Supporting Information

Traceless silylation of β-C(sp^3)–H bonds of alcohols via perfluorinated acetals

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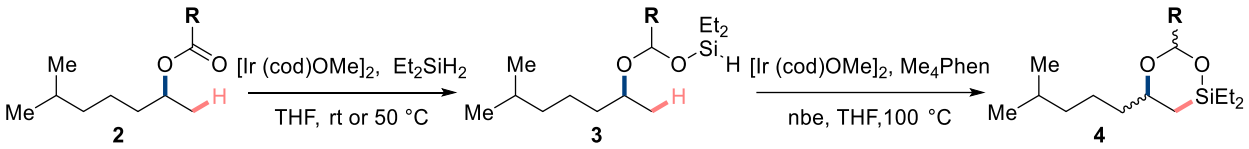
I. General

All reactions were conducted under inert atmosphere in a nitrogen-filled glovebox or with standard Schlenk techniques, unless otherwise specified. Vessels used in air-free reactions were oven-dried prior to use. Vials used as a reaction vessels were sealed with Teflon-lined caps. Silica-gel chromatography was performed with Silicycle SiliaFlash P60 silica gel. Toluene, tetrahydrofuran, and dichloromethane were purged with nitrogen and dried with an Innovative Pure-Solv solvent purification system. Anhydrous dimethylsulfoxide, dimethylformamide, dioxane, *N*-methylpyrrolidone, 1,2,4-trichlorobenzene, and acetonitrile were purchased from Acros Organics. Anhydrous 1,2-dichlorobenzene and 1,2-dichoroethane were purchased from Aldrich. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Brüker AVQ-500 or Brüker AVQ-600 spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (ref: $CHCl_3$ [^{1}H: 7.26, ^{13}C: 77.16], $CHCl_2$-$CHCl_2$ [^{1}H: 6.00, ^{13}C: 73.78], MeOH [^{1}H: 3.31, ^{13}C 49.0], DMSO [^{1}H: 2.50, ^{13}C 39.5]). Coupling constants (*J*) were reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter.

II. Evaluation of reaction conditions

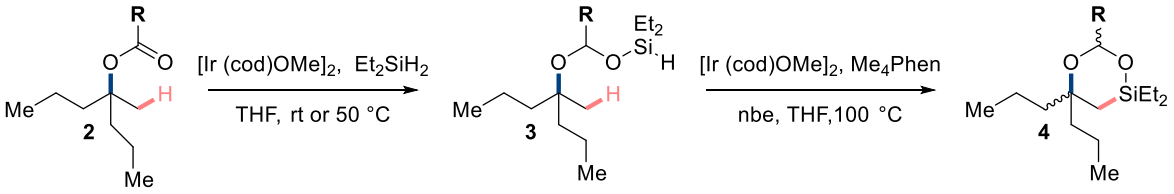
Table S1. Evaluation of directing group for secondary alcohol



Entry	Substrate	Conversion of 2[a,c]	Yield of 4 (^{1}H NMR)[b,d]
1	R = OMe	100%[e]	0%
2	R = CCl_3	50%	0%
3	R = Et	100%	0%
4	R = Ad	100%	0%
5	R = ^{t}Bu	93%	0%
6	R = C_6F_5	70%	0%
7	R = Me	81%	0%
8	R = H	89%	24%
9	R = CF_3	100%	45%
10	R = C_2F_5	100%	68%
11	R = C_3F_7	96%	78%
12	R = CF_2Ph	98%	75%
13	R = C_7F_{15}	95%	84%

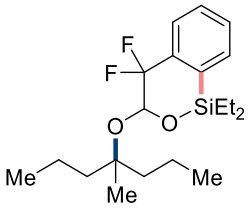
[a]Conditions for hydrosilylation of ester: $[Ir(cod)OMe]_2$ (1.0 mol%), Et_2SiH_2 (4.0 equiv), heptane or THF (0.5 M), rt, 50 or 60 C, 24-48 h, N_2; [b]Conditions for β-C(sp^3)–H silylation: $[Ir(cod)OMe]_2$ (2.0 mol%), Me_4Phen (6.0 mol%), nbe (1.5 equiv), THF (0.1 M), 100 C, 16 h, N_2; [c]Conversion for the hydrosilylation step determined by ^{1}H NMR spectroscopy; [d]Overall yield for the two step determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard; [e]Cleavage of C-OMe bond.

Table S2. Evaluation of directing group for tertyary alcohol



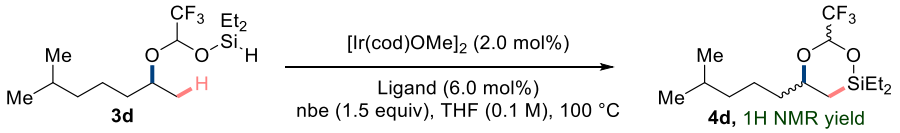
Entry	Substrate	Conversion of 2[a,c]	Yield of 4 (^{1}H NMR)[b,d]
1	R = H	100%	0%
2	R = Me	100%	0%
3	R = Ad	100%	0%
4	R = CF_3	100%	43%
5	R = C_2F_5	28%	-
6	R = C_3F_7	15%	-
7	R = CF_2Ph	100%	36% +18% of **4'**
8	R = C_7F_{15}	13%	-

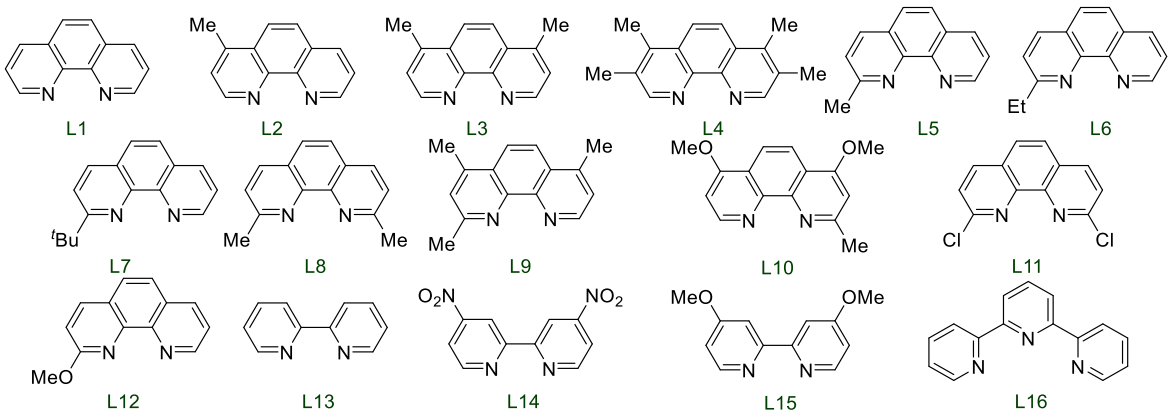
[a]Conditions for hydrosilylation of ester: $[Ir(cod)OMe]_2$ (1.0 mol%), Et_2SiH_2 (4.0 equiv), heptane or THF (0.5 M), rt, 50 or 60 C, 24-48 h, N_2; [b]Conditions for β-C(sp^3)–H silylation: $[Ir(cod)OMe]_2$ (2.0 mol%), Me_4Phen (6.0 mol%), nbe (1.5 equiv), THF (0.1 M), 100 C, 16 h, N_2; [c]Conversion for the hydrosilylation step determined by ^{1}H NMR spectroscopy; [d]Overall yield for the two step determined by ^{1}H NMR spectroscopy using CH_2Br_2 or CH_3NO_2 as internal standard.



4',18%

Table S3. β-C(sp^3)–H silylation of trifluoroacetal **3d**: ligand survey

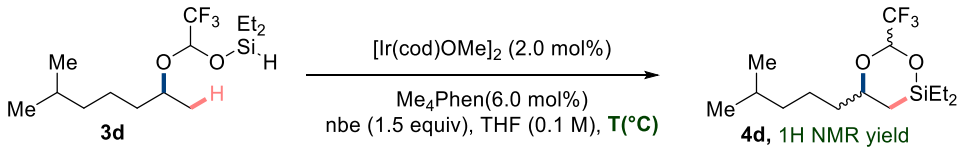




Entry	Ligand	Conversion of 3d[a]	Yield 4d (^{1}H NMR)[a]
1	**L1**	100%	39%
2	**L2**	100%	37%
3	**L3**	100%	34%
4	**L4**	100%	45%
5	**L5**	93%	31%
6	**L6**	85%	13%
7	**L7**	81%	0%
8	**L8**	89%	0%
9	**L9**	93%	16%
10	**L10**	100%	traces
11	**L11**	78%	0%
12	**L12**	100%	0%
13	**L13**	100%	0%
14	**L14**	100%	0%
15	**L15**	78%	9%
16	**L16**	100%	0%

Standard conditions: $[Ir(cod)OMe]_2$ (2.0 mol%), Ligand (6.0 mol%), nbe (1.5 equiv), THF (0.1 M), 100 C, 3 h, N_2, the reactions were conducted in closed vials sealed with Teflon-lined cap; [a]Yield and conversion determined by ^{1}H NMR spectrum using CH_2Br_2 as internal standard.

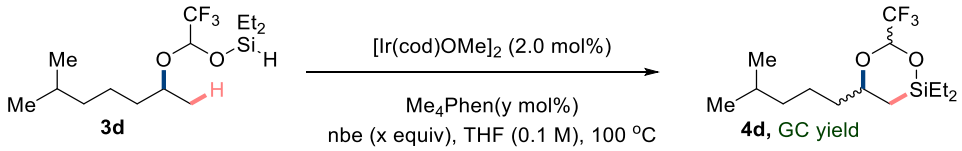
Table S4. β-C(sp^3)–H silylation of trifluoroacetal **3d**: Temperature survey



Entry	T (°C)	Yield 4d (^{1}H NMR)[a]
1	120[b]	44%
2	100	45%
3	80	40%
4	60	6%

Standard conditions: $[Ir(cod)OMe]_2$ (2.0 mol%), Ligand (6.0 mol%), nbe (1.5 equiv), THF (0.1 M), 3 h, N_2, the reactions were conducted in closed vials sealed with Teflon-lined cap; [a]Yield and conversion determined by ^{1}H NMR spectrum using CH_2Br_2 as internal standard. [b] time = 20 min, conversion of **4d** = 78%

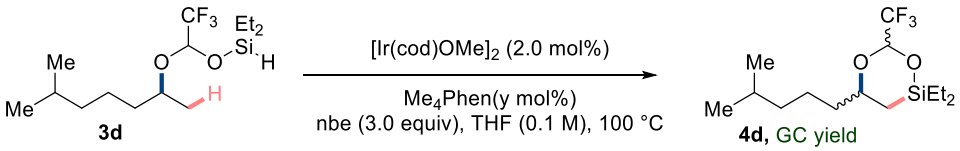
Table S5. β-C(sp^3)–H silylation of trifluoroacetal **3d**: nbe equivalents



Entry	Nbe equiv	Yield 4d (^{1}H NMR)[a]
1	0	0%
2	1.5	45%
3	2.0	41%
4	3.0	39%
5	6.0	35%

Standard conditions: $[Ir(cod)OMe]_2$ (2.0 mol%), Me_4Phen (6.0 mol%), nbe, THF (0.1 M), 100 C, 3 h, N_2, the reactions were conducted in closed vials sealed with Teflon-lined cap; [a]Yield and conversion determined by GC analysis with $^nC_{12}H_{26}$ as internal standard.

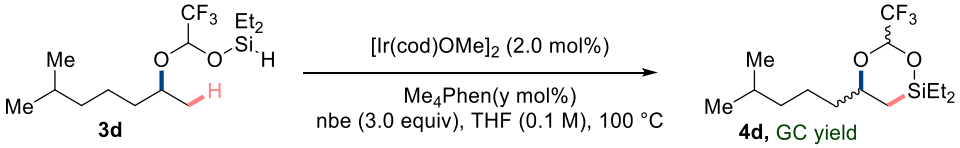
Table S6. β-C(sp^3)–H silylation of trifluoroacetal **3d**: $[Ir(cod)OMe]_2$: Me_4Phen ratio



Entry	$[Ir(cod)OMe]_2$: Me_4Phen ratio	Yield 4d (^{1}H NMR)[a]
1	2 : 4	40%
2	2 : 6	39%
3	2 : 8	30%
4	2 : 12	28%

Standard conditions: $[Ir(cod)OMe]_2$ (2.0 mol%), Me_4Phen, nbe (3.0 equiv), THF (0.1 M), 100 C, 3 h, N_2, the reactions were conducted in closed vials sealed with Teflon-lined cap; [a]Yield and conversion determined by GC analysis with $^nC_{12}H_{26}$ as internal standard.

Table S7. β-C(sp^3)–H silylation of trifluoroacetal **3d**: concentration

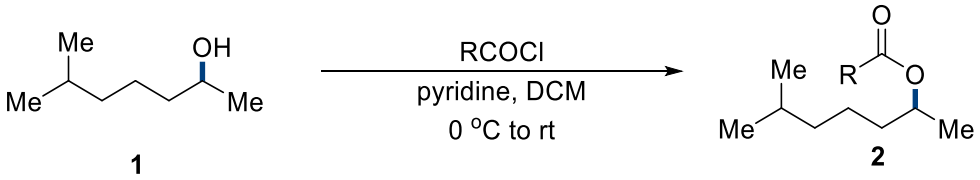


Entry	Concentration	Yield 4d (^{1}H NMR)[a]
1	0.05	38%
2	0.1	39%
3	0.5	23%
4	1.0	17%

Standard conditions: $[Ir(cod)OMe]_2$ (2.0 mol%), Me_4Phen (6.0 mol%), nbe (3.0 equiv), THF, 100 C, 3 h, N_2, the reactions were conducted in closed vials sealed with Teflon-lined cap; [a]Yield and conversion determined by GC analysis with $^nC_{12}H_{26}$ as internal standard.

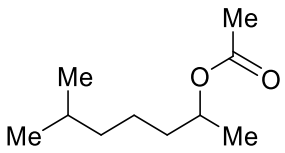
III. Synthesis of starting materials:

III.1. General procedure for the synthesis of 6-methylheptan-2-yl esters:



General Procedure: The alcohol (1.0 equiv) and pyridine (3.0 equiv) were dissolved in DCM (0.5 M), and the resulting reaction mixture was cooled in an ice bath. Subsequently, RC(O)Cl (2.0 equiv) was added dropwise, and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with DCM, washed with aqueous HCl (3.0 M), water, aqueous NaOH (3.0 M), and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, hexane/AcOEt 100:0 to 95:5) to afford the corresponding ester.

6-methylheptan-2-yl acetate



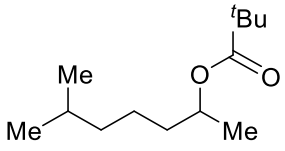
Following the general procedure, the product was obtained as a colorless oil. Yield = 77%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.94 – 4.83 (m, 1H), 2.03 (s, 3H), 1.59 – 1.39 (m, 3H), 1.33 – 1.23 (m, 2H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.18 – 1.13 (m, 2H), 0.86 (d, *J* = 6.6, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 71.0, 38.7, 36.1, 27.8, 23.1, 22.6, 22.5, 21.3, 19.9.

HRMS m/z (EI+) calcd for $C_{10}H_{19}O_2$ [M-H]: 171.1385, found 171.1383.

6-methylheptan-2-yl pivalate



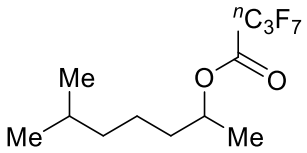
Following the general procedure, the product was obtained as a colorless oil. Yield = 50%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.89 – 4.83 (m, 1H), 1.59 – 1.39 (m, 3H), 1.37 – 1.23 (m, 2H), 1.18 (s, 9H), 1.20 – 1.13 (m, 5H), 0.86 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 69.7, 37.9, 37.8, 35.3, 26.9, 26.3, 26.3, 26.2, 22.7, 21.7, 21.7, 19.1.

HRMS m/z (EI+) calcd for $C_{13}H_{27}O_2$ $[M+H]^+$: 215.2006, found 215.2022.

6-methylheptan-2-yl perfluorobutanoate



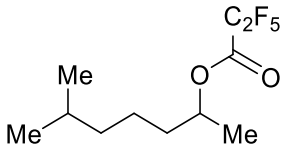
Following the general procedure, the product was obtained as a colorless oil. Yield = 67%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (h, *J* = 6.3 Hz, 1H), 1.70 (dddd, *J* = 14.1, 10.2, 7.6, 5.3 Hz, 1H), 1.61 – 1.49 (m, 2H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.41 – 1.25 (m, 2H), 1.24 – 1.13 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.11 (t, *J* = 29.6 Hz), 77.3, 38.6, 35.7, 27.9, 22.9, 22.6, 22.5, 19.6.

HRMS m/z (EI+) calcd for $C_{12}H_{16}F_7O_2$ [M-H]: 325.1039, found 325.1038.

6-methylheptan-2-yl perfluoropropanoate



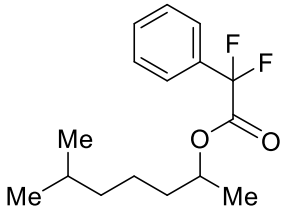
Following the general procedure, the product was obtained as a colorless oil. Yield = 52%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (h, *J* = 6.3 Hz, 1H), 1.70 (dddd, *J* = 14.0, 10.1, 7.6, 5.3 Hz, 1H), 1.62 – 1.48 (m, 2H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.39 – 1.26 (m, 2H), 1.24 – 1.13 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (t, *J* = 29.0 Hz), 117.9 (qt, *J* = 286.4, 34.4 Hz), 106.1 (tq, *J* = 265.0, 40.0 Hz), 77.0, 38.6, 35.8, 27.9, 22.9, 22.6, 22.5, 19.6.

HRMS m/z (EI+) calcd for $C_{12}H_{16}F_5O_2$ [M-H]: 275.1070, found 275.1065.

6-methylheptan-2-yl 2,2-difluoro-2-phenylacetate



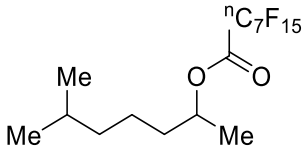
Following the general procedure, the product was obtained as a colorless oil. Yield = 88%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.1 Hz, 2H), 7.50 – 7.40 (m, 3H), 5.05 – 4.97 (m, 1H), 1.63 – 1.56 (m, 1H), 1.52 – 1.39 (m, 2H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.21 – 1.03 (m, 4H), 0.81 (d, *J* = 3.9 Hz, 3H), 0.80 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0 (t, *J* = 34.9 Hz), 133.2 (t, *J* = 25.9 Hz), 131.0, 128.7, 125.5 (t, *J* = 6.1 Hz), 113.5 (t, *J* = 252.0 Hz), 74.8, 38.6, 35.9, 27.9, 22.9, 22.6, 22.5, 19.8.

HRMS m/z (EI+) calcd for $C_{16}H_{22}F_2O_2$ [M+H]: 285.1666, found 285.1671.

6-methylheptan-2-yl perfluorooctanoate



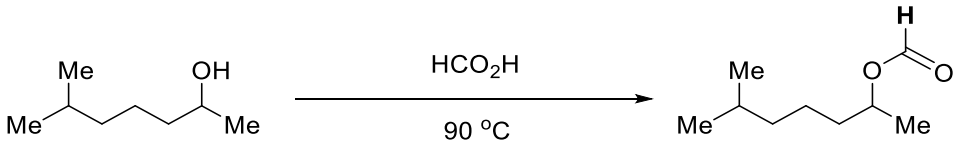
Following the general procedure, the product was obtained as colorless oil. Yield = 57%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (h, *J* = 6.3 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.60 – 1.49 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.39 – 1.27 (m, 2H), 1.24 – 1.13 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.1 Hz), 77.3, 38.6, 35.8, 27.9, 22.9, 22.6, 22.5, 19.6.

HRMS m/z (EI+) calcd for $C_{16}H_{16}F_{15}O_2$ [M+H]: 525.0911, found 525.0889.

6-methylheptan-2-yl formate



The alcohol (1.0 equiv) was dissolved in formic acid (1.5 M) in a screw-capped vial equipped with a magnetic stir bar. The vial was capped with a Teflon-lined screw cap,, and the resulting solution was stirred at 90 °C for 16 hours. Once cooled to room temperature, the reaction mixture was diluted with AcOEt, washed with aqueous NaOH (3.0 M) and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column

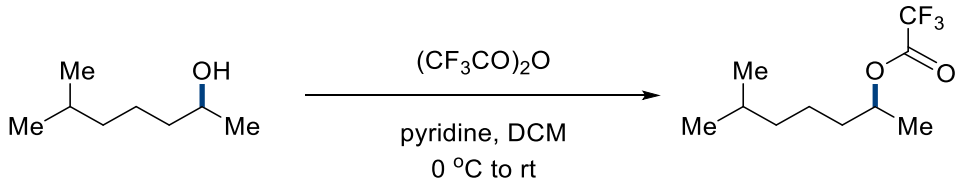
chromatography (SiO_2, hexane/AcOEt 100:0 to 95:5) to afford the corresponding ester as a colorless oil. Yield = 92%.

^{1}H NMR (600 MHz, chloroform-*d*) δ 8.05 (s, 1H), 5.04 – 5.01 (m, 1H), 1.63 – 1.46 (m, 3H), 1.39 – 1.26 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.21 – 1.11 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 71.1, 38.6, 36.0, 27.8, 23.0, 22.5, 22.4, 19.9.

HRMS m/z (EI+) calcd for $C_9H_{19}O_2$ [M+H]: 159.1385, found 159.1385.

6-methylheptan-2-yl trifluoroacetate



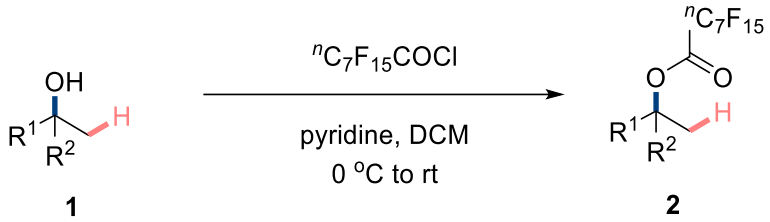
The alcohol (1.0 equiv) and pyridine (3.0 equiv) were dissolved in DCM (0.5 M),, and the resulting reaction mixture was cooled in an ice bath. Subsequently, $(CF_3CO)_2O$ (2.0 equiv) was added dropwise and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with DCM, washed with aqueous HCl (3.0 M), water, aqueous NaOH (3.0 M) and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The ester was purified by flash column chromatography (SiO_2, hexane/AcOEt 100:0 to 95:5) to afford the corresponding ester as a colorless oil. Yield = 82%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 – 5.03 (m, 1H), 1.73 – 1.66 (m, 1H), 1.61 – 1.49 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.40 – 1.26 (m, 2H), 1.22 – 1.15 (m, 2H), 0.87 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1 (q, *J* = 41.8 Hz), 114.6 (q, *J* = 285.8 Hz), 76.5, 38.4, 35.5, 27.7, 22.8, 22.4, 22.4, 22.3, 19.4.

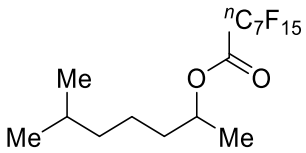
HRMS m/z (CI) calcd for $C_9H_{14}F_3O_2$ [M-Me]: 211.0946, found 211.1004.

III.2. Synthesis of pentadecafluorooctanoate ester:



General Procedure: The alcohol (1.0 equiv) and pyridine (3.0 equiv) were dissolved in DCM (0.5 M),, and the resulting reaction mixture was cooled in an ice bath. Subsequently, $^{n}C_7F_{15}COCl$ (2.0 equiv) was added dropwise, and the reaction mixture was stirred for 2 2 at room temperature. The reaction mixture was diluted with DCM, washed with aqueous HCl (3.0 M), water, aqueous NaOH (3.0 M) and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, hexane/AcOEt 100:0 to 95:5) to afford the corresponding ester.

6-methylheptan-2-yl perfluorooctanoate



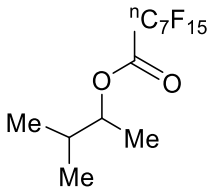
Following the general procedure, the product was obtained as colorless oil. Yield = 57%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (h, *J* = 6.3 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.60 – 1.49 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.39 – 1.27 (m, 2H), 1.24 – 1.13 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.1 Hz), 77.3, 38.6, 35.8, 27.9, 22.9, 22.6, 22.5, 19.6.

HRMS m/z (EI+) calcd for $C_{16}H_{15}F_{15}O_2$ [M-2H]: 524.0833, found 524.0840.

3-methylbut-2-yl perfluorooctanoate



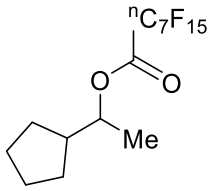
Following the general procedure, the product was obtained as a colorless oil. Yield = 78%

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.97 (p, *J* = 6.2 Hz, 1H), 1.90 (o, *J* = 6.7 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (t, *J* = 29.3 Hz), 81.4, 32.6, 17.9, 17.5, 16.3.

HRMS m/z (EI+) calcd for $C_{10}H_4F_{15}O_2$ [M-^{i}Pr]: 440.9972, found 440.9964.

1-cyclopentyleth-1-yl perfluorooctanoate



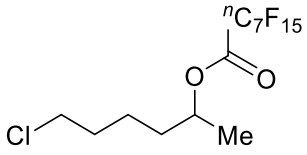
Following the general procedure, the product was obtained as a colorless oil. Yield = 70%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (dq, *J* = 7.8, 6.3 Hz, 1H), 2.11 (h, *J* = 8.3 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.69 – 1.52 (m, 4H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.32 – 1.17 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (t, *J* = 29.1 Hz), 80.9, 45.0, 29.0, 28.8, 25.6, 25.5, 18.7.

HRMS m/z (EI+) calcd for $C_{14}H_{10}F_{15}O_2$ [M-Me]: 495.0441, found 495.0429.

6-chlorohexan-2-yl perfluorooctanoate



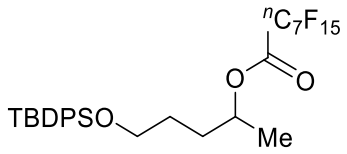
Following the general procedure, the product was obtained as a colorless oil. Yield = 82%

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.15 (h, *J* = 6.3 Hz, 1H), 3.53 (t, *J* = 6.5 Hz, 2H), 1.84 – 1.71 (m, 3H), 1.68 – 1.61 (m, 1H), 1.58 – 1.44 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.2 Hz), 76.8, 44.6, 34.7, 32.2, 22.5, 19.5.

HRMS m/z (EI+) calcd for $C_{14}H_{11}{}^{35}ClF_{15}O_2$ [M-H]: 531.0195, found 533.0208.

1-(tertbutyldiphenyl)siloxypent-4-yl perfluorooctanoate



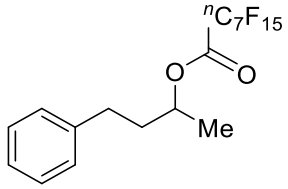
Following the general procedure, after purification by flash chromatography the product was obtained as a yellow oil. Yield = 88%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 4H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 4H), 5.17 (h, *J* = 6.3 Hz, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.69 – 1.52 (m, 2H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.07 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 28.9 Hz), 135.7, 133.9, 129.8, 127.8, 77.1, 63.3, 32.1, 28.1, 26.9, 19.5, 19.3.

HRMS m/z (ESI+) calcd for $C_{29}H_{29}F_{15}NaO_3Si$ $[M+Na]^+$: 761.1539, found 761.1540.

1-phenylbut-3-yl perfluorooctanoate



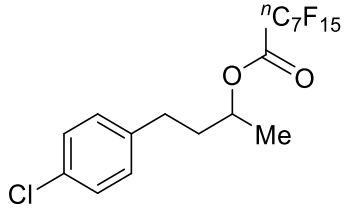
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 68%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.16 (h, *J* = 6.2 Hz, 1H), 2.73 (ddd, *J* = 14.9, 9.9, 5.5 Hz, 1H), 2.64 (ddd, *J* = 14.1, 9.7, 6.6 Hz, 1H), 2.12 – 2.05 (m, 1H), 1.98 – 1.89 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.3 Hz), 140.7, 128.8, 128.4, 126.4, 76.5, 37.2, 31.4, 19.6.

HRMS m/z (EI+) calcd for $C_{18}H_{13}F_{15}O_2$ [M]: 546.0676, found 546.0671.

1-(4-chlorophenyl)but-3-yl perfluorooctanoate



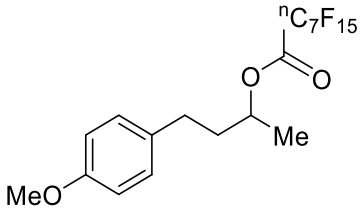
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 91%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.13 (dqd, *J* = 8.1, 6.3, 4.6 Hz, 1H), 2.68 (ddd, *J* = 14.0, 10.0, 5.5 Hz, 1H), 2.60 (ddd, *J* = 14.0, 9.7, 6.6 Hz, 1H), 2.05 (dddd, *J* = 14.2, 9.7, 8.0, 5.5 Hz, 1H), 1.90 (dddd, *J* = 14.4, 9.9, 6.6, 4.7 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.3 Hz), 139.1, 132.2, 129.7, 128.9, 76.3, 37.1, 30.8, 19.6.

HRMS m/z (EI+) calcd for $C_{18}H_{12}{}^{35}ClF_{15}O_2$ [M]: 580.0286, found 580.0281.

1-(4-methoxyphenyl)but-3-yl perfluorooctanoate



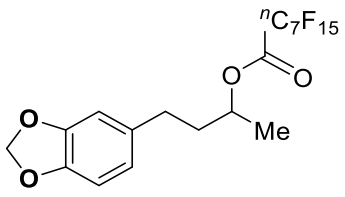
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 89%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.14 (dqd, *J* = 8.0, 6.3, 4.7 Hz, 1H), 3.79 (s, 3H), 2.66 (ddd, *J* = 14.9, 9.7, 5.5 Hz, 1H), 2.58 (ddd, *J* = 14.0, 9.5, 6.7 Hz, 1H), 2.04 (dddd, *J* = 14.4, 9.6, 7.9, 5.6 Hz, 1H), 1.89 (dddd, *J* = 14.4, 9.9, 6.7, 4.8 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 158.1 (t, *J* = 29.1 Hz), 132.7, 129.3, 114.2, 76.5, 55.4, 37.5, 30.5, 19.6.

HRMS m/z (EI+) calcd for $C_{19}H_{15}F_{15}O_3$ [M]: 576.0782, found 576.0784.

4-(benzo[d][1,3]dioxol-5-yl)butan-2-yl perfluoroctanoate



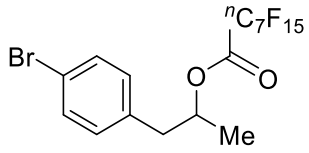
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 62%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.93 (s, 2H), 5.12 (h, *J* = 6.3 Hz, 1H), 2.63 (ddd, *J* = 15.0, 9.9, 5.6 Hz, 1H), 2.55 (ddd, *J* = 15.0, 9.5, 6.6 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.87 (dddd, *J* = 14.3, 9.9, 6.6, 4.7 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8 (t, *J* = 29.4 Hz), 147.7, 145.9, 134.2, 121.0, 108.6, 108.3, 100.8, 76.2, 37.3, 30.9, 19.4.

HRMS m/z (EI+) calcd for $C_{19}H_{13}F_{15}O_4$ [M]: 590.0574, found 590.0574.

1-(4-bromophenyl)prop-2-yl perfluorooctanoate



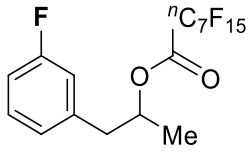
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 51%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.30 (h, *J* = 6.5 Hz, 1H), 2.96 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.86 (dd, *J* = 14.0, 5.8 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (t, *J* = 29.4 Hz), 135.1, 131.9, 131.2, 121.2, 76.9, 41.3, 19.1.

HRMS m/z (EI+) calcd for $C_{17}H_{10}{}^{79}BrF_{15}O_2$ [M]: 609.9625, found 609.9623.

1-(3-fluorophenyl)prop-2-yl perfluorooctanoate



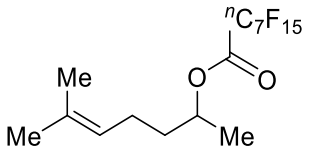
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 51%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 6.98 – 6.87 (m, 3H), 5.36 – 5.28 (m, 1H), 3.05 – 2.86 (m, 2H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.5 Hz), 156.9 (t, *J* = 29.2 Hz), 137.6 (d, *J* = 7.7 Hz), 129.2 (d, *J* = 8.3 Hz), 124.1 (d, *J* = 2.8 Hz), 115.4 (d, *J* = 21.5 Hz), 113.2 (d, *J* = 20.9 Hz), 75.9, 40.6 (d, *J* = 1.7 Hz), 18.2.

HRMS m/z (EI+) calcd for $C_{17}H_9F_{16}O_2$ [M-H]: 549.0347, found 549.0338.

6-methylhept-5-en-2-yl perfluorooctanoate



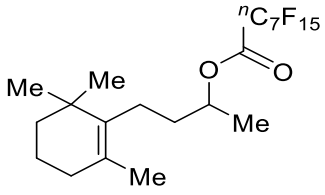
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 58%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (dqd, *J* = 7.9, 6.3, 4.8 Hz, 1H), 5.06 (thept, *J* = 7.2, 1.4 Hz, 1H), 2.10 – 1.98 (m, *J* = 7.3, 6.9 Hz, 2H), 1.77 (dtd, *J* = 14.2, 8.2, 6.2 Hz, 1H), 1.69 (s, 3H), 1.62 (dddd, *J* = 14.0, 8.8, 7.0, 4.9 Hz, 1H), 1.58 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1 (t, *J* = 29.3 Hz), 133.1, 122.6, 76.8, 35.6, 25.8, 23.8, 19.6, 17.6.

HRMS m/z (EI+) calcd for $C_{16}H_{15}F_{15}O_2$ [M]: 524.0833, found 524.0833.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-yl 2,2,2-trifluoroacetate perfluorooctanoate



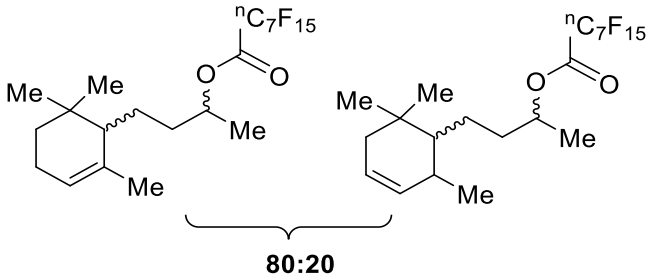
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 54%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (h, *J* = 6.3 Hz, 1H), 2.07 (td, *J* = 13.1, 4.7 Hz, 1H), 1.98 (td, *J* = 12.9, 5.0 Hz, 1H), 1.90 (t, *J* = 6.3 Hz, 2H), 1.80 – 1.66 (m, 2H), 1.57 (s, 3H), 1.59 – 1.54 (m, 2H), 1.43 – 1.40 (m, 2H), 1.37 (d, *J* = 6.3 Hz, 3H), 0.97 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2 (t, *J* = 29.0 Hz), 136.0, 128.1, 77.8, 39.9, 36.1, 35.1, 32.9, 28.6, 28.5, 24.1, 19.7, 19.6, 19.4.

HRMS m/z (EI+) calcd for $C_{21}H_{23}F_{15}O_2$ [M]: 592.1459, found 592.1464.

4-(2,6,6-trimethylcyclohex-2-en-1-yl)butan-2-yl perfluorooctanoate



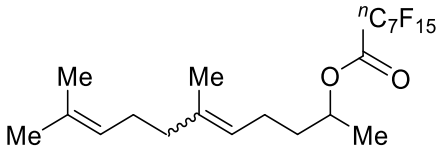
The starting alcohol was purchased as a mixture of isomers. Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 52%. The ^{1}H NMR and ^{13}C NMR analysis for the major constitutional isomer (two diastereoisomers in 1:1 ratio) are:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 – 5.34 (m, 1H), 5.12 – 5.08 (m, 1H), 2.00 – 1.96 (m, 2H), 1.82 – 1.64 (m, 3H), 1.69 – 1.67 (m, 3H), 1.57 – 1.52 (m, 1H), 1.48 – 1.45 (m, 2H), 1.36 (d, *J* = 6.3 Hz, 3H), 1.20 – 1.14 (m, 1H), 0.92 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (t, *J* = 29.5 Hz) 157.8 (t, *J* = 29.5 Hz), 135.6, 135.5, 120.8, 120.7, 77.6, 77.4, 48.8, 48.7, 35.7, 35.5, 32.4, 32.3, 31.5, 31.4, 27.5, 27.4, 27.3, 27.2, 26.1, 25.9, 23.1 (2C), 22.9, 22.8, 19.3, 19.2.

HRMS m/z (EI+) calcd for $C_{21}H_{23}F_{15}O_2$ [M]: 592.1459, found 592.1453.

6,10-dimethylundeca-5,9-dien-2-yl perfluorooctanoate (ratio Z:E= 1:1)



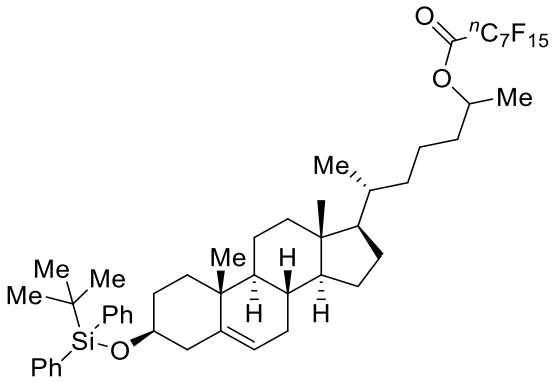
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 54%. The ester is a 1:1 mixture of *Z* and *E* isomers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.16 – 5.10 (m, $1H_Z$+$1H_E$), 5.12 – 5.05 (m, $2H_Z$+$2H_E$), 2.09 – 1.97 (m, $6H_Z$+$6H_E$), 1.82 – 1.72 (m, $1H_Z$+$1H_E$), 1.71 – 1.65 (m, 6H+3H), 1.66 – 1.59 (m, $1H_Z$+$1H_E$), 1.60 – 1.58 (m, 6H+3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.33 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1 (t, *J* = 28.9 Hz, 2C), 135.9, 135.8, 130.9, 130.6, 123.3, 123.2, 122.3, 121.5, 38.8, 34.9, 34.6, 31.0, 25.7, 25.6, 24.8, 24.7, 22.6, 22.5, 22.4, 18.6, 18.5, 16.8, 16.6, 14.9.

HRMS m/z (EI+) calcd for $C_{21}H_{23}F_{15}O_2$ [M]: 592.1459, found 592.1456.

(6R)-6-((3S,8S,9S,10R,13R,14S,17R)-3-((tert-butyldiphenylsilyl)oxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)heptan-2-yl perfluorooctanoate



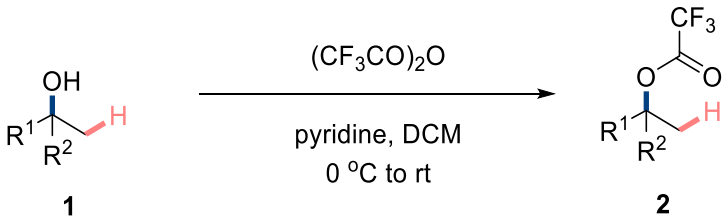
Following the general procedure, the product was obtained as a colorless oil. Yield = 53%. The ester was isolated as 1:1 diastereomeric mixture.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 4H), 7.43 – 7.39 (m, 2H), 7.39 – 7.33 (m, 4H), 5.16 – 5.11 (m, 2H), 3.59 – 3.45 (m, 1H), 2.36 – 2.31 (m, 1H), 2.13 (ddd, *J* = 13.5, 4.9, 2.3 Hz, 1H), 1.95 (dt, *J* = 12.6, 3.4 Hz, 1H), 1.92 – 1.87 (m, 1H), 1.81 – 1.75 (m, 1H), 1.74 – 1.48 (m, 4H), 1.45 – 1.35 (m, 4H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.27 – 1.15 (m, 1H), 1.06 (s, 9H), 1.09 – 1.00 (m, 1H), 0.98 (s, 3H), 0.95 – 0.74 (m, 1H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (t, *J* = 31.5 Hz, 2C), 141.2(2C), 135.8, 135.7, 134.8, 134.7, 129.4, 129.3, 127.4, 127.3, 121.0 (2C), 77.1, 77.0, 73.2(2C), 56.7(2C), 55.9(2C), 50.0(2C), 42.5(2C), 42.3(2C), 39.7, 39.6, 37.2(2C), 36.4(2C), 35.8, 35.7, 35.6, 35.5, 35.4(2C), 31.9(2C), 31.8(2C), 31.7(2C), 28.2, 28.1, 26.9 (2C), 24.2 (2C), 21.5, 21.4, 20.9(2C), 19.5(2C), 19.4(2C), 19.3(2C), 19.1(2C), 18.4(2C), 18.4(2C), 11.7(2C).

HRMS m/z (ESI+) calcd for $C_{50}H_{61}F_{15}NaO_3Si$ $[M+Na]^+$: 1045.4043, found 1045.4042.

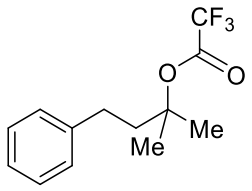
III.3. Synthesis of p trifluoroacetate ester



The alcohol (1.0 equiv) and pyridine (3.0 equiv) were dissolved in DCM (0.5 M), and the resulting reaction mixture was cooled in an ice bath. Subsequently, $(CF_3CO)_2O$ (2.0 equiv) was

added dropwise, and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with DCM, washed with aqueous solution of HCl (3.0 M), aqueous solution of NaOH (3.0 M) and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The ester was used such for the next step or purified by flash column chromatography (SiO_2).

2-methyl-4-phenylbutan-2-yl 2,2,2-trifluoroacetate



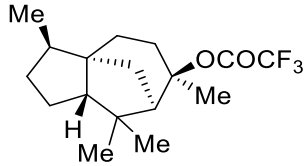
Following the general procedure, after purification by flash chromatography the product was obtained as colorless oil. Yield = 74%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 3H), 2.71 – 2.67 (m, 2H), 2.19 – 2.15 (m, 2H), 1.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2 (q, *J* = 41.3 Hz), 141.1, 128.5, 128.3, 126.1, 114.5 (q, *J* = 265.1 Hz), 88.6, 42.4, 30.1, 25.5.

HRMS m/z (EI+) calcd for $C_{13}H_{15}F_3O_2$ [M]: 260.1024, found 260.1028.

(3R,3aS,6R,7R,8aS)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl 2,2,2-trifluoroacetate



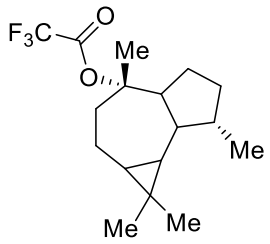
Following the general procedure, the product was obtained as a colorless oil. The product is unstable on silica, but pure material after extraction. Yield = 83%.

^{1}H NMR (600 MHz, $CDCl_3$) 2.40 – 2.38 (m, 1H), 2.17 (ddt, *J* = 13.6, 5.8, 1.7 Hz, 1H), 2.08 (dddd, *J* = 13.6, 12.5, 6.7, 1.1 Hz, 1H), 1.89 (dt, *J* = 12.1, 6.1 Hz, 1H), 1.85 – 1.79 (m, 1H), 1.75 – 1.64 (m, 2H), 1.63 (s, 3H), 1.58 – 1.50 (m, 2H), 1.45 – 1.27 (m, 4H), 1.15 (s, 3H), 0.99 (s, 3H), 0.85 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1 (q, *J* = 41.2 Hz), 113.4 (q, *J* = 286.4 Hz), 93.5, 57.3, 56.7, 54.0, 43.7, 41.3, 41.3, 37.1, 32.8, 31.5, 28.5, 26.8, 25.5, 25.4, 15.6.

HRMS m/z (EI+) calcd for $C_{17}H_{25}F_3O_2$ [M]: 318.1807, found 318.1811.

(4S,7S)-1,1,4,7-tetramethyldecahydro-1H-cyclopropa[e]azulen-4-yl 2,2,2-trifluoroacetate



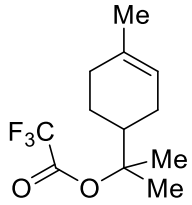
Following the general procedure, the product was obtained as a colorless oil. The product is unstable on silica, but the material obtained after extraction was sufficiently pure for further reactions. Yield = 82%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.52 – 2.44 (m, 1H), 2.37 (td, *J* = 9.3, 5.9 Hz, 1H), 2.02 (dq, *J* = 10.7, 6.8 Hz, 1H), 1.93 – 1.63 (m, 6H), 1.60 (s, 3H), 1.38 – 1.32 (m, 1H), 1.19 – 1.12 (m, 1H), 1.02 (s, 3H), 0.95 (s, 3H), 0.94 (d, *J* = 6.5, 3H), 0.56 (ddd, *J* = 11.4, 9.4, 6.2 Hz, 1H), 0.35 (t, *J* = 9.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2 (q, *J* = 40.7 Hz), 113.7 (q, *J* = 287.5 Hz), 92.9, 52.6, 39.8, 37.6, 33.7, 29.3, 27.7, 25.4, 24.8, 24.1, 22.6, 18.7, 18.0, 15.0, 14.7.

HRMS m/z (EI+) calcd for $C_{17}H_{25}F_3O_2$ [M]: 318.1807, found 318.1811.

2-(4-methylcyclohex-3-en-1-yl)propan-2-yl 2,2,2-trifluoroacetate



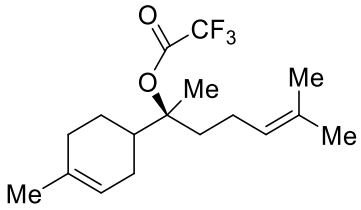
Following the general procedure, the product was obtained as colorless oil. The product is unstable on silica, but the material obtained after extraction was sufficiently pure for further reactions. Yield = 90%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.37 (s, 1H), 2.11 – 1.96 (m, 4H), 1.89 – 1.79 (m, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H), 1.34 (dd, *J* = 12.3, 5.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (q, *J* = 40.7 Hz), 133.1, 118.8, 113.6 (q, *J* = 287.8 Hz), 91.0, 41.8, 29.8, 25.3, 22.8, 22.4, 22.1, 21.9.

HRMS m/z (EI+) calcd for $C_{12}H_{17}F_3O_2$ [M]: 250.1181, found 250.1176.

(2S)-6-methyl-2-(4-methylcyclohex-3-en-1-yl)hept-5-en-2-yl 2,2,2-trifluoroacetate



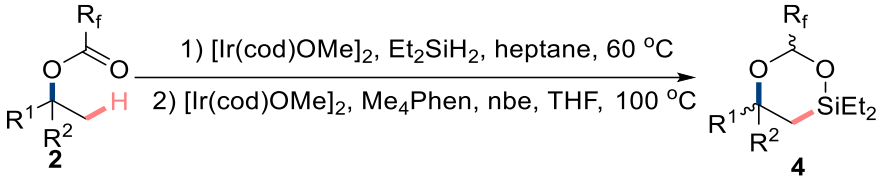
Following the general procedure, the product was obtained as a colorless oil. The product is unstable on silica, but the material obtained after extraction was sufficiently pure for further reactions. Yield = 98%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.36 (s, 1H), 5.08 – 5.06 (m, 1H), 2.22 (tdd, *J* = 11.9, 5.1, 2.4 Hz, 1H), 2.07 – 1.76 (m, 9H), 1.67 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H), 1.51 (s, 3H), 1.37 (qd, *J* = 12.3, 5.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3 (t, *J* = 40.7 Hz), 133.5, 131.6, 122.2, 118.7, 112.7 (q, *J* = 290.7 Hz) 93.3, 39.5, 34.5, 29.8, 25.4, 24.8, 22.6, 22.4, 20.9, 19.4, 16.6.

HRMS m/z (EI+) calcd for $C_{17}H_{25}F_3O_2$ [M]: 318.1807, found 318.1798.

IV. Ir-catalyzed hydrosilylation and C–H silylation of ester:



General procedure for the Ir-catalyzed hydrosilylation of esters: The reactions were conducted on 0.1-2.0 mmol scales. In an N_2-filled glove box, the perfluorinated ester (1.0 equiv) and $[Ir(cod)OMe]_2$ (2.0 mol %) were weighed into screw-capped vials equipped with a magnetic stir bar. To the mixture were added heptane (c = 0.5 M) and Et_2SiH_2 (4.0 equiv). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred at 60 °C for 48 hours. The conversion to the corresponding diethyl(hydrido)silylacetal was observed by ^1H NMR spectroscopy (see Figure S1). The volatile materials from the crude reaction mixture containing the diethyl(hydrido)silylacetal were evaporated with nitrogen at 40-45 °C, placed under high-vacuum for 30 min, and used as such for the next step.

General procedure for the Ir-catalyzed intramolecular aliphatic silylation:
In an N_2-filled glove box, to the screw-capped vial with the crude reaction mixture containing the diethyl(hydrido)silylacetal, were weighed [Ir(cod)OMe]2 (2.0 mol %) and Me_4phen (6.0 mol %). Then, to the reaction mixture were added THF (0.1 M) and nbe (1.5 equiv). The vial was capped with a Teflon-lined screw cap,, and the resulting solution was placed in a pre-heated aluminum block and stirred at 100 °C for 12-16 hours. The volatile materials from the crude reaction mixture containing the diethyl(hydrido)silylacetal were evaporated with a strem of nitrogen at 40-45 °C, and the yield of the 6-membered silinane was determined by ^1H NMR spectroscopy using CH_2Br_2 as internal standard. The crude material was purified by flash column chromatography (C2 deactivated silica gel[1], hexane/acetone 100:0 to 98:2) to afford the purified silinane.

[1] Panne, P.; Fox, J. M., *J. Am. Chem. Soc.* **2007,** *129*, 22-23.

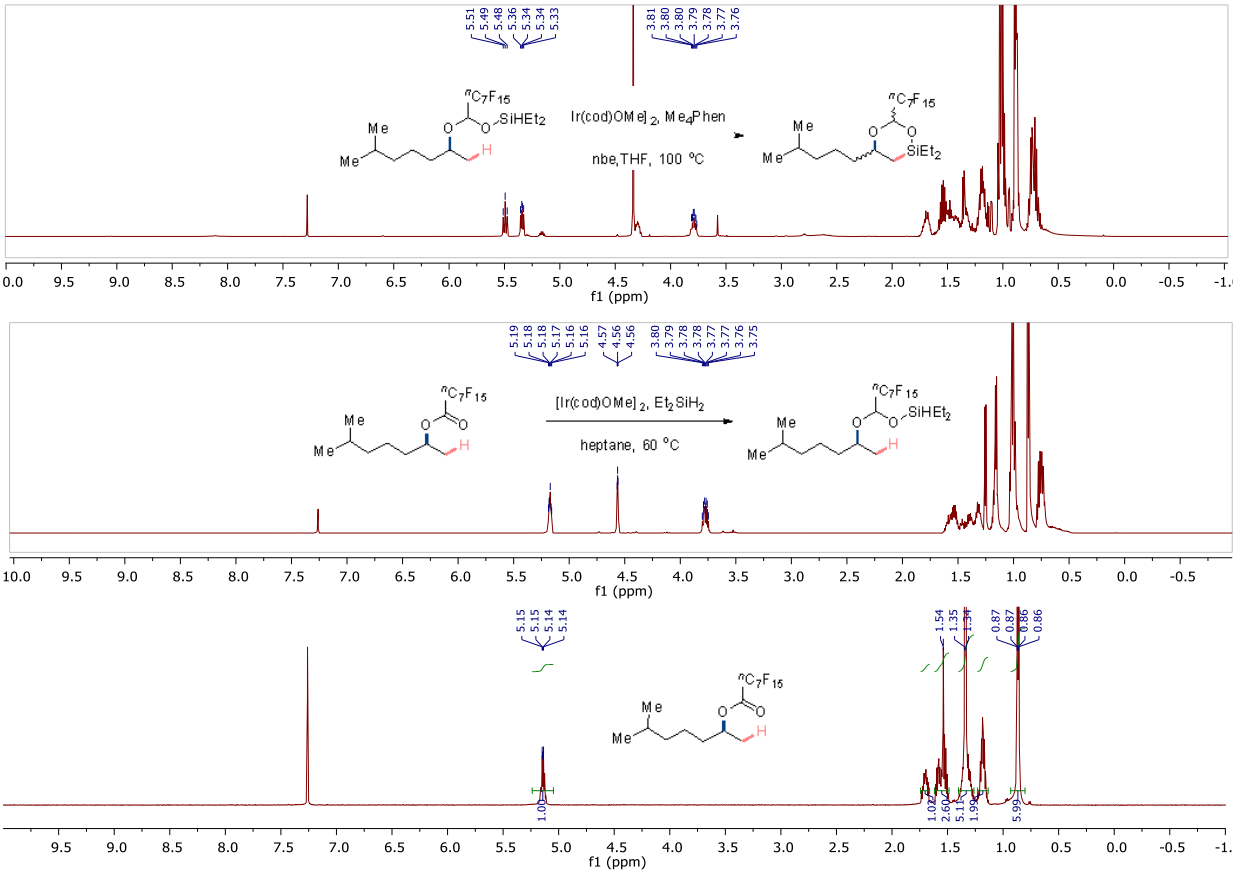
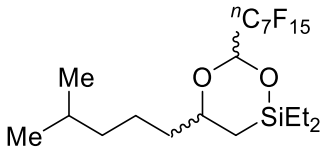


Figure S1[1]H NMR analysis hydrosilylation and C–H silylation reactions

2,2-diethyl-4-(4-methylpentyl)-6-(perfluorooctyl)-1,5,2-dioxasilinane



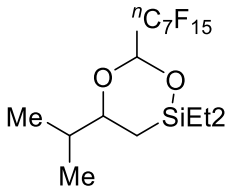
The diastereoisomeric ratio was determined to be 1.3:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 75%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.49 (t, *J* = 9.0 Hz, 1H$_{minor}$), 5.34 (dd, *J* = 8.5, 5.5 Hz, 1H$_{major}$), 4.33 – 4.25 (m, 1H$_{minor}$), 3.79 (ddt, *J* = 11.8, 8.0, 4.0 Hz, 1H$_{major}$), 1.74 – 1.66 (m, 2H$_{minor}$) 1.57 – 1.52 (m, 1H$_{major}$), 1.50– 0.94 (m, 7H$_{minor+major}$), 1.04– 0.97 (m, 6H$_{minor+major}$), 0.89– 0.87 (m, 6H$_{minor+major}$), 0.75– 0.7 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 94.7 (dd, *J* = 27.9, 25.1 Hz), 90.3 (t, *J* = 25.0 Hz), 78.9, 73.3, 40.1, 38.9, 38.8, 38.6, 28.2, 28.1, 23.4, 23.3, 22.7, 22.6(2C), 22.5, 17.6, 16.9, 7.2, 7.1, 6.8, 6.3, 6.2, 6.1, 5.9, 5.8.

HRMS m/z (EI+) calcd for $C_{20}H_{28}F_{15}O_2Si$ [M+H]: 613.1619, found 613.1619.

2,2-diethyl-4-isopropyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



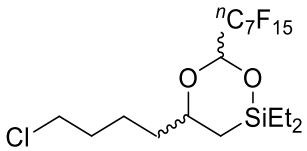
The diastereoisomeric ratio was determined to be 1.6:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 72%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.49 (dd, *J* = 12.4, 6.7 Hz, $1H_{minor}$), 5.34 (dd, *J* = 8.5, 5.7 Hz, $1H_{major}$), 4.03 – 3.92 (m, $1H_{minor}$), 3.53 – 3.46 (m, $1H_{major}$), 1.79 – 1.72 (m, $1H_{minor+major}$), 1.04 – 0.88 (m, $12H_{minor+major}$), 0.77 – 0.67 (m, $4H_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 93.8 (dd, *J* = 28.6, 24.8 Hz), 89.8 (dd, *J* = 26.9, 22.7 Hz), 82.9, 76.9, 34.8, 33.9, 17.5, 17.2, 17.1, 17.03, 13.2, 12.8, 6.3, 6.1, 5.5, 5.4, 5.2(2C), 5.0, 4.8.

HRMS m/z (EI+) calcd for $C_{17}H_{22}F_{15}O_2Si$ [M+H]: 571.1150, found 571.1143.

4-(4-chlorobutyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



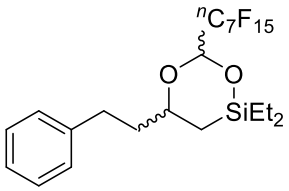
The diastereoisomeric ratio was determined to be 1.6:11 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 65%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.50 (t, *J* = 9.2 Hz, $1H_{minor}$), 5.35 (t, *J* = 6.9 Hz, $1H_{major}$), 4.34 – 4.26 (m, $1H_{minor}$), 3.86 – 3.77 (m, $1H_{major}$), 3.58 – 3.54 (m, $2H_{minor+major}$), 1.84 – 1.50 (m, $6H_{minor+major}$), 1.12 – 0.88 (m, 2H), 1.05 – 0.99 (m, $6H_{minor+major}$), 0.79 – 0.66 (m, $4H_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 94.6 (dd, *J* = 27.6, 25.6 Hz), 89.4 (t, *J* = 25.3 Hz), 77.6, 71.8, 43.9(2C), 37.9, 36.7, 31.5, 31.4, 21.9(2C), 16.5, 15.9, 6.1, 6.1, 5.6, 5.4, 5.2, 5.1, 4.9, 4.8.

HRMS m/z (EI+) calcd for $C_{18}H_{21}{}^{35}ClF_{15}O_2Si$ [M-H]: 617.0760, found 617.0755.

2,2-diethyl-4-phenethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



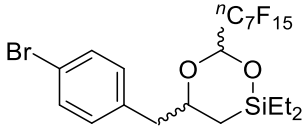
The diastereoisomeric ratio was determined to be 1.5:11 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 74%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H$_{minor+major}$), 7.24 – 7.16 (m, 3H$_{minor+major}$), 5.54 (dd, *J* = 10.2, 7.7 Hz, 1H$_{minor}$), 5.33 (dd, *J* = 7.8, 6.1 Hz, 1H$_{major}$), 4.34 (dt, *J* = 8.3, 4.9 Hz, 1H$_{minor}$), 3.77 (ddt, *J* = 12.1, 8.7, 3.6 Hz, 1H$_{major}$), 2.83 – 2.76 (m, 1H$_{minor+major}$), 2.70 – 2.64 (m, 1H$_{minor+major}$), 2.07 – 2.00 (m, 1H$_{minor+major}$), 1.88 – 1.80 (m, 1H$_{minor+major}$), 1.15 – 0.90 (m, 8H$_{minor+major}$), 0.78 – 0.68 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 140.7, 127.7, 127.6 (2C), 127.5(2C), 125.1, 93.6 (t, *J* = 25.9 Hz), 89.2 (t, *J* = 25.2 Hz), 76.6, 71.8, 40.5, 39.2, 31.0, 30.7, 16.5, 15.8, 6.1, 6.1, 5.7, 5.3, 5.2, 5.1, 4.9, 4.8.

HRMS m/z (EI+) calcd for $C_{22}H_{23}F_{15}O_2Si$ [M]: 632.1228, found 632.1223.

