Cobalt-catalyzed alkene hydrogenation by reductive turnover

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Contents

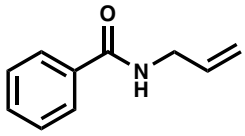
1. General Methods

All reactions were carried out under positive pressure of argon and glassware was oven-dried at 120 ˚C for a minimum of 12 hours or flame-dried with a propane torch under high vacuum unless otherwise stated. Anhydrous solvents were distilled over calcium hydride or purchased and used without further purification. Other commercially available reagents were also used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates purchased from EMD chemicals (TLC Silica gel 60 F_{254}, 250 μm thickness), gas chromatography mass spectrometry (GCMS, Agilent 7820A/5975). Flash column chromatography was performed over Silica gel 60 (particle size 0.04–0.063 mm) from EMD chemicals.

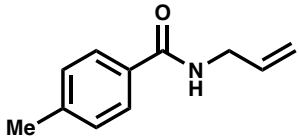
NMR spectra were recorded on Varian-400, Bruker DPX-400, DRX-500 and DRX-600 (cryoprobe) spectrometers. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent, br = broad.

2. Starting Materials

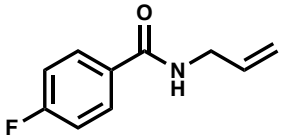
4-phenyl-1-butene, $AlCl_3$, was purchased and used without further purification.



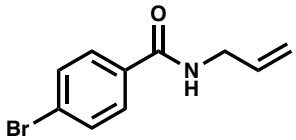
N-allylbenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[1]



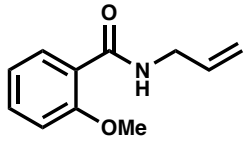
N-allyl-4-methylbenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[2]



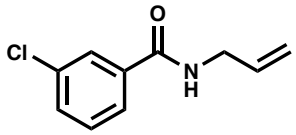
N-allyl-4-fluorobenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[3]



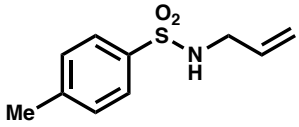
N-allyl-4-bromobenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[3]



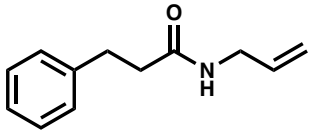
N-allyl-2-methoxybenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[4]



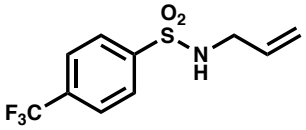
N-allyl-3-chlorobenzamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[2]



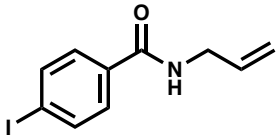
N-allyl-4-methylbenzenesulfonamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[5]



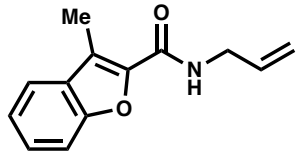
N-allyl-3-phenylpropanamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[6]



N-allyl-4-(trifluoromethyl)benzenesulfonamide was prepared according to literature procedure. Spectral data matched that reported in the literature.[7]

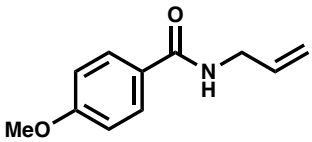


N-allyl-4-iodobenzamide was prepared according to literature procedure.[3] Spectral data matched that reported in the literature.[8]

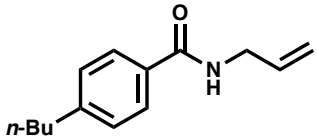


N-allyl-3-methylbenzofuran-2-carboxamide was prepared according to literature procedure.[3] ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.42 (ddd,

J = 8.3, 6.8, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 6.72 (s, 1H), 5.96 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1H), 5.31 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.21 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.11 (tt, *J* = 5.8, 1.6 Hz, 2H), 2.64 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.70, 152.79, 142.17, 133.58, 129.32, 126.56, 122.63, 122.04, 120.49, 116.26, 111.01, 40.93, 8.45. LCMS: found 216.1 (M+H), calc'd 216.1 (M+H).



N-allyl-4-methoxybenzamide was prepared according to literature procedure. Spectral data matched that reported.[9]



N-allyl-4-butylbenzamide was prepared according to literature procedure.[3] ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.67 (m, 2H), 7.26 – 7.21 (m, 2H), 6.16 (s, 1H), 5.94 (ddtd, *J* = 16.9, 10.2, 5.7, 1.0 Hz, 1H), 5.26 (dp, *J* = 17.1, 1.4 Hz, 1H), 5.18 (dp, *J* = 10.1, 1.4 Hz, 1H), 4.09 (tq, *J* = 5.8, 1.5 Hz, 2H), 2.68 – 2.62 (m, 2H), 1.64 – 1.56 (m, 2H), 1.35 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.44, 133.84, 126.44, 116.17, 41.92, 35.06, 32.89, 21.83, 13.45. LCMS: found 218.1 (M+H), calc'd 218.2 (M+H)

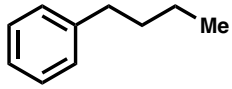
3. Olefin Hydrogenation

General procedure with $AlCl_3$: This reaction may be carried out under ambient temperature and atmosphere. The olefin (0.2 mmol) (if solid), Mn powder (33 mg, 0.3 mmol), $Co(OAc)_2$•$4H_2O$ (14.2 mg, 30 mol%) and $AlCl_3$ (26.6 mg, 0.2 mmol) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A cap is placed on the reaction vessel and *i*-PrOH (2 mL) is added. The reaction is stirred vigorously for 4-20 h at rt. The reaction initially turns blue and over time turns black. The mixture is diluted with CH_2Cl_2, poured into a separating funnel and quenched with saturated aqueous $NaHCO_3$ solution. After phase separation the aqueous phase is extracted twice further with CH_2Cl_2. The combined organic phases are washed with brine, dried over $MgSO_4$ and filtered through a short plug of silica gel. The solvent is removed *in vacuo* to furnish the hydrogenated product without the need for further purification.

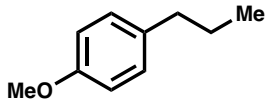
General procedure with HCl: This reaction may be carried out under ambient temperature and atmosphere. A solution of concentrated (12.5 M) HCl is diluted with *i*-PrOH to approximate concentration 1–2M. 0.10 mL of this HCl/*i*-PrOH is diluted with DI H_2O. The resulting solution is titrated with a freshly prepared solution of ~1M NaOH (aqueous) to determine concentration, using pH strips (Cytiva Whatman pH Indicator Papers, pH range 0-14) to monitor for equivalence point. The olefin (0.1 mmol) (if solid), Mn powder (16.5 mg, 0.3 mmol), and $Co(OAc)_2$•$4H_2O$ (7.5 mg, 30 mol%) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A cap is placed on the reaction vessel and *i*-PrOH (2 mL), followed by HCl/*i*-PrOH solution (2 equiv) is added. The reaction is stirred vigorously for 4-20 h at rt. The reaction initially turns blue and over time turns grey. The mixture is diluted with CH_2Cl_2, poured into a separating funnel and quenched

with saturated aqueous $NaHCO_3$ solution. After phase separation the aqueous phase is extracted twice further with CH_2Cl_2. The combined organic phases are washed with brine, dried over $MgSO_4$ and filtered through a short plug of silica gel. The solvent is removed *in vacuo* to furnish the hydrogenated product without the need for further purification.

