

SUPPORTING INFORMATION

Cobalt-Catalyzed Carbonylation of Unactivated C(sp³)-H bonds

Nagaraju Barsu, Bolli Shyam Kumar, Basker Sundararaju*

Fine chemical Laboratory, Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur.
India.

Email: basker@iitk.ac.in

Contents

| | | |
|----|--|---------|
| 1 | General Information | S2 |
| 2 | General procedure for preparation of starting materials | S3-S4 |
| 3 | Analytical Data of Starting Materials (1g, 1h, 1i, 1j, 1m and 1q,) | S5-S6 |
| 4 | General Procedure for Cobalt-Catalyzed Carbonylation of Aliphatic Amides | S6-S14 |
| 5 | H/D exchange experiment | S15-S16 |
| 6 | K _H /K _D and Control Experiments | S16-S19 |
| 7 | Gram scale reaction | S19-S20 |
| 8 | Derivatization | S20-S21 |
| 9 | UV-Vis spectroscopy of cobalt complexes | S21-S22 |
| 10 | Crystallographic Summary | S22-S23 |

1. General information: Unless stated otherwise, all reactions were carried out under Ar in an oven-dried glassware. Chlorobenzene and α, α, α -trifluorotoluene were purchased from commercial provider namely Spectrochem and Alfa aesar. Dichloromethane (CaH_2), methanol (Mg) were purified by distillation over the indicated drying agents under Argon. Flash Column Chromatography was conducted on silica gel (Merck, 100-200 mesh). ^1H and ^{13}C NMR were recorded on JEOL (400 and 500 MHz) using CDCl_3 and $\text{DMSO-}d_6$ as a solvent. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals used as references and the chemicals shifts converted to TMS scale (CDCl_3 : $\delta\text{C} = 77$ ppm; residual CHCl_3 in CDCl_3 : $\delta\text{H} = 7.26$ ppm, $\text{DMSO-}d_6$: ^1H NMR shift for residual $\text{DMSO-}d_6$ at 2.5 ppm and ^{13}C NMR shift at 39.52 ppm). The abbreviations used for ^1H NMR spectra to indicate the signal multiplicity are s (singlet); brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet) and m (multiplet). ESI-MS was recorded on a Waters-Micromass Quattro Micro triplequadrupole mass spectrometer. GC-MS was used to analyse our samples on a Shimadzu GC 2010 plus and MS 2010SE system. All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets precoated with silica gel. Unless stated otherwise, all commercially available compounds (Alfa, Aldrich) were used as received.

2. General Procedure (A) for the Preparation of Starting Materials:

To an oven dried 100 mL flask connected with a CaCl₂ guard tube charged with carboxylic acid (1 eq) in 1M of MeOH. Thionyl chloride (1.2 eq) was then added dropwise to the suspension and stirring continued at the same temperature (r.t.) overnight. After completion of reaction, solvent was evaporated. The crude material was redissolved in EtOAc, washed with sat.NaHCO₃ (3 x 30 ml) and brine (30 mL). The separated organic layers was dried over anhydrous Na₂SO₄, and then evaporated in vacuo to provide the corresponding carboxylate ester as a colourless oil.

A solution of LDA (10 mmol) in THF (30 mL) was prepared from diisopropylamine (1.5 mL, 10.7 mmol) and 1.6 M *n*-BuLi in hexane (4.0 mL, 10 mmol) at -78 °C. Carboxylate ester (10 mmol) in THF (5 ml) was added dropwise to this LDA solution at -78 °C and the mixture was stirred at the same temperature for 1 h. Dropwise addition of alkyl halide (15 mmol) to this solution was performed carefully at -78 °C. After the addition, the mixture was slowly warmed to room temperature and stirring continued at the same temperature overnight. The reaction mixture was quenched with water at 0 °C, extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and then evaporated in vacuum to give the crude ester.

To the ester procured from the previous step, solution of NaOH (2 M, 8.0 mL) and methanol (10 mL) was added. The mixture was stirred overnight at 60 °C. After removal of methanol in vacuo, the pH of the mixture was adjusted to 2 with 3.0 M HCl. The mixture was then saturated with NaCl and extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over MgSO₄, and then evaporated in vacuo to give the crude carboxylic acid, which was used directly for the next step without any further purification.

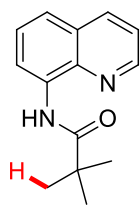
Oxalyl chloride (1.75 mL, 20 mmol) was added slowly to a stirred solution of the carboxylic acid in CH₂Cl₂ (20 mL) and DMF (0.1 mL) at 0 °C. The obtained mixture was stirred for 1 h at 0 °C and another 16 h at room temperature. After its evaporation in vacuo, residue was dissolved in toluene (5 mL), evaporated in vacuo twice, to give the crude acid chloride, which was used directly for the next step without any purification.

The acid chloride was added dropwise to a solution of 8-aminoquinoline (1.01 g, 7.0 mmol) and Et₃N (1.7 mL, 12 mmol) in CH₂Cl₂ (12 mL), which was stirred overnight at room temperature. The reaction was quenched with water after dilution with CH₂Cl₂ (10 mL), washed successively with saturated aqueous NaHCO₃, and brine. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane (1:100 v/v), to afford corresponding 8-aminoquinolinyl amides.¹

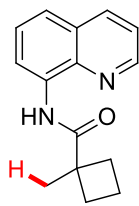
Compound **11** is prepared from reported literature²

¹ a) Wu, X.; Zhao, Y.; and Ge, H. *J. Am. Chem. Soc.* **2015**, *137*, 4924. b) Wu, X.-S.; Yang, K.; Zhao, Y.; Sun, H.; Li, G.-G.; Ge, H. *Nat. Commun.* **2015**, *6*, 6462-6471.

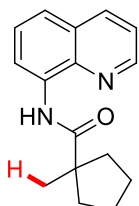
² a) Maity, S.; Agasti, S.; Earsad, A.M.; Hazra, A.; and Maiti, D. *Chem. Eur. J.* **2015**, *21*, 11320 – 11324.



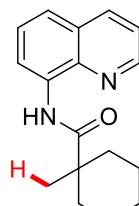
1a; (88%)



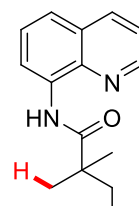
1b; (60%)



1c; (72%)



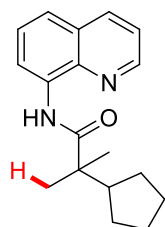
1d; (70%)



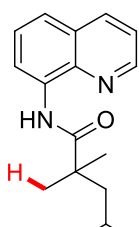
1e; (65%)



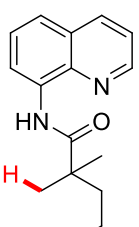
1f; (67%)



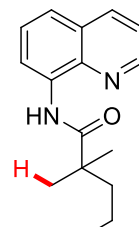
1g; (75%)



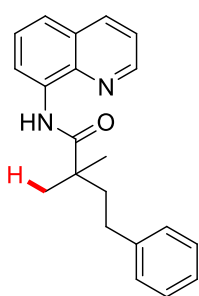
1h; (68%)



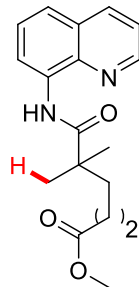
1i; (72%)



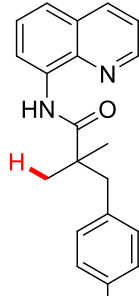
1j; (70%)



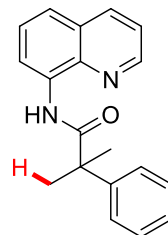
1k; (65%)



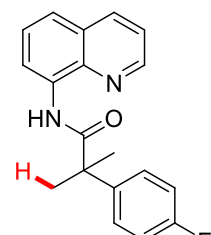
1l; (60%)



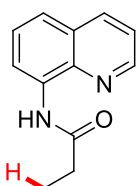
1m; (64%)



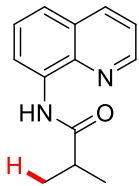
1n; (76%)



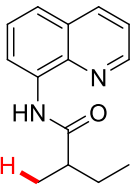
1o; (73%)



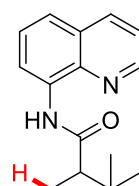
1p; (80%)



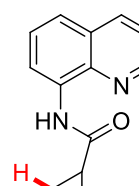
1q; (74%)



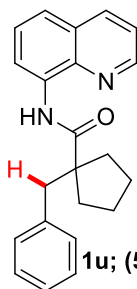
1r; (50%)



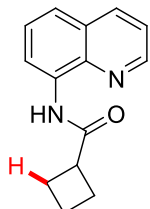
1s; (55%)



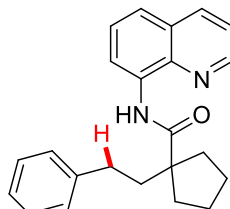
1t; (85%)



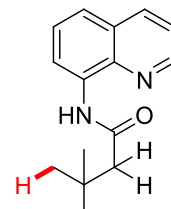
1u; (50%)



1v; (86%)



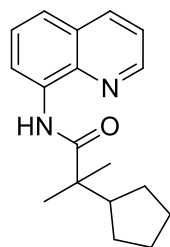
1w; (52%)



1x; (60%)

3. Analytical Data of Starting Materials (1g, 1h, 1i, 1j, 1m and 1q,)

2-cyclopentyl-2-methyl-N-(quinolin-8-yl)propanamide (1g): Compound **1g**, was prepared from cyclopentyl iodide, 8-aminoquinoline and methyl isobutyrate by using general procedure **A** and purified by flash column chromatography (5% EtOAc/Hexane) in 75% yield as light brown liquid. R_f Value = 0.3.

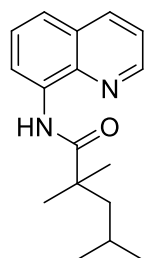


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.26 (s, 1H), 8.81 (dt, J = 5.9, 1.7 Hz, 2H), 8.13 (dd, J = 8.1, 1.8 Hz, 1H), 7.54-7.41 (m, 3H), 2.36-2.28 (m, 1H), 1.76-1.68 (m, 2H), 1.61-1.51 (m, 4H), 1.43-1.39 (m, 2H), 1.37 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 176.8, 148.1, 138.7, 136.2, 134.6, 127.8, 127.3, 121.4, 121.0, 116.0, 48.5, 45.5, 27.4, 25.4, 22.4.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$: 283.1810, found 283.1817.

2,2,4-trimethyl-N-(quinolin-8-yl)pentanamide (1h): Compound **1h**, was prepared from 1-bromo-2-methylpropane, 8-aminoquinoline and methyl isobutyrate by using general procedure **A** and purified by flash column chromatography (4% EtOAc/Hexane) in 68% yield as colourless liquid. R_f Value = 0.3.

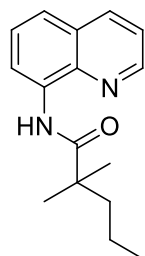


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.27 (s, 1H), 8.82-8.78 (m, 2H), 8.14 (m, 1H), 7.51 (dd, J = 15.7, 8.1 Hz, 2H), 7.46-7.42 (m, 1H), 1.82-1.69 (m, 1H), 1.70 (d, J = 6.1 Hz, 2H), 1.41 (s, 6H), 0.90 (d, J = 6.4 Hz, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 176.9, 148.1, 138.7, 136.2, 134.6, 127.8, 127.4, 121.4, 121.1, 116.1, 50.2, 43.4, 26.4, 25.2, 23.9.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}$: 271.1810, found 271.1811.

2,2-dimethyl-N-(quinolin-8-yl)pentanamide (1i): Compound **1i**, was prepared from bromopropane, 8-aminoquinoline and methyl isobutyrate by using general procedure **A** and purified by flash column chromatography (4% EtOAc/Hexane) in 72% yield as colourless liquid. R_f Value = 0.3.

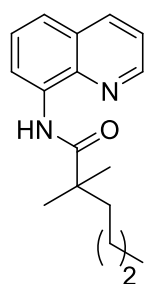


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.25 (s, 1H), 8.81 (d, J = 1.3 Hz, 1H), 8.80 (dd, J = 3.0, 1.5 Hz, 1H), 8.14 (dd, J = 8.2, 1.4 Hz, 1H), 7.54-7.46 (m, 2H), 8.46 (dd, J = 8.4, 4.4 Hz, 1H), 1.71-1.67 (m, 2H), 1.40 (s, 6H), 1.38-1.32 (m, 2H), 0.92 (t, J = 14.8, 7.4 Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 176.7, 148.1, 138.7, 136.2, 134.5, 127.8, 127.3, 121.4, 121.1, 116.0, 43.8, 43.7, 25.5, 18.2, 14.5.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}$: 257.1654, found 257.1653.

2,2-dimethyl-N-(quinolin-8-yl)hexanamide (1j): Compound **1j**, was prepared from bromobutane, 8-aminoquinoline and methyl isobutyrate by using above procedure **A** and purified by flash column chromatography (4% EtOAc/Hexane) in 70% yield as colourless liquid. R_f Value = 0.3.

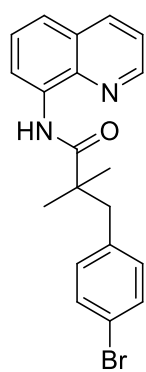


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.26 (s, 1H), 8.81 (m, 2H), 8.12 (m, 1H), 7.54-7.40 (m, 3H), 1.71 (m, 2H), 1.40 (s, 6H), 1.35-1.30 (m, 4H), 0.88 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 176.7, 148.1, 138.6, 136.1, 134.5, 127.8, 127.3, 121.4, 121.1, 116.0, 43.6, 41.2, 27.0, 25.5, 23.1, 13.9.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}$: 271.1810, found 271.1818.

3-(4-bromophenyl)-2,2-dimethyl-N-(quinolin-8-yl)propanamide (1m): Compound **1m**, was



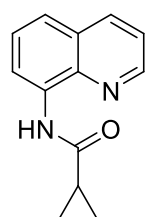
prepared from p-bromo benzyl bromide, 8-aminoquinoline and methyl isobutyrate by using general procedure **A** and purified by flash column chromatography (4% EtOAc/Hexane) in 74% yield as colourless liquid. R_f Value = 0.35.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.13 (s, 1H), 8.77 (m, 2H), 8.13 (d, $J = 8.2$ Hz, 1H), 7.53 (m, 2H), 7.41 (m, 1H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.06 (m, 2H), 2.98 (s, 2H), 1.41 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 175.6, 148.2, 138.6, 136.8, 136.2, 134.1, 131.8, 131.07, 131.01, 127.8, 127.3, 121.5, 120.3, 116.2, 46.2, 44.8, 25.2.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{20}\text{BrN}_2\text{O}$: 383.0759, found 383.0752.

N-(quinolin-8-yl)cyclopropanecarboxamide (1t): Compound **1t**, was prepared from cyclopropane carboxylic acid and 8-aminoquinoline by using general procedure **A** and purified by flash column chromatography (8% EtOAc/Hexane) in 85% yield as light yellow solid. R_f Value = 0.25.



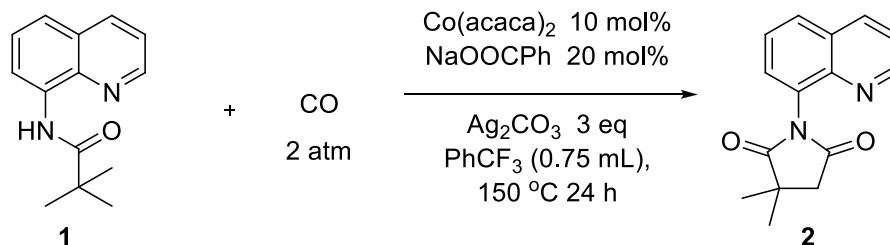
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.02 (s, 1H), 8.80 (dd, $J = 4.2, 1.5$ Hz, 1H), 8.74 (dd, $J = 7.2, 1.5$ Hz, 1H), 8.14 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.53-7.42 (m, 3H), 1.81 (ddd, $J = 15.5, 9.4, 4.6$ Hz, 1H), 1.15 (m, 2H), 0.91 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.2, 148.0, 138.1, 136.3, 134.6, 127.8, 127.4, 121.5, 121.1, 116.3, 16.2, 8.12.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}$: 213.1028, found 213.1020.

4. General Procedure (B) for Cobalt-Catalyzed Carbonylation of Aliphatic Amides

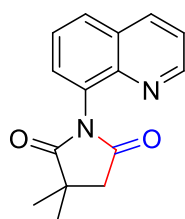
To an oven dried Schlenk tube associate a teflon coated magnetic stir bar was vacuumized and charged with argon. To this added $\text{Co}(\text{acac})_2$ (7.71mg, 0.03mmol, 10 mol%), PhCO_2Na (8.64 mg, 0.06 mmol, 20 mol%), Ag_2CO_3 (247mg, 0.9 mmol, 3 eq), and substituted N-(quinolin-8-yl)pivalamide in 0.75 mL of α, α, α -trifluorotoluene. The resulting mixture was vacuumized quickly and purged with carbon monoxide (either by using "CO" balloon or direct "CO" gas connected to schlenk tube) and placed in preheated oil bath for 24 h. The crude mixture was evaporated to dryness and purified by flash column chromatography using silica gel and petroleum ether / ethyl acetate (50:50 v/v) as the eluent to afford succinamide **2** as white solid in 95% yield (72.5 mg).



4a. Pictorial representation of typical Schlenk tube used for carbonylation



3,3-dimethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2a): Compound (2a) was prepared according to the general procedure **B** from **1a** (68.4 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (50% EtOAc/Hexane) in 95% (72.5 mg) yield as a white solid. R_f Value = 0.2.

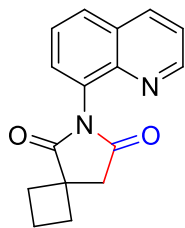


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.84 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.14 (dd, $J = 8.3, 1.7$ Hz, 1H), 7.88 (dd, $J = 7.5, 2.0$ Hz, 1H), 7.59 (m, 2H), 7.38 (dd, $J = 8.2, 4.1$ Hz, 1H), 2.94 (d, $J = 18.0$ Hz, 1H), 2.81 (d, $J = 18.0$ Hz, 1H), 1.60 (s, 3H), 1.49 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 182.8, 175.5, 150.8, 143.4, 135.9, 130.1, 129.4, 129.2, 129.0, 125.8, 121.7, 44.0, 40.8, 26.0, 25.2.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$: 254.1134, found 254.1139.

6-(quinolin-8-yl)-6-azaspiro[3.4]octane-5,7-dione (2b): Compound (2b) was prepared according to the general procedure **B** from **1b** (72 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 87% (70 mg) yield as pale yellow liquid. R_f Value = 0.2.

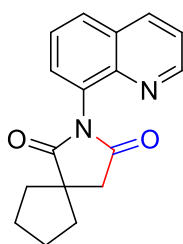


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.85 (dd, $J = 3.9, 1.5$ Hz, 1H), 8.18 (d, $J = 8.2, 1.4$ Hz, 1H), 7.91 (d, $J = 6.8$ Hz, 2.4 Hz, 1H), 7.64-7.59 (m, 2H), 7.42 (dd, $J = 8.1, 4.1$ Hz, 1H), 3.25 (d, $J = 18.2$ Hz, 1H), 3.07 (d, $J = 18.4$ Hz, 1H), 2.94-2.85 (m, 1H), 2.80-2.70 (m, 1H), 2.35-2.05 (m, 4H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 181.6, 175.6, 150.8, 143.4, 136.1, 130.1, 129.5, 129.4, 129.1, 126.0, 121.8, 44.9, 43.2, 32.0, 31.5, 16.3.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2$: 267.1134, found 267.1130.

2-(quinolin-8-yl)-2-azaspiro[4.4]nonane-1,3-dione (2c): Compound (2c) was prepared according to the general procedure **B** from **1c** (76.2 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 71% (60 mg) yield as white solid. R_f Value = 0.2.

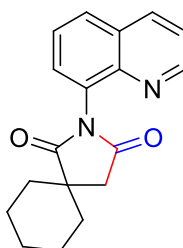


$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.86 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.18 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.93-7.89 (m, 1H), 7.64-7.62 (m, 2H), 7.44-7.41 (m, 1H), 3.00 (d, $J = 18.0$ Hz, 1H), 2.85 (d, $J = 18.0$ Hz, 1H), 2.45-2.29 (m, 2H), 2.01-1.97 (m, 3H), 1.83-1.80 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 182.9, 176.0, 150.9, 143.5, 136.0, 130.4, 129.5, 129.3, 129.1, 126.0, 121.8, 51.0, 44.2, 38.9, 38.1, 25.4, 25.3.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2$: 281.1290, found 281.1292.

2-(quinolin-8-yl)-2-azaspiro[4.5]decane-1,3-dione (2d): Compound (2d) was prepared according to the general procedure **B** from **1d** (80.4 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 67% (59.6 mg) yield as white solid. R_f Value = 0.2.

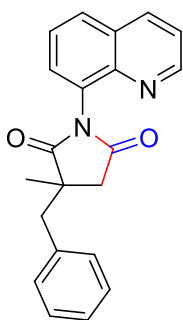


$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.84 (m, 1H), 8.16 (m, 1H), 7.91-7.88 (q, $J = 8.1, 3.3$ Hz, 1H), 7.63-7.59 (m, 2H), 7.41-7.39 (m, 1H), 2.98 (d, $J = 18.1$ Hz, 1H), 2.80 (d, $J = 18.0$ Hz, 1H), 2.02-1.97 (m, 3H), 1.88-1.86 (m, 2H), 1.75-1.73 (m, 2H), 1.44-1.39 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 182.6, 176.0, 150.8, 143.5, 135.9, 130.2, 129.5, 129.3, 129.1, 125.9, 121.8, 45.7, 40.6, 33.6, 33.4, 25.0, 22.2, 22.0.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: 295.1447, found 295.1446.

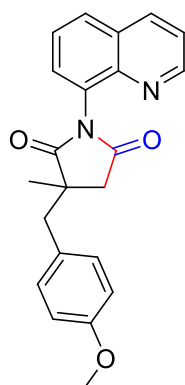
3-benzyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2e): Compound (2e) was prepared according to the general procedure **B** from **1e** (91.2 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (30% EtOAc/Hexane) in 71% (70.4 mg) yield as white solid. R_f Value = 0.2. Characteristic data for **2e** was in accordance with the reported literature^{1a}



$^1\text{H NMR}$ (400 MHz, CDCl_3 , a mixture of atropisomers in ratio 2.6:1.0, the minor one is marked with an *): δ 8.86 (dd, $J = 4.1, 1.3$ Hz, 1H), 8.15 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.88-7.86 (m, 1H), 7.63-7.53 (m, 1H), 7.43-7.28 (m, 6H), 7.17-7.15 (m, 1H), 3.36 (d, $J = 13.5$ Hz, 1H), 3.04 (d, $J = 18.3$ Hz, 1H), 2.85 (d, $J = 13.5$ Hz, 1H), 2.81 (d, $J = 18.1$ Hz, 1H), 1.71 (s, 3H); 8.80 (dd, $J = 4.0, 1.6$ Hz, 1H)*, 8.18 (dd, $J = 8.4, 1.6$ Hz, 1H)*, 7.93-7.90 (m, 1H)*, 7.63-7.53 (m, 1H)*, 7.43-7.28 (m, 6H)*, 7.17-7.15 (m, 1H)*, 3.42 (d, $J = 13.5$ Hz, 1H)*, 3.20 (d, $J = 18.4$ Hz, 1H)*, 2.85 (d, $J = 13.5$ Hz, 1H)*, 2.57 (d, $J = 18.0$ Hz, 1H)*, 1.53 (s, 3H)*.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 181.8, 175.3, 150.9, 143.48, 136.2, 136.0, 130.5, 130.0, 129.52, 129.1, 129.01, 128.6, 127.3, 125.94, 121.82, 46.02, 43.9, 40.1, 25.5; 182.2*, 175.5*, 150.7*, 143.44*, 136.3*, 135.9*, 130.1*, 129.9*, 129.59*, 129.2*, 129.07*, 128.3*, 126.8*, 125.92*, 121.86*, 45.6*, 43.0*, 40.5*, 24.6*.

3-(4-methoxybenzyl)-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2f): Compound (2f)



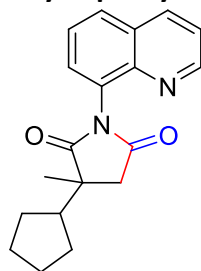
was prepared according to the general procedure **B** from **1f** (100.2 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 71% (77 mg) yield as white solid. R_f Value = 0.2.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , a mixture of atropisomers in ratio 2.5:1.0, the minor one is marked with an *): δ 8.86 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.18 (m, 1H), 7.88 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.58-7.54 (m, 1H), 7.44-7.40 (m, 1H), 7.20-7.17 (m, 3H), 6.91-6.89 (m, 2H), 3.83 (s, 3H), 3.29 (d, $J = 13.4$ Hz, 1H), 3.01 (d, $J = 18.1$ Hz, 1H), 2.83-2.74 (m, 2H), 1.68 (s, 3H); 8.79 (dd, $J = 6.7, 2.9$ Hz, 1H)*, 8.18 (m, 1H)*, 7.92 (dd, $J = 6.7, 2.9$ Hz, 1H)*, 7.65-7.60 (m, 1H)*, 7.44-7.40 (m, 1H)*, 7.23-7.21 (m, 3H)*, 6.87-6.85 (m, 2H)*, 3.82 (s, 3H)*, 3.34 (d, $J = 13.7$ Hz, 1H)*, 3.17 (d, $J = 18.1$ Hz, 1H)*, 2.97 (d, $J = 13.9$ Hz, 1H)*, 2.55 (d, $J = 18.0$ Hz, 1H)*, 1.50 (s, 3H)*.

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 182.0, 175.5, 158.8, 150.9, 143.3, 136.2, 131.0, 129.9, 129.5, 129.4, 129.0, 128.3, 126.09, 121.9, 114.0, 55.25, 46.2, 43.2, 40.5, 25.41; 182.3*, 175.7*, 158.5*, 150.7*, 143.4*, 136.0*, 131.5*, 130.1*, 129.6*, 129.3*, 129.1*, 128.4*, 126.02*, 121.8*, 113.7*, 55.20*, 45.8*, 42.3*, 40.1*, 24.6*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3$: 361.1552, found 361.1552.

3-cyclopentyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2g): Compound (2g) was



prepared according to the general procedure **B** from **1g** (84.6 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 72% (67 mg) yield as pale yellow liquid. R_f Value = 0.2.

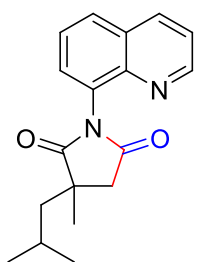
$^1\text{H NMR}$ (400 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.3:1.0, the minor one is marked with an *): δ 8.86 (ddd, $J = 12.7, 8.5, 5.4$ Hz, 1H), 8.19-8.16 (m, 1H), 7.92-7.89 (m, 1H), 7.64-7.54 (m, 2H), 7.42 (dt, $J = 12.8, 7.4$ Hz, 1H), 2.86 (d, $J = 18.2$ Hz, 1H), 2.75 (d, $J = 18.2$ Hz, 1H), 2.49-2.35 (m, 1H), 1.97-1.81 (m, 2H), 1.70-1.64 (m, 4H), 1.60 (s, 3H), 1.43-1.34 (m, 2H);

8.86 (ddd, $J = 12.7, 8.5, 5.4$ Hz, 1H)*, 8.19-8.16 (m, 1H)*, 7.92-7.89 (m, 1H)*, 7.64-7.54 (m, 2H)*, 7.42 (dt, $J = 12.8, 7.4$ Hz, 1H)*, 3.00 (d, $J = 18.4$ Hz, 1H)*, 2.60 (d, $J = 18.0$ Hz, 1H)*, 2.49-2.35 (m, 1H)*, 1.97-1.81 (m, 2H)*, 1.70-1.64 (m, 4H)*, 1.60 (s, 3H)*, 1.43-1.34 (m, 2H)*.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 182.54, 176.3, 151.0, 143.59, 136.0, 130.3, 129.6, 129.3, 129.1, 126.0, 121.9, 46.98, 46.4, 39.0, 27.8, 27.6, 25.5, 25.3, 24.4; 182.55*, 176.1*, 150.7*, 143.57*, 135.9*, 130.2*, 129.5*, 129.2*, 129.1*, 125.9*, 121.8*, 46.99*, 46.1*, 39.4*, 27.9*, 27.7*, 25.9*, 25.6*, 24.3*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2$: 309.1603, found 309.1608.

3-isobutyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2h): Compound (2h) was



prepared according to the general procedure **B** from **1h** (81 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 75% (67 mg) yield as pale yellow liquid. R_f Value = 0.2.

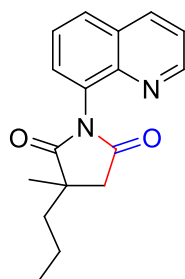
$^1\text{H NMR}$ (500 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.86-8.84 (m, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.90 (m, 1H), 7.61 (m, 2H), 7.41 (dd, $J = 8.0, 3.9$ Hz, 1H), 3.01 (d, $J = 18.2$ Hz, 1H), 2.83 (d, $J = 18.2$ Hz, 1H), 1.91-1.87 (m, 1H), 1.80-1.77 (m, 2H),

1.60 (s, 3H), 1.07-1.00 (m, 6H); 8.86-8.84 (m, 1H)*, 8.17 (d, $J = 8.0$ Hz, 1H)*, 7.90 (m, 1H)*, 7.61 (m, 2H)*, 7.41 (dd, $J = 8.0, 3.9$ Hz, 1H)*, 3.15 (d, $J = 18.5$ Hz, 1H)*, 2.69 (d, $J = 18.1$ Hz, 1H)*, 2.07-2.00 (m, 1H)*, 1.87-1.82 (m, 2H)*, 1.48 (s, 3H)*, 1.07-1.00 (m, 6H)*.

^{13}C NMR (125 MHz, CDCl_3): δ 182.7, 175.9, 150.9, 143.74, 135.97, 130.5, 129.5, 129.24, 129.1, 125.97, 121.8, 46.0, 44.4, 41.7, 25.9, 25.2, 24.6, 23.0; 182.72*, 175.7*, 150.7*, 143.70*, 135.94*, 130.5*, 129.4*, 129.29*, 129.1*, 125.96*, 121.8*, 46.1*, 44.47*, 42.1*, 25.6*, 25.0*, 24.7*, 23.4*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$: 297.1603, found 297.1600.

3-methyl-3-propyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2i): Compound (2i) was prepared according to the general procedure B from 1i (76.8 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 87% (74.2 mg) yield as white solid. R_f Value = 0.2.

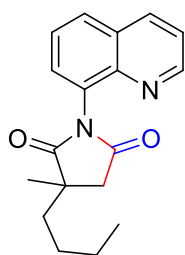


^1H NMR (500 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.87-8.84 (m, 1H), 8.17 (dt, $J = 4.2, 2.1$ Hz, 1H), 7.91-7.88 (m, 1H), 7.63-7.58 (m, 2H), 7.43-7.40 (m, 1H), 2.90 (d, $J = 18.0$ Hz, 1H), 2.84 (d, $J = 18.1$ Hz, 1H), 1.95-1.71 (m, 4H), 1.58 (s, 3H), 1.01 (td, $J = 4.0, 3.0$ Hz, 3H); 8.87-8.84 (m, 1H)*, 8.17 (dt, $J = 4.2, 2.1$ Hz, 1H)*, 7.91-7.88 (m, 1H)*, 7.63-7.58 (m, 2H)*, 7.43-7.40 (m, 1H)*, 3.04 (d, $J = 17.9$ Hz, 1H)*, 2.69 (d, $J = 18.1$ Hz, 1H)*, 1.95-1.71 (m, 4H)*, 1.47 (s, 3H)*, 1.01 (td, $J = 4.0, 3.0$ Hz, 3H)*.

^{13}C NMR (125 MHz, CDCl_3): δ 182.53, 175.9, 150.9, 143.6, 136.0, 129.57, 129.37, 129.18, 125.98, 121.89, 44.66, 41.5, 40.62, 29.6, 24.7, 17.9, 14.31; 182.59*, 175.8*, 150.8*, 143.60*, 135.9*, 129.52*, 129.32*, 129.15*, 125.97*, 121.85*, 44.62*, 41.6*, 40.65*, 29.64*, 24.3*, 17.70*, 14.4*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2$: 283.1447, found 283.1448.

3-butyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2j): Compound (2j) was prepared according to the general procedure B from 1j (81 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 88% (78 mg) yield as pale yellow solid. R_f Value = 0.25.

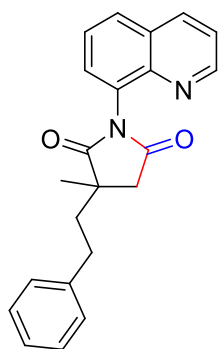


^1H NMR (500 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.85 (m, 1H), 8.15 (d, $J = 8.3$ Hz, 1H), 7.89 (m, 1H), 7.61 (m, 2H), 7.40 (m, 1H), 2.90 (d, $J = 18.3$ Hz, 1H), 2.84 (d, $J = 18.3$ Hz, 1H), 1.83 (m, 2H), 1.58 (s, 3H), 1.39 (m, 4H), 0.98 (m, 3H); 8.85 (m, 1H)*, 8.15 (d, $J = 8.3$ Hz, 1H)*, 7.89 (m, 1H)*, 7.61 (m, 2H)*, 7.40 (m, 1H)*, 3.04 (d, $J = 18.3$ Hz, 1H)*, 2.69 (d, $J = 18.1$ Hz, 1H)*, 1.83 (m, 2H)*, 1.47 (s, 3H)*, 1.39 (m, 4H)*, 0.98 (m, 3H)*.

^{13}C NMR (125 MHz, CDCl_3): δ 182.4, 175.7, 150.8, 143.6, 135.90, 130.4, 129.48, 129.2, 129.14, 125.9, 121.7, 44.55, 41.5, 38.3, 26.6, 24.7, 22.8, 13.9; 182.5*, 175.8*, 150.6*, 143.6*, 135.97*, 130.5*, 129.42*, 129.3*, 129.12*, 125.9*, 121.8*, 44.53*, 41.6*, 38.0*, 26.6*, 24.3*, 23.0*, 13.8*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$: 297.1603, found 297.1600.

3-methyl-3-phenethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2k): Compound (2k) was prepared according to the general procedure **B** from **1k** (95.4 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (30% EtOAc/Hexane) in 88% (91 mg) yield as pale yellow solid. R_f Value = 0.3.

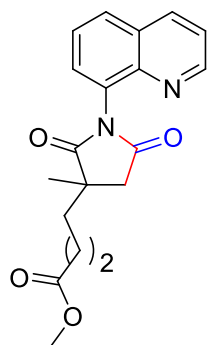


$^1\text{H NMR}$ (500 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.92-8.85 (m, 1H), 8.20 (m, 1H), 7.94 (m, 1H), 7.66 (m, 2H), 7.46-7.41 (m, 1H), 7.37-7.25 (m, 5H), 3.16-2.78 (m, 4H), 2.33-2.06 (m, 2H), 1.58 (s, 3H); 8.92-8.85 (m, 1H)*, 8.20 (m, 1H)*, 7.94 (m, 1H)*, 7.66 (m, 2H)*, 7.46-7.41 (m, 1H)*, 7.37-7.25 (m, 5H)*, 3.16-2.78 (m, 4H)*, 2.33-2.06 (m, 2H)*, 1.69 (s, 3H)*.

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 182.14, 175.6, 150.7, 143.4, 140.8, 136.01, 130.3, 129.8, 129.57, 129.30, 129.1, 128.4, 128.3, 126.1, 125.9, 121.8, 44.5, 41.6, 40.5, 30.90; 182.12*, 175.7*, 150.9*, 141.6*, 140.8*, 136.06*, 130.1*, 129.8*, 129.59*, 129.36*, 129.1*, 128.5*, 128.2*, 126.1*, 125.9*, 121.8*, 44.5*, 41.4*, 40.0*, 30.99*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2$: 345.1603, found 345.1601.

methyl 4-(3-methyl-2,5-dioxo-1-(quinolin-8-yl)pyrrolidin-3-yl)butanoate (2l): Compound (2l) was prepared according to the general procedure **B** from **1l** (94.2 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 61% (63 mg) yield as pale yellow solid. R_f Value = 0.2.



