Electronic Supplementary Information (ESI)

Copper-Catalyzed and Additive Free Decarboxylative Trifluoromethylation of Aromatic and Heteroaromatic Iodides

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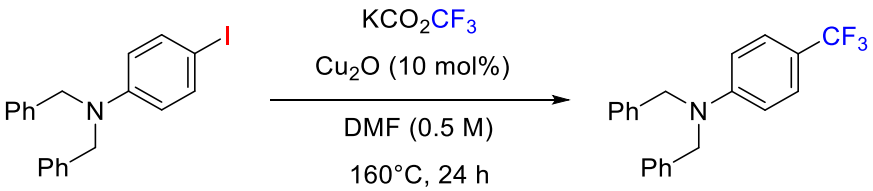
Optimization of copper catalyzed trifluoromethylation of aryl iodides

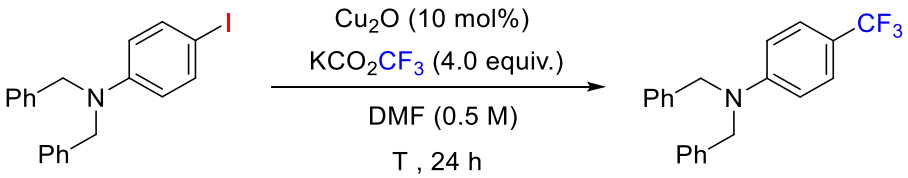
Table SI-1: Loading of potassium trifluoroacetate (KCO_2CF_3)[a]



Entry	KCO_2CF_3 [equiv.]	^{1}H NMR Yield [%][b]	Remaining KCO_2CF_3 [%][c]
I	2	54	39
II	2[d]	68	N.A.
III	3	54	65
IV	3[d]	81	N.A.
V	4	62	84
VI	6	62	85
VII	8	57	N.A.
VIIII	4[e]	65	59
IX	4[f]	63	47
X	4[g]	30	3
XI	4[h]	37	89

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. Remaining KCO_2CF_3 determined by ^{19}F NMR using 2,2,2-trifluoroethanol as an internal standard. [d]20 mol% Cu_2O instead of 10 mol%. [e]Reacion time extended to 48 hours. [f]Reaction time extended to 72 hours. [g]Sodium trifluoroacetate used instead of potassium trifluoroacetate. [h]Cesium trifluoroacetate used instead of potassium trifluoroacetate. N.A. is a denotation for not available.

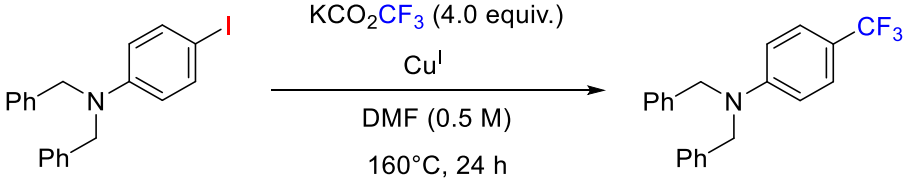
Table SI-2: Temperature[a]



Entry	T [˚C]	^{1}H NMR Yield [%][b]	Remaining KCO_2CF_3 [%][c]
I	140	40	N.A.
II	150	49	N.A.
III	160	62	84
IV	170	53	26
V	180	55	1

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. [c]Remaining KCO_2CF_3 determined by ^{19}F NMR using 2,2,2-trifluoroethanol as an internal standard. N.A. is a denotation for not available.

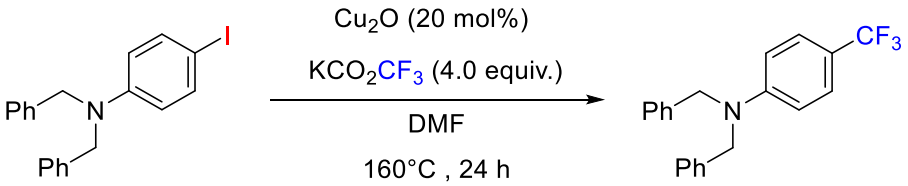
Table SI-3: Loading of copper(I) catalyst[a]



Entry	Cu^{I} [equiv.]	^{1}H NMR Yield [%][b]	Remaining KCO_2CF_3 [%][c]
I	0	0	73
II	0.1 (Cu_2O)	43	N.A.
III	0.2 (Cu_2O)	62	84
IV	0.2 (CuI)	54	N.A.
V	0.4 (Cu_2O)	86	83
VI	0.4 (Cu_2O)[d]	91	N.A.
VII	0.4 (Cu_2O)[e]	87[i]	N.A.
VIII	0.4 (Cu_2O)[f]	30[i]	N.A.
IX	0.4 (CuI)	72	67
X	0.6 (Cu_2O)	96	N.A.
XI	0.6 (CuI)	84	N.A.
XII	0.8 (Cu_2O)	100[g]	N.A.
XIII	0.8 (CuI)	99	N.A.
XIV	1.0 (Cu_2O)	98[g]	N.A.
XV	1.0 (CuI)	97[g]	N.A.
XVI	1.0 (Cu_2O)[h]	87[i]	N.A.
XVII	1.0 (CuI)[h]	100[g,i]	N.A.

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. [c]Remaining KCO_2CF_3 determined by ^{19}F NMR using 2,2,2-trifluoroethanol as an internal standard. [d]0.4 equiv. 1,10-Phenanthroline was added. [e]Experiment performed at near-ambient pressure by installing an empty balloon before heating. [f]The reaction mixture was purged with air for 5 minutes before heating. [g]Full conversion of *N*,*N*-dibenzyl-4-iodoaniline observed in ^{1}H NMR. [h]2 equiv. of KCO_2CF_3 was used instead of 4 equiv. [i]Yield as a ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. N.A. is a denotation for not available.

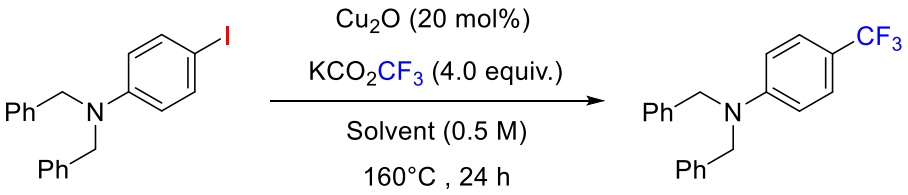
Table SI-4: Volume of DMF[a]



Entry	c [M]	^{1}H NMR Yield [%][b]
I	1.0	90[c]
II	0.67	87
III	0.50	86
IV	0.25	68

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. [c]Viscous reaction mixture.

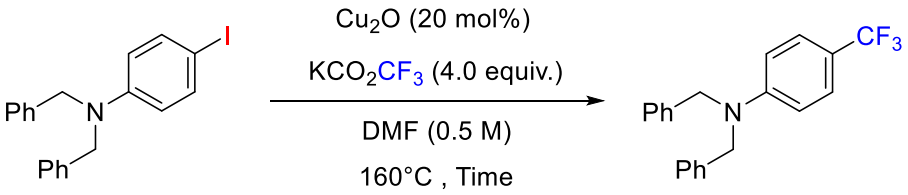
Table SI-5: Solvent Screen[a]



Entry	Solvent	^{1}H NMR Yield [%][b]
I	DMF	86
II	DMSO	0
III	DMPU	0
IV	Butyronitrile	51
V	NMP	85
VI	Diglyme	65
VII	DMAc	52

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard.

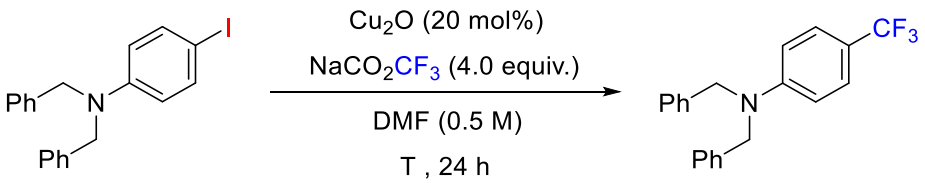
Table SI-6: Reaction time[a]



Entry	Time [h]	^{1}H NMR Yield [%][b]
I	1	23
II	2	31
III	4	44
IV	8	59
V	16	78
VI	24	86

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard.

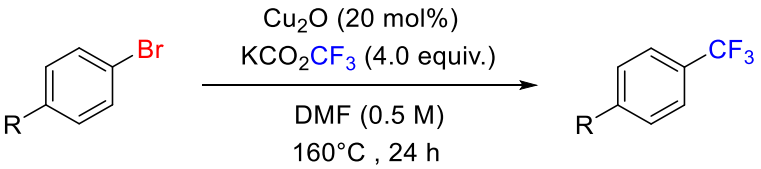
Table SI-7: Reaction temperature for sodium trifluoroacetate ($NaCO_2CF_3$)[a]

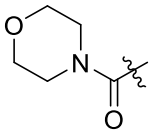
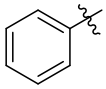
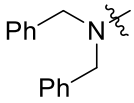
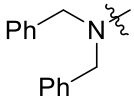
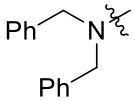
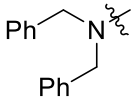
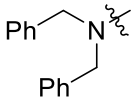
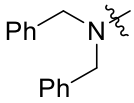


Entry	T [˚C]	^{1}H NMR Yield [%][b]	Remaining $NaCO_2CF_3$ [%][c]
I	130	56	N.A.
II	140	70	84
III	150	66	34
IV	160	68	5
V	160[d]	0	0
VI	160[e]	73	N.A.

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. [c]Remaining $NaCO_2CF_3$ determined by ^{19}F NMR using 2,2,2-trifluoroethanol as an internal standard. [d]Copper(i) oxide omitted. [e]3.50 equiv. sodium trifluoroacetate used with 0.50 equiv. cesium trifluoroacetate. N.A. is a denotation for not available.

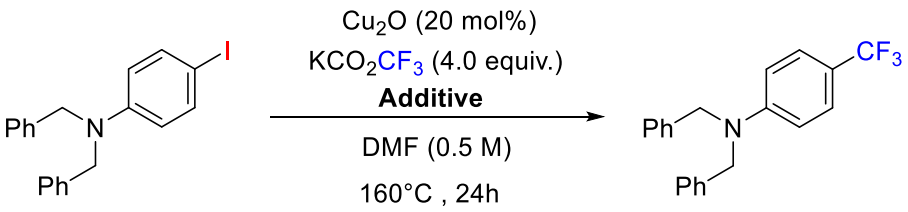
Table SI-8: Experiments with aryl bromide as substrate[a]



Entry	R	Deviation	^{1}H NMR yield
I		-	28[b]
II		-	29[b]
III		-	21[c]
IV		0.5 equiv. Cu_2O	26[c]
V		0.2 equiv. KI	43[c] (10)[d]
VI		1.0 equiv. KI	14[c] (29)[d]
VII		Aryl iodide was used instead	86[c]
VIII		Aryl iodide was used instead and 1.0 equiv. KI	37[c]

[a]Reactions performed using 0.50 mmol of aryl bromide. [b]Yield determined by ^{1}H NMR using 1,3,5-trimethoxybenezene as an internal standard. [c]Yield determined by ^{1}H NMR using using α,α,α-trifluorotoluene as an internal standard. [d]Yield of aryl iodide determined by ^{1}H NMR using using α,α,α-trifluorotoluene as an internal standard in parentheses.

Table SI-9: Attemps of removing iodide *in situ*[a]



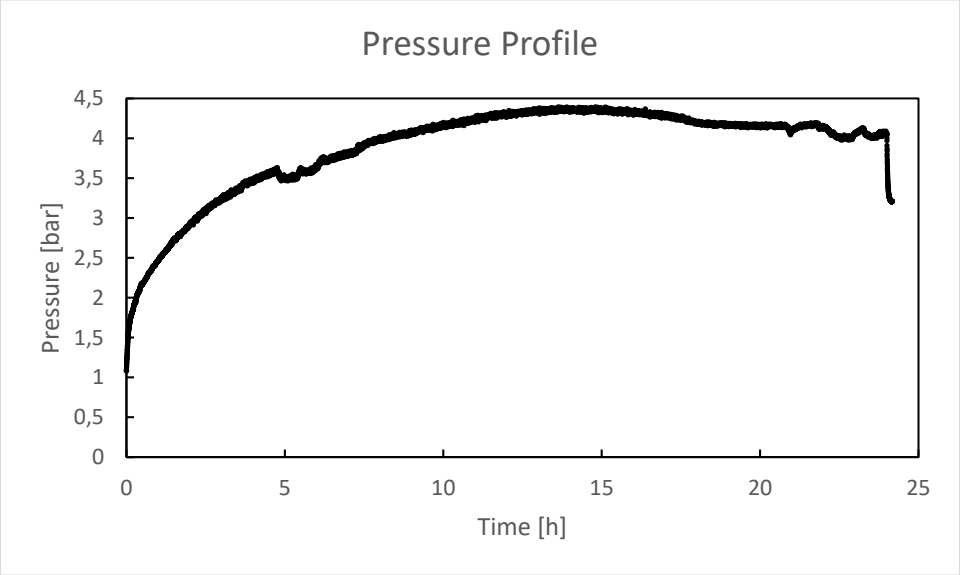
Entry	Additive	^{1}H NMR Yield [%][b]
I	-	86 (43)[c]
II	Silica gel (0.1 g)	0
III	$CaCl_2$ (1.0 equiv.)	19
IV	Tetraethyl orthosilicate (1.0 equiv.)	37
V	Trimethyl borate (1.0 equiv.)[c]	12[d]

[a]Reactions performed using 0.50 mmol of *N*,*N*-dibenzyl-4-iodoaniline. [b]Yield as a ^{1}H NMR yield using α,α,α-trifluorotoluene as an internal standard. [c]5 mol% Cu_2O. [d]Yield as a ^{19}F NMR yield using α,α,α-trifluorotoluene as an internal standard.

Pressure experiment

Using the general procedure for trifluoromethylation with 0.5 mmol of **1a** was a pressure experiment performed by installing a manometer (brand: Keller; type: Digital Manometer LEO record; model: 81710) instead of a Teflon seal.

Collected data:



Start pressure at room temperature before reaction: 1.1 bar

Maximum pressure during reaction: 4.4 bar

End pressure at room temperature after reaction: 3.2 bar

Synthesis and Characterization Data of Starting Materials

Cesium trifluoroacetate. Cesium carbonate (42 mmol, 13.69 g, 1.0 equiv.) was added slowly to a stirred solution of trifluoroacetic acid (84 mmol, 9.58 g, 1.0 equiv.) in 10 mL water. The solution was stirred for 15 minutes at room temperature. The reaction mixture was concentrated under reduced pressure to remove water. The resulting white solid was grounded in a mortar and dried under vacuum overnight at 100˚C to afford the title product (19.9 g, 96 %) as a white solid. ^{13}C NMR (101 MHz, D_2O, uncorrected) δ 165.4 (q, *J* = 34.7 Hz), 119.1 (q, *J* = 292.0 Hz) ppm; ^{19}F NMR (376 MHz, D_2O) δ -75.6 ppm. The NMR data are in agreement with literature.

***N*,*N*-Dibenzyl-4-iodoaniline (1a).** Synthesized by using modified literature procedure.[1] 4-iodoaniline (100.1 mmol, 21.93 g, 1.0 equiv.), Benzyl bromide (25 mL, 2.1 equiv.) and potassium iodide (3.00 g, 0.2 equiv.) was mixed in 100 mL DMF. K_2CO_3 (33.20 g, 2.4 equiv.) was added while stirring. The reaction was stirred overnight. 300 mL of CH_2Cl_2 was added and the reaction mixture was washed with water (3 x 100 mL) and brine (2 x 100 mL). The organic phase was dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recrystallization from 1.5 L EtOH to afford the title compound (29.9 g, 75%) as white needles. mp 123-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.9 Hz, 2H), 7.40-7.34 (m, 4H), 7.33-7.22 (m, 6H), 6.54 (d, *J* = 8.9 Hz, 2H), 4.66 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 138.0, 137.9, 128.9, 127.2, 126.6, 114.9, 77.8, 54.4 ppm; HRMS *m/z* calculated for $C_{20}H_{19}IN$ $[M + H]^+$ 400.0557, found 400.0557. The NMR data are in agreement with literature.[1]

***N*,*N*-Dibenzyl-4-bromoaniline (1b).** Synthesized by the same procedure as **1a**.[1] 4-bromoaniline (10 mmol, 1.72 g, 1.0 equiv.), Benzyl bromide (2.5 mL, 2.1 equiv.) and potassium iodide (0.30 g, 0.2 equiv.) was mixed in 10 mL DMF. K_2CO_3 (3.32 g, 2.4 equiv.) was added while stirring. The reaction was heated and stirred overnight at 40˚C. 30 mL of CH_2Cl_2 was added and the reaction mixture was washed with water (3 x 20 mL) and brine (2 x 20 mL). The organic phase was dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by recrystallization from 100 mL EtOH to afford the title compound (2.79 g, 78%) as white needles. mp 124-126°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 12H), 6.62 (d, *J* = 8.8 Hz, 2H), 4.66 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 138.0, 132.0, 128.9, 127.2, 126.7, 114.3, 108.8, 54.6 ppm; HRMS *m/z* calculated for $C_{20}H_{19}BrN$ $[M + H]^+$ 352.0695, found 352.0704. The NMR data are in agreement with literature.[2]

1-(Benzyloxy)-4-iodobenzene (1d). Synthesized by using modified literature procedure.[3] Benzyl bromide (0.68 mL, 1.15 equiv.) was added dropwise to a suspension of 4-iodophenol (1.10 g, 5.00 mmol, 1.0 equiv.) and K_2CO_3 (0.86 g, 1.25 equiv.) in DMF (5 mL), and the solution was allowed to stir at room temperature for 2 hours. The reaction mixture was diluted with water (20 mL) and extracted with Et_2O (4 x 50 mL). The combined organic phases was washed with brine (2 x 50 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using CH_2Cl_2/pentane (1:9) as eluent to afford title product (1.38 g, 89%) as a white solid. R*f*: 0.22 (in CH_2Cl_2/pentane 1:9); mp 61-62°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.46-7.32 (m, 5H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.04 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 138.4, 136.6, 128.8, 128.2, 127.6, 117.4, 83.2,

[1] S. M. Goldup, D. A. Leigh, P. J. Lusby, R. T. McBurney and A. M. Slawin, *Angew. Chem. Int. Ed.*, 2008, **47**, 3381.
[2] T. Saitoh and J. Ichikawa, *J. Am. Chem. Soc.i*, 2005, **127**, 9696.
[3] J. C. Sarie, C. Thiehoff, R. J. Mudd, C. G. Daniliuc, G. Kehr and R. Gilmour, *J. Org. Chem.*, 2017, **82**, 11792.

70.2 ppm; HRMS *m/z* calculated for $C_{13}H_{12}IO$ $[M + H]^+$ 310.9927, found 310.9924. The NMR data are in agreement with literature.[3]

***N,N*-Diethyl-4-iodobenzenesulfonamide (1i).** 4-iodobenzenesulfonyl chloride (1.51 g, 5.00 mmol, 1.0 equiv.) was dissolved in 10 mL pyridine and the solution was cooled to 0˚C. Diethylamine (0.57 mL, 1.1 equiv.) and *N,N*-dimethyl-4-aminopyridine (2 mg, 0.003 equiv.) was added and the solution was allowed warm to room temperature and stir for 24 hours. The reaction mixture was diluted with water (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic phases was washed with HCl (1 M, 3 x 20 mL), water (3 x 20 mL) and brine (20 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified using a short silica-plug filtration eluting with Et_2O, affording title product (1.03 g, 61%) as an orange solid. mp 59-60°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 4H), 1.13 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.4, 128.6, 99.5, 42.2, 14.3 ppm; HRMS *m/z* calculated for $C_{10}H_{15}INO_2S$ $[M + H]^+$ 339.9863, found 339.9861. The NMR data are in agreement with literature.[4]

4-Iodo-*N*-methoxy-*N*-methylbenzamide (1k). To a suspension of 4-iodobenzoic acid (15.00 g, 60.5 mmol, 1.0 eqiuv.) and oxalyl chloride (10.2 mL, 2.0 equiv.) in 24 mL toluene was added one drop of DMF. The solution was stirred continuously at room temperature for 2 h followed by 1 h at 35˚C. The solvent was removed from the colorless solution under reduced pressure. The off-white solid of crude 4-iodobenzoyl chloride was redissolved in 24 mL CH_2Cl_2 and used without further purification. Triethylamine (6.2 mL, 2.2 equiv.) was added dropwise to a suspension of *N,O*-dimethylhydroxylamine hydrochloride (2.16 g, 1.1 equiv.) in 20 mL CH_2Cl_2 at 0°C. A solution of 4-iodobenzoyl chloride (20.2 mmol, 1.0 equiv.) in CH_2Cl_2 was added slowly at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 42 h. The crude reaction mixture was mixed with sat. $NaHCO_3$ (20 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were washed with brine (2 x 20 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified using a short silica-plug filtration eluting with CH_2Cl_2, affording title product (5.45 g, 93%) as an yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 3.54 (s, 3H), 3.55 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 137.0, 133.2, 129.8, 97.2, 61.0, 33.3 ppm; HRMS *m/z* calculated for $C_9H_{11}INO_2$ $[M + H]^+$ 291.9829, found 291.9830. The NMR data are in agreement with literature.[5]

(4-Iodophenyl)(morpholino)methanone (1l). Triethylamine (3.1 mL, 1.1 equiv.) was added dropwise to a solution of morpholine (1.94 mL, 1.1 equiv.) in 20 mL CH_2Cl_2 at 0°C. A solution of 4-iodobenzoyl chloride (20.2 mmol, 1.0 equiv.) in CH_2Cl_2 was added slowly at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 42 h. The crude reaction mixture was mixed with sat. $NaHCO_3$ (20 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were washed with brine (2 x 20 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified using a short silica-plug filtration eluting with CH_2Cl_2, affording title product (6.15 g, 96%) as a white solid. mp 117-118°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.86-3.24 (m, 8H) ppm; ^{13}C NMR (101

[4] M. Chen, S. Ichikawa and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2015, **54**, 263.
[5] E. J. Emmett, B. R. Hayter and M. C. Willis, *Angew. Chem. Int. Ed.*, 2014, **53**, 10204.

MHz, $CDCl_3$) δ 169.5, 137.8, 134.7, 128.9, 96.2, 66.9, 48.3, 42.7 ppm; HRMS *m/z* calculated for $C_{11}H_{13}INO_2$ $[M + H]^+$ 317.9985, found 317.9985. The NMR data are in agreement with literature.[6]

(4-Bromophenyl)(morpholino)methanone (1l-Br). Triethylamine (3.1 mL, 2.2 equiv.) was added dropwise to a solution of morpholine (0.97 mL, 1.1 equiv.) in 5 mL CH_2Cl_2 at 0°C. A solution of 4-bromobenzoyl chloride (10 mmol, 1.0 equiv.) in CH_2Cl_2 was added slowly at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 13 h. The crude reaction mixture was mixed with sat. $NaHCO_3$ (20 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were washed with brine (2 x 20 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography using CH_2Cl_2/EtOAc (10:1) as eluent to afford the title product (2.36 g, 87%) as a white solid. R*f*: 0.23 (in CH_2Cl_2/EtOAc 10:1). Mp 68-69°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.89 – 3.32 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 134.2, 131.9, 129.0, 124.4, 66.9, 48.4, 42.7 ppm; HRMS *m/z* calculated for $C_{11}H_{13}BrNO_2$ $[M + H]^+$ 270.0124, found 270.0134. The NMR data are in agreement with literature.[6]

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-iodobenzoate (1m). Triethylamine (3.1 mL, 1.1 equiv.) was added dropwise to a solution of L-menthol (3.15 g, 1.0 equiv.) and 4-(dimethylamino)pyridine (109 mg, 0.04 equiv.) in 20 mL CH_2Cl_2 at 0°C. A solution of 4-iodobenzoyl chloride (20.2 mmol, 1.0 equiv.) in CH_2Cl_2 was added slowly at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 42 h. The crude reaction mixture was mixed with sat. $NaHCO_3$ (20 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were washed with 1 M HCl (2 x 20 mL) and brine (2 x 20 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography using pentane/$CHCl_3$ (3:2) as eluent to afford title product (5.16 g, 66%) as a light yellow, viscous oil. Rf: 0.68 (in pentane/$CHCl_3$ 3:2); ^{1}H NMR (400 MHz, CDCl3) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 2.11 (d, J = 11.9 Hz, 1H), 1.96-1.86 (m, 2H), 1.72 (d, *J* = 11.5 Hz, 2H), 1.62-1.47 (m, 2H), 1.19-1.03 (m, 2H), 0.99-0.86 (m, 7H), 0.78 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl3) δ 165.6, 137.6, 131.0, 130.3, 100.4, 75.2, 47.2, 40.9, 34.3, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6 ppm; HRMS m/z calculated for $C_{17}H_{23}INaO_2$ $[M + Na]^+$ 409.0635, found 409.0647. The NMR data are in agreement with literature.[7]

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2,5-diiodobenzoate (1n). To a suspension of 2,5-diiodobenzoic acid (1.87 g, 5.00 mmol, 1.0 equiv.) and oxalyl chloride (0.85 mL, 2.0 equiv.) in 20 mL toluene was added one drop of DMF. The solution was stirred continuously at room temperature for 2 h followed by 1 h at 35˚C. The solvent was removed from the colorless solution under reduced pressure. The off-white solid of 2,5-diiodobenzoyl chloride was redissolved in 8 mL CH_2Cl_2 and used without further purification. Triethylamine (0.77 mL, 1.1 equiv.) was added dropwise to a solution of L-menthol (0.78 g, 1.0 equiv.) and 4-(dimethylamino)pyridine (27 mg, 0.04 equiv.) in 7 mL CH_2Cl_2 at 0°C. A solution of 2,5-diiodobenzoyl chloride (5.00 mmol, 1.0 equiv.) in CH_2Cl_2 was added slowly at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 20 hours. The crude reaction mixture was mixed with sat. $NaHCO_3$ (10 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 x

[6] Y. Tu, L. Yuan, T. Wang, C. Wang, J. Ke J. Zhao, *J. Org. Chem.*, 2017, **82**, 4970.
[7] C. K. W. Jim, J. W. Y. Lam, C. W. T. Leung, A. Qin, F. Mahtab and B. Z. Tang, *Macromolecules*, 2011, **44**, 2427.

10 mL). The combined organic phases were washed with 1 M HCl (2 x 10 mL) and brine (2 x 10 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography using pentane/EtOAc (20:1) as eluent to afford title product (1.47 g, 57%) as a light yellow, viscous oil. Rf: 0.70 (in pentane/EtOAc 20:1); ^{1}H NMR (400 MHz, CDCl3) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.0 Hz, 1H), 4.96 (td, *J* = 10.9, 4.4 Hz, 1H), 2.19-2.10 (m, 1H), 2.02-1.90 (m, 1H), 1.77-1.68 (m, 2H), 1.61-1.49 (m, 2H), 1.23-1.04 (m, 2H), 0.99-0.88 (m, 7H), 0.81 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl3) δ 164.9, 142.7, 141.3, 139.2, 138.0, 93.3, 93.2, 47.1, 40.9, 34.3, 31.7, 26.4, 23.5, 22.2, 21.0, 16.4 ppm; HRMS m/z calculated for $C_{17}H_{23}I_2O_2$ $[M + H]^+$ 512.9782, found 512.9781.

6-((2-Iodobenzyl)oxy)nicotinonitrile (1o). Sodium hydride (60%, 240 mg, 1.2 equiv.) was added in two portions at room temperature to 2-iodobenzyl alcohol (1.17 g, 5.00 mmol, 1.0 equiv.) in 10 mL THF and stirred for 1 hour. 6-Chloro-3-pyridinecarbonitrile (0.83 g, 1.2 equiv.) was added in one portion and the solution was refluxed for 72 hours. The reaction mixture was diluted with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic phases was washed with brine (20 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using pentane/EtOAc (20:1) as eluent to afford title product (1.13 g, 67%) as a white solid. R*f*: 0.23 (in pentane/EtOAc 20:1); mp 104-105°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.82 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.46 (d, *J* = 6.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.8, 1.3 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.44 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 152.1, 141.4, 139.7, 138.6, 130.0, 129.6, 128.5, 117.3, 112.1, 103.1, 98.4, 72.6 ppm; HRMS *m/z* calculated for $C_{13}H_{10}IN_2O$ $[M + H]^+$ 336.9832, found 336.9826.

1-(4-Iodophenyl)-2,5-dimethyl-1*H*-pyrrole (1p). 2,5-Hexanedione (0.62 mL, 1.05 equiv.) was added to a mixture of 4-iodoaniline (1.09 g, 5.00 mmol, 1.0 equiv.) and *p*-TsOH (0.0089 g, 0.01 equiv.) in toluene (20 mL), and the mixture was heated to reflux for 18 hours by using a Dean-Stark apparatus. The cooled reaction mixture was diluted with EtOAc (50 mL), washed with sat. $NaHCO_3$ (20 mL) and brine (2 x 20 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using pentane/EtOAc (9:1) as eluent to afford title product (1.04 g, 70%) as a yellow solid. R*f*: 0.68 (in pentane/EtOAc 9:1); mp 79-80°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.90 (s, 2H), 2.03 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.4, 130.3, 128.8, 106.3, 93.0, 13.1 ppm; HRMS *m/z* calculated for $C_{12}H_{13}IN$ $[M + H]^+$ 298.0087, found 298.0083. The NMR data are in agreement with literature.[8]

4-(5-Iodopyridin-2-yl)morpholine (1q). Morpholine (0.21 mL, 1.1 equiv.) was added to a stirred suspension of 2-fluoro-4-iodopyridine (0.50 g, 2.2 mmol, 1.0 equiv.) and potassium carbonate (0.62 g, 2.0 equiv.) in 4.4 mL DMF at room temperature. The reaction mixture was heated to 80˚C and stirred continuously for 16 hours. The cooled reaction mixture was poured onto ice and the precipitate was filtrated and washed with water (3 x 20 mL) to afford the title compound (0.55 g, 85%) as a white solid. mp 133-134°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.47 (d, *J* = 8.9 Hz, 1H), 3.86 – 3.75 (m, 4H), 3.53 – 3.40 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 153.7,

[8] H. Lee and B. H. Kim, *Tetrahedron*, 2013, **69**, 6698.

145.1, 109.2, 78.1, 66.7, 45.5 ppm; HRMS *m/z* calculated for $C_9H_{12}IN_2O$ $[M + H]^+$ 290.9989, found 290.9991. The NMR data are in agreement with literature.[9]

(2-Iodopyridin-4-yl)(piperidin-1-yl)methanone (1r). Triethylamine (0.29 mL, 1.1 equiv.) and piperidine (0.21 mL, 1.1 equiv.) were added dropwise to a suspension of 2-iodoisonicotinoyl chloride at 0°C. The reaction mixture was allowed to warm to room temperature and stirred continuously for 18 hours. The crude reaction mixture was diluted with EtOAc (40 mL), washed with sat. Na_2CO_3 (3 x 15 mL) and brine (2 x 15 mL), dried above Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified using a short silica-plug filtration eluting with CH_2Cl_2/EtOAc (1:4), affording the title product (0.60 g, 99%) as a yellow, viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.32 (m, 1H), 7.73 – 7.63 (m, 1H), 7.23 – 7.14 (m, 1H), 3.73 – 3.58 (m, 2H), 3.33 – 3.18 (m, 2H), 1.73 – 1.59 (m, 4H), 1.56 – 1.43 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 151.0, 145.8, 132.1, 120.4, 118.3, 48.6, 43.2, 26.6, 25.5, 24.4 ppm; HRMS m/z calculated for $C_{11}H_{14}IN_2O$ $[M + H]^+$ 317.0145, found 317.0152.

1-Benzyl-5-iodo-1*H*-indole (1s). Synthesized by using literature procedure.[10] 5-Iodoindole (1.22 g, 5.00 mmol, 1.0 equiv.) was added portionwise to a stirred suspension of sodium hydride (60%, 600 mg, 3.0 equiv.) in 20 mL DMF at 0˚C and the reaction mixture was allowed to warm to room room temperature and stir for 30 minutes. The suspension was cooled to 0˚C and benzyl bromide (0.27 mL, 1.05 equiv.) was added dropwise. The resulting mixture was allowed to warm to room temperature and stir for 24 hours. The reaction was quenched by slowly adding ice-cooled water, and the mixture was subsequently diluted with ice-cooled until precipitation was visible. The reaction mixture was filtrated and the solids was washed with ice-cooled water (3 x 20 mL). The crude product was purified by recrystallization from 15 mL EtOH/EtOAc (10:1) to afford the title compound (1.20 g, 72%) as off-white flakes. mp 118-119°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.32 (dd, *J* = 10.7, 8.5 Hz, 3H), 7.18-7.05 (m, 4H), 6.50 (d, *J* = 3.0 Hz, 1H), 5.32 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 135.5, 131.4, 130.1, 129.9, 129.2, 129.0, 127.9, 126.8, 111.9, 101.2, 83.2, 50.4 ppm; HRMS *m/z* calculated for $C_{15}H_{13}IN$ $[M + H]^+$ 334.0087, found 334.0080. The NMR data are in agreement with literature.[9]

5-Iodo-1-(2-nitrophenyl)-1*H*-indole (1t). 5-Iodoindole (1.22 g, 5.00 mmol, 1.0 equiv.), 1-fluoro-2-nitrobenzene (0.53 mL, 1.0 equiv.) and Cs_2CO_3 (1.95 g, 1.2 equiv.) in 15 mL anhydrous DMSO were stirred at room temperature for 16 hours. The reaction mixture was diluted with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic phases was washed with saturated NH_4Cl (2 x 20 mL) and brine (2 x 20 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by recrystallization from 25 mL EtOH/EtOAc (7:1) to afford the title compound (1.64 g, 90%) as bright yellow flakes. mp 126-127°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.99 (m, 2H), 7.81-7.72 (m, 1H), 7.64-7.53 (m, 2H), 7.47-7.42 (m, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.65 (d, *J* = 3.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 136.1, 134.0, 132.4, 131.5, 131.4, 130.3, 129.9, 129.0 (2C), 125.8, 111.6, 104.3, 84.6 ppm; HRMS *m/z* calculated for $C_{14}H_{10}IN_2O_2$ $[M + H]^+$ 364.9781, found 364.9777. The NMR data are in agreement with literature.[11]

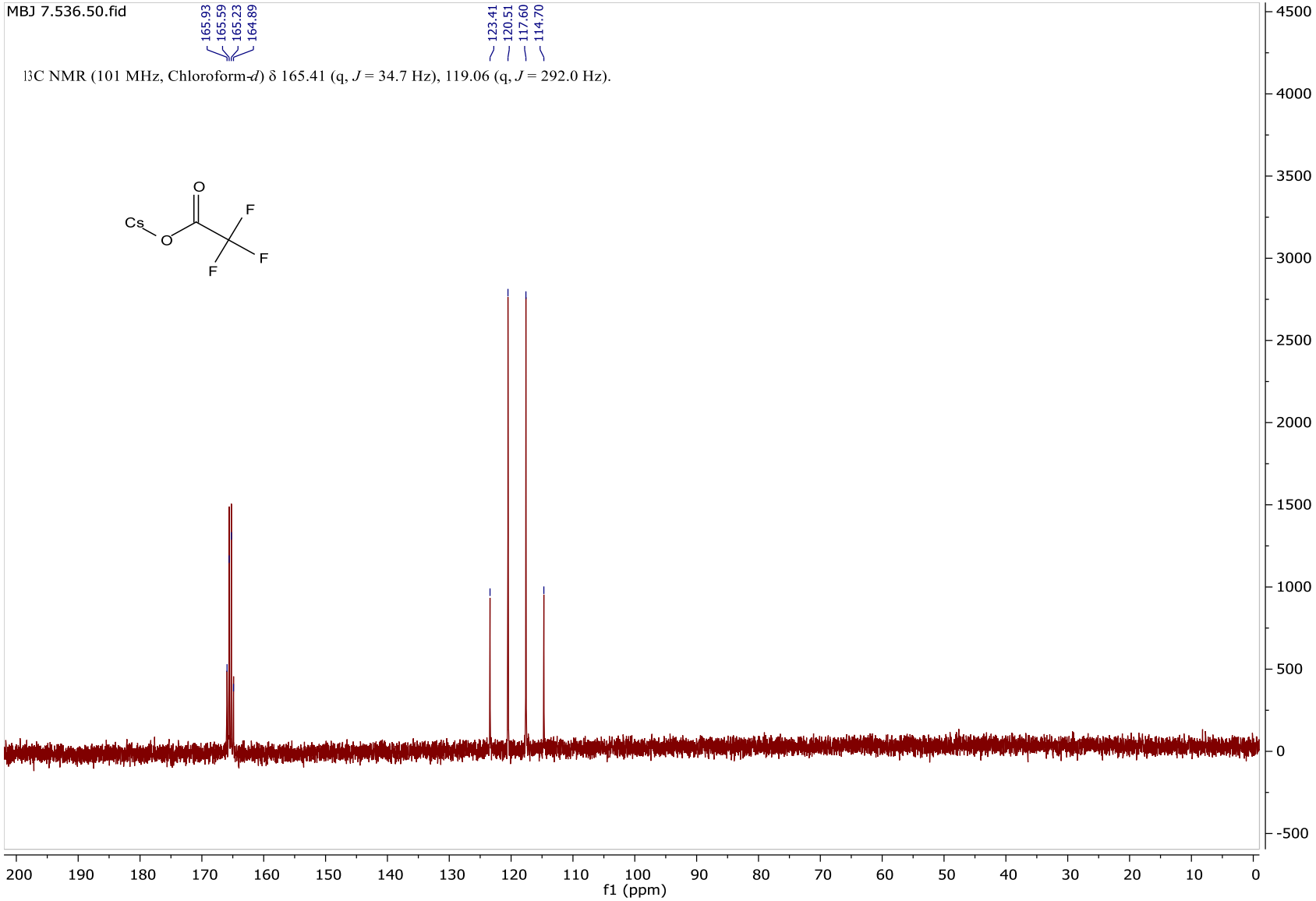
[9] G. J. P. Perry, J. M. Quibell, A. Panigrahi and I. Larrosa, *J. Am. Chem. Soc.*, 2017, **139**, 11527.
[10] Q. Xie, L. Li, Z. Zhu, R. Zhang, C. Ni and J. Hu, *Angew. Chem. Int. Ed.*, 2018, **57**, 13211.
[11] M. Chen and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2013, **52**, 11628.

1-Benzyl-4-iodo-1*H*-pyrazole (1v). Synthesized by using literature procedure.[12] 4-Iodopyrrazole (0.97 g, 5.00 mmol, 1.0 equiv.) was added portionwise to a stirred suspension of sodium hydride (60%, 300 mg, 1.5 equiv.) in 5 mL THF at 0˚C and the reaction mixture was stirred for 30 minutes. Benzyl bromide (0.59 mL, 0.99 equiv.) was added dropwise to the suspension. The resulting mixture was allowed to warm to room temperature and stir for 4 hours. The reaction mixture was diluted with water (20 mL) and extracted with Et_2O (30 mL). The ethereal phase was washed with water (2 x 20 mL) and brine (2 x 50 mL), dried above Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using pentane/EtOAc (15:1) as eluent to afford title product (1.16 g, 83%) as a white solid. R*f*: 0.27 (in pentane/EtOAc 15:1); mp 34-35°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.43 – 7.30 (m, 4H), 7.25 – 7.20 (m, 2H), 5.30 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 135.9, 133.7, 129.1, 128.5, 128.0, 56.6 (2C) ppm; HRMS *m/z* calculated for $C_{10}H_{10}IN_2$ $[M + H]^+$ 284.9883, found 284.9882. The NMR data are in agreement with literature.[12]

2,2,2-Trifluoro-*N*-(3-(4-iodophenoxy)-3-phenylpropyl)-*N*-methylacetamide (1w). 3-(methylamino)-1-phenylpropan-1-ol (1.84 g, 11.2 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to 0°C on an ice bath. Et_3N (2.27 g, 2.0 equiv.) was added followed by dropwise addition of trifluoroacetic anhydride (2.58 g, 1.1 equiv.). The reaction mixture was left to stir at room temperature for 1 hour. The solution was washed with $NaHCO_3$ solution (3 x 10 mL), 0.5 M $KHSO_4$ solution (3 x 10 mL) and brine (3 x 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in CH_3CN (50 mL). $NaHCO_3$ was added (50 mL) and the mixture was stirred for 1 hour at room temperature. The reaction mixture was diluted with water and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4, filtered and concentrated in vacuo affording 2,2,2-trifluoro-*N*-(3-hydroxy-3-phenylpropyl)-*N*-methylacetamide as a clear oil (2.30 g, 79%). The crude product was used in the next step without further purification. A solution of diisopropyl azodicarboxylate (2.16 g, 1.3 equiv.) in anhydrous THF (50 mL) was added dropwise to an ice-bath cooled mixture of 2,2,2-trifluoro-*N*-(3-hydroxy-3-phenylpropyl)-*N*-methylacetamide (2.14 g, 8.2 mmol), PPh_3 (2.81 g, 1.3 equiv.) and 4-iodophenol (2.35 g, 1.3 equiv.) dissolved in anhydrous THF (20 mL). The reaction mixture was stirred for 4 hours at room temperature under argon atmosphere. The organic solvent was evaporated under reduced pressure and a mixture of Et_2O/Hexane (40 mL, 1:1) was added to the residue. The resulting precipitate was filtered off, and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2/Et_2O (1:1, 100 mL) and washed with 1M NaOH (3 x 40mL) and water (50 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2/pentane 1:1) to afford the title compound as a viscous, yellow oil (3.00 g, 79%). R*f*: 0.39 (CH_2Cl_2/pentane 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ *Mixture of rotamers* 7.49 – 7.43 (m, 2H), 7.39 – 7.26 (m, 5H), 6.65 – 6.58 (m, 2H), 5.11 – 5.16 (m, 1H), 3.71 – 3.58 (m, 2H), 3.13 (d, *J* = 1.6 Hz, 2H), 3.04 (s, 1H), 2.35 – 2.21 (m, 1H), 2.21 – 2.10 (m, 1H). ppm. ^{13}C NMR (101 MHz, $CDCl_3$ δ *Mixture of rotamers* 157.6, 157.5, 157.0 (q, *J* = 35.8 Hz), 140.4, 140.0, 138.3 (d, *J* = 2.2 Hz), 129.1, 129.0, 128.3, 128.2, 125.8, 125.6, 118.3, 118.2, 116.5 (q, *J* = 287.9 Hz), 116.6 (q, *J* = 288.9 Hz), 83.5, 83.4, 78.3, 77.6, 47.1, 46.5 (q, *J* = 3.3 Hz), 37.5, 35.5, 35.4 (q, *J* = 4.0 Hz), 34.8. ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ *Mixture of rotamers* -68.9, -69.8 ppm. HRMS m/z calculated for $C_{18}H_{17}F_3INNaO_2$ $[M + Na]^+$ 486.0148, found: 486.0153.

[12] H.-X. Zheng, X.-H. Shan and Y.-B. Kang, *Org. Lett.*, 2017, **19**, 5114.

NMR Spectra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165.59
165.23
164.89
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117.60
114.70
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Cs
O
O
F
F
F
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
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50
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10
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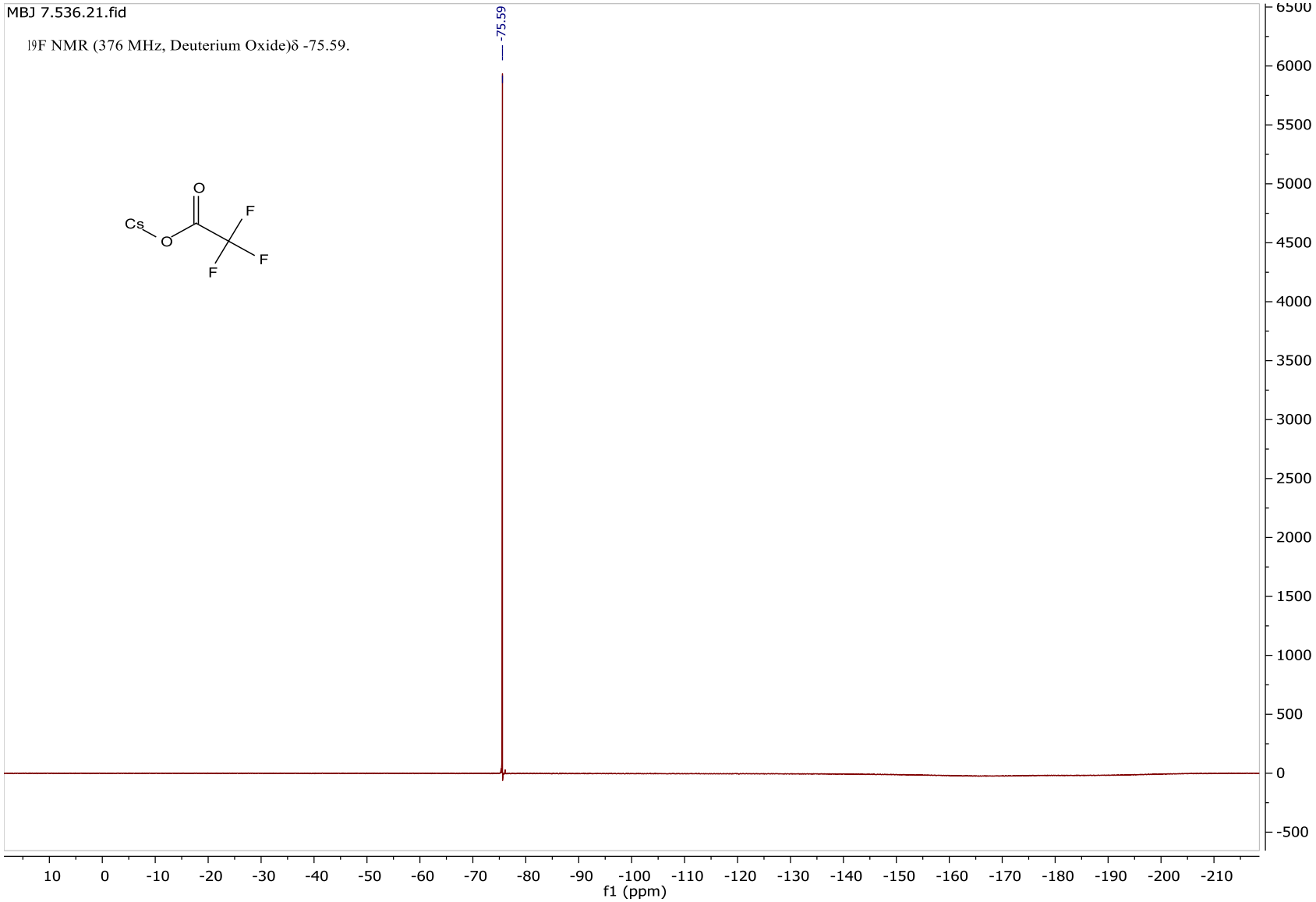
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-75.59
Cs
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O
F
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6000
5500
5000
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4000
3500
3000
2500
2000
1500
1000
500
0
-500
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-10
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-70
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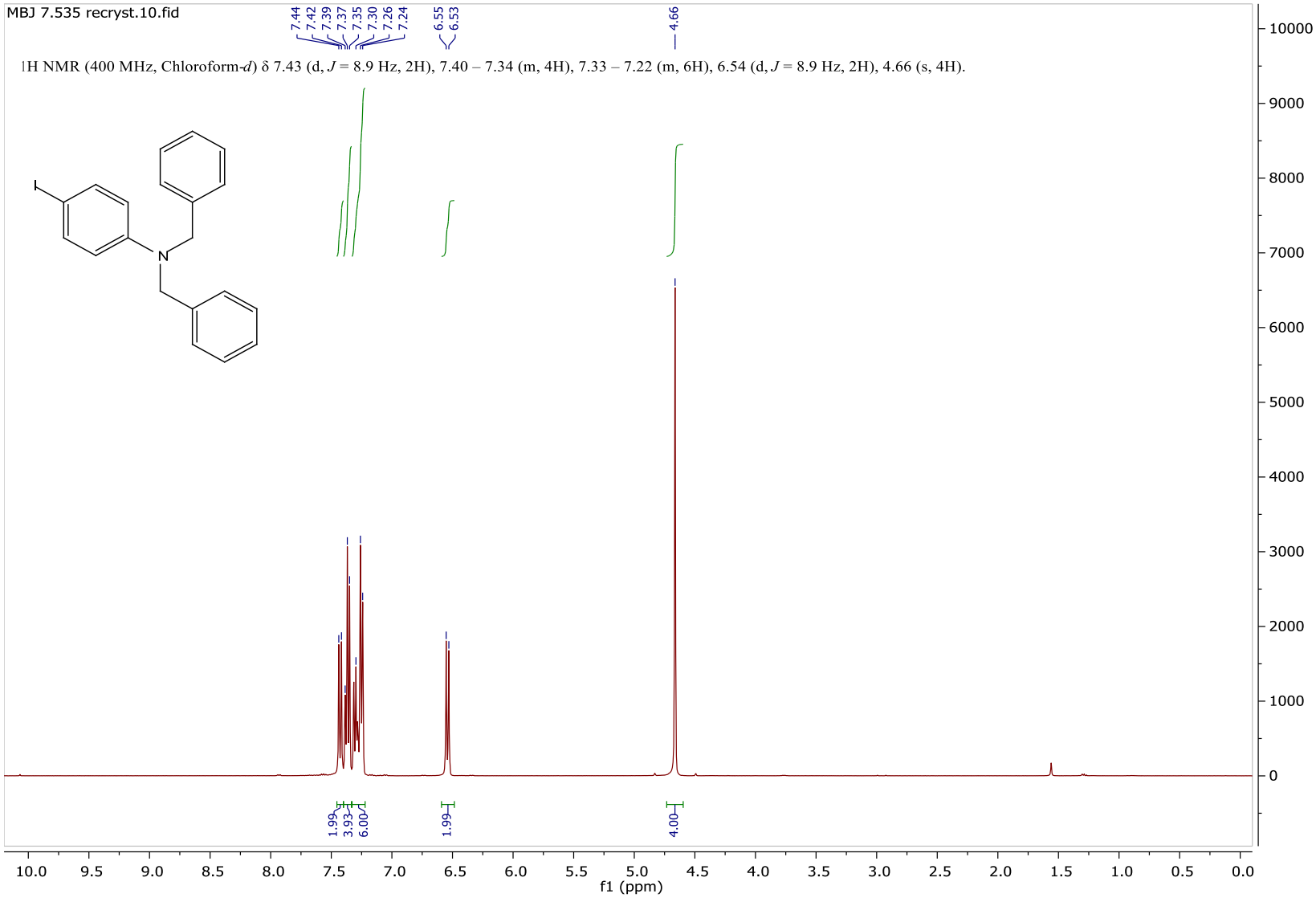
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7.39
7.37
7.35
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7.24
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6.53
4.66
1H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 8.9 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.33 – 7.22 (m, 6H), 6.54 (d, J = 8.9 Hz, 2H), 4.66 (s, 4H).
I
N
1.99
3.93
6.00
1.99
4.00
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
9.5
9.0
8.5
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7.5
7.0
6.5
6.0
5.5
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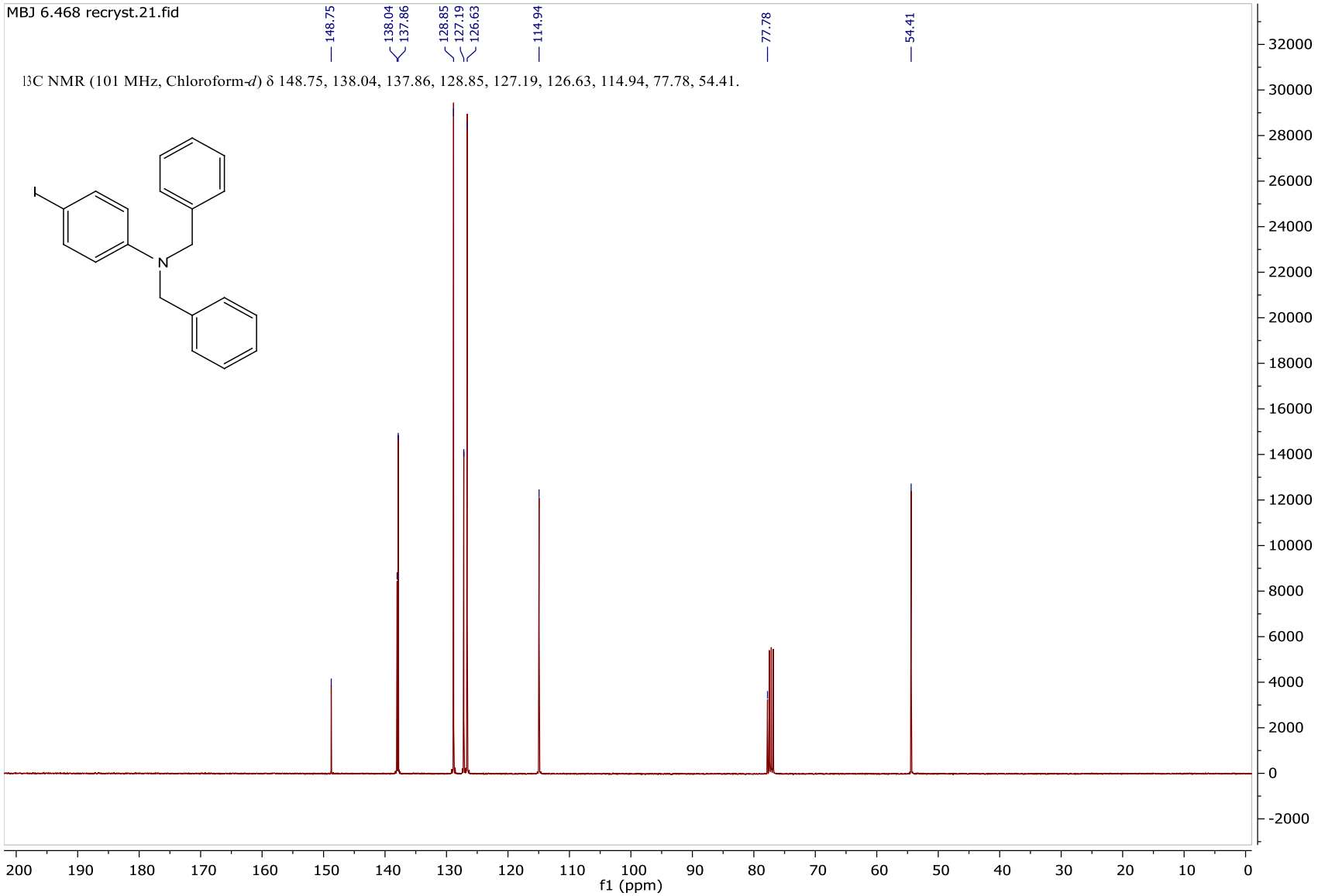
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I
N
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24000
22000
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18000
16000
14000
12000
10000
8000
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4000
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0
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200
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180
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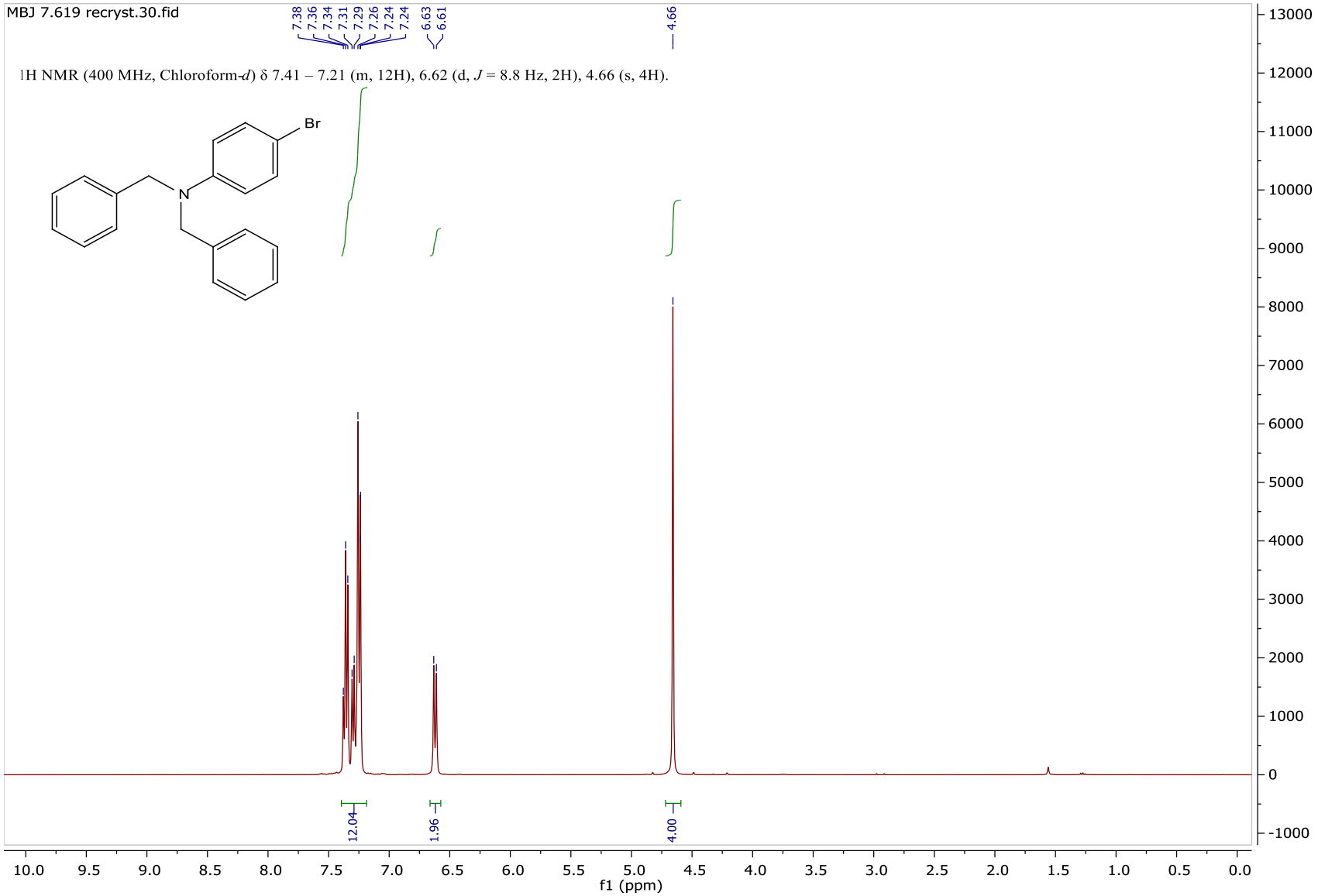
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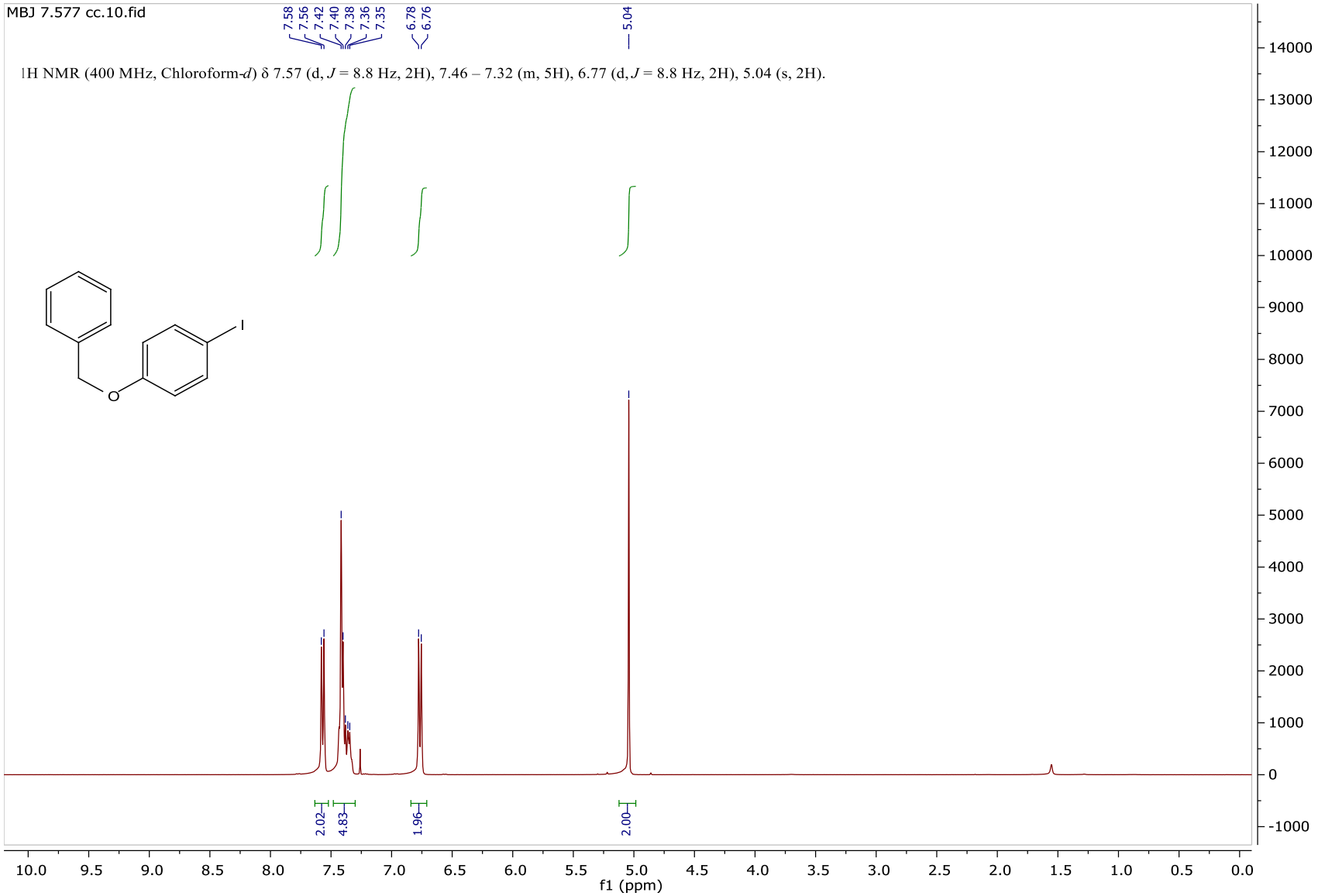
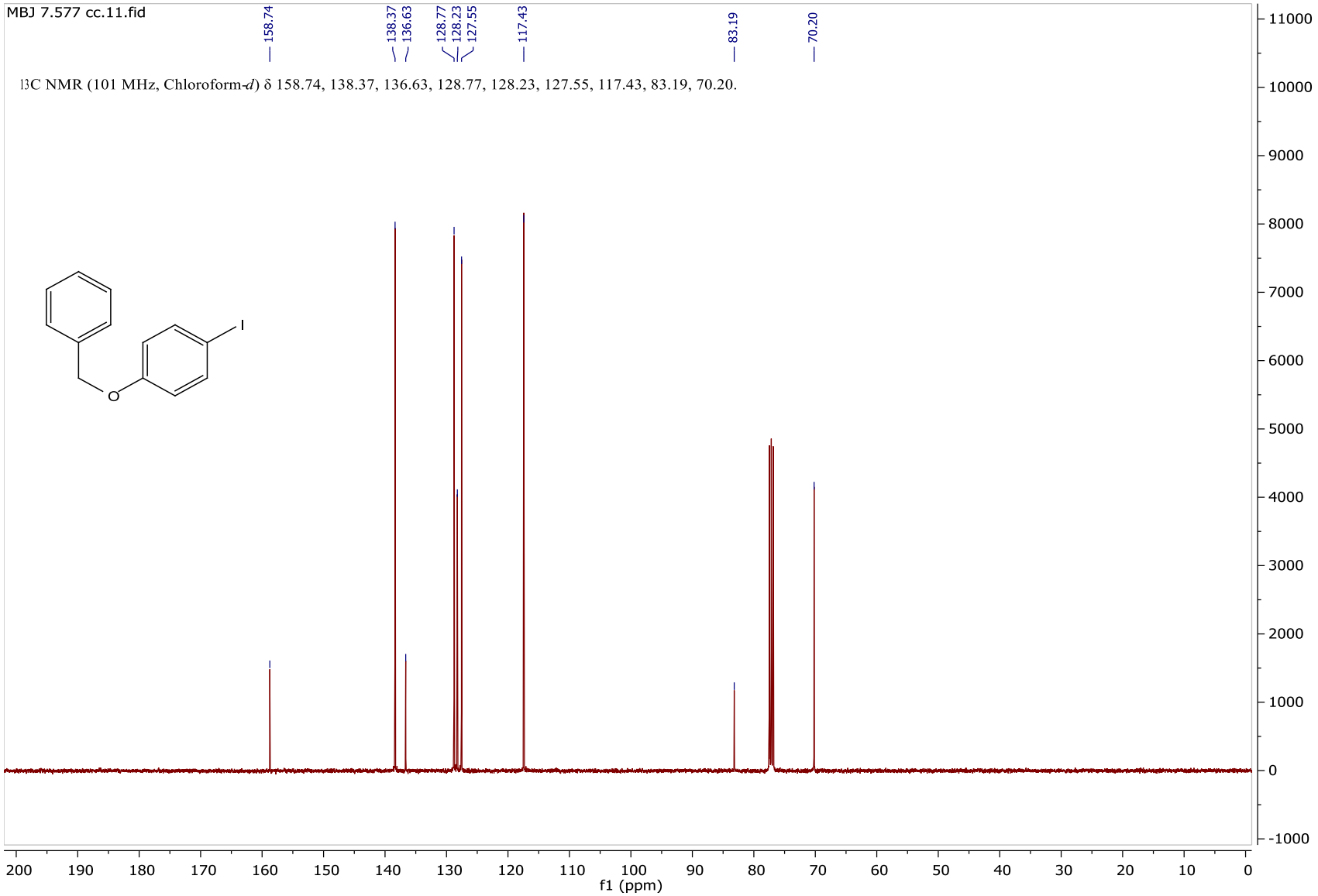
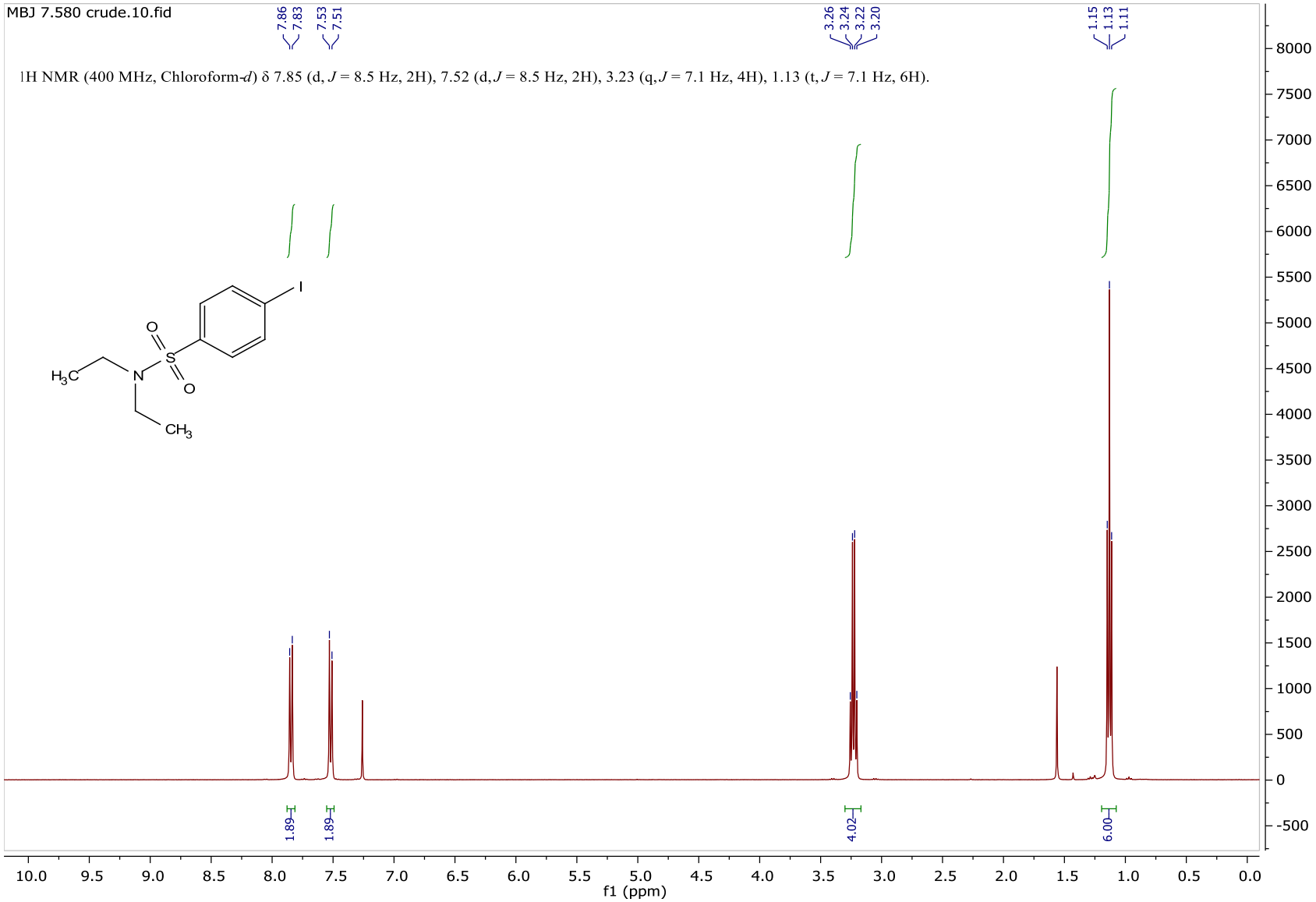
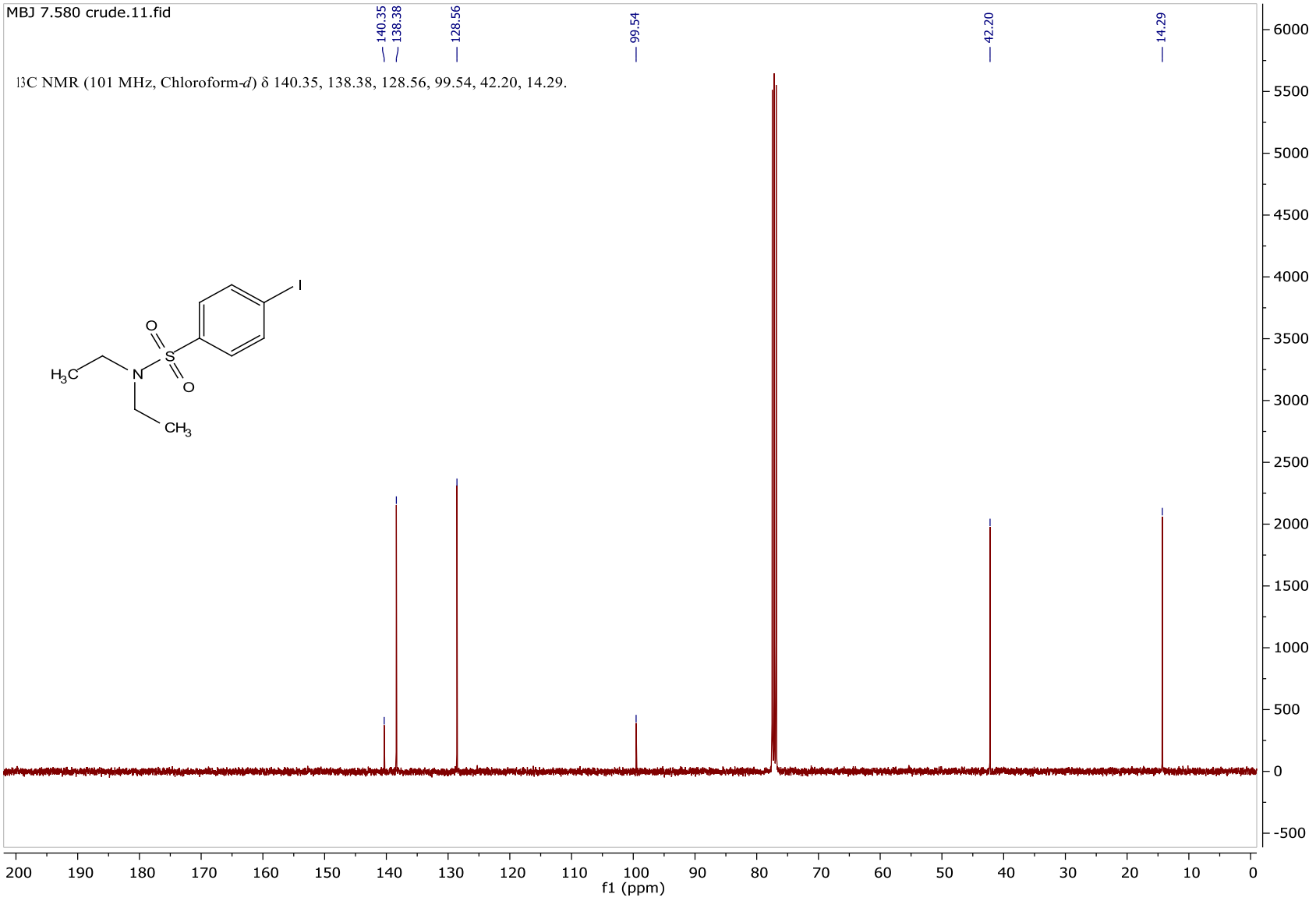
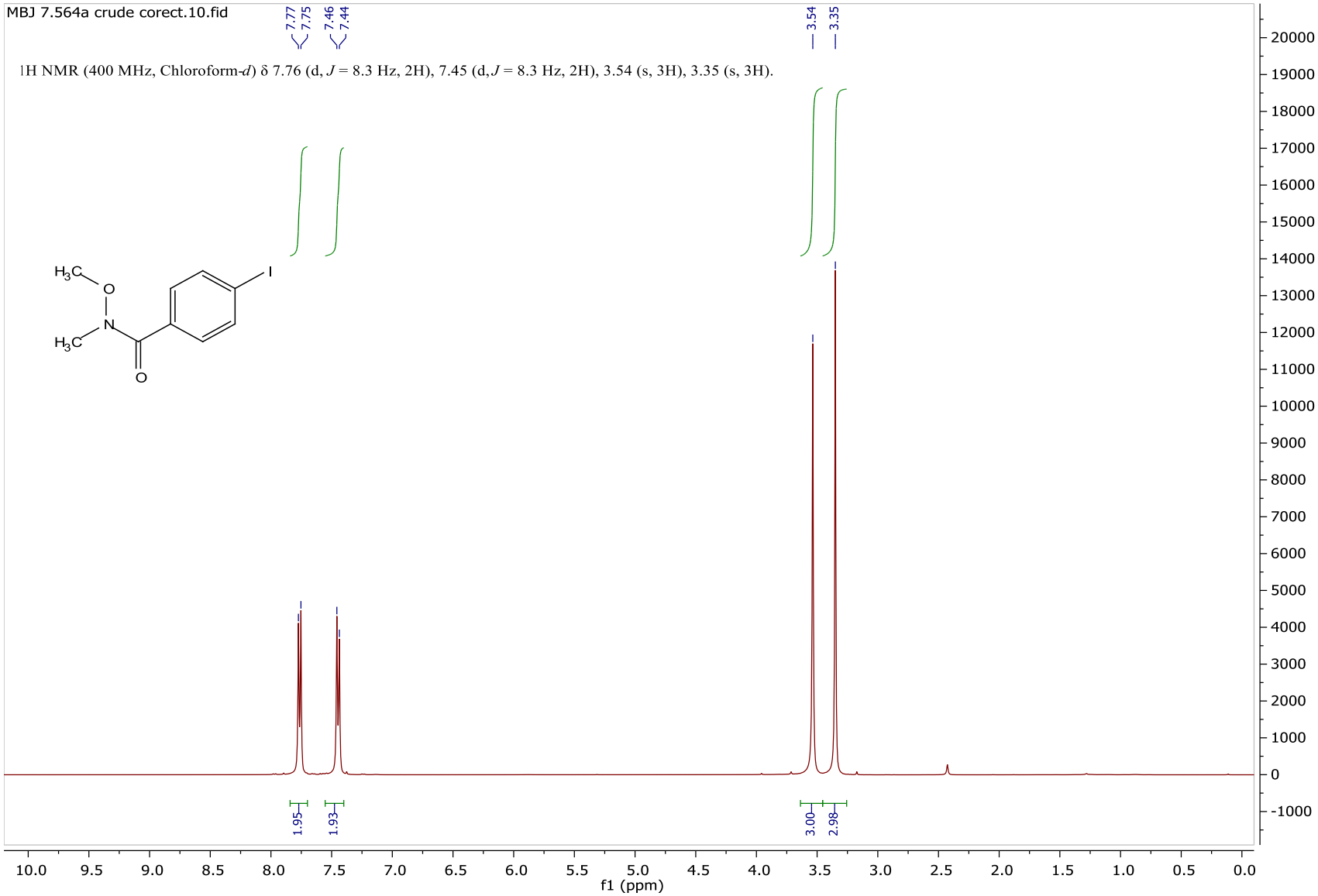
7.34
7.31
7.29
7.26
7.24
7.24
6.63
6.61
4.66
1H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.21 (m, 12H), 6.62 (d, J = 8.8 Hz, 2H), 4.66 (s, 4H).
Br
N
12.04
1.96
4.00
f1 (ppm)

