Electronic Supplementary Material (ESI) for ChemComm.


# Ruthenium Catalyzed β-C($sp^3$)–H Functionalization on the 'Privileged' Piperazine Nucleus

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# Contents:

# 1. General

**Materials and methods:** All reactions were performed in an oven dried glassware or screw cap vials under $N_2$ atmosphere (if required), reactions are magnetically stirred and monitored by analytical thin layer chromatography (TLC). TLC was performed on Merk silica gel 60 $F_{254}$ UV lamp used as visualizing agent, Iodine, 5% aqueous potassium permanganate solution as a developing agents followed by heating. Purification of products was carried out by column chromatography by using silica 60-120, mesh silica and distilled hexane, ethyl acetate, Chloroform, Methanol were used as eluents, concentration under reduced pressure was performed by rotary evaporator at 40-45 $^{o}$C, at appropriate pressure. The yields were given to the purified products.

**Solvents and reagents:** All the reagents are purchased from commercial suppliers from Sigma-Aldrich, Alfa Aesar, and TCI, used without further purification, the ruthenium and iridium catalysts was prepared based on reported procedure.[1] The solvents are distilled according to the traditional methods, distilled solvents are used for purification of the products.

**NMR spectroscopy:** NMR data were recorded on a AVANCE 500, AVANCE 400, AVANCE 300 MHz for $^{1}$H NMR. Chemical shifts are reported in ppm with the solvent resonance employed as the internal standards as TMS via residual solvent as $CDCl_3$. Peaks reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, *J* = coupling constant in Hz. $^{13}$C NMR spectra were recorded with H-decoupling on ANANCE 125, AVANCE 100, AVANCE 75 MHz spectrometer and are reported in ppm with solvent resonance employed as the internal standard as TMS via residual solvent as $CDCl_3$.

**IR spectroscopy**: Infrared spectroscopy was performed neat on a BRUKER FT-IR spectrophotometer in chloroform, IR on KBr pellet spectra were recorded on a Thermo Nicolet-NEXUS 670 FT-IR instrument.

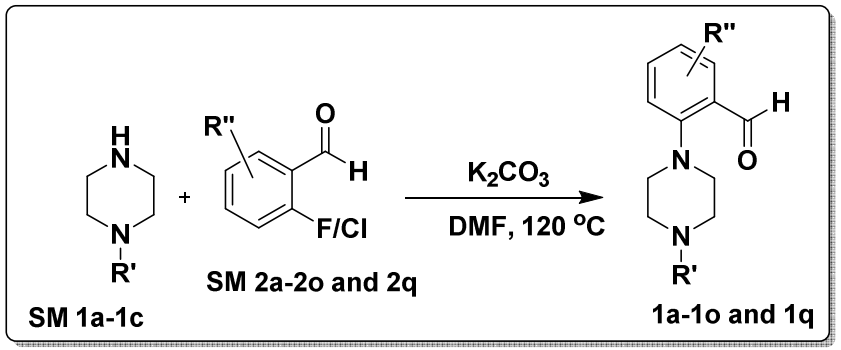
**MASS spectrometry:** Mass spectrometric analyses were performed using ESI techniques, mass spectra obtained on a SHIMADZU LCMS-2020 mass spectrometer. High Resolution Mass Spectra data were obtained on a Thermo scientific Exactive$^{TM}$ Orbitrap mass spectrometer or Q STAR XL Hybrid MS/MS.

**Melting points:** Melting points (MP) were determined using a Super Fit capillary point apparatus. MPs are uncorrected.

# 2. *N*-Arylation of piperazines

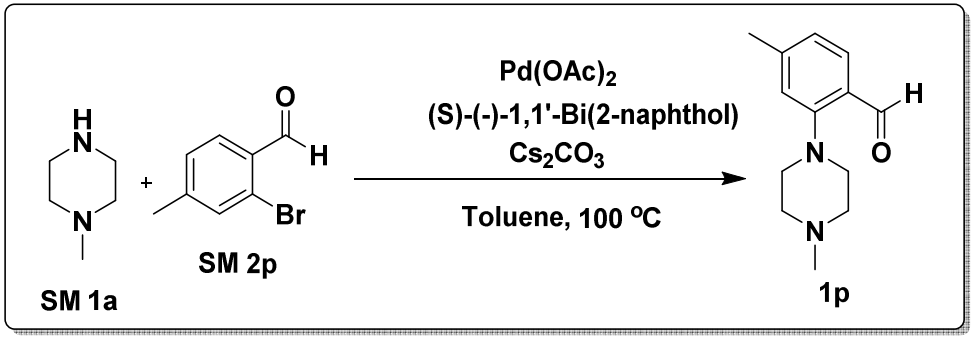
## a. Experimental procedure for 1a-1q

**Method A:**

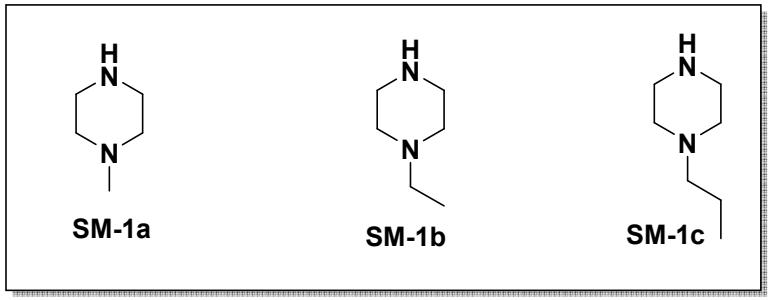



In a screw cap vial $K_2CO_3$ (1.2 equiv.), 2-Fluorobenzaldehyde (1 mmol), were taken then add 4 mL of anhydrous DMF followed by the addition of *N*-protected piperazine, then the reaction mixture was stirred at 120 $^oC$ for 4 h. After completion of reaction, reaction mixture was cooled to room temperature, diluted with cold water, extracted with ethyl acetate (2 x 20 mL), and then washed with brine, dried over anhydrous $Na_2SO_4$, filtered. The solvent was removed under vacuum to afford crude residue. The residue was purified by column chromatography (Chloroform: methanol, 98:2) on silica gel.

**Method B:**




In a sealed tube vial, $Pd(OAc)_2$ (1 mol%), (S)-(−)-1,1′-bi(2-naphthol) (2 mol%), $Cs_2CO_3$ (1.5 equiv) were taken, then add 2-brombenzaldehyde (1 mmol) followed by *N*-protected piperazine (1 mmol), finally toluene (4 mL), then the reaction mixture was stirred at 100 $^{o}$C for 24 h. Then the reaction mixture was cooled to room temperature, diluted with water, extracted with ethyl acetate (2 x 20 mL) washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure to afford crude residue, the residue was purified by flash column chromatography (DCM:Methanol 98:02) on silica gel.


SM-1a
SM-1b
SM-1c

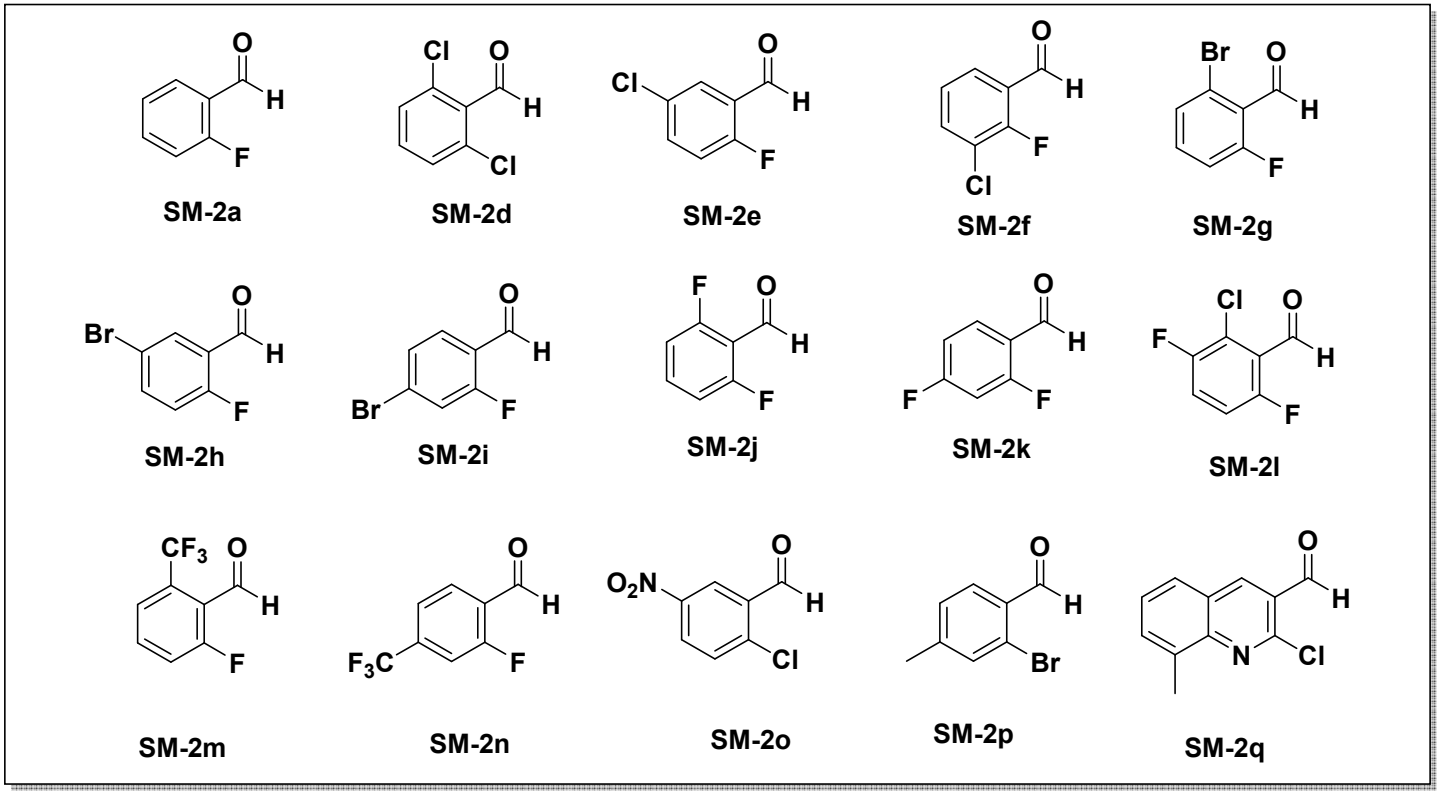
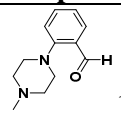
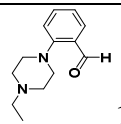
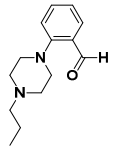
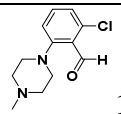
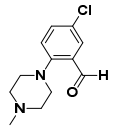
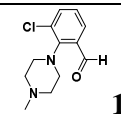
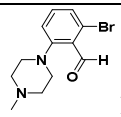
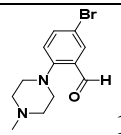
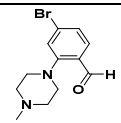
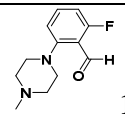
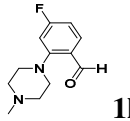
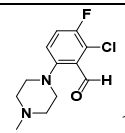
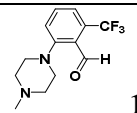
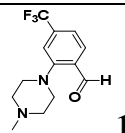
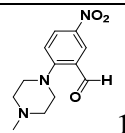
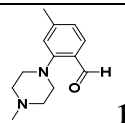
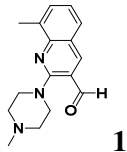
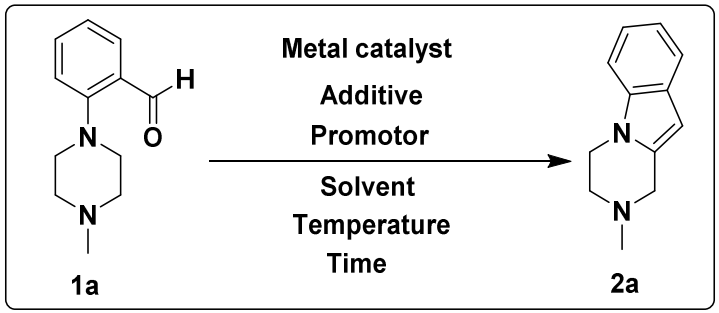

SM-2a
SM-2d
SM-2e
SM-2f
SM-2g
SM-2h
SM-2i
SM-2j
SM-2k
SM-2l
SM-2m
SM-2n
SM-2o
SM-2p
SM-2q

**Table-1**

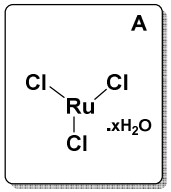
| Entry | SM-1 | SM-2 | Compound 1 | Method | Yield (%) |
|---|---|---|---|---|---|
| 1 | **SM-1a** | **SM-2a** |  **1a** | A | 88 |
| 2 | **SM-1b** | **SM-2a** |  **1b** | A | 79 |
| 3 | **SM-1c** | **SM-2a** |  **1c** | A | 82 |
| 4 | **SM-1a** | **SM-2d** |  **1d** | A | 76 |
| 5 | **SM-1a** | **SM-2e** |  **1e** | A | 65 |
| 6 | **SM-1a** | **SM-2f** |  **1f** | A | 80 |
| 7 | **SM-1a** | **SM-2g** |  **1g** | A | 78 |
| 8 | **SM-1a** | **SM-2h** |  **1h** | A | 83 |
| 9 | **SM-1a** | **SM-2i** |  **1i** | A | 84 |

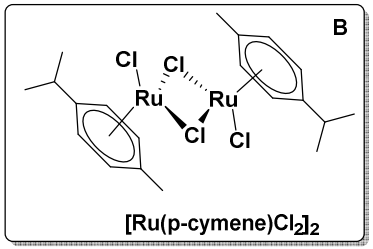
| | | | | | |
|---|---|---|---|---|---|
| 10 | **SM-1a** | **SM-2j** |  **1j** | A | 72 |
| 11 | **SM-1a** | **SM-2k** |  **1k** | B | 57 |
| 12 | **SM-1a** | **SM-2l** |  **1l** | A | 59 |
| 13 | **SM-1a** | **SM-2m** |  **1m** | A | 85 |
| 14 | **SM-1a** | **SM-2n** |  **1n** | A | 86 |
| 15 | **SM-1a** | **SM-2o** |  **1o** | A | 89 |
| 16 | **SM-1a** | **SM-2p** |  **1p** | B | 26 |
| 17 | **SM-1a** | **SM-2q** |  **1q** | A | 69 |

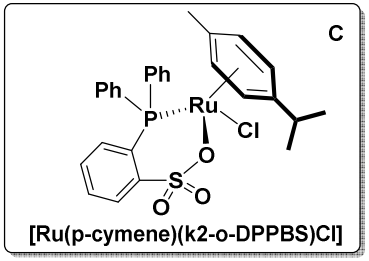
# 3. Optimization survey

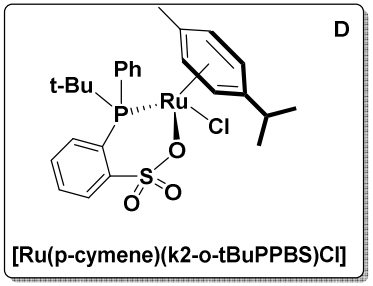


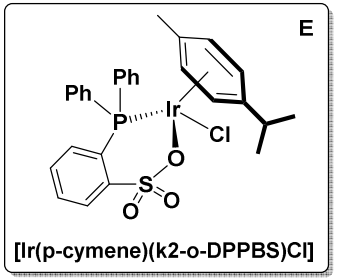

Ruthenium or Iridium Catalysts

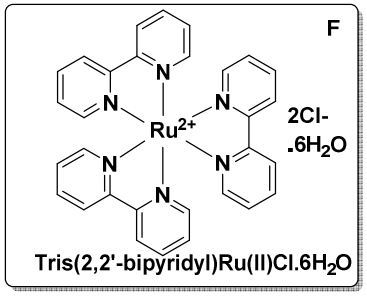


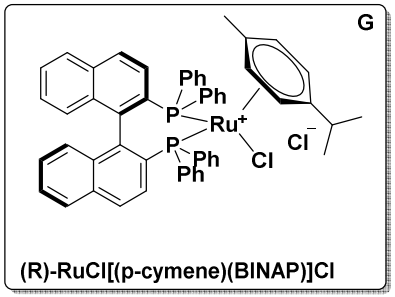



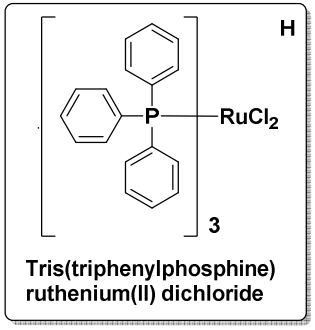



**Experimental procedure for optimization study in table 2- synthesis of 2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole:**

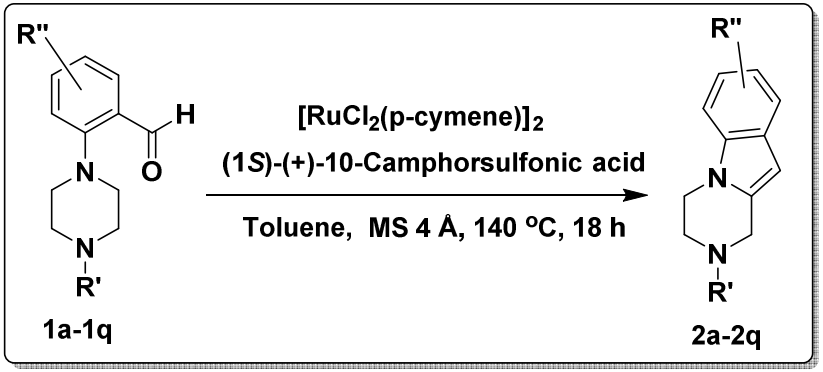
In a sealed cap vial 2-(4-methylpiperazin-1-yl)benzaldehyde (0.6 mmol), metal catalyst (0.03 mmol) and additive were taken, then the reaction vial was closed at atmospheric pressure. The contents were stirred at specified temperature and time as given in the table below. The reaction mixture was cooled to room temperature, diluted with water, then extracted with ethyl acetate (2 x 20 mL), dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under vacuum to afford crude residue. The residue was purified by column chromatography (hexane: ethyl acetate 60:40) on silica gel to obtain 2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole.

**Table-2**

| **S. No** | **Catalyst (mol%)** | **Additive** (mol%) | **Solvent** | **Time (h)** | **T $^{o}$C** | **Yields** |
|---|---|---|---|---|---|---|
| 1. | A(2) | CSA (5) | Toluene | 18 | 140 | **-** |
| 2. | B(2) | CSA (5) | Toluene | 18 | 140 | 38 |
| 3. | C(2) | CSA (5) | Toluene | 18 | 140 | 19 |
| 4. | D(2) | CSA (5) | Toluene | 18 | 140 | 17 |
| 5. | E(2) | CSA (5) | Toluene | 18 | 140 | 21 |
| 6. | F(2) | CSA (5) | Toluene | 18 | 140 | 10 |
| 7. | G(2) | CSA (5) | Toluene | 18 | 140 | 5 |
| 8. | H(2) | CSA (5) | Toluene | 18 | 140 | - |
| 9. | B (2) | CSA (5) | Toluene | 18 | 140 | 42 |
| 10. | B (2) | CSA (50) | Toluene | 18 | 140 | 33 |
| 11. | B (2) | CSA (100) | Toluene | 18 | 140 | Traces |
| 12. | B (2) | CSA (10) | Toluene | 18 | 140 | 38 |
| 13. | B (5) | CSA (10) | Toluene | 18 | 140 | 56 |
| 14. | B (10) | CSA (10) | Toluene | 18 | 140 | 67 |
| 15. | B(5) | CSA (10) | Toluene | 36 | 140 | 37 |
| 16. | B(5) | CSA (10) | Toluene | 48 | 140 | 39 |

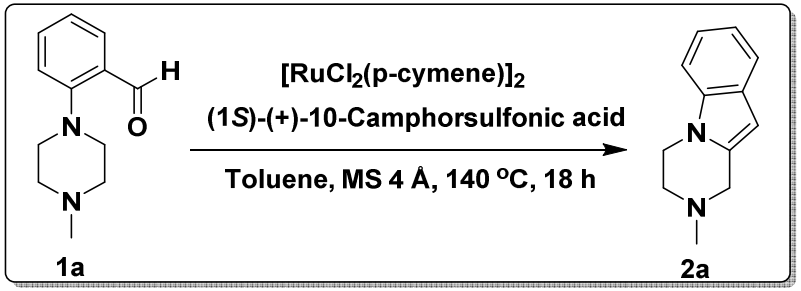
| | | | | | | |
|---|---|---|---|---|---|---|
| 17. | B(5) | $K_2CO_3$ (10) | Toluene | 18 | 140 | 26 |
| 18. | B(5) | Oxalic acid (10) | Toluene | 18 | 140 | - |
| 19. | B(5) | PTSA monohydrate (10) | Toluene | 18 | 140 | 13 |
| 20. | B(5) | Benzoic acid (10) | Toluene | 18 | 140 | - |
| 21. | B(5) | 4-nitrobenzoic acid (10) | Toluene | 18 | 140 | - |
| 22. | B(5) | 3,5-Dinitrobenzoic acid (10) | Toluene | 18 | 140 | - |
| 23. | B(5) | 2-Nitrophenol (10) | Toluene | 18 | 140 | - |
| 24. | B(5) | CSA (10) | *p*-Xylene | 18 | 140 | 36 |
| 25. | B(5) | CSA (10) | DMSO | 18 | 140 | - |
| 26. | B(5) | CSA (10) | DMF | 18 | 140 | 14 |
| 27. | B(5) | CSA (10) + CuI, (1 equiv) | Toluene | 18 | 140 | 20 |
| 28. | B(5) | CSA (10) + $Cu(OAc)_2$(1 equiv) | Toluene | 18 | 140 | 19 |
| 29. | B(5) | CSA (10) + $FeCl_3$ (1 equiv) | Toluene | 18 | 140 | - |
| 30. | B(5) | CSA (10) + $PhI(OAc)_2$ (1 equiv) | Toluene | 18 | 140 | - |
| 31. | B(5) | CSA (10) + Benzoquinone (1 equiv) | Toluene | 18 | 140 | - |
| 32. | B(5) | CSA (10) + BINOL (1 equiv) | Toluene | 18 | 140 | - |
| 33. | B(5) | CSA (10) + Thiourea (1 equiv) | Toluene | 18 | 140 | 40 |
| 34. | **B(5)** | **CSA (10) +4 Å MS** | **Toluene** | **18** | **140** | **66** |
| 35. | B(5) | - | Toluene | 18 | 140 | 32 |
| 36. | - | CSA (10) | Toluene | 18 | 140 | - |

# 4. Experimental procedure for the synthesis of 2a-2q




In a sealed tube vial, $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), CSA (10 mol%), MS 4 Å were taken, then added **1a-1q** (0.6 mmol), followed by the addition of toluene (2 mL). The sealed tube was closed at atmospheric pressure, and then stirred at 140 $^{o}$C for 18 h. Then the reaction mixture was cooled to room temperature, diluted with water, extracted with ethyl acetate (2 x 20 mL), washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure to afford crude residue, the residue was purified by flash column chromatography (hexane: ethyl acetate 60:40) on silica gel.

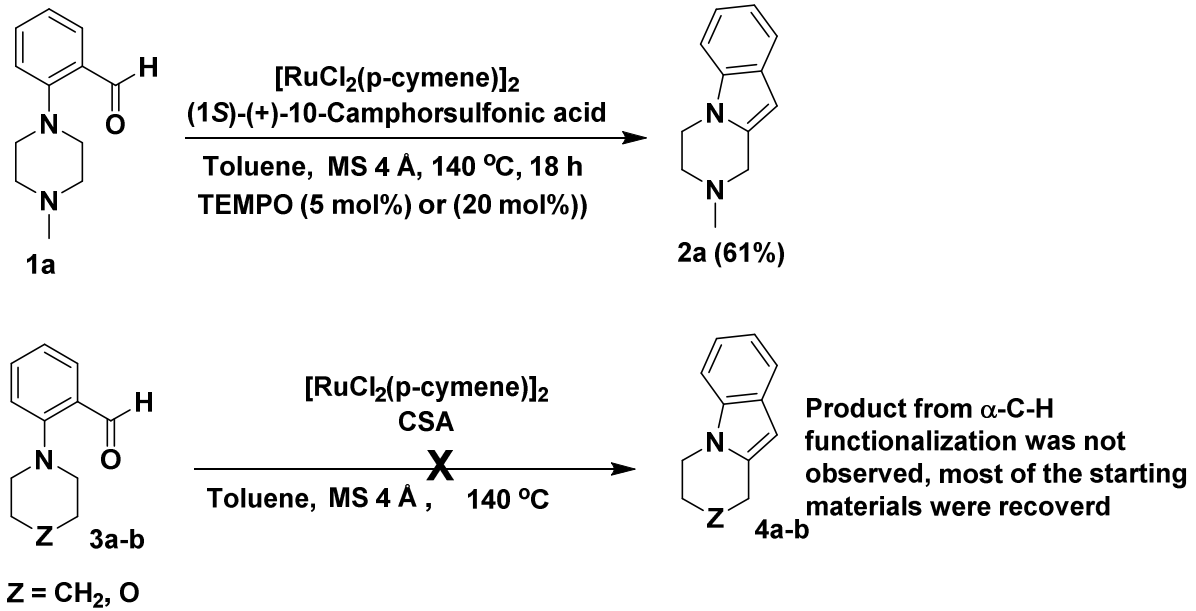
# 5. Experimental procedure for the gram scale synthesis of 2a



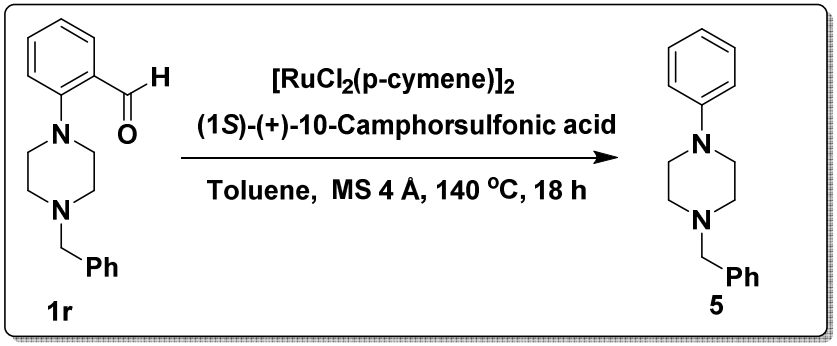

In a sealed tube vial, $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), CSA (10 mol%), MS 4 Å were taken, then added **1a** (10 mmol), followed by the addition of toluene (40 mL), the sealed tube was closed at atmospheric pressure, then stirred at 140 $^oC$ for 18 h. Then the reaction mixture was cooled to room temperature, diluted with water, extracted with ethyl acetate (3 x 80 mL) washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure to afford crude residue, the residue was purified by flash column chromatography (hexane: ethyl acetate 60:40) on silica gel.

# 6. Control experiments and mechanistic studies

In a sealed tube vial, $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), CSA (10 mol%), MS 4 Å, TEMPO (5 mol% or 20 mol%) were taken, then added **1a** (0.6 mmol), followed by the addition of toluene (2 mL), the sealed tube was closed at atmospheric pressure, then stirred at 140 $^{o}$C for 18 h. Then the reaction mixture was cooled to room temperature, diluted with water, extracted with ethyl acetate (2 x 20 mL) washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure to afford crude residue, the residue was purified by flash column chromatography (hexane: ethyl acetate 60:40) on silica gel.



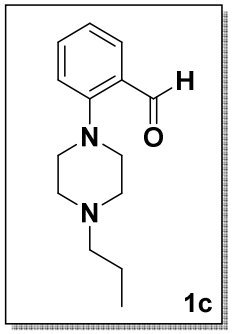
# 7. Ruthenium-catalyzed reaction of 2-(4-benzylpiperazin-1-yl)benzaldehyde 1r




In a sealed tube vial, $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), CSA (10 mol%), MS 4 Å were taken, then added **1r** (0.6 mmol), followed by the addition toluene (2 mL), the sealed tube was closed at atmospheric pressure, then stirred at 140 $^oC$ for 18 h. Then the reaction mixture was cooled to room temperature, diluted with water, extracted with ethyl acetate (2 x 20 mL) washed with brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under reduced pressure to afford crude residue, the residue was purified by flash column chromatography (hexane: ethyl acetate 60:40) on silica gel.

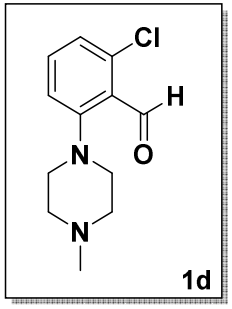
# 8. Spectroscopic data

## a. Spectroscopic data of 1a-1q




**2-(4-propylpiperazin-1-yl)benzaldehyde (1c)**

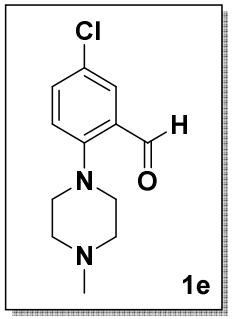
brown oil, 191 mg (0.82 mmol), 82%, $R_f$ = 0.34 (MeOH/Chloroform, 10:90); **IR** 765, 1145, 1284, 1453, 1656, 1685, 2820, 2928, 2958, 3065 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 0.92-0.88 (m, 3H), 1.49-1.58 (m, 2H), 2.35-2.41 (m, 2H), 2.60-2.69 (m, 4H), 3.05-3.15 (m, 4H), 7.05-7.11 (m, 2H), 7.44-7.51 (m, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 10.28 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 11.8, 19.7, 52.9, 53.6, 60.3, 118.8, 122.4, 128.4, 129.7, 134.9, 155.4, 191.2; **MS** (ESI) m/z 233 $[M+H]^+$. **HRMS** (ESI, m/z): calcd for $C_{14}H_{21}N_2O$ $[M+H]^+$ 233.1648, found 233.1656.




**2-chloro-6-(4-methylpiperazin-1-yl)benzaldehyde (1d)**

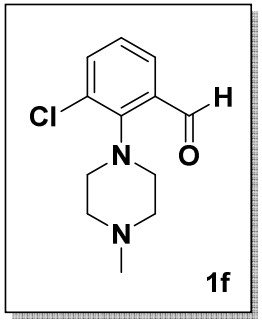
Yellow solid, 182 mg (76 mmol), 76%, $R_f$ = 0.48 (MeOH/Chloroform, 10:90); **MP** 96-98 $^oC$; **IR** 773, 1139, 1241, 1449, 1689, 2745, 2795, 2849, 2924, 3076 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.35 (s, 3H), 2.58-2.63 (m, 4H), 3.07-3.11 (m, 4H), 7.00 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 7.8

Hz, 1H), 7.35 (t, *J* = 8.1 Hz, 1H), 10.29 (s, 1H); **$^{13}$C NMR** (101 MHz) δ = 45.9, 53.3, 54.9, 117.5, 124.3, 125.8, 133.9, 136.4, 155.9, 189.5; **MS** (ESI) m/z 239 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{16}ClN_2O$ $[M+H]^+$ 239.0944 found 239.0946.



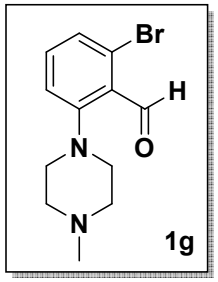

**5-chloro-2-(4-methylpiperazin-1-yl)benzaldehyde (1e)**

Yellow oil, 154 mg (0.65 mmol), 65%, $R_f$ = 0.6 (MeOH/Chloroform, 10:90); **IR** 765, 1145, 1225, 1452, 1595, 1684, 2819, 2873, 2928, 2957, 3056 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.49-2.57 (m, 4H), 2.96-3.03 (m, 4H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 7.27-7.30 (m, 1H), 10.19 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 45.6, 52.9, 54.6, 117.3, 124.0, 125.4, 133.8, 135.9, 155.6, 189.1; **MS** (ESI) m/z 239 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{16}ClN_2O$ $[M+H]^+$ 239.0946, found 239.0943.



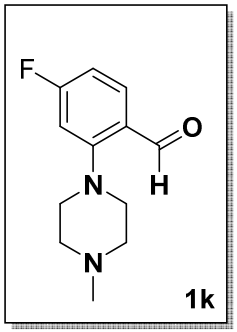

**3-chloro-2-(4-methylpiperazin-1-yl)benzaldehyde (1f)**

Yellow solid, 192 mg (0.8 mmol), 80%, $R_f$ = 0.54 (MeOH/Chloroform, 10:90); **MP** 102-104 °C; **IR** 773, 1139, 1290, 1449, 1584, 1689, 2795, 2845, 2926, 3076 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.35 (s, 3H), 3.05-3.11 (m, 4H), 2.58-2.62 (m, 4H), 6.99 (d, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 8.1 Hz, 1H), 10.29 (s, 1H); **$^{13}$C NMR** (101 MHz) δ = 45.9, 53.3, 54.9, 117.5, 124.3, 125.8, 133.9, 136.4, 155.9, 189.5; **MS** (ESI) m/z 239 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{16}ClN_2O$ $[M+H]^+$ 239.0946 found 239.0943.



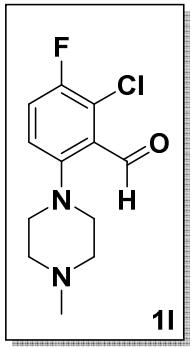

**2-bromo-6-(4-methylpiperazin-1-yl)benzaldehyde (1g)**

Yellow solid, 220 mg (0.78 mmol), 78%, $R_f$ = 0.38 (MeOH/Chloroform, 10:90); **MP** 112-114 °C; **IR** 875, 1143, 1228, 1453, 1681, 2744, 2794, 2840, 2934 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.39 (s, 3H), 2.58-2.69 (m, 4H), 3.01-3.17 (m, 4H), 7.01 (d, $J$ = 8.7 Hz, 1H), 7.60 (dd, $J_1$ = 8.7, $J_2$ = 2.5 Hz, 1H), 7.89 (d, $J$ = 2.5 Hz, 1H), 10.23 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 45.8, 53.7, 54.8, 115.7, 121.0, 129.9, 132.2, 137.4, 154.3, 189.7; **MS** (ESI) m/z 283 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{16}BrN_2O$ $[M+H]^+$ 283.0440, found 283.0438.