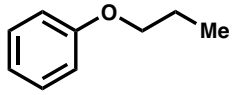
4. Olefin Hydrogenation products



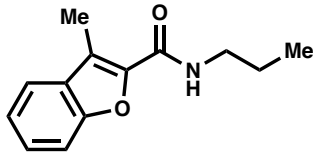
Butylbenzene. The spectral data was in agreement with the literature.[10]



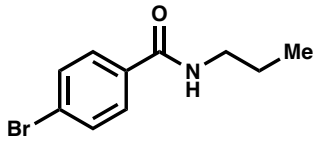
1-methoxy-4-propylbenzene. The spectral data was in agreement with the literature.[11]



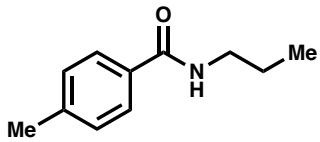
Propoxybenzene. The spectral data was in agreement with the literature.[12]



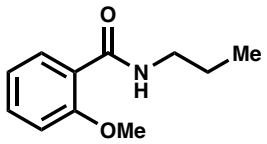
3-methyl-*N*-propylbenzofuran-2-carboxamide. ^{1}H NMR (400 MHz) $CDCl_3$: 7.64 (d, J = 7.8 Hz, 1H, Ar-H), 7.49-7.40 (m, 2H, Ar-H), 7.35-7.29 (m, 1H, Ar-H), 3.46 (app-q, 2H, CH_2), 1.70 (app-h, 2H, CH_2), 1.04 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.70, 152.79, 142.17, 133.58, 129.32, 126.56, 122.63, 122.04, 120.49, 116.26, 111.01, 40.93, 8.45. LCMS: found 216.1 (M+H), Calc'd 216.1 (M+H)



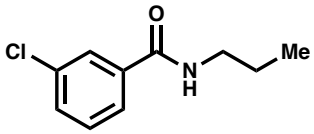
4-bromo-*N*-propylbenzamide. The spectral data was in agreement with the literature.[13]



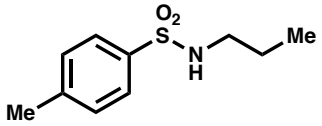
4-methyl-*N*-propylbenzamide. The spectral data was in agreement with the literature.[14]



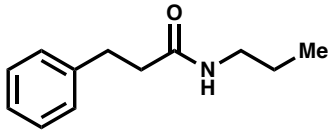
2-methoxy-*N*-propylbenzamide. The spectral data was in agreement with the literature.[15]



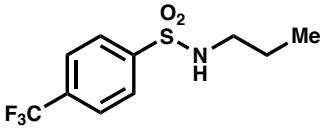
3-chloro-*N*-propylbenzamide. The spectral data was in agreement with the literature.[16]



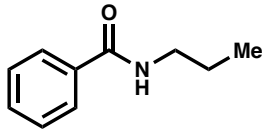
4-methyl-*N*-propylbenzenesulfonamide. The spectral data was in agreement with the literature.[17]



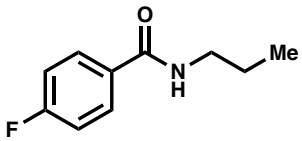
3-Phenyl-*N*-propylpropanamide. The spectral data was in agreement with the literature.[18]



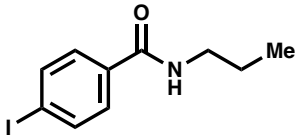
N-propyl-4-(trifluoromethyl)benzenesulfonamide. ^{1}H NMR (400 MHz) $CDCl_3$: 8.03 (d, J = 8.2 Hz, 2H, Ar-H), 7.81 (d, J = 8.2 Hz, 2H, Ar-H), 4.95 (t, J = 5.9 Hz, 1H, NH), 2.97 (app-q, 2H, CH_2), 1.52 (app-h, 2H, CH_2), 0.90 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.30, 127.09, 125.85, 125.82, 125.80, 44.60, 22.59, 10.58. LCMS: found 268.0 (M+H), 268.1 calc'd (M+H).



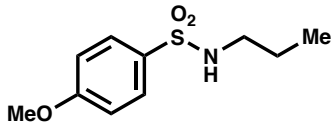
N-propylbenzamide. The spectral data was in agreement with the literature.[19]



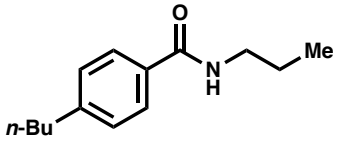
4-Fluoro-*N*-propylbenzamide. The spectral data was in agreement with the literature.[20]



4-iodo-*N*-propylbenzamide. The spectral data was in agreement with the literature.[21]

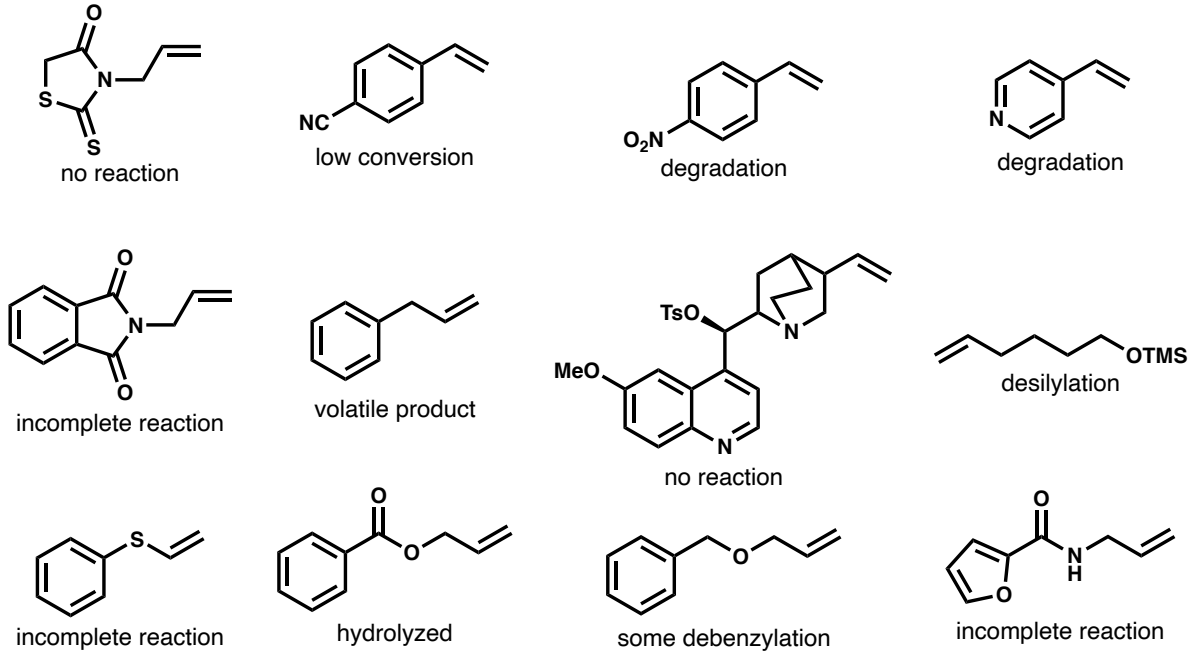


4-methoxy-*N*-propylbenzenesulfonamide. The spectral data was in agreement with the literature.[22]



4-butyl-*N*-propylbenzamide. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H), 7.26 – 7.21 (m, 2H), 6.07 (s, 1H), 3.42 (ddd, *J* = 7.8, 7.1, 5.9 Hz, 2H), 2.67 – 2.62 (m, 2H), 1.67 – 1.58 (m, 4H), 1.35 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.07, 146.19, 131.78, 128.12, 126.36, 41.24, 35.04, 32.91, 22.53, 21.83, 13.45, 10.99. LCMS: found 220.1 (M+H), calc'd 220.2 (M+H)

5. Unsuccessful Substrates



6. Mechanistic Studies

A. Cyclization study: This reaction may be carried out under ambient temperature and atmosphere. Mn powder (16.5 mg, 0.3 mmol), $Co(OAc)_2$•$4H_2O$ (6.5 mg, 30 mol%) and $AlCl_3$ (13.3 mg, 0.1

