Supporting Information

Palladium-catalyzed annulation reactions of quinoline-2-carboxamides via sequential C–H/N–H functionalization

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Table of contents

S1: General experimental details: 3

S2: Preparation of substrates: 4

S3: Method of C-H/N-H annulation reaction: 16

S4: Additional data of optimization of the C-H/N-H coupling reaction: 25

S5: 2D NOESY spectra: 27

S6: Confirmation of the structure of Int-1: 32

S7: NMR chart: 33

Reference 113

S1: General experimental details:

General.

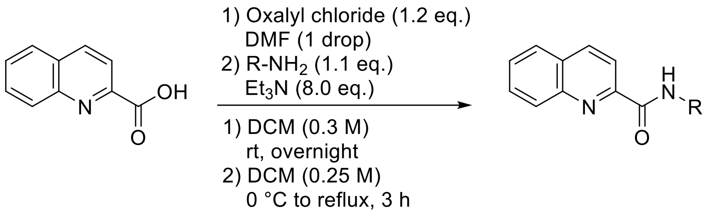
Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 aluminum sheets precoated with a 0.25 mm thickness of silica gel. Flash column chromatography was performed on Wakogel® C-300 (45–75 µm, Fujifilm Wako Pure Chemical Co.). Melting points (Mp) were measured on a Yanaco MP-J3. ^{1}H (400 MHz) and ^{13}C{^{1}H} (100 MHz) NMR spectra were measured on a JEOL ECZ 400 NMR spectrometer at Research Center for Membrane and Film Technology, Kobe University. The chemical shifts were expressed in ppm with tetramethylsilane (0 ppm for ^{1}H as an internal standard in $CDCl_3$) $CDCl_3$ (77.16 ppm for ^{13}C). IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge) by single bounce ATR. HRMS spectra were measured by JEOL JMS-T100L AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment.

Materials.

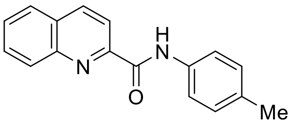
Quinoline-2-carboxylic acid, 2-bromo-4-nitroaniline, 2-iodo-4-methylaniline, and *N*-iodosuccinimide (NIS) were purchased from BLD Pharmatech Ltd. *p*-Toluidine, tris(4-methoxyphenyl)phosphine ($P(4\text{-}MeOC_6H_4)_3$), 1,8-diazabicyclo[5,4,0]undec-2-ene (DBU), 2-bromo-4-*tert*-butylaniline, hydrobromic acid (HBr aq.) (47%), *N*-bromosuccinimide (NBS), tri(*p*-tolyl)phosphine, and tri(*o*-tolyl)phosphine were purchased from Tokyo Chemical Industry Co., Ltd. Aniline, *o*-nitroaniline, acetic anhydride (Ac_2O), nitric acid (HNO_3 aq.), hydrochloric acid (HCl aq.), *o*-xylene, and tris(4-fluorophenly)phosphine were purchased from Fujifilm Wako Pure Chemical Co. *p*-Anisidine, *p*-chloroaniline, *o*-anisidine, acetic acid (AcOH), sulfuric acid (H_2SO_4), triethylamine (Et_3N), *N,N*-dimethylformamide (DMF), cesium carbonate (Cs_2CO_3), sodium nitrile ($NaNO_2$), potassium iodide (KI), acetonitrile (MeCN), *p*-toluenesulfonic acid monohydrate (*p*-TsOH•H_2O), copper(I) bromide (CuBr), zinc powder, and sodium thiosulfate ($Na_2S_2O_3$) were purchased from NAKALAI TESQUE Inc. 4-*tert*-Butylaniline, 4-aminobenzonitrile, and 1-iodo-2-bromobenzene were purchased from Angene International Ltd. 2,4,6-Trimethylaniline, benzylamine, Palladium diacetate ($Pd(OAc)_2$) were purchased from Sigma-Aldrich Co. Oxalyl chloride was purchased from Tokyo Chemical industry Co., Ltd. and NAKALAI TESQUE Inc. Dichloromethane was purchased from Kanto Chemical Co., Inc.

S2: Preparation of substrates:

S2-1: Synthesis of 2-quinolinecarboxamides



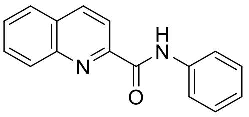
N-(4-Methylphenyl)-2-quinolinecarboxamide (1a)[1)]



To a Schlenk tube equipped with a magnetic stirring bar was added quinoline-2-carboxylic acid (5 mmol, 1.0 eq.) followed by dissolved in dichloromethane (0.3 M). The mixture was cooled to 0 ºC and stirred. To the mixture were added dropwise oxalyl chloride (6.0 mmol, 1.2 eq.) and DMF (1 drop, cat.) via syringe at 0 ºC. The resulting mixture was warmed up to room temperature and stirred for overnight. The solvent was removed under vacuum and the residue was suspended in dichloromethane (0.25 M). To the mixture was added Et_3N (40 mmol, 8.0 eq.) and amine (5.5 mmol, 1.1 eq.) at 0 ºC, then the mixture was stirred at same temperature for 1 hour, followed by warm up to refluxing temperature and stirred for 2 hours. The reaction was quenched with 1 M HCl aq. and extracted thrice with dichloromethane. The organic phases were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give a crude product. The product was separated with silica gel column chromatography (hexane/AcOEt = 2/1) to give a corresponding amide in 89% yield as a light brown solid. ^{1}H NMR ($CDCl_3$): 10.18 (s, 1H), 8.40 (dd, *J* = 8.8, 8.0 Hz, 1H), 8.38 (dd, *J* = 8.8, 8.8 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.81 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.70-7.79 (m, 2H), 7.66 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.17-7.25 (m, 2H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$):162.1, 149.9, 146.4, 137.9, 135.4, 134.1, 130.4, 129.8, 129.7, 129.5, 128.2, 127.9, 119.9, 118.9, 21.1.

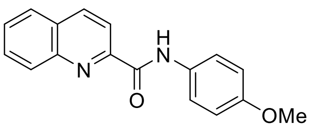
Synthesis of **1b** to **1f** and **1h** to **1k** was carried out in a similar manner, spectroscopic characteristics and analytical properties are shown below.

N-Phenyl-2-quinolinecarboxamide (1b)[1)]



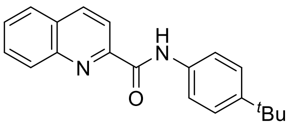
Yield: 76% as a brown solid; ^{1}H NMR ($CDCl_3$): 10.25 (s, 1H), 8.40 (dd, *J* = 8.8, 8.4 Hz, 1H), 8.38 (dd, *J* = 8.8, 8.4 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84-7.89 (m, 2H), 7.82 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.38-7.47 (m, 2H), 7.15-7.21 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.3, 149.8, 146.4, 138.0, 137.9, 130.5, 129.8, 129.5, 129.2, 128.3, 127.9, 124.5, 119.9, 118.9.

_N_-(4-Methoxyphenyl)-2-quinolinecarboxamide (1c)[2)]



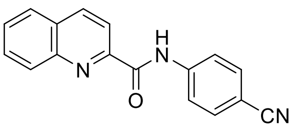
Yield: 82% as a white solid; ^{1}H NMR ($CDCl_3$): 10.13 (s, 1H), 8.32-8.42 (m 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.74-7.79 (m, 2H), 7.64 (ddd, *J* = 8.4, 6.8, 0.8 Hz, 1H), 6.92-6.99 (m, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.0, 156.5, 149.9, 146.4, 137.9, 131.2, 130.4, 129.8, 129.5, 128.2, 127.9, 121.4, 118.8, 114.4, 55.6.

_N_-[4-(_tert_-Butyl)phenyl]-2-quinolinecarboxamide (1d)



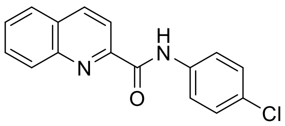
Yield: 45% as a brown solid; Mp: 99.4–101.4 ºC; ^{1}H NMR ($CDCl_3$): 10.19 (s, 1H), 8.35-8.44 (m, 2H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (ddd, *J* = 8.4, 7.6, 0.8 Hz, 1H), 7.74-7.80 (m, 2H), 7.66 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.40-7.48 (m, 2H), 1.35 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.2, 149.9, 147.4, 146.4, 137.9, 135.3, 130.4, 129.8, 127.9, 126.0, 119.7, 118.9, 34.6, 31.5; IR (ATR): 3353, 3343, 2961, 2901, 2870, 1684, 1589, 1529, 1502, 1408, 1320, 1269, 1133, 1114, 1097; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{20}H_{21}N_2O$ 305.1649; found, 305.1662.

_N_-(4-Cyanophenyl)-2-quinolinecarboxamide (1e)[2)]



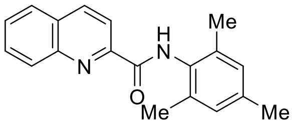
Yield: 63% as a pale yellow solid; ^{1}H NMR ($CDCl_3$): 10.47 (s, 1H), 8.37-8.44 (m, 2H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.97-8.03 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.70-7.74 (m, 2H), 7.69 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.6, 148.8, 146.3, 141.8, 138.3, 133.5, 130.8, 129.7, 128.7, 128.0, 119.8, 119.1, 118.7, 114.5, 107.3.

_N_-(4-Chlorophenyl)-2-quinolinecarboxamide (1f)[1)]



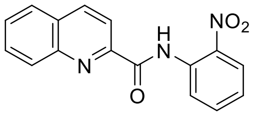
Yield: 81% as a white solid; ^{1}H NMR ($CDCl_3$): 10.25 (s, 1H), 8.35-8.41 (m, 2H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.78-7.85 (m, 3H), 7.66 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.34-7.71 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.3, 149.4, 146.4, 138.1, 136.5, 130.6, 129.7, 129.6, 129.4, 129.2, 128.4, 128.0, 121.1, 118.8.

_N_-Mesityl-2-quinolinecarboxamide (1h)



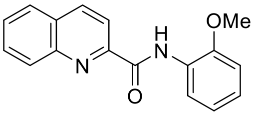
Yield: 65% as a brown solid; Mp: 142.8–144.5 ºC; ^{1}H NMR ($CDCl_3$): 9.64 (s, 1H), 8.34-8.44 (m, 2H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.80 (ddd, *J* = 8.4, 7.2, 0.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.2 Hz, 1H), 6.97 (s, 2H), 2.32 (s, 3H), 2.29 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.9, 149.9, 146.6, 137.7, 136.9, 135.3, 131.3, 130.3, 129.9, 129.5, 129.1, 128.1, 127.9, 119.2, 21.1, 18.7; IR (ATR): 3358, 2920, 1681, 1516, 1496, 1426, 1161; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{19}H_{19}N_2O$ 291.1492; found, 291.1503.

_N_-(2-Nitrophenyl)-2-quinolinecarboxamide (1i)



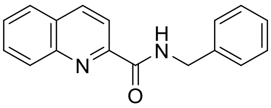
Yield: 71% as a yellow solid; Mp: 175.1–175.6 ºC; ^{1}H NMR ($CDCl_3$): 13.09 (s, 1H), 9.09 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.32-8.39 (m, 2H), 8.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.66 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.23 (ddd, *J* = 8.4, 7.2, 1.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$): 163.7, 149.0, 146.5, 138.0, 137.0, 135.9, 134.8, 130.6, 130.4, 129.7, 128.7, 127.7, 126.1, 123.4, 121.9, 118.7; IR (ATR): 3261, 1698, 1606, 1581, 1503, 1449, 1439, 1424, 1344, 1314, 1273, 1147, 1124; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{16}H_{12}N_3O_3$ 294.0874; found, 294.0882.

_N_-(2-Methoxyphenyl)-2-quinolinecarboxamide (1j)[1)]



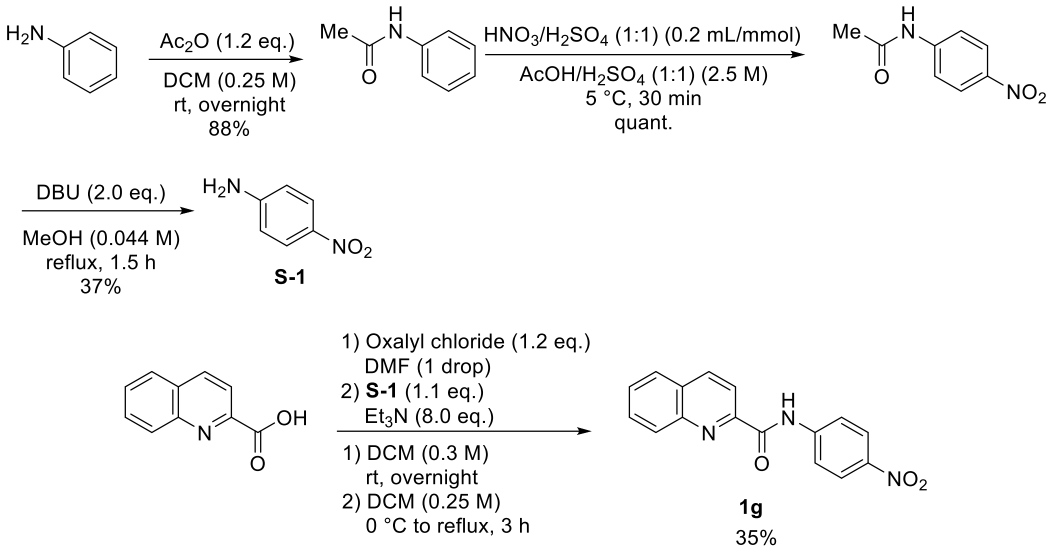
Yield: 86% as a white solid; ^{1}H NMR ($CDCl_3$): 10.82 (s, 1H), 8.67 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.32-8.43 (m, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (ddd, *J* = 8.0, 6.8, 1.6 Hz, 1H), 7.63 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.8, 2.0 Hz, 1H), 7.06 (ddd, *J* = 8.0, 7.8, 1.6 Hz), 4.02 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.3, 150.2, 149.0, 146.5, 137.8, 130.2, 130.1, 129.4, 128.1, 127.9, 127.7, 124.1, 121.2, 119.9, 118.9, 110.2, 56.0.

***N*-Benzyl-2-quinolinecarboxamide (1k)**[3)]



Yield: 82% as a white solid; ^{1}H NMR ($CDCl_3$): 8.61 (br s, 1H), 8.30-8.38 (m, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.40-7.47 (m, 2H), 7.34-7.41 (m, 2H), 7.27-7.34 (m, 1H), 4.75 (d, *J* = 6.0 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): 164.5, 149.7, 146.6, 138.4, 137.6, 130.2, 129.8, 129.4, 128.8, 128.0, 127.8, 127.6, 119.0, 43.7.

S2-2: Synthesis of *N*-(4-nitrophenyl)-2-quinolinecarboxamide (1g).



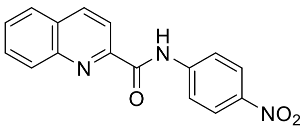
Acetanilide was synthesized according to the literature procedure[4)]. To a round-bottom flask equipped with a magnetic stirring bar were added aniline (10 mmol) and dichloromethane (0.25 M). Ac_2O (12 mmol, 1.2 eq.) was then added dropwise to the stirring mixture. The resulting mixture was stirred for overnight at room temperature. The reaction was monitored by TLC. The solution was replaced to separation funnel and washed with 1 M HCl aq. and sat. $NaHCO_3$ aq.. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure to give 88% of corresponding acetanilide which was used next reaction without further purification.

The nitration product was synthesized according to the literature procedure[5)]. To a round bottom flask equipped with a magnetic stirring bar were added acetanilide (8.8 mmol) and 1:1 mixture of AcOH and H_2SO_4 solution (2.5 M). The mixture was heated until dissolved the sold perfectly. The solution was cooled to 5 ºC, then to the mixture was added 1:1 mixture of HNO_3 and H_2SO_4 (1.76 mL). The resulting mixture was stirred for 30 min at 5 ºC, followed by poured into ice-water. The precipitate was filtered and dried under vacuum to give corresponding 4-nitroacetanilide in quantitative yield which was used next reaction without further purification.

The deprotection product was synthesized according to the literature procedure[6)]. To a round bottom flask equipped with a magnetic stirring bar were added 4-nitroacetanilide (8.8 mmol), MeOH (200 mL), and DBU (17.6 mmol, 2.0 eq.). The mixture was stirred for 1.5 h at reflux. The mixture was poured into H_2O to resulting precipitate. The precipitate was filtered and dried to give corresponding 4-nitroaniline in 37% yield, which was used amidation reaction without further purification.

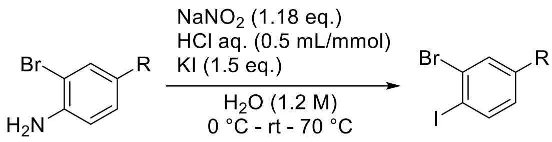
The amide was synthesized according to the general procedure. To a Schlenk tube equipped with a magnetic stirring bar was added quinoline-2-carboxylic acid (2.9 mmol, 1.0 eq.) followed by dissolved in dichloromethane (0.3 M). The mixture was cooled to 0 ºC and stirred. To the mixture were added dropwise oxalyl chloride (3.5 mmol, 1.2 eq.) and DMF (1 drop, cat.) via syringe at 0 ºC. The resulting mixture was warmed up to room temperature and stirred for overnight. The solvent was removed under vacuum and the residue was suspended in dichloromethane (0.25 M). To the mixture was added Et_3N (23.2 mmol, 8.0 eq.) and 4-nitroaniline (3.2 mmol, 1.1 eq.) at 0 ºC, then the mixture was stirred at same temperature for 1 hour, followed by warm up to refluxing temperature and stirred for 2 hours. The reaction was quenched with 1 M HCl aq. and extracted thrice with dichloromethane. The organic phases were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give a crude product. The product was separated with silica gel column chromatography (hexane/AcOEt = 2/1) to give a corresponding amide in 35% yield as a yellow solid.

***N*-(4-Nitrophenyl)-2-quinolinecarboxamide (1g)[1)]**



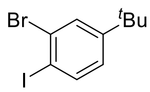
^{1}H NMR ($CDCl_3$): 10.58 (s, 1H), 8.36-8.43 (m, 2H), 8.27-8.34 (m, 2H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.00-8.07 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.84 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 162.7, 148.7, 146.4, 143.73, 143.66, 138.4, 130.9, 129.82, 129.77, 128.8, 128.1, 125.4, 119.4, 118.8.

S2-3: Synthesis of 1-bromo-2-iodobenzene derivatives.



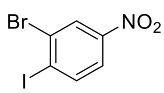
The iodination was carried out according to the literature procedure. [7] To a stirring solution of 2-bromoaniline derivatives (10 mmol, 1.0 eq.) in H_2O (17 mL) and HCl aq. (5 mL) at 0 ºC was added $NaNO_2$ (1.18 eq. 11.8 mmol) in H_2O (17 mL) and the resulting mixture was stirred for 10 minutes at same temperature. To the diazonium solution was then added dropwise KI (1.50 eq. 15 mmol) in H_2O (3.8 mL) at 0 ºC. The mixture was warmed up to room temperature and stirred for 30 minutes, followed by warmed up to 70 ºC and stirred for 1 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted thrice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane) to give corresponding 1-bromo-2-iodobenzene.

