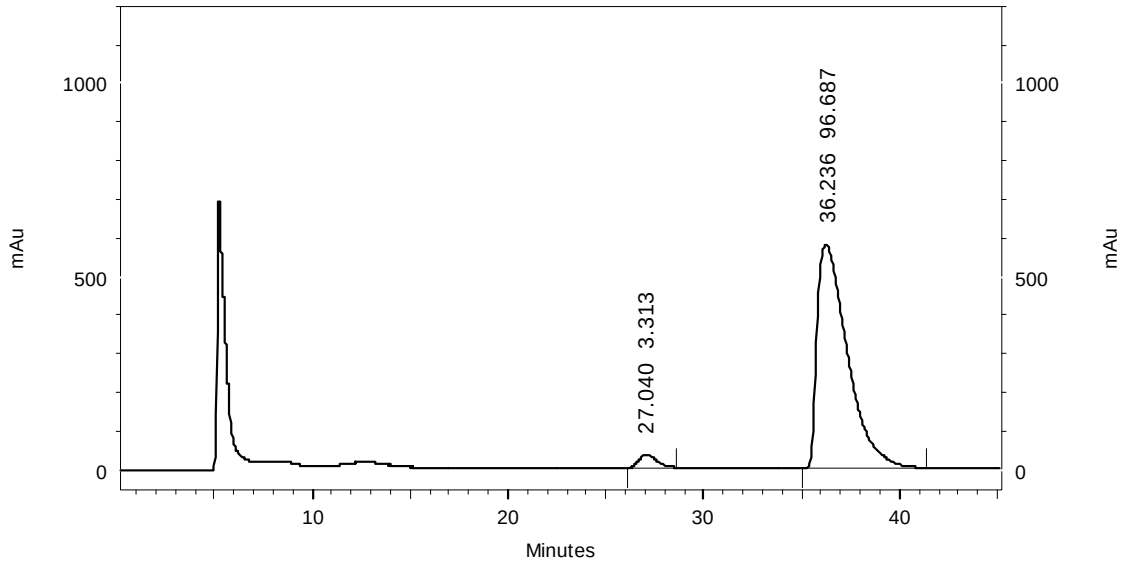
(±)-**3b**

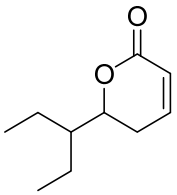
OB-H; 5% IP in Hexane; 0.6 mL/min





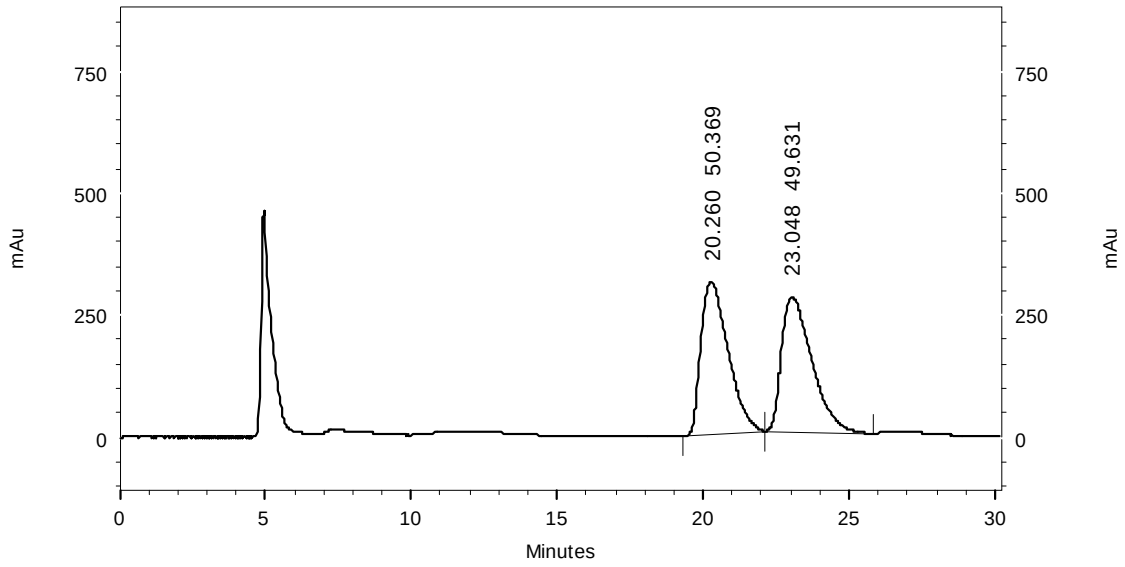
3b

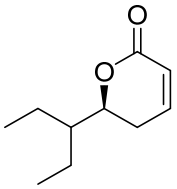




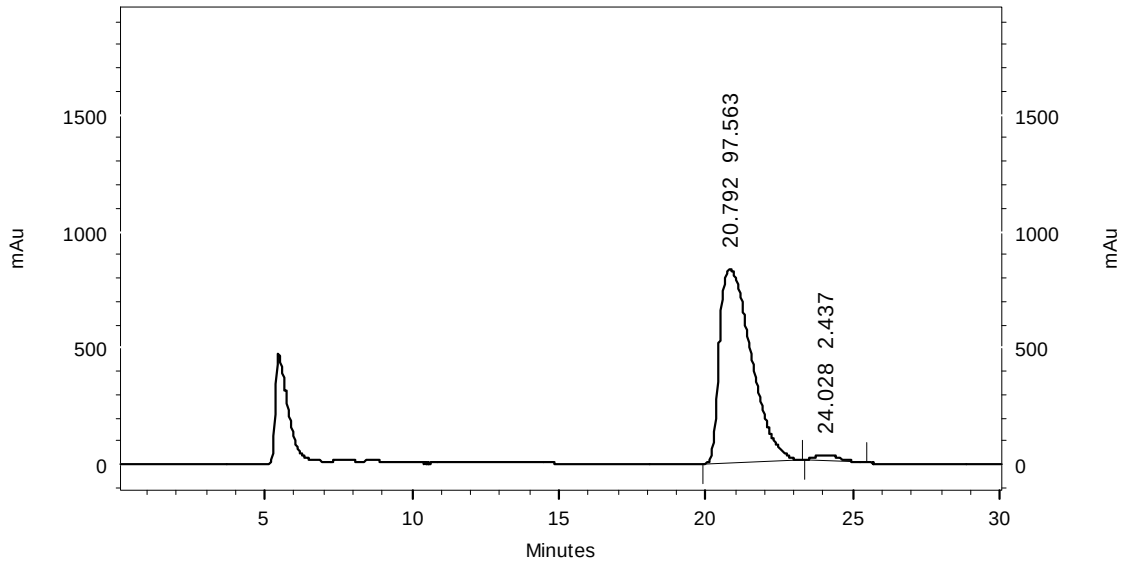
(±)-**3c**

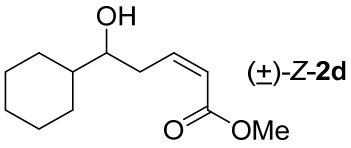
OB-H; 5% IP in Hexane; 0.6 mL/min





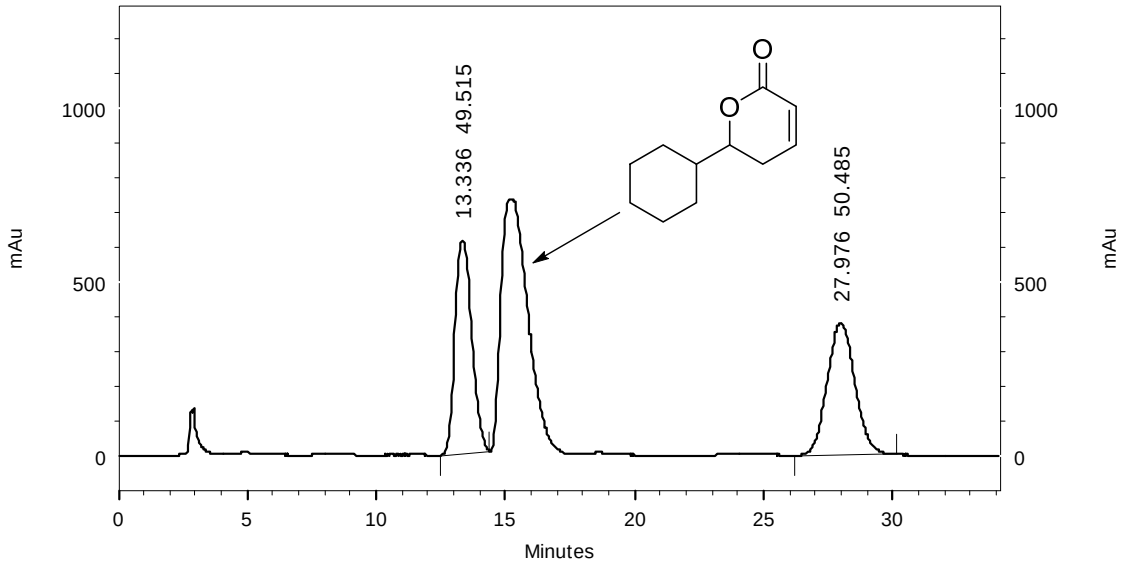
3c

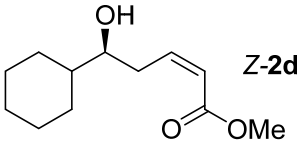




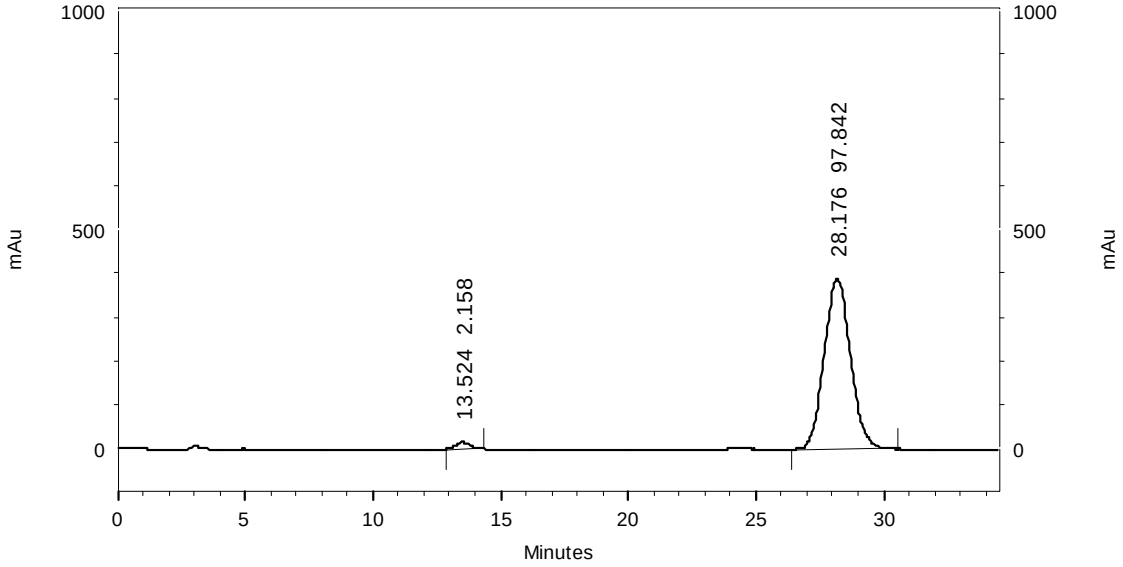
(±)-*Z*-**2d**

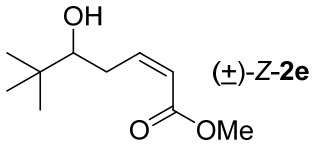
OD-H; 2% IP in Hexane; 1.0 mL/min





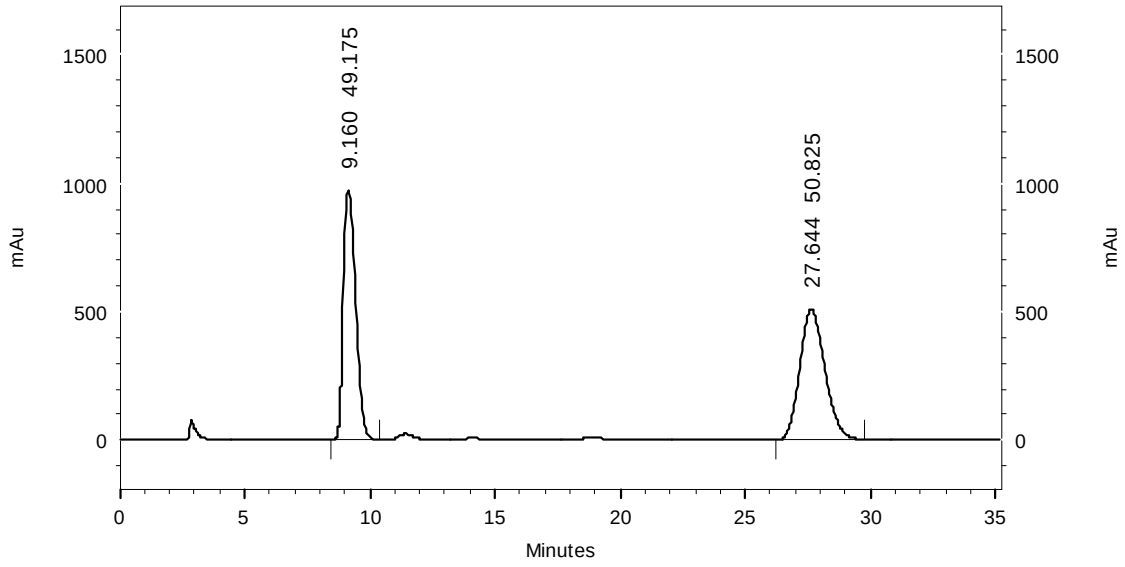
Z-**2d**

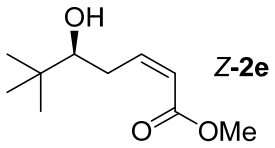




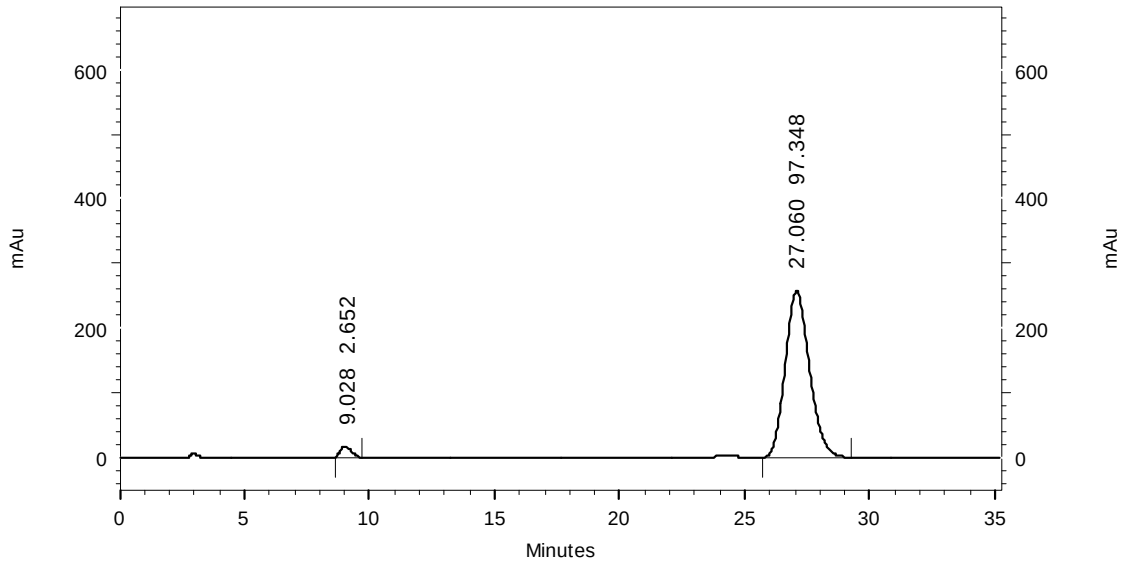
(±)-*Z*-**2e**

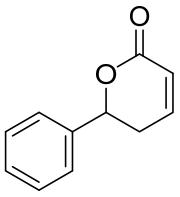
OD-H; 2% IP in Hexane; 1.0 mL/min





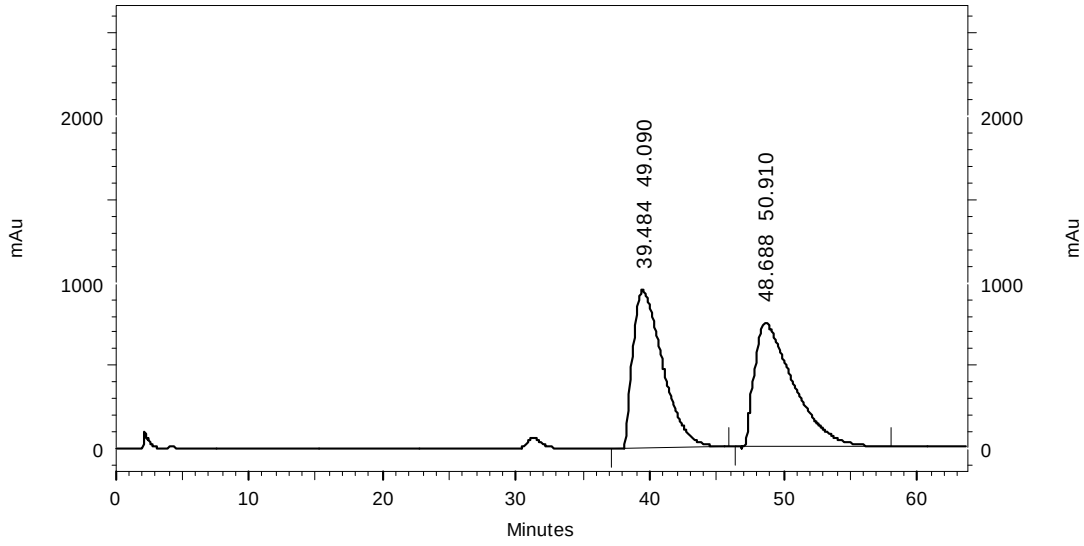
Z-**2e**

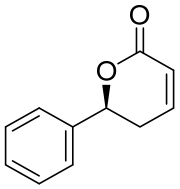




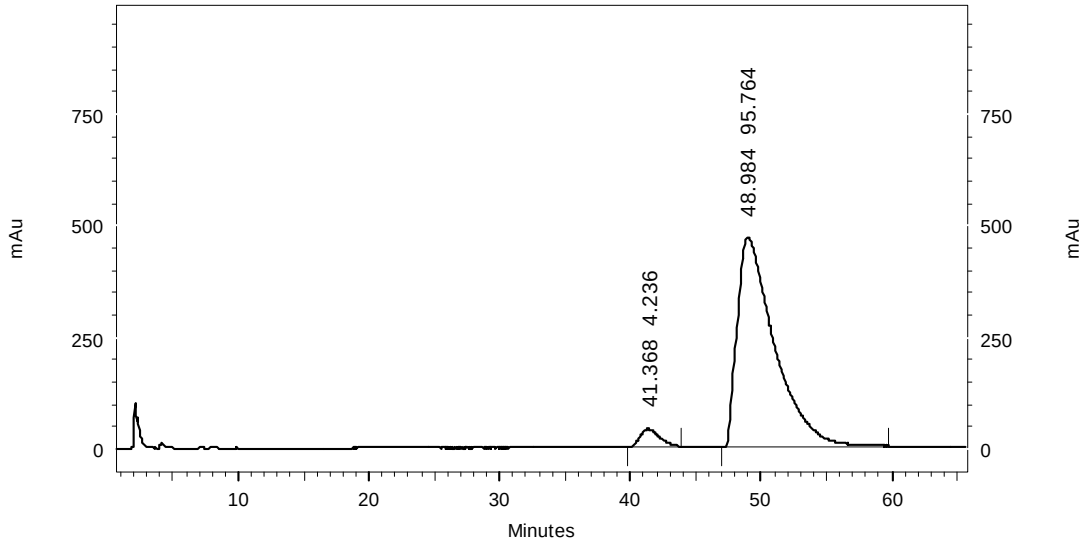
(±)-**3f**

OD-H; 2% IP in Hexane; 1.0 mL/min

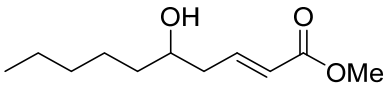




3f

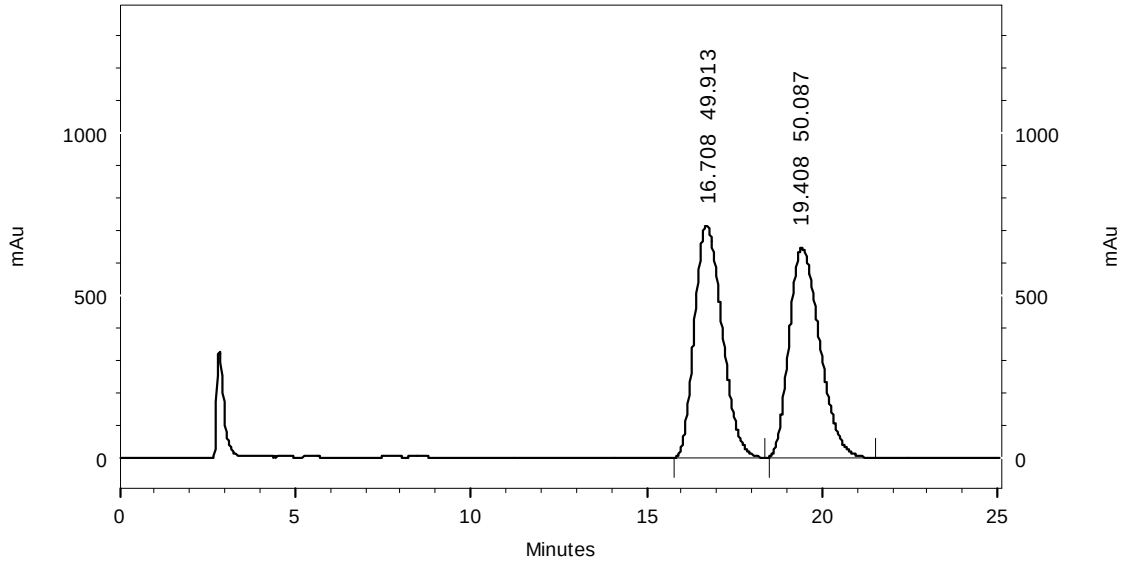


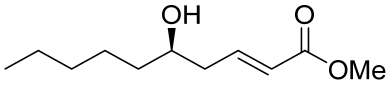
The enantioselectivity of 92% was obtained assuming the peak at 41.368 min for the minor product. Otherwise, the *ee* can be >92%.



