Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information for

# A Palladium/Norbornene Cooperative Catalysis to Access *N*-Containing bridged scaffolds

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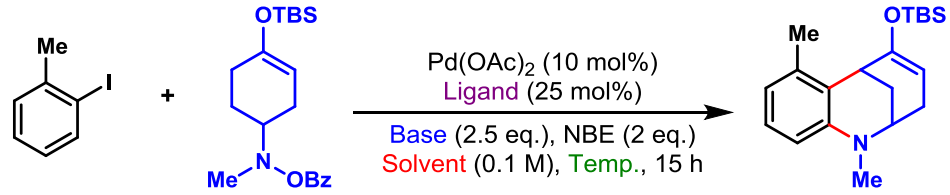
## 1. General information

All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Unless otherwise noted, all solvents were dried by JC Meyer Solvent Drying System. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or basic solution of $KMnO_4$ or acidic solution of *p*-anisaldehyde and heat as a developing agent. Nuclear magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were recorded with a Bruker DMX 400 (400 MHz, $^1$H at 400 MHz, $^{13}$C at 101 MHz). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00 ppm) and were referenced to residual solvent ($CDCl_3$, δ=7.26 ppm ($^1$H) and 77.00 ppm ($^{13}$C)). All the $^{19}$F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for $^1$H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). Gas chromatography (GC) were recorded on Agilent 7890 instrument and with biphenyl as internal standard. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer.

## 2. Optimization of reaction conditions[a].

**Table S1.** Optimization of reaction conditions in terms of solvent, base, temperature and ligand




**1a** (1.0 eq.) **2a'** (2.0 eq.) **3a'**

| Entry[a] | Base | Solvent | Ligand | Temp. (°C) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Cs_2CO_3$ | **$CH_3CN$** | $PPh_3$ | 80 | 2 |
| 2 | $Cs_2CO_3$ | **Toluene** | $PPh_3$ | 80 | 25 |
| 3 | $Cs_2CO_3$ | **DCE** | $PPh_3$ | 80 | 15 |
| 4 | $Cs_2CO_3$ | **DMF** | $PPh_3$ | 80 | trace |
| 5 | $Cs_2CO_3$ | **Dioxane** | $PPh_3$ | 80 | 21 |
| 6 | $Cs_2CO_3$ | **NMP** | $PPh_3$ | 80 | trace |
| 7 | $Cs_2CO_3$ | **DME** | $PPh_3$ | 80 | 16 |
| 8 | **$Cs_2CO_3$** | **THF** | $PPh_3$ | 80 | 35 |
| 9 | **$K_2CO_3$** | THF | $PPh_3$ | 80 | 8 |
| 10 | **CsOAc** | THF | $PPh_3$ | 80 | 0 |
| 11 | **$K_3PO_4$** | THF | $PPh_3$ | **80** | 33 |
| 12 | $Cs_2CO_3$ | THF | $PPh_3$ | **70** | 19 |
| 13 | $Cs_2CO_3$ | THF | $PPh_3$ | **90** | 45 |
| 14 | $Cs_2CO_3$ | THF | **$PPh_3$** | **100** | 30 |
| 15 | $Cs_2CO_3$ | THF | **XPhos** | 90 | 7 |
| 16 | $Cs_2CO_3$ | THF | **$PCy_3$** | 90 | 8 |
| 17 | $Cs_2CO_3$ | THF | **DPPE** | 90 | 0 |
| 18 | $Cs_2CO_3$ | THF | **DavePhos** | 90 | 11 |
| 19 | $Cs_2CO_3$ | THF | **JohnPhos** | 90 | 13 |
| 20 | $Cs_2CO_3$ | THF | **TFP** | 90 | 61 |

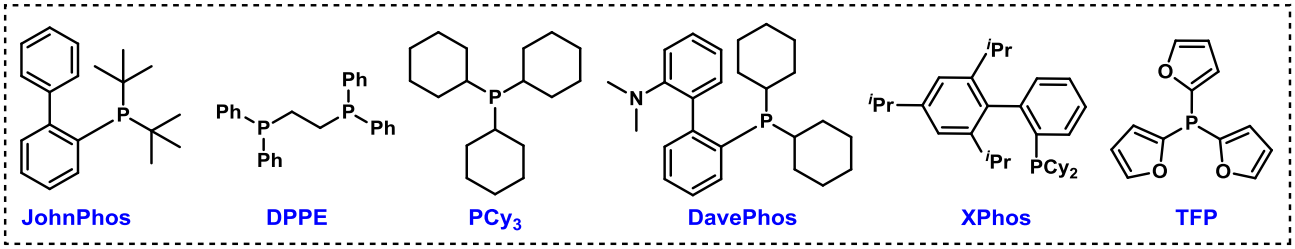
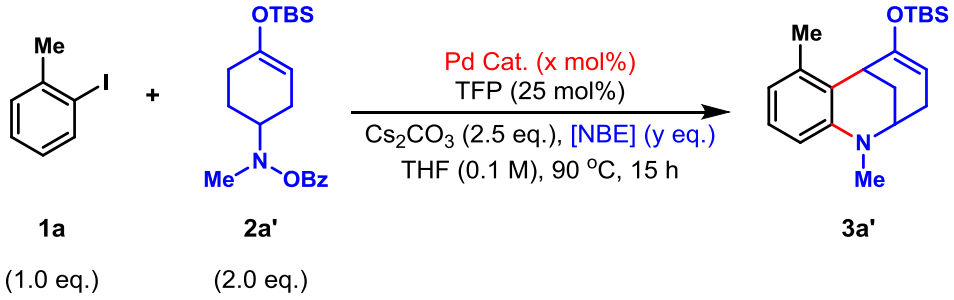
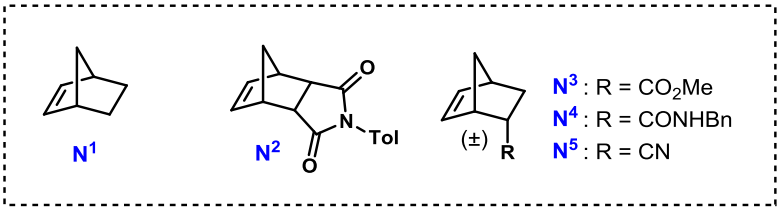


**Table S2.** Further optimization of reaction parameters




**1a** (1.0 eq.) **2a'** (2.0 eq.) **3a'**

| Entry[a] | [NBE] | Pd Cat. | x | y | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $N^1$ | **$Pd(OAc)_2$** | 10 | 2.0 | 61 |
| 2 | $N^1$ | **$Pd(TFA)_2$** | 10 | 2.0 | 62 |
| 3 | $N^1$ | **$[Pd(C_3H_5)Cl]_2$** | 5 | 2.0 | 26 |
| 4 | $N^1$ | **$PdCl_2$** | 10 | 2.0 | 60 |
| 5 | $N^1$ | **$Pd(PPh_3)_4$** | 10 | 2.0 | 44 |
| 6 | $N^1$ | **$Pd_2(dba)_3$** | 5 | 2.0 | 73 |
| 7 | **$N^1$** | $Pd_2(dba)_3$ | 5 | 0.5 | 62 |
| 8 | **$N^2$** | $Pd_2(dba)_3$ | 5 | 0.5 | >99(85)[c] |
| 9 | **$N^3$** | $Pd_2(dba)_3$ | 5 | 0.5 | 61 |
| 10 | **$N^4$** | $Pd_2(dba)_3$ | 5 | 0.5 | 26 |
| 20 | **$N^5$** | $Pd_2(dba)_3$ | 5 | 0.5 | 66 |

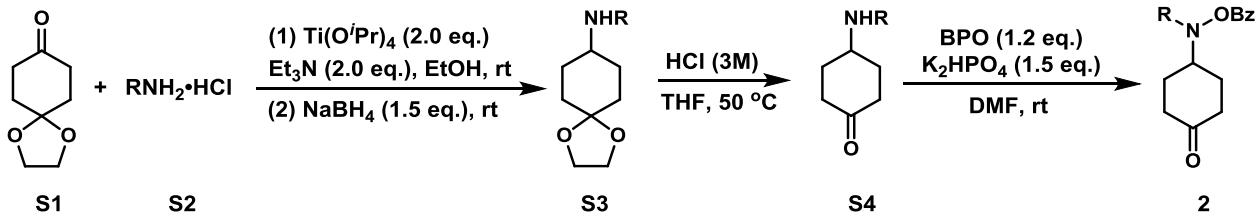



[a]The reaction was performed on 0.1 mmol scale. [b]GC yield with biphenyl as an internal standard. [c]Isolated yield in parentheses.

## 3. Preparation of aryl iodides.

Aryl iodides **1a** to **1c**, **1e** to **1h**, **1k** to **1q, 1s** and **1t** were commercially available and were used without further purification. Aryl iodides **1d**[1], **1i**[2], **1j**[3], **1r**[4] were known compounds and were synthesized by reported procedures.

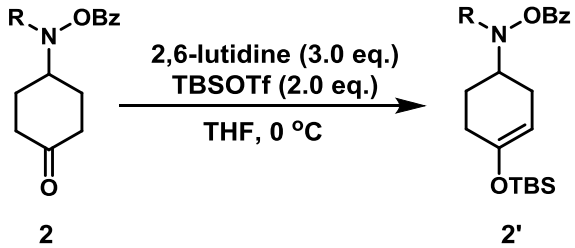
## 4. Preparation of amines.




A mixture of **S1** (0.78 g, 5 mmol, 1.0 eq.), **S2** (0.68 mg, 10mmol, 2.0 eq.), $Ti(O^iPr)_4$ (2.84 g, 10 mmol, 2.0 eq.), and $Et_3N$ (1.01 g, 10 mmol, 2.0 eq.) in absolute EtOH (10 mL) was stirred under Ar at ambient temperature for 10 h. $NaBH_4$ (0.28 g, 7.5 mmol, 1.5 eq.) was then added and stirred for additional 8 h at ambient temperature. The reaction was then quenched by pouring into aqueous ammonia (15 mL), the resulting inorganic precipitate was filtered off, and washed with dichloromethane (30 mL). The organic layer was separated and the remaining aqueous layer was extracted with dichloromethane (3×20 mL) and dried over $Na_2SO_4$. The combined organic extracts was concentrated *in vacuo* to afford **S3**, which was used for the next step without further purification[5].

**S3** was dissolved in THF (5 mL), HCl (3 M, 5 mL) and the solution was stirred at 50 °C for 3 h. The reaction mixture was basified with NaOH (3 M, 5 mL). The organic layer was separated and the remaining aqueous layer was extracted with dichloromethane (3×20 mL) and dried over $Na_2SO_4$. The combined organic extracts was concentrated *in vacuo* to afford **S4**, which was used for the next step without further purification[6].

Benzoyl peroxide (1.45 g, 6 mmol, 1.2 eq.) was added to a solution of **S4**, $K_2HPO_4$ (1.31 g, 7.5 mmol, 1.5 eq.) in DMF (15 mL). The mixture was stirred for 18 h under Ar at ambient temperature. Diluted with $H_2O$ and extracted with EtOAc (3×20 mL) and dried over $Na_2SO_4$. The combined organic extracts was concentrated *in vacuo* to afford **2**, which was used for the next step without further purification[7].

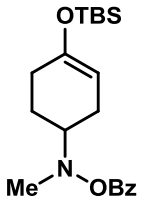



To a solution of **2** in dry THF (10 mL) was added 2,6-lutidine (0.97 mg, 9 mmol, 3.0 eq.)

under Ar at ambient temperature. The reaction mixture was cooled to 0 $^{o}$C and stirred for 5 min before TBSOTf (1.58 g, 6 mmol, 2.0 eq.) was added slowly via a syringe. The mixture was stirred for 1 h and was quenched by addition of sat. $NH_4Cl$. The organic layer was separated and the remaining aqueous layer was extracted with EtOAc (3×10 mL) and dried over $Na_2SO_4$. The combined organic extracts was concentrated *in vacuo*. The residue was purified by silica gel chromatography (Eluent: ethyl acetate / petroleum ether = 1:20) to give the target compound[8].

## 5. Characterization data for compounds 2'.

**_O_-benzoyl-_N_-(4-((_tert_-butyldimethylsilyl)oxy)cyclohex-3-en-1-yl)-_N_-methylhydroxylamine**




**2a'**

**Physical state**: pale oil.

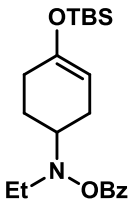
**Yield**: 57% over 4 steps from **S1**.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.42 (m, 2H), 4.79 (d, *J* = 7.8 Hz, 1H), 3.05-2.98 (m, 1H), 2.91 (s, 3H), 2.33-2.04 (m, 5H), 1.77-1.66 (m, 1H), 0.91 (s, 9H), 0.12 (d, *J* = 1.5 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.36, 150.39, 133.21, 129.61, 129.43, 128.57, 101.41, 63.80, 43.94, 29.21, 25.79, 18.14, -4.21, -4.39.

**HRMS** (ESI-TOF): calc'd for $C_{20}H_{31}NNaO_3Si$ [M+$Na^+$] 384.1965, found 384.1963.

**_O_-benzoyl-_N_-(4-((_tert_-butyldimethylsilyl)oxy)cyclohex-3-en-1-yl)-_N_-ethylhydroxylamine**




**2b'**

**Physical state**: pale oil.

**Yield**: 15% over 4 steps from **S1**.

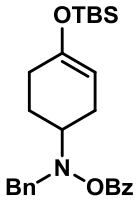
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.42 (m, 2H),

4.79-4.77 (m, 1H), 3.17-3.06 (m, 3H), 2.31-2.01 (m, 5H), 1.76-1.69 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.11 (s, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.12, 150.36, 133.20, 129.68, 129.23, 128.57, 101.57, 62.15, 50.18, 29.36, 25.76, 18.11, 12.03, -4.24, -4.40.

**HRMS** (ESI-TOF): calc'd for $C_{21}H_{33}NNaO_3Si$ [M+$Na^+$] 398.2122, found 398.2119.

**_O_-benzoyl-_N_-benzyl-_N_-(4-((_tert_-butyldimethylsilyl)oxy)cyclohex-3-en-1-yl)hydroxylamine**




**2c'**

**Physical state**: white solid.

**Melting point**: 63-65 ℃.

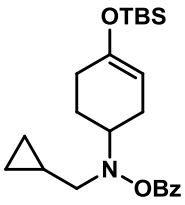
**Yield**: 37% over 4 steps from **S1**.

**$^{1}$H NMR** (4 00 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.5 Hz, 2H), 7.54-7.50 (m, 1H), 7.43-7.37 (m, 4H), 7.29-7.20 (m, 3H), 4.81-4.78 (m, 1H), 4.23 (q, *J* = 13.6 Hz, 3H), 3.21-3.14 (m, 1H), 2.40-2.29 (m, 2H), 2.22-2.04 (m, 3H), 1.83-1.73 (m, 1H), 0.90 (s, 9H), 0.12 (d, *J* = 1.9 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.36, 150.39, 136.21, 133.00, 129.62, 129.51, 129.34, 128.46, 128.40, 127.67, 101.56, 61.73, 59.94, 29.34, 25.79, 18.13, -4.24, -4.36.

**HRMS** (ESI-TOF): calc'd for $C_{26}H_{35}NNaO_3Si$ [M+$Na^+$] 460.2278, found 460.2271.

**_O_-benzoyl-_N_-(4-((_tert_-butyldimethylsilyl)oxy)cyclohex-3-en-1-yl)-_N_-(cyclopropylmethyl)hydroxylamine**




**2d'**

**Physical state**: pale oil.

**Yield**: 23% over 4 steps from **S1**.

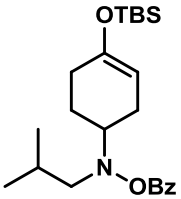
**$^{1}$H NMR** (4 00 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz,

2H), 4.78-4.76 (m, 1H), 3.17-3.10 (m, 1H), 2.91 (s, 2H), 2.31-2.14 (m, 3H), 2.07-2.01 (m, 2H), 1.77-1.66 (m, 1H), 1.10-1.01 (m, 1H), 0.89 (s, 9H), 0.46-0.42 (m, 2H), 0.14-0.06 (m, 8H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.87, 150.34, 133.07, 129.62, 129.49, 128.53, 101.58, 62.10, 60.86, 29.36, 25.75, 18.09, 8.66, -4.27, -4.41.

**HRMS** (ESI-TOF): calc'd for $C_{23}H_{35}NNaO_3Si$ [M+Na$^+$] 424.2278, found 424.2276.

***O*-benzoyl-*N*-(4-((*tert*-butyldimethylsilyl)oxy)cyclohex-3-en-1-yl)-*N*-isobutylhydroxylamine**




2e'

**Physical state**: pale oil.

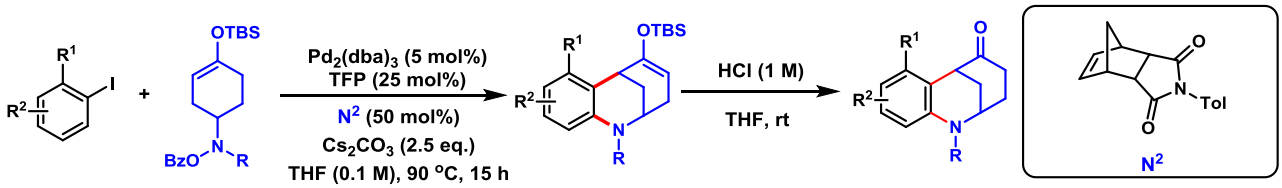
**Yield**: 46% over 4 steps from **S1**.

**$^1$H NMR** (4 00 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.42 (m, 2H), 4.79-4.76 (m, 1H), 3.07-3.05 (m, 1H), 2.84-2.73 (m, 2H), 2.28-2.14 (m, 3H), 2.07-2.01 (m, 2H), 1.80-1.61 (m, 2H), 0.97 (dd, *J* = 6.6, 2.3 Hz, 6H), 0.90 (s, 9H), 0.11 (s, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.78, 150.36, 133.09, 129.67, 129.50, 128.55, 101.79, 63.87, 63.06, 29.44, 26.58, 25.79, 21.18, 21.16, 18.13, -4.25, -4.38.

**HRMS** (ESI-TOF): calc'd for $C_{23}H_{37}NNaO_3Si$ [M+Na$^+$] 426.2435, found 424.2428.

## 6. General procedure for the synthesis of compound 3.

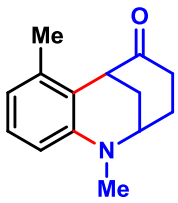



A 25 mL of oven-dried Schlenk tube equipped with a magnetic stir bar was charged under argon with $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.05 eq.), TFP (11.6 mg, 0.05 mmol, 0.25 eq.), $Cs_2CO_3$ (163.0 mg, 0.5 mmol, 2.5 eq.), **N$^2$** (26.0 mg, 0.1 mmol, 0.5 eq.) and dry THF (2.0 mL). Aryl iodide **1** (0.20 mmol, 1.0 eq.) and amine **2'** (0.40 mmol, 2.0 eq.) were added, then the reaction was heated to 90 $^o$C and stirred for 15 h. After the reaction mixture was cooled to r.t., it

was filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated *in vacuo*. The residue **3'** was dissolved in THF (3 mL), and 1M HCl (2 mL) was added. The reaction was stirred for additional 5 h at ambient temperature. Then, the reaction mixture was basified with saturated $NaHCO_3$. The organic layer was separated and the remaining aqueous layer was extracted with dichloromethane (3×10 mL) and dried over $Na_2SO_4$. The combined organic extracts was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel or purified by PTLC to give the desired product.

## 7. Characterization data for compounds 3.

**1,7-dimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3a**

**Physical state**: colorless oil.

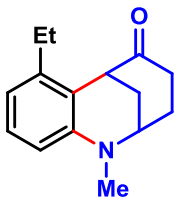
**Yield**: 77%.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 6.46 (d, *J* = 7.4 Hz, 1H), 3.90 (s, 1H), 3.58 (s, 1H), 3.09 (s, 3H), 2.44-2.32 (m, 2H), 2.27 (s, 3H), 2.19-2.14 (m, 2H), 2.08-2.02 (m, 1H), 1.89-1.80 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.11, 145.72, 137.22, 128.00, 117.74, 117.40, 107.93, 53.15, 47.49, 37.70, 34.72, 33.76, 29.53, 19.62.

**HRMS** (ESI-TOF): calc'd for $C_{14}H_{18}NO$ [M+H$^+$] 216.1383, found 216.1376.

**7-ethyl-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3b**

**Physical state**: yellow oil.

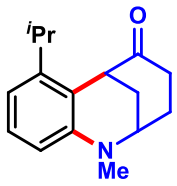
**Yield**: 82%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.9 Hz, 1H), 6.52 (t, *J* = 7.0 Hz, 2H), 3.97-3.96 (m, 1H), 3.58-3.57 (m, 1H), 3.09 (s, 3H), 2.81-2.72 (m, 1H), 2.57-2.42 (m, 1H), 2.40-2.34 (m, 2H), 2.19-2.14 (m, 2H), 2.08-2.02 (m, 1H), 1.88-1.79 (m, 1H), 1.16 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.70, 145.74, 143.17, 128.21, 116.77, 115.91, 107.80, 53.10, 46.93, 37.78, 34.81, 33.90, 29.73, 25.34, 15.09.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{20}NO$ [M+H$^+$] 230.1539, found 230.1539.

**7-isopropyl-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3c**

**Physical state**: white solid.

**Melting point**: 44-46 ℃.

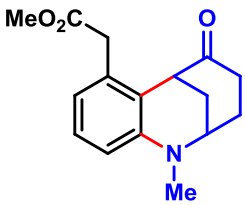
**Yield**: 76%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.51 (dd, *J* = 8.2, 1.4 Hz, 1H), 4.07-4.05 (m, 1H), 3.58-3.56 (m, 1H), 3.38-3.31 (m, 1H), 3.09 (s, 3H), 2.43-2.33 (m, 2H), 2.20-2.16 (m, 2H), 2.07-2.01 (m, 1H), 1.89-1.80 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.97, 147.87, 145.65, 128.32, 116.12, 112.67, 107.50, 52.94, 46.55, 37.81, 34.82, 33.94, 29.82, 28.13, 24.56, 23.06.

**HRMS** (ESI-TOF): calc'd for $C_{16}H_{22}NO$ [M+H$^+$] 244.1696, found 244.1689.

**methyl 2-(1-methyl-5-oxo-1,2,3,4,5,6-hexahydro-2,6-methanobenzo[*b*]azocin-7-yl)acetate**




**3d**

**Physical state**: yellow oil.

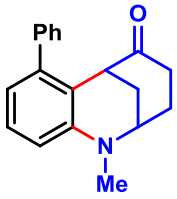
**Yield**: 71%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.9 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 6.49 (d, *J* = 7.4 Hz, 1H), 3.97-3.95 (m, 1H), 3.88 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H), 3.60-3.58 (m, 1H), 3.49 (d, *J* = 16.0 Hz, 1H), 3.09 (s, 3H), 2.43-2.29 (m, 2H), 2.20-2.14 (m, 2H), 2.09-2.04 (m, 1H), 1.88-1.80 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.09, 172.20, 145.99, 133.28, 128.34, 117.78, 117.67, 109.25, 53.06, 52.12, 47.33, 38.10, 37.71, 34.54, 33.64, 29.35.

**HRMS** (ESI-TOF): calc'd for $C_{16}H_{19}NNaO_3$ [M+$Na^+$] 296.1257, found 296.1263.

**1-methyl-7-phenyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3e**

**Physical state**: white solid.

**Melting point**: 122-124 ℃.

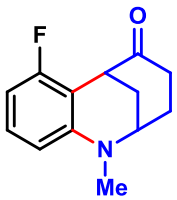
**Yield**: 88%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 3H), 7.21-7.17 (m, 3H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 1H), 3.69-3.68 (m, 1H), 3.59-3.57 (m, 1H), 3.15 (s, 3H), 2.53-2.41 (m, 2H), 2.23-2.19 (m, 1H), 2.06-1.96 (m, 2H), 1.87-1.78 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.76, 145.71, 143.10, 141.12, 129.79, 127.84, 127.77, 127.16, 117.89, 116.60, 108.85, 53.40, 48.15, 37.68, 35.38, 34.35, 30.24.

**HRMS** (ESI-TOF): calc'd for $C_{19}H_{19}NNaO$ [M+$Na^+$] 300.1359, found 300.1361.

**7-fluoro-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3f**

**Physical state**: yellow oil.

**Yield**: 34%.

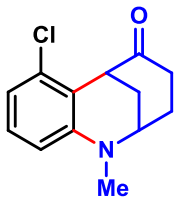
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.10-7.04 (m, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 6.35-6.31 (m, 1H), 4.03-4.01 (m, 1H), 3.60-3.59 (m, 1H), 3.10 (s, 3H), 2.43-2.31 (m, 2H), 2.23-2.15 (m, 2H), 2.05-2.00 (m, 1H), 1.90-1.81 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.07, 160.63 (d, *J* = 243.6 Hz), 146.92 (d, *J* = 7.2 Hz), 129.01 (d, *J* = 10.8 Hz), 106.15 (d, *J* = 20.7 Hz), 105.31 (d, *J* = 2.5 Hz), 102.20 (d, *J* = 22.4 Hz), 53.23, 43.34 (d, *J* = 3.4 Hz), 37.69, 34.56, 33.59, 28.94.

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -118.99.

**HRMS** (ESI-TOF): calc'd for $C_{13}H_{14}FKNO$ $[M+K^+]$ 258.0691, found 258.0697.

**7-chloro-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3g**

**Physical state**: white solid.

**Melting point**: 57-59 ℃.

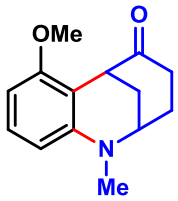
**Yield**: 48%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 8.1 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.54 (dd, *J* = 8.0, 0.9 Hz, 1H), 4.23-4.21 (m, 1H), 3.61-3.58 (m, 1H), 3.10 (s, 3H), 2.43-2.28 (m, 2H), 2.23-2.16 (m, 2H), 2.06-2.01 (m, 1H), 1.90-1.82 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 208.75, 146.95, 134.42, 128.87, 116.34, 116.28, 108.25, 53.41, 47.65, 37.69, 34.86, 33.85, 29.51.

**HRMS** (ESI-TOF): calc'd for $C_{13}H_{14}ClNNaO$ $[M+Na^+]$ 258.0656, found 258.0659.

**7-methoxy-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3h**

**Physical state**: white solid.

**Melting point**: 92-94 ℃.

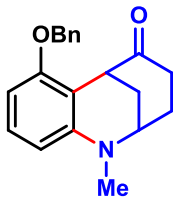
**Yield**: 46%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.3 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 4.13-4.11 (m, 1H), 3.78 (s, 3H), 3.55-3.54 (m, 1H), 3.09 (s, 3H), 2.42-2.34 (m, 2H), 2.15-2.11 (m, 2H), 2.02-1.98 (m, 1H), 1.89-1.79 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.54, 157.40, 146.61, 128.56, 106.97, 103.19, 98.34, 55.72, 53.23, 43.73, 37.68, 34.86, 33.97, 29.43.

**HRMS** (ESI-TOF): calc'd for $C_{14}H_{17}NNaO_2$ [M+$Na^+$] 254.1151, found 254.1153.

**7-(benzyloxy)-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3i**

**Physical state**: yellow solid.

**Melting point**: 74-76 ℃.

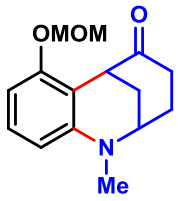
**Yield**: 37%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.41-7.37 (m, 2H), 7.32-7.27 (m, 1H), 7.07 (t, *J* = 8.3 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 6.25 (dd, *J* = 8.2, 0.9 Hz, 1H), 5.10-5.00 (m, 2H), 4.26-4.25 (m, 1H), 3.57-3.54 (m, 1H), 3.10 (s, 3H), 2.47-2.37 (m, 2H), 2.20-2.12 (m, 2H), 2.06-1.99 (m, 1H), 1.91-1.81 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.10, 156.31, 146.74, 137.67, 128.56, 128.54, 127.60, 126.97, 107.53, 103.39, 99.66, 69.85, 53.28, 43.87, 37.68, 34.91, 33.95, 29.44.

**HRMS** (ESI-TOF): calc'd for $C_{20}H_{21}NNaO_2$ [M+$Na^+$] 330.1465, found 330.1463.

**7-(methoxymethoxy)-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3j**

**Physical state**: yellow oil.

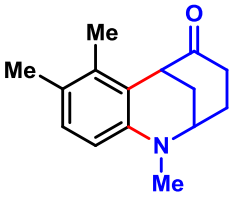
**Yield**: 77%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 8.3 Hz, 1H), 6.36 (dd, *J* = 14.0, 8.3 Hz, 2H), 5.16 (q, *J* = 6.7 Hz, 2H), 4.17-4.15 (m, 1H), 3.56-3.55 (m, 1H), 3.44 (s, 3H), 3.09 (s, 3H), 2.43-2.34 (m, 2H), 2.18-2.11 (m, 2H), 2.04-1.98 (m, 1H), 1.88-1.80 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.28, 154.78, 146.70, 128.61, 107.85, 103.88, 101.16, 94.02, 56.15, 53.20, 43.89, 37.67, 34.83, 33.91, 29.39.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{19}NNaO_3$ [M+$Na^+$] 284.1257, found 284.1257.

**1,7,8-trimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3k**

**Physical state**: white solid.

**Melting point**: 114-116 ℃.

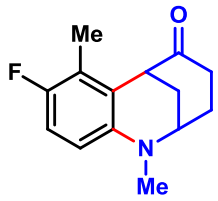
**Yield**: 74%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.3 Hz, 1H), 6.46 (d, *J* = 8.3 Hz, 1H), 3.98-3.97 (m, 1H), 3.56-3.53 (m, 1H), 3.07 (s, 3H), 2.43-2.31 (m, 2H), 2.19 (s, 3H), 2.18-2.12 (m, 5H), 2.07-2.01 (m, 1H), 1.89-1.78 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.56, 144.12, 135.64, 129.54, 123.63, 117.85, 107.41, 52.80, 47.77, 37.62, 34.84, 33.82, 29.99, 19.95, 15.25.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{20}NO$ [M+$H^+$] 230.1539, found 230.1536.

**8-fluoro-1,7-dimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3l**

**Physical state**: yellow solid.

**Melting point**: 101-103 ℃.

**Yield**: 79%.

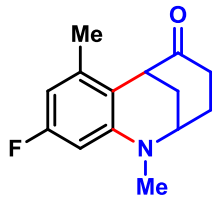
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 6.84 (t, *J* = 9.1 Hz, 1H), 6.41 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.90-3.89 (m, 1H), 3.56-3.55 (m, 1H), 3.06 (s, 3H), 2.42-2.27 (m, 2H), 2.20-2.15 (m, 5H), 2.06-2.00 (m, 1H), 1.87-1.79 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.67, 153.20 (d, *J* = 232.5 Hz), 142.12, 123.75 (d, *J* = 16.9 Hz), 118.48, 114.35 (d, *J* = 24.0 Hz), 107.53 (d, *J* = 7.9 Hz), 52.86, 47.65 (d, *J* = 2.1 Hz), 37.82, 34.72, 33.64, 29.63, 10.65 (d, *J* = 5.1 Hz).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -132.62.

**HRMS** (ESI-TOF): calc'd for $C_{14}H_{16}FNNaO$ [M+$Na^+$] 256.1108, found 256.1110.

**9-fluoro-1,7-dimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3m**

**Physical state**: yellow solid.

**Melting point**: 48-50 ℃.

**Yield**: 87%.

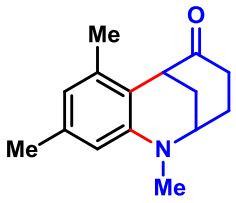
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 6.23-6.16 (m, 2H), 3.84-3.83 (m, 1H), 3.58-3.57 (m, 1H), 3.06 (s, 3H), 2.43-2.29 (m, 2H), 2.23 (s, 3H), 2.19-2.14 (m, 2H), 2.05-2.00 (m, 1H), 1.89-1.82 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.72, 163.03 (d, *J* = 240.9 Hz), 147.14 (d, *J* = 11.7 Hz), 138.90 (d, *J* = 10.0 Hz), 113.09 (d, *J* = 2.3 Hz), 104.04 (d, *J* = 21.6 Hz), 94.92 (d, *J* = 26.4 Hz), 53.13, 46.86, 37.79, 34.46, 33.63, 29.53, 19.76 (d, *J* = 2.0 Hz).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -114.74.

**HRMS** (ESI-TOF): calc'd for $C_{14}H_{16}FNNaO$ [M+$Na^+$] 256.1108, found 256.1109.

**1,7,9-trimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3n**

**Physical state**: yellow oil.

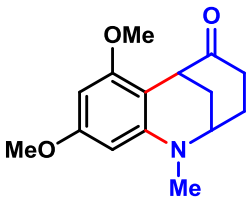
**Yield**: 76%.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 6.31 (s, 1H), 3.86-3.85 (m, 1H), 3.55 (s, 1H), 3.08 (s, 3H), 2.42-2.32 (m, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 2.17-2.12 (m, 2H), 2.07-2.01 (m, 1H), 1.87-1.78 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.30, 145.72, 137.71, 137.05, 118.73, 114.78, 108.58, 53.19, 47.24, 37.71, 34.65, 33.75, 29.75, 21.76, 19.51.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{19}NNaO$ [M+$Na^+$] 252.1359, found 252.1360.

**7,9-dimethoxy-1-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3o**

**Physical state**: white solid.

**Melting point**: 110-112 ℃.

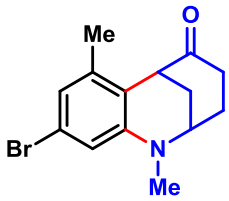
**Yield**: 65%.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.88 (d, *J* = 2.2 Hz, 1H), 5.83 (d, *J* = 2.2 Hz, 1H), 4.01-3.99 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.53-3.52 (m, 1H), 3.08 (s, 3H), 2.45-2.33 (m, 2H), 2.15-2.08 (m, 2H), 2.01-1.96 (m, 1H), 1.89-1.76 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.69, 160.65, 158.16, 147.09, 100.18, 88.81, 85.91, 55.68, 55.22, 53.46, 43.22, 37.72, 34.58, 33.81, 29.65.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{19}NNaO_3$ [M+$Na^+$] 284.1257, found 284.1262.