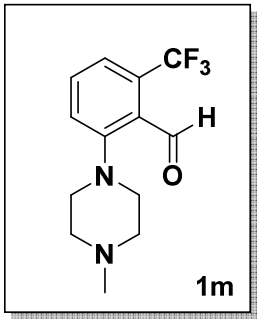

**4-fluoro-2-(4-methylpiperazin-1-yl)benzaldehyde (1k)**

Yellow oil, 126 mg (0.57 mmol), 57%, $R_f$ = 0.5 (MeOH/Chloroform, 10:90)**; $^1$H NMR** (500 MHz, $CDCl_3$) δ 2.85 (s, 3H), 2.90-3.02 (m, 2H), 3.46-3.67 (m, 2H), 3.84-3.93 (m, 4H), 6.54 (dd, $J$ = 13.5, 2.1 Hz, 1H), 6.67-6.75 (m, 1H), 7.80 (t, $J$ = 8.5 Hz, 1H), 10.16 (s, 1H); **MS** (ESI) m/z 222 $[M+H]^+$.



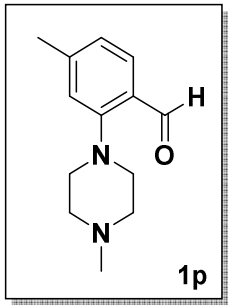

**2-chloro-3-fluoro-6-(4-methylpiperazin-1-yl)benzaldehyde (1l)**

Yellow oil, 151 mg (0.59 mmol), 59%, $R_f$ = 0.5 (MeOH/Chloroform, 10:90)**;** **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.57-2.66 (m, 4H), 3.07-3.13 (m, 4H), 7.07 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 10.23 (s, 1H); **MS** (ESI) m/z 257 $[M+H]^+$.



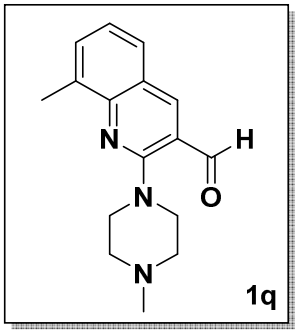

**2-(4-methylpiperazin-1-yl)-6-(trifluoromethyl)benzaldehyde (1m)**

Yellow oil, 232 mg (0.85 mmol), 85%, $R_f$ = 0.4 (MeOH/Chloroform, 10:90); **IR** 831, 1130, 1170, 1311, 1427, 1690, 2746, 2797, 2849, 2925 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.32 (s, 3H), 2.55-2.61 (m, 4H), 3.08-3.12 (m, 4H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 10.24 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 45.9, 53.7, 54.8, 115.9, 118.9, 122.1, 124.8, 130.5 (*J* = 19.8), 135.9 (*J* = 32), 155.4, 190.2; **MS** (ESI) m/z 273 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{13}H_{16}F_3N_2O$ $[M+H]^+$ 273.1209, found 273.1233.




**4-methyl-2-(4-methylpiperazin-1-yl)benzaldehyde (1p)**

Wight semi solid, 57 mg (0.26 mmol), 26%, $R_f$ = 0.54 (MeOH/Chloroform, 10:90); **IR** 772, 1041, 1458, 1643, 1692, 2794, 2852, 2924, 3617 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.73 (s, 3H), 3.10-3.23 (m, 4H), 3.32-3.42 (m, 4H), 6.92 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 10.12 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 22.0, 44.3, 50.8, 54.3, 119.9, 124.3, 127.2, 133.6, 146.7, 152.9, 190.6; **MS** (ESI) m/z 219 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{13}H_{19}N_2O$ $[M+H]^+$ 219.1492, found 219.1499.

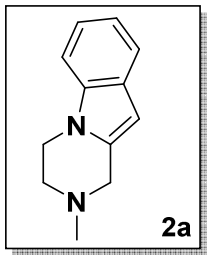



**8-methyl-2-(4-methylpiperazin-1-yl)quinoline-3-carbaldehyde (1q)**

Yellow solid, 186 mg (0.69 mmol), 69%, $R_f$ = 0.31 (MeOH/Chloroform, 10:90); **MP** 108-110 $^oC$; **IR** 772, 1003, 1173, 1437, 1643, 1691, 2795, 2852, 2923, 3241 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 2.86 (s, 3H), 3.23-3.49 (m, 4H), 3.85-4.01 (m, 4H), 7.33-7.40 (m, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 8.46-8.60 (m, 1H), 10.10 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 17.7, 43.9, 47.2, 53.6, 121.2, 124.1, 125.3, 126.8, 133.5, 135.9, 147.7, 148.3, 154.9, 189.9; **MS** (ESI) m/z 270 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{20}N_3O$ $[M+H]^+$ 270.1601, found 270.1609.

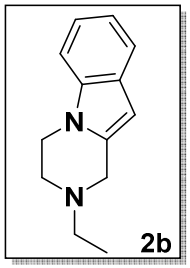
Remaining starting materials were prepared according to the general experimental method A (vide supra). The spectral data were in good agreement with the reported data as follows: **1a**[2a], **1b**[2b], **1h**[2c], **1i**[2c], **1j**[2d], **1n**[2e], **1o**[2f],**3a**[2g], **3b**[2h]

## b. Spectroscopic data for 2a-2q



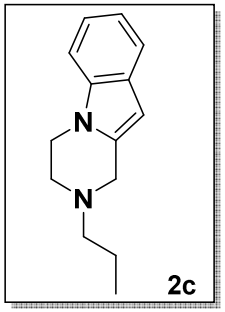

**2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2a)**

Yellow solid, 73 mg (0.39 mmol), 66%, $R_f$ = 0.2 (EtOAc/Hexane, 90:10); **MP** 129-131 $^oC$; **IR** 738, 1181, 1457, 2768, 2850, 2924, 3046, 3423 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.52 (s, 3H), 2.93 (t, *J* = 5.6 Hz, 2H), 3.79 (s, 2H), 4.11 (t, *J* = 5.6 Hz, 2H), 6.22 (s, 1H), 7.08-7.13 (m, 1H), 7.14-7.19 (m, 1H), 7.27-7.30 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 41.7, 45.8, 52.4, 53.4, 96.3, 108.5, 119.7, 119.9, 120.5, 128.3, 134.2, 135.9; **MS** (ESI) m/z 187 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{15}N_2$ $[M+H]^+$ 187.1229, found 187.1219.



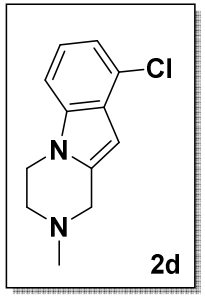

**2-ethyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2b)**

Yellow solid, 59 mg (0.30 mmol), 49%, $R_f$ = 0.36 (EtOAc/Hexane, 90:10); **MP** 144-146 $^oC$; **IR** 746, 1223, 1327, 1454, 1939, 2057, 2852, 2924, 3025 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 1.19 (t, *J* = 7.2 Hz, 3H), 2.62 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 5.6 Hz, 2H), 3.82 (s, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 6.19 (s, 1H), 7.04-7.10 (m, 1H), 7.10-7.15 (m, 1H), 7.24 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 12.4, 41.7, 50.3, 51.1, 51.7, 96.5, 108.5, 119.7, 119.9, 120.5, 128.3, 134.3, 135.9; **MS** (ESI) m/z 201 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{13}H_{17}N_2$ $[M+H]^+$ 201.1392, found 201.1388.



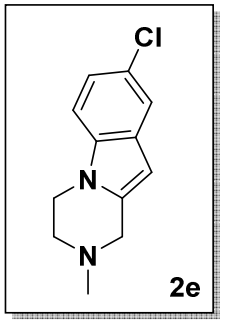

**2-propyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2c)**

Red solid, 58 mg (0.27 mmol), 47%, $R_f$ = 0.47 (EtOAc/Hexane, 70:30); **MP** 130-132 $^oC$; **IR** 748, 1178, 1325, 1453, 2766, 2852, 2924, 2957, 3052 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 0.95 (t, *J* = 7.4 Hz, 3H), 1.60 (dt, *J* = 14.8, 7.4 Hz, 2H), 2.51 (dd, $J_1$ = 8.3, $J_2$ = 6.8 Hz, 2H), 2.94-2.98 (m, 2H), 3.82 (s, 2H), 4.05-4.09 (m, 2H), 6.19 (s, 1H), 7.07 (td, *J* = 7.5, 1.1 Hz, 1H), 7.11-7.16 (m, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 11.8, 20.3, 41.7, 50.5, 51.4, 59.7, 96.5, 108.5, 119.7, 120.5, 128.3, 134.3, 135.9; **MS** (ESI) m/z 215 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{14}H_{19}N_2$ $[M+H]^+$ 215.1543 found 215.1558.



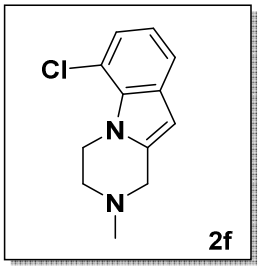

**9-chloro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2d)**

White solid, 79 mg (0.36 mmol), 60%, $R_f$ = 0.32 (EtOAc/Hexane, 90:10); **MP** 146-148 $^oC$; **IR** 751, 1117, 1169, 1329, 1434, 1990, 2058, 2790, 2848, 2939 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.51 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.79 (s, 2H), 4.10 (t, *J* = 5.6 Hz, 2H), 6.30 (s, 1H), 7.03-7.11 (m, 2H), 7.15-7.18 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 42.1, 45.8, 52.2, 53.3, 95.1, 107.2, 119.5, 121.1, 125.3, 127.0, 135.0, 136.7; **MS** (ESI) m/z 221 $[M+H]^+$, **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2Cl$ $[M+H]^+$ 221.0840, found 221.0829.



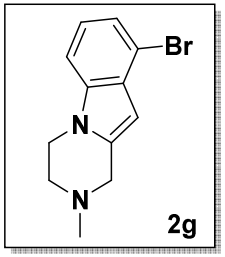

**8-chloro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2e)**

White solid, 82 mg (0.37 mmol), 62%, $R_f$ = 0.28 (EtOAc/Hexane, 90:10); **MP** 142-144 $^oC$; **IR** 780, 1057, 1445, 1993, 2025, 2789, 2850, 2923 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.76 (s, 2H), 4.07 (t, *J* = 5.6 Hz, 2H), 6.14 (s, 1H), 7.09 (dd, $J_1$ = 8.6 Hz, $J_2$ = 1.9 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 41.9, 45.8, 52.3, 53.3, 96.1, 109.5, 119.4, 120.7, 125.4, 129.3, 134.4, 135.7; **MS** (ESI) m/z 221 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2Cl$ $[M+H]^+$ 221.0840, found 221.0823.



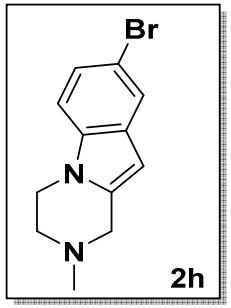

**6-chloro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2f)**

White solid, 52 mg (0.24 mmol), 39%, $R_f$ = 0.34 (EtOAc/Hexane, 90:10); **MP** 143-145 $^oC$; **IR** 761, 1119, 1331, 1437, 1991, 2058, 2851, 2925, 3095 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.78 (s, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 6.25 (s, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.24-7.25 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 42.1, 45.7, 52.2, 53.3, 96.8, 107.7, 114.0, 121.4, 122.7, 128.9, 135.0, 136.3; **MS** (ESI) m/z 221 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2Cl$ $[M+H]^+$ 221.0840, found 221.0840.



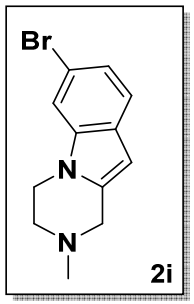

**9-bromo-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2g)**

Yellow solid, 89 mg (0.33 mmol), 55%, $R_f$ = 0.26 (EtOAc/Hexane, 90:10); **MP** 127-129 $^oC$; **IR** 771, 1136, 1220, 1434, 1550, 1992, 2059, 2852, 2923 $cm^{-1}$; **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 2.49 (s, 3H), 2.90 (t, *J* = 5.6 Hz, 2H), 3.77 (s, 2H), 4.07 (t, *J* = 5.6 Hz, 2H), 6.24 (s, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 2.7 Hz, 1H); **$^{13}$C NMR** (101 MHz) δ = 42.1, 45.7, 52.2, 53.3, 96.8, 107.7, 114.0, 121.4, 122.7, 128.9, 135.0, 136.2; **MS** (ESI) m/z 265 $[M+H]^+$, **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2Br$ $[M+H]^+$ 265.0335, found 265.0316.



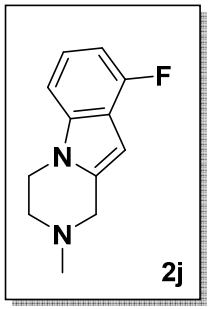

**8-bromo-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2h)**

White solid, 91 mg (0.34 mmol), 69%, $R_f$ = 0.29 (EtOAc/Hexane, 90:10); **MP** 148-150 $^oC$; **IR** 772. 1220, 1325, 1448, 1563, 2767, 2846, 2943 $cm^{-1}$; **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.91 (t, *J* = 5.6 Hz, 2H), 3.75 (s, 2H), 4.06 (t, *J* = 5.6 Hz, 2H), 6.14 (s, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 7.17-7.25 (m, 1H), 7.66 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 41.9, 45.8, 52.2, 53.3, 96.0, 109.9, 113.0, 122.5, 123.3, 129.9, 134.7, 135.6; **MS** (ESI) m/z 265 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2Br$ $[M+H]^+$ 265.0335, found 265.0318.



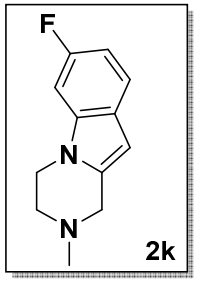

**7-bromo-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2i)**

White solid, 106 mg (0.4 mmol), 67%, $R_f$ = 0.4 (EtOAc/Hexane, 90:10); **MP** 128-130 °C; **IR** 772, 1219, 1420, 1564, 2725, 2768, 2846, 2944 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.91 (t, *J* = 5.6 Hz, 2H), 3.74 (s, 2H), 4.04 (t, *J* = 5.6 Hz, 2H), 6.17 (s, 1H), 7.18 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.7 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 41.9, 45.7, 52.3, 53.3, 96.6, 111.7, 113.9, 121.2, 122.9, 127.1, 135.0, 136.8; **MS** (ESI) m/z 265 $[M+H]^+$ **HRMS** (ESI, m/z):calcd for $C_{12}H_{14}N_2Br$ $[M+H]^+$ 265.0335, found 265.0318.



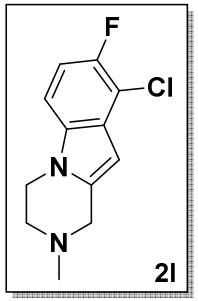

**9-fluoro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2j)**

White solid, 71 mg (0.35 mmol), 59%, $R_f$ = 0.25 (EtOAc/Hexane, 90:10); **MP** 137-139 °C; **IR** 771, 1228, 1336, 1578, 1993, 2060, 2852, 2923 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.51 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.77 (s, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 6.28 (s, 1H), 6.72-6.80 (m, 1H), 7.01-7.09 (m, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 42.2, 45.8, 52.3, 53.4, 92.4, 104.7 (*J* = 7.5 Hz), 117.1 (*J* = 22.6 Hz), 120.9 (*J* = 7.5 Hz), 134.3, 138.7 (*J* = 11.3 Hz), 155.1, 157.0; **MS** (ESI) m/z 205 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{14}N_2F$ $[M+H]^+$ 205.1135, found 205.1124




**7-fluoro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2k)**

White solid, 53 mg (0.26 mmol), 43%, $R_f$ = 0.24 (EtOAc/Hexane, 90:10); **MP** 135-137 °C; **IR** 772, 1168, 1608, 1650, 1936, 2852, 2923 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.91 (t, *J* = 5.6 Hz, 2H), 3.75 (s, 2H), 4.05 (t, *J* = 5.6 Hz, 2H), 6.19 (s, 1H), 7.18 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.7 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 41.9, 45.8, 52.3, 53.4, 96.6, 111.7, 113.9, 121.2, 122.9, 127.1, 135.0, 136.8; **MS** (ESI) m/z 205 $[M+H]^+$ **HRMS** (ESI, m/z): $C_{12}H_{14}N_2F$ $[M+H]^+$ 205.1135, found 205.1145.




**9-chloro-8-fluoro-2-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2l)**

White solid, 52 mg (0.21 mmol), 37%, $R_f$ = 0.23 (EtOAc/Hexane, 90:10); **MP** 140-142 °C; **IR** 769, 1203, 1334, 1439, 1547, 2731, 2849, 2939 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.51 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.78 (s, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 6.30 (s, 1H), 6.92-6.98 (m, 1H), 7.07 (dd, $J_1$ = 8.7 Hz, $J_2$ = 3.7 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 42.1, 45.7, 52.1, 53.3, 95.4 (*J* = 5), 107.3 (*J* = 9), 109.3 (*J* = 25), 127.8, 132.7, 136.6, 152.1, 154.4; **MS** (ESI) m/z 239 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{12}H_{13}ClFN_2$ $[M+H]^+$ 239.0751 found 239.0748

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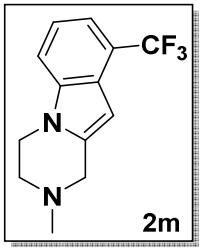
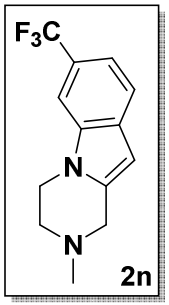


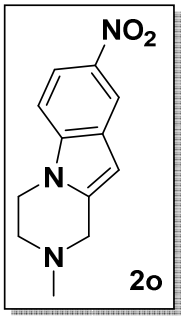

**2-methyl-9-(trifluoromethyl)-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2m)**

Yellow solid, 89 mg (0.35 mmol), 58%, $R_f$ = 0.32 (EtOAc/Hexane, 90:10); **MP** 158-160 $^oC$; **IR** 772, 1115, 1168, 1422, 1997, 2063, 2852, 2925, 3050 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.50 (s, 3H), 2.91 (t, *J* = 5.6 Hz, 2H), 3.77 (s, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 6.25 (s, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.24-7.26 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 41.9, 45.7, 52.2, 53.3, 96.8, 106.0 (*J* = 3.8 Hz), 116.5 (*J* = 3.7 Hz), 120.2, 122.5 (*J* = 31 Hz), 126.5, 130.4 (*J* = 59 Hz), 134.9, 137.2; **MS** (ESI) m/z 255 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{13}H_{14}F_3N_2$ $[M+H]^+$ 255.1109, found 255.1106.



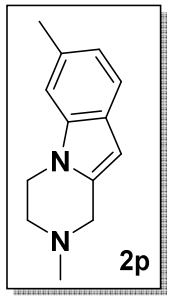

**2-methyl-7-(trifluoromethyl)-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2n)**

Off white solid, 70 mg (0.28 mmol), 46%, $R_f$ = 0.52 (EtOAc/Hexane, 90:10); **MP** 154-156 $^oC$; **IR** 772, 1341, 1455, 1996, 2062, 2794, 2853, 2928 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.51 (s, 3H), 2.94 (t, *J* = 5.6 Hz, 2H), 3.79 (s, 2H), 4.14 (t, *J* = 5.6 Hz, 2H), 6.25 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 41.9, 45.7, 52.2, 53.3, 96.8, 106.1 (*J* = 3.7 Hz), 116.5 (*J* = 3.7), 120.2, 122.5 (*J* = 31), 126.5, 130.4 (*J* = 59), 134.9, 137.2; **MS** (ESI) m/z 255 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{13}H_{14}F_3N_2$ $[M+H]^+$ 255.1109, found 255.1109.



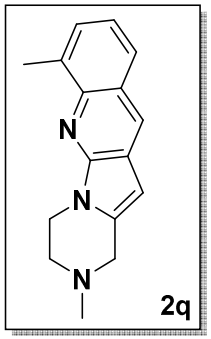

**2-methyl-8-nitro-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2o)**

Yellow solid, 73 mg (0.32 mmol), 64%, $R_f$ = 0.24 (EtOAc/Hexane, 90:10); **MP** 152-154 $^oC$; **IR** 773, 1338, 1512, 2738, 2808, 2855, 2926 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 2.53 (s, 3H), 2.96 (t, *J* = 5.6 Hz, 2H), 3.80 (s, 2H), 4.16 (t, *J* = 5.6 Hz, 2H), 6.38 (s, 1H), 7.28 (s, 1H), 8.07 (dd, $J_1$ = 9.0 Hz, $J_2$ = 2.2 Hz, 1H), 8.50 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ = 42.3, 45.8, 52.0, 53.3, 98.8, 108.3, 116.4, 117.2, 127.5, 137.7, 138.7, 141.9; **MS** (ESI) m/z 232 $[M+H]^+$ **HRMS** (ESI, m/z):calcd for $C_{12}H_{14}O_2N_3$ $[M+H]^+$ 232.1080, found 232.1065.




**2,7-dimethyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (2p)**

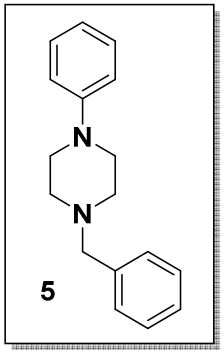
White solid, 68 mg (0.34 mmol), 56%, $R_f$ = 0.22 (EtOAc/Hexane, 90:10); **MP** 132-134 $^oC$; **IR** 771, 1077, 1220, 1326, 1453, 1989, 2057, 2790, 2852, 2922 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 2.49 (s, 3H), 2.50 (s, 3H), 2.92 (t, *J* = 5.6 Hz, 2H), 3.77 (s, 2H), 4.06 (t, *J* = 5.6 Hz, 2H), 6.15 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 21.8, 41.7, 45.8, 52.5, 53.5, 96.2, 108.7, 119.7, 121.4, 126.1, 130.3, 133.5, 136.5; **MS** (ESI) m/z 201 $[M+H]^+$ **HRMS** (ESI, m/z):calcd for $C_{13}H_{17}N_2$ $[M+H]^+$ 201.1386, found 201.1374.




**2,7-dimethyl-1,2,3,4-tetrahydropyrazino[1',2':1,5]pyrrolo[2,3-*b*]quinoline (2q)**

Brownish solid, 108 mg (0.43 mmol), 72%, $R_f$ = 0.35 (EtOAc/Hexane, 90:10); **MP** 133-135 $^{o}$C; **IR** 771, 1129, 1257, 1383, 1429, 1563, 2769, 2849, 2921, 3041 $cm^{-1}$; **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ = 2.53 (s, 3H), 2.88 (s, 3H), 2.96 (t, *J* = 5.6 Hz, 2H), 3.83 (s, 2H), (t, *J* = 5.6 Hz, 2H), 6.25 (s, 1H), 7.29-7.32 (m, 1H), 7.49 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 8.22 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 18.3, 40.9, 45.8, 52.4, 53.7, 93.7, 121.8, 122.3, 124.8, 126.0, 126.1, 127.1, 135.4, 139.2, 143.5, 148.9; **MS** (ESI) m/z 252 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{18}N_3$ $[M+H]^+$ 252.1495, found 252.1474.

## c. Spectroscopic data of 5




**1-benzyl-4-phenylpiperazine**[3]

Wight solid, 28 mg (0.11 mmol), 11%; $R_f$ = 0.5 (EtOAc/Hexane, 95:5); **IR** 693, 738, 1007, 1226, 1451, 1496, 1598, 2770, 2813, 2878, 2921, 3027, 3060 $cm^{-1}$; **$^1$H NMR** (500 MHz, $CDCl_3$) ) δ 2.60-2.64 (m, 4H), 3.18-3.23 (m, 4H), 3.57 (s, 2H), 6.82-6.87 (m, 1H), 6.92 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.23-7.29 (m, 3H), 7.31-7.39 (m, 4H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 49.1, 53.1, 63.1, 116.0, 119.6, 127.1, 128.3, 129.1, 129.2, 137.9, 151.4; **MS** (ESI) m/z 253 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{21}N_2$ $[M+H]^+$ 253.1699, found 253.1731.

# 9. References


1. Ru and Ir catalysts preparation.

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2. For spectral data for **1a-1q** and **3a, 3b**

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3. For spectral data of decarbonylation product (**3**)

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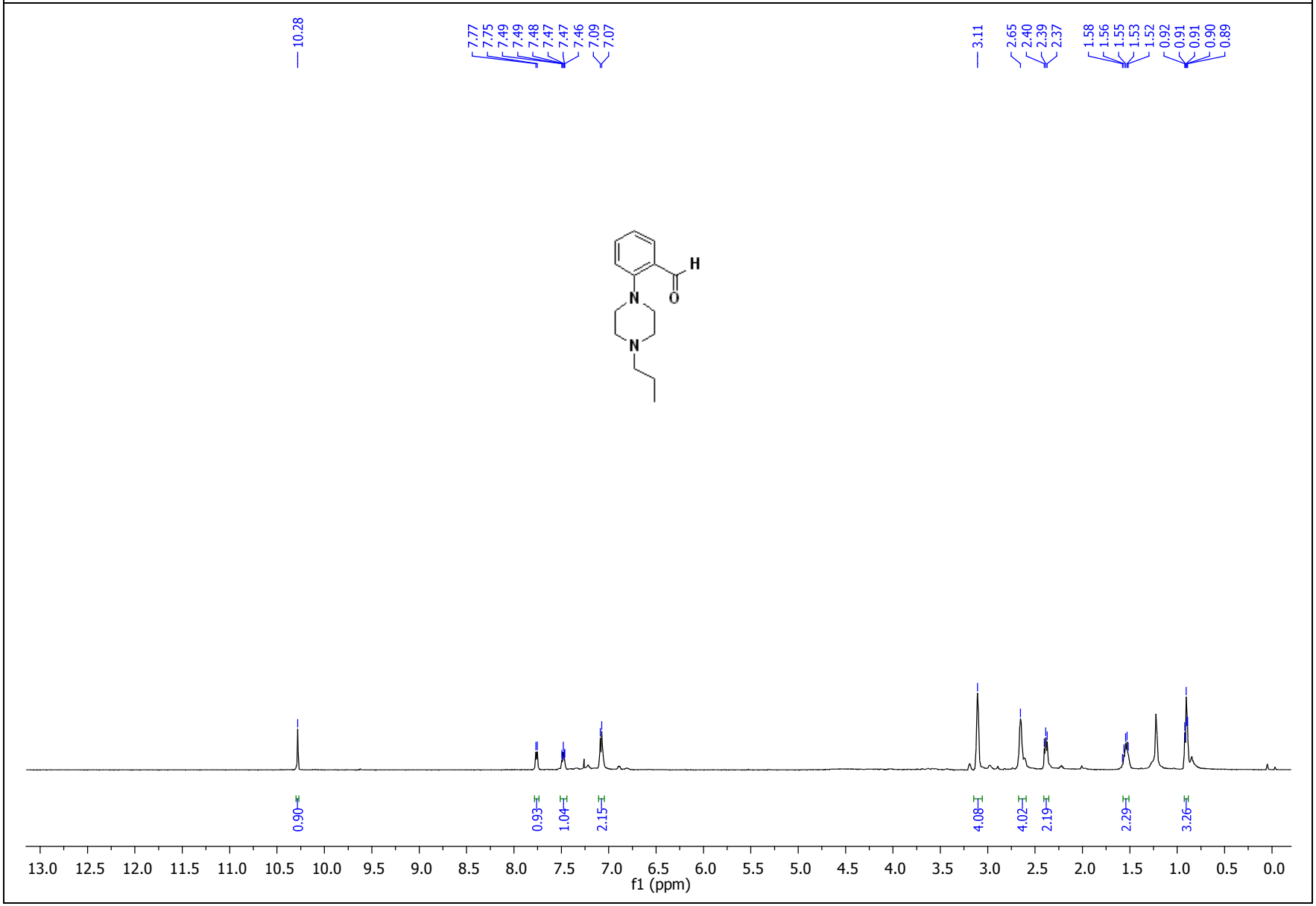
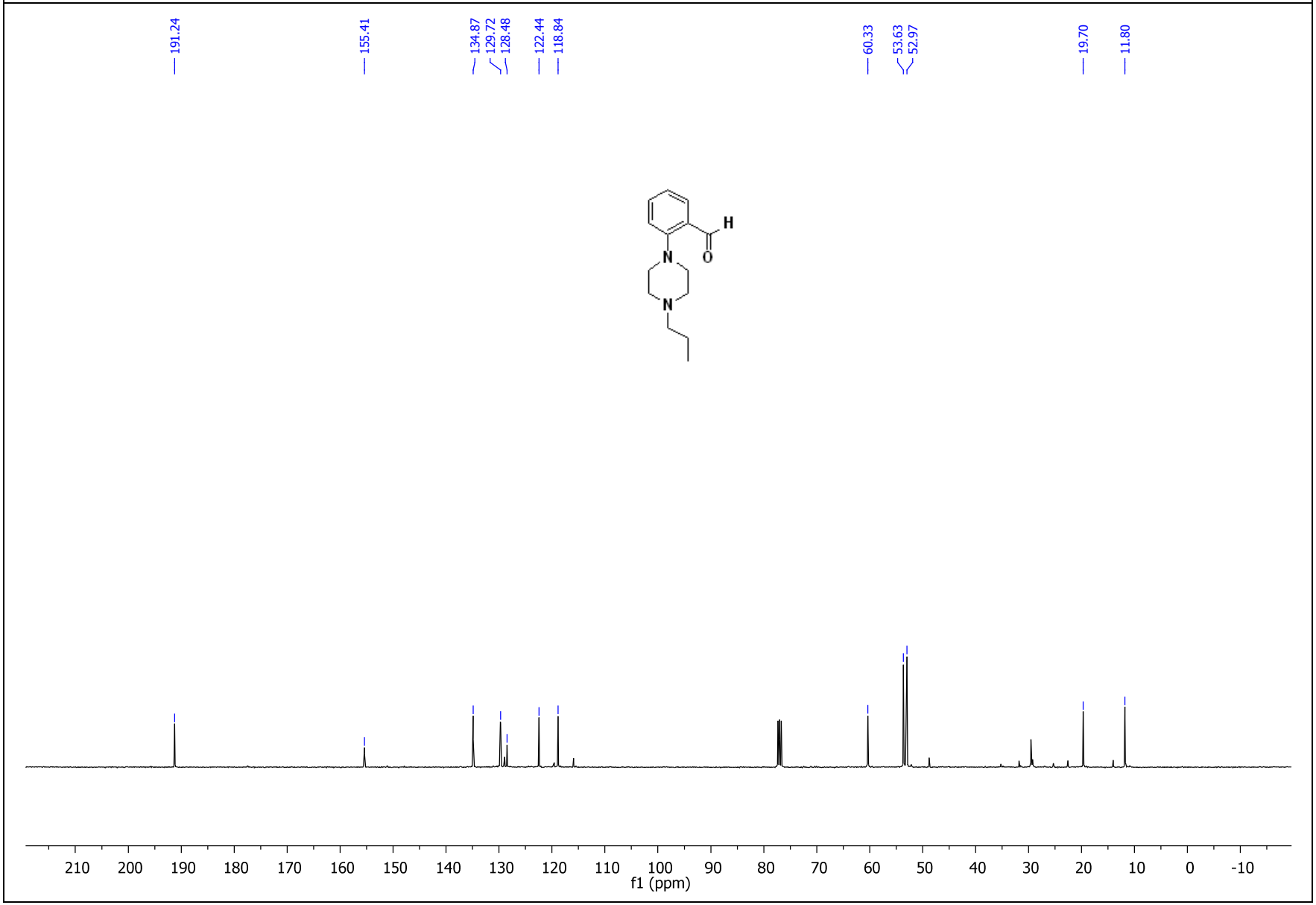
## 10. Copies of $^{1}H$ and $^{13}C$ NMR spectra:

$^{1}H$ NMR of **1c**



$^{13}$C NMR of **1c**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155.41
134.87
129.72
128.48
122.44
118.84
60.33
53.63
52.97
19.70
11.80
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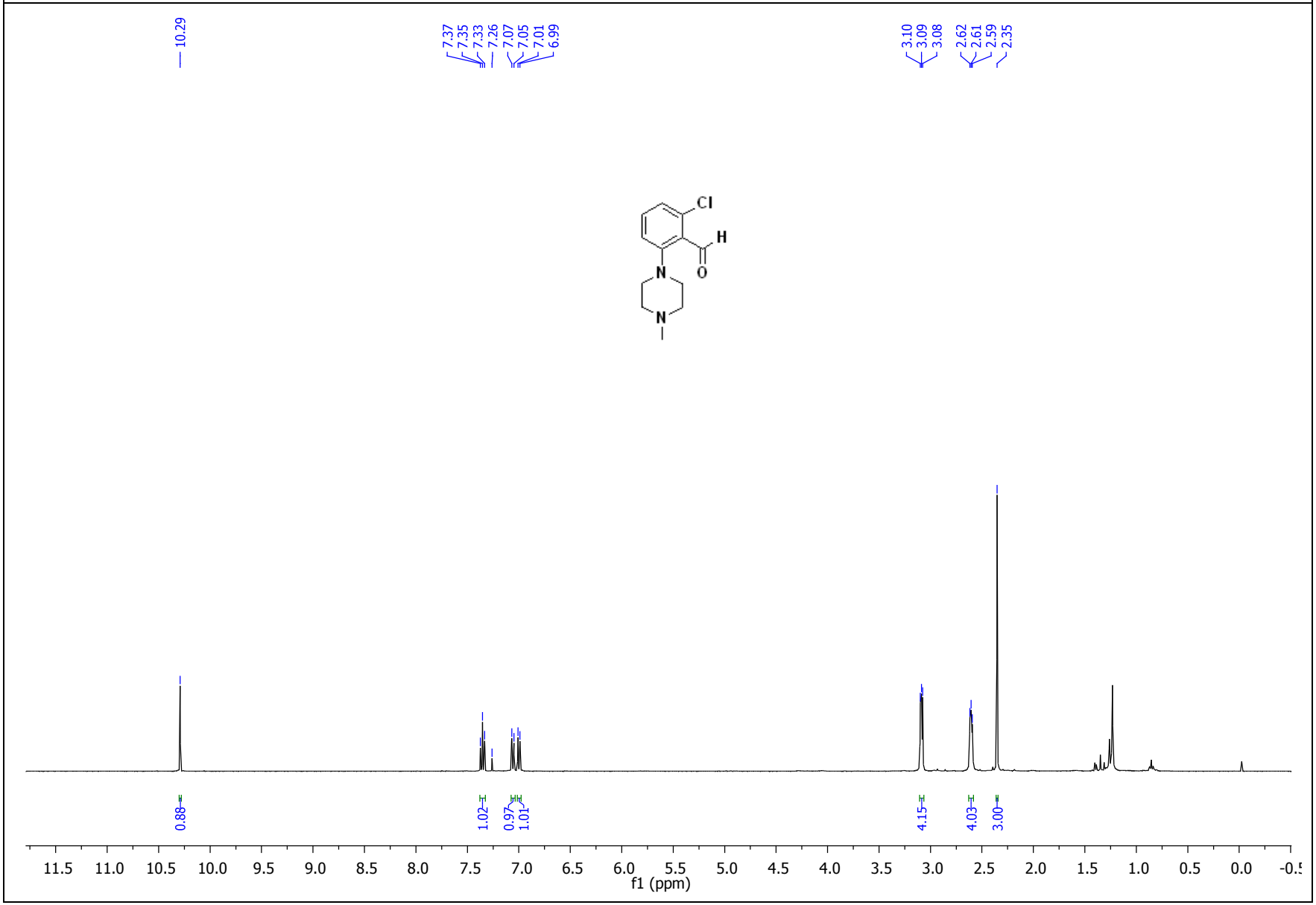
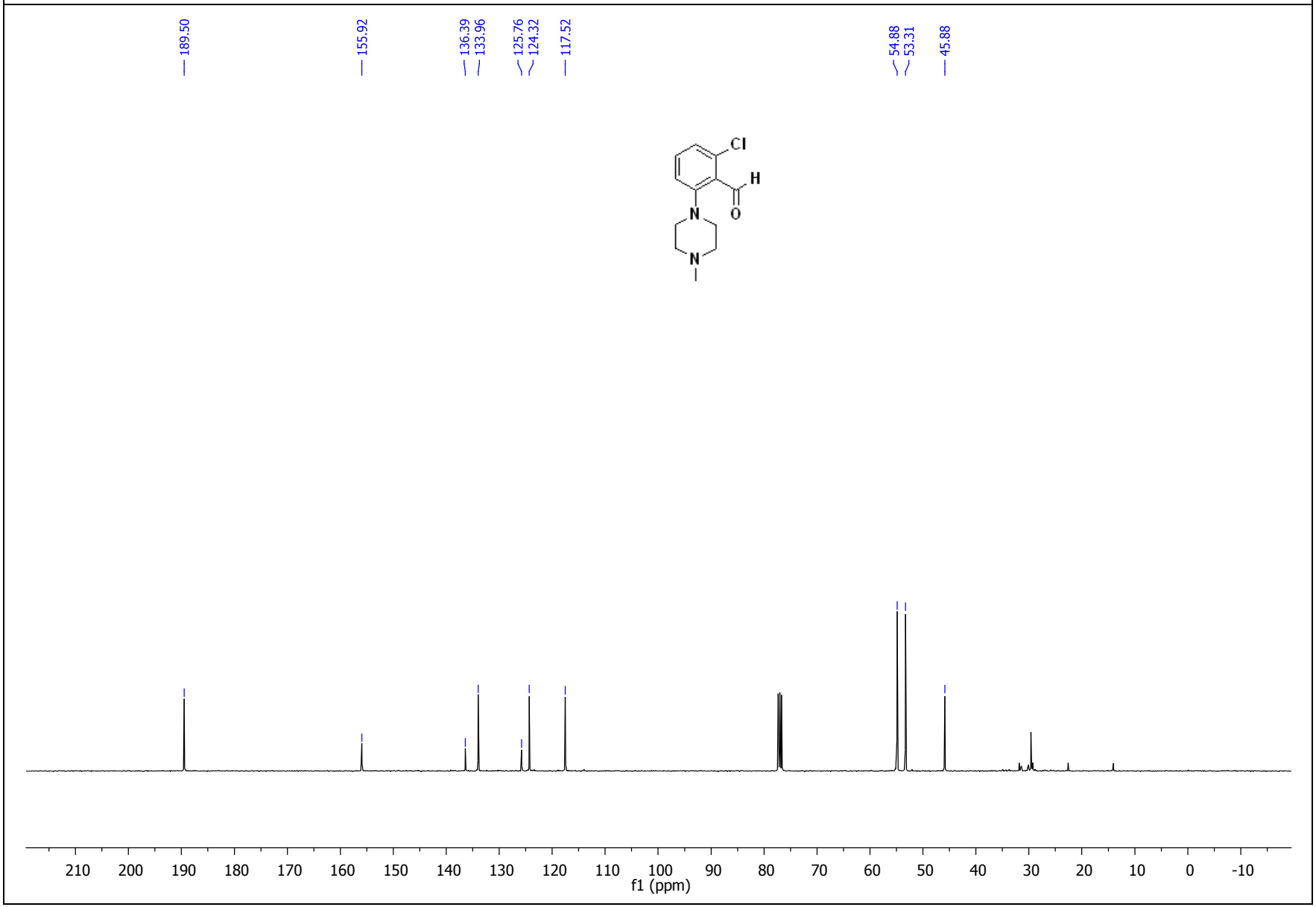
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

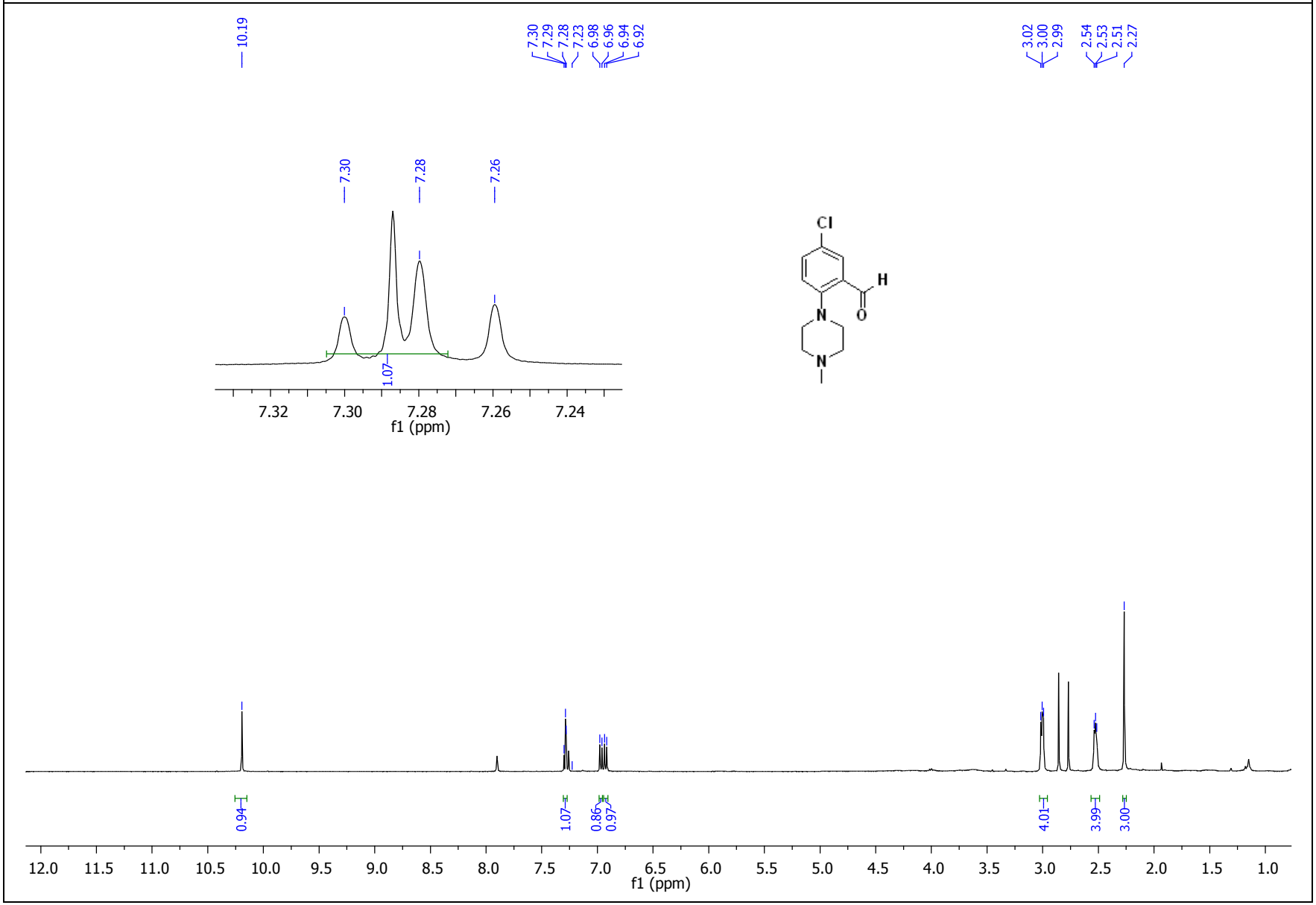
$^{1}$H NMR of **1d**


10.29
7.37
7.35
7.33
7.26
7.07
7.05
7.01
6.99
3.10
3.09
3.08
2.62
2.61
2.59
2.35
Cl
H
O
N
N
0.88
1.02
0.97
1.01
4.15
4.03
3.00
f1 (ppm)

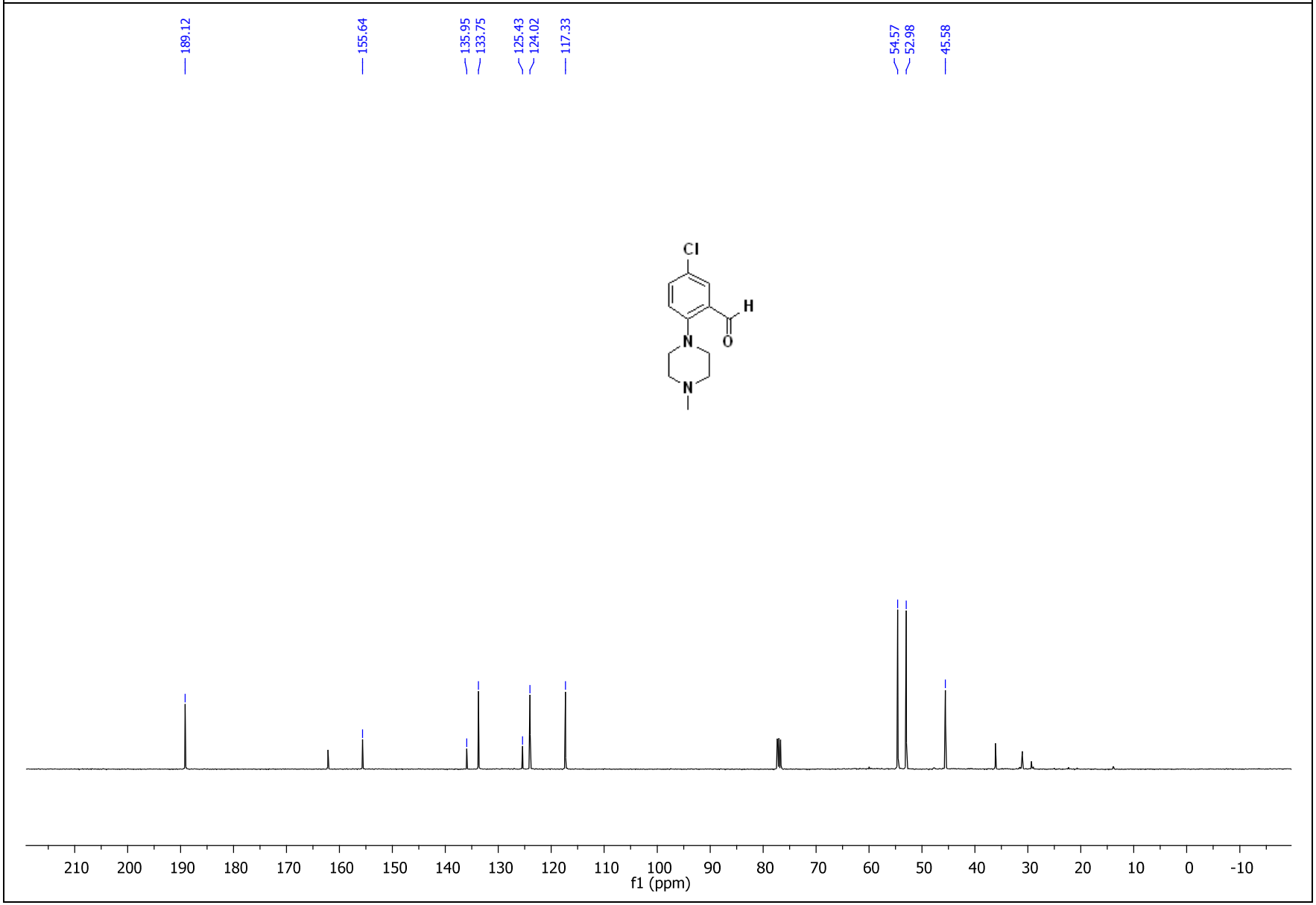
$^{13}$C NMR of **1d**


189.50
155.92
136.39
133.96
125.76
124.32
117.52
54.88
53.31
45.88
Cl
H
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

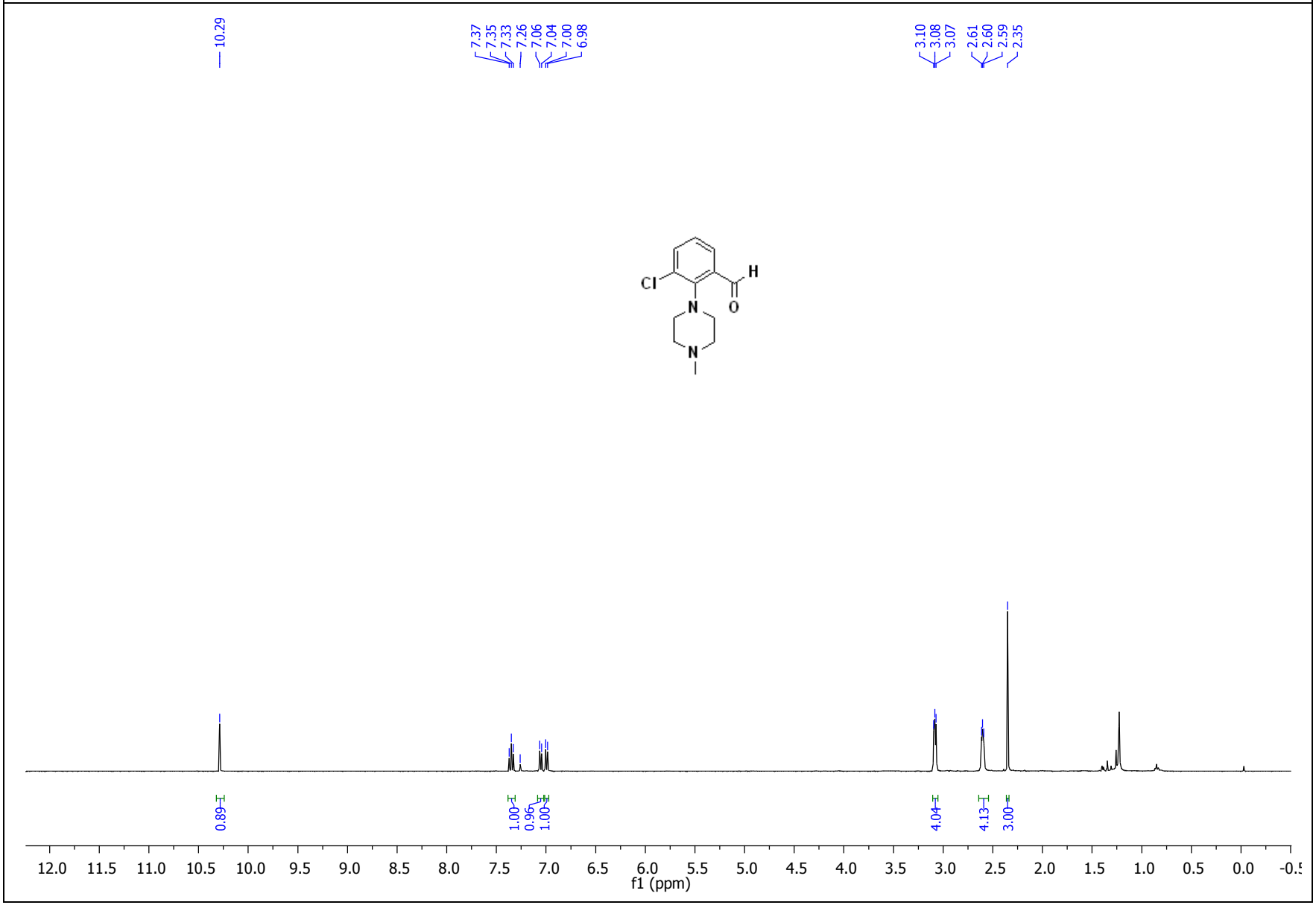
$^{1}$H NMR of **1e**


10.19
7.30
7.29
7.28
7.23
6.98
6.96
6.94
6.92
3.02
3.00
2.99
2.54
2.53
2.51
2.27
7.30
7.28
7.26
1.07
7.32
7.30
7.28
7.26
7.24
f1 (ppm)
Cl
H
O
N
N
0.94
1.07
0.86
0.97
4.01
3.99
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

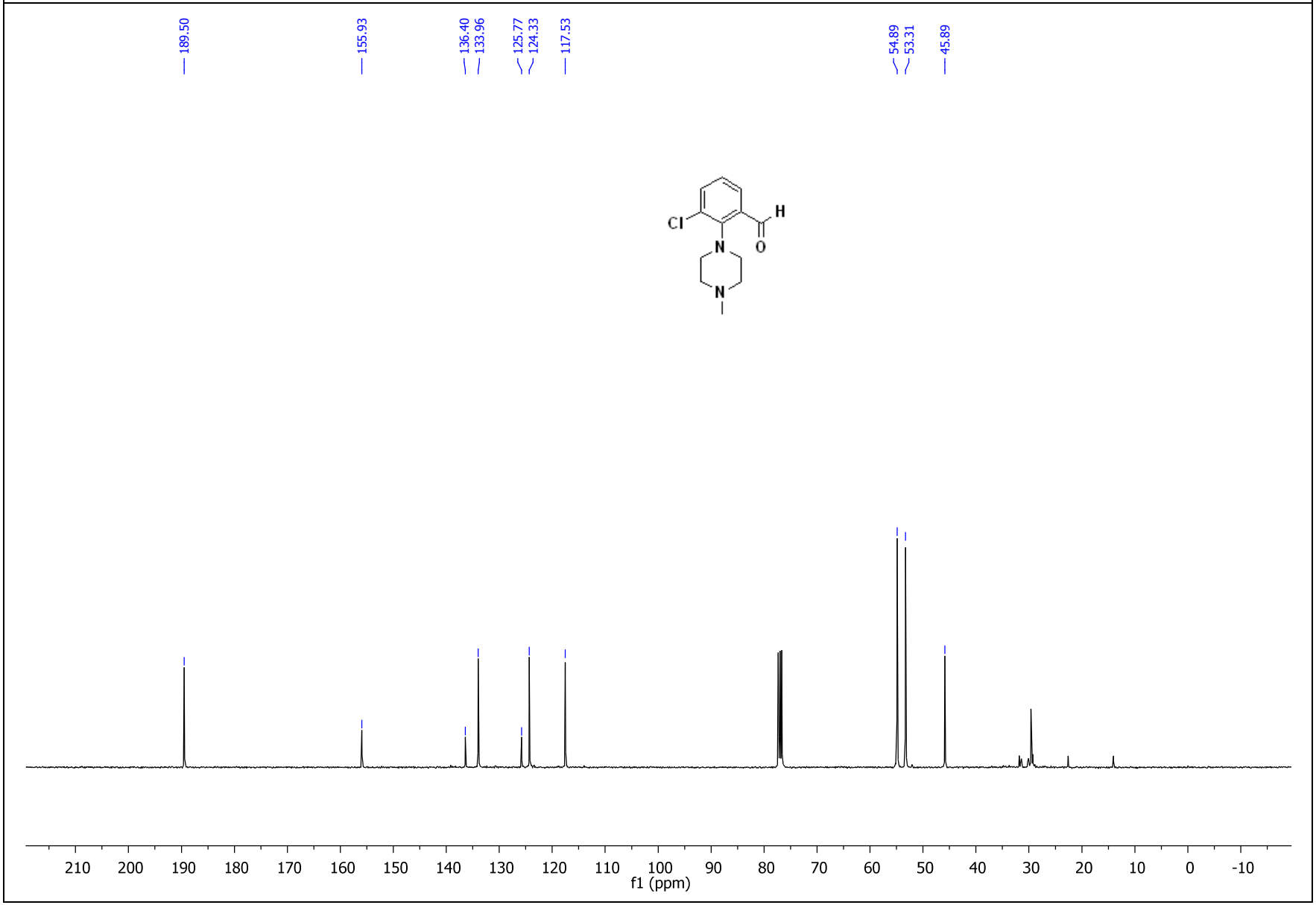
$^{13}$C NMR of **1e**


189.12
155.64
135.95
133.75
125.43
124.02
117.33
54.57
52.98
45.58
Cl
H
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

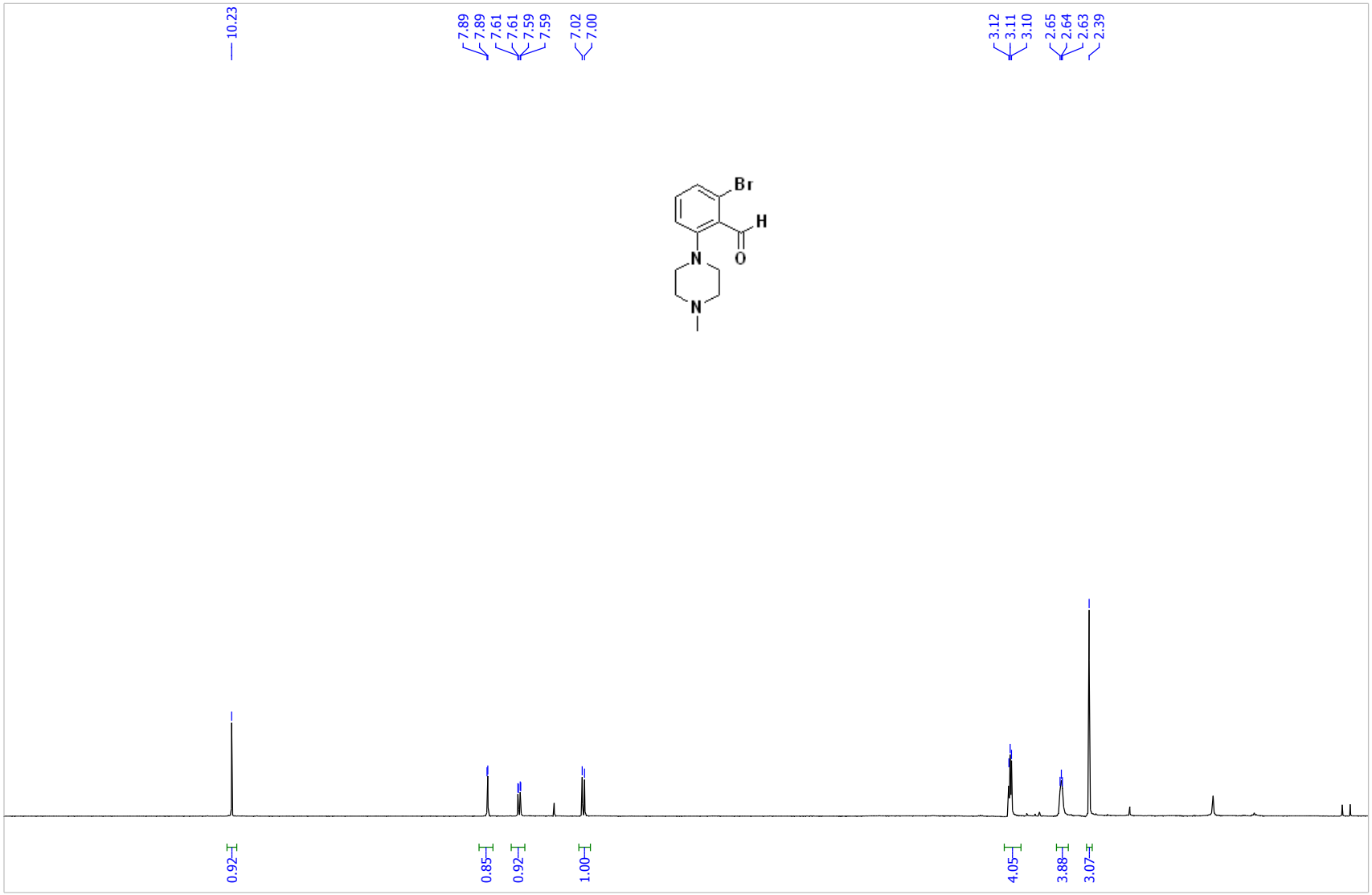
$^{1}$H NMR of **1f**


10.29
7.37
7.35
7.33
7.26
7.06
7.04
7.00
6.98
3.10
3.08
3.07
2.61
2.60
2.59
2.35
Cl
N
N
O
H
0.89
1.00
0.96
1.00
4.04
4.13
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

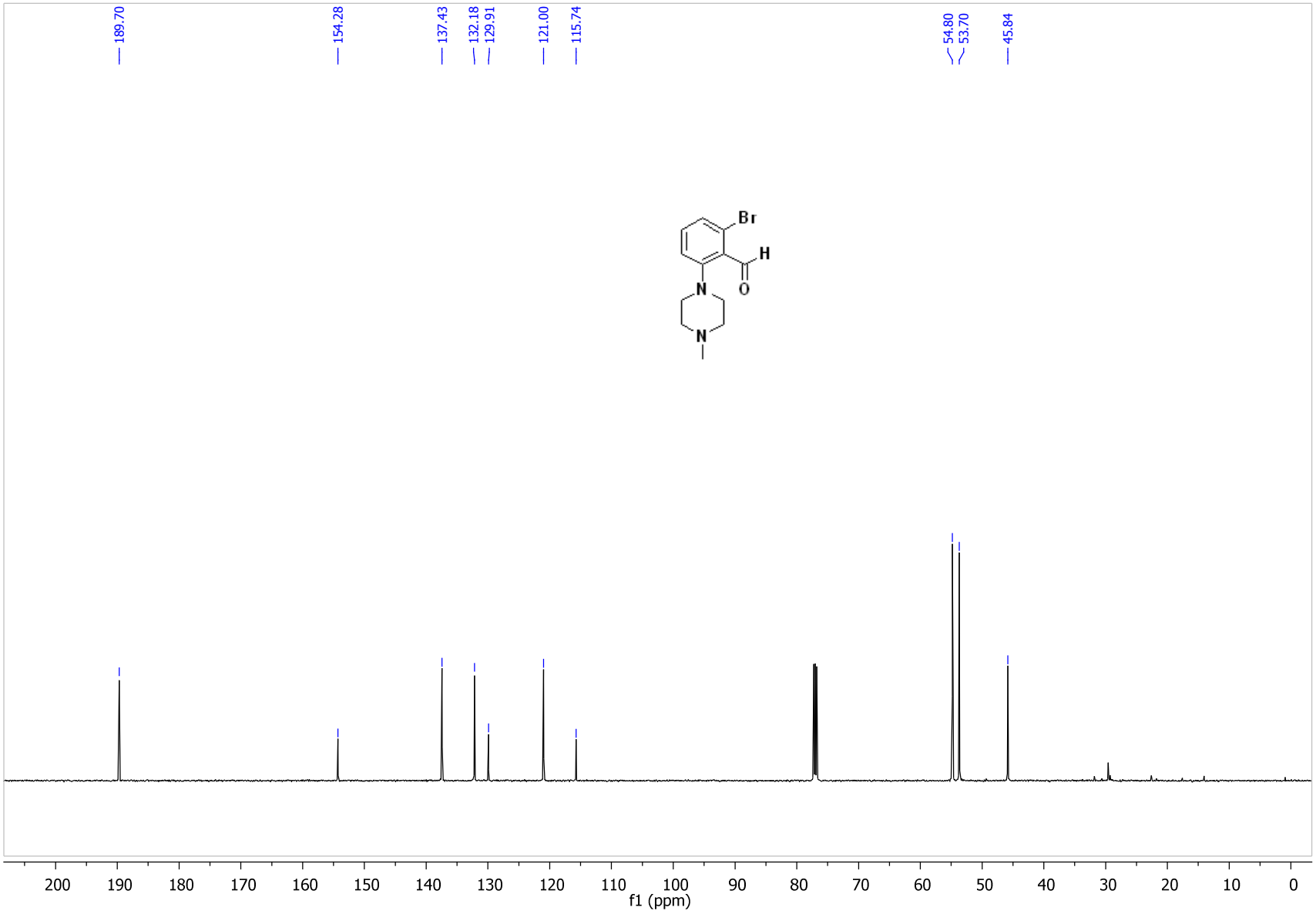
$^{13}$C NMR of **1f**


189.50
155.93
136.40
133.96
125.77
124.33
117.53
54.89
53.31
45.89
Cl
H
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

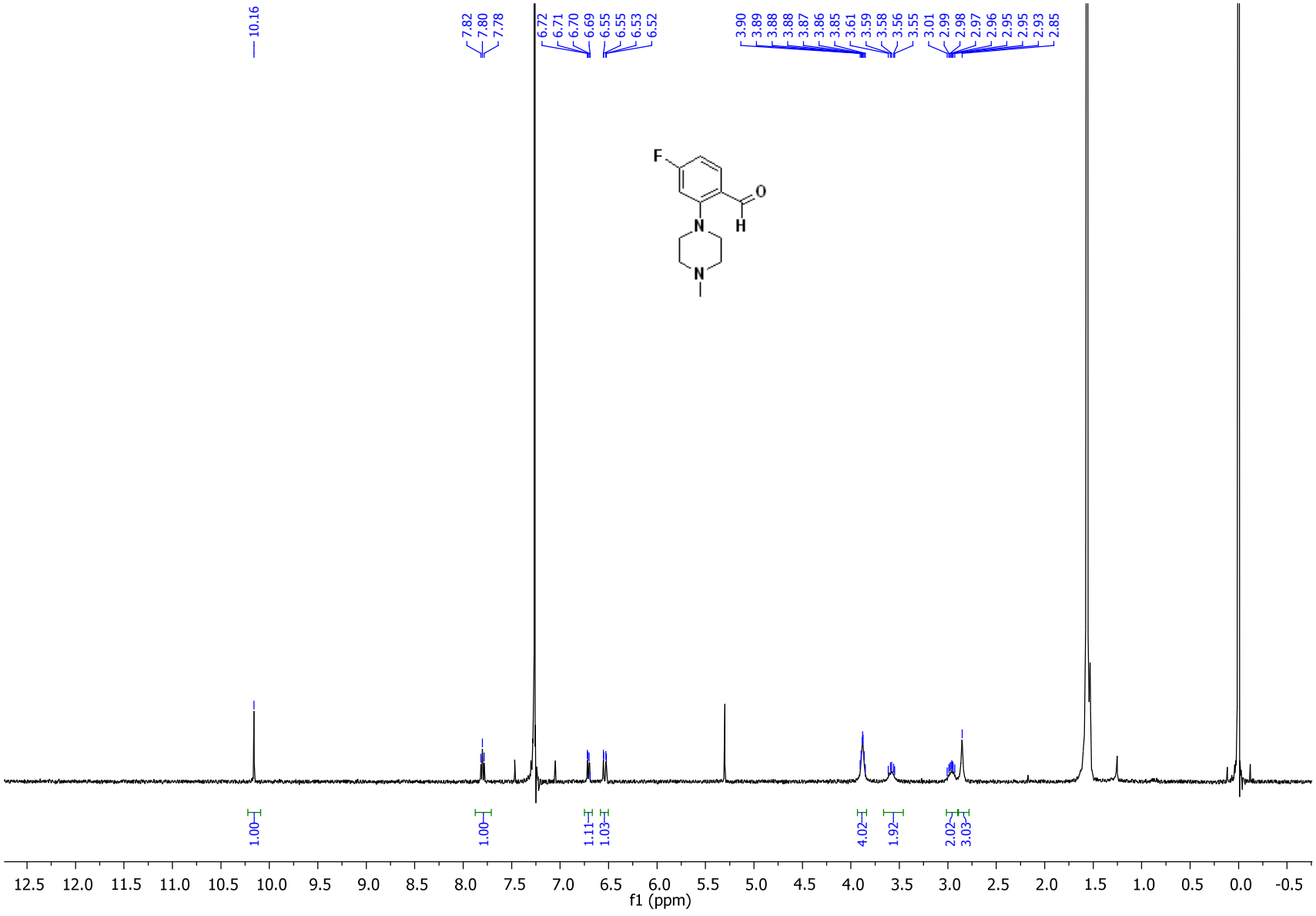
$^{1}$H NMR of **1g**


10.23
7.89
7.89
7.61
7.61
7.59
7.59
7.02
7.00
3.12
3.11
3.10
2.65
2.64
2.63
2.39
Br
H
O
N
N
0.92
0.85
0.92
1.00
4.05
3.88
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

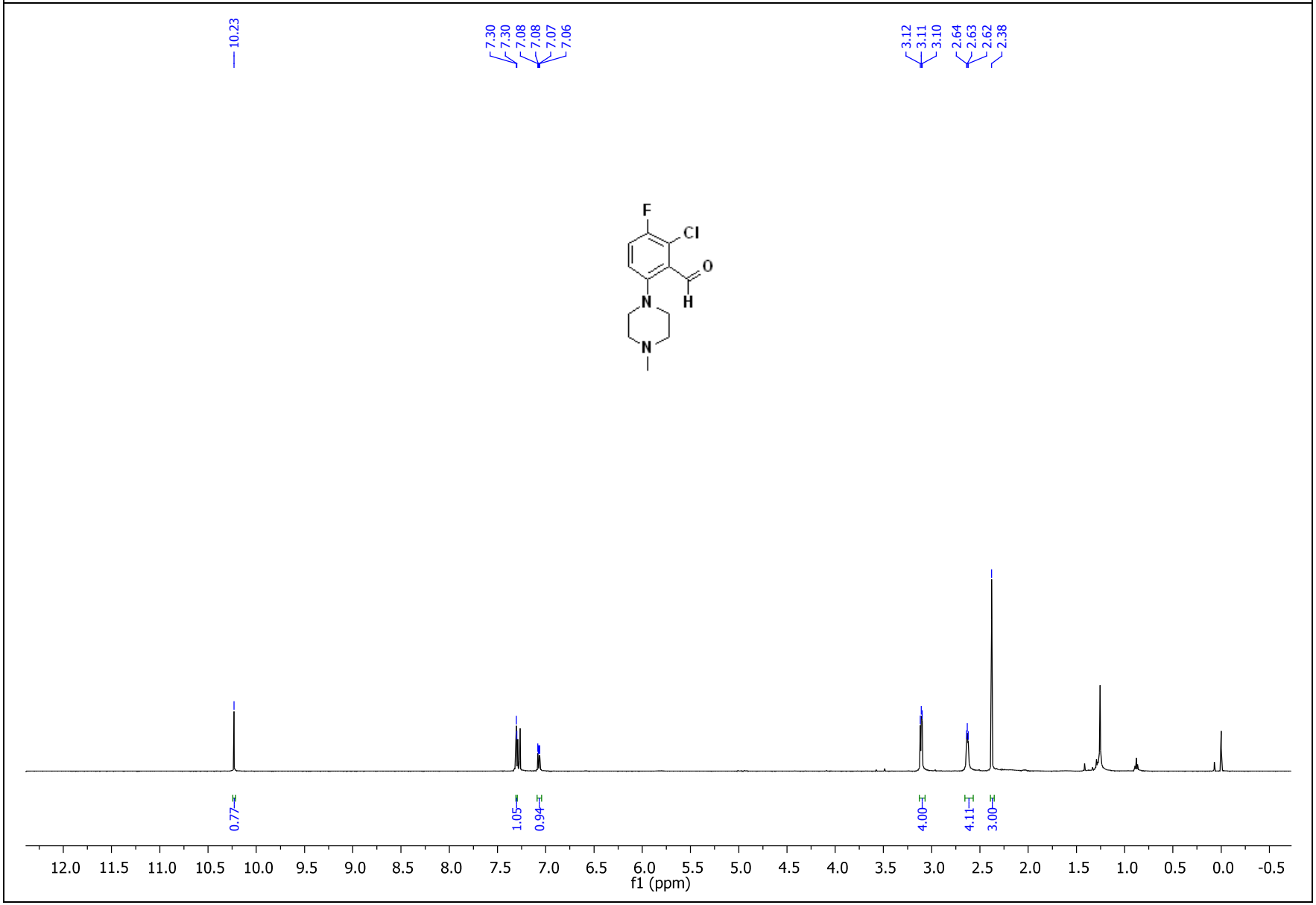
$^{13}$C NMR of **1g**


189.70
154.28
137.43
132.18
129.91
121.00
115.74
54.80
53.70
45.84
Br
H
O
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