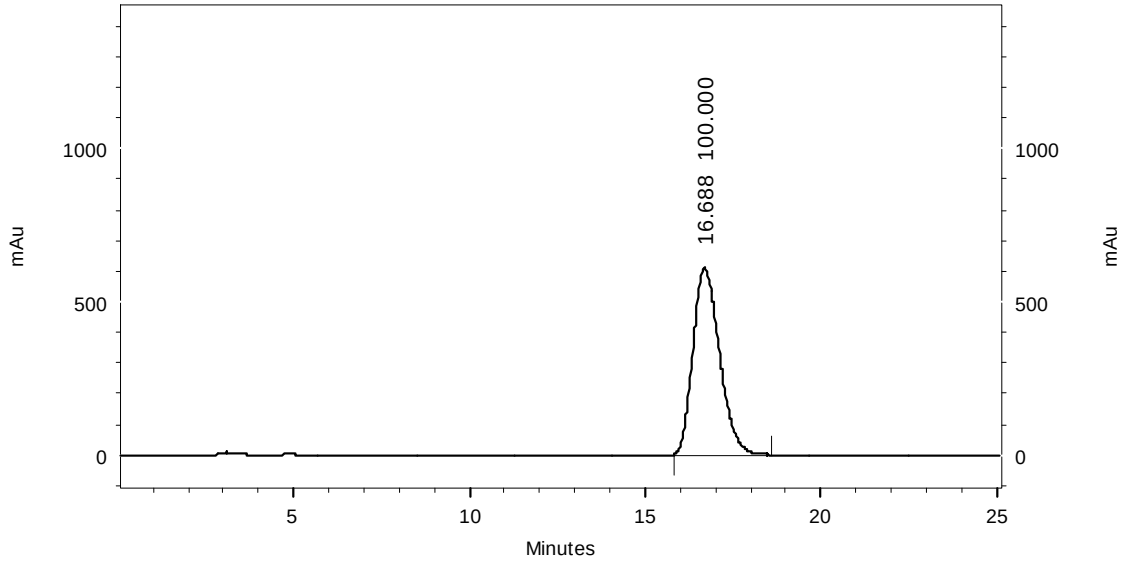
(±)-*E*-**2a**

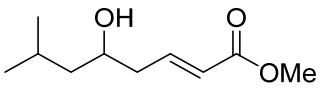
OD-H; 2% IP in Hexane; 1.0 mL/min





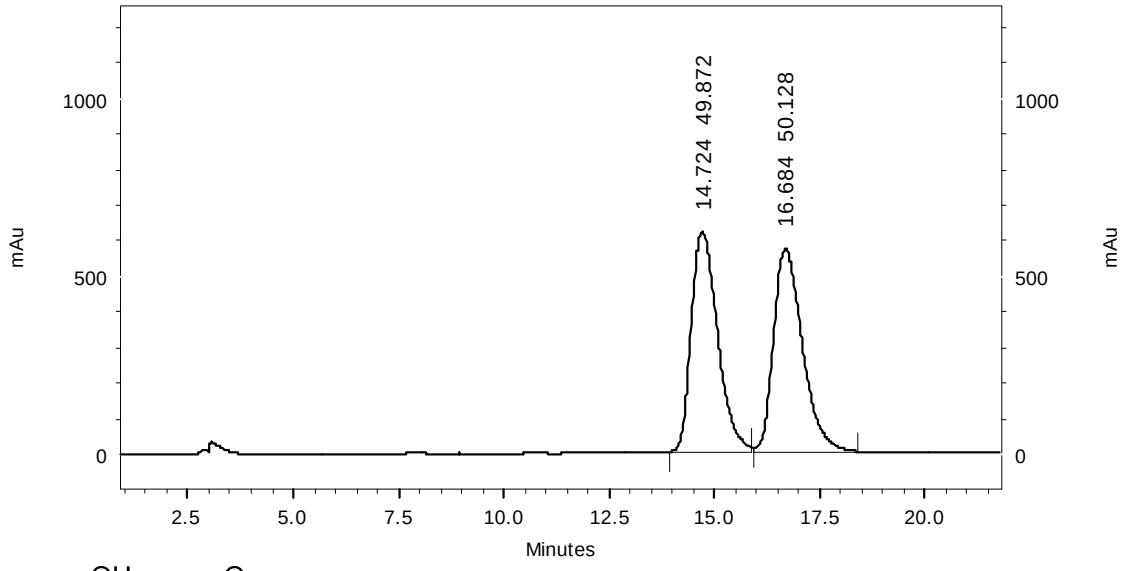
E-**2a**

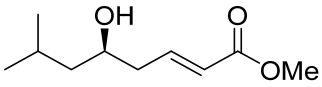




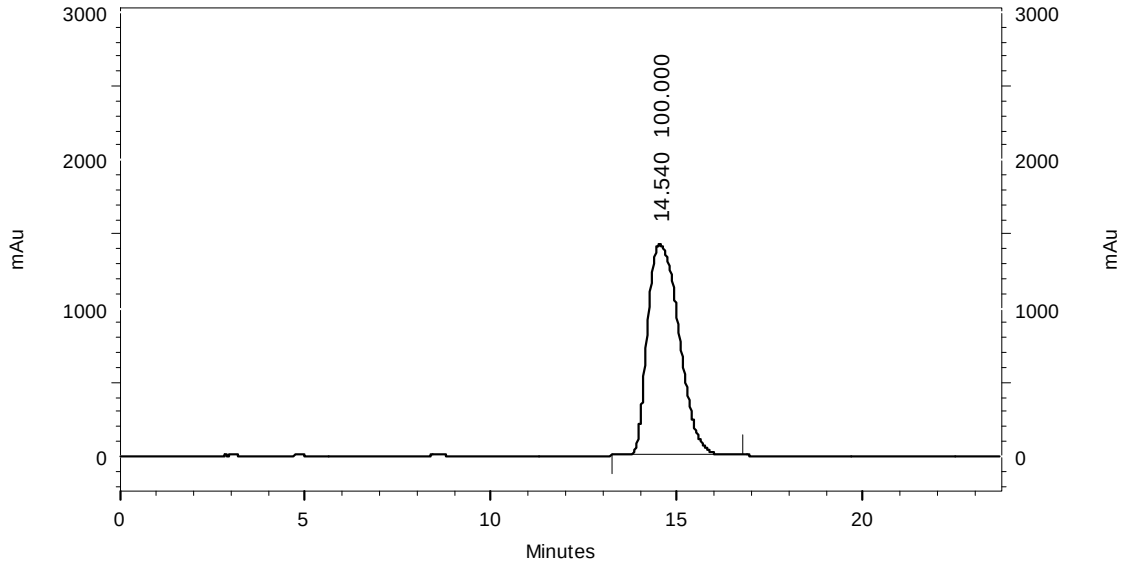
(±)-*E*-**2b**

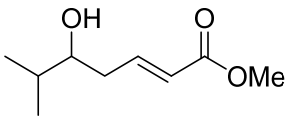
OD-H; 2% IP in Hexane; 1.0 mL/min





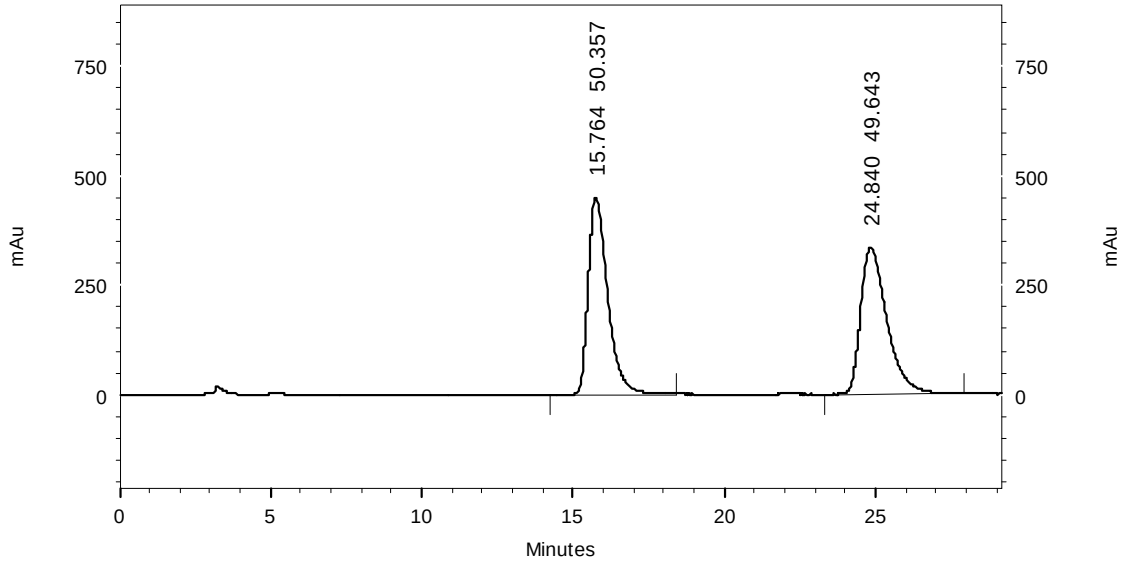
E-**2b**

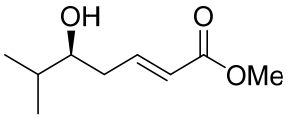




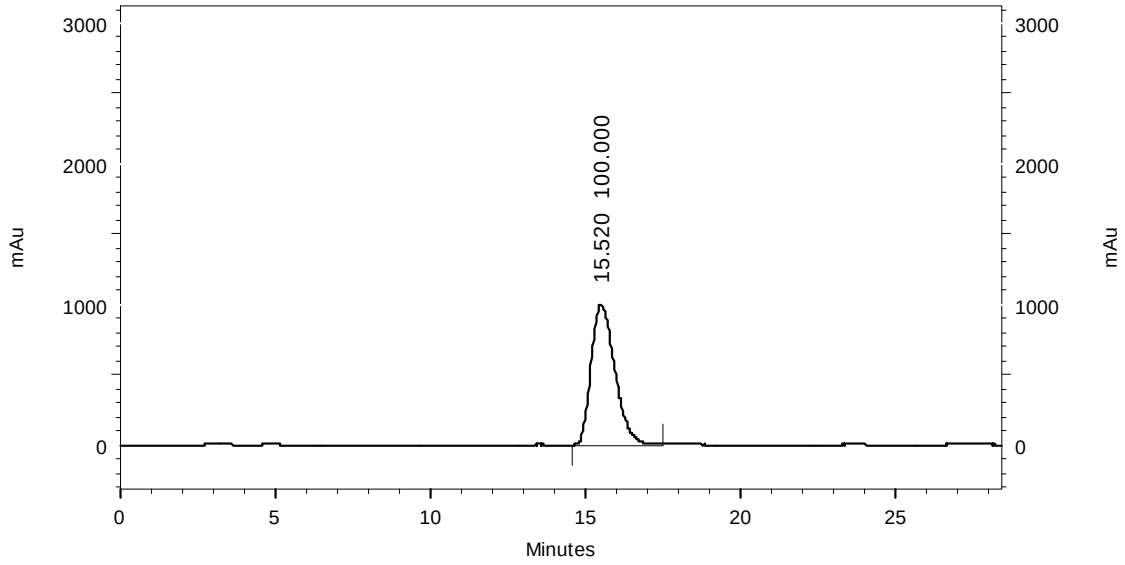
(±)-*E*-**2c**

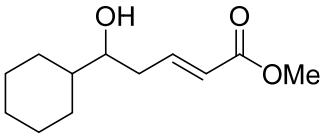
OD-H; 2% IP in Hexane; 1.0 mL/min





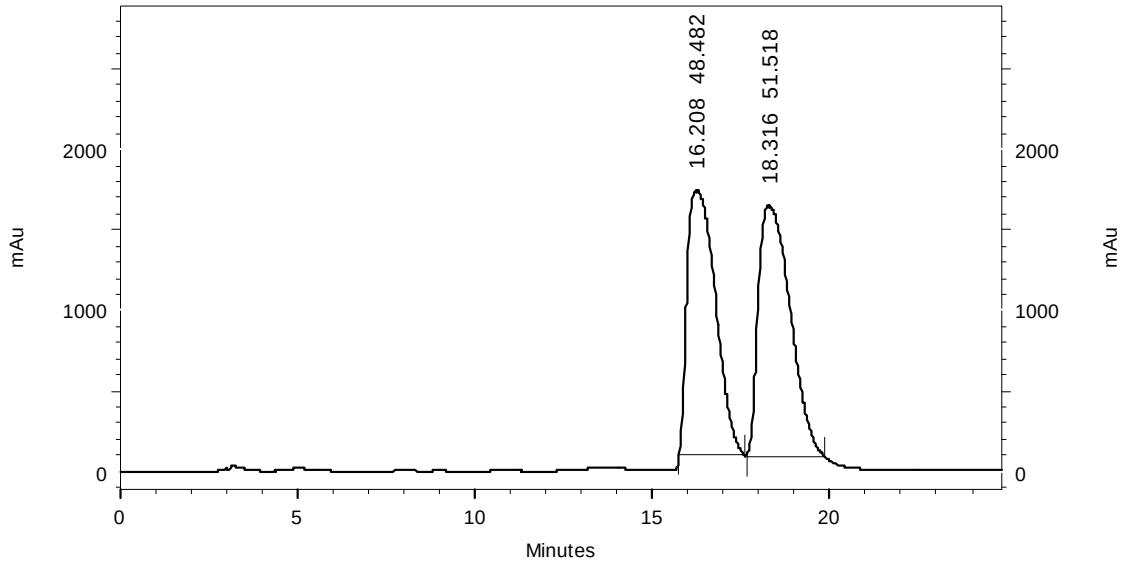
E-**2c**

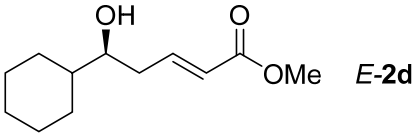




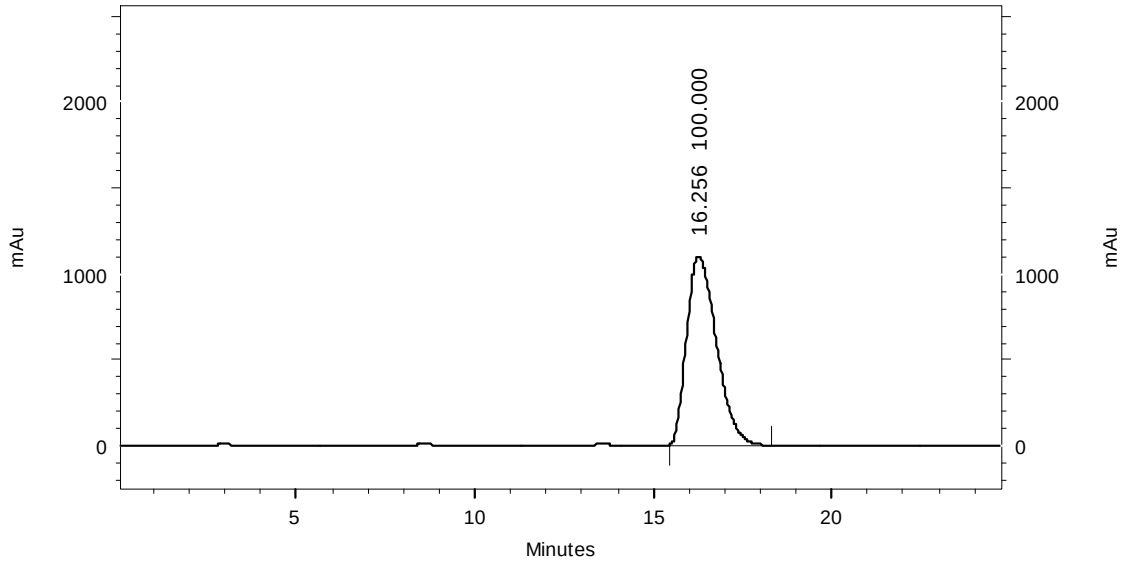
(±)-*E*-**2d**

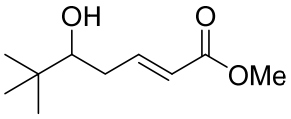
OD-H; 2% IP in Hexane; 1.0 mL/min





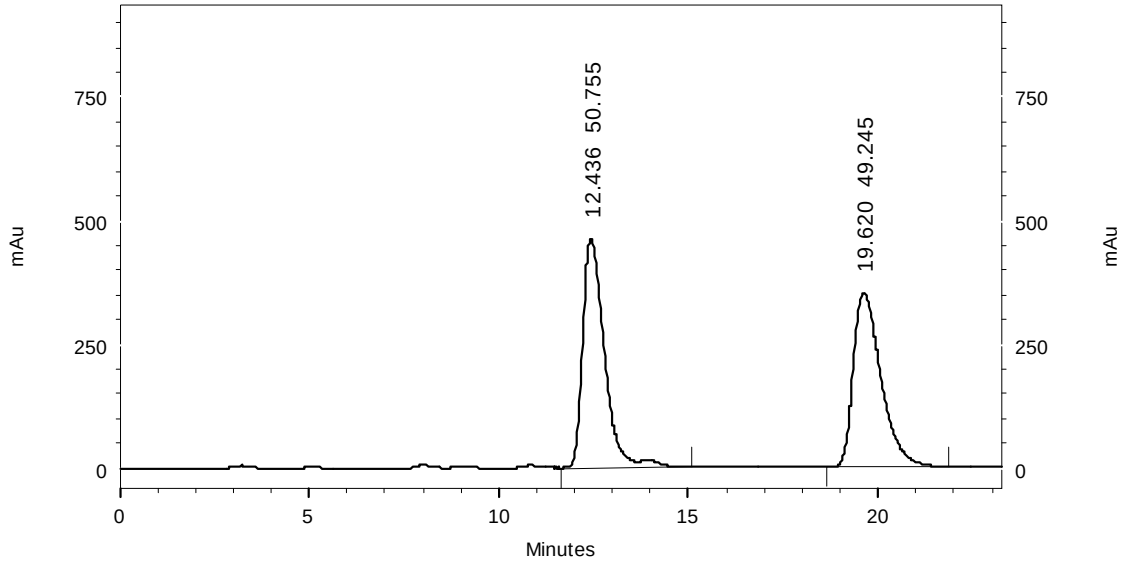
E-**2d**

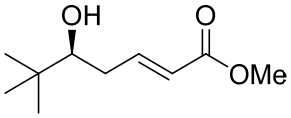




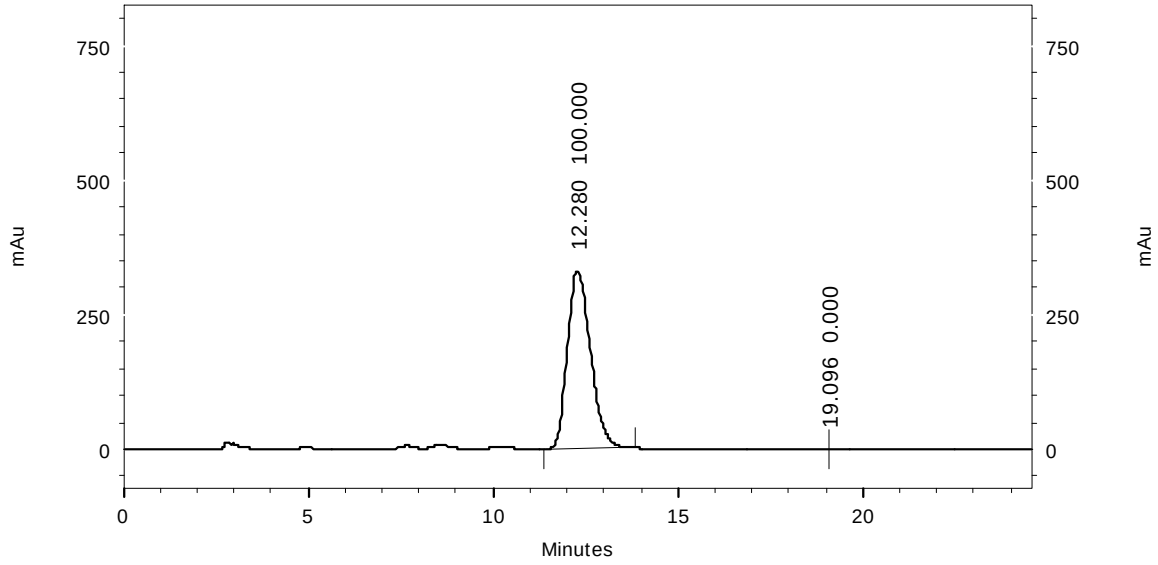
(±)-*E*-**2e**

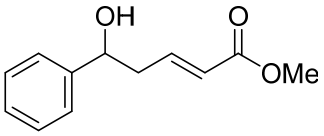
OD-H; 2% IP in Hexane; 1.0 mL/min





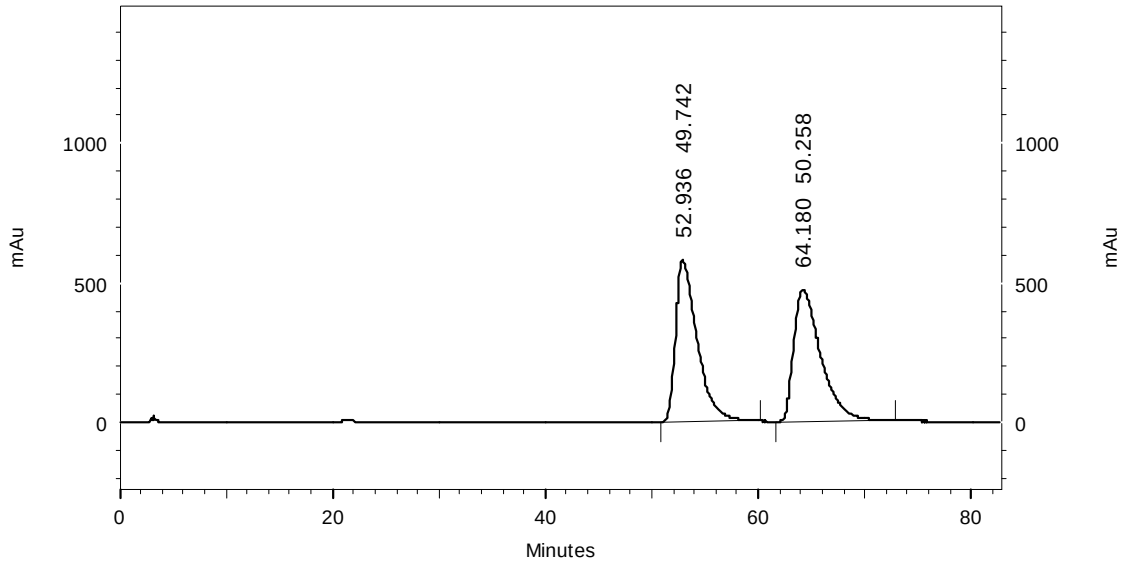
E-**2e**

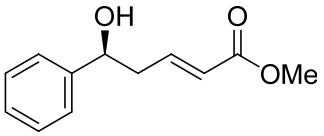




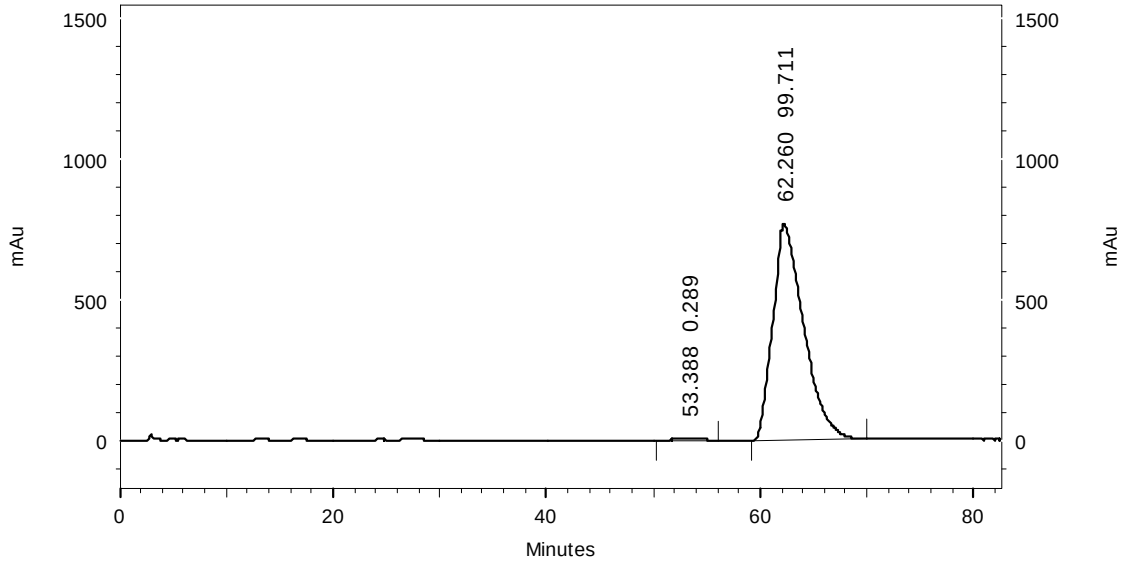
(±)-*E*-**2f**

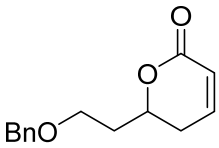
OD-H; 2% IP in Hexane; 1.0 mL/min





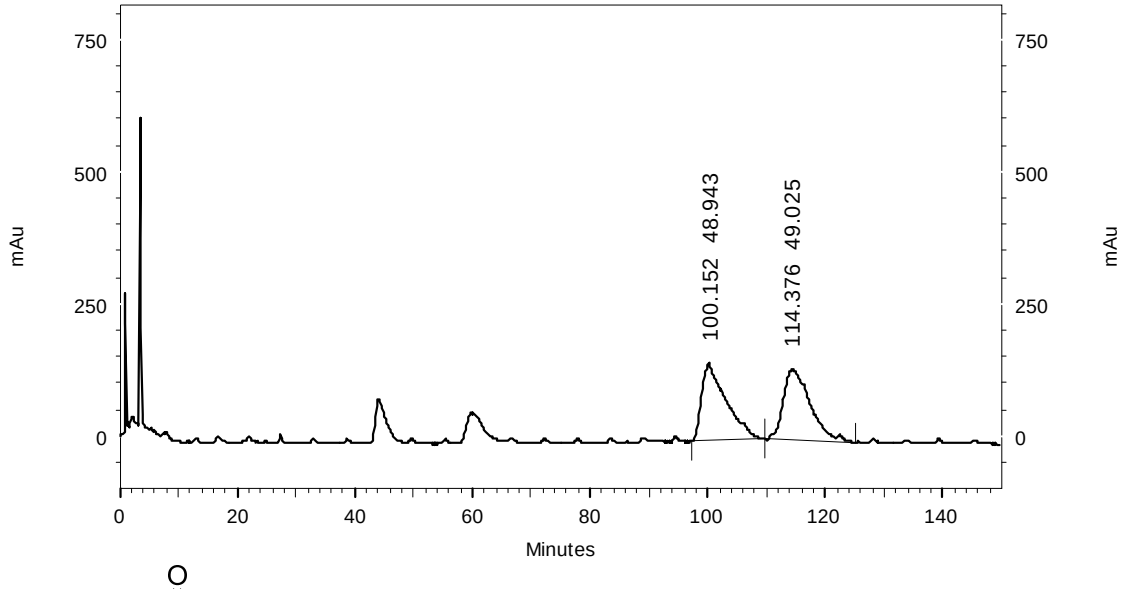
E-**2f**

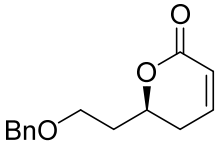




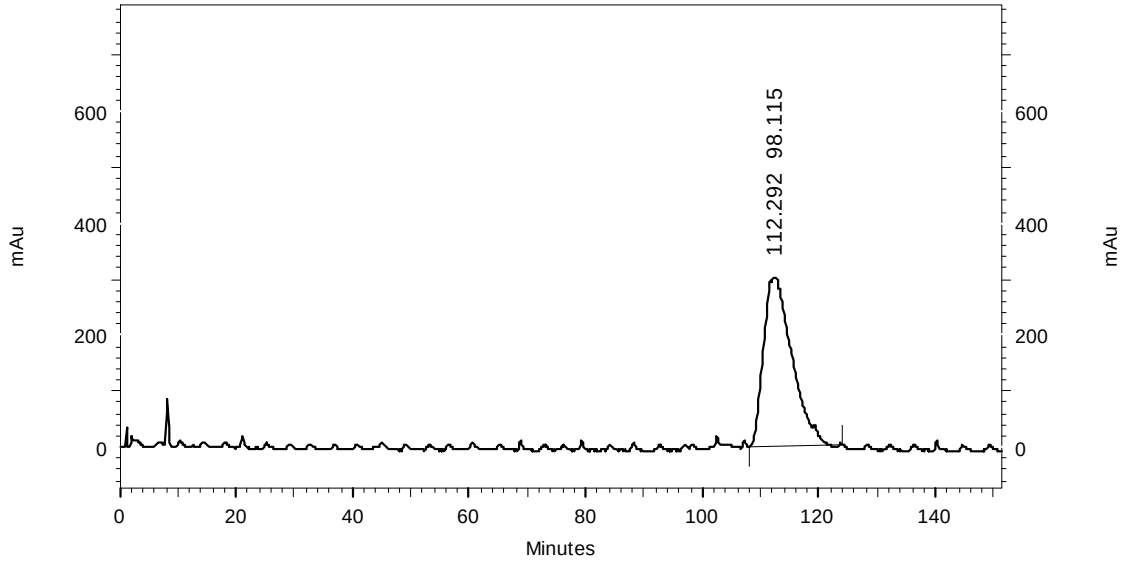
(±)-**8**

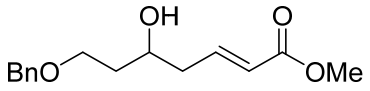
OB-H; 5% IP in Hexane; 1.50 mL/min





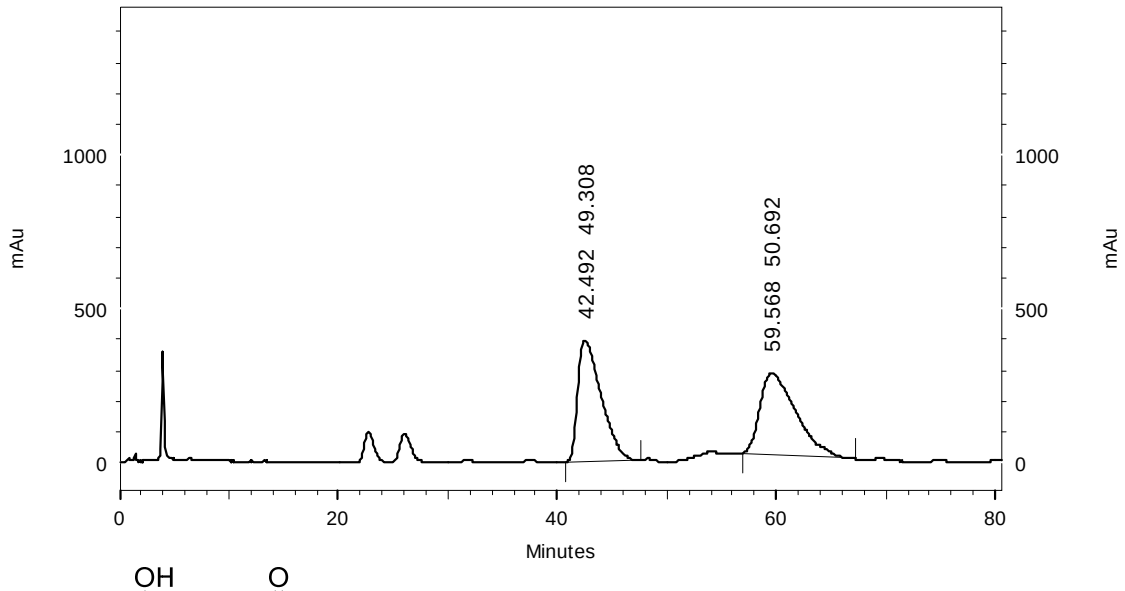
8

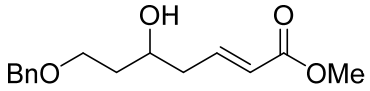




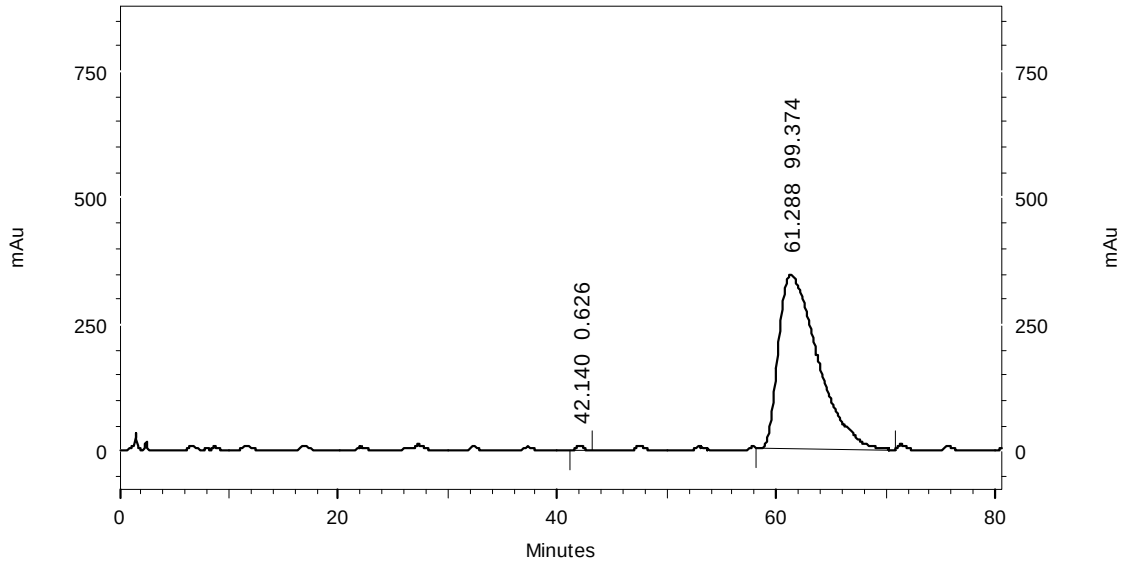
(±)-*E*-**7**

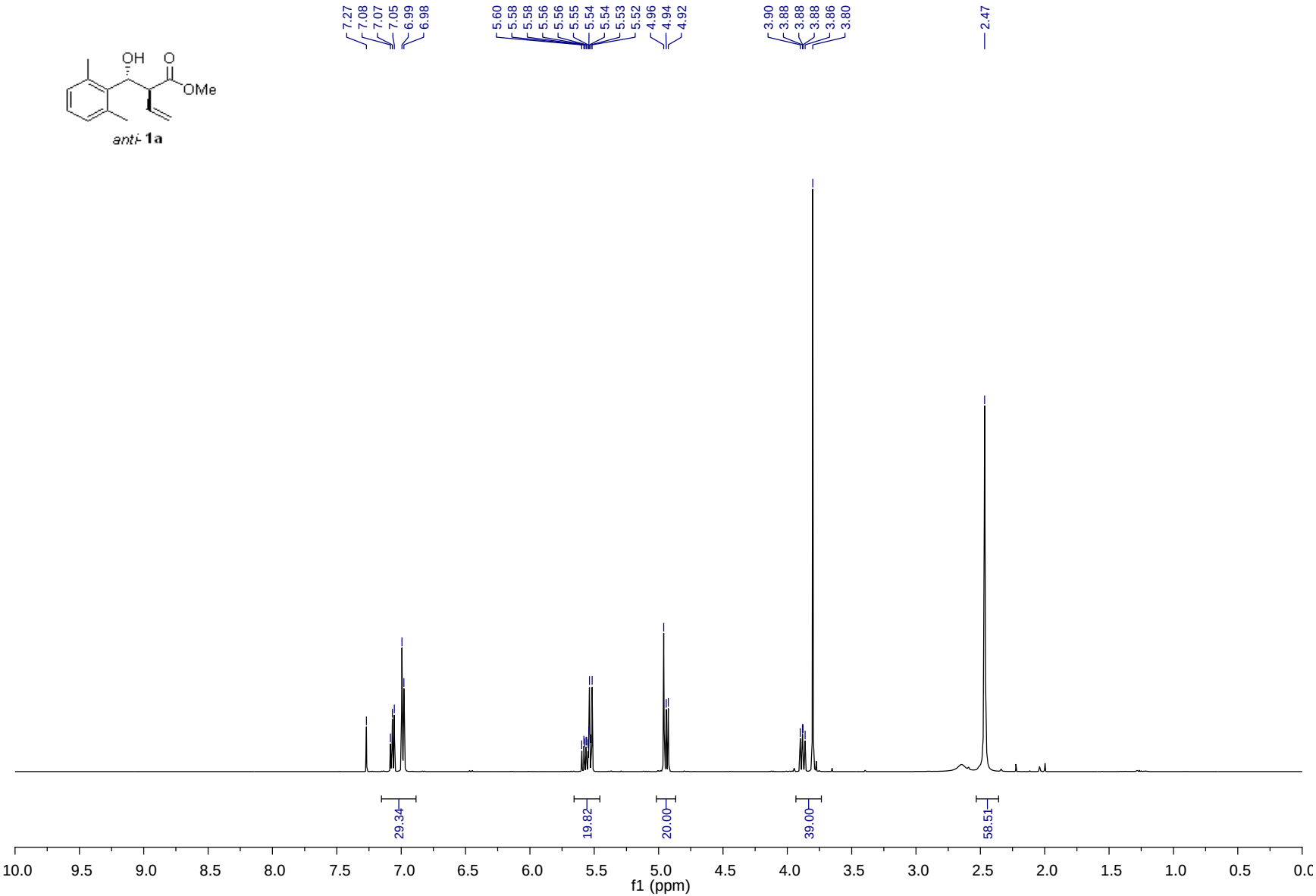
OB-H; 5% IP in Hexane; 1.50 mL/min

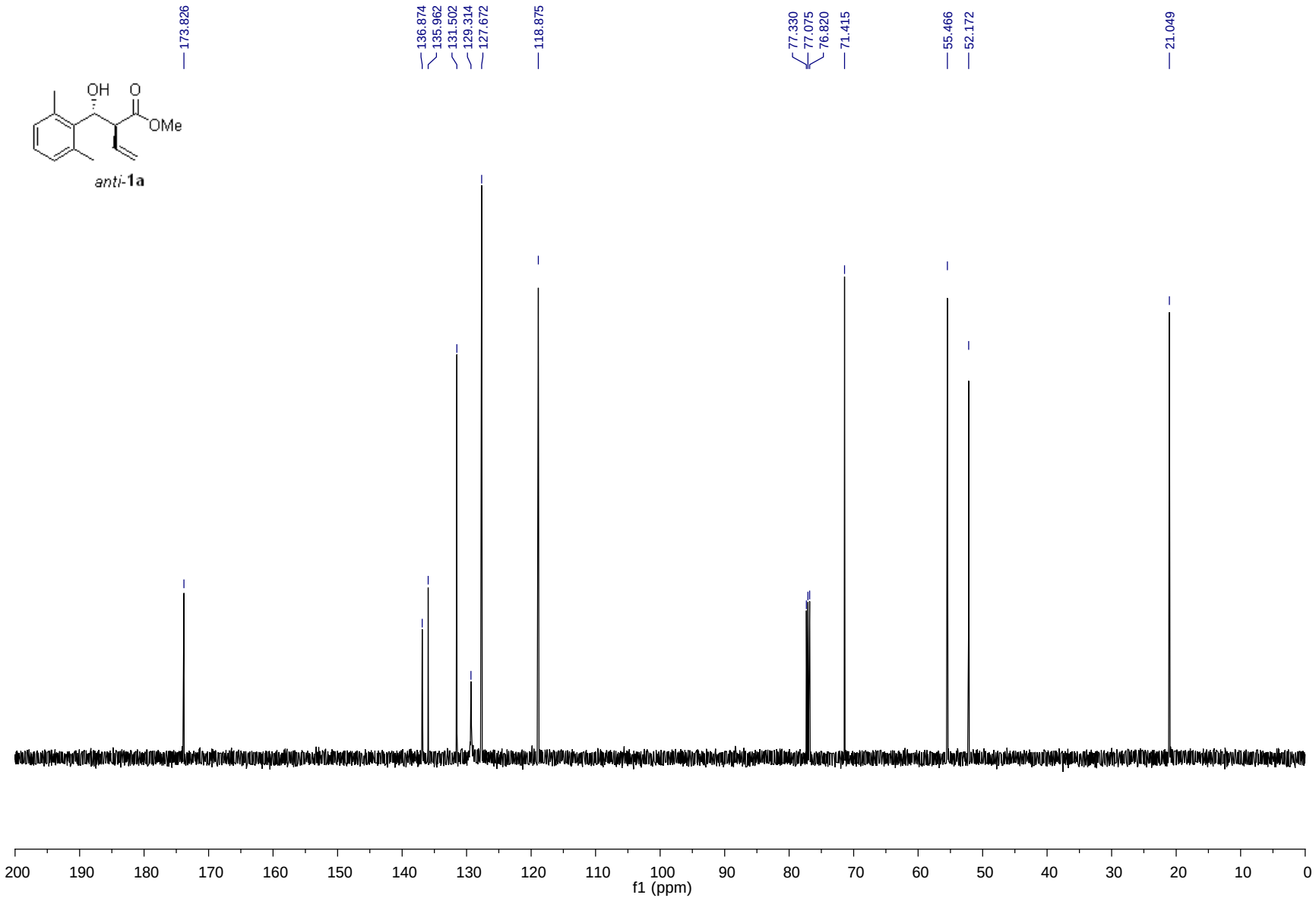


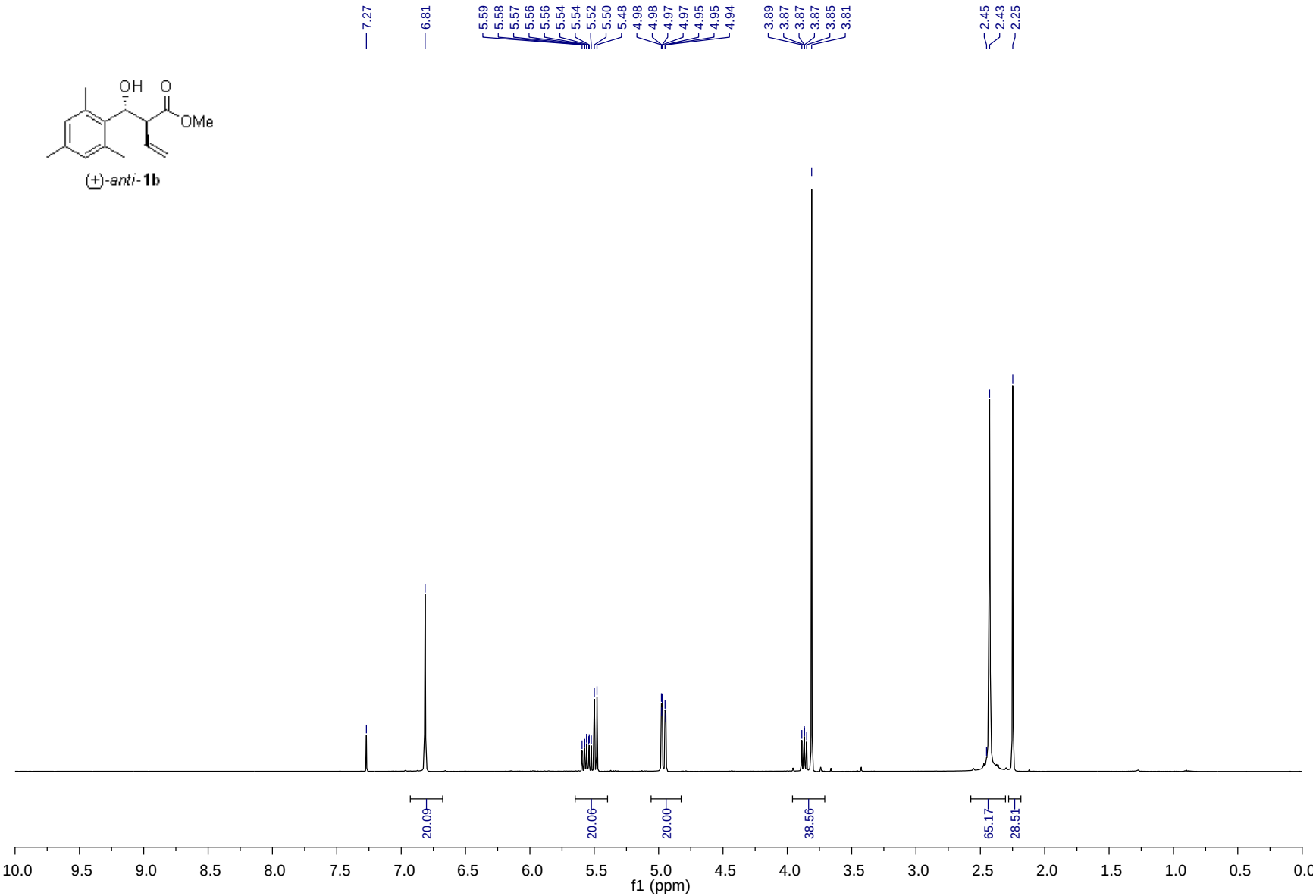


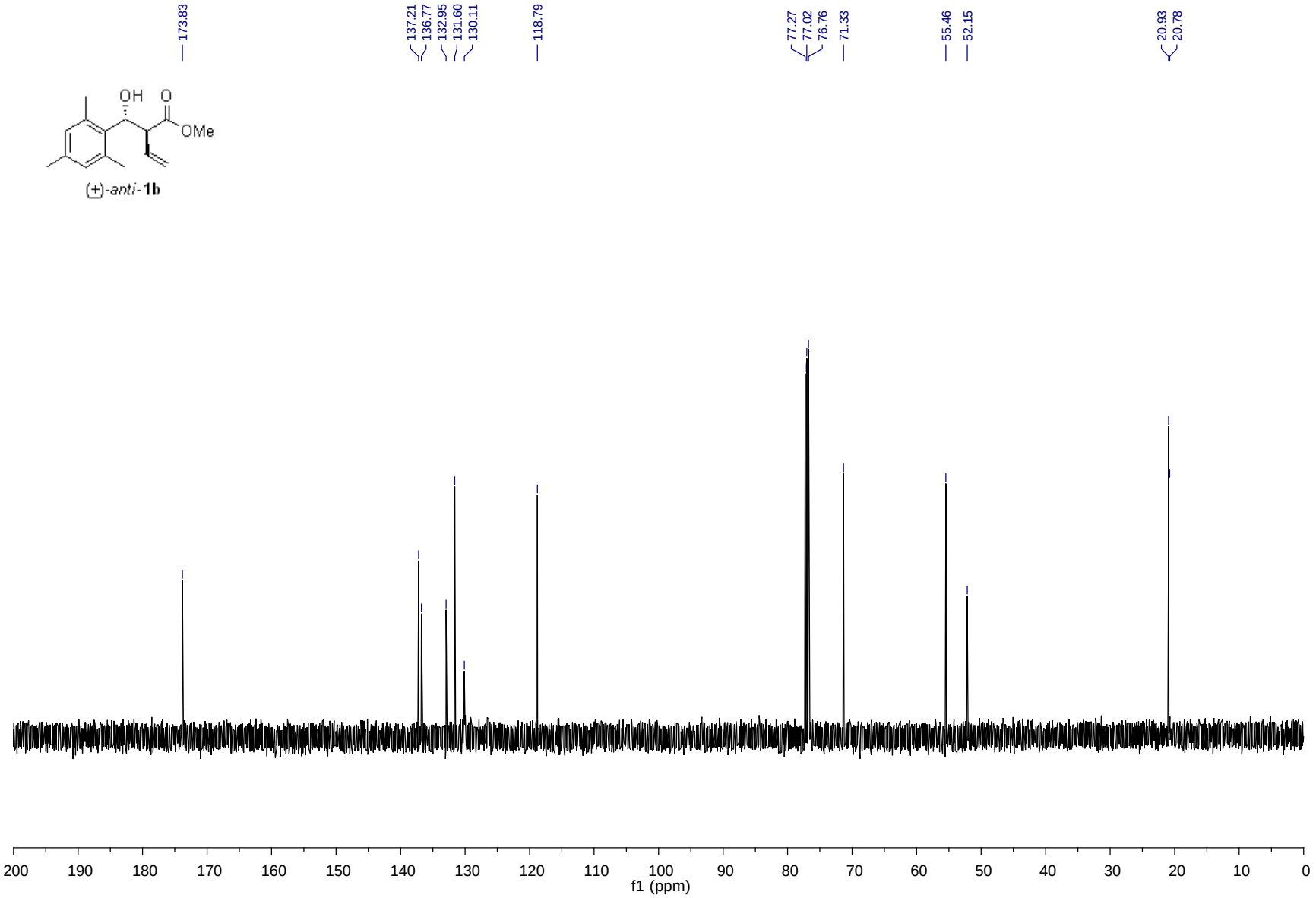
E-**7**

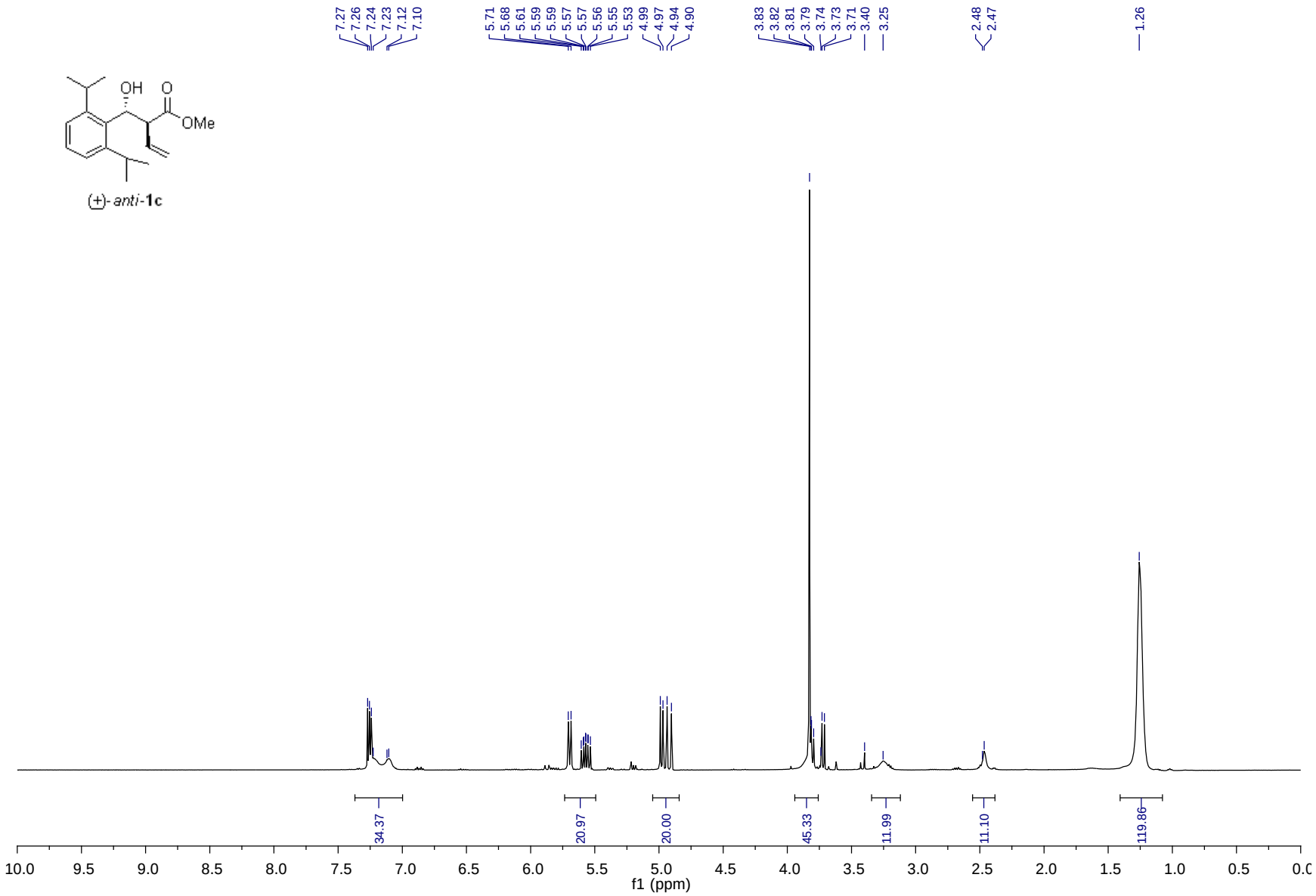


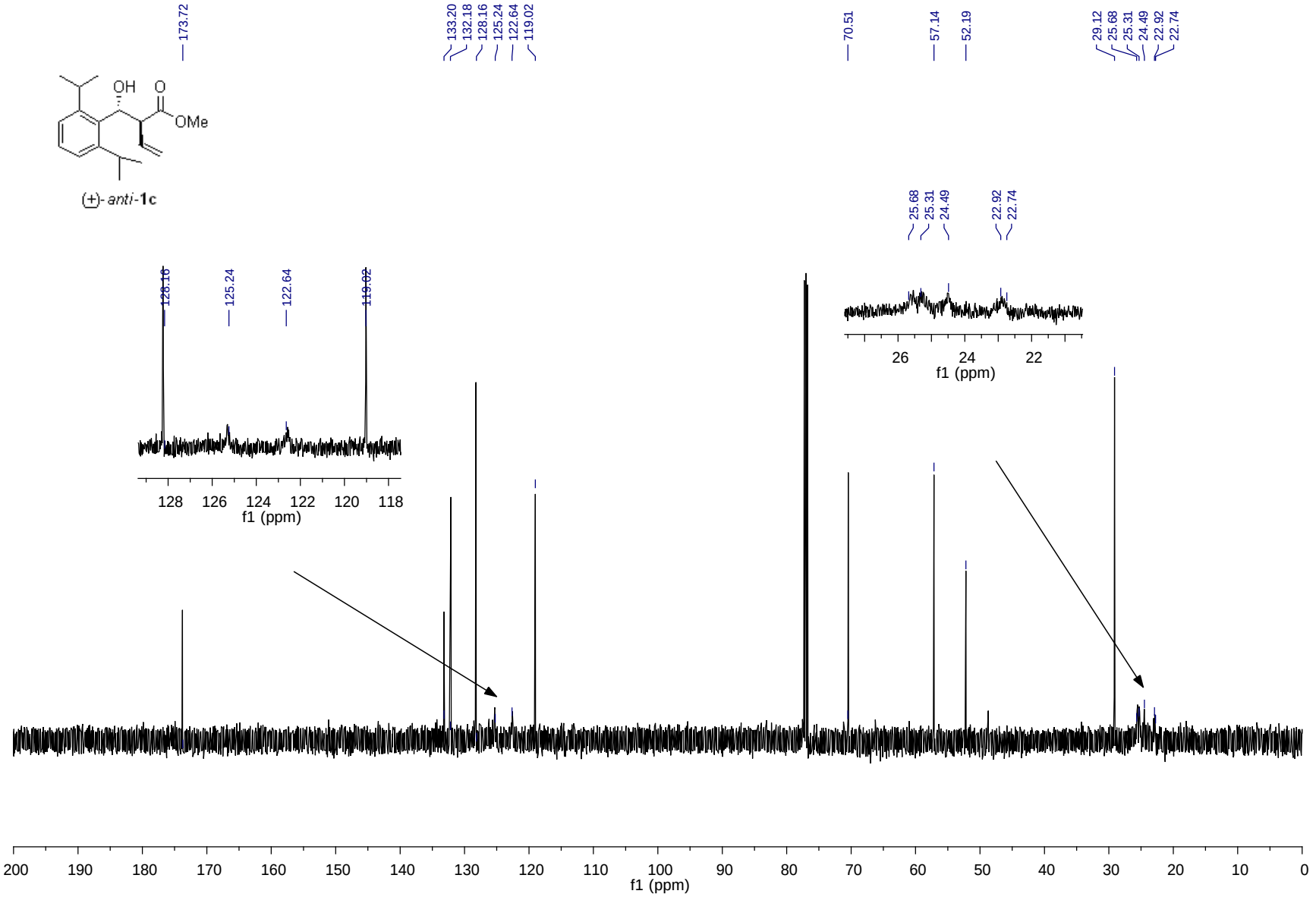

OH
O
OMe
anti-1a
7.27
7.08
7.07
7.05
6.99
6.98
5.60
5.58
5.58
5.56
5.56
5.55
5.54
5.54
5.53
5.52
4.96
4.94
4.92
3.90
3.88
3.88
3.86
3.80
2.47
29.34
19.82
20.00
39.00
58.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