**9-bromo-1,7-dimethyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3p**

**Physical state**: yellow solid.

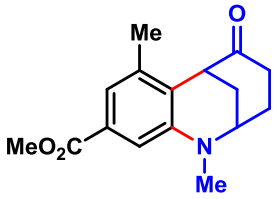
**Melting point**: 82-84 ℃.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 6.63 (d, *J* = 1.8 Hz, 1H), 6.59 (d, *J* = 1.9 Hz, 1H), 3.84-3.82 (m, 1H), 3.58-3.56 (m, 1H), 3.07 (s, 3H), 2.41-2.26 (m, 2H), 2.21 (s, 3H), 2.19-2.13 (m, 2H), 2.02-1.96 (m, 1H), 1.88-1.81 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.32, 146.77, 138.87, 122.05, 120.26, 116.27, 110.59, 53.17, 47.10, 37.76, 34.54, 33.59, 29.30, 19.39.

**HRMS** (ESI-TOF): calc'd for $C_{14}H_{17}BrNO$ $[M+H^+]$ 294.0488, found 294.0500.

**methyl 1,7-dimethyl-5-oxo-1,2,3,4,5,6-hexahydro-2,6-methanobenzo[*b*] azocine-9-carboxylate**




**3q**

**Physical state**: yellow oil.

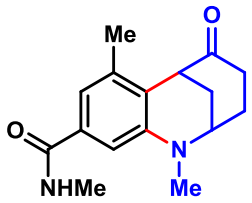
**Yield**: 72%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 1.6 Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 3.95-3.94 (m, 1H), 3.89 (s, 3H), 3.61 (s, 1H), 3.15 (s, 3H), 2.45-2.38 (m, 1H), 2.33-2.24 (m, 4H), 2.22-2.16 (m, 2H), 2.06-2.00 (m, 1H), 1.90-1.82 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.16, 167.90, 145.72, 137.34, 129.47, 122.00, 118.76, 108.69, 53.11, 52.17, 47.81, 37.82, 34.80, 33.71, 29.28, 19.67.

**HRMS** (ESI-TOF): calc'd for $C_{16}H_{19}NNaO_3$ $[M+Na^+]$ 296.1257, found 296.1263.

***N*,1,7-trimethyl-5-oxo-1,2,3,4,5,6-hexahydro-2,6-methanobenzo[*b*]azocine-9-carboxamide**




**3r**

**Physical state**: white solid.

**Melting point**: 196-198 ℃.

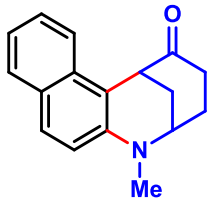
**Yield**: 83%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.70 (s, 1H), 6.12 (s, 1H), 3.92-3.91 (m, 1H), 3.60 (s, 1H), 3.14 (s, 3H), 2.99 (d, *J* = 4.9 Hz, 3H), 2.44-2.38 (m, 1H), 2.33-2.24 (m, 4H), 2.21-2.15 (m, 2H), 2.05-1.99 (m, 1H), 1.90-1.81 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.33, 169.10, 145.96, 137.31, 134.43, 120.30, 115.21, 107.02, 53.17, 47.61, 37.87, 34.71, 33.67, 29.28, 26.94, 19.77.

**HRMS** (ESI-TOF): calc'd for $C_{16}H_{20}N_2NaO_2$ [M+$Na^+$] 295.1417, found 295.1417.

**6-methyl-3,4,5,6-tetrahydro-1,5-methanonaphtho[2,1-*b*]azocin-2(1*H*)-one**




**3s**

**Physical state**: yellow oil.

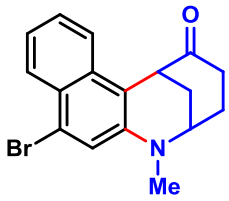
**Yield**: 71%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.70-7.68 (m, 1H), 7.66 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 9.1 Hz, 1H), 4.37 (s, 1H), 3.64 (s, 1H), 3.24 (s, 3H), 2.51-2.27 (m, 3H), 2.21-2.12 (m, 2H), 1.96-1.87 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.91, 143.48, 132.61, 129.04, 128.40, 127.24, 126.36, 121.50, 121.35, 113.57, 109.28, 53.35, 46.19, 37.87, 34.70, 33.86, 29.11.

**HRMS** (ESI-TOF): calc'd for $C_{17}H_{17}NNaO$ [M+$Na^+$] 274.1202, found 274.1204.

**8-bromo-6-methyl-3,4,5,6-tetrahydro-1,5-methanonaphtho[2,1-*b*]azocin-2(1*H*)-one**




**3t**

**Physical state**: yellow solid.

**Melting point**: 137-139 ℃.

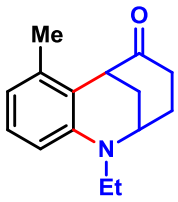
**Yield**: 74%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.48-7.44 (m, 2H), 7.28-7.24 (m, 1H), 4.35-4.33 (m, 1H), 3.65-3.62 (m, 1H), 3.22 (s, 3H), 2.49-2.42 (m, 1H), 2.38-2.26 (m, 2H), 2.22-2.18 (m, 1H), 2.12-2.06 (m, 1H), 1.96-1.87 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 209.31, 143.66, 133.48, 127.92, 127.68, 124.66, 123.99, 122.67, 121.72, 117.44, 109.31, 53.32, 46.08, 37.80, 34.61, 33.75, 28.96.

**HRMS** (ESI-TOF): calc'd for $C_{17}H_{16}BrNNaO$ [M+$Na^+$] 352.0307, found 352.0310.

**1-ethyl-7-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3ab**

**Physical state**: yellow oil.

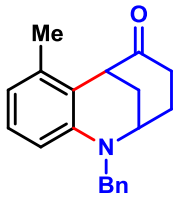
**Yield**: 35%.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.05-7.01 (m, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 6.44 (d, *J* = 7.3 Hz, 1H), 3.92-3.90 (m, 1H), 3.62-3.61 (m, 1H), 3.59-3.53 (m, 1H), 3.47-3.38 (m, 1H), 2.43-2.30 (m, 2H), 2.27 (s, 3H), 2.21-2.13 (m, 2H), 1.95-1.90 (m, 1H), 1.88-1.81 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.13, 144.25, 137.60, 127.95, 117.28, 117.16, 107.93, 51.28, 47.62, 44.27, 34.99, 34.84, 29.65, 19.71, 12.46.

**HRMS** (ESI-TOF): calc'd for $C_{15}H_{20}NO$ [M+$H^+$] 230.1539, found 230.1546.

**1-benzyl-7-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3ac**

**Physical state**: white solid.

**Melting point**: 93-95 ℃.

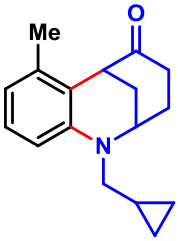
**Yield**: 31% (The reaction was run in DCE with 2.0 equiv of **N**[2] as the mediator).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.26 (d, *J* = 7.1 Hz, 3H), 6.92 (t, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.77 (d, *J* = 17.4 Hz, 1H), 4.60 (d, *J* = 17.5 Hz, 1H), 3.98 (s, 1H), 3.70 (s, 1H), 2.53-2.38 (m, 2H), 2.30 (s, 3H), 2.27-2.13 (m, 3H), 1.91-1.83 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.03, 145.07, 138.58, 137.47, 128.91, 128.05, 127.12, 126.13, 118.03, 117.22, 108.73, 53.01, 51.74, 47.59, 35.01, 34.08, 29.83, 19.67.

**HRMS** (ESI-TOF): calc'd for $C_{20}H_{22}NO$ [M+H$^+$] 292.1696, found 292.1687.

**1-(cyclopropylmethyl)-7-methyl-1,3,4,6-tetrahydro-2,6-methanobenzo[*b*]azocin-5(2*H*)-one**




**3ad**

**Physical state**: brown oil.

**Yield**: 50% (10 mol % $Pd_2(dba)_3$ and 50 mol % TFP were applied).

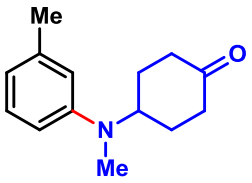
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.03 (t, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 7.3 Hz, 1H), 3.92-3.90 (m, 1H), 3.70-3.69 (m, 1H), 3.51 (dd, *J* = 15.2, 5.4 Hz, 1H), 3.17 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.44-2.35 (m, 2H), 2.27 (s, 3H), 2.19-2.13 (m, 2H), 2.04-1.99 (m, 1H), 1.89-1.79 (m, 1H), 1.21-1.13 (m, 1H), 0.58-0.54 (m, 2H), 0.35-0.30 (m, 1H), 0.25-0.21 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.32, 144.97, 137.60, 127.91, 117.45, 117.08, 108.34, 54.24, 51.90, 47.58, 34.96, 34.82, 29.51, 19.73, 9.66, 4.28, 3.59.

**HRMS** (ESI-TOF): calc'd for $C_{17}H_{22}NO$ [M+H$^+$] 256.1696, found 256.1698.

## 8. Characterization data for compounds 4.

**4-(methyl(*m*-tolyl)amino)cyclohexan-1-one**




**4a**

**Physical state**: yellow oil.

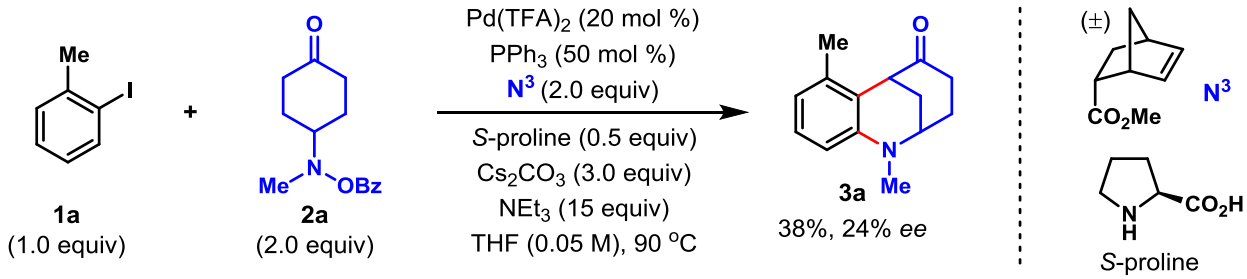
**Yield**: 17%.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.14 (m, 1H), 6.70-6.67 (m, 2H), 6.61 (d, *J* = 7.4 Hz, 1H), 4.12-4.04 (m, 1H), 2.77 (s, 3H), 2.52-2.48 (m, 4H), 2.34 (s, 3H), 2.13-2.06 (m, 2H), 2.01-1.90 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 210.47, 150.21, 139.10, 129.23, 118.67, 115.04, 111.42, 56.70, 40.30, 31.79, 28.89, 22.07.

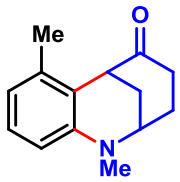
**HRMS** (ESI-TOF): calc'd for $C_{14}H_{20}NO$ [M+H$^+$] 218.1539, found 218.1534.

## 9. Preliminary asymmetric studies.




A 25 mL of oven-dried Schlenk tube equipped with a magnetic stir bar was charged under argon with $Pd(TFA)_2$ (6.7 mg, 0.02 mmol, 0.2 eq.), $PPh_3$ (13.2 mg, 0.05 mmol, 0.5 eq.), $Cs_2CO_3$ (98.0 mg, 0.3 mmol, 3.0 eq.), *S*-proline (5.8 mg, 0.05 mmol, 0.5 eq.) and dry THF (2.0 mL). $NEt_3$ (151.8 mg, 1.5 mmol, 15.0 eq.), **N$^3$** (30.5 mg, 0.2 mmol, 2.0 eq.), Aryl iodide **1a** (21.8 mg, 0.10 mmol, 1.0 eq.) and amine **2a** (50.0 mg, 0.20 mmol, 2.0 eq.) were added, then the reaction was heated to 90 $^o$C and stirred for 12 h. After the reaction mixture was cooled to r.t., it was

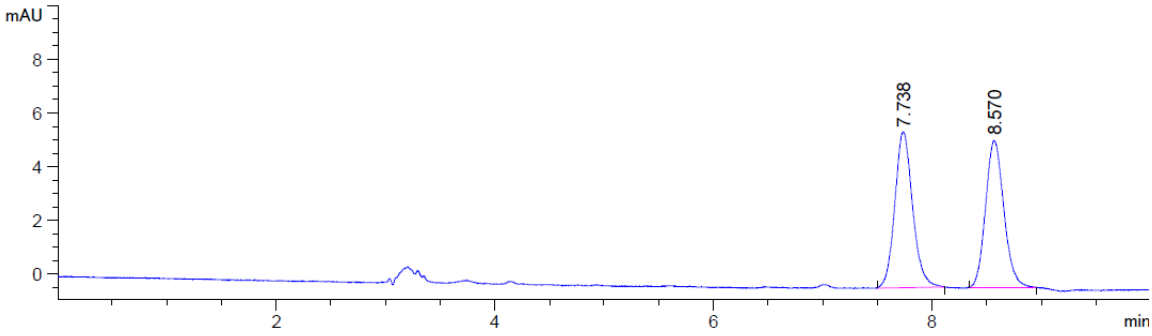
filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel or purified by PTLC to give the desired product **3a**.




**3a**

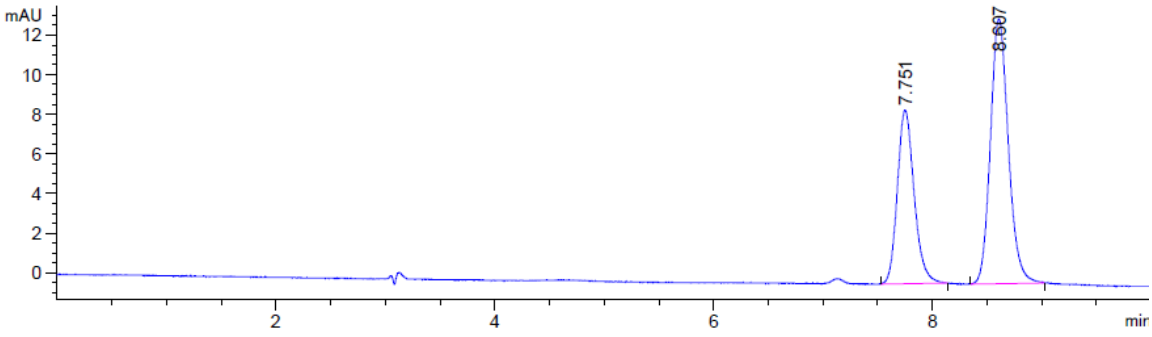
Colorless oil, 38% yield, 24% *ee*. The *ee* was determined by HPLC (Daicel Chiralpak OJ-H column, n-hexane/i-PrOH, 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm). t (minor) = 7.751 min; t (major) = 8.607 min.

Racemic sample of **3a**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.738 | BB | 0.1369 | 65.55648 | 5.79680 | 50.7399 |
| 2 | 8.570 | BB | 0.1373 | 63.64460 | 5.46652 | 49.2601 |

Enantioenriched sample of **3a**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.751 | BB | 0.1393 | 93.31808 | 8.76079 | 38.0800 |
| 2 | 8.607 | BB | 0.1651 | 151.74010 | 13.35140 | 61.9200 |

**10. X-ray crystallographic data for 3t.**

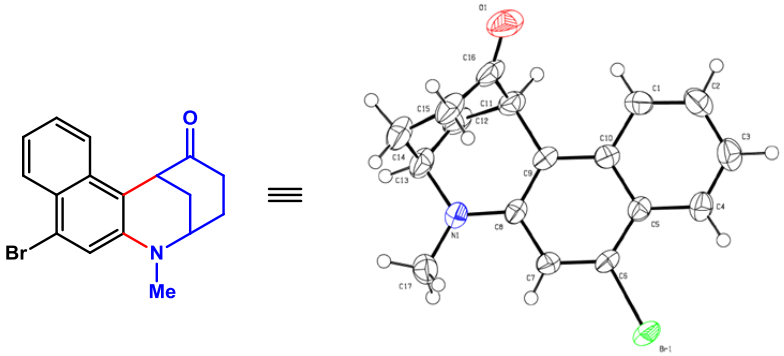



**Table 3.** Crystal data for **3t**

| | | |
|---|---|---|
| Identification code | CCDC 1911279 | |
| Empirical formula | C17H16BrNO | |
| Molecular formula | C17H16BrNO | |
| Formula weight | 330.22 | |
| Temperature | 296(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 23.7222(13) Å | α= 90 °. |

| | | |
|---|---|---|
| | b = 10.0218(6) Å | β= 125.646(2) °. |
| | c = 14.5030(8) Å | γ = 90 °. |
| Volume | 2801.9(3) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.566 $Mg/m^3$ | |
| Absorption coefficient | 3.945 $mm^{-1}$ | |
| F(000) | 1344 | |
| Crystal size | 0.120 x 0.060 x 0.060 $mm^3$ | |
| Theta range for data collection | 4.587 to 68.871 °. | |
| Index ranges | -28<=h<=28, -12<=k<=12, -16<=l<=16 | |
| Reflections collected | 17347 | |
| Independent reflections | 2573 [R(int) = 0.0515] | |
| Completeness to theta = 67.679 ° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2573 / 0 / 234 | |
| Goodness-of-fit on $F^2$ | 1.120 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0387, wR2 = 0.1021 | |
| R indices (all data) | R1 = 0.0390, wR2 = 0.1024 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.718 and -0.681 $e.Å^{-3}$ | |

**11. Reference.**


[1] E. Marchal, P. Uriac, B. Legouin, L. Toupet, P. Weghe, *Tetrahedron* **2007**, *63*, 9979-9990.

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[7] Z. Dong, G. Dong, *J. Am. Chem. Soc.* **2013**, *135*, 18350-18353.

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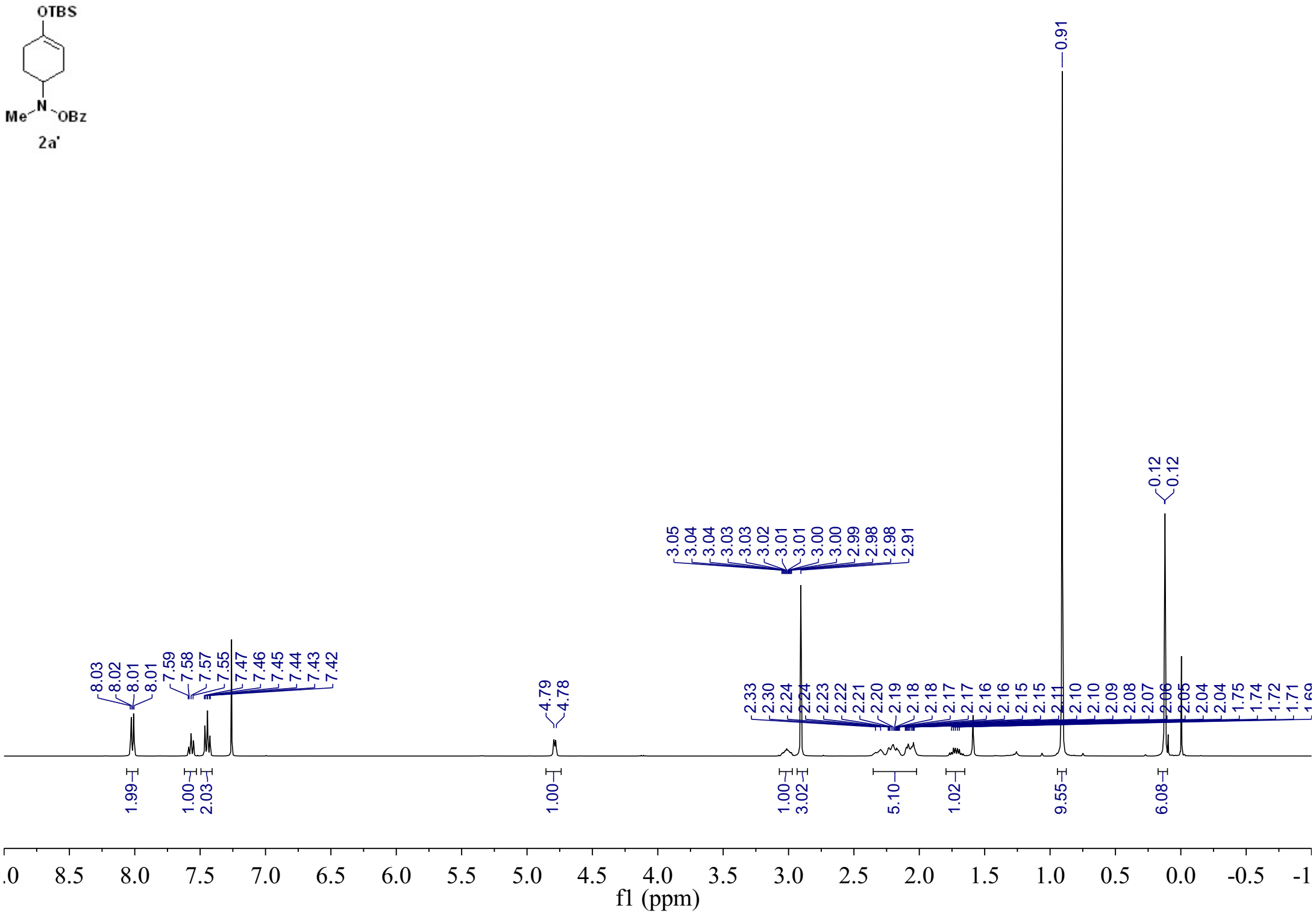
**12. NMR Spectra.**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OBz
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8.01
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7.58
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7.47
7.46
7.45
7.44
7.43
7.42
4.79
4.78
3.05
3.04
3.04
3.03
3.03
3.02
3.01
3.01
3.00
3.00
2.99
2.98
2.98
2.91
2.33
2.30
2.24
2.24
2.23
2.22
2.21
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.11
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.04
1.75
1.74
1.72
1.71
0.91
0.12
0.12
1.99
1.00
2.03
1.00
1.00
3.02
5.10
1.02
9.55
6.08
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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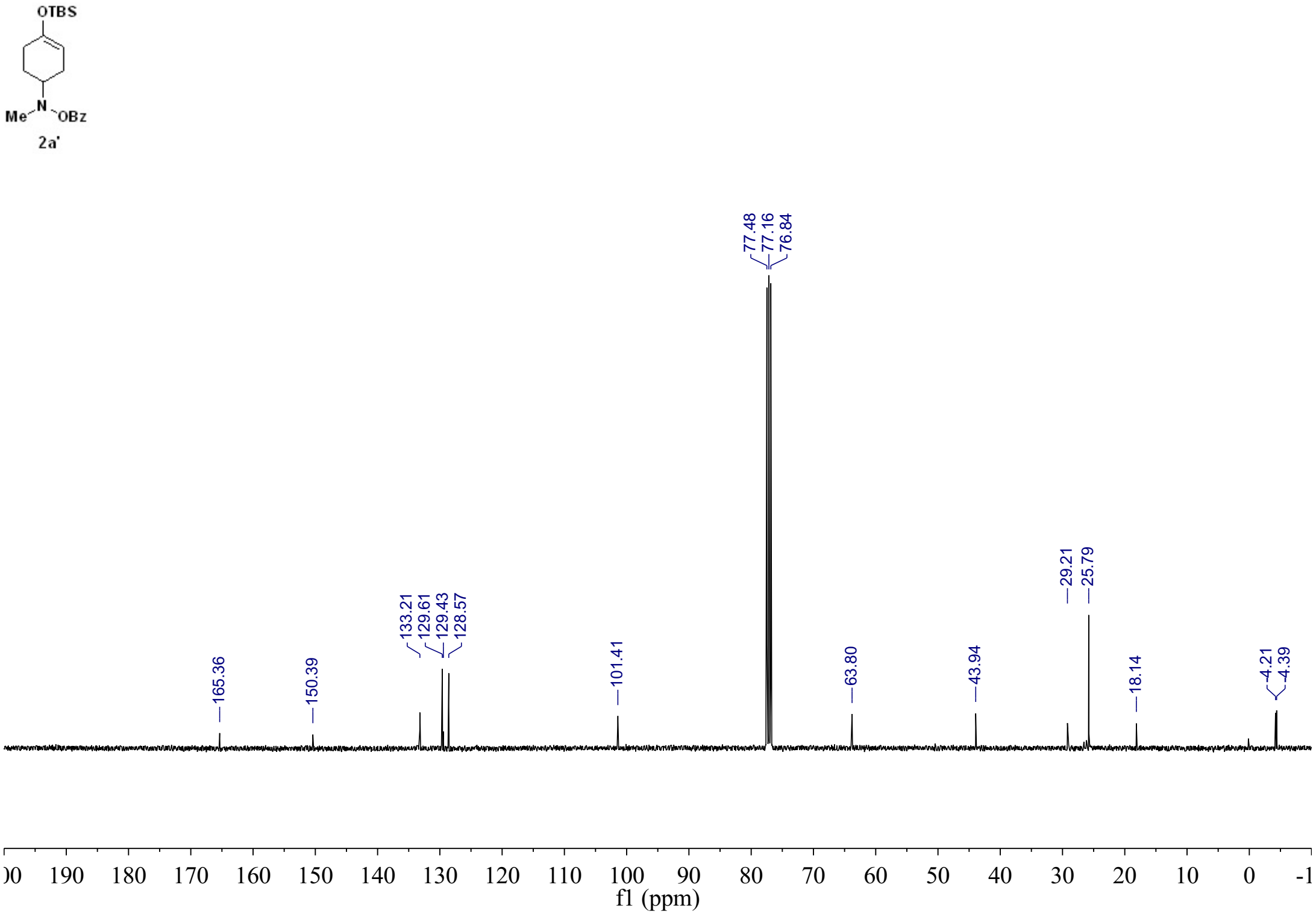
0.0
-0.5
-1
f1 (ppm)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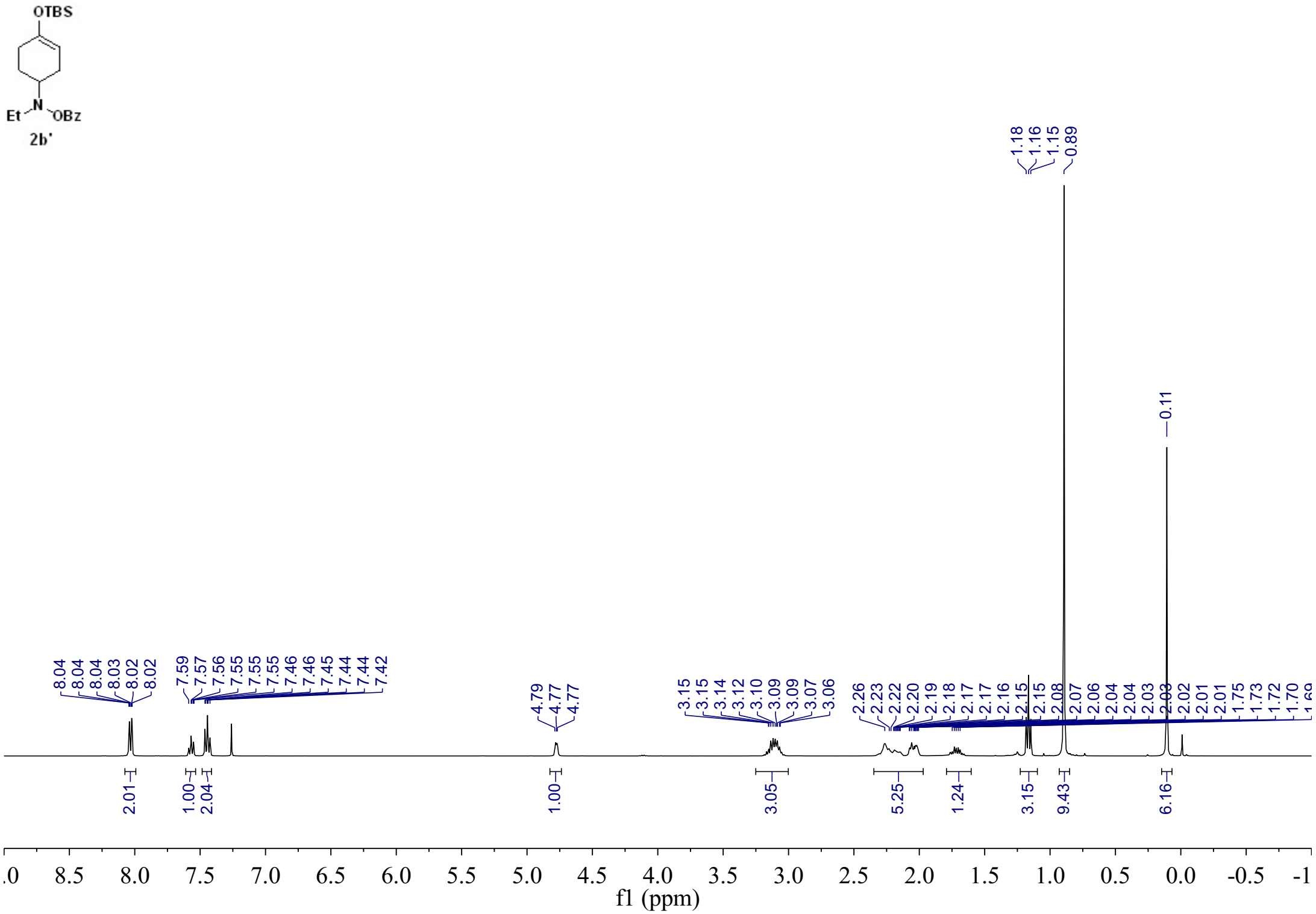
4.39
f1 (ppm)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Et
N
OBz
2b'
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8.04
8.03
8.02
8.02
7.59
7.57
7.56
7.55
7.55
7.55
7.46
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3.15
3.15
3.14
3.12
3.10
3.09
3.09
3.07
3.06
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2.16
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2.07
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2.04
2.03
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1.72
1.70
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2.04
1.00
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1.24
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7.0
6.5
6.0
5.5
5.0
4.5
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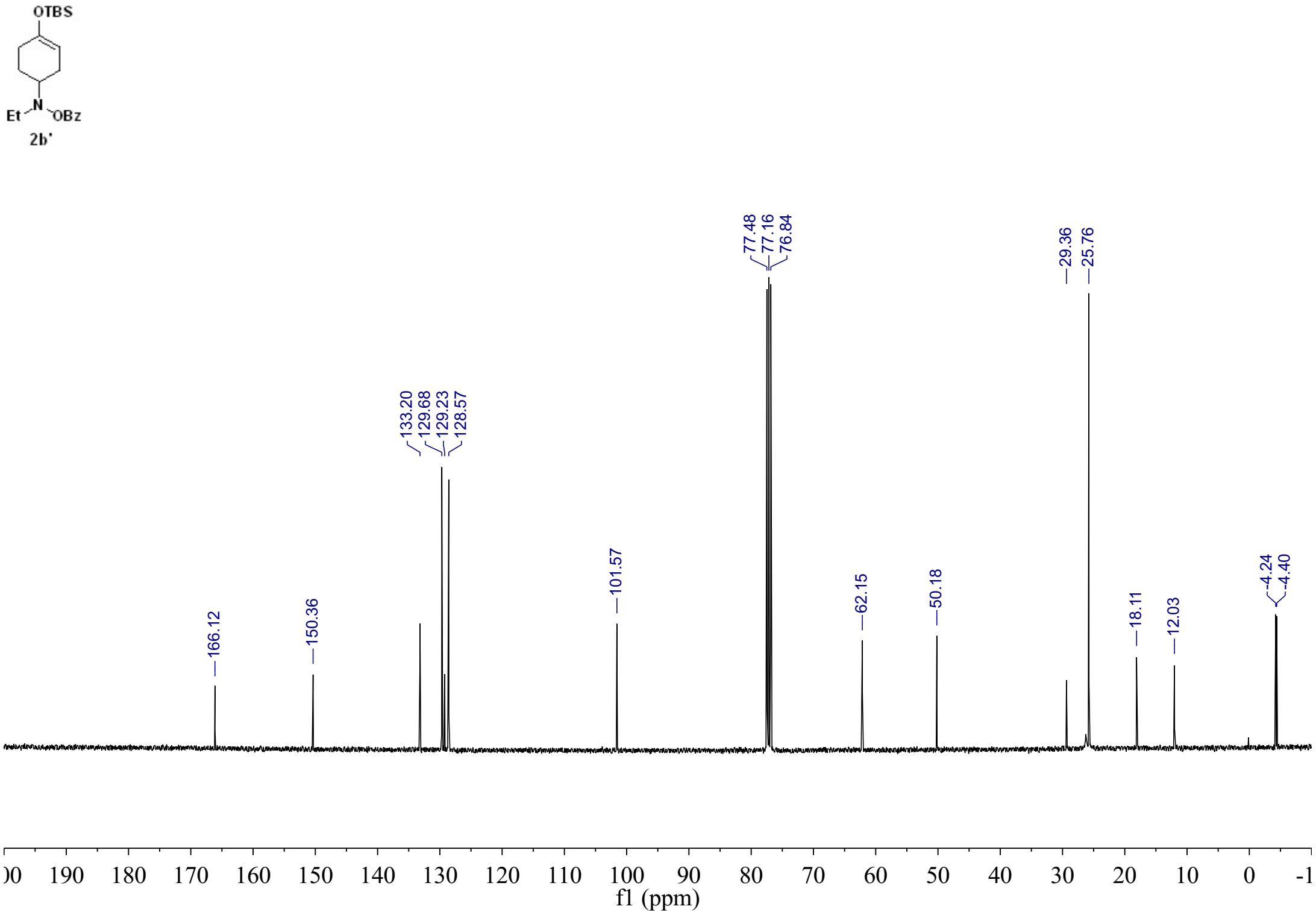
f1 (ppm)