1-Bromo-2-iodo-5-*tert*-butylbenzene (2d)[8]

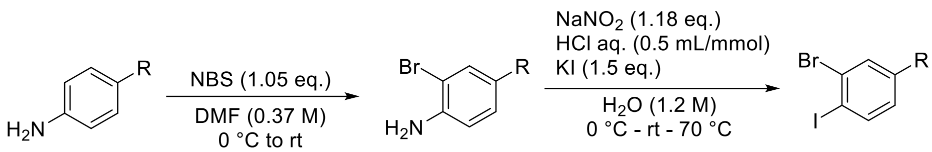


Yield: 81% as a colorless oil; ^{1}H NMR ($CDCl_3$): 7.75 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.02 (dd, J = 8.4, 2.0 Hz, 1H), 1.29 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): 153.5, 139.9, 130.2, 129.6, 126.1, 97.2, 34.8, 31.1.

1-Bromo-2-iodo-5-nitrobenzene (2i)[9]



Yield: 62% as a yellow solid; ^{1}H NMR ($CDCl_3$): 8.44 (d, J = 3.0 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 7.84 (dd, J = 8.8, 3.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$); 148.3, 141.1, 131.0, 127.4, 122.8, 110.4.

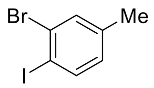


The bromination was carried out according to the literature procedure.[10] To a solution of 4-

substituted aniline (10 mmol, 1.0 eq.) in DMF (0.37 M) was added portionwise NBS (10.5 mmol, 1.05 eq.) at 0 ºC. The reaction mixture was stirred for 30 min at 0 ºC, then warmed up to room temperature and stirred for 18 hours at same temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with brine. The organic phase was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (Hexane/AcOEt = 20/1) to give the corresponding 2-bromo-4-substituted aniline.[11,12)]

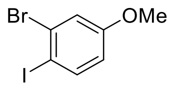
The iodination was carried out according to the literature procedure.[7)] To a stirring solution of 2-bromoaniline derivatives (10 mmol, 1 eq.) in H_2O (17 mL) and HCl aq. (5 mL) at 0 ºC was added $NaNO_2$ (1.18 eq. 11.8 mmol) in H_2O (17 mL) and the resulting mixture was stirred for 10 minutes at same temperature. To the diazonium solution was then added dropwise KI (1.50 eq. 15 mmol) in H_2O (3.8 mL) at 0 ºC. The mixture was warmed up to room temperature and stirred for 30 minutes, followed by warmed up to 70 ºC and stirred for 1 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted thrice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane) to give corresponding 1-bromo-2-iodobenzene.

3-Bromo-4-iodotoluene (2b)



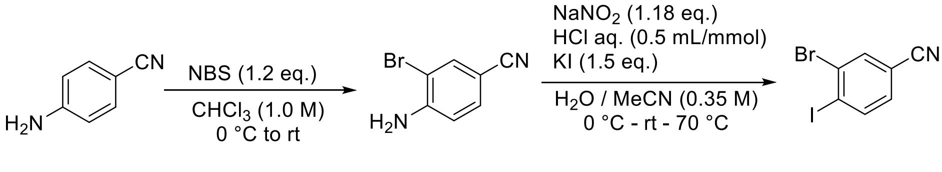
Yield: 65% as a colorless oil; ^{1}H NMR ($CDCl_3$): 7.70 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 140.02, 139.98, 133.5, 129.7, 129.5, 97.0, 20.8; IR (ATR): 2921, 1458, 1370, 1259, 1208, 1097, 1006; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_7H_6{}^{79}BrI$ 295.8698; found, 295.8689.

3-Bromo-4-iodoanisole (2f)[13)]



Yield: 54% as a colorless oil; ^{1}H NMR ($CDCl_3$): 7.67 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 3.2 Hz, 1H), 6.59 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 160.3, 140.3, 130.0, 118.5, 115.4, 89.6, 55.7.

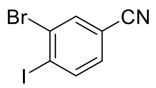
Synthesis of 3-bromo-4-iodobenzonitrile (2h)



To a stirred solution 4-aminobenzonitrile (7.5 mmol, 1.0 eq.) in chloroform (7.5 mL, 1.0 M) was added portionwise NBS (9.0 mmol, 1.2 eq.) during 1 hour at 0 ºC. The reaction mixture was warmed up to room temperature and stirred for 4 h, then the resulting precipitate was filtered off. The filtrate was washed with H_2O, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane/AcOEt = 2/1) to give 3-bromo-4-aminobenzonitrile in 58% yield.

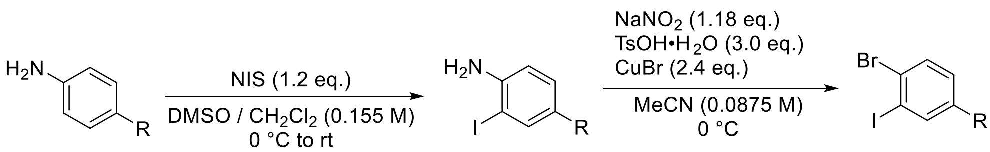
The iodination was carried out according to the modified literature procedure. [7] To a stirring solution of 3-bromo-4-aminobenzonitrile (4.3 mmol, 1.0 eq.) in H_2O/acetonitrile (3/2, 0.35 M) and HCl aq. (2.25 mL) at 0 ºC was added $NaNO_2$ (5.1 mmol, 1.18 eq.) in H_2O (1.9 mL) and the resulting mixture was stirred for 10 minutes at same temperature. To the diazonium solution was then added dropwise KI (6.5 mmol, 1.50 eq.) in H_2O (1.9 mL) at 0 ºC. The mixture was warmed up to room temperature and stirred for 30 minutes, followed by warmed up to 70 ºC and stirred for 1 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted thrice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane) to give 3-bromo-4-iodobenzonitrile.

3-Bromo-4-iodobenzonitrile (2h)[14]



Yield: 59% as a colorless solid; ^1H NMR ($CDCl_3$): 7.99 (dd, J = 8.4, 0.8 Hz, 1H), 7.87 (m, 1H), 7.26 (dd, J = 8.4, 1.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 141.2, 135.3, 131.1, 131.0, 117.0, 113.6, 108.3.

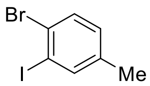
Synthesis of 4-substituted 1-bromo-2-iodobenzene derivatives



The iodination was carried out according to the literature procedure.[15] To a stirring solution of 4-substituted aniline (10 mmol, 1.0 eq.) in DMSO/dichloromethane (2/1) (0.155 M) was added *N*-iodosuccinimide (12 mmol, 1.2 eq.) at 0 ºC. The mixture was stirred for same temperature for 10 minutes. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. The biphasic layer was extracted thrice with dichloromethane. The combined organic layers were washed with brine. The organic phase was dried over Na_2SO_4, filtered, and evaporated. The crude product was purified with silica gel column chromatography (hexane/AcOEt = 10/1) to give corresponding 2-iodo-4-substituted aniline.

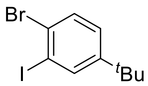
The iodination was carried out according to the literature procedure.[16] To a stirring solution of 2-iodo-4-substituted aniline (10.0 mmol, 1.0 eq.) in MeCN (0.0875 M) was added *p*-TsOH•H_2O (30.0 mmol, 3.0 eq.) at 0 ºC. To the mixture was added dropwise a solution of $NaNO_2$ (19.4 mmol, 1.94 eq.) in H_2O (7.8 mL) at same temperature. The mixture was stirred for 2 hours at 0 ºC. To the resulting diazonium solution was added CuBr (24.0 mmol, 2.4 eq.) at 0 ºC. The reaction mixture was stirred for additional 1 hour at same temperature. The reaction mixture was diluted with H_2O. The biphasic layer was extracted thrice with AcOEt. The combined organic layers were washed with brine. The organic phase was dried over Na_2SO_4, filtered, and evaporated. The crude product was purified with silica gel column chromatography (hexane) to give corresponding 1-bromo-2-iodo-4-substituted benzene.

4-Bromo-3-iodotoluele (2c)



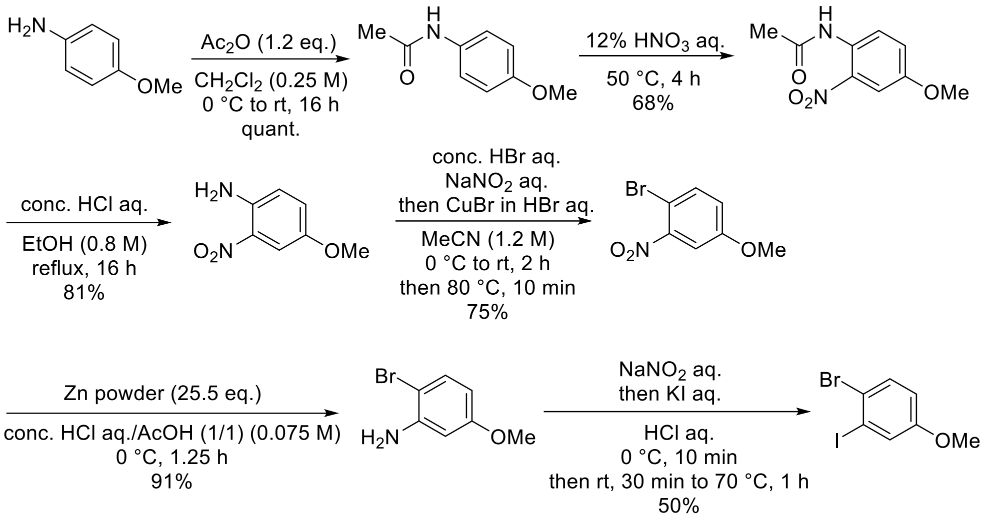
Yield: 65% as a colorless oil; ^{1}H NMR ($CDCl_3$): 7.69 (d, *J* = 1.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 140.9, 138.8, 132.3, 130.5, 126.3, 101.1, 20.5; IR (ATR): 2920, 1456, 1369, 1257, 1100, 1010; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_7H_6{}^{79}BrI$ 295.8698; found, 295.8707.

1-Bromo-2-iodo-4-*tert*-butylbenzene (2e)[17)]



Yield: 79% as a colorless oil; ^{1}H NMR ($CDCl_3$): 7.84 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 1.28 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 152.2, 137.6, 132.3, 127.1, 126.5, 101.3, 34.6, 31.2.

Synthesis of 4-bromo-3-iodoanisole



To a solution of *p*-anisidine (10 mmol, 1.0 eq.) in CH_2Cl_2 (0.25 M) at 0 ºC was added acetic anhydride (12 mmol, 1.2 eq.), then the reaction mixture was warmed up to room temperature and stirred for 16 h. The mixture was washed with sat. $NaHCO_3$ aq., 1.0 M HCl aq., H_2O, and brine. The organic phase was dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give *p*-acetanisidide as a colorless solid.[18) The product was used next reaction without further purification.

To a solution of *p*-acetanisidide (10 mmol, 1.0 eq.) in 12% of HNO_3 aq. was stirred at 50 ºC for 4 h, then the reaction mixture was cooled to room temperature. After the reaction, cold H_2O was added to the reaction mixture. The resulting precipitate was filtered and washed with H_2O, then the precipitate was dried under vacuum to *N*-(4-methoxy-2-nitrophenyl)acetamide in 68% yield (in 2 steps) as a yellow solid.[19)] The product was used next reaction without further purification.

To a solution of *N*-(4-methoxy-2-nitrophenyl)acetamide (6.8 mmol, 1 eq.) in EtOH (0.8 M) was added dropwise conc. HCl aq. (4.2 mL), then the reaction mixture was stirred for 16 h at reflux. The reaction mixture was cooled to room temperature and quenched with 28% NH_3 aq. (3.4 mL) under iced bath. The resulting precipitate was filtered and washed with H_2O. The precipitate was dried under vacuum to give 4-methoxy-2-nitroaniline in 81% yield as a red solid.[20)] The product was used next reaction without further purification.

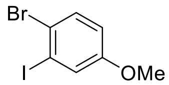
The bromination was carried out to the literature procedure.[21)] To a suspension of 4-methoxy-2-nitroaniline (5.5 mmol, 1 eq.) in MeCN (1.2 M) was added HBr (47%, 5.5 mL) and the mixture was cooled to 0 ºC. A solution of $NaNO_2$ (1.0 eq.) in H_2O (2.3 mL) was added dropwise to the reaction mixture at same temperature, then the mixture was warmed up to room temperature and stirred for 2 hours. To the mixture was added a solution of CuBr (0.9 eq.) in HBr (47%, 2.3 mL) and the reaction mixture was heated to 80 ºC for 10 minutes. The mixture was cooled to room temperature and the NaOH tablet was added until the red color changed blue-green. The mixture was extracted thrice with AcOEt and the organic layers were washed with brine, dried over Na_2SO_4, and concentrated at reduced pressure. The residue was purified with silica gel column chromatography (hexane/AcOEt =

5/1) to give 1-bromo-4-methoxy-2-nitrobenzene in 75% yield as a yellow solid.[21]

The reduction was carried out to the literature procedure.[22] To a mixture of concentrated HCl aq./AcOH (1/1, 0.075 M) at 0 ºC was added 1-bromo-4-methoxy-2-nitrobenzene (4.1 mmol 1.0 eq.). Zinc powder (6.9 g, 25.5 eq.) was then added portionwise to the mixture over 1 hour after which point the reaction mixture was stirred for an additional 15 minutes at 0 ºC and then quenched by addition of ammonium hydroxide until slightly basic. The crude product was extracted thrice with DCM and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/AcOEt = 5/1) to give 2-bromo-5-methoxyaniline in 91% yield as a brown oil.

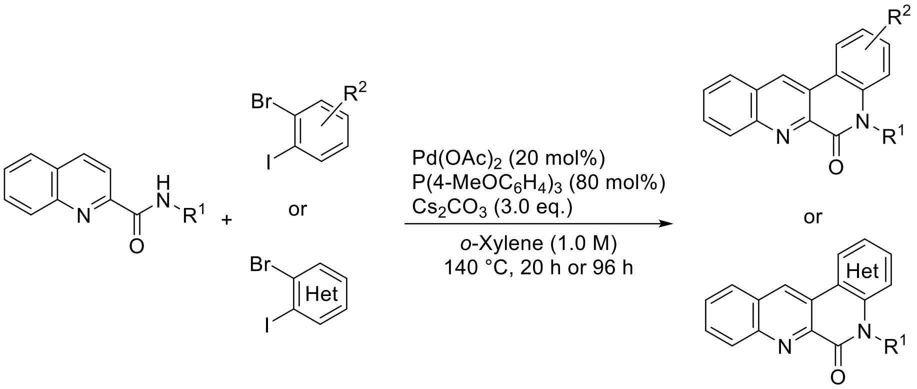
The iodination was carried out according to the literature procedure.[7] To a stirring solution of 2-bromo-5-methoxyaniline (3.8 mmol, 1.0 eq.) in H_2O and HCl aq. at 0 ºC was added $NaNO_2$ in H_2O and the resulting mixture was stirred for 10 minutes at same temperature. To the diazonium solution was then added dropwise KI in H_2O at 0 ºC. The mixture was warmed up to room temperature and stirred for 30 minutes, followed by warmed up to 70 ºC and stirred for 1 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted thrice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane) to give 4-bromo-3-iodoanisole in 50% yield as a colorless oil.

4-Bromo-3-iodoanisole (2g)[23]



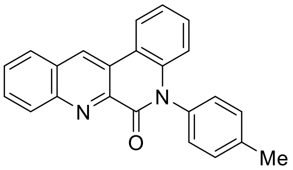
^{1}H NMR ($CDCl_3$): 7.46 (d, J = 9.2 Hz, 1H), 7.38 (d, J = 2.8 Hz, 1H), 6.76 (dd, J = 8.0, 2.8 Hz, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 158.7, 132.7, 125.4, 120.3, 116.1, 101.2, 55.8.

S3: Method of C–H/N–H annulation reaction:



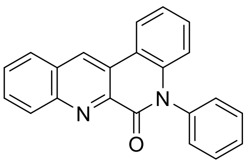
To a screw capped test tube equipped with a magnetic stirring bar were added quinoline-2-carboxamide (0.05 mmol, 1.0 eq.), $Pd(OAc)_2$ (0.01 mmol, 20 mol%), $P(4\text{-}MeOC_6H_4)_3$ (0.04 mmol, 80 mol%), Cs_2CO_3 (0.15 mmol, 3.0 eq.), and 1-iodo-2-bromobenzene derivatives (0.1 mmol, 2.0 eq.), followed by dissolved in *o*-xylene (1.0 M). The test tube was backfilled with N_2 atmosphere and sealed with screw cap. The mixture was stirred at 140 ºC for 20 hours (Method A) or 96 hours (Method B). The reaction mixture was quenched with H_2O and extracted thrice with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography (hexane to hexane/AcOEt = 1/9 gradient) to give the corresponding lactam.

5-(4-Methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3aa)



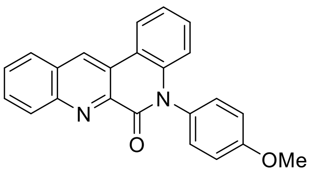
Method A; Yield: 81% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.15 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.36-8.44 (m, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.83 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.30-7.38 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.71-6.79 (m, 1H), 3.15 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.3, 148.4, 142.4, 139.0, 138.8, 135.3, 131.2, 131.0, 130.5, 130.2, 129.6, 129.3, 128.8, 128.6, 127.7, 126.7, 123.2, 123.0, 117.9, 117.4, 21.3; IR (ATR): 2980, 2964, 2936, 2925, 1673, 1605, 1511, 1493, 1351, 1331, 1315; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_{23}H_{17}N_2O$ 337.1341; found, 337.1349.

5-Phenyldibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ba)



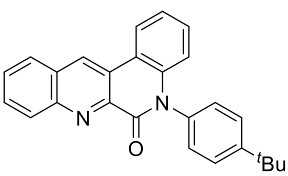
Method A; Yield: 81% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.16 (s, 1H), 8.48 (d, *J* = 8.8 Hz, 1H), 8.38-8.45 (m, 1H), 8.08 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.85 (ddd, *J* = 8.8, 6.8, 1.6 Hz, 1H), 7.72 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.61-7.69 (m, 2H). 7.56) 7.53-7.60 (m, 1H), 7.36-7.41 (m. 2H), 7.32-7.37 (m, 2H), 6.68-6.24 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.3, 148.6, 142.4, 138.9, 138.1, 131.2, 130.7, 130.4, 129.8, 129.4, 129.1, 129.04, 128.99, 127.8, 126.9, 123.4, 123.2, 118.0, 117.4; IR (ATR): 3059, 2980, 2961, 2921, 2849, 1672, 1604, 1493, 1465, 1412, 1384, 1352, 1331, 1315, 1283, 1225, 1149, 1125; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{22}H_{15}N_2O$ 323.1184; found, 323.1186.

5-(4-Methoxyphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ca)



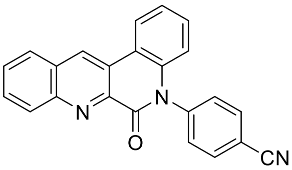
Method A; Yield: 68% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.16 (s, 1H), 8.48 (d, *J* = 8.8 Hz, 1H), 8.38-8.44 (m, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.31-7.39 (m, 1H), 7.26-7.31 (m, 2H), 7.11-7.18 (m, 2H), 6.74-6.81 (m, 1H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.6, 159.8, 148.5, 142.5, 139.3, 131.2, 130.6, 130.3, 130.0, 129.8, 129.4, 128.9, 127.8, 126.9, 123.4, 123.1, 118.0, 117.5, 115.6, 55.6; IR (ATR): 3071, 2975, 2961, 2934, 2912, 1671, 1605, 1510, 1464, 1352, 1329, 1315, 1299, 1249, 1225, 1169, 1149, 1125, 1105, 1030; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{23}H_{17}N_2O_2$ 353.1290; found, 353.1280.