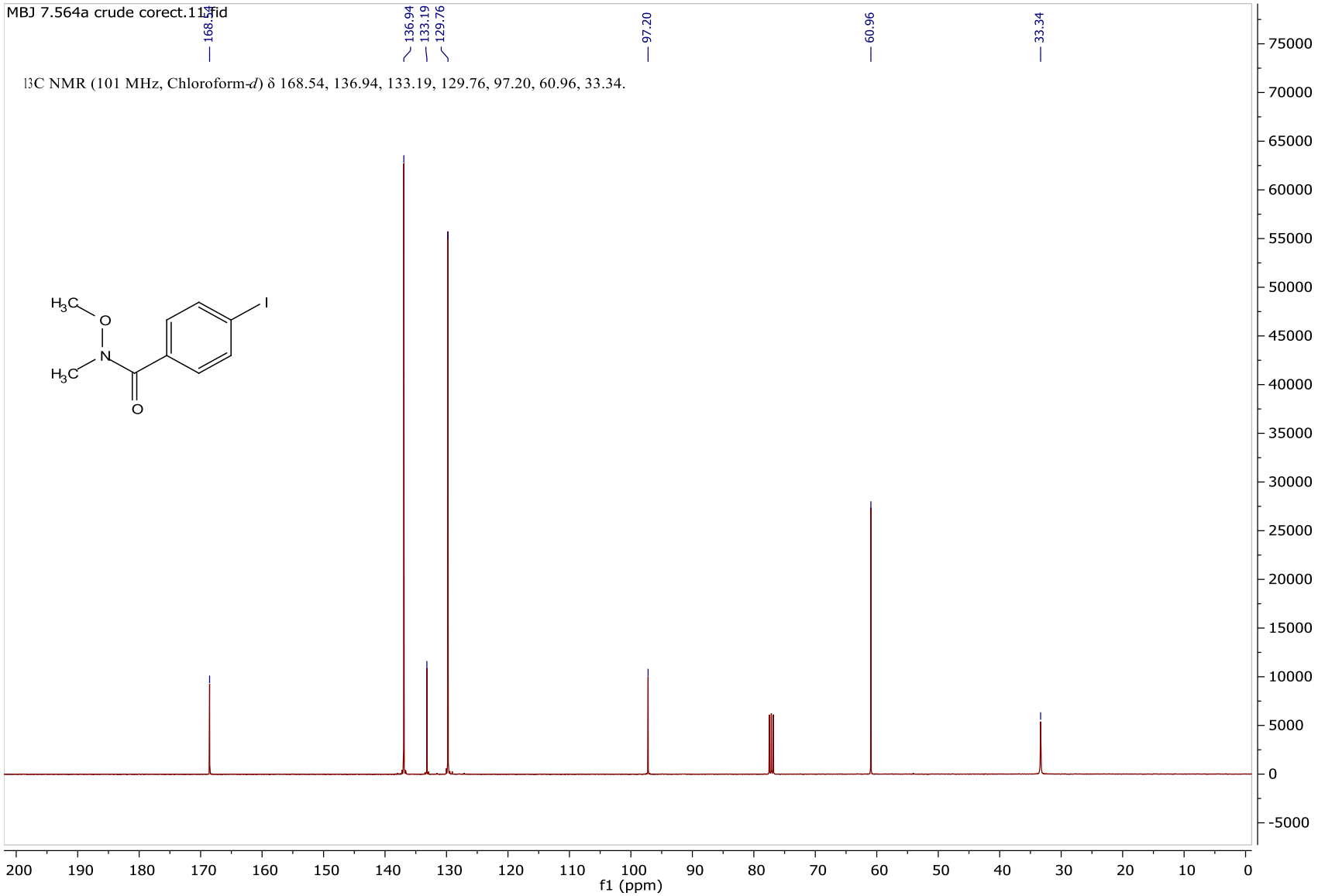

MBJ 7.577 cc.10.fid
7.58
7.56
7.42
7.40
7.38
7.36
7.35
6.78
6.76
5.04
1H NMR (400 MHz, Chloroform-d) δ 7.57 (d, J = 8.8 Hz, 2H), 7.46 – 7.32 (m, 5H), 6.77 (d, J = 8.8 Hz, 2H), 5.04 (s, 2H).
I
O
2.02
4.83
1.96
2.00
f1 (ppm)

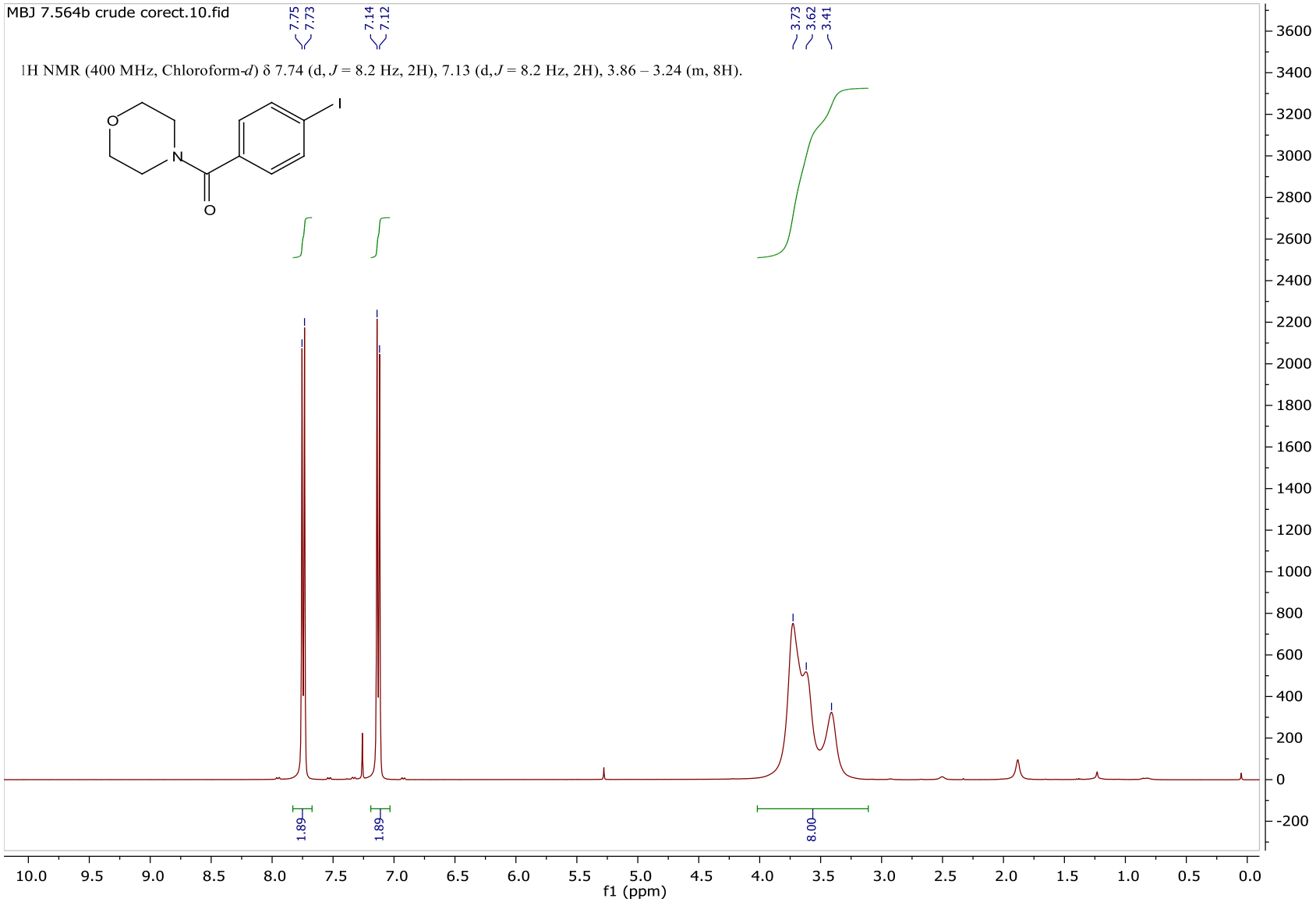

MBJ 7.577 cc.11.fid
158.74
138.37
136.63
128.77
128.23
127.55
117.43
83.19
70.20
13C NMR (101 MHz, Chloroform-d) δ 158.74, 138.37, 136.63, 128.77, 128.23, 127.55, 117.43, 83.19, 70.20.
I
O
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

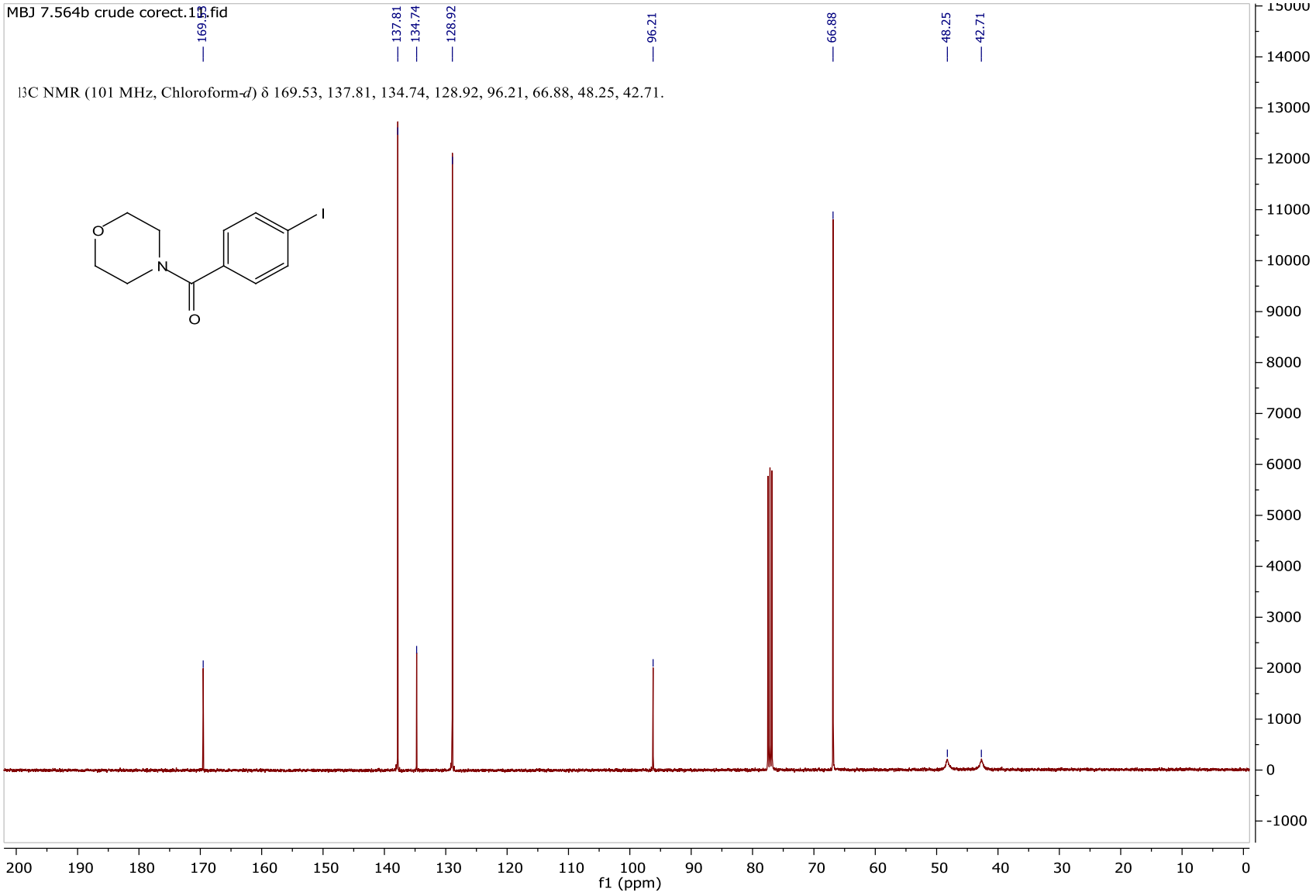

MBJ 7.580 crude.10.fid
7.86
7.83
7.53
7.51
3.26
3.24
3.22
3.20
1.15
1.13
1.11
1H NMR (400 MHz, Chloroform-d) δ 7.85 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 3.23 (q, J = 7.1 Hz, 4H), 1.13 (t, J = 7.1 Hz, 6H).
I
O
S
O
H3C
N
CH3
1.89
1.89
4.02
6.00
f1 (ppm)

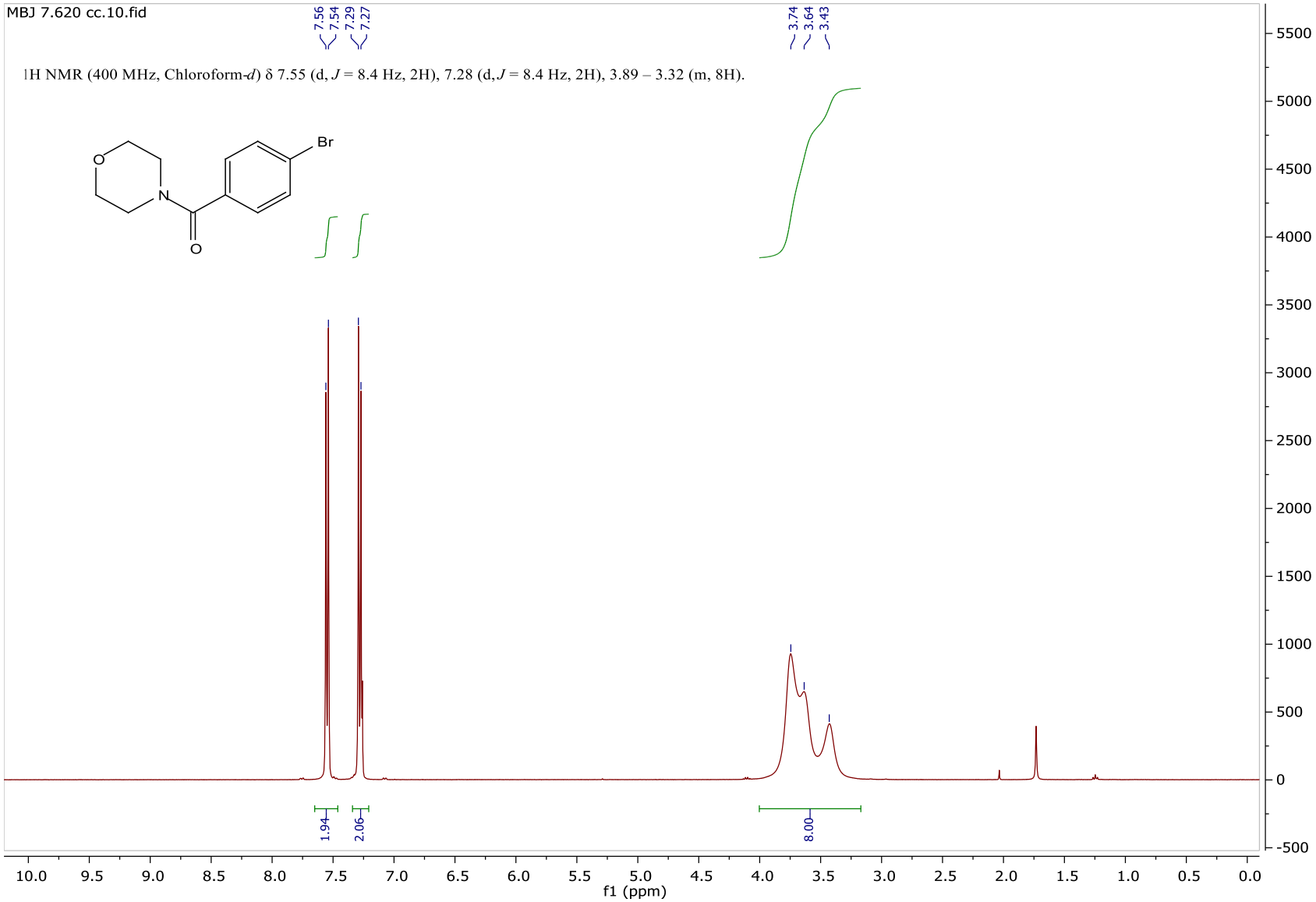

MBJ 7.580 crude.11.fid
140.35
138.38
128.56
99.54
42.20
14.29
13C NMR (101 MHz, Chloroform-d) δ 140.35, 138.38, 128.56, 99.54, 42.20, 14.29.
I
O
S
O
H3C
N
CH3
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

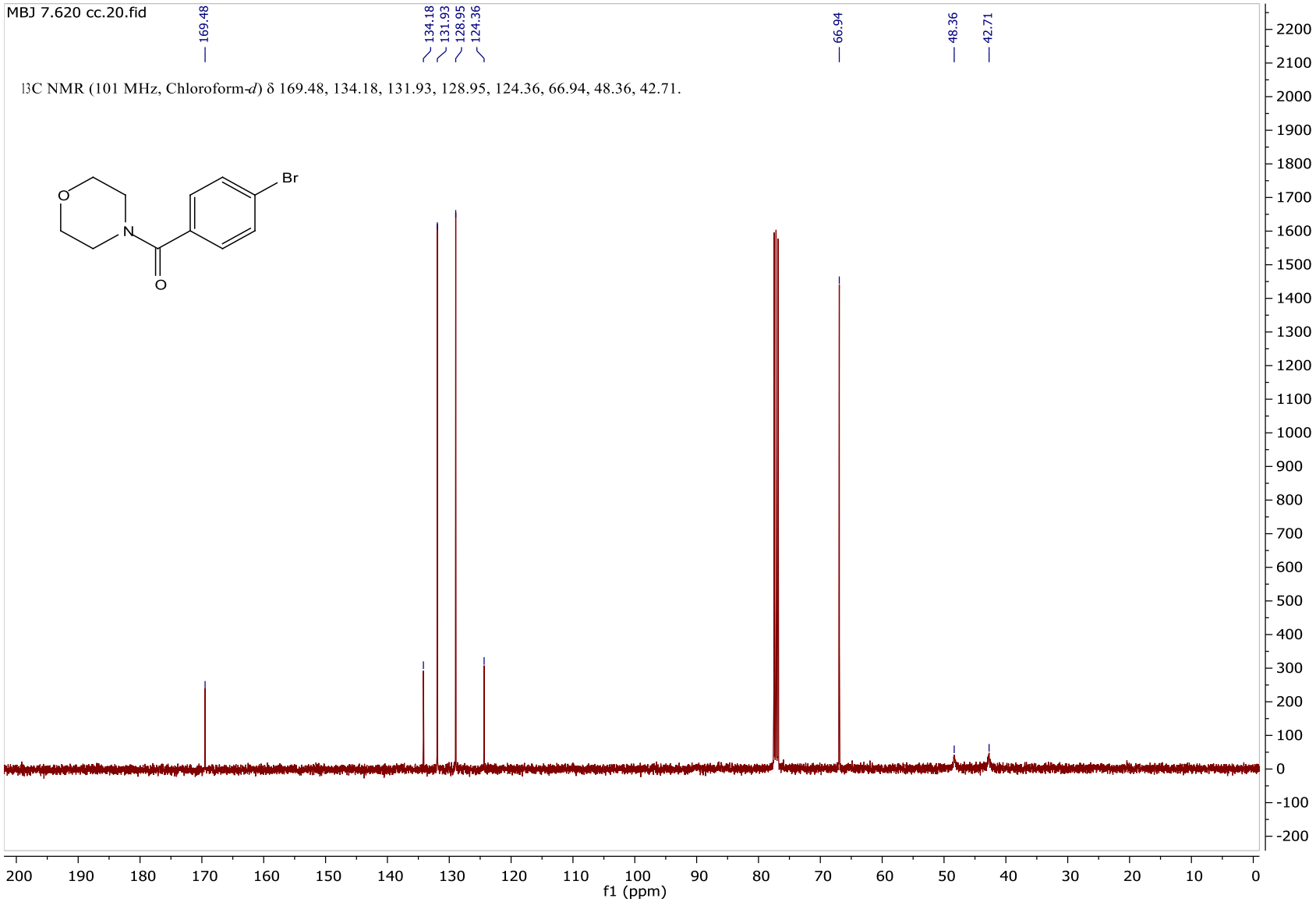

MBJ 7.564a crude corect.10.fid
7.77
7.75
7.46
7.44
3.54
3.35
1H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 3.54 (s, 3H), 3.35 (s, 3H).
H3C
O
N
H3C
O
I
1.95
1.93
3.00
2.98
f1 (ppm)

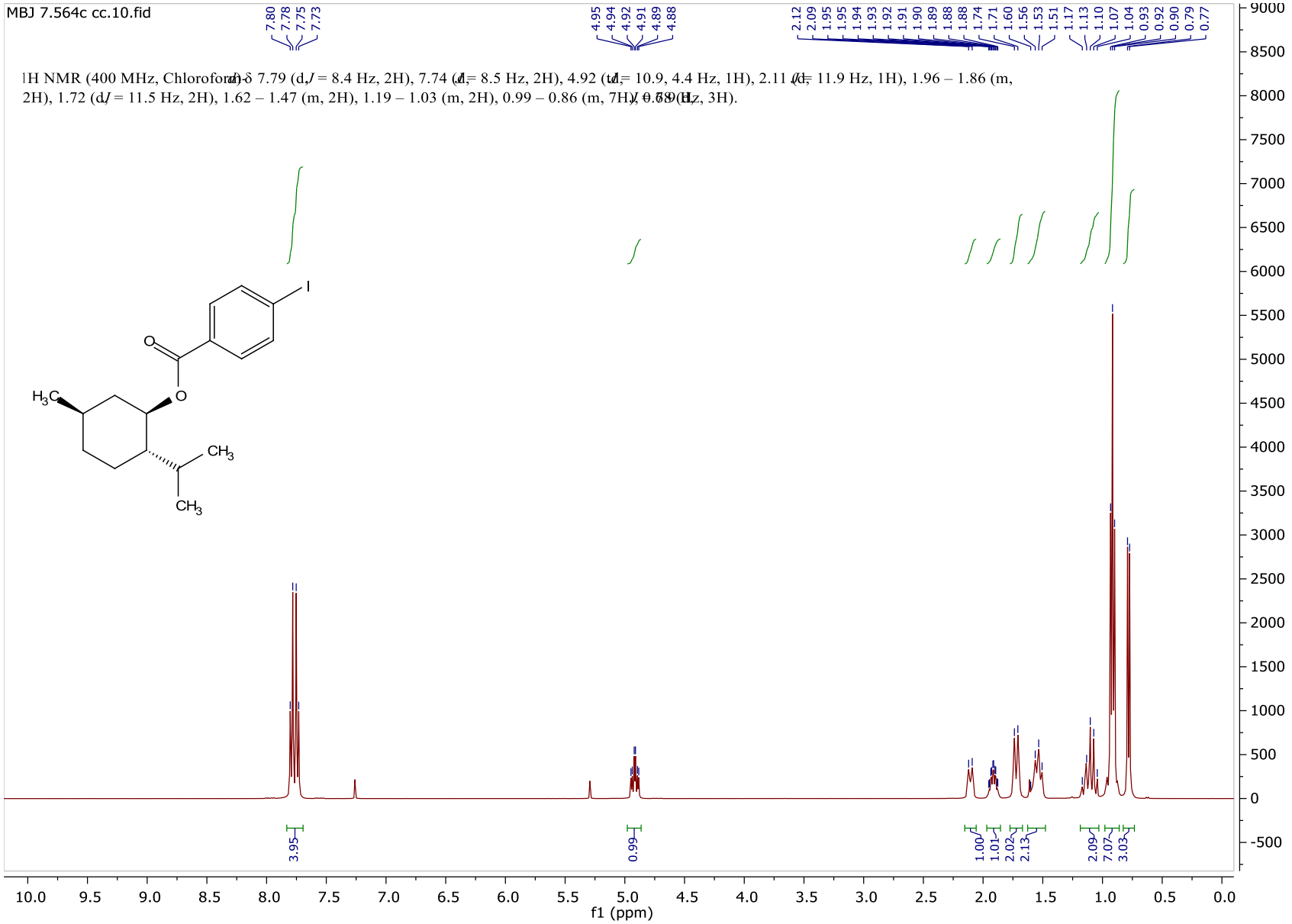

MBJ 7.564a crude corect.11.fid
168.54
136.94
133.19
129.76
97.20
60.96
33.34
13C NMR (101 MHz, Chloroform-d) δ 168.54, 136.94, 133.19, 129.76, 97.20, 60.96, 33.34.
H3C
O
N
H3C
O
I
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

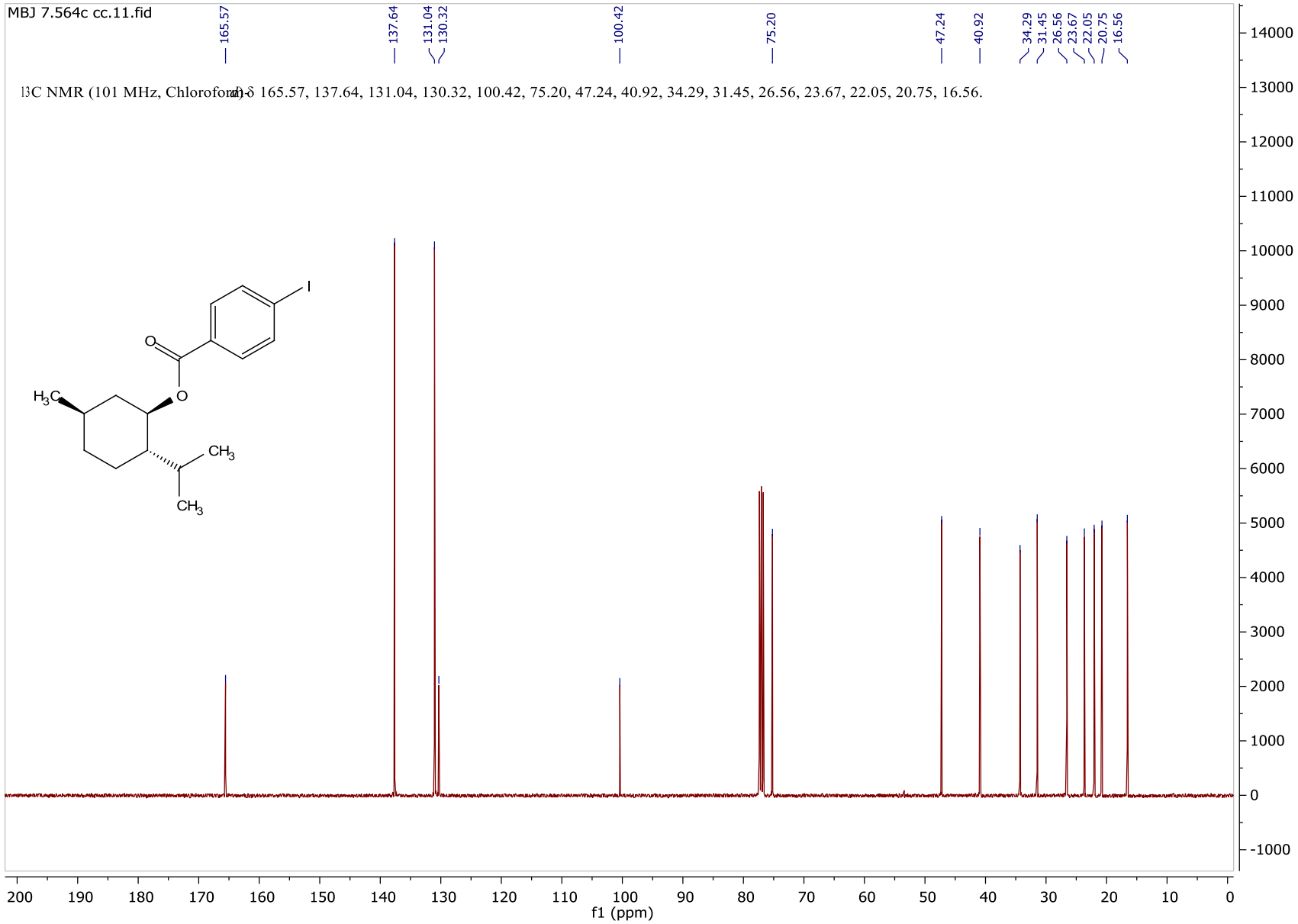

MBJ 7.564b crude corect.10.fid
7.75
7.73
7.14
7.12
3.73
3.62
3.41
1H NMR (400 MHz, Chloroform-d) δ 7.74 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 3.86 – 3.24 (m, 8H).
O
N
O
I
1.89
1.89
8.00
f1 (ppm)

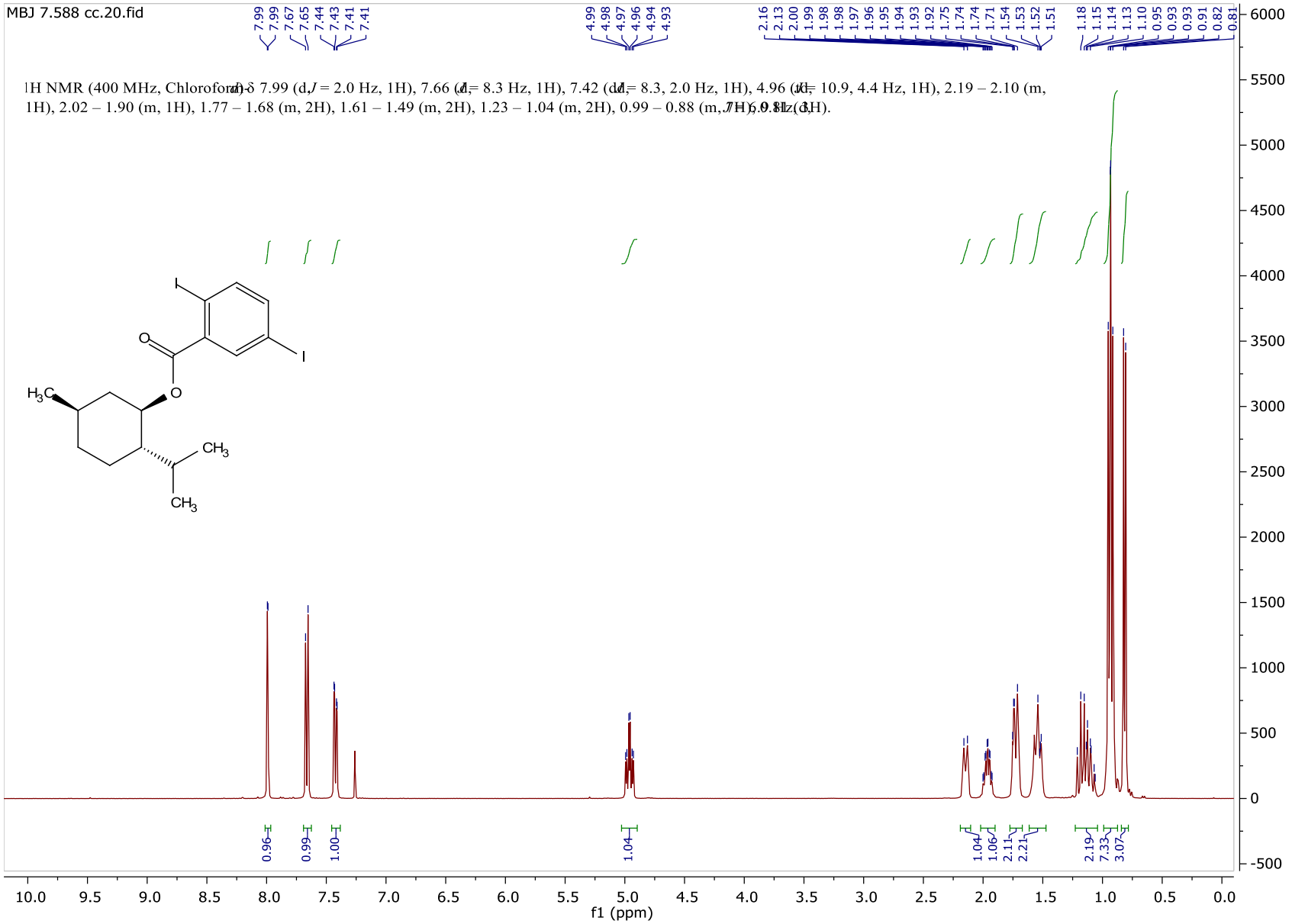

MBJ 7.564b crude corect.11.fid
169.53
137.81
134.74
128.92
96.21
66.88
48.25
42.71
13C NMR (101 MHz, Chloroform-d) δ 169.53, 137.81, 134.74, 128.92, 96.21, 66.88, 48.25, 42.71.
O
N
O
I
f1 (ppm)

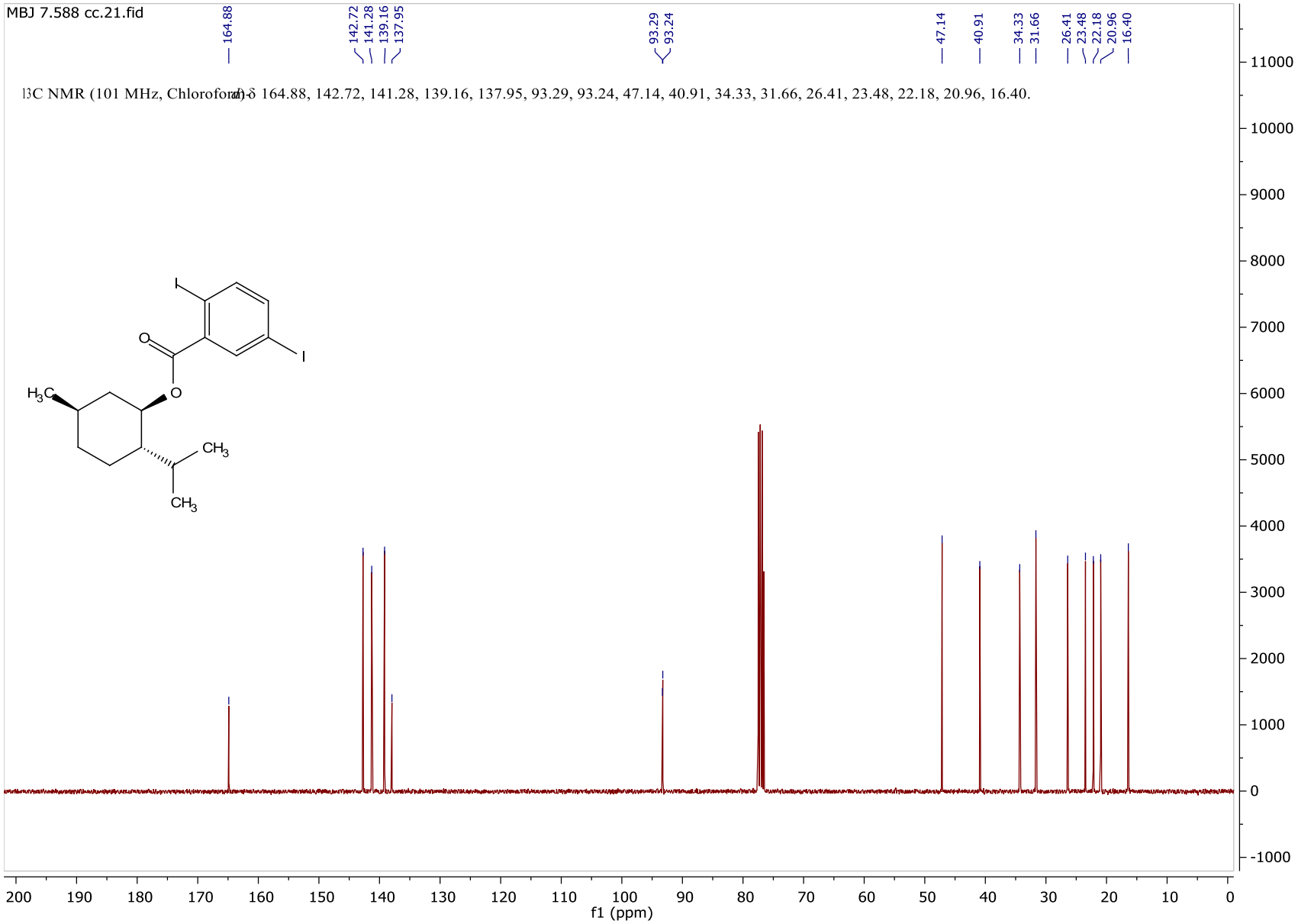

MBJ 7.620 cc.10.fid
7.56
7.54
7.29
7.27
3.74
3.64
3.43
1H NMR (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.89 – 3.32 (m, 8H).
Br
O
N
O
1.94
2.06
8.00
f1 (ppm)

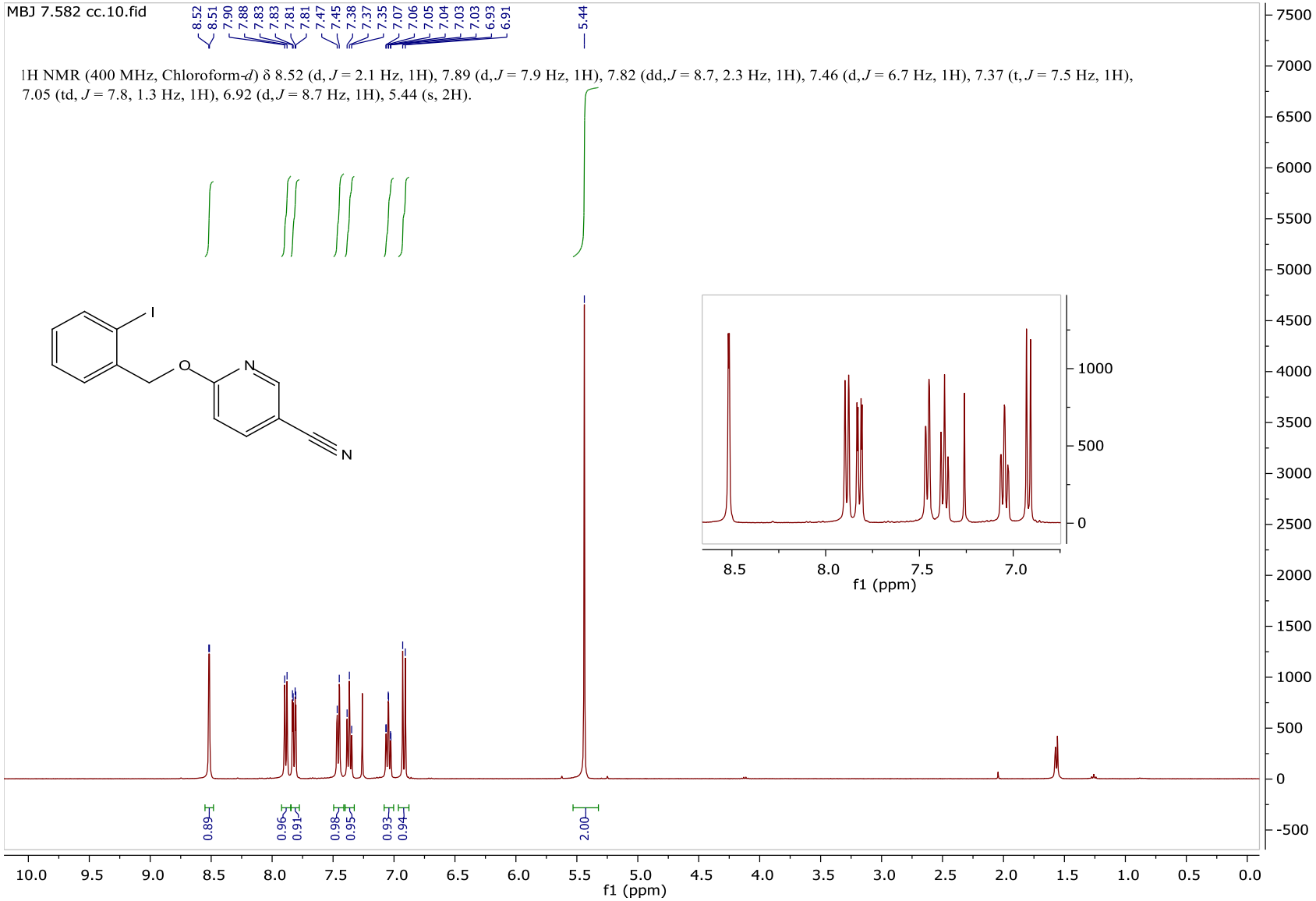

MBJ 7.620 cc.20.fid
169.48
134.18
131.93
128.95
124.36
66.94
48.36
42.71
13C NMR (101 MHz, Chloroform-d) δ 169.48, 134.18, 131.93, 128.95, 124.36, 66.94, 48.36, 42.71.
Br
O
N
O
f1 (ppm)

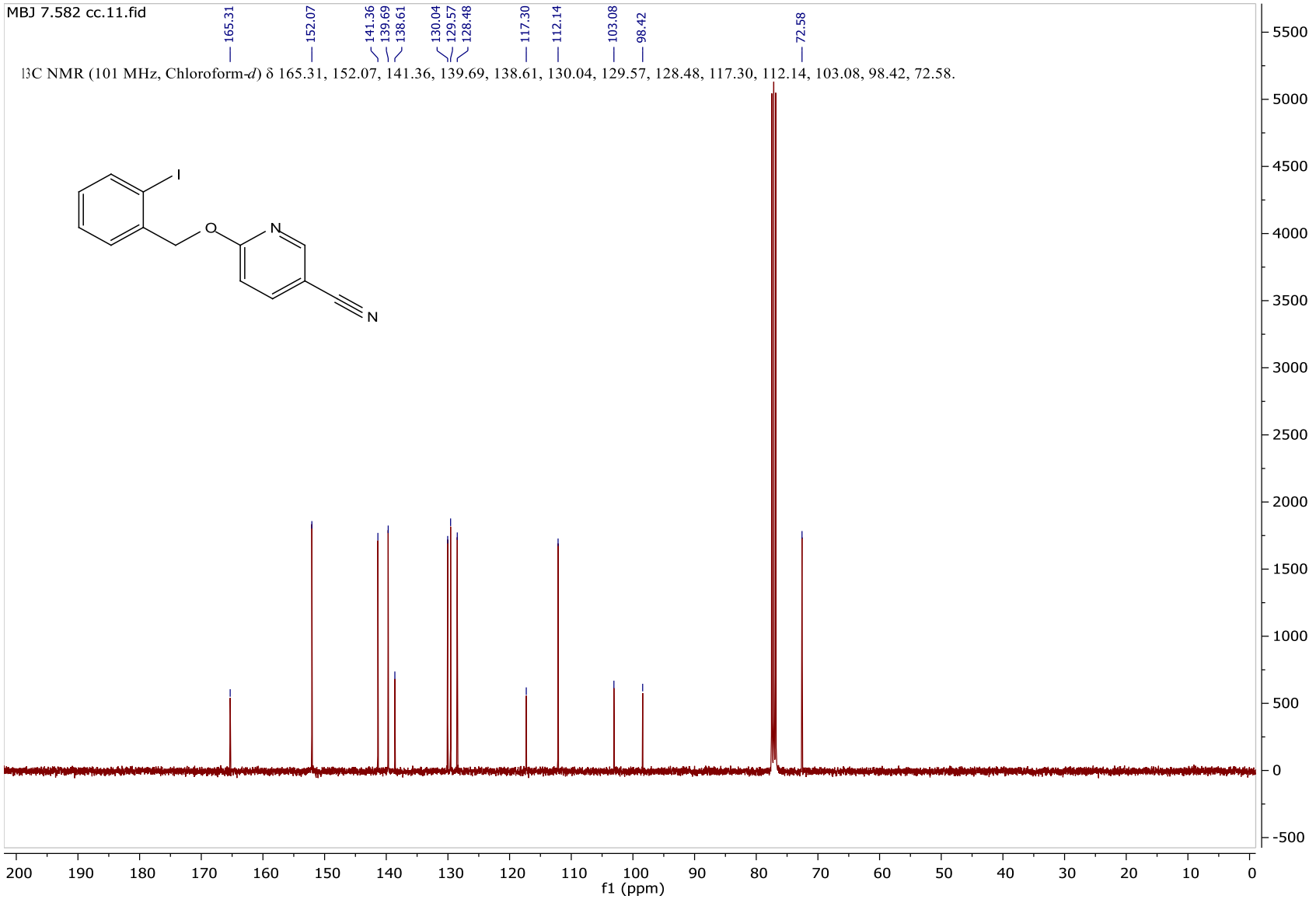

MBJ 7.564c cc.10.fid
7.80
7.78
7.75
7.73
4.95
4.94
4.92
4.91
4.89
4.88
2.12
2.09
1.95
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.88
1.88
1.74
1.71
1.60
1.56
1.53
1.51
1.17
1.13
1.10
1.07
1.04
0.93
0.92
0.90
0.79
0.77
1H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 4.92 (td, J = 10.9, 4.4 Hz, 1H), 2.11 (d, J = 11.9 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.72 (d, J = 11.5 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.19 – 1.03 (m, 2H), 0.99 – 0.86 (m, 7H), 0.78 (d, J = 6.9 Hz, 3H).
I
O
O
H3C
CH3
CH3
3.95
0.99
1.00
1.01
2.02
2.13
2.09
7.07
3.03
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