OTBS
Et
N
OBz
2b'
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133.20
129.68
129.23
128.57
101.57
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77.16
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62.15
50.18
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25.76
18.11
12.03
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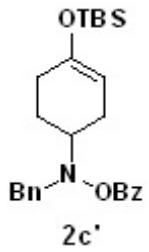
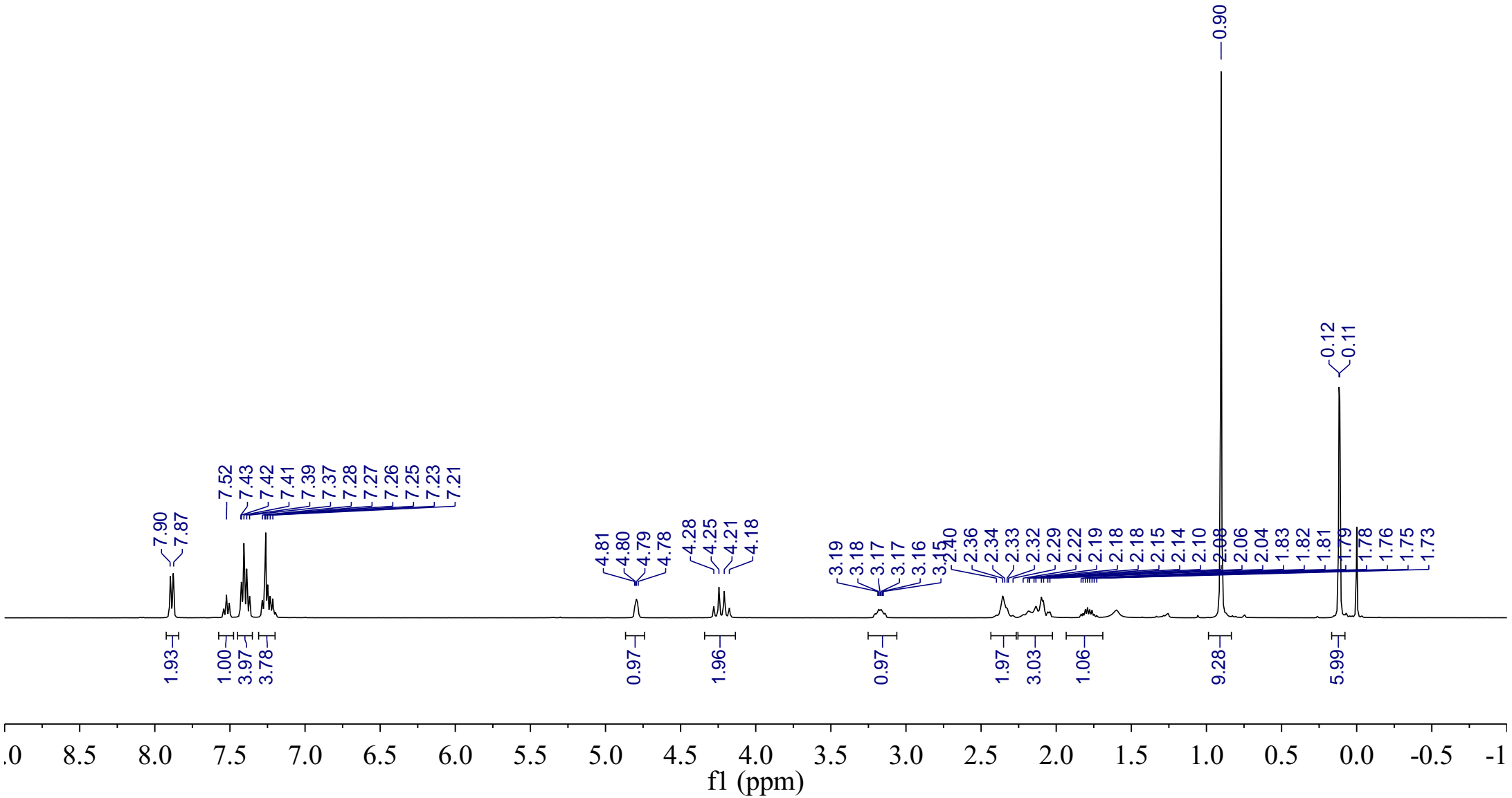
f1 (ppm)


OTBS
Bn
N
OBz

2c'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2.10
2.08
2.06
2.04
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1.82
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1.96
0.97
1.97
3.03
1.06
9.28
5.99
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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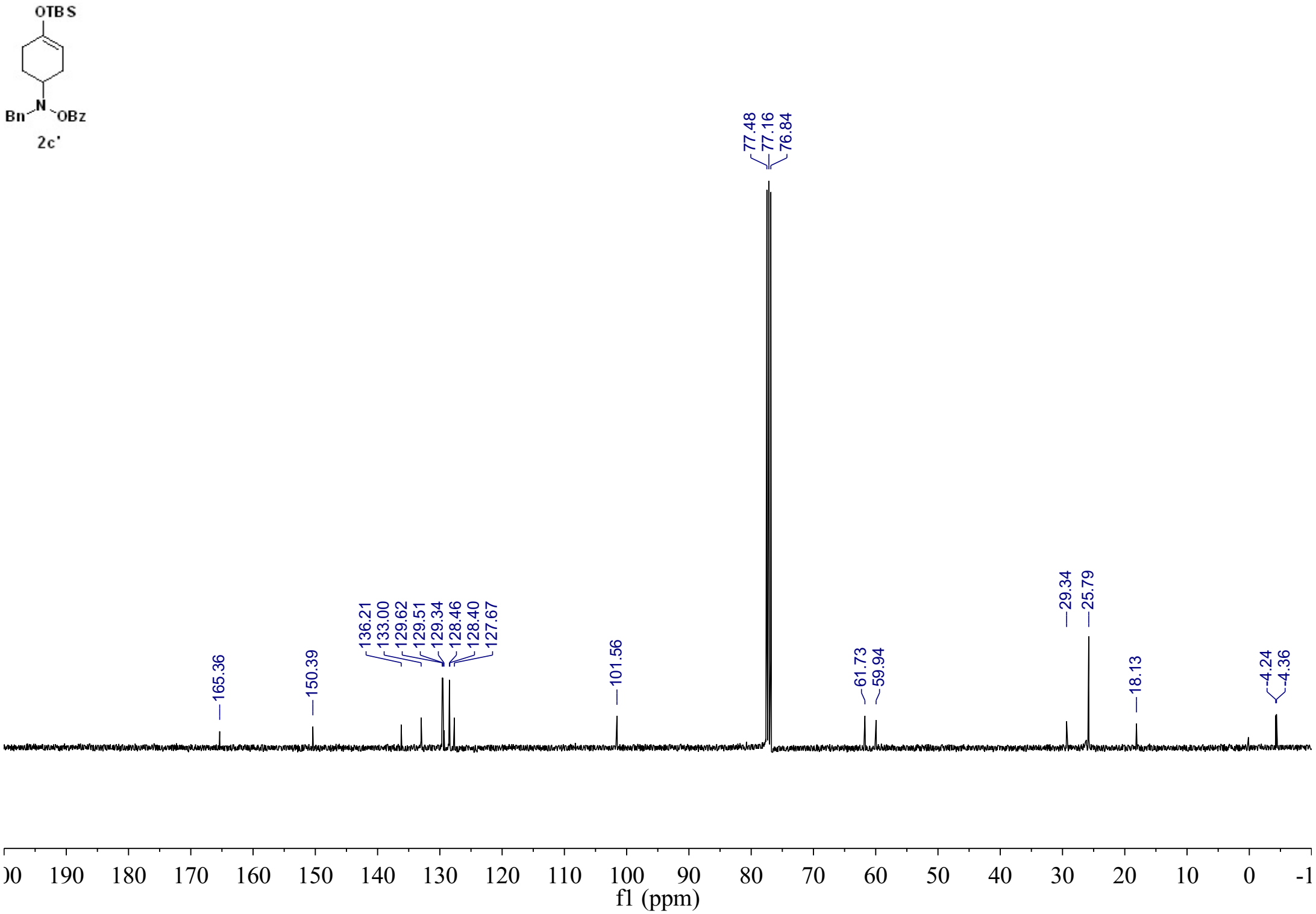
f1 (ppm)


OTBS
Bn
N
OBz
2c'
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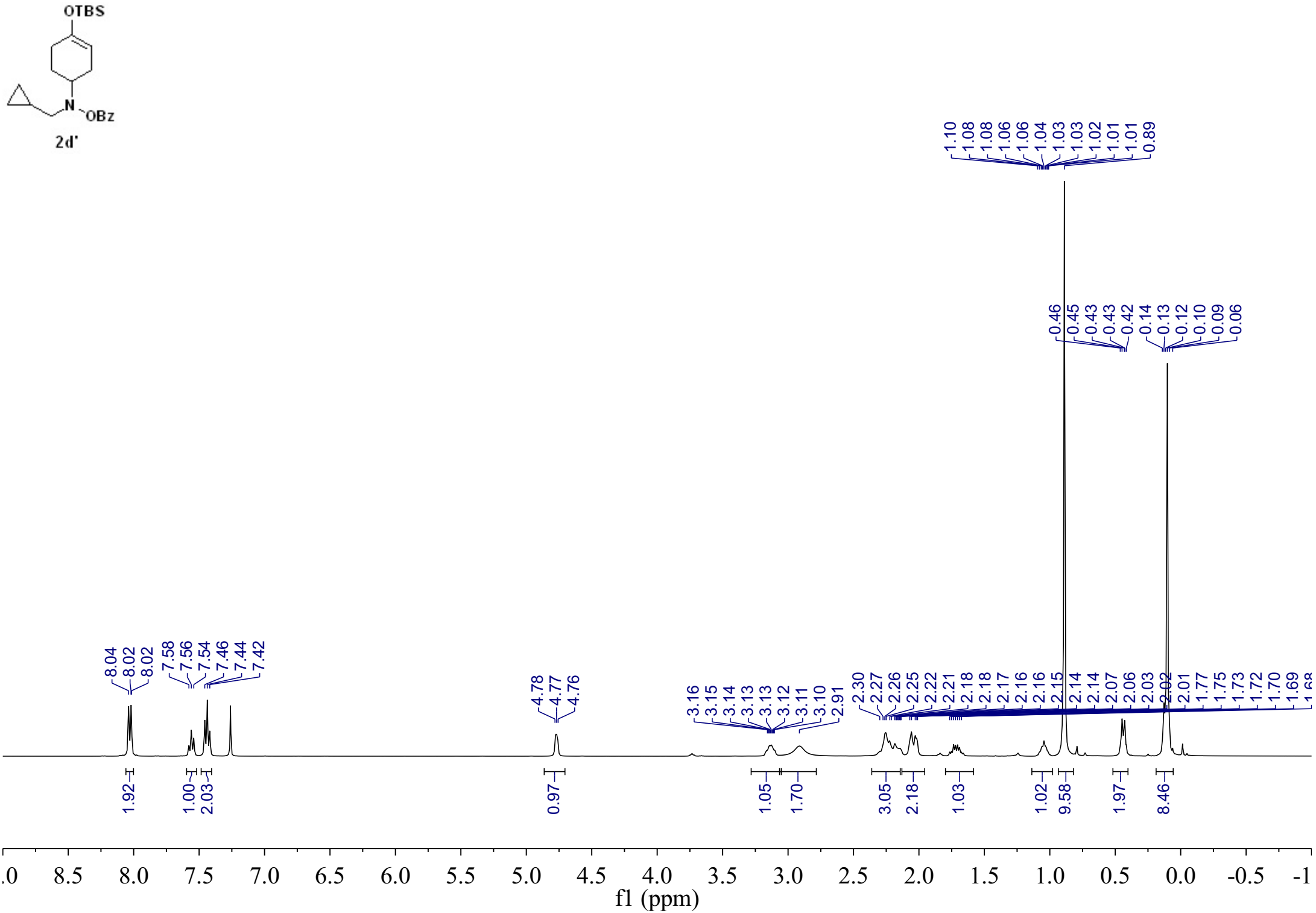
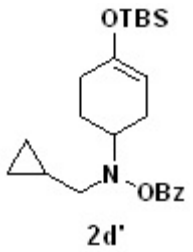
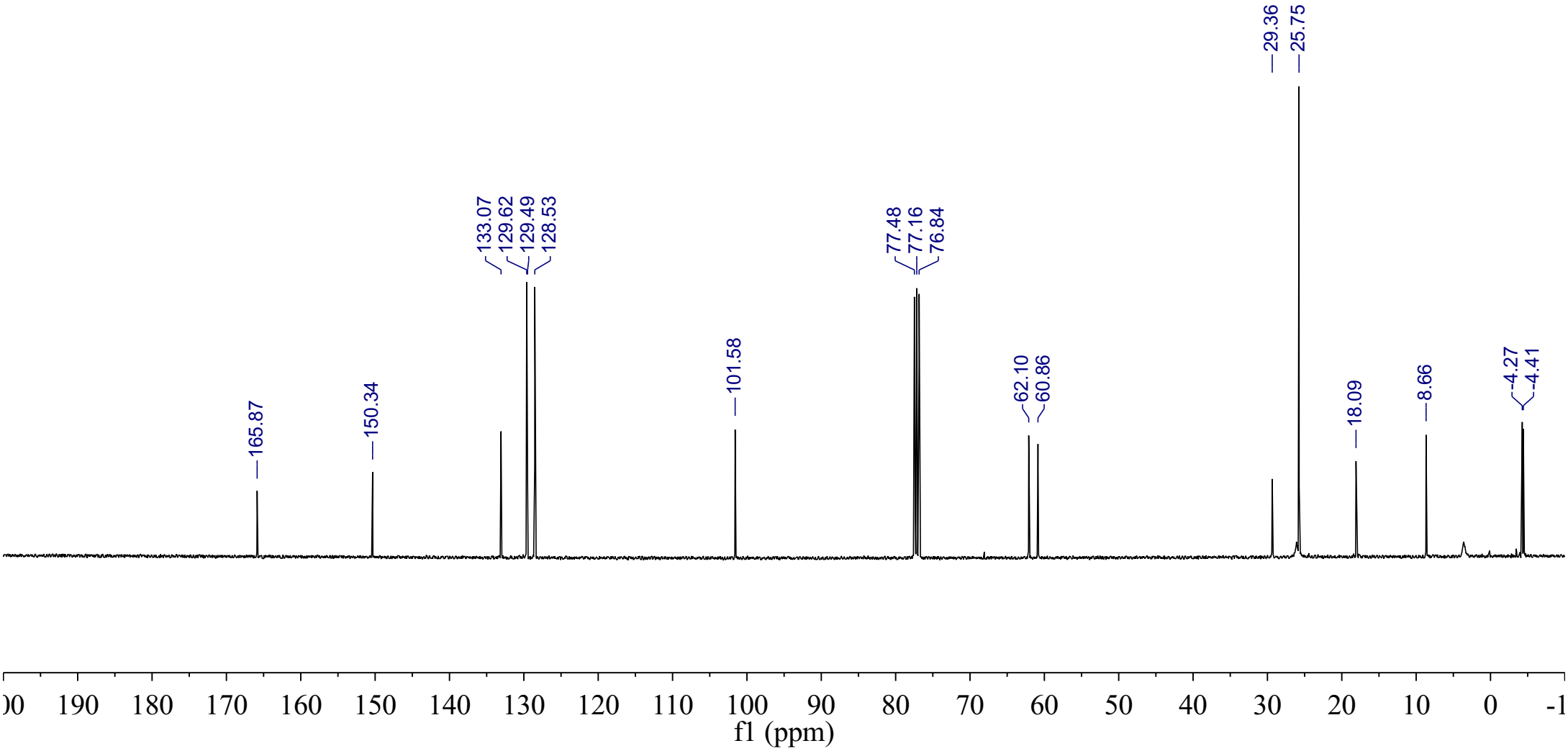
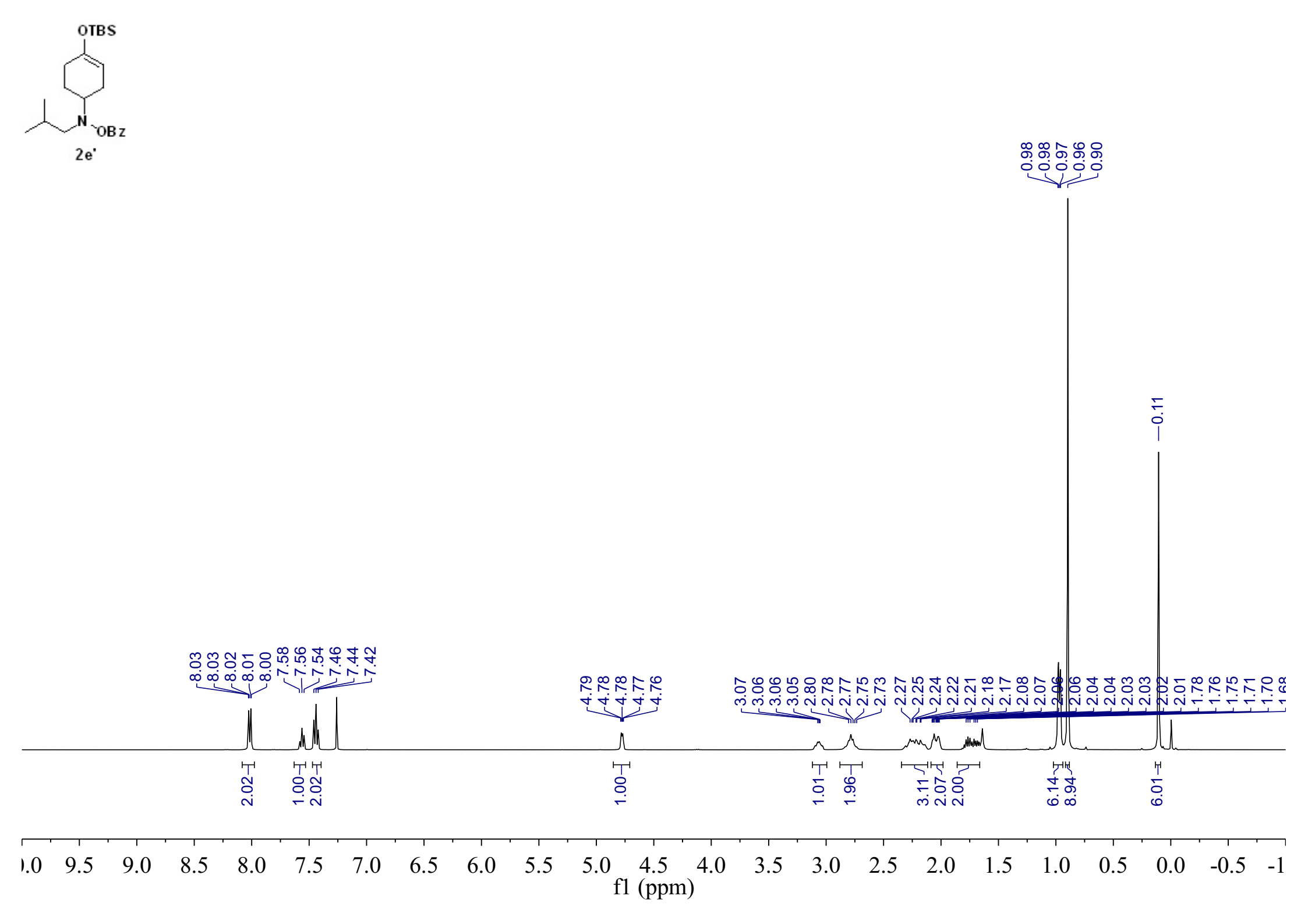
129.51
129.34
128.46
128.40
127.67
101.56
61.73
59.94
29.34
25.79
18.13
-4.24
-4.36
f1 (ppm)

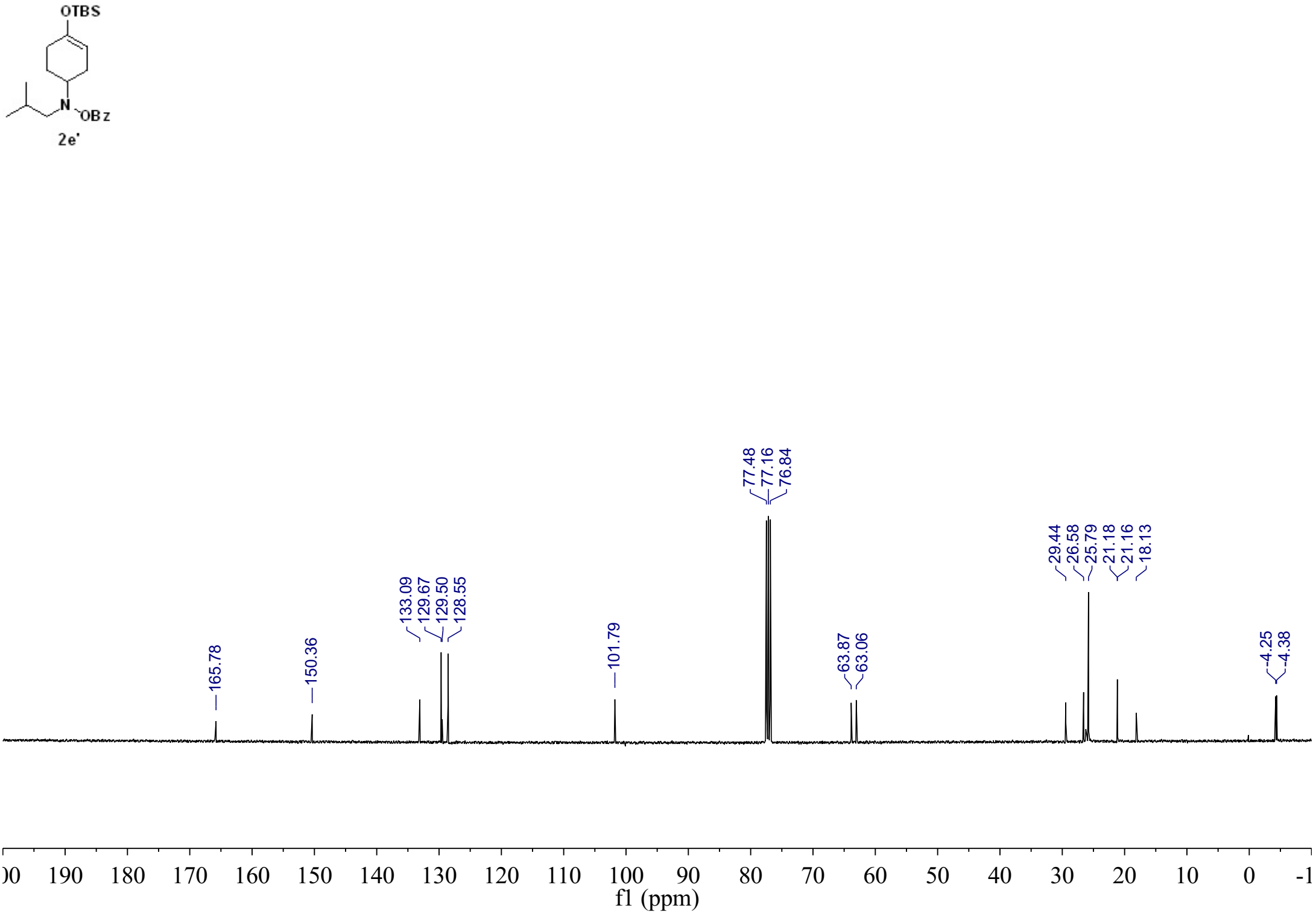

OTBS
N
OBz
2d'
1.10
1.08
1.08
1.06
1.06
1.04
1.03
1.03
1.02
1.01
1.01
0.89
0.46
0.45
0.43
0.43
0.42
0.14
0.13
0.12
0.10
0.09
0.06
8.04
8.02
8.02
7.58
7.56
7.54
7.46
7.44
7.42
4.78
4.77
4.76
3.16
3.15
3.14
3.13
3.13
3.12
3.11
3.10
2.91
2.30
2.27
2.26
2.25
2.22
2.21
2.18
2.18
2.17
2.16
2.16
2.15
2.14
2.14
2.07
2.06
2.03
2.02
2.01
1.77
1.75
1.73
1.72
1.70
1.69
1.92
1.00
2.03
0.97
1.05
1.70
3.05
2.18
1.03
1.02
9.58
1.97
8.46
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

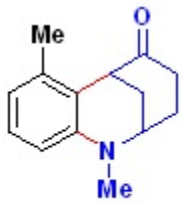

OTBS
N
OBz

2d'

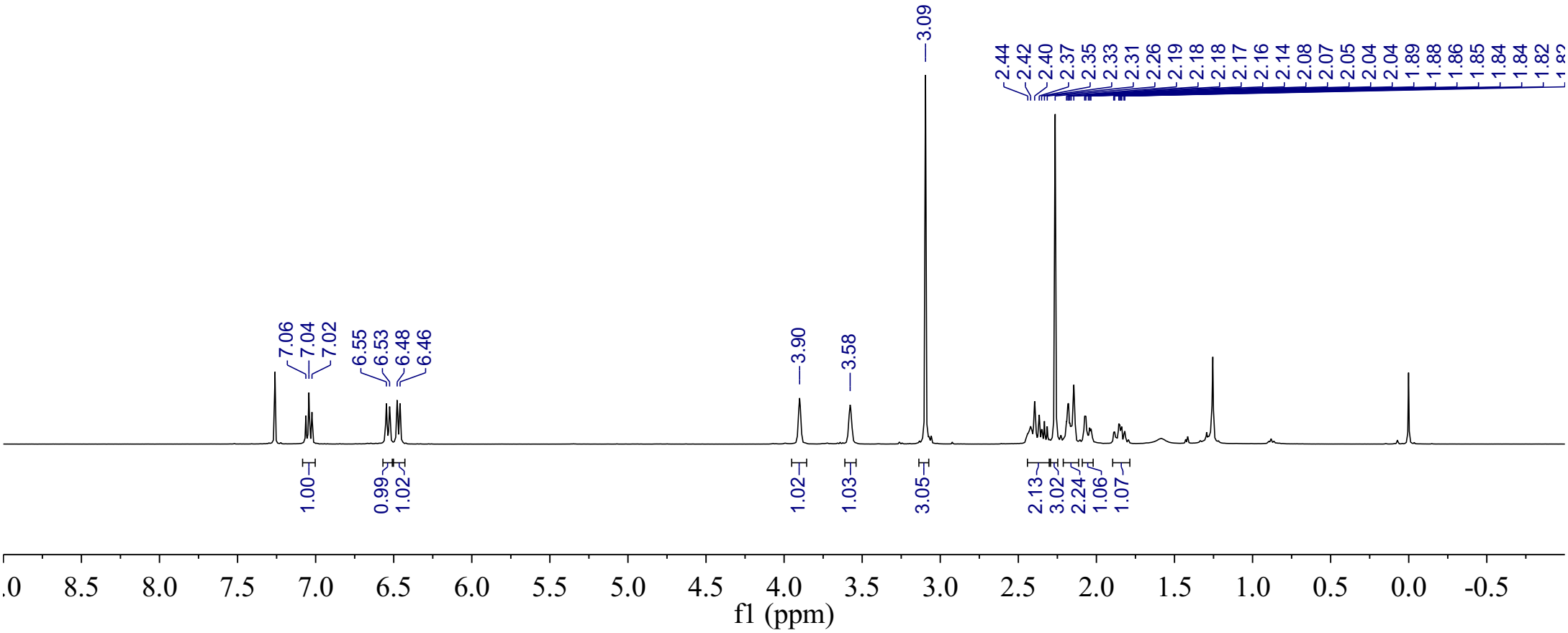

165.87
150.34
133.07
129.62
129.49
128.53
101.58
77.48
77.16
76.84
62.10
60.86
29.36
25.75
18.09
8.66
-4.27
-4.41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

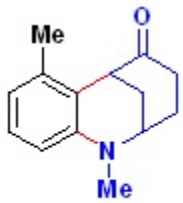

OTBS
N
OBz
2e'
8.03
8.03
8.02
8.01
8.00
7.58
7.56
7.54
7.46
7.44
7.42
4.79
4.78
4.78
4.77
4.76
3.07
3.06
3.06
3.05
2.80
2.78
2.77
2.75
2.73
2.27
2.25
2.24
2.22
2.21
2.18
2.17
2.08
2.07
2.06
2.06
2.04
2.04
2.03
2.03
2.02
2.01
1.78
1.76
1.75
1.71
1.70
0.98
0.98
0.97
0.96
0.90
0.11
2.02
1.00
2.02
1.00
1.01
1.96
3.11
2.07
2.00
6.14
8.94
6.01
f1 (ppm)


OTBS
N
OBz
2e'
165.78
150.36
133.09
129.67
129.50
128.55
101.79
77.48
77.16
76.84
63.87
63.06
29.44
26.58
25.79
21.18
21.16
18.13
-4.25
-4.38
f1 (ppm)

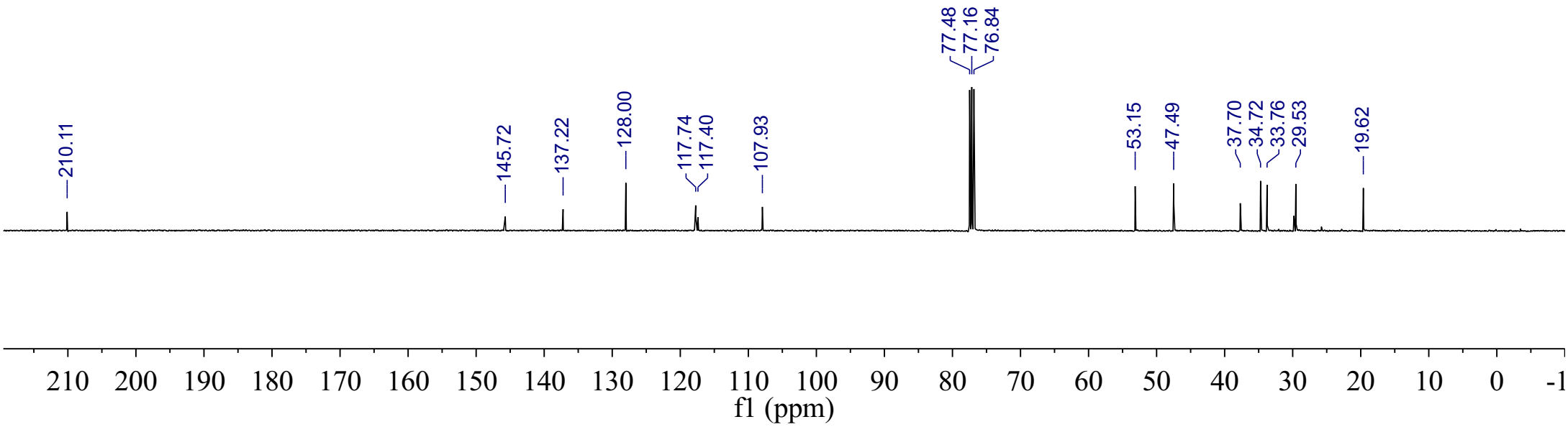

Me
O
N
Me

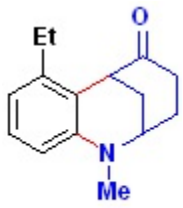
3a


7.06
7.04
7.02
6.55
6.53
6.48
6.46
3.90
3.58
3.09
2.44
2.42
2.40
2.37
2.35
2.33
2.31
2.26
2.19
2.18
2.18
2.17
2.16
2.14
2.08
2.07
2.05
2.04
2.04
1.89
1.88
1.86
1.85
1.84
1.84
1.82
1.00
0.99
1.02
1.02
1.03
3.05
2.13
3.02
2.24
1.06
1.07
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

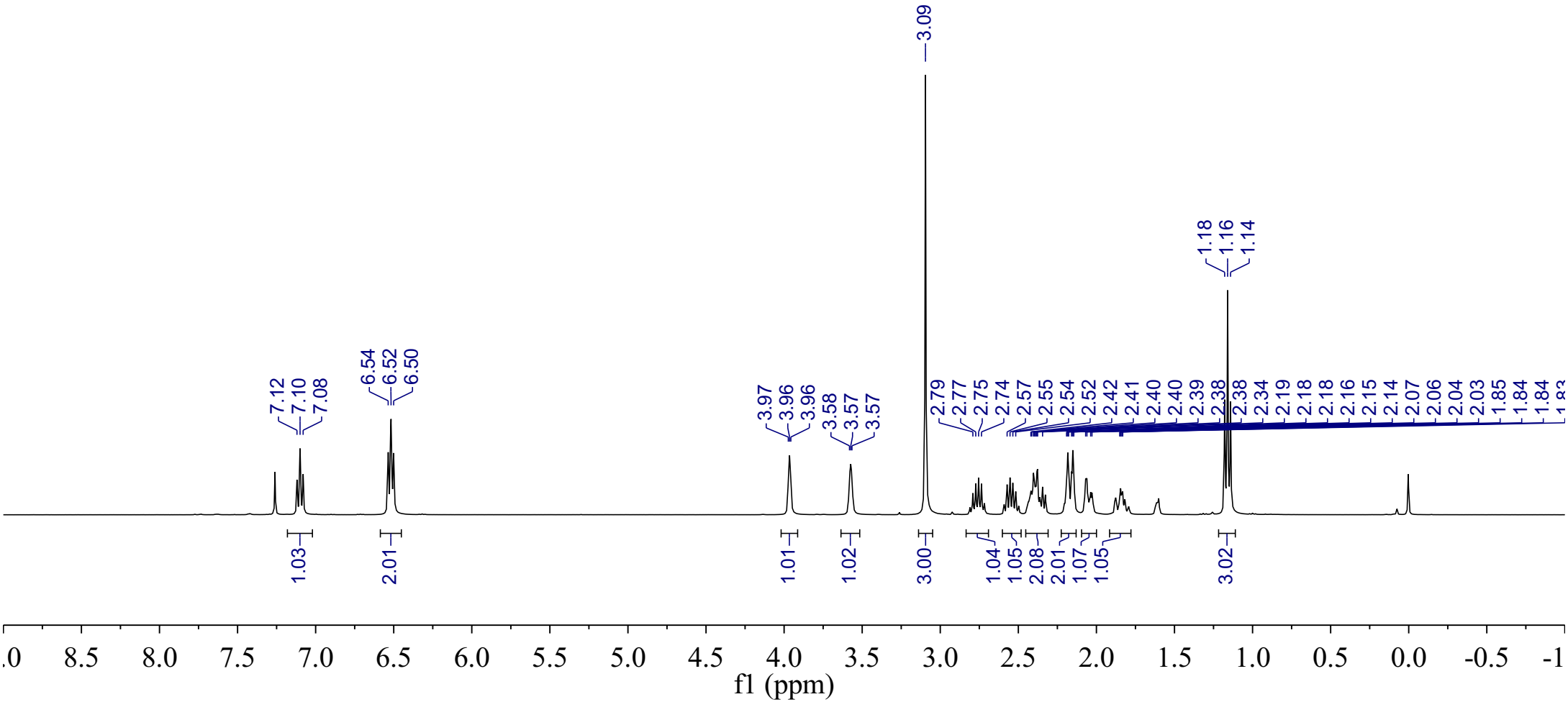

Me
O
N
Me

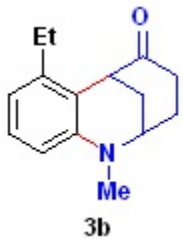
3a


210.11
145.72
137.22
128.00
117.74
117.40
107.93
77.48
77.16
76.84
53.15
47.49
37.70
34.72
33.76
29.53
19.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

