Iridium-Catalyzed Regio- and Enantioselective Allylation of Trimethylsiloxyfuran

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Supporting Information

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General Experimental Details

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. DCM and THF was degassed by purging with argon for 15 minutes and dried with a solvent purification system containing a one-meter column of activated alumina. Cinnamyl alcohol, butyraldehyde, cyclohexanecarboxaldehyde, benzaldehyde, 4-methoxybenzaldehyde, 4-fluorobenzaldehyde, 3-fluorobenzaldehyde and 4-chlorobenzaldehyde were purchased from Sigma-Aldrich and used without further purification. Vinylmagnesium chloride was purchased as a 1.6 M solution in THF from Sigma-Aldrich. Trimethylsiloxyfuran was purchased from TCI and used without further purification. Different substituted methyl trimethylsiloxyfurans were prepared according to known procedures.[1] All the allylic carbonates and benzoates were prepared according to literature procedures.[2] The racemic sample was prepared by using racemic catalyst.

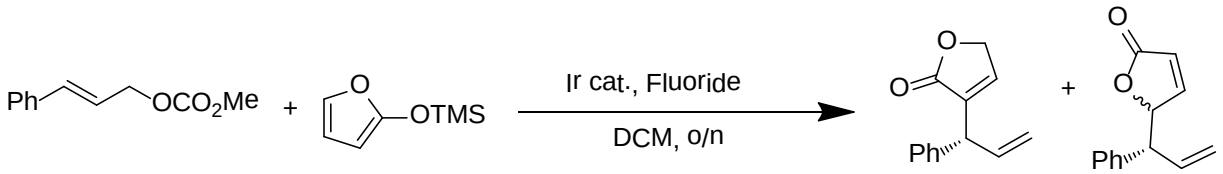
$[Ir(COD)Cl]_2$ was obtained from Johnson-Matthey and used without further purification. Phosphoramidite ligands **L1** and **L2** were synthesized according to literature procedures.[3] [Ir(COD)(κ^2-**L1**)(ethylene) (**1**) and [Ir(COD)(κ^2-**L2**)(ethylene) (**2**) were prepared according to literature procedures.[4] GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 m film) and an FID detector. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector) with using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High resolution

mass spectra and elemental analyses were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. NMR spectra were acquired on Bruker AVQ-400, AVB-400, and AV-600 spectrometers. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H and 77.23 ppm for ^{13}C). Coupling constants are reported in hertz. Flash column chromatography was performed on Silicylce Silica-P silica gel. Products were visualized on TLC plates by UV or by staining with $KMnO_4$.

Condition Screening for Iridium-catalyzed Asymmetric Allylic Substitution of Trimethylsiloxyfuran 3 with Cinnamyl Carbonate 4a

In a nitrogen-filled dry-box, the cinnamyl carbonate **4a** (48.0 mg, 0.250 mmol, 1.00 equiv), trimethylsiloxyfuran (46.8 mg, 0.300 mmol, 1.20 equiv), and the additive (0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, the catalyst precursor (0.00250 mmol, 0.010 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature overnight. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 µL) was added as an internal standard. The yield and the ratio of isomers were then determined by ^1H NMR analysis.

TABLE 1. Effect of catalyst and fluorie on the iridium catalyzed allylic substitution of trimethylsiloxyfuran



4a **3a** **5a** **6a**

Entry	Cat.[a]	Fluoride	Yield(%)[b]	**5a**:**6a**[c]	ee(%)[d]
1	1	CsF	13	-	-
2	2	CsF	32	20:1	99
3	2	ZnF_2	87(85)	20:1	99
4[e]	2	TBAF	trace	-	-
5	2	TBAT	trace	-	-
6	2	None	40	20:1	99
7[f]	2	None	89	20:1	99

[a] 1% Ir catalyst was used unless otherwise noted. [b]The yield was determined from ^1H NMR analysis with mesitylene as internal standard. [c] The ratio was determined from ^1H NMR analysis of the crude reaction mixtures. [d]ee was determined by chiral HPLC analysis [(Chiralpak AD-H) hexane/i-PrOH, 97:3, 1.o mL/min]. [e]Branched alllic alcohol was identified in 69% yield. [f] 2% Ir catalyst was used.

Procedure for Palladium-catalyzed Allylation of Trimethylsiloxyfuran

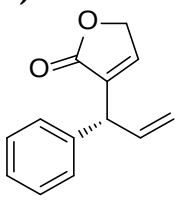
In a nitrogen-filled dry-box, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.100 equiv) and Trost Ligand (25.9 mg, 0.0375 mmol, 0.150 equiv) was dissolved in DCM (1 mL) in a 1-dram vial. After stirring at room temperature for 15 min, a solution of trimethylsiloxyfuran (46.8 mg, 0.300 mmol, 1.20 equiv) in DCM (0.5 mL) was added and stirred for another 15 min. The vial was sealed with a PTFE/silicone-lined septum cap and removed from the dry-box. Cinnamyl acetate (42.0 mg, 0.250 mmol, 1.00 equiv) in DCM (0.5 mL) was added over 30 min at 0 ^{o}C. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 6:1 to 3:1) to yield an inseparable mixture (1:0.8) of 3-cinnamyl-2-furanone and **6a** in 30% yield (15 mg). 3-cinnamyl-2-furanone: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.26 (m, 5H), 7.23 (t, *J* = 1.6 Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.85 (d, *J* = 1.9 Hz, 2H), 3.25 (d, *J* = 6.8 Hz, 2H). **6a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.8, 1.4 Hz, 1H), 7.43-7.26 (m, 5H), 6.11 (dd, *J* = 7.0, 2.0 Hz, 1H), 6.09 (ddd, *J* = 8.4, 10.0, 17.6 Hz, 1H), 5.37-5.28 (m, 3H), 3.75 (dd, *J* = 8.0, 6.4 Hz, 1H).

General Procedure for Iridium-catalyzed Allylic Substitution of Trimethylsiloxyfuran 3a

General Procedure 1 (for aromatic allylic carbonates): In a nitrogen-filled dry-box, the allylic carbonate (0.250 mmol, 1.00 equiv), trimethylsiloxyfuran (0.300 mmol, 1.20 equiv), and ZnF_2 (0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, the catalyst precursor (0.0025 mmol, 0.010 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature overnight. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 μL) was added as an internal standard. The site selectivity was then determined by ^{1}H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 6:1 to 3:1) to yield the product.

General Procedure 2 (for aliphatic allylic carbonates): In a nitrogen-filled dry-box, the allylic benzoate (0.250 mmol, 1.00 equiv), trimethylsiloxyfuran (0.550 mmol, 2.20 equiv), and ZnF_2 (0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, the catalyst precursor (0.0075 mmol, 0.030 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at 50 ^{o}C for 12 hours. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 μL) was added as an internal standard. The site selectivity was then determined by ^{1}H NMR spectroscopy. After this analysis, the crude reaction mixture was washed with 1 M NaOH (1 mL) to remove the benzoate formed. Then the mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 6:1 to 3:1) to yield the product.

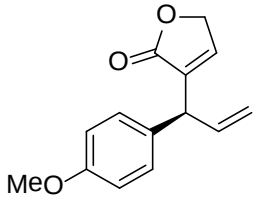
(*R*)-3-(1-phenylallyl)furan-2(5H)-one (5a)



5a

Prepared according to the general procedure 1 from **4a** (48.0 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*R, R, R*)-**2** (2.6 mg, 0.0025 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5a** as a light yellow oil in 85% yield (42.5 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.7 min (major); t_R 13.6 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = -35.7° (c 0.75, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.33 – 7.22 (m, 3H), 7.19 – 7.10 (q, *J* = 1.6 Hz, 1H), 6.20 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.28 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.11 (dt, *J* = 17.2, 1.1 Hz, 1H), 4.87 (dt, A of AB-system, *J* = 18.0, 1.6 Hz, 1H), 4.82 (dt, B of AB-system, *J* = 18.0, 1.6 Hz, 1H), 4.54 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 146.1, 139.7, 137.1, 136.1, 128.7, 128.1, 127.1, 117.0, 70.2, 45.8. HRMS (ESI) Calcd. for $C_{13}H_{13}O_2$ ($[M+H]^+$): 201.0910. Found: 201.0914. Calcd. for $C_{13}H_{12}NO_2Na$ ($[M+Na]^+$): 223.0732. Found: 223.0735.

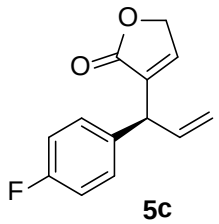
(*S*)-3-(1-(4-methoxyphenyl)allyl)furan-2(5H)-one (5b)



5b

Prepared according to the general procedure 1 from **4b** (55.5 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*S, S, S*)-**2** (2.6 mg, 0.00250 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5b** as a colorless oil in 70% yield (40.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 28.5 min (major); t_R 24.1 min (minor) (Chiralcel OD-H) [hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = +49.6° (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 7.10 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.14 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.21 (dd, *J* = 10.0, 0.8 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.83 (d, A of AB-system, *J* = 18.0 Hz, 1H), 4.78 (d, B of AB-system, *J* = 18.0 Hz, 1H), 4.45 (d, *J* = 6.6 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 158.6, 145.9, 137.4, 136.4, 131.7, 129.2, 116.8, 114.1, 70.2, 55.2, 45.0. HRMS (ESI) Calcd. for $C_{14}H_{14}O_3$ ($[M+H]^+$): 231.1016. Found: 231.1024.

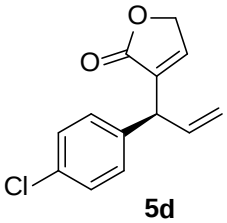
(*S*)-3-(1-(4-fluorophenyl)allyl)furan-2(5H)-one (5c)



5c

Prepared according to the general procedure 1 from **4c** (52.5 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*S, S, S*)-**2** (2.6 mg, 0.00250 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5c** as a colorless oil in 83% yield (45.2 mg).The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 44.5 min (major); t_R 43.5 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 97:3, 0.5 mL/min] to be 95%. $[\alpha]_D^{25}$ = +40.0° (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.11 (m, 3H), 7.04-7.00 (m, 2H), 6.13 (ddd, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.05 (dd, *J* = 17.0, 0.8 Hz, 1H), 4.85 (d, A of AB-system, *J* = 19.2 Hz, 1H), 4.81 (d, B of AB-system, *J* = 19.2 Hz, 1H), 4.48 (d, *J* = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 161.8 (d, *J* = 245.6 Hz), 146.1, 137.0, 136.0, 135.3 (d, *J* = 12.0 Hz), 129.7 (d, *J* = 8.0 Hz), 117.3, 115.5 (d, *J* = 21.4 Hz), 70.2, 45.1. HRMS (ESI) Calcd. for $C_{13}H_{12}O_2F$ ($[M+H]^+$): 219.0816. Found: 219.0824. Calcd. for $C_{13}H_{15}NO_2$ ($[M+NH_4]^+$): 236.1081. Found: 236.1090.

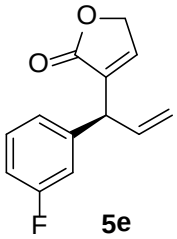
(*S*)-3-(1-(4-chlorophenyl)allyl)furan-2(5H)-one (5d)



5d

Prepared according to the general procedure 1 from **4d** (56.6 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*S, S, S*)-**2** (2.6 mg, 0.00250 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5d** as a pale yellow oil in 78% yield (45.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 24.1 min (major); t_R 23.1 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = +53.0° (c 1.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 6.12 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.86 (d, A of AB-system, *J* = 18.0 Hz, 1H), 4.81 (d, B of AB-system, *J* = 18.0 Hz, 1H),4.47 (d, *J* = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 146.2, 138.1, 136.6, 135.8, 133.0, 129.5, 128.8, 117.5, 70.2, 45.2. Anal. Calcd. for $C_{13}H_{11}O_2Cl$: C, 66.53; H, 4.72; N, 0.00; found: C, 66.37; H, 4.89; N, <0.02.

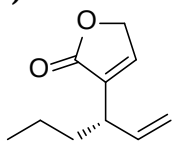
(*S*)-3-(1-(3-fluorophenyl)allyl)furan-2(5H)-one (5e)



5e

Prepared according to the general procedure 1 from **4e** (52.5 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*S, S, S*)-**2** (5.1 mg, 0.00500 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5e** as a colorless oil in 91% yield (49.5 mg). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 14.0 min (major); t_R 13.2 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = +51.8° (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.35 – 7.24 (m, 1H), 7.15 (s, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.13 (ddd, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.27 (dd, *J* = 10.2, 0.7 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 4.86 (d, A of AB-system, *J* = 19.2 Hz, 1H), 4.81 (d, B of AB-system, *J* = 18.4 Hz, 1H), 4.50 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 162.9 (d, *J* = 246.3 Hz), 146.4, 142.2 (d, *J* = 7.0 Hz), 136.4, 135.6, 130.2 (d, *J* = 8.3 Hz), 123.8 (d, *J* = 2.8 Hz), 117.6, 115.0 (d, *J* = 21.1 Hz), 114.0 (d, *J* = 21.1 Hz), 70.2, 45.5. HRMS (ESI) Calcd. for $C_{13}H_{11}FO_2Na$ ($[M+Na]^+$): 241.0635. Found: 241.0644. Calcd. for $C_{13}H_{15}FNO_2$ ($[M+NH_4]^+$): 236.1081. Found: 236.1088.

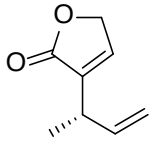
(*S*)-3-(hex-1-en-3-yl)furan-2(5H)-one (5f)



5f

Prepared according to the general procedure 2 from **4g** (44.0 mg, 0.250 mmol) and **3** (85.8 mg, 0.550 mmol) with (*R, R, R*)-**2** (7.6 mg, 0.00750 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5f** (10:1 mixture of regioisomers) as a colorless oil in 71% yield (33.2 mg).The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 14.0 min (major); t_R 13.6 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = +40.8° (c 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 5.81 (dt, *J* = 17.2, 8.8 Hz, 1H), 5.11 (d, *J* = 18.4 Hz, 1H), 5.10 (d, *J* = 8.8 Hz, 1H), 4.79 (s, 2H), 3.16 (q, *J* = 7.1 Hz, 1H), 1.87 – 1.62 (m, 1H), 1.58-1.48 (m, 1H), 1.44 – 1.20 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 143.9, 138.2, 136.8, 116.1, 70.1, 40.4, 35.2, 20.3, 13.8. HRMS (ESI) Calcd. for $C_{10}H_{15}O_2$ ($[M+H]^+$): 167.1067. Found: 167.1072. Calcd. for $C_{10}H_{18}NO_2$ ($[M+NH_4]^+$): 184.1338. Found: 184.1338.

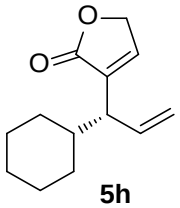
(*S*)-3-(but-3-en-2-yl)furan-2(5H)-one (5g)



5g

Prepared according to the general procedure 2 from **4h** (51.0 mg, 0.250 mmol) and **3** (85.8 mg, 0.550 mmol) with (*R, R, R*)-**2** (7.6 mg, 0.00750 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5g** (10:1 mixture of regioisomers) as a colorless oil in 80% yield (33.2 mg).The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 62.1 min (major); t_R 65.4 min (minor) [(Chiralpak AS-H) hexane/*i*-PrOH, 99:1, 0.5 mL/min] to be 97%. $[\alpha]_D^{25}$ = +28.8° (c 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (q, *J* = 1.6 Hz, 1H), 5.92 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.13 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.09 (dt, *J* = 10.0, 1.2 Hz, 1H), 4.78 (t, *J* = 1.7 Hz, 2H), 3.53 – 3.11 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 143.7, 139.2, 137.7, 114.9, 70.1, 34.3, 18.1. HRMS (EI) Calcd. for $C_8H_{10}O_2$ ($[M]^+$): 138.0681. Found: 138.0677.

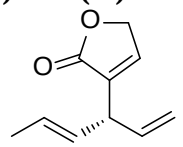
(R)-3-(1-cyclohexylallyl)furan-2(5H)-one (5h)



5h

Prepared according to the general procedure 2 from **4i** (61.0 mg, 0.250 mmol) and **3** (85.8 mg, 0.550 mmol) with (*R, R, R)*-**2** (7.6 mg, 0.00750 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5h** (8:1 mixture of regioisomers) as a colorless oil in 60% yield (31.0 mg).The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 14.6 min (major); t_R 14.1 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = +14.8° (c 1.0, CH_2Cl_2). ^{1}H NMR (8:1 inseparable regioisomer mixture, major regioisomer reported) (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 5.87 (dt, *J* = 16.7, 9.9 Hz, 1H), 5.08 (d, *J* = 9.4 Hz, 2H), 5.07 (d, *J* = 17.6 Hz, 2H), 4.80 (s, 2H), 2.96 (t, *J* = 8.4 Hz, 1H), 1.67 (m, 5H), 1.34 – 1.02 (m, 4H), 1.02 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 144.5, 136.9, 135.7, 116.8, 70.1, 47.5, 39.8, 31.2, 30.1, 26.3, 26.2, 26.1. HRMS (ESI) Calcd. for $C_{13}H_{19}O_2$ ($[M+H]^+$): 207.1380. Found: 207.1388. Calcd. for $C_{13}H_{22}NO_2$ ($[M+NH_4]^+$): 224.1650. Found: 224.1651.

(R,E)-3-(hexa-1,4-dien-3-yl)furan-2(5H)-one (5i)



5i

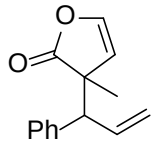
Prepared according to the general procedure 1 from **4j** (61.0 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with $[(dbcot)IrCl]_2$[5] (2.2 mg, 0.00250 mmol), (*R, R, R*)-**L2** (3.0 mg, 0.0050 mmol) and 5 μL $PrNH_2$. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **5i** (3:1 mixture of regioisomers) as a colorless oil in 83% yield (34.0 mg). The enantiomeric excess was determined by HPLC analysis (220 nm, 25 °C) t_R 50.1 min (major); t_R 49.2 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.5:0.5, 0.5 mL/min]

to be 99%. $[\alpha]_D^{25}$ = -51.1° (c 0.9, CH_2Cl_2). ^{1}H NMR (3:1 inseparable regioisomer mixture, major regioisomer reported) (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 5.90 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 1H), 5.62 – 5.52 (m, 2H), 5.13 (d, *J* = 9.6 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 4.79 (s, 2H), 3.83 (t, *J* = 6.4 Hz, 1H), 1.70 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 154.6, 144.8, 137.0, 128.8, 127.8, 116.1, 70.1, 42.8, 17.9. HRMS (ESI) Calcd. for $C_{10}H_{13}O_2$ ($[M+H]^+$): 165.0910. Found: 165.0916. Calcd. for $C_{10}H_{16}NO_2$ ($[M+NH_4]^+$): 182.1181. Found: 182.1181.

Procedure and Characterization Data for 3-Allylation of 3-Methyl Trimethylsiloxyfuran

In a nitrogen-filled dry-box, the cinnamyl carbonate **4a** (48.0 mg, 0.250 mmol, 1.00 equiv), 3-methyl trimethylsiloxyfuran **3b** (48.0 mg, 0.300 mmol, 1.20 equiv), and ZnF_2 (25.8 mg, 0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, (*S, S, S*)-**2** (5.1 mg, 0.0050 mmol, 0.020 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature overnight. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the mixture was heated to 50 °C and stirred for one more hour. Then the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure, and then purified by flash column silica gel chromatography (eluting with hexanes:EtOAc,6:1 to 3:1) to yield the product **5j** as a colorless oil in 42% yield (22.5 mg) and **6j** as a colorless oil in 38% yield (20.3 mg).

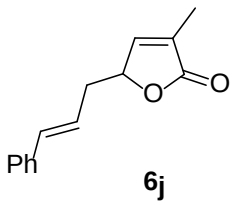
3-methyl-3-(1-phenylallyl)furan-2(3H)-one (5j)



5j

The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 11.7 min (major); t_R 10.9 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be 97%. $[\alpha]_D^{25}$ = +163° (c 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 5H), 6.80 (d, *J* = 3.6 Hz, 1H), 6.06 (dt, *J* =17.2, 9.6 Hz, 1H), 5.58 (d, *J* = 3.6 Hz, 1H), 5.17 (d, *J* = 16.0 Hz, 2H), 5.16 (d, *J* = 9.6 Hz, 2H), 3.53 (d, *J* = 9.4 Hz, 1H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 141.4, 139.1, 135.6, 128.64, 128.58, 127.3, 118.7, 112.9, 56.6, 52.0, 22.2. HRMS (ESI) Calcd. for $C_{14}H_{15}O_2$ ($[M+H]^+$): 215.1067. Found: 215.1071. Calcd. for $C_{14}H_{14}O_2Na$ ($[M+Na]^+$): 237.0892. Found: 237.0889.

5-cinnamyl-3-methylfuran-2(5H)-one (6j)



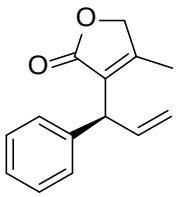
6j

The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 24.1 min (major); t_R 28.6 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 92%. $[\alpha]_D^{25}$ = +63.7° (c 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 5H), 7.10 (d, *J* = 0.8 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.99 (t, *J* = 5.9 Hz, 1H), 2.86 – 2.40 (m, 2H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 148.1, 136.7, 134.1, 130.5, 128.6, 127.6, 126.2, 122.8, 80.4, 37.0, 10.7. HRMS (ESI) Calcd. for $C_{14}H_{15}O_2$ ($[M+H]^+$): 215.1067. Found: 215.1070.

Procedure and Characterization Data for 3-Allylation of 4-Methyl Trimethylsiloxyfuran

In a nitrogen-filled dry-box, the cinnamyl carbonate **4a** (48.0 mg, 0.250 mmol, 1.00 equiv), 4-methyl trimethylsiloxyfuran (48.0 mg, 0.300 mmol, 1.20 equiv), and ZnF_2 (25.8 mg, 0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, (*S, S, S*)-**2** (5.1 mg, 0.0050 mmol, 0.020 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature overnight. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure, and the mixture was separated by flash column silica gel chromatography (eluting with hexanes:EtOAc,6:1 to 3:1) to yield the product **5k′** as a 1:1 diastereomeric mixture in 21% yield (11.3 mg), **5k** in 30% yield (17.0 mg), and **6k** in 38% yield as a 2:1 diastereomeric mixture (20.4 mg). The diastereomeric mixture of **5k′** (11.3 mg, 0.0500 mmol, 1.00 equiv) was dissolved in 1 mL of DCM, and then the O-desmethyl quinine[6] (3.3 mg, 0.0100 mmol, 0.200 equiv) was added. The mixture was stirred overnight. The crude reaction mixture was directly loaded on silica gel and then purified by flash column chromatography (eluting with hexanes:EtOAc 3:1) to give a colorless oil **5k** in 95% yield (10.7 mg).

(*S*)-4-methyl-3-(1-phenylallyl)furan-2(5H)-one (5k)



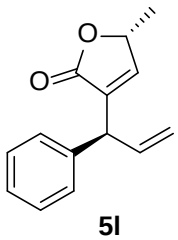
5k

The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 17.1 min (major); t_R 19.1 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 93%. $[\alpha]_D^{25}$ = +3.8° (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.04 (m, 5H), 6.40 (ddd, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 4.68 (s, 2H), 4.67 (d, *J* = 10.5 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 157.7, 140.3, 136.6, 128.5, 128.2, 127.8, 126.8, 117.0, 72.5, 45.0, 12.7. HRMS (ESI) Calcd. for $C_{13}H_{15}O_2$ ($[M+H]^+$): 215.1067. Found: 215.1075. Calcd. for $C_{13}H_{18}NO_2$ ($[M+NH_4]^+$): 236.1332. Found: 232.1338.