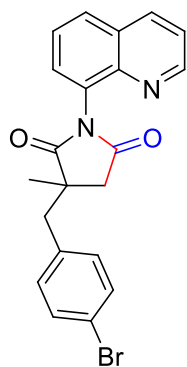
$^1\text{H NMR}$ (400 MHz, CDCl_3 , a mixture of atropisomers in ratio 1.0:1.0, the minor one is marked with an *): δ 8.85 (m, 1H), 8.17 (dt, $J = 12.0$, 1.9 Hz, 1H), 7.91-7.89 (m, 1H), 7.61-7.59 (m, 2H), 7.41 (dd, $J = 8.2$, 4.2 Hz, 1H), 3.69 (s, 3H), 2.94 (d, $J = 18.3$ Hz, 1H), 2.85 (d, $J = 18.2$ Hz, 1H), 2.42-2.38 (m, 2H), 1.97-1.70 (m, 4H), 1.48 (s, 3H); 8.85 (m, 1H)*, 8.17 (dt, $J = 12.0$, 1.9 Hz, 1H)*, 7.91-7.89 (m, 1H)*, 7.61-7.59 (m, 2H)*, 7.41 (dd, $J = 8.2$, 4.2 Hz, 1H)*, 3.69 (s, 3H)*, 3.06 (d, $J = 18.3$ Hz, 1H)*, 2.71 (d, $J = 18.1$ Hz, 1H)*,

2.42-2.38 (m, 2H)*, 1.97-1.70 (m, 4H)*, 1.59 (s, 3H)*.

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 182.27, 175.71, 173.6, 150.9, 143.43, 136.01, 130.2, 129.65, 129.2, 129.1, 125.9, 121.9, 51.5, 44.3, 41.4, 37.7, 34.0, 24.4, 20.0; 182.22*, 175.77*, 173.3*, 150.8*, 143.41*, 136.11*, 130.0*, 129.60*, 129.4*, 129.0*, 126.0*, 121.9*, 51.6*, 44.4*, 41.3*, 37.3*, 33.7*, 24.6*, 19.9*.

HRMS: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$: 341.1501, found 341.1500.

3-methyl-3-phenyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2m): Compound (2m) was prepared according to the general procedure **B** from **1m** (114.6 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 58% (70 mg) yield as white solid. R_f Value = 0.25.



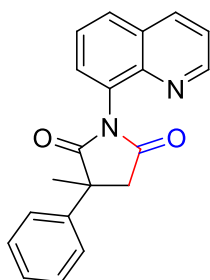
$^1\text{H NMR}$ (400 MHz, CDCl_3 , a mixture of atropisomers in ratio 2.4:1.0, the minor one is marked with an *): δ 8.88 (dd, $J = 4.1$, 1.5 Hz, 1H), 8.18 (m, 1H), 7.91 (m, 1H), 7.64-7.60 (m, 1H), 7.50 (m, 2H), 7.45-7.40 (m, 2H), 7.17-7.14 (m, 2H), 3.29 (d, $J = 13.2$ Hz, 1H), 2.96 (d, $J = 18.2$ Hz, 1H), 2.82-2.77 (m, 2H), 1.69 (s, 3H); 8.76 (dd, $J = 4.2$, 2.0 Hz, 1H)*, 8.18 (m, 1H)*, 7.91 (m, 1H)*, 7.58-7.56 (m, 1H)*, 7.50 (m, 2H)*, 7.45-7.40 (m, 2H)*, 7.21-7.18 (m, 2H)*, 3.36 (d, $J = 13.4$ Hz, 1H)*, 3.11 (d, $J = 17.6$ Hz, 1H)*, 2.95 (d, $J = 13.1$ Hz,

1H)*, 2.60 (d, $J = 18.4$ Hz, 1H)*, 1.52 (s, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 181.6, 175.20, 151.0, 143.4, 136.0, 135.3, 132.2, 131.79, 129.8, 129.6, 129.2, 129.0, 126.0, 121.93, 121.4, 45.9, 43.0, 40.0, 25.6; 181.8*, 175.29*, 150.7*, 143.3*, 135.9*, 135.2*, 131.75*, 131.5*, 130.0*, 129.7*, 129.2*, 129.1*, 125.9*, 121.97*, 121.0*, 45.5*, 42.6*, 40.3*, 25.0*.

HRMS: [M+H]⁺ calculated for C₂₁H₁₈BrN₂O₂: 409.0552, found 409.0551.

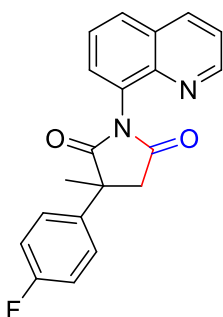
3-methyl-3-phenyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2n): Compound (2n) was prepared according to the general procedure B from 1n (87 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (30% EtOAc/Hexane) in 51% (49 mg) of sp³ and 14% (14 mg) sp² carbonylated product yield. R_f Value = 0.3. Characteristic data for 2n was in accordance with the reported literature^{1a}



¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.0:1.0, the minor one is marked with an *): δ 8.90 (td, *J* = 3.7, 1.5 Hz, 1H), 8.19 (m, 1H), 7.95-7.91 (m, 1H), 7.79-7.76 (m, 1H), 7.71-7.62 (m, 2H), 7.58-7.55 (m, 1H), 7.46-7.36 (m, 3H), 7.36-7.31 (m, 1H), 3.42 (d, *J* = 18.3 Hz, 1H), 3.13 (d, *J* = 18.3 Hz, 1H), 2.02 (s, 3H); 8.90 (td, *J* = 3.7, 1.5 Hz, 1H), 8.19 (m, 1H), 7.95-7.91 (m, 1H), 7.79-7.76 (m, 1H), 7.71-7.62 (m, 2H), 7.58-7.55 (m, 1H), 7.46-7.36 (m, 3H), 7.36-7.31 (m, 1H), 3.38 (d, *J* = 18.1 Hz, 1H), 3.28 (d, *J* = 17.9 Hz, 1H), 1.93 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 180.6, 175.45, 151.0, 143.5, 142.4, 136.1, 130.2, 129.76, 129.4, 129.18, 128.9, 127.4, 126.3, 125.7, 121.9, 48.5, 45.52, 26.1; 180.9*, 175.43*, 150.8*, 143.4*, 142.0*, 136.0*, 130.1*, 129.70*, 129.3*, 129.12*, 128.7*, 127.3*, 126.3*, 126.0*, 121.9*, 48.7*, 45.56*, 24.9*.

3-(4-fluorophenyl)-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2o): Compound (2o) was prepared according to the general procedure B from 1o (92.4 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (30% EtOAc/Hexane) in 50% (50 mg) sp³ and 15% (15mg) sp² carbonylated product yield R_f Value = 0.3.

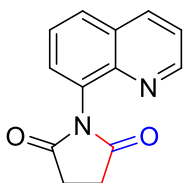


¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.3:1.0, the minor one is marked with an *): δ 8.89 (m, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.93 (m, 1H), 7.78-7.75 (m, 1H), 7.70-7.62 (m, 2H), 7.53 (m, 1H), 7.45 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.14-7.09 (m, 2H), 3.35 (d, *J* = 18.7 Hz, 1H) 3.12 (d, *J* = 18.4 Hz, 1H), 1.91 (s, 3H); δ 8.89 (m, 1H)*, 8.20 (d, *J* = 8.4 Hz, 1H)*, 7.93 (m, 1H)*, 7.78-7.75 (m, 1H)*, 7.70-7.62 (m, 2H)*, 7.53 (m, 1H)*, 7.45 (dd, *J* = 8.2, 4.1 Hz, 1H)*, 7.14-7.09 (m, 2H)*, 3.35 (d, *J* = 18.7 Hz, 1H)*, 3.26 (d, *J* = 18.0 Hz, 1H)*, 2.01 (s, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 180.7, 175.16, 163.1, 150.8, 143.4, 138.26, 137.7, 136.14, 130.17, 129.7, 129.3, 129.1, 128.2, 127.6, 126.05, 122.03, 115.8, 115.65, 48.03, 46.5, 25.03; 180.4*, 175.11*, 160.7*, 151.0*, 143.5*, 138.29*, 137.8*, 136.10*, 130.12*, 129.8*, 129.4*, 129.2*, 128.1*, 127.5*, 126.02*, 122.02*, 115.63*, 115.4*, 48.2*, 45.4*, 26.8*.

HRMS: [M+H]⁺ calculated for C₂₀H₁₆FN₂O₂: 335.1196, found 335.1193.

1-(quinolin-8-yl)pyrrolidine-2,5-dione (2p): Compound (2p) was prepared according to the general procedure B from 1p (60 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (80% EtOAc/Hexane) in 31% (21 mg) yield as pale yellow solid. R_f Value = 0.2.

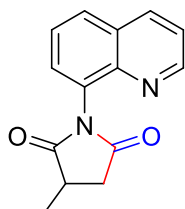


¹H NMR (500 MHz, CDCl₃): δ 8.88 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.21 (m, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 (m, 2H), 7.46 (dd, *J* = 8.3, 3.9 Hz, 1H), 3.17-3.10 (m, 2H), 3.03-2.95 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 176.9, 150.9, 143.4, 136.3, 130.1, 129.7, 129.5, 129.2, 126.1, 122.0, 28.9.

HRMS: [M+H]⁺ calculated for C₁₃H₁₁N₂O₂: 227.0821, found 227.0822.

3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2q): Compound (2q) was prepared according to the general procedure B from 1q (64.2 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (70% EtOAc/Hexane) in 45% (32.5 mg) yield as pale yellow solid. R_f Value = 0.2.

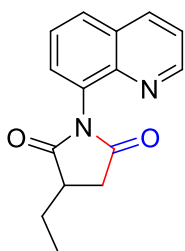


¹H NMR (500 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.87 (m, 1H), 8.19 (m, 1H), 7.92 (m, 1H), 7.64-7.60 (m, 2H), 7.43 (dt, *J* = 8.5, 4.5 Hz, 1H), 3.34-3.28 (m, 1H), 3.19-3.11 (m, 1H), 2.62-2.56 (m, 1H), 1.50 (d, *J* = 6.8 Hz, 3H); 8.87 (m, 1H)*, 8.19 (m, 1H)*, 7.92 (m, 1H)*, 7.64-7.60 (m, 2H)*, 7.43 (dt, *J* = 8.5, 4.5 Hz, 1H)*, 3.34-3.28 (m, 1H)*, 3.19-3.11 (m, 1H)*, 2.77-2.73 (m, 1H)*, 1.59 (d, *J* = 7.3 Hz, 3H)*.

¹³C NMR (125 MHz, CDCl₃): δ 180.1, 175.9, 150.8, 143.53, 136.2, 130.3, 129.59, 129.4, 129.27, 126.03, 121.89, 37.16, 35.3, 17.19; 180.2*, 176.1*, 150.9*, 143.57*, 136.0*, 130.4*, 129.57*, 129.3*, 129.20*, 126.05*, 121.89*, 37.10*, 35.6*, 16.77*.

HRMS: [M+H]⁺ calculated for C₁₄H₁₃N₂O₂: 241.0977, found 241.0978.

3-ethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2r): Compound (2r) was prepared according to the general procedure B from 1r (68.4 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (50% EtOAc/Hexane) in 48% (37.2 mg) yield as pale yellow solid. R_f Value = 0.2.

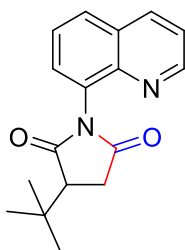


¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.86 (m, 1H), 8.18 (t, *J* = 15.2, 8.0 Hz, 1H), 7.91 (m, 1H), 7.61 (m, 2H), 7.42 (m, 1H), 3.23 (m, 2H), 2.66 (m, 1H), 2.12 (m, 1H), 1.94 (m, 1H), 1.11 (t, *J* = 14.7, 7.1 Hz, 3H); 8.86 (m, 1H)*, 8.18 (t, *J* = 15.2, 8.0 Hz, 1H)*, 7.91 (m, 1H)*, 7.61 (m, 2H)*, 7.42 (m, 1H)*, 3.06 (m, 2H)*, 2.82 (m, 1H)*, 2.12 (m, 1H)*, 1.79 (m, 1H)*, 1.17 (t, *J* = 14.7, 7.3 Hz, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 179.5, 176.3, 150.8, 143.35, 136.3, 130.0, 129.6, 129.4, 129.2, 126.06, 121.9, 41.7, 34.4, 24.4, 10.95; 179.6*, 176.5*, 150.9*, 143.37*, 136.0*, 130.2*, 129.5*, 129.3*, 129.1*, 126.01*, 121.8*, 41.9*, 34.2*, 24.5*, 10.93*.

HRMS: [M+H]⁺ calculated for C₁₅H₁₅N₂O₂: 255.1134, found 255.1133.

3-tert-butyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2s): Compound (2s) was prepared according to the general procedure B from 1s (76.8 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (50% EtOAc/Hexane) in 60% (51.2 mg) yield as yellow liquid. R_f Value = 0.3.

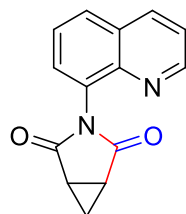


¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.89-8.83 (m, 1H), 7.94-7.89 (m, 1H), 7.94-7.89 (m, 1H), 7.64-7.54 (m, 2H), 7.46-7.40 (m, 1H), 3.18-3.04 (m, 1H), 2.97-2.77 (m, 2H), 1.17 (s, 9H); 8.89-8.83 (m, 1H)*, 7.94-7.89 (m, 1H)*, 7.94-7.89 (m, 1H)*, 7.64-7.54 (m, 2H)*, 7.46-7.40 (m, 1H)*, 3.18-3.04 (m, 1H)*, 2.97-2.77 (m, 2H)*, 1.23 (s, 9H)*.

¹³C NMR (125 MHz, CDCl₃); δ 177.9, 176.28, 143.3, 136.3, 130.1, 129.6, 129.2, 129.06, 128.3, 127.5, 126.0, 121.88, 50.3, 33.5, 32.3, 27.4, 27.2; 178.0*, 176.25*, 150.6*, 143.4*, 135.8*, 130.3*, 129.5*, 129.4*, 129.7*, 128.0*, 127.5*, 125.9*, 121.80*, 50.5*, 33.7*, 32.3*, 27.2*, 27.1*.

HRMS: [M+H]⁺ calculated for C₁₇H₁₉N₂O₂: 283.1447, found 283.1443.

3-(quinolin-8-yl)-3-azabicyclo[3.1.0]hexane-2,4-dione (2t): Compound (2t) was prepared according to the general procedure B from 1t (63.6 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (50% EtOAc/Hexane) in 84% (60.3 mg) yield as white solid. R_f Value = 0.3.

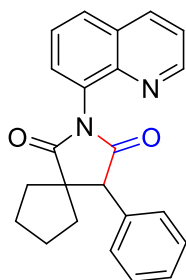


¹H NMR (500 MHz, CDCl₃, a mixture of atropisomers in ratio 5.0:1.0, the minor one is marked with an *): δ 8.82 (d, J = 4.0 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 6.9 Hz, 1H), 7.59 (t, J = 15.7, 8.0 Hz, 1H), 7.39-7.37 (m, 1H), 2.67 (dd, J = 8.1, 3.4 Hz, 2H), 2.42 (m, 1H), 1.69-1.64 (m, 1H); 8.91 (d, J = 4.0 Hz, 1H)*, 8.17 (d, J = 7.8 Hz, 1H)*, 7.89 (d, J = 8.5 Hz, 1H)*, 7.66 (dd, J = 6.9 Hz, 1H)*, 7.55 (d, J = 8.0 Hz, 1H)*, 7.43-7.41 (m, 1H)*, 2.75 (dd, J = 8.1, 3.3 Hz, 2H)*, 2.42 (m, 1H)*, 1.69-1.64 (m, 1H)*.

¹³C NMR (125 MHz, CDCl₃); δ 174.7, 150.7, 143.32, 135.9, 130.5, 129.8, 129.29, 128.9, 128.7, 125.9, 121.7, 21.2, 20.7, 19.9; 174.7*, 150.0*, 143.35*, 136.1*, 130.5*, 129.4*, 129.21*, 129.0*, 128.7*, 125.8*, 121.9*, 21.2*, 20.8*, 19.9*.

HRMS: [M+H]⁺ calculated for C₁₄H₁₁N₂O₂: 239.0821, found 239.0824.

4-phenyl-2-(quinolin-8-yl)-2-azaspiro[4.4]nonane-1,3-dione (2u): Compound (2u) was prepared according to the general procedure B from 1u (99 mg, 0.3 mmol, 1 eq) and purified by flash column chromatography (70% EtOAc/Hexane) in 26% (28.6 mg) yield as pale yellow solid. R_f Value = 0.2.

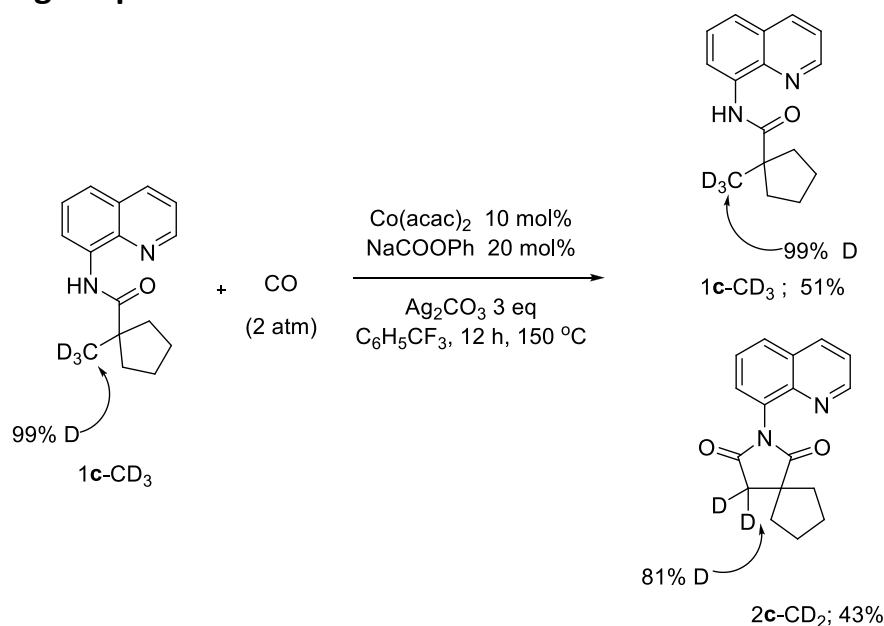


¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 5.0:1.0, the minor one is marked with an *): δ 8.82 (dd, J = 4.0, 1.7 Hz, 1H), 8.15 (dd, J = 8.1, 1.6 Hz, 1H), 7.86 (dd, J = 8.3, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.41-7.28 (m, 6H), 7.07 (dd, J = 7.4, 1.4 Hz, 1H), 3.54-3.47 (m, 1H), 3.21 (m, 1H), 2.84 (d, J = 13.0 Hz, 1H), 2.60-2.55 (m, 1H), 2.37-2.21 (m, 2H), 2.11-2.06 (m, 1H), 1.93-1.78 (m, 2H); 8.75 (dd, J = 4.1, 1.9 Hz, 1H)*, 8.15 (dd, J = 8.1, 1.6 Hz, 1H)*, 7.90 (dd, J = 7.6, 1.5 Hz, 1H)*, 7.62-7.57 (m, 1H)*, 7.41-7.28 (m, 6H)*, 7.07 (d, J = 7.4, 1.4 Hz, 1H)*, 3.54-3.47 (m, 1H)*, 3.37-3.35 (m, 1H)*, 3.05 (d, J = 13.6 Hz, 1H)*, 2.60-2.55 (m, 1H)*, 2.37-2.21 (m, 2H)*, 2.11-2.06 (m, 1H)*, 1.93-1.78 (m, 2H)*.

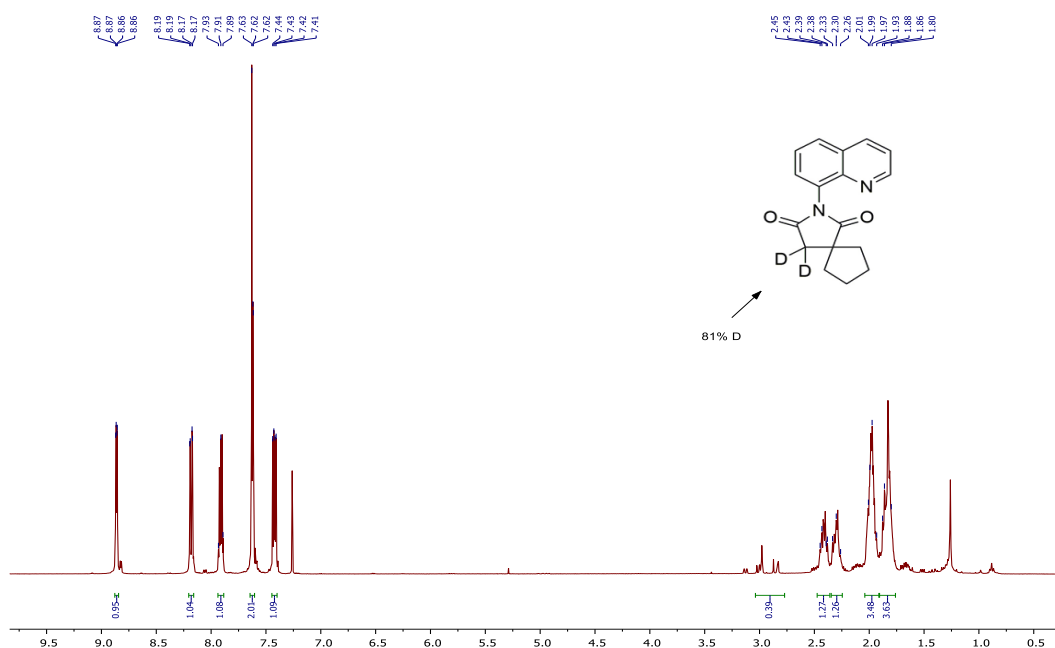
¹³C NMR (100 MHz, CDCl₃); δ 181.95, 179.5, 151.02, 143.5, 136.9, 135.89, 129.8, 129.4, 129.1, 128.6, 127.2, 126.0, 121.8, 58.4, 48.8, 41.7, 38.3, 31.2, 25.04; 181.13*, 179.3*, 151.79*, 143.4*, 136.7*, 135.84*, 129.8*, 129.5*, 129.0*, 128.4*, 126.7*, 125.9*, 121.8*, 57.3*, 49.1*, 40.9*, 36.9*, 30.7*, 25.26*.

HRMS: [M+H]⁺ calculated for C₂₃H₂₁N₂O₂: 357.1603, found 357.1608.

5. H/D Exchange experiment:

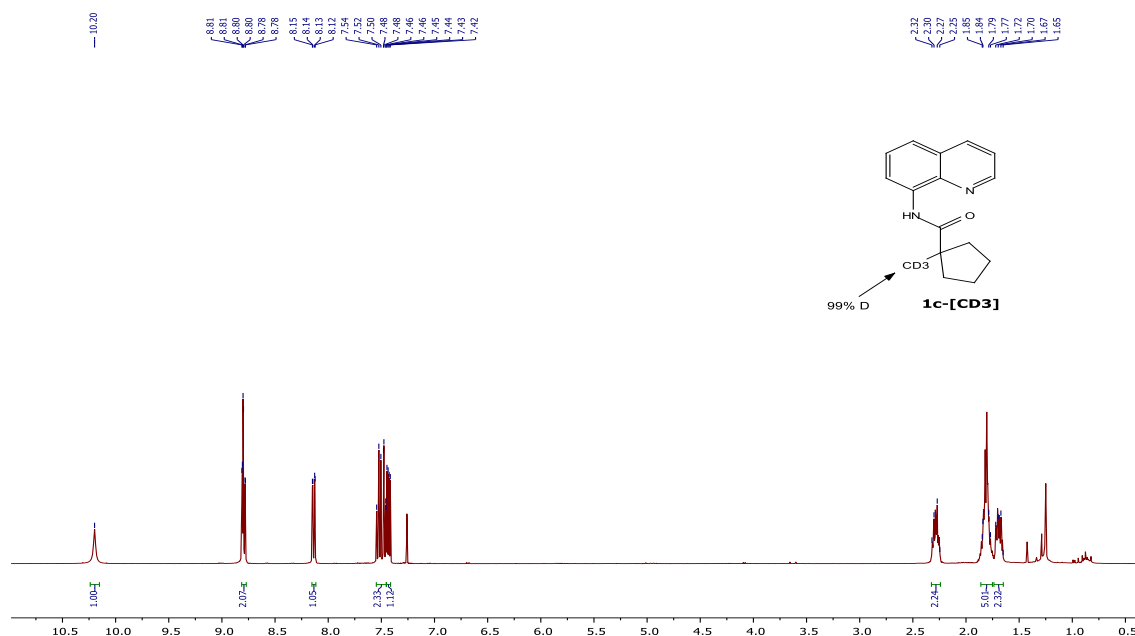


To an oven dried Schlenk tube associate with a teflon coated magnetic stir bar was vaccumised and purged with argon, to this Co(acac)₂ (7.71mg, 0.03mmol, 10 mol%), PhCO₂Na (8.64 mg, 0.06 mmol, 20 mol%), Ag₂CO₃ (247mg, 0.9 mmol, 3 eq), followed by 1c-[CD₃] (77.1 mg, 0.3 mmol, 1 eq) in 0.75 mL of α,α,α- trifluoro toluene solvent was added. Finally, schlenk was capped, vaccumised and pressurized to 2 atm of carbon monoxide and placed in preheated oil bath for 12 h. After 12 h, upon completion of reaction, it was cooled to room temperature. Then concentration of solvent followed by purification by column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate (50:50 v/v) as the eluent to give the desired product 2c-[CD₂] (37 mg, 43%) and recovered 1c-[CD₃] (39.9 mg, 51%). The ratio of deuterium incorporated was determined by ¹H NMR.



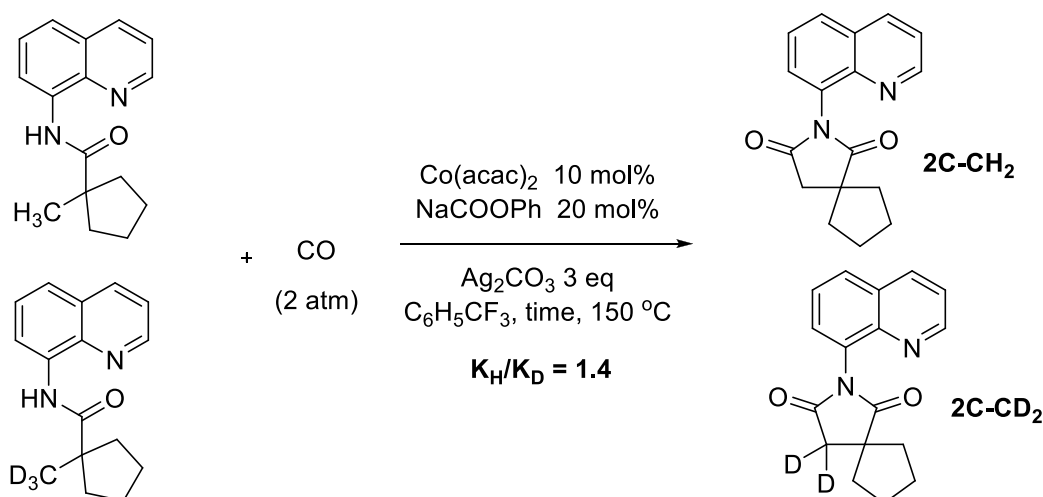
2c-[CD₂], ¹H NMR (400 MHz, CDCl₃): 8.86 (dd, *J* = 4.2, 1.9 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.93-7.89 (m, 1H), 7.62 (m, 2H), 7.42 (dd, *J* = 8.3, 4.0 Hz, 1H), 2.45-2.38 (m, 1H), 2.33-2.26 (m, 1H), 2.10-1.93 (m, 3H), 1.88-1.80 (m, 3H).

Recovered 1c-[CD₃], ¹H NMR (400 MHz, CDCl₃): 10.20 (s, 1H), 8.80 (m, 2H), 8.14 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.50 (m, 2H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.32-2.25 (m, 2H), 1.85-1.77 (m, 5H), 1.72-1.65 (m, 2H).



6. Deuterium and Control Experiments:

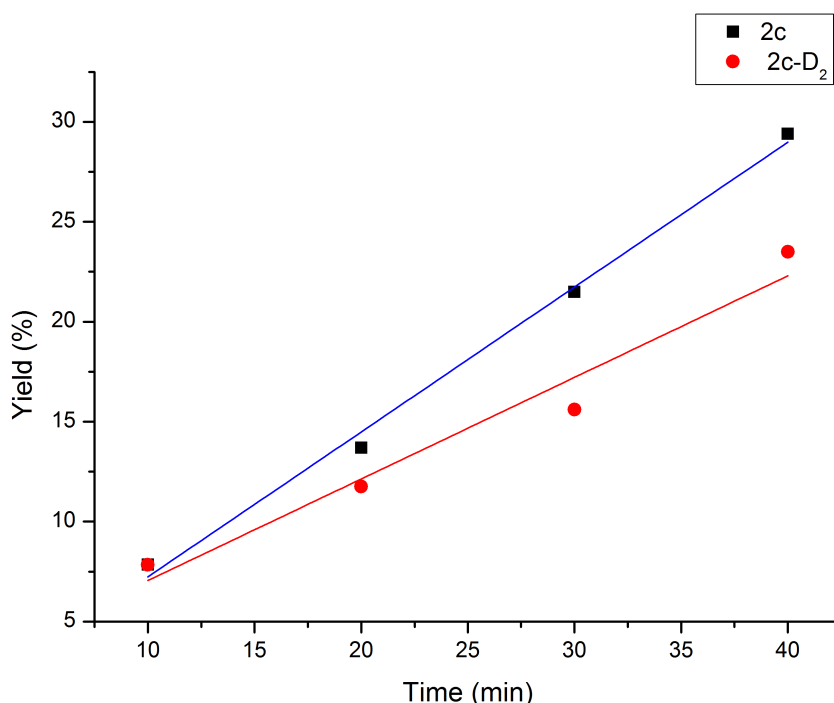
6.1. Parallel KIE Experiment:



To an oven dried Schlenk tube associate with a teflon coated magnetic stir bar was vaccumised and charged with argon, to this added Co(acac)₂ (2.57 mg, 0.01mmol, 10 mol%), PhCO₂Na (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (82.5 mg, 0.3 mmol, 3 eq), and 1c-[CD₃](25.7 mg, 0.1 mmol, 1 eq) in 0.3 mL of α,α,α- trifluoro toluene on one side. On the other hand, in another dried Schlenk tube Co(acac)₂ (2.57 mg, 0.01 mmol, 10 mol%),

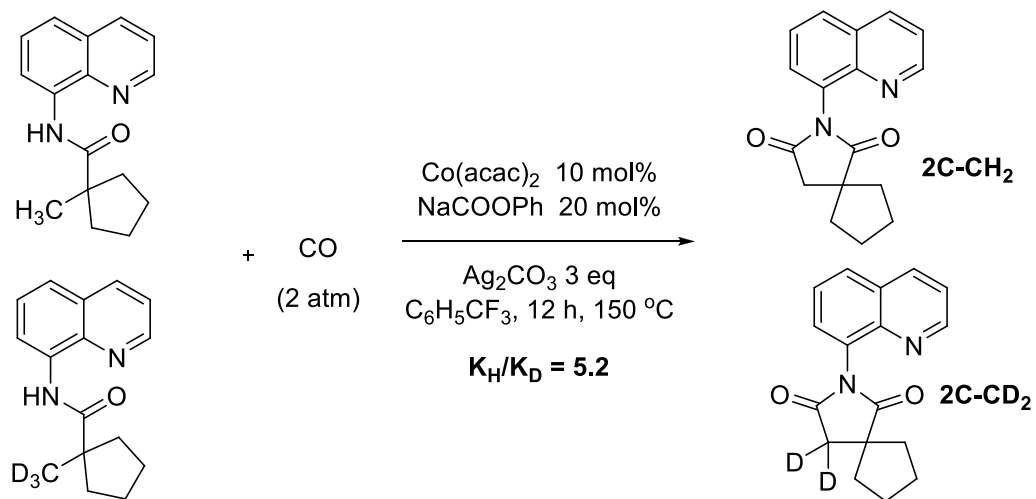
PhCO₂Na (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (82.5 mg, 0.3 mmol, 3 eq), and **1c** – [CH₃](25.4 mg, 0.1 mmol, 1 eq) and 0.3 mL of α,α,α- trifluoro toluene was added sequentially. Finally both the Schlenks were closed, vaccumised and pressurized to 2 atm of carbon monoxide and placed in preheated oil bath for 10, 20, 30, 40 min and immediately quenched separately with 1ml EtOAc. Next, the reaction mixture was diluted with 5 mL of EtOAc, and filtered using a silica pad. The solvent was then removed under reduced pressure and ¹H NMR was taken using Anisole (7 mg) as the internal standard. The K_H/K_D value for parallel experiment is 1.42 determined by ¹H NMR spectroscopy by plotting NMR yield vs time (min).

| | | | | |
|---|------|-------|------|------|
| Time (min) | 10 | 20 | 30 | 40 |
| Yield of 2c (%) | 7.84 | 13.7 | 21.5 | 29.4 |
| Yield of [D ₂]- 2c (%) | 7.84 | 11.76 | 15.6 | 23.5 |

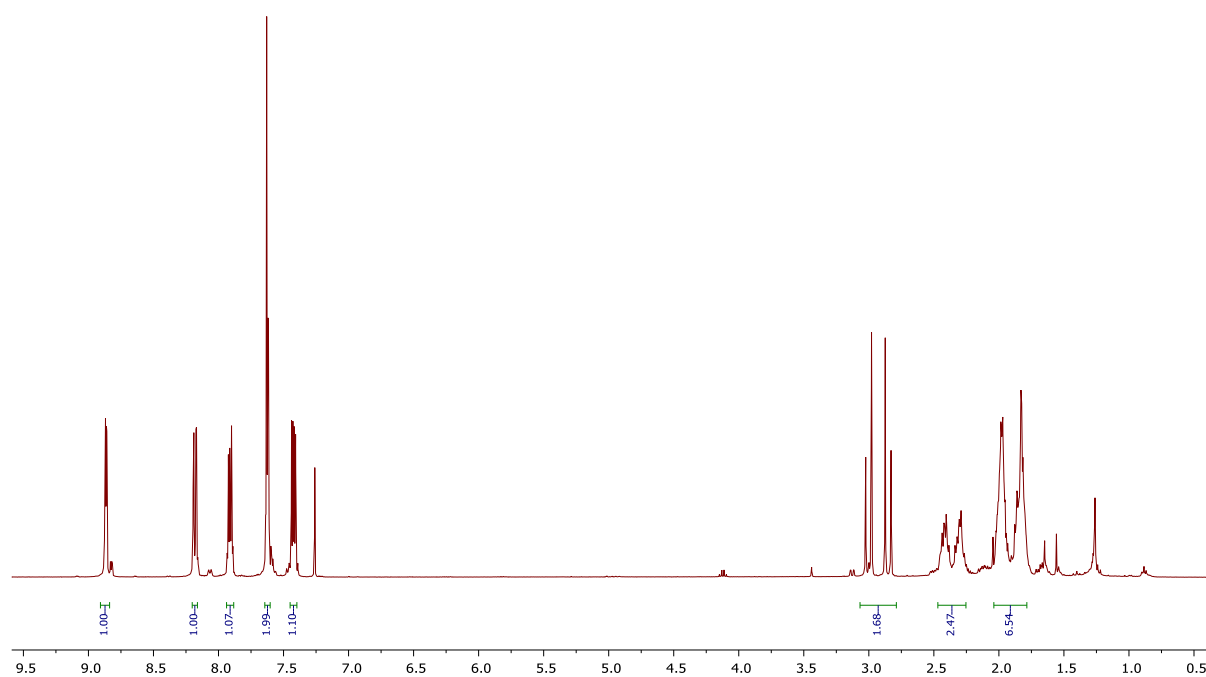


6.2. One pot KIE Experiment:

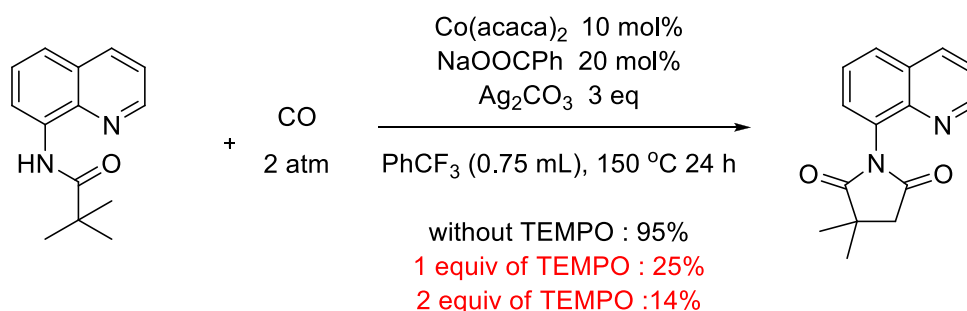
To an oven dried Schlenk tube, Co(acac)₂ (7.71mg, 0.03mmol, 10 mol%), PhCO₂Na (8.64 mg, 0.06 mmol, 20 mol%), Ag₂CO₃ (247mg, 0.9 mmol, 3 eq), was added along with **1c** – [CD₃](77.1 mg, 0.3 mmol, 1 eq) and **1c** – [CH₃](76.2 mg, 0.3 mmol, 1 eq) in 0.75 mL of α,α,α- trifluoro toluene as solvent. After addition is over it was again vaccumised and purged with carbon monoxide with 2 atm pressure and placed in preheated oil bath for 12 h. After 12 h, upon completion of reaction, it was cooled to room temperature. The crude mixtures was purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate (50:50 v/v) as the eluent, gave mixture of 2C-CH₂ and 2C-CD₂. The K_H/K_D value for one pot experiment is 5.2, determined by ¹H NMR spectroscopy.