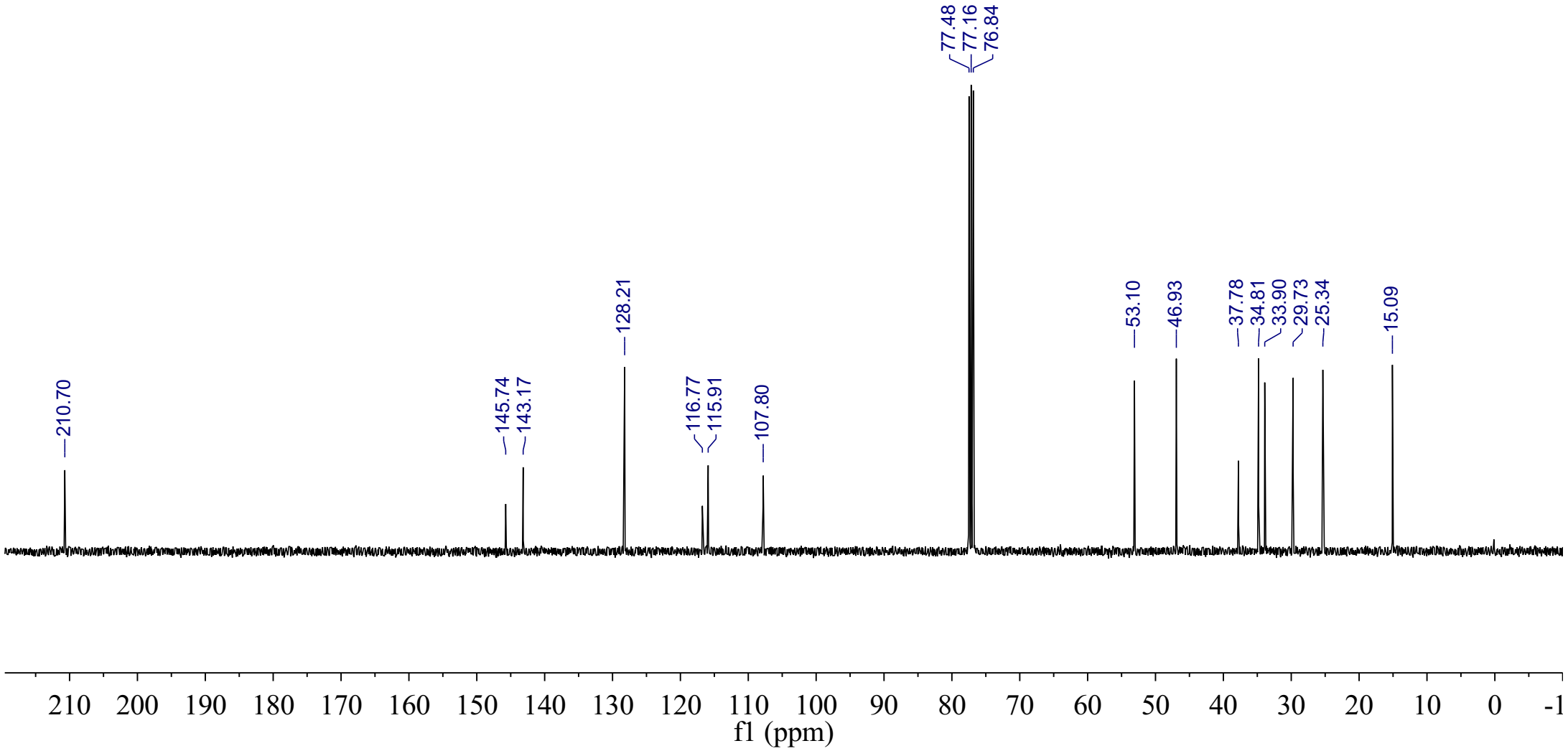

Et
O
N
Me

3b


7.12
7.10
7.08
6.54
6.52
6.50
3.97
3.96
3.96
3.58
3.57
3.57
3.09
2.79
2.77
2.75
2.74
2.57
2.55
2.54
2.52
2.42
2.41
2.40
2.40
2.39
2.38
2.38
2.34
2.19
2.18
2.18
2.16
2.15
2.14
2.07
2.06
2.04
2.03
1.85
1.84
1.84
1.18
1.16
1.14
1.03
2.01
1.01
1.02
3.00
1.04
1.05
2.08
2.01
1.07
1.05
3.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Et
O
N
Me

3b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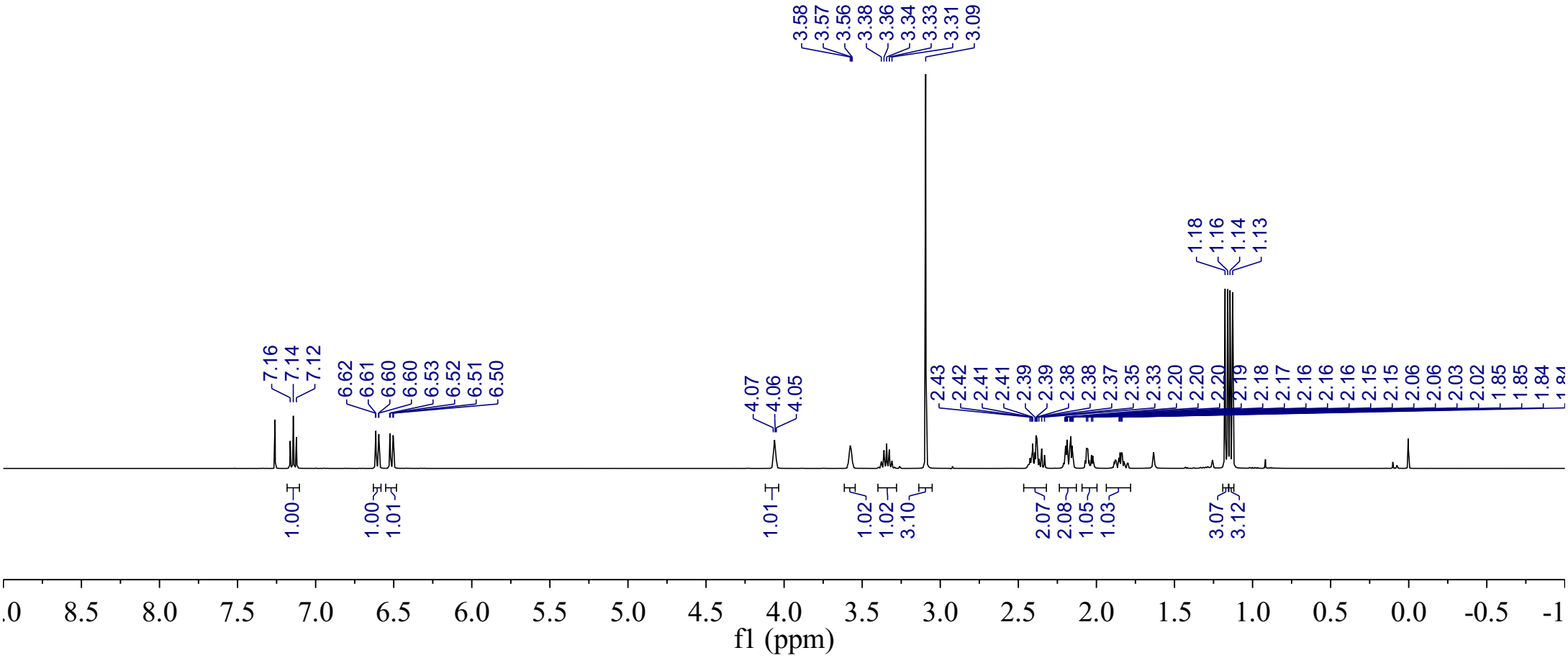
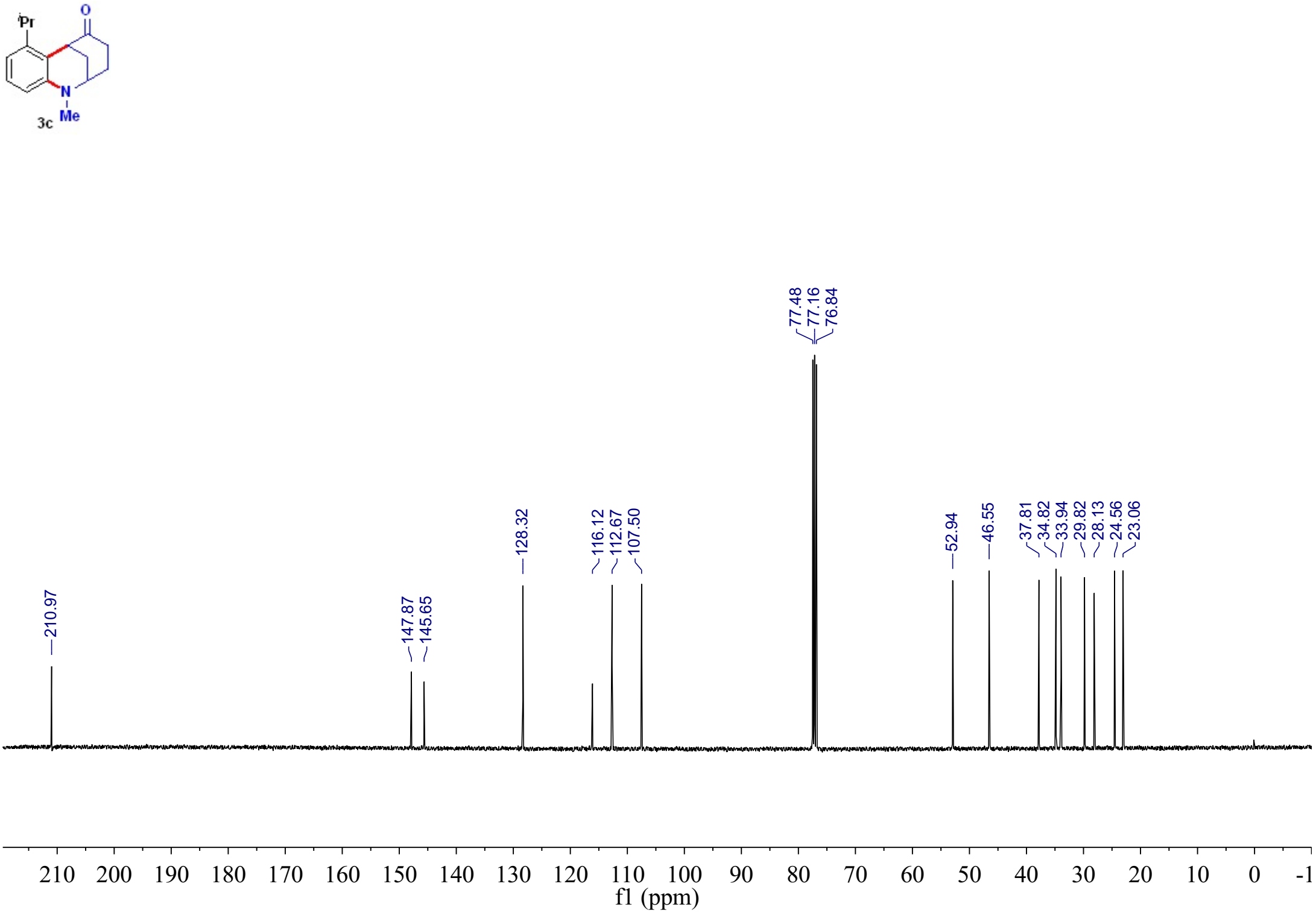
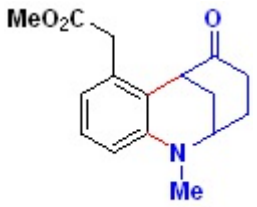
143.17
128.21
116.77
115.91
107.80
77.48
77.16
76.84
53.10
46.93
37.78
34.81
33.90
29.73
25.34
15.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


iPr
O
N
Me

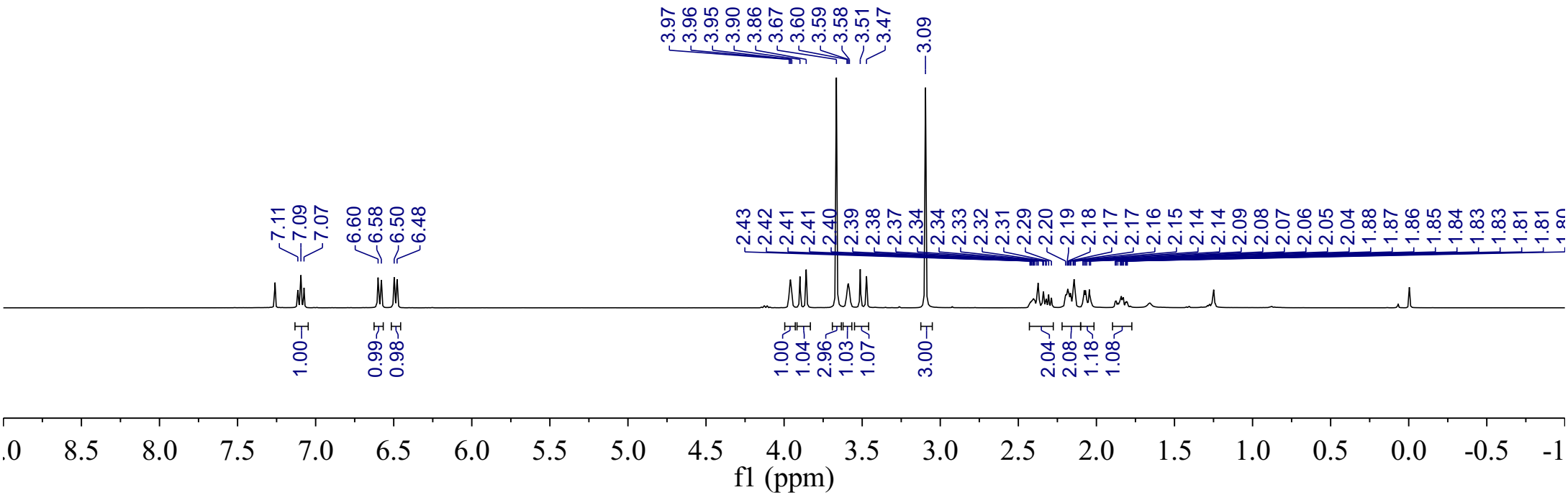
3c

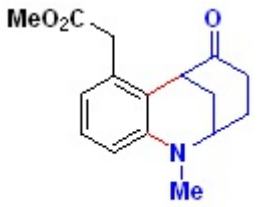

7.16
7.14
7.12
6.62
6.61
6.60
6.60
6.53
6.52
6.51
6.50
4.07
4.06
4.05
3.58
3.57
3.56
3.38
3.36
3.34
3.33
3.31
3.09
2.43
2.42
2.41
2.41
2.39
2.39
2.38
2.38
2.37
2.35
2.33
2.20
2.20
2.20
2.19
2.18
2.17
2.16
2.16
2.16
2.15
2.15
2.06
2.06
2.03
2.02
1.85
1.85
1.84
1.18
1.16
1.14
1.13
1.00
1.00
1.01
1.01
1.02
1.02
3.10
2.07
2.08
1.05
1.03
3.07
3.12
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


iPr
O
N
Me
3c
210.97
147.87
145.65
128.32
116.12
112.67
107.50
77.48
77.16
76.84
52.94
46.55
37.81
34.82
33.94
29.82
28.13
24.56
23.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

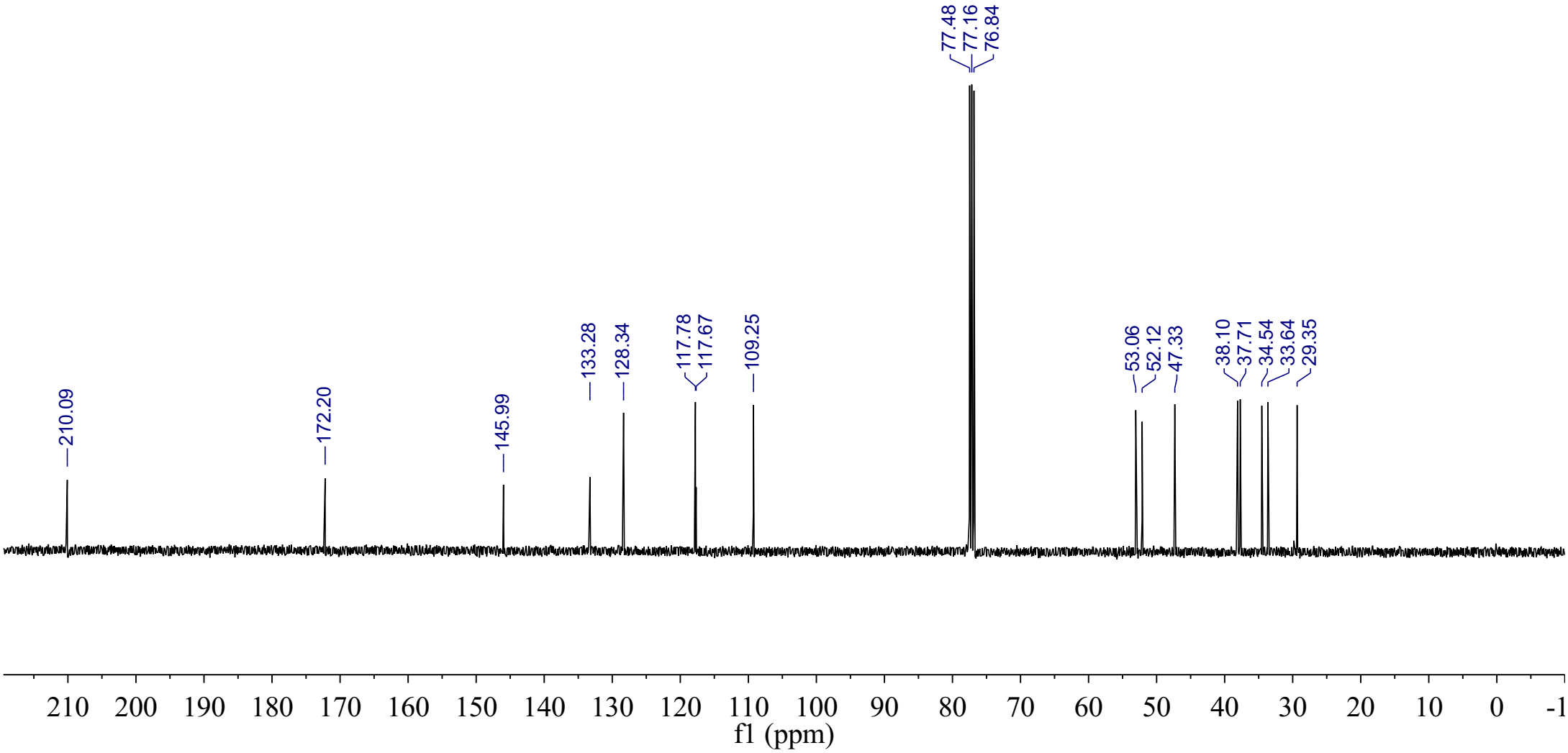

MeO2C
O
N
Me

3d


3.97
3.96
3.95
3.90
3.86
3.67
3.60
3.59
3.58
3.51
3.47
3.09
7.11
7.09
7.07
6.60
6.58
6.50
6.48
2.43
2.42
2.41
2.41
2.40
2.39
2.38
2.37
2.34
2.34
2.33
2.32
2.31
2.29
2.20
2.19
2.18
2.17
2.17
2.16
2.15
2.14
2.14
2.09
2.08
2.07
2.06
2.05
2.04
1.88
1.87
1.86
1.85
1.84
1.83
1.83
1.81
1.81
1.00
0.99
0.98
1.00
1.04
2.96
1.03
1.07
3.00
2.04
2.08
1.18
1.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


MeO2C
O
N
Me

3d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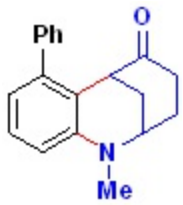
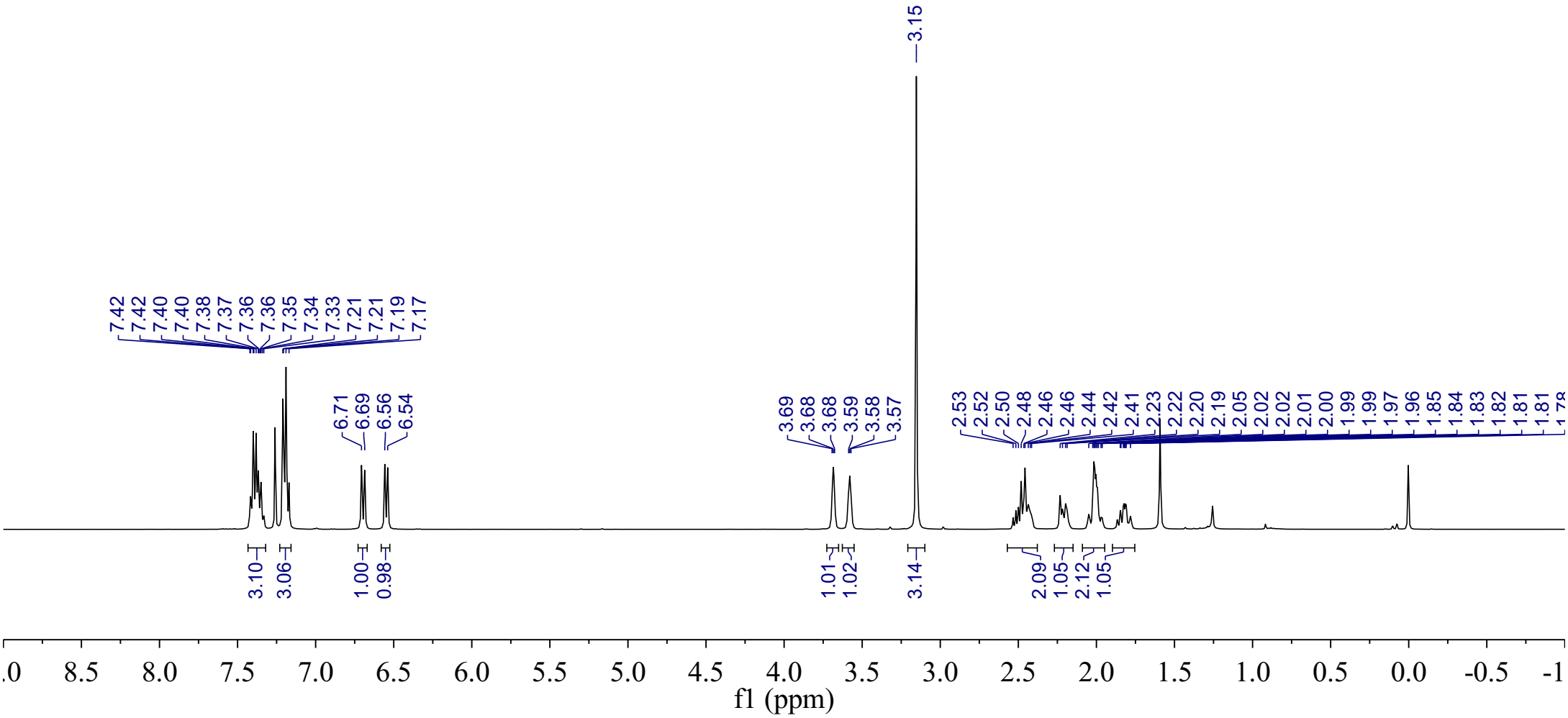
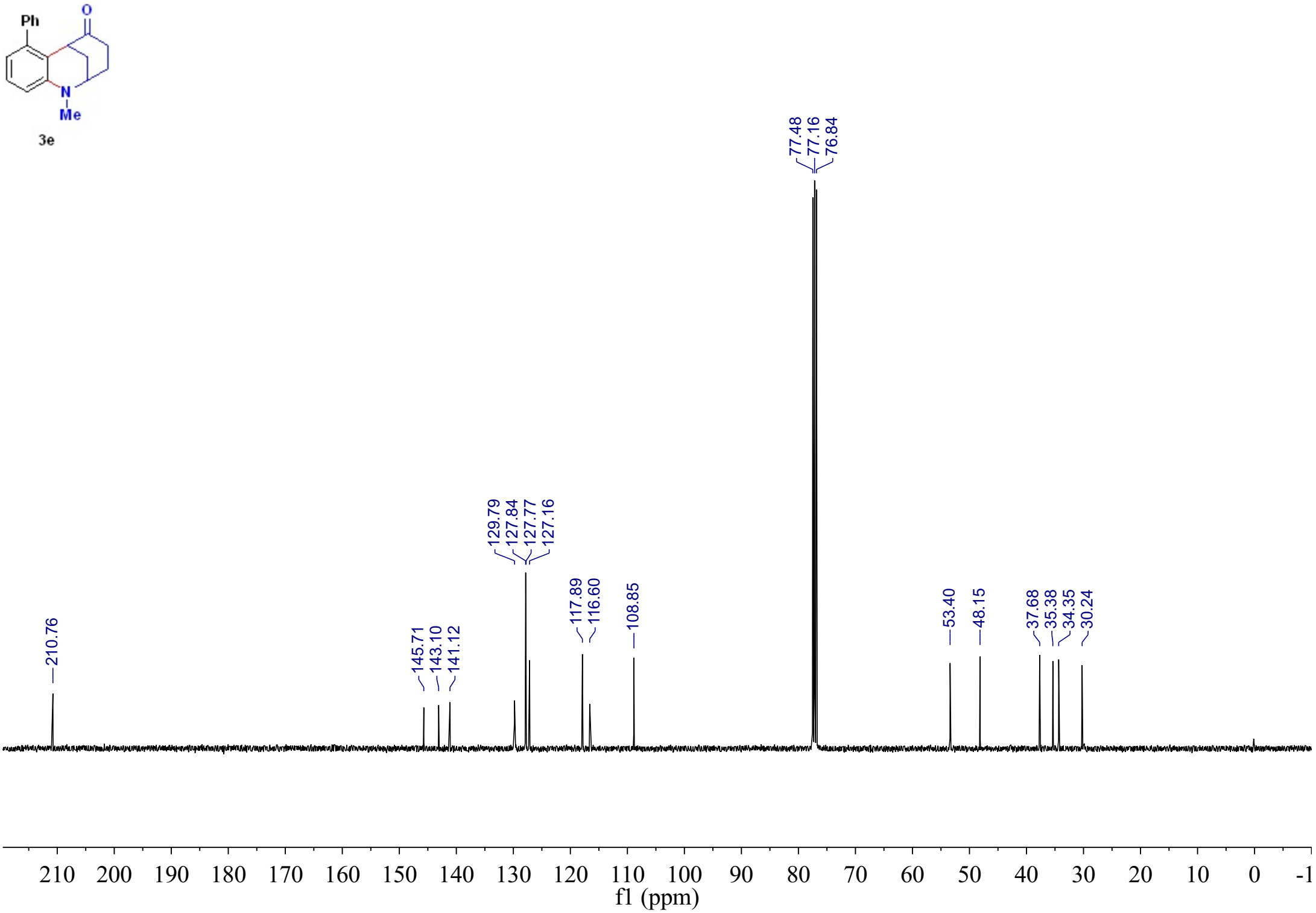
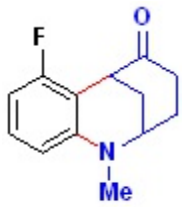
172.20
145.99
133.28
128.34
117.78
117.67
109.25
77.48
77.16
76.84
53.06
52.12
47.33
38.10
37.71
34.54
33.64
29.35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Ph
O
N
Me

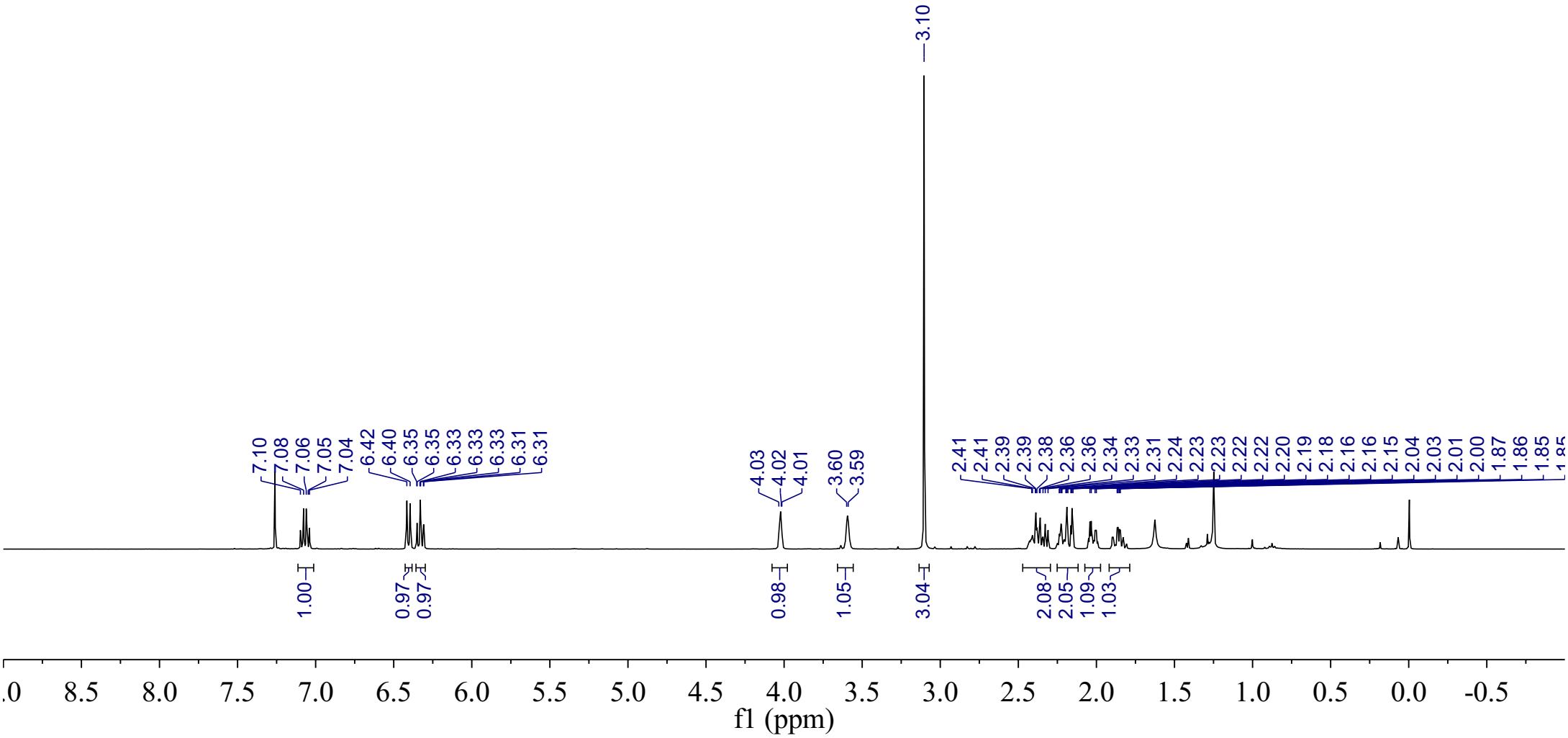
3e

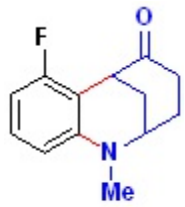

7.42
7.42
7.40
7.40
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.21
7.21
7.19
7.17
6.71
6.69
6.56
6.54
3.69
3.68
3.68
3.59
3.58
3.57
3.15
2.53
2.52
2.50
2.48
2.46
2.46
2.44
2.42
2.41
2.23
2.22
2.20
2.19
2.05
2.02
2.02
2.01
2.00
1.99
1.99
1.97
1.96
1.85
1.84
1.83
1.82
1.81
1.81
3.10
3.06
1.00
0.98
1.01
1.02
3.14
2.09
1.05
2.12
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Ph
O
N
Me
3e
210.76
145.71
143.10
141.12
129.79
127.84
127.77
127.16
117.89
116.60
108.85
77.48
77.16
76.84
53.40
48.15
37.68
35.38
34.35
30.24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


F
O
N
Me

3f


7.10
7.08
7.06
7.05
7.04
6.42
6.40
6.35
6.35
6.33
6.33
6.33
6.31
6.31
4.03
4.02
4.01
3.60
3.59
3.10
2.41
2.41
2.39
2.39
2.38
2.36
2.36
2.34
2.33
2.31
2.24
2.23
2.23
2.22
2.22
2.20
2.19
2.18
2.16
2.16
2.15
2.04
2.03
2.01
2.00
1.87
1.86
1.85
1.00
0.97
0.97
0.98
1.05
3.04
2.08
2.05
1.09
1.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