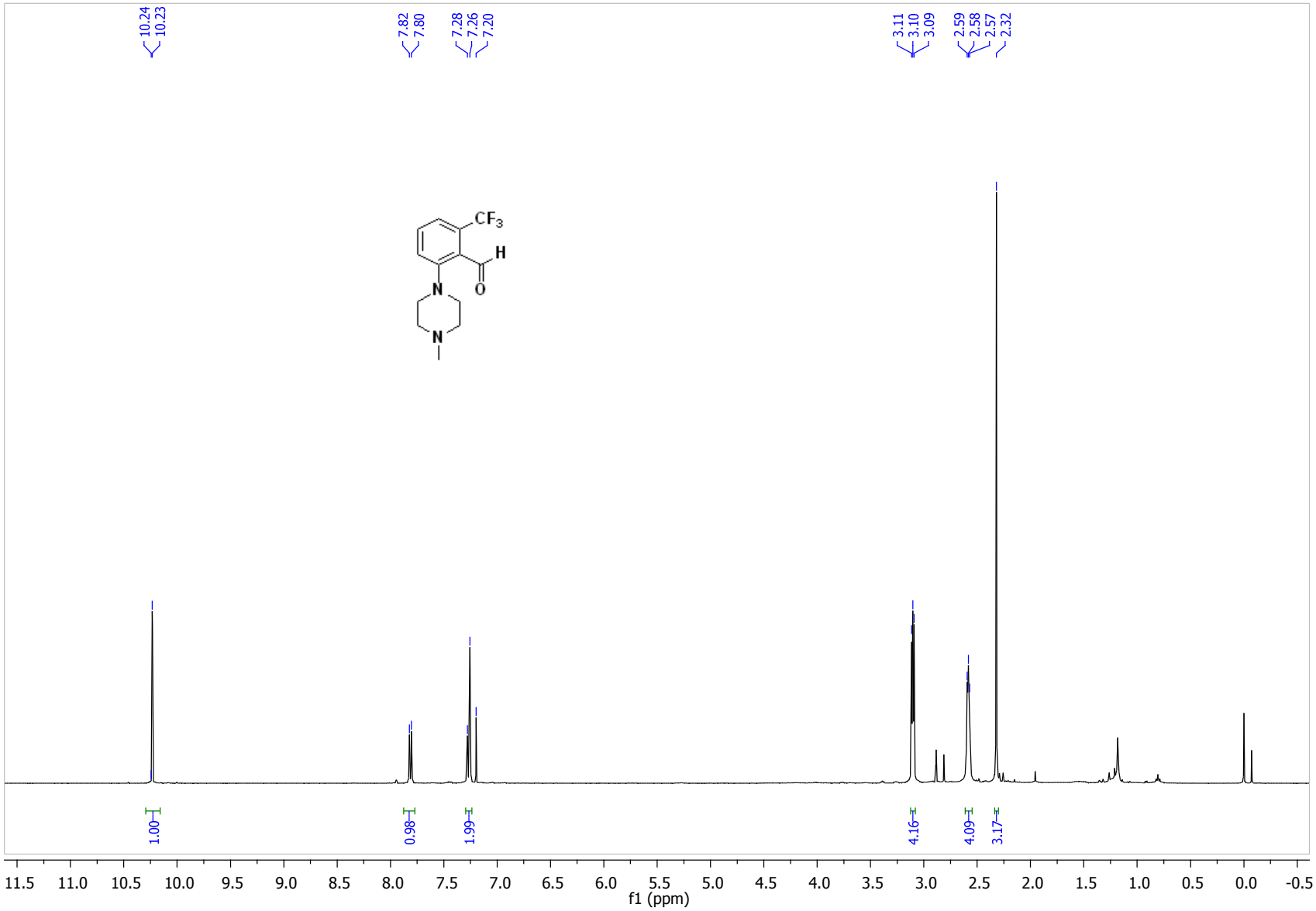
$^{1}$H NMR of **1k**


10.16
7.82
7.80
7.78
6.72
6.71
6.70
6.69
6.55
6.55
6.53
6.52
3.90
3.89
3.88
3.88
3.87
3.86
3.85
3.61
3.59
3.58
3.56
3.55
3.01
2.99
2.98
2.97
2.96
2.95
2.95
2.93
2.85
F
O
H
N
N
1.00
1.00
1.11
1.03
4.02
1.92
2.02
3.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

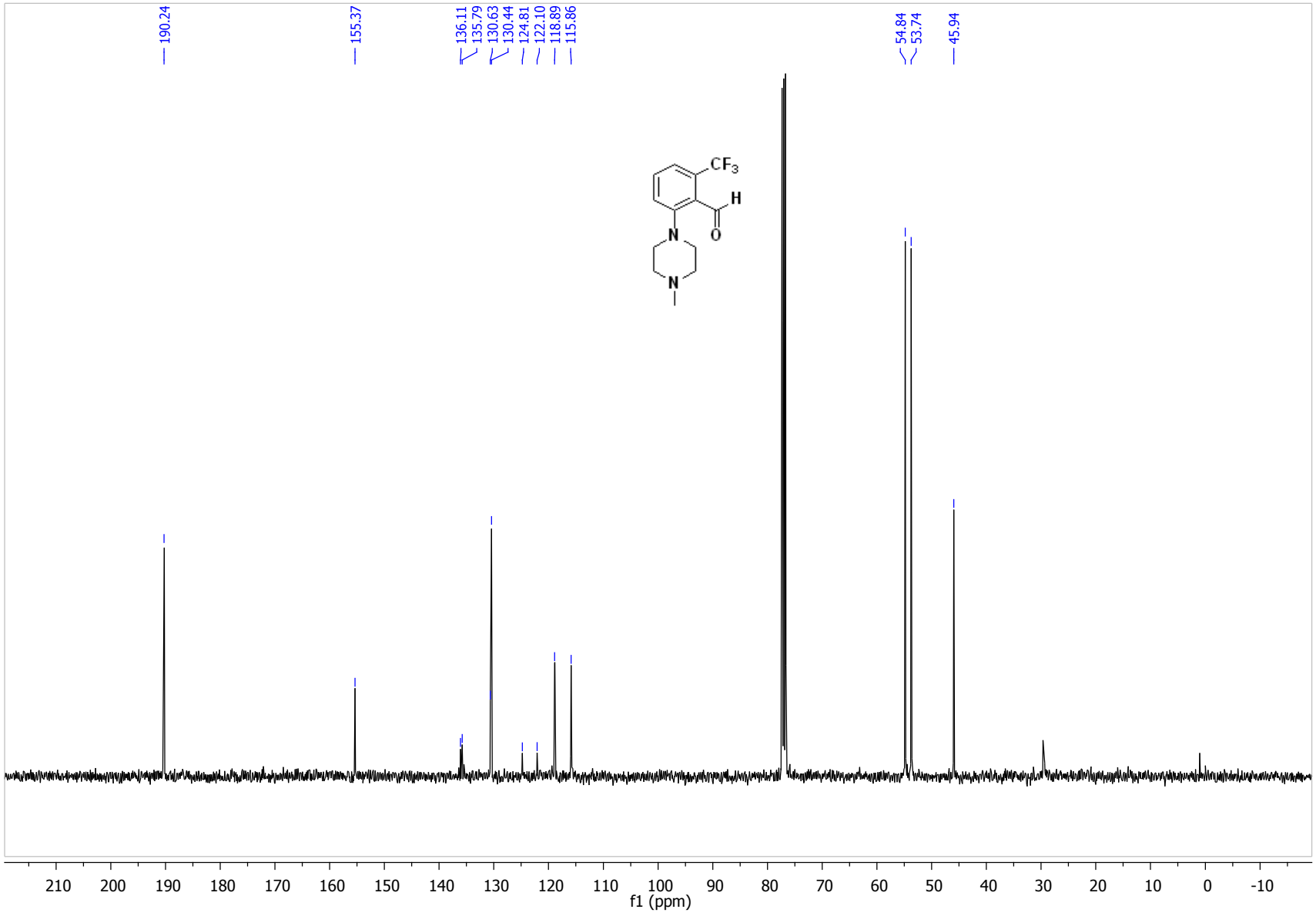
$^{1}$H NMR of **1l**


10.23
7.30
7.30
7.08
7.08
7.07
7.06
3.12
3.11
3.10
2.64
2.63
2.62
2.38
F
Cl
O
H
N
N
0.77
1.05
0.94
4.00
4.11
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

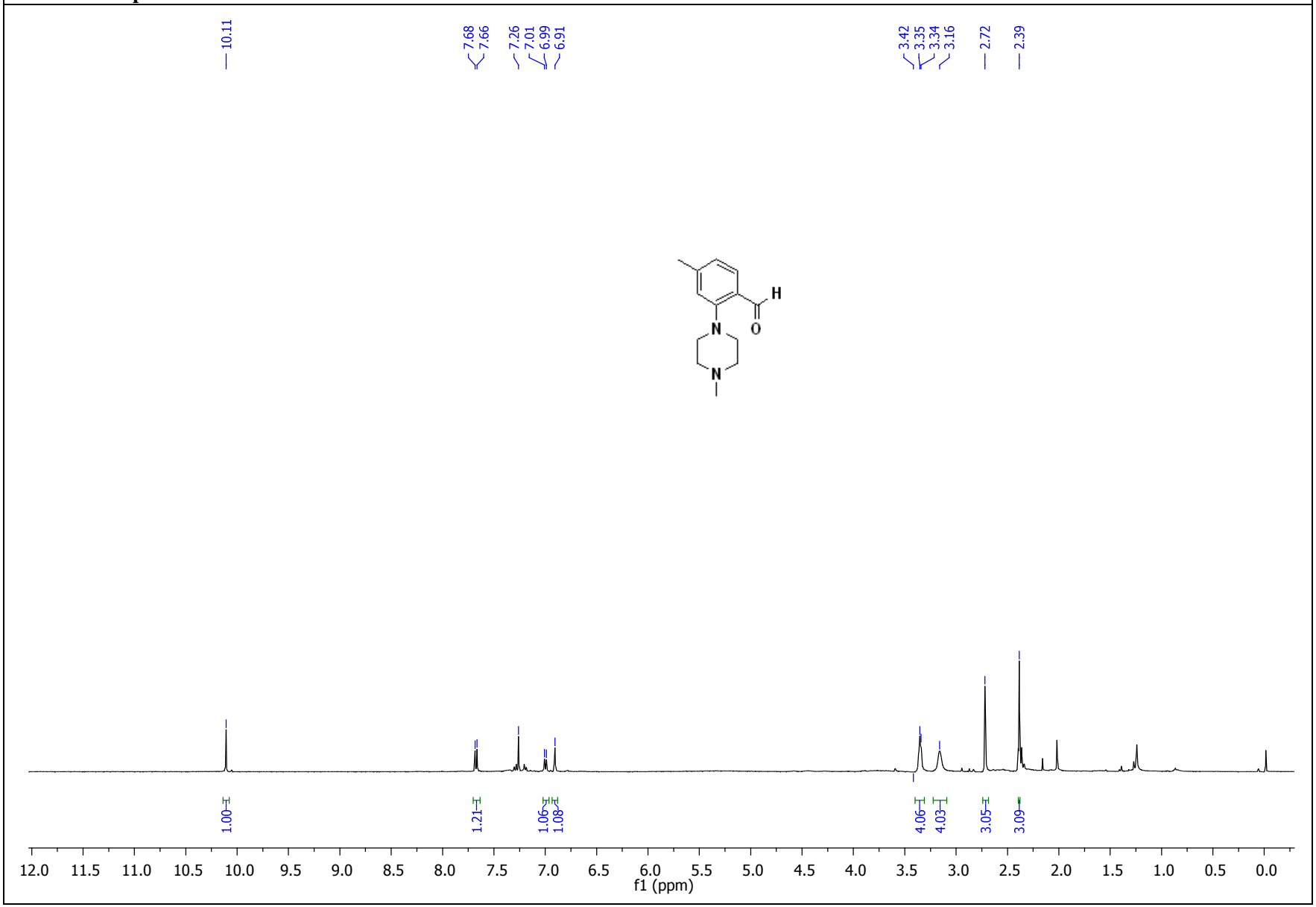
$^{1}$H NMR of **1m**


10.24
10.23
7.82
7.80
7.28
7.26
7.20
3.11
3.10
3.09
2.59
2.58
2.57
2.32
CF3
H
O
N
N
1.00
0.98
1.99
4.16
4.09
3.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

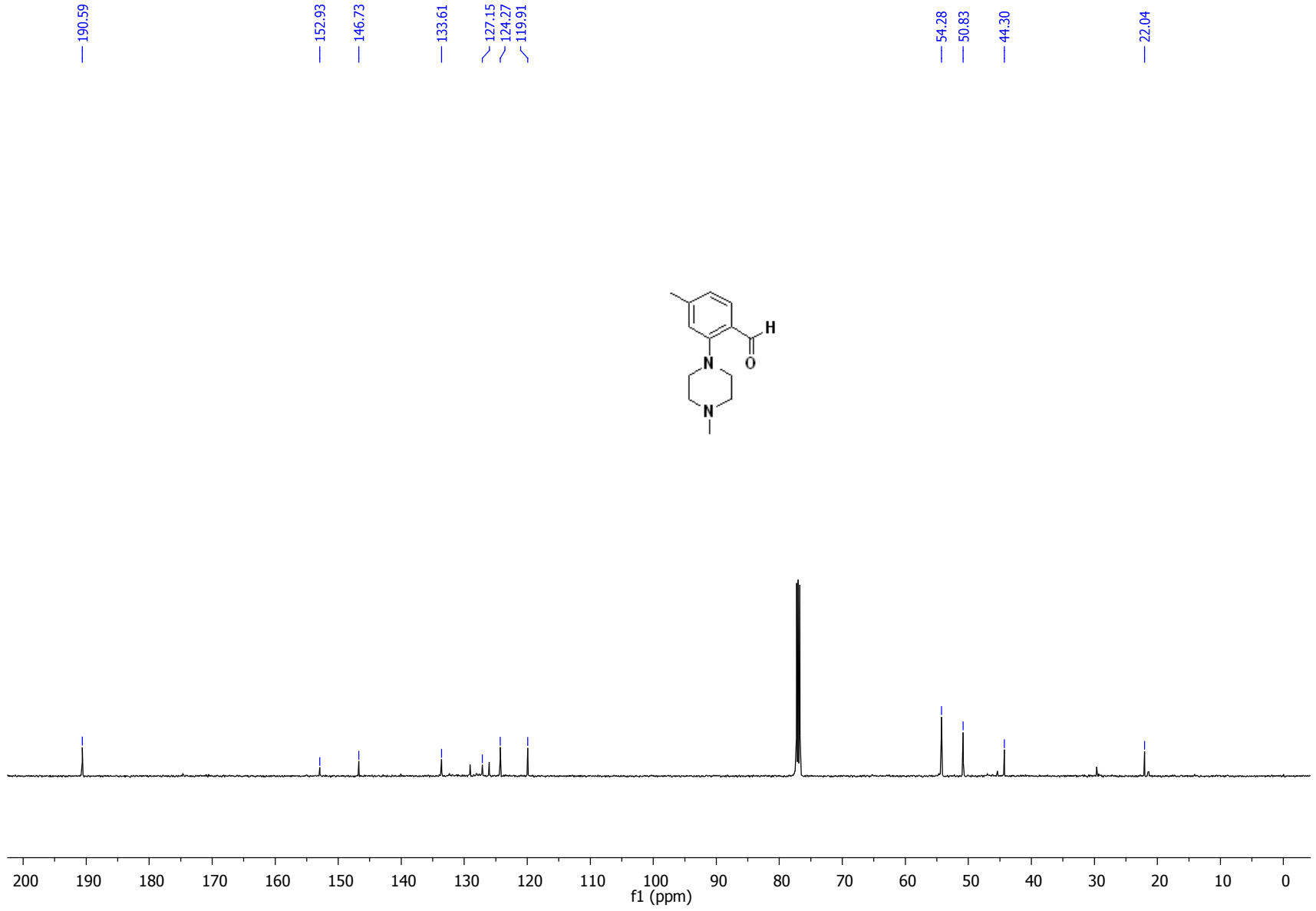
$^{13}$C NMR of **1m**


190.24
155.37
136.11
135.79
130.63
130.44
124.81
122.10
118.89
115.86
54.84
53.74
45.94
CF3
H
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

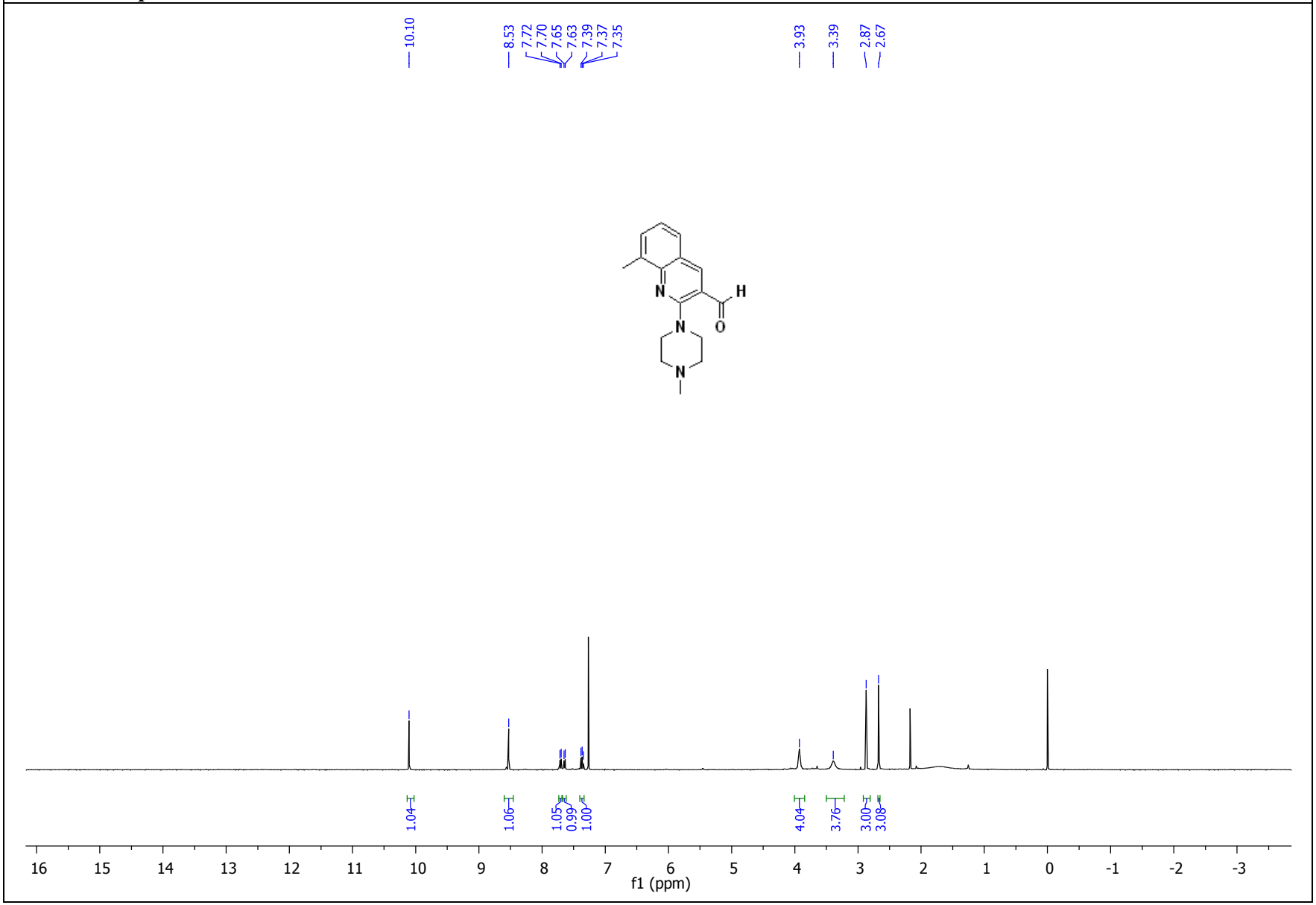
$^{1}$H NMR of **1p**


10.11
7.68
7.66
7.26
7.01
6.99
6.91
3.42
3.35
3.34
3.16
2.72
2.39
H
O
N
N
1.00
1.21
1.06
1.08
4.06
4.03
3.05
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

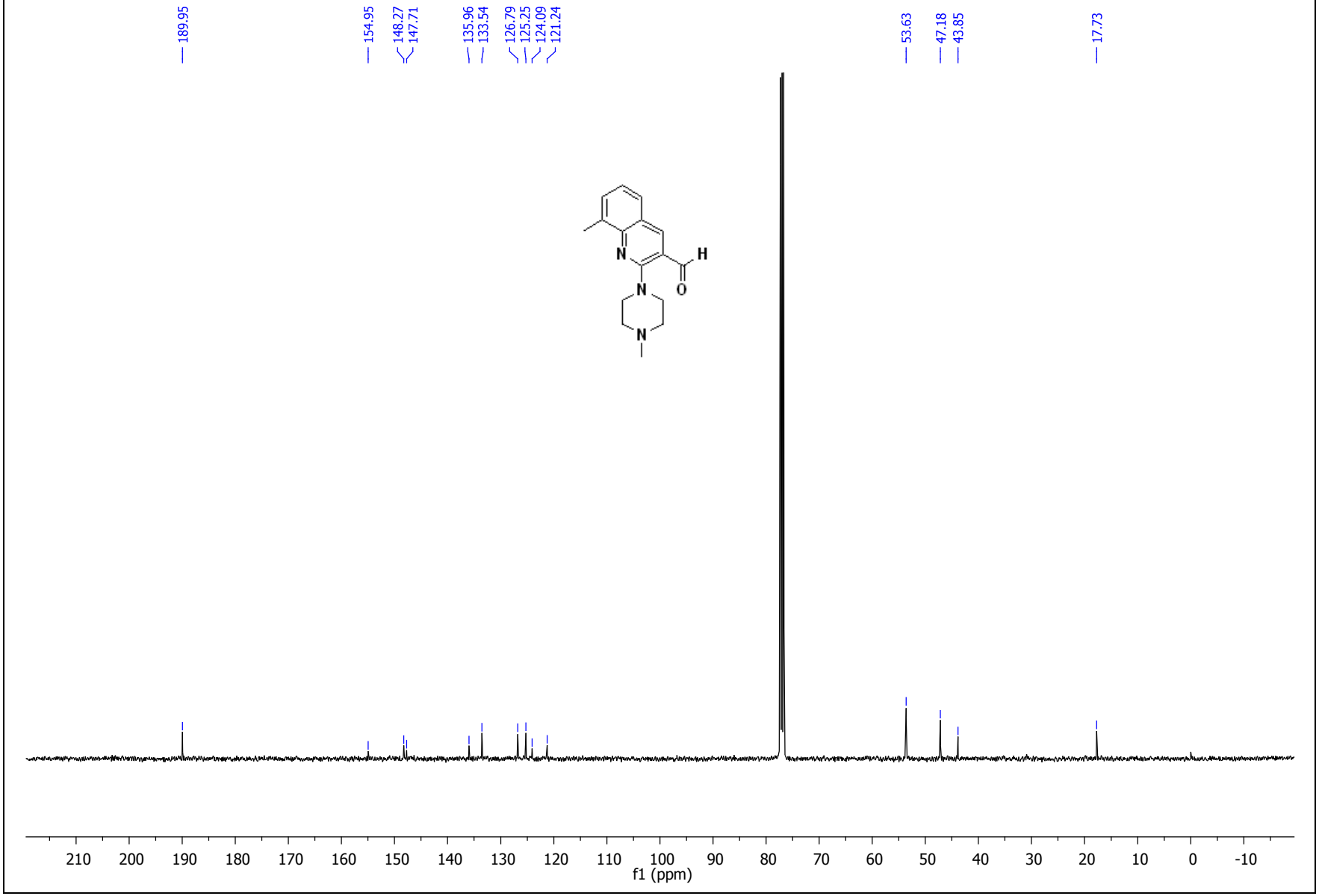
$^{13}$C NMR of **1p**


190.59
152.93
146.73
133.61
127.15
124.27
119.91
54.28
50.83
44.30
22.04
H
O
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

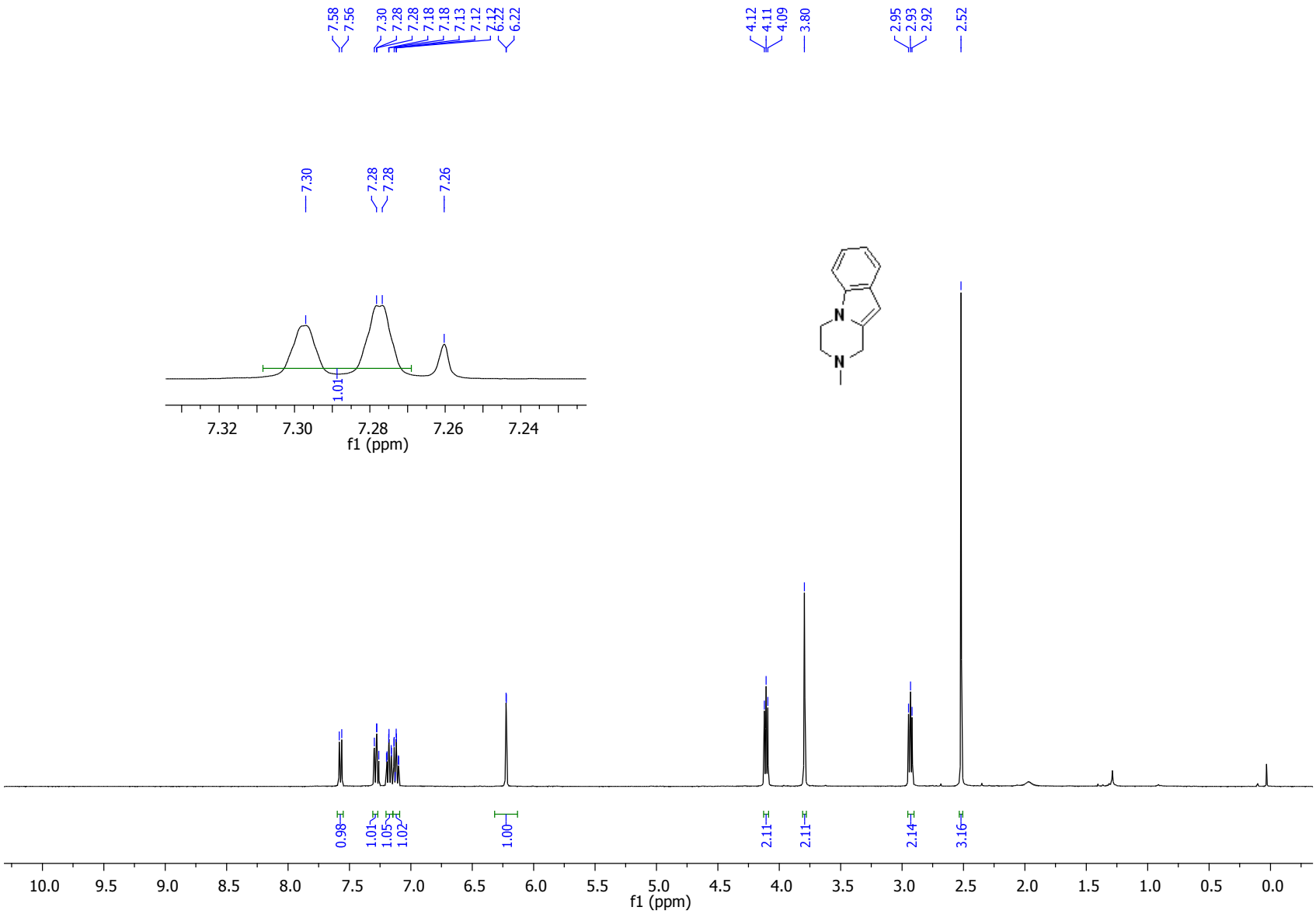
$^{1}$H NMR of **1q**


10.10
8.53
7.72
7.70
7.65
7.63
7.39
7.37
7.35
3.93
3.39
2.87
2.67
1.04
1.06
1.05
0.99
1.00
4.04
3.76
3.00
3.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

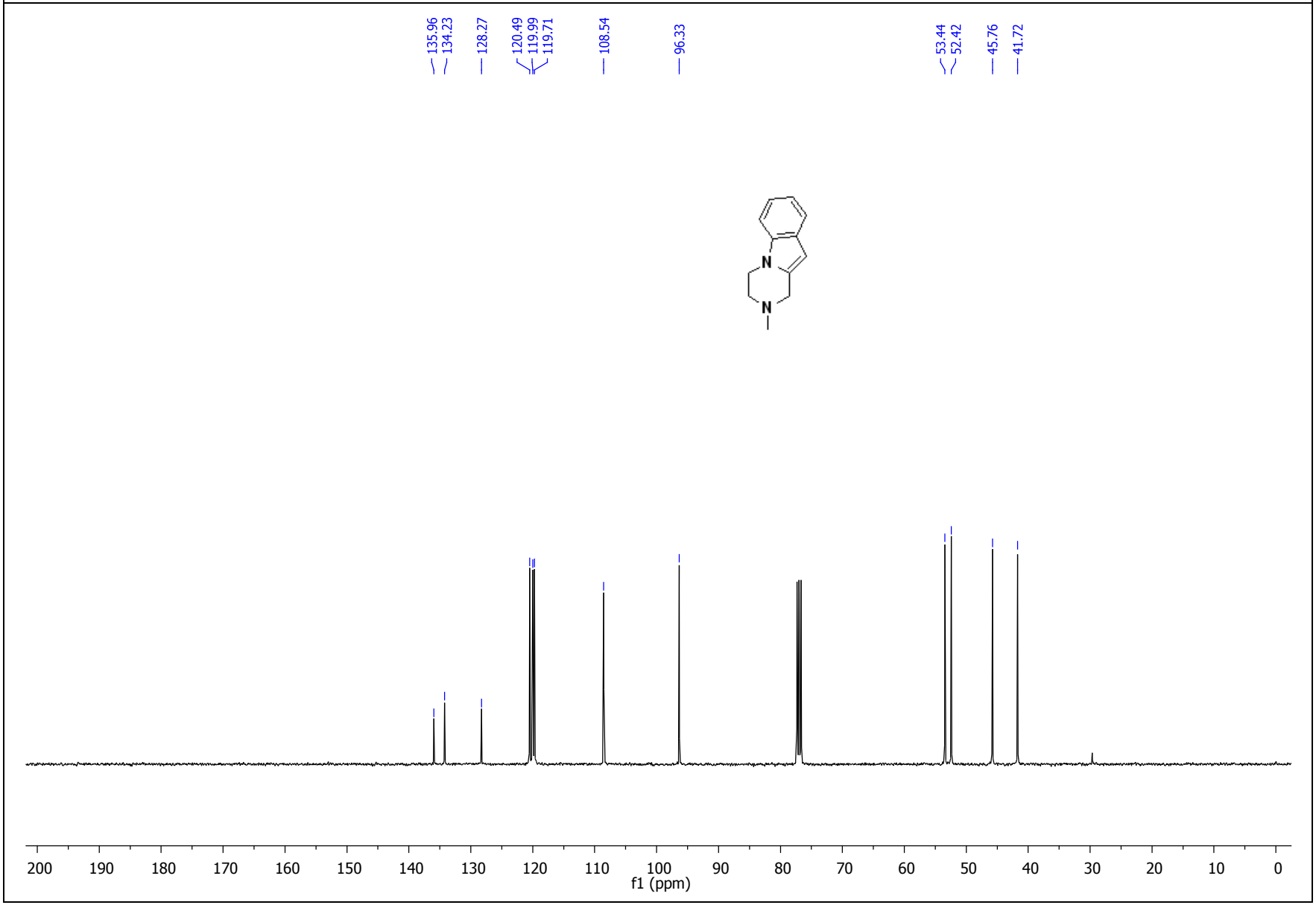
$^{13}$CNMR of **1q**


189.95
154.95
148.27
147.71
135.96
133.54
126.79
125.25
124.09
121.24
53.63
47.18
43.85
17.73
N
N
N
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