Procedure and Characterization Data for 3-Allylation of 5-methyl trimethylsiloxyfuran

In a nitrogen-filled dry-box, the cinnamyl carbonate **4a** (48.0 mg, 0.250 mmol, 1.00 equiv), 5-methyl trimethylsiloxyfuran **3d** (48.0 mg, 0.300 mmol, 1.20 equiv), and ZnF_2 (25.8 mg, 0.250 mmol, 1.00 equiv) were added to a 1-dram vial. Then, (*S, S, S*)-**2** (5.1 mg, 0.00500 mmol, 0.020 equiv) and DCM (0.3 mL) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature overnight. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure, and the mixture was separated by flash column silica gel chromatography (eluting with hexanes:EtOAc, 6:1 to 3:1) to yield the product **5l′** in nearly 100% yield and 1:1 dr (56.0 mg). The diastereomeric mixture **5l′** (56.0 mg, 0.250 mmol, 1.00 equiv) was dissolved in 1 mL DCM, and then the O-desmethyl quinine (15.6 mg, 0.0500 mmol, 0.200 equiv) was added. The mixture was stirred overnight. The crude reaction mixture was directly loaded on silica gel and then purified by flash column chromatography (eluting with hexanes:EtOAc 3:1) to give the product **5l** as a colorless oil in 88% yield and 6:1 dr. (49.3 mg).

(*R*)-5-methyl-3-((*S*)-1-phenylallyl)furan-2(5H)-one (5l)

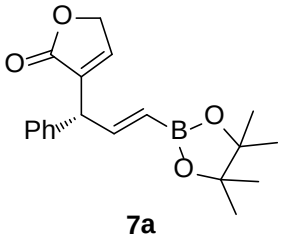


5l

The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 27.0 min (major); t_R 22.9 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 98:2, 0.6 mL/min] to be 99%. $[\alpha]_D^{25}$ = +13.8° (c 1.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.14 (m, 5H), 7.03 (d, *J* = 1.2 Hz, 1H), 6.19 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 5.07 – 5.00 (m, 1H), 4.52 (d, *J* = 6.6 Hz, 1H), 1.48 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 150.9, 139.8, 137.2, 135.9, 128.7, 128.1, 127.0, 116.9, 77.5, 45.6, 19.2. HRMS (ESI) Calcd. for $C_{13}H_{15}O_2$ ($[M+H]^+$): 215.1067. Found: 215.1075. Calcd. for $C_{13}H_{18}NO_2$ ($[M+NH_4]^+$): 236.1332. Found: 232.1339.

Functionalization of the Compound 5a, 5g and 5l

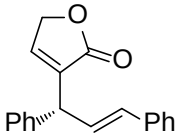
(*R,E*)-3-(1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)furan-2(5H)-one (7a)



7a

To a stirred solution of the compound **5a** (100 mg, 0.500 mmol, 1.00 equiv) and vinyl boronate (1.16 g, 7.50 mmol, 15.0 equiv) in CH_2Cl_2 (3 mL) at 22 °C was added the Hoveyda–Grubbs second generation catalyst (6.3 mg, 0.010 mmol, 0.020 equiv). The reaction mixture was warmed to 40 °C and stirred at that temperature for 3 h before a second portion of catalyst (6.3 mg, 0.010 mmol, 0.020 equiv) was added, and the resulting mixture was stirred at 40 °C for 12 h. The solvent was then removed in vacuum, and the residue was purified by flash column chromatography, eluting with Hexane/EtOAc (3:1) to give the alkenyl boronate **7a** in 82% yield (132 mg, exclusively *E*) as a light red oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 5H), 7.16 (s, 1H), 6.86 (dd, *J* = 17.9, 6.1 Hz, 1H), 5.44 (d, *J* = 17.9 Hz, 1H), 4.82 (d, A of AB-system, *J* = 19.2 Hz, 1H), 4.77 (d, B of AB-system, *J* = 20.0 Hz, 1H), 4.56 (d, *J* = 5.3 Hz, 1H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 150.8, 146.4, 139.1, 135.4, 128.7, 128.4, 127.2, 83.3, 70.2, 47.3, 24.78, 24.75. HRMS (ESI) Calcd. for $C_{19}H_{24}O_4B$ ($[M+H]^+$): 327.1762. Found: 327.1775. Calcd. for $C_{19}H_{27}NO_4B$ ($[M+NH_4]^+$): 344.2033. Found: 344.2041.

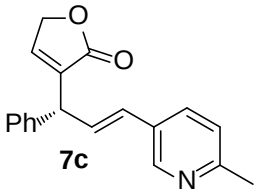
(*R*,*E*)-3-(1,3-diphenylallyl)furan-2(5H)-one (7b)



7b

In a glovebox, to a stirred solution of the compound **7a** (20.0 mg, 0.0621 mmol, 1.00 equiv), K_2CO_3·1.5 H_2O (20.5 mg, 0.124 mmol, 2.00 equiv) and bromobenzene (19.5 mg, 0.124 mmol, 2.00 equiv) in acetonitrile (1 mL) at 22 °C was added Pd(Qphos)(crotyl)Cl (2.8 mg, 0.0031 mmol, 0.050 equiv). The reaction mixture was warmed to 40 °C and stirred at that temperature for 2 h. The reaction was monitored by GC. When the reaction was judged to be complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography, eluting with Hexane/EtOAc (3:1) to give **7b** in 72% yield (12.3 mg) as a colorless oil.
The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 25.0 min (major); t_R 27.2 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = +12.2° (c 0.9, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.20 (m, 10H), 7.18 (s, 1H), 6.52 (dd, *J* = 15.9, 7.3 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.86 (A of d AB-system, *J* = 18.0 Hz, 1H), 4.83 (B of d AB-system, *J* = 18.0 Hz, 1H), 4.67 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 145.9, 140.1, 136.7, 136.4, 132.1, 128.8, 128.7, 128.5, 128.1, 127.6, 127.2, 126.4, 70.2, 45.2.

(R,E)-3-(3-(6-methylpyridin-3-yl)-1-phenylallyl)furan-2(5H)-one (7c)

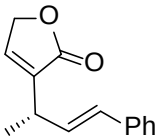


7c

In a glovebox, to a stirred solution of the compound **7a** (20.0 mg, 0.0621 mmol, 1.00 equiv), $K_2CO_3 \cdot 1.5\ H_2O$ (20.5 mg, 0.124 mmol, 2.00 equiv) and 5-bromo-2-methylpyridine(21.6 mg, 0.124 mmol, 2.00 equiv) in acetonitrile (1 mL) at 22 °C was added Pd(Qphos)(crotyl)Cl (2.8 mg, 0.0031 mmol, 0.050 equiv). The reaction mixture was warmed to 40 °C and stirred at that temperature for 2 h. The reaction was monitored by GC. When the reaction was judged to be complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography, eluting with Hexane/EtOAc (3:1) to pure EtOAc to give **7c** in 63% yield (11.3 mg) as a colorless oil.

^{1}H NMR (600 MHz, CDCl3) δ 8.44 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.37-7.35 (m, 2H), 7.31-7.27 (m, 3H), 7.16 (s, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.54 (dd, J = 15.9, 7.1 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 4.87 (A of d AB-system, J = 18.2 Hz, 1H),, 4.82 (B of d AB-system, J = 18.2 Hz, 1H), 4.67 (d, J = 7.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 157.5, 147.5, 146.1, 139.7, 136.1, 133.2, 129.9, 129.5, 128.9, 128.6, 128.1, 127.3, 123.0, 70.2, 45.4, 24.1. HRMS (ESI) Calcd. for $C_{19}H_{28}O_2N$ ($[M+H]^+$): 292.1332. Found: 292.1333.

(*S*,*E*)-3-(4-phenylbut-3-en-2-yl)furan-2(5H)-one (7d)[7]

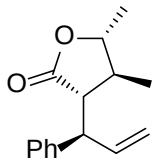


7d

In a glovebox, to a stirred solution of the compound **5g** (20.0 mg, 0.145 mmol, 1.00 equiv) and styrene (75.2 mg, 0.725 mmol, 5.00 equiv) in CH_2Cl_2 (0.3 mL) was added Schrock's catalyst (11.1 mg, 0.0145 mmol, 0.100 equiv). The reaction mixture was stirred at room temperature for 3 h. The reaction progress was monitored by GC. When the reaction was judged to be complete, the solvent was evaporated under vacuum. The residue was purified by flash column chromatography, eluting with Hexane/EtOAc (3:1) to give **7d** as a colorless oil in 88% yield (27.3 mg, exclusively *E*).

The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 21.8 min (major); t_R 25.5 min (minor) [(Chiralpak AS-H) hexane/*i*-PrOH, 97:3, 1.0 mL/min] to be 96%; or, t_R 28.3 min (major); t_R 35.1 min (minor) [(Chiralpak AS-H) heptane/*i*-PrOH, 97:3, 1.0 mL/min] to be 96%. $[\alpha]_D^{25}$ = +6.0° (c 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 4H), 7.20-7.25 (m, 1H), 7.15 (s, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.9, 7.2 Hz, 1H), 4.79 (br s, 2H), 3.82 – 3.13 (m, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 143.6, 137.9, 137.0, 130.8, 130.2, 128.5, 127.4, 126.2, 70.0, 33.9, 18.7.

(*3S*,*4S*,*5R*)-4,5-dimethyl-3-((R)-1-phenylallyl)dihydrofuran-2(3H)-one (7e)



7e

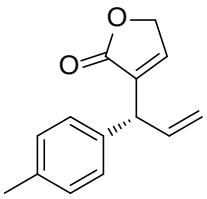
To a stirred solution of MeLi (0.374 mmol, 4.00 equiv) in ether (1.00 mL) at -20 °C was added CuI (35.7 mg, 0.187 mmol, 2.00 equiv). The mixture was stirred at that temperature for 1 h. Then the compound **5l** (20.0 mg, 0.0934 mmol, 1.00 equiv) in 0.5 mL ether was added to the mixture. The reaction progress was monitored by GC. When the reaction was judged to be complete, the solvent was removed under vacuum. The residue was purified by flash column chromatography, eluting with Hexane/EtOAc (6:1) to give **7e** as a colorless oil in 82% yield (17.5 mg).
$[\alpha]_D^{25}$ = +41.6° (c 0.8, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 6.91 (m, 5H), 6.37 (ddd, *J* = 16.7, 10.5, 8.6 Hz, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 5.21 (dd, *J* = 18.0, 0.6 Hz, 1H), 3.97 (dq, *J* = 9.1, 6.2 Hz, 1H), 3.85 (dd, *J* = 8.6, 4.6 Hz, 1H), 2.68 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.05 – 1.81 (m, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 140.8, 136.7, 128.6, 128.2, 126.9, 117.7, 81.0, 54.3, 48.3, 40.5, 18.8, 16.0. HRMS (ESI) Calcd. for $C_{15}H_{19}O_2$ ($[M+H]^+$):231.1380. Found: 231.1378. Calcd. for $C_{15}H_{22}NO_2$ ($[M+NH_4]^+$): 248.1650. Found: 248.1641.

Procedure for Stoichiometric Reaction of 3-Allylation with Trimethylsiloxyfuran

To a stirred solution of the Ir-allyl complex[8] (20.0 mg, 0.0181 mmol, 1.00 equiv) and ZnF_2 (1.9 mg, 0.018 mmol, 1.0 equiv) in CH_2Cl_2 (0.3 mL) at room temperature was added trimethylsiloxyfuran **3** (4.2 mg, 0.027 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 12 h and was then analyzed by GC. No product was detected. Then Bu_4NOAc (5.4 mg, 0.018 mmol, 1.0 equiv) was added to the mixture. After 2 h, GC analysis showed the formation of the desired product **5a**. The reaction mixture was purified by preparative TLC, eluting with Hexane/EtOAc (3:1) to give the product **5a** in 92% yield. HPLC analysis showed that the product from this reaction was the same major enantiomer as was formed from the catalytic reaction.

To a stirred solution of the Ir-allyl complex (20.0 mg, 0.0181 mmol, 1.00 equiv), p-tolyl allylacetate (17.2 mg, 0.0905 mmol, 5.00 equiv), mesitylene (11.6 mg, 0.0967 mmol) and ZnF_2 (5.7 mg, 0.054 mmol, 3.0 equiv) in CH_2Cl_2 (0.3 mL) at room temperature was added trimethylsiloxyfuran **3a** (16.8 mg, 0.108 mmol, 6.00 equiv) and Bu_4NOAc (5.4 mg, 0.0181 mmol, 1.00 equiv). The reaction mixture was stirred at room temperature for 2 h. GC analysis at this time showed the formation of the compound **5a** in 92% yield and **S1** in 37% yield.

(*R*)-3-(1-tolylallyl)furan-2(5H)-one (S1)



S1

Prepared according to the general procedure 1 from **4a** (48.0 mg, 0.250 mmol) and **3** (46.8 mg, 0.300 mmol) with (*R, R, R*)-**2** (2.6 mg, 0.0025 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give **S1** as a light yellow oil in 83% yield (44.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 6.98 (m, 5H), 6.20 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.23 (dt, J = 10.2, 1.1 Hz, 1H), 5.07 (dt, J = 17.1, 1.2 Hz, 1H), 4.83 (dt, A of AB-system, *J* = 18.0, 1.6 Hz, 1H), 4.77 (dt, B of AB-system, *J* = 18.0, 1.6 Hz, 1H), 4.47 (d, J = 6.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 145.9, 137.3, 136.7, 136.2, 129.4, 128.0, 116.8, 70.2, 45.5, 21.0. HRMS (ESI) Calcd. for $C_{14}H_{14}O_2Na$ ($[M+Na]^+$): 237.0886. Found: 237.0887.

