Control of Diastereoselectivity for Iridium-catalyzed Allylation of a Prochiral Nucleophile with a Phosphate Counterion

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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, toluene, THF were 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, 4-nitrocinnamyl alcohol, 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. Azlactones were prepared according to literature procedures.[1] All the allylic carbonates and phosphates were prepared according to literature procedures.[2] The racemic samples were prepared by using racemic catalyst.

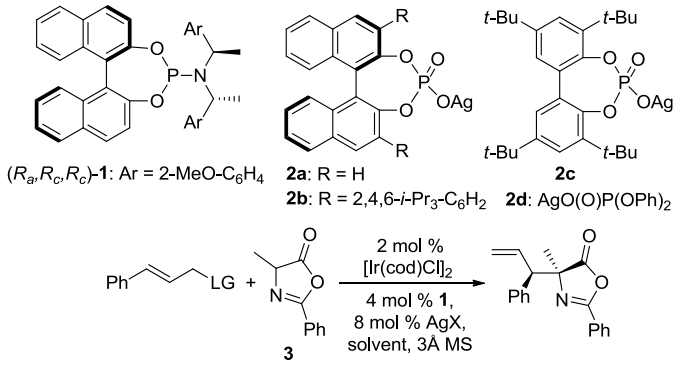
$[Ir(cod)Cl]_2$ was obtained from Johnson-Matthey and used without further purification. Phosphoramidite ligands **1** were synthesized according to literature procedures.[3] [Ir(COD)(κ^2-**1**)(ethylene) (**1**) was prepared according to literature procedures.[4] GC analyses were obtained on an Agilent 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, DRX 500, and AV-600 spectrometers. Chemical shifts were reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H and 77.00 ppm for ^{13}C). Coupling constants were 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 $KMnO_4$.

General Procedure for Evaluation of Reaction Conditions

In a nitrogen-filled dry-box, the cinnamyl carbonate (0.250 mmol, 1.00 equiv), $[Ir(cod)Cl]_2$ (0.0050 mmol, 0.0200 equiv), ligand **1** (0.0100 mmol, 0.0400 equiv), AgX (0.0200 mmol, 0.0800 equiv) and toluene (0.25 mL) were added to a 1-dram vial. The mixture was stirred for 20 min before azlactone **3** (0.550 mmol, 2.20 equiv) and 3 Å MS (50 mg) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature for 8 h. 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 diastereoselectivity was then determined by ^1H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 6:1) to yield the product.

Table 1. Evaluation of Ligand, Leaving Group, Solvent and Counterion Effect on the Ir-Catalyzed Allylation of azlactone 3[a]

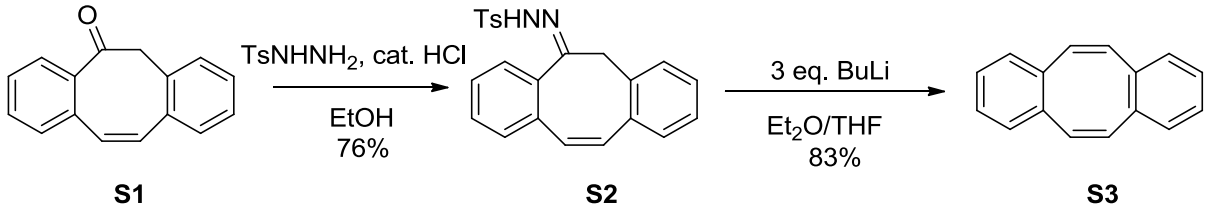


Entry	ligand	LG	Solvent	AgX	Yield(%)[b]	dr[c]	ee(%)[d]
1[e]	**1**	OCOOMe	toluene	$AgBF_4$	31	7:1	98
2	**1**	OCOOMe	toluene	**2a**	83	8:1	98
3	**1**	OCOOMe	toluene	**2b**	87	>20:1	98
4[f]	**1**	OCOOMe	toluene	**2b**	57	>20:1	98
5[g]	**1**	OCOOMe	toluene	**2b**	70	>20:1	98
6	ent-**1**	OCOOMe	toluene	**2b**	88	20:1	-98
7	**1**	OCOOMe	toluene	**2c**	89(87)	>20:1	98
8	**1**	OCOOMe	toluene	**2d**	81	18:1	98
9	**1**	OCOOMe	THF	**2b**	90	6:1	92

10	**1**	OCOOMe	dioxane	**2b**	62	6:1	97
11	**1**	OCOOMe	DCM	**2b**	52	5:1	92
12	**1**	OBoc	Toluene	**2c**	58	14:1	95
13	**1**	OTroc	Toluene	**2c**	85	4:1	-
14	**1**	$OPO(OEt)_2$	Toluene	**2c**	36	2:1	-

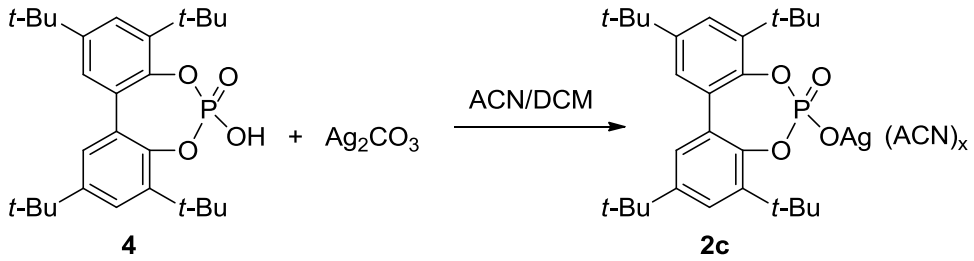
[a]See the Supporting Information (SI) for experimental details. Absolute configuration of the allylation product was determined by chemical correlation. [b]Determined by ^{1}H NMR analysis with mesitylene as the internal standard. Numbers in parentheses correspond to isolated yield. [c]Determined by ^{1}H NMR analysis of crude reaction mixtures. [d]Determined by chiral HPLC analysis of the major diastereomer. [e]90% conversion of cinnamyl carbonate. [f]4 mol % **2b** was used. 64% conversion of cinnamyl carbonate. [g]Without molecular sieves. 80% conversion of cinnamyl carbonate.

Procedure for the Synthesis of DBCOT



To the 20 mL absolute ethanol solution of **S1**[5] (782 mg, 1.00 euqiv, 3.55 mmol) and $TsNHNH_2$ (727mg, 1.10 equiv, 3.91 mmol) was added 10 μL concentrated hydrochloric acid. The solution was stirred for 12 h. After the reaction was complete, the white precipitate formed was collected by filtration. The precipitate was washed with 1 mL ice-cold ethanol, and was then dried in vaccuum to yield white powder **S2** in 76% yield (1.05 g). In a glovebox, **S2** (500 mg, 1.00 equiv, 1.29 mmol) was dissolved in 8 mL THF and 24 mL of ether in a round bottom flask. BuLi (2.42 mL, 1.6 M in hexane, 3.0 equiv, 3.9 mmol) was added to the solution. During this time, the reaction mixture changed to a dark red solution. When the reaction was determined to be complete, according to TLC, in 1 h, the flask was removed from glovebox. The reaction mixture became light yellow when the reaction was quenched with 5 mL saturated NH_4Cl solution. The mixture was poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted by EtOAc (2 x 5 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography over silica gel with hexanes afforded **S3** in 83% (215 mg) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 5.5, 2.5 Hz, 1H), 7.07 (d, J = 3.2 Hz, 1H), 6.76 (s, 1H).

Procedure for the Synthesis of 2c

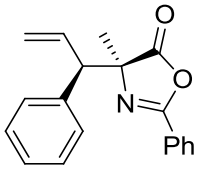


To the 3 mL ACN/DCM (1/1) solution of **4**[6] (2 g, 1.00 eqiuv, 4.24 mmol) and was added Ag_2CO_3 (643 mg, 0.55 eqiuv, 2.33 mmol). The solution was stirred for 2 h. After the reaction was complete, the precipitate was filtered. The solvent was removed to afford **2c** in 95% (2.33 g) yield as an off-white powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.3 Hz, 2H), 7.18 (d, *J* = 2.4 Hz, 2H), 1.55 (s, 18H), 1.33 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 139.60, 139.57, 130.7, 126.5, 124.7, 35.5, 34.6, 31.52, 31.46. Anal. Calcd. for $C_{28}H_{40}AgO_4P \cdot CH_3CN$: C, 58.07; H, 6.98; N, 2.26; found: C, 58.16; H, 6.98; N, 1.96.

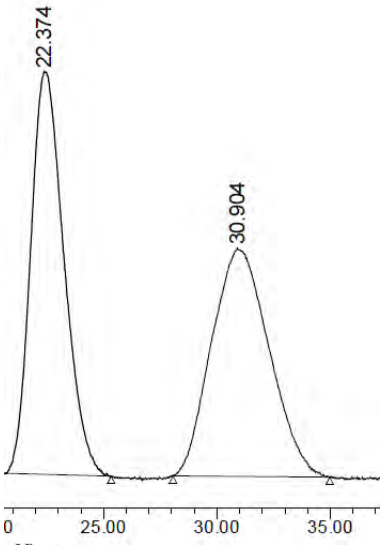
General Procedure for Ir-catalyzed Allylation of Azlactones

In a nitrogen-filled dry-box, the allylic carbonate (0.250 mmol, 1.00 equiv), $[Ir(cod)Cl]_2$ (0.0050 mmol, 0.0200 equiv), **1** (0.0100 mmol, 0.0400 equiv), **2c** (0.0200 mmol, 0.0800 equiv) and toluene (0.25 mL) were added to a 1-dram vial. The mixture was stirred for 20 min before azlactone (0.550 mmol, 2.20 equiv) and 3 Å MS (50 mg) were added. The vial was sealed with a PTFE/silicone-lined septum cap, removed from the dry-box, and stirred at room temperature for 1-24 h. 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. The diastereoselectivity 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, 16:1 to 3:1) to yield the product.

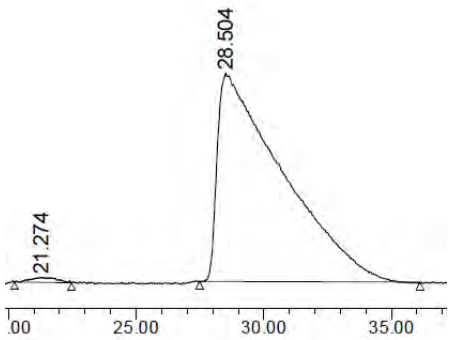
(*S*)-4-methyl-2-phenyl-4-((*R*)-1-phenylallyl)oxazol-5(4H)-one



Prepared according to the general procedure using cinnamyl methyl carbonate (48.0 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 87% yield (63.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 28.5 min (major); t_R 21.4 min (minor) [(Chiralcel OJ-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = -72.3° (c 0.7, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.52-7.45 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.23 (m, 1H), 6.03 (dt, *J* = 16.8, 9.6 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 3.71 (d, *J* = 9.5 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.6, 159.8, 138.4, 135.5, 132.6, 129.1, 128.7, 128.5, 128.0, 127.4, 125.8, 118.9, 73.5, 57.5, 22.4.

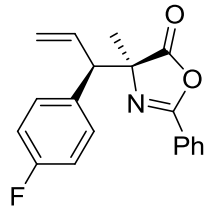


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	22.374	29768389	50.54	291769	63.82
2	30.904	29129743	49.46	165412	36.18

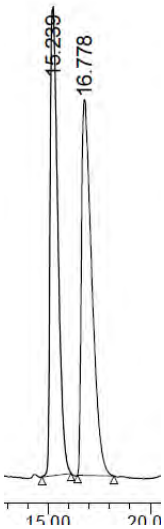


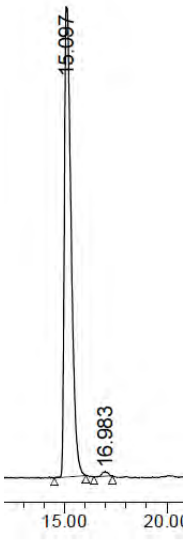
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	21.274	647490	0.91	8750	2.17
2	28.504	70318582	99.09	395152	97.83

(*S*)-4-((*R*)-1-(4-fluorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 4-fluorocinnamyl methyl carbonate (52.5 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 85% yield (65.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 15.1 min (major); t_R 17.0 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.5:0.5, 0.5 mL/min] to be 98%. $[\alpha]_D^{25}$ = -98.0° (c 0.4, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.03 (t, *J* = 8.1 Hz, 2H), 5.97 (dt, *J* = 16.8, 10.2 Hz, 1H), 5.18 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 3.69 (d, *J* = 9.4 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.4, 162.1 (d, *J* = 246 Hz), 159.9, 135.3, 134.1(d, *J* = 3.8 Hz), 132.7, 130.7 (d, *J* = 7.9 Hz), 128.7, 127.9, 125.7, 119.0, 115.3 (d, *J* = 21.2 Hz), 73.3, 56.6, 22.4.

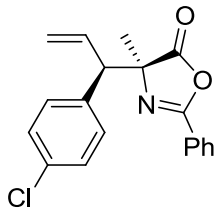




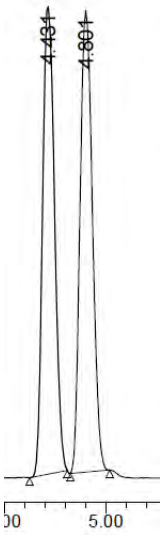
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.239	41408107	48.10	1575794	55.47
2	16.778	44681139	51.90	1264908	44.53

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.097	28034297	99.09	1225476	99.01
2	16.983	258300	0.91	12223	0.99

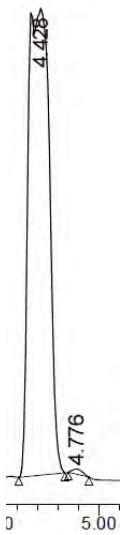
(*S*)-4-((*R*)-1-(4-chlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 4-chlorocinnamyl methyl carbonate (56.6 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as white wax in 84% yield (68.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.43 min (major); t_R 4.78 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = -121° (c 2.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.96 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.94 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.19 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 3.68 (d, *J* = 9.4 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 180.4, 160.1, 136.9, 135.1, 133.3, 132.9, 130.5, 128.8, 128.7, 128.0, 125.7, 119.3, 73.3, 56.8, 22.5.



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.431	14823878	49.33	1842141	50.40
2	4.801	15229299	50.67	1813217	49.60



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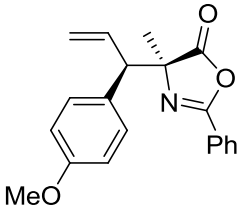
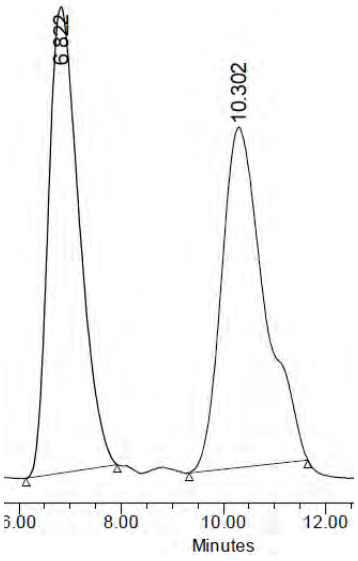
1	4.428	34020501	99.44	2405438	98.92
2	4.776	192890	0.56	26207	1.08

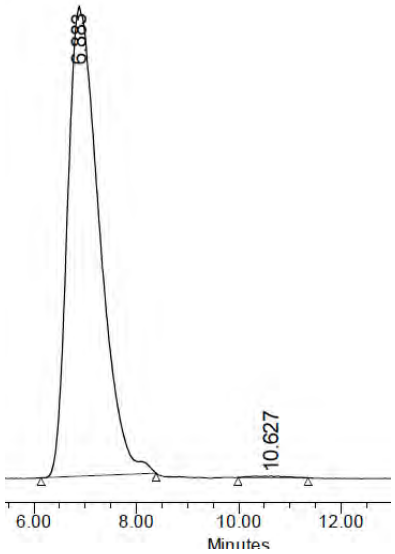
(*S*)-4-((*R*)-1-(4-methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 4-methoxycinnamyl methyl carbonate (55.5 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 68% yield (54.6 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.88 min (major); t_R 10.30 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be >99%. $[\alpha]_D^{25}$ = -105° (c 1.7, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.99 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.18 (d, *J* = 16.9 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 3.79 (s, 3H), 3.66 (d, *J* = 9.4 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.7, 159.8, 158.8, 135.7, 132.6, 130.4, 130.1, 128.7, 127.9, 125.9, 118.5, 113.8, 73.6, 56.7, 55.2, 22.4.

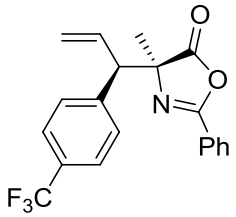


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.822	25245277	49.73	601903	57.82
2	10.302	25517071	50.27	439029	42.18

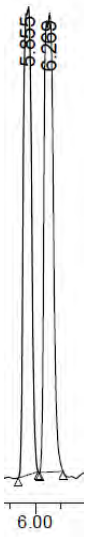


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.883	56108477	99.67	1296065	99.67
2	10.627	184042	0.33	4307	0.33

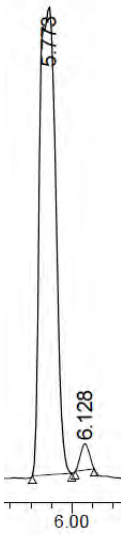
(*S*)-4-methyl-2-phenyl-4-((*R*)-1-(4-(trifluoromethyl)phenyl)allyl)oxazol-5(4H)-one



Prepared according to the general procedure using 4-trifluoromethylcinnamyl methyl carbonate (65.0 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 82% yield (73.6 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.74 min (major); t_R 6.13 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = -105° (c 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 7.95 (m, 2H), 7.69 – 7.56 (m, 5H), 7.51 (t, *J* = 7.7 Hz, 2H), 5.95 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.22 (d, *J* = 16.9 Hz, 1H), 5.13 (dd, *J* = 10.2, 0.8 Hz, 1H), 3.77 (d, *J* = 9.4 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.2, 160.2, 142.5, 134.8, 132.9, 129.62, 129.63 (q, *J* = 32.6 Hz), 128.9, 128.0, 125.6, 125.5 (q, *J* = 3.78 Hz), 124.1 (q, *J* = 272 Hz), 119.8, 73.2, 57.1, 22.4. HRMS (ESI) Calcd. for $C_{20}H_{16}NO_2F_3$ ($[M]^+$): 359.1133. Found: 359.1132.

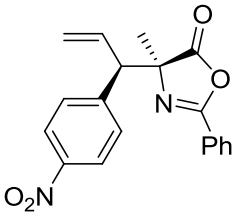


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.855	20743189	47.47	1923289	50.75
2	6.269	22950009	52.53	1866143	49.25

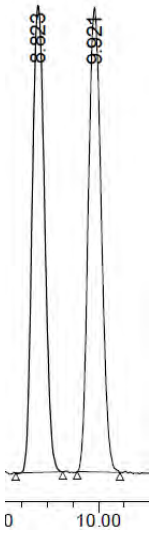


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.773	21623668	96.98	2022752	94.70
2	6.128	674481	3.02	113201	5.30

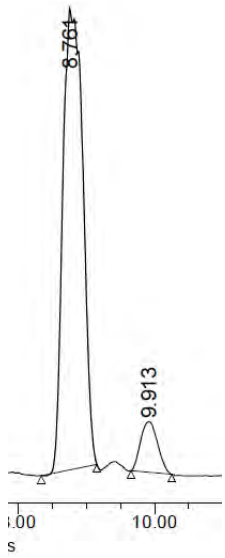
(*S*)-4-methyl-4-((*R*)-1-(4-nitrophenyl)allyl)-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 4-nitrocinnamyl methyl carbonate (59.3 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give the title compound as colorless oil in 83% yield (69.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.76 min (major); t_R 9.91 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be 84%. $[\alpha]_D^{25}$ = -185° (c 1.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 8.07 – 7.96 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 5.94 (dt, *J* = 16.9, 9.8 Hz, 1H), 5.23 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 3.83 (d, *J* = 9.4 Hz, 1H), 1.35 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 160.4, 147.3, 146.0, 134.2, 133.1, 130.2, 128.9, 128.0, 125.4, 123.7, 120.3, 73.0, 57.0, 22.5. HRMS (ESI) Calcd. for $C_{19}H_{17}N_2O_4$ ($[M+H]^+$): 337.1188. Found: 337.1189.

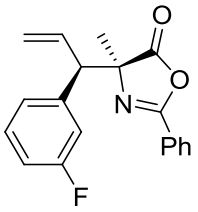


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.823	11489593	48.95	688510	50.16
2	9.921	11983036	51.05	684230	49.84

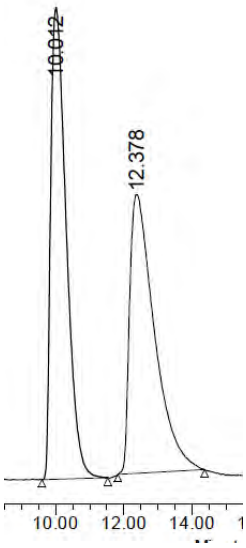


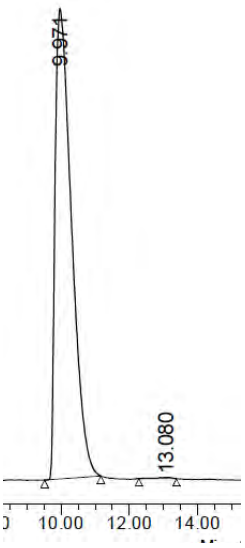
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.761	33909565	91.42	1675712	90.15
2	9.913	3183306	8.58	183090	9.85

(*S*)-4-((*R*)-1-(3-fluorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 3-fluorocinnamyl methyl carbonate (52.5 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 96% yield (74.2 mg). The enantiomeric excess was determined by HPLC analysis of methanolysis product (254 nm, 25 °C) t_R 9.97 min (major); t_R 13.08 min (minor) [(Chiralpak AS-H) hexane/*i*-PrOH, 98:2, 1.0 mL/min] to be >99%. $[\alpha]_D^{25}$ = -82.7° (c 2.5, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.1 Hz, 2H), 7.37 – 7.25 (m, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 8.2 Hz, 1H), 6.06 – 5.82 (dt, *J* = 16.9, 10.0 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.70 (d, *J* = 9.2 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.3, 162.7 (d, *J* = 246 Hz), 160.0, 140.8 (d, *J* = 7.1 Hz), 135.0, 132.8, 129.9 (d, *J* = 8.2 Hz), 128.8, 128.0, 125.7, 125.0 (d, *J* = 2.7 Hz), 119.3, 116.0 (d, *J* = 21.9 Hz), 114.3 (d, *J* = 21.1 Hz), 73.3, 57.1, 22.4. HRMS (ESI) Calcd. for $C_{19}H_{16}NO_2F$ ($[M]^+$): 309.1165. Found: 309.1166.

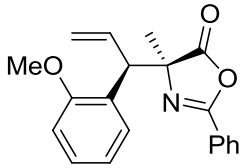




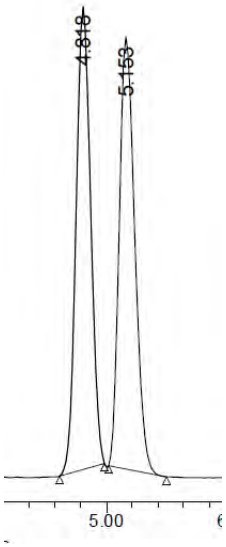
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.012	22290353	51.54	703273	62.86
2	12.378	20954892	48.46	415570	37.14

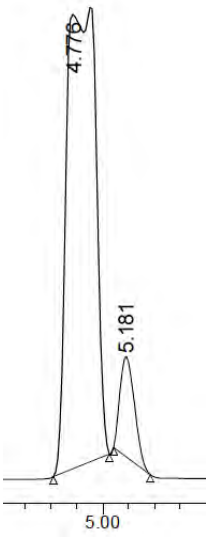
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.971	40784869	99.75	1219811	99.71
2	13.080	101820	0.25	3582	0.29

(*S*)-4-((*R*)-1-(2-methoxyphenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using 2-methoxycinnamyl methyl carbonate (55.5 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (7:1 mixture of diastereomers) as colorless oil in 81% yield (65.0 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.69 min (major); t_R 5.09 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 92.5:7.5, 1.0 mL/min] to be 80%. $[\alpha]_D^{25}$ = -83.9° (c 3.5, CH_2Cl_2). 7:1 diastereomer mixtures ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55-7.48 (m, 2H), 7.27 (dd, *J* = 10.7, 3.9 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.08 – 5.80 (dt, *J* = 16.9, 10.1 Hz, 1H), 5.24 (d, *J* = 16.9 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.52 (d, *J* = 9.4 Hz, 1H), 3.88 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.0, 159.6, 157.2, 135.6, 132.6, 129.7, 128.7, 128.2, 127.9, 126.7, 126.0, 120.7, 118.9, 110.6, 73.8, 55.5, 47.2, 21.8. HRMS (ESI) Calcd. for $C_{20}H_{20}NO_3$ ($[M+H]^+$): 322.1438. Found: 322.1436.

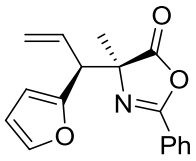




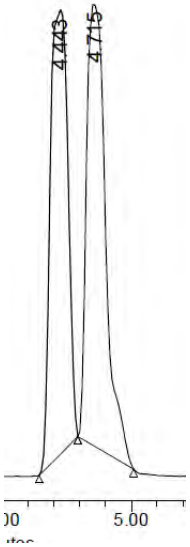
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.818	11137861	50.10	1409785	51.63
2	5.153	11094822	49.90	1320604	48.37

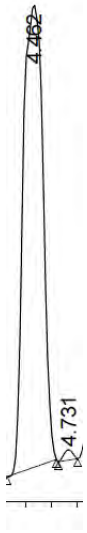
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.776	32613357	90.06	2091786	81.99
2	5.181	3600590	9.94	459408	18.01

(*S*)-4-((*S*)-1-(furan-2-yl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using (E)-3-(furan-3-yl)allyl methyl carbonate (45.5 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (15:1 mixture of diastereomers) as colorless oil in 90% yield (63.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.46 min (major); t_R 4.73 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 92.5:7.5, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = -69.0° (c 2.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.63 – 7.53 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.36-7.33 (m, 1H), 6.43 – 6.26 (m, 2H), 6.00 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.24 (d, *J* = 17.0 Hz, 1H), 5.19 (dd, *J* = 10.1, 1.1 Hz, 1H), 3.90 (d, *J* = 9.4 Hz, 1H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 160.2, 151.7, 141.8, 132.6, 132.6, 128.7, 127.9, 125.7, 119.6, 110.3, 107.8, 72.5, 50.9, 22.3. HRMS (ESI) Calcd. for $C_{17}H_{16}NO_3$ ($[M+H]^+$): 282.1130. Found: 282.1121.

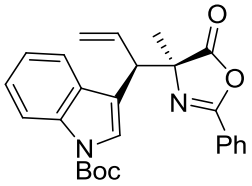




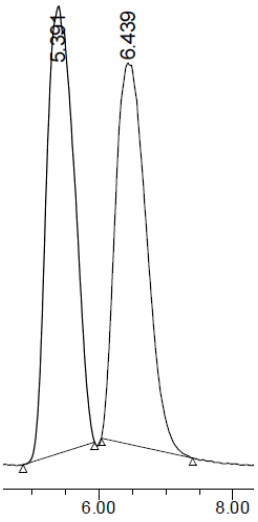
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.443	19501809	48.26	2051690	50.27
2	4.715	20908536	51.74	2029753	49.73

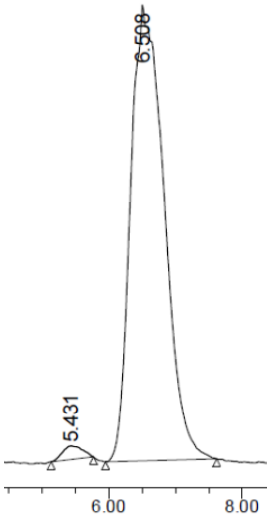
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.462	18390618	98.99	1724947	97.79
2	4.731	187360	1.01	38960	2.21

tert-Butyl 3-((*R*)-1-((*S*)-4-methyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)allyl)-1H-indole-1-carboxylate



Prepared according to the general procedure using (E)-tert-butyl 3-(3-((methoxycarbonyl)oxy)prop-1-en-1-yl)-1H-indole-1-carboxylate (82.8 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (15:1 mixture of diastereomers) as colorless oil in 81% yield (87.1 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.46 min (major); t_R 4.73 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 95%. $[\alpha]_D^{25}$ = -71.9° (c 3.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.87 (br s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.63-7.58 (m, 1H), 7.54-7.48 (m, 2H), 7.37-7.27 (m, 2H), 5.97 (d, *J* = 16.8, 10.1 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.1 Hz, 1H), 4.08 (d, *J* = 9.2 Hz, 1H), 1.74 (s, 9H), 1.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.5, 160.0, 149.8, 135.1, 134.7, 132.7, 130.3, 128.8, 128.0, 127.99, 125.7, 124.4, 122.5, 119.6, 119.0, 117.4, 115.2, 83.8, 73.7, 48.1, 28.2, 22.5. HRMS (ESI) Calcd. for $C_{26}H_{27}N_2O_4$ ($[M+H]^+$): 431.1965. Found: 431.1965.