5-(4-*tert*-Butylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3da)



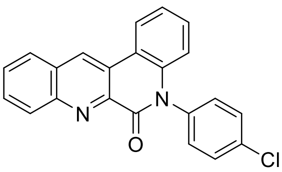
Method A; Yield: 72% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.16 (s, 1H), 8.48 (d, *J* = 8.8 Hz, 1H), 8.38-8.44 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (ddd, *J* = 8.4, 6.8, 0.8 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.8, 0.8 Hz, 1H), 7.60-7.68 (m, 2H), 7.33-7.37 (m, 1H), 6.70-6.71 (m, 1H), 6.70-6.75 (m, 1H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.3, 151.8, 148.6, 142.5, 139.2, 135.3, 131.3, 130.6, 130.3, 129.8, 129.4, 128.9, 128.4, 127.8, 127.3, 126.9, 123.3, 123.1, 118.0, 117.6, 34.9, 31.5; IR (ATR): 2964, 2913, 2866, 1674, 1605, 1502, 1464, 1412, 1384, 1352, 1330, 1314, 1283, 1227, 1210, 1153, 1112, 1102; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{26}H_{23}N_2O$ 379.1810; found, 379.1800.

5-(4-Cyanophenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ea)



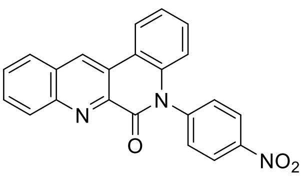
Method A; Yield: 67% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.17 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.39-8.46 (m, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.92-8.00 (m, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.51-7.61 (m, 2H), 7.35-7.43 (m, 2H), 6.59-6.67 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.0, 148.7, 148.6, 142.3, 141.9. 138.0, 134.3, 131.2, 131.0, 130.60, 130.56, 130.0, 129.5, 129.3, 127.9, 126.7, 123.7, 118.2, 118.2, 116.8, 113.3; IR (ATR): 3040, 2935, 2230, 1683, 1605, 1558, 1465, 1411, 1384, 1351, 1339, 1330, 1316, 1285, 1226, 1149, 1125; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{23}H_{14}N_3O$ 348.1137; found, 348.1127.

5-(4-Chlorophenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3fa)



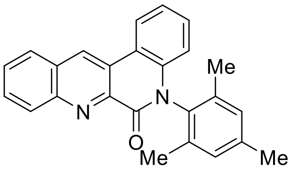
Method A; Yield: 75% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.16 (s, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.38-8.45 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.73 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.58-7.66 (m, 2H), 7.34-7.42 (m, 2H), 7.31-7.36 (m, 2H), 6.68-6.75 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.3, 148.6, 142.2, 138.6, 136.6, 135.0, 131.2, 130.1, 130.7, 130.6, 130.5, 129.9, 129.4, 129.1, 127.8, 126.8, 123.5, 123.4, 118.1, 117.2; IR (ATR): 3073, 3059, 2988, 2977, 2967, 1674, 1604, 1492, 1465, 1412, 1383, 1352, 1330, 1316, 1284, 1261, 1226, 1149, 1126, 1090, 1017; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{22}H_{14}{}^{35}ClN_2O$ 357.0795; found, 357.0790.

5-(4-Nitrophenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ga)



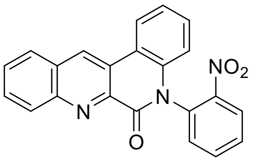
Method A; Yield: 18% as a yellow solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.18 (s, 1H), 8.50-8.56 (m, 2H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.43-8.47 (m, 1H), 8.10 (d, *J* = 8.0 Hz), 7.88 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.76 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.60-7.65 (m, 2H), 7.36-7.44 (m, 1H), 6.62-6.68 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.1, 148.7, 148.1, 144.0, 141.9, 138.0, 131.3, 131.1, 130.8, 130.7, 130.1, 129.6, 129.4, 127.9, 126.8, 125.9, 123.9, 123.8, 118.3, 116.8; IR (ATR): 3087, 1678, 1606, 1593, 1523, 1494, 1466, 1348, 1312, 1225, 1149, 1127, 1103, 1089; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_{22}H_{14}N_3O_3$ 368.1035; found, 368.1028.

5-Mesityldibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ha)



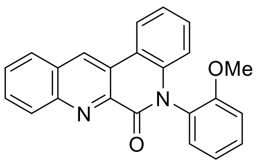
Method A; Yield: 21% as a brown solid; Mp: over 89.4–94.1 ºC; ^{1}H NMR ($CDCl_3$): 9.18 (s, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.41-8.46 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.72 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.32-7.42 (m, 2H), 7.10 (s, 2H), 6.58-6.68 (m, 1H), 2.40 (s, 3H), 2.01 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$): 159.4, 148.5, 142.5, 138.9, 137.5, 135.8, 133.3, 131.4, 130.7, 130.48, 130.45, 130.1, 129.5, 129.1, 127.8, 127.1, 123.6, 123.4, 118.3, 116.2, 21.4, 17.7; IR (ATR): 2954, 2924, 2848, 1671, 1605, 1493, 1464, 1410, 1383, 1352, 1329, 1315, 1284, 1260, 1224, 1100, 1030; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_{25}H_{21}N_2O$ 365.1654; found, 365.1650.

5-(2-Nitrophenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ia)



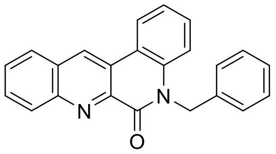
Method A; Yield: 14% as a yellow solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.17 (s, 1H), 8.41-8.50 (m, 2H), 8.38 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.91 (ddd, *J* = 8.0, 7.6, 1.2 Hz, 1H), 7.86 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.34-7.42 (m, 2H), 6.59-6.65 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): 148.6, 146.9, 138.0, 135.3, 132.21, 132.16, 131.4, 130.9, 130.7, 130.5, 130.1, 129.9, 129.6, 129.3, 127.9, 127.0, 126.7, 123.85, 123.78, 123.3, 118.5, 116.4; IR (ATR): 2926, 1679, 1616, 1529, 1465, 1353, 1339, 1315, 1290, 1262; HRMS (DART$^+$) *m/z* $[M+H]^+$ calcd. for $C_{22}H_{14}N_3O_3$ 368.1035; found, 368.1047.

5-(2-Methoxyphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ja)



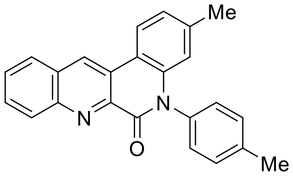
Method B; Yield: 17% as a brown solid; Mp: 207.0–211.2 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.15 (s, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.37-8.44 (m, 1H), 8.07 (d, J = 8.8 Hz, 1H), 7.83 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.71 (ddd, J = 8.0, 7.2, 0.8 Hz, 1H), 7.54 (ddd, J = 9.2, 8.4, 1.6 Hz, 1H), 7.30-7.40 (m, 1H), 7.31 (dd, J = 8.8, 1.2 Hz, 1H), 7.14-7.22 (m, 1H), 6.69-6.77 (m, 1H), 3.14 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.0, 155.7, 148.5, 142.7, 138.7, 131.4, 130.7, 130.6, 130.34, 130.33, 130.0, 129.4, 128.9, 127.8, 127.1, 126.5, 123.4, 123.1, 121.8, 118.1, 116.9, 112.9, 56.0; IR (ATR): 2939, 2851, 1674, 1603, 1500, 1465, 1412, 1384, 1352, 1340, 1330, 1316, 1281, 1255, 1222, 1180, 1162, 1148, 1119, 1101, 1045, 1025; HRMS (DART^{+}) *m/z* [M+H]$^{+}$ calcd. for $C_{23}H_{17}N_2O_2$ 353.1290; found, 353.1295.

5-Benzyldibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ka)



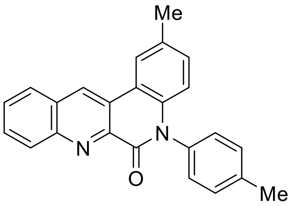
Method B; Yield: 21% as a brown solid; Mp: 232.0–235.5 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.13 (s, 1H), 8.51 (dd, J = 8.4, 0.8 Hz, 1H), 8.40 (dd, J = 8.0, 1.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.86 (ddd, J = 8.8, 6.8, 1.6 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.45 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.34-7.40 (m, 3H), 7.28-7.34 (m, 3H), 7.21-7.26 (m, 1H), 5.75 (br s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.9, 148.6, 142.1, 137.0, 136.4, 131.3, 130.8, 130.34, 130.32, 129.4, 129.03, 128.96, 127.9, 127.5, 127.0, 126.7, 123.7, 123.2, 118.5, 116.5, 47.3; IR (ATR): 2963, 2926, 2859, 1664, 1606, 1496, 1467, 1456, 1412, 1386, 1371, 1332, 1306, 1243, 1210, 1162, 1152, 1124, 1081; HRMS (DART^{+}) *m/z* [M+H]$^{+}$ calcd. for $C_{23}H_{17}N_2O$ 337.1349; found, 337.1339.

3-Methyl-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ab)



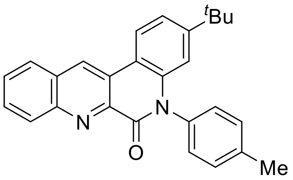
Method B; Yield: 79% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.10 (s, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.82 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.70 (ddd, J = 8.4, 6.8, 0.8 Hz, 1H), 7.40-7.47 (m, 2H), 7.22-7.30 (m, 2H), 7.16 (dd, J = 8.0, 0.8 Hz, 1H), 6.53 (s, 1H), 2.51 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.5, 148.3, 142.3, 140.4, 139.1, 138.8, 135.5, 131.3, 131.0, 130.4, 129.9, 129.4, 128.8, 128.7, 127.7, 127.0, 124.3, 123.3, 117.7, 115.5, 21.9, 21.5; IR (ATR): 2972, 2961, 2930, 2921, 2873, 1722, 1673, 1616, 1592, 1541, 1513, 1490, 1456, 1400, 1381, 1352, 1340, 1326, 1286, 1227, 1211, 1192, 1159, 1147, 1106, 1066, 1047; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{24}H_{19}N_2O$ 351.1497; found, 351.1486.

2-Methyl-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ac)



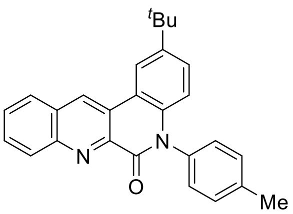
Method B; Yield: 83% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.14 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.20 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.83 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.39-7.46 (m, 2H), 7.21-7.27 (m, 2H), 7.15 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 2.50 (s, 3H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.2, 148.5, 142.6, 138.8, 137.0, 135.6, 132.6, 131.2, 131.0, 130.8, 130.5, 130.3, 129.3, 128.8, 128.7, 127.8, 126.8, 123.5, 117.8, 117.4, 21.5, 21.0; IR (ATR): 2970, 2922, 1673, 1620, 1510, 1486, 1462, 1381, 1339, 1315, 1280, 1226; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{24}H_{19}N_2O$ 351.1497; found, 351.1500.

3-*tert*-Butyl-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ad)



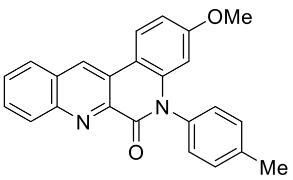
Method B; Yield: 55% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.09 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz), 7.80 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.68 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.38-7.47 (m, 2H), 7.36 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.21-7.29 (m, 2H), 6.74 (d, *J* = 2.0 Hz, 1H), 2.49 (s, 3H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.6, 153.5, 148.4, 142.5, 138.9, 138.8, 135.5, 131.3, 131.0, 130.4, 129.9, 129.4, 128.8, 128.7, 127.7, 126.9, 123.1, 120.6, 115.5, 114.4, 35.1, 31.1, 21.5; IR (ATR): 2963, 2929, 2907, 1673, 1613, 1511, 1488, 1400, 1383, 1340, 1326, 1284, 1256, 1233, 1211, 1166, 1147, 1124; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{27}H_{25}N_2O$ 393.1967; found, 393.1966.

2-*tert*-Butyl-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ae)



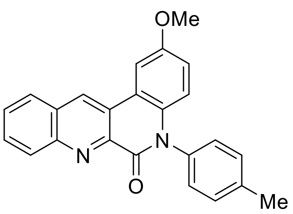
Method B; Yield: 81% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.16 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 2.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.83 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 0.8 Hz, 1H), 7.37-7.46 (m, 3H), 7.22-7.29 (m, 2H), 6.69, (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H), 1.44 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 160.3, 148.5, 146.0, 142.7, 138.9, 137.0, 135.5, 131.4, 131.1, 130.6, 130.1, 129.4, 128.9, 128.8, 127.8, 127.5, 127.2, 119.5, 117.4, 34.8, 31.6, 21.5; IR (ATR): 2963, 2954, 2930, 2918, 2904, 2871, 1674, 1613, 1597, 1511, 1485, 1462, 1380, 1366, 1340, 1315, 1282, 1262, 1231, 1209; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{27}H_{25}N_2O$ 393.1967; found, 393.1967.

3-Methoxy-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3af)



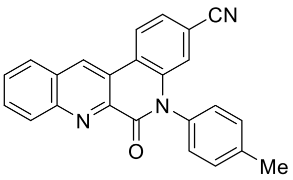
Method B; Yield: 51% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 8.98 (s, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.67 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.36-7.44 (m, 2H), 7.20-7.27 (m, 2H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 3.71 (s, 3H), 2.47 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 160.8, 160.7, 148.0, 141.8, 140.6, 138.9, 135.4, 131.3, 131.1, 130.1, 129.5, 129.2, 128.9, 128.6, 127.6, 127.1, 124.8, 111.4, 109.5, 102.7, 55.5, 21.5; IR (ATR): 2963, 2923, 2852, 1673, 1612, 1512, 1491, 1452, 1406, 1383, 1352, 1341, 1327, 1304, 1283, 1229, 1179, 1150, 1130, 1105, 1048; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{24}H_{19}N_2O_2$ 367.1447; found, 367.1431.

2-Methoxy-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ag)



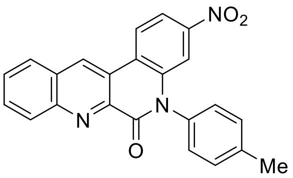
Method B; Yield: 82% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.08 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.79-7.91 (m, 2H), 7.70 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.38-7.46 (m, 2H), 7.21-7.29 (m, 2H), 6.93 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.67 (d, *J* = 9.2 Hz, 1H), 3.94 (s, 3H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 159.9, 155.6, 148.6, 142.7, 138.9, 135.7, 133.4, 131.3, 131.1, 130.7, 130.5, 129.3, 129.0, 128.8, 127.8, 126.6, 118.9, 118.8, 116.6, 107.3, 56.0, 21.5; IR (ATR): 2921, 1669, 1618, 1598, 1581, 1507, 1488, 1469, 1440, 1403, 1383, 1340, 1326, 1299, 1239, 1223, 1184, 1146, 1105, 1043; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{24}H_{19}N_2O_2$ 367.1447; found, 367.1434.

3-Cyano-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ah)



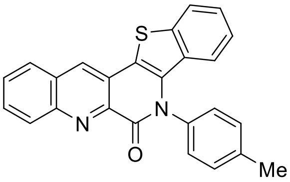
Method A; Yield: 26% as a brown solid; Mp: over 250 ºC (decomp.); ^1H NMR ($CDCl_3$): 9.18 (s, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.91 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.78 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44-7.50 (m, 2H), 7.20-7.25 (m, 2H), 7.03 (d, *J* = 2.0 Hz, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 160.0, 149.3, 142.5, 139.9, 139.4, 134.4, 131.8, 131.6, 131.4, 129.6, 129.3, 128.5, 128.1, 125.9, 125.4, 124.3, 121.9, 121.2, 118.4, 112.9, 21.5; IR (ATR): 2928, 2918, 2228, 1678, 1592, 1521, 1503, 1481, 1445, 1408, 1377, 1335, 1317, 1298, 1258, 1226, 1192; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{24}H_{16}N_3O$ 362.1293; found, 362.1305.

3-Nitro-5-(4-methylphenyl)dibenzo[*b*,*f*][1,7]naphthylidin-6(5*H*)-one (3ai)



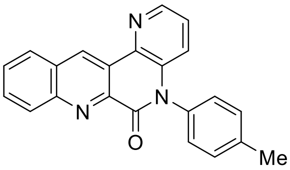
Method A; Yield: 7% as a yellow solid; Mp: over 250 ºC (decomp.); ^1H NMR ($CDCl_3$): 9.22 (s, 1H), 8.56 (d, *J* = 9.2 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.17 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.93 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.79 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.45-7.51 (m, 2H), 7.23-7.29 (m, 2H), 2.53 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): 160.1, 149.5, 148.2, 139.9, 139.7, 134.4, 132.1, 132.0, 131.6, 131.4, 129.7, 129.3, 128.4, 128.2, 125.1, 124.5, 123.4, 117.5, 112.8, 21.6; IR (ATR): 2926, 2854, 1718, 1678, 1618, 1588, 1526, 1491, 1448, 1382, 1342, 1317, 1287, 1263, 1221, 1149, 1131, 1118, 1093; HRMS (DART$^+$) *m/z* [M+H]$^+$ calcd. for $C_{23}H_{16}N_3O_3$ 382.1192; found, 382.1193.

5-(4-Methylpehnyl)benzothieno[2,3-*f*]benzo[*b*][1,7]naphthylidine-6(5*H*)-one (3aj)



Method A; Yield: 21% as a yellow solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 8.61 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.81 (ddd, *J* = 8.8, 7.2, 1.2 Hz, 1H), 7.71 (ddd, *J* = 7.6, 6.8, 0.8 Hz, 1H), 7.41-7.47 (m, 2H), 7.34-7.40 (m, 2H), 7.31 (dd, *J* = 8.8, 7.6 Hz, 1H), 7.03 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 6.13 (d, *J* = 8.4 Hz, 1H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 161.5, 148.4, 141.4, 139.7, 138.6, 136.4, 133.1, 131.6, 131.2, 130.9, 130.7, 130.5, 129.6, 129.3, 128.9, 127.5, 126.1, 124.7, 124.0, 123.4, 115.5, 21.7; IR (ATR): 2969, 2958, 2925, 2908, 1661, 1622, 1540, 1511, 1395, 1376, 1263; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{25}H_{17}N_2OS$ 393.1062; found, 393.1070.

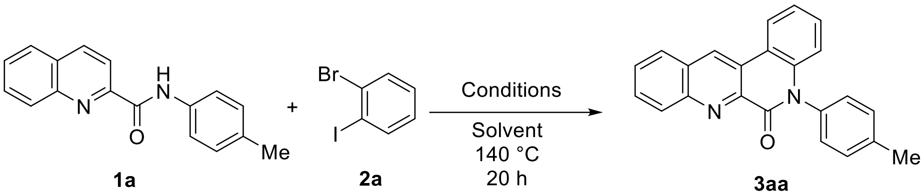
1-(4-Methylphenyl)quino[2,3-*c*][1,5]naphthylidin-2(1*H*)-one (3ak)



Method A; Yield: 31% as a brown solid; Mp: over 250 ºC (decomp.); ^{1}H NMR ($CDCl_3$): 9.78 (s, 1H), 8.60 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.89 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.41-7.48 (m, 2H), 7.29 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.23-7.28 (m, 2H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): 160.1, 149.6, 144.4, 143.1, 139.4, 136.3, 135.5, 134.5, 133.2, 131.34, 131.29, 129.7, 129.1, 128.7, 128.6, 128.0, 124.2, 124.0, 106.3, 21.5; IR (ATR): 2922, 2854, 1680, 1606, 1511, 1464, 1438, 1417, 1382, 1355, 1318, 1262, 1213, 1197, 1145, 1128, 1109; HRMS (DART^{+}) *m/z* $[M+H]^{+}$ calcd. for $C_{22}H_{16}N_3O$ 338.1293; found, 338.1303.