References

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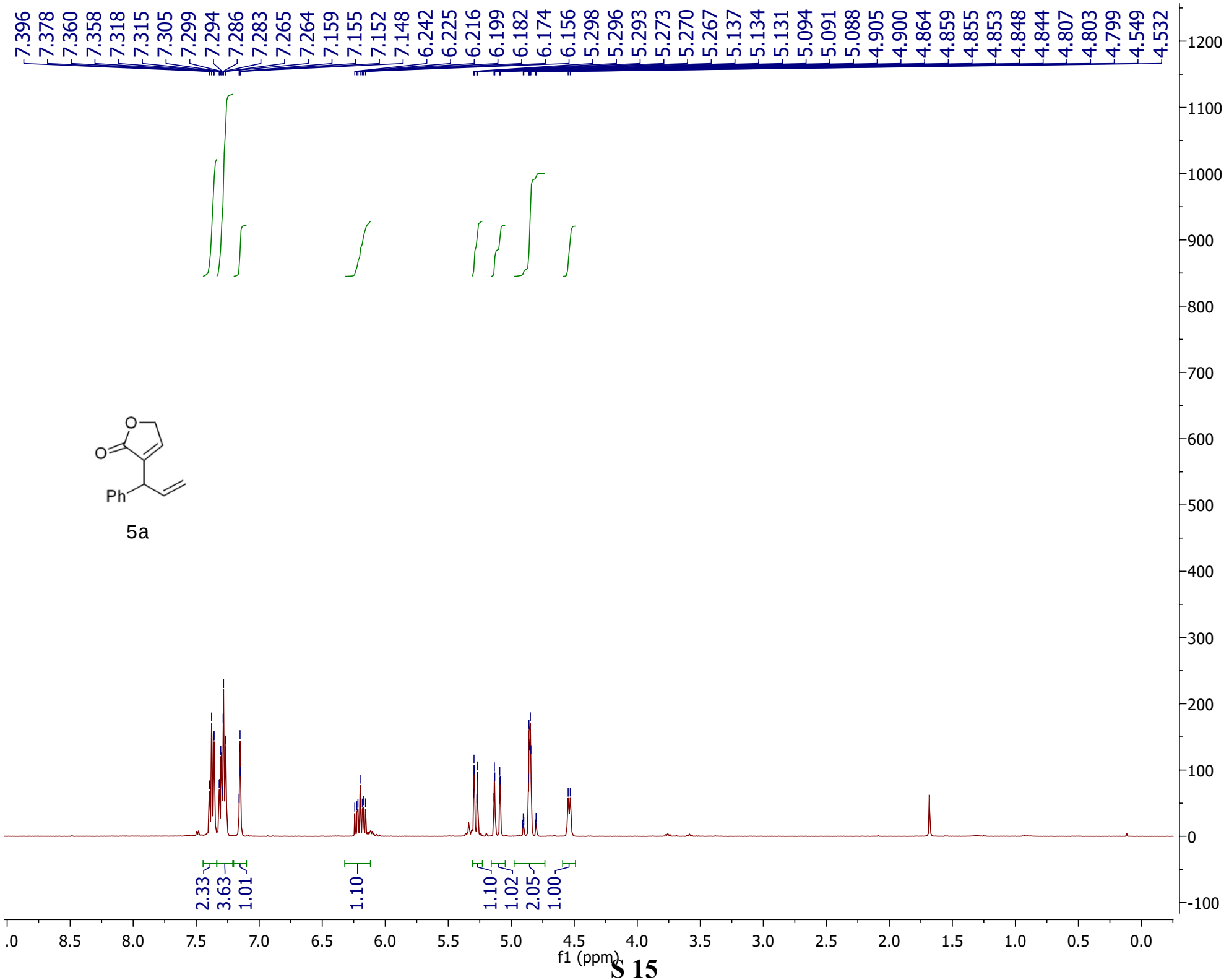
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6.174
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5.091
5.088
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4.900
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4.853
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4.844
4.807
4.803
4.799
4.549
4.532
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1.02
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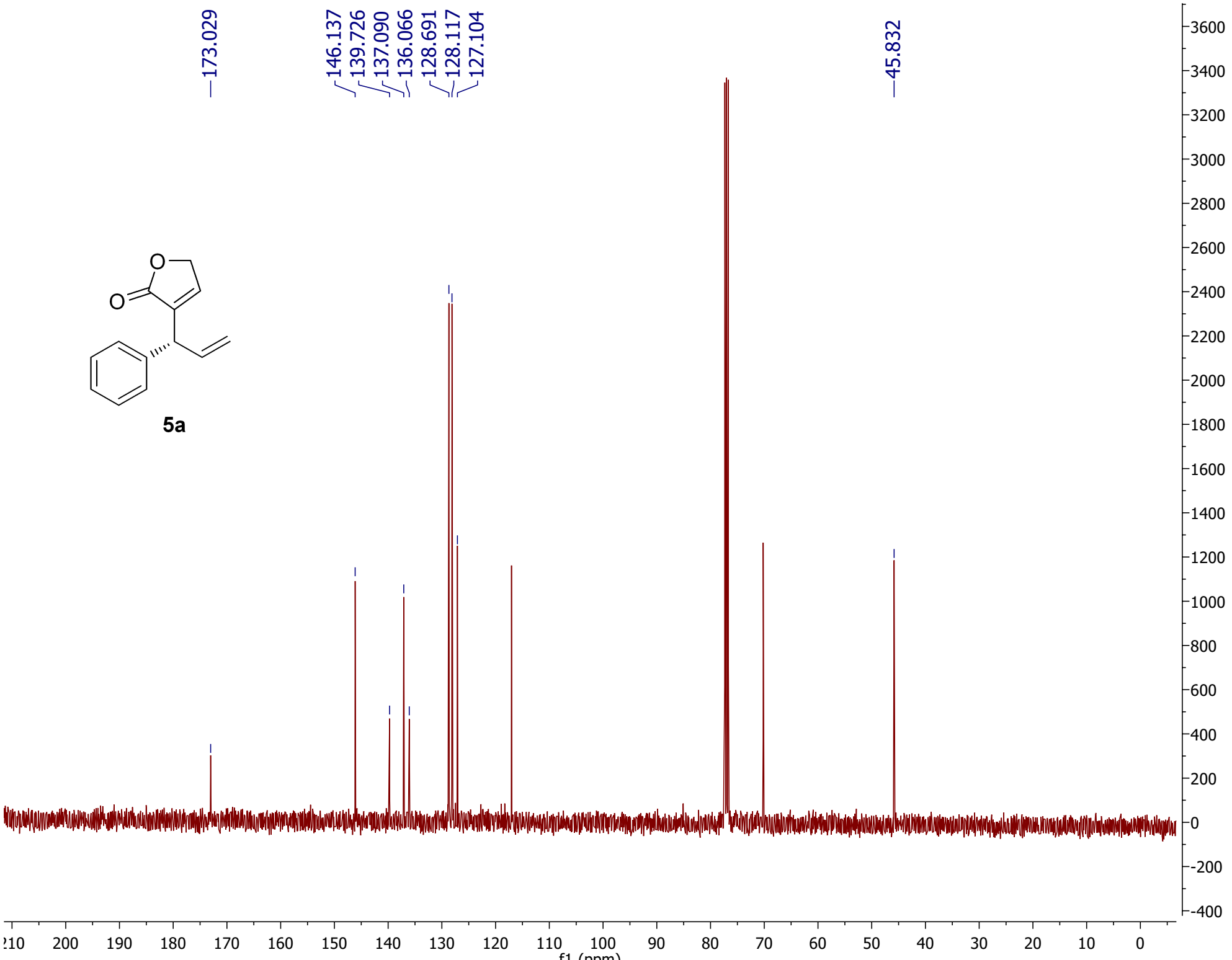
f1 (ppm)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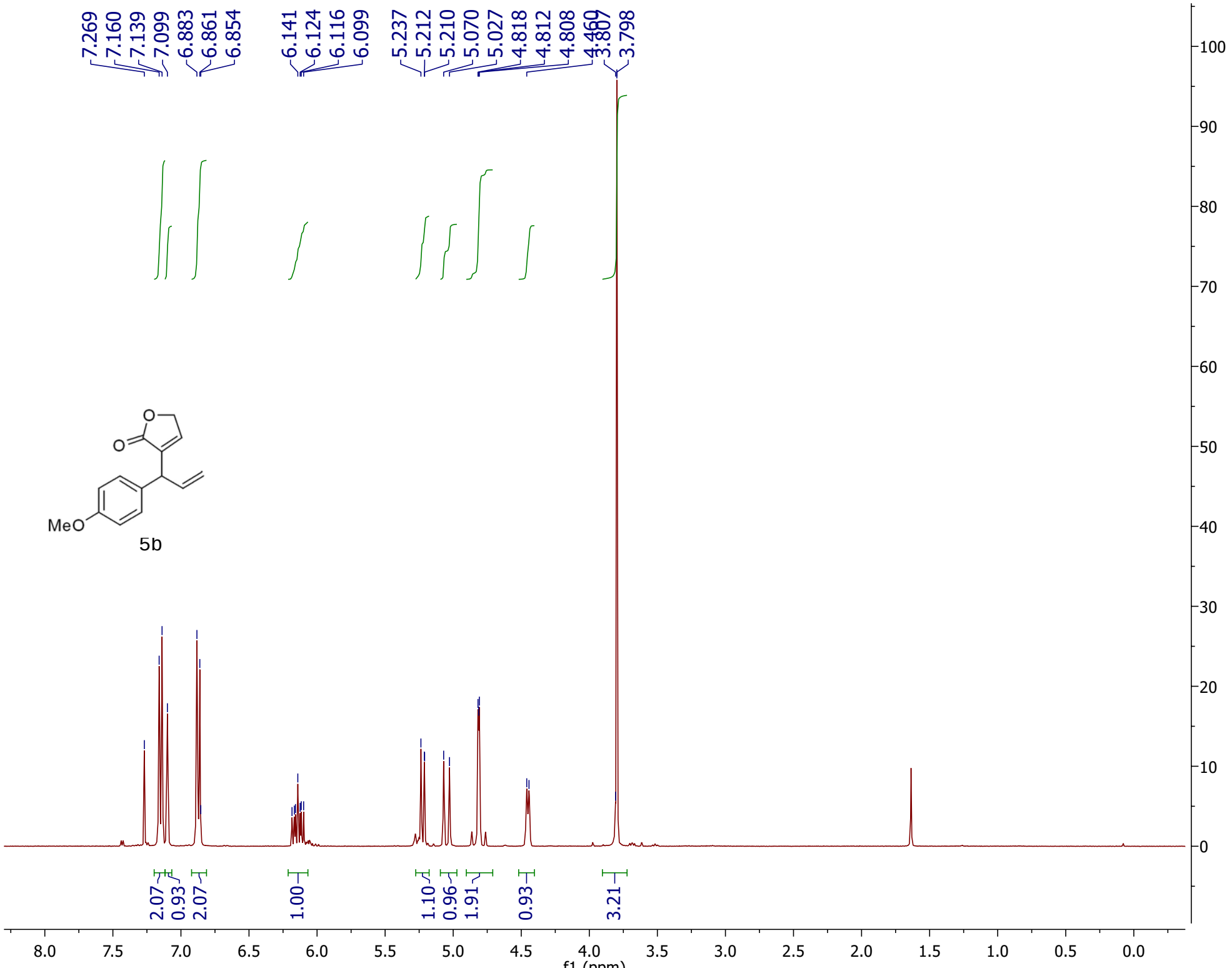
f1 (ppm)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5.210
5.070
5.027
4.818
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4.808
4.460
3.807
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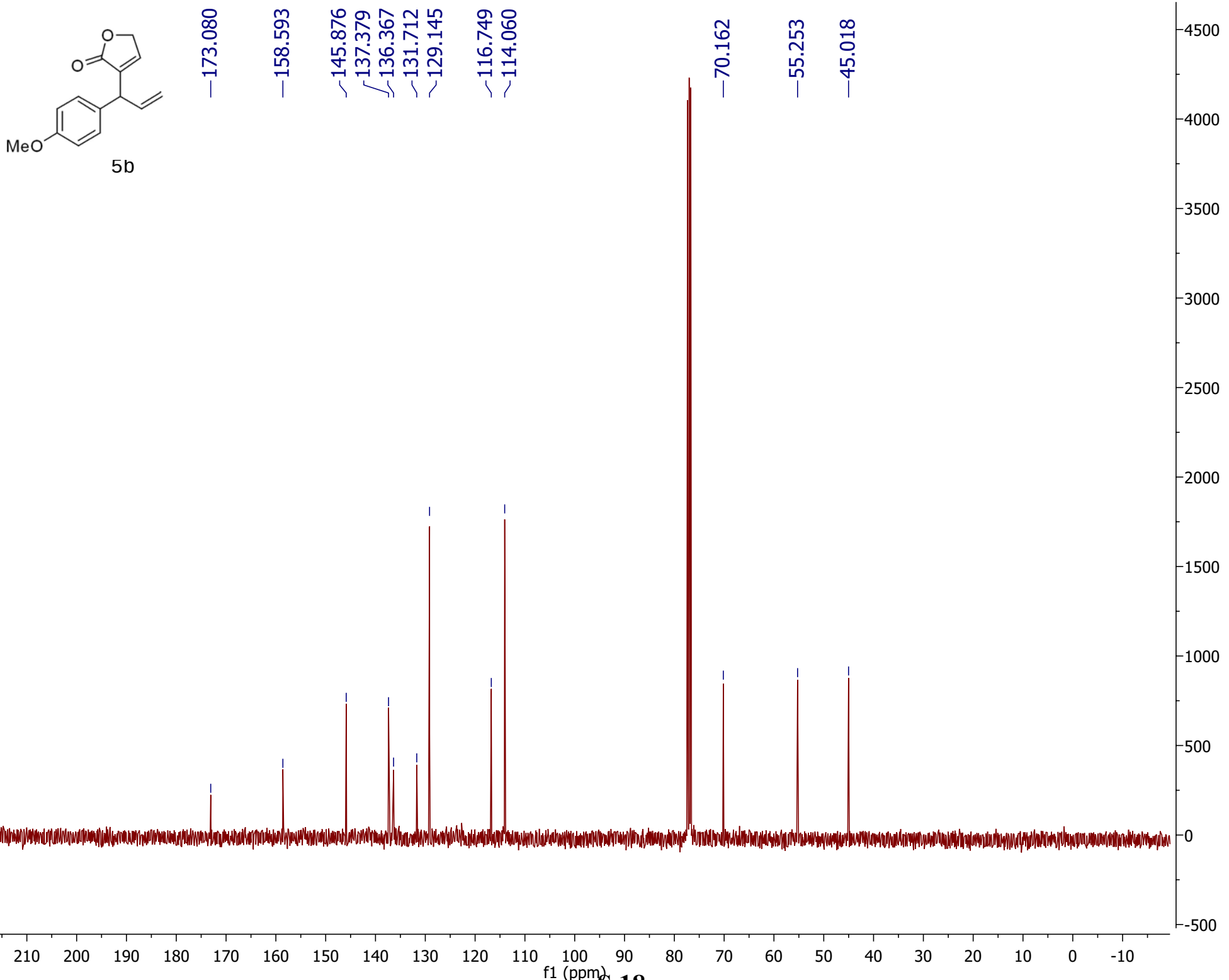
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3000
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500
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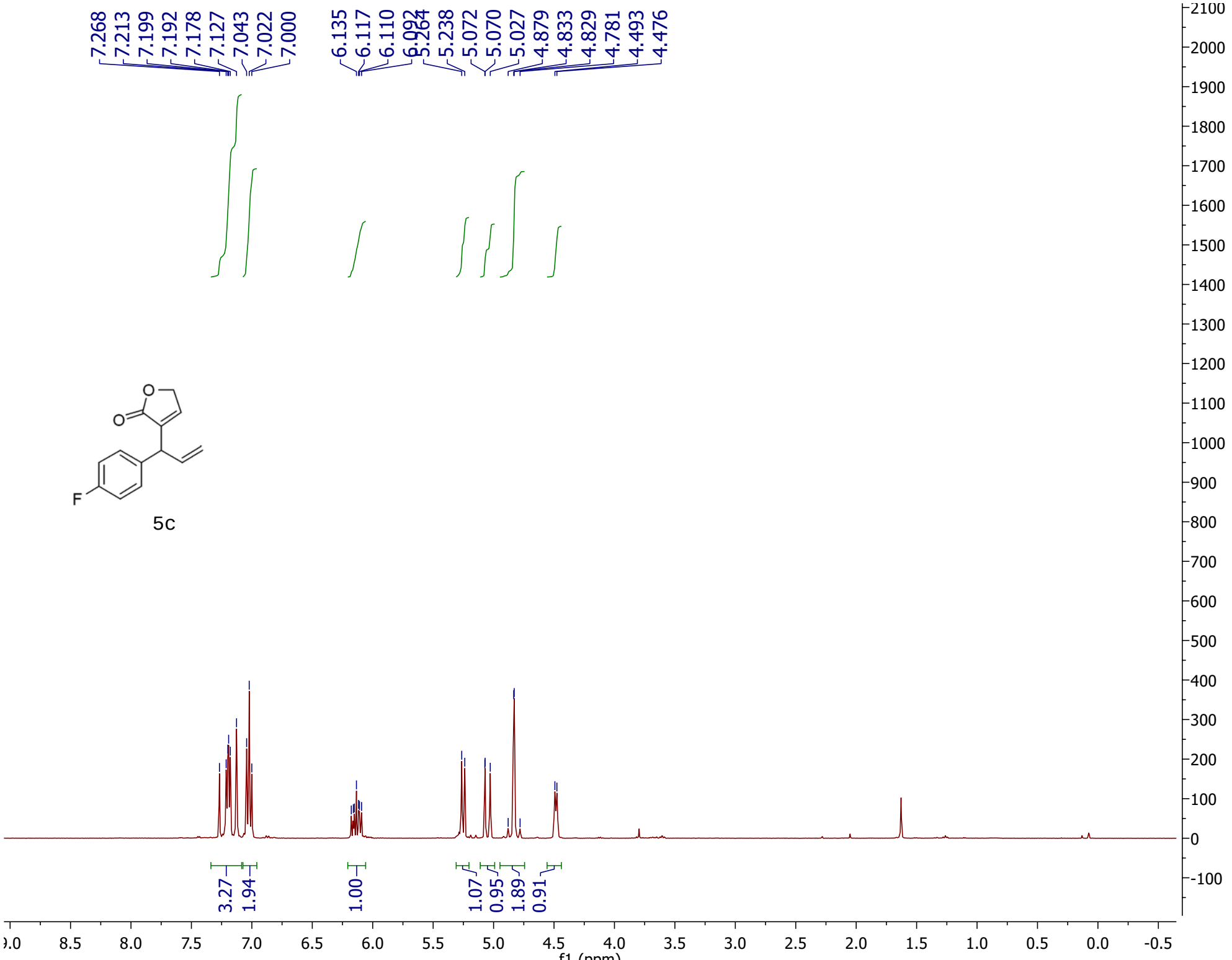
f1 (ppm)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5.027
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4.833
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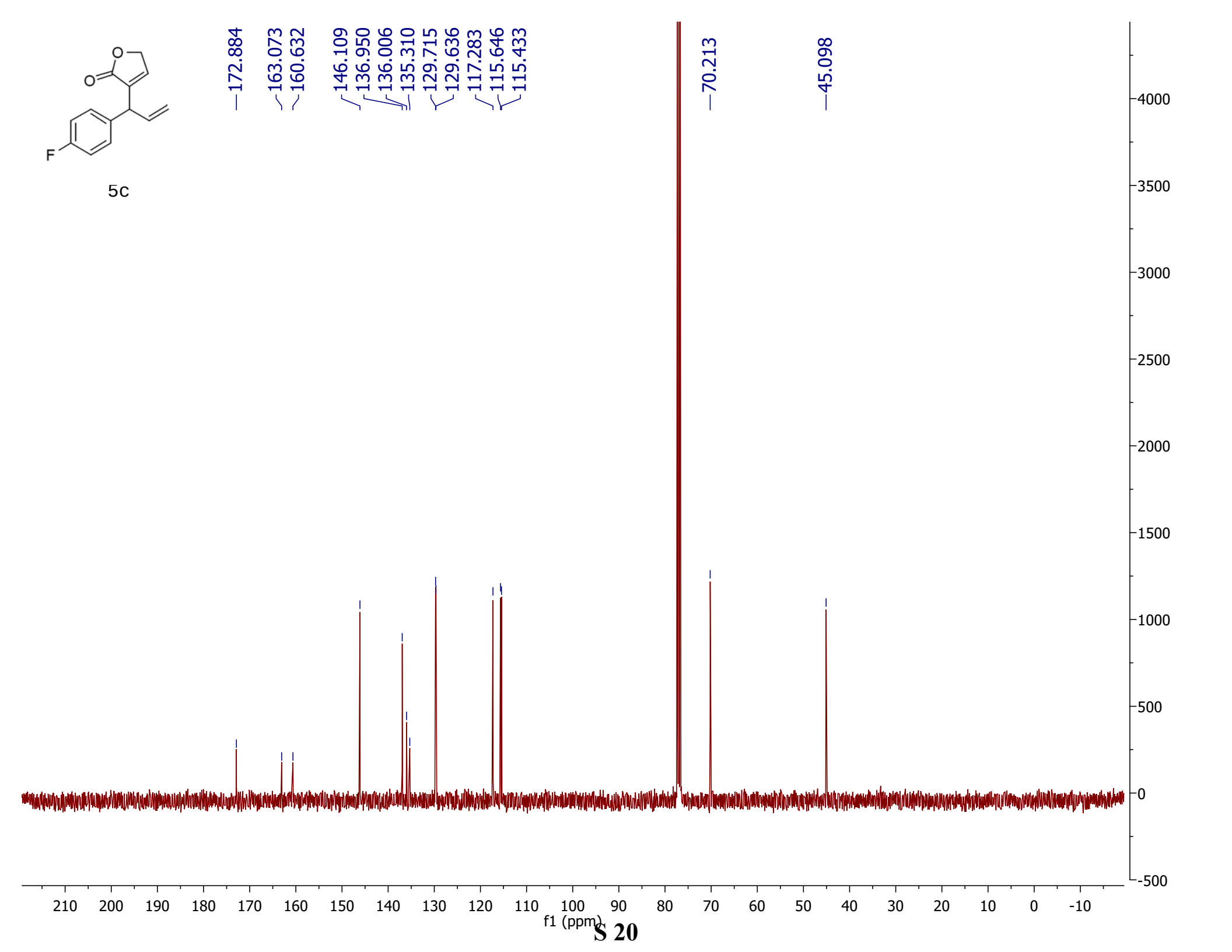
f1 (ppm)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O
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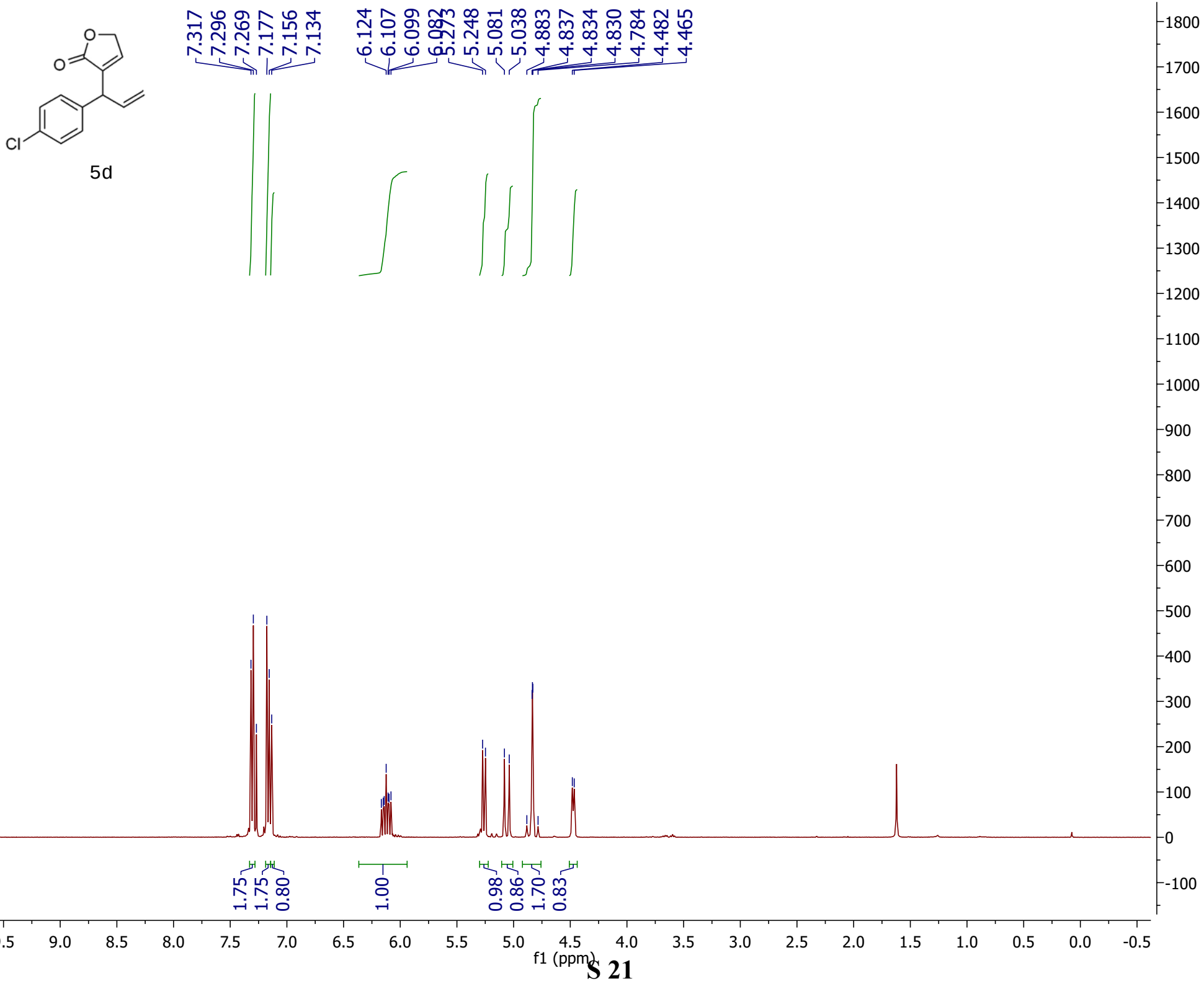
f1 (ppm)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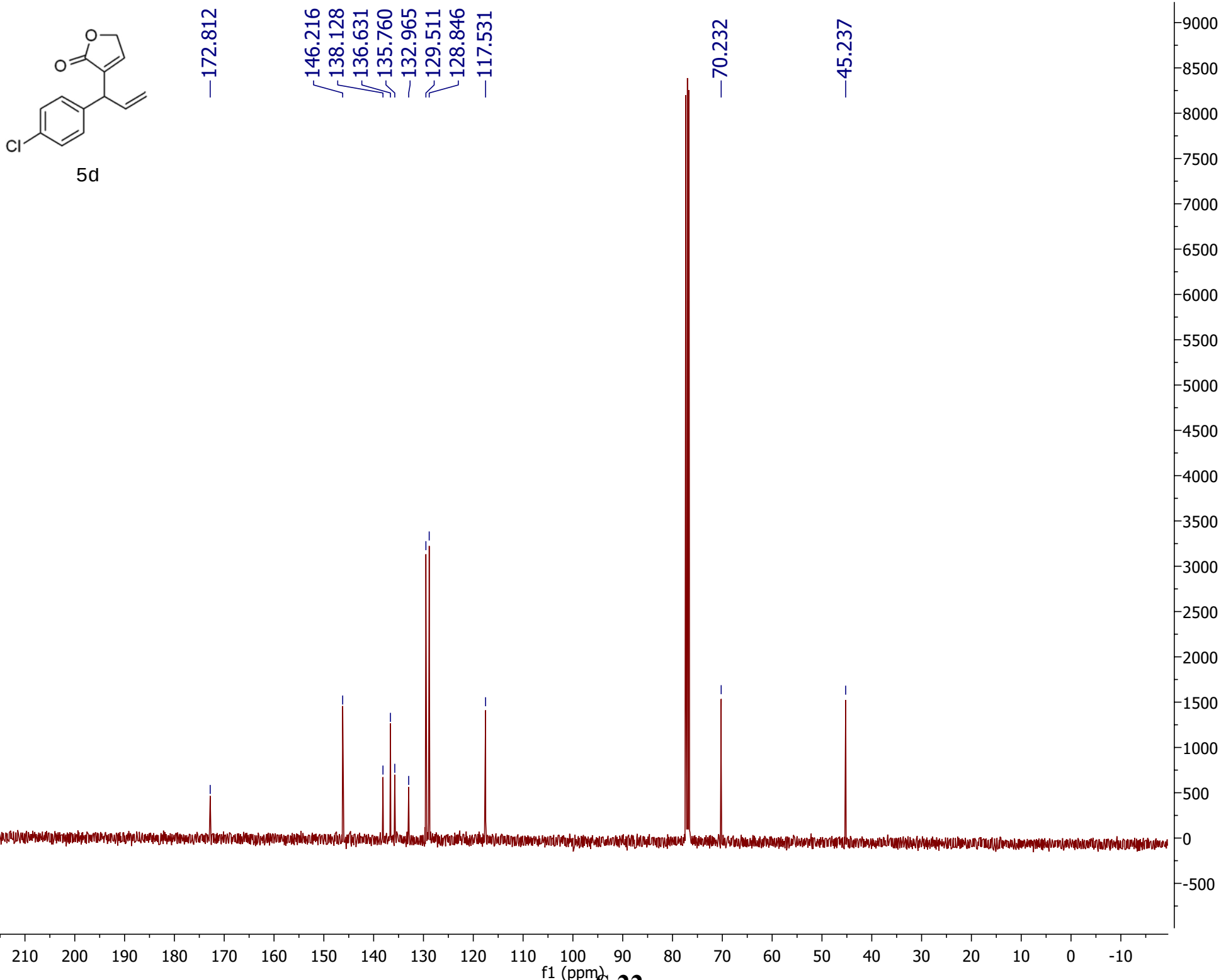
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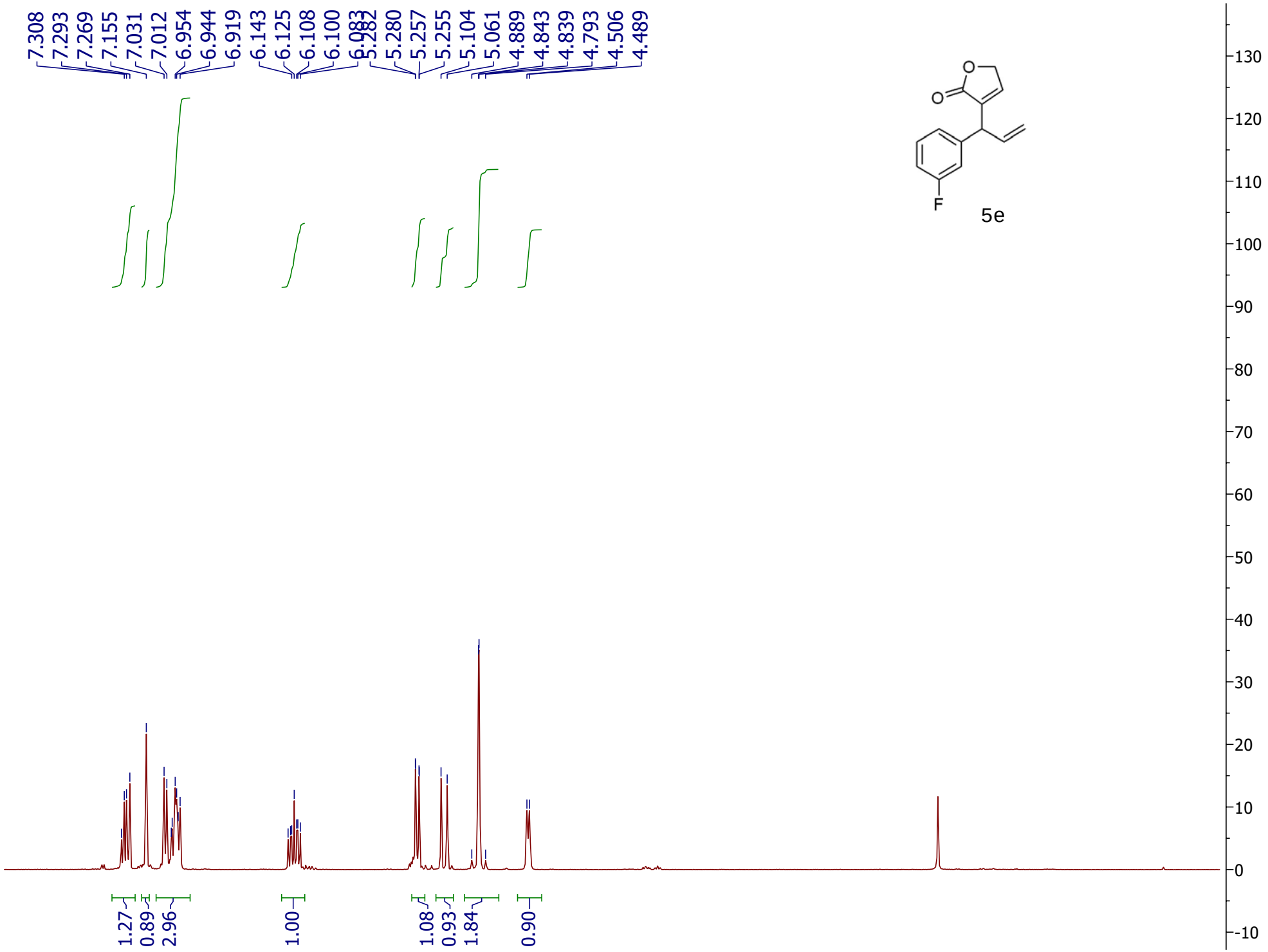
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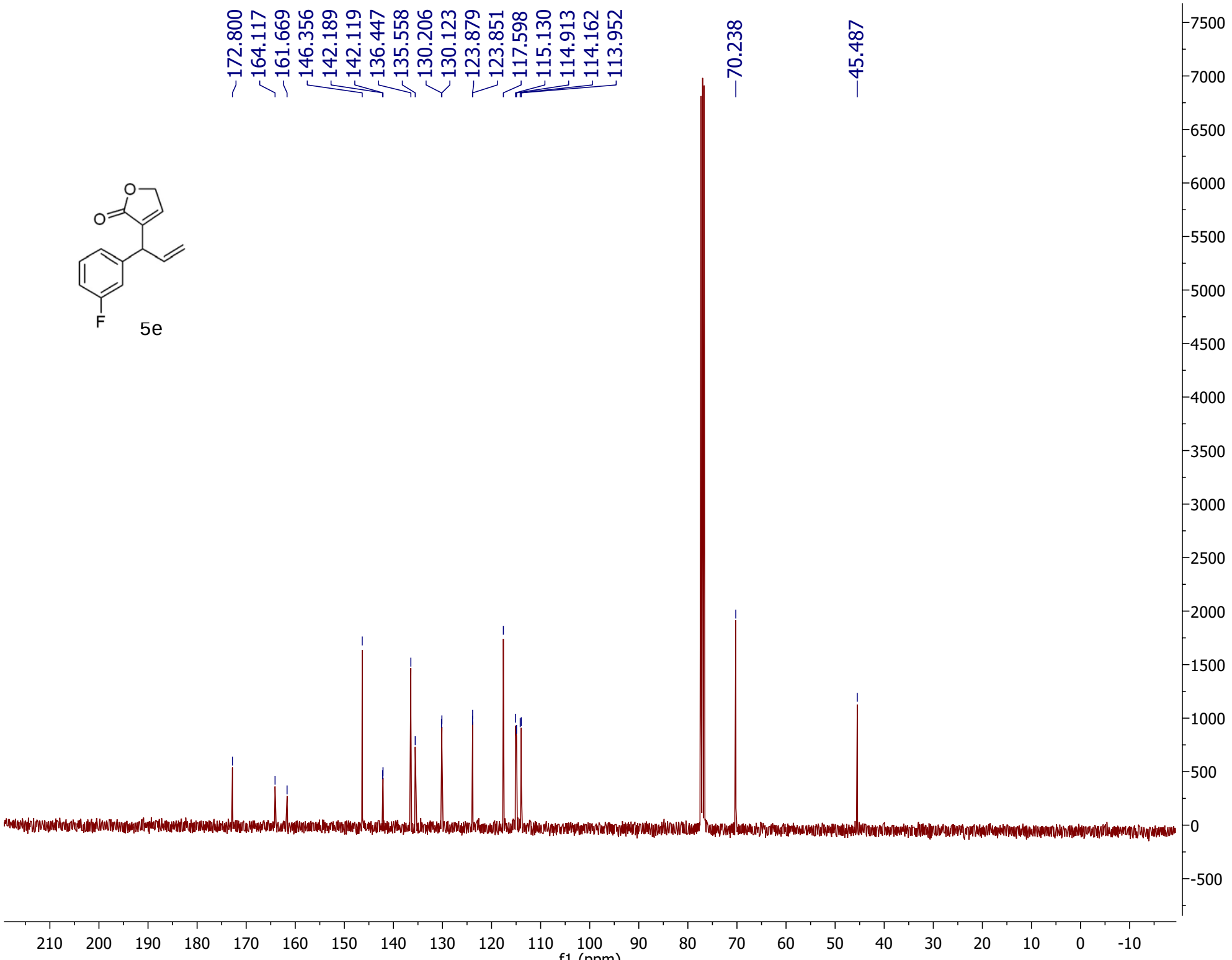
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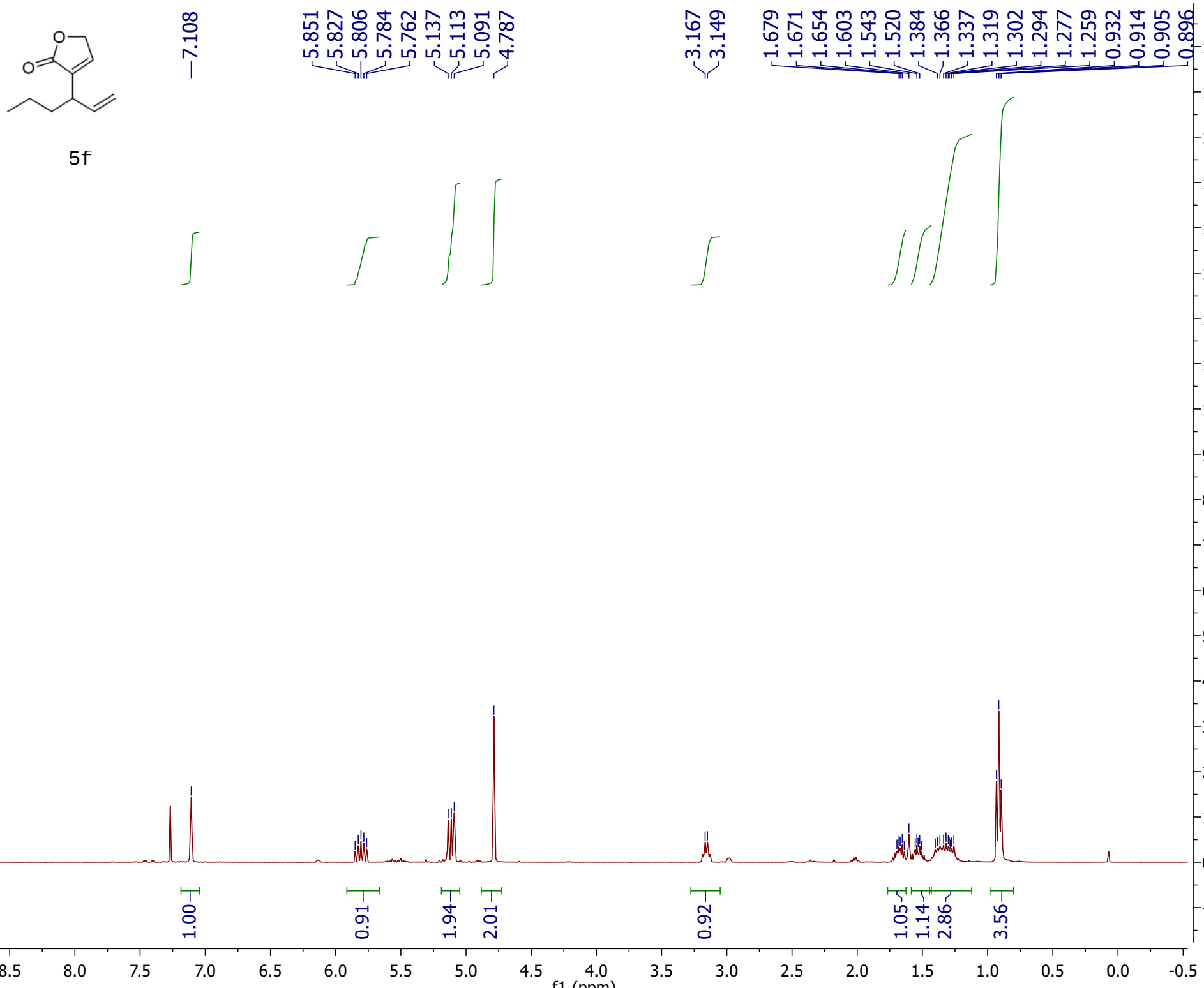
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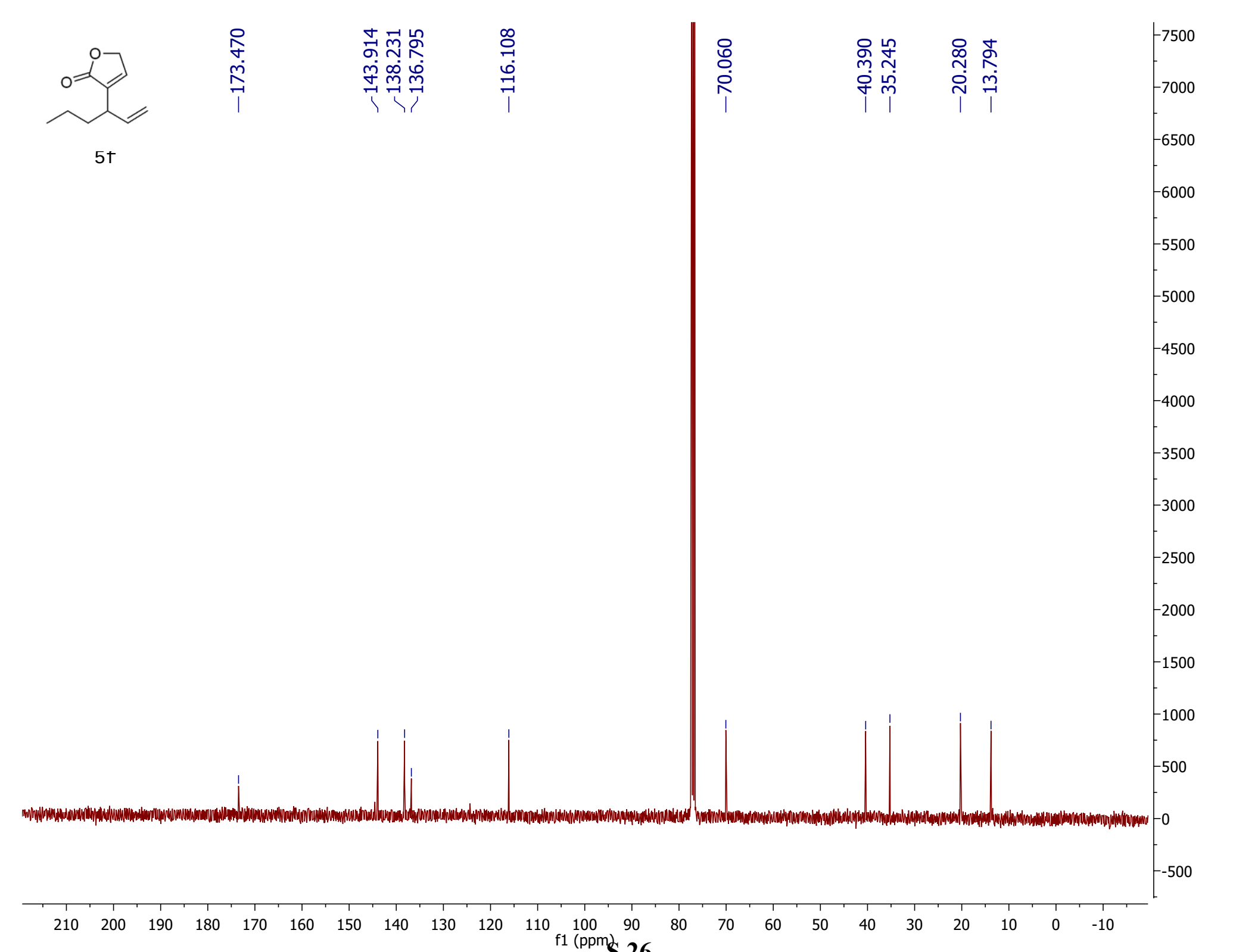
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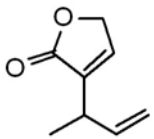