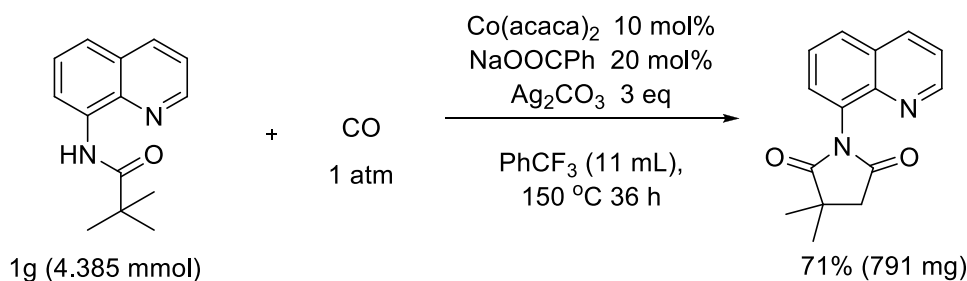
KIE value determined from one pot reaction = 5.25



6.3. Radical quenching Experiment: To an oven dried Schlenk tubes, was added $\text{Co}(\text{acac})_2$ (7.71mg, 0.03mmol, 10 mol%), PhCO_2Na (8.64 mg, 0.06 mmol, 20 mol%), Ag_2CO_3 (247mg, 0.9 mmol, 3 eq), and amide **1a** (68.4 mg, 0.3 mmol, 1 eq) in 0.75 mL of α,α,α -trifluoro toluene along with 1 equiv of TEMPO (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (46.8 mg, 0.3 mmol, 1 eq). Similarly the reaction was conducted with 2 equiv of TEMPO (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (93.6 mg, 0.6 mmol, 2 eq) using the same procedure. The closed Schlenk tubes was vaccumised and pressurized to 2 atm of carbon monoxide and placed in preheated oil bath for 24 h. After 24 h, removal of solvent followed by purification through column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate (50;50 v/v) as the eluent gave **2a** 25% (19.2 mg) as white solid.

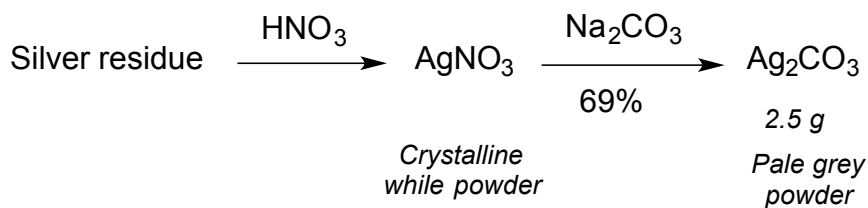


7. Gram scale reaction:



To an oven dried Schlenk tube associate with a teflon coated magnetic stir bar was vaccumized and charged with argon, to this added $\text{Co}(\text{acac})_2$ (112.7 mg, 0.43 mmol, 10 mol%), PhCO_2Na (126.31 mg, 0.877 mmol, 20 mol%), Ag_2CO_3 (3618 mg, 13.15 mmol, 3 eq), and substituted N-(quinolin-8-yl)pivalamide in 11 mL of α,α,α -trifluoro toluene as solvent. The closed Schlenk tube was vaccumised and filled with 1 atm of carbon monoxide using "CO" baloon and placed in preheated oil bath for 36 h. After 36 h removal of solvent followed by purification was done through column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate (50:50 v/v) as the eluent to afford **2a** as white solid (791 mg, 71% yield). Residual silver was recycled according to the literature procedure in 69% (2.5 g) after two steps as pale grey powder.³

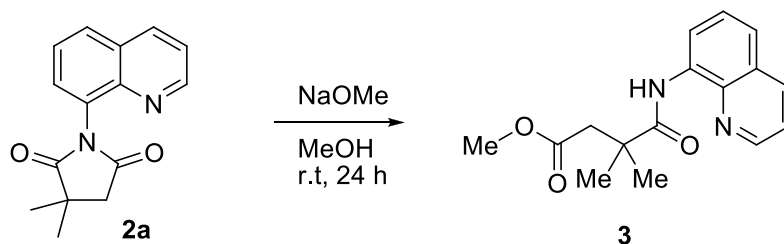
³ Tan, G.; He, S.; Huang, X.; Liao, X.; Cheng, Y.; You, J. -S. *Angew. Chem. Int. Ed.* **2016**, *55*, 10414-10418.



Caution: It should be noted that the resulting filtrate at the end of the first step (ie. after silver nitrate formation) should not be recovered and free from EtOH. The second crop of AgNO₃ may potentially produce EXPLOSIVE silver fulminate, which should be avoided. Also, Do not wash with ethanol, instead you may wash with isopropanol and then dry the silver nitrate.⁴

8. Derivatization of 3,3-dimethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione:

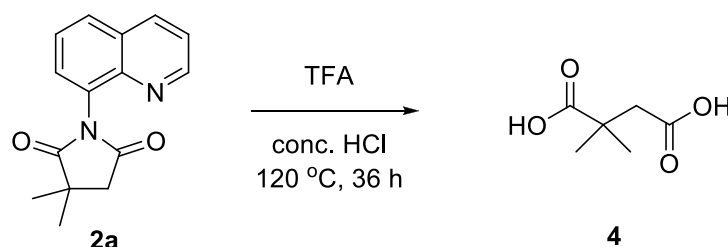
To an oven dried Schlenk tube associate with a teflon coated magnetic stir bar was vacuumised and charged with argon, to this added compound **2a** (38 mg, 0.15 mmol) added dry MeONa (12.4 mg, 0.23 mmol) in MeOH (distilled) (1 mL) was stirred for 48 h at room temperature. The reaction mixture was diluted with EtOAc (10 mL). The organic layer was washed with saturated aqueous NaHCO₃, brine, dried over Na₂SO₄, and then evaporated in vacuo. The residue was purified by flash column chromatography on silica gel, eluted with EtOAc/hexane (1:20, v/v), to afford 60% (26 mg) of compound **3** as colourless oil.



¹H NMR (500 MHz, CDCl₃): δ 9.85 (s, 1H), 8.79-8.73 (m, 2H), 8.13 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51-7.42 (m, 3H), 3.76 (s, 3H), 2.86 (s, 2H), 1.37 (s, 6H).

¹³C NMR (125 MHz, CDCl₃): δ 177.5, 169.1, 148.0, 138.2, 136.3, 134.3, 127.8, 127.3, 121.5, 121.4, 116.5, 52.2, 47.8, 41.2, 29.6, 25.5.

HRMS: [M+H]⁺ calculated for C₁₆H₁₉N₂O₃: 287.1396, found 287.1394.



A 25 mL Schlenk tube was charged with **2a** (150 mg, 0.59 mmol), trifluoroacetic acid (1.5 mL) and conc. HCl (1.5 mL). The reaction mixture was stirred at 120 °C for 36 h. After cooling to room temperature, the crude mixture was concentrated under reduced pressure and the

⁴ Henderson, K. O.; Garlin, D. L. *J. Chem. Educ.* **1970**, *47*, 741.

residue was diluted with 3N HCl (3 mL) and extracted with EtOAc (10 mL x 3). The combined organic layer were washed with brine, dried over Na₂SO₄, and then evaporated in vacuo to afford 91% (79 mg) of the carboxylic acid **5** as white solid. Characteristic data of diacid **5** was in accordance with the literature.⁵

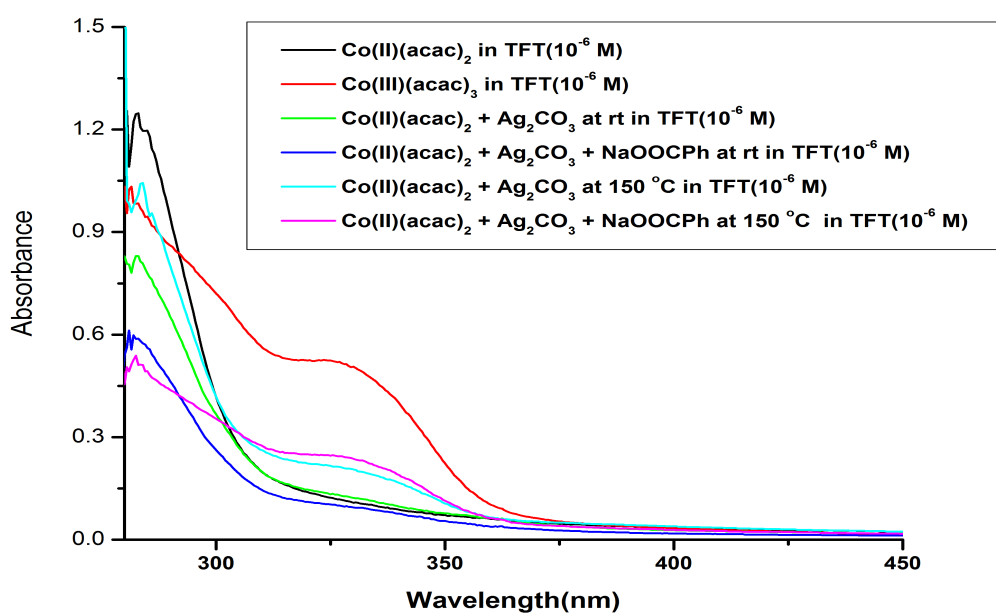
¹H NMR (500 MHz, DMSO-*d*₆): δ 12.05 (s, 2H), 2.43 (s, 2H), 1.15 (s, 6H);

¹³C NMR (125 MHz, DMSO-*d*₆): δ 177.9, 172.4, 43.6, 25.2.

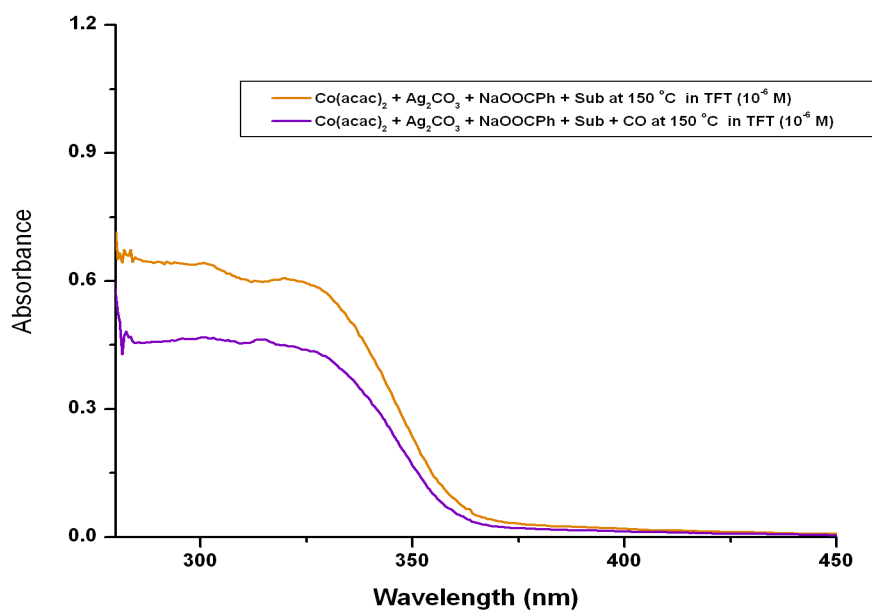
9. UV-Vis spectra of cobalt complexes:

To probe the oxidation state of the active cobalt species in the reaction media, we have monitored the progress of the reaction stoichiometrically through UV-Vis spectra. In an oven dried schlenk tube Co(acac)₂ (20 mg, 0.07 mmol), Ag₂CO₃ (40 mg, 0.15 mmol) and sodium benzoate (22 mg, 0.15 mmol) was added along with N-(quinolin-8-yl)pivalamide **1a** (17.7 mg, 0.07 mmol) in 1 mL of α,α,α- trifluoro toluene under 2 atm CO pressure. The UV-Vis spectra was measured by diluting to 10⁻⁶ M concentration. The conditions were altered as mentioned in the spectra and carried out for 2h both at r.t and 150 °C and monitored the reaction mixture by UV-Vis spectra. Analysis of the spectral data suggest that the conversion of Co(II) to Co(III) observed only using Ag₂CO₃ at 150 °C for 2h. Further there is no significant change in the spectra even after addition of the “CO” suggesting involvement of Co(III) species in the catalytic cycle.

The typical peak appears at 325 nm is responsible for the Co(III) (transition of e⁻ from t_{2g}-e_g) and it is in accordance with the literature.



⁵ Yoo, E. J.; Wasa, M.; and Yu, J. -Q. *J. Am. Chem. Soc.* **2010**, *132*, 17378–17380.



10. Crystallographic Summary:

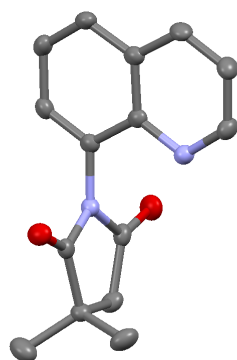


Figure S1: Structure of compound **2a** in solid state. Hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis : C₁₅H₁₄N₂O₂, MW = 254.28 g.mol⁻¹, colourless, crystal size = 0.20 x 0.12 x 0.14 mm, monoclinic, space group: P2(1)/n, a = 8.730(5) Å, b = 13.396(5) Å, c = 11.372(5) Å, T = 293 K, Z = 4, Dcalc = 1.298 g.cm⁻¹, λ = 0.71073 Å (Mo-Kα), CCD Bruker SMART APEX diffractometer, 1.9 < q < 25.4, 3766 measured reflections, structures were solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F².

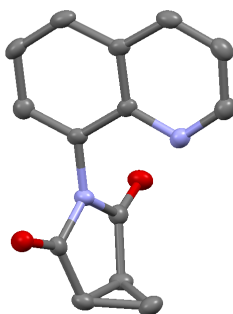
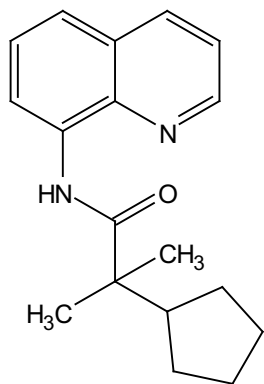
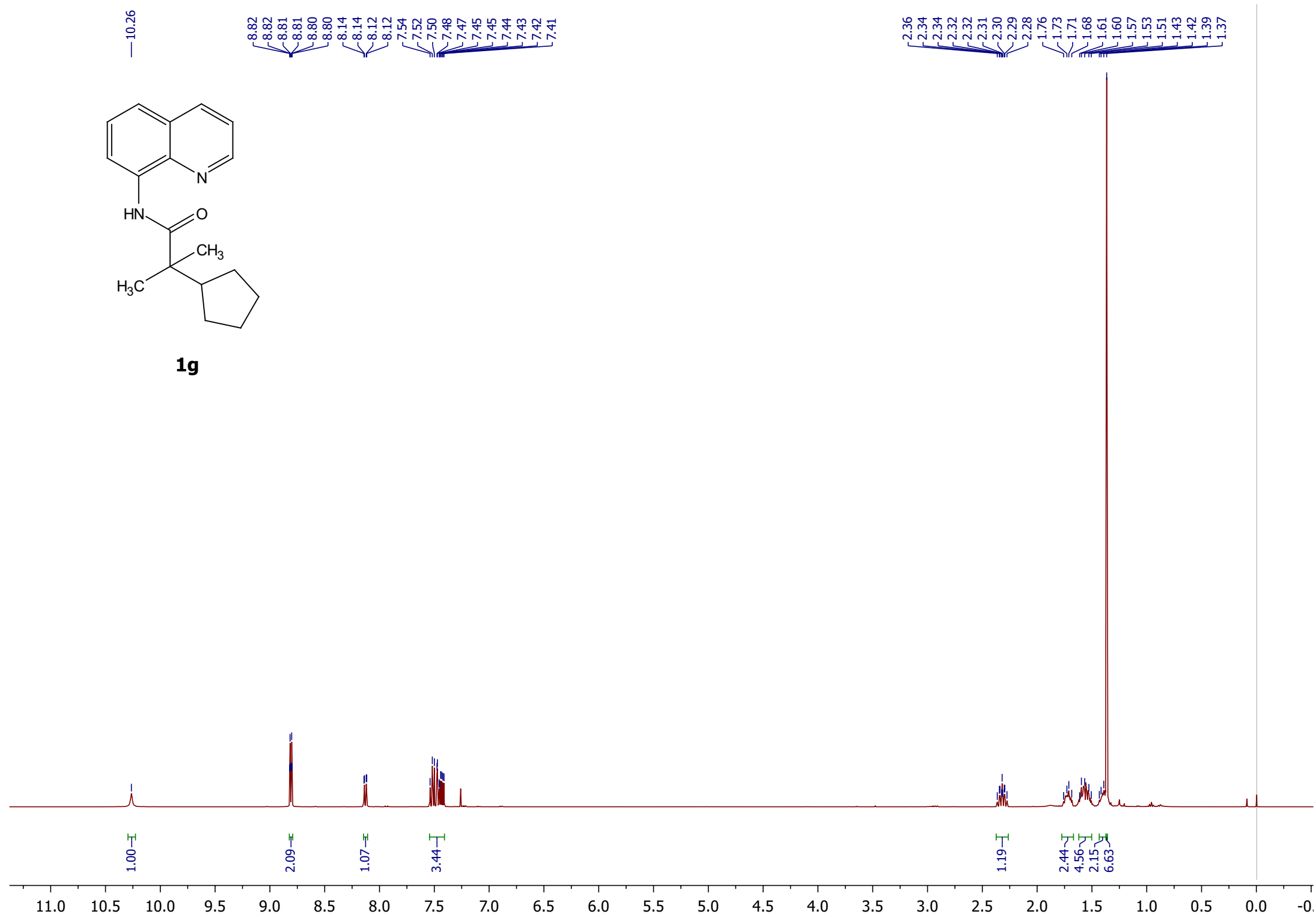


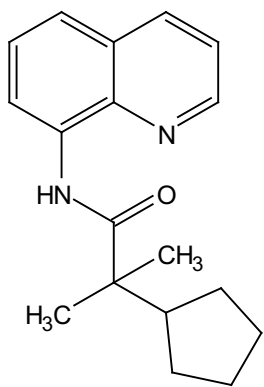
Figure S2: Structure of compound **2t** in solid state. Hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis : $C_{14}H_{10}N_2O_2$, MW = 238.24 g.mol⁻¹ colourless, crystal size = 0.20 x 0.15 x 0.14 mm, orthorhombic, space group: Pbc_a, a = 8.2000(8) Å, b = 12.4012(12) Å, c = 21.182(2) Å, T = 293 K, Z = 8, D_{calc} = 1.469 g.cm⁻³, λ = 0.71073 Å (Mo-Kα), CCD Bruker SMART APEX diffractometer, 1.9 < q < 25.4, 3766 measured reflections, structures were solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F².

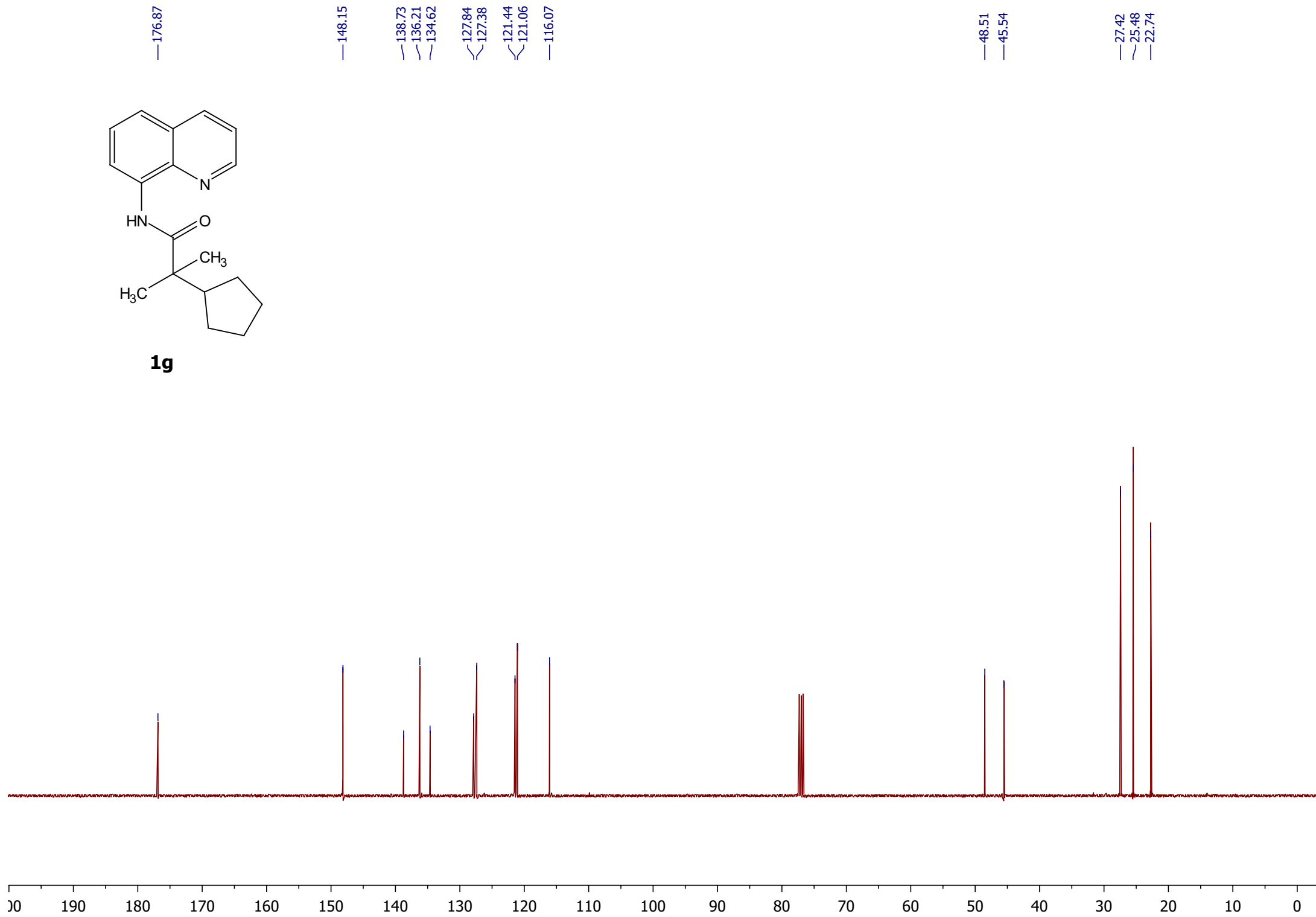


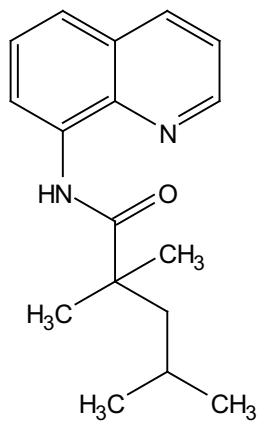
1g



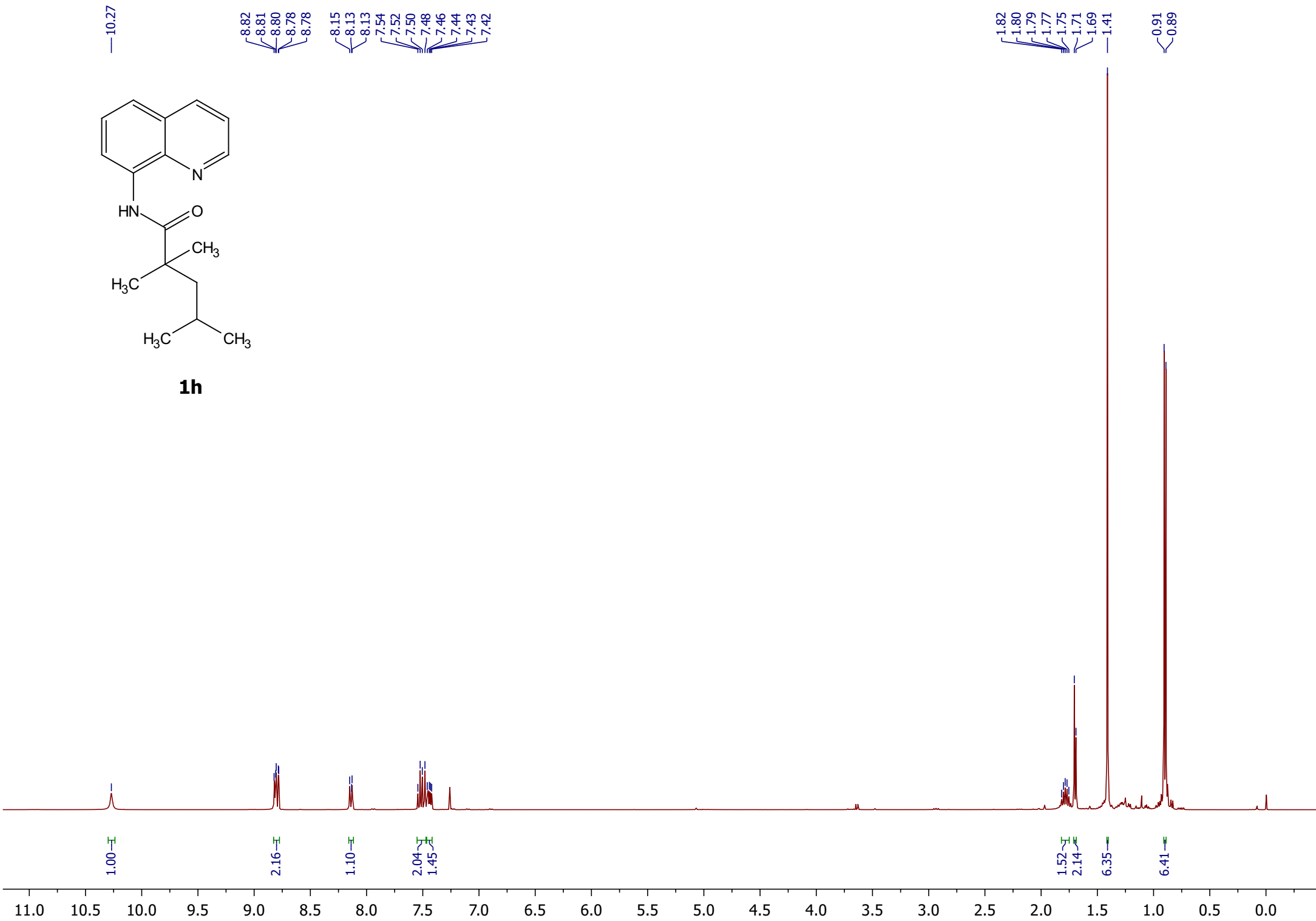


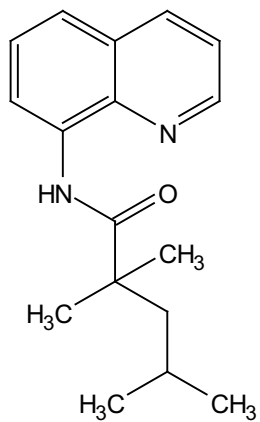
1g



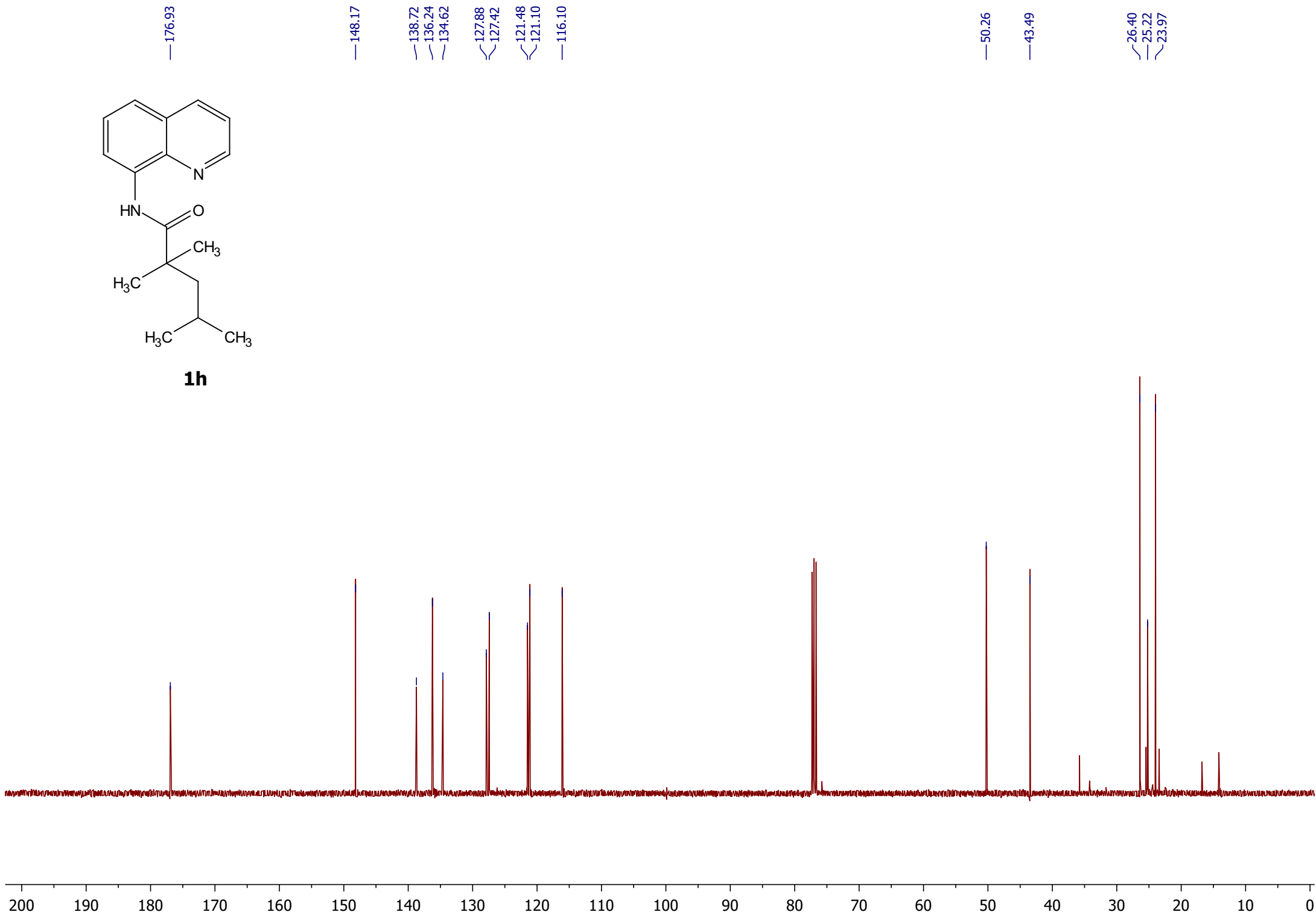


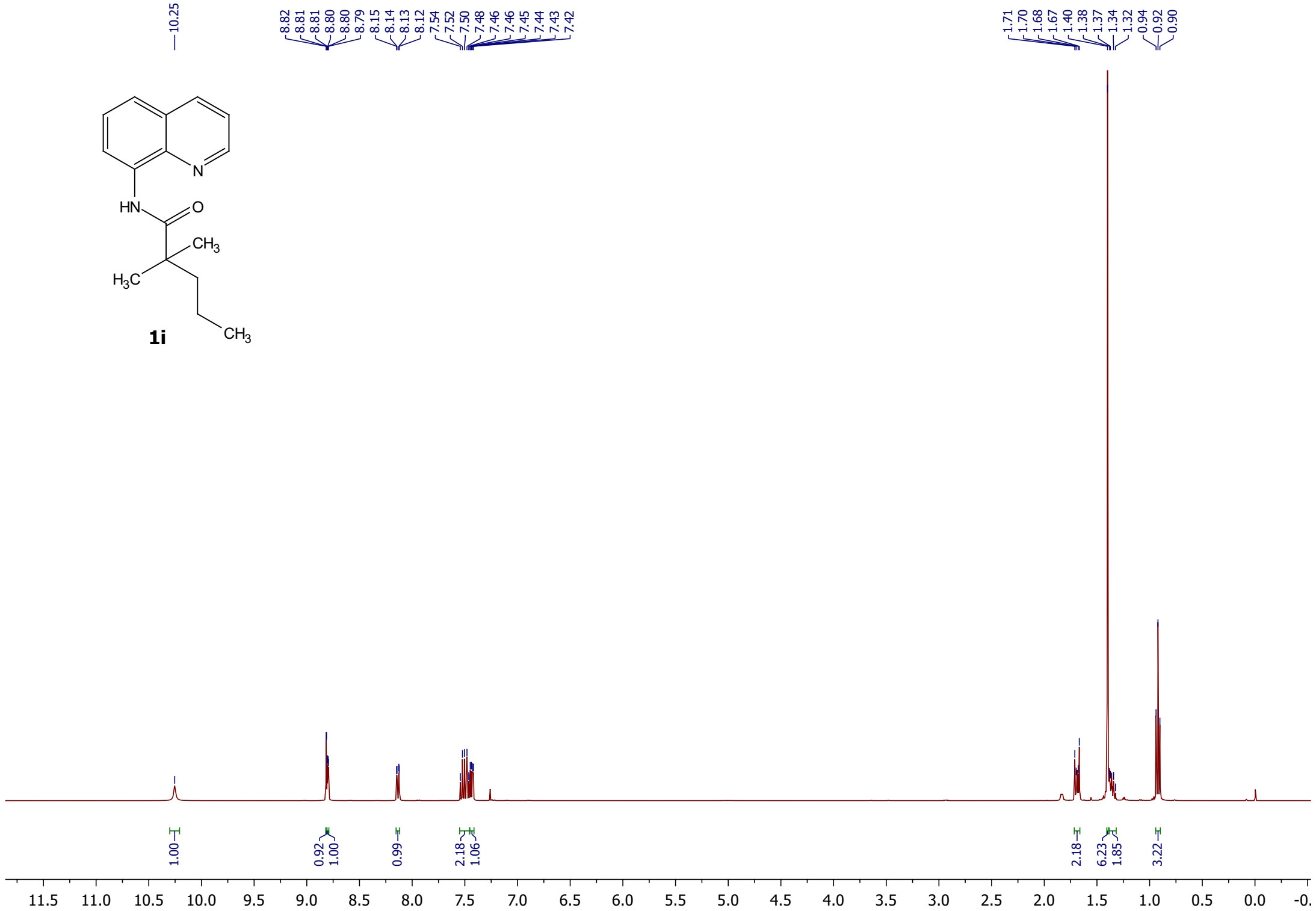
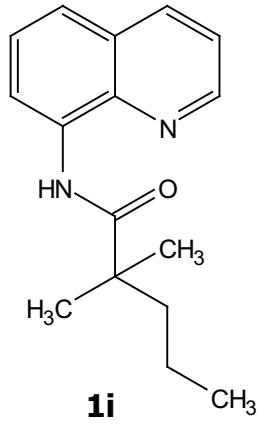
1h