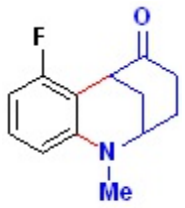



3f

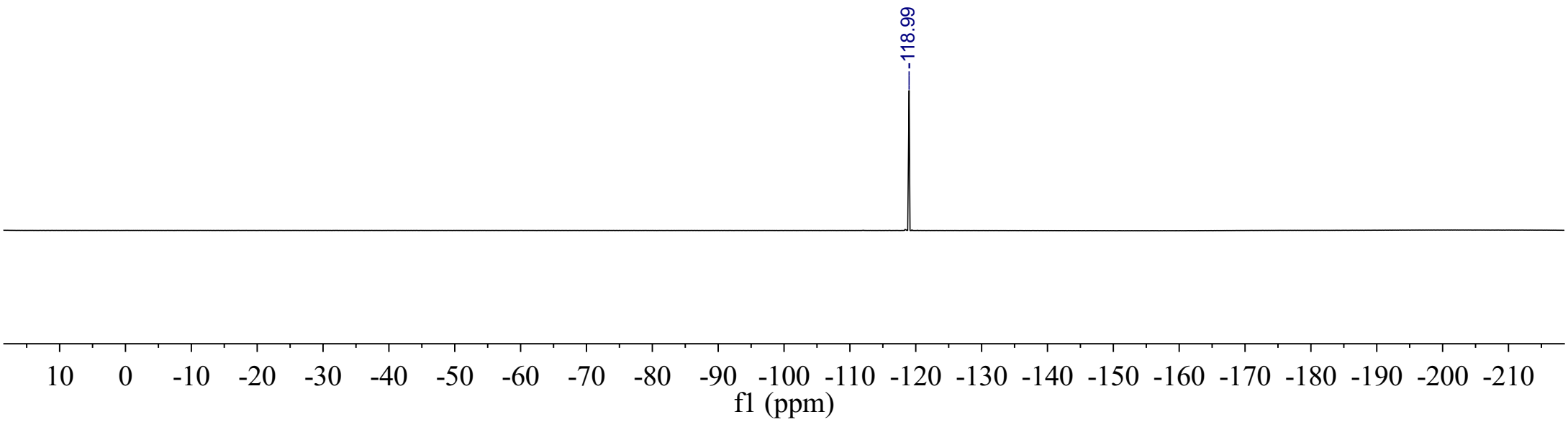
209.07
161.84
159.42
146.96
146.89
129.06
128.96
106.25
106.05
105.32
105.30
102.31
102.08
77.48
77.16
76.84
53.23
43.35
43.32
37.69
34.56
33.59
28.94

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

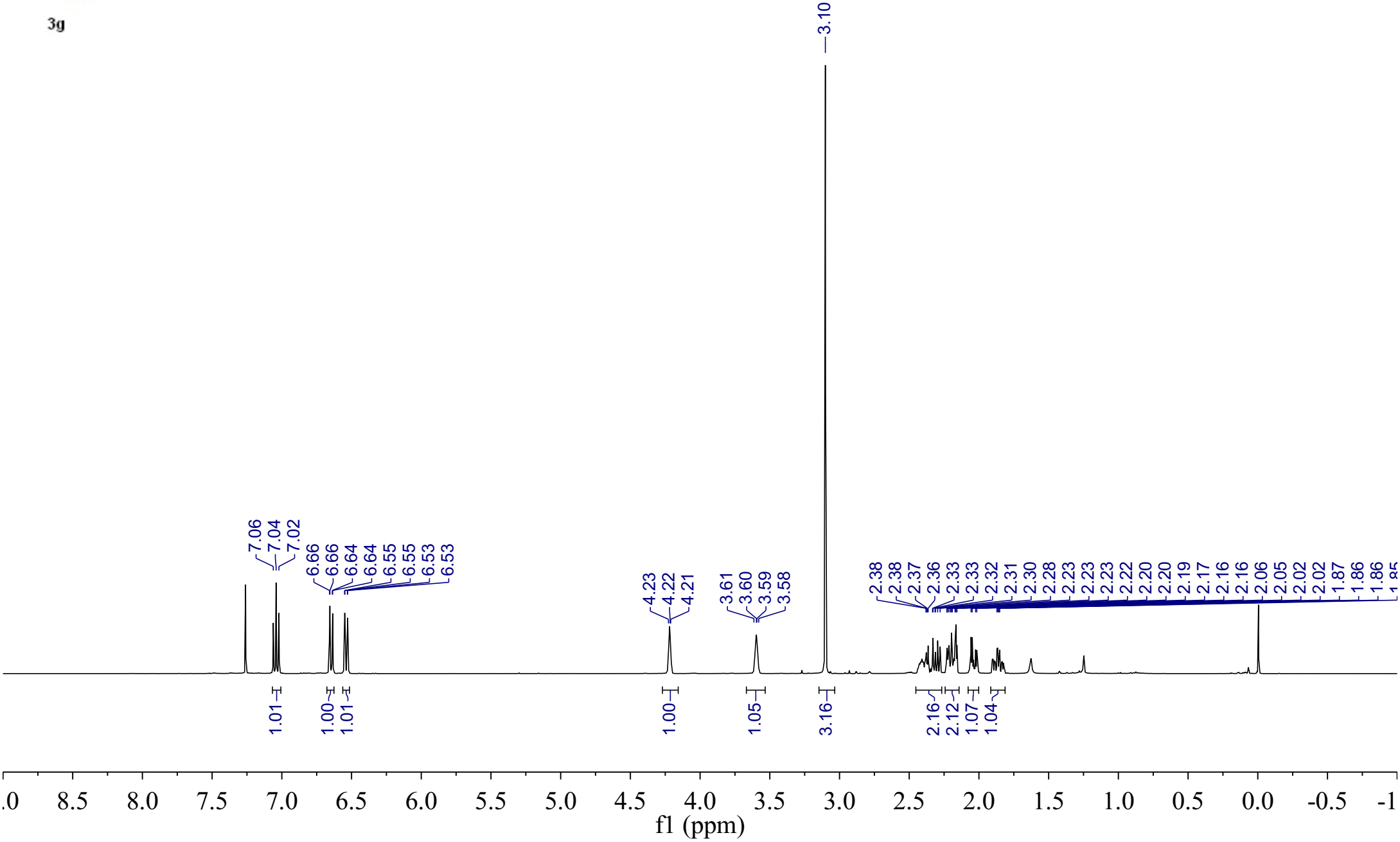

F
O
N
Me

3f


-118.99
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)


Cl
O
N
Me

3g


3.10
7.06
7.04
7.02
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6.66
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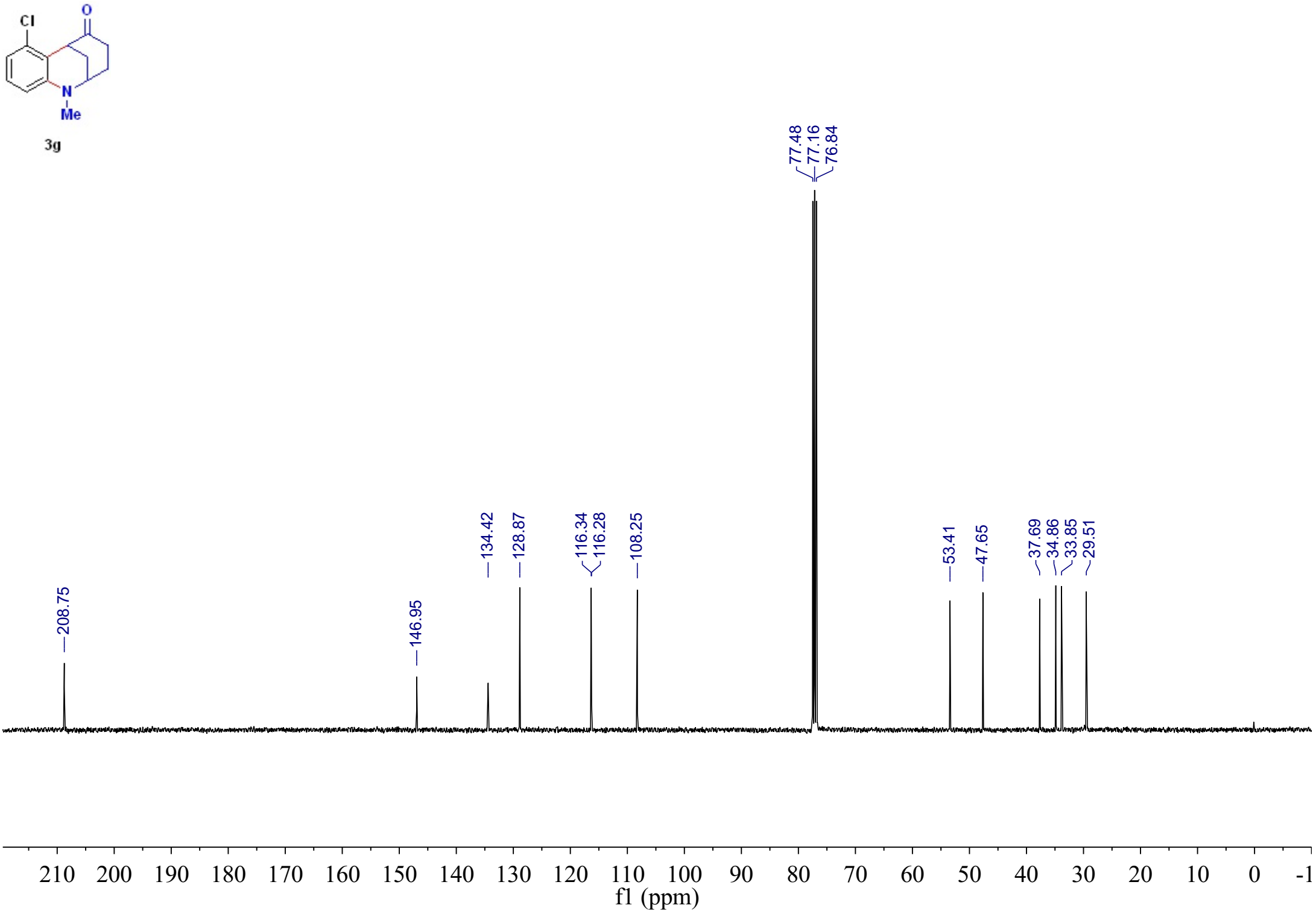
6.64
6.55
6.55
6.53
6.53
4.23
4.22
4.21
3.61
3.60
3.59
3.58
2.38
2.38
2.37
2.36
2.33
2.33
2.32
2.31
2.30
2.28
2.23
2.23
2.23
2.22
2.20
2.20
2.19
2.17
2.16
2.16
2.06
2.05
2.02
2.02
1.87
1.86
1.86
1.01
1.00
1.01
1.00
1.05
3.16
2.16
2.12
1.07
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Cl
O
N
Me
3g
208.75
146.95
134.42
128.87
116.34
116.28
108.25
77.48
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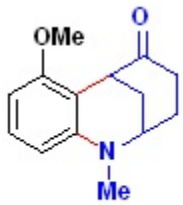
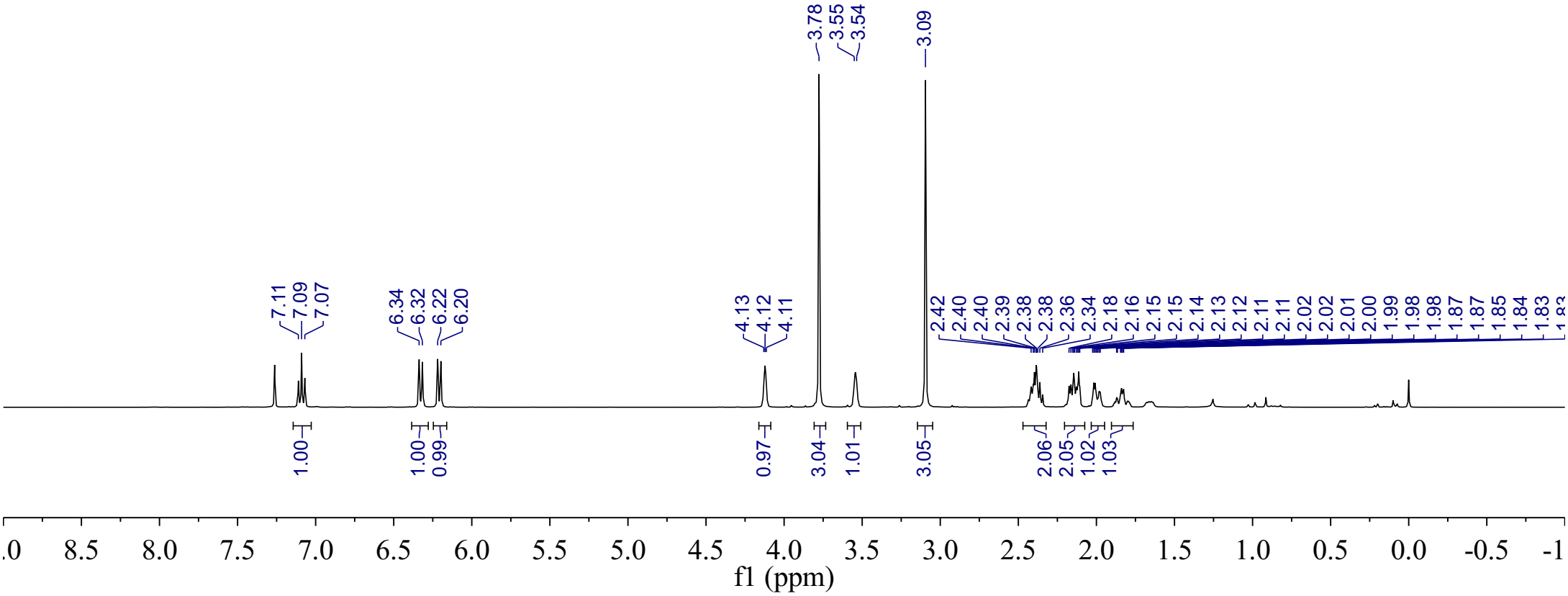
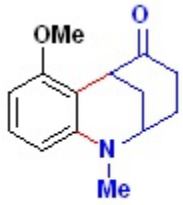
76.84
53.41
47.65
37.69
34.86
33.85
29.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

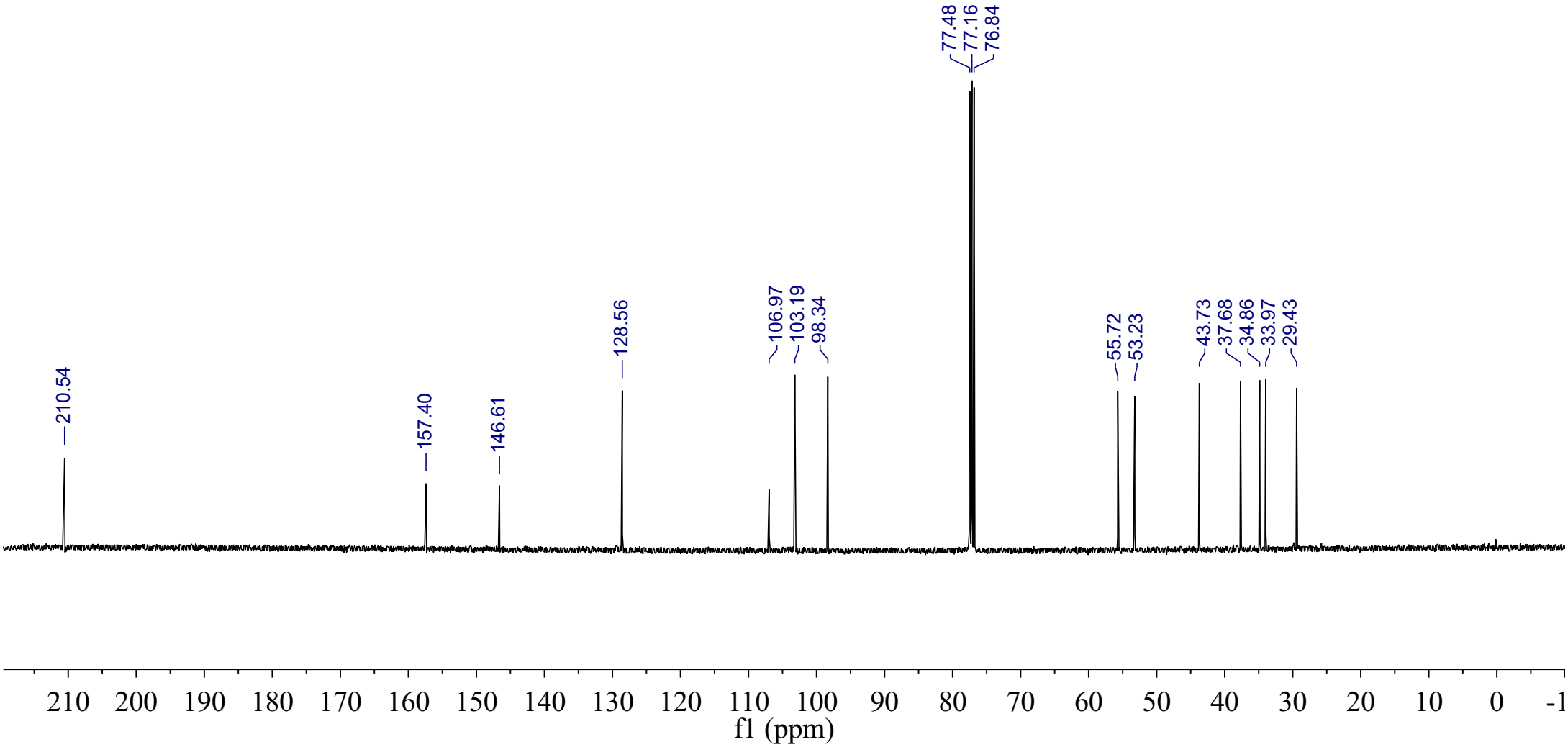

OMe
O
N
Me

3h


7.11
7.09
7.07
6.34
6.32
6.22
6.20
4.13
4.12
4.11
3.78
3.55
3.54
3.09
2.42
2.40
2.40
2.39
2.38
2.38
2.36
2.34
2.18
2.16
2.15
2.15
2.14
2.13
2.12
2.11
2.11
2.02
2.02
2.01
2.00
1.99
1.98
1.98
1.87
1.87
1.85
1.84
1.83
1.00
1.00
0.99
0.97
3.04
1.01
3.05
2.06
2.05
1.02
1.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


OMe
O
N
Me

3h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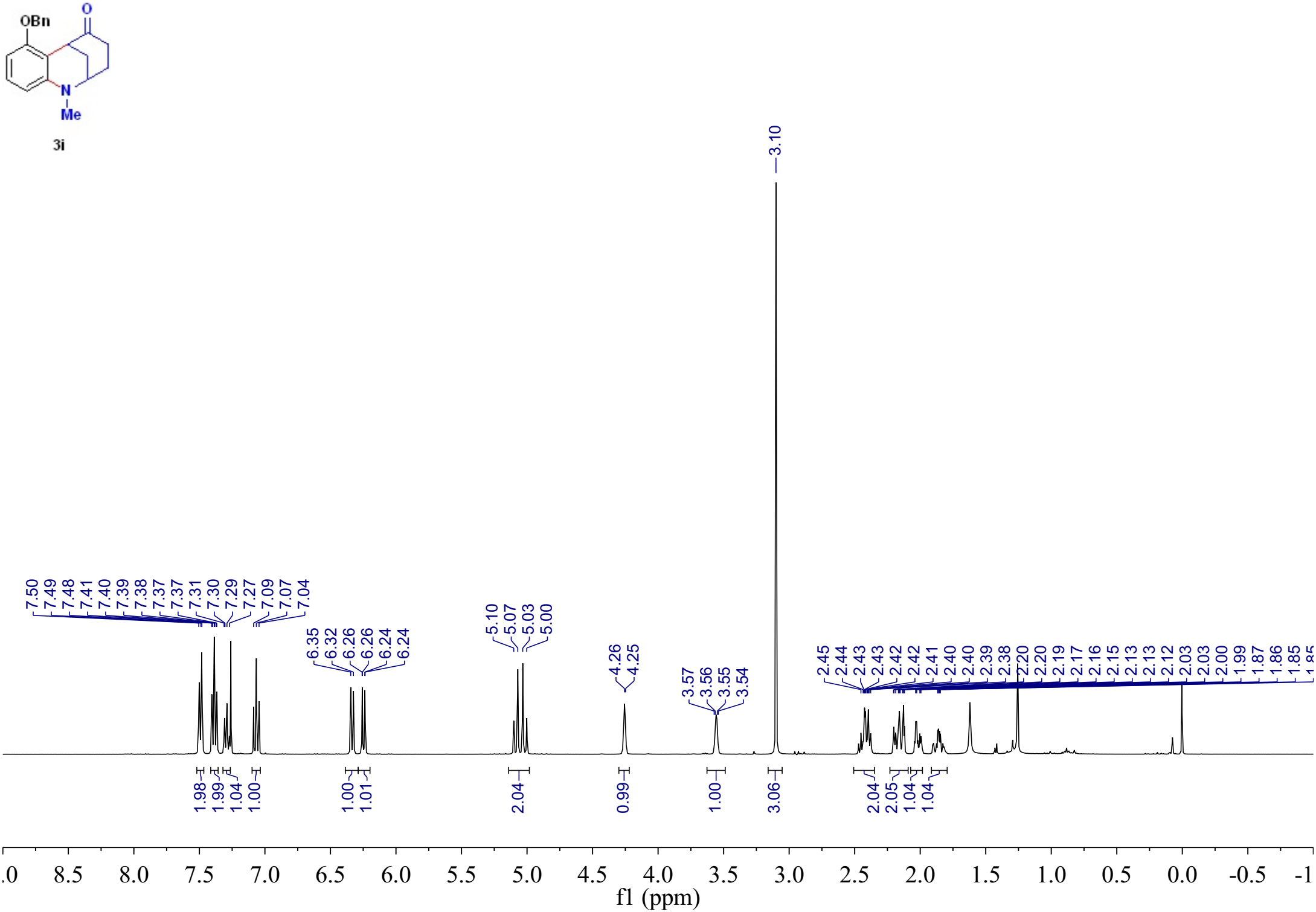
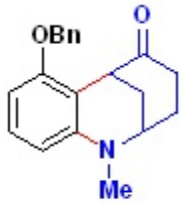
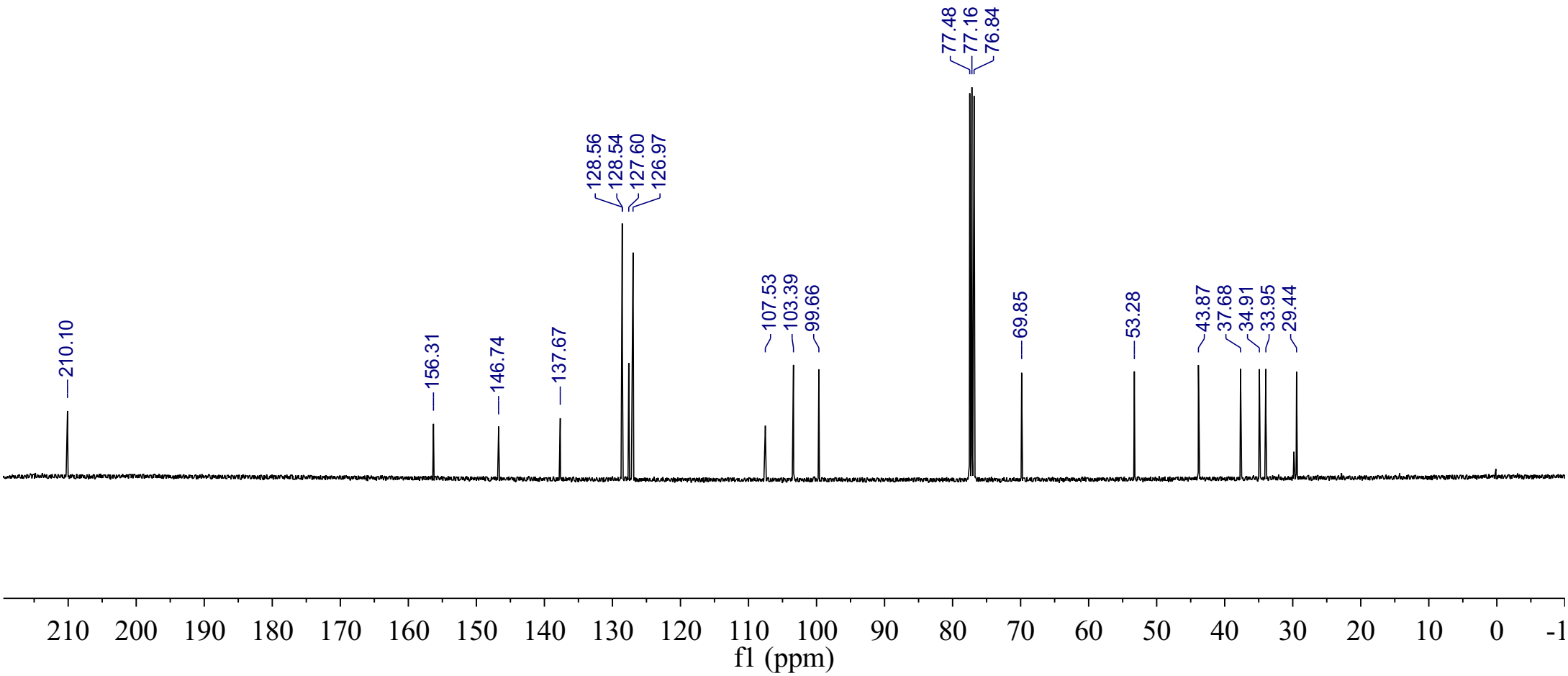
157.40
146.61
128.56
106.97
103.19
98.34
77.48
77.16
76.84
55.72
53.23
43.73
37.68
34.86
33.97
29.43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


OBn
O
N
Me
3i
3.10
7.50
7.49
7.48
7.41
7.40
7.39
7.38
7.37
7.37
7.31
7.30
7.29
7.27
7.09
7.07
7.04
6.35
6.32
6.26
6.26
6.24
6.24
5.10
5.07
5.03
5.00
4.26
4.25
3.57
3.56
3.55
3.54
2.45
2.44
2.43
2.43
2.42
2.42
2.41
2.40
2.40
2.39
2.38
2.20
2.20
2.19
2.17
2.16
2.15
2.13
2.13
2.12
2.03
2.03
2.00
1.99
1.87
1.86
1.85
1.98
1.99
1.04
1.00
1.00
1.01
2.04
0.99
1.00
3.06
2.04
2.05
1.04
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


OBn
O
N
Me

3i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156.31
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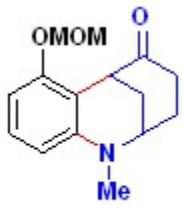
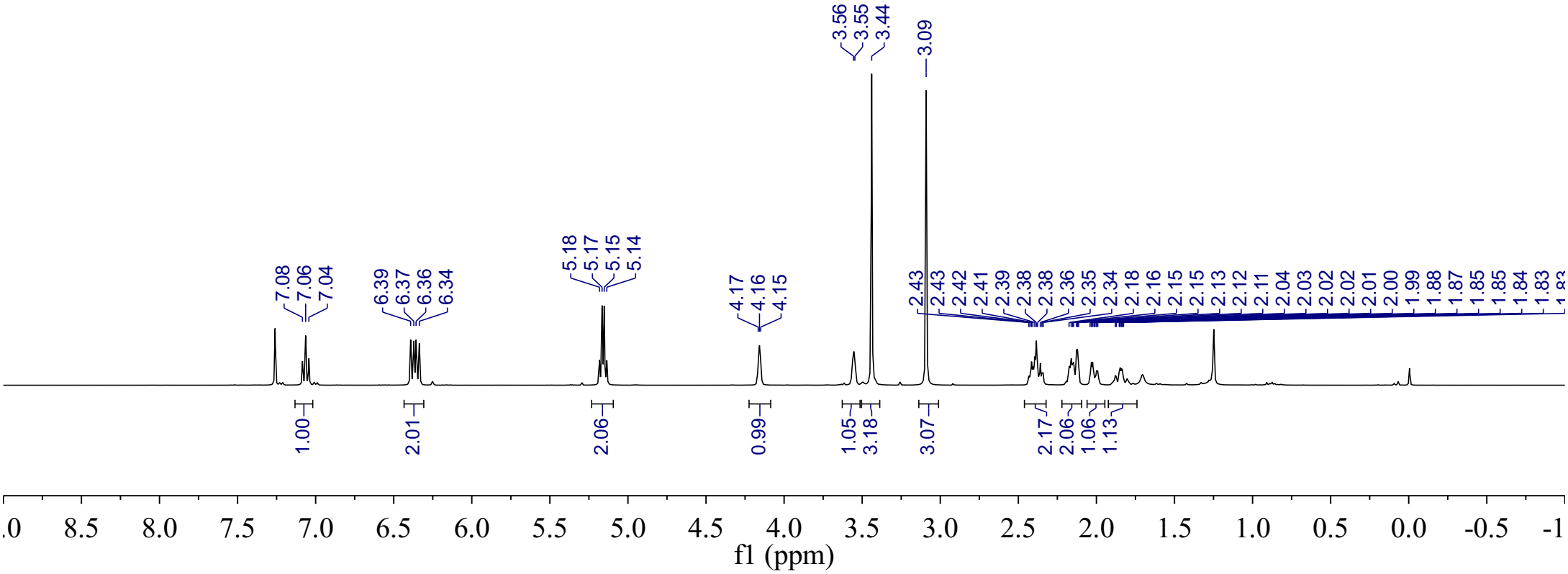
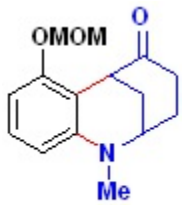
137.67
128.56
128.54
127.60
126.97
107.53
103.39
99.66
77.48
77.16
76.84
69.85
53.28
43.87
37.68
34.91
33.95
29.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

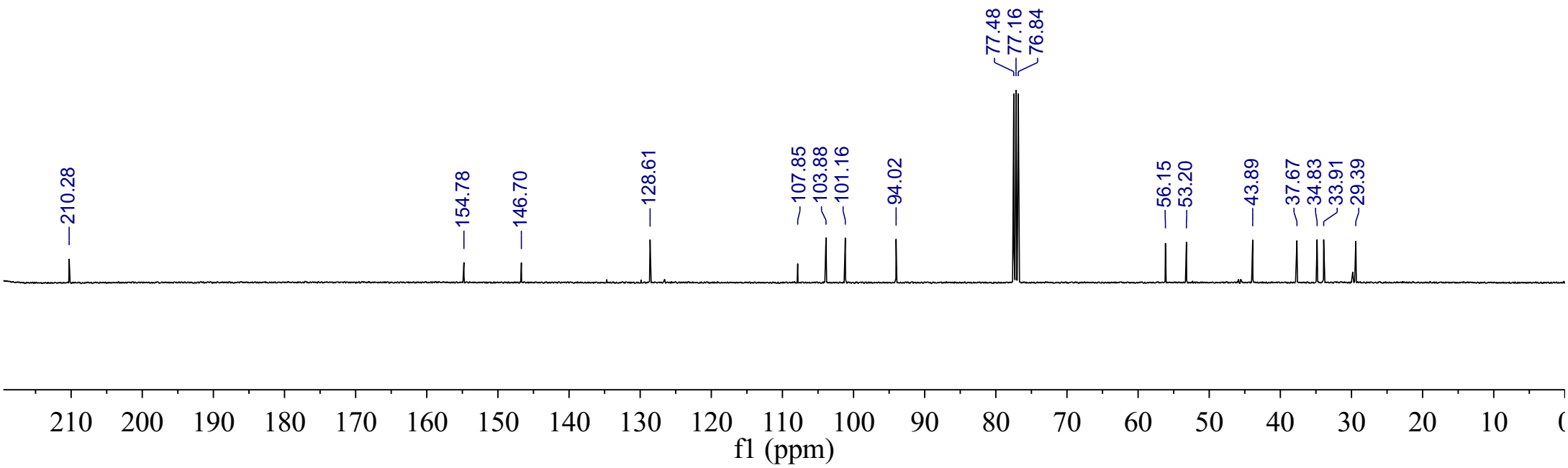

OMOM
O
N
Me

3j


7.08
7.06
7.04
6.39
6.37
6.36
6.34
5.18
5.17
5.15
5.14
4.17
4.16
4.15
3.56
3.55
3.44
3.09
2.43
2.43
2.42
2.41
2.39
2.38
2.38
2.36
2.35
2.34
2.18
2.16
2.15
2.15
2.13
2.12
2.11
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.88
1.87
1.85
1.85
1.84
1.83
1.00
2.01
2.06
0.99
1.05
3.18
3.07
2.17
2.06
1.06
1.13
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