4-(4-bromobenzyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



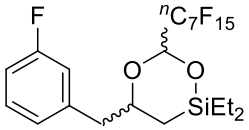
The diastereoisomeric ratio was determined to be 1.4:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 73%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H$_{minor+major}$), 7.13 – 7.06 (m, 2H$_{minor+major}$), 5.51 (t, *J* = 9.4 Hz, 1H$_{minor}$), 5.26 (t, *J* = 6.9 Hz, 2H$_{major}$), 4.52 – 4.42 (m, 1H$_{minor}$), 4.01 – 3.92 (m, 1H$_{major}$), 3.07 – 2.92 (m, 1H$_{minor+major}$), 2.82 – 2.71 (m, 1H$_{minor+major}$), 1.11 – 0.89 (m, 8H$_{minor+major}$), 0.79 – 0.65 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7, 136.4, 131.5, 131.4(3C), 120.6(2C), 94.3 (t, *J* = 27.1 Hz), 90.9 (t, *J* = 25.2 Hz), 79.2, 73.1, 45.2, 44.2, 17.2, 16.3, 7.1, 6.9, 6.4, 6.3, 6.2, 6.0, 5.9, 5.8.

HRMS m/z (EI+) calcd for $C_{21}H_{20}BrF_{15}O_2Si$ [M]: 696.0176, found 666.0167.

4-(3-fluorobenzyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



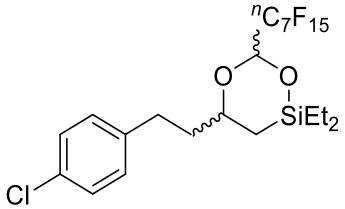
The diastereoisomeric ratio was determined to be 1.5:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 75%.

^{1}H NMR (600 MHz $CDCl_3$) 7.26 – 7.21 (m, 1H$_{minor+major}$), 6.98 – 6.90 (m, 3H$_{minor+major}$), 5.49 (t, *J* = 9.3 Hz, 1H$_{minor}$), 5.25 (dd, *J* = 7.8, 5.8 Hz, 1H$_{major}$), 4.48 (dq, *J* = 10.7, 6.0 Hz, 1H$_{minor}$), 4.03 – 3.92 (m, 1H$_{major}$), 3.02 – 2.94 (m, 1H$_{minor+major}$), 2.82 – 2.76 (m, 1H$_{minor+major}$), 1.13 – 0.90 (m, 8H$_{minor+major}$), 0.75 – 0.63 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8 (d, *J* = 245.1 Hz), 162.7 (d, *J* = 245.4 Hz), 140.1 (d, *J* = 7.7 Hz), 139.7 (d, *J* = 7.7 Hz), 129.7 (d, *J* = 8.2 Hz), 129.5 (d, *J* = 8.2 Hz), 125.1 (d, *J* = 2.6 Hz), 125.0 (d, *J* = 2.8 Hz), 116.3 (d, *J* = 21.1 Hz), 116.1 (d, *J* = 21.1 Hz), 113.2 (d, *J* = 20.9 Hz), 113.1 (d, *J* = 20.9 Hz), 94.3 (t, *J* = 26.9 Hz), 90.6 (t, *J* = 24.8 Hz), 79.0, 72.9, 45.3, 44.3, 17.1, 16.2, 6.9, 6.8, 6.3, 6.2, 5.9, 5.8, 5.7, 5.6.

HRMS m/z (EI+) calcd for $C_{21}H_{20}F_{16}O_2Si$ [M]: 636.0977, found 636.0969.

4-(4-chlorophenethyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



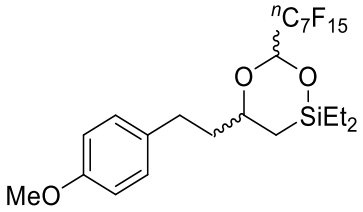
The diastereoisomeric ratio was determined to be 1.3:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 76%.

^{1}H NMR (600 MHz, $CDCl_3$) 7.28 – 7.23 (m, 2H$_{minor+major}$), 7.12 – 7.08 (m, 2H$_{minor+major}$), 5.51 (dd, *J* = 10.5, 7.4 Hz, 1H$_{minor}$), 5.30 (t, *J* = 6.9 Hz, 1H$_{major}$), 4.29 (dt, *J* = 8.7, 4.8 Hz, 1H$_{minor}$), 3.73 (ddt, *J* = 12.3, 9.0, 3.6 Hz, 1H$_{major}$), 2.78– 2.72 (m, 1H$_{minor+major}$), 2.65– 2.58 (m, 1H$_{minor+major}$), 2.01 – 1.94 (m, 1H$_{minor+major}$), 1.82 – 1.75 (m, 1H$_{minor+major}$), 1.12 – 0.87 (m, 8H$_{minor+major}$), 0.78 – 0.64 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 140.2, 131.9, 131.8, 129.9, 129.8, 128.7, 128.6, 94.6 (t, *J* = 25.9 Hz), 90.3 (t, *J* = 24.5 Hz), 77.4, 72.4, 41.3, 40.2, 31.32, 31.1, 17.5, 17.0, 7.1, 7.0, 6.6, 6.3, 6.2, 6.1, 5.9, 5.8.

HRMS m/z (EI+) calcd for $C_{22}H_{22}{}^{35}ClF_{15}O_2Si$ [M]: 666.0838, found 666.0835.

4-(4-metoxyphenethyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



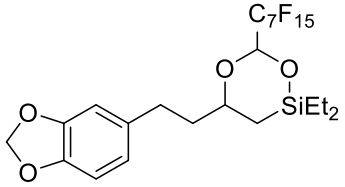
The diastereoisomeric ratio was determined to be 1.3:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 76%.

^{1}H NMR (600 MHz, $CDCl_3$) 7.12 – 7.07 (m, 2H$_{minor+major}$), 6.86 – 6.83 (m, 2H$_{minor+major}$), 5.53 (dd, *J* = 10.2, 7.5 Hz, 1H$_{minor}$), 5.32 (t, *J* = 6.9 Hz, 2H$_{major}$), 4.32 (dt, *J* = 8.7, 4.8 Hz, 1H$_{minor}$), 3.80 – 3.80 (m, 3H$_{minor+major}$), 3.78 – 3.73 (m, 1H$_{major}$), 2.77 – 2.68 (m, 1H$_{minor+major}$), 2.64 – 2.57 (m, 1H$_{minor+major}$), 2.04 – 1.96 (m, 1H$_{minor+major}$), 1.83 – 1.75 (m, 1H$_{minor+major}$), 1.24 – 0.89 (m, 8H$_{minor+major}$), 0.76 – 0.65 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 157.0, 132.8, 132.7, 128.5, 128.4, 113.1, 113.0, 93.6 (dd, *J* = 27.7, 25.7 Hz), 89.2 (t, *J* = 25.4 Hz), 76.5, 71.7, 54.4(2C), 40.7, 39.3, 30.0, 29.7, 16.5, 15.8, 6.1, 6.1, 5.7, 5.3, 5.2, 5.1, 4.9, 4.8.

HRMS m/z (EI+) calcd for $C_{23}H_{25}F_{15}O_3Si$ [M]: 666.1333, found 666.1342.

4-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-2,2-diethyl-6-(perfluorooctyl)-1,5,2-dioxasilinane



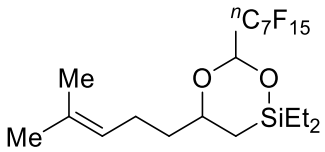
The diastereoisomeric ratio was determined to be 1.5:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 68%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.74 (s, 1H$_{minor}$), 6.72 (s, 1H$_{major}$), 6.70 – 6.64 (m, 1H$_{minor+major}$), 6.63 (dd, *J* = 7.9, 1.8 Hz, 1H$_{minor}$), 6.61 (dd, *J* = 7.8, 1.8 Hz, 1H$_{major}$), 5.93 (s, 2H$_{major}$), 5.92 (s, 2H$_{minor}$), 5.51 (dd, *J* = 10.4, 7.7 Hz, 1H$_{minor}$), 5.30 (t, *J* = 7.0 Hz, 1H$_{major}$), 4.30 (tt, *J* = 9.6, 4.8 Hz, 1H$_{minor}$), 3.77 – 3.71 (m, 1H$_{major}$), 2.73 – 2.65 (m, 1H$_{minor+major}$), 2.60 – 2.53 (m, 1H$_{minor+major}$), 2.00 – 1.93 (m, 1H$_{minor+major}$), 1.80 – 1.73 (m, 1H$_{minor+major}$), 1.13 – 0.88 (m, 8H$_{minor+major}$), 0.77 – 0.63 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 146.7, 144.8 (2C), 134.6, 134.5, 120.3, 120.2, 108.0, 107.9, 107.3(2C), 100.0, 99.9, 93.6 (t, *J* = 25.1 Hz), 89.2 (t, *J* = 23.7 Hz), 75.4, 71.5, 40.7, 39.4, 30.7, 30.4, 16.5, 15.8, 6.1, 6.0, 5.7, 5.4, 5.2, 5.10, 4.9, 4.8.

HRMS m/z (EI+) calcd for $C_{23}H_{23}F_{15}O_4Si$ [M]: 676.1126, found 676.1132.

2,2-diethyl-4-(4-methylpent-3-en-1-yl)-6-(perfluorooctyl)-1,5,2-dioxasilinane



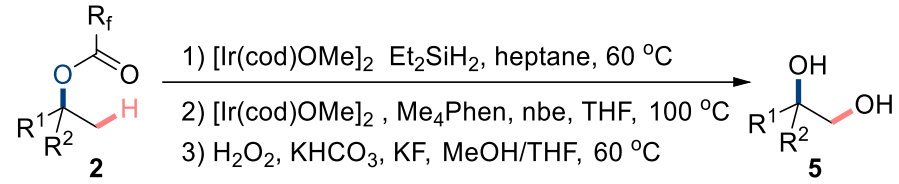
The diastereoisomeric ratio was determined to be 1.7:1 by ^{1}H NMR analysis of the crude reaction mixture. Following the general procedure, the product was obtained as a colorless oil. Yield = 69%.

^{1}H NMR (600 MHz, $CDCl_3$) 5.48 (t, *J* = 8.9 Hz, 1H$_{minor}$), 5.31 (dd, *J* = 8.0, 6.0 Hz, 1H$_{major}$), 5.12 – 5.05 (m, 1H$_{minor+major}$), 4.29 (dq, *J* = 9.6, 5.5 Hz, 1H$_{minor}$), 3.76 (ddt, *J* = 11.9, 7.8, 3.8 Hz, 1H$_{major}$), 2.14 – 1.99 (m, 2H$_{minor+major}$), 1.75 – 1.71 (m, 1H$_{minor+major}$), 1.71 – 1.67 (m, 3H$_{minor+major}$), 1.62 – 1.57 (m, 3H$_{minor+major}$), 1.55 – 1.49 (m, 1H$_{minor+major}$), 1.16 – 0.83 (m, 8H$_{minor+major}$), 0.77 – 0.64 (m, 4H$_{minor+major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 131.4, 131.3, 122.7, 122.6, 93.7 (t, *J* = 27.1 Hz), 89.1 (t, *J* = 25.7 Hz), 77.2, 71.9, 38.8, 37.15, 24.8, 24.8, 23.1, 23.0, 16.7, 16.6, 16.5, 15.7, 6.2, 6.1, 5.8, 5.4, 5.2, 5.1, 4.9, 4.8.

HRMS m/z (EI+) calcd for $C_{20}H_{25}F_{15}O_2Si$ [M]: 610.1384, found 610.1388.

V. Hydrosilylation/C–H silylation/oxidation sequence



if R^1 = H, R_f = $^nC_7F_{15}$

if $R^1 \neq H$, R_f = CF_3

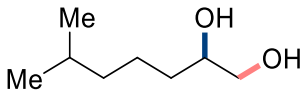
General procedure for Ir-catalyzed hydrosilylation of esters: The reactions were conducted on 0.03-1.0 mmol scales. In an N_2-filled glove box, the perfluorinated ester (1.0 equiv) and $[Ir(cod)OMe]_2$ (2.0 mol %) were weighed into a screw-capped vial equipped with a magnetic stir bar. To the mixture were added heptane (c = 0.5 M) and Et_2SiH_2 (4.0 equiv). The vial was capped with a Teflon-lined screw cap, and the resulting solution was stirred at 60 °C for 48 h. The conversion to the corresponding diethyl(hydrido)silylacetal was observed by ^1H NMR spectroscopy. The volatile materials from the crude reaction mixture containing the diethyl(hydrido)silylacetal were evaporated by a stream of nitrogen at 40-45 °C, placed under high-vacuum for 30 min, and used as such for the next step.

General procedure for Ir-catalyzed intramolecular aliphatic silylation:
In an N_2-filled glove box, to the screw-capped vial with the crude reaction mixture containing the diethyl(hydrido)silylacetal were weighed $[Ir(cod)OMe]_2$ (2.0 mol %) and Me_4phen (6.0 mol %). Then, to the reaction mixture were added THF (0.1 M) and nbe (1.5 equiv). The vial was capped with a Teflon-lined screw cap, and the resulting solution was placed in a pre-heated aluminum block and stirred at 100 °C for 12-16 hours. The volatile materials from crude reaction mixture containing the diethyl(hydrido)silylacetal were evaporated by a stream of nitrogen at 40-45 °C, and the yield of the 6-membered silinane was determined by ^1H NMR spectroscopy using CH_2Br_2 as internal standard. The crude product was filtered through a pad of C2-deactivated silica gel (hexane/acetone 98:3).[2] The solvent was evaporated, and the material was used as such for the oxidation step.

General procedure for Tamao-Fleming oxidation:
On the bench top, to the vial containing the oxasilolane (1.0 equiv) were added $KHCO_3$ (4.0 equiv), KF (4.0 equiv), MeOH (0.1 M), and H_2O_2 (50% solution in H_2O, 10 equiv). The vial was closed with a pressure-relief, open-top cap and placed on a pre-heated aluminum block and stirred at 60 °C for 2 h. The reaction mixture was diluted with AcOEt, washed with aqueous NaOH (3.0 M) and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (SiO_2, hexane/acetone 95:5 to 90:10 to 70:30) to afford the corresponding diol.

[2] Panne, P.; Fox, J. M., *J. Am. Chem. Soc.* **2007,** *129*, 22-23.

6-methylheptane-1,2-diol



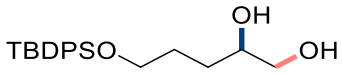
Following the general procedure, the product was obtained as a colorless oil. Yield = 59% (8.6 mg, 0.06 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 – 3.69 (m, 1H), 3.66 (dd, *J* = 11.0, 2.9 Hz, 1H), 3.44 (dd, *J* = 11.0, 7.7 Hz, 1H), 1.99 (s, 2OH), 1.54 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.48 – 1.13 (m, 6H), 0.87 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 71.5, 66.0, 38.1, 32.6, 27.1, 22.5, 21.8, 21.7.

HRMS m/z (EI+) calcd for $C_8H_{17}O_2$ [M-H]: 145.1229 found 145.1233.

5-((tert-butyldiphenylsilyl)oxy)pentane-1,2-diol



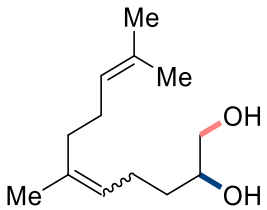
Following the general procedure, the product was obtained as a colorless oil. Yield = 40% (28.6 mg, 0.08 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) 7.67 (dd, *J* = 6.3, 1.9 Hz, 4H), 7.46 – 7.41 (m, 2H), 7.40 – 7.38 (m, 4H), 3.76 – 3.71 (m, 1H), 3.73 – 3.68 (m, 1H), 3.63 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.46 (dd, *J* = 11.0, 7.5 Hz, 1H), 1.73 – 1.64 (m, 2H), 1.66 – 1.58 (m, 1H), 1.56 – 1.49 (m, 1H), 1.06 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 134.6, 132.6(2C), 128.8 (2C), 126.8(2C), 71.1, 66.0, 63.3, 29.5, 27.8, 26.0, 18.3.

HRMS m/z (ESI+) calcd for $C_{21}H_{31}O_3Si$ $[M+H]^+$: 359.2037 found 359.2034.

6,10-dimethylundeca-5,9-diene-1,2-diol (ratio Z:E= 1:1)



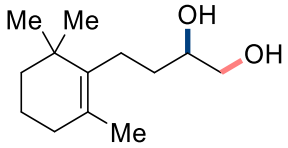
Following the general procedure, the product was obtained as a colorless oil. Yield = 48% (20.2 mg, 0.095 mmol).

^{1}H NMR (600 MHz, chloroform-*d*) 5.15 – 5.07 (m, $2H_Z$+$2H_E$), 3.75 – 3.71 (m, $1H_Z$+$1H_E$), 3.68 – 3.62 (m, $1H_Z$+$1H_E$), 3.47 – 3.43 (m, $1H_Z$+$1H_E$), 2.15 – 1.98 (m, $6H_Z$+$6H_E$), 1.73 – 1.59 (m, $9H_Z$+$9H_E$), 1.53 – 1.44 (m, $2H_Z$+$2H_E$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 135.3, 130.9, 130.7, 123.6, 123.4, 123.3, 122.74, 71.2, 71.1, 66.0($2C_{Z+E}$), 38.9, 32.5, 32.3, 31.1, 25.8, 25.7, 24.9, 24.9, 23.2, 23.1, 22.5, 16.9, 16.8, 15.2.

HRMS m/z (ESI-) calcd for $C_{13}H_{23}O_2$ $[M-H]^-$: 211.1704, found 211.1703.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)butane-1,2-diol



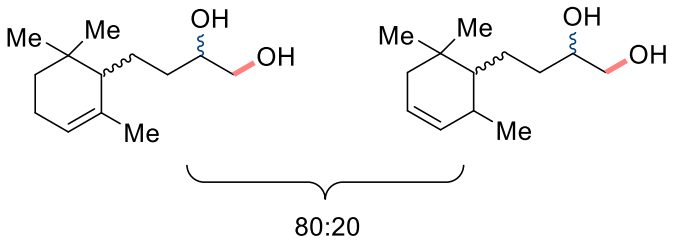
Following the general procedure, the product was obtained as a colorless oil. Yield = 54% (22.4 mg, 0.11 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) 3.75 – 3.67 (m, 1H), 3.67 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.46 (dd, *J* = 11.1, 7.7 Hz, 1H), 2.32 (s, 2OH), 2.23 – 2.14 (m, 1H), 2.01 – 1.91 (m, 1H), 1.89 (t, *J* = 6.4 Hz, 2H), 1.59 (s, 3H), 1.58 – 1.48 (m, 4H), 1.42 – 1.39 (m, 2H), 0.98 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.8, 126.5, 72.2,65.9, 38.9, 34.1, 33.0, 31.9, 27.7, 23.7, 18.9, 18.6.

HRMS m/z (ESI-) calcd for $C_{13}H_{23}O_2$ $[M-H]^-$: 211.1704, found 211.1703.

4-(2,6,6-trimethylcyclohex-2-en-1-yl)butane-1,2-diol



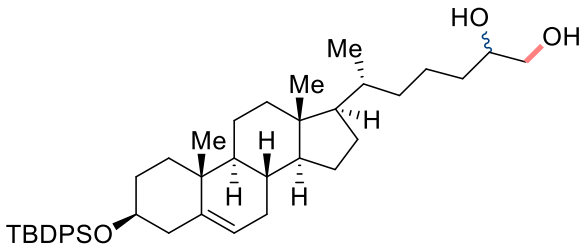
The starting alcohol was purchased as mixture of isomers. Following the general procedure, the diol was obtained as a colorless oil. Yield = 47% (19.8 mg, 0.093 mmol). The ^{1}H NMR and ^{13}C NMR analysis for the major regioisomer (two diasterioisomer 1:1 ratio) are:

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.30 (s, 1H), 3.67 – 3.61 (m, 2H), 3.43 (dd, *J* = 11.7, 8.3 Hz, 1H), 2.40 (brs, 2OH), 1.95 – 1.93 (m, 2H), 1.69 – 1.65 (m, 3H), 093 – 0.92 (m, 6H), 0.86 – 0.86 (m, 3H), 0.86 – 0.86 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3, 135.2, 119.6, 119.5, 72.2, 72.0, 65.9, 65.8, 48.4, 48.3, 32.8, 32.7, 31.7, 31.6, 30.8, 30.6, 26.78, 26.7(2C), 26.6, 25.9, 25.8, 22.7, 22.6, 22.1 (2C).

HRMS m/z (ESI-) calcd for $C_{13}H_{23}O_2$ $[M-H]^-$: 211.1704, found 211.1703.

(6R)-6-((3S,8S,9S,10R,13R,14S,17R)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)heptane-1,2-diol



Following the general procedure, the product was obtained as mixture of two diasterioisomer 1:1 ratio. Tamao-Fleming oxidation was condcuted in the mixture of MeOH/THF (5/1, 0.1M). Yield = 41% (7.9 mg, 0.012 mmol).

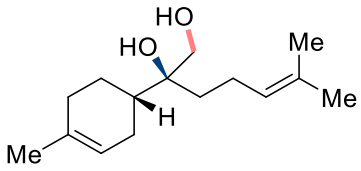
^{1}H NMR (600 MHz, $CDCl_3$) 5.38 – 5.33 (m, 1H), 3.75 – 3.68 (m, 1H), 3.70 – 3.63 (m, 1H), 3.56 – 3.49 (m, 1H), 3.44 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.32 – 2.19 (m, 2H), 2.03 – 1.94 (m, 2H), 1.85 – 1.79 (m, 3H), 1.60 – 1.04 (m, 11H), 1.01 (s, 3H), 0.99 – 0.82 (m, 9H) 0.93 (d, *J* = 6.9 Hz, 3H), 0.68 (s, 3H).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.65 (m, 4H), 7.43 – 7.38 (m, 2H), 7.37 – 7.34 (m, *J* 4H), 5.14 – 5.10 (m, 1H), 3.73 – 3.68 (m, 1H), 3.68 – 3.63 (m, 1H), 3.57 – 3.49 (m, 1H), 3.43 (dd, *J* = 11.0, 7.6 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.16 – 2.10 (m, 1H), 1.99 – 1.94 (m, 2H), 1.91 – 1.15 (m, 18H), 1.05 (s, 3H), 1.12 – 0.78 (m, 5H), 1.05 (s, 9H), 0.98 (s, 3H), 0.90 (d, *J* = 6.6 Hz, 1H), 0.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5 (2C), 135.0, 134.9, 134.1, 134.0, 128.6, 128.5, 126.6, 126.5, 120.3(2C), 72.4(2C), 71.6, 71.5, 66.1, 66.0, 55.9(2C), 55.2, 55.1, 49.2(2C), 41.7(2C), 41.5(2C), 38.9(2C), 36.4(2C), 35.7(2C), 35.1, 35.0, 34.9, 34.8, 32.9, 32.8, 31.1(2C), 31.0(2C), 27.4(2C), 26.2(2C), 23.4(2C), 21.2, 21.1, 20.2(2C), 18.6(2C), 18.3(2C), 17.8(2C), 11.0(2C).

HRMS m/z (EI+) calcd for C38H53O3Si [M-^{t}Bu]: 585.3764, found 585.3761.

(S)-6-methyl-2-((S)-4-methylcyclohex-3-en-1-yl)hept-5-ene-1,2-diol



Following the general procedure, the product was obtained as colorless oil. Tamao-Fleming oxidation was condcuted in the mixture of MeOH/THF (5/1, 0.1M). Yield = 26% (12.0 mg, 0.05 mmol).

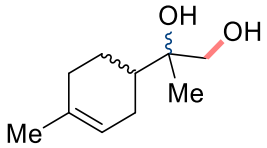
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.40 – 5.35 (m, 1H), 5.12 (t, *J* = 7.0 Hz, 1H), 3.63 (d, *J* = 11.1 Hz, 1H), 3.50 (d, *J* = 11.1 Hz, 1H), 2.06 – 1.73 (m, 10H), 1.68 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.57 (q, *J* = 7.7 Hz, 1H), 1.27 – 1.73 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.3, 131.3, 123.5, 119.6, 74.9, 64.9, 38.4, 33.5, 30.2, 25.3, 24.9, 22.6, 22.6, 21.1, 16.9.

HRMS m/z (ESI-) calcd for $C_{26}H_{43}O_3$ $[M-H]^-$: 403.3216, found 403.3218.

$[\alpha]_D^{25} = -21.7^o$ (c 2.9, CH_2Cl_2).

2-(4-methylcyclohex-3-en-1-yl)propane-1,2-diol



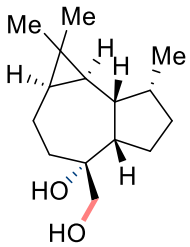
Following the general procedure, the product was obtained as mixture of two diasterioisomer 1:1.3 ratio. Tamao-Fleming oxidation was condcuted in the mixture of MeOH/THF (5/1, 0.1M). Yield = 36% (61.9 mg, 0.36 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) 5.39 (dd, *J* = 3.6, 1.7 Hz, $1H_{minor}$), 5.34 (dd, *J* = 4.0, 2.3 Hz, $1H_{major}$), 3.59 (d, *J* = 11.0 Hz, $1H_{minor}$), 3.54 (d, *J* = 11.0 Hz, $1H_{major}$), 3.44 (d, *J* = 11.0 Hz, $1H_{minor}$), 3.40 (d, *J* = 11.0 Hz, $1H_{major}$), 2.38 (s, $2OH_{minor+major}$), 2.12 – 1.65 (m, $4H_{minor+major}$), 1.63 (s, $3H_{minor+major}$), 1.37 – 1.17 (m, $3H_{minor+major}$), 1.11 (s, $3H_{minor}$), 1.07 (s, $3H_{major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.4, 133.0, 119.6, 119.2, 74.0, 73.9, 67.7, 67.4, 39.9, 39.7, 30.0, 29.9, 26.0, 24.9, 23.4, 22.5, 22.4, 22.2, 19.6, 18.5.

HRMS m/z (EI+) calcd for $C_{10}H_{16}O$ [M-OH]: 152.1201, found 152.1200.

(1aR,4R,4aS,7R,7aS,7bS)-4-(hydroxymethyl)-1,1,7-trimethyldecahydro-1H-cyclopropa[e]azulen-4-ol



Following the general procedure, the product was obtained as a colorless oil. Tamao-Fleming oxidation was condcuted in the mixture of MeOH/THF (5/1, 0.1M). Yield = 21% (0.021 mmol, 5.0 mg).

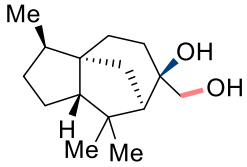
^{1}H NMR (600 MHz, $CDCl_3$*d*) 3.45 (d, *J* = 10.9 Hz, 1H), 3.35 (d, *J* = 10.9 Hz, 1H), 2.11 – 1.62 (m, 9H), 1.35 – 1.28 (m, 1H), 1.23 – 1.14 (m, 1H), 1.04 (s, 3H), 0.97 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.70 (ddd, *J* = 10.5, 9.1, 6.6 Hz, 1H), 0.34 (dd, *J* = 10.5, 9.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 75.4, 69.2, 49.2, 39.9, 37.4, 32.8, 29.5, 27.8, 24.2, 23.0, 22.6, 18.4, 18.3, 15.1, 14.7.

HRMS m/z (ESI-) calcd for $C_{15}H_{25}O_2$ $[M-H]^-$: 237.1860, found 237.1861.

$[\alpha]_D^{25}$ = –11.5^{o} (c 2.0, CH_2Cl_2).

(3R,3aS,6R,7R,8aS)-6-(hydroxymethyl)-3,8,8-trimethyloctahydro-1H-3a,7-methanoazulen-6-ol



Following the general procedure, the product was obtained as a colorless oil. Tamao-Fleming oxidation was condcuted in the mixture of MeOH/THF (5/1, 0.1 M). Yield = 25% (0.025 mmol, 6.0 mg). Yield=23% (0.23 mmol, 54.8 mg).

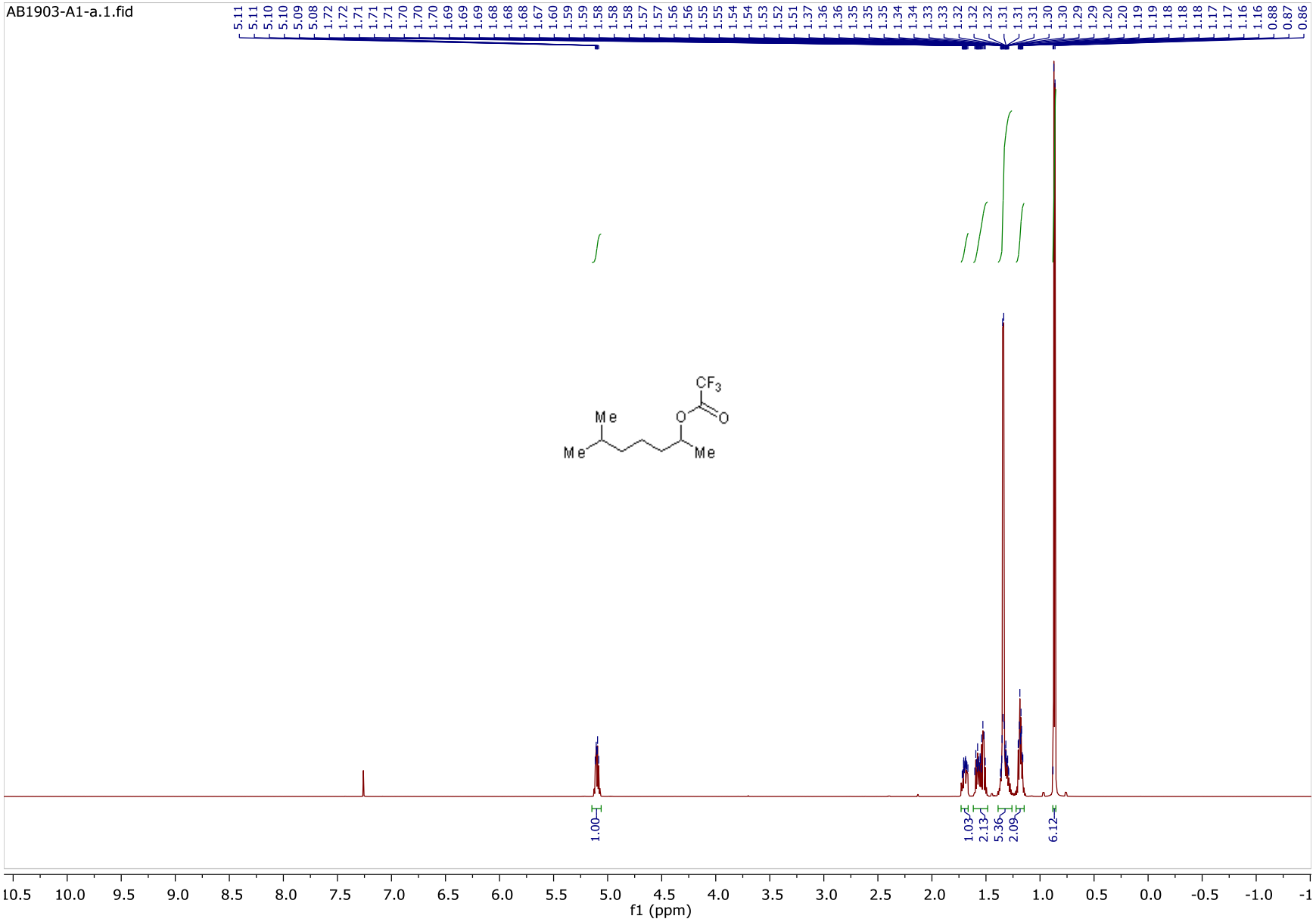
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.56 (d, *J* = 10.1 Hz, 1H), 3.49 (d, *J* = 10.1 Hz, 1H), 2.09 (brs, 1OH), 1.99 (brs, 1OH), 1.91 – 1.82 (m, 2H), 1.75 – 1.50 (m, 6H), 1.47 – 1.37 (m, 2H), 1.36 – 1.24 (m, 3H), 1.33 (s, 3H), 1.01 (s, 3H), 0.83 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 75.4, 67.6, 56.1, 55.5, 53.1, 42.7, 40.6, 39.7, 36.2, 30.4, 29.2, 27.9, 26.8, 24.5, 14.7.

HRMS m/z (ESI-) calcd for $C_{15}H_{25}O_2$ $[M-H]^-$: 237.1860, found 237.1861.

$[\alpha]_D^{25}$ = +15.5^{o} (c 2.0, CH_2Cl_2).

