Supporting Information for

Stereodivergent Allylic Substitutions with Aryl Acetic Acid Esters by Synergistic Iridium and Lewis Base Catalysis

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General Experimental Details

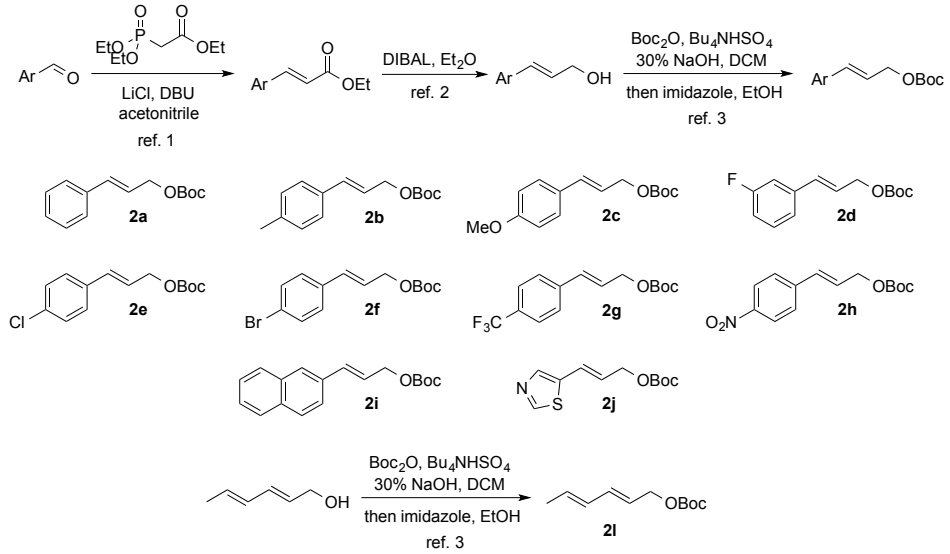
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. Tetrahydrofuran was purified by passing it through a solvent column composed of activated A-1 alumina and degassed by freeze-pump-thaw method. $[Ir(cod)Cl]_2$ was obtained from Johnson-Matthey and used without further purification. (*R*)-BTM was obtained from Apollo Scientific. (*S*)-BTM was obtained from TCI America.

Chiral SFC analysis was conducted on a JASCO SF-2000 integrated analytical SFC system. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (300, 400, 500 and 600 MHz) at the NMR facility of University of California, Berkeley. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 100, 126 and 151 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were acquired at 376 MHz. The proton signal for residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.16 resonance of $CDCl_3$. For ^{19}F NMR spectra, chemical shifts are reported relative to the δ -113.15 resonance of PhF used as an external reference. Coupling constants are reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer at the Micro Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

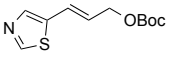
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} glass plates pre-coated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with $KMnO_4$. For the purification of substrates and allylation products, column chromatography was generally performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns.

Syntheses of Substrates and Iridium Catalysts

1) In general, allylic *t*-butyl carbonates were prepared according to the procedure as shown below.[1-3]



(*E*)-*tert*-butyl (3-(thiazol-5-yl)allyl) carbonate (2j)



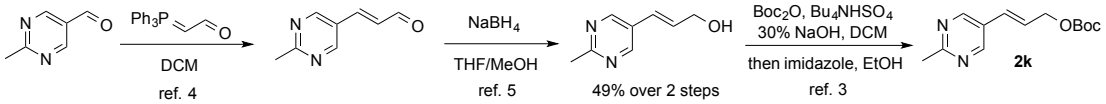
The title compound was isolated (0.33 g, 1.4 mmol, 99% starting from 1.4 mmol of the corresponding allylic alcohol) as a slightly yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.77 (s, 1H), 6.83 (d, J = 15.7 Hz, 1H), 6.14 (dt, J = 15.7, 6.2 Hz, 1H), 4.69 (dd, J = 6.3, 1.4 Hz, 2H), 1.50 (s, 9H).

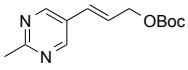
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3, 152.2, 142.3, 136.4, 126.6, 123.7, 82.9, 66.7, 27.9.

HRMS (ESI): *m/z* for $C_{11}H_{16}NO_3S$ $[M+H]^+$ calcd.: 242.0845, found: 242.0842.

2k was prepared according to the procedure as shown below.[3-5]



(*E*)-*tert*-butyl (3-(2-methylpyrimidin-5-yl)allyl) carbonate (2k)



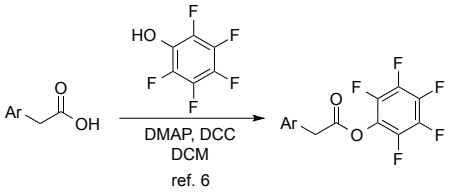
The title compound was isolated (0.26 g, 1.0 mmol, 83% starting from 1.2 mmol of the corresponding allylic alcohol) as a white solid.

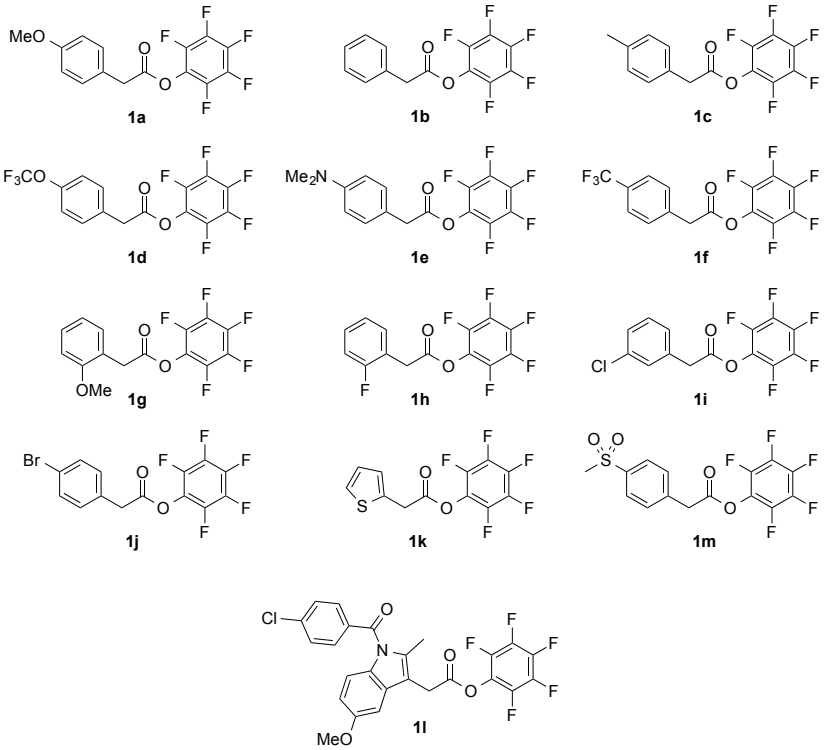
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (s, 2H), 6.58 (d, J = 16.1 Hz, 1H), 6.39 (dt, J = 16.1, 6.0 Hz, 1H), 4.73 (d, J = 6.0 Hz, 2H), 2.73 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 154.8, 153.3, 126.9, 126.8, 126.6, 82.8, 66.8, 27.9, 25.9.

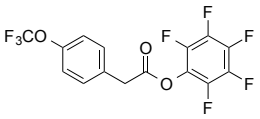
HRMS (ESI): *m/z* for $C_{13}H_{19}N_2O_3$ $[M+H]^+$ calcd.: 251.1390, found: 251.1391.

2) Aryl acetic acid esters were prepared according to the procedure as shown below.[6]





perfluorophenyl 2-(4-(trifluoromethoxy)phenyl)acetate (1d)



The title compound was isolated (1.41 g, 3.65 mmol, 73% starting from 5.00 mmol of the corresponding carboxylic acid) as a colorless oil.

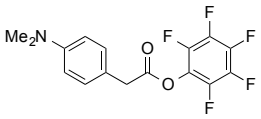
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.98 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 149.0, 130.9, 130.8, 121.5, 120.6 (q, *J* = 257.8 Hz), 39.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0 (s, 3F), -152.5 – -152.9 (m, 2F), -157.5 (t, *J* = 21.7 Hz, 1F), -162.0 – -162.3 (m, 2F).

HRMS (EI): *m/z* for $C_{15}H_6F_8O_3$ $[M]^+$ calcd.: 386.0189, found: 386.0190.

perfluorophenyl 2-(4-(dimethylamino)phenyl)acetate (1e)



The title compound was isolated (0.78 g, 2.3 mmol, 45% yield starting from 5.00 mmol of the corresponding carboxylic acid) as a white solid.

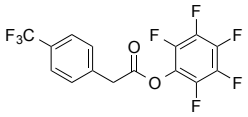
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 2H), 2.96 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 150.2, 130.0, 119.6, 112.9, 40.7, 39.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.4 – -152.8 (m, 2F), -158.2 (t, *J* = 21.8 Hz, 1F), -161.9 – -163.3 (m, 2F).

HRMS (ESI): *m/z* for $C_{16}H_{13}F_5NO_2$ $[M+H]^+$ calcd.: 346.0861, found: 346.0863.

perfluorophenyl 2-(4-(trifluoromethyl)phenyl)acetate (1f)



The title compound was isolated (1.15 g, 3.10 mmol, 62% starting from 5.00 mmol of the corresponding carboxylic acid) as a white solid.

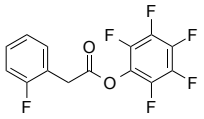
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 4.04 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 136.1, 130.4 (q, *J* = 33.1 Hz), 129.8, 126.0 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 272.2 Hz), 40.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F), -152.5 – -152.8 (m, 2F), -157.4 (t, *J* = 21.7 Hz, 1F), -161.8 – -162.3 (m, 2F).

HRMS (EI): *m/z* for $C_{15}H_6F_8O_2$ $[M]^+$ calcd.: 370.0240, found: 370.0237.

perfluorophenyl 2-(2-fluorophenyl)acetate (1h)



The title compound was isolated (1.07 g, 3.34 mmol, 67% starting from 5.00 mmol of the corresponding carboxylic acid) as a colorless oil.

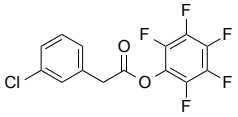
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 9.0 Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 161.2 (d, *J* = 247.3 Hz), 131.4 (d, *J* = 3.6 Hz), 130.0 (d, *J* = 8.1 Hz), 124.6 (d, *J* = 3.7 Hz), 119.7 (d, *J* = 15.7 Hz), 115.8 (d, *J* = 21.4 Hz), 33.7 (d, *J* = 3.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8 (s, 1F), -152.1 – -153.1 (m, 2F), -157.8 (t, *J* = 21.7 Hz, 1F), -161.5 – -163.0 (m, 2F).

HRMS (EI): *m/z* for $C_{14}H_6F_6O_2$ $[M]^+$ calcd.: 320.0272, found: 320.0274.

perfluorophenyl 2-(3-chlorophenyl)acetate (1i)



The title compound was isolated (0.71 g, 2.1 mmol, 42% starting from 5.00 mmol of the corresponding carboxylic acid) as a colorless oil.

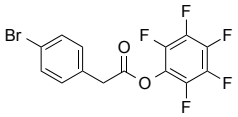
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 1H), 3.95 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 134.9, 133.9, 130.3, 129.6, 128.3, 127.6, 39.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.4 – -152.9 (m, 2F), -157.6 (t, *J* = 21.8 Hz, 1F), -161.8 – -162.4 (m, 2F).

HRMS (EI): *m/z* for $C_{14}H_6ClF_5O_2$ $[M]^+$ calcd.: 335.9976, found: 335.9980.

perfluorophenyl 2-(4-bromophenyl)acetate (1j)



The title compound was isolated (1.46 g, 3.84 mmol, 77% starting from 5.00 mmol of the corresponding carboxylic acid) as a colorless oil.

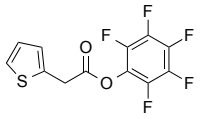
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 132.2, 131.1, 122.1, 39.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.5 – -153.1 (m, 2F), -157.6 (t, *J* = 21.7 Hz, 1F), -162.0 – -162.5 (m, 2F).

HRMS (EI): *m/z* for $C_{14}H_6BrF_5O_2$ $[M]^+$ calcd.: 379.9471, found: 379.9474.

perfluorophenyl 2-(thiophen-2-yl)acetate (1k)



The title compound was isolated (0.87 g, 2.8 mmol, 56% starting from 5.00 mmol of the corresponding carboxylic acid) as a colorless oil.

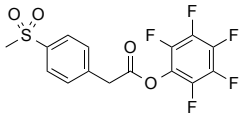
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.07 (dd, *J* = 3.4, 1.2 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.20 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 132.7, 127.8, 127.3, 126.0, 34.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.2 – -152.8 (m, 2F), -157.6 (t, *J* = 21.7 Hz, 1F), -161.9 – -162.4 (m, 2F).

HRMS (EI): *m/z* for $C_{12}H_5F_5O_2S$ $[M]^+$ calcd.: 307.9930, found: 307.9931.

perfluorophenyl 2-(4-(methylsulfonyl)phenyl)acetate (1m)



The title compound was isolated (0.76 g, 2.0 mmol, 40% starting from 5.00 mmol of the corresponding carboxylic acid) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 4.08 (s, 2H), 3.07 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 140.4, 138.2, 130.5, 128.2, 44.6, 40.0.

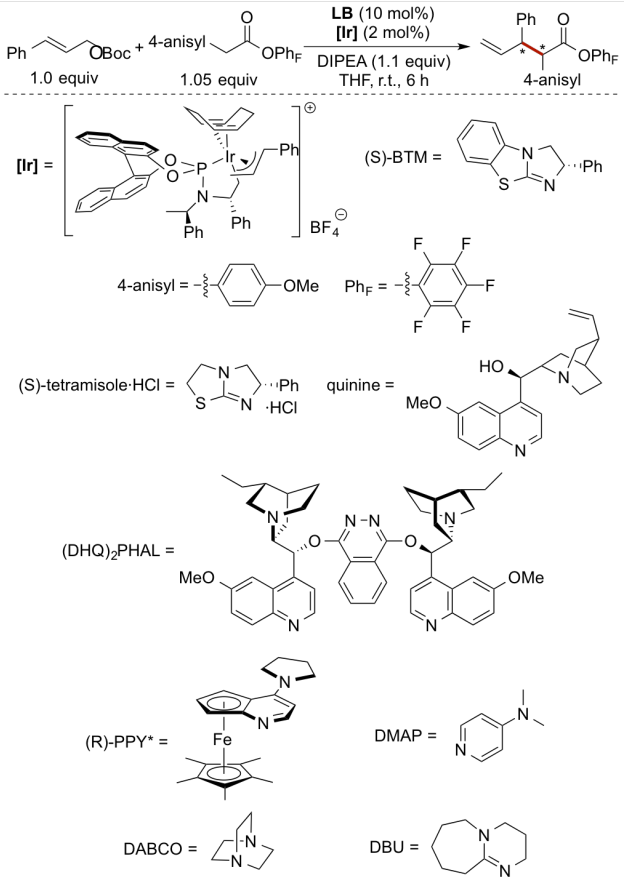
^{19}F NMR (376 MHz, $CDCl_3$) δ -152.4 – -153.0 (m, 2F), -157.1 (t, *J* = 21.7 Hz, 1F), -161.7 – -162.1 (m, 2F).

HRMS (EI): *m/z* for $C_{15}H_{10}F_5O_4S$ $[M+H]^+$ calcd.: 381.0214, found: 381.0216.

3) Iridium catalysts were prepared according to published procedures.[7] Specifically, Iridium catalysts **[Ir]-1**, **[Ir]-2**, **[Ir]-3**, **[Ir]-4** were prepared from the corresponding (*R_a, R, R*)-phosphoramidite ligands. Iridium catalysts *ent*-**[Ir]-1**, *ent*-**[Ir]-2**, *ent*-**[Ir]-3**, *ent*-**[Ir]-4** were prepared from the corresponding (*S_a, S, S*)-phosphoramidite ligands.

Evaluation of Reaction Conditions (Additional Results)

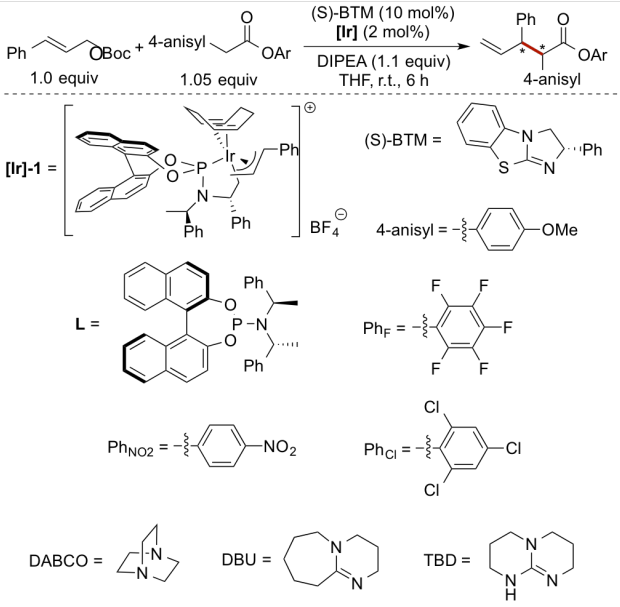
Table S1. Evaluation of Lewis Base Catalysts.



Entry	**LB**	Conv./%[a]	dr[b]	Yield/%[c]
1	(S)-BTM	100	>20:1	>99
2	(S)-tetramisole·HCl	25	4:1	24
3	quinine	41	1:3	39
4	$(DHQ)_2PHAL$	33	1:3	32
5	(R)-PPY*	98	1.9:1	94
6	DMAP	97	1:1.6	92
7	DABCO	100	1:3	97
8	DBU	82	1:3	79

Reactions were conducted on a 0.1 mmol scale. [a] Determined by ^{1}H NMR analysis with mesitylene as internal standard. [b] Determined by ^{1}H NMR analysis of crude reaction mixtures. [c] Combined yield of two diastereomers. Determined by ^{1}H NMR analysis with mesitylene as internal standard. LB = lewis base. DIPEA = diisopropylethylamine.

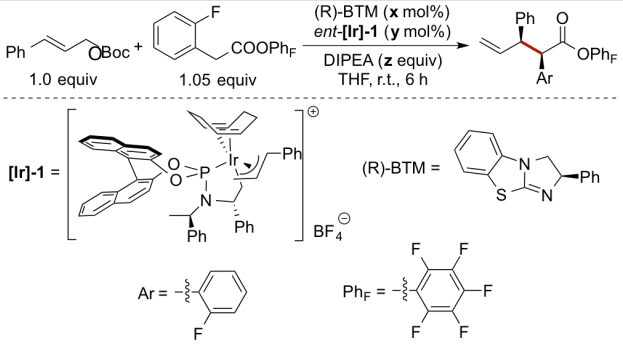
Table S2. Evaluation of Aryl Acetic Acid Esters and Iridium Catalysts.



Entry	[Ir]	activator[a]	Ar	Conv./%[b]	dr[c]	Yield/%[d]
1	**[Ir]-1**	no	Ph_F	100	>20:1	>99
2	-	no	Ph_{NO2}	94	18:1	92
3	-	no	Ph_{Cl}	25	4:1	16
4	-	no	Ph	6	n.d.	0
5	$[Ir(cod)Cl]_2$ + **L**	DBU	Ph_F	6	n.d.	0
6	-	DABCO	-	0	n.d.	0
7	-	TBD	-	0	n.d.	0
8	-	no	-	0	n.d.	0

Reactions were conducted on a 0.1 mmol scale. [a] 5 mol% of activator was added to the solution of $[Ir(cod)Cl]_2$ (1 mol%) and ligand (2 mol%). The mixture was stirred for 10 min at room temperature and then transferred to the vial containing solution of other reaction components. [b] Determined by ^{1}H NMR analysis with mesitylene as internal standard. [c] Determined by ^{1}H NMR analysis of crude reaction mixtures. [d] Combined yield of two diastereomers. Determined by ^{1}H NMR analysis with mesitylene as internal standard. DIPEA = diisopropylethylamine. n.d. = not determined.

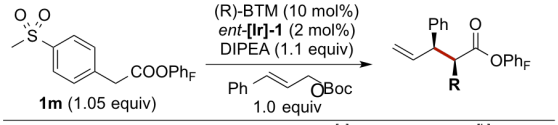
Table S3. Evaluation of Stoichiometry of Reaction Components.



Entry	x	y	z	dr[a]	Yield/%[b]
1	20	2	1.1	10.0:1	>99
2	15	-	-	9.1:1	>99
3	10	-	-	7.6:1	>99
4	5	-	-	4.7:1	>99
5	0	-	-	1:2.1	93
6	10	4	1.1	7.4:1	>99
7	-	3	-	7.9:1	>99
3	-	2	-	7.6:1	>99
8	-	1	-	5.9:1	>99
9	-	0	-		0
10	10	2	2	7.6:1	>99
3	-	-	1.1	7.6:1	>99
11	-	-	0.1	8.8:1	>99
12	-	-	0	9.0:1	>99

Reactions were conducted on a 0.1 mmol scale. [a] Determined by ^{1}H NMR analysis of crude reaction mixtures. [b] Combined yield of two diastereomers. Determined by ^{1}H NMR analysis with mesitylene as internal standard. DIPEA = diisopropylethylamine.

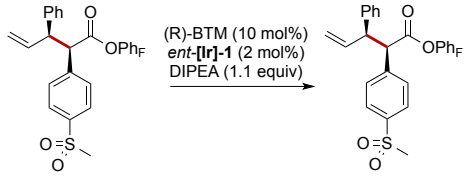
Table S4. Investigations on the Low Diastereoselectivity.



Entry	Changes	dr[a]	Yield/%[b]
1	no	1.7:1	78
2	20% BTM cat.	2.7:1	73
3	no DIPEA	3.8:1	88
4	0.1 equiv DIPEA	3.6:1	85
5	no BTM cat.	1:1.8	91
6	no BTM cat., no DIPEA	1:1.9	15

Reactions were conducted on a 0.1 mmol scale. [a] Determined by ^{1}H NMR analysis of crude reaction mixtures. [b] Combined yield of two diastereomers. Determined by ^{1}H NMR analysis with mesitylene as internal standard. DIPEA = diisopropylethylamine.

product was subjected to the reaction condition:



start 4.7:1 dr

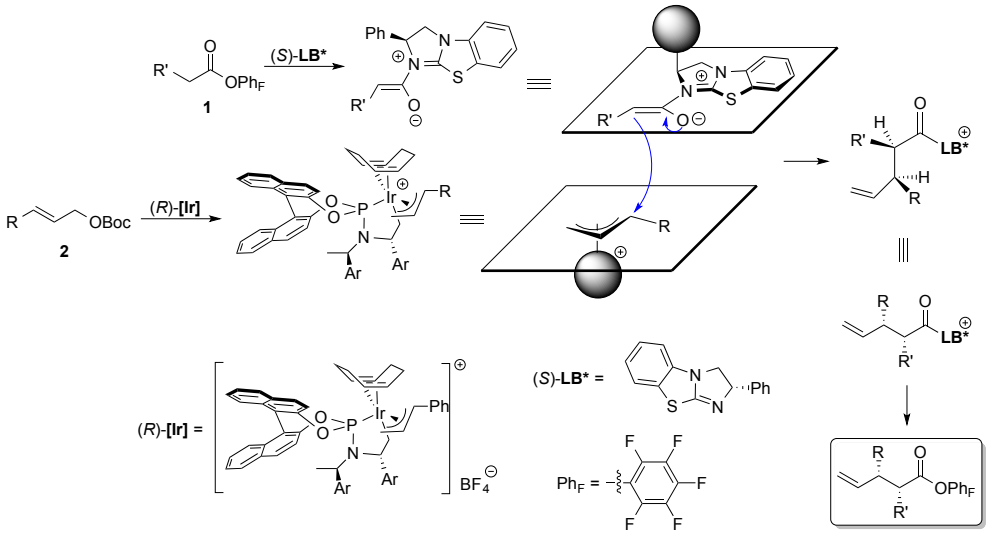
start 1:1.3 dr

end 4.6:1 dr

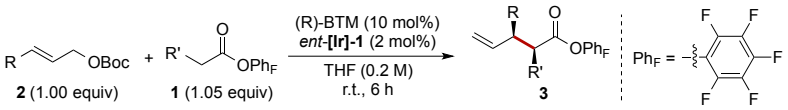
end 1:1.2 dr

The allylation reaction occurred with **1m** in the absence of BTM catalyst (entry 5, Table S4), affording the product **3ma** with low diastereoselectivity. No significant racemization of the product was observed when subjecting the product to the reaction condition. Thus, it is likely that the low diastereoselectivity obtained for the reaction with **1m** results from the competing background allylation of **1m** occurring without participation of BTM, not racemization of the product.

Scheme S1. Stereochemical Model



General Procedure for the Ir-Catalyzed Allylation of Aryl Acetic Acid Esters

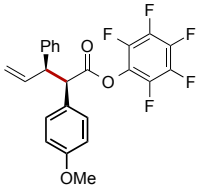


In a nitrogen-filled dry-box, the allyl *t*-butyl carbonate **2** (0.100 mmol, 1.00 equiv) and aryl acetic acid ester **1** (0.105 mmol, 1.05 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. Thereafter, *ent*-**[Ir]-1** (8 mM in THF, 0.25 mL, 0.002 mmol, 2 mol%) and (R)-BTM (40 mM in THF, 0.25 mL, 0.010 mmol, 10 mol%) were added sequentially via syringe. The vial was sealed with a cap containing PTFE/silicone septa and removed from the dry box. The reaction mixture was stirred at r.t. for 6 h. Then the mixture was diluted with 2 mL of hexanes, and filtered through a 0.5-inch plug of silica gel (eluting with 1:1 hexanes:EtOAc, 8 mL). After removal of solvent under vacuum, the crude mixture was purified by column chromatography performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns (4-gram silica gel column, 100/0 to 90/10 of hexanes/EtOAc).

The ratio of diastereomers was determined by ^{1}H NMR analysis of crude reaction mixture. In general, the product was obtained as a mixture of two diastereomers strongly favoring one diastereomer over the other. For characterizations, an additional preparative TLC separation was performed to decrease the amount of the minor diastereomer in the product with 1:1 hexanes:toluene as eluent system. For polar substrates, 1:1 hexanes:ethyl acetate was employed instead.

Scope of Aryl Acetic Acid Esters

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3aa)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (43.1 mg, 0.0962 mmol, 96%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 2.01 min (major) and t_R = 2.67 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –86.4^o (c 0.29, CH_2Cl_2).

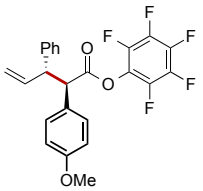
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 5H), 7.06 – 7.02 (m, 2H), 6.74 – 6.69 (m, 2H), 6.18 (ddd, *J* = 17.1, 10.4, 7.8 Hz, 1H), 5.33 – 5.18 (m, 2H), 4.25 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.72 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 159.2, 139.8, 138.6, 129.8, 128.6, 128.4, 127.0, 126.8, 116.9, 114.1, 55.8, 55.2, 53.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.1 (m, 2F), -158.1 (t, *J* = 21.8 Hz, 1F), -162.4 – -162.7 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{17}F_5O_3$ $[M]^+$ calcd.: 448.1098, found: 448.1100.

perfluorophenyl (2*R*,3*S*)-2-(4-methoxyphenyl)-3-phenylpent-4-enoate ((*R*,*S*)-3aa)



Prepared according to the general procedure as described above (**[Ir]-1** was used instead of *ent*-**[Ir]-1**). The diastereomeric ratio was determined to be >20:1. The branched/linear selectivity was determined to be 10:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (43.6 mg, 0.0973 mmol, 97%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 3.76 min (major) and t_R = 3.37 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –77.1^o (c 0.24, CH_2Cl_2).

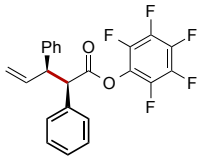
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 6H), 7.32 – 7.26 (m, 1H), 6.96 – 6.91 (m, 2H), 5.77 (ddd, *J* = 17.0, 10.3, 7.7 Hz, 1H), 4.94 (d, *J* = 10.3 Hz, 1H), 4.82 (d, *J* = 17.0 Hz, 1H), 4.28 (d, *J* = 11.6 Hz, 1H), 4.11 (dd, *J* = 11.6, 7.7 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 159.6, 140.9, 138.1, 130.1, 129.0, 128.1, 127.4, 127.4, 117.5, 114.4, 55.9, 55.4, 53.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.1 – -152.4 (m, 2F), -158.3 (t, *J* = 21.8 Hz, 1F), -162.5 – -162.9 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{17}F_5O_3$ $[M]^+$ calcd.: 448.1098, found: 448.1093.

perfluorophenyl (2*R*,3*R*)-2,3-diphenylpent-4-enoate ((*R*,*R*)-3ba)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 18:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (40.7 mg, 0.0974 mmol, 97%).

The **enantiomeric excess** was determined by SFC analysis to be 99% with t_R = 2.55 min (major) and t_R = 3.55 min (minor) [AD-H, 2.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –70.6^o (c 0.29, CH_2Cl_2).

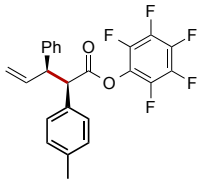
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 7H), 7.11 – 7.07 (m, 1H), 7.06 – 7.03 (m, 2H), 6.20 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 4.14 (dd, *J* = 11.5, 7.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 139.6, 138.5, 135.0, 128.7, 128.7, 128.5, 128.4, 128.0, 126.9, 116.9, 56.6, 53.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.5 – -152.9 (m, 2F), -158.0 (t, *J* = 21.8 Hz, 1F), -162.2 – -163.3 (m, 2F).

HRMS (EI): *m/z* for $C_{23}H_{15}F_5O_2$ $[M]^+$ calcd.: 418.0992, found: 418.0996.

perfluorophenyl (2*R*,3*R*)-3-phenyl-2-(*p*-tolyl)pent-4-enoate ((*R*,*R*)-3ca)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (43.4 mg, 0.100 mmol, >99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.36 min (major) and t_R = 1.65 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –77.4^o (c 0.37, CH_2Cl_2).

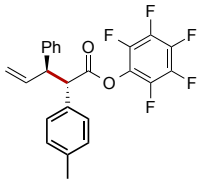
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 2H), 7.12 – 7.08 (m, 3H), 7.07 – 7.03 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.18 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.28 (d, *J* = 11.4 Hz, 1H), 4.12 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 139.8, 138.6, 137.6, 131.9, 129.4, 128.5, 128.5, 128.4, 126.8, 116.9, 56.1, 53.1, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.4 – -152.7 (m, 2F), -158.1 (t, *J* = 21.7 Hz, 1F), -161.9 – -162.8 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{17}F_5O_2$ $[M]^+$ calcd.: 432.1149, found: 432.1152.

Perfluorophenyl (2*S*,3*R*)-3-phenyl-2-(*p*-tolyl)pent-4-enoate ((*S*,*R*)-3ca)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be 19:1. The branched/linear selectivity was determined to be 8:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (43.2 mg, 0.0999 mmol, >99%). For characterization, an additional recrystallization from pentane was performed to decrease the amount of the minor diastereomer and linear product in the sample.

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.94 min (major) and t_R = 2.10 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 225 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = +84.2^o (c 0.31, $CHCl_3$).

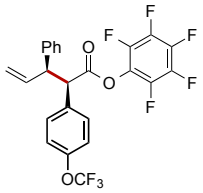
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 6H), 7.32 – 7.27 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 5.77 (ddd, *J* = 17.5, 10.3, 7.6 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.81 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.13 (dd, *J* = 11.6, 7.6 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 140.8, 138.0, 137.9, 132.2, 129.6, 128.8, 128.6, 127.9, 127.2, 117.3, 56.2, 52.7, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.7 (m, 2F), –158.3 (t, *J* = 21.7 Hz, 1F), –162.7 (dd, *J* = 22.0, 17.4 Hz, 2F).

HRMS (EI): *m/z* for $C_{24}H_{17}F_5O_2$ $[M]^+$ calcd.: 432.1149, found: 432.1149.

perfluorophenyl (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethoxy)phenyl)pent-4-enoate ((*R*,*R*)-3da)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 16:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (49.3 mg, 0.0982 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be 97% with t_R = 1.67 min (major) and t_R = 2.21 min (minor) [AD-H, 2.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –69.9^o (c 0.44, CH_2Cl_2).

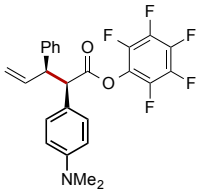
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 7.15 – 7.08 (m, 1H), 7.06 – 6.97 (m, 4H), 6.19 (ddd, *J* = 17.1, 10.4, 7.8 Hz, 1H), 5.32 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 4.08 (dd, *J* = 11.4, 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 148.9, 139.3, 138.0, 133.8, 130.1, 128.7, 128.3, 127.2, 121.4, 120.5 (q, *J* = 257.4 Hz,), 117.3, 56.0, 53.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0 (s, 3F), -150.6 – -152.1 (m, 2F), -157.6 (t, *J* = 21.7 Hz, 1F), -161.5 – -163.6 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{14}F_8O_3$ $[M]^+$ calcd.: 502.0815, found: 502.0816.

perfluorophenyl (2*R*,3*R*)-2-(4-(dimethylamino)phenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3ea)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (35.3 mg, 0.0766 mmol, 77%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 2.78 min (major) and t_R = 4.64 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –90.9^o (c 0.21, CH_2Cl_2).

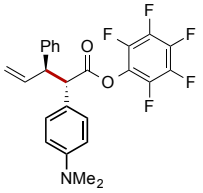
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 7.12 – 7.03 (m, 5H), 6.53 (d, *J* = 8.8 Hz, 2H), 6.17 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.21 (d, *J* = 11.4 Hz, 1H), 4.10 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.87 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 150.0, 140.2, 139.0, 129.4, 128.5, 128.4, 126.7, 122.3, 116.7, 112.4, 55.6, 53.0, 40.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.5 – -152.0 (m, 2F), -158.4 (t, *J* = 21.7 Hz, 1F), -162.6 – -162.9 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{20}F_5NO_2$ $[M]^+$ calcd.: 461.1414, found: 461.1414.

Perfluorophenyl (2*S*,3*R*)-2-(4-(dimethylamino)phenyl)-3-phenylpent-4-enoate ((*S*,*R*)-3ea)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be 16:1. The branched/linear selectivity was determined to be 13:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (46.9 mg, 0.102 mmol, >99%). For characterization, an additional preparative TLC separation was performed to decrease the amount of the minor diastereomer and linear product in the sample with 1:1 hexanes:toluene as the eluent system.

The **enantiomeric excess** was determined by SFC analysis to be 99% with t_R = 3.49 min (major) and t_R = 3.13 min (minor) [OJ-H, 3.0% ^{i}PrOH, 2.5 mL/min, 269 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = +89.0^o (c 1.56, $CHCl_3$).

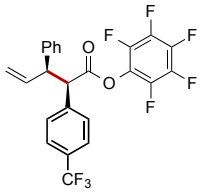
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 7.29 – 7.24 (m, 2H), 6.74 (app d, *J* = 8.4 Hz, 2H), 5.80 (ddd, *J* = 17.4, 10.3, 7.4 Hz, 1H), 4.94 (dt, *J* = 10.3, 1.2 Hz, 1H), 4.82 (dt, *J* = 17.1, 1.3 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.11 (ddt, *J* = 11.6, 7.4, 1.2 Hz, 1H), 2.98 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 141.1, 138.3, 129.5, 128.7, 128.0, 127.1, 117.1, 112.5, 55.7, 52.6, 40.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.6 – -152.7 (m, 2F), -158.6 (t, *J* = 21.7 Hz, 1F), -162.1 – -163.5 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{20}F_5NO_2$ $[M]^+$ calcd.: 461.1414, found: 461.1416.

perfluorophenyl (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)pent-4-enoate ((*R*,*R*)-3fa)



Prepared according to the general procedure as described above (20 mol% of (R)-BTM catalyst was used instead of 10 mol%). The diastereomeric ratio was determined to be 11:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (43.6 mg, 0.0897 mmol, 90%).

The **enantiomeric excess** was determined by SFC analysis to be 98% with t_R = 1.14 min (major) and t_R = 1.46 min (minor) [AD-H, 3.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –62.9° (c 0.35, CH_2Cl_2).

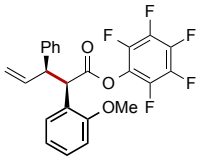
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 7.06 – 7.01 (m, 2H), 6.19 (ddd, *J* = 17.2, 10.4, 7.8 Hz, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.37 (d, *J* = 11.4 Hz, 1H), 4.12 (dd, *J* = 11.4, 7.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 139.0, 137.9, 130.2 (q, *J* = 32.8 Hz), 129.0, 128.8, 128.2, 127.2, 125.6 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 272.3 Hz), 117.4, 56.4, 53.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F), -151.6 – -152.3 (m, 2F), -157.5 (t, *J* = 21.6 Hz, 1F), -161.9 – -162.5 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{14}F_8O_2$ $[M]^+$ calcd.: 486.0866, found: 486.0862.

perfluorophenyl (2*R*,3*R*)-2-(2-methoxyphenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3ga)



Prepared according to the general procedure as described above (reaction time was extended to 9 h, and 1.1 equiv of diisopropylethylamine was added into reaction mixture). The diastereomeric ratio was determined to be 11:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (42.8 mg, 0.0955 mmol, 96%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.31 min (major) and t_R = 2.13 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 °C].

$[\alpha]_D^{25}$ = –49.5° (c 0.33, CH_2Cl_2).

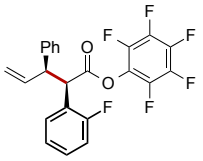
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.16 – 7.11 (m, 3H), 7.10 – 7.05 (m, 3H), 6.86 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.21 (ddd, *J* = 17.4, 10.3, 7.8 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.14 (dd, *J* = 11.0, 7.8 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 157.0, 140.1, 139.0, 129.0, 128.9, 128.4, 128.1, 126.6, 123.9, 120.8, 116.6, 110.8, 55.6, 52.4, 47.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.2 (m, 2F), -158.4 (t, *J* = 21.8 Hz, 1F), -162.4 – -163.1 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{17}F_5O_3$ $[M]^+$ calcd.: 448.1098, found: 448.1099.

perfluorophenyl (2*R*,3*R*)-2-(2-fluorophenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3ha)



Prepared according to the general procedure as described above (20 mol% of (R)-BTM catalyst was used instead of 10 mol%). The diastereomeric ratio was determined to be 12:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (38.7 mg, 0.0888 mmol, 89%).

The **enantiomeric excess** was determined by SFC analysis to be 98% with t_R = 3.31 min (major) and t_R = 3.10 min (minor) [OD-H, 3.0% ^{i}PrOH, 2.0 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –49.2^o (c 0.24, CH_2Cl_2).

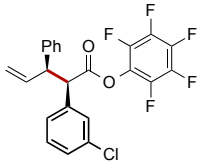
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 1H), 7.19 – 7.12 (m, 3H), 7.12 – 7.02 (m, 4H), 6.90 – 6.83 (m, 1H), 6.19 (ddd, *J* = 17.2, 10.3, 7.8 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.16 (dd, *J* = 11.3, 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 160.5 (d, *J* = 247.0 Hz), 139.4, 138.4, 129.7 (d, *J* = 8.6 Hz), 129.3 (d, *J* = 2.6 Hz), 128.5, 128.2, 127.0, 124.5 (d, *J* = 3.4 Hz), 122.5 (d, *J* = 14.3 Hz), 117.12, 115.6 (d, *J* = 22.8 Hz), 52.4, 47.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2 – -117.4 (m, 1F), -151.8 – -152.6 (m, 2F), -157.8 (t, *J* = 21.7 Hz, 1F), -161.9 – -162.7 (m, 2F).

HRMS (EI): *m/z* for $C_{23}H_{14}F_6O_2$ $[M]^+$ calcd.: 436.0898, found: 436.0897.

perfluorophenyl (2*R*,3*R*)-2-(3-chlorophenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3ia)



Prepared according to the general procedure as described above (20 mol% of (R)-BTM catalyst was used instead of 10 mol%). The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (42.8 mg, 0.0945 mmol, 94%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.50 min (major) and t_R = 1.88 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –74.5^o (c 0.24, CH_2Cl_2).

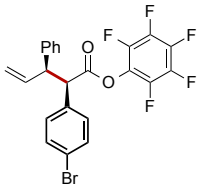
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 1.9 Hz, 1H), 7.21 – 7.06 (m, 6H), 7.06 – 7.02 (m, 2H), 6.18 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 11.4, 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 139.2, 138.1, 137.0, 134.5, 129.9, 128.8, 128.7, 128.3, 127.2, 127.0, 117.3, 56.3, 53.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.7 – -152.2 (m, 2F), -157.6 (t, *J* = 21.6 Hz, 1F), -162.1 – -162.2 (m, 2F).

HRMS (EI): *m/z* for $C_{23}H_{14}ClF_5O_2$ $[M]^+$ calcd.: 452.0602, found: 452.0603.

perfluorophenyl (2*R*,3*R*)-2-(4-bromophenyl)-3-phenylpent-4-enoate ((*R*,*R*)-3ja)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 18:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (49.9 mg, 0.100 mmol, >99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 4.27 min (major) and t_R = 6.19 min (minor) [AD-H, 3.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –82.7^o (c 0.22, CH_2Cl_2).

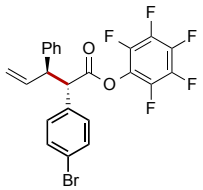
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 7.15 – 7.07 (m, 3H), 7.05 – 6.99 (m, 2H), 6.17 (ddd, *J* = 17.1, 10.4, 7.8 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 4.26 (d, *J* = 11.4 Hz, 1H), 4.07 (dd, *J* = 11.5, 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 139.3, 138.2, 134.2, 131.9, 130.3, 128.7, 128.3, 127.2, 122.2, 117.2, 56.1, 53.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.1 (m, 2F), -157.6 (t, *J* = 21.7 Hz, 1F), -162.1 – -162.4 (m, 2F).

HRMS (EI): *m/z* for $C_{23}H_{14}BrF_5O_2$ $[M]^+$ calcd.: 496.0097, found: 496.0098.

Perfluorophenyl (2*S*,3*R*)-2-(4-bromophenyl)-3-phenylpent-4-enoate ((*S*,*R*)-3ja)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be 16:1. The branched/linear selectivity was determined to be 8:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (50.8 mg, 0.102 mmol, >99%). For characterization, an additional an additional recrystallization from 99:1 hexanes:toluene was performed to decrease the amount of the minor diastereomer and linear product in the sample.

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.66 min (major) and t_R = 2.02 min (minor) [AD-H, 10% ^{i}PrOH, 2.5 mL/min, 230 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = +71.1^o (c 0.72, $CHCl_3$).

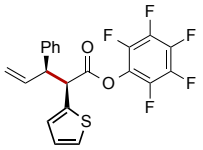
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.27 (m, 7H), 5.75 (ddd, *J* = 16.9, 10.3, 7.9 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 4.84 (dd, *J* = 17.0, 1.3 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 4.09 (dd, *J* = 11.5, 7.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 140.3, 137.4, 134.4, 132.1, 130.5, 128.9, 127.8, 127.4, 122.4, 117.8, 56.1, 52.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.5 – -153.3 (m, 2F), -157.9 (t, *J* = 21.7 Hz, 1F), -162.4 (td, *J* = 22.8, 22.4, 4.9 Hz, 2F).

HRMS (EI): *m/z* for $C_{23}H_{14}F_5BrO_2$ $[M]^+$ calcd.: 498.0077, found: 498.0069.

perfluorophenyl (2*S*,3*R*)-3-phenyl-2-(thiophen-2-yl)pent-4-enoate ((*S*,*R*)-3ka)



Prepared according to the general procedure as described above (20 mol% of (R)-BTM catalyst was used instead of 10 mol%). The diastereomeric ratio was determined to be 17:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (41.5 mg, 0.0979 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.42 min (major) and t_R = 1.61 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –37.4^o (c 0.35, CH_2Cl_2).

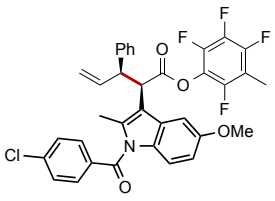
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 7.14 – 7.10 (m, 3H), 6.85 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.81 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.18 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 1H), 5.32 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.58 (d, *J* = 11.3 Hz, 1H), 4.08 (dd, *J* = 11.3, 8.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 139.6, 137.9, 136.8, 128.7, 128.2, 127.3, 127.2, 126.8, 125.8, 117.6, 54.7, 52.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.4 – -151.8 (m, 2F), -157.8 (t, *J* = 21.7 Hz, 1F), -162.1 – -162.7 (m, 2F).

HRMS (EI): *m/z* for $C_{21}H_{13}F_5O_2S$ $[M]^+$ calcd.: 424.0556, found: 424.0555.

2,3,4,6-tetrafluoro-5-methylphenyl (2*R*,3*R*)-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-3-phenylpent-4-enoate ((*R*,*R*)-3la)



Prepared according to the general procedure as described above (1.1 equiv of diisopropylethylamine was added into reaction mixture). The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a yellow oil (58.8 mg, 0.0918 mmol, 92%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 6.54 min (major) and t_R = 3.90 min (minor) [AD-H, 8.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –129.6^{o} (c 0.56, CH_2Cl_2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.18 – 7.11 (m, 4H), 7.07 (d, *J* = 9.0 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.27 (ddd, *J* = 17.3, 10.4, 6.9 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.56 – 4.42 (m, 2H), 3.88 (s, 3H), 2.02 (s, 3H).

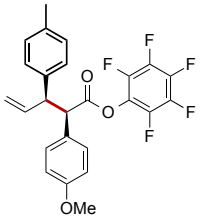
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 168.1, 156.0, 140.1, 139.6, 138.3, 135.9, 133.7, 131.3, 131.2, 129.2, 128.4, 128.1, 127.0, 117.2, 114.7, 112.9, 111.9, 103.0, 55.9, 49.9, 47.9, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.6 – -152.1 (m, 2F), -157.8 (t, *J* = 21.7 Hz, 1F), -162.0 – -162.6 (m, 2F).

HRMS (EI): *m/z* for $C_{34}H_{23}ClF_5NO_4$ $[M]^+$ calcd.: 639.1236, found: 639.1230.

Scope of Allylic *t*-Butyl Carbonates

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(*p*-tolyl)pent-4-enoate ((*R*,*R*)-3ab)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (45.1 mg, 0.0976 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be 98% with t_R = 2.10 min (major) and t_R = 2.60 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –76.4^o (c 0.28, CH_2Cl_2).

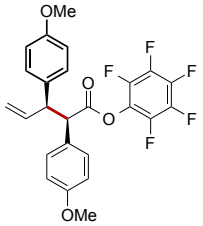
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.16 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 11.4 Hz, 1H), 4.07 (dd, *J* = 11.4, 7.8 Hz, 1H), 3.73 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 159.1, 138.9, 136.7, 136.4, 129.8, 129.3, 128.1, 127.1, 116.6, 114.0, 55.7, 55.2, 52.7, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.0 (m, 2F), -158.1 (t, *J* = 21.8 Hz, 1F), -162.4 – -162.8 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{19}F_5O_3$ $[M]^+$ calcd.: 462.1254, found: 462.1257.

perfluorophenyl (2*R*,3*R*)-2,3-bis(4-methoxyphenyl)pent-4-enoate ((*R*,*R*)-3ac)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (47.4 mg, 0.0991 mmol, 99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 3.93 min (major) and t_R = 5.89 min (minor) [AD-H, 4.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –88.5^o (c 0.30, CH_2Cl_2).

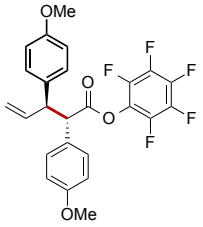
^{1}H NMR (600 MHz, $CDCl_3$)) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.77 – 6.65 (m, 4H), 6.15 (ddd, *J* = 17.6, 10.3, 7.7 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.1 Hz, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 4.05 (dd, *J* = 11.4, 7.7 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 159.2, 158.4, 138.9, 131.8, 129.8, 129.3, 127.2, 116.5, 114.1, 114.0, 55.9, 55.3, 52.3.

^{19}F NMR (376 MHz, $CDCl_3$)) δ -151.6 – -152.5 (m, 2F), -158.1 (t, *J* = 21.5 Hz, 1F), -162.2 – -163.1 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{19}F_5O_4$ $[M]^+$ calcd.: 478.1204, found: 478.1206.

Perfluorophenyl (2*S*,3*R*)-2,3-bis(4-methoxyphenyl)pent-4-enoate ((*S*,*R*)-3ac)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be >20:1. The branched/linear selectivity was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (46.5 mg, 0.973 mmol, 97%). For characterization, an additional an additional recrystallization from hexanes was performed to decrease the amount of the minor diastereomer and linear product in the sample. The **enantiomeric excess** was determined by SFC analysis to be 98% with t_R = 1.85 min (major) and t_R = 1.58 min (minor) [AD-H, 10% ^{i}PrOH, 2.5 mL/min, 230 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = +72.8^o (c 1.09, $CHCl_3$).

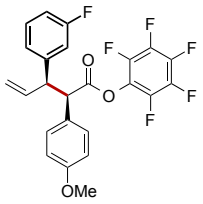
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (m, *J* = 8.7 Hz, 2H), 7.33 – 7.21 (m, 2H), 6.93 (m, *J* = 8.7 Hz, 2H), 6.91 (m, *J* = 8.7 Hz, 2H), 5.76 (ddd, *J* = 17.2, 10.3, 7.5 Hz, 1H), 4.93 (dt, *J* = 10.3, 1.2 Hz, 1H), 4.82 (d, *J* = 17.1 Hz, 1H), 4.24 (d, *J* = 11.5 Hz, 1H), 4.08 (dd, *J* = 11.6, 7.6 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 159.5, 158.7, 138.2, 132.8, 129.9, 128.9, 127.4, 117.0, 114.3, 114.2, 56.0, 55.3, 55.2, 51.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.3 – -152.9 (m, 2F), -158.4 (t, *J* = 21.7 Hz, 1F), -162.3 – -163.2 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{19}F_5O_4$ $[M]^+$ calcd.: 478.1204, found: 478.1197.

perfluorophenyl (2*R*,3*R*)-3-(3-fluorophenyl)-2-(4-methoxyphenyl)pent-4-enoate ((*R*,*R*)-3ad)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 17:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (46.7 mg, 0.100 mmol, >99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.86 min (major) and t_R = 2.92 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –85.3^o (c 0.36, CH_2Cl_2).

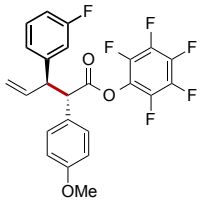
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 3H), 6.84 – 6.71 (m, 5H), 6.13 (ddd, *J* = 17.1, 10.4, 7.7 Hz, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.27 – 5.21 (m, 1H), 4.21 (d, *J* = 11.4 Hz, 1H), 4.10 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 162.9 (d, *J* = 246.0 Hz), 159.3, 142.4 (d, *J* = 7.0 Hz), 138.0, 130.0 (d, *J* = 8.4 Hz), 129.7, 126.6, 124.2 (d, *J* = 2.7 Hz), 117.4, 115.2 (d, *J* = 21.7 Hz), 114.2, 113.8 (d, *J* = 21.1 Hz), 55.6, 55.3, 52.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.7 – -115.5 (m, 1F), -151.9 – -152.1 (m, 2F), -157.9 (t, *J* = 21.8 Hz, 1F), -161.8 – -163.0 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{16}F_6O_3$ $[M]^+$ calcd.: 466.1004, found: 466.1009.

Perfluorophenyl (2*S*,3*R*)-3-(3-fluorophenyl)-2-(4-methoxyphenyl)pent-4-enoate ((*S*,*R*)-3ad)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be 12:1. The branched/linear selectivity was determined to be 6:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (46.1 mg, 0.989 mmol, 99%). For characterization, an additional an additional recrystallization from hexanes was performed to decrease the amount of the minor diastereomer and linear product in the sample.

The **enantiomeric excess** was determined by SFC analysis to be 95% with t_R = 1.58 min (major) and t_R = 1.81 min (minor) [AD-H, 8.0% ^{i}PrOH, 2.5 mL/min, 235 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = +77.2^o (c 1.54, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, *J* = 6.9 Hz, 2H), 7.33 (td, *J* = 8.0, 5.9 Hz, 1H), 7.13 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.05 (dt, *J* = 9.8, 2.1 Hz, 1H), 6.98 (tdd, *J* = 8.5, 2.6, 0.9 Hz, 1H), 6.95 – 6.91 (m, 2H), 5.73 (ddd,

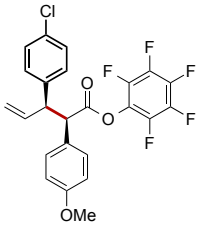
J = 17.0, 10.3, 7.6 Hz, 1H), 4.96 (dt, *J* = 10.3, 1.1 Hz, 1H), 4.82 (d, *J* = 17.0 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 4.10 (dd, *J* = 11.6, 7.7 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 163.0 (d, *J* = 246.3 Hz), 159.6, 143.4 (d, *J* = 6.9 Hz), 137.3, 130.3 (d, *J* = 8.3 Hz), 129.8, 126.9, 123.6 (d, *J* = 2.8 Hz), 117.8, 115.0 (d, *J* = 21.7 Hz), 114.4, 114.2 (d, *J* = 21.1 Hz), 55.6, 55.3, 52.5 (d, *J* = 1.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 (q, *J* = 8.5 Hz, 1F), -148.3 – -155.6 (m, 2F), -158.1 (t, *J* = 21.6 Hz, 1F), -162.5 (dd, *J* = 22.6, 18.0 Hz, 2F).

HRMS (EI): *m/z* for $C_{24}H_{16}F_6O_3$ $[M]^+$ calcd.: 466.1004, found: 466.0997.

perfluorophenyl (2*R*,3*R*)-3-(4-chlorophenyl)-2-(4-methoxyphenyl)pent-4-enoate ((*R*,*R*)-3ae)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (46.8 mg, 0.0969 mmol, 97%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 3.04 min (major) and t_R = 4.15 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –90.9^o (c 0.54, CH_2Cl_2).

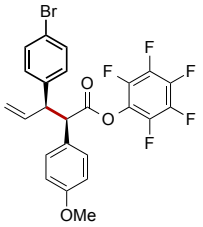
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 4H), 7.00 – 6.94 (m, 2H), 6.77 – 6.70 (m, 2H), 6.13 (ddd, *J* = 17.6, 10.3, 7.5 Hz, 1H), 5.36 – 5.20 (m, 2H), 4.19 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 11.5, 7.6 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 159.4, 138.4, 138.2, 132.6, 129.7, 128.7, 126.7, 117.3, 114.2, 55.6, 55.3, 52.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.3 (m, 2F), -157.9 (t, *J* = 21.7 Hz, 1F), -162.4 (td, *J* = 22.6, 5.2 Hz, 2F).

HRMS (EI): *m/z* for $C_{24}H_{16}ClF_5O_3$ $[M]^+$ calcd.: 482.0708, found: 482.0711.

perfluorophenyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(4-methoxyphenyl)pent-4-enoate ((*R*,*R*)-3af)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (52.4 mg, 0.0994 mmol, >99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 4.12 min (major) and t_R = 5.90 min (minor) [AD-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –77.2^o (c 0.59, CH_2Cl_2).

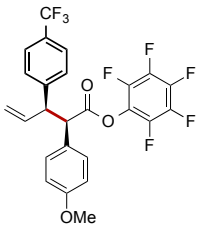
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.12 (ddd, *J* = 17.1, 10.3, 7.6 Hz, 1H), 5.34 – 5.20 (m, 2H), 4.19 (d, *J* = 11.5 Hz, 1H), 4.07 (dd, *J* = 11.5, 7.6 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 159.4, 138.9, 138.1, 131.7, 130.1, 129.7, 126.6, 120.8, 117.3, 114.3, 55.6, 55.3, 52.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8 – -152.2 (m, 2F), -157.9 (t, *J* = 21.7 Hz, 1F), -162.1 – -162.5 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{16}BrF_5O_3$ $[M]^+$ calcd.: 526.0203, found: 526.0197.

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)pent-4-enoate ((*R*,*R*)-3ag)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (49.0 mg, 0.0 949mmol, 95%).

The **enantiomeric excess** was determined by SFC analysis to be 99% with t_R = 2.26 min (major) and t_R = 3.17 min (minor) [AD-H, 3.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –82.2^o (c 0.33, CH_2Cl_2).

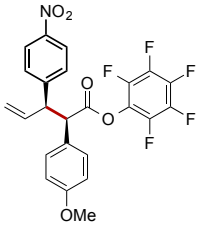
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.14 (ddd, *J* = 17.0, 10.3, 7.5 Hz, 1H), 5.31 (d, *J* = 17.1 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.25 (d, *J* = 11.5 Hz, 1H), 4.18 (dd, *J* = 11.5, 7.6 Hz, 1H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 159.4, 144.0, 137.8, 129.7, 129.2 (q, *J* = 32.4 Hz), 128.8, 126.4, 125.5 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.0 Hz), 117.8, 114.3, 55.5, 55.3, 52.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F), -150.6 – -154.0 (m, 2F), -157.8 (t, *J* = 21.7 Hz, 1F), -161.7 – -165.6 (m, 2F).

HRMS (EI): *m/z* for $C_{25}H_{16}F_8O_3$ $[M]^+$ calcd.: 516.0972, found: 516.0974.

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(4-nitrophenyl)pent-4-enoate ((*R*,*R*)-3ah)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (44.6 mg, 0.0904 mmol, 90%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 4.05 min (major) and t_R = 3.82 min (minor) [AD-H, 7.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –99.6^o (c 0.35, CH_2Cl_2).

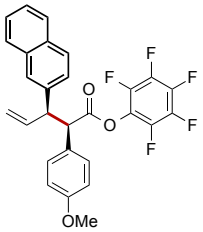
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.13 (dddd, *J* = 17.4, 10.3, 4.5, 2.8 Hz, 1H), 5.39 – 5.27 (m, 2H), 4.26 – 4.22 (m, 2H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 159.5, 147.6, 146.9, 137.1, 129.6, 129.3, 126.0, 123.8, 118.4, 114.4, 55.4, 55.3, 52.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.9 – -152.3 (m, 2F), -157.6 (t, *J* = 21.7 Hz, 1F), -162.0 – -162.5 (m, 2F).

HRMS (EI): *m/z* for $C_{24}H_{16}F_5NO_5$ $[M]^+$ calcd.: 493.0949, found: 493.0945.

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(naphthalen-2-yl)pent-4-enoate ((*R*,*R*)-3ai)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography to give the title compound as a colorless oil (46.5 mg, 0.0934 mmol, 93%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 3.90 min (major) and t_R = 5.42 min (minor) [AD-H, 6.0% ^{i}PrOH, 3.0 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –85.6^o (c 0.30, CH_2Cl_2).