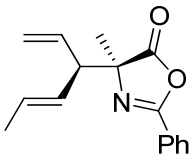




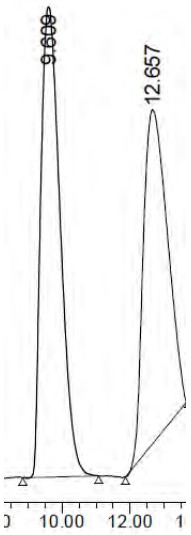
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.391	36707934	51.06	1274681	54.06
2	6.439	35188871	48.94	1083056	45.94

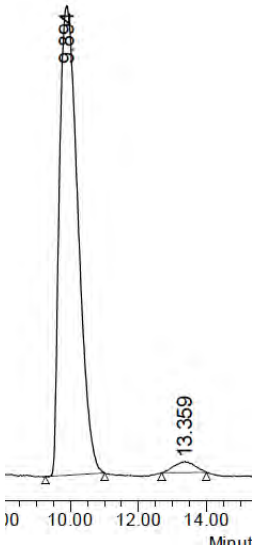
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.431	883566	1.72	42203	2.84
2	6.508	50466422	98.28	1445280	97.16

(*S*)-4-((*R*,*E*)-hexa-1,4-dien-3-yl)-4-methyl-2-phenyloxazol-5(4H)-one



Prepared according to the general procedure using (2E,4E)-hexa-2,4-dien-1-yl methyl carbonate (39.0 mg, 0.250 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (96.3 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (14:1:1 mixture of diastereomers and the linear product) as colorless oil in 83% yield (52.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.89 min (major); t_R 13.36 min (minor) [(Chiralpak AS-H) hexane/*i*-PrOH, 98:2, 0.8 mL/min] to be 94%. $[\alpha]_D^{25}$ = -4.5° (c 2.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.62-7.57(m, 1H), 7.55 – 7.47 (m, 2H), 5.77 – 5.61 (m, 2H), 5.63 – 5.50 (m, 1H), 5.17 (d, *J* = 17.7 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.1 Hz, 1H), 3.12 (t, *J* = 8.6 Hz, 1H), 1.74 (d, *J* = 6.0 Hz, 3H), 1.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 159.9, 134.9, 132.6, 130.1, 128.7, 127.9, 126.9, 125.9, 118.3, 72.6, 54.7, 22.2, 18.1. HRMS (ESI) Calcd. for $C_{16}H_{18}NO_2$ ($[M+H]^+$): 256.1338. Found: 256.1334.

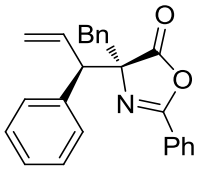




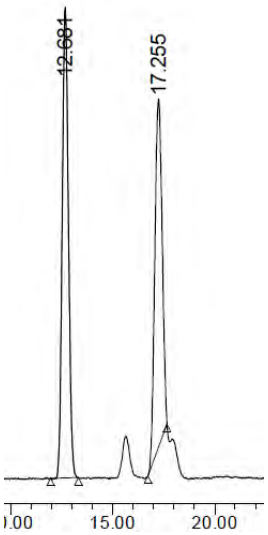
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.609	21249948	53.13	540097	58.46
2	12.657	18749532	46.87	383838	41.54

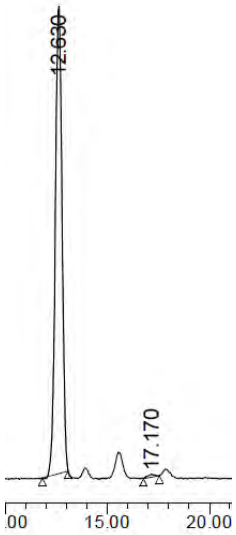
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.894	29386639	97.43	778916	97.72
2	13.359	775744	2.57	18176	2.28

(*S*)-4-benzyl-2-phenyl-4-((*R*)-1-phenylallyl)oxazol-5(4H)-one



Prepared according to the general procedure using cinnamyl methyl carbonate (48.0 mg, 0.250 mmol), 4-benzyl-2-phenyloxazol-5(4H)-one (138 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (12:1 mixture of diastereomers) as colorless oil in 83% yield (76.2 mg). The enantiomeric excess was determined by HPLC analysis of methanolysis product (254 nm, 25 °C) t_R 12.62 min (major); t_R 17.25 min (minor) [(Chiralpak AD-H) hexane/i-PrOH, 95:5, 1.0 mL/min] to be >99%. $[\alpha]_D^{25}$ = -305° (c 0.6, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46 – 7.36 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.01 (m, 5H), 6.08 (d, *J* = 16.9, 10.1 Hz, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 3.91 (d, *J* = 9.4 Hz, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.93 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.3, 159.8, 138.5, 135.6, 134.3, 132.4, 130.18, 130.12, 129.2, 128.5, 127.9, 127.8, 127.4, 127.0, 125.6, 118.9, 78.7, 57.4, 42.0.

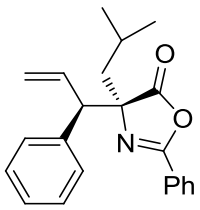




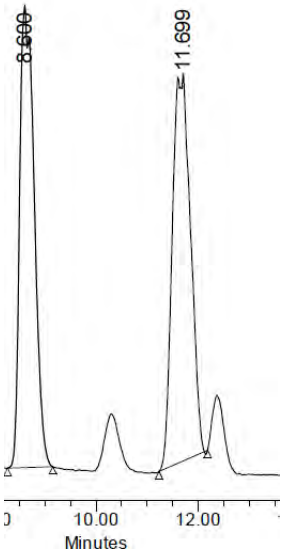
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.681	19454968	53.42	921431	57.48
2	17.255	16961458	46.58	681720	42.52

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.630	30002840	99.40	1321059	99.39
2	17.170	182344	0.60	8129	0.61

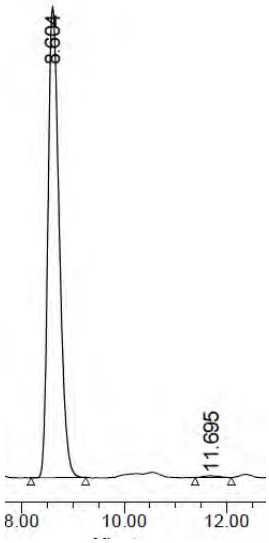
(*S*)-4-benzyl-2-phenyl-4-((*R*)-1-phenylallyl)oxazol-5(4H)-one



Prepared according to the general procedure using cinnamyl methyl carbonate (48.0 mg, 0.250 mmol), 4-*iso*-butyl-2-phenyloxazol-5(4H)-one (119 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound (14:1 mixture of diastereomers) as colorless oil in 84% yield (76.2 mg). The enantiomeric excess was determined by HPLC analysis of methanolysis product (254 nm, 25 °C) t_R 8.63 min (major); t_R 11.65 min (minor) [(Chiralpak AD-H) hexane/i-PrOH, 95:5, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = -110° (c 2.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (dd, *J* = 13.8, 6.5 Hz, 1H), 6.07 (dt, *J* = 17.0, 9.9 Hz, 1H), 5.22 (d, *J* = 16.9 Hz, 1H), 5.14 (dd, *J* = 10.1, 0.9 Hz, 1H), 3.70 (d, *J* = 9.6 Hz, 1H), 1.83 (dd, *J* = 14.2, 6.7 Hz, 1H), 1.74 (dd, *J* = 14.2, 5.9 Hz, 1H), 1.52 (dsep, *J* = 13.0, 6.5 Hz, 1H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.7, 159.6, 138.6, 135.2, 132.6, 129.1, 128.7, 128.4, 127.9, 127.3, 125.8, 118.9, 77.1, 58.5, 44.4, 25.0, 23.9, 23.3. HRMS (ESI) Calcd. for $C_{22}H_{24}NO_2$ ($[M+H]^+$): 334.1802. Found: 334.1800.

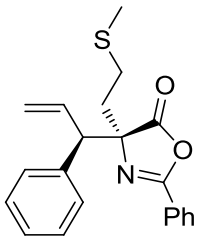


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.600	33554212	48.74	1692008	54.47
2	11.699	35286848	51.26	1414123	45.53

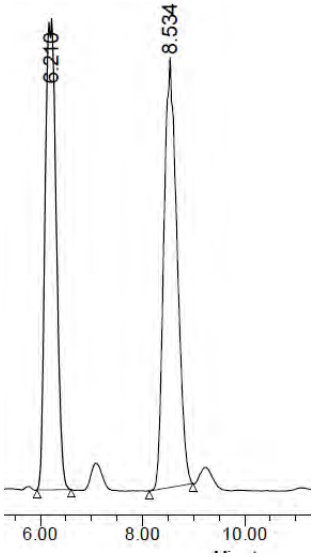


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.604	18482583	99.47	1215999	99.65
2	11.695	97653	0.53	4317	0.35

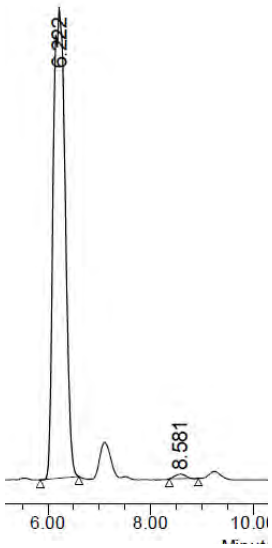
(*S*)-4-(2-(methylthio)ethyl)-2-phenyl-4-((*R*)-1-phenylallyl)oxazol-5(4H)-one



Prepared according to the general procedure using cinnamyl methyl carbonate (48.0 mg, 0.250 mmol), 4-methylthioethyl-2-phenyloxazol-5(4H)-one (129 mg, 0.550 mmol), $[Ir(cod)Cl]_2$ (3.36 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 93% yield (81.6 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.21 min (major); t_R 8.53 min (minor) [(Chiralpak AD-H) hexane/i-PrOH, 98:2, 1.0 mL/min] to be 98%. $[\alpha]_D^{25}$ = -71.8° (c 4.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.65 – 7.58 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.23 (m, 1H), 6.05 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.23 (d, *J* = 16.5 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.2 Hz, 1H), 3.74 (d, *J* = 9.5 Hz, 1H), 2.38 (ddd, *J* = 12.5, 10.5, 4.5 Hz, 1H), 2.30 (ddd, *J* = 12.9, 10.4, 6.3 Hz, 1H), 2.21 (ddd, *J* = 13.9, 10.4, 6.3 Hz, 1H), 2.01 (ddd, *J* = 14.5, 10.4, 4.5 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 160.6, 138.2, 135.0, 132.8, 129.1, 128.8, 128.5, 128.0, 127.5, 125.6, 119.2, 76.6, 57.5, 34.9, 28.6, 15.2. HRMS (ESI) Calcd. for $C_{21}H_{22}NO_2S$ ($[M+H]^+$): 352.1366. Found: 352.1364.

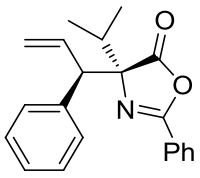


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.210	30483752	47.99	1993724	52.39
2	8.534	33041950	52.01	1811519	47.61

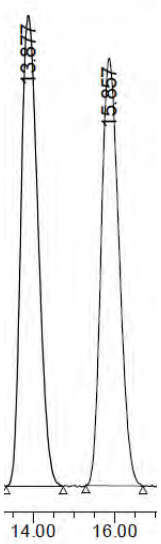


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.222	37469676	99.14	2311017	99.06
2	8.581	324512	0.86	21861	0.94

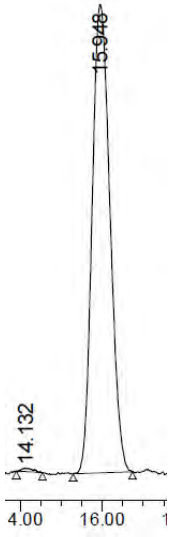
(*S*)-4-benzyl-2-phenyl-4-((*R*)-1-phenylallyl)oxazol-5(4H)-one



Prepared according to the general procedure using cinnamyl methyl carbonate (48.0 mg, 0.250 mmol), 4-*iso*-propyl-2-phenyloxazol-5(4H)-one (112 mg, 0.550 mmol), $[Ir(dbcot)Cl]_2$ (4.32 mg, 0.0050 mmol,), **1** (6.00 mg, 0.0100 mmol) and **2c** (11.6 mg, 0.0200 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 16:1 to 6:1) to give the title compound as colorless oil in 69% yield (55.0 mg). The enantiomeric excess was determined by HPLC analysis of methanolysis product (254 nm, 25 °C) t_R 15.94 min (major); t_R 14.13 min (minor) [(Chiralpak AD-H) hexane/i-PrOH, 98:2, 1.0 mL/min] to be 99%. $[\alpha]_D^{25}$ = -50.3° (c 1.9, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52-7.47 (m, 4H), 7.34-7.27 (m, 2H), 7.26-7.21 (m, 1H), 6.14 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.1 Hz, 1H), 3.95 (d, *J* = 9.6 Hz, 1H), 2.19 (dsep, *J* = 13.6, 6.8 Hz, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.3, 159.8, 138.7, 135.7, 132.5, 129.2, 128.7, 128.3, 127.9, 127.2, 125.8, 118.4, 80.3, 54.3, 32.3, 16.7, 16.1. HRMS (ESI) Calcd. for $C_{21}H_{22}NO_2$ ($[M+H]^+$): 320.1651. Found: 320.1645.



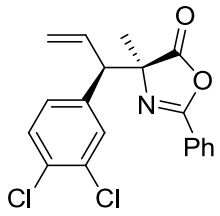
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.877	10518464	51.42	361068	52.43
2	15.857	9936648	48.58	327615	47.57



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	14.132	32722	0.45	1720	0.71
2	15.948	7267014	99.55	240490	99.29

Procedure for Synthesis of 6e

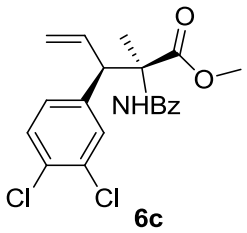
(*S*)-4-((*R*)-1-(3,4-dichlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one(6b)



6b

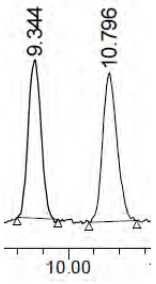
Prepared according to the general procedure using 3,4-dichlorocinnamyl methyl carbonate **6a** (500 mg, 1.92 mmol), 4-methyl-2-phenyloxazol-5(4H)-one (740 mg, 4.22 mmol), $[Ir(cod)Cl]_2$ (25.8 mg, 0.0384 mmol,), **1** (46.1 mg, 0.0768 mmol) and **2c** (89.1 mg, 0.154 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 3:1) to give the title compound **6b** as white wax in 93% yield (634 mg). $[\alpha]_D^{25}$ = -110° (c 3.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 – 7.92 (m, 2H), 7.66 – 7.60 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.90 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.22 (d, *J* = 16.9 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 3.69 (d, *J* = 9.3 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 160.3, 138.6, 134.6, 132.9, 132.4, 131.5, 131.1, 130.4, 128.8, 128.6, 128.0, 125.5, 119.8, 73.1, 56.4, 22.4. HRMS (ESI) Calcd. for $C_{19}H_{17}NO_2Cl_2$ ($[M+H]^+$): 360.0553. Found: 360.0552.

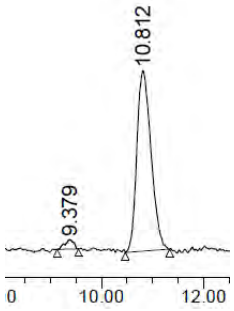
(*2S,3R*)-methyl 2-benzamido-3-(3,4-dichlorophenyl)-2-methylpent-4-enoate(6c)



6c

(*S*)-4-((*R*)-1-(3,4-dichlorophenyl)allyl)-4-methyl-2-phenyloxazol-5(4H)-one **6b** (200 mg, 0.557 mmol) was dissolved in 10 mL methanol with anhydrous K_2CO_3 (20 mg, 0.144 mmol). The mixture was stirred for 1 h. After removing the solvent, the crude mixture was purified by flash column chromatography (hexanes:EtOAc, 6:1 to 2:1) to give the title compound **6c** as white wax in 95% yield (207 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.81 min (major); t_R 9.38 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 92.5:7.5, 1.0 mL/min] to be 94%. $[\alpha]_D^{25}$ = +11.0° (c 0.9, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.53 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 6.99 – 6.89 (m, 2H), 6.38 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.44 (d, *J* = 16.9 Hz, 1H), 5.40 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.35 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 166.4, 139.1, 134.9, 134.4, 132.4, 131.7, 131.5, 130.3, 130.2, 128.7, 127.8, 126.7, 120.5, 63.3, 54.4, 52.8, 19.8. HRMS (ESI) Calcd. for $C_{20}H_{20}Cl_2NO_3$ ($[M+H]^+$): 392.0820. Found: 392.0814. Calcd. for $C_{20}H_{19}Cl_2NO_3Na$ ($[M+Na]^+$): 414.0640. Found: 414.0634.

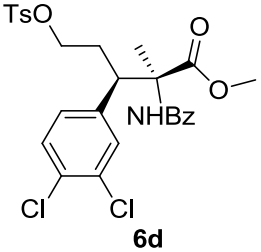




	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.344	3030579	48.87	174036	51.62
2	10.796	3170224	51.13	163134	48.38

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.379	170864	3.25	14223	5.09
2	10.812	5085635	96.75	265100	94.91

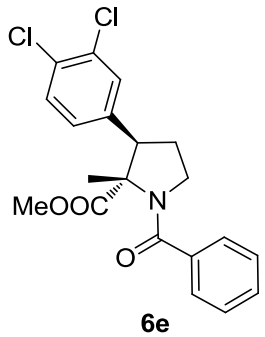
(*2S*,*3R*)-methyl 2-benzamido-3-(3,4-dichlorophenyl)-2-methyl-5-(tosyloxy)pentanoate(6d)



6d

(*2S,3R*)-methyl 2-benzamido-3-(3,4-dichlorophenyl)-2-methylpent-4-enoate **6c** (50 mg, 0.128 mmole) was dissolved in dry, degassed THF (0.5 mL) and cooled to -78 °C. Then 9-BBN (0.56 mL as a 0.5 M solution in THF, 0.282 mmol) was added to the reaction vessel. The reaction mixture was stirred for 1 h at -78 °C, then allowed to warm slowly to room temperature and stirred overnight. The resulting solution was cooled to 0 °C, at which time water (1.0 mL), and $NaBO_3 \cdot 4H_2O$ (295 mg, 1.92 mmol) were added. The reaction was allowed to warm to room temperature and was stirred for an additional 6 h. The reaction mixture was diluted with DCM, and then extracted with DCM (3*3 mL). The organic layer was combined, dried over MgSO4, filtered, and concentrated. The crude product was dissolved in DCM (1 mL) and cooled to 0 °C, at which time triethylamine (38.8 mg, 0.383 mmol) and TsCl (53.8 mg, 0.283 mmol) were added. The reaction was allowed to warm to room temperature and stirred for 1 h. The resulted solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the polar residue. After removing the solvent, the mixture was purified by flash column silica gel chromatography (hexanes:EtOAc, 6:1 to 2:1) to give the title compound **6d** as an colorless oil in 56% yield (40.4 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.87 (s, 1H), 6.80 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.99 (ddd, *J* = 10.7, 6.7, 4.0 Hz, 1H), 3.86 – 3.78 (m, 4H), 3.70 (td, *J* = 9.5, 5.6 Hz, 1H), 2.56 – 2.44 (m, 4H), 2.28 – 2.19 (m, 1H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 166.8, 145.0, 138.0, 134.5, 132.5, 132.4, 131.8, 131.7, 130.5, 130.3, 129.8, 128.6, 127.8, 126.7, 68.2, 63.9, 52.9, 46.1, 29.3, 21.7, 21.2.

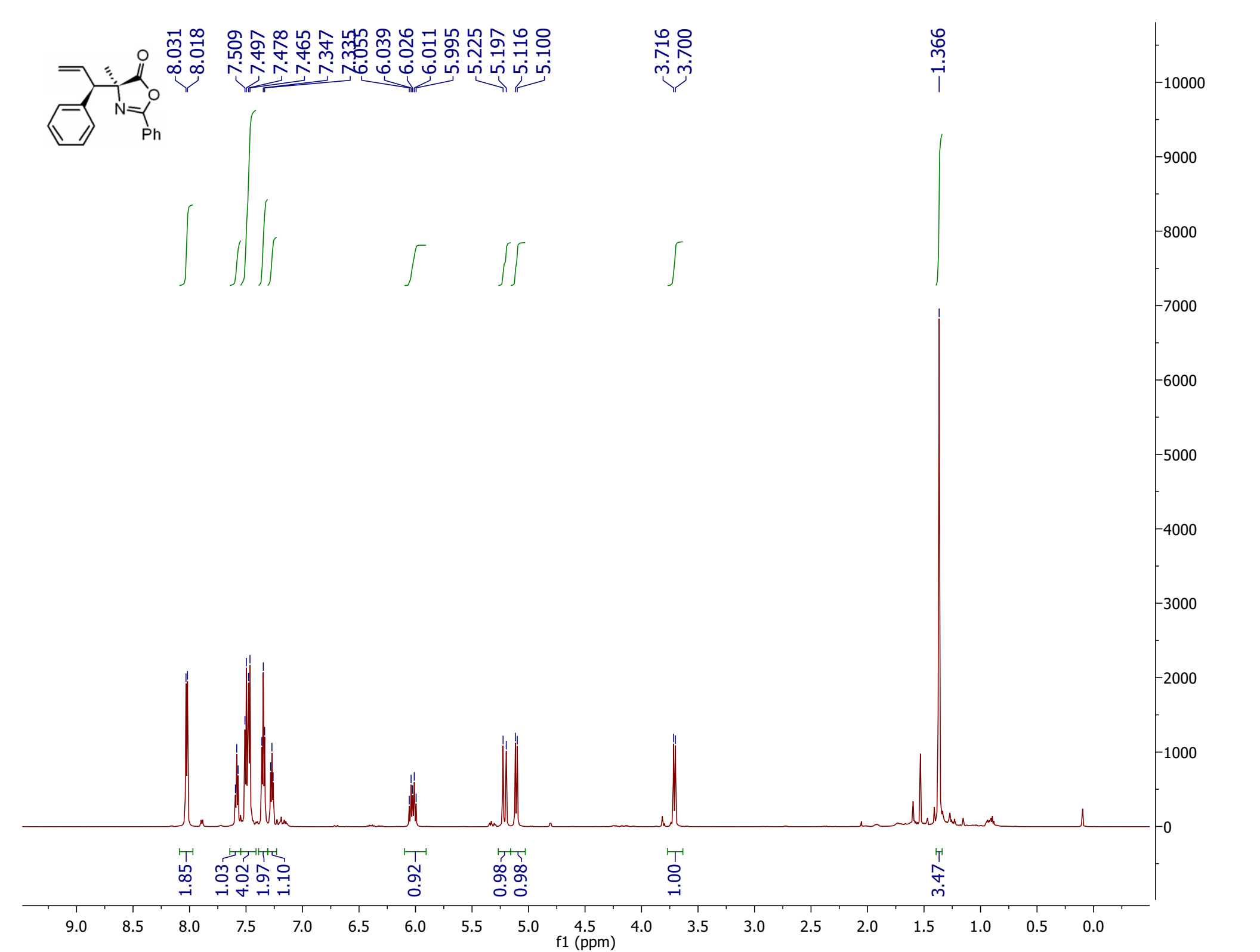
(*2S,3R*)-methyl 1-benzoyl-3-(3,4-dichlorophenyl)-2-methylpyrrolidine-2-carboxylate(6e)



6e

(*2S,3R*)-methyl 2-benzamido-3-(3,4-dichlorophenyl)-2-methyl-5-(tosyloxy)pentanoate **6d** (20mg, 0.0355 mmol) and NaH (1.35 mg, 0.0563 mmol) were dissolved in dry DMF (0.5 mL). The mixture was stirred for 12 h at room temperature. After removing the solvent in vacuum, the mixture was purified by flash column silica gel chromatography (hexanes:EtOAc, 6:1 to 3:1) to give the title compound **6e** as an colorless oil in 95% yield (13.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.47 – 7.37 (m, 4H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 8.3, 1.8 Hz, 1H), 3.86 (s, 3H), 3.79 (td, *J* = 10.8, 6.2 Hz, 1H), 3.72 (dd, *J* = 12.9, 5.6 Hz, 1H), 3.70 – 3.64 (m, 1H), 2.49-2.35 (m, 1H), 2.30 – 2.18 (m, 1H), 1.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 169.1, 136.6, 136.6, 132.6, 131.8, 130.4, 130.1, 129.8, 128.4, 127.8, 126.5, 68.7, 52.7, 51.5, 48.8, 28.3, 16.7. HRMS (ESI) Calcd. for $C_{20}H_{19}NO_3Na$ ($[M+Na]^+$): 414.0640. Found: 414.0633.