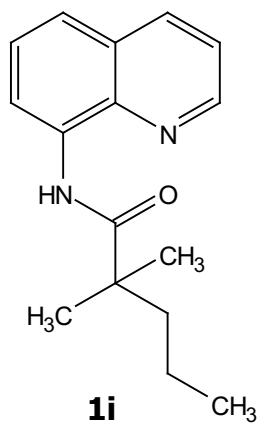




1h







—176.71

—148.16

—138.71

—136.23

—134.58

—127.85

—127.38

—121.47

—121.14

—116.08

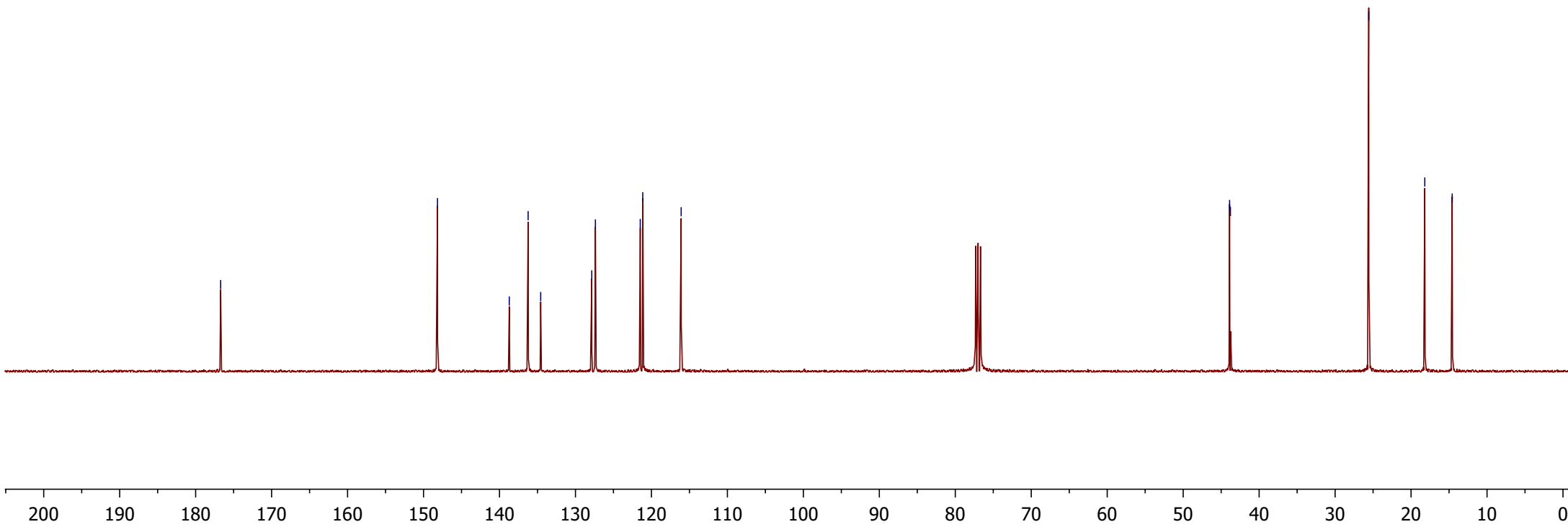
—43.89

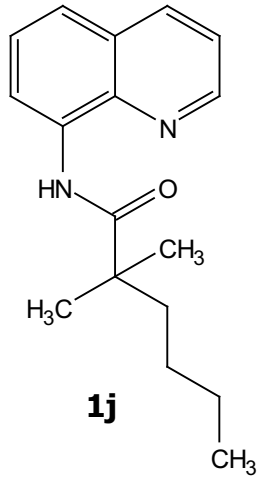
—43.78

—25.57

—18.20

—14.58





10.26

8.82
8.81
8.80

8.14
8.13
8.12
8.11

7.54
7.52
7.48

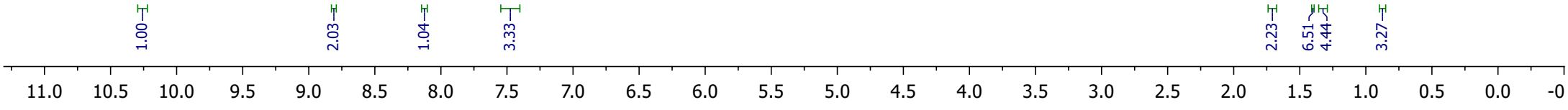
7.43
7.41
7.40

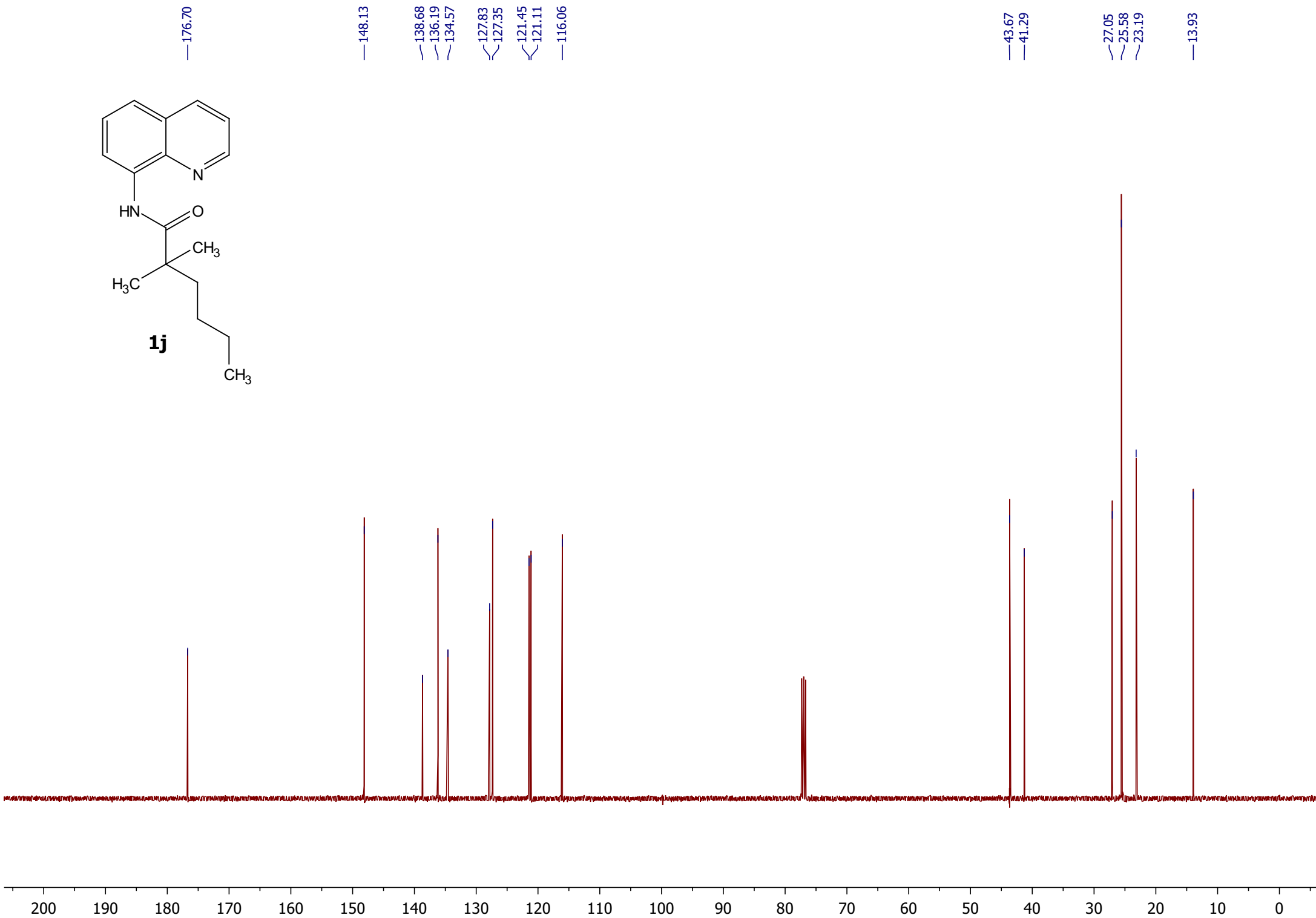
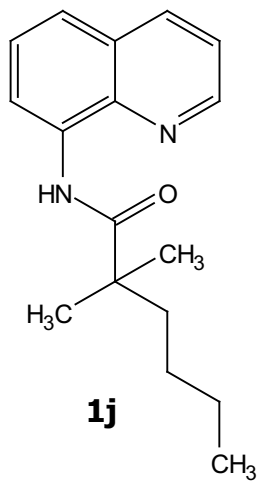
1.73
1.71
1.69

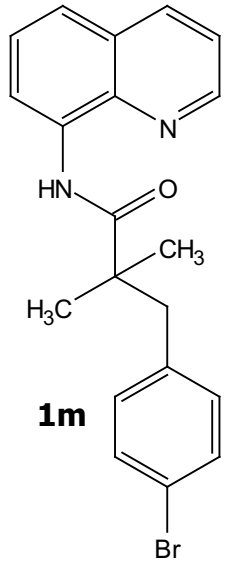
1.40

1.35
1.32

1.30
0.89
0.87
0.86



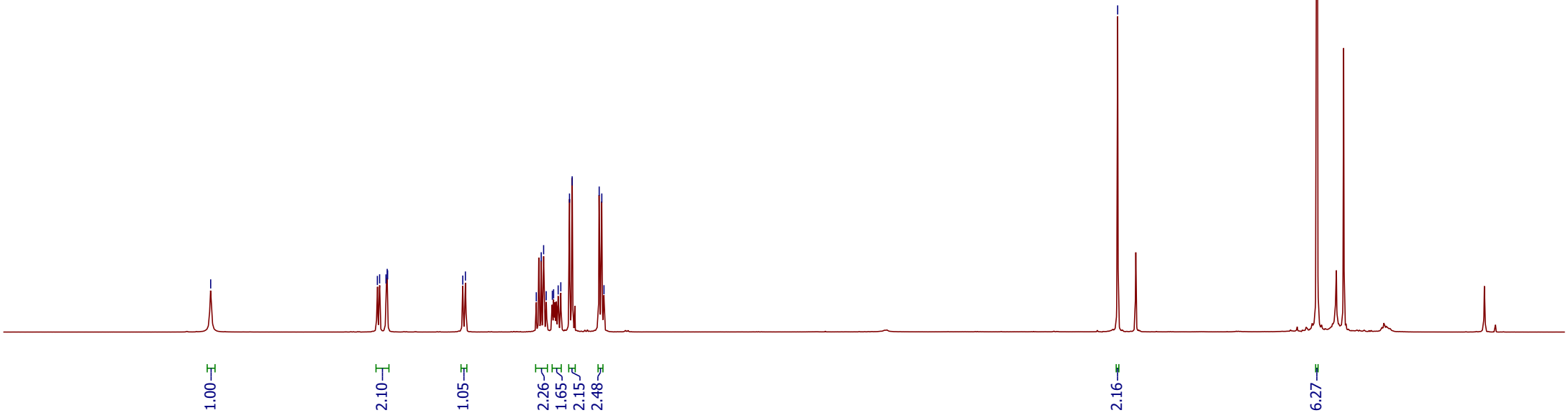




10.13
8.82
8.80
8.75
8.74
8.74
8.14
8.12
7.56
7.53
7.51
7.49
7.44
7.43
7.39
7.37
7.30
7.28
7.07
7.05
7.03

2.98

1.41



1.00

2.10

1.05

2.26

1.65

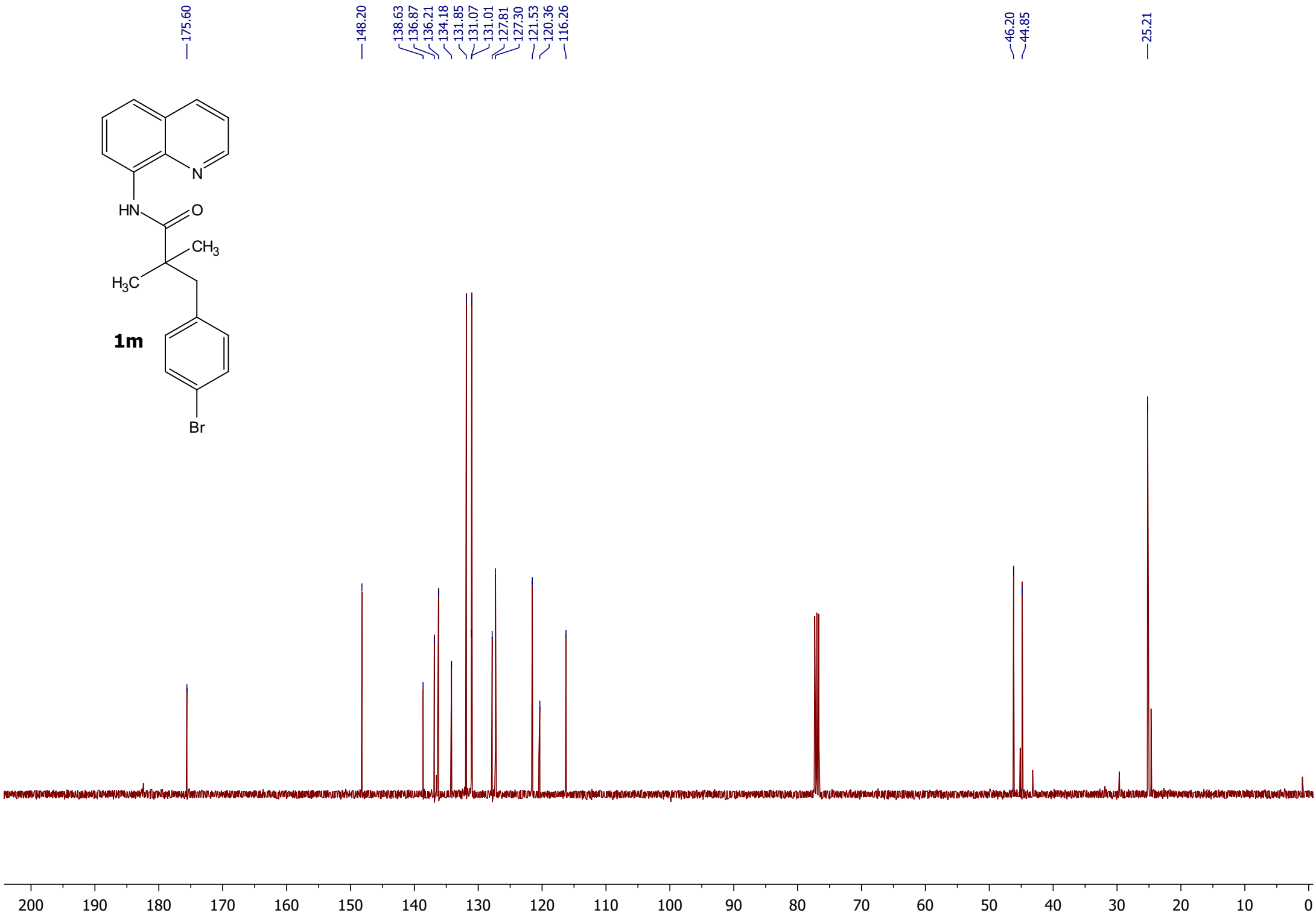
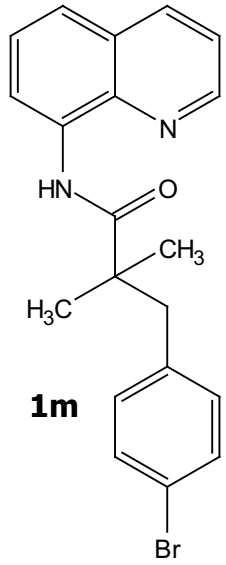
2.15

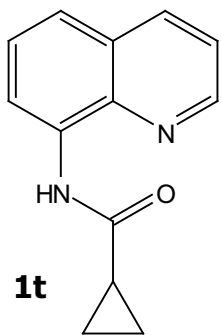
2.48

2.16

6.27

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

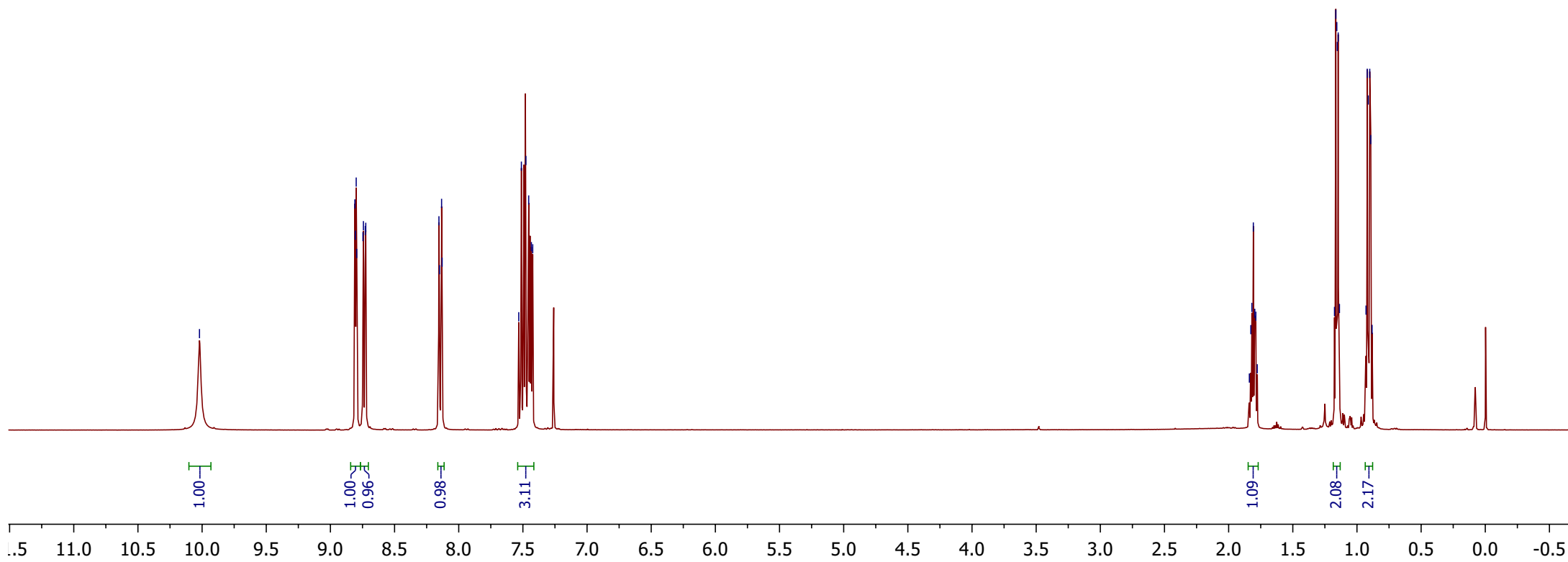


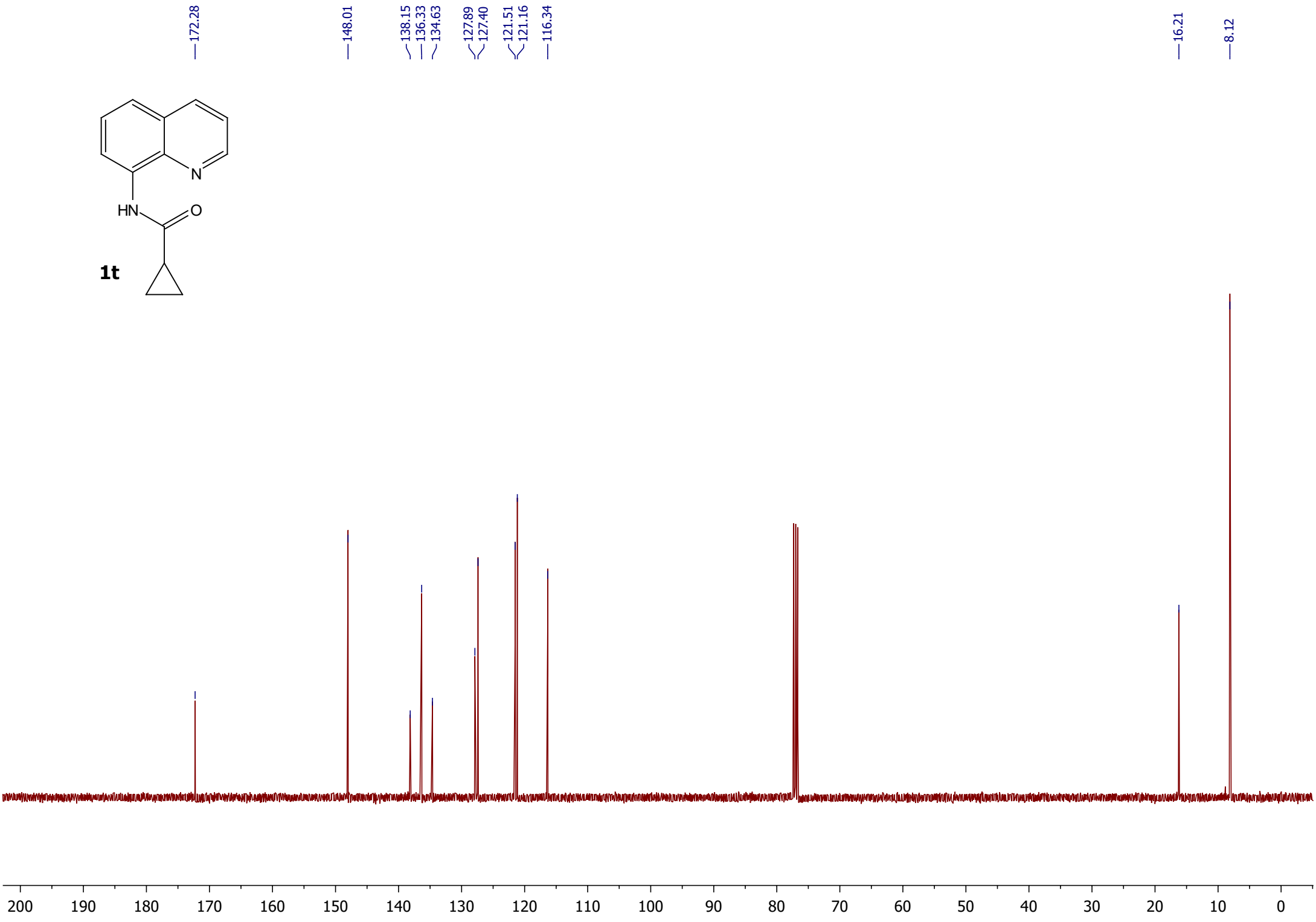
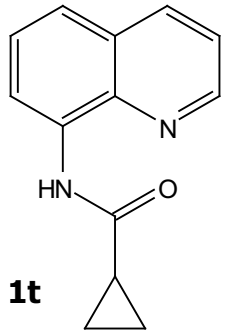


10.02

8.81
8.81
8.80
8.79
8.75
8.74
8.73
8.72
8.15
8.15
8.13
8.13
7.53
7.51
7.48
7.45
7.43
7.42

1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.18
1.16
1.16
1.15
1.15
1.14
0.93
0.92
0.91
0.90
0.89
0.88

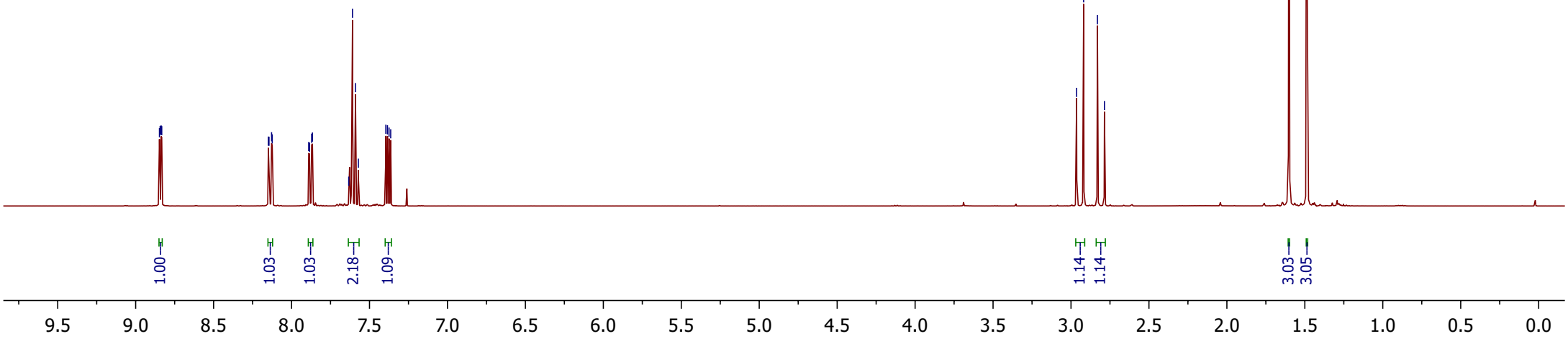
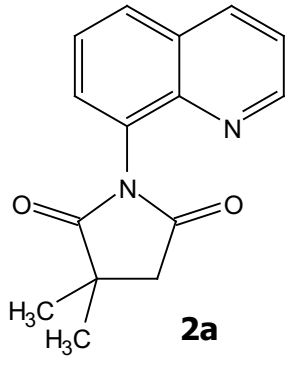


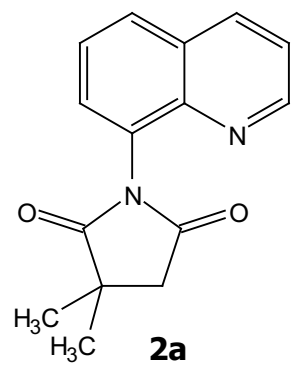


8.85
8.84
8.84
8.83
8.15
8.14
8.13
8.12
7.89
7.88
7.87
7.87
7.63
7.61
7.59
7.57
7.40
7.38
7.37
7.36

2.96
2.92
2.83
2.79

1.60
1.49





—182.87

—175.58

—150.82

—143.45

—135.92

130.14

129.49

129.22

129.01

125.85

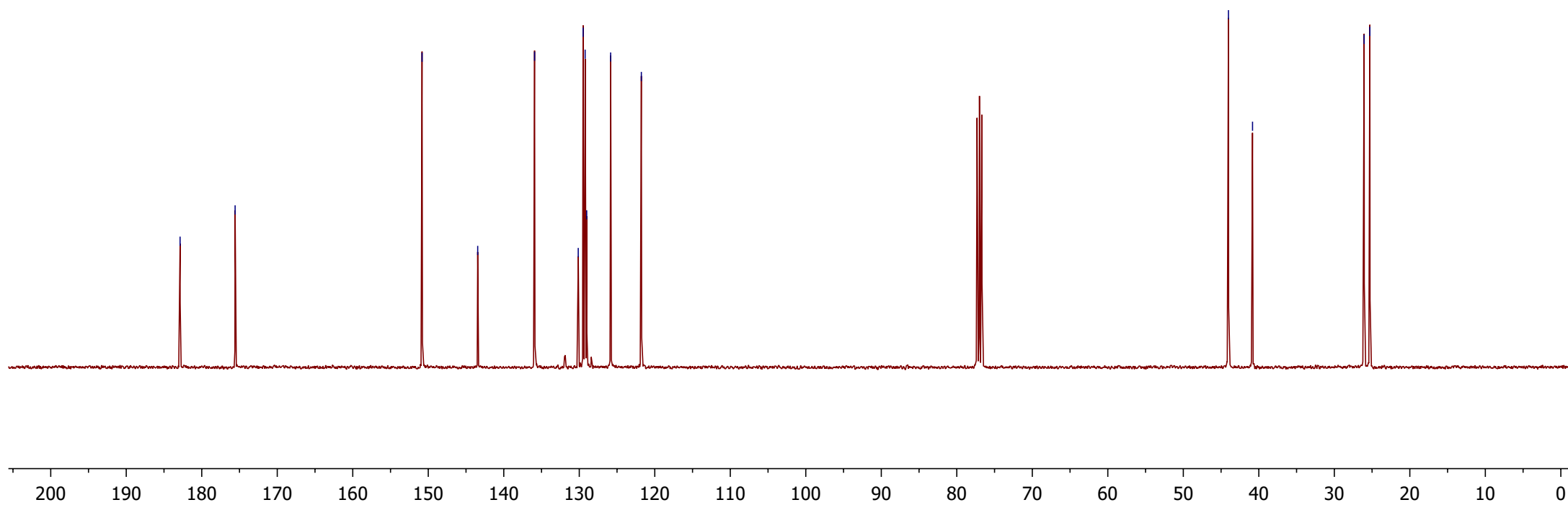
121.78

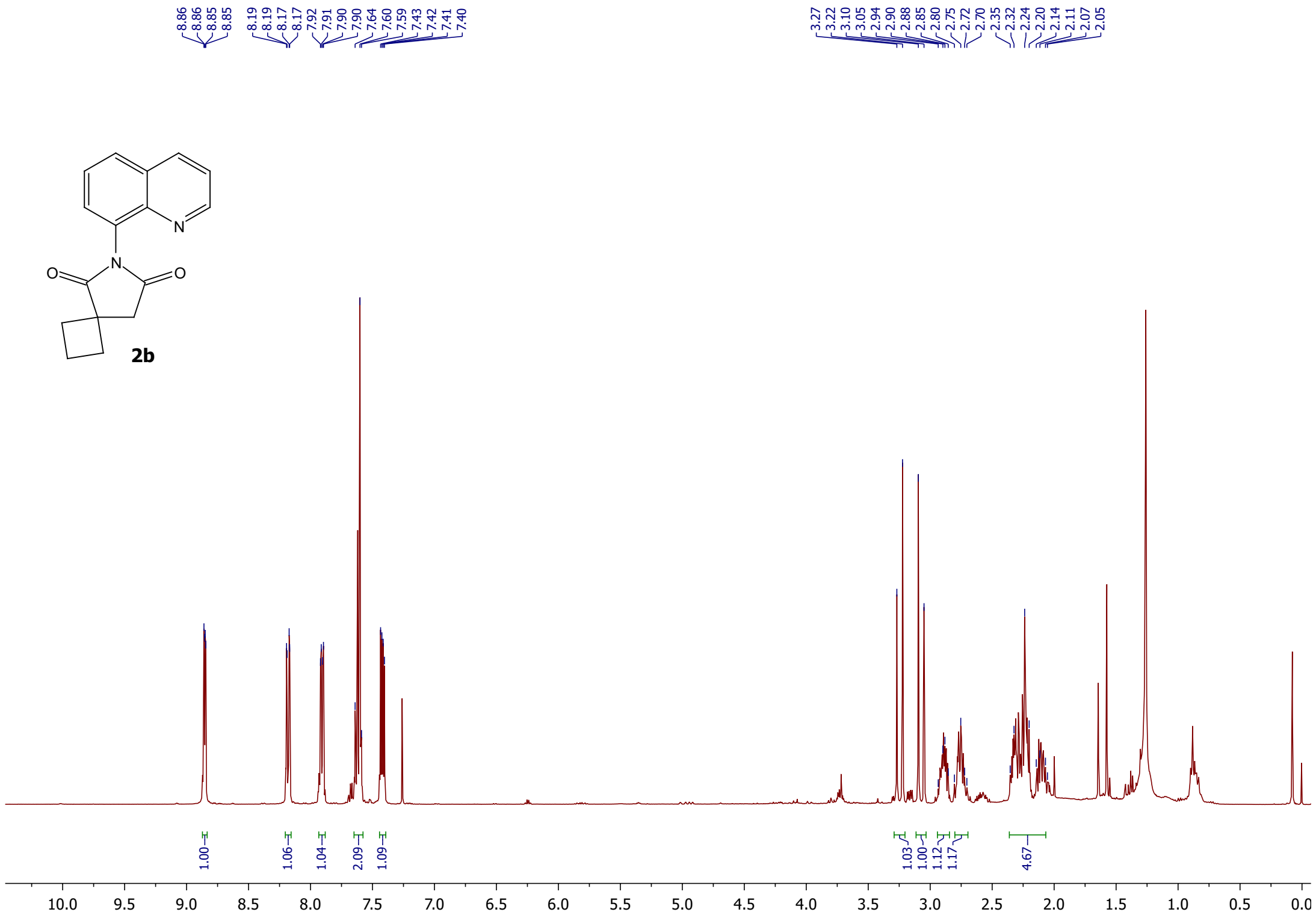
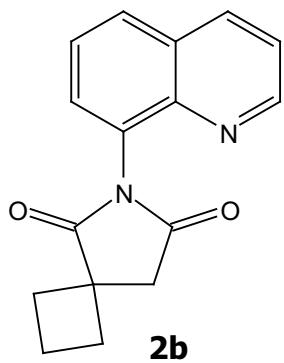
—44.02