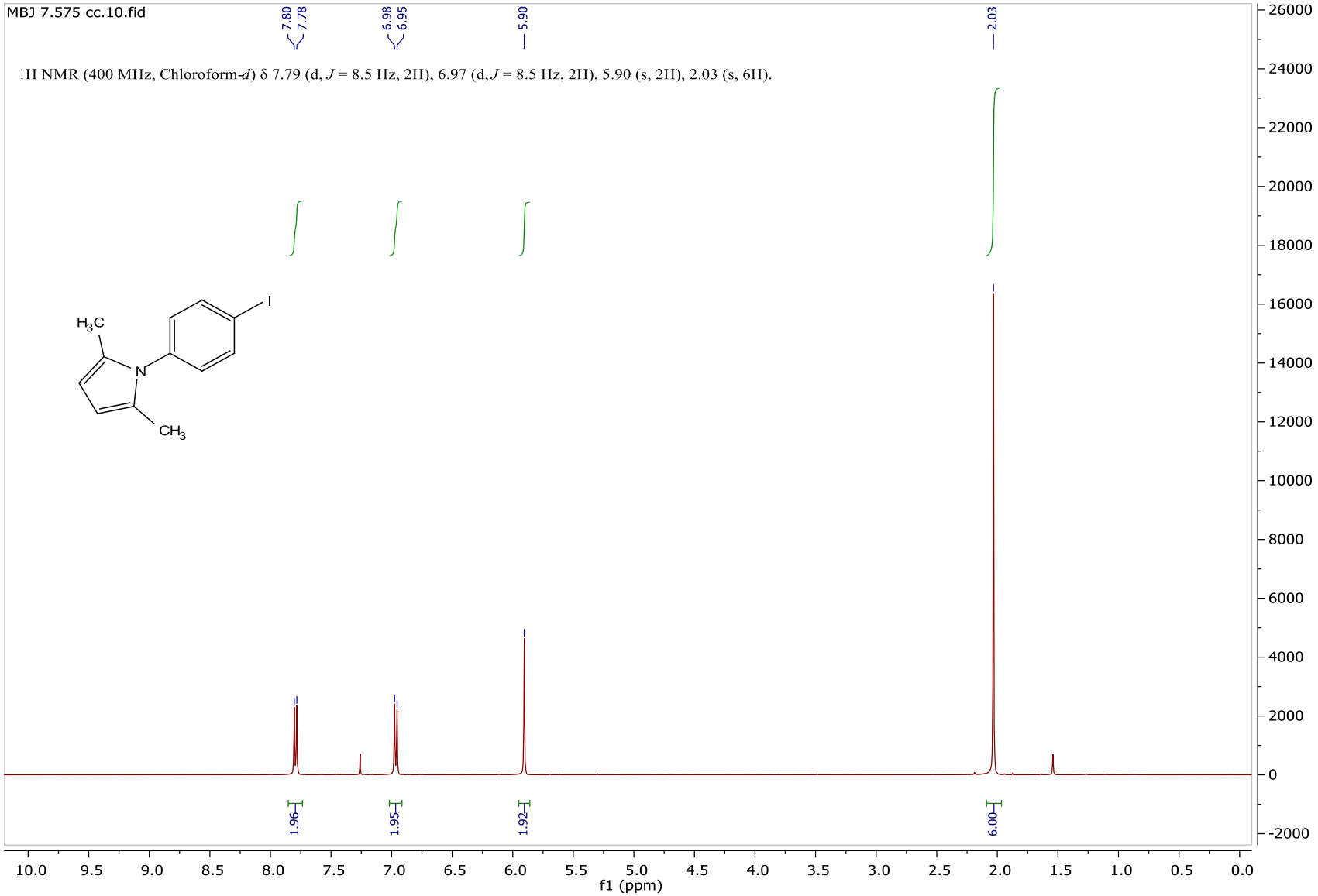

MBJ 7.564c cc.11.fid
165.57
137.64
131.04
130.32
100.42
75.20
47.24
40.92
34.29
31.45
26.56
23.67
22.05
20.75
16.56
13C NMR (101 MHz, Chloroform-d) δ 165.57, 137.64, 131.04, 130.32, 100.42, 75.20, 47.24, 40.92, 34.29, 31.45, 26.56, 23.67, 22.05, 20.75, 16.56.
I
O
O
H3C
CH3
CH3
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

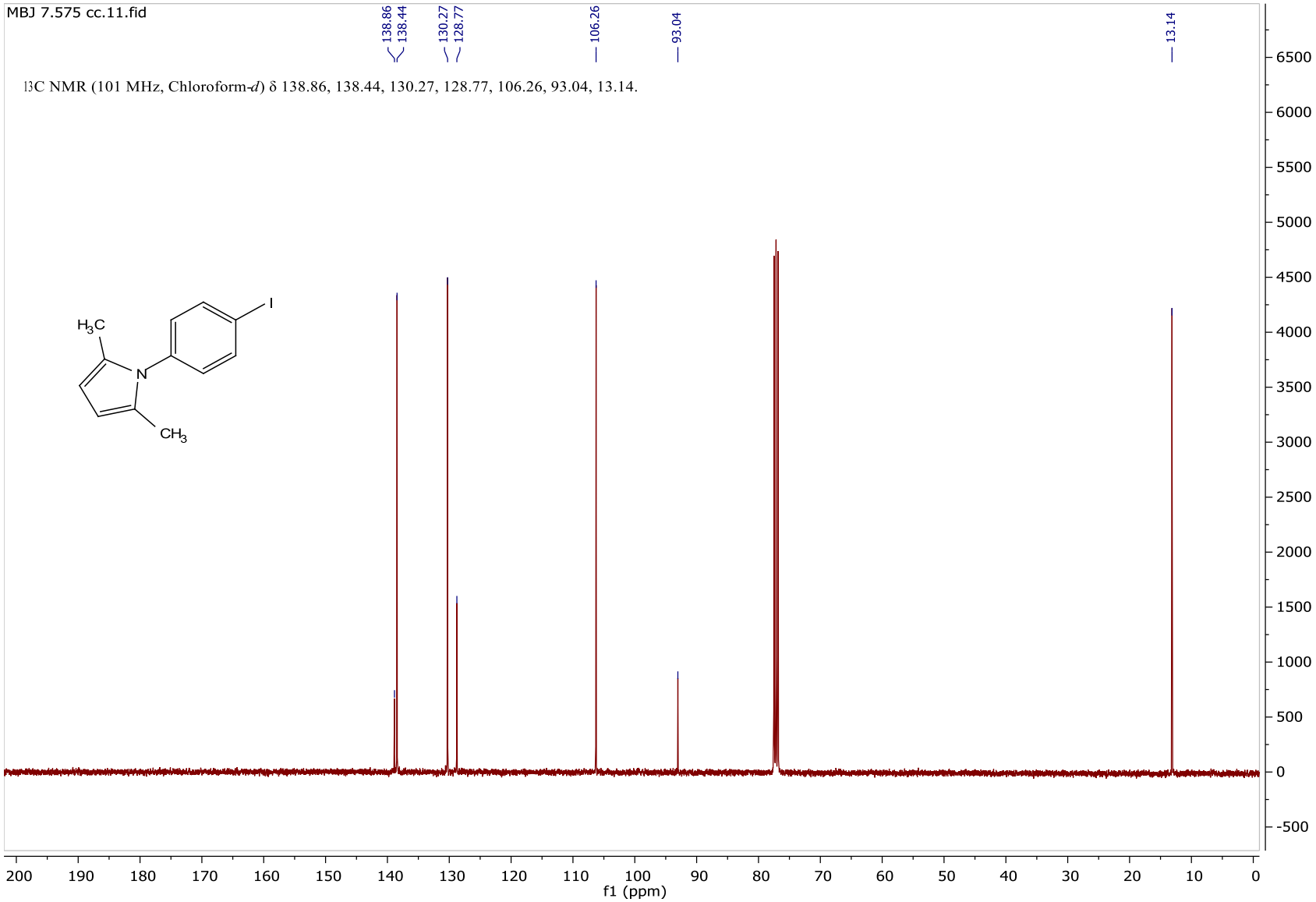

MBJ 7.588 cc.20.fid
1H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 2.0 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.42 (dd, J = 8.3, 2.0 Hz, 1H), 4.96 (dt, J = 10.9, 4.4 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.02 – 1.90 (m, 1H), 1.77 – 1.68 (m, 2H), 1.61 – 1.49 (m, 2H), 1.23 – 1.04 (m, 2H), 0.99 – 0.88 (m, 7H), 0.81 (d, J = 6.9 Hz, 3H).
f1 (ppm)

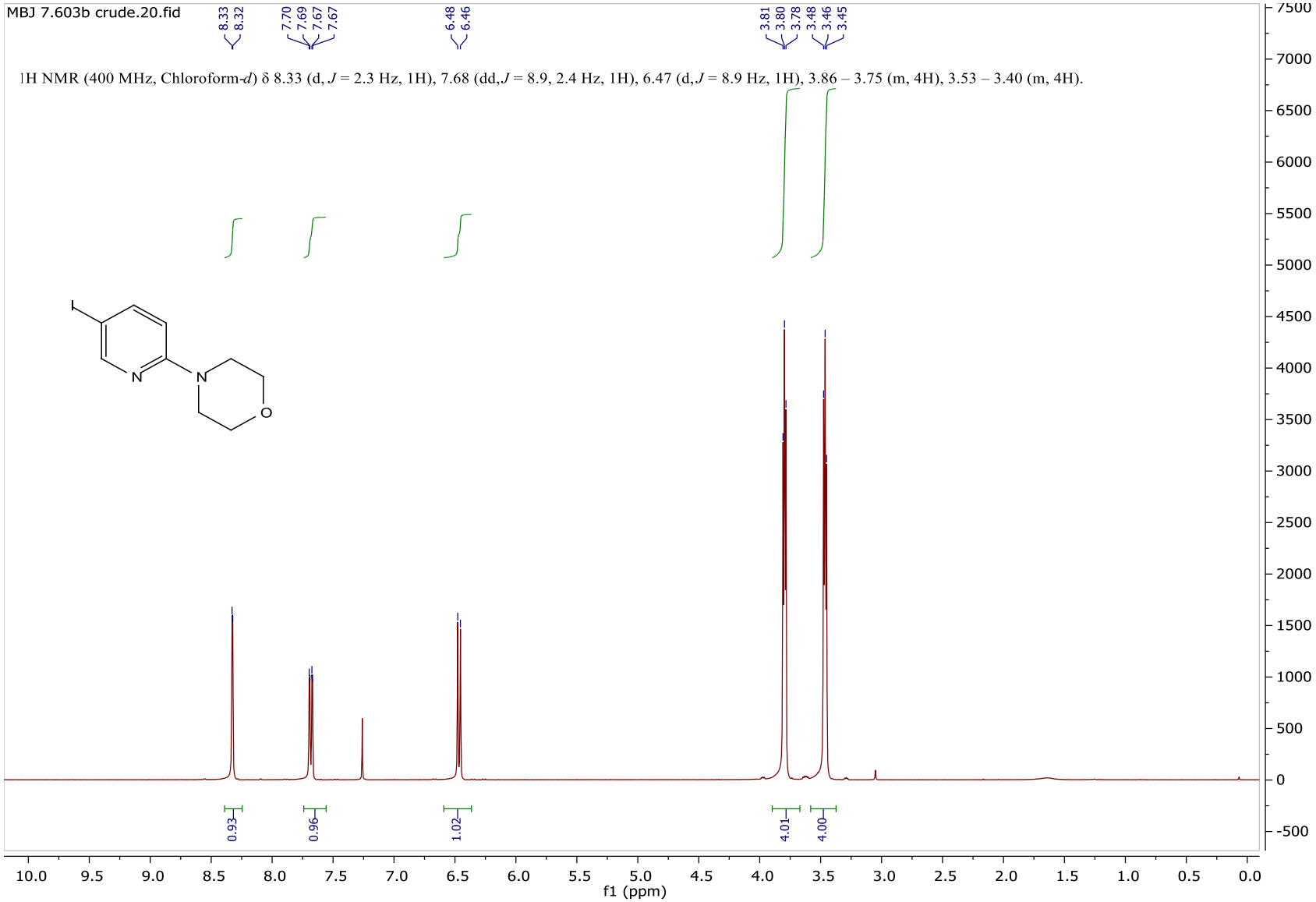

MBJ 7.588 cc.21.fid
164.88
142.72
141.28
139.16
137.95
93.29
93.24
47.14
40.91
34.33
31.66
26.41
23.48
22.18
20.96
16.40
13C NMR (101 MHz, Chloroform-d) δ 164.88, 142.72, 141.28, 139.16, 137.95, 93.29, 93.24, 47.14, 40.91, 34.33, 31.66, 26.41, 23.48, 22.18, 20.96, 16.40.
I
O
I
O
H3C
CH3
CH3
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

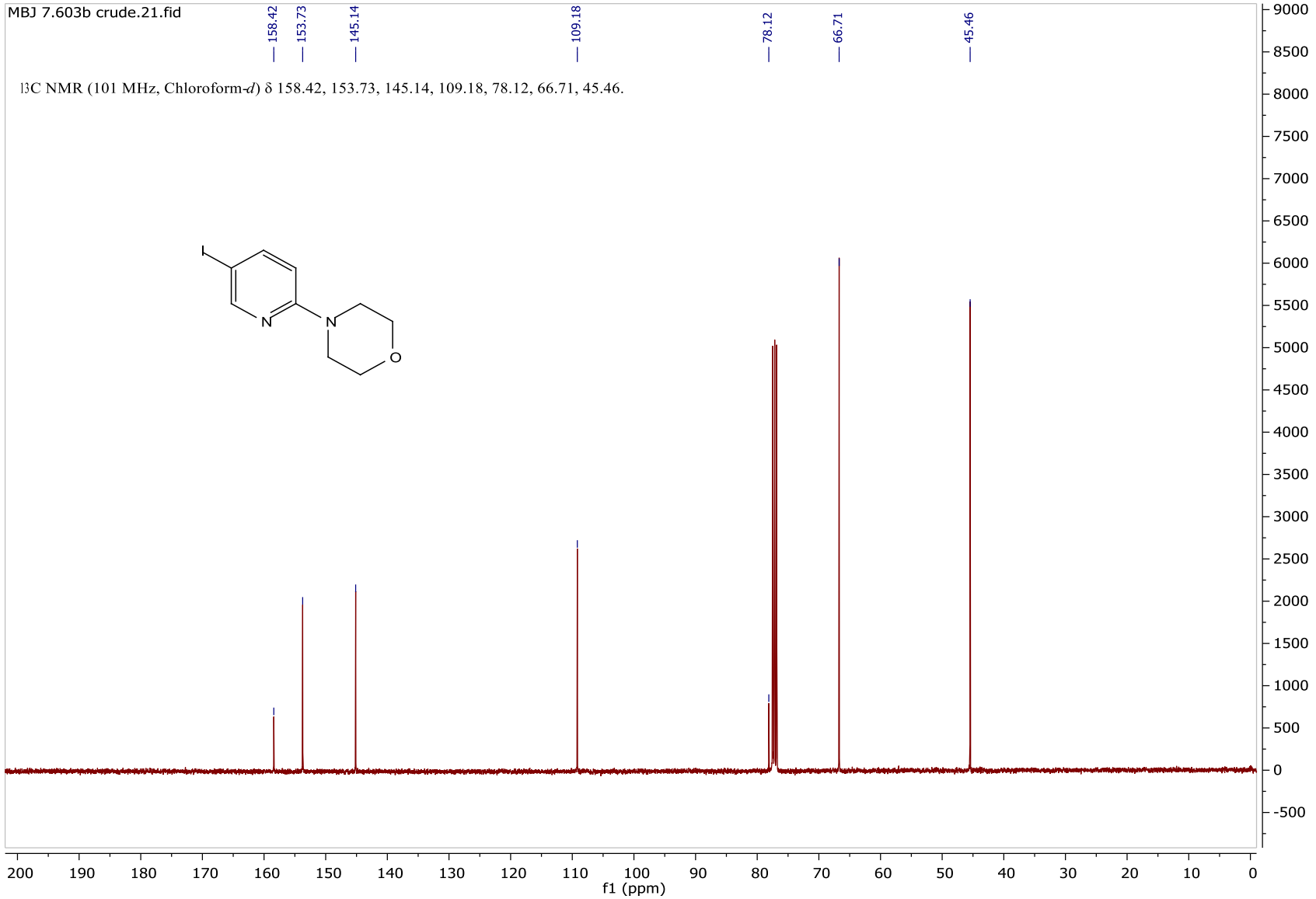

MBJ 7.582 cc.10.fid
8.52
8.51
7.90
7.88
7.83
7.83
7.81
7.81
7.47
7.45
7.38
7.37
7.35
7.07
7.06
7.05
7.04
7.03
7.03
6.93
6.91
5.44
1H NMR (400 MHz, Chloroform-d) δ 8.52 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.82 (dd, J = 8.7, 2.3 Hz, 1H), 7.46 (d, J = 6.7 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.05 (td, J = 7.8, 1.3 Hz, 1H), 6.92 (d, J = 8.7 Hz, 1H), 5.44 (s, 2H).
I
O
N
N
0.89
0.96
0.91
0.98
0.95
0.93
0.94
2.00
f1 (ppm)
f1 (ppm)

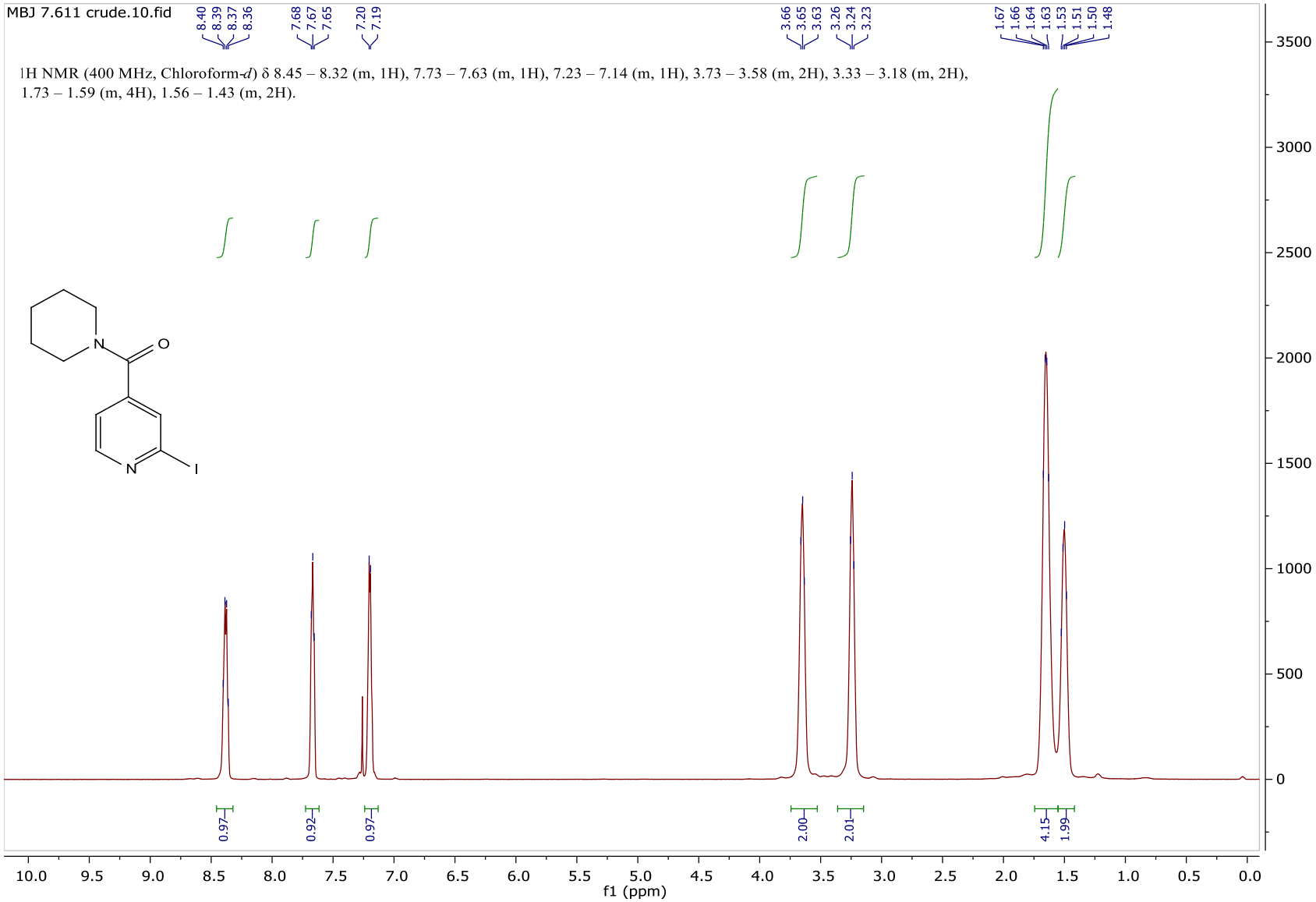

MBJ 7.582 cc.11.fid
165.31
152.07
141.36
139.69
138.61
130.04
129.57
128.48
117.30
112.14
103.08
98.42
72.58
13C NMR (101 MHz, Chloroform-d) δ 165.31, 152.07, 141.36, 139.69, 138.61, 130.04, 129.57, 128.48, 117.30, 112.14, 103.08, 98.42, 72.58.
I
O
N
N
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

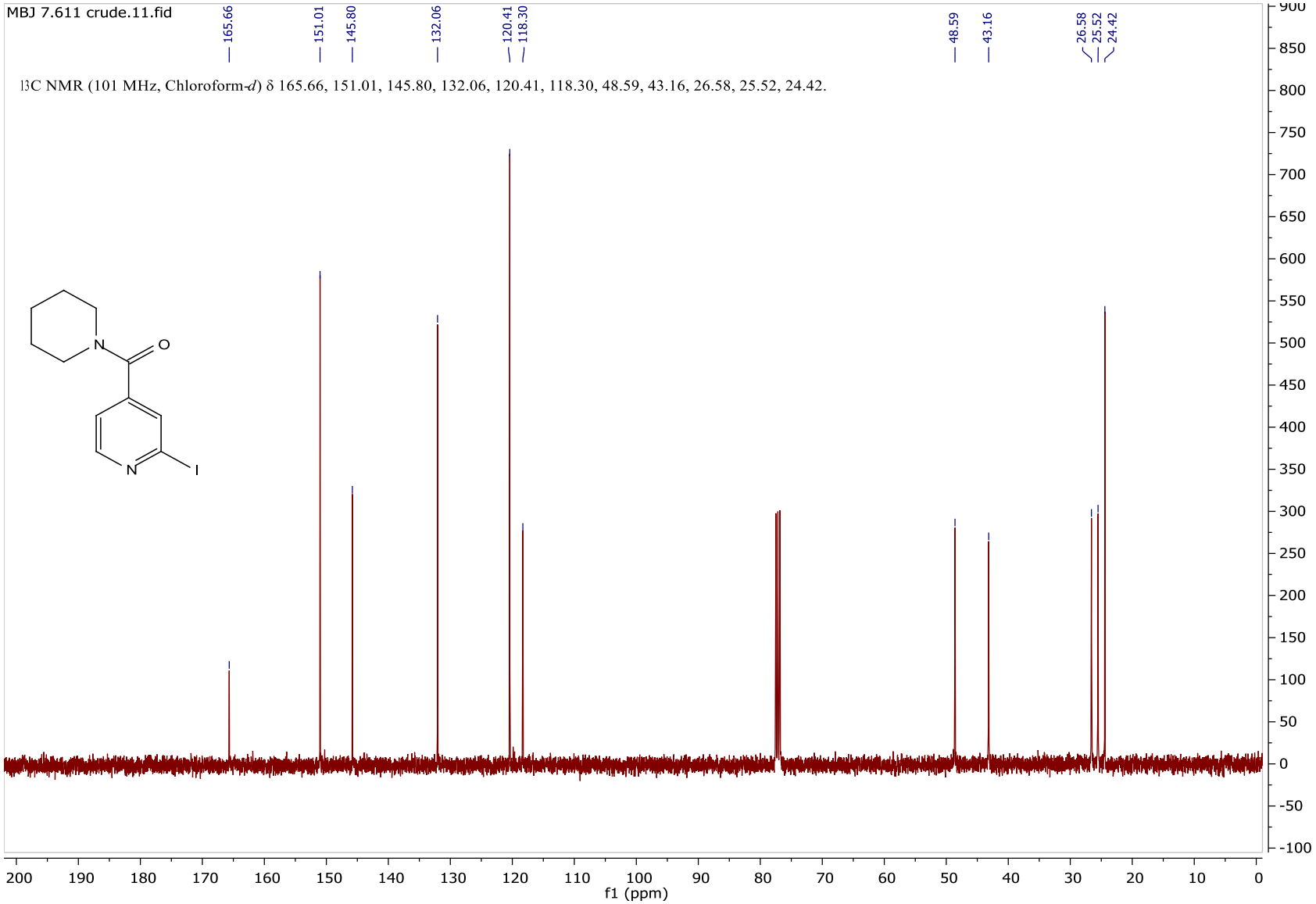

MBJ 7.575 cc.10.fid
7.80
7.78
6.98
6.95
5.90
2.03
1H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 5.90 (s, 2H), 2.03 (s, 6H).
H3C
N
CH3
I
1.96
1.95
1.92
6.00
f1 (ppm)

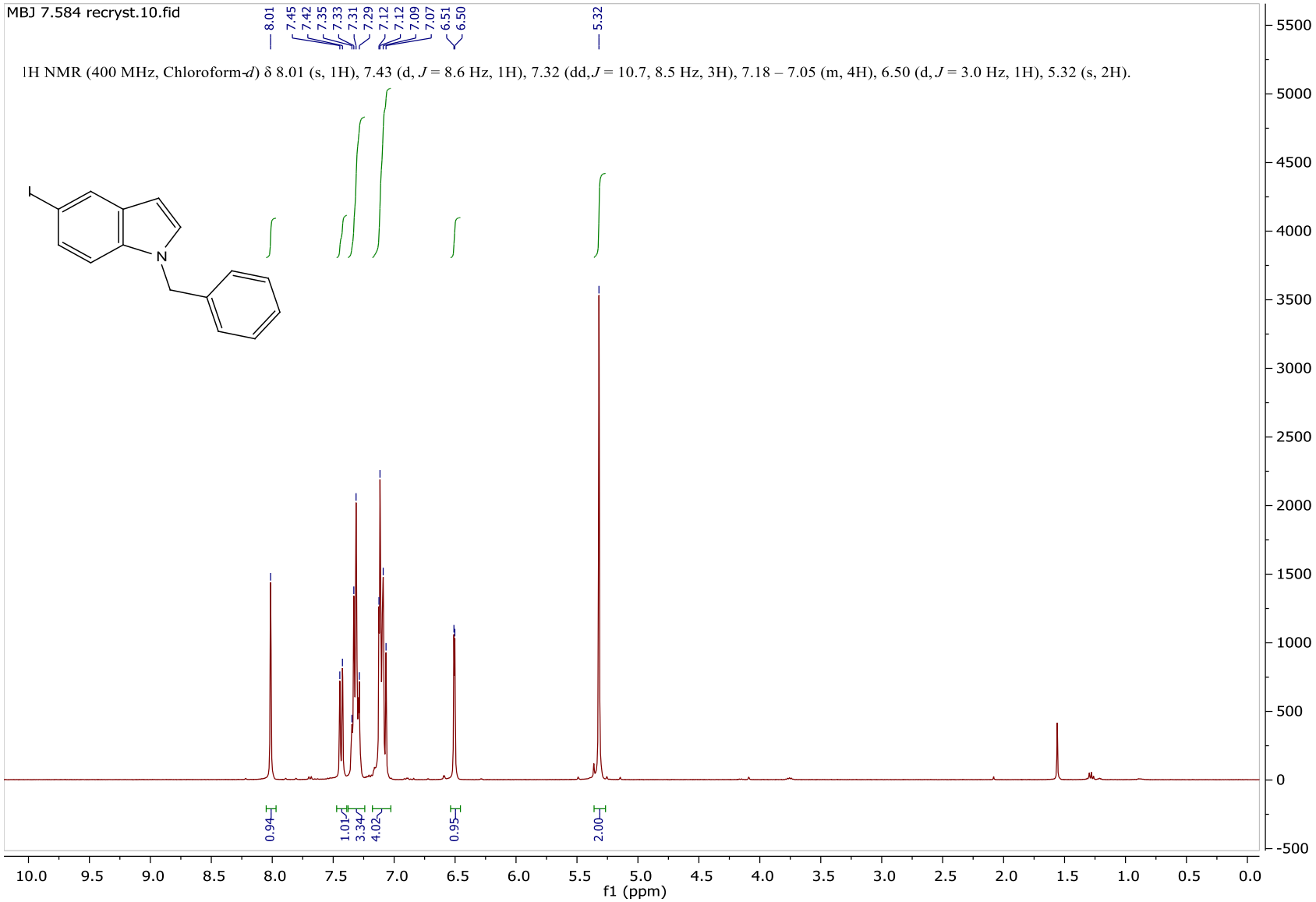

MBJ 7.575 cc.11.fid
138.86
138.44
130.27
128.77
106.26
93.04
13.14
13C NMR (101 MHz, Chloroform-d) δ 138.86, 138.44, 130.27, 128.77, 106.26, 93.04, 13.14.
H3C
N
CH3
I
f1 (ppm)

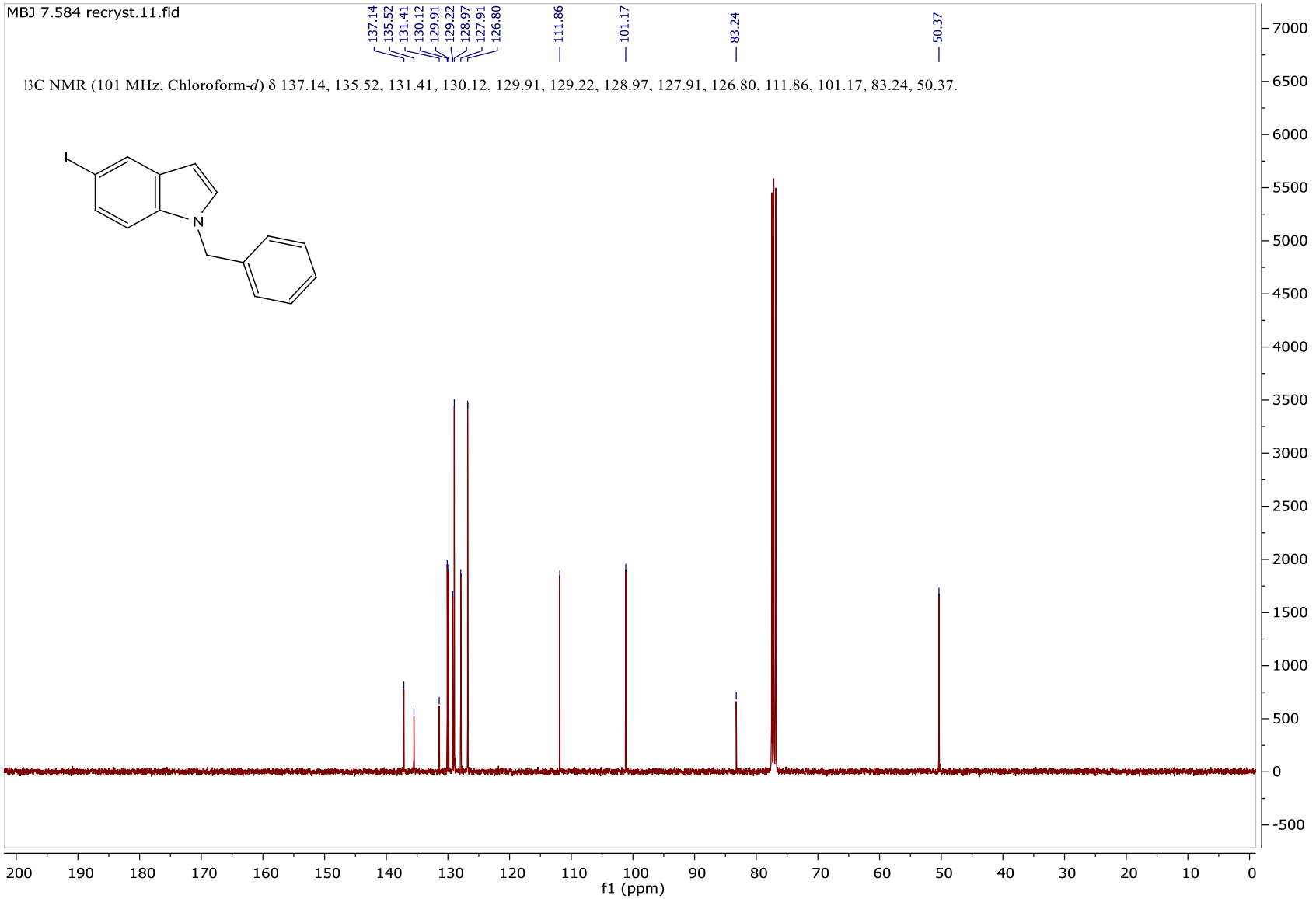

MBJ 7.603b crude.20.fid
8.33
8.32
7.70
7.69
7.67
7.67
6.48
6.46
3.81
3.80
3.78
3.48
3.46
3.45
1H NMR (400 MHz, Chloroform-d) δ 8.33 (d, J = 2.3 Hz, 1H), 7.68 (dd, J = 8.9, 2.4 Hz, 1H), 6.47 (d, J = 8.9 Hz, 1H), 3.86 – 3.75 (m, 4H), 3.53 – 3.40 (m, 4H).
I
N
N
O
0.93
0.96
1.02
4.01
4.00
f1 (ppm)

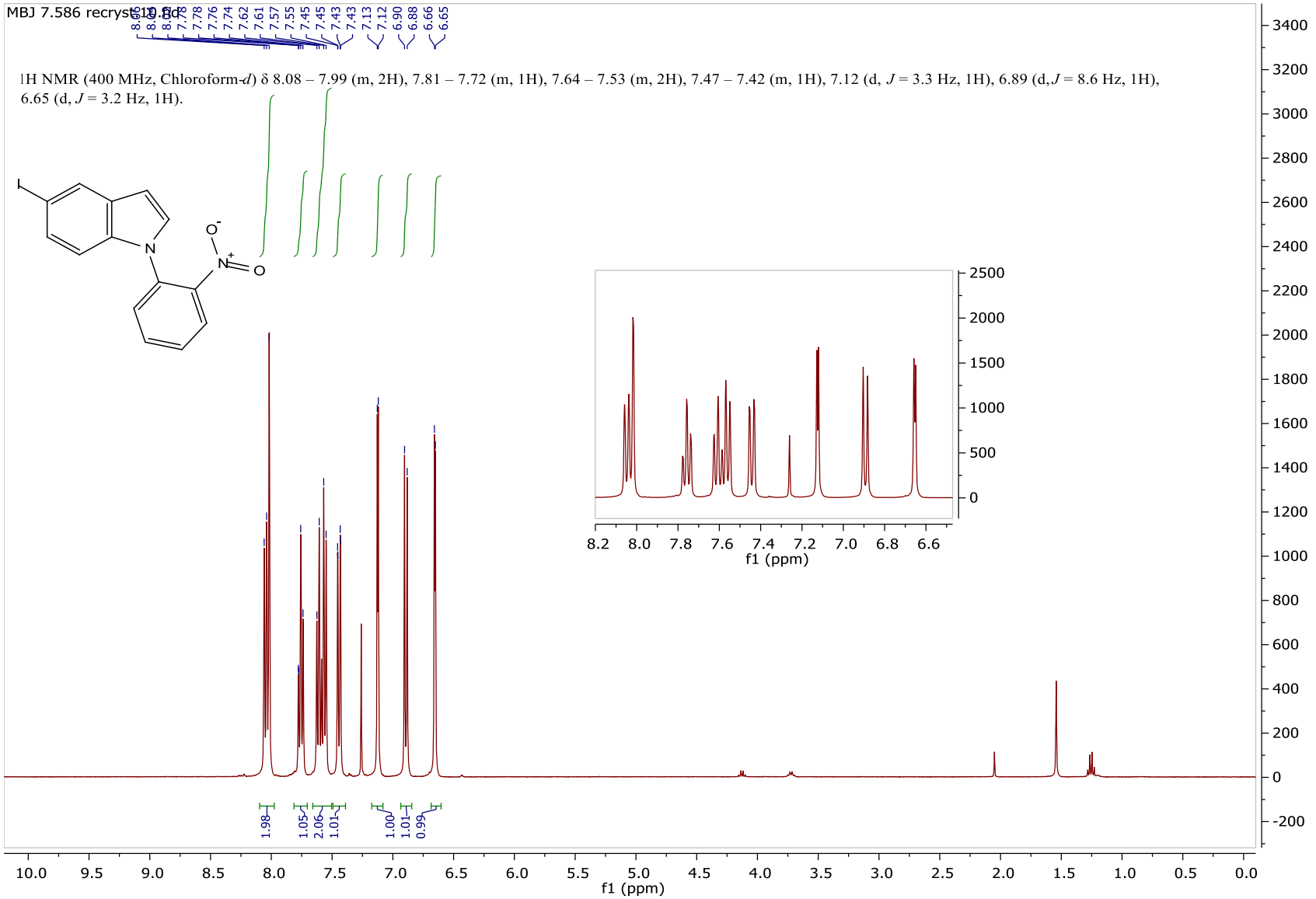

MBJ 7.603b crude.21.fid
158.42
153.73
145.14
109.18
78.12
66.71
45.46
13C NMR (101 MHz, Chloroform-d) δ 158.42, 153.73, 145.14, 109.18, 78.12, 66.71, 45.46.
I
N
N
O
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

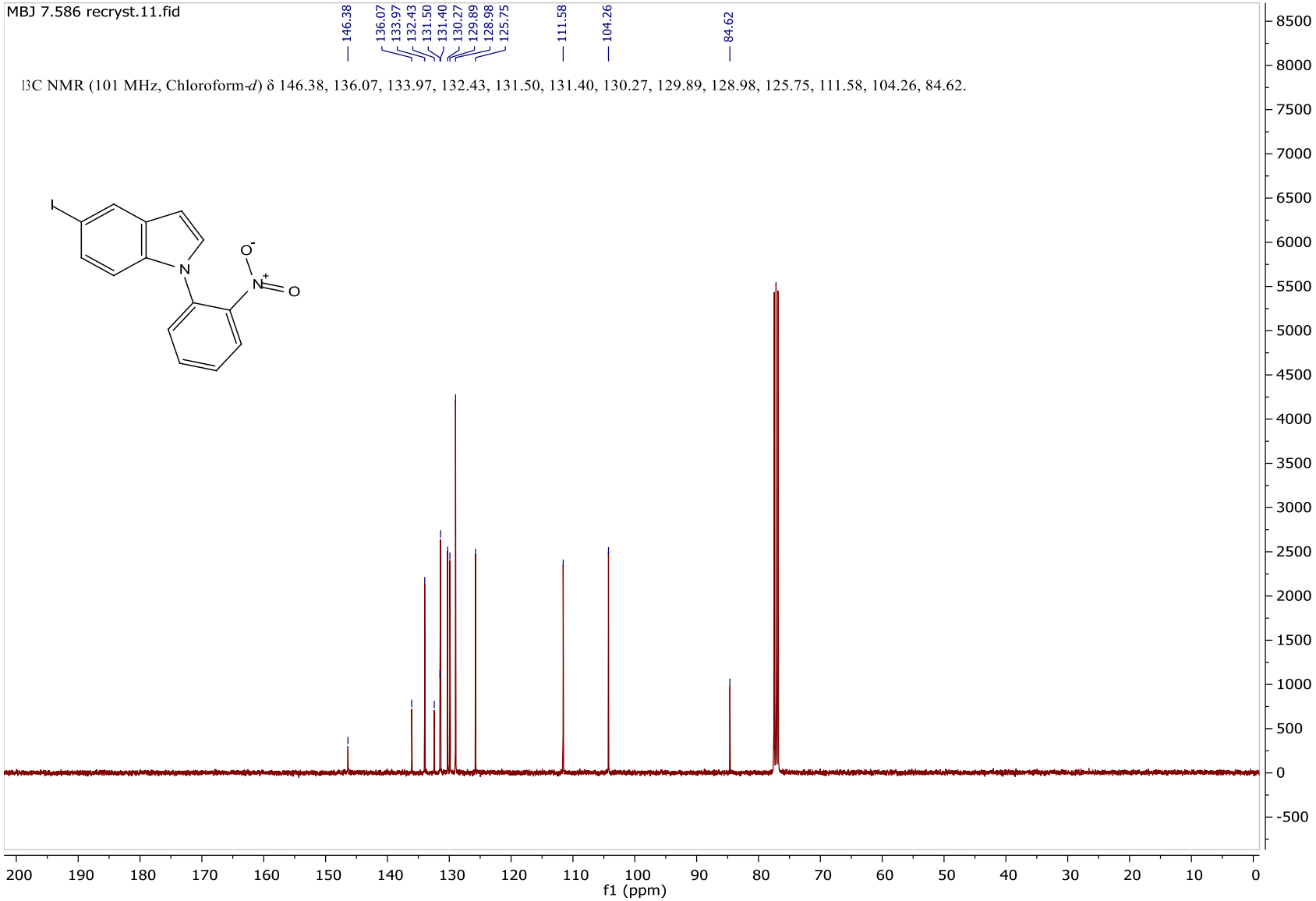

MBJ 7.611 crude.10.fid
8.40
8.39
8.37
8.36
7.68
7.67
7.65
7.20
7.19
3.66
3.65
3.63
3.26
3.24
3.23
1.67
1.66
1.64
1.63
1.53
1.51
1.50
1.48
1H NMR (400 MHz, Chloroform-d) δ 8.45 – 8.32 (m, 1H), 7.73 – 7.63 (m, 1H), 7.23 – 7.14 (m, 1H), 3.73 – 3.58 (m, 2H), 3.33 – 3.18 (m, 2H), 1.73 – 1.59 (m, 4H), 1.56 – 1.43 (m, 2H).
N
O
N
I
0.97
0.92
0.97
2.00
2.01
4.15
1.99
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

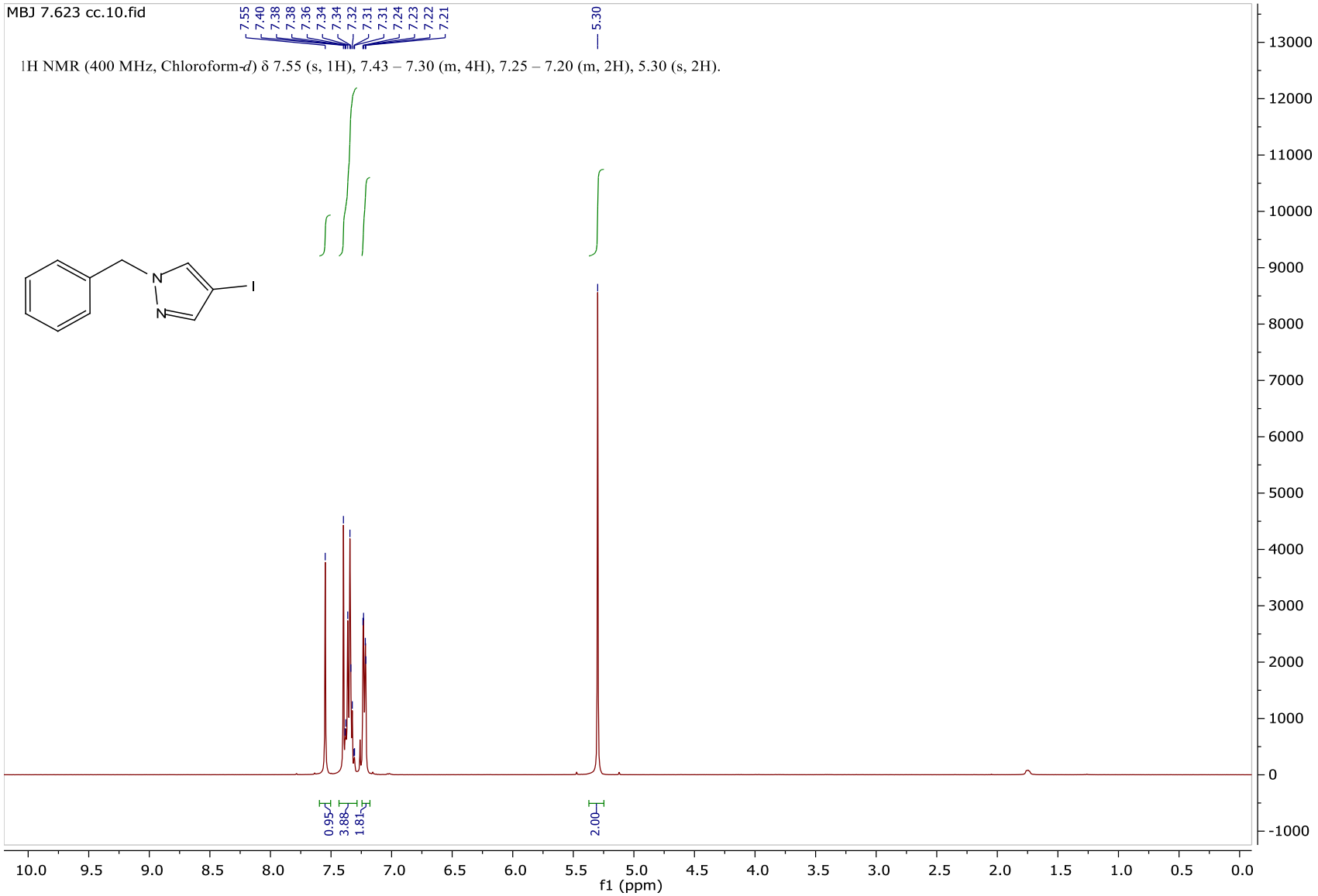

MBJ 7.611 crude.11.fid
165.66
151.01
145.80
132.06
120.41
118.30
48.59
43.16
26.58
25.52
24.42
13C NMR (101 MHz, Chloroform-d) δ 165.66, 151.01, 145.80, 132.06, 120.41, 118.30, 48.59, 43.16, 26.58, 25.52, 24.42.
N
O
N
I
f1 (ppm)

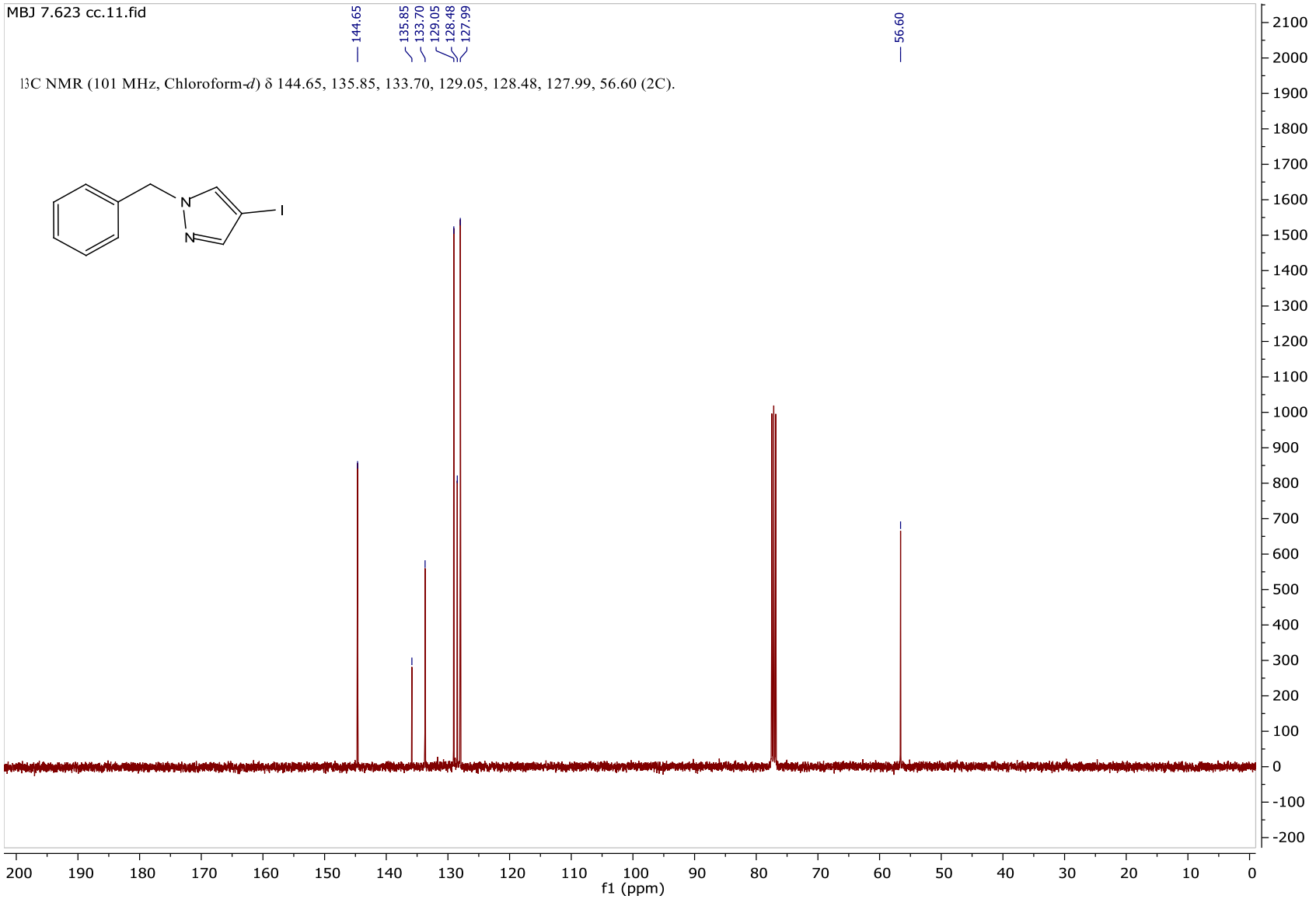

MBJ 7.584 recryst.10.fid
8.01
7.45
7.42
7.35
7.33
7.31
7.29
7.12
7.12
7.09
7.07
6.51
6.50
5.32
1H NMR (400 MHz, Chloroform-d) δ 8.01 (s, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.32 (dd, J = 10.7, 8.5 Hz, 3H), 7.18 – 7.05 (m, 4H), 6.50 (d, J = 3.0 Hz, 1H), 5.32 (s, 2H).
I
N
0.94
1.01
3.34
4.02
0.95
2.00
f1 (ppm)

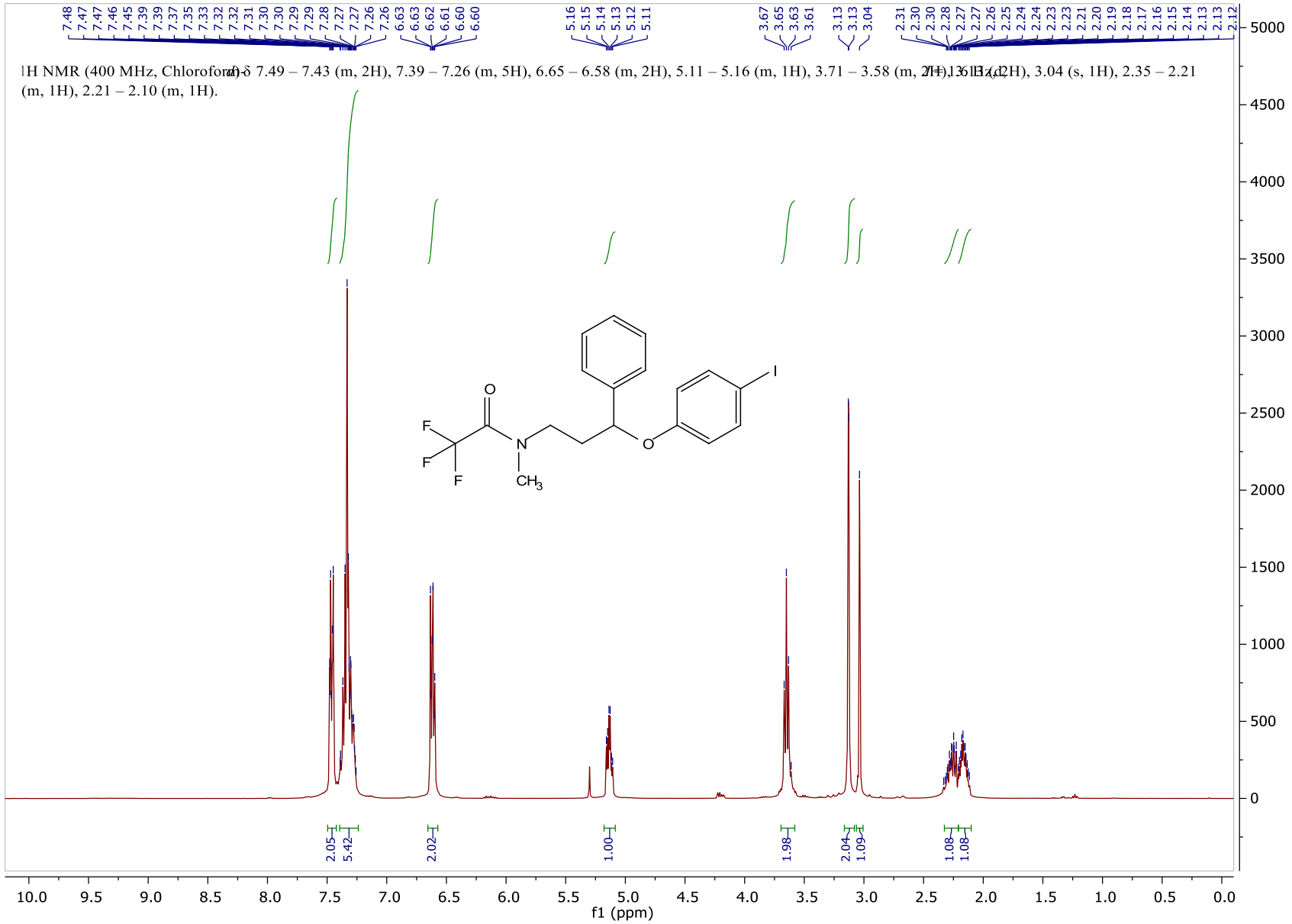

MBJ 7.584 recryst.11.fid
137.14
135.52
131.41
130.12
129.91
129.22
128.97
127.91
126.80
111.86
101.17
83.24
50.37
13C NMR (101 MHz, Chloroform-d) δ 137.14, 135.52, 131.41, 130.12, 129.91, 129.22, 128.97, 127.91, 126.80, 111.86, 101.17, 83.24, 50.37.
I
N
f1 (ppm)


MBJ 7.586 recryst 1D.fid
8.08
8.06
8.02
7.99
7.81
7.78
7.76
7.74
7.62
7.61
7.57
7.55
7.45
7.45
7.43
7.43
7.13
7.12
6.90
6.88
6.66
6.65
1H NMR (400 MHz, Chloroform-d) δ 8.08 – 7.99 (m, 2H), 7.81 – 7.72 (m, 1H), 7.64 – 7.53 (m, 2H), 7.47 – 7.42 (m, 1H), 7.12 (d, J = 3.3 Hz, 1H), 6.89 (d,J = 8.6 Hz, 1H), 6.65 (d, J = 3.2 Hz, 1H).
I
N
O
N
O
1.98
1.05
2.06
1.01
1.00
1.01
0.99
f1 (ppm)
f1 (ppm)

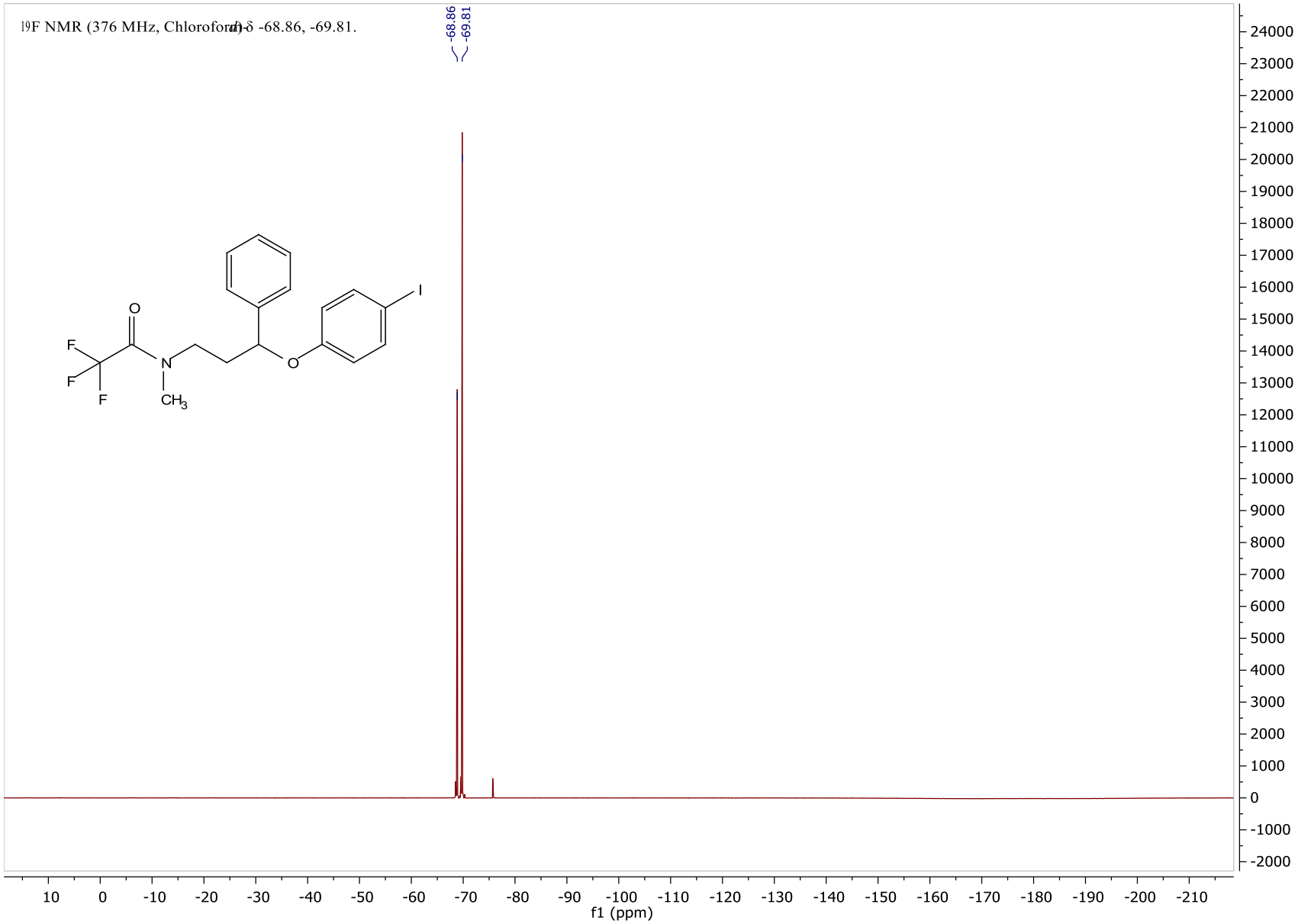

MBJ 7.586 recryst.11.fid
146.38
136.07
133.97
132.43
131.50
131.40
130.27
129.89
128.98
125.75
111.58
104.26
84.62
13C NMR (101 MHz, Chloroform-d) δ 146.38, 136.07, 133.97, 132.43, 131.50, 131.40, 130.27, 129.89, 128.98, 125.75, 111.58, 104.26, 84.62.
f1 (ppm)