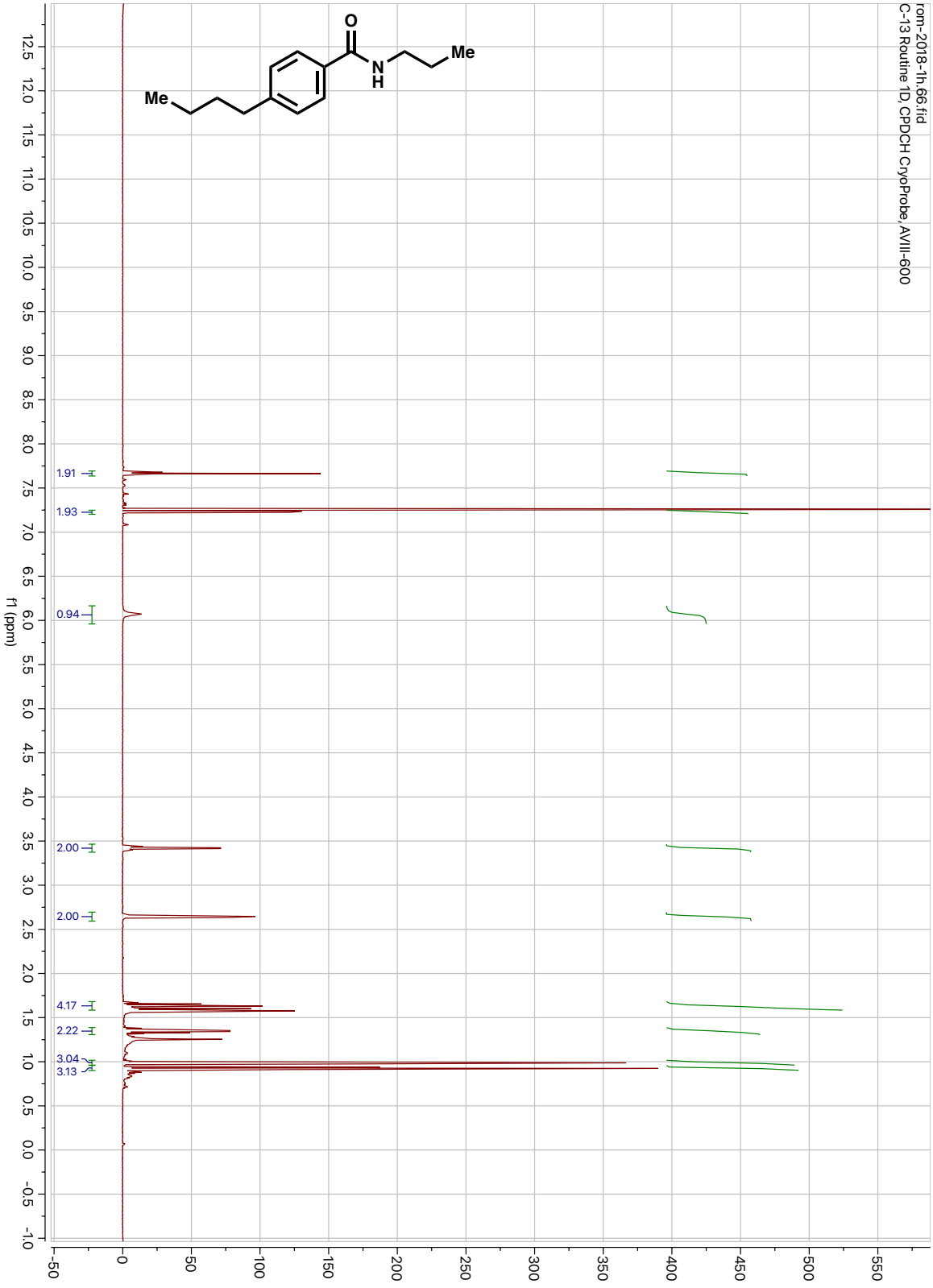
mmol) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A septum cap is placed on the reaction vessel and *i*-PrOH (1 mL) is added. Allyl ether (12 µL, 0.1 mmol) is added via syringe through septum. The reaction is stirred vigorously for 4 h at rt. 10 µL of reaction solution is diluted with 2 mL EtOAc and filtered through a short plug of silica into a 2 mL vial. The sample is submitted for GC/MS analysis. Only propyl ether is observed, no cyclized product.

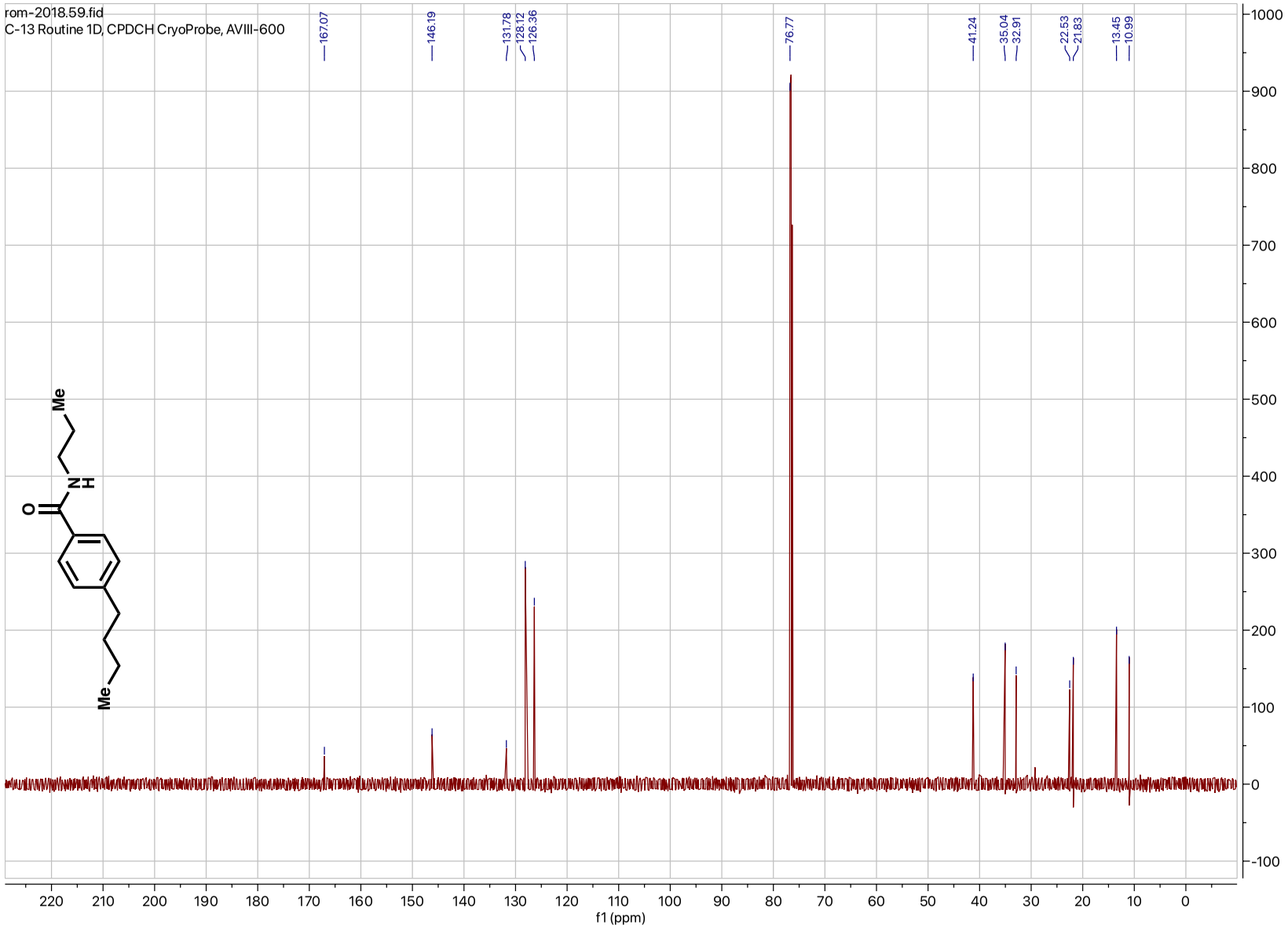
B. Reaction purge with argon: Mn powder (16.5 mg, 0.3 mmol), $Co(OAc)_2•4H_2O$ (6.5 mg, 30 mol%) and $AlCl_3$ (13.3 mg, 0.1 mmol) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A septum cap is placed on the reaction vessel and *i*-PrOH (1 mL) is added. Argon is bubbled through the solution slightly above atmospheric pressure (via balloon) for five minutes. 4-phenylbutene (15 µL, 0.1 mmol) is added via syringe through septum. The reaction is stirred vigorously for 24 h at rt. 10 µL of reaction solution is diluted with 2 mL EtOAc and filtered through a short plug of silica. The sample is submitted for GC/MS analysis. Butylbenzene is detected. No starting material is observed in the chromatogram.