1. Melhado, A. D.; Luparia, M.; Toste, F. D. *J. Am. Chem. Soc.* **2007,** *129*, 12638.
2. Stanley, L. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2009,** *48*, 7841.
3. Polet, D.; Alexakis, A.; Tissot-Croset, K.; Corminboeuf, C.; Ditrich, K. *Chem. -Eur. J* **2006,** *12*, 3596.
4. Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009,** *131*, 8971.
5. Chaffins, S.; Brettreich, M.; Wudl, F. *Synthesis* **2002**, 1191.
6. Wuennemann, S.; Froehlich, R.; Hoppe, D. *Eur. J. Org. Chem.* **2008**, 684.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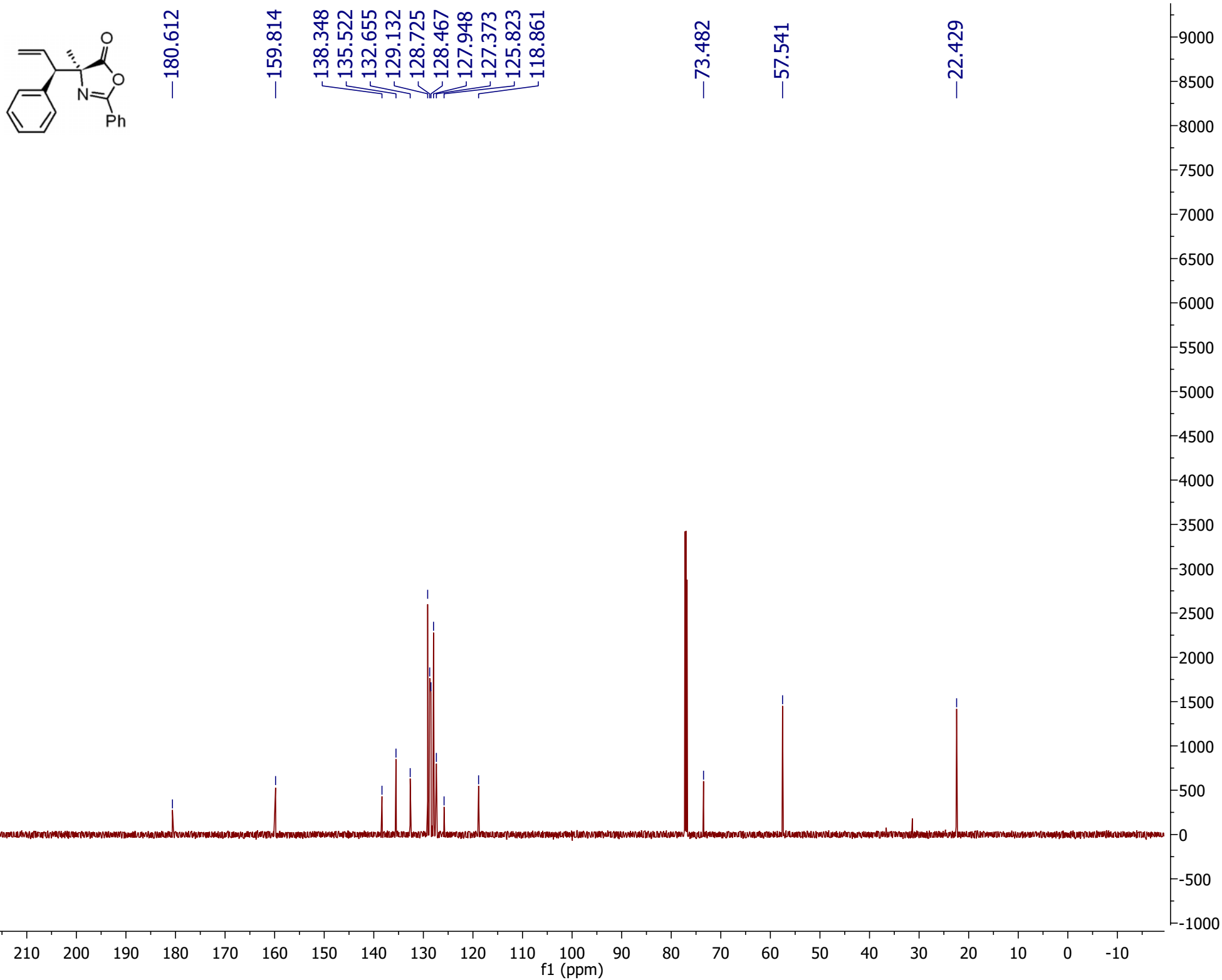
7.497
7.478
7.465
7.347
7.335
6.055
6.039
6.026
6.011
5.995
5.225
5.197
5.116
5.100
3.716
3.700
1.366
O
O
N
Ph
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.85
1.03
4.02
1.97
1.10
0.92
0.98
0.98
1.00
3.47
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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O
N
Ph
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138.348
135.522
132.655
129.132
128.725
128.467
127.948
127.373
125.823
118.861
73.482
57.541
22.429
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
210
200
190
180
170
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140
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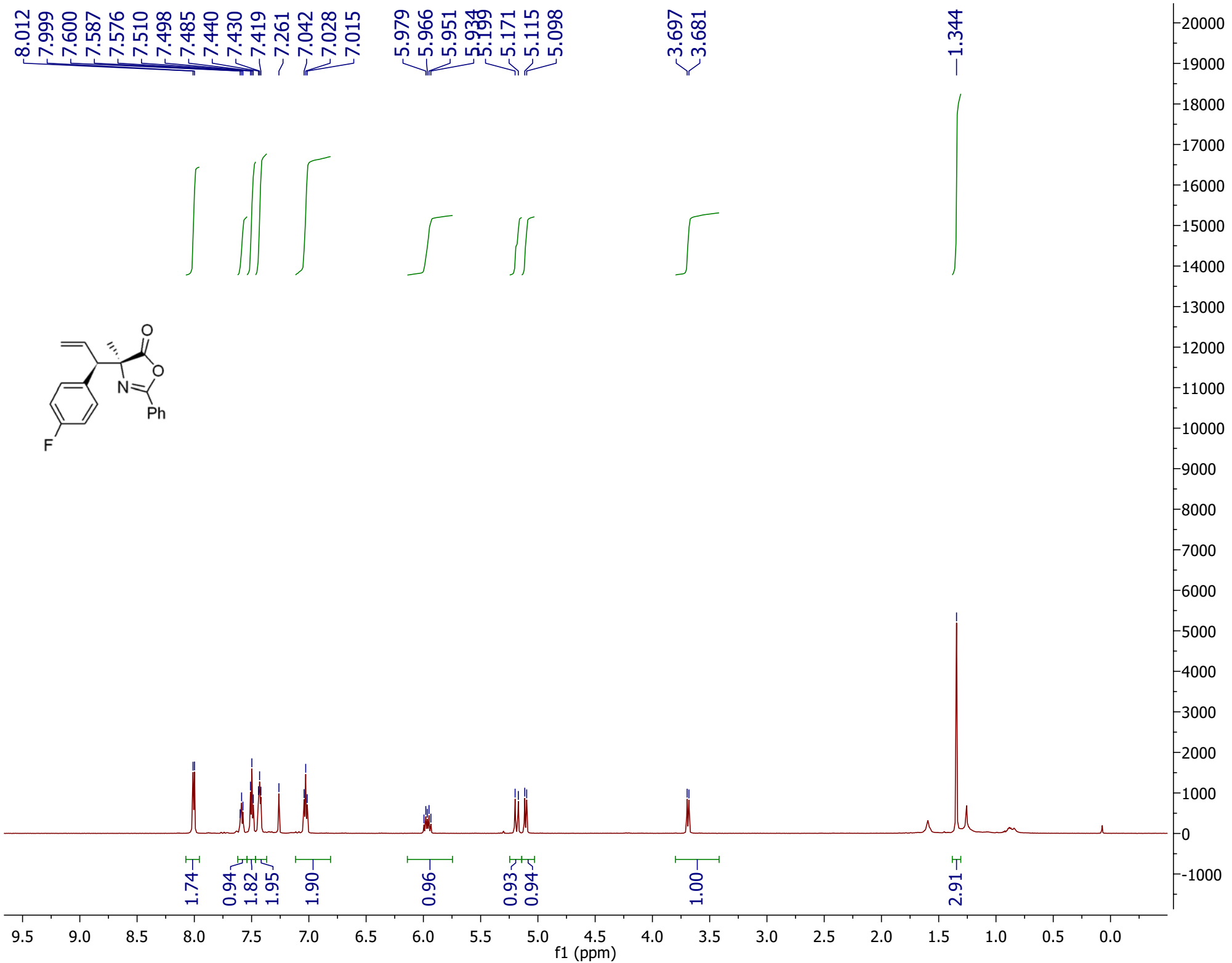
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.510
7.498
7.485
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7.430
7.419
7.261
7.042
7.028
7.015
5.979
5.966
5.951
5.934
5.199
5.171
5.115
5.098
3.697
3.681
1.344
O
O
N
Ph
F
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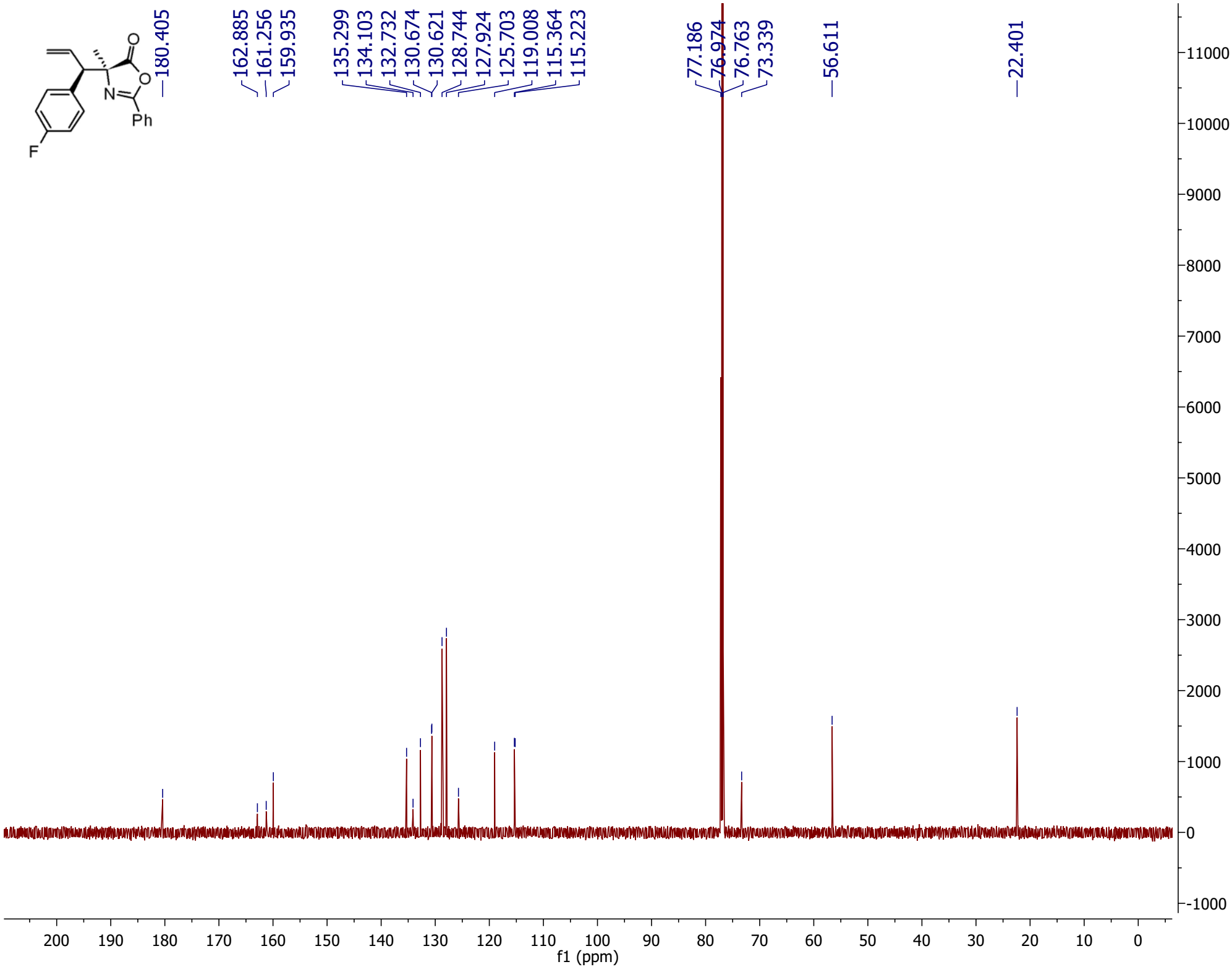
1.82
1.95
1.90
0.96
0.93
0.94
1.00
2.91
f1 (ppm)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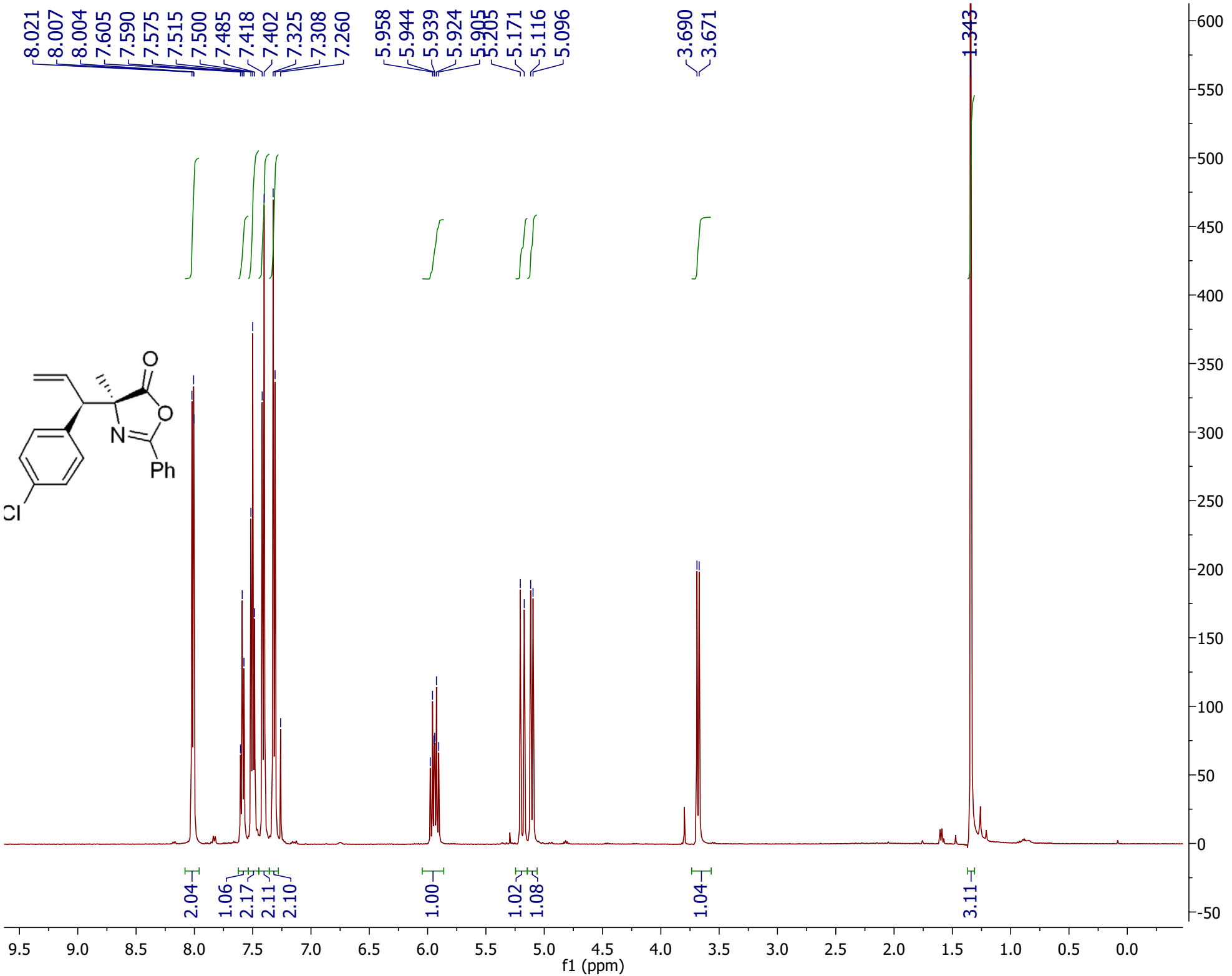
161.256
159.935
135.299
134.103
132.732
130.674
130.621
128.744
127.924
125.703
119.008
115.364
115.223
77.186
76.974
76.763
73.339
56.611
22.401
O
O
N
Ph
F
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.007
8.004
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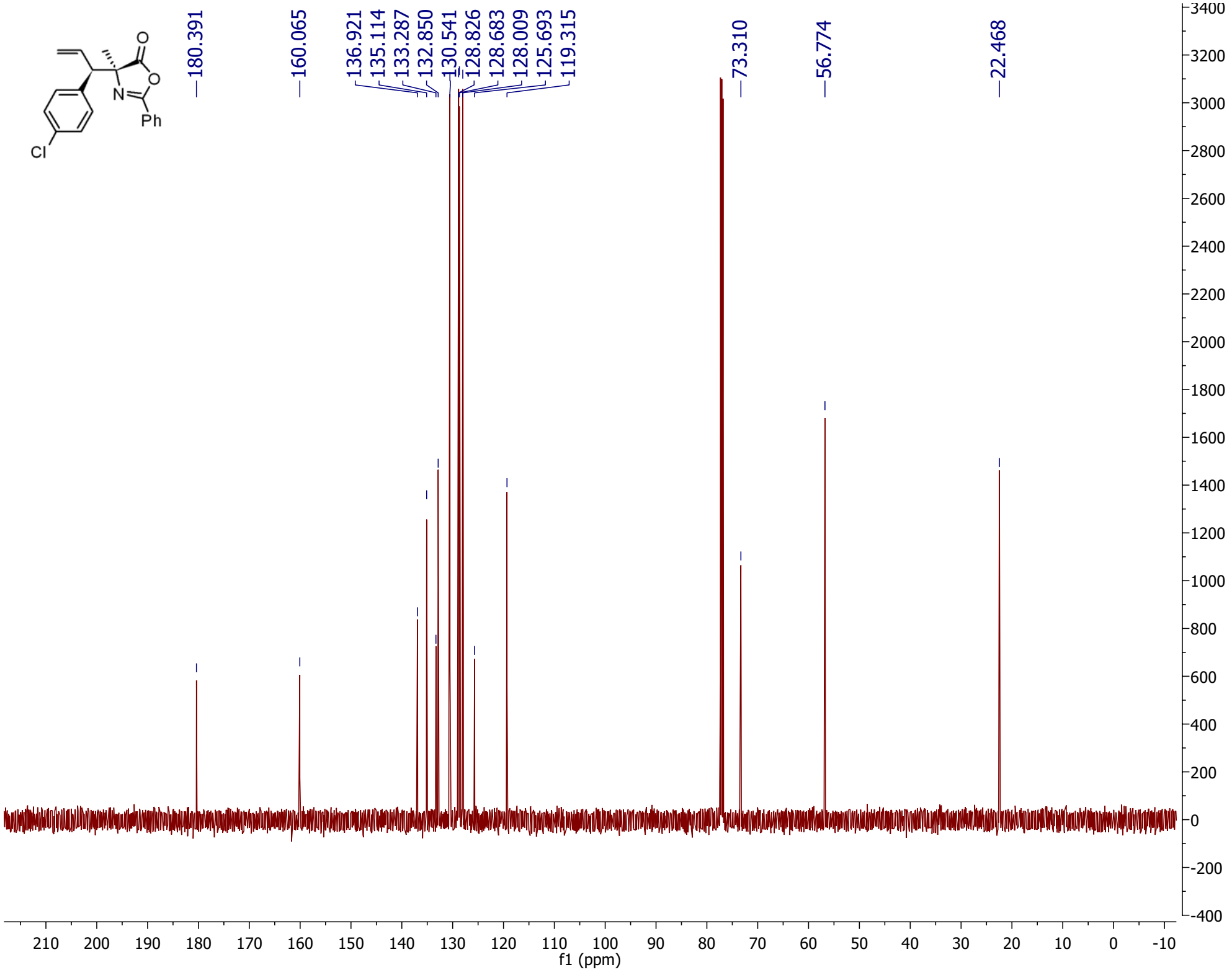
7.590
7.575
7.515
7.500
7.485
7.418
7.402
7.325
7.308
7.260
5.958
5.944
5.939
5.924
5.205
5.171
5.116
5.096
3.690
3.671
1.343
O
O
N
Ph
Cl
2.04
1.06
2.17
2.11
2.10
1.00
1.02
1.08
1.04
3.11
f1 (ppm)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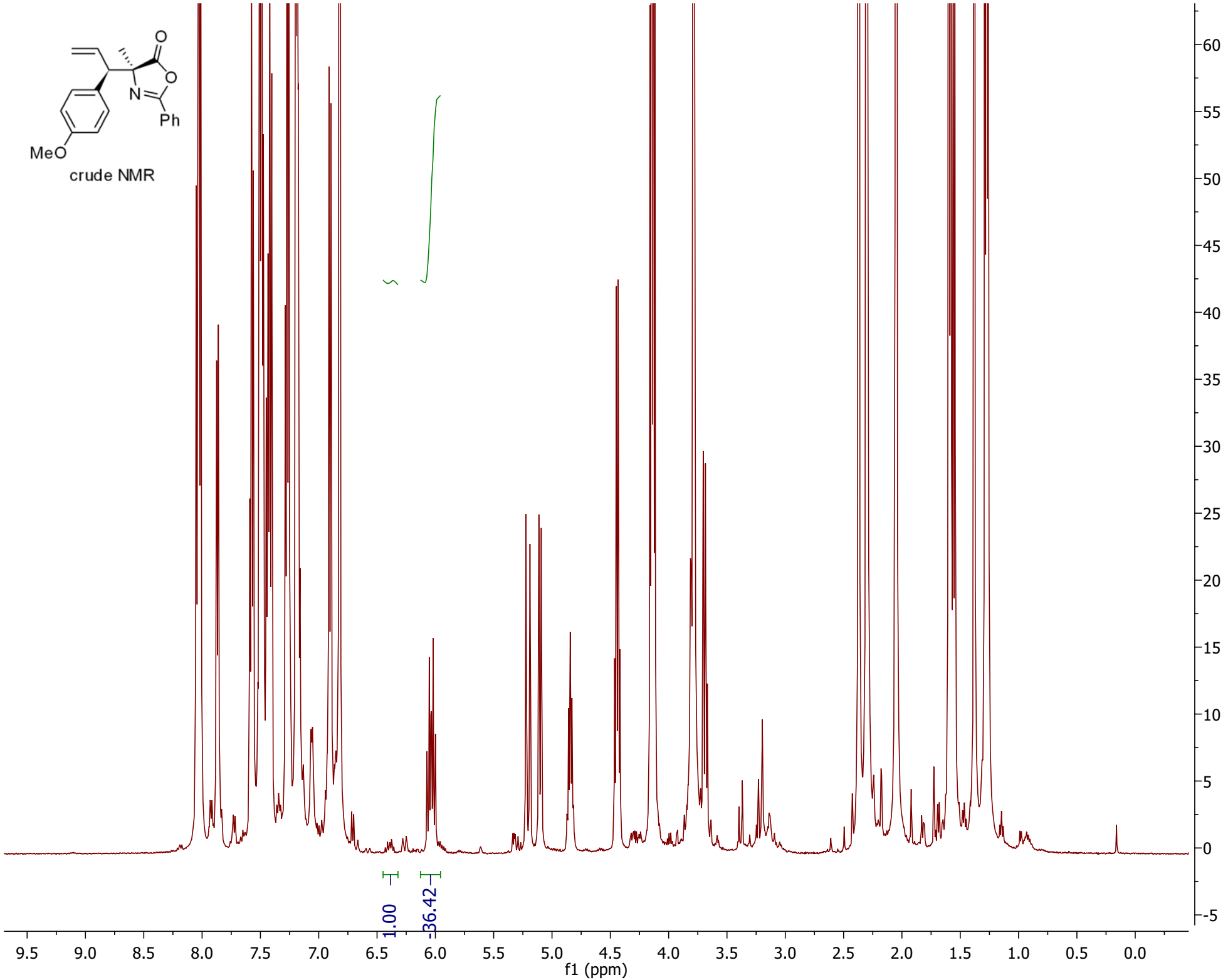
135.114
133.287
132.850
130.541
128.826
128.683
128.009
125.693
119.315
73.310
56.774
22.468
O
O
N
Ph
Cl
f1 (ppm)


