C-H and N-H Bond Annulation of Aryl Amides with Unactivated Olefins by Merging Cobalt(III) and Photoredox Catalysis

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Contents

1. Experimental Section

1. General Information

Unless otherwise mentioned, all reactions were carried out under argon atmosphere. Reagent grade 2,2,2-trifluoroethanol (TFE), 1,2-dichloroethane (DCE), 1,4-dioxane, methanol used as such and distilled dichloromethane dried with calcium hydride was used. ^{1}H, ^{13}C and ^{19}F NMR were recorded on JEOL (400 and 500 MHz) using $CDCl_3$ and 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 a references and the chemicals shifts converted to TMS scale ($CDCl_3$: δC = 77 ppm; residual $CHCl_3$ in $CDCl_3$: δH = 7.26 ppm) and (DMSO-d_6: δC = 40 ppm; δH = 2.5 ppm). All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets precoated with silica gel. Column chromatography was conducted on silica gel (Merck, 200-400 mesh). EI-MS/ESI-MS was recorded on Waters-Micromass Quattro Micro triplequadrupole mass spectrometers. GC-MS was used to analyze our samples on a Shimadzu GC 2010 plus and MS 2010 SE system, and an Agilent 7890A GC and 5975C MS system. All other chemicals were received and used as such from the commercial sources.

All cobalt precursors Co(acac)2, $Co(OAc)_2.4H2O$ were purchased from Sigma Aldrich/Merck.

All amides were prepared from the corresponding carboxylic acids using reported protocol.[1]

2. General Procedure for Catalytic C-H and N-H Bond Annulation of Substituted Benzamides with Alkenes

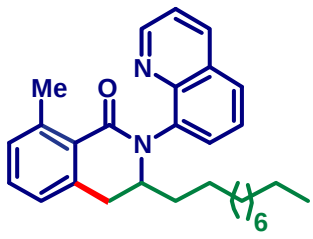
An oven dried Schlenk tube was charged with Teflon coated magnetic stir bar, benzamide **1** (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2-trifluoroethanol (1.5 mL). Subsequently to the reaction mixture alkene **2** (0.24 mmol, 2 equiv.) was introduced under air. The Schlenk was vacuumized and sparged with oxygen

(approximately 2 atm). The resulting reaction mixture was stirred, in the presence of white LEDs (4 x 7 watts) for 48 h. Removal of solvent in *vacuo*, followed by flash column chromatography (EtOAc/hexane) on silica gel afforded the corresponding 3,4 dihydro isoquinolinones **3** in good yields.

3. Analytical Data for the Substrate Scope of Arylamides

3-decyl-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3aa) : Compound **3aa** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 82% yield as a pale yellow oil.

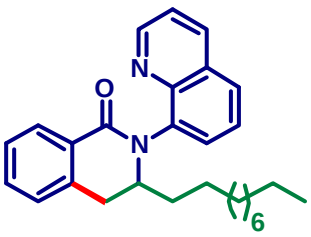
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 1.8, 4.0 Hz, 1H), 8.19 (dd, J = 8.5, 1.8 Hz, 1H), 7.83 (dd, J = 7.9, 1.5 Hz, 1H), 7.74-7.25 (m, 1H), 7.62-7.58 (m, 1H), 7.41 (dd, J = 8.2, 4.1 Hz, 1H), 7.32 (t, J = 8.1 Hz, 1H), 7.16-7.10 (m, 2H), 4.07 (brs, 1H), 3.98-3.95 (m, 1H), 2.93-2.86 (m, 1H), 2.70 (s, 3H), 1.66-1.60 (m, 2H), 1.29-1.25 (m, 4H), 1.22-1.17 (m, 4H), 1.15-1.07 (m, 8H), 0.87 (t, J = 7.16 Hz, 3H).



^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 150.5, 150.3, 144.6, 141.0, 136.2, 130.9, 130.7, 130.4, 129.7, 128.2, 127.7, 126.5, 126.2, 125.8, 121.4, 59.2, 32.3, 31.9, 29.76, 29.74, 29.6, 29.5, 29.4, 29.3, 26.5, 22.7, 22.4, 14.1.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{37}N_2O$: 429.2906, found 429.2904.

3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ba): Compound **3ba** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 82% yield as a pale yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.2, 1.6 Hz, 1H), 8.19 (dd, J = 8.1, 1.3 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.84-7.82 (m, 1H), 7.77 (d, J = 7.1 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.48 (td, J = 7.8, 1.3 Hz, 1H), 7.41 (dd, J = 8.5, 4.2 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 4.17-4.11 (m, 1H), 3.96 (brs, 1H), 2.98 (d, J = 14.8 Hz, 1H), 1.63-1.58 (m, 2H), 1.28-1.26 (m, 4H), 1.21-1.17 (m, 4H), 1.13-1.06 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H).

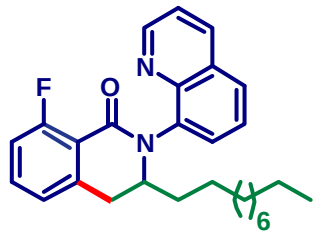
^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 150.4, 144.3, 138.9, 137.5, 136.2, 131.8, 130.5, 129.8, 129.6, 128.4, 127.69, 127.63, 126.7, 126.0, 121.3, 59.3, 32.3, 31.8, 31.7, 29.6, 29.4, 29.35, 29.32, 29.1, 26.2, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{35}N_2O$: 415.2749, found 415.2749.

3-decyl-8-fluoro-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ca):

Compound **3ca** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 60% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.2, 1.5 Hz, 1H), 8.18-8.16 (m, 1H), 7.82-7.76 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.06-7.01 (m, 2H), 4.18-4.03 (m, 2H), 2.95 (d, J = 14.4 Hz, 1H), 1.67-1.58 (m, 2H), 1.26-1.25 (m, 4H), 1.20-1.16 (m, 4H), 1.11-1.08 (m, 8H), 0.85 (t, J = 6.7 Hz, 3H).

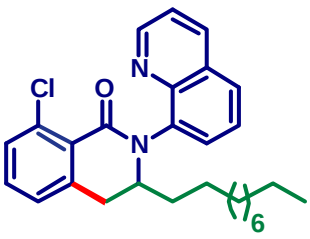


^{13}C NMR (101 MHz, $CDCl_3$): δ 163.6, 161.3, 150.4, 144.3, 140.7, 136.2, 132.9, 132.8, 130.5, 129.6, 127.7, 126.0, 123.4, 121.3, 118.1, 115.7, 59.3, 32.4, 32.1, 31.7, 29.6, 29.4, 29.34, 29.31, 29.2, 26.4, 22.6, 14.0.

^{19}F NMR (373 MHz, $CDCl_3$): -111.79.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}FN_2O$: 433.2655, found 433.2654.

8-chloro-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2H)-one (3da):



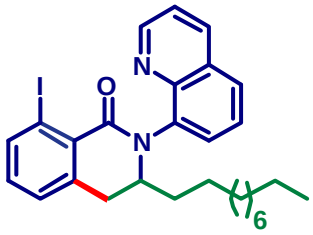
Compound **3da** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 73% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.0, 1.2 Hz, 1H), 8.19 (dd, J = 8.3, 1.4 Hz, 1H), 7.83-7.81 (m, 1H), 7.76 (d, J = 6.8 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.42-7.37 (m, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.1 Hz, 1H), 4.18-4.14 (m, 1H), 3.99-3.97 (m, 1H), 2.92 (d, J = 14.0 Hz, 1H), 1.72-1.54 (m, 2H), 1.28-1.26 (m, 4H), 1.18-1.16 (m, 4H), 1.16-1.06 (m, 8H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 150.4, 144.1, 140.8, 139.4, 136.2, 134.9, 131.5, 130.3, 129.5, 127.7, 127.0, 126.5, 126.3 126.1, 121.3, 59.0, 32.1, 31.7, 29.6, 29.3, 29.29, 29.23, 29.1, 26.9, 26.4, 22.5, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}ClN_2O$: 449.2360, found 449.2360.

3-decyl-8-iodo-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ea):



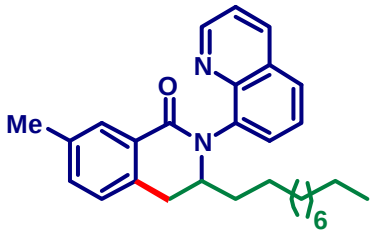
Compound **3ea** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 25:75) in 28% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (m, 1H), 8.2-8.17 (m, 1H), 8.0 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H) 7.74 (d, J = 7.2 Hz, 1H),7.59 (t, J = 7.6 Hz, 1H), 7.41 (dd, J = 8.1, 3.8 Hz, 1H), 7.27 (d, J = 6.1 Hz, 1H), 7.05 (t, J = 7.3 Hz, 1H), 4.18-4.14 (m, 1H), 3.98-3.95 (m, 1H), 2.96-2.83 (m, 1H), 1.62-1.58 (m, 2H), 1.24-1.26 (m, 4H), 1.21-1.17 (m, 4H), 1.15-1.09 (m, 8H), 0.86 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 150.4, 144.2, 141.2, 140.0, 136.2, 131.9, 130.5, 130.1, 129.6, 129.1, 128.2, 127.7, 126.2, 126.2, 121.3, 94.9, 58.9, 32.2, 31.8, 29.6, 29.4, 29.3, 29.28, 29.22, 26.4, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}IN_2O$: 541.1710, found 541.1716.

3-decyl-7-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3fa):



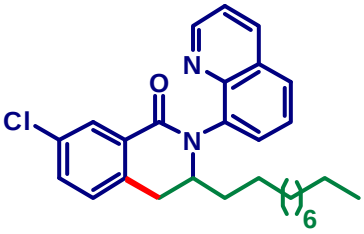
Compound **3fa** was prepared according to the general procedure in 0.12 mmol scale. The product shown here, the major isomer was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 90% yield as pale oil in 3.98:1.0 mixture of regioisomers. Structure and NMR data for major isomer is shown.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91-8.90 (m, 1H), 8.14-8.15 (m, 1H), 7.97 (brs, 1H), 7.82-7.76 (m, 2H), 7.60 (t, J = 7.47 Hz, 1H), 7.39 (dd, J = 7.9, 3.8 Hz, 1H), 7.29-7.27 (m, 1H), 7.17 (d, J = 7.3 Hz, 1H), 4.13-4.09 (m, 1H), 3.92 (brs, 1H), 2.94 (d, J = 15.5 Hz, 1H), 2.39 (s, 3H), 1.62-1.60 (m, 2H), 1.29-1.23 (m, 4H), 1.21-1.18 (m, 4H), 1.13-1.07 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.5, 150.3, 144.1, 140.2, 139.0, 136.2, 134.3, 133.2, 132.5, 130.4, 129.3, 128.6, 127.6, 127.4, 125.9, 121.2, 59.2, 32.0, 31.6, 31.0, 29.5, 29.4, 29.3, 29.2, 29.0, 26.1, 22.4, 20.9, 13.9.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{37}N_2O$: 429.2906, found 429.2903.

7-chloro-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ga):



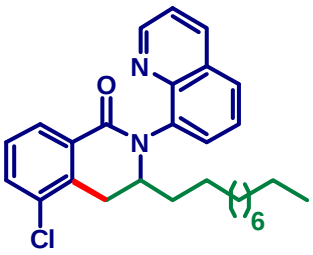
Compound **3ga** was prepared according to the general procedure 2b in 0.12 mmol scale. The product shown here, the major isomer was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 62% yield as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): 8.92-8.89 (m, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.13-8.10 (brs, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.44-7.40 (m, 2H), 7.23 (d, *J* = 7.93 Hz, 1H), 4.16-4.13 (m, 1H), 3.99-3.89 (brs, 1H), 2.99-2.91 (m, 1H), 1.63-1.58 (m, 2H), 1.27-1.24 (m, 4H), 1.20-1.17 (m, 4H), 1.13-1.07 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 163.1, 150.4, 144.2, 136.3, 135.8, 132.7, 131.7, 131.4, 130.4, 129.6, 129.1, 128.4, 127.8, 126.0, 121.4, 115.2, 59.2, 32.3, 31.8, 31.1, 29.6, 29.4, 29.35, 29.30, 29.20, 26.2, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}ClN_2O$: 449.2360, found 449.2360.

5-chloro-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3g'a):



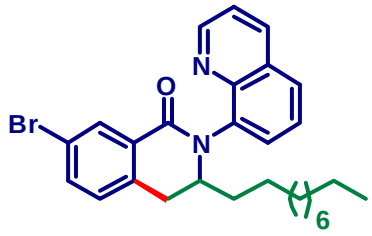
Compound **3g'a** was prepared according to the general procedure in 0.12 mmol scale. The product shown here, the minor isomer was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 30% yield as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.09-8.06 (m, 1H), 7.85 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.57-7.53 (m, 1H), 7.43 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 4.20-4.15 (m, 1H), 3.90-3.75 (brs, 1H), 3.39-3.31 (m, 1H), 1.62-1.57 (m, 2H), 1.26-1.25 (m, 4H), 1.20-1.17 (m, 4H), 1.13-1.08 (m, 8H), 0.86 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 163.4, 150.5, 144.2, 136.2, 135.5, 132.8, 132.4, 131.7, 130.3, 129.6, 127.9, 127.4, 127.1, 126.0, 121.4, 115.2, 58.8, 32.6, 31.9, 31.8, 29.6, 29.4, 29.3, 29.29, 29.22, 26.2, 22.6, 14.0

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}ClN_2O$: 449.2360, found 449.2360.

7-bromo-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ha):



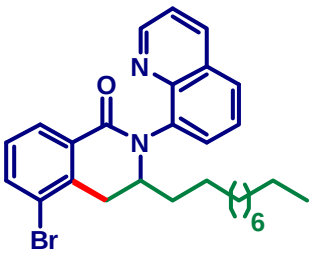
Compound **3ha** was prepared according to the general procedure in 0.12 mmol scale. The product shown here, the major isomer was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 64% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (m, 1H), 8.26 (m, 1H), 8.21 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 6.9 Hz, 1H), 7.63-7.57 (m, 2H), 7.43 (dd, J = 8.2, 4.1 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 4.155-4.11 (m, 1H), 3.91 (brs, 1H), 2.94 (d, J = 12.8 Hz, 1H), 1.60-1.58 (m, 2H), 1.26-1.25 (m, 4H), 1.20-1.16 (m, 4H), 1.13-1.0 (m, 8H), 0.87 (t, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 150.3, 144.0, 138.4, 136.5, 136.3, 134.7, 131.6, 131.3, 130.4, 129.6, 129.4, 127.9, 126.1, 121.4, 120.5, 59.3, 32.3, 31.8, 31.2, 29.6, 29.4, 29.3, 29.2, 29.1, 26.2, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}BrN_2O$: 493.1855, found 493.1854.

5-bromo-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3h'a):



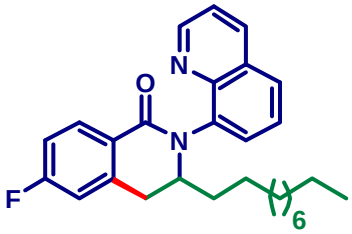
Compound **3h'a** was prepared according to the general procedure in 0.12 mmol scale. The product shown here, the minor isomer was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 30% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (dd, J = 4.1, 1.4 Hz, 1H), 8.21 (dd, J = 8.2, 1.4 Hz, 1H), 8.12 (d, J = 7.3 Hz, 1H), 7.85-7.83 (m, 1H), 7.77-7.71 (m, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.2, 3.7 Hz, 1H), 7.26-7.22 (m, 1H), 4.18-4.15 (m, 1H), 3.84 (brs, 1H), 3.3 (d, J = 14.3 Hz, 1H), 1.63-1.55 (m, 2H), 1.25 (m, 4H), 1.20-1.16 (m, 4H), 1.14-1.0 (m, 8H),0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 150.5, 144.2, 137.3, 136.2, 135.6, 131.9, 130.3, 130.2, 129.6, 127.9, 127.8, 126.0, 123.3, 121.4, 58.8, 32.5, 31.9, 31.8, 29.6, 29.4, 29.3, 29.29, 29.26, 29.22, 26.5, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}BrN_2O$: 493.1855, found 493.1854.

3-decyl-6-fluoro-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ia):



Compound **3ia** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 94% yield as a pale yellow oil.

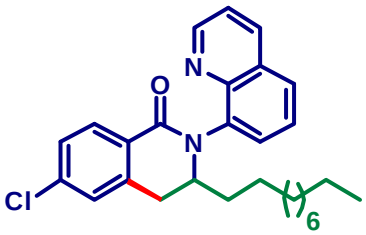
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.1, 1.9 Hz, 1H), 8.19 (dd, J = 8.4, 1.7 Hz, 1H), 8.16-8.12 (m, 1H), 7.84-7.82 (m, 1H), 7.76 (d, J = 6.6 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.41 (dd, J = 8.1, 4.8 Hz, 1H), 7.04 (td, J = 8.4, 2.5 Hz, 1H), 6.98 (dd, J = 8.7, 2.3 Hz, 1H), 4.15-4.12 (m, 1H), 3.98 (brs, 1H), 2.95 (d, J = 15.5 Hz, 1H), 1.64-1.60 (m, 2H), 1.26-1.25 (m, 4H), 1.24-1.18 (m, 4H), 1.15-1.06 (m, 8H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2, 163.4, 150.4, 144.2, 140.4, 136.2, 131.2, 131.1, 130.4, 129.6, 127.7, 126.1, 126.0, 126.3, 114.1, 59.0, 32.3, 31.8, 31.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.2, 22.5, 14.0.

^{19}F NMR (373 MHz, $CDCl_3$): δ -107.91.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}FN_2O$: 433.2655, found 433.2652.

6-chloro-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ja):



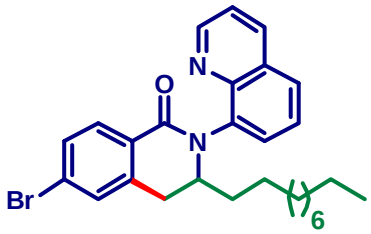
Compound **3ja** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 73% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.2, 1.2 Hz, 1H), 8.19 (dd, J = 8.3, 1.5 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 8.1 Hz, 1H), 7.42 (dd, J = 8.1, 4.4 Hz, 1H), 7.34-7.32 (m, 1H), 7.28 (brs, 1H), 4.13-4.11 (m, 1H), 3.95 (brs, 1H), 2.94 (d, J = 15.6 Hz, 1H), 1.67-1.55 (m, 2H), 1.25-1.23 (m, 4H), 1.18-1.16 (m, 4H), 1.14-1.07 (m, 8H), 0.86 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.4, 150.4, 144.2, 139.3, 137.8, 136.3, 130.4, 130.0, 129.6, 129.3, 128.3, 127.8, 127.6, 127.0, 126.0, 121.3, 59.1, 32.1, 31.7, 29.6, 29.4, 29.36, 29.31, 29.2, 29.1, 26.2, 22.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}ClN_2O$: 449.2360, found 449.2361.

6-bromo-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2H)-one (3ka):



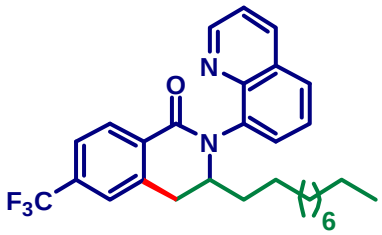
Compound **3ka** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 30:70) in 79% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.19 (dd, *J* = 7.8, 0.97 Hz, 1H), 8.0 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.76 (d, *J* = 6.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.45 (s, 1H), 7.42 (dd, *J* = 8.4, 4.1 Hz, 1H), 4.15-4.11 (m, 1H), 3.96 (brs, 1H), 2.94 (d, *J* = 15.3 Hz, 1H), 1.65-1.55 (m, 2H), 1.27-1.25 (m, 4H), 1.21-1.18 (m, 4H), 1.15-1.0 (m, 8H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5, 150.4, 144.1, 139.5, 138.5, 136.3, 130.5, 130.2, 130.0, 129.6, 128.8, 127.8, 126.4, 126.0, 121.3, 59.2, 32.3, 31.7, 31.4, 29.6, 29.4, 29.35, 29.30, 29.2, 29.1, 26.2, 22.5, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}BrN_2O$: 493.1855, found 493.1856.

3-decyl-2-(quinolin-8-yl)-6-(trifluoromethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3la):



Compound **3la** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 58% yield as a pale yellow oil.

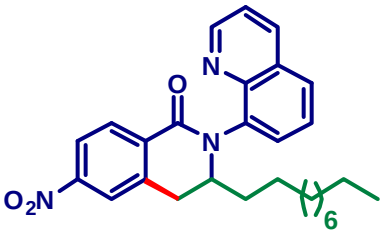
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.63-7.59 (m, 2H), 7.56 (brs, 1H), 7.43 (dd, *J* = 8.2, 4.1 Hz, 1H), 4.21-4.15 (m, 1H), 4.03 (brs, 1H), 3.05 (d, *J* = 14.5 Hz, 1H), 1.66-1.56 (m, 2H), 1.24-1.23 (m, 4H), 1.19-1.16 (m, 4H), 1.12-1.07 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 150.5, 144.1, 138.3, 136.3, 133.5, 132.9, 129.6, 129.0, 128.0, 126.0, 125.2, 124.6, 123.6, 122.4, 121.4, 59.2, 32.4, 31.8, 31.8, 29.6, 29.4, 29.3, 29.29, 29.25, 29.20, 26.2, 22.6, 14.0.

^{19}F NMR (373 MHz, $CDCl_3$): δ -62.73.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{34}F_3N_2O$: 483.2623, found 483.2621.

3-decyl-6-nitro-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ma):



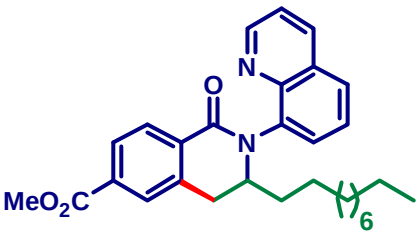
Compound **3ma** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 85% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (dd, J = 4.2, 1.7 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.23-8.17 (m, 3H), 7.87 (dd, J = 8.6, 1.0 Hz, 1H), 7.76 (d, J = 6.7 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.44 (dd, J = 8.1, 3.9 Hz, 1H), 4.22-4.16 (m, 1H), 4.06 (brs, 1H), 3.11 (d, J = 15.2 Hz, 1H), 1.70-1.56 (m, 2H), 1.26-1.24 (m, 4H), 1.19-1.16 (m, 4H), 1.14-1.08 (m, 8H), 0.85 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3, 150.6, 149.7, 143.9, 139.2, 138.0, 136.4, 135.1, 130.1, 129.8, 129.6, 128.1, 126.0, 122.7, 121.8, 121.5, 59.2, 32.4, 31.7, 29.6, 29.39, 29.33, 29.26, 29.23, 29.1, 26.3, 22.5, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{34}N_3O_3$: 460.2600, found 460.2602.

methyl3-decyl-1-oxo-2-(quinolin-8-yl)-1,2,3,4-tetrahydroisoquinoline-6-carboxylate (3na):



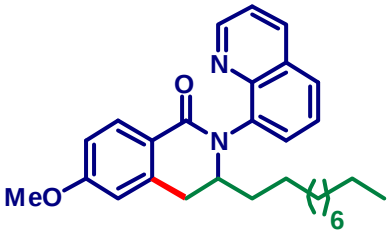
Compound **3na** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 30:70) in 80% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.1, 1.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.04-8.01 (m, 1H), 7.98 (brs, 1H), 7.86-7.83 (m, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.42 (dd, J = 8.3, 4.0 Hz, 1H), 4.18-4.13 (m, 1H), 4.06-3.96 (brs, 1H), 3.96 (s, 3H), 3.05 (d, J = 14.9 Hz, 1H), 1.65-1.55 (m, 2H), 1.27-1.24 (m, 4H), 1.20-1.16 (m, 4H), 1.13-1.07 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 163.4, 150.5, 144.1, 137.6, 136.3, 133.6, 132.8, 130.4, 130.3, 129.6, 128.9, 128.5, 127.9, 127.8, 126.0, 121.4, 59.3, 52.4, 32.2, 31.7, 29.6, 29.4, 29.35, 29.30, 29.2, 29.1, 26.3, 22.5, 140.

HRMS: $[M+H]^+$ calculated for $C_{30}H_{37}N_2O_3$: 473.2804, found 473.2804.

3-decyl-6-methoxy-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (30a):



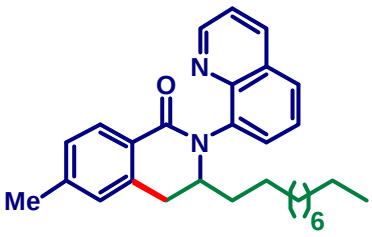
Compound **30a** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 40:60) in 56% yield as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92-8.89 (m, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.78-7.74 (m, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.41 (dd, J = 8.1, 4.0 Hz, 1H), 6.88-6.85 (m, 1H), 6.78-6.76 (m, 1H), 4.15-4.10 (m, 1H), 4.00-3.92 (m, 1H), 3.89 (s, 3H), 2.96-2.88 (m, 1H), 1.62-1.58 (m, 2H), 1.27-1.24 (m, 4H), 1.20-1.17 (m, 4H), 1.12-1.07 (m, 8H), 0.85 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.4, 162.6, 150.5, 144.5, 139.8, 136.3, 130.6, 129.7, 129.3, 127.7, 126.1, 122.8, 121.3, 115.4, 113.0, 112.0, 59.3, 55.4, 32.4, 32.1, 31.9, 29.7, 29.56, 29.50, 29.4, 29.3, 26.4, 22.7, 14.1.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{37}N_2O_2$: 445.2855, found 445.2859.

3-decyl-6-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3pa):



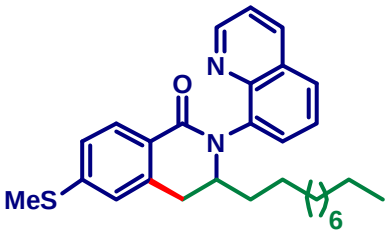
Compound **3pa** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 25:75) in 76% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.0, 1.7 Hz, 1H), 8.18 (dd, J = 8.9, 1.9 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.82 (dd, J = 8.4, 1.4 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.40 (dd, J = 8.1, 4.1 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 7.08 (brs, 1H), 4.14-4.11 (m, 1H), 3.91 (brs, 1H), 2.92 (d, J = 15.1 Hz, 1H), 2.42 (s, 3H), 1.69-1.59 (m, 2H), 1.27-1.24 (m, 4H), 1.20-1.17 (m, 4H), 1.13-1.07 (m, 8H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.4, 150.3, 144.4, 142.2, 137.4, 136.2, 130.5, 130.4, 129.6, 128.4, 128.2, 127.6, 127.5, 127.1, 126.0, 121.2, 59.2, 32.2, 31.8, 31.6, 29.6, 29.4, 29.37, 29.35, 29.2, 26.3, 22.6, 21.6, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{37}N_2O$: 429.2906, found 429.2905.

3-decyl-6-(methylthio)-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one



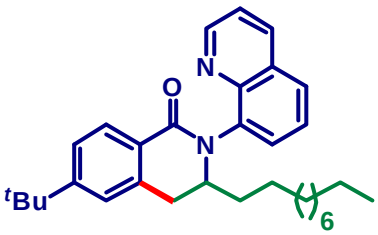
(3qa): Compound **3qa** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 42% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.0, 1.4 Hz, 1H), 8.19 (dd, J = 8.1, 1.4 Hz, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.83 (dd, J = 8.2 Hz, 1H), 7.76 (d, J = 6.8 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.41 (dd, J = 8.3, 3.8 Hz, 1H),7.20-7.18 (m, 1H), 7.11 (brs, 1H), 4.13-4.11 (m, 1H), 3.92 (brs, 1H), 2.92 (d, J = 15.1 Hz, 1H), 2.54 (s, 3H), 1.62-1.59 (m, 2H), 1.28-1.24 (m, 4H), 1.20-1.16 (m, 4H), 1.14-1.02 (m, 8H), 0.86 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 150.3, 144.1, 143.6, 138.6, 137.9, 136.2, 130.5, 129.5, 128.7, 127.6, 126.1, 125.9, 124.1, 123.3, 121.2, 59.1, 32.1, 31.7, 29.5, 29.3, 29.29, 29.26, 29.22, 29.1, 26.2, 22.5, 14.8, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{29}H_{37}N_2OS$: 461.2627, found 461.2624.

6-(*tert*-butyl)-3-decyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ra):



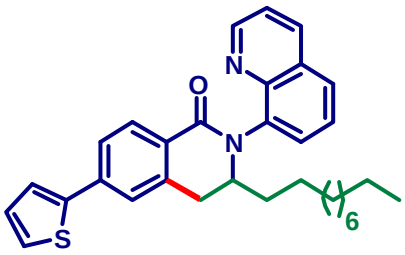
Compound **3ra** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 91% yield as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (dd, J = 1.6, 4.1 Hz, 1H), 8.18 (dd, J = 1.6, 8.2 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.83-7.80 (m, 1H), 7.76 (d, J = 7.0 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.26 (m, 1H), 4.16-4.13 (m, 1H), 3.90 (brs, 1H), 2.95 (d, J = 13.9 Hz, 1H), 1.63-1.59 (m, 2H), 1.37 (s, 9H), 1.25-1.24 (m, 4H), 1.20-1.17 (m, 4H), 1.13-1.06 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 155.5, 150.5, 144.6, 139.0, 137.4, 136.3, 130.7, 129.7, 128.3, 127.7, 127.2, 126.1, 124.6, 124.0, 121.4, 59.3, 35.0, 32.5, 31.9, 31.3, 29.8, 29.58, 29.50, 29.46, 29.41, 29.3, 26.4, 22.7, 14.2.

HRMS: $[M+H]^+$ calculated for $C_{32}H_{43}N_2O$: 471.3375, found 471.3376.

3-decyl-2-(quinolin-8-yl)-6-(thiophen-2-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3sa): Compound **3sa** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc: Hexane = 20:80) in 70% yield as a pale yellow oil.

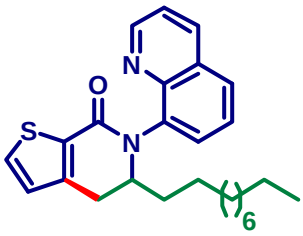


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92-8.91 (m, 1H), 8.17 (dd, J = 19.5, 8.5 Hz, 2H), 7.84-7.77 (m, 2H), 7.63-7.59 (m, 2H), 7.52 (s, 1H), 7.44-7.40 (m, 2H), 7.36-7.34 (m, 1H), 7.13 (dd, J = 5.0, 3.6 Hz, 1H), 4.17-4.16 (m, 1H), 3.99 (brs, 1H), 3.01 (d, J = 14.6 Hz, 1H), 1.65-1.63 (m, 2H), 1.29-1.26 (m, 4H), 1.20-1.16 (m, 4H), 1.15-1.05 (m, 8H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 150.4, 144.3, 143.5, 138.2, 137.5, 136.2, 130.5, 129.6, 129.1, 128.7, 128.1, 127.7, 126.0, 125.7, 124.7, 124.0, 124.0, 121.3, 59.3, 32.3, 31.8, 31.7, 29.6, 29.6, 29.4, 29.37, 29.33, 29.1, 26.3, 22.5, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{32}H_{37}N_2OS$: 497.2627, found 497.2628.

5-decyl-6-(quinolin-8-yl)-5,6-dihydrothieno[2,3-c]pyridin-7(4*H*)-one (3ta): Compound **3ta** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 40:60) in 80% yield as a colorless solid in 1.14:1.0 mixture of regioisomers with the alkyl chain α to and β to the dihydroisoquinoline nitrogen. NMR data for both isomers is shown.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91-8.90 (m, 2H), 8.18-8.15 (m, 2H), 7.81-7.79 (m, 3H), 7.74-7.72 (m, 1H), 7.60-7.55 (m, 2H), 7.52-7.49 (m, 2H), 7.39 (dd, J = 8.2, 3.9 Hz, 2H), 7.02 (d, J = 5.0 Hz, 1H), 6.98 (d, J = 5.3 Hz, 1H), 4.32-4.29 (m, 2H), 3.86-3.68 (m, 2H), 3.25-3.19 (m, 1H), 3.0 (dd, J = 16.0, 3.1 Hz, 1H), 1.68-1.55 (m, 4H), 1.26-1.25 (m, 8H), 1.21-1.15 (m, 8H), 1.12-1.09 (m, 16H), 0.87-0.84 (m, 6H).

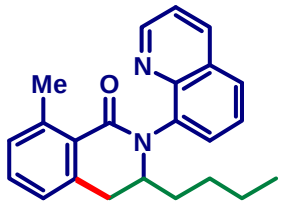
^{13}C NMR: 161.8, 161.1, 150.5, 150.4, 149.2, 144.5, 144.4, 143.3, 140.2, 139.3, 137.9, 136.5, 136.4, 131.9, 131.2, 131.1, 129.6, 129.0, 127.9, 127.8, 127.2, 126.5, 126.1, 124.5, 124.0, 121.5, 121.4, 114.2, 61.0, 56.4, 36.0, 33.9, 32.7, 32.5, 32.03, 32.00, 31.9, 29.8, 29.78, 29.71, 29.6, 29.5, 29.5, 29.4, 29.3, 28.4, 27.2, 27.1, 26.3, 22.79, 22.76, 14.2.

HRMS: $[M+H]^+$ calculated for $C_{26}H_{33}N_2OS$: 421.2314, found 421.2312.

4. Analytical Data for the Substrate Scope of Alkenes

3-butyl-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ab): Compound **3ab** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 82% yield as a pale yellow oil.