VI. Copies of 1H and 13C NMR spectra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Me
Me
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2.09
6.12
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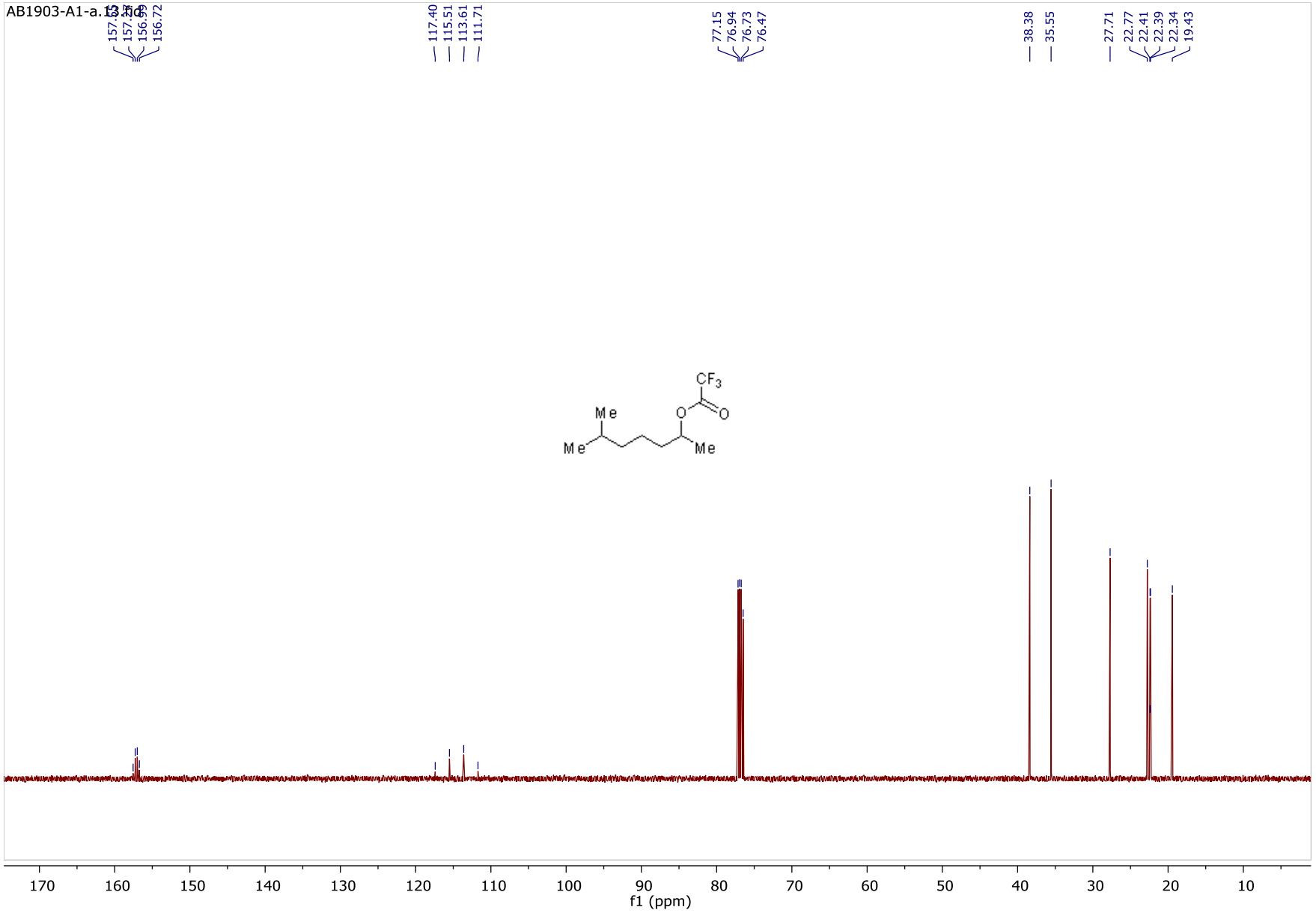
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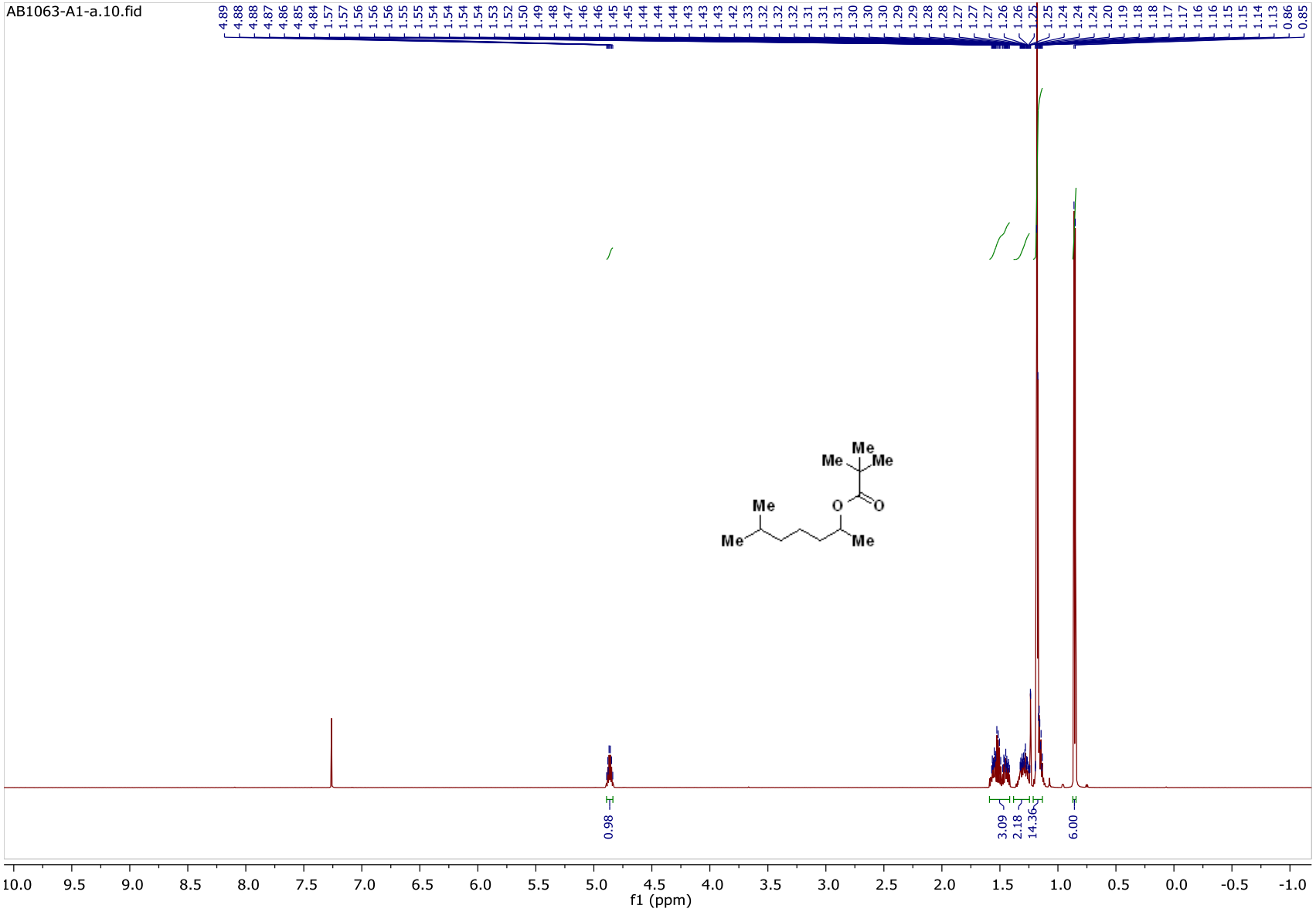
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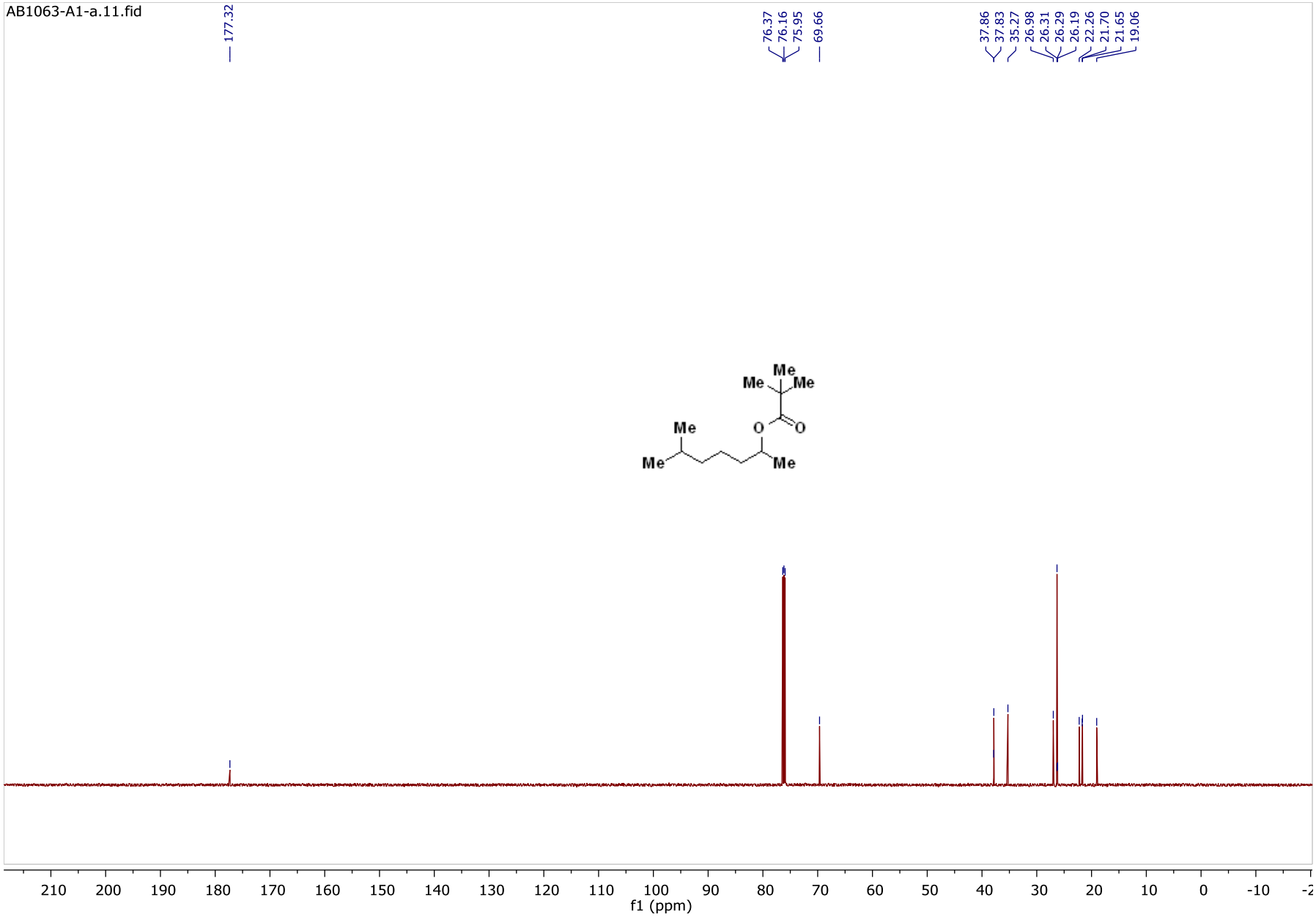
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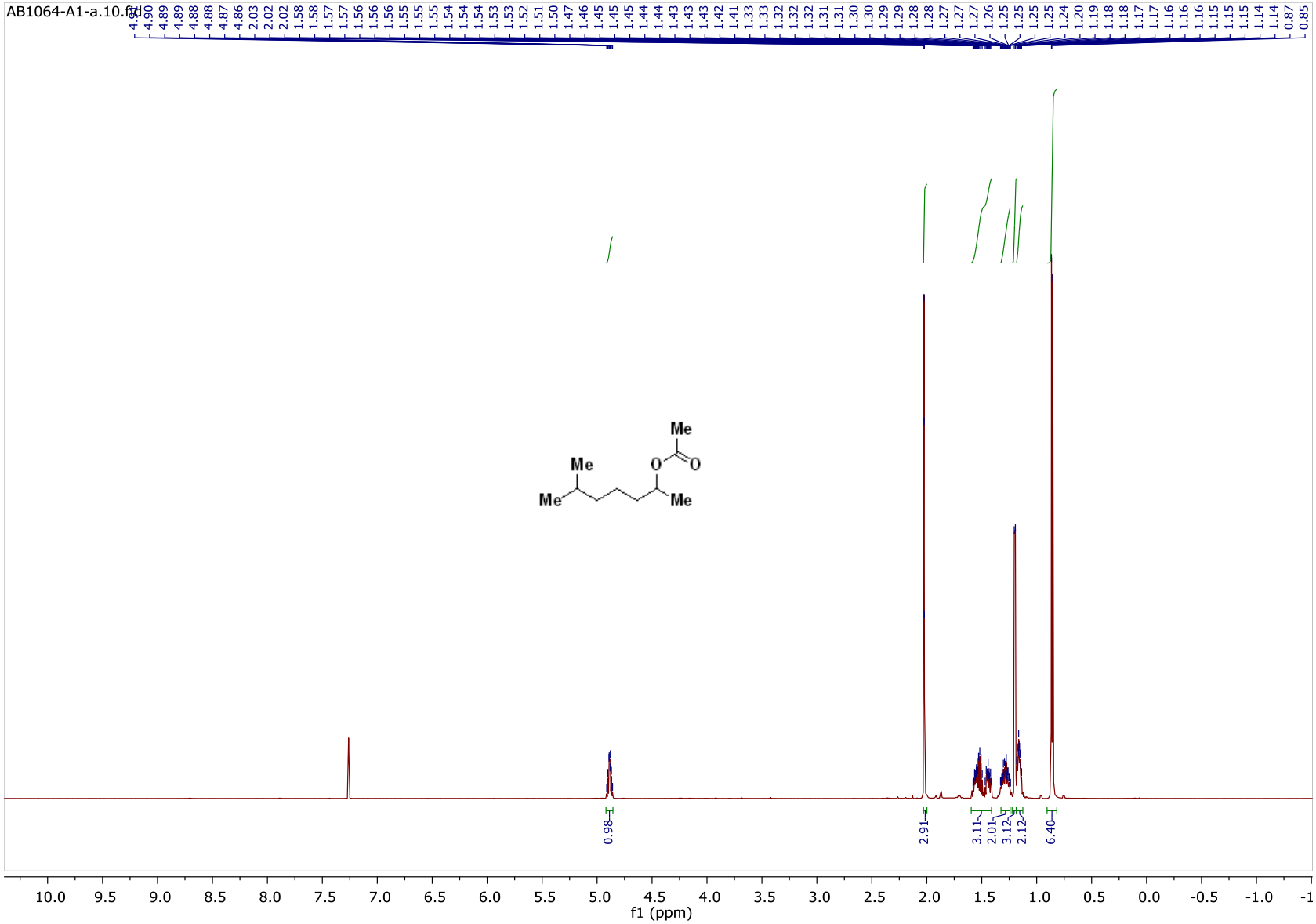
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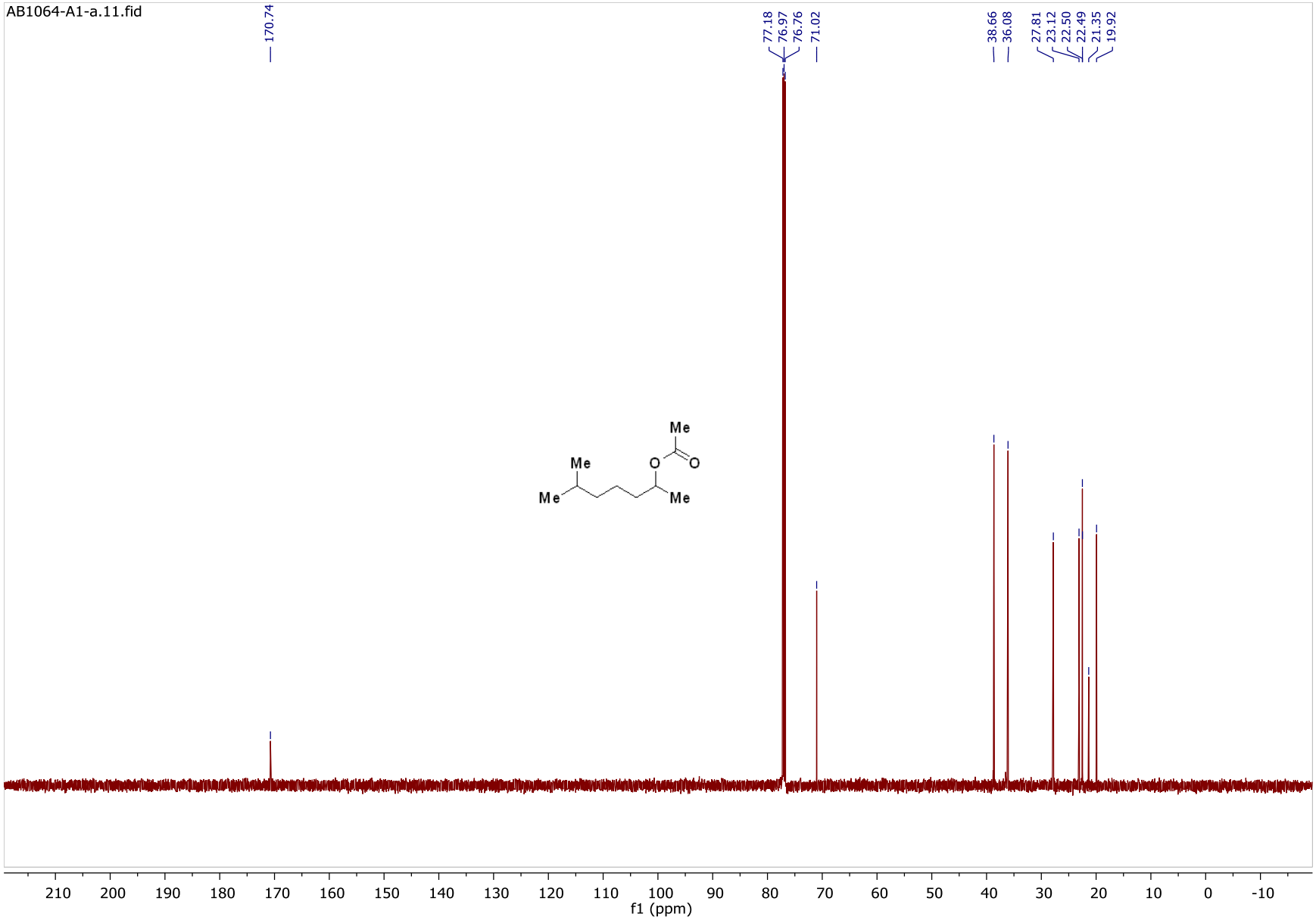
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Me
Me
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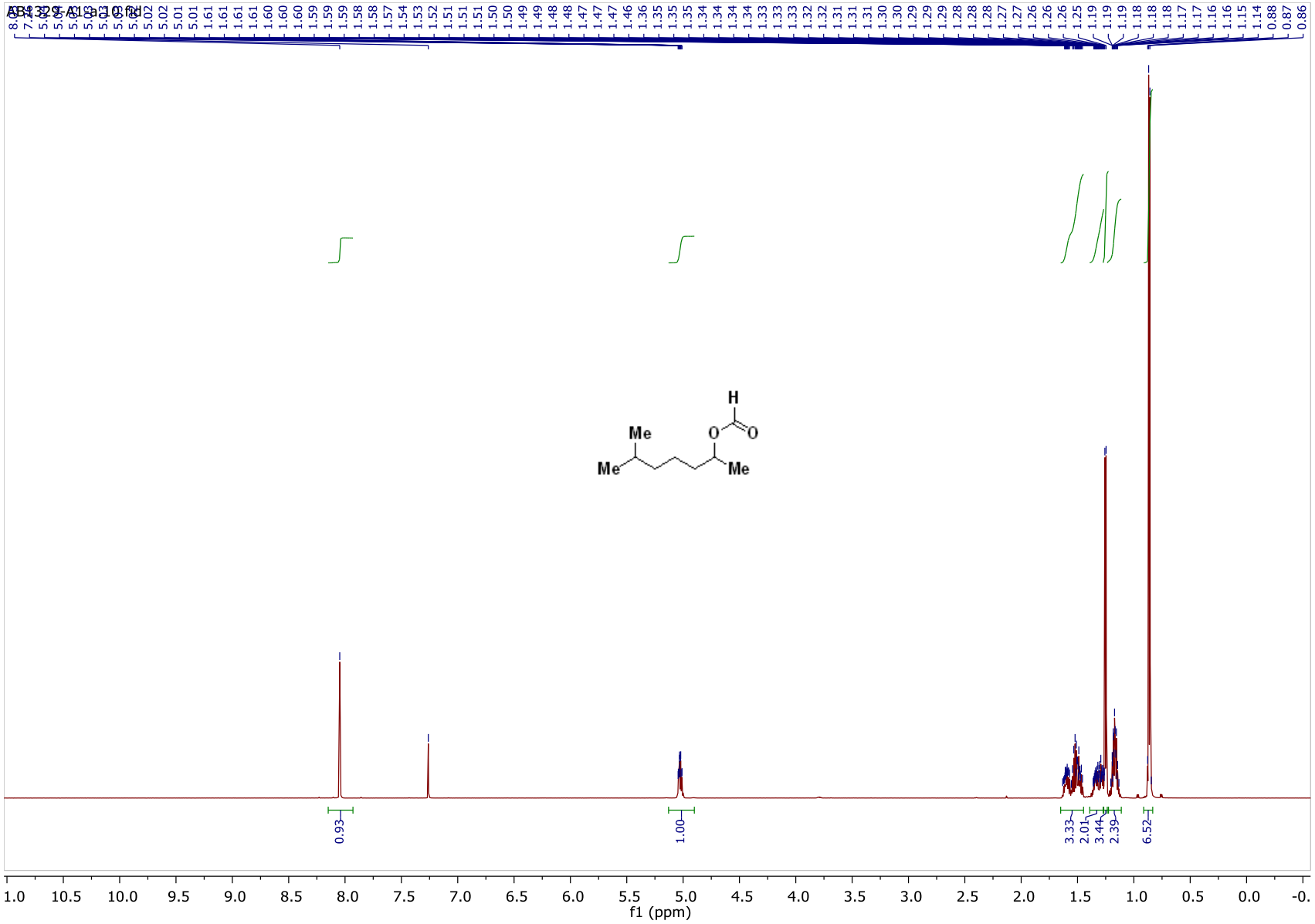
f1 (ppm)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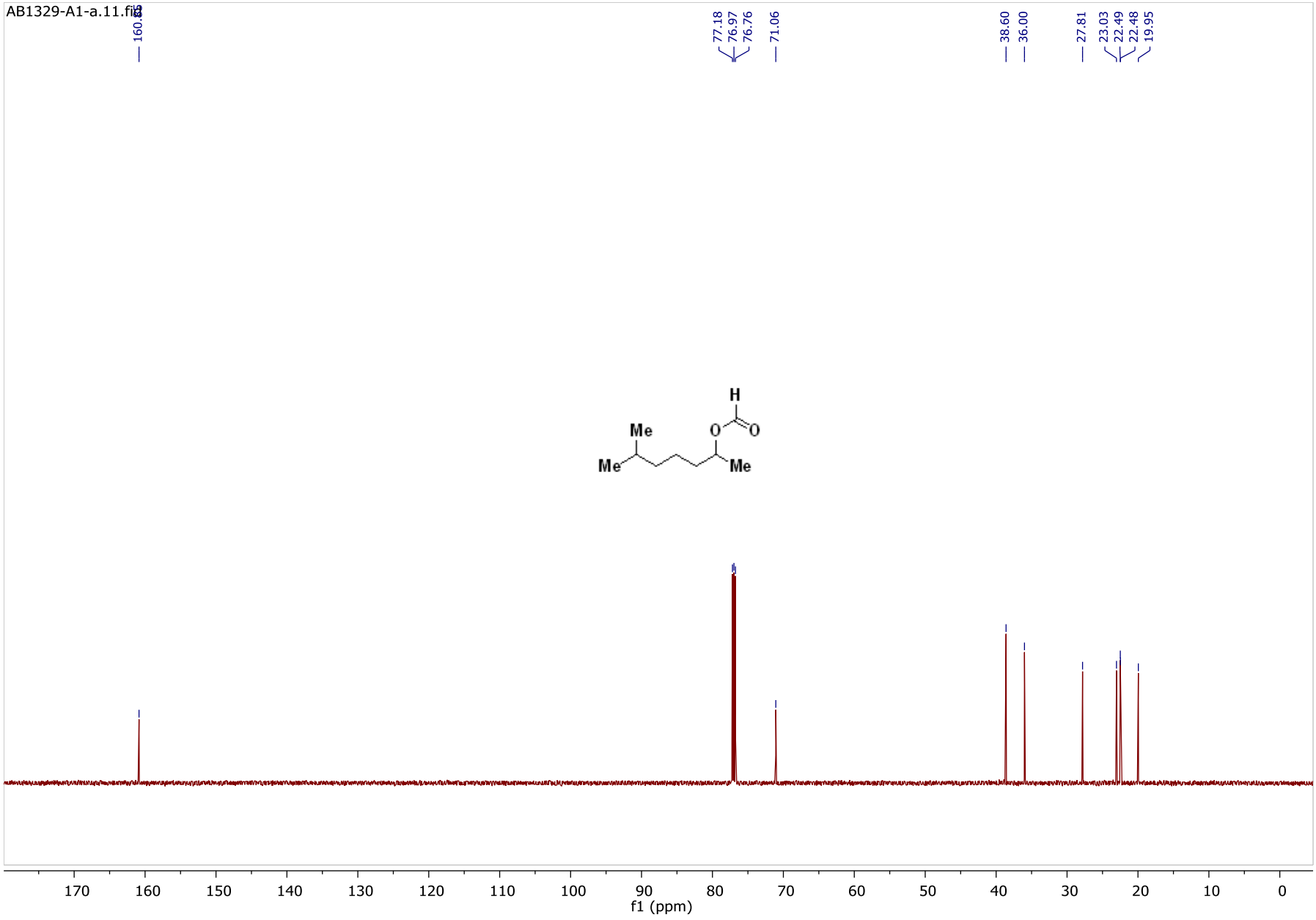
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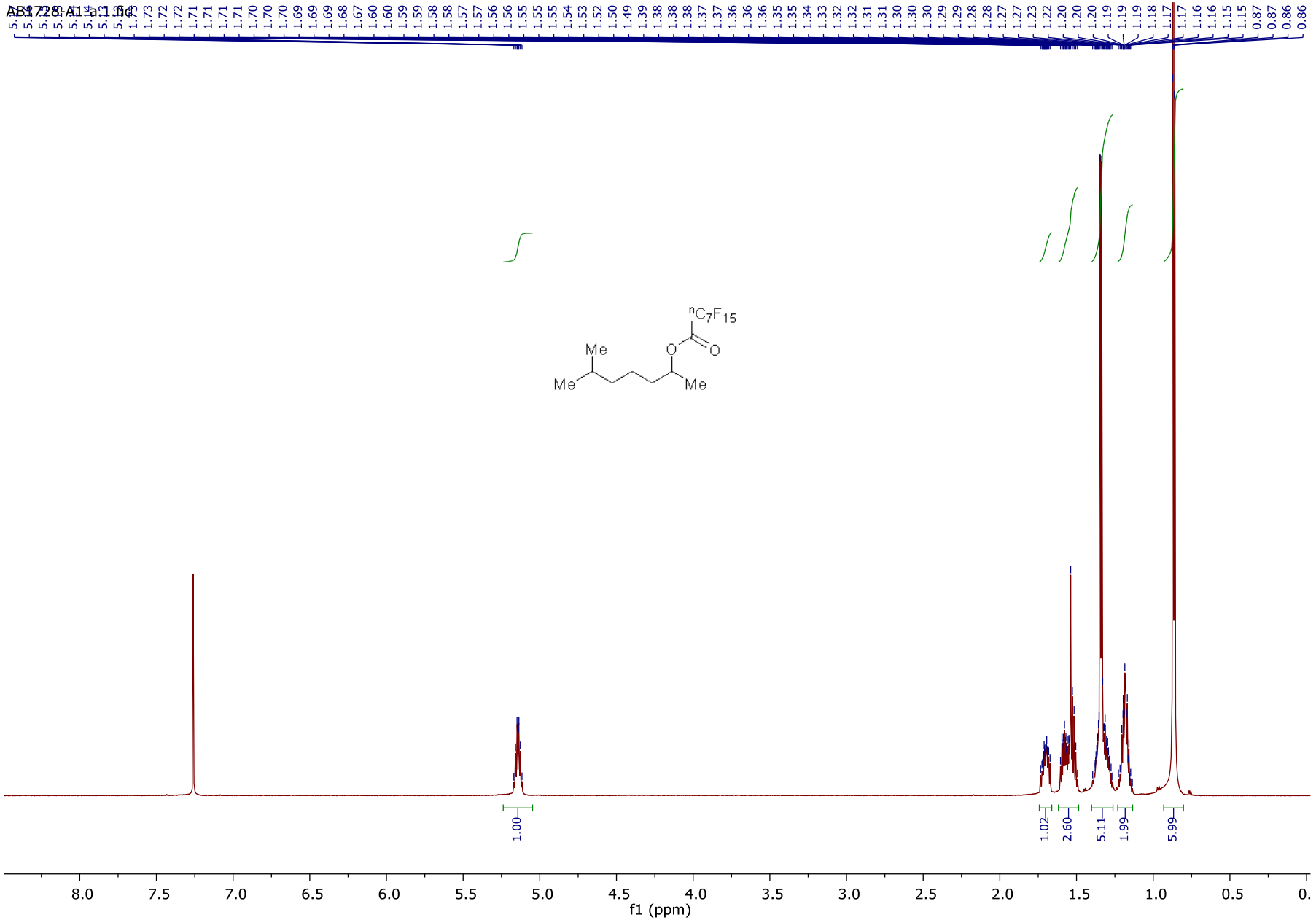
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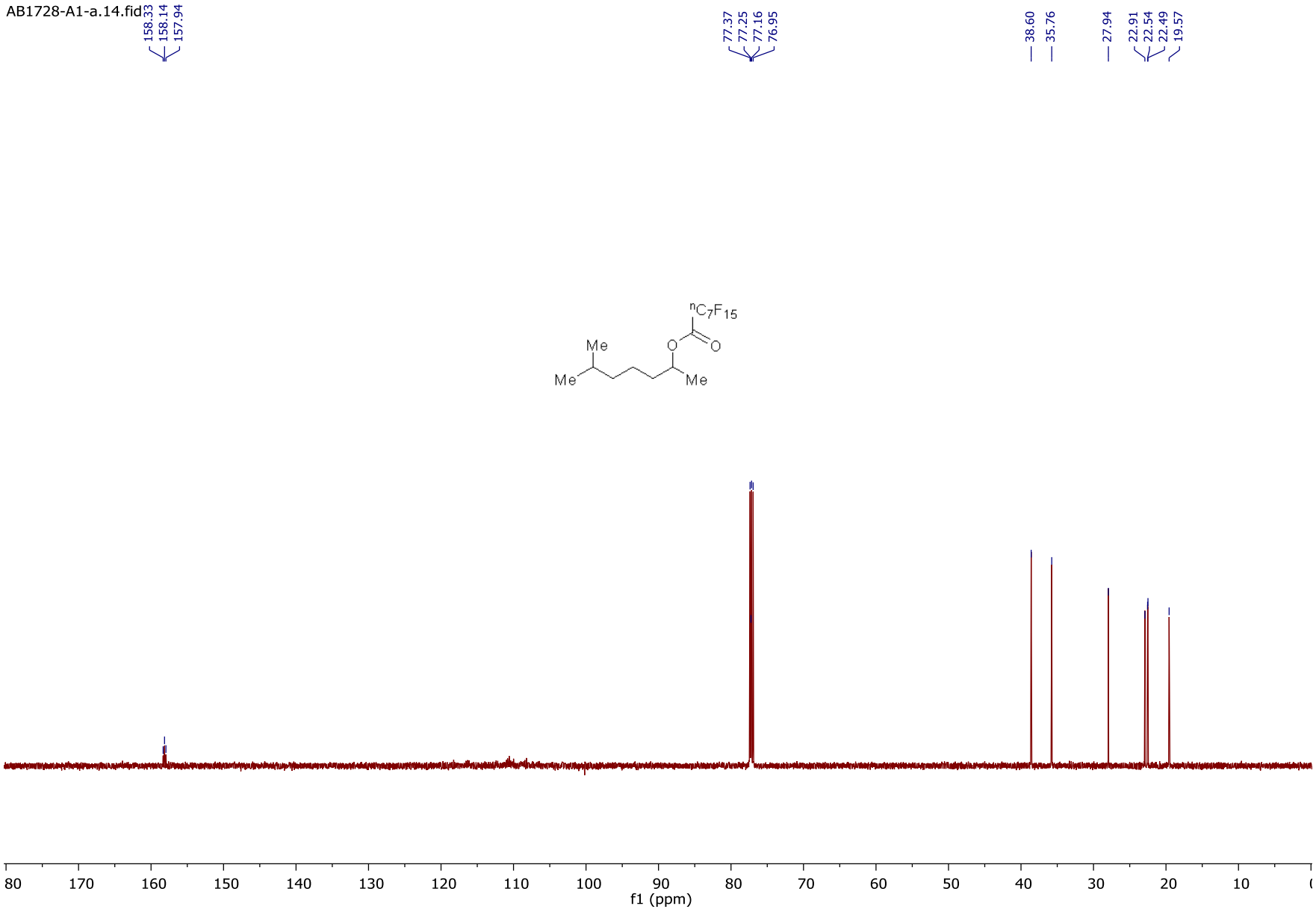
f1 (ppm)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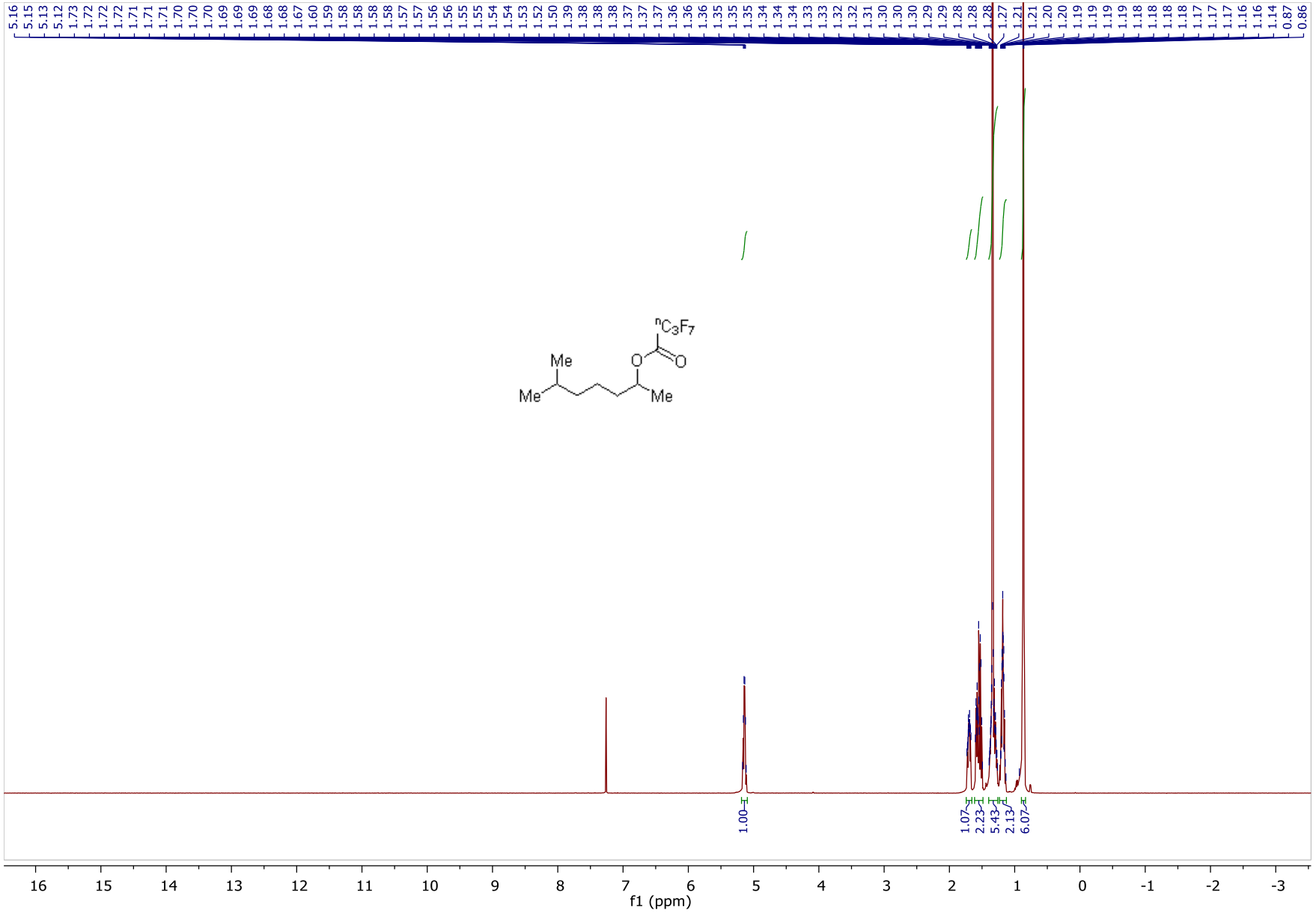
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O
O
Me
Me
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6.07
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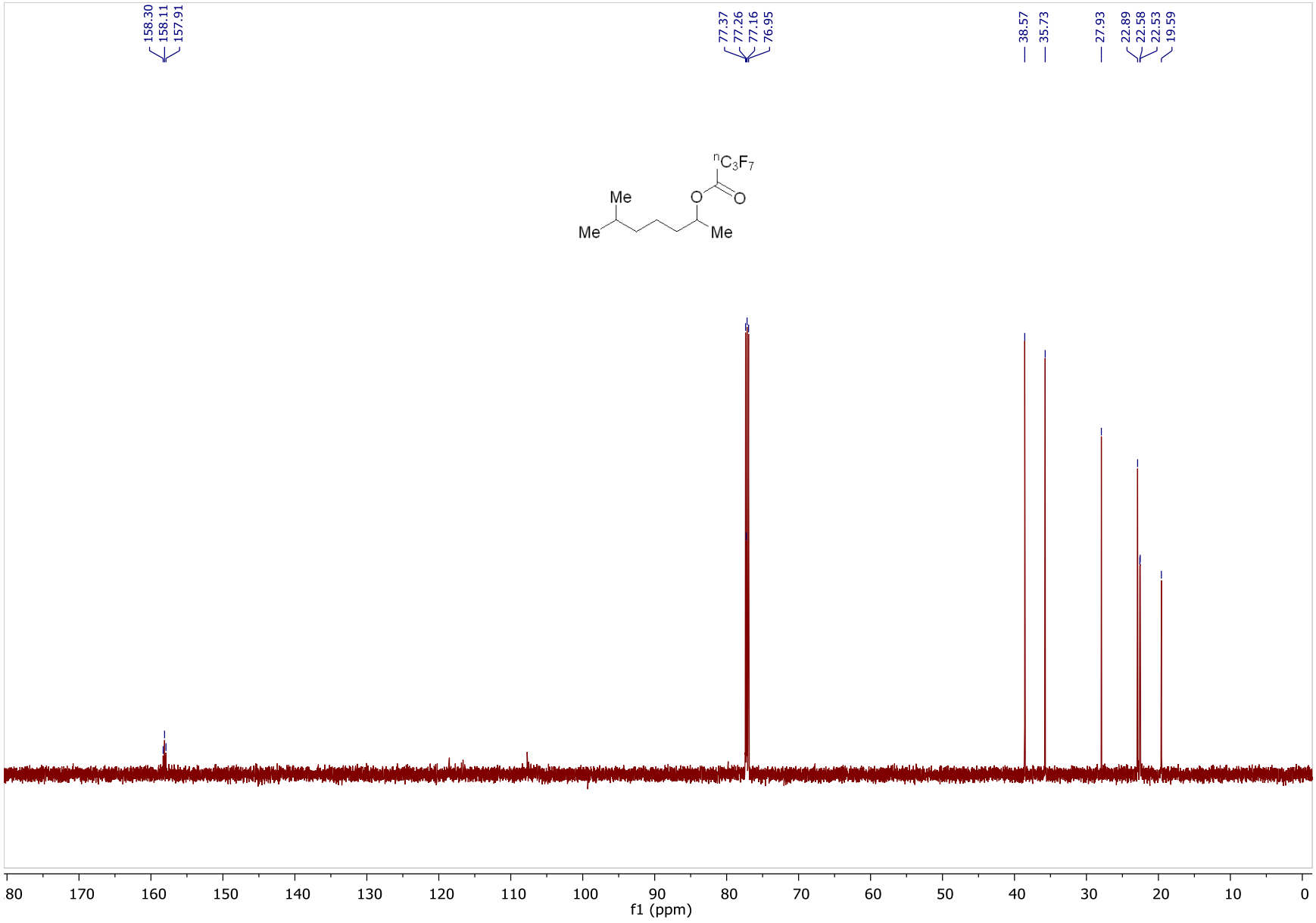
f1 (ppm)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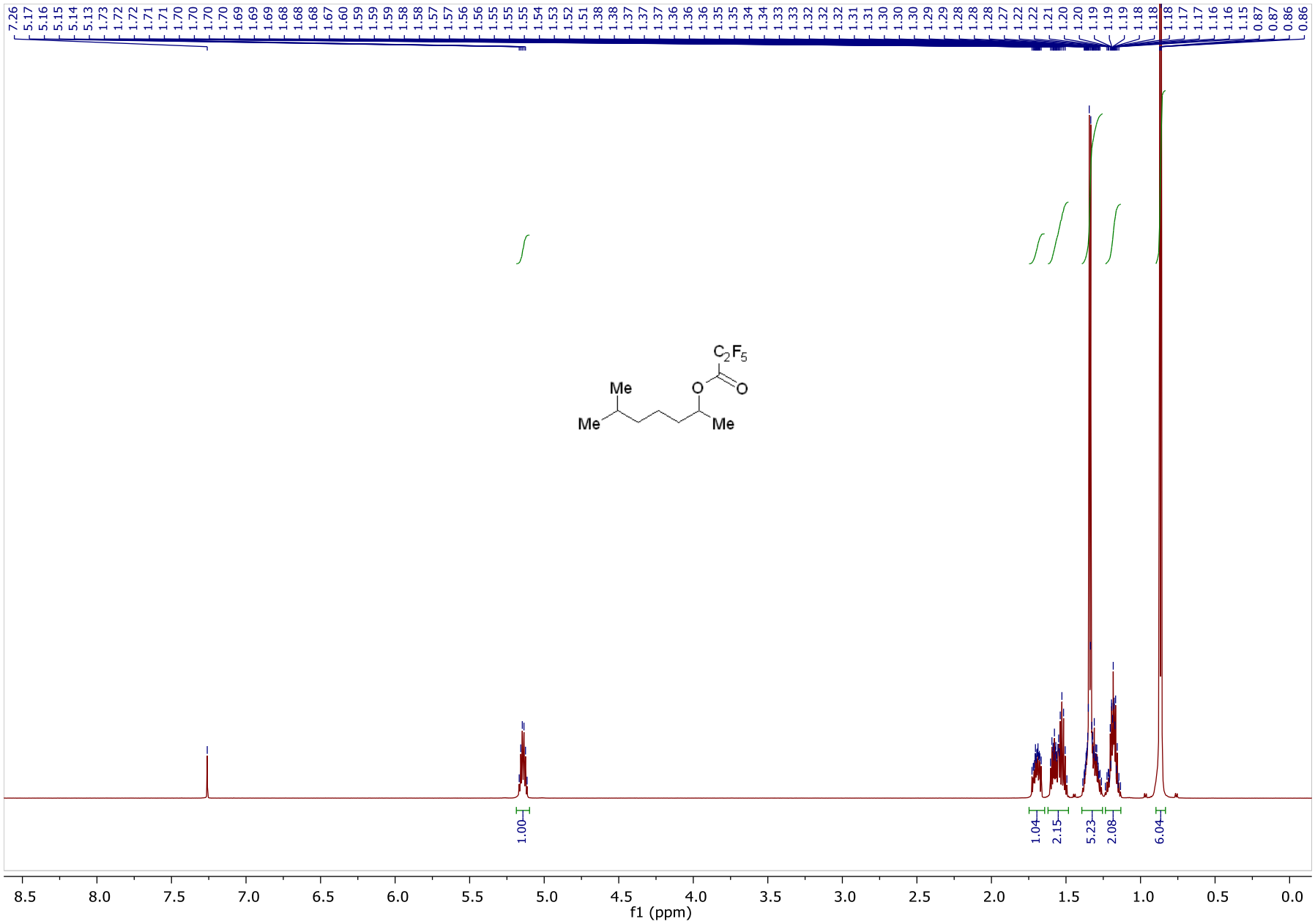
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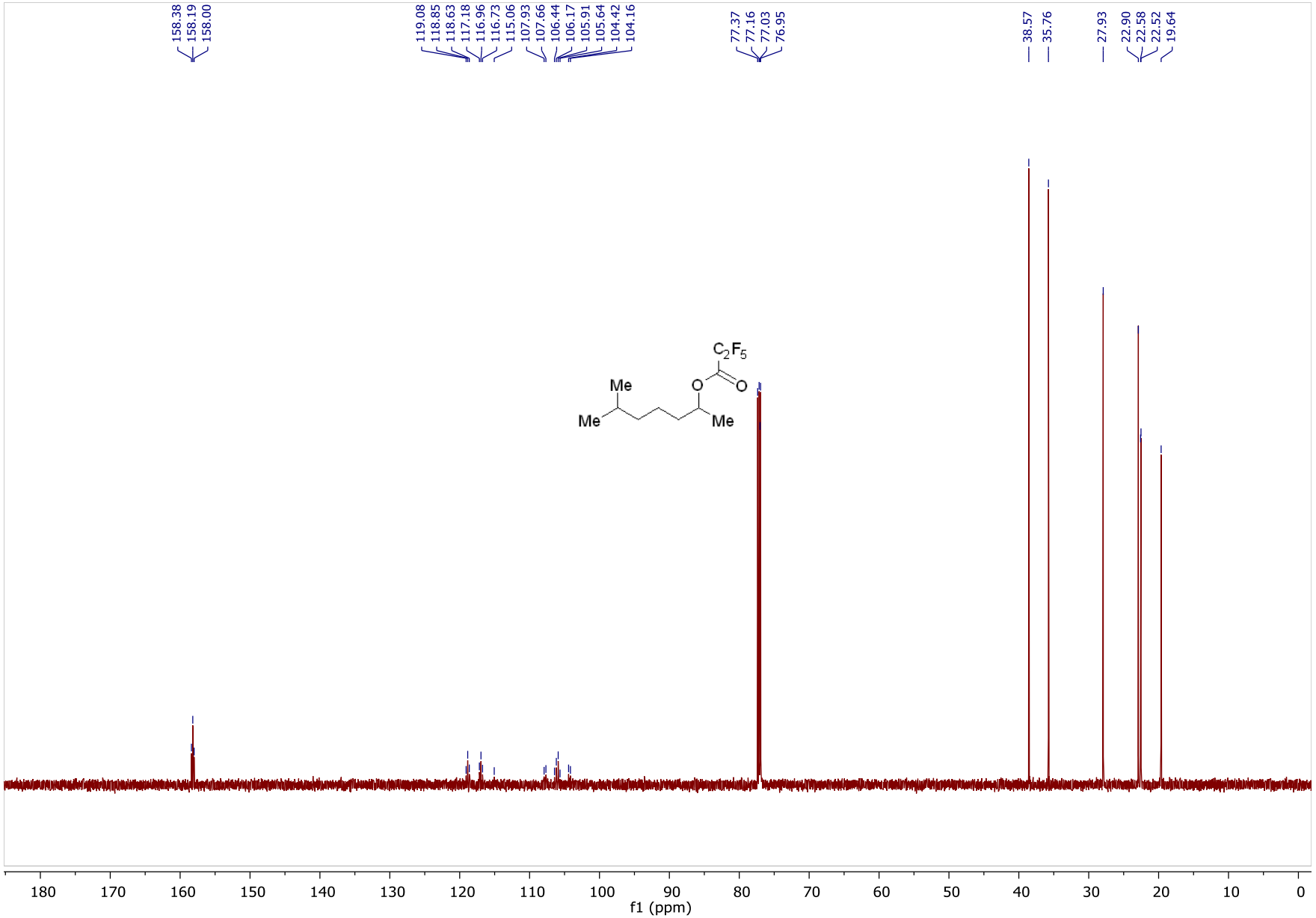
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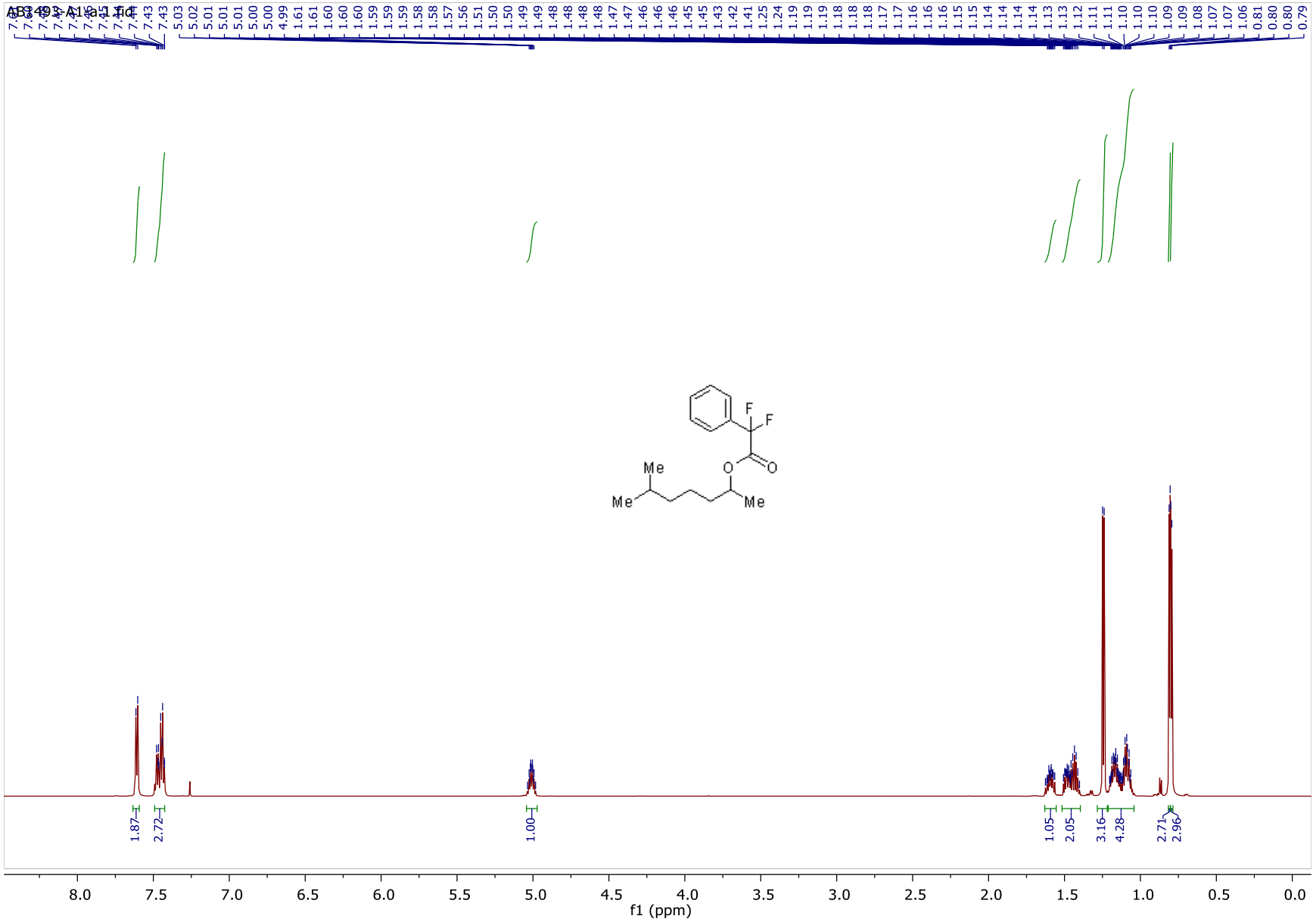
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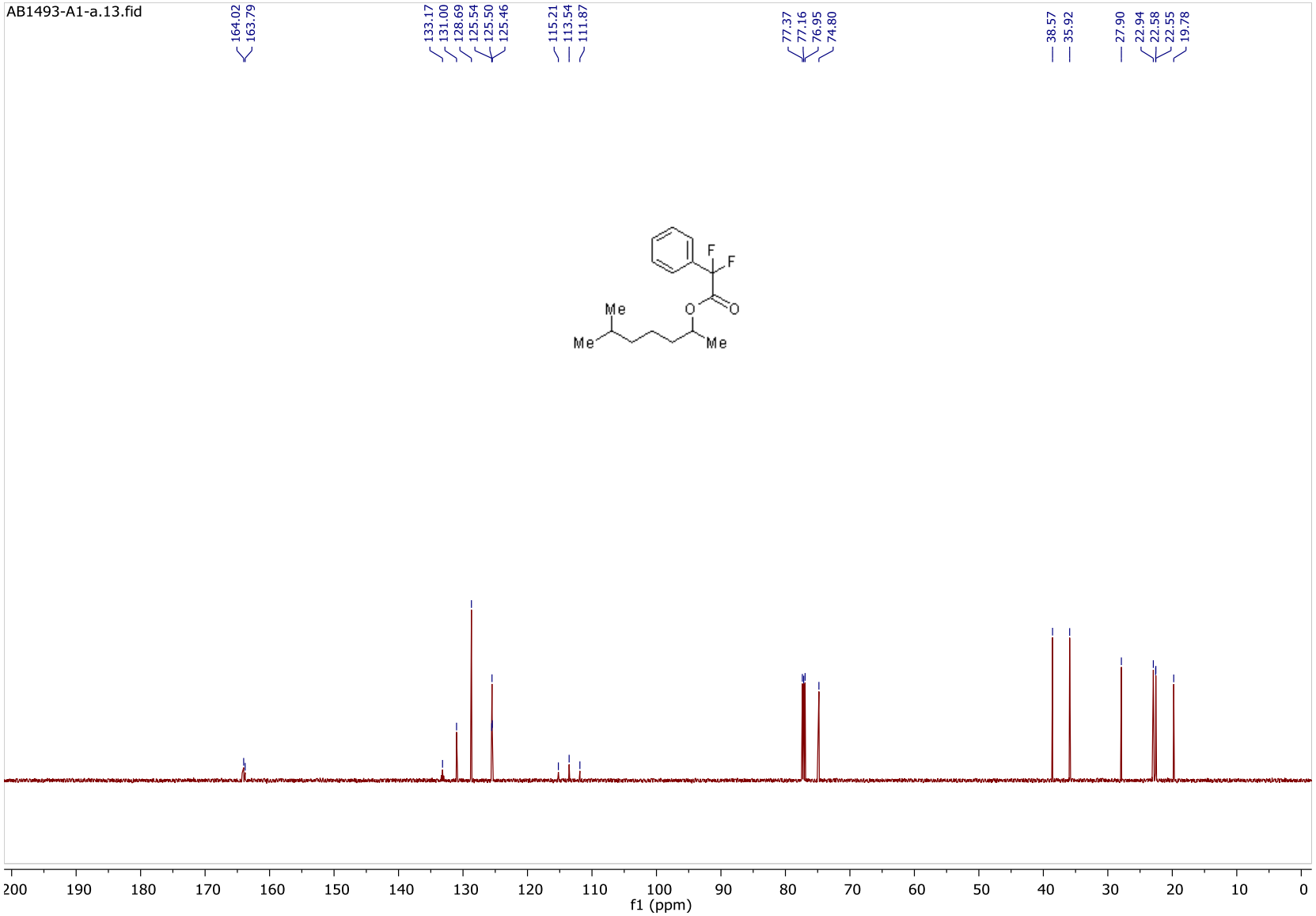
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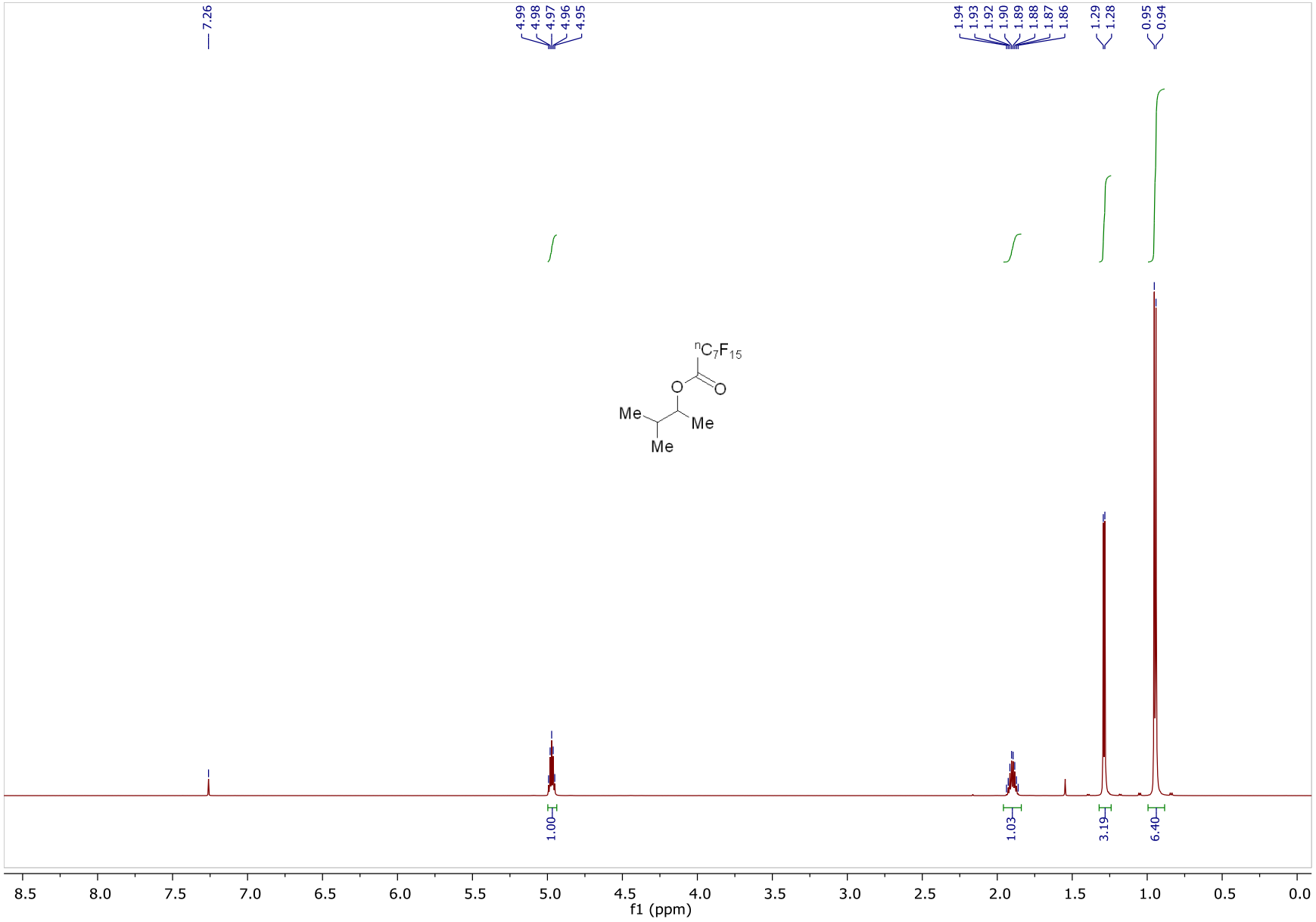
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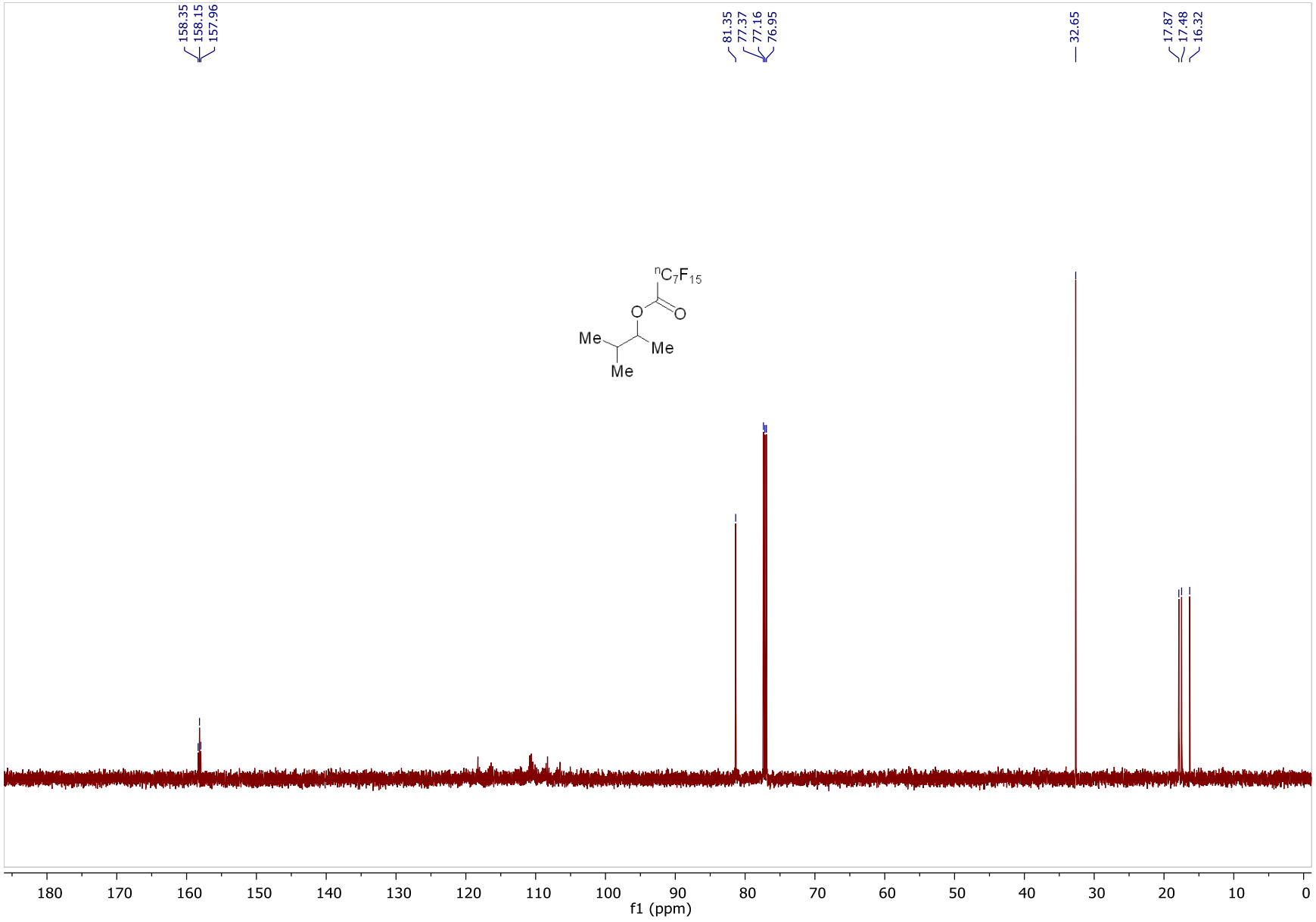
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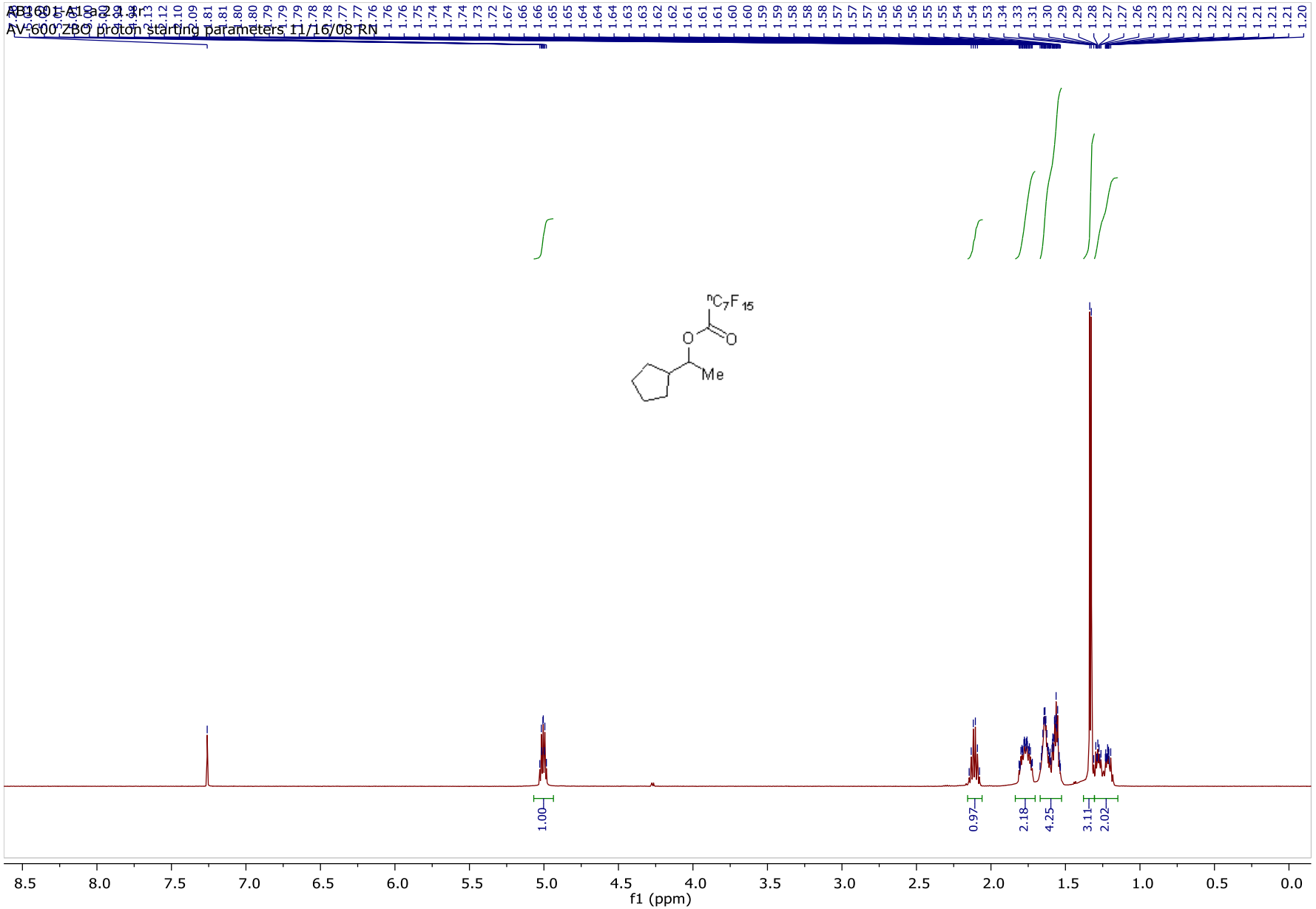
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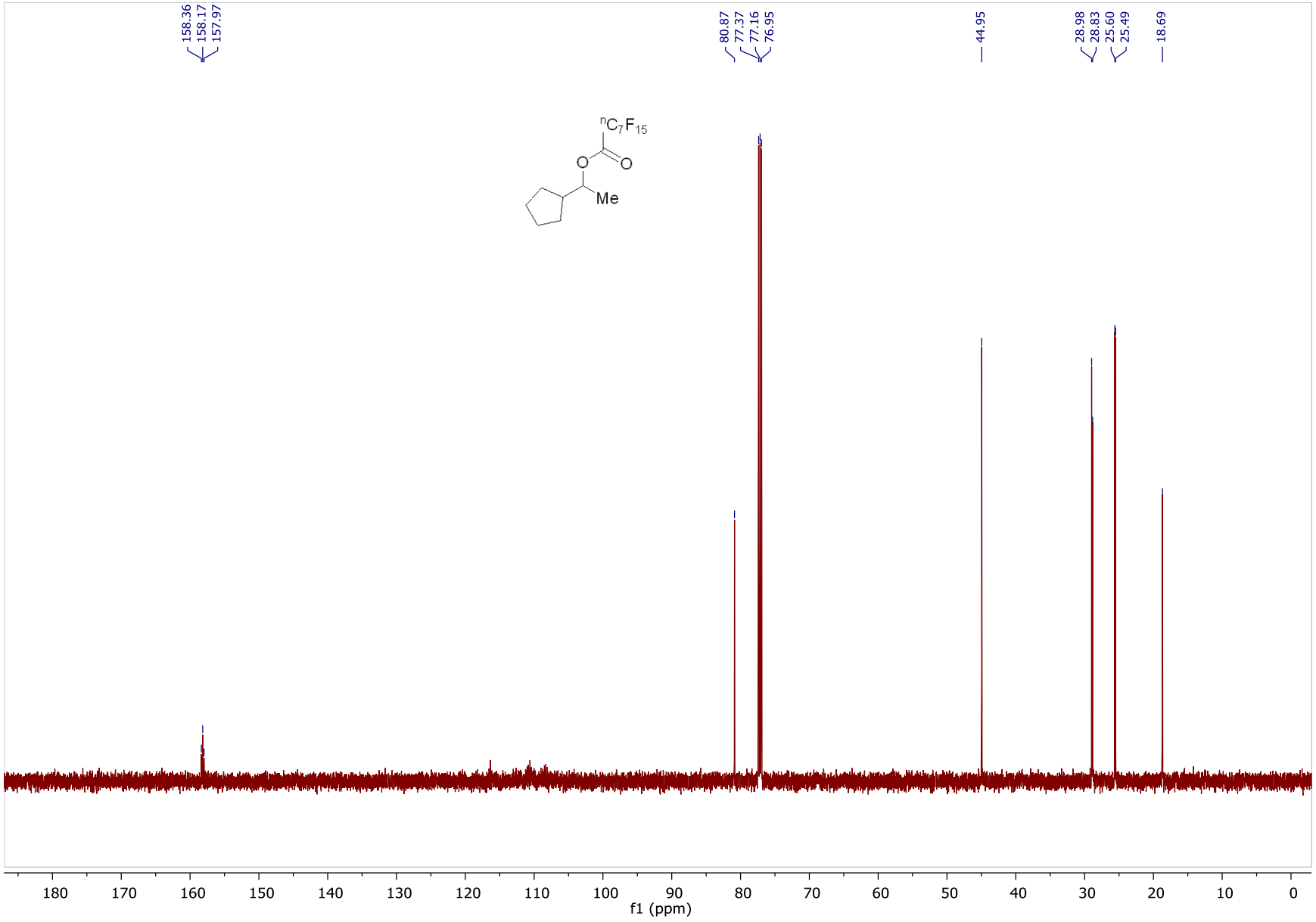
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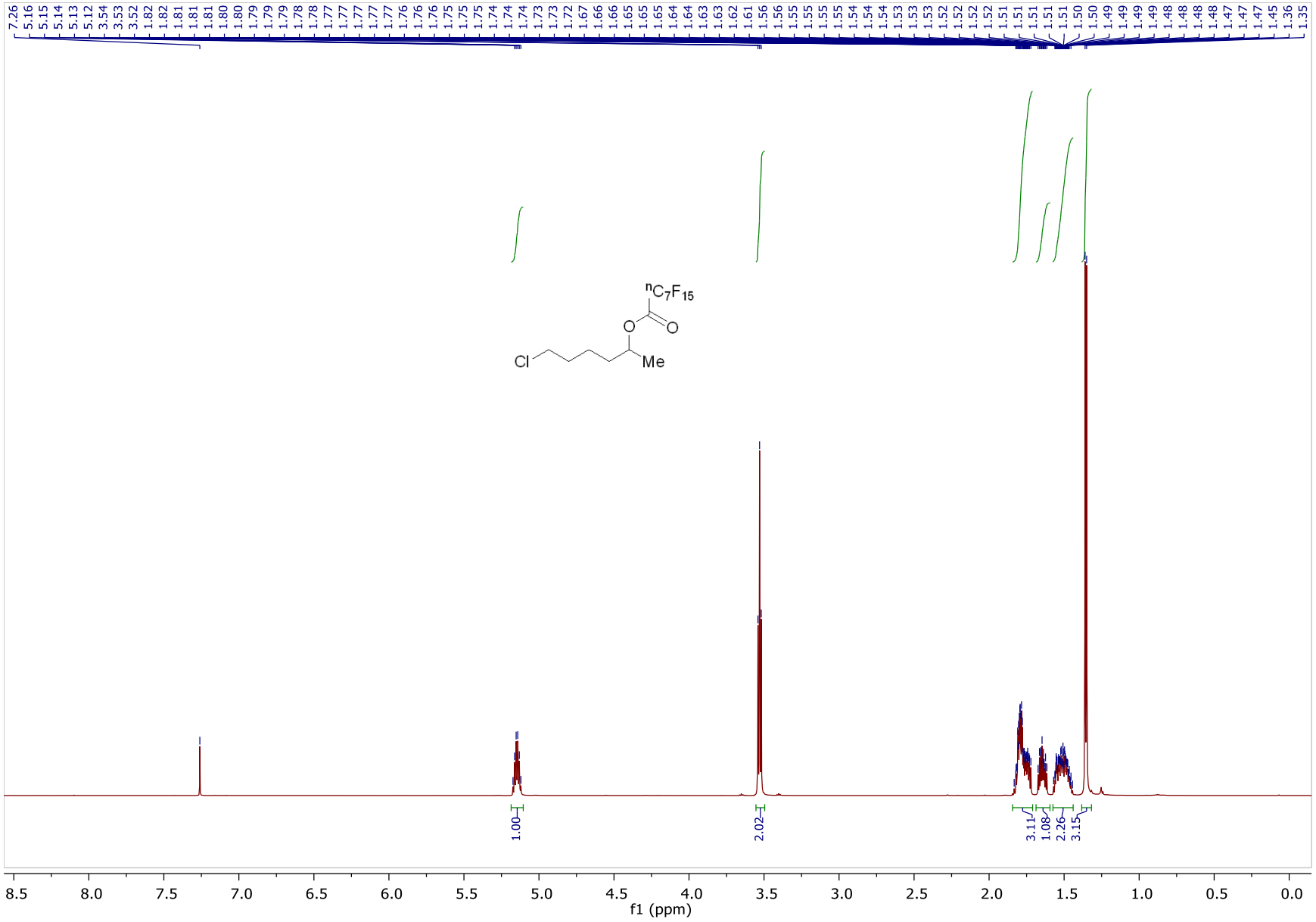
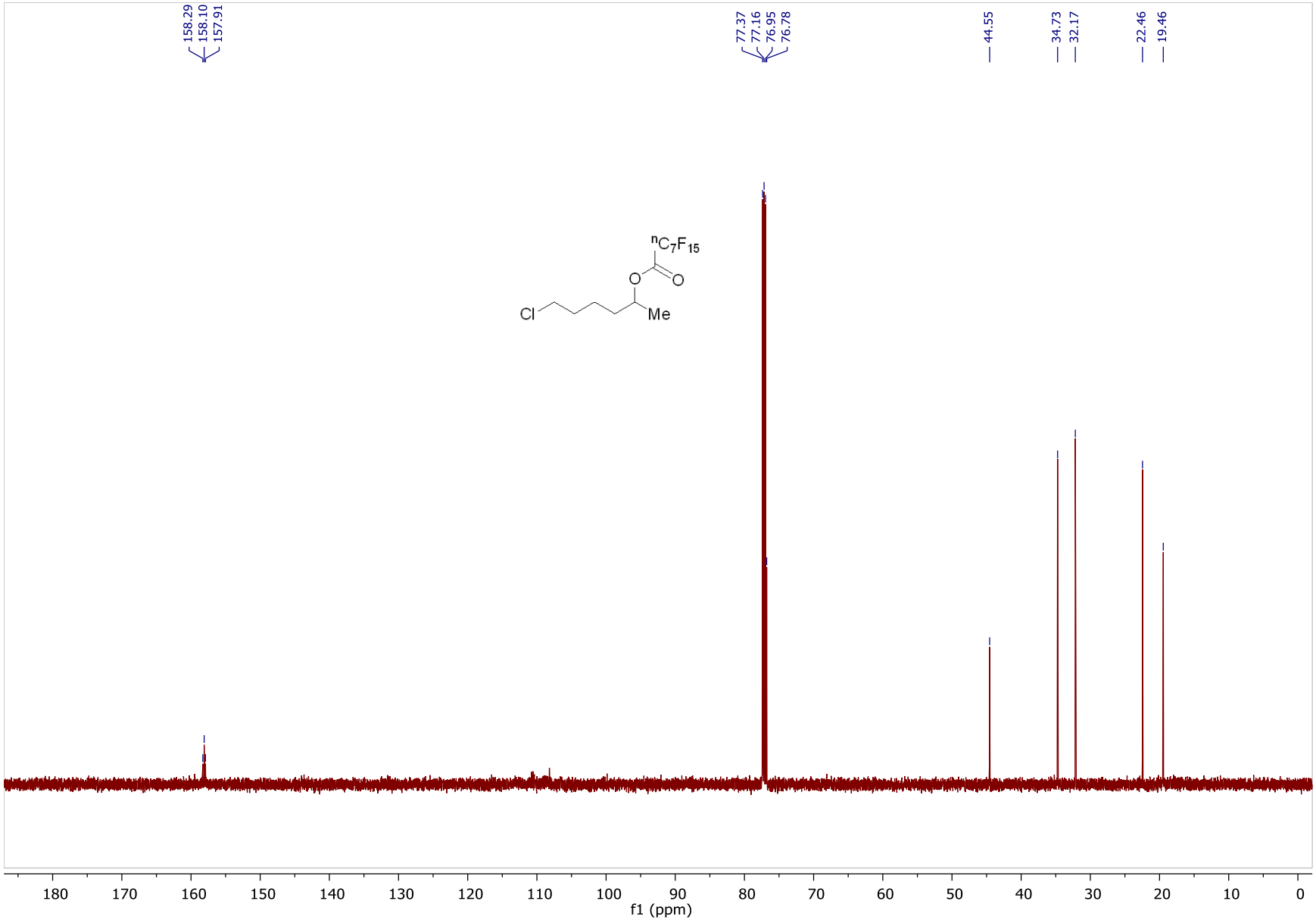
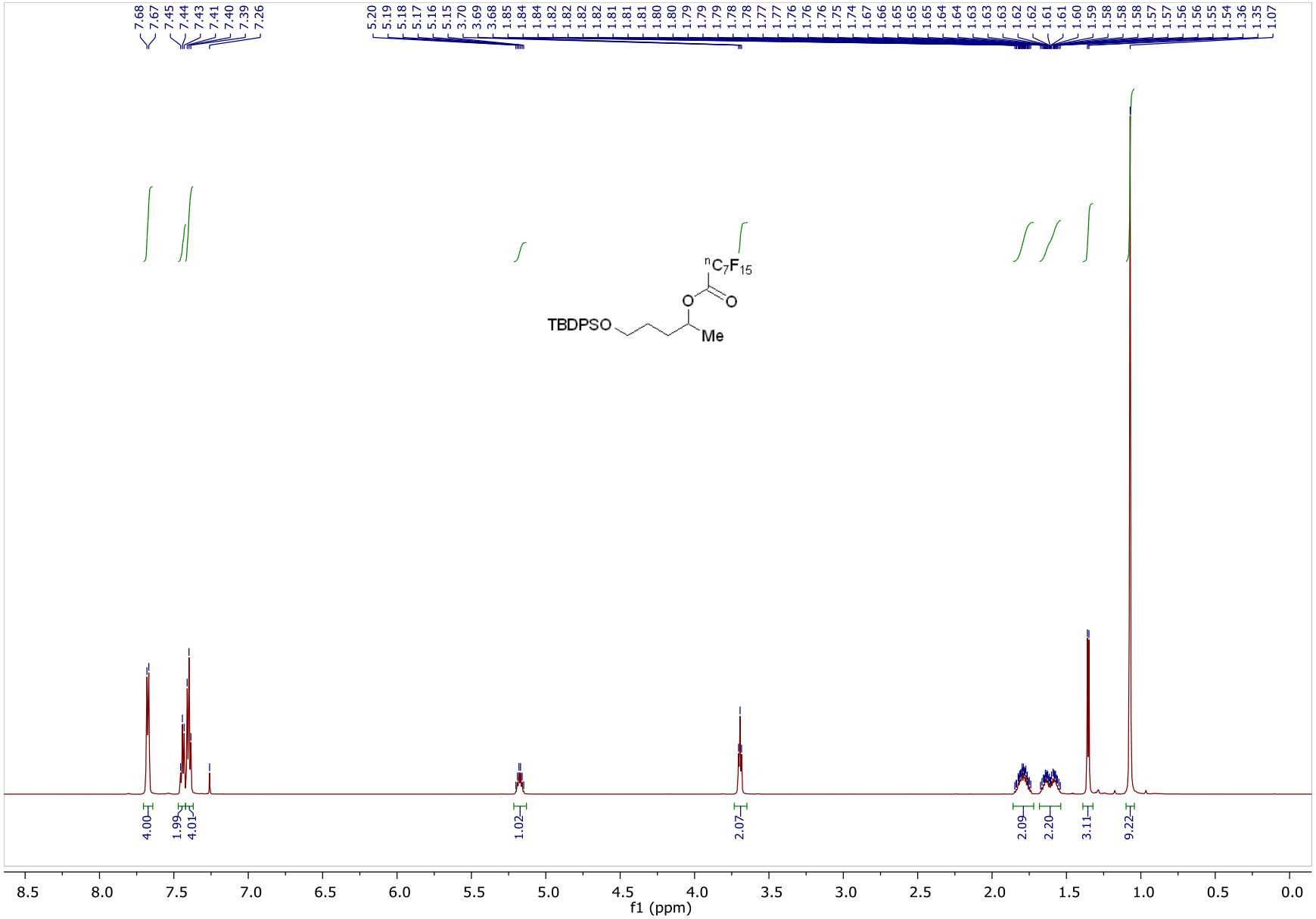
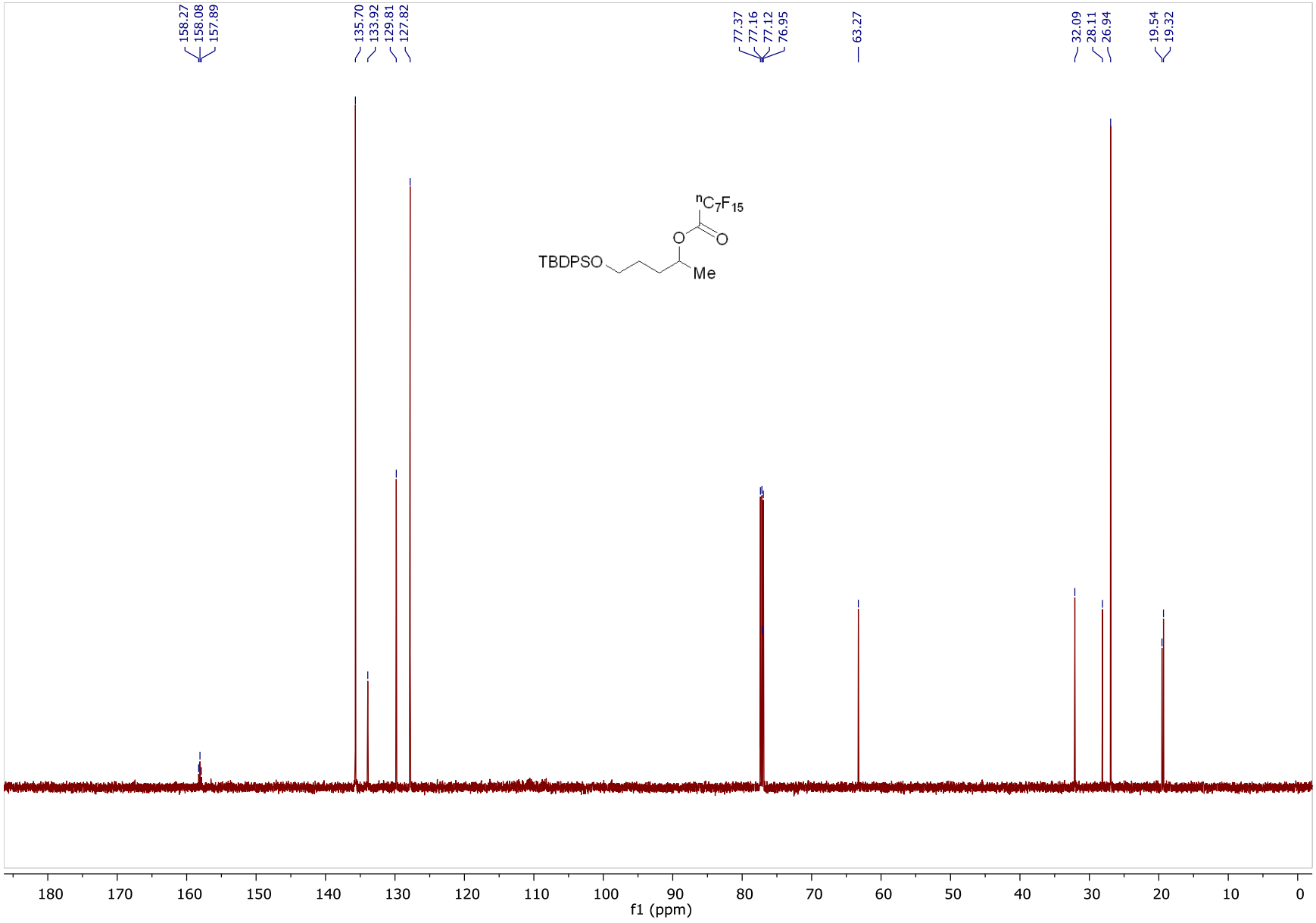
0
f1 (ppm)