MeO
Ph
O
N
O
crude NMR
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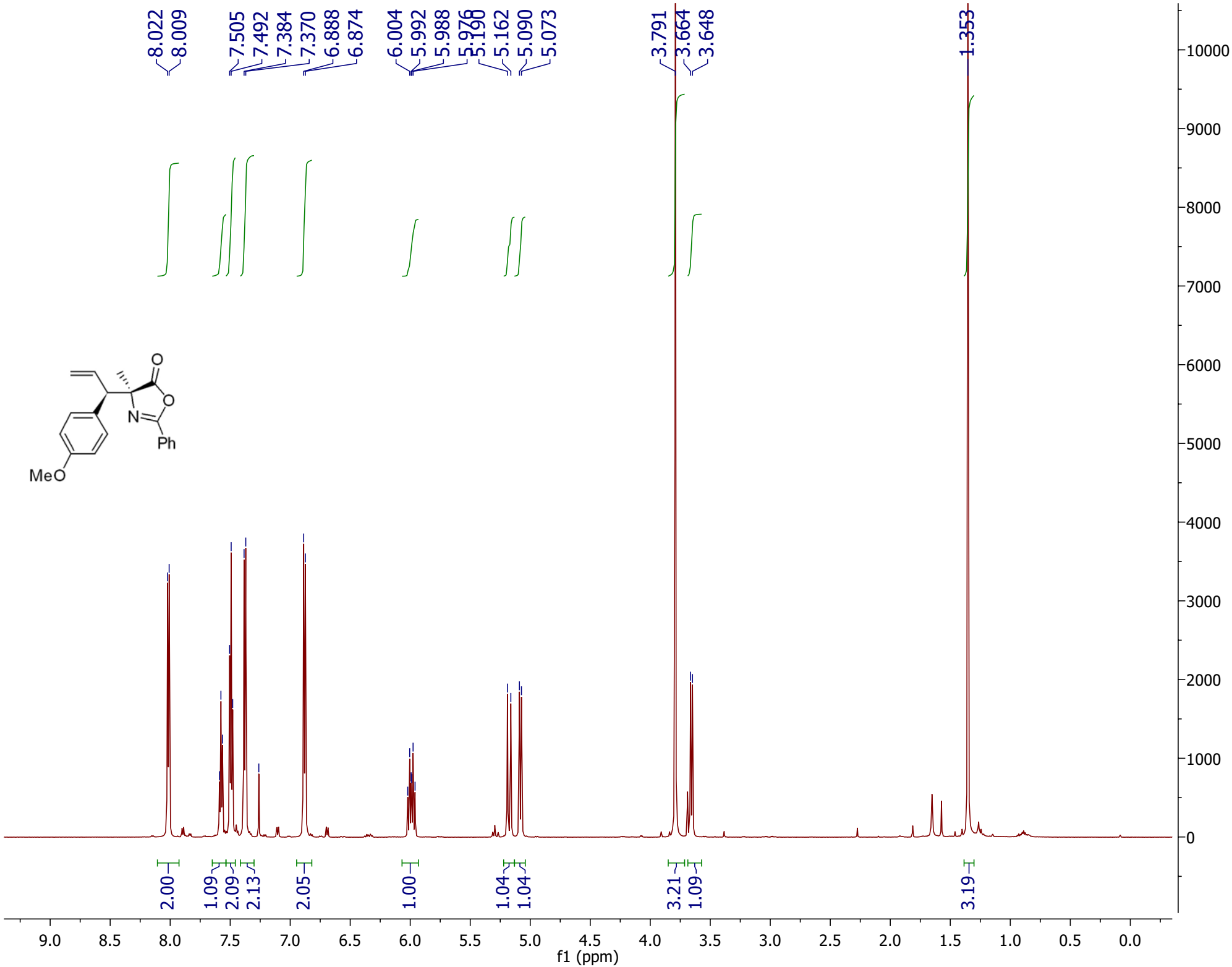
36.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
60
55
50
45
40
35
30
25
20
15
10
5
0
-5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7.505
7.492
7.384
7.370
6.888
6.874
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5.988
5.976
5.190
5.162
5.090
5.073
3.791
3.664
3.648
1.353
O
O
N
Ph
MeO
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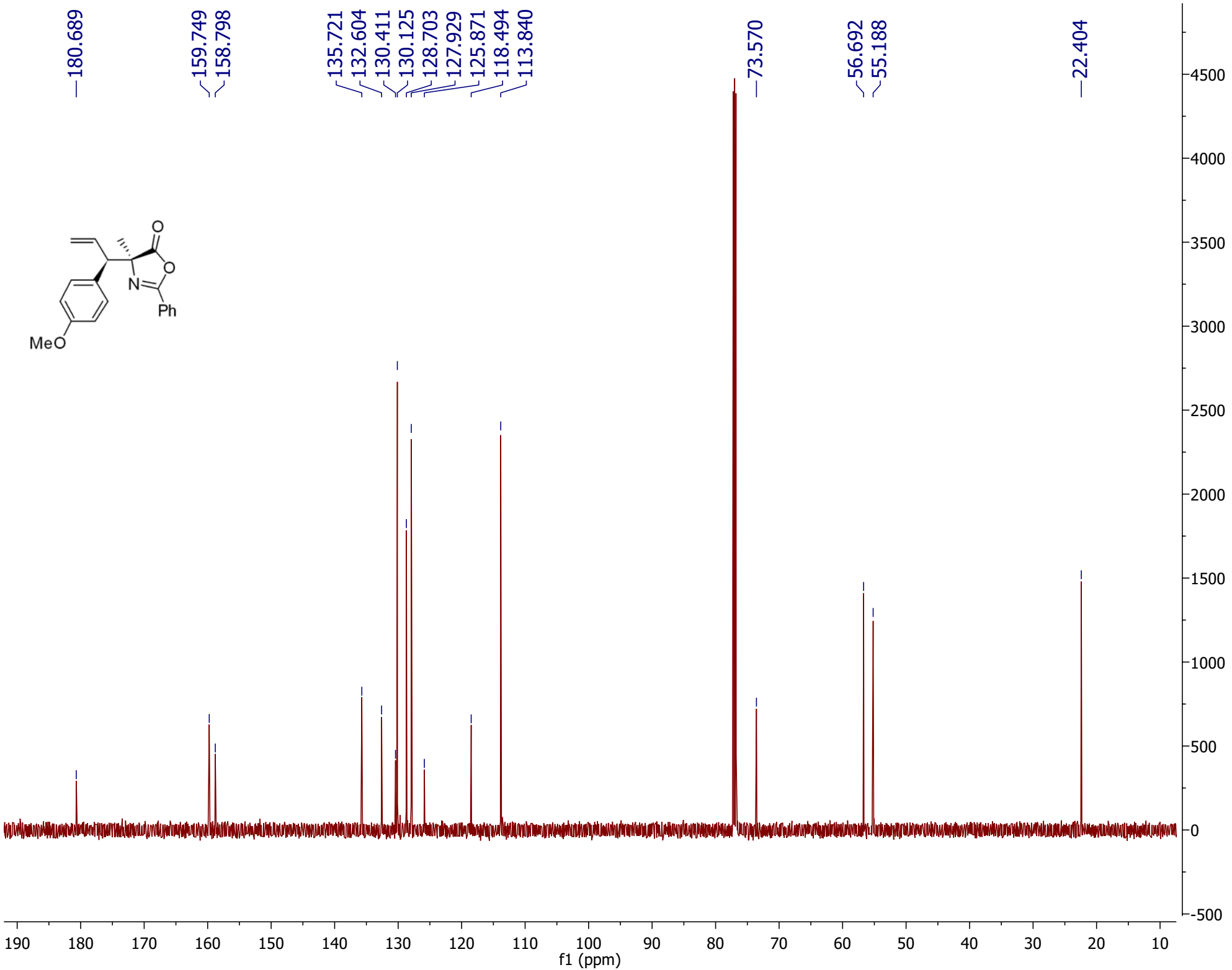
2.09
2.13
2.05
1.00
1.04
1.04
3.21
1.09
3.19
f1 (ppm)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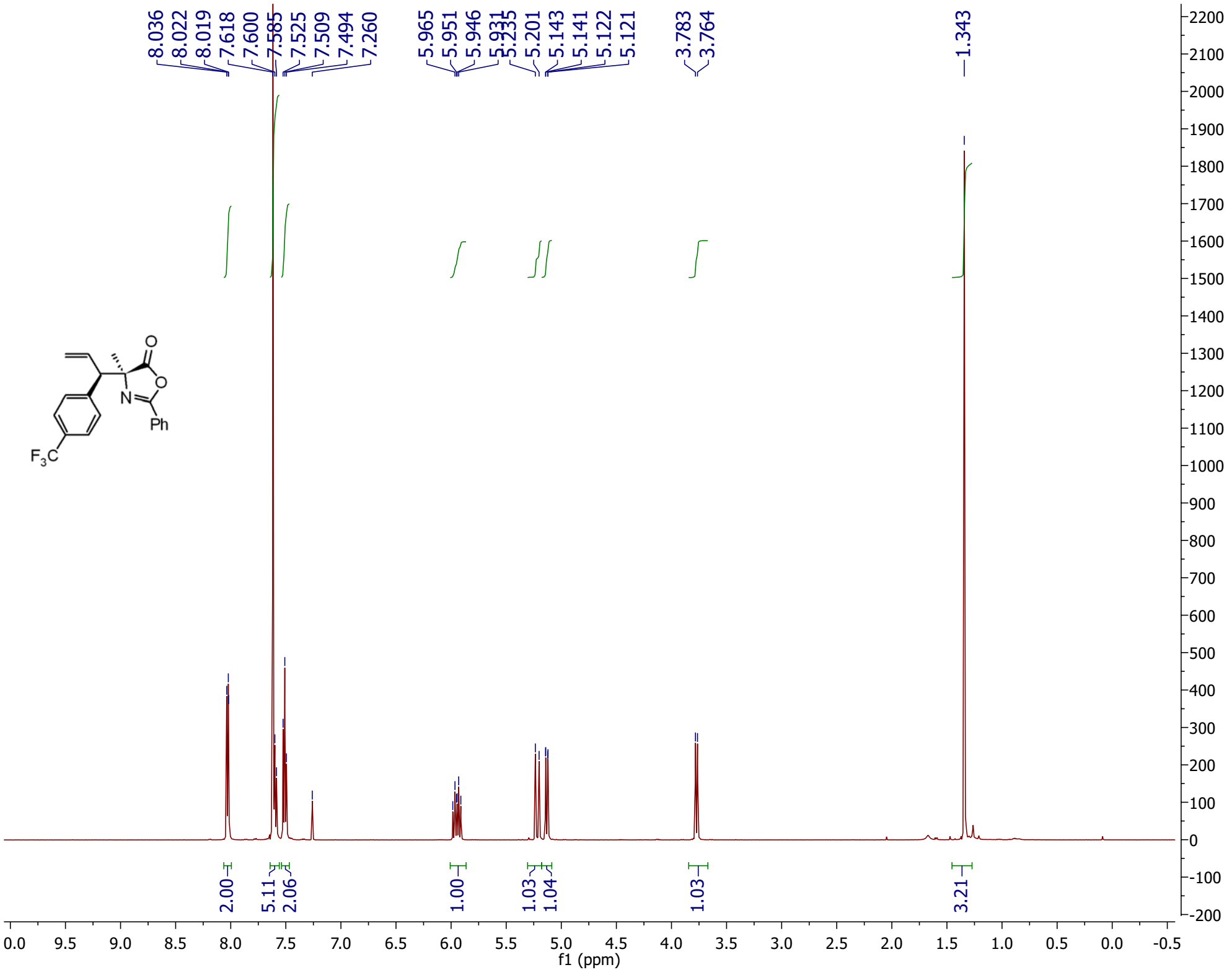
158.798
135.721
132.604
130.411
130.125
128.703
127.929
125.871
118.494
113.840
73.570
56.692
55.188
22.404
MeO
N
O
Ph
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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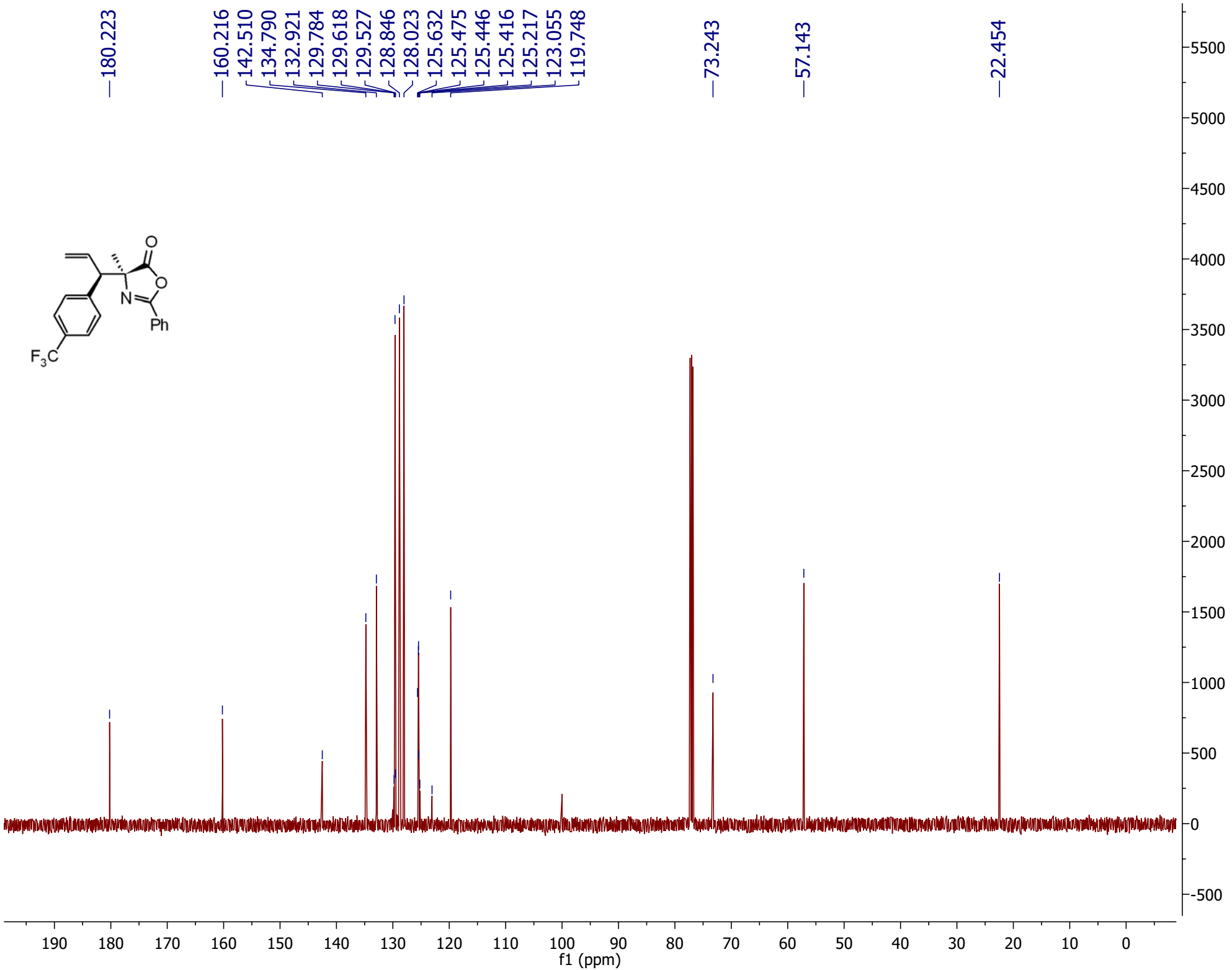
8.019
7.618
7.600
7.585
7.525
7.509
7.494
7.260
5.965
5.951
5.946
5.931
5.235
5.201
5.143
5.141
5.122
5.121
3.783
3.764
1.343
O
O
N
Ph
F3C
2.00
5.11
2.06
1.00
1.03
1.04
1.03
3.21
f1 (ppm)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142.510
134.790
132.921
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129.527
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128.023
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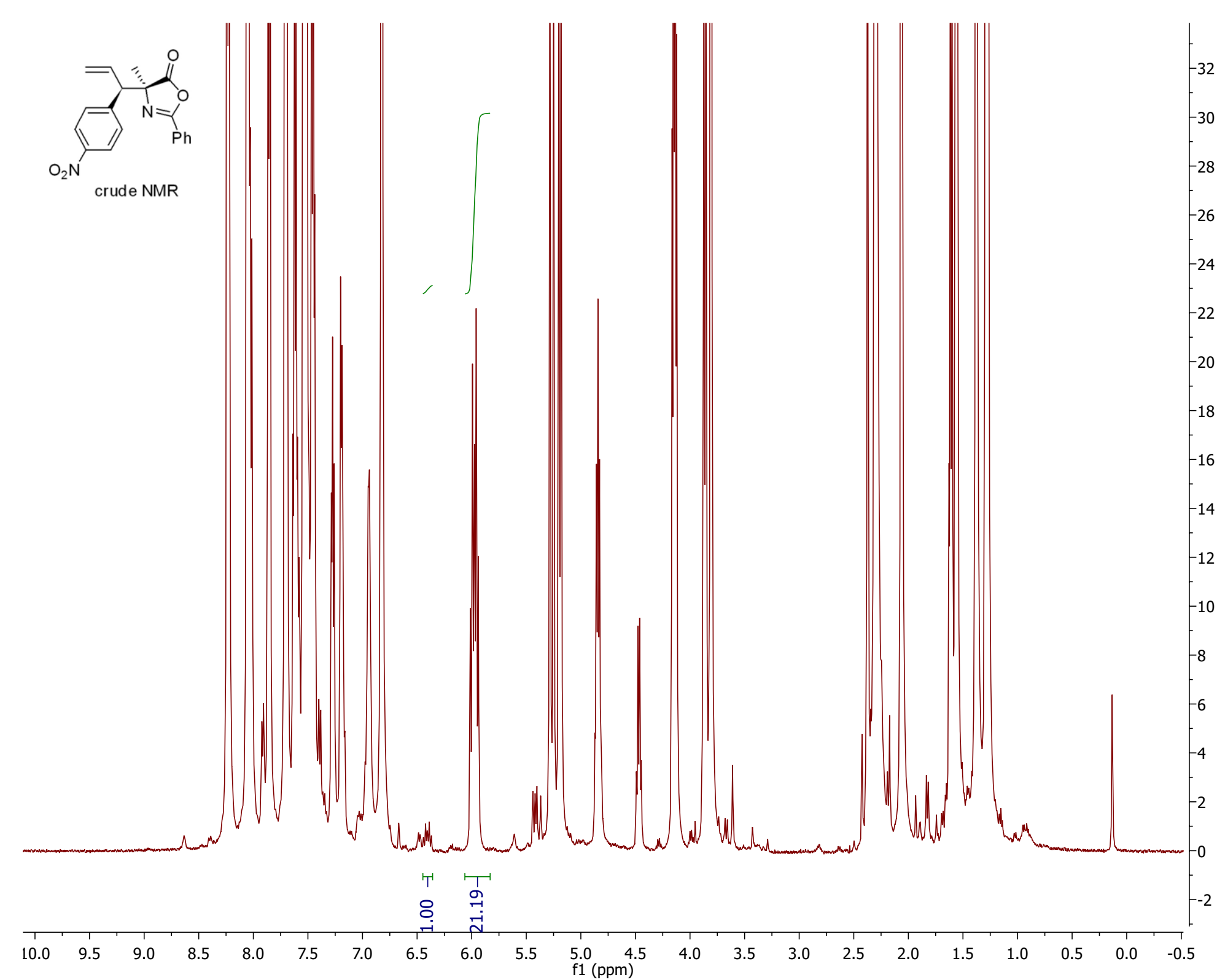
125.475
125.446
125.416
125.217
123.055
119.748
73.243
57.143
22.454
O
O
N
Ph
F3C
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N
Ph
O_2N
crude NMR
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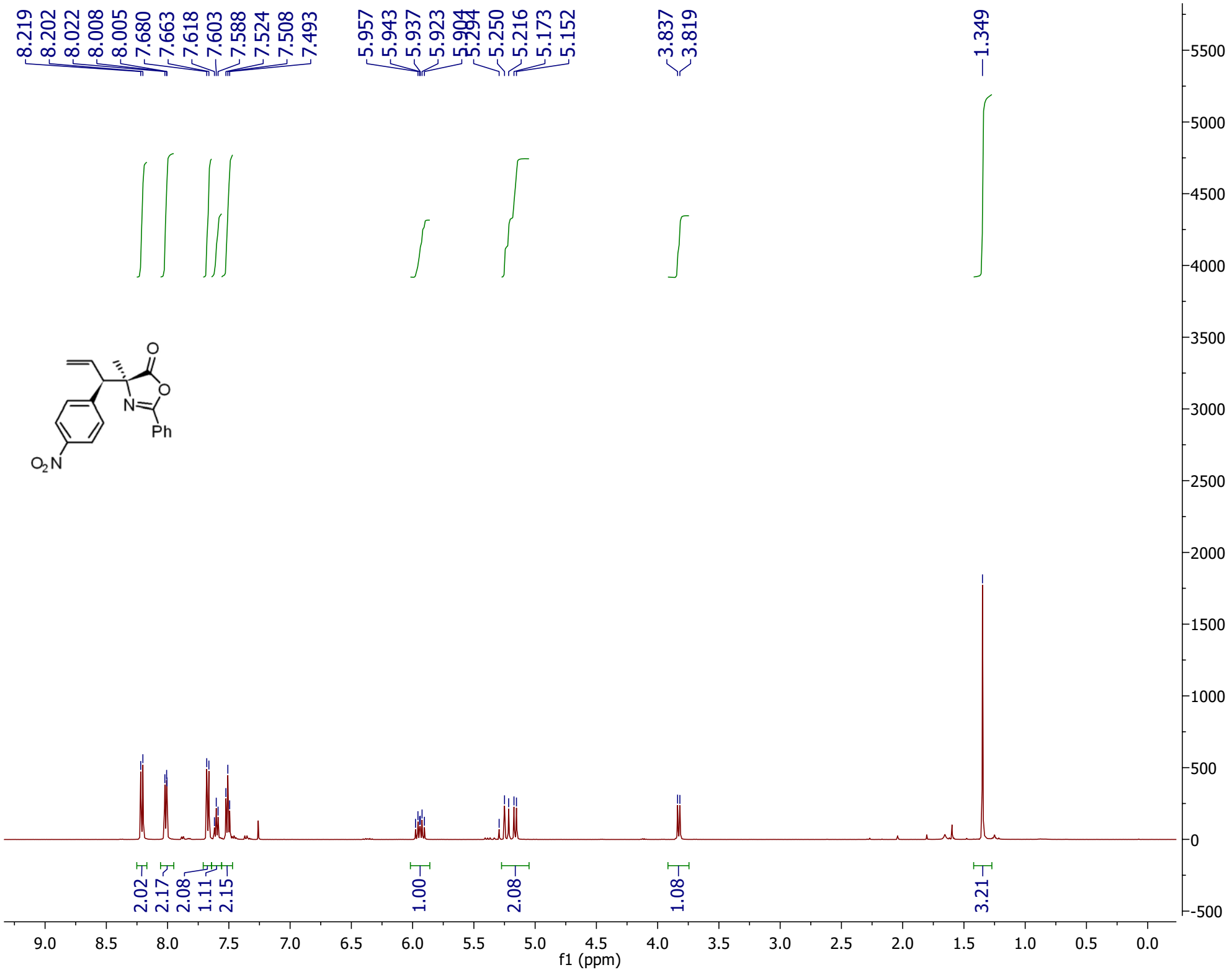
21.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2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7.508
7.493
5.957
5.943
5.937
5.923
5.904
5.294
5.250
5.216
5.173
5.152
3.837
3.819
1.349
O
O
N
Ph
O2N
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2.17
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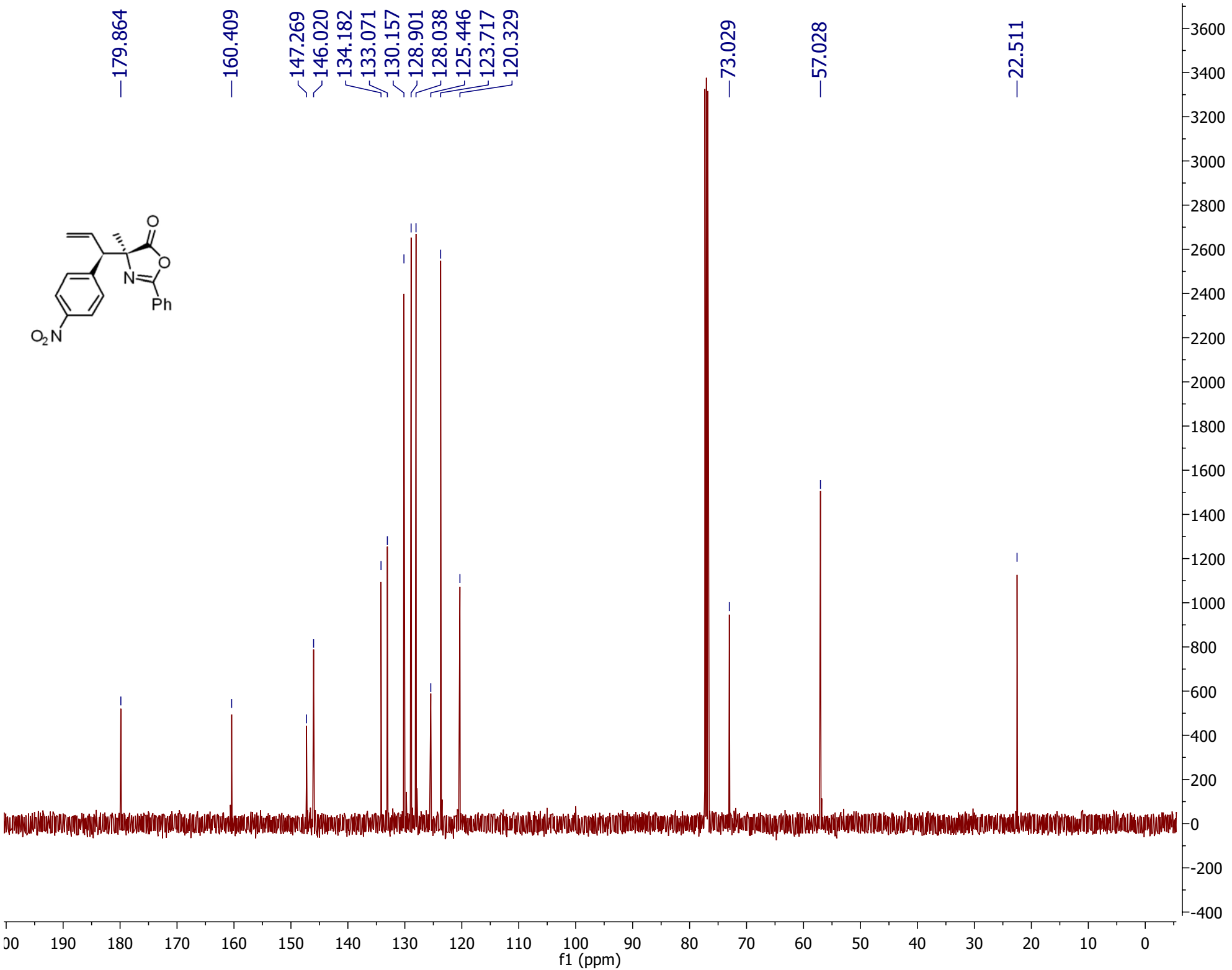
1.11
2.15
1.00
2.08
1.08
3.21
f1 (ppm)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128.901
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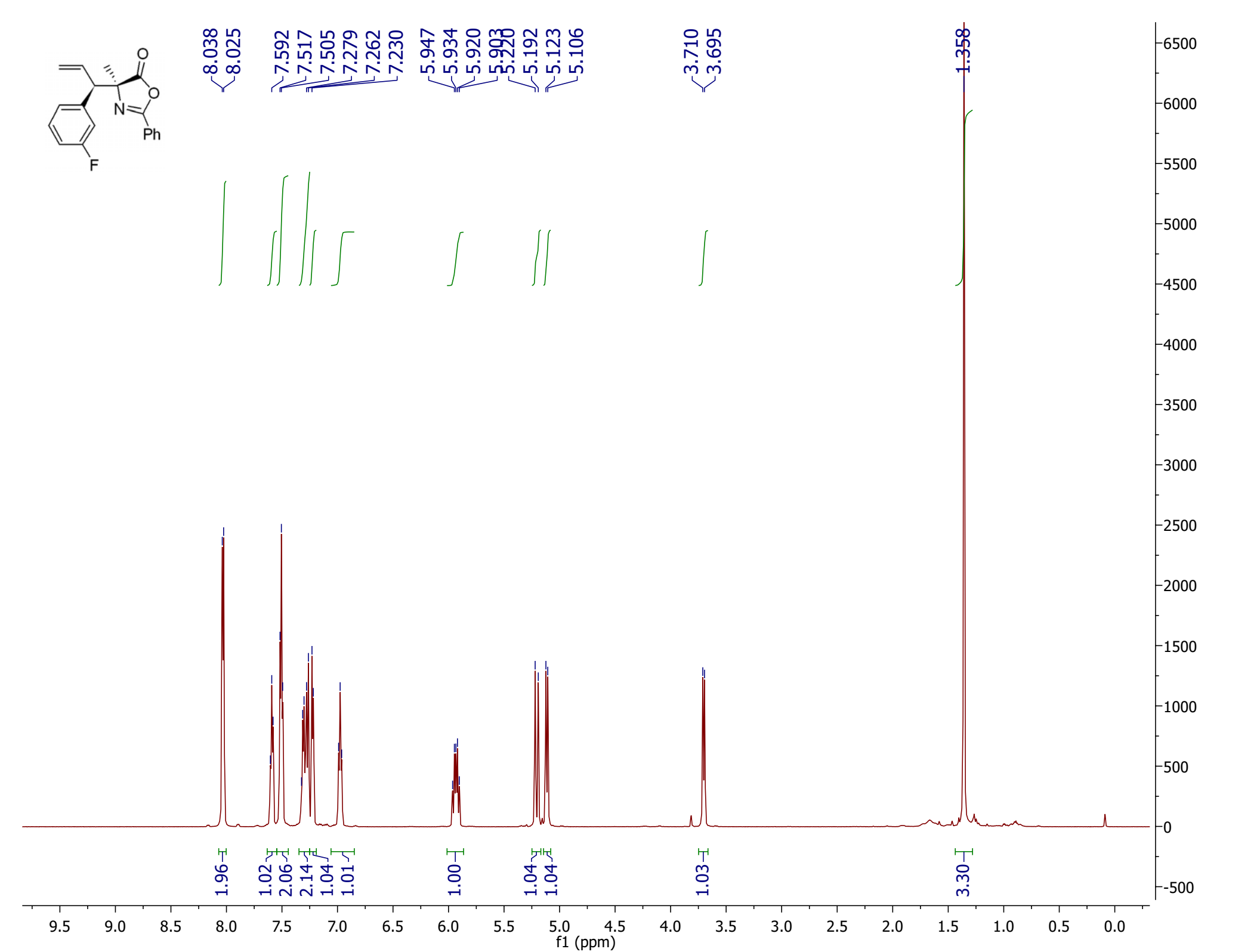
123.717
120.329
73.029
57.028
22.511
O
O
N
Ph
O2N
f1 (ppm)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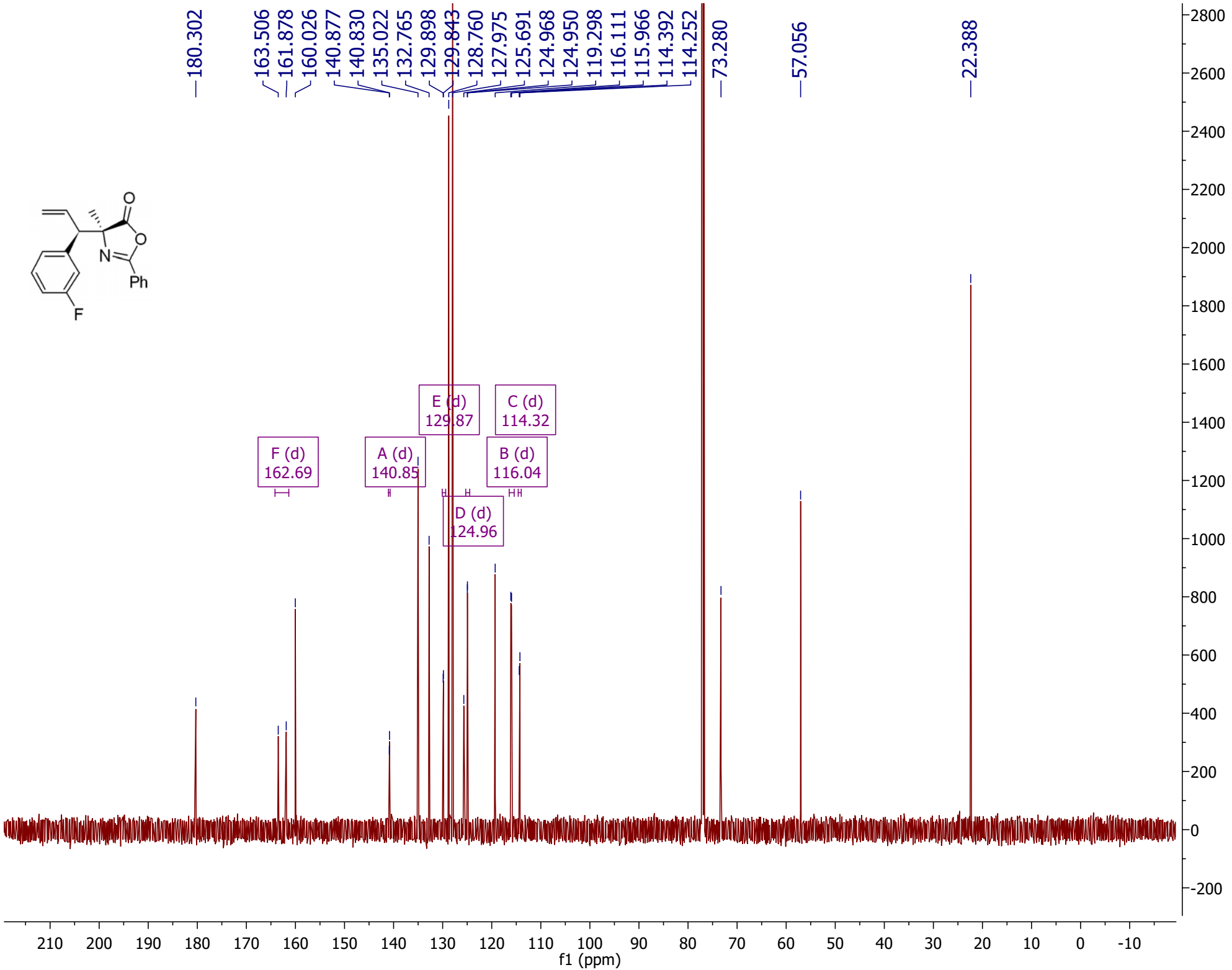
7.279
7.262
7.230
5.947
5.934
5.920
5.903
5.220
5.192
5.123
5.106
3.710
3.695
1.358
O
O
N
Ph
F
1.96
1.02
2.06
2.14
1.04
1.01
1.00
1.04
1.04
1.03
3.30
f1 (ppm)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132.765
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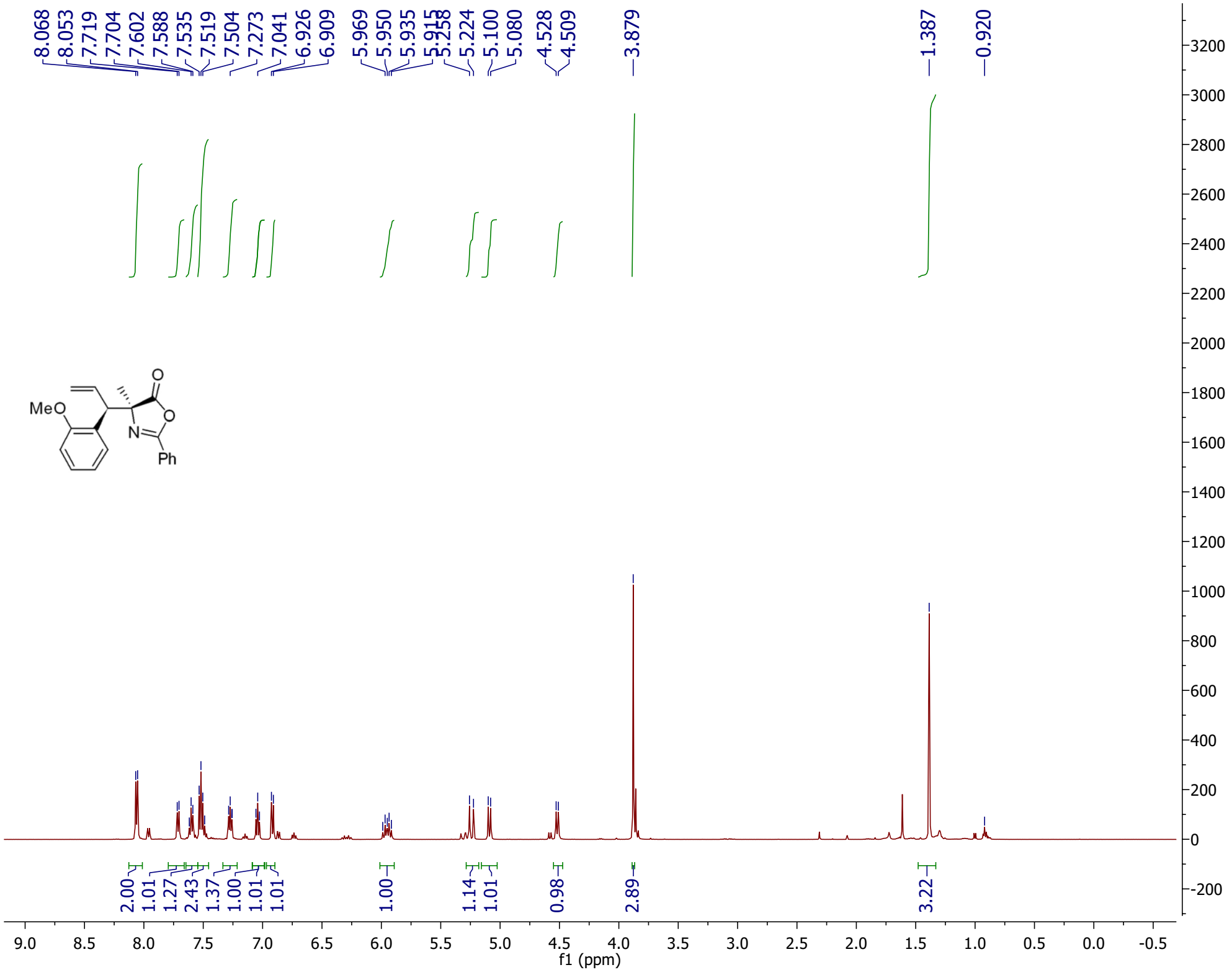