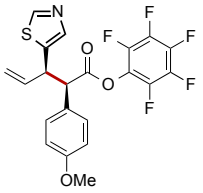
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.71 – 7.69 (m, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.44 – 7.38 (m, 2H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.25 (ddd, *J* = 17.2, 10.3, 7.6 Hz, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.30 (dd, *J* = 11.5, 7.6 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 159.1, 138.6, 137.3, 133.5, 132.4, 129.7, 128.2, 127.8, 127.7, 127.40, 126.8, 126.2, 126.1, 125.8, 117.1, 114.1, 55.5, 55.2, 53.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.7 – -152.3 (m, 2F), -158.0 (t, *J* = 21.8 Hz, 1F), -162.2 – -162.9 (m, 2F).

HRMS (EI): *m/z* for $C_{28}H_{19}F_5O_3$ $[M]^+$ calcd.: 498.1254, found: 498.1255.

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(thiazol-5-yl)pent-4-enoate ((*R*,*R*)-3aj)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography (100/0 to 70/30 of hexanes/ethyl acetate) to give the title compound as a white solid (36.7 mg, 0.0807 mmol, 81%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 2.93 min (major) and t_R = 2.59 min (minor) [AD-H, 8.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –87.8^o (c 0.59, CH_2Cl_2).

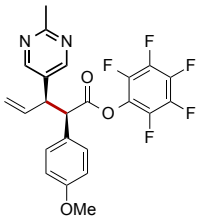
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.41 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.15 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.43 – 5.30 (m, 2H), 4.47 (dd, *J* = 11.0, 7.8 Hz, 1H), 4.13 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 159.7, 152.6, 141.6, 137.7, 137.1, 129.8, 126.1, 118.5, 114.4, 56.6, 55.3, 45.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.9 – -152.2 (m, 2F), -157.7 (t, *J* = 21.5 Hz, 1F), -162.1 – -162.4 (m, 2F).

HRMS (EI): *m/z* for $C_{21}H_{14}F_5NO_3S$ $[M]^+$ calcd.: 455.0615, found: 455.0622.

perfluorophenyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-(2-methylpyrimidin-5-yl)pent-4-enoate ((*R*,*R*)-3ak)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be >20:1. The crude mixture was purified by column chromatography (100/0 to 40/60 of hexanes/ethyl acetate) to give the title compound as a white solid (43.9 mg, 0.0946 mmol, 95%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 3.13 min (major) and t_R = 2.80 min (minor) [AD-H, 7.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –98.5° (c 0.20, CH_2Cl_2).

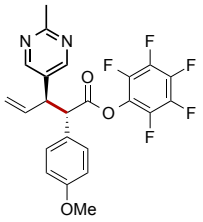
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.12 (ddd, *J* = 17.1, 10.4, 7.4 Hz, 1H), 5.41 – 5.28 (m, 2H), 4.21 (d, *J* = 11.4 Hz, 1H), 4.11 (dd, *J* = 11.3, 7.4 Hz, 1H), 3.74 (s, 3H), 2.62 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 166.8, 159.7, 156.9, 136.7, 129.8, 129.7, 125.8, 118.7, 114.7, 55.3, 55.1, 48.1, 25.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.9 – -152.4 (m, 2F), -157.5 (t, *J* = 21.7 Hz, 1F), -161.9 – -162.4 (m, 2F).

HRMS (EI): *m/z* for $C_{23}H_{17}F_5N_2O_3$ $[M]^+$ calcd.: 464.1159, found: 464.1165.

Perfluorophenyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-(2-methylpyrimidin-5-yl)pent-4-enoate ((*S*,*R*)-3ak)



Prepared according to the general procedure as described above ((*S*)-BTM was used instead of (*R*)-BTM). The diastereomeric ratio was determined to be 9:1. The branched/linear selectivity was determined to be >20:1. The crude mixture was purified by column chromatography (15% EtOAc in hexanes) to give the title compound as a very pale yellow semi-solid (34.2 mg, 0.737 mmol, 74%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 2.77 min (major) and t_R = 2.30 min (minor) [AD-H, 10% ^{i}PrOH, 2.5 mL/min, 223 nm, 40 °C].

$[\alpha]_D^{25}$ = +70.2° (c 1.07, $CHCl_3$).

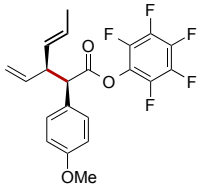
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.78 (ddd, *J* = 17.3, 10.3, 7.3 Hz, 1H), 5.06 (dt, *J* = 10.4, 1.0 Hz, 1H), 4.87 (dt, *J* = 17.1, 1.1 Hz, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.82 (s, 3H), 2.75 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 167.2, 159.8, 156.7, 136.0, 130.7, 129.7, 126.1, 118.9, 114.5, 55.3, 55.2, 47.8, 25.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -152.4 – -153.1 (m, 2F), -157.6 (t, *J* = 21.6 Hz, 1F), -162.2 (td, *J* = 22.8, 5.4 Hz, 2F).

HRMS (EI): *m/z* for $C_{23}H_{17}F_5N_2O_3$ $[M]^+$ calcd.: 464.1159, found: 464.1161.

perfluorophenyl (2*R*,3*S*,*E*)-2-(4-methoxyphenyl)-3-vinylhex-4-enoate ((*R*,*R*)-3al)



Prepared according to the general procedure as described above. The diastereomeric ratio was determined to be 17:1. The crude mixture was purified by column chromatography to give the title compound as a white solid (37.1 mg, 0.0900 mmol, 90%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.95 min (major) and t_R = 2.60 min (minor) [AD-H, 2.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –62.9^{o} (c 0.20, CH_2Cl_2).

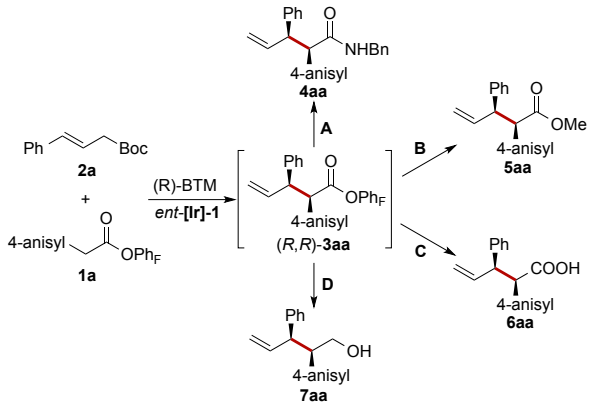
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 6.91 – 6.86 (m, 2H), 5.88 (ddd, *J* = 17.2, 10.3, 7.9 Hz, 1H), 5.44 – 5.35 (m, 1H), 5.23 – 5.14 (m, 3H), 3.85 (d, *J* = 10.3 Hz, 1H), 3.82 (s, 3H), 3.54 – 3.47 (m, 1H), 1.54 (d, *J* = 5.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 159.3, 137.9, 130.1, 129.2, 128.4, 127.3, 117.0, 114.1, 55.4, 55.4, 49.8, 18.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -151.3 – -152.8 (m, 2F), -158.3 (t, *J* = 21.6 Hz, 1F), -161.9 – -163.9 (m, 2F).

HRMS (EI): *m/z* for $C_{21}H_{17}F_5O_3$ $[M]^+$ calcd.: 412.1098, found: 412.1102.

Procedures for Derivatization of the Allylated Esters

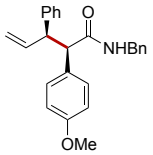


A) One-Pot Synthesis of Amide 4aa:

In a nitrogen-filled dry-box, the allyl *t*-butyl carbonate **2a** (23.4 mg, 0.100 mmol, 1.00 equiv) and aryl acetic acid ester **1a** (34.9 mg, 0.105 mmol, 1.05 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. Thereafter, *ent*-**[Ir]-1** (8 mM in THF, 0.25 mL, 0.002 mmol, 2 mol%) and (R)-BTM (40 mM in THF, 0.25 mL, 0.010 mmol, 10 mol%) were added sequentially via syringe. The vial was sealed with a cap containing PTFE/silicone septa, and the reaction mixture was stirred at r.t. for 6 h. Thereafter, DIPEA (26 μL, 0.150 mmol, 1.50 equiv) and benzylamine (14 μL, 0.130 mmol, 1.30 equiv) were added. The vial was removed from the dry box, and the reaction mixture was stirred at r.t. for another 12 h.

The mixture was diluted with 2 mL of hexanes, and filtered through a 0.5-inch plug of silica gel (eluting with 1:1 hexanes:EtOAc, 8 mL). After removal of solvent under vacuum, the crude mixture was purified by column chromatography performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns (4-gram silica gel column, 100/0 to 60/40 of hexanes/EtOAc).

(2*R*,3*R*)-*N*-benzyl-2-(4-methoxyphenyl)-3-phenylpent-4-enamide (4aa)



The diastereomeric ratio was determined to be >20:1. The title compound was obtained as a white solid (36.5 mg, 0.0983 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be 98% with t_R = 6.46 min (major) and t_R = 4.55 min (minor) [AD-H, 20.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –4.9^o (c 0.16, CH_2Cl_2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 3H), 7.10 – 7.06 (m, 2H), 7.06 – 7.00 (m, 4H), 6.99 – 6.94 (m, 1H), 6.94 – 6.90 (m, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 6.04 (ddd, *J* = 17.0, 10.3, 7.6 Hz, 1H), 5.82 (t, *J* =

5.7 Hz, 1H), 5.07 (d, J = 17.1 Hz, 1H), 5.02 (d, J = 10.3 Hz, 1H), 4.44 (dd, J = 14.8, 6.1 Hz, 1H), 4.19 (dd, J = 14.8, 5.2 Hz, 1H), 4.08 (dd, J = 10.8, 7.7 Hz, 1H), 3.61 (s, 3H), 3.52 (d, J = 10.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 158.6, 141.2, 139.8, 138.4, 130.0, 129.6, 128.7, 128.6, 128.3, 127.9, 127.5, 126.3, 116.2, 113.8, 58.2, 55.2, 53.0, 43.8.

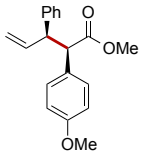
HRMS (EI): *m/z* for $C_{25}H_{25}NO_2$ $[M]^+$ calcd.: 371.1885, found: 371.1892.

B) One-Pot Synthesis of Methyl Ester 5aa:

In a nitrogen-filled dry-box, the allyl *t*-butyl carbonate **2a** (23.4 mg, 0.100 mmol, 1.00 equiv) and aryl acetic acid ester **1a** (34.9 mg, 0.105 mmol, 1.05 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. Thereafter, *ent*-**[Ir]-1** (8 mM in THF, 0.25 mL, 0.002 mmol, 2 mol%) and (R)-BTM (40 mM in THF, 0.25 mL, 0.010 mmol, 10 mol%) were added sequentially via syringe. The vial was sealed with a cap containing PTFE/silicone septa and removed from the dry box. The reaction mixture was stirred at r.t. for 6 h. Thereafter, DMAP (2.4 mg, 0.020 mmol, 0.20 equiv), triethylamine (70 μL, 0.50 mmol, 5.0 equiv) and 0.50 mL of MeOH were added. The reaction mixture was stirred at 65 ^{o}C for another 12 h.

The mixture was diluted with 2 mL of hexanes, and filtered through a 0.5-inch plug of silica gel (eluting with 1:1 hexanes:EtOAc, 8 mL). After removal of solvent under vacuum, the crude mixture was purified by column chromatography performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns (4-gram silica gel column, 100/0 to 85/15 of hexanes/EtOAc).

methyl (2*R*,3*R*)-2-(4-methoxyphenyl)-3-phenylpent-4-enoate (5aa)



The diastereomeric ratio was determined to be >20:1. The title compound was obtained as a colorless oil (29.1 mg, 0.0983 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.85 min (major) and t_R = 2.28 min (minor) [OJ-H, 5.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^{o}C].

$[\alpha]_D^{25}$ = –54.0^{o} (c 0.18, CH_2Cl_2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 4H), 7.08 – 7.03 (m, 1H), 7.01 – 6.98 (m, 2H), 6.67 (d, J = 8.7 Hz, 2H), 6.08 (ddd, J = 17.1, 10.3, 7.9 Hz, 1H), 5.18 (d, J = 17.1 Hz, 1H), 5.10 (d, J = 10.3 Hz, 1H), 4.01 (dd, J = 11.5, 7.9 Hz, 1H), 3.91 (d, J = 11.5 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 158.7, 140.7, 139.7, 129.8, 128.8, 128.4, 128.4, 126.5, 116.0, 113.8, 56.3, 55.2, 53.6, 52.0.

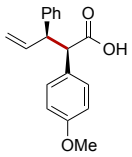
HRMS (EI): *m/z* for $C_{19}H_{20}O_3$ $[M]^+$ calcd.: 296.1412, found: 296.1416.

C) One-Pot Synthesis of Carboxylic Acid 6aa:

In a nitrogen-filled dry-box, the allyl *t*-butyl carbonate **2a** (23.4 mg, 0.100 mmol, 1.00 equiv) and aryl acetic acid ester **1a** (34.9 mg, 0.105 mmol, 1.05 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. Thereafter, *ent*-**[Ir]-1** (8 mM in THF, 0.25 mL, 0.002 mmol, 2 mol%) and (R)-BTM (40 mM in THF, 0.25 mL, 0.010 mmol, 10 mol%) were added sequentially via syringe. The vial was sealed with a cap containing PTFE/silicone septa and removed from the dry box. The reaction mixture was stirred at r.t. for 6 h. Thereafter, DMAP (2.4 mg, 0.020 mmol, 0.20 equiv), triethylamine (70 μL, 0.50 mmol, 5.0 equiv) and 0.50 mL of H_2O were added. The reaction mixture was stirred at 65 ^oC for another 12 h.

The mixture was acidified with aqueous HCl solution (1 M, 5 mL), and extracted with Et_2O (3 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude mixture was purified by column chromatography performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns (4-gram silica gel column, 100/0 to 50/50 of hexanes/EtOAc).

(2*R*,3*R*)-2-(4-methoxyphenyl)-3-phenylpent-4-enoic acid (6aa)



The diastereomeric ratio was determined to be 19:1. The title compound was obtained as a white solid (27.8 mg, 0.0985 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 4.77 min (major) and t_R = 5.36 min (minor) [AD-H, 10.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^oC].

$[\alpha]_D^{25}$ = –50.1^o (c 0.21, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 4H), 7.09 – 7.03 (m, 1H), 7.03 – 6.98 (m, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.10 (ddd, *J* = 17.6, 10.3, 7.7 Hz, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.01 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.2, 158.9, 140.4, 139.3, 129.8, 128.4, 128.4, 128.2, 126.6, 116.4, 113.8, 56.2, 55.2, 53.1.

HRMS (EI): *m/z* for $C_{18}H_{18}O_3$ $[M]^+$ calcd.: 282.1256, found: 282.1252.

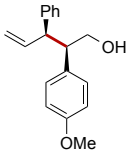
D) Synthesis of Primary Alcohol 7aa:

In a nitrogen-filled dry-box, the allyl *t*-butyl carbonate **2a** (23.4 mg, 0.100 mmol, 1.00 equiv) and aryl acetic acid ester **1a** (34.9 mg, 0.105 mmol, 1.05 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. Thereafter, *ent*-**[Ir]-1** (8 mM in THF, 0.25 mL, 0.002 mmol, 2 mol%) and (R)-BTM (40 mM in THF, 0.25 mL, 0.010 mmol, 10 mol%) were added sequentially via syringe. The vial was sealed with a cap containing PTFE/silicone septa and removed from the dry box. The reaction mixture was stirred at r.t. for 6 h. The mixture was diluted with 2 mL of hexanes, and filtered through a 0.5-inch plug of silica gel (eluting with 1:1 hexanes:EtOAc, 8 mL). After removal of solvent under vacuum, the crude mixture

was dissolved with dry THF (2 mL). Then $LiAlH_4$ (5.7 mg, 0.15 mmol, 1.5 equiv) was added under 0 ^oC. The reaction mixture was stirred at r.t. for another 12 h.

The mixture was quenched with aqueous HCl (1 M, 5 mL) under 0 ^oC, and extracted with Et_2O (3 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude mixture was purified by column chromatography performed on a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns (4-gram silica gel column, 100/0 to 65/35 of hexanes/EtOAc).

(2*R*,3*R*)-2-(4-methoxyphenyl)-3-phenylpent-4-en-1-ol (7aa)



The diastereomeric ratio was determined to be >20:1. The title compound was obtained as a colorless oil (26.4 mg, 0.0984 mmol, 98%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 4.14 min (major) and t_R = 5.03 min (minor) [AD-H, 10.0% ^{i}PrOH, 2.5 mL/min, 240 nm, 40 ^oC].

$[\alpha]_D^{25}$ = +53.0^o (c 0.34, CH_2Cl_2).

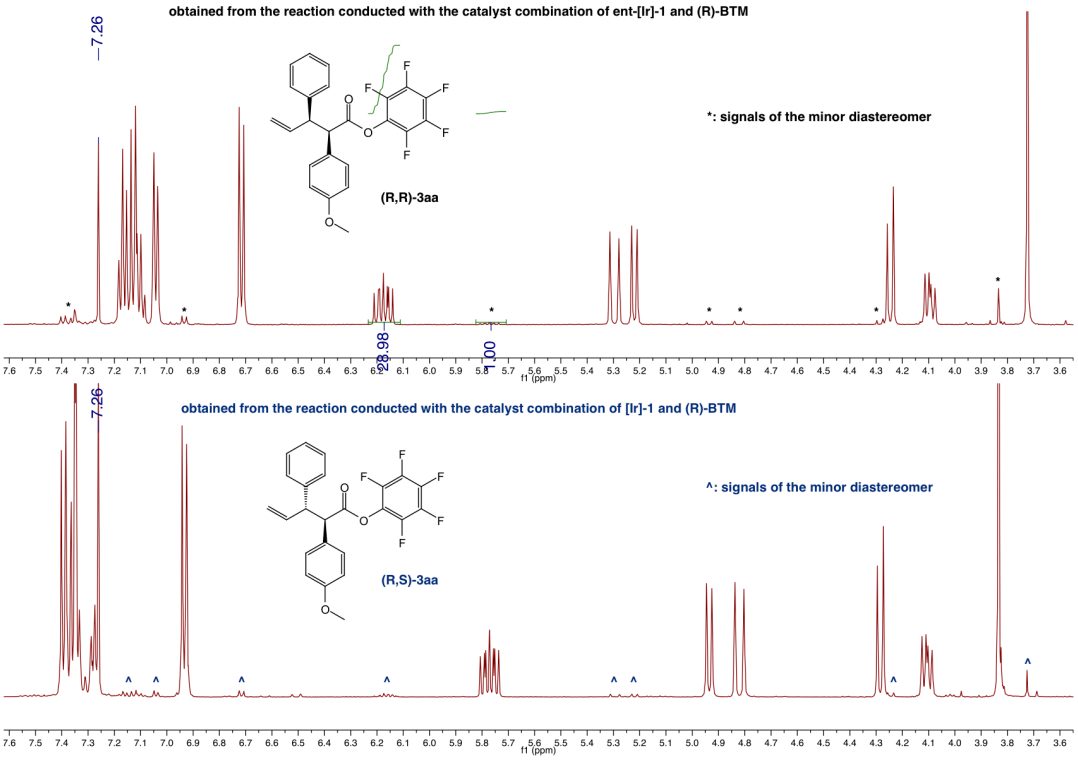
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 7.02 – 6.95 (m, 4H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.09 (dt, *J* = 16.9, 9.7 Hz, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 5.09 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.98 (dd, *J* = 11.1, 4.8 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.71 (s, 3H), 3.59 (t, *J* = 9.9 Hz, 1H), 3.16 (ddd, *J* = 10.4, 8.0, 4.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 142.5, 140.9, 132.2, 129.8, 128.3, 128.1, 126.2, 115.6, 113.9, 66.0, 55.2, 53.9, 52.1.

HRMS (EI): *m/z* for $C_{18}H_{20}O_2$ $[M]^+$ calcd.: 268.1463, found: 268.1465.

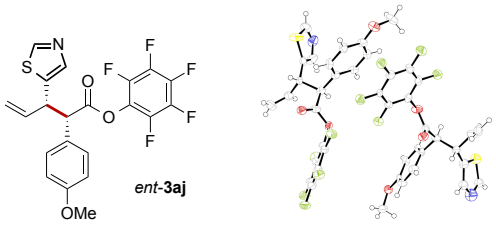
Comparison between ^{1}H NMR Spectra of (*R,R*)-3aa and (*R,S*)-3aa

In general, the product was obtained as a mixture of two diastereomers strongly favoring one diastereomer over the other. Small peaks in the ^{1}H NMR spectra of the allylation products are generally the signals of the minor diastereomers. For example, a comparison between ^{1}H NMR spectra of (*R,R*)-**3aa** and (*R,S*)-**3aa** is shown below.



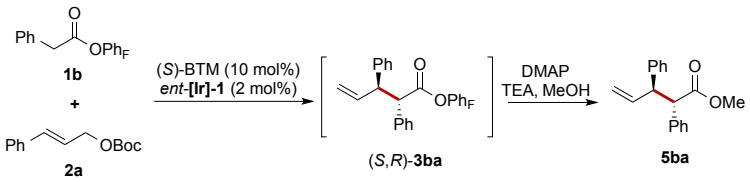
Determination of Absolute Configuration

1) Absolute configuration of the enantiomer of **3aj** was determined by X-ray analysis (see X-Ray Analysis Section for details).

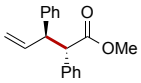


ent-**3aj**

2) The absolute configuration of (*S,R*)-**3ba** was assigned by converting it to the ester **5ba** following the procedure for the synthesis of **5aa** and comparing the optical rotation of this material with that reported by Corey and Lee.[8]



methyl (2*S*,3*R*)-2,3-diphenylpent-4-enoate (5ba)



The diastereomeric ratio was determined to be 18:1. The branched/linear selectivity was determined to be 7:1. The title compound was obtained as a white solid (26.9 mg, 0.100 mmol, >99%).

The **enantiomeric excess** was determined by SFC analysis to be >99% with t_R = 1.90 min (major) and t_R = 1.80 min (minor) [OJ-H, 5.0% ^{i}PrOH, 2.5 mL/min, 220 nm, 40 ^{o}C].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.37 – 7.27 (m, 7H), 7.25 – 7.22 (m, 1H), 5.72 (ddd, *J* = 17.5, 10.3, 7.7 Hz, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 4.75 (d, *J* = 17.0 Hz, 1H), 4.07 (dd, *J* = 11.7, 7.7 Hz, 1H), 3.98 (d, *J* = 11.6 Hz, 1H), 3.40 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 141.8, 138.7, 137.2, 129.0, 128.7, 128.7, 128.2, 127.7, 126.9, 116.9, 57.4, 53.2, 51.9.

HRMS (EI): *m/z* for $C_{18}H_{18}O_2$ $[M]^+$ calcd.: 266.1307, found: 266.1310.

$[\alpha]_D^{25}$ = +110.4^o (c 0.29, $CHCl_3$).

Lit[8]: $[\alpha]_D^{25}$ = +119.9^o (c 1.46, $CHCl_3$).

3) The absolute configurations of all other products shown in this paper were assigned by analogy.

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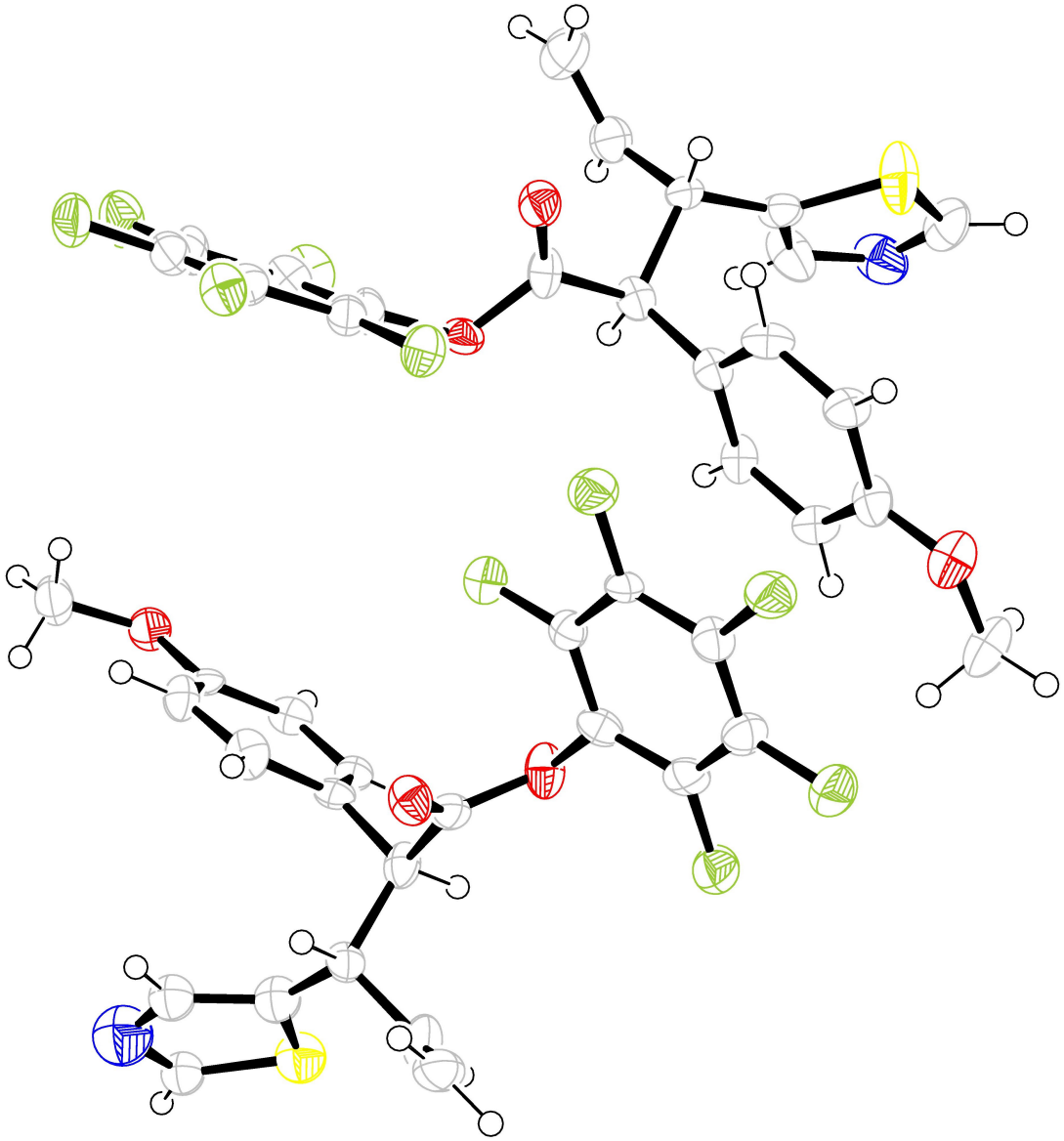
ent-3aj



A colorless rod 0.060 x 0.030 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.9% complete to 67.000° in θ. A total of 45422 reflections were collected covering the indices, -5<=*h*<=7, -32<=*k*<=32, -14<=*l*<=14. 6869 reflections were found to be symmetry independent, with an R_{int} of 0.0498. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2016). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2016. Absolute stereochemistry was unambiguously determined to be *S* at all chiral centers.

Table S5. Crystal data and structure refinement for *ent*-**3aj**.

X-ray ID	***ent*-3aj**	
Empirical formula	$C_{21}H_{14}F_5NO_3S$	
Formula weight	455.39	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.9674(3) Å	α= 90°.
	b = 26.9049(15) Å	β= 90.059(4)°.
	c = 12.1120(7) Å	γ = 90°.
Volume	1944.61(18) $Å^3$	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	2.148 mm^{-1}	
F(000)	928	
Crystal size	0.060 x 0.030 x 0.030 mm^3	
Theta range for data collection	3.285 to 68.579°.	
Index ranges	-5<=h<=7, -32<=k<=32, -14<=l<=14	
Reflections collected	45422	
Independent reflections	6869 [R(int) = 0.0498]	
Completeness to theta = 67.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.729	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6869 / 13 / 551	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1194	
R indices (all data)	R1 = 0.0548, wR2 = 0.1207	
Absolute structure parameter	0.038(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.449 and -0.331 $e.Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *ent*-**3aj**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3828(13)	6148(3)	-46(6)	27(2)
C(2)	5513(14)	6558(3)	-169(6)	32(2)
C(3)	7795(15)	6517(4)	-292(9)	49(2)
C(4)	7636(17)	7317(4)	-352(8)	47(2)
C(5)	4092(16)	5775(3)	-947(7)	39(2)
C(6)	2519(18)	5625(4)	-1639(9)	49(2)
C(7)	4089(13)	5877(3)	1120(7)	29(2)
C(8)	4265(13)	6238(3)	2070(6)	28(2)
C(9)	6229(13)	6272(3)	2659(7)	28(2)
C(10)	6559(13)	6619(3)	3484(6)	29(2)
C(11)	4823(14)	6952(3)	3736(7)	33(2)
C(12)	2828(14)	6918(3)	3148(7)	31(2)
C(13)	2568(13)	6572(3)	2297(6)	30(2)
C(14)	7019(16)	7390(3)	5046(8)	45(2)
C(15)	2131(15)	5528(3)	1235(7)	32(2)
C(16)	1188(15)	4711(3)	1707(7)	34(2)
C(17)	1582(14)	4290(3)	1053(7)	33(2)
C(18)	54(15)	3904(3)	1002(8)	34(2)
C(19)	-1876(15)	3938(3)	1608(7)	34(2)
C(20)	-2307(13)	4344(3)	2246(7)	31(2)
C(21)	-766(13)	4726(3)	2305(7)	29(2)
C(22)	8988(14)	4131(3)	7451(6)	29(2)
C(23)	10443(10)	3693(2)	7512(6)	40(2)
C(24)	12470(40)	2902(6)	7857(9)	37(3)
C(25)	12749(15)	3695(6)	7503(9)	50(2)
C(24A)	13270(30)	3008(7)	7711(9)	37(3)
C(25A)	9750(20)	3198(3)	7504(9)	39(1)
C(26)	9350(16)	4495(3)	8386(8)	40(2)
C(27)	7774(18)	4666(3)	9024(7)	43(2)
C(28)	9258(14)	4400(3)	6330(7)	31(2)
C(29)	9384(12)	4045(3)	5357(6)	24(2)

C(30)	11304(15)	4025(3)	4693(6)	30(2)
C(31)	11483(13)	3673(3)	3838(6)	30(2)
C(32)	9820(15)	3330(3)	3693(6)	27(2)
C(33)	7872(14)	3344(3)	4340(7)	33(2)
C(34)	7690(14)	3706(3)	5160(8)	38(2)
C(35)	8566(17)	2595(3)	2744(8)	43(2)
C(36)	7306(15)	4751(3)	6195(6)	31(2)
C(37)	6219(14)	5550(3)	5654(6)	29(2)
C(38)	6334(15)	5955(3)	6313(6)	31(2)
C(39)	4629(15)	6305(3)	6296(6)	33(2)
C(40)	2836(13)	6247(3)	5619(7)	31(2)
C(41)	2737(13)	5844(3)	4924(7)	28(2)
C(42)	4405(13)	5493(3)	4928(6)	26(2)
N(1)	8961(14)	6936(3)	-417(8)	52(2)
N(2)	13860(20)	3273(5)	7687(11)	37(4)
N(2A)	11150(40)	2843(3)	7605(11)	70(5)
O(1)	4898(10)	7307(2)	4511(5)	39(1)
O(2)	217(10)	5603(2)	973(5)	34(1)
O(3)	2786(9)	5083(2)	1687(4)	30(1)
O(4)	10192(11)	2993(2)	2840(5)	37(1)
O(5)	5402(10)	4668(2)	6446(5)	36(1)
O(6)	7928(9)	5192(2)	5698(5)	37(1)
F(1)	3432(9)	4271(2)	434(4)	44(1)
F(2)	462(10)	3515(2)	358(4)	47(1)
F(3)	-3410(8)	3573(2)	1528(4)	42(1)
F(4)	-4174(7)	4365(2)	2839(4)	33(1)
F(5)	-1168(8)	5115(2)	2967(4)	35(1)
F(6)	8060(9)	6008(2)	7024(4)	42(1)
F(7)	4755(9)	6699(2)	7000(4)	44(1)
F(8)	1182(8)	6583(2)	5600(4)	39(1)
F(9)	969(8)	5792(2)	4248(4)	39(1)
F(10)	4291(8)	5102(2)	4255(4)	38(1)
S(1)	4837(4)	7171(1)	-175(3)	56(1)
S(2)	9631(9)	3108(2)	7775(4)	39(1)
S(2A)	13246(8)	3633(2)	7671(4)	50(2)

Table S7. Bond lengths [Å] and angles [°] for *ent*-**3aj**.

C(1)-C(5)	1.491(12)	C(15)-O(3)	1.374(9)
C(1)-C(2)	1.500(10)	C(16)-C(21)	1.374(12)
C(1)-C(7)	1.596(10)	C(16)-O(3)	1.383(10)
C(1)-H(1)	1.0000	C(16)-C(17)	1.401(11)
C(2)-C(3)	1.375(12)	C(17)-F(1)	1.336(9)
C(2)-S(1)	1.698(8)	C(17)-C(18)	1.384(11)
C(3)-N(1)	1.335(12)	C(18)-F(2)	1.326(9)
C(3)-H(3)	0.9500	C(18)-C(19)	1.370(12)
C(4)-N(1)	1.296(13)	C(19)-F(3)	1.347(9)
C(4)-S(1)	1.729(10)	C(19)-C(20)	1.363(12)
C(4)-H(4)	0.9500	C(20)-F(4)	1.327(9)
C(5)-C(6)	1.321(13)	C(20)-C(21)	1.380(11)
C(5)-H(5)	0.9500	C(21)-F(5)	1.341(9)
C(6)-H(6A)	0.9500	C(22)-C(23)	1.466(9)
C(6)-H(6B)	0.9500	C(22)-C(26)	1.512(11)
C(7)-C(15)	1.506(11)	C(22)-C(28)	1.547(11)
C(7)-C(8)	1.508(11)	C(22)-H(22)	1.0000
C(7)-H(7)	1.0000	C(23)-C(25)	1.376(7)
C(8)-C(9)	1.374(11)	C(23)-C(25A)	1.395(7)
C(8)-C(13)	1.383(10)	C(23)-S(2)	1.679(6)
C(9)-C(10)	1.381(11)	C(23)-S(2A)	1.691(6)
C(9)-H(9)	0.9500	C(24a)-N(2)	1.315(7)
C(10)-C(11)	1.403(11)	C(24a)-S(2)	1.78(2)
C(10)-H(10)	0.9500	C(24a)-H(24)	0.9500
C(11)-O(1)	1.340(10)	C(25a)-N(2)	1.334(7)
C(11)-C(12)	1.389(12)	C(25a)-H(25)	0.9500
C(12)-C(13)	1.397(11)	C(24Ab)-N(2A)	1.35(3)
C(12)-H(12)	0.9500	C(24Ab)-S(2A)	1.683(19)
C(13)-H(13)	0.9500	C(24Ab)-H(24A)	0.9500
C(14)-O(1)	1.438(11)	C(25Ab)-N(2A)	1.276(19)
C(14)-H(14A)	0.9800	C(25Ab)-H(25A)	0.9500
C(14)-H(14B)	0.9800	C(26)-C(27)	1.302(13)
C(14)-H(14C)	0.9800	C(26)-H(26)	0.9500
C(15)-O(2)	1.202(10)	C(27)-H(27A)	0.9500

C(27)-H(27B)	0.9500	C(35)-H(35B)	0.9800
C(28)-C(36)	1.508(11)	C(35)-H(35C)	0.9800
C(28)-C(29)	1.519(10)	C(36)-O(5)	1.198(10)
C(28)-H(28)	1.0000	C(36)-O(6)	1.381(9)
C(29)-C(34)	1.384(11)	C(37)-C(38)	1.354(11)
C(29)-C(30)	1.402(11)	C(37)-O(6)	1.403(9)
C(30)-C(31)	1.408(11)	C(37)-C(42)	1.403(11)
C(30)-H(30)	0.9500	C(38)-F(6)	1.350(10)
C(31)-C(32)	1.366(11)	C(38)-C(39)	1.386(12)
C(31)-H(31)	0.9500	C(39)-C(40)	1.357(12)
C(32)-O(4)	1.392(9)	C(39)-F(7)	1.362(9)
C(32)-C(33)	1.403(11)	C(40)-F(8)	1.338(9)
C(33)-C(34)	1.395(12)	C(40)-C(41)	1.373(11)
C(33)-H(33)	0.9500	C(41)-F(9)	1.342(9)
C(34)-H(34)	0.9500	C(41)-C(42)	1.373(11)
C(35)-O(4)	1.449(10)	C(42)-F(10)	1.332(8)
C(35)-H(35A)	0.9800		

C(5)-C(1)-C(2)	110.5(7)	C(5)-C(6)-H(6A)	120.0
C(5)-C(1)-C(7)	109.3(6)	C(5)-C(6)-H(6B)	120.0
C(2)-C(1)-C(7)	111.0(6)	H(6A)-C(6)-H(6B)	120.0
C(5)-C(1)-H(1)	108.7	C(15)-C(7)-C(8)	112.6(7)
C(2)-C(1)-H(1)	108.7	C(15)-C(7)-C(1)	107.0(7)
C(7)-C(1)-H(1)	108.7	C(8)-C(7)-C(1)	112.9(6)
C(3)-C(2)-C(1)	128.0(8)	C(15)-C(7)-H(7)	108.1
C(3)-C(2)-S(1)	108.2(6)	C(8)-C(7)-H(7)	108.1
C(1)-C(2)-S(1)	123.8(6)	C(1)-C(7)-H(7)	108.1
N(1)-C(3)-C(2)	117.5(9)	C(9)-C(8)-C(13)	118.5(7)
N(1)-C(3)-H(3)	121.3	C(9)-C(8)-C(7)	119.9(7)
C(2)-C(3)-H(3)	121.3	C(13)-C(8)-C(7)	121.3(7)
N(1)-C(4)-S(1)	114.7(7)	C(8)-C(9)-C(10)	122.8(7)
N(1)-C(4)-H(4)	122.6	C(8)-C(9)-H(9)	118.6
S(1)-C(4)-H(4)	122.6	C(10)-C(9)-H(9)	118.6
C(6)-C(5)-C(1)	126.4(9)	C(9)-C(10)-C(11)	119.0(8)
C(6)-C(5)-H(5)	116.8	C(9)-C(10)-H(10)	120.5
C(1)-C(5)-H(5)	116.8	C(11)-C(10)-H(10)	120.5

O(1)-C(11)-C(12)	115.7(7)	C(23)-C(22)-C(26)	113.5(7)
O(1)-C(11)-C(10)	125.7(8)	C(23)-C(22)-C(28)	111.0(6)
C(12)-C(11)-C(10)	118.6(8)	C(26)-C(22)-C(28)	109.9(6)
C(11)-C(12)-C(13)	121.1(7)	C(23)-C(22)-H(22)	107.4
C(11)-C(12)-H(12)	119.5	C(26)-C(22)-H(22)	107.4
C(13)-C(12)-H(12)	119.5	C(28)-C(22)-H(22)	107.4
C(8)-C(13)-C(12)	120.0(7)	C(25a)-C(23)-C(22)	126.0(8)
C(8)-C(13)-H(13)	120.0	C(25Ab)-C(23)-C(22)	126.2(8)
C(12)-C(13)-H(13)	120.0	C(25a)-C(23)-S(2)	107.1(8)
O(1)-C(14)-H(14A)	109.5	C(22)-C(23)-S(2)	126.4(5)
O(1)-C(14)-H(14B)	109.5	C(25Ab)-C(23)-S(2A)	101.8(8)
H(14A)-C(14)-H(14B)	109.5	C(22)-C(23)-S(2A)	132.0(5)
O(1)-C(14)-H(14C)	109.5	N(2a)-C(24a)-S(2)	110.9(14)
H(14A)-C(14)-H(14C)	109.5	N(2a)-C(24a)-H(24)	124.6
H(14B)-C(14)-H(14C)	109.5	S(2a)-C(24a)-H(24)	124.6
O(2)-C(15)-O(3)	121.5(7)	N(2a)-C(25a)-C(23)	119.5(13)
O(2)-C(15)-C(7)	127.4(7)	N(2a)-C(25a)-H(25)	120.3
O(3)-C(15)-C(7)	111.1(7)	C(23)-C(25a)-H(25)	120.3
C(21)-C(16)-O(3)	125.0(7)	N(2Ab)-C(24Ab)-S(2A)	108.3(11)
C(21)-C(16)-C(17)	117.7(7)	N(2Ab)-C(24Ab)-H(24A)	125.8
O(3)-C(16)-C(17)	117.3(7)	S(2Ab)-C(24Ab)-H(24A)	125.8
F(1)-C(17)-C(18)	119.4(7)	N(2Ab)-C(25Ab)-C(23)	121.2(14)
F(1)-C(17)-C(16)	119.2(7)	N(2Ab)-C(25Ab)-H(25A)	119.4
C(18)-C(17)-C(16)	121.4(7)	C(23)-C(25Ab)-H(25A)	119.4
F(2)-C(18)-C(19)	121.5(7)	C(27)-C(26)-C(22)	124.8(9)
F(2)-C(18)-C(17)	119.8(8)	C(27)-C(26)-H(26)	117.6
C(19)-C(18)-C(17)	118.7(7)	C(22)-C(26)-H(26)	117.6
F(3)-C(19)-C(20)	119.8(8)	C(26)-C(27)-H(27A)	120.0
F(3)-C(19)-C(18)	119.0(7)	C(26)-C(27)-H(27B)	120.0
C(20)-C(19)-C(18)	121.2(8)	H(27A)-C(27)-H(27B)	120.0
F(4)-C(20)-C(19)	120.0(7)	C(36)-C(28)-C(29)	110.3(6)
F(4)-C(20)-C(21)	120.0(7)	C(36)-C(28)-C(22)	107.9(7)
C(19)-C(20)-C(21)	120.0(8)	C(29)-C(28)-C(22)	113.1(6)
F(5)-C(21)-C(16)	119.4(7)	C(36)-C(28)-H(28)	108.4
F(5)-C(21)-C(20)	119.5(7)	C(29)-C(28)-H(28)	108.4
C(16)-C(21)-C(20)	121.1(7)	C(22)-C(28)-H(28)	108.4

C(34)-C(29)-C(30)	118.2(7)	C(38)-C(37)-C(42)	119.7(7)
C(34)-C(29)-C(28)	120.8(7)	O(6)-C(37)-C(42)	120.6(7)
C(30)-C(29)-C(28)	120.8(7)	F(6)-C(38)-C(37)	119.9(7)
C(29)-C(30)-C(31)	120.7(7)	F(6)-C(38)-C(39)	119.9(7)
C(29)-C(30)-H(30)	119.6	C(37)-C(38)-C(39)	120.1(8)
C(31)-C(30)-H(30)	119.6	C(40)-C(39)-F(7)	120.7(7)
C(32)-C(31)-C(30)	119.6(7)	C(40)-C(39)-C(38)	120.6(7)
C(32)-C(31)-H(31)	120.2	F(7)-C(39)-C(38)	118.6(8)
C(30)-C(31)-H(31)	120.2	F(8)-C(40)-C(39)	120.9(7)
C(31)-C(32)-O(4)	114.7(7)	F(8)-C(40)-C(41)	119.4(7)
C(31)-C(32)-C(33)	120.8(7)	C(39)-C(40)-C(41)	119.6(7)
O(4)-C(32)-C(33)	124.4(7)	F(9)-C(41)-C(42)	120.0(7)
C(34)-C(33)-C(32)	118.8(7)	F(9)-C(41)-C(40)	119.3(7)
C(34)-C(33)-H(33)	120.6	C(42)-C(41)-C(40)	120.7(7)
C(32)-C(33)-H(33)	120.6	F(10)-C(42)-C(41)	120.4(7)
C(29)-C(34)-C(33)	121.8(8)	F(10)-C(42)-C(37)	120.5(7)
C(29)-C(34)-H(34)	119.1	C(41)-C(42)-C(37)	119.1(7)
C(33)-C(34)-H(34)	119.1	C(4)-N(1)-C(3)	110.0(8)
O(4)-C(35)-H(35A)	109.5	C(24a)-N(2a)-C(25)	111.0(15)
O(4)-C(35)-H(35B)	109.5	C(25Ab)-N(2Ab)-C(24A)	112.4(11)
H(35A)-C(35)-H(35B)	109.5	C(11)-O(1)-C(14)	117.1(6)
O(4)-C(35)-H(35C)	109.5	C(15)-O(3)-C(16)	116.2(6)
H(35A)-C(35)-H(35C)	109.5	C(32)-O(4)-C(35)	115.7(7)
H(35B)-C(35)-H(35C)	109.5	C(36)-O(6)-C(37)	114.2(6)
O(5)-C(36)-O(6)	121.7(8)	C(2)-S(1)-C(4)	89.5(4)
O(5)-C(36)-C(28)	126.0(7)	C(23)-S(2a)-C(24)	91.5(6)
O(6)-C(36)-C(28)	112.2(7)	C(24Ab)-S(2Ab)-C(23)	96.3(6)
C(38)-C(37)-O(6)	119.6(8)		

Symmetry transformations used to generate equivalent atoms:

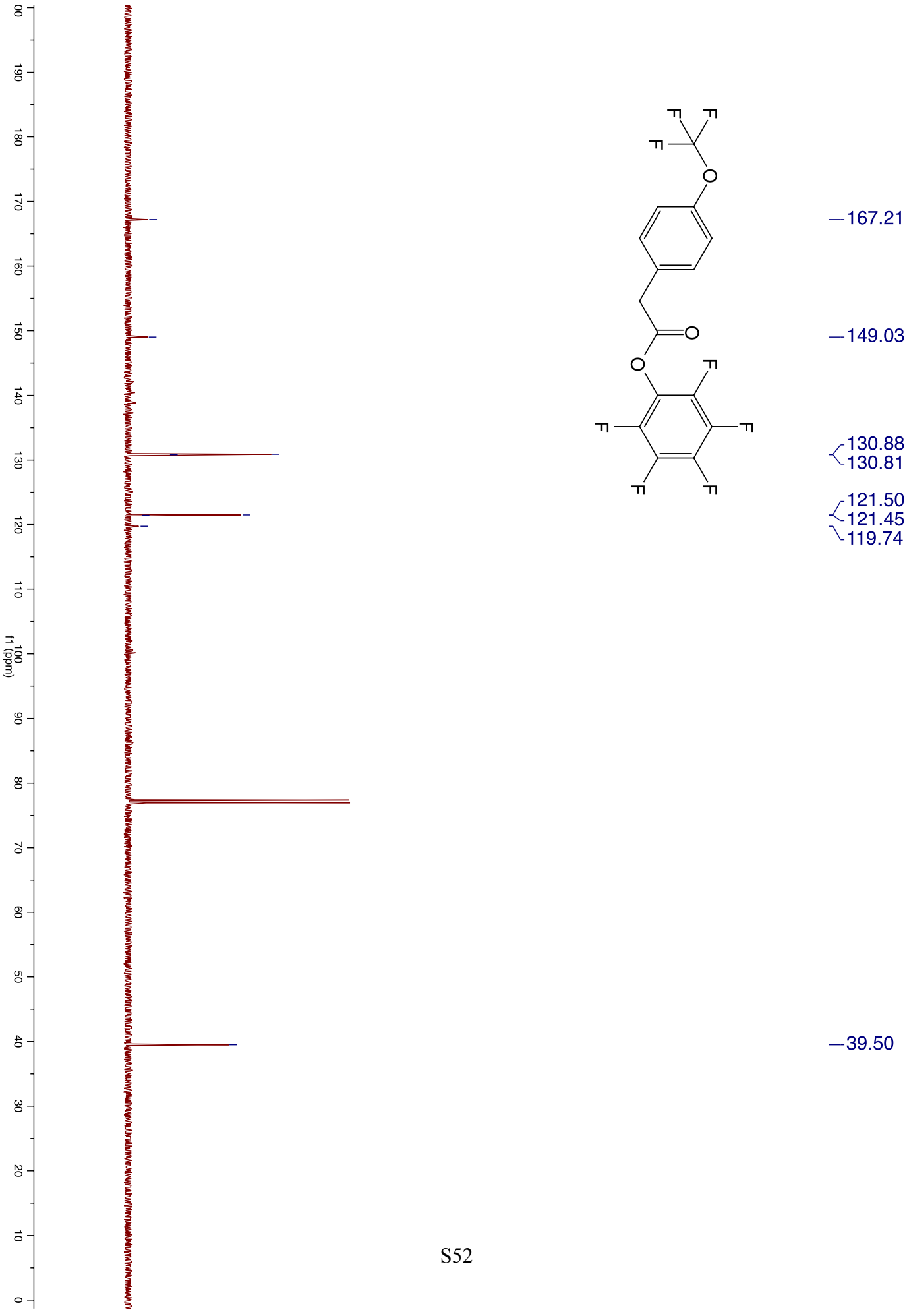
Table S8. Anisotropic displacement parameters ($Å^2$x 10^3)for *ent*-**3aj**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(4)	28(4)	24(4)	1(3)	-5(3)	-3(3)
C(2)	32(4)	41(4)	22(4)	4(3)	-3(3)	-8(3)
C(3)	24(4)	45(5)	77(7)	23(5)	5(5)	4(4)
C(4)	47(6)	50(5)	44(5)	1(4)	6(5)	-25(4)
C(5)	39(5)	39(4)	39(5)	6(4)	1(4)	-10(4)
C(6)	47(6)	54(6)	46(6)	-5(4)	1(5)	-16(5)
C(7)	21(4)	28(4)	39(4)	3(3)	3(4)	2(3)
C(8)	22(4)	27(4)	35(4)	3(3)	3(3)	2(3)
C(9)	20(4)	24(3)	40(4)	-2(3)	10(4)	0(3)
C(10)	19(4)	40(4)	27(4)	0(3)	3(3)	2(3)
C(11)	18(4)	28(4)	52(5)	2(4)	2(4)	-4(3)
C(12)	22(4)	36(4)	34(4)	-1(3)	-2(4)	6(3)
C(13)	18(4)	47(5)	25(4)	2(4)	1(3)	5(3)
C(14)	34(5)	44(5)	58(6)	-25(4)	5(5)	-4(4)
C(15)	31(5)	24(4)	40(5)	-3(3)	9(4)	-5(3)
C(16)	39(5)	19(3)	42(5)	2(3)	-2(4)	-2(3)
C(17)	27(4)	36(4)	36(4)	6(3)	9(4)	5(3)
C(18)	35(5)	16(3)	50(5)	-1(3)	-4(4)	5(3)
C(19)	31(5)	28(4)	43(5)	7(3)	-6(4)	-2(3)
C(20)	19(4)	34(4)	41(5)	6(4)	-8(4)	0(3)
C(21)	27(4)	25(3)	34(4)	1(3)	-6(4)	0(3)
C(22)	24(4)	27(4)	37(4)	4(3)	-10(4)	2(3)
C(26)	42(5)	31(4)	47(5)	-5(4)	9(4)	-9(4)
C(27)	58(6)	40(5)	30(5)	-3(4)	-3(4)	8(4)
C(28)	21(4)	26(4)	45(5)	-2(3)	-3(4)	-2(3)
C(29)	18(4)	31(4)	23(4)	5(3)	-3(3)	3(3)
C(30)	41(5)	30(4)	18(3)	2(3)	2(4)	-4(3)
C(31)	18(4)	42(4)	29(4)	6(3)	4(3)	1(3)
C(32)	43(5)	29(4)	11(3)	-1(3)	-4(3)	0(3)
C(33)	30(4)	27(4)	42(5)	0(3)	2(4)	-5(3)
C(34)	21(4)	40(4)	52(5)	4(4)	3(4)	-2(3)

C(35)	55(6)	29(4)	45(5)	1(4)	4(5)	-3(4)
C(36)	36(5)	36(4)	22(4)	2(3)	-2(4)	-8(4)
C(37)	27(4)	35(4)	24(4)	6(3)	4(3)	4(3)
C(38)	34(5)	40(4)	18(4)	4(3)	5(3)	-6(4)
C(39)	38(5)	35(4)	26(4)	-5(3)	2(4)	0(4)
C(40)	23(4)	30(4)	39(4)	3(3)	-3(4)	2(3)
C(41)	29(4)	27(4)	28(4)	7(3)	-14(3)	-5(3)
C(42)	23(4)	26(3)	28(4)	2(3)	2(3)	-3(3)
N(1)	37(5)	58(5)	61(5)	21(4)	1(4)	-10(4)
O(1)	24(3)	42(3)	52(4)	-12(3)	8(3)	-3(2)
O(2)	25(3)	31(3)	46(3)	2(2)	-2(3)	-3(2)
O(3)	25(3)	33(3)	31(3)	8(2)	-5(2)	-2(2)
O(4)	43(4)	36(3)	32(3)	-1(2)	5(3)	-1(3)
O(5)	29(3)	35(3)	43(3)	6(3)	4(3)	-5(2)
O(6)	28(3)	27(3)	56(4)	-3(3)	7(3)	2(2)
F(1)	34(3)	44(3)	53(3)	3(2)	12(2)	7(2)
F(2)	63(4)	29(2)	49(3)	-4(2)	8(3)	5(2)
F(3)	40(3)	29(2)	55(3)	5(2)	-4(3)	-10(2)
F(4)	22(2)	35(2)	44(3)	4(2)	7(2)	-1(2)
F(5)	33(3)	32(2)	39(3)	-5(2)	5(2)	-1(2)
F(6)	41(3)	38(3)	47(3)	0(2)	-8(3)	-1(2)
F(7)	52(3)	36(2)	44(3)	-9(2)	-4(3)	2(2)
F(8)	36(3)	40(3)	42(3)	-1(2)	-8(2)	8(2)
F(9)	35(3)	44(3)	39(3)	3(2)	-4(2)	-6(2)
F(10)	42(3)	32(2)	41(3)	-1(2)	-2(2)	-2(2)
S(1)	45(1)	29(1)	93(2)	-1(1)	19(1)	-7(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for *ent*-**3aj**.