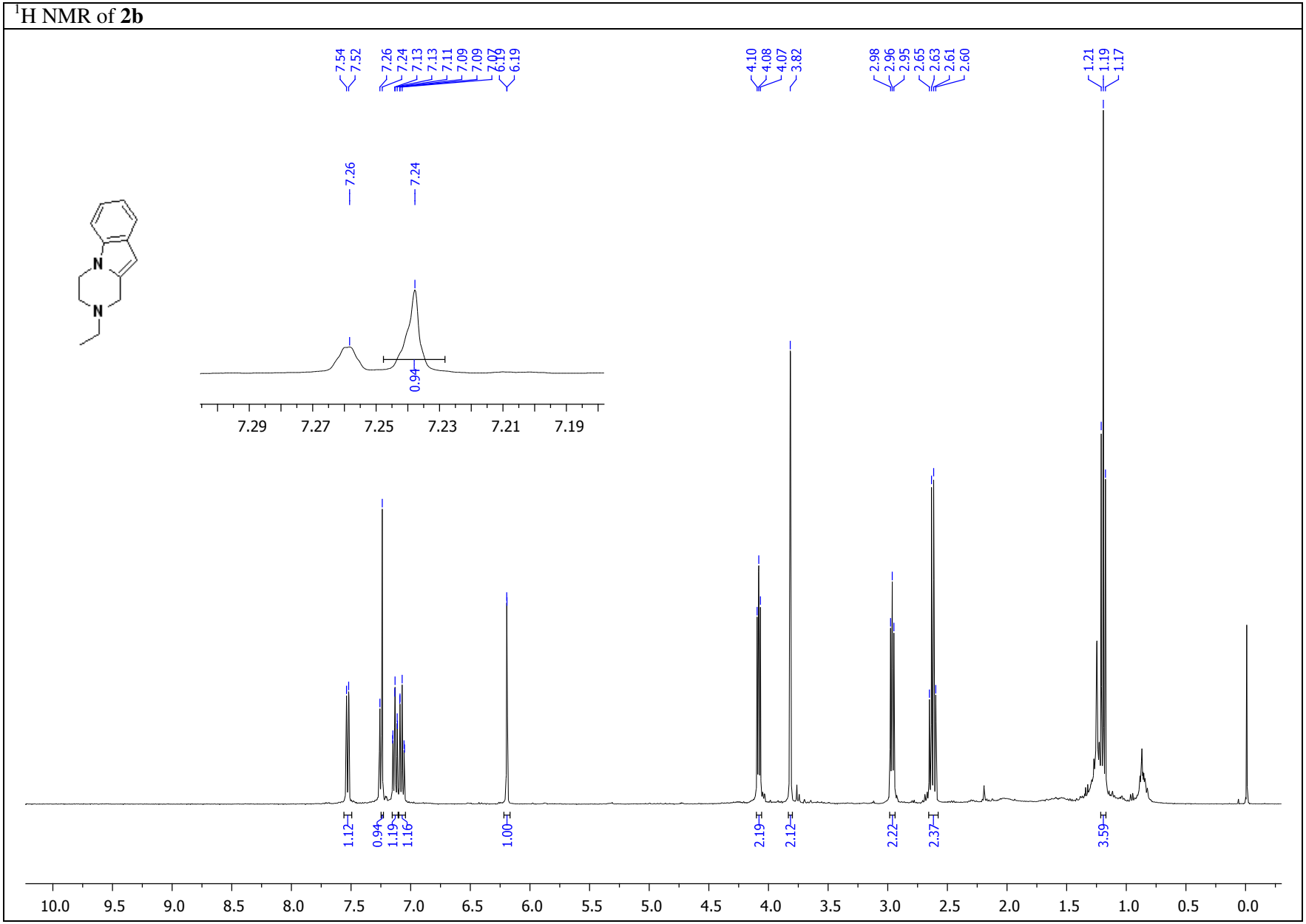
$^{1}$H NMR of **2a**


7.58
7.56
7.30
7.28
7.28
7.18
7.18
7.13
7.12
6.22
6.22
4.12
4.11
4.09
3.80
2.95
2.93
2.92
2.52
7.30
7.28
7.28
7.26
1.01
7.32
7.30
7.28
7.26
7.24
f1 (ppm)
N
N
0.98
1.01
1.05
1.02
1.00
2.11
2.11
2.14
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

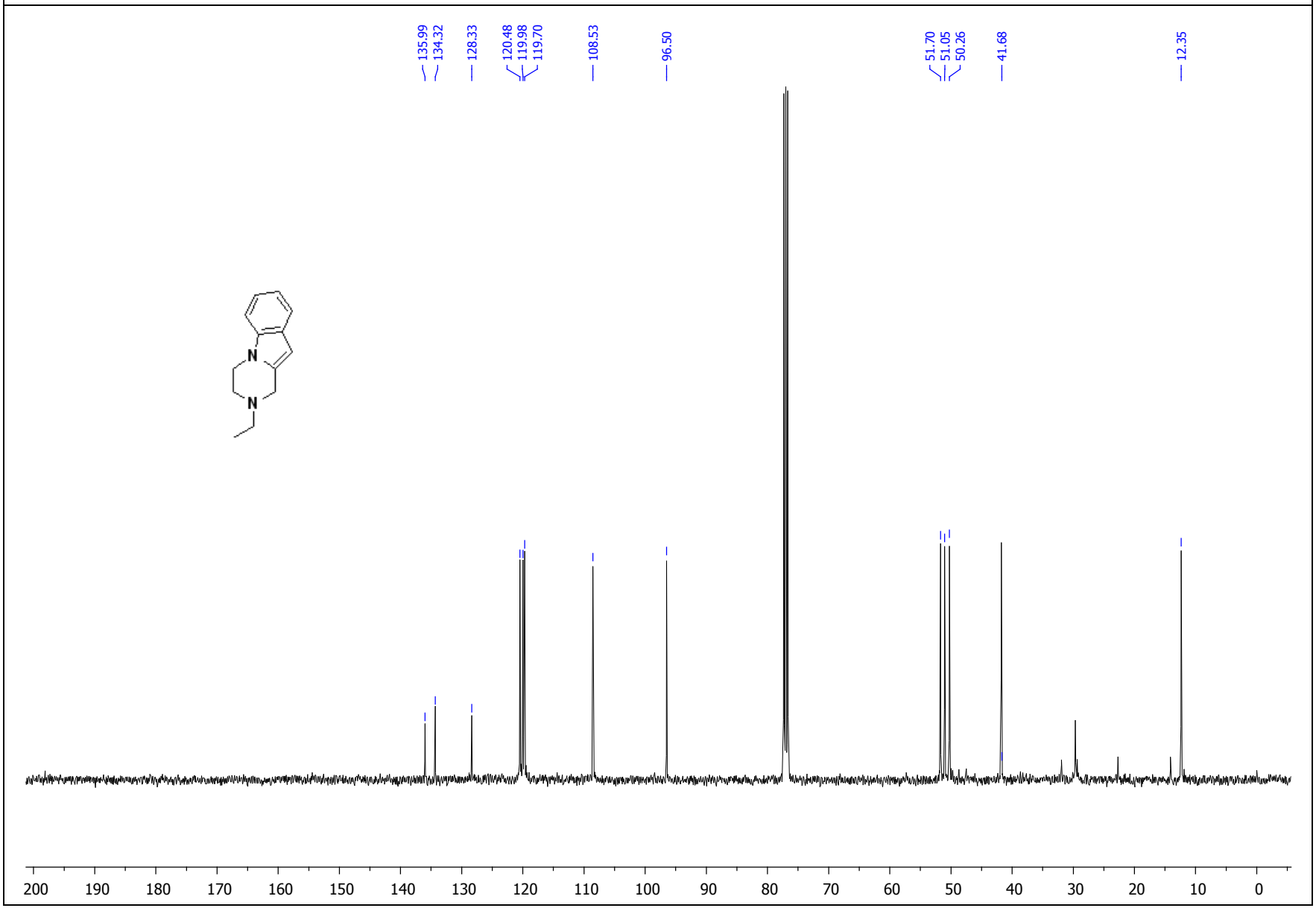
$^{13}$C NMR of **2a**


135.96
134.23
128.27
120.49
119.99
119.71
108.54
96.33
53.44
52.42
45.76
41.72
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

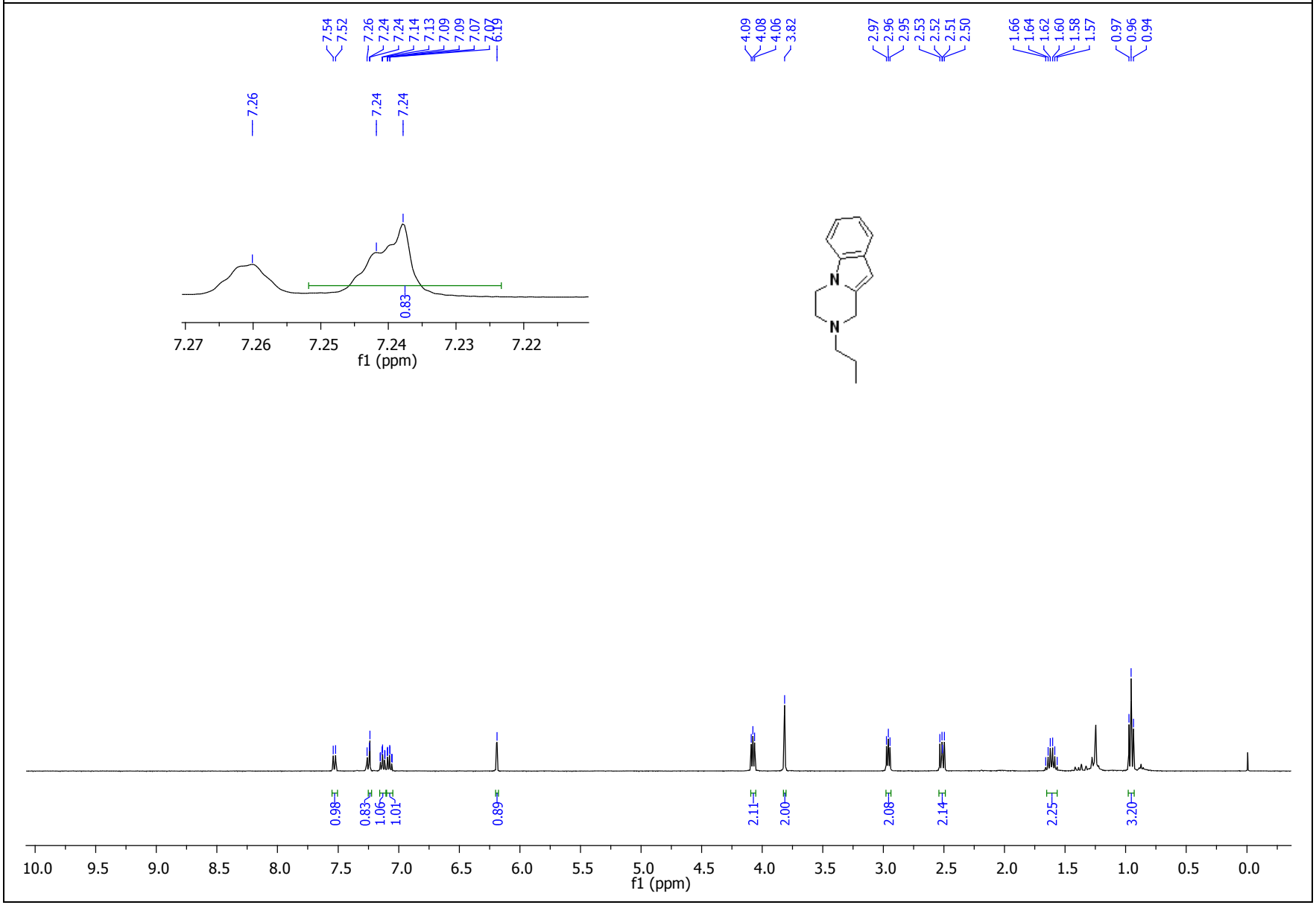
$^{1}$H NMR of **2b**


7.54
7.52
7.26
7.24
7.13
7.11
7.09
7.09
7.07
6.19
4.10
4.08
4.07
3.82
2.98
2.96
2.95
2.65
2.63
2.61
2.60
1.21
1.19
1.17
7.26
7.24
0.94
7.29
7.27
7.25
7.23
7.21
7.19
1.12
0.94
1.19
1.16
1.00
2.19
2.12
2.22
2.37
3.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

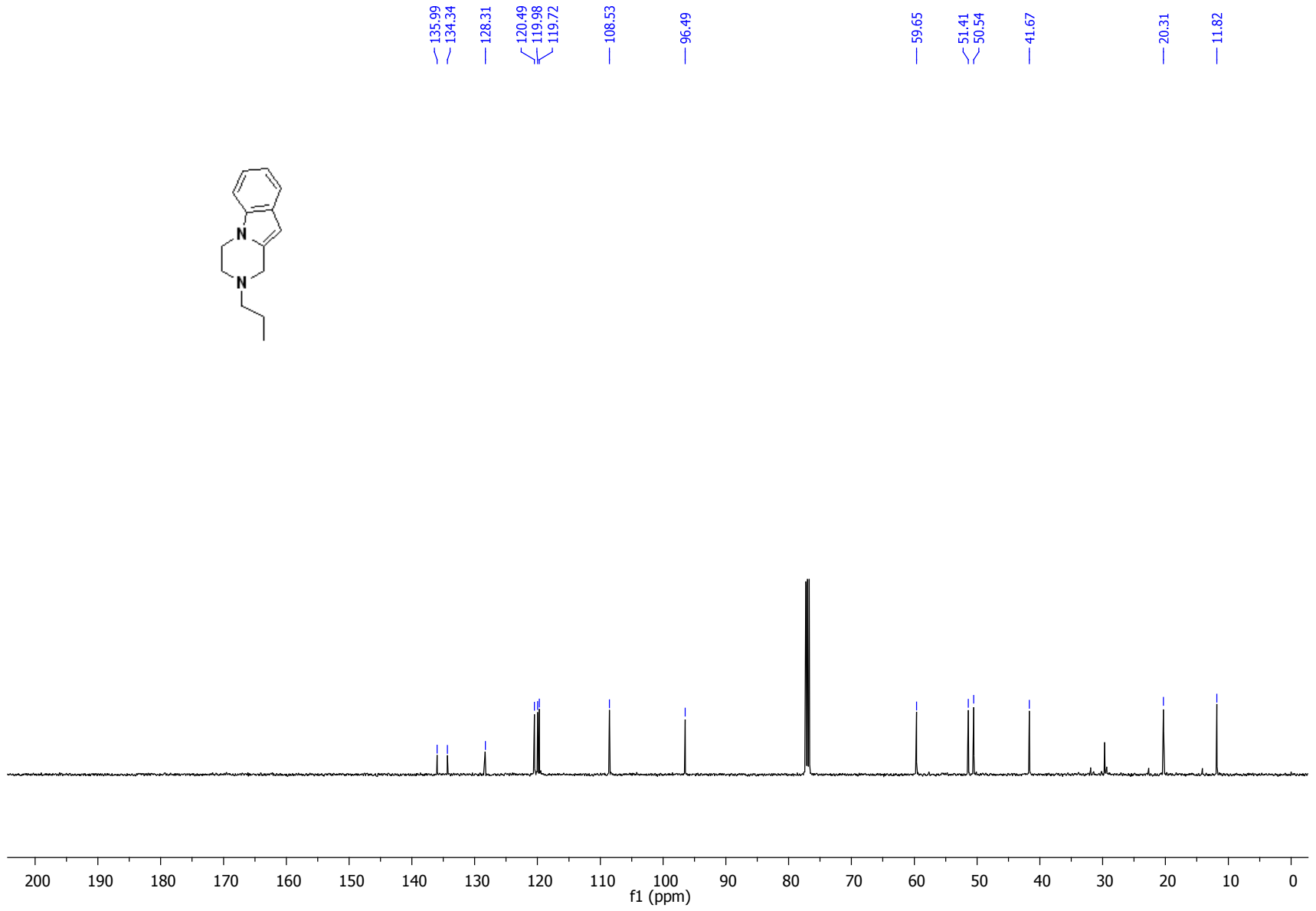
$^{13}$C NMR of **2b**


135.99
134.32
128.33
120.48
119.98
119.70
108.53
96.50
51.70
51.05
50.26
41.68
12.35
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

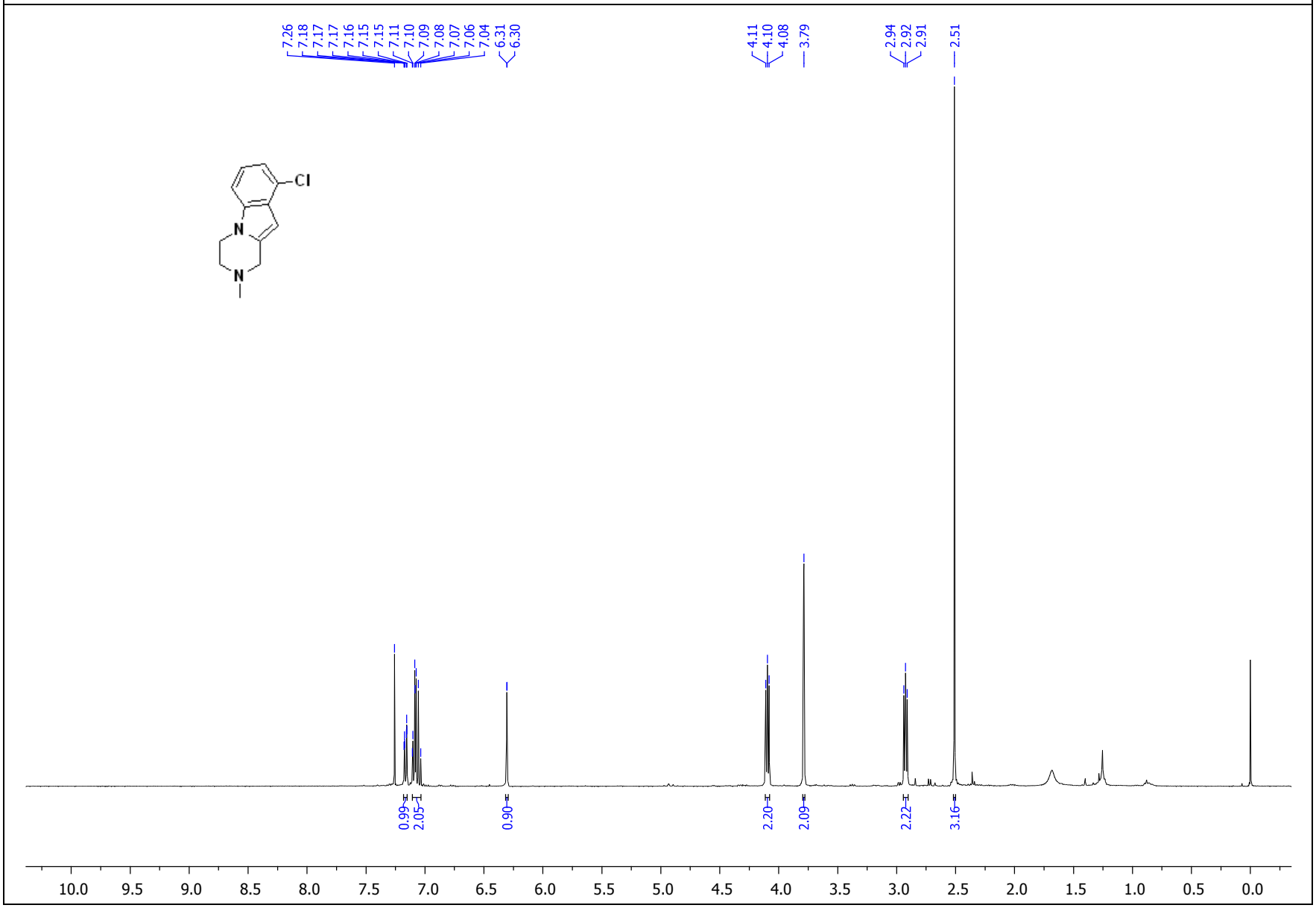
$^{1}$H NMR of **2c**


7.54
7.52
7.26
7.24
7.24
7.14
7.13
7.09
7.09
7.07
7.07
6.19
4.09
4.08
4.06
3.82
2.97
2.96
2.95
2.53
2.52
2.51
2.50
1.66
1.64
1.62
1.60
1.58
1.57
0.97
0.96
0.94
7.26
7.24
7.24
0.83
7.27
7.26
7.25
7.24
7.23
7.22
f1 (ppm)
N
N
0.98
0.83
1.06
1.01
0.89
2.11
2.00
2.08
2.14
2.25
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

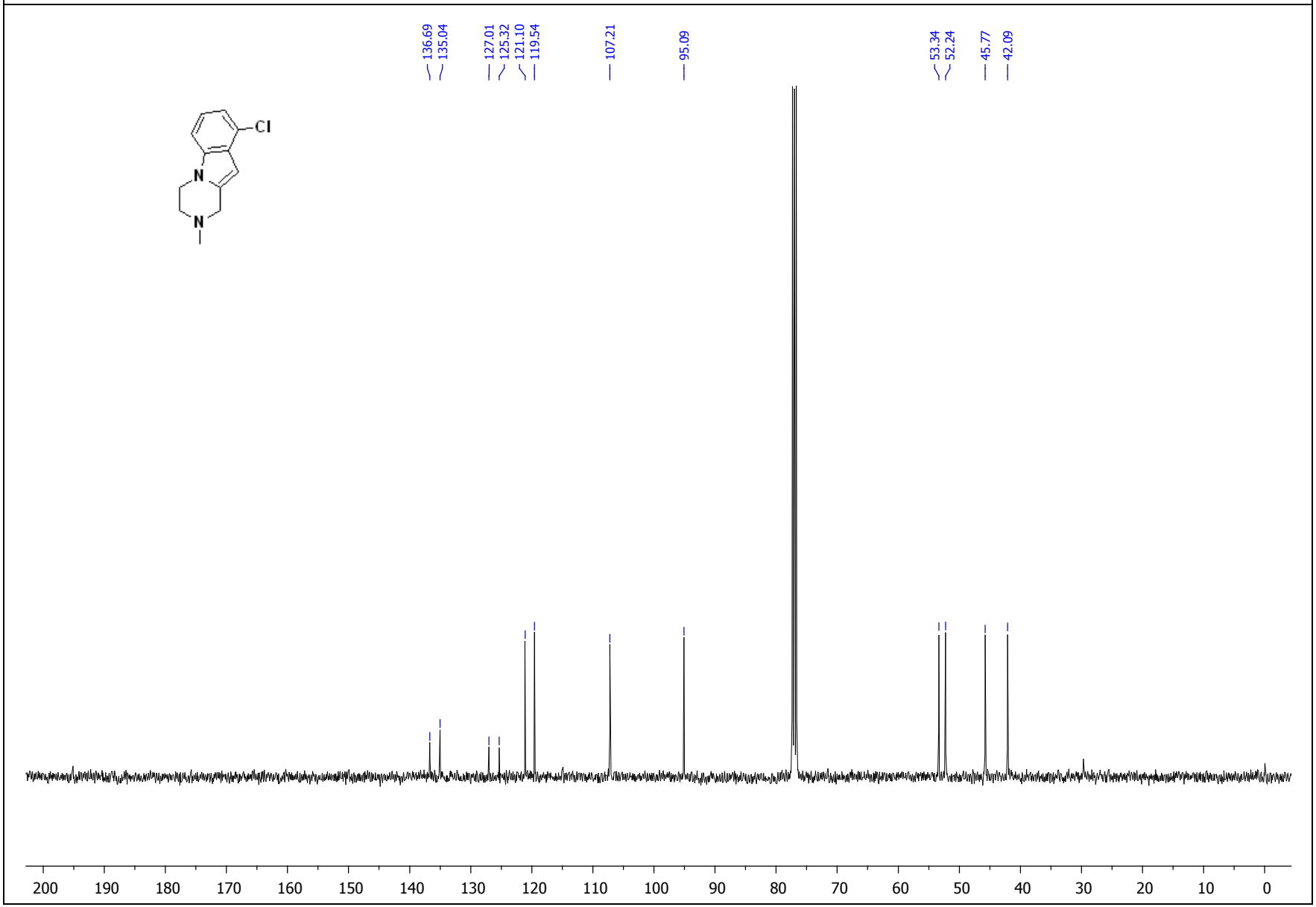
$^{13}$C NMR of **2c**


135.99
134.34
128.31
120.49
119.98
119.72
108.53
96.49
59.65
51.41
50.54
41.67
20.31
11.82
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

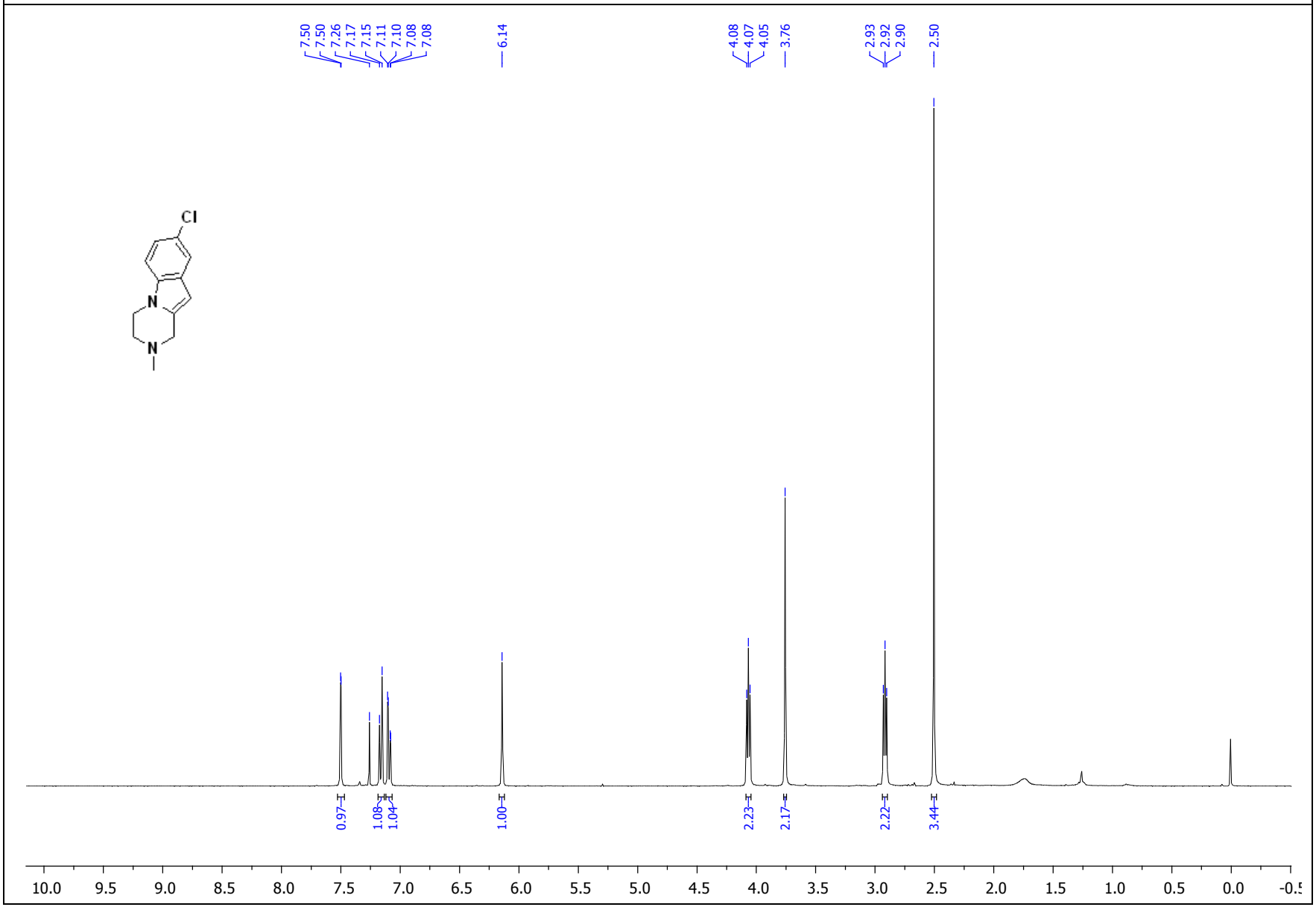
$^{1}$H NMR of **2d**


7.26
7.18
7.17
7.17
7.16
7.15
7.15
7.11
7.10
7.09
7.08
7.07
7.06
7.04
6.31
6.30
4.11
4.10
4.08
3.79
2.94
2.92
2.91
2.51
Cl
N
N
0.99
2.05
0.90
2.20
2.09
2.22
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

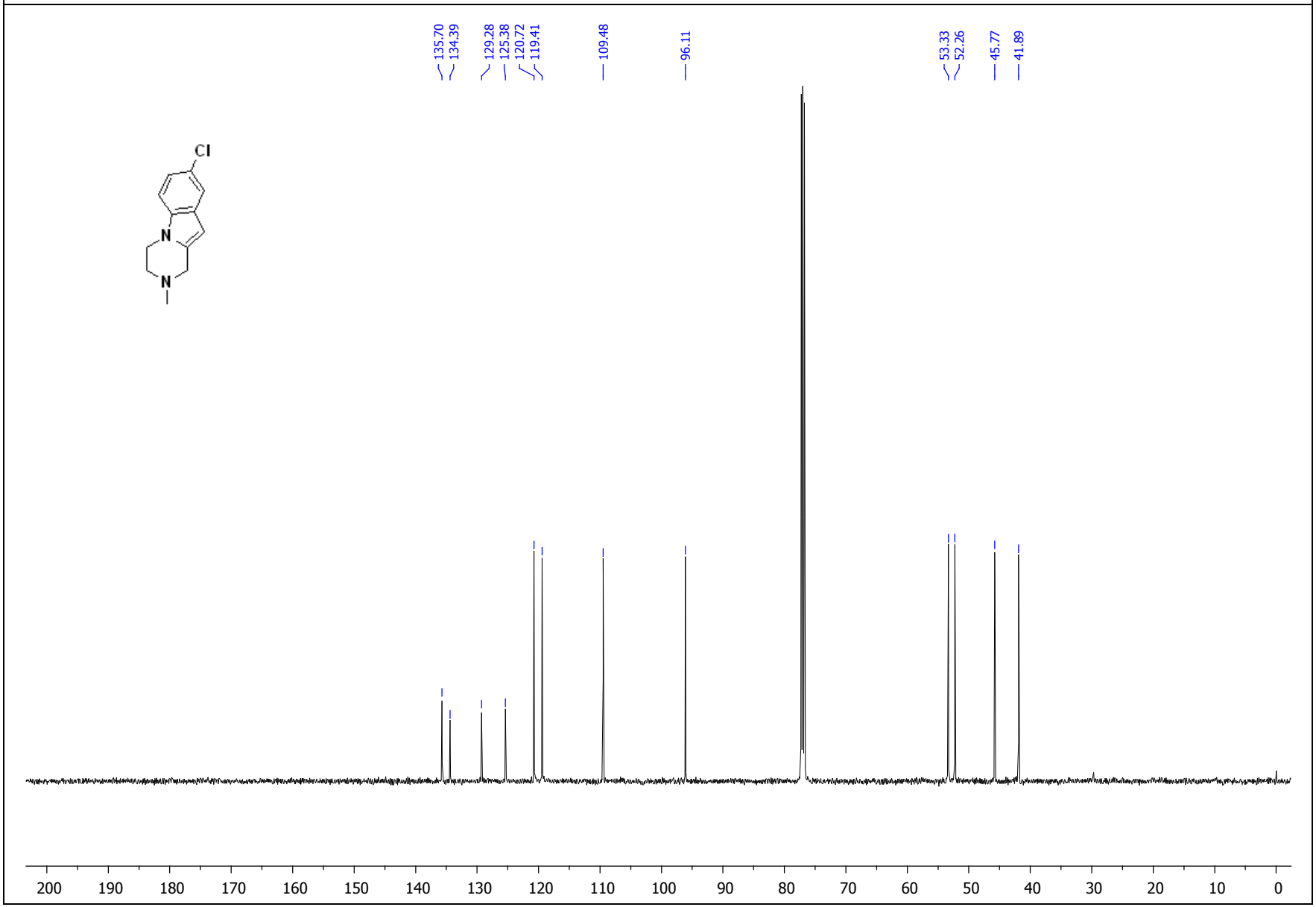
$^{13}$C NMR of **2d**


136.69
135.04
127.01
125.32
121.10
119.54
107.21
95.09
53.34
52.24
45.77
42.09
Cl
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

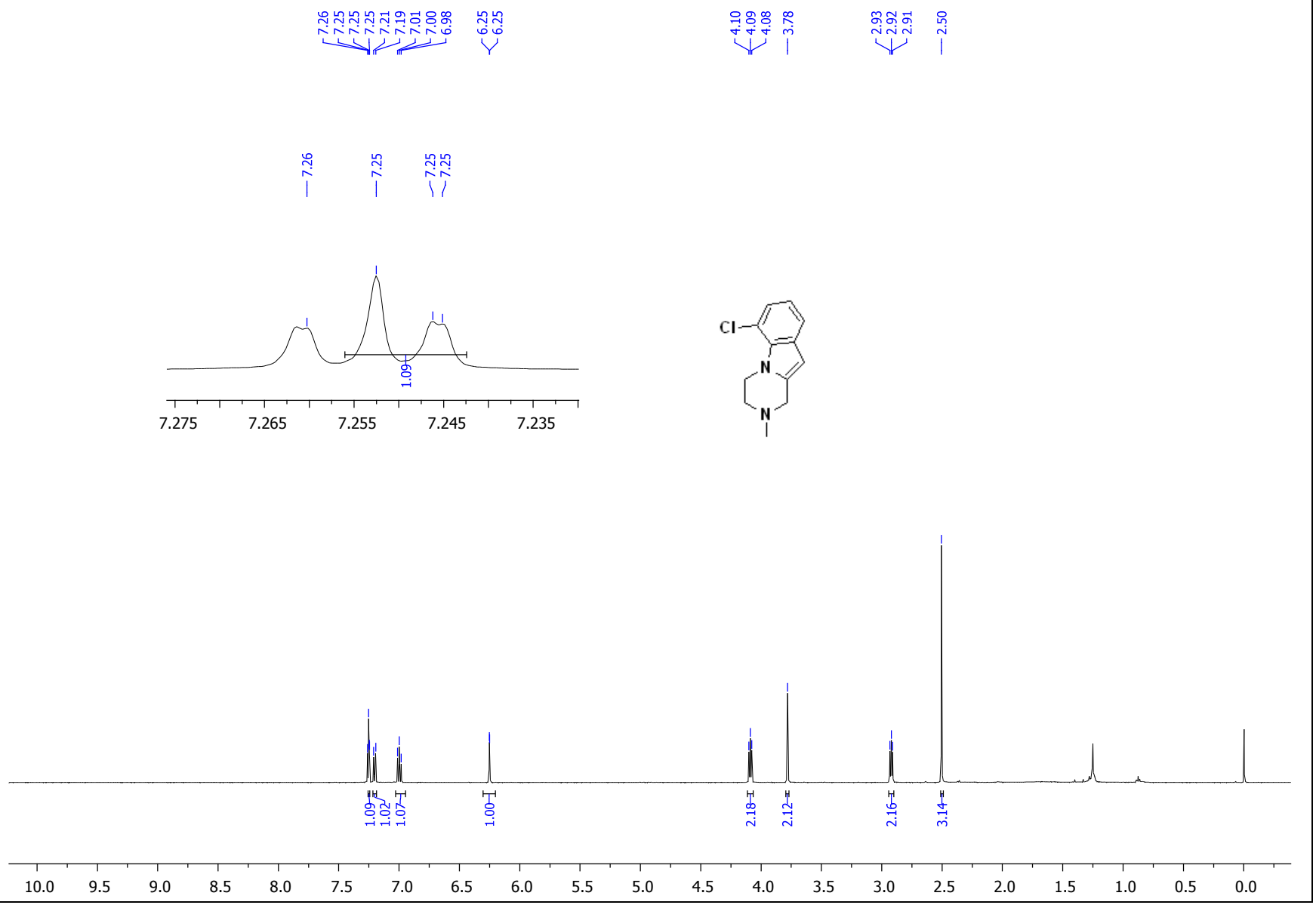
$^{1}$H NMR of **2e**


7.50
7.50
7.26
7.17
7.15
7.11
7.10
7.08
7.08
6.14
4.08
4.07
4.05
3.76
2.93
2.92
2.90
2.50
Cl
N
N
0.97
1.08
1.04
1.00
2.23
2.17
2.22
3.44
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