7.26 5.16 5.15 5.14 5.13 5.12 3.54 3.53 3.52 1.82 1.82 1.81 1.81 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.77 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.75 1.74 1.74 1.74 1.73 1.73 1.72 1.67 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.61 1.56 1.56 1.55 1.55 1.55 1.55 1.54 1.54 1.54 1.53 1.53 1.53 1.52 1.52 1.52 1.52 1.52 1.51 1.51 1.51 1.51 1.51 1.51 1.50 1.50 1.49 1.49 1.49 1.49 1.48 1.48 1.48 1.48 1.47 1.47 1.47 1.45 1.36 1.35
nC7F15
O
O
Cl
Me
1.00
2.02
3.11
1.08
2.26
3.15
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)


158.29
158.10
157.91
77.37
77.16
76.95
76.78
44.55
34.73
32.17
22.46
19.46
nC7F15
O
O
Cl
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.68 7.67 7.45 7.44 7.43 7.41 7.40 7.39 7.26
5.20 5.19 5.18 5.17 5.16 5.15 3.70 3.69 3.68 1.85 1.84 1.82 1.82 1.82 1.81 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.74 1.67 1.66 1.65 1.65 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.61 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.54 1.36 1.35 1.07
nC7F15
O
O
TBDPSO
Me
4.00
1.99
4.01
1.02
2.07
2.09
2.20
3.11
9.22
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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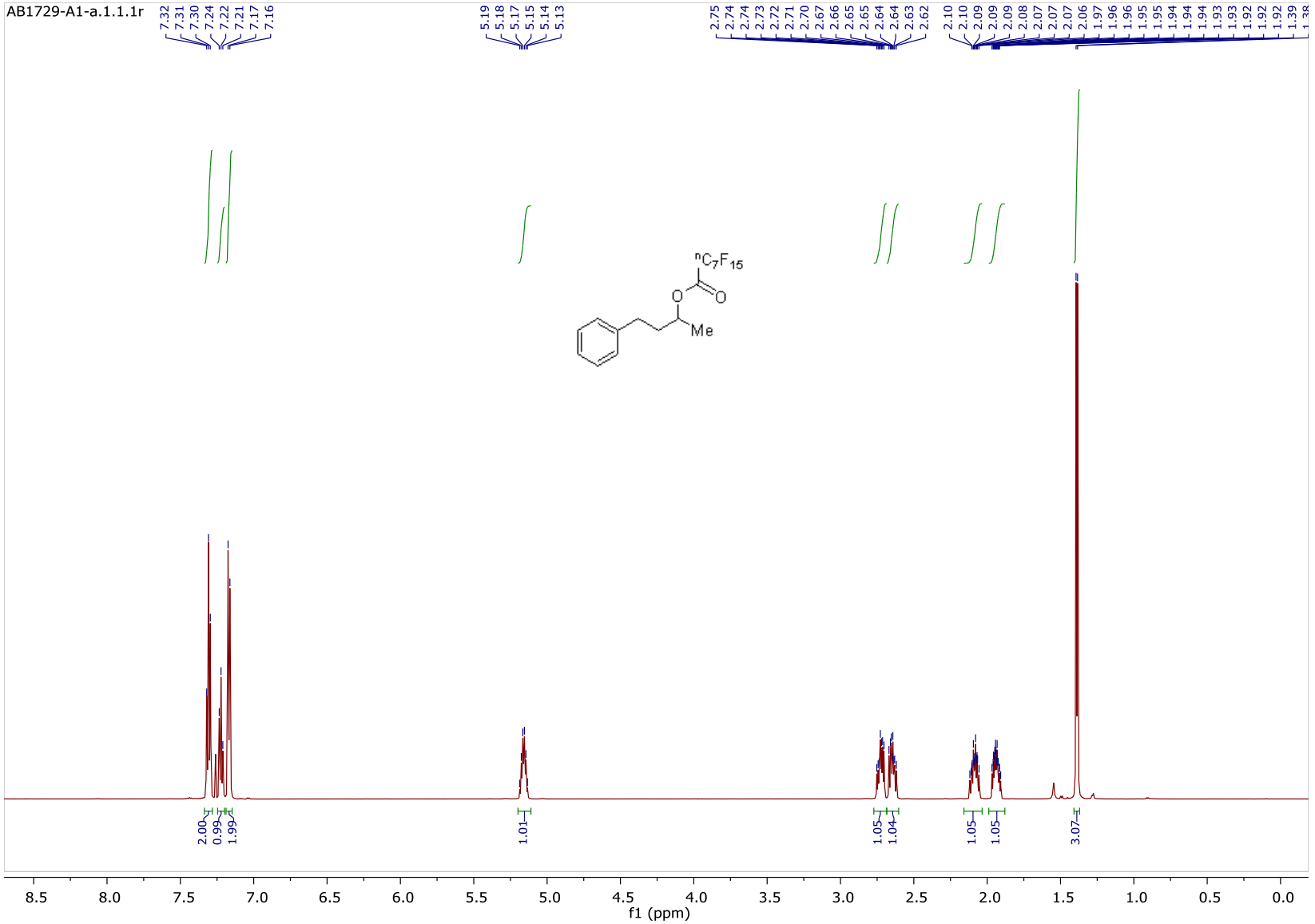
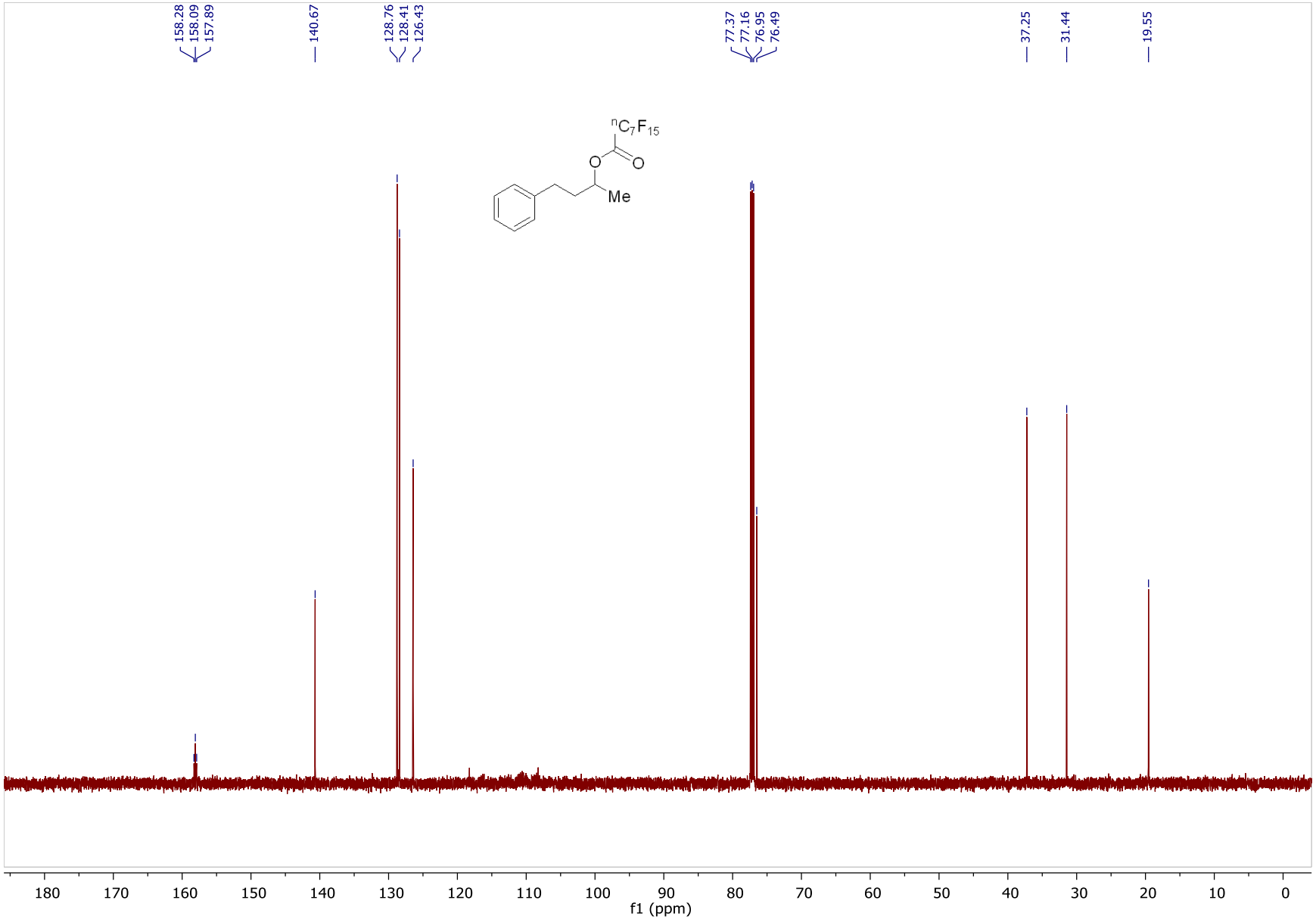
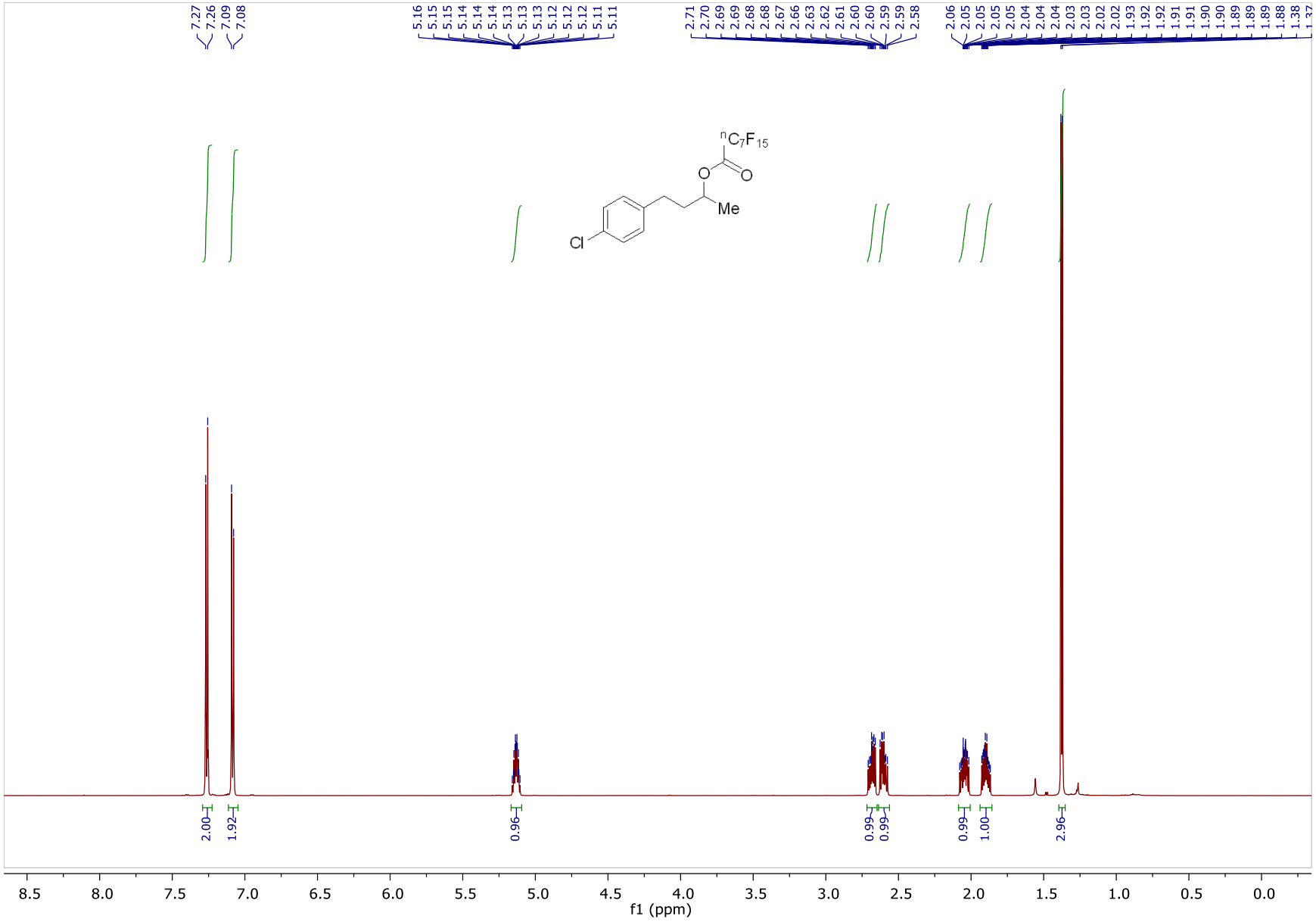
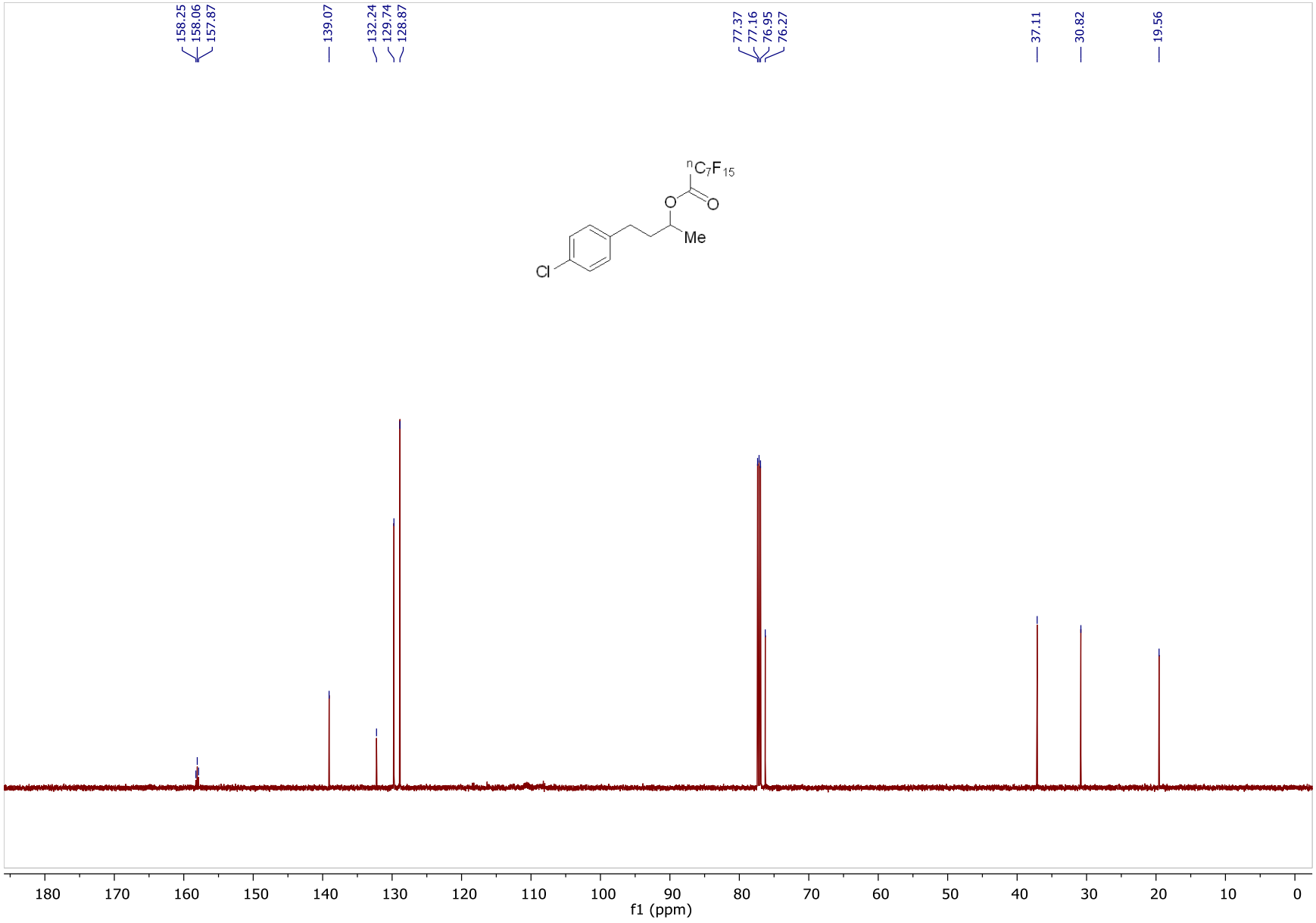
158.08
157.89
135.70
133.92
129.81
127.82
77.37
77.16
77.12
76.95
63.27
32.09
28.11
26.94
19.54
19.32
$^{n}C_7F_{15}$
O
O
TBDPSO
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


AB1729-A1-a.1.1.1r
7.32 7.31 7.30 7.24 7.22 7.21 7.17 7.16
5.19 5.18 5.17 5.15 5.14 5.13
2.75 2.74 2.74 2.73 2.72 2.71 2.70 2.67 2.66 2.65 2.65 2.64 2.64 2.63 2.62
2.10 2.10 2.09 2.09 2.09 2.08 2.07 2.07 2.07 2.06 1.97 1.96 1.96 1.95 1.95 1.94 1.94 1.94 1.93 1.93 1.92 1.92 1.92 1.39
nC7F15
O
O
Me
2.00
0.99
1.99
1.01
1.05
1.04
1.05
1.05
3.07
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)


158.28
158.09
157.89
140.67
128.76
128.41
126.43
77.37
77.16
76.95
76.49
37.25
31.44
19.55
nC7F15
O
O
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.26
7.09
7.08
5.16
5.15
5.15
5.14
5.14
5.14
5.13
5.13
5.13
5.12
5.12
5.11
5.11
2.71
2.70
2.69
2.69
2.68
2.68
2.67
2.66
2.63
2.62
2.61
2.60
2.60
2.59
2.59
2.58
2.06
2.05
2.05
2.05
2.05
2.04
2.04
2.04
2.03
2.03
2.02
2.02
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.89
1.89
1.89
1.88
1.38
nC7F15
O
O
Me
Cl
2.00
1.92
0.96
0.99
0.99
0.99
1.00
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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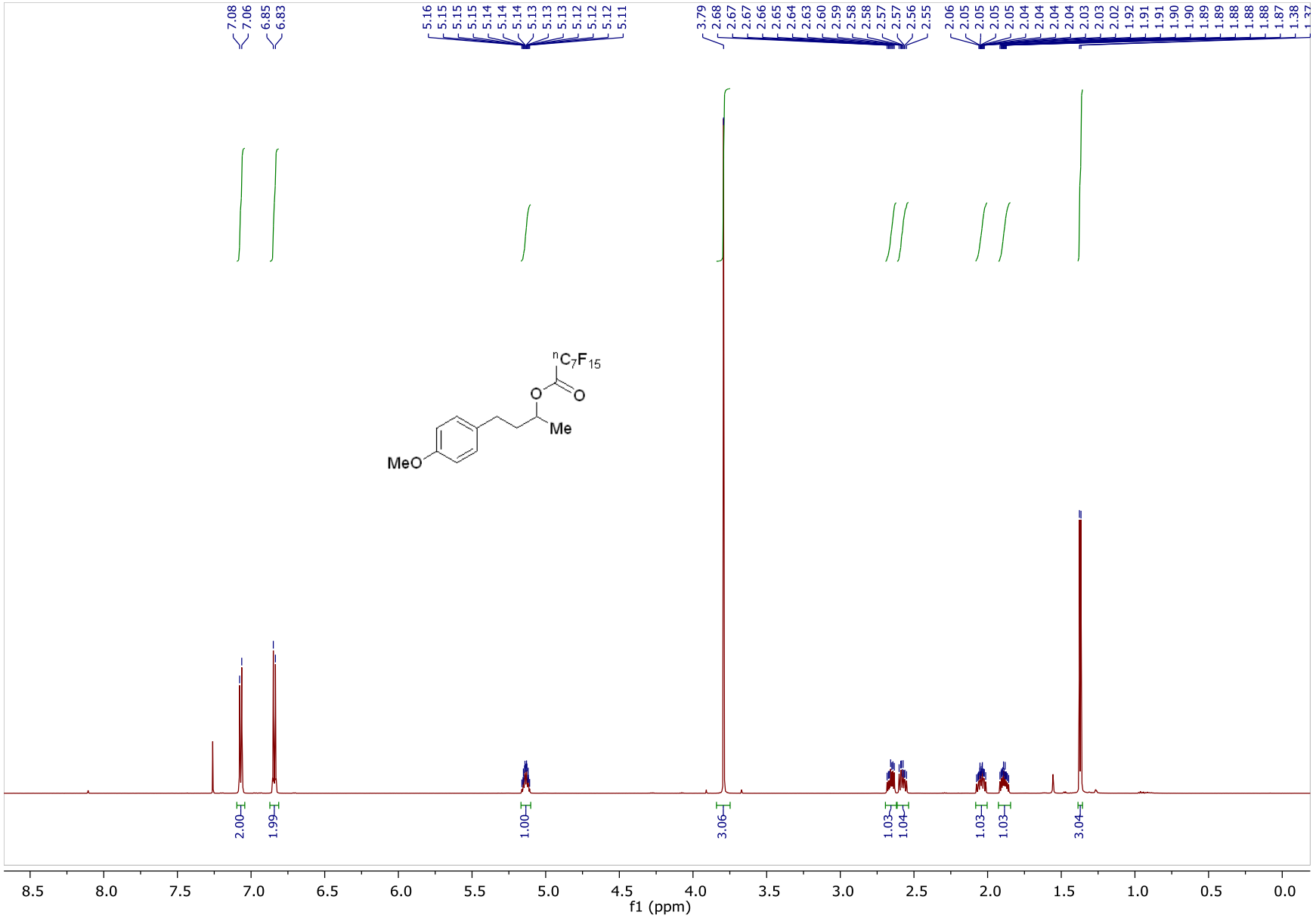
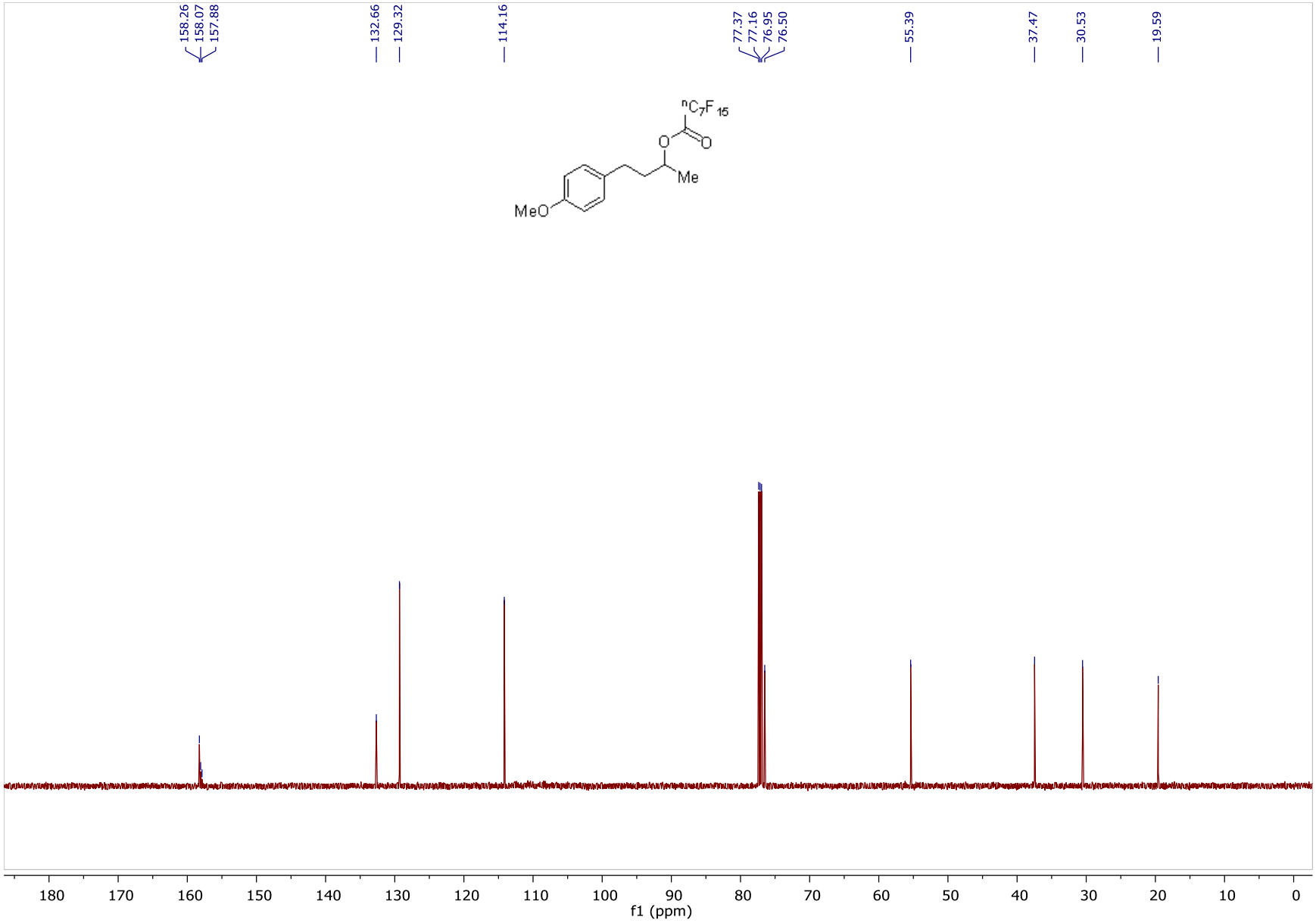
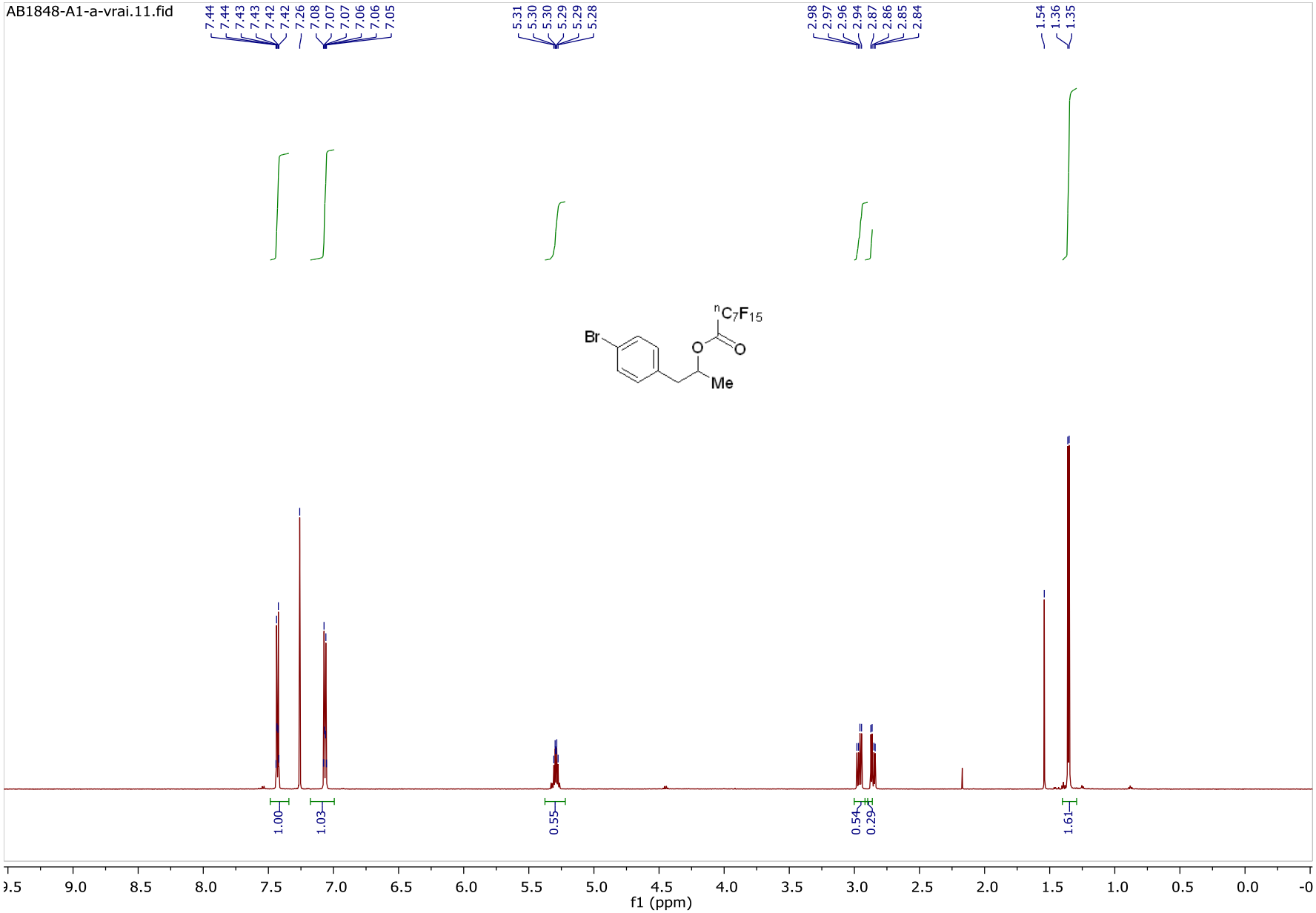
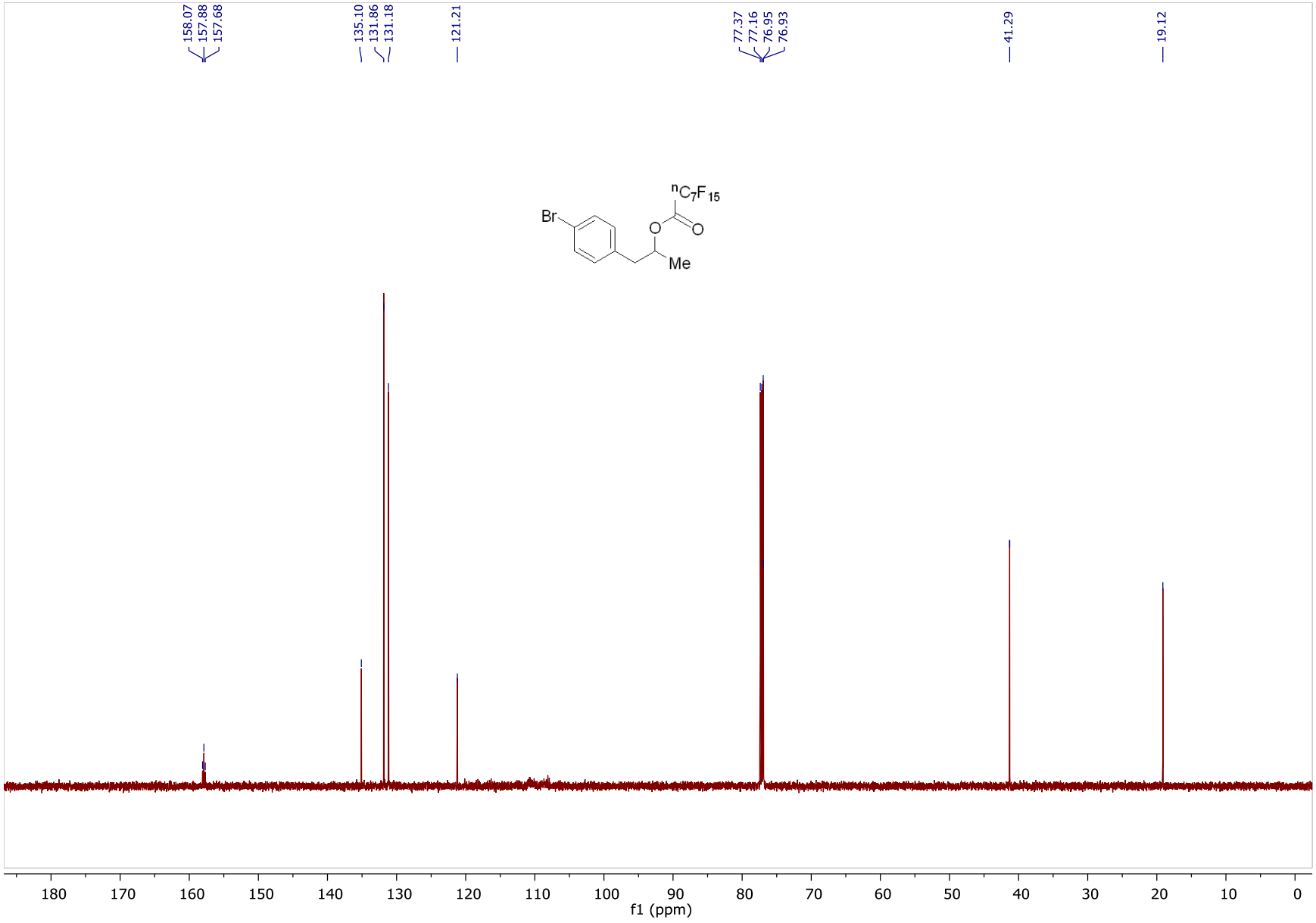
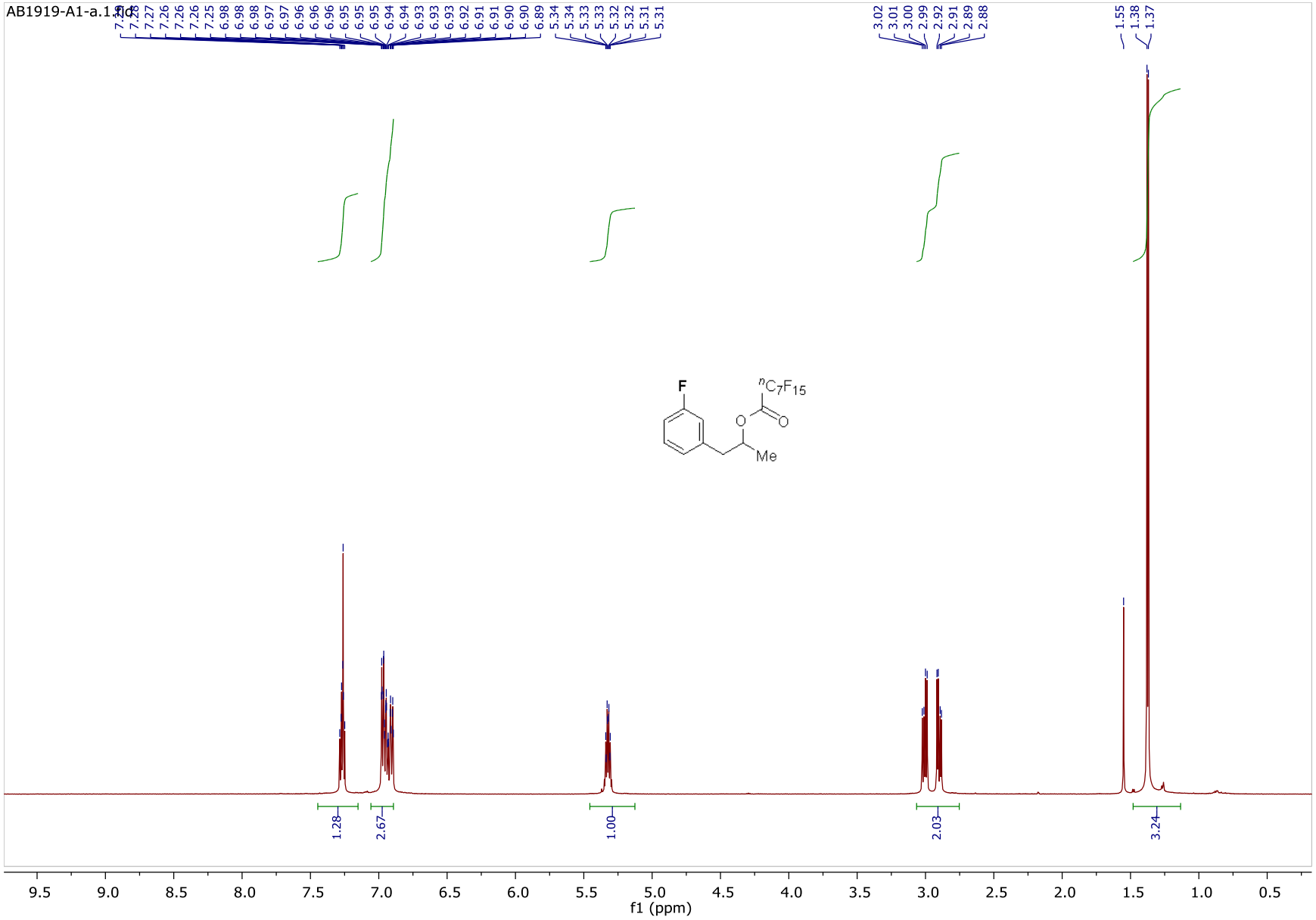
158.06
157.87
139.07
132.24
129.74
128.87
77.37
77.16
76.95
76.27
37.11
30.82
19.56
nC7F15
O
O
Me
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

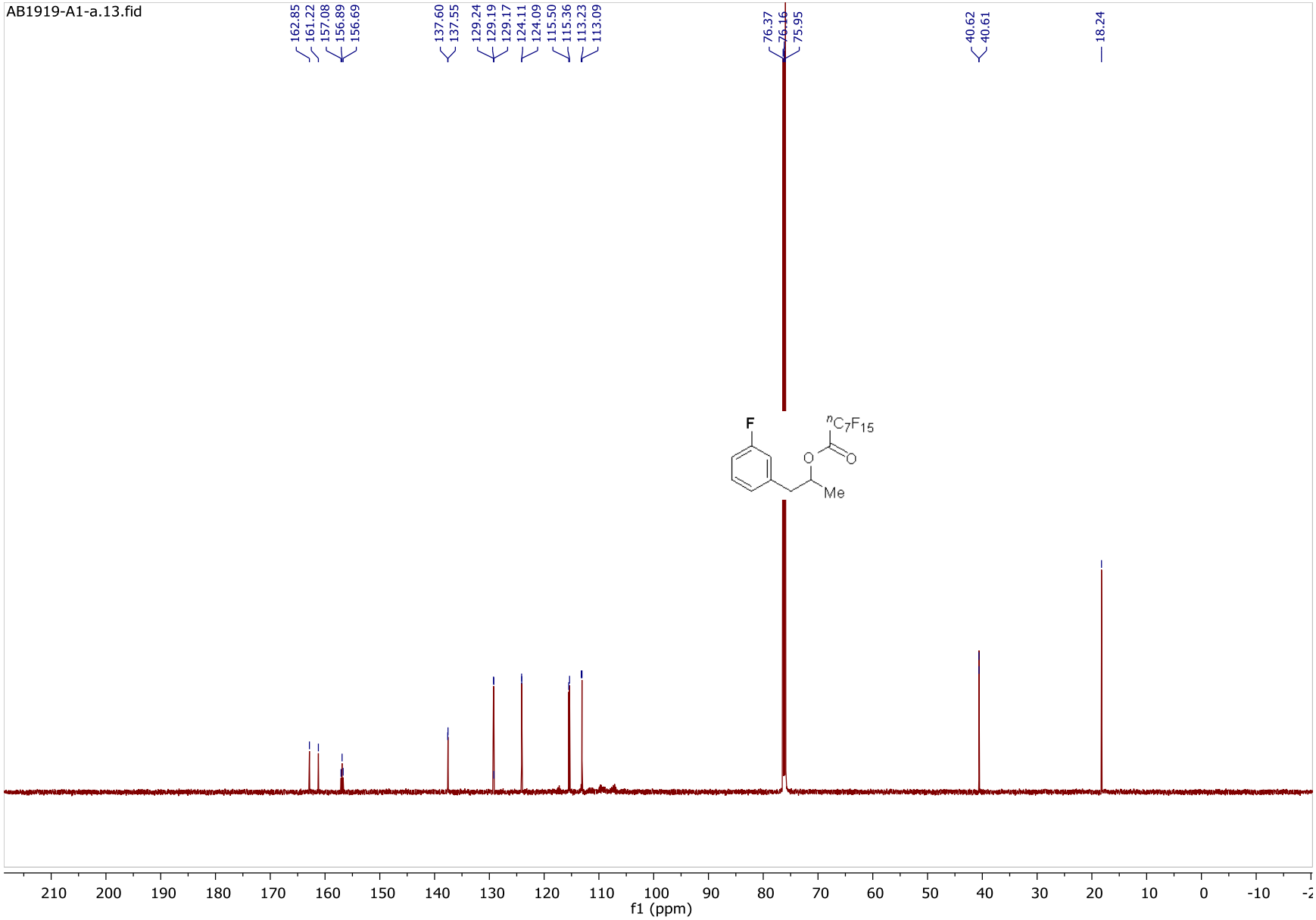

7.08
7.06
6.85
6.83
5.16
5.15
5.15
5.15
5.14
5.14
5.14
5.13
5.13
5.13
5.12
5.12
5.12
5.11
3.79
2.68
2.67
2.67
2.66
2.65
2.64
2.63
2.60
2.59
2.58
2.58
2.57
2.57
2.56
2.55
2.06
2.05
2.05
2.05
2.05
2.04
2.04
2.04
2.04
2.03
2.03
2.02
1.92
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.88
1.88
1.87
1.38
nC7F15
O
O
Me
MeO
2.00
1.99
1.00
3.06
1.03
1.04
1.03
1.03
3.04
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)

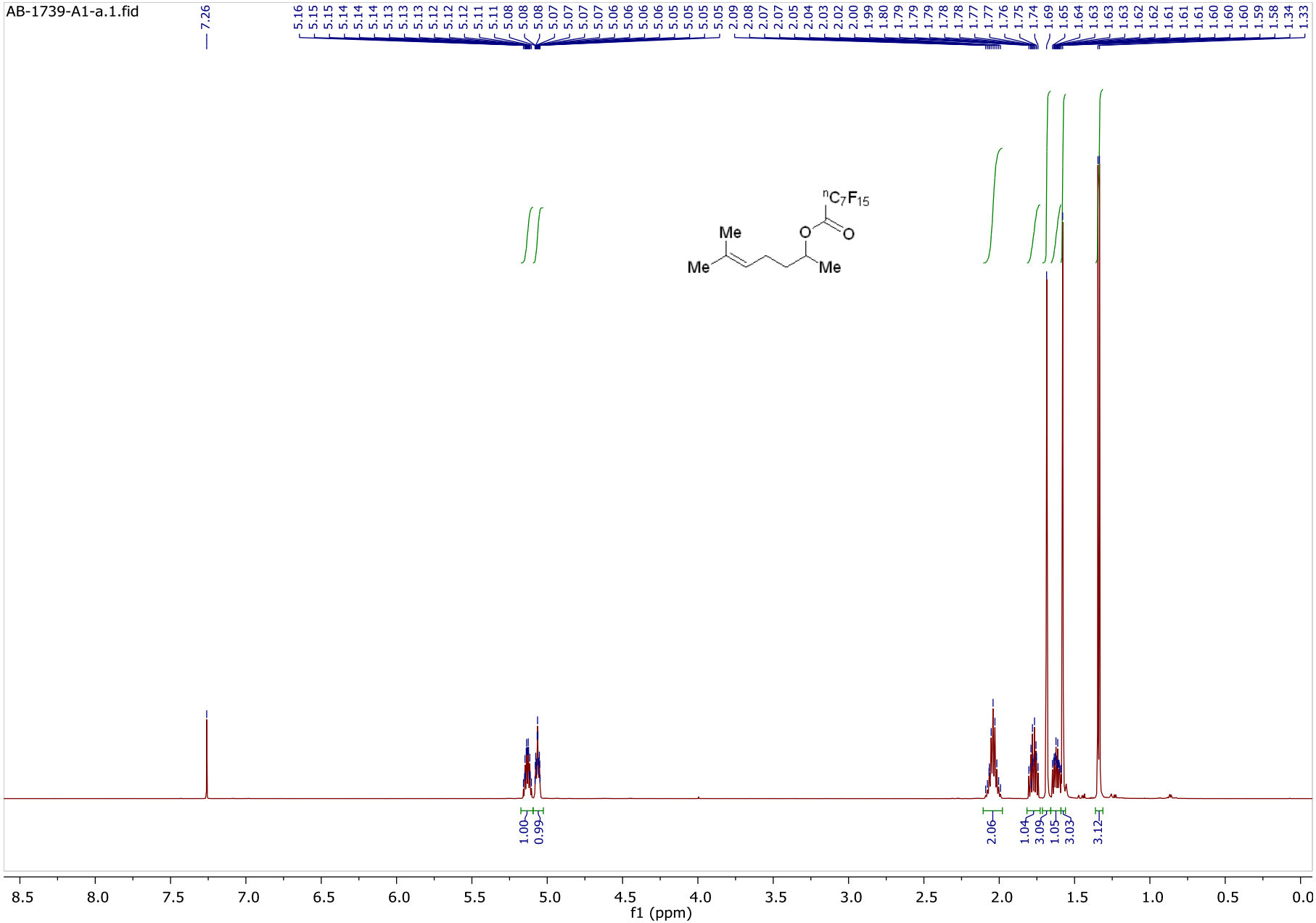

158.26
158.07
157.88
132.66
129.32
114.16
77.37
77.16
76.95
76.50
55.39
37.47
30.53
19.59
nC7F15
O
O
Me
MeO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

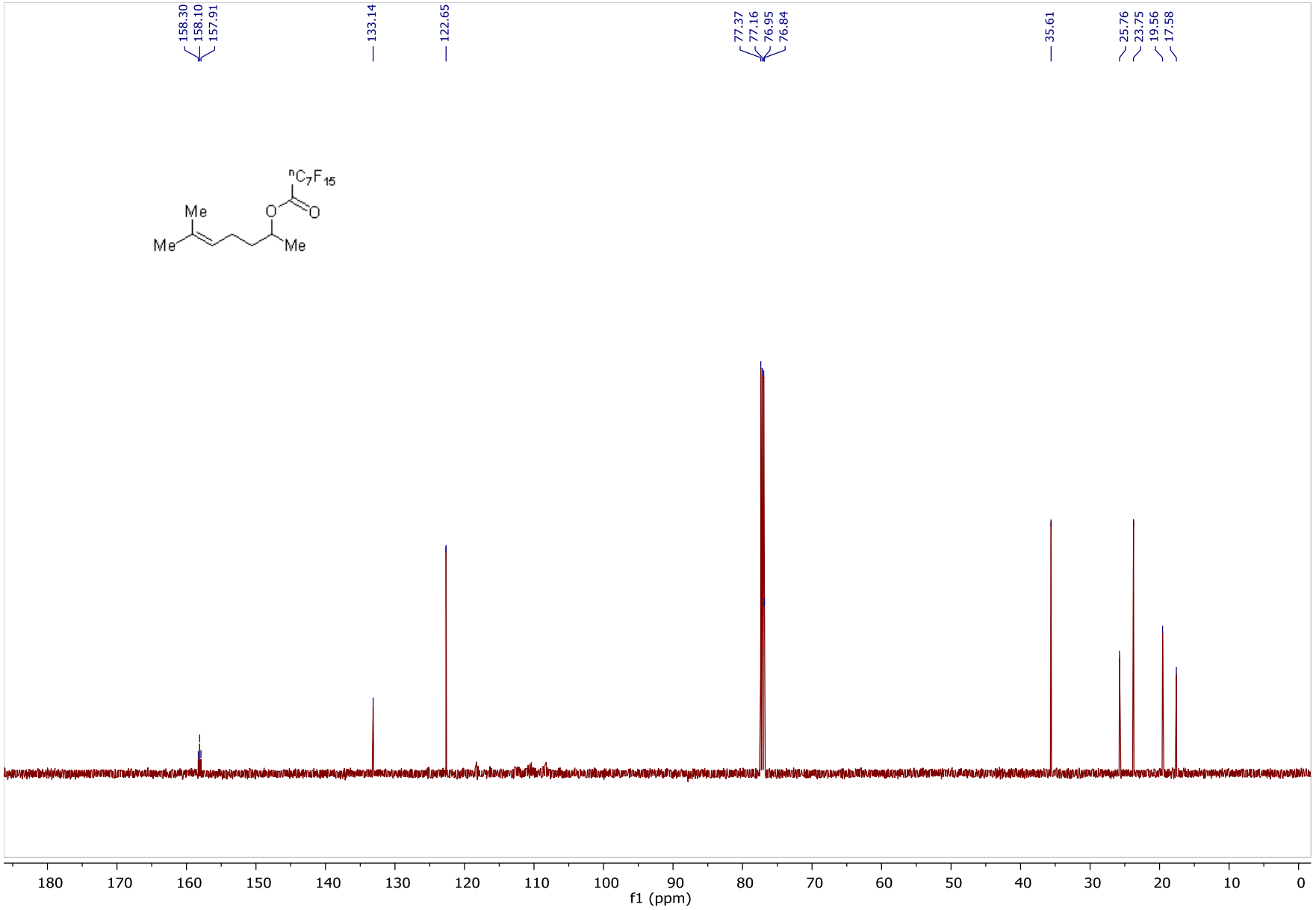

AB1848-A1-a-vrai.11.fid
7.44
7.44
7.43
7.43
7.42
7.42
7.26
7.08
7.07
7.07
7.06
7.06
7.05
5.31
5.30
5.30
5.29
5.29
5.28
2.98
2.97
2.96
2.94
2.87
2.86
2.85
2.84
1.54
1.36
1.35
Br
O
O
nC7F15
Me
1.00
1.03
0.55
0.54
0.29
1.61
f1 (ppm)

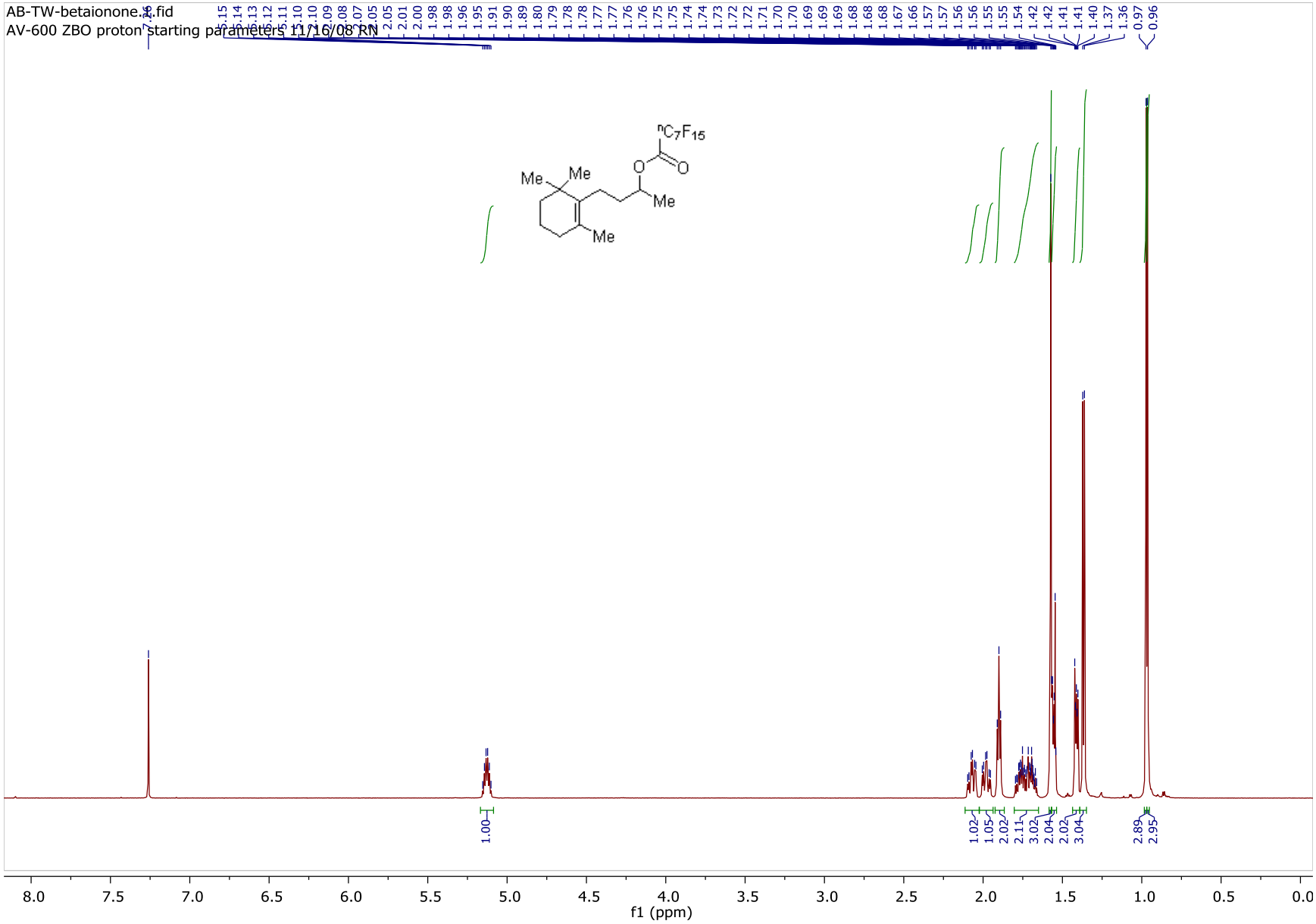

158.07
157.88
157.68
135.10
131.86
131.18
121.21
77.37
77.16
76.95
76.93
41.29
19.12
Br
O
O
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

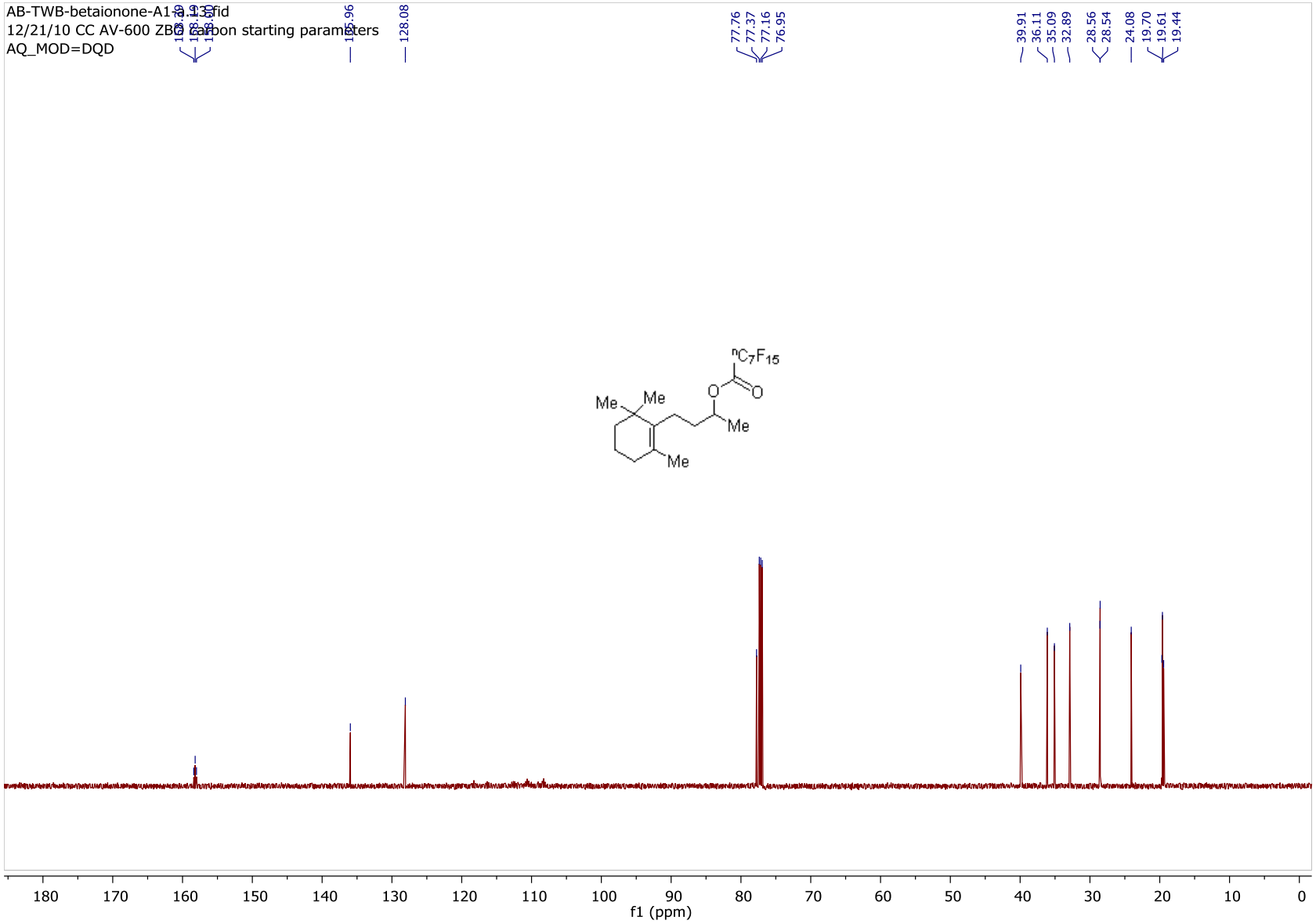

AB1919-A1-a.1.1d
F
$^{n}C_7F_{15}$
O
O
O
Me
1.28
2.67
1.00
2.03
3.24
f1 (ppm)

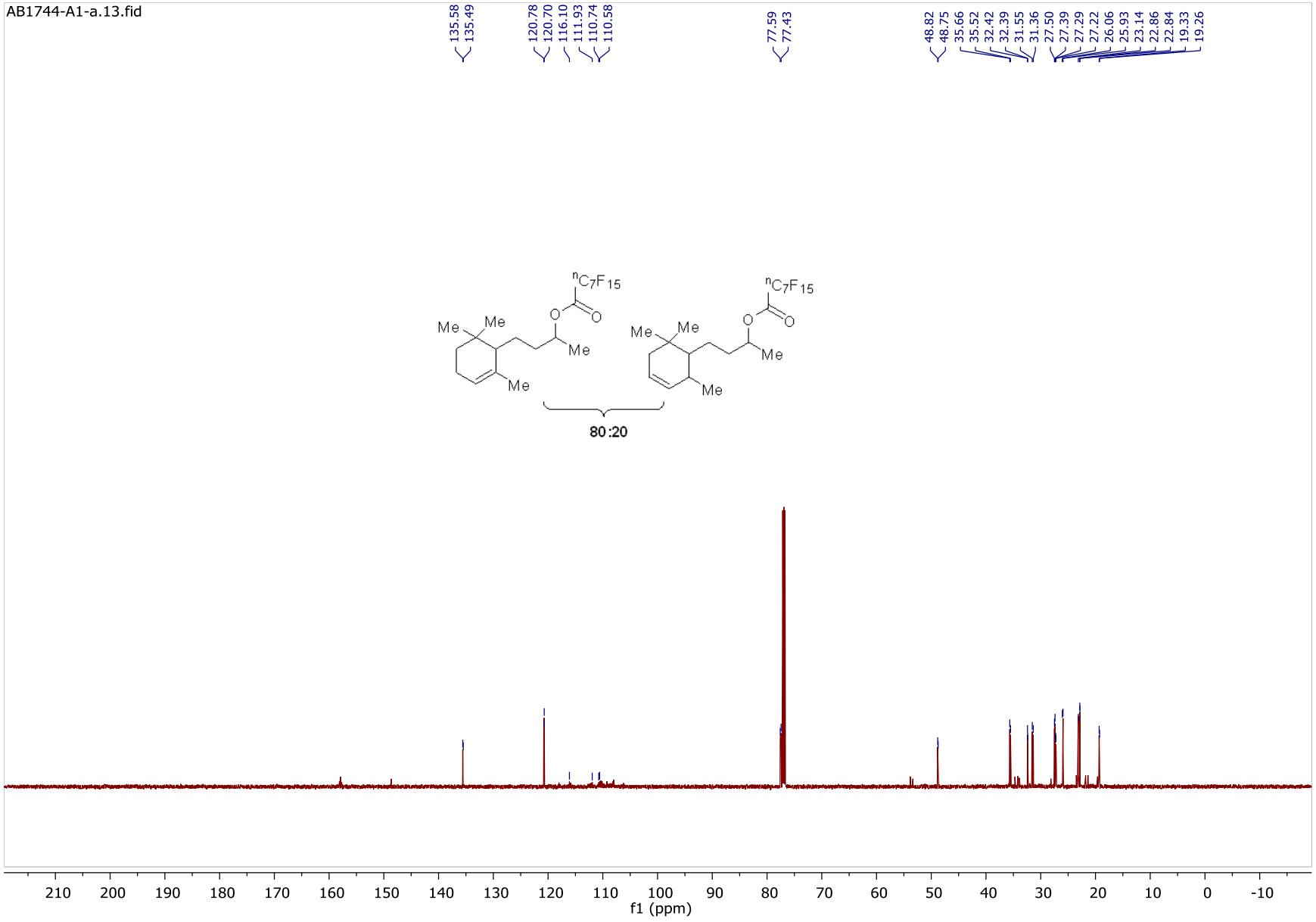

AB1919-A1-a.13.fid
162.85
161.22
157.08
156.89
156.69
137.60
137.55
129.24
129.19
129.17
124.11
124.09
115.50
115.36
113.23
113.09
76.37
76.16
75.95
40.62
40.61
18.24
F
$^{n}C_7F_{15}$
O
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