129.843
128.760
127.975
125.691
124.968
124.950
119.298
116.111
115.966
114.392
114.252
73.280
57.056
22.388
F (d)
162.69
A (d)
140.85
E (d)
129.87
C (d)
114.32
B (d)
116.04
D (d)
124.96
O
O
N
Ph
F
f1 (ppm)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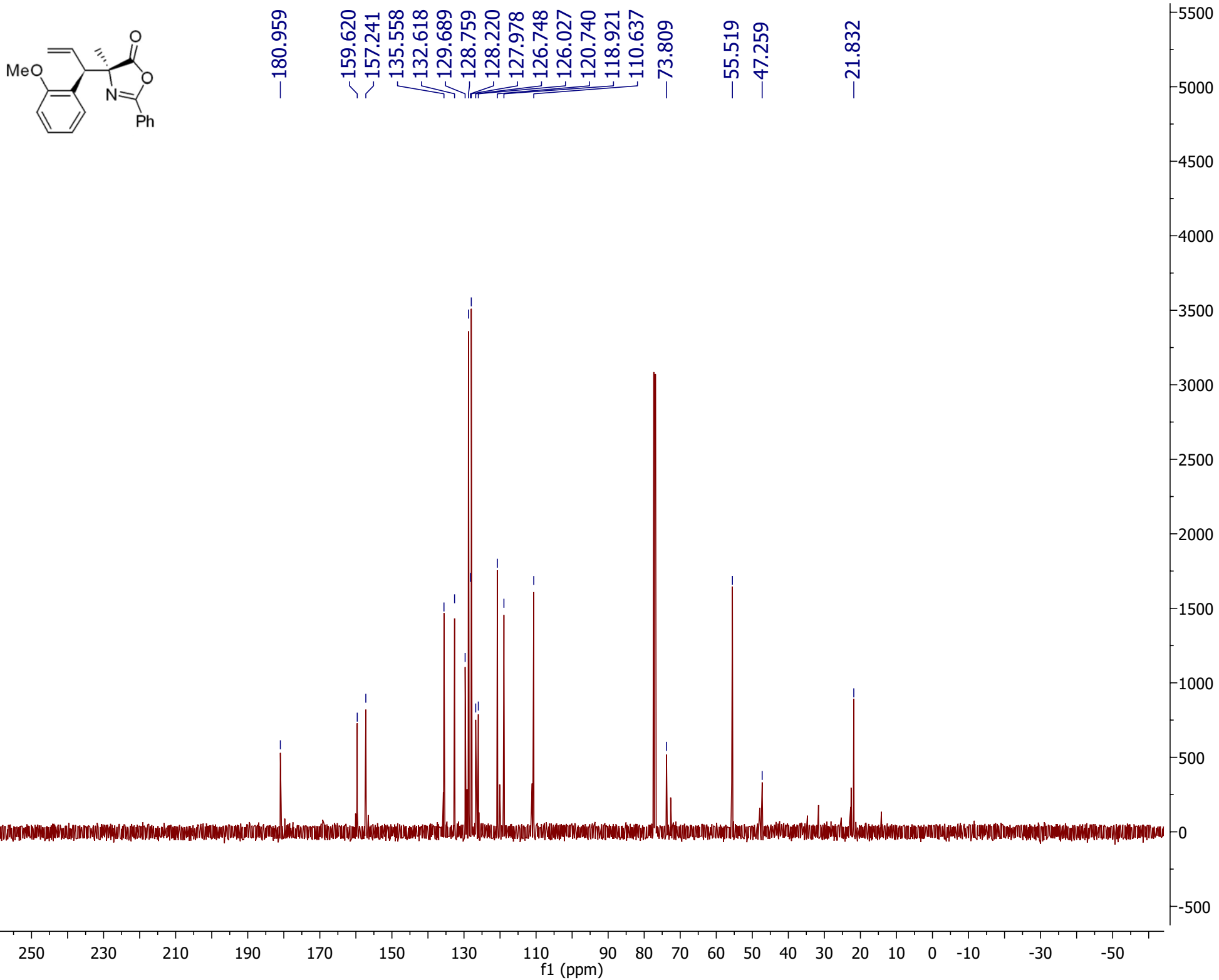
7.602
7.588
7.535
7.519
7.504
7.273
7.041
6.926
6.909
5.969
5.950
5.935
5.915
5.258
5.224
5.100
5.080
4.528
4.509
3.879
1.387
0.920
MeO
O
O
N
Ph
2.00
1.01
1.27
2.43
1.37
1.00
1.01
1.01
1.00
1.14
1.01
0.98
2.89
3.22
f1 (ppm)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O
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N
Ph
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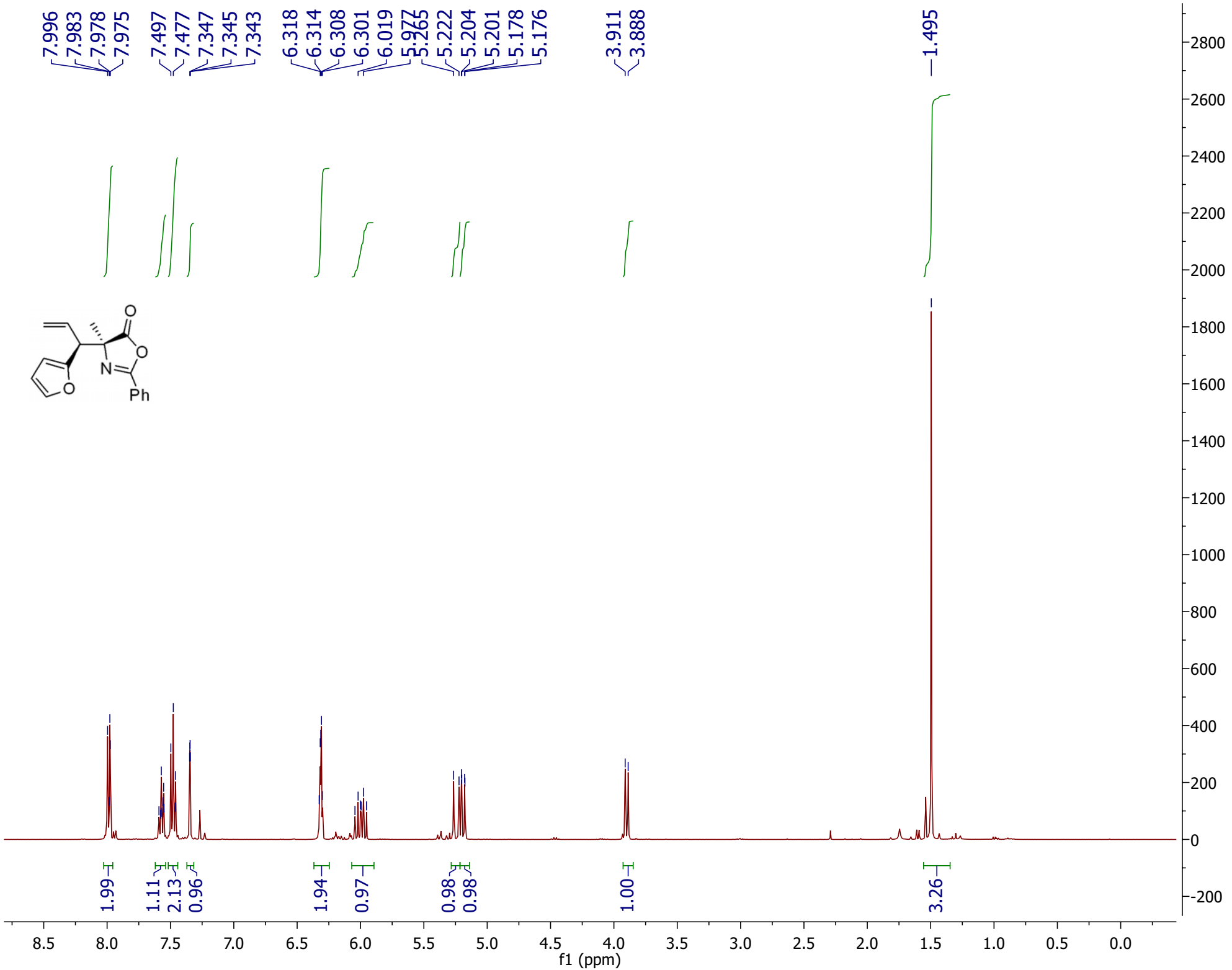
126.748
126.027
120.740
118.921
110.637
73.809
55.519
47.259
21.832
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)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7.345
7.343
6.318
6.314
6.308
6.301
6.019
5.977
5.265
5.222
5.204
5.201
5.178
5.176
3.911
3.888
1.495
O
O
N
O
Ph
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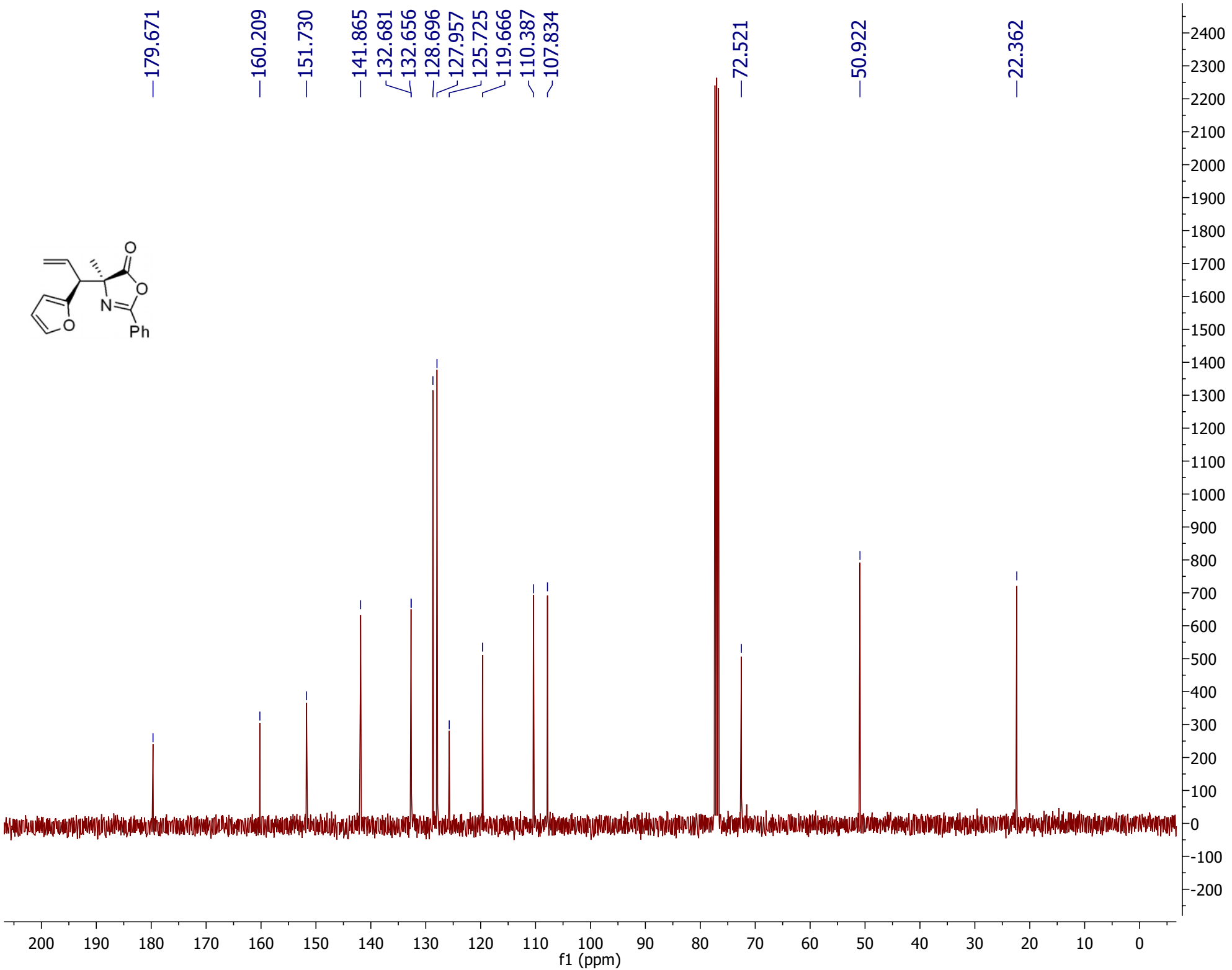
2.13
0.96
1.94
0.97
0.98
0.98
1.00
3.26
f1 (ppm)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127.957
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107.834
72.521
50.922
22.362
O
O
N
O
Ph
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
200
190
180
170
160
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130
120
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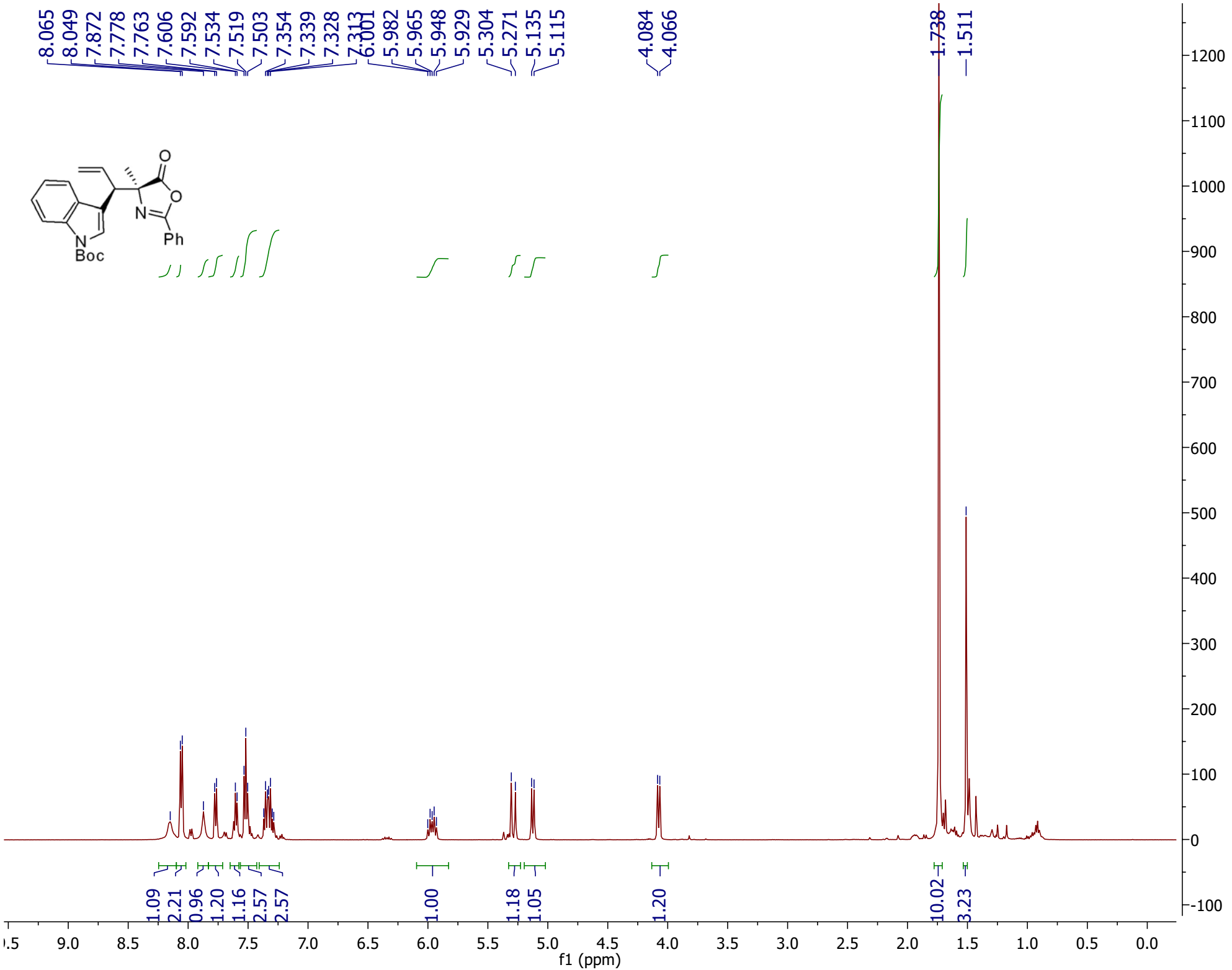
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.503
7.354
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7.328
7.313
6.001
5.982
5.965
5.948
5.929
5.304
5.271
5.135
5.115
4.084
4.066
1.738
1.511
O
O
N
Ph
N
Boc
1.09
2.21
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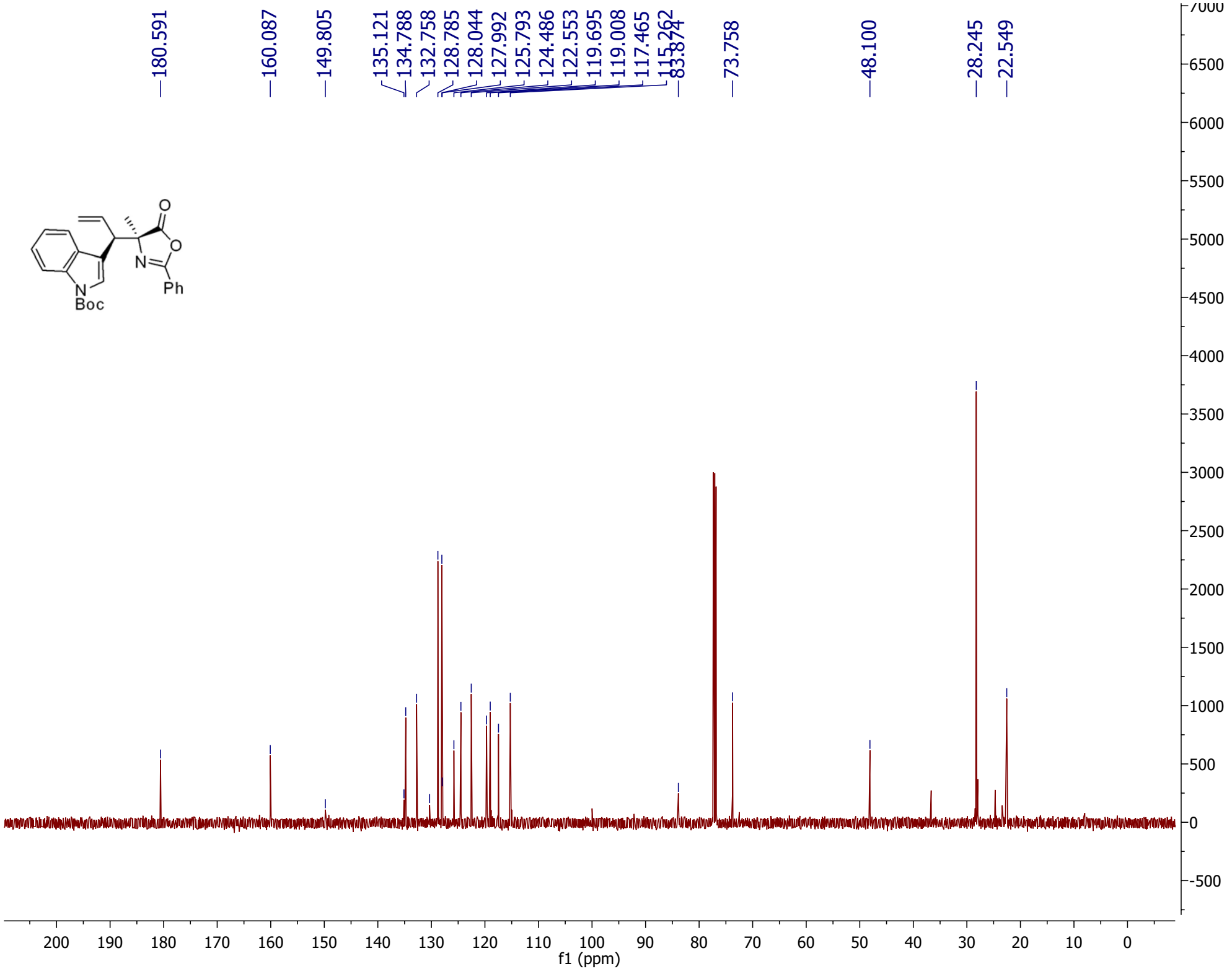
2.57
2.57
1.00
1.18
1.05
1.20
10.02
3.23
f1 (ppm)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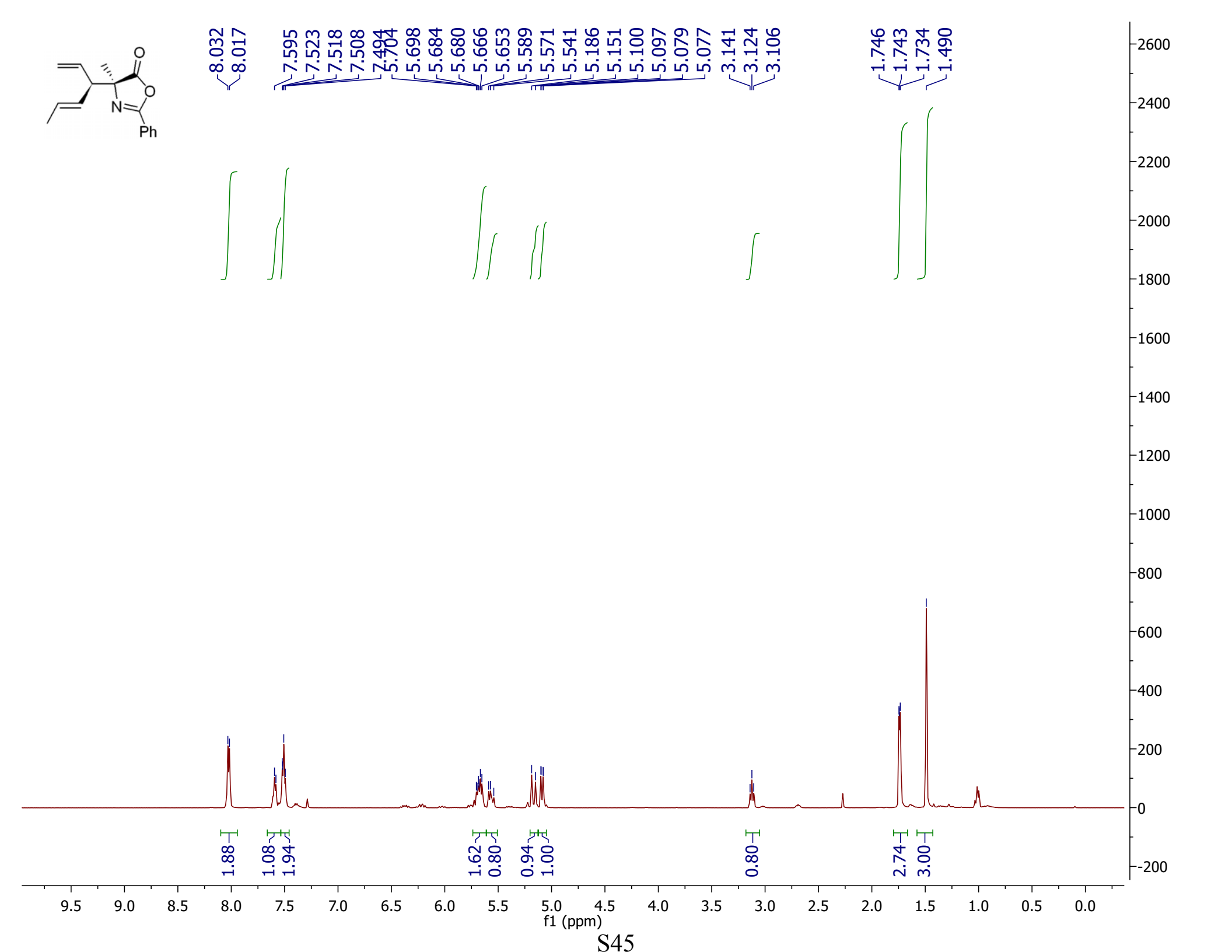
128.785
128.044
127.992
125.793
124.486
122.553
119.695
119.008
117.465
115.262
83.874
73.758
48.100
28.245
22.549
O
O
N
Ph
N
Boc
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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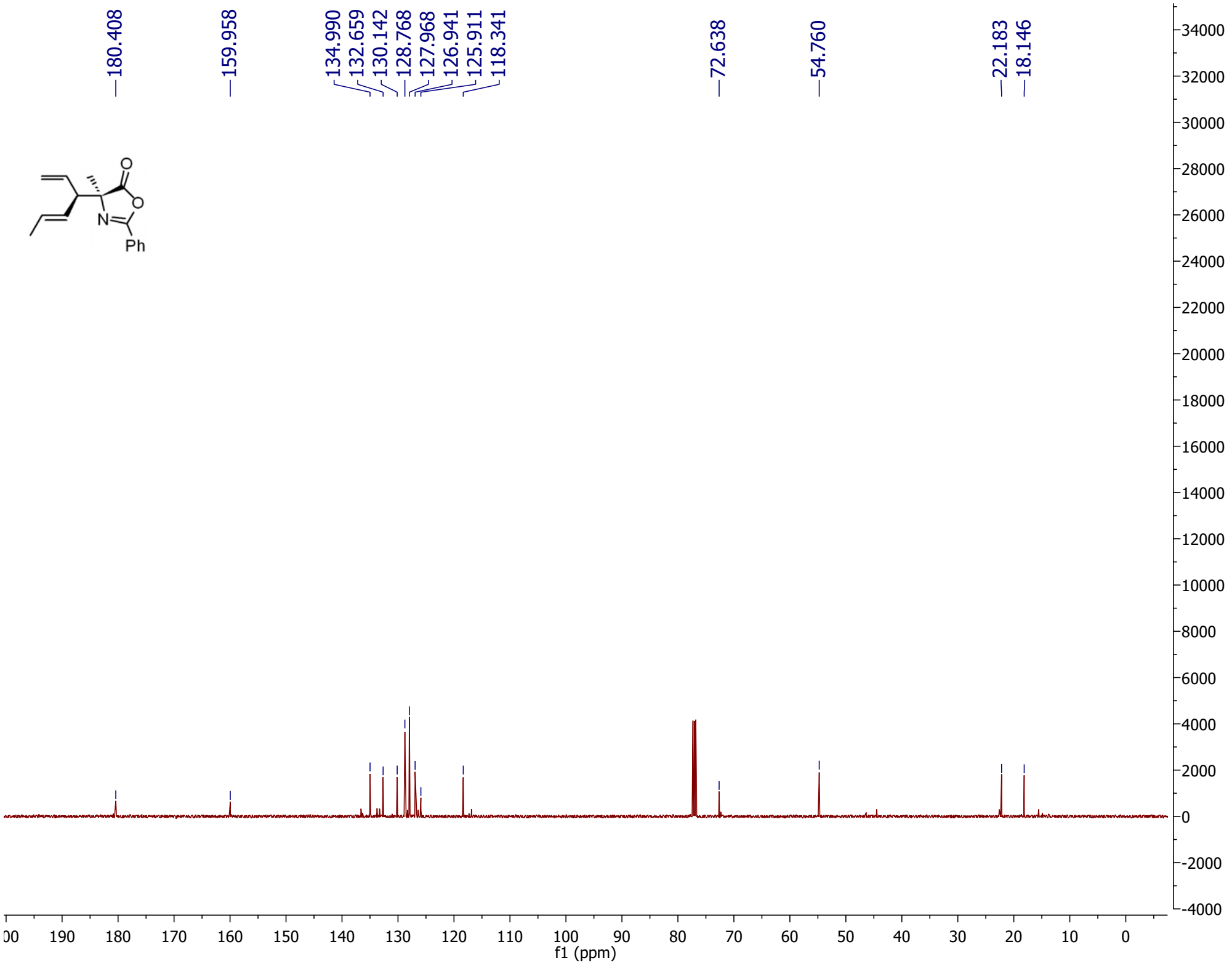
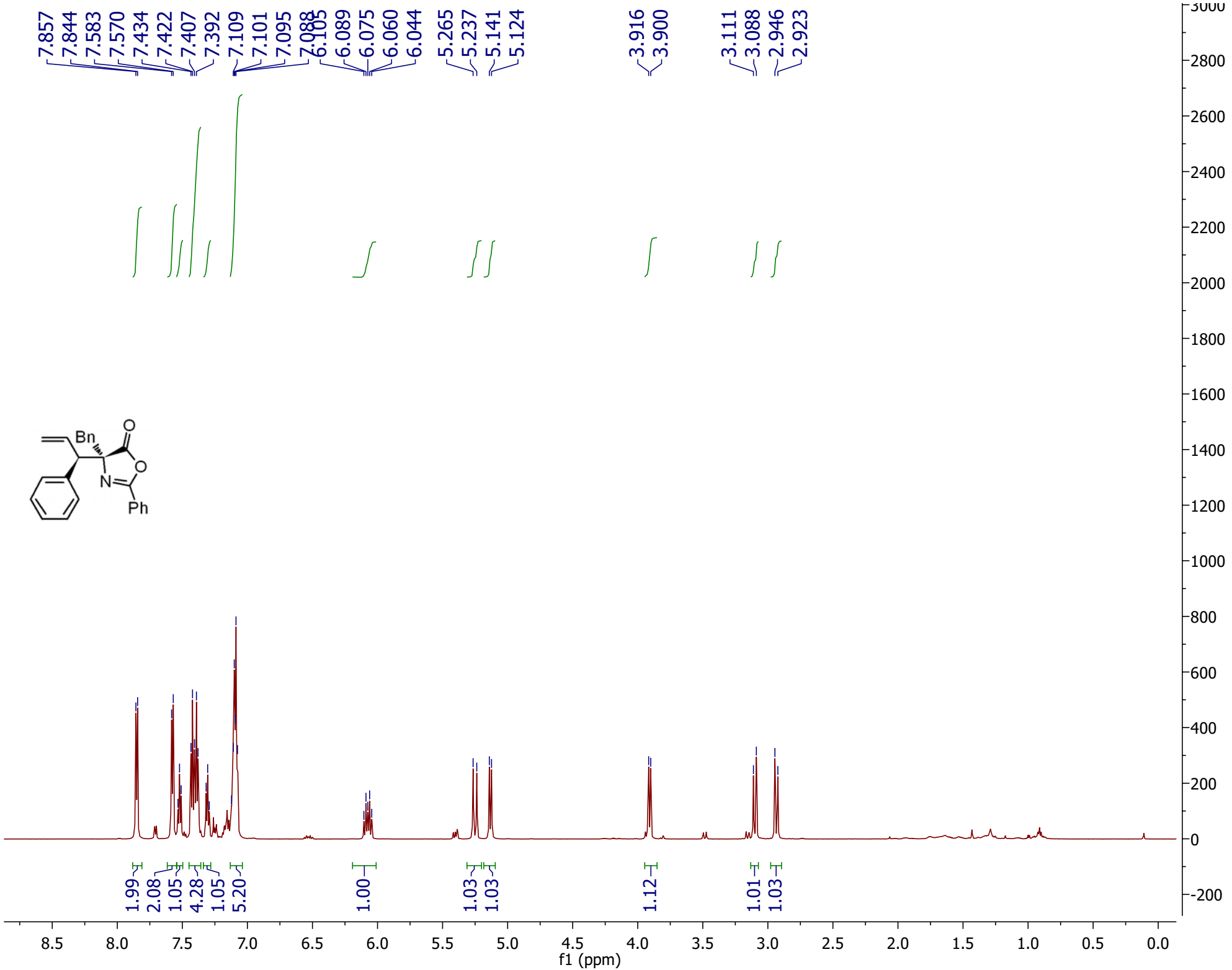
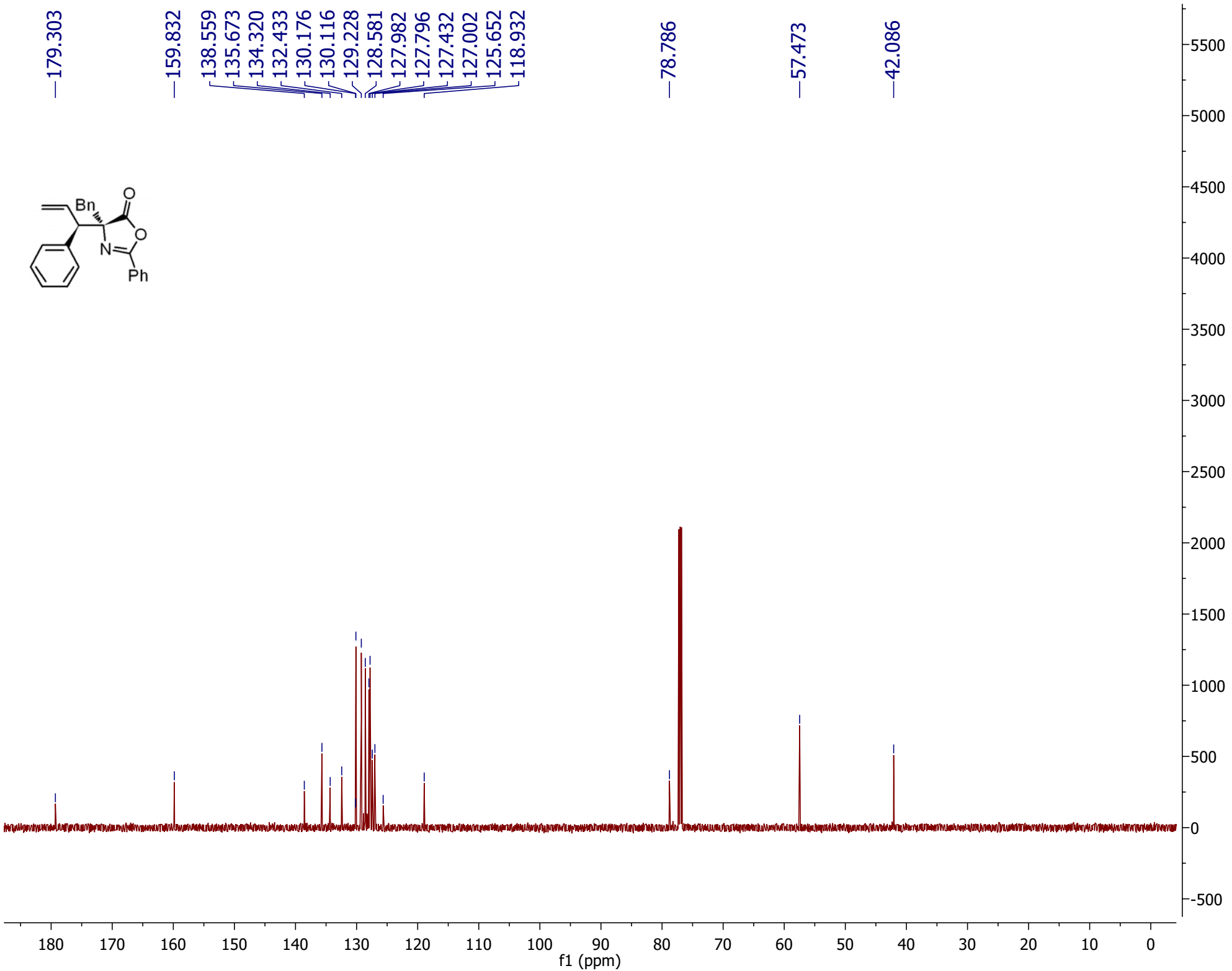
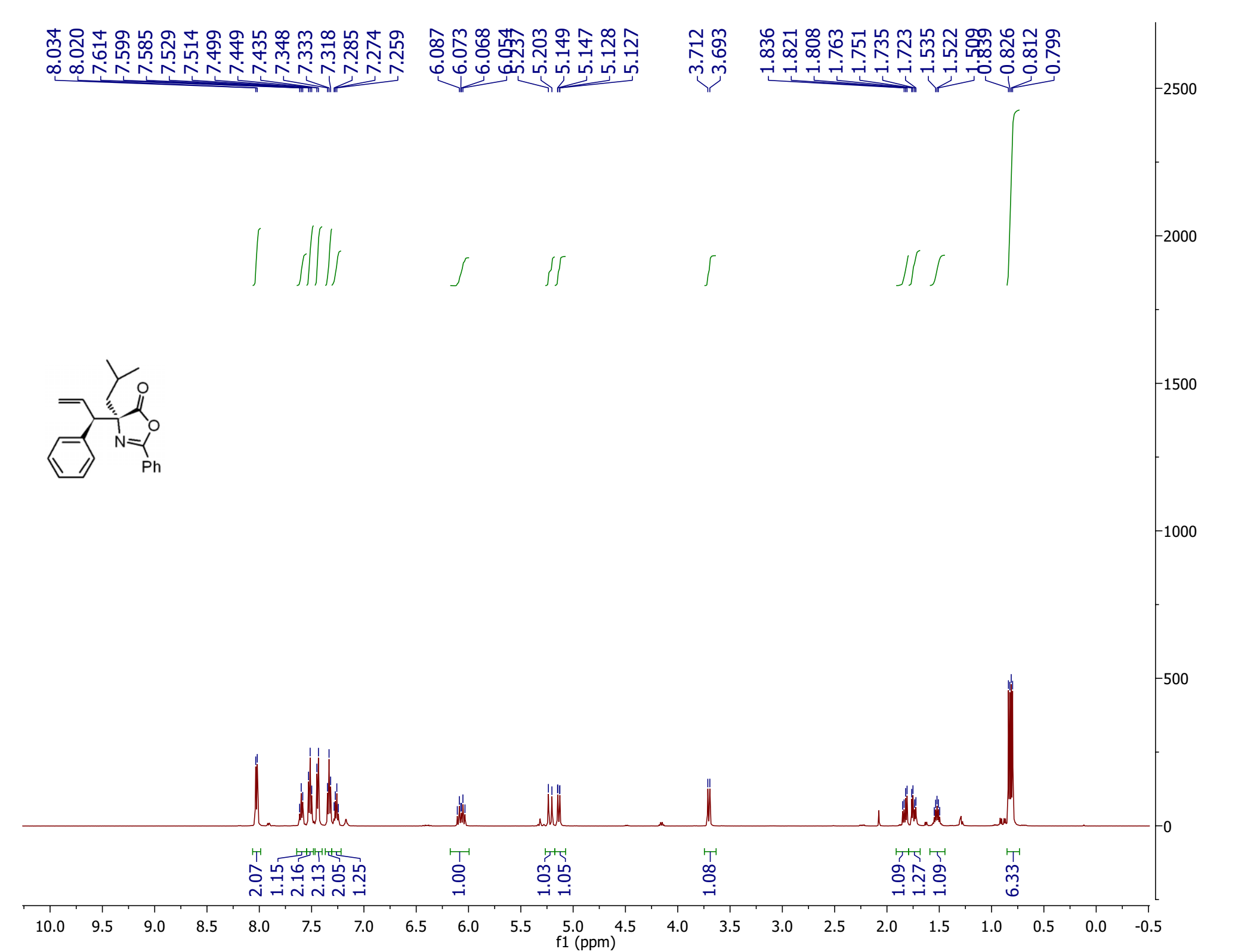
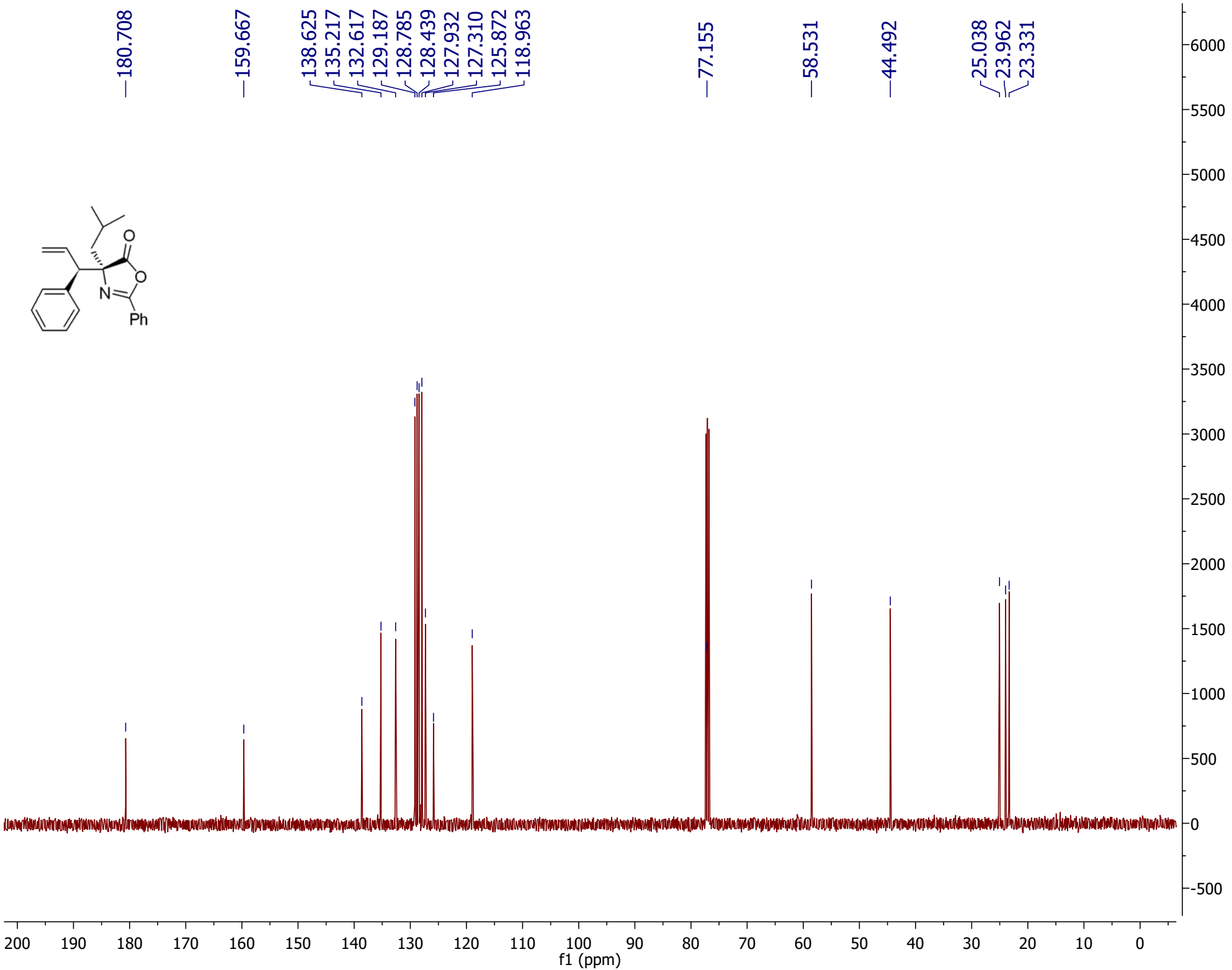
8.017
7.595
7.523
7.518
7.508
7.494
5.704
5.698
5.684
5.680
5.666
5.653
5.589
5.571
5.541
5.186
5.151
5.100
5.097
5.079
5.077
3.141
3.124
3.106
1.746
1.743
1.734
1.490
O
O
N
Ph
1.88
1.08
1.94
1.62
0.80
0.94
1.00
0.80
2.74
3.00
f1 (ppm)