S4: Additional data of optimization of the C–H/N–H coupling reaction:

Table S1.



Entry	Catalyst (mol%)	Ligand (mol%)	Base (eq.)	**2a** (eq.)	Solvent (M)	Yield (%)[a]
S1	$Pd(OAc)_2$ (10)	PPh_3 (40)	Cs_2CO_3 (3.0)	1.0	DMF (0.1)	19 (52)
S2	$PdCl_2(PPh_3)_2$ (10)	none	Cs_2CO_3 (3.0)	1.0	DMF (0.1)	10 (85)
S3	$Pd(TFA)_2$ (10)	PPh_3 (40)	Cs_2CO_3 (3.0)	1.0	DMF (0.1)	39 (32)
S4	$Pd(OAc)_2$ (10)	PPh_3 (40)	K_2CO_3 (3.0)	1.0	DMF (0.1)	6 (72)
S5	$Pd(OAc)_2$ (10)	PPh_3 (40)	*t*-BuOK (3.0)	1.0	DMF (0.1)	N. R.
S6	$Pd(OAc)_2$ (10)	PPh_3 (40)	*t*-BuONa (3.0)	1.0	DMF (0.1)	9 (63)
S7	$Pd(OAc)_2$ (10)	PPh_3 (40)	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	46 (28)
S8	$Pd(OAc)_2$ (10)	PhDave-Phos (40)	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	9 (55)
S9	$Pd(OAc)_2$ (10)	P(*p*-tolyl)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	15 (18)
S10	$Pd(OAc)_2$ (10)	PPh_3 (20)	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	7 (57)
S11	$Pd(OAc)_2$ (10)	None	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	N. R.
S12	$Pd(TFA)_2$ (10)	PPh_3 (40)	Cs_2CO_3 (3.0)	1.0	DMF (1.0)	39 (32)
S13	$Pd(OAc)_2$ (10)	PPh_3 (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	34 (58)

Entry	Catalyst (mol%)	Ligand (mol%)	Base (eq.)	**2a** (eq.)	Solvent (M)	Yield (%)[a]
S14	$Pd(OAc)_2$ (10)	PPh_3 (100)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	39 (30)
S15	$Pd(OAc)_2$ (10)	P(*p*-tolyl)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	35 (30)
S16	$Pd(OAc)_2$ (10)	P(*p*-MeOC$_6$H$_4$)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	44 (33)
S17	$Pd(OAc)_2$ (10)	P(4-FC$_6$H$_4$)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	21 (55)
S18	$Pd(OAc)_2$ (10)	P(*o*-tolyl)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	N. R.
S19	$Pd(OAc)_2$ (10)	PhDave-Phos (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	15 (58)
S20	$Pd(OAc)_2$ (10)	Xantphos (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	16 (59)
S21	$Pd(OAc)_2$ (10)	P(2-fulyl)$_3$ (40)	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	9 (62)
S22	Herrmann's catalyst (10)	none	Cs_2CO_3 (3.0)	1.0	*o*-Xylene (1.0)	N. R.
S23[b)]	$Pd(OAc)_2$ (10)	P(*p*-MeOC$_6$H$_4$)$_3$ (40)	Cs_2CO_3 (3.0)	1.0 + 1.0	*o*-Xylene (1.0)	53 (15)
S24	$Pd(OAc)_2$ (10)	P(*p*-MeOC$_6$H$_4$)$_3$ (80)	Cs_2CO_3 (3.0)	2.0	*o*-Xylene (1.0)	45 (34)
S25	$Pd(OAc)_2$ (20)	P(*p*-MeOC$_6$H$_4$)$_3$ (80)	Cs_2CO_3 (3.0)	2.0	*o*-Xylene (1.0)	81[c)]

a) Yields in parentheses were for the recovered **1a**. The yields were determined by ^{1}H NMR spectrum used 1,1,2,2-tetrachloroethane as an internal standard.

b) After stirring for 20 hours at 140 ºC, an additional one equivalent of **2a** was added to the reaction system and the reaction was carried out for further 20 hours at 140 ºC.

c) Isolated yield.

S5: 2D NOESY spectra:

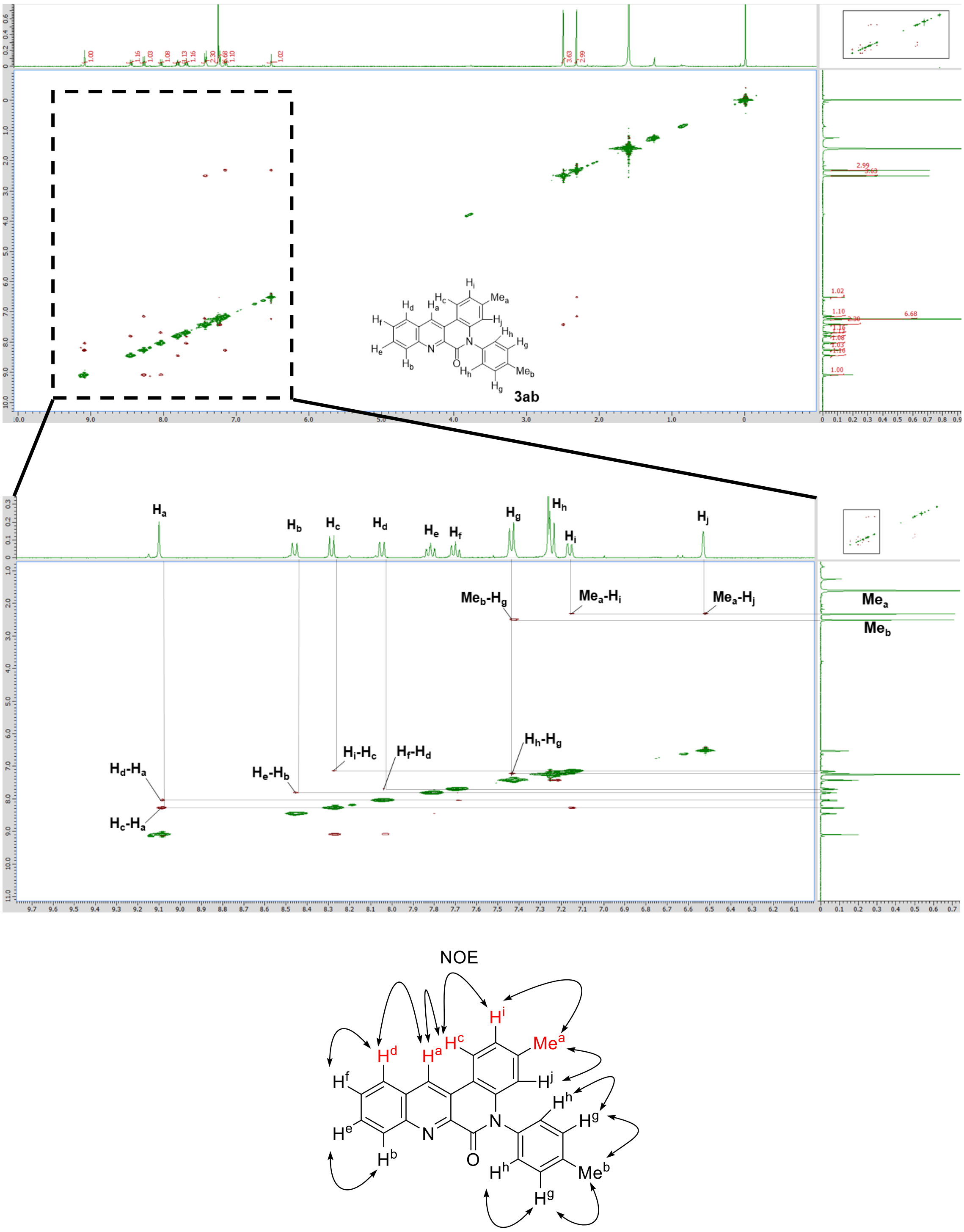


Figure S1. NOESY spectrum of **3ab**.

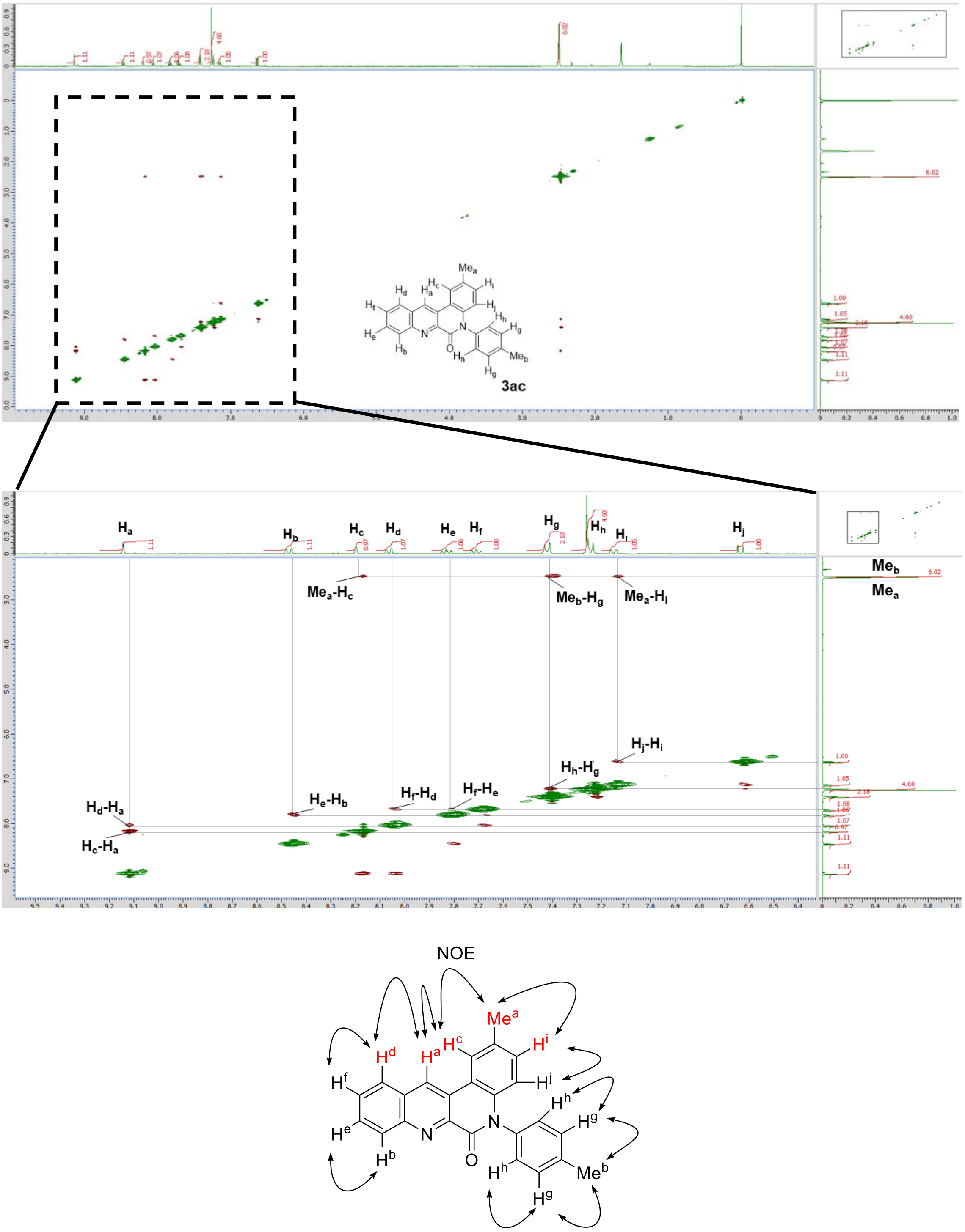


Figure S2. NOESY spectrum of **3ac**.

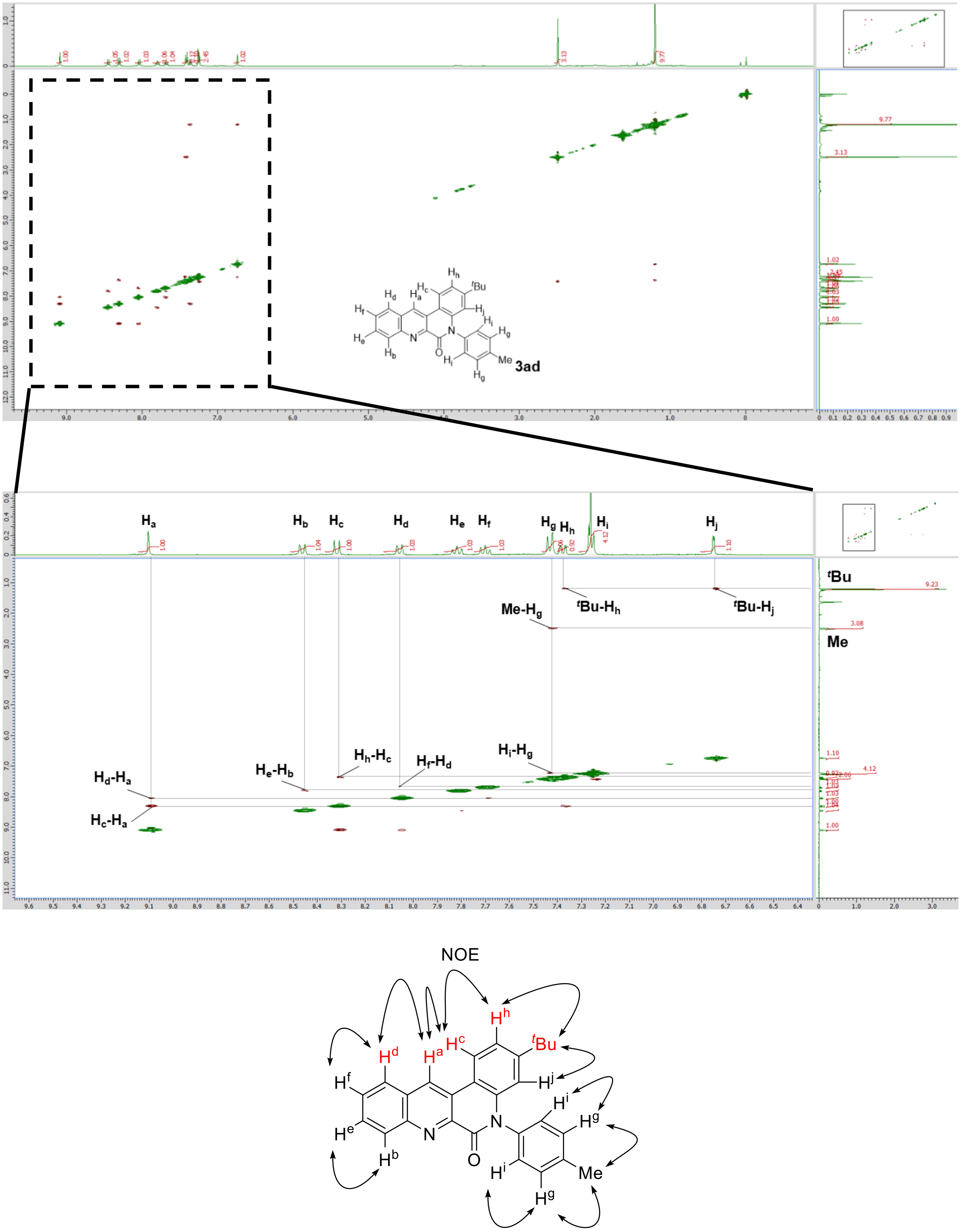


Figure S3. NOESY spectrum of **3ad**.

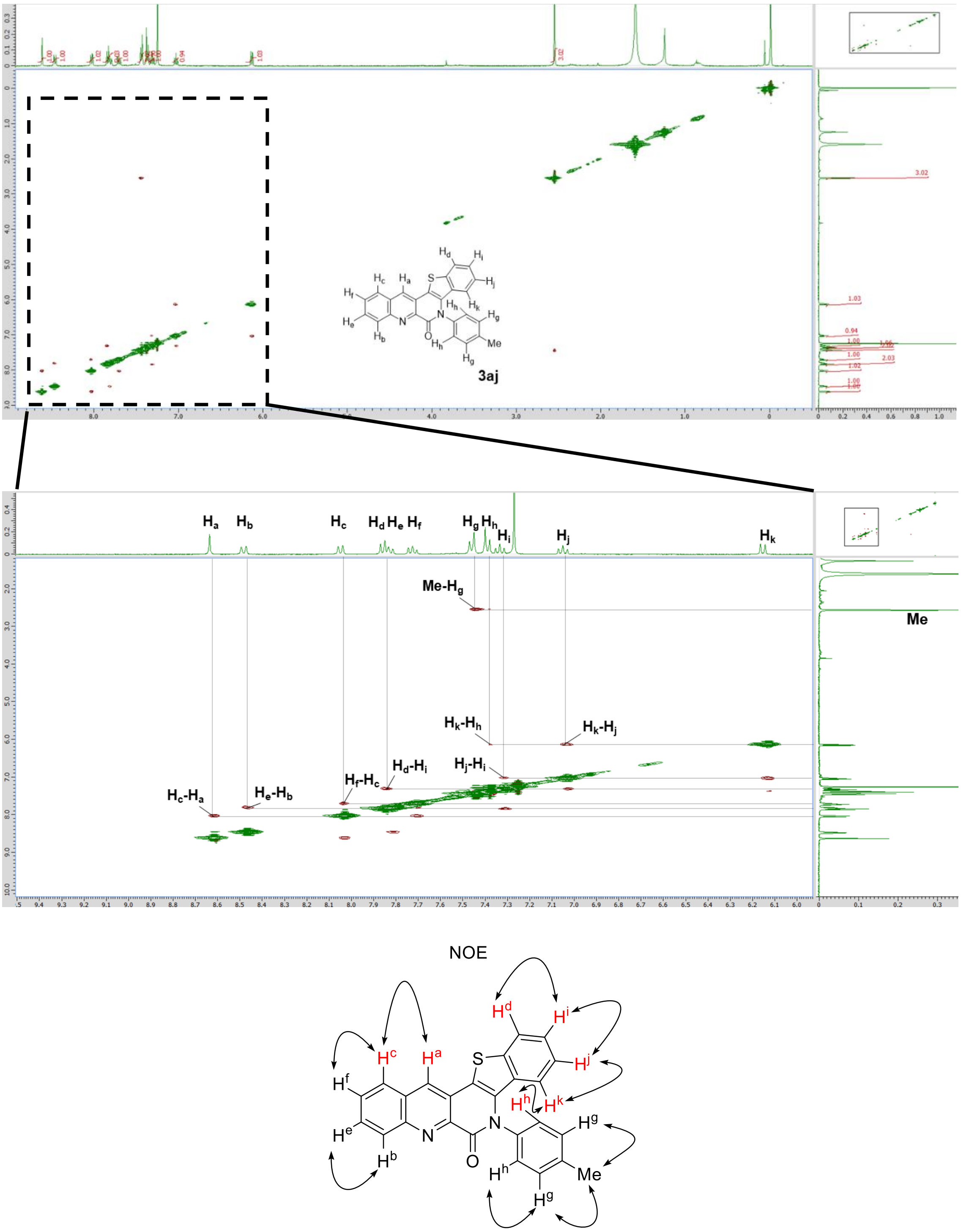


Figure S4. NOESY spectrum of **3aj**.