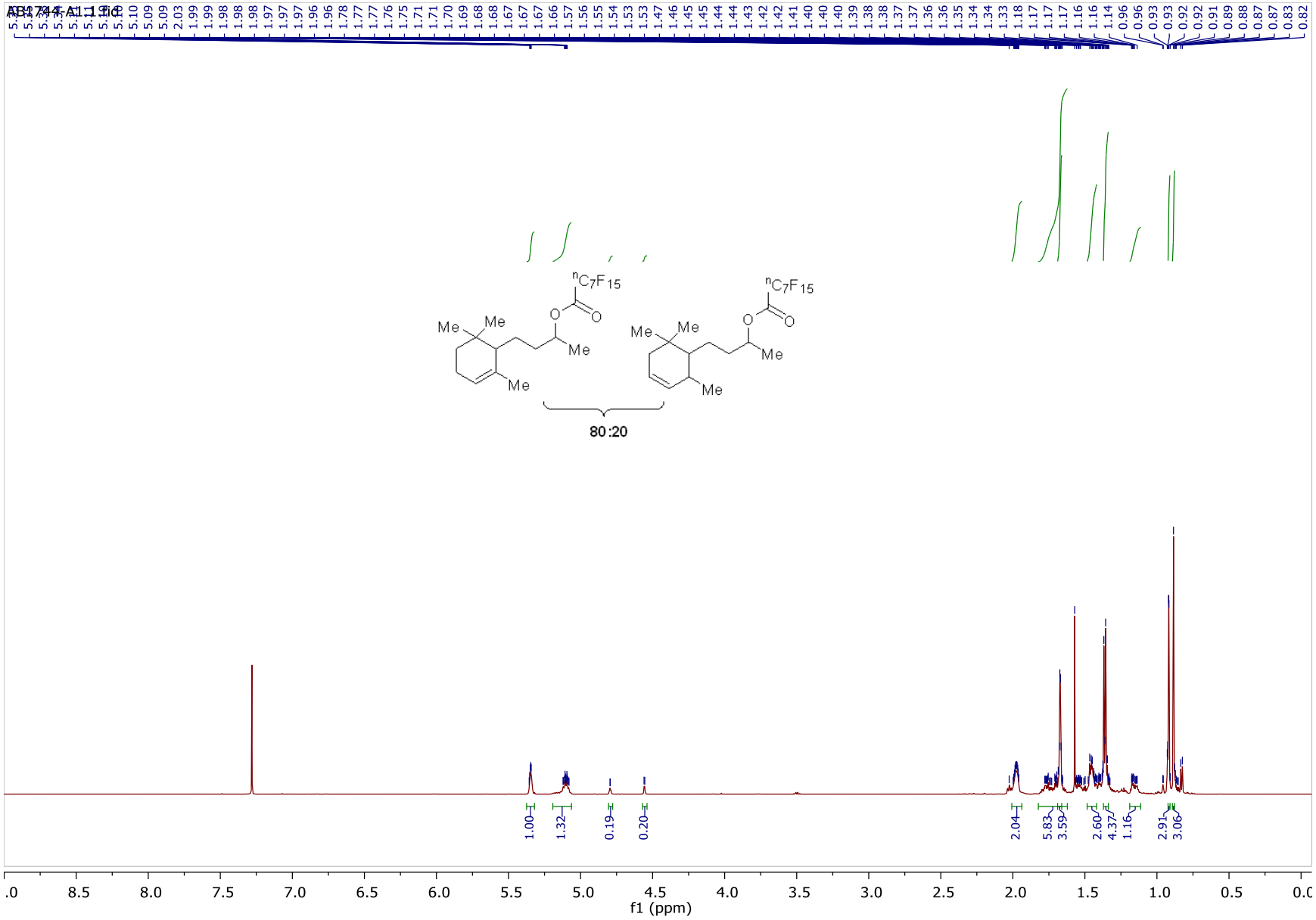

AB-1739-A1-a.1.fid
7.26
5.16 5.15 5.15 5.14 5.14 5.14 5.13 5.13 5.13 5.12 5.12 5.12 5.11 5.11 5.08 5.08 5.08 5.07 5.07 5.07 5.07 5.06 5.06 5.06 5.06 5.05 5.05 5.05 5.05
2.09 2.08 2.07 2.07 2.05 2.04 2.03 2.02 2.00 1.99 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.74 1.69 1.65 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.61 1.61 1.60 1.60 1.60 1.59 1.58 1.34 1.33
nC7F15
O
O
Me
Me
Me
1.00
0.99
2.06
1.04
3.09
1.05
3.03
3.12
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)

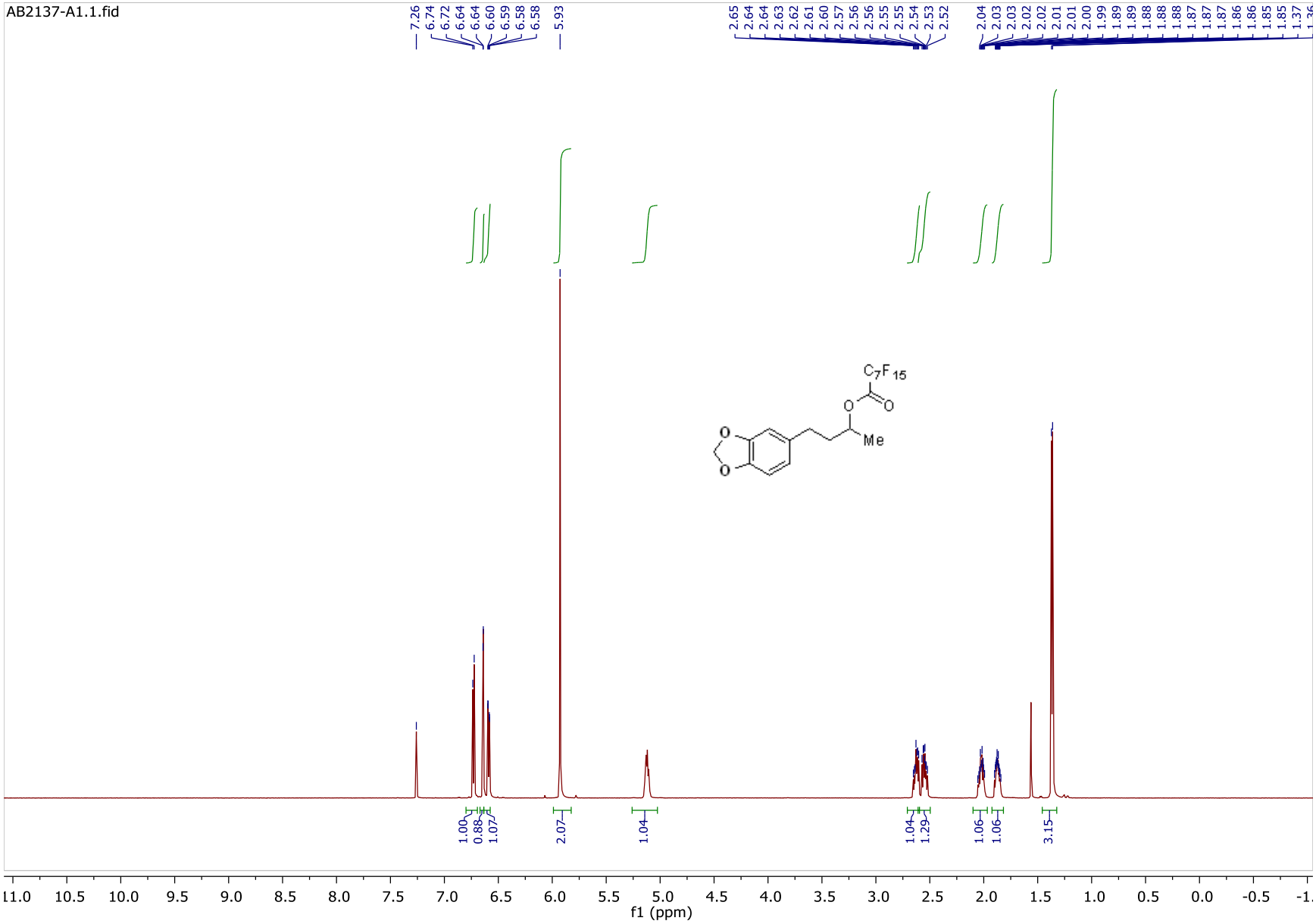

158.30
158.10
157.91
133.14
122.65
77.37
77.16
76.95
76.84
35.61
25.76
23.75
19.56
17.58
$^{n}C_7F_{15}$
Me
Me
O
O
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

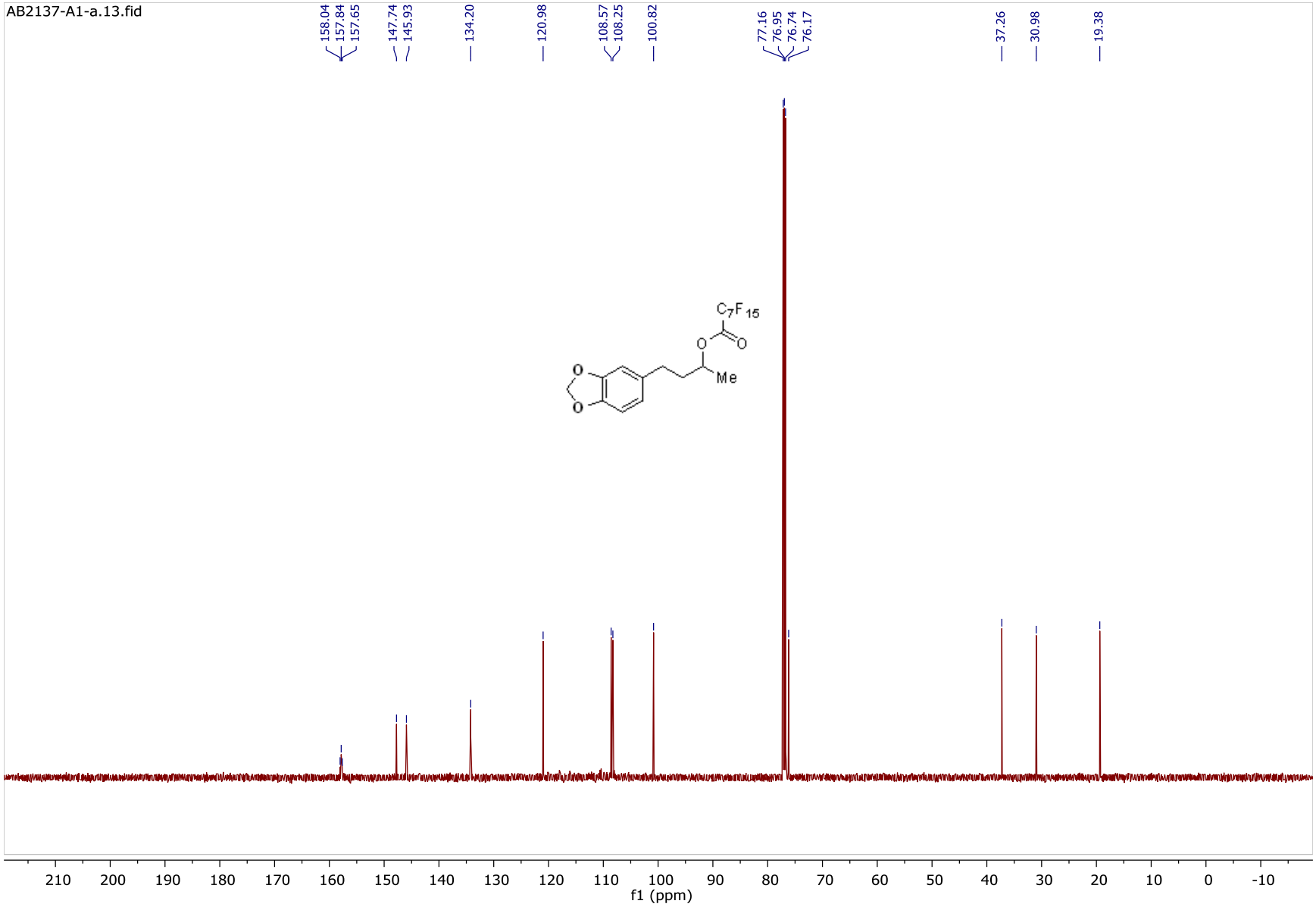

AB-TW-betaionone.4.fid
AV-600 ZBO proton starting parameters 11/16/08 RN
nC7F15
O
O
Me
Me
Me
Me
1.00
1.02
1.05
2.02
2.11
3.02
2.04
2.02
3.04
2.89
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

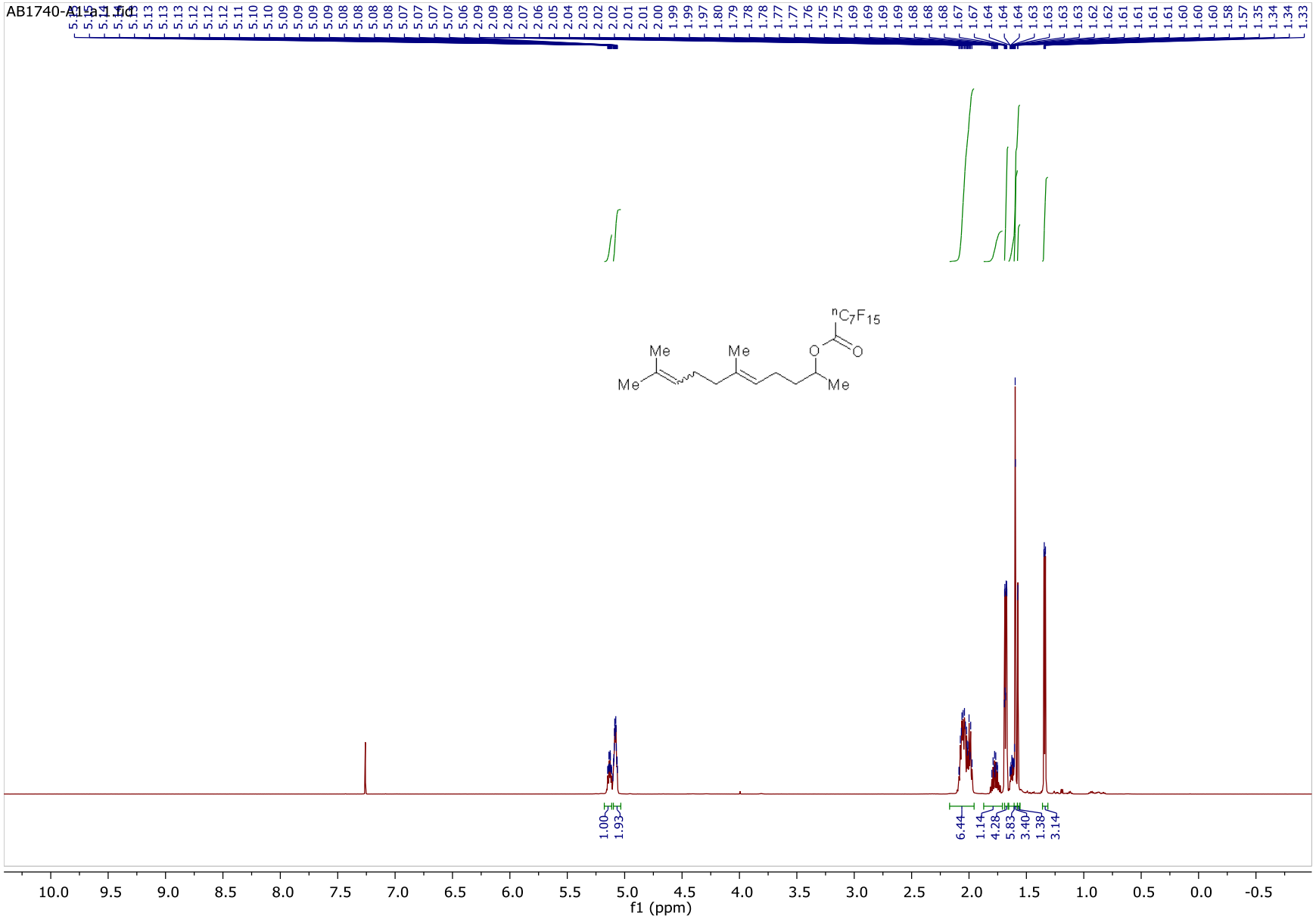

AB-TWB-betaionone-A1a-1.13.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
158.96
128.08
77.76
77.37
77.16
76.95
39.91
36.11
35.09
32.89
28.56
28.54
24.08
19.70
19.61
19.44
nC7F15
O
O
Me
Me
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

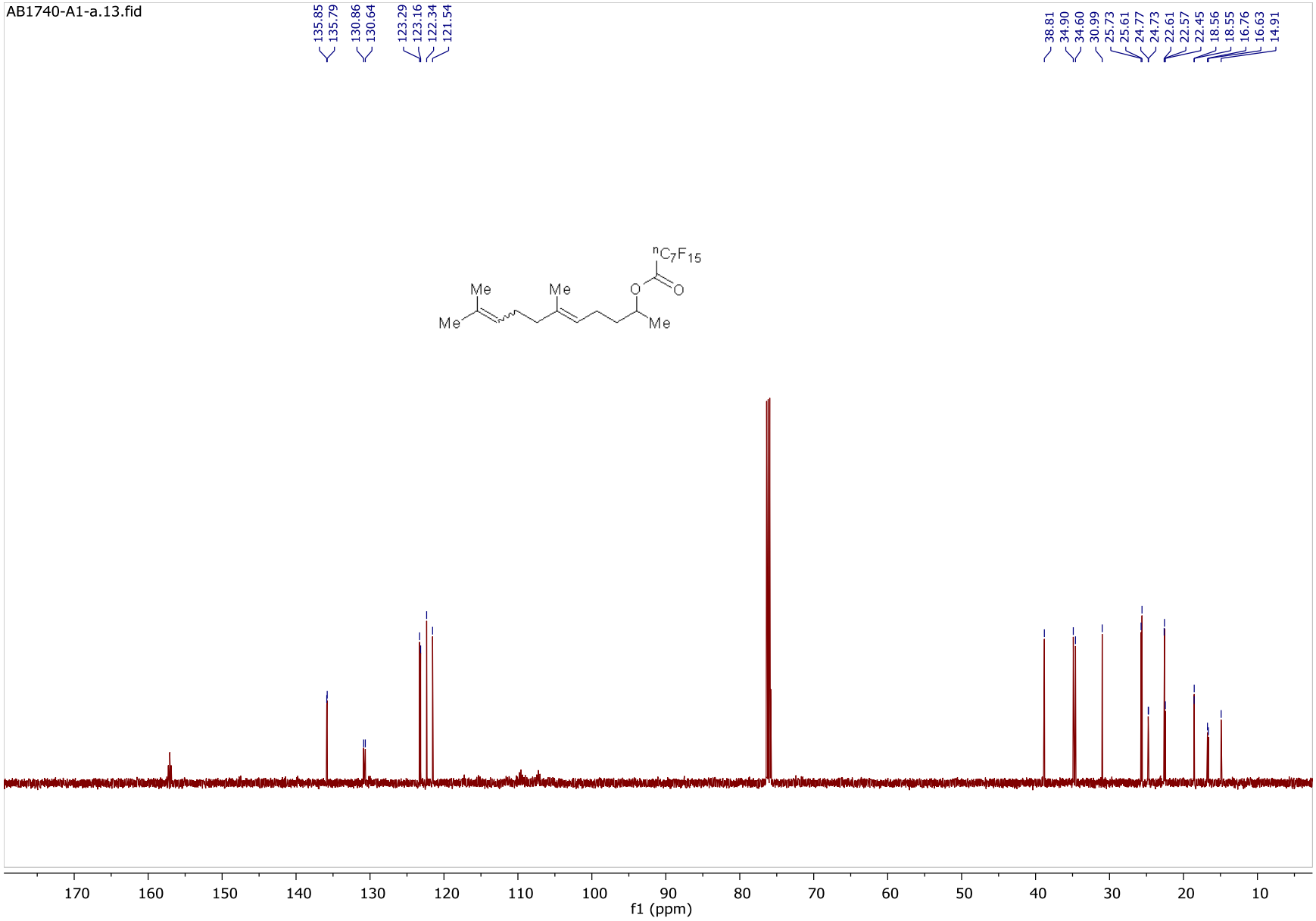

AB1744-A1-a.13.fid
135.58
135.49
120.78
120.70
116.10
111.93
110.74
110.58
77.59
77.43
48.82
48.75
35.66
35.52
32.42
32.39
31.55
31.36
27.50
27.39
27.29
27.22
26.06
25.93
23.14
22.86
22.84
19.33
19.26
nC7F15
O
O
Me
Me
Me
Me
nC7F15
O
O
Me
Me
Me
Me
80:20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

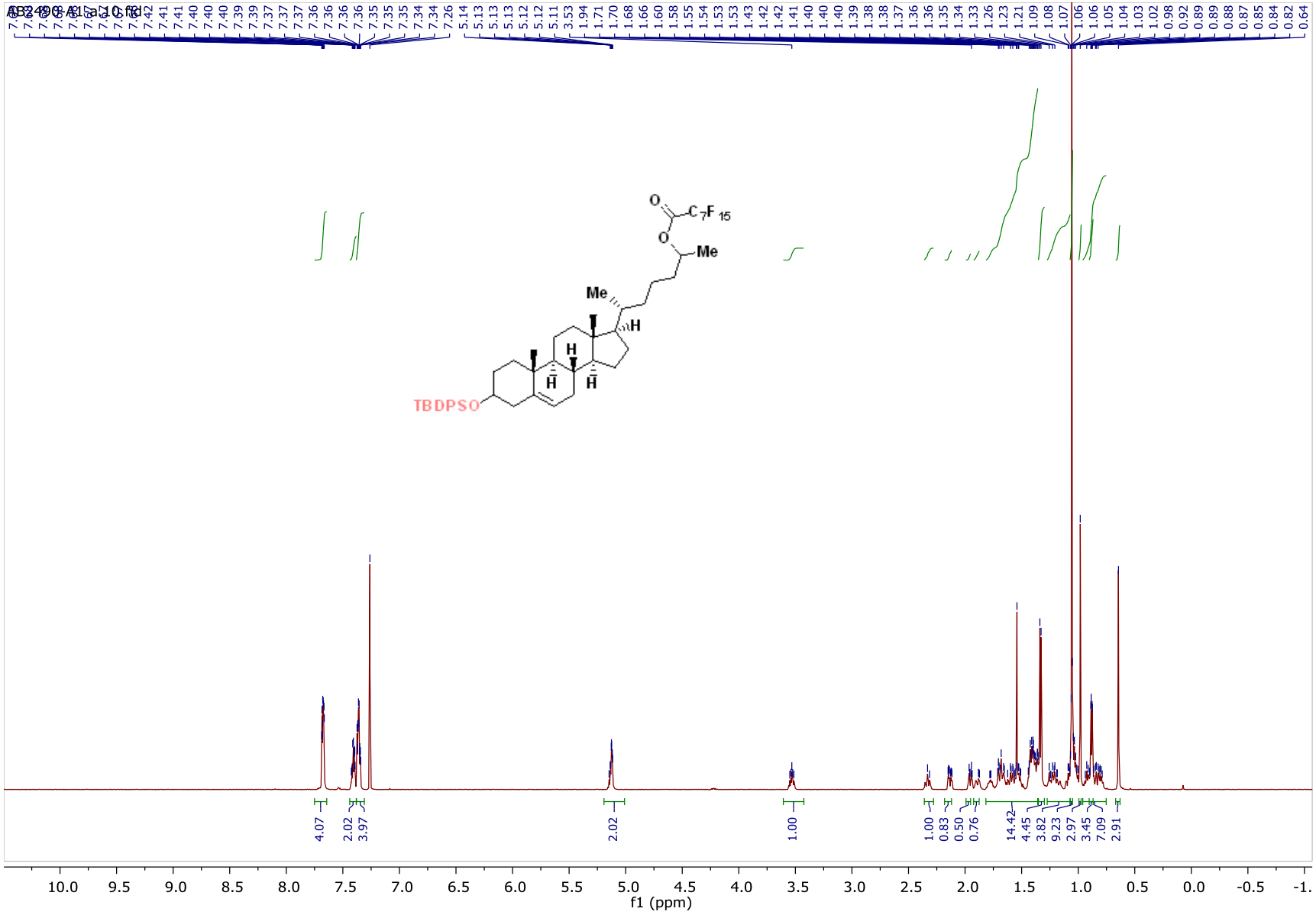

AB1744-A1-13d
nC7F15
O
O
Me
Me
Me
Me
80:20
1.00
1.32
0.19
0.20
2.04
5.83
3.59
2.60
4.37
1.16
2.91
3.06
f1 (ppm)

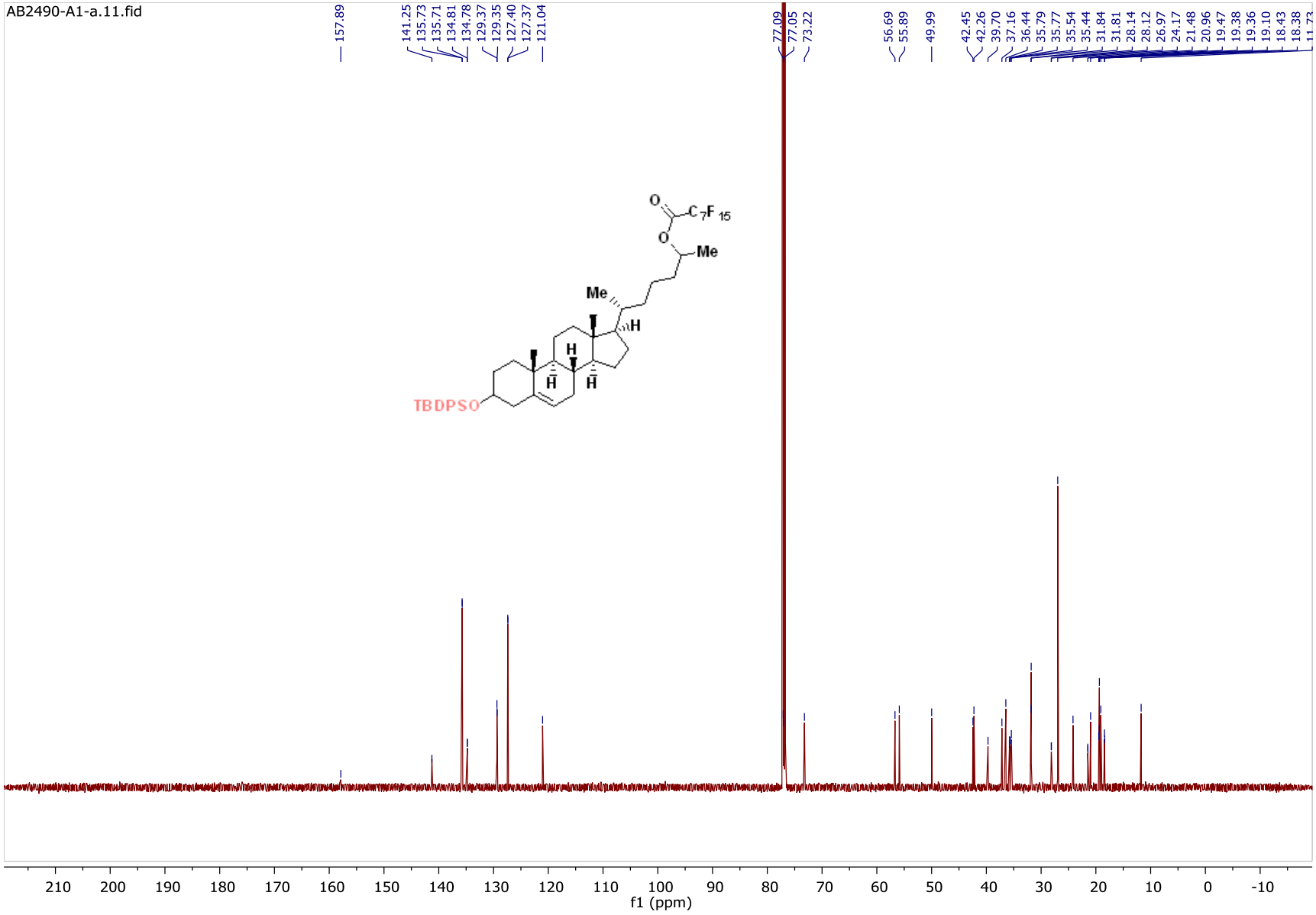

AB2137-A1.1.fid
7.26
6.74
6.72
6.64
6.64
6.60
6.59
6.58
6.58
5.93
2.65
2.64
2.64
2.63
2.62
2.61
2.60
2.57
2.56
2.56
2.55
2.55
2.54
2.53
2.52
2.04
2.03
2.03
2.02
2.02
2.01
2.01
2.00
1.99
1.89
1.89
1.88
1.88
1.88
1.87
1.87
1.87
1.86
1.86
1.85
1.85
1.37
C7F15
O
O
O
O
Me
1.00
0.88
1.07
2.07
1.04
1.04
1.29
1.06
1.06
3.15
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

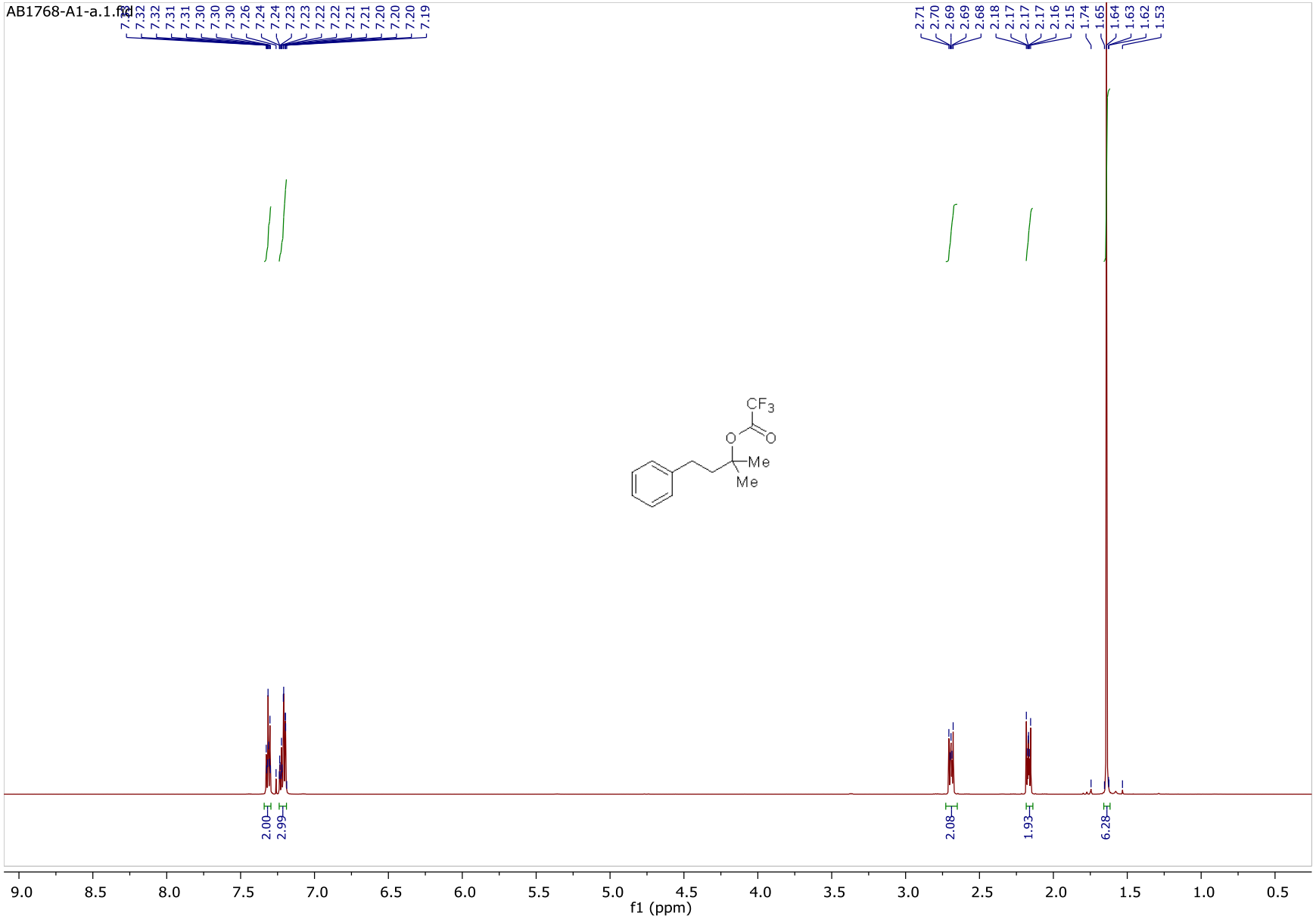

AB2137-A1-a.13.fid
158.04
157.84
157.65
147.74
145.93
134.20
120.98
108.57
108.25
100.82
77.16
76.95
76.74
76.17
37.26
30.98
19.38
C7F15
O
O
O
O
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

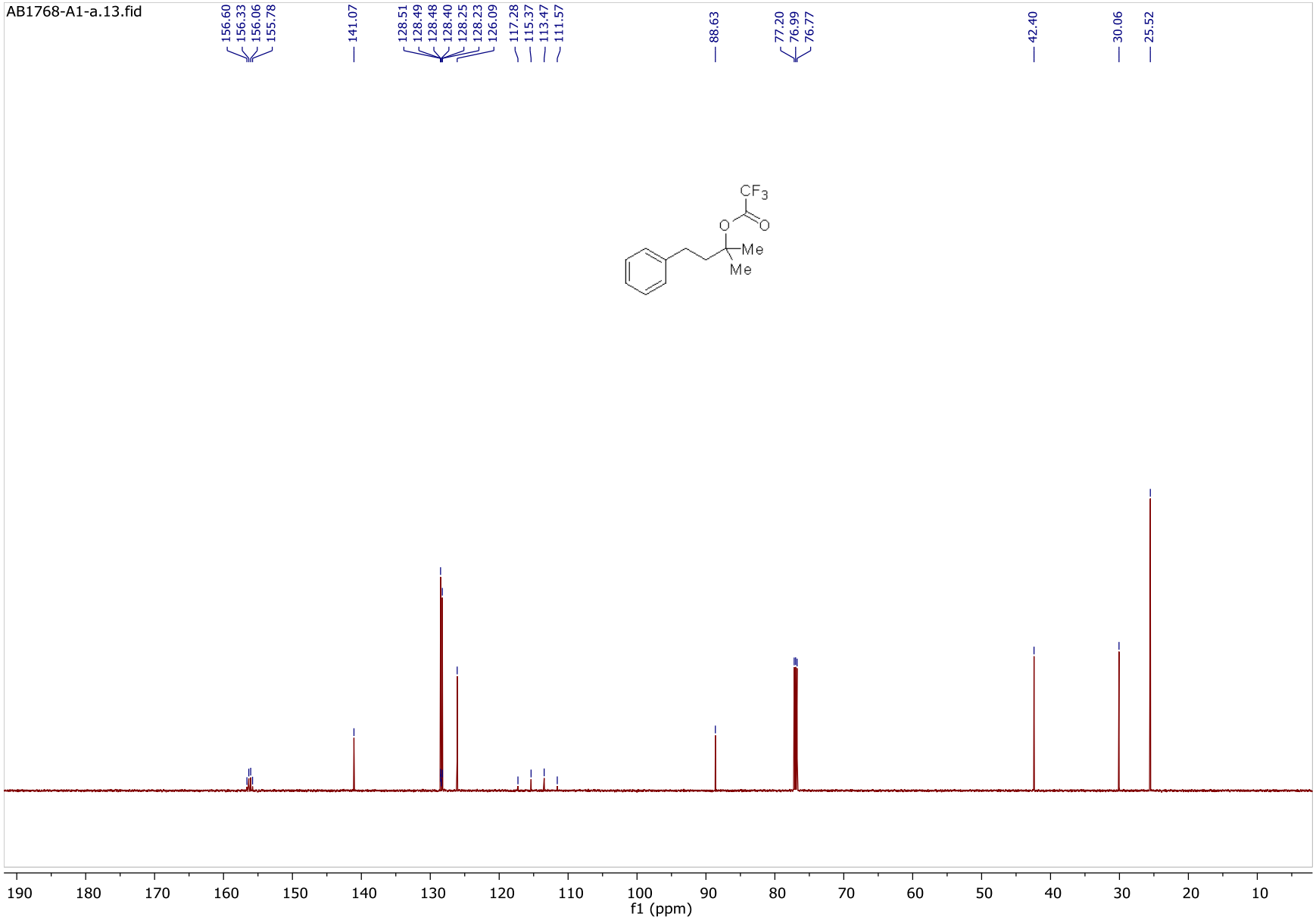

AB1740-A1-a-1.fid
Me
Me
Me
O
O
Me
nC7F15
1.00
1.93
6.44
1.14
4.28
5.83
3.40
1.38
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

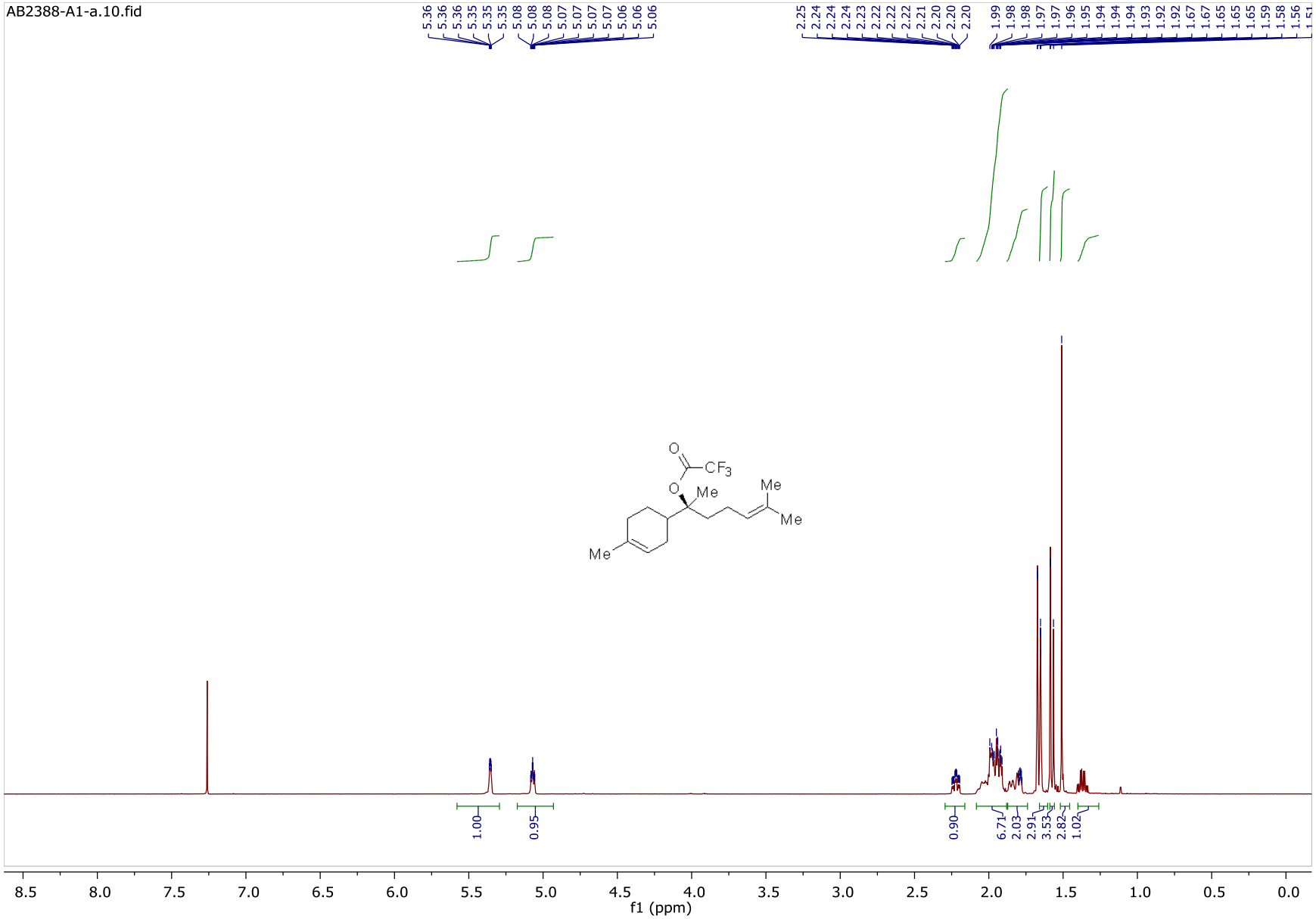

AB1740-A1-a.13.fid
135.85
135.79
130.86
130.64
123.29
123.16
122.34
121.54
38.81
34.90
34.60
30.99
25.73
25.61
24.77
24.73
22.61
22.57
22.45
18.56
18.55
16.76
16.63
14.91
nC7F15
Me
Me
Me
O
O
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

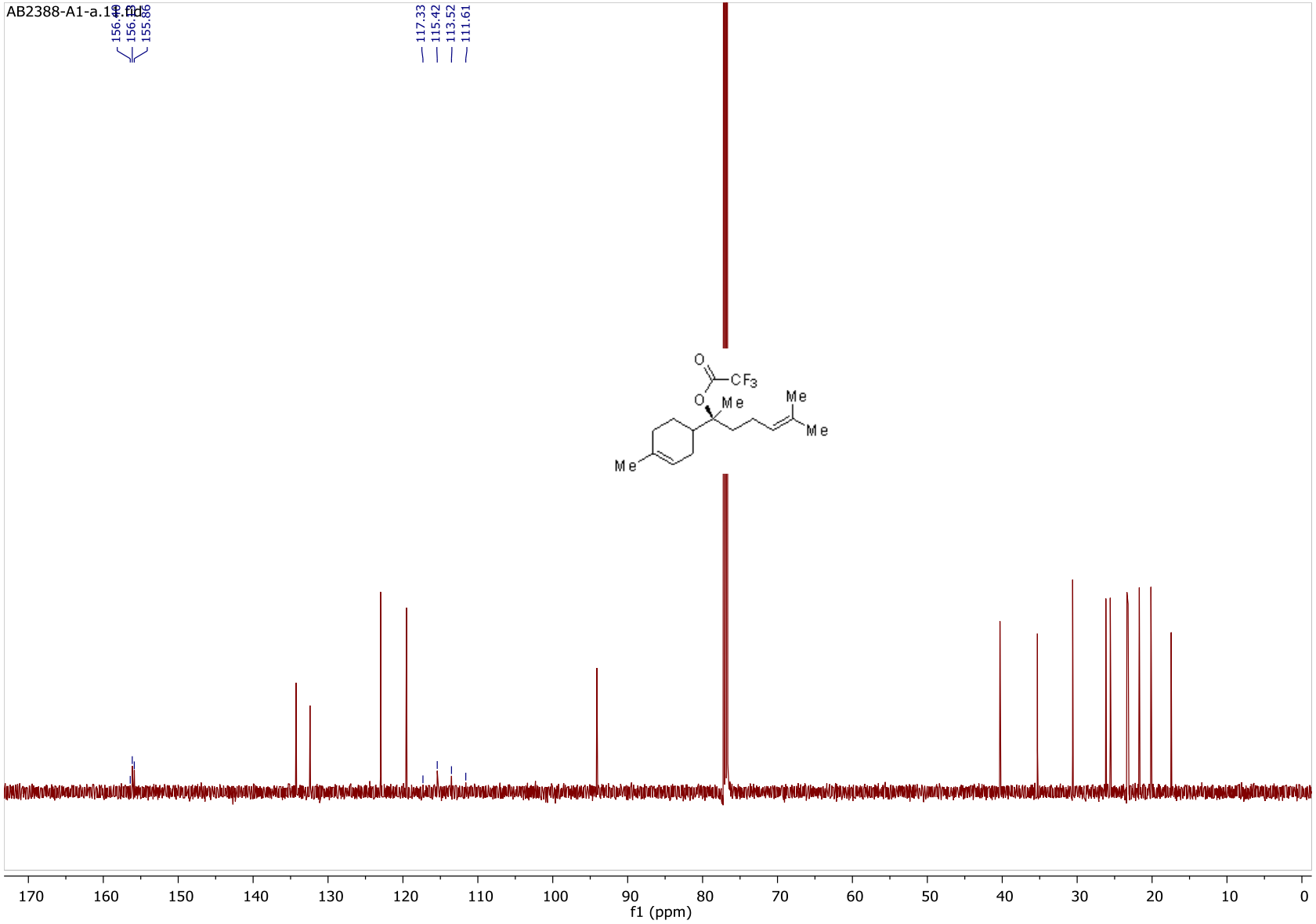

AB2496-A1-a-10-f1
O
C7F15
O
Me
Me
H
H
H
H
TBDPSO
4.07
2.02
3.97
2.02
1.00
1.00
0.83
0.50
0.76
14.42
4.45
3.82
9.23
2.97
3.45
7.09
2.91
f1 (ppm)

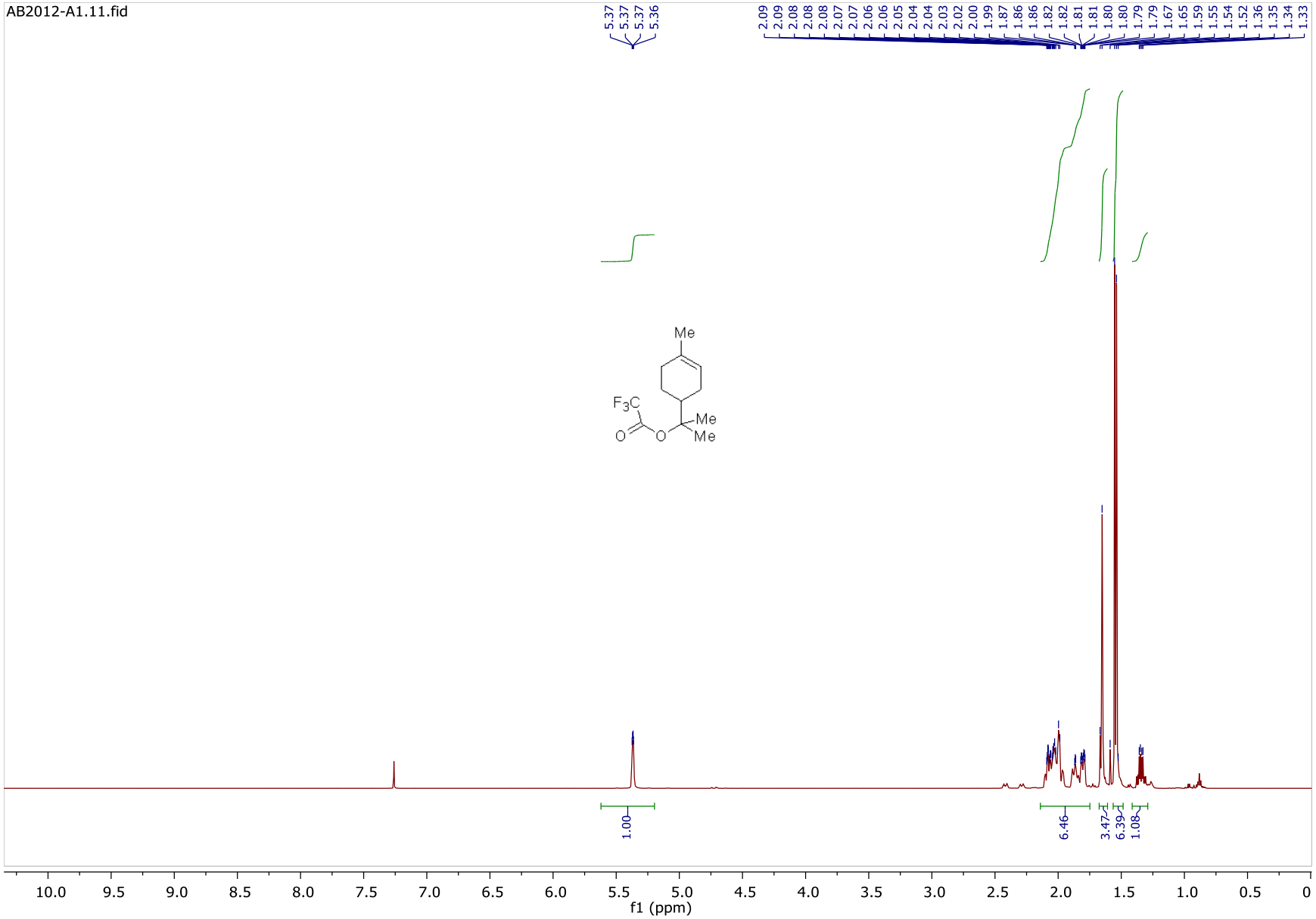

AB2490-A1-a.11.fid
157.89
141.25
135.73
135.71
134.81
134.78
129.37
129.35
127.40
127.37
121.04
77.09
77.05
73.22
56.69
55.89
49.99
42.45
42.26
39.70
37.16
36.44
35.79
35.77
35.54
35.44
31.84
31.81
28.14
28.12
26.97
24.17
21.48
20.96
19.47
19.38
19.36
19.10
18.43
18.38
11.73
O
C7F15
O
Me
Me
H
H
H
H
TBDPSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

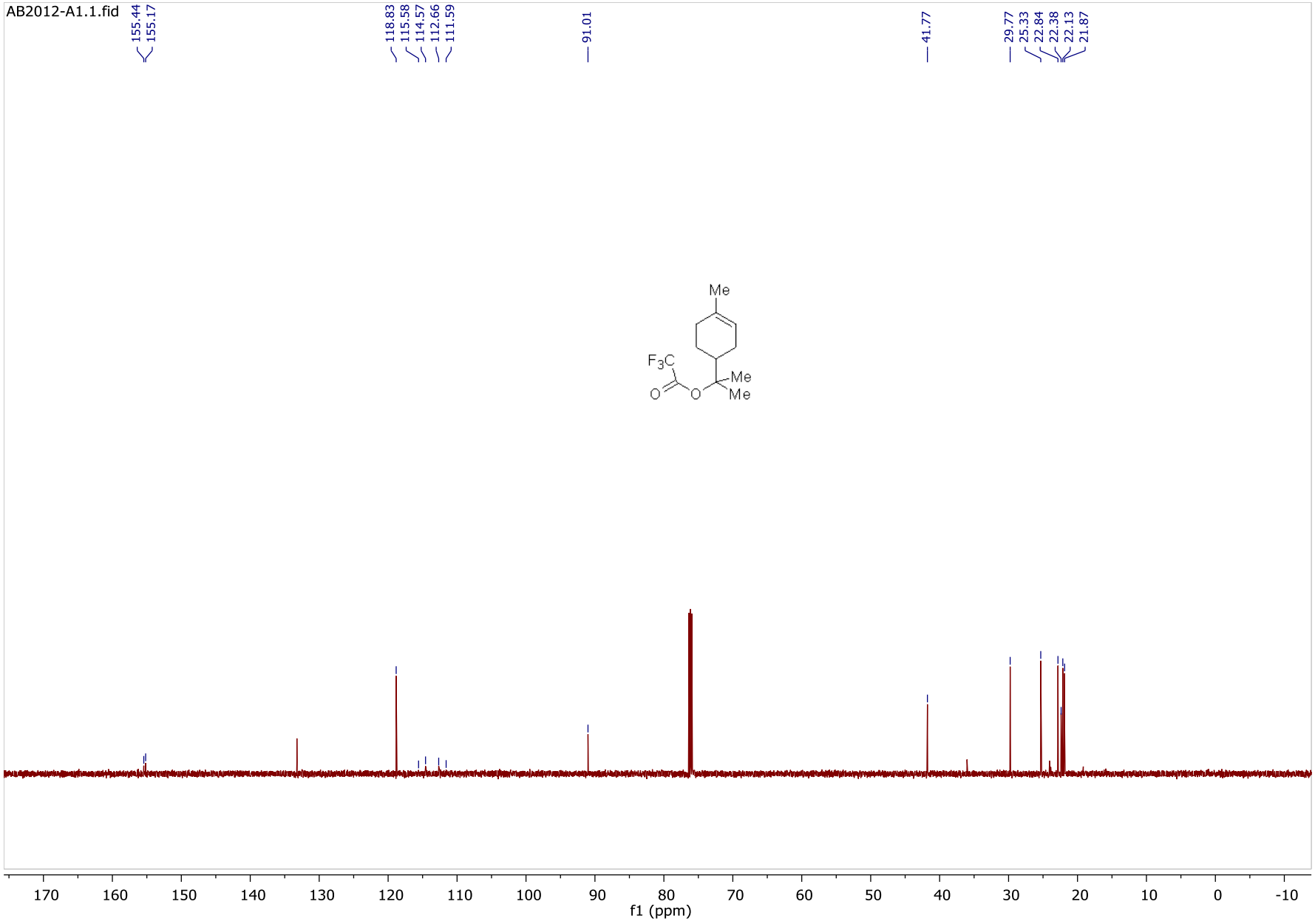

AB1768-A1-a.1.fid
7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.26 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.20 7.19
2.71 2.70 2.69 2.69 2.68 2.18 2.17 2.17 2.17 2.16 2.15 1.74 1.65 1.64 1.63 1.62 1.53
CF3
O
O
Me
Me
2.00
2.99
2.08
1.93
6.28
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

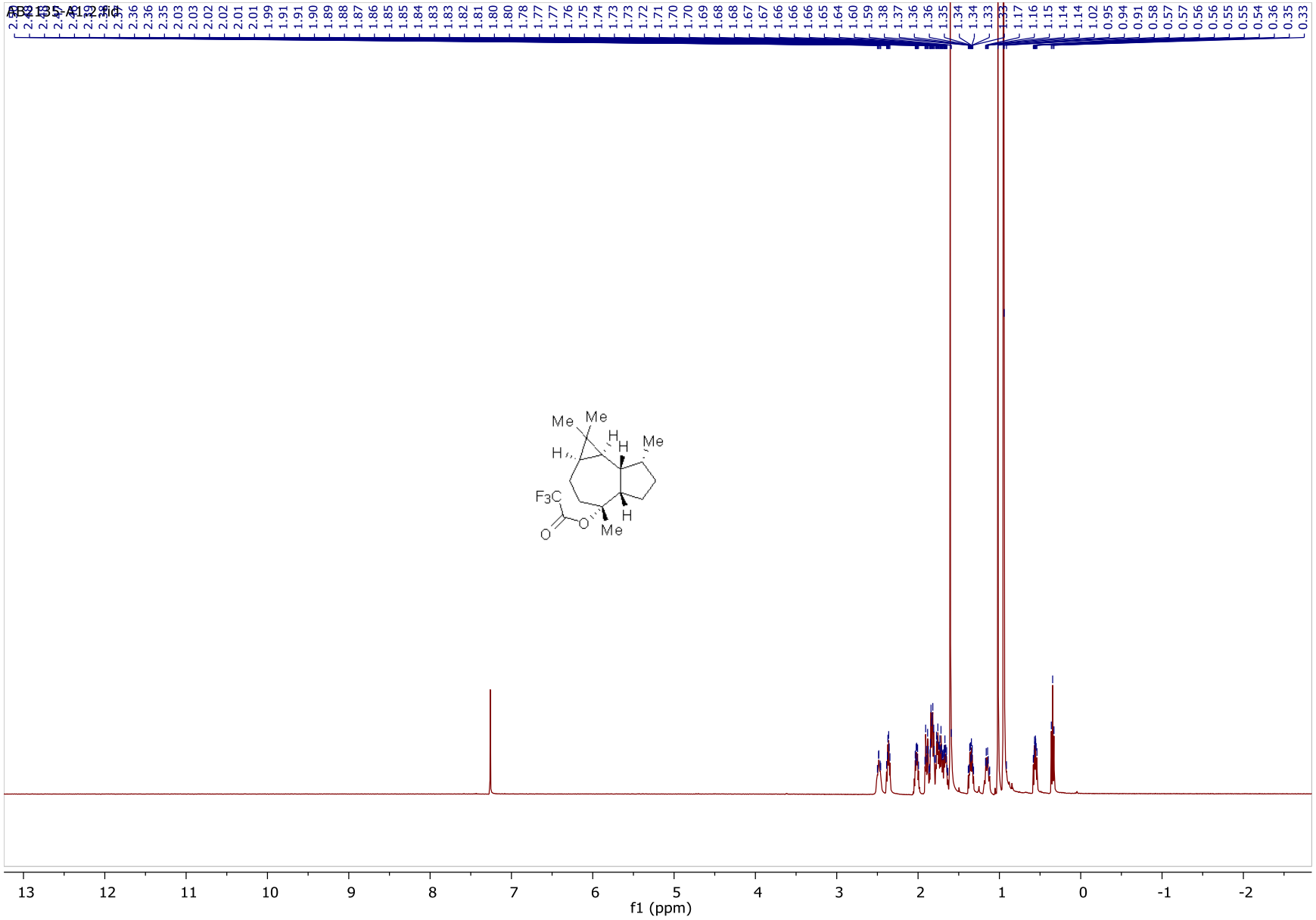

AB1768-A1-a.13.fid
156.60
156.33
156.06
155.78
141.07
128.51
128.49
128.48
128.40
128.25
128.23
126.09
117.28
115.37
113.47
111.57
88.63
77.20
76.99
76.77
42.40
30.06
25.52
CF3
O
O
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