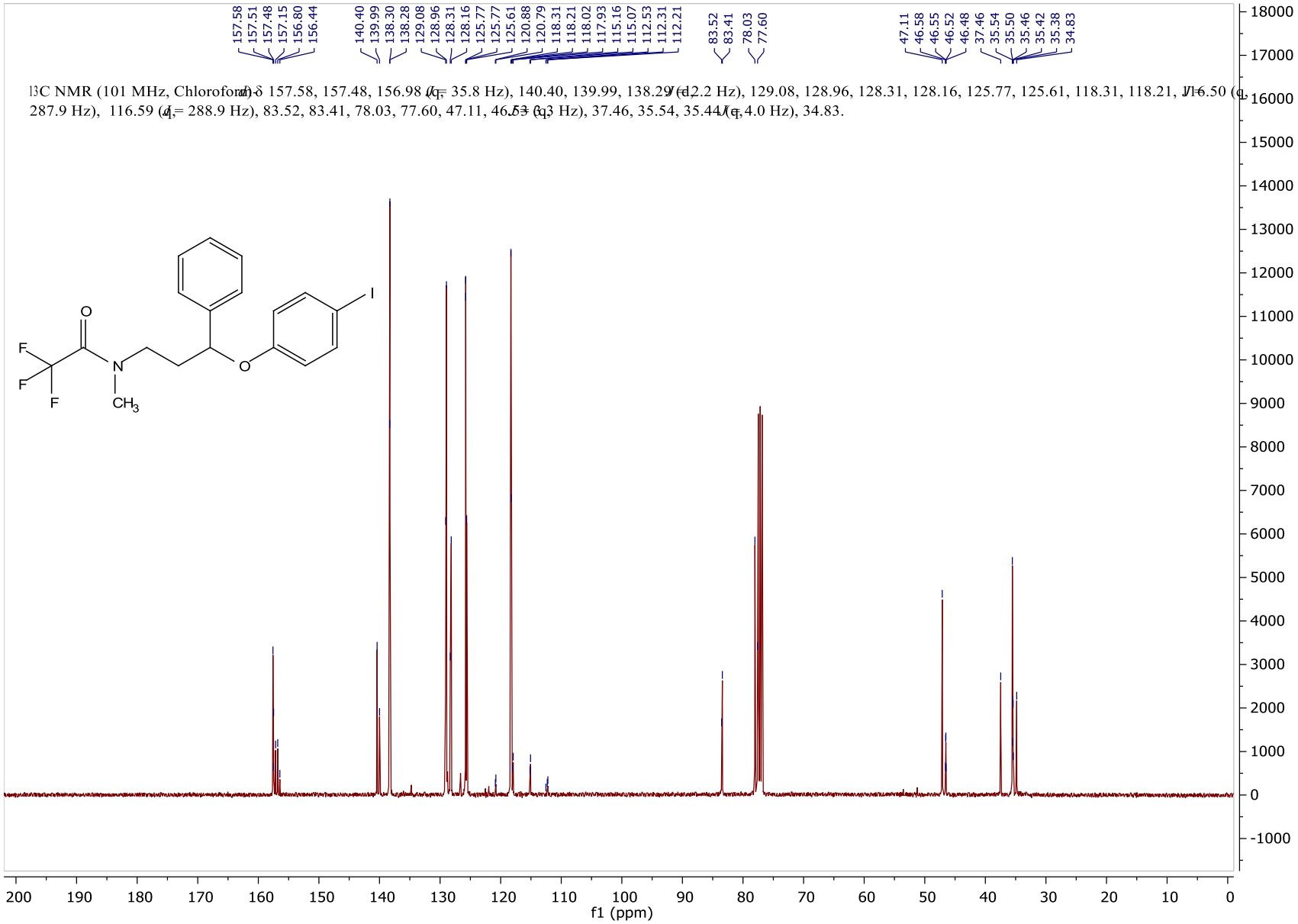

MBJ 7.623 cc.10.fid
7.55
7.40
7.38
7.38
7.36
7.34
7.34
7.32
7.31
7.31
7.24
7.23
7.22
7.21
5.30
1H NMR (400 MHz, Chloroform-d) δ 7.55 (s, 1H), 7.43 – 7.30 (m, 4H), 7.25 – 7.20 (m, 2H), 5.30 (s, 2H).
N
N
I
0.95
3.88
1.81
2.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

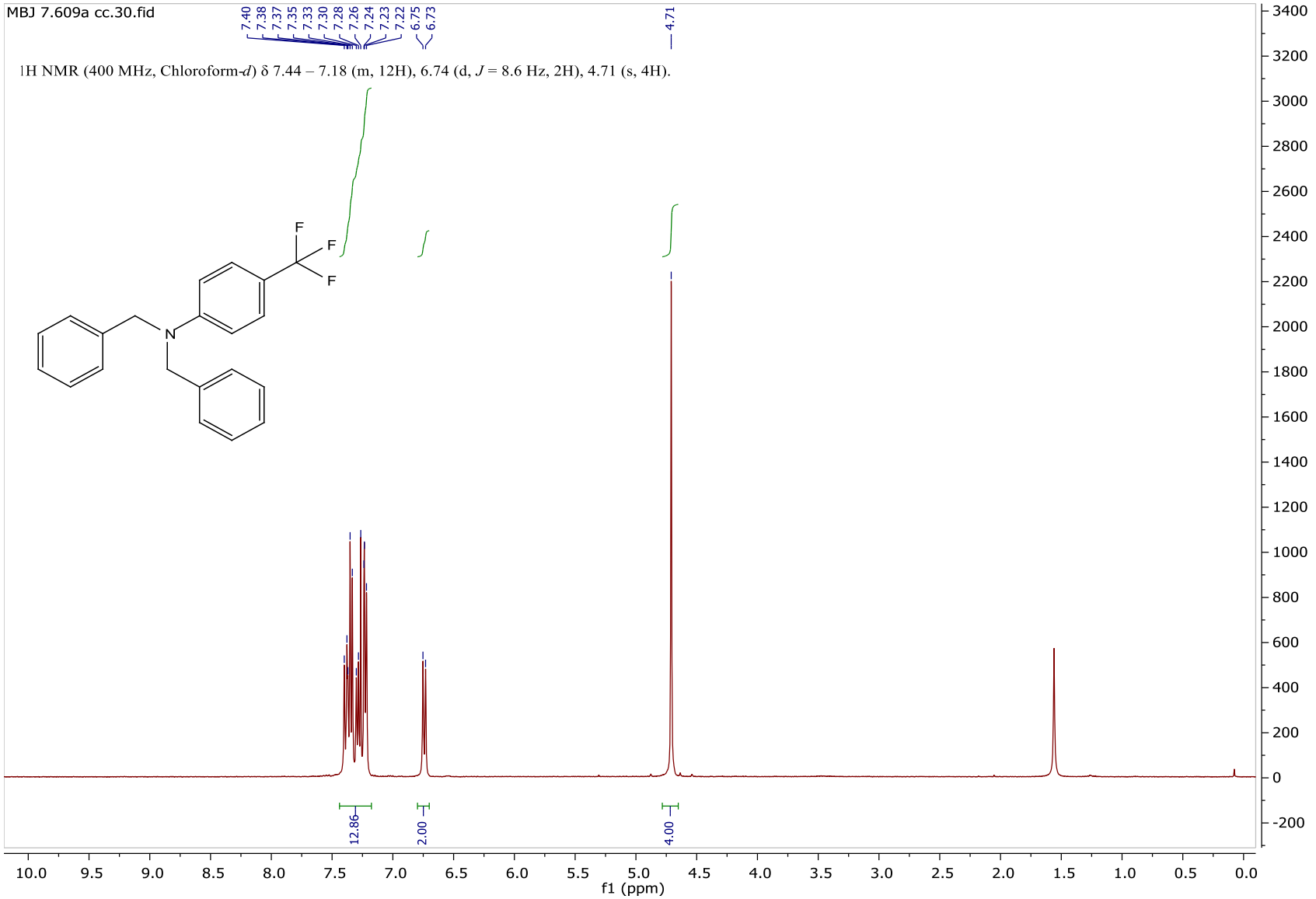

MBJ 7.623 cc.11.fid
144.65
135.85
133.70
129.05
128.48
127.99
56.60
13C NMR (101 MHz, Chloroform-d) δ 144.65, 135.85, 133.70, 129.05, 128.48, 127.99, 56.60 (2C).
N
N
I
f1 (ppm)

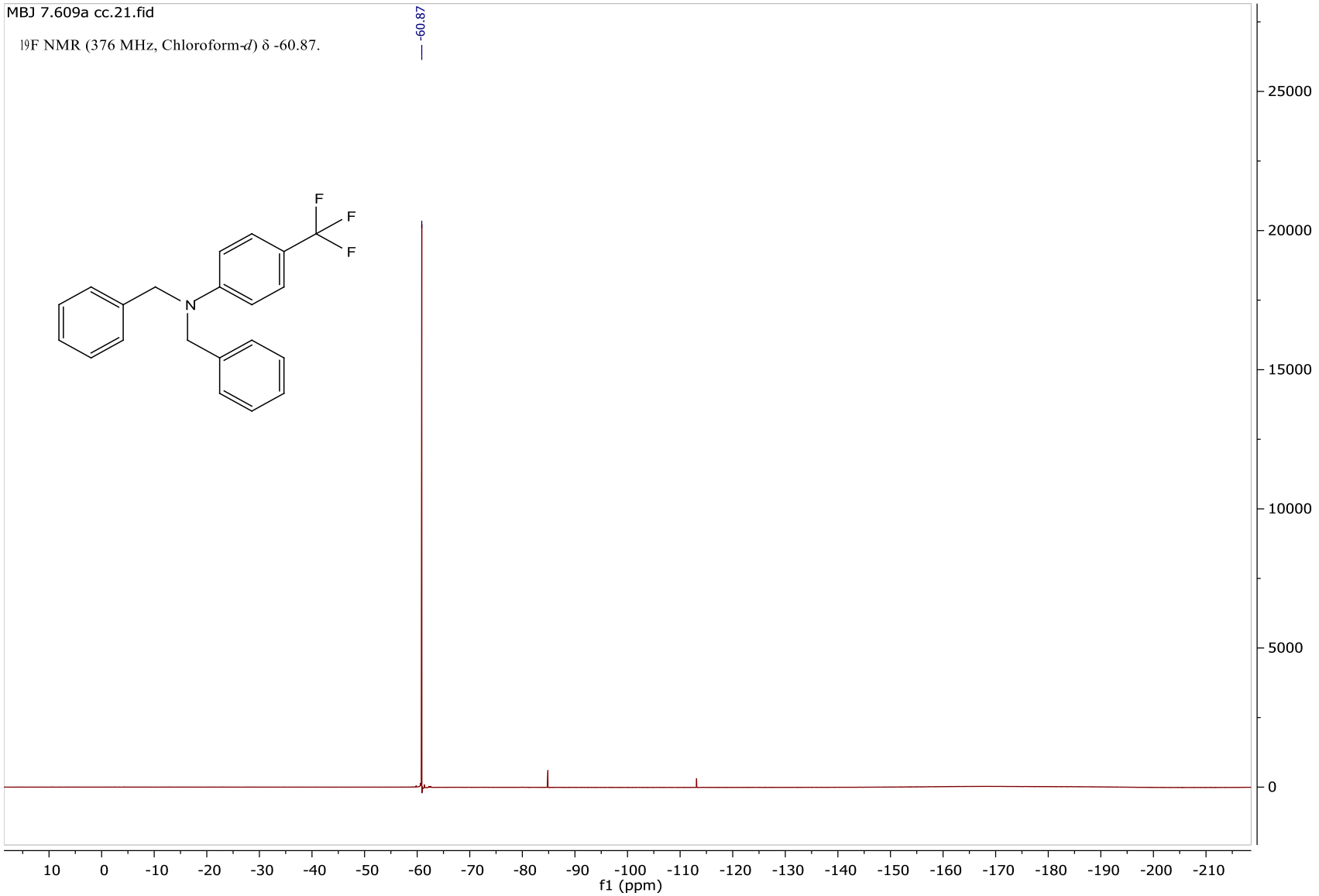

1H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.39 – 7.26 (m, 5H), 6.65 – 6.58 (m, 2H), 5.11 – 5.16 (m, 1H), 3.71 – 3.58 (m, 2H), 3.61 (t, J = 7.2 Hz, 2H), 3.04 (s, 1H), 2.35 – 2.21 (m, 1H), 2.21 – 2.10 (m, 1H).
O
F
F
F
N
CH3
O
I
f1 (ppm)

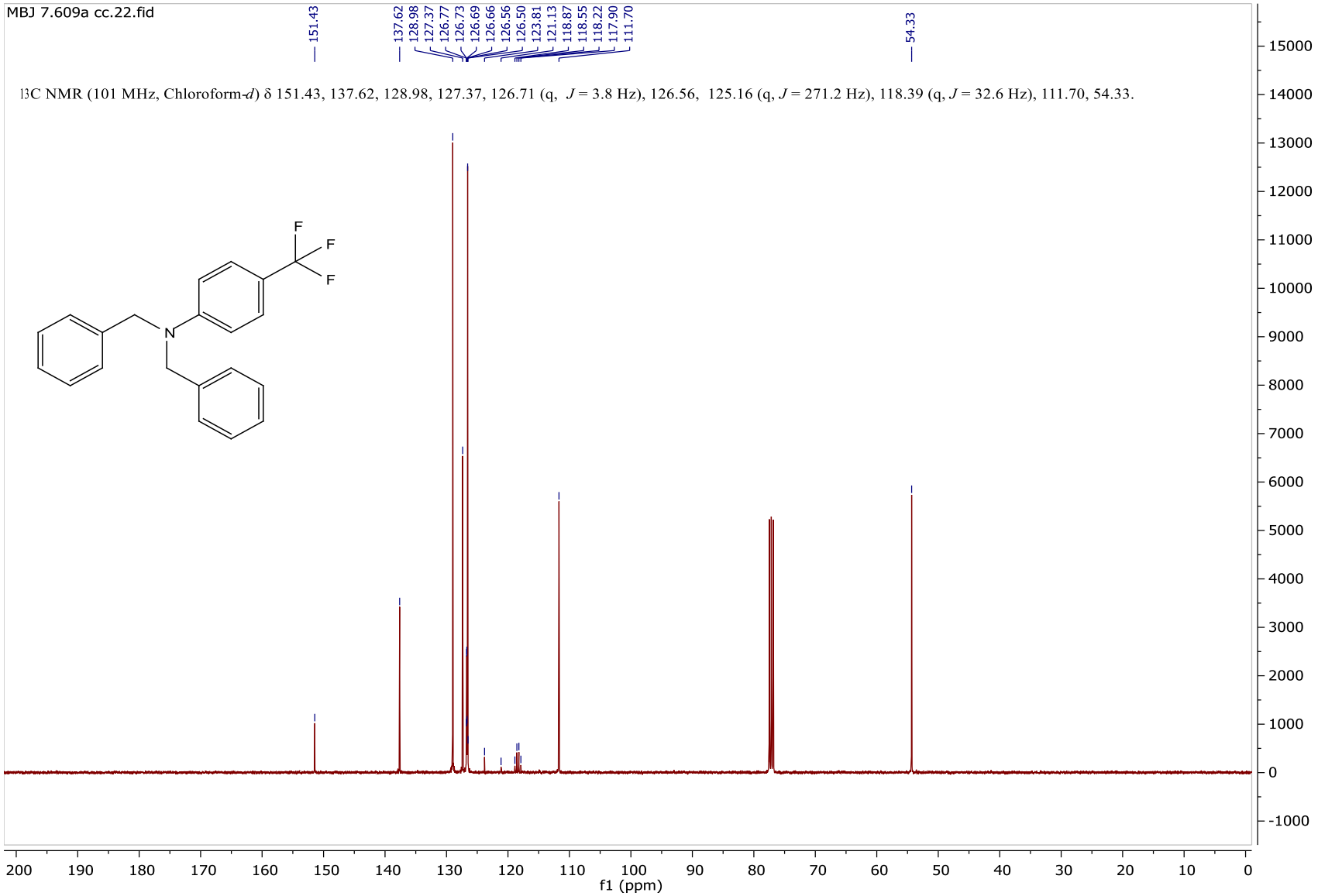
^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.86, -69.81.

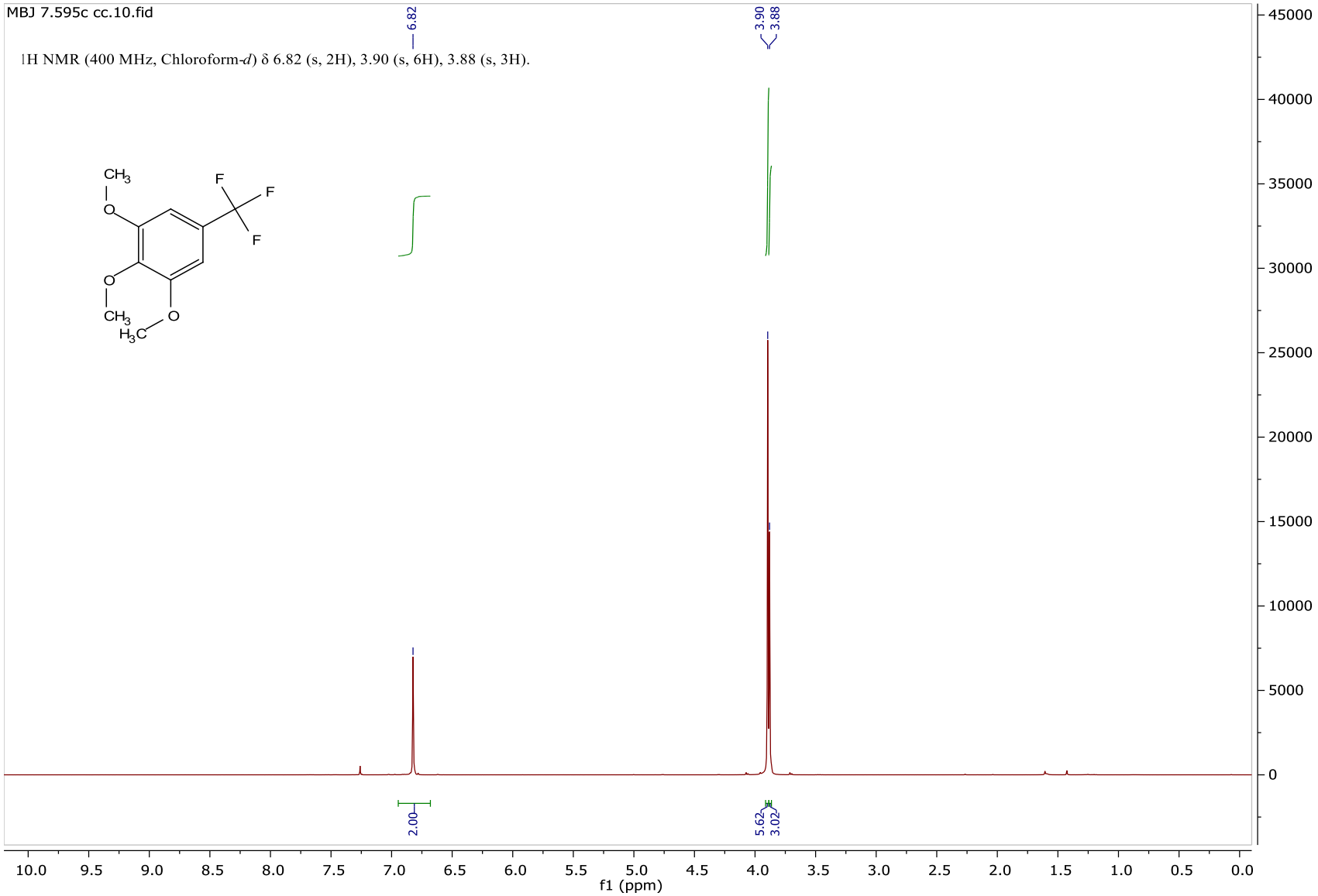


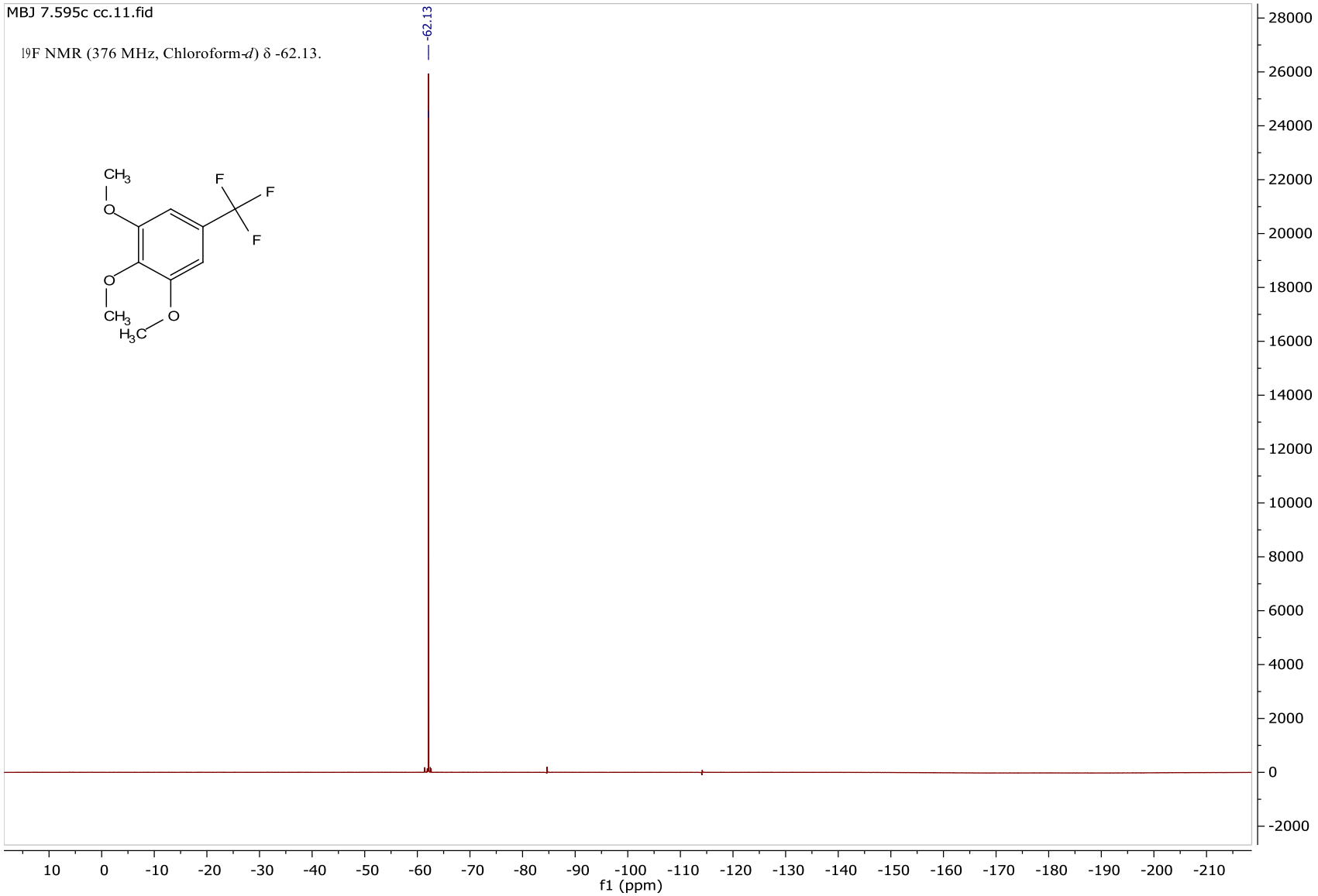

157.58
157.51
157.48
157.15
156.80
156.44
140.40
139.99
138.30
138.28
129.08
128.96
128.31
128.16
125.77
125.77
125.61
120.88
120.79
118.31
118.21
118.02
117.93
115.16
115.07
112.53
112.31
112.21
83.52
83.41
78.03
77.60
47.11
46.58
46.55
46.52
46.48
37.46
35.54
35.50
35.46
35.42
35.38
34.83
13C NMR (101 MHz, Chloroform-d) δ 157.58, 157.48, 156.98 (q, J = 35.8 Hz), 140.40, 139.99, 138.29 (d, J = 2.2 Hz), 129.08, 128.96, 128.31, 128.16, 125.77, 125.61, 118.31, 118.21, 116.50 (q, J = 287.9 Hz), 116.59 (q, J = 288.9 Hz), 83.52, 83.41, 78.03, 77.60, 47.11, 46.53 (q, J = 3.3 Hz), 37.46, 35.54, 35.44 (q, J = 4.0 Hz), 34.83.
O
F
F
F
N
CH3
O
I
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

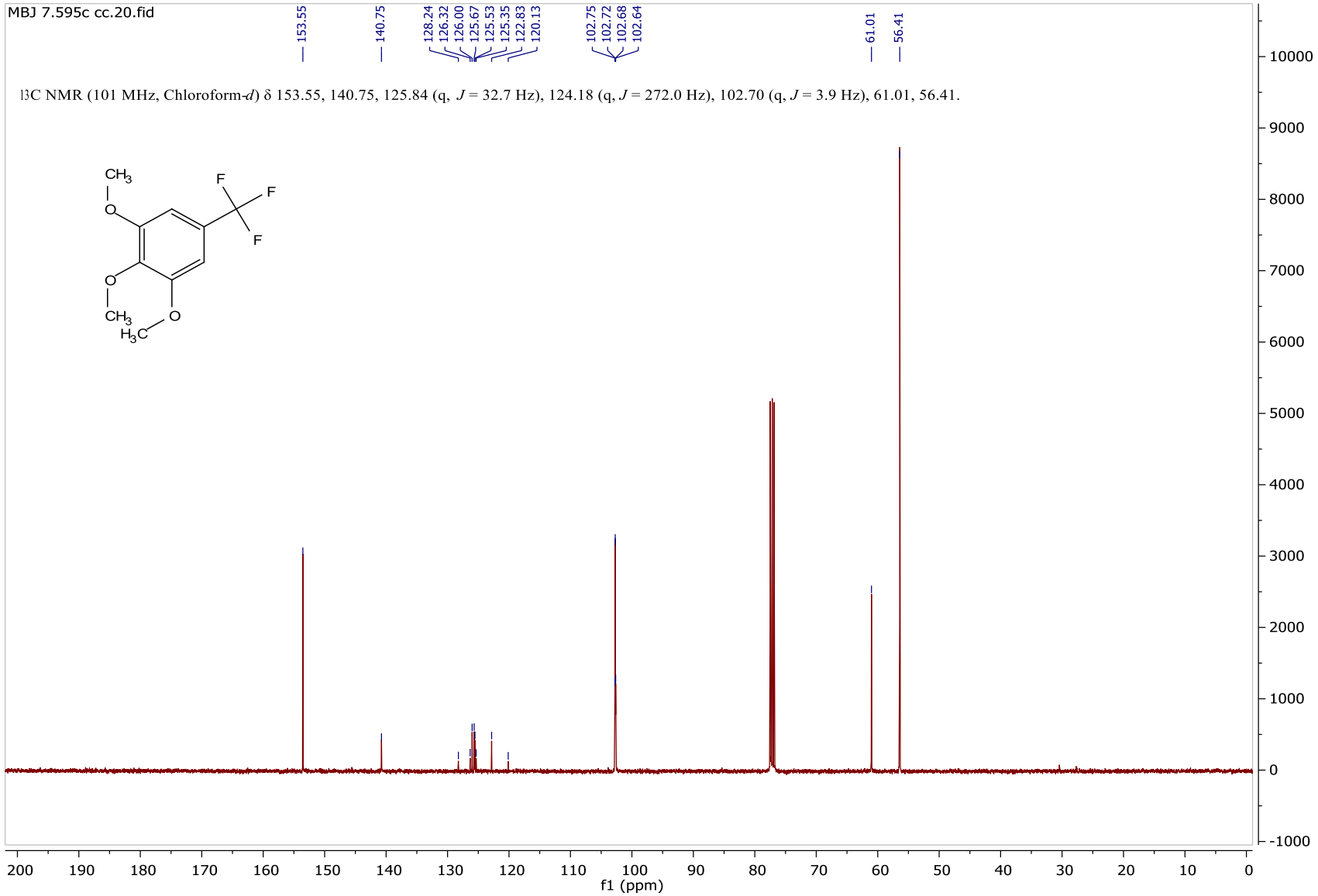

MBJ 7.609a cc.30.fid
7.40
7.38
7.37
7.35
7.33
7.30
7.28
7.26
7.24
7.23
7.22
6.75
6.73
4.71
1H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.18 (m, 12H), 6.74 (d, J = 8.6 Hz, 2H), 4.71 (s, 4H).
F
F
F
N
12.86
2.00
4.00
f1 (ppm)

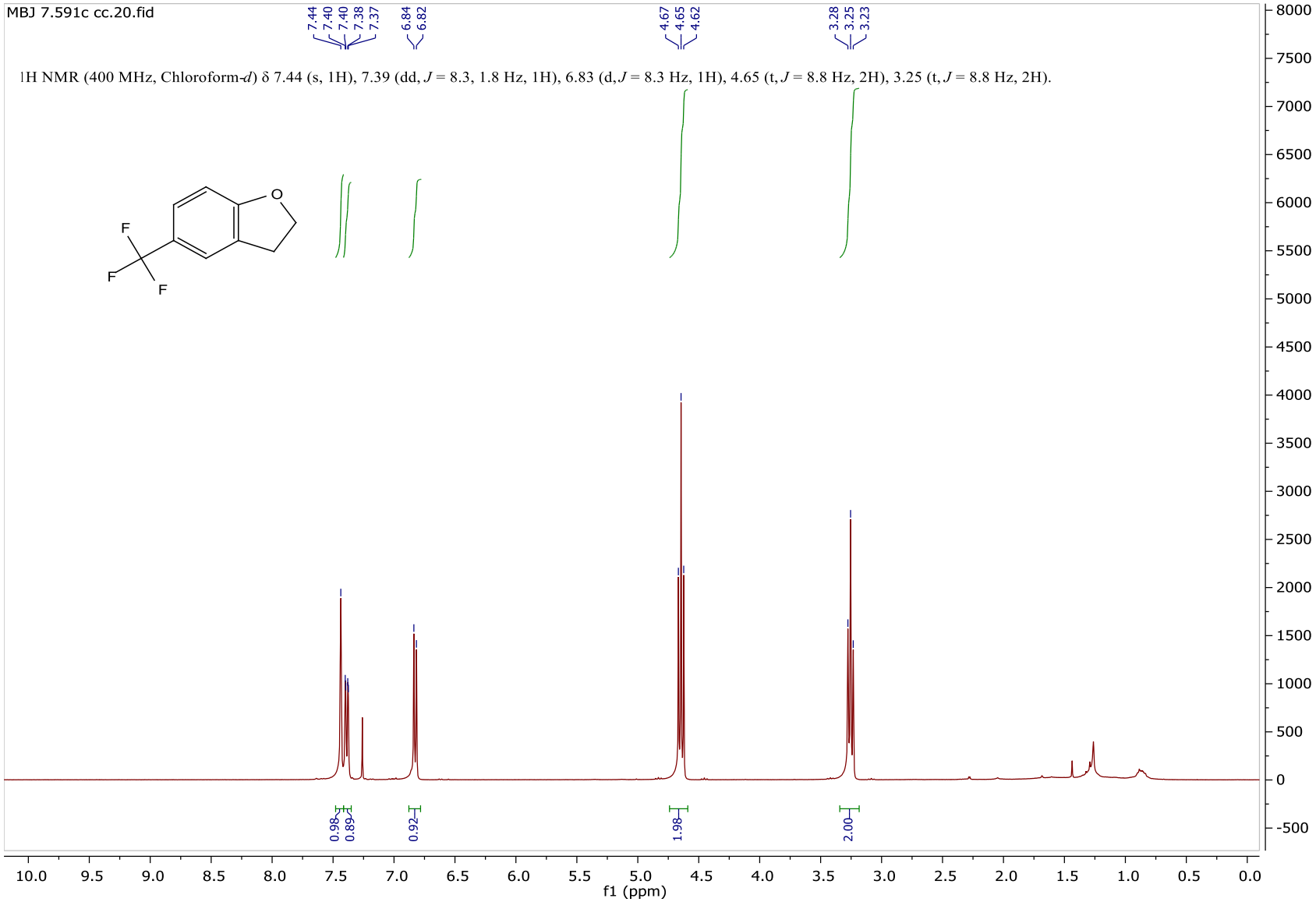

MBJ 7.609a cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -60.87.
-60.87
F
F
F
N
25000
20000
15000
10000
5000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

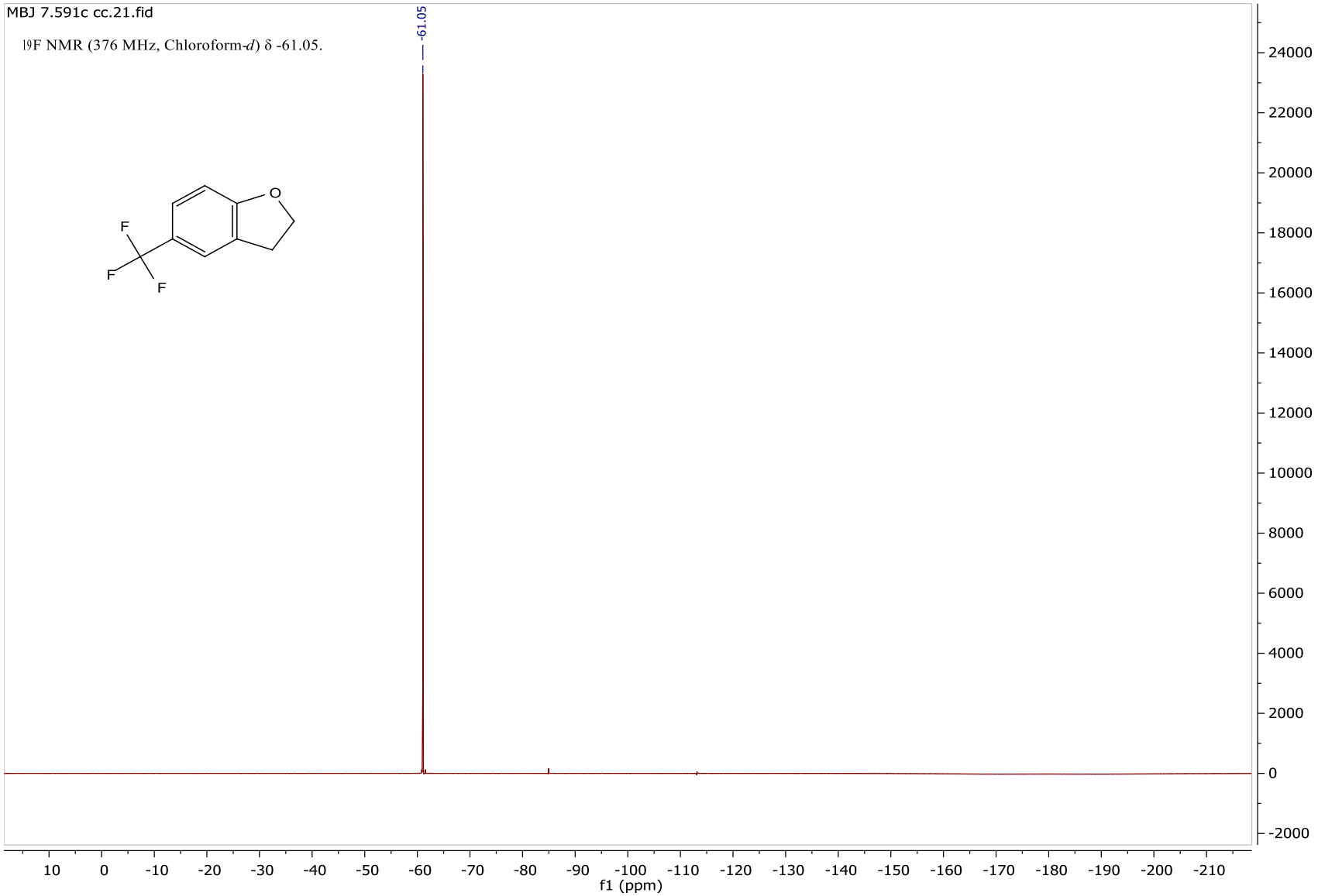

MBJ 7.609a cc.22.fid
151.43
137.62
128.98
127.37
126.77
126.73
126.69
126.66
126.56
126.50
123.81
121.13
118.87
118.55
118.22
117.90
111.70
54.33
13C NMR (101 MHz, Chloroform-d) δ 151.43, 137.62, 128.98, 127.37, 126.71 (q, J = 3.8 Hz), 126.56, 125.16 (q, J = 271.2 Hz), 118.39 (q, J = 32.6 Hz), 111.70, 54.33.
F
F
F
N
f1 (ppm)

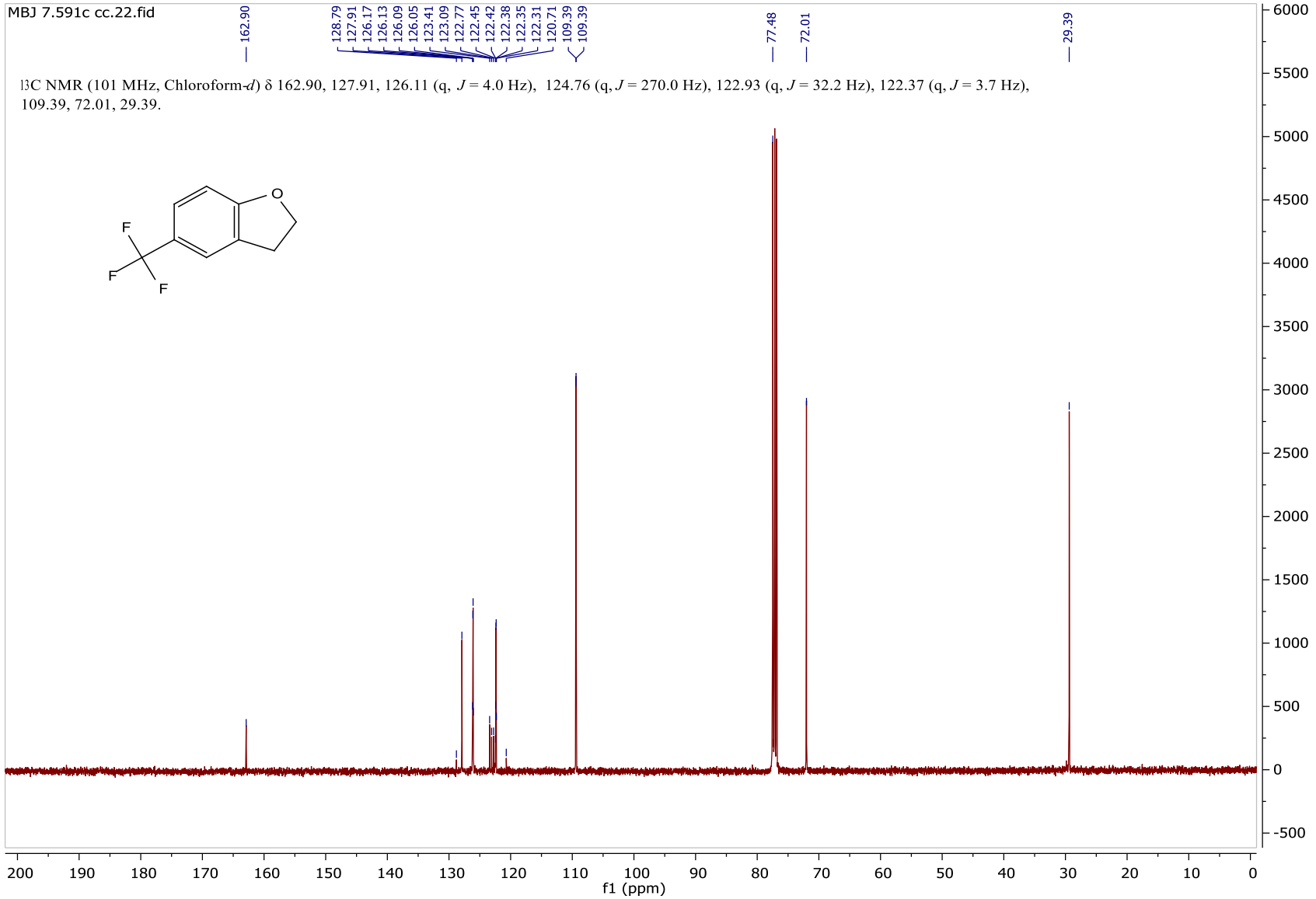

MBJ 7.595c cc.10.fid
6.82
3.90
3.88
1H NMR (400 MHz, Chloroform-d) δ 6.82 (s, 2H), 3.90 (s, 6H), 3.88 (s, 3H).
CH3
O
O
CH3
H3C
O
F
F
F
2.00
5.62
3.02
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

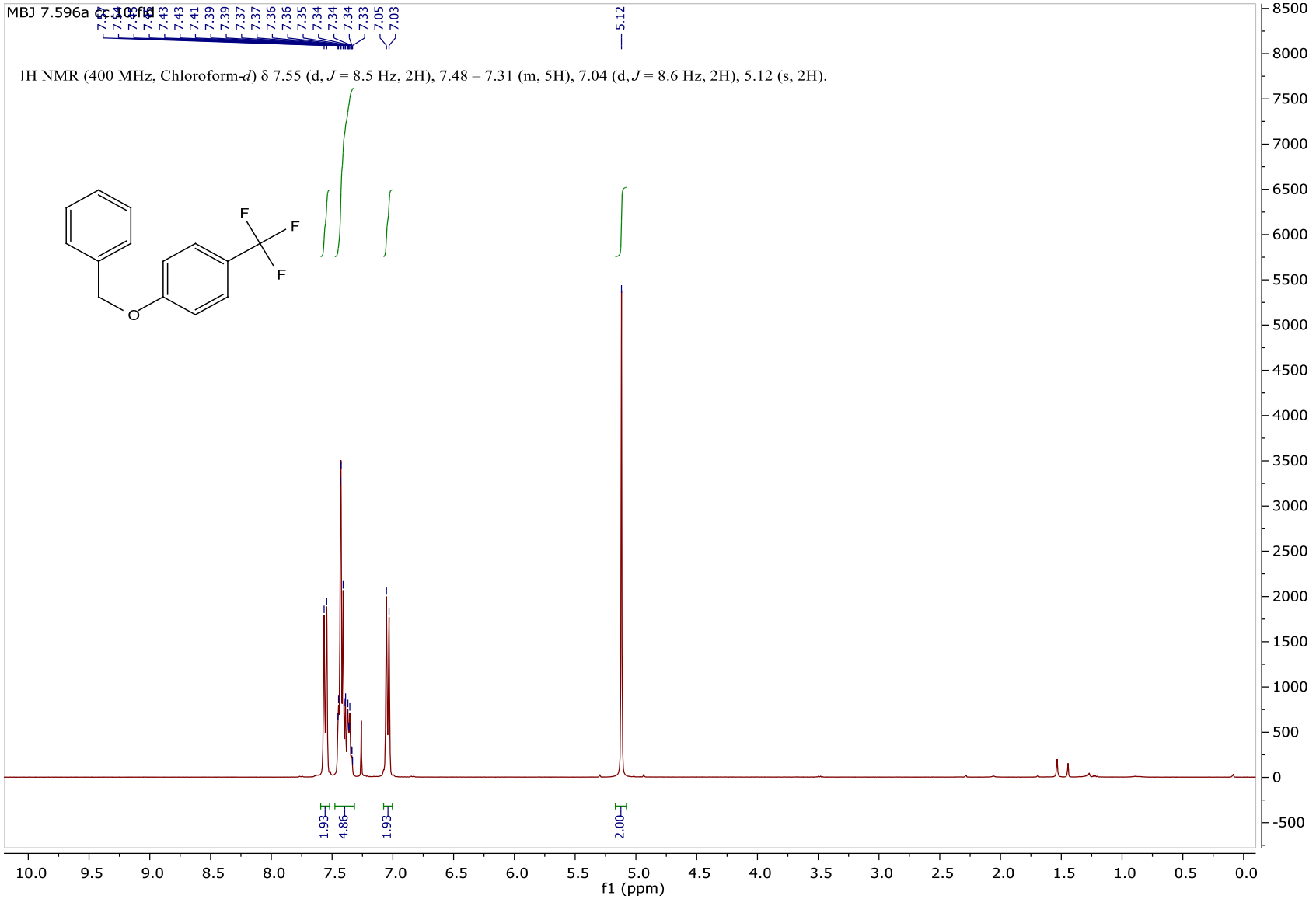

MBJ 7.595c cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -62.13.
-62.13
CH3
O
O
CH3
H3C
O
F
F
F
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

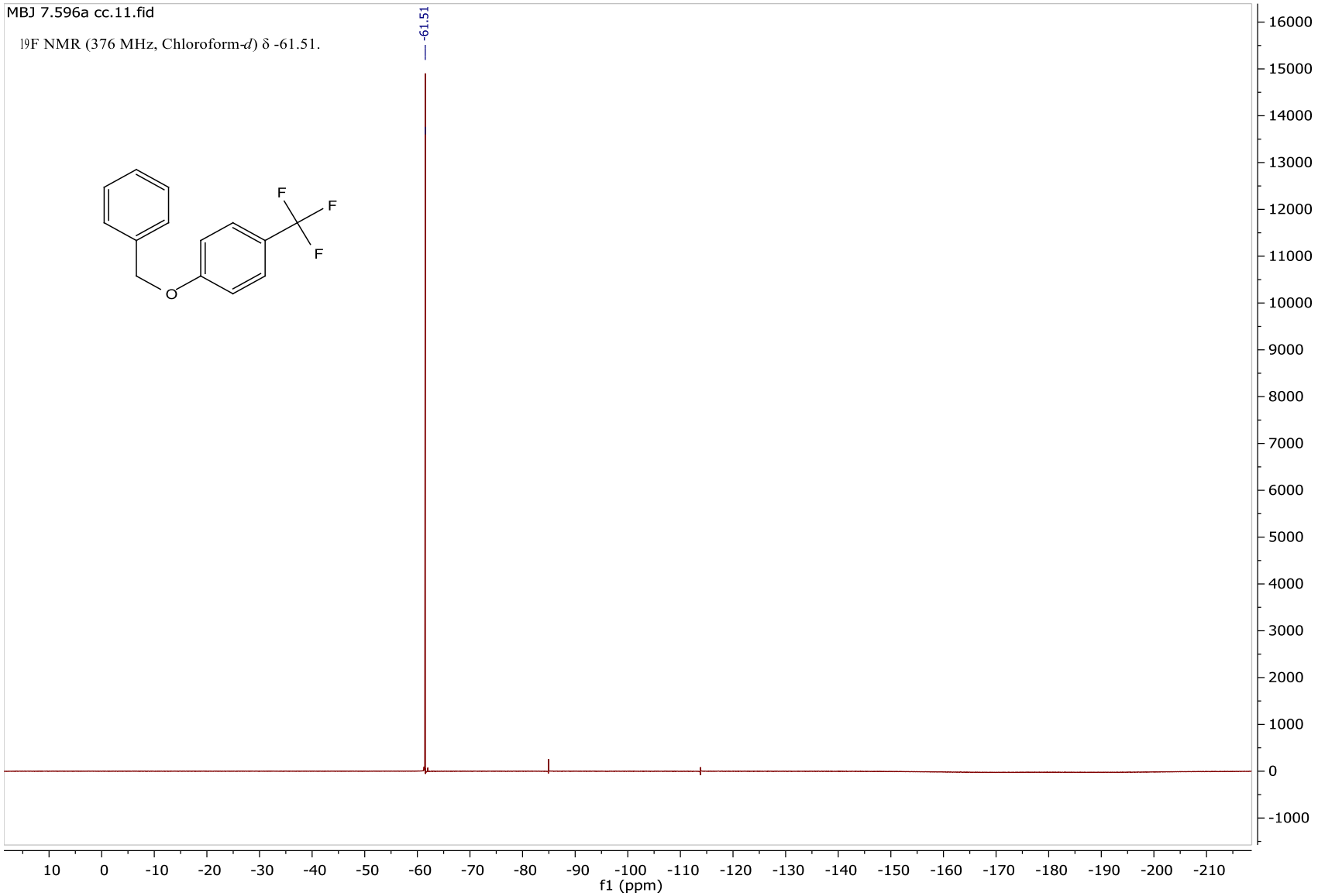

MBJ 7.595c cc.20.fid
153.55
140.75
128.24
126.32
126.00
125.67
125.53
125.35
122.83
120.13
102.75
102.72
102.68
102.64
61.01
56.41
13C NMR (101 MHz, Chloroform-d) δ 153.55, 140.75, 125.84 (q, J = 32.7 Hz), 124.18 (q, J = 272.0 Hz), 102.70 (q, J = 3.9 Hz), 61.01, 56.41.
CH3
O
O
CH3
H3C
O
F
F
F
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

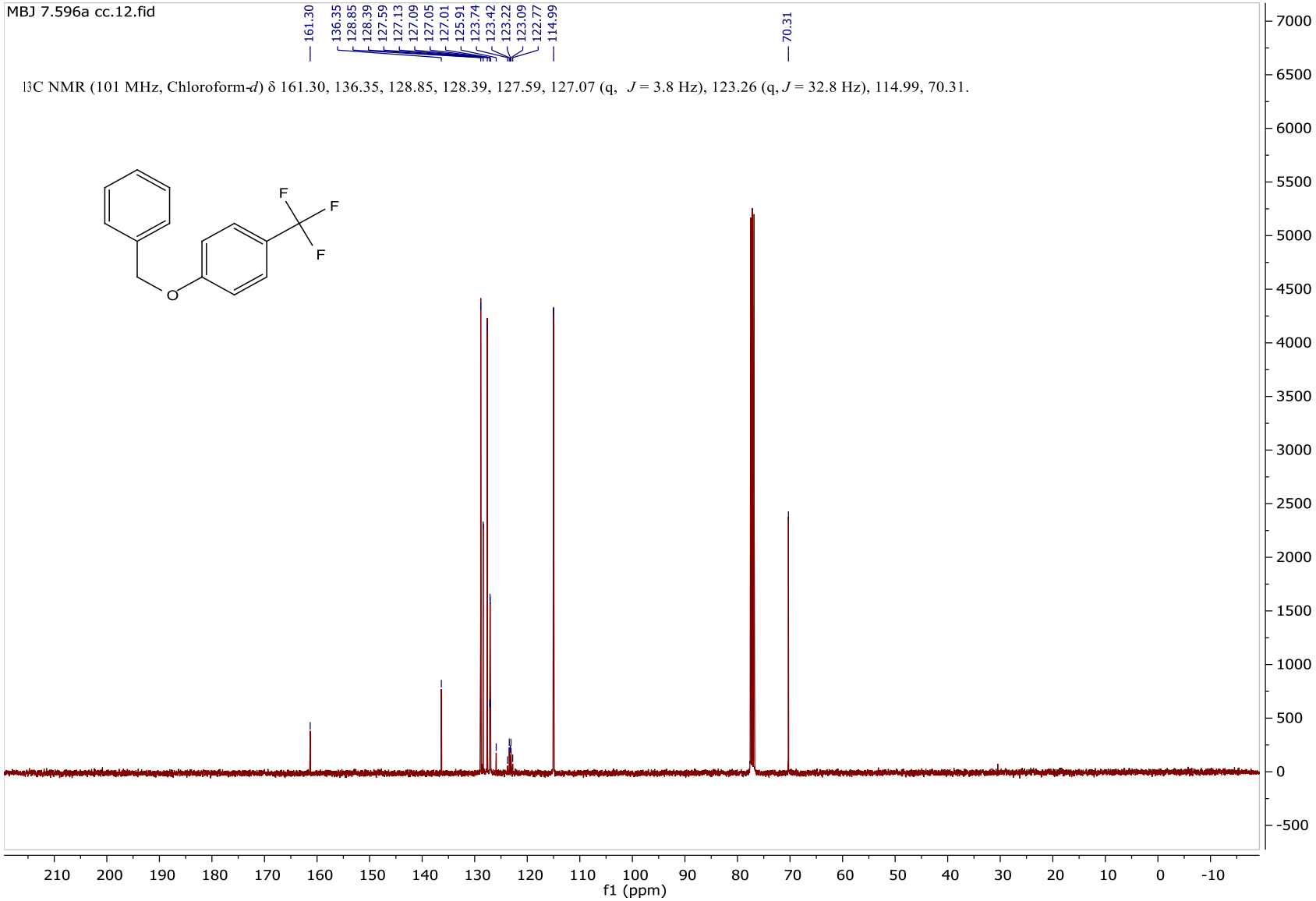

MBJ 7.591c cc.20.fid
7.44
7.40
7.40
7.38
7.37
6.84
6.82
4.67
4.65
4.62
3.28
3.25
3.23
1H NMR (400 MHz, Chloroform-d) δ 7.44 (s, 1H), 7.39 (dd, J = 8.3, 1.8 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 4.65 (t, J = 8.8 Hz, 2H), 3.25 (t, J = 8.8 Hz, 2H).
O
F
F
F
0.98
0.89
0.92
1.98
2.00
f1 (ppm)


MBJ 7.591c cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -61.05.
-61.05
F
F
F
O
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

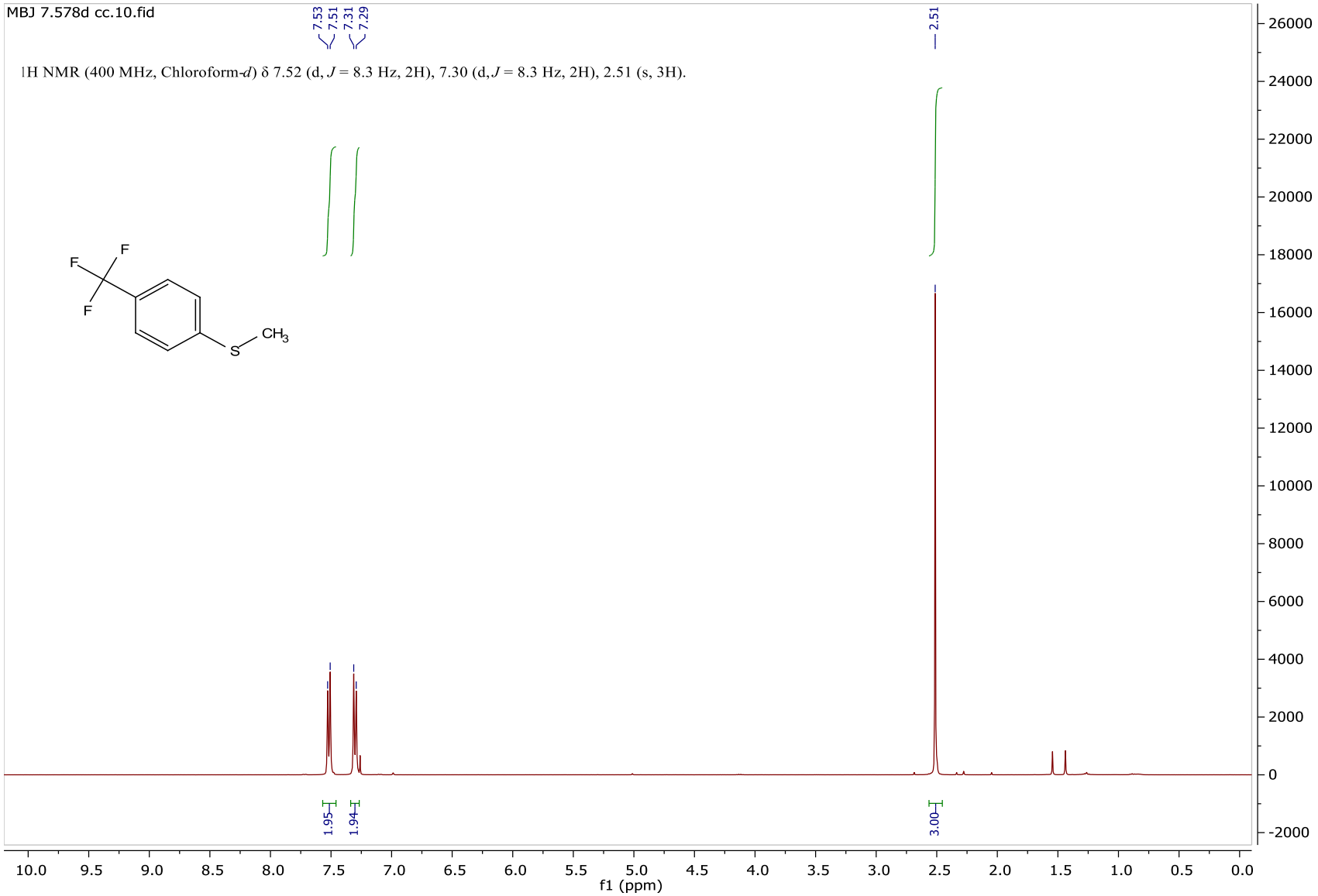

MBJ 7.591c cc.22.fid
162.90
128.79
127.91
126.17
126.13
126.09
126.05
123.41
123.09
122.77
122.45
122.42
122.38
122.35
122.31
120.71
109.39
109.39
77.48
72.01
29.39
13C NMR (101 MHz, Chloroform-d) δ 162.90, 127.91, 126.11 (q, J = 4.0 Hz), 124.76 (q, J = 270.0 Hz), 122.93 (q, J = 32.2 Hz), 122.37 (q, J = 3.7 Hz), 109.39, 72.01, 29.39.
O
F
F
F
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

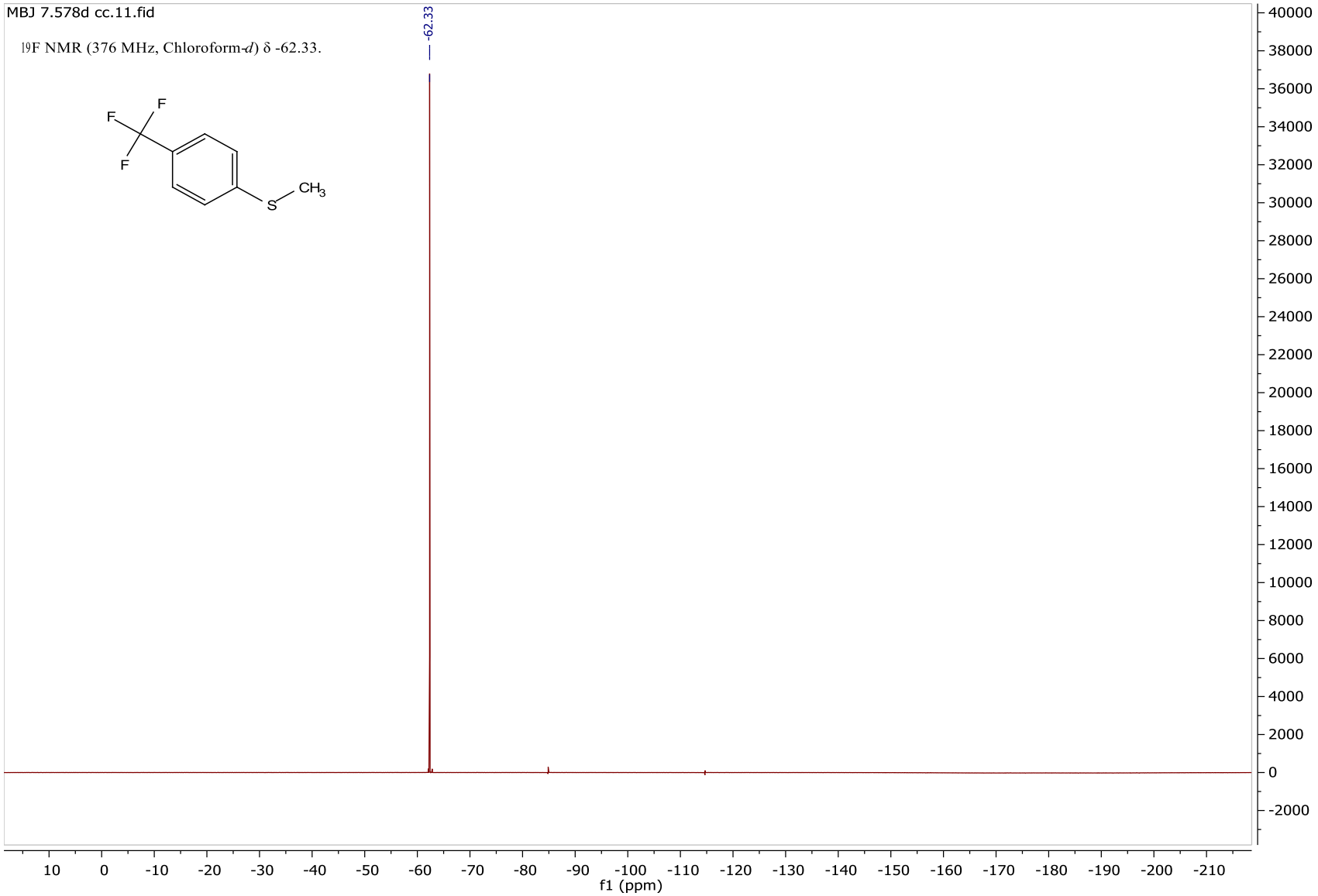

MBJ 7.596a cc.10.fid
7.55 7.55 7.48 7.48 7.43 7.43 7.41 7.39 7.39 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.05 7.03
5.12
1H NMR (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.5 Hz, 2H), 7.48 – 7.31 (m, 5H), 7.04 (d, J = 8.6 Hz, 2H), 5.12 (s, 2H).
F
F
F
O
1.93
4.86
1.93
2.00
f1 (ppm)