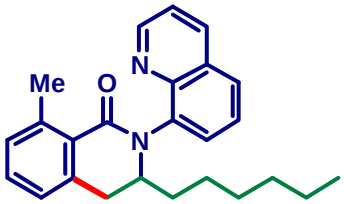
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.0, 1.5 Hz, 1H), 8.19 (dd, J = 8.1, 0.9 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 6.7 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.40 (dd, J = 8.2, 4.1 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 4.1 (brs, 1H), 4.01-3.95 (m, 1H), 2.98-2.86 (m, 1H), 2.71 (s, 3H), 1.70-1.57 (m, 2H), 1.27 (s, 1H), 1.17-1.08 (m, 3H), 0.75 (t, J = 6.4 Hz, 3H).



^{13}C NMR (101 MHz, $CDCl_3$): δ 165.18, 150.39, 144.55, 140.89, 139.97, 138.76, 136.12, 130.80, 130.57, 130.20, 129.59, 128.07, 127.54, 126.11, 125.71, 121.27, 59.00, 39.66, 31.91, 28.58, 22.39, 22.28, 13.80.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{25}N_2O$: 345.1967, found 345.1968.

3-hexyl-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ac): Compound **3ac** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 87% yield as a pale yellow oil.



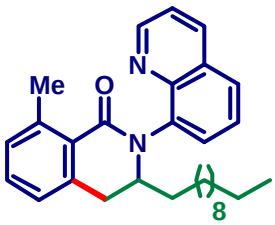
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.1, 1.7 Hz, 1H), 8.19 (dd, J = 8.3, 1.5 Hz, 1H), 7.82 (dd, J = 8.2, 1.1 Hz, 1H), 7.74 (dd, J = 7.2, 1.0 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.40 (dd, J = 8.2, 4.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 4.12 (brs, 1H), 4.01-3.95 (m, 1H), 2.96-2.85 (m, 1H), 2.71 (s, 3H), 1.68-1.56 (m, 2H), 1.27-1.10 (m, 8H), 0.79 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.25, 150.44, 144.58, 140.96, 140.01, 138.79, 136.17, 130.83, 130.62, 130.27, 129.66, 128.12, 127.57, 126.16, 125.74, 121.32, 59.05, 33.01, 31.57, 29.65, 29.00, 26.41, 22.39, 22.31, 13.90.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{29}N_2O$: 373.2280, found 373.2294.

8-methyl-2-(quinolin-8-yl)-3-undecyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ad): Compound **3ad** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 67% yield as a pale yellow oil.

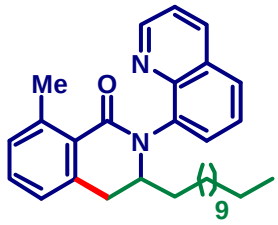
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 4.1, 1.6 Hz, 1H), 8.10 (dd, J = 8.0, 1.3 Hz, 1H), 8.18 (dd, J = 1.6, 8.3 Hz, 1H), 7.81 (dd, J = 7.9, 0.8 Hz, 1H), 7.73 (d, J = 7.1 Hz, 1H), 7.59 (t, J = 7.9 Hz, 1H), 7.39 (dd, J = 8.3, 4.3 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H), 4.16-4.09 (brs, 1H), 4.02-3.94 (m, 1H), 2.96-2.85 (m, 1H), 2.71 (s, 3H), 1.69-1.55 (m, 2H), 1.28-1.08 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H).



^{13}C NMR (101 MHz, $CDCl_3$): δ 165.85, 150.24, 144.27, 140.69, 140.01, 136.21, 130.90, 130.31, 130.04, 129.69, 128.39, 127.33, 126.37, 125.98, 125.15, 121.21, 63.99, 51.61, 46.02, 41.09, 31.55, 30.84, 29.64, 26.34, 26.31, 26.20, 26.16, 22.64, 22.29, 14.07.

HRMS: $[M+H]^+$ calculated for $C_{30}H_{39}N_2O$: 443.3062, found 443.3062.

3-dodecyl-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ae): Compound **3ae** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 67% yield as a pale yellow oil.



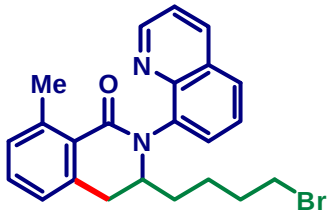
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.2, 1.8 Hz, 1H), 8.19 (dd, J = 8.4, 1.7 Hz, 1H), 7.83 (dd, J = 8.1, 1.1 Hz, 1H), 7.74 (dd, J = 7.1, 0.9 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.2, 4.2 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 7.4 Hz, 1H), 4.10 (brs, 1H), 4.01-3.95 (m ,1H), 2.97-2.85 (m, 1H), 2.72 (s, 3H), 1.70-1.56 (m, 2H), 1.30-1.11 (m, 20H), 0.89 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.21, 150.44, 144.50, 140.91, 139.94, 138.82, 136.15, 130.83, 130.60, 130.23, 129.63, 128.03, 127.57, 126.14, 125.74, 121.31, 58.98, 32.86, 32.20, 31.84, 29.64, 29.60, 29.53, 29.47, 29.35, 29.30, 29.26, 26.41, 22.62, 22.34, 14.06.

HRMS: $[M+H]^+$ calculated for $C_{31}H_{41}N_2O$: 457.3219, found 457.3214.

3-(4-bromobutyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one(3af): Compound **3af** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 25:75) in 82% yield as a pale yellow oil.

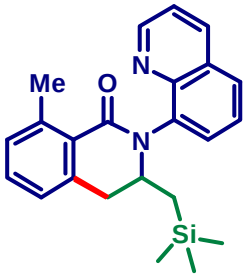
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.1, 1.7 Hz, 1H), 8.20 (dd, J = 8.2, 1.6 Hz, 1H), 7.83 (dd, J = 8.4, 1.2 Hz, 1H), 7.73 (dd, J = 7.3, 1.2 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.42 (dd, J = 8.3, 4.1 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.14 (dd, J = 16.8, 7.7 Hz, 2H), 4.23-4.01 (brs, 1H), 4.03-3.98 (m, 1H), 3.29-3.20 (m, 2H), 2.97-2.85 (brs, 1H), 2.7 (s, 3H), 1.72-1.60 (m, 2H), 1.26 (m, 2H), 0.91-0.83 (m, 2H).



^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 150.4, 144.4, 141.0, 139.7, 138.5, 136.2, 130.9, 130.7, 130.2, 129.6, 127.9, 127.7, 126.1, 125.7, 121.4, 58.6, 33.4, 32.2, 29.6, 25.0, 22.3, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{24}BrN_2O$: 423.1072, found 423.1079.

8-methyl-2-(quinolin-8-yl)-3-((trimethylsilyl)methyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ag): Compound **3ag** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 40% yield as a pale yellow oil.

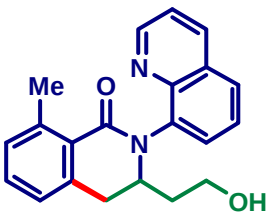


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (dd, J = 4.1, 1.6 Hz, 1H), 8.19 (dd, J = 1.5, 8.2 Hz, 1H) 7.83 (dd, J = 8.4, 1.1 Hz, 1H), 7.72 (dd, J = 7.1, 1.2 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.41 (dd, J = 8.4, 4.2 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 4.20-4.13 (m, 1H), 2.92-2.78 (m, 1H), 2.71 (s, 3H), 1.29-1.25 (m, 2H), 1.17-1.10 (m, 1H), -0.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.01, 150.50, 144.64, 141.03, 139.64, 138.60, 136.19, 130.82, 130.70, 130.00, 129.64, 128.05, 127.62, 126.22, 125.94, 121.34, 56.98, 35.65, 29.65, 22.40, -1.06.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{27}N_2OSi$: 375.1893, found 375.1882.

3-(2-hydroxyethyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ah): Compound **3ah** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 71% yield as a pale yellow oil.



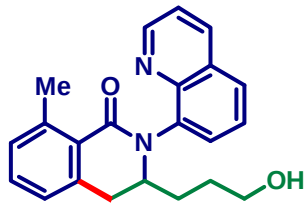
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (dd, J = 3.9, 1.5 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 6.5 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.38 (dd, J = 7.8, 3.9 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 4.16 (brs,

1H), 3.50-3.40 (m, 2H), 2.95-2.82 (m, 1H), 2.66 (s, 3H), 1.93-1.75 (m, 2H), 1.29-1.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.31, 150.37, 150.16, 144.34, 140.95, 138.40, 136.38, 130.96, 130.69, 129.60, 127.73, 126.43, 126.18, 125.71, 125.01, 121.42, 59.48, 56.23, 35.12, 29.62, 22.18.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{21}N_2O_2$: 333.1603, found 333.1600.

3-(3-hydroxypropyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ai): Compound **3ai** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 70% yield as a pale yellow oil.

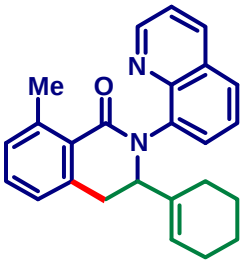


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (m, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 6.7 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.38 (dd, J = 8.2, 4.1 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 7.3 Hz, 1H), 4.10 (brs, 1H), 3.99 (brs, 1H), 3.37 (brs, 1H), 2.94-2.81 (m, 1H), 2.67 (s, 3H), 1.74-1.68 (m, 1H), 1.64-1.56 (m, 1H), 1.49-1.40 (m, 1H), 1.33-1.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.20, 150.45, 150.20, 144.66, 144.46, 140.98, 136.24, 130.96, 130.71, 130.36, 129.65, 128.00, 127.68, 126.20, 125.74, 121.37, 62.34, 58.88, 33.02, 29.48, 28.60, 22.27.

HRMS: $[M+H]^+$ calculated for $C_{22}H_{23}N_2O_2$: 347.1760, found 347.1769.

3-(cyclohex-1-en-1-yl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (3aj): Compound **3aj** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 66% yield as a pale yellow oil.

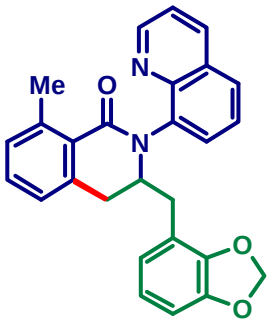


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (dd, J = 3.9, 1.3 Hz, 1H), 7.82-7.74 (m, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.40 (dd, J = 8.2, 4.1 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.18-7.03 (m, 2H), 4.32-4.12 (m, 1H), 3.87-3.77 (brs, 1H), 2.99 (d, J = 15.3 Hz, 1H), 2.70 (s, 3H), 1.73-1.56 (m, 4H), 1.26 (s, 1H), 1.11-0.93 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)**:** δ 165.8, 150.2, 144.2, 143.1, 140.7, 139.9, 136.2, 130.9, 130.3, 130.0, 129.7, 128.3, 127.3, 126.4, 126.3, 125.9, 125.1, 121.2, 63.9, 41.0, 30.8, 29.6, 26.3, 26.1, 22.3.

HRMS: $[M+H]^+$ calculated for $C_{22}H_{23}N_2O_2$: 369.1967, found 369.1963.

3-(benzo[d][1,3]dioxol-4-ylmethyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquin- olin -1(2*H*)-one (3ak) : Compound **3ak** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 82% yield as a pale yellow oil.

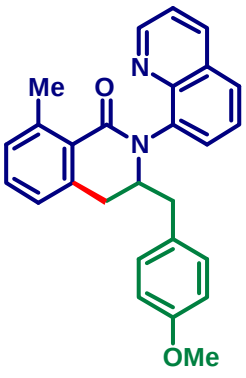


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (m, 1H), 8.20 (dd, J = 8.2, 1.5 Hz, 1H), 7.84 (dd, J = 8.0, 0.9 Hz, 1H), 7.67-7.57 (m, 2H), 7.42 (dd, J = 8.0, 3.9 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.4, 1H),6.65 (d, J = 7.8 Hz, 1H), 6.39 (s, 1H), 5.88-5.87 (m, 2H) 4.15-4.10 (m, 2H), 2.99-2.90 (m, 1H), 2.72 (s, 3H), 2.04 (s, 1H), 1.28-1.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 150.6, 147.6, 146.1, 144.5, 141.2, 138.6, 136.3, 132.1, 131.2, 130.9, 130.1, 129.8, 128.2, 127.9, 126.3, 126.1, 122.2, 121.5, 109.5, 108.2, 100.9, 60.5, 38.2, 32.1, 22.4, 14.3.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{23}N_2O_3$: 423.1760, found 423.1687.

3-(4-methoxybenzyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2H)-one (3la): Compound **3la** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 51% yield as a pale yellow oil.

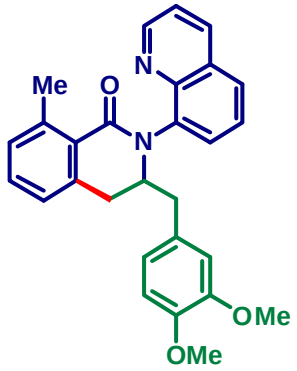


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 3.9, 1.3 Hz, 1H), 8.20 (dd, J = 8.2, 1.6 Hz, 1H), 7.84 (dd, J = 8.0, 1.5 Hz, 1H), 7.67-7.55 (m, 2H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.76-6.73 (m, 2H), 4.17-4.11 (m, 1H), 3.76 (s, 3H), 3.01 (dd, J = 13.4, 4.8 Hz, 1H), 2.81-2.78 (m, 1H), 2.75 (s, 3H), 1.35-1.27 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.18, 158.11, 150.52, 144.49, 141.09, 139.94, 138.63, 136.18, 131.05, 130.72, 130.28, 130.08, 129.67, 128.14, 127.71, 126.22, 125.99, 125.24, 121.39, 113.76, 60.67, 55.17, 32.01, 29.65, 22.33.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{24}N_2O_2$: 409.1916, found 409.1914.

3-(3,4-dimethoxybenzyl)-8-methyl-2-(quinolin-8-yl)-3,4-dihydroisoquinolin-1(2H)-one (3am): Compound **3am** was prepared according to the general procedure in 0.12 mmol scale. The product was isolated from the reaction mixture using flash column chromatography (EtOAc:Hexane = 20:80) in 79% yield as a pale yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (dd, J = 3.7, 1.2 Hz, 1H), 8.20 (dd, J = 8.2, 1.6 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.63-7.57 (m, 2H), 7.42 (dd, J = 8.3, 4.0 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.4 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 1.7 Hz, 1H), 4.19-4.14 (m, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.01 (dd, J = 13.4, 5.1 Hz, 1H), 2.86-2.76 (m, 1H), 2.73 (s, 3H), 1.28-1.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.12, 150.42, 148.67, 147.49, 144.39, 141.02, 139.83, 138.52, 136.11, 130.93, 130.66, 130.00, 129.56, 128.11, 127.64, 127.2, 126.12, 125.83, 121.31, 121.09, 112.33, 111.16, 60.36, 55.65, 37.90, 32.14, 29.54, 22.21.

HRMS: $[M+H]^+$ calculated for $C_{28}H_{27}N_2O_3$: 439.2022, found 439.2020.

5. Mechanistic Investigations

5.1. Radical Quenching Experiment

An oven dried Schlenk tube was charged with magnetic stir bar, benzamide **1a** (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol), TEMPO (1.0 equiv., 0.12 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2 trifluoroethanol (1.5 mL). Subsequently, to this reaction mixture alkene **2a** (0.24 mmol, 2 equiv.) was introduced under air. The Schlenk was vacuumized and sparged with oxygen (approximately 2 atm). The reaction mixture was stirred at room temperature in presence of white LEDs (4 x 7 watts) for 48 h. The reaction was monitored by thin-layer chromatography, only trace amount of product was observed.

5.2. DABCO Experiment

An oven dried Schlenk tube was charged with magnetic stir bar, benzamide **1a** (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol), DABCO (1 equiv., 0.12 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2

trifluoroethanol (1.5 mL). Subsequently, to this reaction mixture alkene **2a** (0.24 mmol, 2 equiv.) was introduced under air. The Schlenk was vacuumized and sparged with oxygen (approximately 2 atm). The reaction mixture was stirred at room temperature in presence of white LEDs (4 x 7 watts) for 48 h. The removal of solvent in *vacuo*, followed by flash column chromatography (EtOAc/hexane) on silica gel afforded the product in 82% yield.

5.3. Deuterium Labeling Experiments

5.3a. H/D Exchange of 1a

An oven dried Schlenk tube was charged with Teflon coated magnetic stir bar, deuterated benzamide **1b** (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2 trifluoroethanol (1.5 mL). The Schlenk was vacuumized and sparged with oxygen (approximately 2 atm). The mixture was stirred magnetically, in the presence of white LEDs (4 x 7 watts) for 2 h. The removal of solvent in *vacuo*, followed by flash column chromatography (EtOAc:hexane = 10:90) to isolate the compound. ^{1}H analysis revealedthat there is no H/D exchange on the substrate.

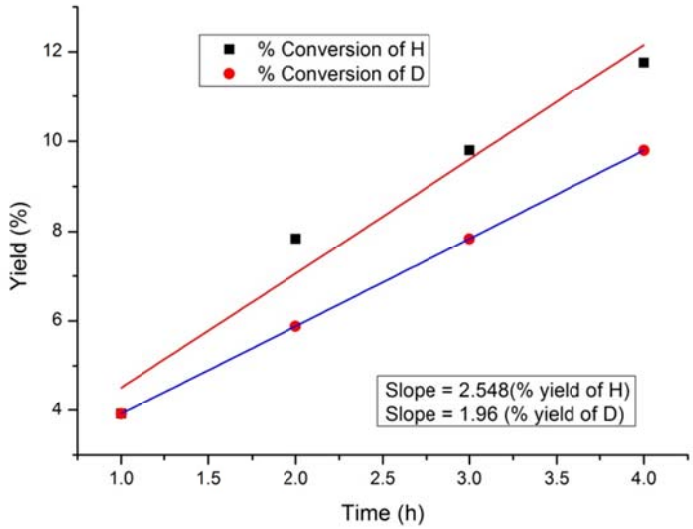
5.3b. H/D Exchange in Presence of Alkene

An oven dried Schlenk tube was charged with Teflon coated magnetic stir bar, deuterated benzamide (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2 trifluoroethanol (1.5 mL). Subsequently, to this reaction mixture dodecene (2 equiv., 0.24 mmol) was introduced. The Schlenk was vacuumized and sparged with oxygen (approximately 2 atm). The reaction mixture was stirred at room temperature in presence of white LEDs (4 x 7 watts) for 2 h. The removal of solvent in *vacuo*, followed by flash column chromatography (EtOAc/hexane) on silica gel afforded the product **3ba**-D_4 as well as the starting material **1b**-D_5. ^{1}H analysis revealed that there is no H/D exchange takes place.

5.4 Parallel Kinetic Isotope Effect Experiments

An oven dried Schlenk tube was charged with Teflon coated magnetic stir bar, deuterated benzamide **1b**-D_5(0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol) and Na_2EosinY (10 mol%, 0.012 mmol**)** followed by 2,2,2 trifluoroethanol. Subsequently, to this reaction mixture alkene **2a** (0.24 mmol, 2 equiv.) was introduced under air. The Schlenk was vacuumized and sparged with oxygen (approx. 2 atm). The same procedure is followed for the benzamide **1b**-H_5 in another oven dried Schlenk tube. The reaction mixtures were stirred at room temperature in presence of white LEDs (4 x 7 watts) for 1 h. The same reactions were repeated for 2, 3, 4 h. After the completion of the reaction, immediately quenched with 1 mL of ethyl acetate. Then the reaction mixture was diluted with 5 mL ethyl acetate and filtered using a silica pad. The solvent was removed under reduced pressure and ^{1}H NMR is taken using anisole (7 mg) as the internal standard. The k_H/k_D value is 1.3 ± 0.06 as determined from a plot of the NMR yields *versus* the time of the reaction (in minutes).

Time (in hours)	1	2	3	4
Yield of H (in per cent)	3.92	7.84	9.80	11.76
Yield of D (in per cent)	3.92	5.88	7.84	9.80

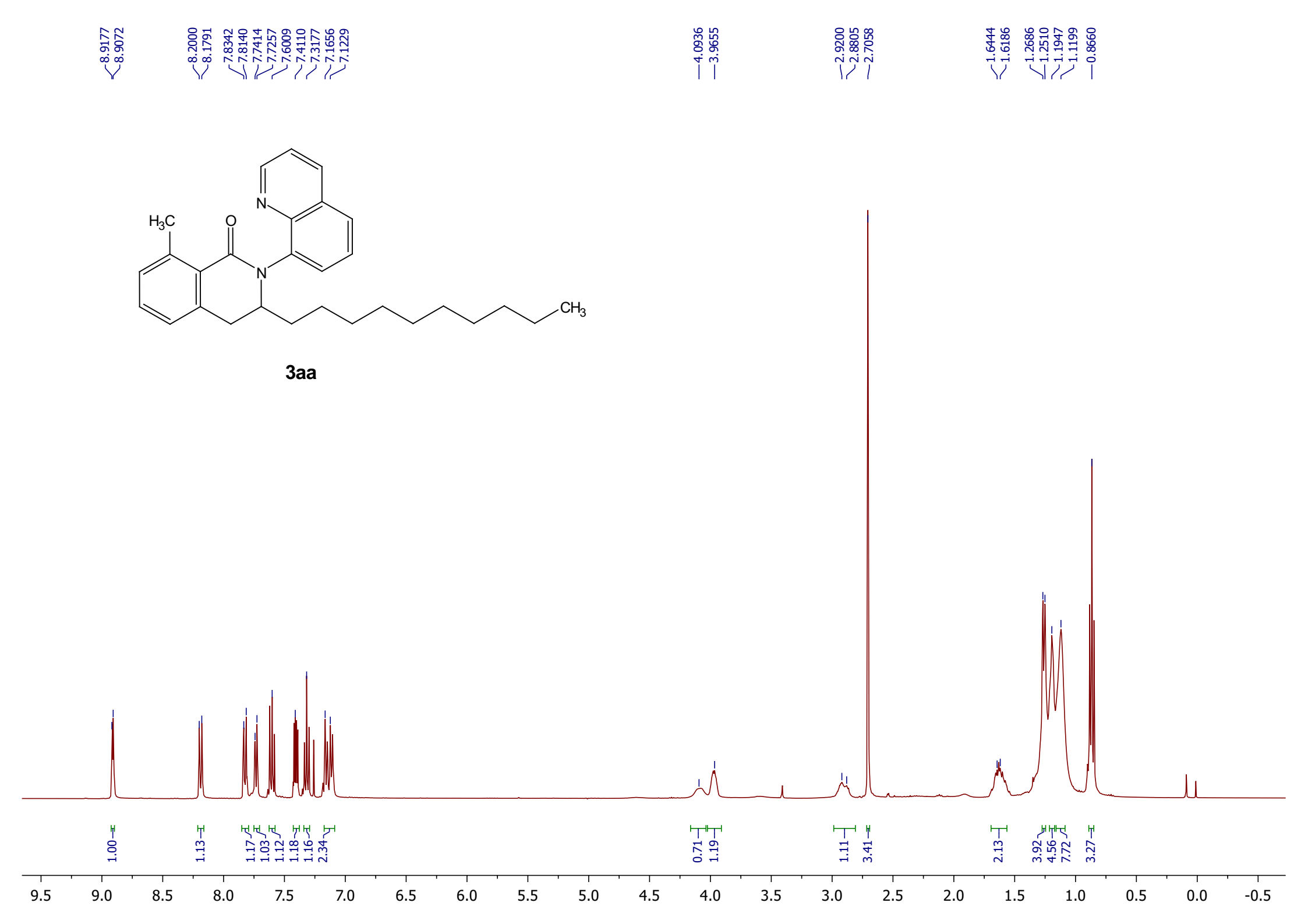


5.5. KI/Starch Experiment

An oven dried Schlenk tube was charged with Teflon coated magnetic stir bar, deuterated benzamide **1b** (0.12 mmol), $Co(acac)_2$ (20 mol%, 0.024 mmol), Sodium triflate (50 mol%, 0.06 mmol), KI (1 equiv., 0.12 mmol) and Na_2EosinY (10 mol%, 0.012 mmol) followed by 2,2,2 trifluoroethanol (1.5 mL). Subsequently, to this reaction mixture alkene **2a** (0.24 mmol, 2 equiv.) was introduced under air. The Schlenk was vacuumized and sparged with oxygen (approximately 2 atm). The reaction mixture was stirred at room temperature in presence of white LEDs (4 x 7 watts) for 48 h. After the reaction time, starch solution was added to the reaction mixture which led to a colour change from blue black solution. This indicated the presence of superoxide anion in the reaction mixture.