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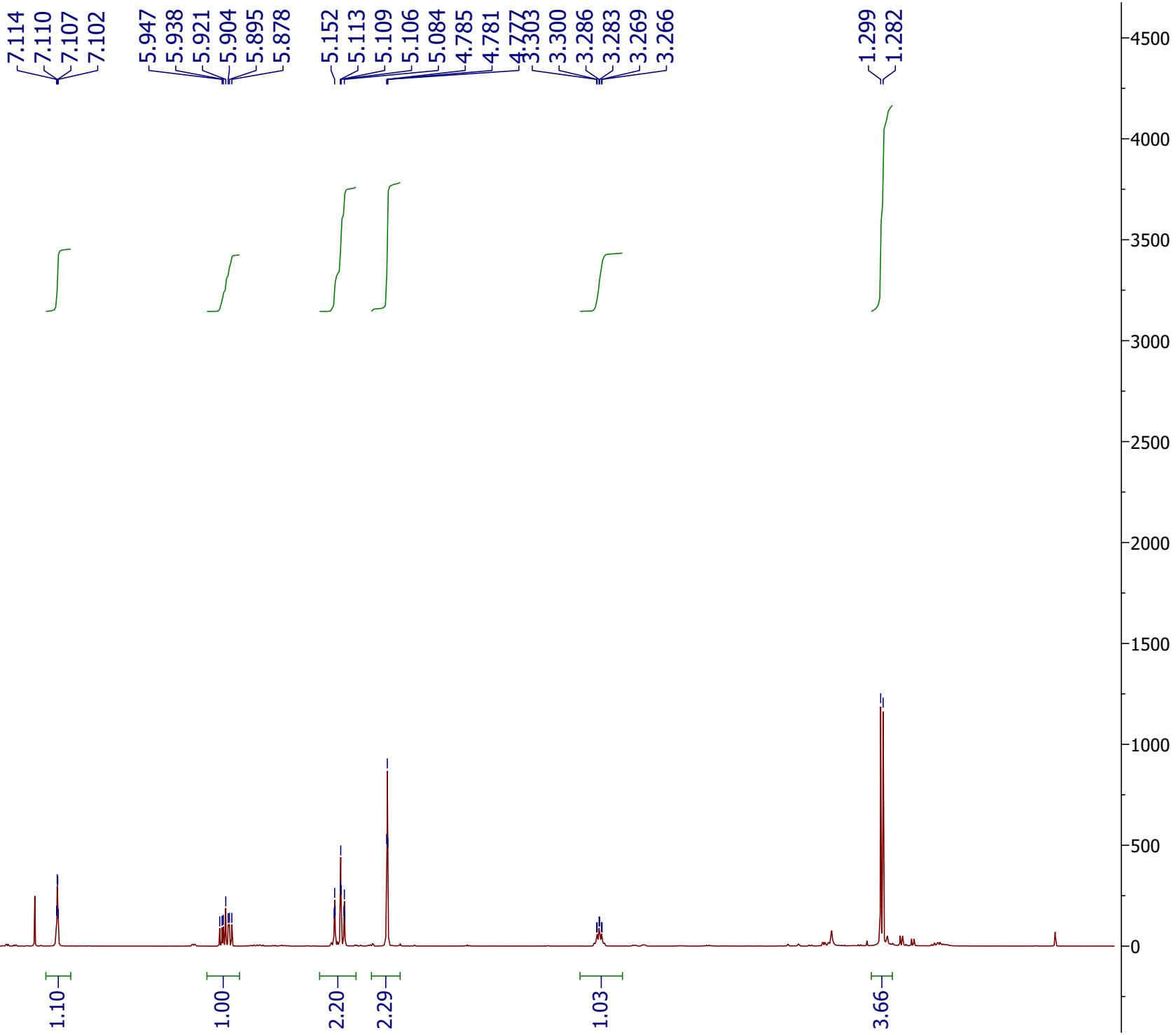
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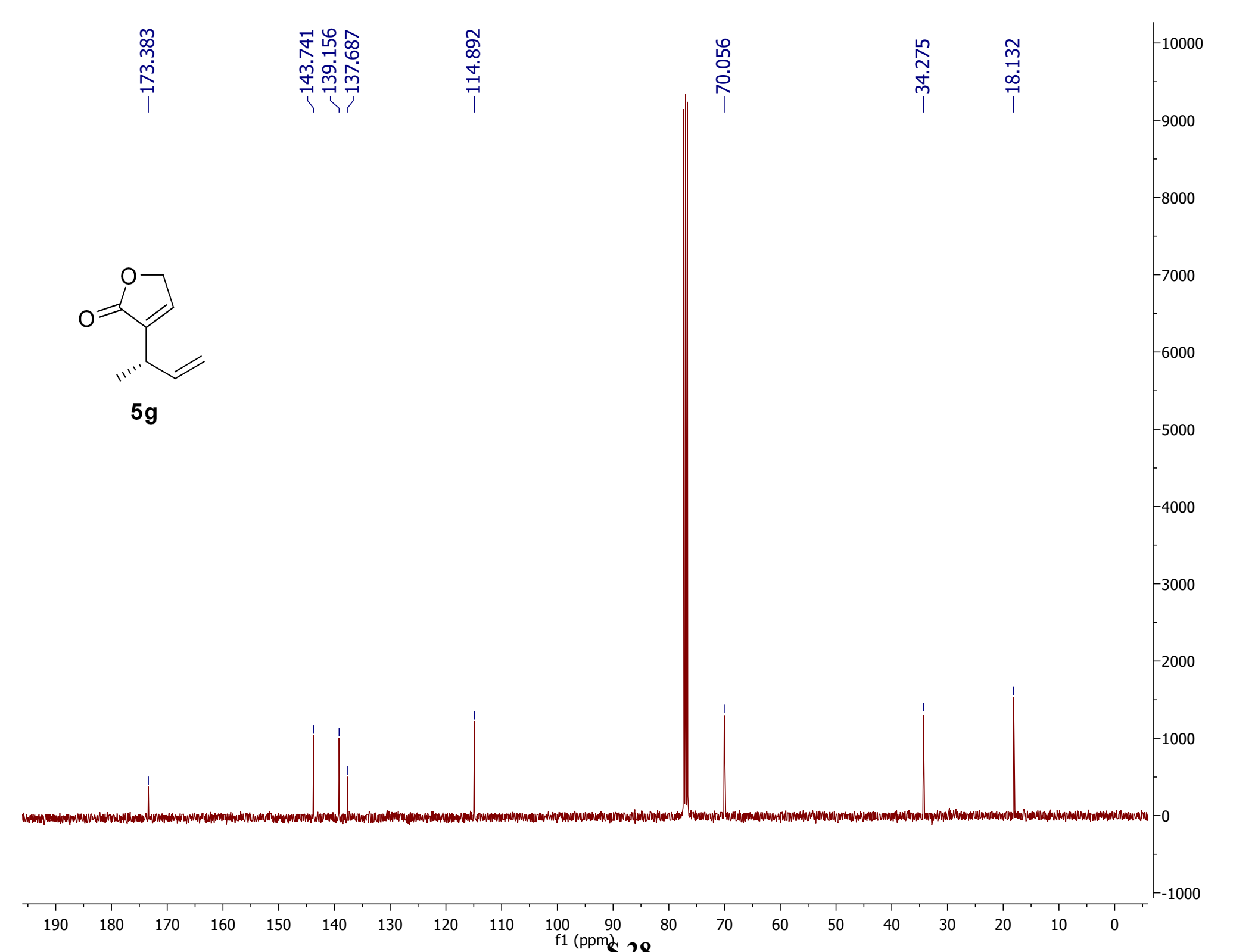
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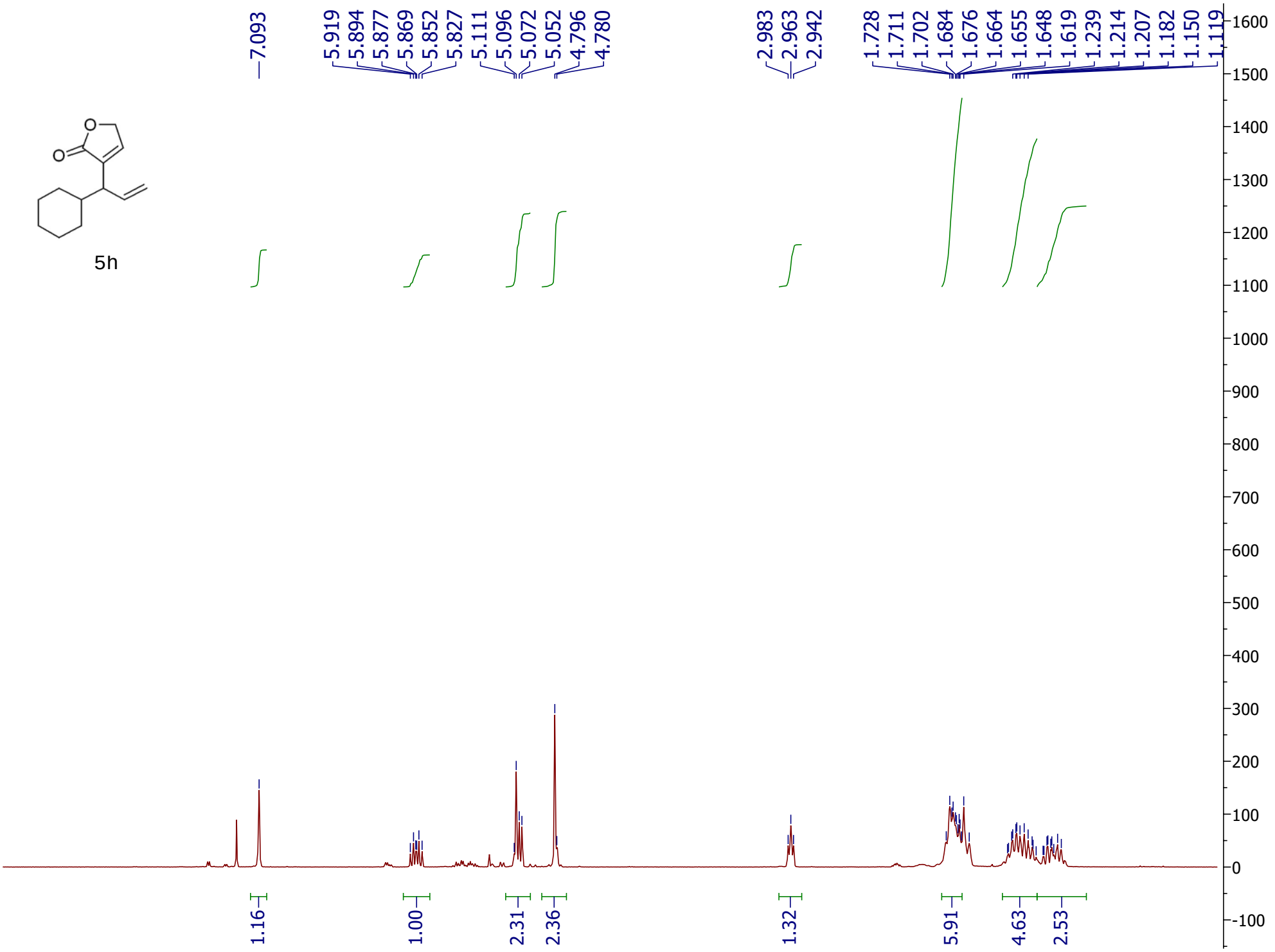
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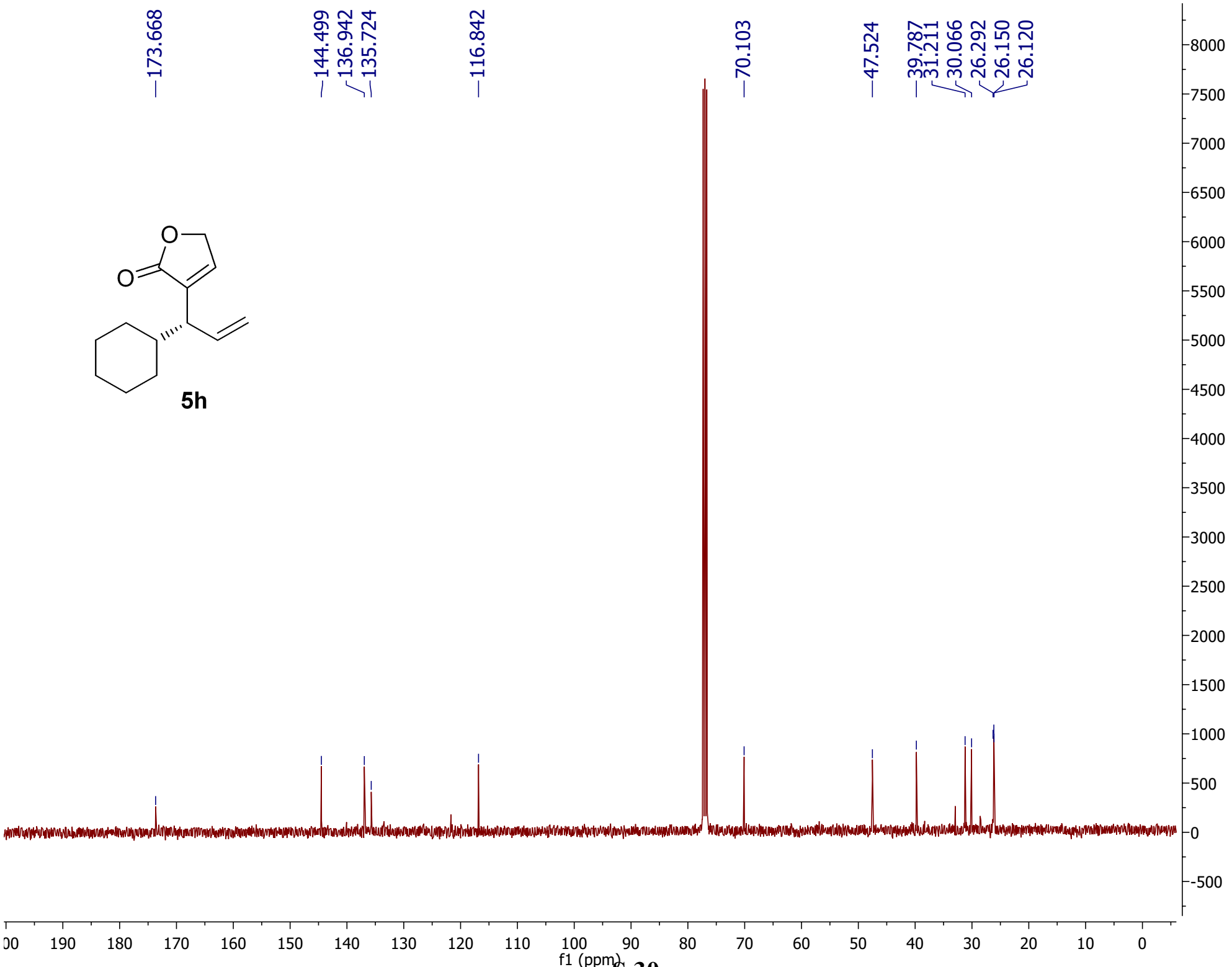
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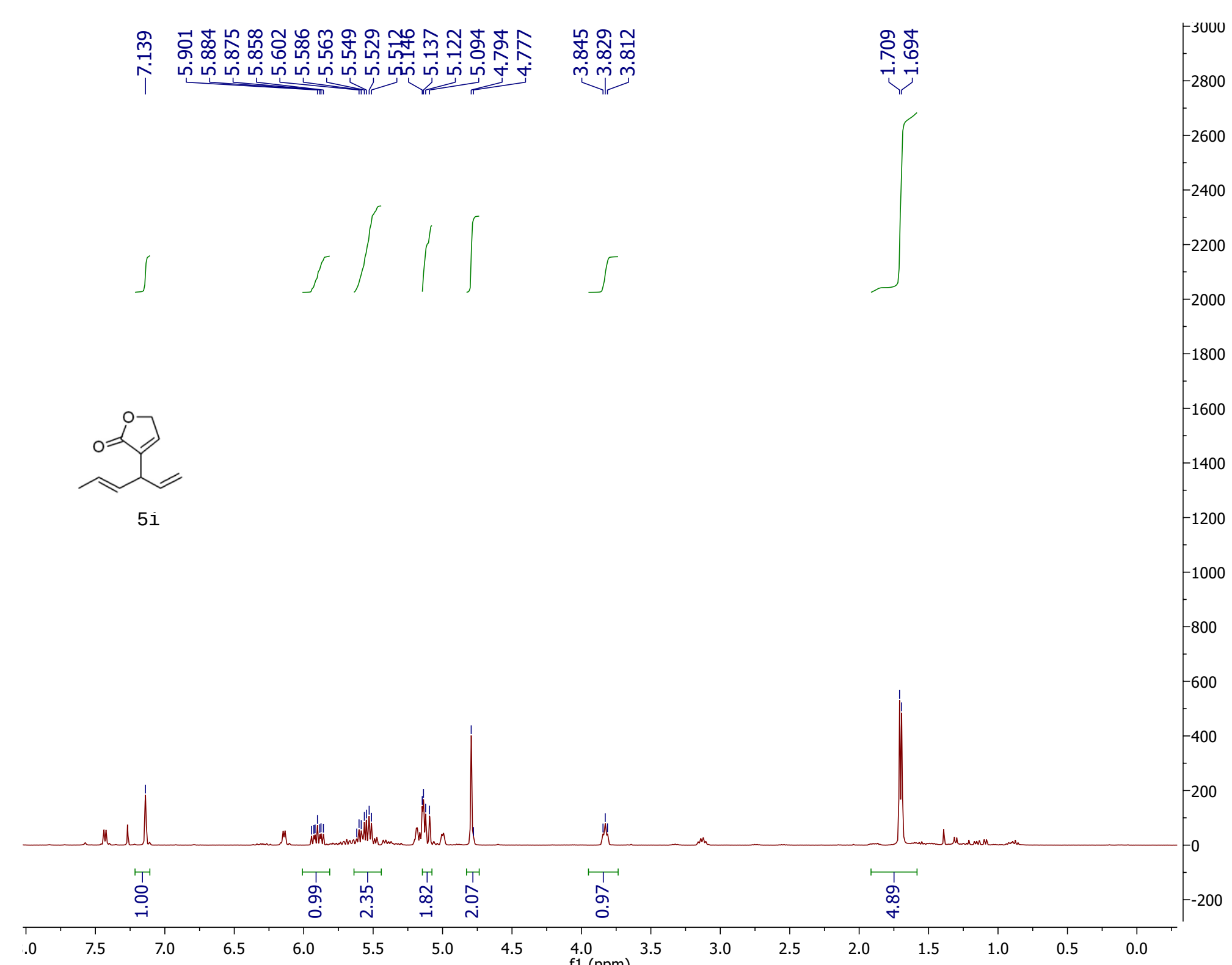
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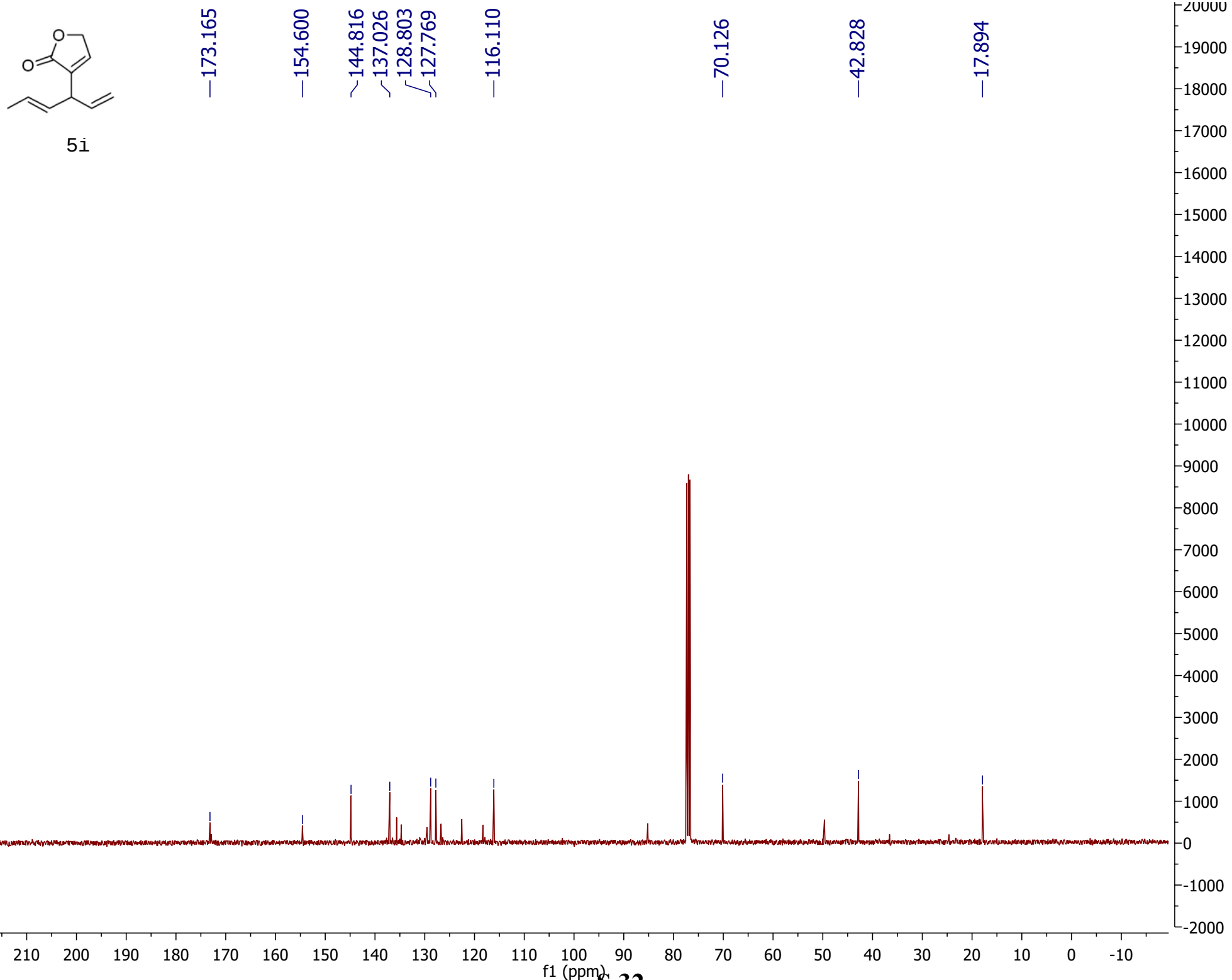
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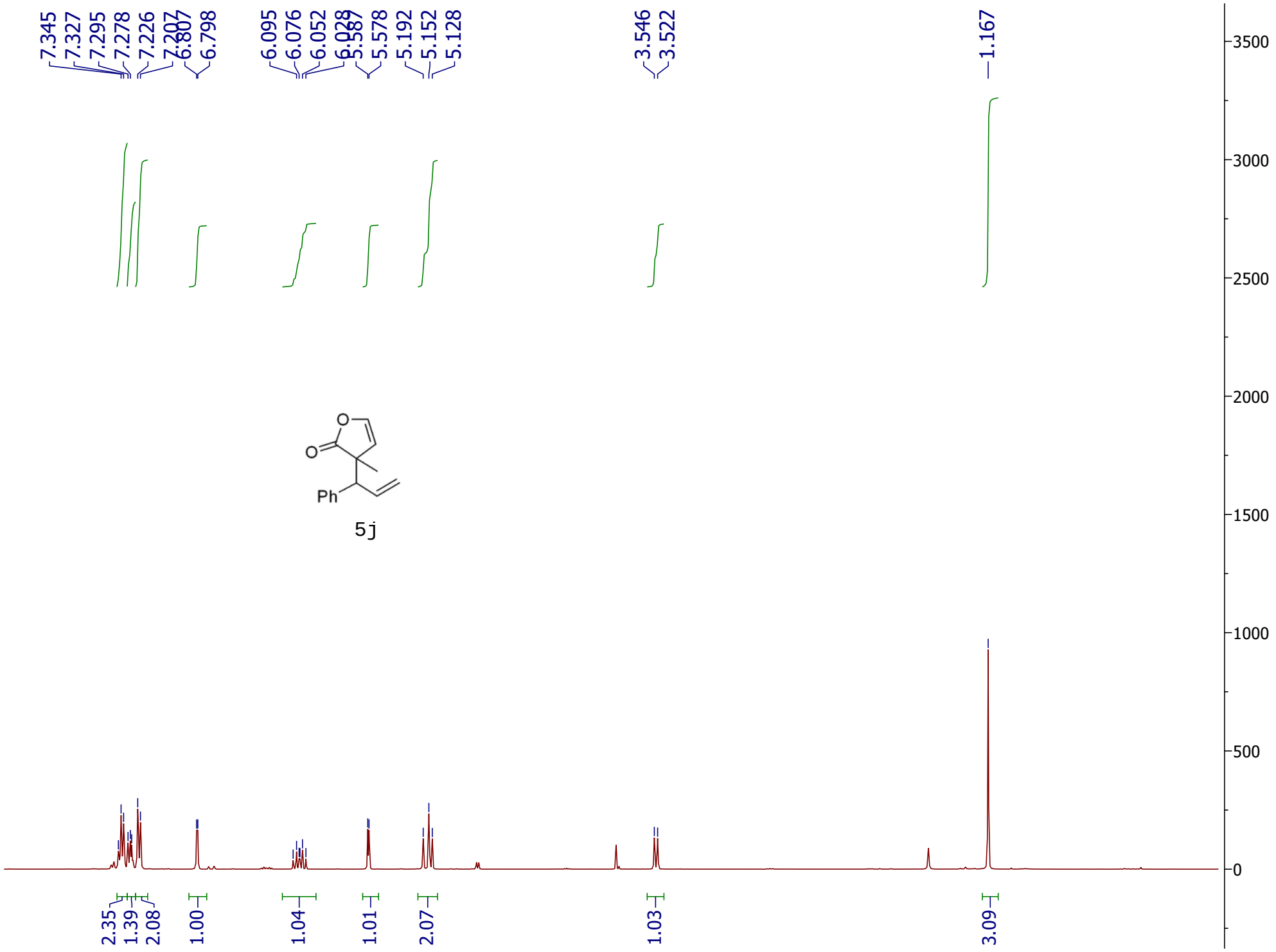