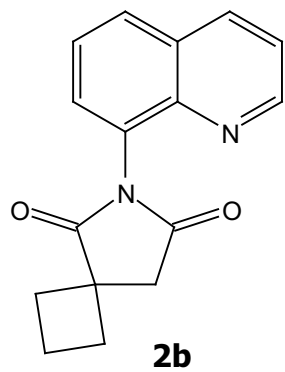
—40.83

26.05

25.29







—181.67

—175.69

—150.88

—143.45

—136.18

130.18

129.57

129.40

129.15

126.03

121.88

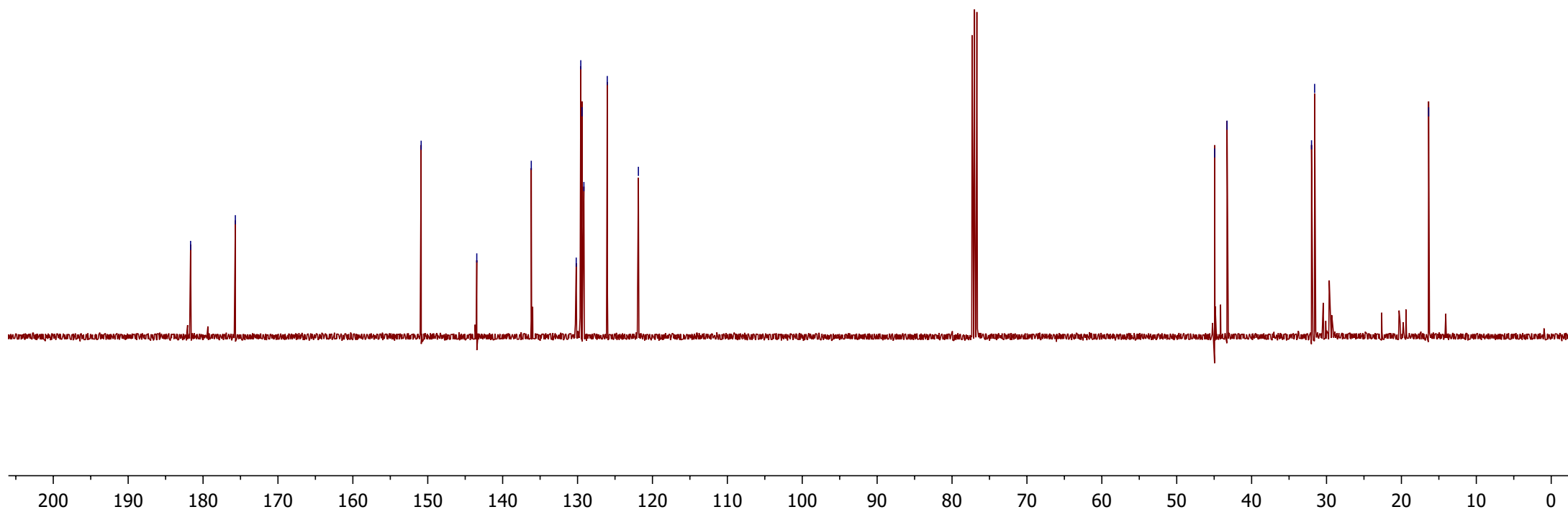
44.94

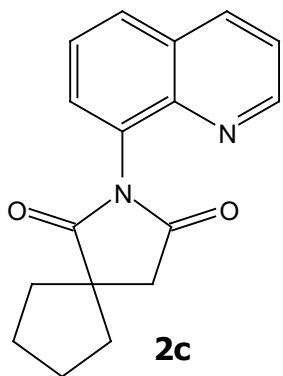
43.28

32.00

31.59

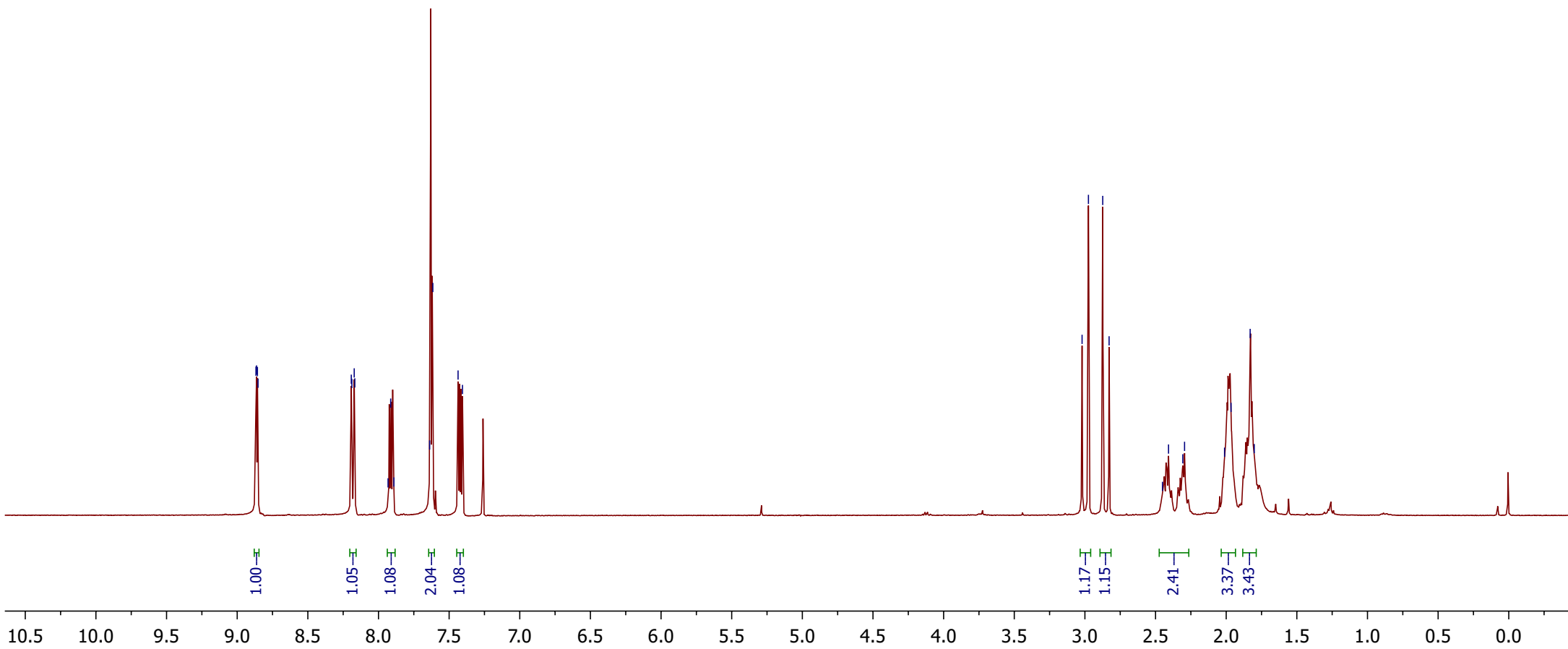
—16.37

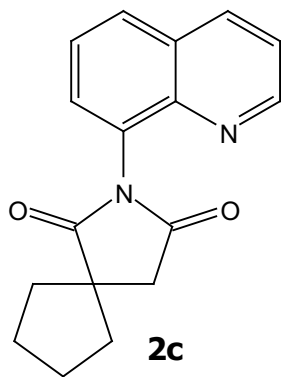




8.87
8.86
8.86
8.85
8.19
8.19
8.17
8.17
7.93
7.91
7.89
7.64
7.62
7.44
7.41

3.02
2.98
2.87
2.83
2.45
2.41
2.31
2.29
2.01
1.97
1.83
1.80





— 182.98

— 176.04

— 150.94

— 143.59

— 136.03

130.47

129.53

129.37

129.18

126.01

121.88

— 51.05

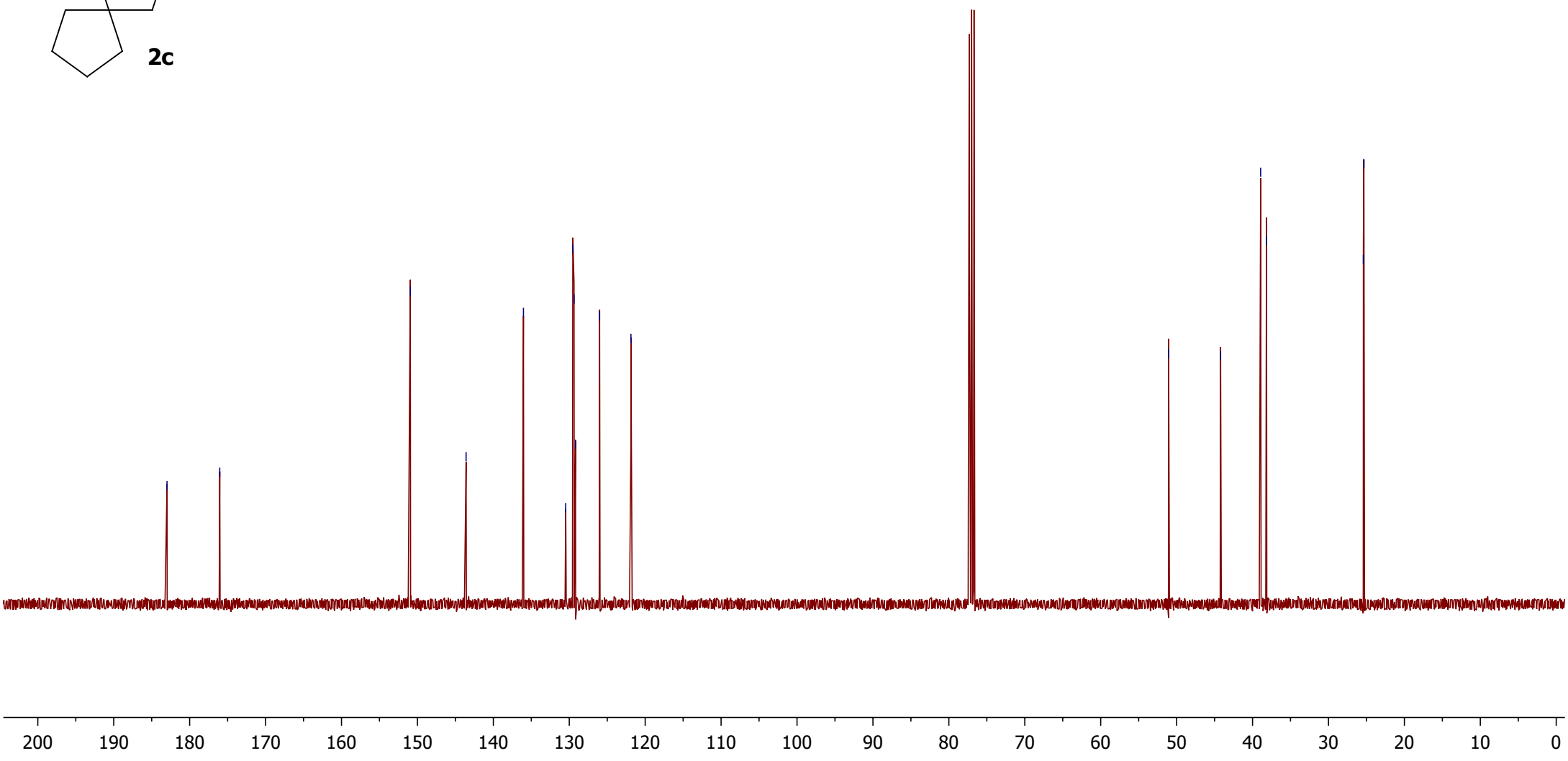
— 44.21

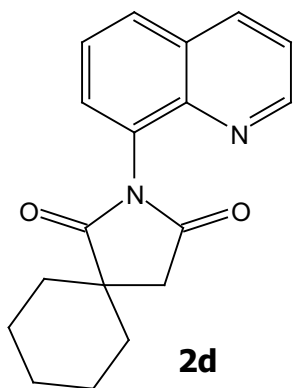
38.93

38.16

25.40

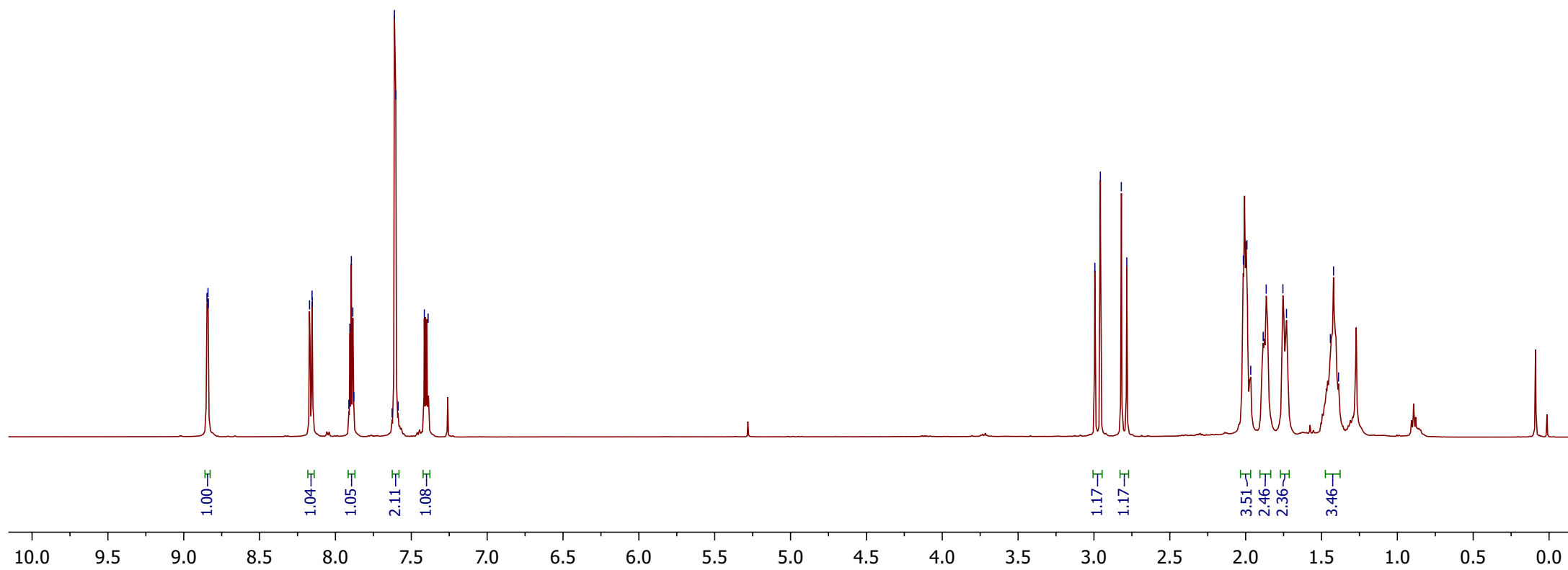
25.34

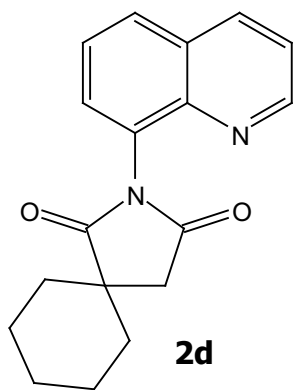




8.85
8.84
8.84
8.17
8.15
8.15
7.91
7.90
7.89
7.88
7.63
7.61
7.60
7.59
7.41
7.39

2.99
2.96
2.82
2.78
2.02
1.99
1.97
1.88
1.86
1.75
1.73
1.44
1.42
1.39





— 182.63

— 176.02

— 150.89

— 143.53

— 135.99

130.24

129.51

129.36

129.14

125.95

121.84

— 45.70

— 40.60

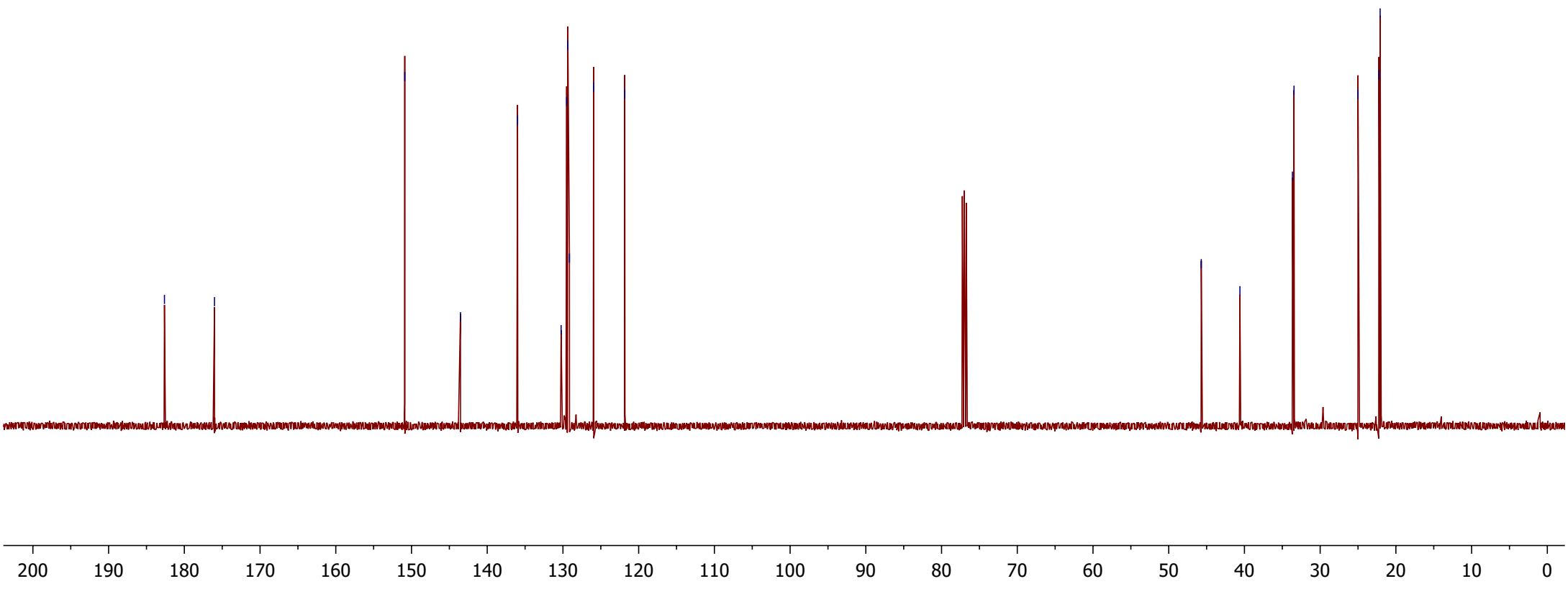
33.66

33.45

25.00

22.24

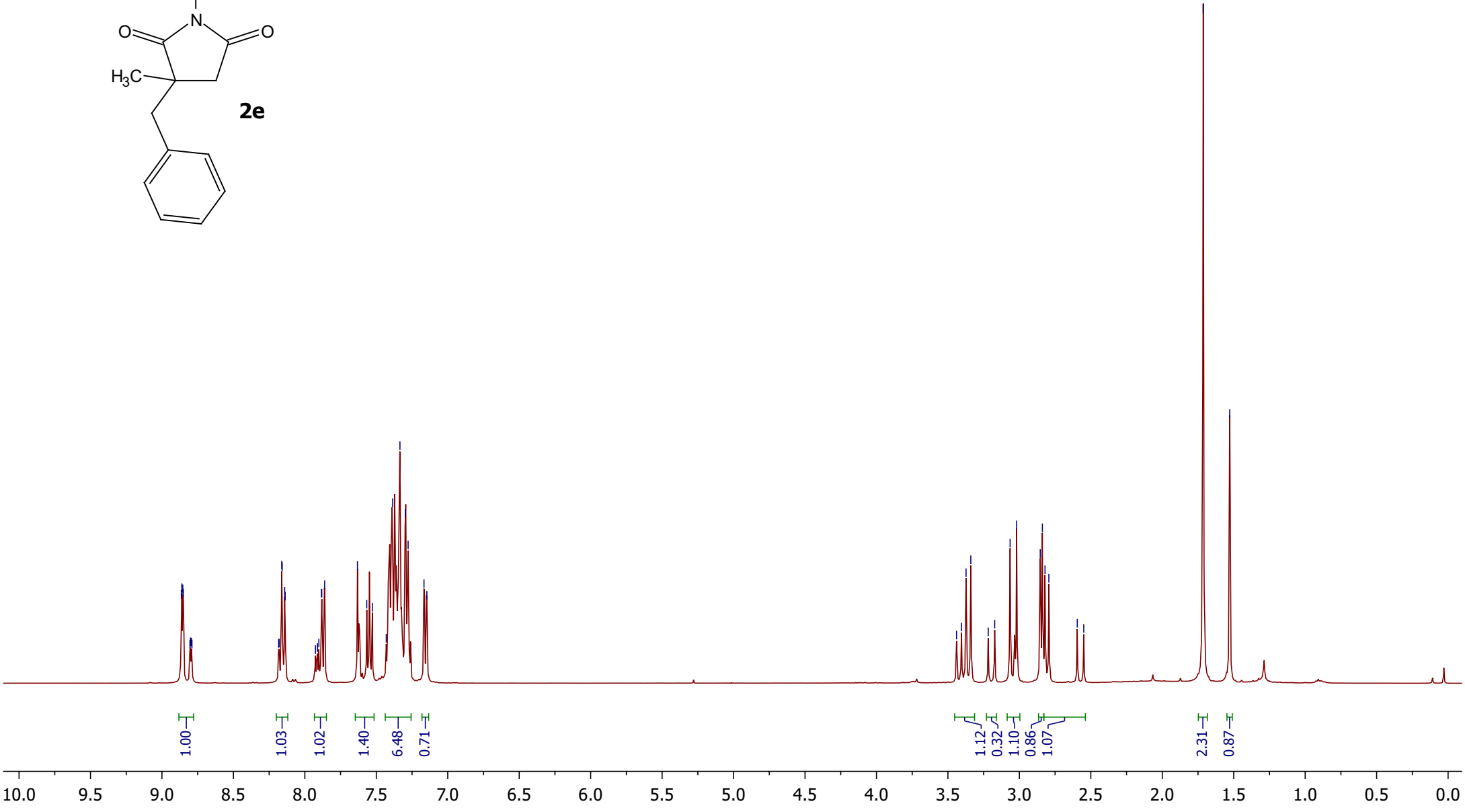
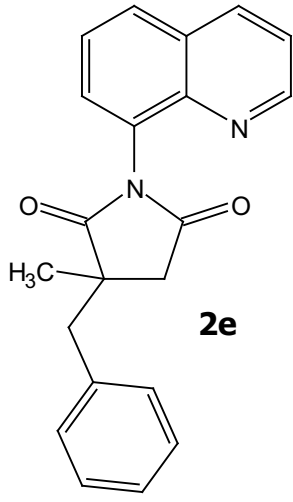
22.08



8.86
8.86
8.85
8.85
8.80
8.80
8.79
8.79
8.18
8.18
8.16
8.16
8.14
8.14
8.14
7.93
7.91
7.90
7.88
7.88
7.86
7.86
7.63
7.57
7.53
7.43
7.39
7.39
7.33
7.33
7.30
7.28
7.17
7.15

3.44
3.41
3.37
3.34
3.22
3.17
3.06
3.02
2.85
2.84
2.82
2.79
2.59
2.55

1.71
1.53



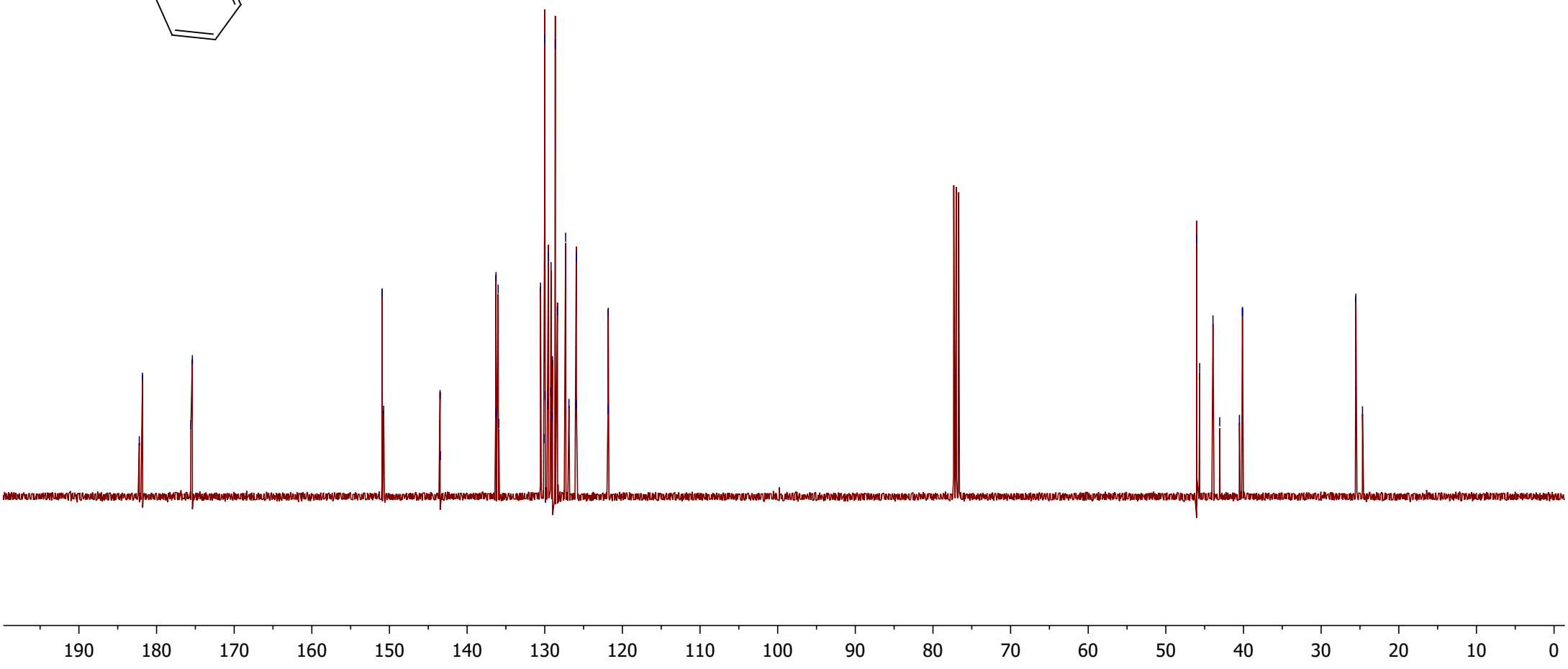
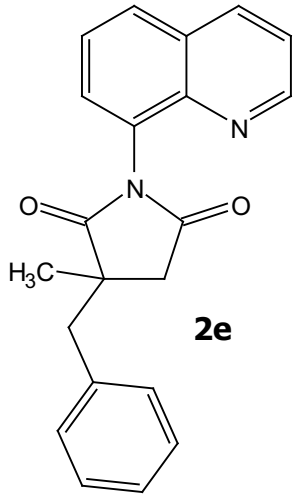
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

182.22
181.81
175.58
175.39

150.94
150.75
143.48
143.44
136.32
136.28
136.00
135.91
130.54
130.11
130.01
129.96
129.59
129.52
129.22
129.19
129.07
129.01
128.64
128.37
127.32
126.88
125.94
125.92
121.86
121.82

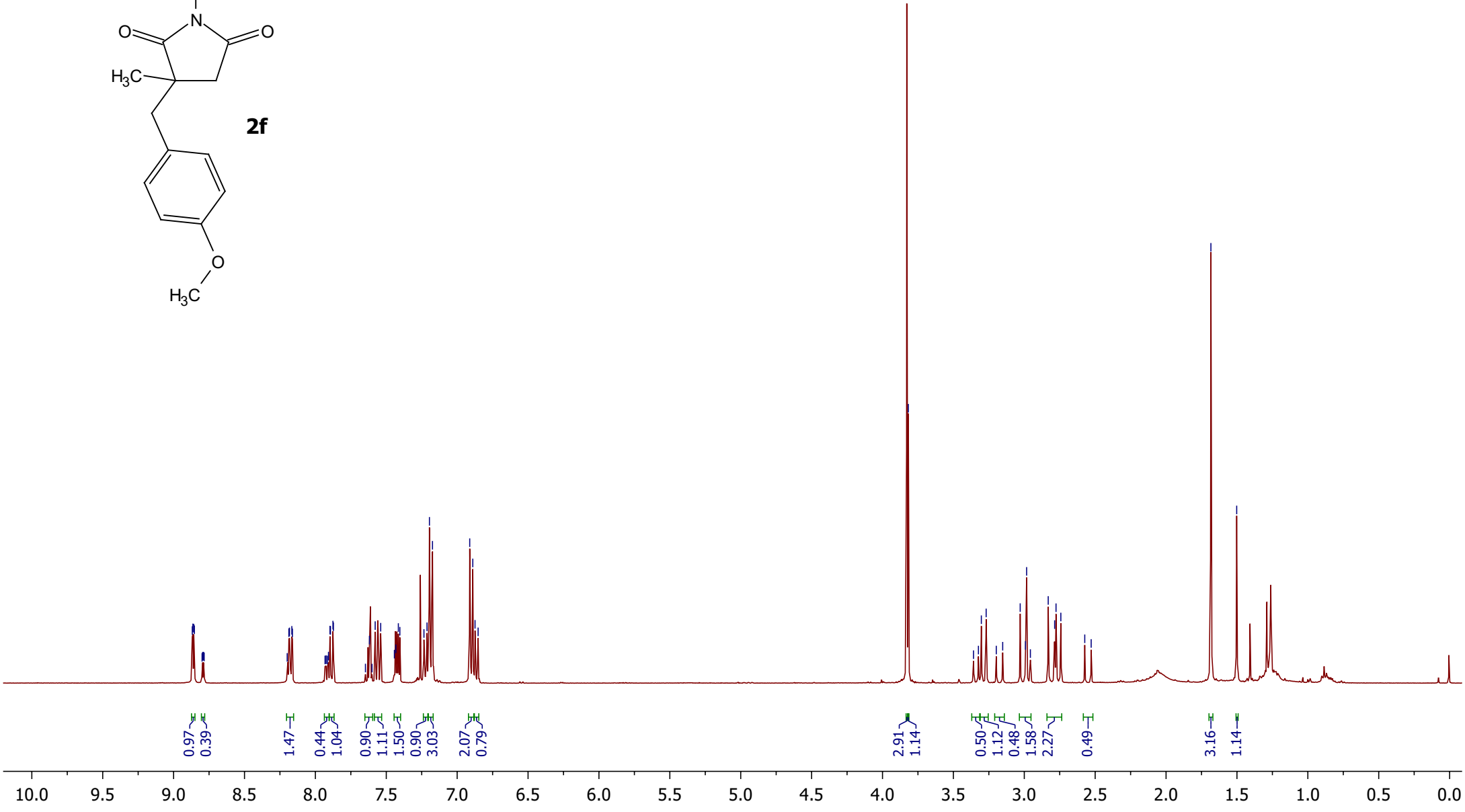
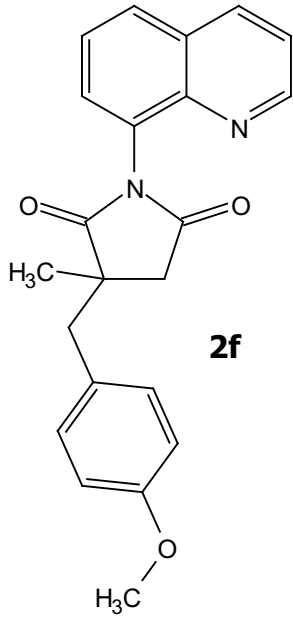
46.02
45.65
43.93
43.06
40.52
40.14

25.53
24.67

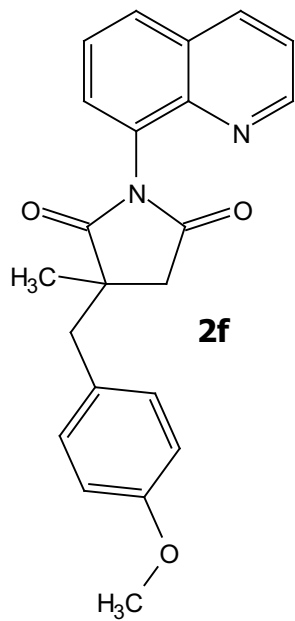


8.87
8.86
8.86
8.85
8.80
8.79
8.78
8.20
8.19
8.18
8.17
8.16
7.93
7.92
7.92
7.91
7.90
7.89
7.88
7.87
7.65
7.62
7.60
7.58
7.54
7.44
7.43
7.41
7.40
7.23
7.21
7.20
7.17
6.91
6.89
6.87
6.85

3.82
3.36
3.32
3.30
3.27
3.20
3.15
3.03
2.99
2.98
2.96
2.83
2.79
2.78
2.74
2.57
2.53
1.68
1.50



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



182.35
182.02
175.74
175.58

158.83
158.58

150.92
150.74

143.44
143.38

136.25
136.05

131.57
131.07

130.12
129.94

129.63
129.57

129.40
129.34

129.14
129.09

128.40
128.30

126.09
126.02

121.91
121.88

114.02
113.77

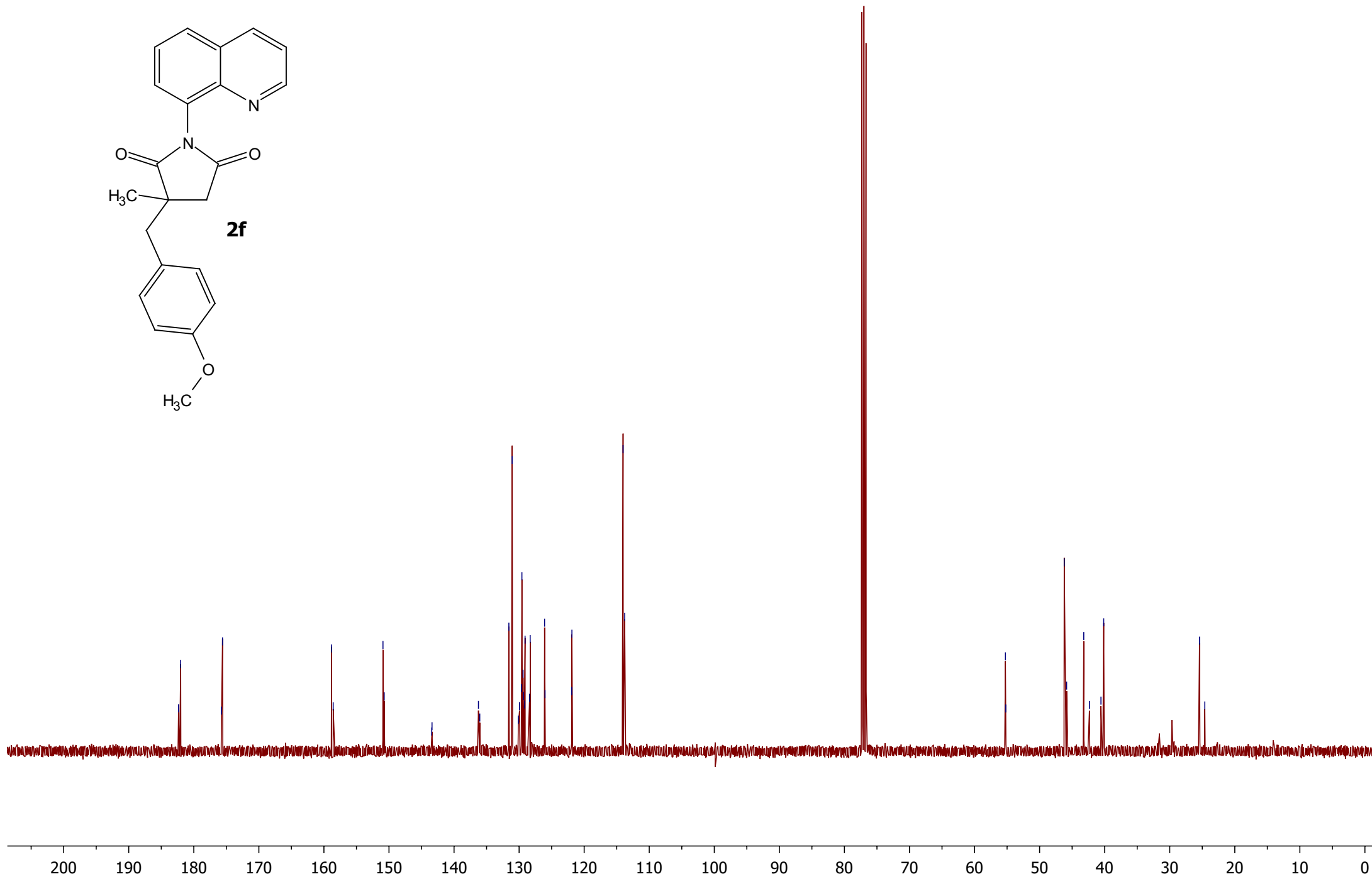
55.25
55.20

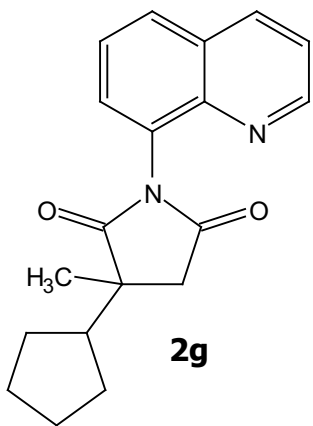
46.22
45.85

43.21
42.35

40.57
40.15

25.42
24.61



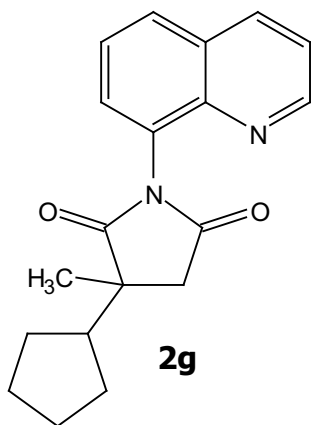


8.88
8.87
8.87
8.86
8.85
8.84
8.19
8.18
8.17
8.16
7.92
7.89
7.64
7.57
7.46
7.44
7.40

3.03
2.98
2.88
2.84
2.77
2.73
2.63
2.58
2.49
2.42
2.35
1.97
1.81
1.70
1.64
1.60
1.50
1.43
1.34