	x	y	z	U(eq)
H(1)	2290	6294	-94	33
H(3)	8515	6202	-289	58
H(4)	8160	7650	-398	57
H(5)	5534	5630	-1031	47
H(6A)	1049	5759	-1589	59
H(6B)	2857	5384	-2188	59
H(7)	5492	5674	1101	35
H(9)	7409	6047	2492	34
H(10)	7939	6632	3874	34
H(12)	1621	7133	3328	37
H(13)	1225	6567	1875	36
H(14A)	7502	7084	5416	68
H(14B)	6863	7657	5591	68
H(14C)	8137	7486	4493	68
H(22)	7404	4012	7498	35
H(24)	12913	2570	8003	44
H(25)	13542	3995	7366	59
H(24A)	14567	2805	7795	44
H(25A)	8199	3124	7421	47
H(26)	10837	4606	8518	48
H(27A)	6267	4563	8917	52
H(27B)	8132	4894	9596	52
H(28)	10669	4600	6353	37
H(30)	12498	4251	4821	35
H(31)	12752	3673	3365	35
H(33)	6699	3111	4221	40
H(34)	6367	3719	5595	45
H(35A)	8341	2441	3468	65
H(35B)	9117	2346	2221	65
H(35C)	7140	2731	2477	65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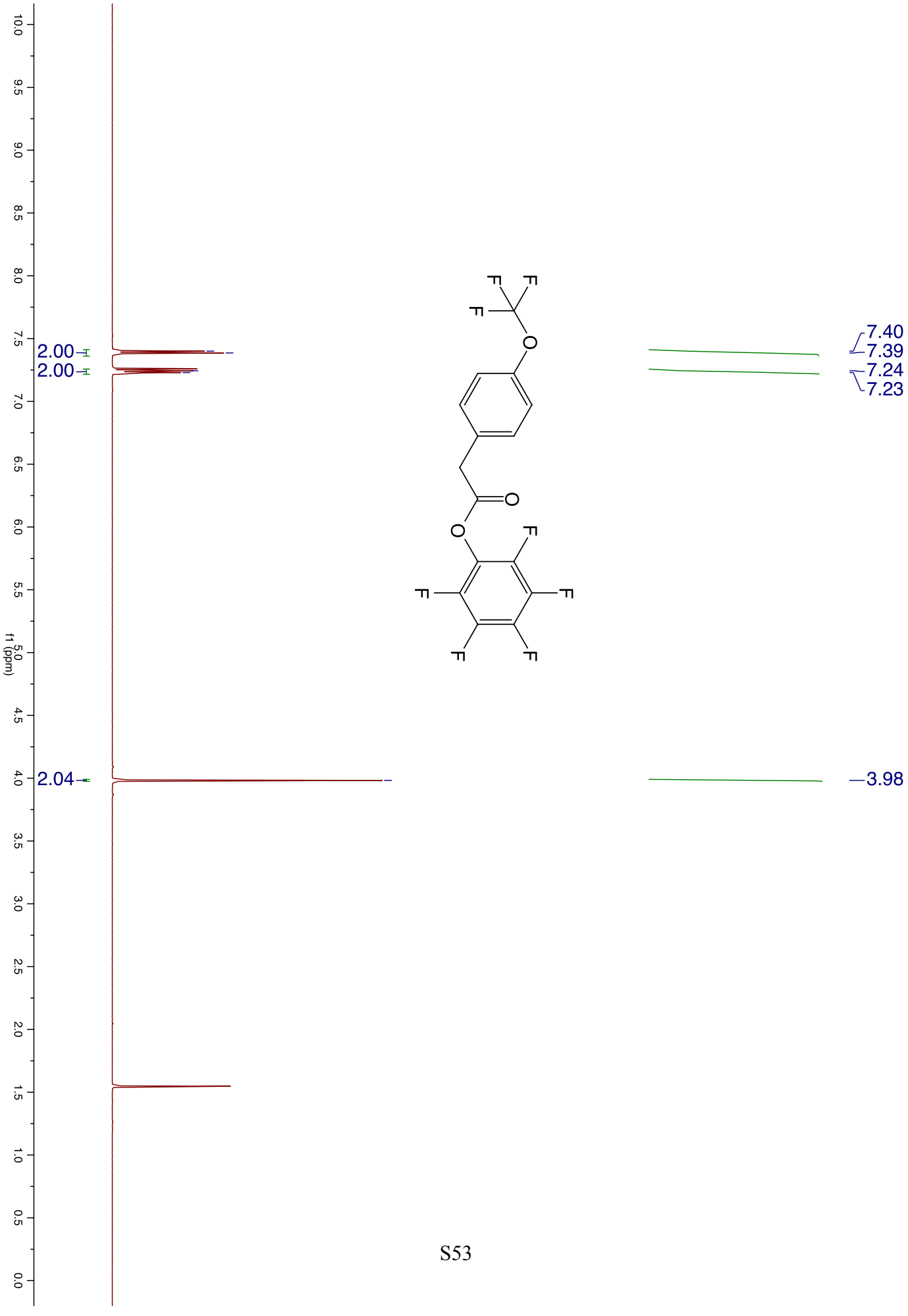
f1 (ppm)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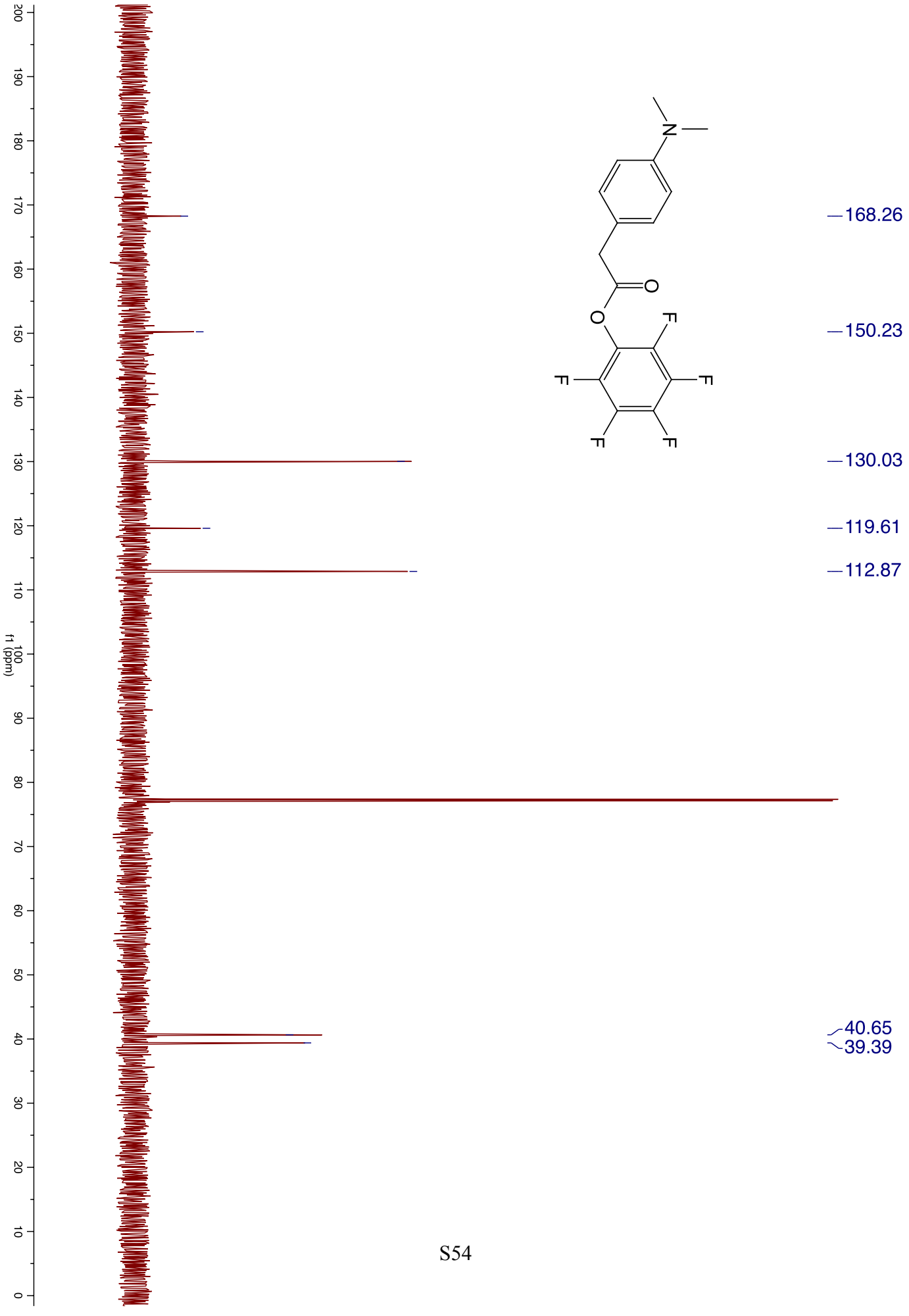
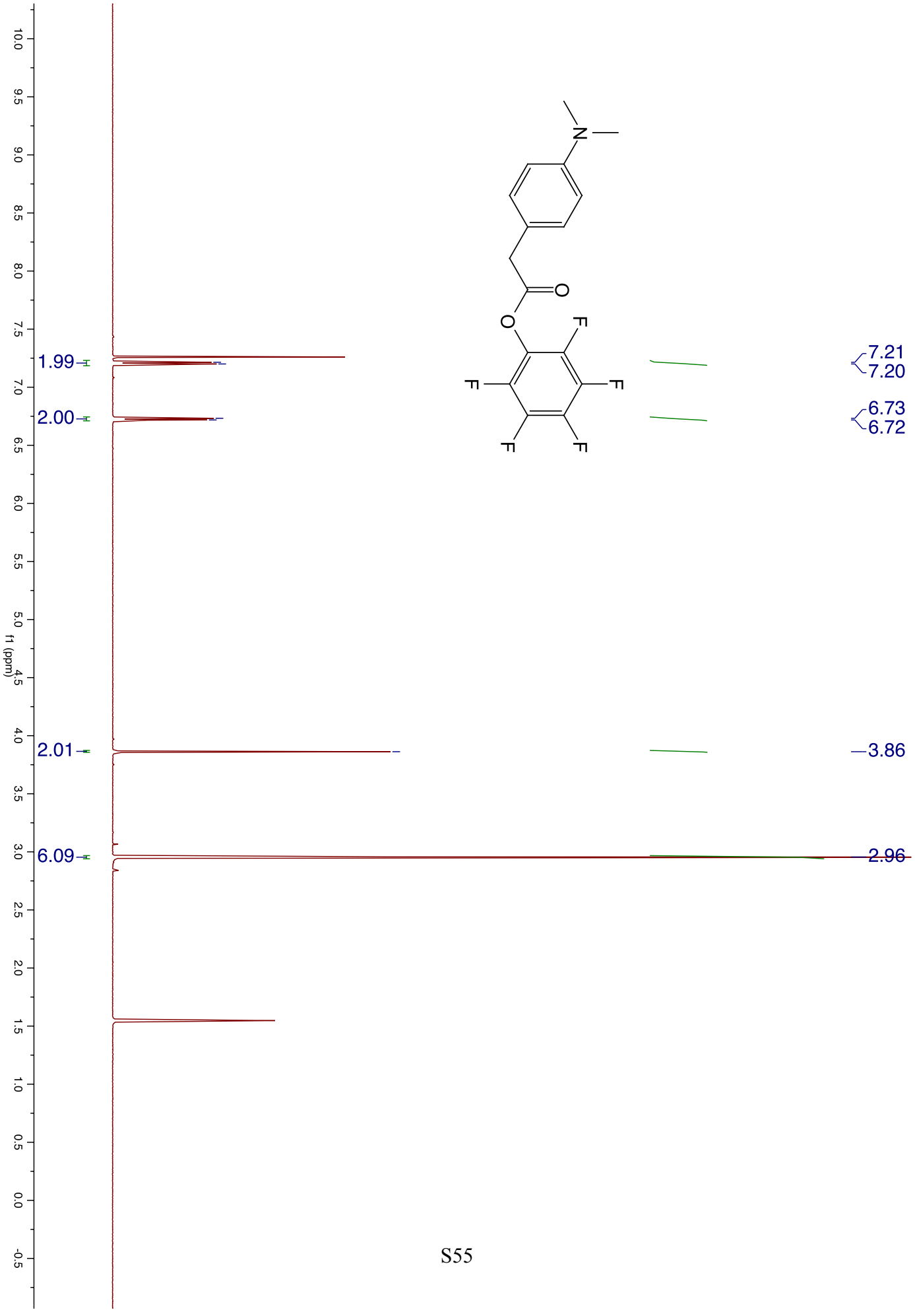
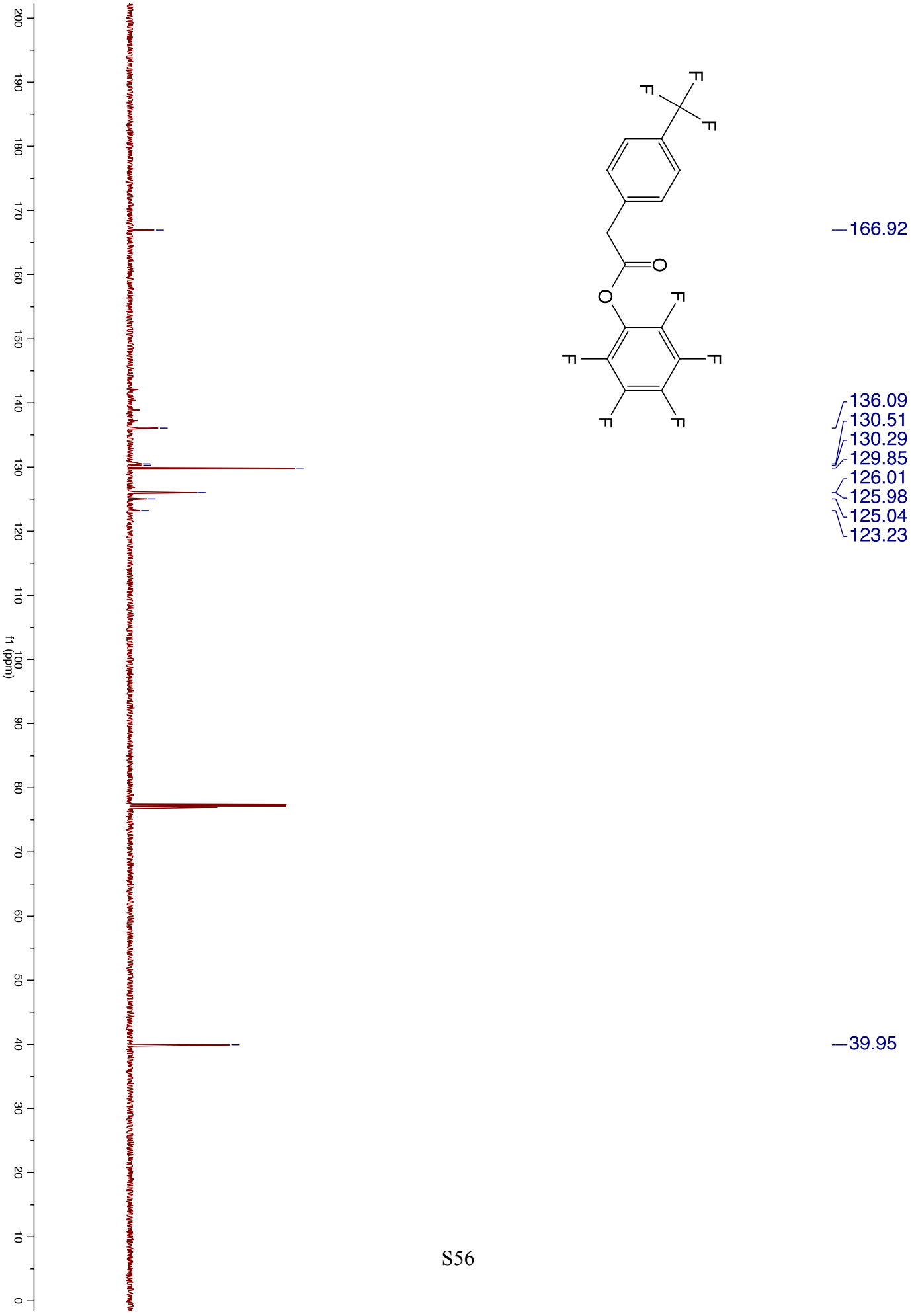
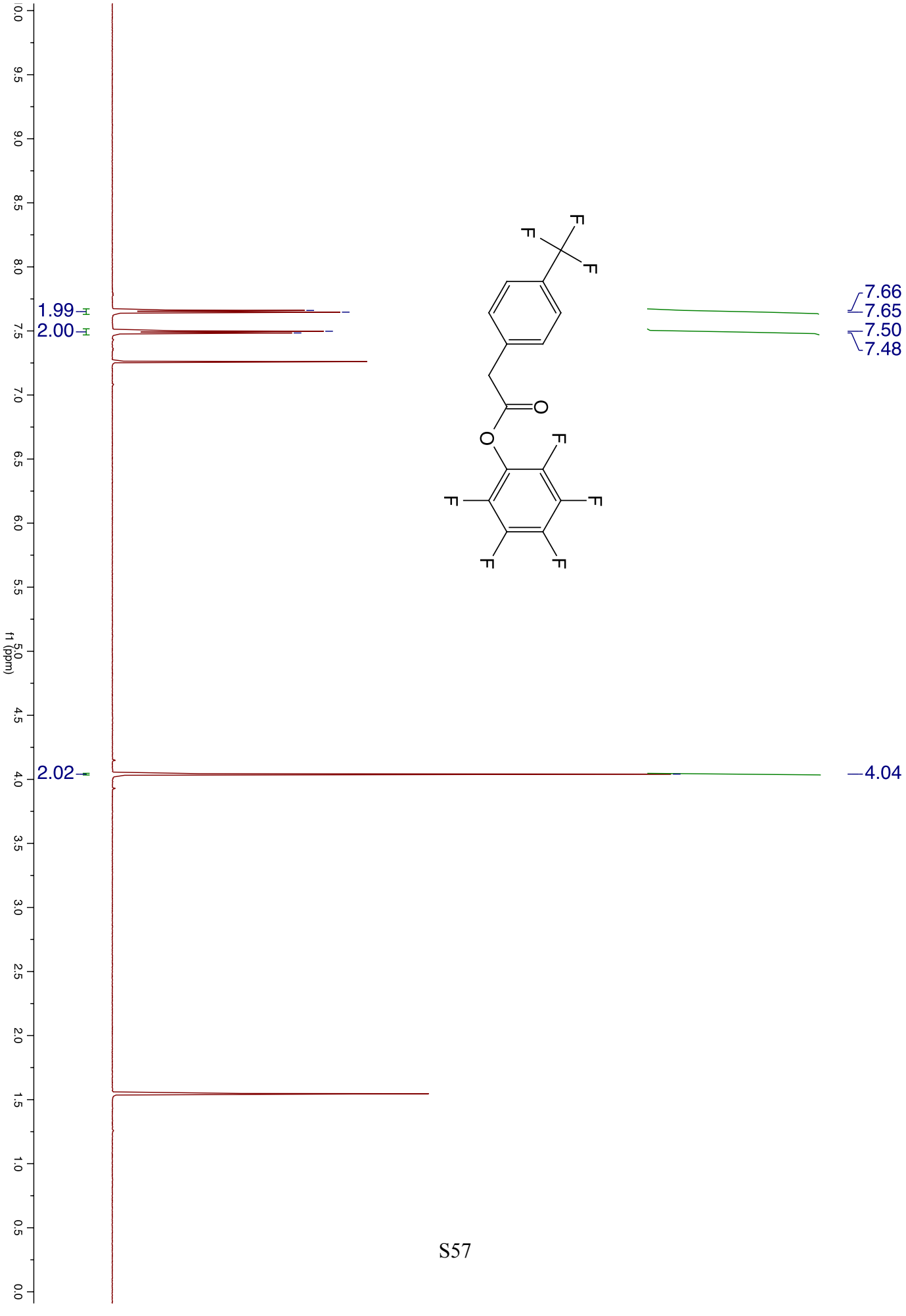
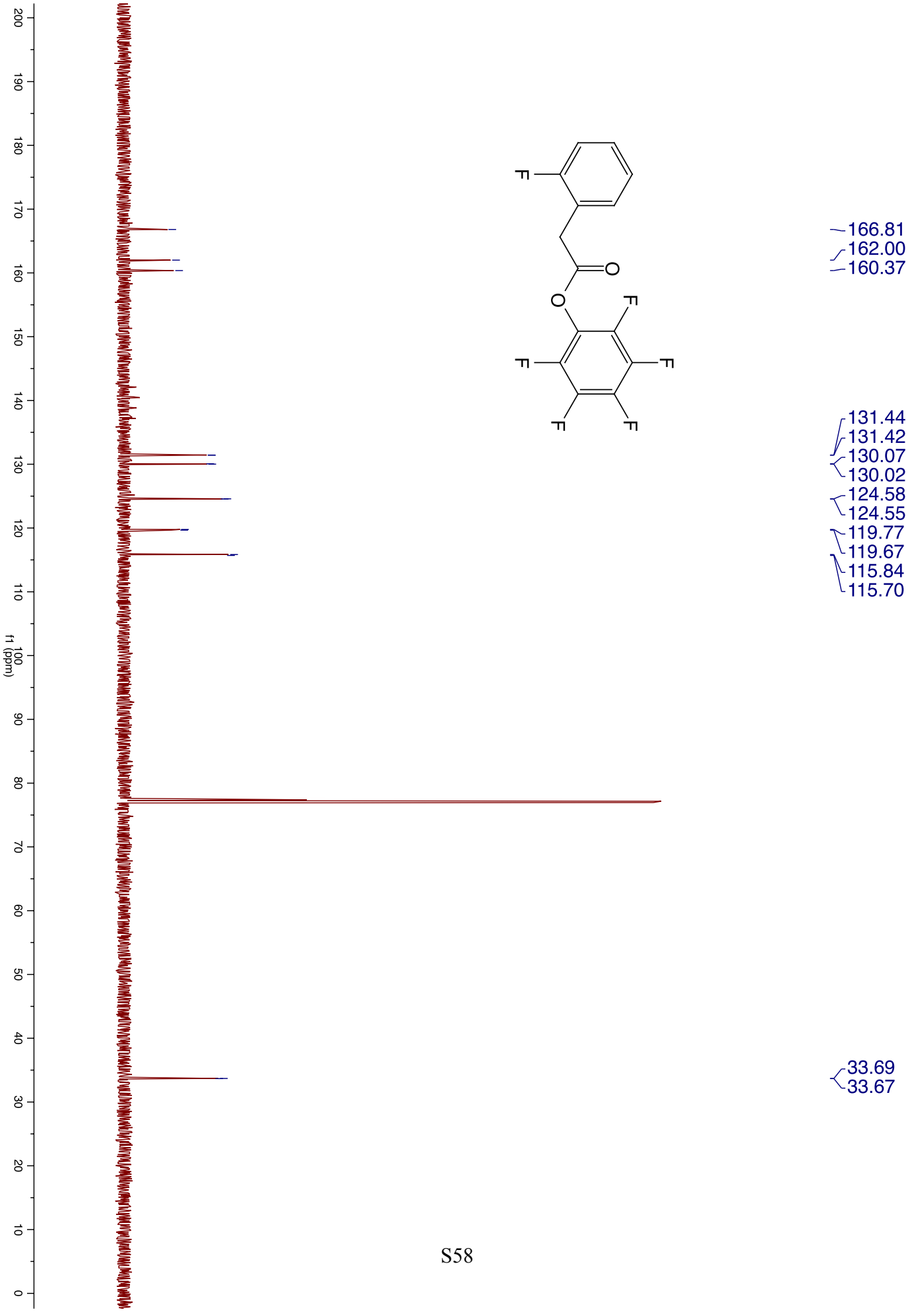
7.24
7.23
3.98
f1 (ppm)

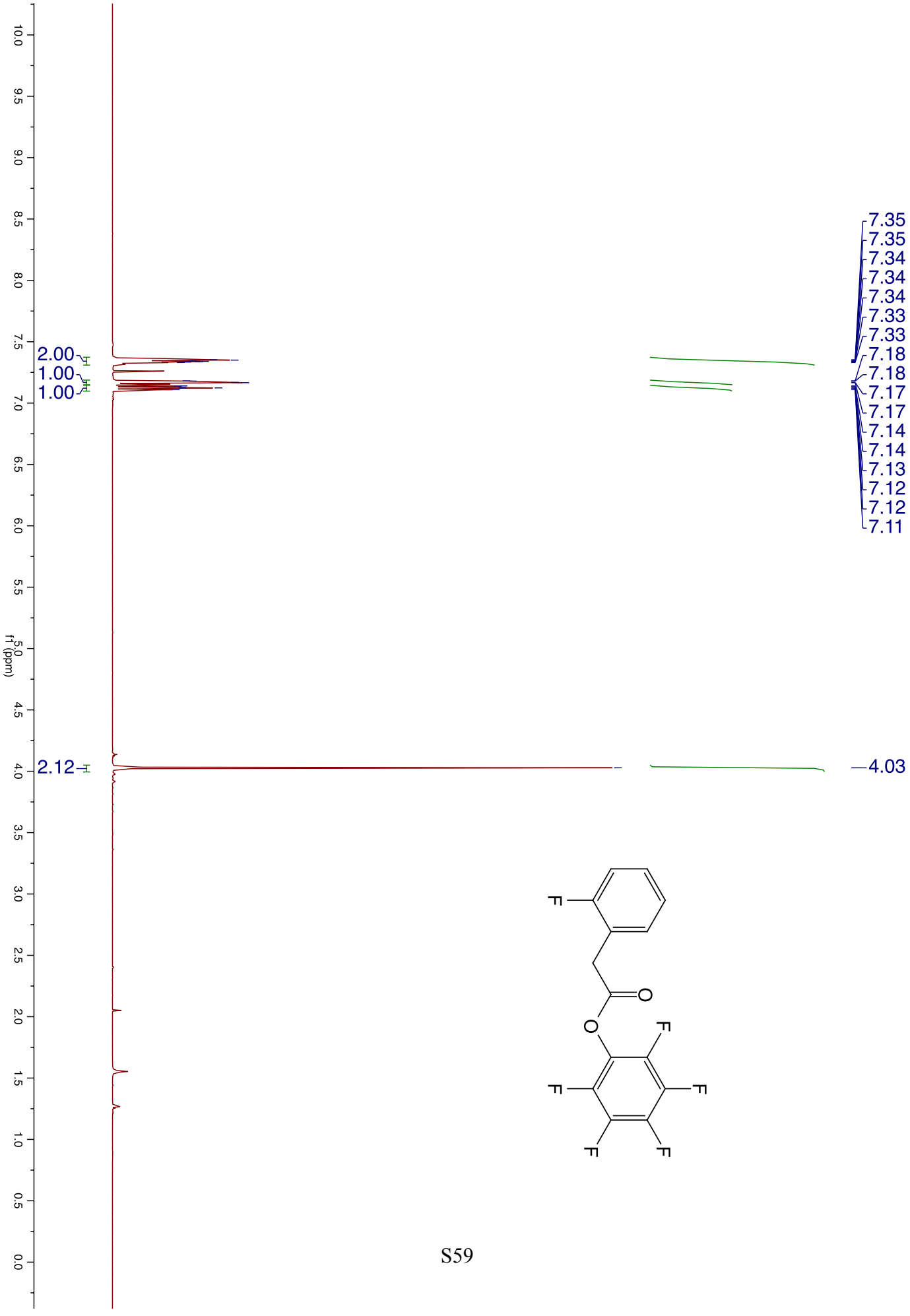

168.26
150.23
130.03
119.61
112.87
40.65
39.39
f1 (ppm)

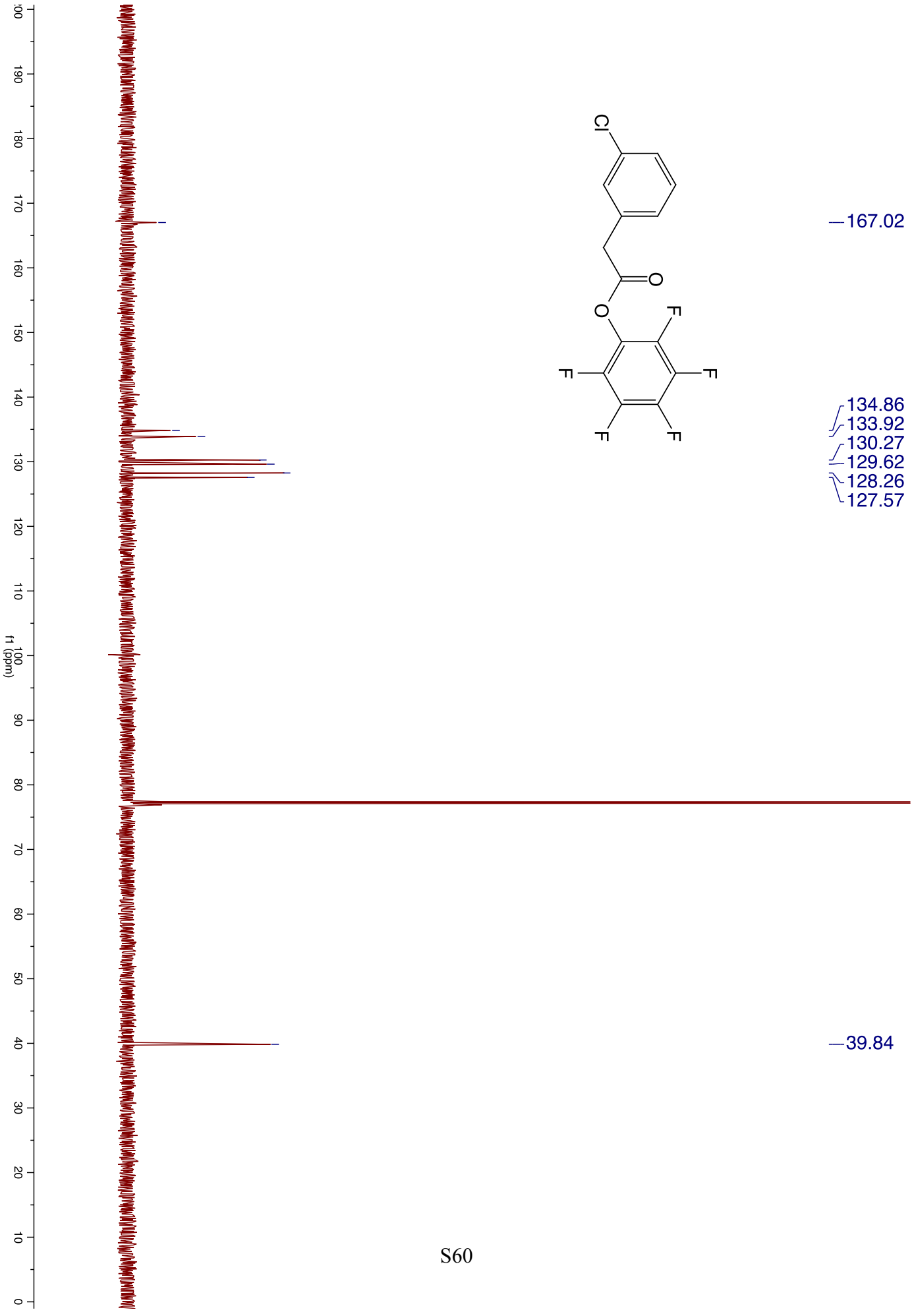

f1 (ppm)
1.99
2.00
2.01
6.09
7.21
7.20
6.73
6.72
3.86
2.96
N
O
O
F
F
F
F
F

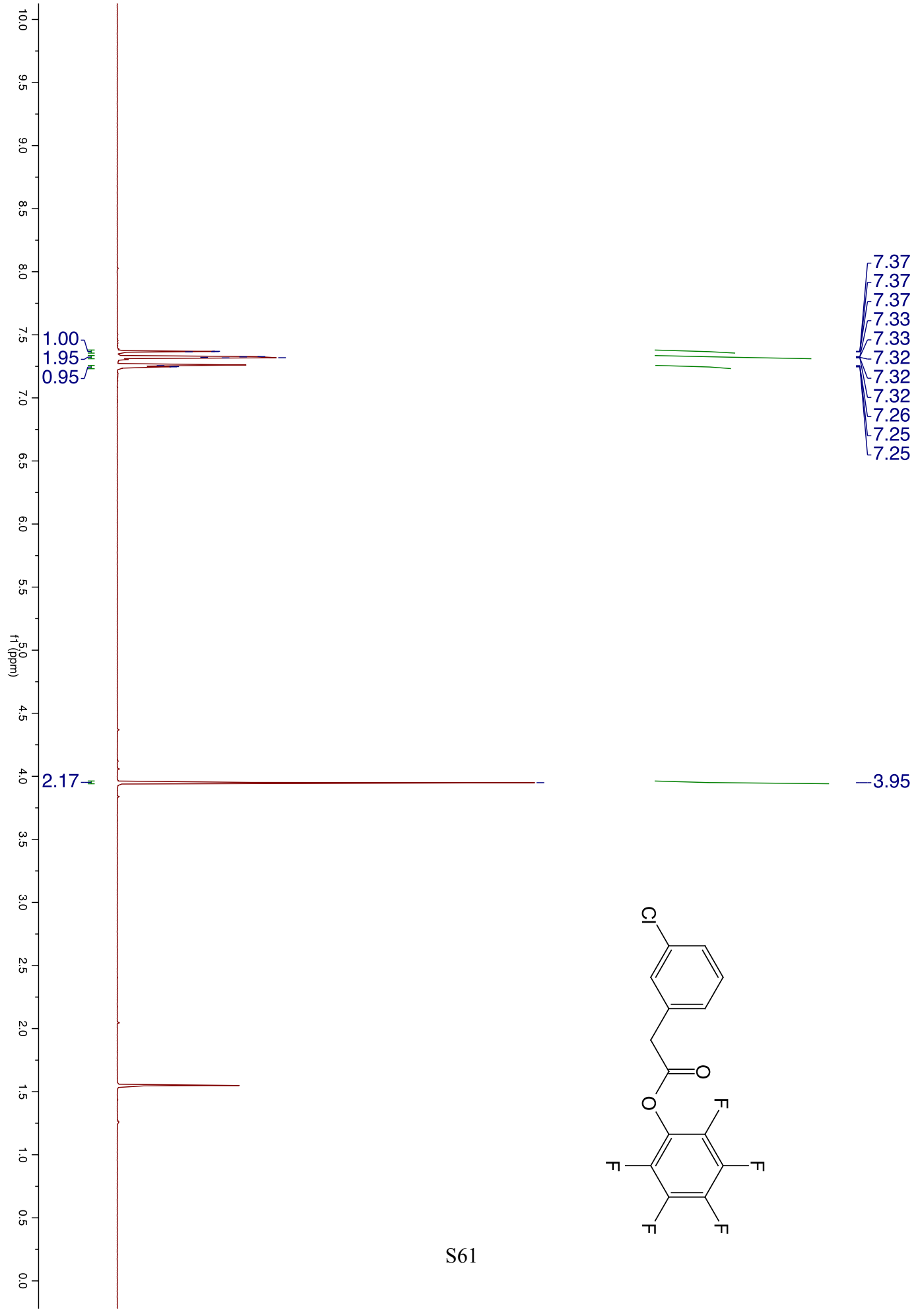

F
F
F
O
O
F
F
F
F
F
166.92
136.09
130.51
130.29
129.85
126.01
125.98
125.04
123.23
39.95
f1 (ppm)

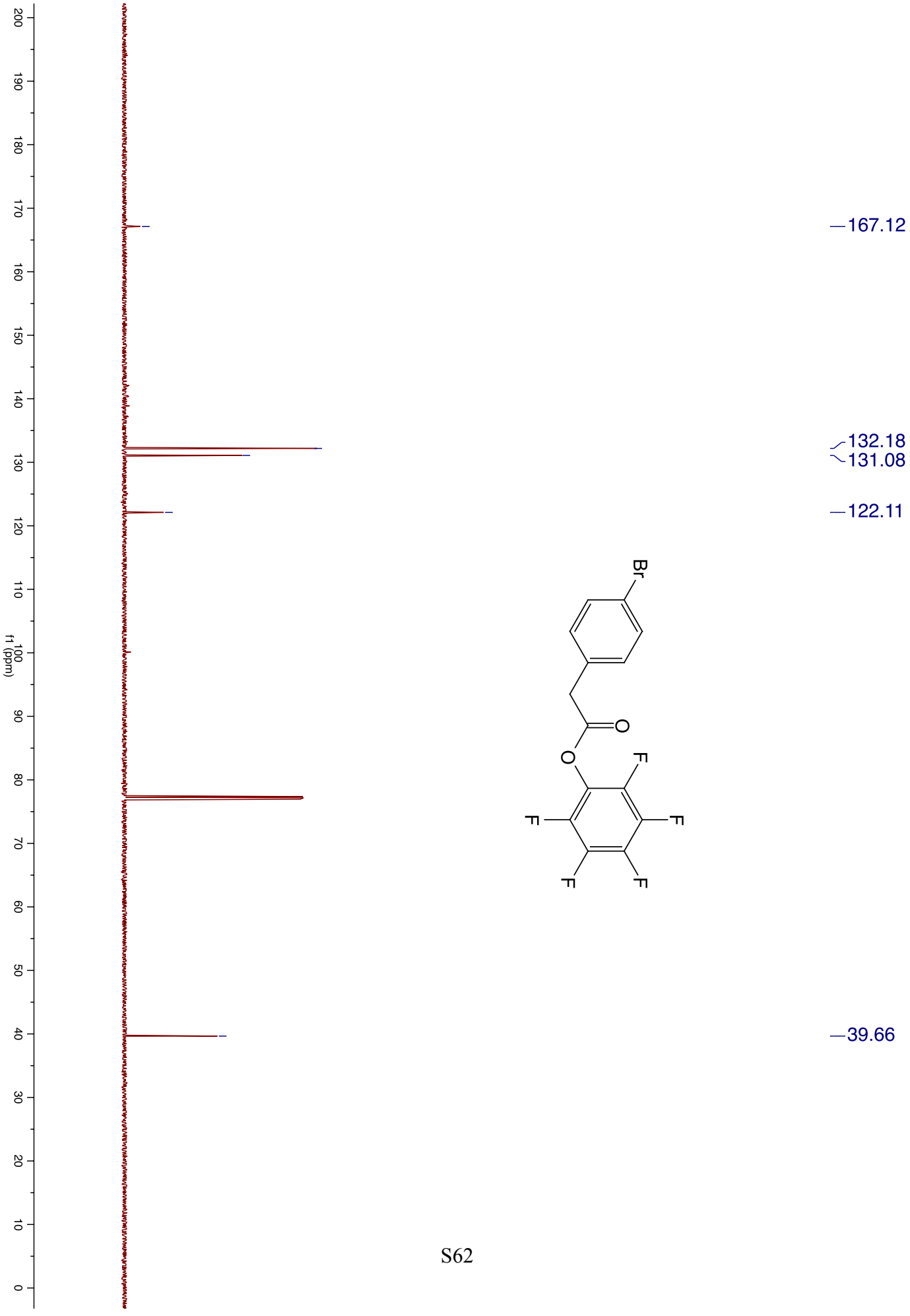

1.99
2.00
2.02
7.66
7.65
7.50
7.48
4.04
F
F
F
O
O
F
F
F
F
F
f1 (ppm)

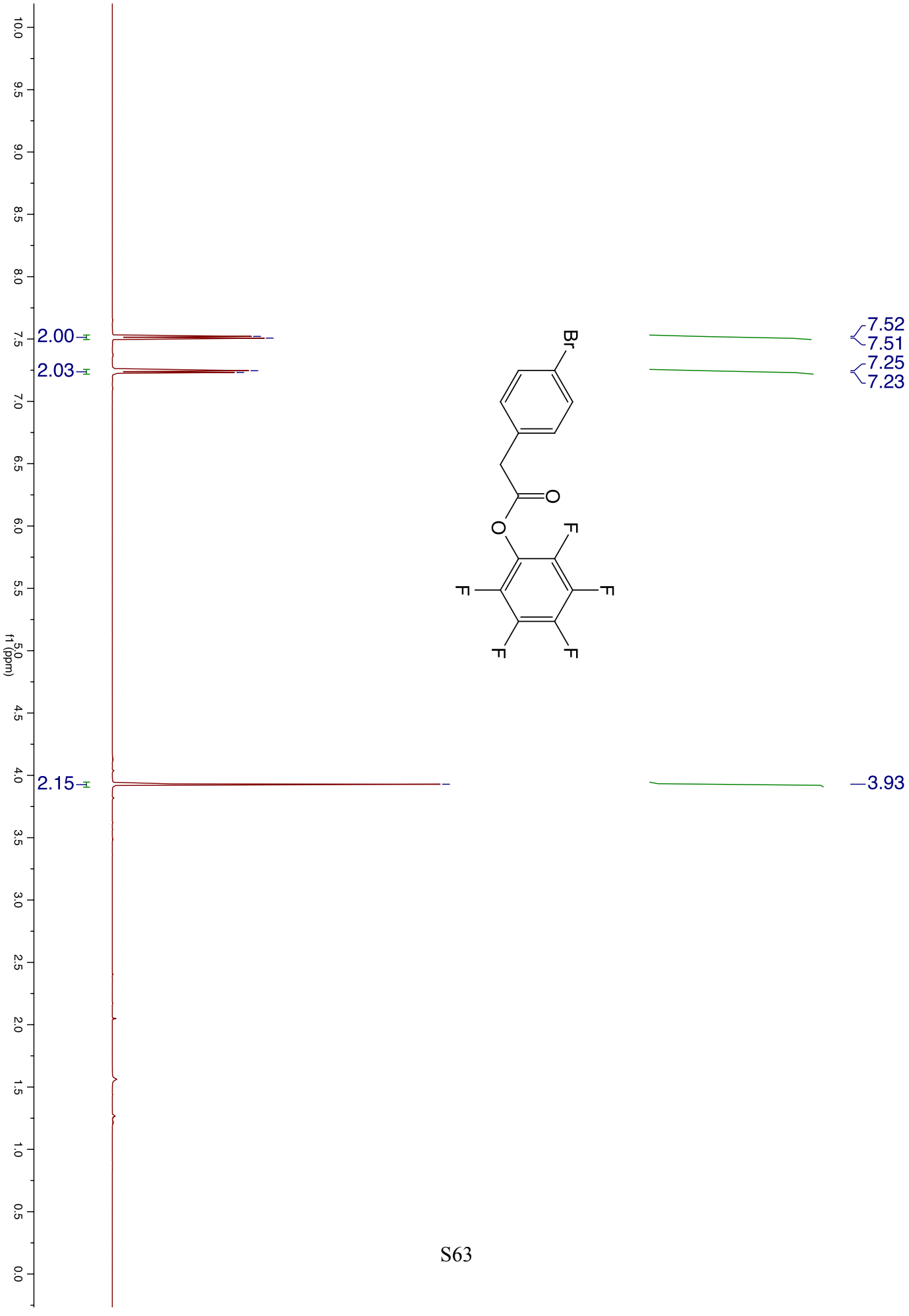

166.81
162.00
160.37
131.44
131.42
130.07
130.02
124.58
124.55
119.77
119.67
115.84
115.70
33.69
33.67
f1 (ppm)

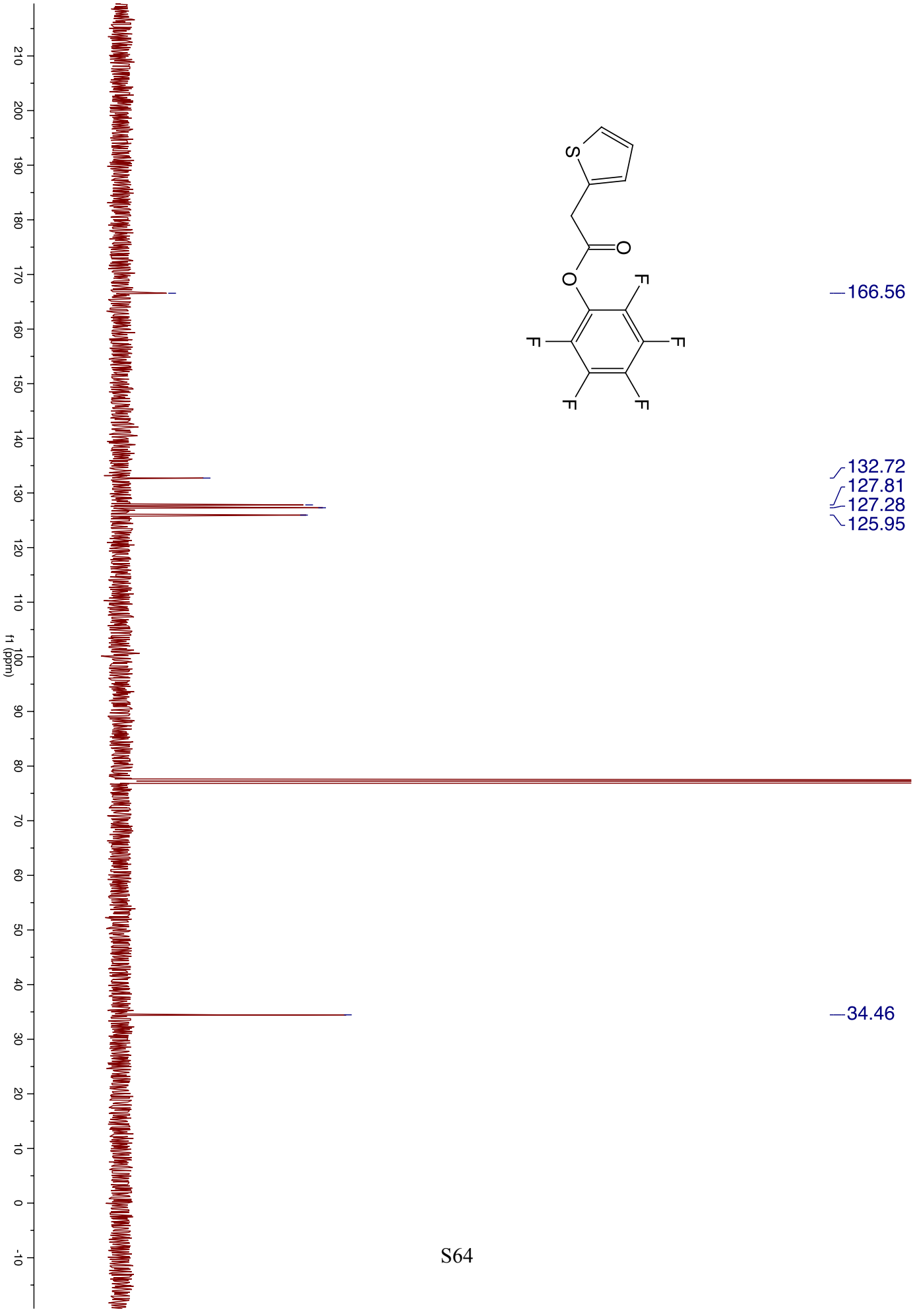

7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.18
7.18
7.17
7.17
7.14
7.14
7.13
7.12
7.12
7.11
2.00
1.00
1.00
2.12
4.03
f1 (ppm)
F
O
O
F
F
F
F
F

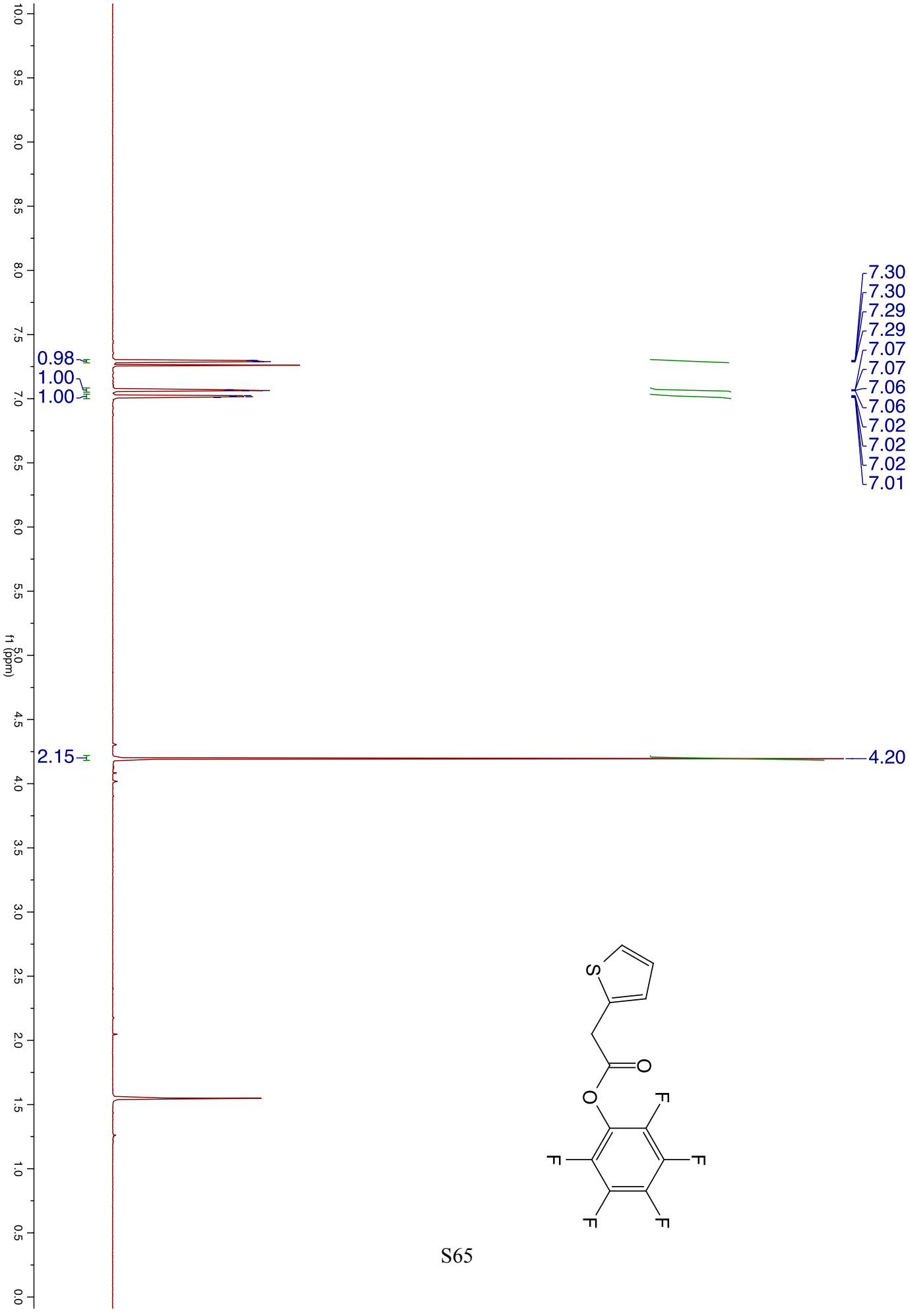

Cl
O
O
F
F
F
F
F
167.02
134.86
133.92
130.27
129.62
128.26
127.57
39.84
f1 (ppm)

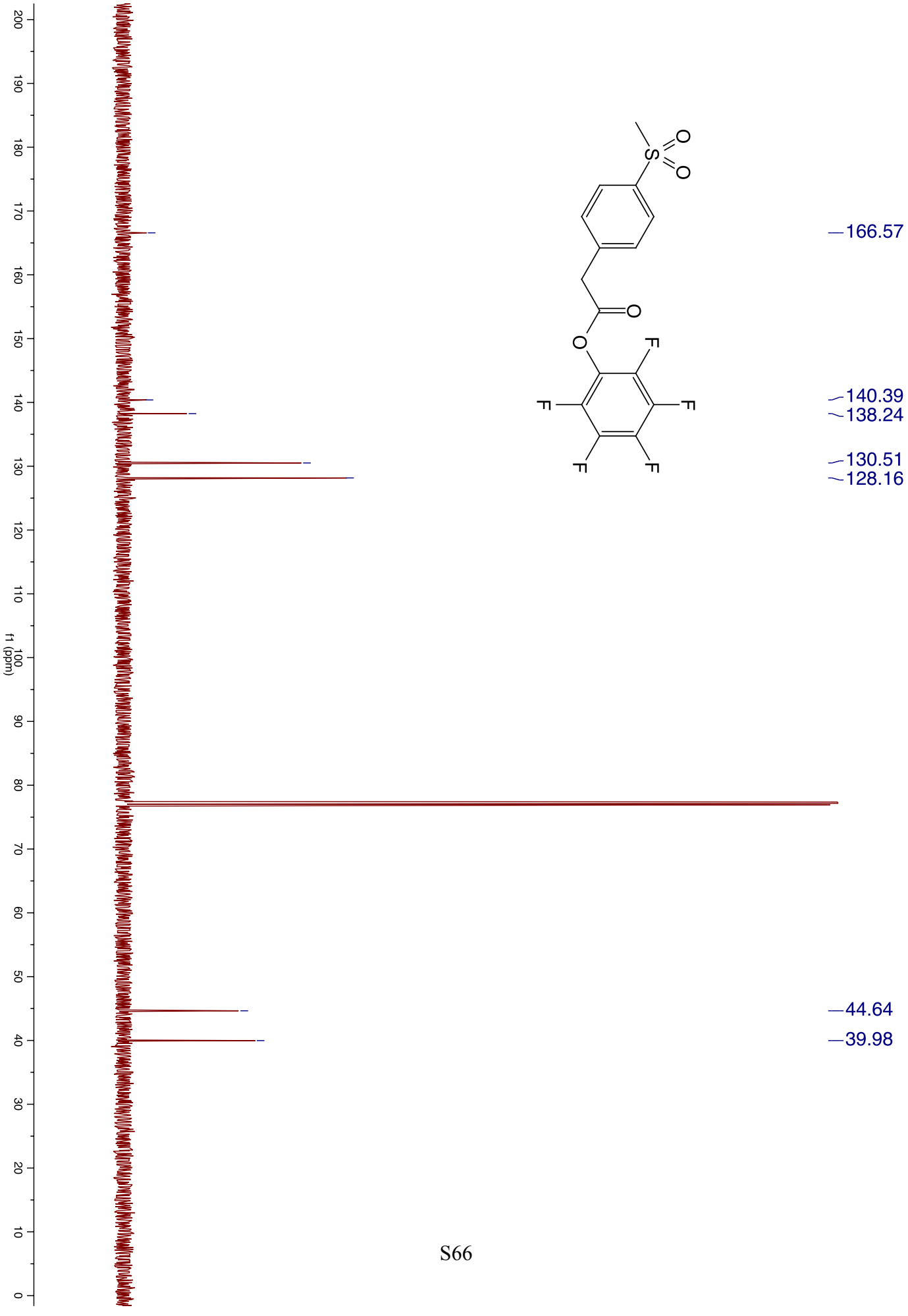

1.00
1.95
0.95
2.17
7.37
7.37
7.37
7.33
7.33
7.32
7.32
7.32
7.26
7.25
7.25
3.95
f1 (ppm)
Cl
O
O
F
F
F
F

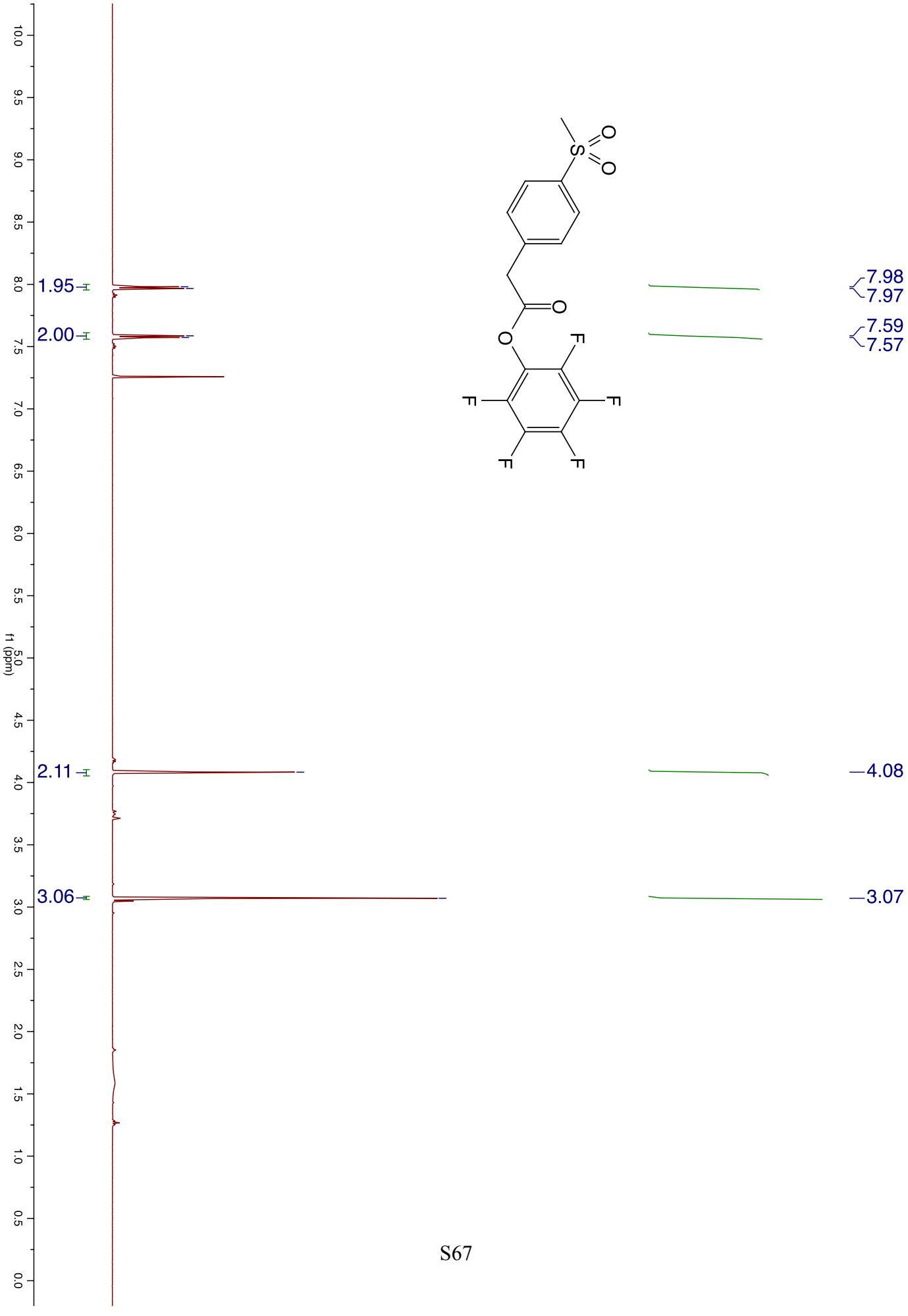

167.12
132.18
131.08
122.11
39.66
Br
O
O
F
F
F
F
F
f1 (ppm)

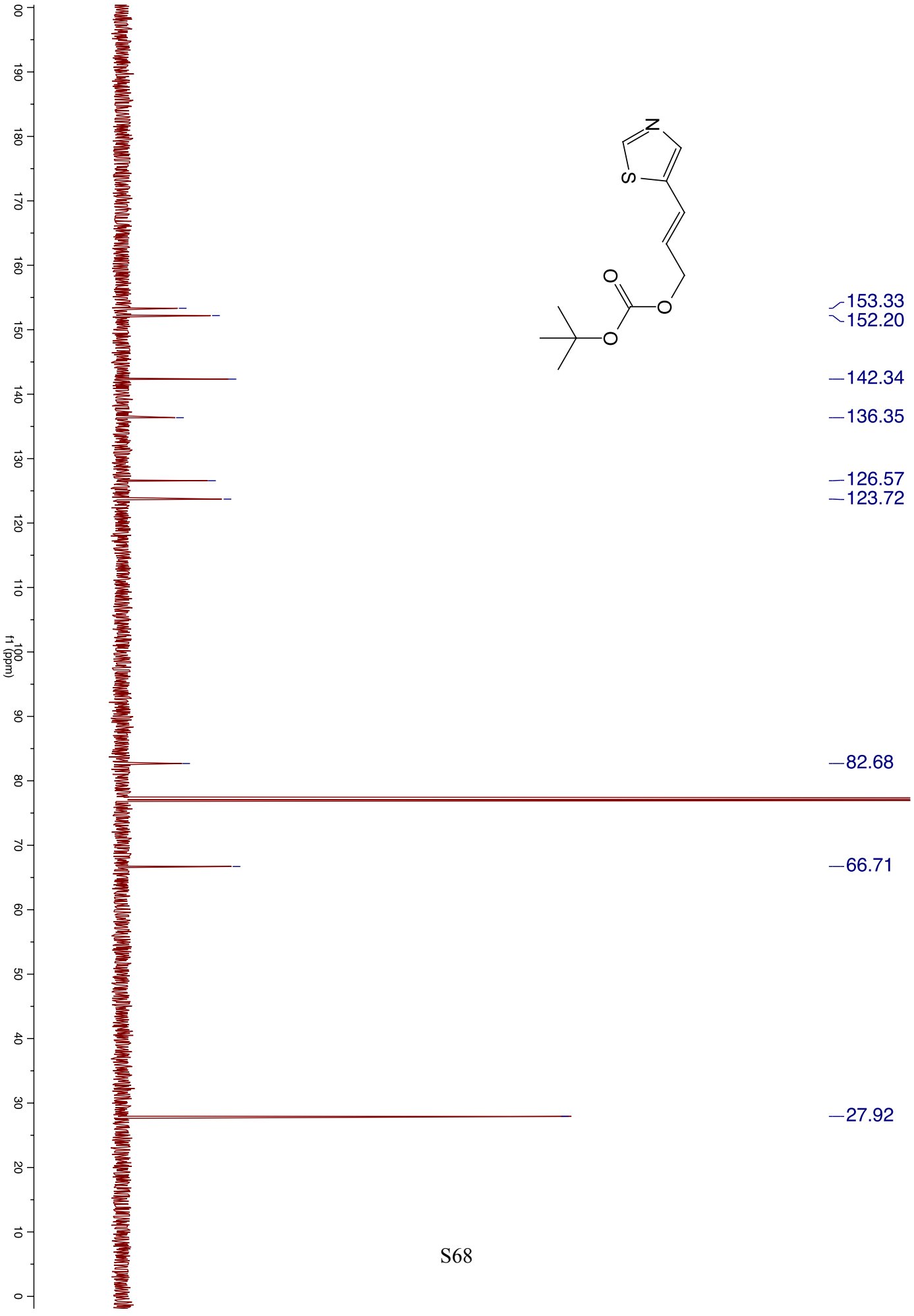

2.00
2.03
2.15
7.52
7.51
7.25
7.23
3.93
Br
O
O
F
F
F
F
F
f1 (ppm)

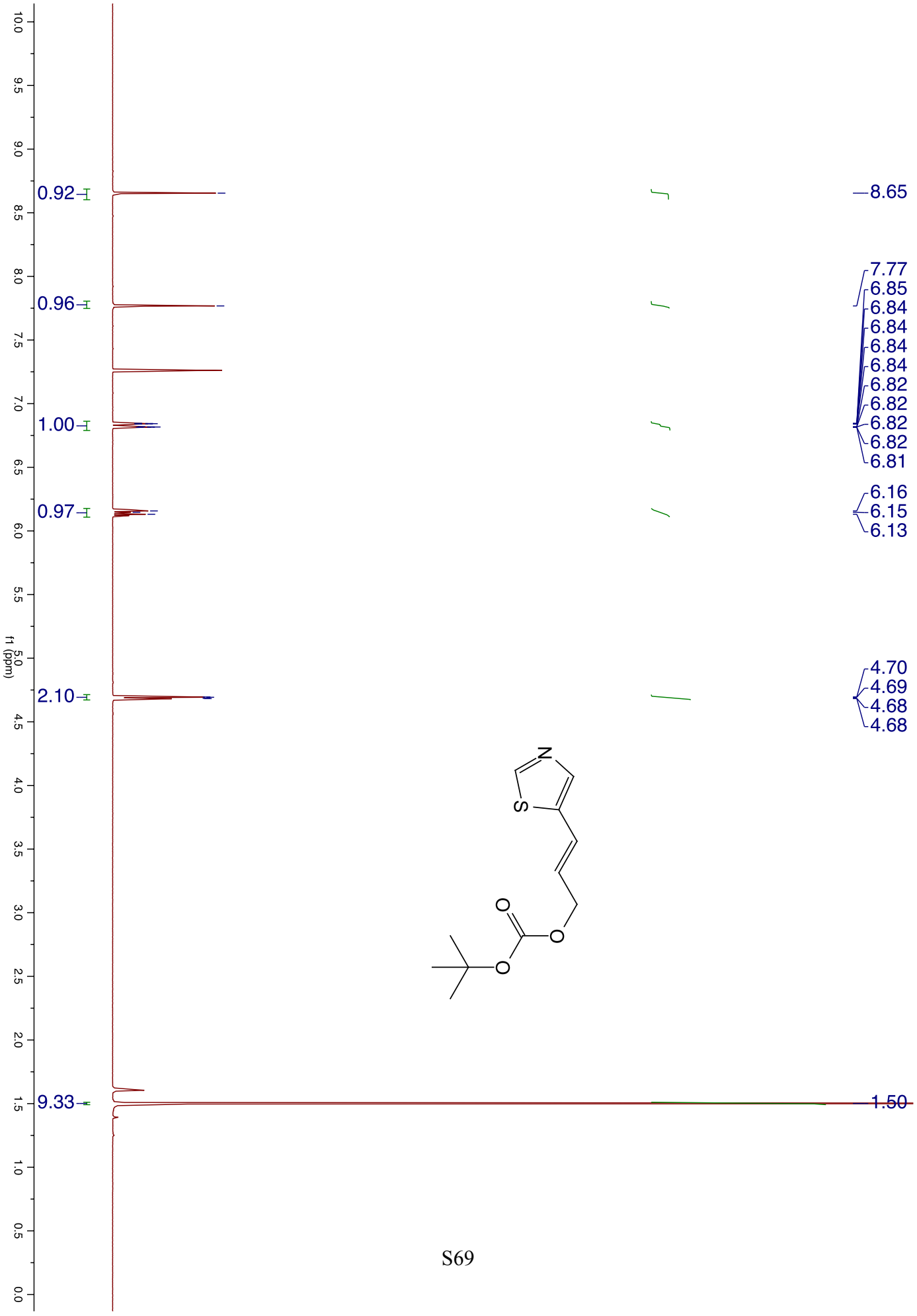

166.56
132.72
127.81
127.28
125.95
34.46
f1 (ppm)