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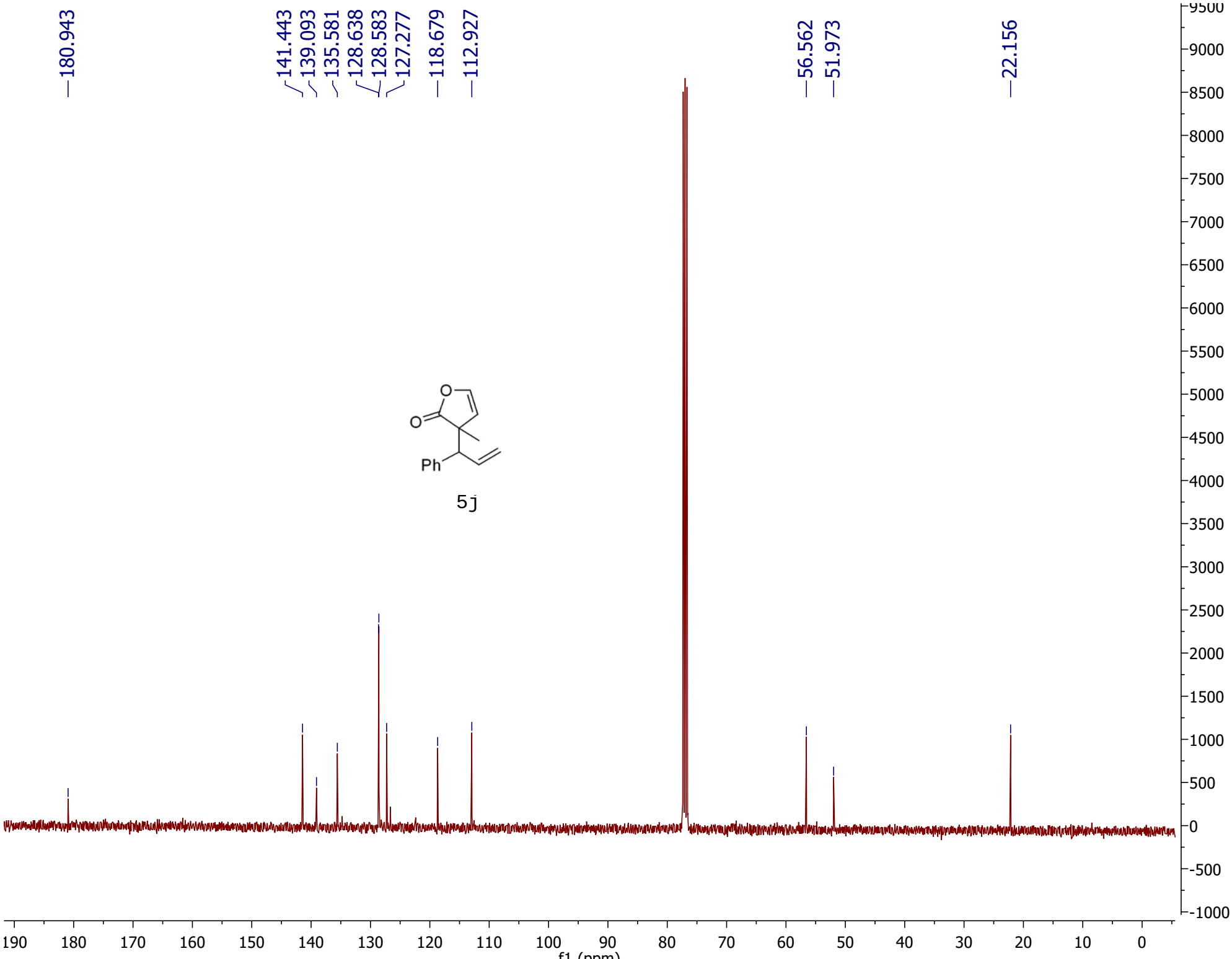
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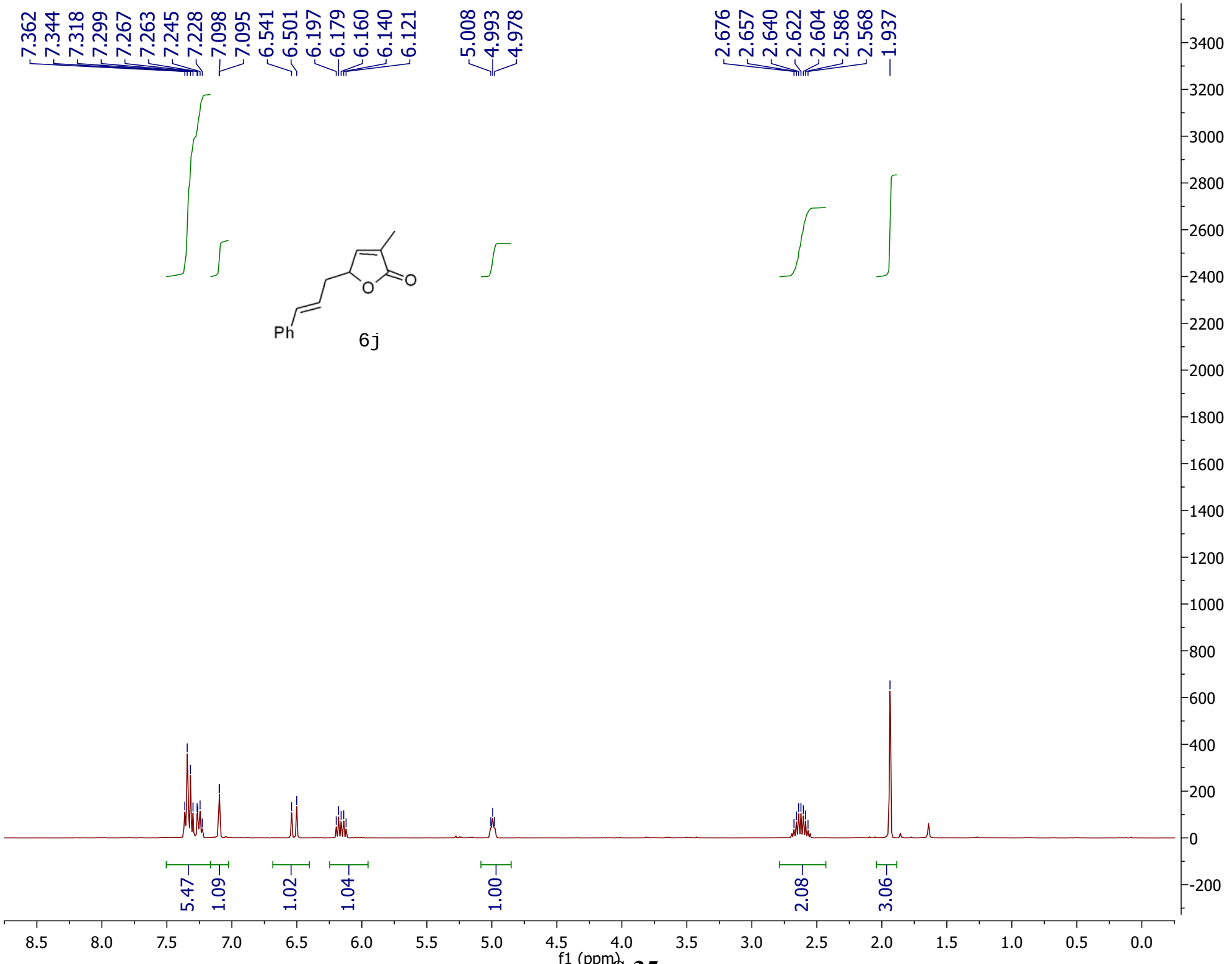
f1 (ppm)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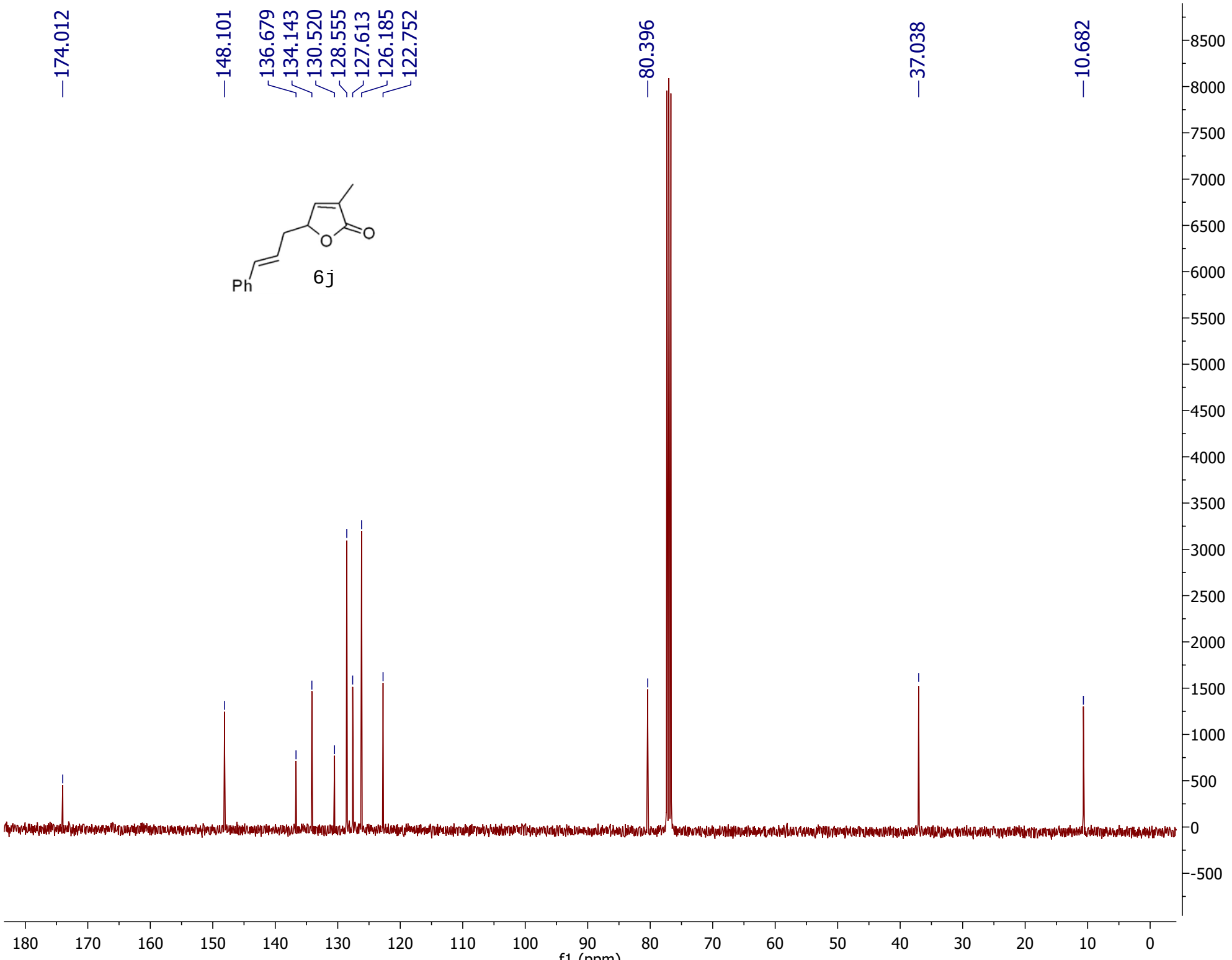
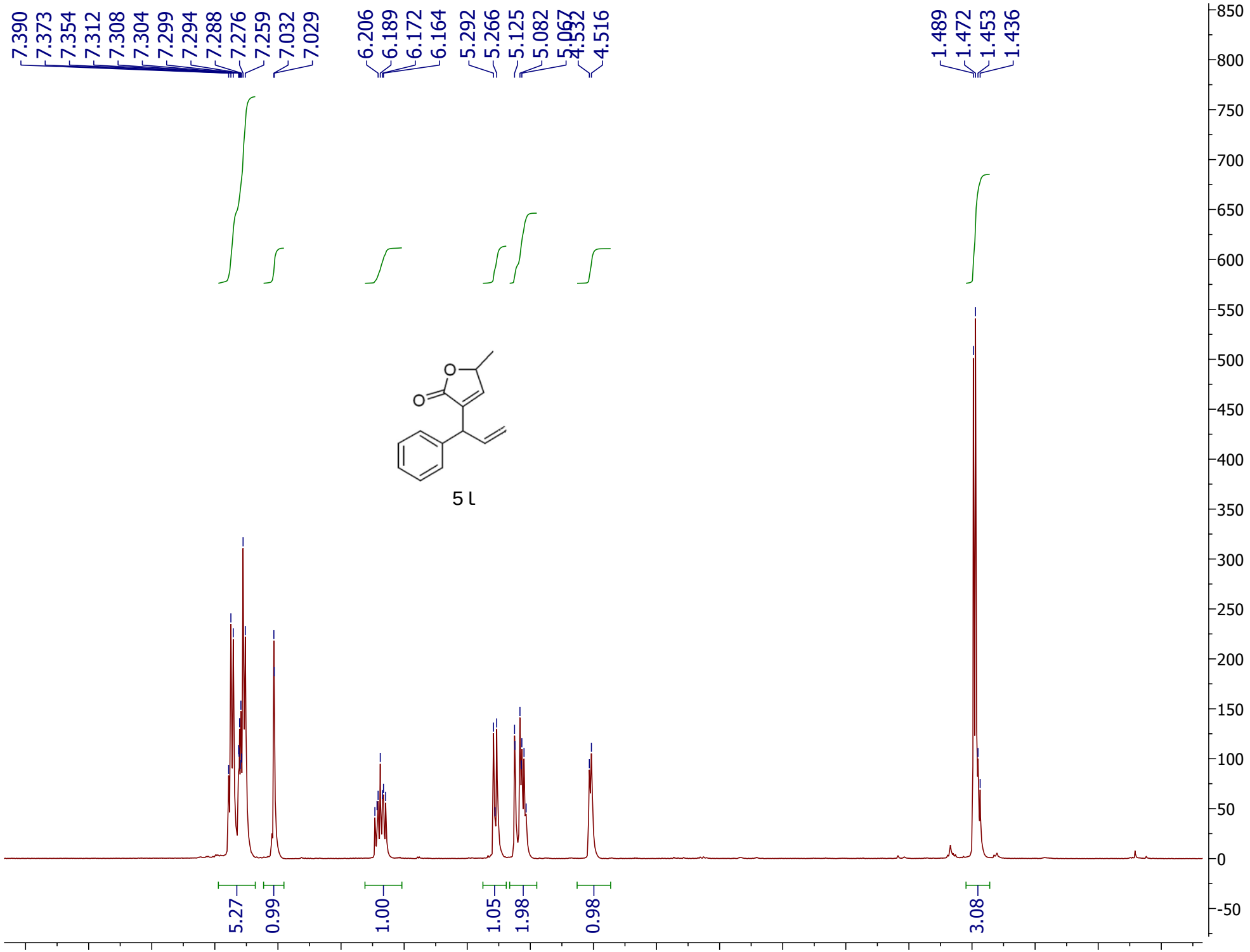
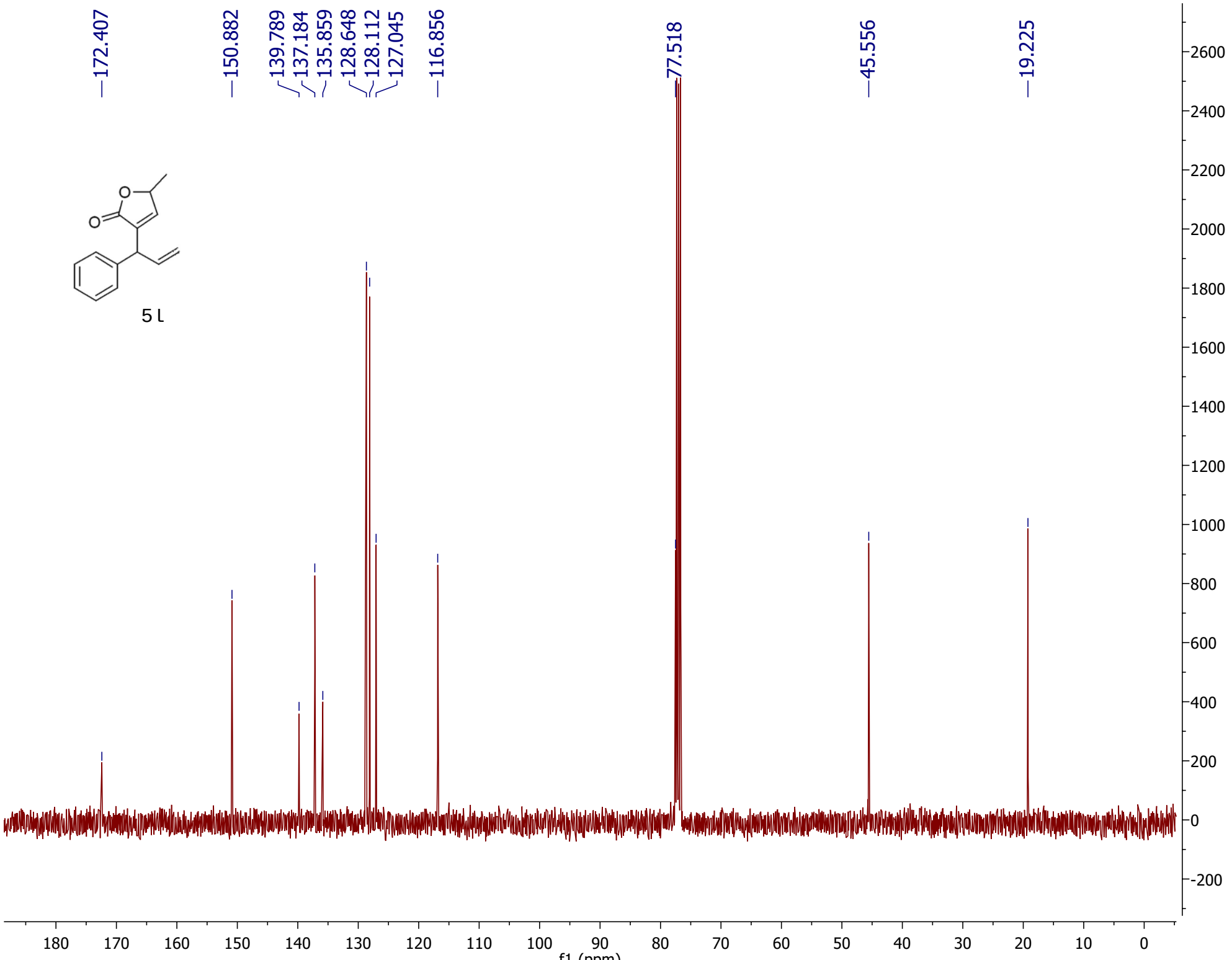
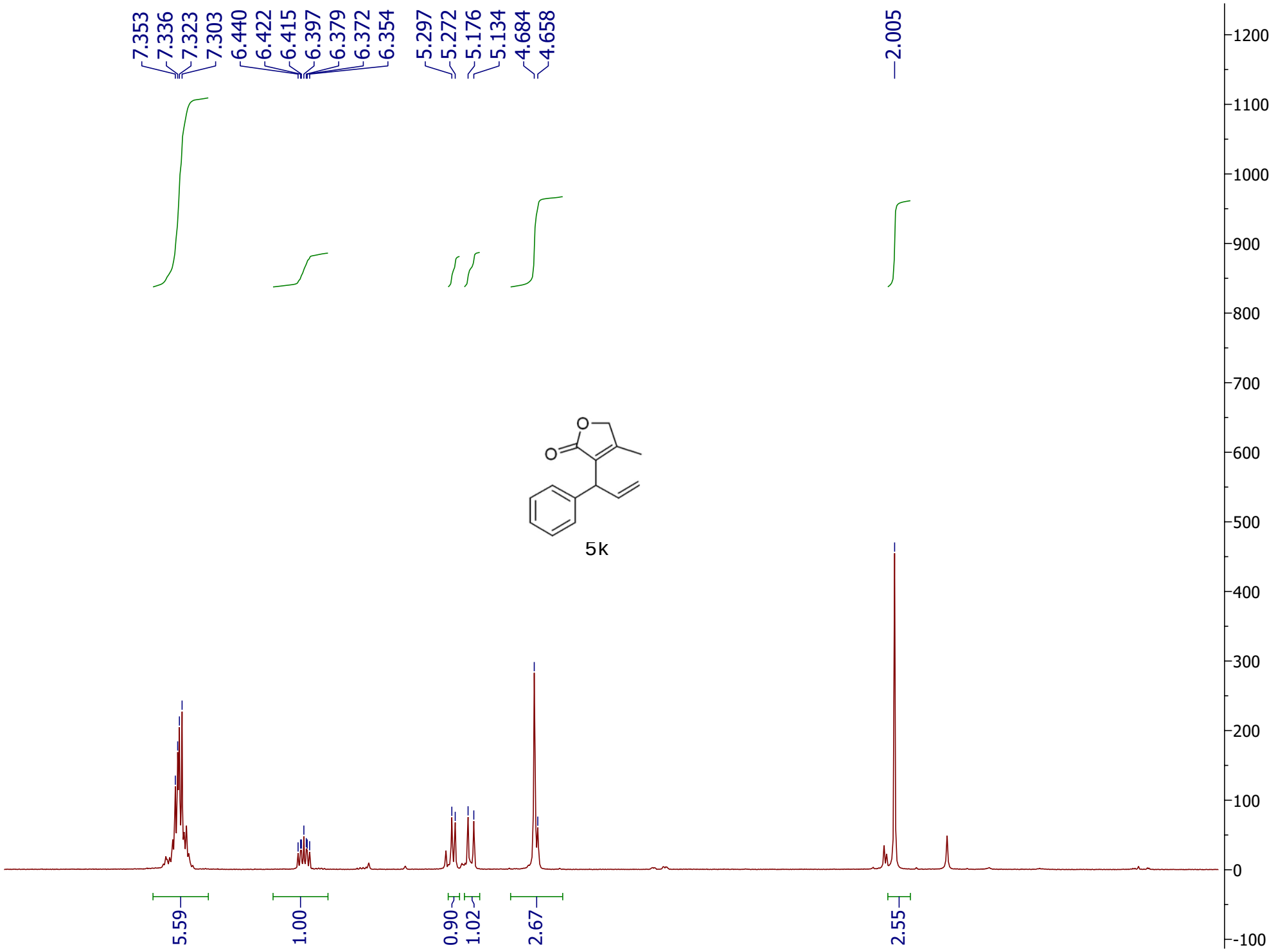
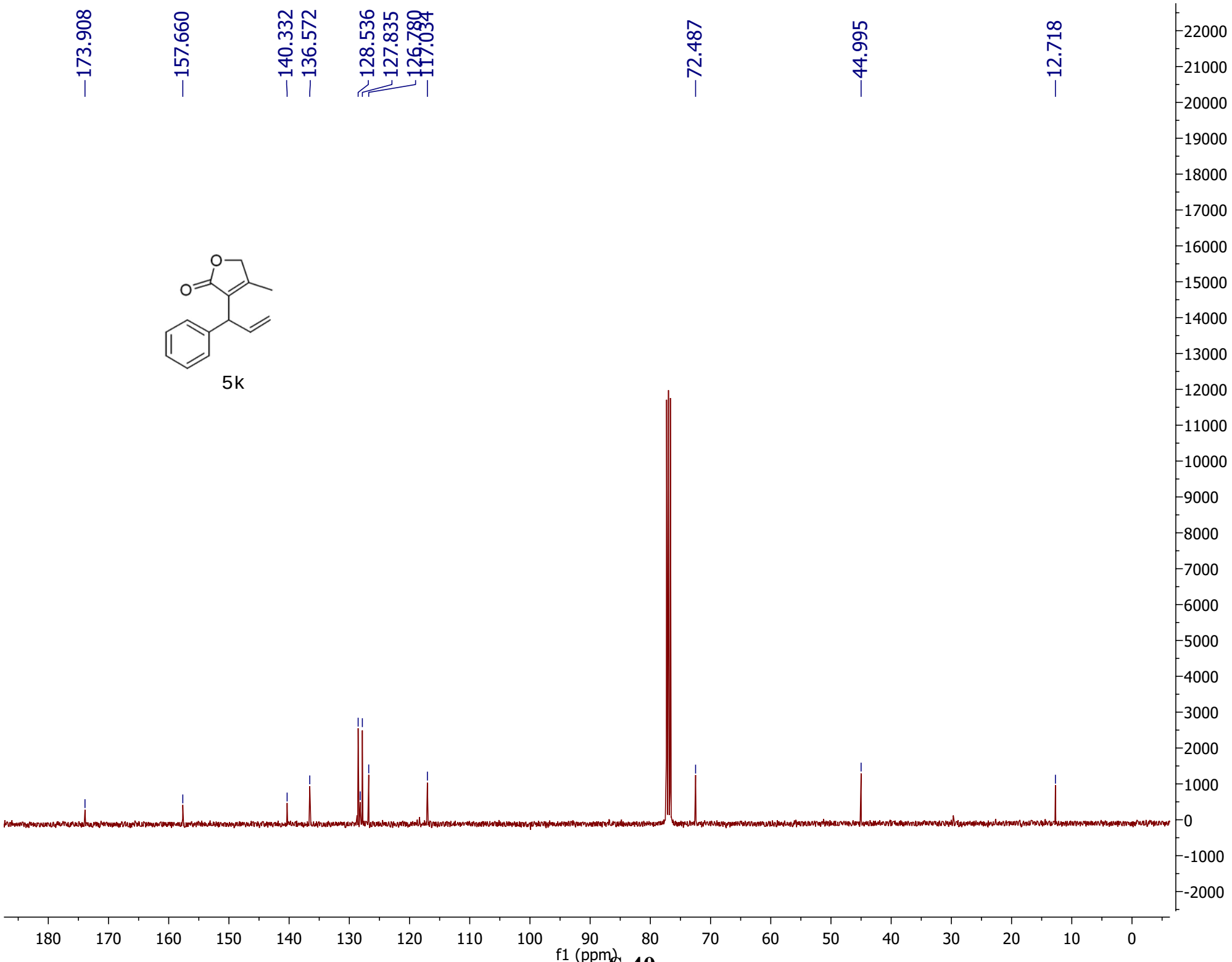
6.121
5.008
4.993
4.978
2.676
2.657
2.640
2.622
2.604
2.586
2.568
1.937
Ph
O
O
6j
5.47
1.09
1.02
1.04
1.00
2.08
3.06
f1 (ppm)