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



182.55
182.54

176.32
176.19

151.00
150.78

143.59
143.57

136.07
135.94

130.37
130.25

129.61
129.52

129.34
129.27

129.16
129.12

126.01
125.96

121.91
121.86

46.99
46.98

46.42
46.12

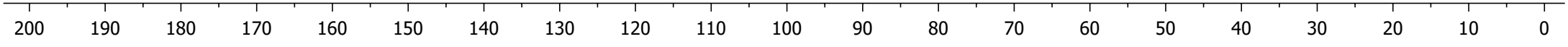
39.42
39.00

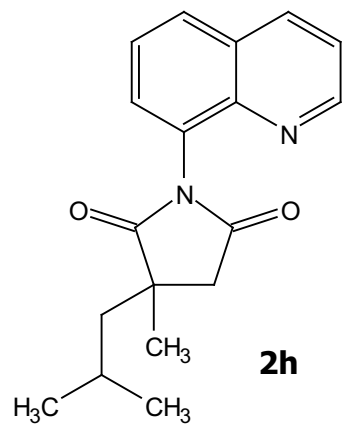
27.91
27.83
27.78

27.67
25.91

25.62
25.54

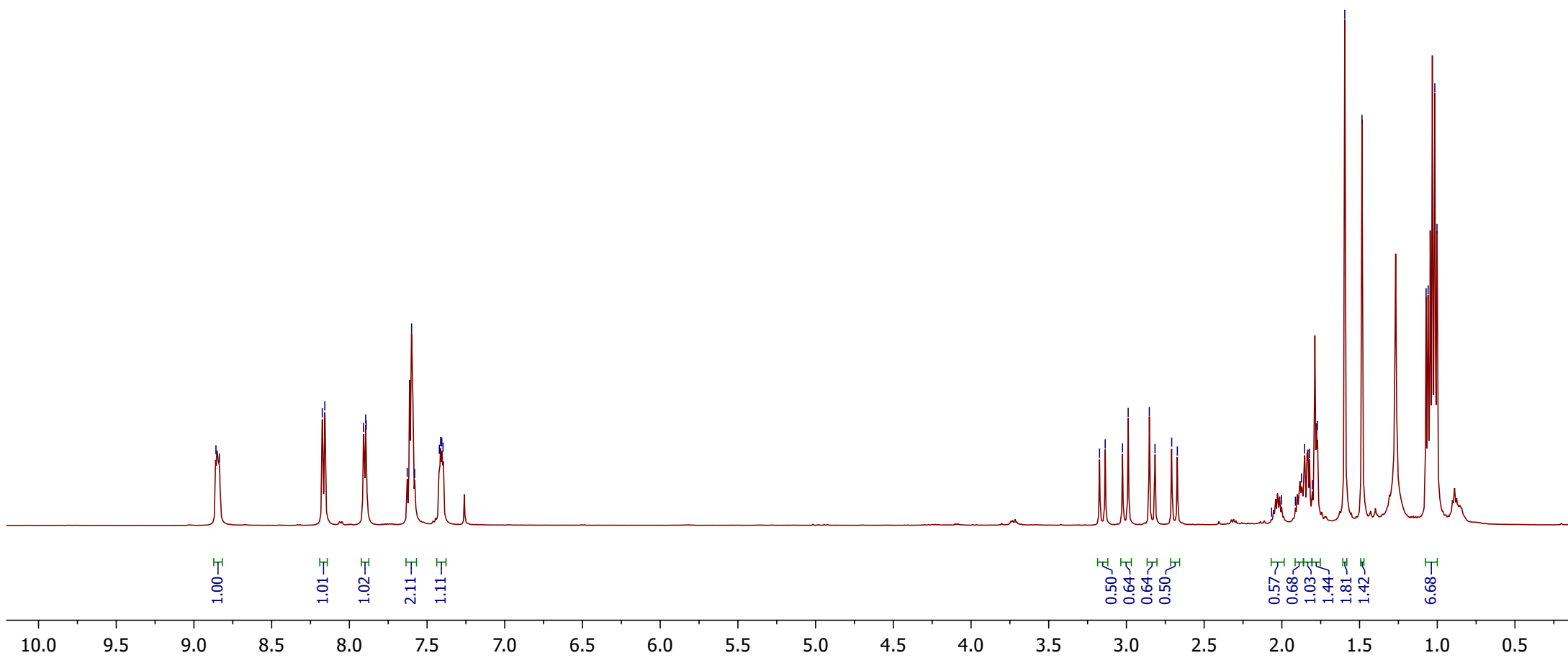
25.36
24.41
24.34

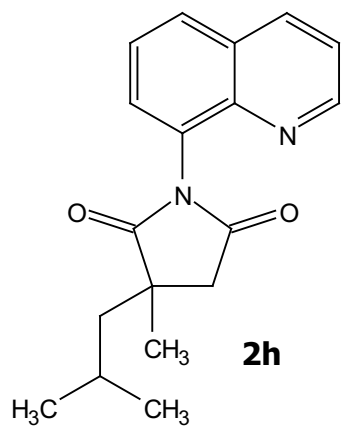




8.86
8.84
8.17
8.16
7.91
7.90
7.89
7.63
7.60
7.58
7.42
7.41
7.41
7.40

3.17
3.14
3.03
2.99
2.85
2.82
2.71
2.67
2.07
2.00
1.91
1.87
1.85
1.82
1.80
1.77
1.60
1.48
1.07
1.06
1.02
1.00





182.79
182.72

175.98
175.79

150.90
150.70

143.74
143.70

135.97
135.94

130.50

129.51

129.48

129.29

129.24

129.19

125.97

125.96

121.85

46.13

46.06

44.47

44.40

42.11

41.77

25.97

25.66

25.25

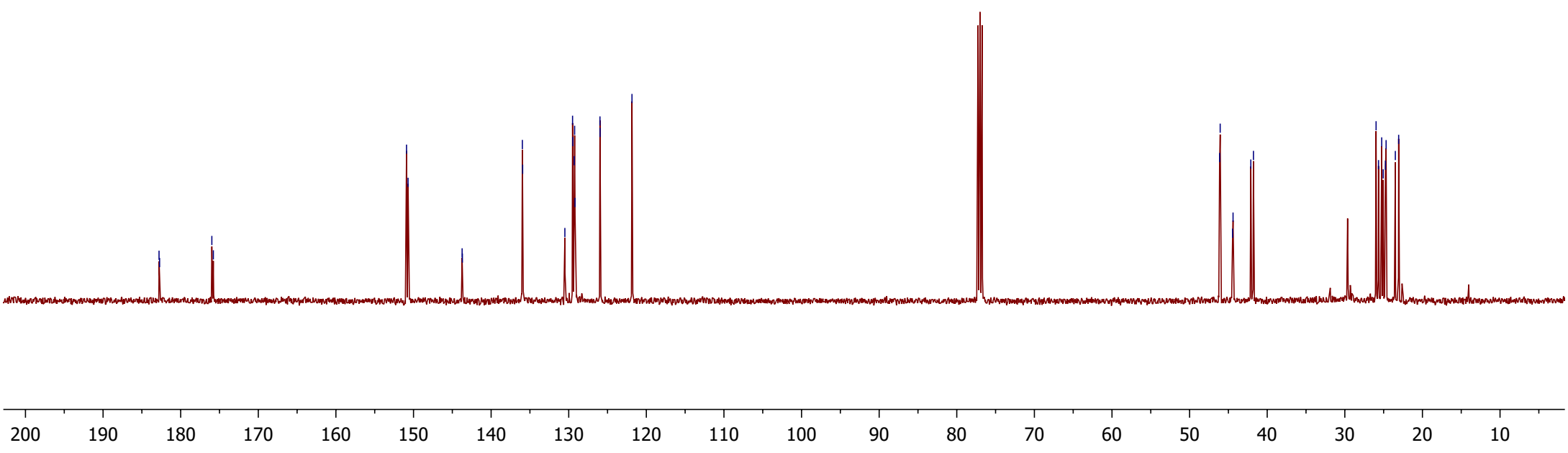
25.06

24.76

24.68

23.49

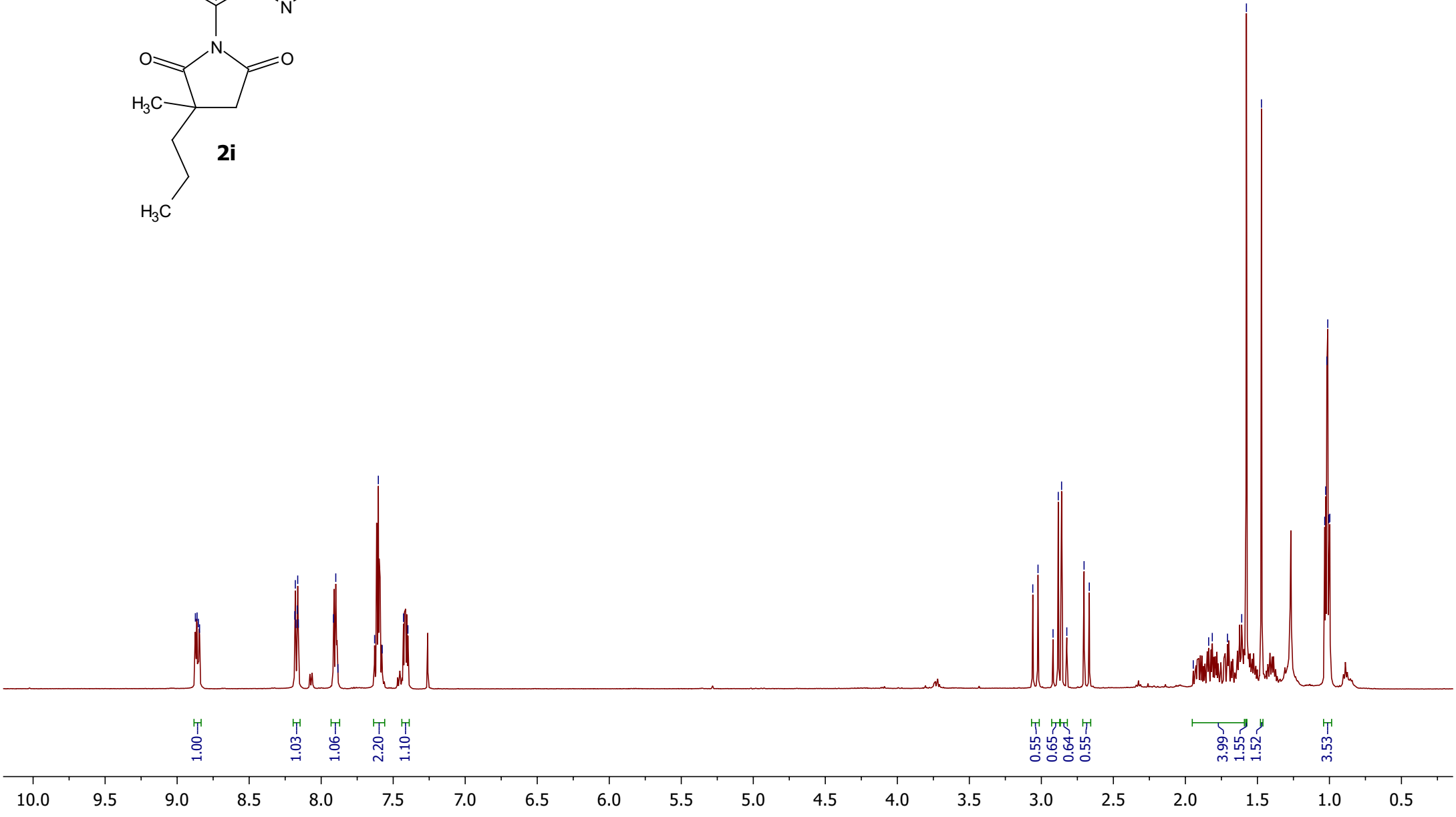
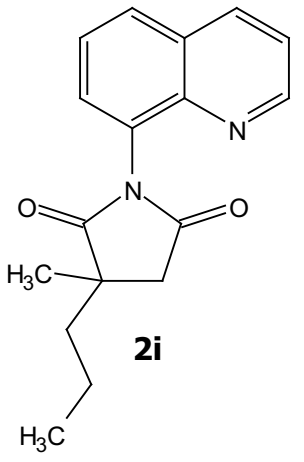
23.06

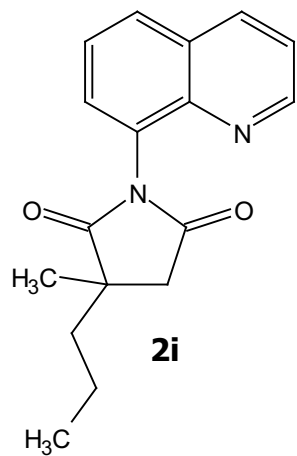


8.87
8.86
8.85
8.84
8.18
8.18
8.17
8.16
8.16
7.91
7.90
7.88
7.63
7.60
7.58
7.43
7.40

3.06
3.02
2.92
2.88
2.86
2.82
2.70
2.67

1.95
1.84
1.81
1.71
1.61
1.58
1.47
1.03
1.02
1.01
1.00
1.00





182.59
182.53

175.98
175.89

150.95
150.80

143.60

136.06
135.98

129.57
129.52

129.37
129.32

129.18
129.15

125.98
125.97

121.89
121.85

44.66
44.62

41.68
41.52

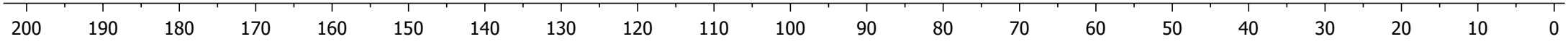
40.65
40.62

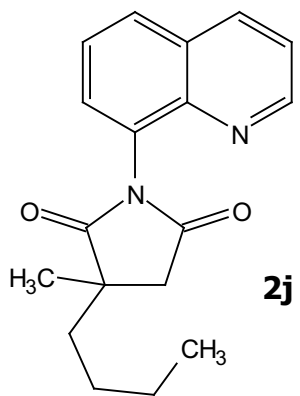
29.64

24.76
24.33

17.91
17.75

14.43
14.31

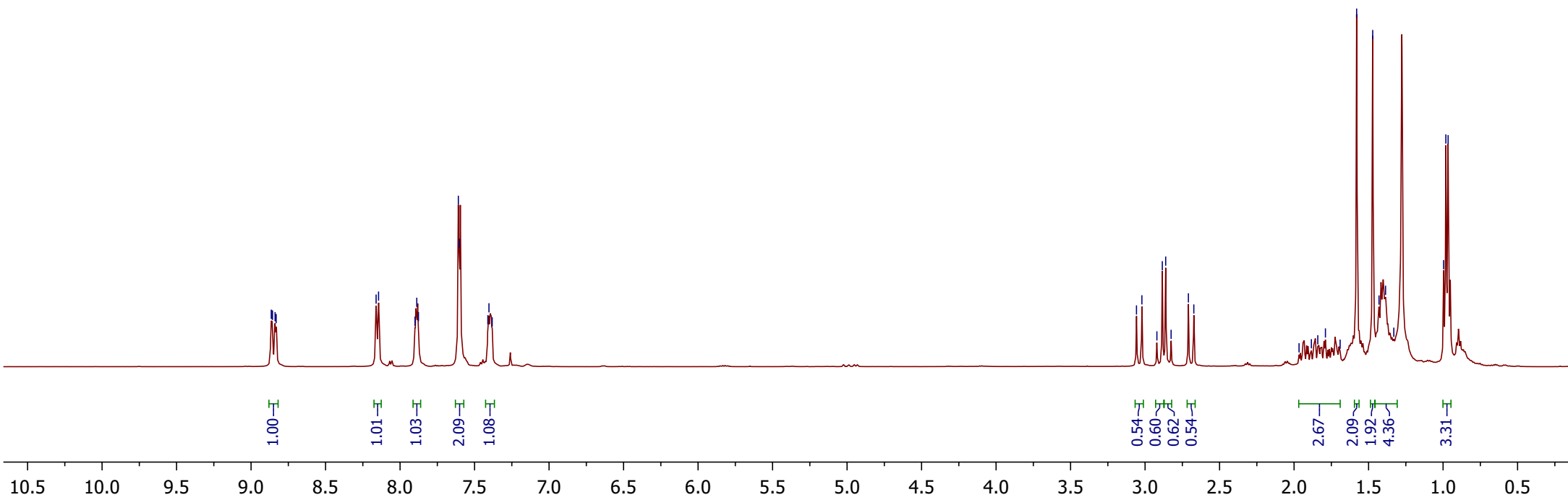


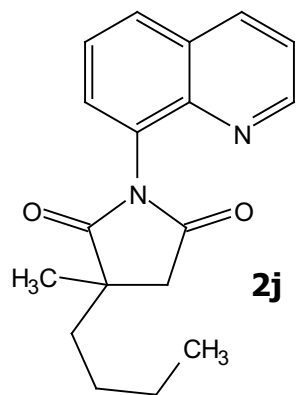


8.86
8.86
8.84
8.83

8.16
8.14
7.90
7.89
7.88
7.61
7.60
7.41
7.40
7.38

3.06
3.02
2.92
2.88
2.86
2.83
2.71
2.67
1.97
1.88
1.84
1.79
1.69
1.58
1.47
1.43
1.39
1.33
1.00
0.98
0.97





182.51
182.44

175.83
175.75

150.86
150.64

143.63

135.97
135.90

130.52
130.41

129.48
129.42

129.32
129.29

129.14
129.12

125.90
121.81
121.79

44.55
44.53

41.69
41.54

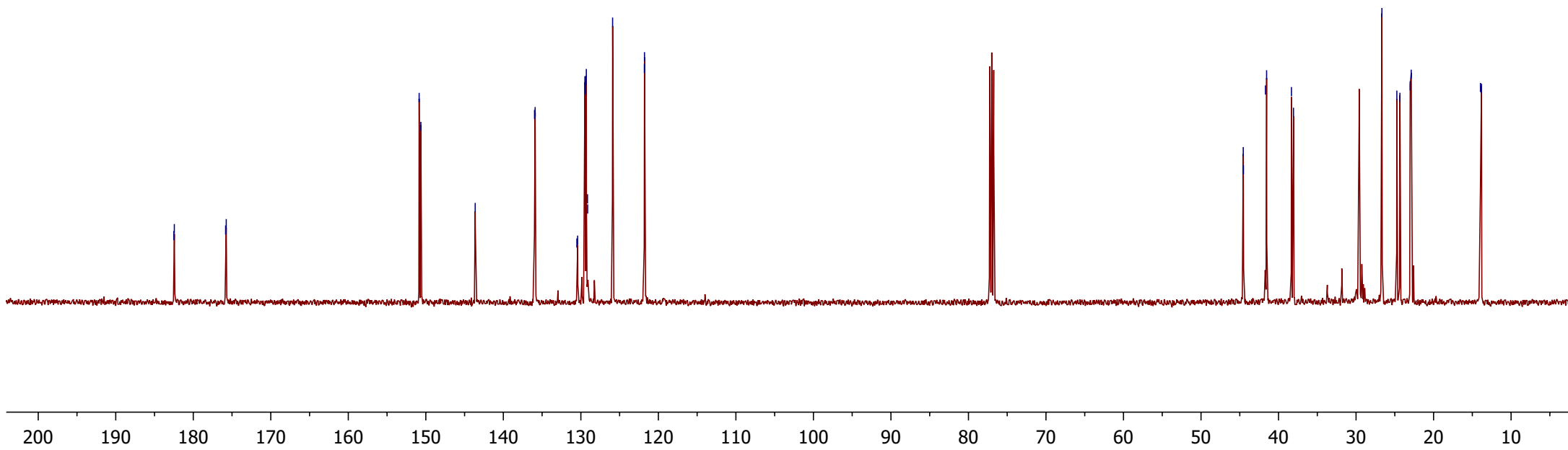
38.33
38.07

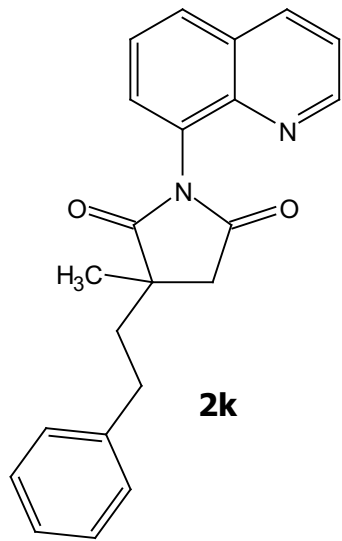
26.67
24.74

24.34
23.02

22.88

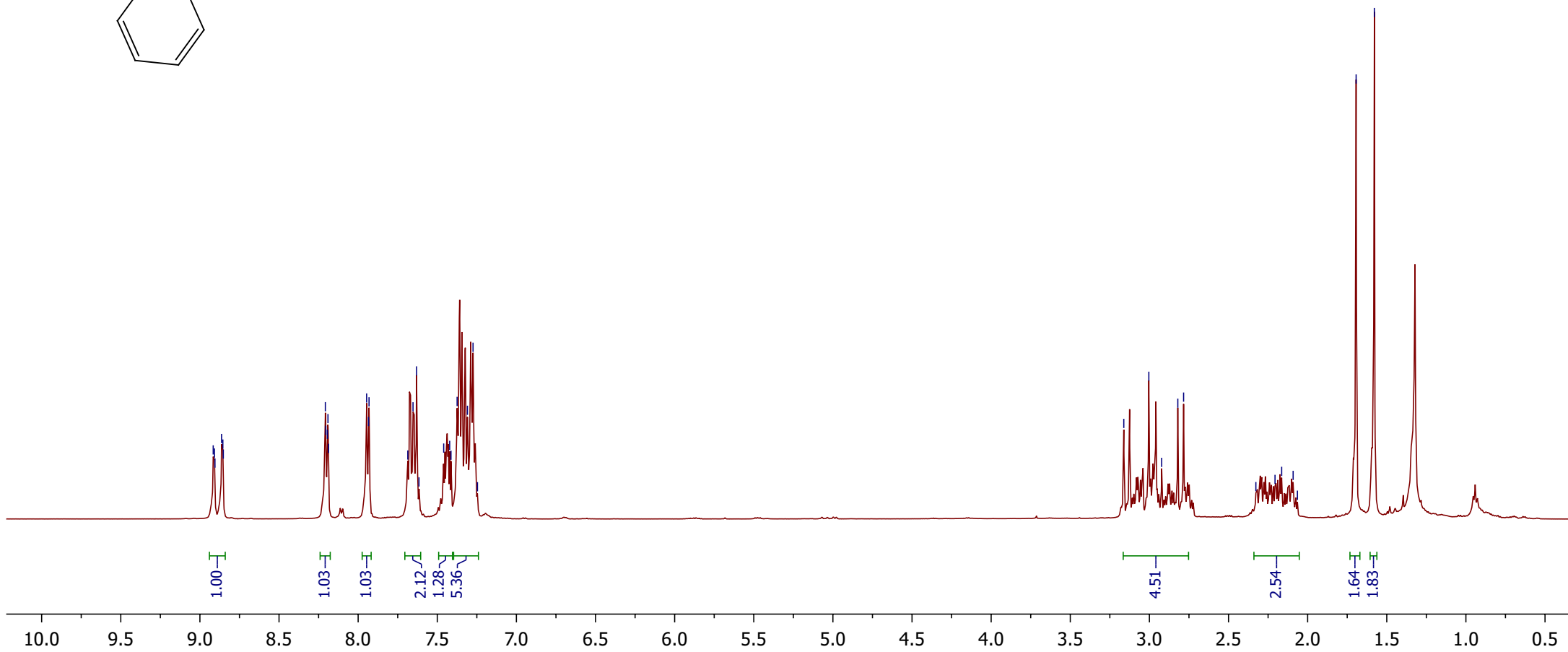
13.95
13.82

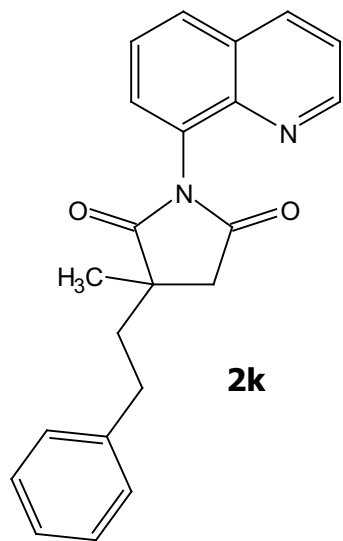




8.92
8.91
8.90
8.86
8.86
8.85
8.21
8.20
8.19
8.19
8.19
7.95
7.93
7.69
7.65
7.65
7.63
7.62
7.46
7.42
7.41
7.37
7.31
7.27
7.25

3.16
3.00
2.92
2.82
2.78
2.33
2.21
2.16
2.09
2.06
1.69
1.58





182.14
182.12

175.70
175.65

150.91
150.79

143.48
141.67

140.81

136.06
136.01

130.30
130.13

129.85
129.59

129.57
129.36

129.30
129.12

128.52
128.43

128.32
128.26

126.18
125.94

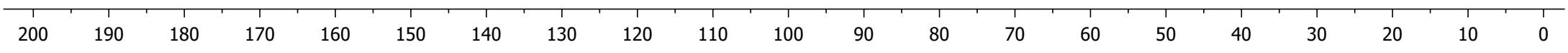
121.87

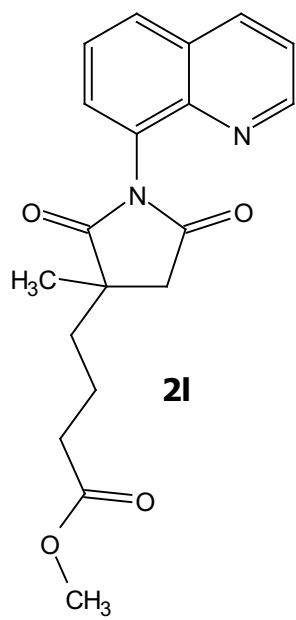
44.56
41.66

41.46
40.57

40.03

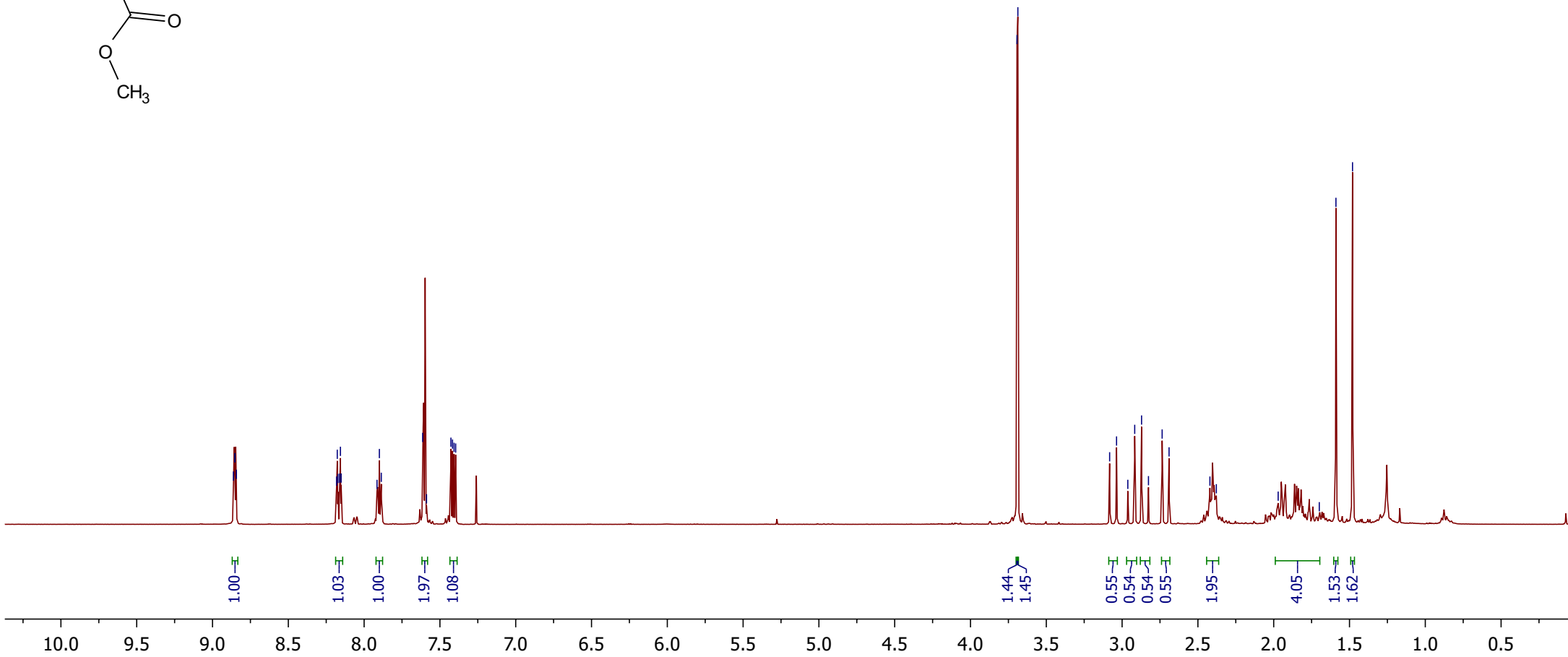
30.99
30.90

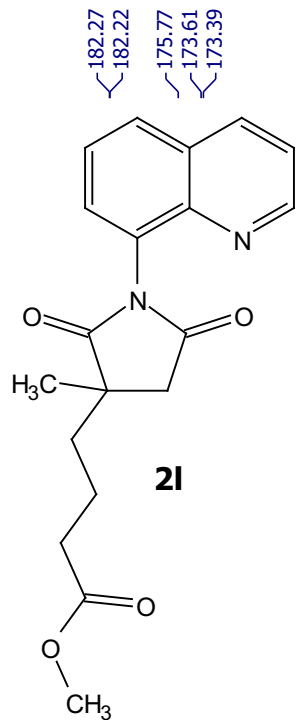




8.86
8.85
8.84
8.18
8.18
8.17
8.16
8.16
8.15
7.91
7.90
7.89
7.61
7.59
7.43
7.42
7.41
7.40

3.69
3.69
3.08
3.04
2.96
2.92
2.87
2.83
2.74
2.69
2.42
2.38
1.97
1.70
1.59
1.48



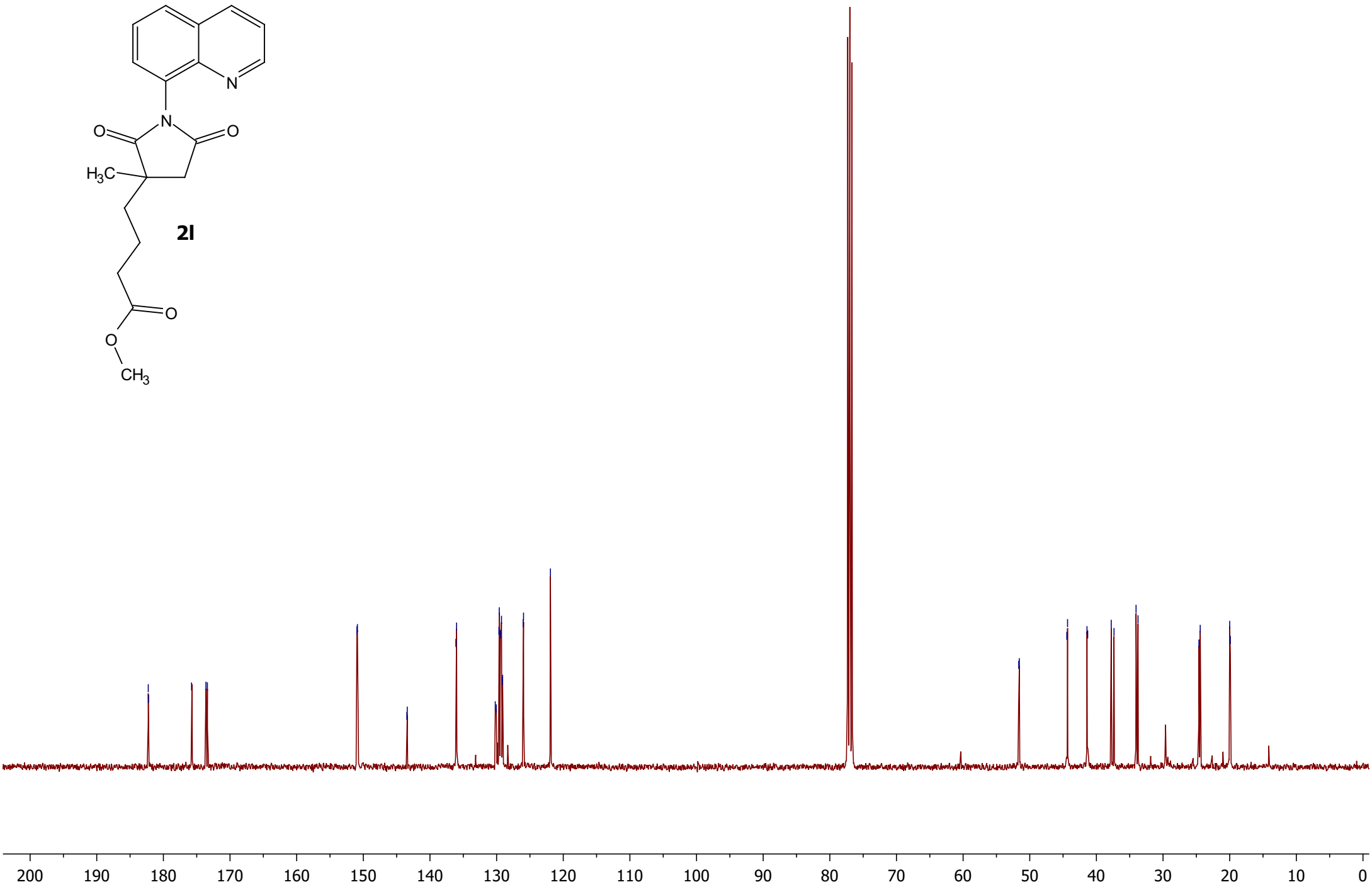


182.27
182.22
175.77
173.61
173.39

150.96
150.89
143.47
143.41
136.11
136.01
130.20
130.05
129.65
129.60
129.43
129.27
129.13
129.09
126.02
125.96
121.92

51.66
51.57
44.44
44.33
41.41
41.30
37.78
37.36
34.05
33.75

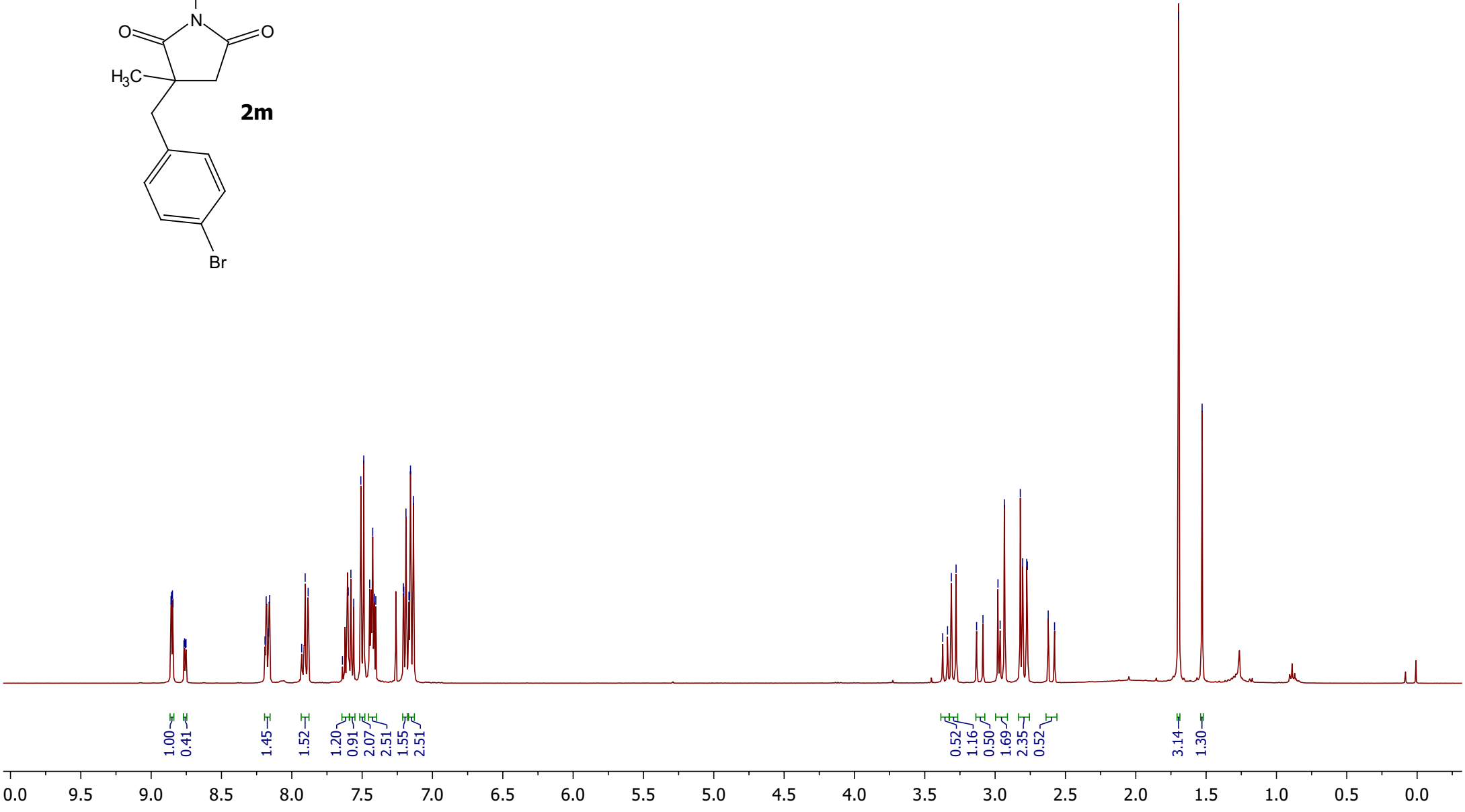
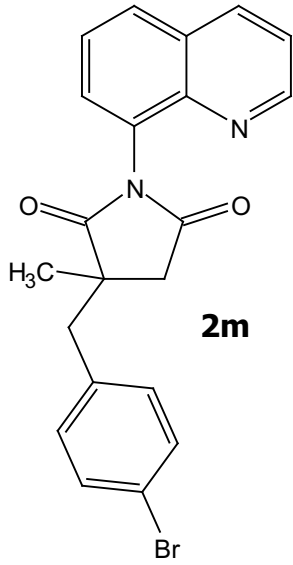
24.62
24.42
20.00
19.91

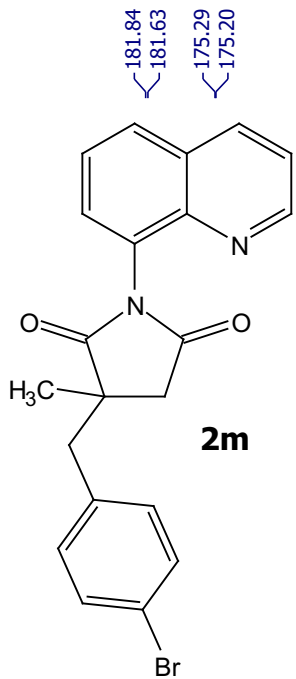


8.86
8.85
8.85
8.84
8.77
8.76
8.76
8.75
8.19
8.18
8.17
8.16
7.93
7.90
7.88
7.64
7.60
7.60
7.58
7.56
7.51
7.49
7.45
7.42
7.41
7.40
7.21
7.20
7.19
7.17
7.16
7.14