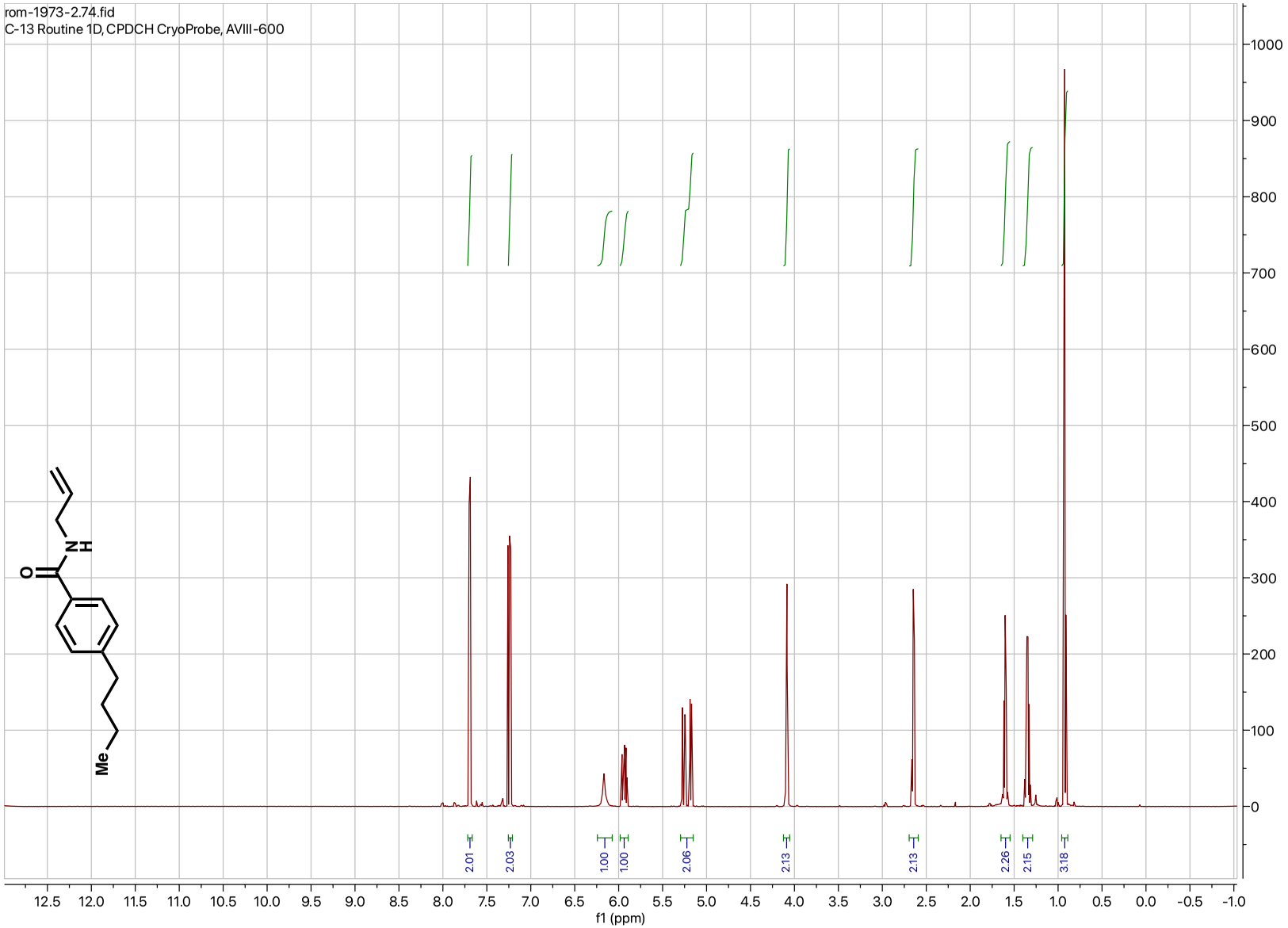
C. Catalytic Mn with hydrogen atmosphere. *N*-allyl-4-bromobenzamide (24 mg, 0.1 mmol), Mn powder (0.6 mg, 0.01 mmol), $Co(OAc)_2•4H_2O$ (6.5 mg, 30 mol%) and $AlCl_3$ (13.3 mg, 0.1 mmol) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A septum cap is placed on the reaction vessel and *i*-PrOH (1 mL) is added. Hydrogen is bubbled through the solution slightly above atmospheric pressure (via balloon) for five minutes. The hydrogen balloon is removed from solution but left inserted through septum to maintain a positive pressure of hydrogen above the reacting solution. The reaction is stirred vigorously for 24 h at rt. 10 µL of reaction solution is diluted with 2 mL MeOH and filtered through a short plug of silica. The sample is submitted for LC/MS analysis. No *N*-propyl-4-bromobenzamide is detected.

D. $MnCl_2$ and $PhSiH_3$: This reaction may be carried out under ambient temperature and atmosphere. *N*-allyl-4-bromobenzamide (24 mg, 0.1 mmol), $MnCl_2•4H_2O$ powder (59.1 mg, 0.3 mmol), $Co(OAc)_2•4H_2O$ (6.5 mg, 30 mol%) are weighed out and added to a 5 mL one-dram vial equipped with a stirring bar. A septum cap is placed on the reaction vessel and *i*-PrOH (1 mL) is added. $PhSiH_3$ is added The reaction is stirred vigorously for 24 h at rt. 10 µL of reaction solution is diluted with 2 mL MeOH and filtered through a short plug of silica. The sample is submitted for LC/MS analysis. No *N*-propyl-4-bromobenzamide is detected.