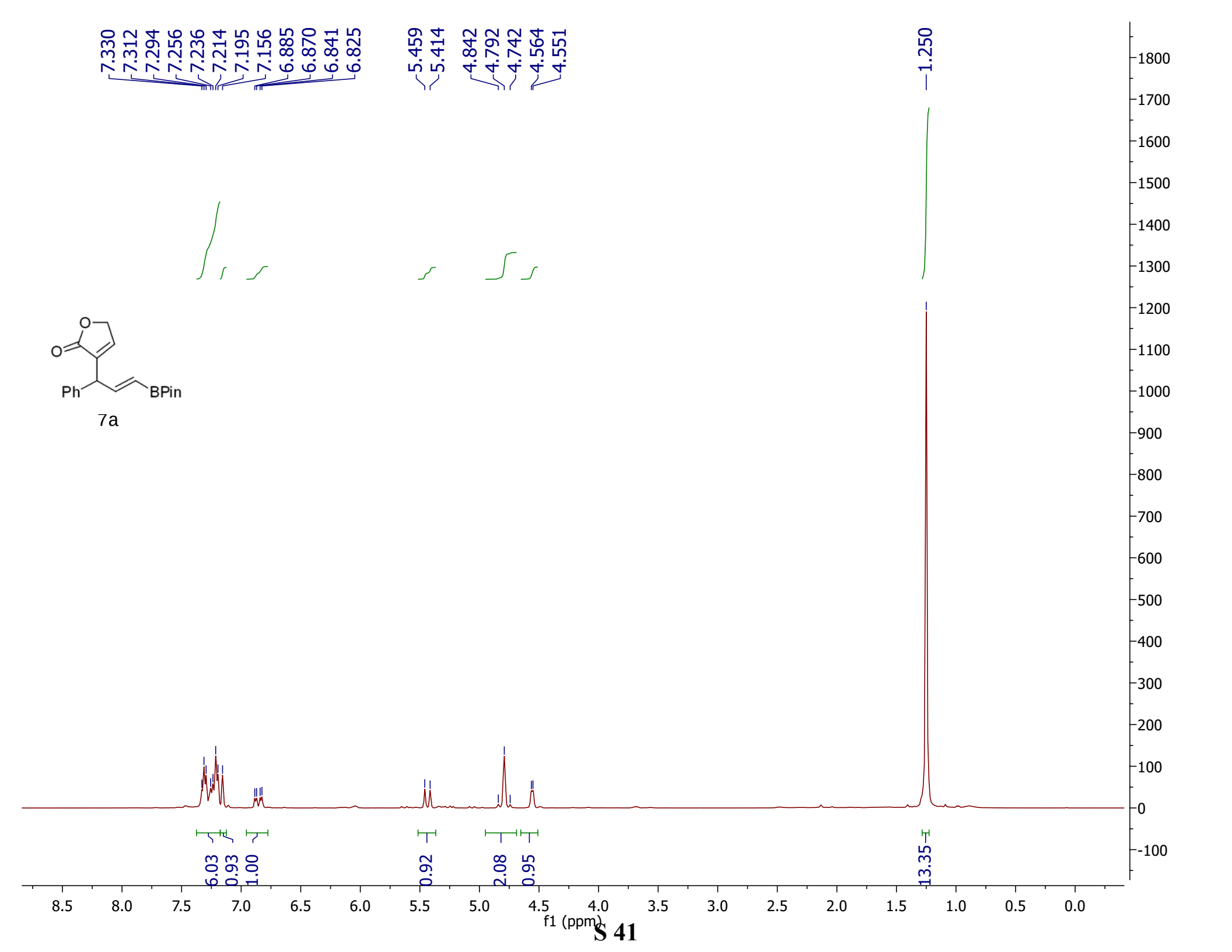

174.012
148.101
136.679
134.143
130.520
128.555
127.613
126.185
122.752
80.396
37.038
10.682
Ph
O
O
6j
f1 (ppm)

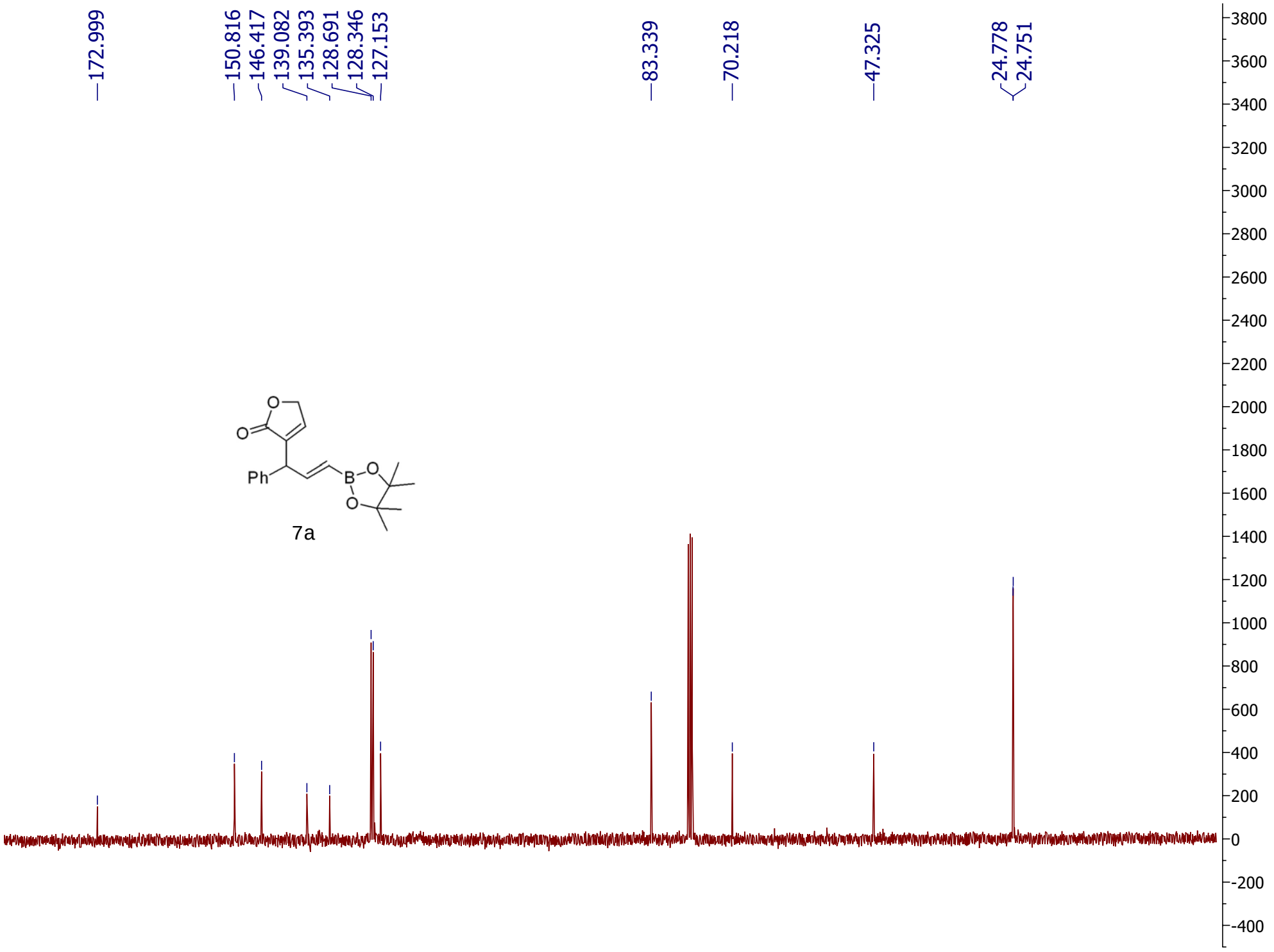

7.390
7.373
7.354
7.312
7.308
7.304
7.299
7.294
7.288
7.276
7.259
7.032
7.029
6.206
6.189
6.172
6.164
5.292
5.266
5.125
5.082
5.067
4.532
4.516
1.489
1.472
1.453
1.436
5 l
5.27
0.99
1.00
1.05
1.98
0.98
3.08
f1 (ppm)