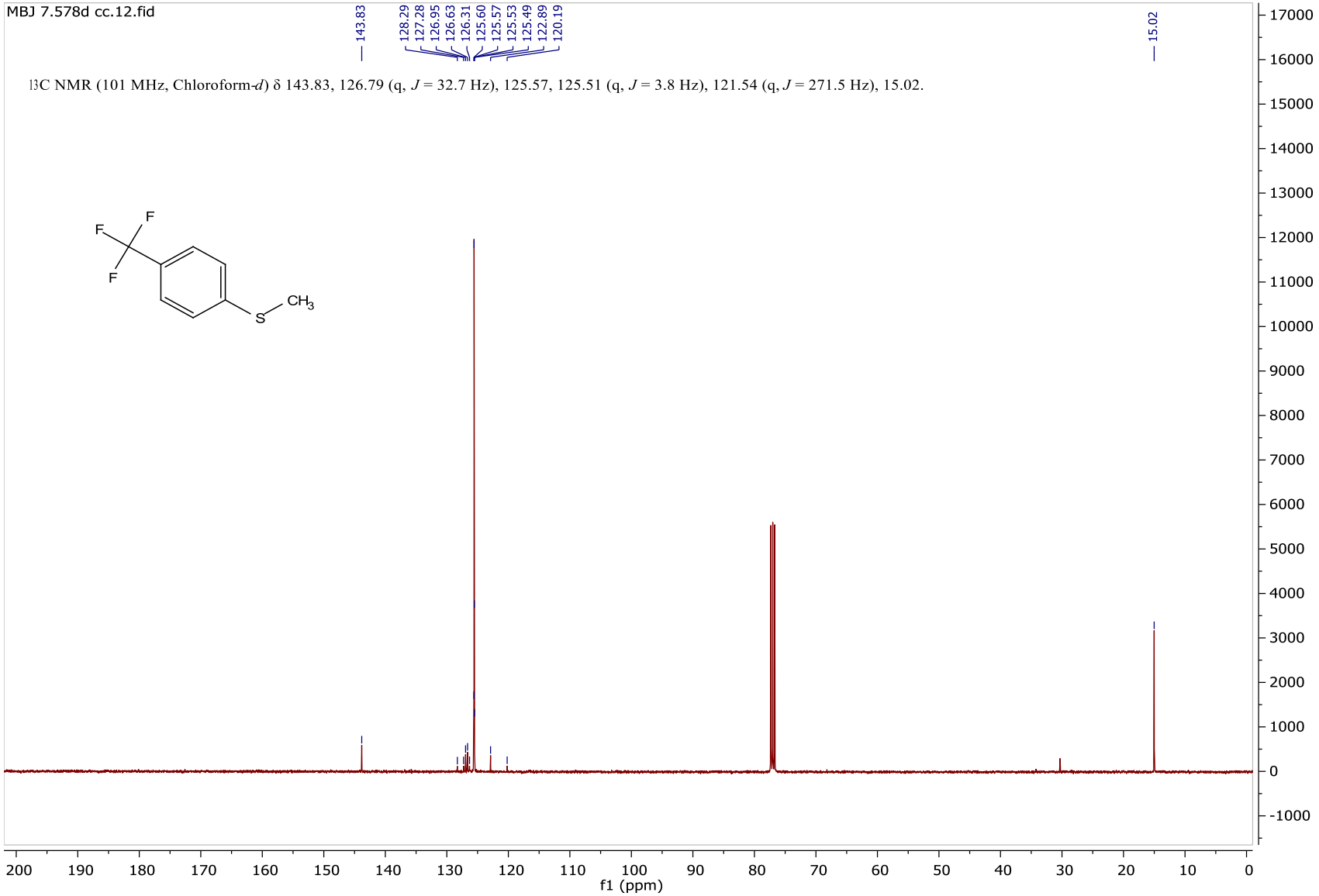

MBJ 7.596a cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -61.51.
-61.51
F
F
F
O
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

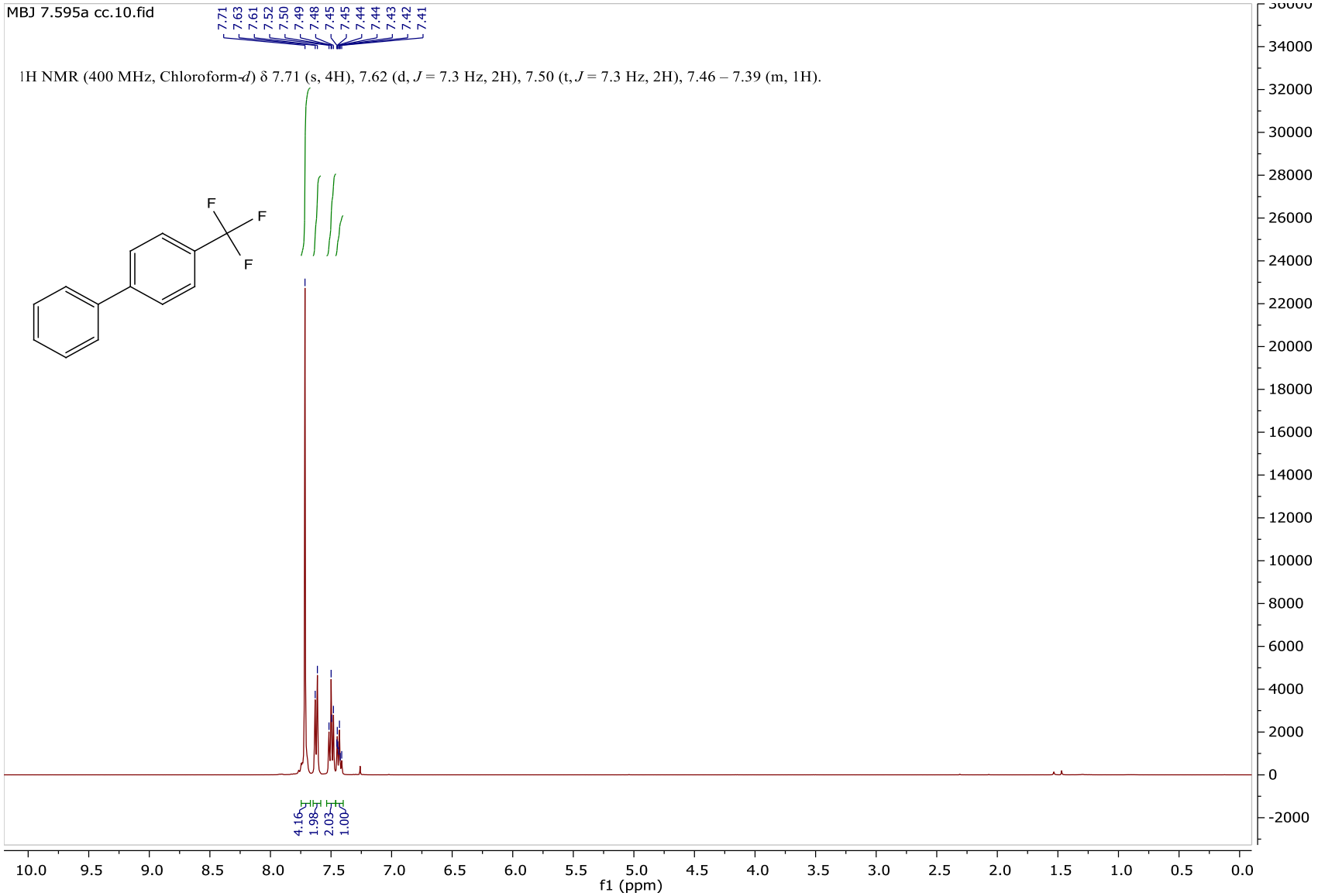


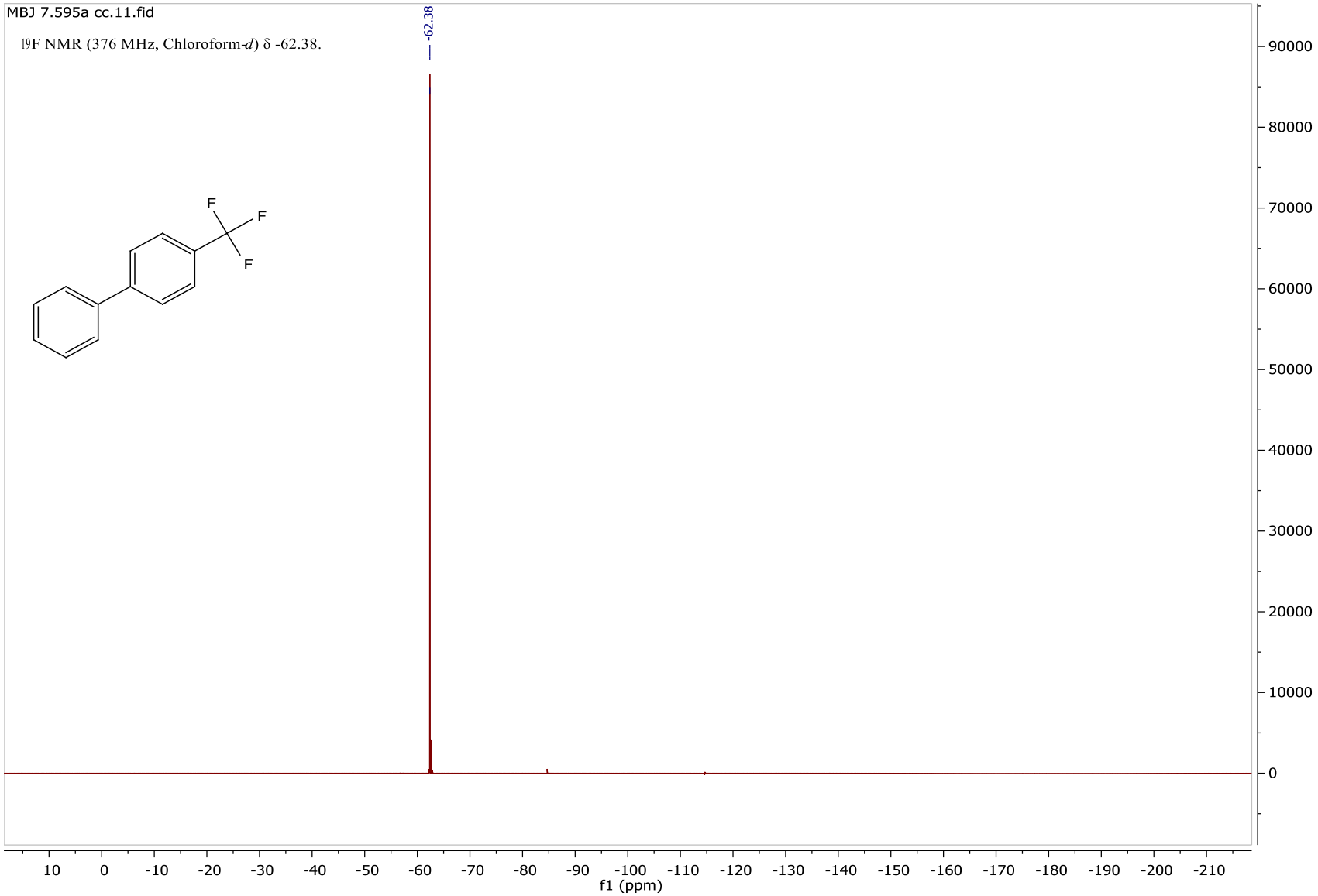
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.30, 136.35, 128.85, 128.39, 127.59, 127.07 (q, J = 3.8 Hz), 123.26 (q, J = 32.8 Hz), 114.99, 70.31.

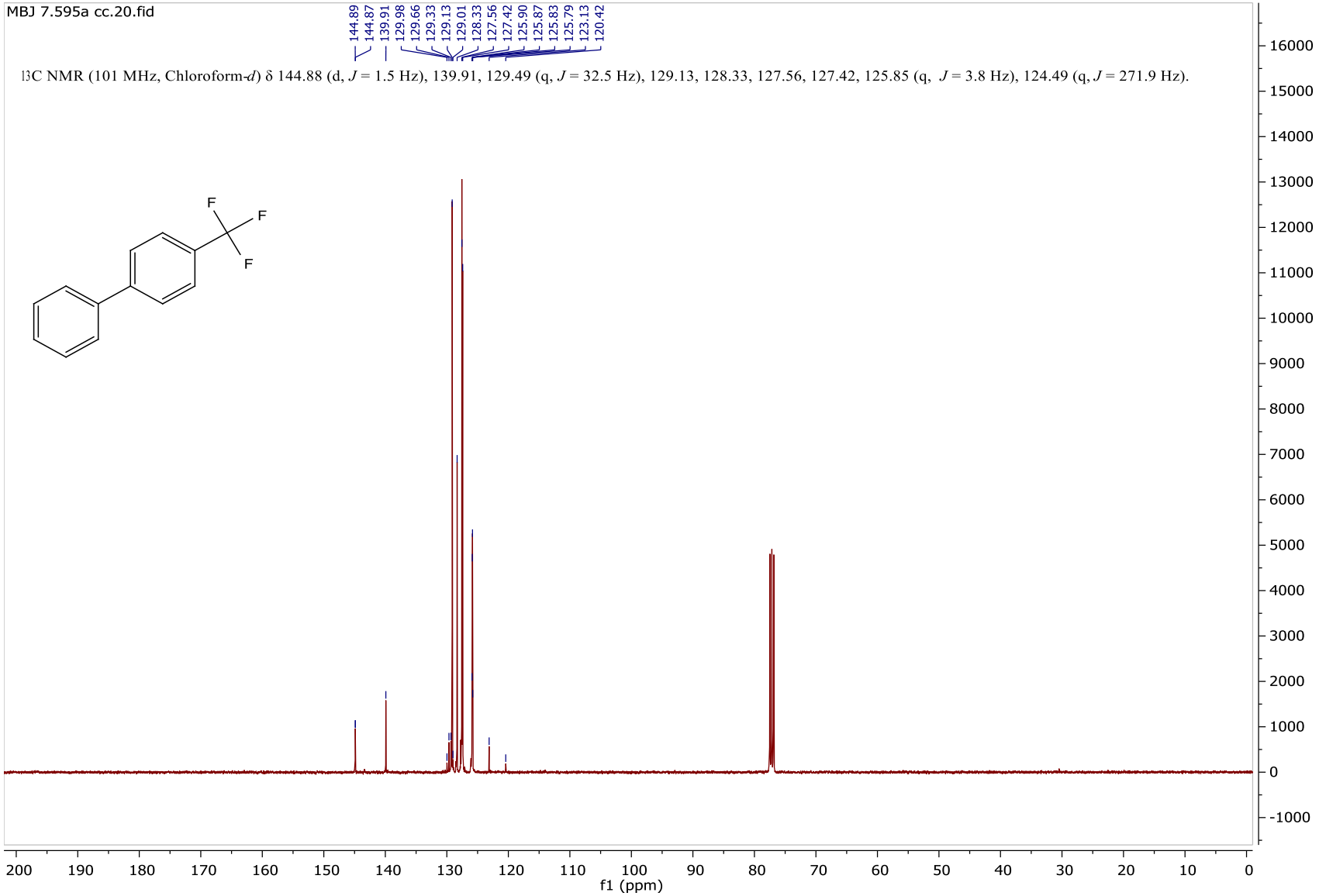

MBJ 7.578d cc.10.fid
7.53
7.51
7.31
7.29
2.51
1H NMR (400 MHz, Chloroform-d) δ 7.52 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 2.51 (s, 3H).
F
F
F
S
CH3
1.95
1.94
3.00
f1 (ppm)

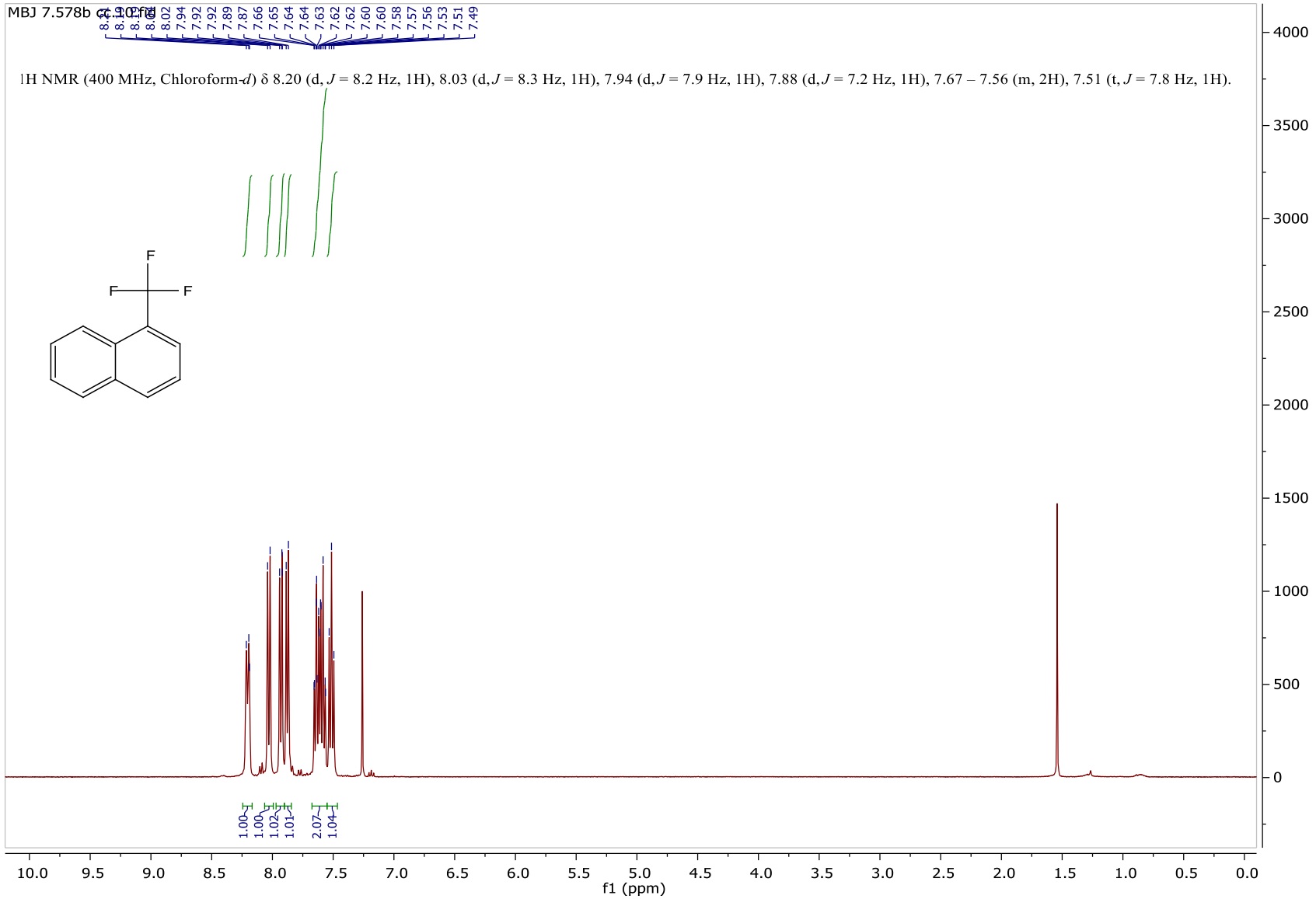

MBJ 7.578d cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -62.33.
-62.33
F
F
F
S
CH3
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

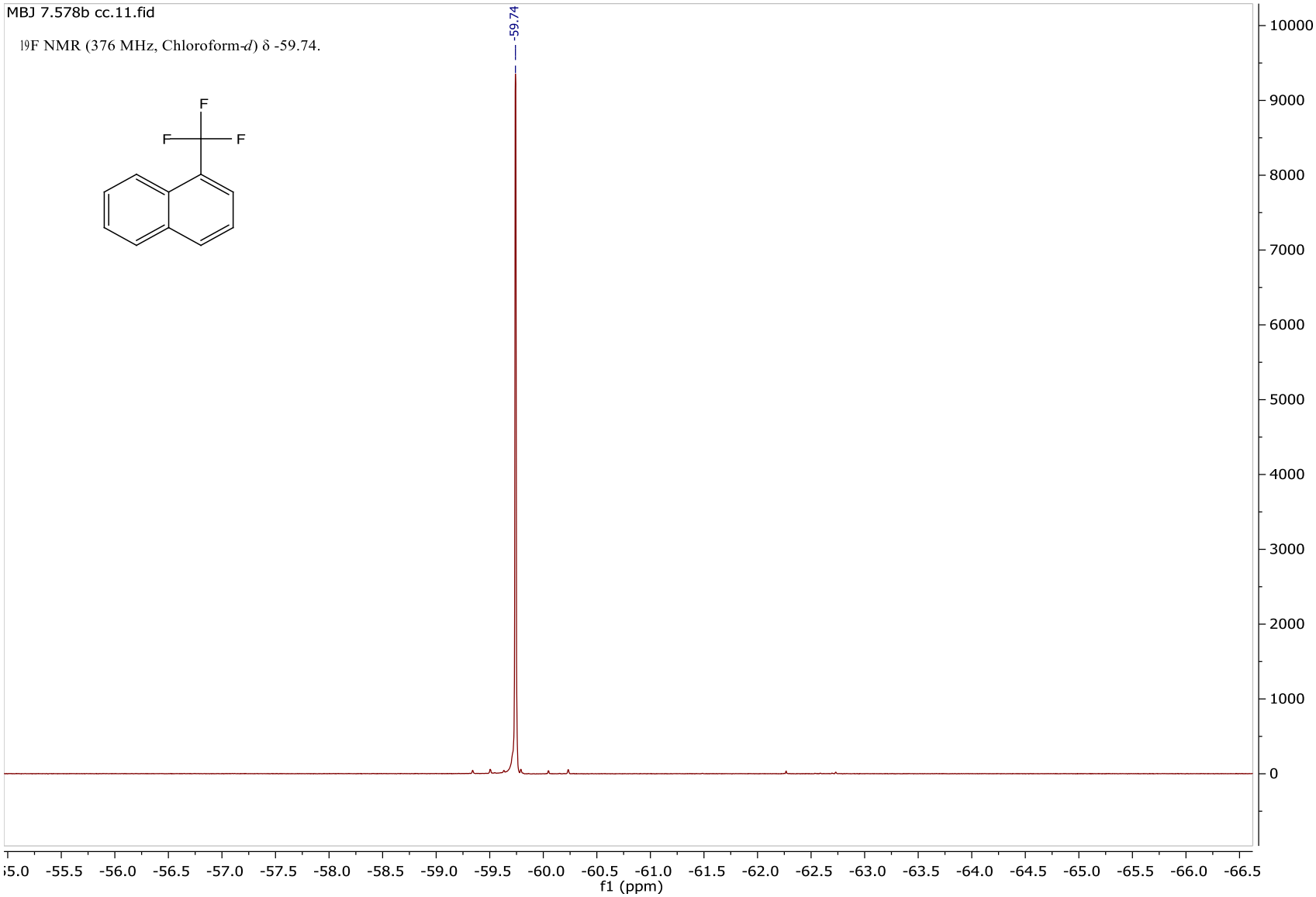

MBJ 7.578d cc.12.fid
143.83
128.29
127.28
126.95
126.63
126.31
125.60
125.57
125.53
125.49
122.89
120.19
15.02
13C NMR (101 MHz, Chloroform-d) δ 143.83, 126.79 (q, J = 32.7 Hz), 125.57, 125.51 (q, J = 3.8 Hz), 121.54 (q, J = 271.5 Hz), 15.02.
F
F
F
CH3
S
f1 (ppm)

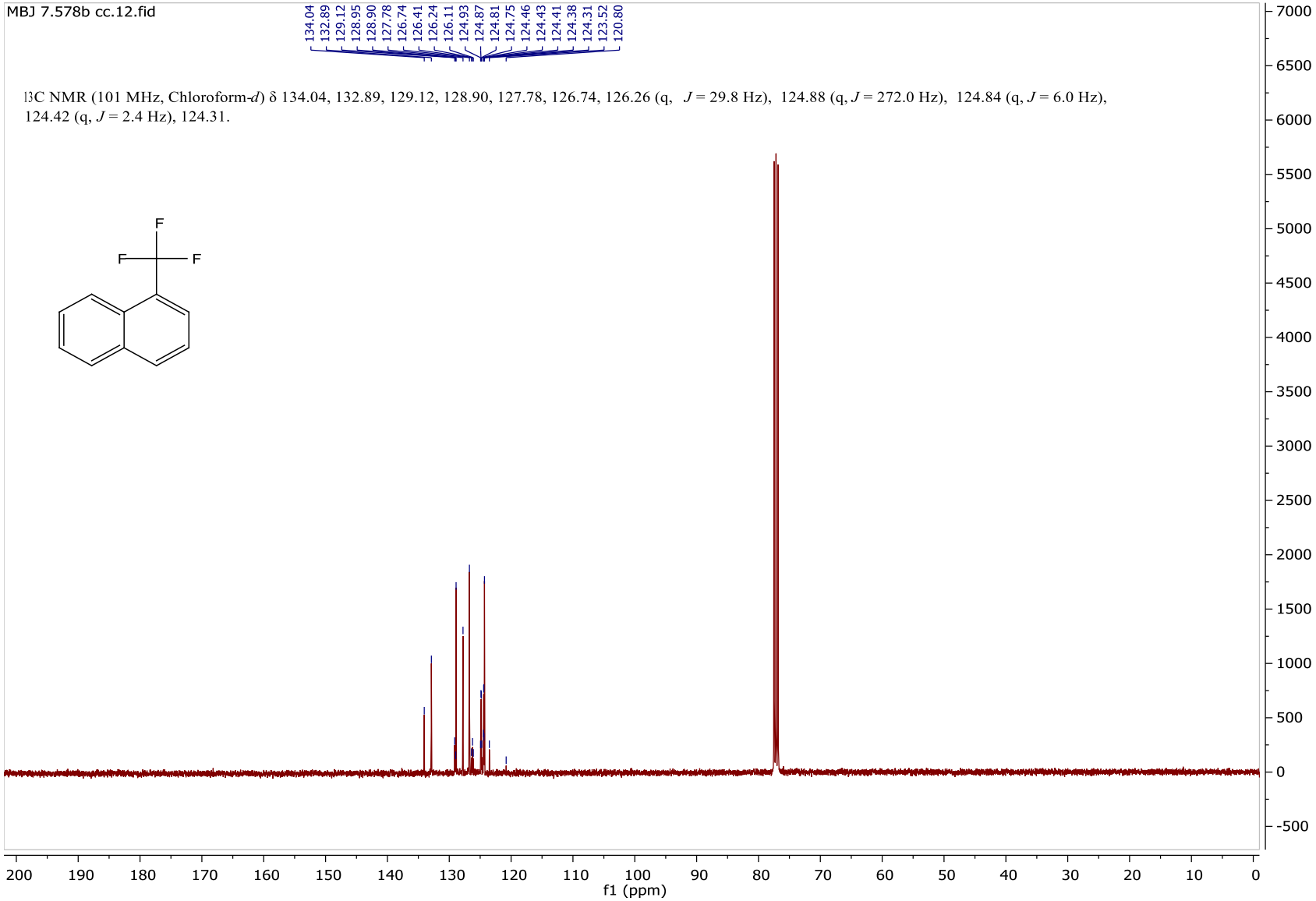

MBJ 7.595a cc.10.fid
7.71
7.63
7.61
7.52
7.50
7.49
7.48
7.45
7.45
7.44
7.44
7.43
7.42
7.41
1H NMR (400 MHz, Chloroform-d) δ 7.71 (s, 4H), 7.62 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 2H), 7.46 – 7.39 (m, 1H).
F
F
F
4.16
1.98
2.03
1.00
f1 (ppm)


MBJ 7.595a cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -62.38.
-62.38
F
F
F
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

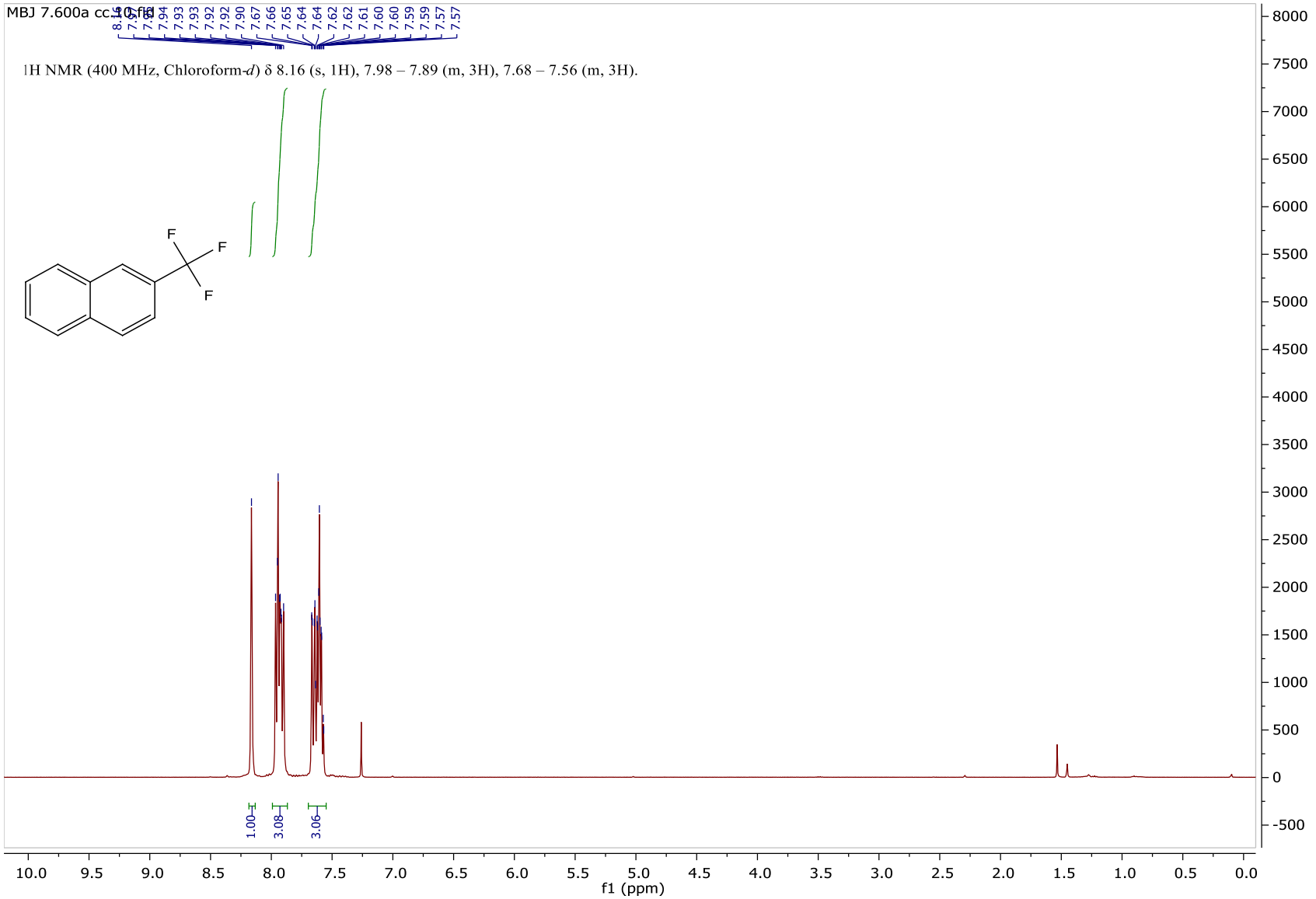

MBJ 7.595a cc.20.fid
144.89
144.87
139.91
129.98
129.66
129.33
129.13
129.01
128.33
127.56
127.42
125.90
125.87
125.83
125.79
123.13
120.42
13C NMR (101 MHz, Chloroform-d) δ 144.88 (d, J = 1.5 Hz), 139.91, 129.49 (q, J = 32.5 Hz), 129.13, 128.33, 127.56, 127.42, 125.85 (q, J = 3.8 Hz), 124.49 (q, J = 271.9 Hz).
F
F
F
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

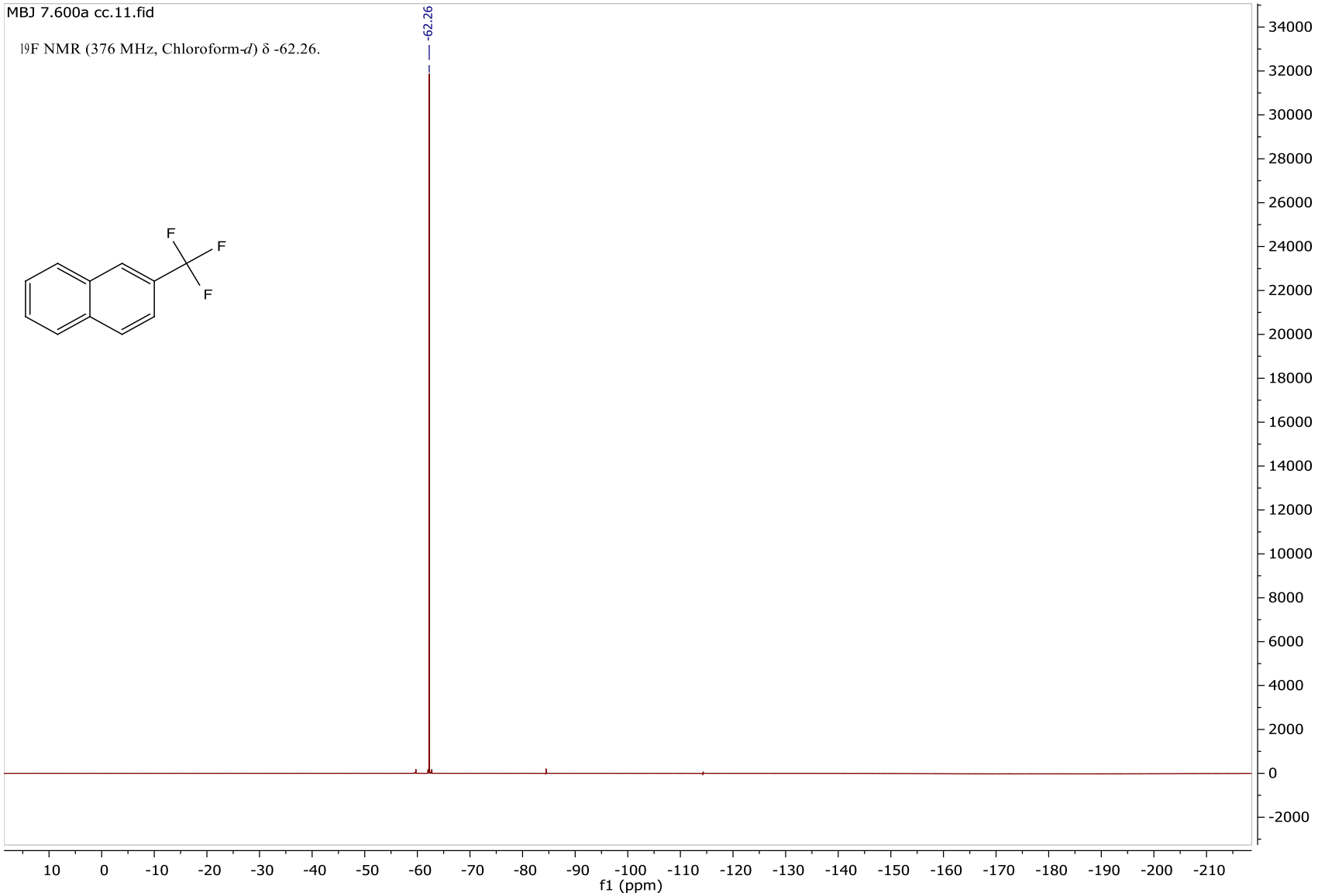

MBJ 7.578b cc 10.fid
8.20
8.19
8.03
8.02
7.94
7.92
7.92
7.89
7.87
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.60
7.60
7.58
7.57
7.56
7.53
7.51
7.49
1H NMR (400 MHz, Chloroform-d) δ 8.20 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H).
F
F
F
1.00
1.00
1.02
1.01
2.07
1.04
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

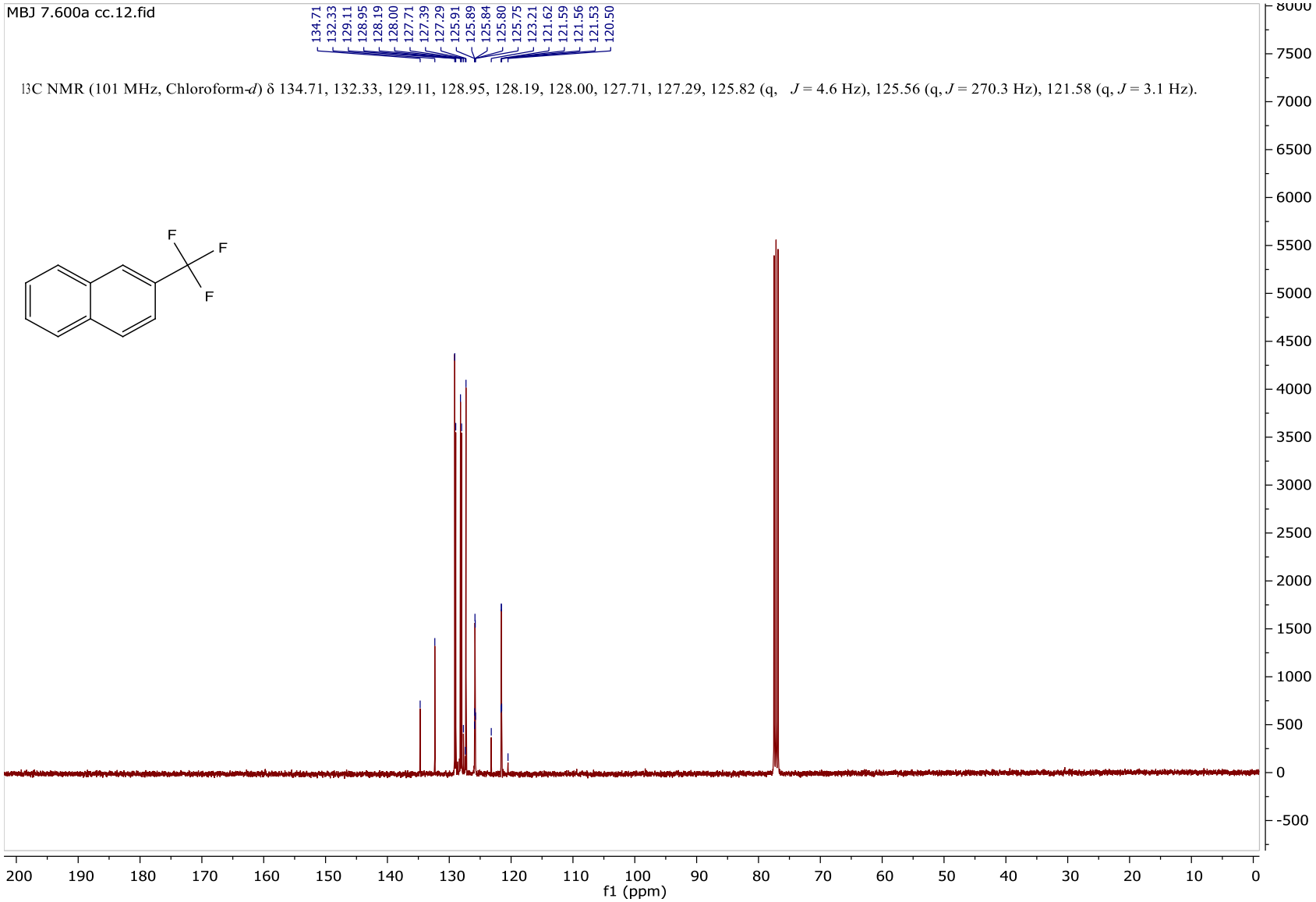

MBJ 7.578b cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -59.74.
F
F
F
-59.74
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
f1 (ppm)



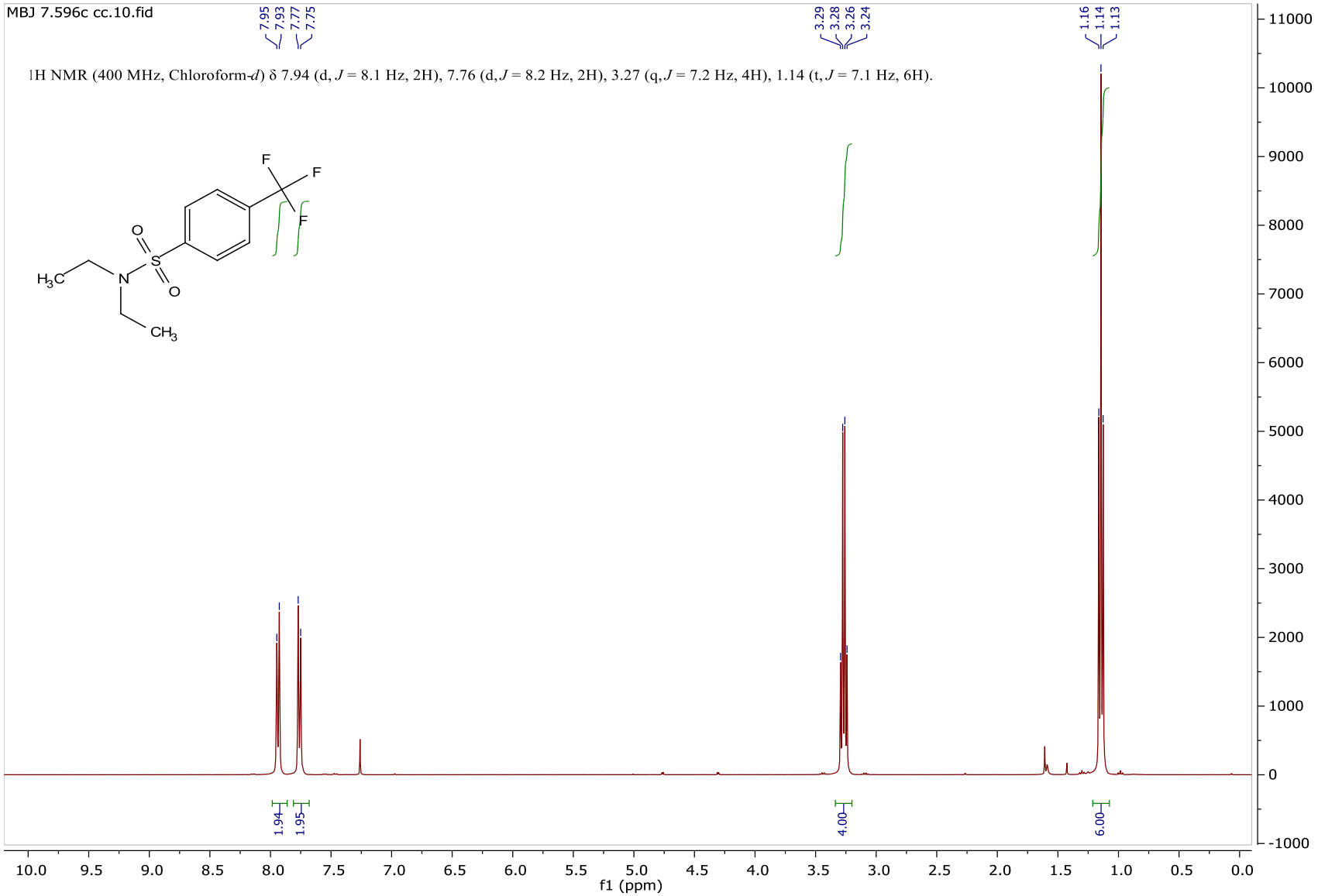
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.04, 132.89, 129.12, 128.90, 127.78, 126.74, 126.26 (q, *J* = 29.8 Hz), 124.88 (q, *J* = 272.0 Hz), 124.84 (q, *J* = 6.0 Hz), 124.42 (q, *J* = 2.4 Hz), 124.31.

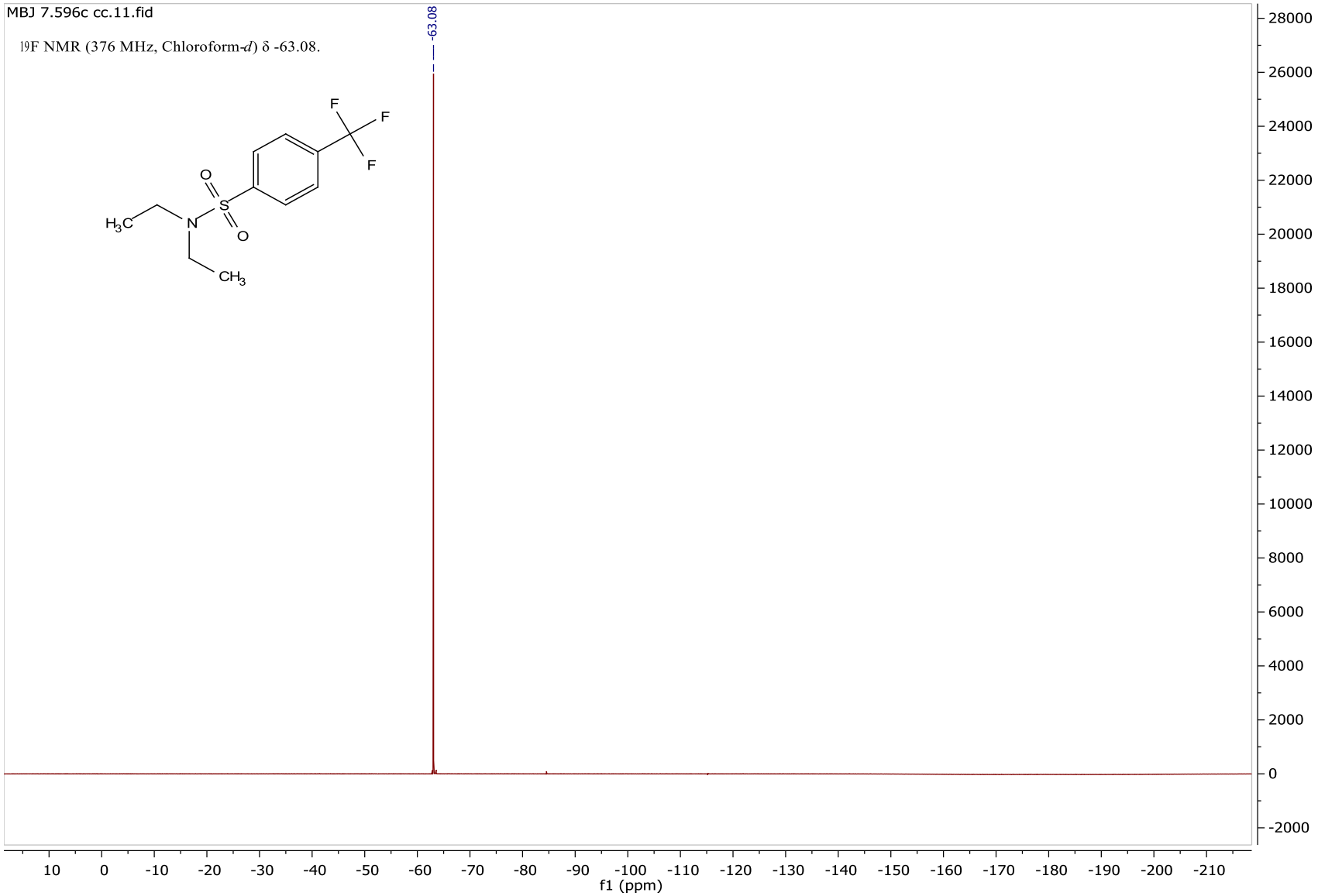

MBJ 7.600a cc.10.fid
8.16 7.98 7.98 7.94 7.93 7.93 7.92 7.92 7.90 7.67 7.66 7.65 7.64 7.64 7.62 7.62 7.61 7.60 7.60 7.59 7.59 7.57 7.57
1H NMR (400 MHz, Chloroform-d) δ 8.16 (s, 1H), 7.98 – 7.89 (m, 3H), 7.68 – 7.56 (m, 3H).
F
F
F
1.00
3.08
3.06
f1 (ppm)

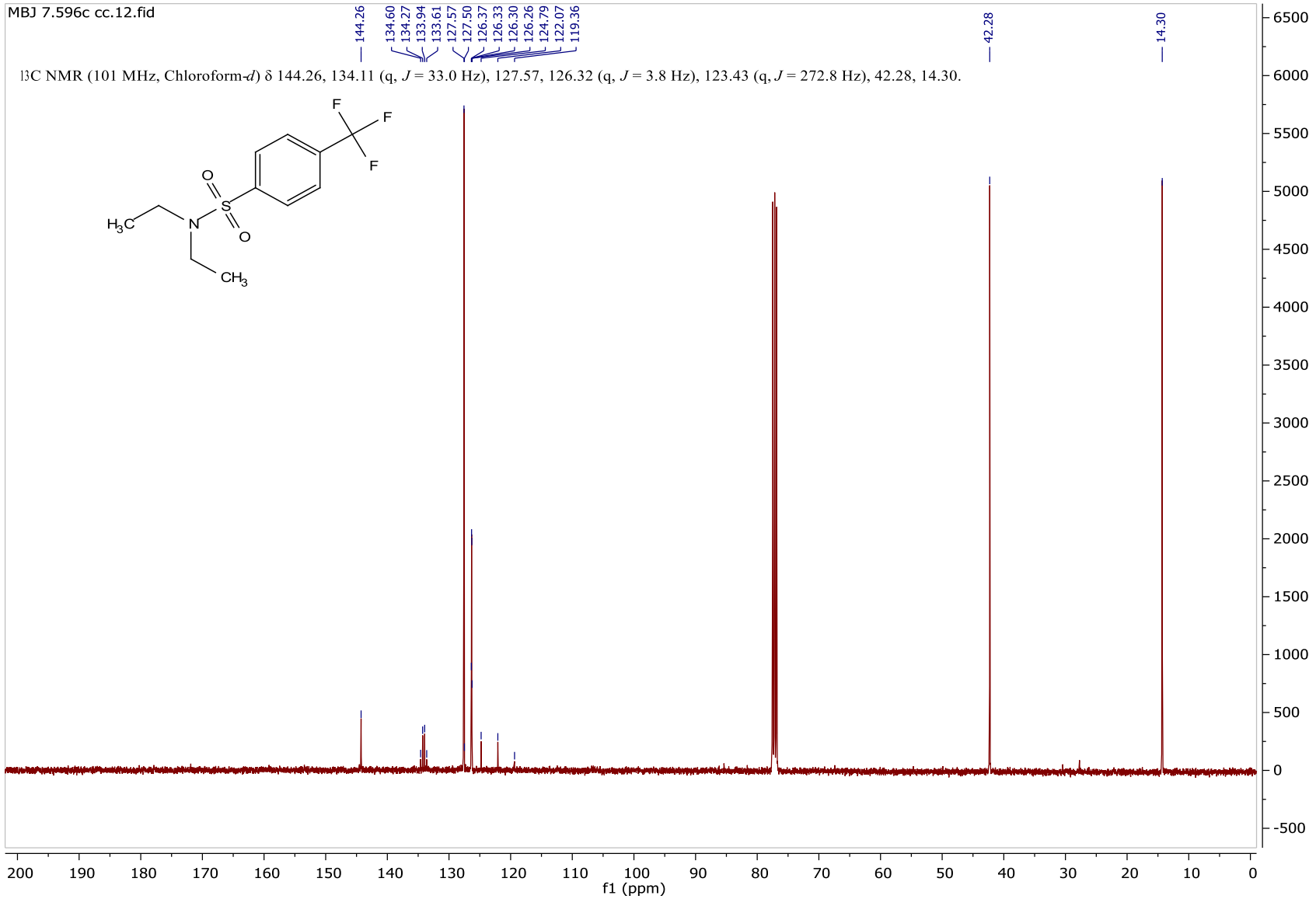

MBJ 7.600a cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -62.26.
-62.26
F
F
F
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

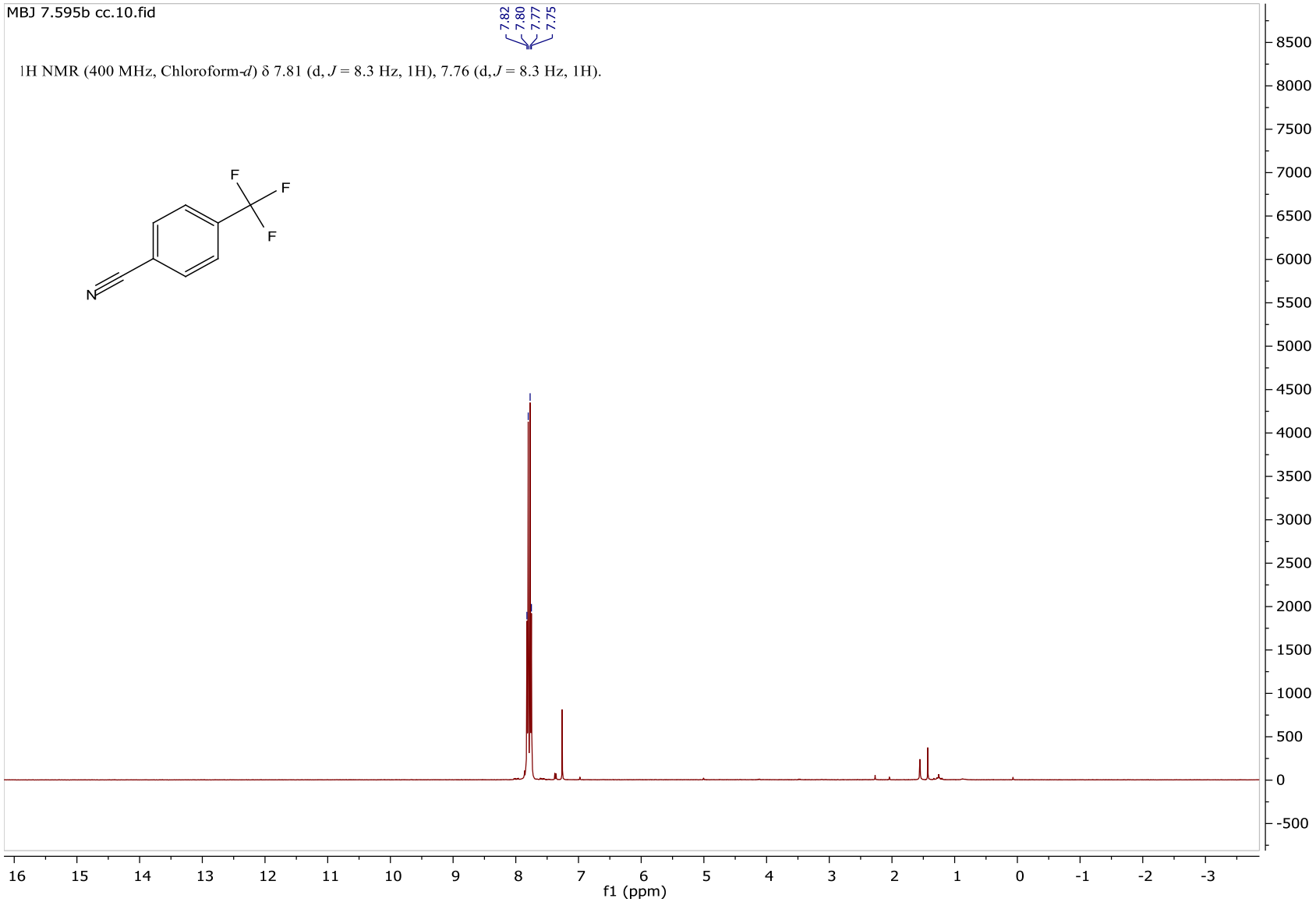


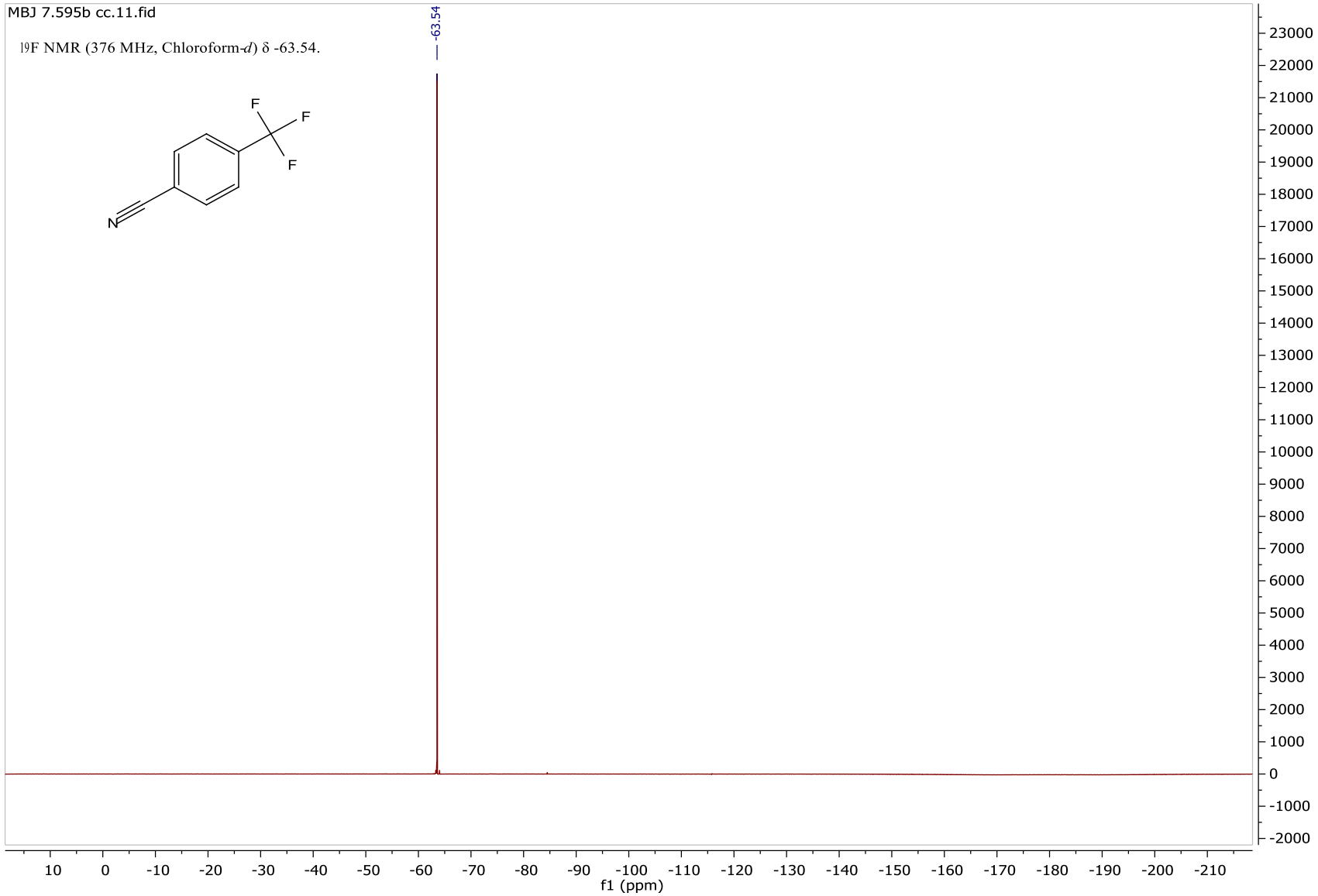
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.71, 132.33, 129.11, 128.95, 128.19, 128.00, 127.71, 127.29, 125.82 (q, J = 4.6 Hz), 125.56 (q, J = 270.3 Hz), 121.58 (q, J = 3.1 Hz).