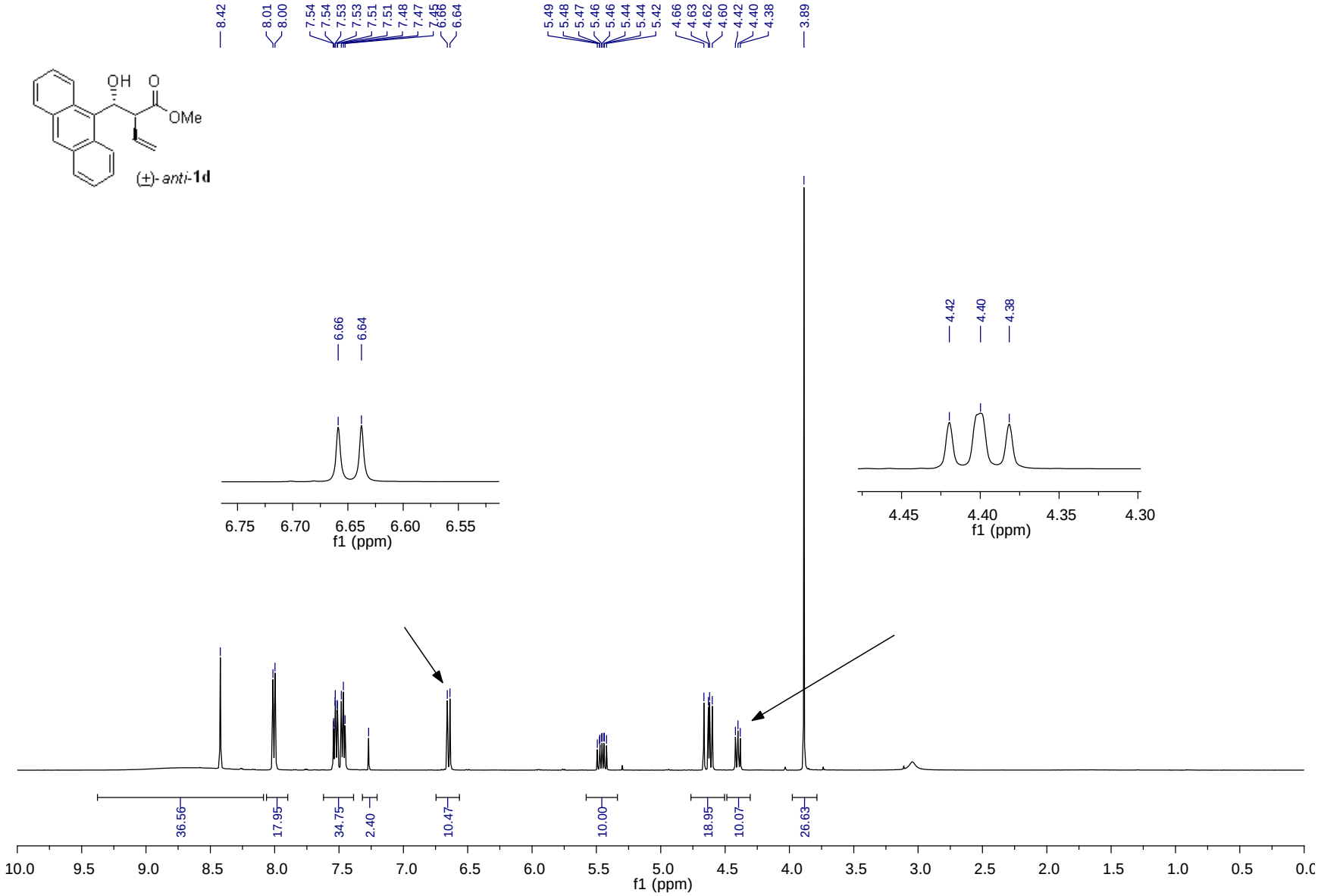

173.826
136.874
135.962
131.502
129.314
127.672
118.875
77.330
77.075
76.820
71.415
55.466
52.172
21.049
OH
O
OMe
anti-1a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
6.81
5.59
5.58
5.57
5.56
5.56
5.54
5.54
5.52
5.50
5.48
4.98
4.98
4.97
4.97
4.95
4.95
4.94
3.89
3.87
3.87
3.87
3.85
3.81
2.45
2.43
2.25
OH
O
OMe
(±)-anti-1b
20.09
20.06
20.00
38.56
65.17
28.51
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)


173.83
137.21
136.77
132.95
131.60
130.11
118.79
77.27
77.02
76.76
71.33
55.46
52.15
20.93
20.78
OH
O
OMe
(±)-anti-1b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.26
7.24
7.23
7.12
7.10
5.71
5.68
5.61
5.59
5.59
5.57
5.57
5.56
5.55
5.53
4.99
4.97
4.94
4.90
3.83
3.82
3.81
3.79
3.74
3.73
3.71
3.40
3.25
2.48
2.47
1.26
OH
O
OMe
(+)-anti-1c
34.37
20.97
20.00
45.33
11.99
11.10
119.86
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
0.0
f1 (ppm)


173.72
133.20
132.18
128.16
125.24
122.64
119.02
70.51
57.14
52.19
29.12
25.68
25.31
24.49
22.92
22.74
OH
O
OMe
(±)-anti-1c
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.42
8.01
8.00
7.54
7.54
7.53
7.53
7.51
7.51
7.48
7.47
7.45
6.66
6.64
5.49
5.48
5.47
5.46
5.46
5.44
5.44
5.42
4.66
4.63
4.62
4.60
4.42
4.40
4.38
3.89
OH
O
OMe
(±)-anti-1d
6.66
6.64
6.75
6.70
6.65
6.60
6.55
f1 (ppm)
4.42
4.40
4.38
4.45
4.40
4.35
4.30
f1 (ppm)
36.56
17.95
34.75
2.40
10.47
10.00
18.95
10.07
26.63
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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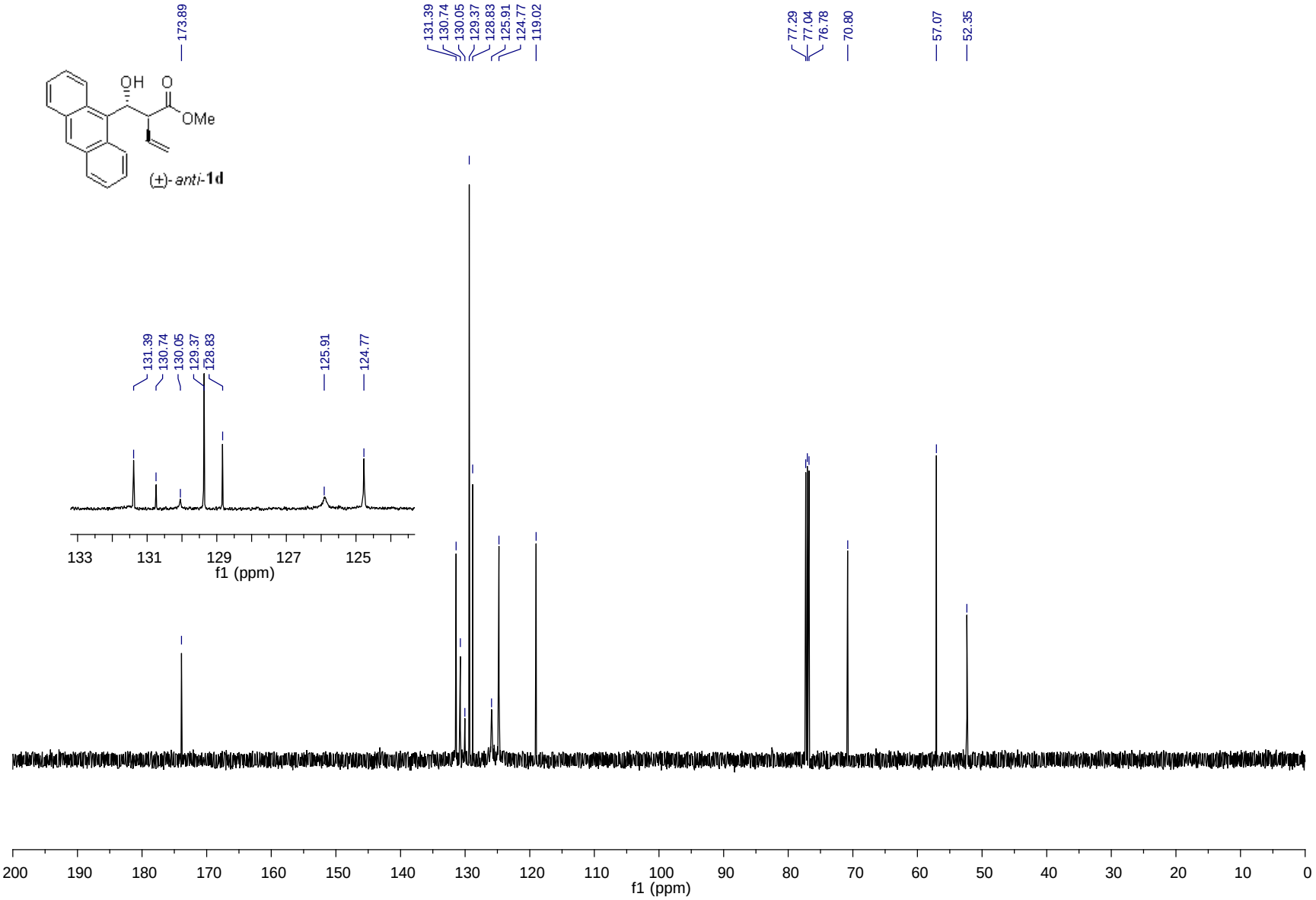
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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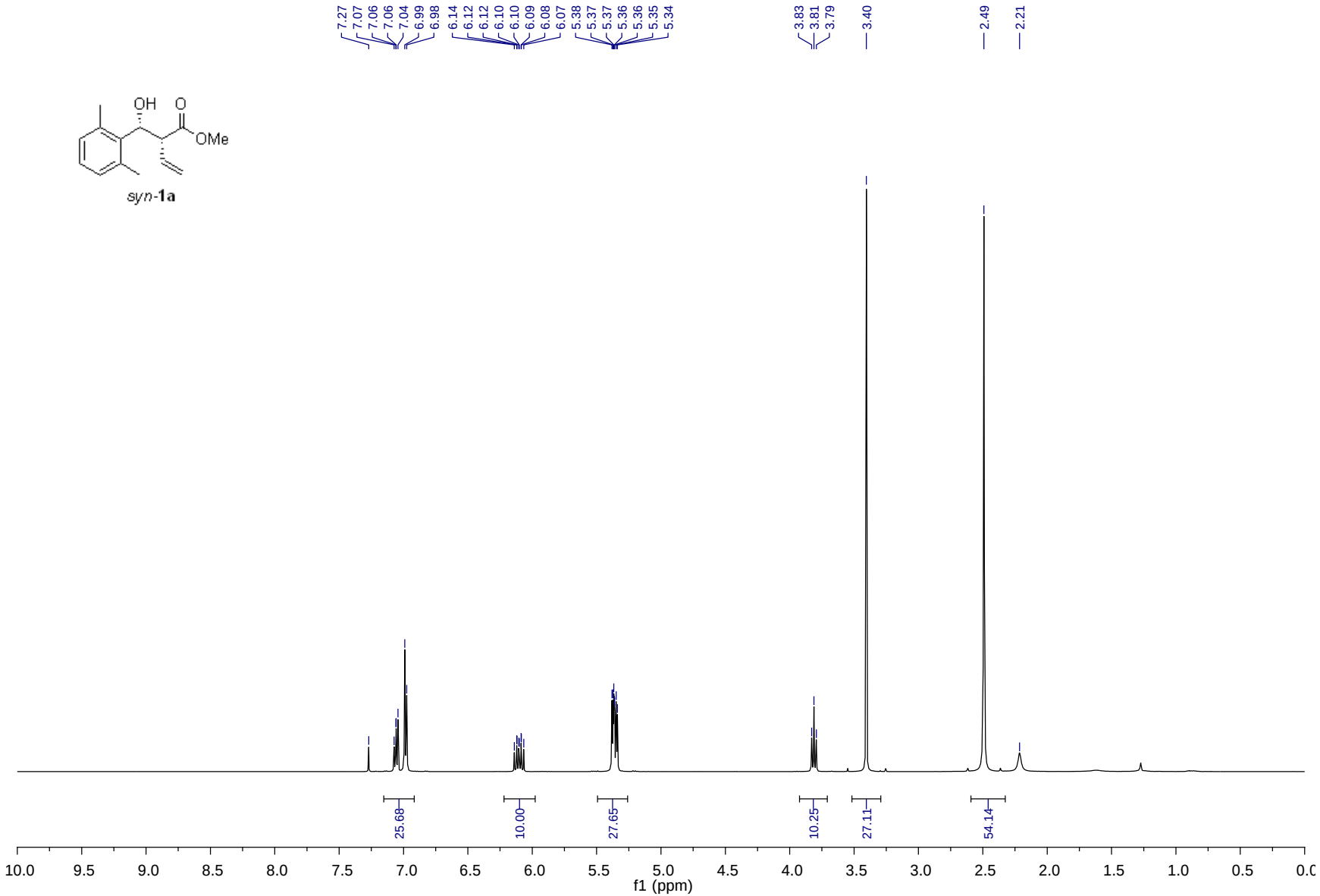
131.39
130.74
130.05
129.37
128.83
125.91
124.77
119.02
77.29
77.04
76.78
70.80
57.07
52.35
OH
O
OMe
(±)-anti-1d
f1 (ppm)
f1 (ppm)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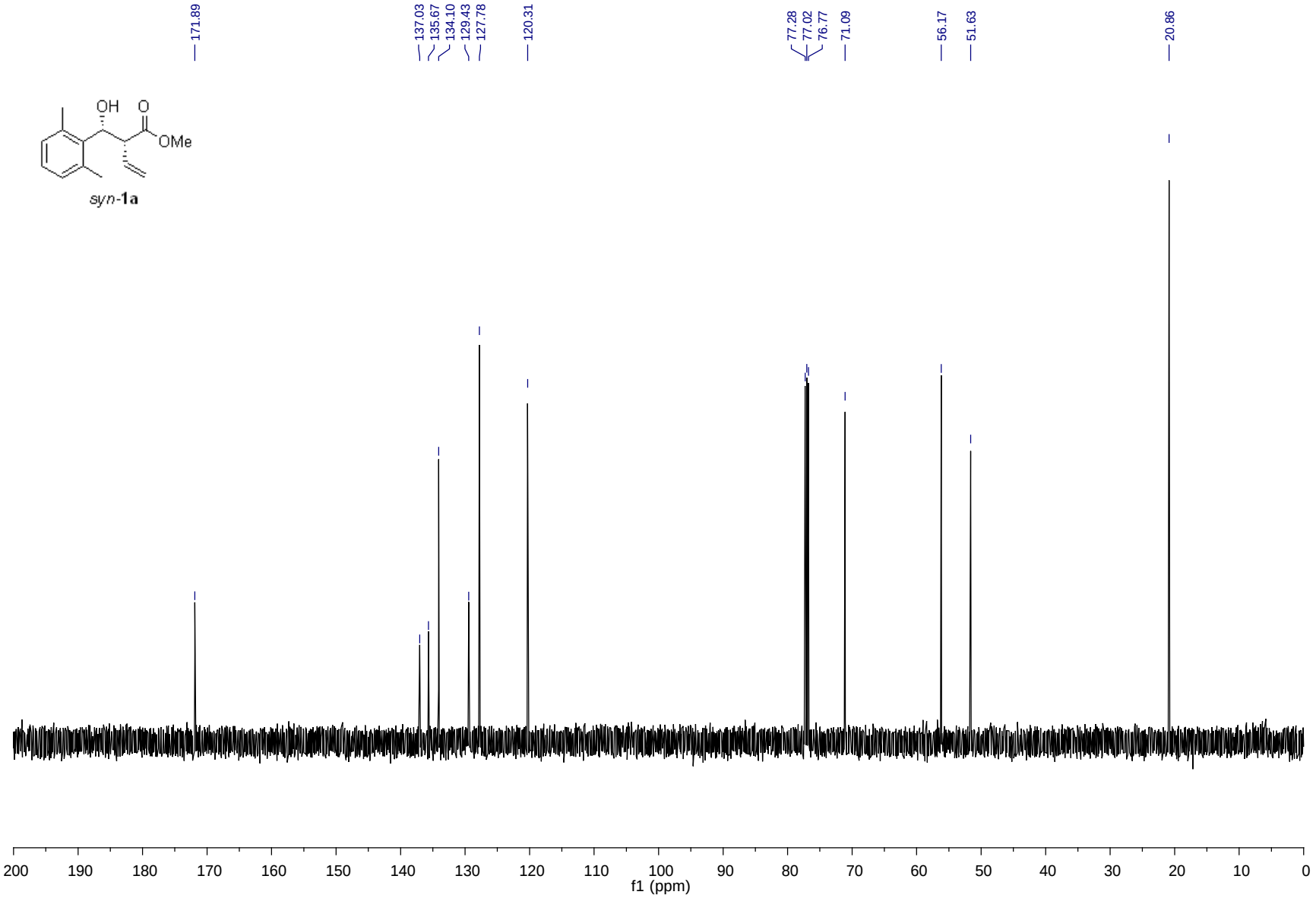
7.06
7.04
6.99
6.98
6.14
6.12
6.12
6.10
6.10
6.09
6.08
6.07
5.38
5.37
5.37
5.36
5.36
5.35
5.34
3.83
3.81
3.79
3.40
2.49
2.21
OH
O
OMe
syn-1a
25.68
10.00
27.65
10.25
27.11
54.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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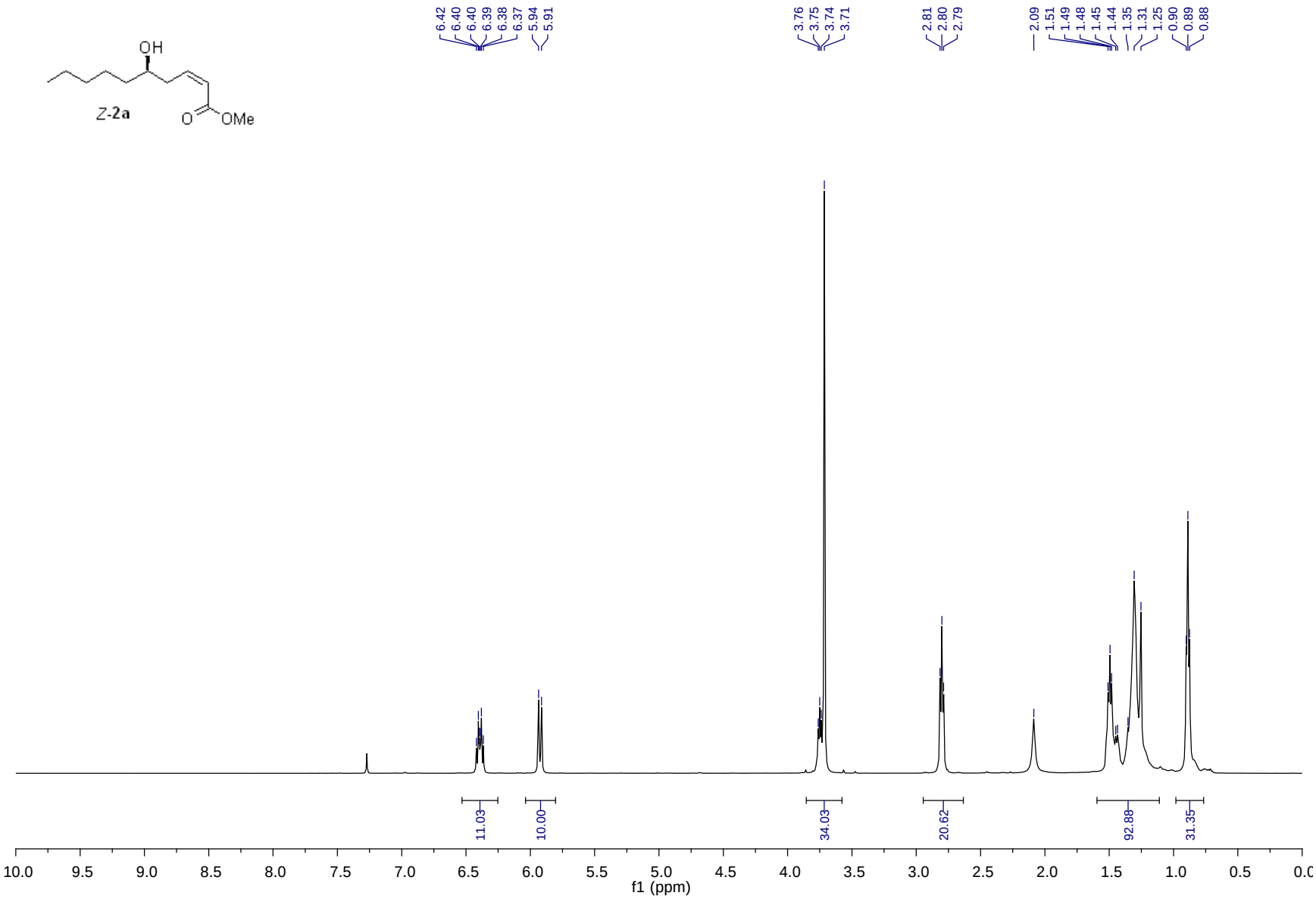
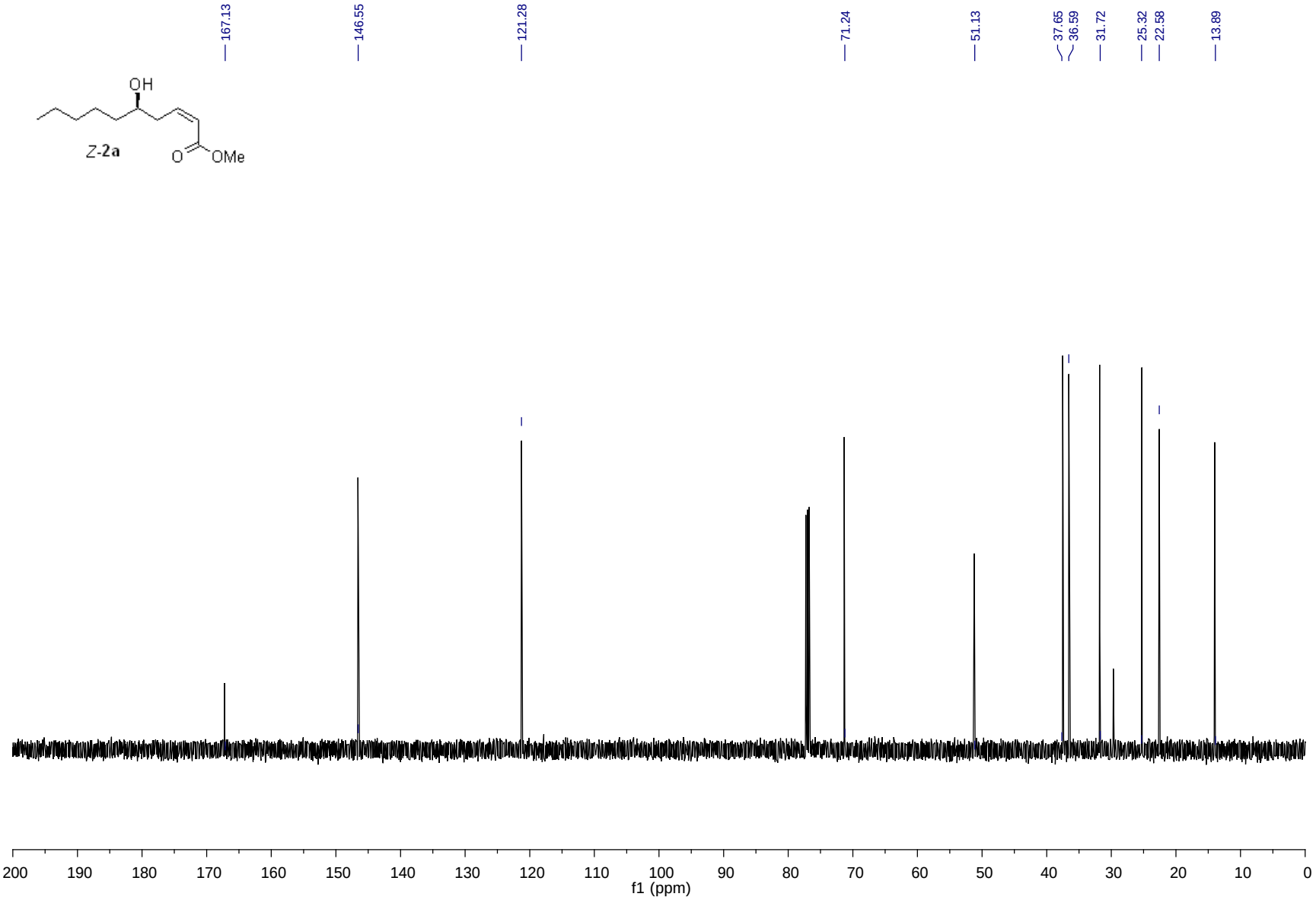
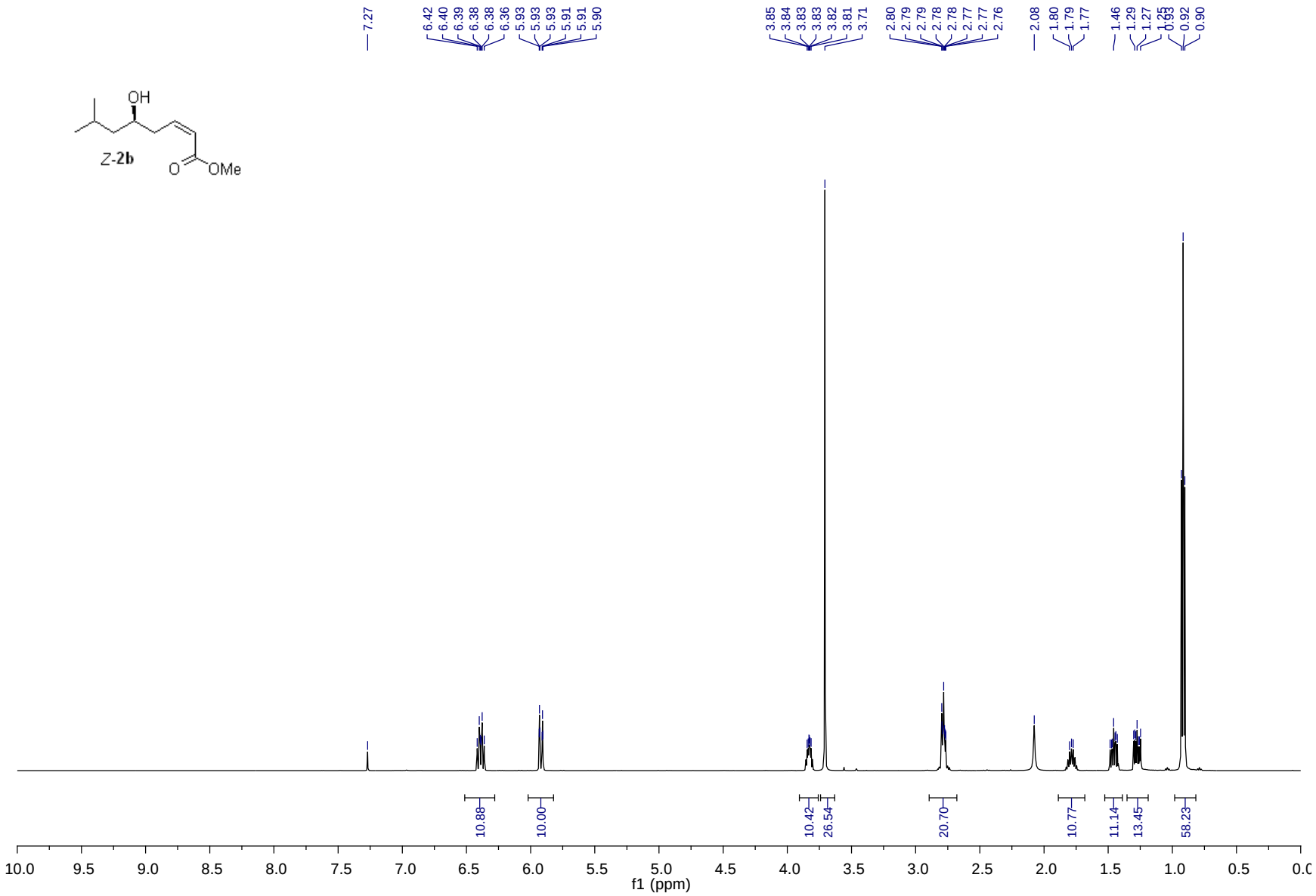
135.67
134.10
129.43
127.78
120.31
77.28
77.02
76.77
71.09
56.17
51.63
20.86
OH
O
OMe
syn-1a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Z-2a
O
OMe
6.42
6.40
6.40
6.39
6.38
6.37
5.94
5.91
3.76
3.75
3.74
3.71
2.81
2.80
2.79
2.09
1.51
1.49
1.48
1.45
1.44
1.35
1.31
1.25
0.90
0.89
0.88
11.03
10.00
34.03
20.62
92.88
31.35
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
0.0
f1 (ppm)