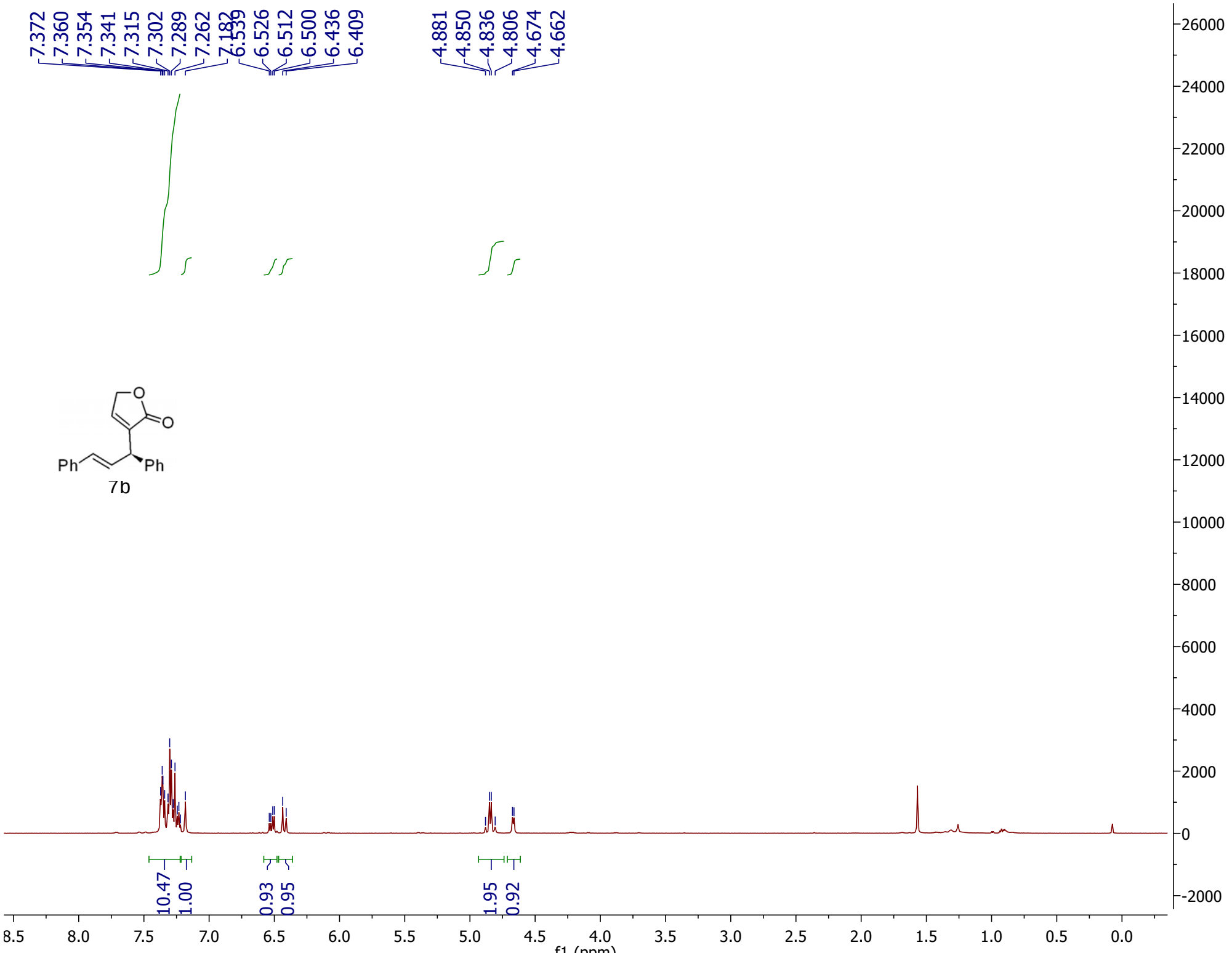

172.407
150.882
139.789
137.184
135.859
128.648
128.112
127.045
116.856
77.518
45.556
19.225
5 l
f1 (ppm)

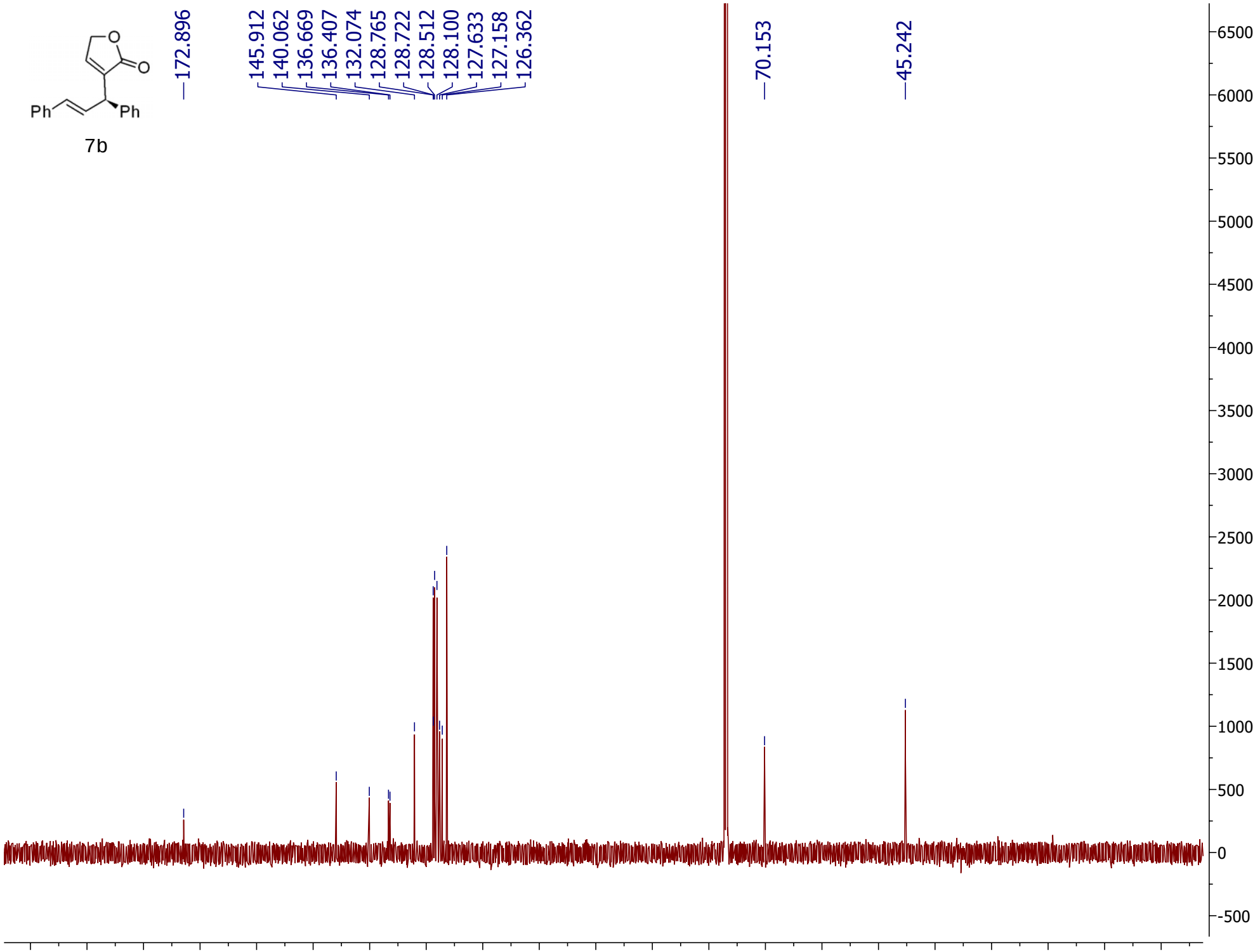

7.353
7.336
7.323
7.303
6.440
6.422
6.415
6.397
6.379
6.372
6.354
5.297
5.272
5.176
5.134
4.684
4.658
2.005
5k
5.59
1.00
0.90
1.02
2.67
2.55
f1 (ppm)

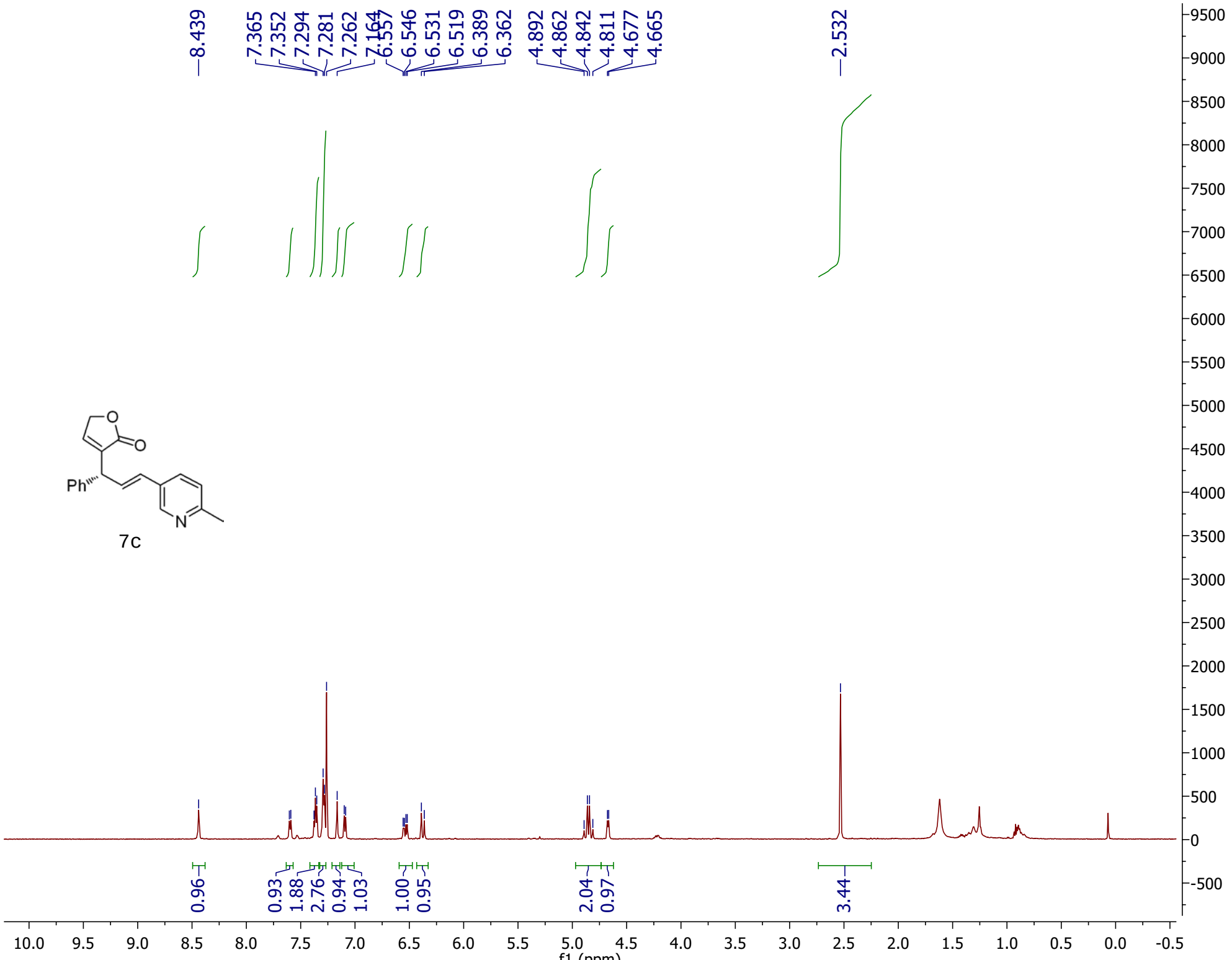

173.908
157.660
140.332
136.572
128.536
127.835
126.780
117.034
72.487
44.995
12.718
5k
f1 (ppm)

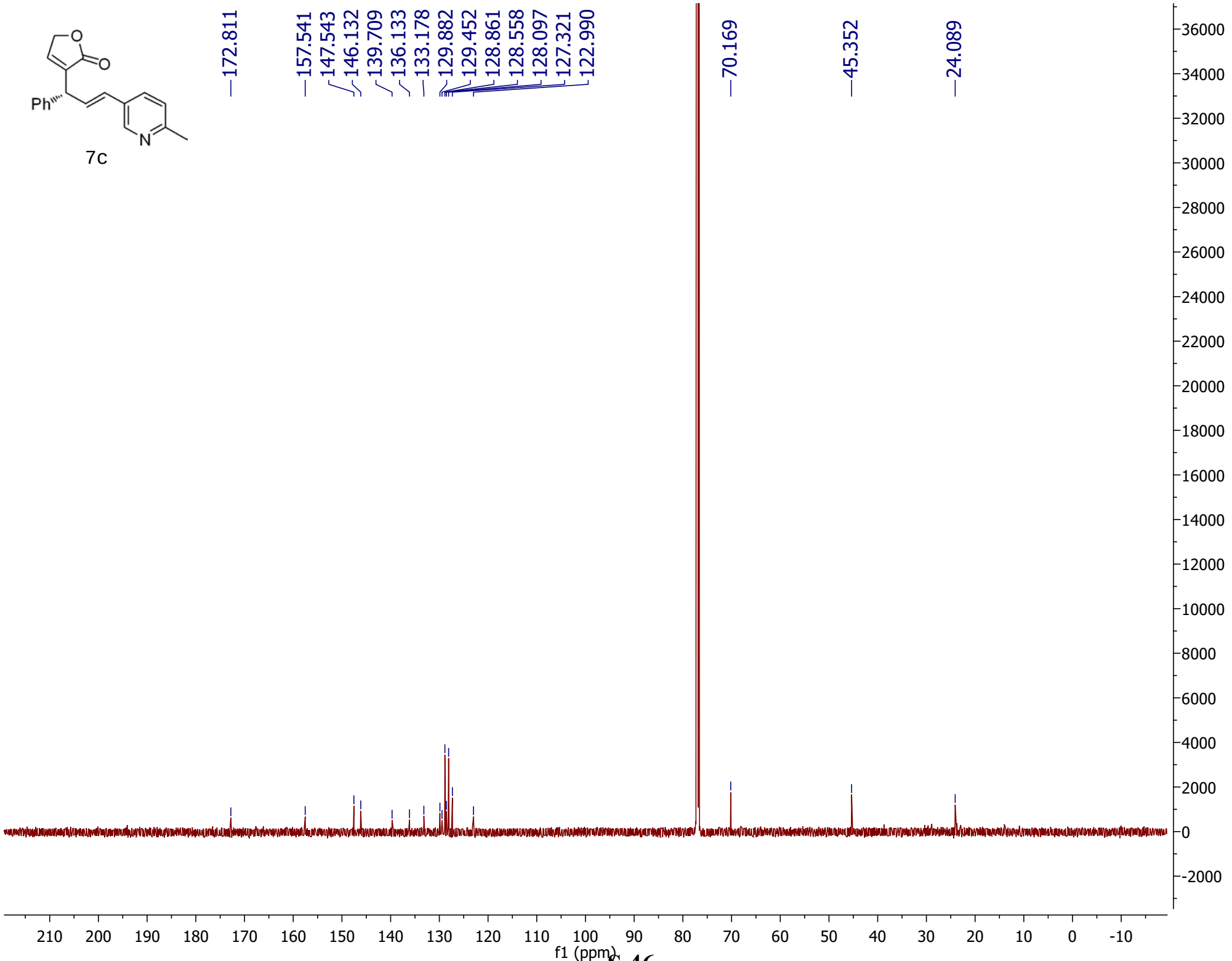

7.330
7.312
7.294
7.256
7.236
7.214
7.195
7.156
6.885
6.870
6.841
6.825
5.459
5.414
4.842
4.792
4.742
4.564
4.551
1.250
O
O
Ph
BPin
7a
6.03
0.93
1.00
0.92
2.08
0.95
13.35
f1 (ppm)

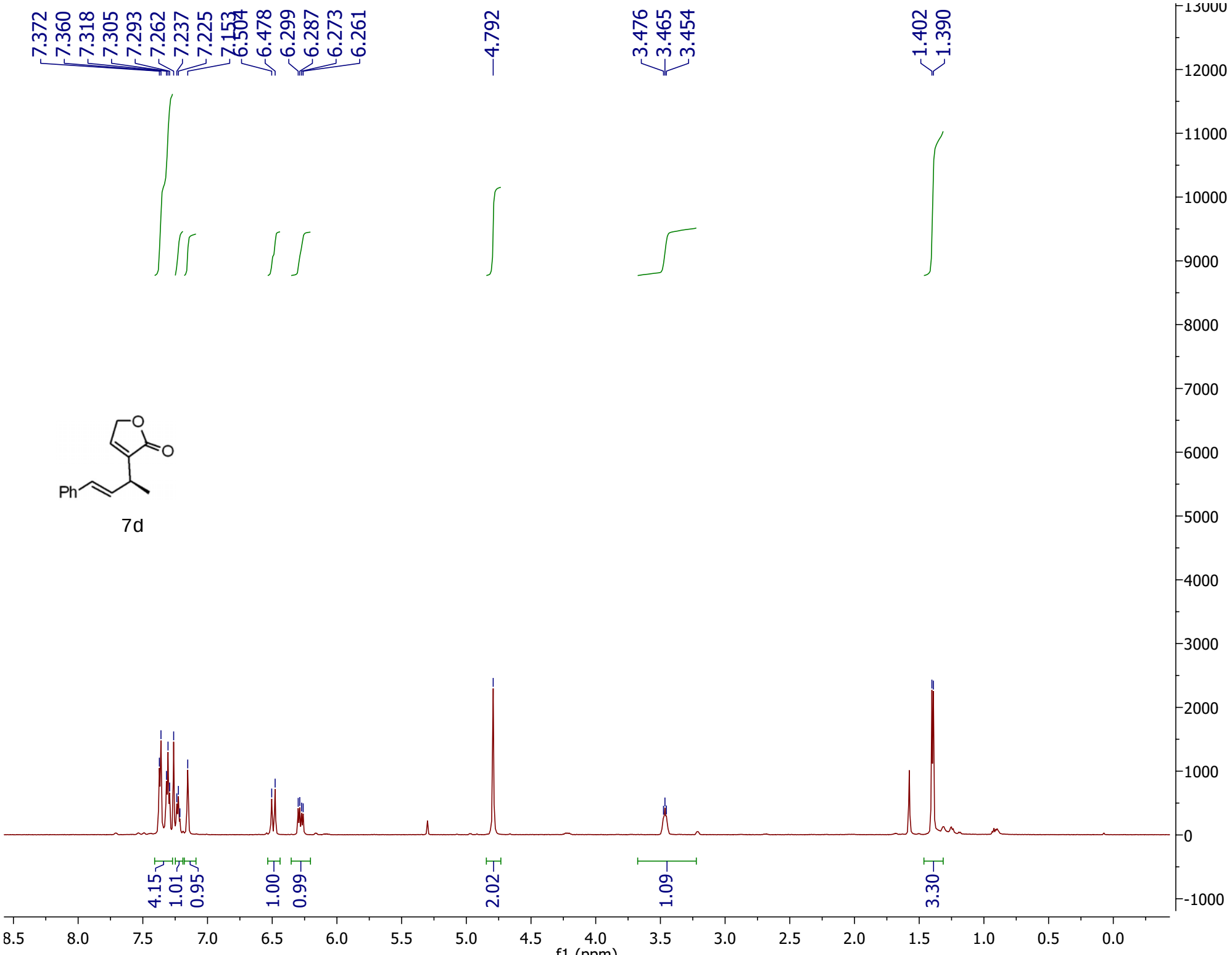

172.999
150.816
146.417
139.082
135.393
128.691
128.346
127.153
83.339
70.218
47.325
24.778
24.751
O
O
Ph
B
O
O
7a
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