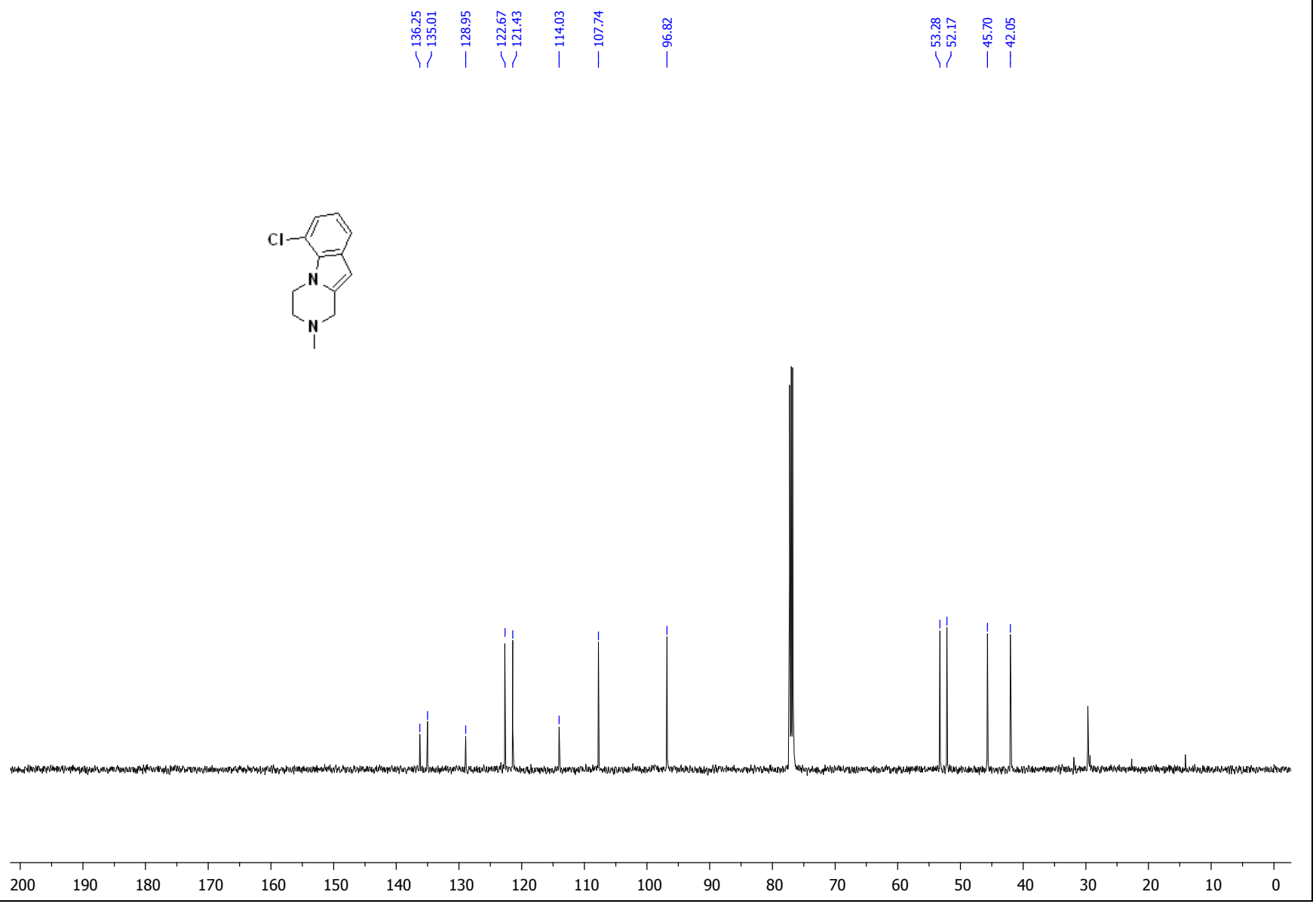
$^{13}$C NMR of **2e**


135.70
134.39
129.28
125.38
120.72
119.41
109.48
96.11
53.33
52.26
45.77
41.89
Cl
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

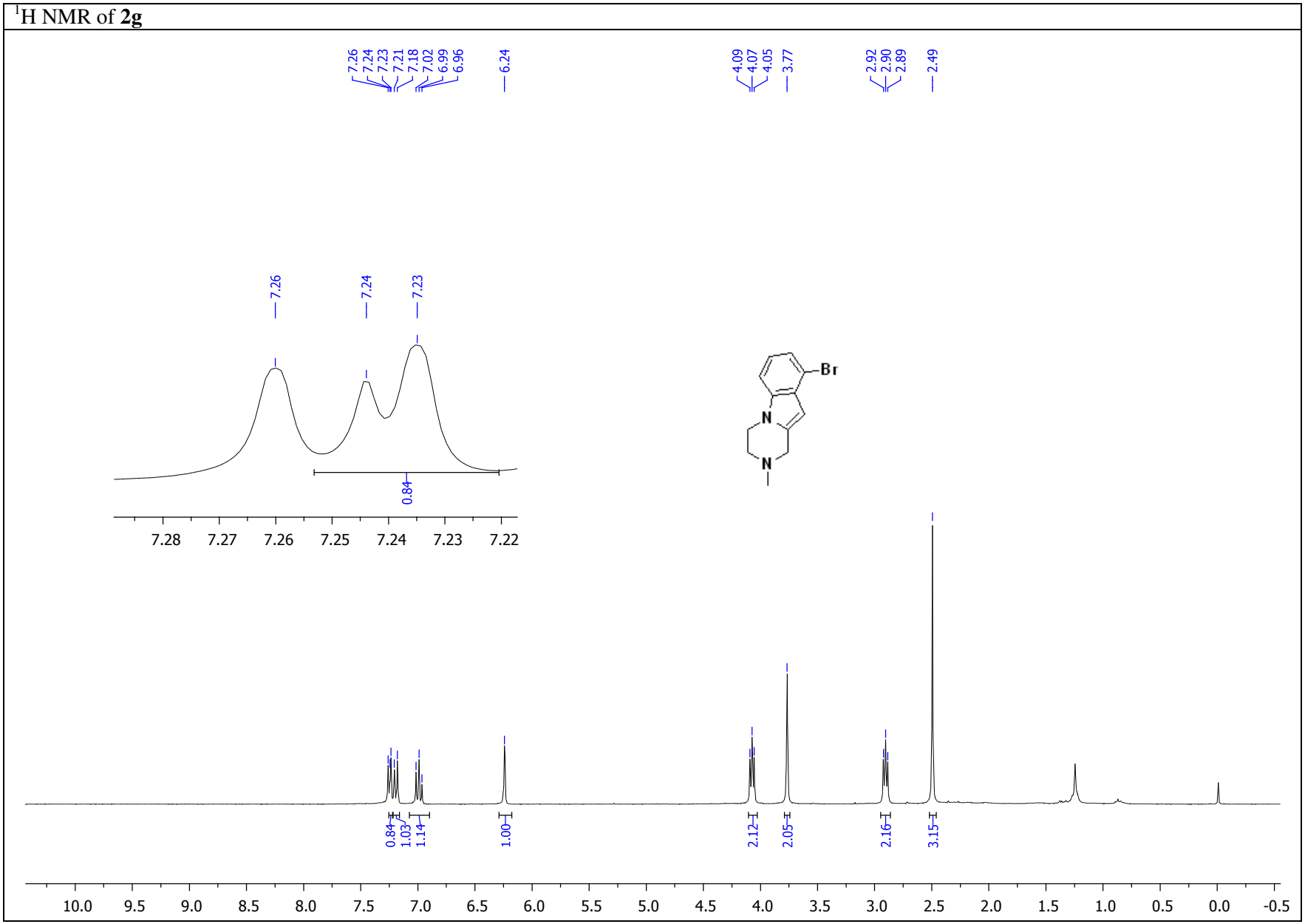
[1]H NMR of **2f**


7.26
7.25
7.25
7.25
7.21
7.19
7.01
7.00
6.98
6.25
6.25
4.10
4.09
4.08
3.78
2.93
2.92
2.91
2.50
7.26
7.25
7.25
7.25
1.09
7.275
7.265
7.255
7.245
7.235
Cl
N
N
1.09
1.02
1.07
1.00
2.18
2.12
2.16
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

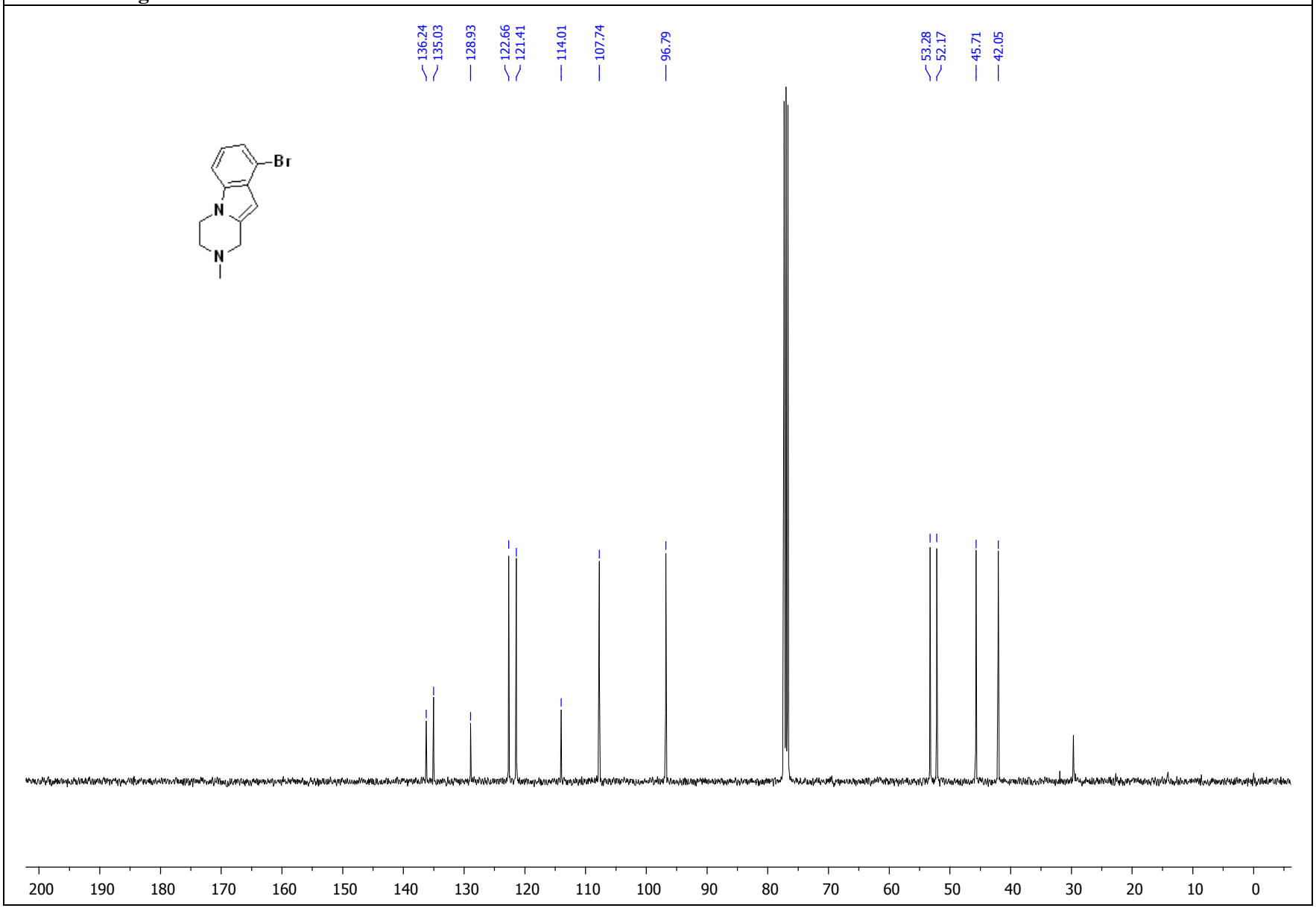
$^{13}$C NMR of **2f**


136.25
135.01
128.95
122.67
121.43
114.03
107.74
96.82
53.28
52.17
45.70
42.05
Cl
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

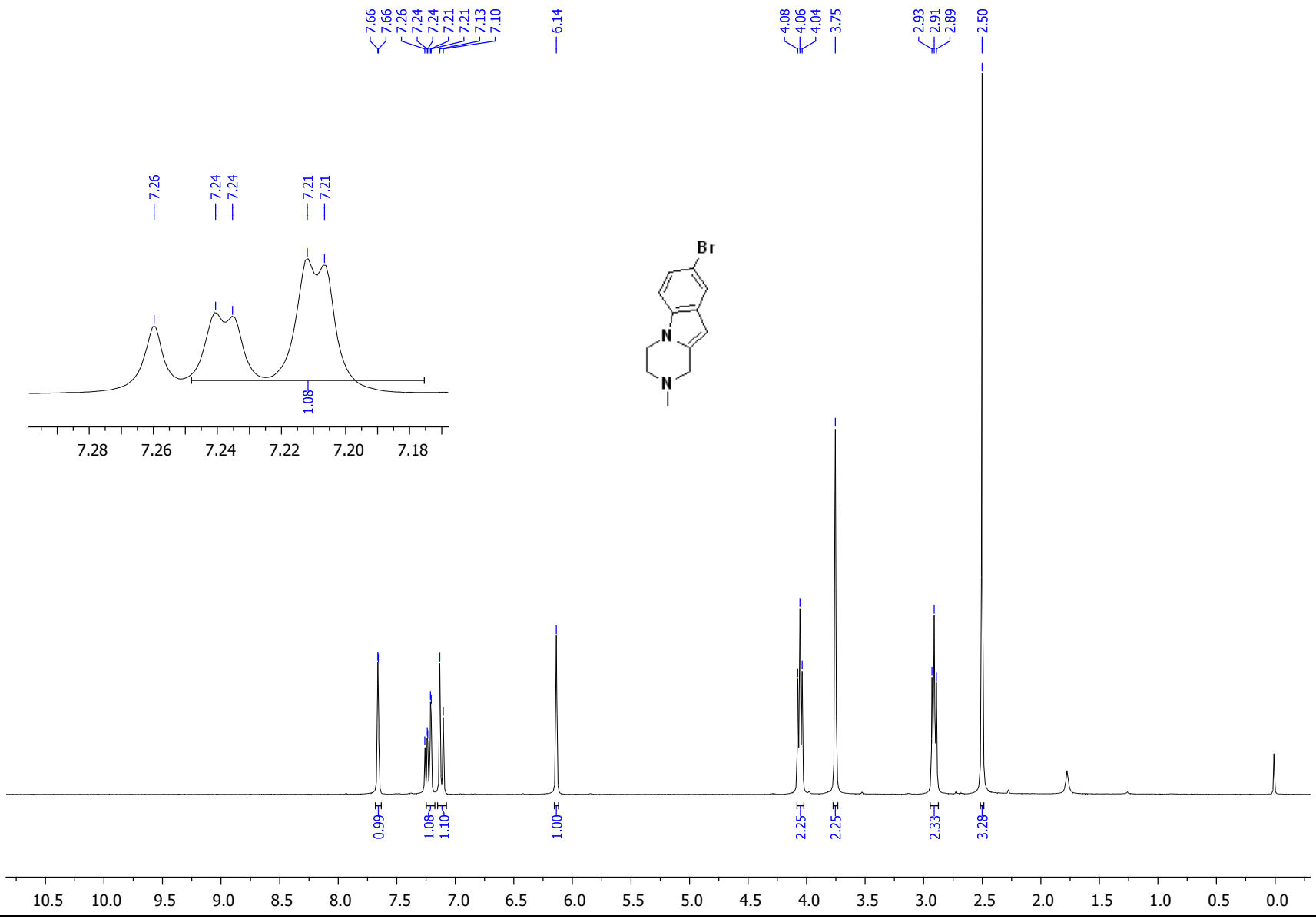
$^{1}$H NMR of **2g**


7.26
7.24
7.23
7.21
7.18
7.02
6.99
6.96
6.24
4.09
4.07
4.05
3.77
2.92
2.90
2.89
2.49
Br
N
N
0.84
1.03
1.14
1.00
2.12
2.05
2.16
3.15

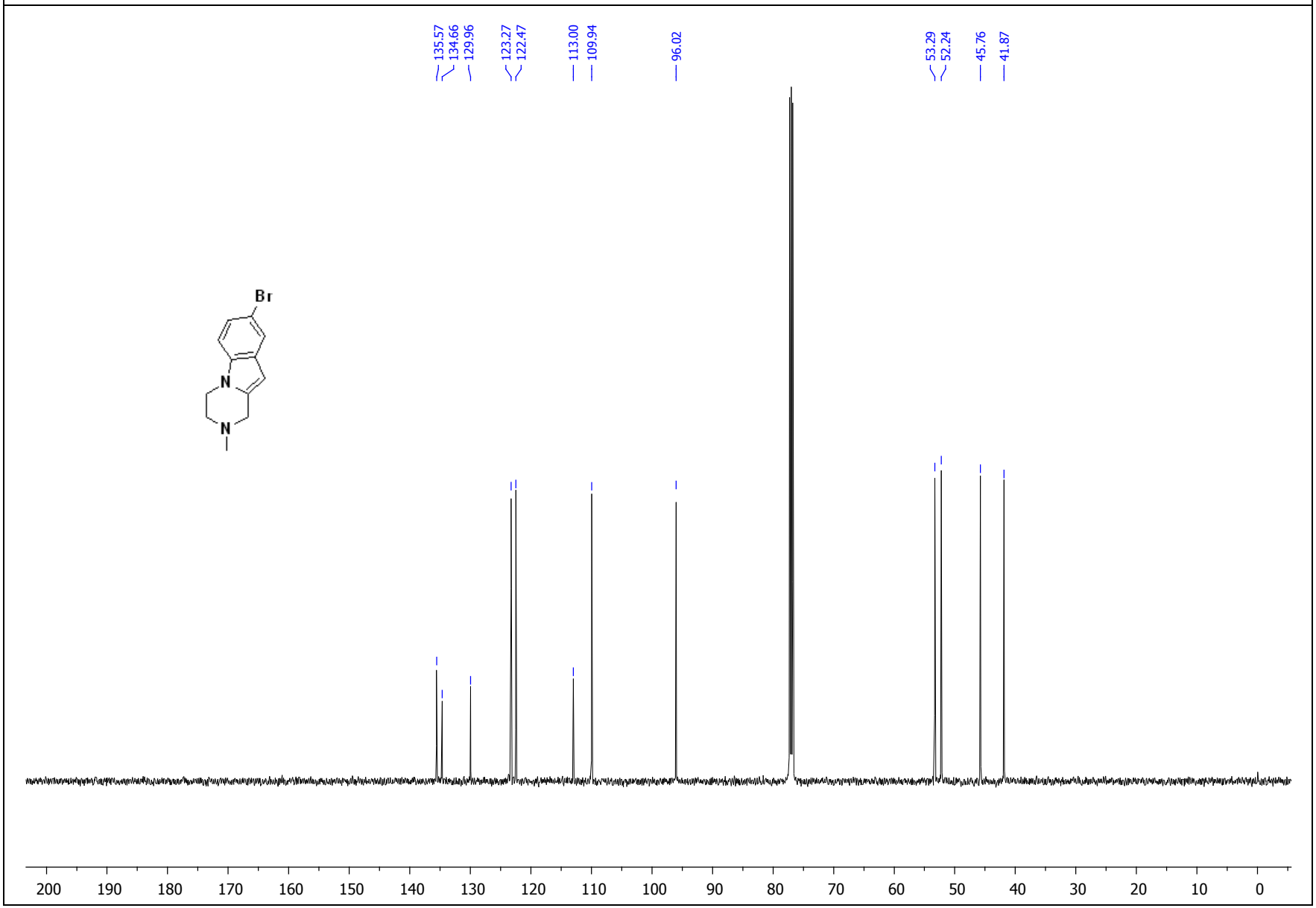
$^{13}$C NMR of **2g**


136.24
135.03
128.93
122.66
121.41
114.01
107.74
96.79
53.28
52.17
45.71
42.05
Br
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

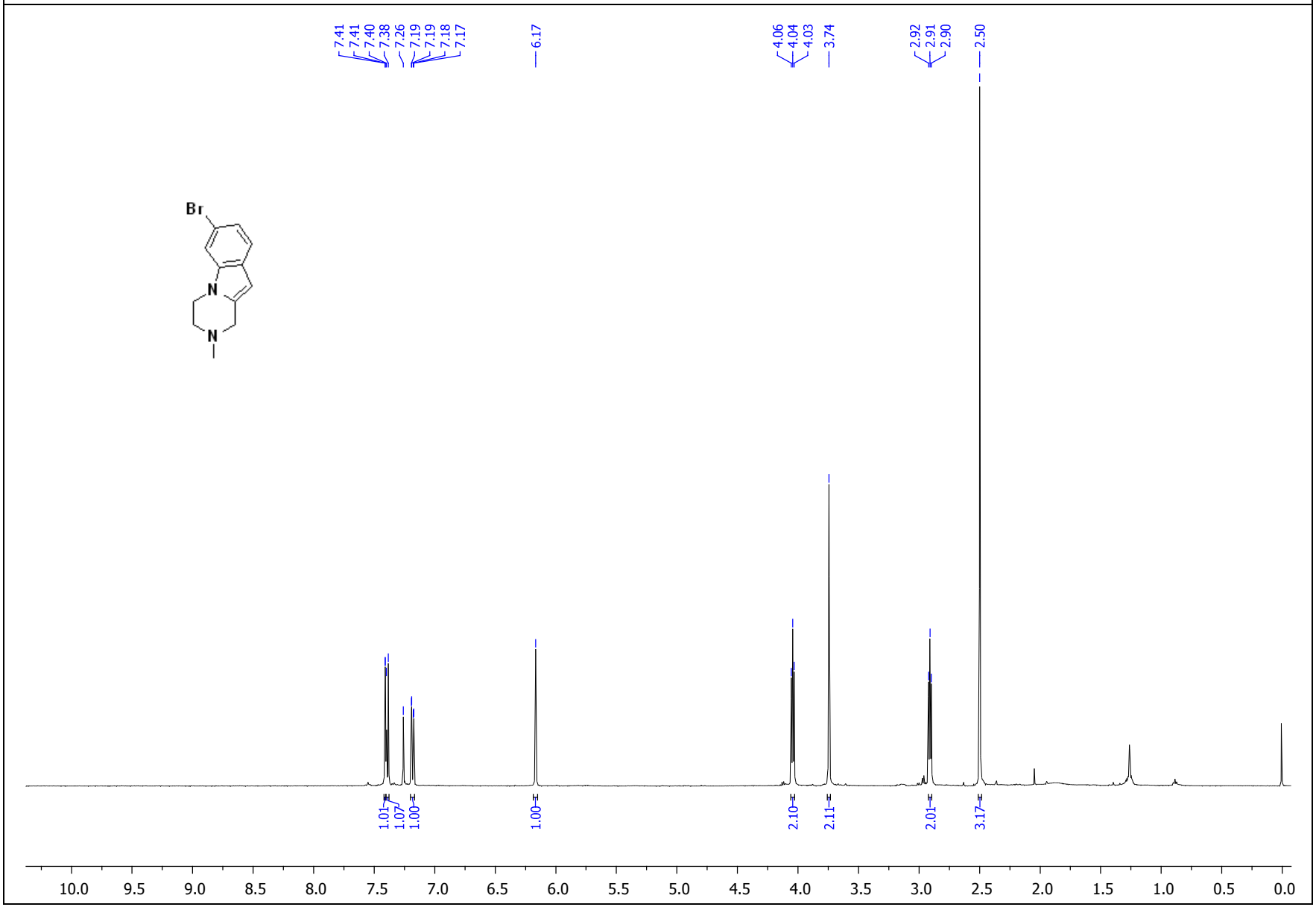
[1]H NMR of **2h**


7.66
7.66
7.26
7.24
7.24
7.21
7.21
7.13
7.10
6.14
4.08
4.06
4.04
3.75
2.93
2.91
2.89
2.50
7.26
7.24
7.24
7.21
7.21
1.08
7.28
7.26
7.24
7.22
7.20
7.18
Br
N
N
0.99
1.08
1.10
1.00
2.25
2.25
2.33
3.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

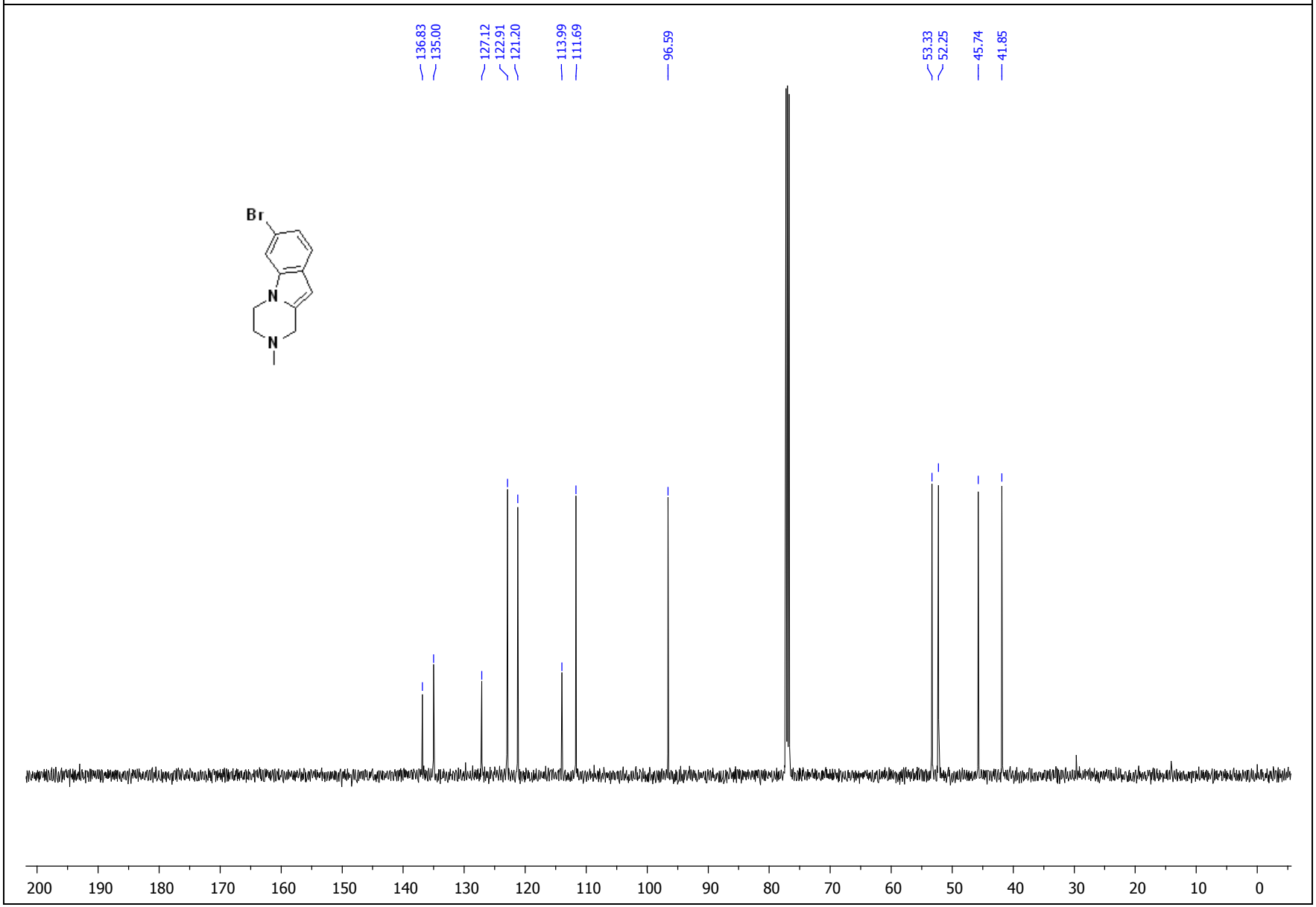
$^{13}$C NMR of **2h**


135.57
134.66
129.96
123.27
122.47
113.00
109.94
96.02
53.29
52.24
45.76
41.87
Br
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

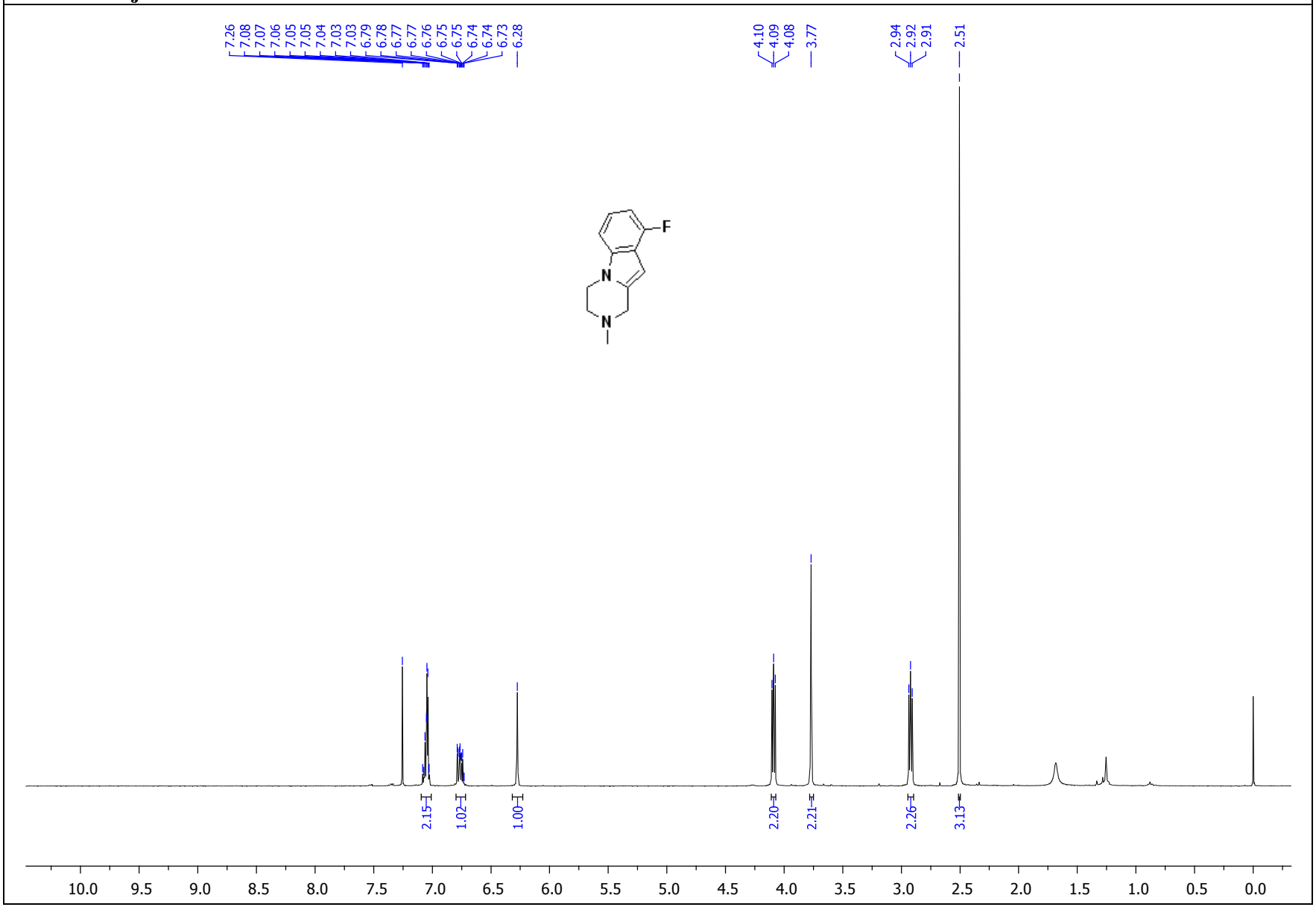
$^{1}$H NMR of **2i**


7.41
7.41
7.40
7.38
7.26
7.19
7.19
7.18
7.17
6.17
4.06
4.04
4.03
3.74
2.92
2.91
2.90
2.50
Br
N
N
1.01
1.07
1.00
1.00
2.10
2.11
2.01
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

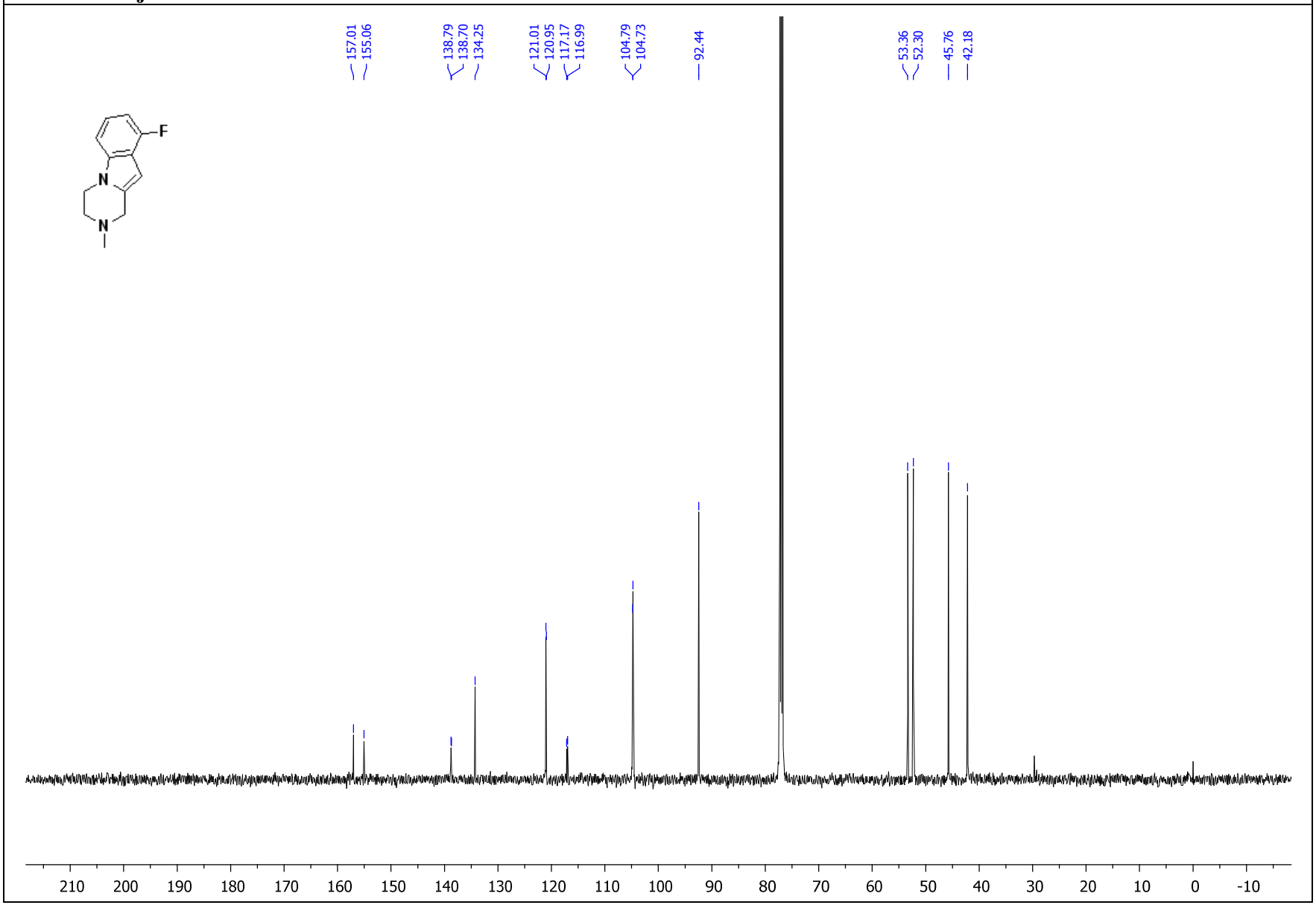
$^{13}$C NMR of **2i**


136.83
135.00
127.12
122.91
121.20
113.99
111.69
96.59
53.33
52.25
45.74
41.85
Br
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