167.13
146.55
121.28
71.24
51.13
37.65
36.59
31.72
25.32
22.58
13.89
OH
Z-2a
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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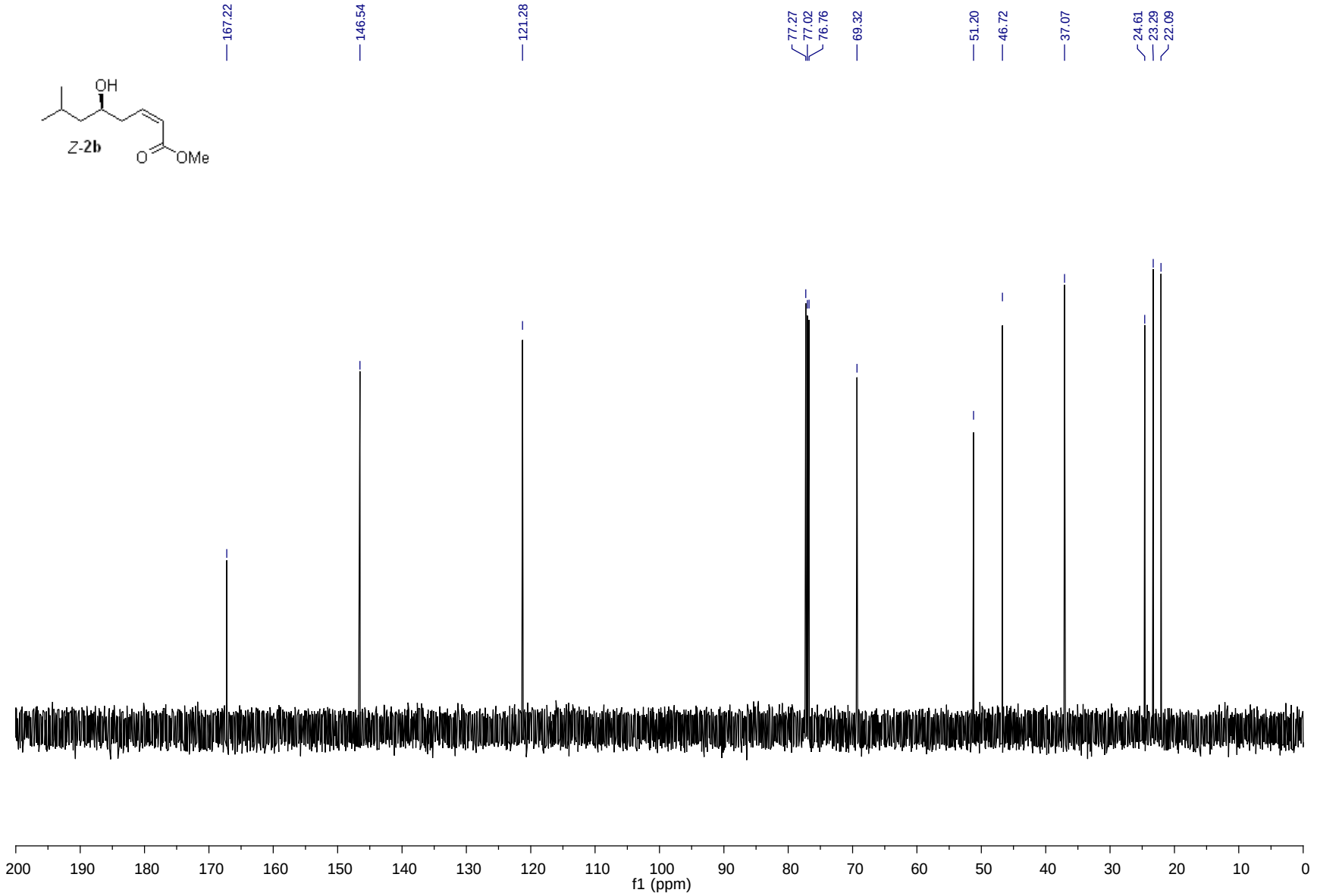
6.42
6.40
6.39
6.38
6.38
6.36
5.93
5.93
5.93
5.91
5.91
5.90
3.85
3.84
3.83
3.83
3.82
3.81
3.71
2.80
2.79
2.79
2.78
2.78
2.77
2.77
2.76
2.08
1.80
1.79
1.77
1.46
1.29
1.27
1.25
0.93
0.92
0.90
OH
Z-2b
O
OMe
10.88
10.00
10.42
26.54
20.70
10.77
11.14
13.45
58.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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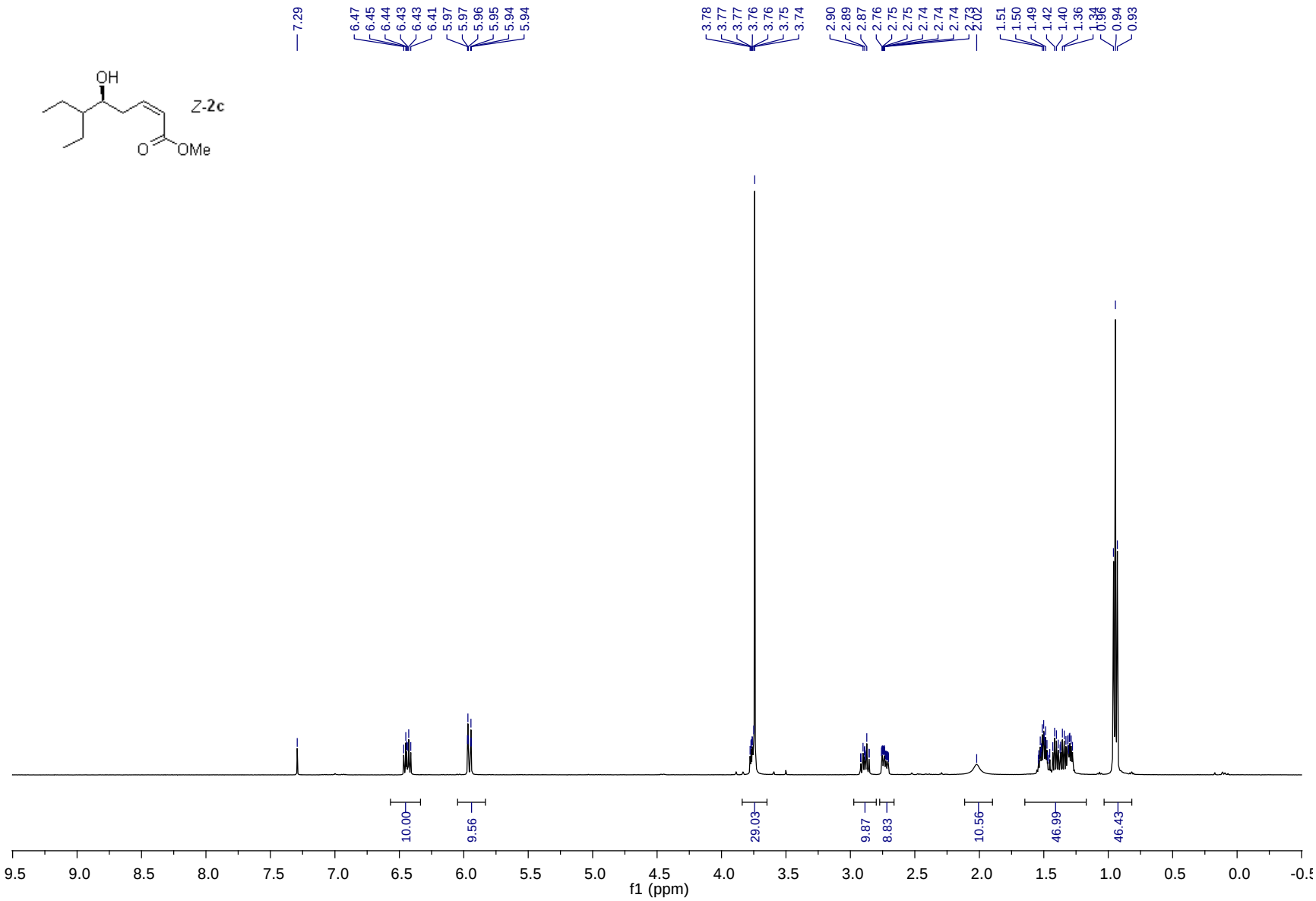
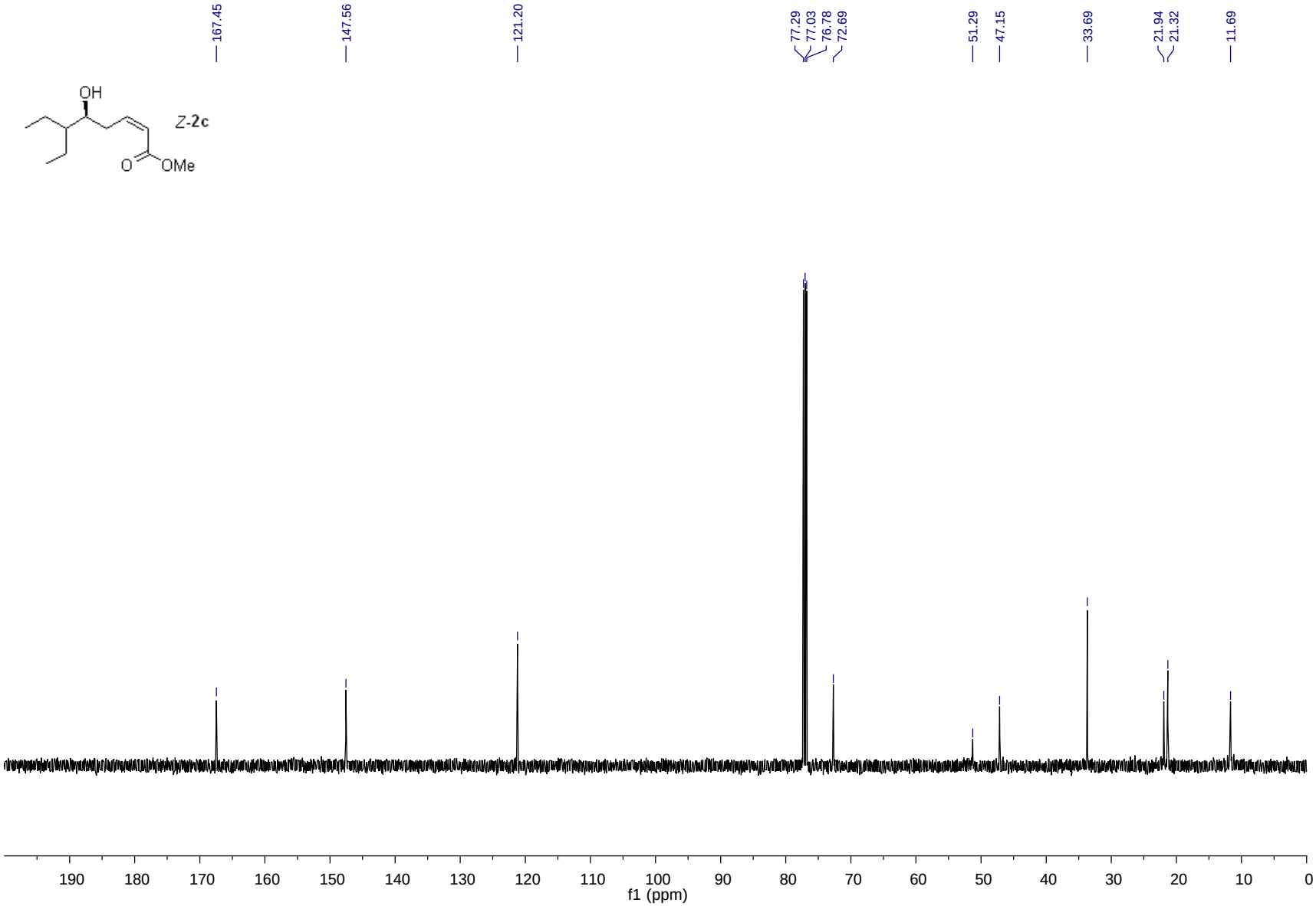
146.54
121.28
77.27
77.02
76.76
69.32
51.20
46.72
37.07
24.61
23.29
22.09
OH
Z-2b
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Z-2c
O
OMe
7.29
6.47
6.45
6.44
6.43
6.43
6.41
5.97
5.97
5.96
5.95
5.94
5.94
3.78
3.77
3.77
3.76
3.76
3.75
3.74
2.90
2.89
2.87
2.76
2.75
2.75
2.74
2.74
2.74
2.73
2.02
1.51
1.50
1.49
1.42
1.40
1.36
0.96
0.94
0.93
10.00
9.56
29.03
9.87
8.83
10.56
46.99
46.43
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
0.0
f1 (ppm)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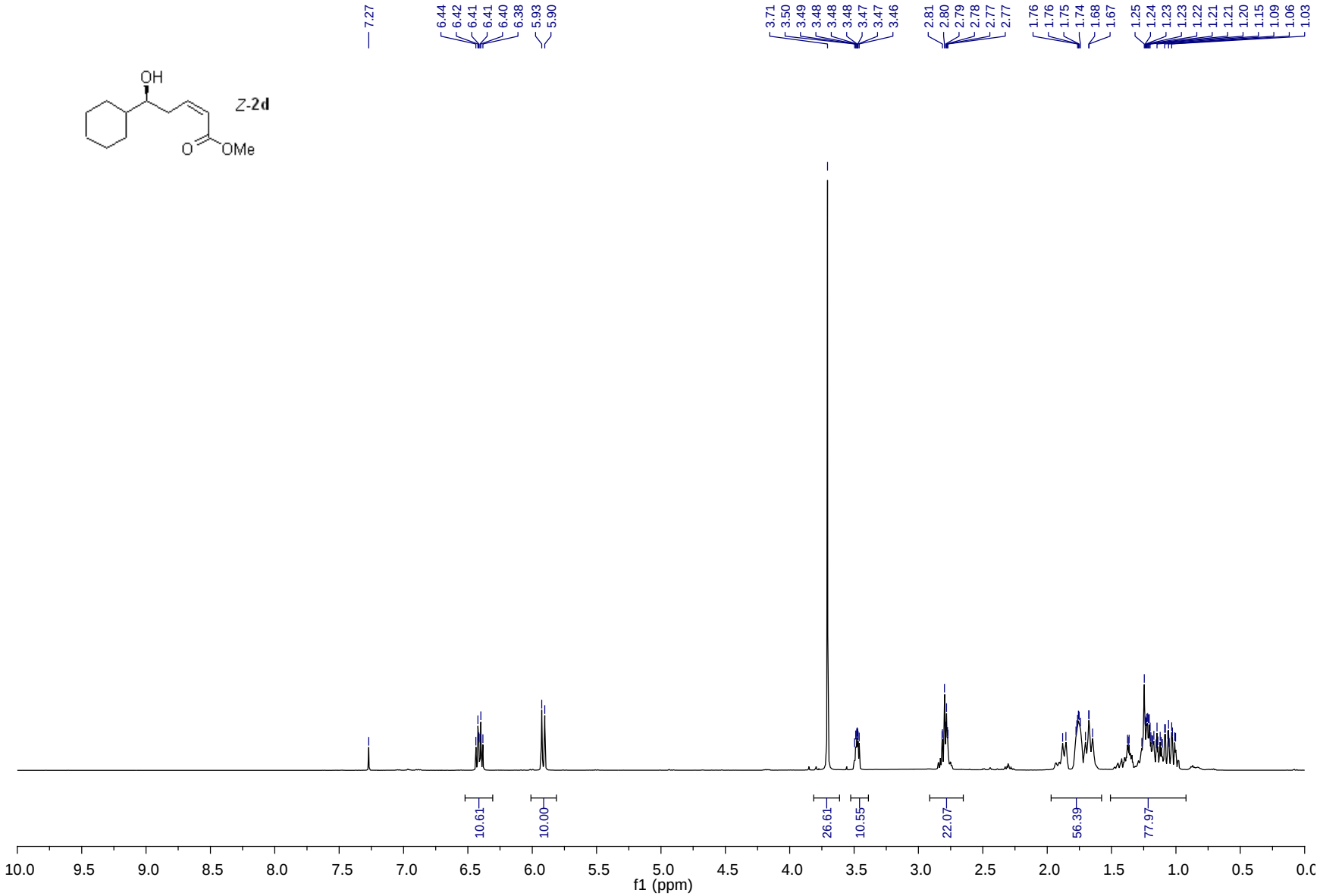
147.56
121.20
77.29
77.03
76.78
72.69
51.29
47.15
33.69
21.94
21.32
11.69
OH
Z-2c
O
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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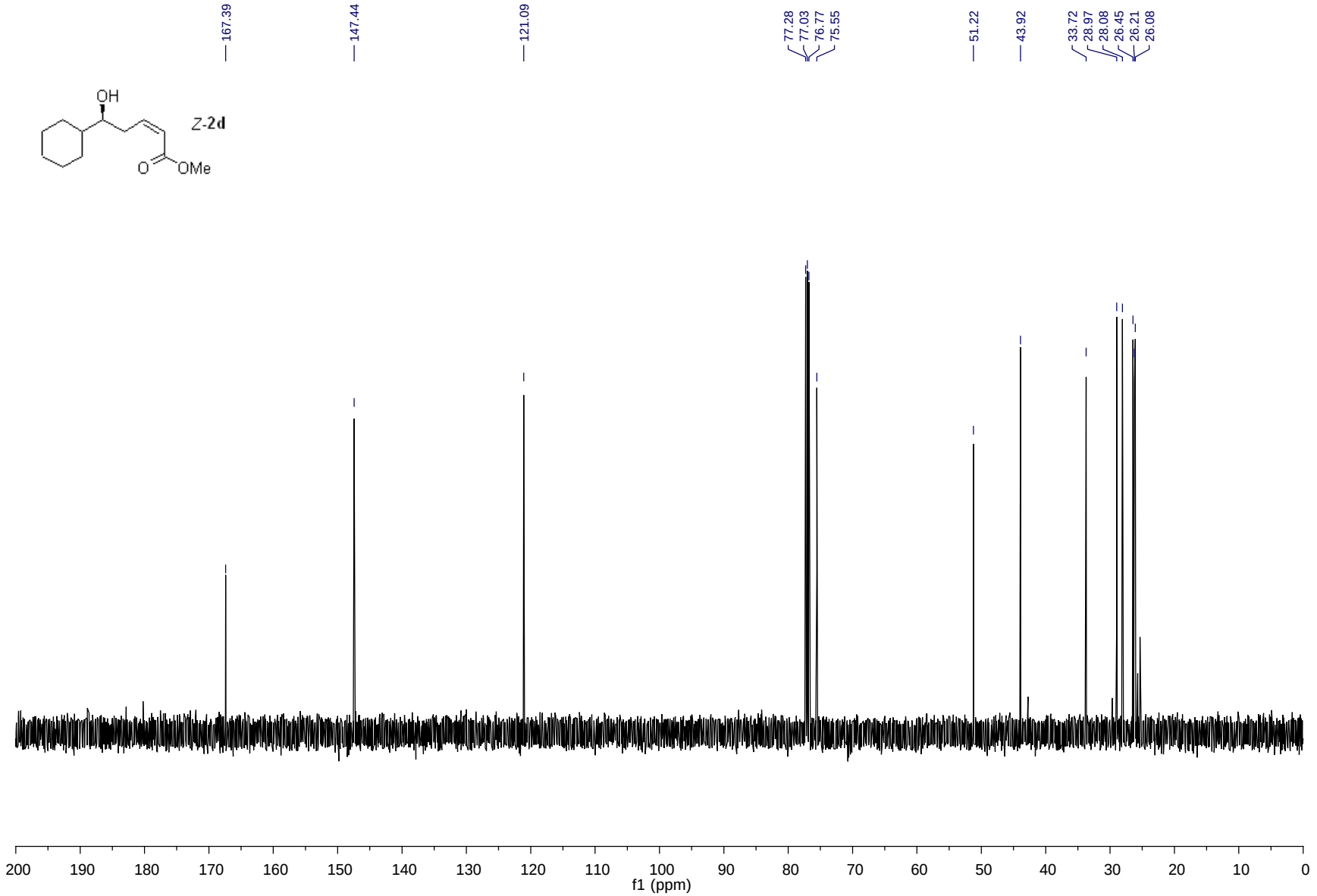
6.44
6.42
6.41
6.41
6.40
6.38
5.93
5.90
3.71
3.50
3.49
3.48
3.48
3.48
3.47
3.47
3.46
2.81
2.80
2.79
2.78
2.77
2.77
1.76
1.76
1.75
1.74
1.68
1.67
1.25
1.24
1.23
1.23
1.22
1.21
1.21
1.20
1.15
1.09
1.06
1.03
OH
Z-2d
O
OMe
10.61
10.00
26.61
10.55
22.07
56.39
77.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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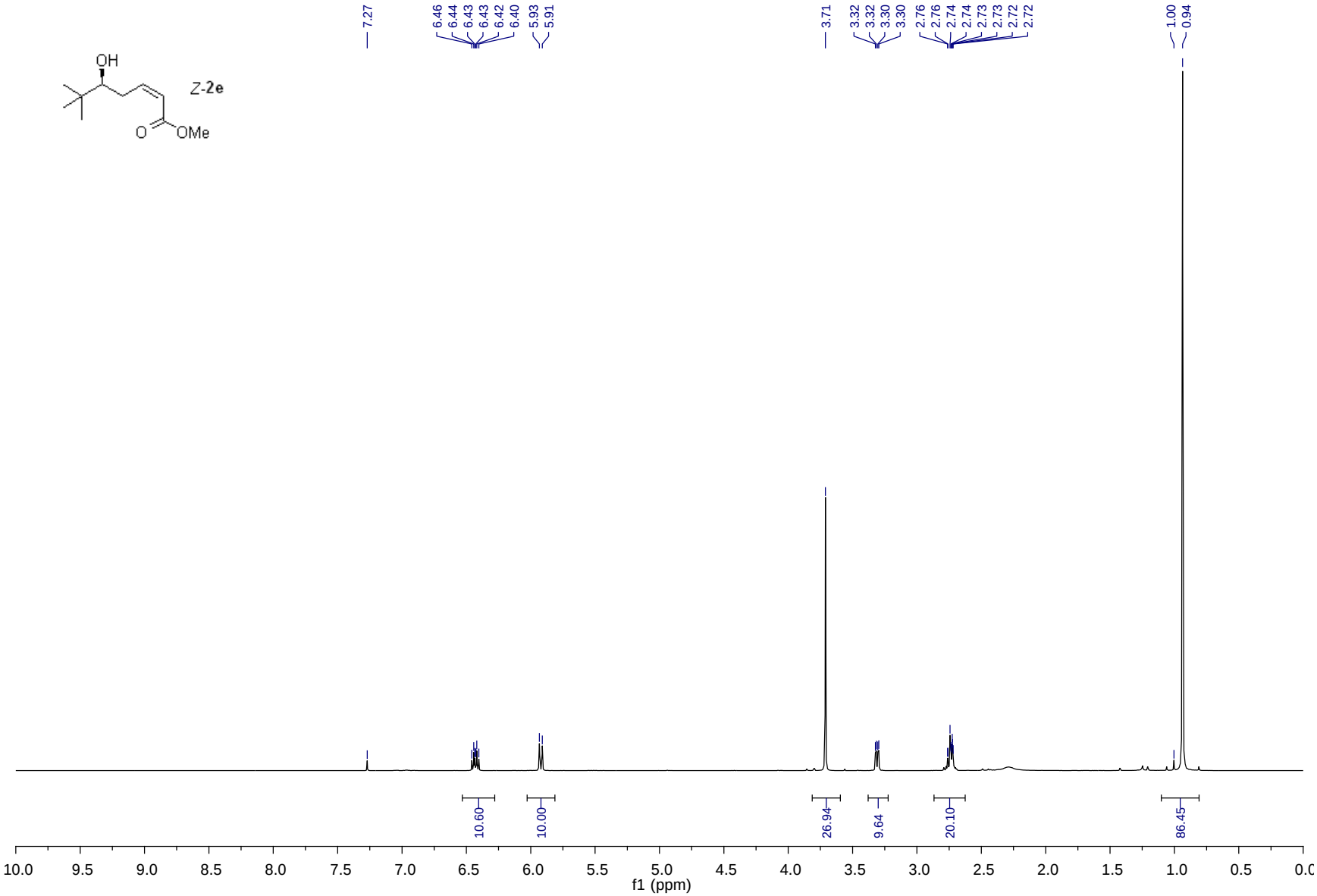
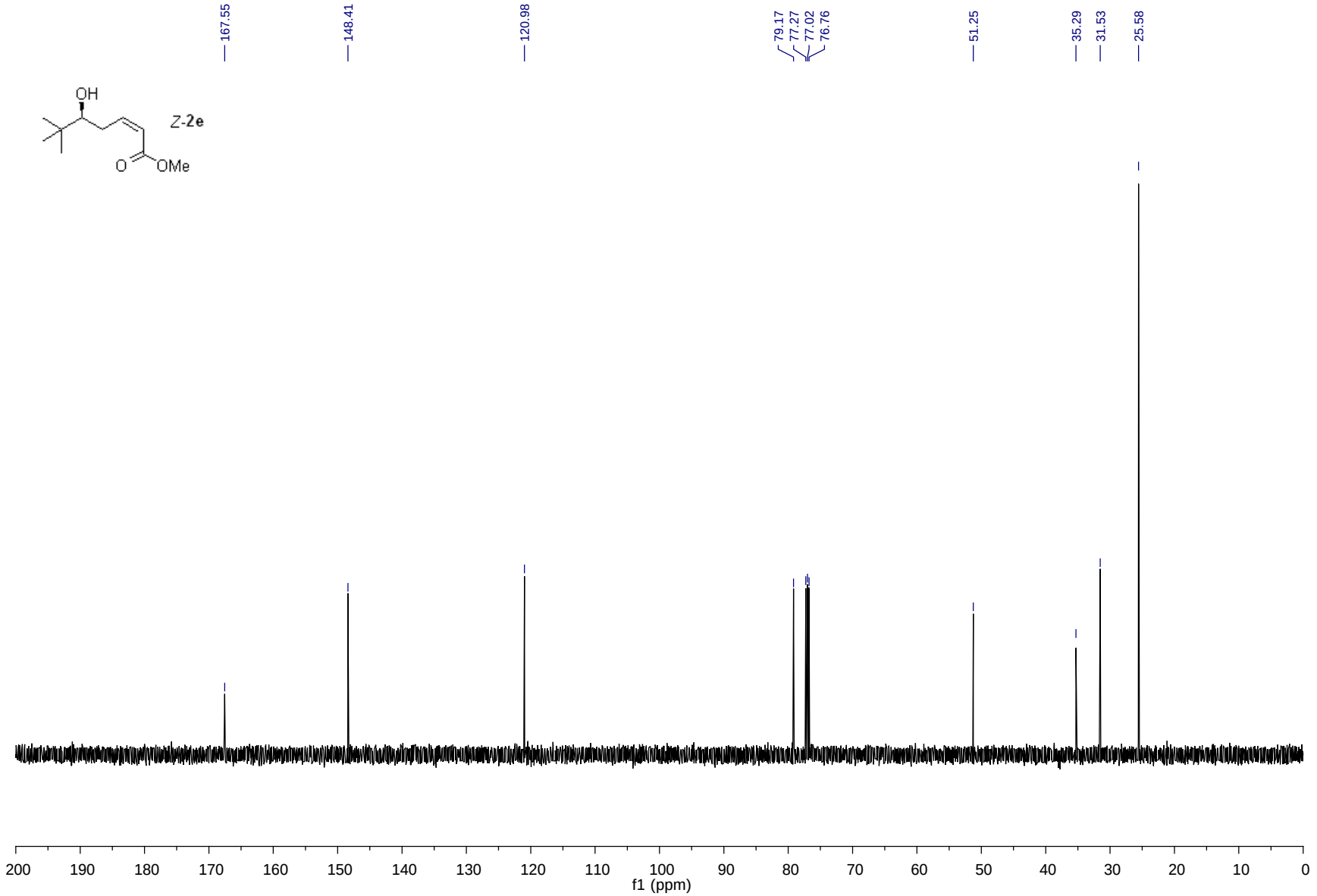
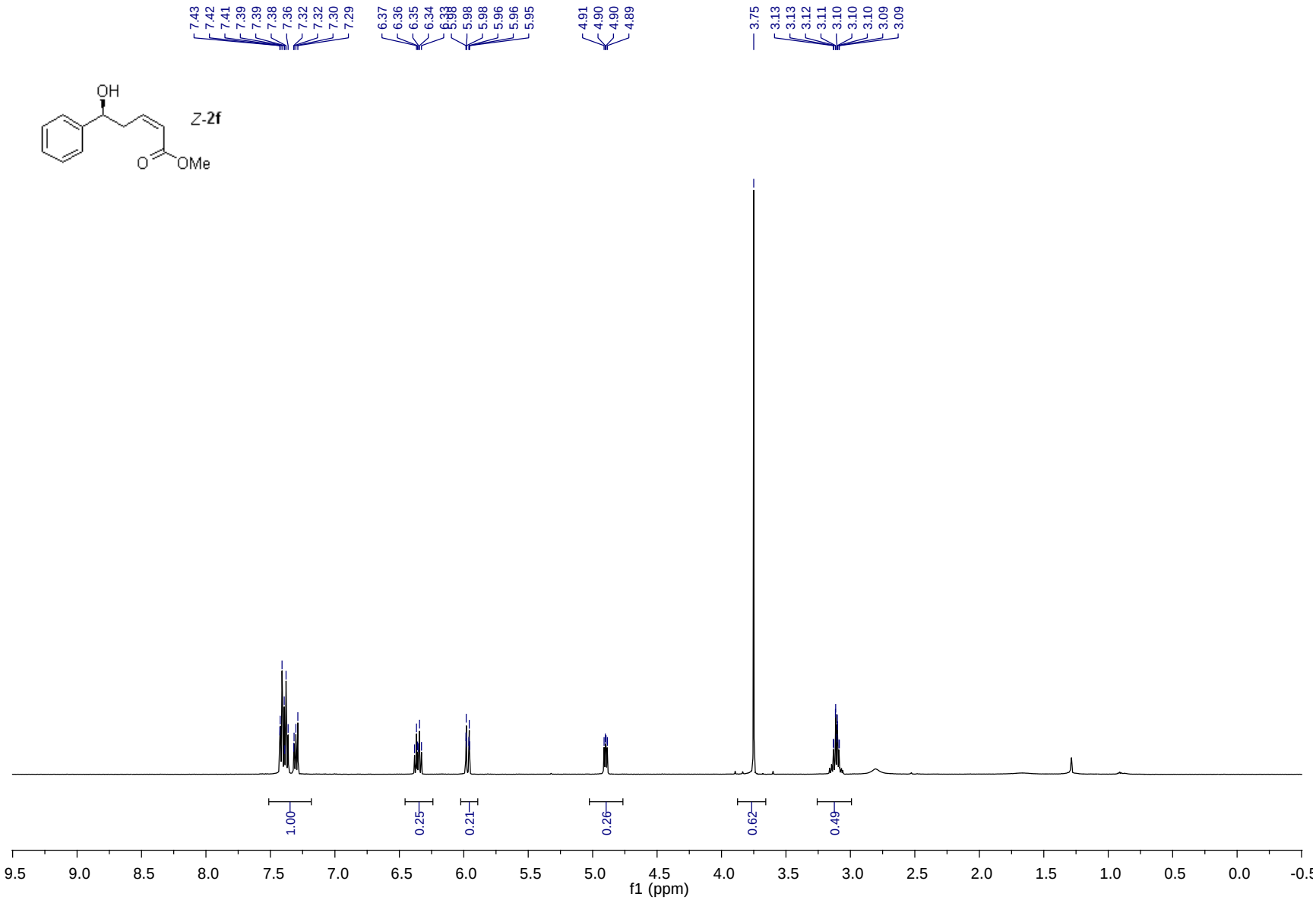
147.44
121.09
77.28
77.03
76.77
75.55
51.22
43.92
33.72
28.97
28.08
26.45
26.21
26.08
OH
Z-2d
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Z-2e
O
OMe
7.27
6.46
6.44
6.43
6.43
6.42
6.40
5.93
5.91
3.71
3.32
3.32
3.30
3.30
2.76
2.76
2.74
2.74
2.73
2.73
2.72
2.72
1.00
0.94
10.60
10.00
26.94
9.64
20.10
86.45
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)