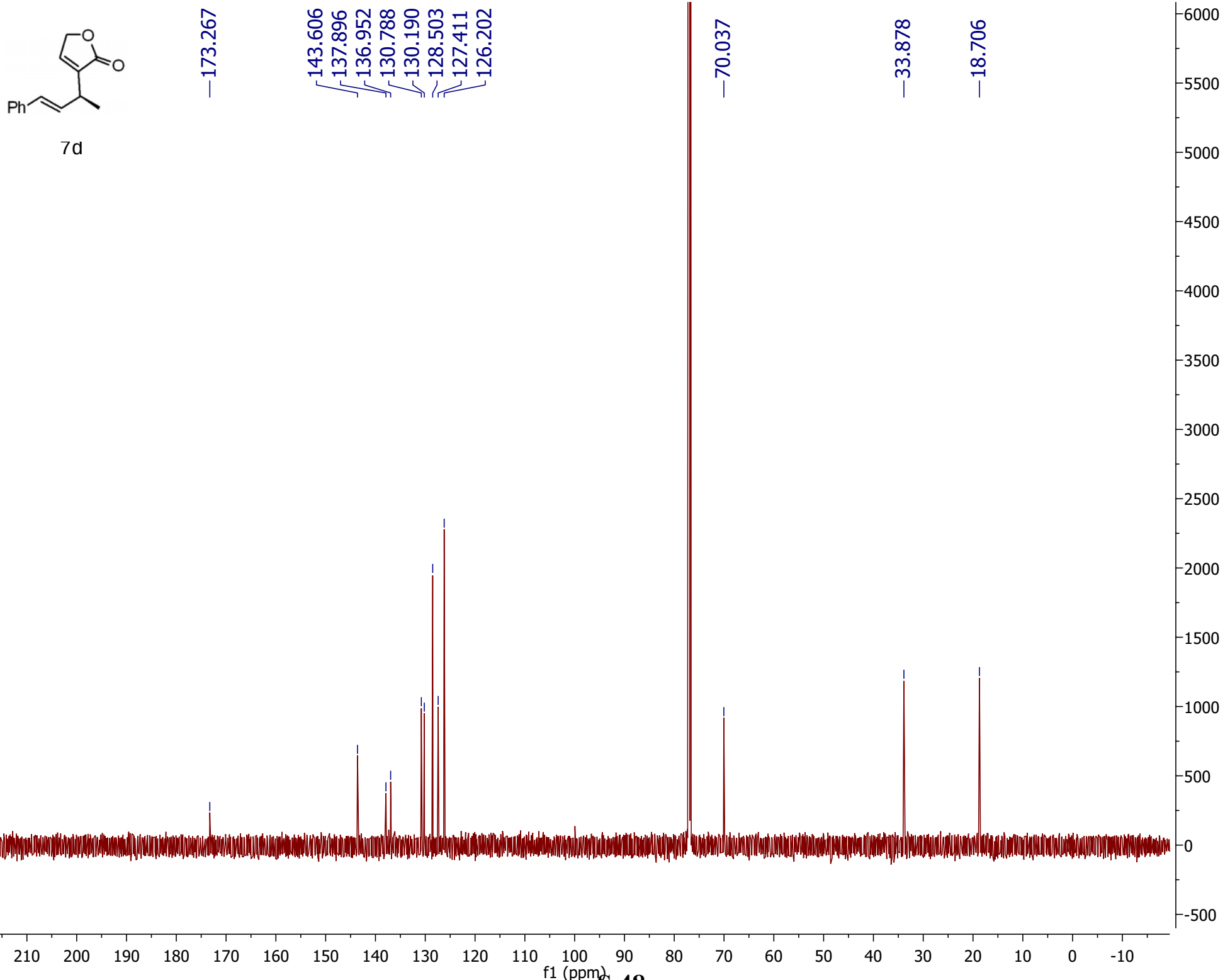

7.372
7.360
7.354
7.341
7.315
7.302
7.289
7.262
7.182
6.539
6.526
6.512
6.500
6.436
6.409
4.881
4.850
4.836
4.806
4.674
4.662
O
O
Ph
Ph
7b
10.47
1.00
0.93
0.95
1.95
0.92
f1 (ppm)

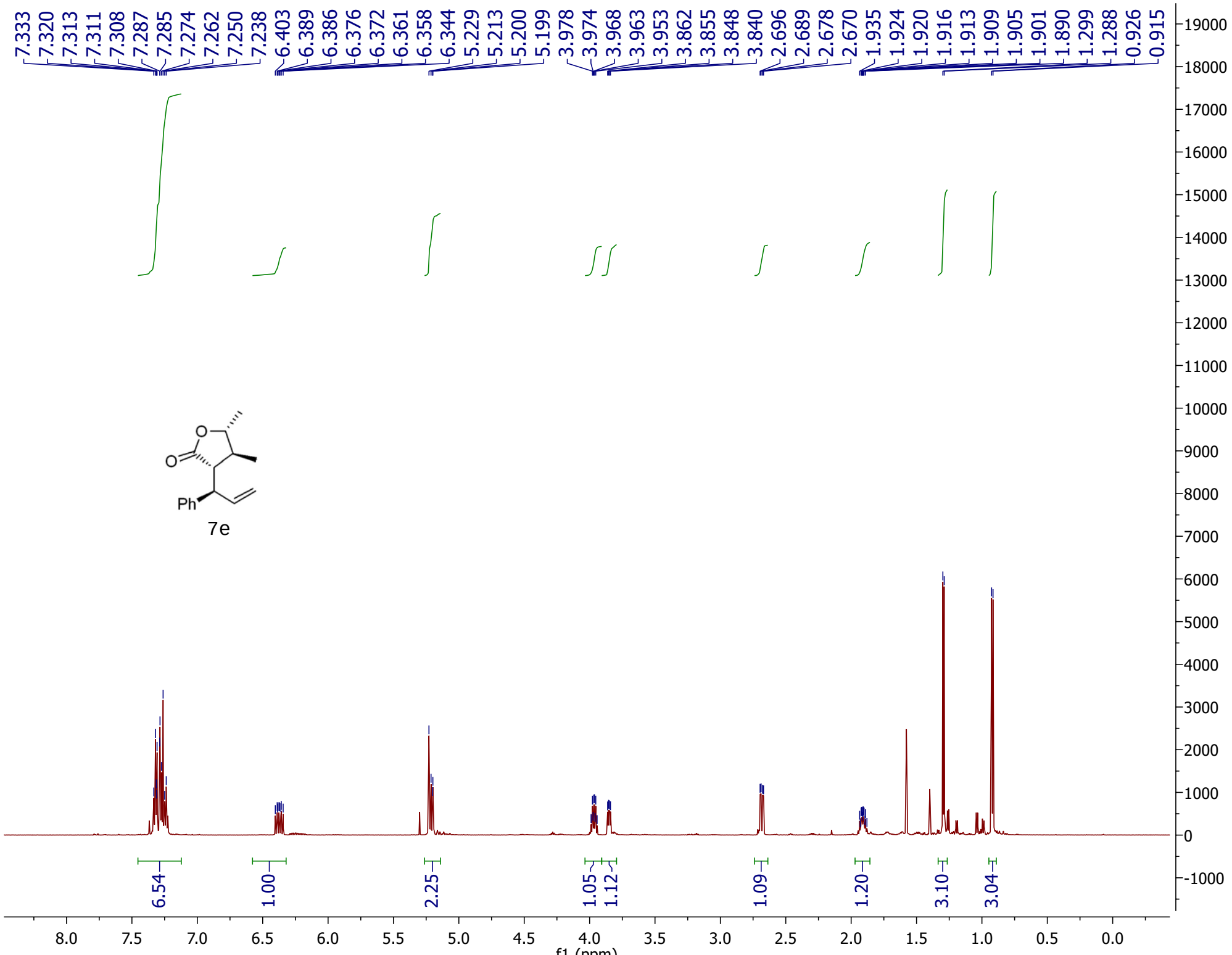

172.896
145.912
140.062
136.669
136.407
132.074
128.765
128.722
128.512
128.100
127.633
127.158
126.362
70.153
45.242
Ph
Ph
O
O
7b
f1 (ppm)

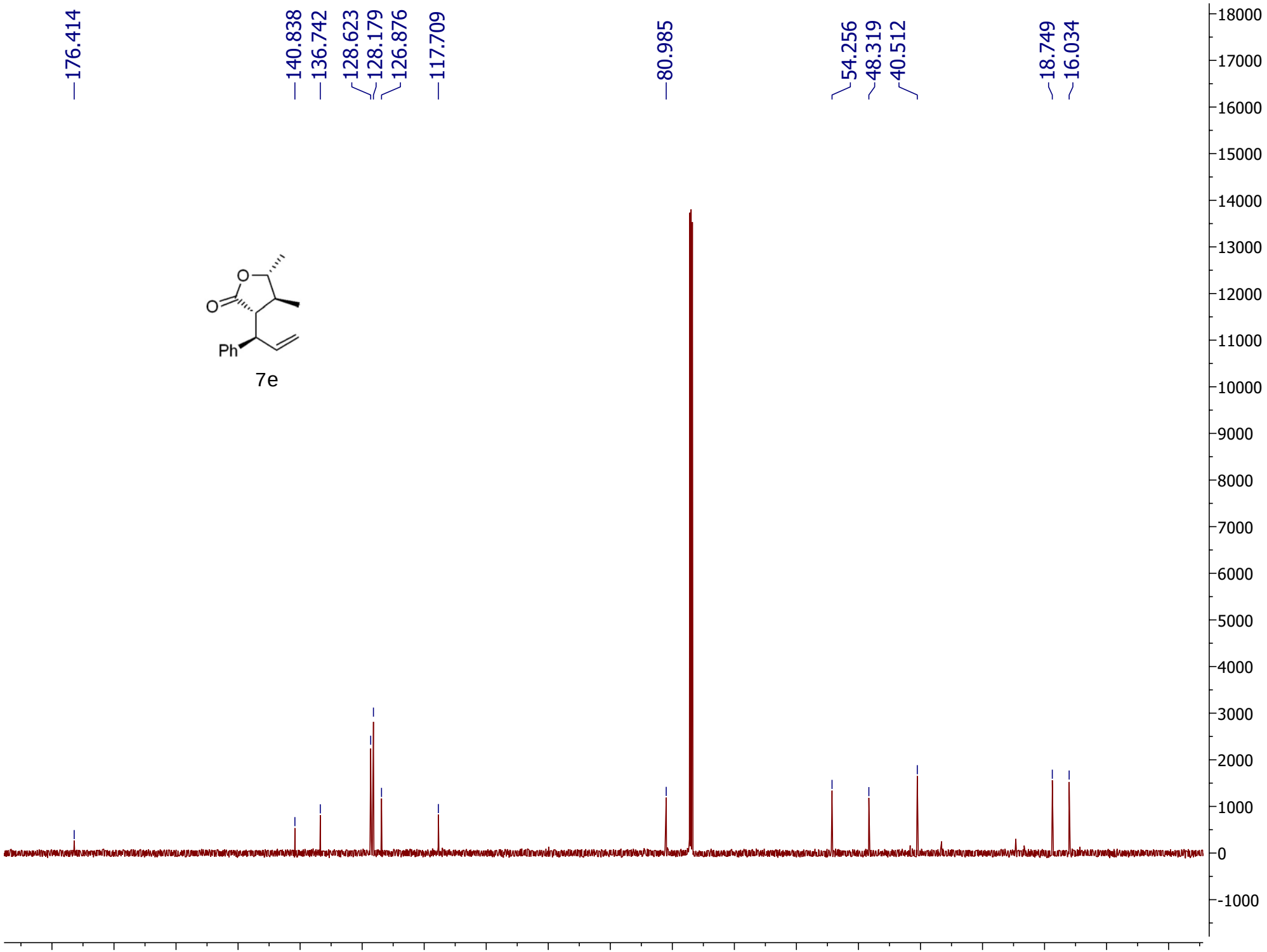

8.439
7.365
7.352
7.294
7.281
7.262
7.164
6.557
6.546
6.531
6.519
6.389
6.362
4.892
4.862
4.842
4.811
4.677
4.665
2.532
Ph
O
O
N
7c
0.96
0.93
1.88
2.76
0.94
1.03
1.00
0.95
2.04
0.97
3.44
f1 (ppm)

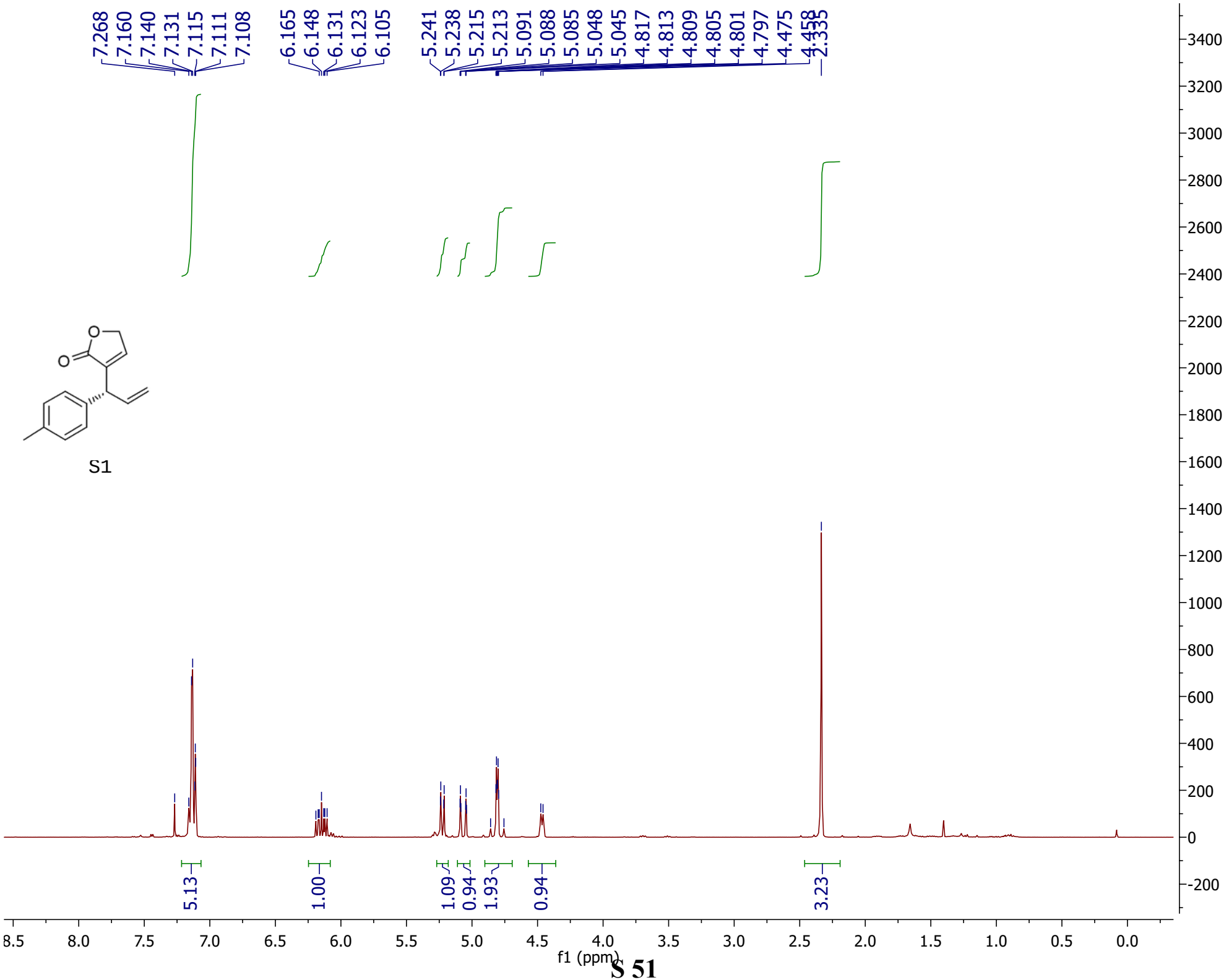

172.811
157.541
147.543
146.132
139.709
136.133
133.178
129.882
129.452
128.861
128.558
128.097
127.321
122.990
70.169
45.352
24.089
Ph
O
O
N
7c
f1 (ppm)

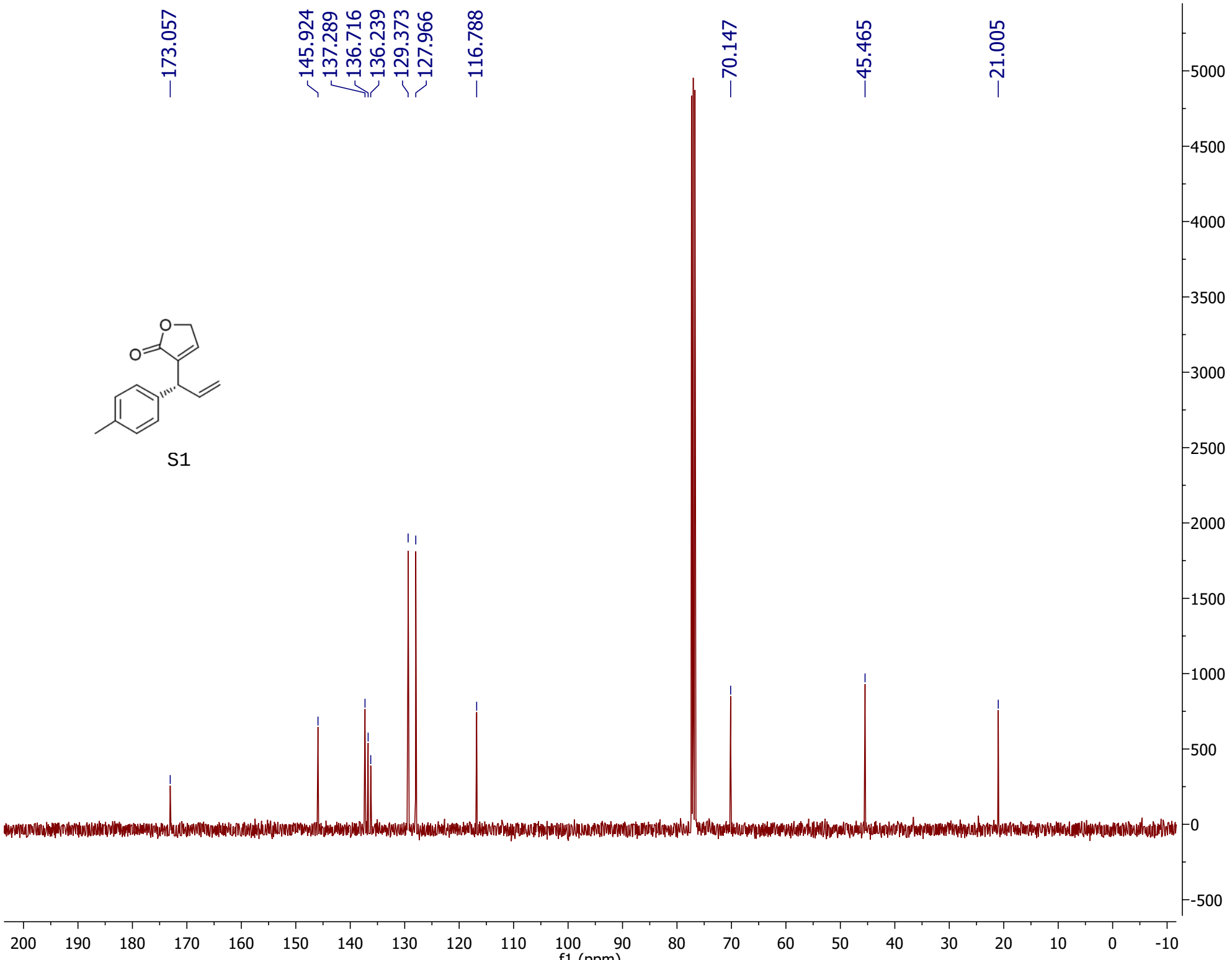

7.372
7.360
7.318
7.305
7.293
7.262
7.237
7.225
7.153
6.504
6.478
6.299
6.287
6.273
6.261
4.792
3.476
3.465
3.454
1.402
1.390
Ph
7d
4.15
1.01
0.95
1.00
0.99
2.02
1.09
3.30
f1 (ppm)

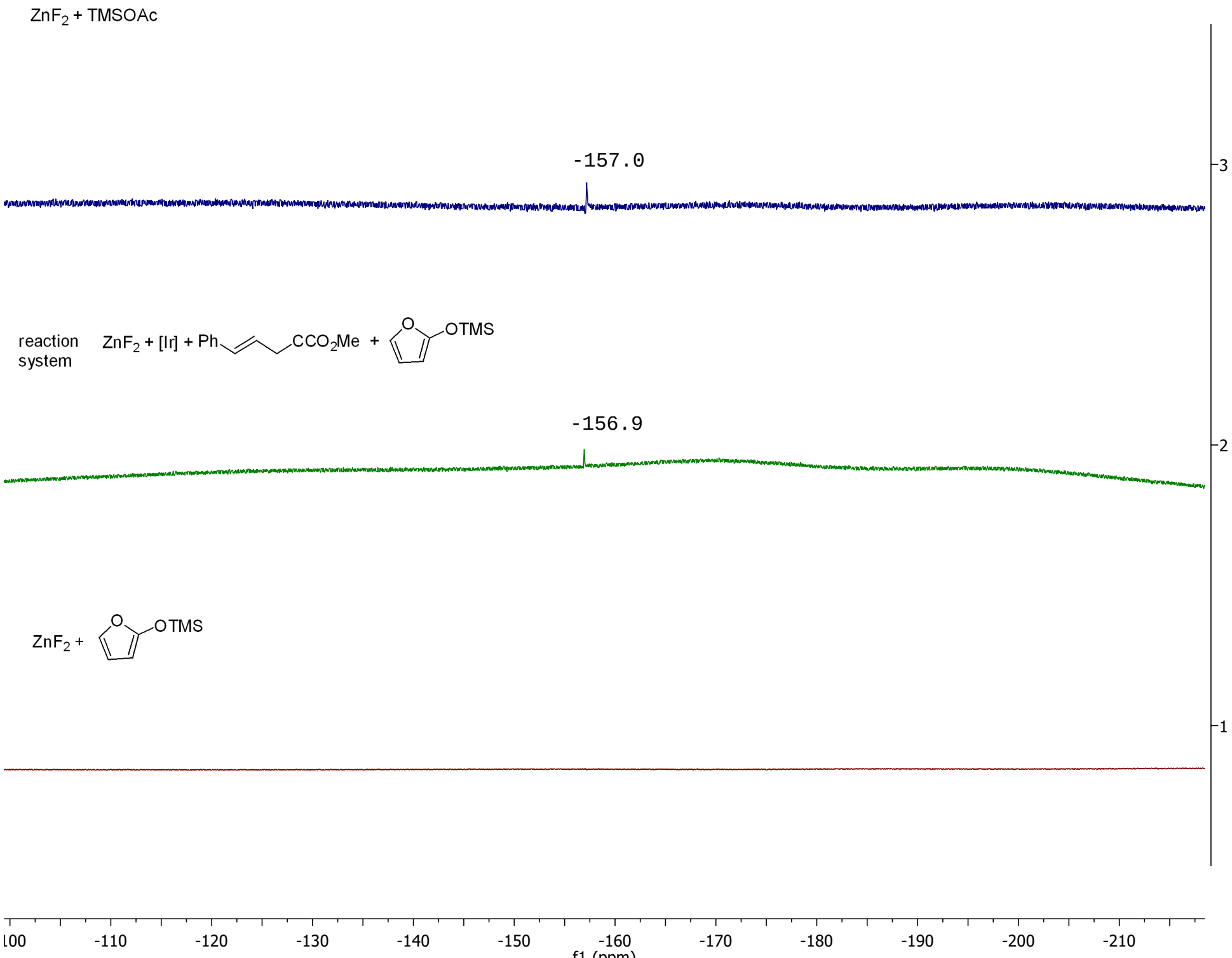

Ph
7d
173.267
143.606
137.896
136.952
130.788
130.190
128.503
127.411
126.202
70.037
33.878
18.706
f1 (ppm)


7.333
7.320
7.313
7.311
7.308
7.287
7.285
7.274
7.262
7.250
7.238
6.403
6.389
6.386
6.376
6.372
6.361
6.358
6.344
5.229
5.213
5.200
5.199
3.978
3.974
3.968
3.963
3.953
3.862
3.855
3.848
3.840
2.696
2.689
2.678
2.670
1.935
1.924
1.920
1.916
1.913
1.909
1.905
1.901
1.890
1.299
1.288
0.926
0.915
O
O
Ph
7e
6.54
1.00
2.25
1.05
1.12
1.09
1.20
3.10
3.04
f1 (ppm)


176.414
140.838
136.742
128.623
128.179
126.876
117.709
80.985
54.256
48.319
40.512
18.749
16.034
O
O
Ph
7e
f1 (ppm)


7.268
7.160
7.140
7.131
7.115
7.111
7.108
6.165
6.148
6.131
6.123
6.105
5.241
5.238
5.215
5.213
5.091
5.088
5.085
5.048
5.045
4.817
4.813
4.809
4.805
4.801
4.797
4.475
4.458
2.335
S1
5.13
1.00
1.09
0.94
1.93
0.94
3.23
f1 (ppm)


173.057
145.924
137.289
136.716
136.239
129.373
127.966
116.788
70.147
45.465
21.005
S1
f1 (ppm)


ZnF2 + TMSOAc
-157.0
reaction system
ZnF2 + [Ir] + Ph
CCO2Me +
OTMS
-156.9
ZnF2 +
OTMS
3
2
1
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)