6. References

[1] (a) Aihara, Y.; Chatani, N., Nickel-Catalyzed Direct Alkylation of C–H Bonds in Benzamides and Acrylamides with Functionalized Alkyl Halides via Bidentate-Chelation Assistance. *J. Am. Chem. Soc.* **2013,** *135*, 5308-5311. (b) Barsu, N.; Kalsi, D.; Sundararaju, B., Carboxylate Assisted Ni-Catalyzed C-H Bond Allylation of Benzamides. *Chem. Eur. J.*, **2015,** *21*, 9364-9368. (c) Yamashita, Y.; Katsuki, T., Asymmetric Diels-Alder Reaction Using Oxo(salen)manganese(V) Complex as a Lewis Acid Catalyst. *Synlett* **1995,** *1995*, 829-830. (d) Sommai, P.-A.; Tetsuya, S.; Yoshiki, K.; Masahiro, M.; Masakatsu, N., Palladium-Catalyzed Arylation of Azole Compounds with Aryl Halides in the Presence of Alkali Metal Carbonates and the Use of Copper Iodide in the Reaction. *Bull. Chem. Soc. Jpn.* **1998,** *71*, 467-473.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CH3
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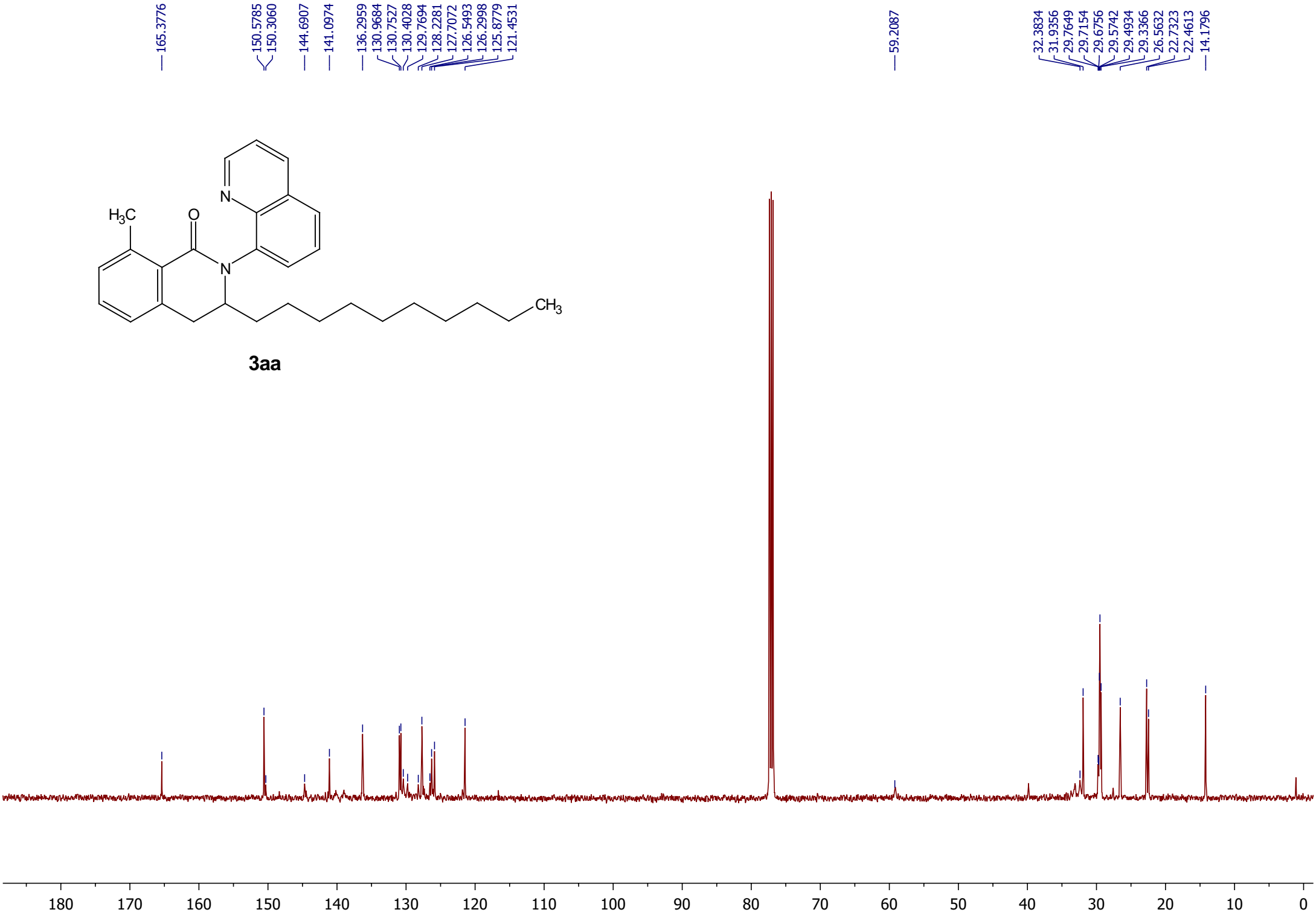
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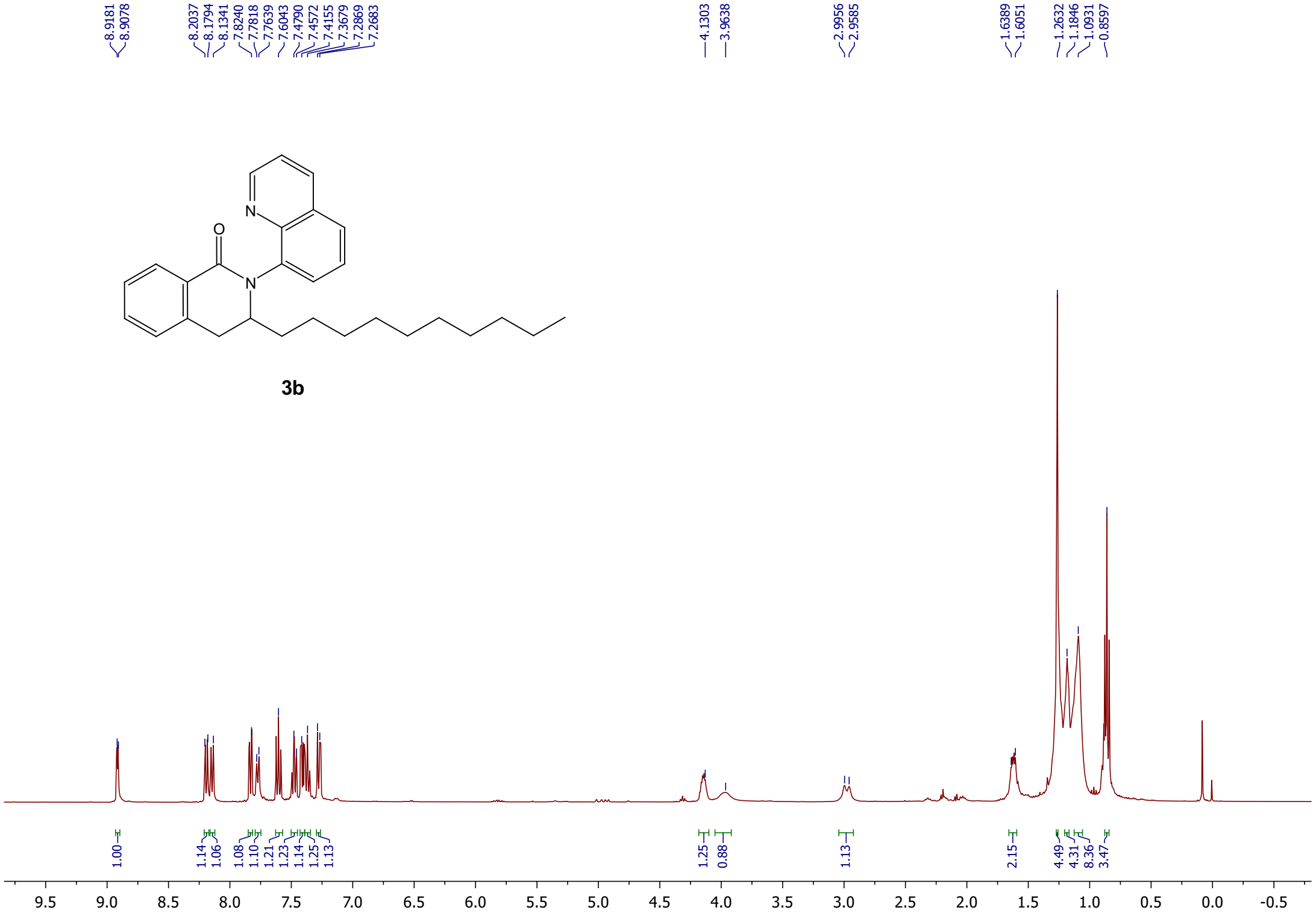
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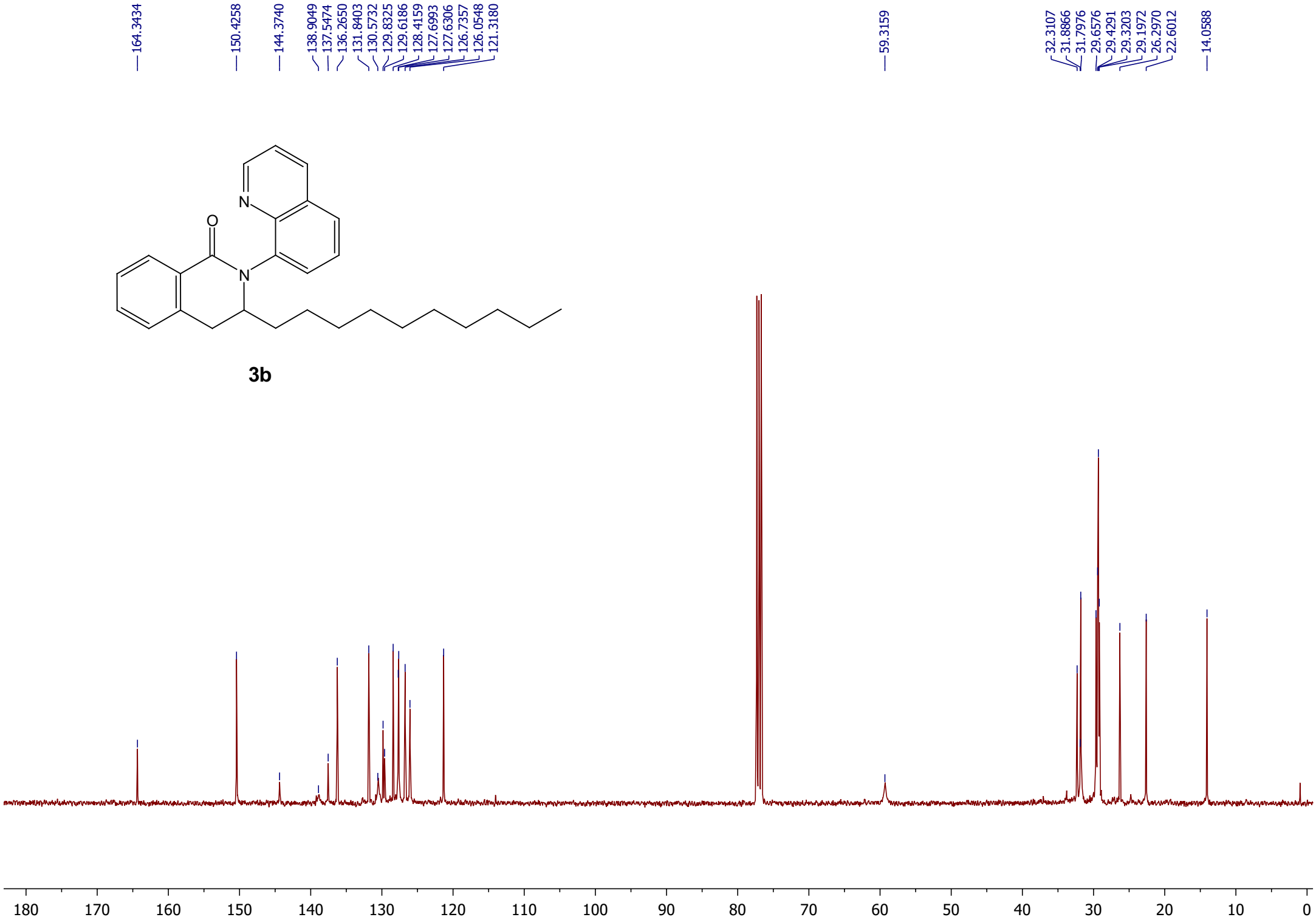
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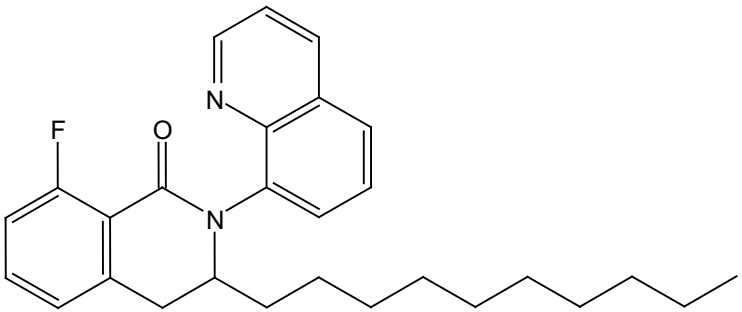
3b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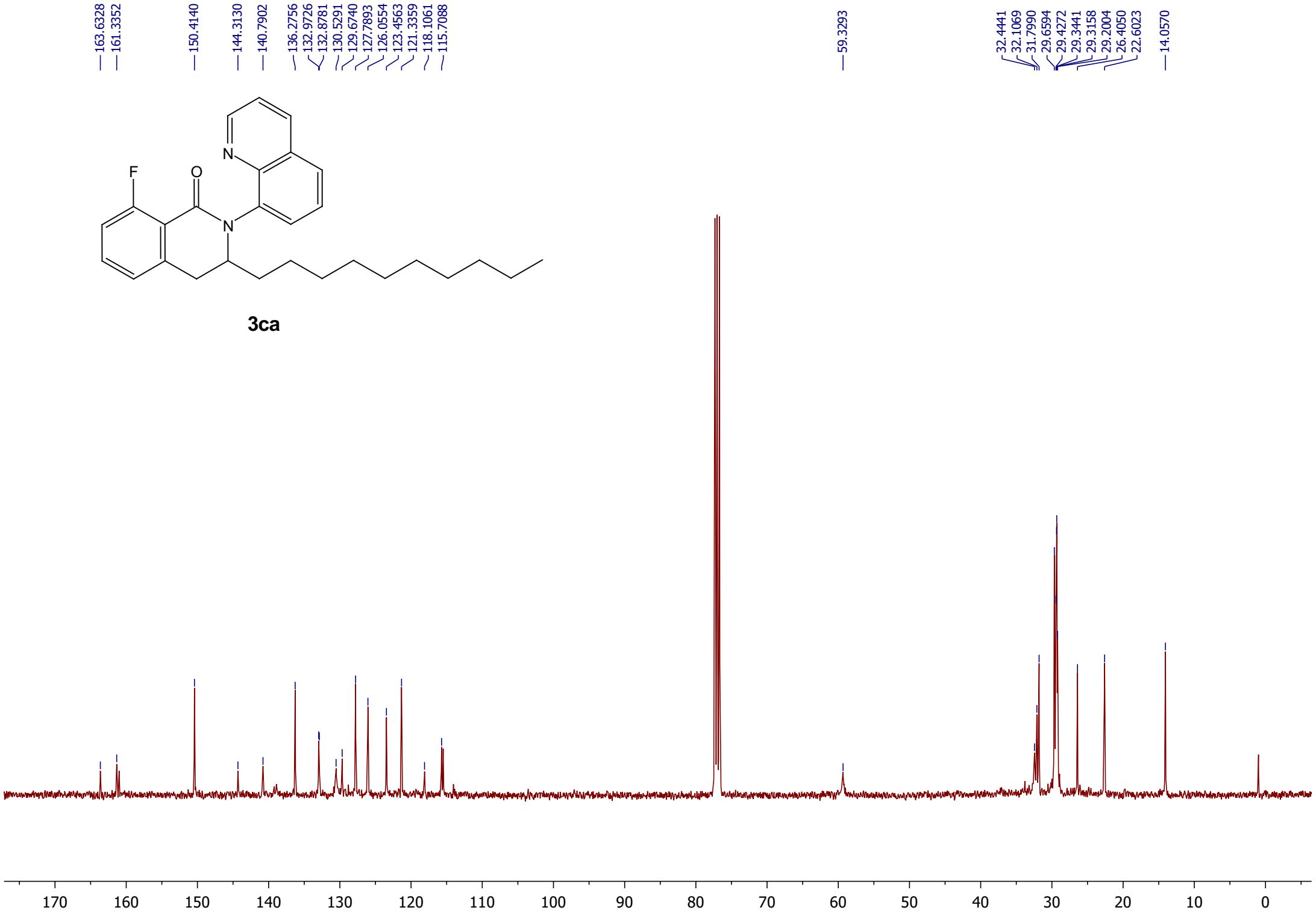
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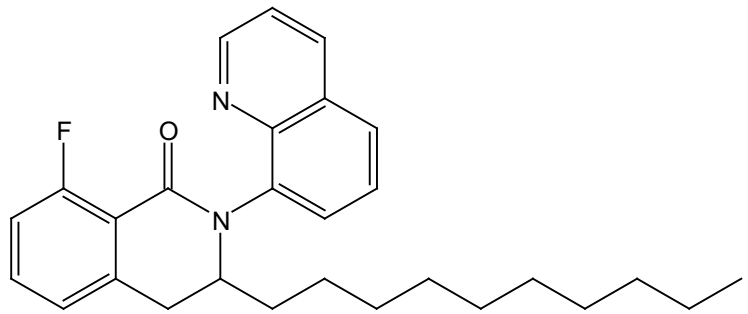
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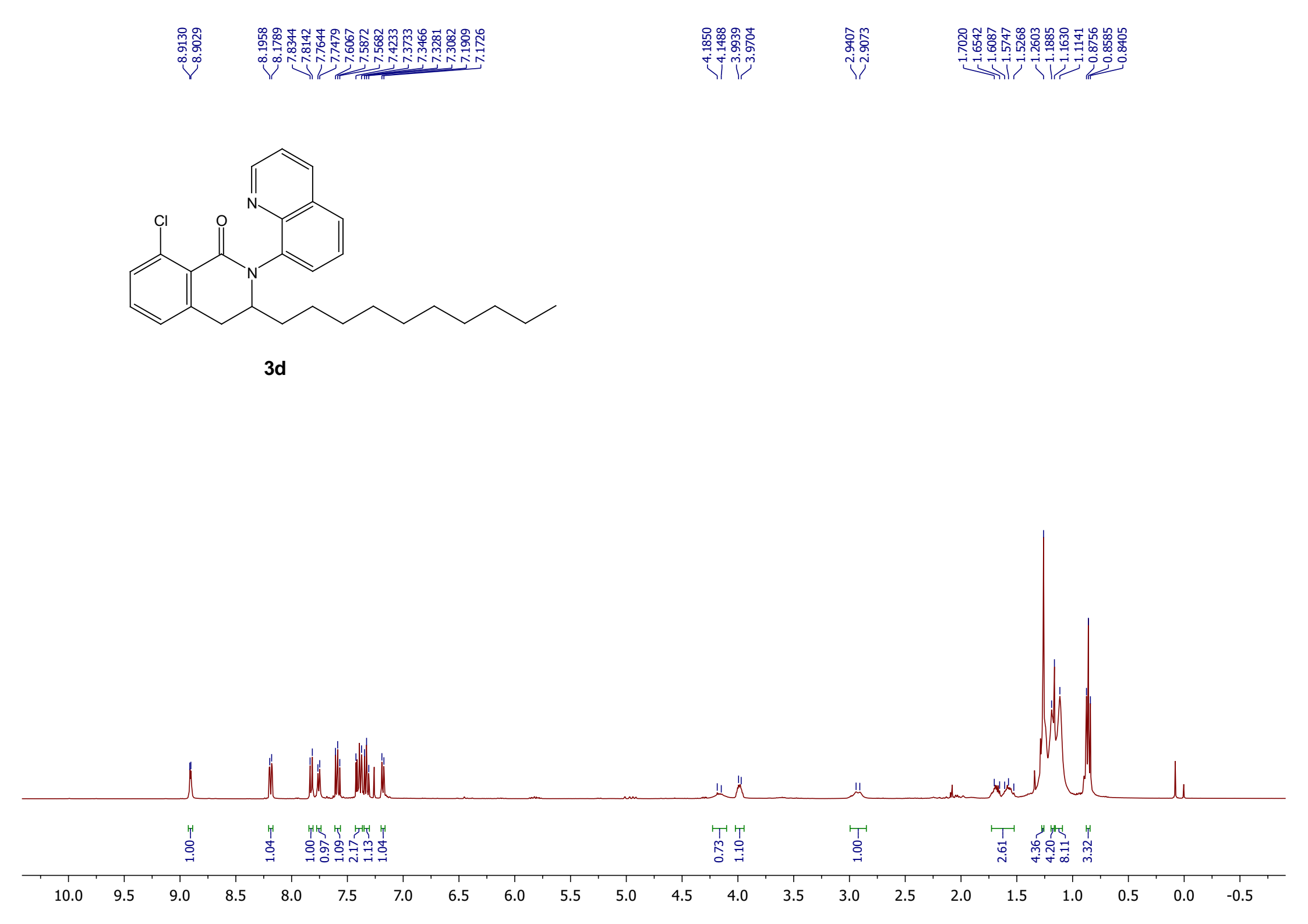
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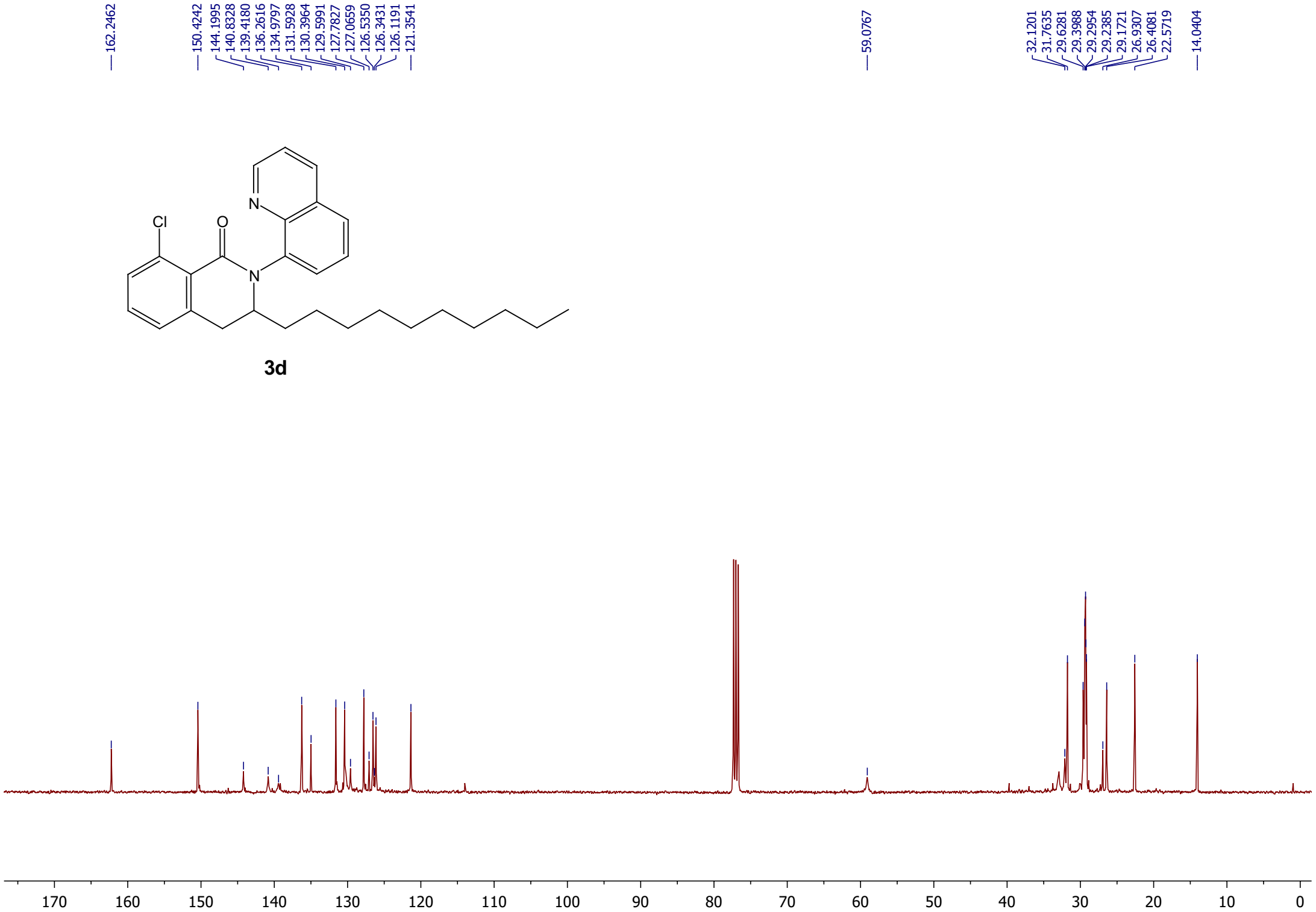
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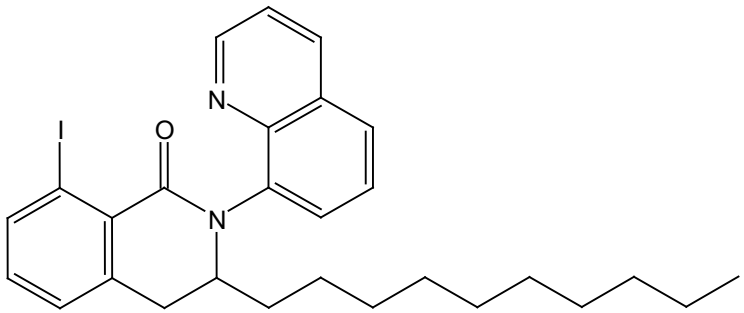
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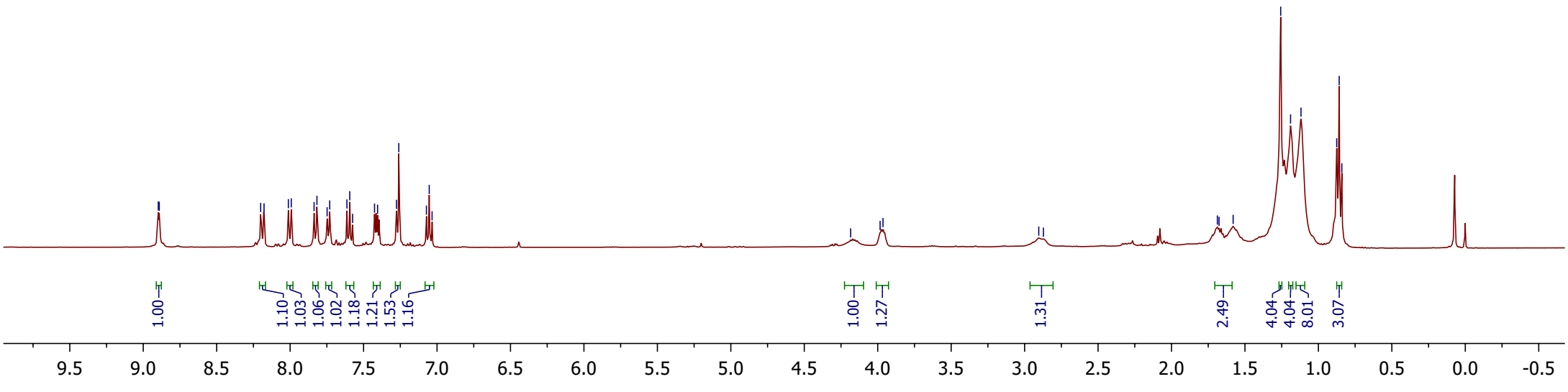
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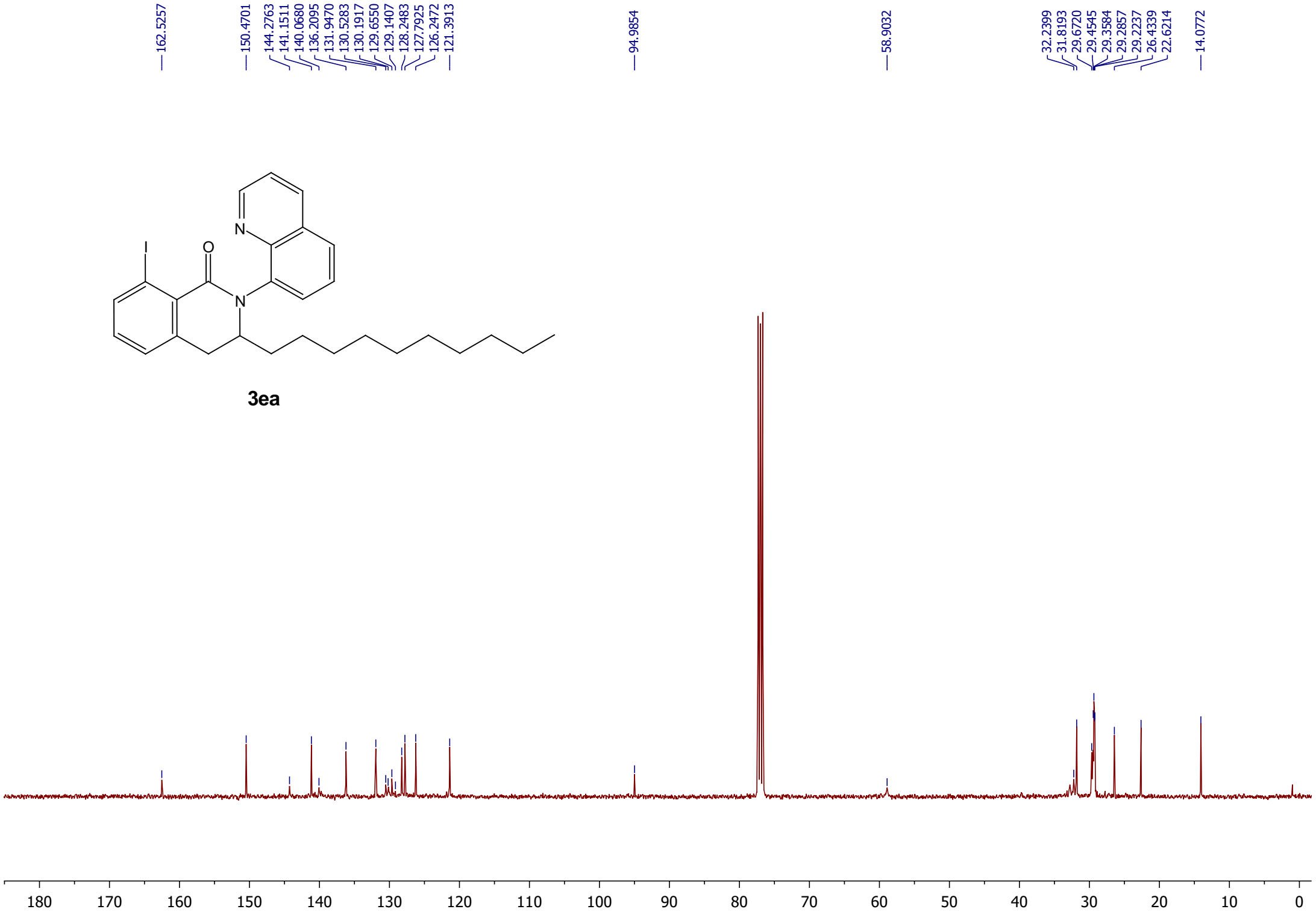
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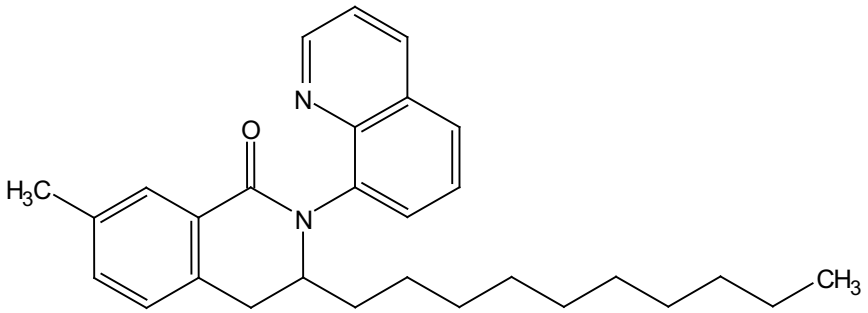

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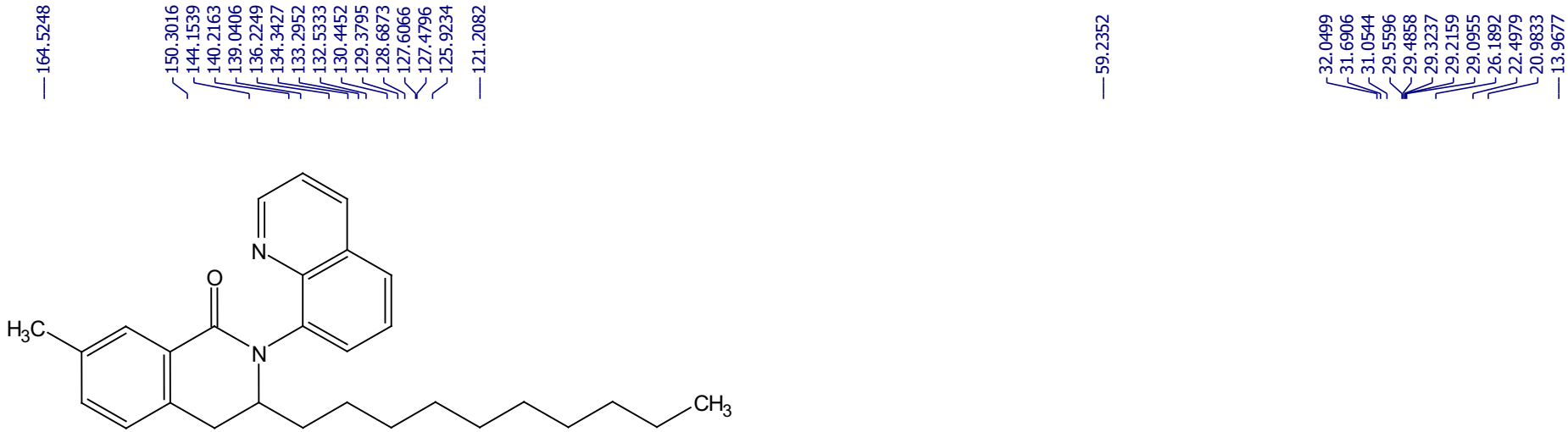

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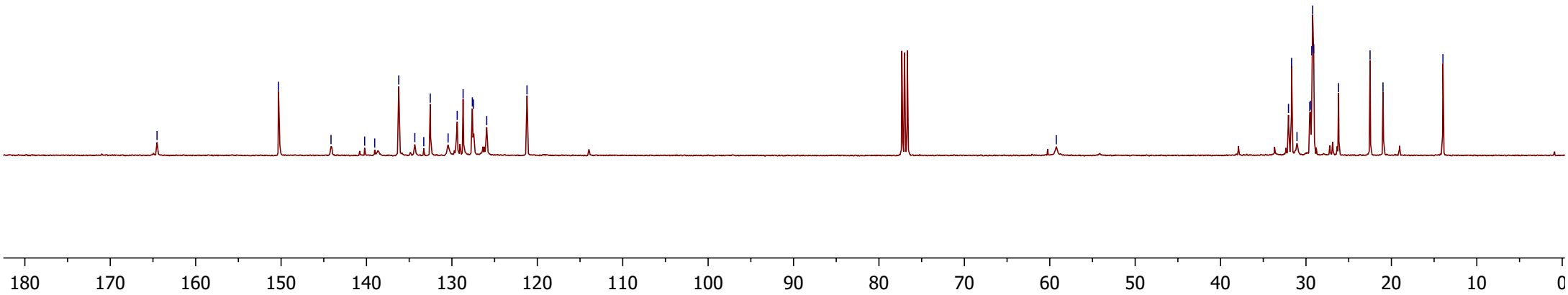