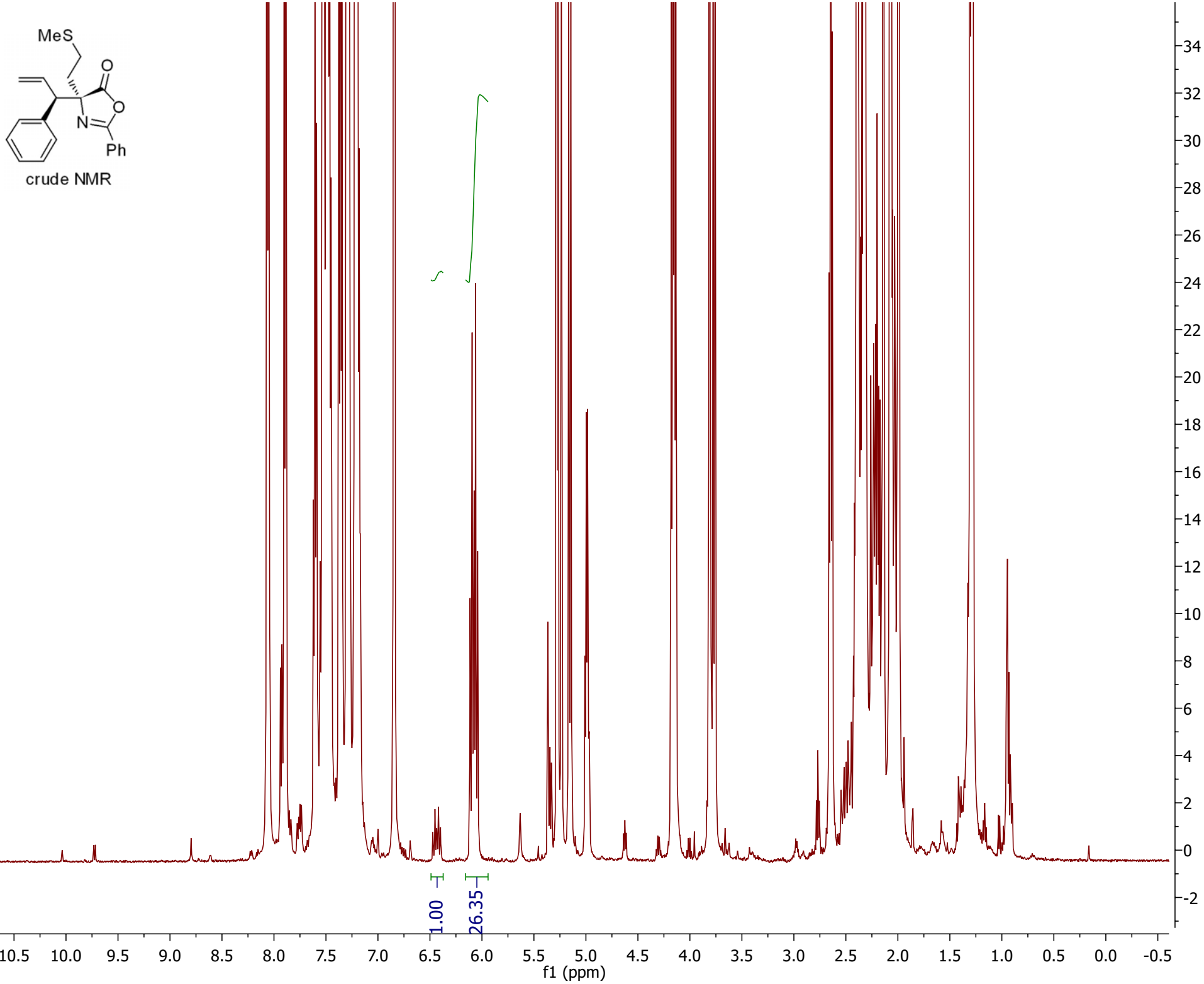

180.408
159.958
134.990
132.659
130.142
128.768
127.968
126.941
125.911
118.341
72.638
54.760
22.183
18.146
O
O
N
Ph
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

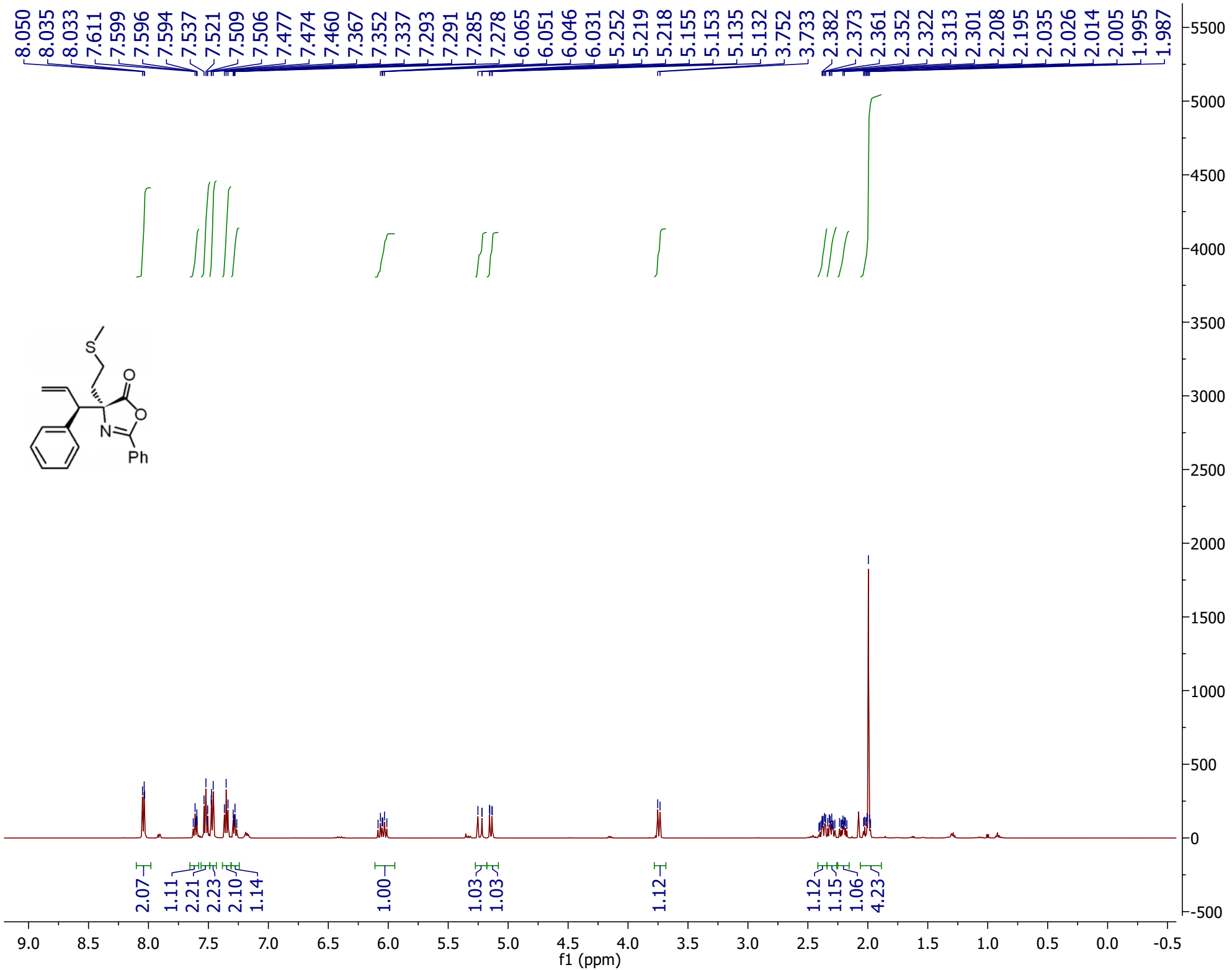

7.857
7.844
7.583
7.570
7.434
7.422
7.407
7.392
7.109
7.101
7.095
7.088
6.105
6.089
6.075
6.060
6.044
5.265
5.237
5.141
5.124
3.916
3.900
3.111
3.088
2.946
2.923
Bn
O
O
N
Ph
1.99
2.08
1.05
4.28
1.05
5.20
1.00
1.03
1.03
1.12
1.01
1.03
f1 (ppm)

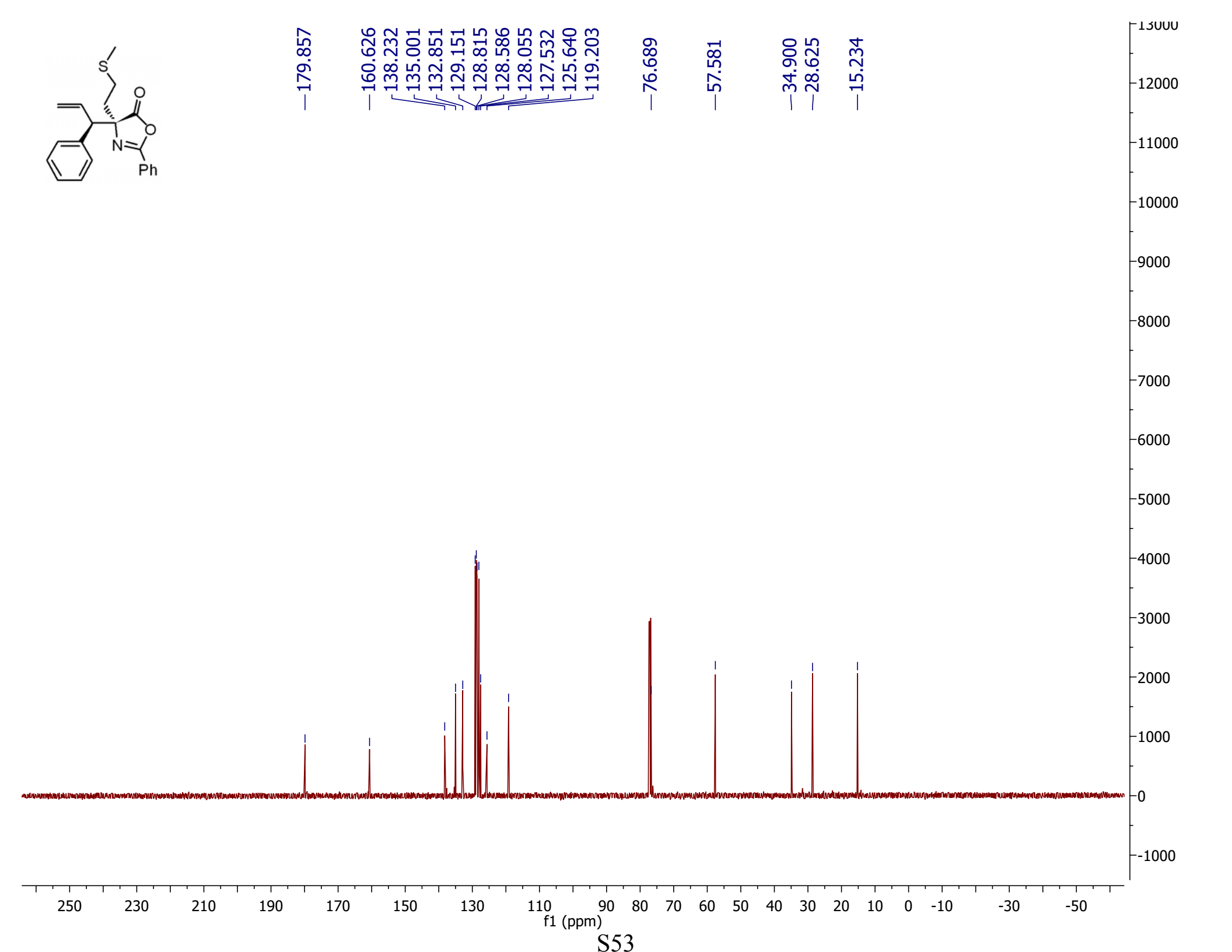

179.303
159.832
138.559
135.673
134.320
132.433
130.176
130.116
129.228
128.581
127.982
127.796
127.432
127.002
125.652
118.932
78.786
57.473
42.086
Bn
O
O
N
Ph
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

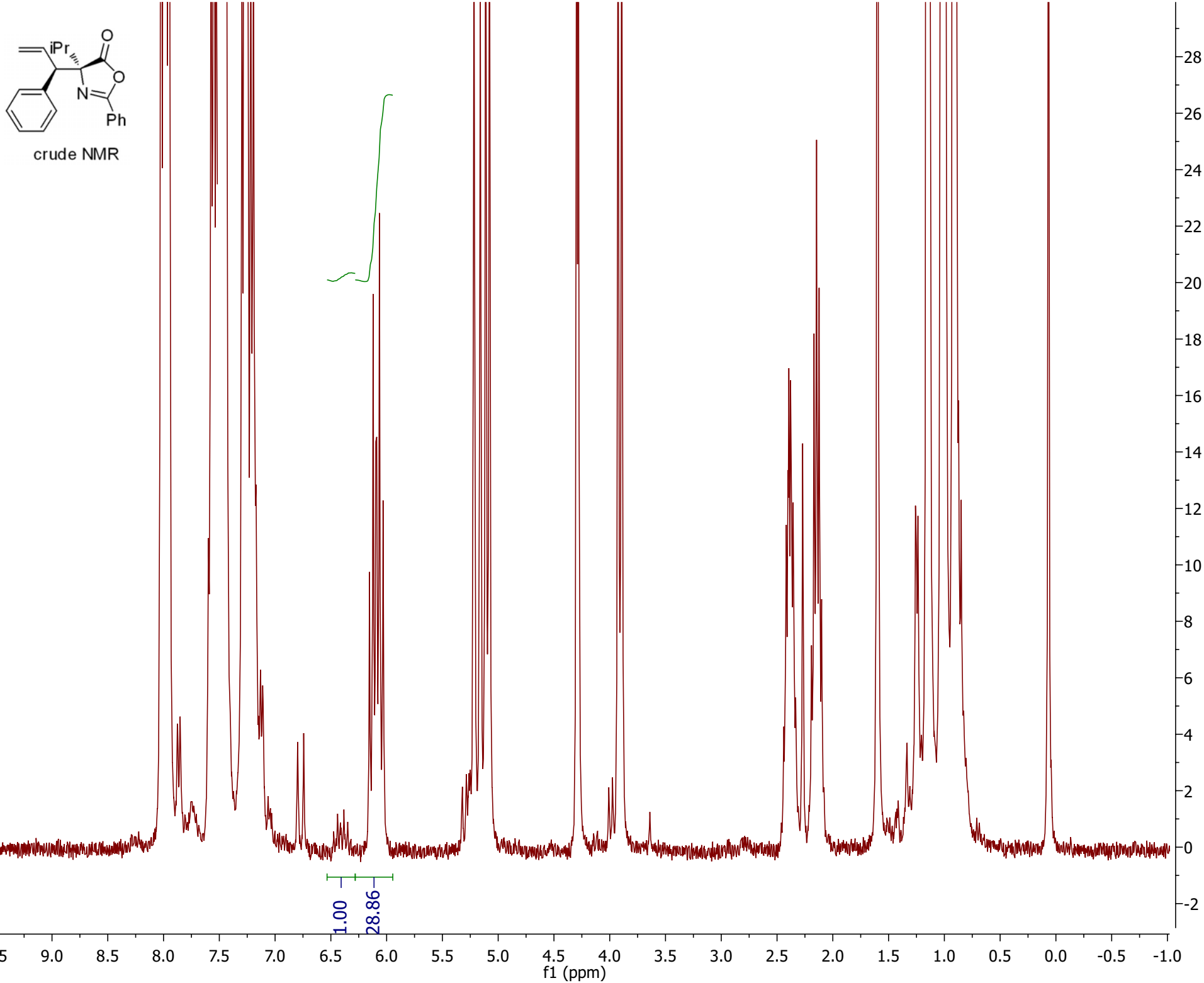

8.034
8.020
7.614
7.599
7.585
7.529
7.514
7.499
7.449
7.435
7.348
7.333
7.318
7.285
7.274
7.259
6.087
6.073
6.068
5.237
5.203
5.149
5.147
5.128
5.127
3.712
3.693
1.836
1.821
1.808
1.763
1.751
1.735
1.723
1.535
1.522
0.826
0.812
0.799
O
O
N
Ph
2.07
1.15
2.16
2.13
2.05
1.25
1.00
1.03
1.05
1.08
1.09
1.27
1.09
6.33
2500
2000
1500
1000
500
0
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
-0.5
f1 (ppm)