167.55
148.41
120.98
79.17
77.27
77.02
76.76
51.25
35.29
31.53
25.58
OH
Z-2e
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.43
7.42
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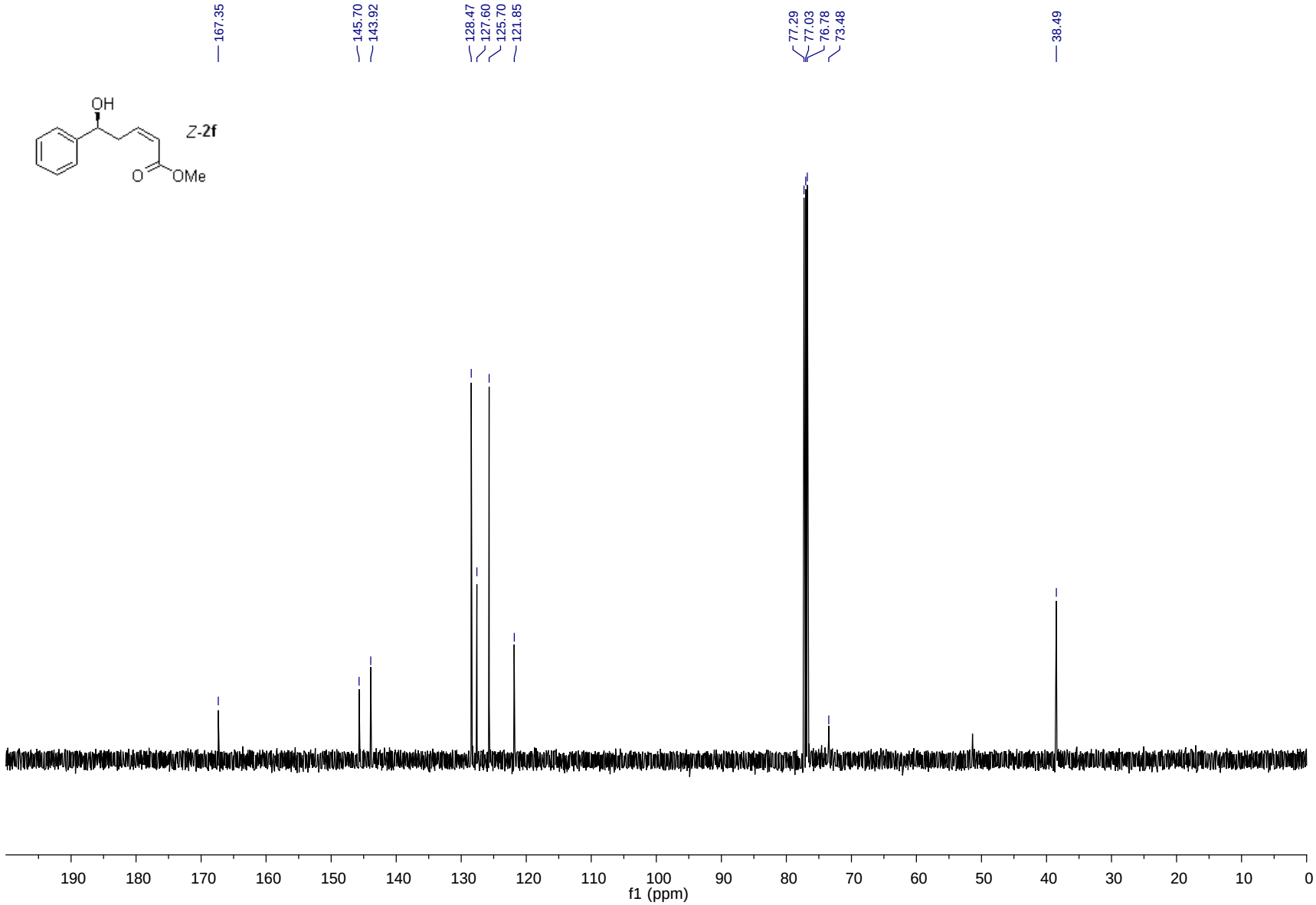
7.38
7.36
7.32
7.32
7.30
7.29
6.37
6.36
6.35
6.34
5.98
5.98
5.96
5.96
5.95
4.91
4.90
4.90
4.89
3.75
3.13
3.13
3.12
3.11
3.10
3.10
3.10
3.09
3.09
OH
Z-2f
O
OMe
1.00
0.25
0.21
0.26
0.62
0.49
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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143.92
128.47
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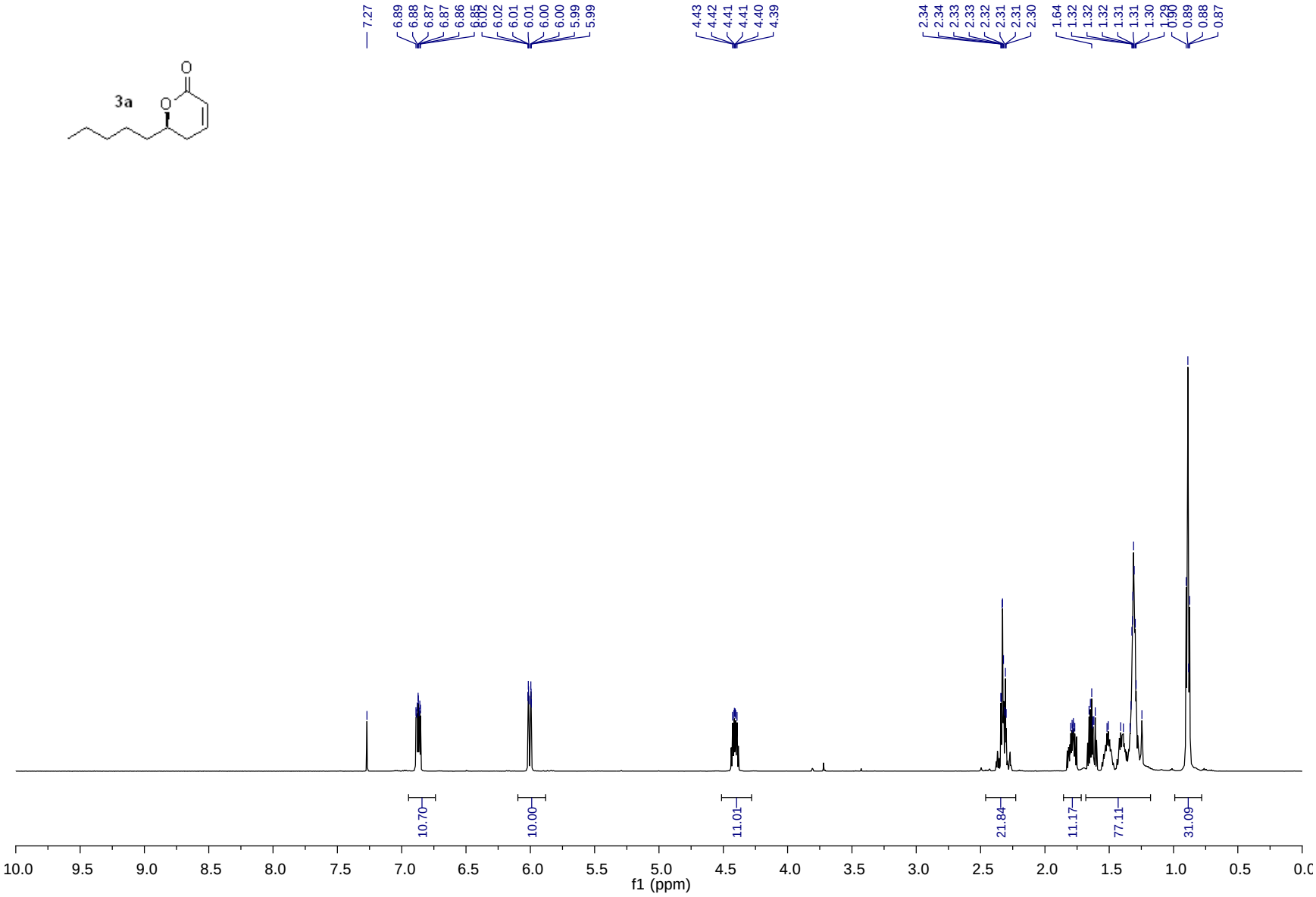
125.70
121.85
77.29
77.03
76.78
73.48
38.49
OH
Z-2f
O
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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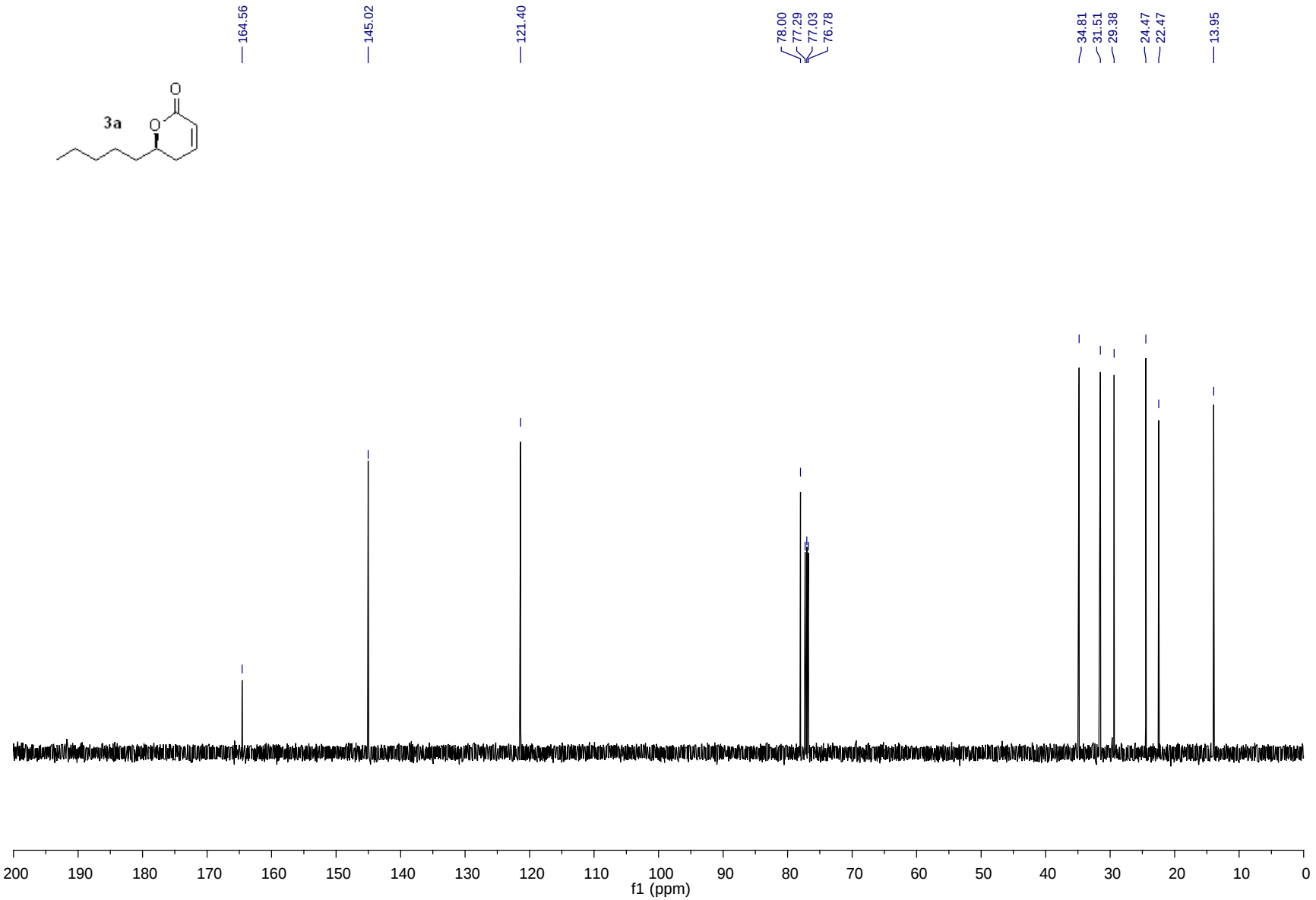
6.88
6.87
6.87
6.86
6.85
6.02
6.02
6.01
6.01
6.00
6.00
5.99
5.99
4.43
4.42
4.41
4.41
4.40
4.39
2.34
2.34
2.33
2.33
2.32
2.31
2.31
2.30
1.64
1.32
1.32
1.32
1.31
1.31
1.30
0.90
0.89
0.88
0.87
3a
O
O
10.70
10.00
11.01
21.84
11.17
77.11
31.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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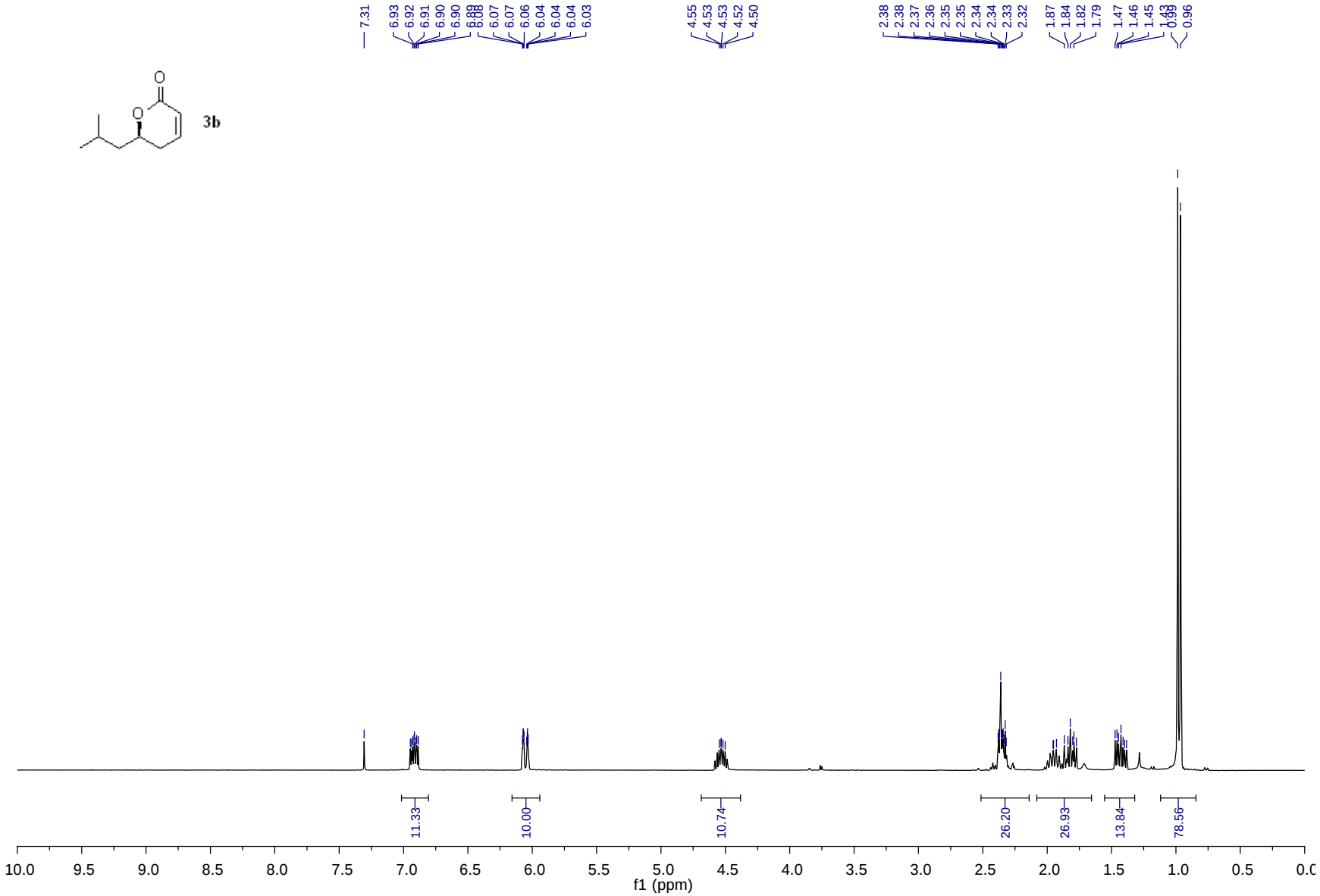
77.03
76.78
34.81
31.51
29.38
24.47
22.47
13.95
3a
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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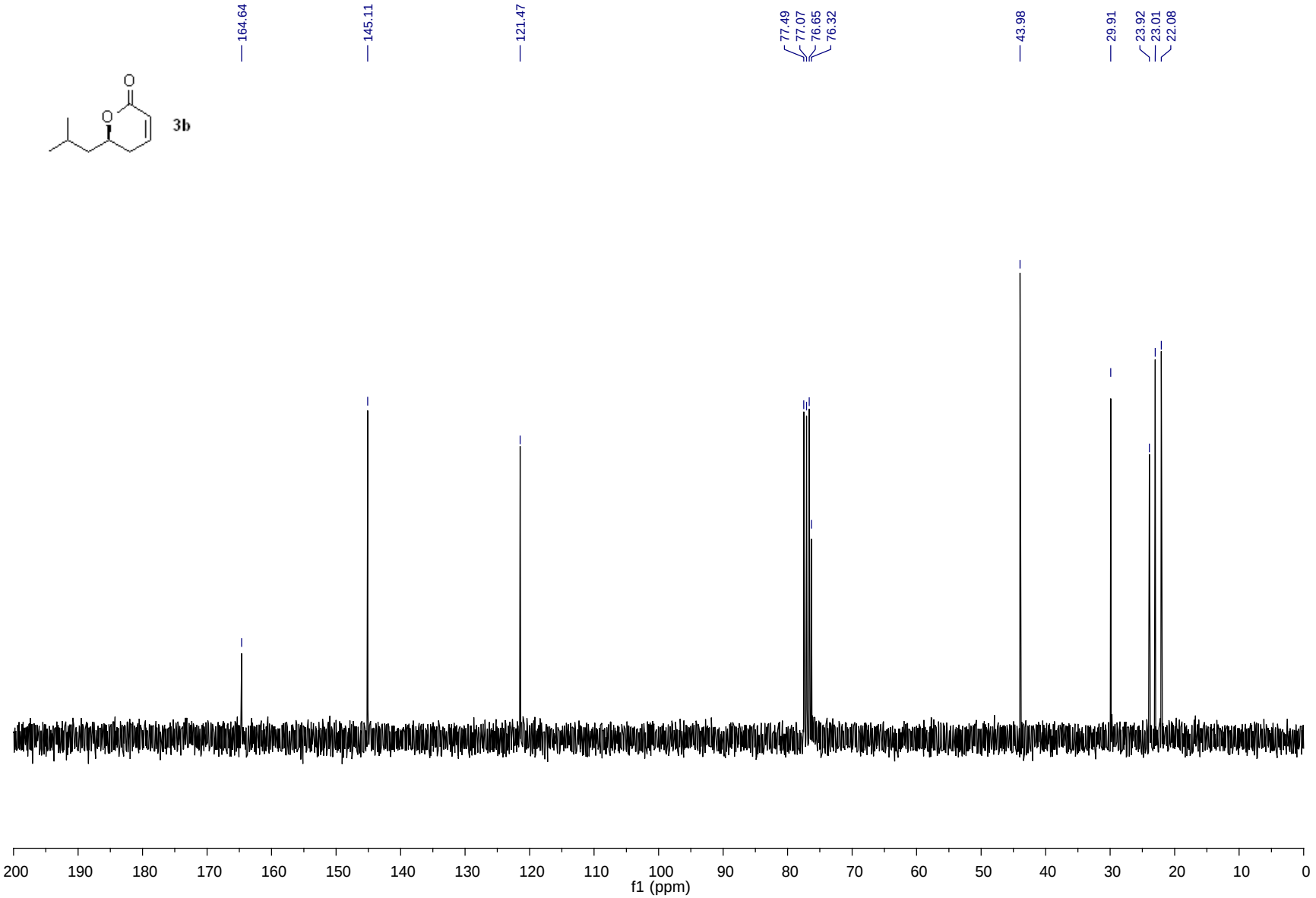
6.90
6.89
6.08
6.07
6.07
6.06
6.04
6.04
6.04
6.03
4.55
4.53
4.53
4.52
4.50
2.38
2.38
2.37
2.36
2.35
2.35
2.34
2.34
2.33
2.32
1.87
1.84
1.82
1.79
1.47
1.46
1.45
1.43
0.99
0.96
3b
11.33
10.00
10.74
26.20
26.93
13.84
78.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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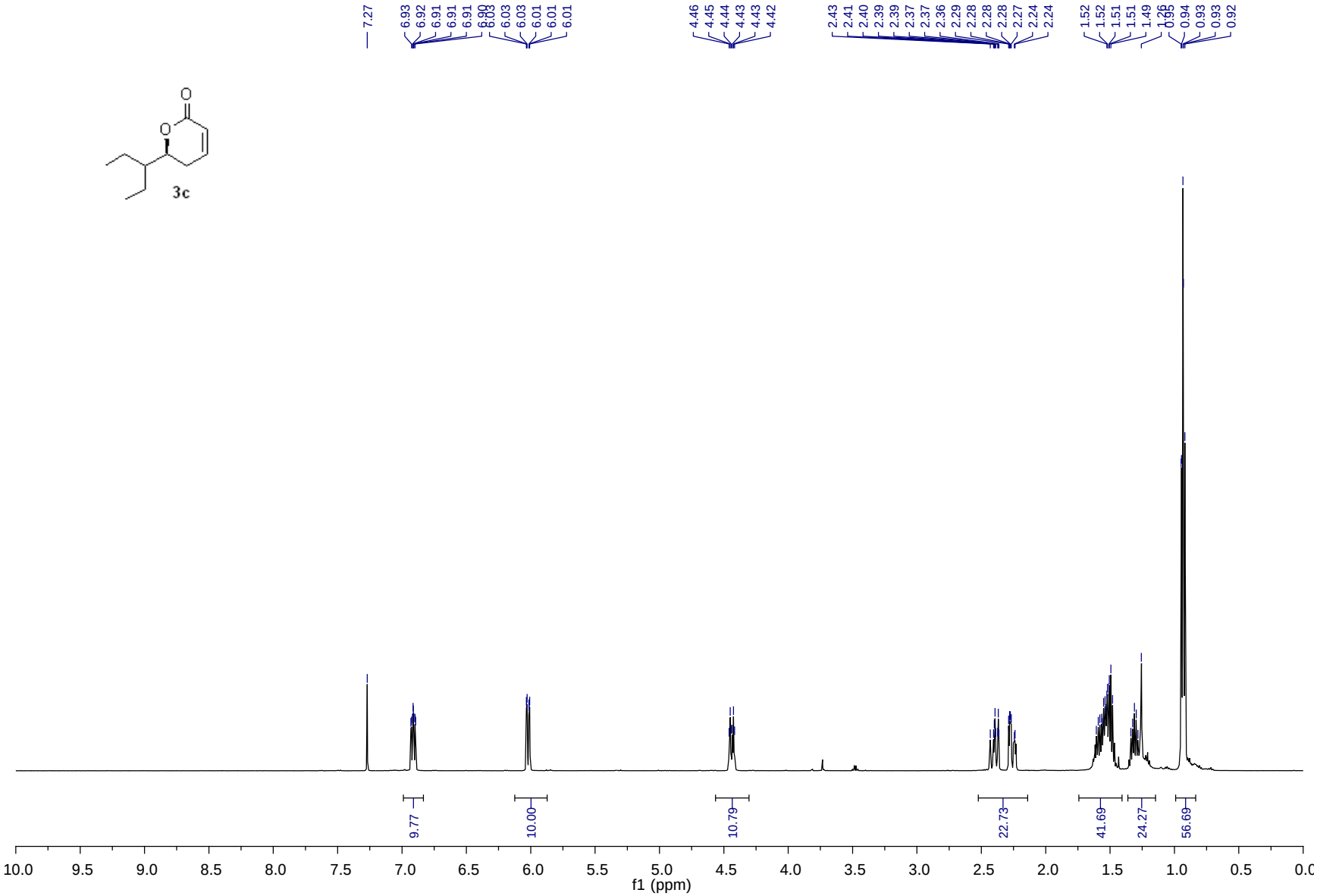
77.07
76.65
76.32
43.98
29.91
23.92
23.01
22.08
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.93
6.92
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6.91
6.90
6.03
6.03
6.03
6.01
6.01
6.01
4.46
4.45
4.44
4.43
4.43
4.42
2.43
2.41
2.40
2.39
2.39
2.37
2.37
2.36
2.29
2.28
2.28
2.28
2.27
2.24
2.24
1.52
1.52
1.51
1.51
1.49
1.26
0.95
0.94
0.93
0.93
0.92
O
O
3c
9.77
10.00
10.79
22.73
41.69
24.27
56.69
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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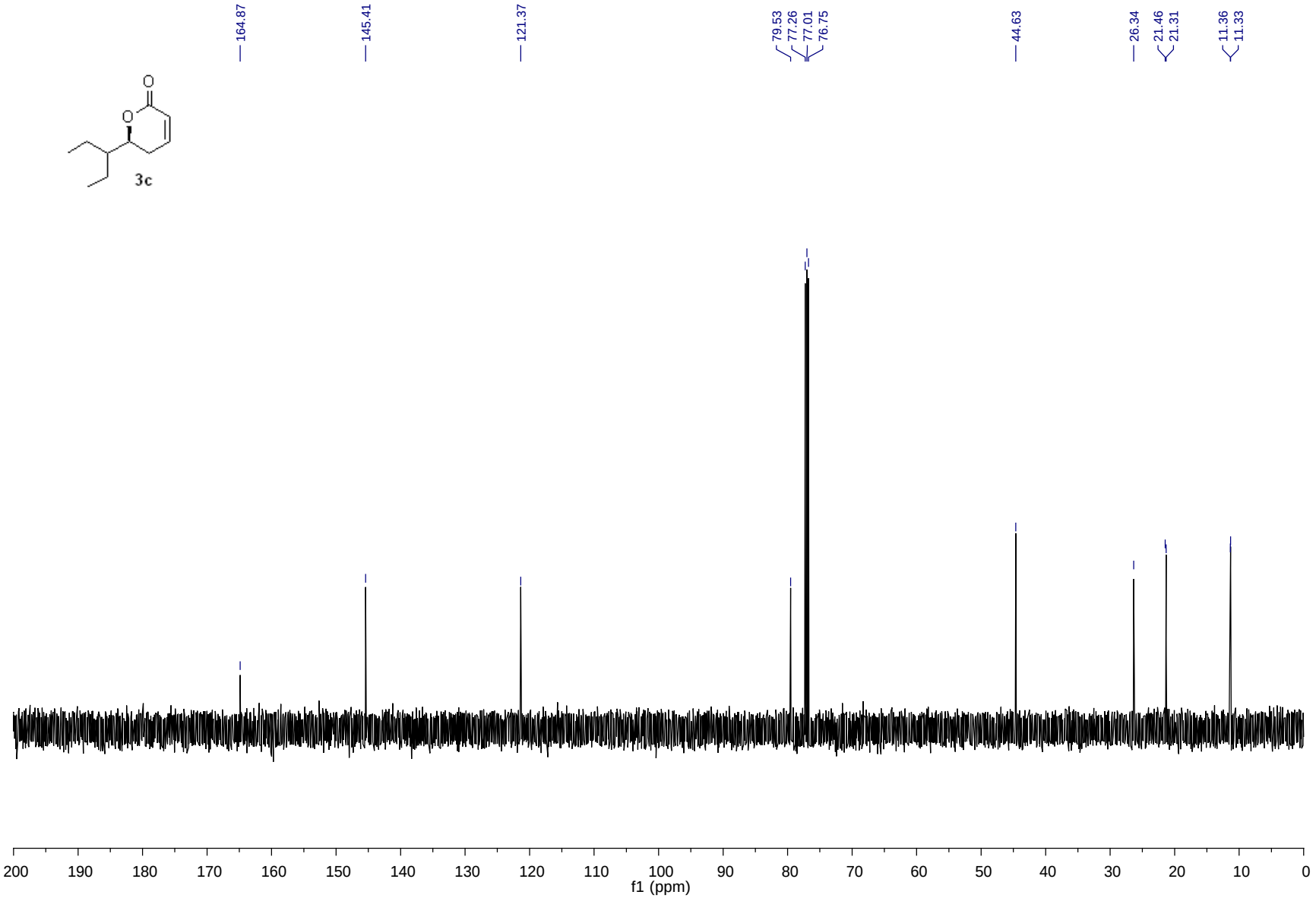
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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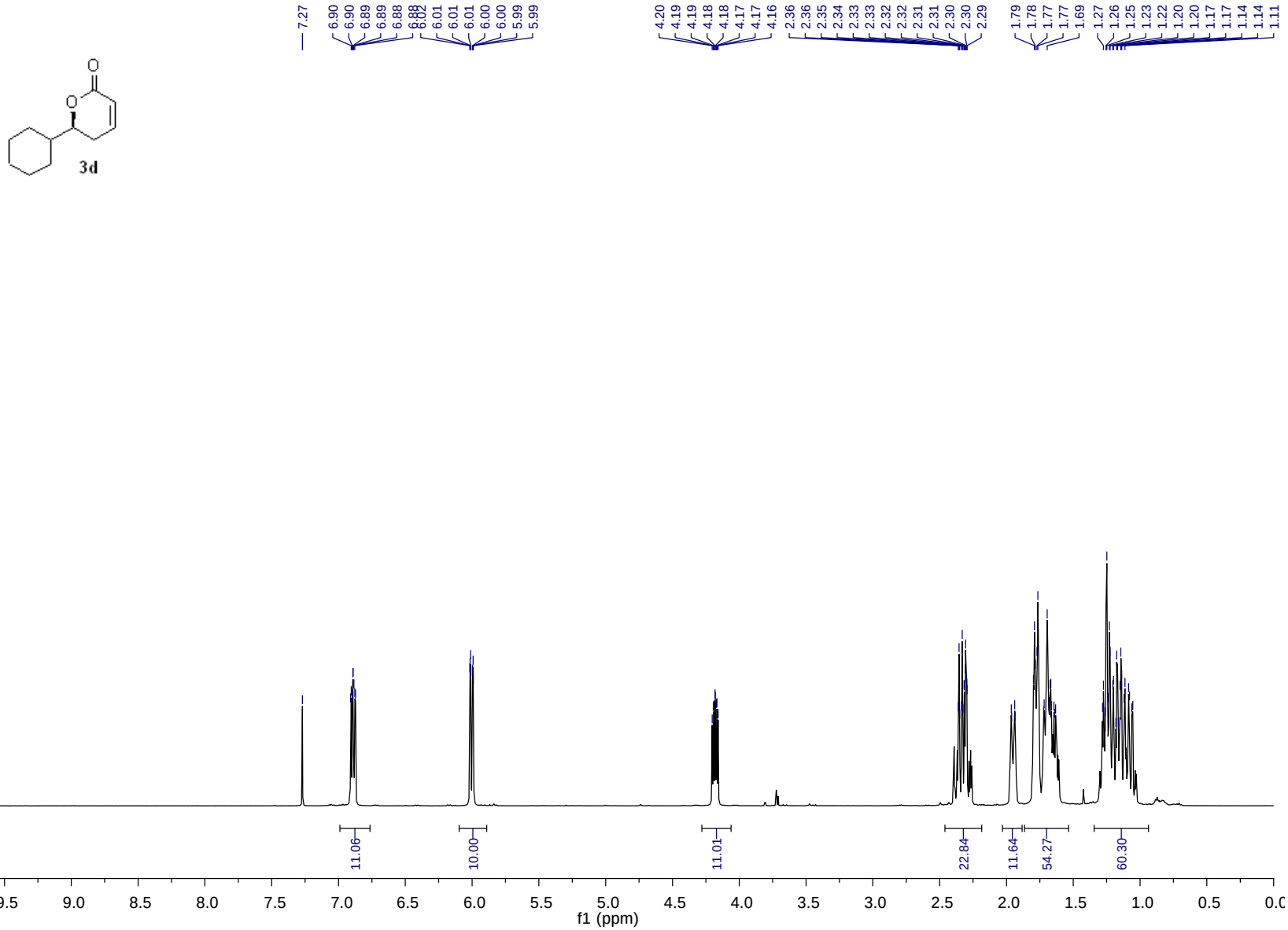
79.53
77.26
77.01
76.75
44.63
26.34
21.46
21.31
11.36
11.33
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.90
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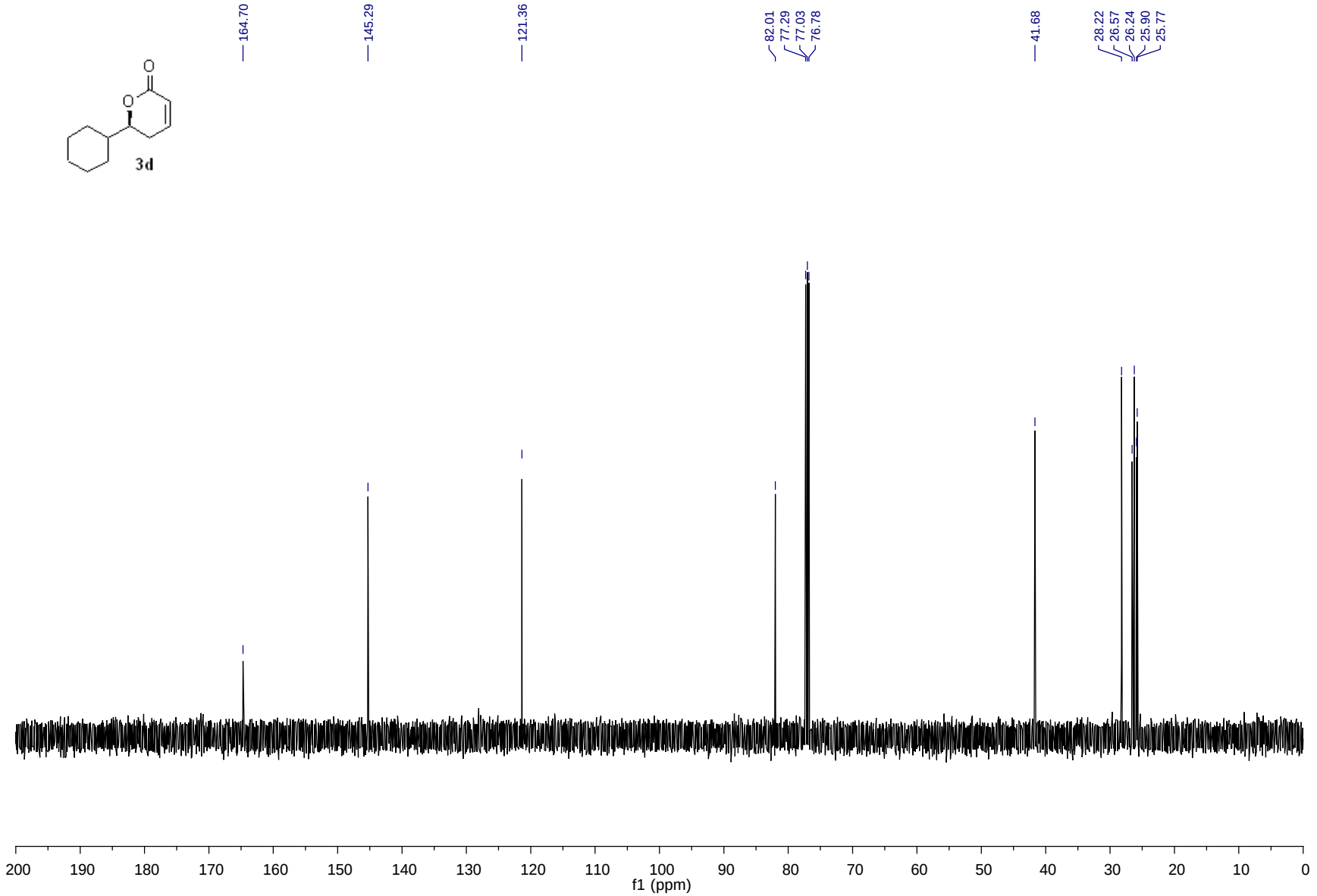
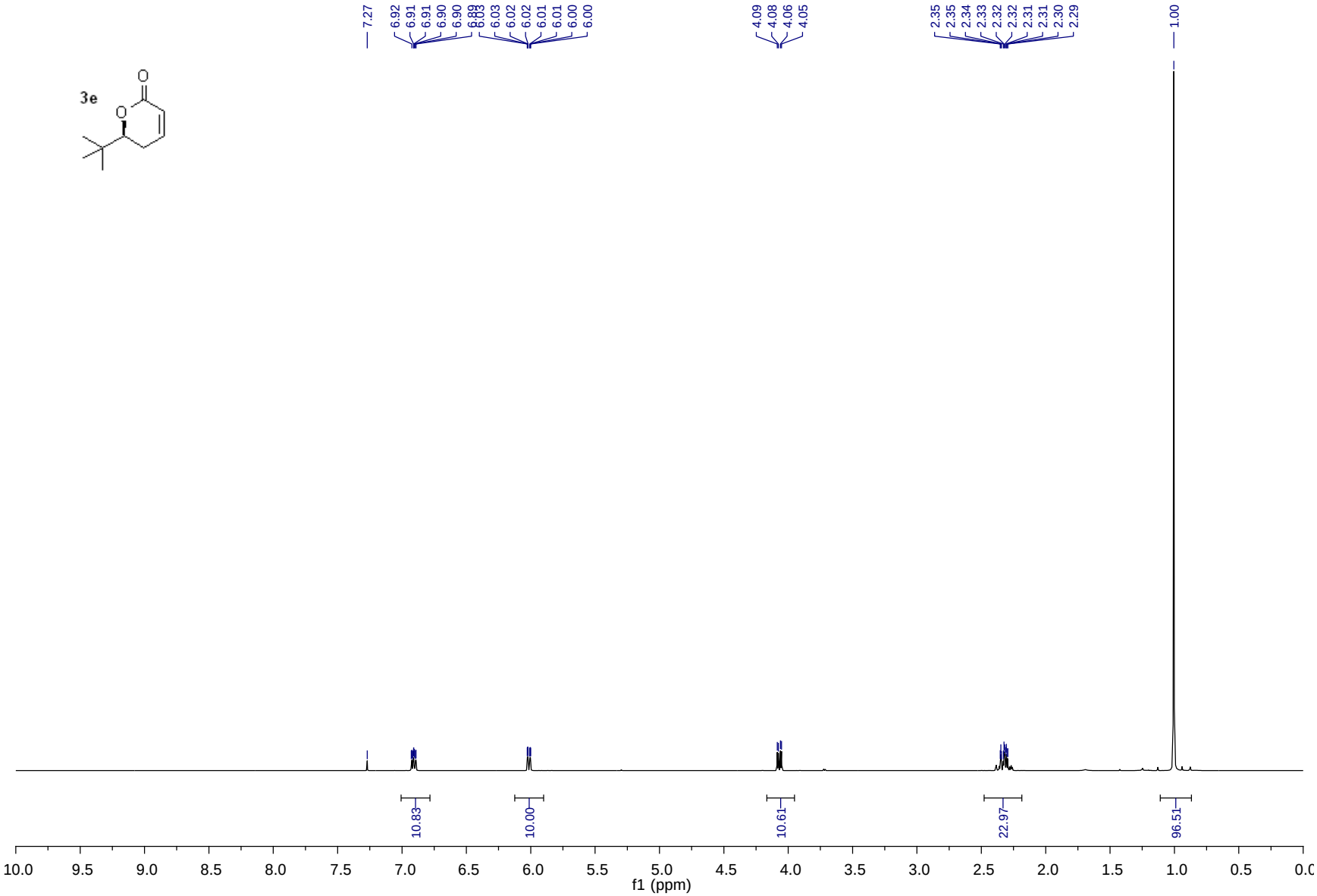
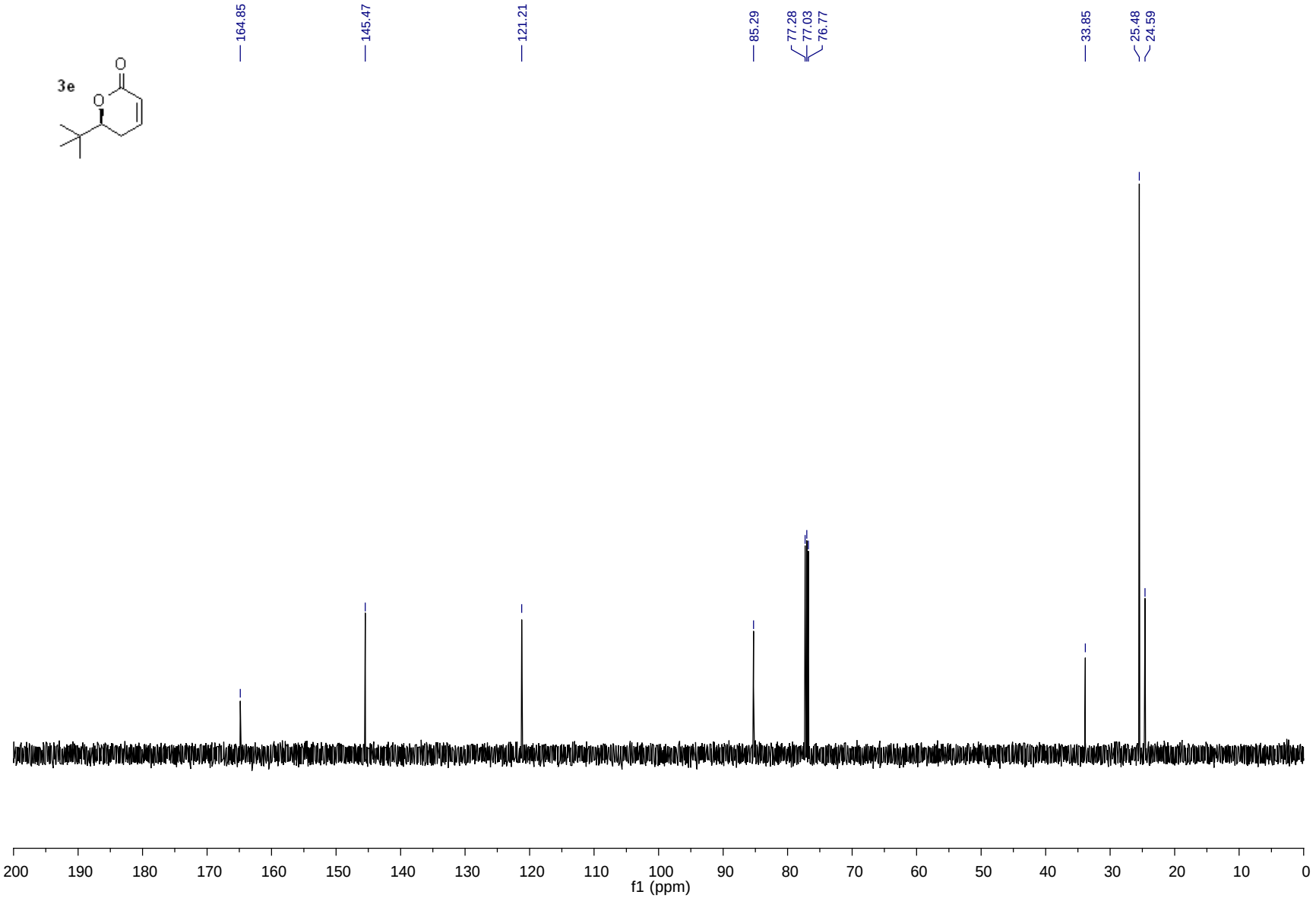
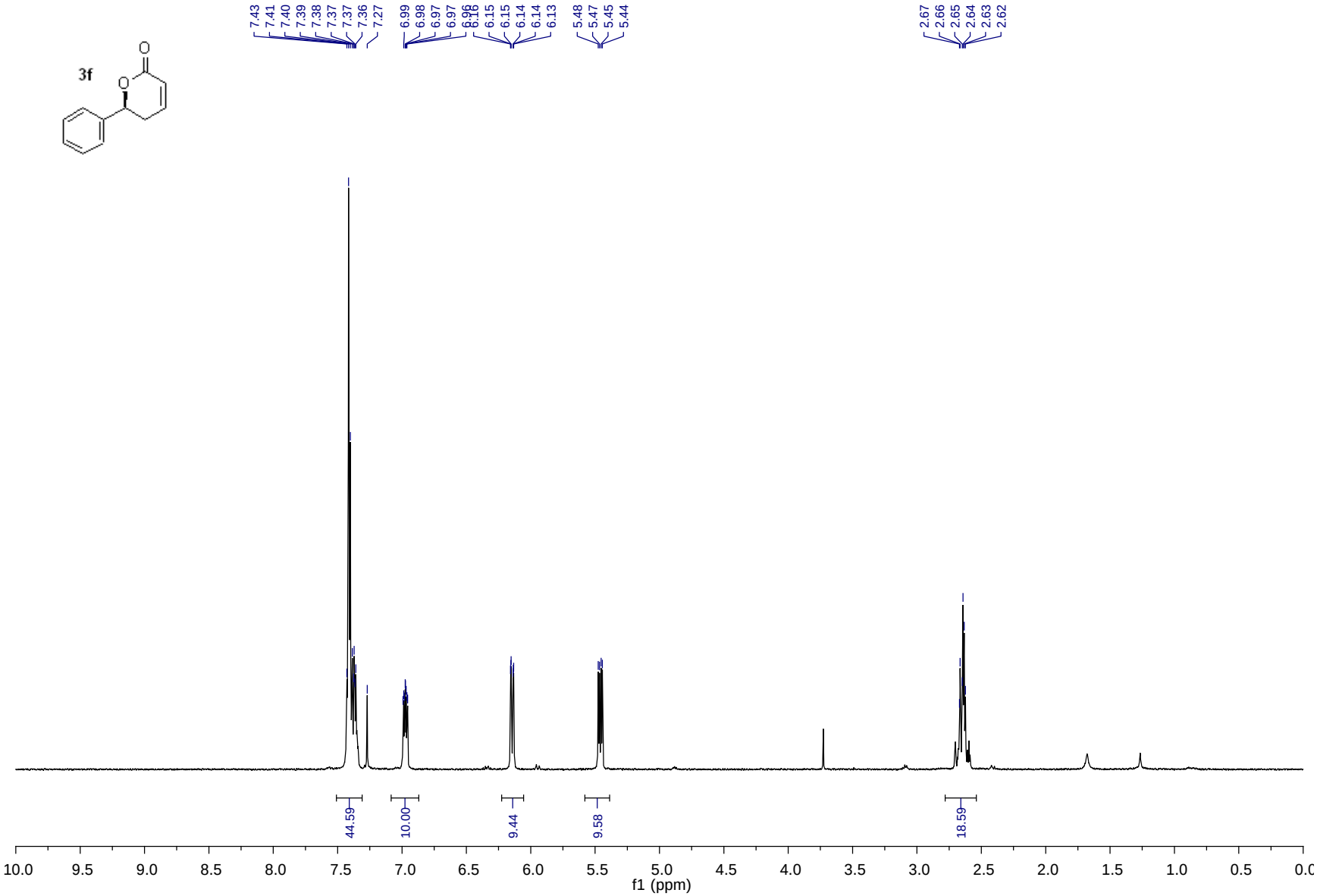
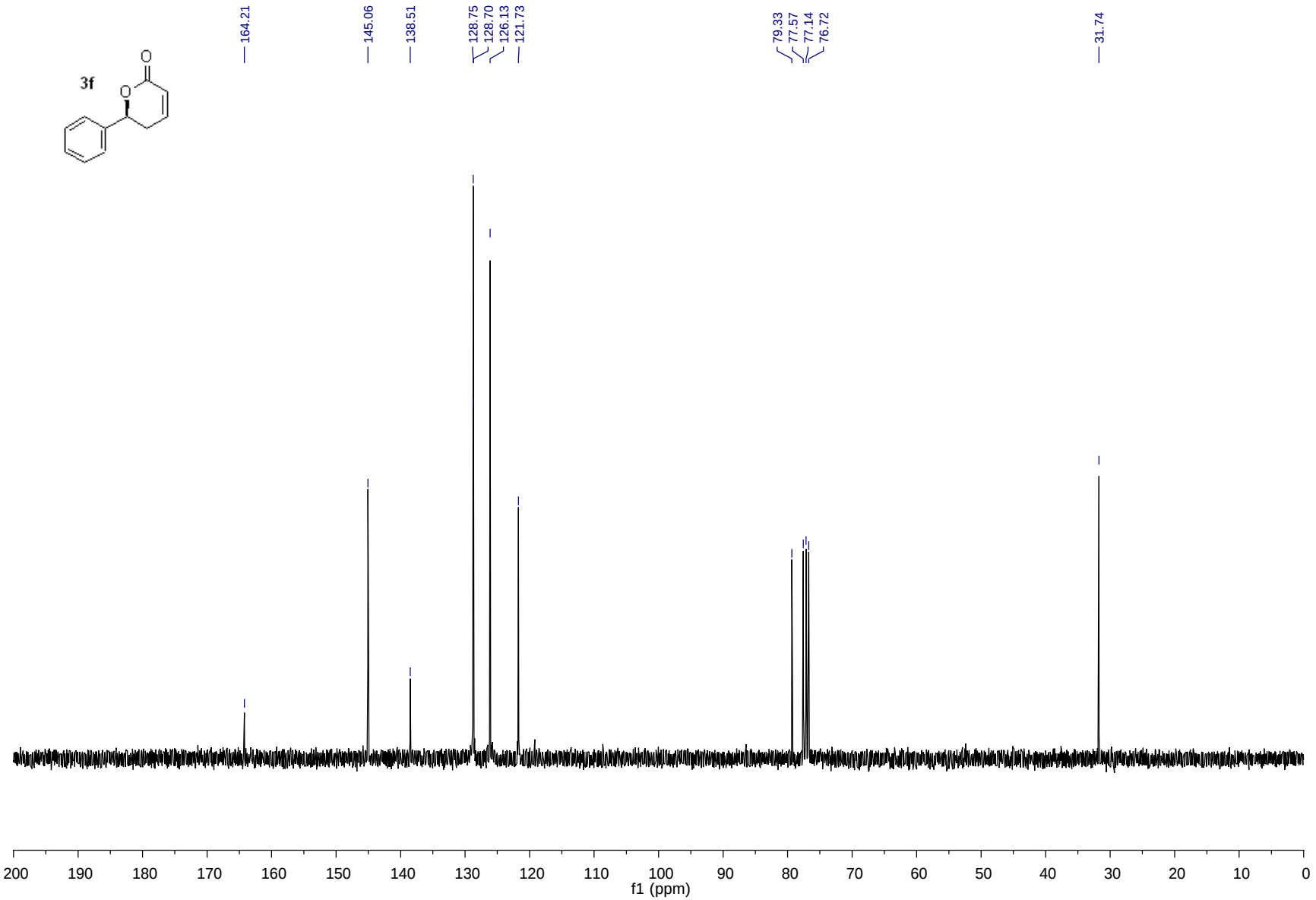
6.89
6.88
6.88
6.02
6.01
6.01
6.00
6.00
5.99
5.99
4.20
4.19
4.19
4.18
4.18
4.17
4.17
4.16
2.36
2.36
2.35
2.34
2.33
2.33
2.32
2.32
2.31
2.31
2.30
2.30
2.29
1.79
1.78
1.77
1.77
1.69
1.27
1.26
1.25
1.23
1.22
1.20
1.20
1.17
1.17
1.14
1.14
1.11
O
O
3d
11.06
10.00
11.01
22.84
11.64
54.27
60.30
10.0
9.5
9.0
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)