OMOM
O
N
Me

3j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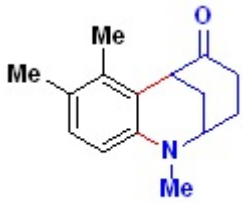
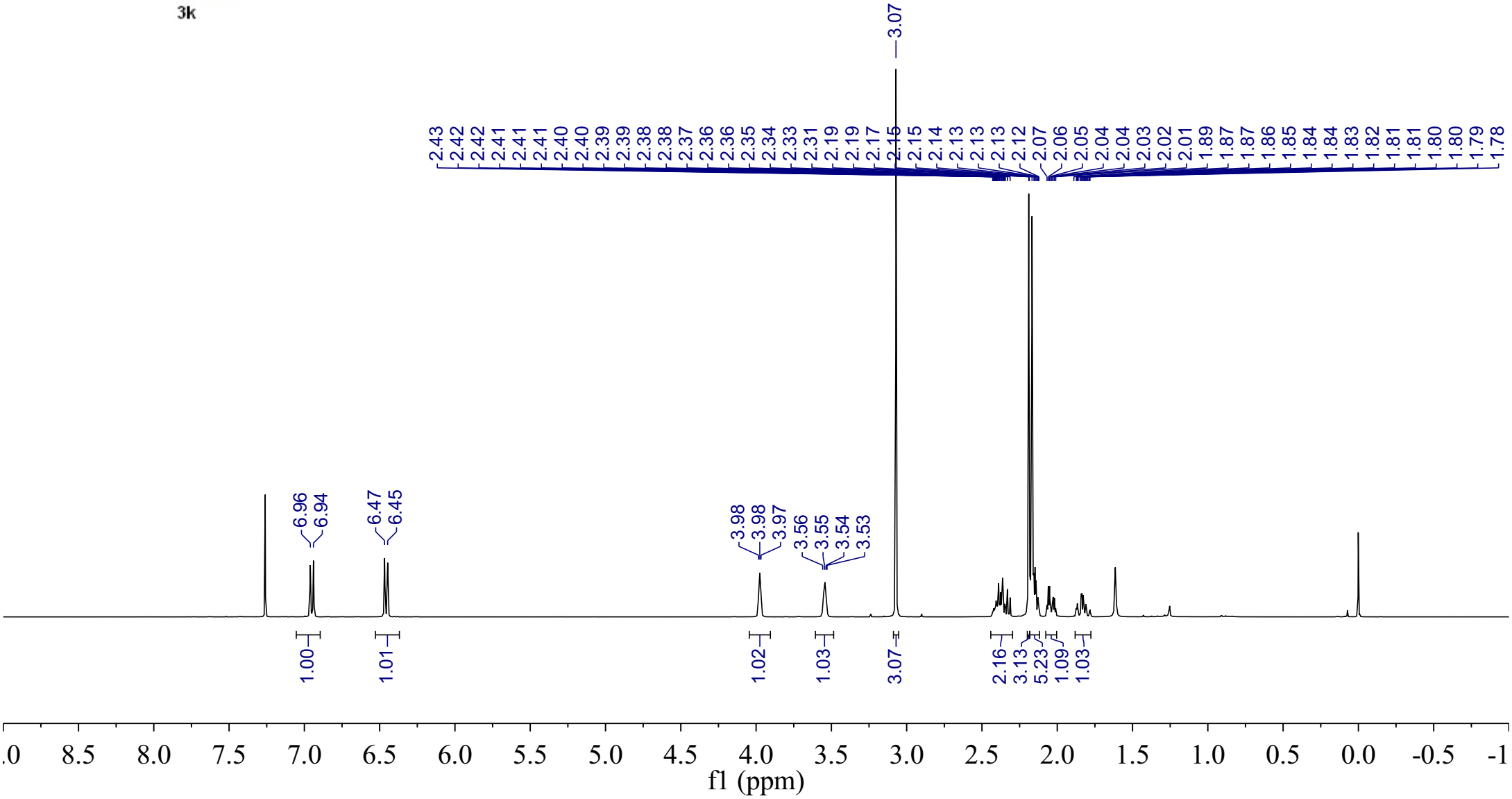
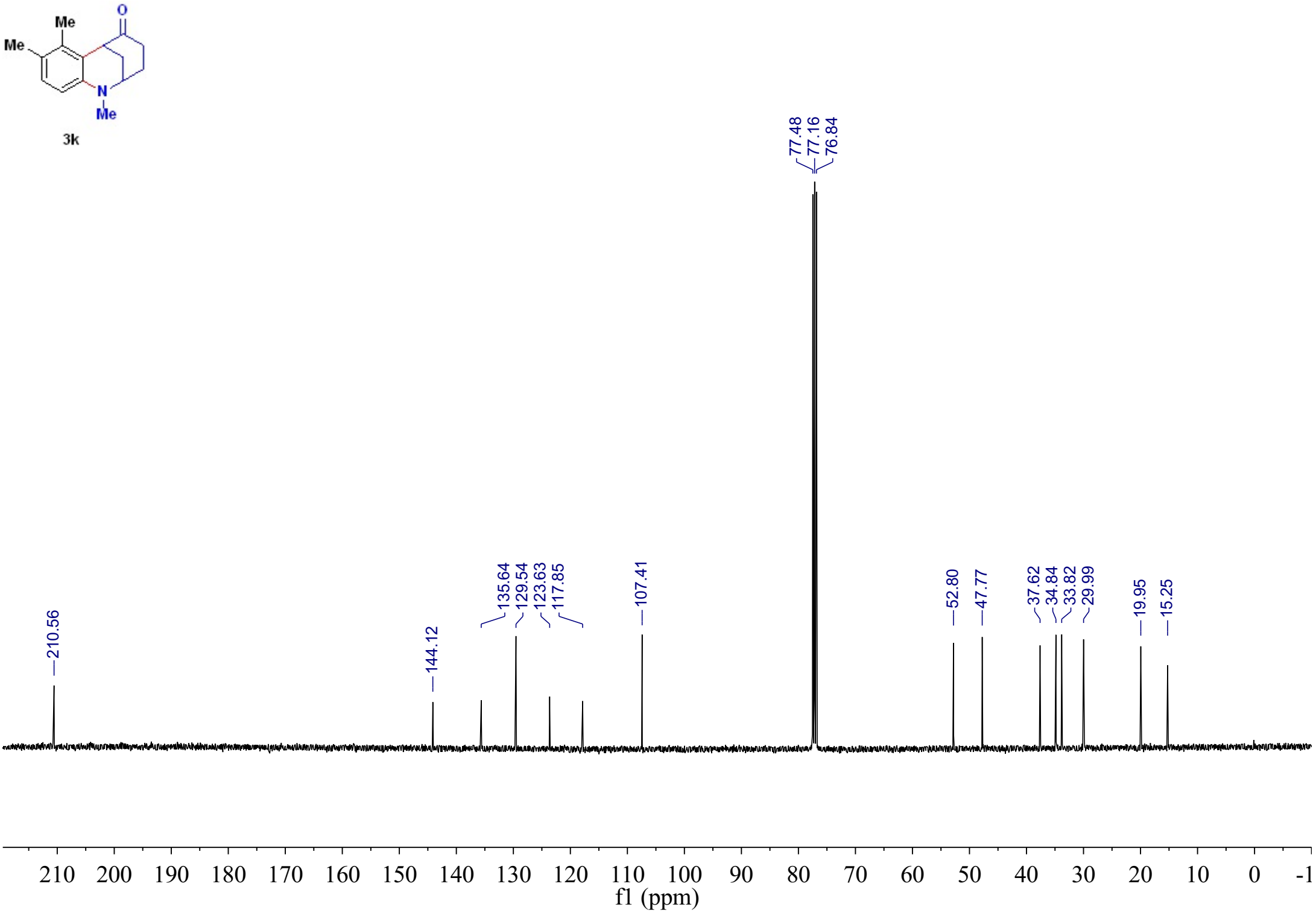
154.78
146.70
128.61
107.85
103.88
101.16
94.02
77.48
77.16
76.84
56.15
53.20
43.89
37.67
34.83
33.91
29.39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
Me
O
N
Me

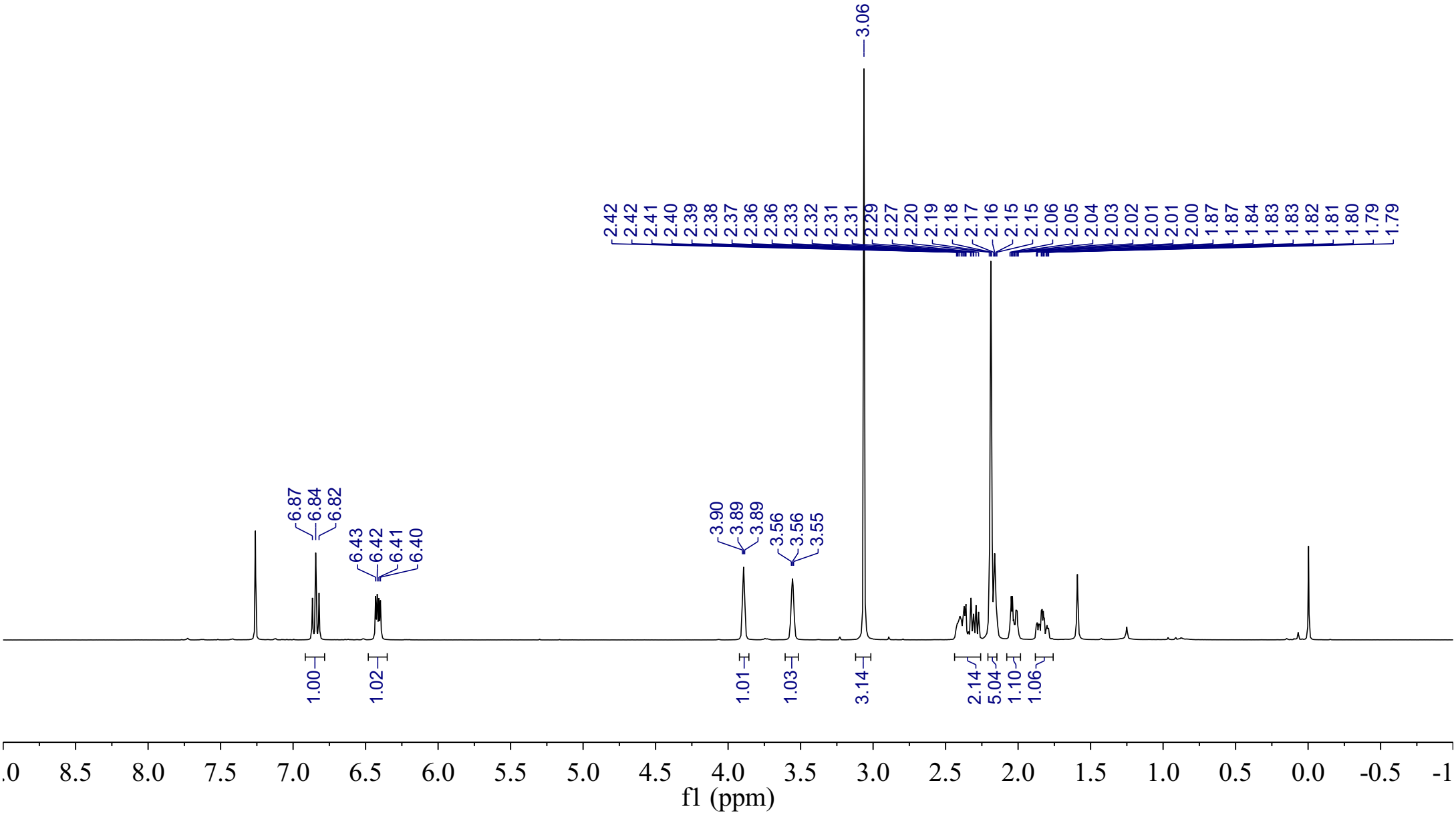
3k


3.07
2.43 2.42 2.42 2.41 2.41 2.41 2.40 2.40 2.39 2.39 2.38 2.38 2.37 2.36 2.36 2.35 2.34 2.33 2.31 2.19 2.19 2.17 2.15 2.15 2.14 2.13 2.13 2.13 2.12 2.07 2.06 2.05 2.04 2.04 2.03 2.02 2.01 1.89 1.87 1.87 1.86 1.85 1.84 1.84 1.83 1.82 1.81 1.81 1.80 1.80 1.79 1.78
6.96 6.94
6.47 6.45
3.98 3.98 3.97 3.56 3.55 3.54 3.53
1.00 1.01 1.02 1.03 3.07 2.16 3.13 5.23 1.09 1.03
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


Me
Me
O
N
Me
3k
210.56
144.12
135.64
129.54
123.63
117.85
107.41
77.48
77.16
76.84
52.80
47.77
37.62
34.84
33.82
29.99
19.95
15.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
F
N
Me

3l


3.06
2.42 2.42 2.41 2.40 2.39 2.38 2.37 2.36 2.36 2.33 2.32 2.31 2.31 2.29 2.27 2.20 2.19 2.18 2.17 2.16 2.15 2.15 2.06 2.05 2.04 2.03 2.02 2.01 2.01 2.00 1.87 1.87 1.84 1.83 1.83 1.82 1.81 1.80 1.79 1.79
6.87 6.84 6.82
6.43 6.42 6.41 6.40
3.90 3.89 3.89
3.56 3.56 3.55
1.00 1.02 1.01 1.03 3.14 2.14 5.04 1.10 1.06
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

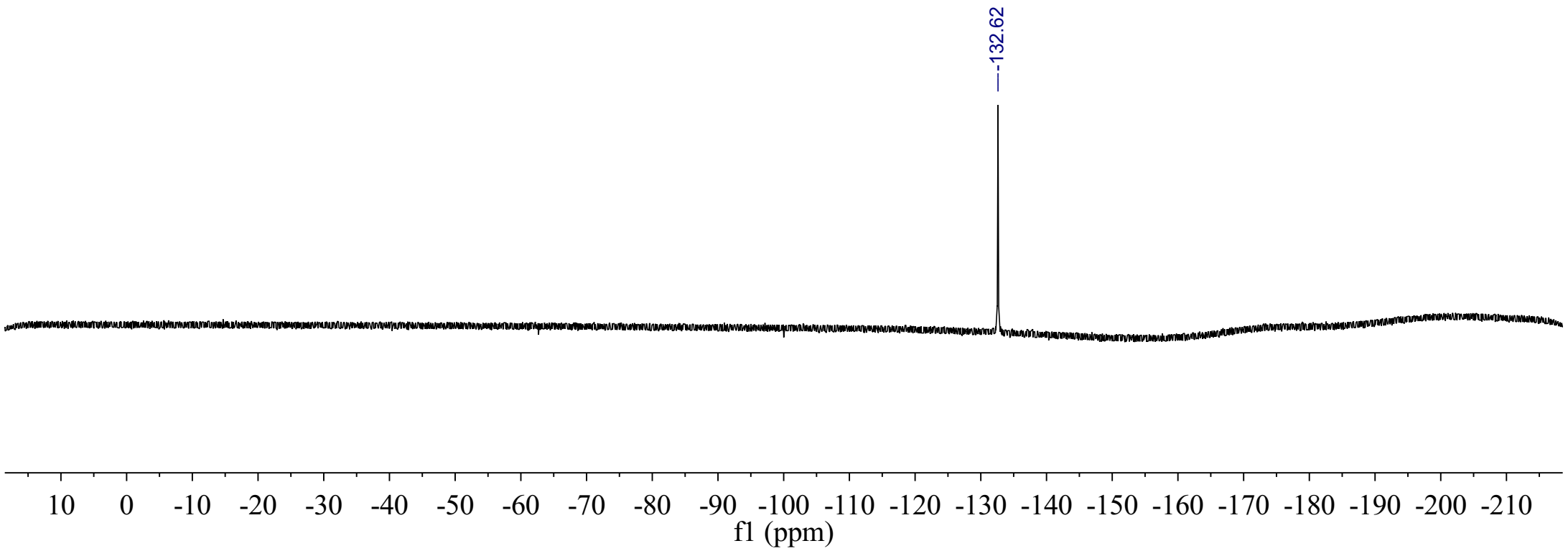

Me
O
F
N
Me

3l


77.48
77.16
76.84
209.67
154.35
152.04
142.12
123.83
123.66
118.48
114.47
114.24
107.57
107.49
52.86
47.66
47.64
37.82
34.72
33.64
29.63
10.68
10.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
F
N
Me

3l


-132.62
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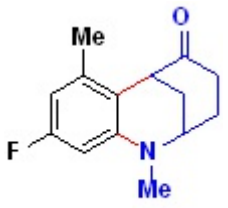
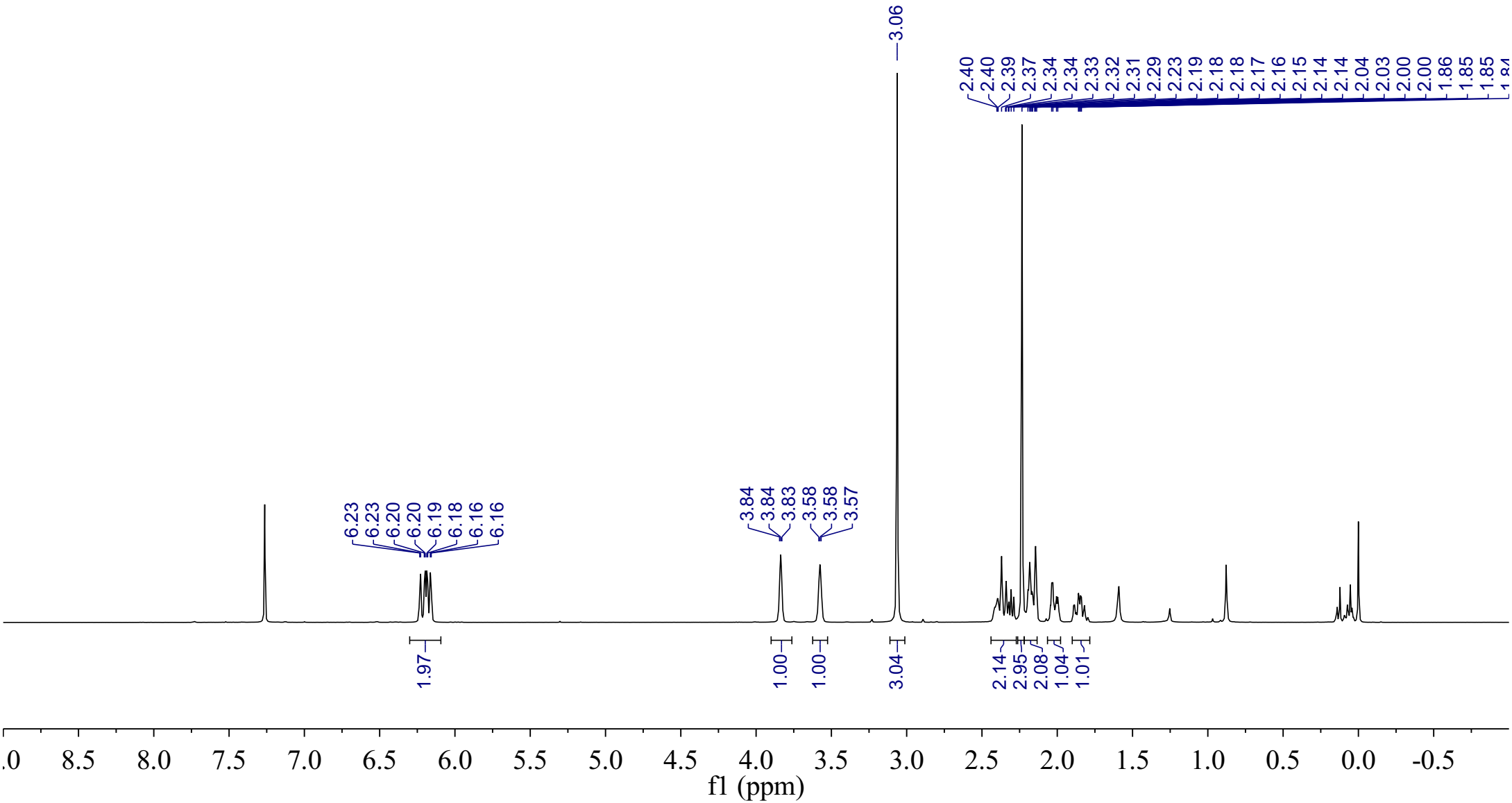
f1 (ppm)


Me
O
F
N
Me

3m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6.18
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6.16
3.84
3.84
3.83
3.58
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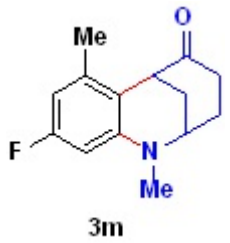
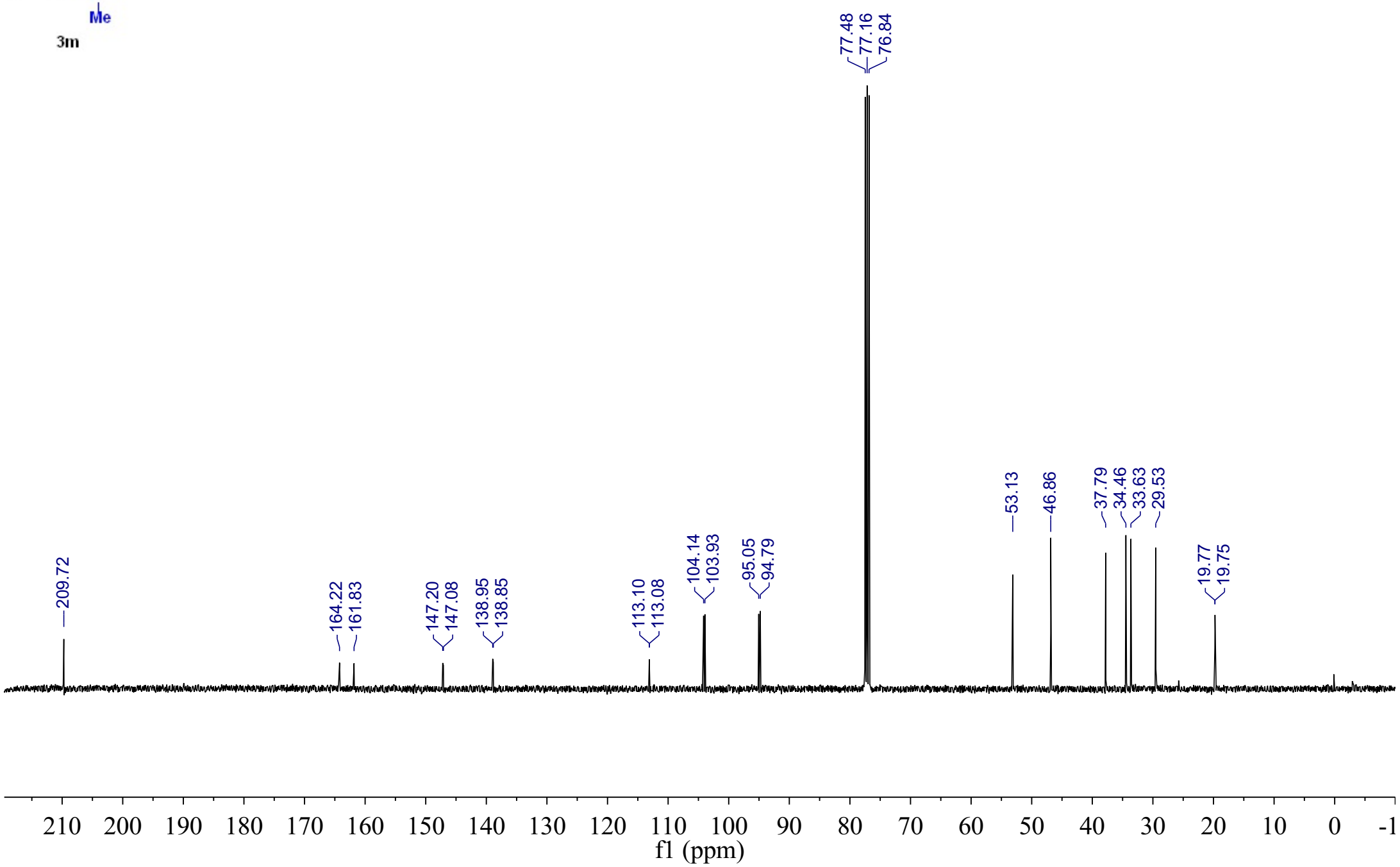
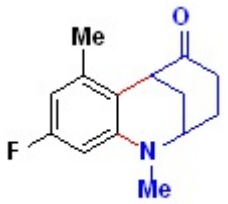
3.57
3.06
2.40
2.40
2.39
2.37
2.34
2.34
2.33
2.32
2.31
2.29
2.23
2.19
2.18
2.18
2.17
2.16
2.15
2.14
2.14
2.04
2.03
2.00
2.00
1.86
1.85
1.85
1.97
1.00
1.00
3.04
2.14
2.95
2.08
1.04
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

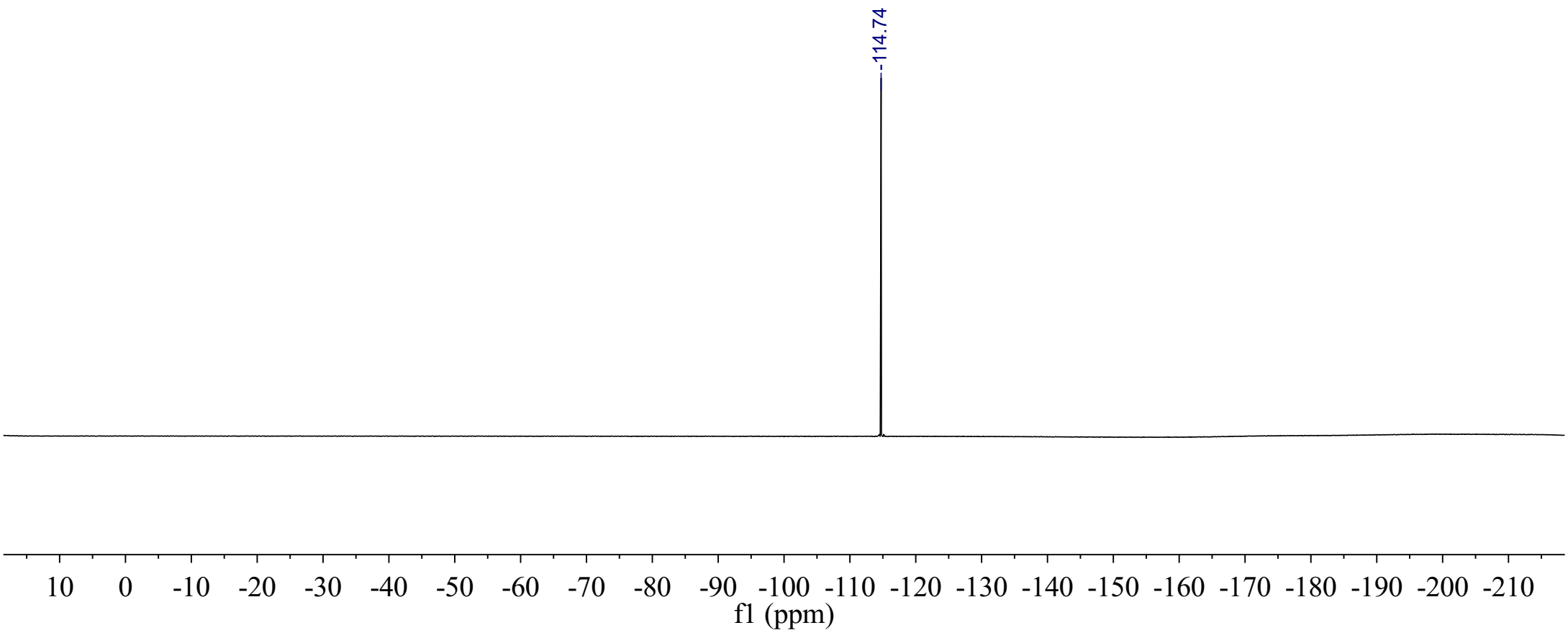

Me
O
F
N
Me

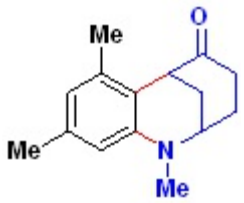
3m


77.48
77.16
76.84
209.72
164.22
161.83
147.20
147.08
138.95
138.85
113.10
113.08
104.14
103.93
95.05
94.79
53.13
46.86
37.79
34.46
33.63
29.53
19.77
19.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

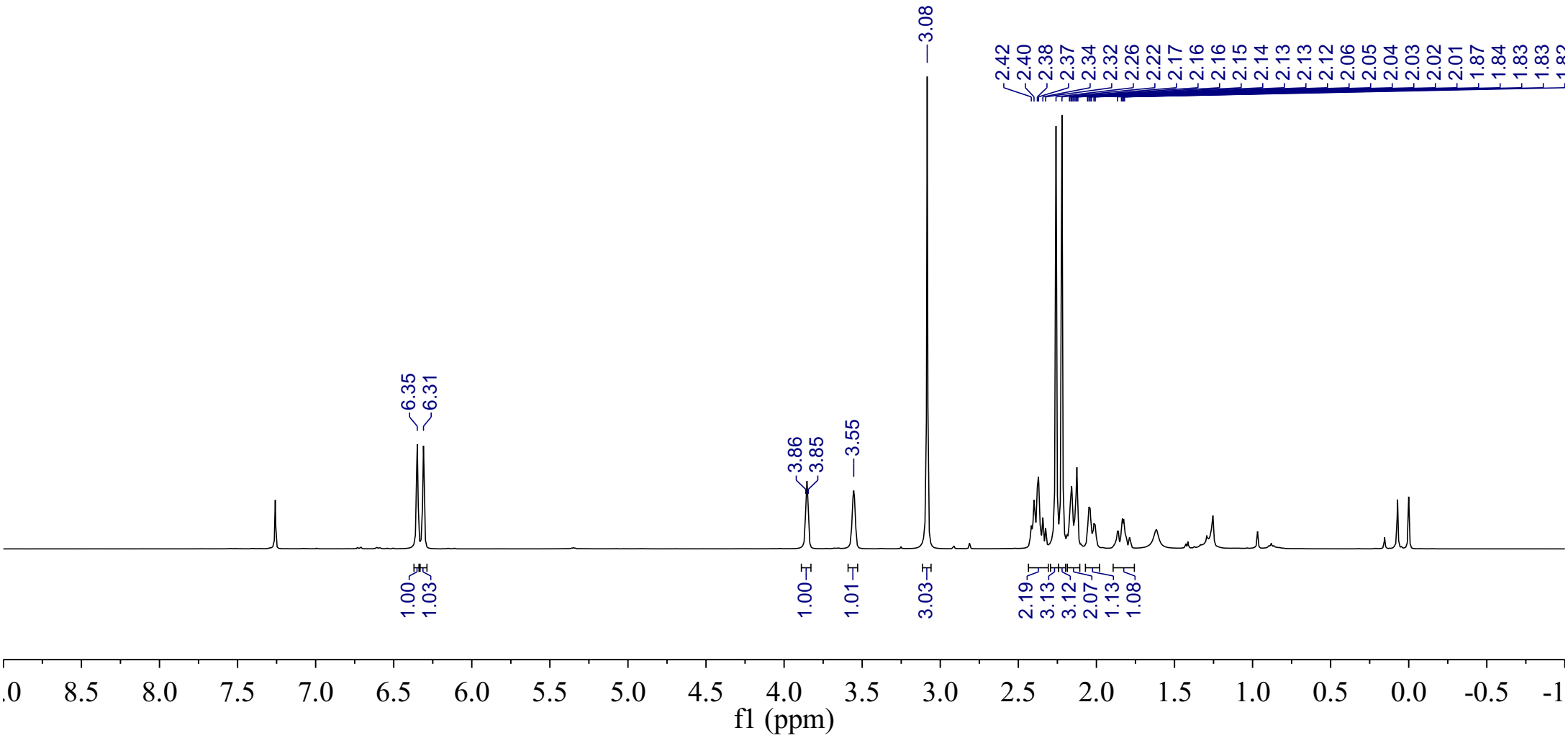

Me
O
F
N
Me

3m


-114.74
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)


Me
O
Me
N
Me

3n


6.35
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3.08
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2.40
2.38
2.37
2.34
2.32
2.26
2.22
2.17
2.16
2.16
2.15
2.14
2.13
2.13
2.12
2.06
2.05
2.04
2.03
2.02
2.01
1.87
1.84
1.83
1.83
1.00
1.03
1.00
1.01
3.03
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3.13
3.12
2.07
1.13
1.08
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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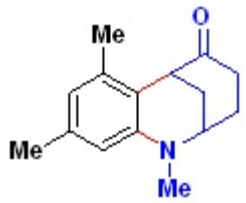
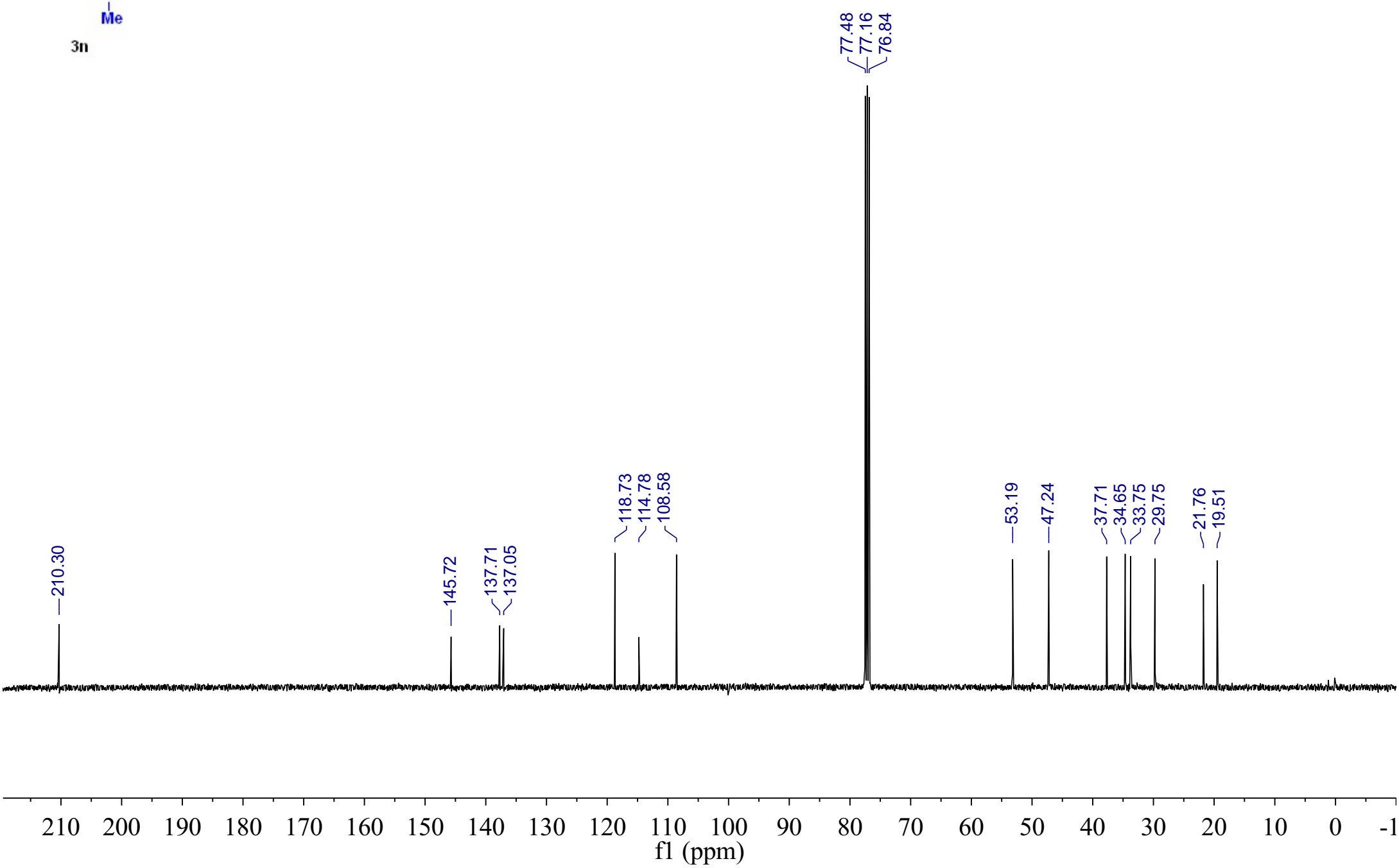
0.5
0.0
-0.5
f1 (ppm)