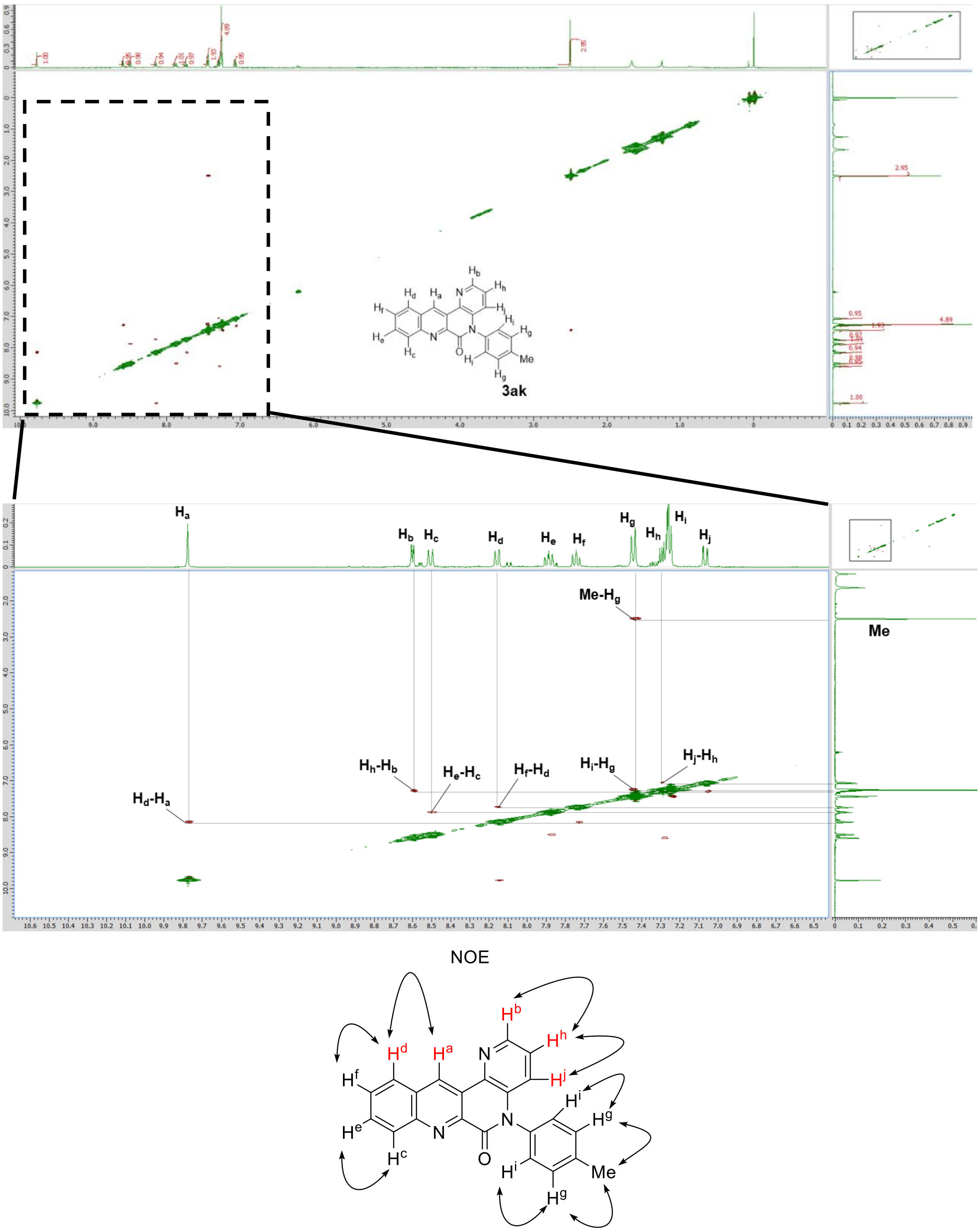
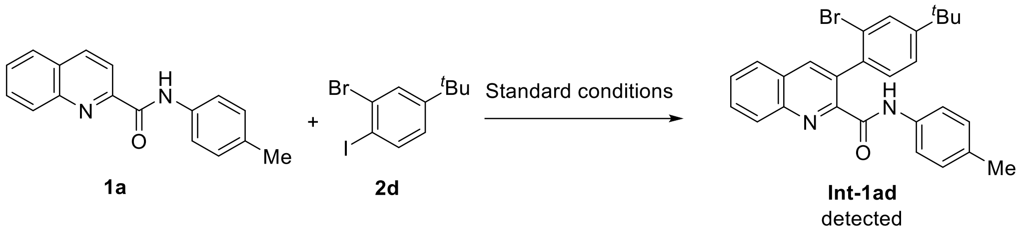


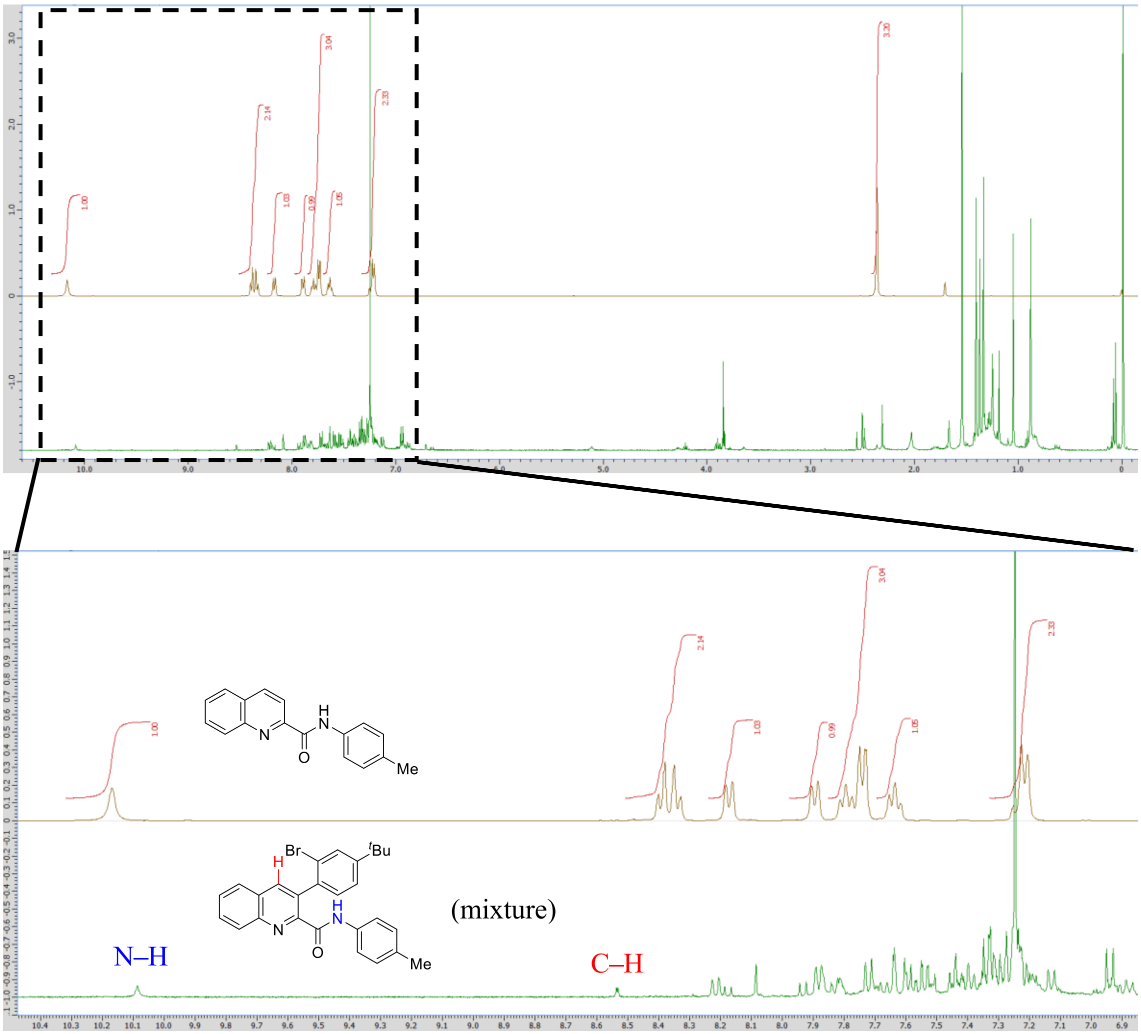
Figure S5. NOESY spectrum of **3ak**.

S6: Confirmation of the structure of Int-1ad:



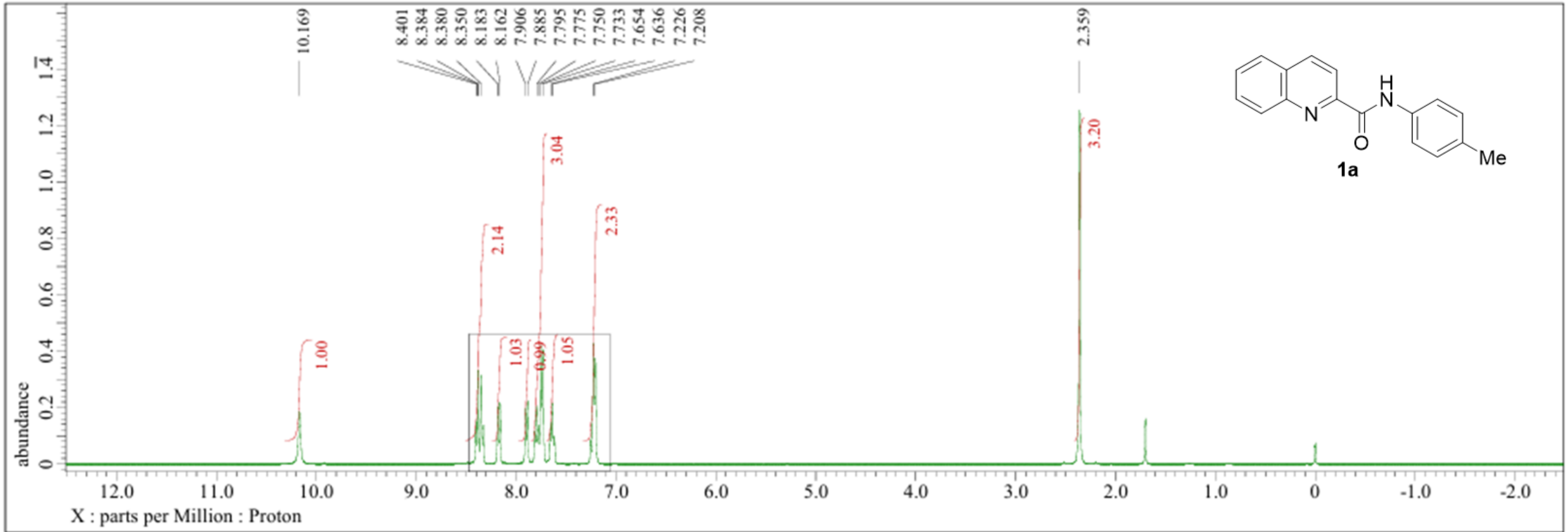
Int-1ad

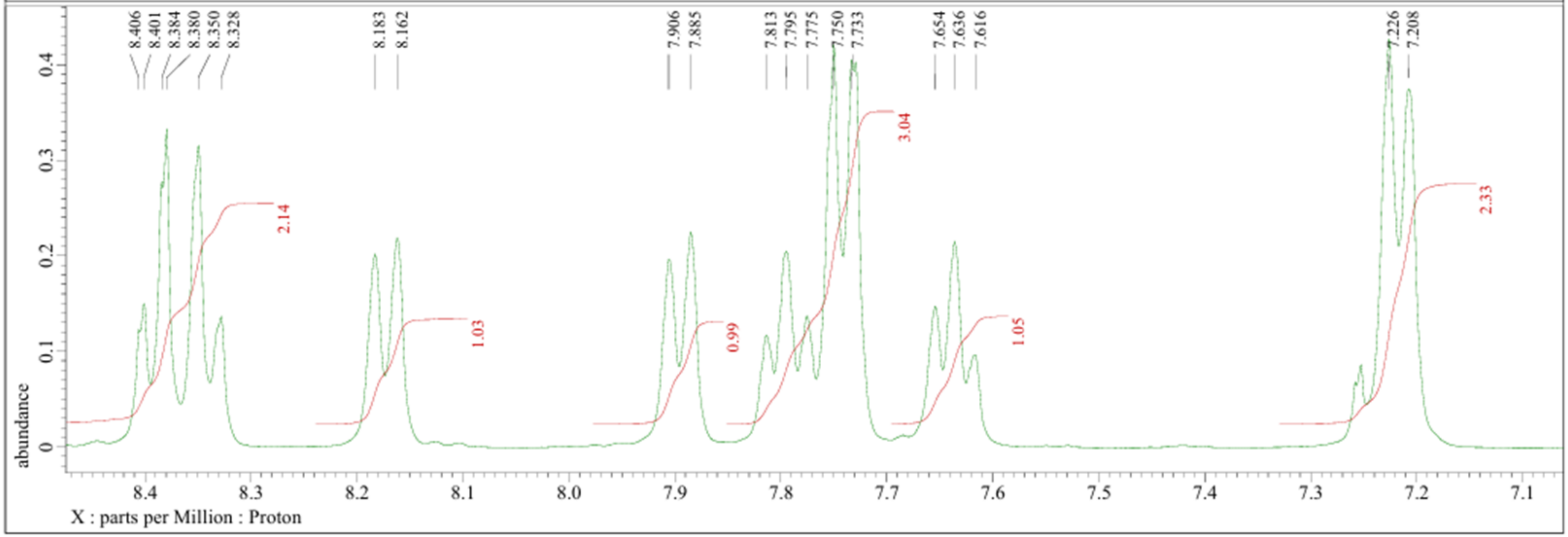
HRMS (DART$^+$) *m/z* [M+Na]$^+$ calcd. for $C_{27}H_{25}{}^{79}BrN_2ONa$ calcd. for 495.1024; found, 495.1043.



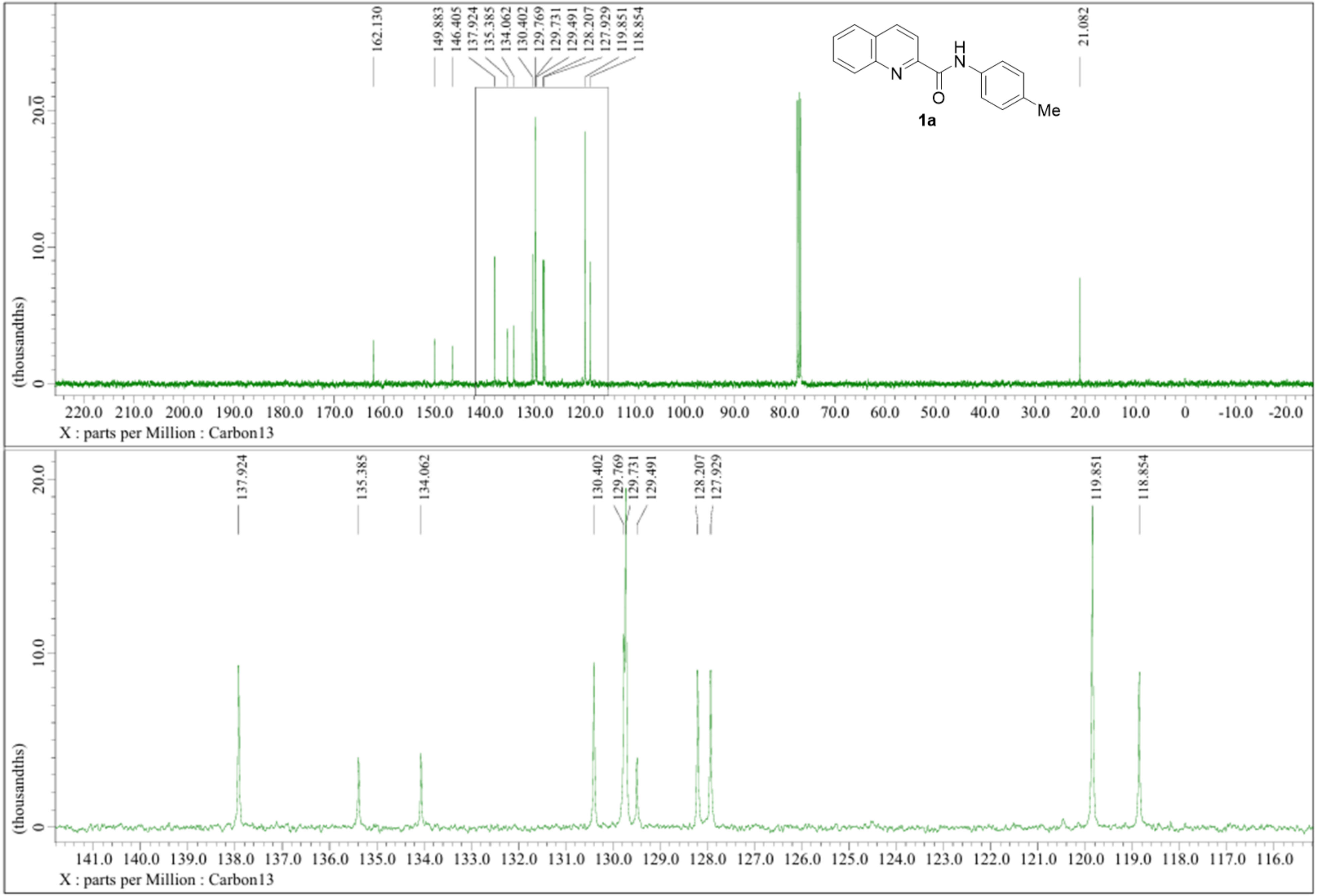
S7: NMR chart:

^{1}H NMR (400 MHz, $CDCl_3$)