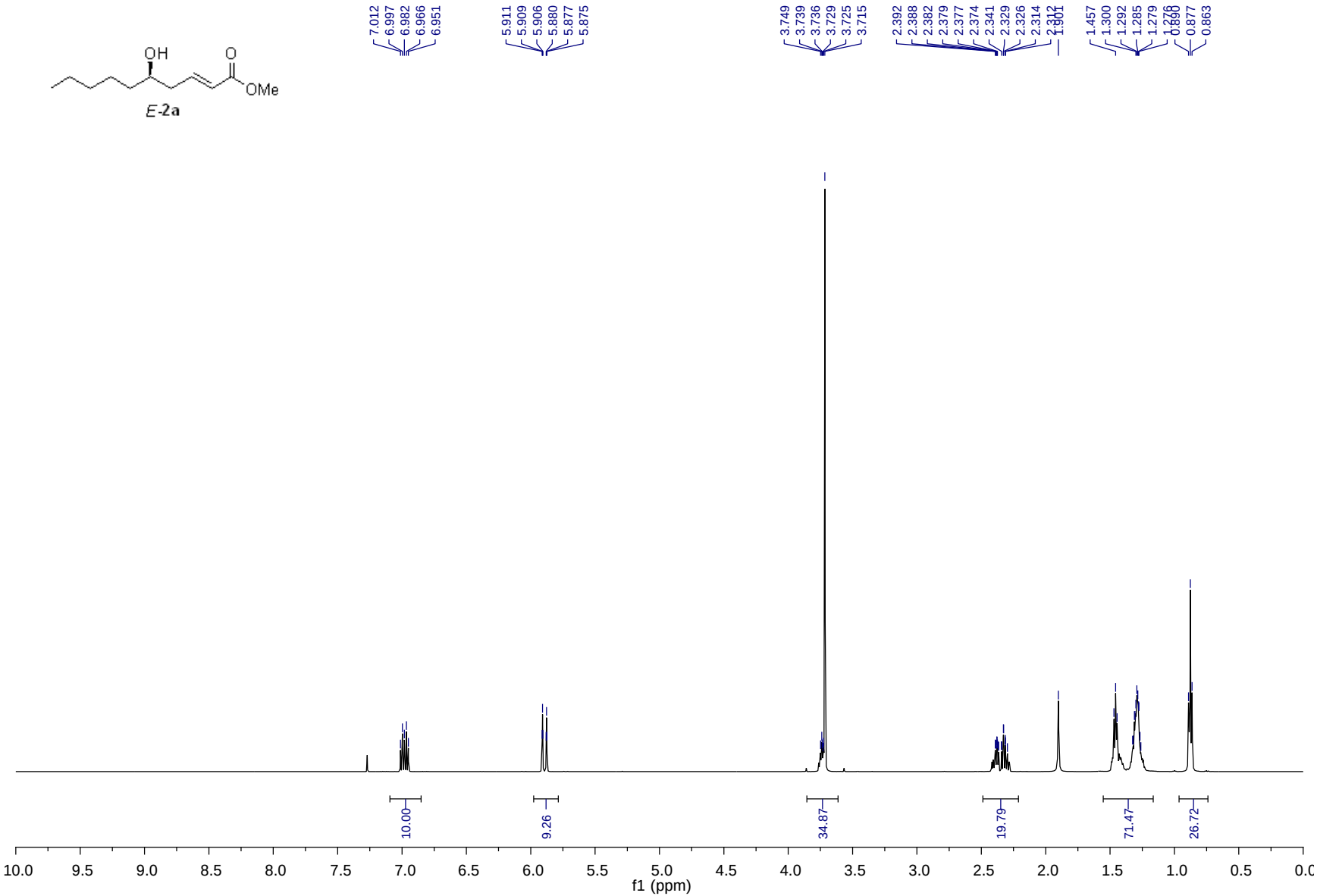

164.70
145.29
121.36
82.01
77.29
77.03
76.78
41.68
28.22
26.57
26.24
25.90
25.77
O
O
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

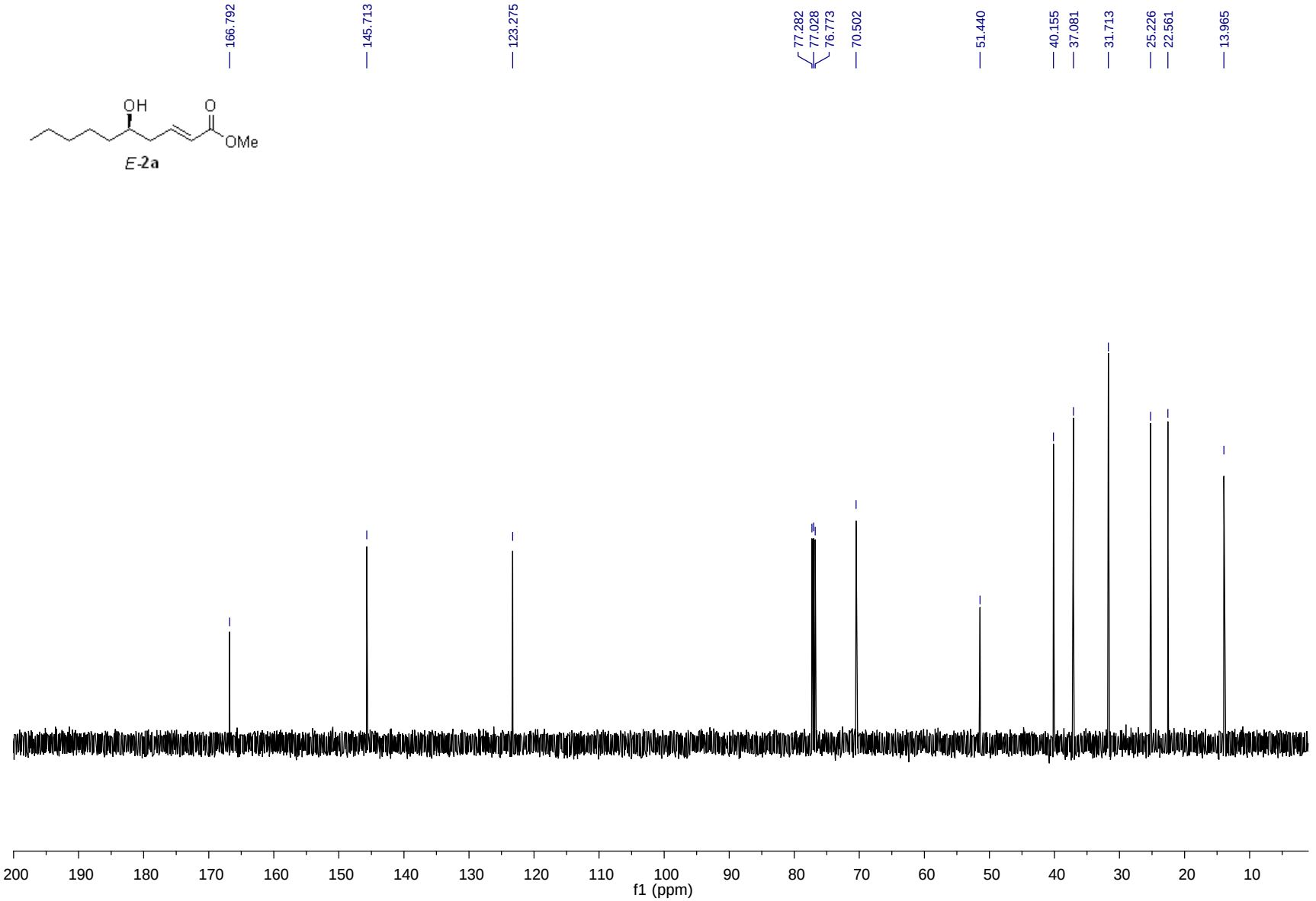

3e
7.27
6.92
6.91
6.91
6.90
6.90
6.89
6.03
6.02
6.02
6.01
6.00
6.00
4.09
4.08
4.06
4.05
2.35
2.35
2.34
2.33
2.32
2.32
2.31
2.31
2.30
2.29
1.00
10.83
10.00
10.61
22.97
96.51
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


3e
164.85
145.47
121.21
85.29
77.28
77.03
76.77
33.85
25.48
24.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3f
7.43
7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.27
6.99
6.98
6.97
6.97
6.16
6.15
6.15
6.14
6.14
6.13
5.48
5.47
5.45
5.44
2.67
2.66
2.65
2.64
2.63
2.62
44.59
10.00
9.44
9.58
18.59
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
0.0
f1 (ppm)