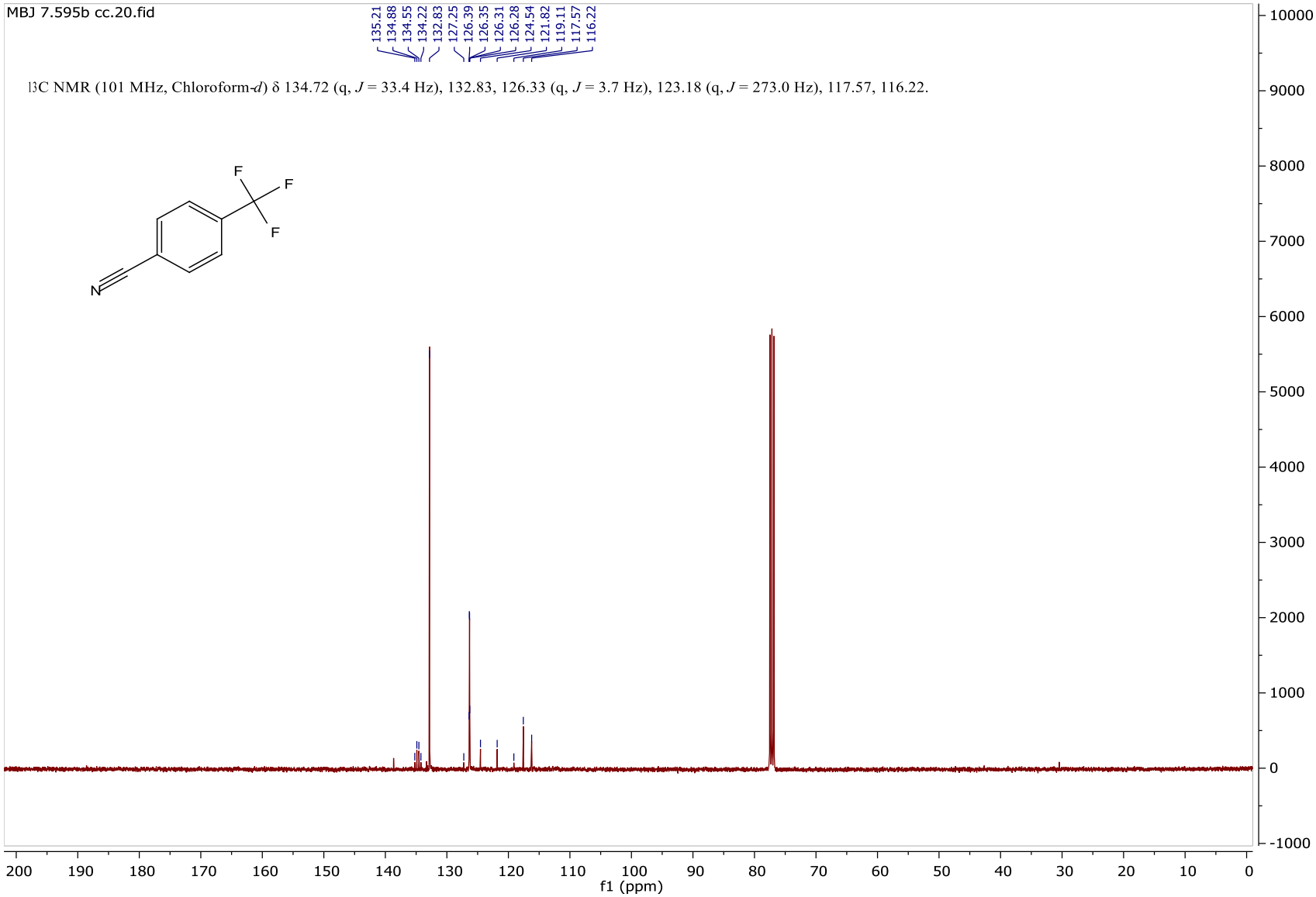

MBJ 7.596c cc.10.fid
7.95
7.93
7.77
7.75
3.29
3.28
3.26
3.24
1.16
1.14
1.13
1H NMR (400 MHz, Chloroform-d) δ 7.94 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 3.27 (q, J = 7.2 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H).
F
F
F
O
S
O
N
H3C
CH3
1.94
1.95
4.00
6.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

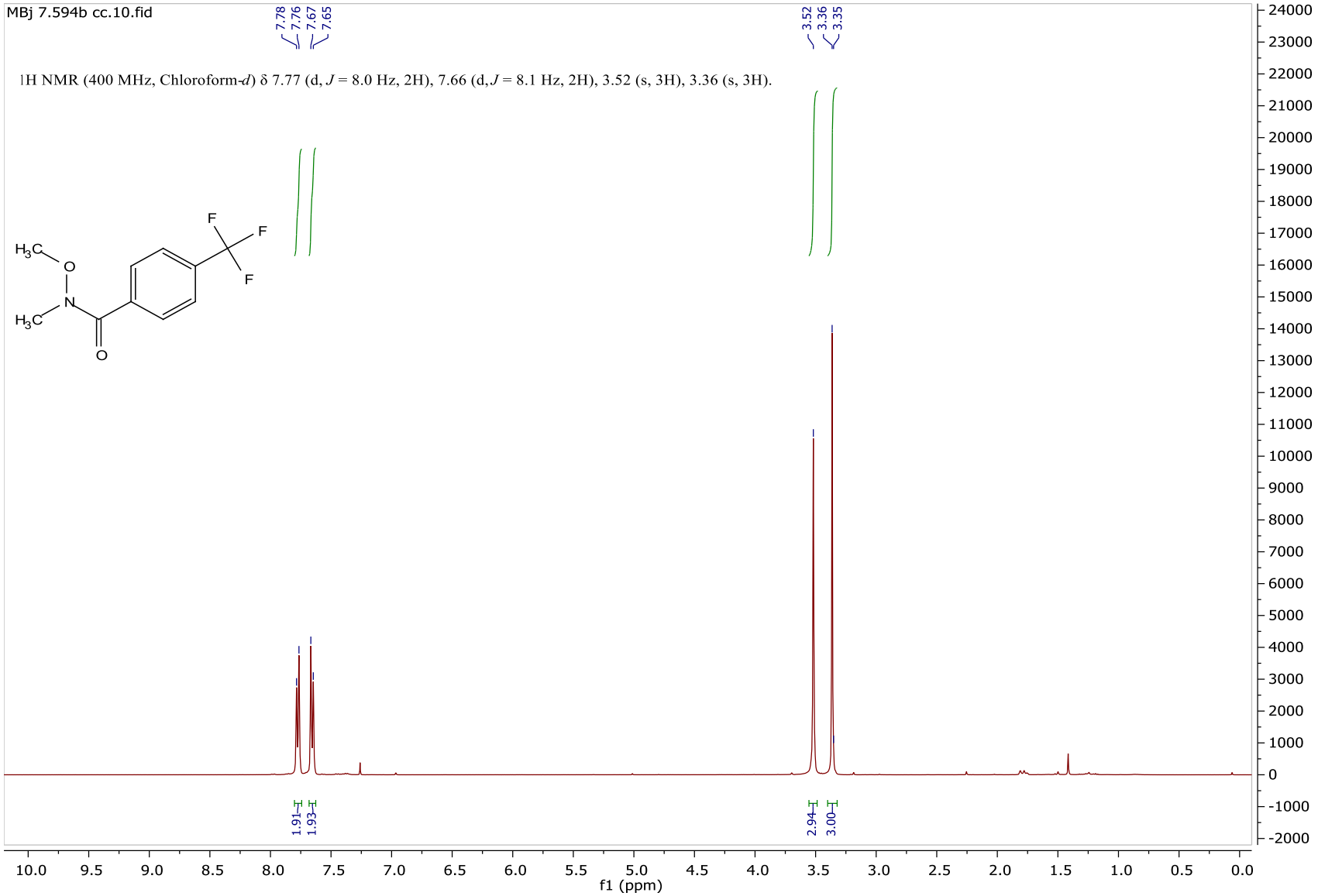

MBJ 7.596c cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -63.08.
-63.08
F
F
F
O
S
O
H3C
N
CH3
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

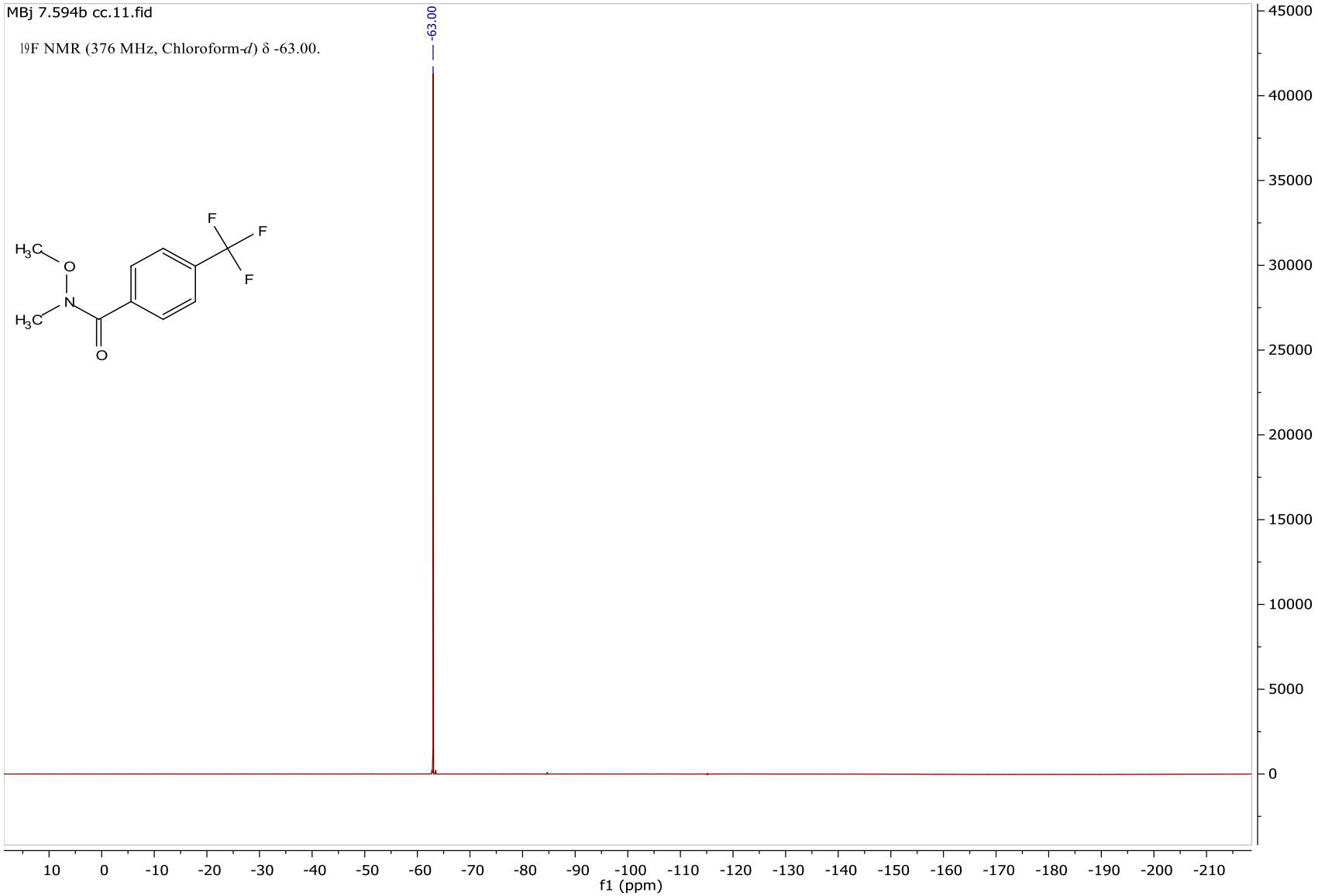

MBJ 7.596c cc.12.fid
144.26
134.60
134.27
133.94
133.61
127.57
127.50
126.37
126.33
126.30
126.26
124.79
122.07
119.36
42.28
14.30
13C NMR (101 MHz, Chloroform-d) δ 144.26, 134.11 (q, J = 33.0 Hz), 127.57, 126.32 (q, J = 3.8 Hz), 123.43 (q, J = 272.8 Hz), 42.28, 14.30.
F
F
F
O
S
O
H3C
N
CH3
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

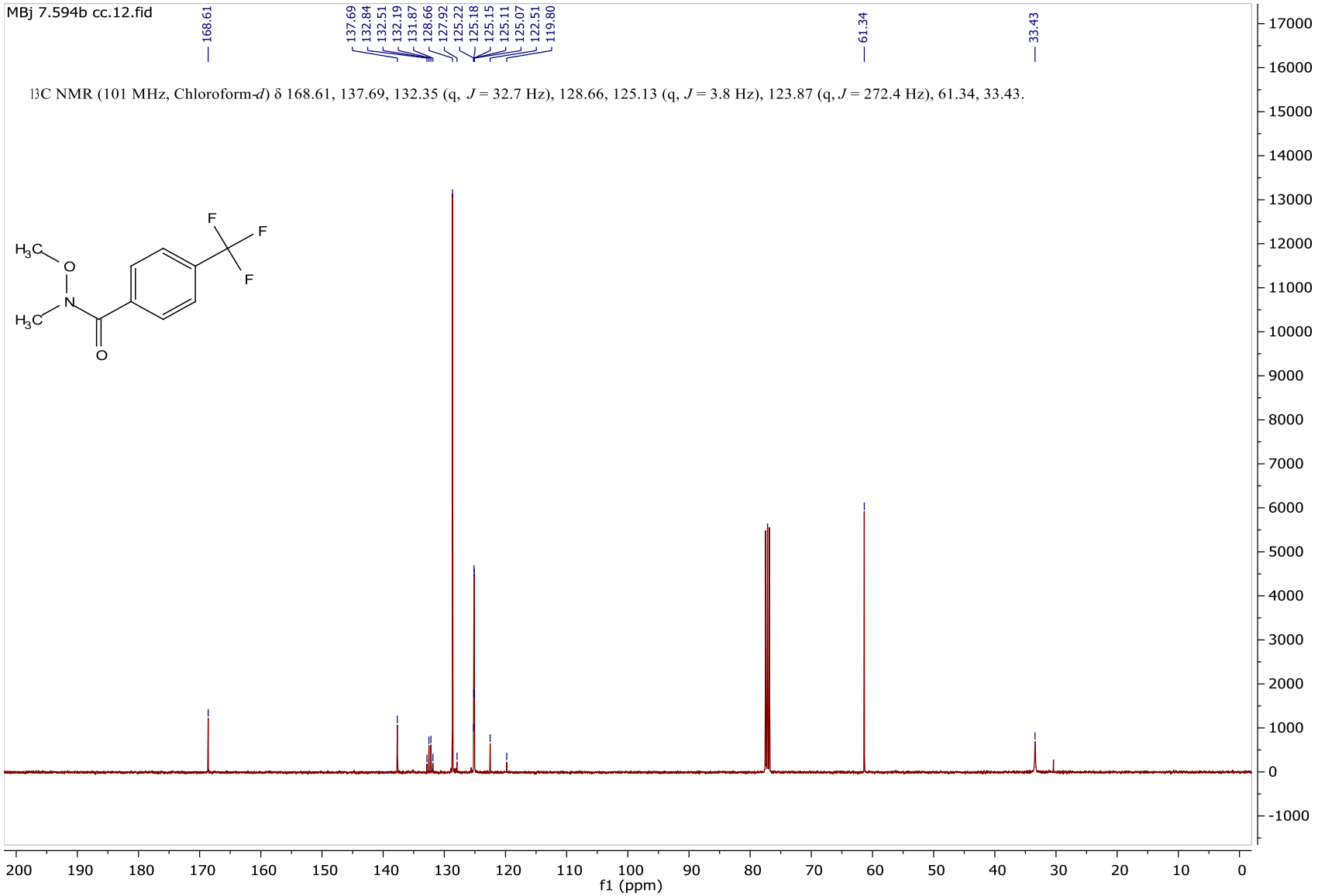

MBJ 7.595b cc.10.fid
7.82
7.80
7.77
7.75
1H NMR (400 MHz, Chloroform-d) δ 7.81 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H).
F
F
F
N
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

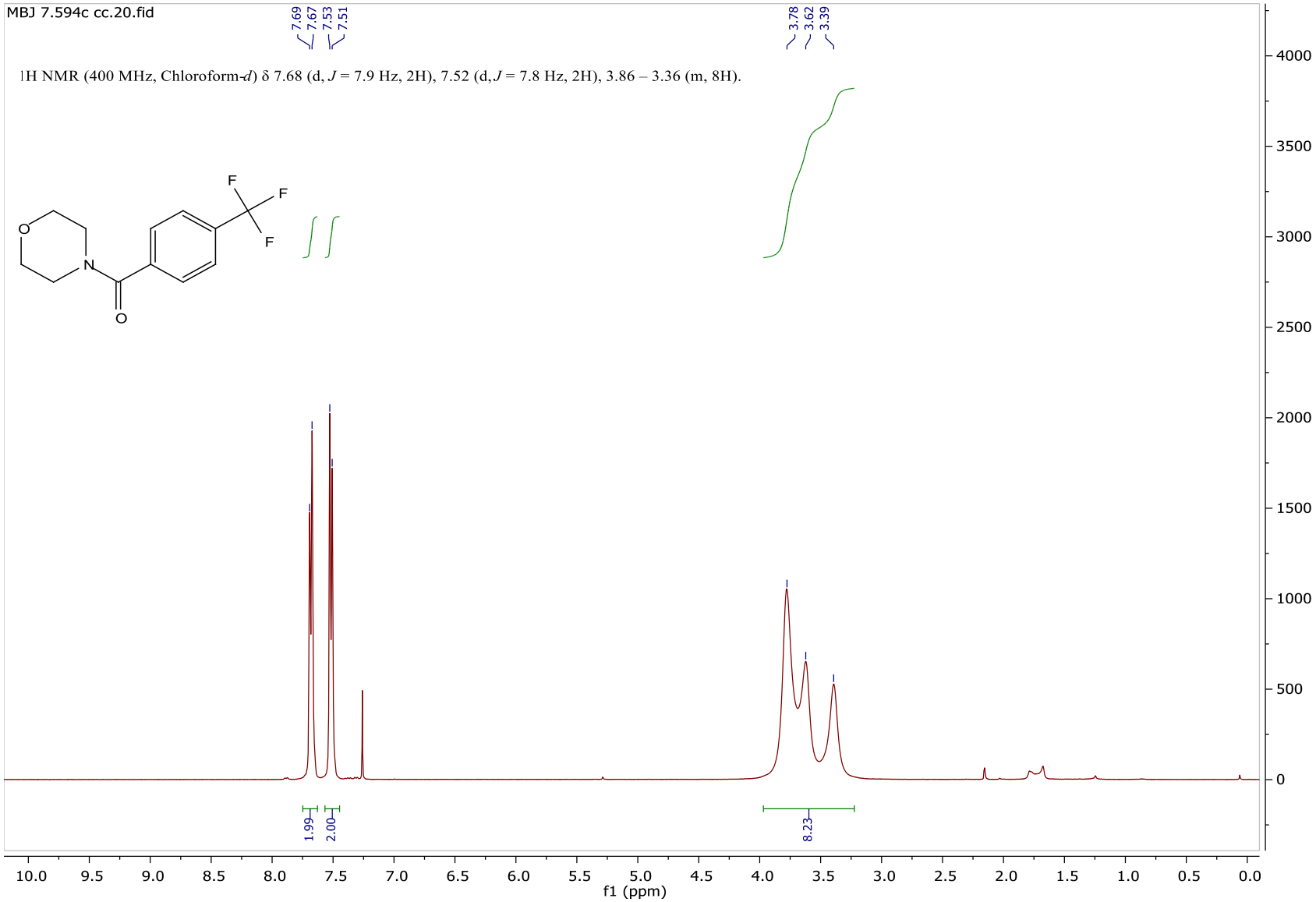

MBJ 7.595b cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -63.54.
-63.54
F
F
F
N
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

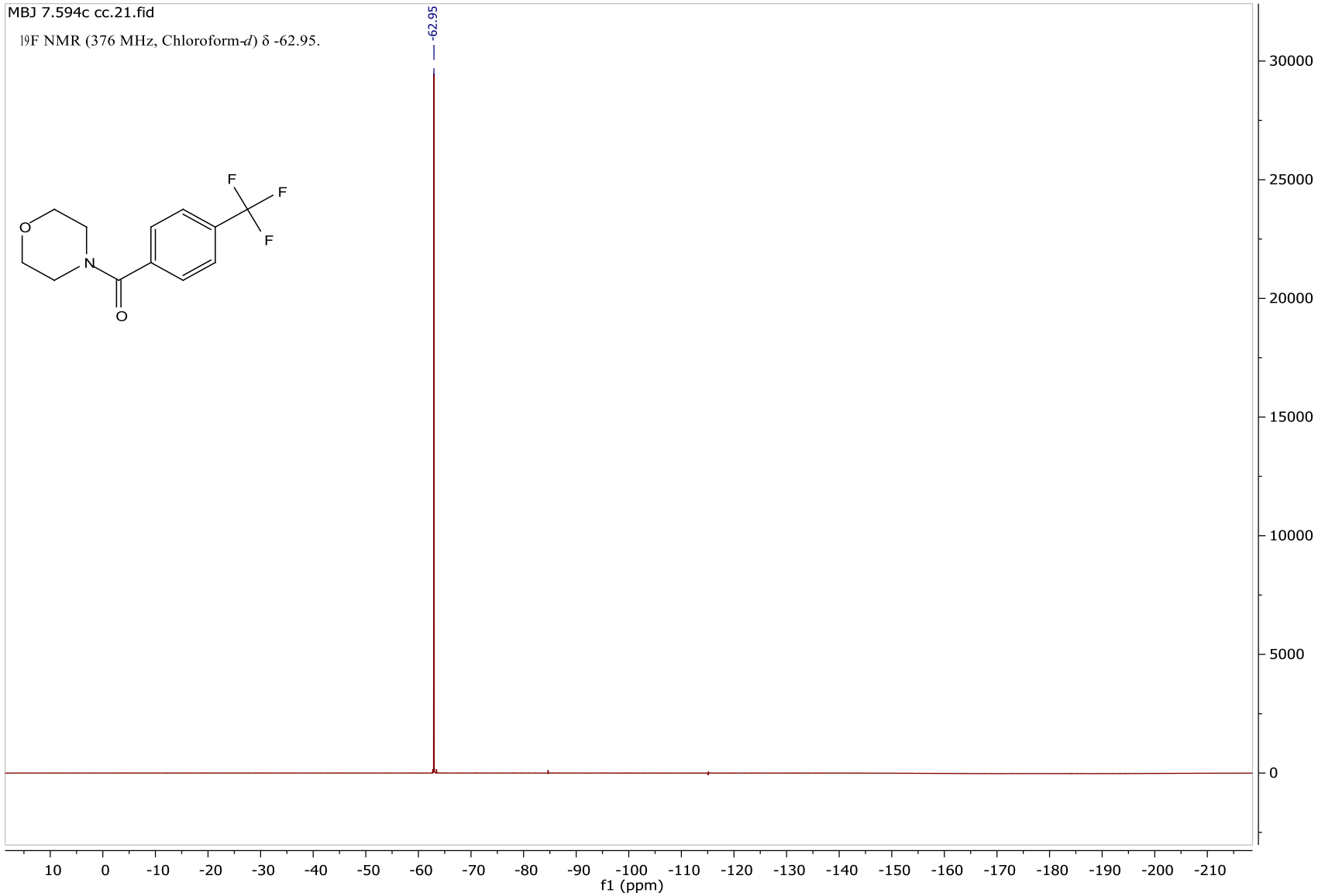

MBJ 7.595b cc.20.fid
135.21
134.88
134.55
134.22
132.83
127.25
126.39
126.35
126.31
126.28
124.54
121.82
119.11
117.57
116.22
13C NMR (101 MHz, Chloroform-d) δ 134.72 (q, J = 33.4 Hz), 132.83, 126.33 (q, J = 3.7 Hz), 123.18 (q, J = 273.0 Hz), 117.57, 116.22.
F
F
F
N
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

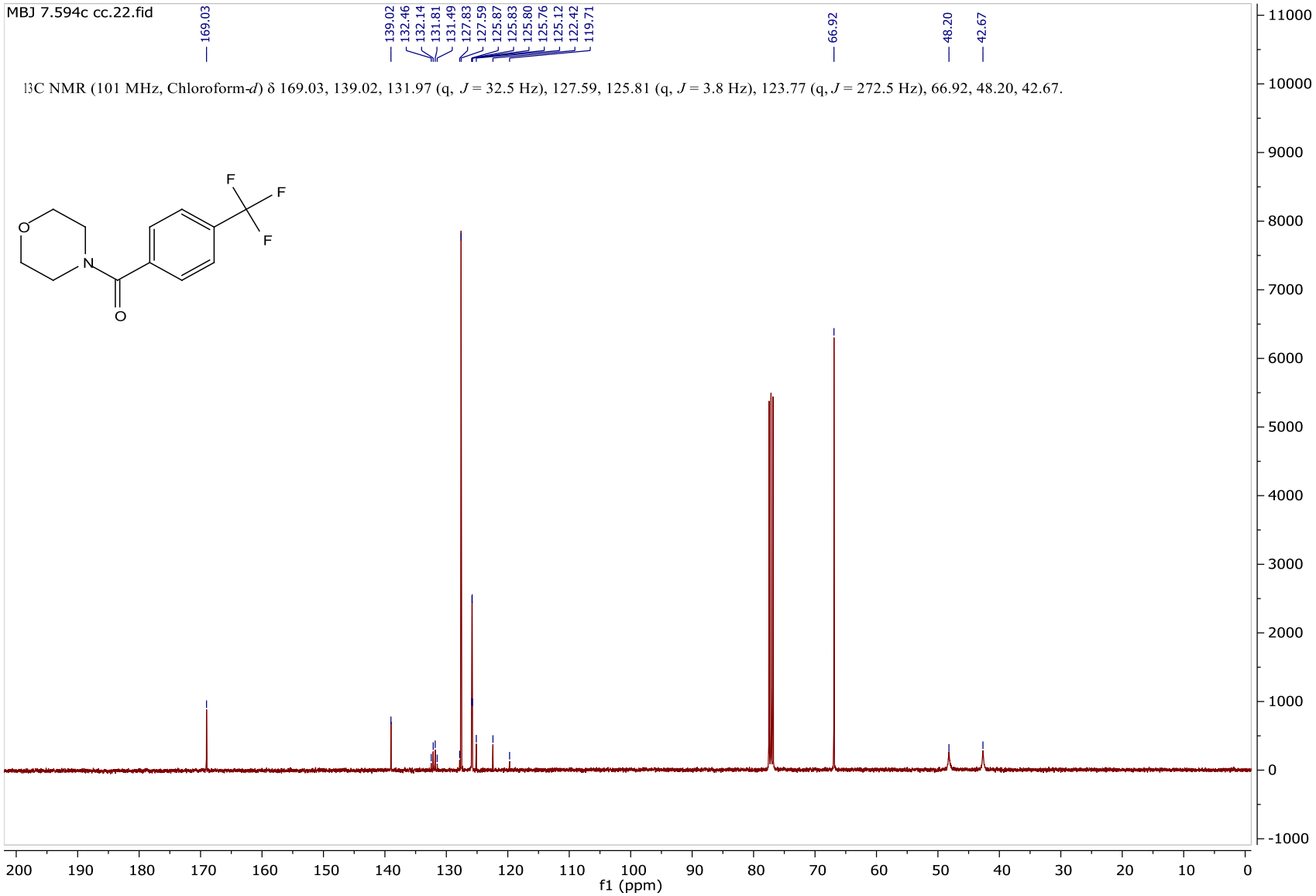

MBj 7.594b cc.10.fid
7.78
7.76
7.67
7.65
3.52
3.36
3.35
1H NMR (400 MHz, Chloroform-d) δ 7.77 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 3.52 (s, 3H), 3.36 (s, 3H).
F
F
F
H3C
O
N
H3C
O
1.91
1.93
2.94
3.00
f1 (ppm)


MBj 7.594b cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -63.00.
-63.00
H3C
O
N
H3C
O
F
F
F
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

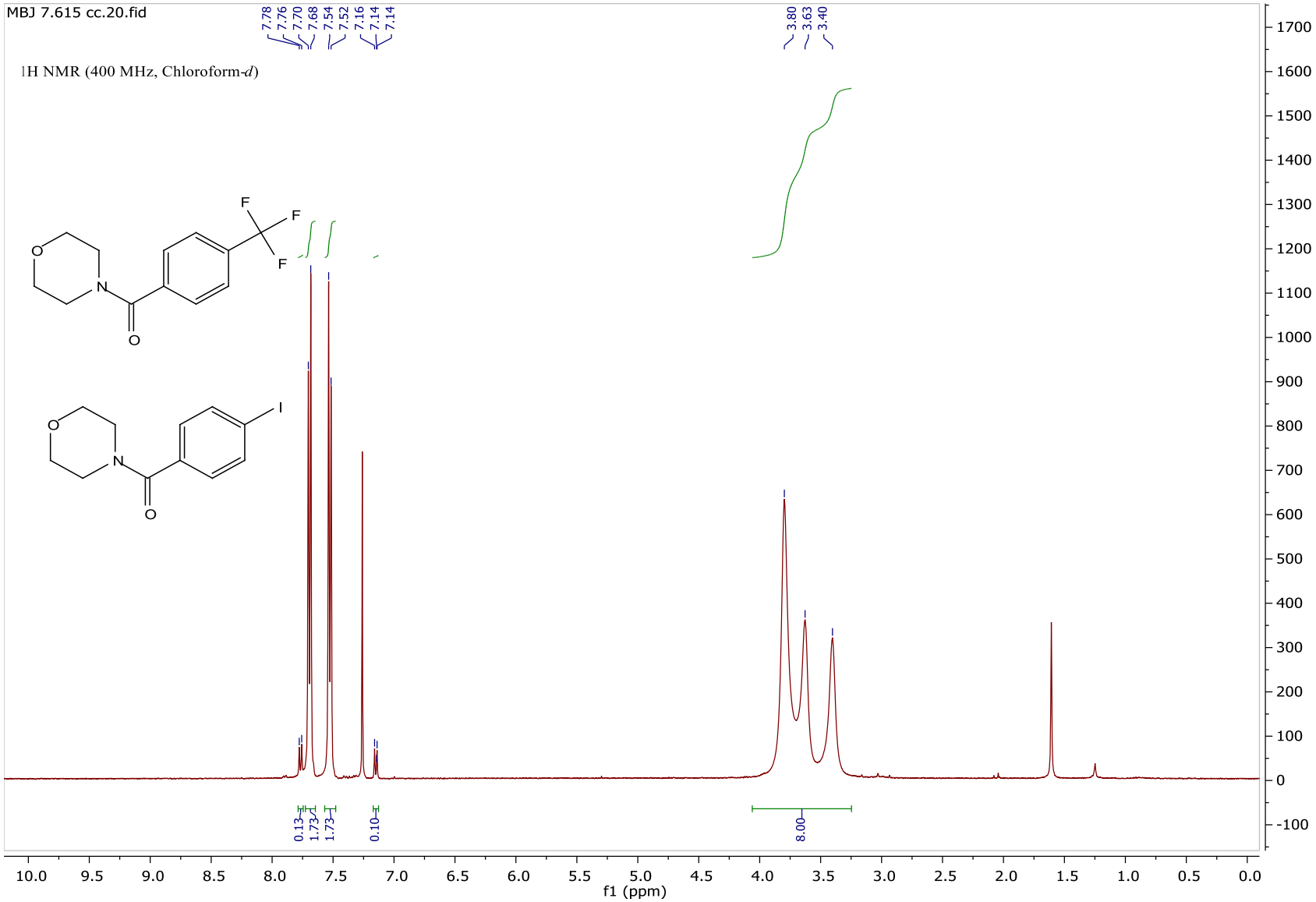

MBj 7.594b cc.12.fid
168.61
137.69
132.84
132.51
132.19
131.87
128.66
127.92
125.22
125.18
125.15
125.11
125.07
122.51
119.80
61.34
33.43
13C NMR (101 MHz, Chloroform-d) δ 168.61, 137.69, 132.35 (q, J = 32.7 Hz), 128.66, 125.13 (q, J = 3.8 Hz), 123.87 (q, J = 272.4 Hz), 61.34, 33.43.
F
F
F
H3C
O
N
H3C
O
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

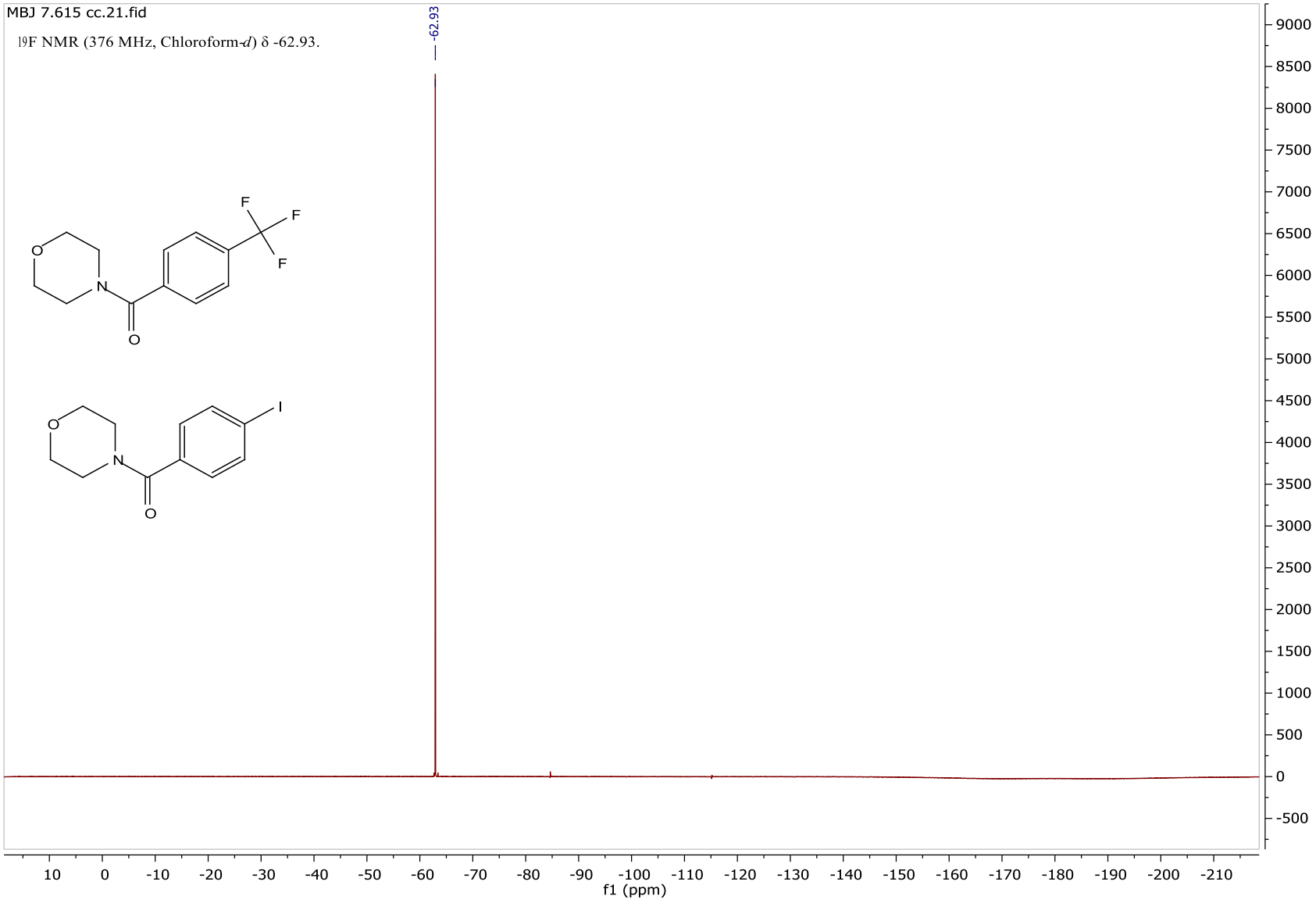

MBJ 7.594c cc.20.fid
7.69
7.67
7.53
7.51
3.78
3.62
3.39
1H NMR (400 MHz, Chloroform-d) δ 7.68 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 3.86 – 3.36 (m, 8H).
F
F
F
O
N
O
1.99
2.00
8.23
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

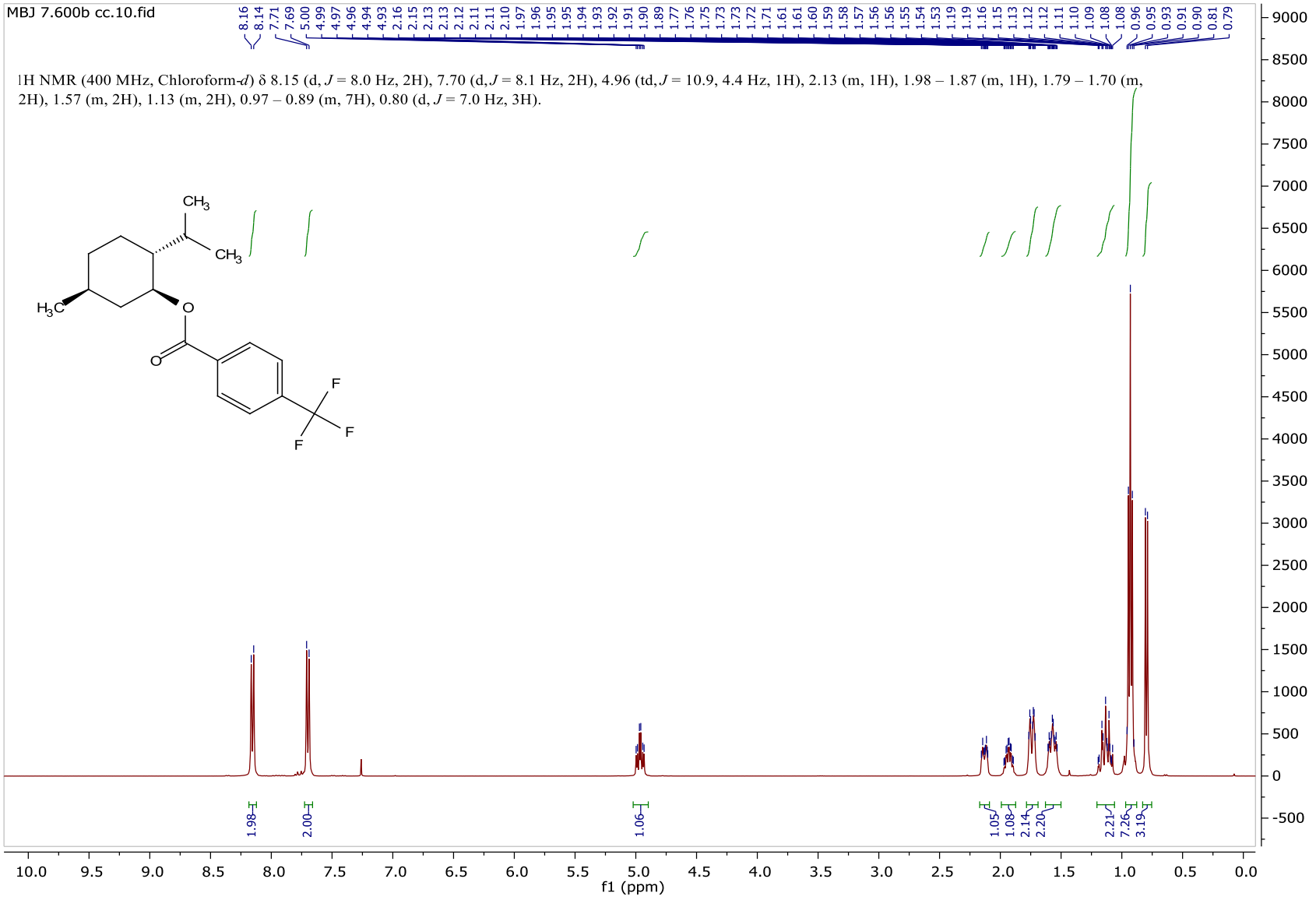

MBJ 7.594c cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -62.95.
-62.95
F
F
F
O
N
O
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

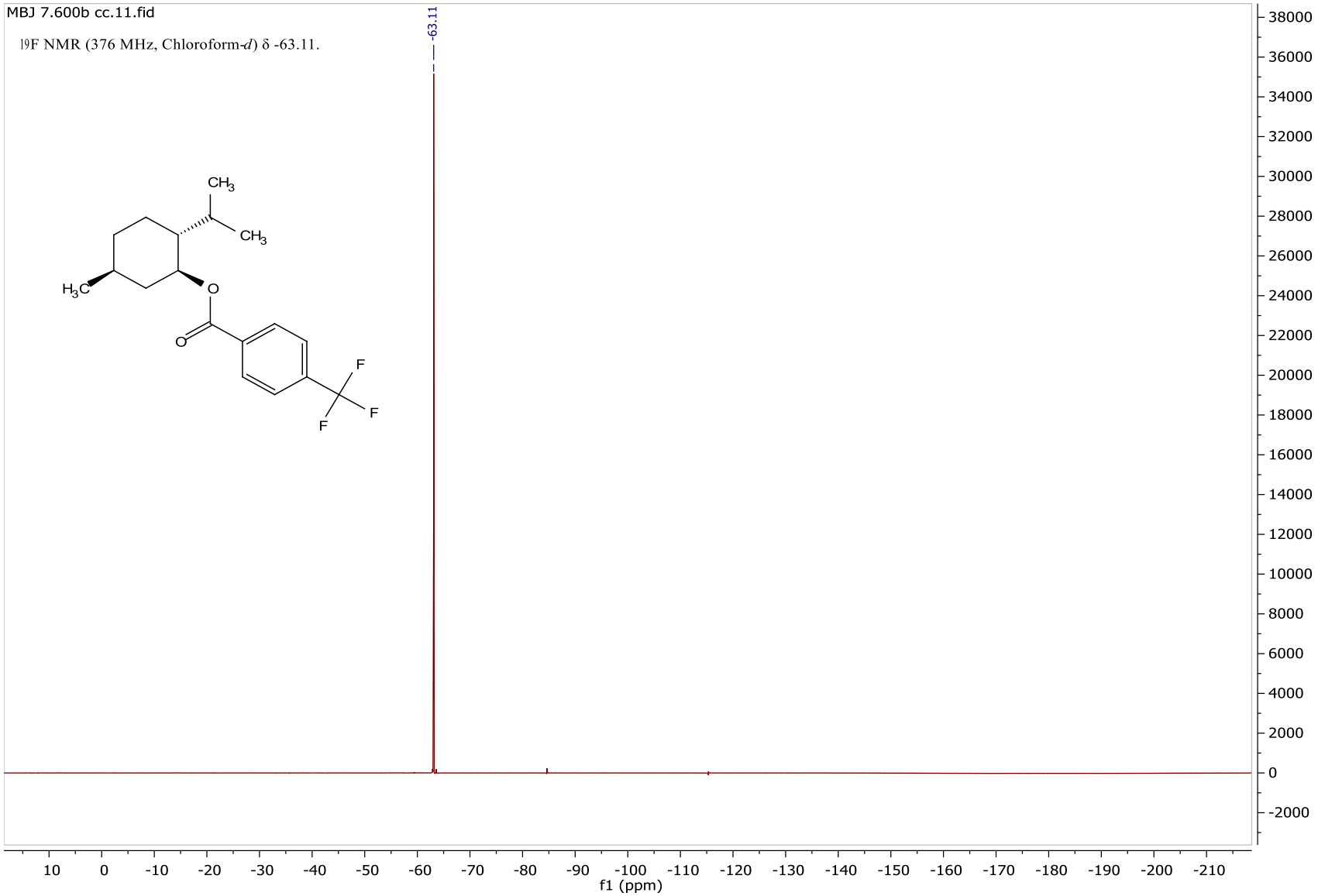


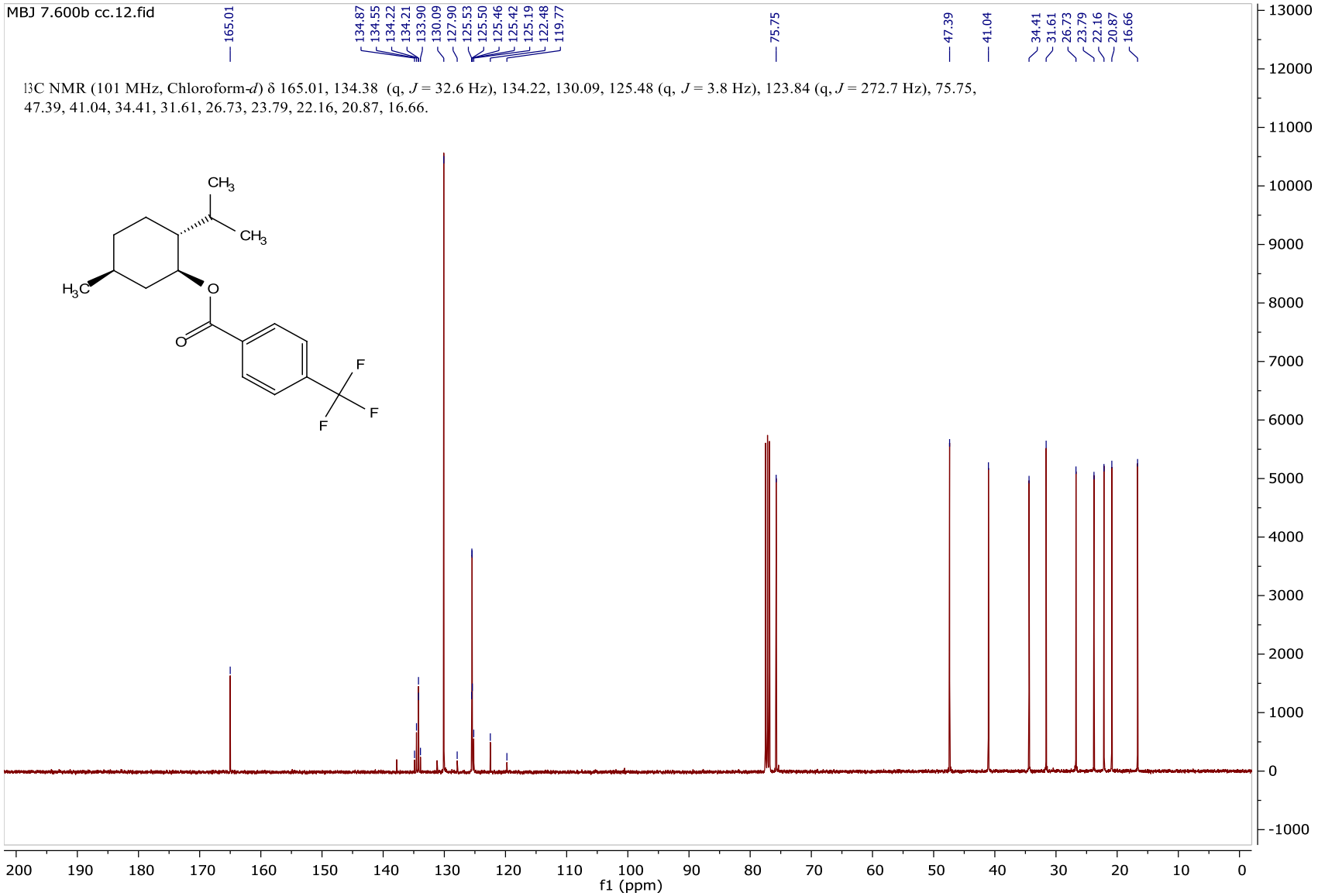
13C NMR (101 MHz, Chloroform-*d*) δ 169.03, 139.02, 131.97 (q, *J* = 32.5 Hz), 127.59, 125.81 (q, *J* = 3.8 Hz), 123.77 (q, *J* = 272.5 Hz), 66.92, 48.20, 42.67.

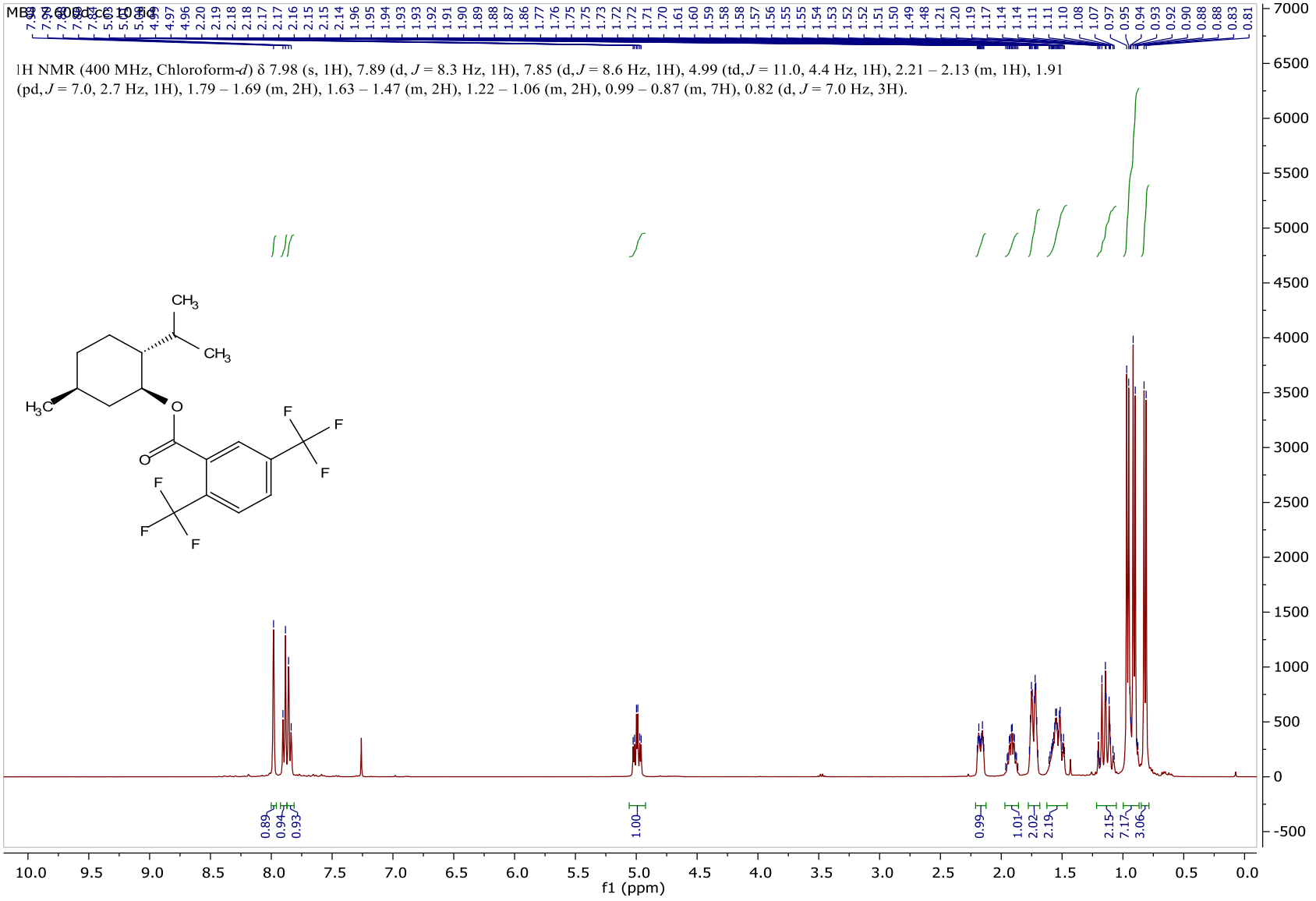

MBJ 7.615 cc.20.fid
1H NMR (400 MHz, Chloroform-d)
7.78
7.76
7.70
7.68
7.54
7.52
7.16
7.14
7.14
3.80
3.63
3.40
F
F
F
O
N
O
O
N
O
I
0.13
1.73
1.73
0.10
8.00
f1 (ppm)

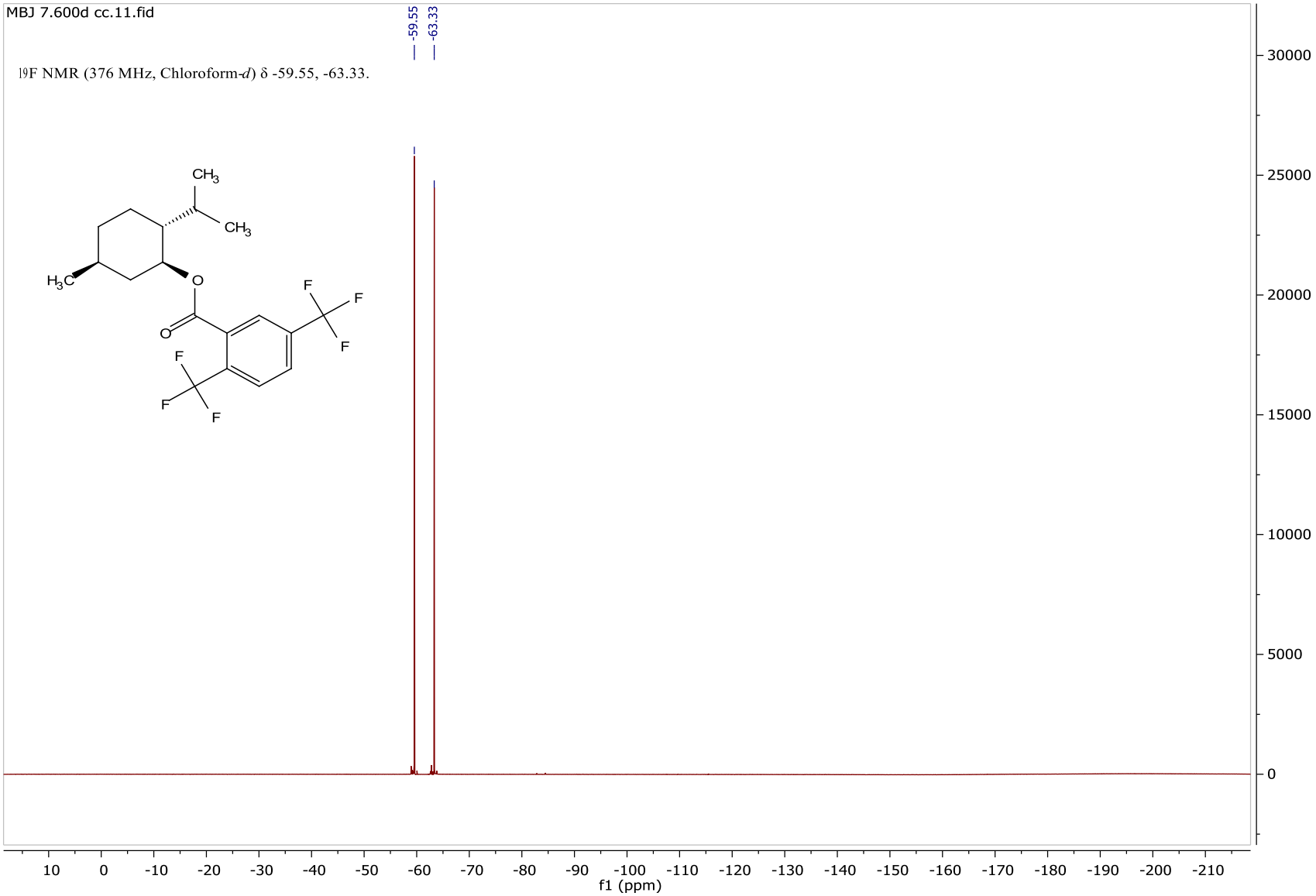

MBJ 7.615 cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -62.93.
-62.93
F
F
F
O
N
O
O
N
O
I
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

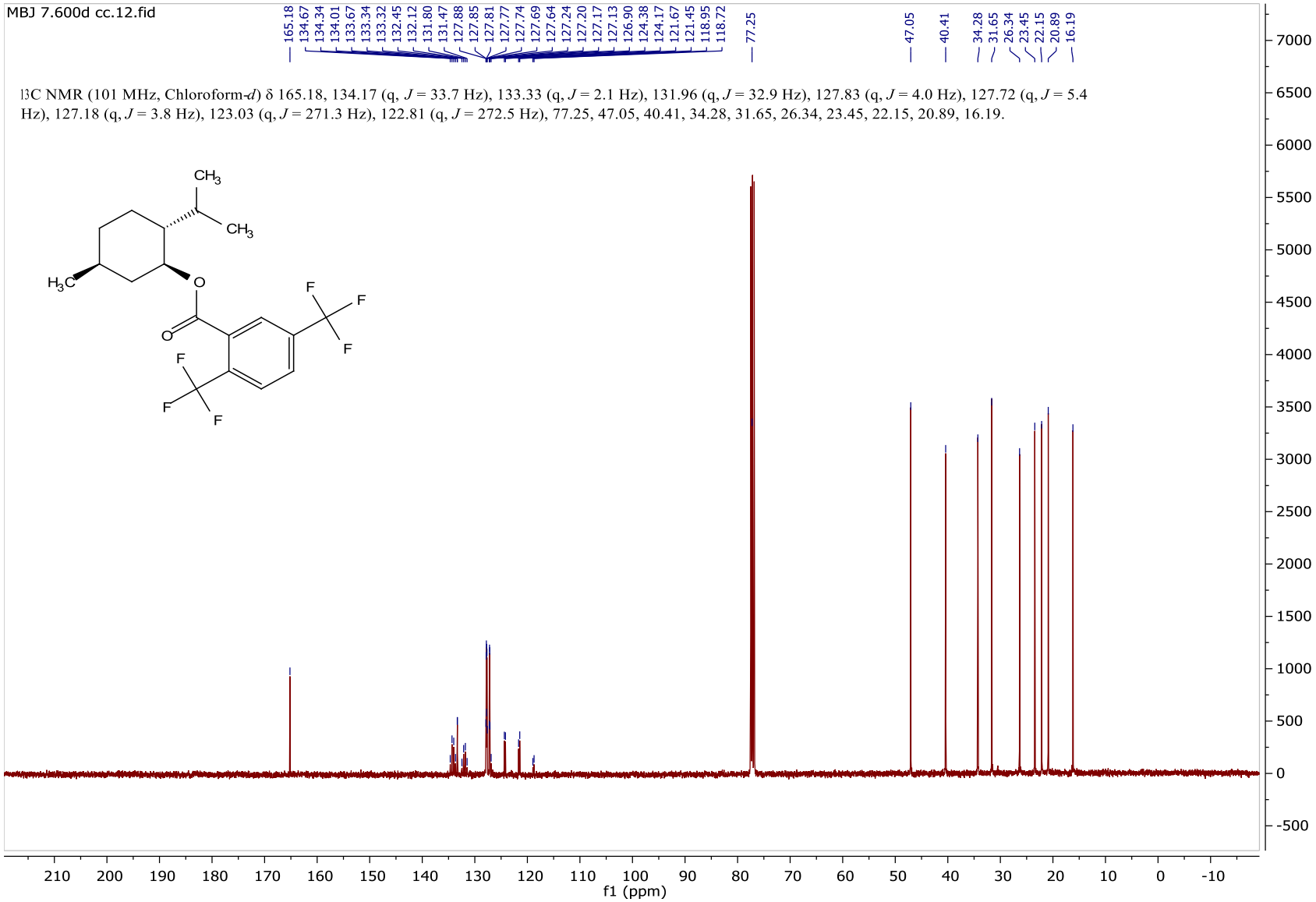

MBJ 7.600b cc.10.fid
8.16 8.14 7.71 7.69 5.00 4.99 4.97 4.96 4.94 4.93 2.16 2.15 2.13 2.13 2.12 2.11 2.11 2.10 1.97 1.96 1.95 1.95 1.94 1.93 1.92 1.91 1.90 1.89 1.77 1.76 1.75 1.73 1.73 1.72 1.71 1.61 1.61 1.60 1.59 1.58 1.57 1.56 1.56 1.55 1.54 1.53 1.19 1.19 1.16 1.15 1.13 1.12 1.12 1.11 1.10 1.09 1.08 0.96 0.95 0.93 0.91 0.90 0.81 0.79
1H NMR (400 MHz, Chloroform-d) δ 8.15 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 4.96 (td, J = 10.9, 4.4 Hz, 1H), 2.13 (m, 1H), 1.98 – 1.87 (m, 1H), 1.79 – 1.70 (m, 2H), 1.57 (m, 2H), 1.13 (m, 2H), 0.97 – 0.89 (m, 7H), 0.80 (d, J = 7.0 Hz, 3H).
CH3
CH3
H3C
O
O
F
F
F
1.98 2.00 1.06 1.05 1.08 2.14 2.20 2.21 7.26 3.19
f1 (ppm)

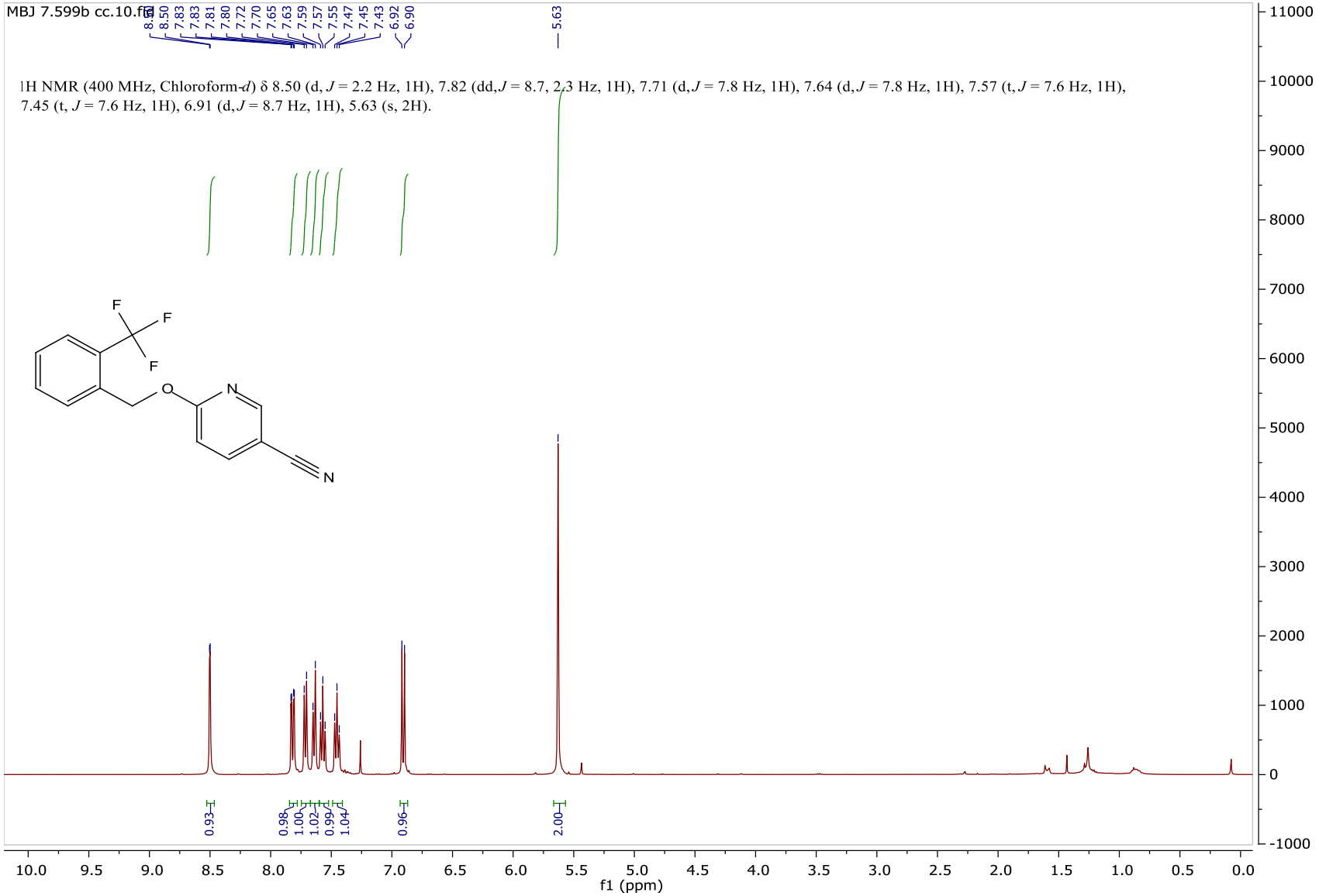

MBJ 7.600b cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -63.11.
-63.11
CH3
CH3
H3C
O
O
F
F
F
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