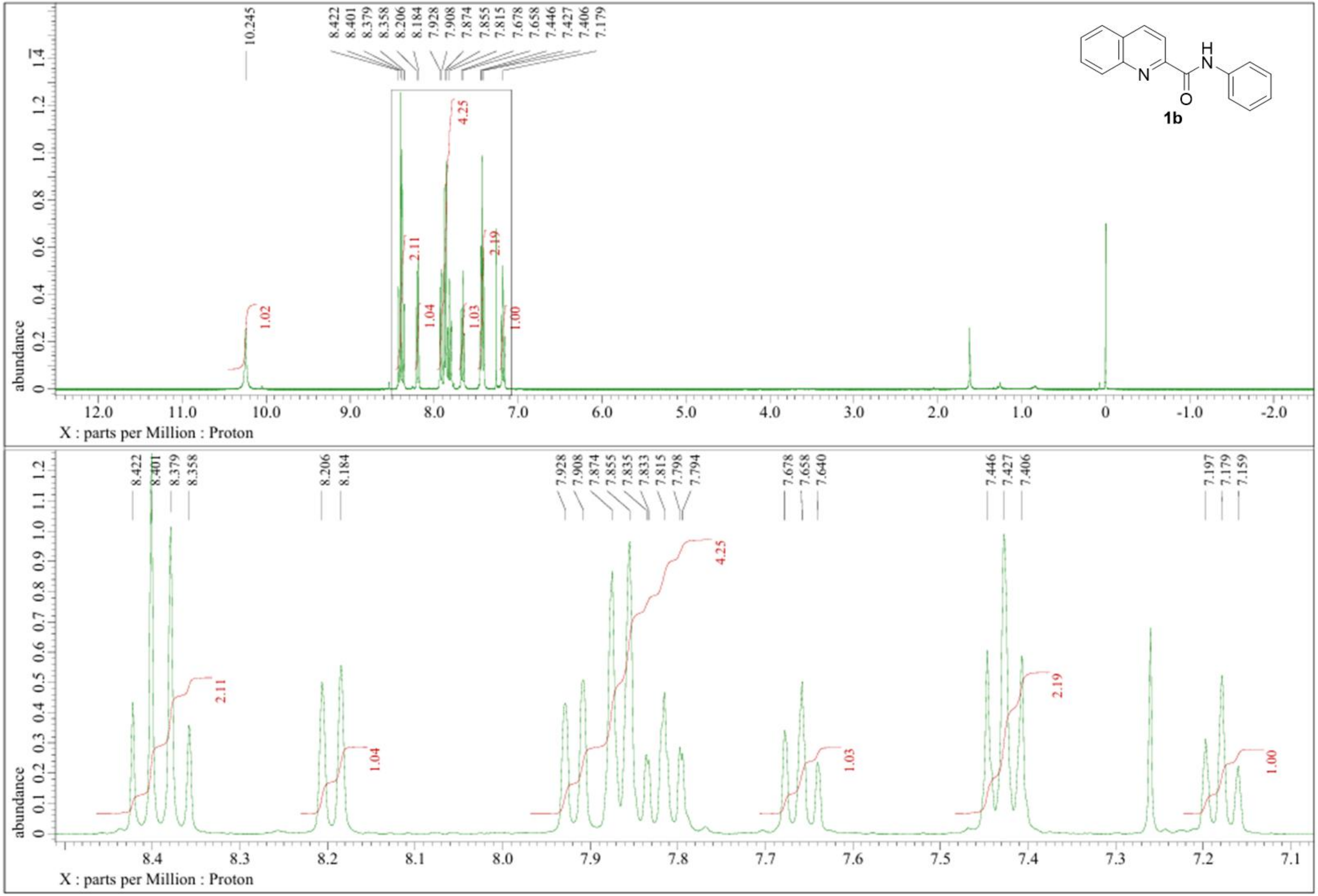




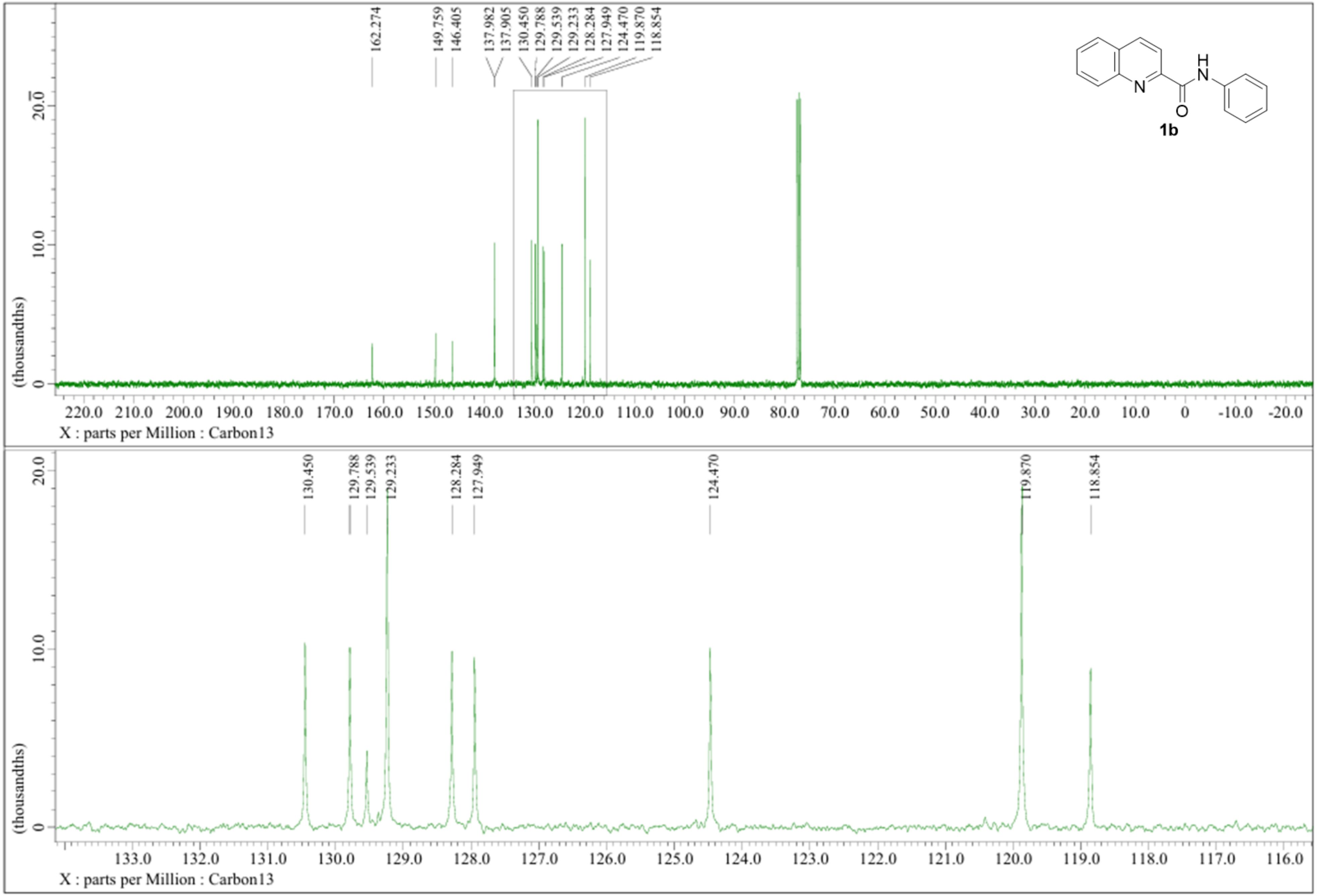
$^{13}C\{^1H\}$ **NMR (100 MHz, $CDCl_3$)**



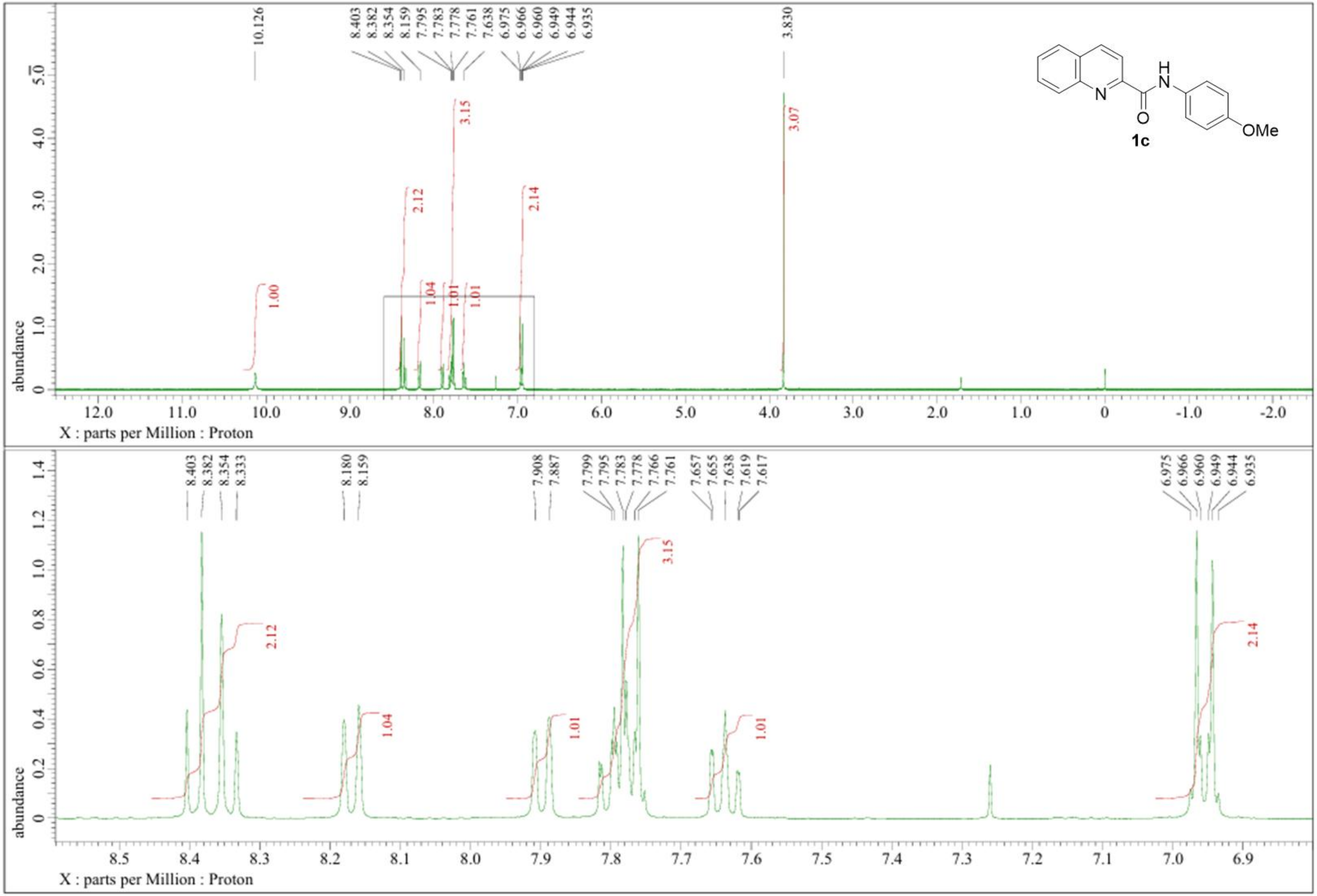
[1]H NMR (400 MHz, $CDCl_3$)



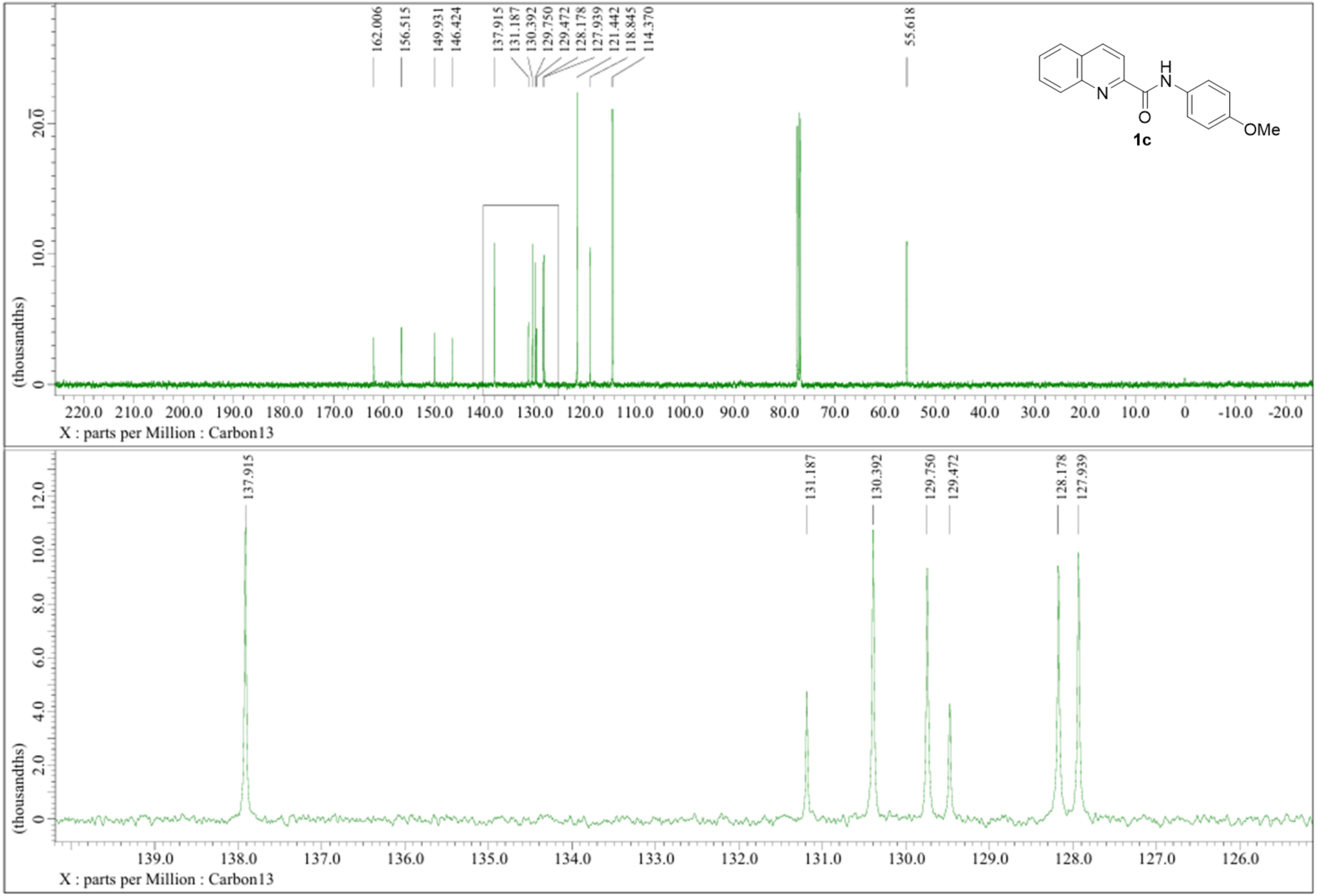
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



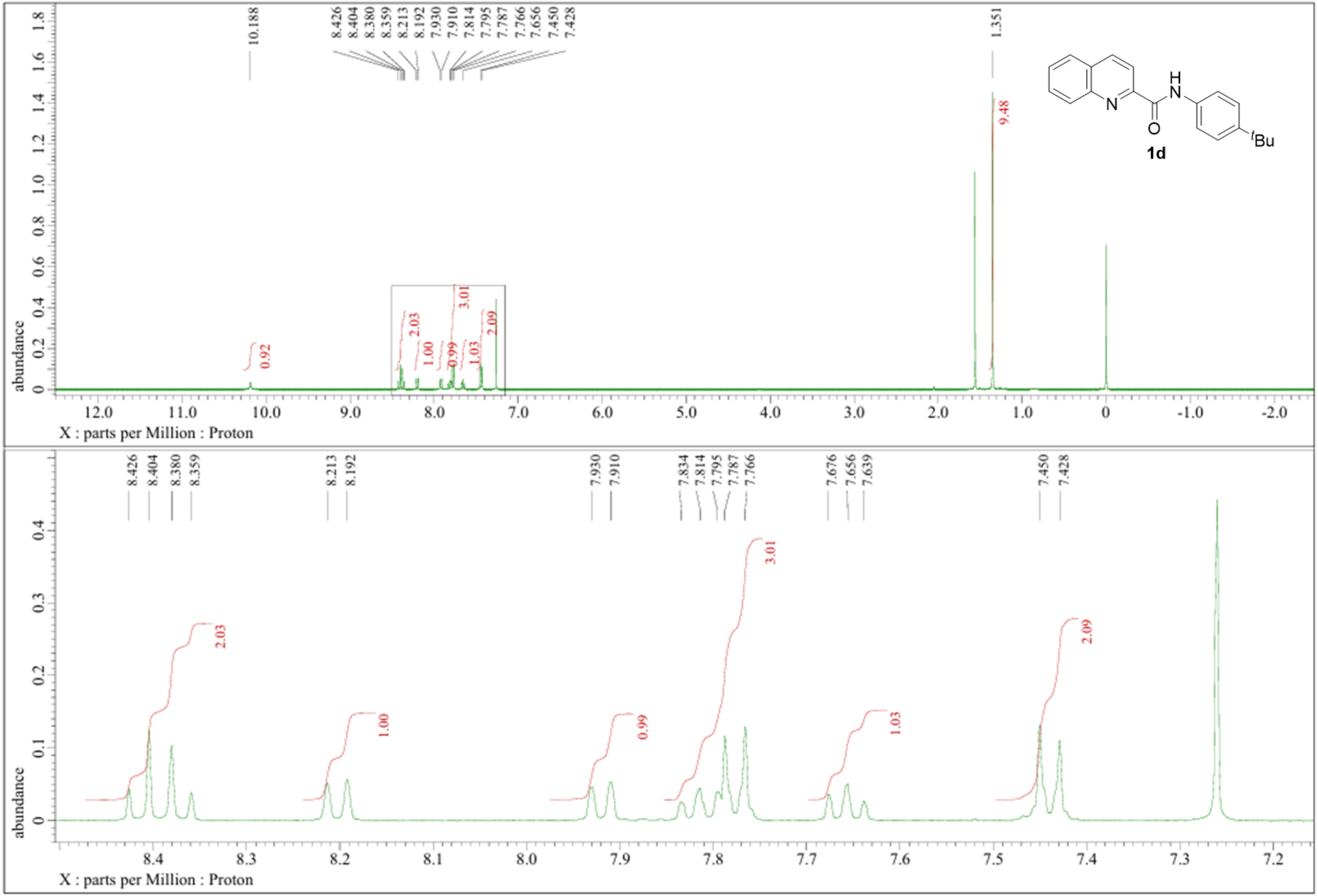
^{1}H NMR (400 MHz, $CDCl_3$)



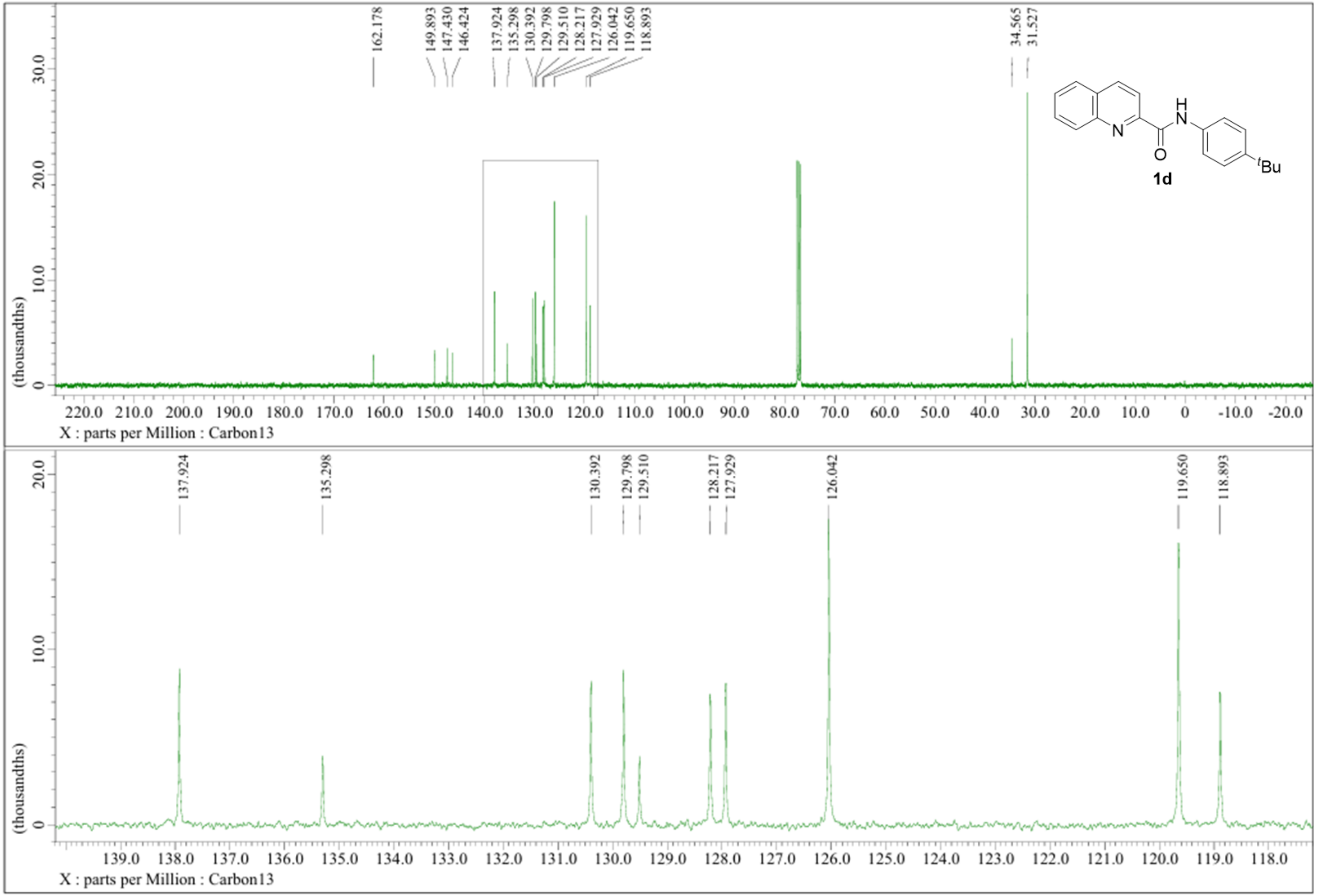
$^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl$_3$)