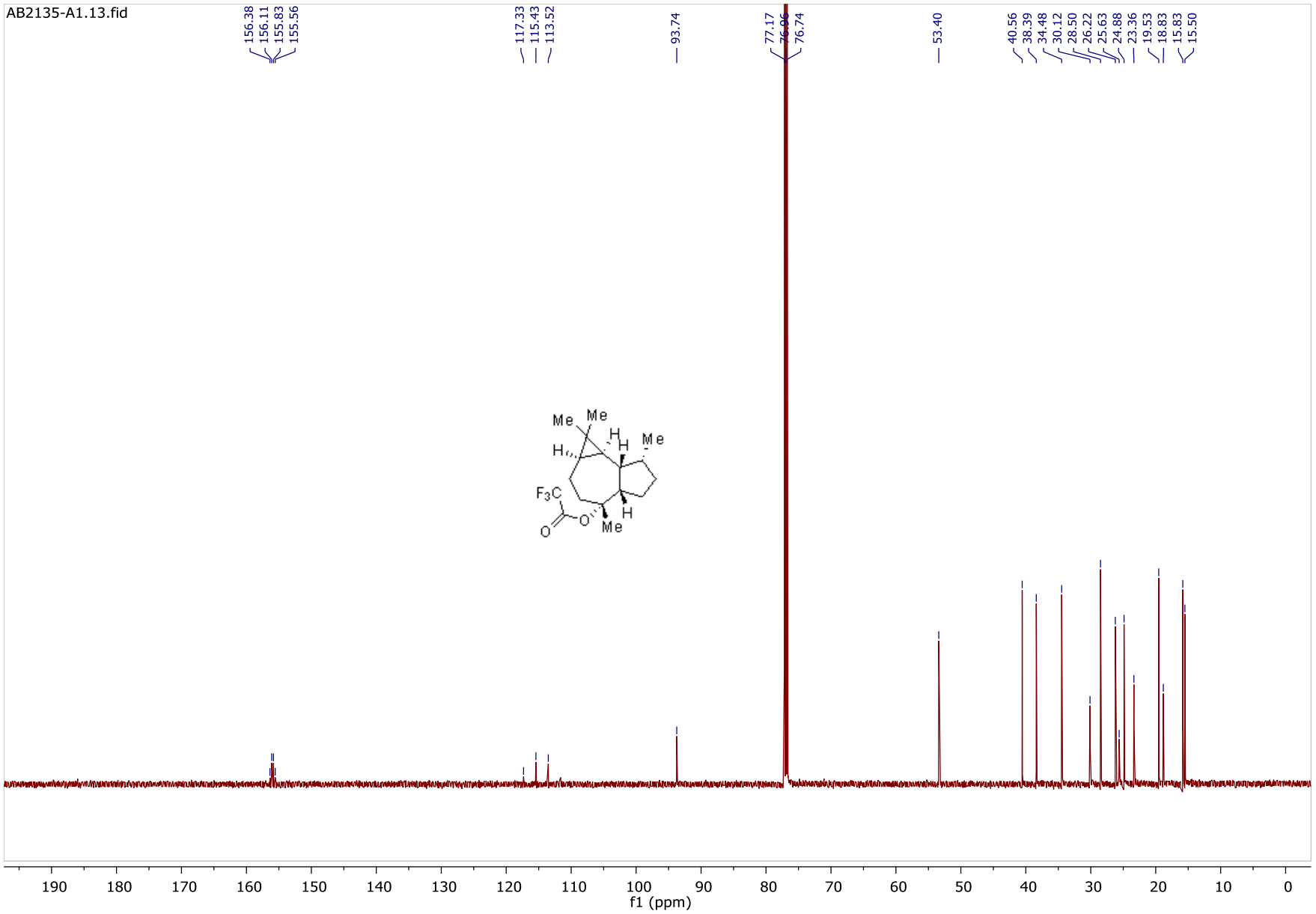

AB2388-A1-a.10.fid
5.36 5.36 5.36 5.35 5.35 5.35 5.08 5.08 5.08 5.07 5.07 5.07 5.06 5.06 5.06
2.25 2.24 2.24 2.24 2.23 2.22 2.22 2.22 2.21 2.20 2.20 2.20
1.99 1.98 1.98 1.97 1.97 1.96 1.95 1.94 1.94 1.94 1.93 1.92 1.92 1.67 1.67 1.65 1.65 1.65 1.59 1.58 1.56
O
CF3
O
Me
Me
Me
Me
1.00
0.95
0.90
6.71
2.03
2.91
3.53
2.82
1.02
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)

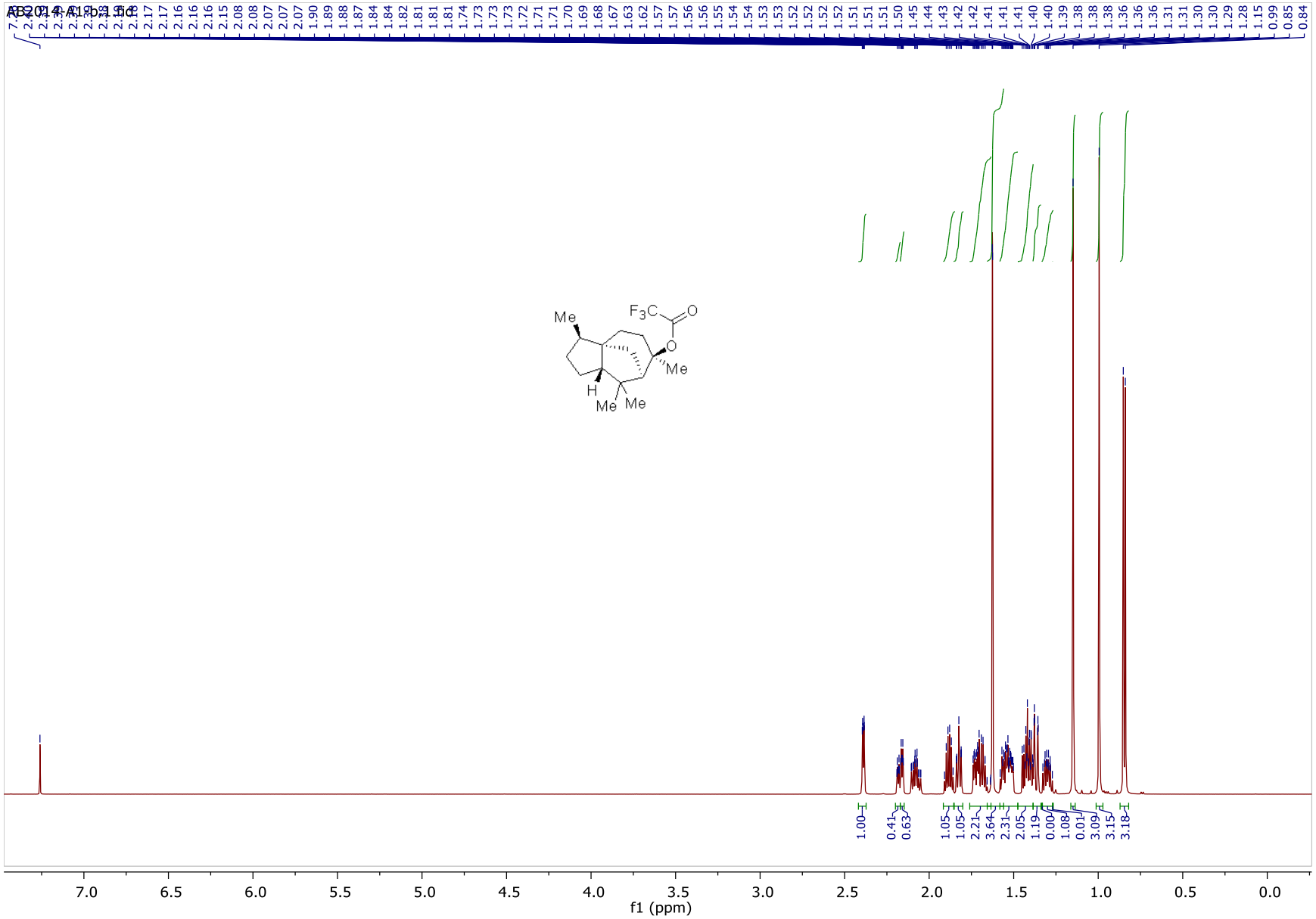

AB2388-A1-a.11.fid
156.41
156.16
155.86
117.33
115.42
113.52
111.61
O
CF3
O
Me
Me
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

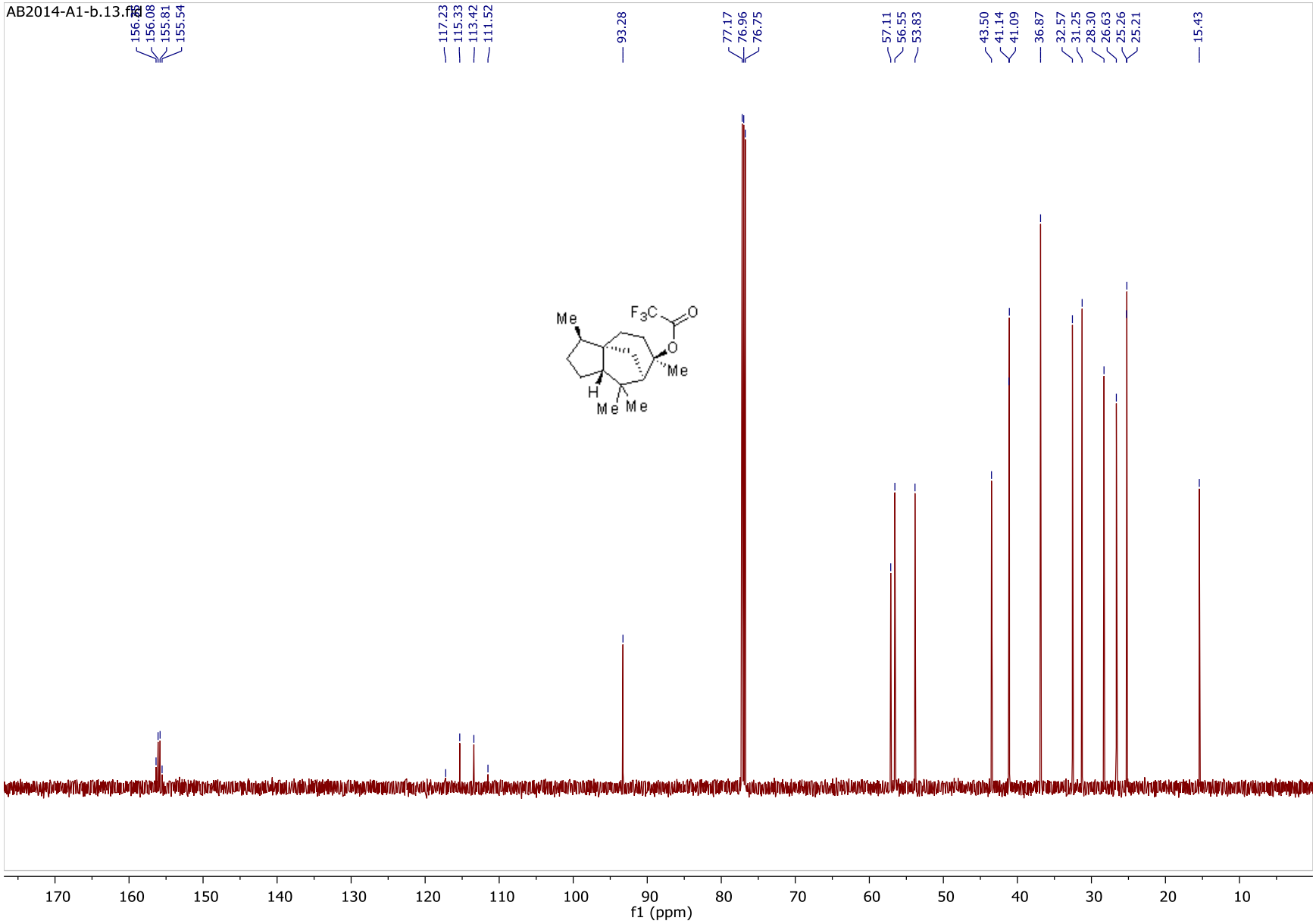

AB2012-A1.11.fid
5.37
5.37
5.37
5.36
2.09
2.09
2.08
2.08
2.08
2.07
2.07
2.06
2.06
2.05
2.04
2.04
2.03
2.02
2.00
1.99
1.87
1.86
1.86
1.82
1.82
1.81
1.81
1.80
1.80
1.79
1.79
1.67
1.65
1.59
1.55
1.54
1.52
1.36
1.35
1.34
1.33
Me
F3C
O
O
Me
Me
1.00
6.46
3.47
6.39
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

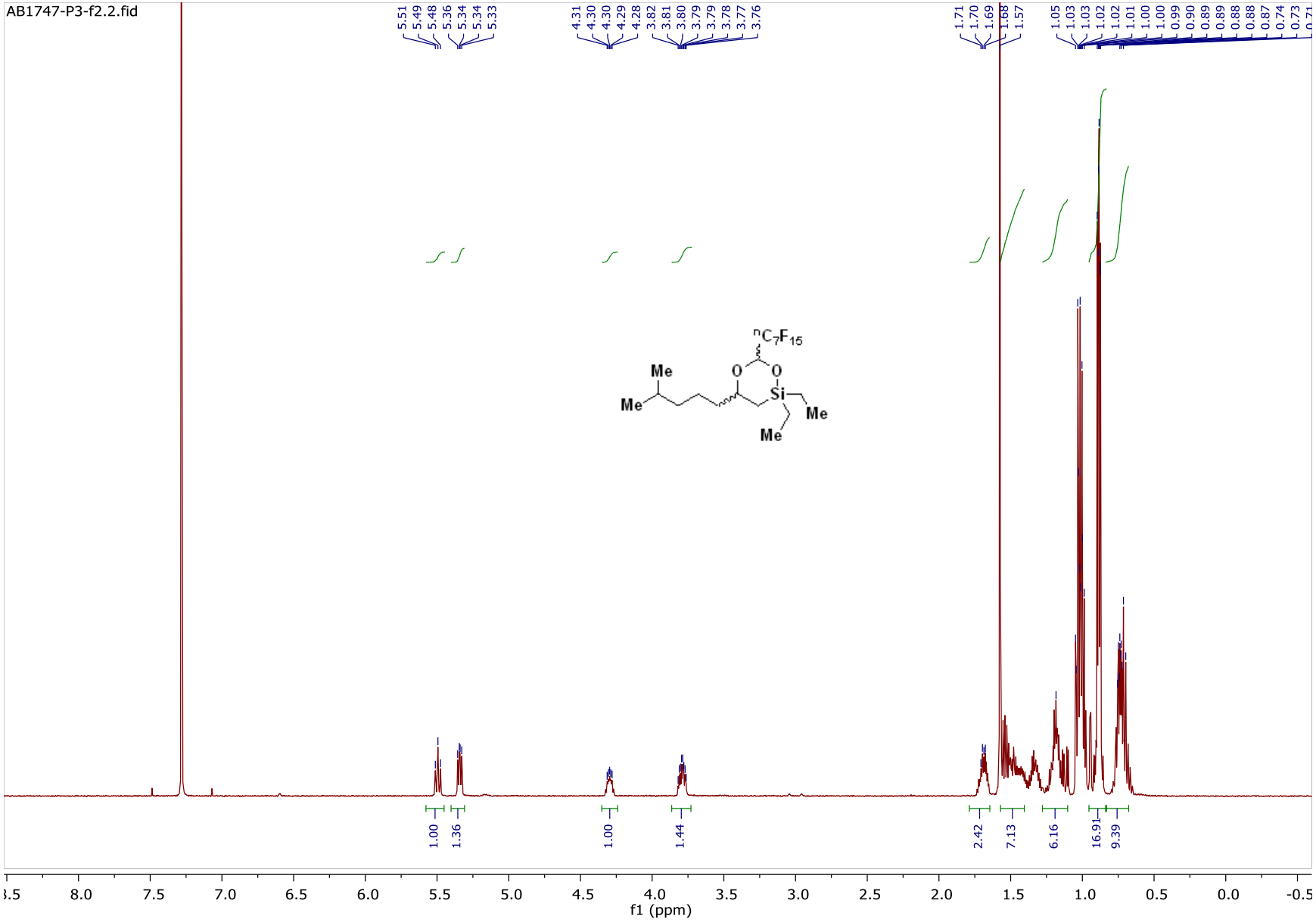

AB2012-A1.1.fid
155.44
155.17
118.83
115.58
114.57
112.66
111.59
91.01
41.77
29.77
25.33
22.84
22.38
22.13
21.87
Me
F3C
O
O
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

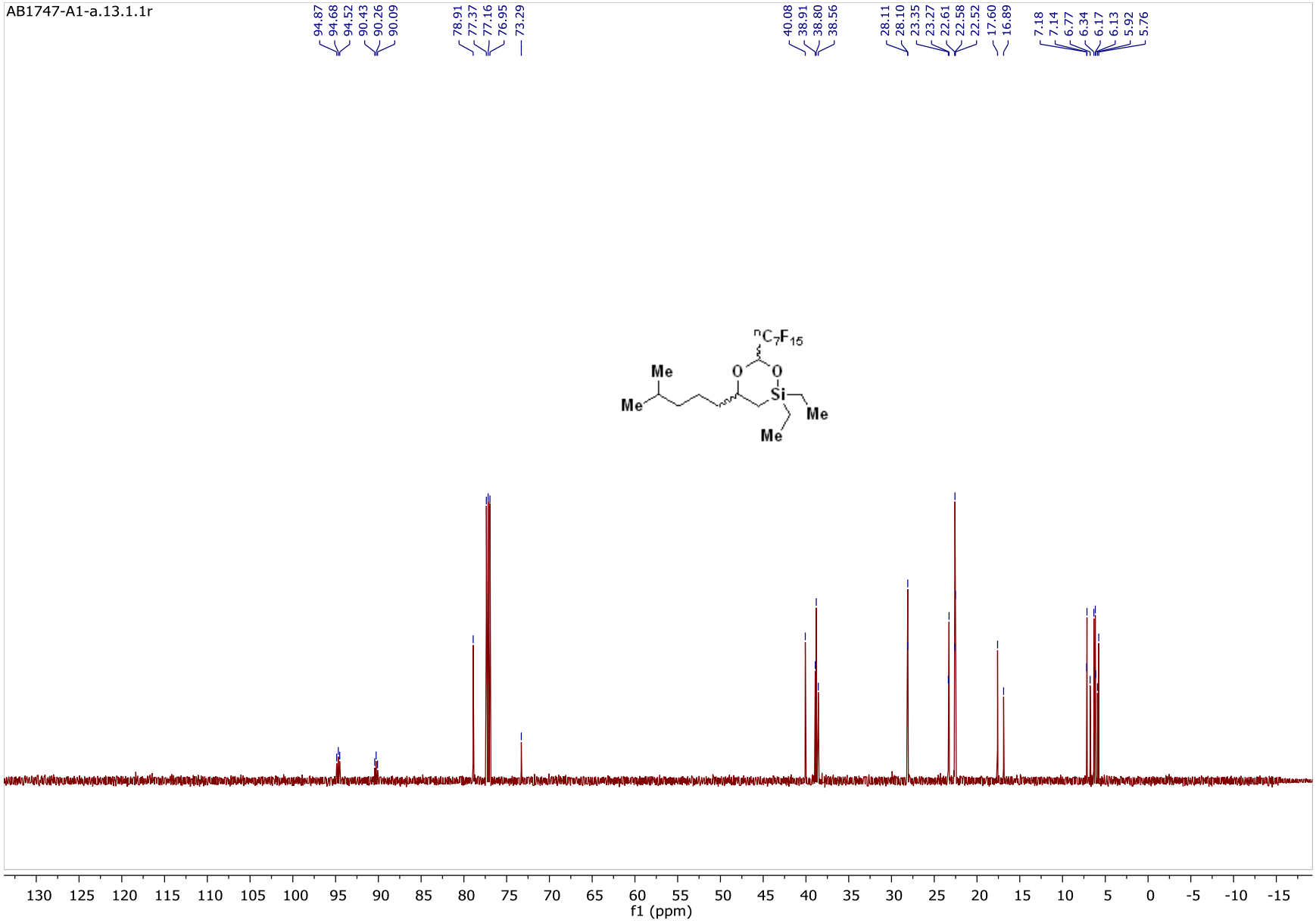

AB2135-A1-2-fid
Me
Me
H
H
Me
H
F3C
O
O
H
Me
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

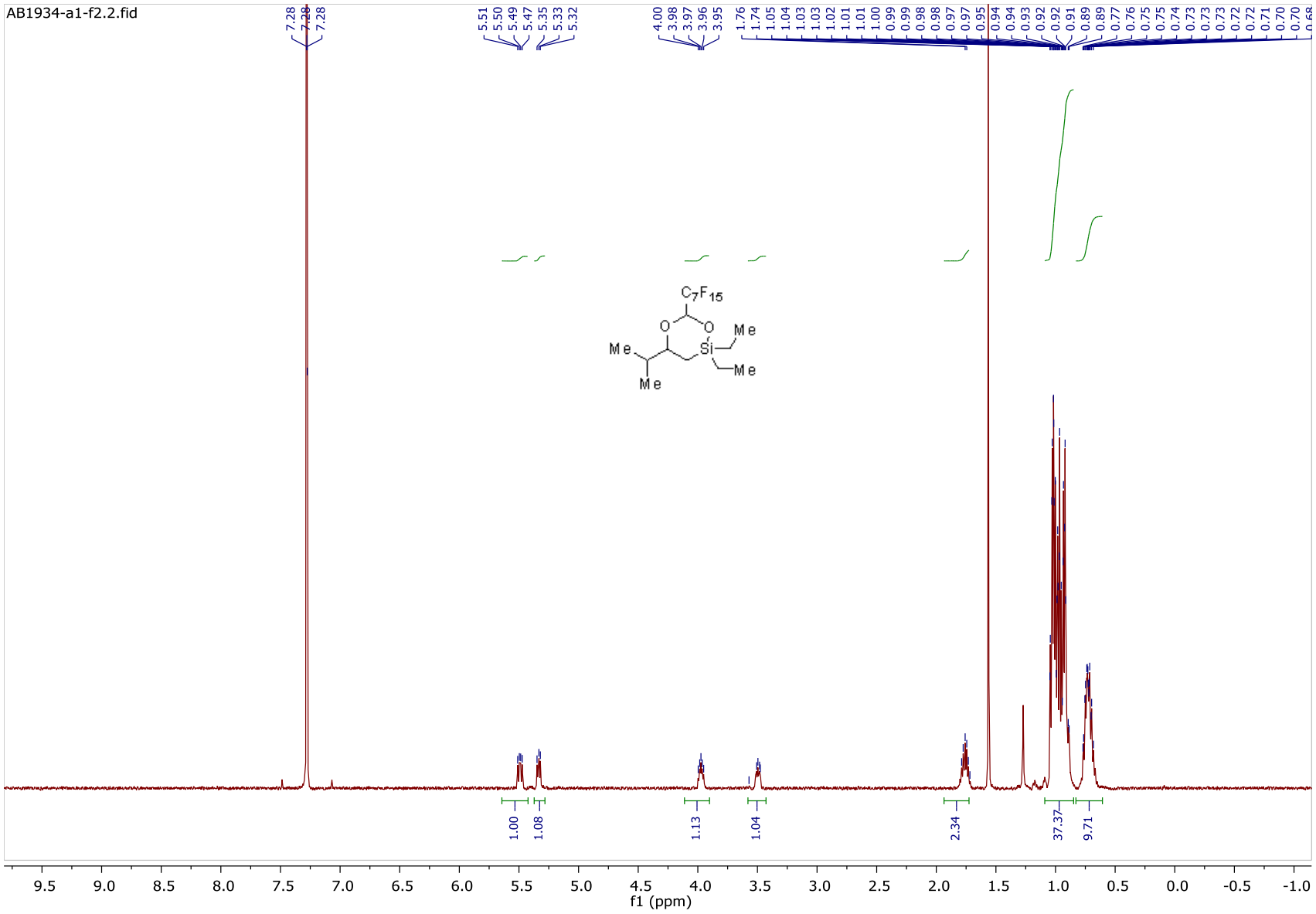

AB2135-A1.13.fid
156.38
156.11
155.83
155.56
117.33
115.43
113.52
93.74
77.17
76.96
76.74
53.40
40.56
38.39
34.48
30.12
28.50
26.22
25.63
24.88
23.36
19.53
18.83
15.83
15.50
Me
Me
H
H
Me
H
F3C
O
O
H
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

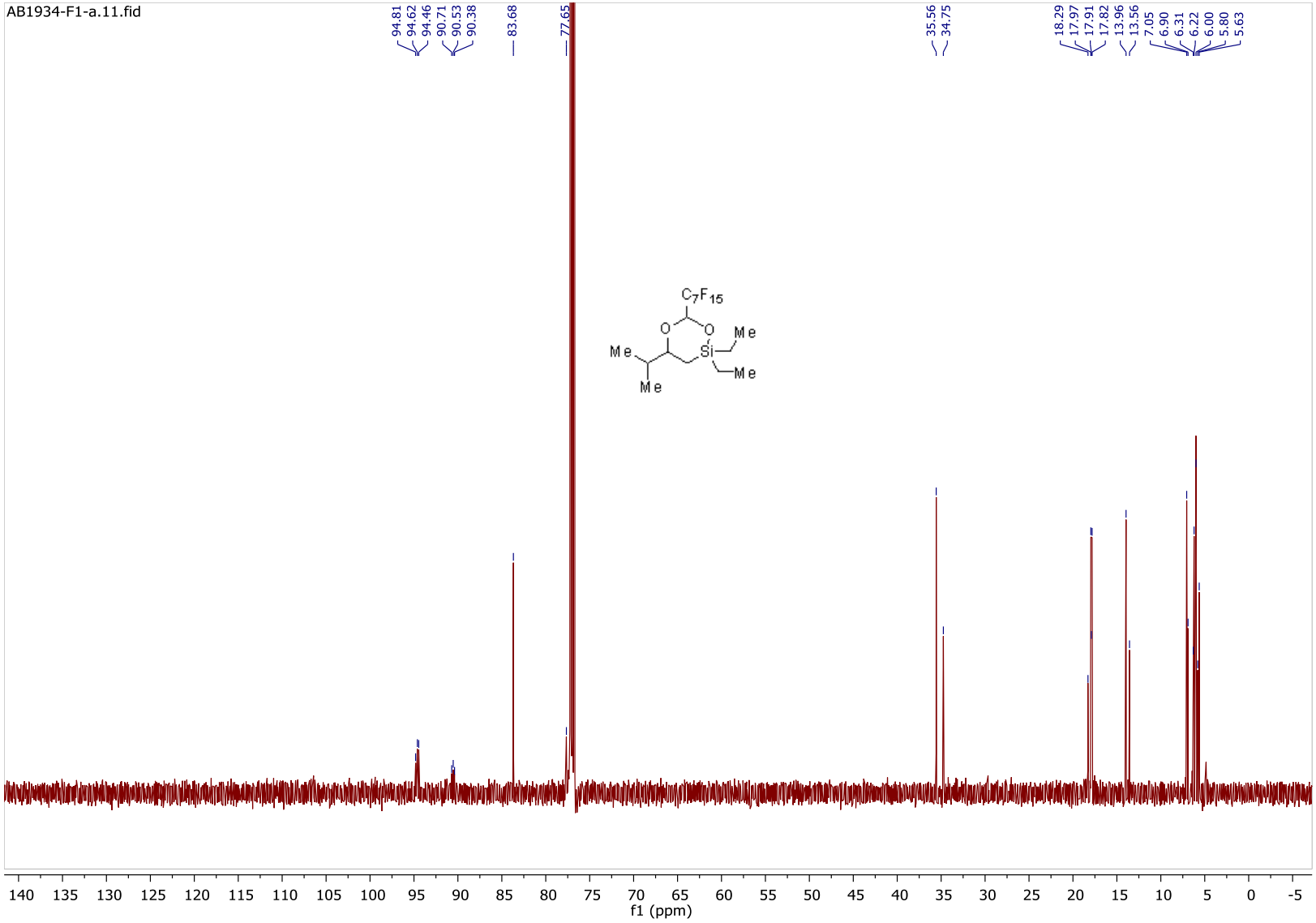

AB2014-A12b1.fid
Me
F3C
O
O
Me
H
Me
Me
1.00
0.41
0.63
1.05
1.05
2.21
3.64
2.31
2.05
1.19
0.00
1.08
0.01
3.09
3.15
3.18
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

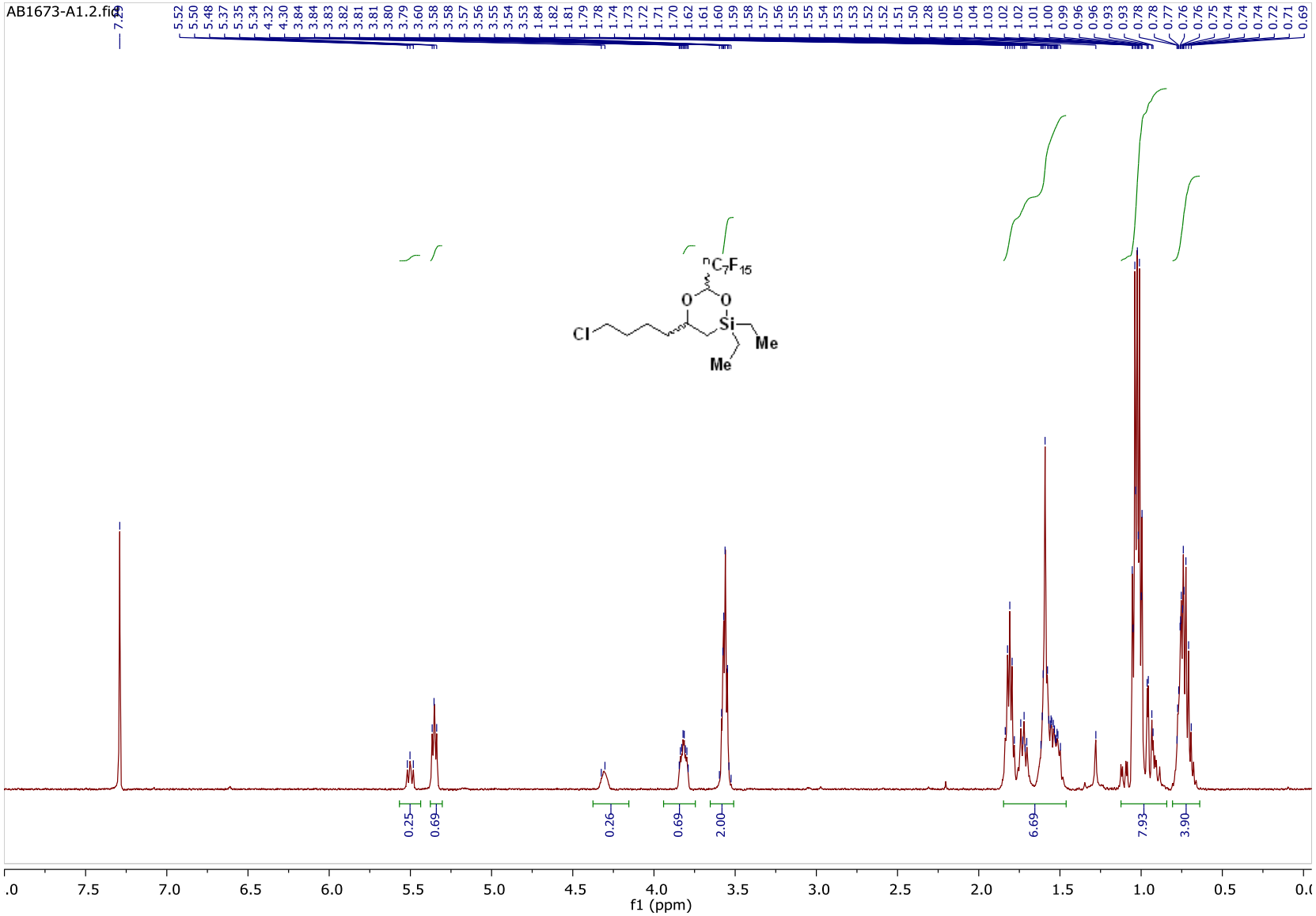

AB2014-A1-b.13.fid
156.28
156.08
155.81
155.54
117.23
115.33
113.42
111.52
93.28
77.17
76.96
76.75
57.11
56.55
53.83
43.50
41.14
41.09
36.87
32.57
31.25
28.30
26.63
25.26
25.21
15.43
Me
F3C
O
O
Me
H
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

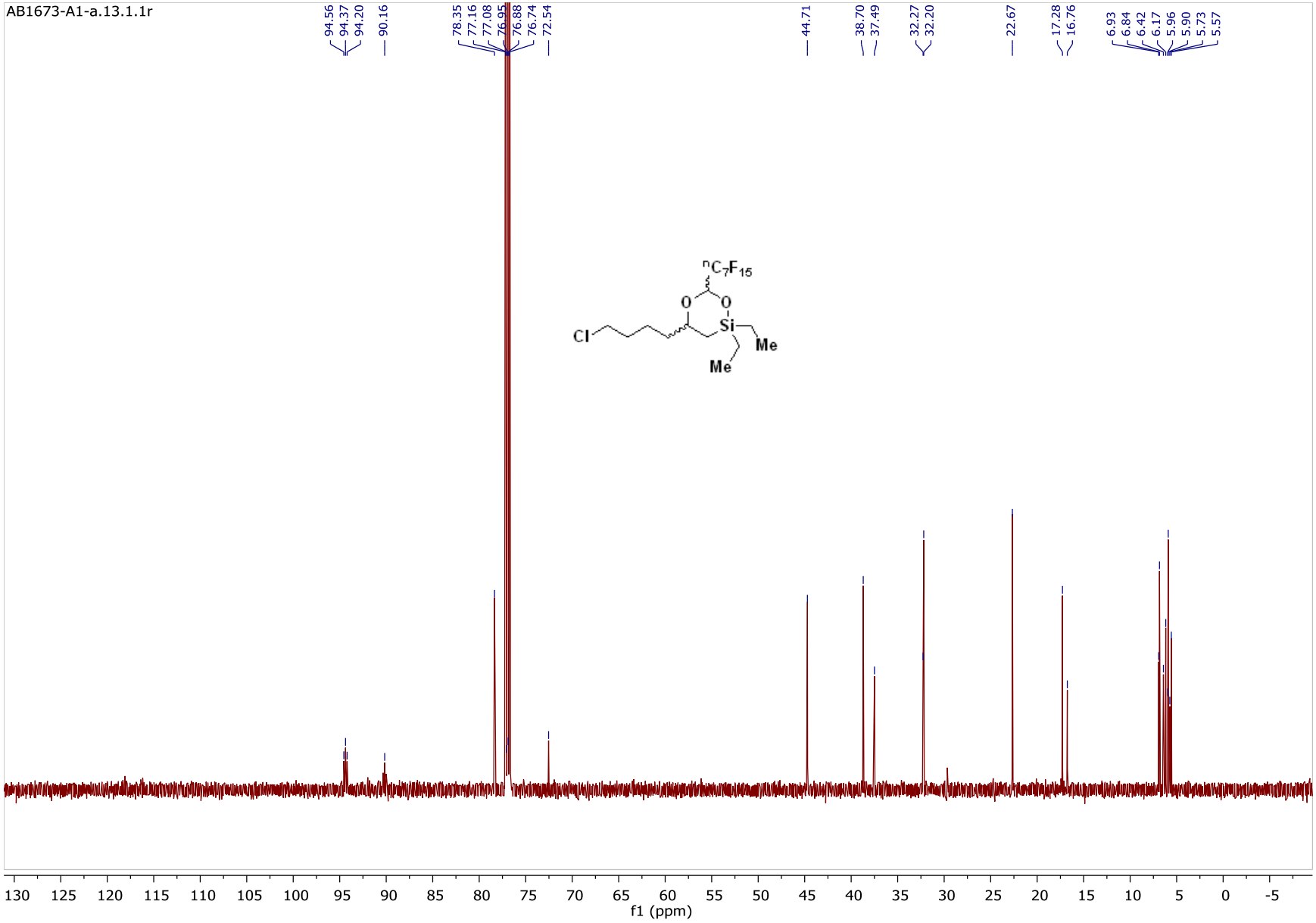

AB1747-P3-f2.2.fid
5.51 5.49 5.48 5.36 5.34 5.34 5.33
4.31 4.30 4.30 4.29 4.28 3.82 3.81 3.80 3.79 3.79 3.78 3.77 3.76
1.71 1.70 1.69 1.68 1.57
1.05 1.03 1.03 1.02 1.02 1.01 1.00 1.00 0.99 0.90 0.89 0.89 0.88 0.88 0.87 0.74 0.73
nC7F15
Me
Me
O
O
Si
Me
Me
1.00 1.36 1.00 1.44 2.42 7.13 6.16 16.91 9.39
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

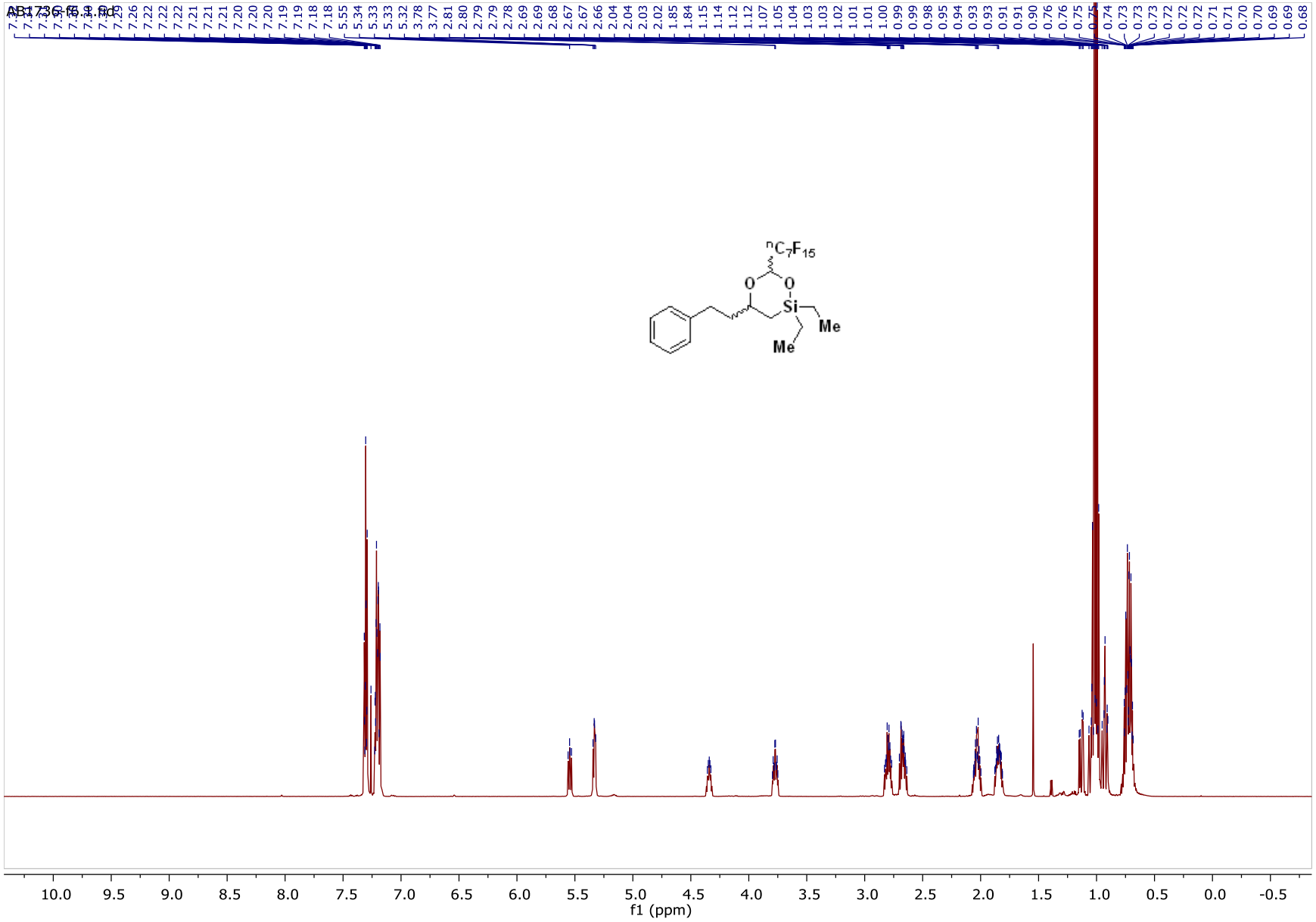

AB1747-A1-a.13.1.1r
94.87
94.68
94.52
90.43
90.26
90.09
78.91
77.37
77.16
76.95
73.29
40.08
38.91
38.80
38.56
28.11
28.10
23.35
23.27
22.61
22.58
22.52
17.60
16.89
7.18
7.14
6.77
6.34
6.17
6.13
5.92
5.76
nC7F15
Me
Me
O
O
Si
Me
Me
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

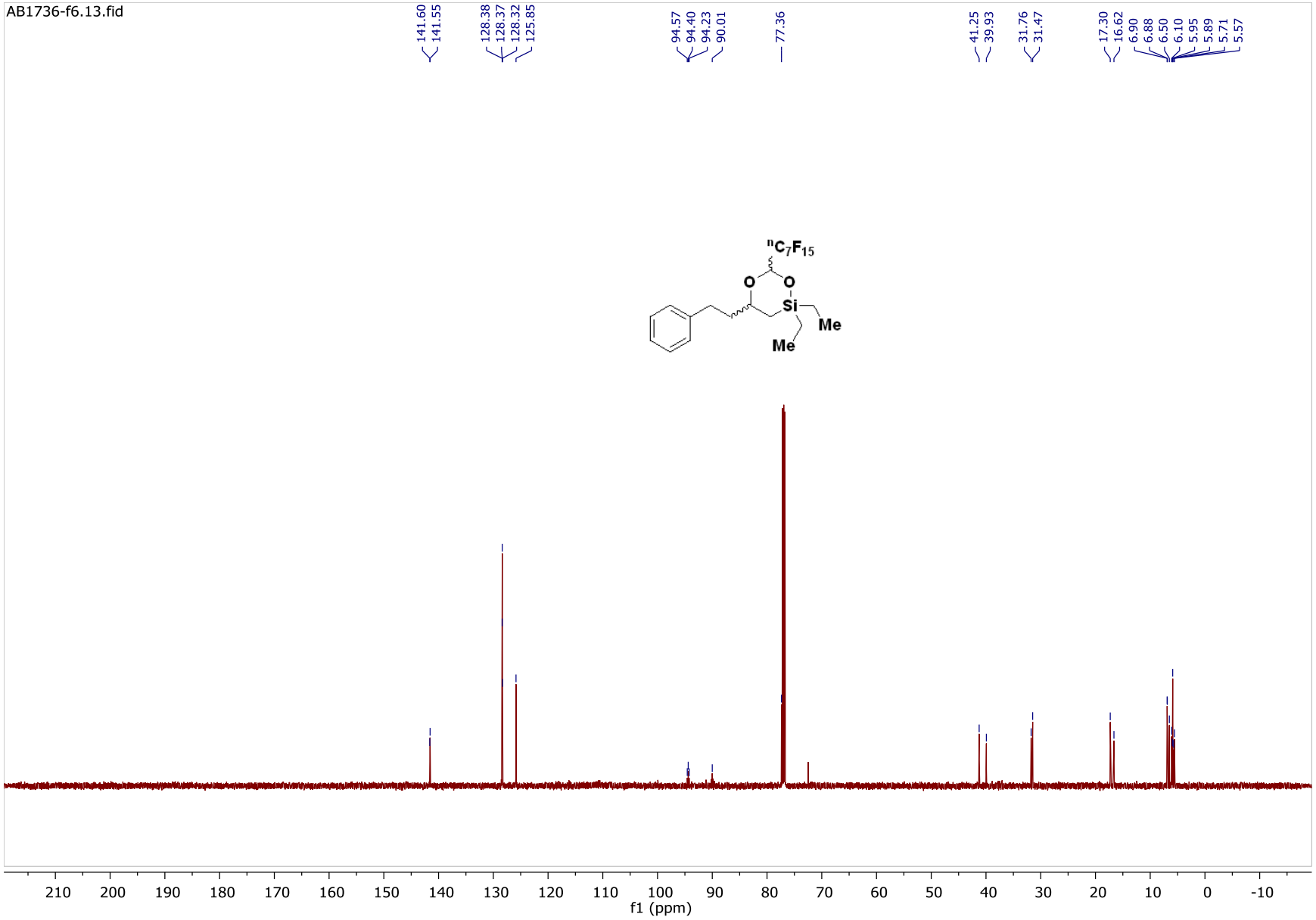

AB1934-a1-f2.2.fid
7.28
7.28
7.28
5.51
5.50
5.49
5.47
5.35
5.33
5.32
4.00
3.98
3.97
3.96
3.95
1.76
1.74
1.05
1.04
1.03
1.03
1.02
1.01
1.01
1.00
0.99
0.99
0.98
0.98
0.97
0.97
0.95
0.94
0.94
0.93
0.92
0.92
0.91
0.89
0.89
0.77
0.76
0.75
0.75
0.74
0.73
0.73
0.72
0.72
0.71
0.70
0.70
C7F15
O
O
Si
Me
Me
Me
Me
1.00
1.08
1.13
1.04
2.34
37.37
9.71
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

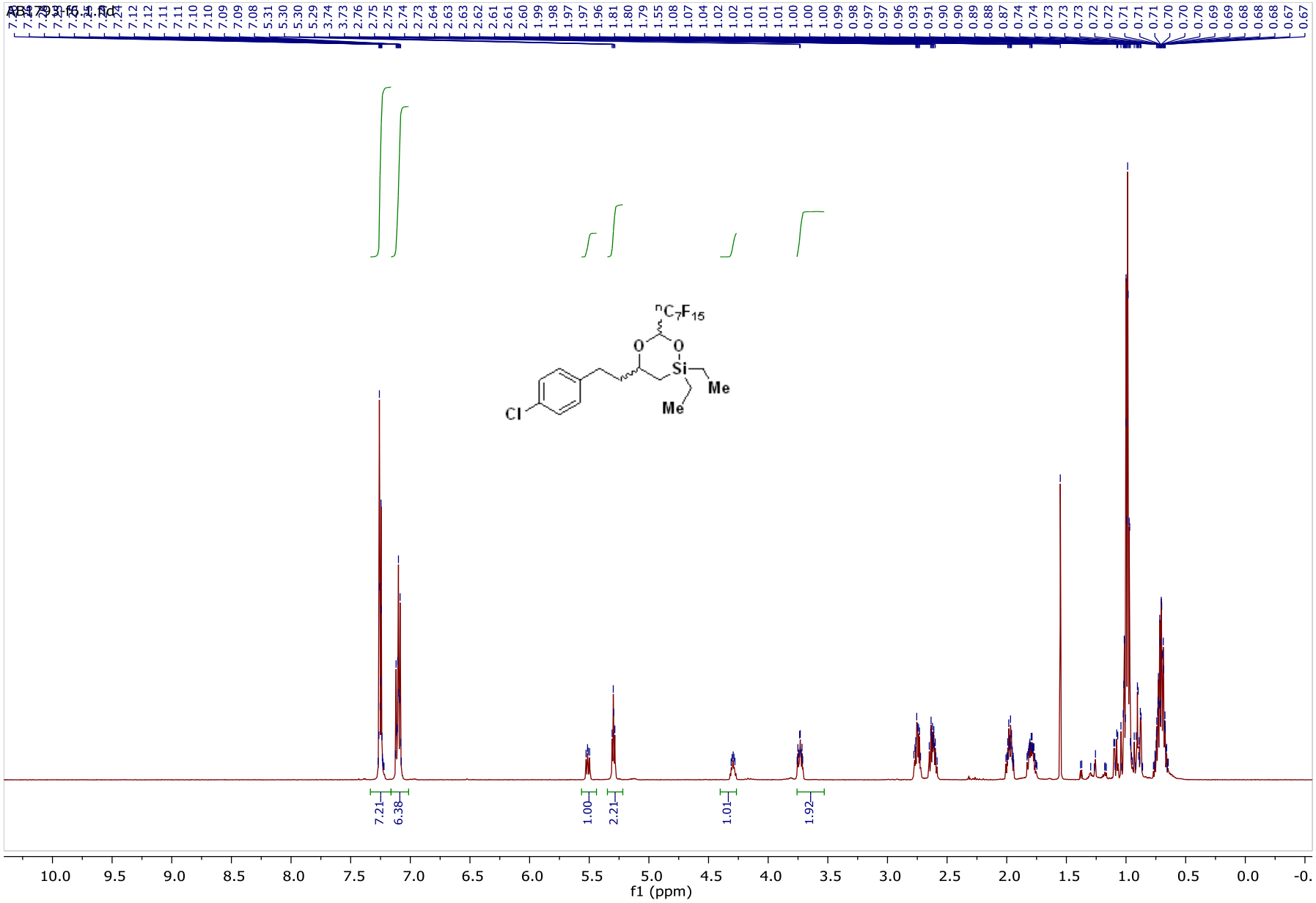

AB1934-F1-a.11.fid
94.81
94.62
94.46
90.71
90.53
90.38
83.68
77.65
35.56
34.75
18.29
17.97
17.91
17.82
13.96
13.56
7.05
6.90
6.31
6.22
6.00
5.80
5.63
C7F15
O
O
Si
Me
Me
Me
Me
Me
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

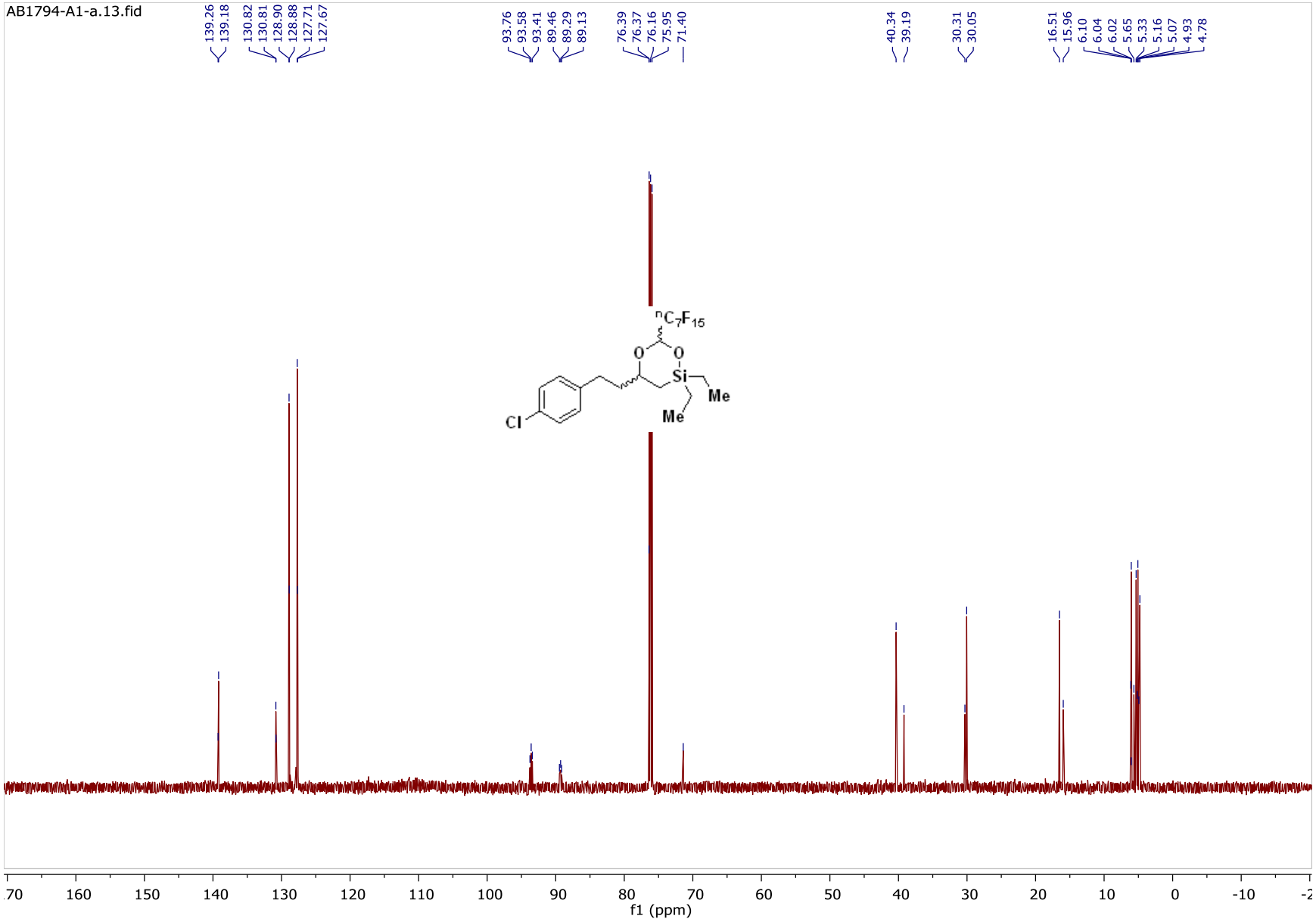

AB1673-A1.2.fid
f1 (ppm)
0.25
0.69
0.26
0.69
2.00
6.69
7.93
3.90

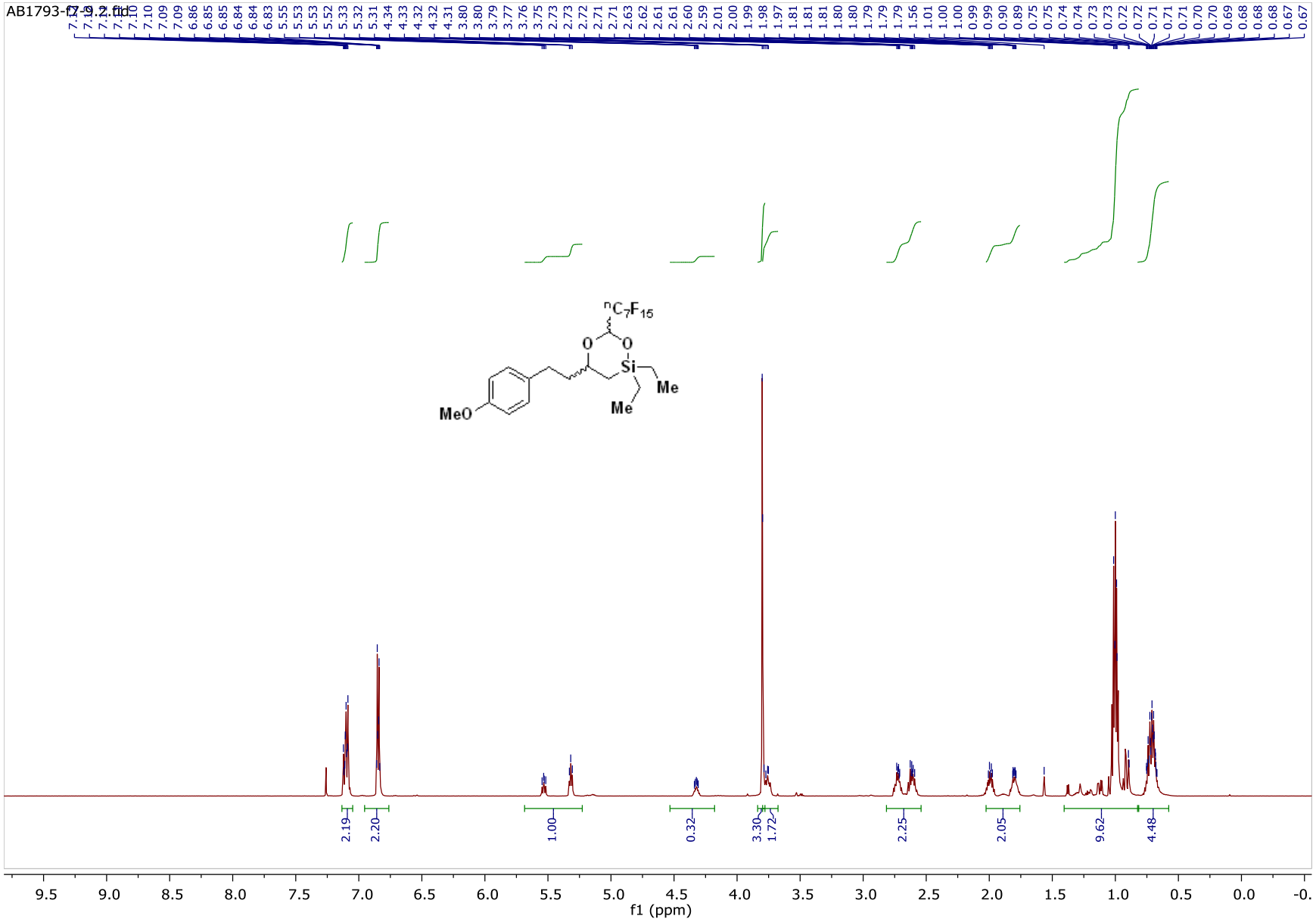

AB1673-A1-a.13.1.1r
94.56
94.37
94.20
90.16
78.35
77.16
77.08
76.95
76.88
76.74
72.54
44.71
38.70
37.49
32.27
32.20
22.67
17.28
16.76
6.93
6.84
6.42
6.17
5.96
5.90
5.73
5.57
nC7F15
O
O
Si
Cl
Me
Me
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

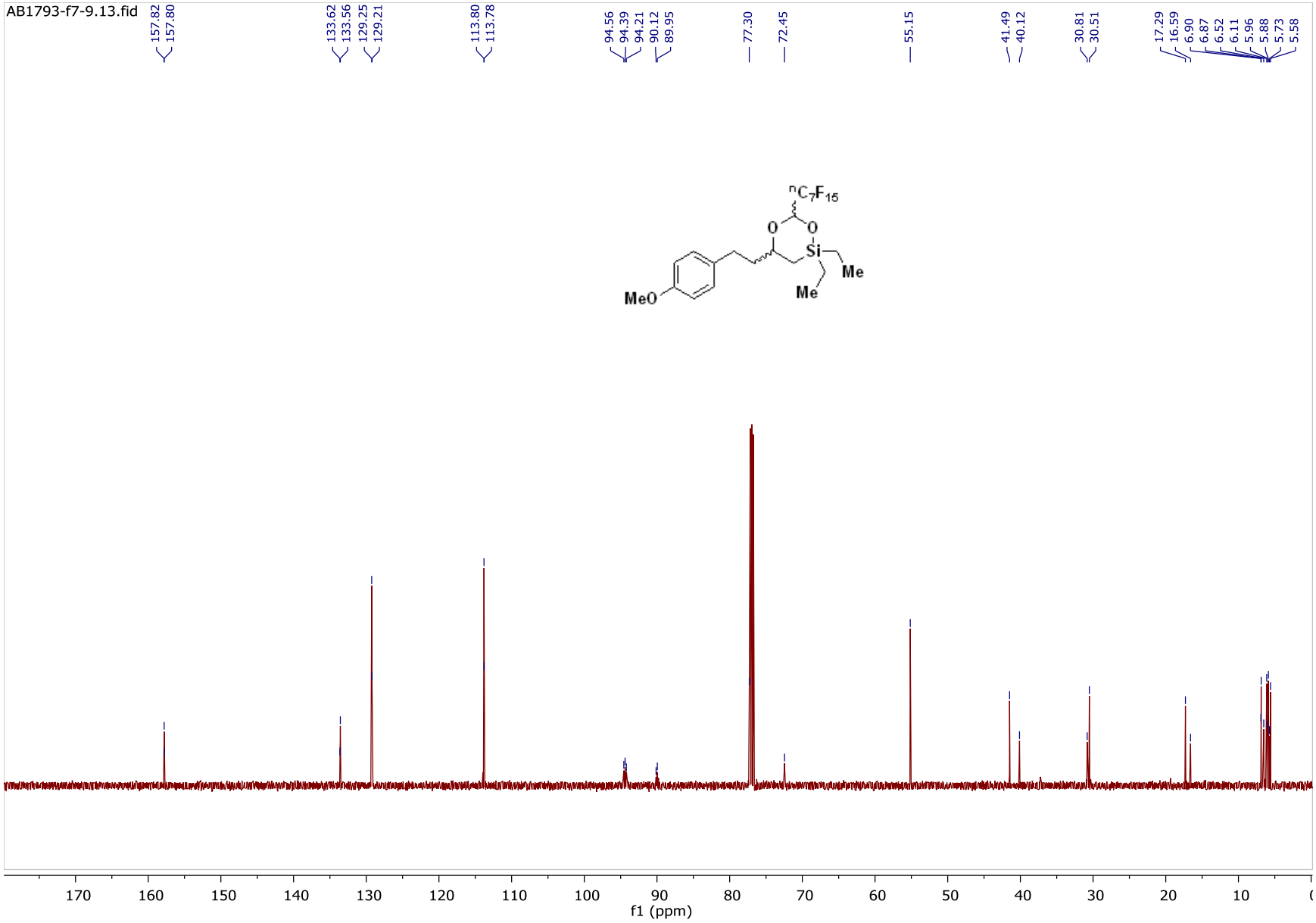

AB1736-6-1-8d
nC7F15
O
O
Si
Me
Me
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