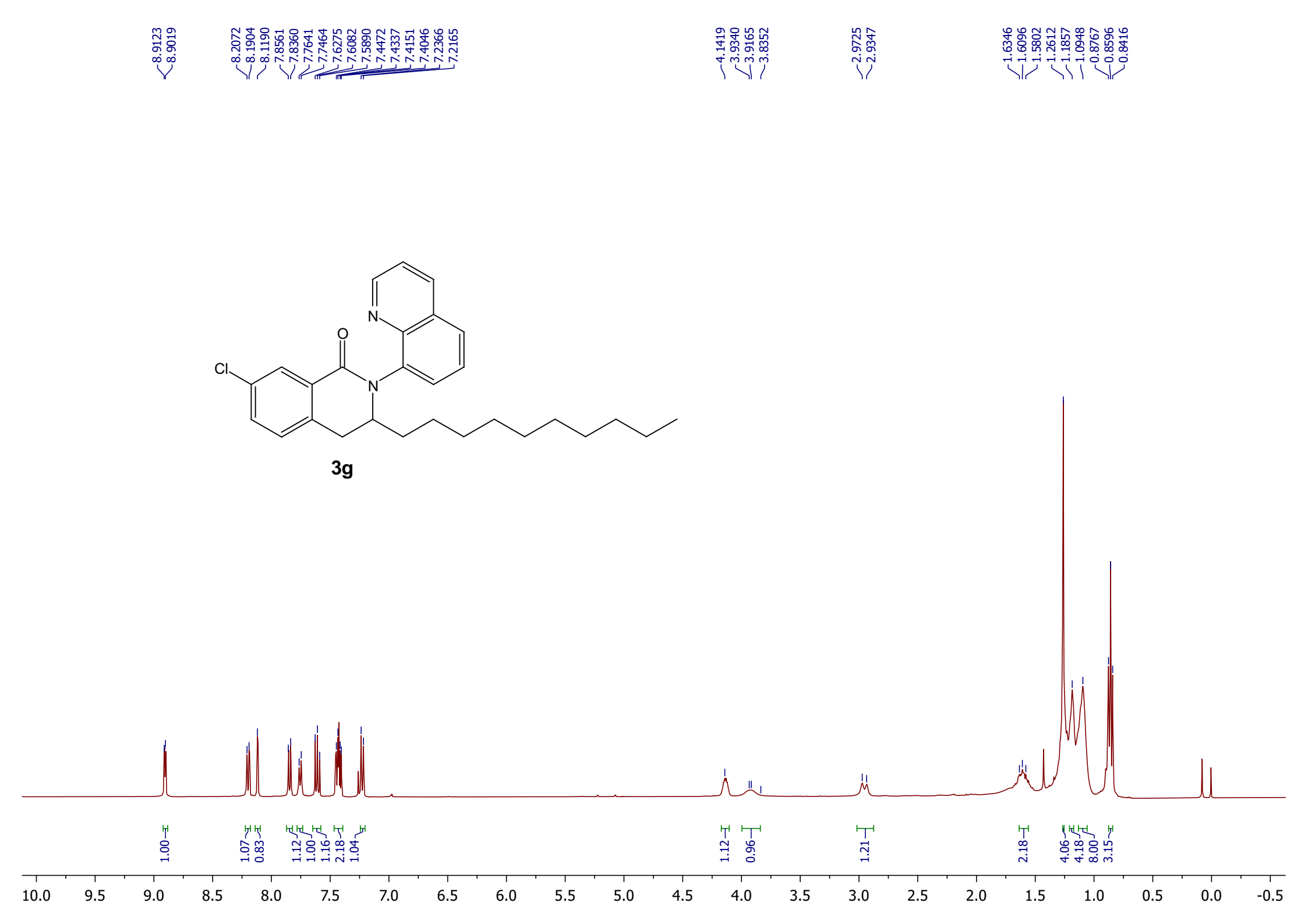
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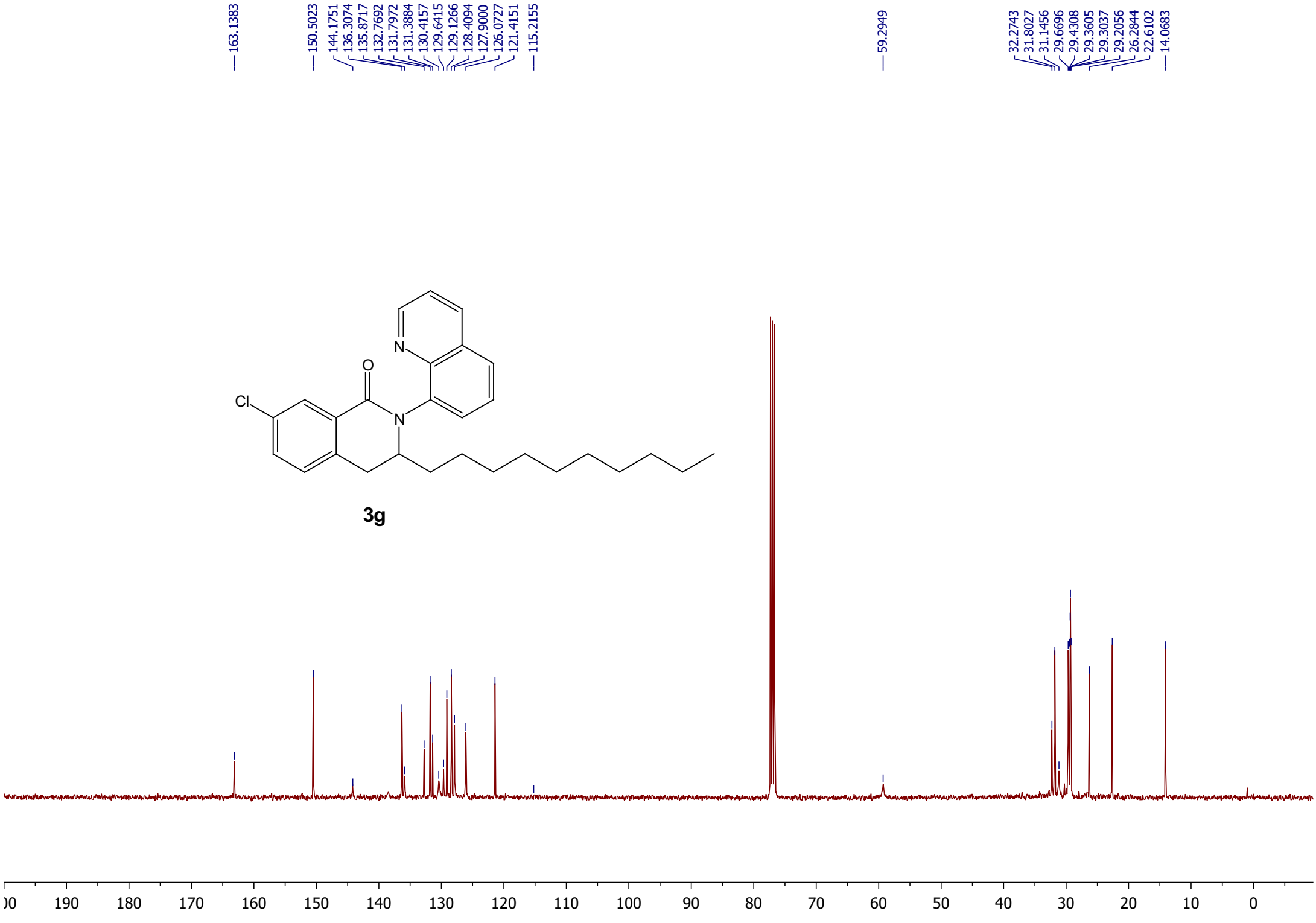
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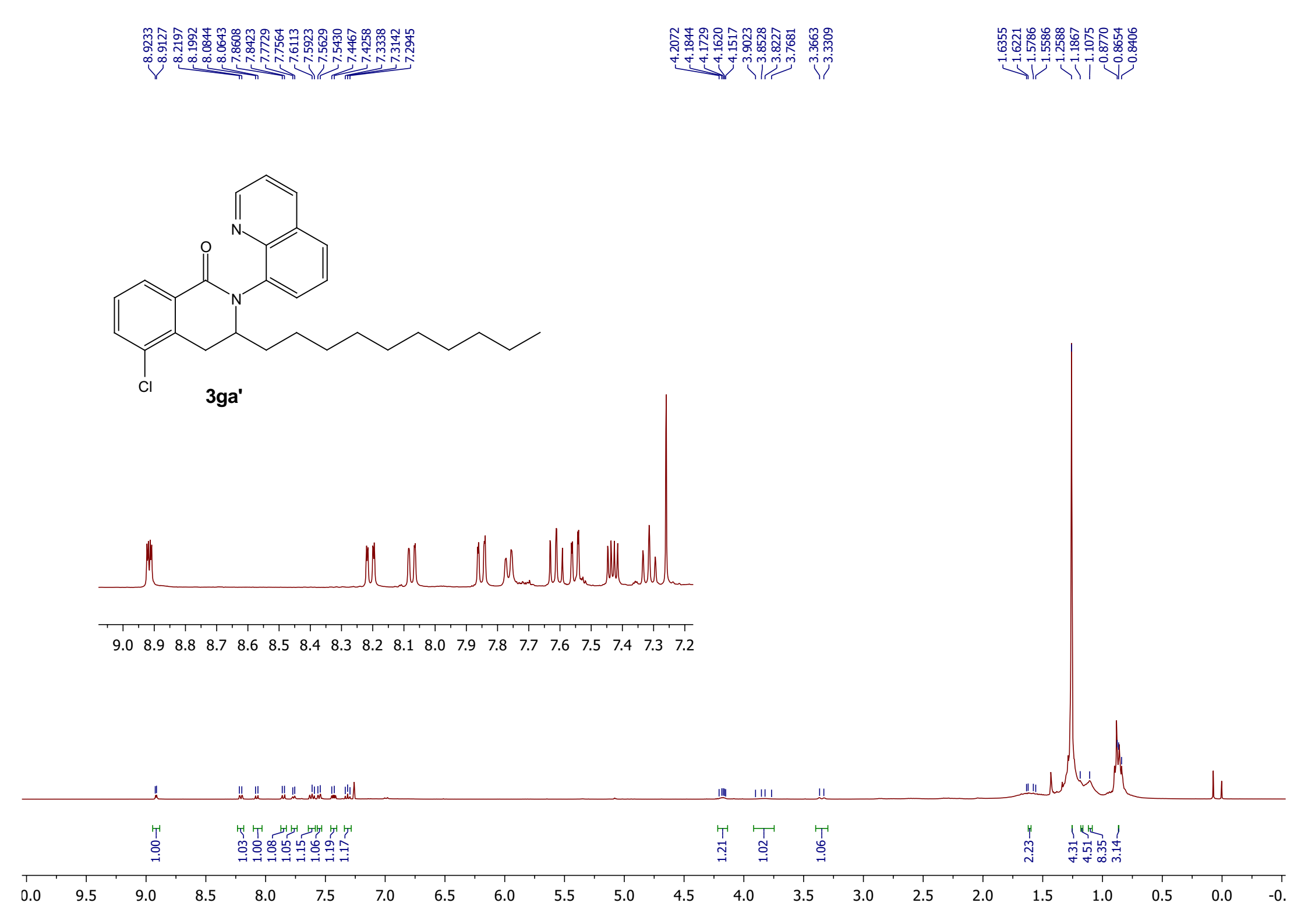
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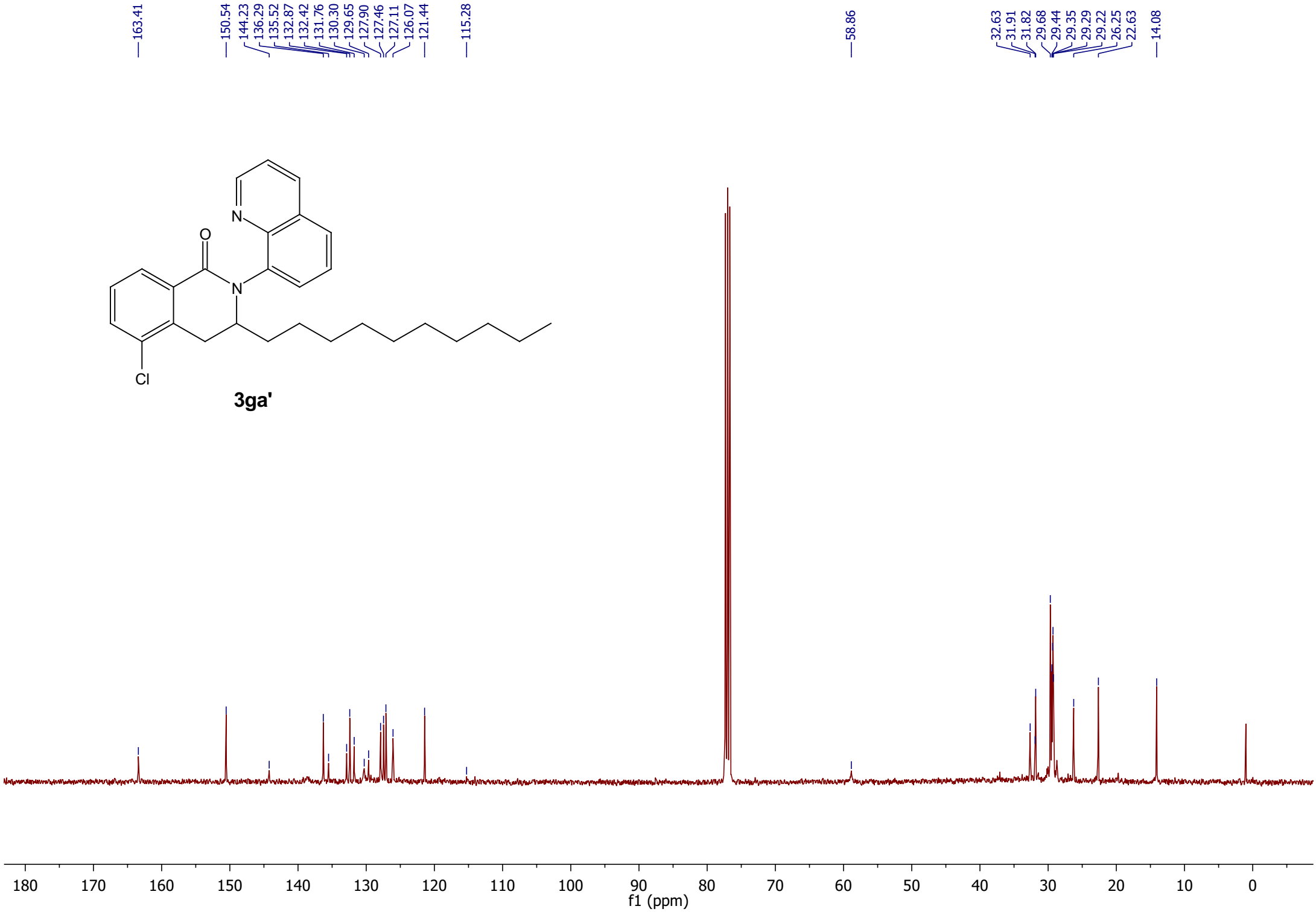
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22.63
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O
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Cl
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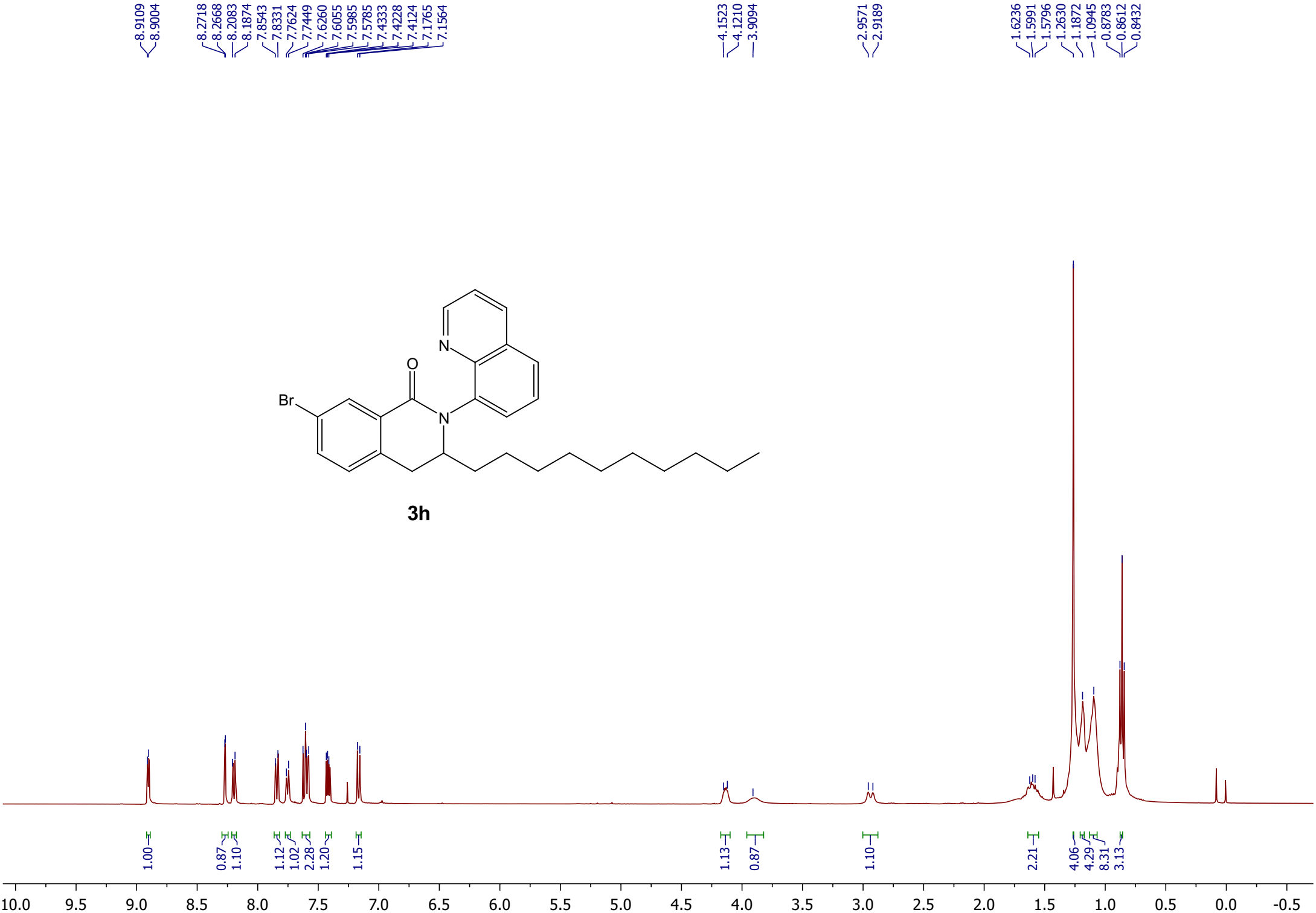
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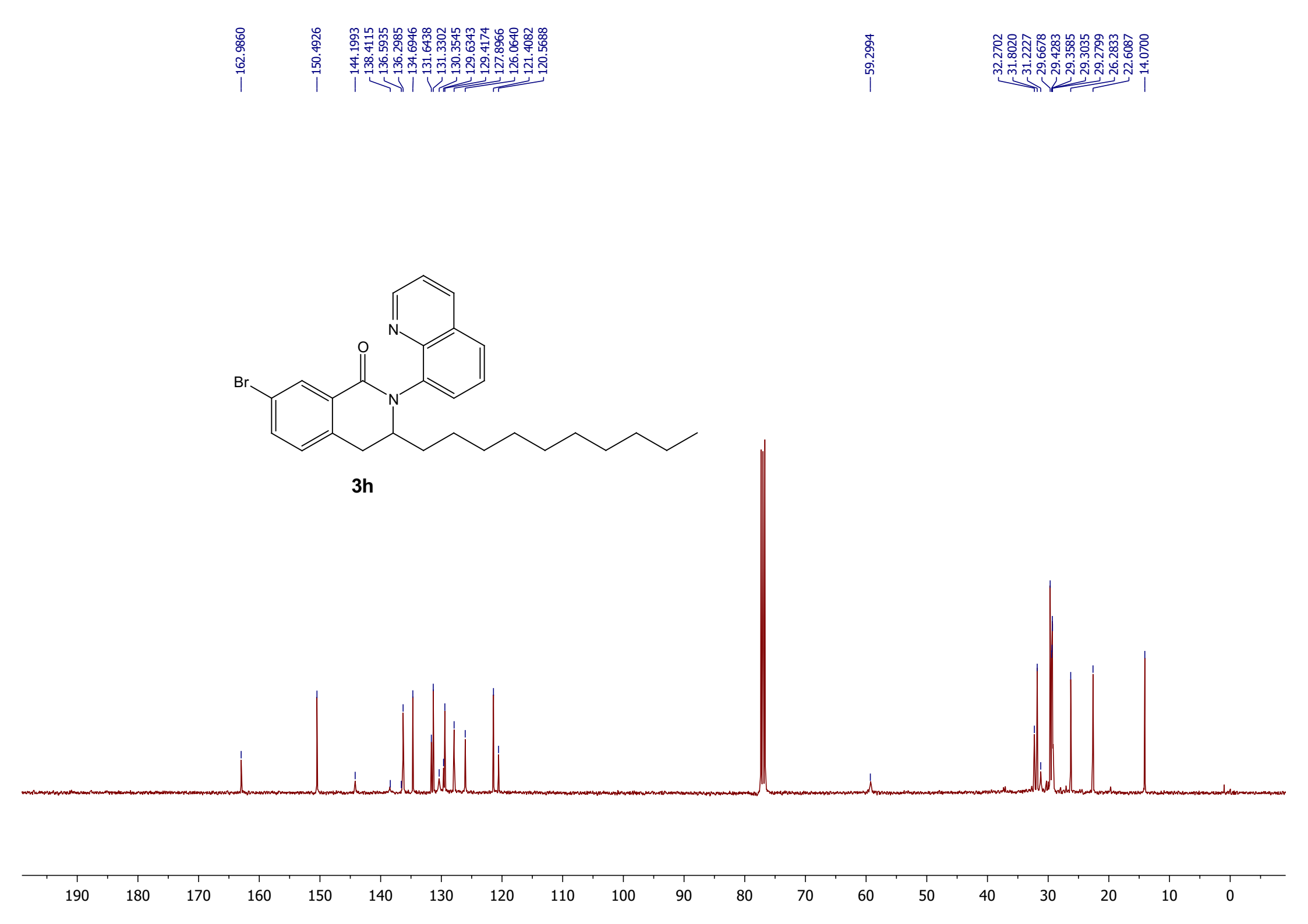
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Br
O
N
N
3h
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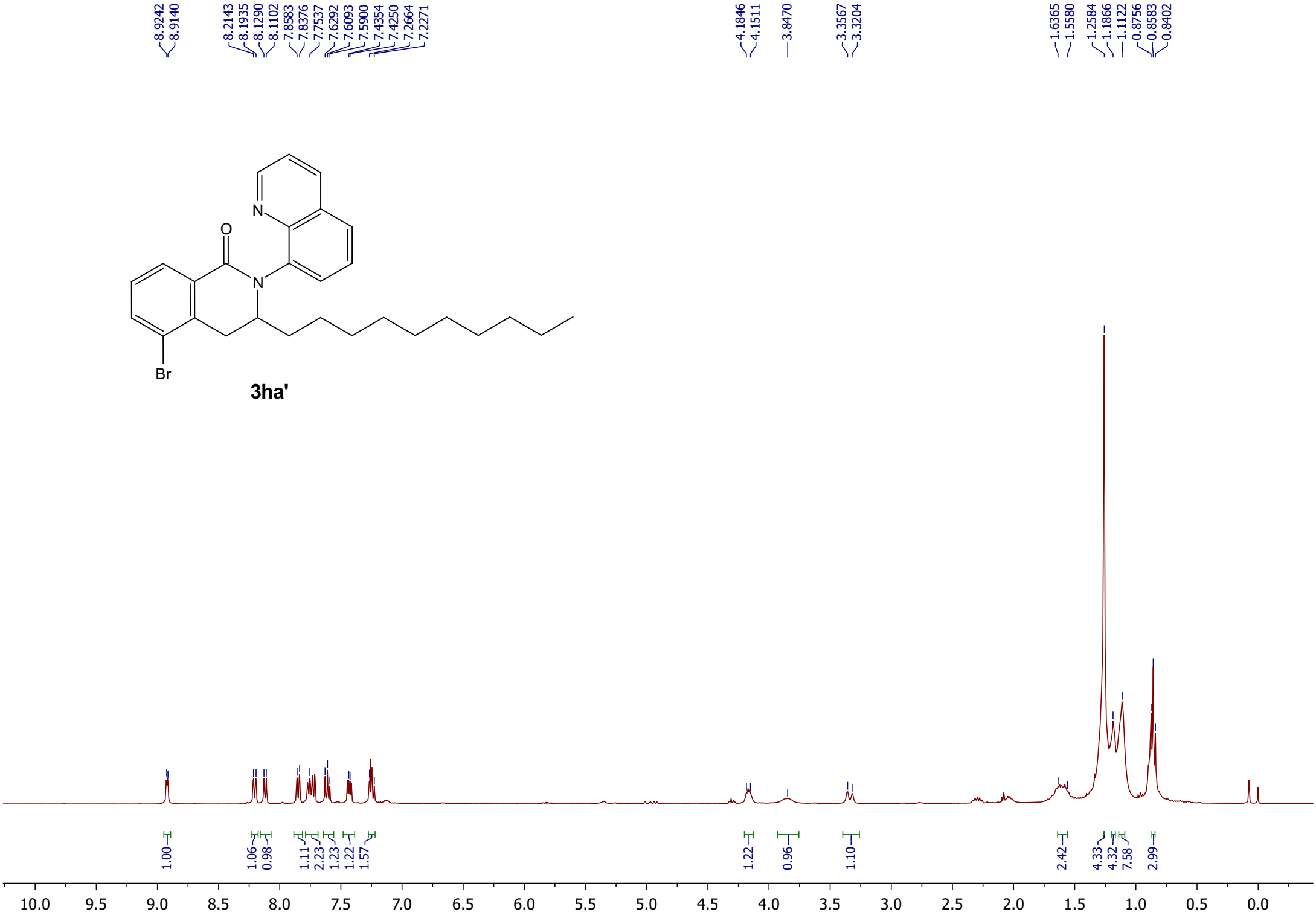
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Br
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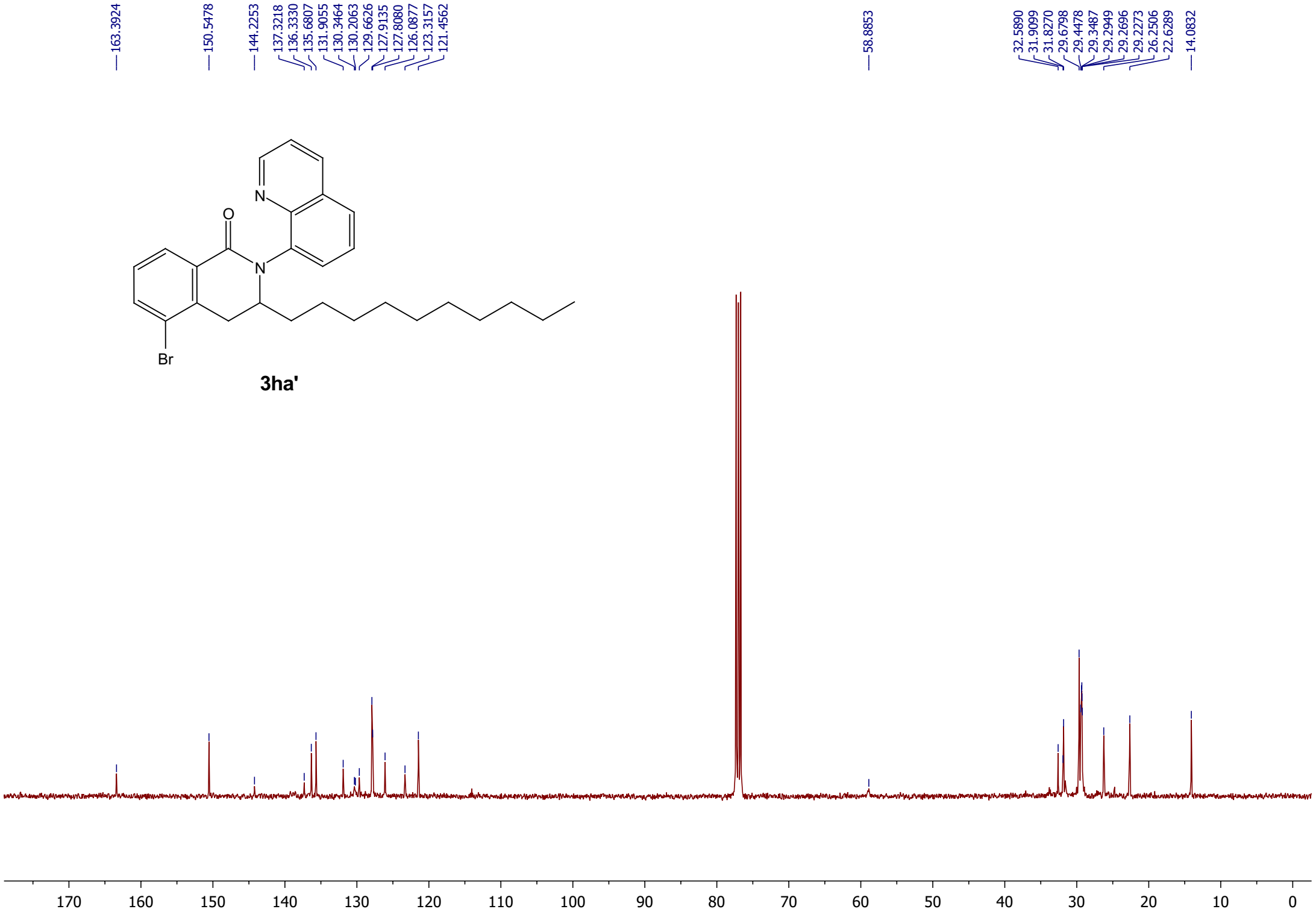
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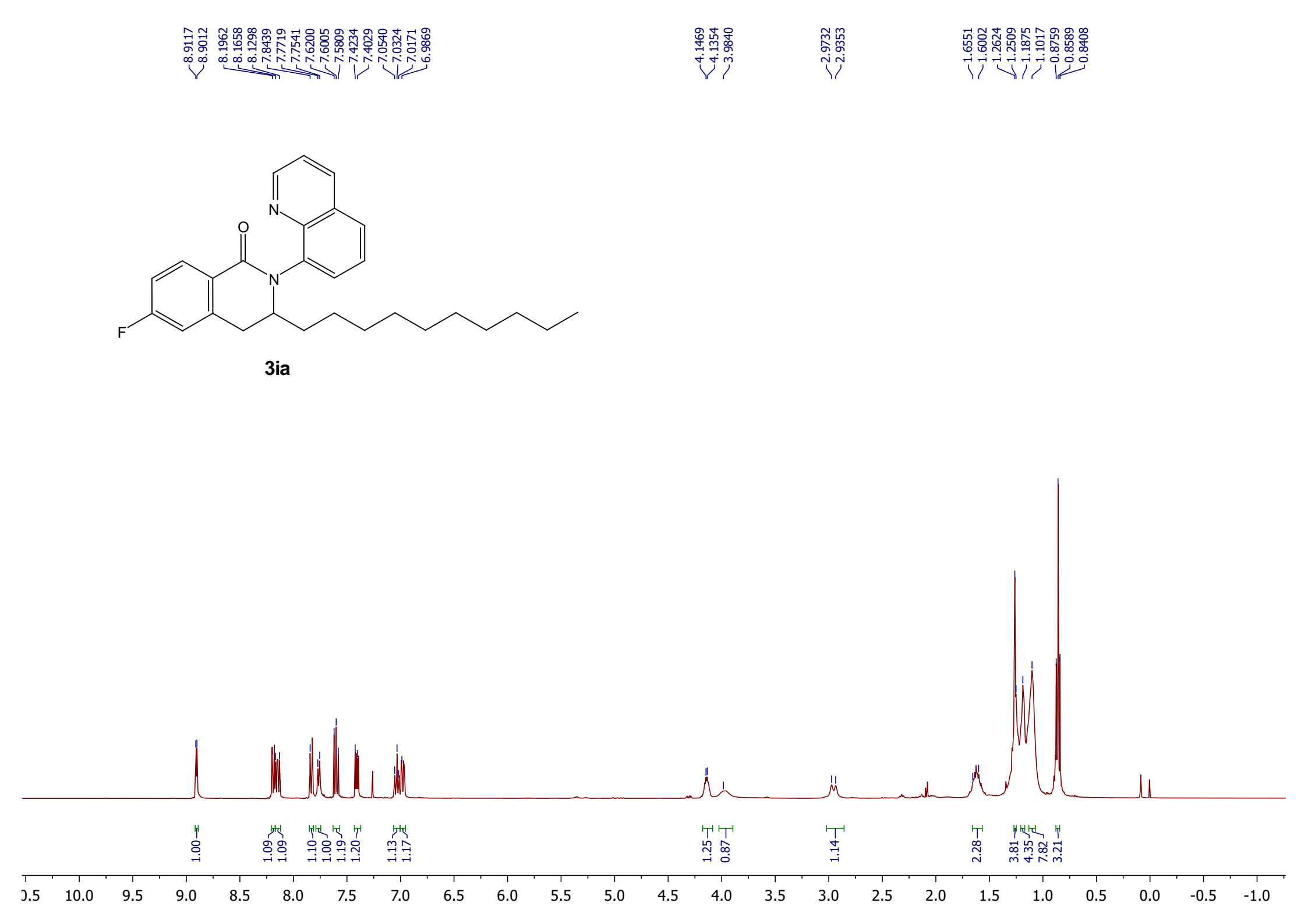
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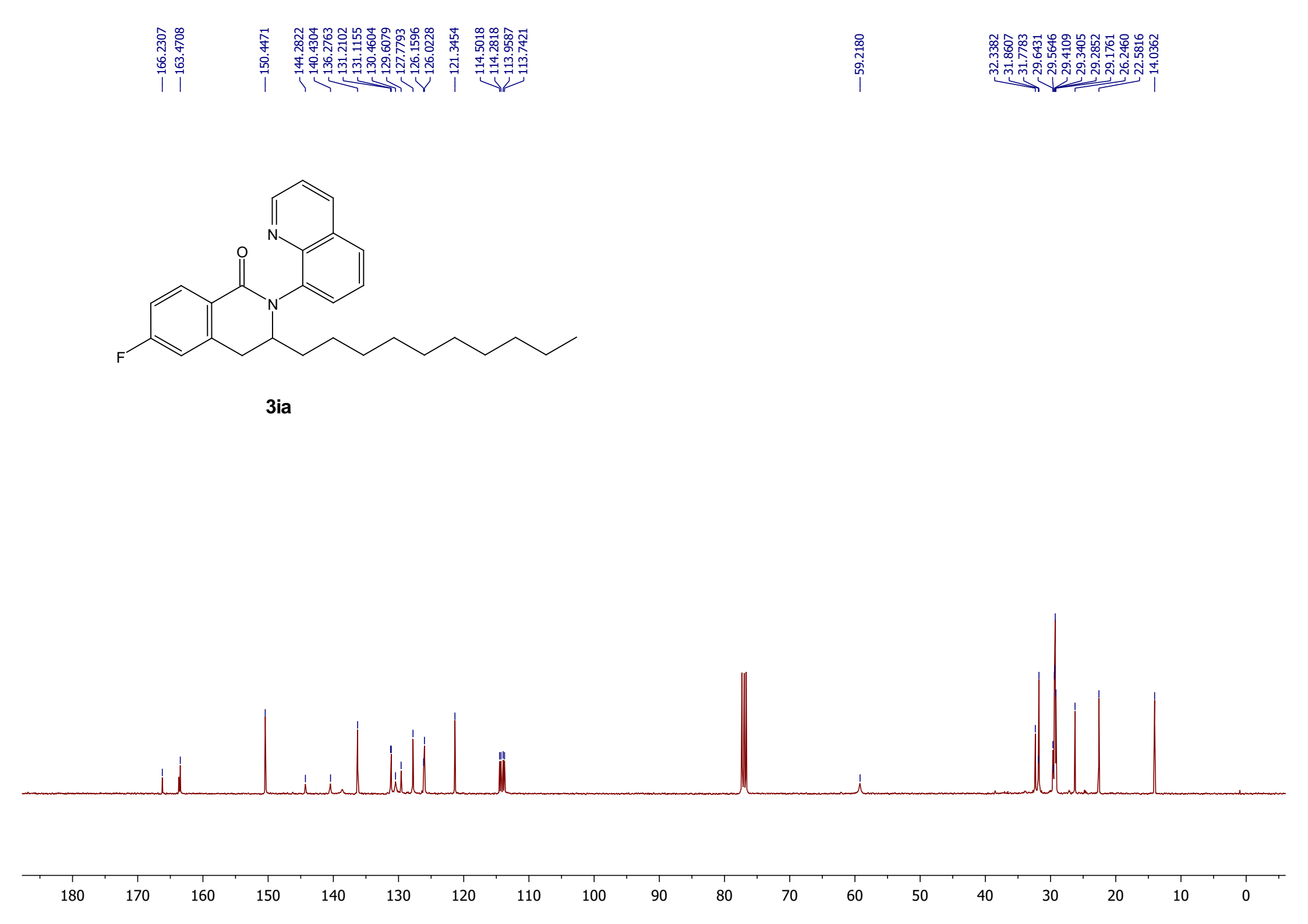
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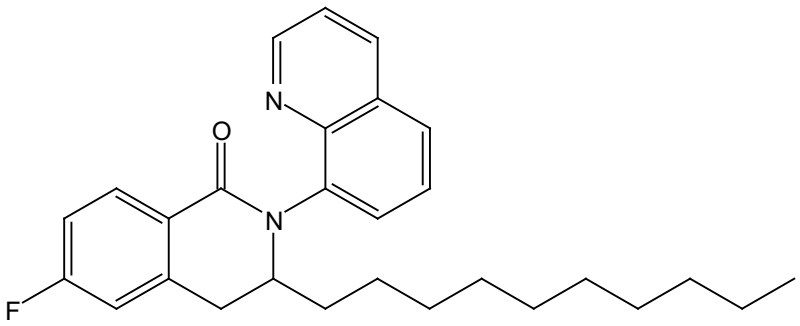
O
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N
F

3ia

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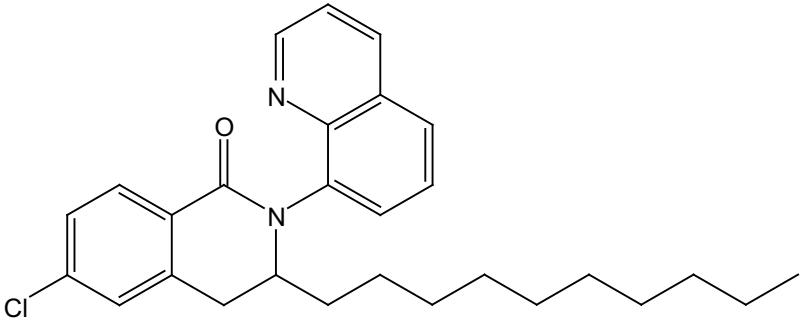