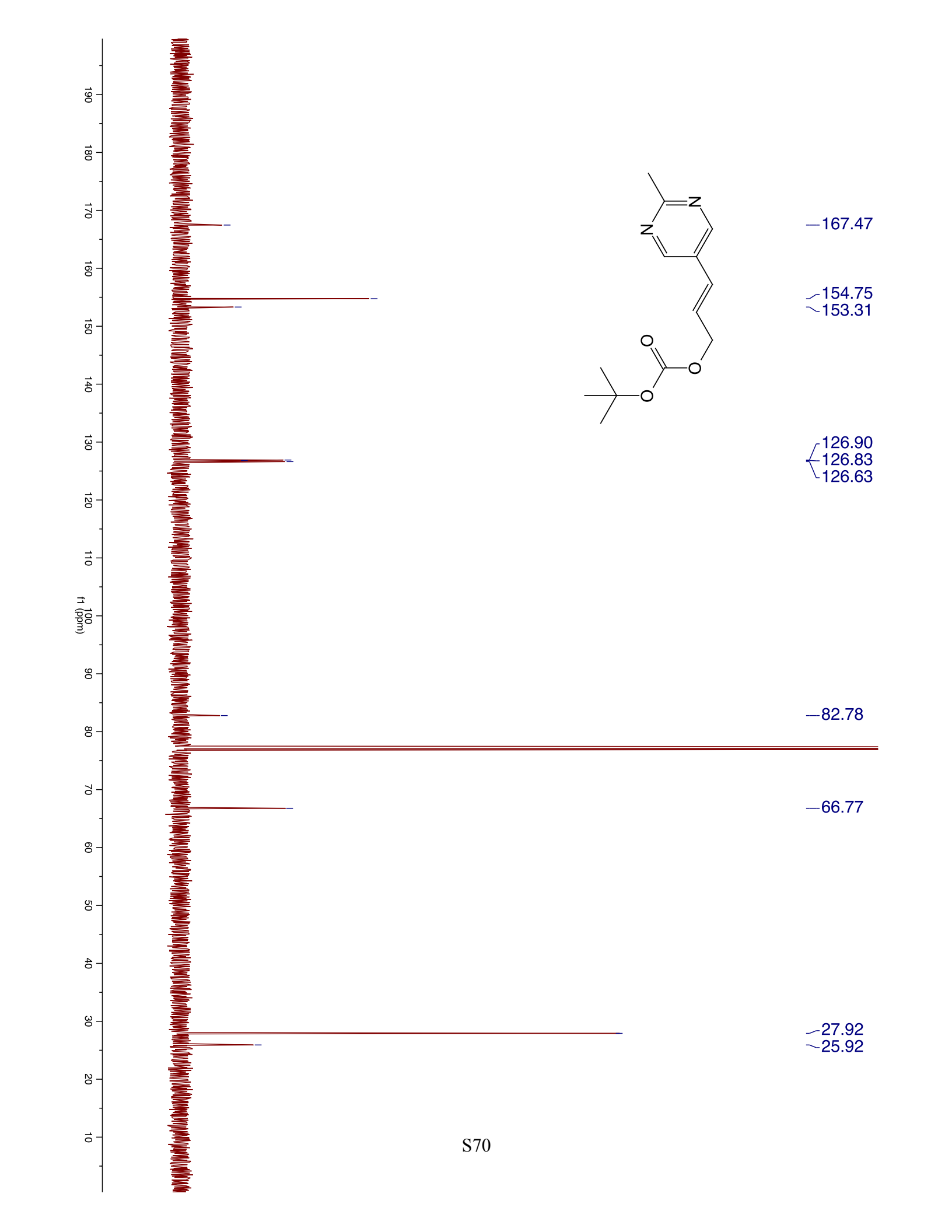

0.98
1.00
1.00
2.15
7.30
7.30
7.29
7.29
7.07
7.07
7.06
7.06
7.02
7.02
7.02
7.01
4.20
f1 (ppm)
S
O
O
F
F
F
F
F

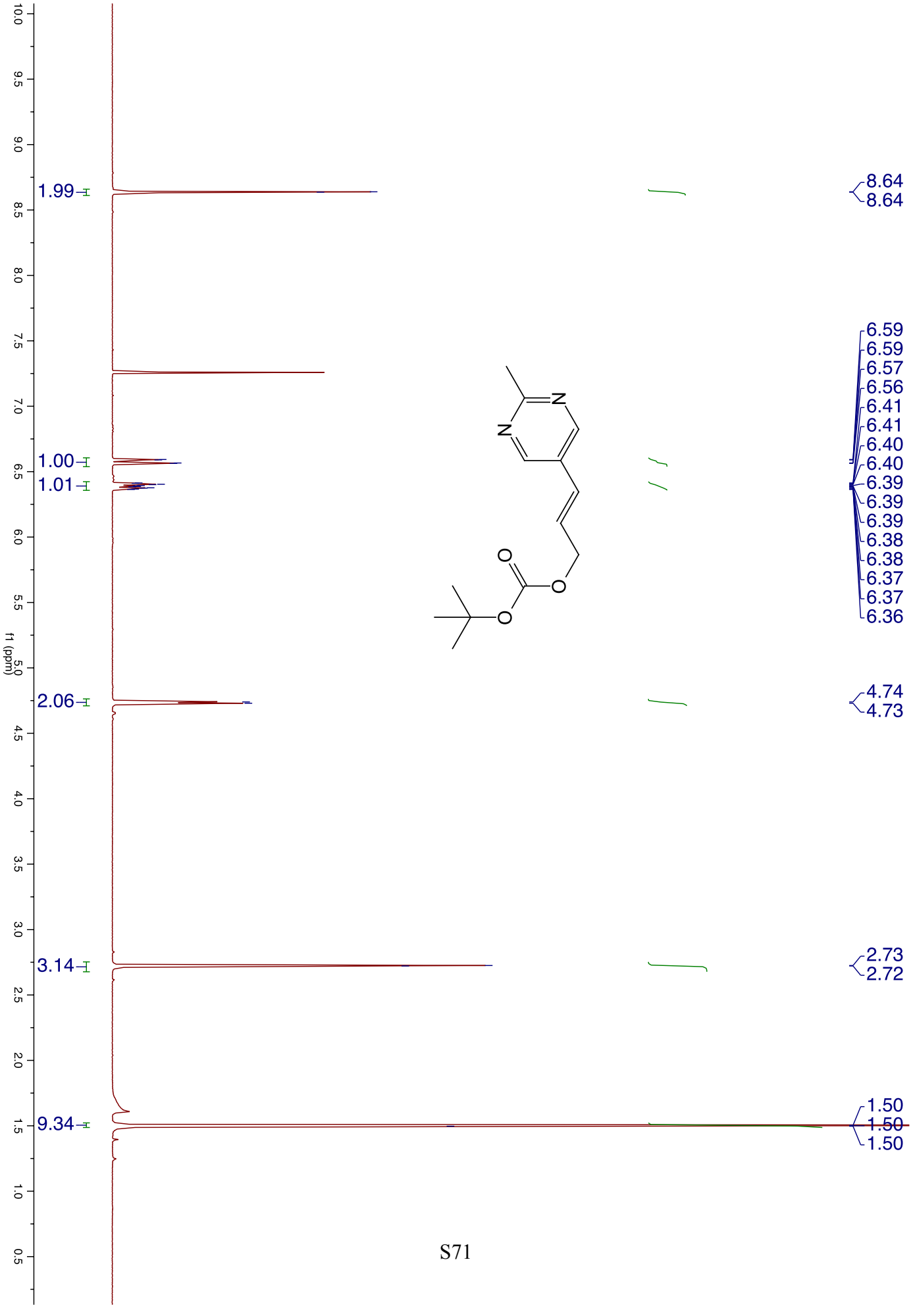

166.57
140.39
138.24
130.51
128.16
44.64
39.98
f1 (ppm)

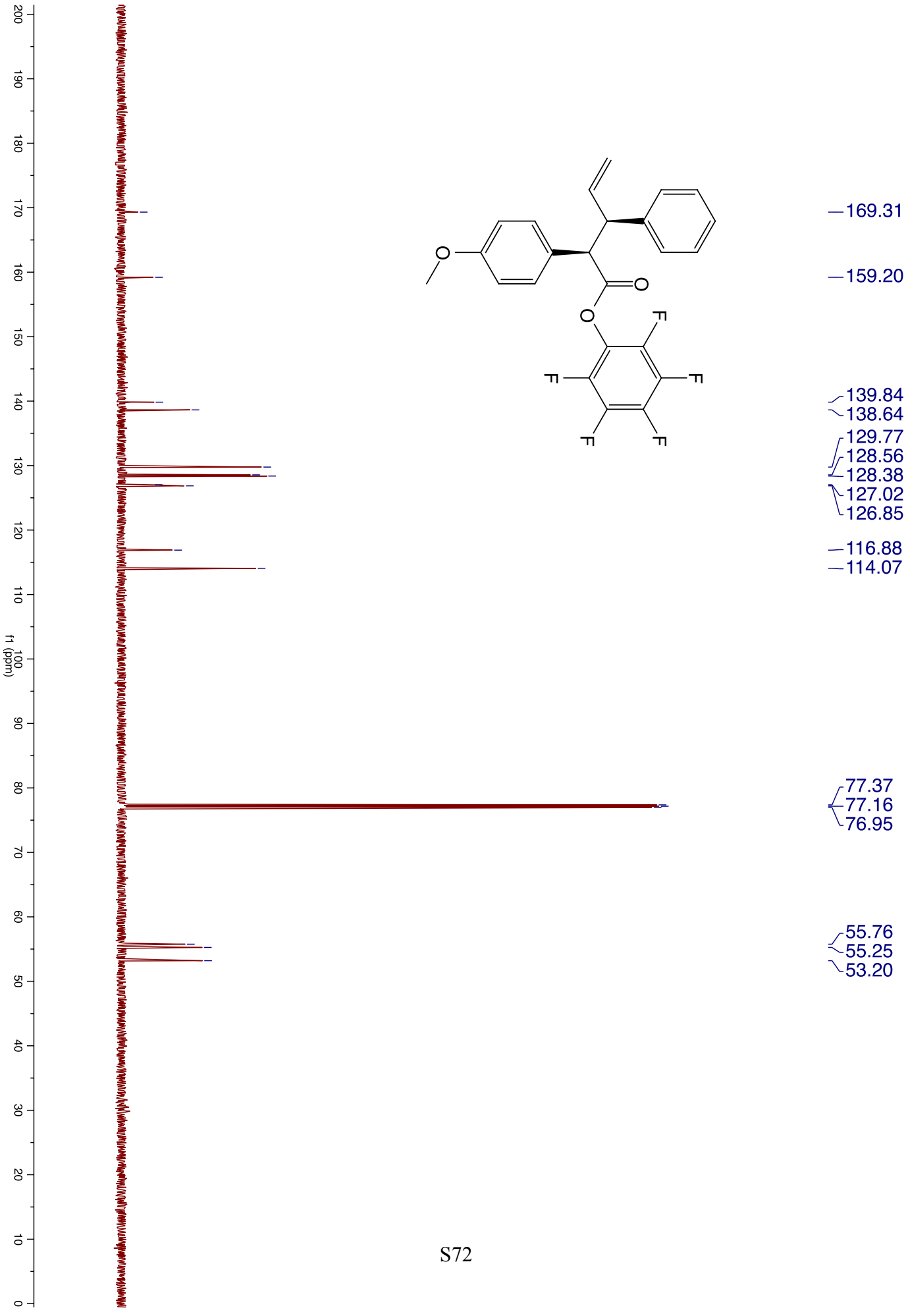

1.95
2.00
2.11
3.06
7.98
7.97
7.59
7.57
4.08
3.07
f1 (ppm)

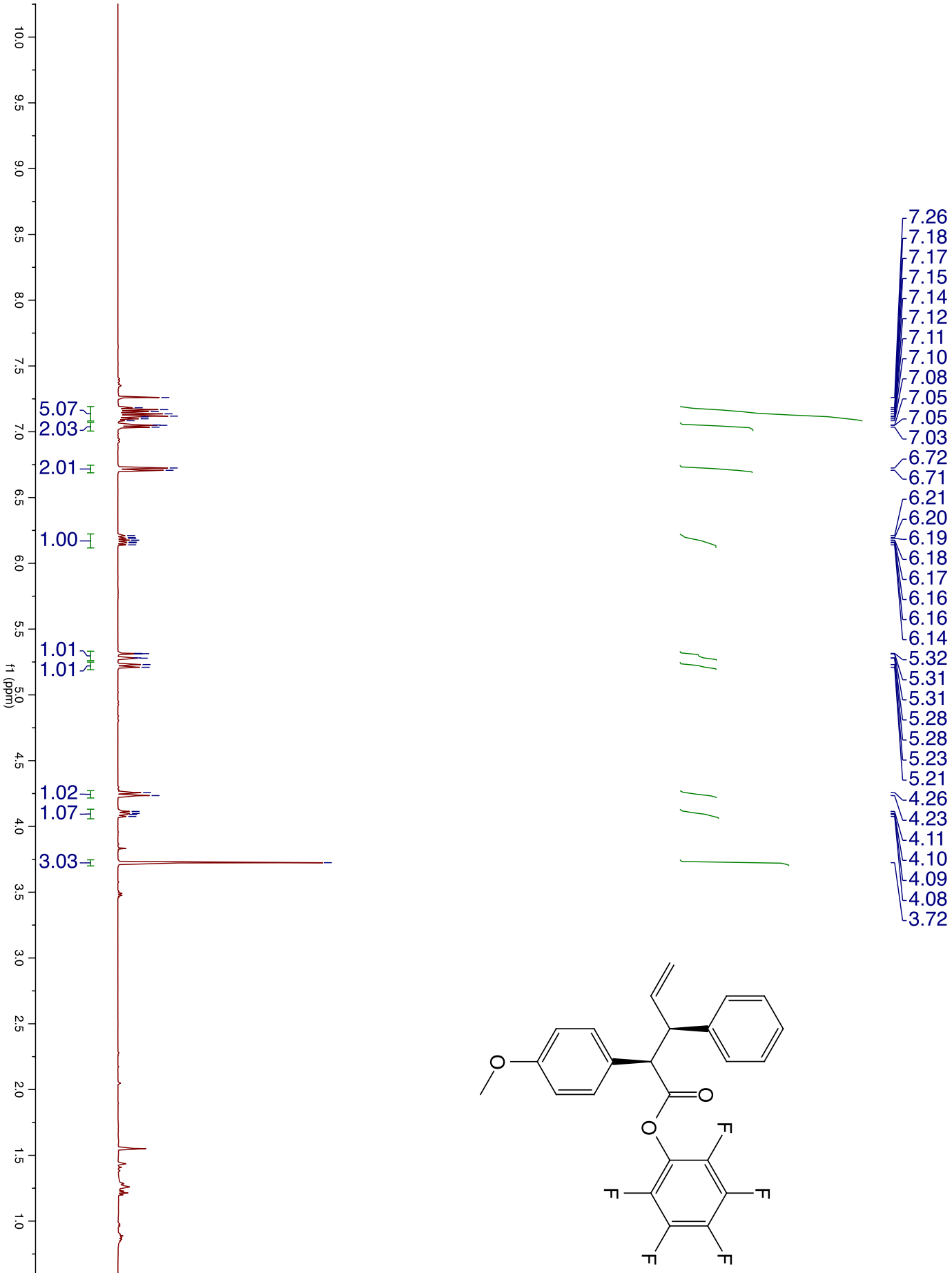

153.33
152.20
142.34
136.35
126.57
123.72
82.68
66.71
27.92
f1 (ppm)

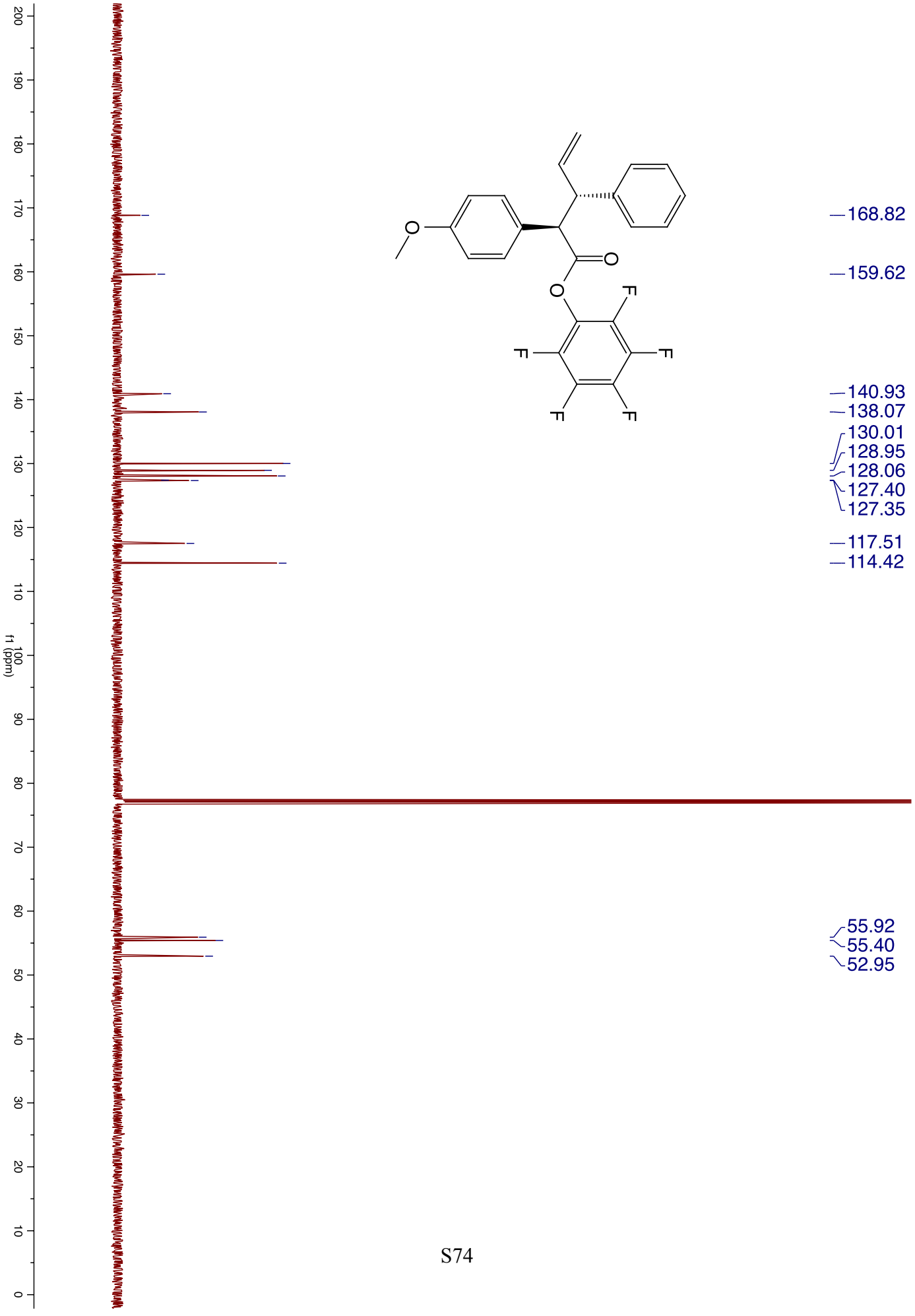

0.92
0.96
1.00
0.97
2.10
9.33
8.65
7.77
6.85
6.84
6.84
6.84
6.84
6.82
6.82
6.82
6.82
6.81
6.16
6.15
6.13
4.70
4.69
4.68
4.68
1.50
f1 (ppm)
N
S
O
O
O

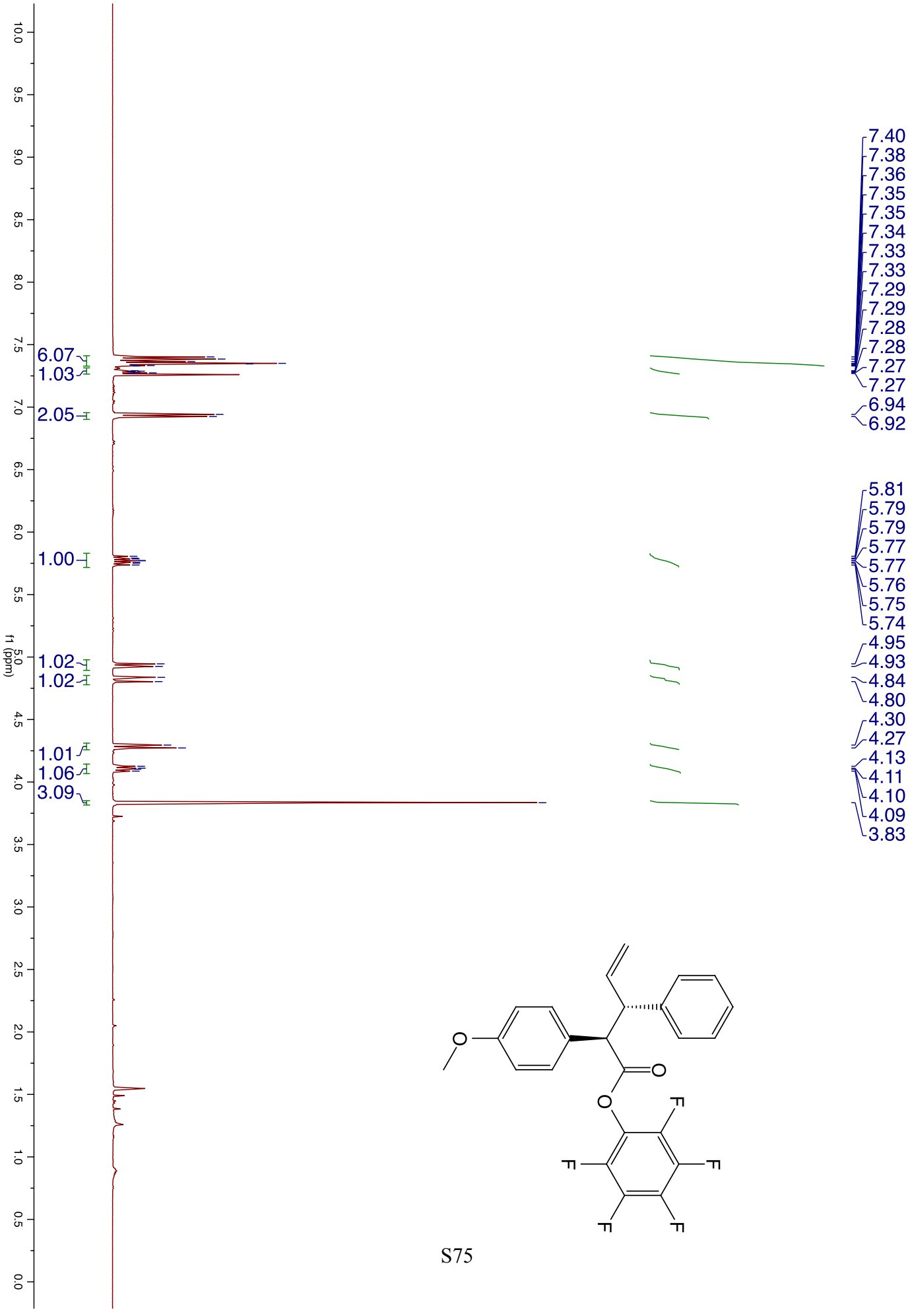

167.47
154.75
153.31
126.90
126.83
126.63
82.78
66.77
27.92
25.92
f1 (ppm)

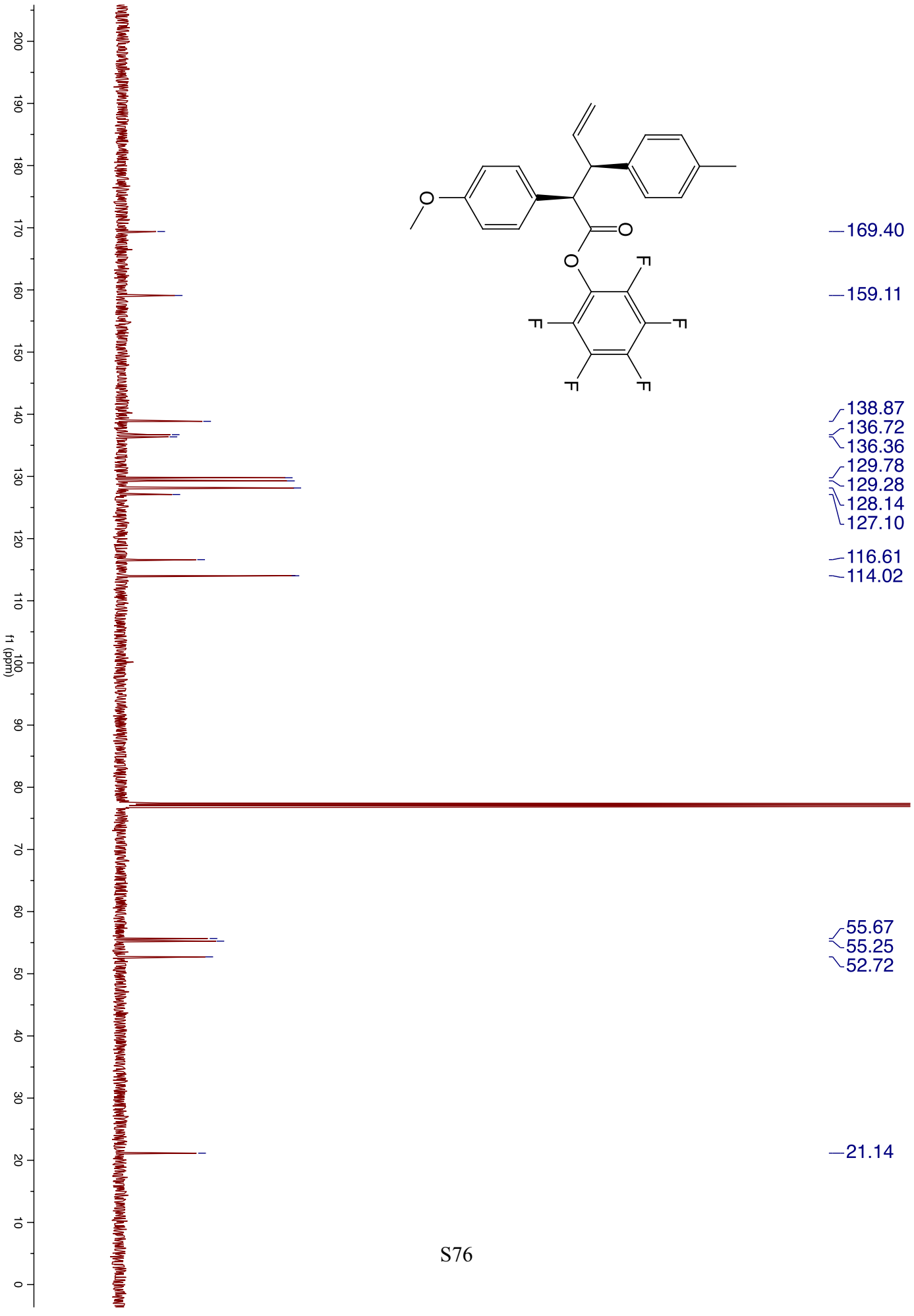

f1 (ppm)
1.99
1.00
1.01
2.06
3.14
9.34
8.64
8.64
6.59
6.59
6.57
6.56
6.41
6.41
6.40
6.40
6.39
6.39
6.39
6.38
6.38
6.37
6.37
6.36
4.74
4.73
2.73
2.72
1.50
1.50
1.50
N
N
O
O
O

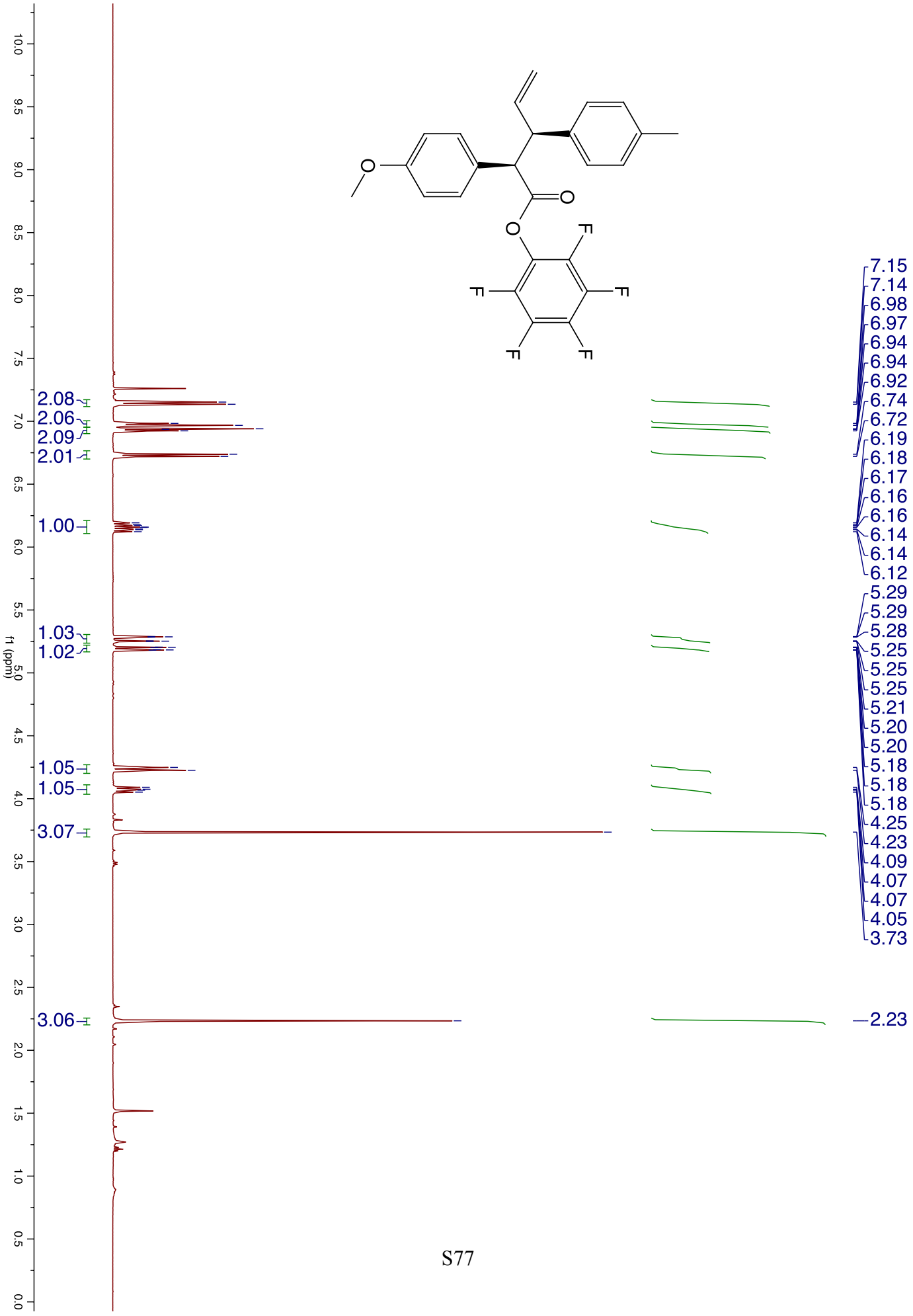

169.31
159.20
139.84
138.64
129.77
128.56
128.38
127.02
126.85
116.88
114.07
77.37
77.16
76.95
55.76
55.25
53.20
f1 (ppm)

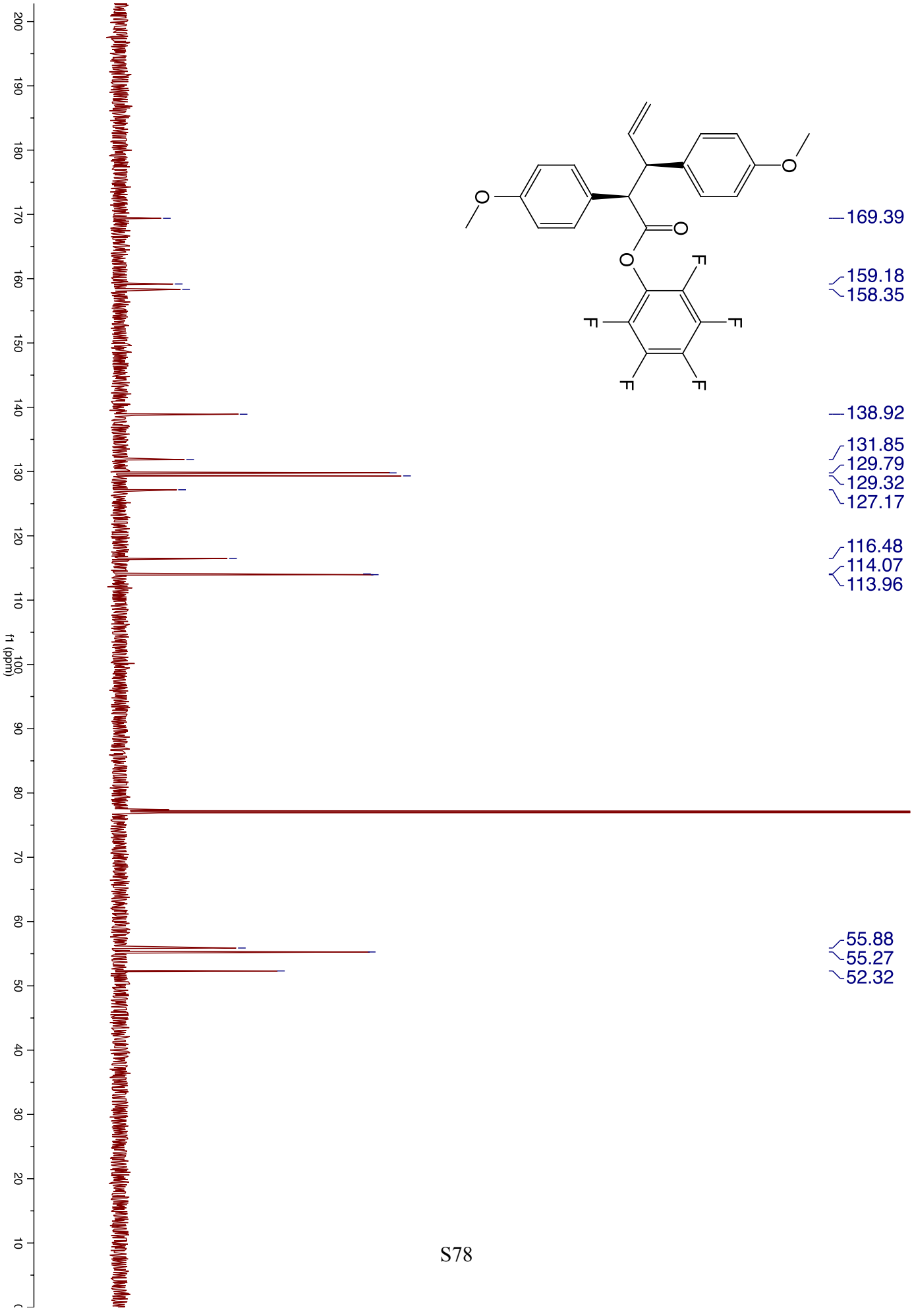

7.26
7.18
7.17
7.15
7.14
7.12
7.11
7.10
7.08
7.05
7.05
7.03
6.72
6.71
6.21
6.20
6.19
6.18
6.17
6.16
6.16
6.14
5.32
5.31
5.31
5.28
5.28
5.23
5.21
4.26
4.23
4.11
4.10
4.09
4.08
3.72
5.07
2.03
2.01
1.00
1.01
1.01
1.02
1.07
3.03
f1 (ppm)
O
O
O
F
F
F
F
F

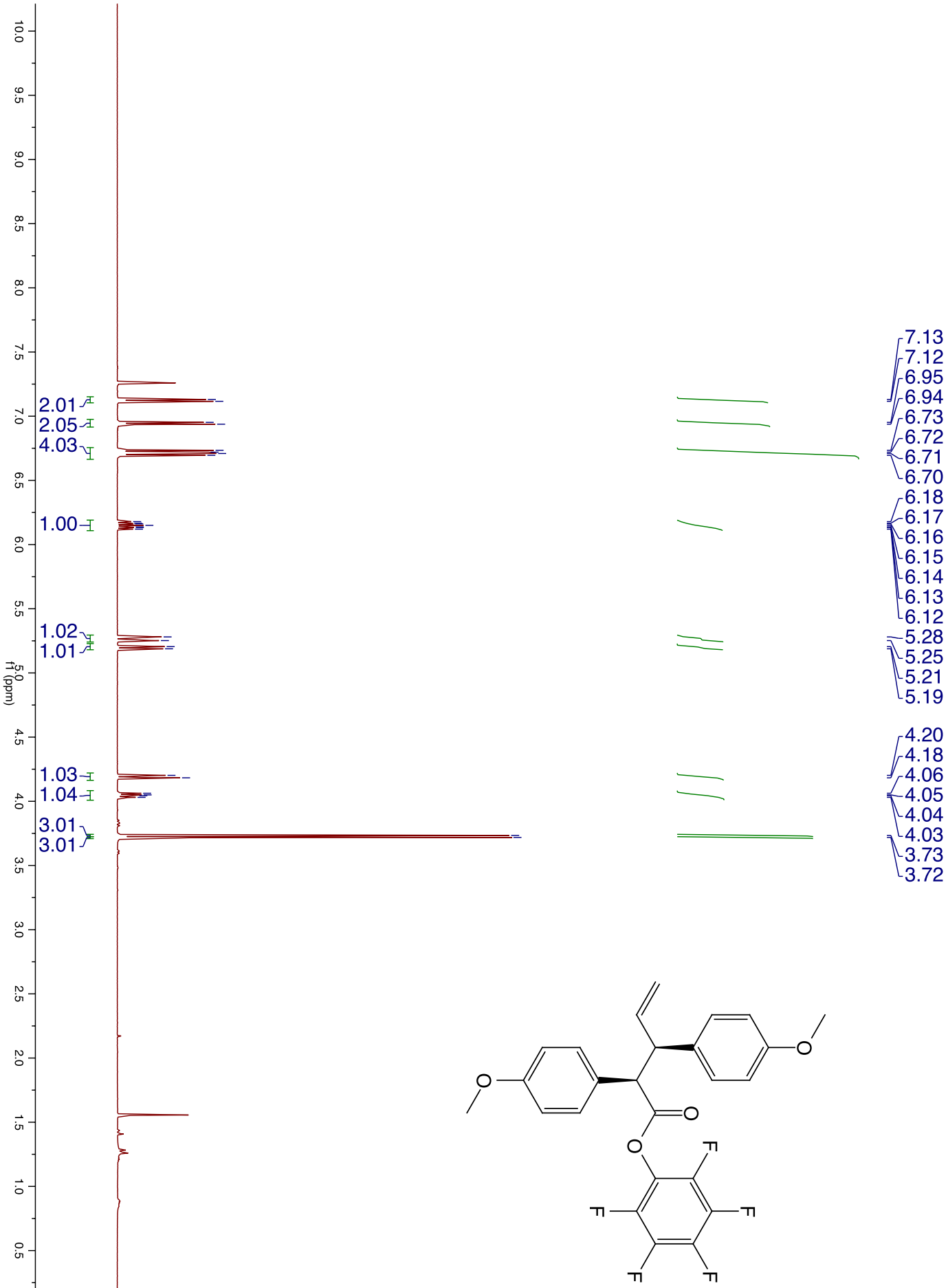

168.82
159.62
140.93
138.07
130.01
128.95
128.06
127.40
127.35
117.51
114.42
55.92
55.40
52.95
f1 (ppm)

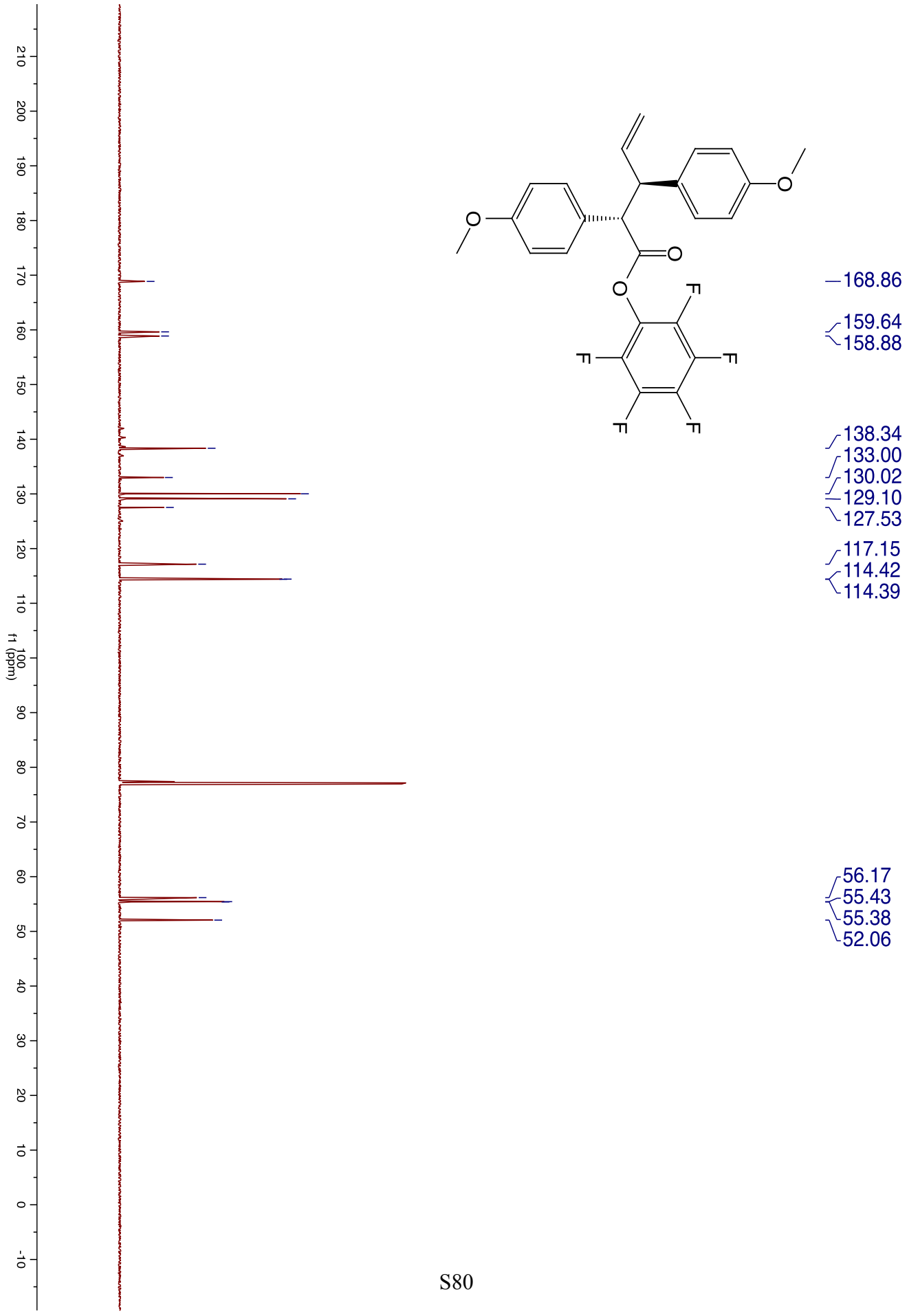

f1 (ppm)
6.07
1.03
2.05
1.00
1.02
1.02
1.01
1.06
3.09
7.40
7.38
7.36
7.35
7.35
7.34
7.33
7.33
7.29
7.29
7.28
7.28
7.27
7.27
6.94
6.92
5.81
5.79
5.79
5.77
5.77
5.76
5.75
5.74
4.95
4.93
4.84
4.80
4.30
4.27
4.13
4.11
4.10
4.09
3.83
O
O
O
F
F
F
F
F

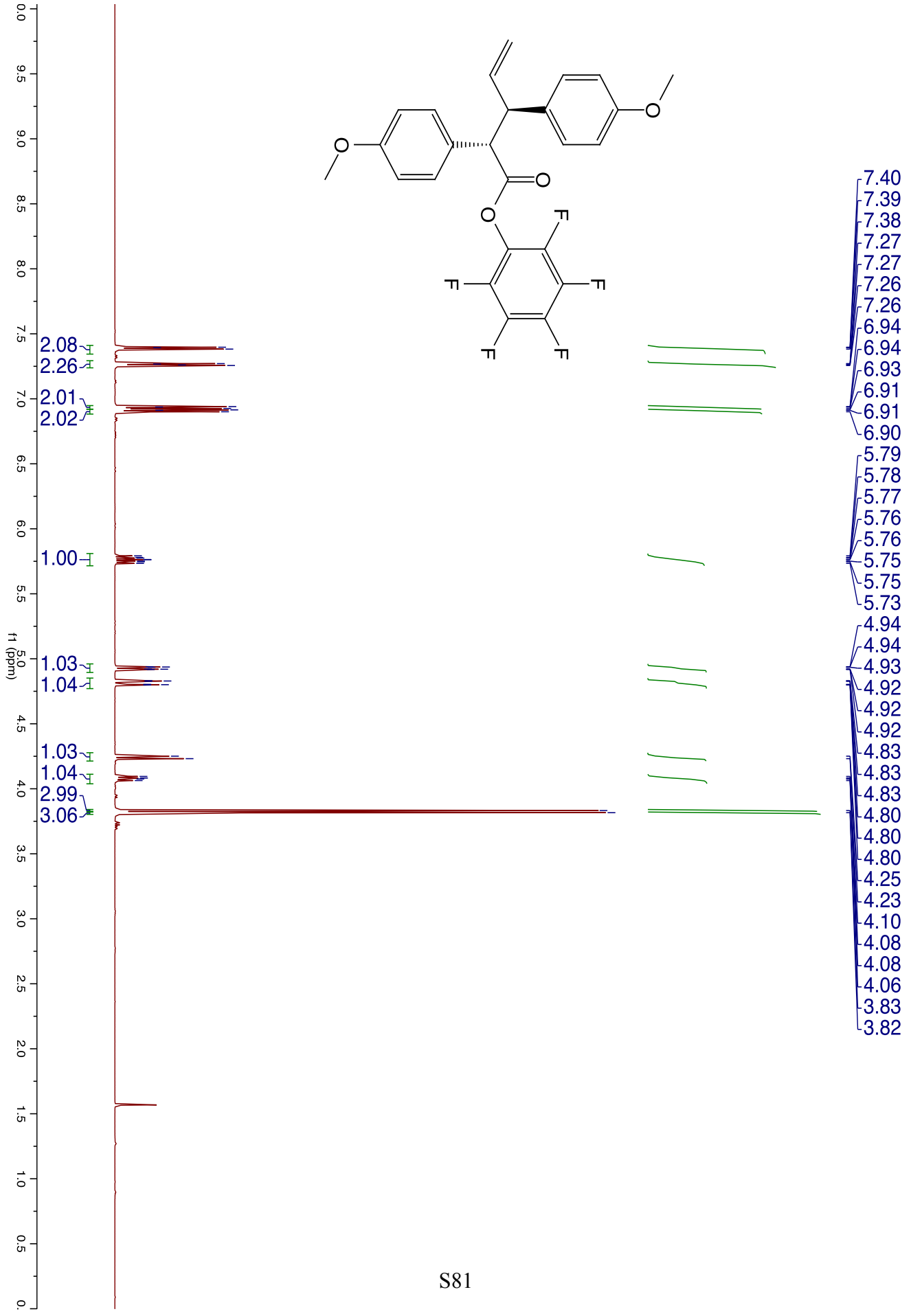

169.40
159.11
138.87
136.72
136.36
129.78
129.28
128.14
127.10
116.61
114.02
55.67
55.25
52.72
21.14
f1 (ppm)

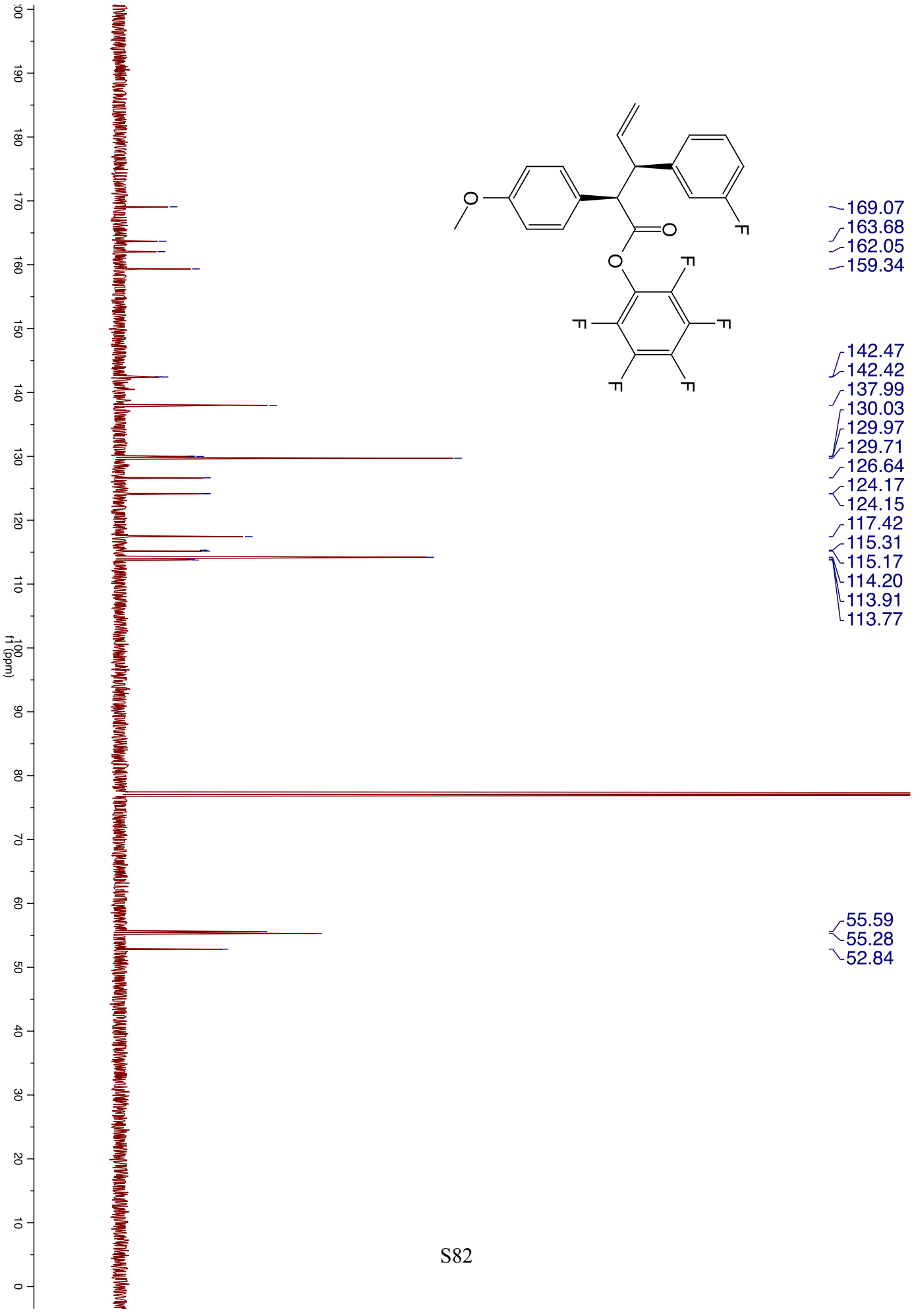

f1 (ppm)
2.08
2.06
2.09
2.01
1.00
1.03
1.02
1.05
1.05
3.07
3.06
7.15
7.14
6.98
6.97
6.94
6.94
6.92
6.74
6.72
6.19
6.18
6.17
6.16
6.16
6.14
6.14
6.12
5.29
5.29
5.28
5.25
5.25
5.25
5.21
5.20
5.20
5.18
5.18
5.18
4.25
4.23
4.09
4.07
4.07
4.05
3.73
2.23
O
O
O
F
F
F
F
F

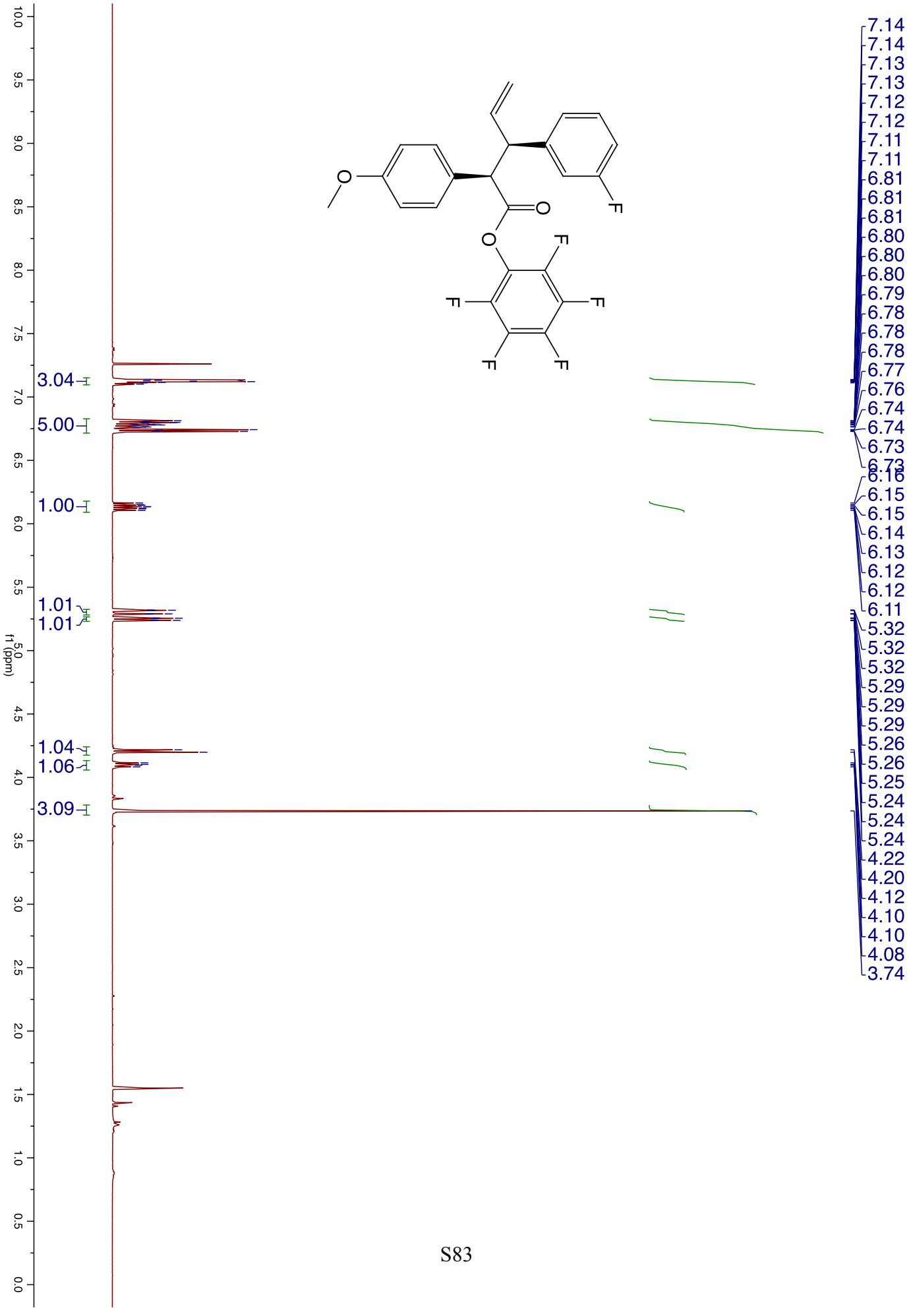

169.39
159.18
158.35
138.92
131.85
129.79
129.32
127.17
116.48
114.07
113.96
55.88
55.27
52.32
f1 (ppm)