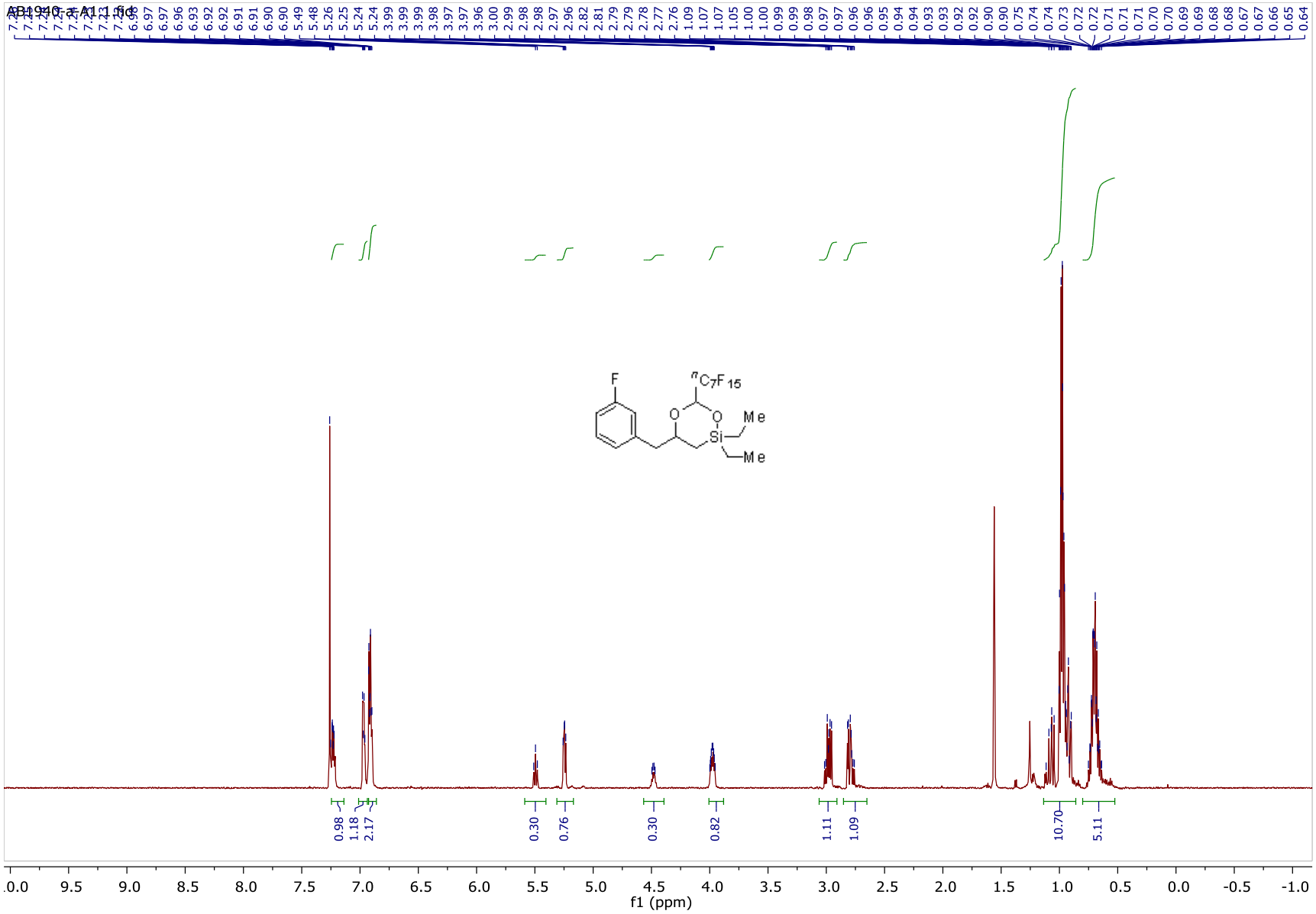

AB1736-f6.13.fid
141.60
141.55
128.38
128.37
128.32
125.85
94.57
94.40
94.23
90.01
77.36
41.25
39.93
31.76
31.47
17.30
16.62
6.90
6.88
6.50
6.10
5.95
5.89
5.71
5.57
$^{n}C_7F_{15}$
O
O
Si
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

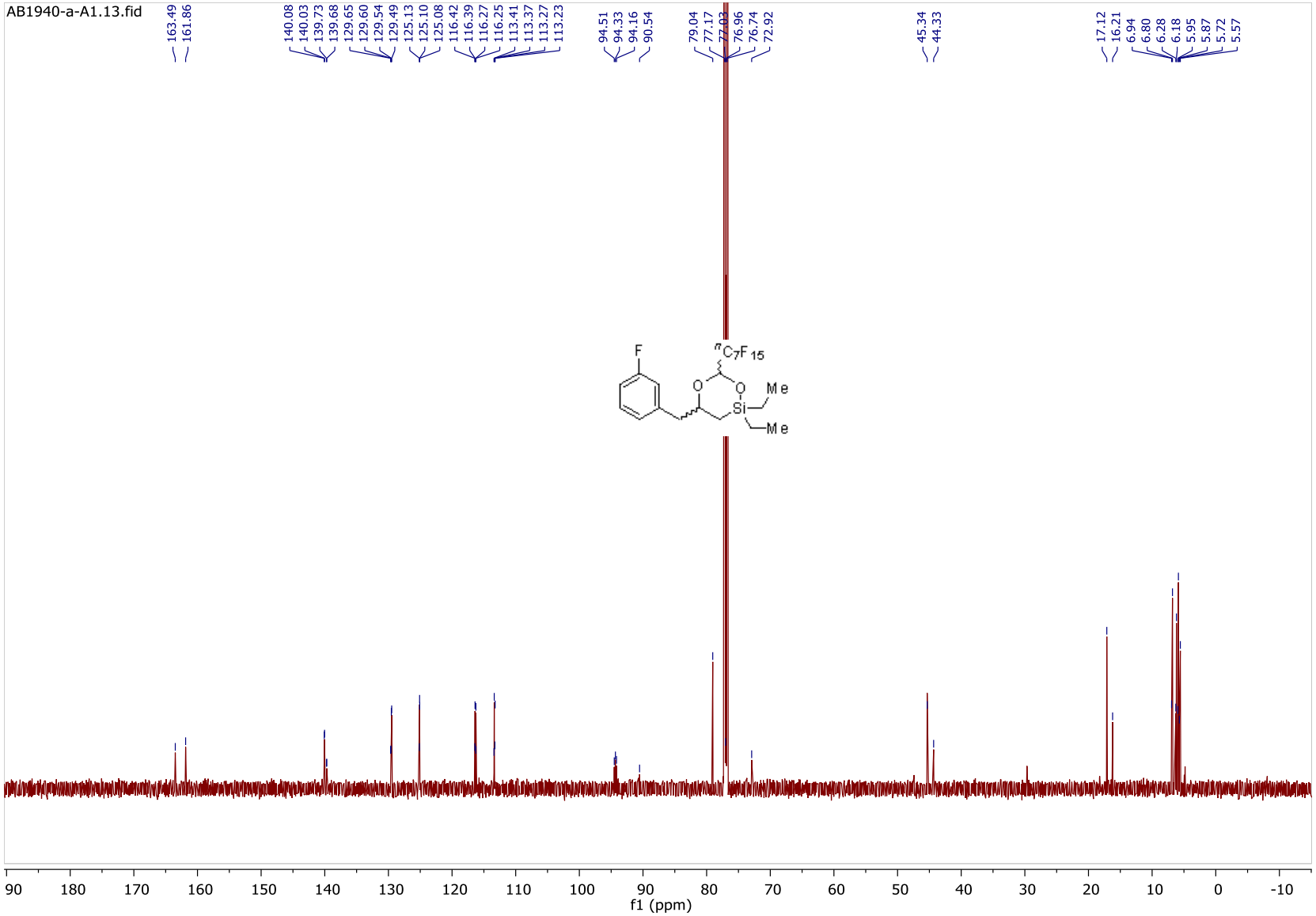

AB3793-f6-1.5d
nC7F15
O
O
Si
Me
Me
Cl
7.21
6.38
1.00
2.21
1.01
1.92
f1 (ppm)

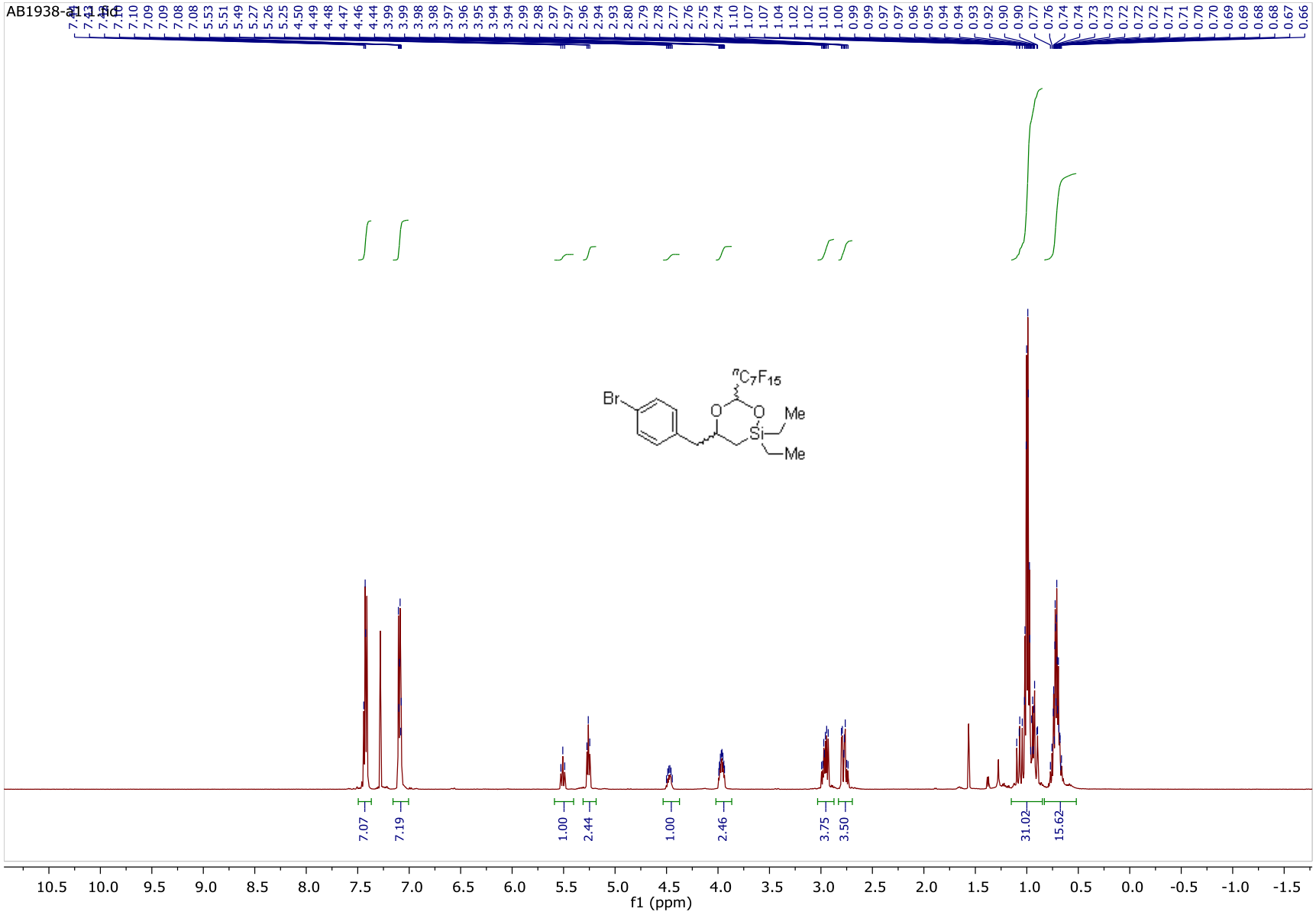

AB1794-A1-a.13.fid
139.26
139.18
130.82
130.81
128.90
128.88
127.71
127.67
93.76
93.58
93.41
89.46
89.29
89.13
76.39
76.37
76.16
75.95
71.40
40.34
39.19
30.31
30.05
16.51
15.96
6.10
6.04
6.02
5.65
5.33
5.16
5.07
4.93
4.78
nC7F15
O
O
Si
Me
Me
Cl
f1 (ppm)

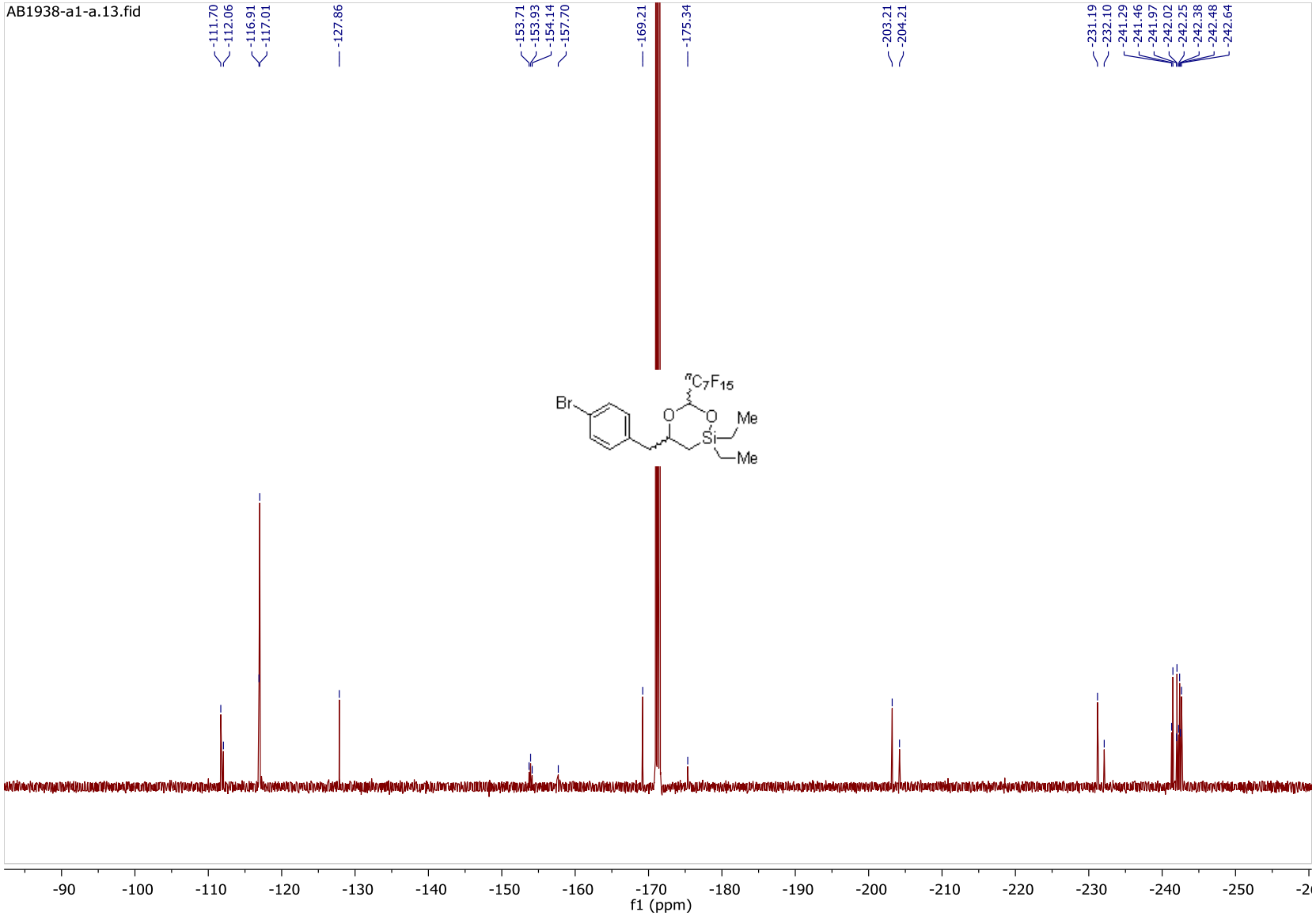

AB1793-f2-9.2.fid
nC7F15
O
O
Si
Me
Me
MeO
2.19
2.20
1.00
0.32
3.30
1.72
2.25
2.05
9.62
4.48
f1 (ppm)

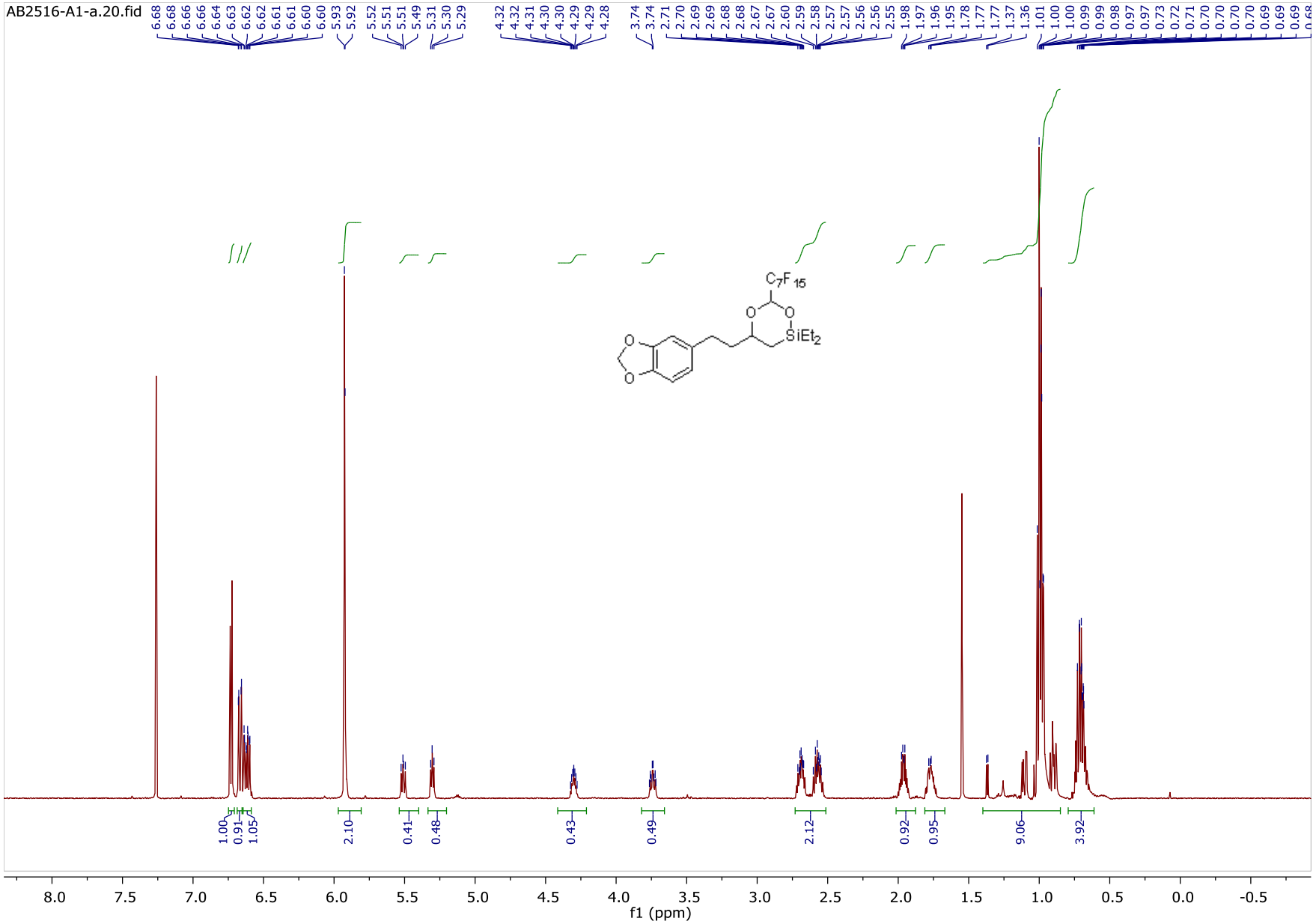

AB1793-f7-9.13.fid
157.82
157.80
133.62
133.56
129.25
129.21
113.80
113.78
94.56
94.39
94.21
90.12
89.95
77.30
72.45
55.15
41.49
40.12
30.81
30.51
17.29
16.59
6.90
6.87
6.52
6.11
5.96
5.88
5.73
5.58
nC7F15
O
O
Si
Me
Me
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

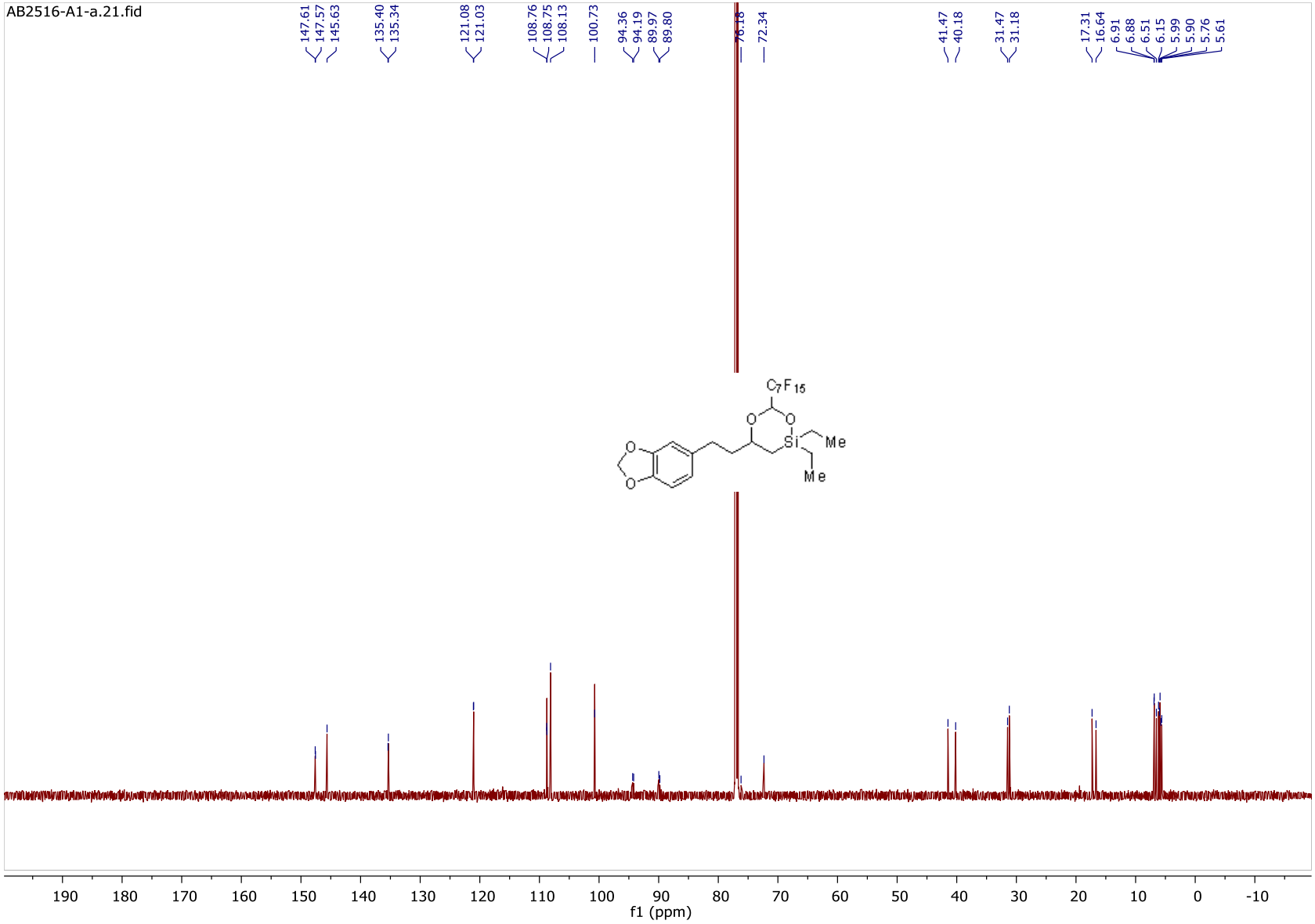

AB1916-1-A1.1.fid
F
$^{n}C_7F_{15}$
O
O
Si
Me
Me
0.98
1.18
2.17
0.30
0.76
0.30
0.82
1.11
1.09
10.70
5.11
f1 (ppm)

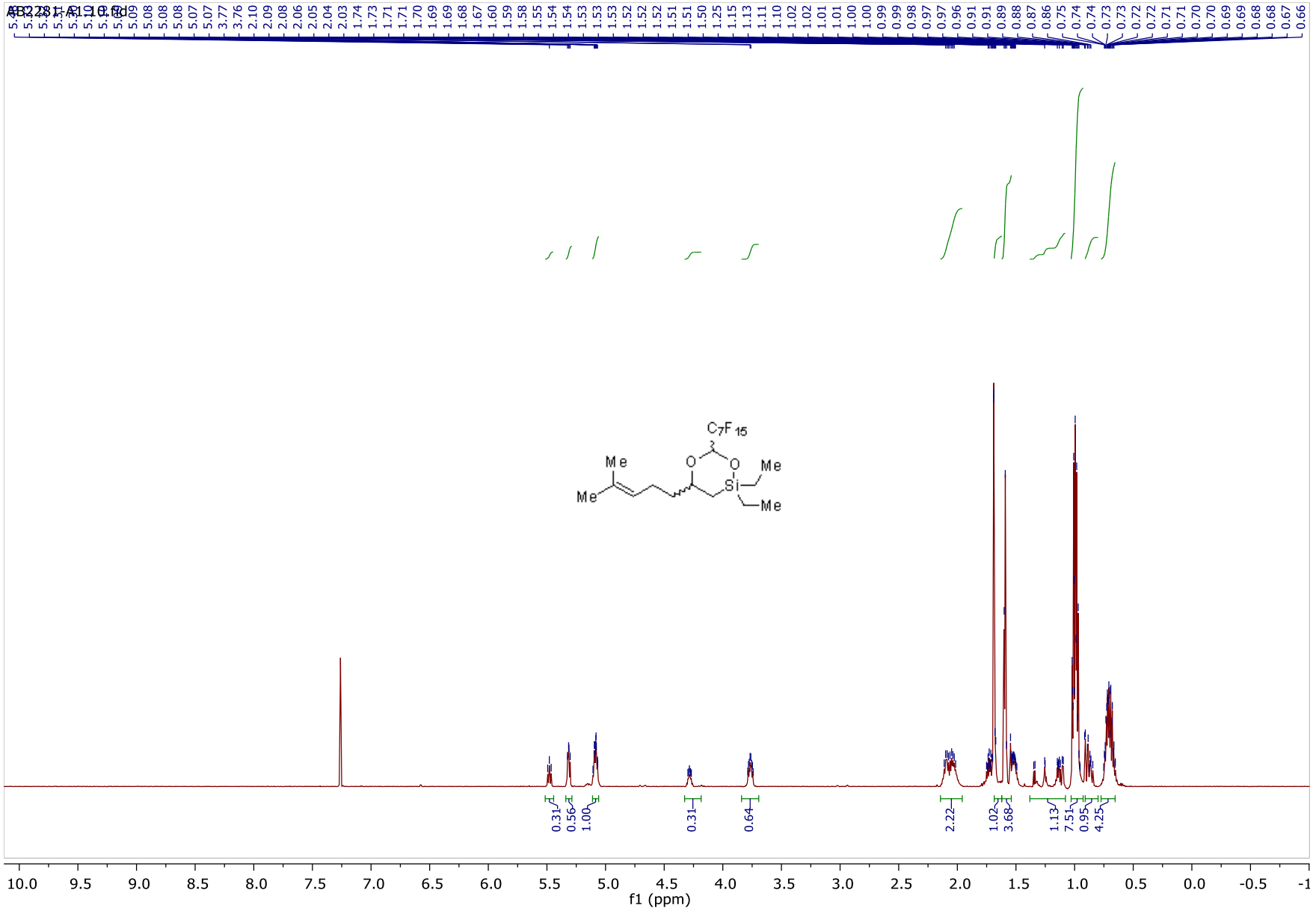

AB1940-a-A1.13.fid
163.49
161.86
140.08
140.03
139.73
139.68
129.65
129.60
129.54
129.49
125.13
125.10
125.08
116.42
116.39
116.27
116.25
113.41
113.37
113.27
113.23
94.51
94.33
94.16
90.54
79.04
77.17
77.03
76.96
76.74
72.92
45.34
44.33
17.12
16.21
6.94
6.80
6.28
6.18
5.95
5.87
5.72
5.57
F
C7F15
O
O
Si
Me
Me
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

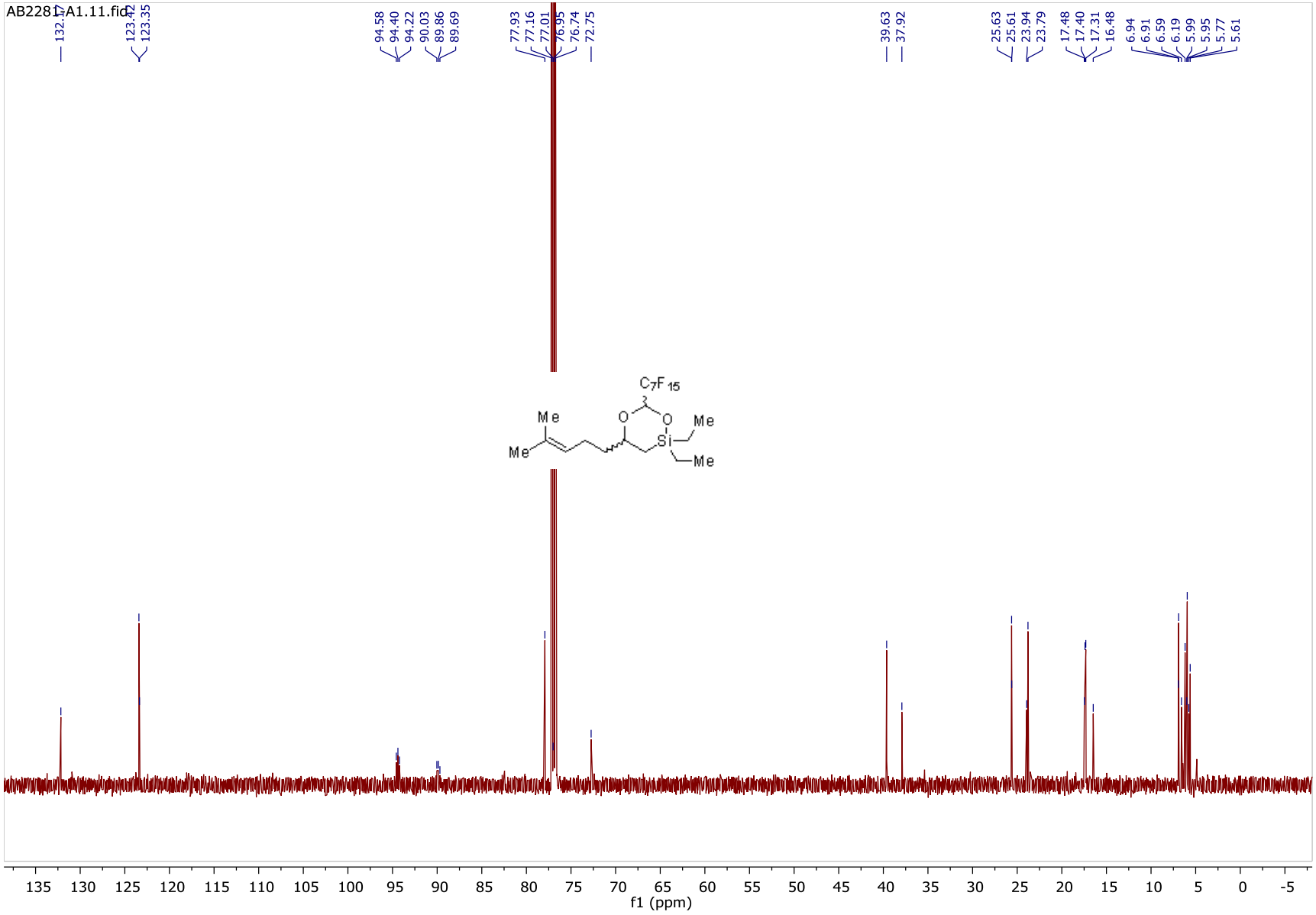

AB1938-a1-1-1d
Br
$^{n}C_7F_{15}$
O
O
Si
Me
Me
7.07
7.19
1.00
2.44
1.00
2.46
3.75
3.50
31.02
15.62
f1 (ppm)

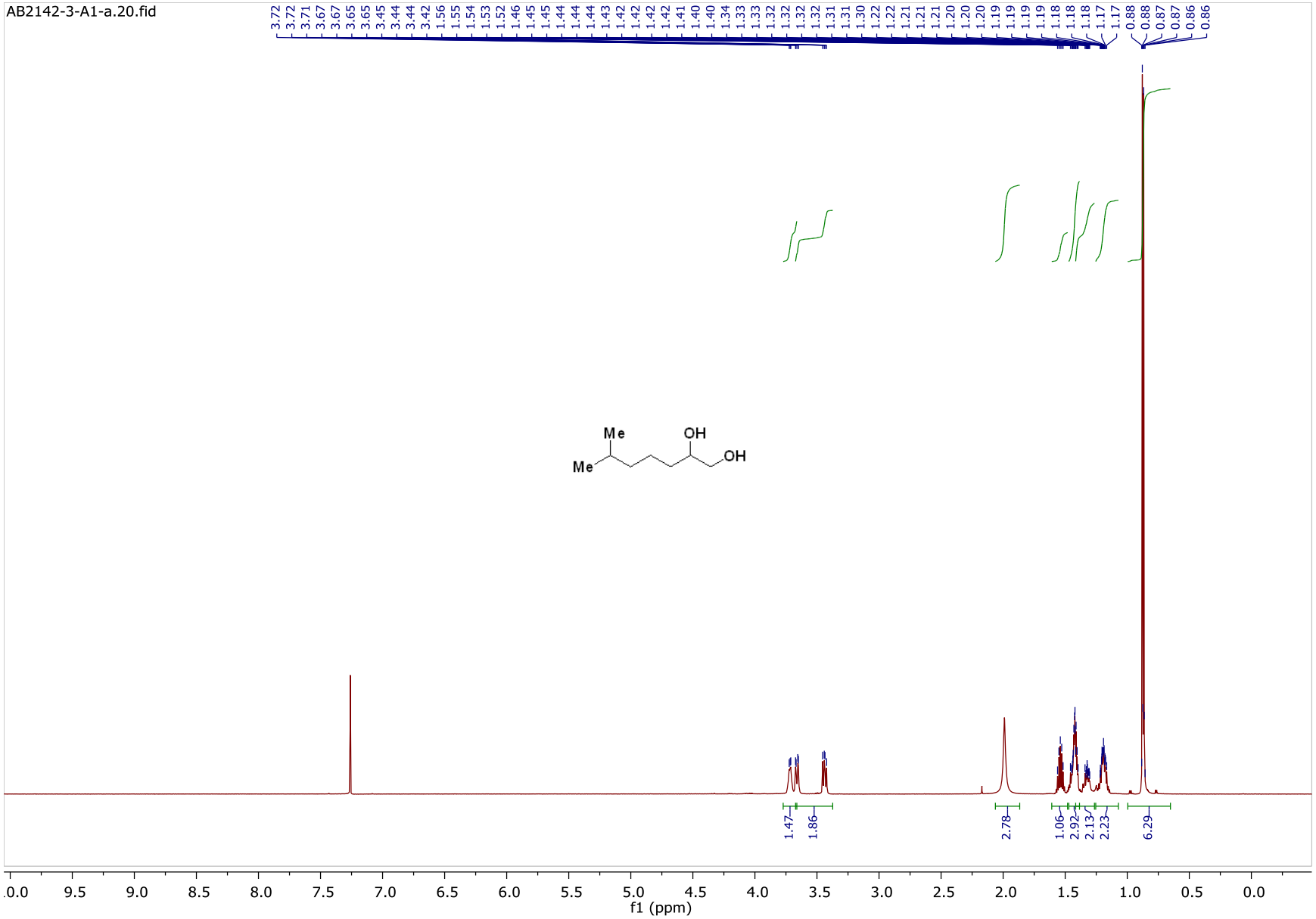

AB1938-a1-a.13.fid
-111.70
-112.06
-116.91
-117.01
-127.86
-153.71
-153.93
-154.14
-157.70
-169.21
-175.34
-203.21
-204.21
-231.19
-232.10
-241.29
-241.46
-241.97
-242.02
-242.25
-242.38
-242.48
-242.64
Br
$^{n}C_7F_{15}$
O
O
Si
Me
Me
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

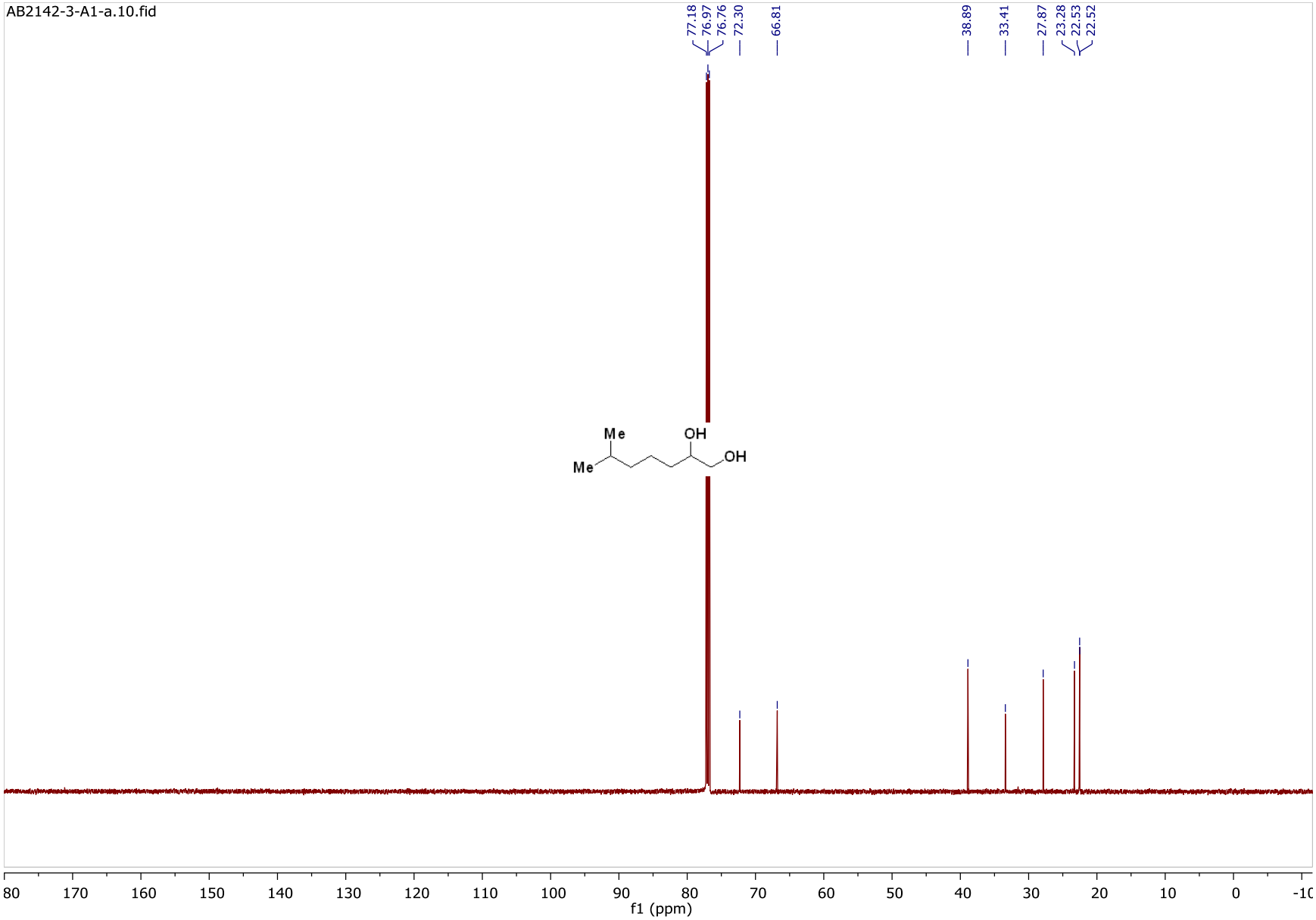

AB2516-A1-a.20.fid
C7F15
SiEt2
f1 (ppm)

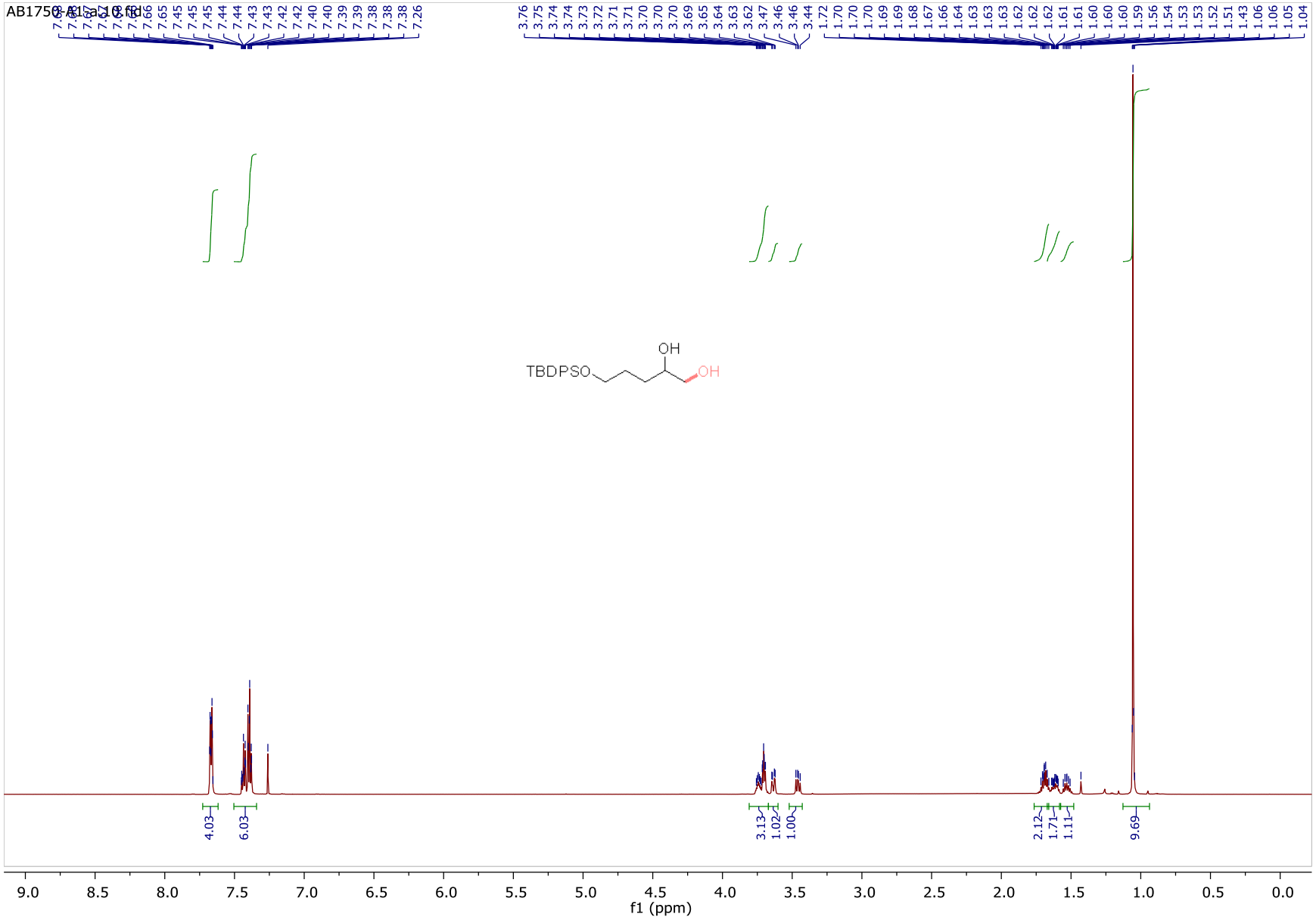

AB2516-A1-a.21.fid
147.61
147.57
145.63
135.40
135.34
121.08
121.03
108.76
108.75
108.13
100.73
94.36
94.19
89.97
89.80
76.18
72.34
41.47
40.18
31.47
31.18
17.31
16.64
6.91
6.88
6.51
6.15
5.99
5.90
5.76
5.61
C7F15
O
O
O
O
Si
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

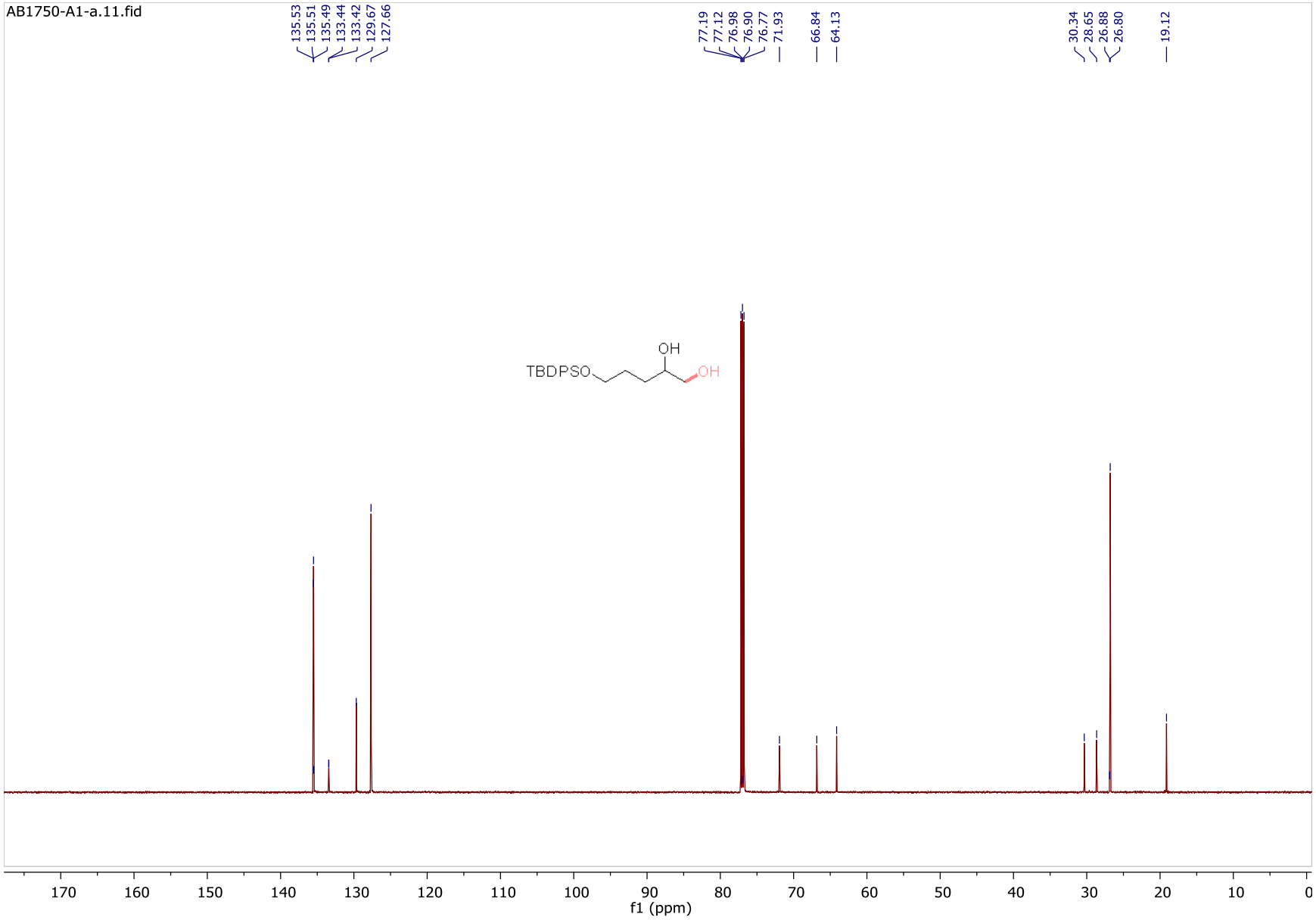

AB2281-A1-10.fid
C7F15
Me
Me
Me
Me
Si
O
O
0.31
0.56
1.00
0.31
0.64
2.22
1.02
3.68
1.13
7.51
0.95
4.25
f1 (ppm)

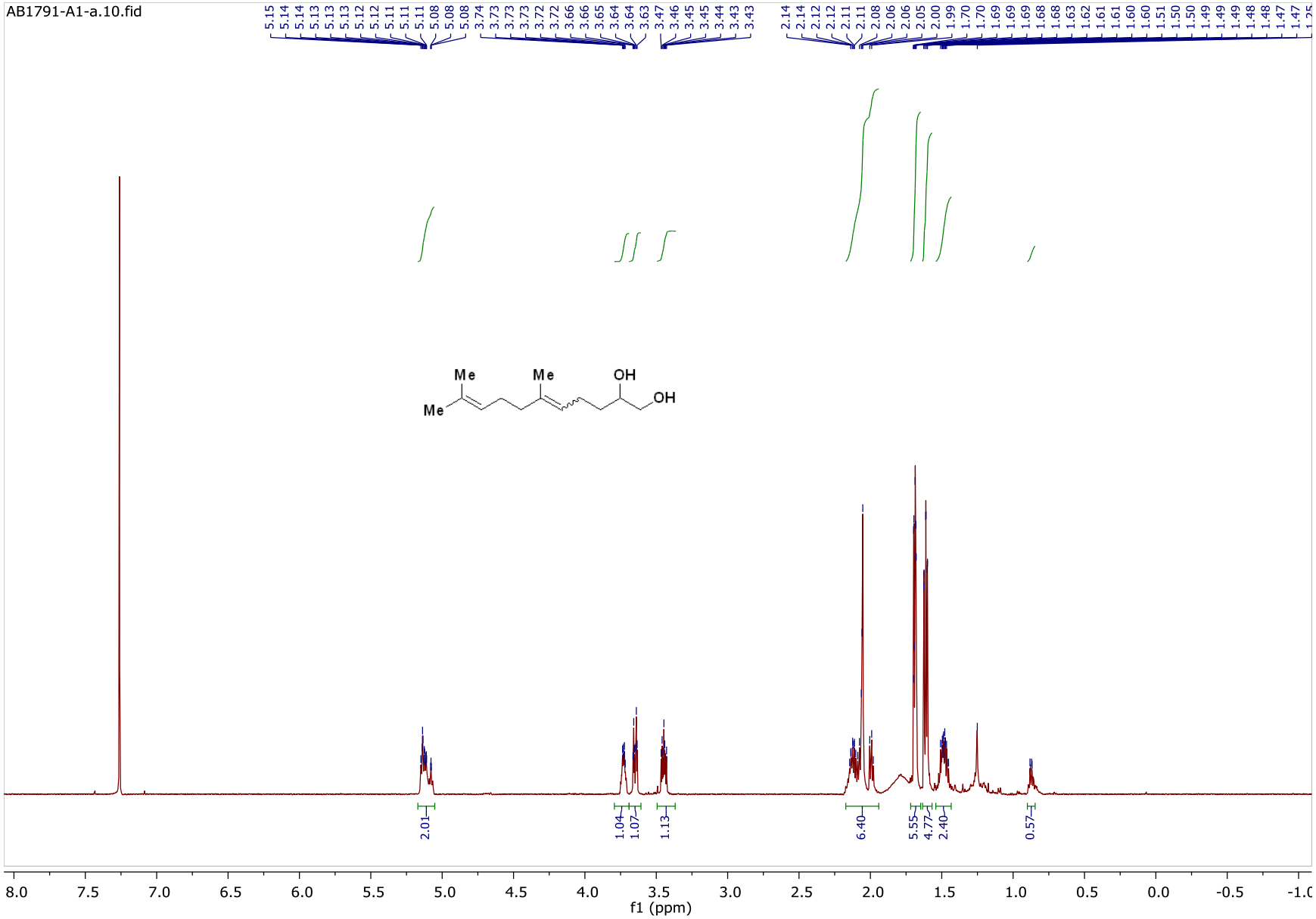

AB2281-A1.11.fid
132.17
123.42
123.35
94.58
94.40
94.22
90.03
89.86
89.69
77.93
77.16
77.01
76.95
76.74
72.75
39.63
37.92
25.63
25.61
23.94
23.79
17.48
17.40
17.31
16.48
6.94
6.91
6.59
6.19
5.99
5.95
5.77
5.61
C7F15
Me
Me
O
O
Si
Me
Me
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

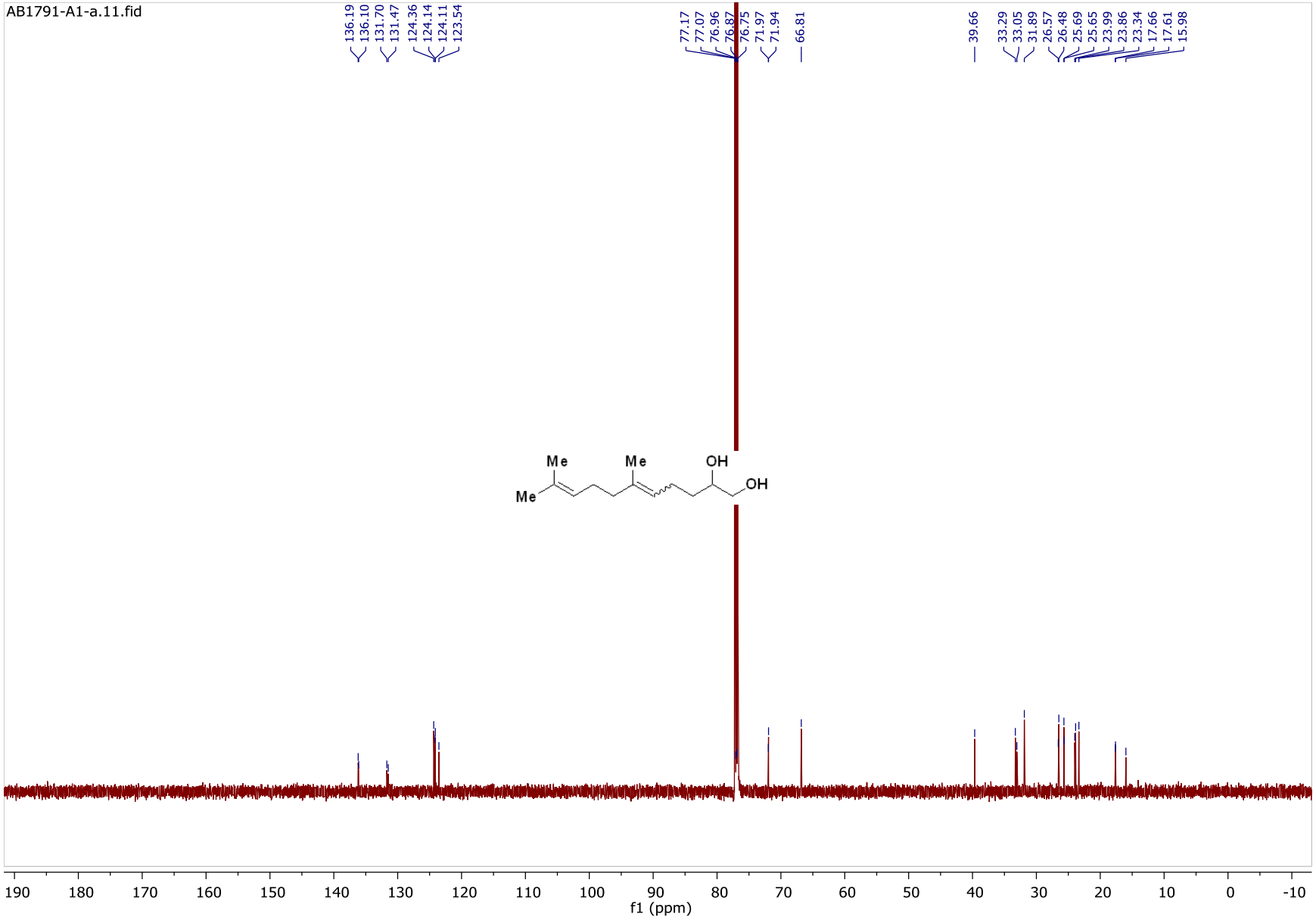

AB2142-3-A1-a.20.fid
3.72 3.72 3.71 3.67 3.67 3.65 3.65 3.45 3.44 3.44 3.42 1.56 1.55 1.54 1.53 1.52 1.46 1.45 1.45 1.44 1.44 1.44 1.43 1.42 1.42 1.42 1.42 1.41 1.40 1.40 1.34 1.33 1.33 1.32 1.32 1.32 1.31 1.31 1.30 1.22 1.22 1.21 1.21 1.21 1.20 1.20 1.20 1.19 1.19 1.19 1.19 1.18 1.18 1.18 1.17 1.17 0.88 0.88 0.87 0.87 0.86 0.86
Me
OH
Me
OH
1.47
1.86
2.78
1.06
2.92
2.13
2.23
6.29
.0.0 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)