7. ^{1}H and ^{13}C NMR Spectra of Novel Compounds




rom-2018.59.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
167.07
146.19
131.78
128.12
126.36
76.77
41.24
35.04
32.91
22.53
21.83
13.45
10.99
Me
N
H
O
Me
f1 (ppm)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O
N
H
Me
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2.03
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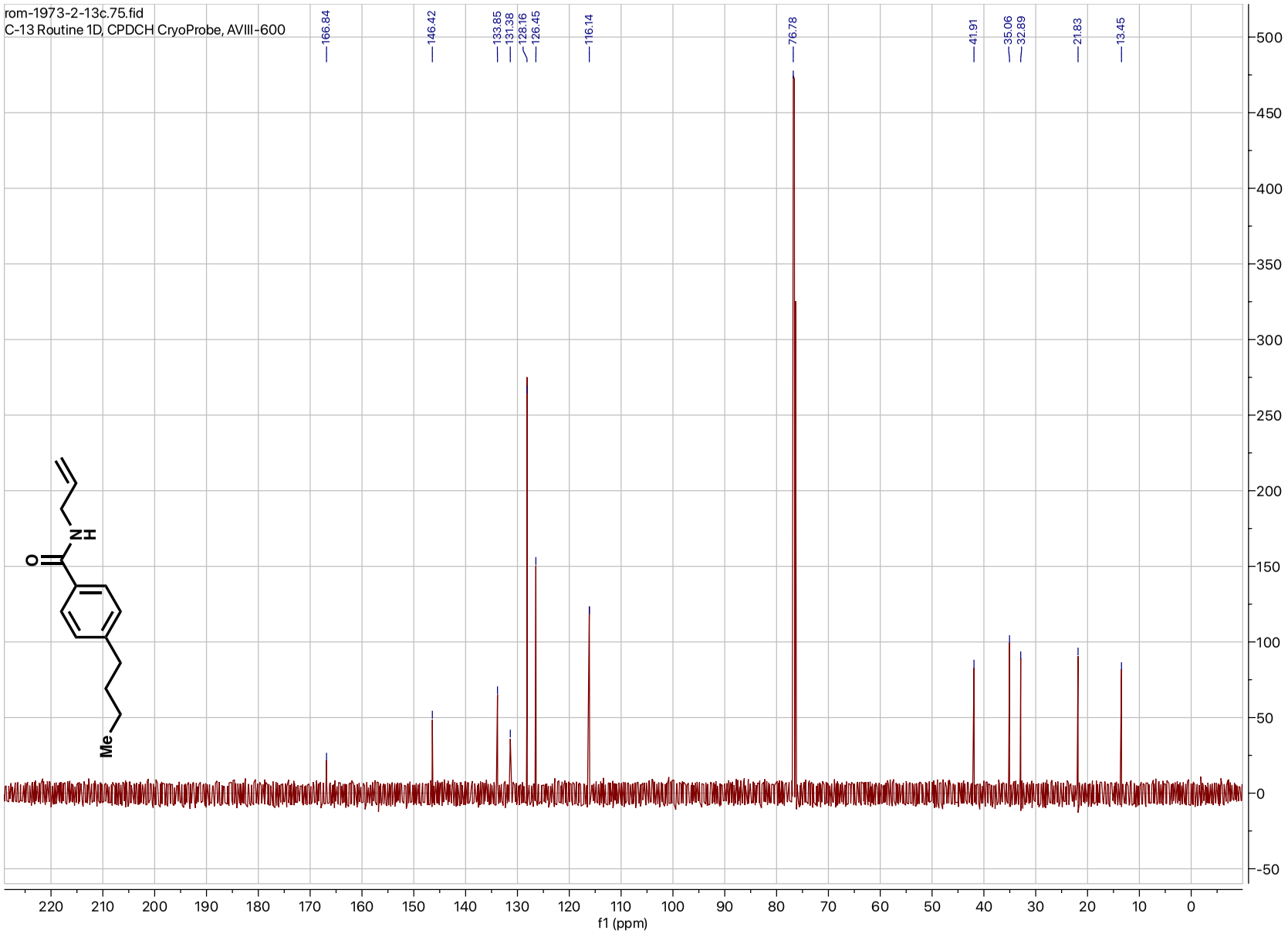
2.13
2.13
2.26
2.15
3.18
f1 (ppm)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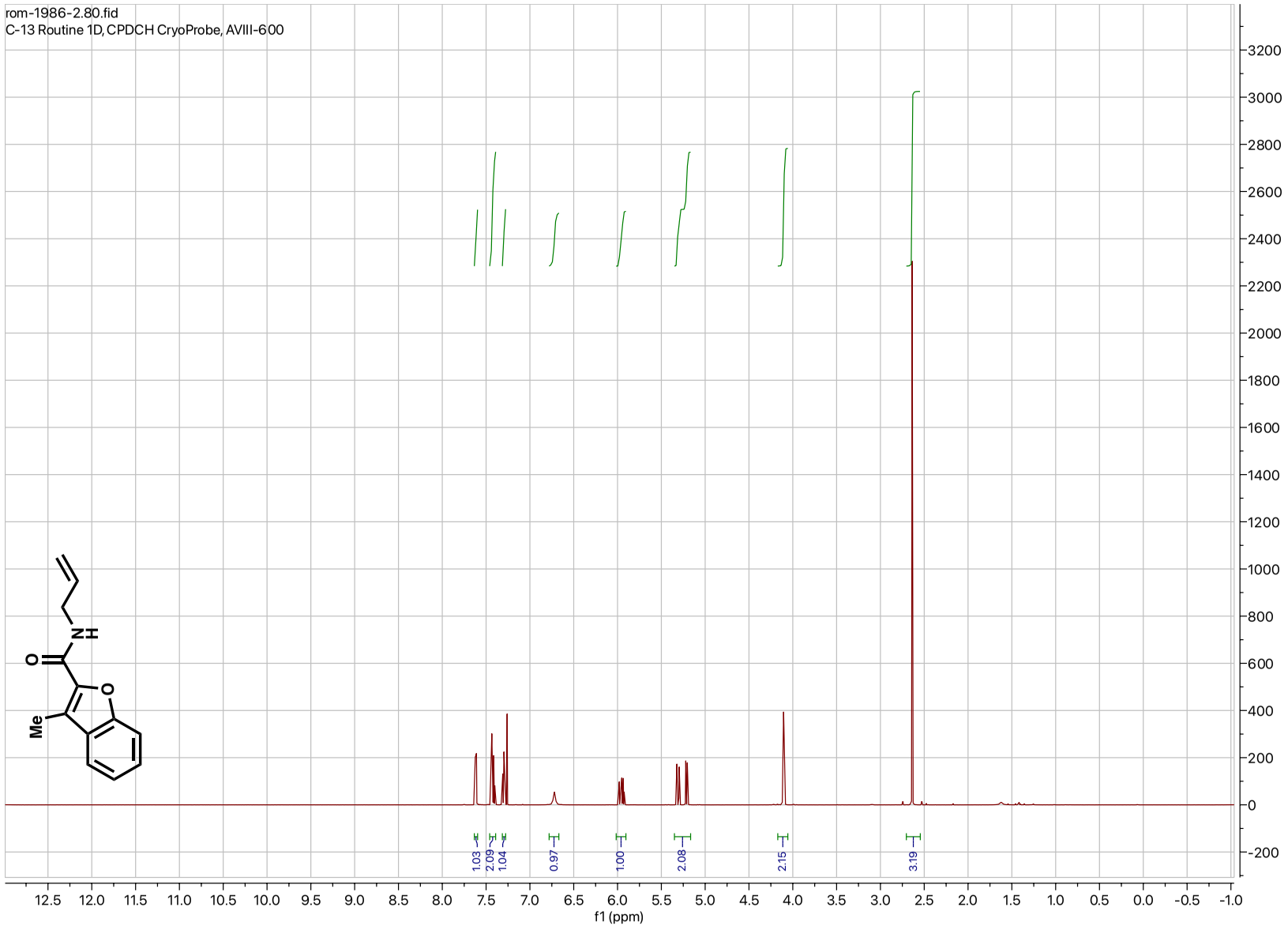
146.42
133.85
131.38
128.16
126.45
116.14
76.78
41.91
35.06
32.89