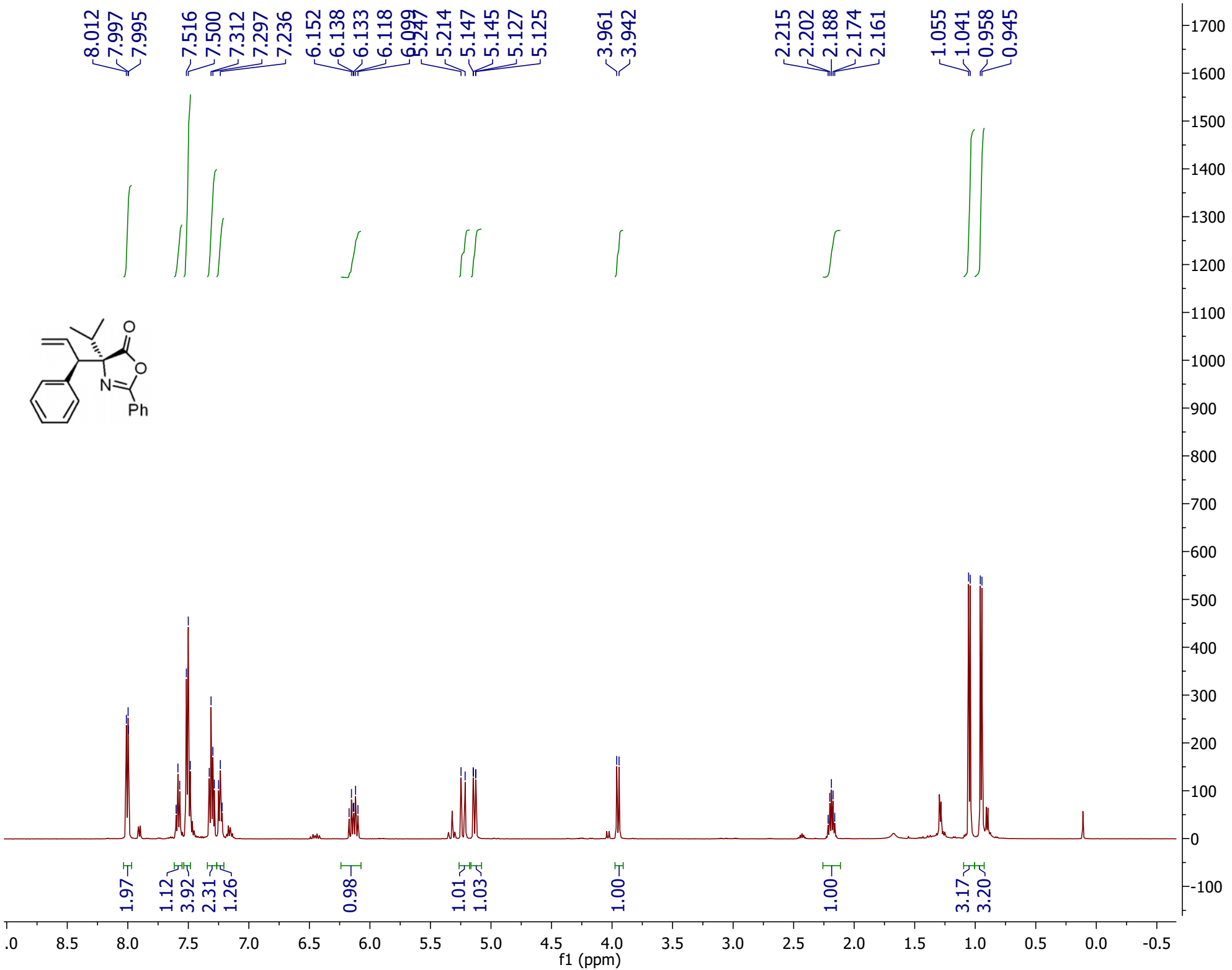

180.708
159.667
138.625
135.217
132.617
129.187
128.785
128.439
127.932
127.310
125.872
118.963
77.155
58.531
44.492
25.038
23.962
23.331
O
O
N
Ph
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

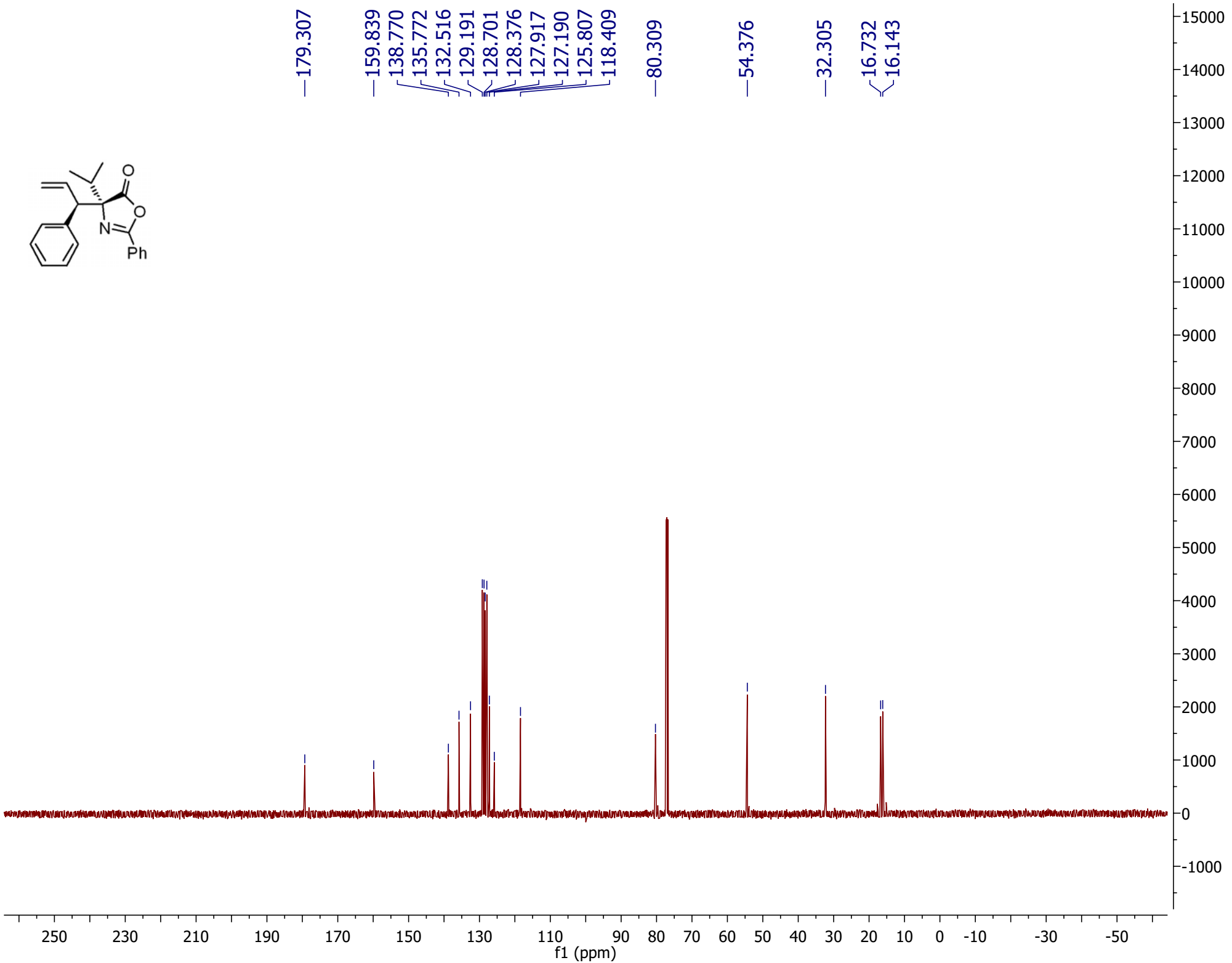

MeS
O
O
N
Ph
crude NMR
1.00
26.35
f1 (ppm)


8.050
8.035
8.033
7.611
7.599
7.596
7.594
7.537
7.521
7.509
7.506
7.477
7.474
7.460
7.367
7.352
7.337
7.293
7.291
7.285
7.278
6.065
6.051
6.046
6.031
5.252
5.219
5.218
5.155
5.153
5.135
5.132
3.752
3.733
2.382
2.373
2.361
2.352
2.322
2.313
2.301
2.208
2.195
2.035
2.026
2.014
2.005
1.995
1.987
S
O
O
N
Ph
2.07
1.11
2.21
2.23
2.10
1.14
1.00
1.03
1.03
1.12
1.12
1.15
1.06
4.23
f1 (ppm)


179.857
160.626
138.232
135.001
132.851
129.151
128.815
128.586
128.055
127.532
125.640
119.203
76.689
57.581
34.900
28.625
15.234
S
O
O
N
Ph
f1 (ppm)


iPr
O
O
N
Ph
crude NMR
1.00
28.86
f1 (ppm)


8.012
7.997
7.995
7.516
7.500
7.312
7.297
7.236
6.152
6.138
6.133
6.118
5.214
5.147
5.145
5.127
5.125
3.961
3.942
2.215
2.202
2.188
2.174
2.161
1.055
1.041
0.958
0.945
O
O
N
Ph
1.97
1.12
3.92
2.31
1.26
0.98
1.01
1.03
1.00
1.00
3.17
3.20
f1 (ppm)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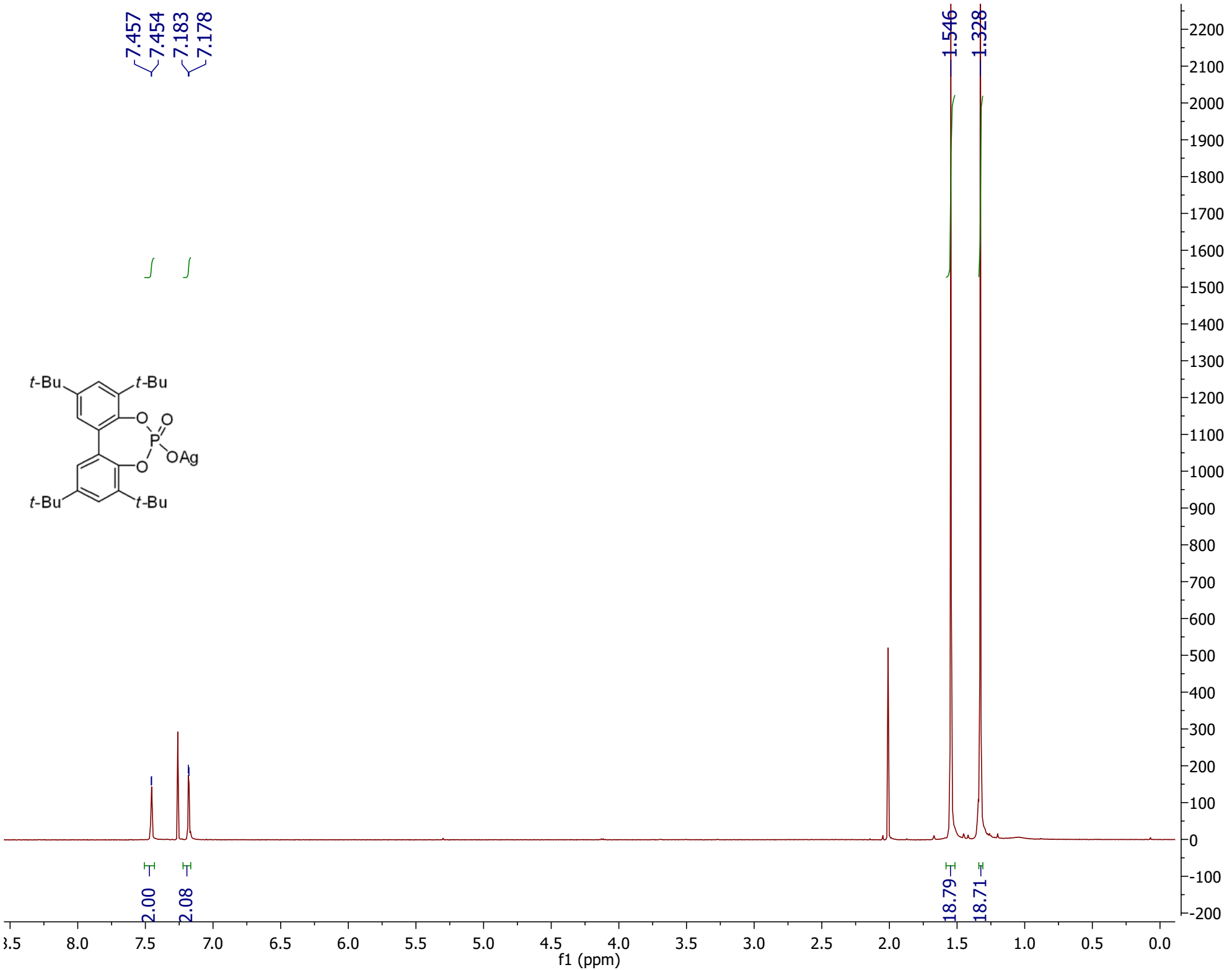
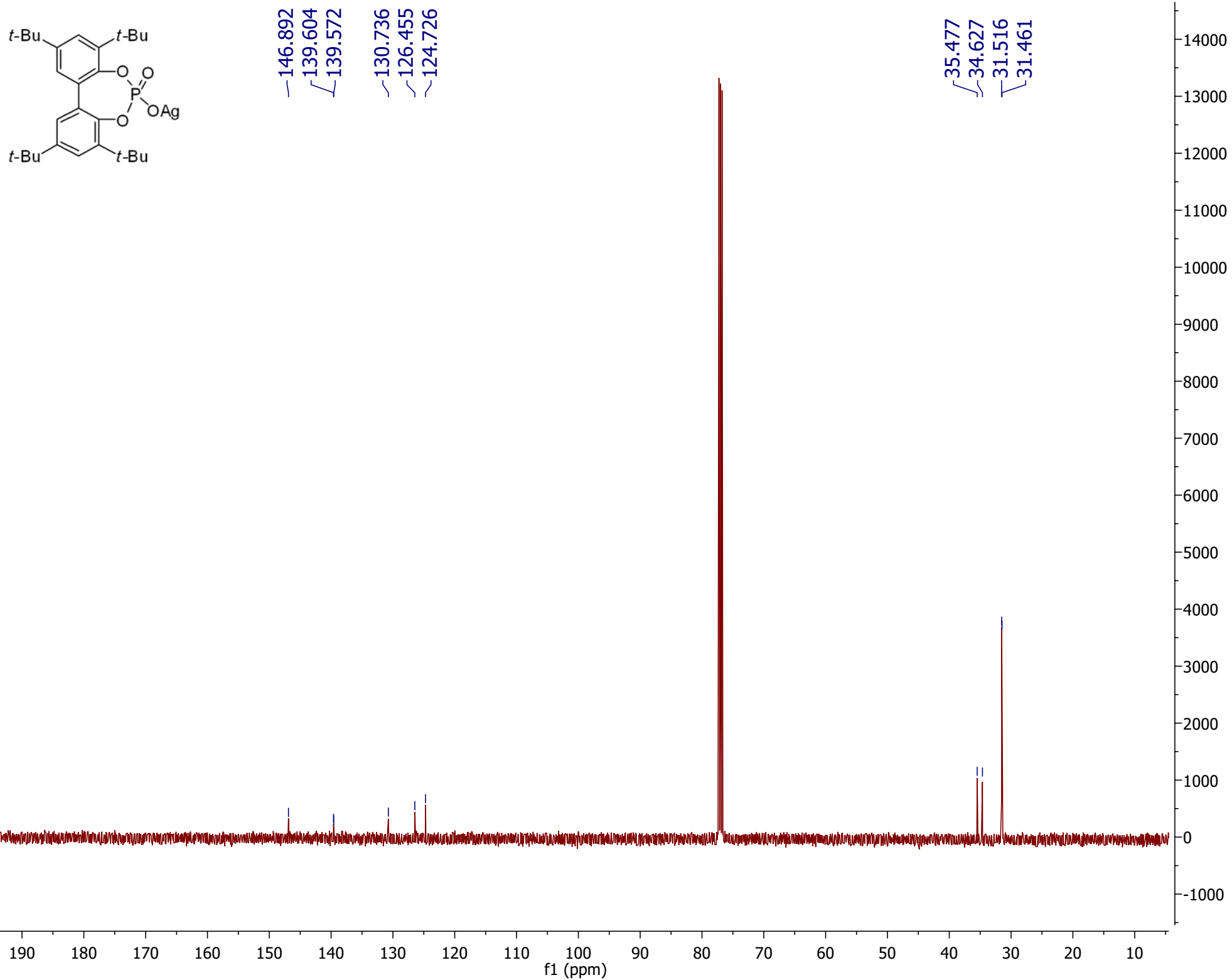
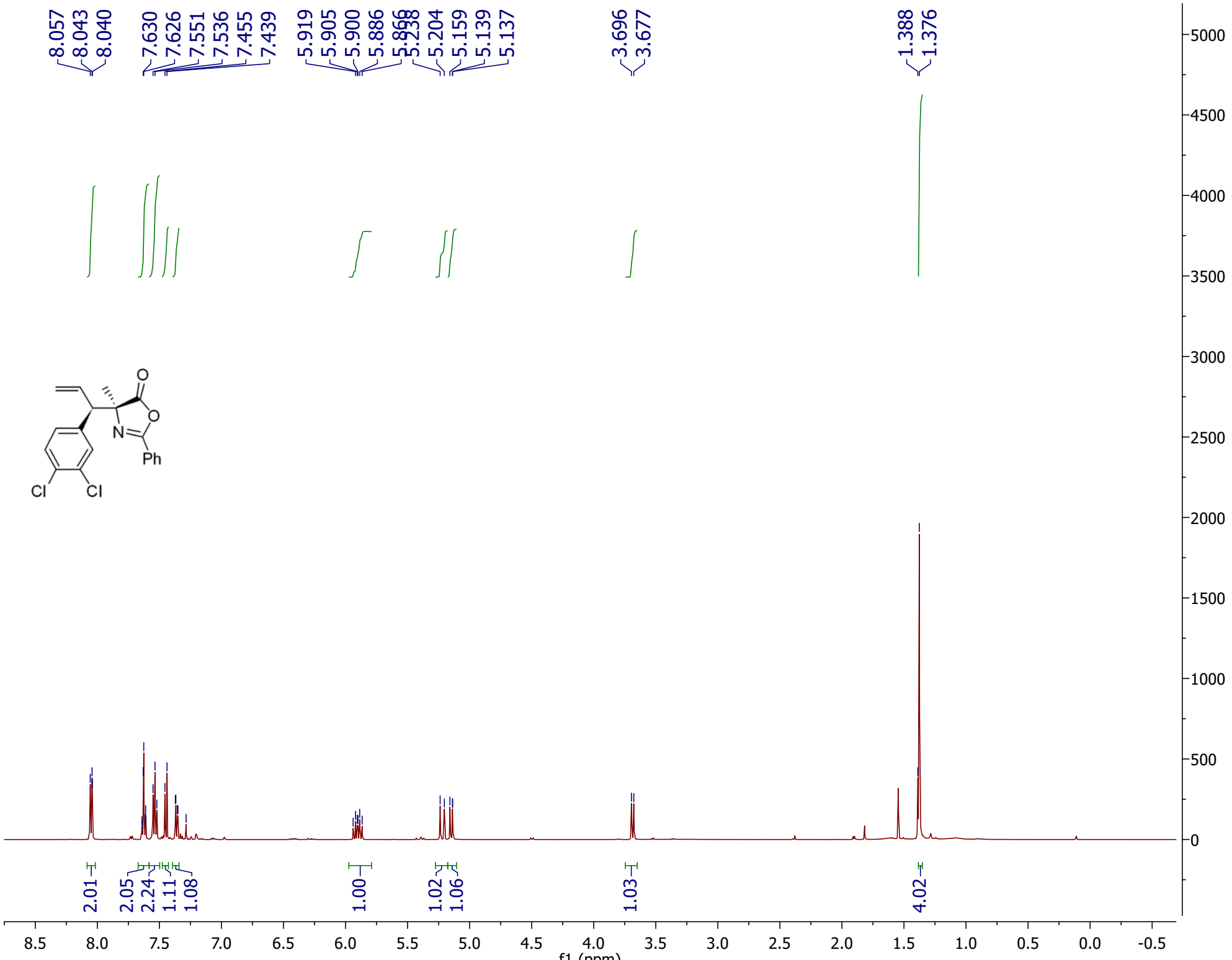
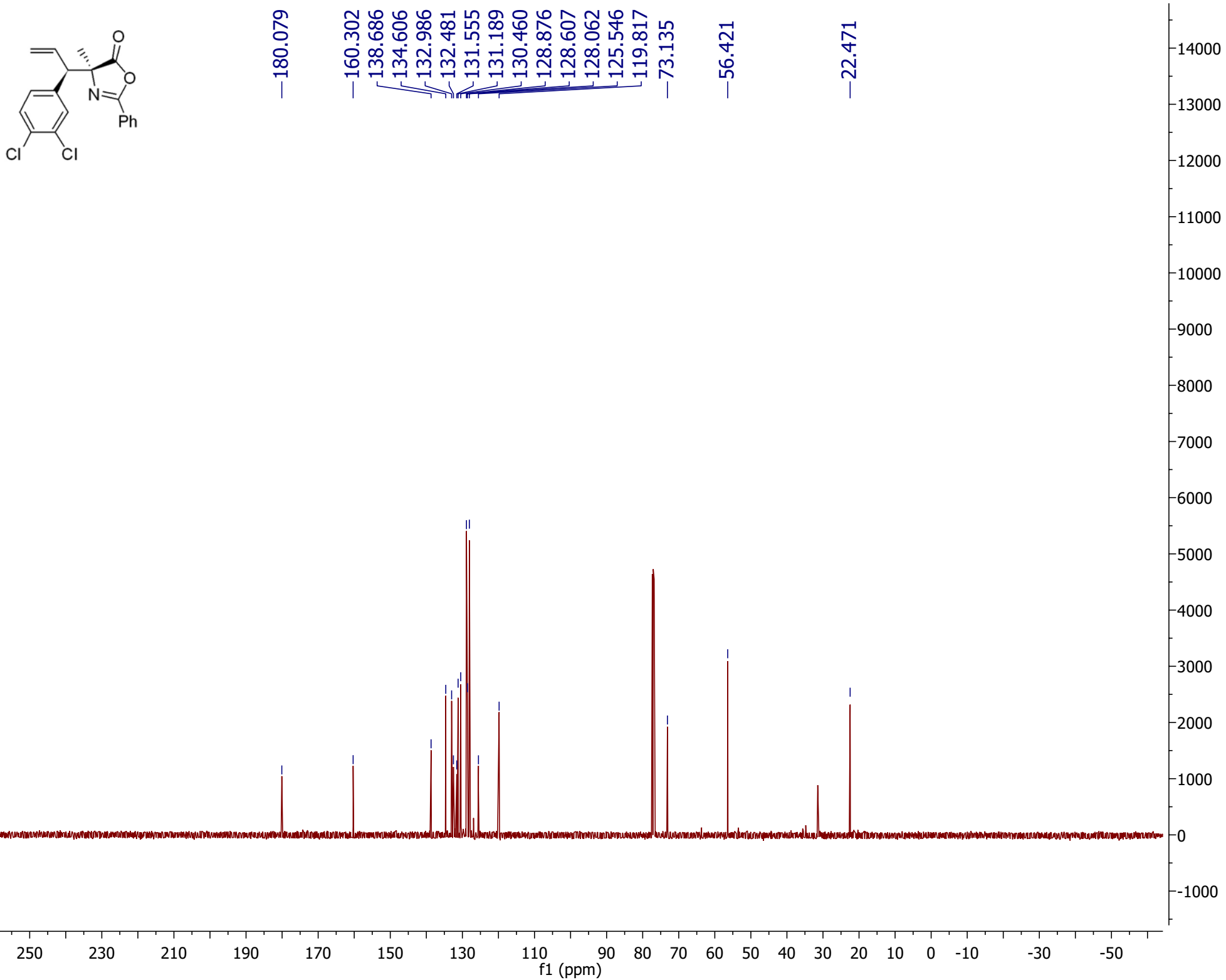
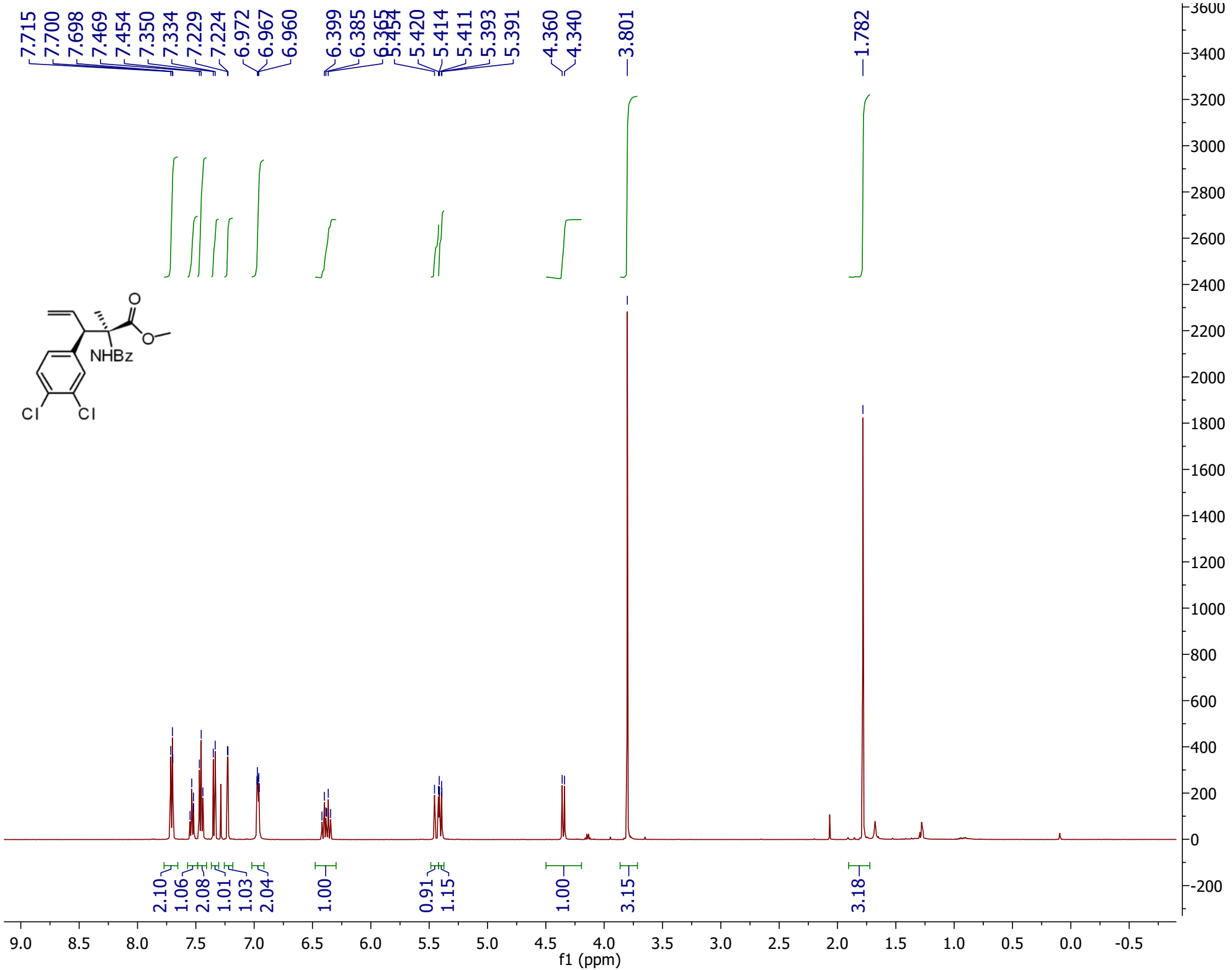
159.839
138.770
135.772
132.516
129.191
128.701
128.376
127.917
127.190
125.807
118.409
80.309
54.376
32.305
16.732
16.143
O
O
N
Ph
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)