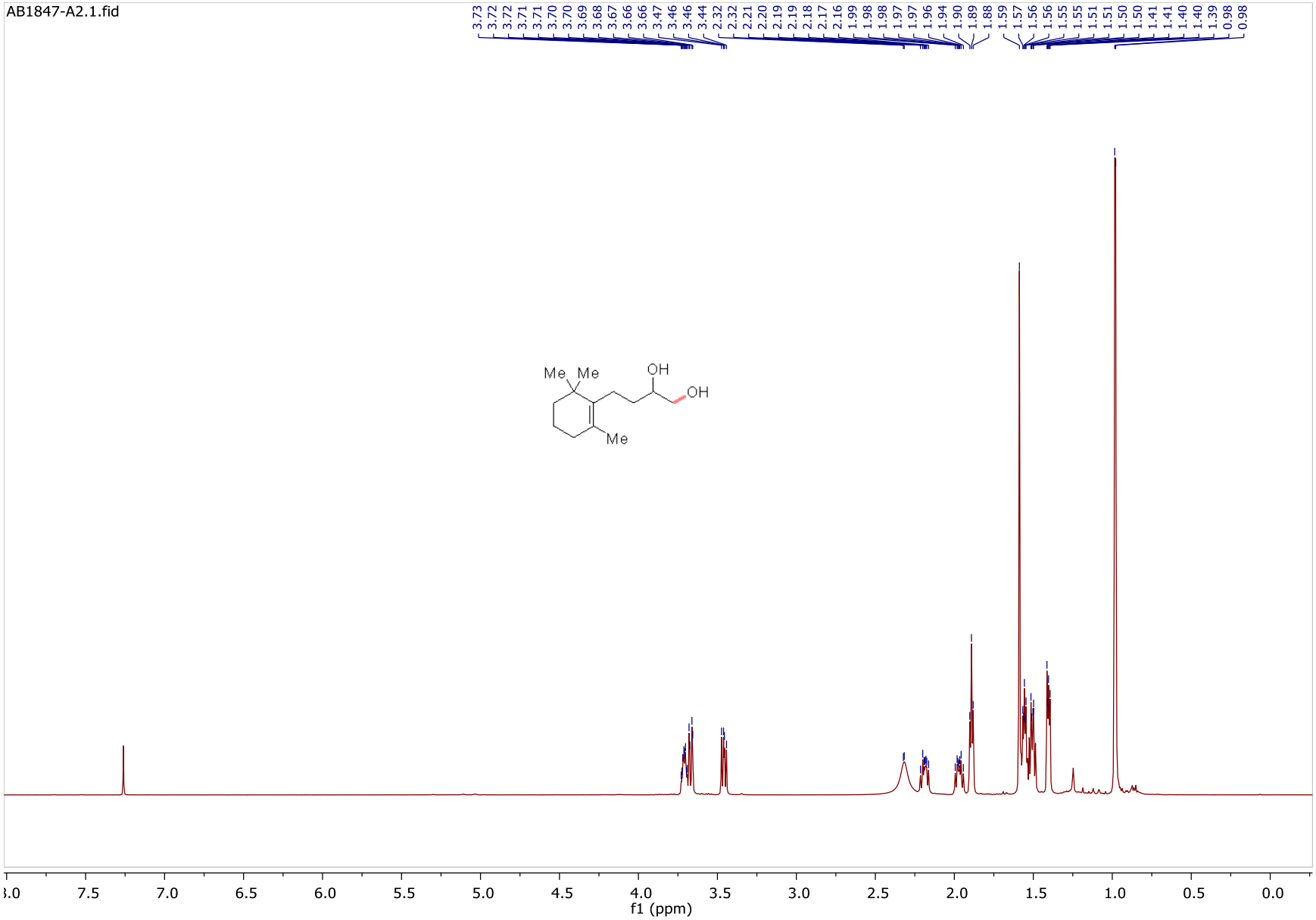

AB2142-3-A1-a.10.fid
77.18
76.97
76.76
72.30
66.81
38.89
33.41
27.87
23.28
22.53
22.52
Me
OH
Me
OH
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

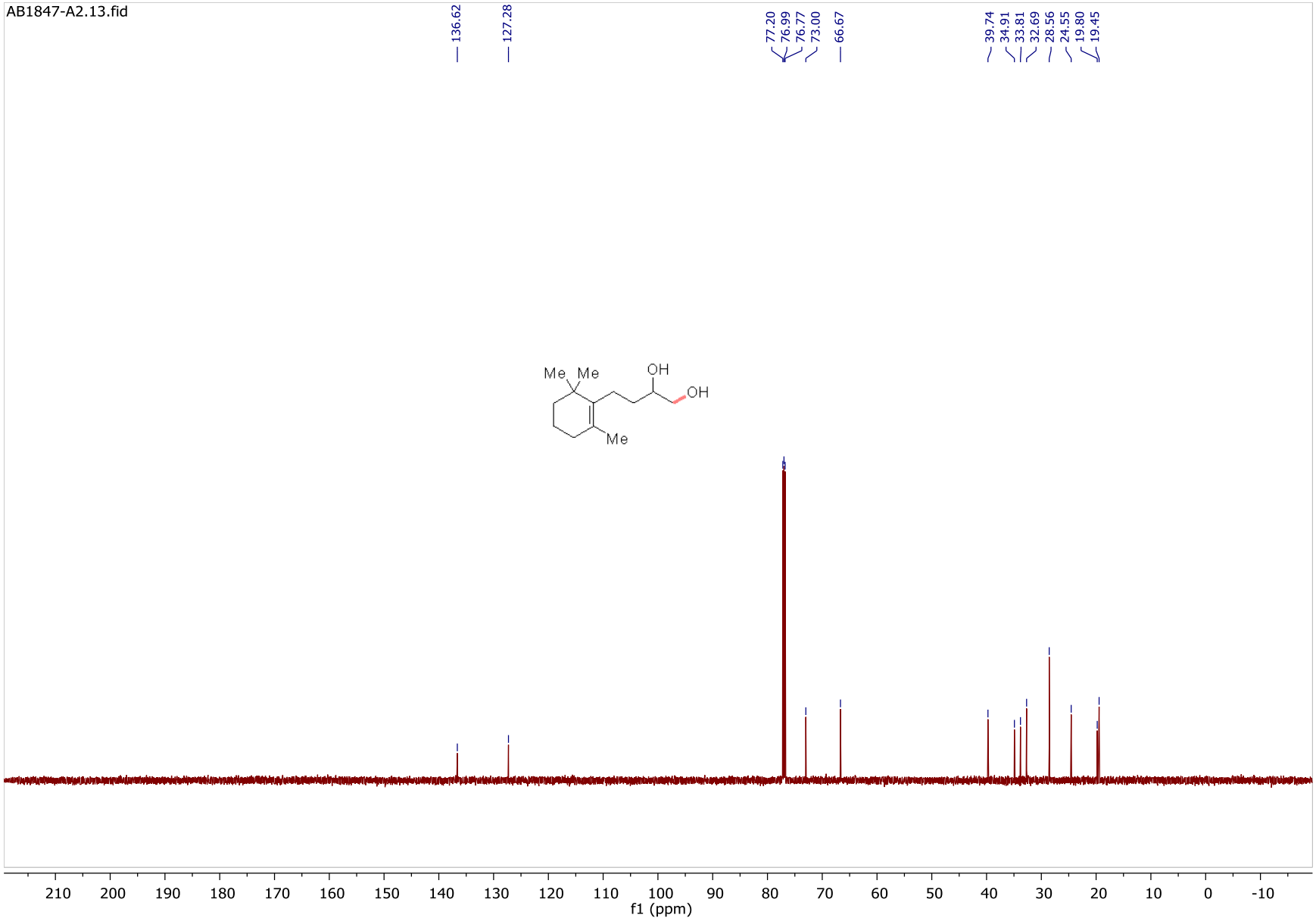

AB1756-A1-a1@1fid
TBDPSO
OH
OH
4.03
6.03
3.13
1.02
1.00
2.12
1.71
1.11
9.69
f1 (ppm)

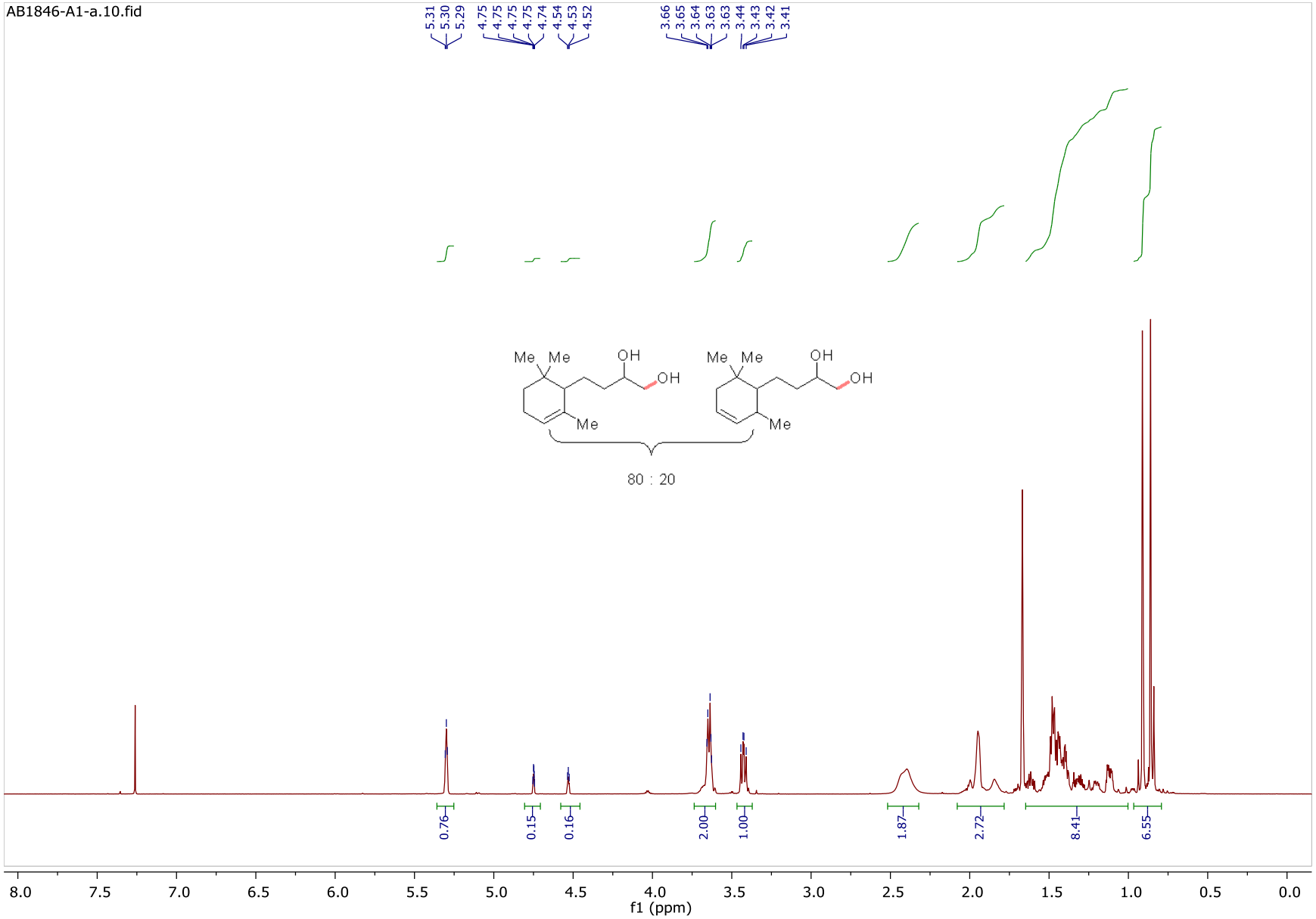

AB1750-A1-a.11.fid
135.53
135.51
135.49
133.44
133.42
129.67
127.66
77.19
77.12
76.98
76.90
76.77
71.93
66.84
64.13
30.34
28.65
26.88
26.80
19.12
TBDPSO
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

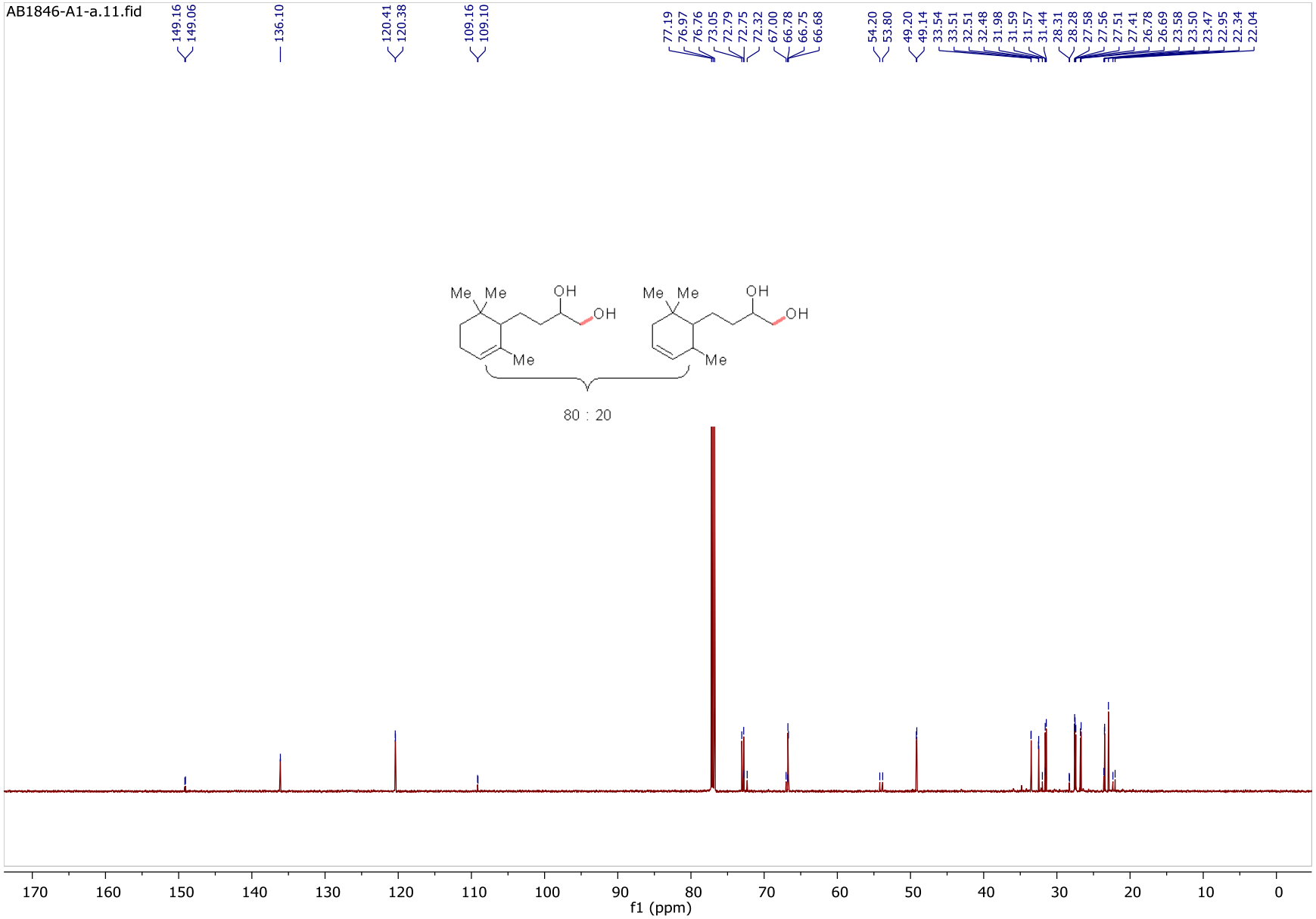

AB1791-A1-a.10.fid
Me
Me
Me
OH
OH
2.01
1.04
1.07
1.13
6.40
5.55
4.77
2.40
0.57
f1 (ppm)

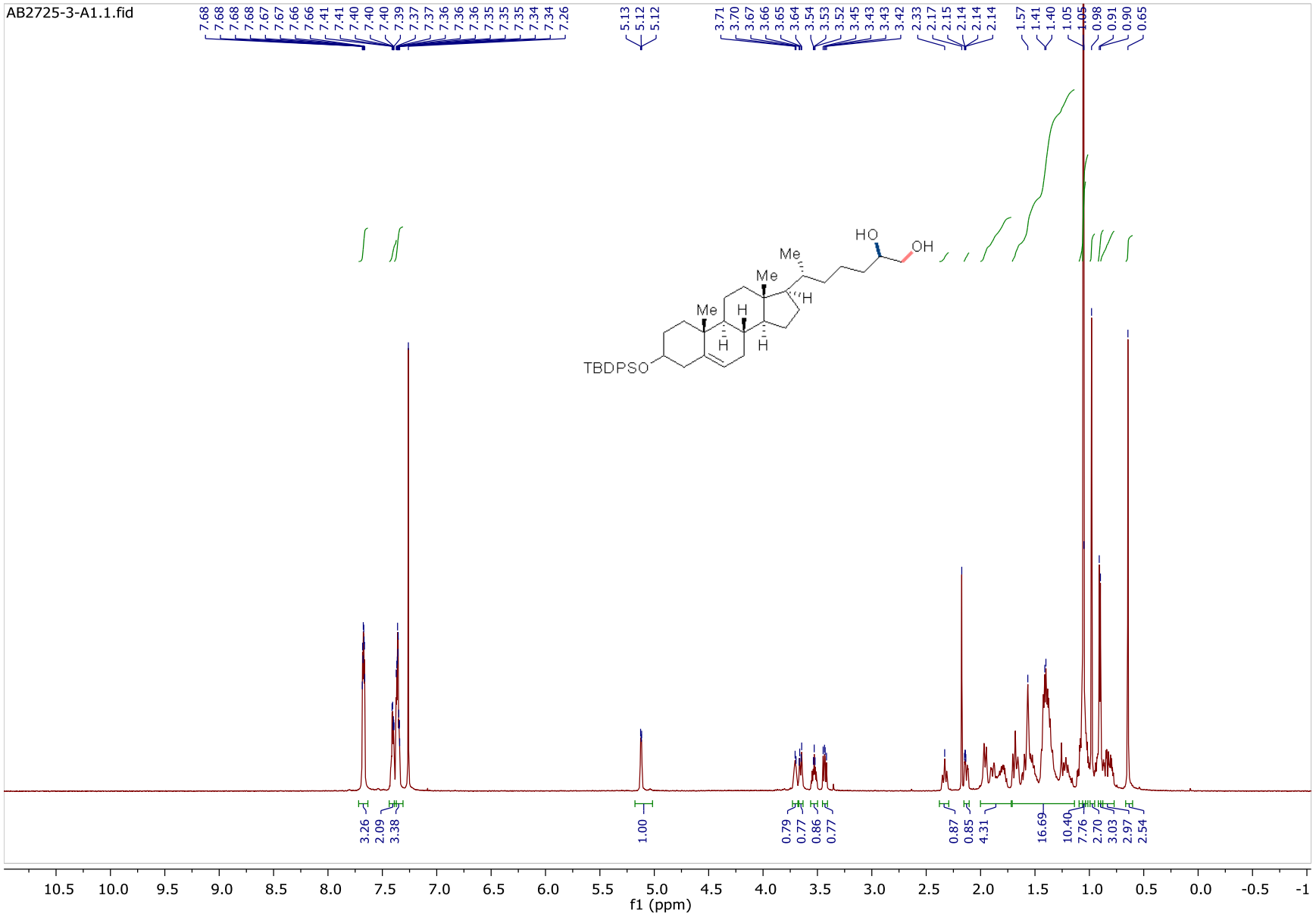

AB1791-A1-a.11.fid
136.19
136.10
131.70
131.47
124.36
124.14
124.11
123.54
77.17
77.07
76.96
76.87
76.75
71.97
71.94
66.81
39.66
33.29
33.05
31.89
26.57
26.48
25.69
25.65
23.99
23.86
23.34
17.66
17.61
15.98
Me
Me
OH
OH
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

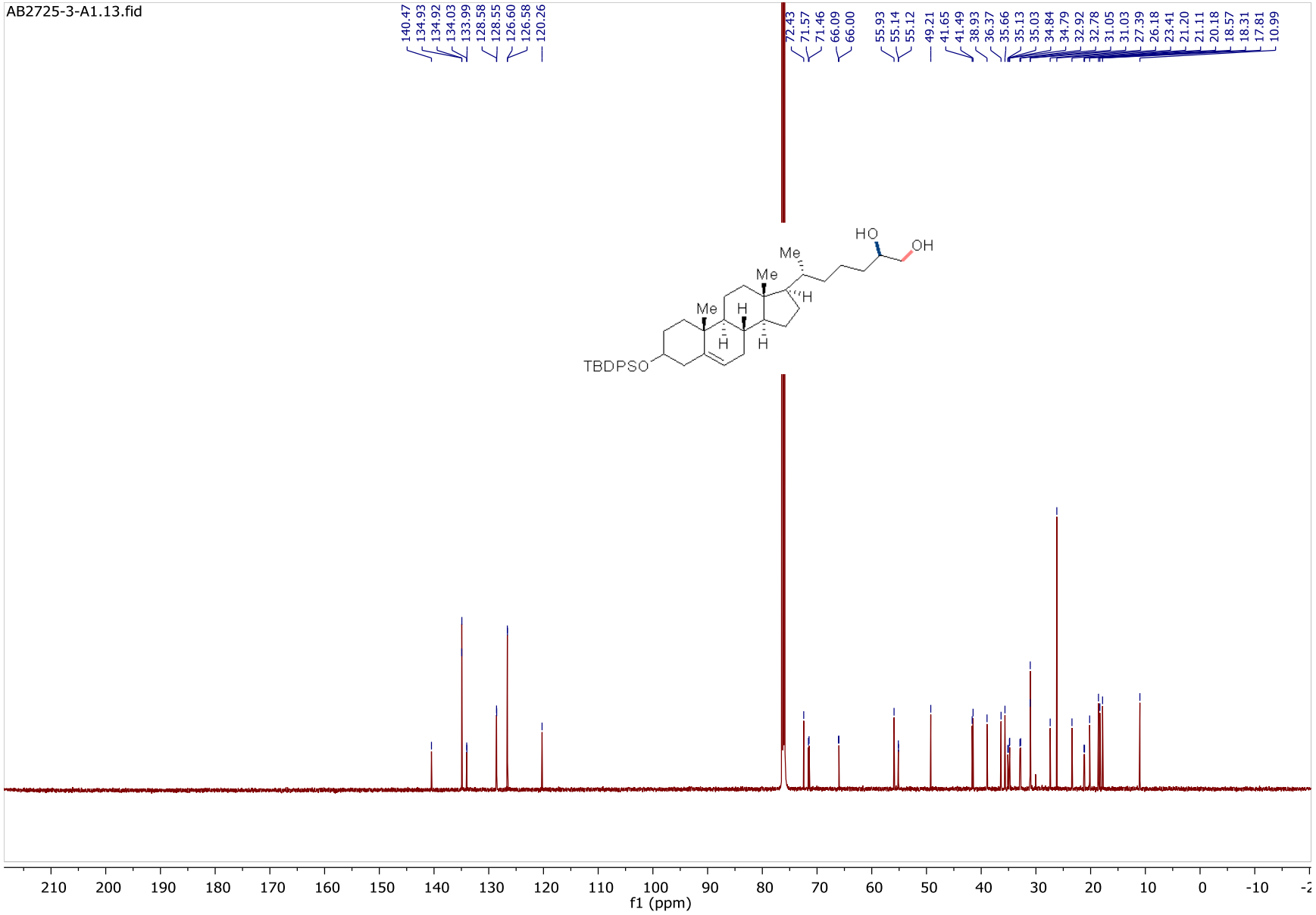

AB1847-A2.1.fid
3.73 3.72 3.72 3.71 3.71 3.70 3.70 3.69 3.68 3.67 3.66 3.66 3.47 3.46 3.44 2.32 2.32 2.21 2.20 2.19 2.19 2.18 2.17 2.16 1.99 1.98 1.98 1.97 1.97 1.96 1.94 1.90 1.89 1.88 1.59 1.57 1.56 1.56 1.55 1.55 1.51 1.51 1.50 1.50 1.41 1.41 1.40 1.40 1.39 0.98 0.98
Me Me
OH
OH
Me
8.0 7.5 7.0 6.5 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)

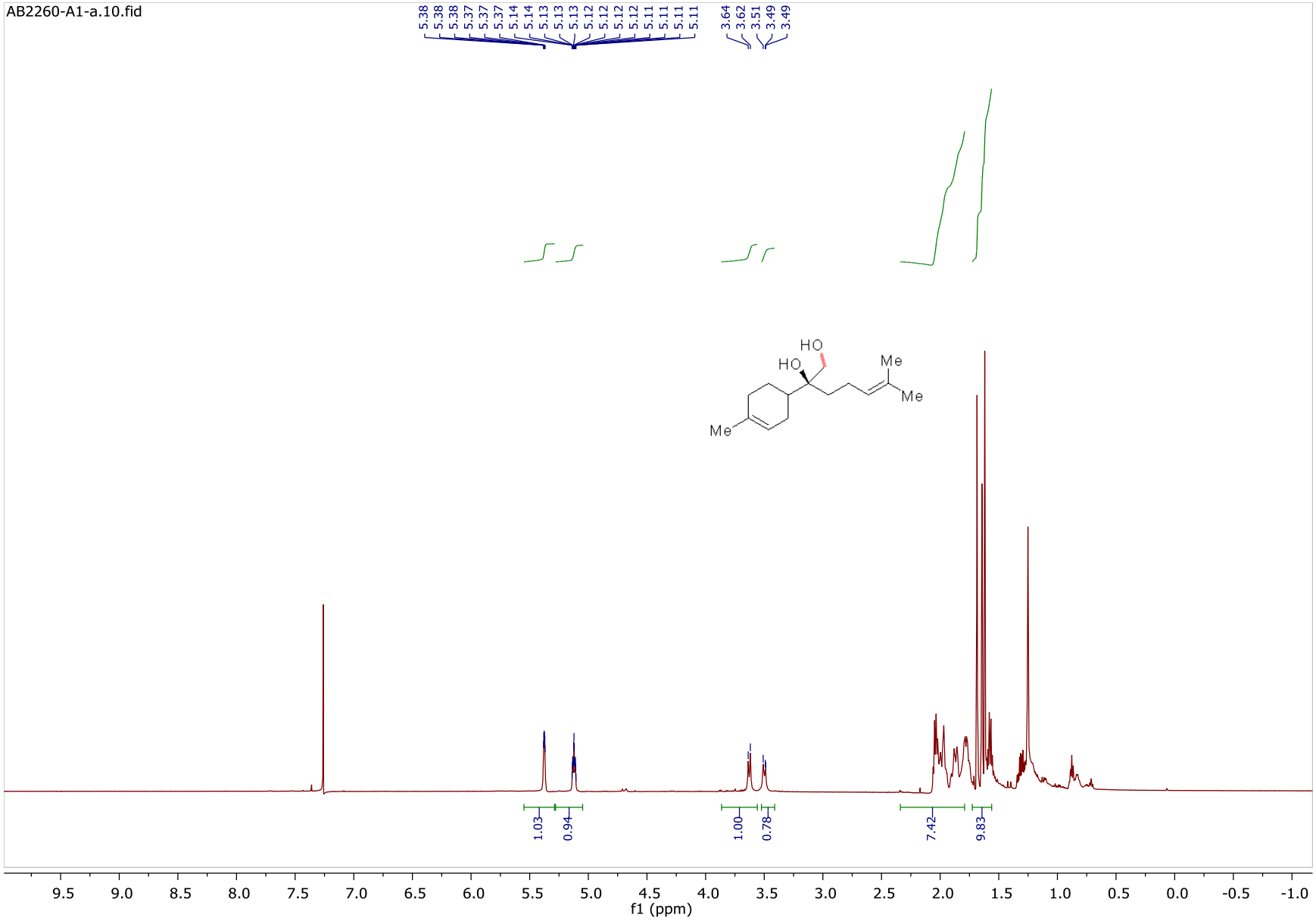

AB1847-A2.13.fid
136.62
127.28
77.20
76.99
76.77
73.00
66.67
39.74
34.91
33.81
32.69
28.56
24.55
19.80
19.45
Me
Me
OH
OH
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AB1846-A1-a.10.fid
5.31
5.30
5.29
4.75
4.75
4.75
4.75
4.74
4.54
4.53
4.52
3.66
3.65
3.64
3.63
3.63
3.44
3.43
3.42
3.41
Me
Me
OH
OH
Me
Me
Me
OH
OH
Me
80 : 20
0.76
0.15
0.16
2.00
1.00
1.87
2.72
8.41
6.55
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)


AB1846-A1-a.11.fid
149.16
149.06
136.10
120.41
120.38
109.16
109.10
77.19
76.97
76.76
73.05
72.79
72.75
72.32
67.00
66.78
66.75
66.68
54.20
53.80
49.20
49.14
33.54
33.51
32.51
32.48
31.98
31.59
31.57
31.44
28.31
28.28
27.58
27.56
27.51
27.41
26.78
26.69
23.58
23.50
23.47
22.95
22.34
22.04
Me
Me
OH
OH
Me
Me
Me
OH
OH
Me
80 : 20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


AB2725-3-A1.1.fid
7.68 7.68 7.68 7.68 7.67 7.67 7.66 7.66 7.41 7.41 7.40 7.40 7.40 7.39 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.26
5.13 5.12 5.12
3.71 3.70 3.67 3.66 3.65 3.64 3.54 3.53 3.52 3.45 3.43 3.43 3.42
2.33 2.17 2.15 2.14 2.14 2.14
1.57 1.41 1.40 1.05 1.05 0.98 0.91 0.90 0.65
HO
OH
Me
Me
Me
H
H
H
H
TBDPSO
3.26 2.09 3.38
1.00
0.79 0.77 0.86 0.77
0.87 0.85 4.31
16.69
10.40 7.76 2.70 3.03 2.97 2.54
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


AB2725-3-A1.13.fid
140.47
134.93
134.92
134.03
133.99
128.58
128.55
126.60
126.58
120.26
72.43
71.57
71.46
66.09
66.00
55.93
55.14
55.12
49.21
41.65
41.49
38.93
36.37
35.66
35.13
35.03
34.84
34.79
32.92
32.78
31.05
31.03
27.39
26.18
23.41
21.20
21.11
20.18
18.57
18.31
17.81
10.99
HO
OH
Me
Me
Me
H
H
H
H
TBDPSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AB2260-A1-a.10.fid
5.38
5.38
5.38
5.37
5.37
5.37
5.14
5.14
5.13
5.13
5.13
5.12
5.12
5.12
5.12
5.11
5.11
5.11
3.64
3.62
3.51
3.49
3.49
HO
HO
Me
Me
Me
1.03
0.94
1.00
0.78
7.42
9.83
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
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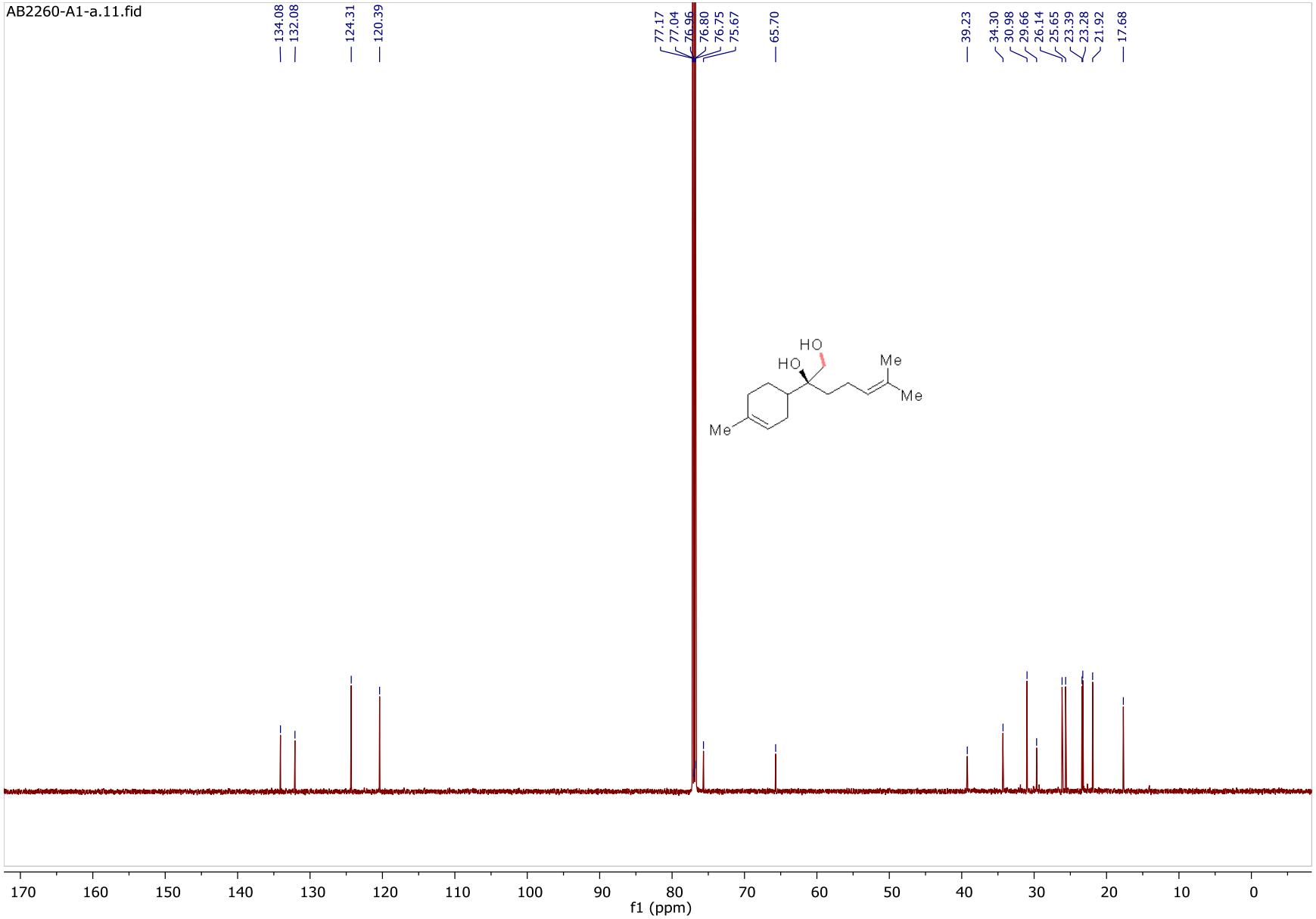
0.5
0.0
-0.5
-1.0
f1 (ppm)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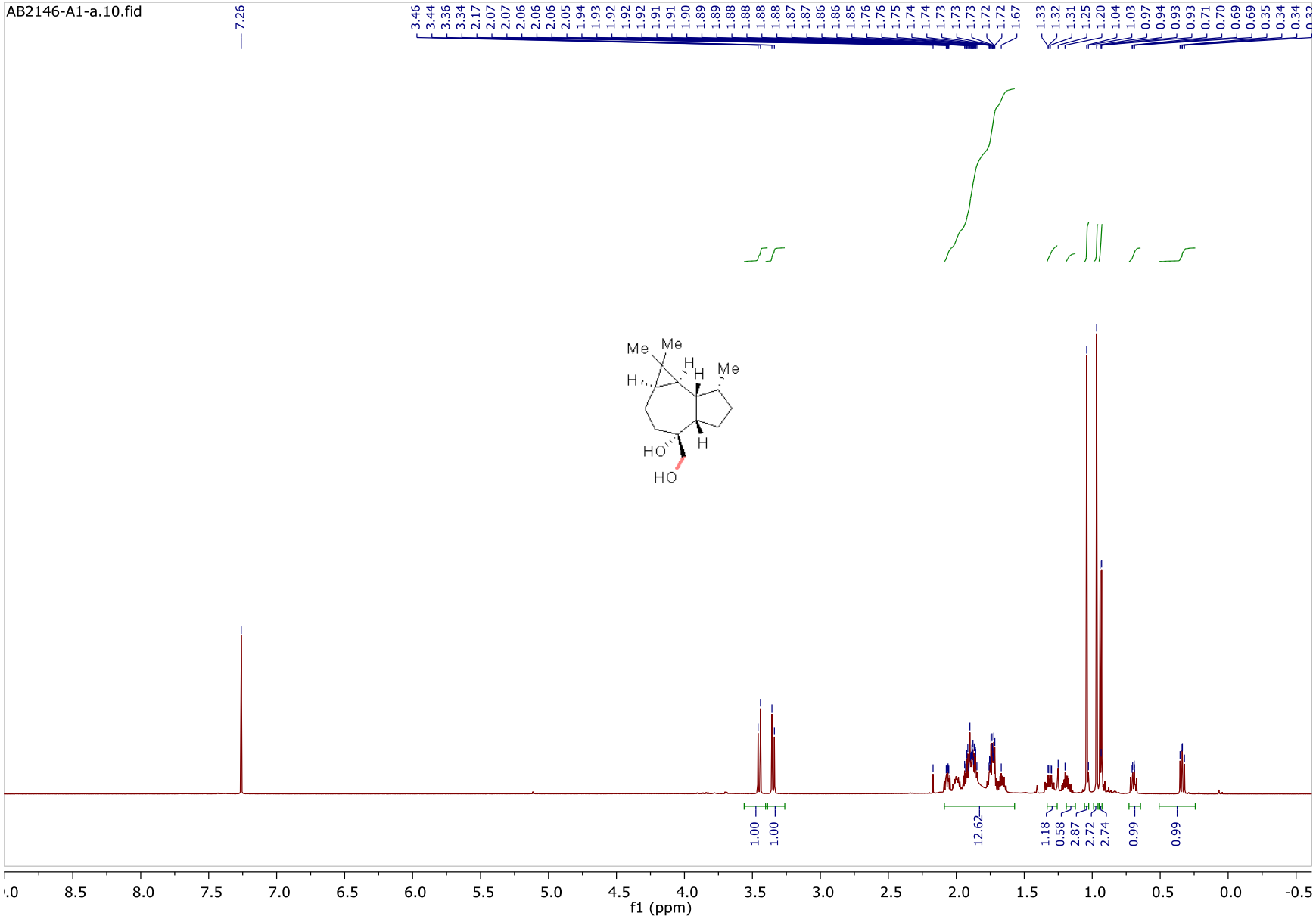
132.08
124.31
120.39
77.17
77.04
76.96
76.80
76.75
75.67
65.70
39.23
34.30
30.98
29.66
26.14
25.65
23.39
23.28
21.92
17.68
HO
HO
Me
Me
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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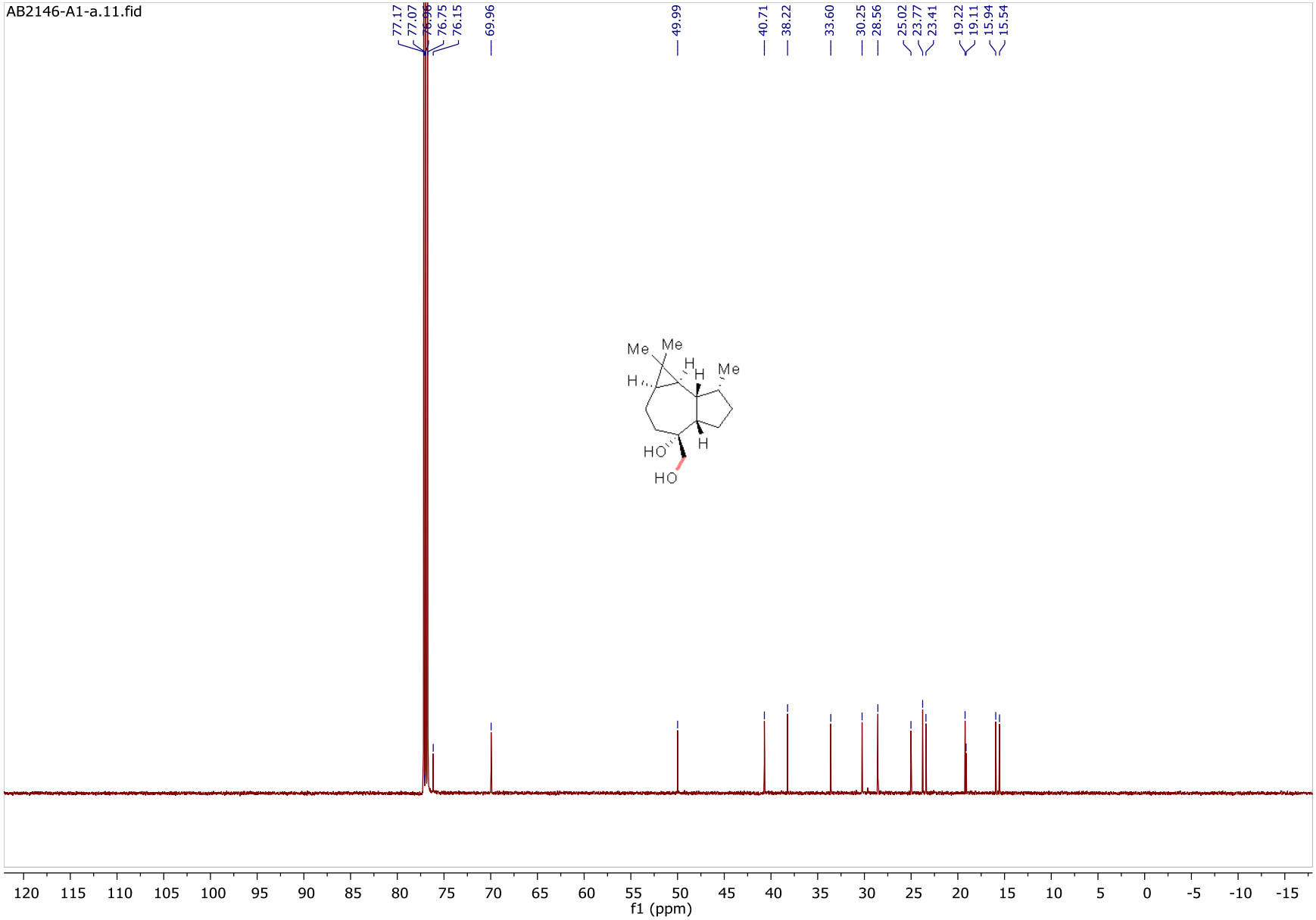
3.46 3.44 3.36 3.34 2.17 2.07 2.07 2.06 2.06 2.06 2.05 1.94 1.93 1.92 1.92 1.92 1.91 1.91 1.90 1.89 1.89 1.88 1.88 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.76 1.76 1.75 1.74 1.74 1.73 1.73 1.73 1.72 1.72 1.67
1.33 1.32 1.31 1.25 1.20 1.04 1.03 0.97 0.94 0.93 0.93 0.71 0.70 0.69 0.69 0.35 0.34 0.34
Me
Me
H
H
Me
H
H
HO
HO
1.00
1.00
12.62
1.18
0.58
2.87
2.72
2.74
0.99
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


AB2146-A1-a.11.fid
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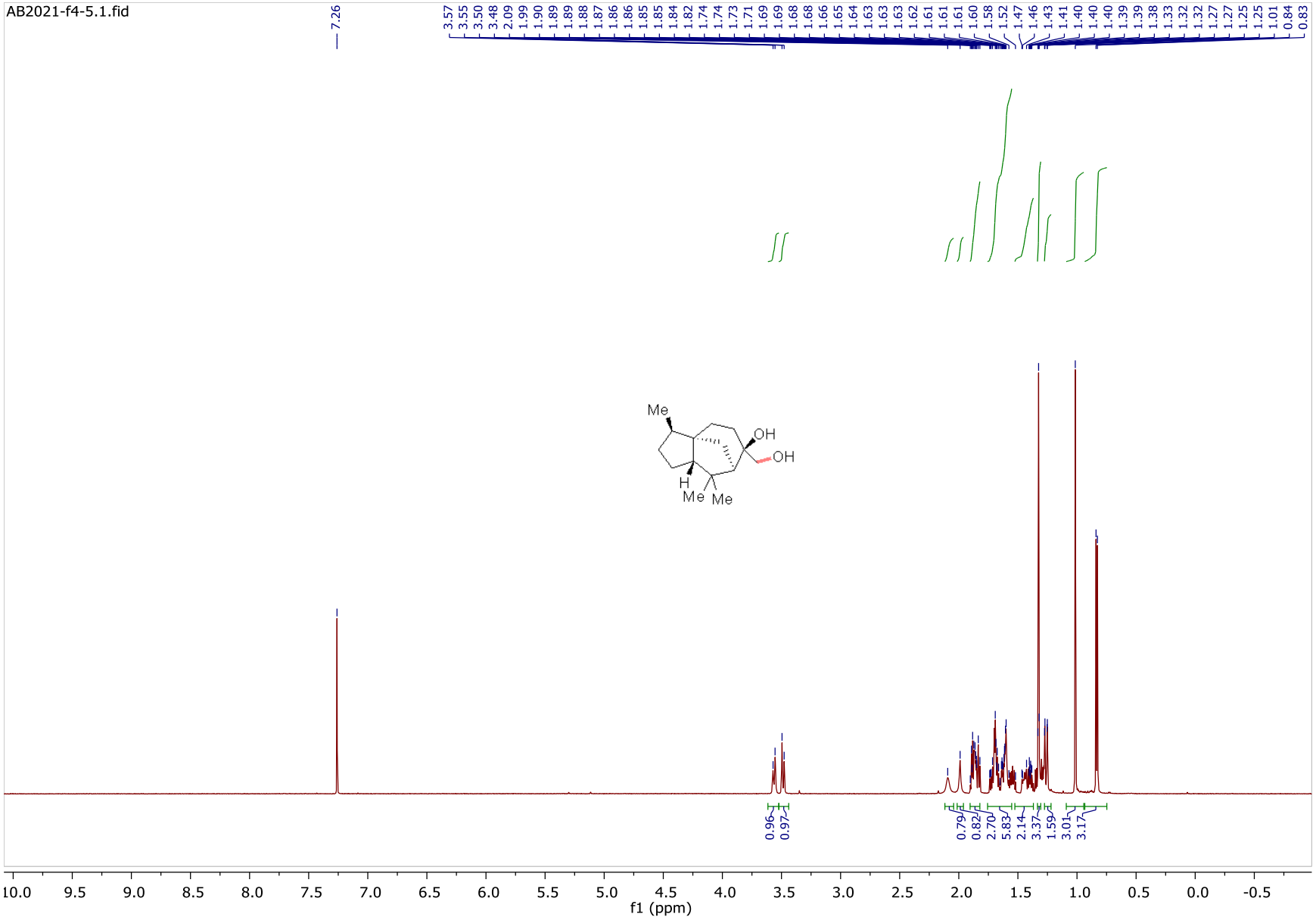
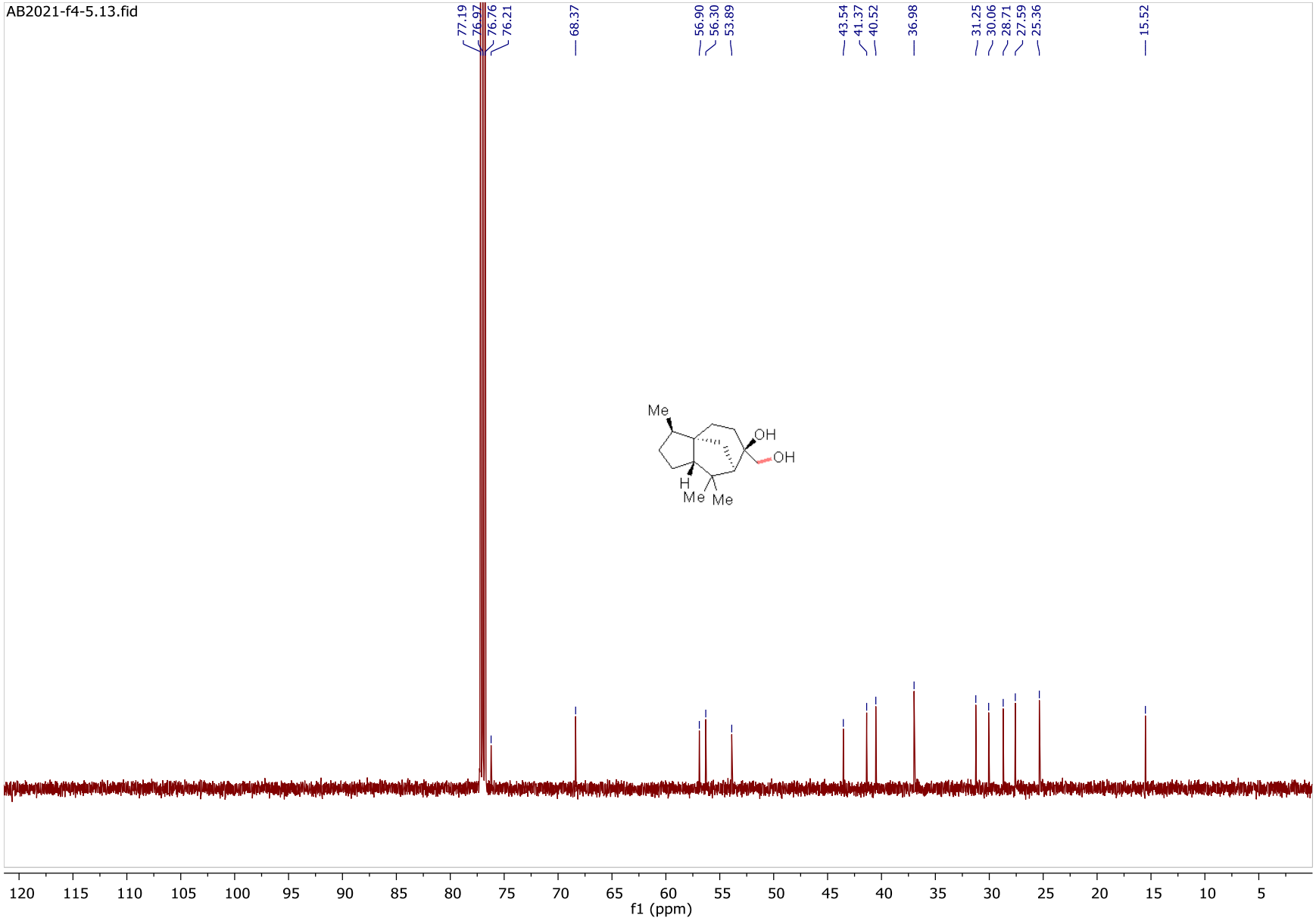
77.07
76.96
76.75
76.15
69.96
49.99
40.71
38.22
33.60
30.25
28.56
25.02
23.77
23.41
19.22
19.11
15.94
15.54
Me
Me
H
H
Me
H
H
HO
HO
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)


AB2021-f4-5.1.fid
7.26
3.57 3.55 3.50 3.48 2.09 1.99 1.90 1.89 1.89 1.88 1.87 1.86 1.86 1.85 1.85 1.84 1.82 1.74 1.74 1.73 1.71 1.69 1.69 1.68 1.68 1.66 1.65 1.64 1.63 1.63 1.63 1.62 1.61 1.61 1.61 1.60 1.58 1.52 1.47 1.46 1.43 1.41 1.40 1.40 1.40 1.39 1.39 1.38 1.33 1.32 1.32 1.27 1.27 1.25 1.25 1.01 0.84 0.83
Me
OH
OH
H
Me
Me
0.96
0.97
0.79
0.82
2.70
5.83
2.14
3.37
1.59
3.01
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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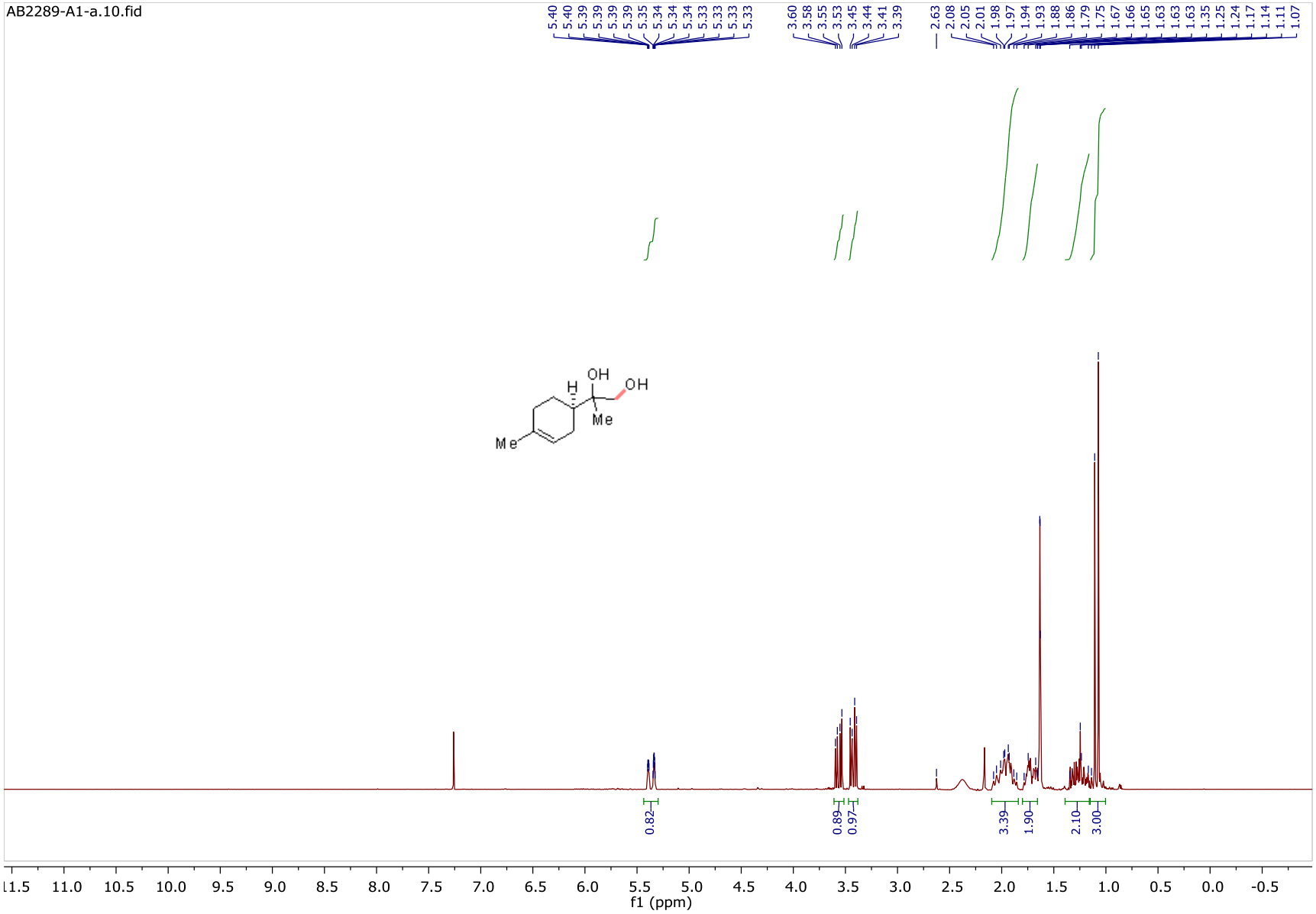
76.76
76.21
68.37
56.90
56.30
53.89
43.54
41.37
40.52
36.98
31.25
30.06
28.71
27.59
25.36
15.52
Me
OH
OH
H
Me
Me
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


AB2289-A1-a.10.fid
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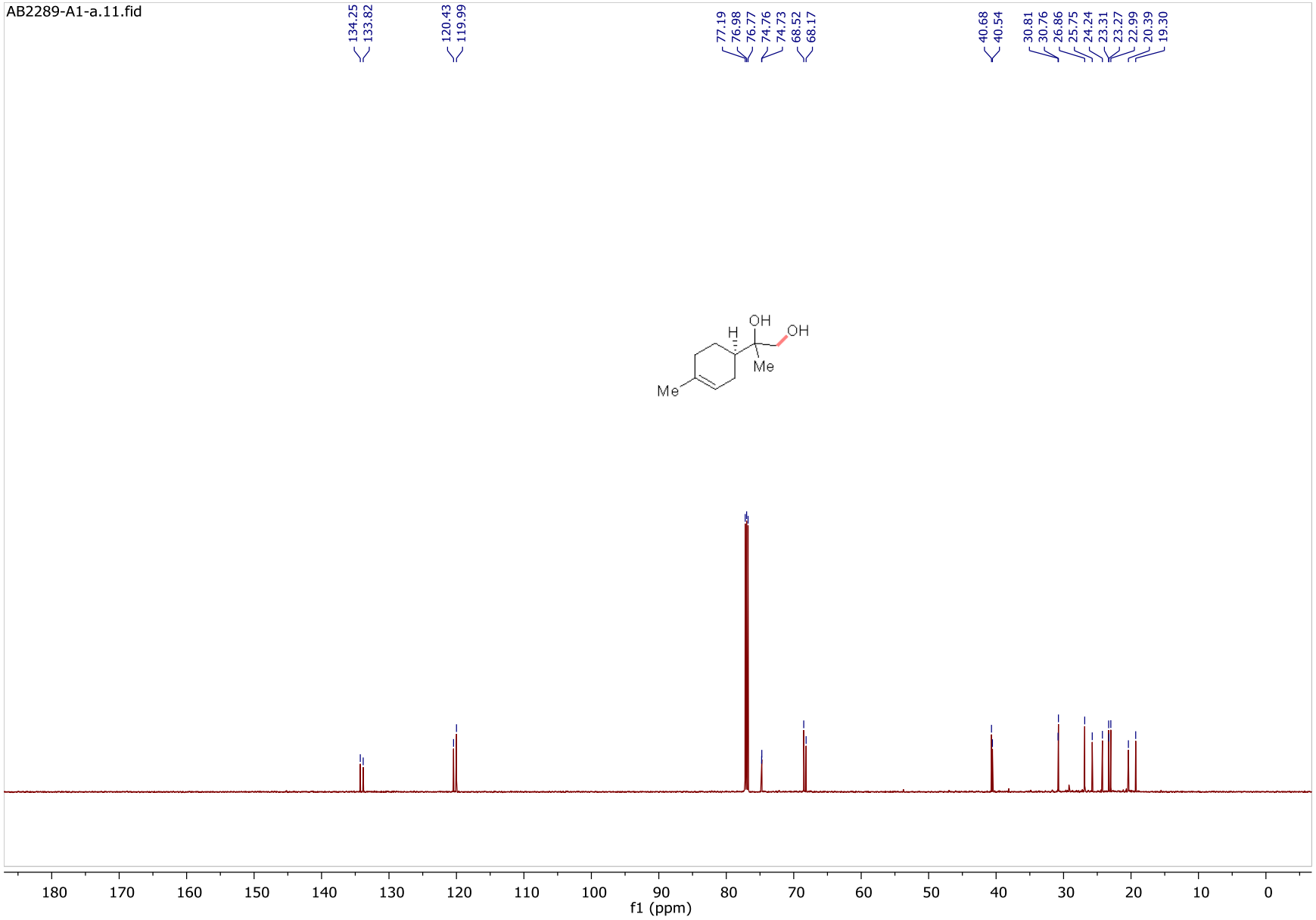
3.60 3.58 3.55 3.53 3.45 3.44 3.41 3.39
2.63 2.08 2.05 2.01 1.98 1.97 1.94 1.93 1.88 1.86 1.79 1.75 1.67 1.66 1.65 1.63 1.63 1.63 1.35 1.25 1.24 1.17 1.14 1.11 1.07
OH
OH
H
Me
Me
0.82
0.89
0.97
3.39
1.90
2.10
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


AB2289-A1-a.11.fid
134.25
133.82
120.43
119.99
77.19
76.98
76.77
74.76
74.73
68.52
68.17
40.68
40.54
30.81
30.76
26.86
25.75
24.24
23.31
23.27
22.99
20.39
19.30
OH
OH
H
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)