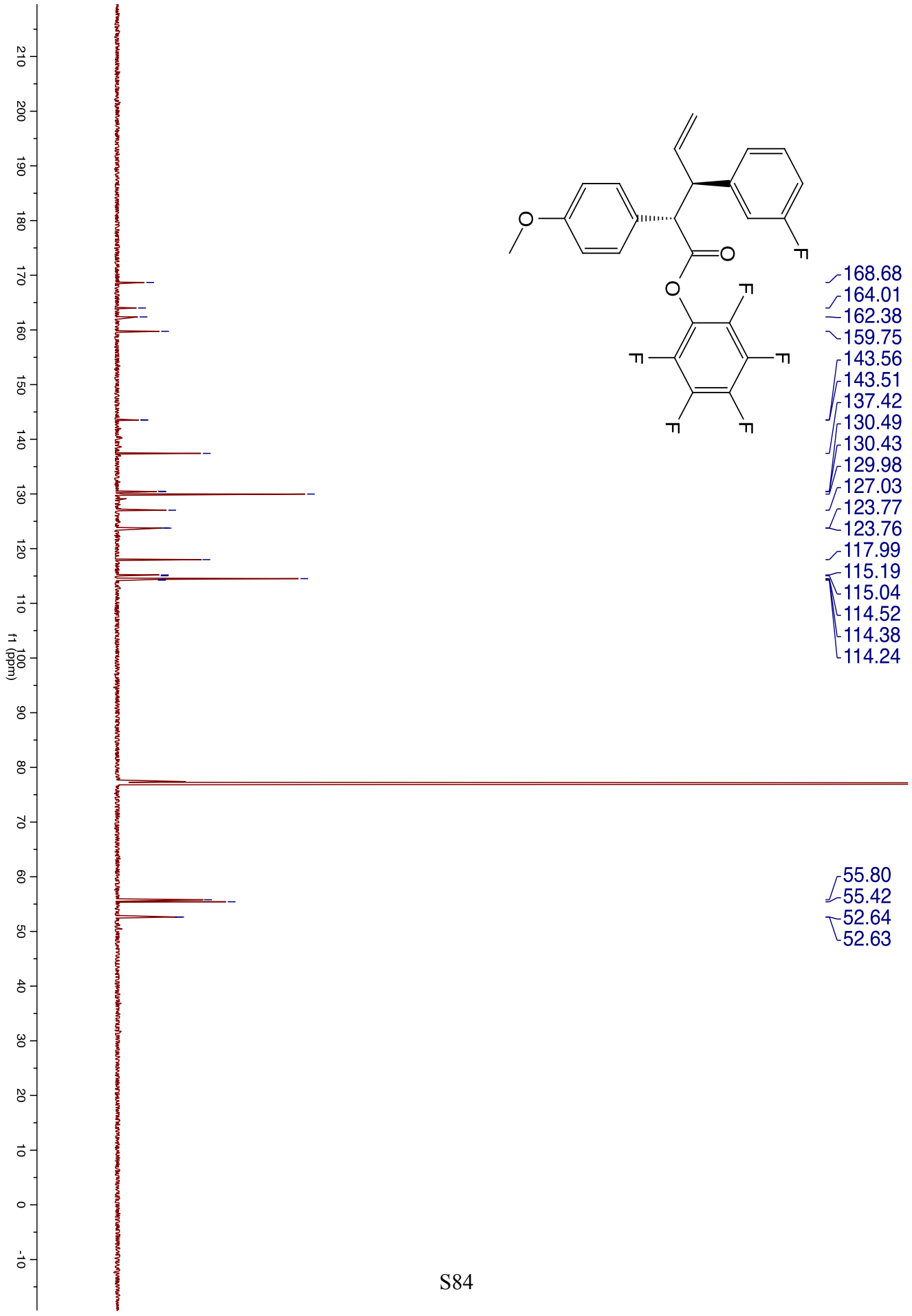

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.01
2.05
4.03
1.00
1.02
1.01
1.03
1.04
3.01
3.01
7.13
7.12
6.95
6.94
6.73
6.72
6.71
6.70
6.18
6.17
6.16
6.15
6.14
6.13
6.12
5.28
5.25
5.21
5.19
4.20
4.18
4.06
4.05
4.04
4.03
3.73
3.72
O
O
O
O
F
F
F
F
F

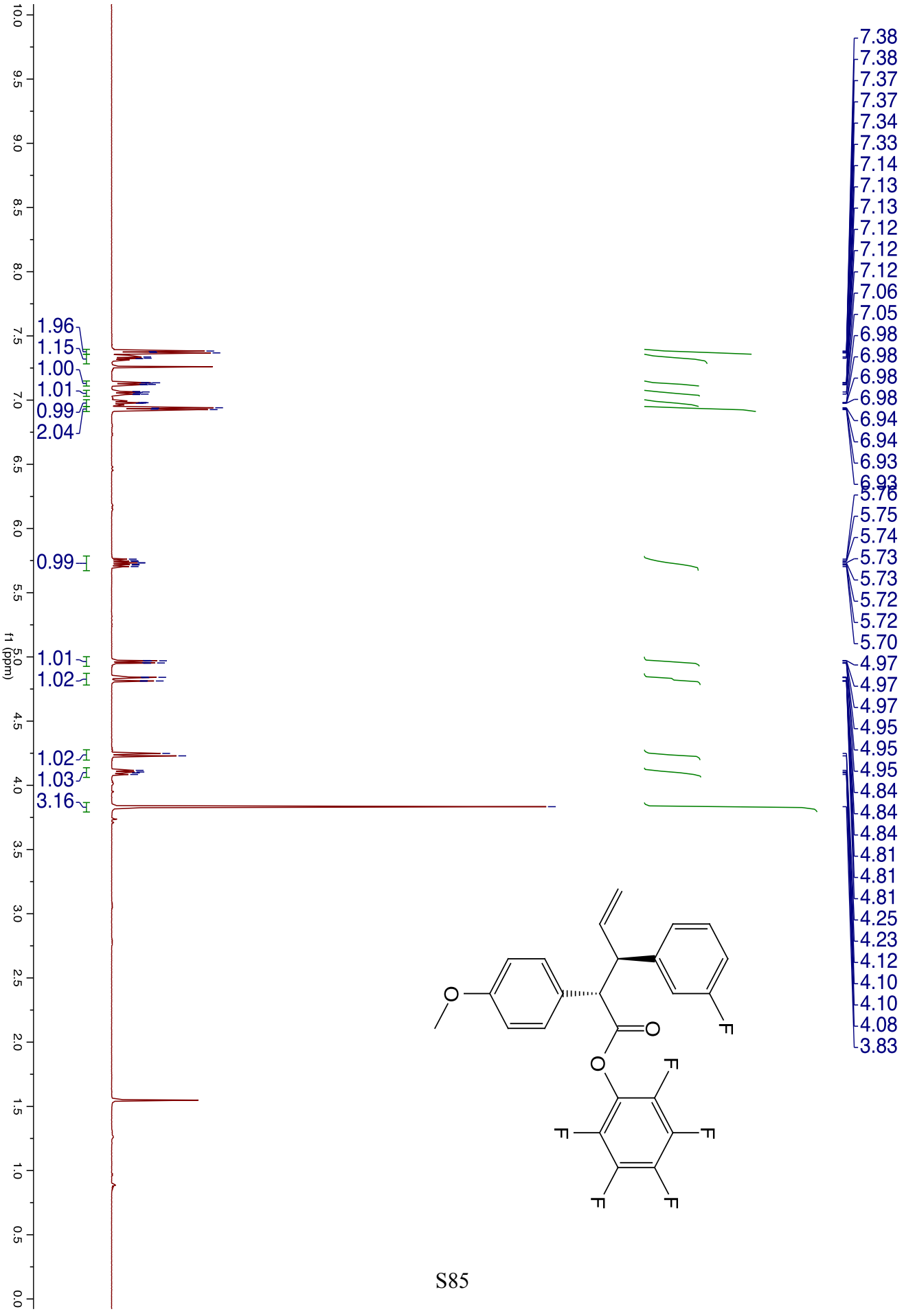

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
O
O
O
F
F
F
F
F
168.86
159.64
158.88
138.34
133.00
130.02
129.10
127.53
117.15
114.42
114.39
56.17
55.43
55.38
52.06

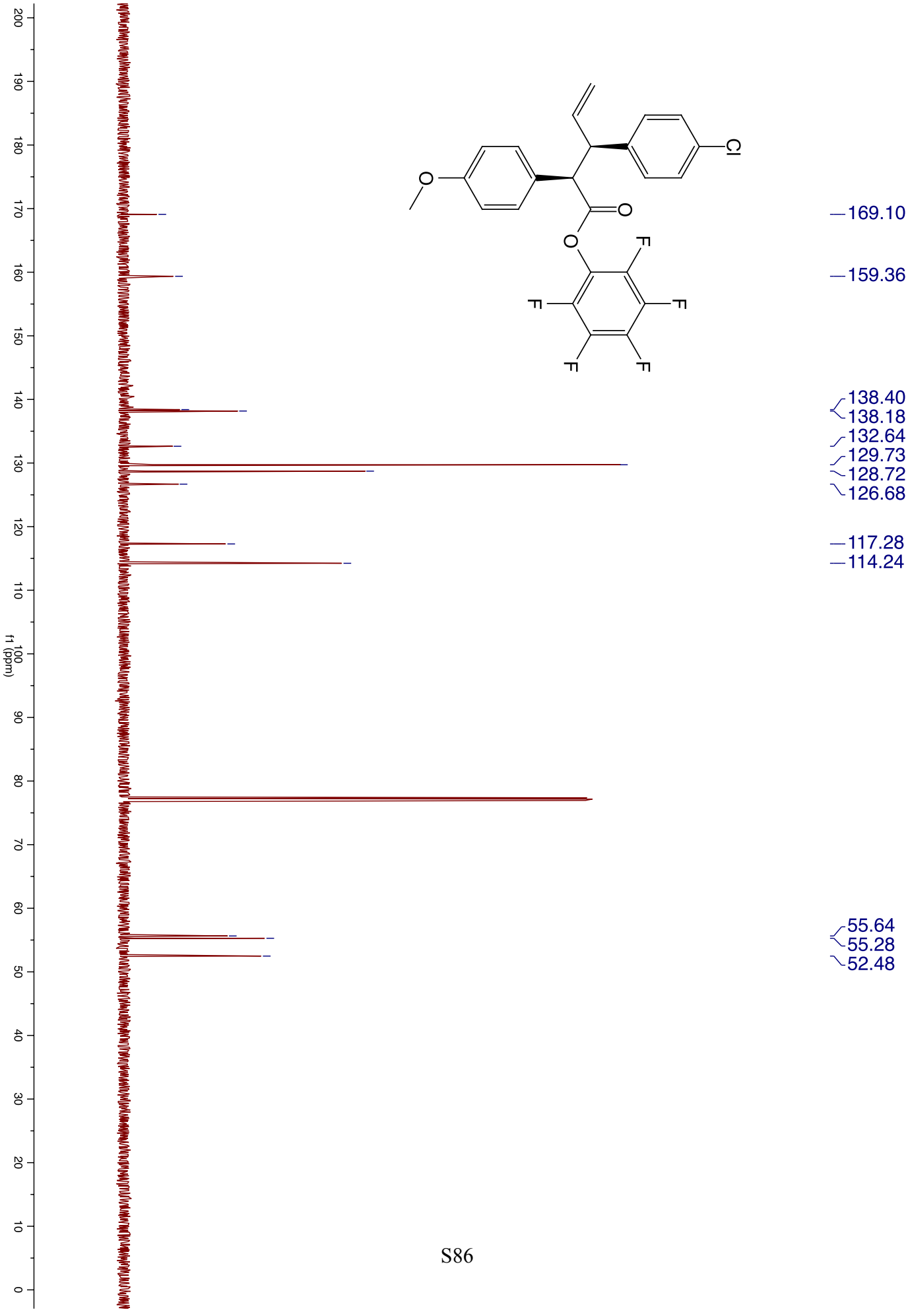

f1 (ppm)
2.08
2.26
2.01
2.02
1.00
1.03
1.04
1.03
1.04
2.99
3.06
7.40
7.39
7.38
7.27
7.27
7.26
7.26
6.94
6.94
6.93
6.91
6.91
6.90
5.79
5.78
5.77
5.76
5.76
5.75
5.75
5.73
4.94
4.94
4.93
4.92
4.92
4.92
4.83
4.83
4.83
4.80
4.80
4.80
4.25
4.23
4.10
4.08
4.08
4.06
3.83
3.82

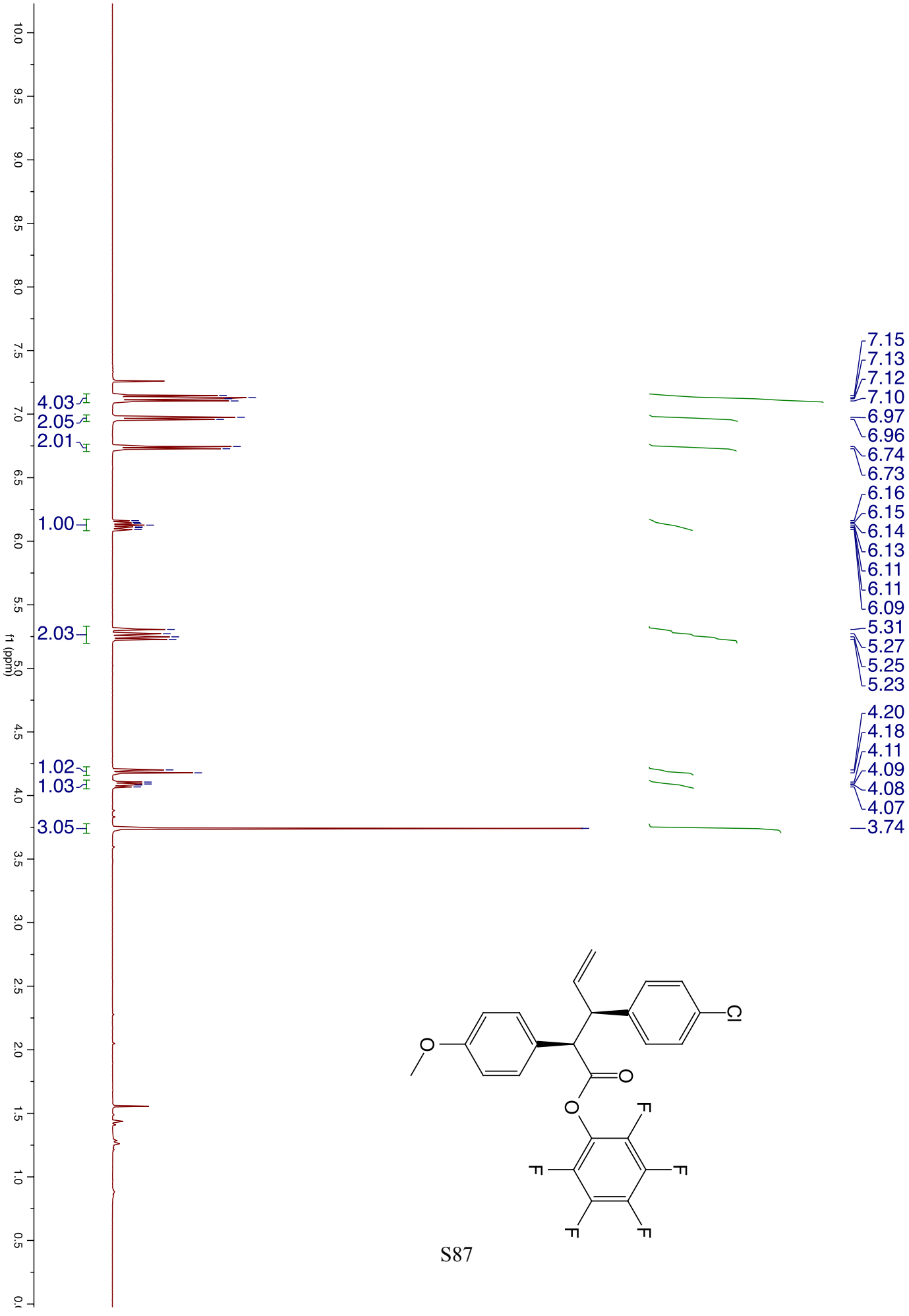

O
O
O
F
F
F
F
F
169.07
163.68
162.05
159.34
142.47
142.42
137.99
130.03
129.97
129.71
126.64
124.17
124.15
117.42
115.31
115.17
114.20
113.91
113.77
55.59
55.28
52.84
f1 (ppm)

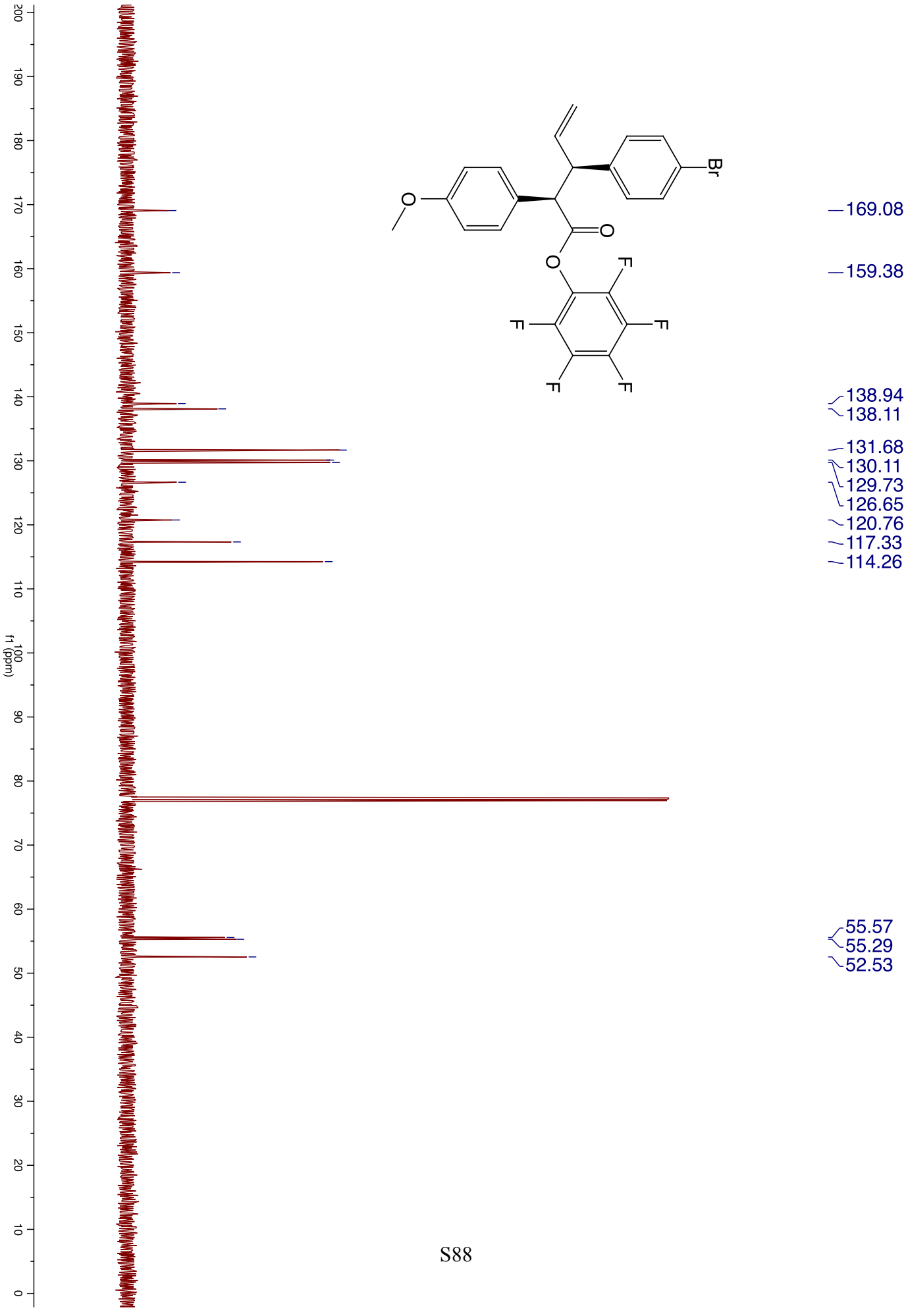

3.04
5.00
1.00
1.01
1.01
1.04
1.06
3.09
f1 (ppm)
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
6.81
6.81
6.81
6.80
6.80
6.80
6.79
6.78
6.78
6.78
6.77
6.76
6.74
6.74
6.73
6.73
6.16
6.15
6.15
6.14
6.13
6.12
6.12
6.11
5.32
5.32
5.32
5.29
5.29
5.29
5.26
5.26
5.25
5.24
5.24
5.24
4.22
4.20
4.12
4.10
4.10
4.08
3.74

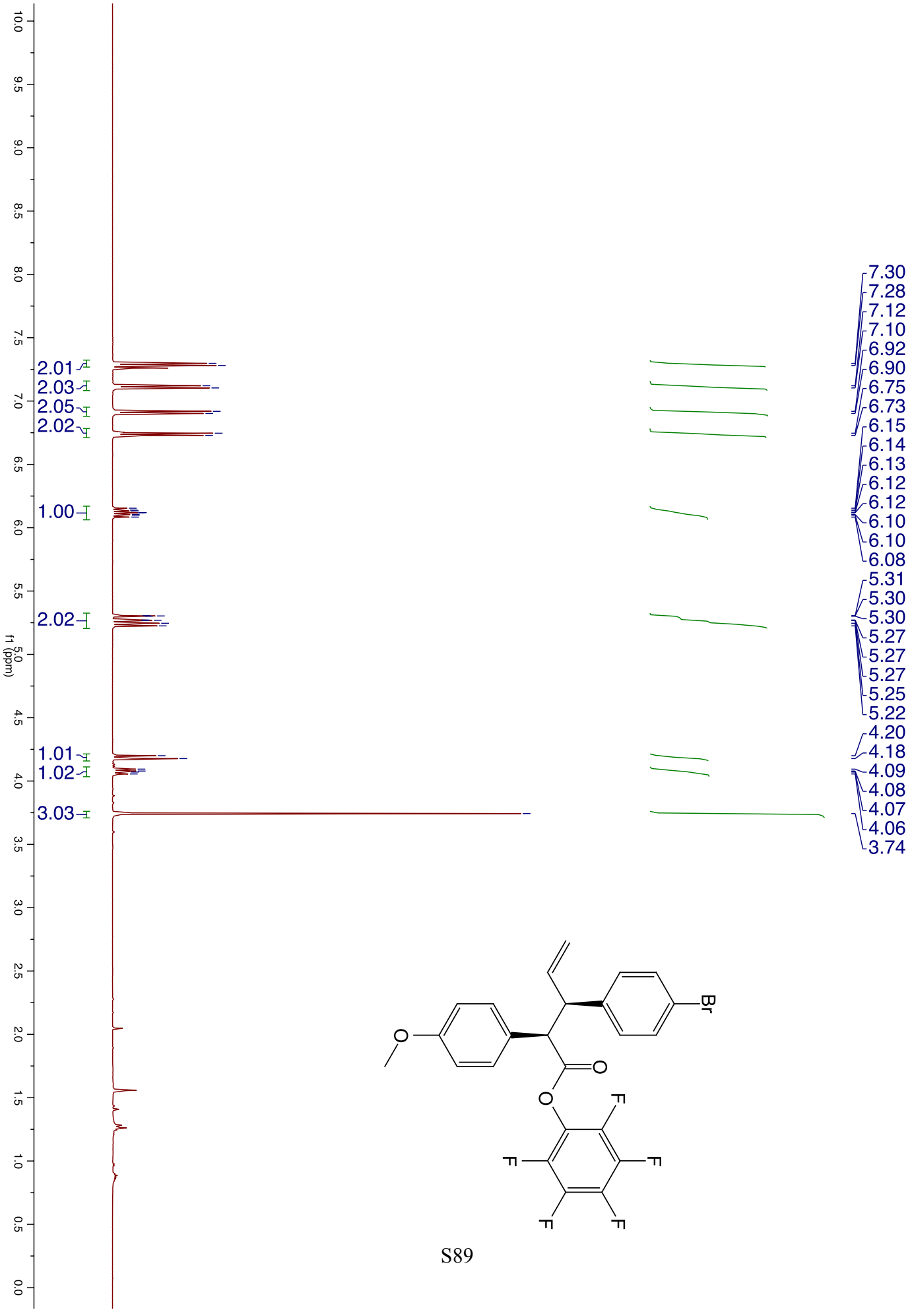

168.68
164.01
162.38
159.75
143.56
143.51
137.42
130.49
130.43
129.98
127.03
123.77
123.76
117.99
115.19
115.04
114.52
114.38
114.24
55.80
55.42
52.64
52.63
f1 (ppm)

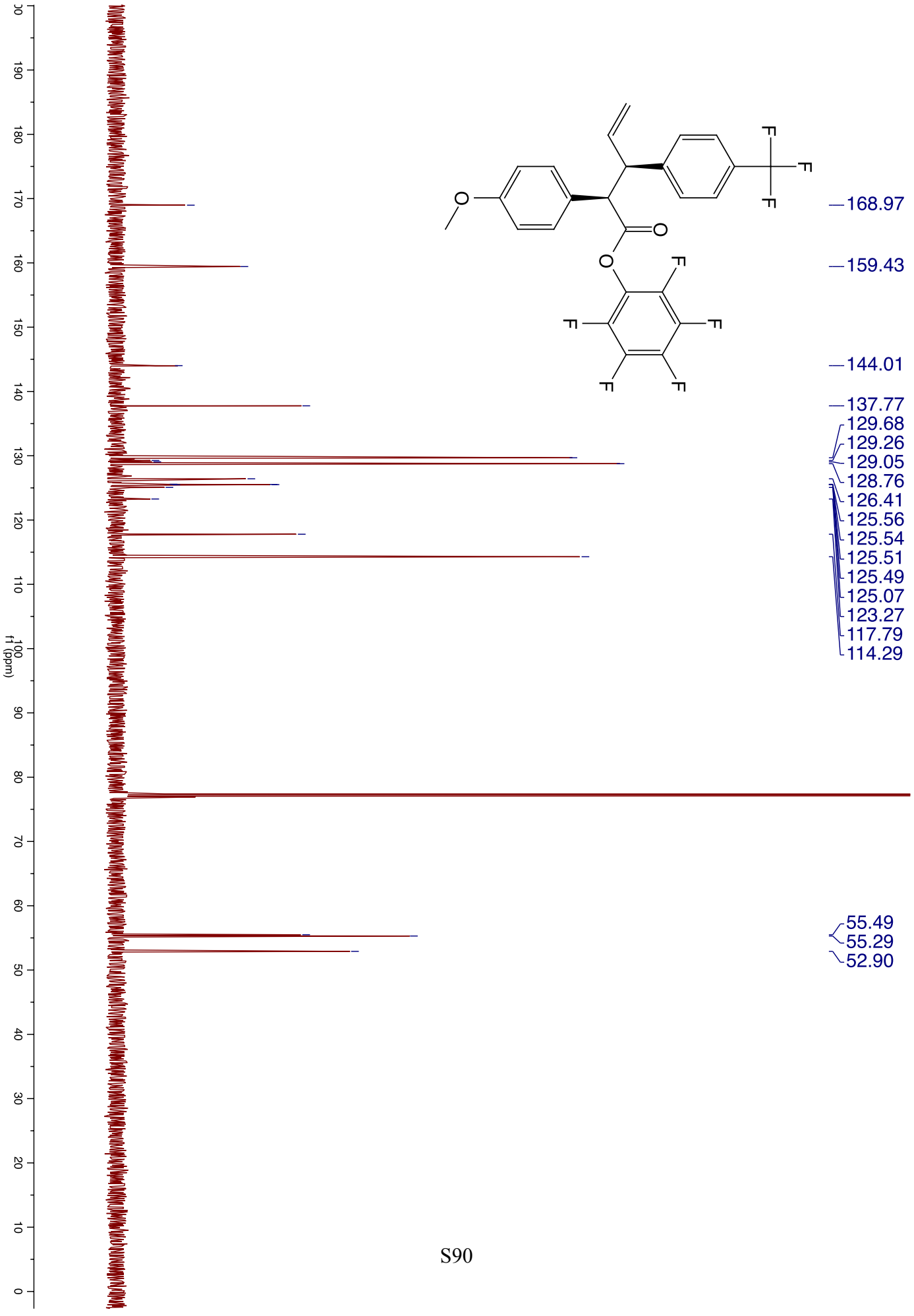

f1 (ppm)
1.96
1.15
1.00
1.01
0.99
2.04
0.99
1.01
1.02
1.02
1.03
3.16
7.38
7.38
7.37
7.37
7.34
7.33
7.14
7.13
7.13
7.12
7.12
7.12
7.06
7.05
6.98
6.98
6.98
6.98
6.94
6.94
6.93
6.93
5.76
5.75
5.74
5.73
5.73
5.72
5.72
5.70
4.97
4.97
4.97
4.95
4.95
4.95
4.84
4.84
4.84
4.81
4.81
4.81
4.25
4.23
4.12
4.10
4.10
4.08
3.83
O
O
O
F
F
F
F
F

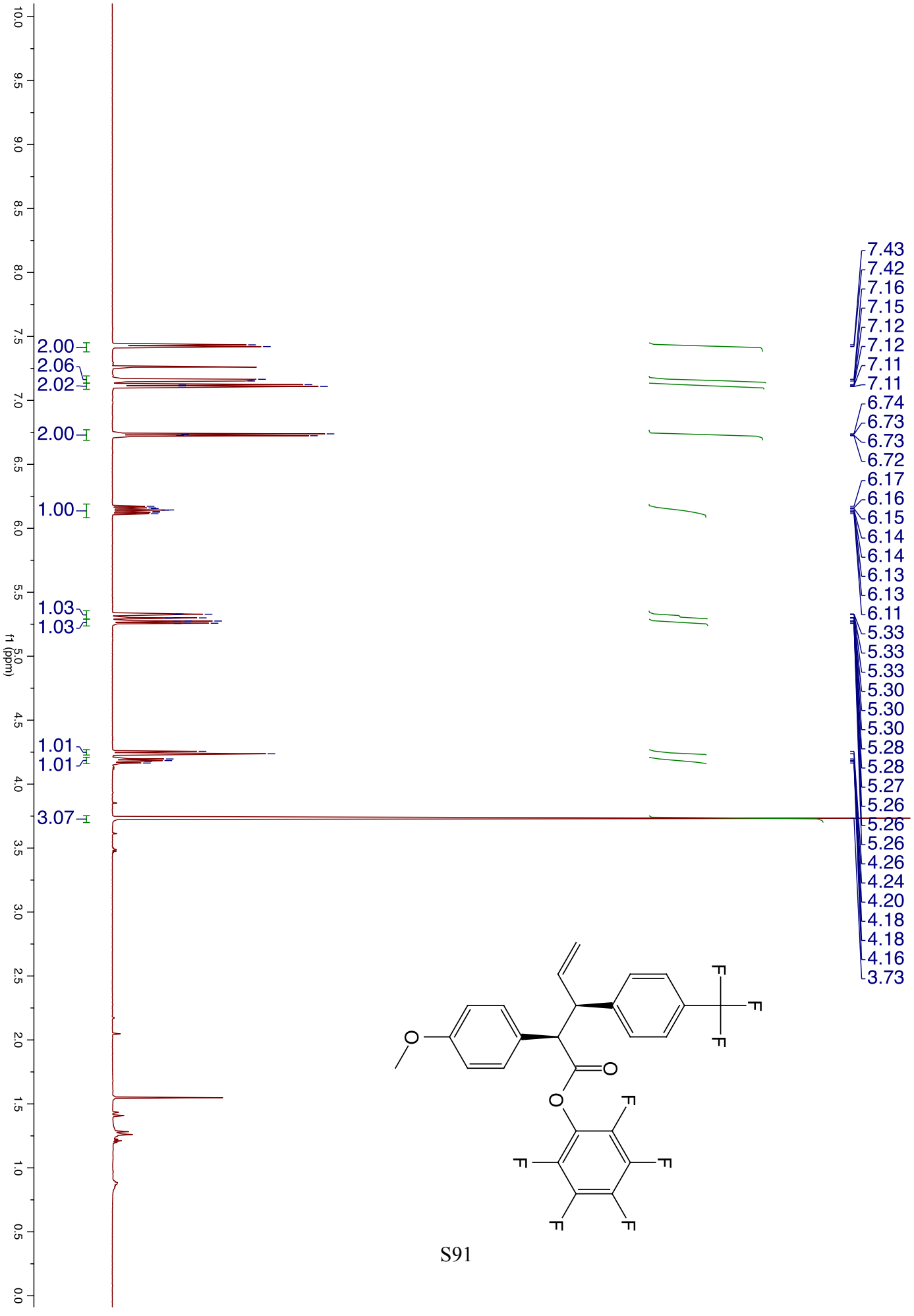

Cl
O
O
O
F
F
F
F
F
169.10
159.36
138.40
138.18
132.64
129.73
128.72
126.68
117.28
114.24
55.64
55.28
52.48
f1 (ppm)

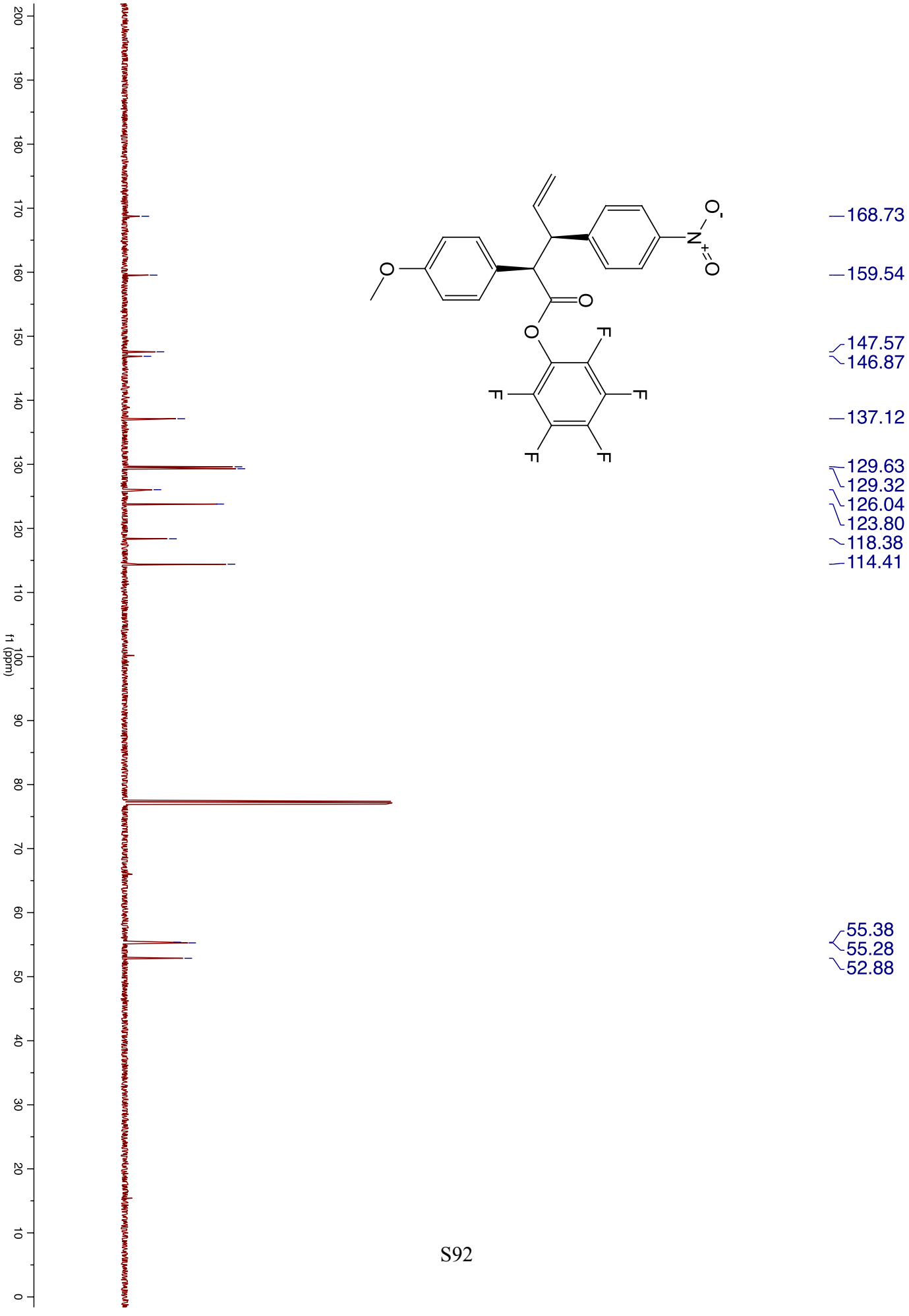

f1 (ppm)
4.03
2.05
2.01
1.00
2.03
1.02
1.03
3.05
7.15
7.13
7.12
7.10
6.97
6.96
6.74
6.73
6.16
6.15
6.14
6.13
6.11
6.11
6.09
5.31
5.27
5.25
5.23
4.20
4.18
4.11
4.09
4.08
4.07
3.74
O
O
O
Cl
F
F
F
F
F

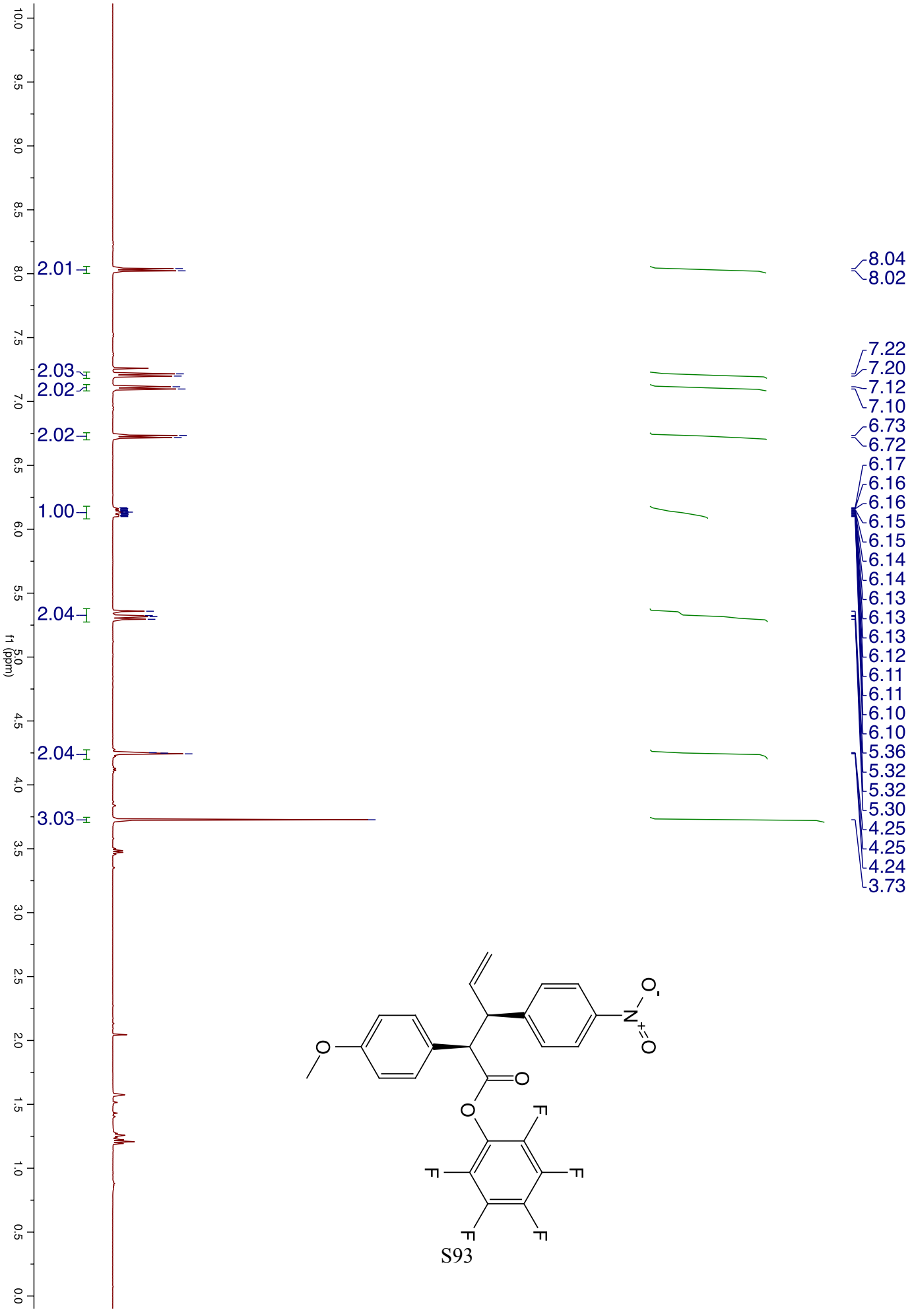

Br
O
O
O
F
F
F
F
F
169.08
159.38
138.94
138.11
131.68
130.11
129.73
126.65
120.76
117.33
114.26
55.57
55.29
52.53
f1 (ppm)

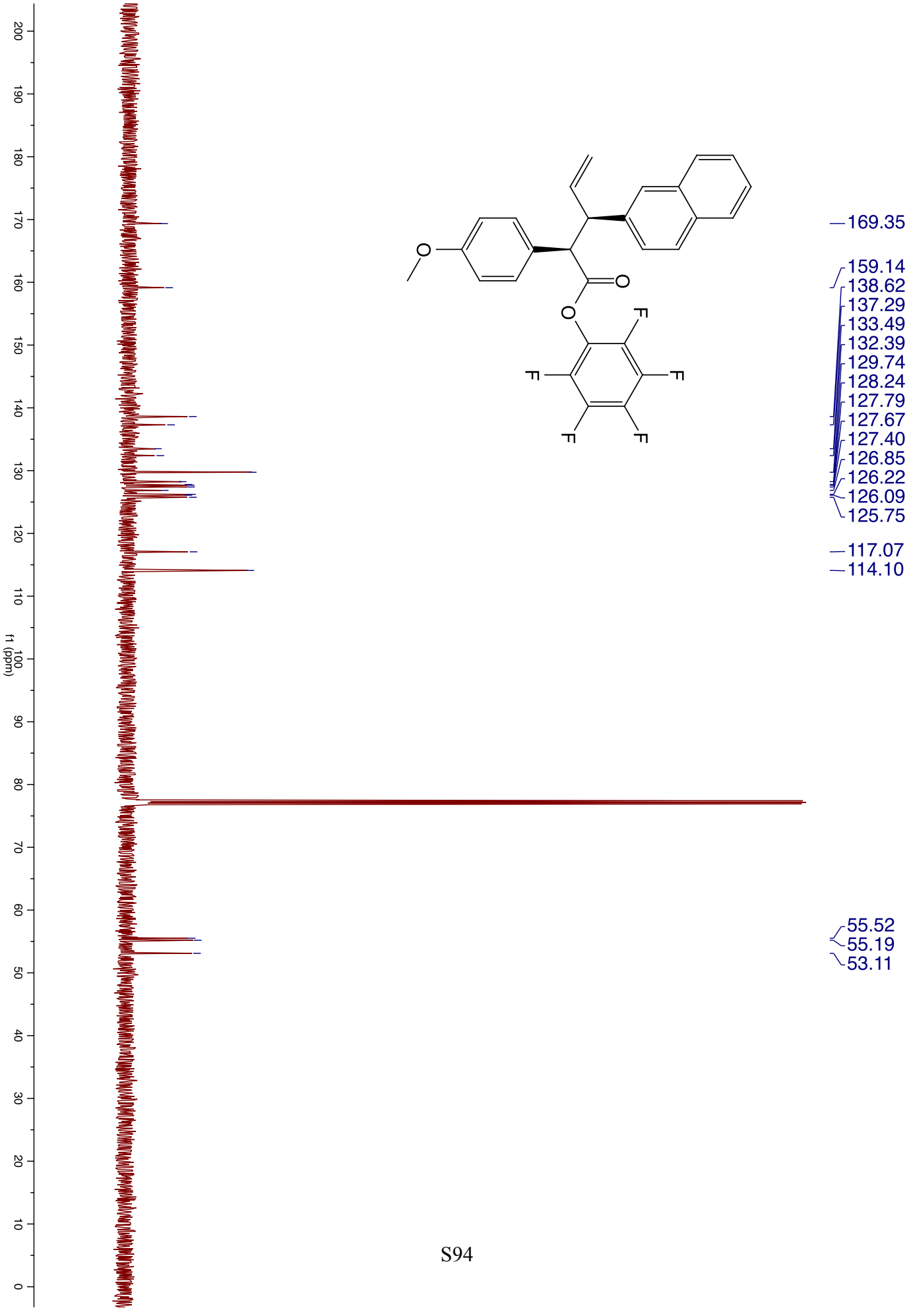

f1 (ppm)
2.01
2.03
2.05
2.02
1.00
2.02
1.01
1.02
3.03
7.30
7.28
7.12
7.10
6.92
6.90
6.75
6.73
6.15
6.14
6.13
6.12
6.12
6.10
6.10
6.08
5.31
5.30
5.30
5.27
5.27
5.27
5.25
5.22
4.20
4.18
4.09
4.08
4.07
4.06
3.74
Br
O
O
O
F
F
F
F
F

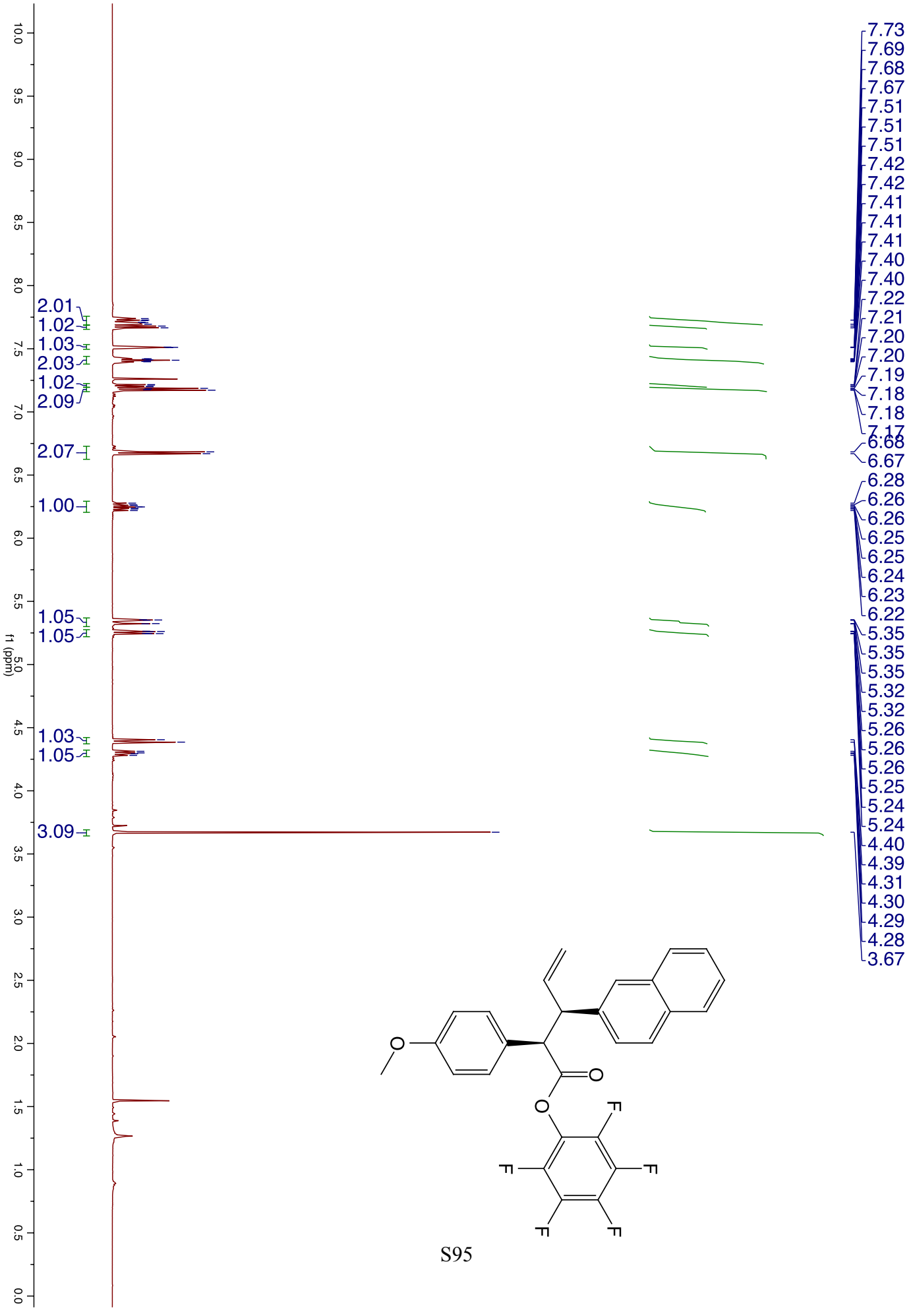

168.97
159.43
144.01
137.77
129.68
129.26
129.05
128.76
126.41
125.56
125.54
125.51
125.49
125.07
123.27
117.79
114.29
55.49
55.29
52.90
f1 (ppm)

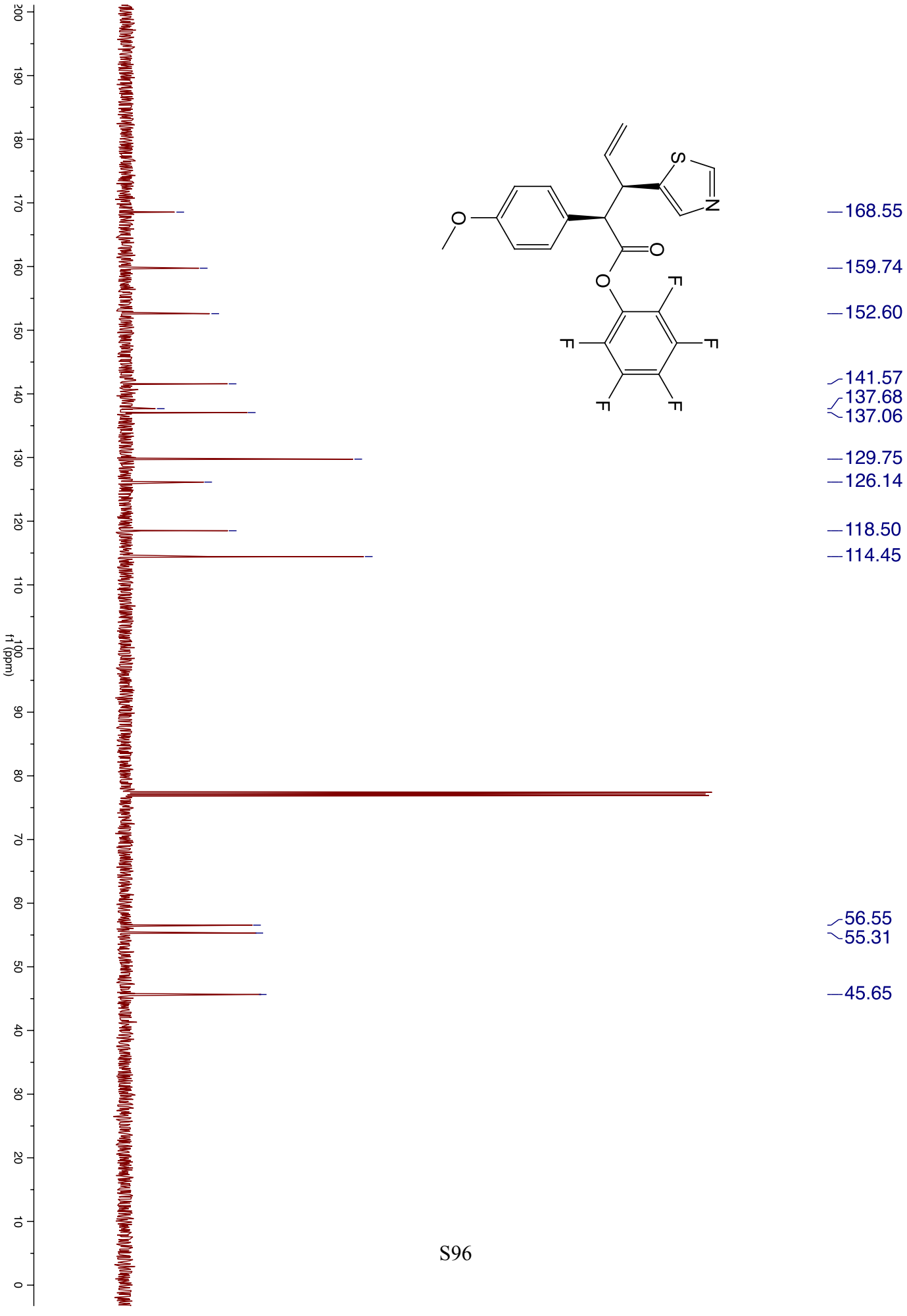

f1 (ppm)
2.00
2.06
2.02
2.00
1.00
1.03
1.03
1.01
1.01
3.07
7.43
7.42
7.16
7.15
7.12
7.12
7.11
7.11
6.74
6.73
6.73
6.72
6.17
6.16
6.15
6.14
6.14
6.13
6.13
6.11
5.33
5.33
5.33
5.30
5.30
5.30
5.28
5.28
5.27
5.26
5.26
5.26
4.26
4.24
4.20
4.18
4.18
4.16
3.73
O
O
O
F
F
F
F
F
F
F

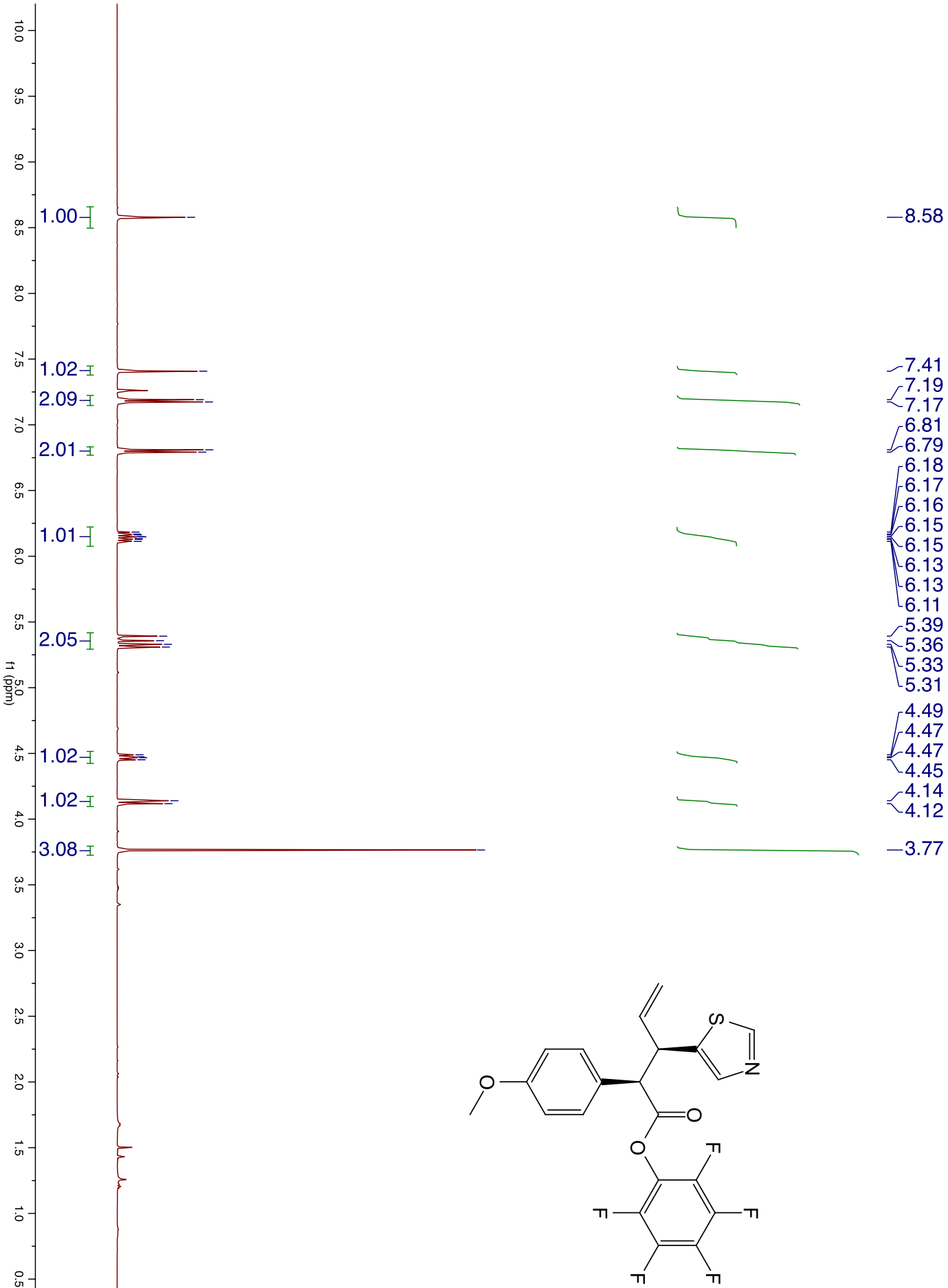

f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
N
O
O
F
F
F
F
F
168.73
159.54
147.57
146.87
137.12
129.63
129.32
126.04
123.80
118.38
114.41
55.38
55.28
52.88

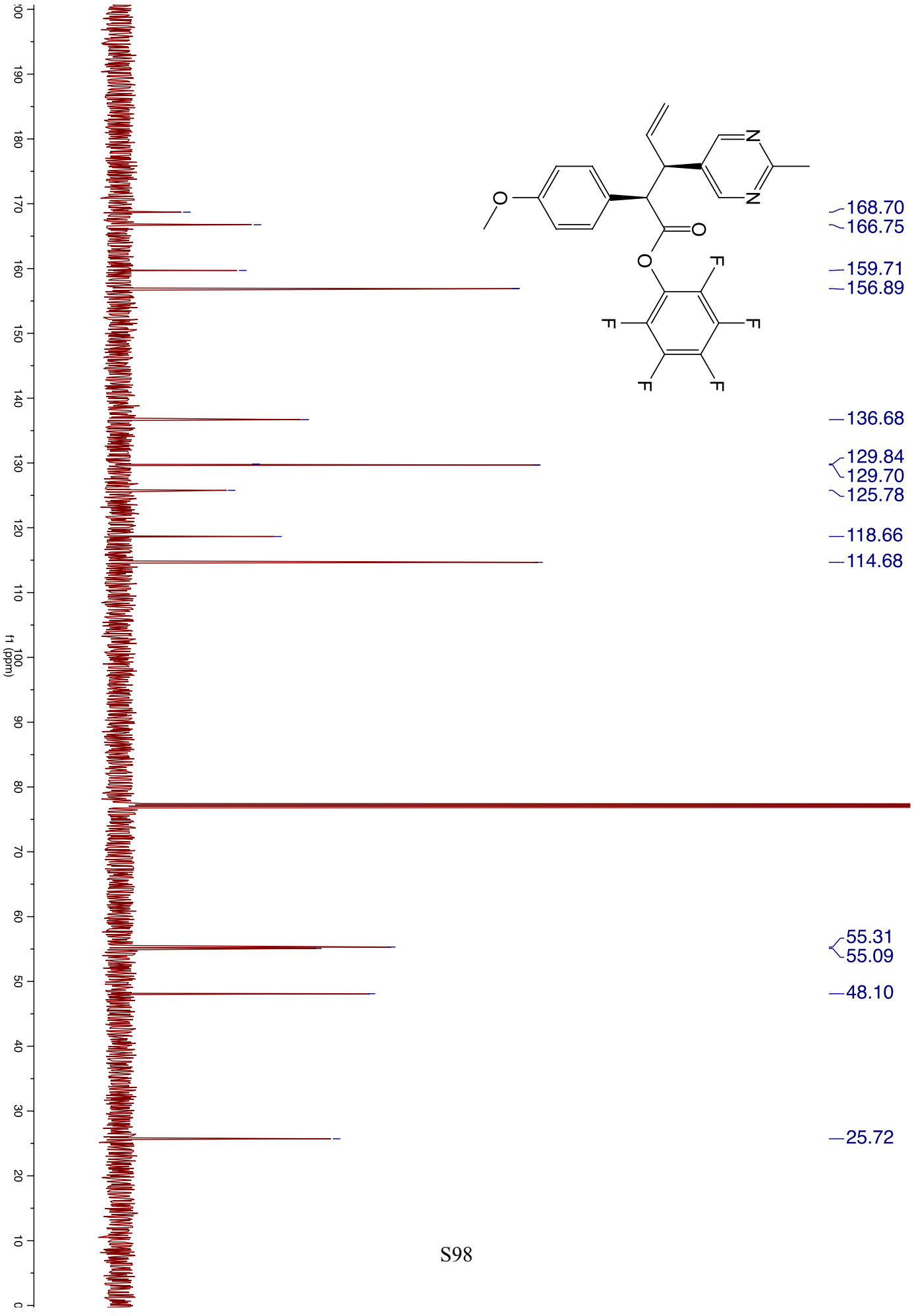

f1 (ppm)
2.01
2.03
2.02
2.02
1.00
2.04
2.04
3.03
8.04
8.02
7.22
7.20
7.12
7.10
6.73
6.72
6.17
6.16
6.16
6.15
6.15
6.14
6.14
6.13
6.13
6.13
6.12
6.11
6.11
6.10
6.10
5.36
5.32
5.32
5.30
4.25
4.25
4.24
3.73
O
O
O
O
N
O
O
F
F
F
F
F