Me
O
Me
N
Me

3n


77.48
77.16
76.84
210.30
145.72
137.71
137.05
118.73
114.78
108.58
53.19
47.24
37.71
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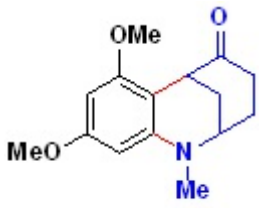
29.75
21.76
19.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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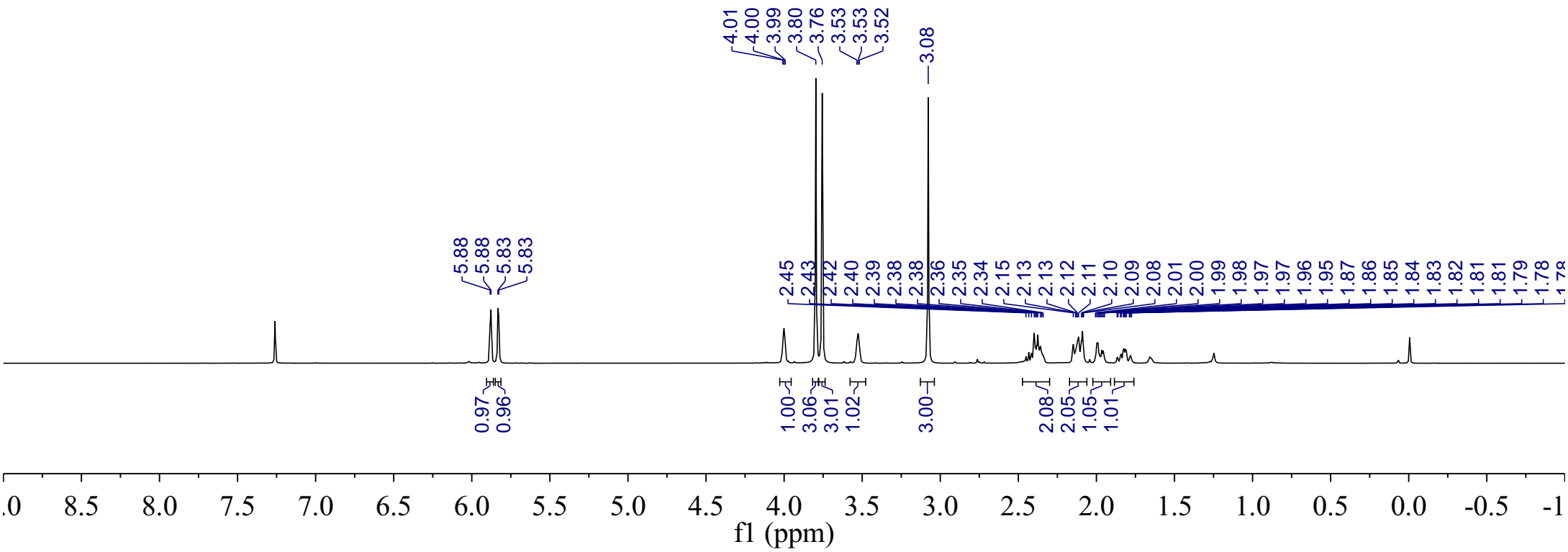
O
MeO
N
Me

3o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5.88
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5.83
2.45
2.43
2.42
2.40
2.39
2.38
2.38
2.36
2.35
2.34
2.15
2.13
2.13
2.12
2.11
2.10
2.09
2.08
2.01
2.00
1.99
1.98
1.97
1.97
1.96
1.95
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.81
1.79
1.78
0.97
0.96
1.00
3.06
3.01
1.02
3.00
2.08
2.05
1.05
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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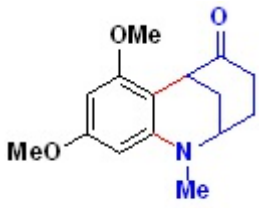
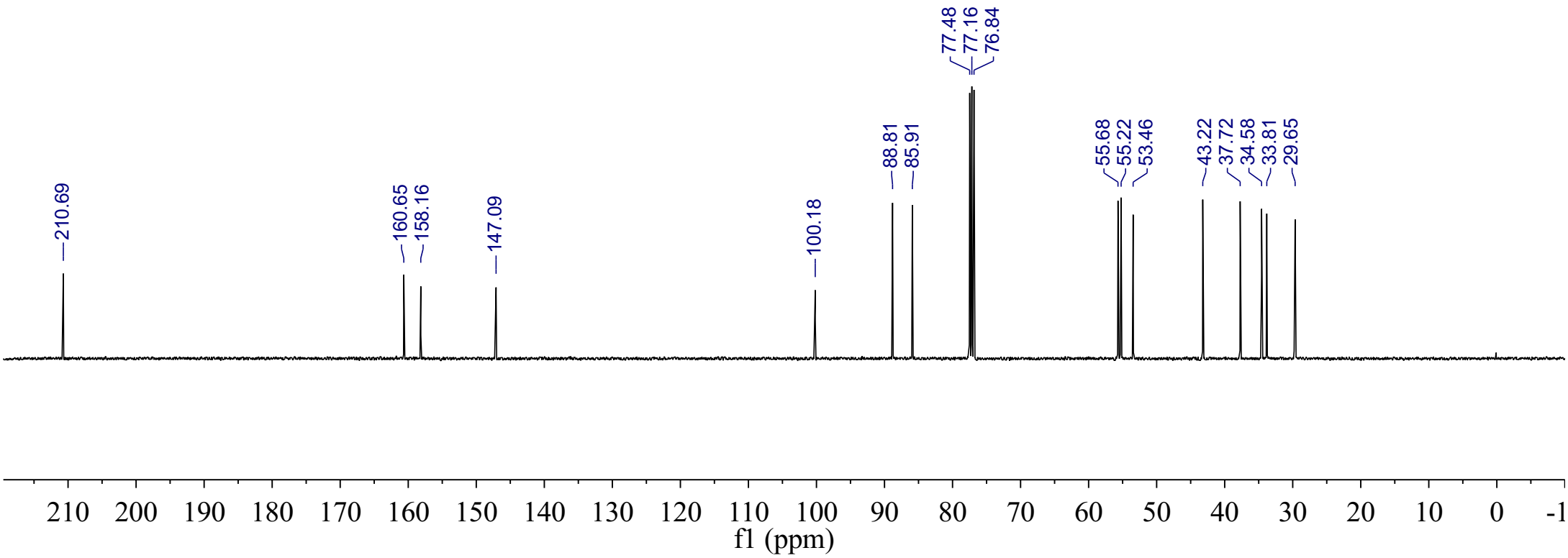
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


OMe
O
MeO
N
Me

3o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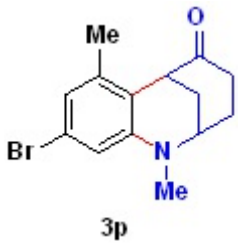
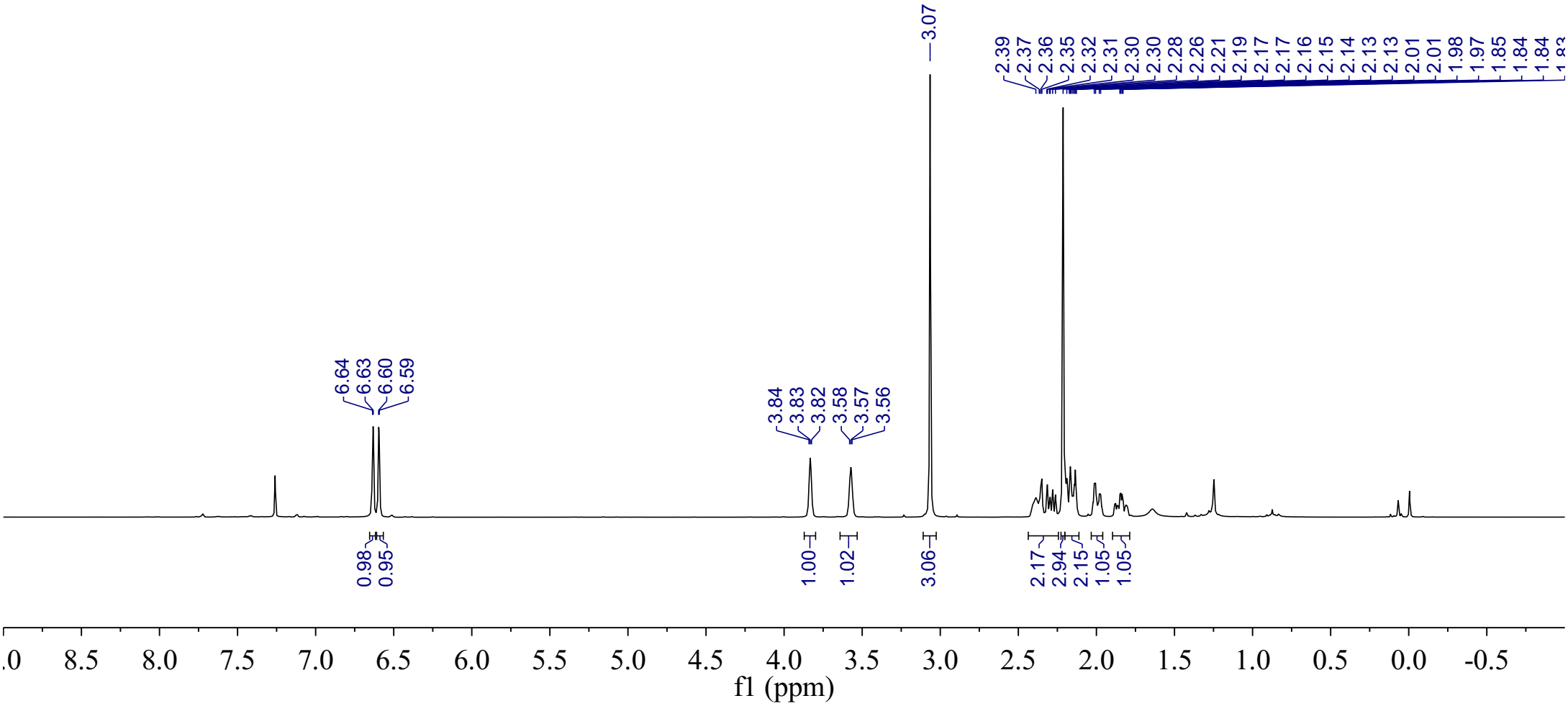
100.18
88.81
85.91
77.48
77.16
76.84
55.68
55.22
53.46
43.22
37.72
34.58
33.81
29.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
Br
N
Me

3p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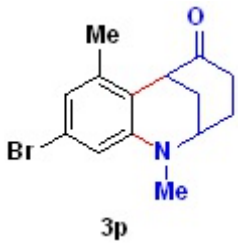
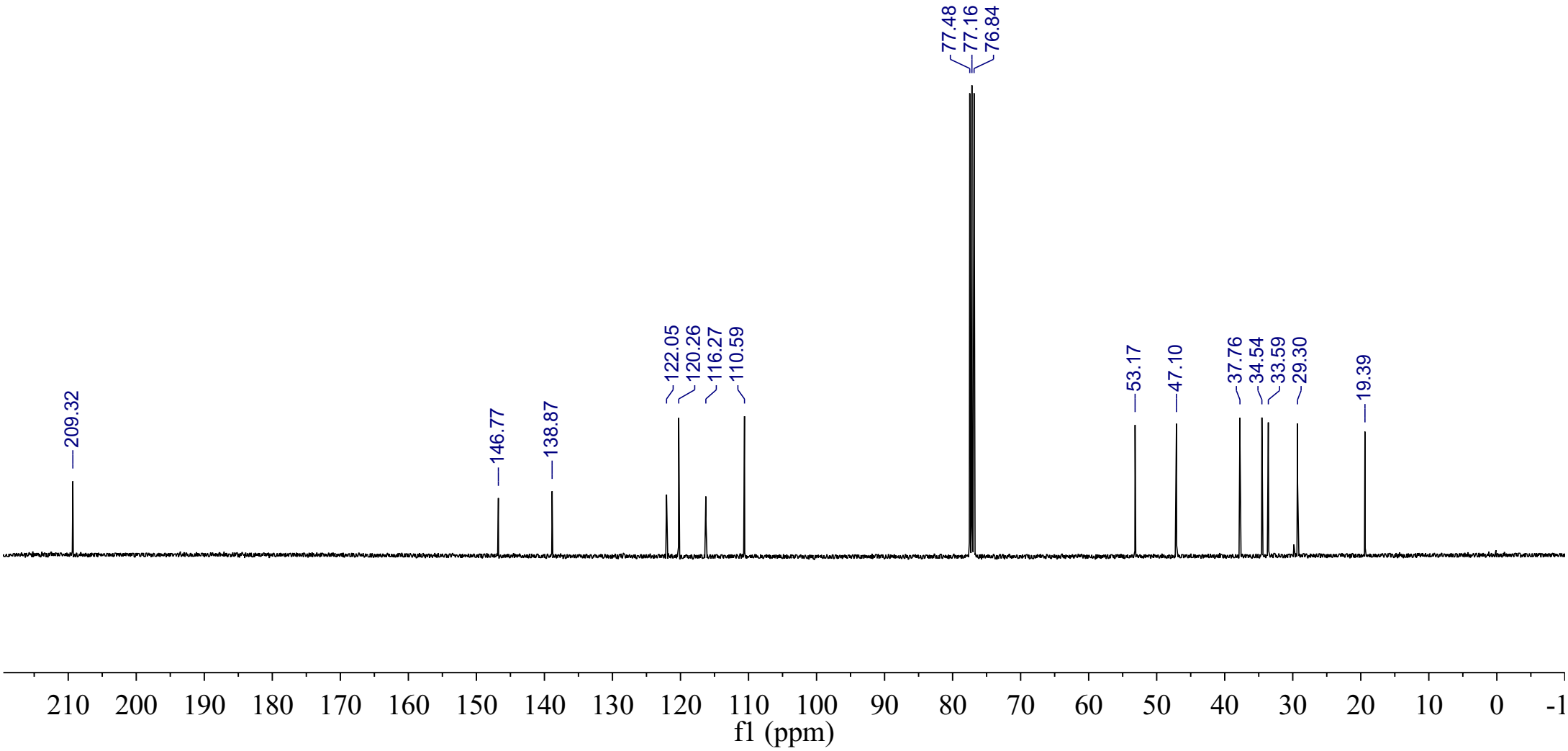
6.63
6.60
6.59
3.84
3.83
3.82
3.58
3.57
3.56
3.07
2.39
2.37
2.36
2.35
2.32
2.31
2.30
2.30
2.28
2.26
2.21
2.19
2.17
2.17
2.16
2.15
2.14
2.13
2.13
2.01
2.01
1.98
1.97
1.85
1.84
1.84
0.98
0.95
1.00
1.02
3.06
2.17
2.94
2.15
1.05
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
O
Br
N
Me

3p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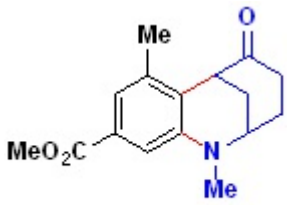
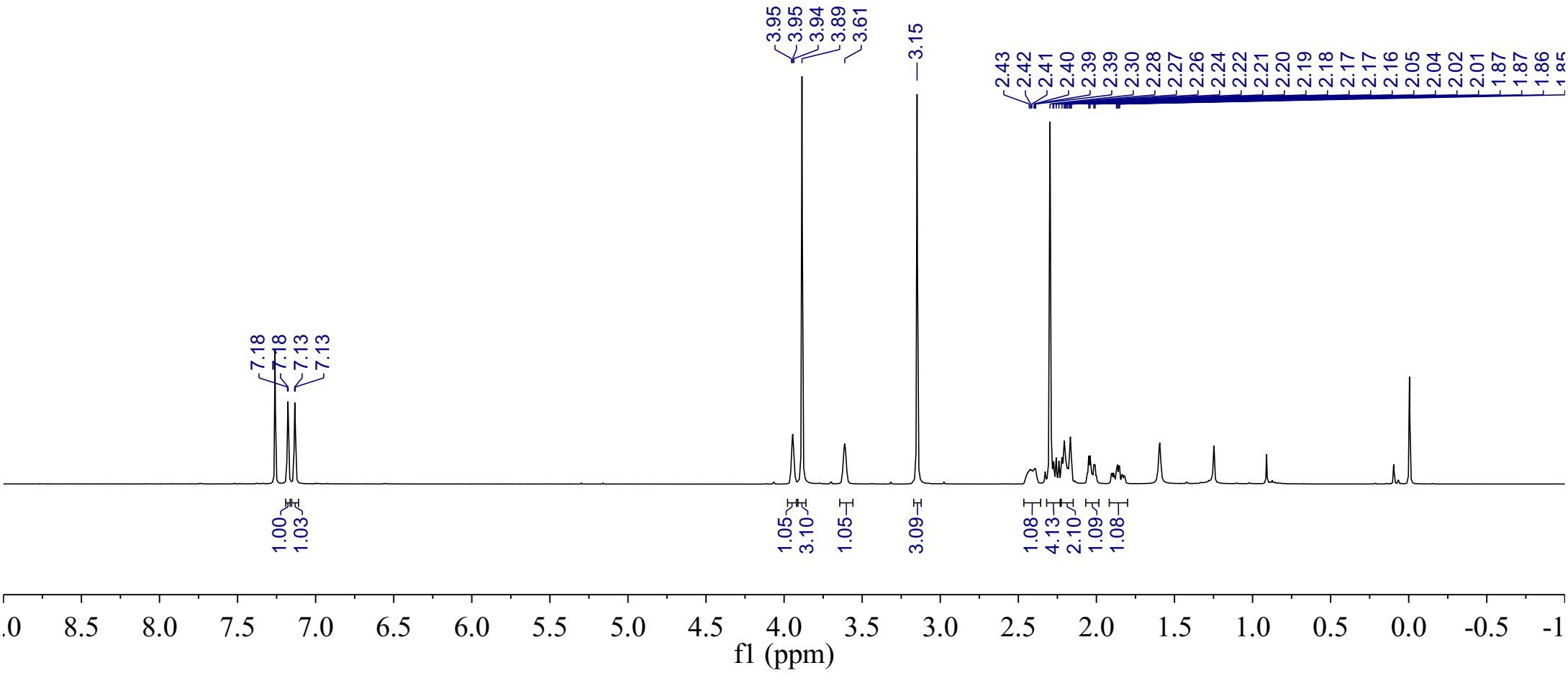
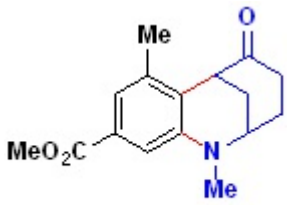
120.26
116.27
110.59
77.48
77.16
76.84
53.17
47.10
37.76
34.54
33.59
29.30
19.39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

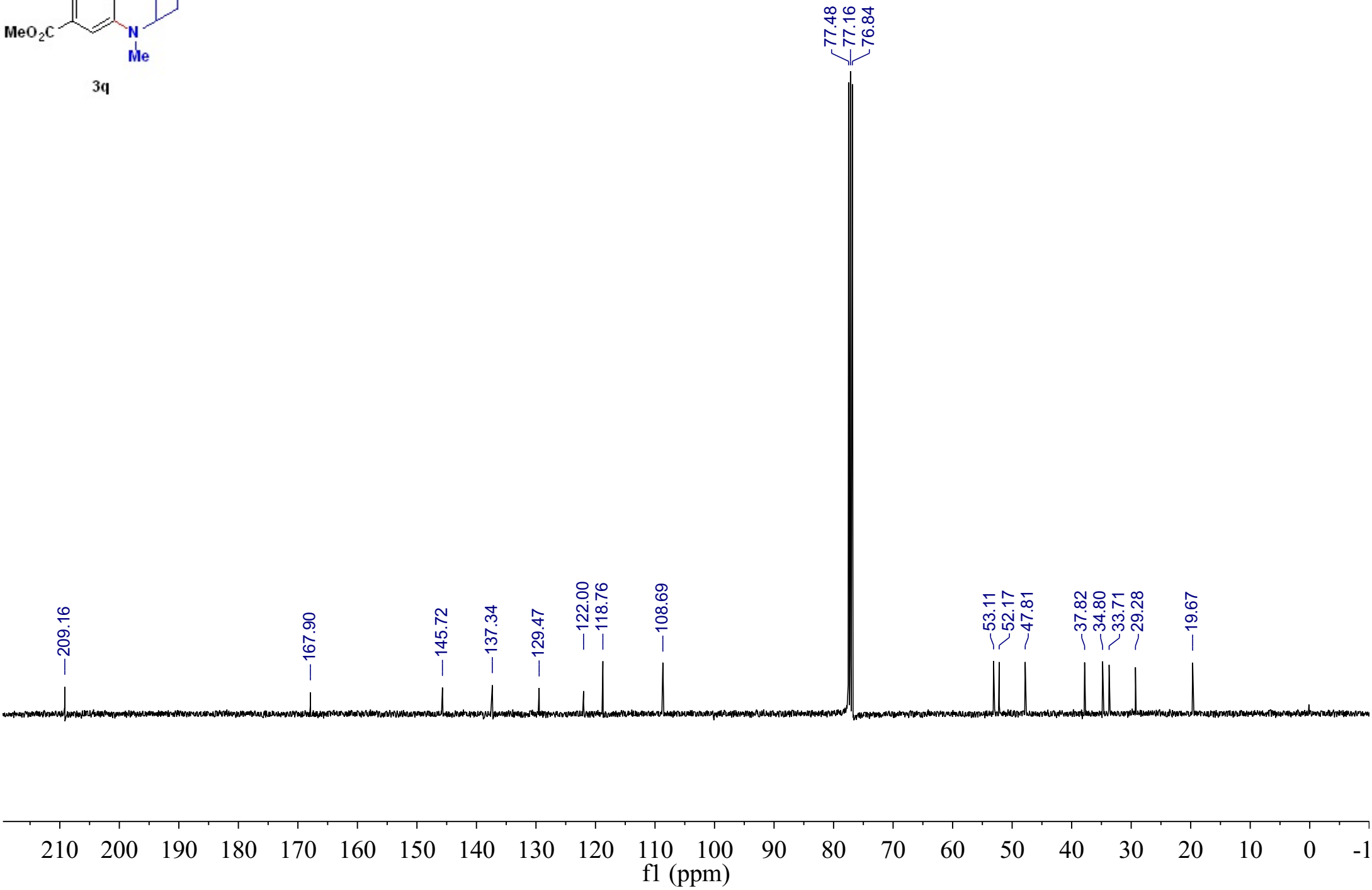

Me
O
MeO2C
N
Me

3q


3.95
3.95
3.94
3.89
3.61
3.15
2.43
2.42
2.41
2.40
2.40
2.39
2.39
2.30
2.28
2.27
2.26
2.24
2.22
2.21
2.20
2.19
2.18
2.17
2.17
2.16
2.05
2.04
2.02
2.01
1.87
1.87
1.86
7.18
7.18
7.13
7.13
1.00
1.03
1.05
3.10
1.05
3.09
1.08
4.13
2.10
1.09
1.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Me
O
MeO2C
N
Me

3q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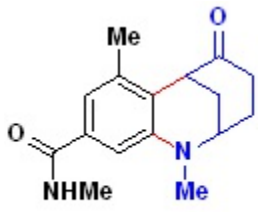
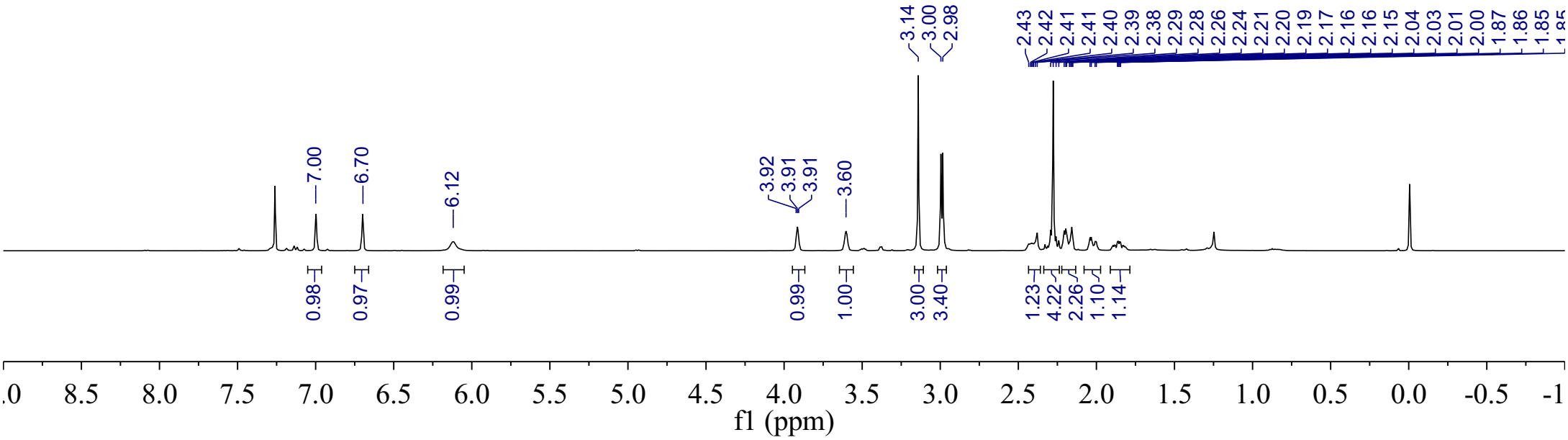
76.84
209.16
167.90
145.72
137.34
129.47
122.00
118.76
108.69
53.11
52.17
47.81
37.82
34.80
33.71
29.28
19.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
O
N
NHMe
Me

3r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2.42
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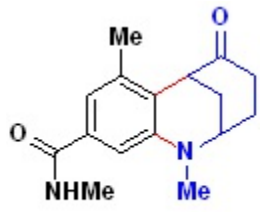
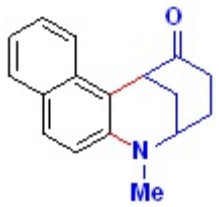
2.41
2.40
2.39
2.38
2.29
2.28
2.26
2.24
2.21
2.20
2.19
2.17
2.16
2.16
2.15
2.04
2.03
2.01
2.00
1.87
1.86
1.85
7.00
6.70
6.12
3.92
3.91
3.91
3.60
0.98
0.97
0.99
0.99
1.00
3.00
3.40
1.23
4.22
2.26
1.10
1.14
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

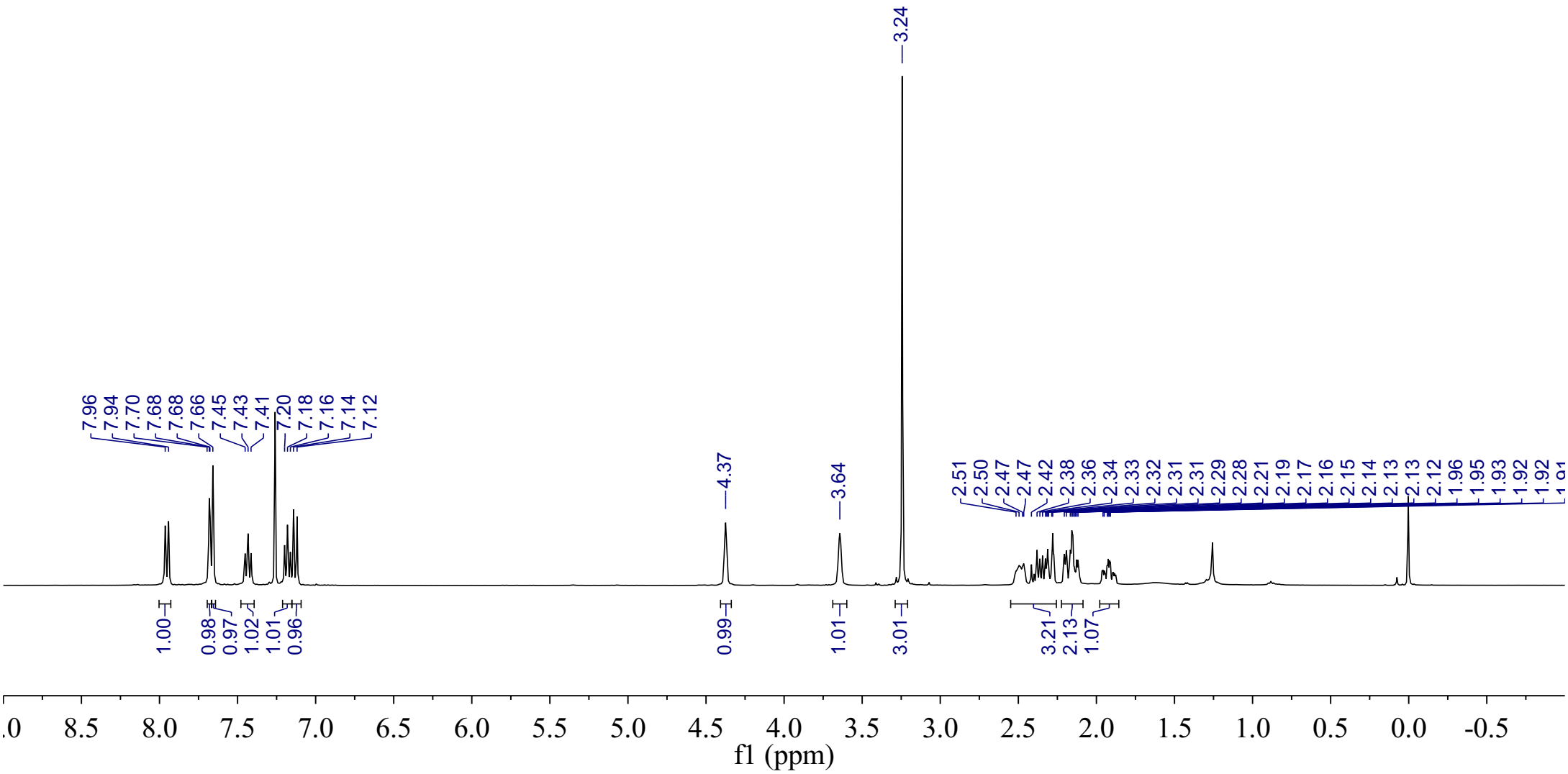

Me
O
O
N
NHMe
Me

3r


77.48
77.16
76.84
209.33
169.10
145.96
137.31
134.43
120.30
115.21
107.02
53.17
47.61
37.87
34.71
33.67
29.28
26.94
19.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O
N
Me

3s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7.43
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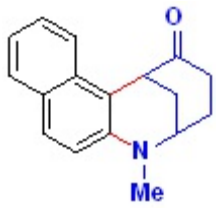
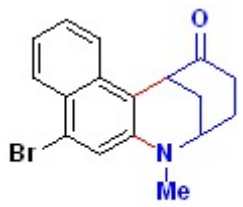
7.20
7.18
7.16
7.14
7.12
4.37
3.64
3.24
2.51
2.50
2.47
2.47
2.42
2.38
2.36
2.34
2.33
2.32
2.31
2.31
2.29
2.28
2.21
2.19
2.17
2.16
2.15
2.14
2.13
2.13
2.12
1.96
1.95
1.93
1.92
1.92
1.00
0.98
0.97
1.02
1.01
0.96
0.99
1.01
3.01
3.21
2.13
1.07
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

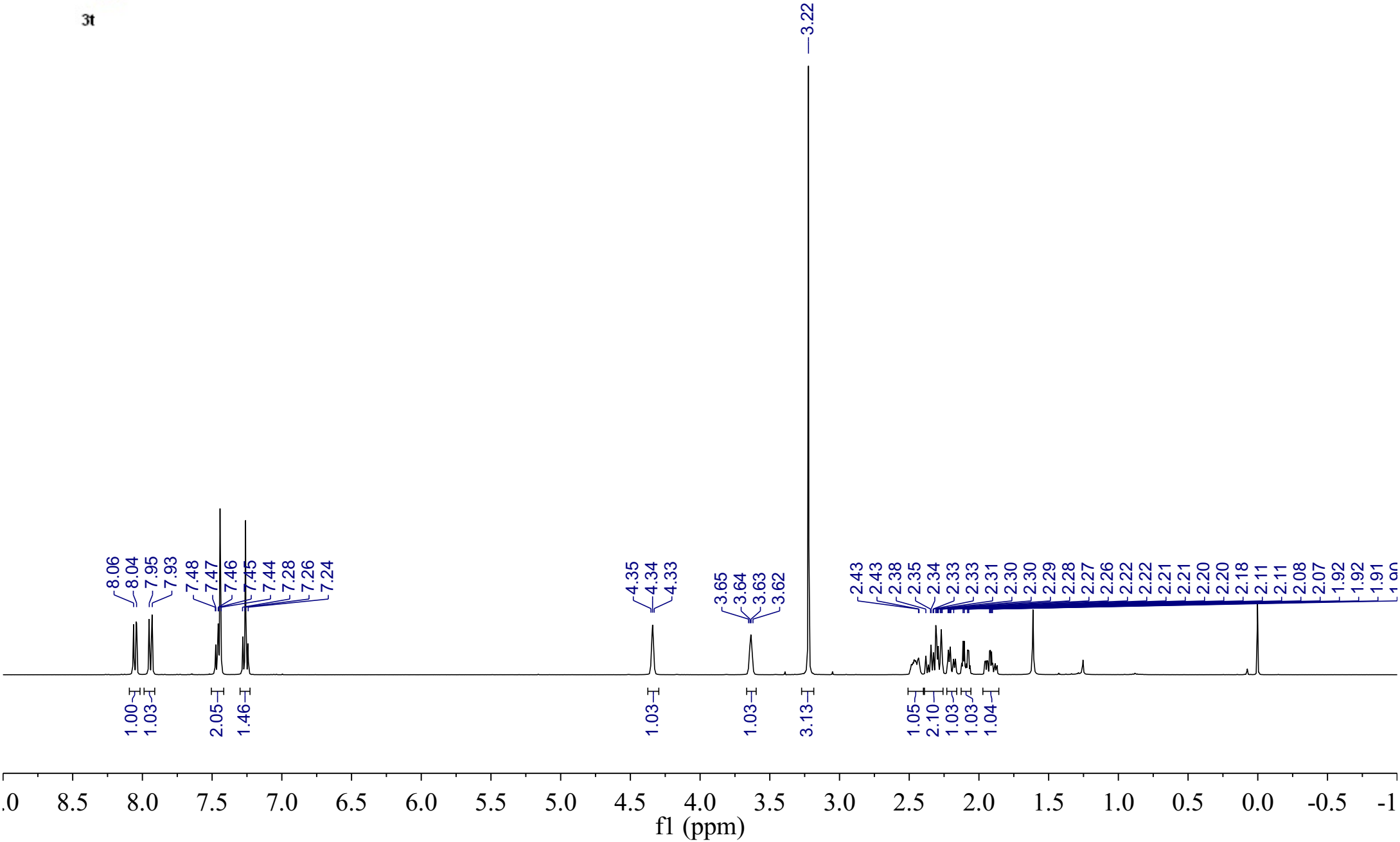

O
N
Me

3s


77.48
77.16
76.84
209.91
143.48
132.61
129.04
128.40
127.24
121.50
121.35
113.57
109.28
53.35
46.19
37.87
34.70
33.86
29.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