21.83
13.45
O
N
H
Me
f1 (ppm)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C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
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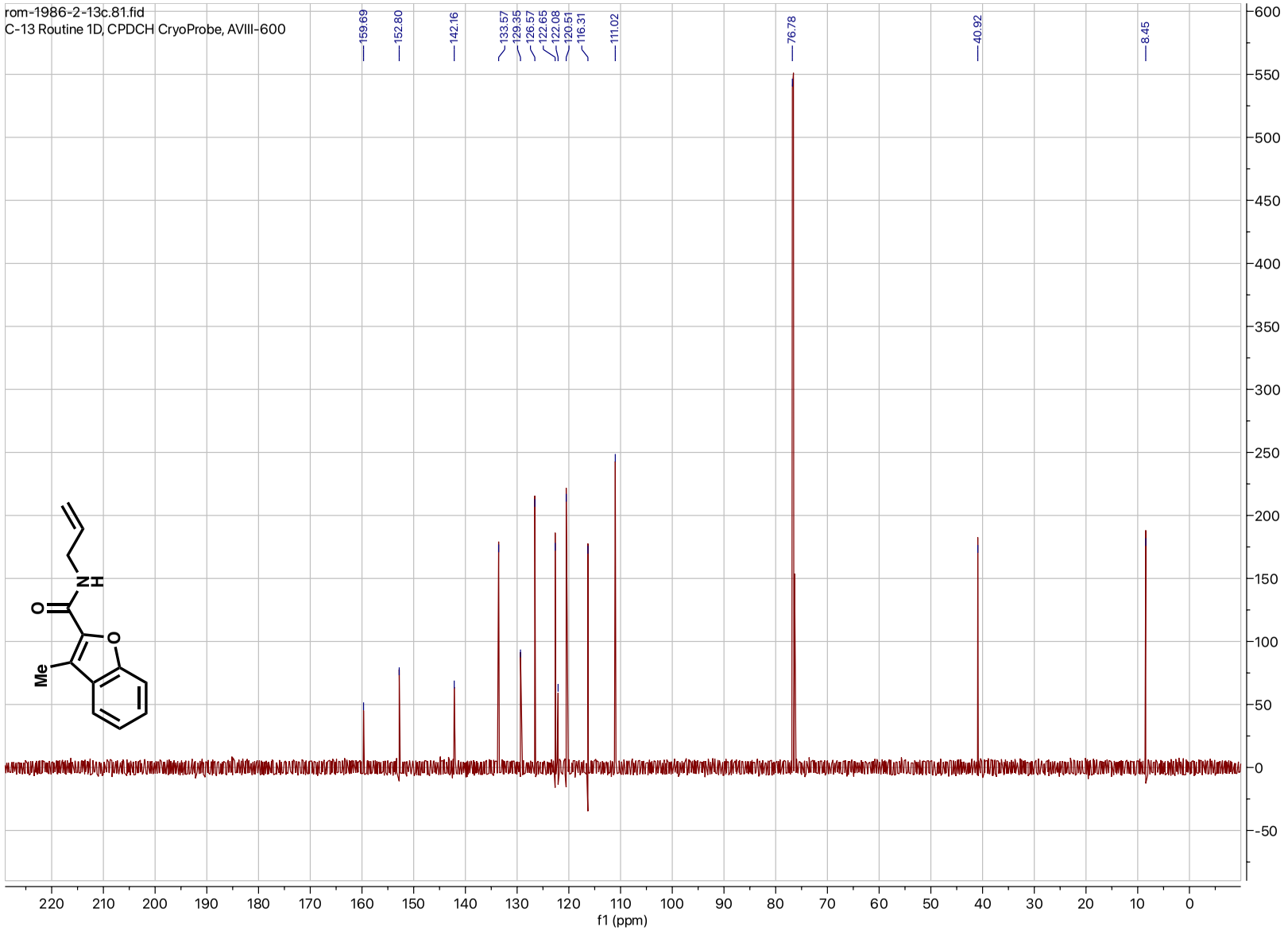
2.09
1.04
0.97
1.00
2.08
2.15
3.19
f1 (ppm)
O
N
H
O
Me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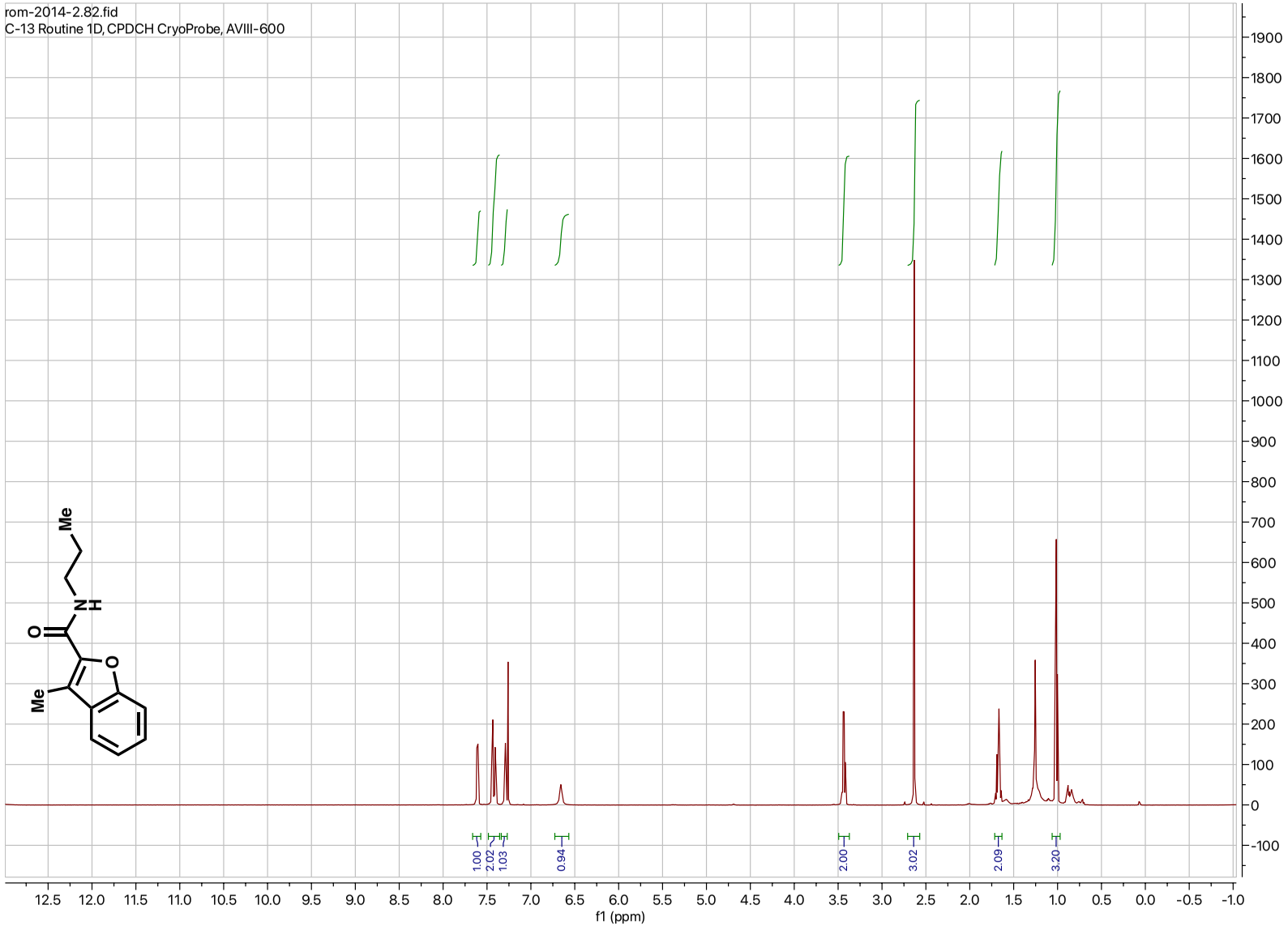
152.80
142.16
133.57
129.35
126.57
122.65
122.08
120.51
116.31
111.02
76.78
40.92
8.45
O
N
H
O
Me
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
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N
H
O
O
Me