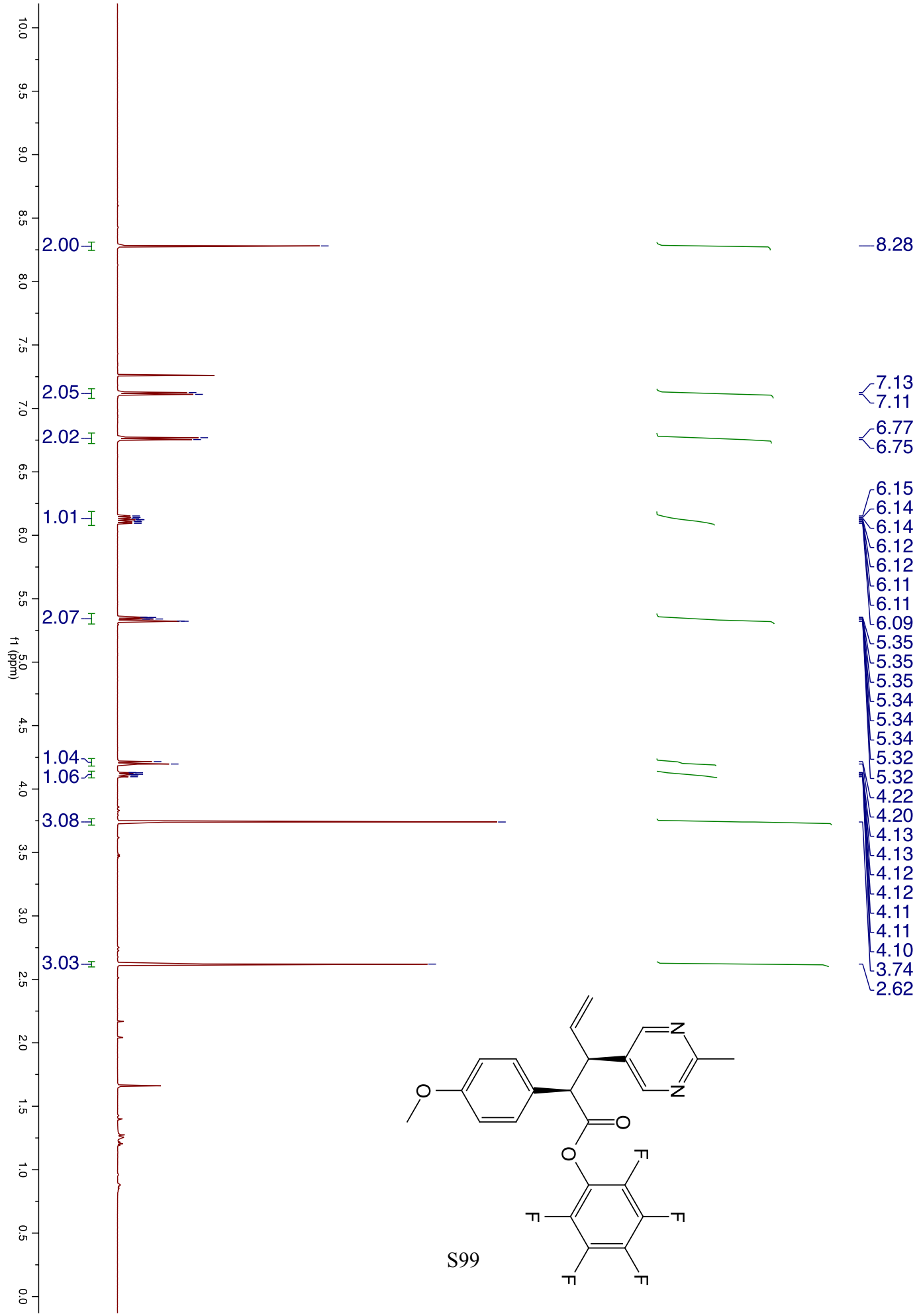

169.35
159.14
138.62
137.29
133.49
132.39
129.74
128.24
127.79
127.67
127.40
126.85
126.22
126.09
125.75
117.07
114.10
55.52
55.19
53.11
f1 (ppm)

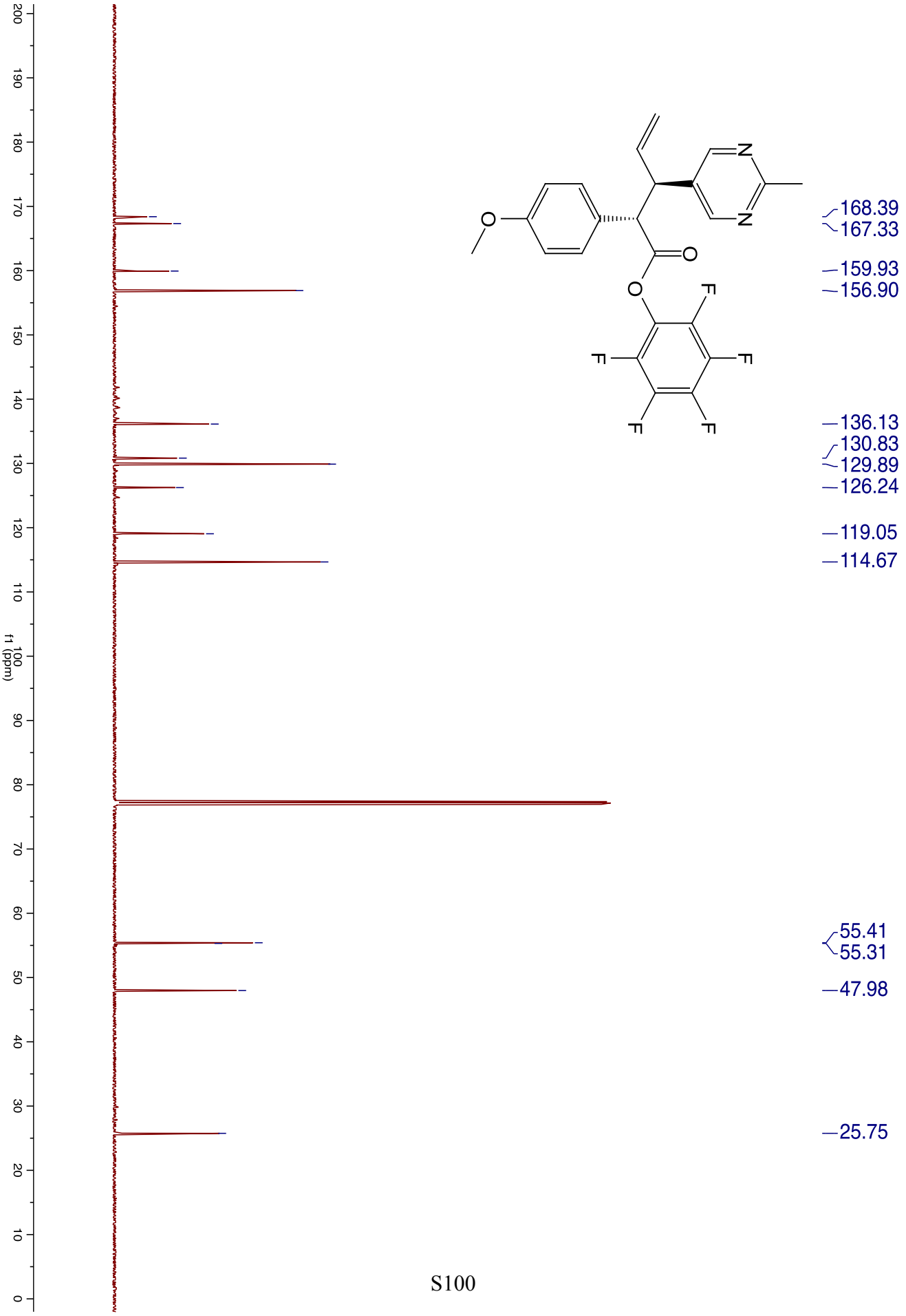

f1 (ppm)
2.01
1.02
1.03
2.03
1.02
2.09
2.07
1.00
1.05
1.05
1.03
1.05
3.09
7.73
7.69
7.68
7.67
7.51
7.51
7.51
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
6.68
6.67
6.28
6.26
6.26
6.25
6.25
6.24
6.23
6.22
5.35
5.35
5.35
5.32
5.32
5.26
5.26
5.26
5.25
5.24
5.24
4.40
4.39
4.31
4.30
4.29
4.28
3.67
O
O
O
F
F
F
F
F

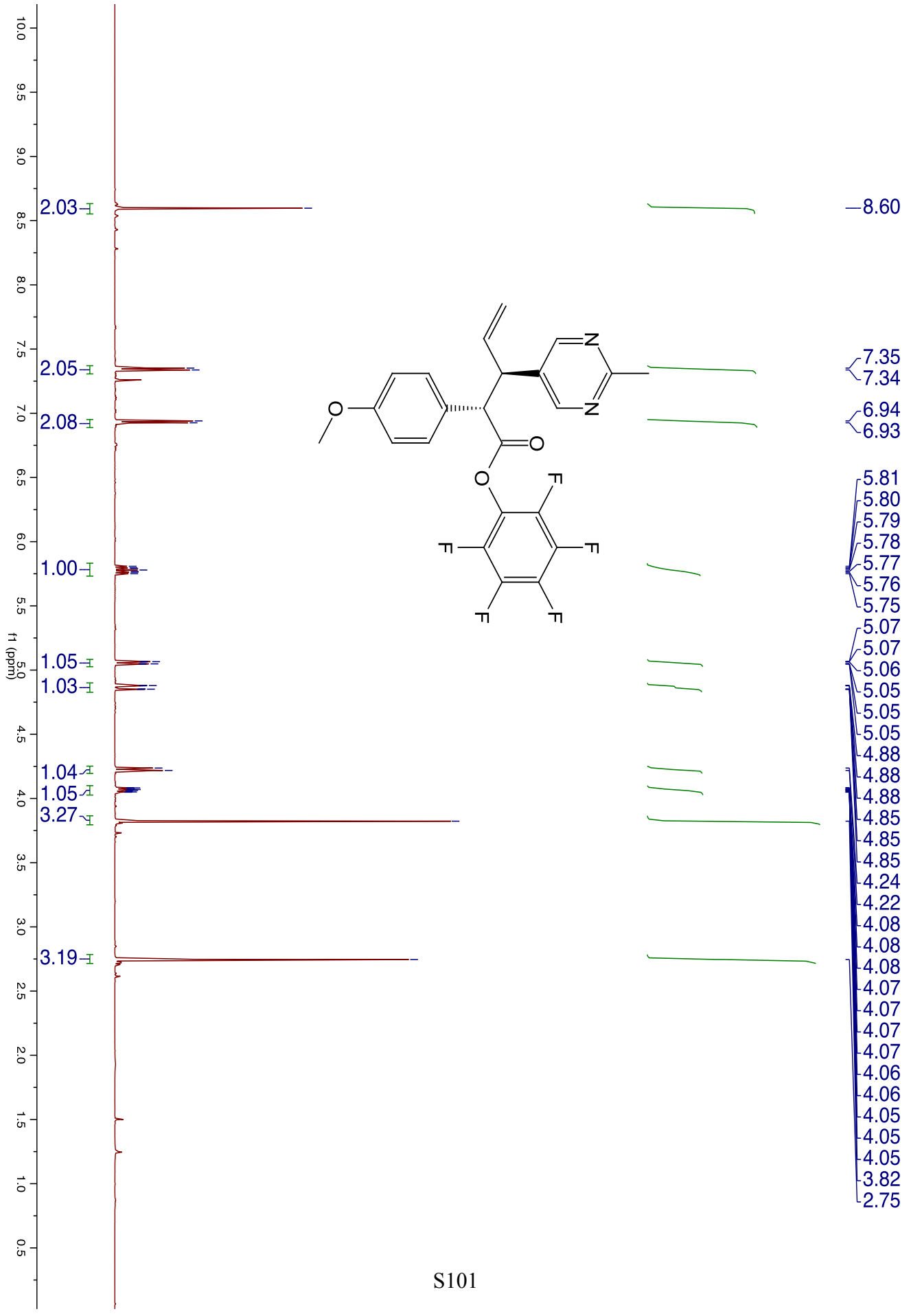

168.55
159.74
152.60
141.57
137.68
137.06
129.75
126.14
118.50
114.45
56.55
55.31
45.65
f1 (ppm)

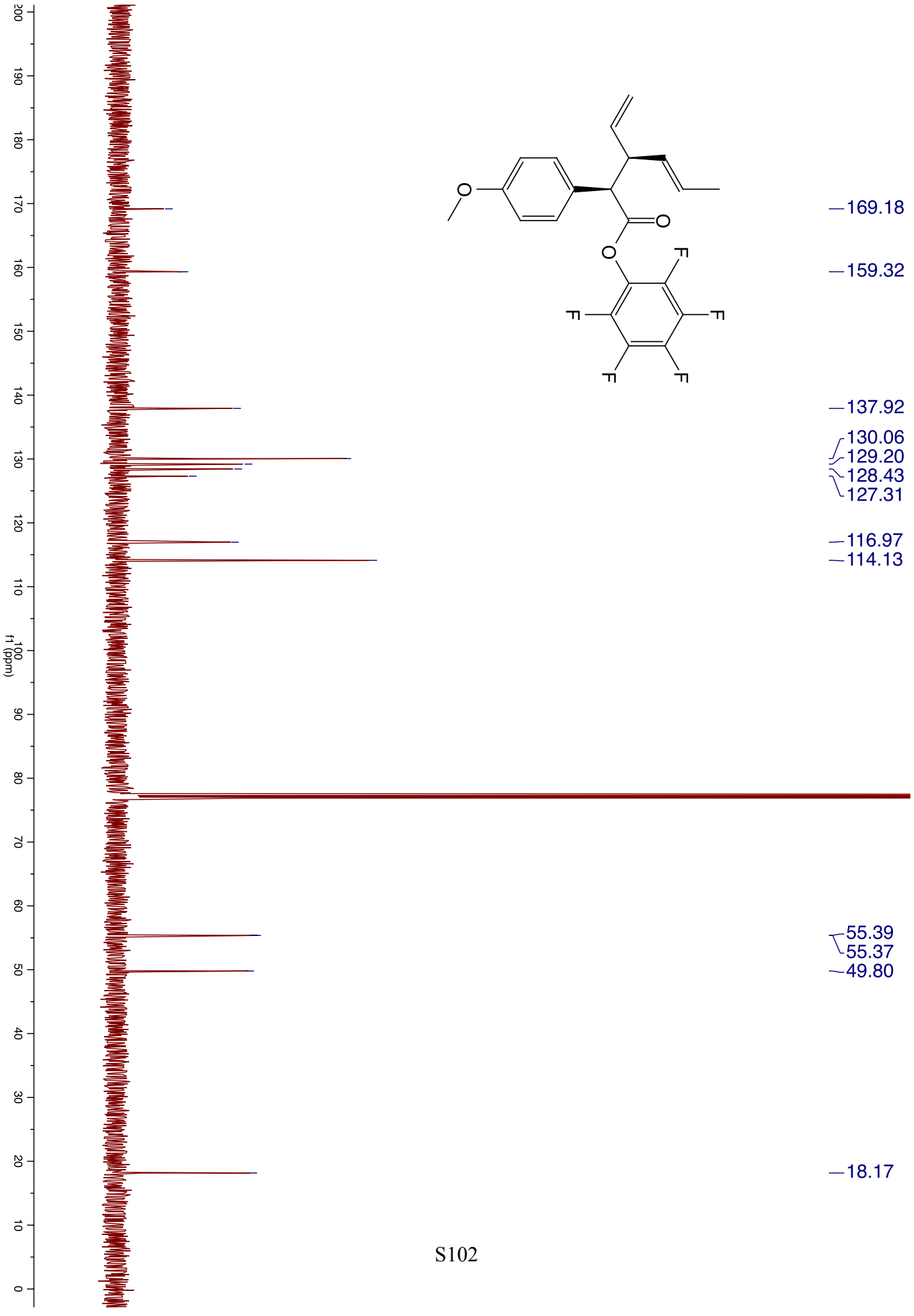

1.00
1.02
2.09
2.01
1.01
2.05
1.02
1.02
3.08
8.58
7.41
7.19
7.17
6.81
6.79
6.18
6.17
6.16
6.15
6.15
6.13
6.13
6.11
5.39
5.36
5.33
5.31
4.49
4.47
4.47
4.45
4.14
4.12
3.77
f1 (ppm)
O
S
N
O
O
F
F
F
F
F

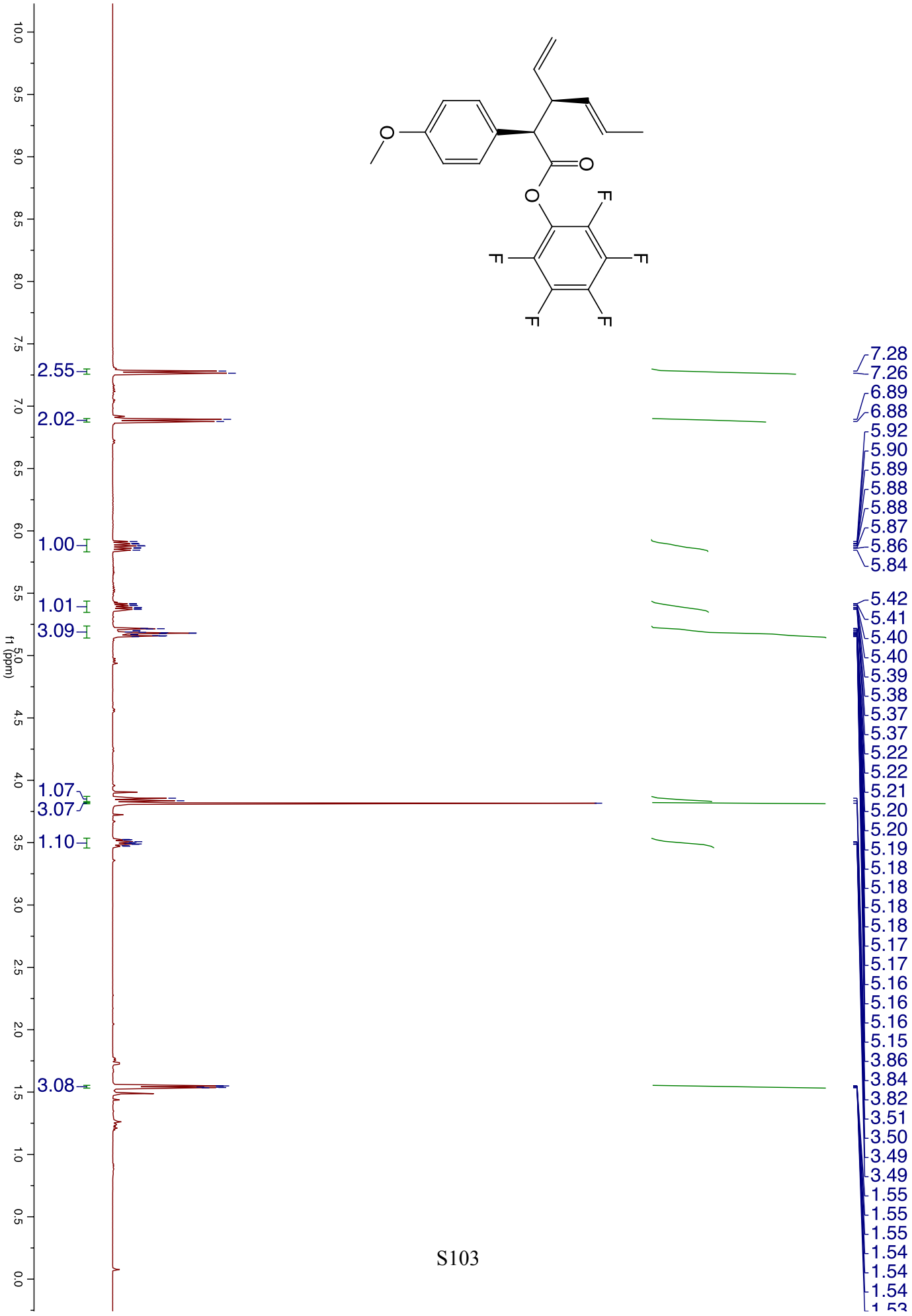

168.70
166.75
159.71
156.89
136.68
129.84
129.70
125.78
118.66
114.68
55.31
55.09
48.10
25.72
f1 (ppm)


2.00
2.05
2.02
1.01
2.07
1.04
1.06
3.08
3.03
f1 (ppm)
8.28
7.13
7.11
6.77
6.75
6.15
6.14
6.14
6.12
6.12
6.11
6.11
6.09
5.35
5.35
5.35
5.34
5.34
5.34
5.32
5.32
4.22
4.20
4.13
4.13
4.12
4.12
4.11
4.11
4.10
3.74
2.62
N
N
O
O
O
F
F
F
F
F


168.39
167.33
159.93
156.90
136.13
130.83
129.89
126.24
119.05
114.67
55.41
55.31
47.98
25.75
f1 (ppm)


f1 (ppm)
2.03
2.05
2.08
1.00
1.05
1.03
1.04
1.05
3.27
3.19
8.60
7.35
7.34
6.94
6.93
5.81
5.80
5.79
5.78
5.77
5.76
5.75
5.07
5.07
5.06
5.05
5.05
5.05
4.88
4.88
4.88
4.85
4.85
4.85
4.24
4.22
4.08
4.08
4.08
4.07
4.07
4.07
4.07
4.06
4.06
4.05
4.05
4.05
3.82
2.75


O
O
O
F
F
F
F
169.18
159.32
137.92
130.06
129.20
128.43
127.31
116.97
114.13
55.39
55.37
49.80
18.17
f1 (ppm)


O
O
O
F
F
F
F
2.55
2.02
1.00
1.01
3.09
1.07
3.07
1.10
3.08
f1 (ppm)
7.28
7.26
6.89
6.88
5.92
5.90
5.89
5.88
5.88
5.87
5.86
5.84
5.42
5.41
5.40
5.40
5.39
5.38
5.37
5.37
5.22
5.22
5.21
5.20
5.20
5.19
5.18
5.18
5.18
5.18
5.17
5.17
5.16
5.16
5.16
5.15
3.86
3.84
3.82
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3.50
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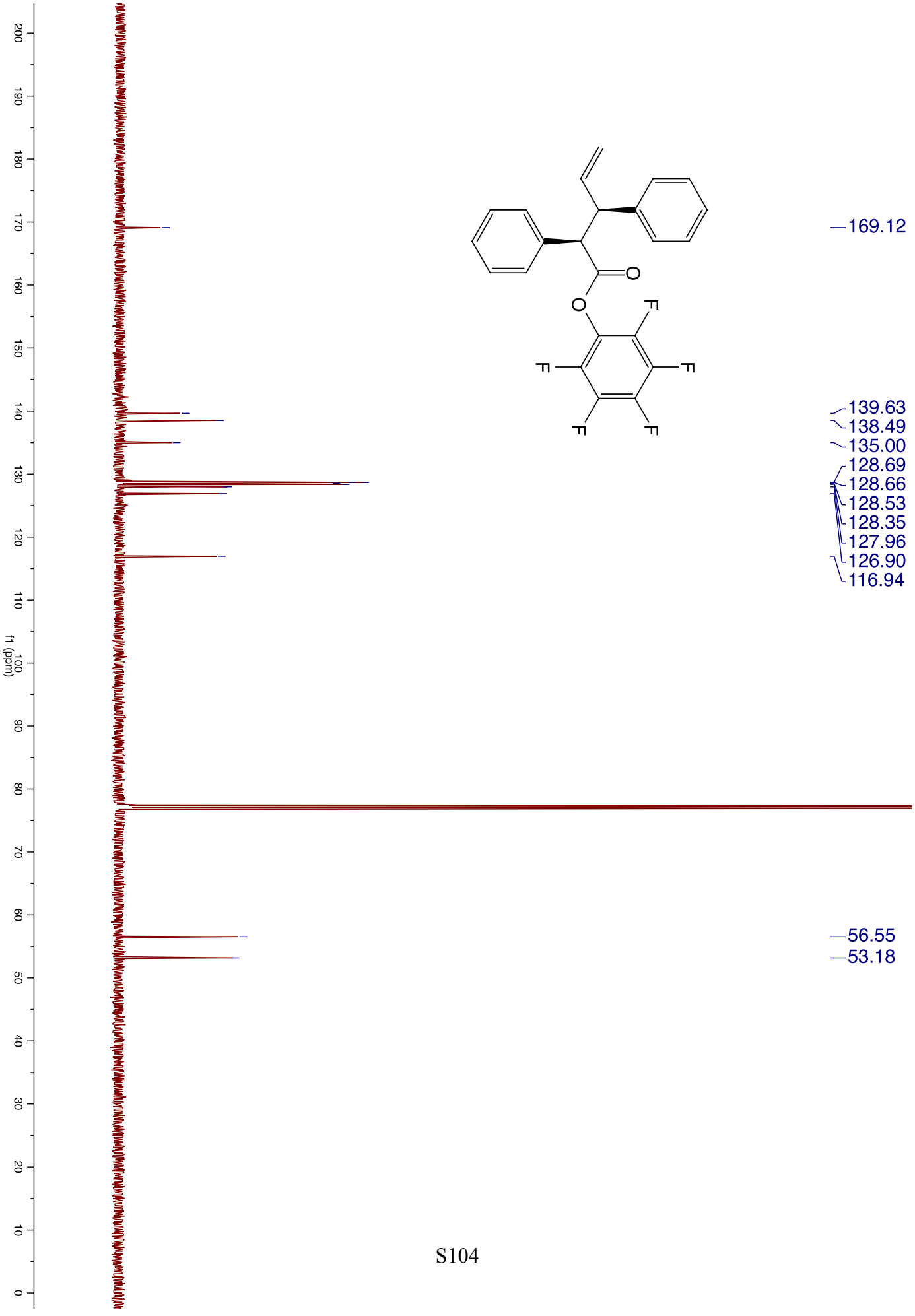
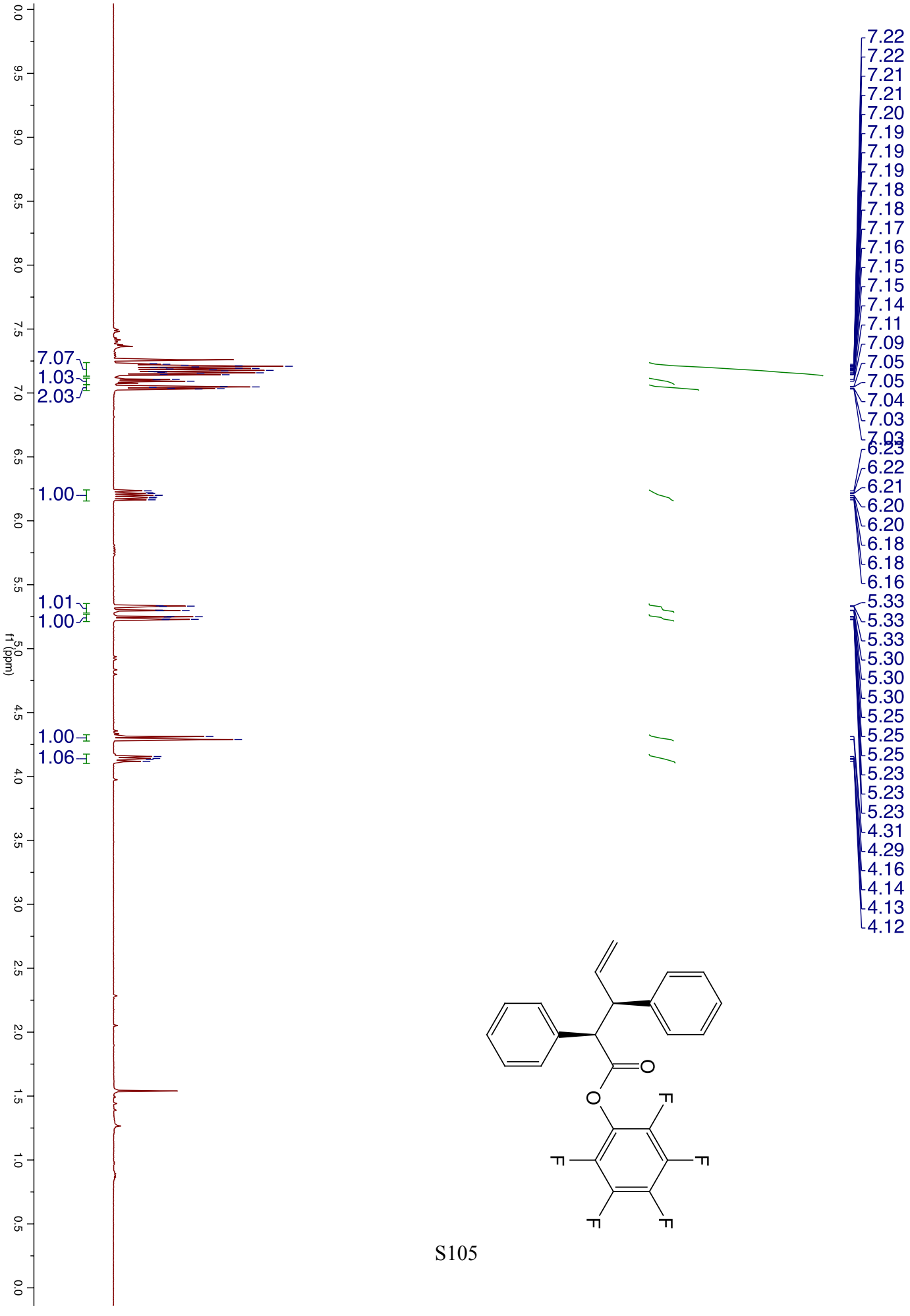
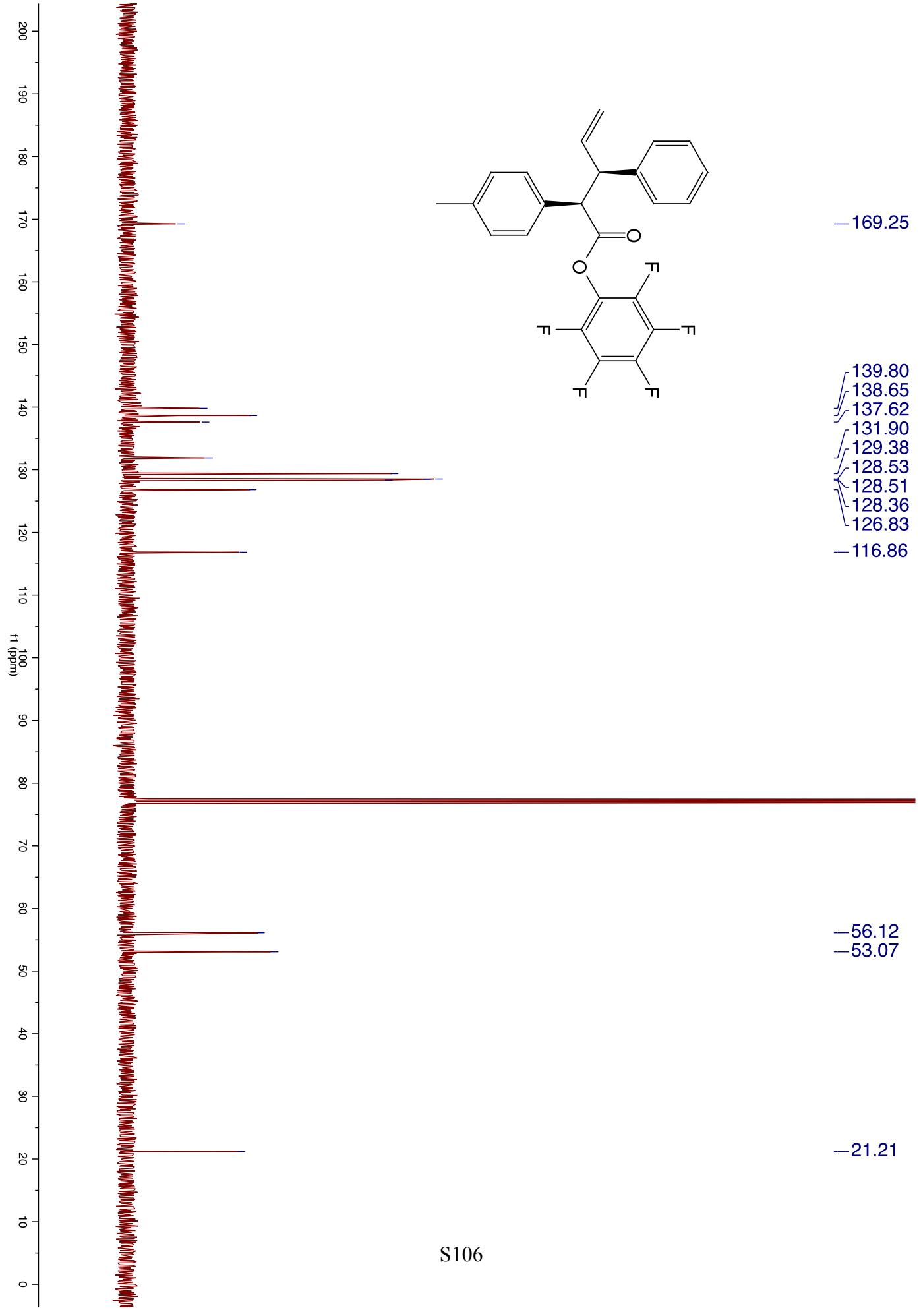
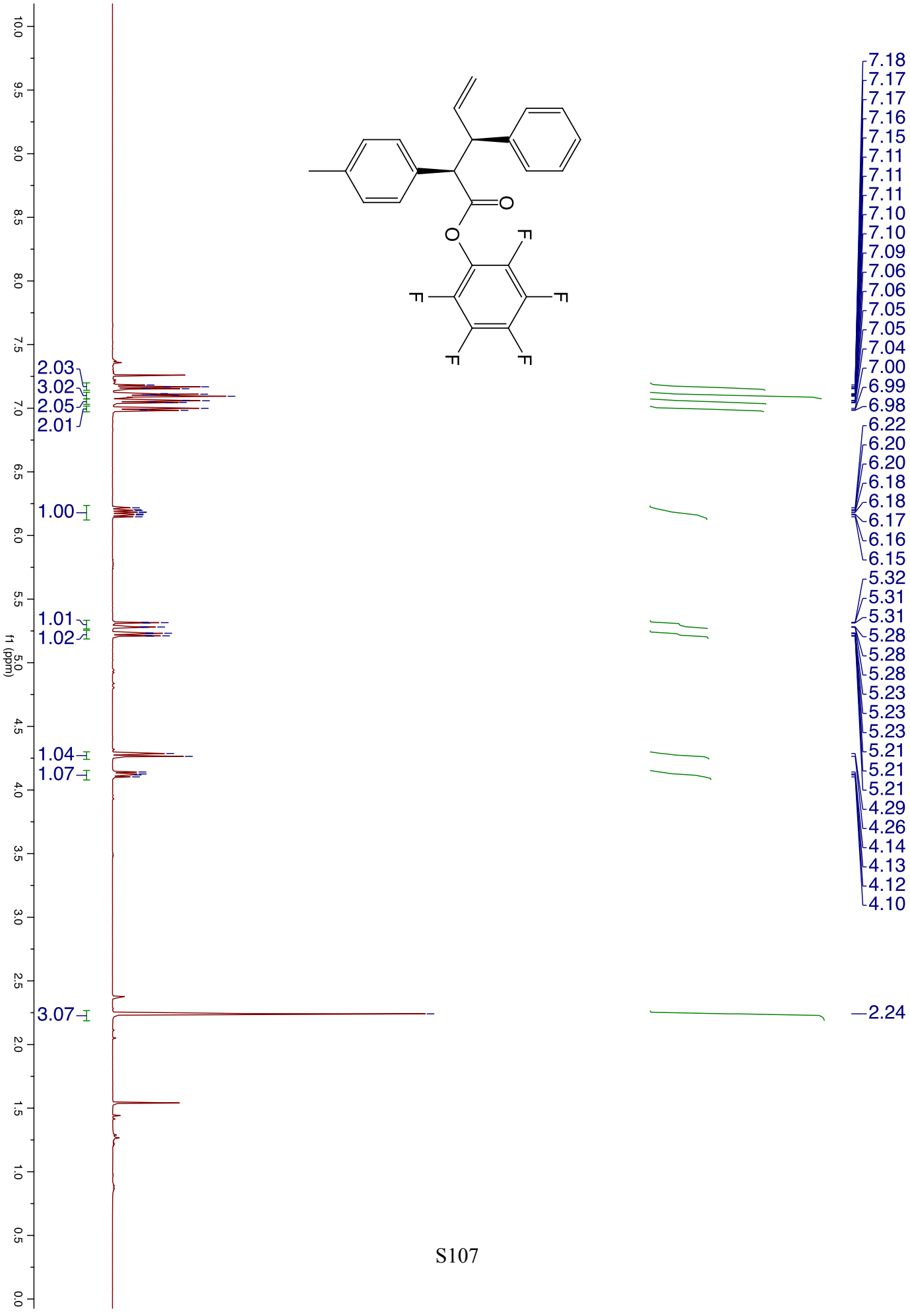
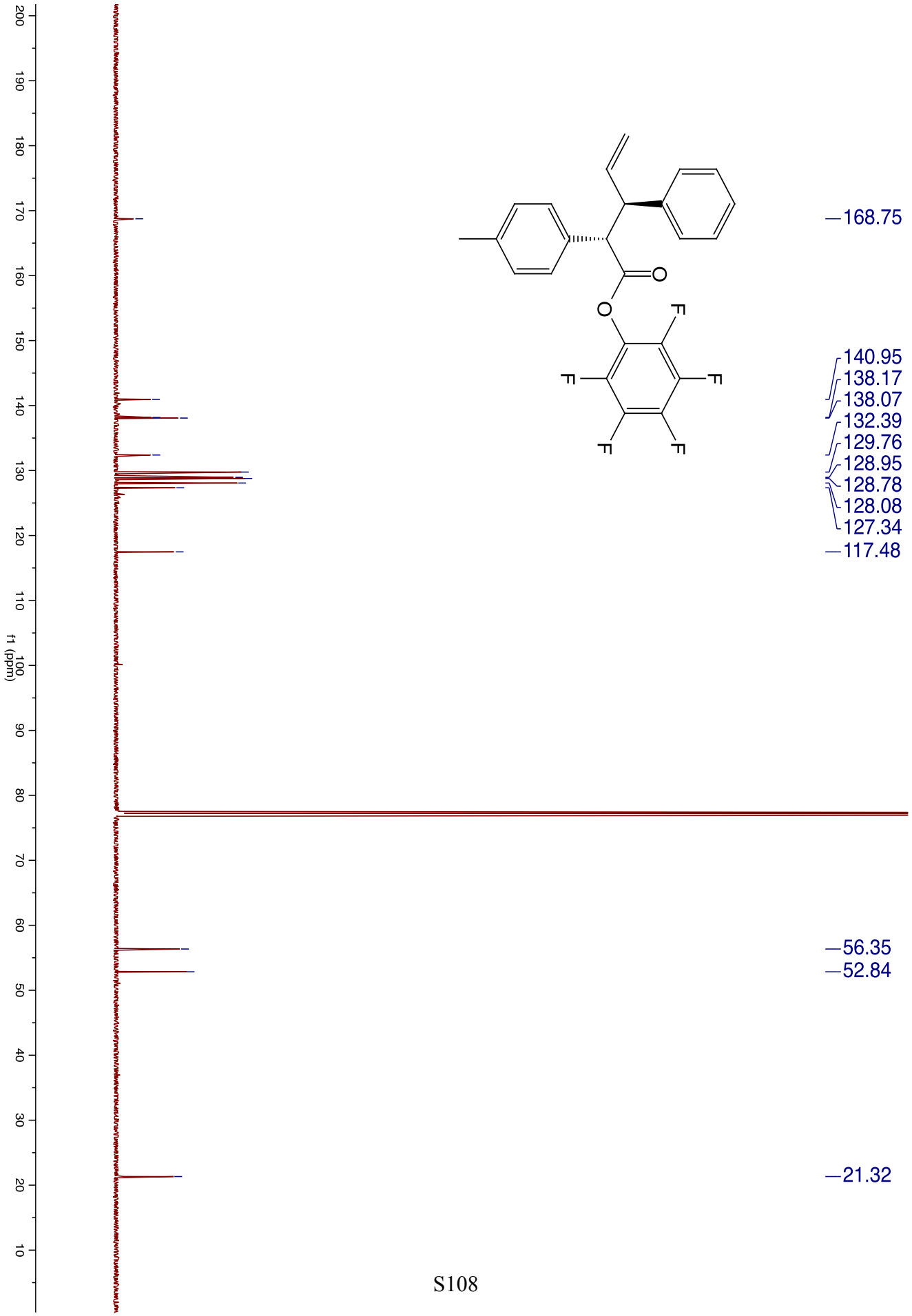
1.55
1.55
1.55
1.54
1.54
1.54

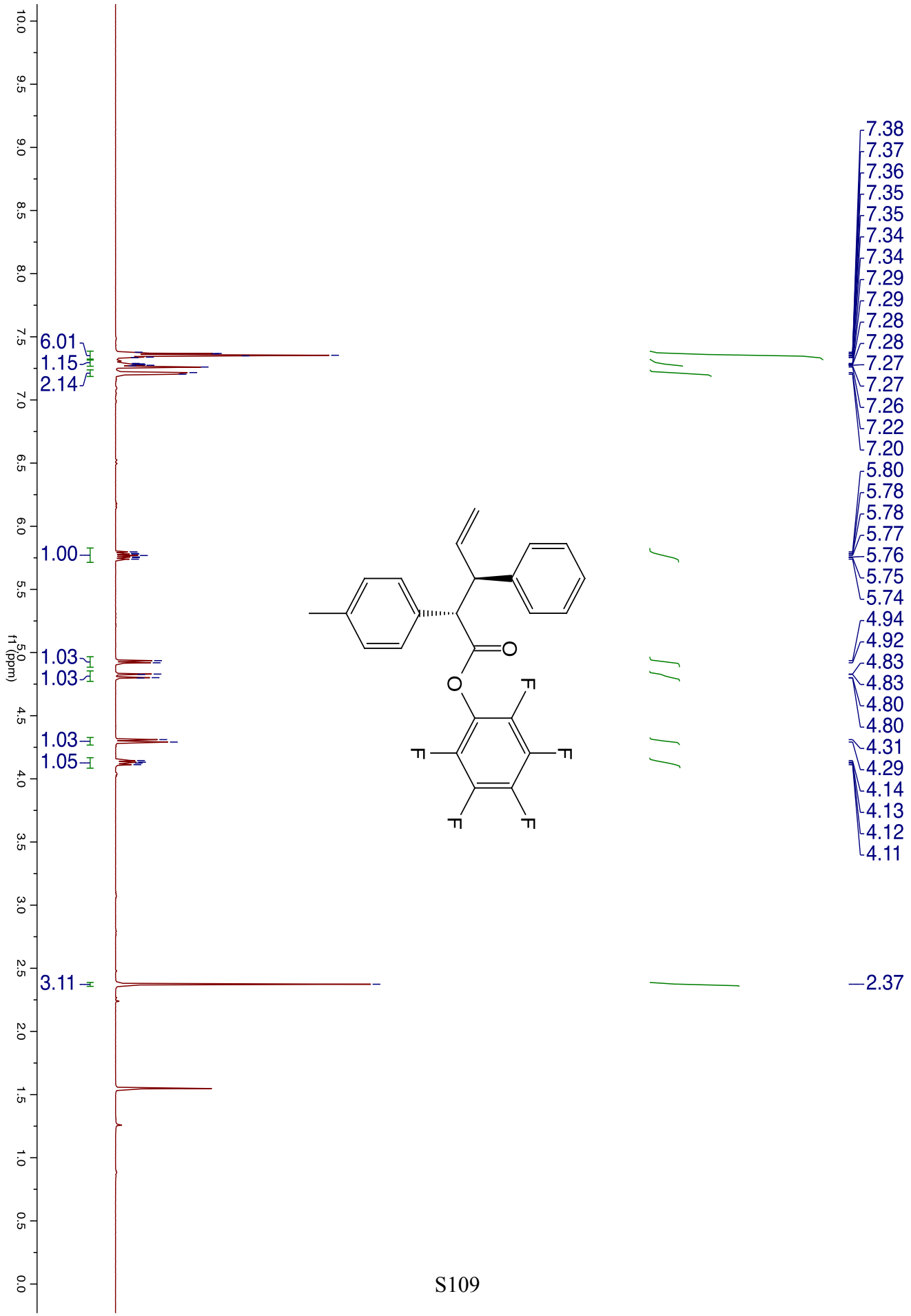

169.12
139.63
138.49
135.00
128.69
128.66
128.53
128.35
127.96
126.90
116.94
56.55
53.18
O
O
F
F
F
F
F
f1 (ppm)

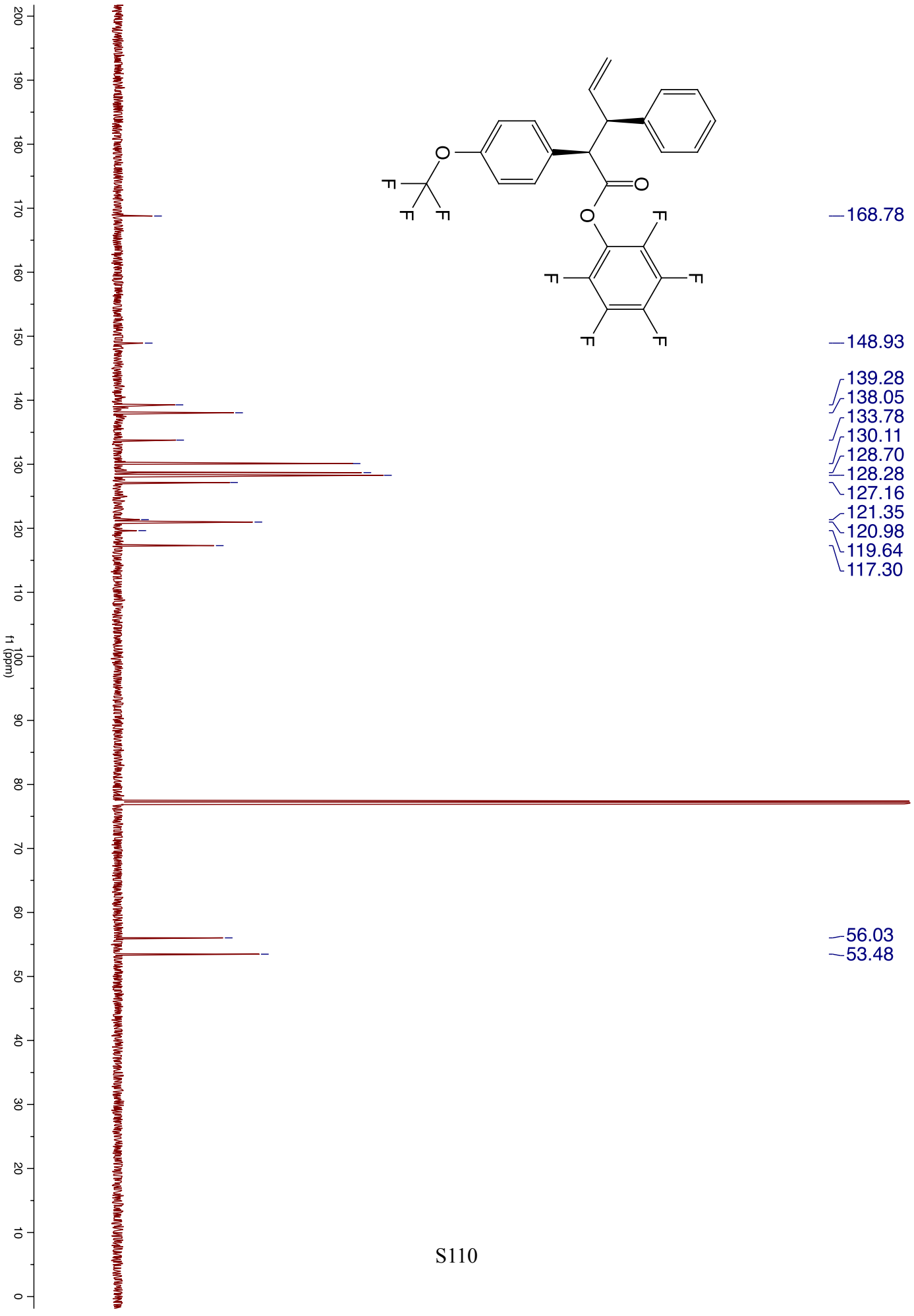

7.07
1.03
2.03
1.00
1.01
1.00
1.00
1.06
f1 (ppm)
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.16
7.15
7.15
7.14
7.11
7.09
7.05
7.05
7.04
7.03
7.03
6.23
6.22
6.21
6.20
6.20
6.18
6.18
6.16
5.33
5.33
5.33
5.30
5.30
5.30
5.25
5.25
5.25
5.23
5.23
5.23
4.31
4.29
4.16
4.14
4.13
4.12
O
O
F
F
F
F
F


169.25
139.80
138.65
137.62
131.90
129.38
128.53
128.51
128.36
126.83
116.86
56.12
53.07
21.21
f1 (ppm)


f1 (ppm)
2.03
3.02
2.05
2.01
1.00
1.01
1.02
1.04
1.07
3.07
7.18
7.17
7.17
7.16
7.15
7.11
7.11
7.11
7.10
7.10
7.09
7.06
7.06
7.05
7.05
7.04
7.00
6.99
6.98
6.22
6.20
6.20
6.18
6.18
6.17
6.16
6.15
5.32
5.31
5.31
5.28
5.28
5.28
5.23
5.23
5.23
5.21
5.21
5.21
4.29
4.26
4.14
4.13
4.12
4.10
2.24
F
F
F
F
F
O
O


168.75
140.95
138.17
138.07
132.39
129.76
128.95
128.78
128.08
127.34
117.48
56.35
52.84
21.32
f1 (ppm)