O
Br
N
Me

3t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7.93
7.48
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7.46
7.45
7.44
7.28
7.26
7.24
4.35
4.34
4.33
3.65
3.64
3.63
3.62
2.43
2.43
2.38
2.35
2.34
2.33
2.33
2.31
2.30
2.30
2.29
2.28
2.27
2.26
2.22
2.22
2.21
2.21
2.20
2.20
2.18
2.11
2.11
2.08
2.07
1.92
1.92
1.91
1.00
1.03
2.05
1.46
1.03
1.03
3.13
1.05
2.10
1.03
1.03
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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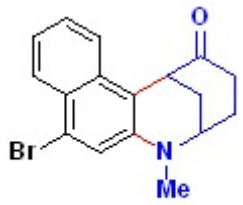
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

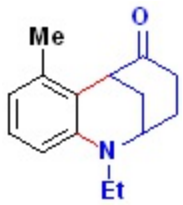



3t

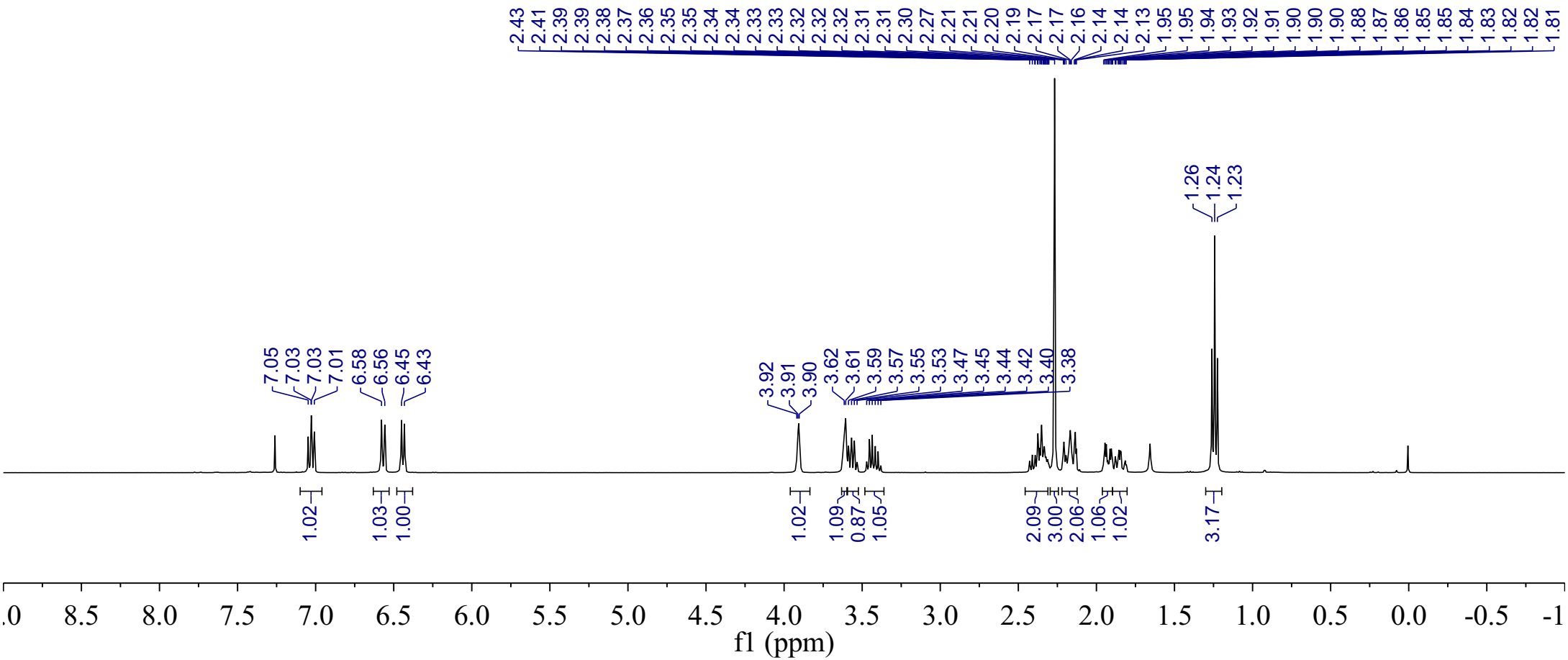
209.31
143.66
133.48
127.92
127.68
124.66
122.67
121.72
117.44
109.31
77.48
77.16
76.84
53.32
46.08
37.80
34.61
33.75
28.96

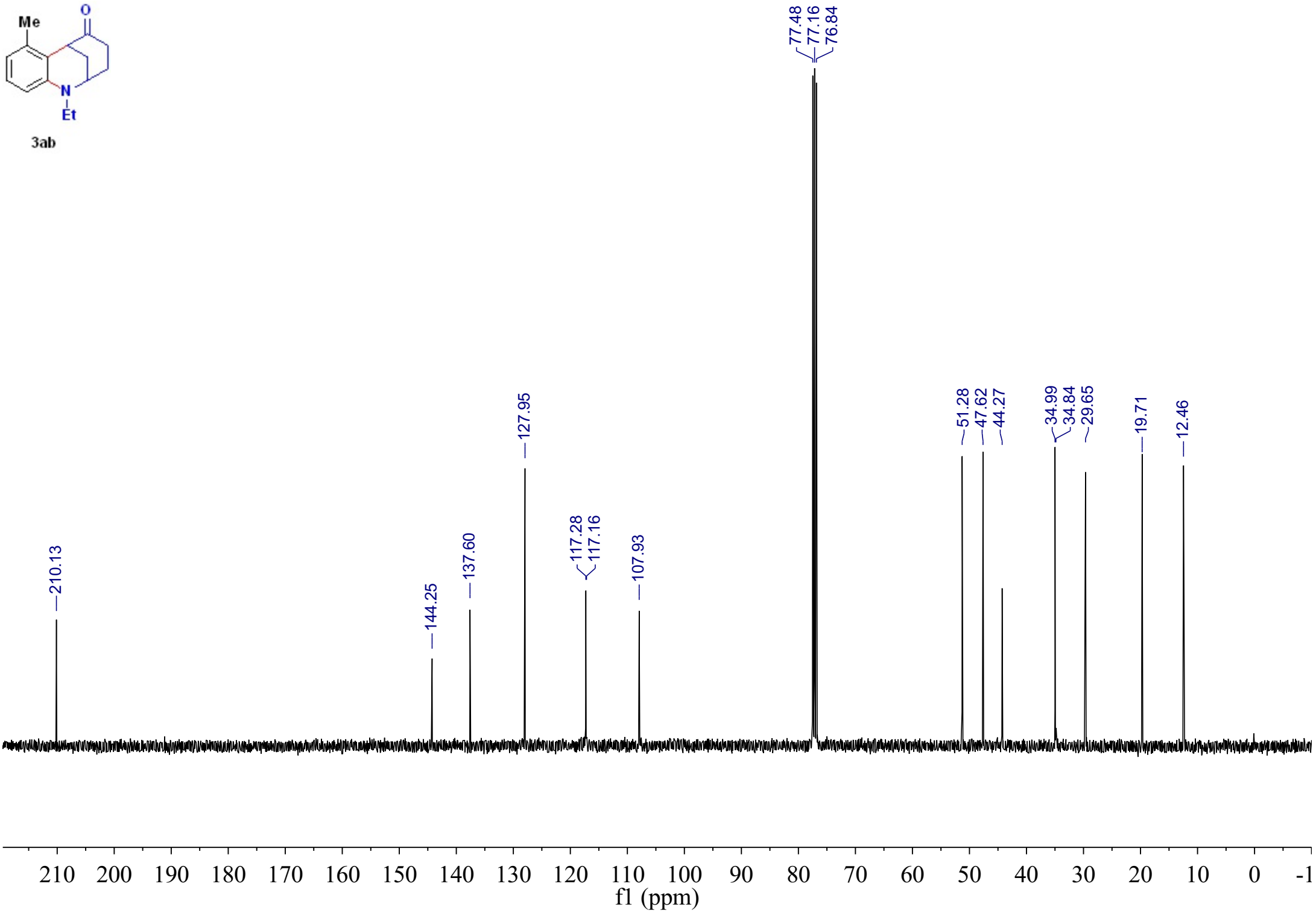
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

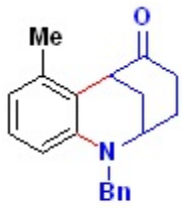
f1 (ppm)


Me
O
N
Et

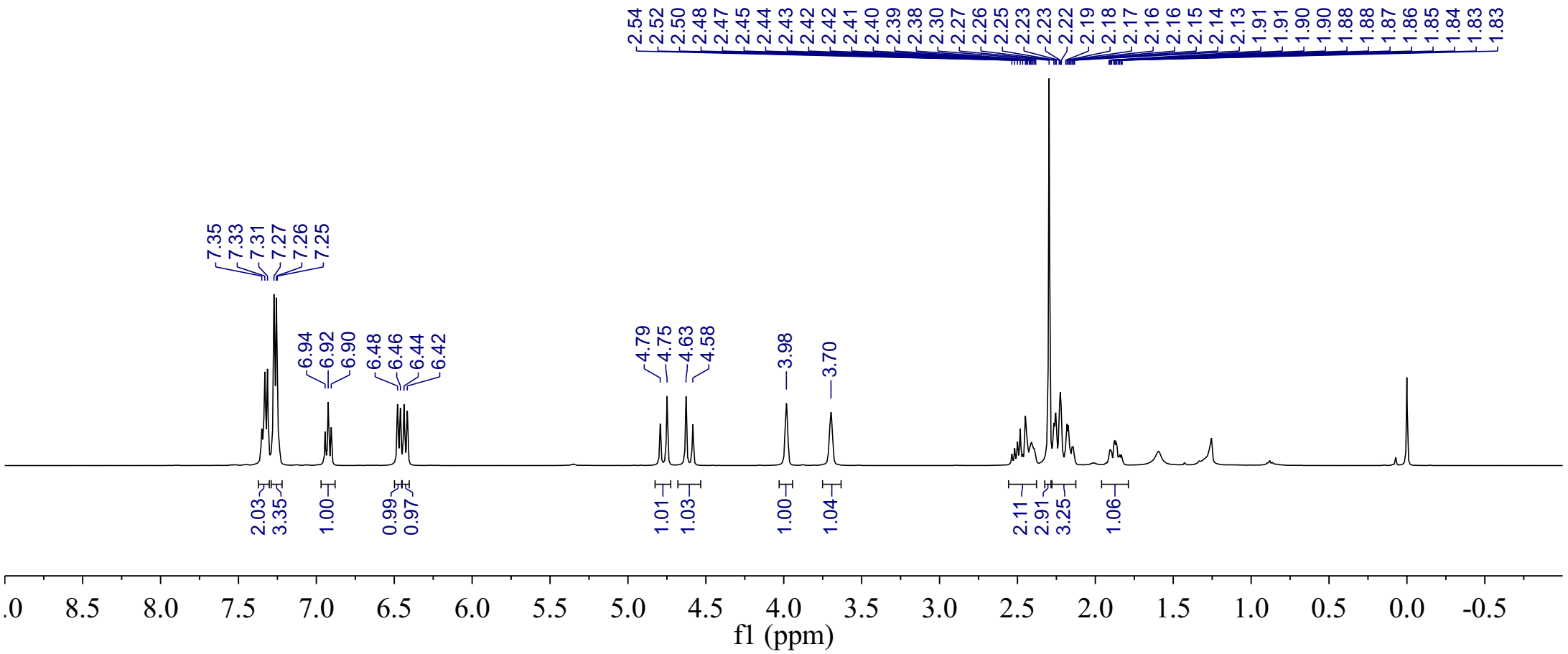
3ab


2.43 2.41 2.39 2.39 2.38 2.37 2.36 2.35 2.35 2.34 2.34 2.33 2.33 2.32 2.32 2.32 2.31 2.31 2.30 2.27 2.21 2.21 2.20 2.19 2.17 2.17 2.16 2.14 2.14 2.13 1.95 1.95 1.94 1.93 1.92 1.91 1.90 1.90 1.90 1.88 1.87 1.86 1.85 1.85 1.84 1.83 1.82 1.82 1.81
1.26 1.24 1.23
7.05 7.03 7.03 7.01 6.58 6.56 6.45 6.43
3.92 3.91 3.90 3.62 3.61 3.59 3.57 3.55 3.53 3.47 3.45 3.44 3.42 3.40 3.38
1.02 1.03 1.00 1.02 1.09 0.87 1.05 2.09 3.00 2.06 1.06 1.02 3.17
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


Me
O
N
Et
3ab
77.48
77.16
76.84
210.13
144.25
137.60
127.95
117.28
117.16
107.93
51.28
47.62
44.27
34.99
34.84
29.65
19.71
12.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
N
Bn

3ac


2.54
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2.47
2.45
2.44
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2.41
2.40
2.39
2.38
2.30
2.27
2.26
2.25
2.23
2.23
2.22
2.19
2.18
2.17
2.16
2.16
2.15
2.14
2.13
1.91
1.91
1.90
1.90
1.88
1.88
1.87
1.86
1.85
1.84
1.83
1.83
7.35
7.33
7.31
7.27
7.26
7.25
6.94
6.92
6.90
6.48
6.46
6.44
6.42
4.79
4.75
4.63
4.58
3.98
3.70
2.03
3.35
1.00
0.99
0.97
1.01
1.03
1.00
1.04
2.11
2.91
3.25
1.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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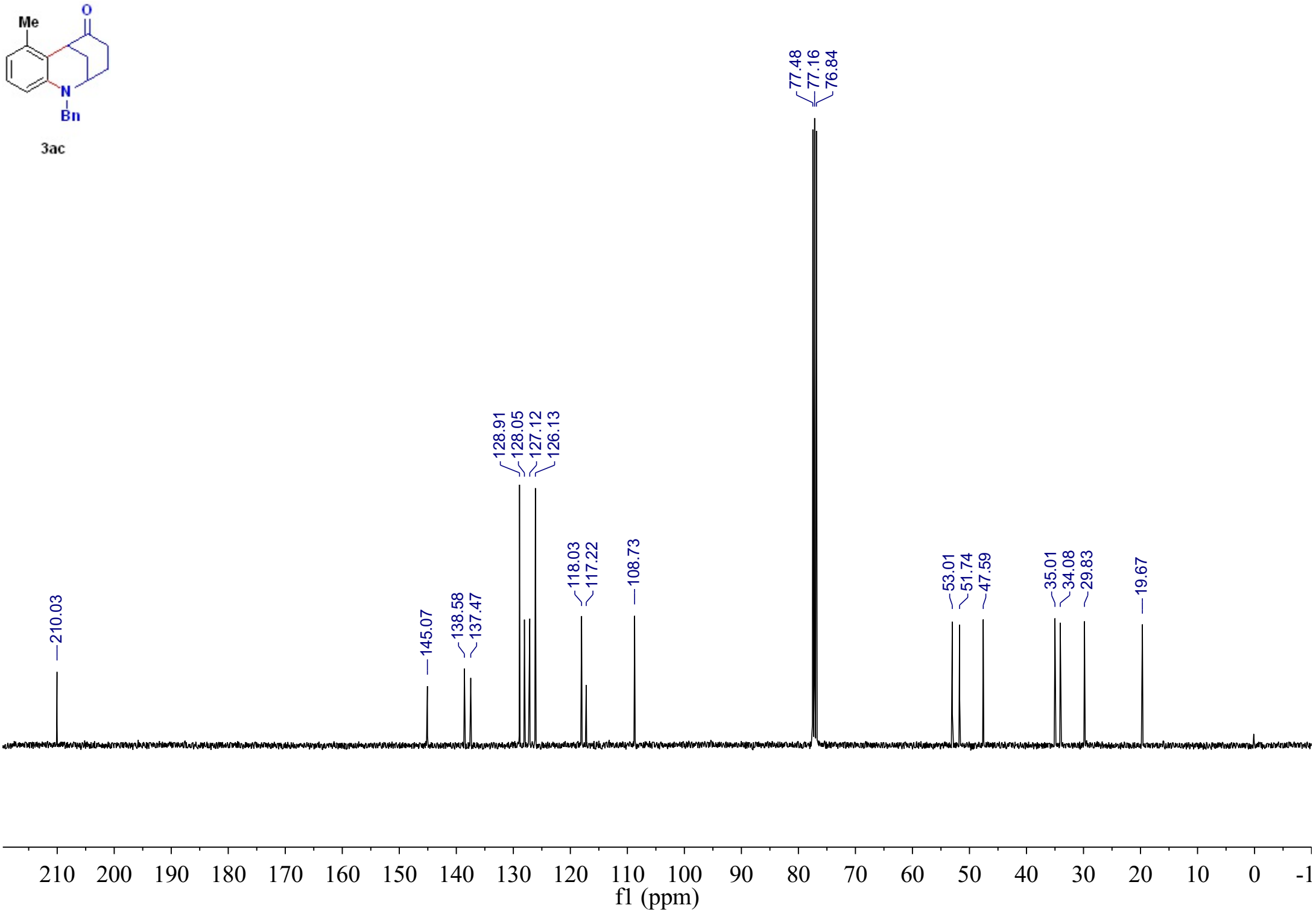
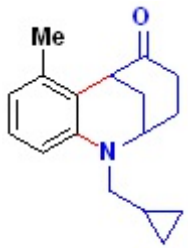
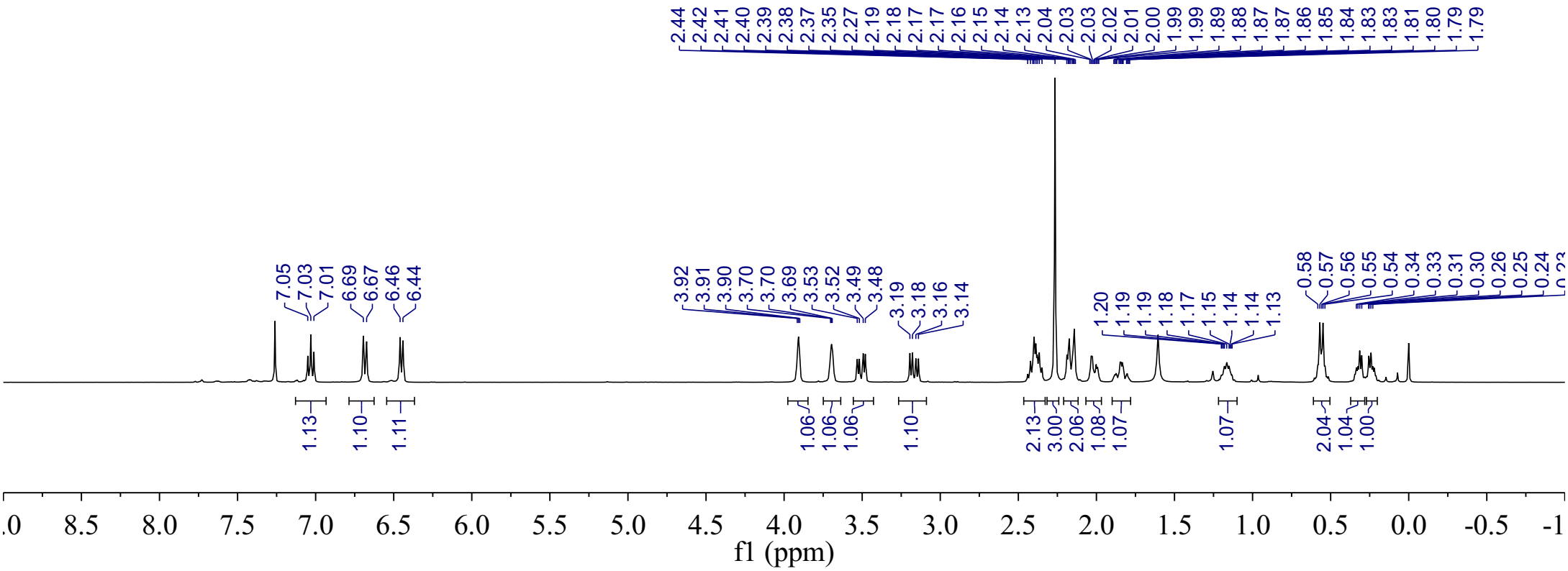
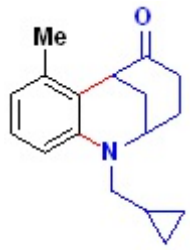
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
O
N
Bn
3ac
210.03
145.07
138.58
137.47
128.91
128.05
127.12
126.13
118.03
117.22
108.73
77.48
77.16
76.84
53.01
51.74
47.59
35.01
34.08
29.83
19.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

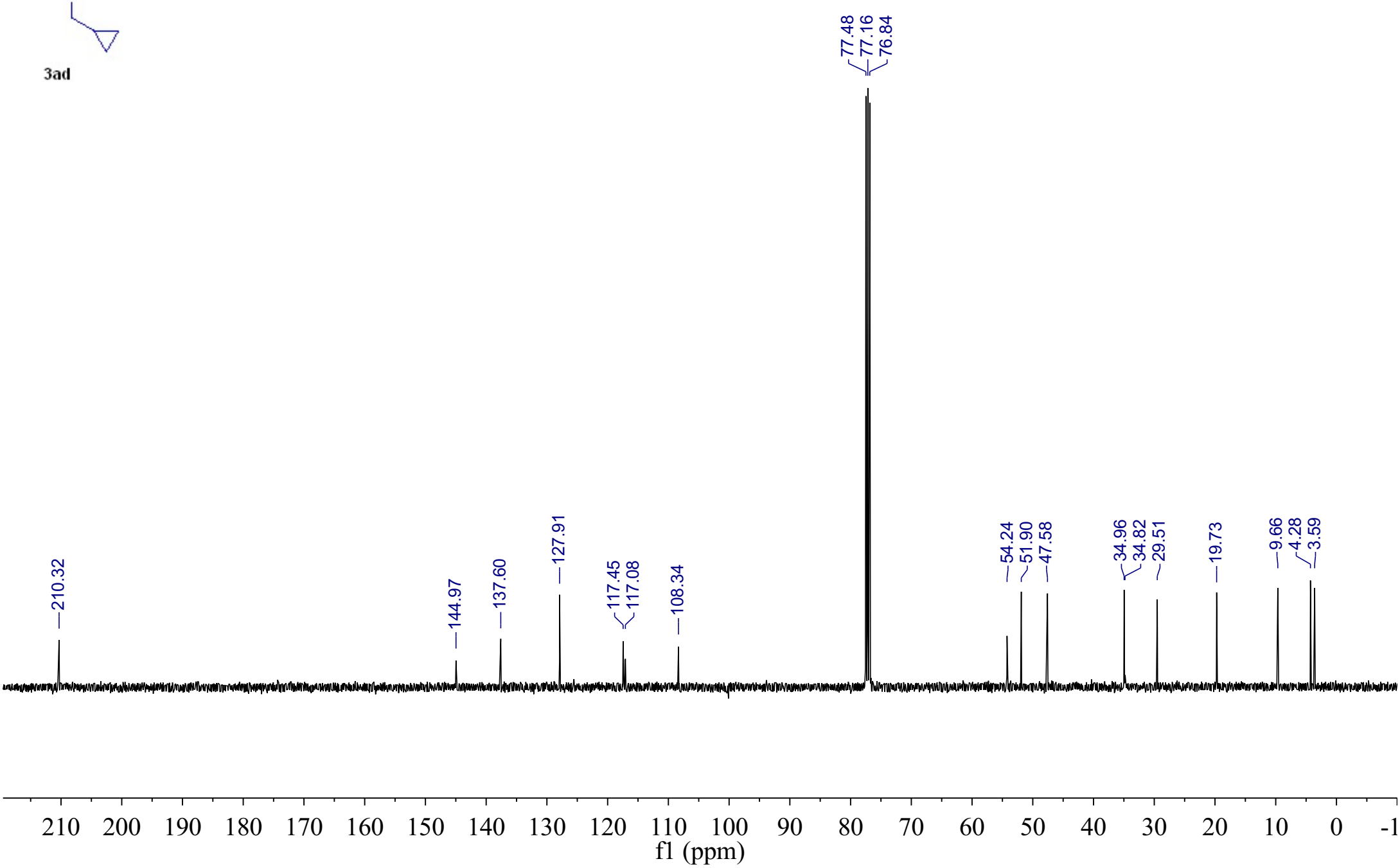

Me
O
N

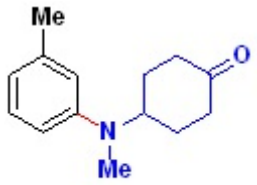
3ad


2.44 2.42 2.41 2.40 2.39 2.38 2.37 2.35 2.27 2.19 2.18 2.17 2.17 2.16 2.15 2.14 2.13 2.04 2.03 2.03 2.02 2.01 2.00 1.99 1.99 1.89 1.88 1.87 1.87 1.86 1.85 1.84 1.83 1.83 1.81 1.80 1.79 1.79
7.05 7.03 7.01 6.69 6.67 6.46 6.44
3.92 3.91 3.90 3.70 3.70 3.69 3.53 3.52 3.49 3.48 3.19 3.18 3.16 3.14
1.20 1.19 1.19 1.18 1.17 1.15 1.14 1.14 1.13
0.58 0.57 0.56 0.55 0.54 0.34 0.33 0.31 0.30 0.26 0.25 0.24
1.13 1.10 1.11 1.06 1.06 1.06 1.10 2.13 3.00 2.06 1.08 1.07 1.07 2.04 1.04 1.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

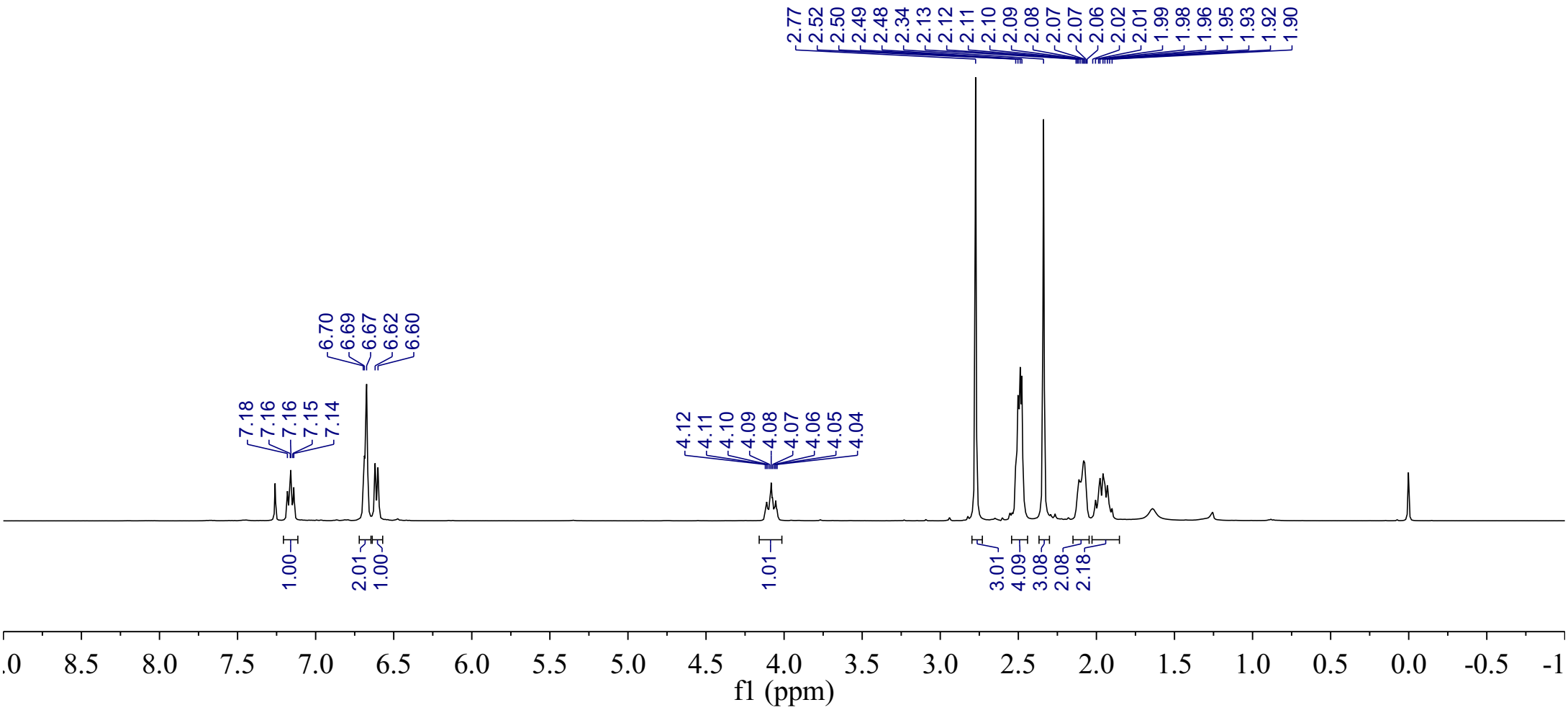

Me
O
N

3ad


77.48
77.16
76.84
210.32
144.97
137.60
127.91
117.45
117.08
108.34
54.24
51.90
47.58
34.96
34.82
29.51
19.73
9.66
4.28
3.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Me
O
N
Me

4a


2.77
2.52
2.50
2.49
2.48
2.34
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.07
2.06
2.02
2.01
1.99
1.98
1.96
1.95
1.93
1.92
1.90
6.70
6.69
6.67
6.62
6.60
7.18
7.16
7.16
7.15
7.14
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
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1.00
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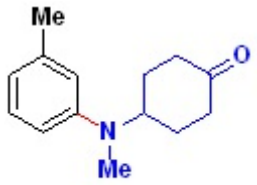
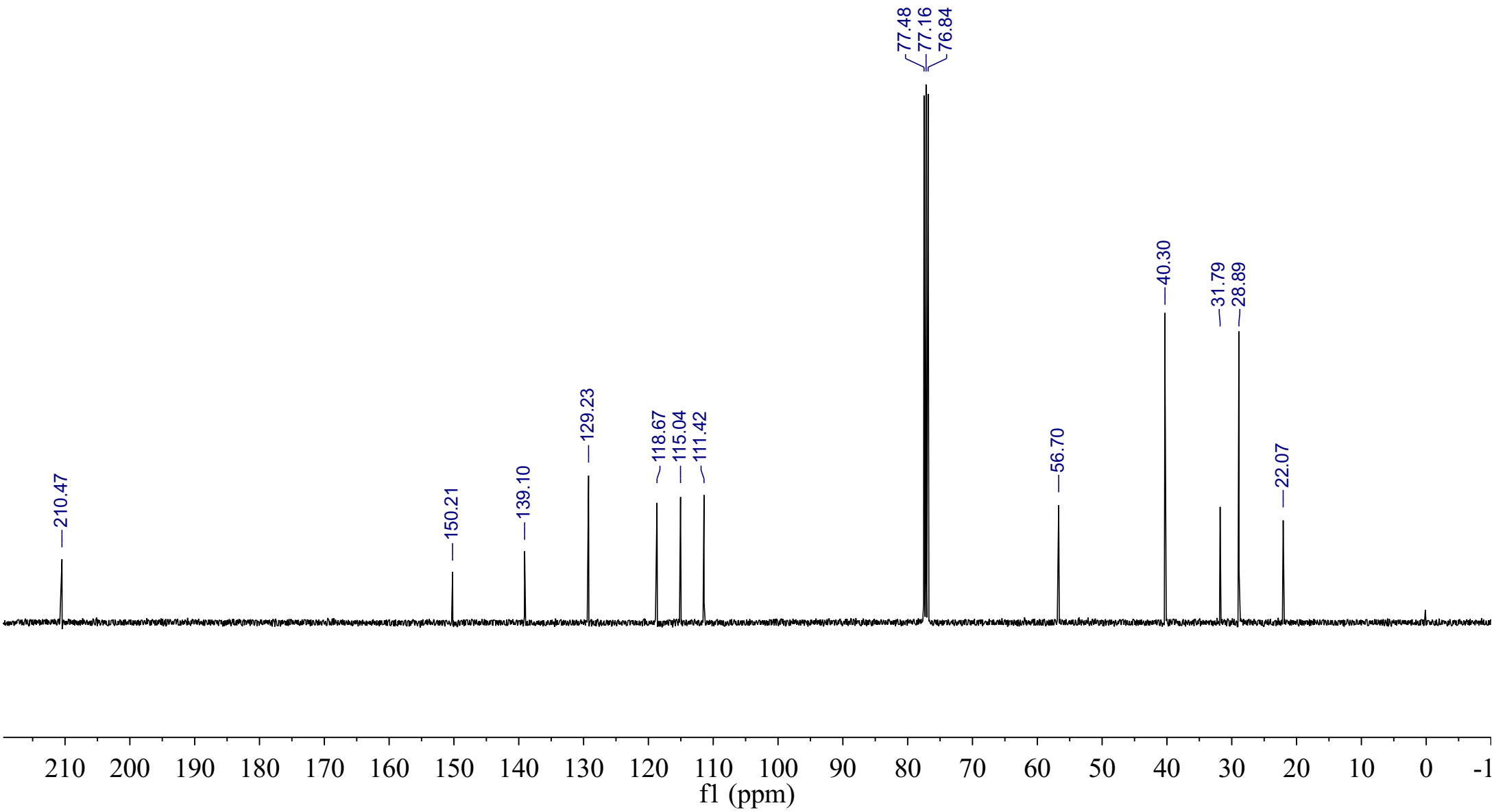
3.01
4.09
3.08
2.08
2.18
f1 (ppm)


Me
O
N
Me

4a


210.47
150.21
139.10
129.23
118.67
115.04
111.42
77.48
77.16
76.84
56.70
40.30
31.79
28.89
22.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)