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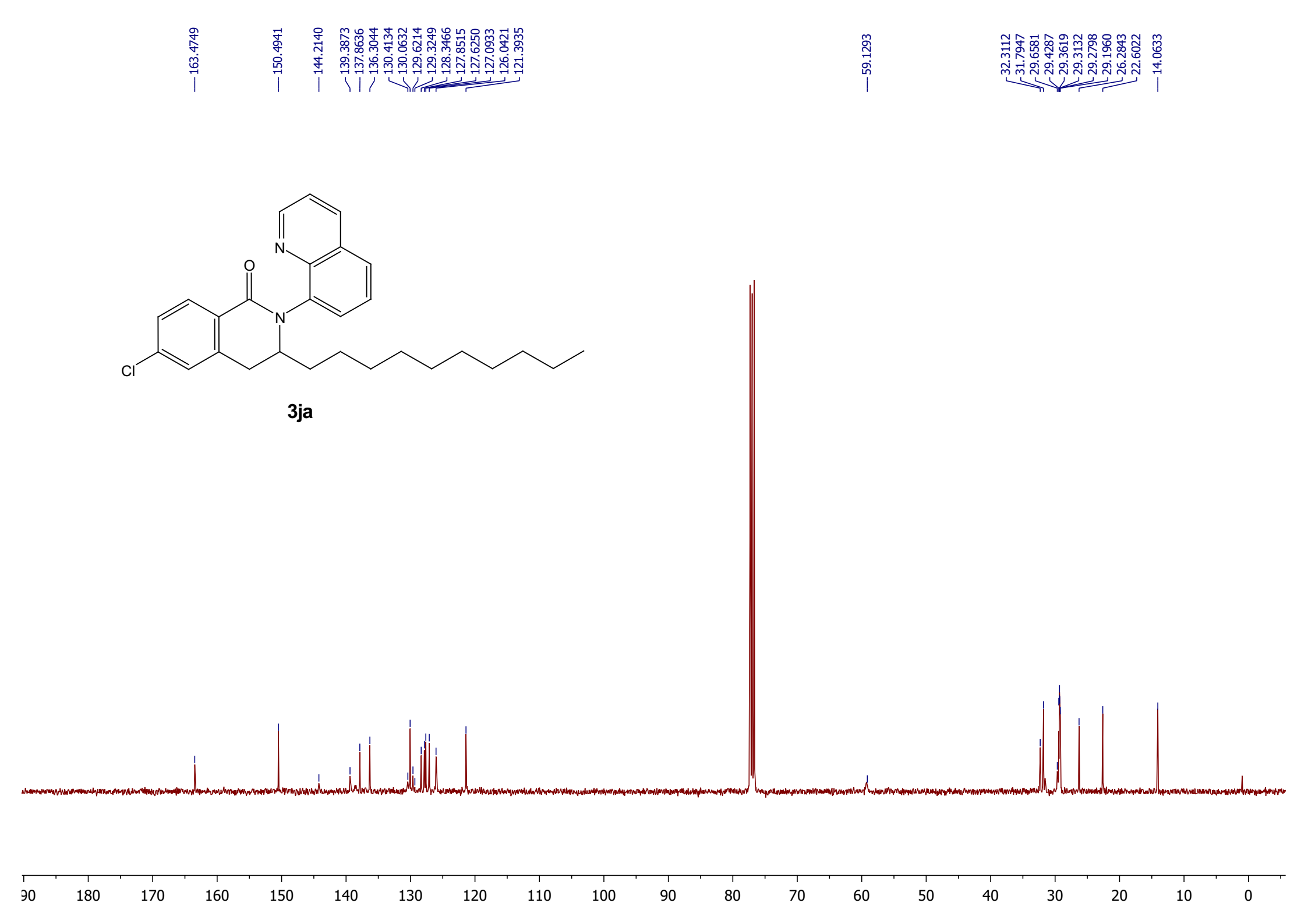
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O
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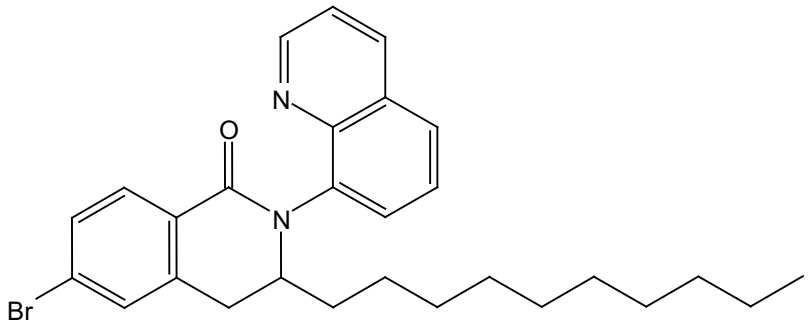
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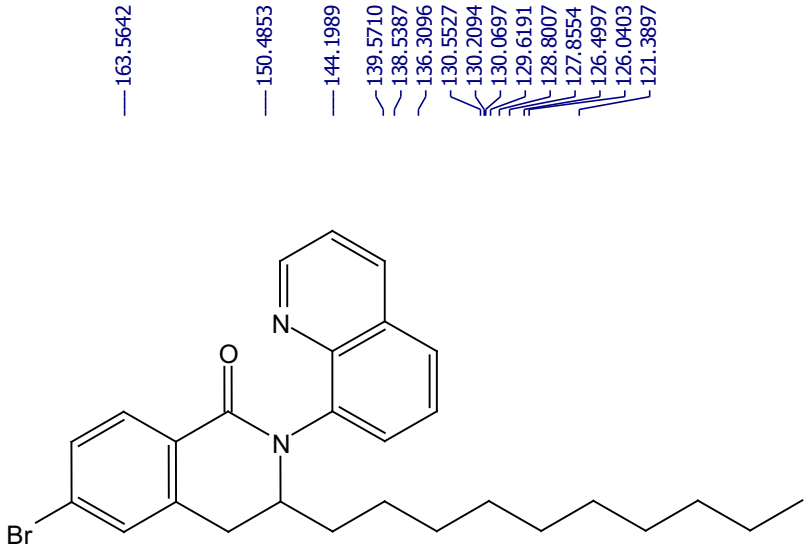
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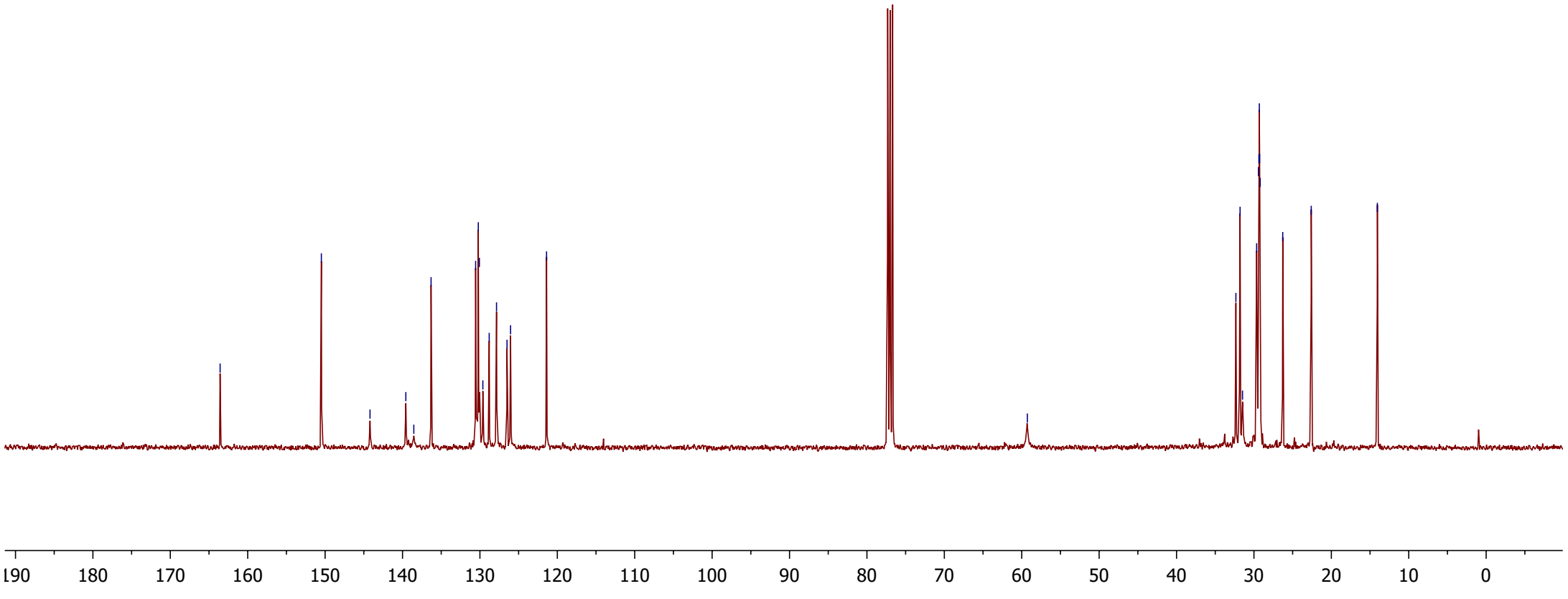
Br

3ka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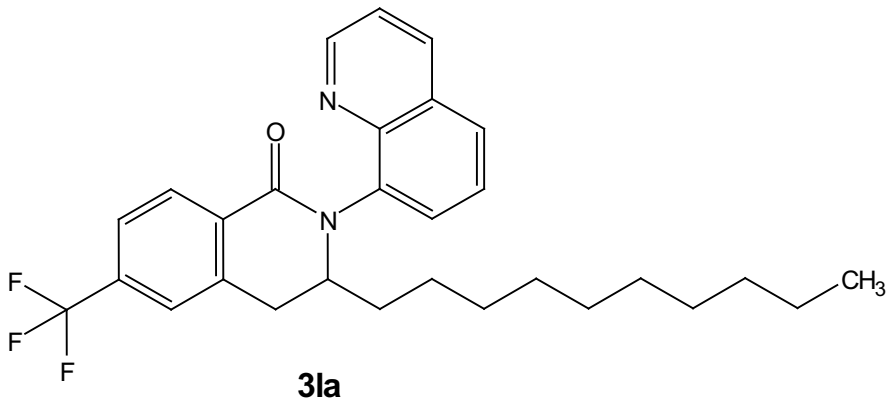

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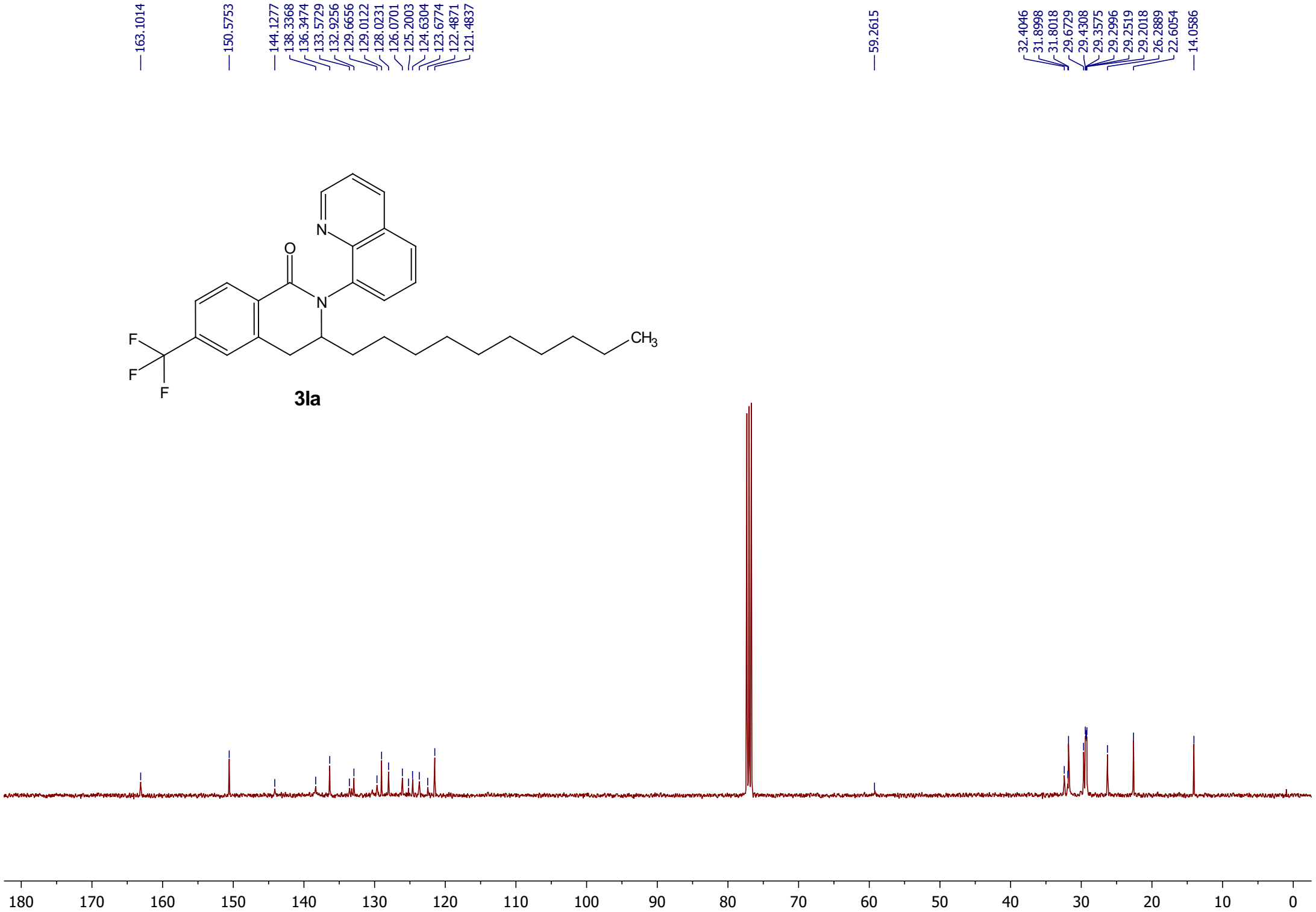
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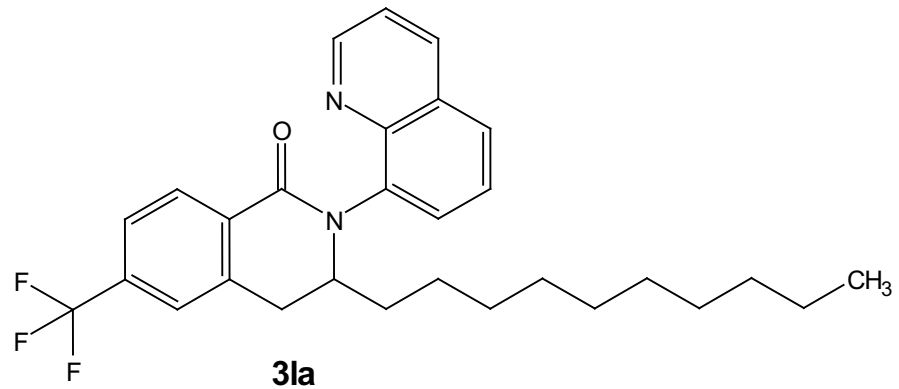
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CH3

3la

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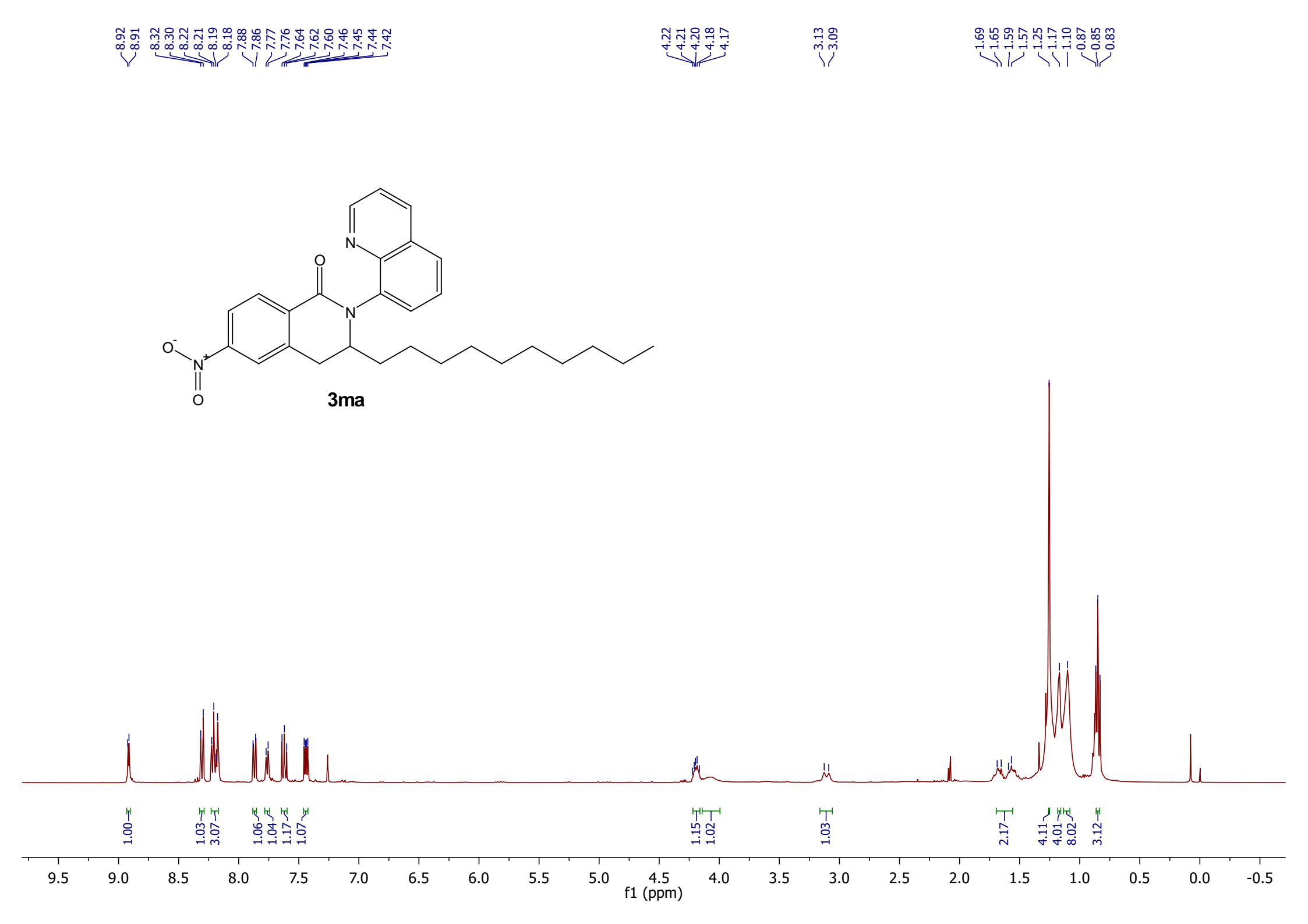
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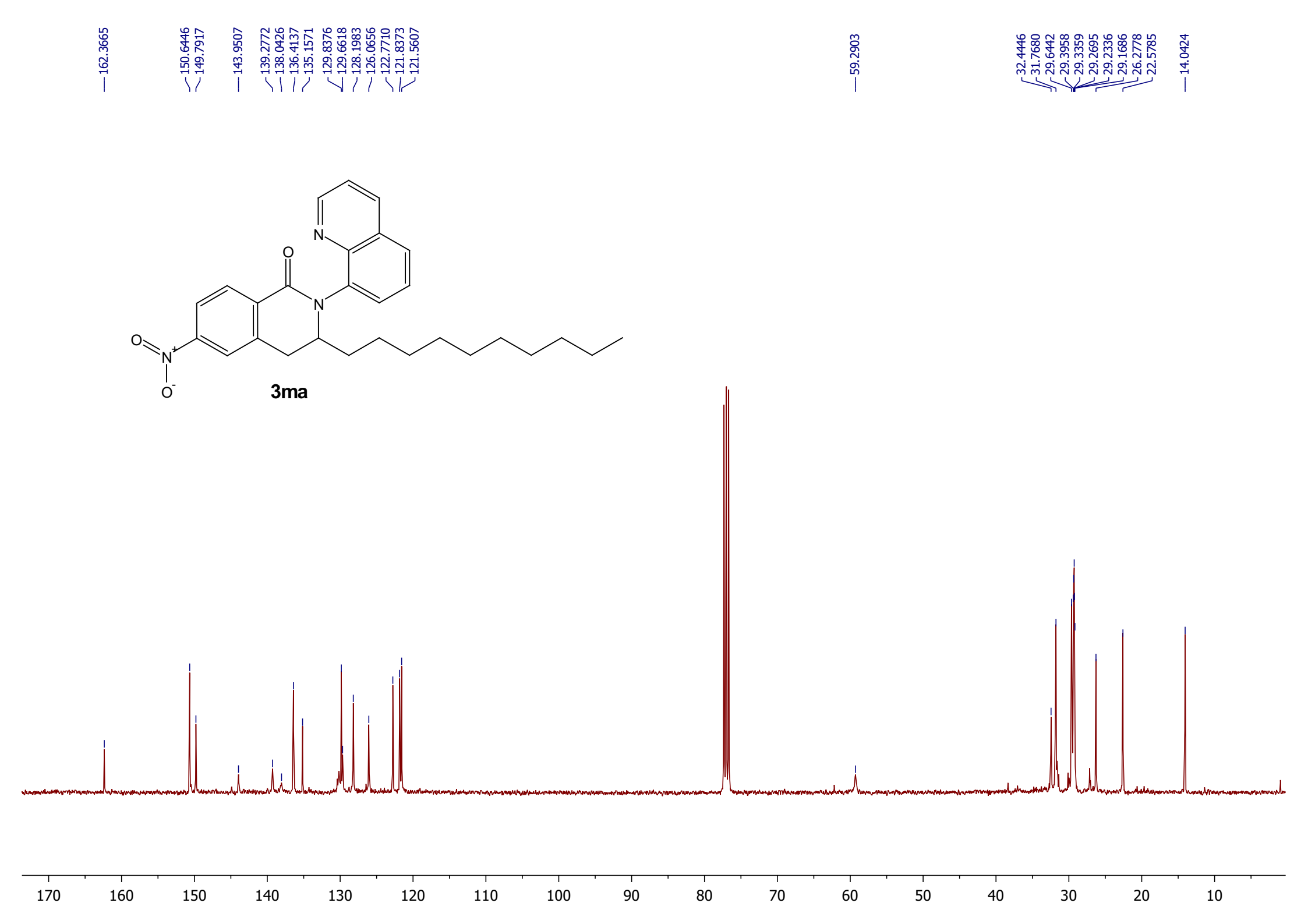
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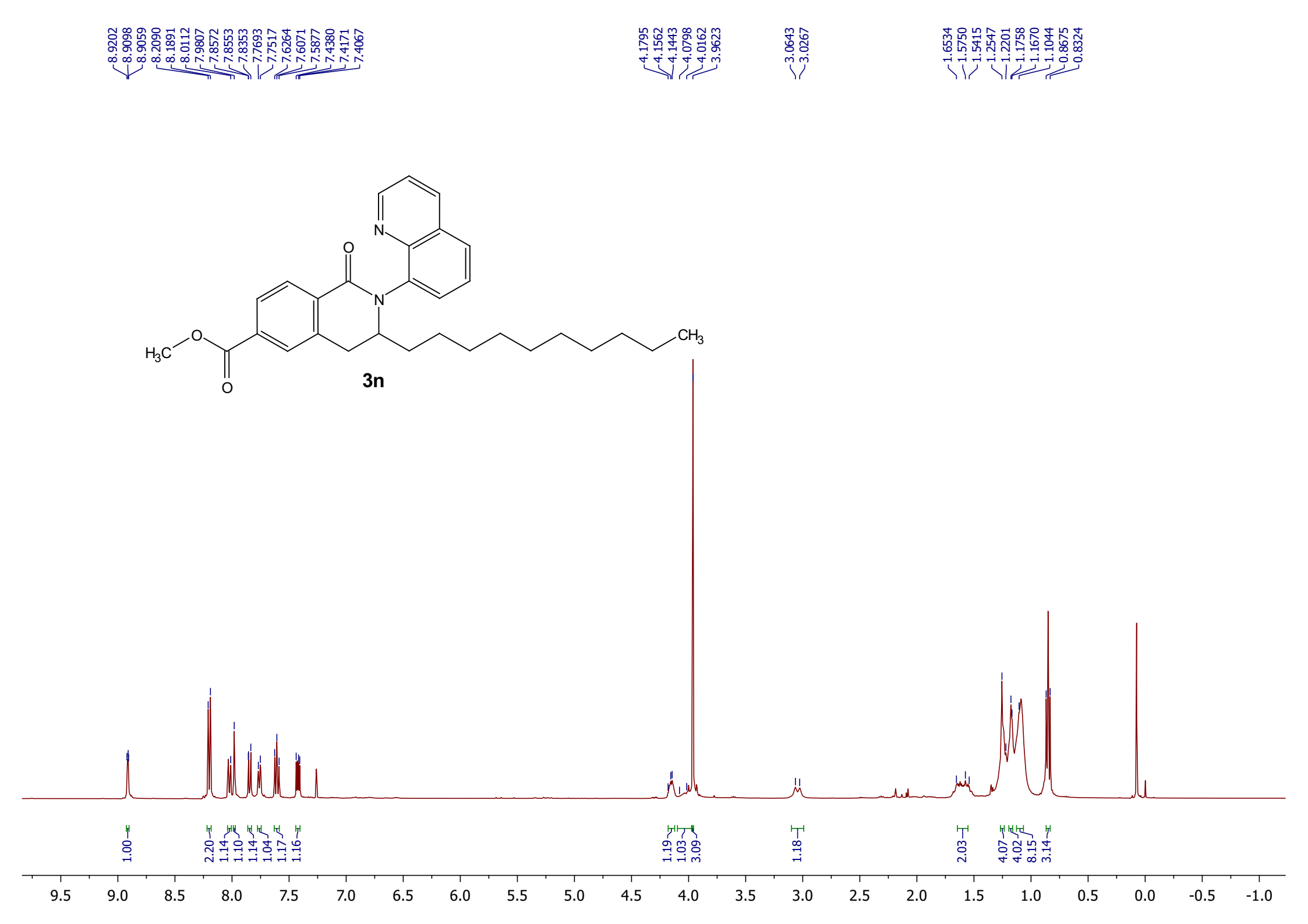
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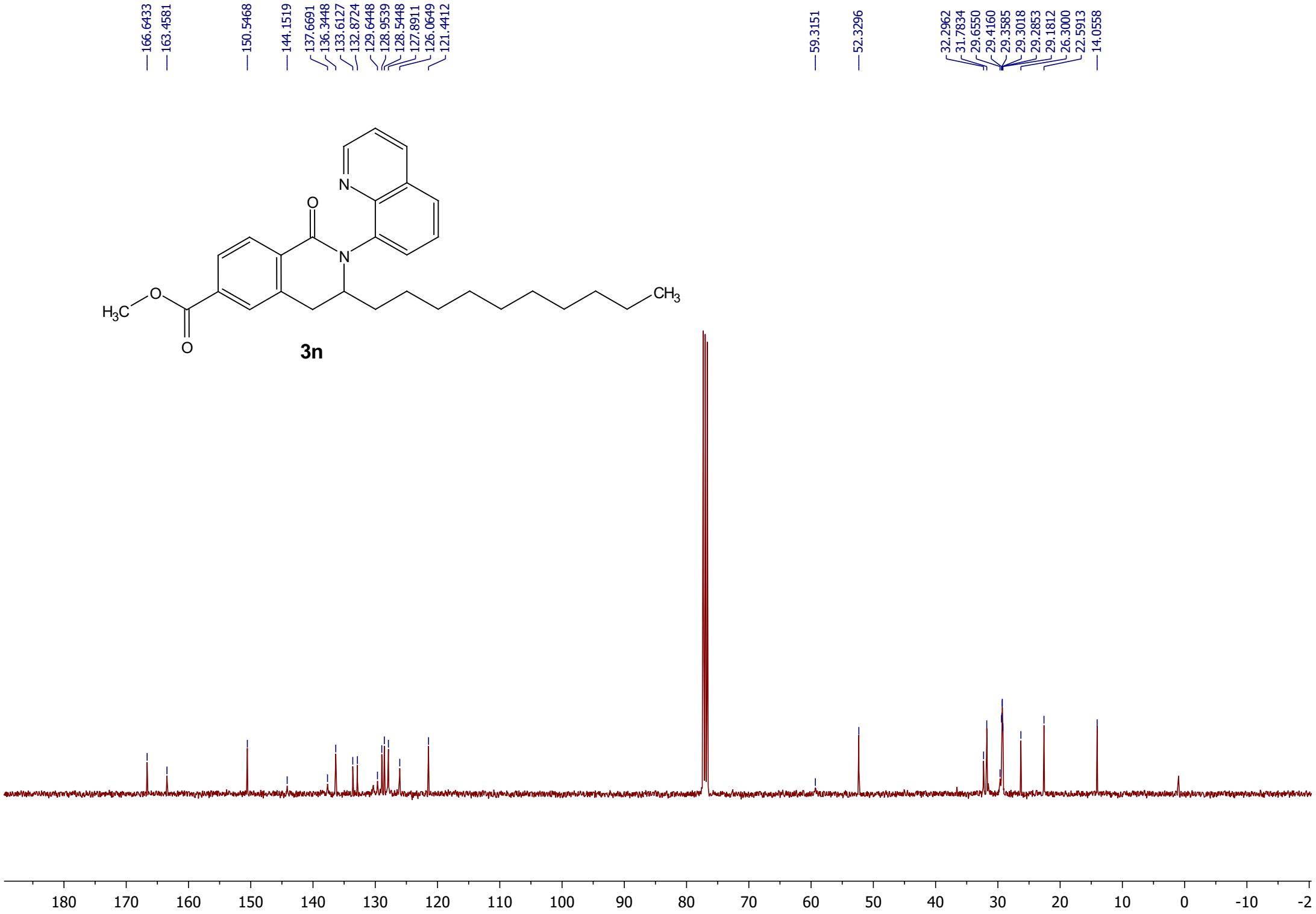
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CH3
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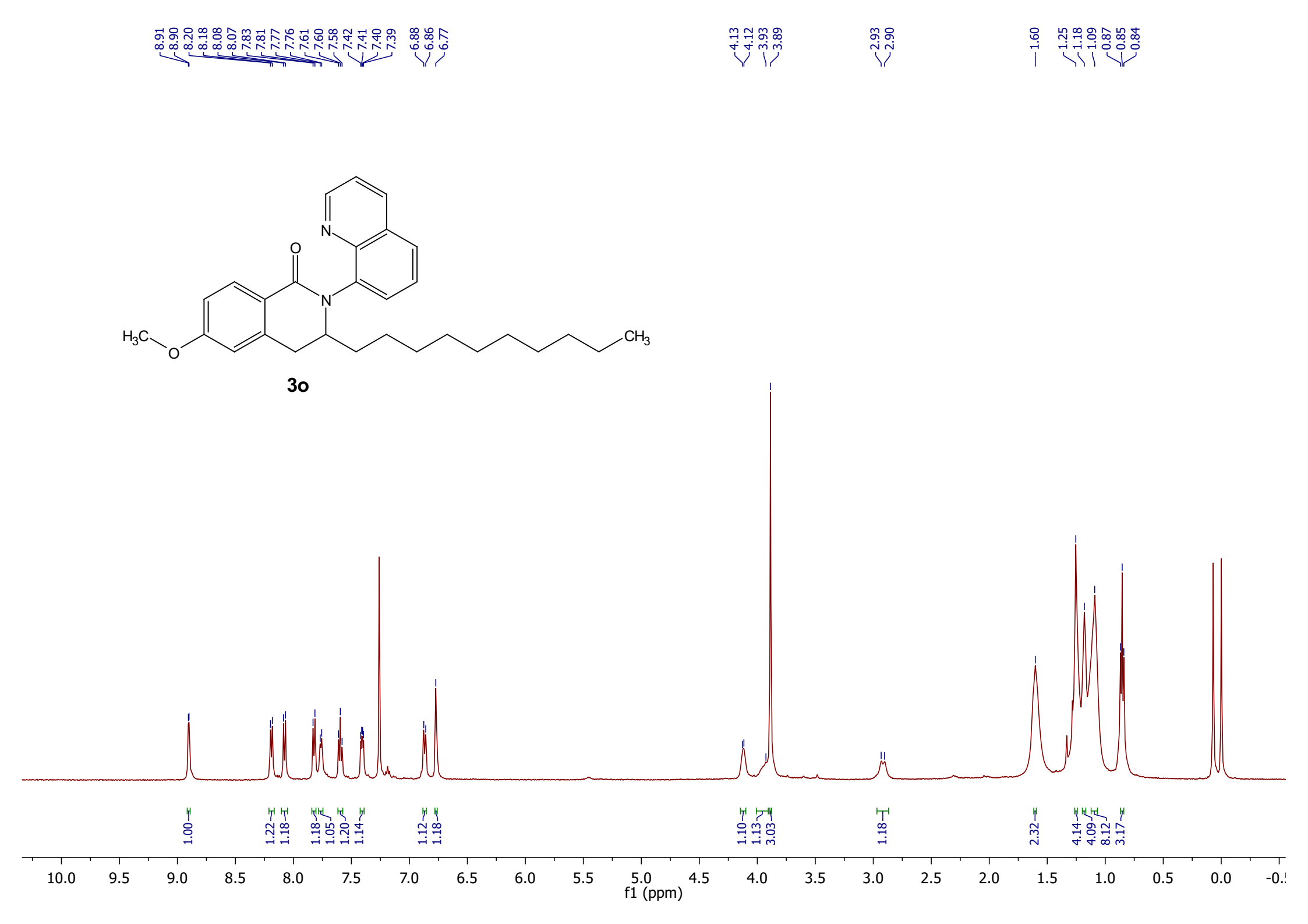
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CH3
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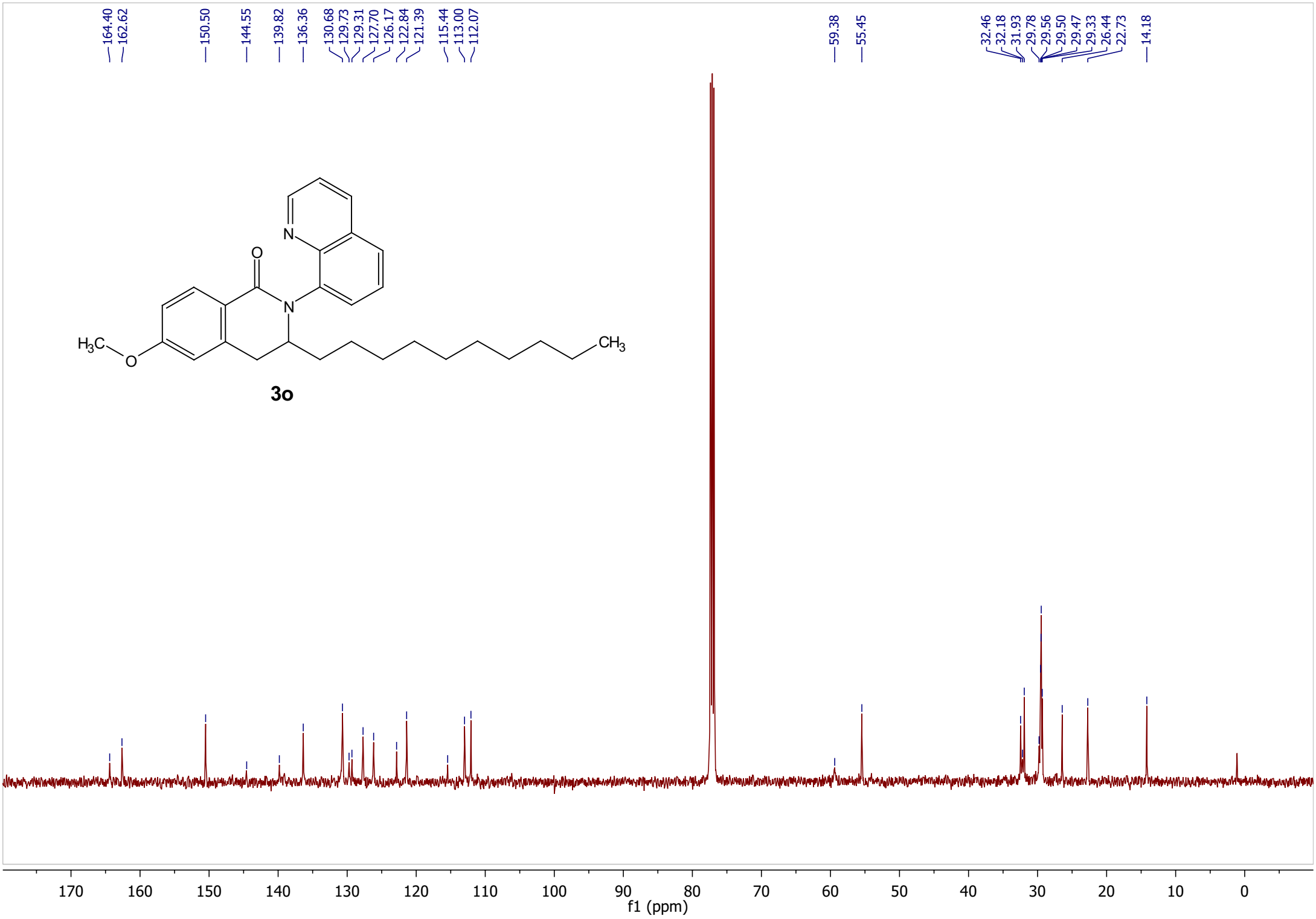
f1 (ppm)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126.17
122.84
121.39
115.44
113.00
112.07
59.38
55.45
32.46
32.18
31.93
29.78
29.56
29.50
29.47
29.33
26.44
22.73
14.18
N
O
N
H3C
O
CH3
3o
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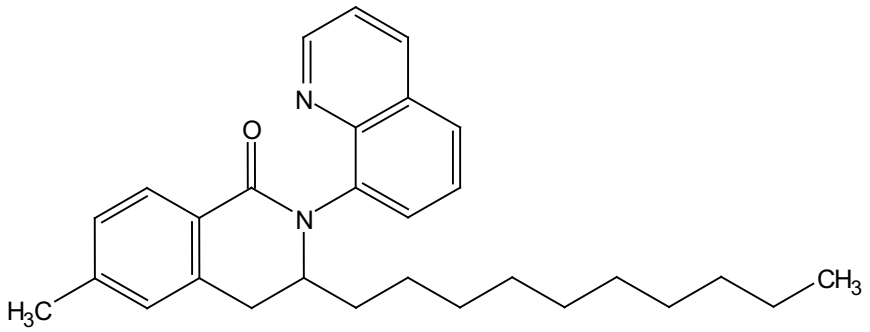
f1 (ppm)