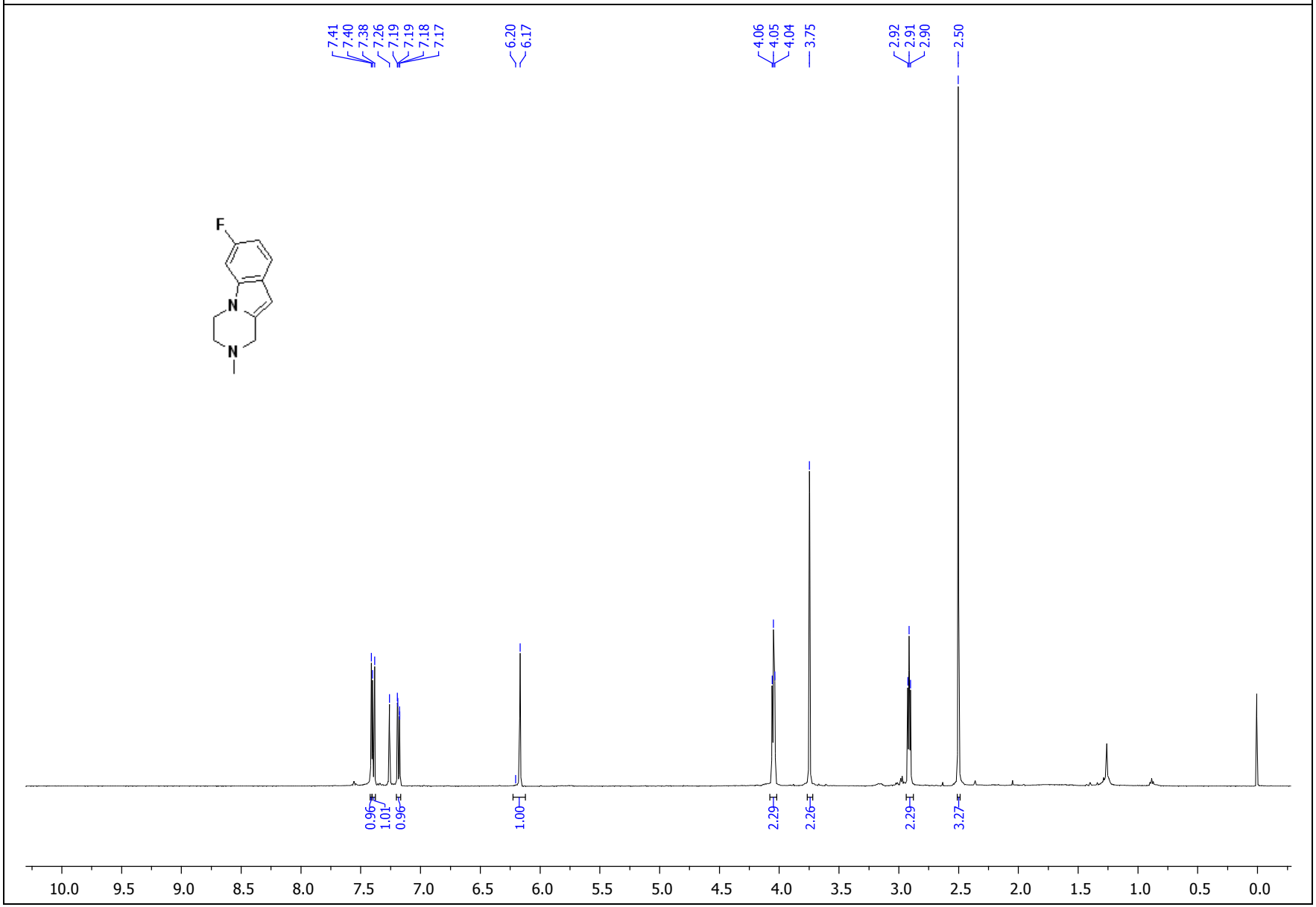
$^{1}$H NMR of **2j**


7.26
7.08
7.07
7.06
7.05
7.05
7.04
7.03
7.03
6.79
6.78
6.77
6.77
6.76
6.75
6.75
6.74
6.74
6.73
6.28
4.10
4.09
4.08
3.77
2.94
2.92
2.91
2.51
F
N
N
2.15
1.02
1.00
2.20
2.21
2.26
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

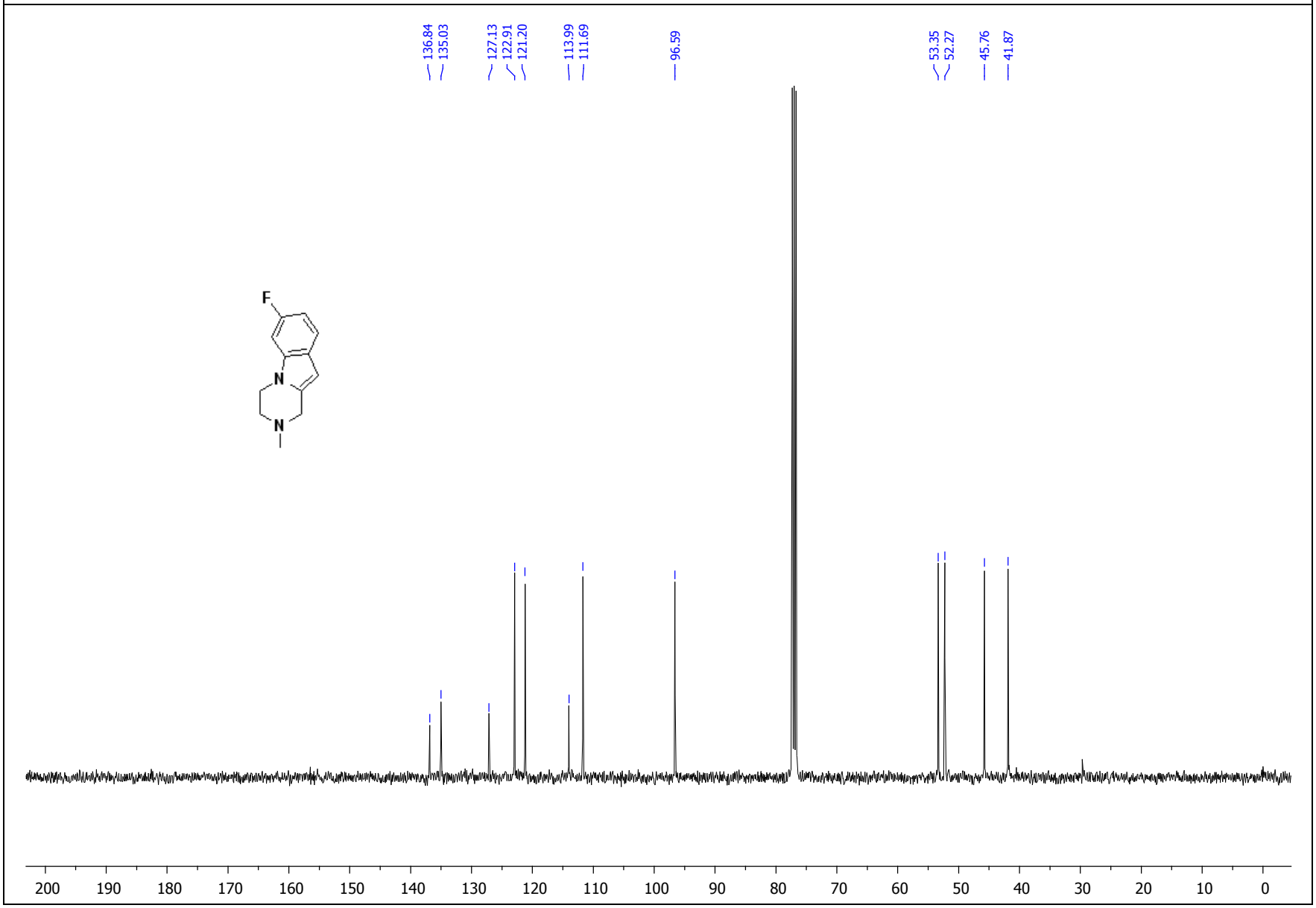
$^{13}$C NMR of **2j**


157.01
155.06
138.79
138.70
134.25
121.01
120.95
117.17
116.99
104.79
104.73
92.44
53.36
52.30
45.76
42.18
F
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

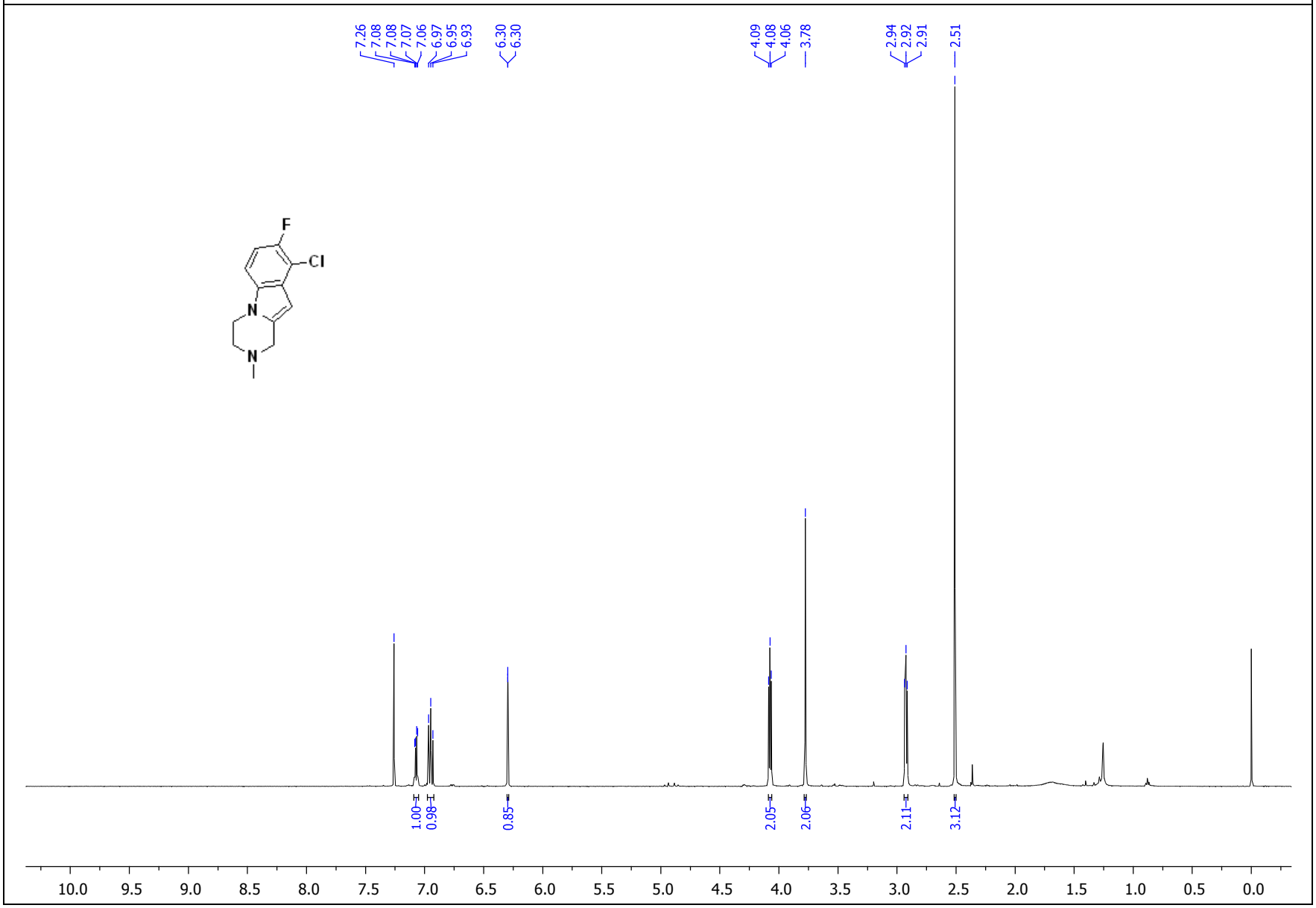
$^{1}$H NMR of **2k**


7.41
7.40
7.38
7.26
7.19
7.19
7.18
7.17
6.20
6.17
4.06
4.05
4.04
3.75
2.92
2.91
2.90
2.50
F
N
N
0.96
1.01
0.96
1.00
2.29
2.26
2.29
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

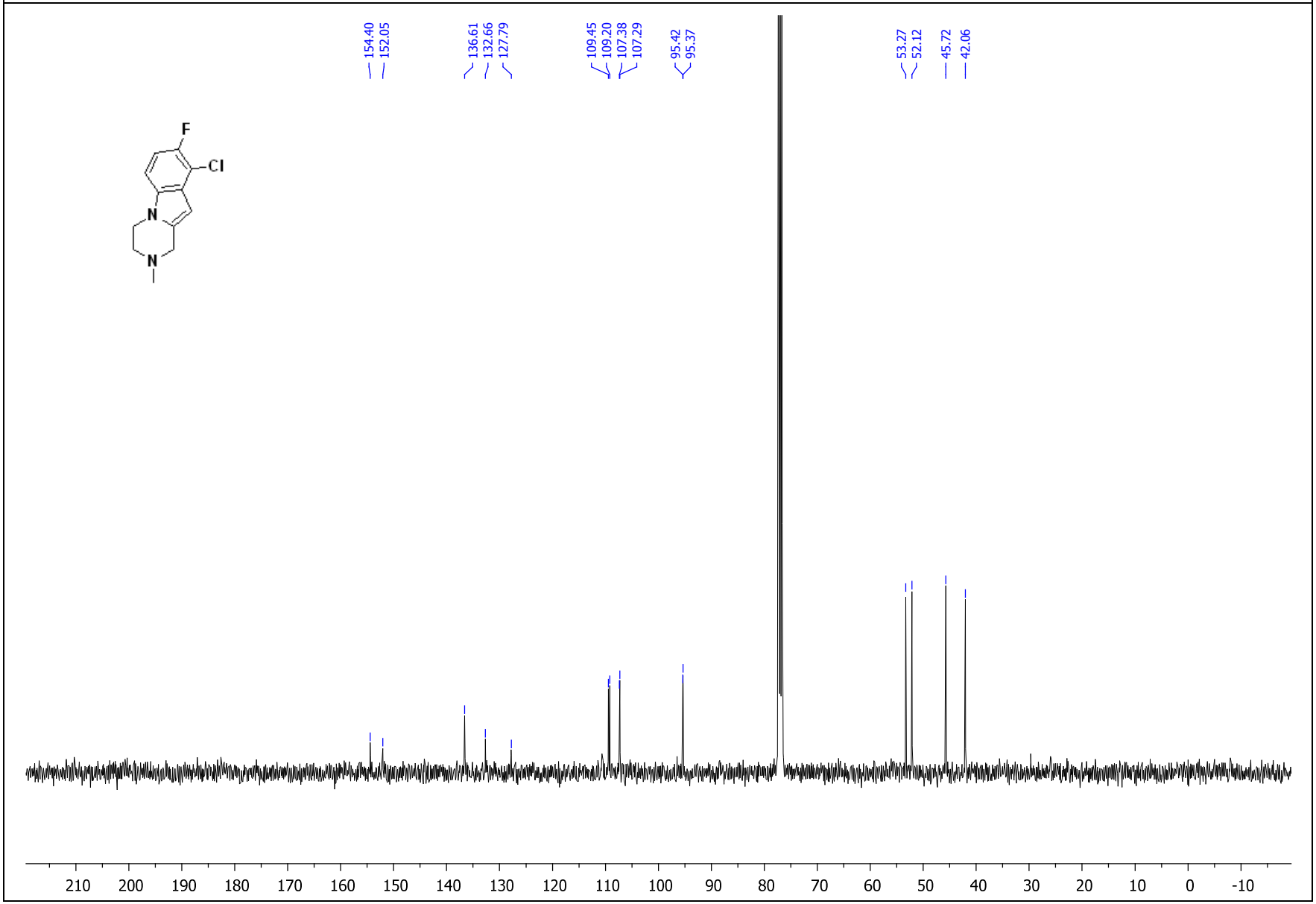
$^{13}$C NMR of **2k**


136.84
135.03
127.13
122.91
121.20
113.99
111.69
96.59
53.35
52.27
45.76
41.87
F
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

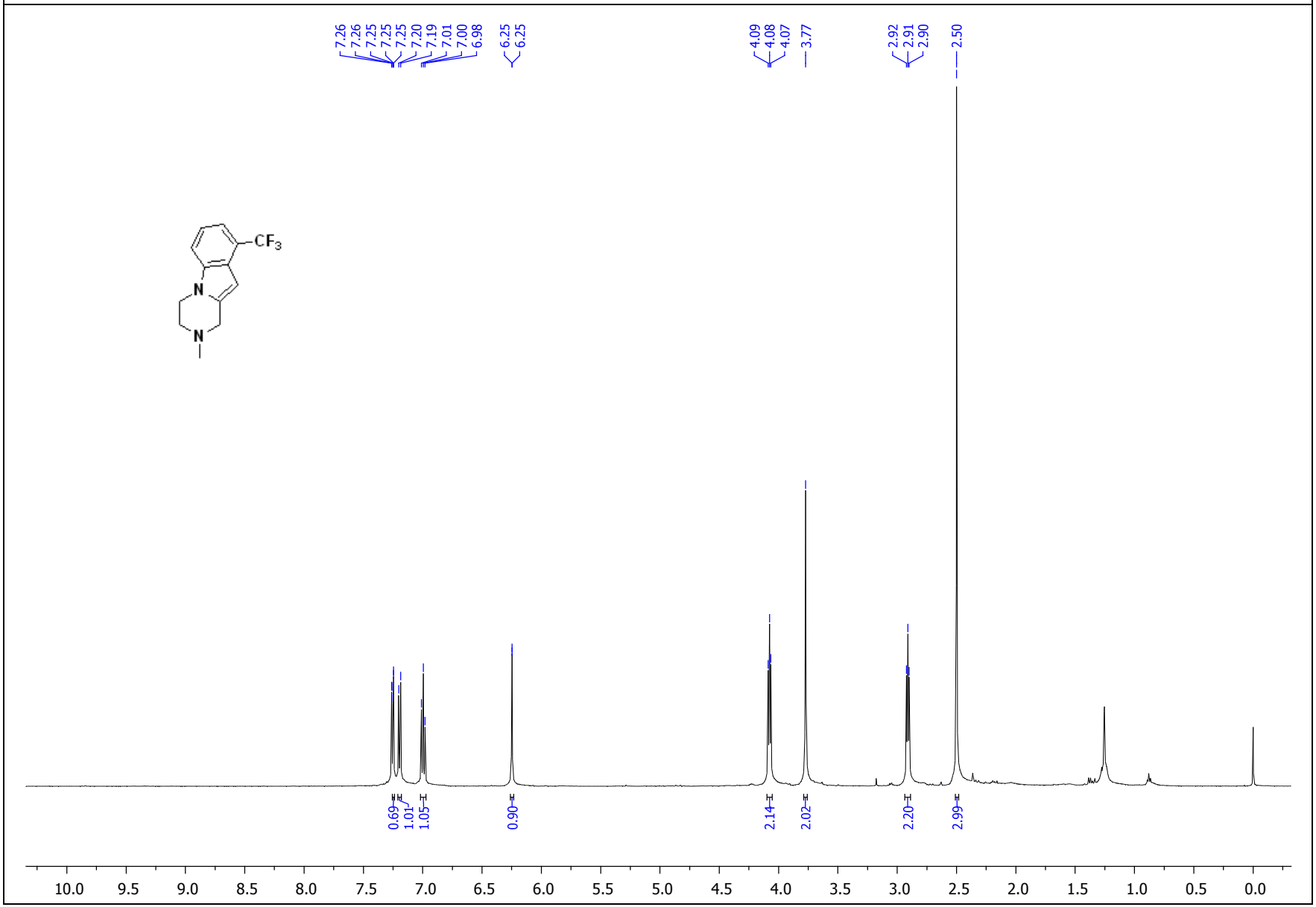
$^{1}$H NMR of **2l**


7.26
7.08
7.08
7.07
7.06
6.97
6.95
6.93
6.30
6.30
4.09
4.08
4.06
3.78
2.94
2.92
2.91
2.51
F
Cl
N
N
1.00
0.98
0.85
2.05
2.06
2.11
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

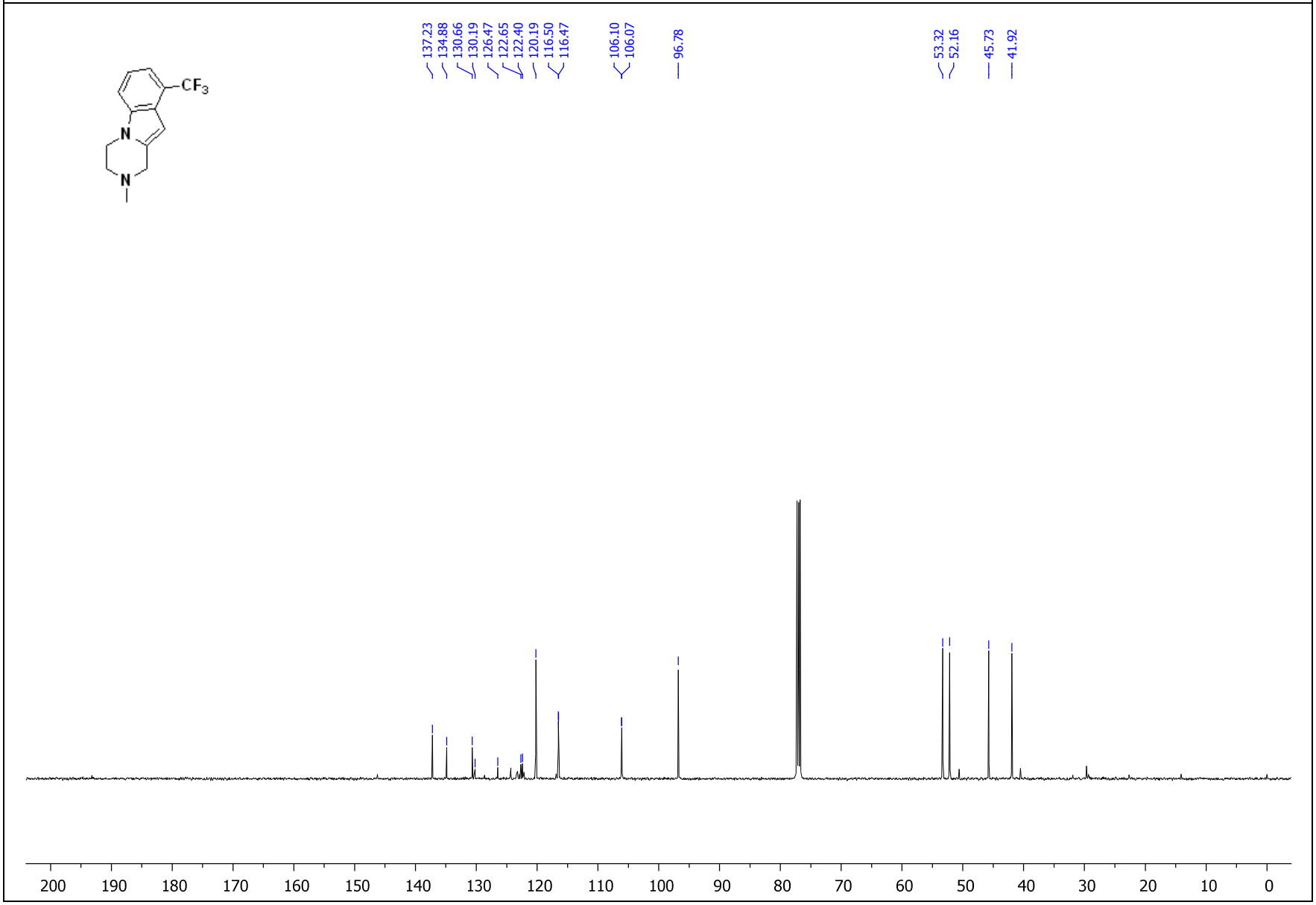
$^{13}$C NMR of **2l**


154.40
152.05
136.61
132.66
127.79
109.45
109.20
107.38
107.29
95.42
95.37
53.27
52.12
45.72
42.06
F
Cl
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

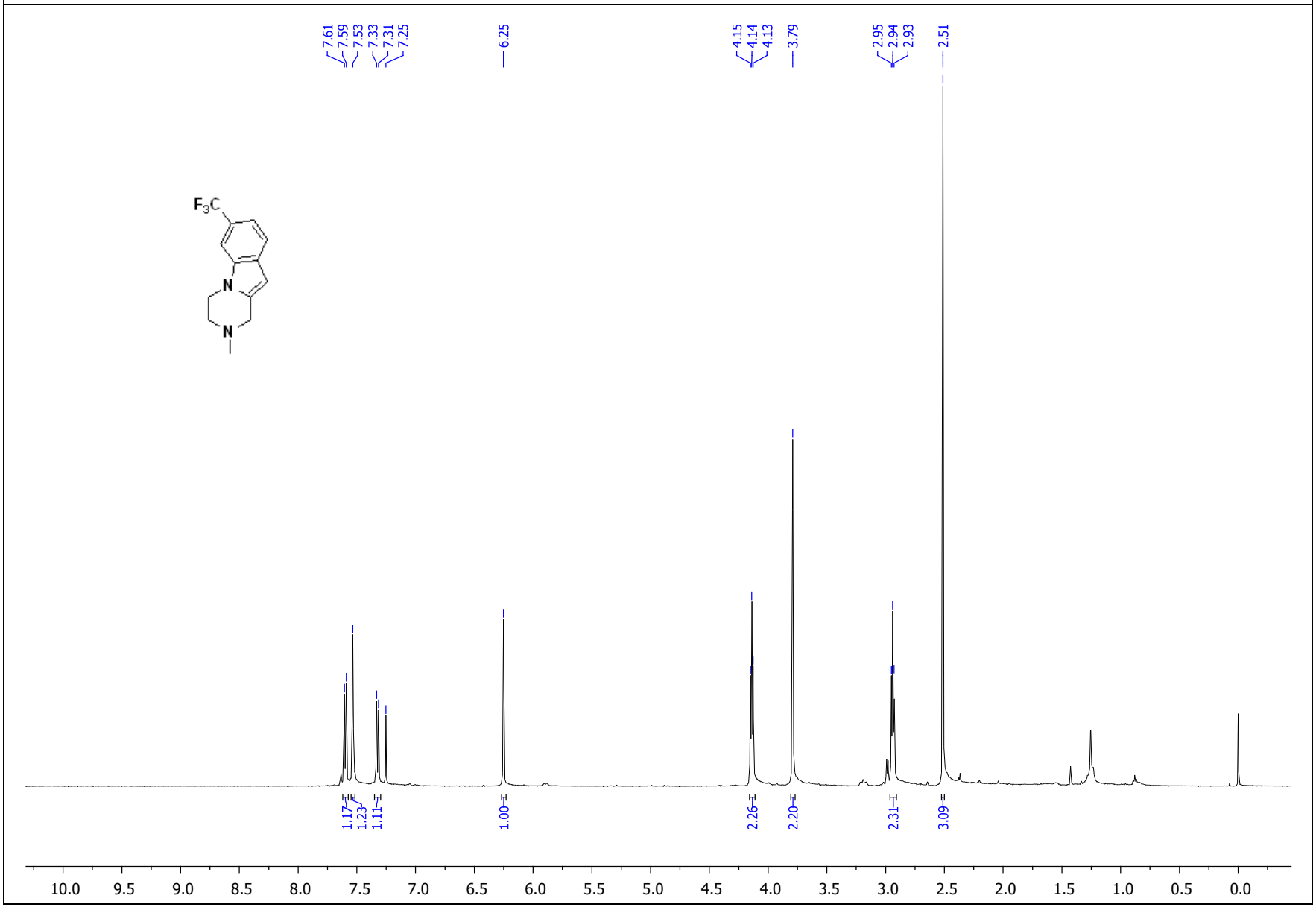
$^{1}$H NMR of **2m**


7.26
7.26
7.25
7.25
7.25
7.20
7.19
7.01
7.00
6.98
6.25
6.25
4.09
4.08
4.07
3.77
2.92
2.91
2.90
2.50
CF3
N
N
0.69
1.01
1.05
0.90
2.14
2.02
2.20
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

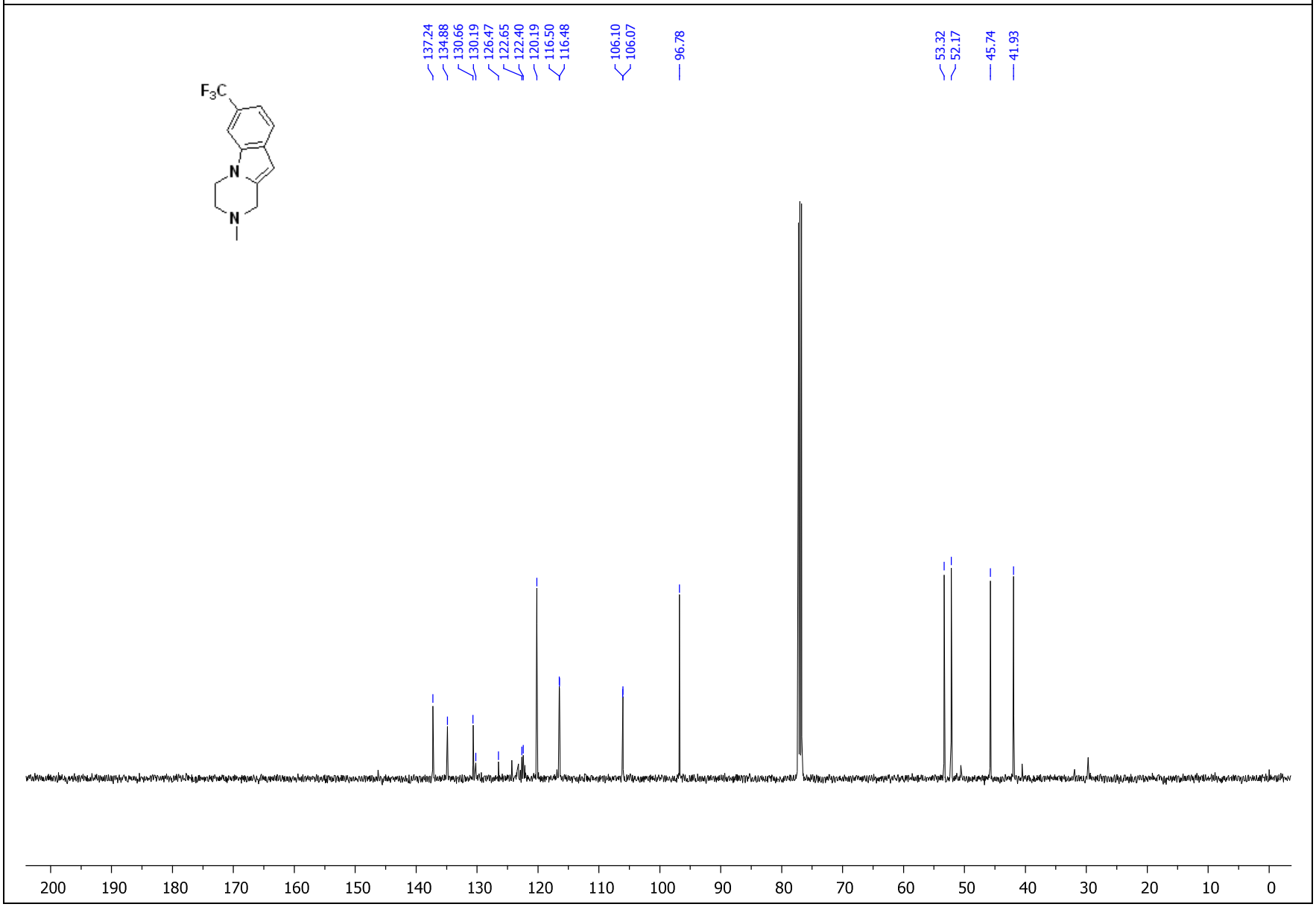
$^{13}$C NMR of **2m**


137.23
134.88
130.66
130.19
126.47
122.65
122.40
120.19
116.50
116.47
106.10
106.07
96.78
53.32
52.16
45.73
41.92
CF3
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