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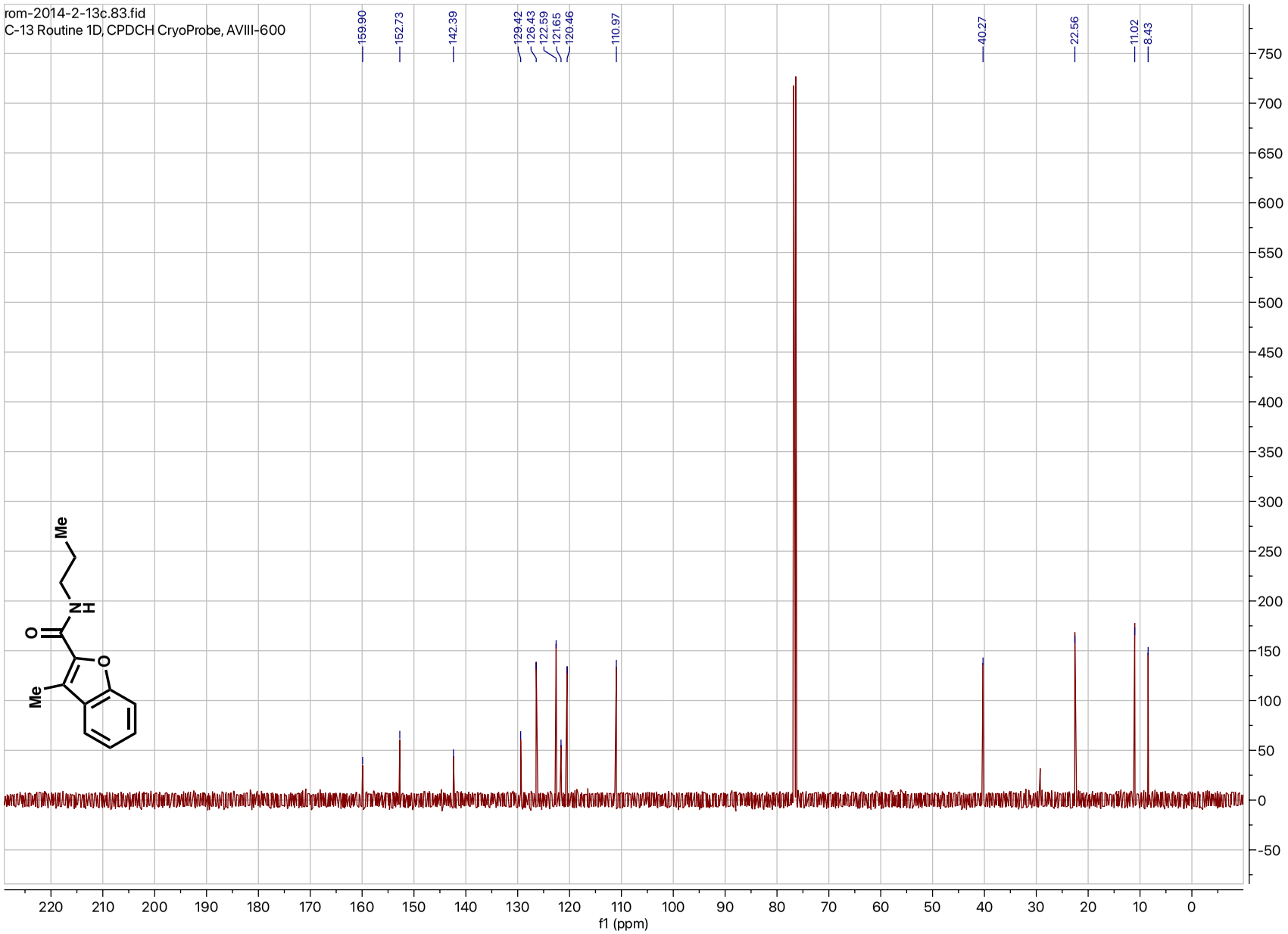
1.03
0.94
2.00
3.02
2.09
3.20
f1 (ppm)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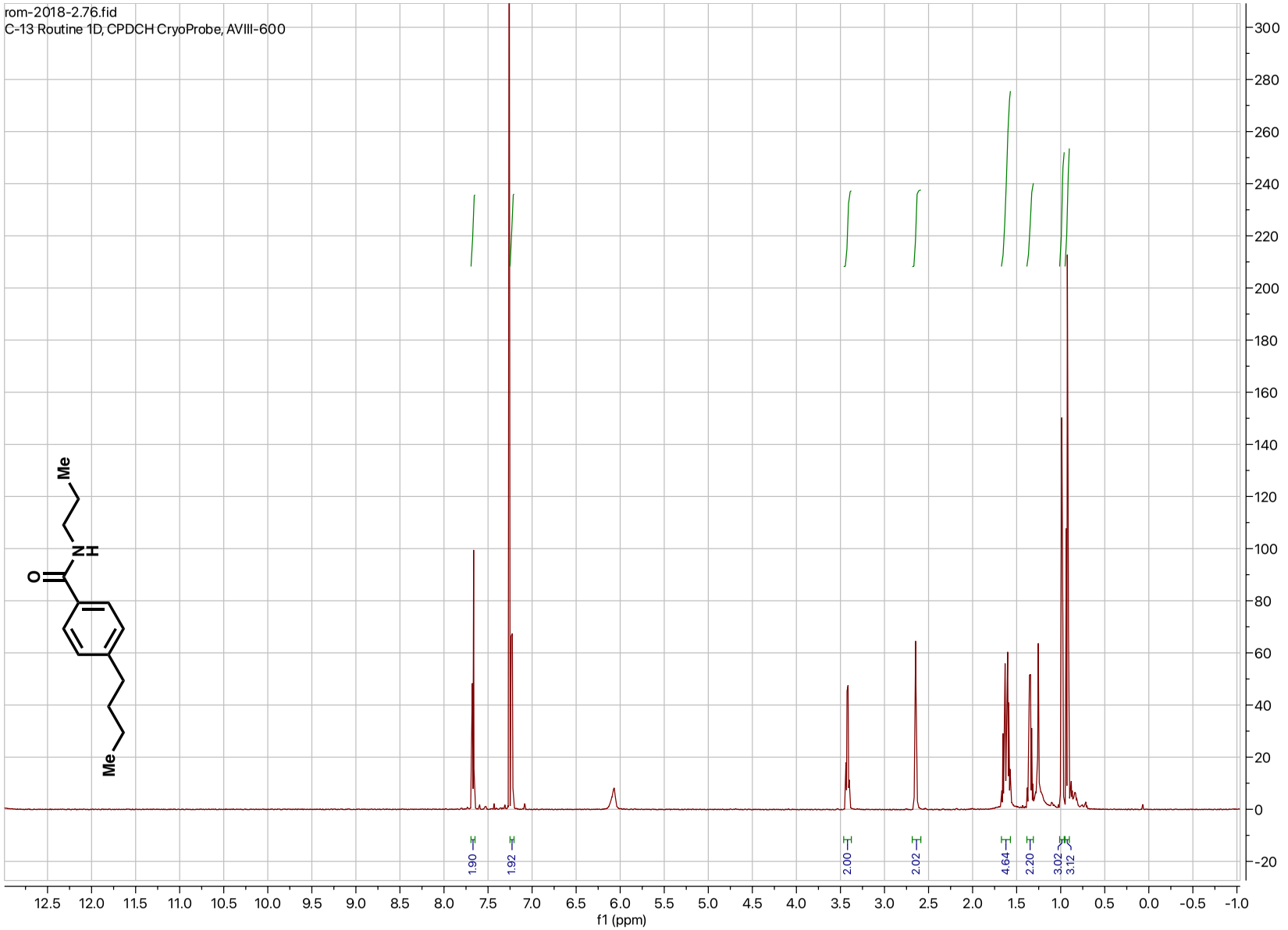
142.39
129.42
126.43
122.59
121.65
120.46
110.97
40.27
22.56
11.02
8.43
Me
N
H
O
O
Me
f1 (ppm)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C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
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N
H
O
Me
1.90
1.92
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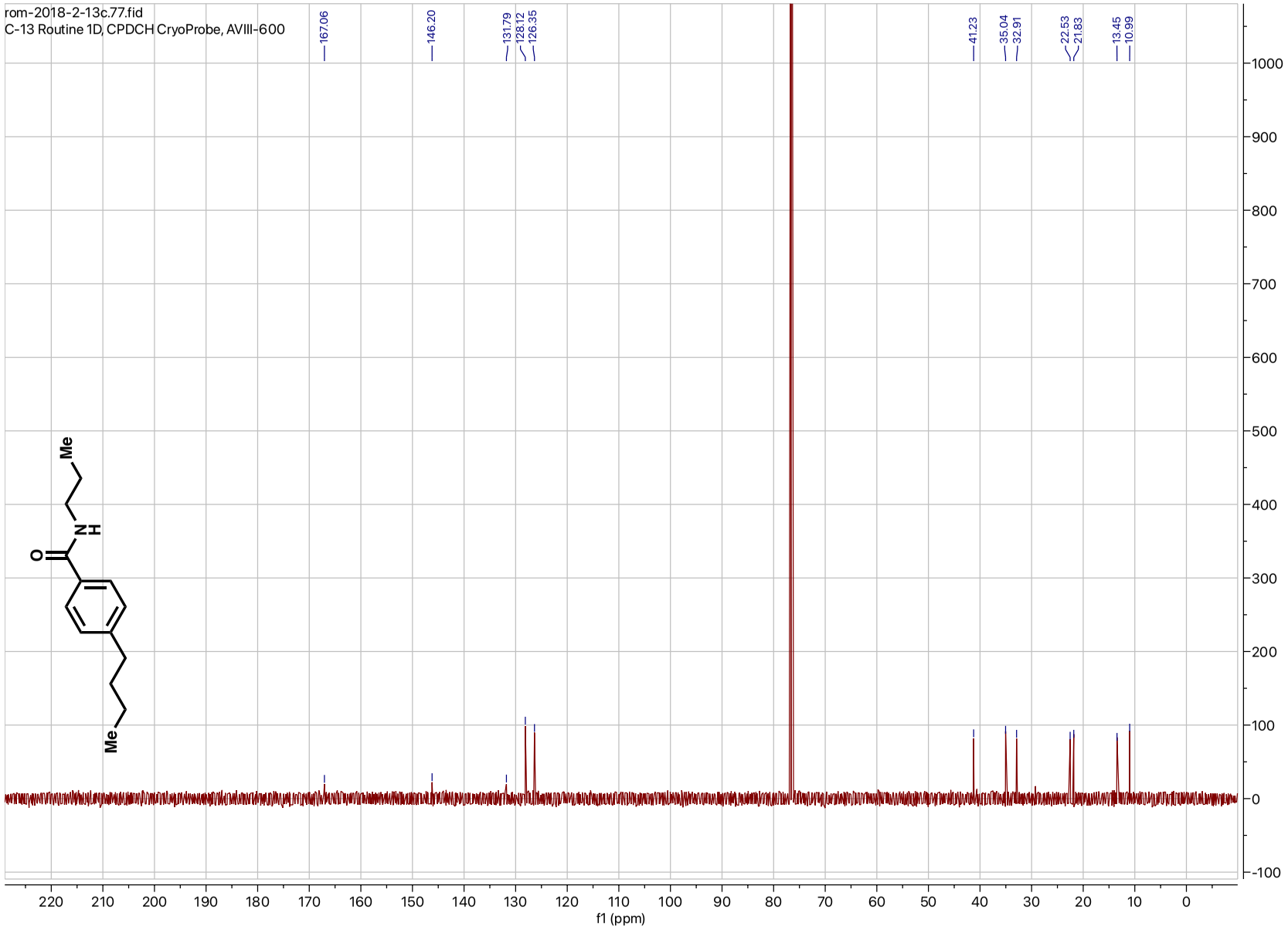
2.02
4.64
2.20
3.02
3.12