3.37
3.34
3.31
3.28
3.13
3.09
2.98
2.96
2.93
2.82
2.80
2.78
2.77
2.62
2.58

1.69
1.53





181.84
181.63

175.29
175.20

151.01
150.79

143.46
143.37

136.07
135.96

135.33
135.27

132.27
131.79

131.75
131.53

130.01
129.87

129.70
129.67

129.20
129.12

129.09
126.04

125.95
121.97

121.93
121.44

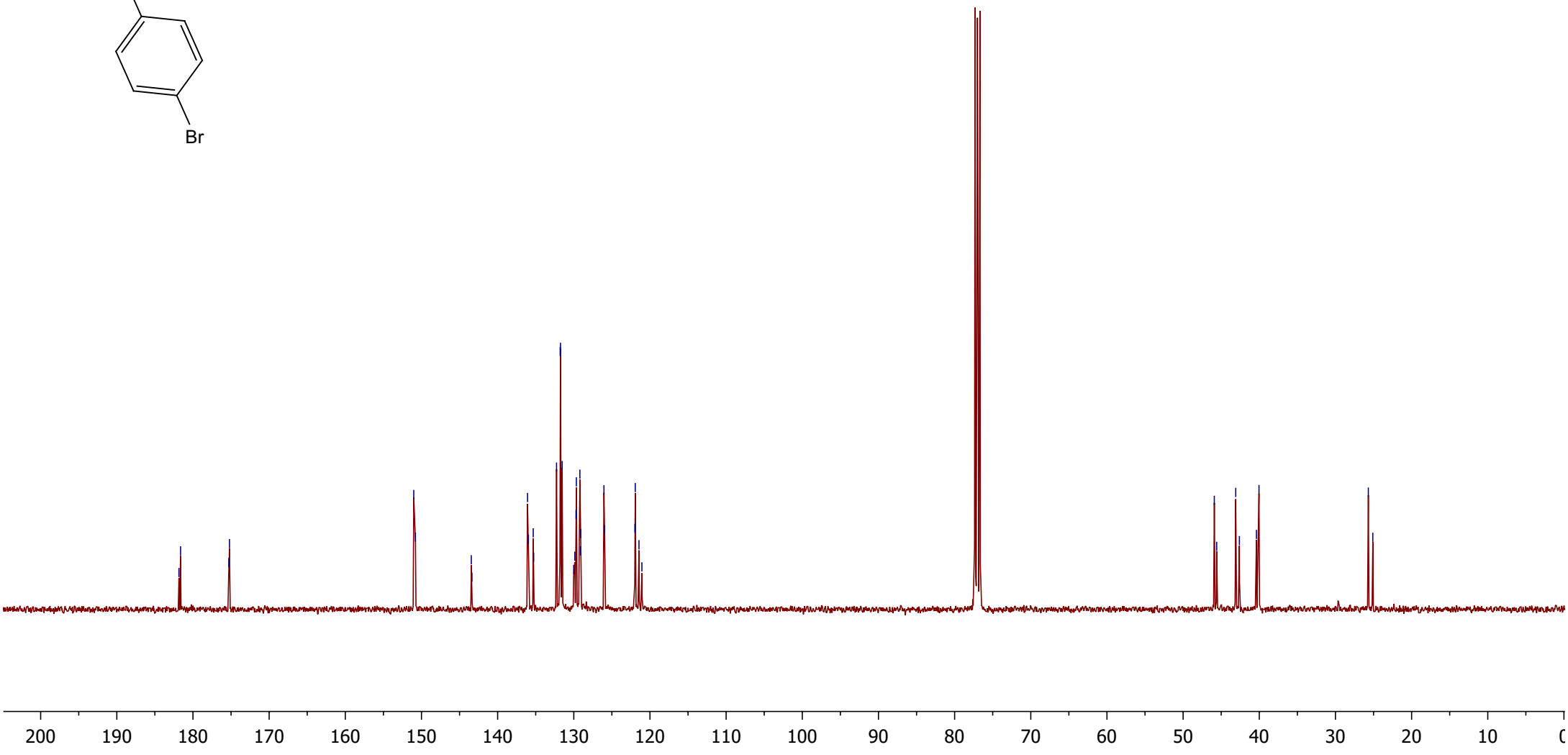
121.06

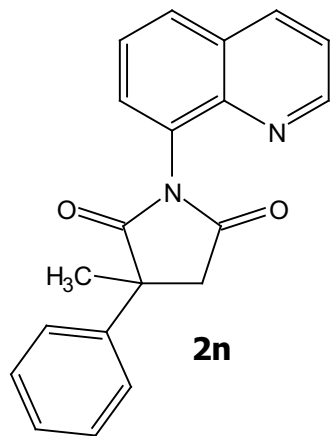
45.91
45.59

43.09
42.61

40.37
40.04

25.68
25.09

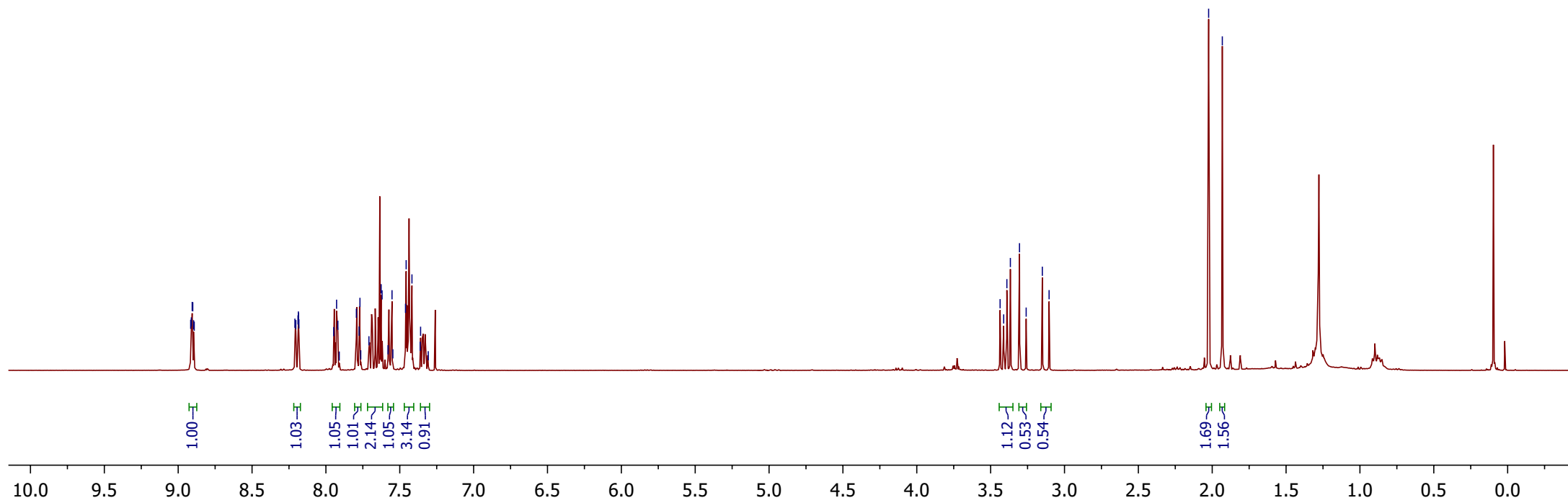


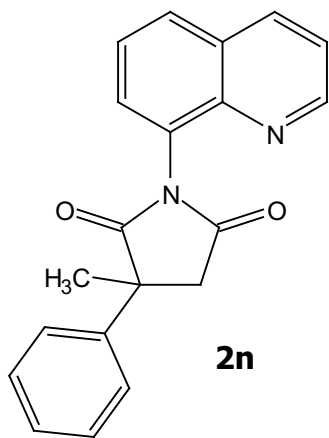


8.92
8.91
8.91
8.90
8.90
8.89
8.21
8.20
8.19
8.19
8.19
8.18
7.95
7.93
7.92
7.91
7.79
7.78
7.77
7.76
7.71
7.63
7.62
7.58
7.55
7.55
7.46
7.46
7.42
7.36
7.36
7.31

3.44
3.41
3.39
3.37
3.30
3.26
3.15
3.10

2.02
1.93



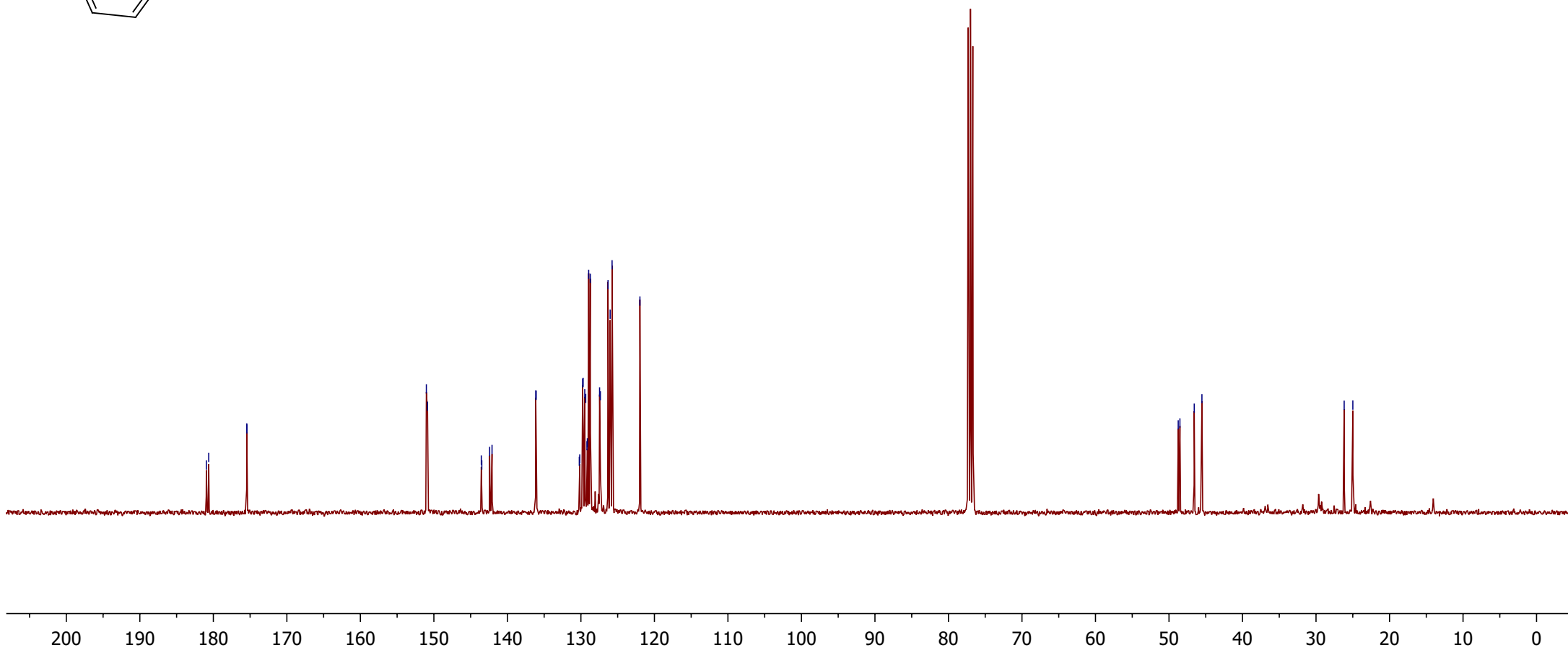


180.95
180.63
175.45
175.43

151.02
150.87
143.55
143.48
142.41
142.09
136.14
136.08
130.22
130.16
129.76
129.70
129.47
129.35
129.18
129.12
128.94
128.72
127.46
127.35
126.31
126.02
125.76
121.97

48.74
48.51
46.56
45.52

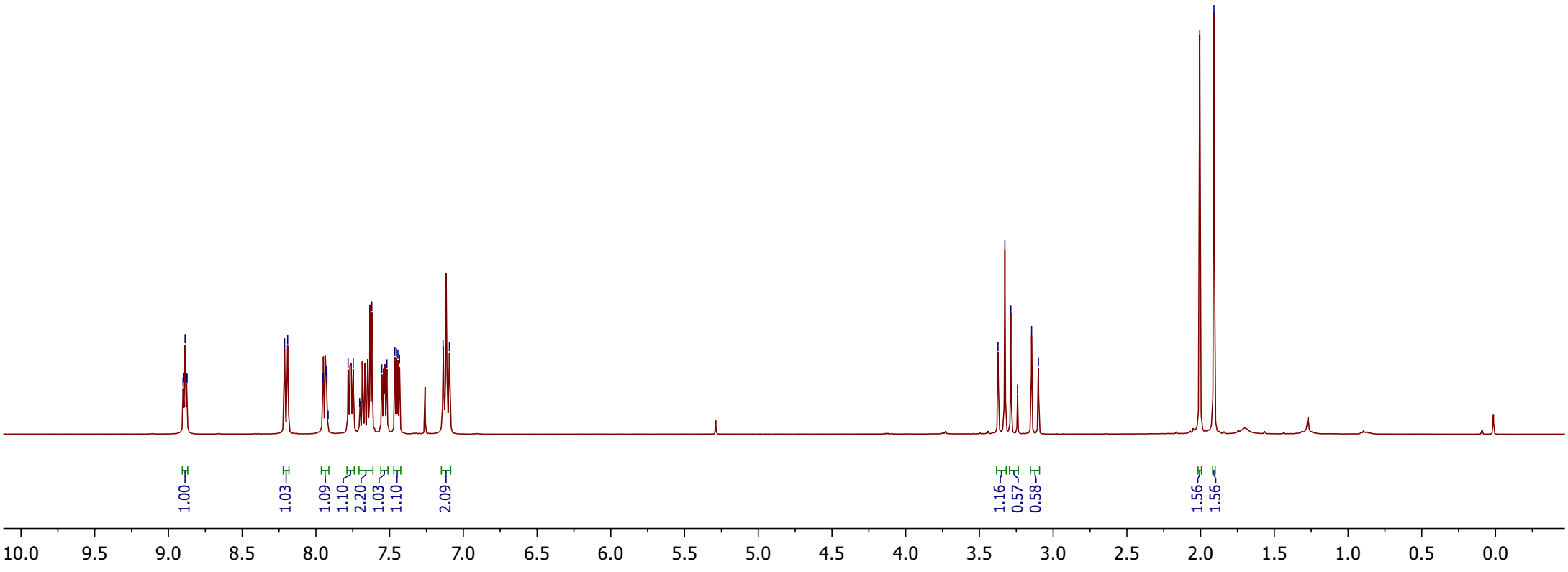
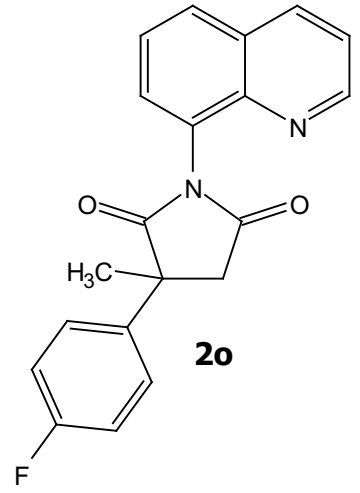
26.17
24.99

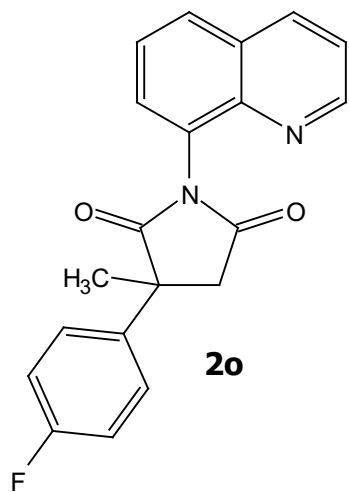


8.90
8.90
8.89
8.88
8.87
8.21
8.19
7.95
7.93
7.93
7.92
7.78
7.75
7.70
7.62
7.55
7.52
7.46
7.45
7.44
7.43
7.14
7.09

3.37
3.33
3.29
3.24
3.15
3.10

2.01
1.91



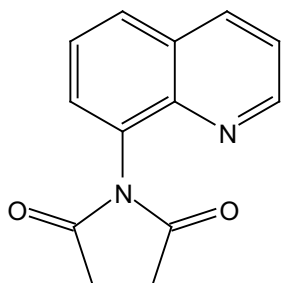


180.76
180.49
175.16
175.11
163.17
160.71
151.05
150.87
143.56
143.46
138.29
138.26
137.82
137.79
136.14
136.10
130.17
130.12
129.82
129.77
129.43
129.36
129.20
129.16
128.20
128.12
127.67
127.59
126.05
126.02
122.03
122.02
115.87
115.65
115.63
115.42

48.25
48.03
46.56
45.42

26.82
25.03

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10



2p

8.89
8.88
8.88
8.88

8.22
8.21
8.21

7.95
7.95

7.93

7.66
7.65

7.63
7.62

7.62
7.61

7.60
7.47

7.46
7.45
7.44

3.17
3.13

3.10

3.03
2.97

1.00

1.09

1.05

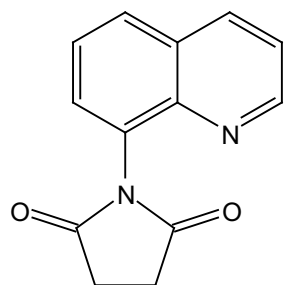
2.13

1.07

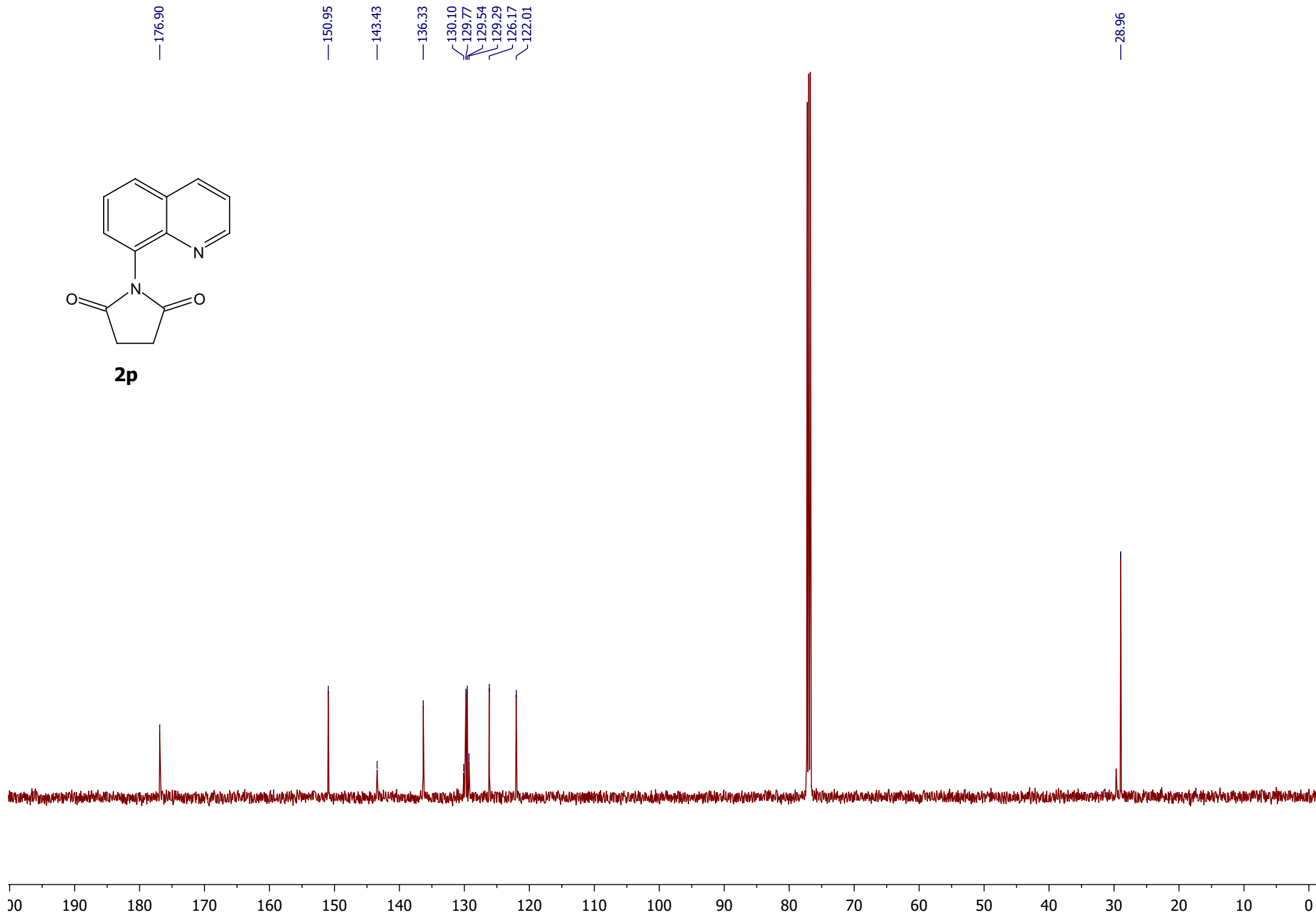
2.50

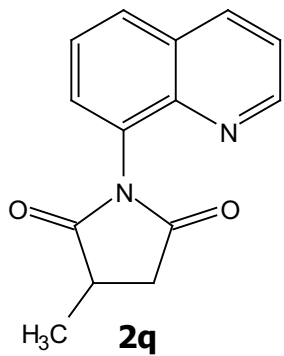
2.58

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



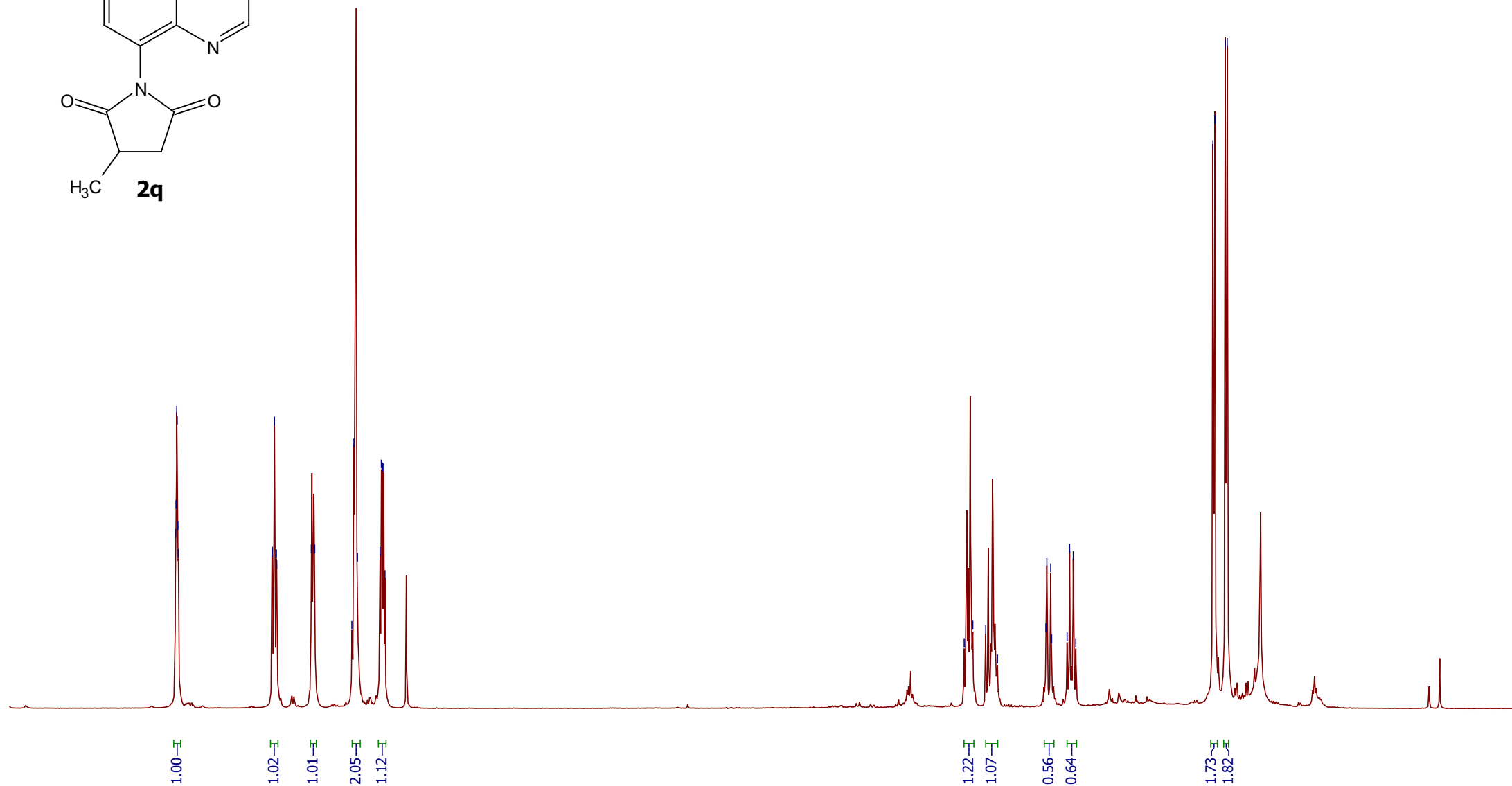
2p



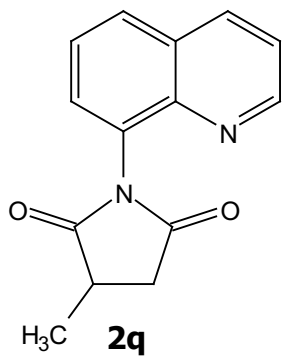


8.88
8.88
8.87
8.87
8.86
8.86
8.20
8.20
8.19
8.17
8.17
7.93
7.90
7.64
7.63
7.60
7.44
7.44
7.43
7.42
7.41

3.34
3.28
3.19
3.11
2.77
2.76
2.74
2.73
2.62
2.60
2.58
2.56
1.60
1.58
1.51
1.50



0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0



180.22
180.11
176.16
175.90

150.95
150.84

143.57
143.53

136.21
136.03

130.42
130.31

129.59
129.57

129.45
129.39

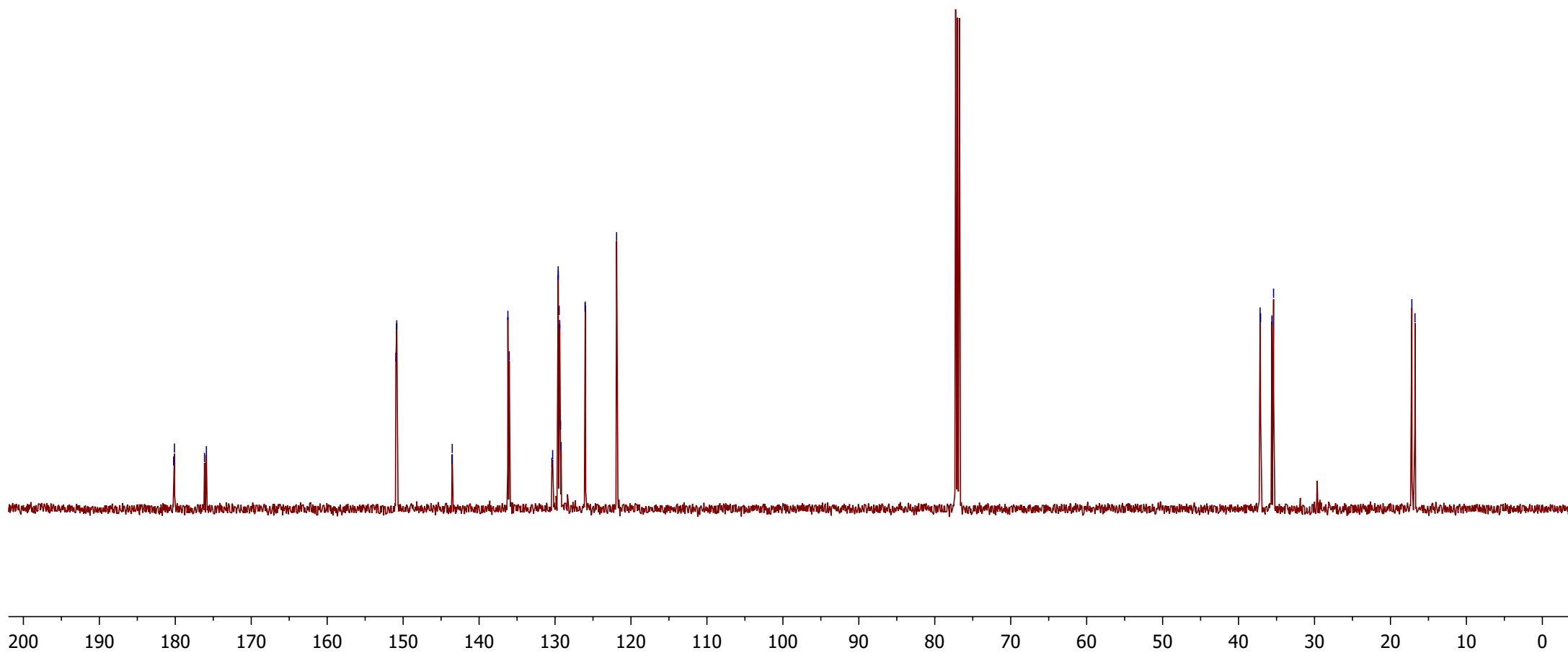
129.27
129.20

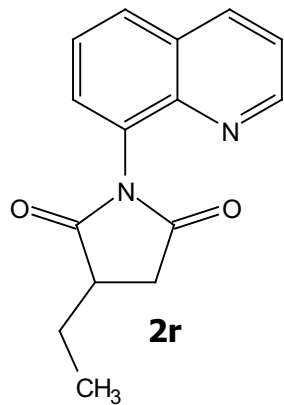
126.05
126.03

121.89

37.16
37.10
35.61
35.39

17.19
16.77

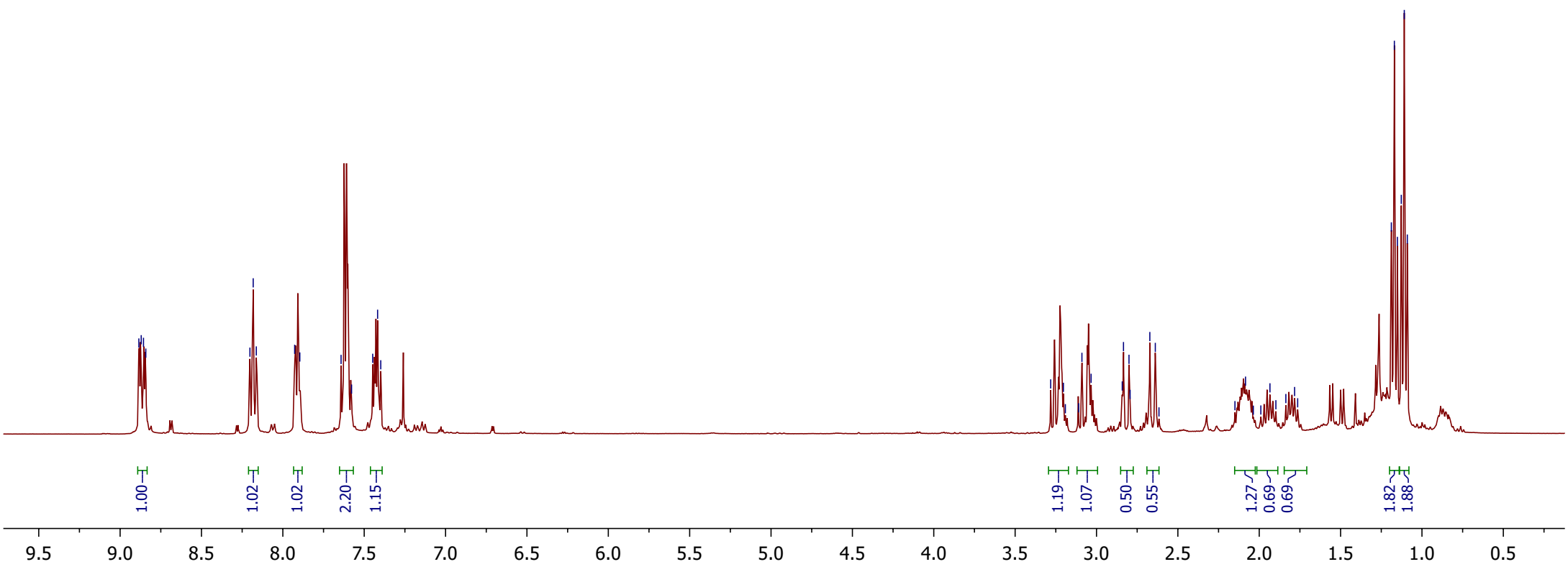




8.88
8.87
8.86
8.84

8.20
8.18
8.16
7.93
7.90
7.64
7.58
7.45
7.42
7.40

3.28
3.20
3.19
3.11
3.09
3.03
2.84
2.83
2.80
2.79
2.67
2.64
2.62
2.15
2.08
2.04
1.99
1.93
1.90
1.84
1.78
1.76
1.19
1.17
1.15
1.13
1.11
1.09



179.69
179.51
176.57
176.38

150.90
150.85

143.37
143.35

136.31
136.03

130.22
130.02

129.67
129.59

129.47
129.33

129.21
129.11

126.06
126.01

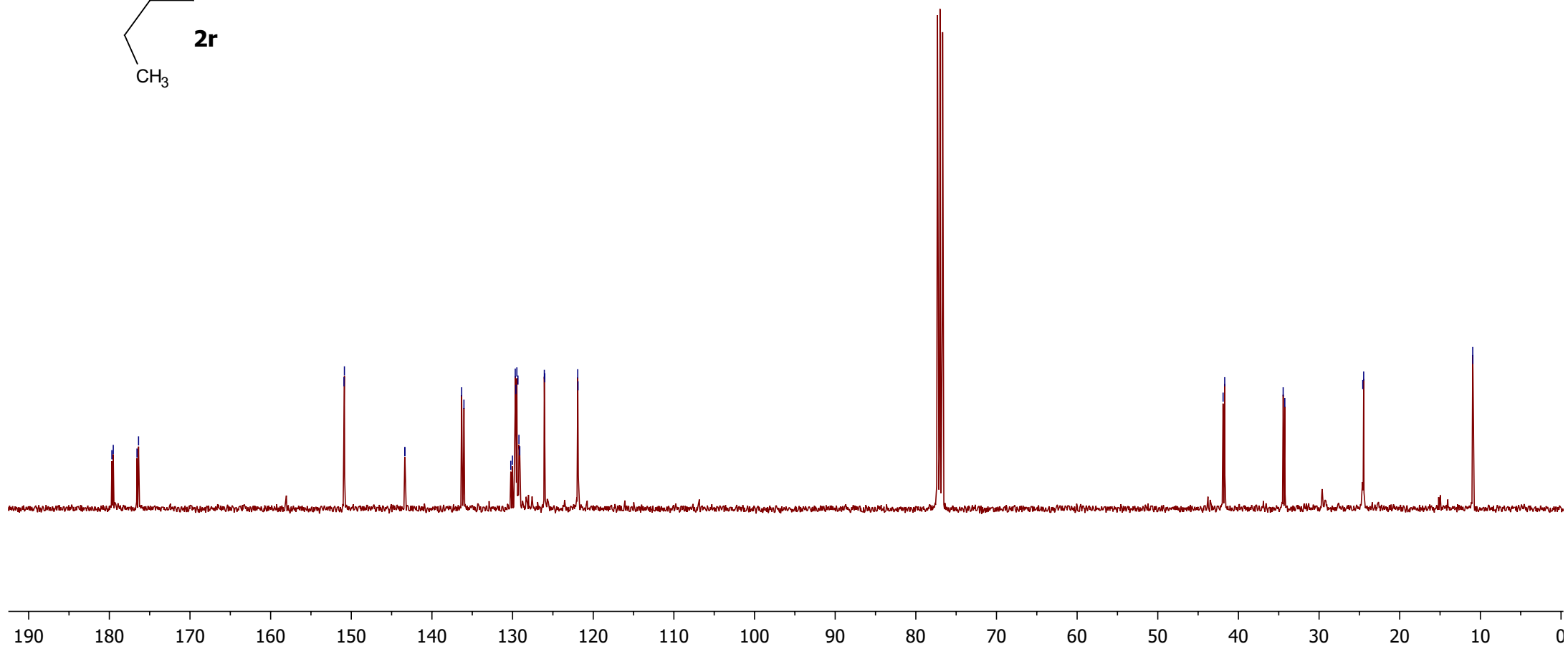
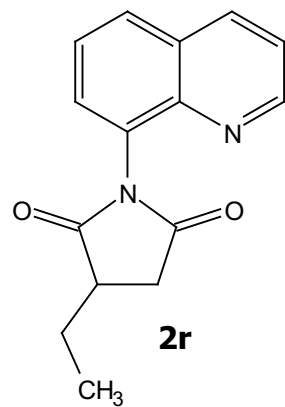
121.92
121.89