10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6.01
1.15
2.14
1.00
1.03
1.03
1.03
1.05
3.11
O
O
F
F
F
F
F
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.22
7.20
5.80
5.78
5.78
5.77
5.76
5.75
5.74
4.94
4.92
4.83
4.83
4.80
4.80
4.31
4.29
4.14
4.13
4.12
4.11
2.37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139.28
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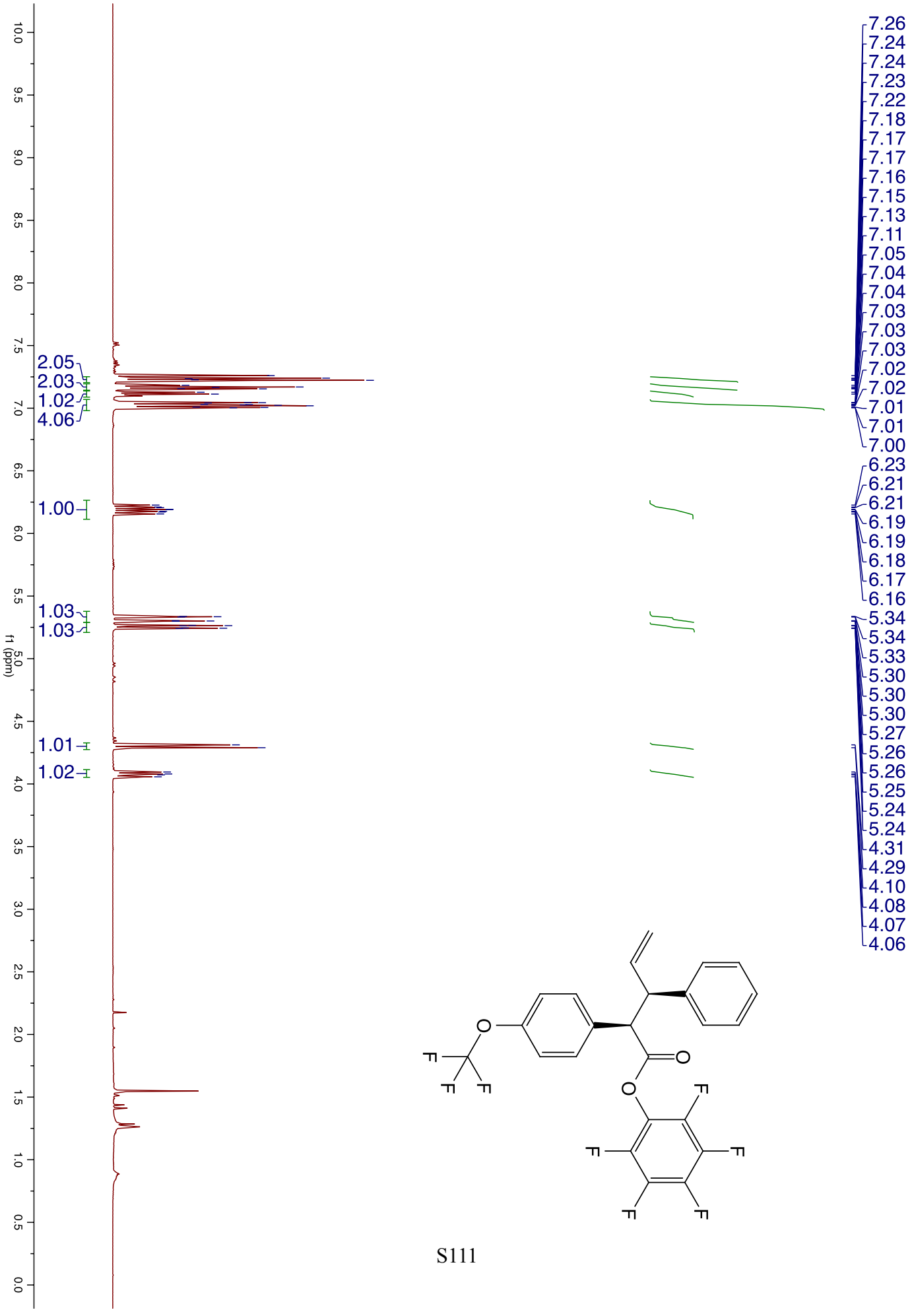
128.28
127.16
121.35
120.98
119.64
117.30
56.03
53.48
f1 (ppm)


f1 (ppm)
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2.03
1.02
4.06
1.00
1.03
1.03
1.01
1.02
7.26
7.24
7.24
7.23
7.22
7.18
7.17
7.17
7.16
7.15
7.13
7.11
7.05
7.04
7.04
7.03
7.03
7.03
7.02
7.02
7.01
7.01
7.00
6.23
6.21
6.21
6.19
6.19
6.18
6.17
6.16
5.34
5.34
5.33
5.30
5.30
5.30
5.27
5.26
5.26
5.25
5.24
5.24
4.31
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4.08
4.07
4.06
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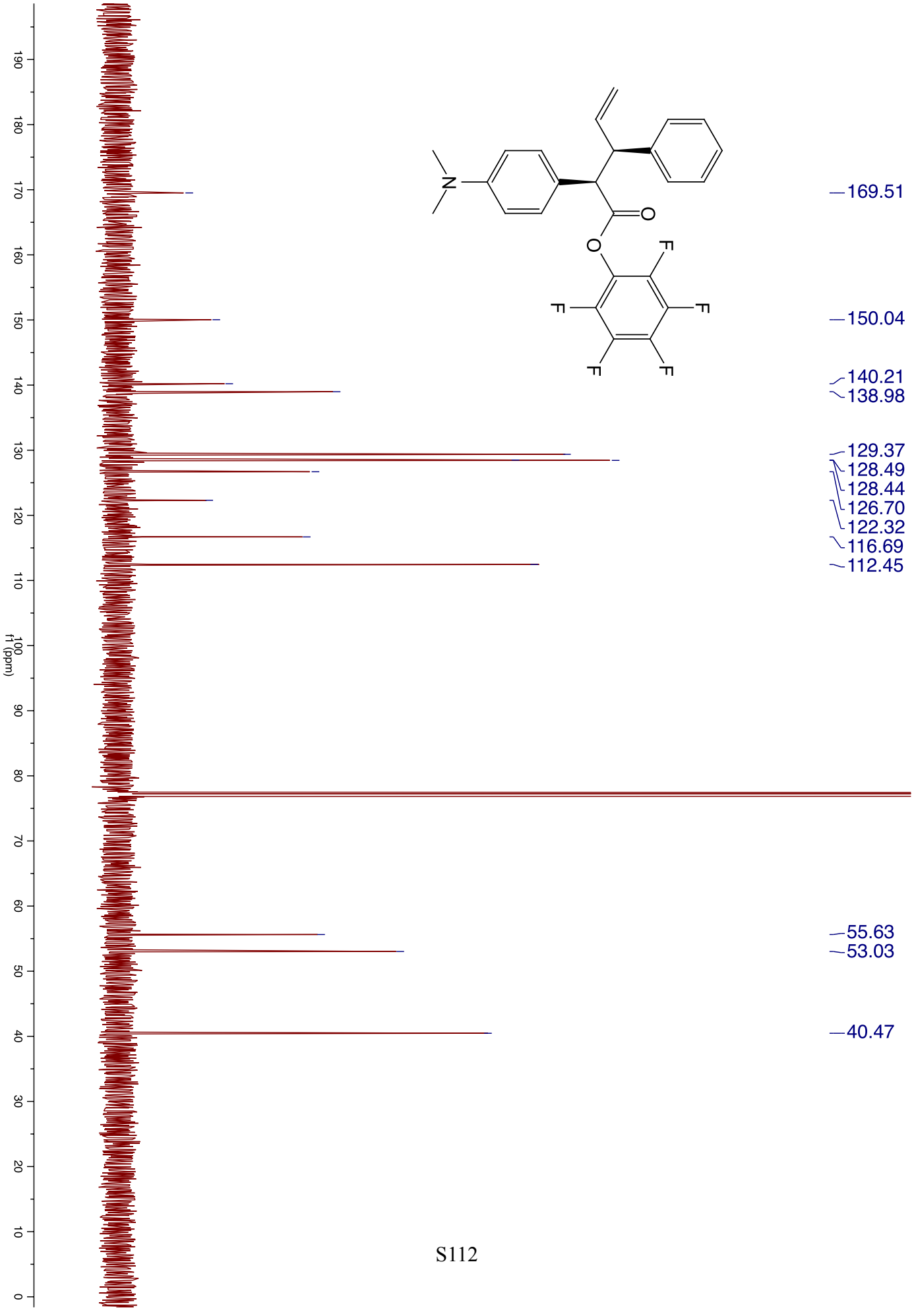
F
F
O
O
F
F
F
F
F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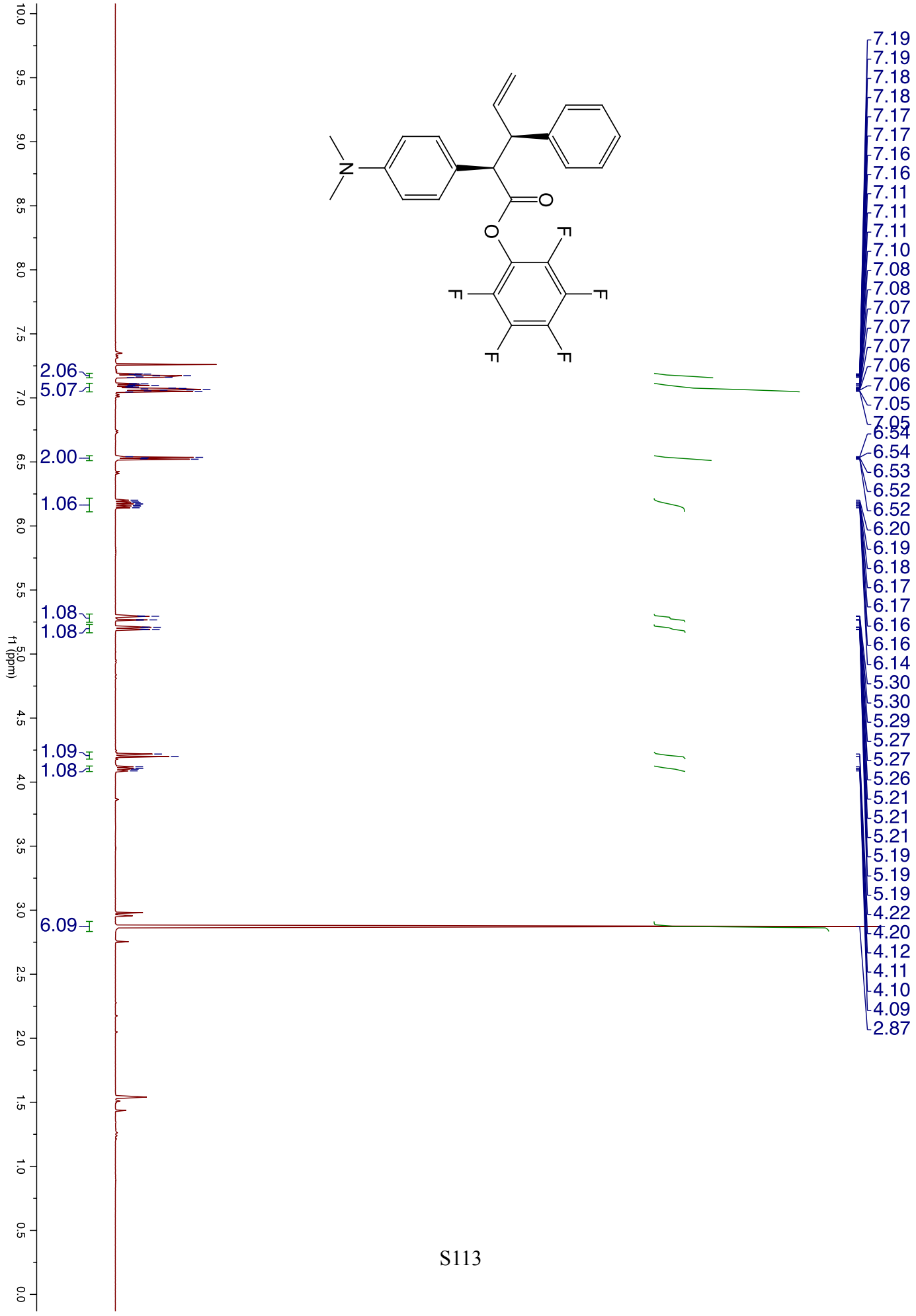
126.70
122.32
116.69
112.45
55.63
53.03
40.47
f1 (ppm)


f1 (ppm)
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5.07
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1.08
1.08
1.09
1.08
6.09
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.11
7.11
7.11
7.10
7.08
7.08
7.07
7.07
7.07
7.06
7.06
7.05
7.05
6.54
6.54
6.53
6.52
6.52
6.20
6.19
6.18
6.17
6.17
6.16
6.16
6.14
5.30
5.30
5.29
5.27
5.27
5.26
5.21
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5.19
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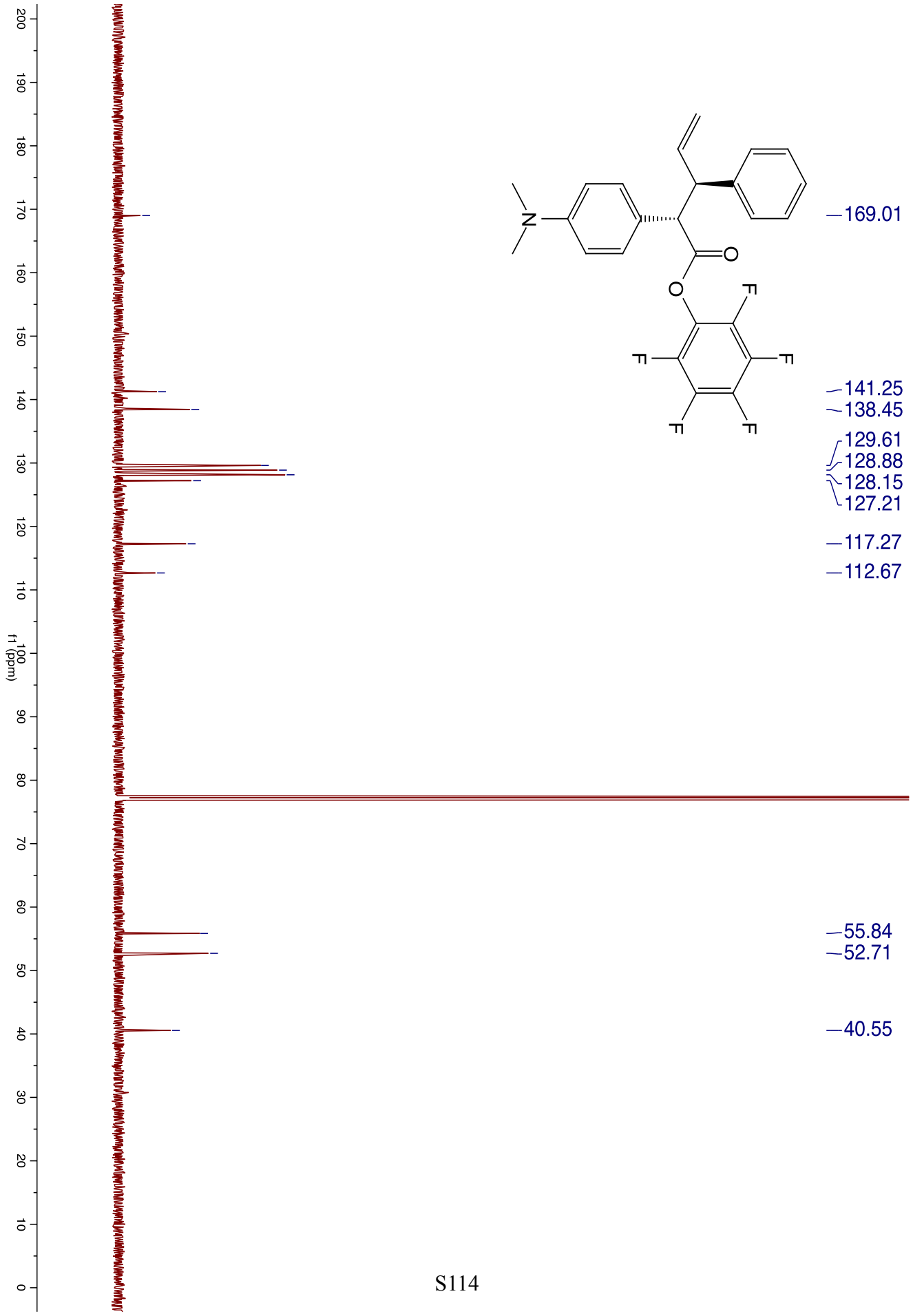
4.20
4.12
4.11
4.10
4.09
2.87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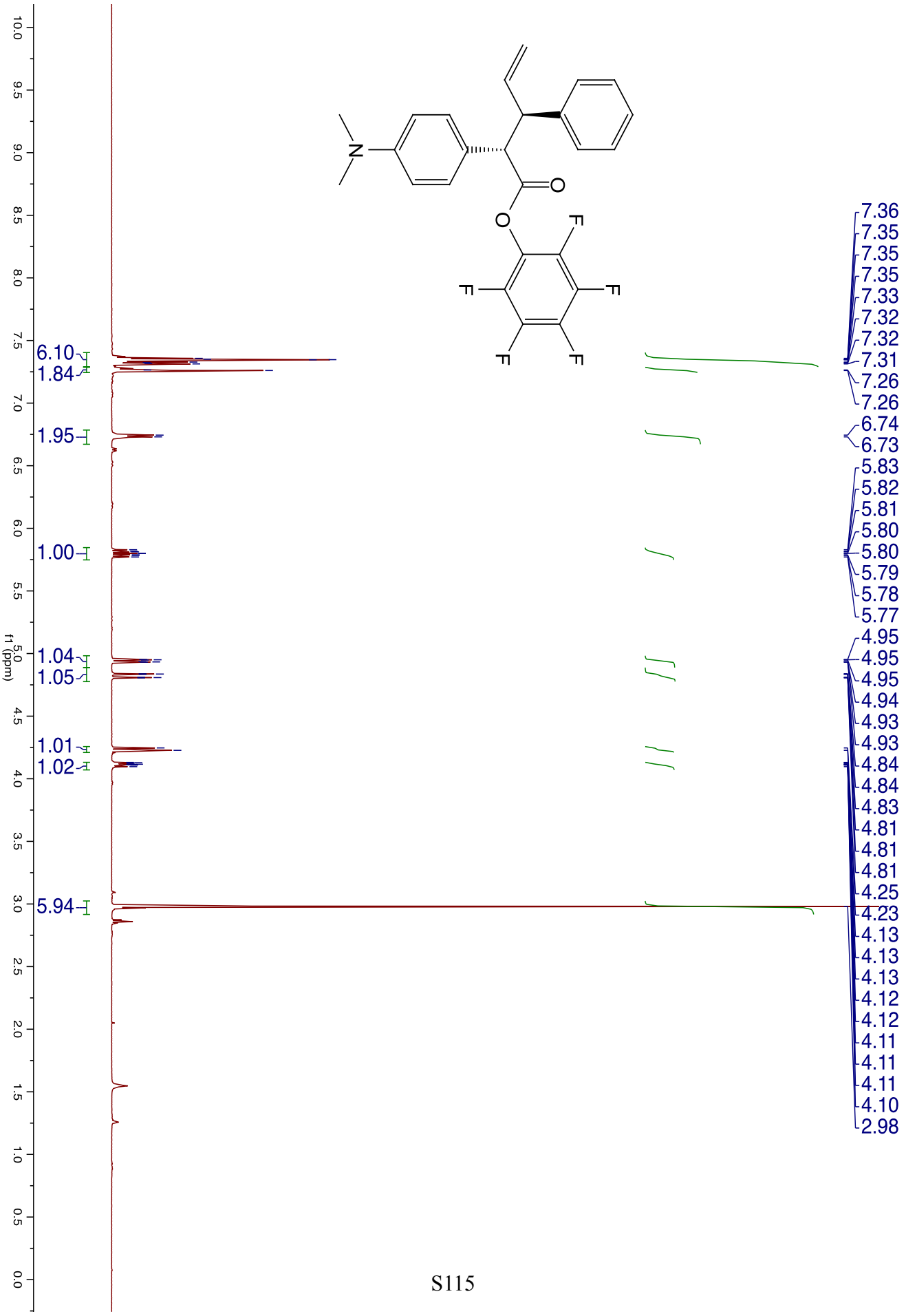
128.15
127.21
117.27
112.67
55.84
52.71
40.55
f1 (ppm)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1.95
1.00
1.04
1.05
1.01
1.02
5.94
7.36
7.35
7.35
7.35
7.33
7.32
7.32
7.31
7.26
7.26
6.74
6.73
5.83
5.82
5.81
5.80
5.80
5.79
5.78
5.77
4.95
4.95
4.95
4.94
4.93
4.93
4.84
4.84
4.83
4.81
4.81
4.81
4.25
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4.13
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4.12
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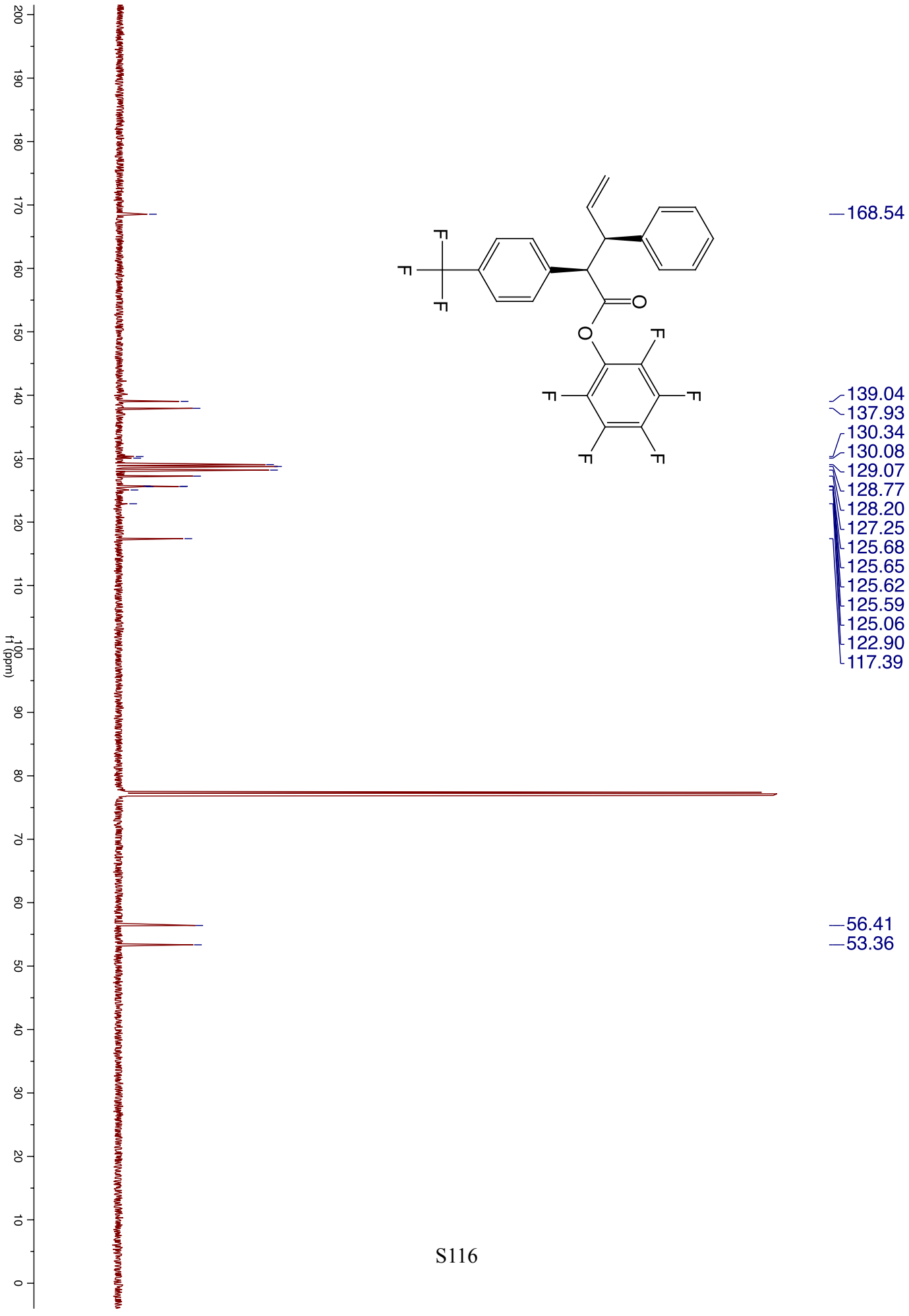
4.11
4.11
4.10
2.98
f1 (ppm)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130.08
129.07
128.77
128.20
127.25
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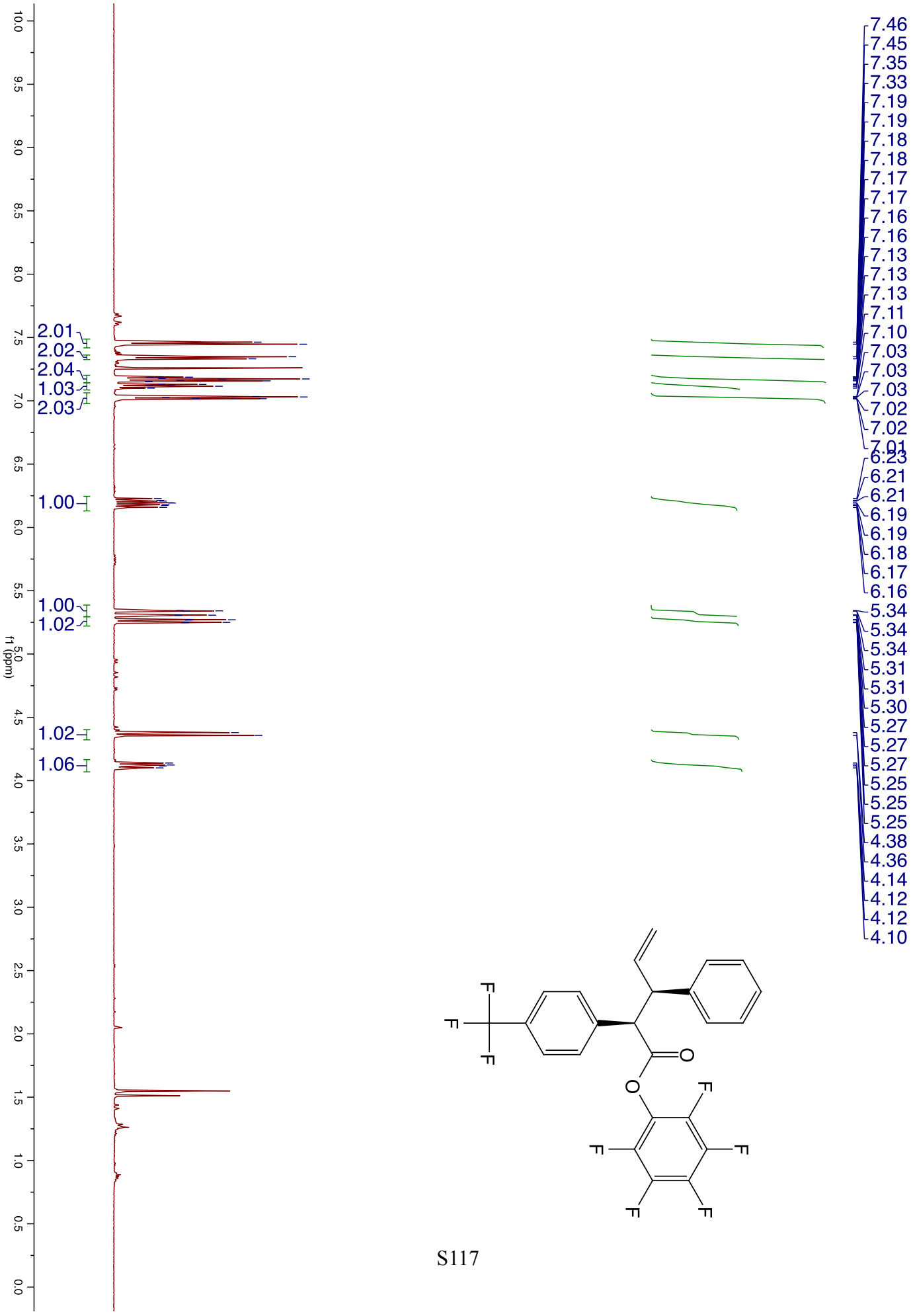
125.65
125.62
125.59
125.06
122.90
117.39
56.41
53.36
f1 (ppm)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9.0
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.01
2.02
2.04
1.03
2.03
1.00
1.00
1.02
1.02
1.06
7.46
7.45
7.35
7.33
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.13
7.13
7.13
7.11
7.10
7.03
7.03
7.03
7.02
7.02
7.01
6.23
6.21
6.21
6.19
6.19
6.18
6.17
6.16
5.34
5.34
5.34
5.31
5.31
5.30
5.27
5.27
5.27
5.25
5.25
5.25
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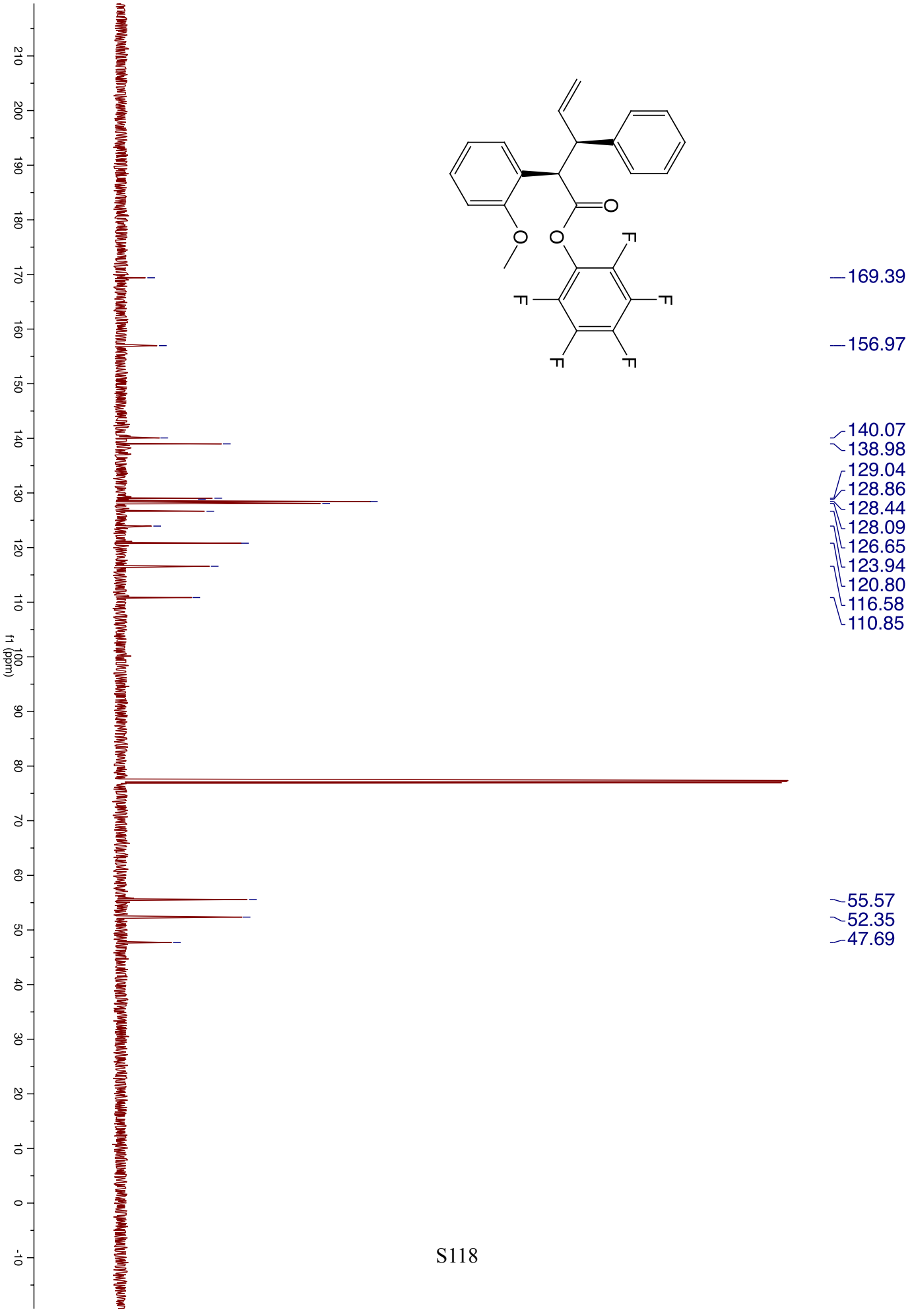
4.36
4.14
4.12
4.12
4.10
F
F
F
O
O
F
F
F
F
F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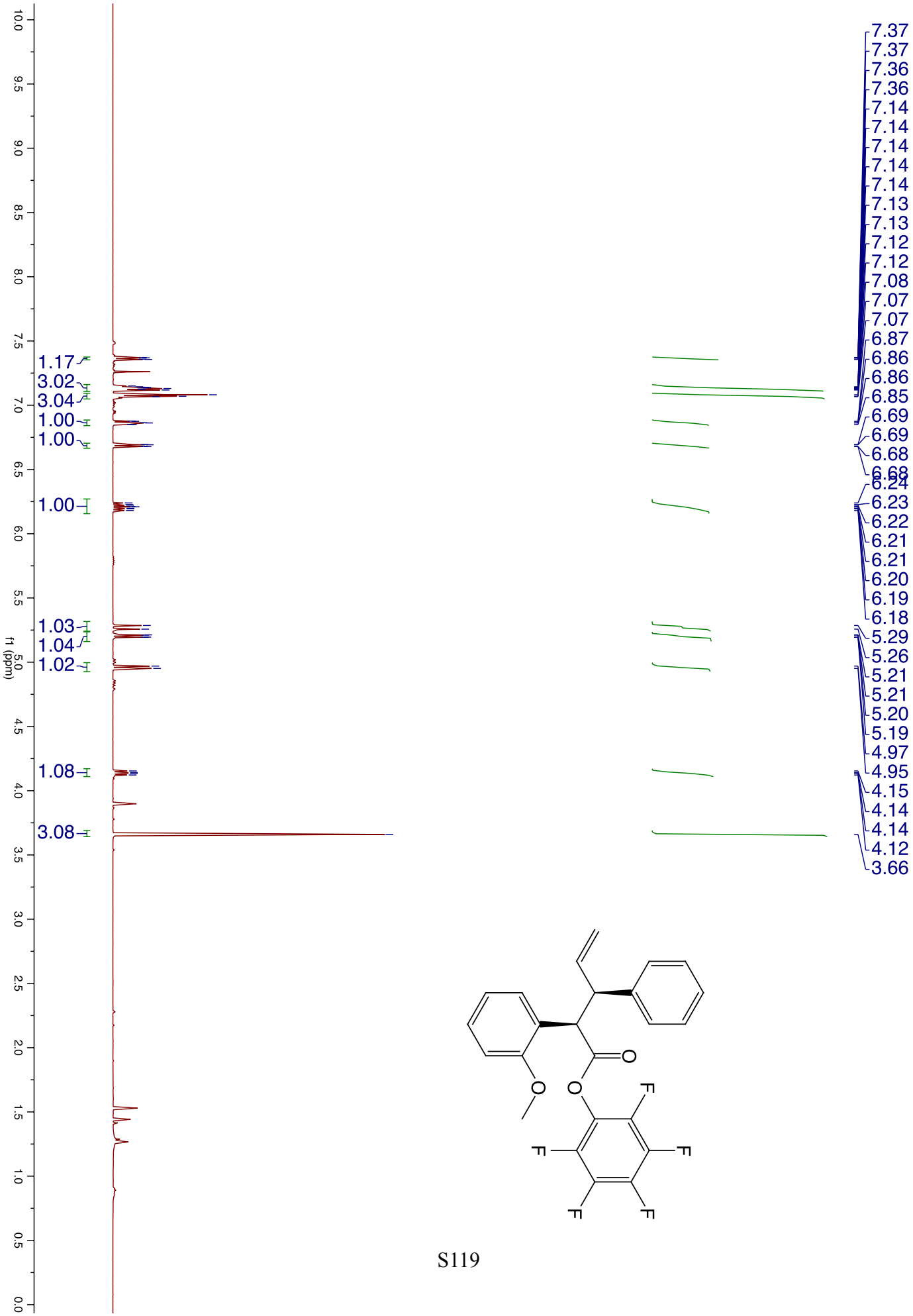
128.44
128.09
126.65
123.94
120.80
116.58
110.85
55.57
52.35
47.69
f1 (ppm)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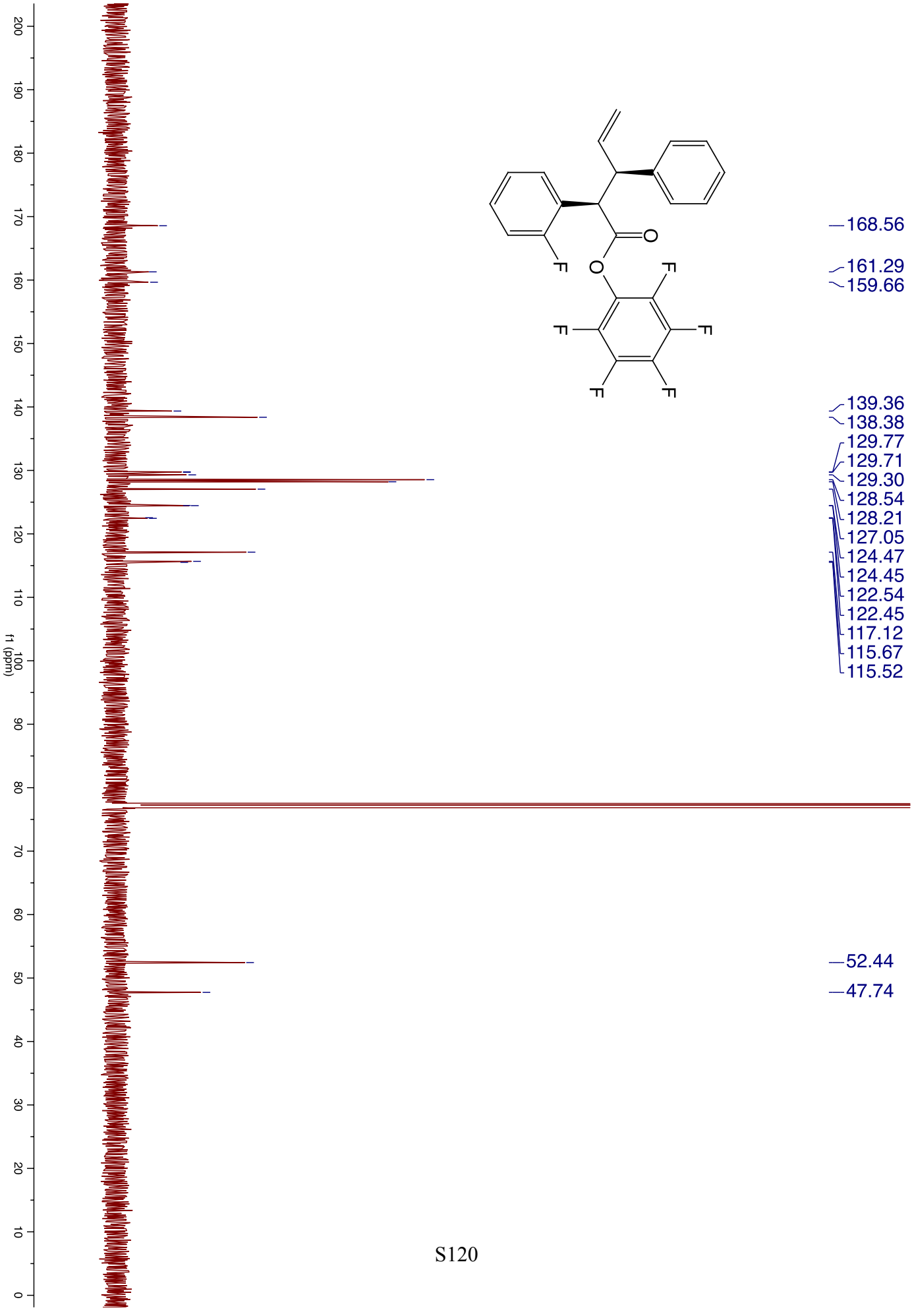
7.14
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.08
7.07
7.07
6.87
6.86
6.86
6.85
6.69
6.69
6.68
6.24
6.23
6.22
6.21
6.21
6.20
6.19
6.18
5.29
5.26
5.21
5.21
5.20
5.19
4.97
4.95
4.15
4.14
4.14
4.12
3.66
1.17
3.02
3.04
1.00
1.00
1.00
1.03
1.04
1.02
1.08
3.08
f1 (ppm)
O
O
O
F
F
F
F
F


168.56
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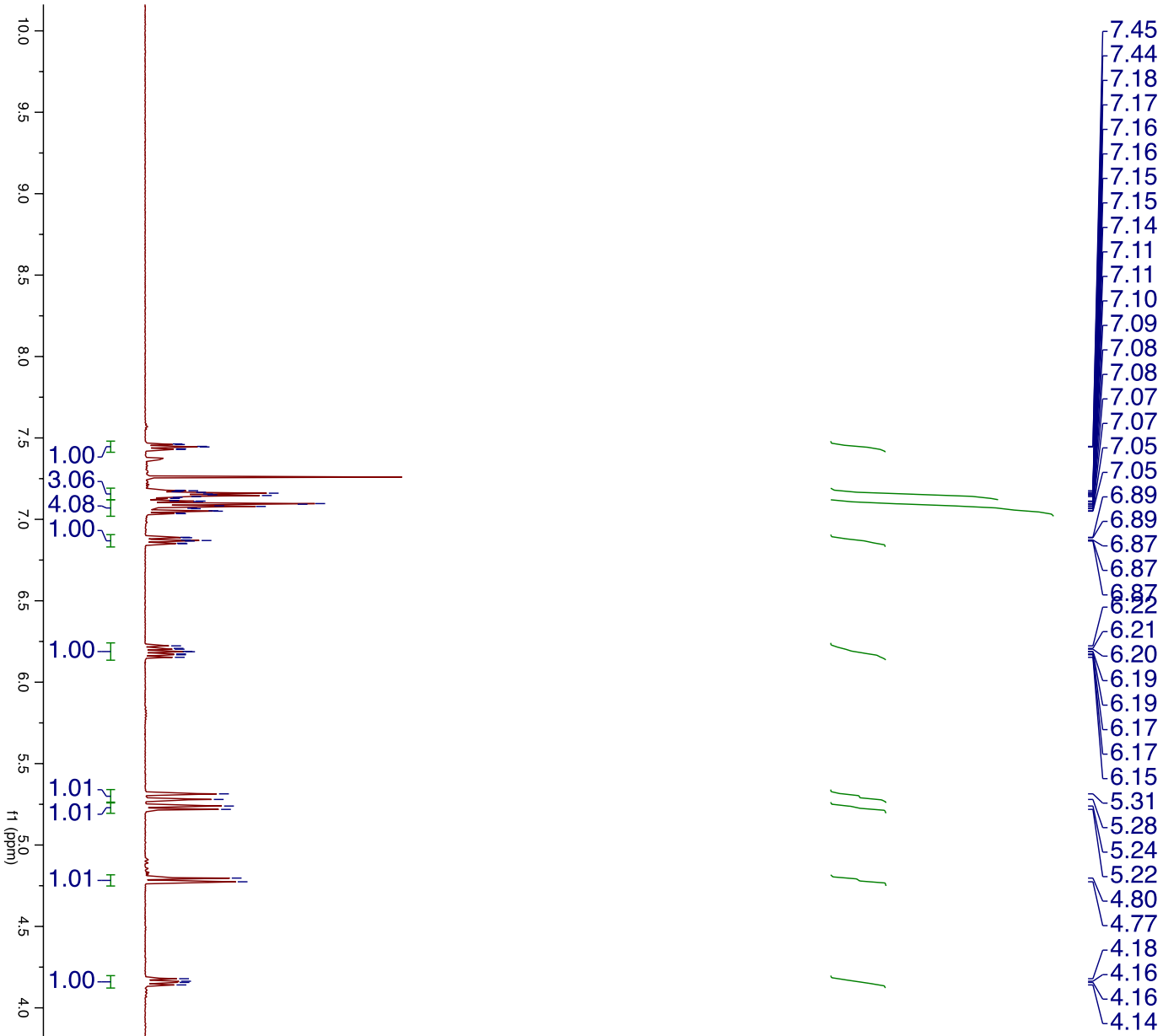
159.66
139.36
138.38
129.77
129.71
129.30
128.54
128.21
127.05
124.47
124.45
122.54
122.45
117.12
115.67
115.52
52.44
47.74
f1 (ppm)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7.44
7.18
7.17
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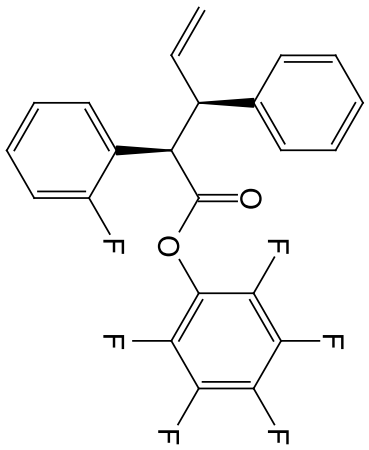
7.16
7.15
7.15
7.14
7.11
7.11
7.10
7.09
7.08
7.08
7.07
7.07
7.05
7.05
6.89
6.89
6.87
6.87
6.87
6.22
6.21
6.20
6.19
6.19
6.17
6.17
6.15
5.31
5.28
5.24
5.22
4.80
4.77
4.18
4.16
4.16
4.14
1.00
3.06
4.08
1.00
1.00
1.01
1.01
1.01
1.00
f1 (ppm)


O
O
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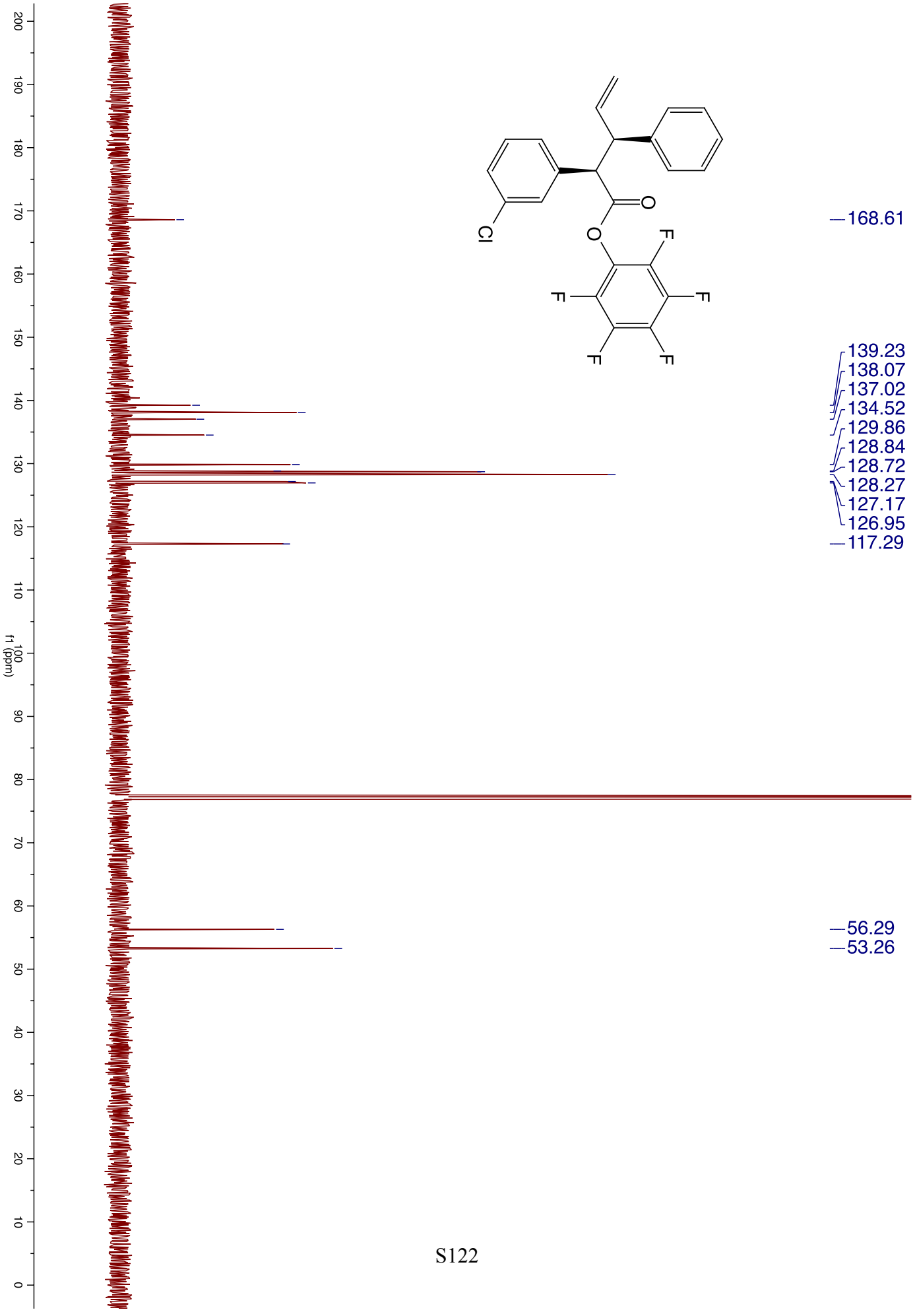
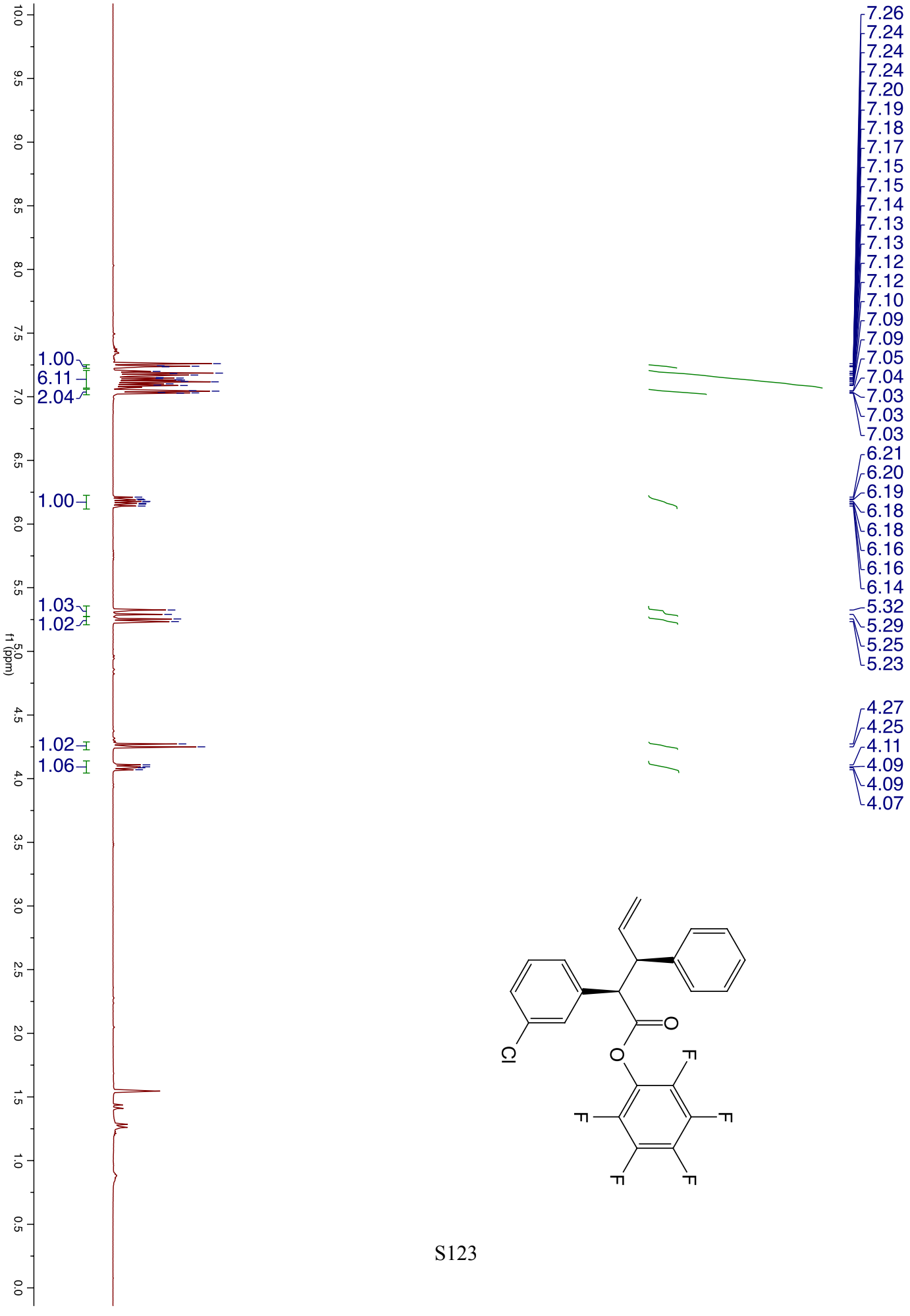
F
F
F
F
F


Cl
O
O
F
F
F
F
F
168.61
139.23
138.07
137.02
134.52
129.86
128.84
128.72
128.27
127.17
126.95
117.29
56.29
53.26
f1 (ppm)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8.0
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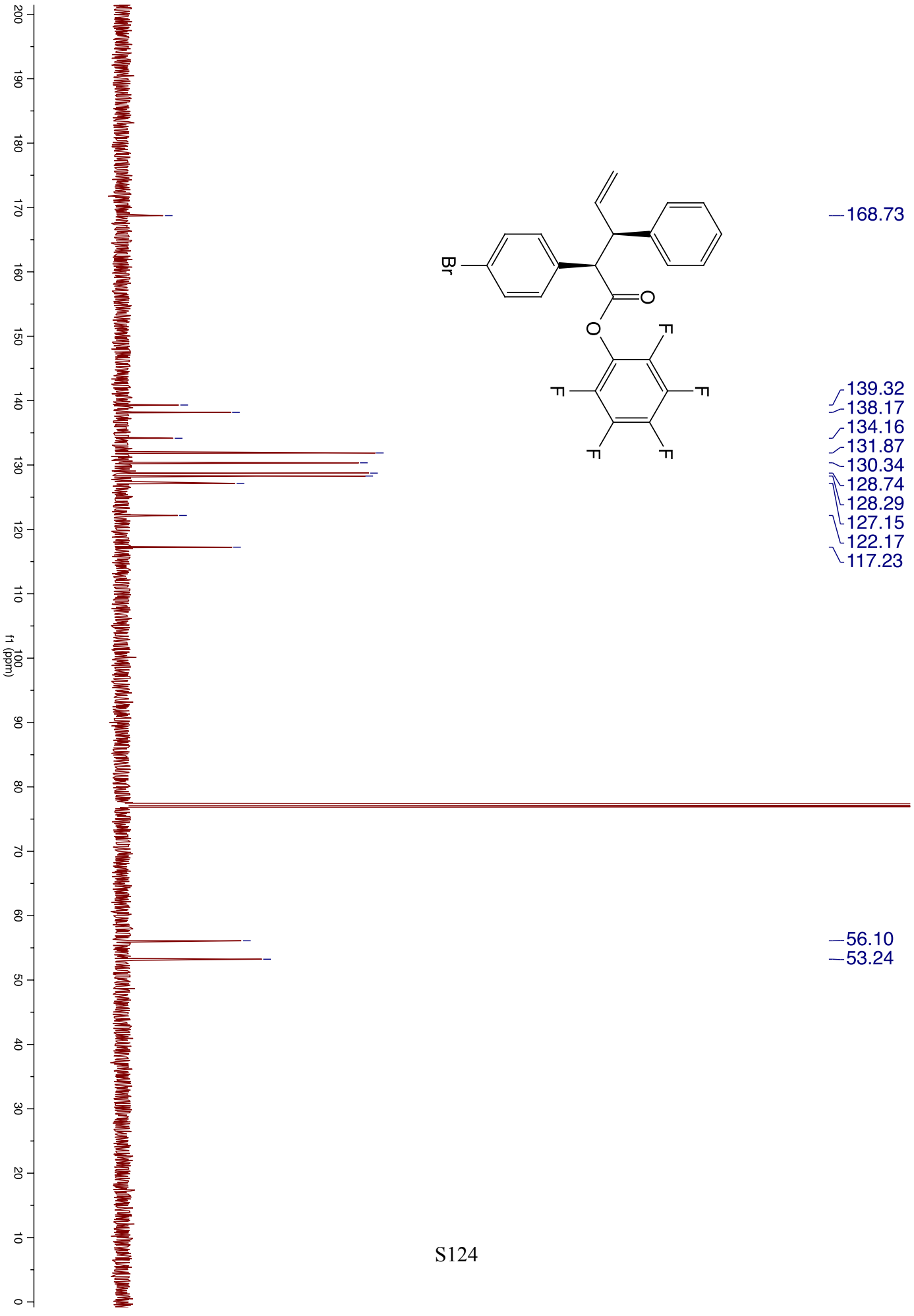
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
6.11
2.04
1.00
1.03
1.02
1.02
1.06
7.26
7.24
7.24
7.24
7.20
7.19
7.18
7.17
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.10
7.09
7.09
7.05
7.04
7.03
7.03
7.03
6.21
6.20
6.19
6.18
6.18
6.16
6.16
6.14
5.32
5.29
5.25
5.23
4.27
4.25
4.11
4.09
4.09
4.07
Cl
O
O
F
F
F
F
F


Br
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O
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F
F
F
F
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134.16
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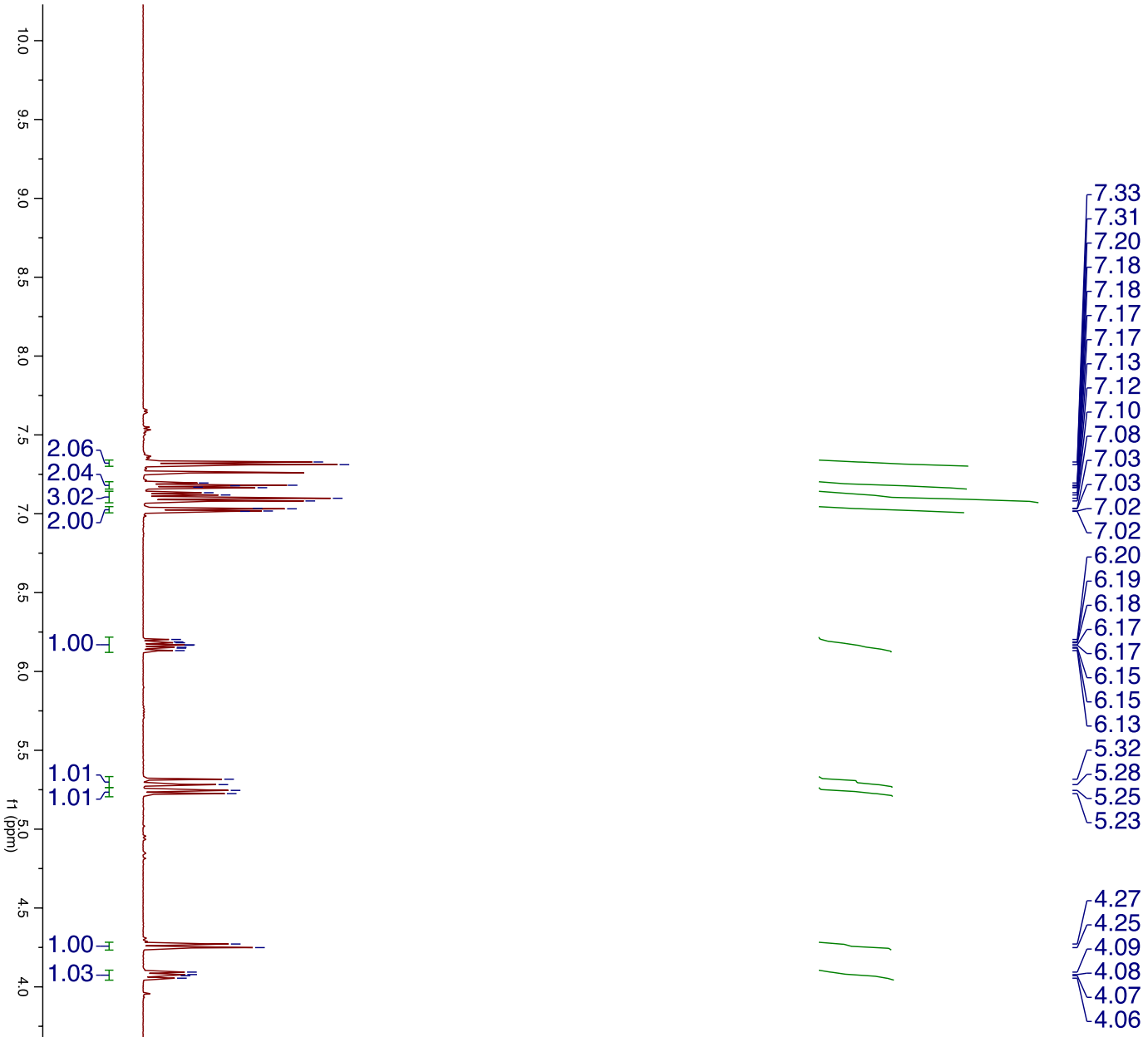
130.34
128.74
128.29
127.15
122.17
117.23
56.10
53.24
f1 (ppm)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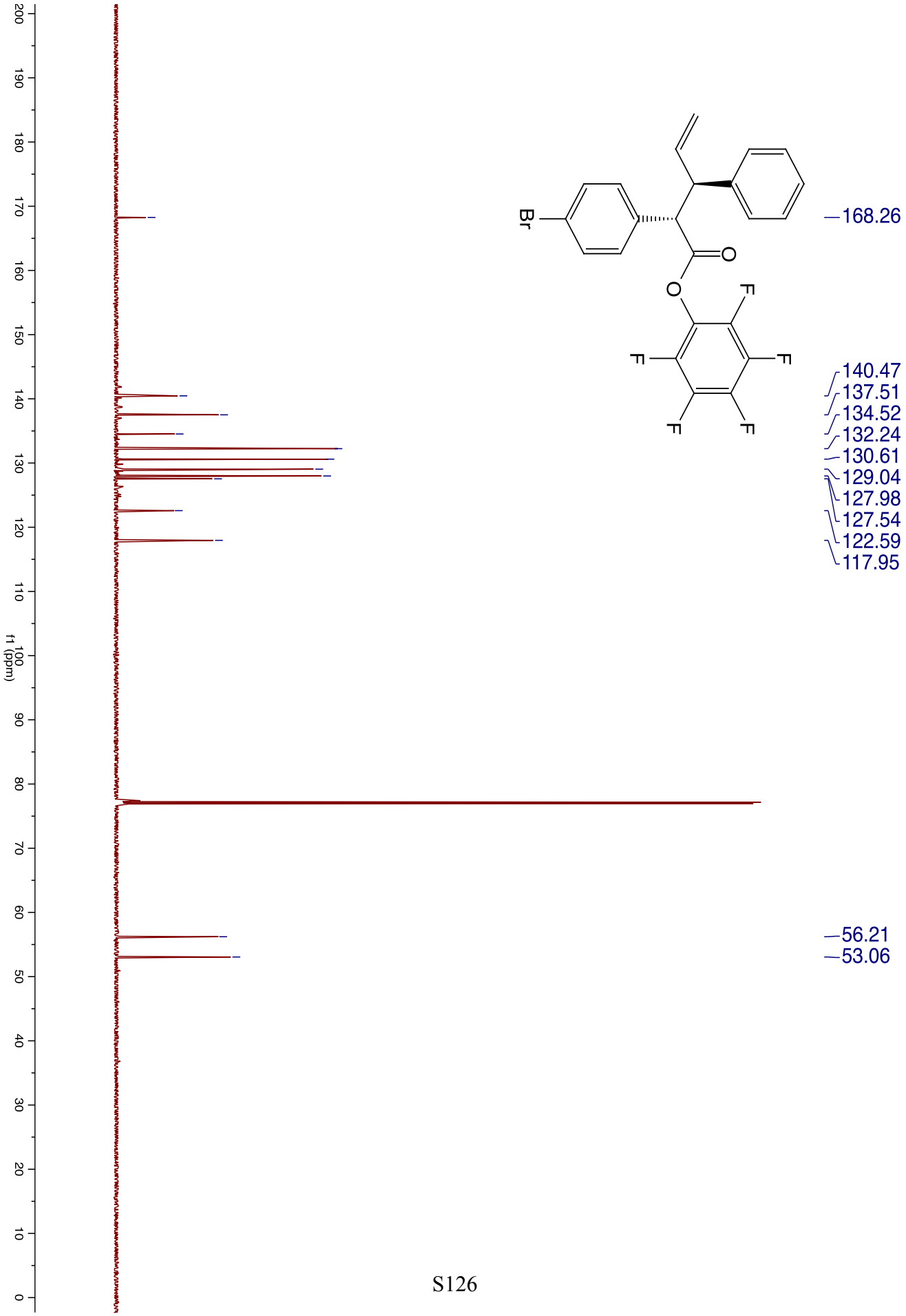
7.13
7.12
7.10
7.08
7.03
7.03
7.02
7.02
6.20
6.19
6.18
6.17
6.17
6.15
6.15
6.13
5.32
5.28
5.25
5.23
4.27
4.25
4.09
4.08
4.07
4.06
2.06
2.04
3.02
2.00
1.00
1.01
1.01
1.00
1.03
f1 (ppm)
Br
O
O
F
F
F
F
F