3f
164.21
145.06
138.51
128.75
128.70
126.13
121.73
79.33
77.57
77.14
76.72
31.74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
O
OMe
E-2a
7.012
6.997
6.982
6.966
6.951
5.911
5.909
5.906
5.880
5.877
5.875
3.749
3.739
3.736
3.729
3.725
3.715
2.392
2.388
2.382
2.379
2.377
2.374
2.341
2.329
2.326
2.314
1.457
1.300
1.292
1.285
1.279
0.890
0.877
0.863
10.00
9.26
34.87
19.79
71.47
26.72
f1 (ppm)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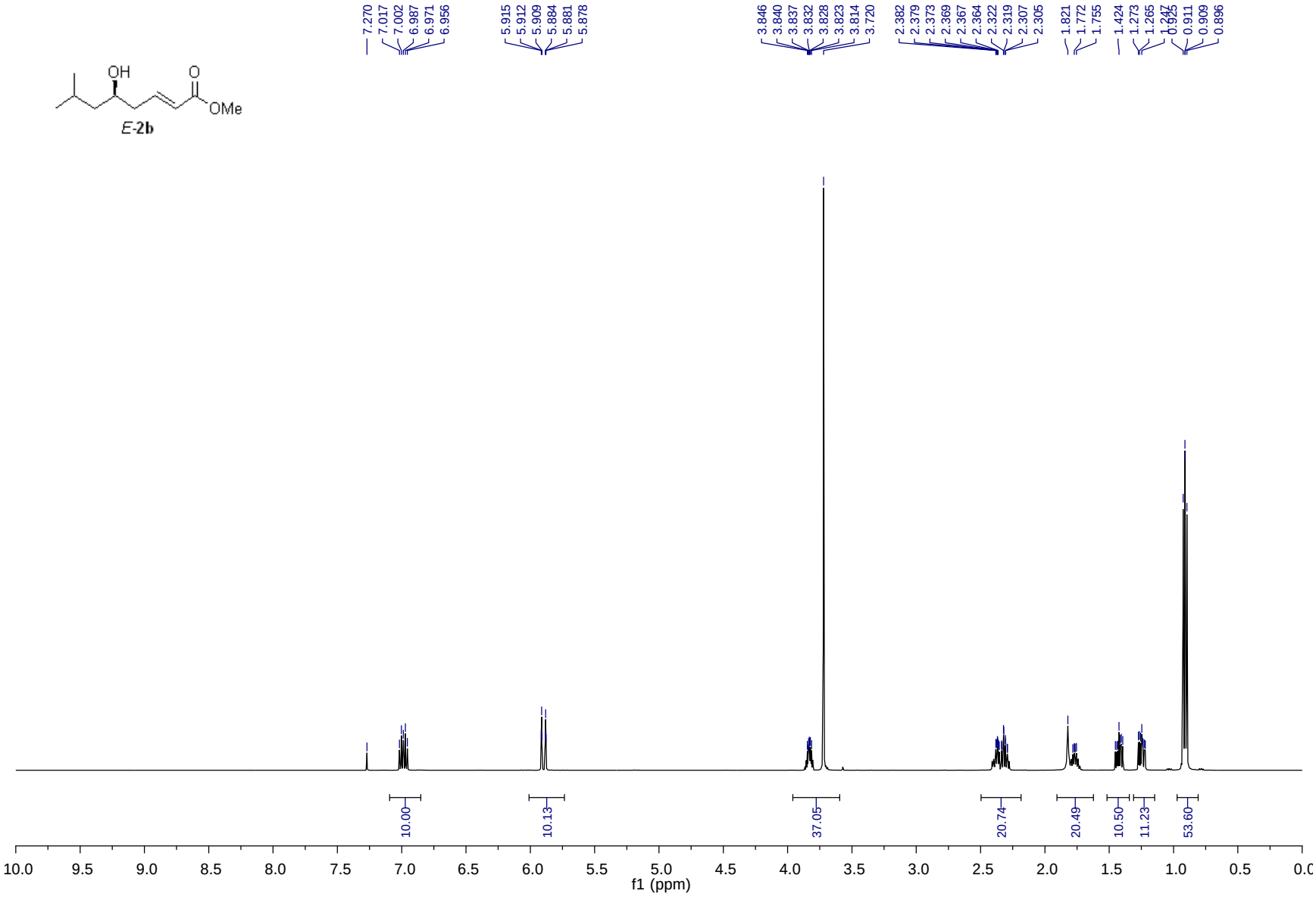
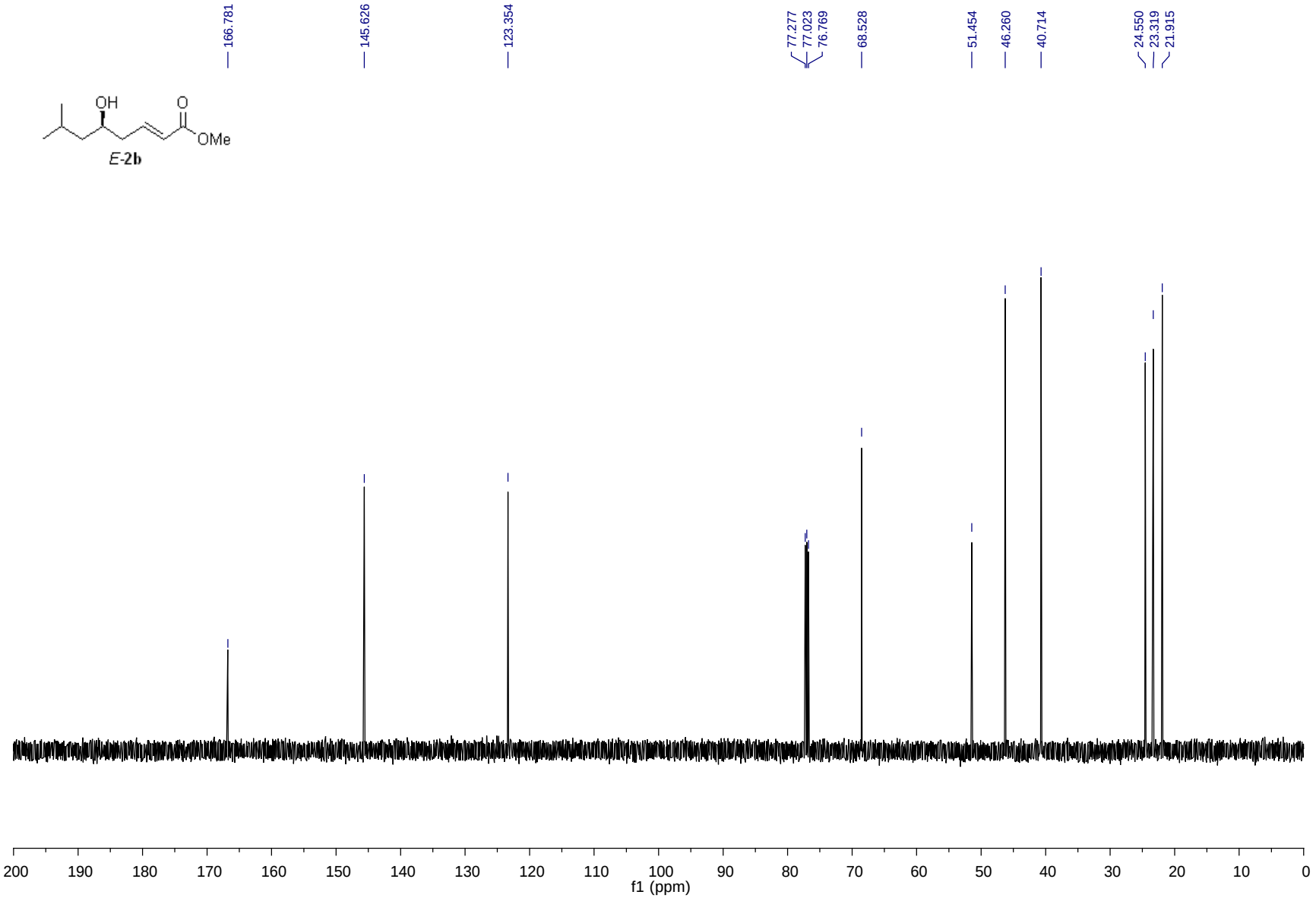
145.713
123.275
77.282
77.028
76.773
70.502
51.440
40.155
37.081
31.713
25.226
22.561
13.965
OH
O
OMe
E-2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.270
7.017
7.002
6.987
6.971
6.956
5.915
5.912
5.909
5.884
5.881
5.878
3.846
3.840
3.837
3.832
3.828
3.823
3.814
3.720
2.382
2.379
2.373
2.369
2.367
2.364
2.322
2.319
2.307
2.305
1.821
1.772
1.755
1.424
1.273
1.265
0.925
0.911
0.909
0.896
OH
O
OMe
E-2b
10.00
10.13
37.05
20.74
20.49
10.50
11.23
53.60
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)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145.626
123.354
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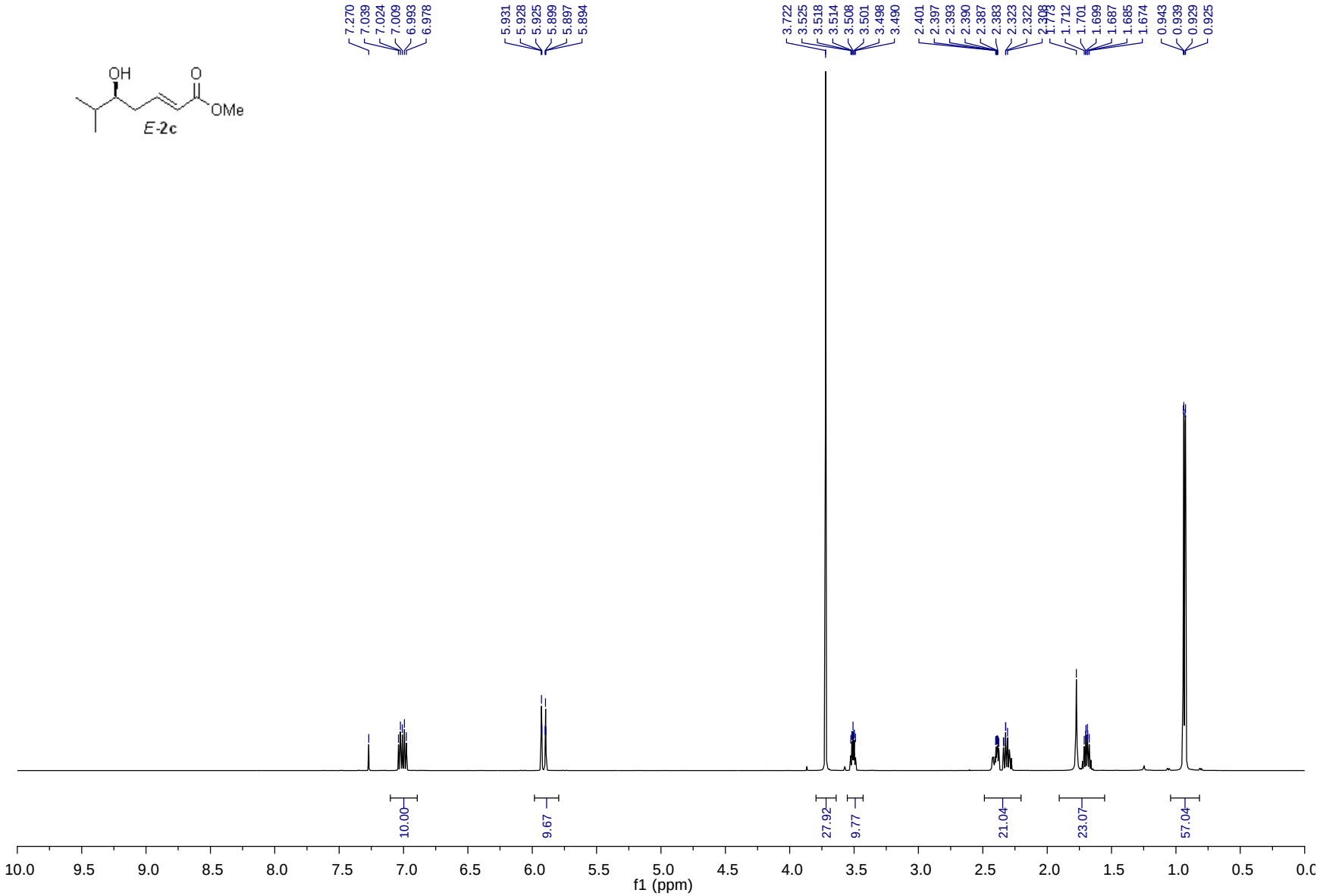
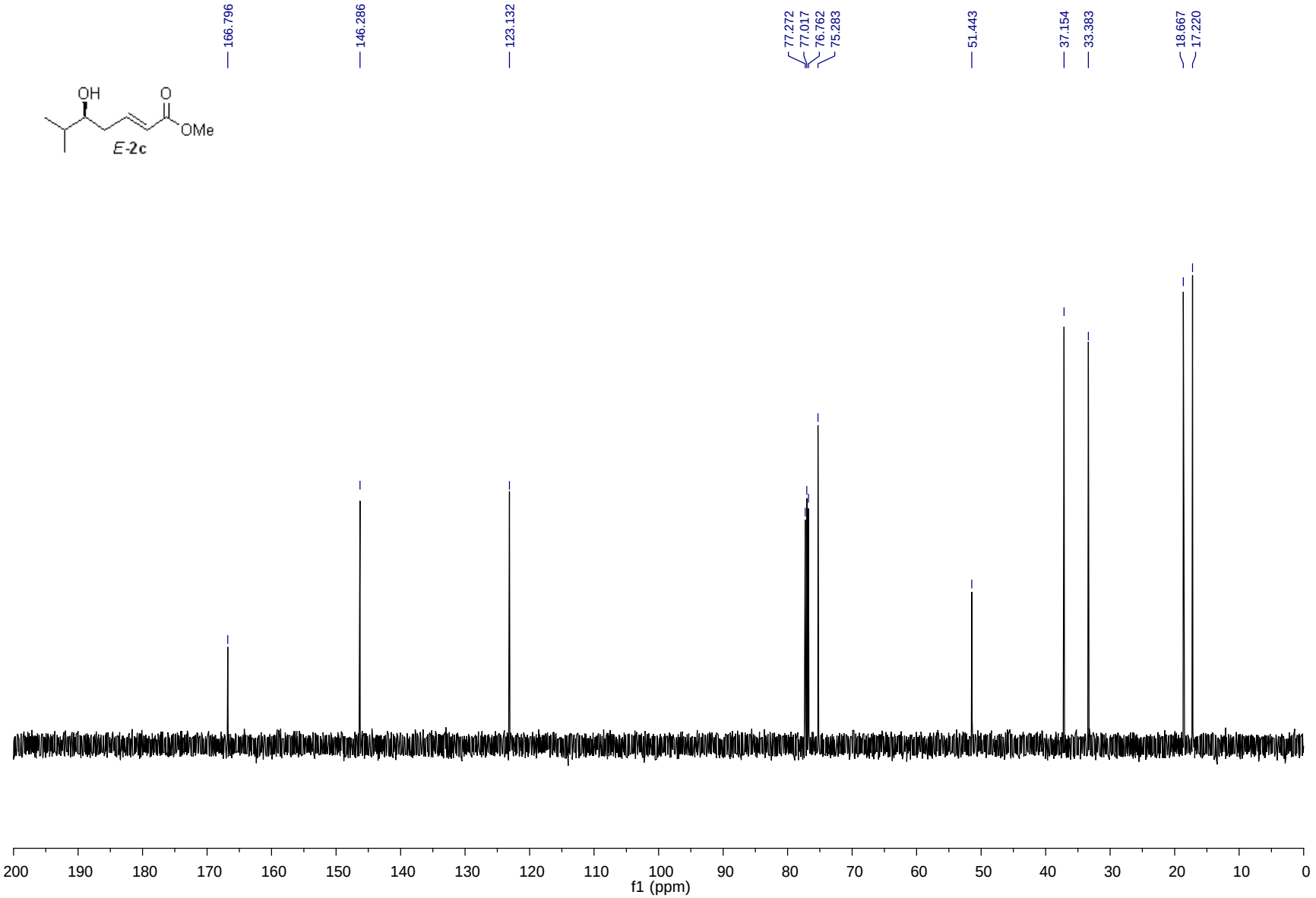
77.023
76.769
68.528
51.454
46.260
40.714
24.550
23.319
21.915
OH
O
OMe
E-2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.270
7.039
7.024
7.009
6.993
6.978
5.931
5.928
5.925
5.899
5.897
5.894
3.722
3.525
3.518
3.514
3.508
3.501
3.498
3.490
2.401
2.397
2.393
2.390
2.387
2.383
2.323
2.322
1.773
1.712
1.701
1.699
1.687
1.685
1.674
0.943
0.939
0.929
0.925
OH
O
OMe
E-2c
10.00
9.67
27.92
9.77
21.04
23.07
57.04
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
0.0
f1 (ppm)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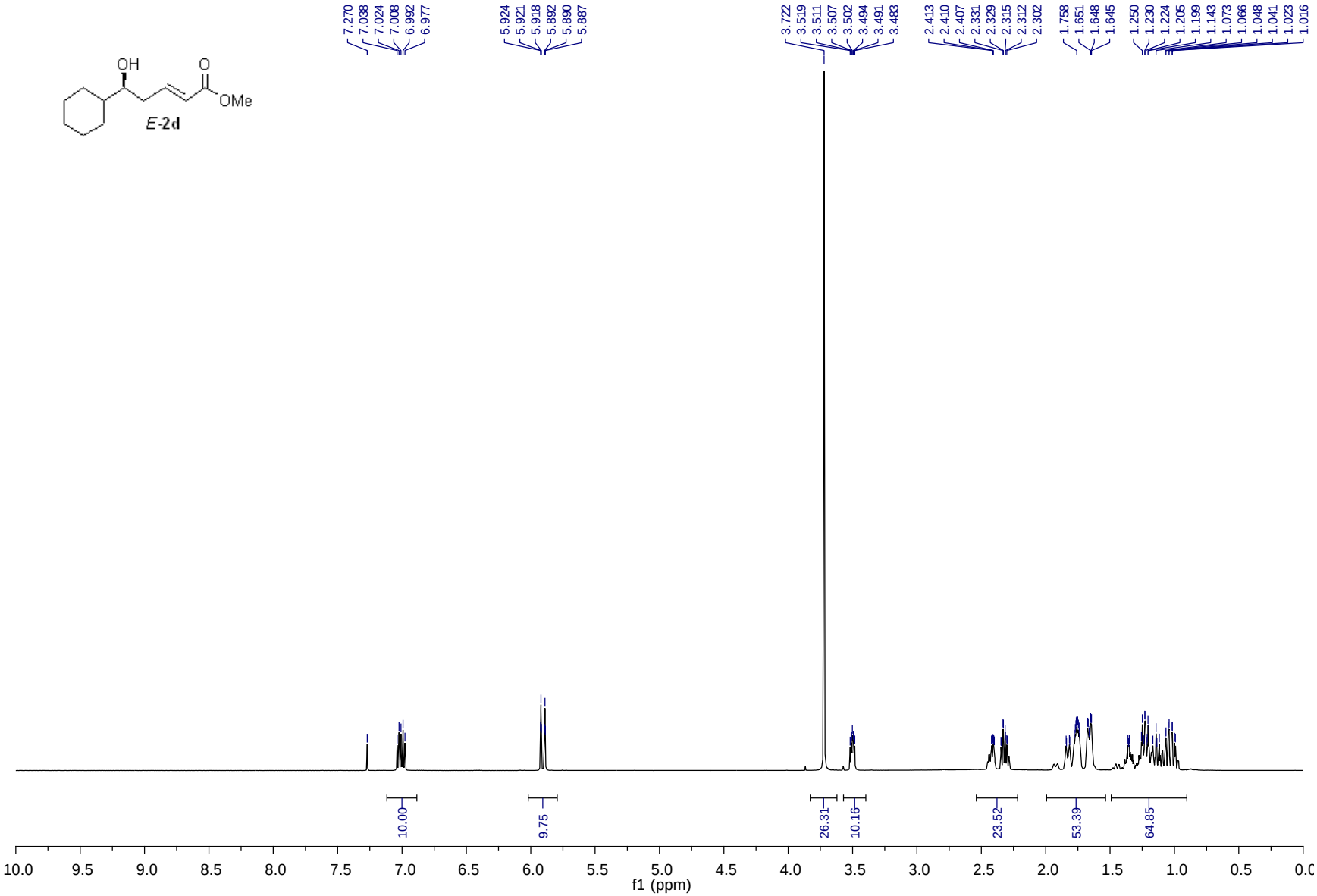
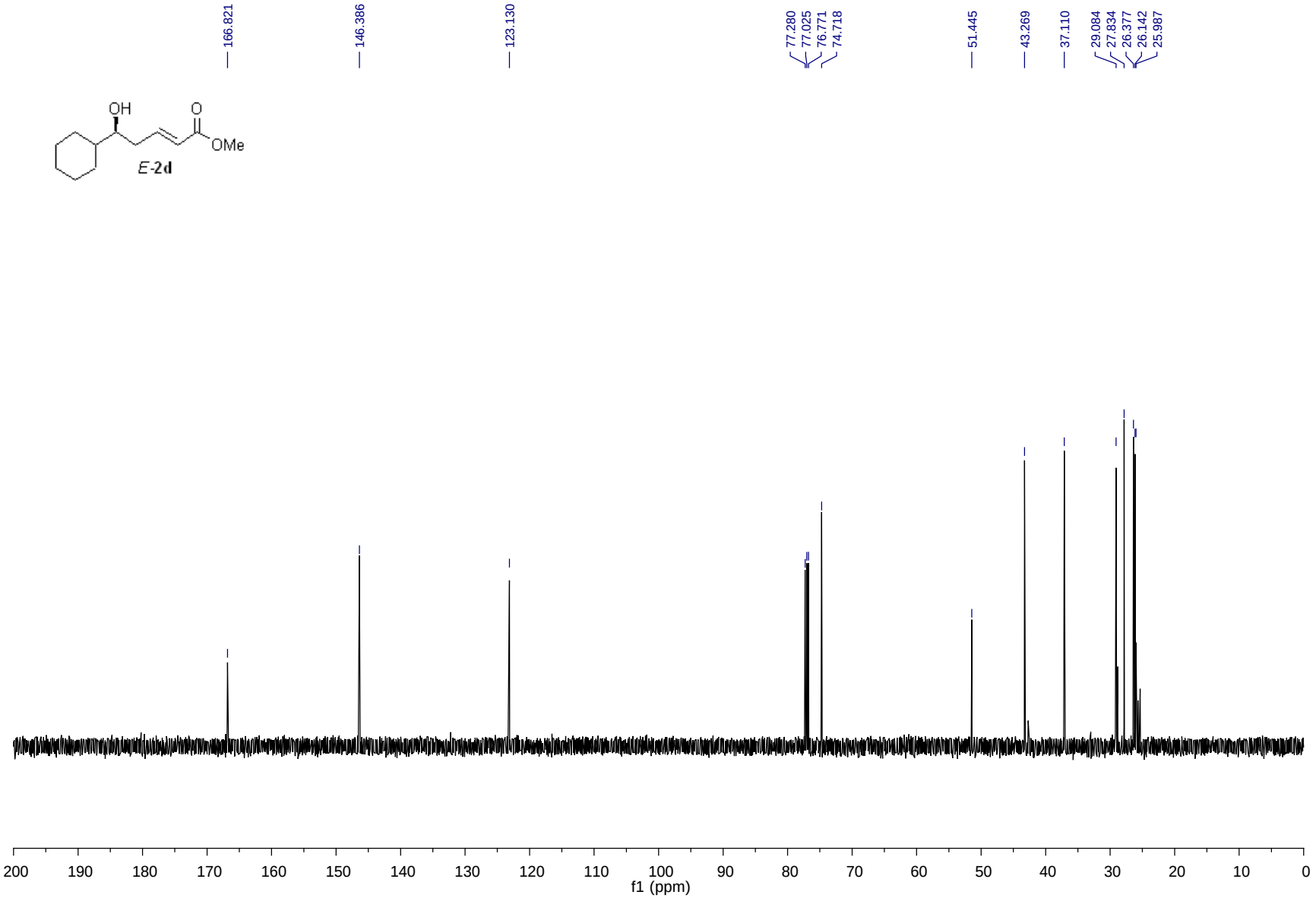
123.132
77.272
77.017
76.762
75.283
51.443
37.154
33.383
18.667
17.220
OH
O
OMe
E-2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
O
OMe
E-2d
7.270
7.038
7.024
7.008
6.992
6.977
5.924
5.921
5.918
5.892
5.890
5.887
3.722
3.519
3.511
3.507
3.502
3.494
3.491
3.483
2.413
2.410
2.407
2.331
2.329
2.315
2.312
2.302
1.758
1.651
1.648
1.645
1.250
1.230
1.224
1.205
1.199
1.143
1.073
1.066
1.048
1.041
1.023
1.016
10.00
9.75
26.31
10.16
23.52
53.39
64.85
f1 (ppm)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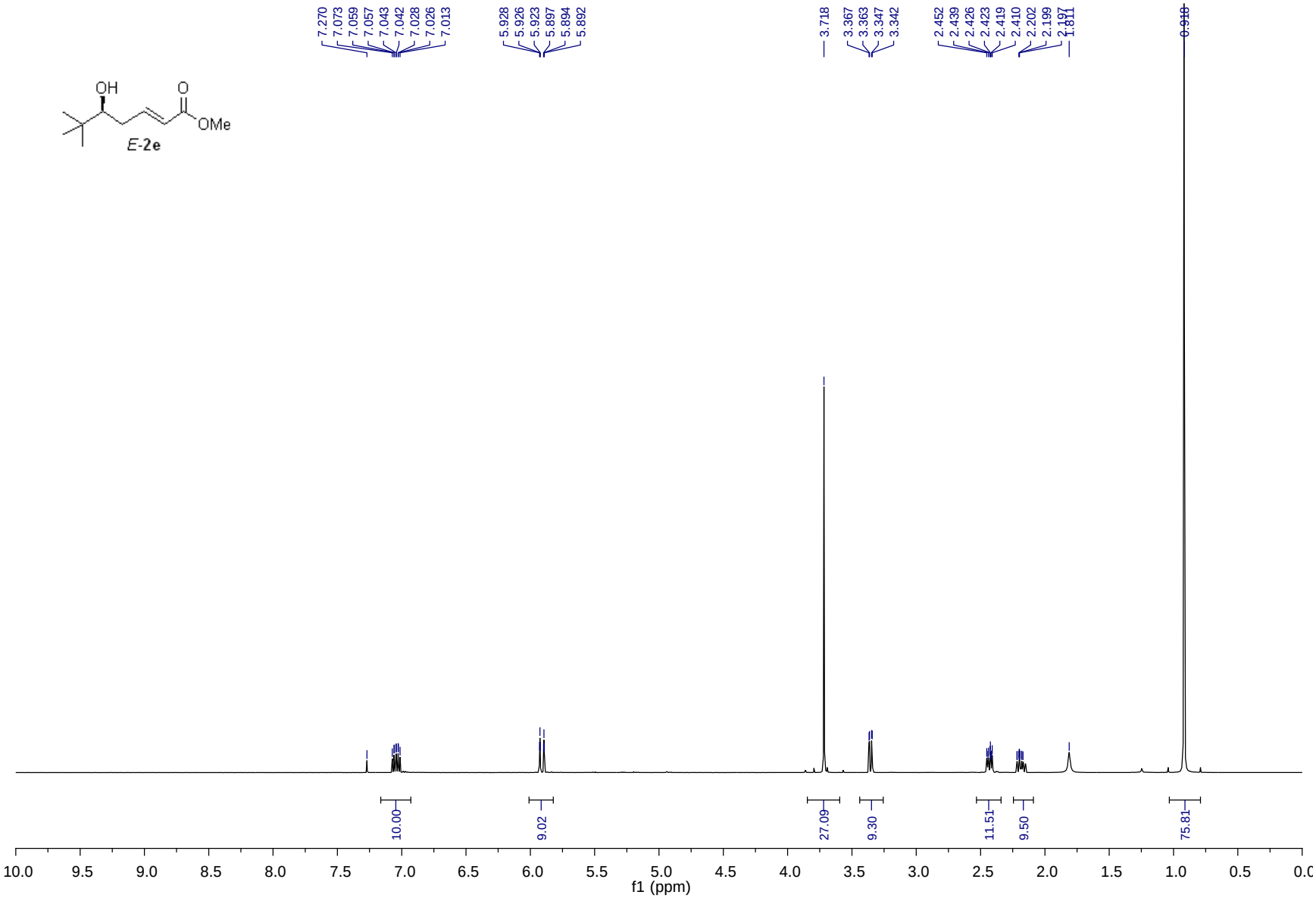
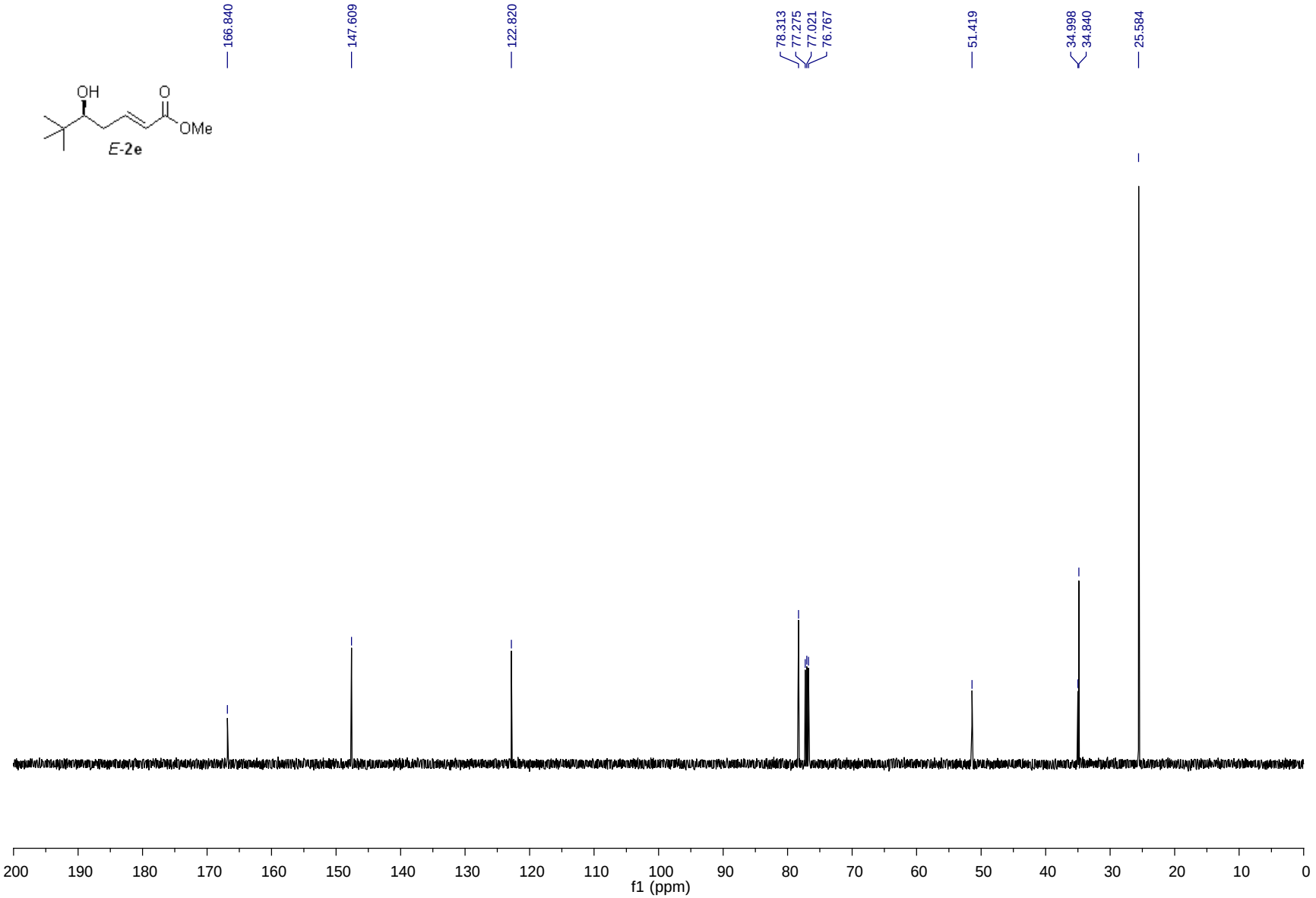
76.771
74.718
51.445
43.269
37.110
29.084
27.834
26.377
26.142
25.987
OH
O
OMe
E-2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.270
7.073
7.059
7.057
7.043
7.042
7.028
7.026
7.013
5.928
5.926
5.923
5.897
5.894
5.892
3.718
3.367
3.363
3.347
3.342
2.452
2.439
2.426
2.423
2.419
2.410
2.202
2.199
1.811
0.910
OH
O
OMe
E-2e
10.00
9.02
27.09
9.30
11.51
9.50
75.81
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)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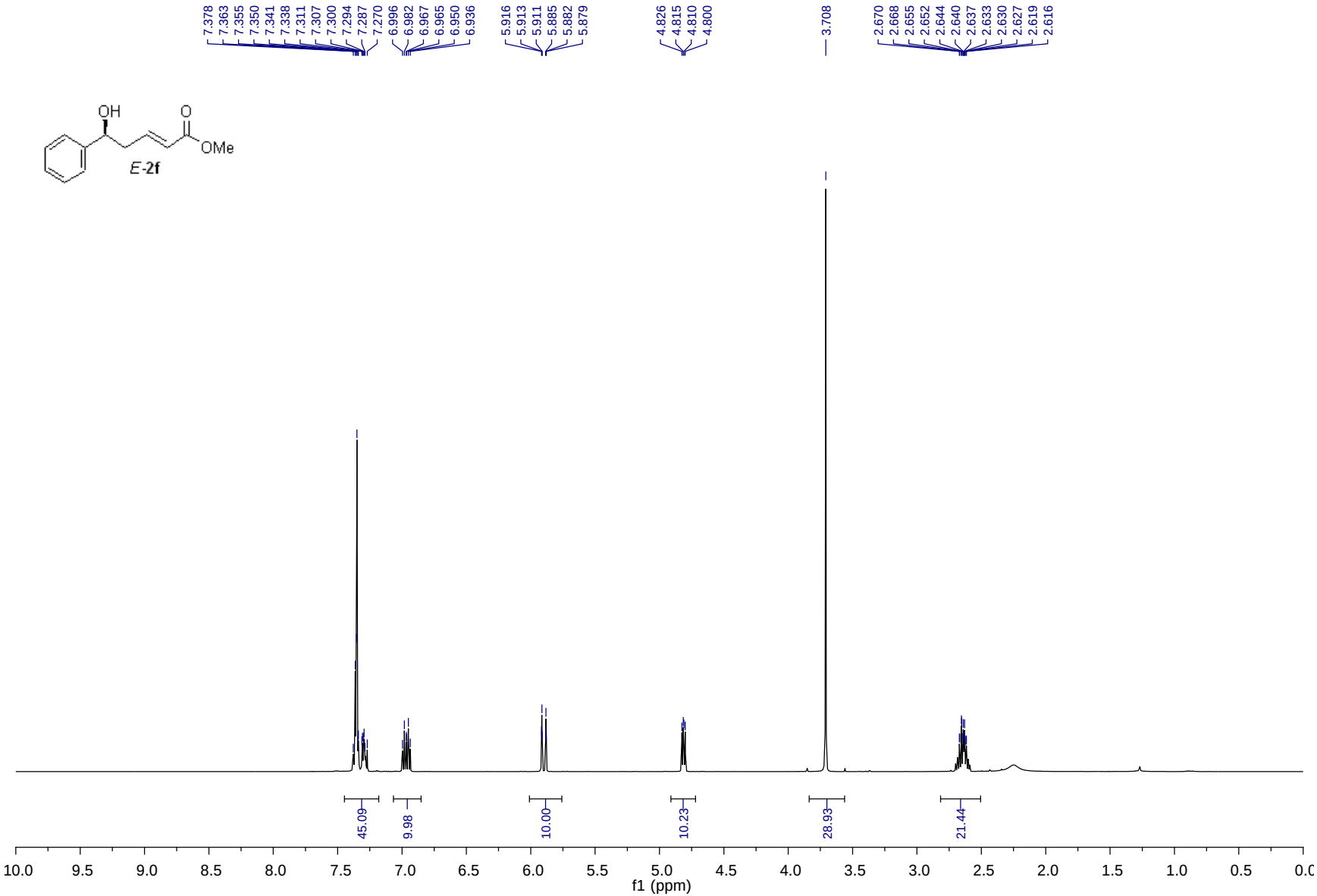
122.820
78.313
77.275
77.021
76.767
51.419
34.998
34.840
25.584
OH
O
OMe
E-2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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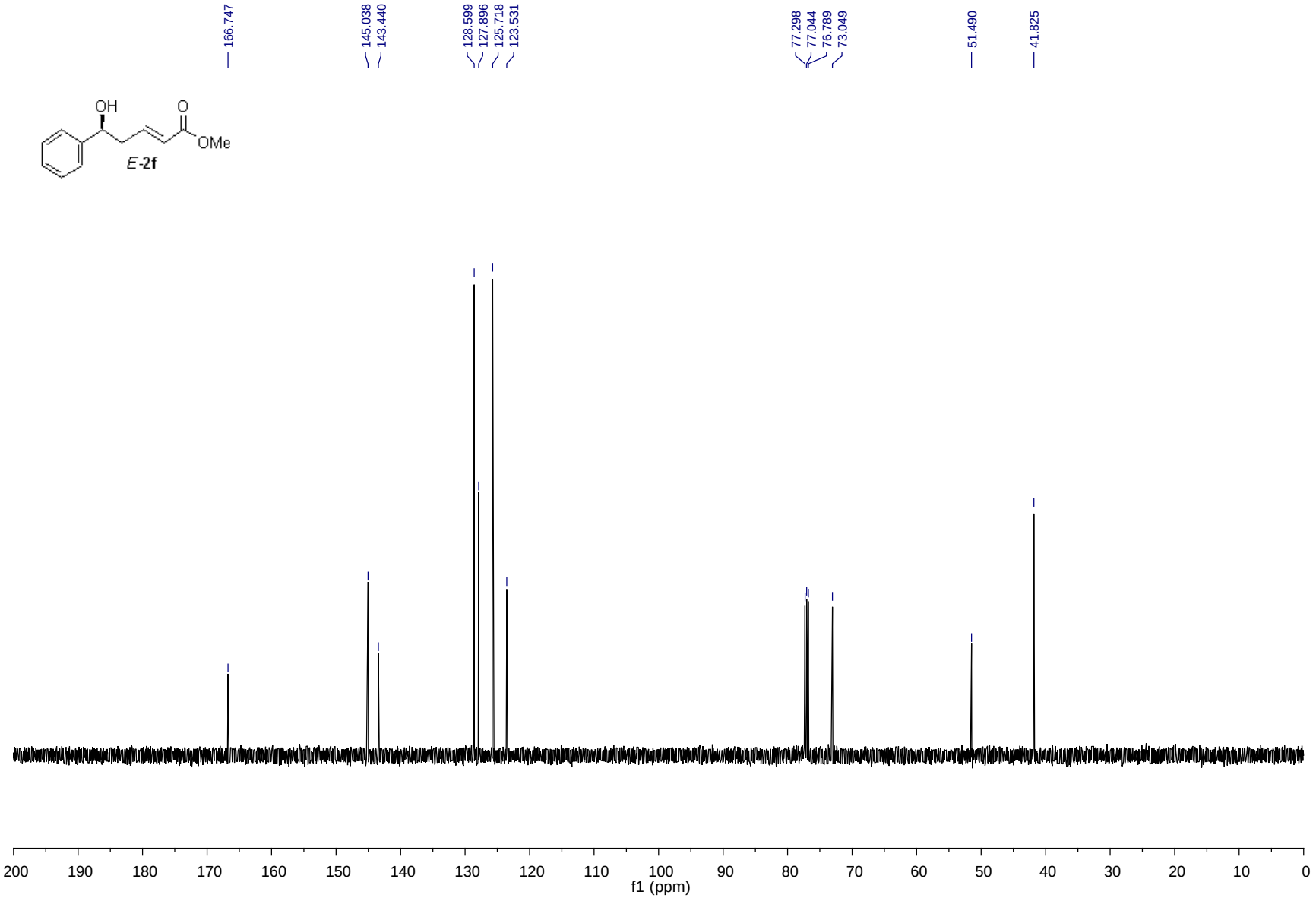
7.338
7.311
7.307
7.300
7.294
7.287
7.270
6.996
6.982
6.967
6.965
6.950
6.936
5.916
5.913
5.911
5.885
5.882
5.879
4.826
4.815
4.810
4.800
3.708
2.670
2.668
2.655
2.652
2.644
2.640
2.637
2.633
2.630
2.627
2.619
2.616
OH
O
OMe
E-2f
45.09
9.98
10.00
10.23
28.93
21.44
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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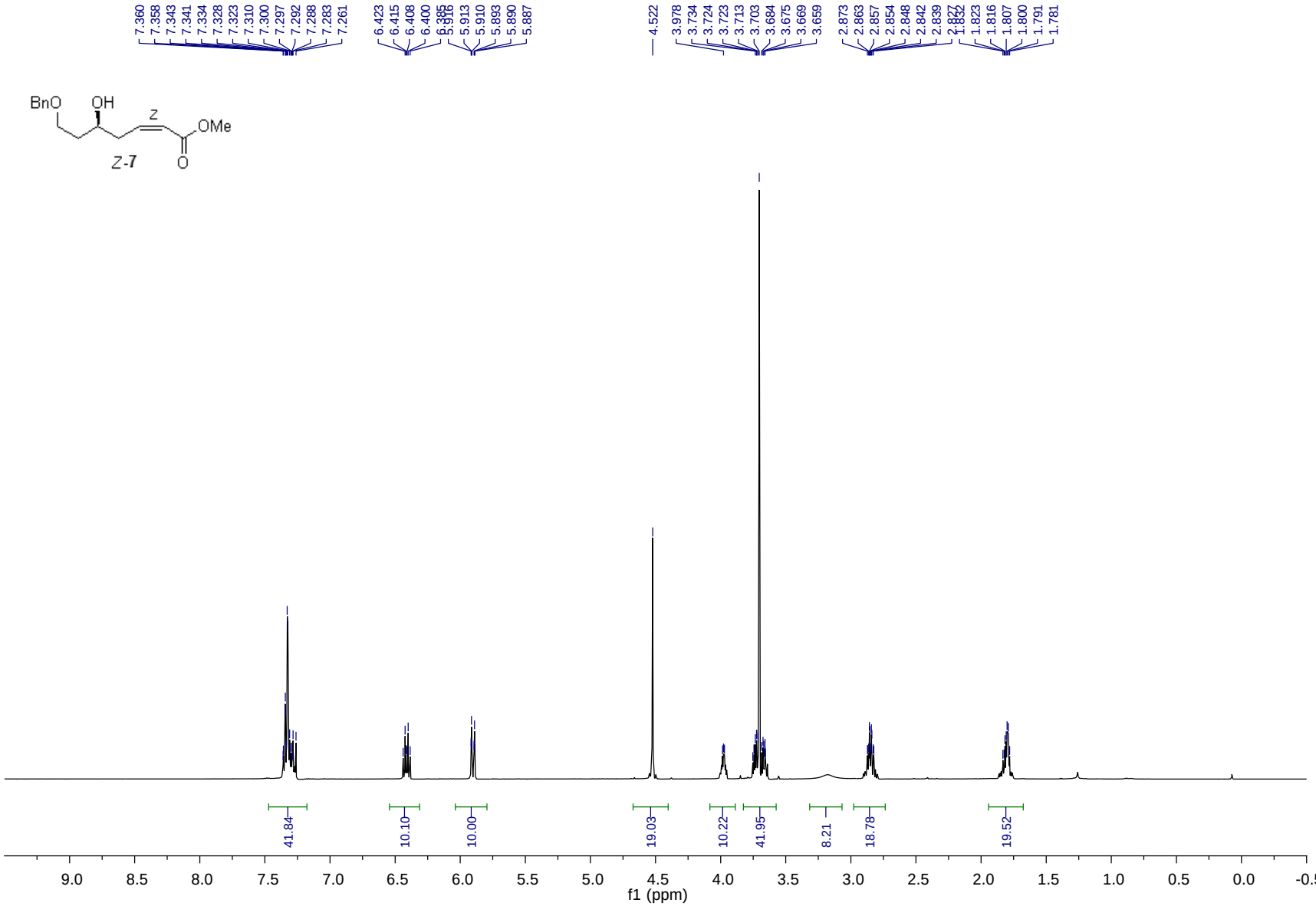
143.440
128.599
127.896
125.718
123.531
77.298
77.044
76.789
73.049
51.490
41.825
OH
O
OMe
E-2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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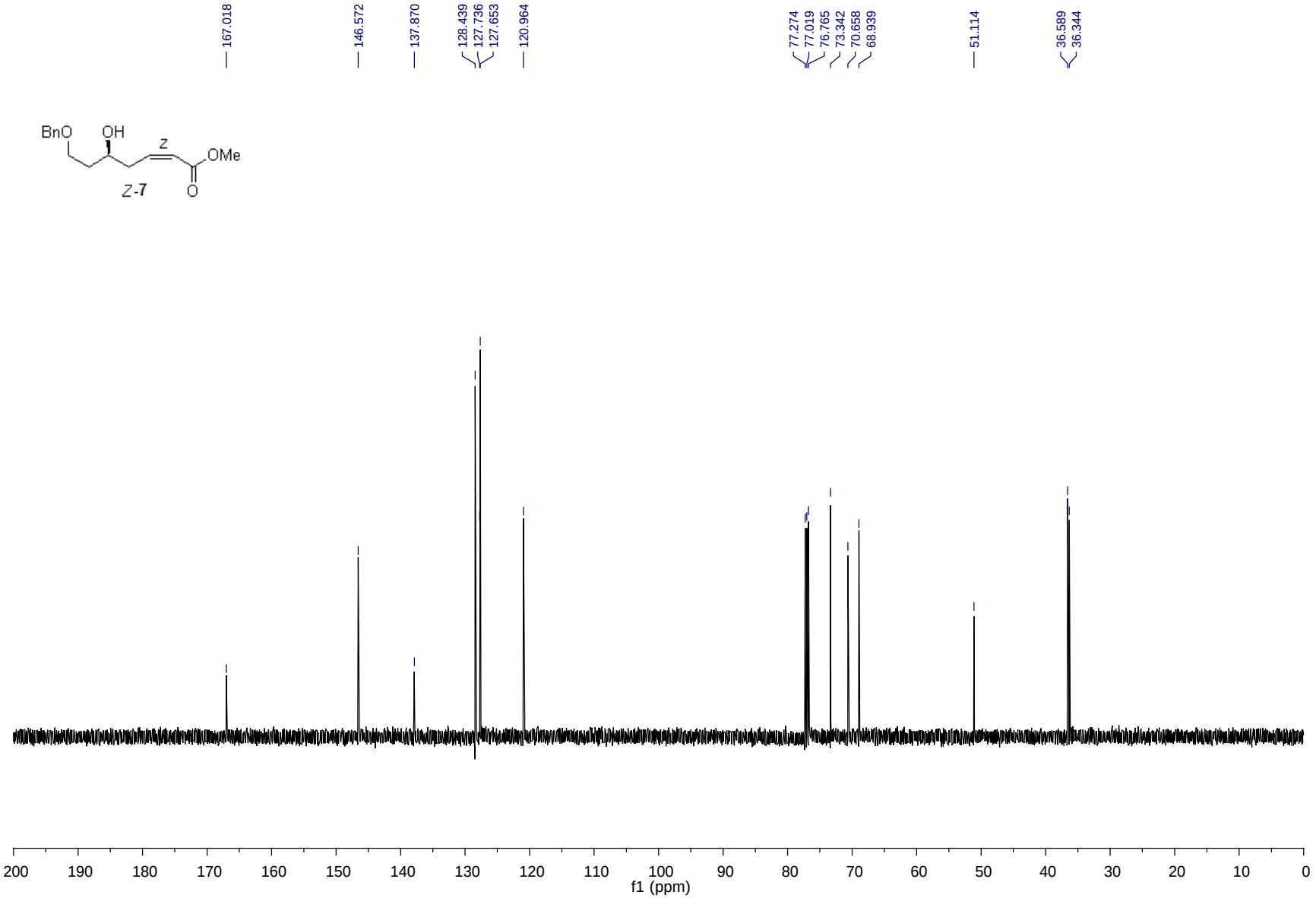
7.341
7.334
7.328
7.323
7.310
7.300
7.297
7.292
7.288
7.283
7.261
6.423
6.415
6.408
6.400
5.913
5.910
5.893
5.890
5.887
4.522
3.978
3.734
3.724
3.723
3.713
3.703
3.684
3.675
3.669
3.659
2.873
2.863
2.857
2.854
2.848
2.842
2.839
1.823
1.816
1.807
1.800
1.791
1.781
BnO
OH
Z
OMe
O
Z-7
41.84
10.10
10.00
19.03
10.22
41.95
8.21
18.78
19.52
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
0.0
f1 (ppm)


167.018
146.572
137.870
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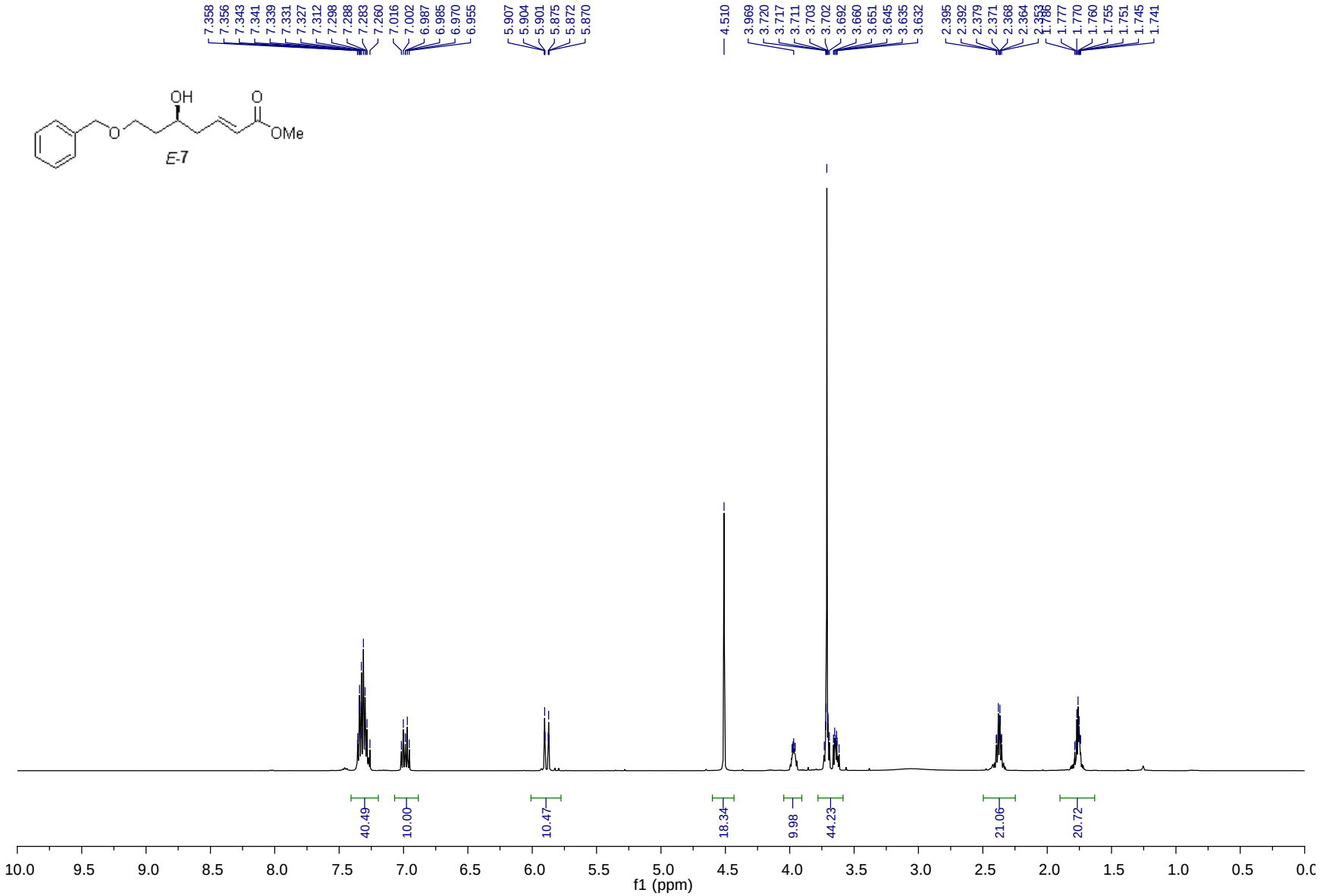
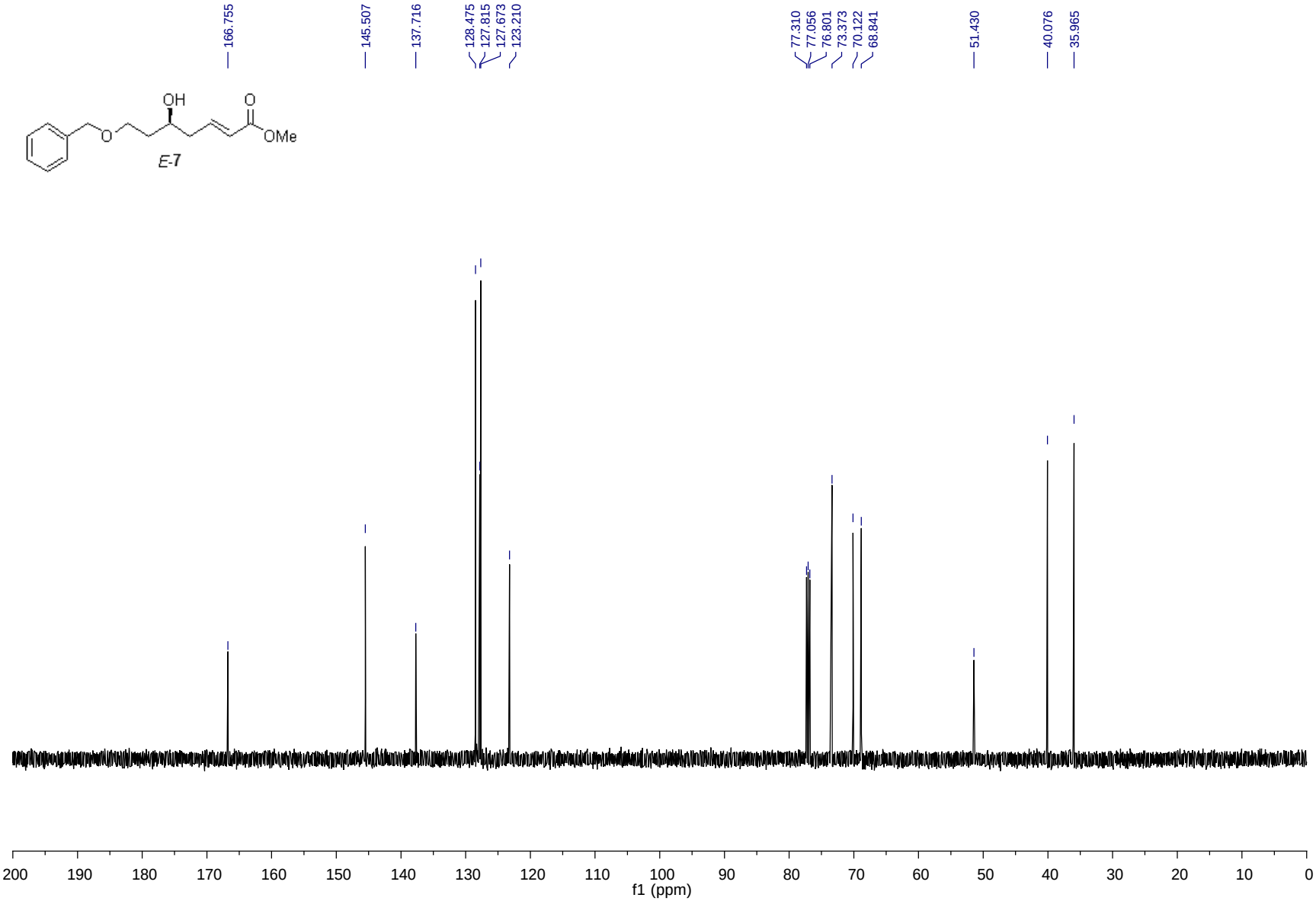
127.736
127.653
120.964
77.274
77.019
76.765
73.342
70.658
68.939
51.114
36.589
36.344
BnO
OH
Z
OMe
O
Z-7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.358
7.356
7.343
7.341
7.339
7.331
7.327
7.312
7.298
7.288
7.283
7.260
7.016
7.002
6.987
6.985
6.970
6.955
5.907
5.904
5.901
5.875
5.872
5.870
4.510
3.969
3.720
3.717
3.711
3.703
3.702
3.692
3.660
3.651
3.645
3.635
3.632
2.395
2.392
2.379
2.371
2.368
2.364
1.777
1.770
1.760
1.755
1.751
1.745
1.741
OH
O
O
OMe
E-7
40.49
10.00
10.47
18.34
9.98
44.23
21.06
20.72
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)