O
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N
H3C
CH3

3p

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8.1718
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8.0136
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7.3969
7.1773
7.0831
4.1329
3.9136
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2.9014
2.4206
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1.2626
1.1861
1.0943
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1.12
1.03
1.16
1.07
1.18
1.18
1.14
1.12
1.17
0.88
1.10
3.11
2.74
3.75
4.07
8.54
3.27
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9.5
9.0
8.5
8.0
7.5
7.0
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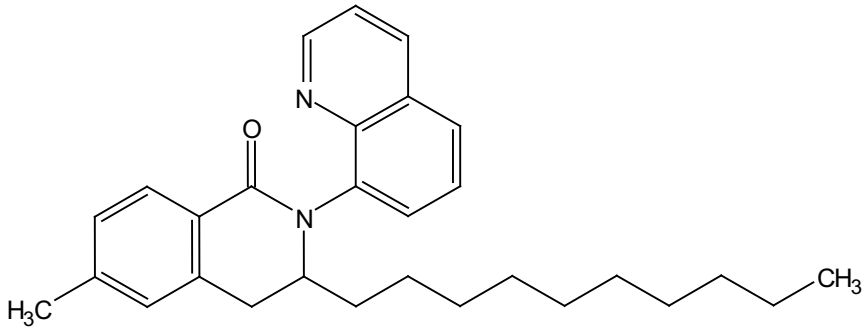
O
N
N
H3C
CH3

3p

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129.6016
128.4587
128.2907
127.6043
127.5416
127.1900
126.0389
121.2716
59.2469
32.2583
31.8062
31.6648
29.6629
29.4439
29.3769
29.3509
29.3141
29.2077
26.3285
22.6081
21.6043
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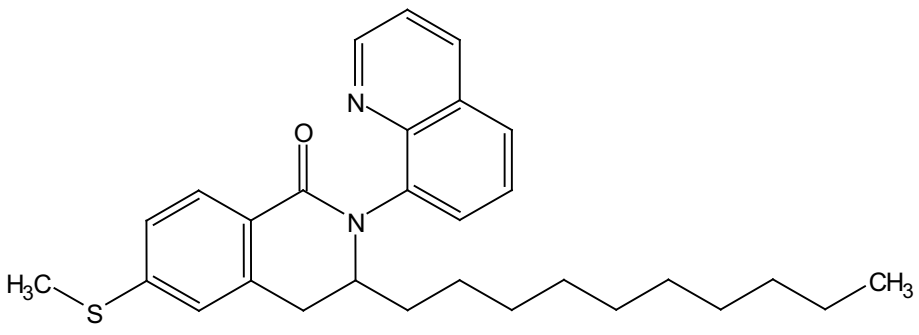
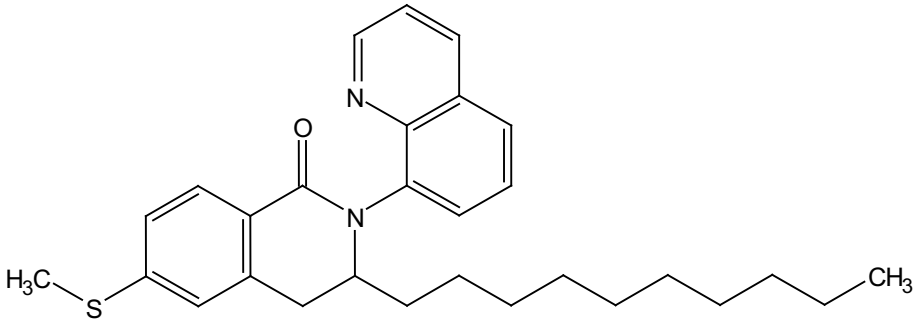


3q


O
N
N
H3C
S
CH3

3q

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136.2592
130.5149
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125.9536
124.1603
123.3812
121.2520
59.1463
32.1964
31.5999
29.5781
29.3545
29.2978
29.2606
29.2237
29.1225
26.2278
22.5269
14.8069
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150
140
130
120
110
100
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80
70
60
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20
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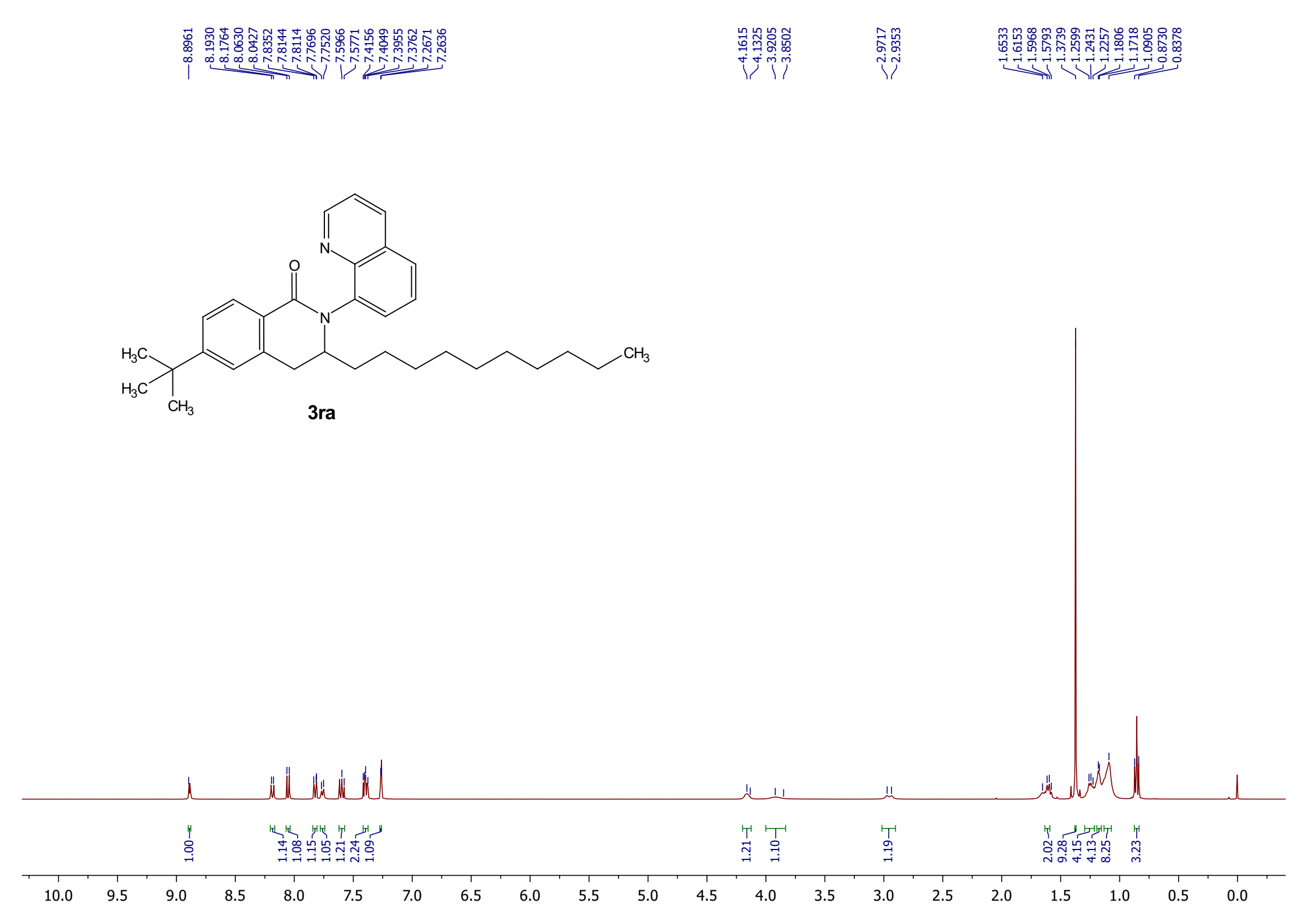
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7.5966
7.5771
7.4156
7.4049
7.3955
7.3762
7.2671
7.2636
4.1615
4.1325
3.9205
3.8502
2.9717
2.9353
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1.5968
1.5793
1.3739
1.2599
1.2431
1.2257
1.1806
1.1718
1.0905
0.8730
0.8378
O
N
N
H3C
H3C
CH3
CH3
3ra
1.00
1.14
1.08
1.15
1.05
1.21
2.24
1.09
1.21
1.10
1.19
2.02
9.28
4.15
4.13
8.25
3.23
10.0
9.5
9.0
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8.0
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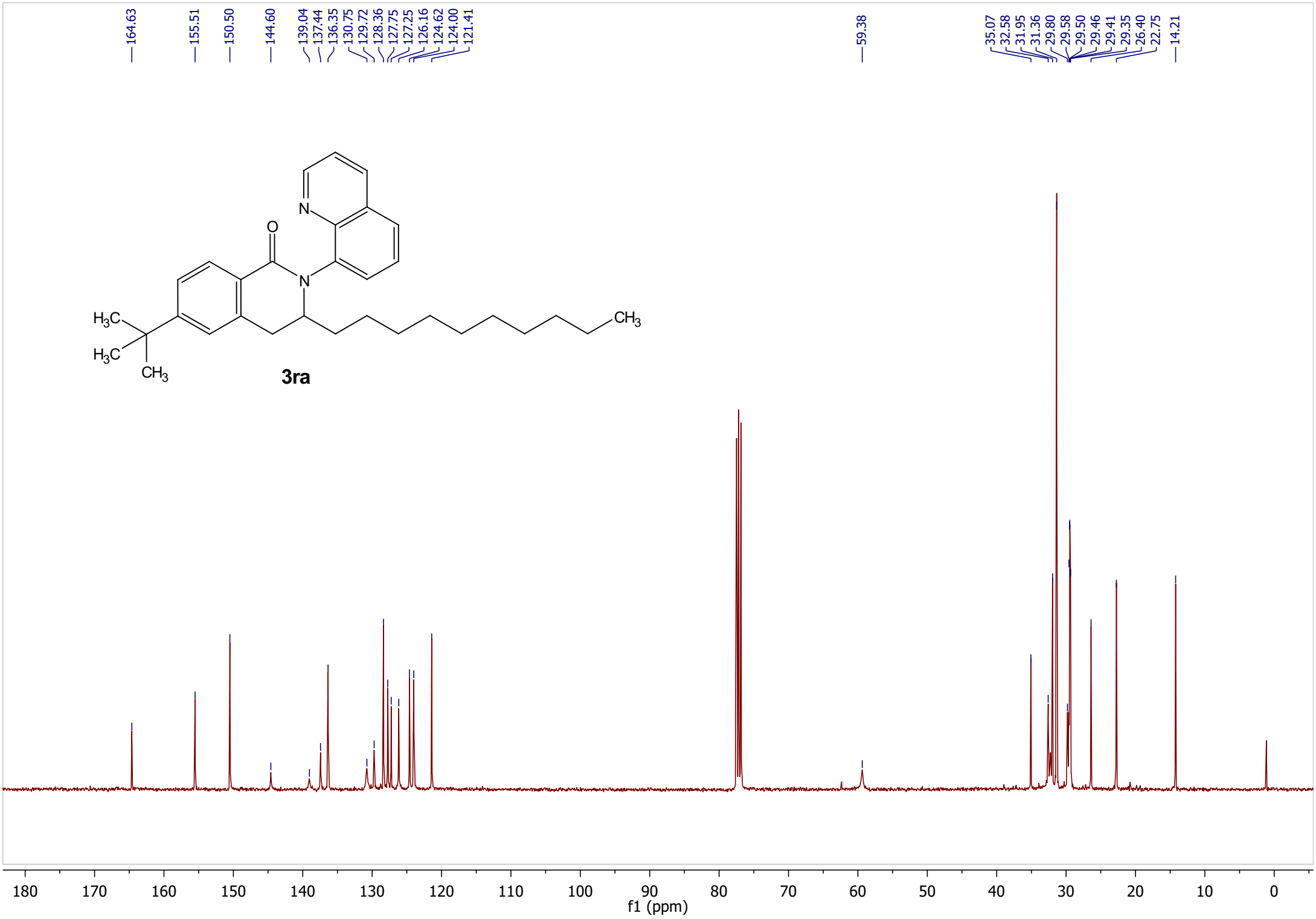
0.0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137.44
136.35
130.75
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128.36
127.75
127.25
126.16
124.62
124.00
121.41
59.38
35.07
32.58
31.95
31.36
29.80
29.58
29.50
29.46
29.41
29.35
26.40
22.75
14.21
O
N
N
H3C
H3C
CH3
CH3
3ra
180
170
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140
130
120
110
100
90
80
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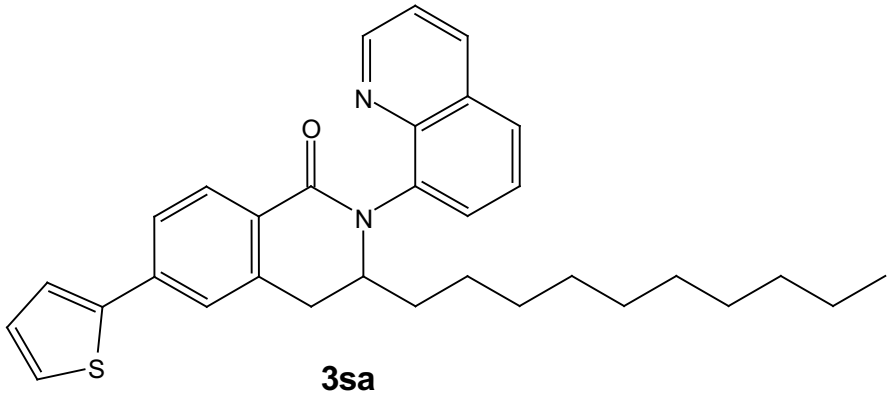
50
40
30
20
10
0
f1 (ppm)


O
N
N
S

3sa

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8.9170
8.2033
8.1827
8.1552
8.1350
7.8452
7.8251
7.7938
7.7761
7.6313
7.6118
7.5916
7.5248
7.4479
7.4197
7.4000
7.3616
7.3495
7.1377
7.1284
7.1256
7.1161
4.1720
4.1603
3.9962
3.0290
2.9924
1.6565
1.6393
1.2617
1.1762
1.1029
0.8685
0.8514
0.8337
1.00
2.22
2.21
2.22
1.03
2.34
1.05
1.04
1.15
0.94
1.11
1.98
3.46
4.12
7.95
2.88
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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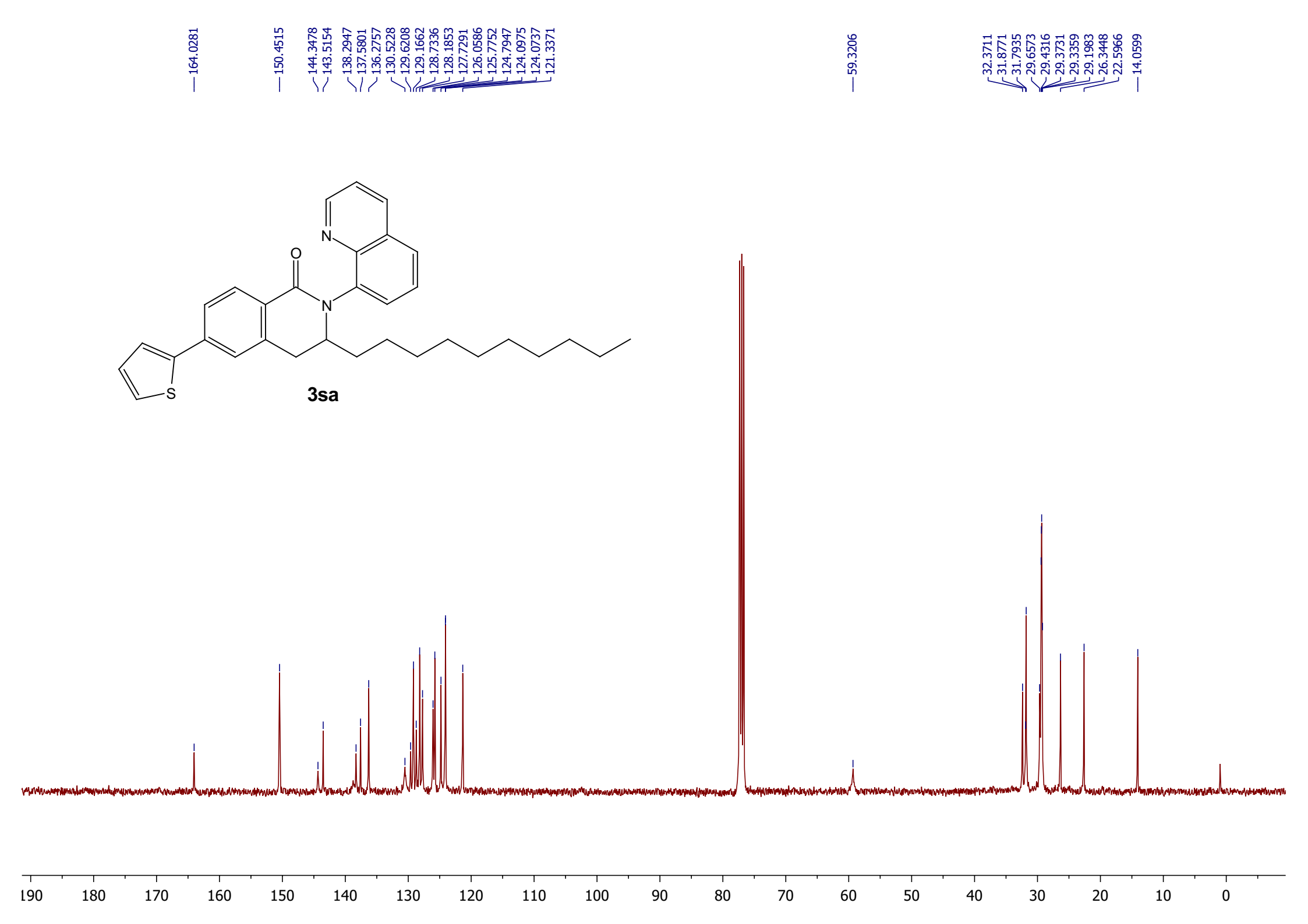
2.0
1.5
1.0
0.5
0.0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138.2947
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136.2757
130.5228
129.6208
129.1662
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128.1853
127.7291
126.0586
125.7752
124.7947
124.0975
124.0737
121.3371
59.3206
32.3711
31.8771
31.7935
29.6573
29.4316
29.3731
29.3359
29.1983
26.3448
22.5966
14.0599
O
N
N
S
3sa
190
180
170
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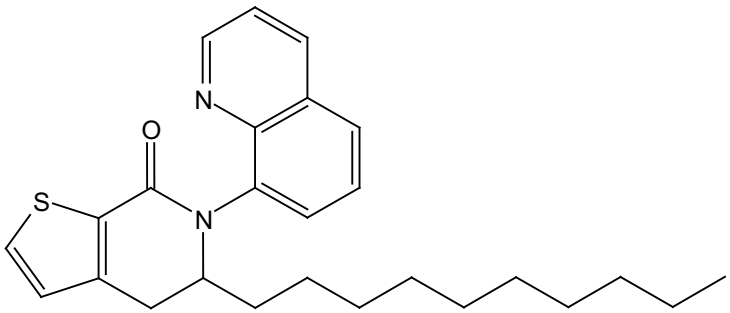
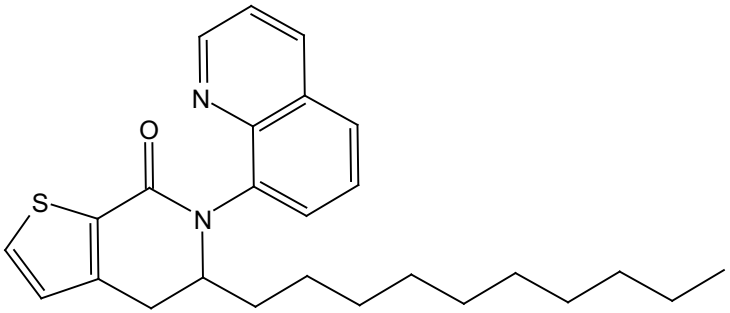
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3ta


N
O
S
N

3ta

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131.2361
131.1765
129.6907
129.0847
127.9189
127.8508
127.2505
126.5376
126.1530
124.5805
124.0859
121.5712
121.4422
114.2064
61.0313
56.4473
36.0116
33.9411
32.7921
32.5355
32.0359
32.0022
31.9536
29.8167
29.7841
29.7119
29.6192
29.5887
29.5242
29.4733
29.3539
28.4491
27.2597
27.1934
26.3575
22.7933
22.7637
14.2435
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160
150
140
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120
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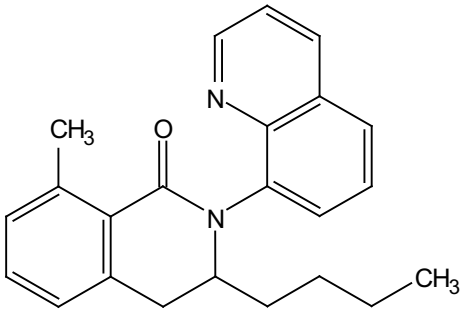
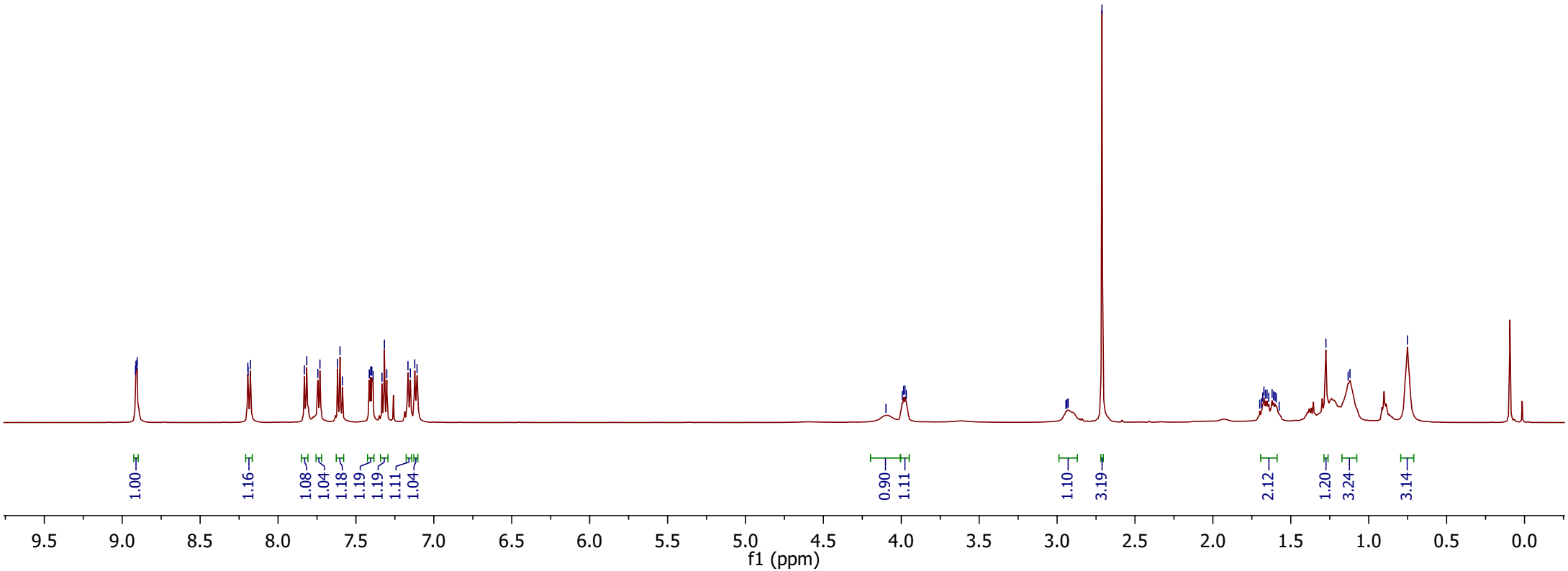
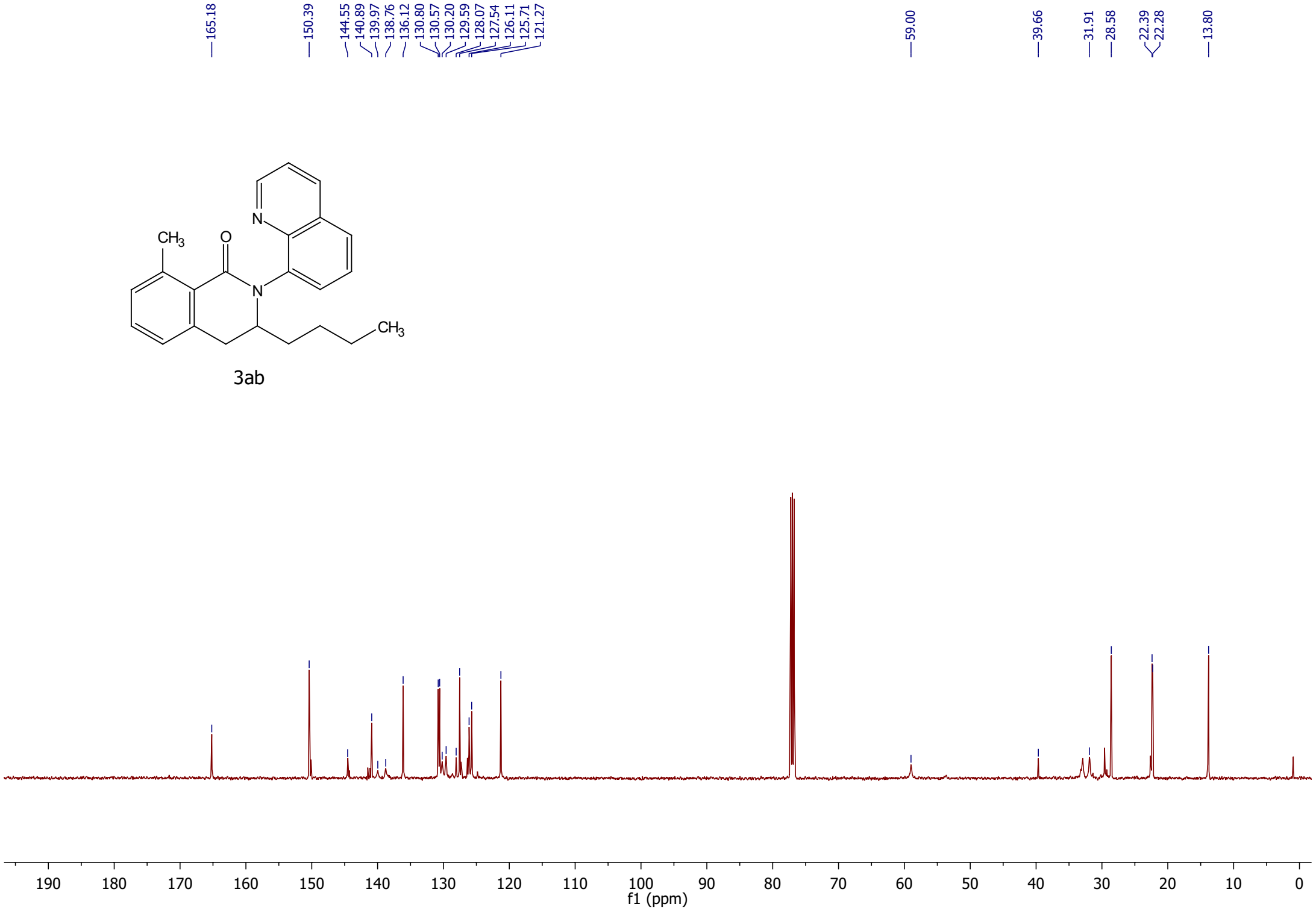
80
70
60
50
40
30
20
10



3ab

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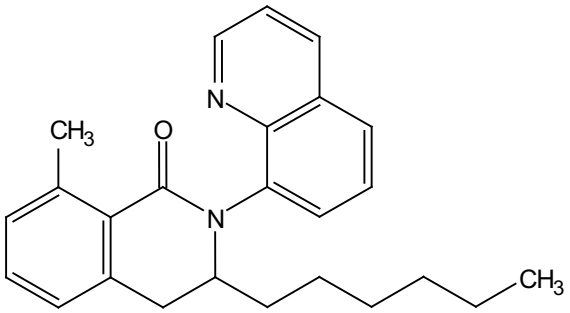
139.97
138.76
136.12
130.80
130.57
130.20
129.59
128.07
127.54
126.11
125.71
121.27
59.00
39.66
31.91
28.58
22.39
22.28
13.80
CH3
O
N
N
CH3
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
O
N
N
CH3