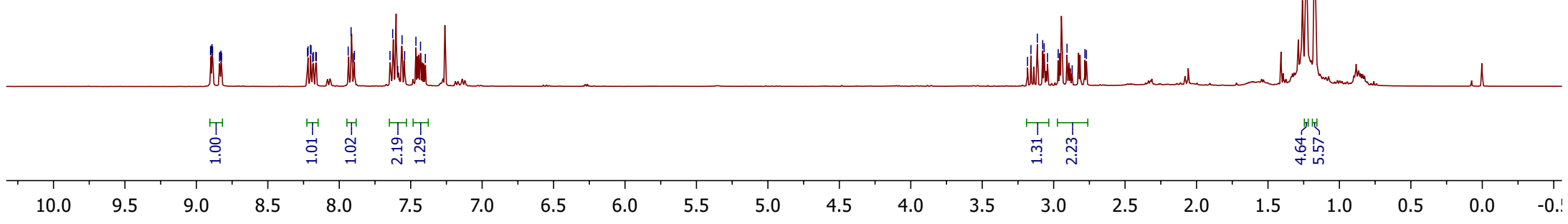
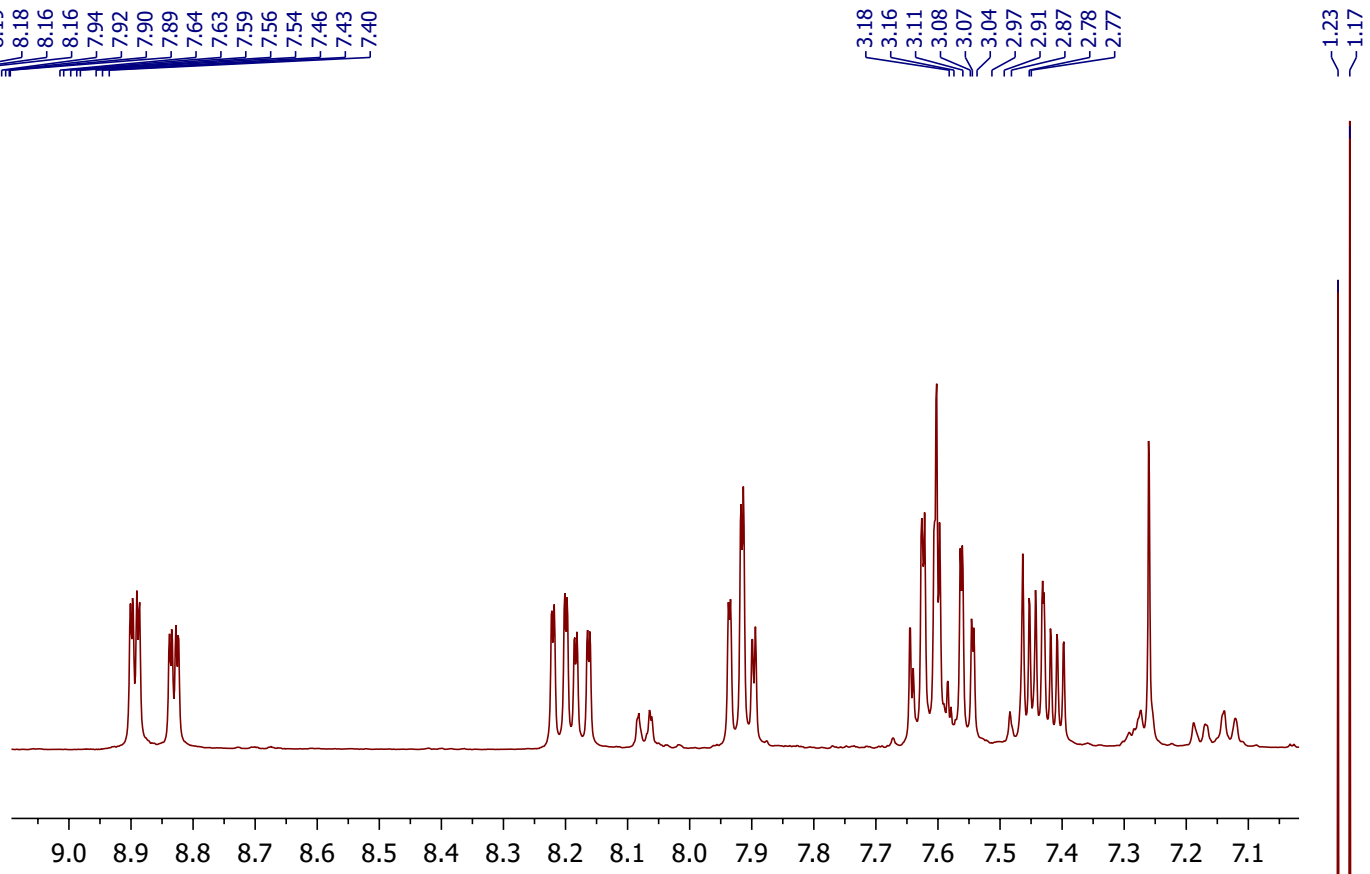
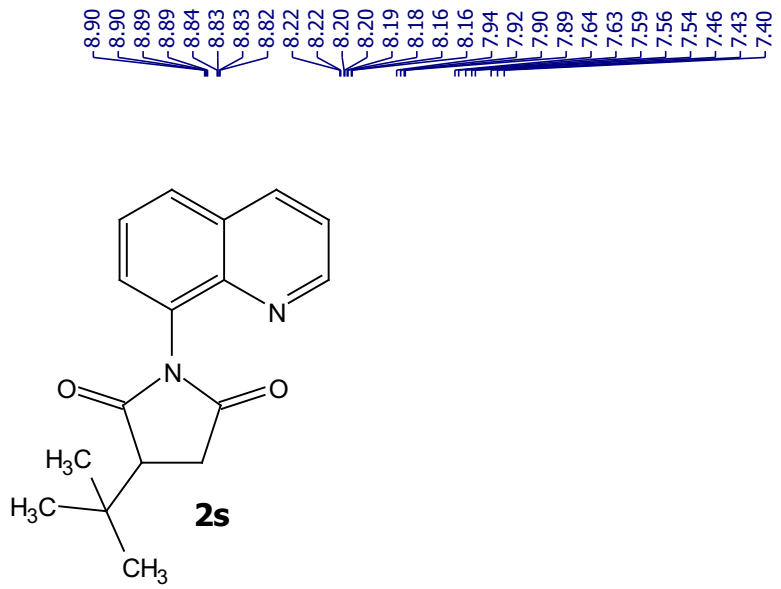
41.90
41.70

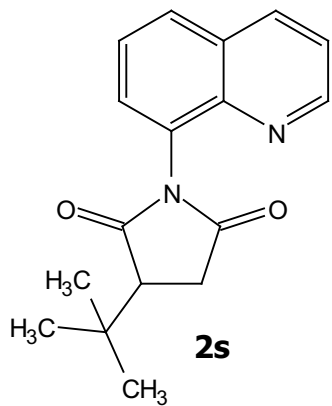
34.45
34.25

24.58
24.47

10.95
10.93







178.07
177.97
176.28
176.25

150.86
150.69

143.47
143.37

136.37
135.87

130.39
130.17

129.77
129.64

129.54
129.42

129.22
129.06

128.30
128.04

127.57
126.06

125.92
121.88

121.80

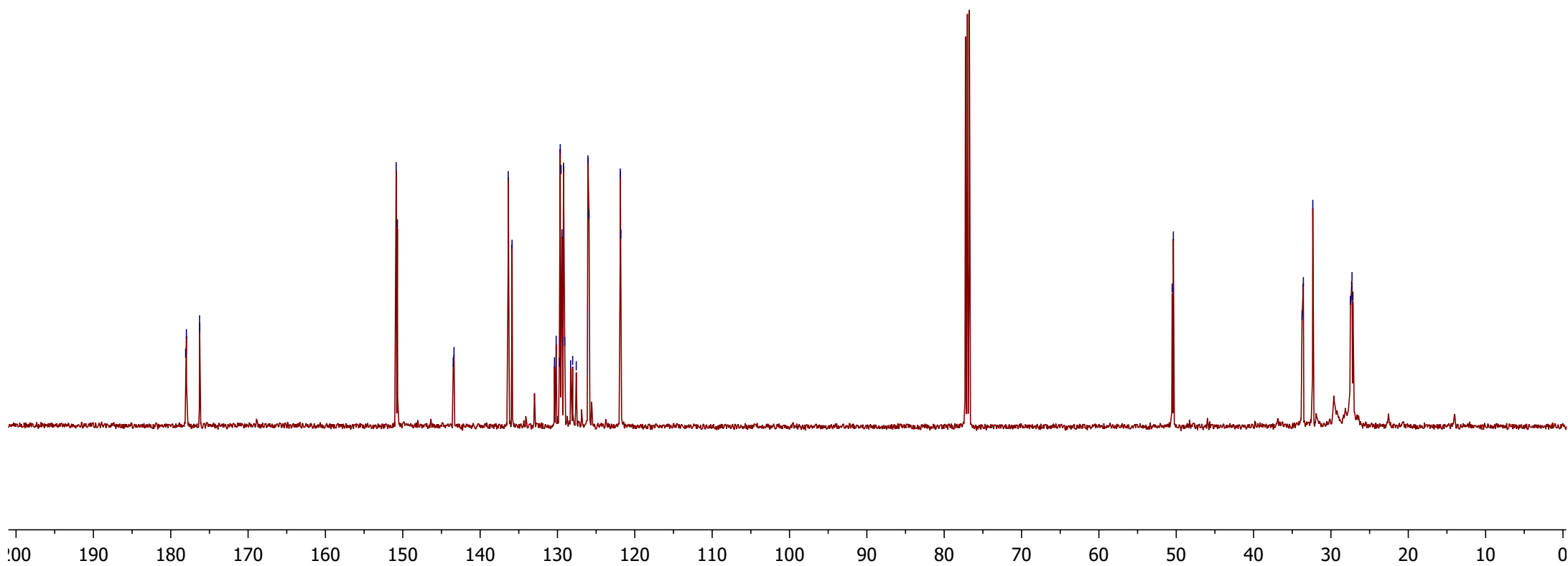
50.53
50.37

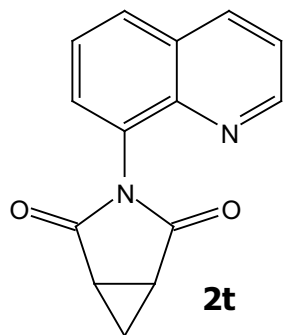
33.74
33.56

32.34
27.48

27.33
27.27

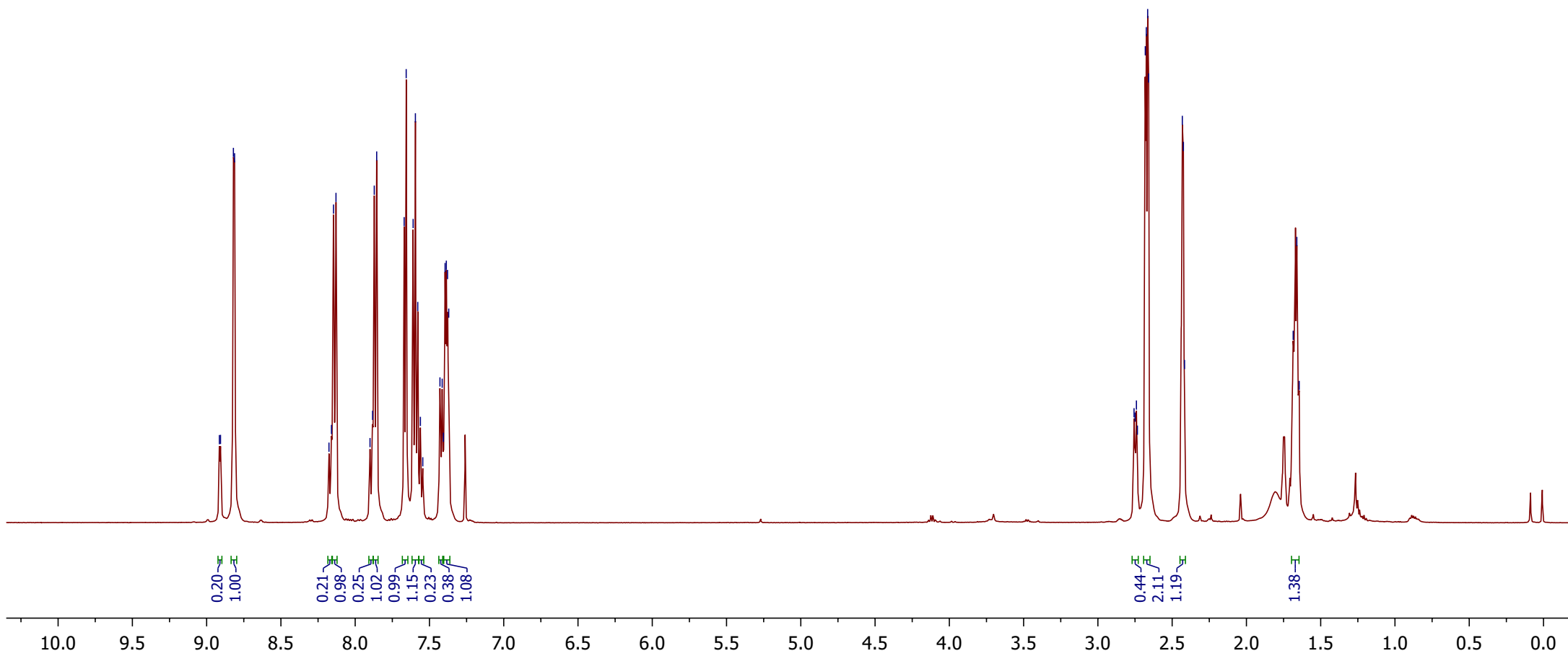
27.15

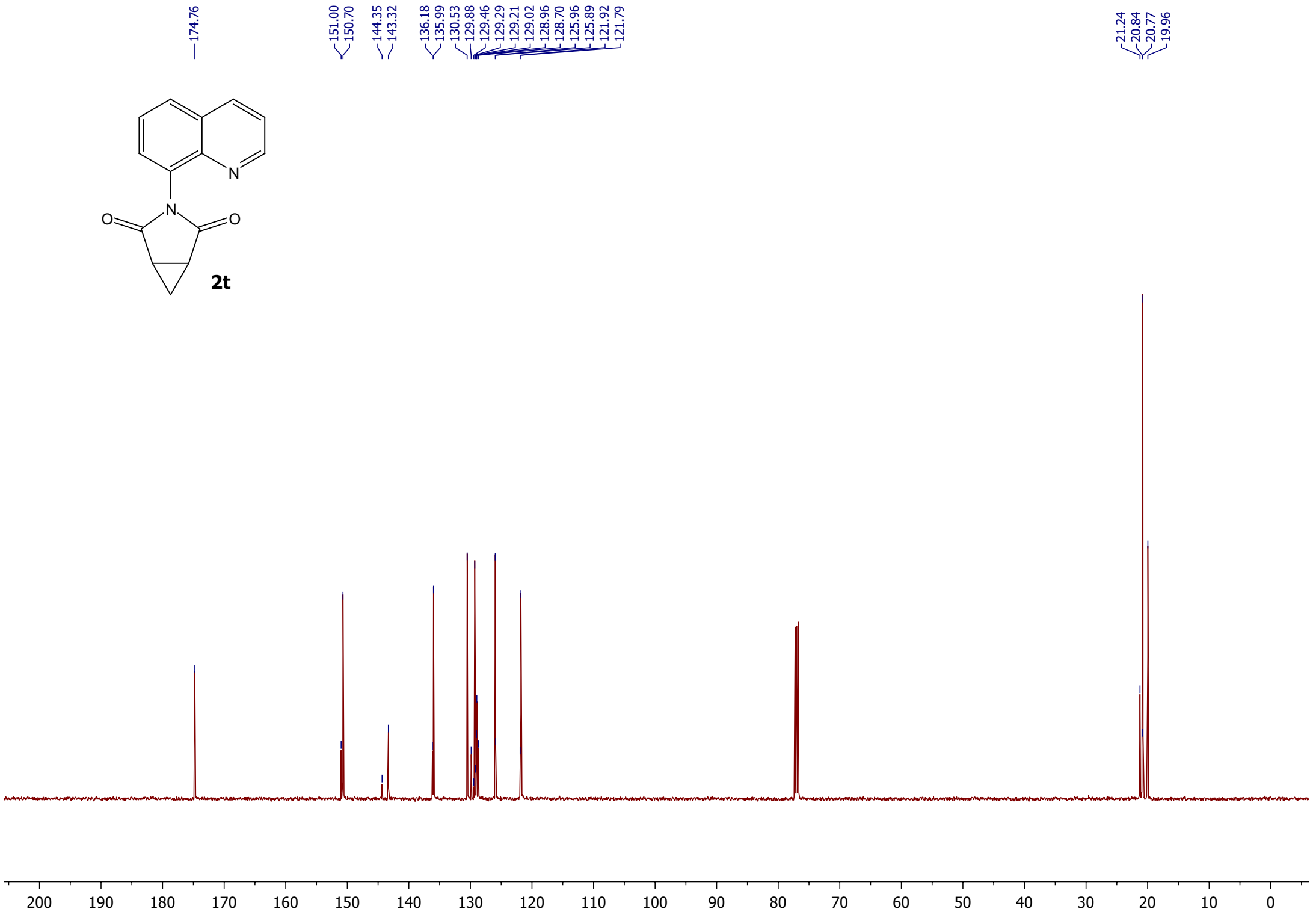
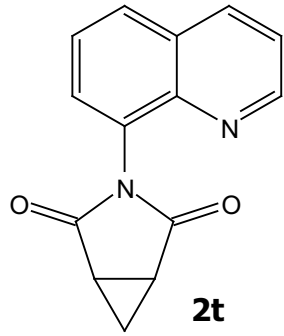


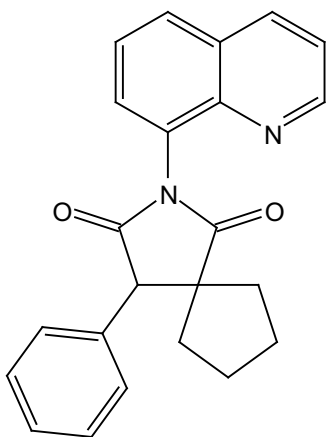


8.91
8.91
8.82
8.81
8.18
8.16
8.15
8.13
7.90
7.88
7.87
7.86
7.67
7.66
7.61
7.59
7.58
7.56
7.54
7.43
7.41
7.41
7.39
7.39
7.38
7.37

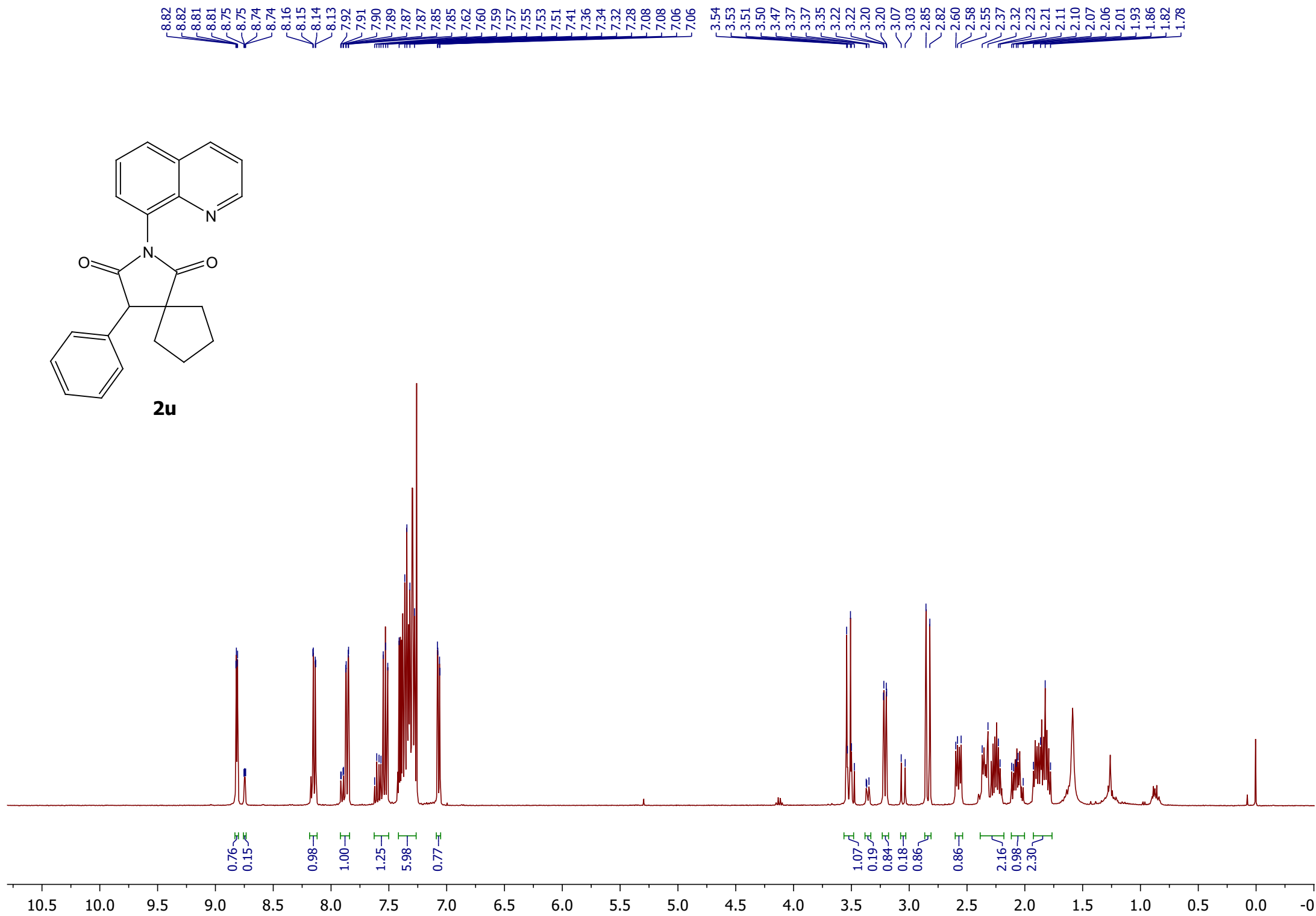
2.76
2.75
2.74
2.73
2.68
2.67
2.66
2.66
2.43
2.42
2.42
1.69
1.66
1.64

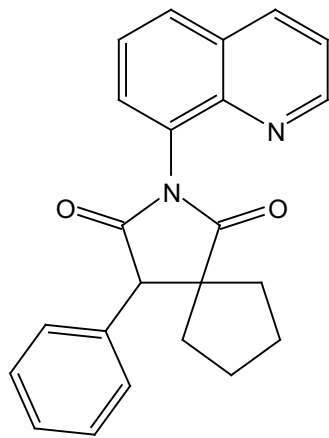




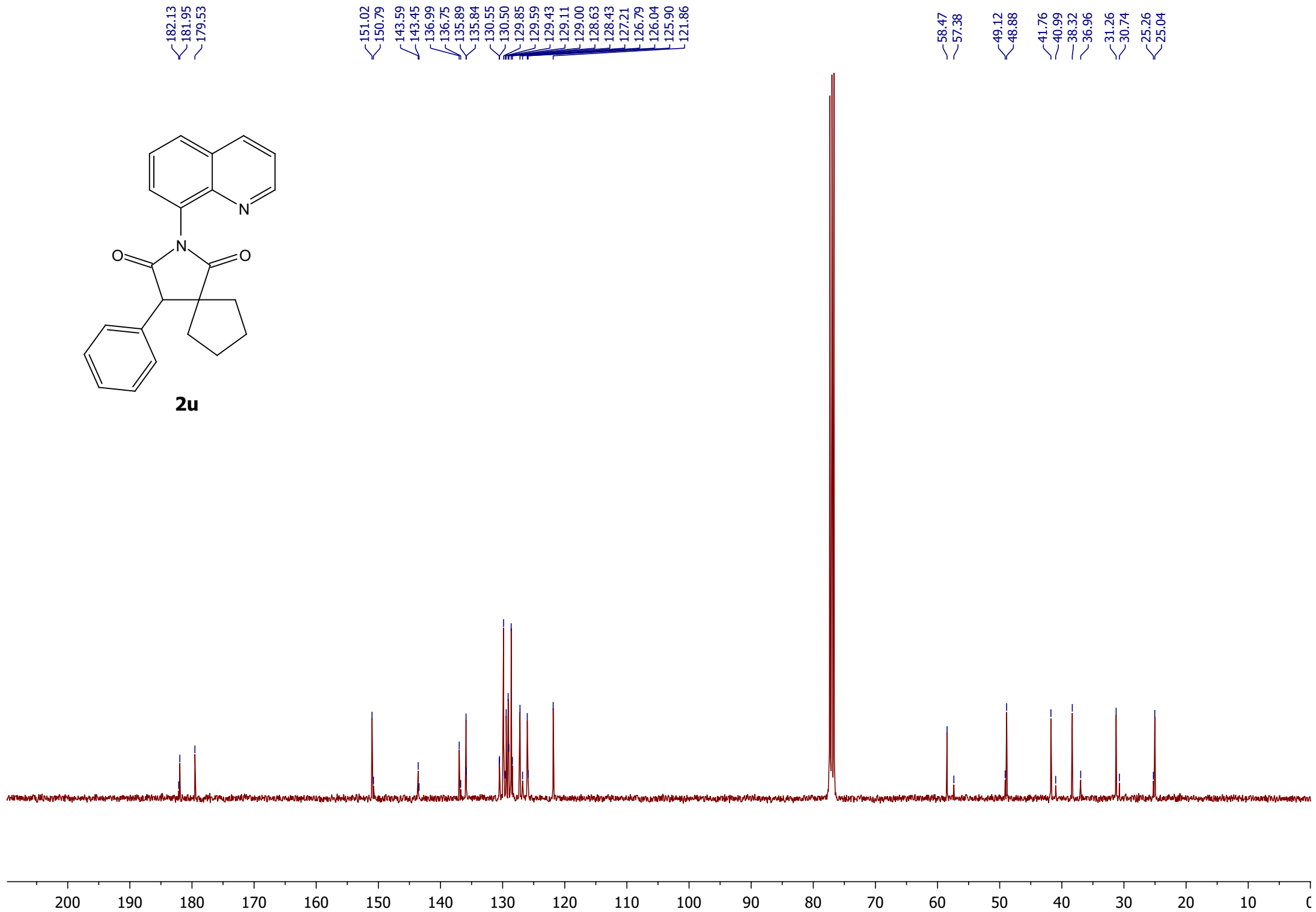


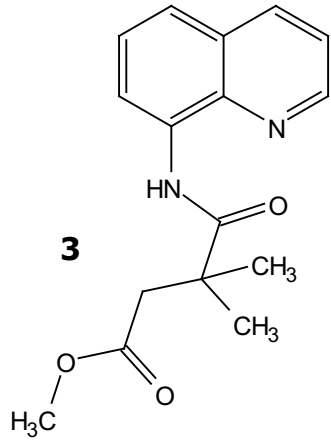
2u





2u





9.85

8.79

8.78

8.75

8.74

8.73

8.14

8.14

8.13

8.12

7.51

7.48

7.43

7.42

3.76

2.86

1.37

1.00

2.01

1.03

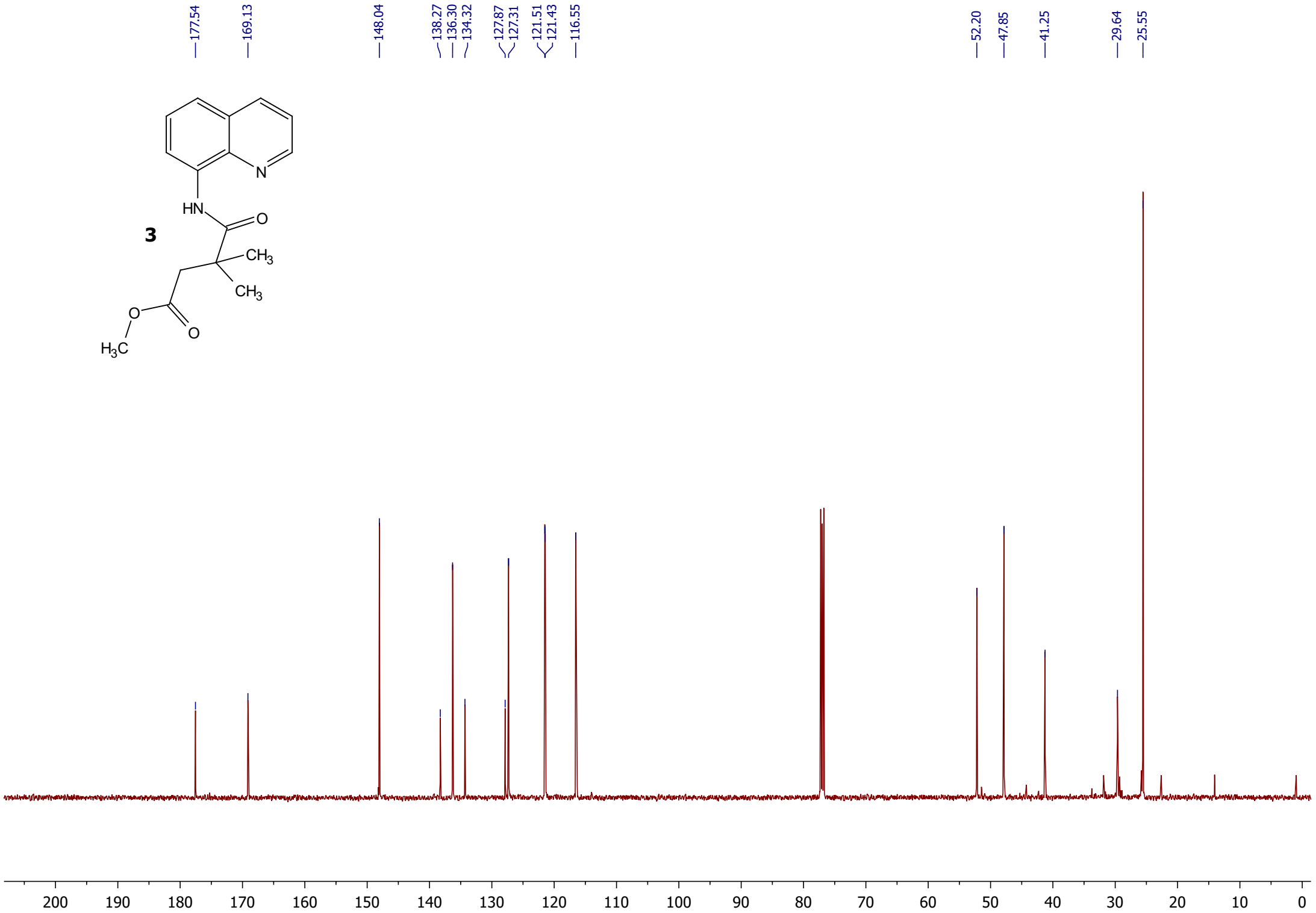
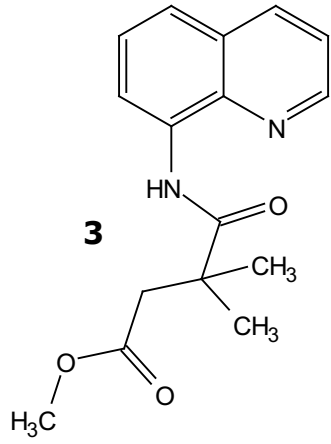
3.33

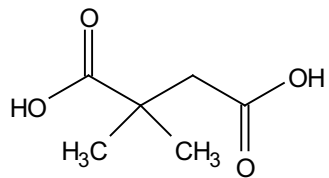
3.11

2.20

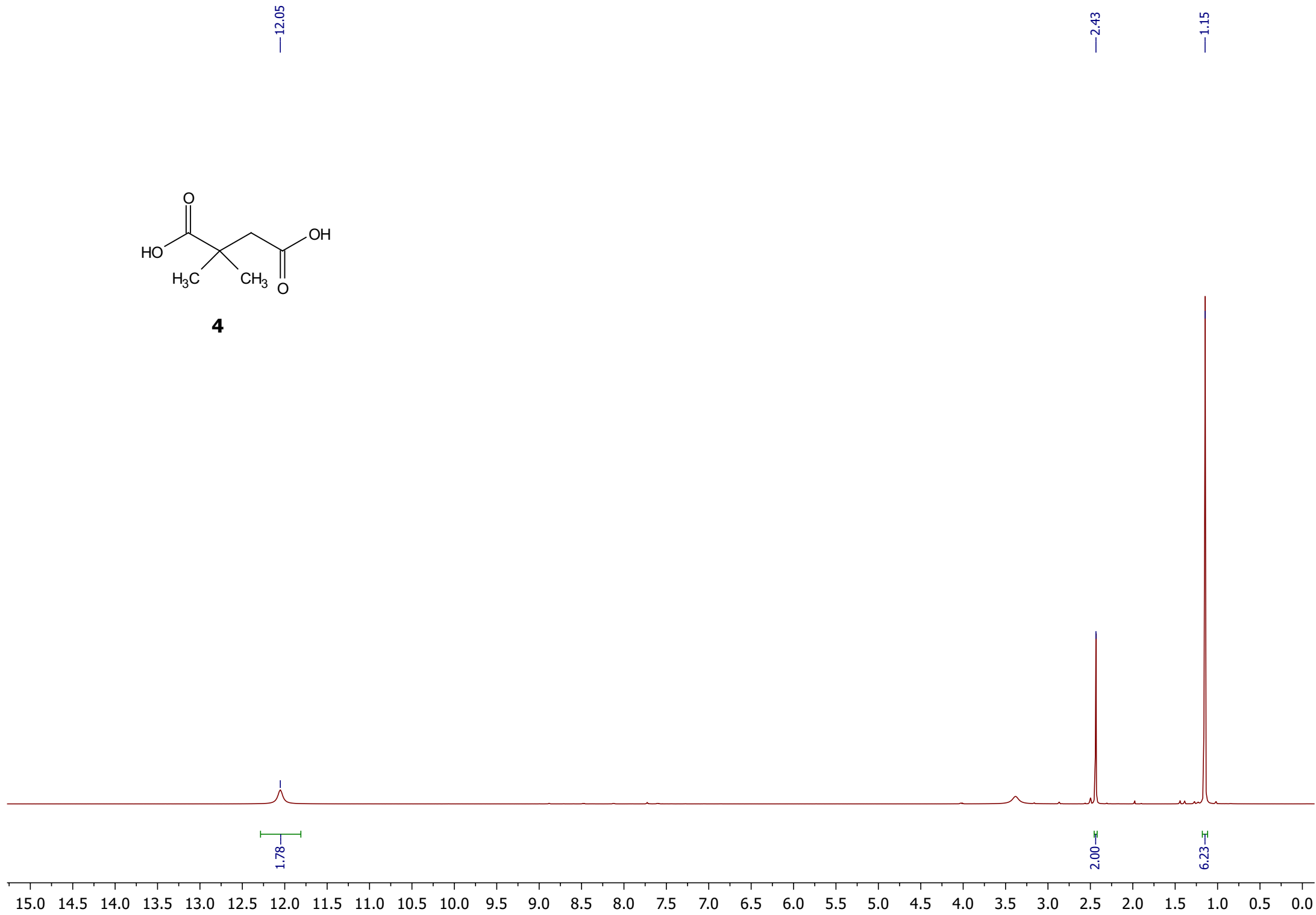
6.45

1.5 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





4

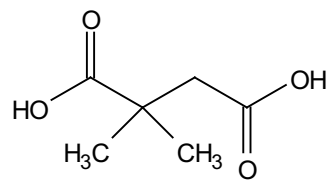


—177.98

—172.47

—43.62

—25.22



4