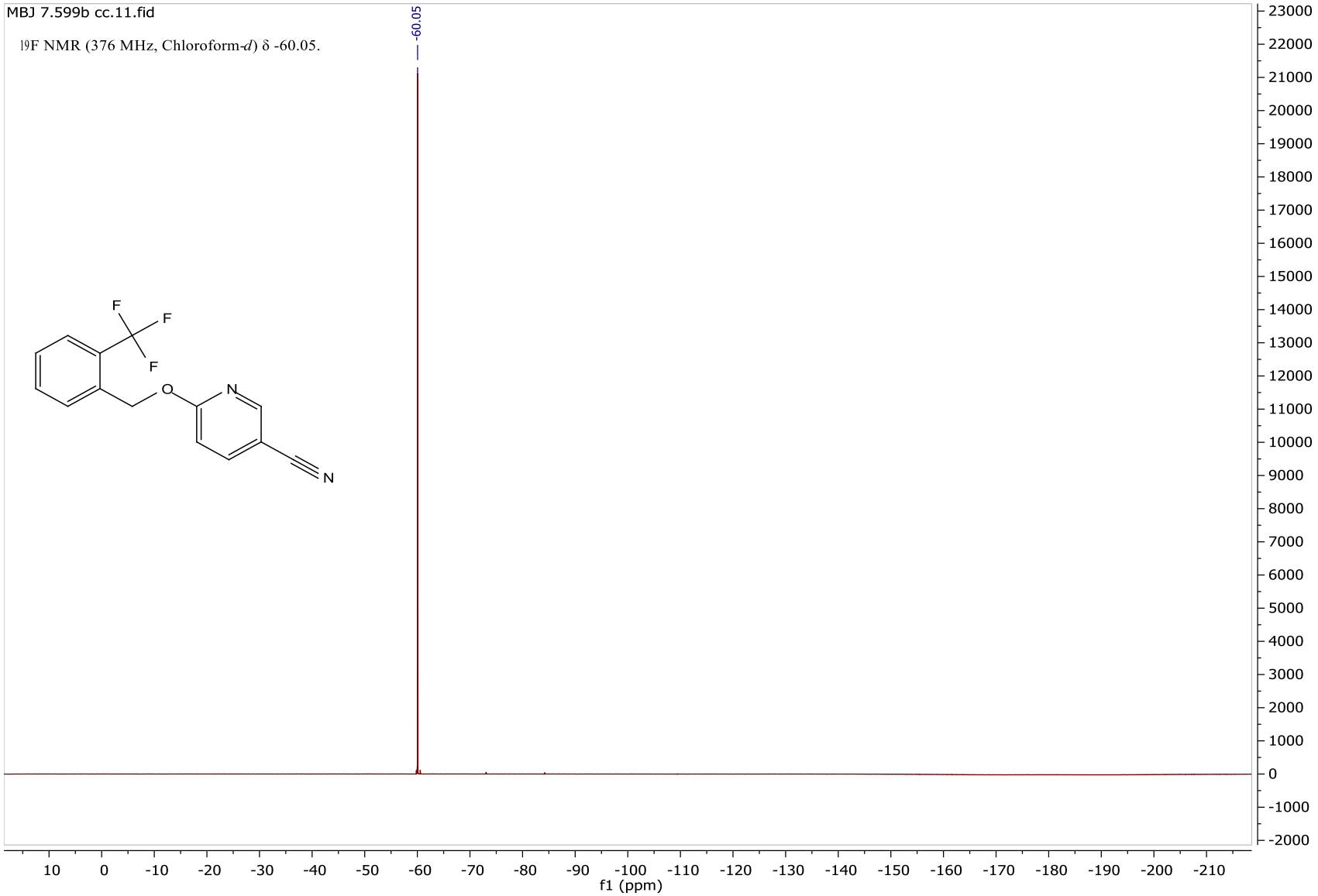

MBJ 7.600b cc.12.fid
165.01
134.87
134.55
134.22
134.21
133.90
130.09
127.90
125.53
125.50
125.46
125.42
125.19
122.48
119.77
75.75
47.39
41.04
34.41
31.61
26.73
23.79
22.16
20.87
16.66
13C NMR (101 MHz, Chloroform-d) δ 165.01, 134.38 (q, J = 32.6 Hz), 134.22, 130.09, 125.48 (q, J = 3.8 Hz), 123.84 (q, J = 272.7 Hz), 75.75, 47.39, 41.04, 34.41, 31.61, 26.73, 23.79, 22.16, 20.87, 16.66.
CH3
CH3
H3C
O
O
F
F
F
f1 (ppm)

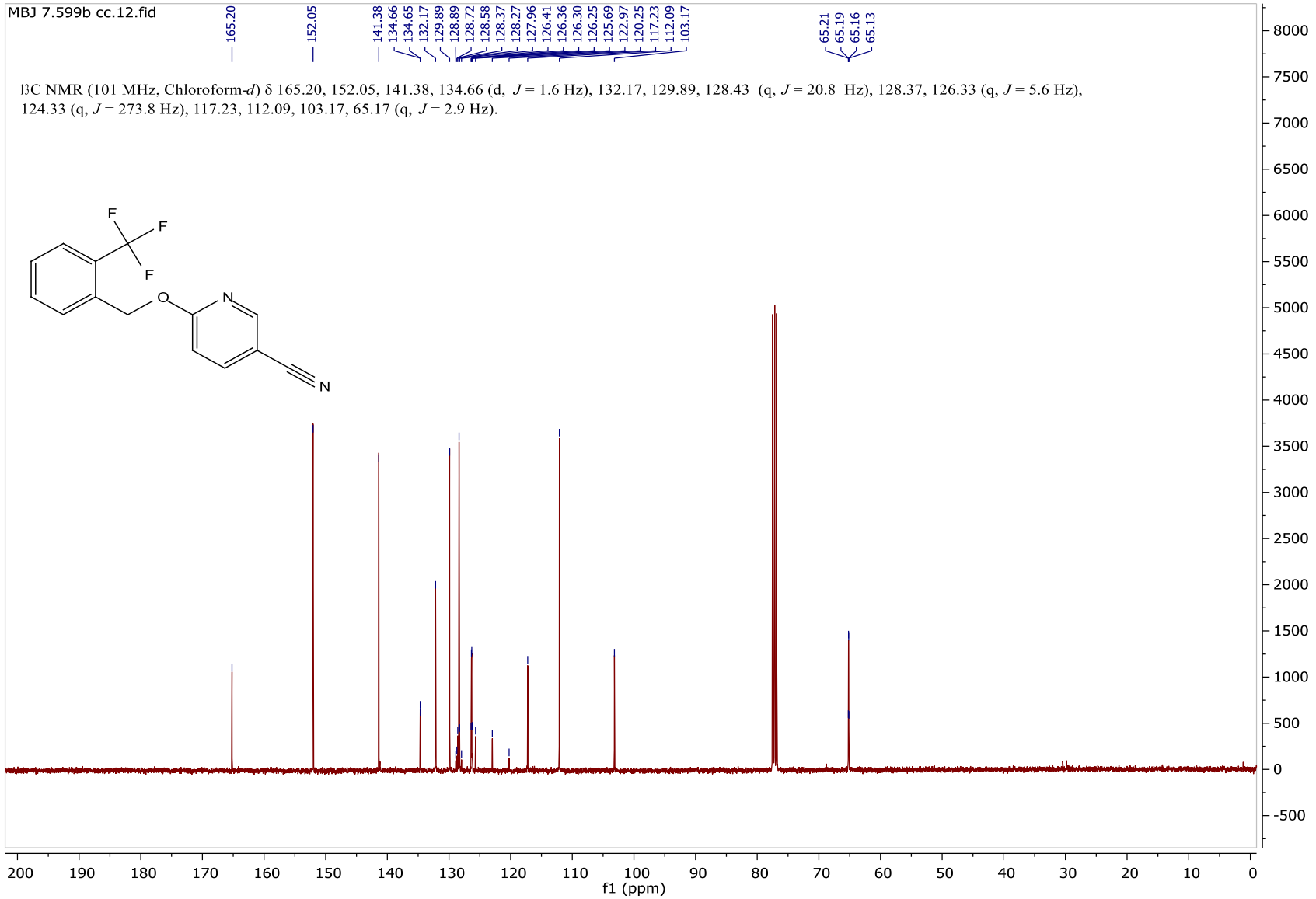

1H NMR (400 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 4.99 (td, J = 11.0, 4.4 Hz, 1H), 2.21 – 2.13 (m, 1H), 1.91 (pd, J = 7.0, 2.7 Hz, 1H), 1.79 – 1.69 (m, 2H), 1.63 – 1.47 (m, 2H), 1.22 – 1.06 (m, 2H), 0.99 – 0.87 (m, 7H), 0.82 (d, J = 7.0 Hz, 3H).
f1 (ppm)


MBJ 7.600d cc.11.fid
-59.55
-63.33
19F NMR (376 MHz, Chloroform-d) δ -59.55, -63.33.
CH3
CH3
H3C
O
O
F
F
F
F
F
F
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

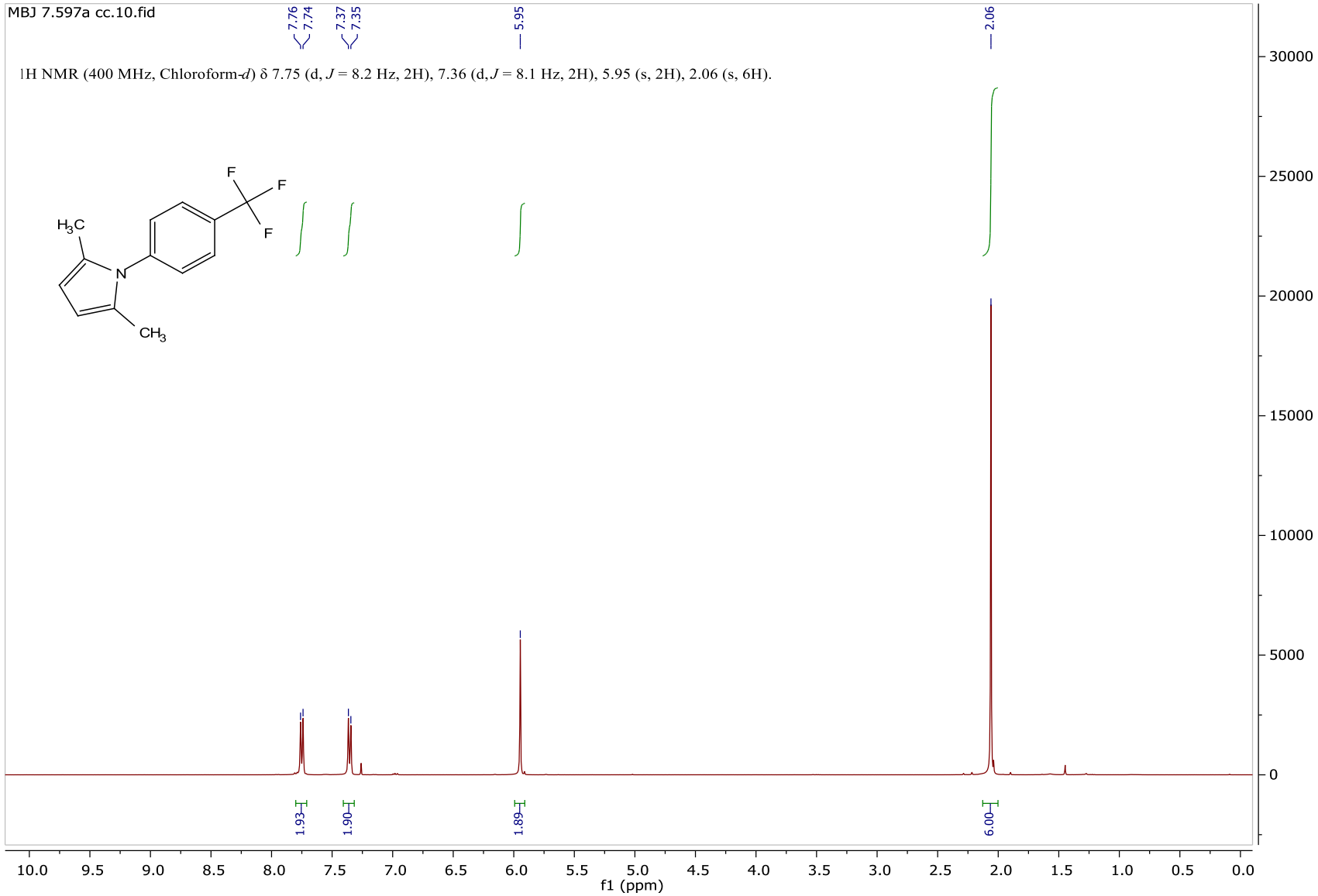

MBJ 7.600d cc.12.fid
165.18
134.67
134.34
134.01
133.67
133.34
133.32
132.45
132.12
131.80
131.47
127.88
127.85
127.81
127.77
127.74
127.69
127.64
127.24
127.20
127.17
127.13
126.90
124.38
124.17
121.67
121.45
118.95
118.72
77.25
47.05
40.41
34.28
31.65
26.34
23.45
22.15
20.89
16.19
13C NMR (101 MHz, Chloroform-d) δ 165.18, 134.17 (q, J = 33.7 Hz), 133.33 (q, J = 2.1 Hz), 131.96 (q, J = 32.9 Hz), 127.83 (q, J = 4.0 Hz), 127.72 (q, J = 5.4 Hz), 127.18 (q, J = 3.8 Hz), 123.03 (q, J = 271.3 Hz), 122.81 (q, J = 272.5 Hz), 77.25, 47.05, 40.41, 34.28, 31.65, 26.34, 23.45, 22.15, 20.89, 16.19.
CH3
CH3
H3C
O
O
F
F
F
F
F
F
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

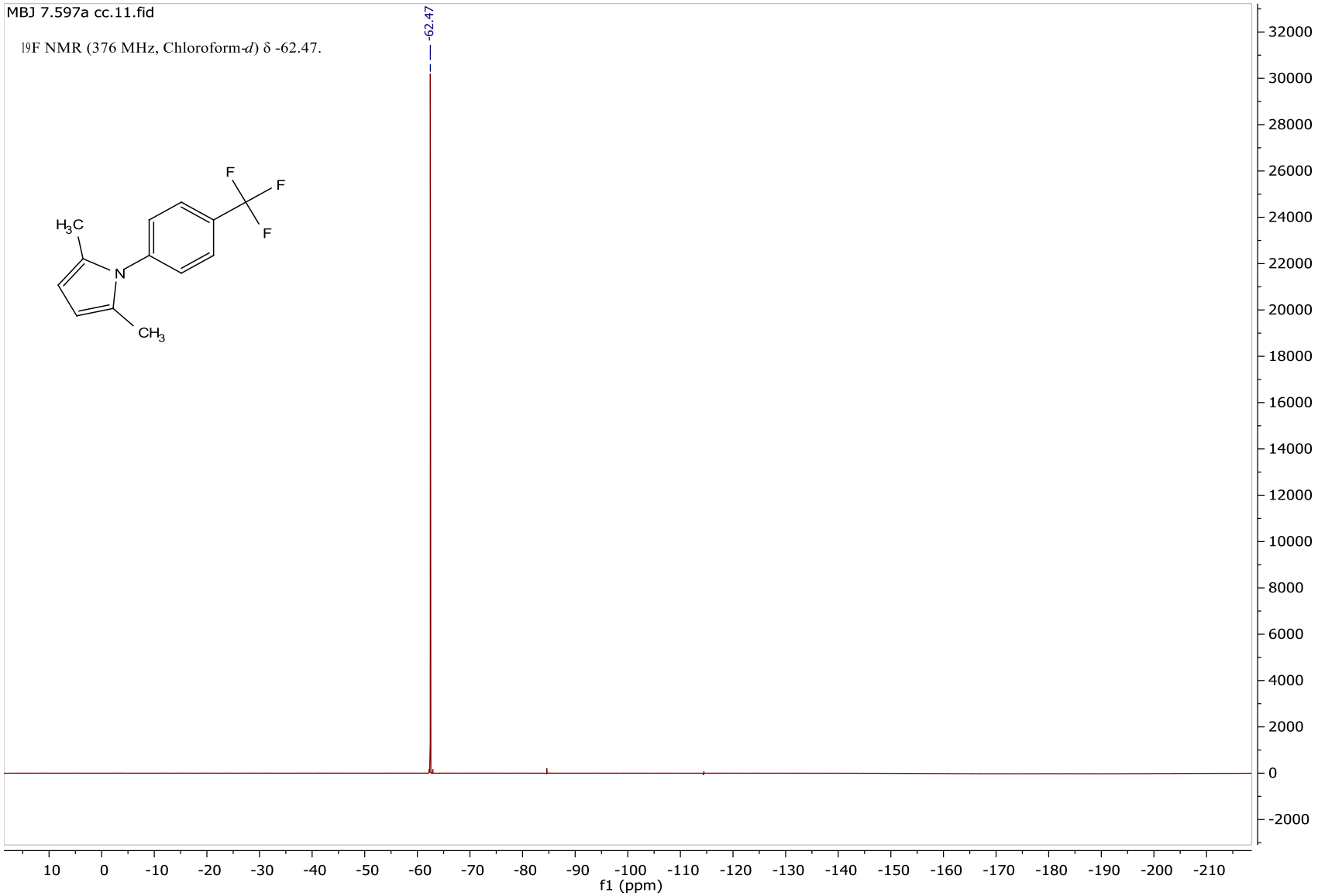

MBJ 7.599b cc.10.fid
8.50
7.83
7.83
7.81
7.80
7.72
7.70
7.65
7.63
7.59
7.57
7.55
7.47
7.45
7.43
6.92
6.90
5.63
1H NMR (400 MHz, Chloroform-d) δ 8.50 (d, J = 2.2 Hz, 1H), 7.82 (dd, J = 8.7, 2.3 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 5.63 (s, 2H).
F
F
F
O
N
N
0.93
0.98
1.00
1.02
0.99
1.04
0.96
2.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

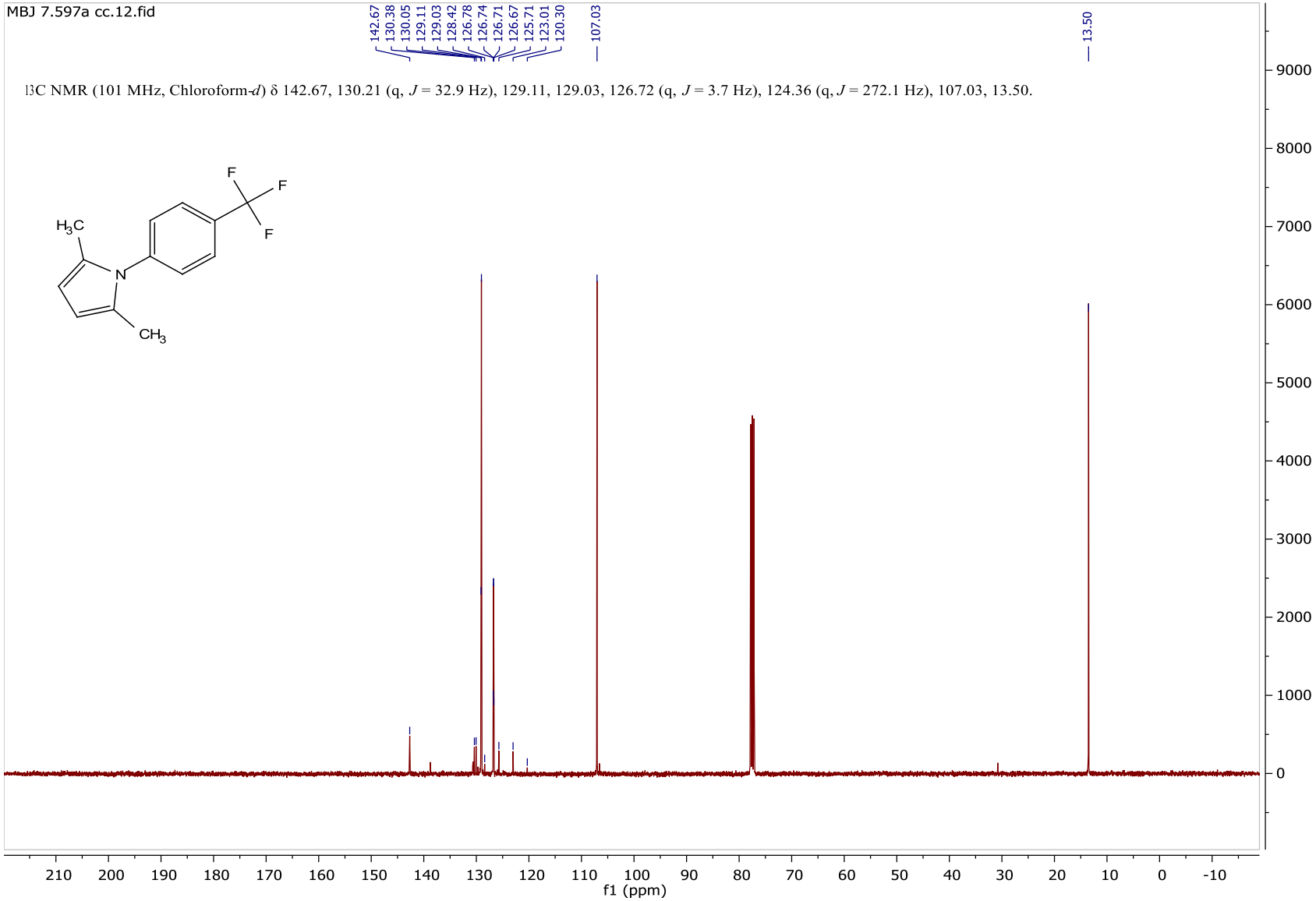

MBJ 7.599b cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -60.05.
-60.05
F
F
F
O
N
N
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



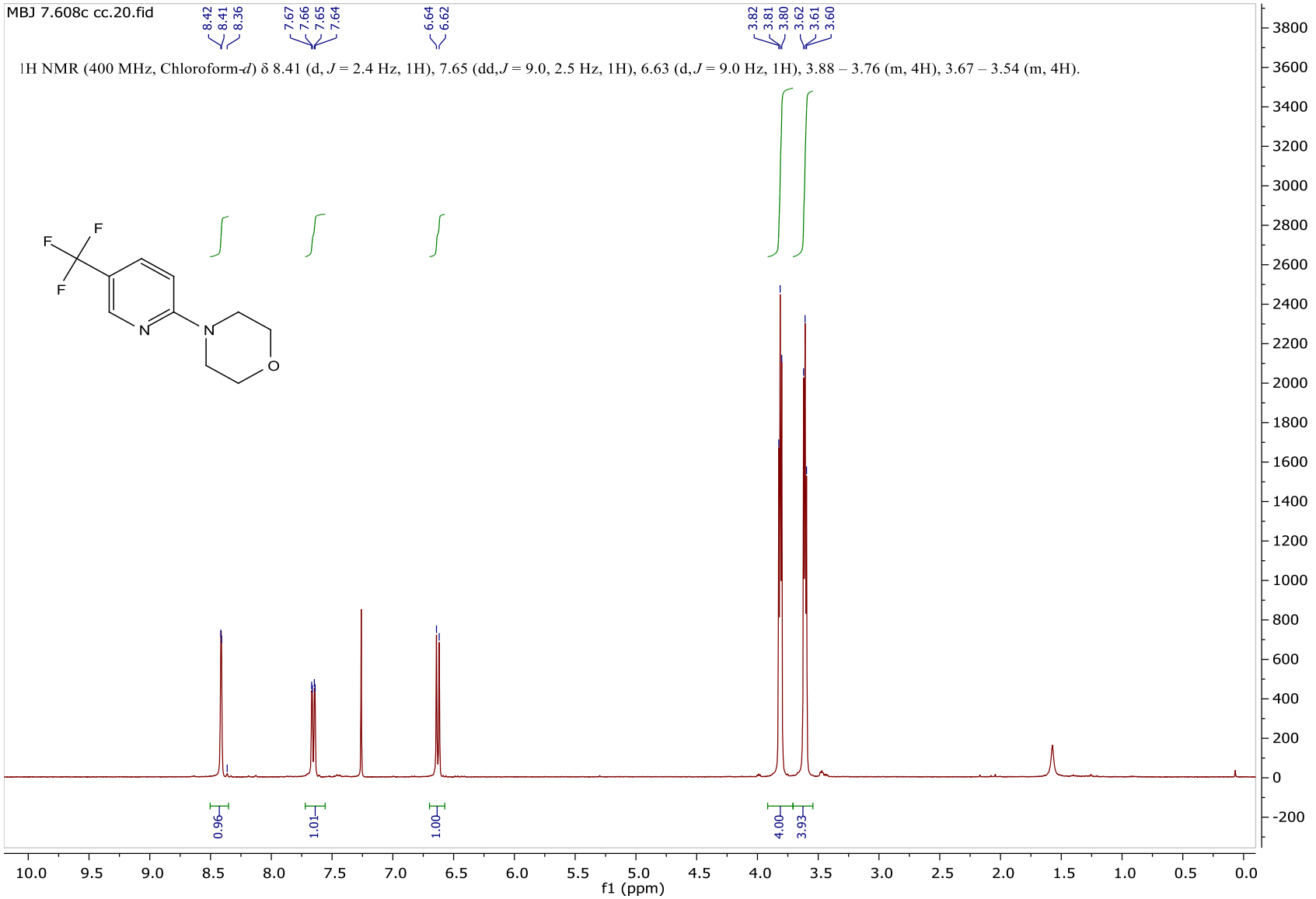
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.20, 152.05, 141.38, 134.66 (d, J = 1.6 Hz), 132.17, 129.89, 128.43 (q, J = 20.8 Hz), 128.37, 126.33 (q, J = 5.6 Hz), 124.33 (q, J = 273.8 Hz), 117.23, 112.09, 103.17, 65.17 (q, J = 2.9 Hz).

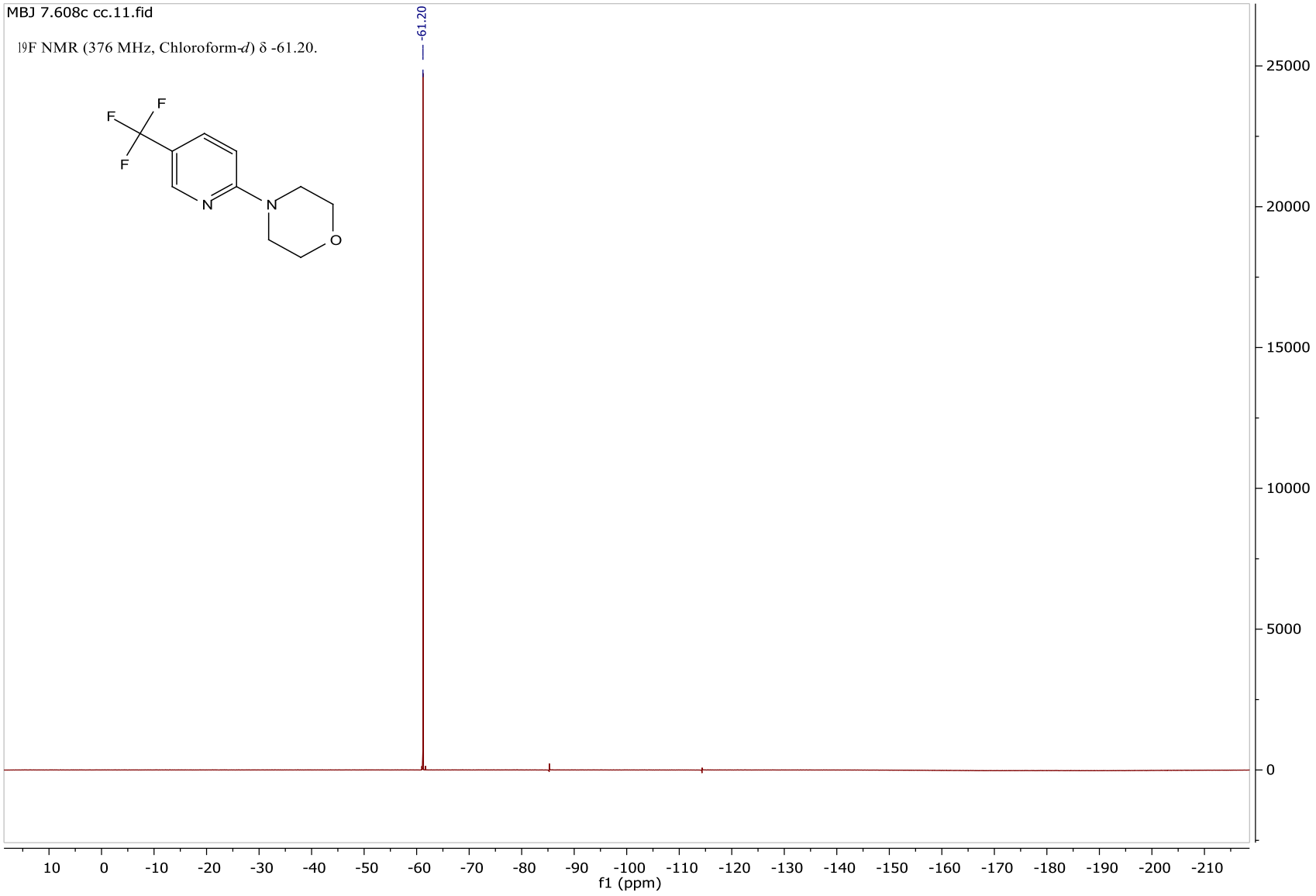

MBJ 7.597a cc.10.fid
7.76
7.74
7.37
7.35
5.95
2.06
1H NMR (400 MHz, Chloroform-d) δ 7.75 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.95 (s, 2H), 2.06 (s, 6H).
F
F
F
H3C
N
CH3
30000
25000
20000
15000
10000
5000
0
1.93
1.90
1.89
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

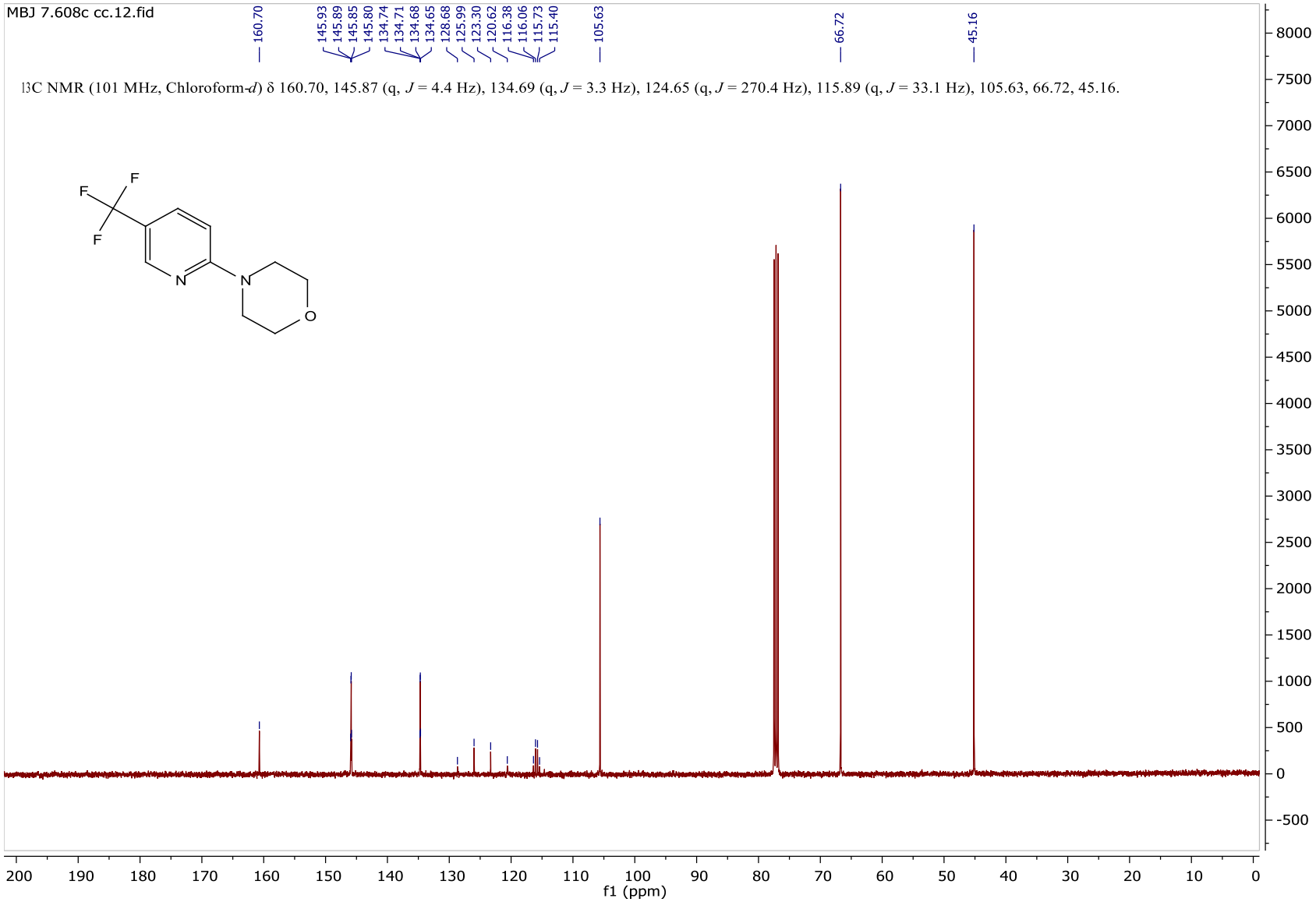

MBJ 7.597a cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -62.47.
-62.47
F
F
F
H3C
N
CH3
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



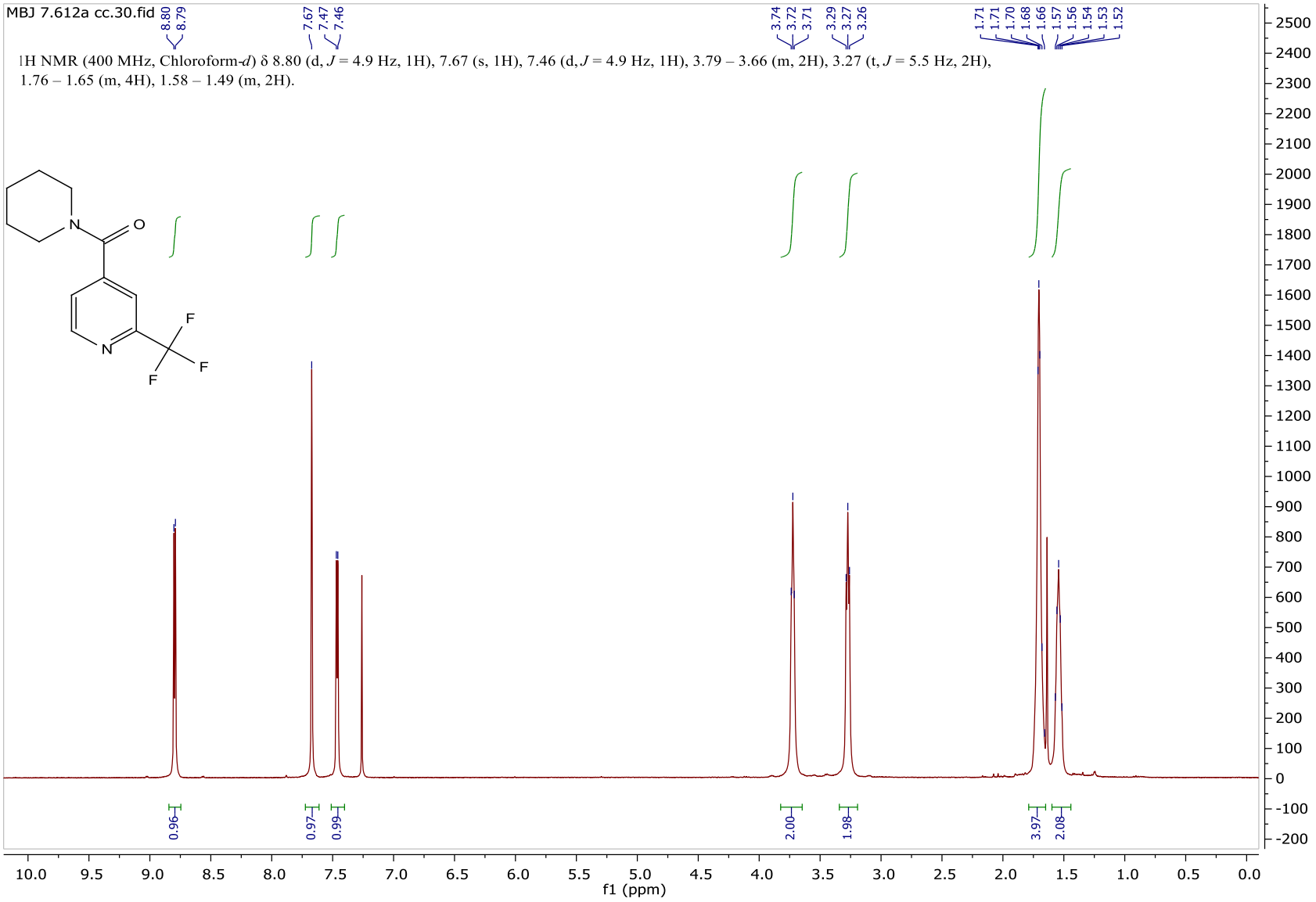
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.67, 130.21 (q, *J* = 32.9 Hz), 129.11, 129.03, 126.72 (q, *J* = 3.7 Hz), 124.36 (q, *J* = 272.1 Hz), 107.03, 13.50.

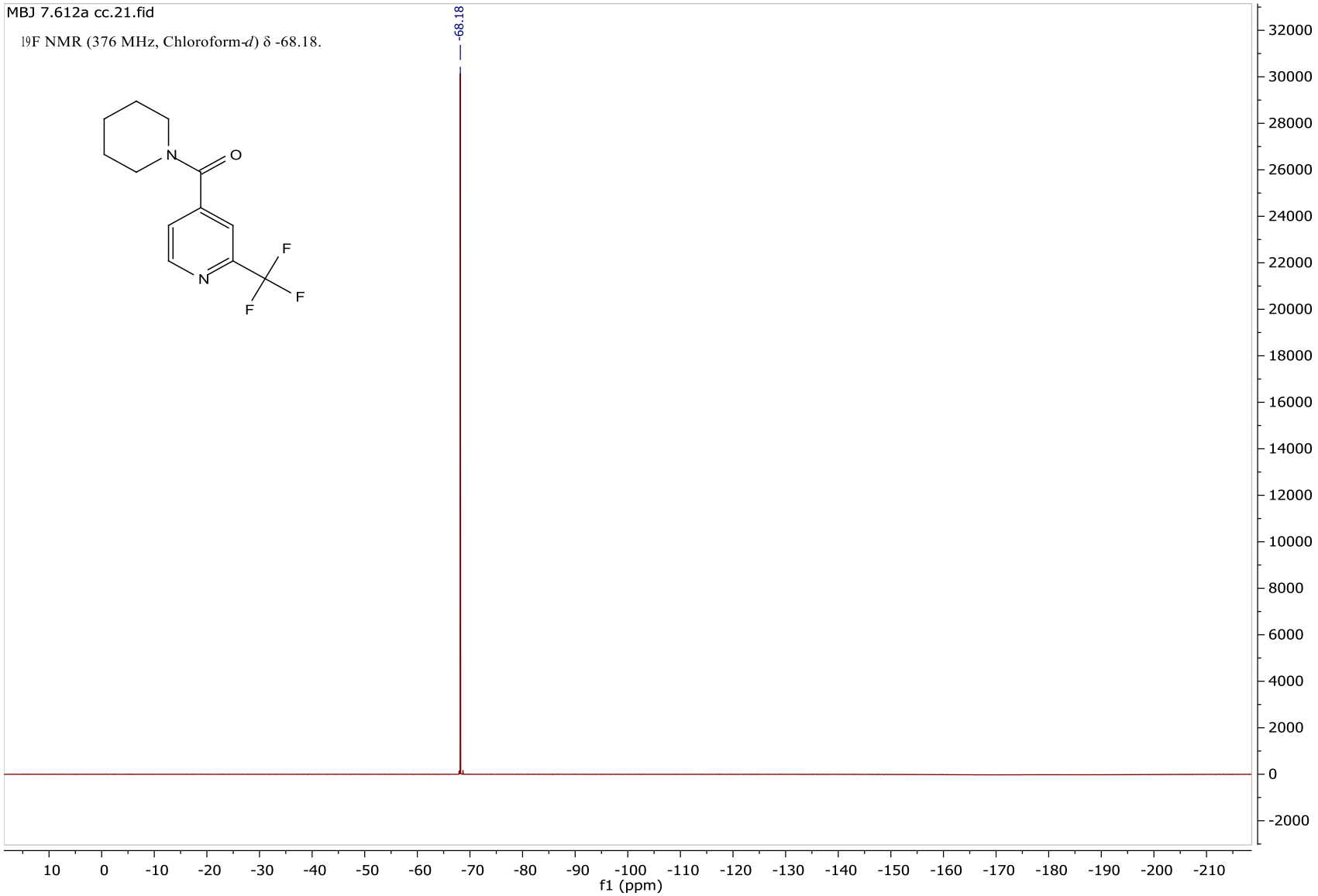

MBJ 7.608c cc.20.fid
8.42
8.41
8.36
7.67
7.66
7.65
7.64
6.64
6.62
3.82
3.81
3.80
3.62
3.61
3.60
1H NMR (400 MHz, Chloroform-d) δ 8.41 (d, J = 2.4 Hz, 1H), 7.65 (dd,J = 9.0, 2.5 Hz, 1H), 6.63 (d,J = 9.0 Hz, 1H), 3.88 – 3.76 (m, 4H), 3.67 – 3.54 (m, 4H).
F
F
F
N
N
O
0.96
1.01
1.00
4.00
3.93
f1 (ppm)

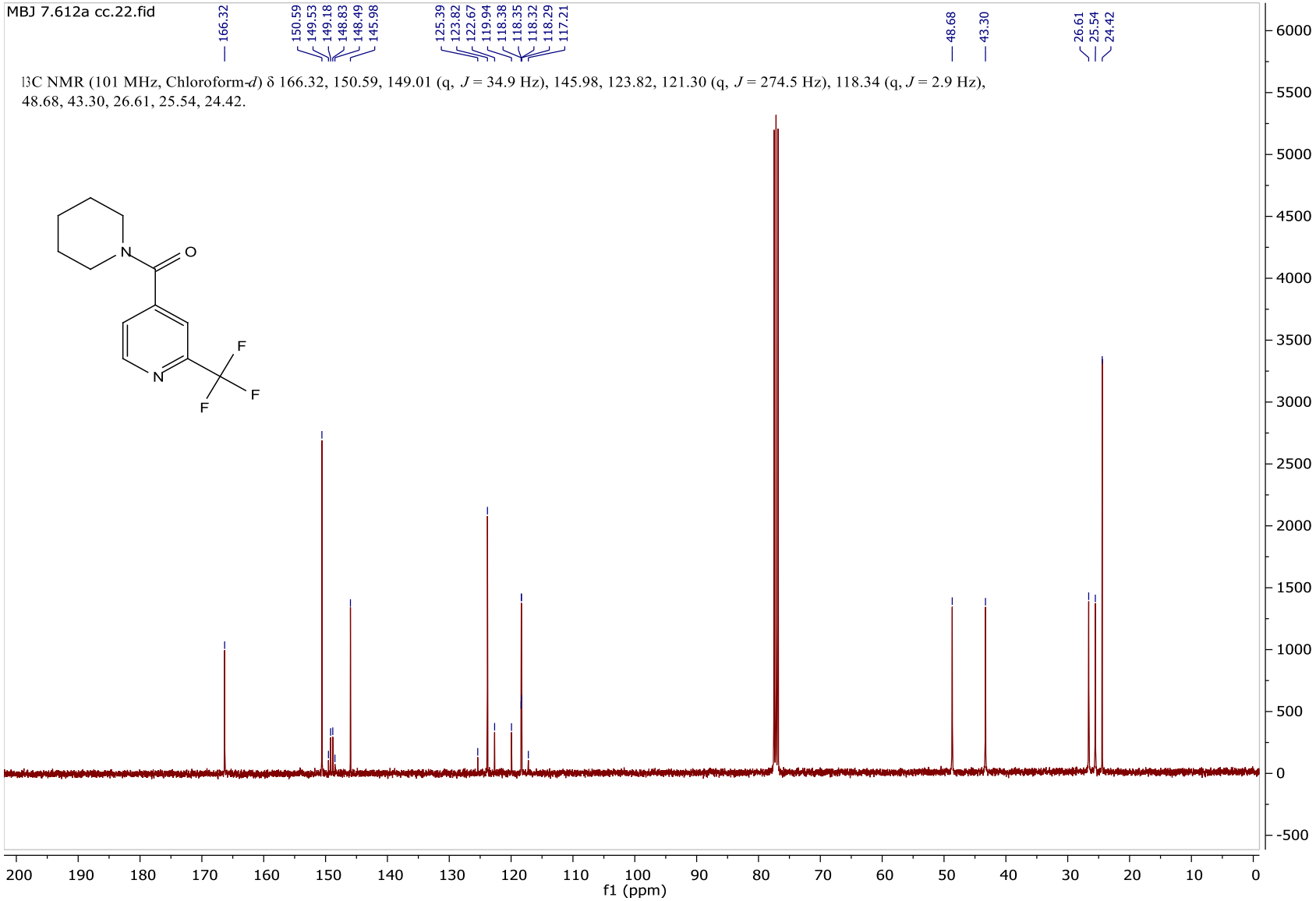

MBJ 7.608c cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -61.20.
-61.20
F
F
F
N
N
O
25000
20000
15000
10000
5000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

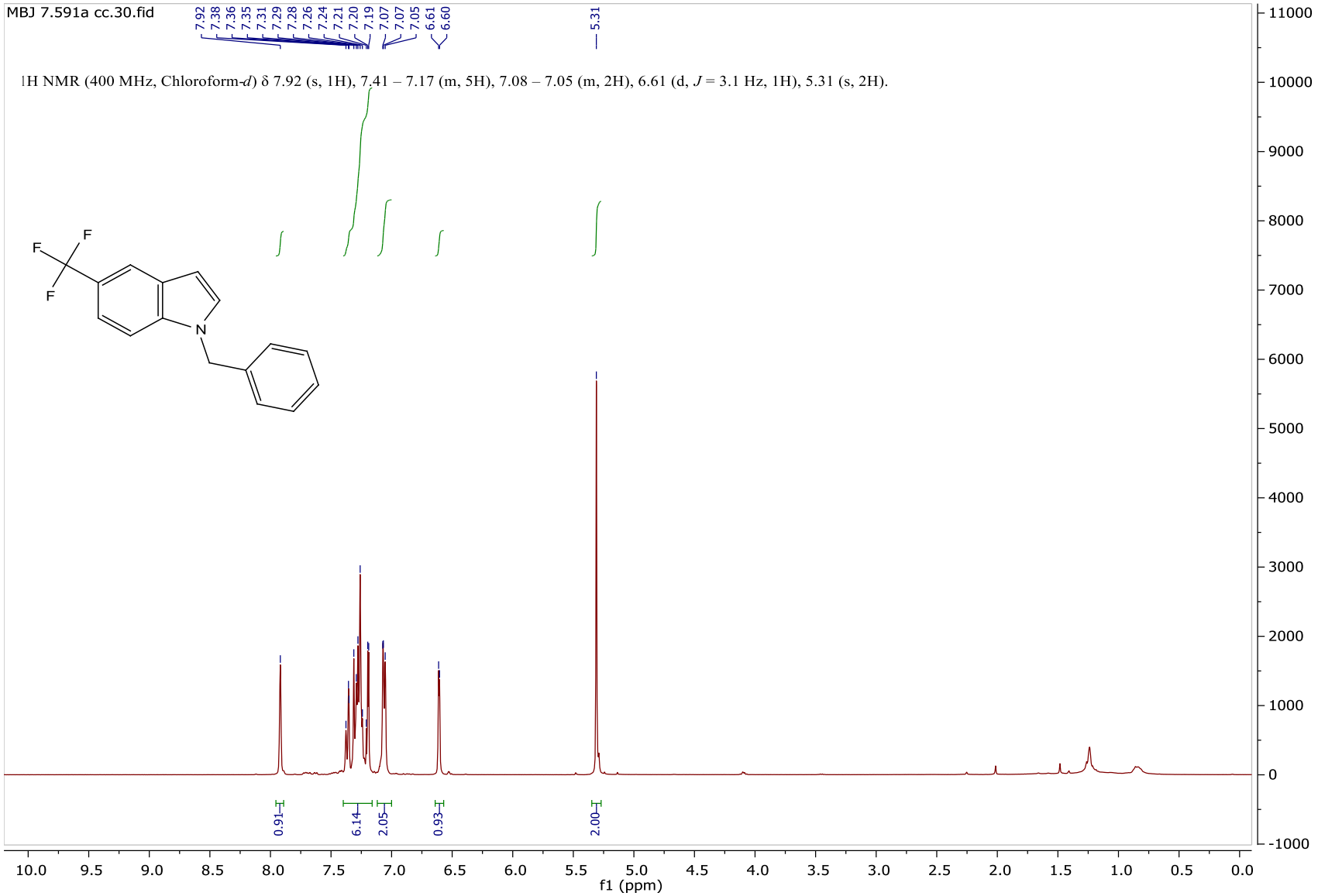


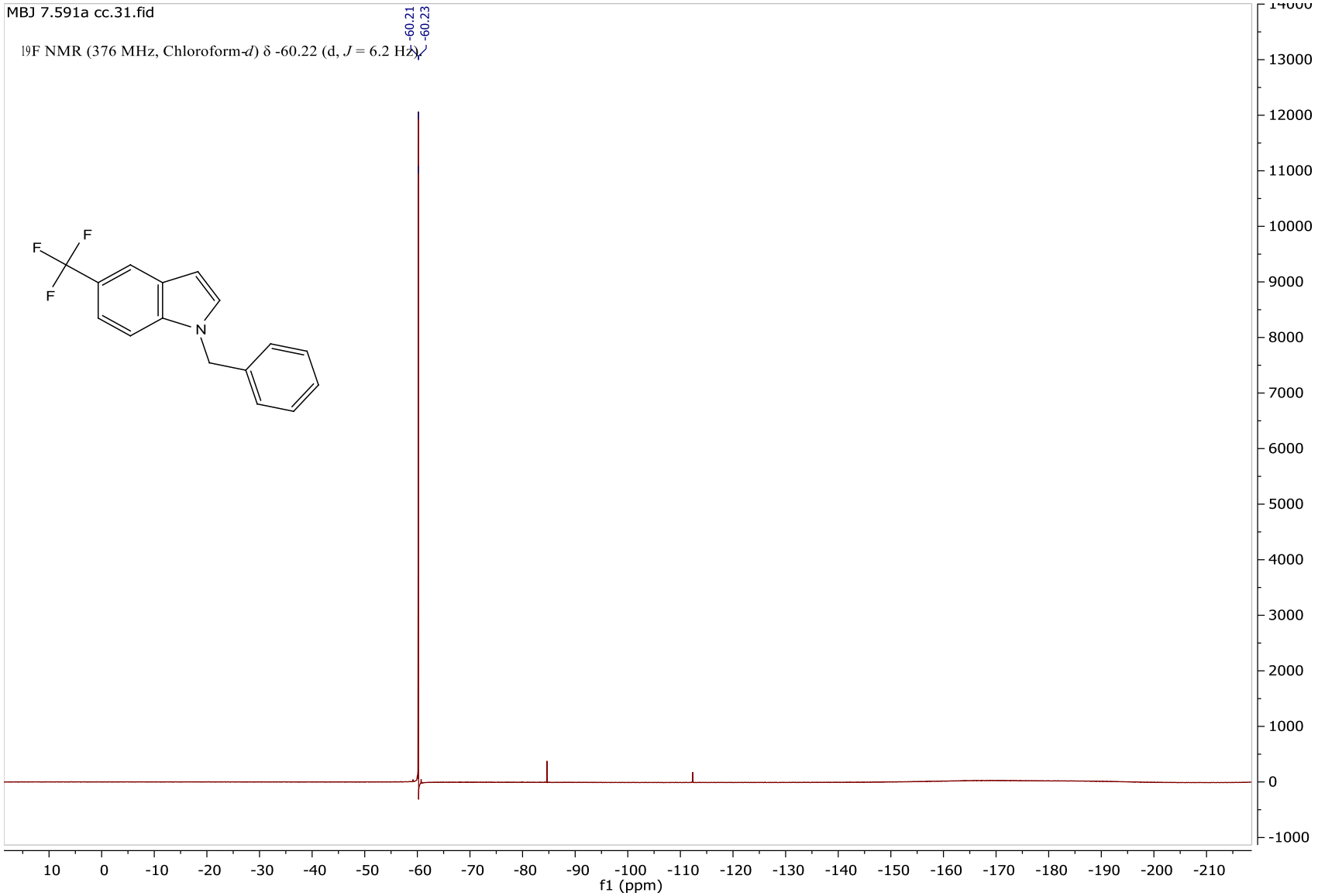
13C NMR (101 MHz, Chloroform-*d*) δ 160.70, 145.87 (q, *J* = 4.4 Hz), 134.69 (q, *J* = 3.3 Hz), 124.65 (q, *J* = 270.4 Hz), 115.89 (q, *J* = 33.1 Hz), 105.63, 66.72, 45.16.