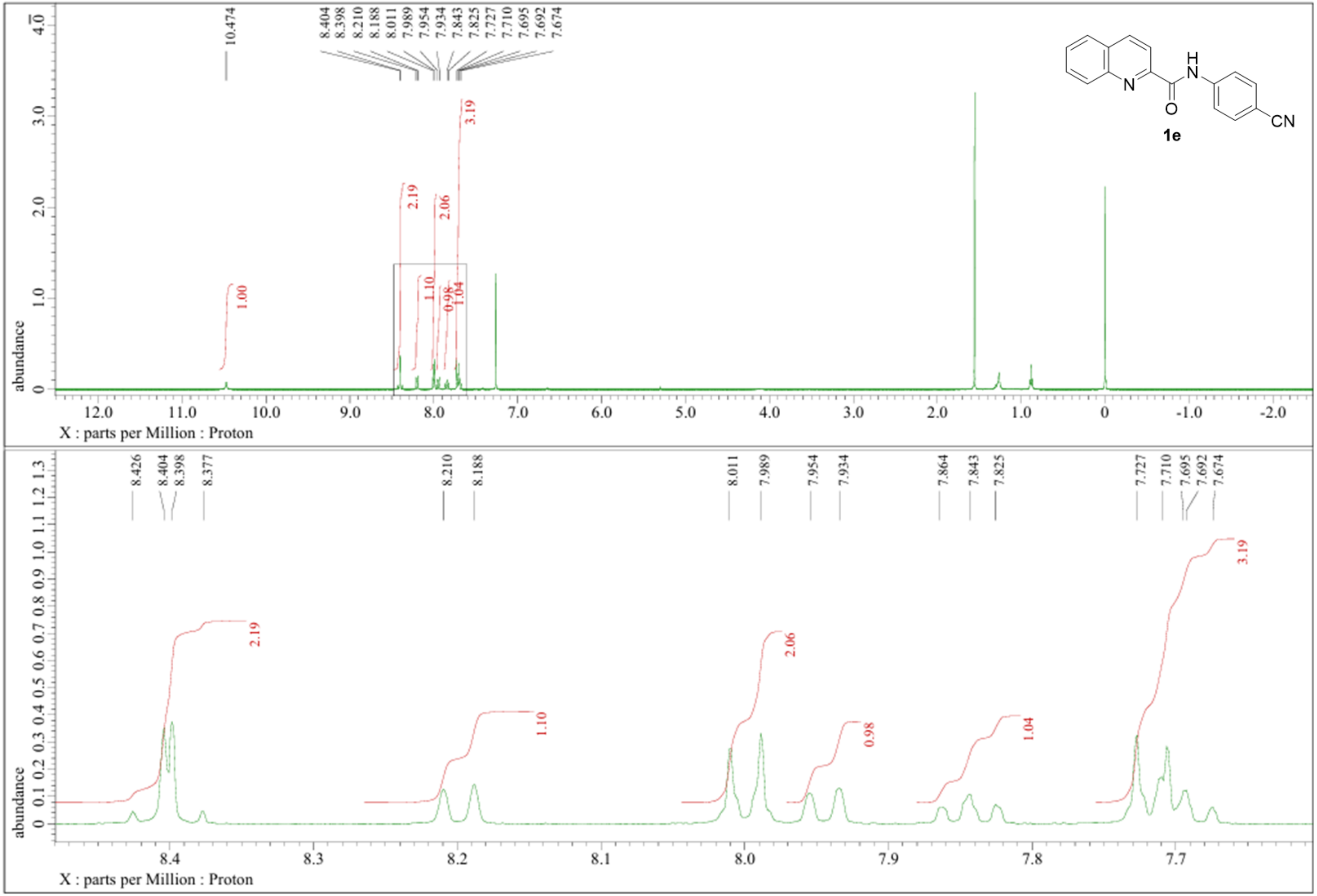
^{1}H NMR (400 MHz, $CDCl_3$)



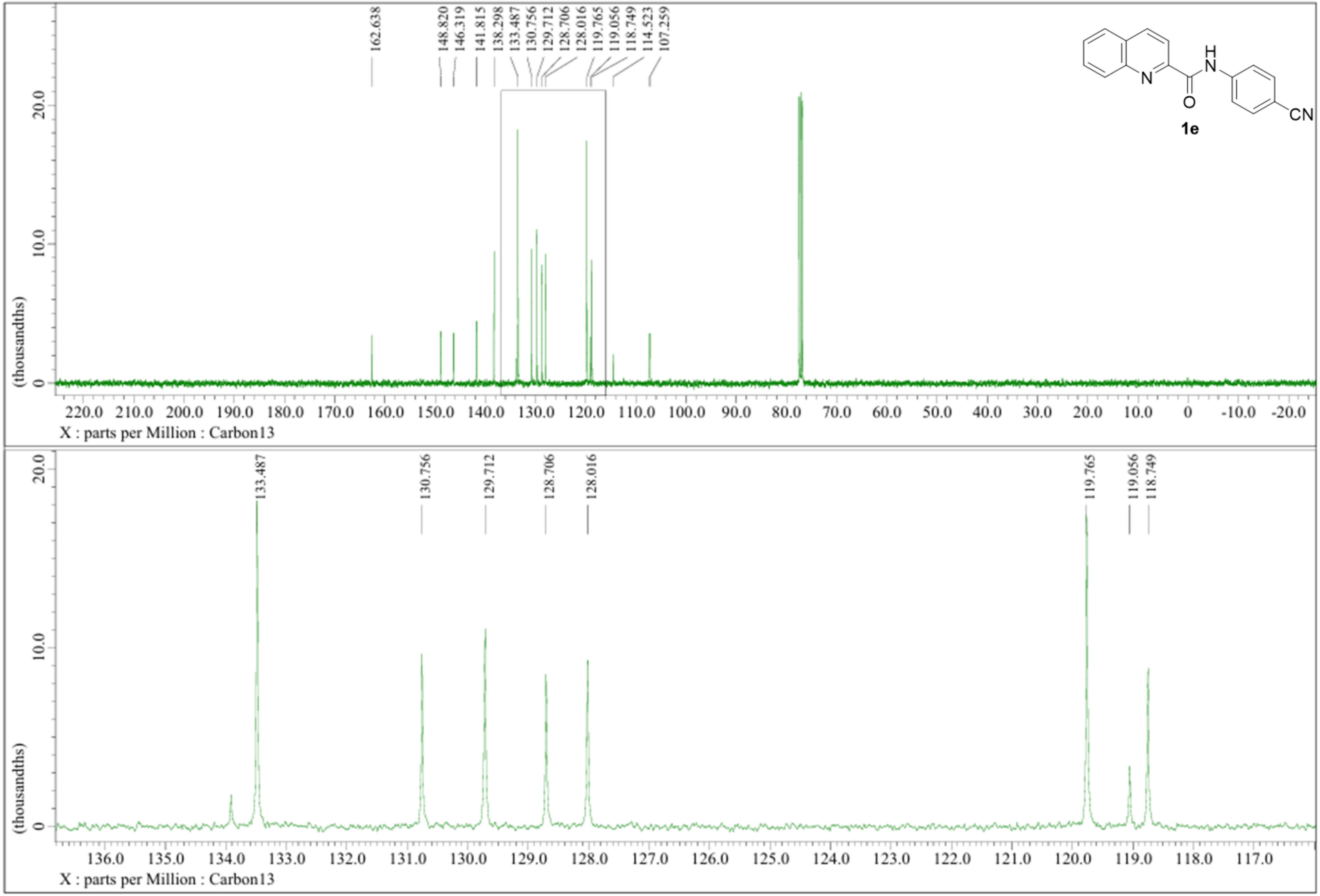
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



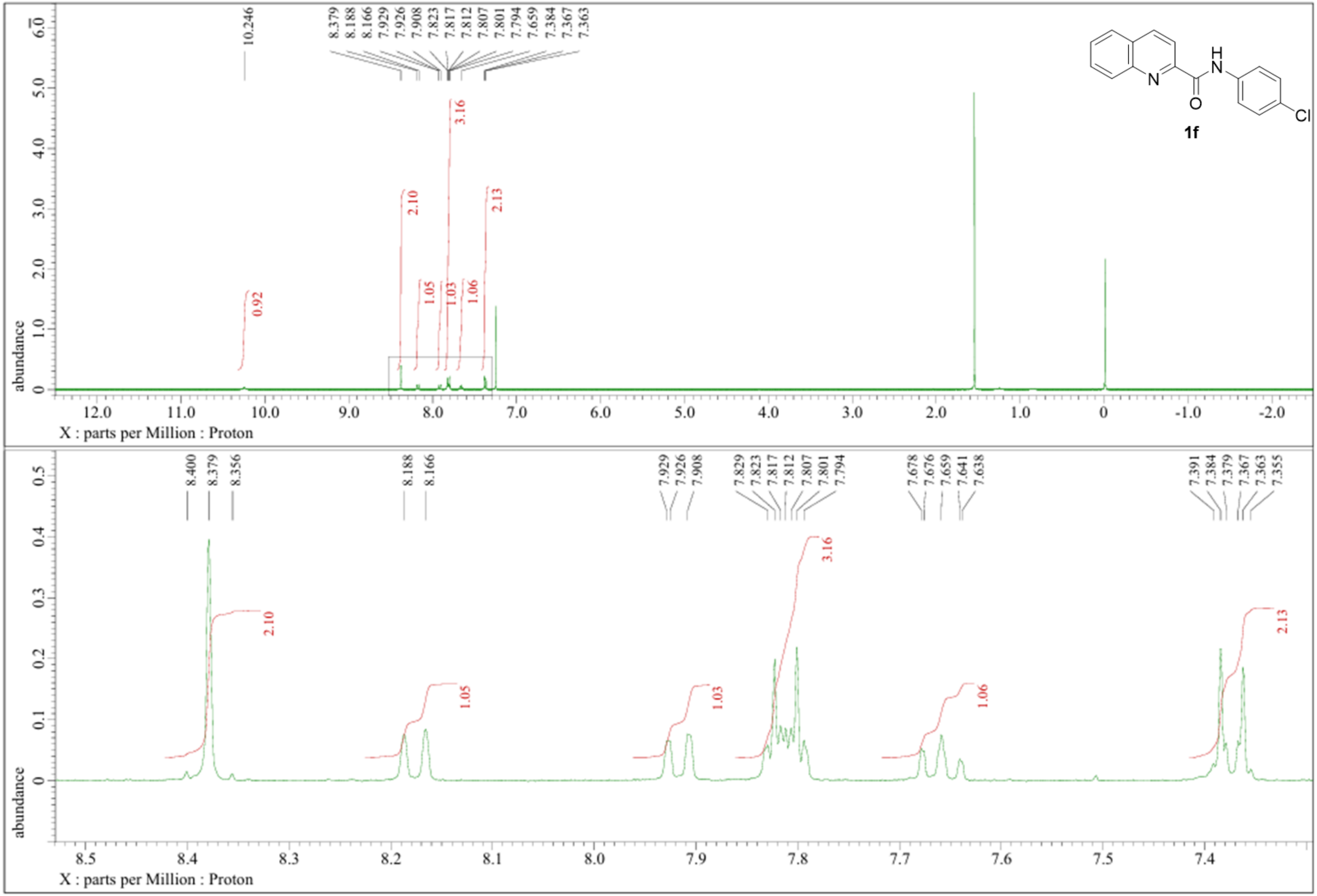
^{1}H NMR (400 MHz, $CDCl_3$)



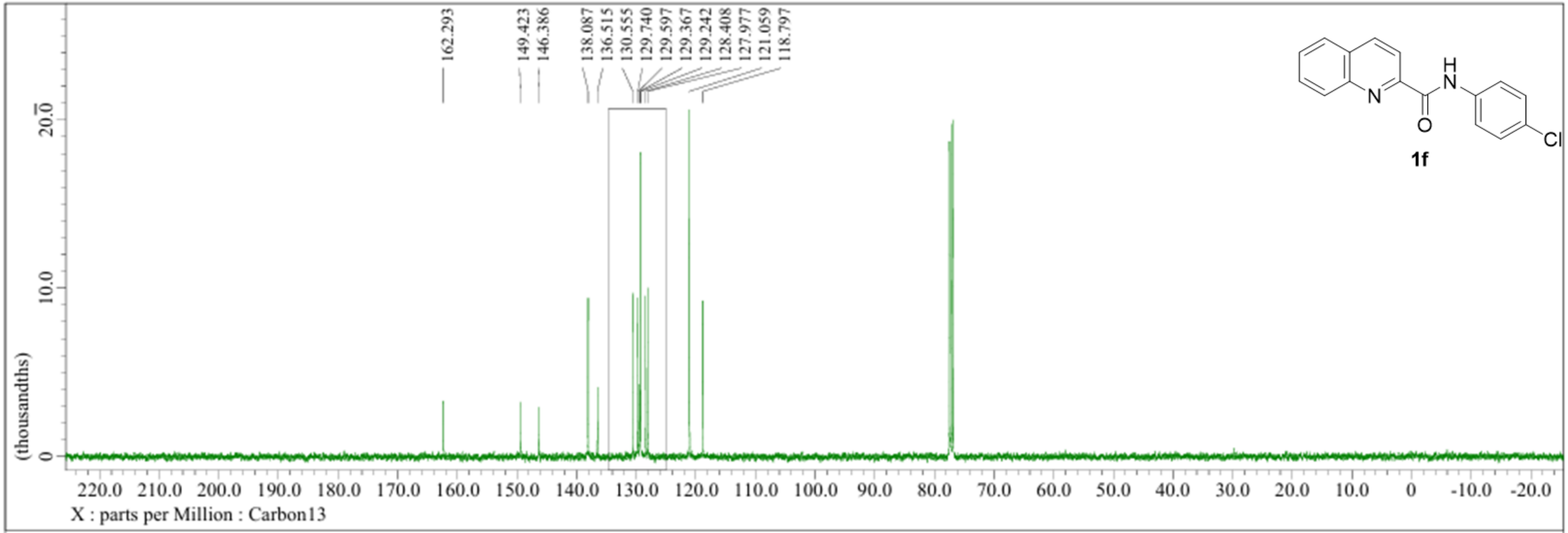
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

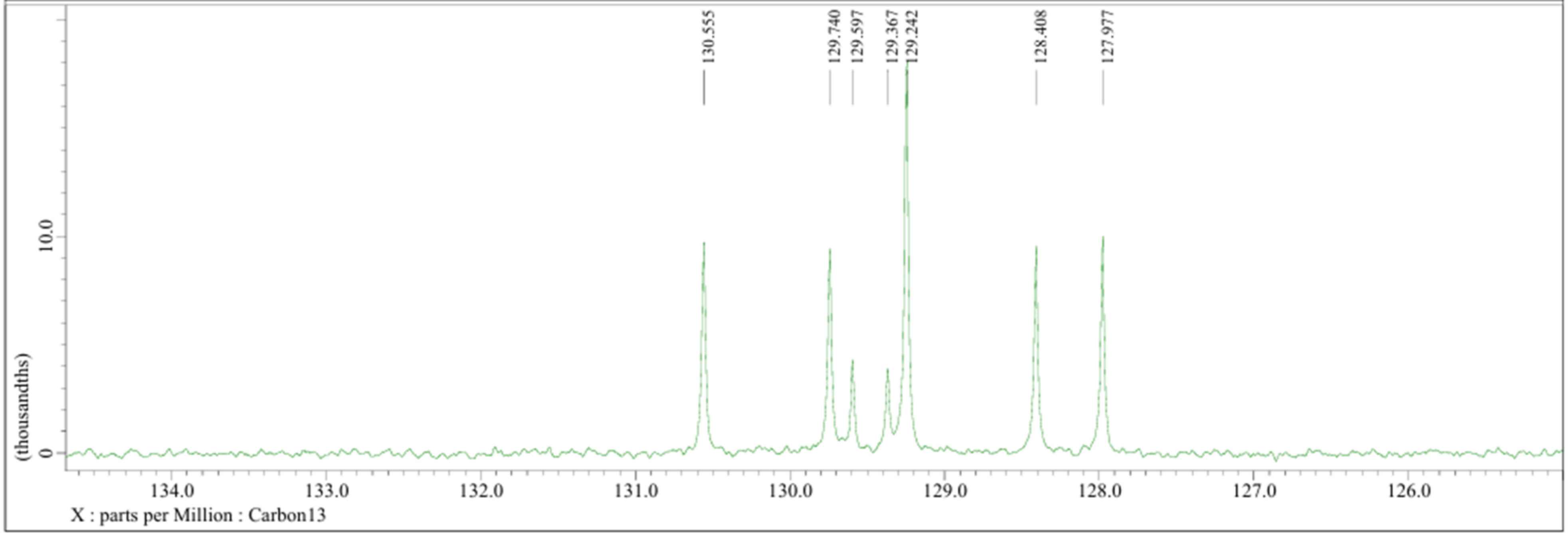


[1]H NMR (400 MHz, $CDCl_3$)