3ac

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8.91
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8.90
8.20
8.19
8.18
8.18
7.83
7.83
7.82
7.81
7.74
7.74
7.73
7.73
7.62
7.60
7.59
7.42
7.41
7.40
7.39
7.33
7.32
7.30
7.17
7.15
7.12
7.11
4.15
4.09
3.99
3.99
3.98
3.97
3.15
2.99
2.94
2.92
2.89
2.84
2.71
1.69
1.64
1.60
1.58
1.27
1.22
1.16
1.11
0.80
0.79
0.77
1.01
1.03
1.04
0.97
1.06
1.05
1.04
1.00
1.03
0.82
1.04
1.00
3.12
2.12
8.31
2.84
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
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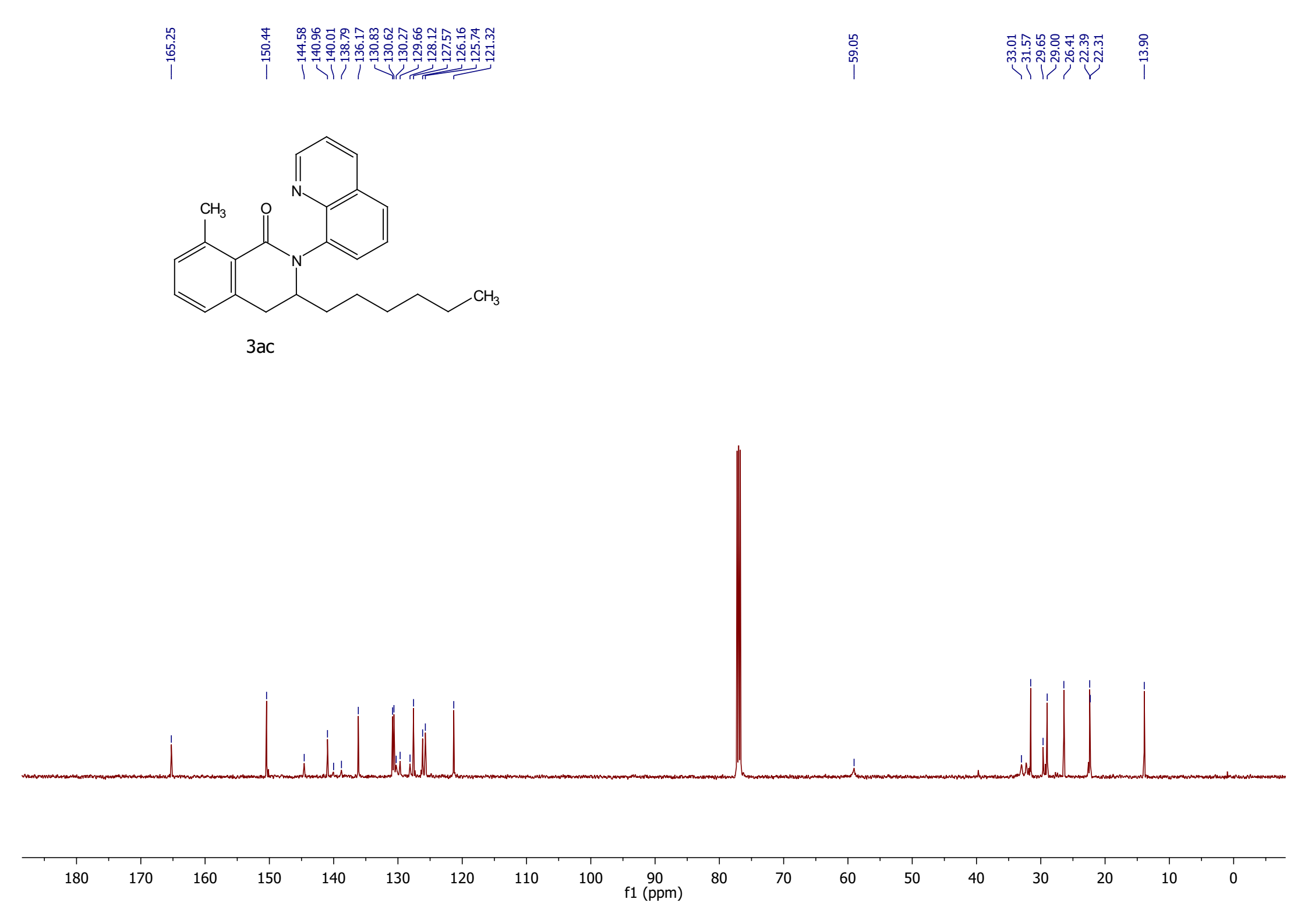
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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130.83
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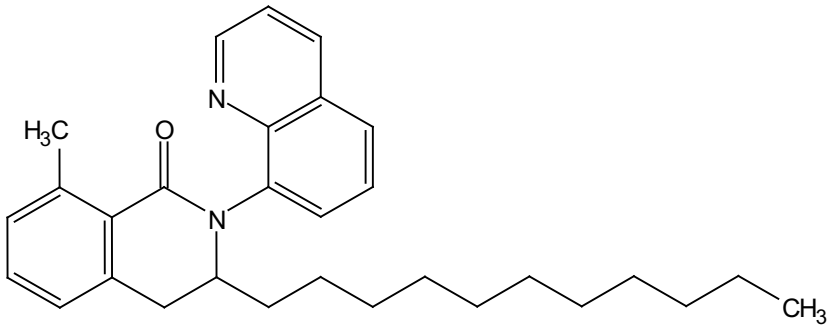
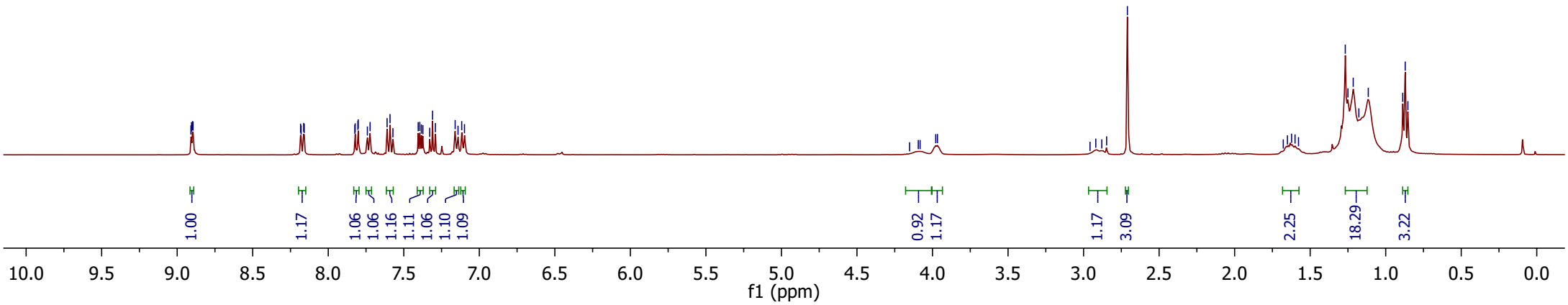
130.27
129.66
128.12
127.57
126.16
125.74
121.32
59.05
33.01
31.57
29.65
29.00
26.41
22.39
22.31
13.90
CH3
O
N
N
CH3
3ac
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H3C
O
N
N
CH3

3ad


8.91
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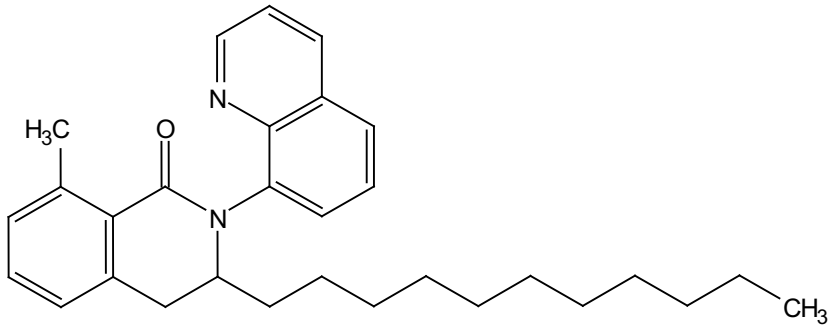
7.82
7.80
7.80
7.74
7.72
7.61
7.59
7.57
7.40
7.39
7.38
7.37
7.33
7.31
7.29
7.16
7.14
7.12
7.10
4.15
4.09
4.08
3.98
3.97
2.96
2.92
2.88
2.85
2.71
1.68
1.65
1.62
1.60
1.58
1.27
1.25
1.22
1.18
1.12
0.89
0.87
0.85
1.00
1.17
1.06
1.06
1.16
1.11
1.06
1.10
1.09
0.92
1.17
1.17
3.09
2.25
18.29
3.22
10.0
9.5
9.0
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)


H3C
O
N
N
CH3

3ad

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140.69
140.01
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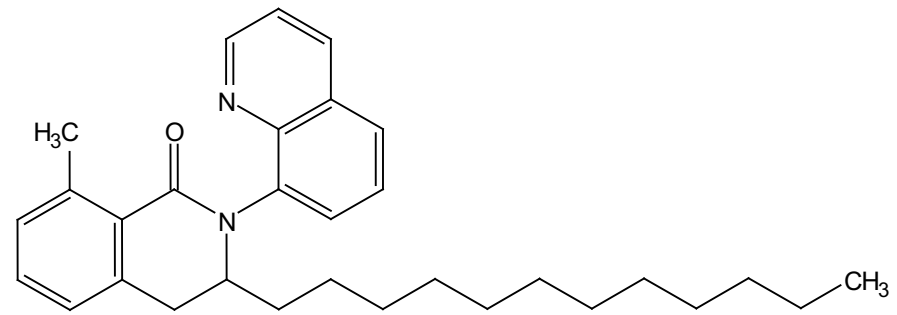
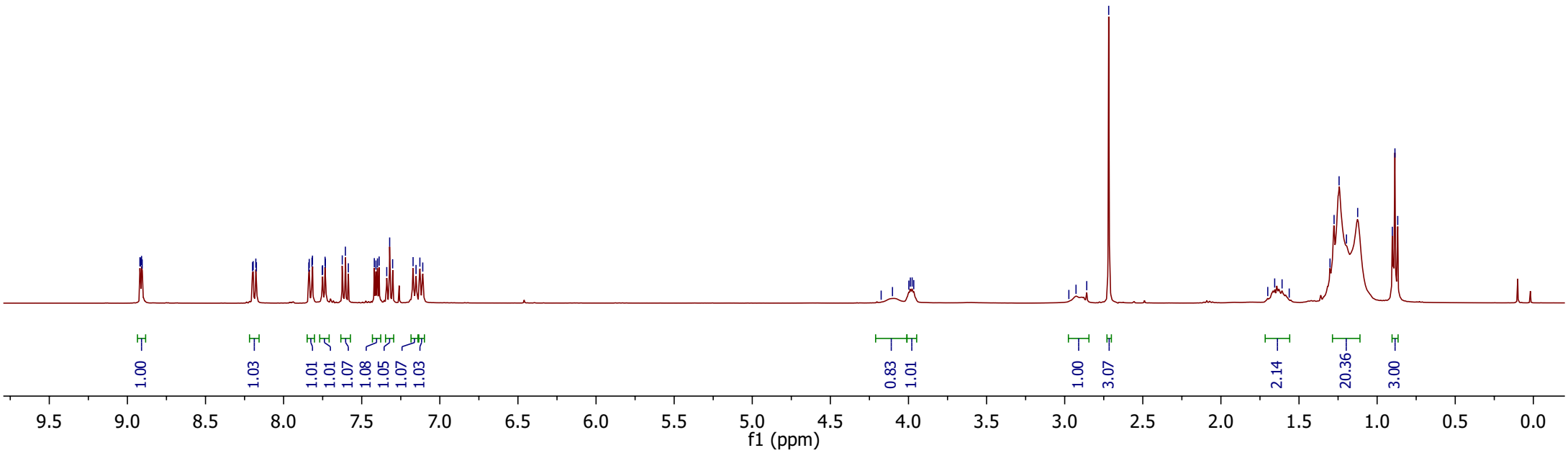
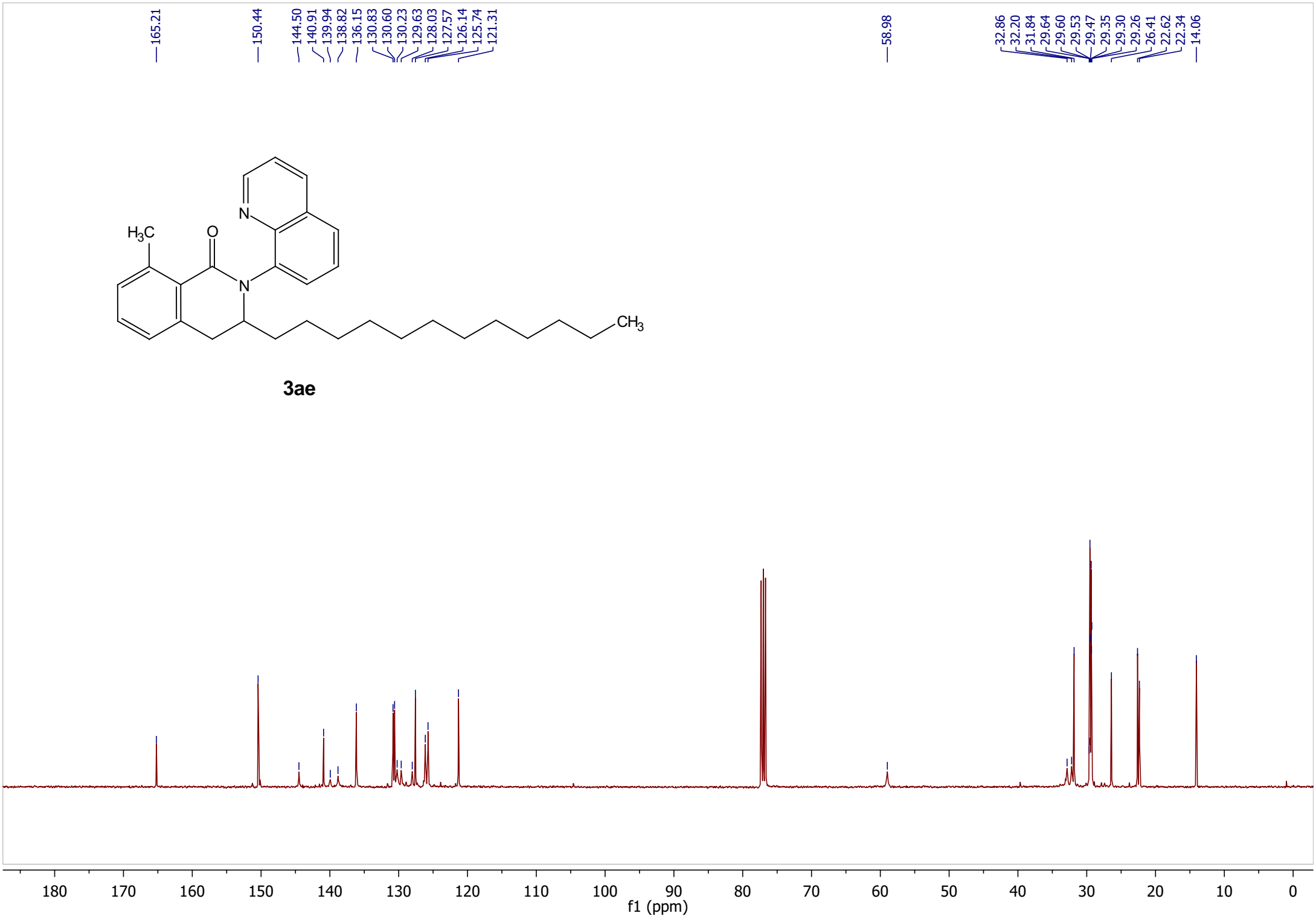
130.31
130.04
129.69
128.39
127.33
126.37
125.98
125.15
121.21
63.99
51.61
46.02
41.09
34.62
31.87
31.55
30.84
30.15
29.64
29.31
26.34
26.31
26.20
26.16
25.22
22.64
22.50
22.29
20.63
14.07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ae

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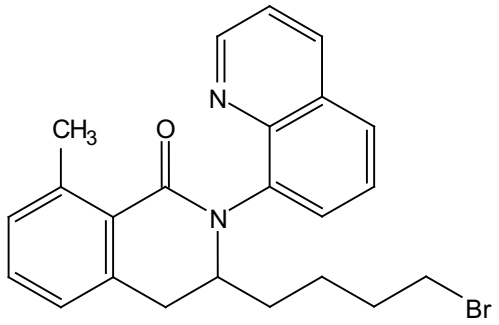
139.94
138.82
136.15
130.83
130.60
130.23
129.63
128.03
127.57
126.14
125.74
121.31
58.98
32.86
32.20
31.84
29.64
29.60
29.53
29.47
29.35
29.30
29.26
26.41
22.62
22.34
14.06
H3C
O
N
N
CH3
3ae
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
O
N
N
Br

3af

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8.5235
8.1857
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7.5126
7.4705
7.4520
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4.3628
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3.5914
3.5825
3.2658
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3.0397
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2.0034
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1.6053
1.2174
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1.09
1.10
1.00
1.12
1.16
1.14
2.17
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1.00
2.06
1.04
2.96
2.23
1.95
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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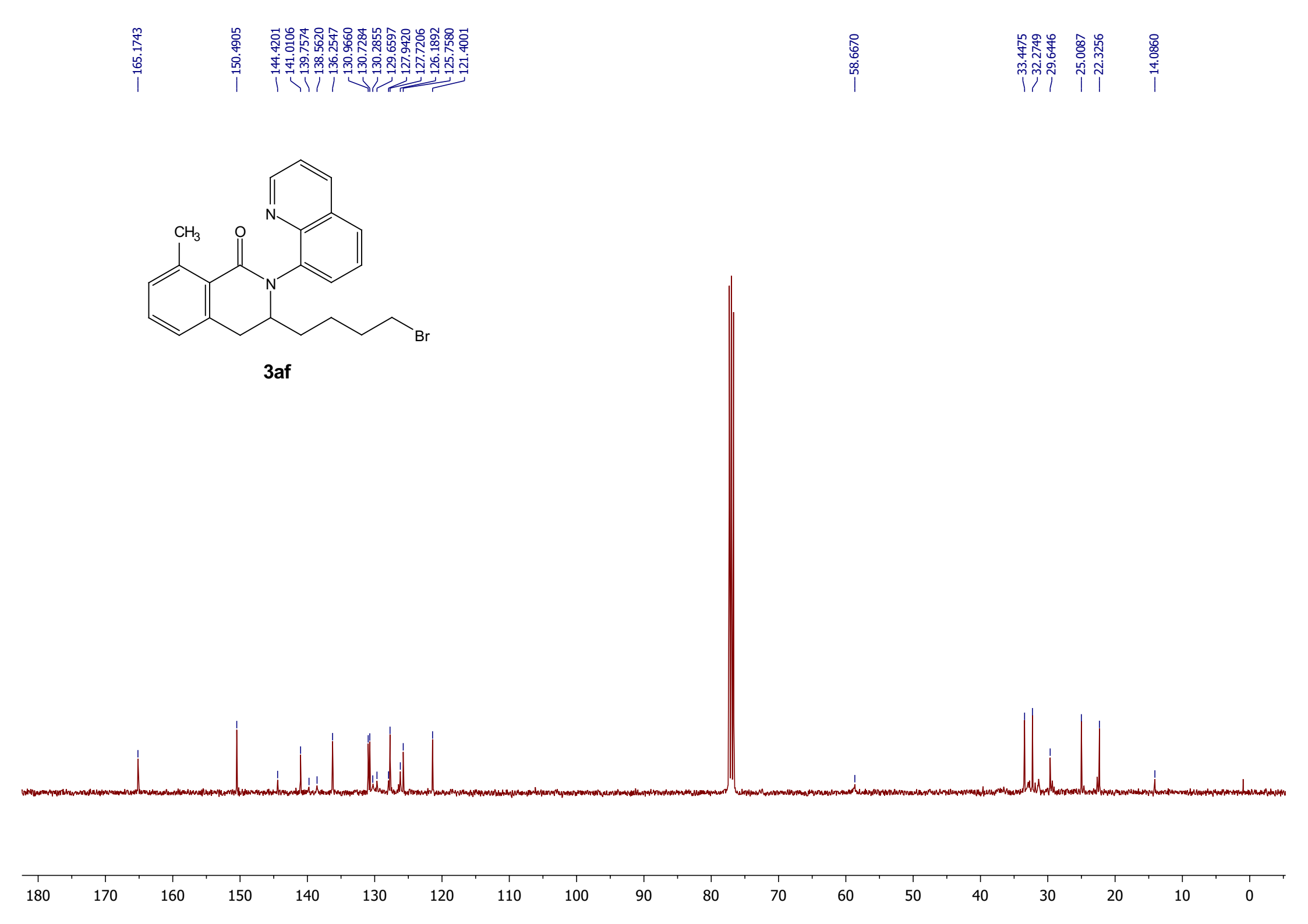
1.0
0.5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136.2547
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129.6597
127.9420
127.7206
126.1892
125.7580
121.4001
58.6670
33.4475
32.2749
29.6446
25.0087
22.3256
14.0860
CH3
O
N
N
Br
3af
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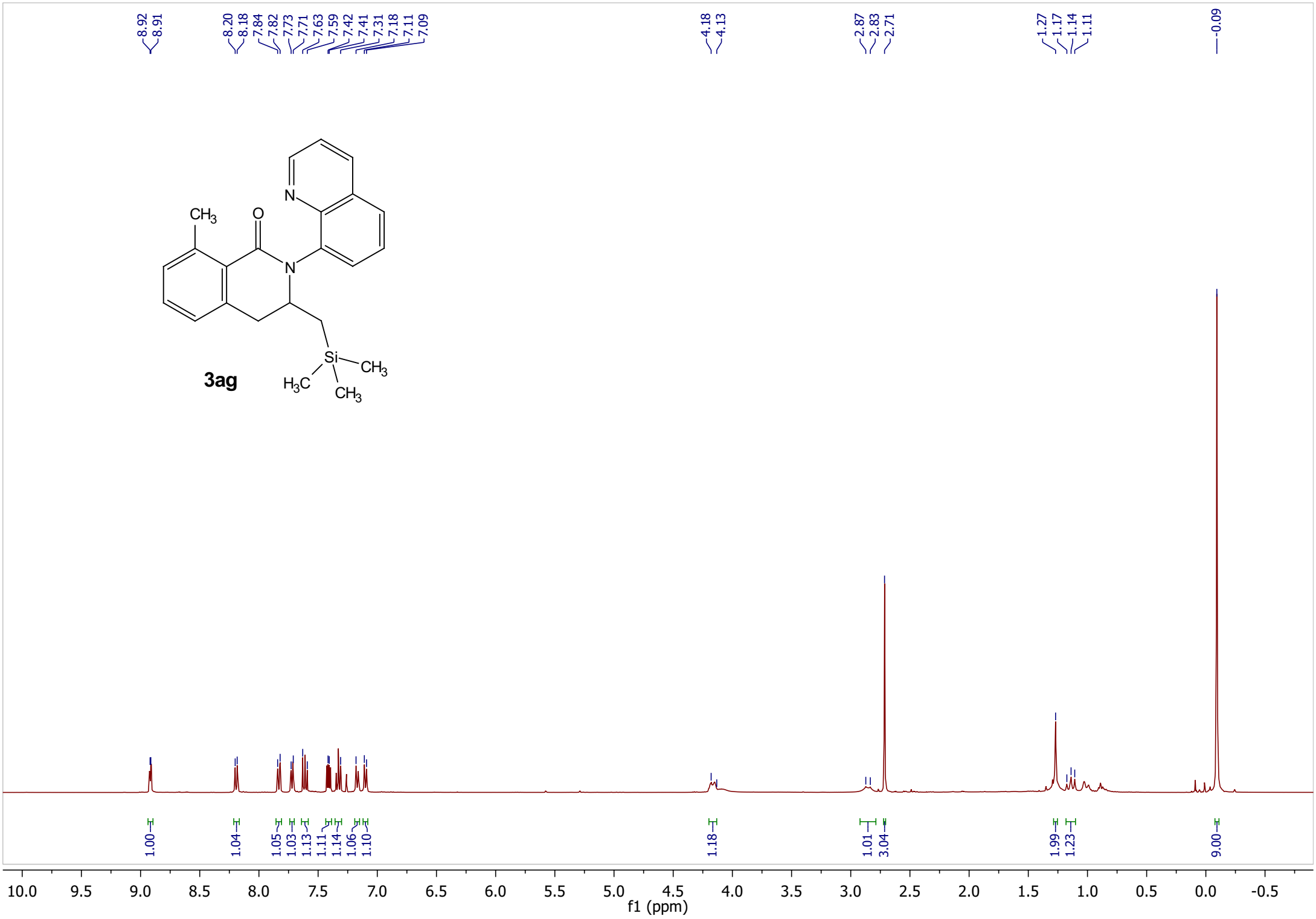
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7.73
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7.42
7.41
7.31
7.18
7.11
7.09
4.18
4.13
2.87
2.83
2.71
1.27
1.17
1.14
1.11
-0.09
CH3
O
N
N
Si
CH3
H3C
CH3
3ag
1.00
1.04
1.05
1.03
1.13
1.11
1.14
1.06
1.10
1.18
1.01
3.04
1.99
1.23
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
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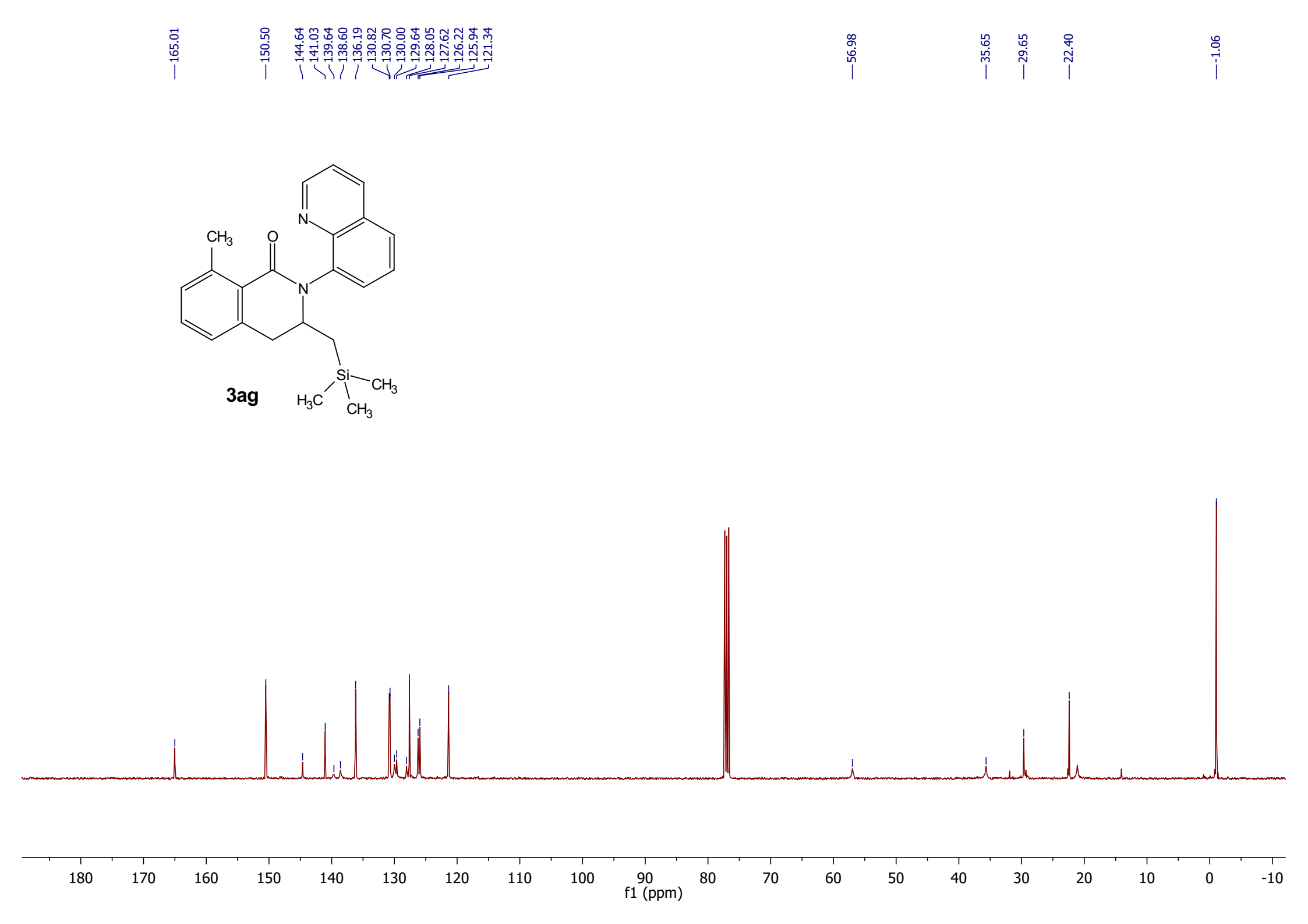
-0.5
f1 (ppm)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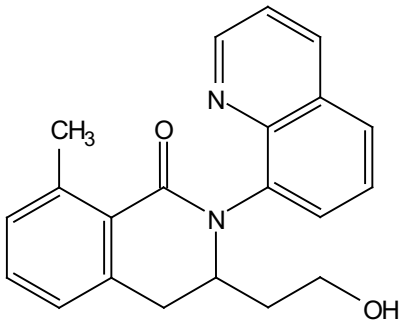
138.60
136.19
130.82
130.70
130.00
129.64
128.05
127.62
126.22
125.94
121.34
56.98
35.65
29.65
22.40
-1.06
CH3
O
N
N
Si
CH3
H3C
CH3
3ag
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CH3
O
N
N
OH