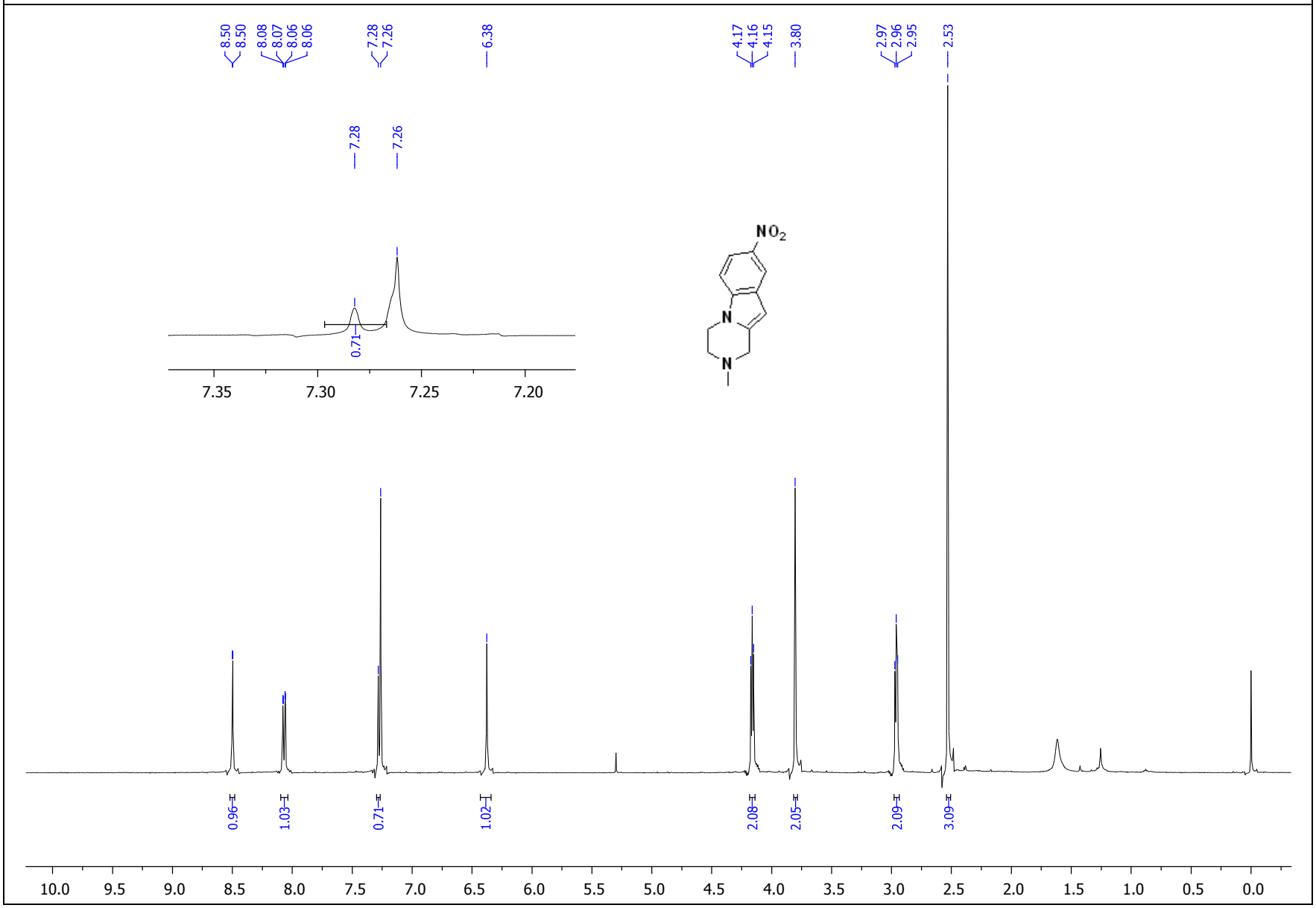
$^{1}$H NMR of **2n**


7.61
7.59
7.53
7.33
7.31
7.25
6.25
4.15
4.14
4.13
3.79
2.95
2.94
2.93
2.51
F3C
N
N
1.17
1.23
1.11
1.00
2.26
2.20
2.31
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

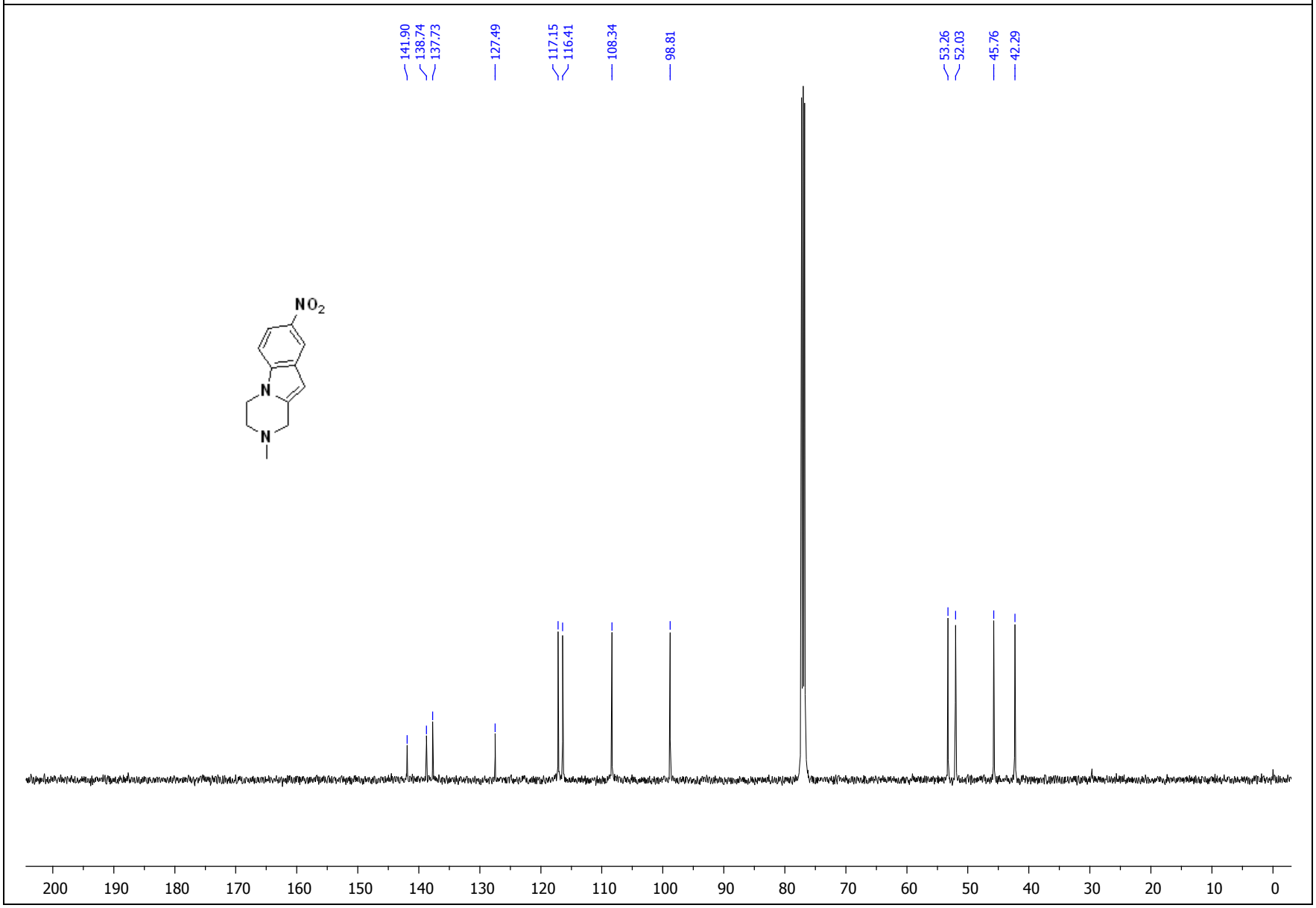
$^{13}$C NMR of **2n**


137.24
134.88
130.66
130.19
126.47
122.65
122.40
120.19
116.50
116.48
106.10
106.07
96.78
53.32
52.17
45.74
41.93
F3C
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

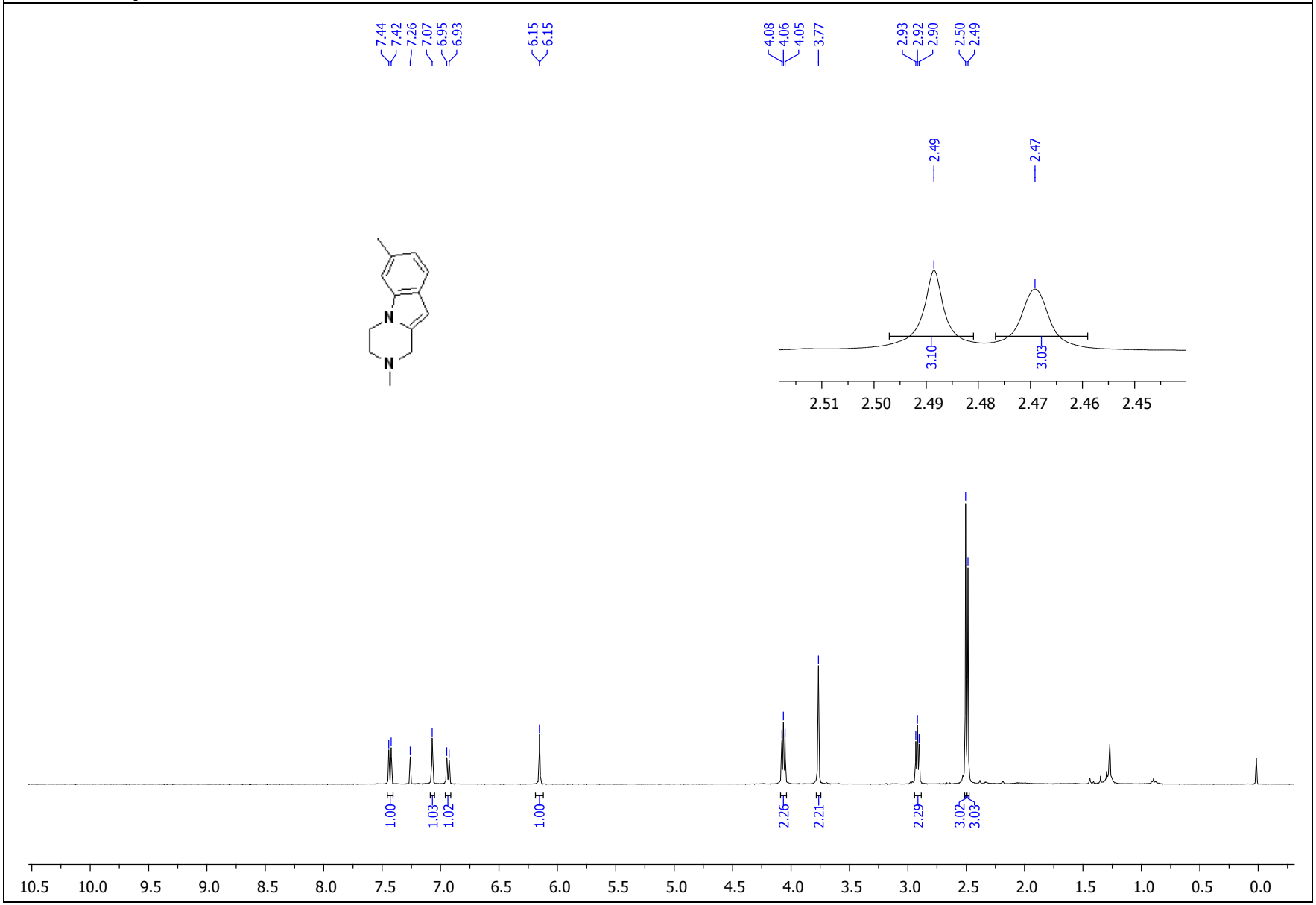
$^{1}$H NMR of **2o**


8.50
8.50
8.08
8.07
8.06
8.06
7.28
7.26
6.38
4.17
4.16
4.15
3.80
2.97
2.96
2.95
2.53
7.28
7.26
0.71
7.35
7.30
7.25
7.20
NO2
N
N
0.96
1.03
0.71
1.02
2.08
2.05
2.09
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

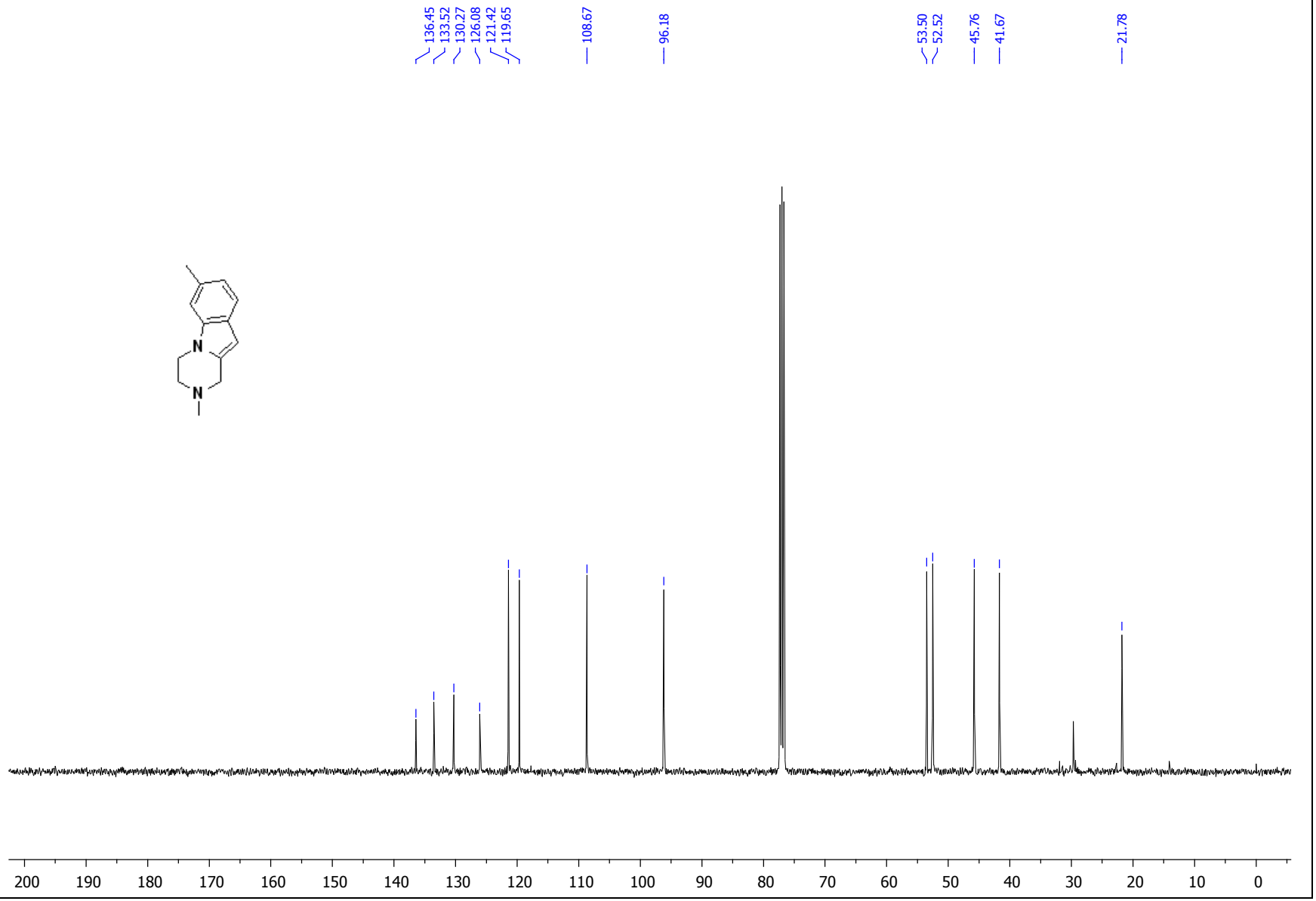
$^{13}$C NMR of **2o**


141.90
138.74
137.73
127.49
117.15
116.41
108.34
98.81
53.26
52.03
45.76
42.29
NO2
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

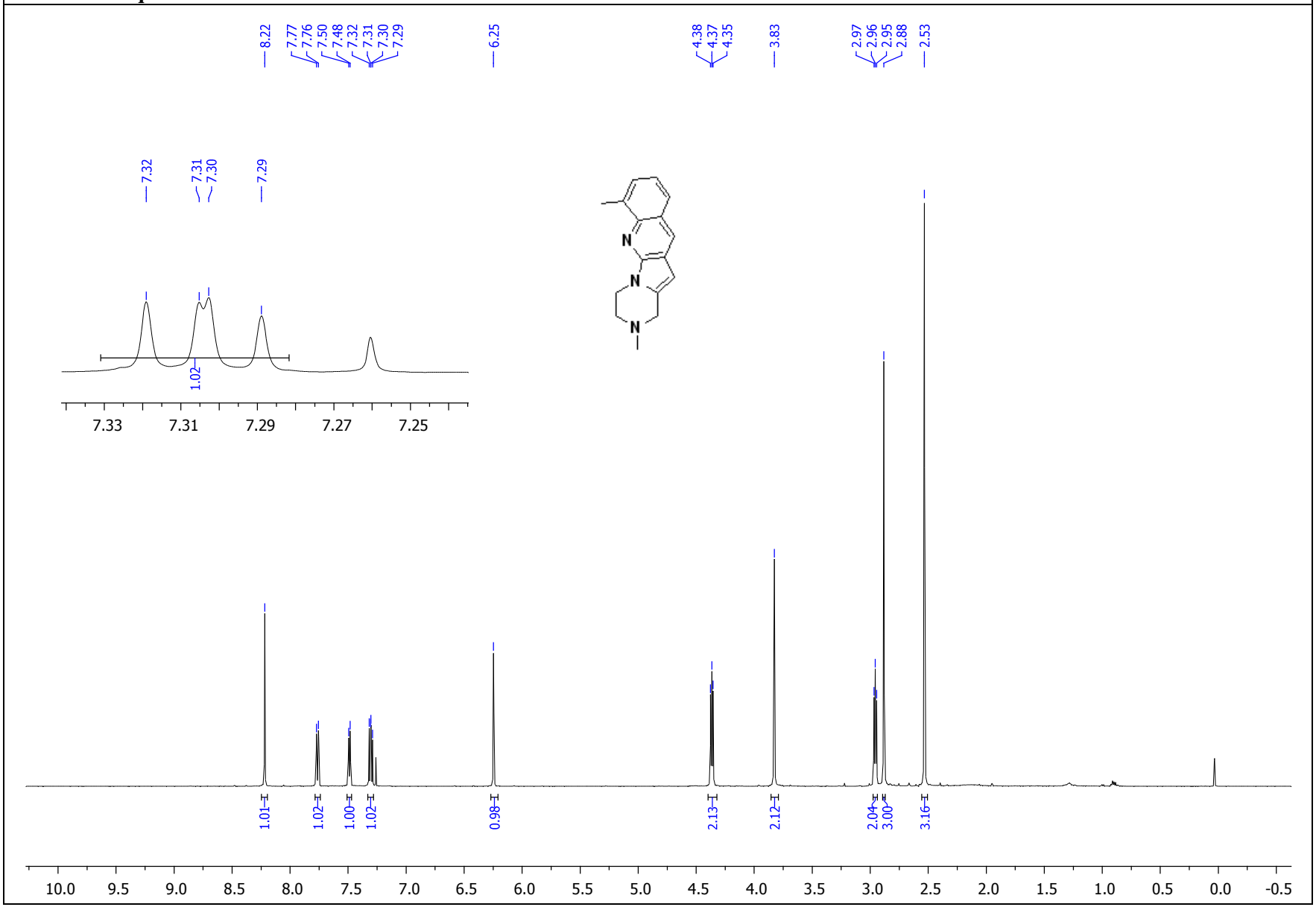
$^{1}$H NMR of **2p**


7.44
7.42
7.26
7.07
6.95
6.93
6.15
6.15
4.08
4.06
4.05
3.77
2.93
2.92
2.90
2.50
2.49
2.49
2.47
3.10
3.03
2.51 2.50 2.49 2.48 2.47 2.46 2.45
1.00
1.03
1.02
1.00
2.26
2.21
2.29
3.02
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

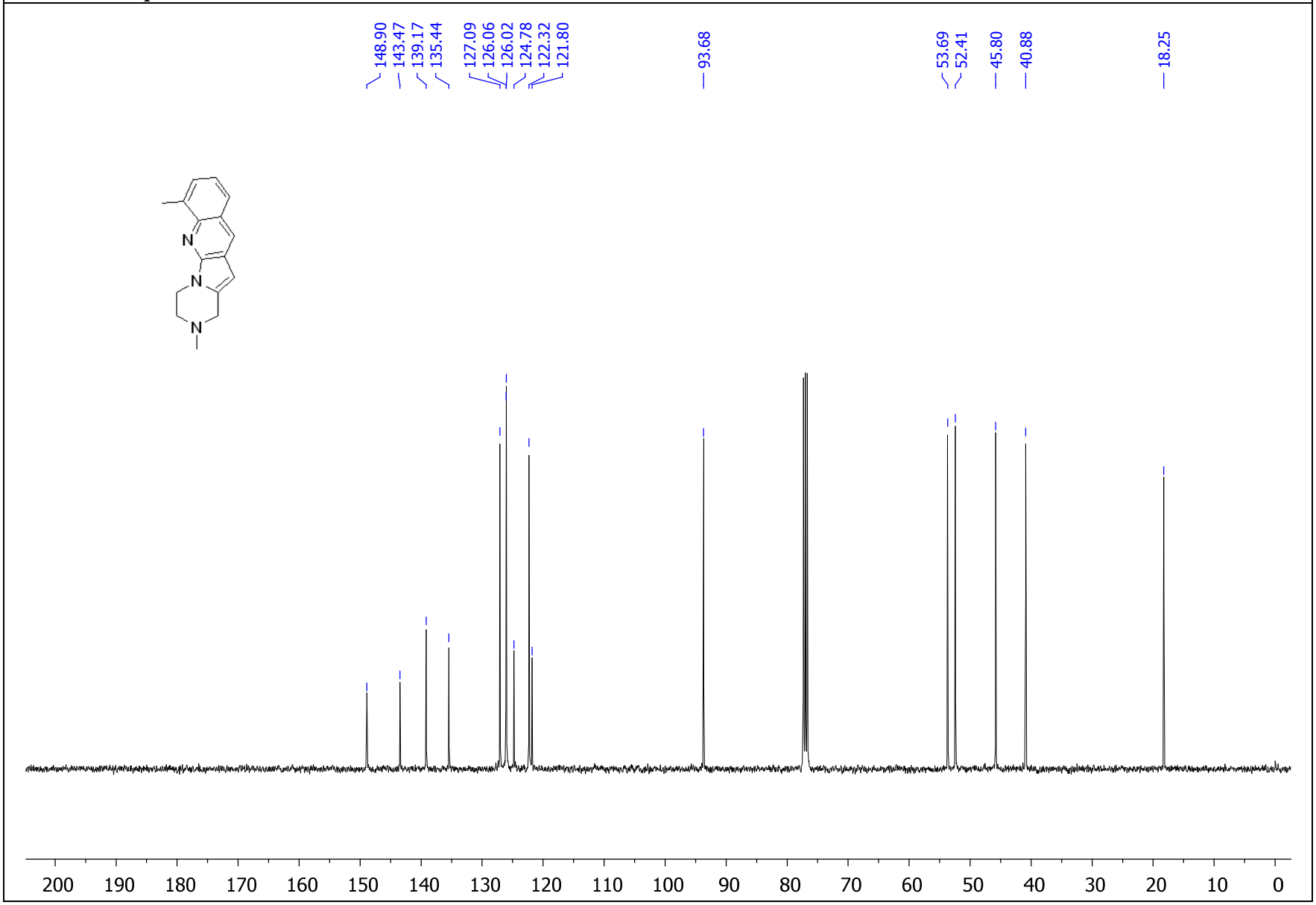
$^{13}$C NMR of **2p**


136.45
133.52
130.27
126.08
121.42
119.65
108.67
96.18
53.50
52.52
45.76
41.67
21.78
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

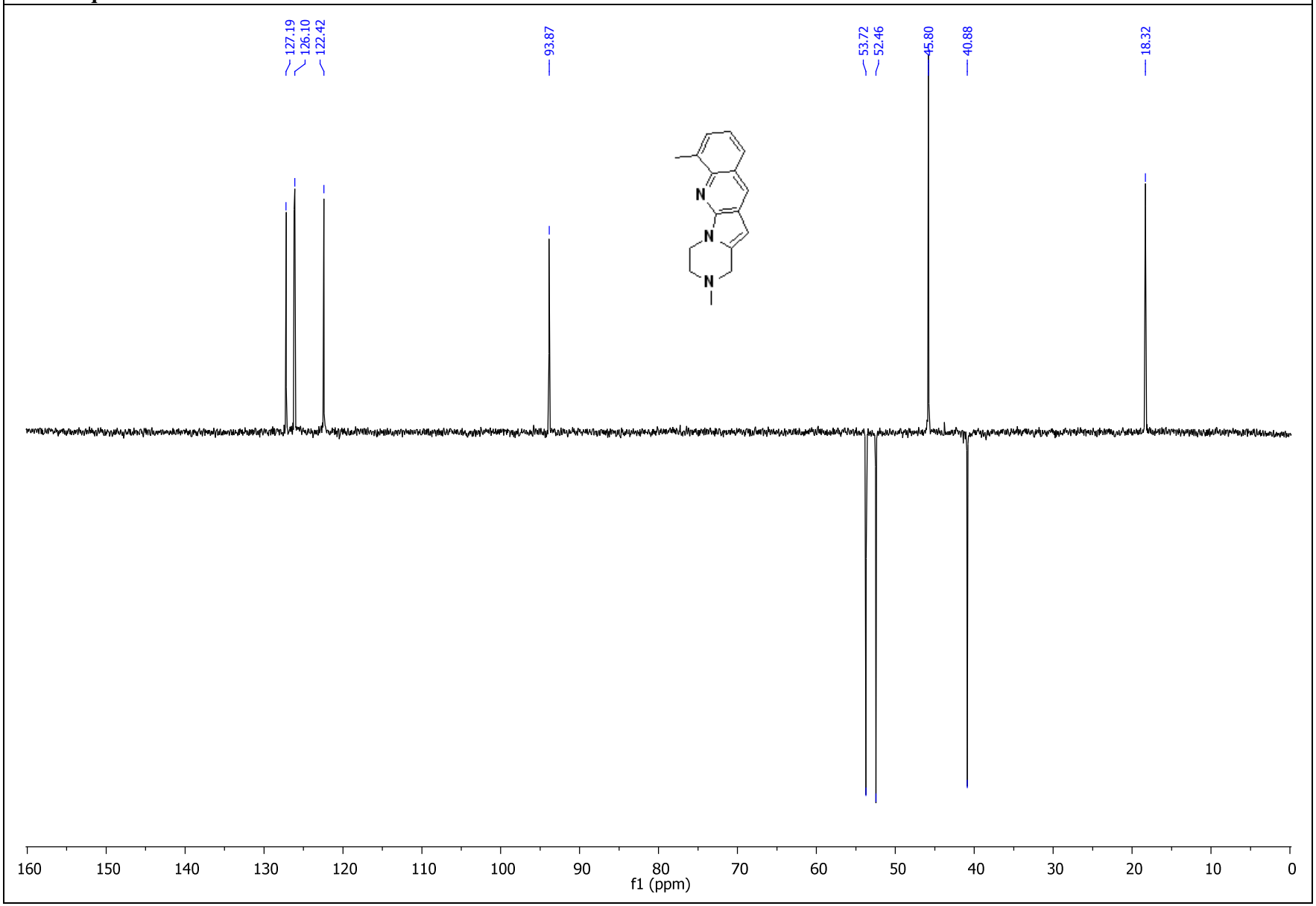
$^{1}$H NMR of **2q**


8.22
7.77
7.76
7.50
7.48
7.32
7.31
7.30
7.29
6.25
4.38
4.37
4.35
3.83
2.97
2.96
2.95
2.88
2.53
7.32
7.31
7.30
7.29
1.02
7.33
7.31
7.29
7.27
7.25
N
N
N
1.01
1.02
1.00
1.02
0.98
2.13
2.12
2.04
3.00
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

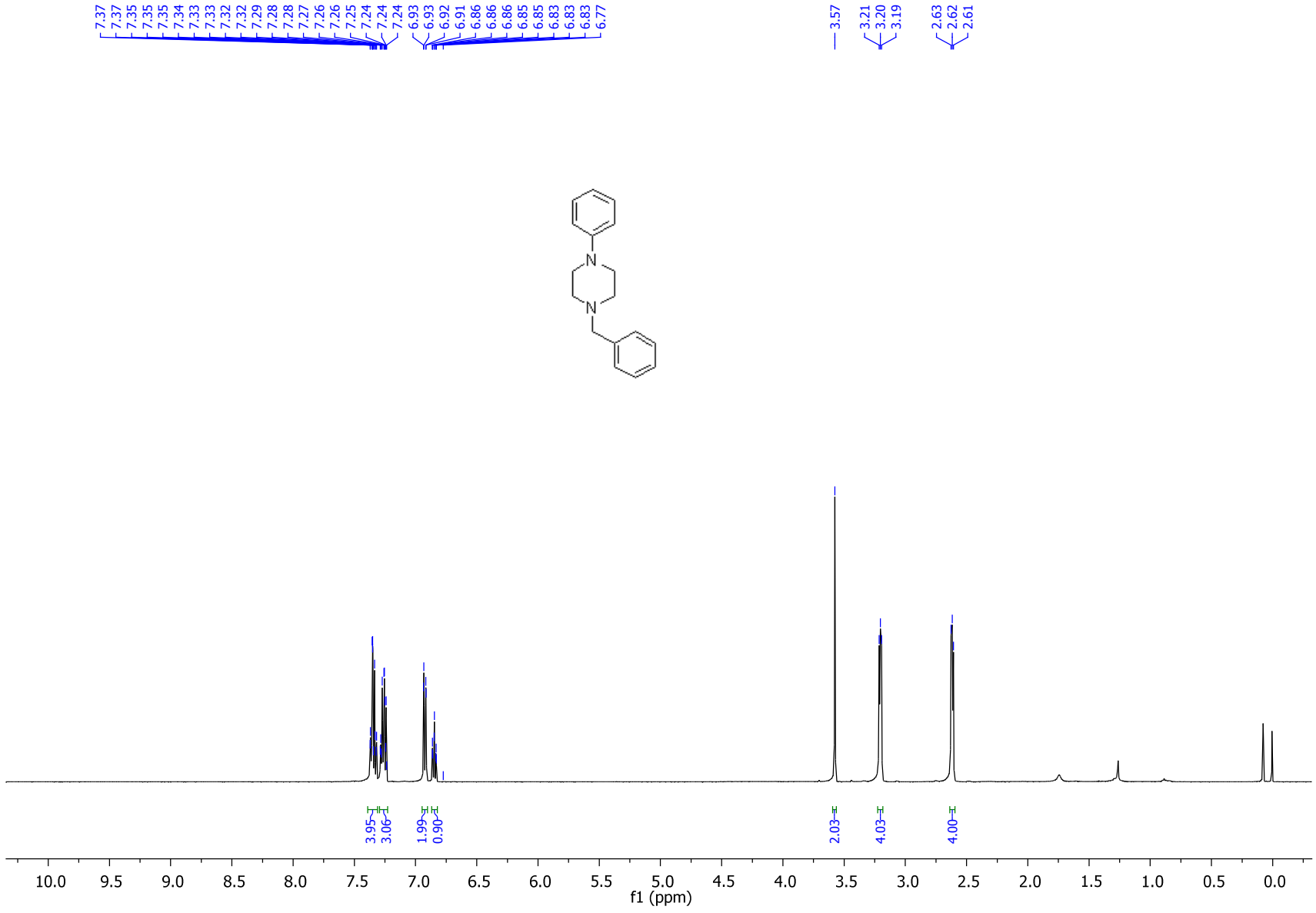
$^{13}$C NMR of **2q**


148.90
143.47
139.17
135.44
127.09
126.06
126.02
124.78
122.32
121.80
93.68
53.69
52.41
45.80
40.88
18.25
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

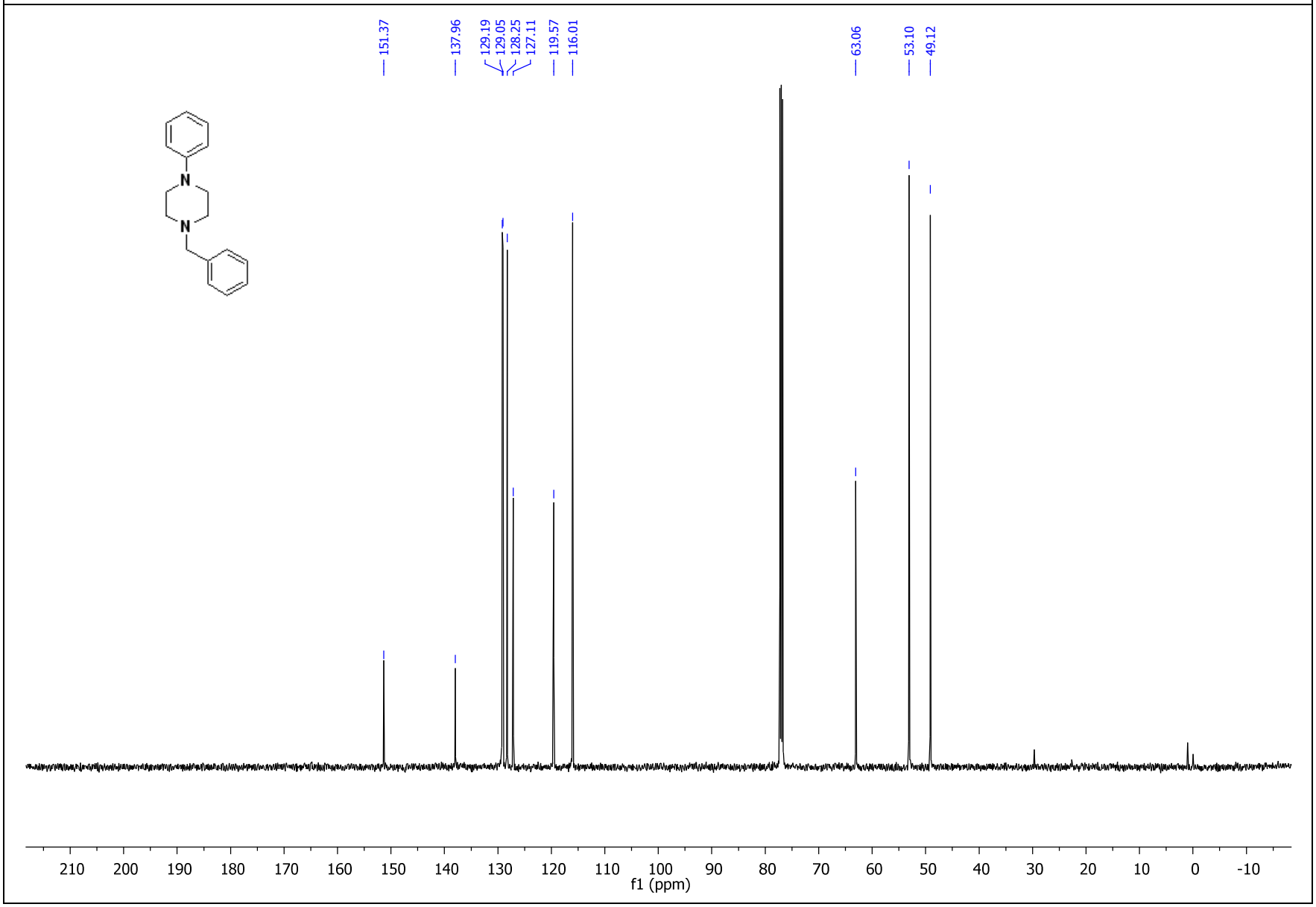
DEPT **2q**


127.19
126.10
122.42
93.87
53.72
52.46
45.80
40.88
18.32
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

H[1] NMR of **5**


7.37
7.37
7.35
7.35
7.34
7.33
7.32
7.32
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.24
6.93
6.93
6.92
6.91
6.86
6.86
6.86
6.85
6.85
6.83
6.83
6.83
6.77
3.57
3.21
3.20
3.19
2.63
2.62
2.61
N
N
3.95
3.06
1.99
0.90
2.03
4.03
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

$^{13}$C NMR of **5**


151.37
137.96
129.19
129.05
128.25
127.11
119.57
116.01
63.06
53.10
49.12
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)