f1 (ppm)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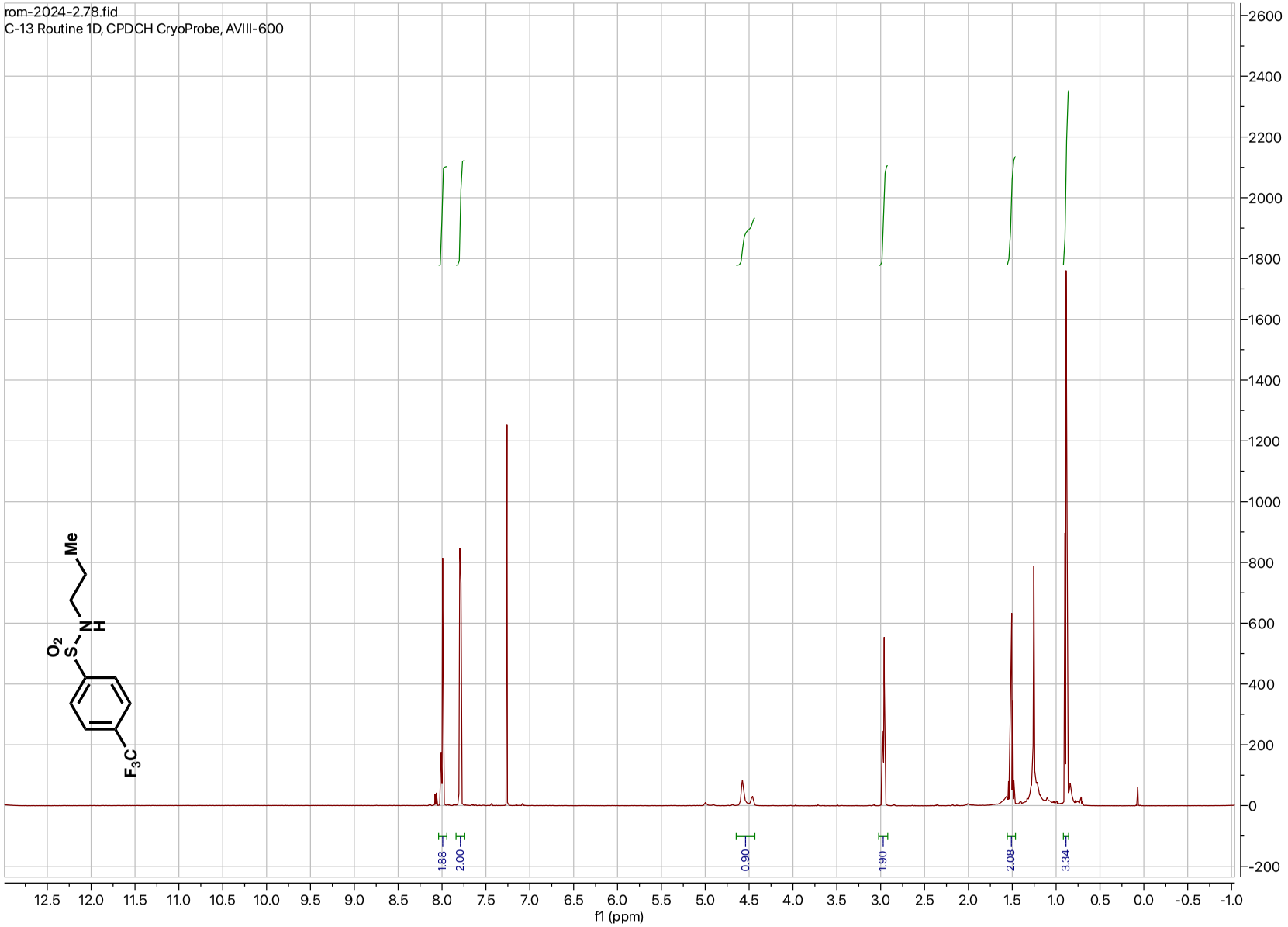
131.79
128.12
126.35
41.23
35.04
32.91
22.53
21.83
13.45
10.99
Me
N
H
O
Me
f1 (ppm)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C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
Me
N
H
O2
S
F3C
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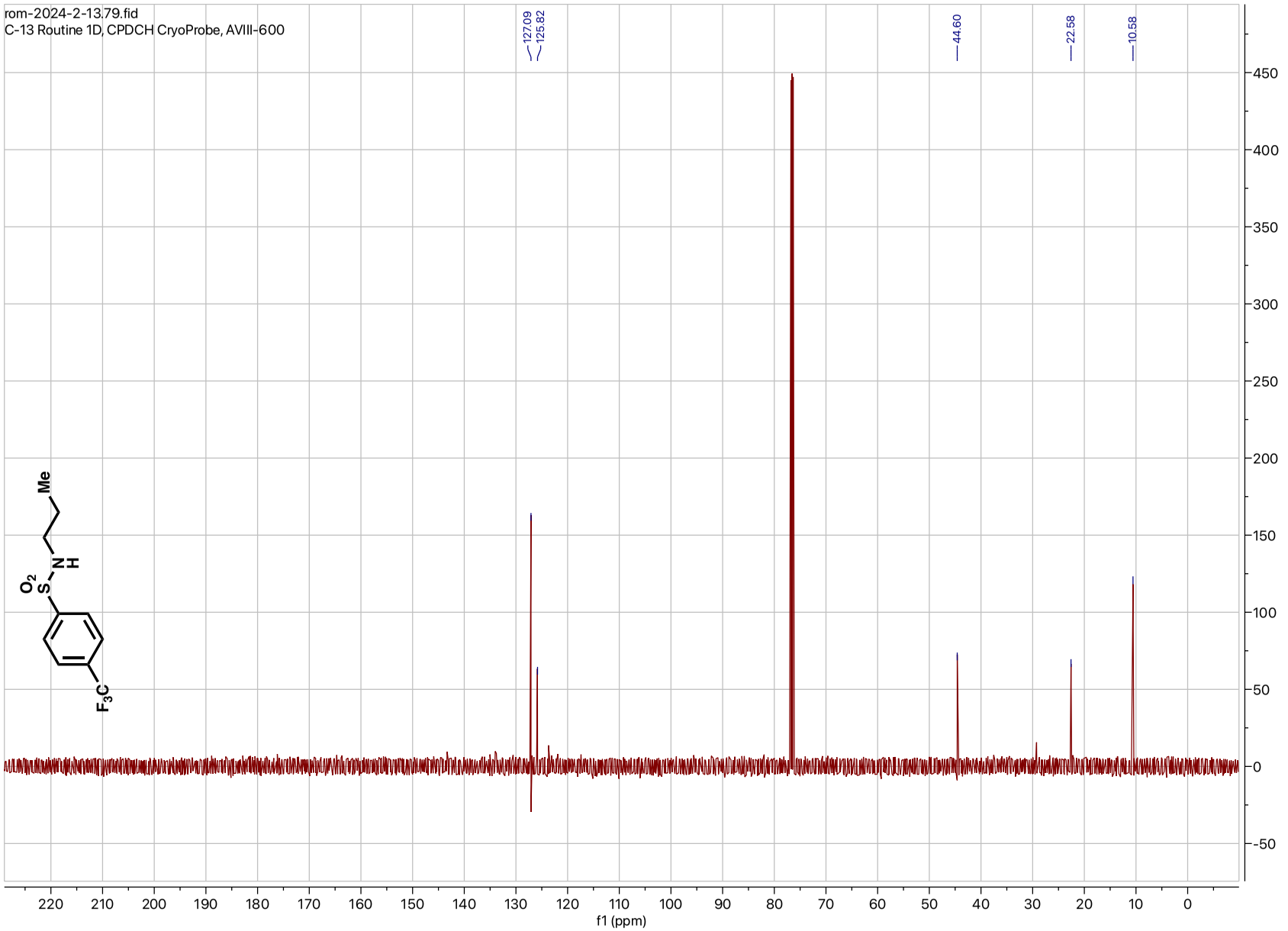
2.00
0.90
1.90
2.08
3.34
f1 (ppm)


rom-2024-2-13.79.fid
C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
127.09
125.82
44.60
22.58
10.58
Me
N
H
S
O2
F3C
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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