3ah

8.87
8.86
8.16
8.15
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7.57
7.55
7.54
7.38
7.37
7.37
7.29
7.28
7.14
7.13
7.07
4.23
4.16
4.10
3.52
3.45
3.40
2.95
2.89
2.85
2.66
1.94
1.91
1.87
1.79
1.29
1.27
1.00
1.02
1.04
1.04
1.07
1.04
1.04
1.08
0.88
1.27
1.95
1.04
3.09
2.21
2.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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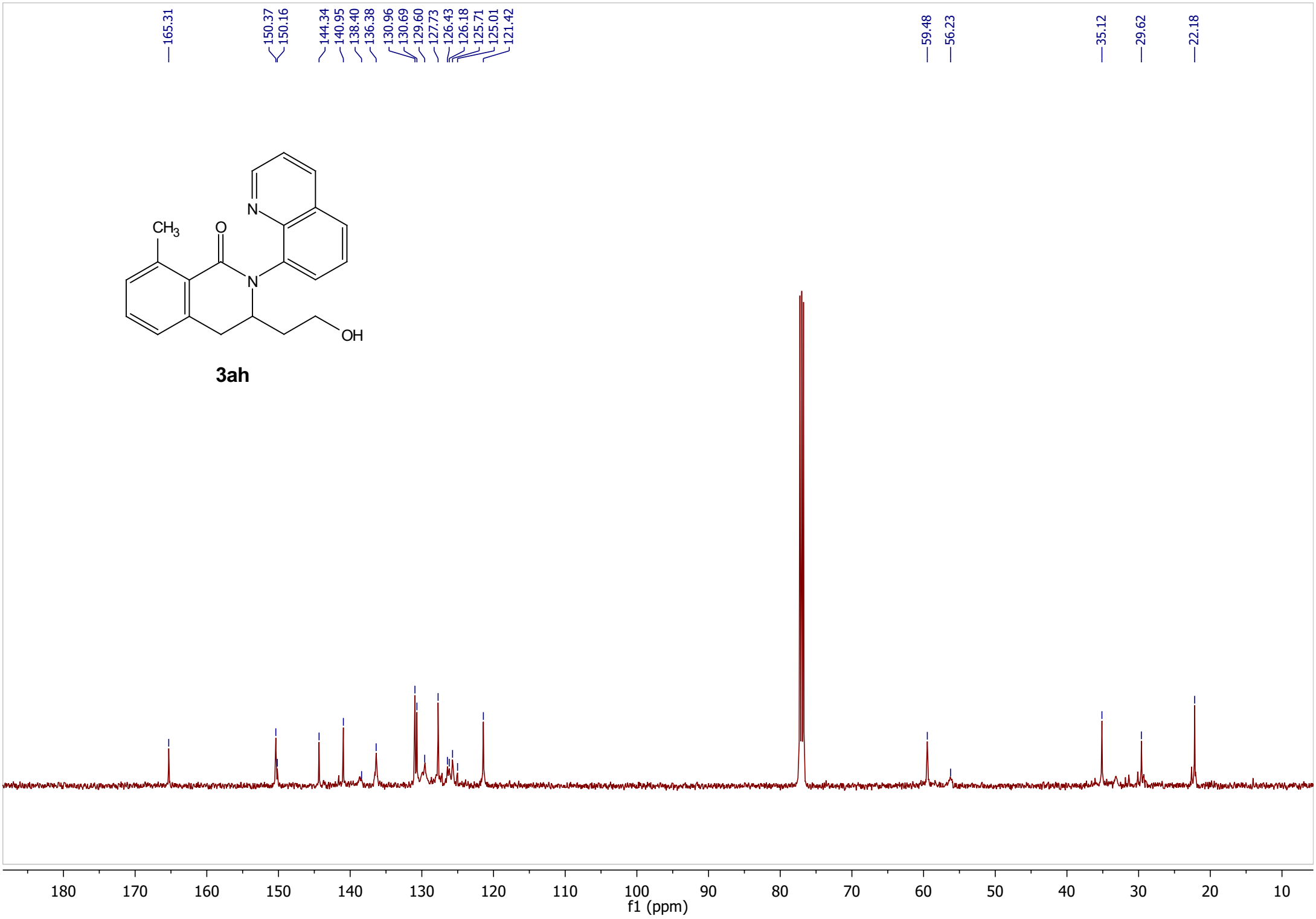
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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129.60
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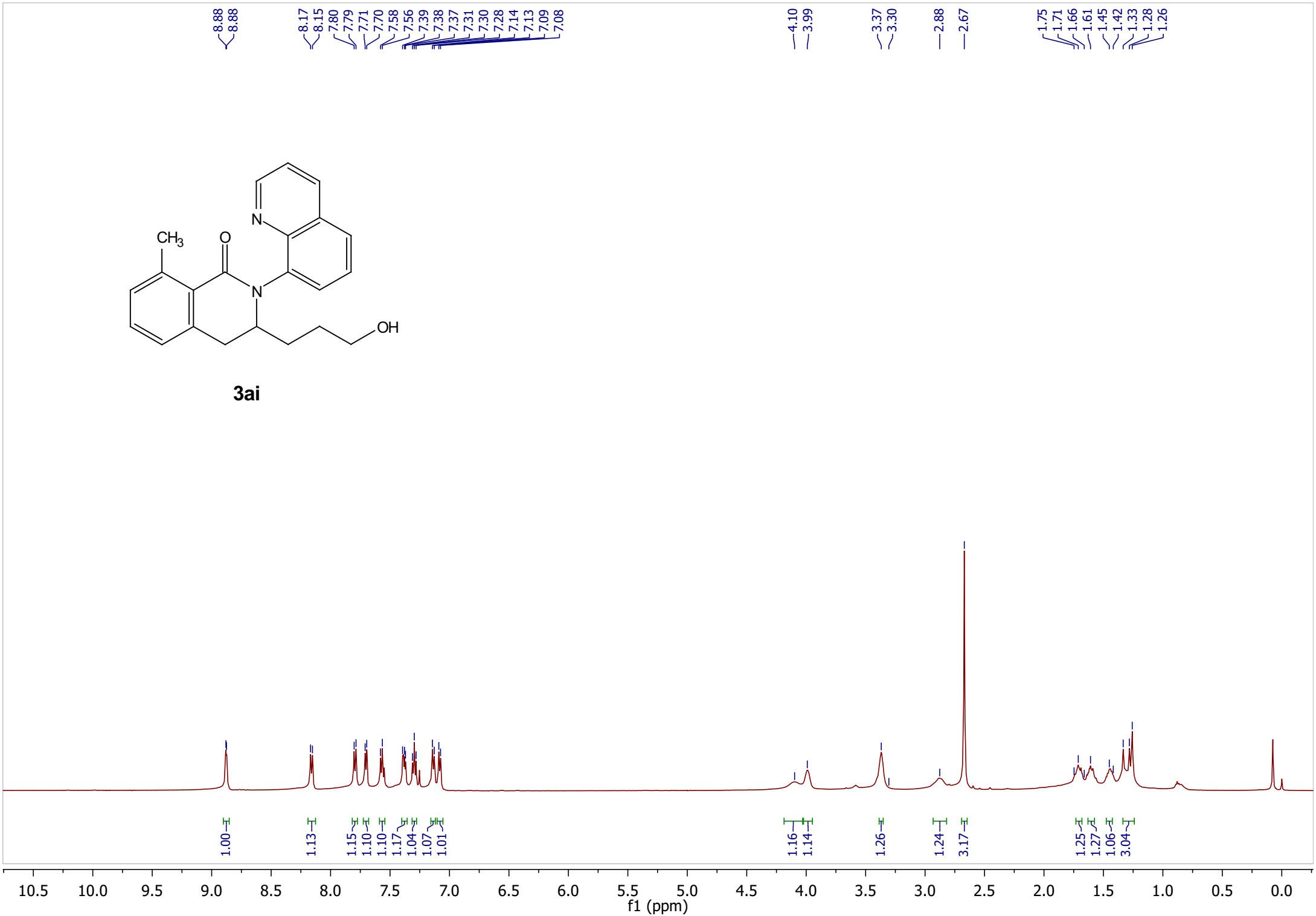
126.43
126.18
125.71
125.01
121.42
59.48
56.23
35.12
29.62
22.18
CH3
O
N
N
OH
3ah
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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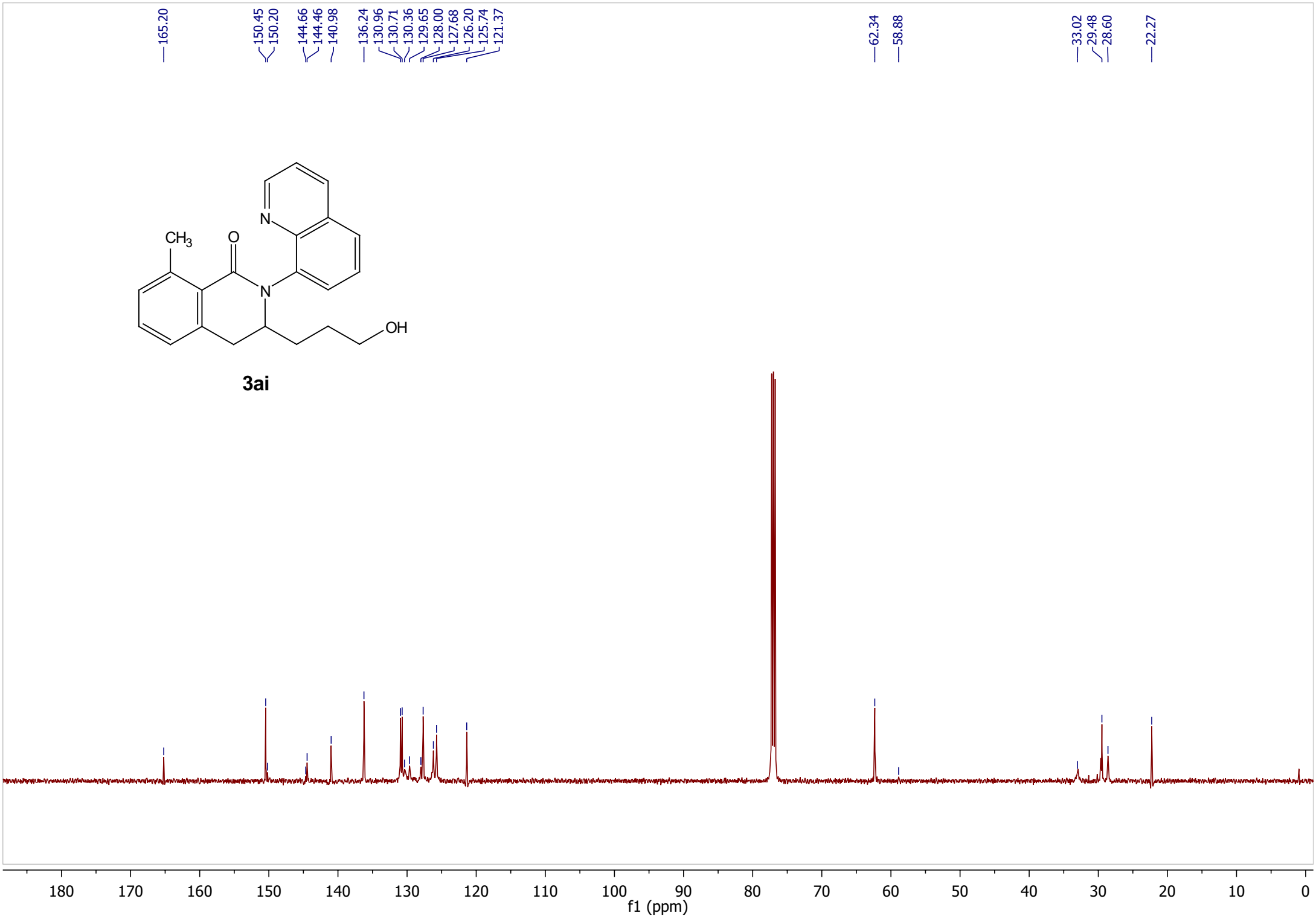
7.56
7.39
7.38
7.37
7.31
7.30
7.28
7.14
7.13
7.09
7.08
4.10
3.99
3.37
3.30
2.88
2.67
1.75
1.71
1.66
1.61
1.45
1.42
1.33
1.28
1.26
CH3
O
N
N
OH
1.00
1.13
1.15
1.10
1.10
1.17
1.04
1.07
1.01
1.16
1.14
1.26
1.24
3.17
1.25
1.27
1.06
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3ai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130.36
129.65
128.00
127.68
126.20
125.74
121.37
62.34
58.88
33.02
29.48
28.60
22.27
CH3
O
N
N
OH
3ai
180
170
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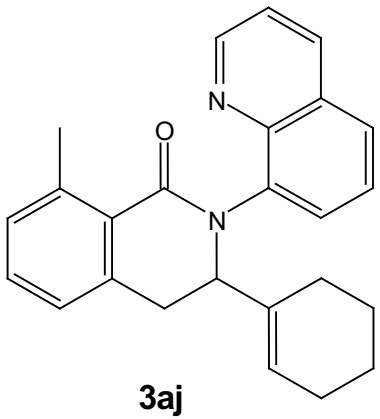
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N

3aj

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7.4151
7.3943
7.3841
7.2834
7.1212
7.1009
7.0824
4.3258
4.2847
4.2428
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3.0133
2.9752
2.6980
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1.5840
1.1158
1.0443
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1.00
1.03
2.03
1.06
1.01
1.09
2.26
1.09
1.02
0.96
3.16
4.20
1.21
4.26
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9.5
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8.5
8.0
7.5
7.0
6.5
6.0
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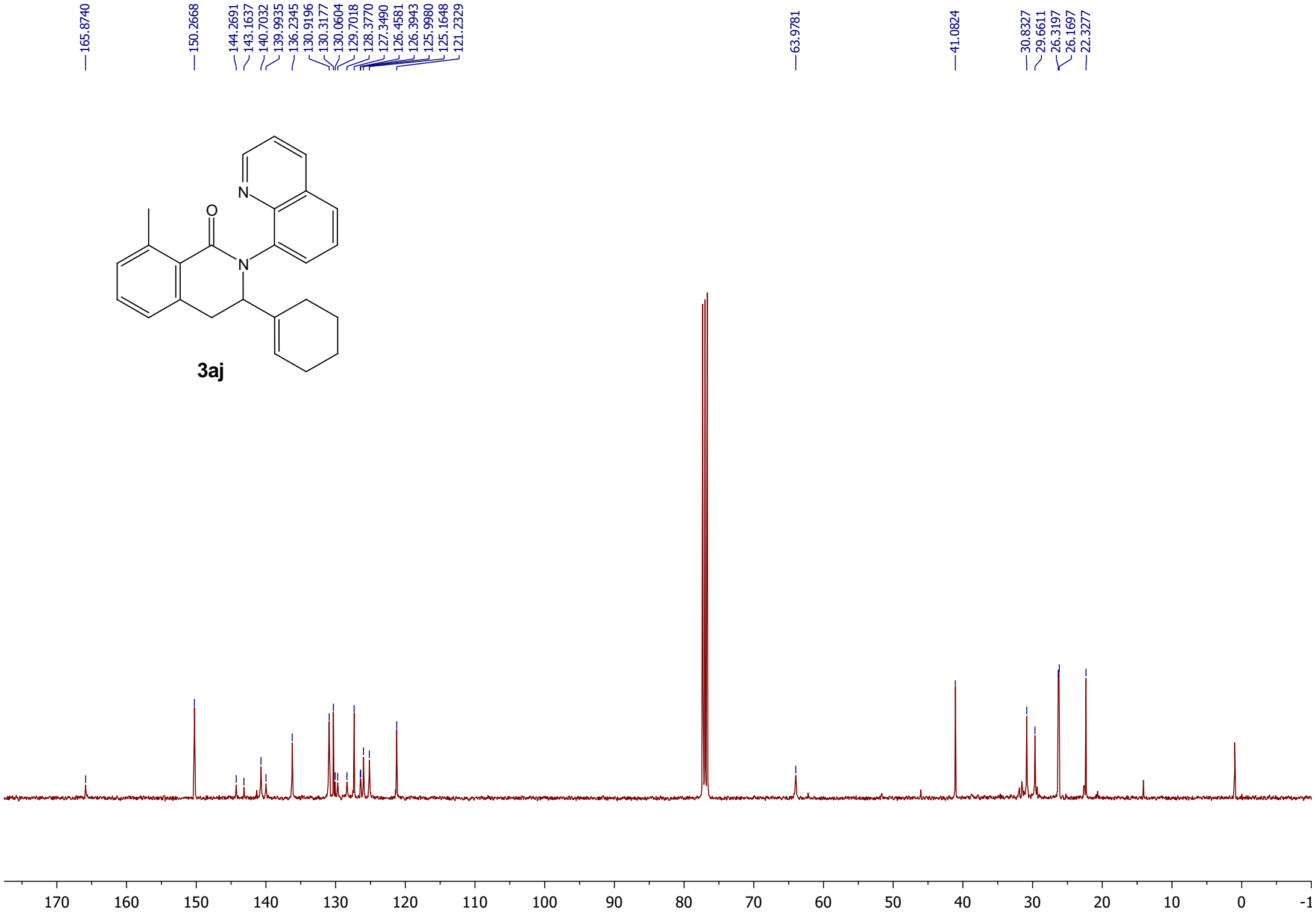
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130.3177
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128.3770
127.3490
126.4581
126.3943
125.9980
125.1648
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29.6611
26.3197
26.1697
22.3277
N
O
N
3aj
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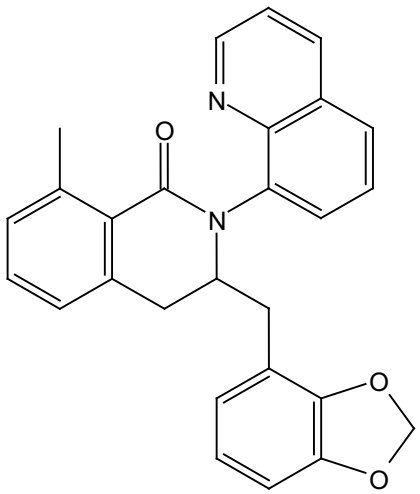
O
N
N
O
O

3ak

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7.4123
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7.0884
7.0699
6.6591
6.6395
6.3895
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4.1173
2.9836
2.9615
2.7294
2.0492
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1.00
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1.04
2.07
1.07
1.02
1.02
1.01
1.00
1.07
2.07
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1.17
3.01
1.00
2.23
9.5
9.0
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7.0
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6.0
5.5
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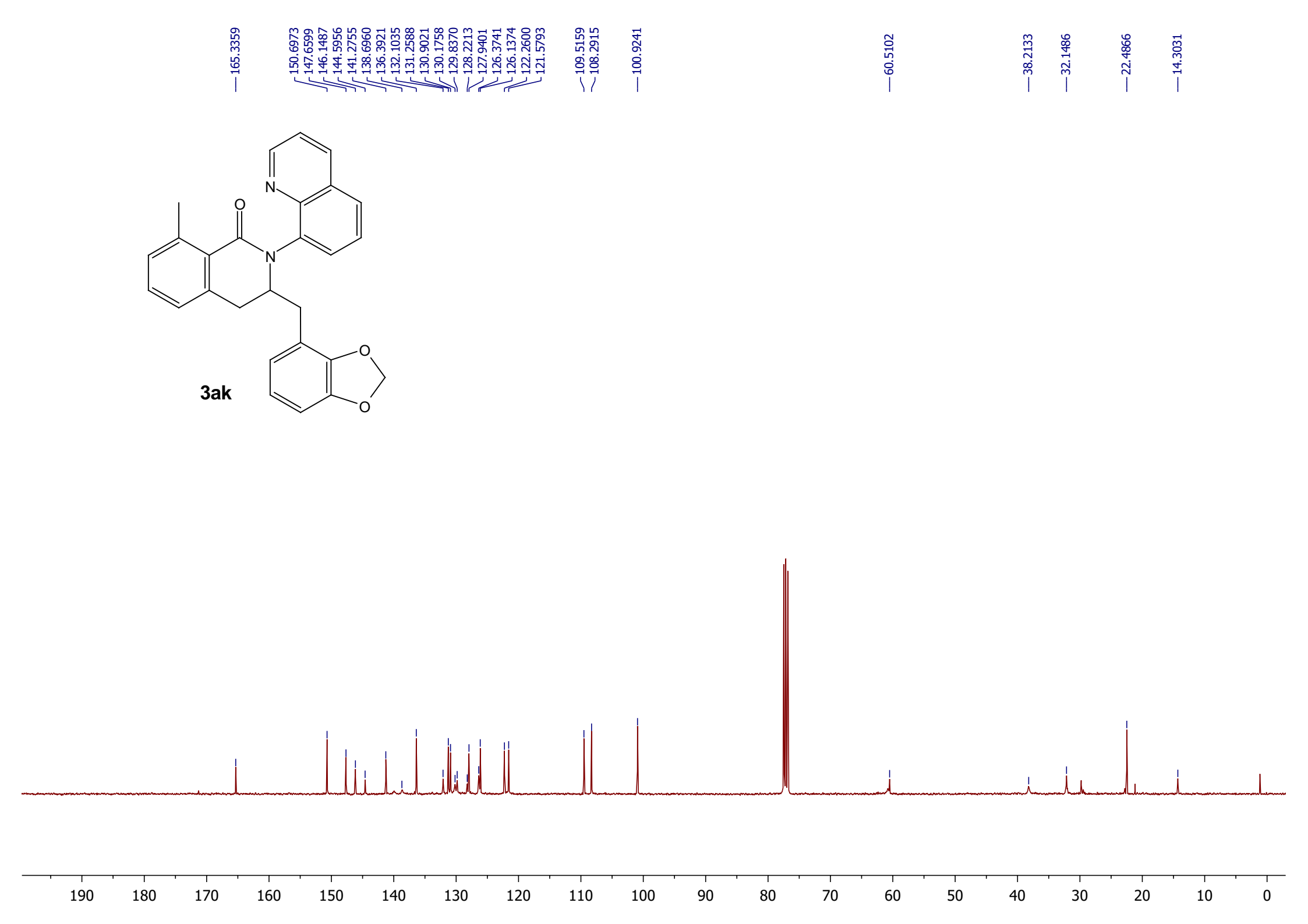
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129.8370
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126.3741
126.1374
122.2600
121.5793
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108.2915
100.9241
60.5102
38.2133
32.1486
22.4866
14.3031
N
O
N
O
O
3ak
190
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150
140
130
120
110
100
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70
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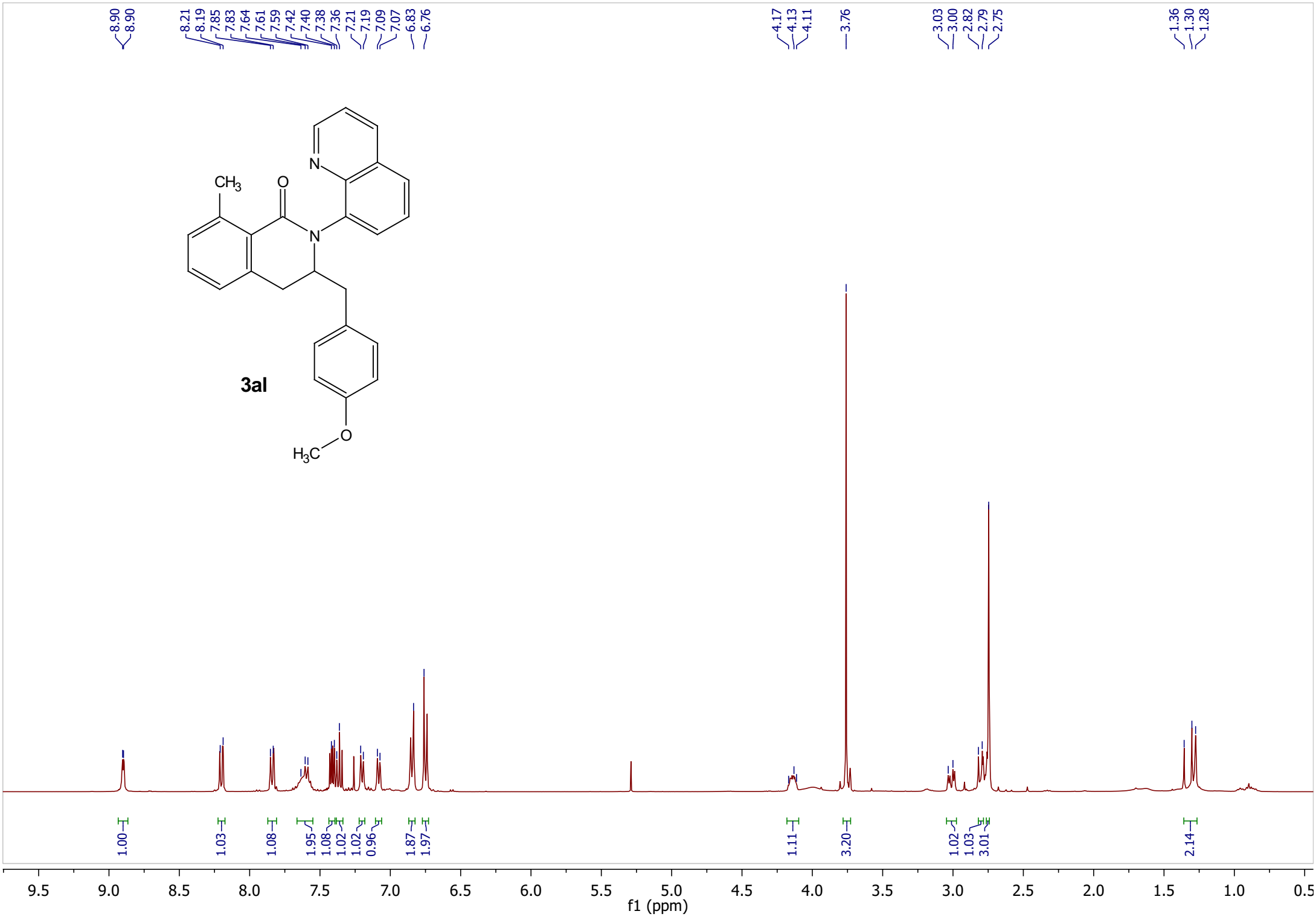
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7.42
7.40
7.38
7.36
7.21
7.19
7.09
7.07
6.83
6.76
4.17
4.13
4.11
3.76
3.03
3.00
2.82
2.79
2.75
1.36
1.30
1.28
CH3
O
N
N
O
H3C
3al
1.00
1.03
1.08
1.95
1.08
1.02
1.02
0.96
1.87
1.97
1.11
3.20
1.02
1.03
3.01
2.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.5
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1.5
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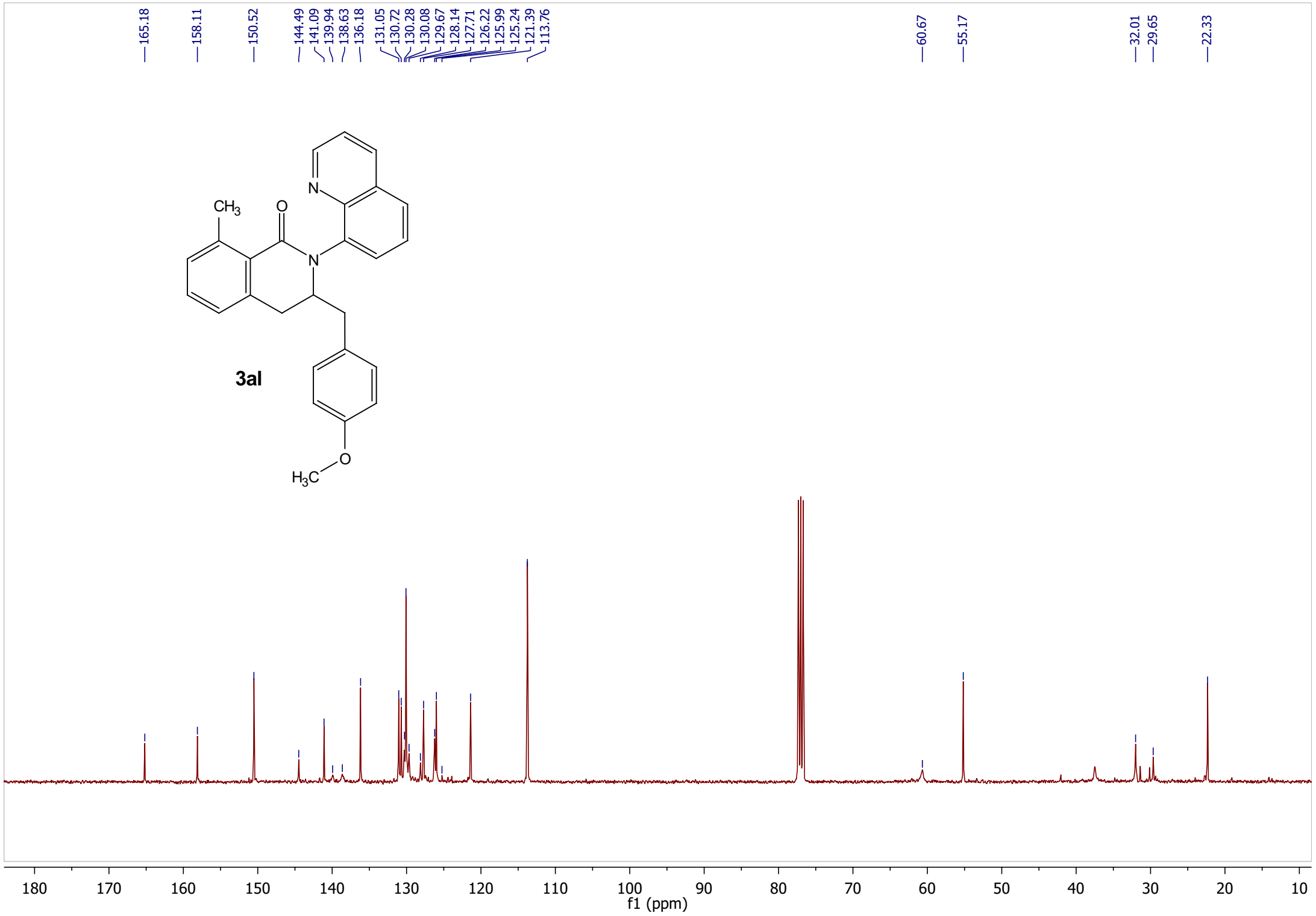
f1 (ppm)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129.67
128.14
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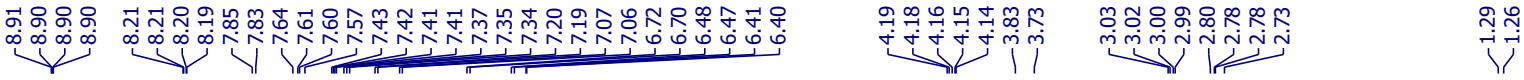
126.22
125.99
125.24
121.39
113.76
60.67
55.17
32.01
29.65
22.33
CH3
O
N
N
O
H3C
3al
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.61
7.60
7.57
7.43
7.42
7.41
7.41
7.37
7.35
7.34
7.20
7.19
7.07
7.06
6.72
6.70
6.48
6.47
6.41
6.40
4.19
4.18
4.16
4.15
4.14
3.83
3.73
3.03
3.02
3.00
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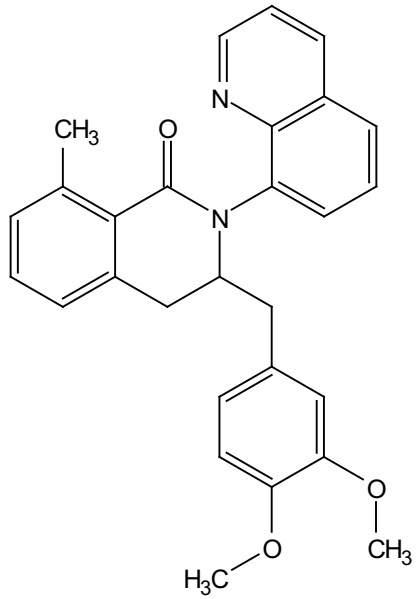
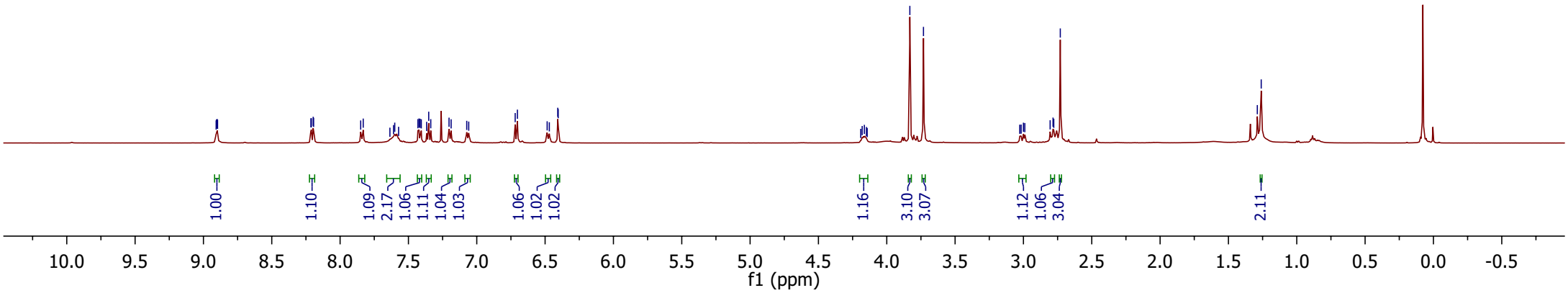
2.80
2.78
2.78
2.73
1.29
1.26


N
CH3
O
N
O
O
CH3
H3C

3am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2.17
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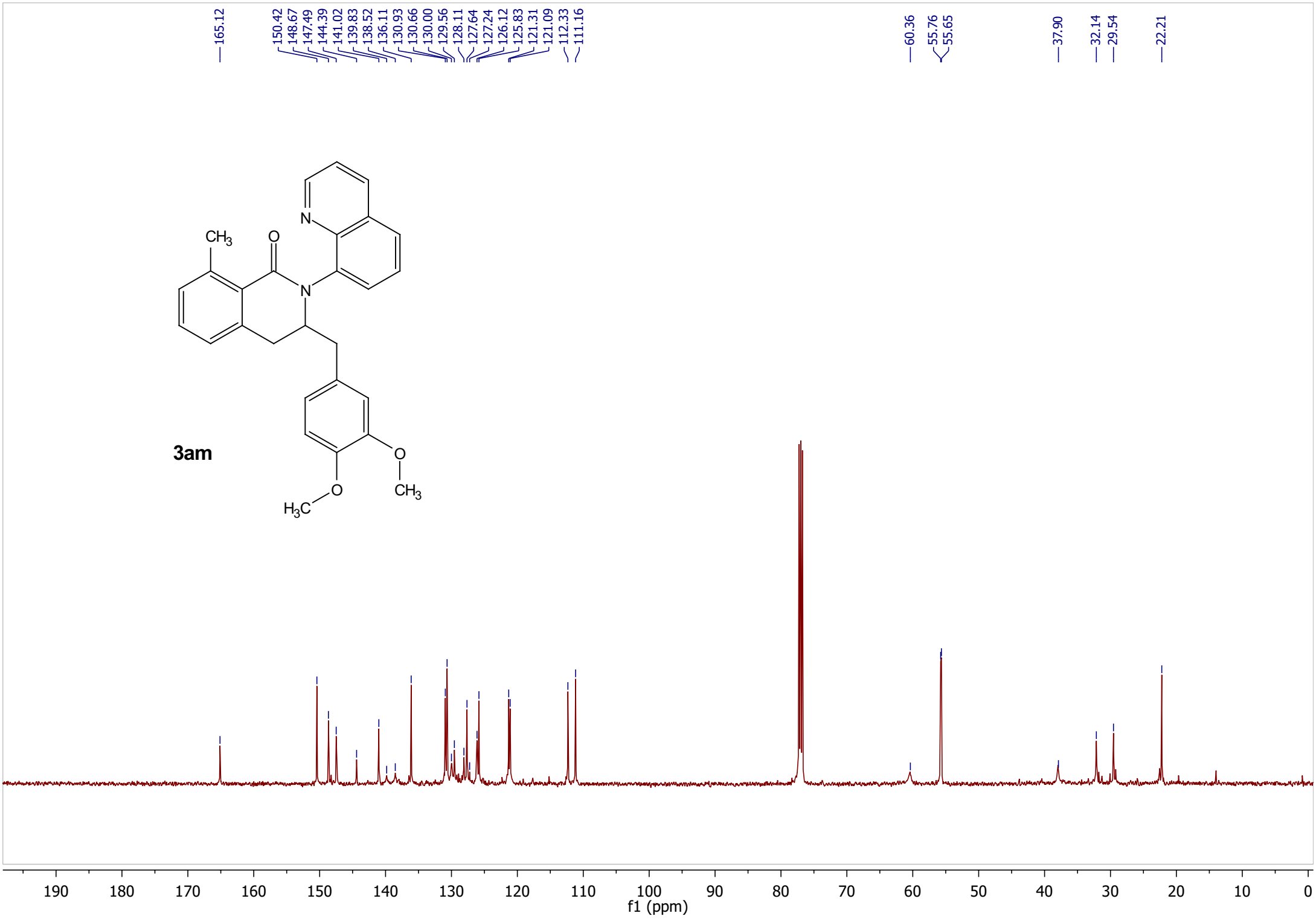
1.11
1.04
1.03
1.06
1.02
1.02
1.16
3.10
3.07
1.12
1.06
3.04
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.11
127.64
127.24
126.12
125.83
121.31
121.09
112.33
111.16
60.36
55.76
55.65
37.90
32.14
29.54
22.21
CH3
O
N
N
O
O
H3C
CH3
3am
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)