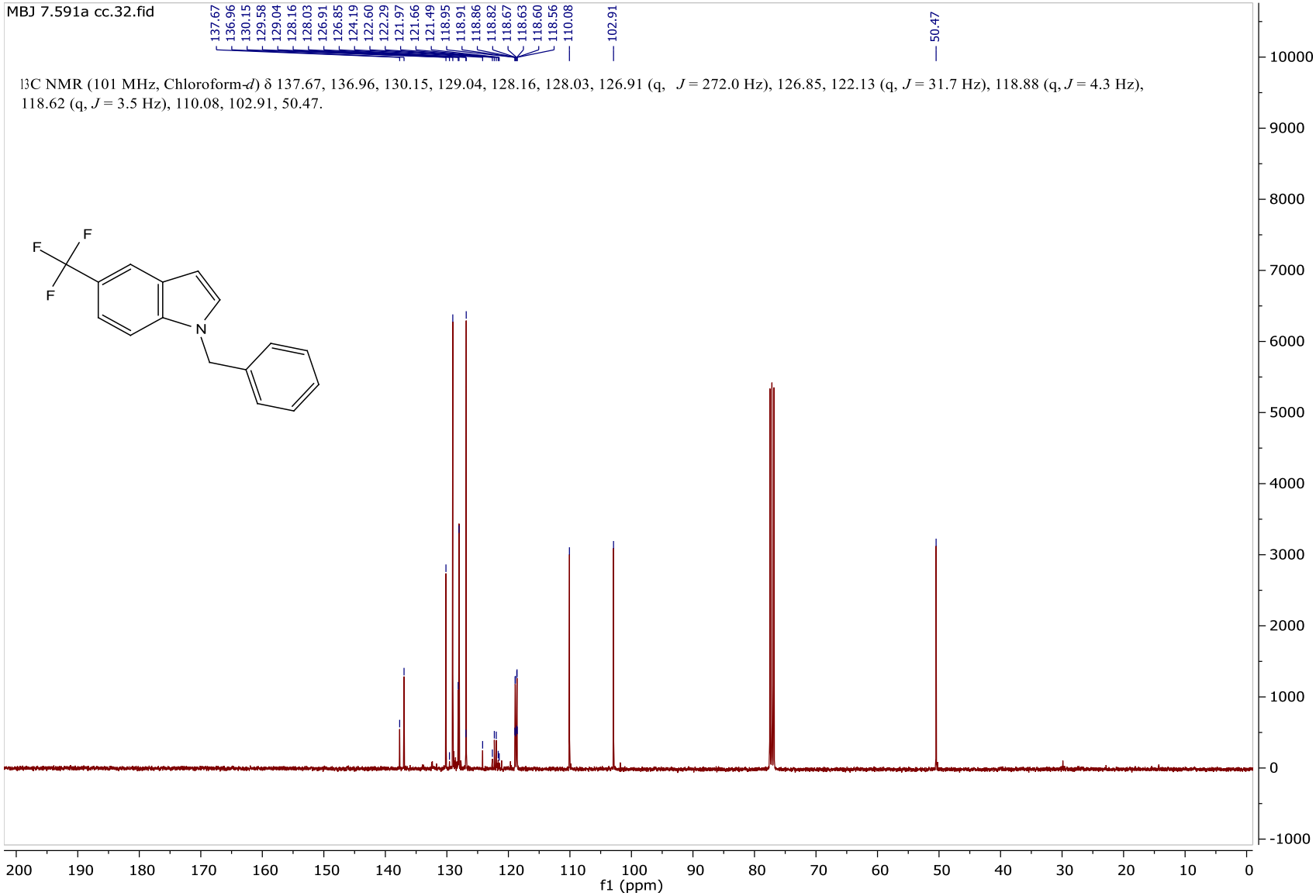

MBJ 7.612a cc.30.fid
8.80
8.79
7.67
7.47
7.46
3.74
3.72
3.71
3.29
3.27
3.26
1.71
1.71
1.70
1.68
1.66
1.57
1.56
1.54
1.53
1.52
1H NMR (400 MHz, Chloroform-d) δ 8.80 (d, J = 4.9 Hz, 1H), 7.67 (s, 1H), 7.46 (d, J = 4.9 Hz, 1H), 3.79 – 3.66 (m, 2H), 3.27 (t, J = 5.5 Hz, 2H), 1.76 – 1.65 (m, 4H), 1.58 – 1.49 (m, 2H).
N
O
N
F
F
F
0.96
0.97
0.99
2.00
1.98
3.97
2.08
f1 (ppm)

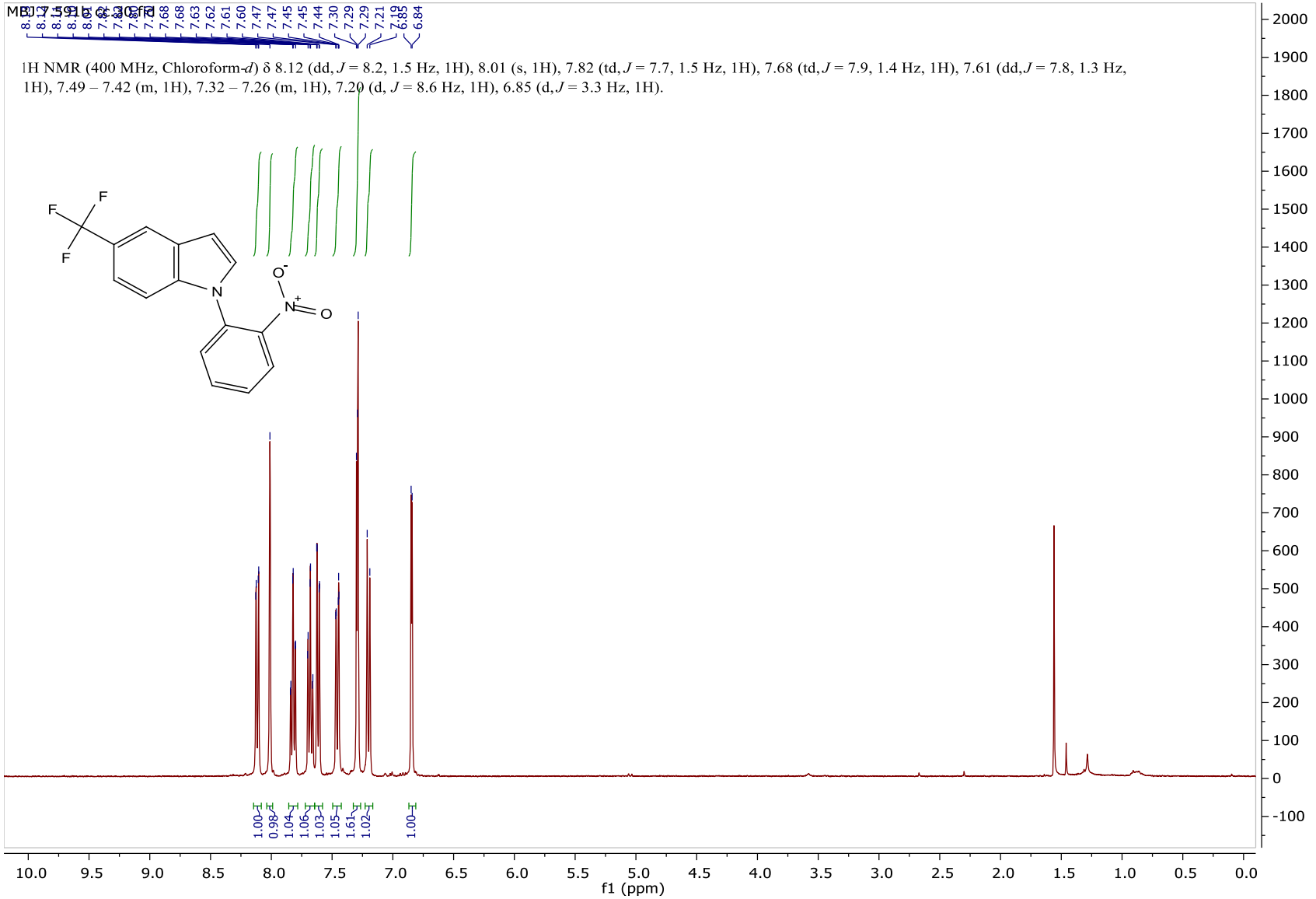

MBJ 7.612a cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -68.18.
-68.18
N
O
N
F
F
F
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


MBJ 7.612a cc.22.fid
166.32
150.59
149.53
149.18
148.83
148.49
145.98
125.39
123.82
122.67
119.94
118.38
118.35
118.32
118.29
117.21
48.68
43.30
26.61
25.54
24.42
13C NMR (101 MHz, Chloroform-d) δ 166.32, 150.59, 149.01 (q, J = 34.9 Hz), 145.98, 123.82, 121.30 (q, J = 274.5 Hz), 118.34 (q, J = 2.9 Hz), 48.68, 43.30, 26.61, 25.54, 24.42.
N
O
F
F
F
N
f1 (ppm)

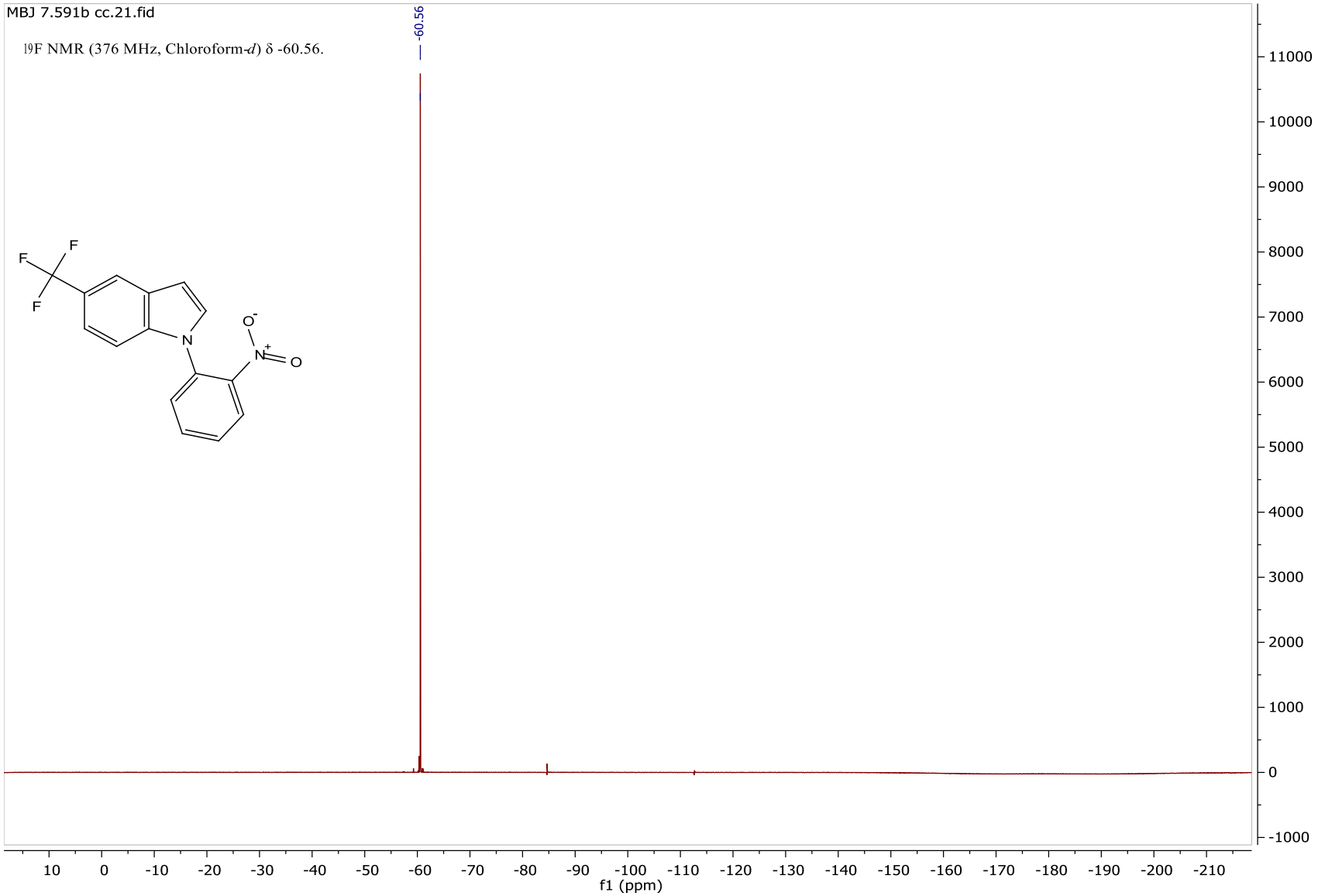

MBJ 7.591a cc.30.fid
7.92
7.38
7.36
7.35
7.31
7.29
7.28
7.26
7.24
7.21
7.20
7.19
7.07
7.07
7.05
6.61
6.60
5.31
1H NMR (400 MHz, Chloroform-d) δ 7.92 (s, 1H), 7.41 – 7.17 (m, 5H), 7.08 – 7.05 (m, 2H), 6.61 (d, J = 3.1 Hz, 1H), 5.31 (s, 2H).
F
F
F
N
0.91
6.14
2.05
0.93
2.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

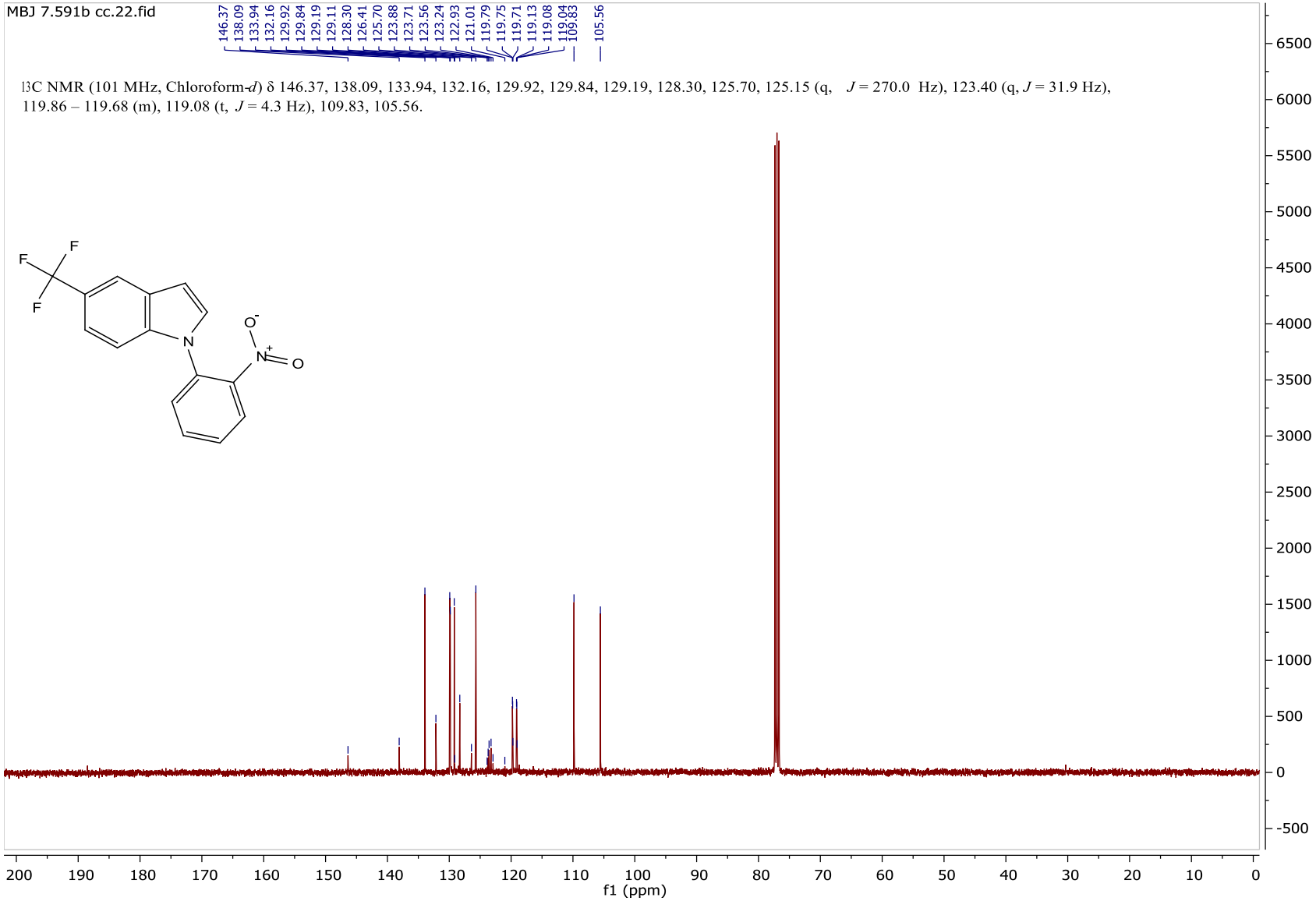

MBJ 7.591a cc.31.fid
19F NMR (376 MHz, Chloroform-d) δ -60.22 (d, J = 6.2 Hz)
-60.21
-60.23
F
F
F
N
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

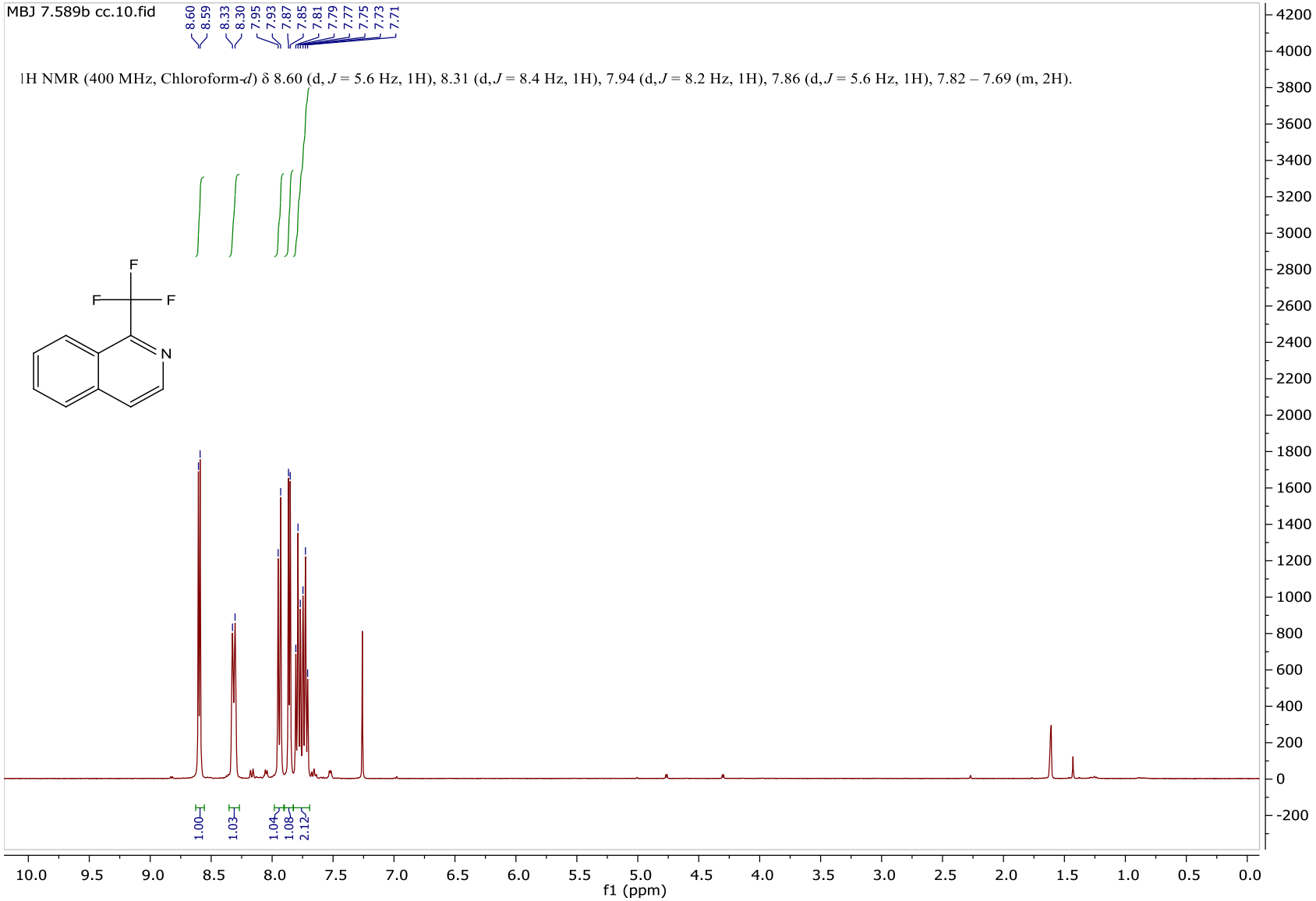

MBJ 7.591a cc.32.fid
137.67
136.96
130.15
129.58
129.04
128.16
128.03
126.91
126.85
124.19
122.60
122.29
121.97
121.66
121.49
118.95
118.91
118.86
118.82
118.67
118.63
118.60
118.56
110.08
102.91
50.47
13C NMR (101 MHz, Chloroform-d) δ 137.67, 136.96, 130.15, 129.04, 128.16, 128.03, 126.91 (q, J = 272.0 Hz), 126.85, 122.13 (q, J = 31.7 Hz), 118.88 (q, J = 4.3 Hz), 118.62 (q, J = 3.5 Hz), 110.08, 102.91, 50.47.
F
F
F
N
f1 (ppm)

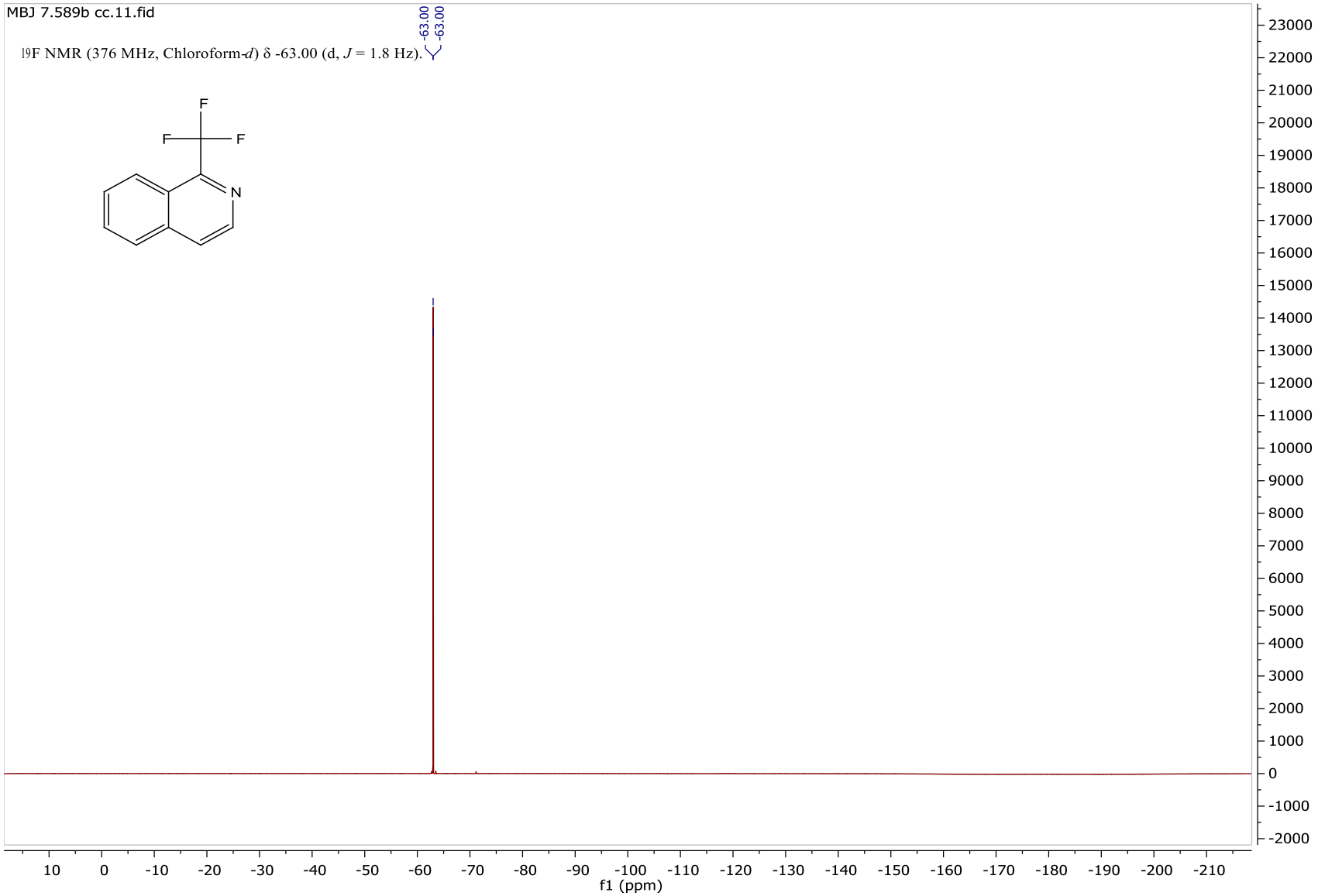


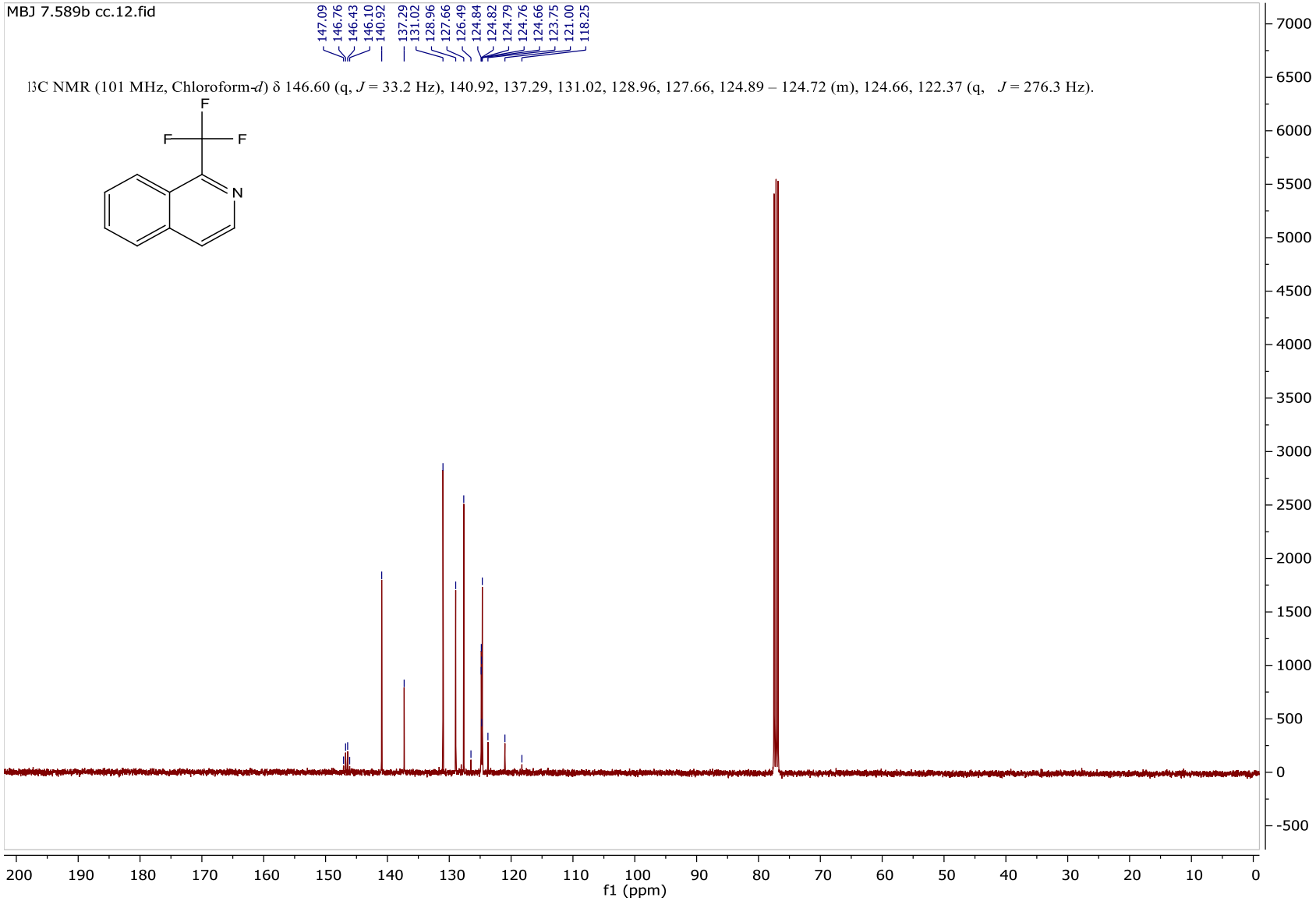
1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.01 (s, 1H), 7.82 (td, *J* = 7.7, 1.5 Hz, 1H), 7.68 (td, *J* = 7.9, 1.4 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.32 – 7.26 (m, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 3.3 Hz, 1H).


MBJ 7.591b cc.21.fid
19F NMR (376 MHz, Chloroform-d) δ -60.56.
-60.56
F
F
F
N
O
N
O
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

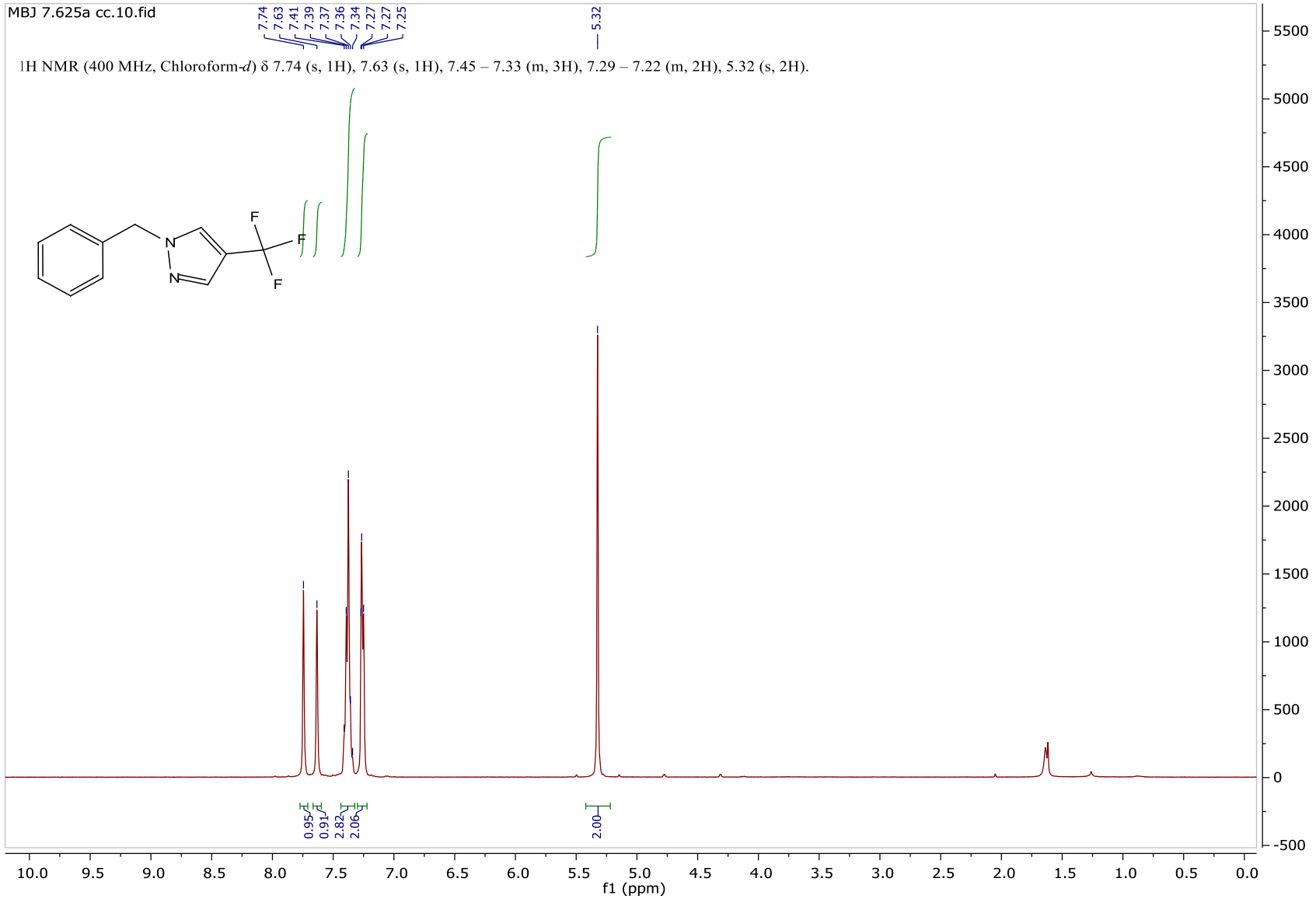

MBJ 7.591b cc.22.fid
146.37
138.09
133.94
132.16
129.92
129.84
129.19
129.11
128.30
126.41
125.70
123.88
123.71
123.56
123.24
122.93
121.01
119.79
119.75
119.71
119.13
119.08
119.04
109.83
105.56
13C NMR (101 MHz, Chloroform-d) δ 146.37, 138.09, 133.94, 132.16, 129.92, 129.84, 129.19, 128.30, 125.70, 125.15 (q, J = 270.0 Hz), 123.40 (q, J = 31.9 Hz), 119.86 – 119.68 (m), 119.08 (t, J = 4.3 Hz), 109.83, 105.56.
F
F
F
N
O-
N+
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

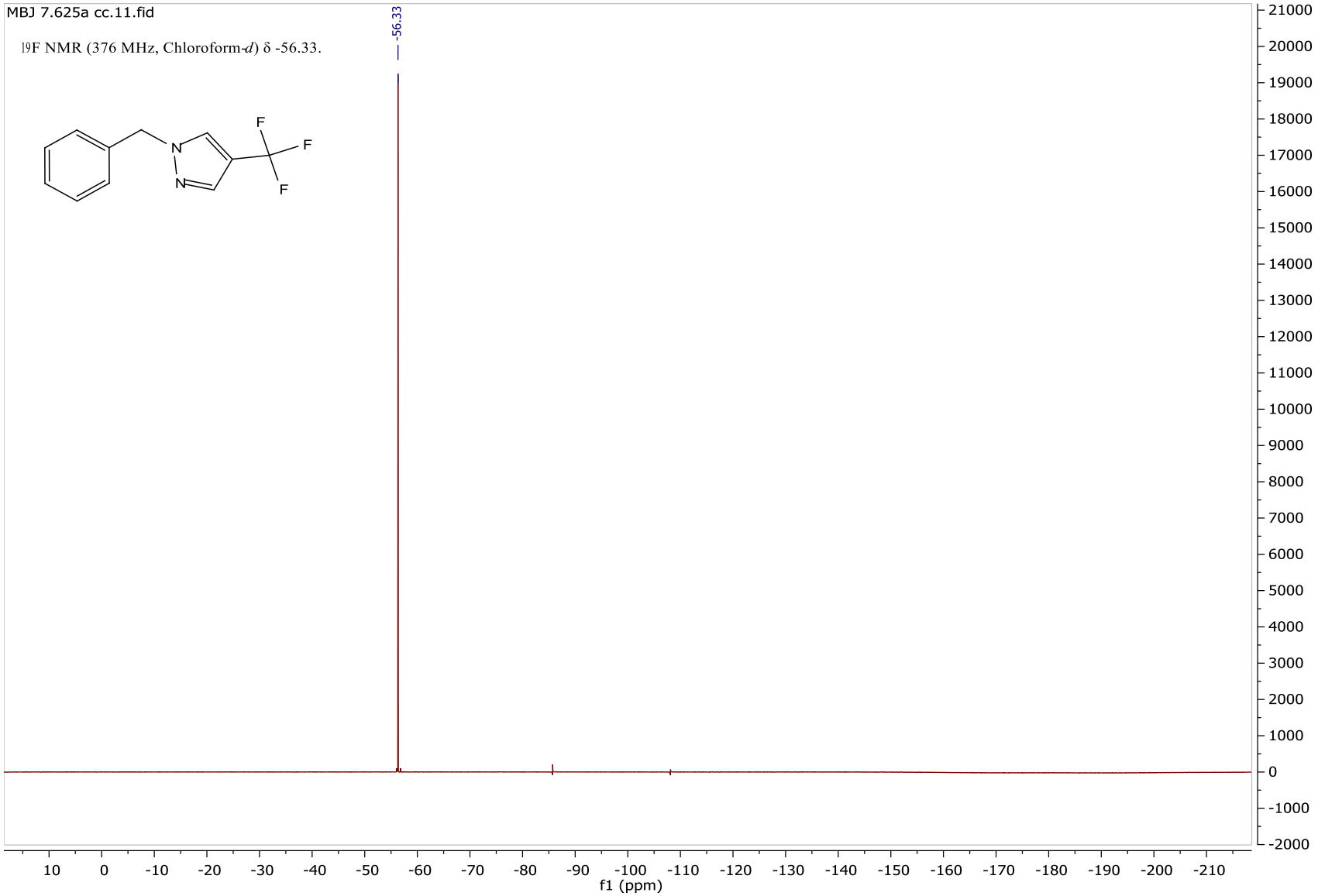

MBJ 7.589b cc.10.fid
8.60
8.59
8.33
8.30
7.95
7.93
7.87
7.85
7.81
7.79
7.77
7.75
7.73
7.71
1H NMR (400 MHz, Chloroform-d) δ 8.60 (d, J = 5.6 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 5.6 Hz, 1H), 7.82 – 7.69 (m, 2H).
F
F
F
N
1.00
1.03
1.04
1.08
2.12
f1 (ppm)

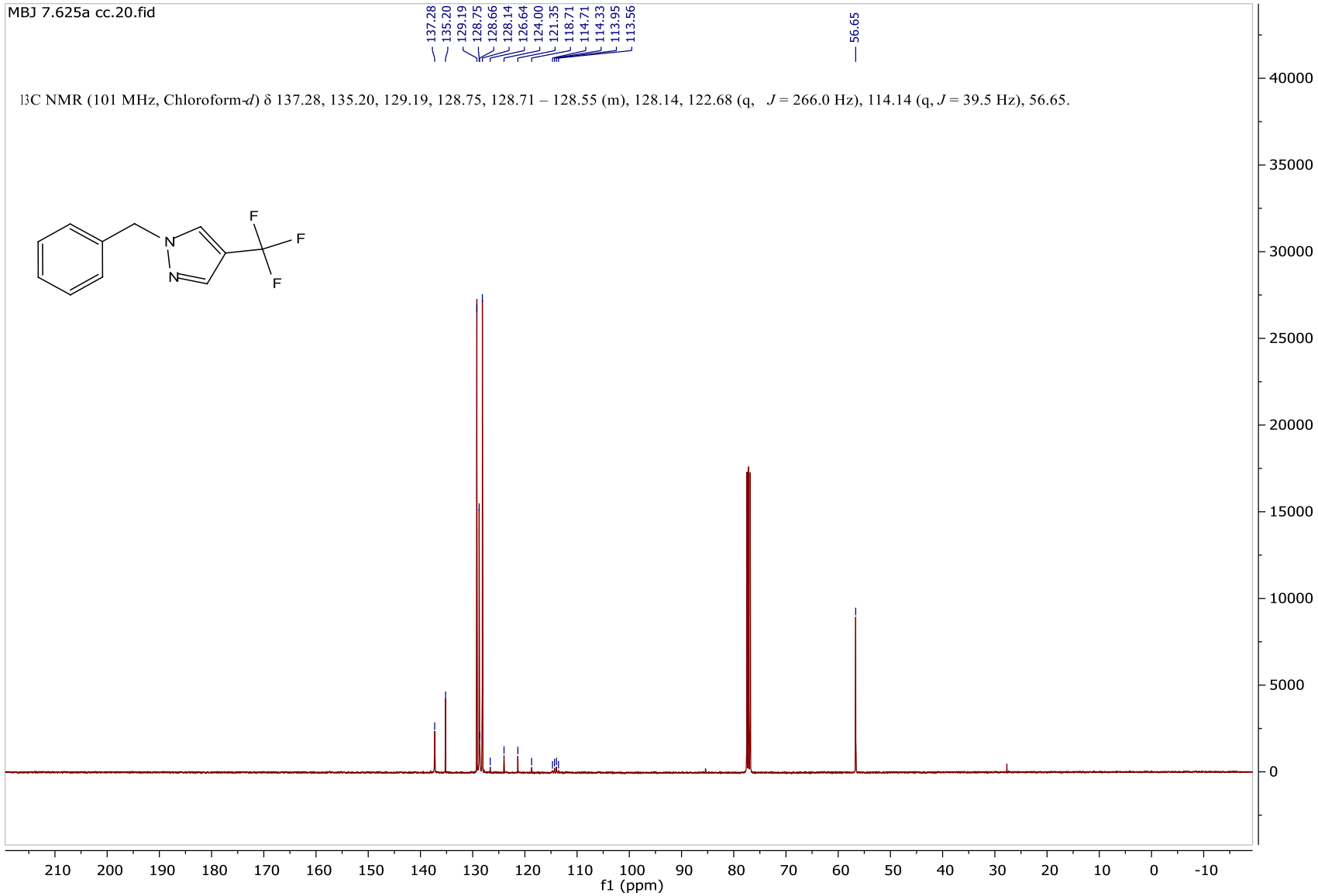

MBJ 7.589b cc.11.fid
-63.00
-63.00
19F NMR (376 MHz, Chloroform-d) δ -63.00 (d, J = 1.8 Hz).
F
F
F
N
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

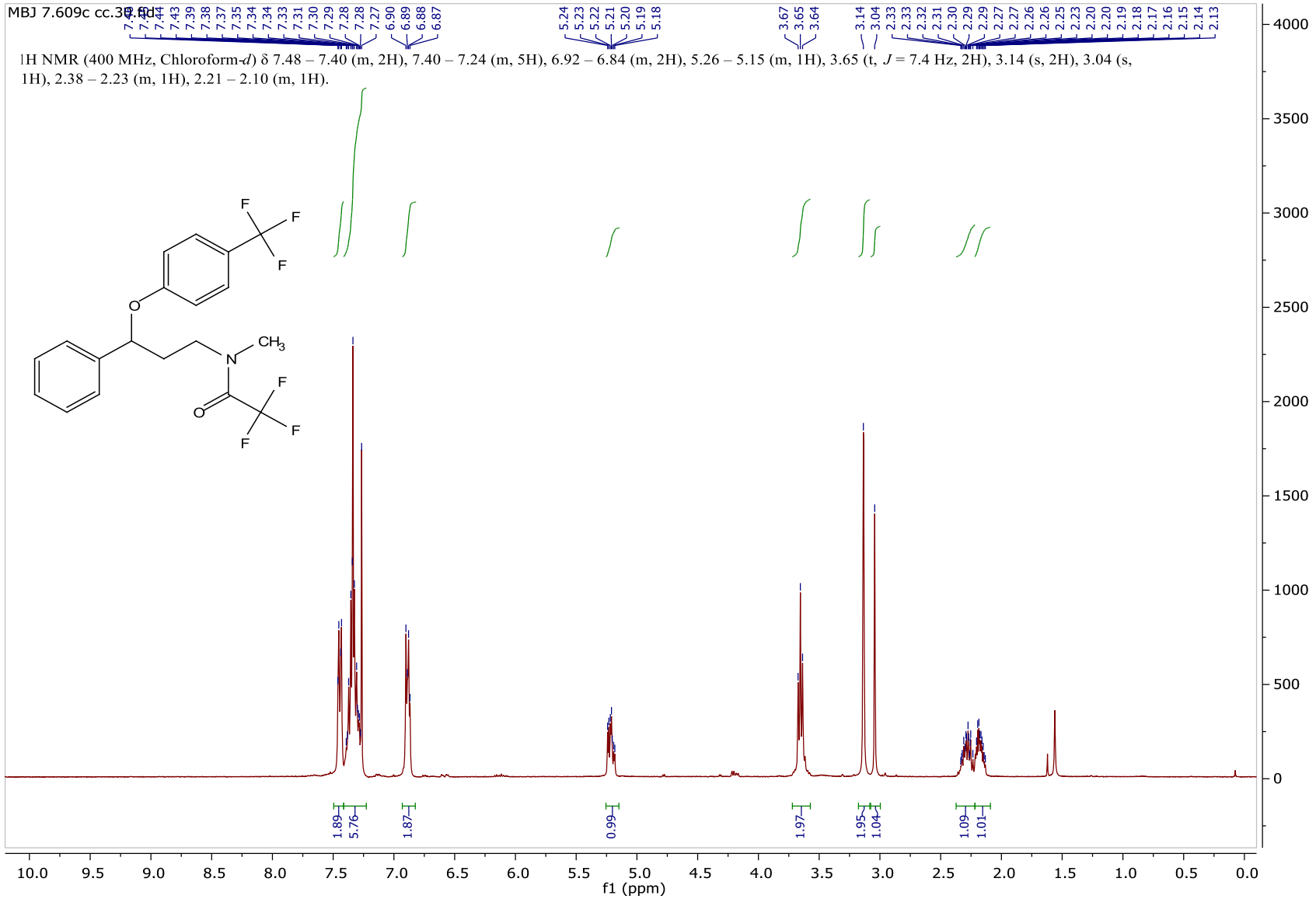


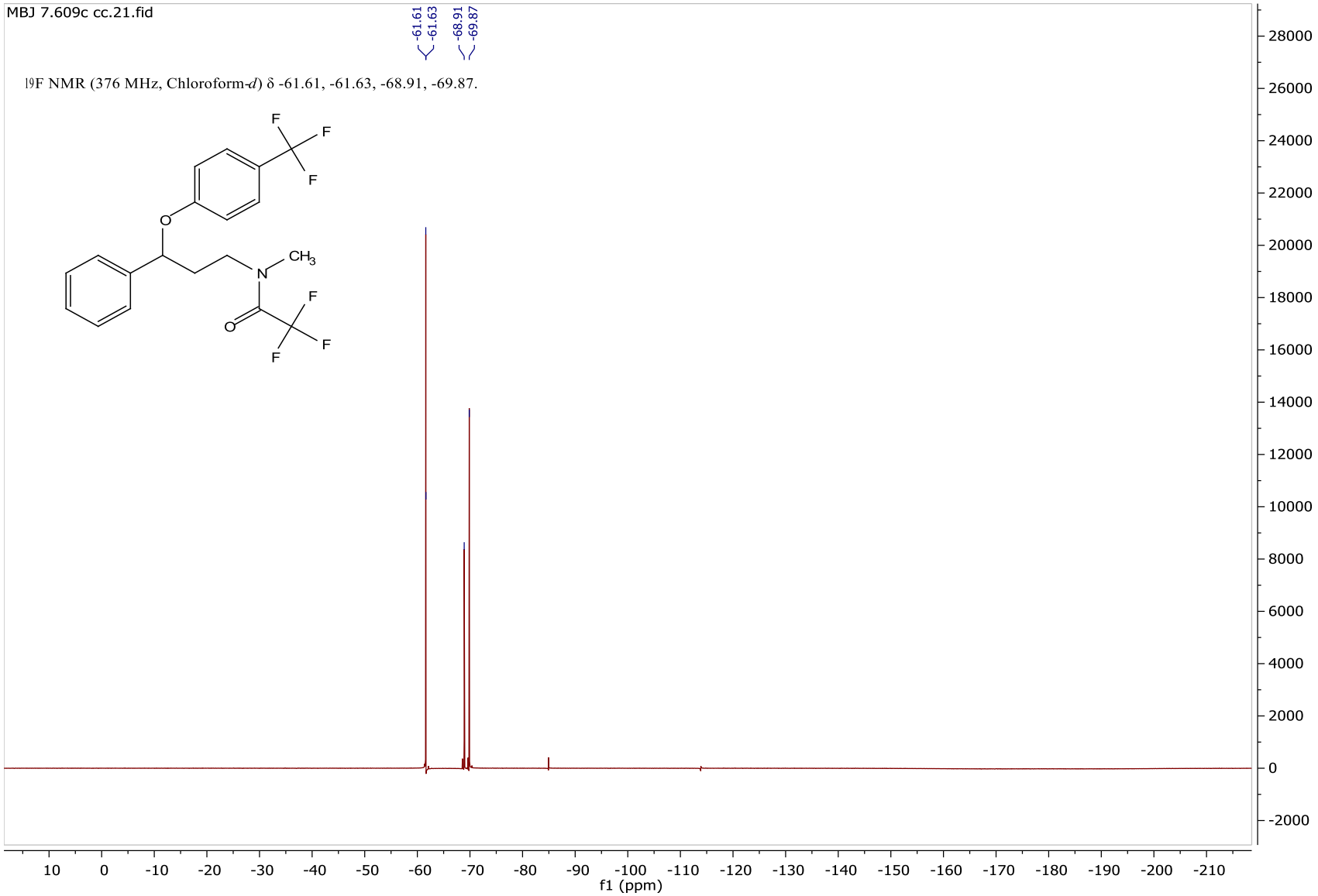
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.60 (q, *J* = 33.2 Hz), 140.92, 137.29, 131.02, 128.96, 127.66, 124.89 – 124.72 (m), 124.66, 122.37 (q, *J* = 276.3 Hz).

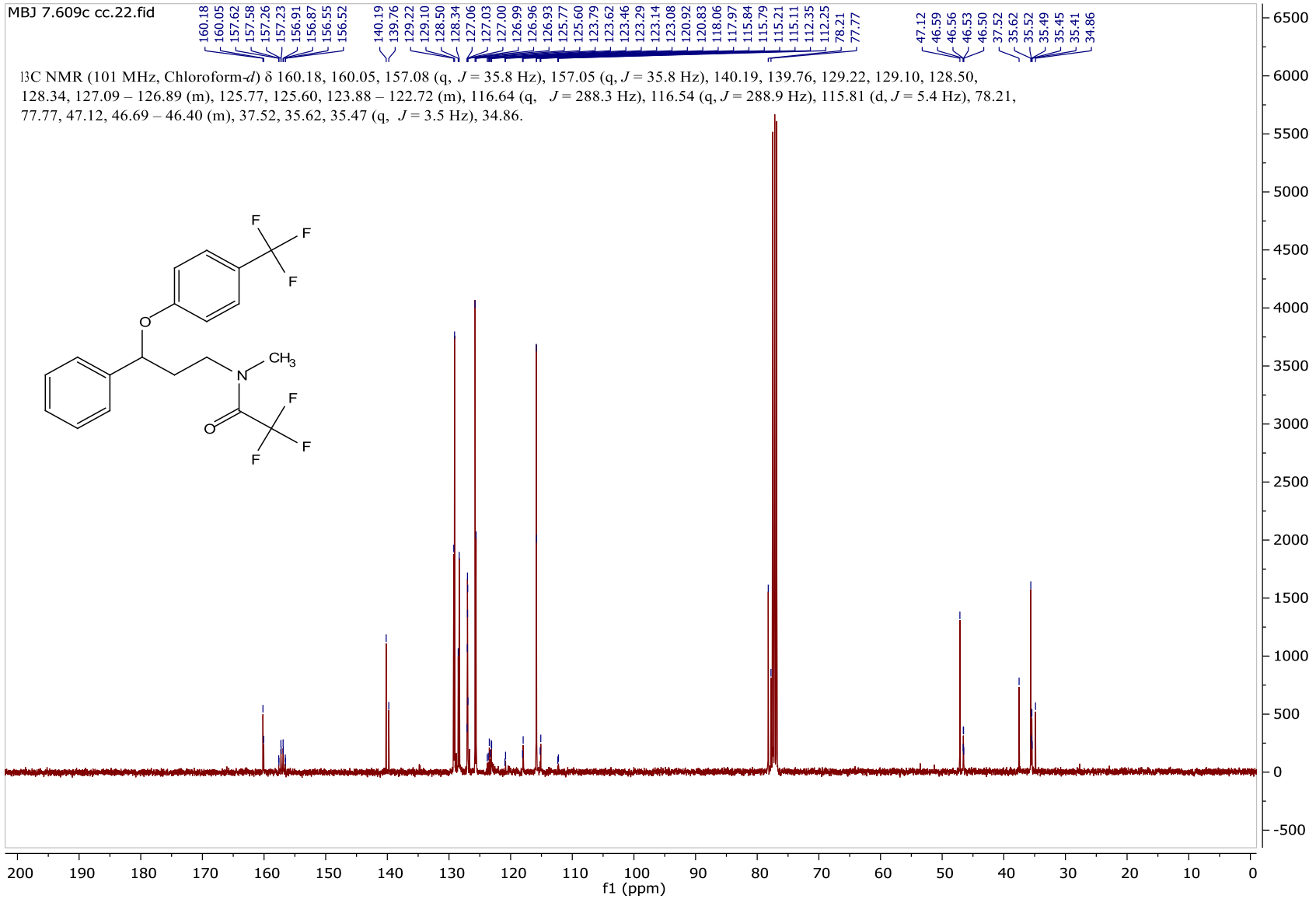

MBJ 7.625a cc.10.fid
7.74
7.63
7.41
7.39
7.37
7.36
7.34
7.27
7.27
7.25
5.32
1H NMR (400 MHz, Chloroform-d) δ 7.74 (s, 1H), 7.63 (s, 1H), 7.45 – 7.33 (m, 3H), 7.29 – 7.22 (m, 2H), 5.32 (s, 2H).
F
F
F
N
N
0.95
0.91
2.82
2.06
2.00
f1 (ppm)

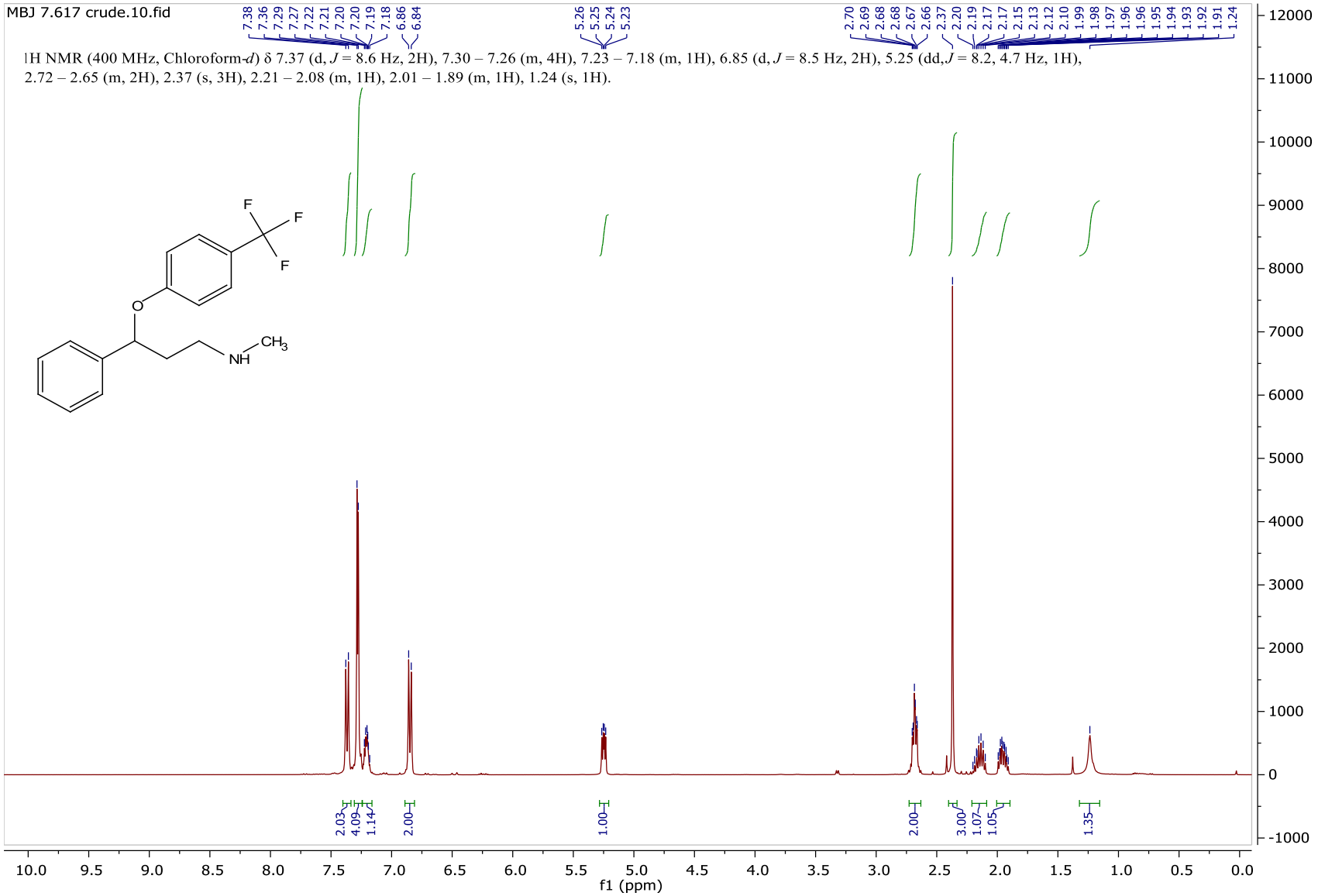

MBJ 7.625a cc.11.fid
19F NMR (376 MHz, Chloroform-d) δ -56.33.
-56.33
F
F
F
N
N
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

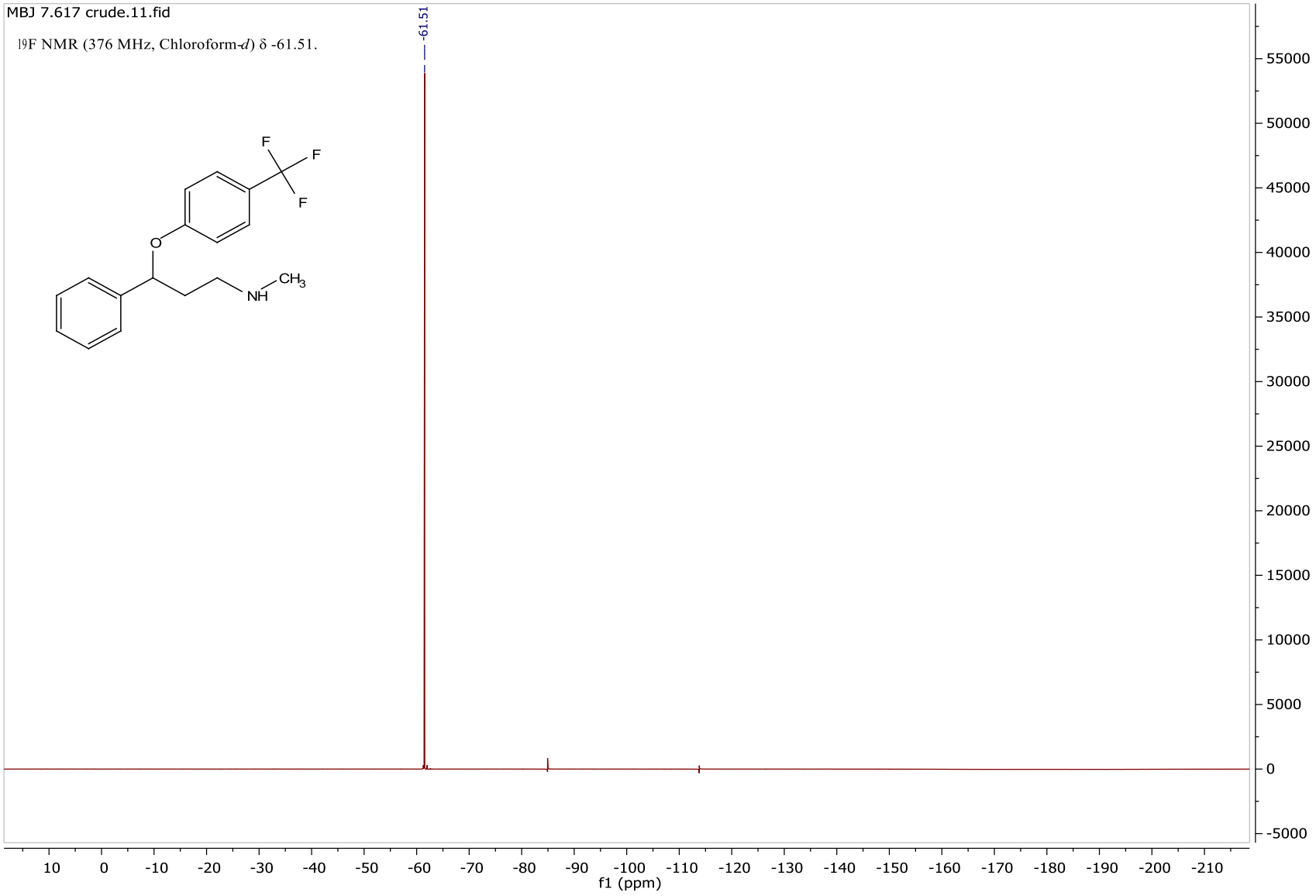

MBJ 7.625a cc.20.fid
137.28
135.20
129.19
128.75
128.66
128.14
126.64
124.00
121.35
118.71
114.71
114.33
113.95
113.56
56.65
13C NMR (101 MHz, Chloroform-d) δ 137.28, 135.20, 129.19, 128.75, 128.71 – 128.55 (m), 128.14, 122.68 (q, J = 266.0 Hz), 114.14 (q, J = 39.5 Hz), 56.65.
F
F
F
N
N
40000
35000
30000
25000
20000
15000
10000
5000
0
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)

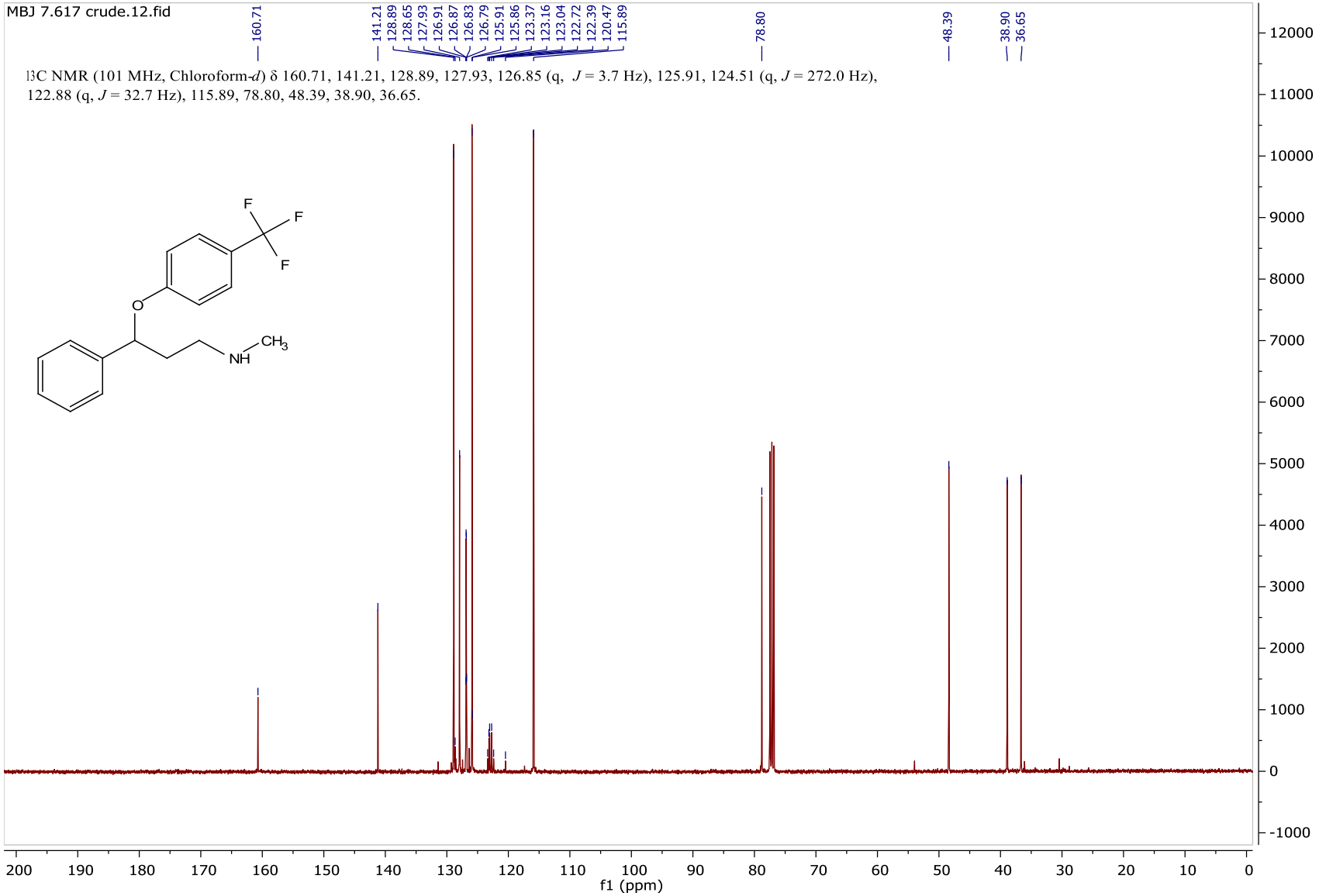

MBJ 7.609c cc.3H.fid
1H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.40 (m, 2H), 7.40 – 7.24 (m, 5H), 6.92 – 6.84 (m, 2H), 5.26 – 5.15 (m, 1H), 3.65 (t, J = 7.4 Hz, 2H), 3.14 (s, 2H), 3.04 (s, 1H), 2.38 – 2.23 (m, 1H), 2.21 – 2.10 (m, 1H).
F
F
F
O
CH3
N
O
F
F
F
1.89
5.76
1.87
0.99
1.97
1.95
1.04
1.09
1.01
f1 (ppm)


MBJ 7.609c cc.21.fid
-61.61
-61.63
-68.91
-69.87
19F NMR (376 MHz, Chloroform-d) δ -61.61, -61.63, -68.91, -69.87.
F
F
F
O
CH3
N
F
O
F
F
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


MBJ 7.609c cc.22.fid
160.18 160.05 157.62 157.58 157.26 157.23 156.91 156.87 156.55 156.52
140.19 139.76 129.22 129.10 128.50 128.34 127.06 127.03 127.00 126.99 126.96 126.93 125.77 125.60 123.79 123.62 123.46 123.29 123.14 123.08 120.92 120.83 118.06 117.97 115.84 115.79 115.21 115.11 112.35 112.25 78.21 77.77
47.12 46.59 46.56 46.53 46.50 37.52 35.62 35.52 35.49 35.45 35.41 34.86
13C NMR (101 MHz, Chloroform-d) δ 160.18, 160.05, 157.08 (q, J = 35.8 Hz), 157.05 (q, J = 35.8 Hz), 140.19, 139.76, 129.22, 129.10, 128.50, 128.34, 127.09 – 126.89 (m), 125.77, 125.60, 123.88 – 122.72 (m), 116.64 (q, J = 288.3 Hz), 116.54 (q, J = 288.9 Hz), 115.81 (d, J = 5.4 Hz), 78.21, 77.77, 47.12, 46.69 – 46.40 (m), 37.52, 35.62, 35.47 (q, J = 3.5 Hz), 34.86.
F
F
F
O
CH3
N
F
O
F
F
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MBJ 7.617 crude.10.fid
1H NMR (400 MHz, Chloroform-d) δ 7.37 (d, J = 8.6 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 6.85 (d, J = 8.5 Hz, 2H), 5.25 (dd, J = 8.2, 4.7 Hz, 1H), 2.72 – 2.65 (m, 2H), 2.37 (s, 3H), 2.21 – 2.08 (m, 1H), 2.01 – 1.89 (m, 1H), 1.24 (s, 1H).
F
F
F
O
NH
CH3
f1 (ppm)


MBJ 7.617 crude.11.fid
19F NMR (376 MHz, Chloroform-d) δ -61.51.
-61.51
F
F
F
O
NH
CH3
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


MBJ 7.617 crude.12.fid
160.71
141.21
128.89
128.65
127.93
126.91
126.87
126.83
126.79
125.91
125.86
123.37
123.16
123.04
122.72
122.39
120.47
115.89
78.80
48.39
38.90
36.65
13C NMR (101 MHz, Chloroform-d) δ 160.71, 141.21, 128.89, 127.93, 126.85 (q, J = 3.7 Hz), 125.91, 124.51 (q, J = 272.0 Hz), 122.88 (q, J = 32.7 Hz), 115.89, 78.80, 48.39, 38.90, 36.65.
F
F
F
O
NH
CH3
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)