166.755
145.507
137.716
128.475
127.815
127.673
123.210
77.310
77.056
76.801
73.373
70.122
68.841
51.430
40.076
35.965
OH
O
O
OMe
E-7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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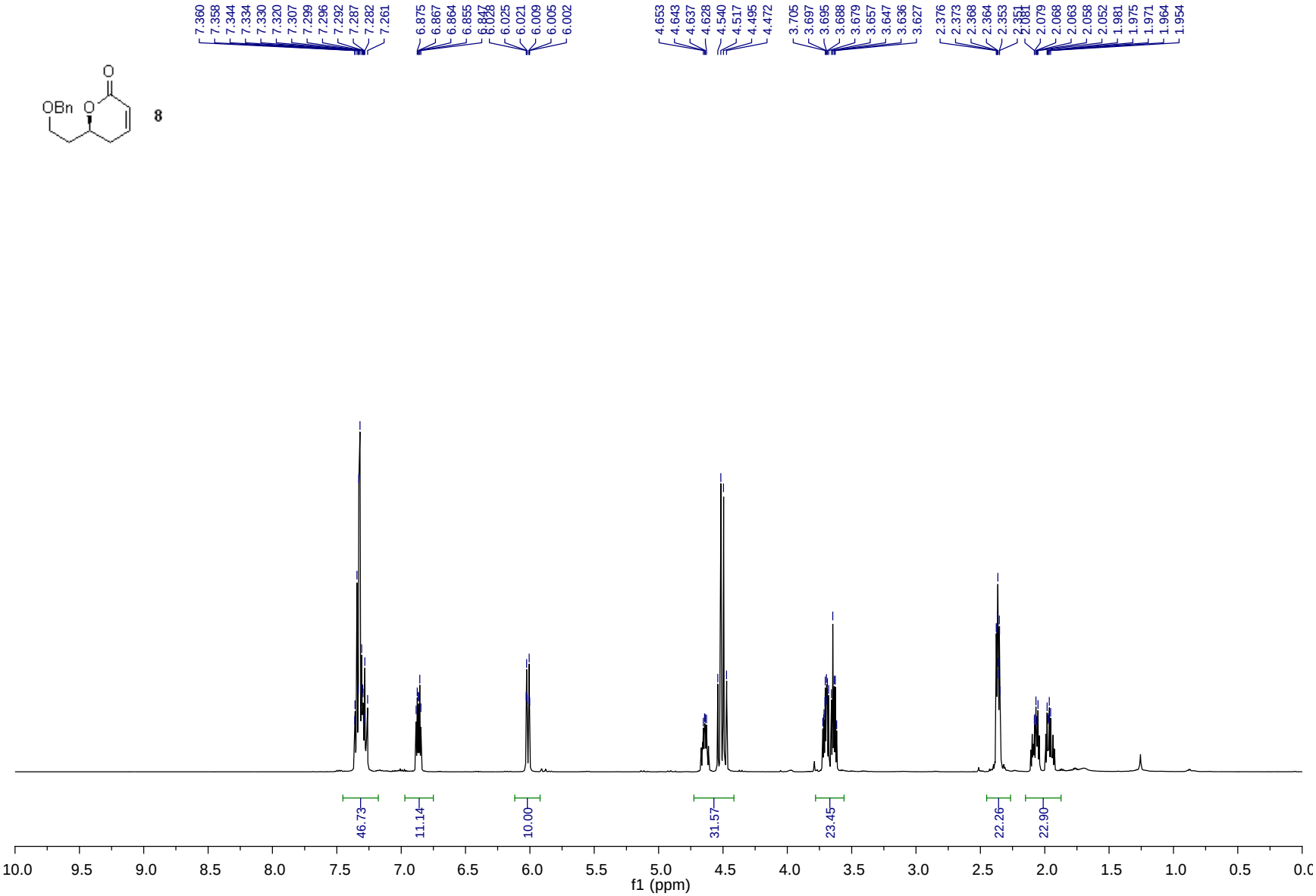
f1 (ppm)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7.358
7.344
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7.330
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7.299
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7.287
7.282
7.261
6.875
6.867
6.864
6.855
6.847
6.028
6.025
6.021
6.009
6.005
6.002
4.653
4.643
4.637
4.628
4.540
4.517
4.495
4.472
3.705
3.697
3.695
3.688
3.679
3.657
3.647
3.636
3.627
2.376
2.373
2.368
2.364
2.353
2.351
2.081
2.079
2.068
2.063
2.058
2.052
1.981
1.975
1.971
1.964
1.954
OBn
O
O
8
46.73
11.14
10.00
31.57
23.45
22.26
22.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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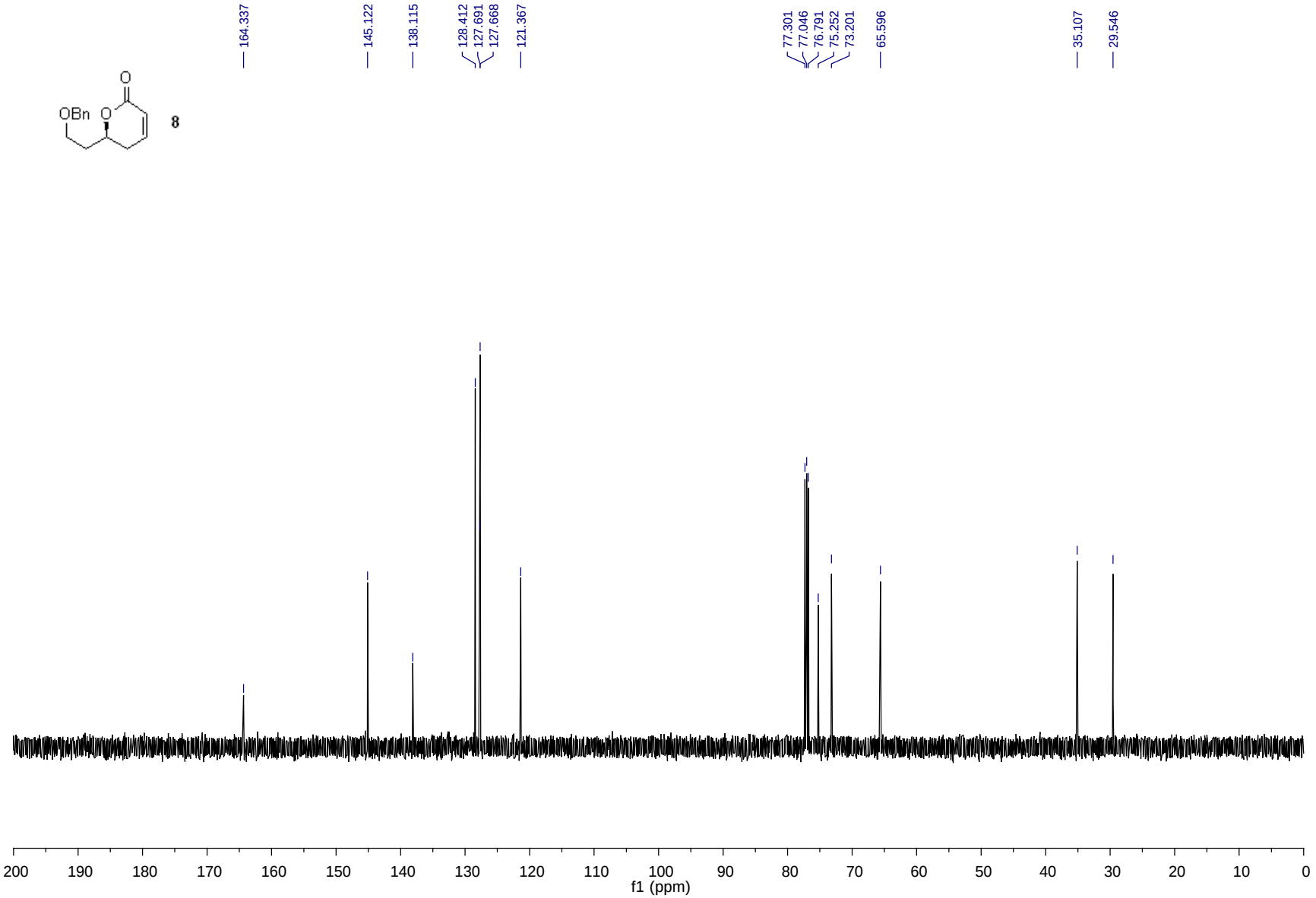
0.0
f1 (ppm)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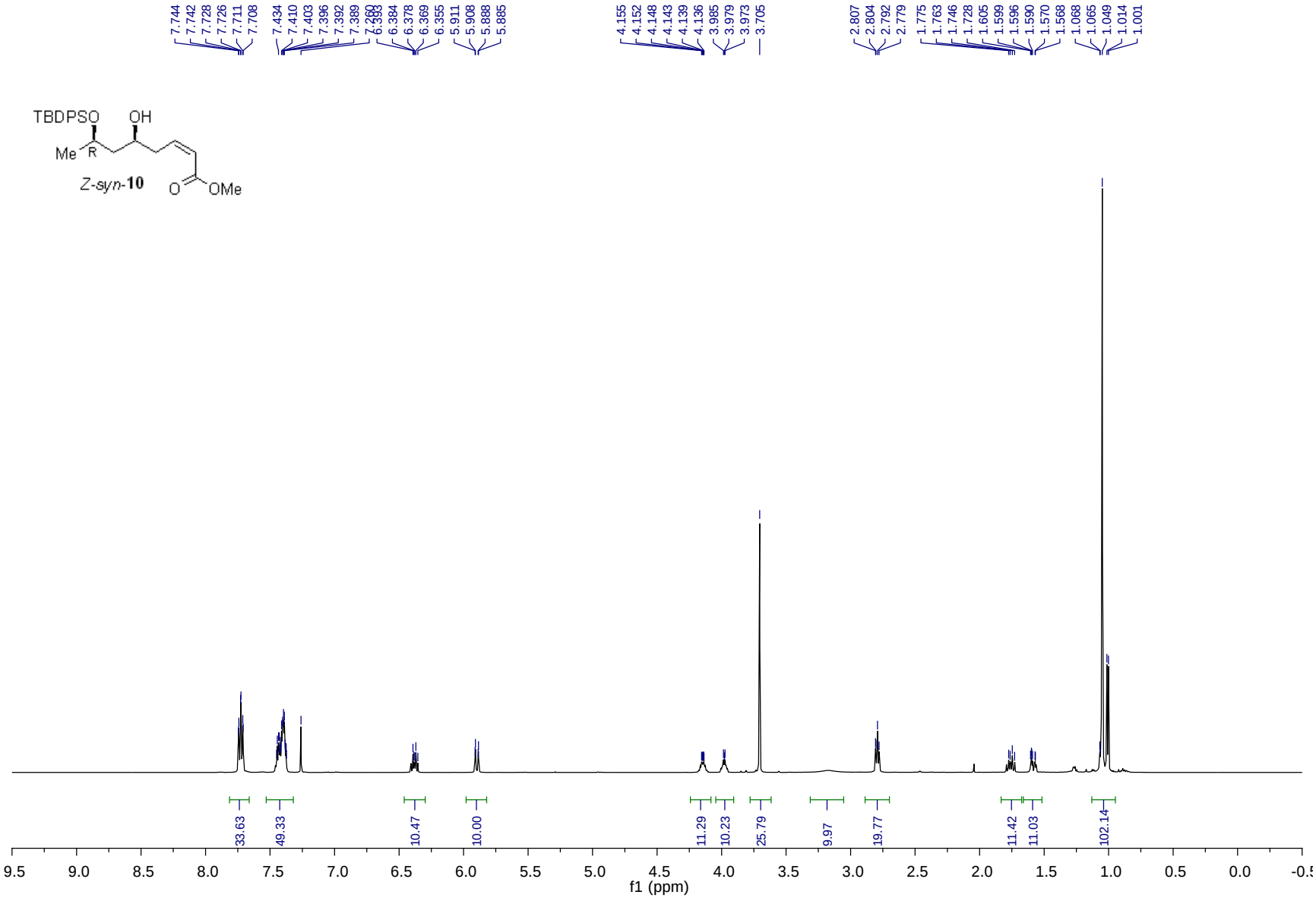
145.122
138.115
128.412
127.691
127.668
121.367
77.301
77.046
76.791
75.252
73.201
65.596
35.107
29.546
OBn
O
O
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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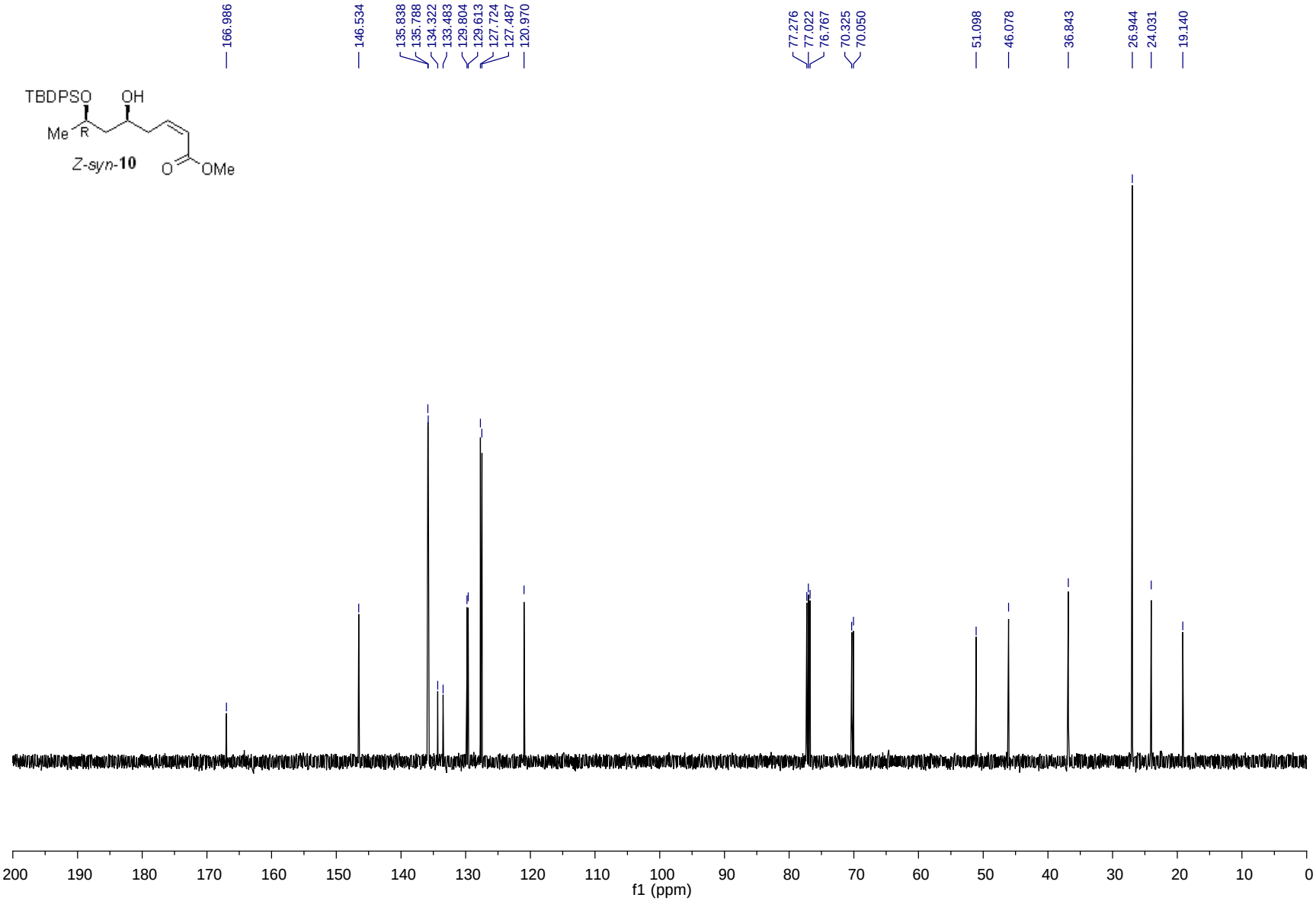
7.742
7.728
7.726
7.711
7.708
7.434
7.410
7.403
7.396
7.392
7.389
6.384
6.378
6.369
6.355
5.911
5.908
5.888
5.885
4.155
4.152
4.148
4.143
4.139
4.136
3.985
3.979
3.973
3.705
2.807
2.804
2.792
2.779
1.775
1.763
1.746
1.728
1.605
1.599
1.596
1.590
1.570
1.568
1.068
1.065
1.049
1.014
1.001
TBDPSO
OH
Me
R
Z-syn-10
O
OMe
33.63
49.33
10.47
10.00
11.29
10.23
25.79
9.97
19.77
11.42
11.03
102.14
f1 (ppm)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135.838
135.788
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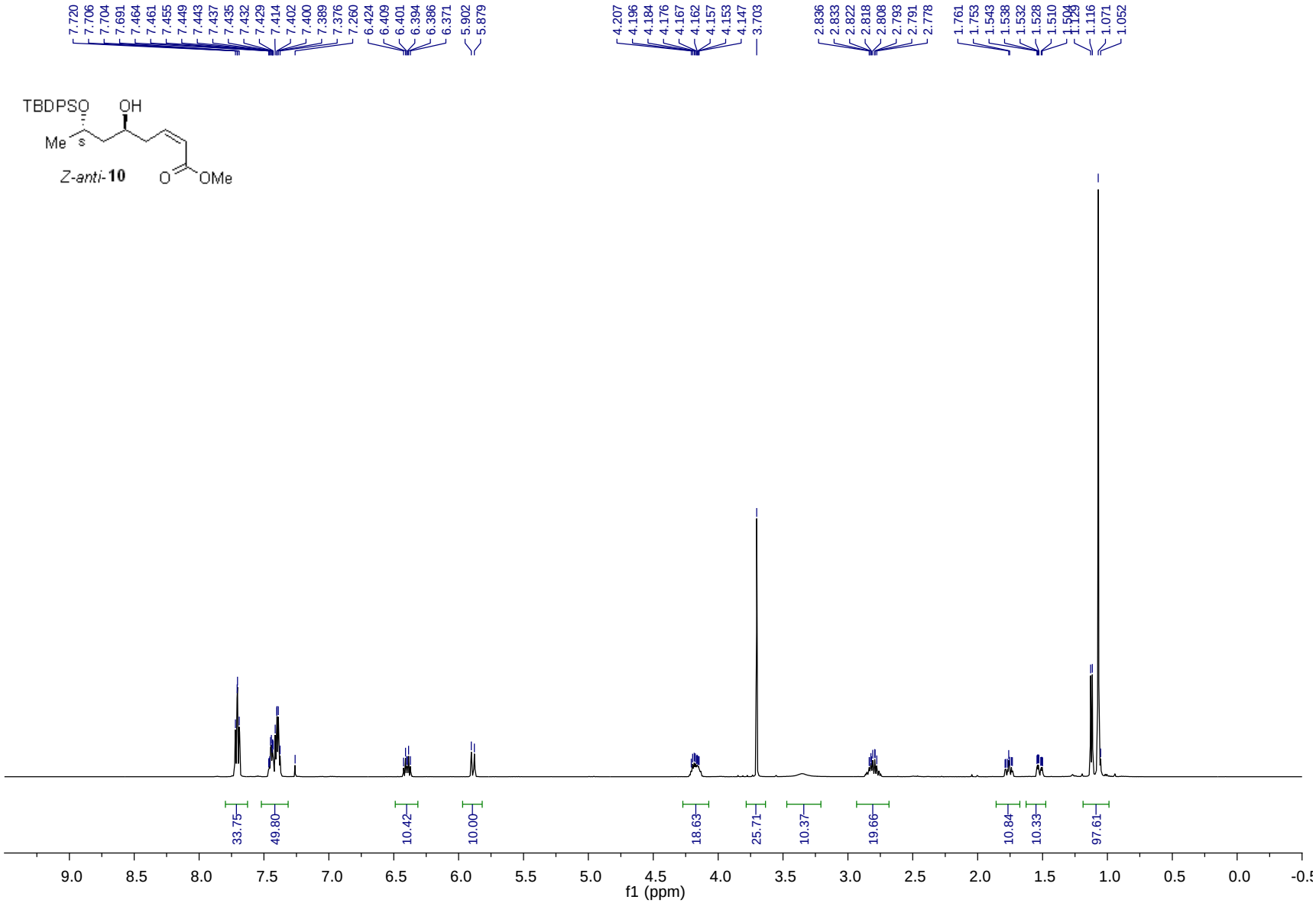
129.613
127.724
127.487
120.970
77.276
77.022
76.767
70.325
70.050
51.098
46.078
36.843
26.944
24.031
19.140
TBDPSO
OH
Me
R
Z-syn-10
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.706
7.704
7.691
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7.461
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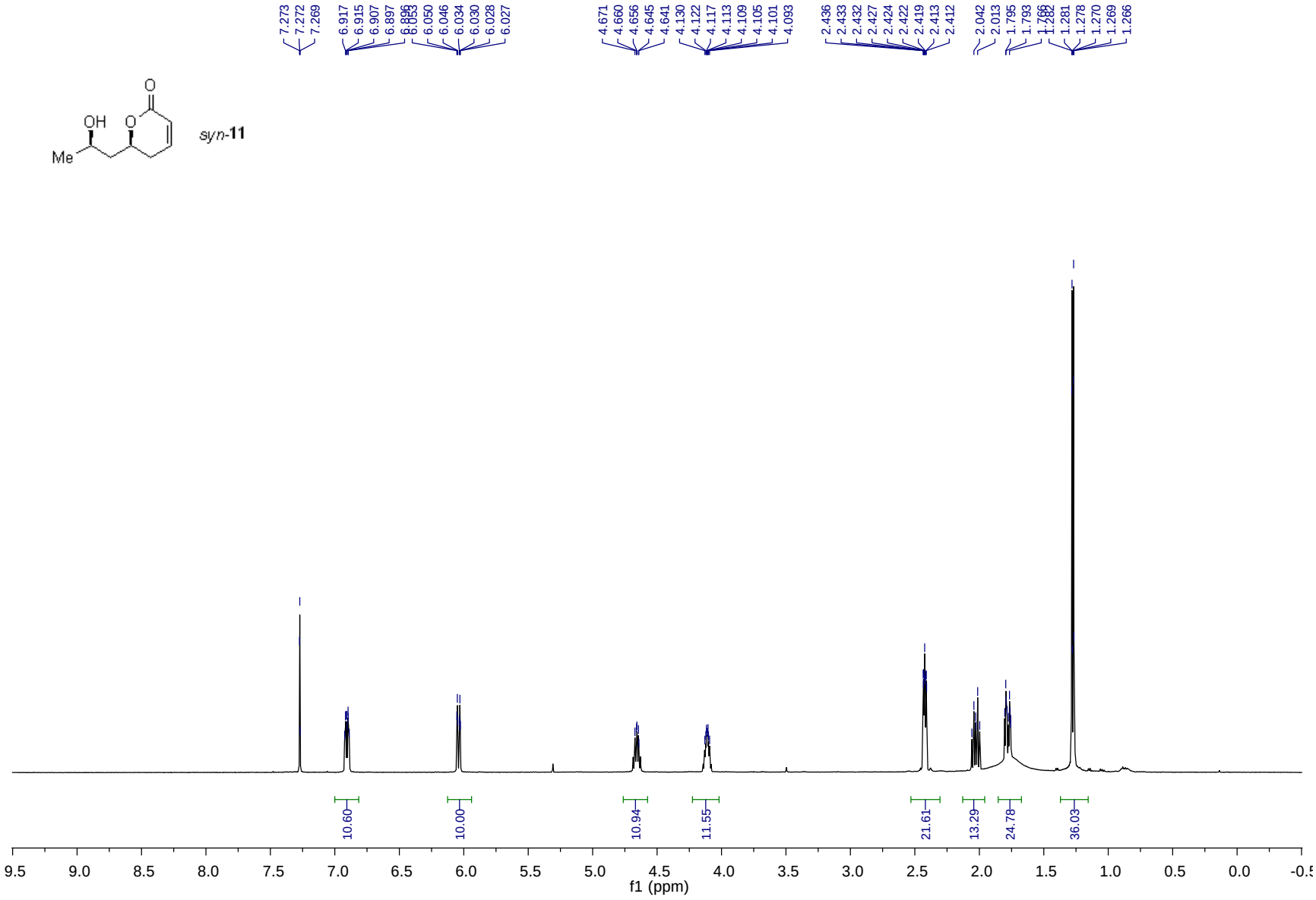
7.449
7.443
7.437
7.435
7.432
7.429
7.414
7.402
7.400
7.389
7.376
7.260
6.424
6.409
6.401
6.394
6.386
6.371
5.902
5.879
4.207
4.196
4.184
4.176
4.167
4.162
4.157
4.153
4.147
3.703
2.836
2.833
2.822
2.818
2.808
2.793
2.791
2.778
1.761
1.753
1.543
1.538
1.532
1.528
1.510
1.504
1.129
1.116
1.071
1.052
TBDPSO
OH
Me
S
Z-anti-10
O
OMe
33.75
49.80
10.42
10.00
18.63
25.71
10.37
19.66
10.84
10.33
97.61
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
0.0
f1 (ppm)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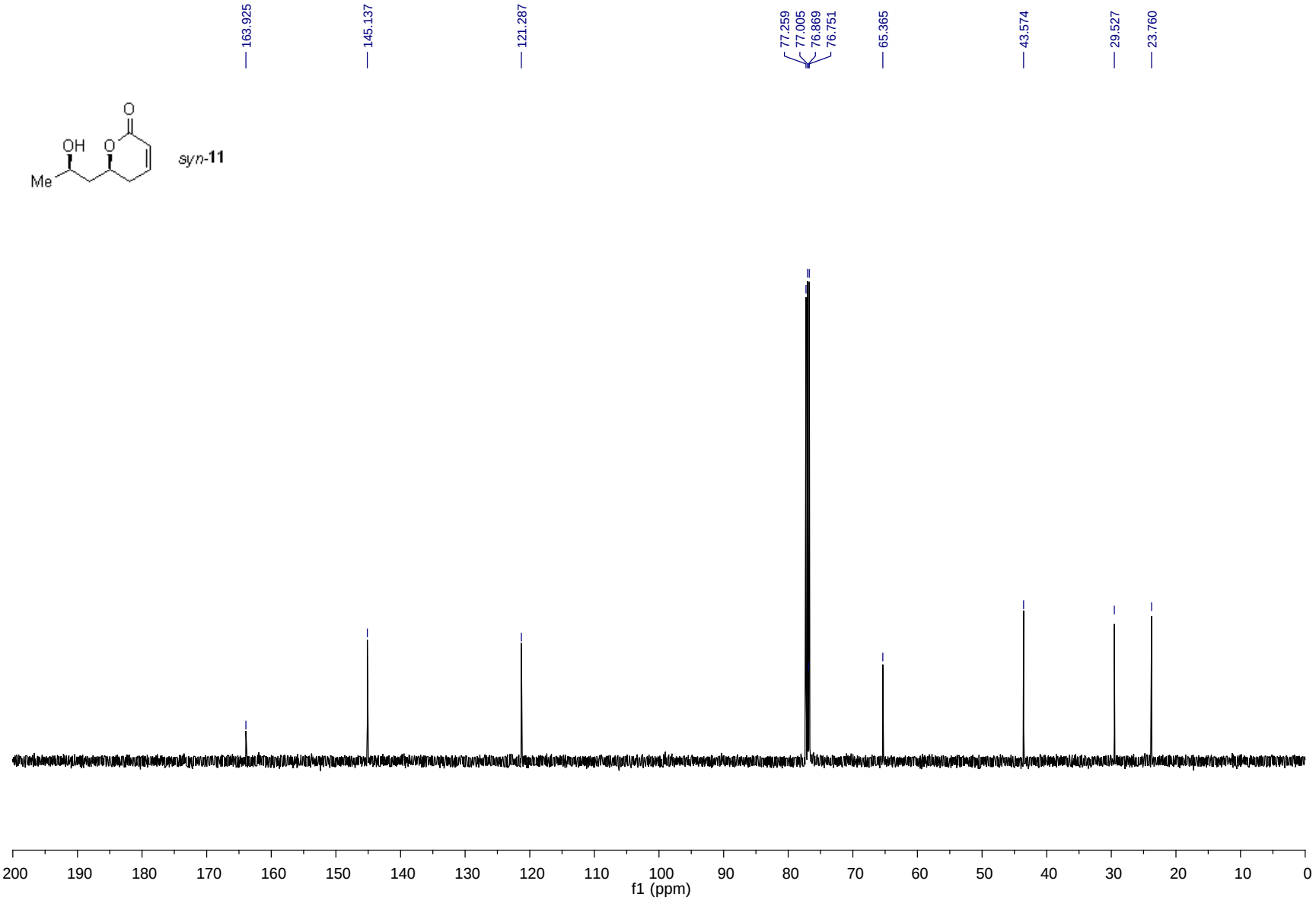
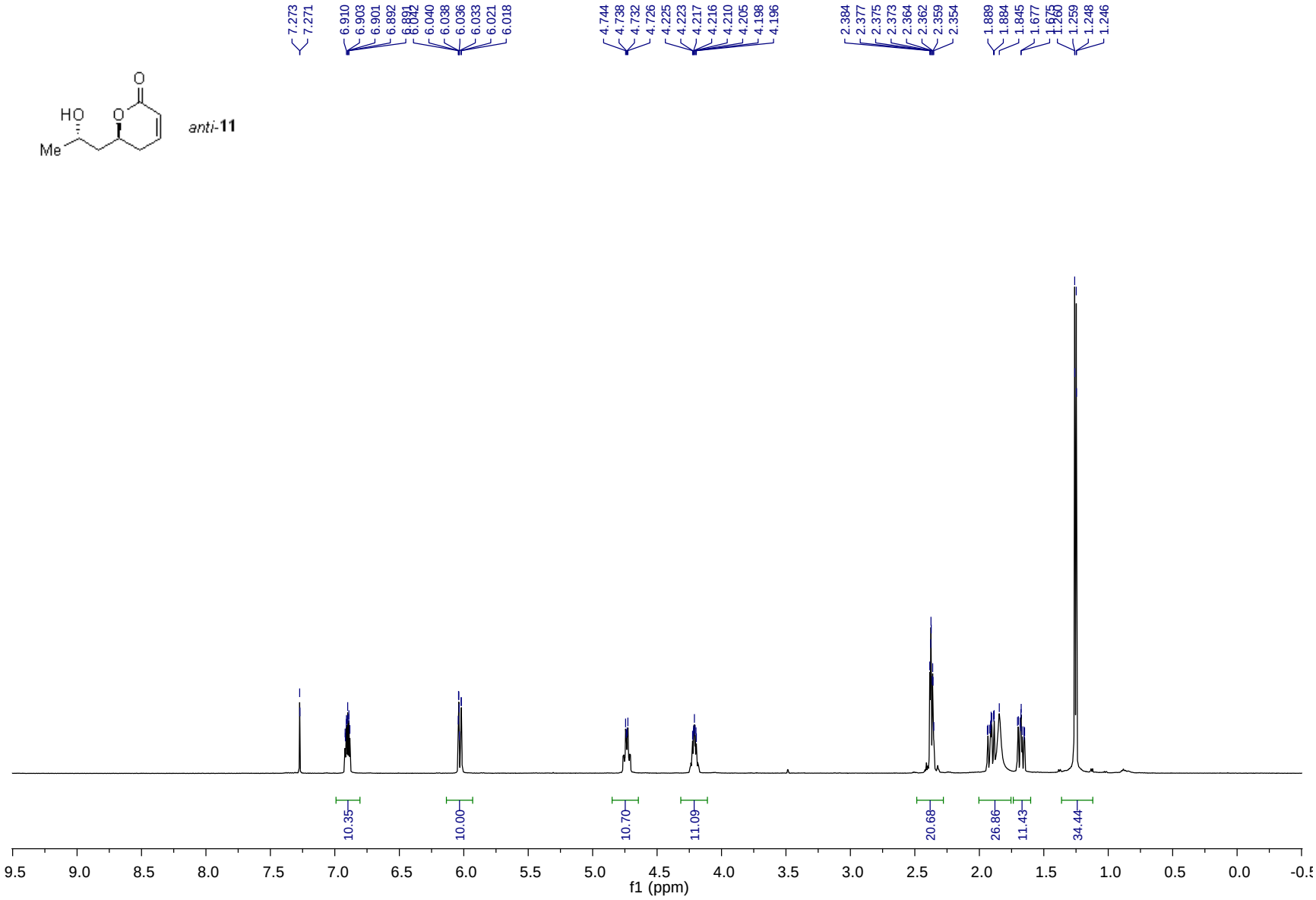
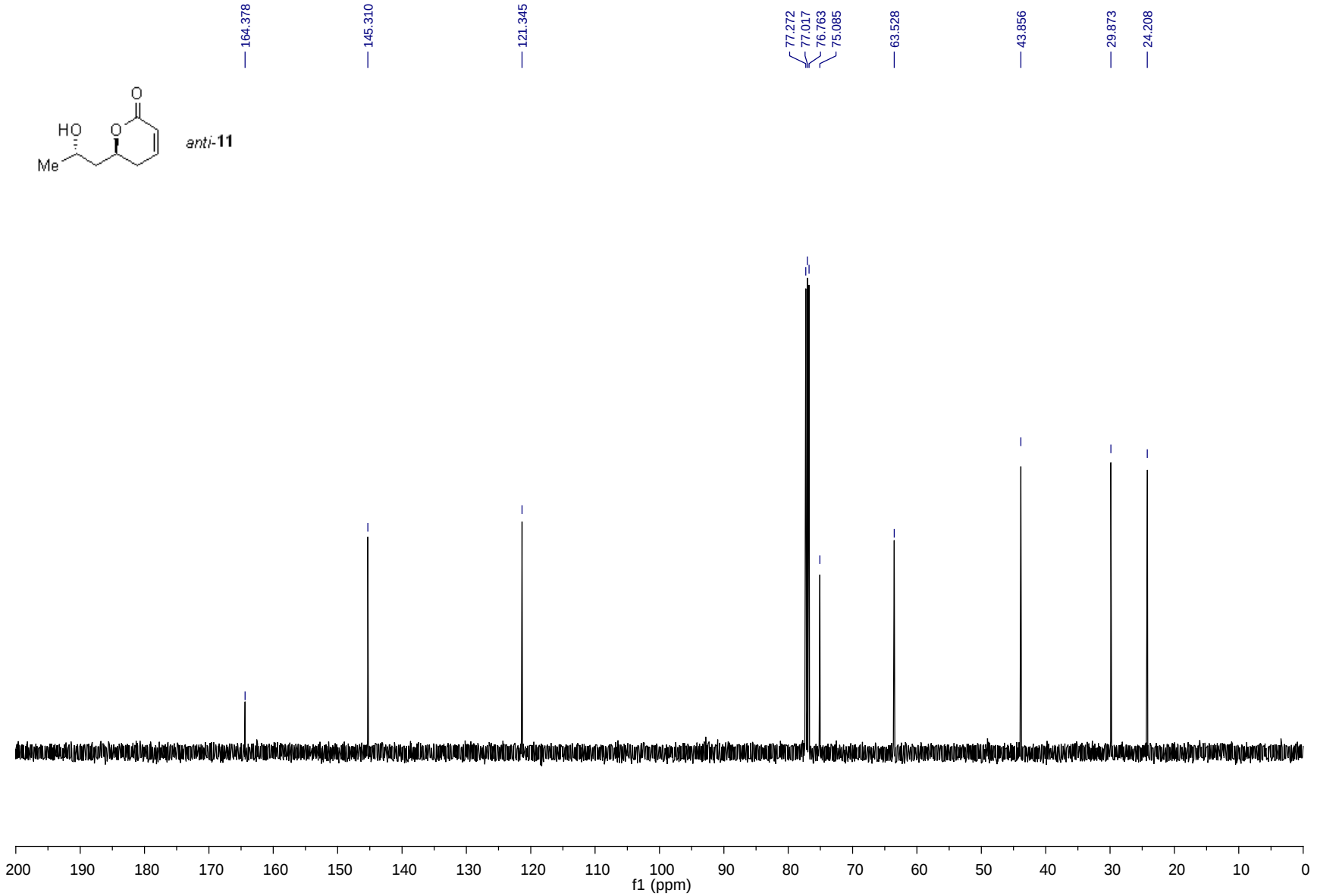
7.272
7.269
6.917
6.915
6.907
6.897
6.896
6.053
6.050
6.046
6.034
6.030
6.028
6.027
4.671
4.660
4.656
4.645
4.641
4.130
4.122
4.117
4.113
4.109
4.105
4.101
4.093
2.436
2.433
2.432
2.427
2.424
2.422
2.419
2.413
2.412
2.042
2.013
1.795
1.793
1.766
1.282
1.281
1.278
1.270
1.269
1.266
OH
O
O
Me
syn-11
10.60
10.00
10.94
11.55
21.61
13.29
24.78
36.03
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
0.0
f1 (ppm)


163.925
145.137
121.287
77.259
77.005
76.869
76.751
65.365
43.574
29.527
23.760
OH
O
O
Me
syn-11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.273
7.271
6.910
6.903
6.901
6.892
6.891
6.042
6.040
6.038
6.036
6.033
6.021
6.018
4.744
4.738
4.732
4.726
4.225
4.223
4.217
4.216
4.210
4.205
4.198
4.196
2.384
2.377
2.375
2.373
2.364
2.362
2.359
2.354
1.889
1.884
1.845
1.677
1.675
1.260
1.259
1.248
1.246
HO
O
O
Me
anti-11
10.35
10.00
10.70
11.09
20.68
26.86
11.43
34.44
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
0.0
f1 (ppm)


164.378
145.310
121.345
77.272
77.017
76.763
75.085
63.528
43.856
29.873
24.208
HO
O
O
Me
anti-11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)