Br
O
O
F
F
F
F
F
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140.47
137.51
134.52
132.24
130.61
129.04
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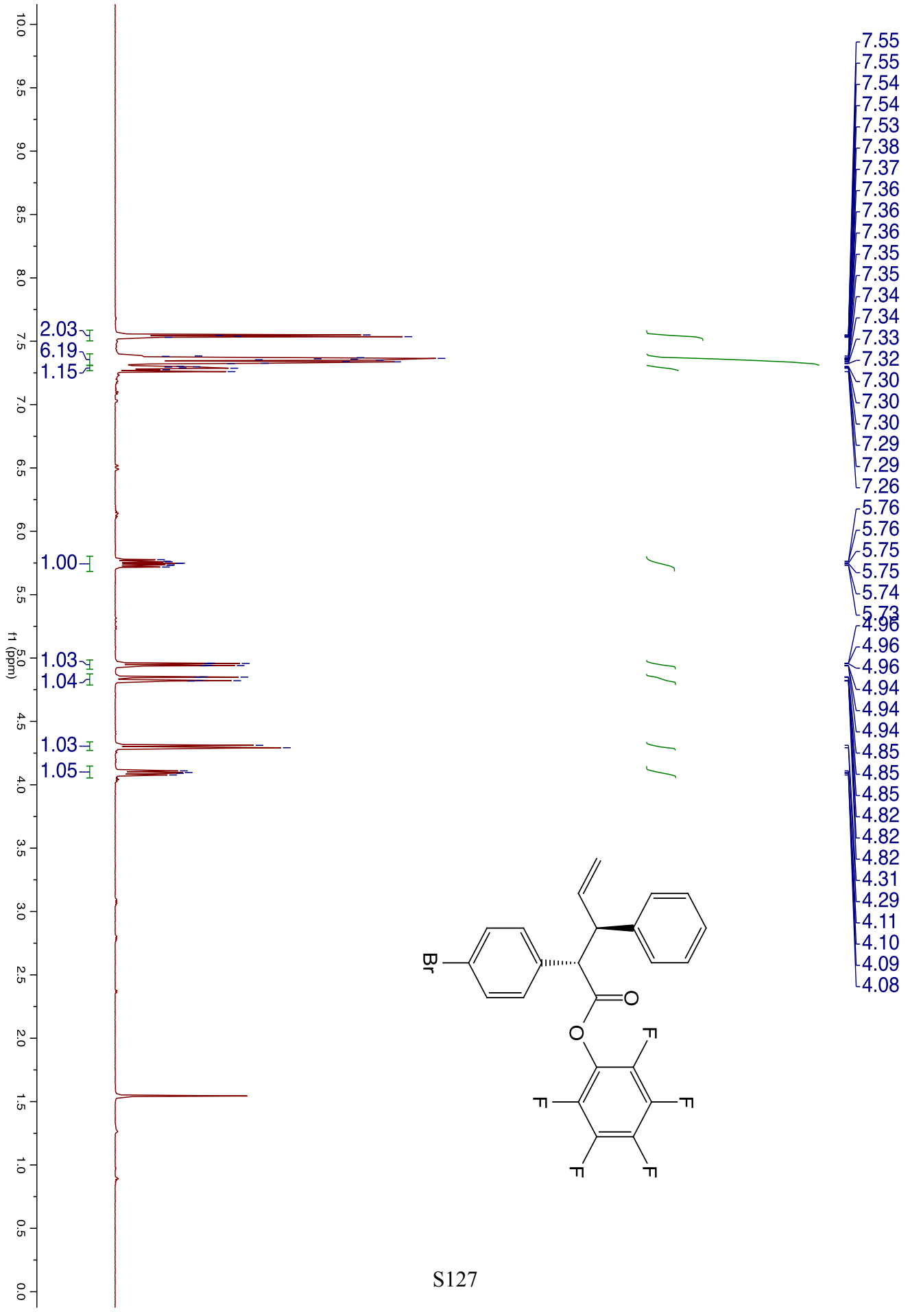
122.59
117.95
56.21
53.06
f1 (ppm)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6.19
1.15
1.00
1.03
1.04
1.03
1.05
f1 (ppm)
7.55
7.55
7.54
7.54
7.53
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.30
7.29
7.29
7.26
5.76
5.76
5.75
5.75
5.74
4.96
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4.94
4.94
4.94
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4.85
4.82
4.82
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4.29
4.11
4.10
4.09
4.08
Br
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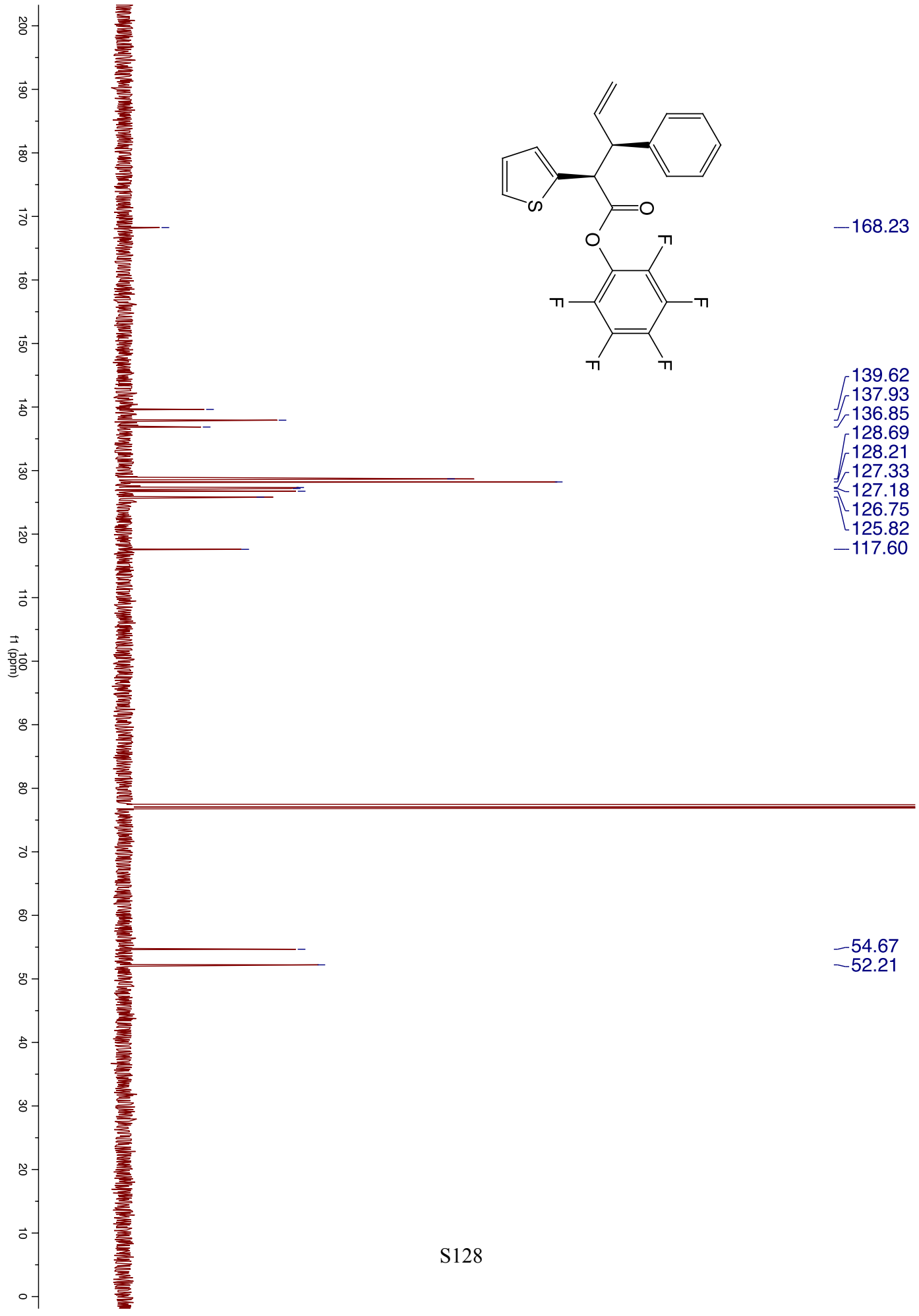
O
F
F
F
F
F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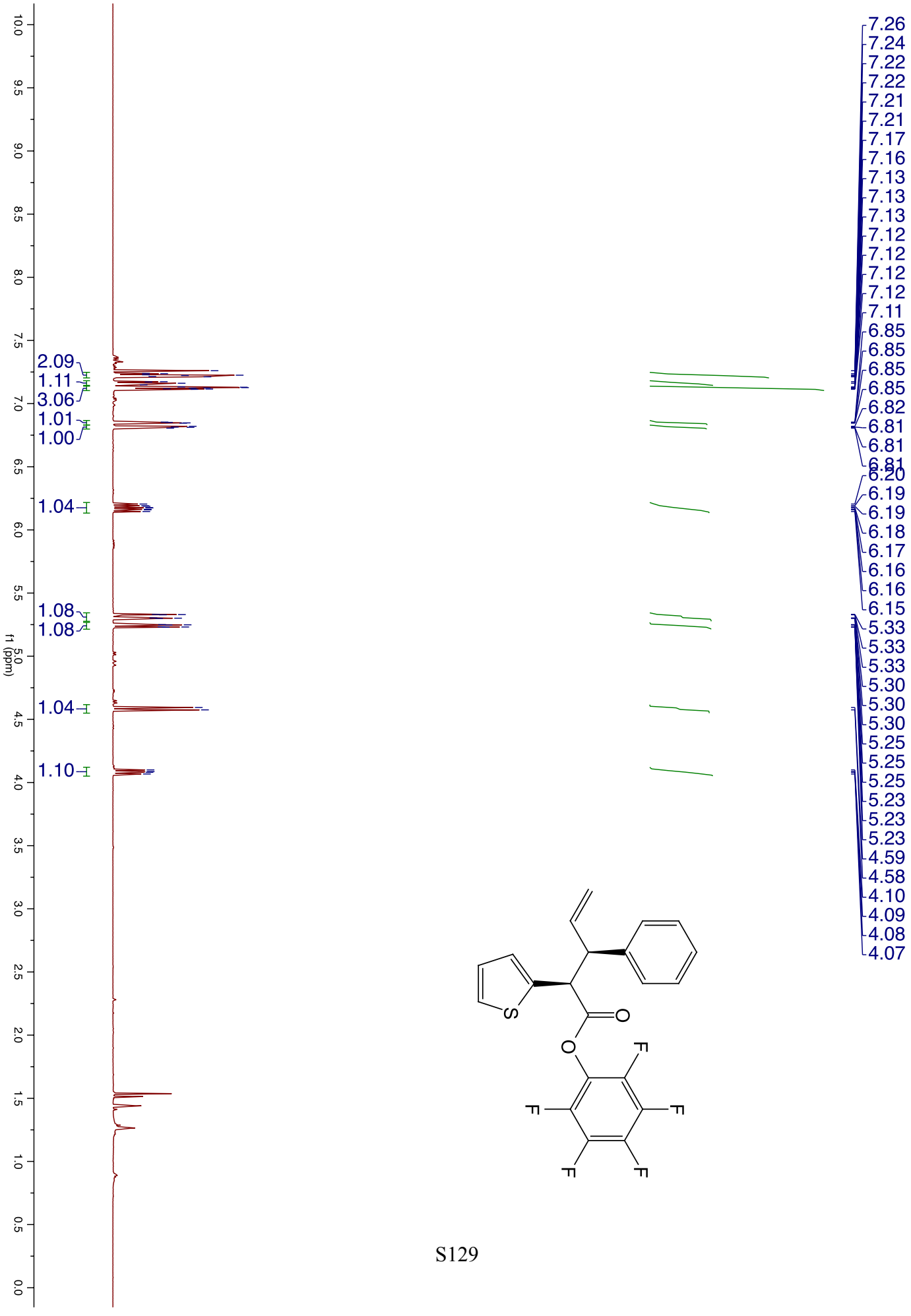
128.21
127.33
127.18
126.75
125.82
117.60
54.67
52.21
f1 (ppm)


f1 (ppm)
2.09
1.11
3.06
1.01
1.00
1.04
1.08
1.08
1.04
1.10
7.26
7.24
7.22
7.22
7.21
7.21
7.17
7.16
7.13
7.13
7.13
7.12
7.12
7.12
7.12
7.11
6.85
6.85
6.85
6.85
6.82
6.81
6.81
6.81
6.20
6.19
6.19
6.18
6.17
6.16
6.16
6.15
5.33
5.33
5.33
5.30
5.30
5.30
5.25
5.25
5.25
5.23
5.23
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4.58
4.10
4.09
4.08
4.07
S
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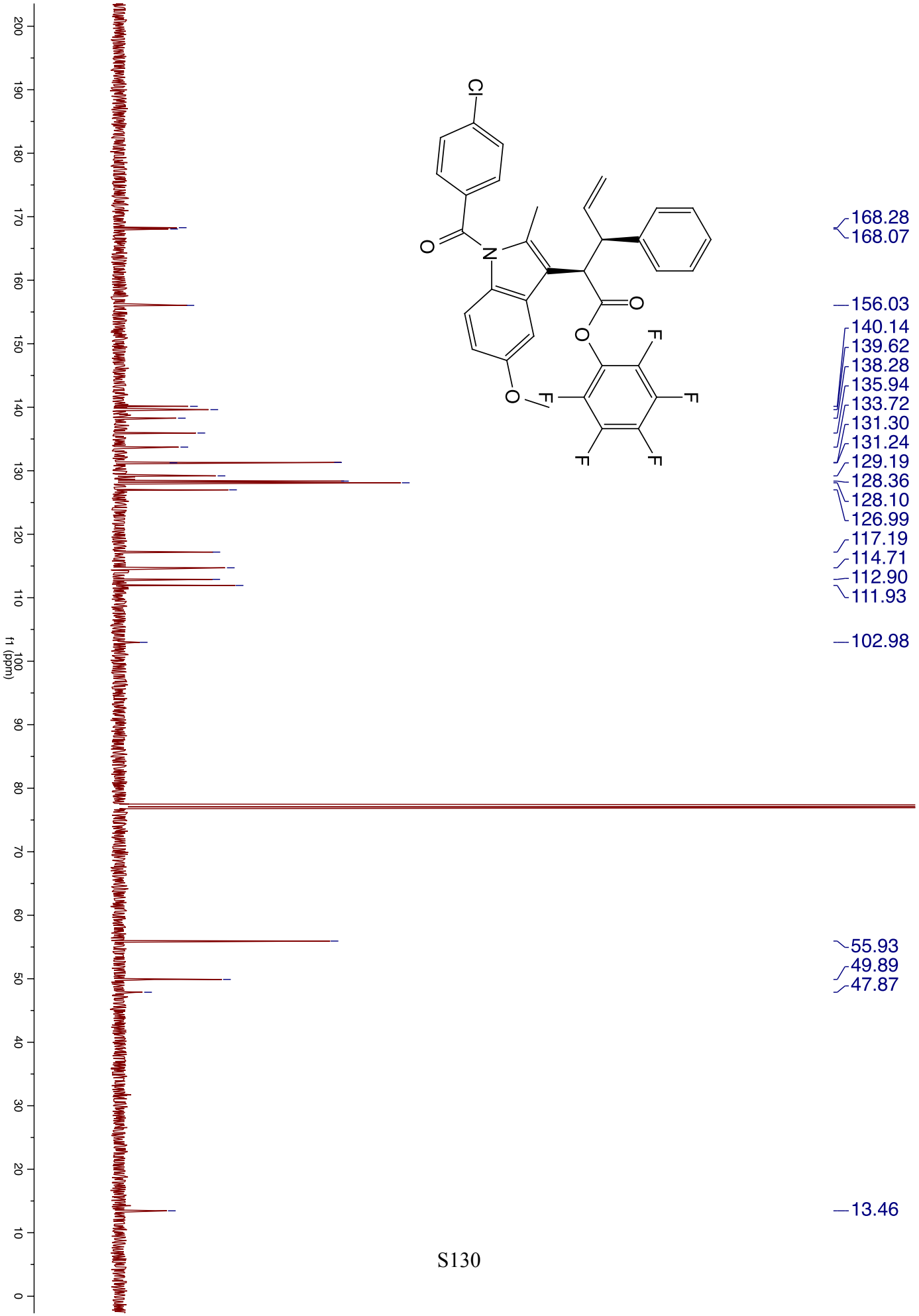
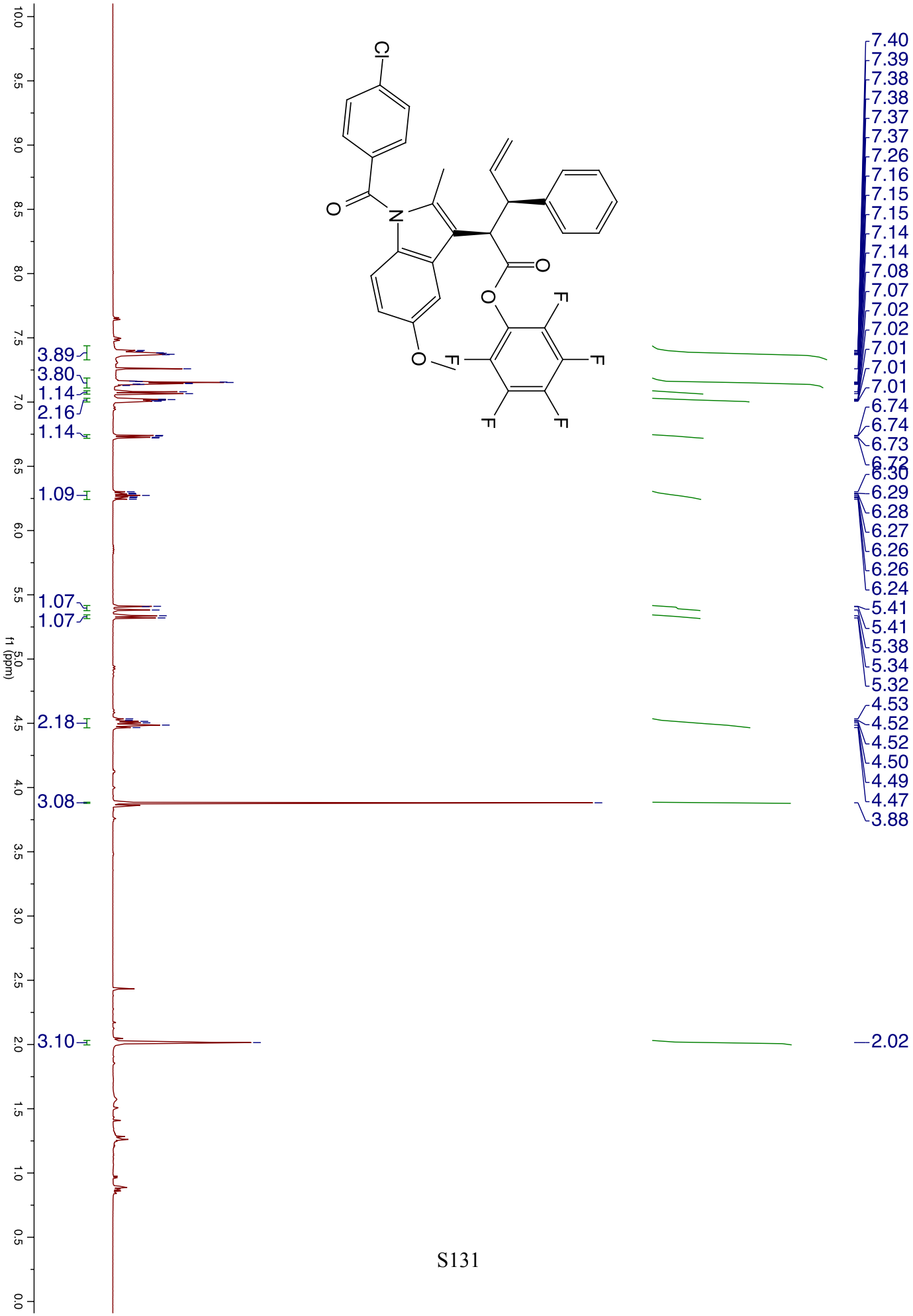
F
F
F
F
F


Cl
O
N
O
O
O
F
F
F
F
F
168.28
168.07
156.03
140.14
139.62
138.28
135.94
133.72
131.30
131.24
129.19
128.36
128.10
126.99
117.19
114.71
112.90
111.93
102.98
55.93
49.89
47.87
13.46
f1 (ppm)


Cl
O
N
O
O
O
F
F
F
F
F
3.89
3.80
1.14
2.16
1.14
1.09
1.07
1.07
2.18
3.08
3.10
2.02
7.40
7.39
7.38
7.38
7.37
7.37
7.26
7.16
7.15
7.15
7.14
7.14
7.08
7.07
7.02
7.02
7.01
7.01
7.01
6.74
6.74
6.73
6.72
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6.28
6.27
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6.26
6.24
5.41
5.41
5.38
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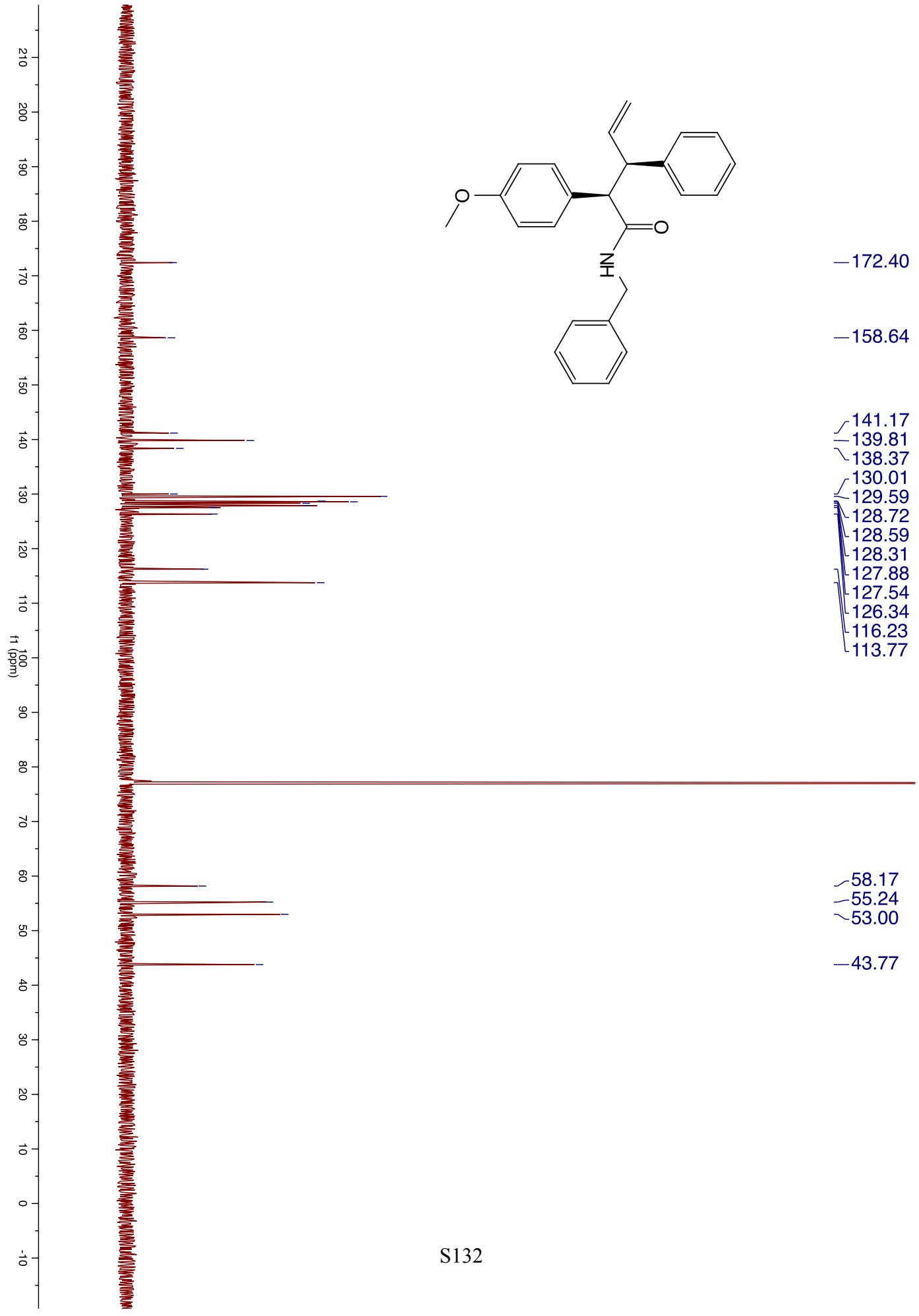
5.32
4.53
4.52
4.52
4.50
4.49
4.47
3.88
f1 (ppm)


O
O
HN
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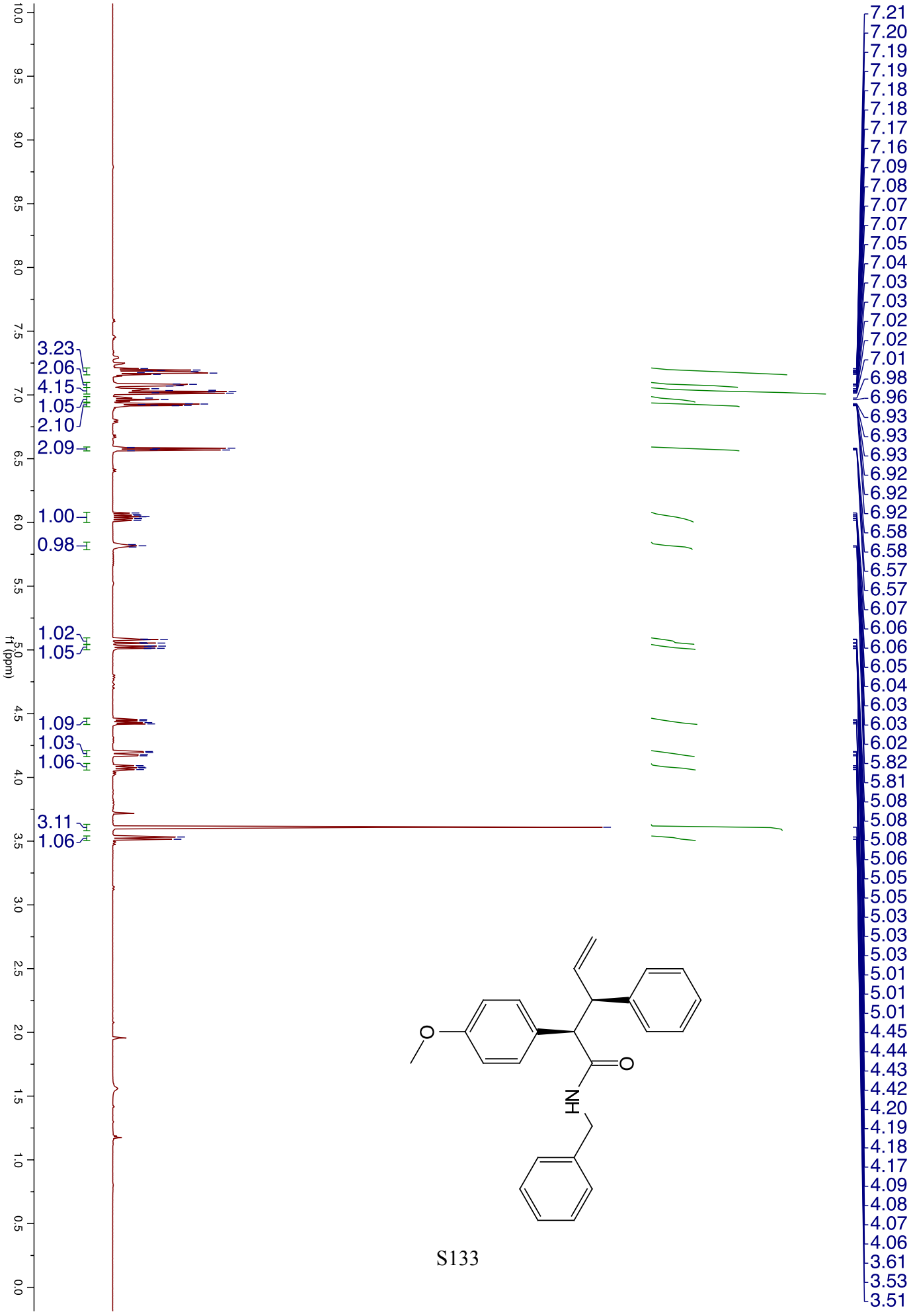
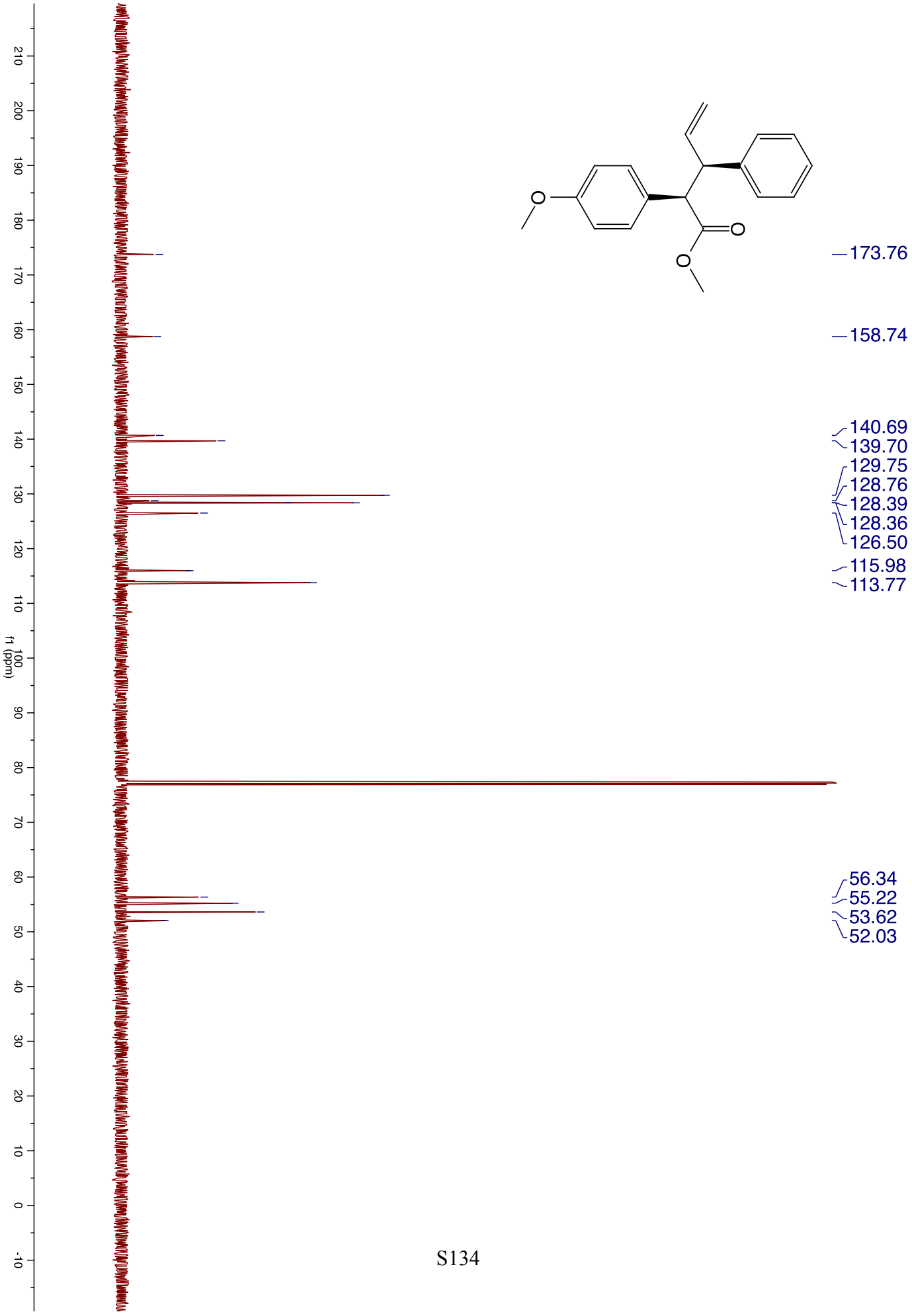
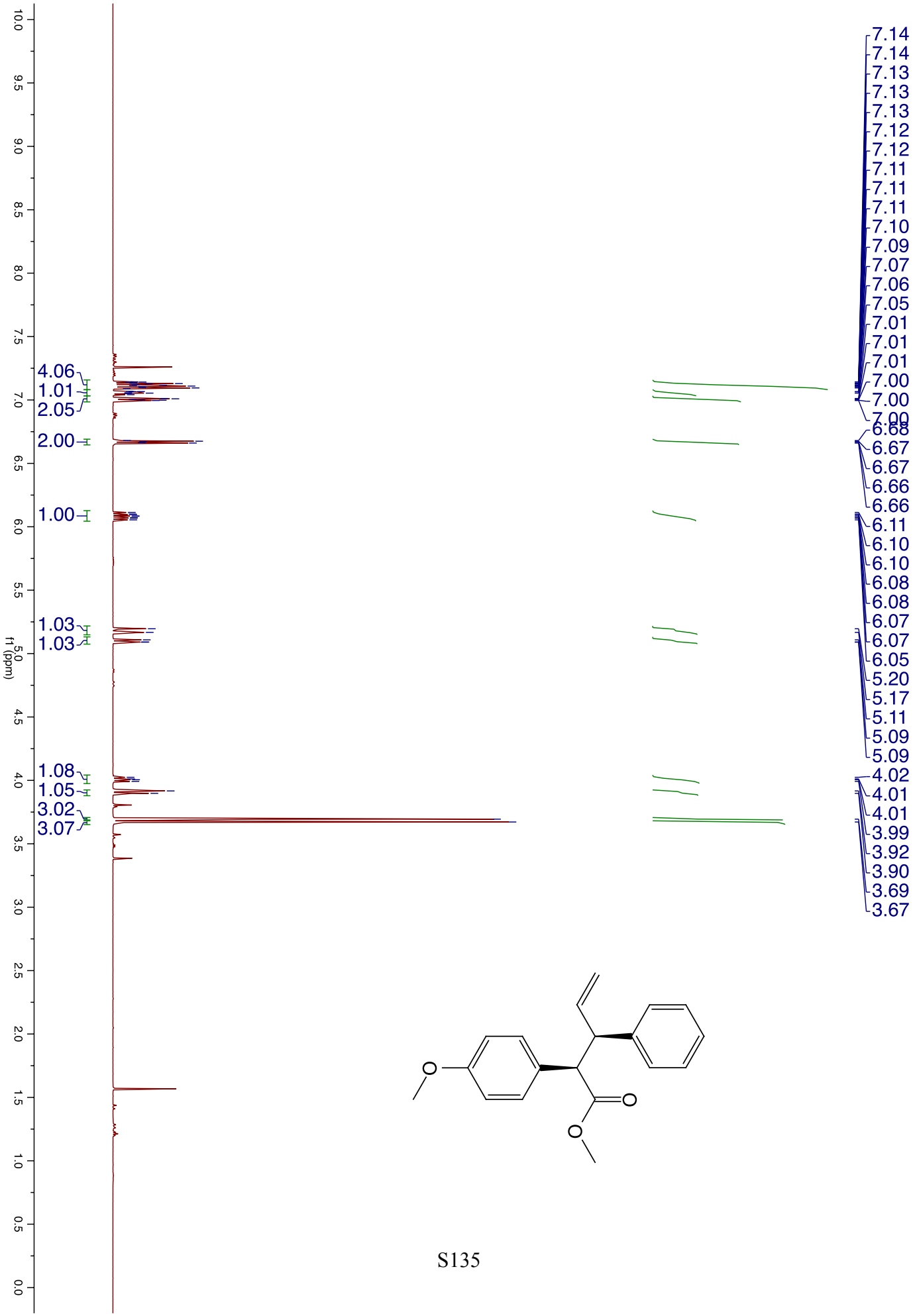
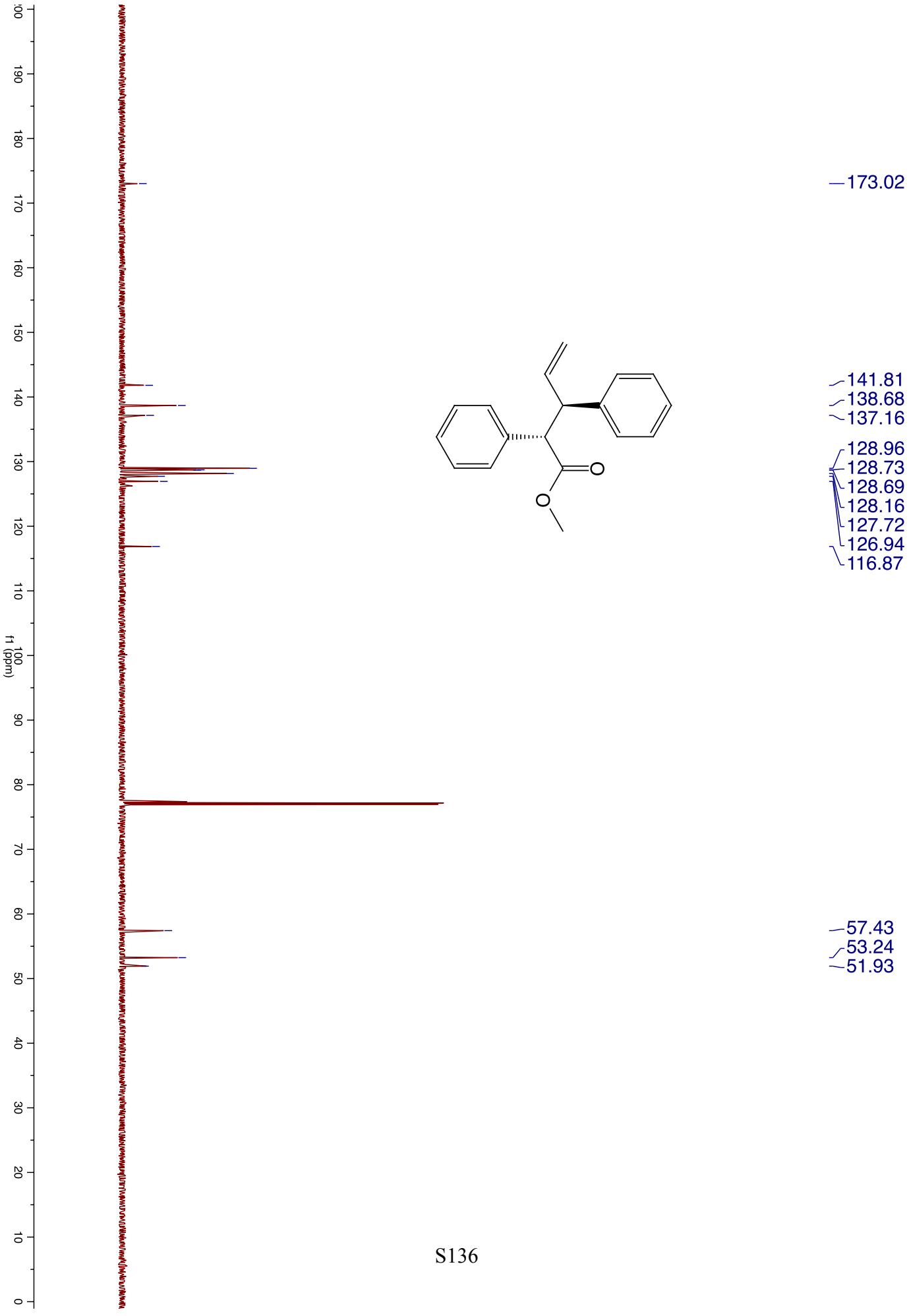
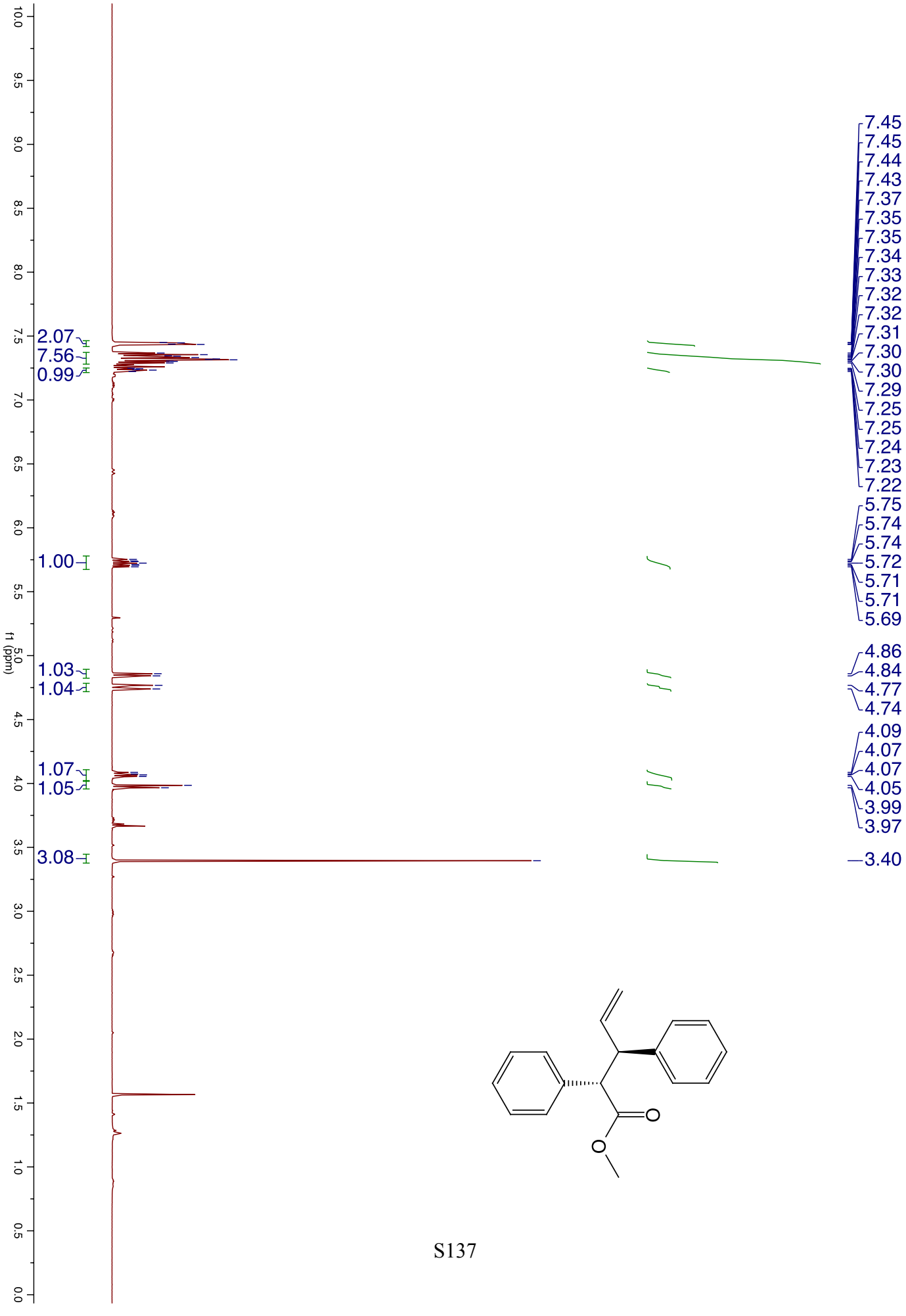
158.64
141.17
139.81
138.37
130.01
129.59
128.72
128.59
128.31
127.88
127.54
126.34
116.23
113.77
58.17
55.24
53.00
43.77
f1 (ppm)

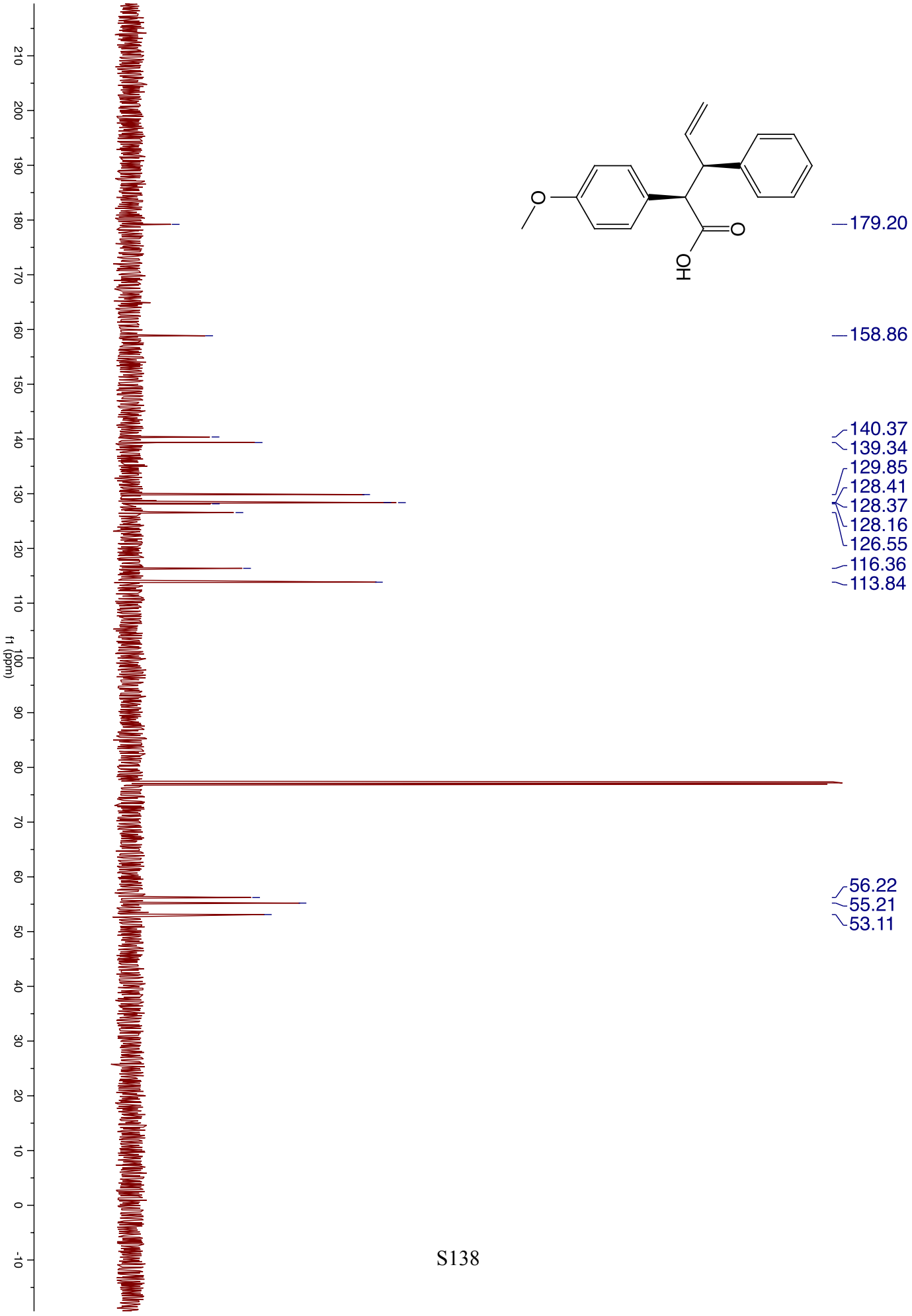

3.23
2.06
4.15
1.05
2.10
2.09
1.00
0.98
1.02
1.05
1.09
1.03
1.06
3.11
1.06
f1 (ppm)
O
O
HN

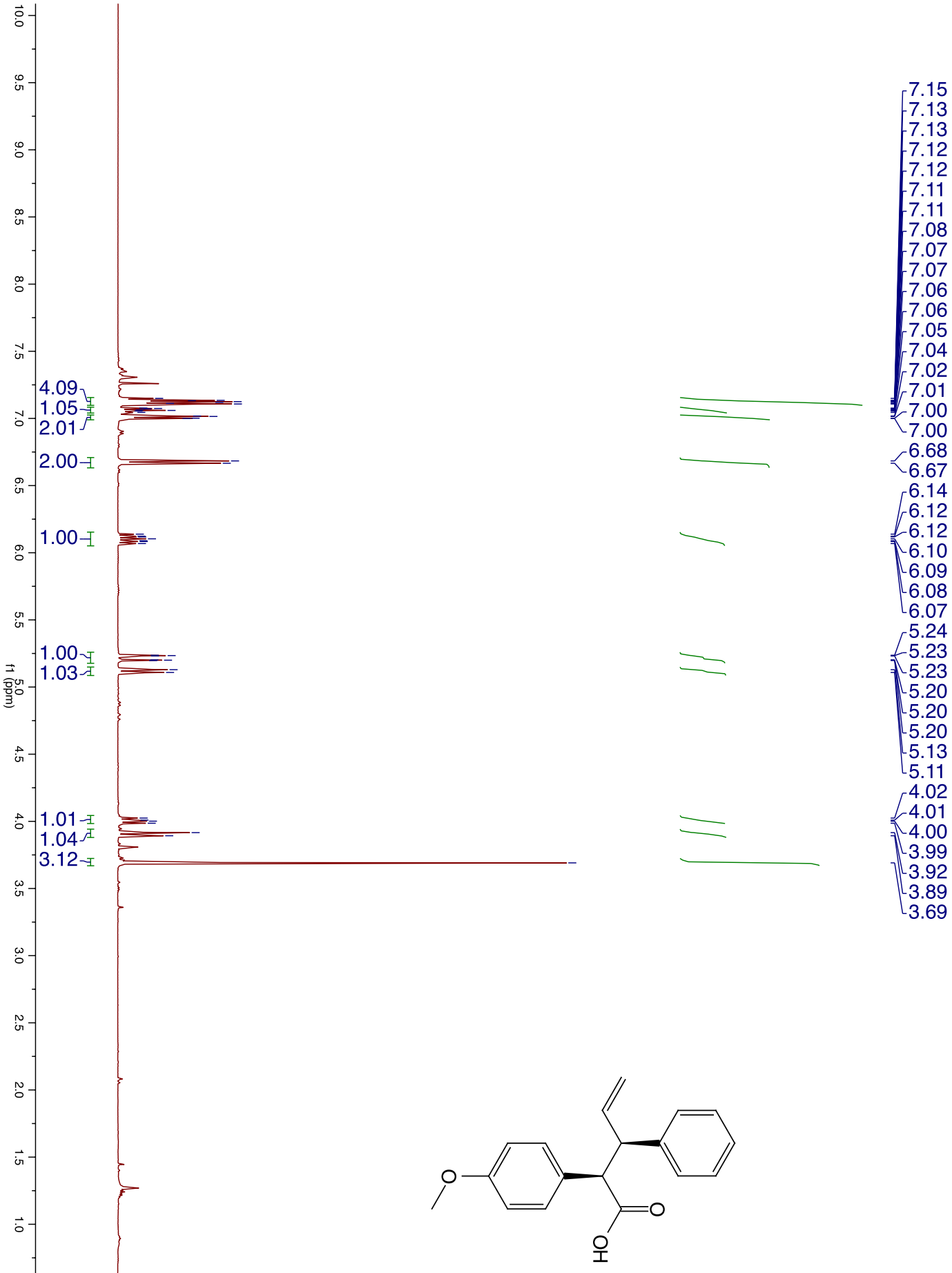

173.76
158.74
140.69
139.70
129.75
128.76
128.39
128.36
126.50
115.98
113.77
56.34
55.22
53.62
52.03
f1 (ppm)

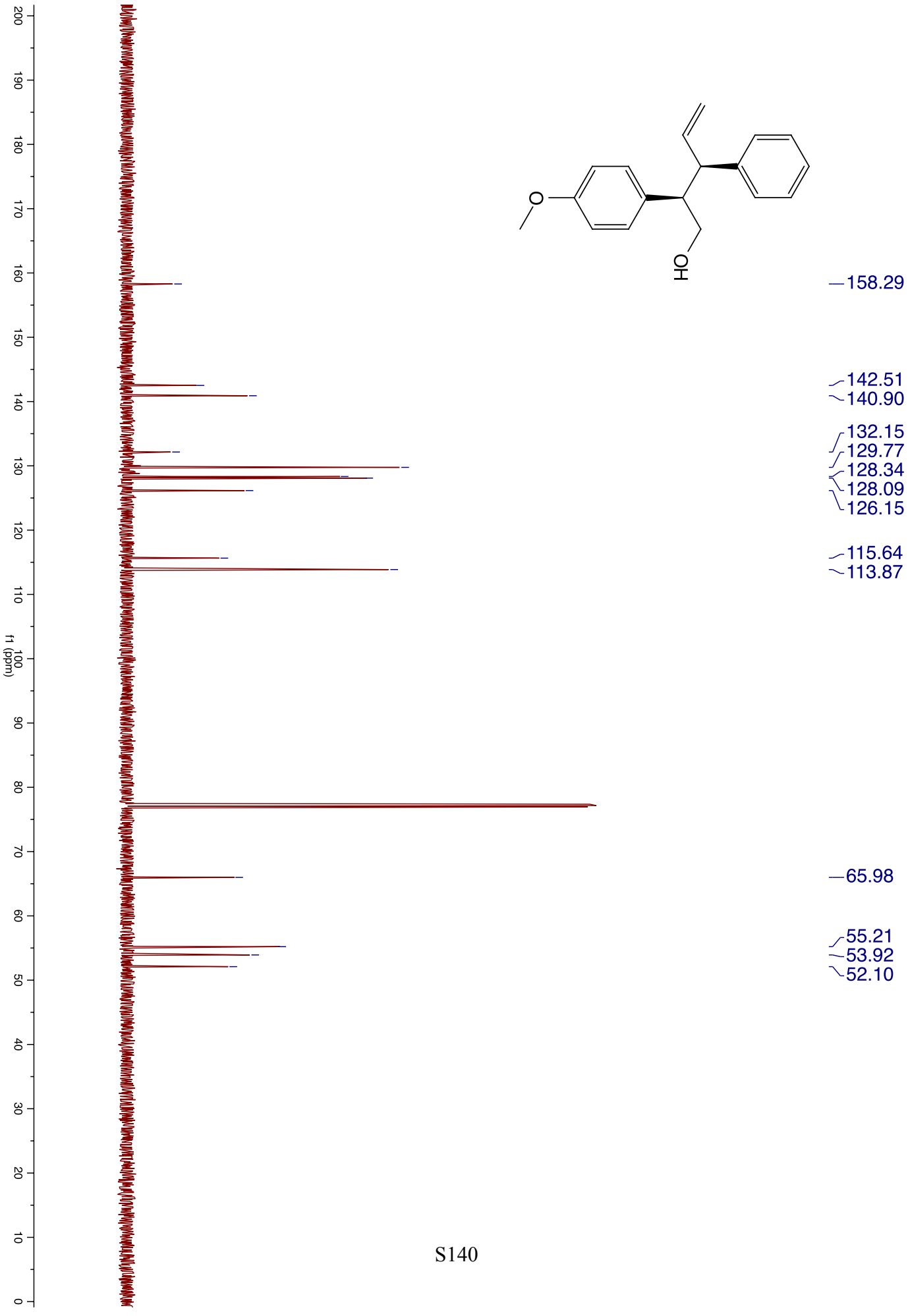

f1 (ppm)
4.06
1.01
2.05
2.00
1.00
1.03
1.03
1.08
1.05
3.02
3.07
7.14
7.14
7.13
7.13
7.13
7.12
7.12
7.11
7.11
7.11
7.10
7.09
7.07
7.06
7.05
7.01
7.01
7.01
7.00
7.00
7.00
6.68
6.67
6.67
6.66
6.66
6.11
6.10
6.10
6.08
6.08
6.07
6.07
6.05
5.20
5.17
5.11
5.09
5.09
4.02
4.01
4.01
3.99
3.92
3.90
3.69
3.67
O
O
O

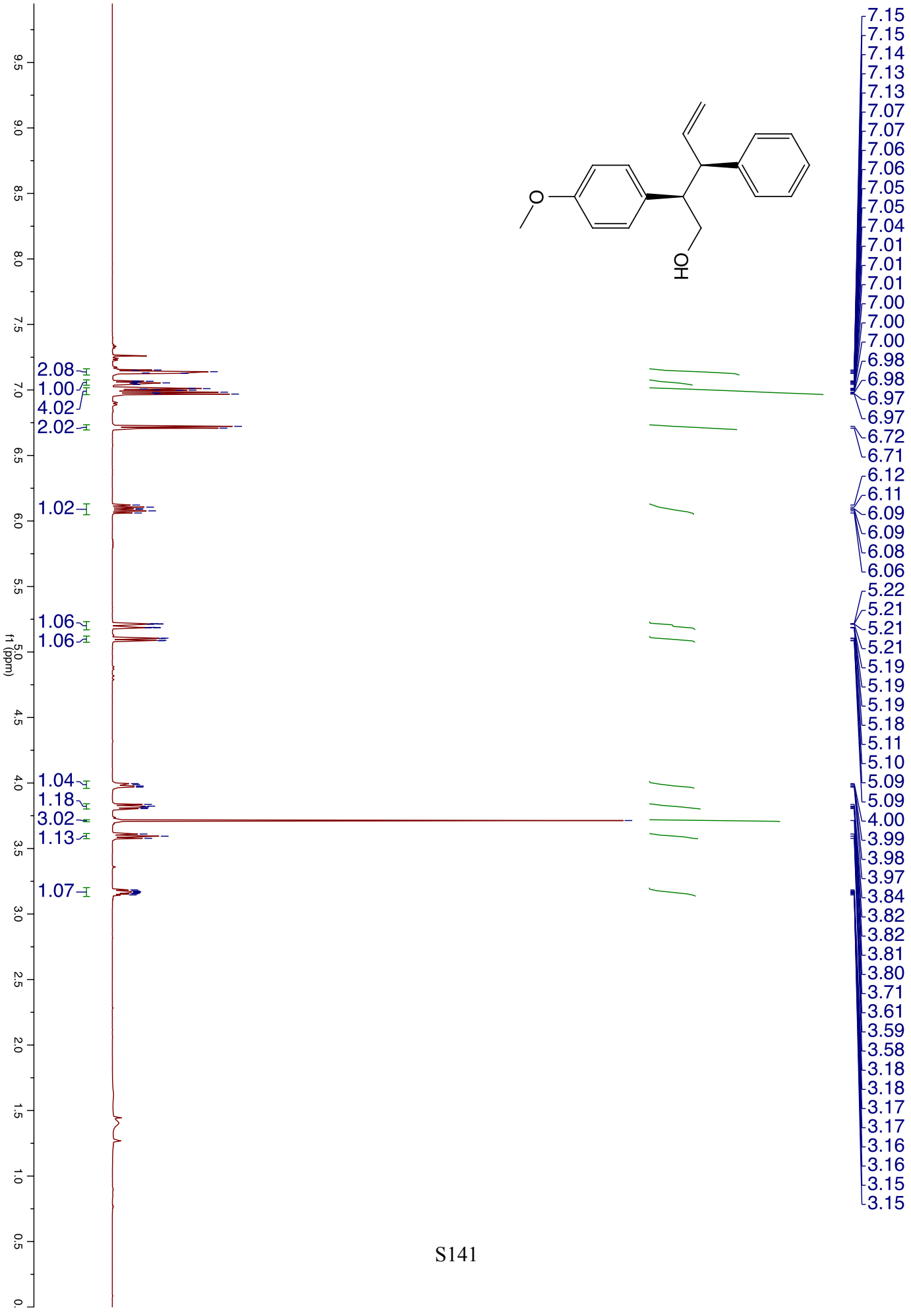

173.02
141.81
138.68
137.16
128.96
128.73
128.69
128.16
127.72
126.94
116.87
57.43
53.24
51.93
f1 (ppm)


f1 (ppm)
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
2.07
7.56
0.99
1.00
1.03
1.04
1.07
1.05
3.08
7.45
7.45
7.44
7.43
7.37
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.25
7.25
7.24
7.23
7.22
5.75
5.74
5.74
5.72
5.71
5.71
5.69
4.86
4.84
4.77
4.74
4.09
4.07
4.07
4.05
3.99
3.97
3.40
O
O


179.20
158.86
140.37
139.34
129.85
128.41
128.37
128.16
126.55
116.36
113.84
56.22
55.21
53.11
f1 (ppm)


f1 (ppm)
4.09
1.05
2.01
2.00
1.00
1.00
1.03
1.01
1.04
3.12
7.15
7.13
7.13
7.12
7.12
7.11
7.11
7.08
7.07
7.07
7.06
7.06
7.05
7.04
7.02
7.01
7.00
7.00
6.68
6.67
6.14
6.12
6.12
6.10
6.09
6.08
6.07
5.24
5.23
5.23
5.20
5.20
5.20
5.13
5.11
4.02
4.01
4.00
3.99
3.92
3.89
3.69
O
O
HO


O
HO
158.29
142.51
140.90
132.15
129.77
128.34
128.09
126.15
115.64
113.87
65.98
55.21
53.92
52.10
f1 (ppm)


f1 (ppm)
2.08
1.00
4.02
2.02
1.02
1.06
1.06
1.04
1.18
3.02
1.13
1.07
HO
7.15
7.15
7.14
7.13
7.13
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.01
7.01
7.01
7.00
7.00
7.00
6.98
6.98
6.97
6.97
6.72
6.71
6.12
6.11
6.09
6.09
6.08
6.06
5.22
5.21
5.21
5.21
5.19
5.19
5.19
5.18
5.11
5.10
5.09
5.09
4.00
3.99
3.98
3.97
3.84
3.82
3.82
3.81
3.80
3.71
3.61
3.59
3.58
3.18
3.18
3.17
3.17
3.16
3.16
3.15
3.15