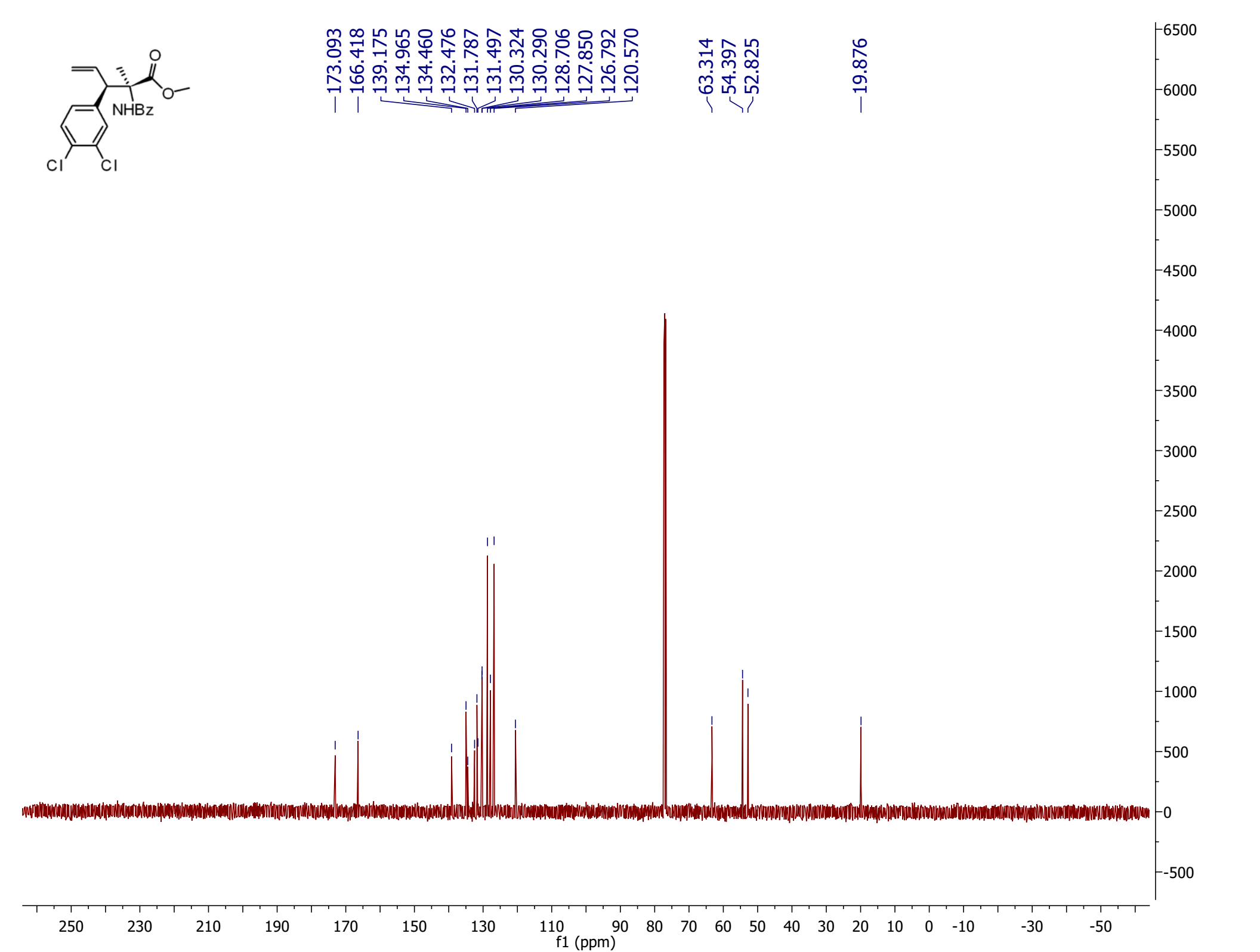

7.457
7.454
7.183
7.178
1.546
1.328
t-Bu
t-Bu
t-Bu
t-Bu
O
O
P
O
OAg
2.00
2.08
18.79
18.71
f1 (ppm)

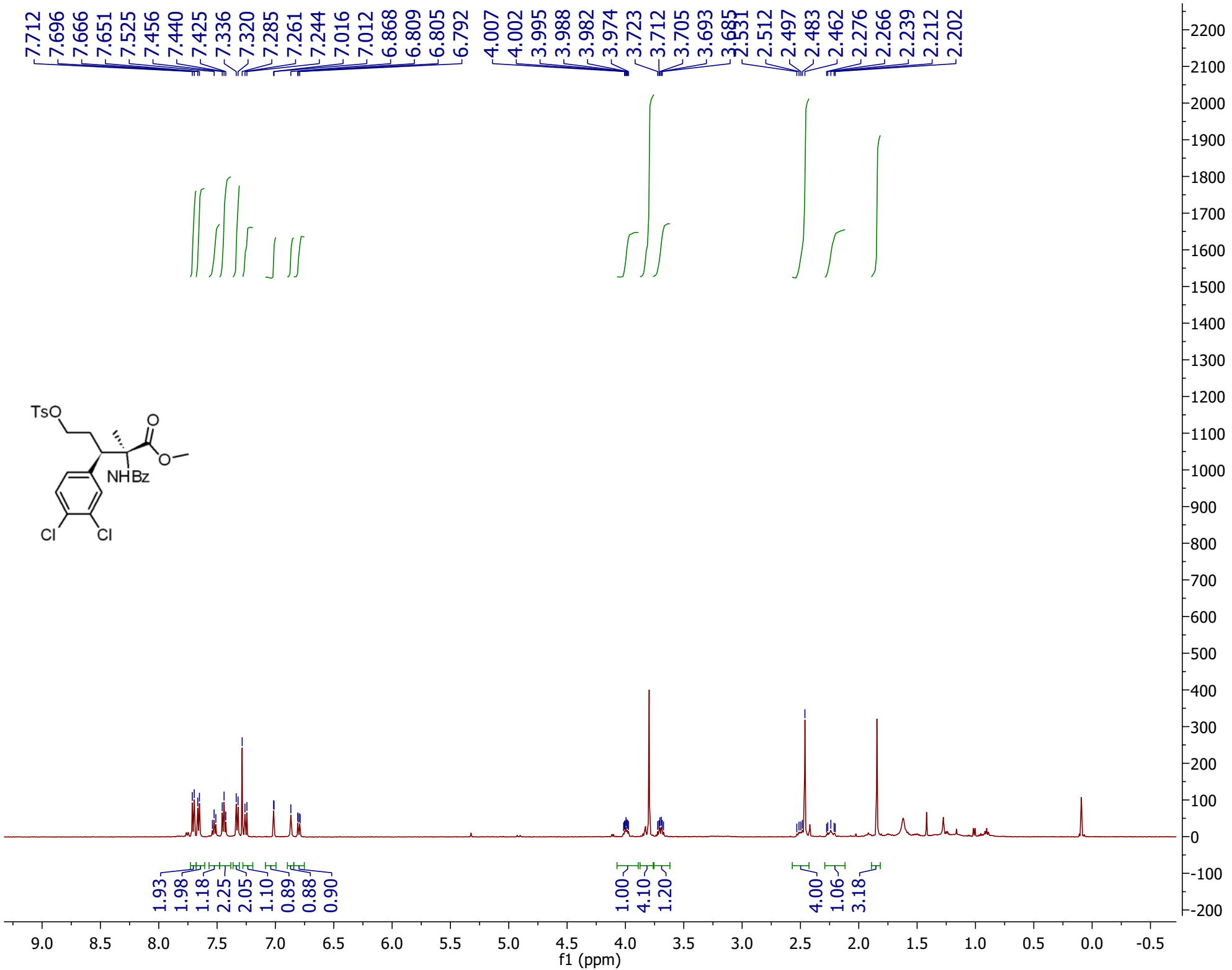

t-Bu
t-Bu
O
O
P
OAg
O
t-Bu
t-Bu
146.892
139.604
139.572
130.736
126.455
124.726
35.477
34.627
31.516
31.461
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

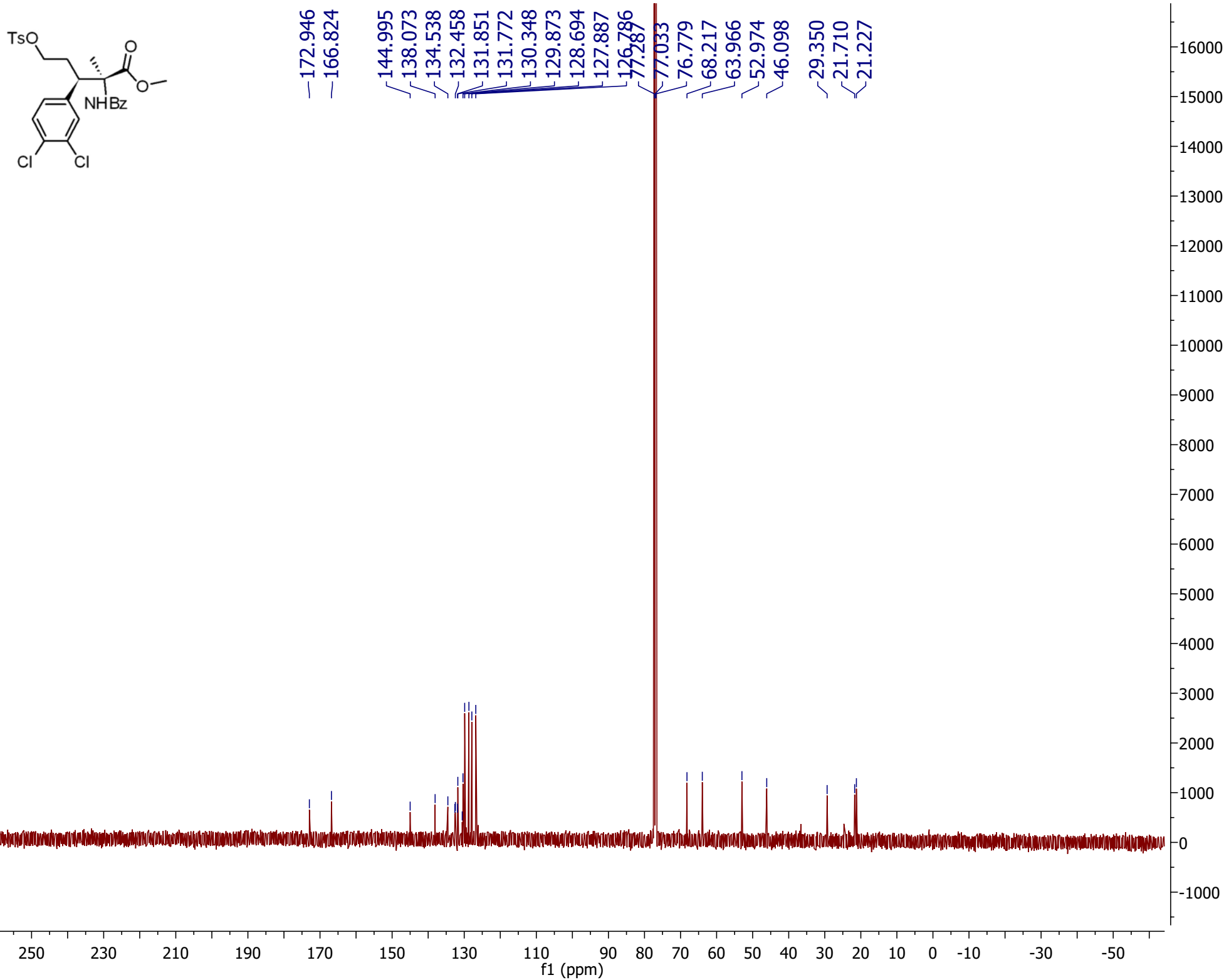

8.057
8.043
8.040
7.630
7.626
7.551
7.536
7.455
7.439
5.919
5.905
5.900
5.886
5.866
5.238
5.204
5.159
5.139
5.137
3.696
3.677
1.388
1.376
O
O
N
Ph
Cl
Cl
2.01
2.05
2.24
1.11
1.08
1.00
1.02
1.06
1.03
4.02
f1 (ppm)

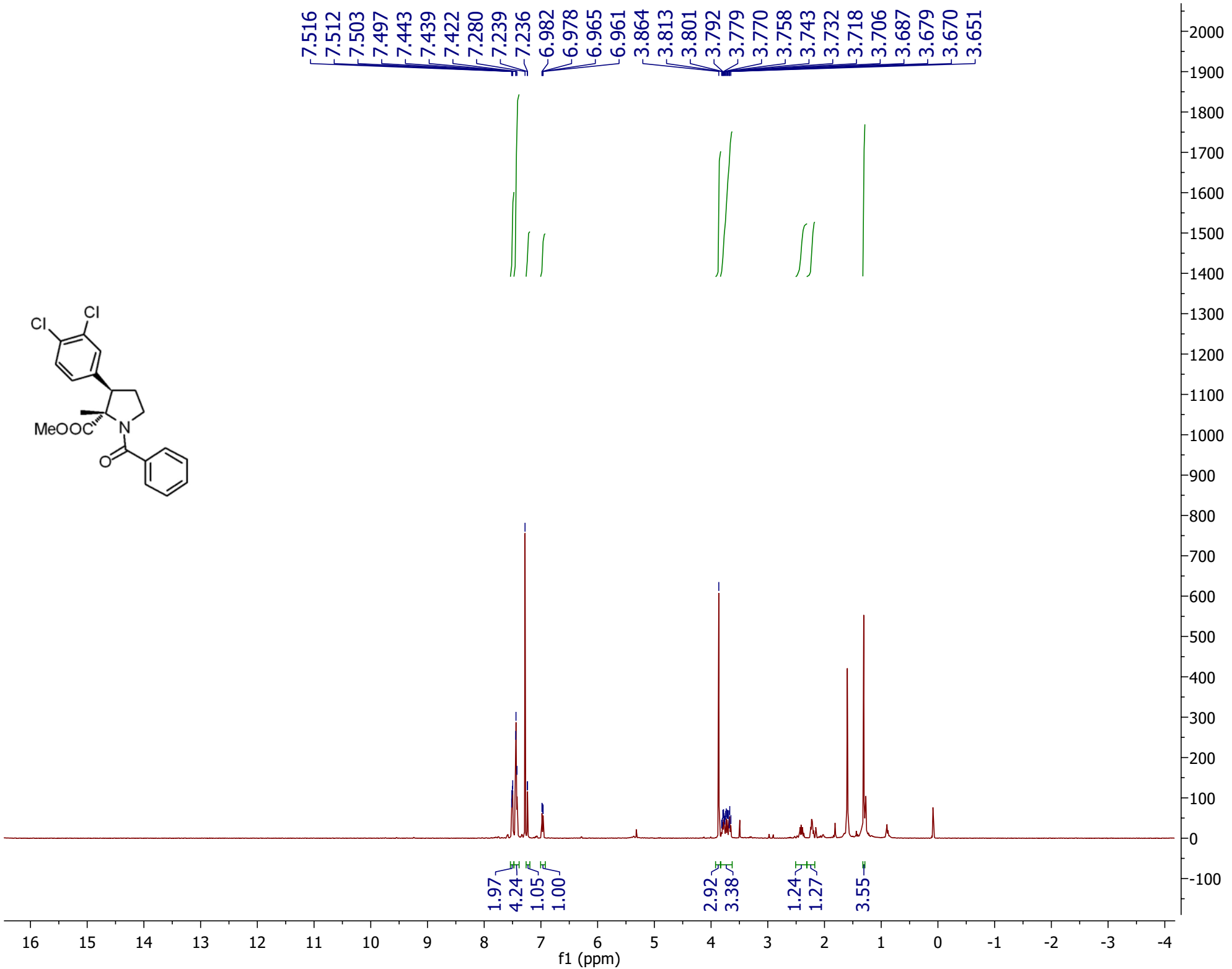

180.079
160.302
138.686
134.606
132.986
132.481
131.555
131.189
130.460
128.876
128.607
128.062
125.546
119.817
73.135
56.421
22.471
O
O
N
Ph
Cl
Cl
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)

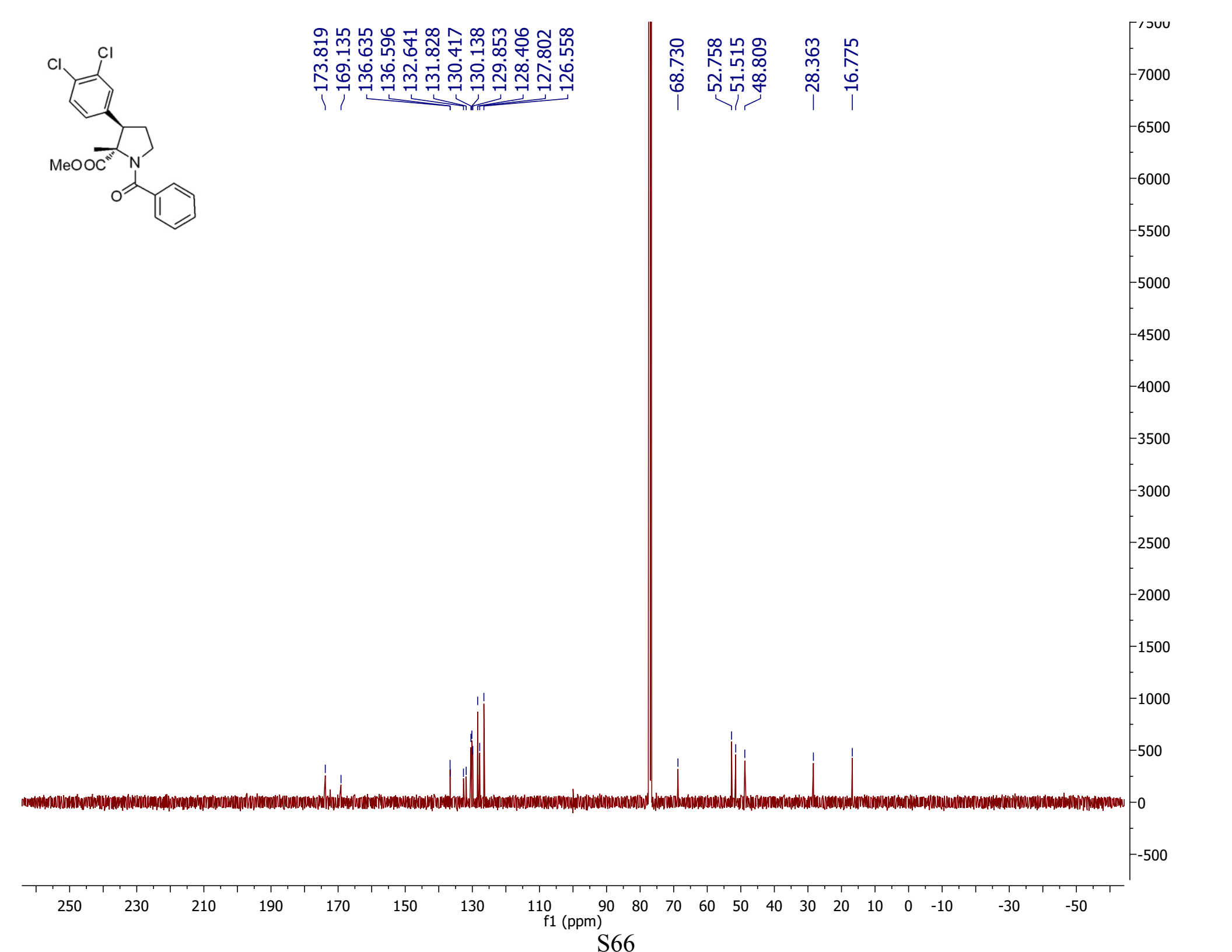

7.715
7.700
7.698
7.469
7.454
7.350
7.334
7.229
7.224
6.972
6.967
6.960
6.399
6.385
5.420
5.414
5.411
5.393
5.391
4.360
4.340
3.801
1.782
NHBz
Cl
Cl
2.10
1.06
2.08
1.01
1.03
2.04
1.00
0.91
1.15
1.00
3.15
3.18
f1 (ppm)

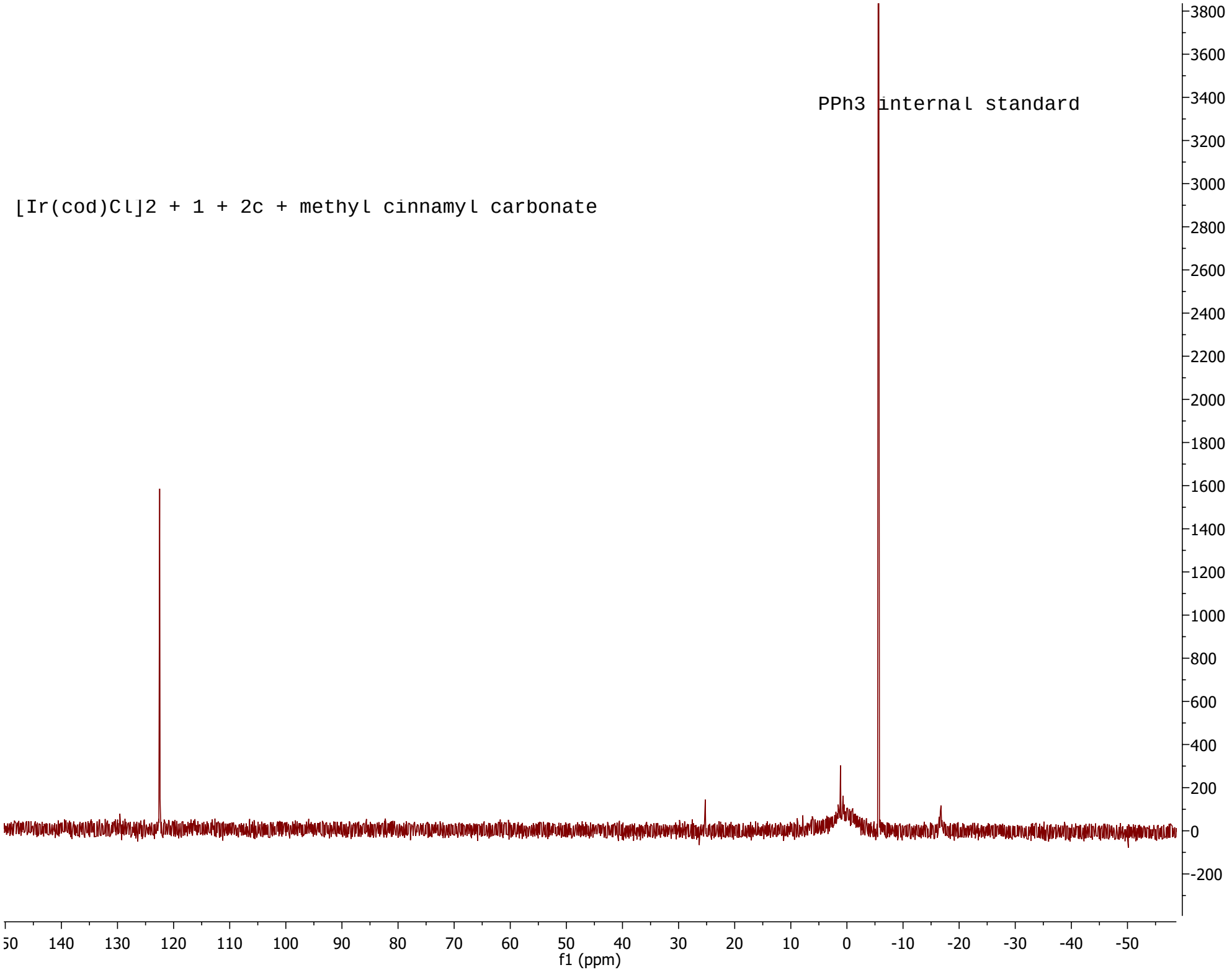

NHBz
Cl
Cl
O
O
173.093
166.418
139.175
134.965
134.460
132.476
131.787
131.497
130.324
130.290
128.706
127.850
126.792
120.570
63.314
54.397
52.825
19.876
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)

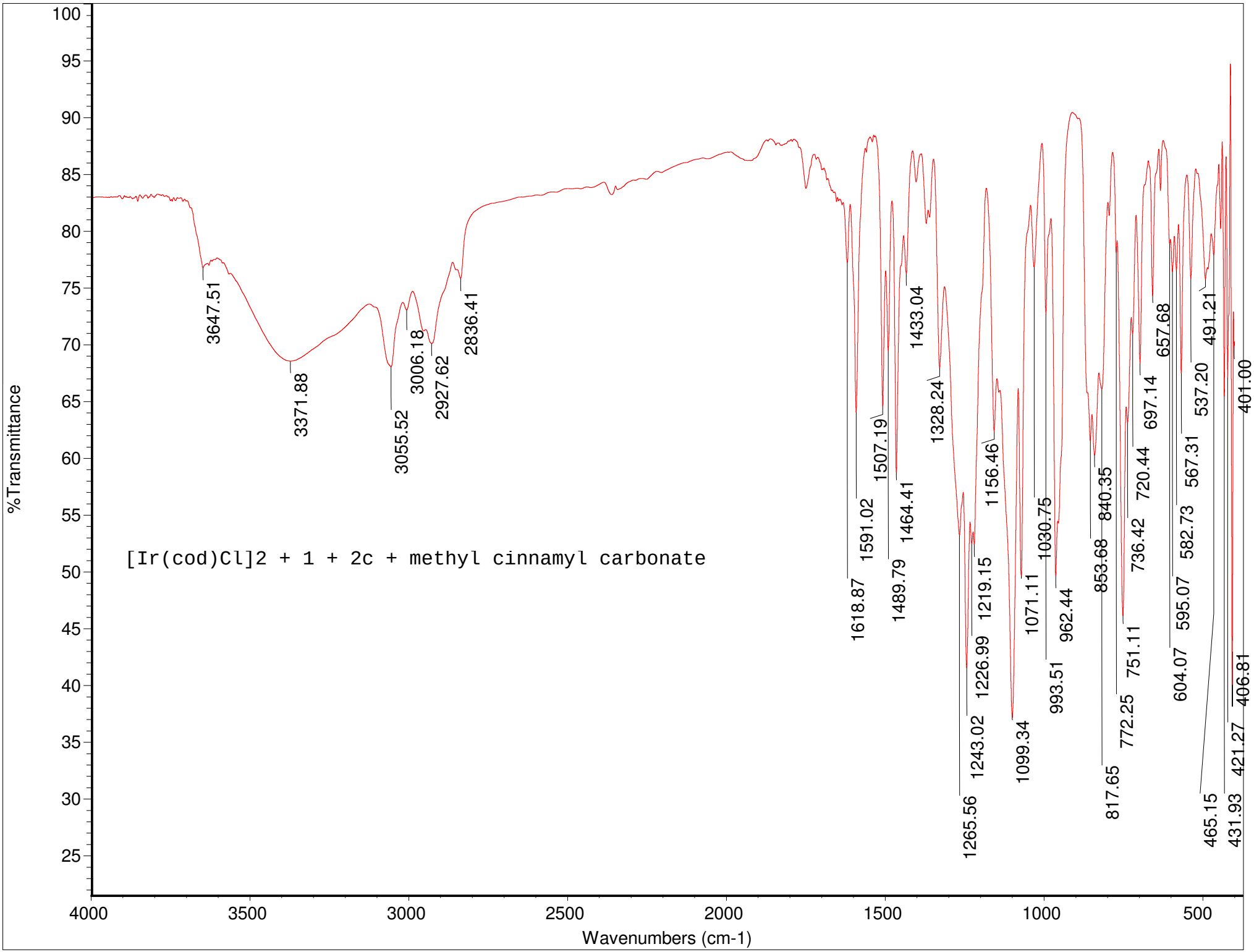

7.712
7.696
7.666
7.651
7.525
7.456
7.440
7.425
7.336
7.320
7.285
7.261
7.244
7.016
7.012
6.868
6.809
6.805
6.792
4.007
4.002
3.995
3.988
3.982
3.974
3.723
3.712
3.705
3.693
3.685
2.531
2.512
2.497
2.483
2.462
2.276
2.266
2.239
2.212
2.202
TsO
O
O
NHBz
Cl
Cl
1.93
1.98
1.18
2.25
2.05
1.10
0.89
0.88
0.90
1.00
4.10
1.20
4.00
1.06
3.18
f1 (ppm)


TsO
O
O
NHBz
Cl
Cl
172.946
166.824
144.995
138.073
134.538
132.458
131.851
131.772
130.348
129.873
128.694
127.887
126.786
77.287
77.033
76.779
68.217
63.966
52.974
46.098
29.350
21.710
21.227
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)


7.516
7.512
7.503
7.497
7.443
7.439
7.422
7.280
7.239
7.236
6.982
6.978
6.965
6.961
3.864
3.813
3.801
3.792
3.779
3.770
3.758
3.743
3.732
3.718
3.706
3.687
3.679
3.670
3.651
Cl
Cl
MeOOC
N
O
1.97
4.24
1.05
1.00
2.92
3.38
1.24
1.27
3.55
f1 (ppm)


Cl
Cl
MeOOC
N
O
173.819
169.135
136.635
136.596
132.641
131.828
130.417
130.138
129.853
128.406
127.802
126.558
68.730
52.758
51.515
48.809
28.363
16.775
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
f1 (ppm)


PPh3 internal standard
[Ir(cod)Cl]2 + 1 + 2c + methyl cinnamyl carbonate
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)


[Ir(cod)Cl]2 + 1 + 2c + methyl cinnamyl carbonate
%Transmittance
Wavenumbers (cm-1)
100
95
90
85
80
75
70
65
60
55
50
45
40
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