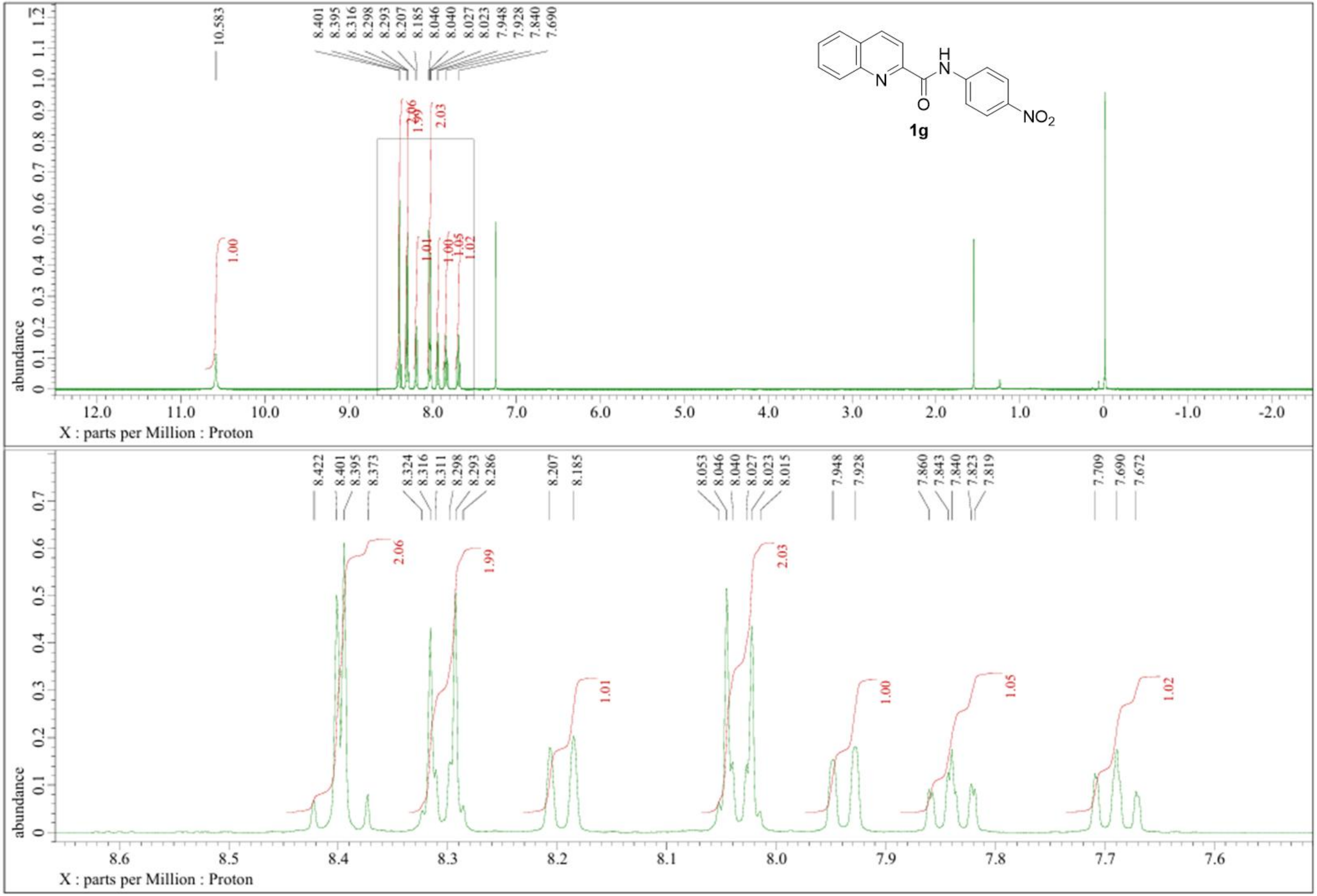


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

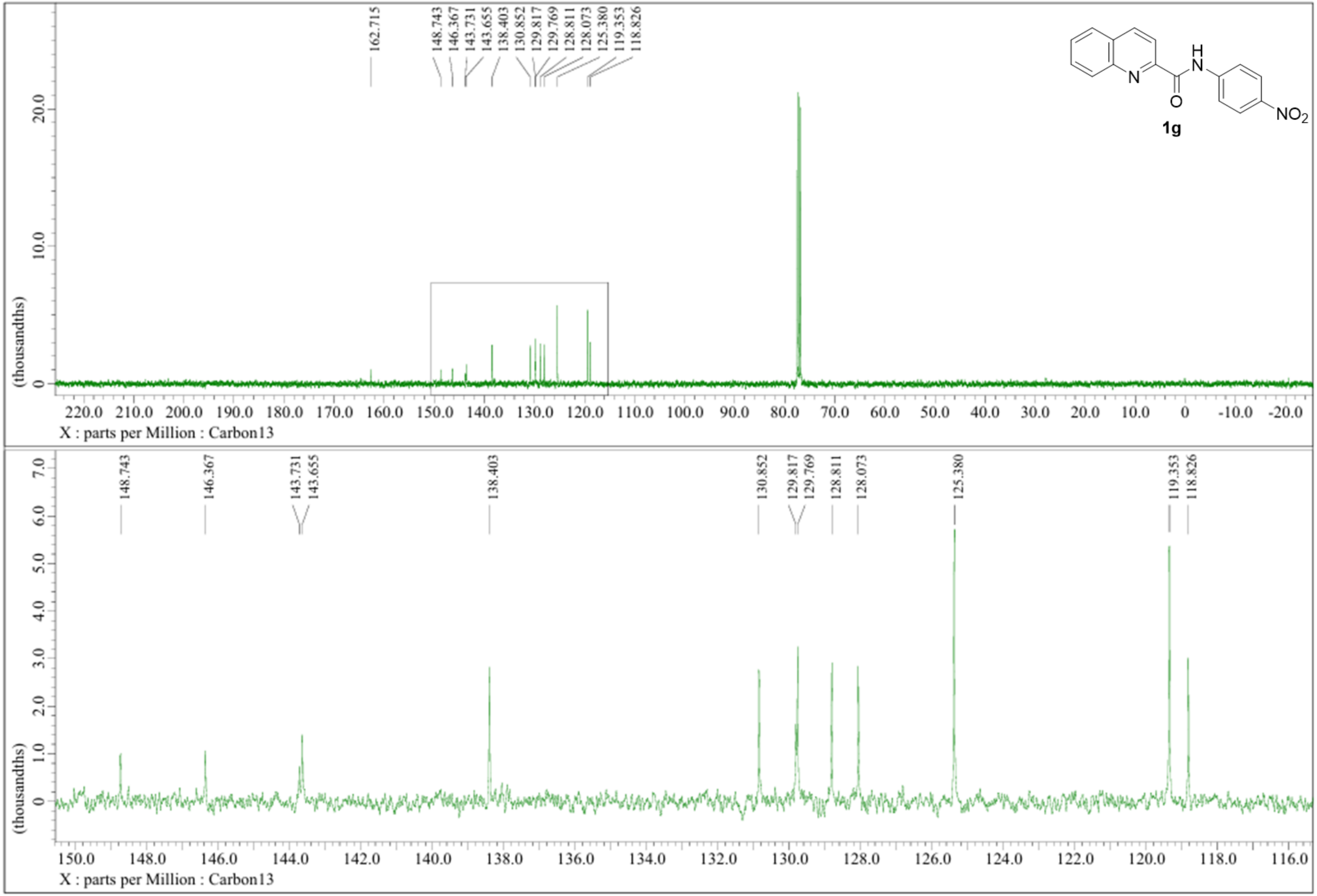




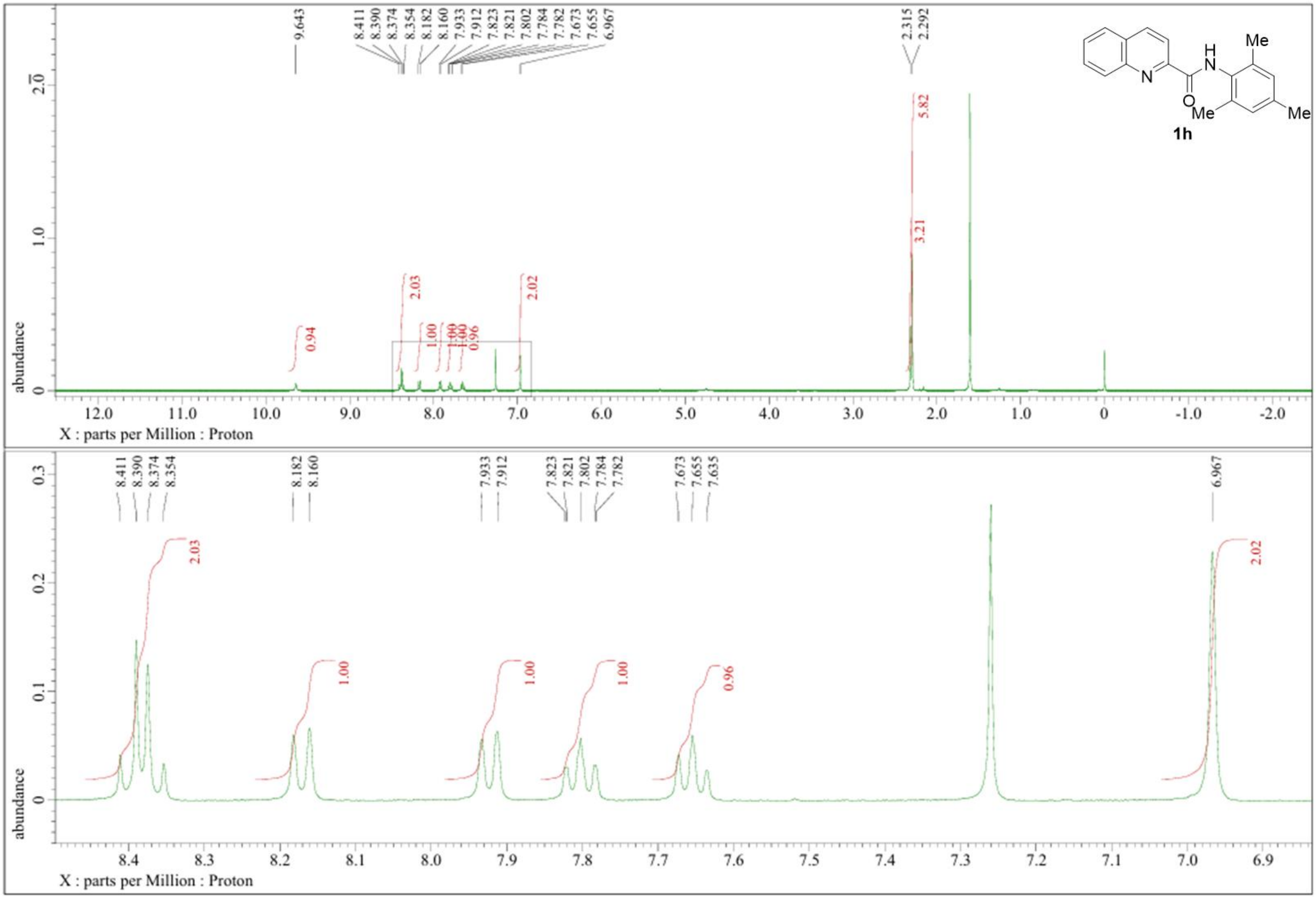
^{1}H NMR (400 MHz, $CDCl_3$)



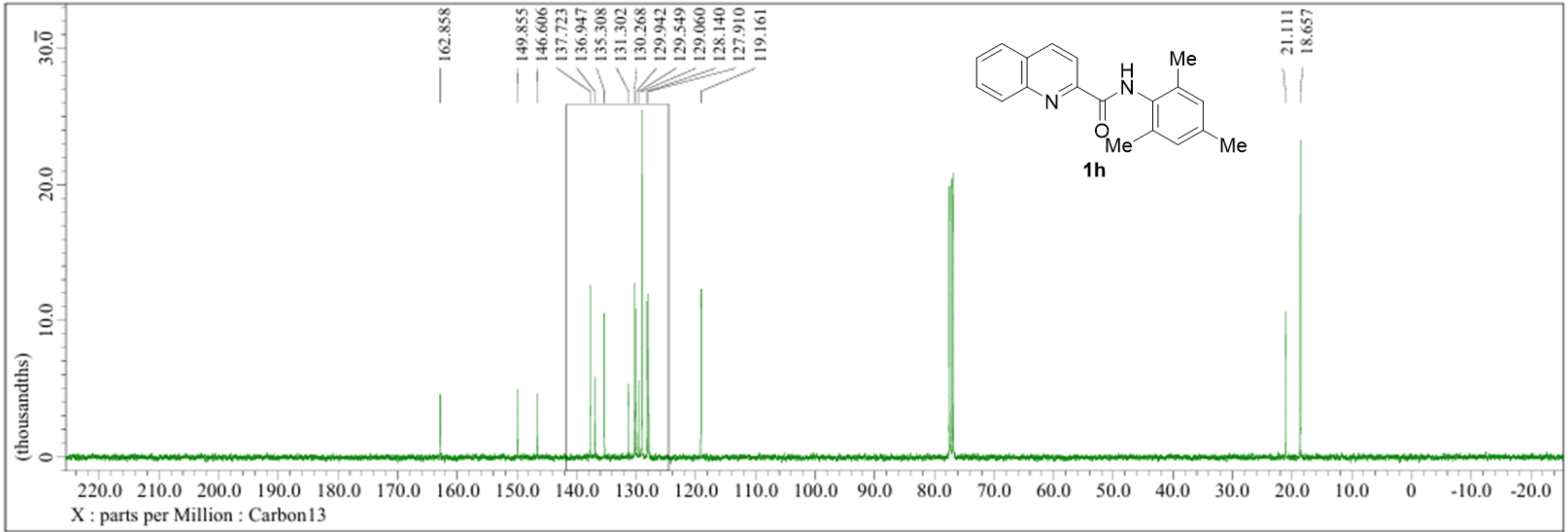
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

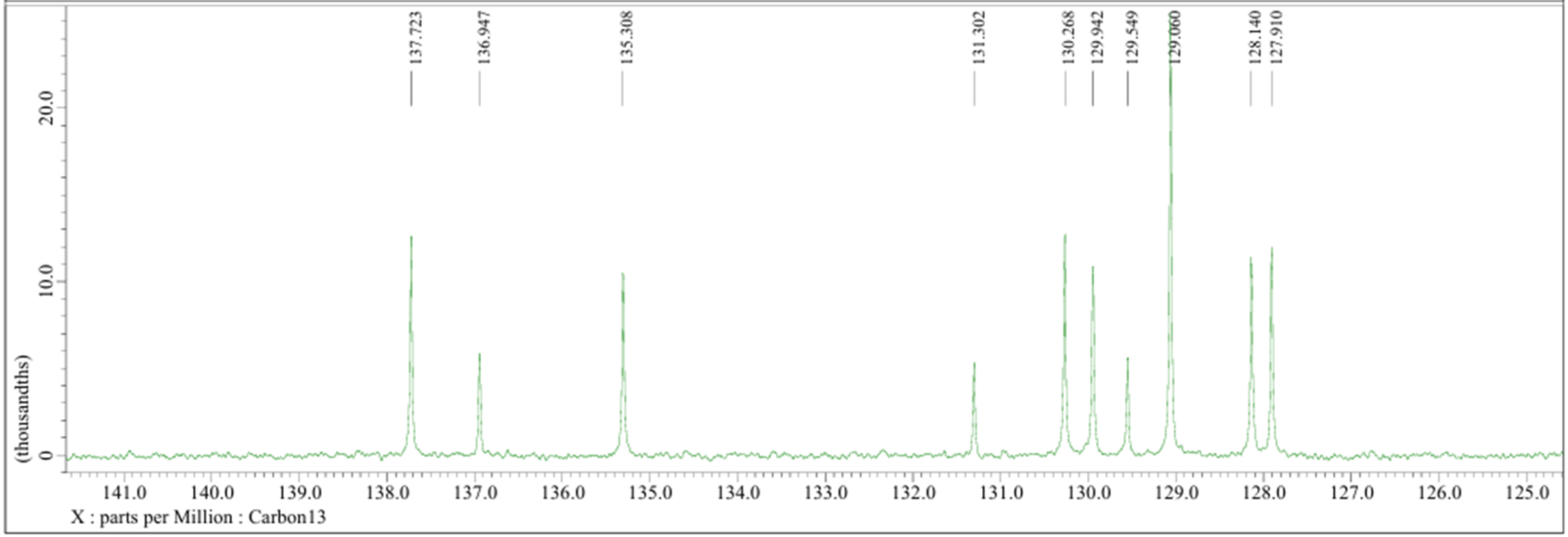


[1]H NMR (400 MHz, $CDCl_3$)

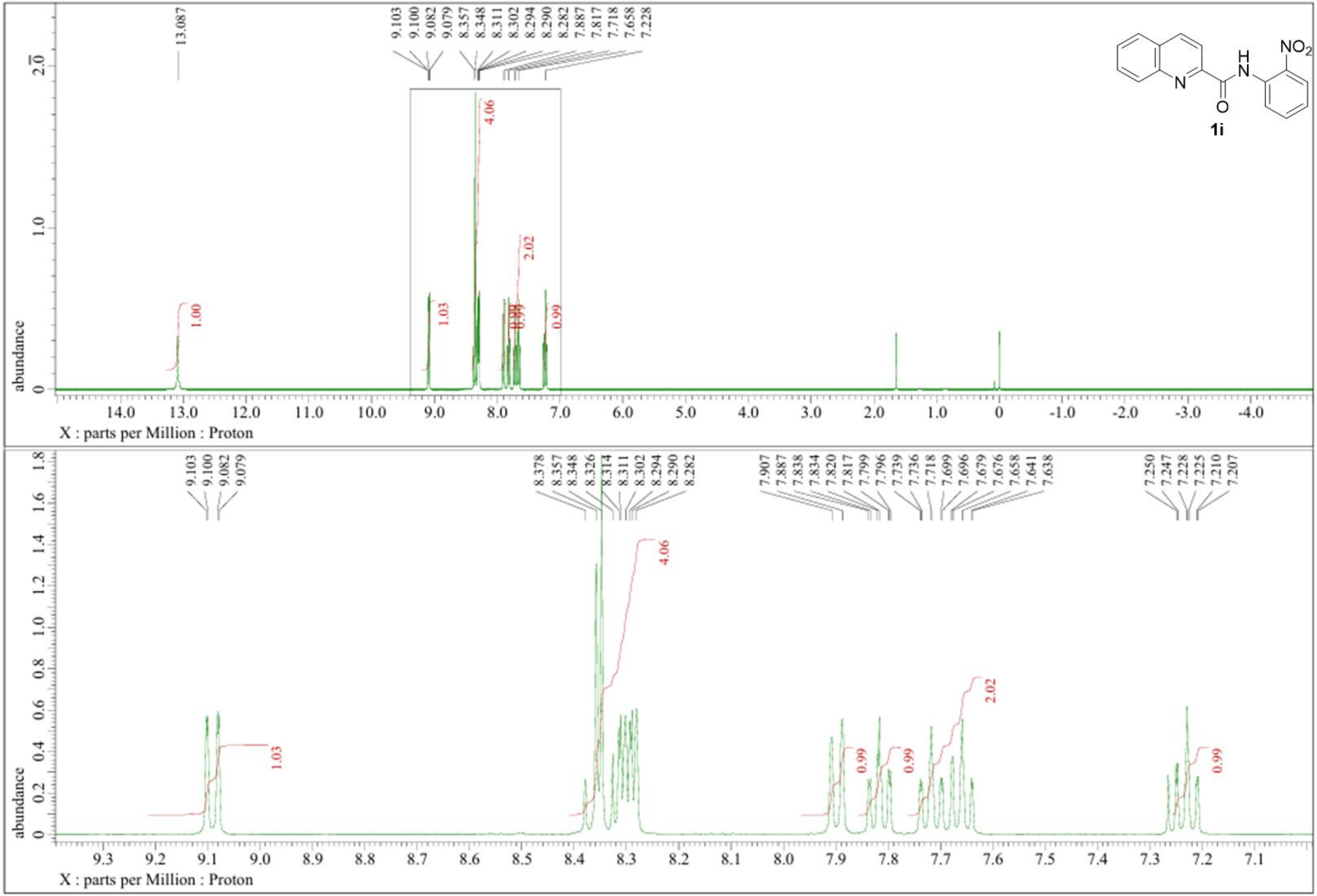


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

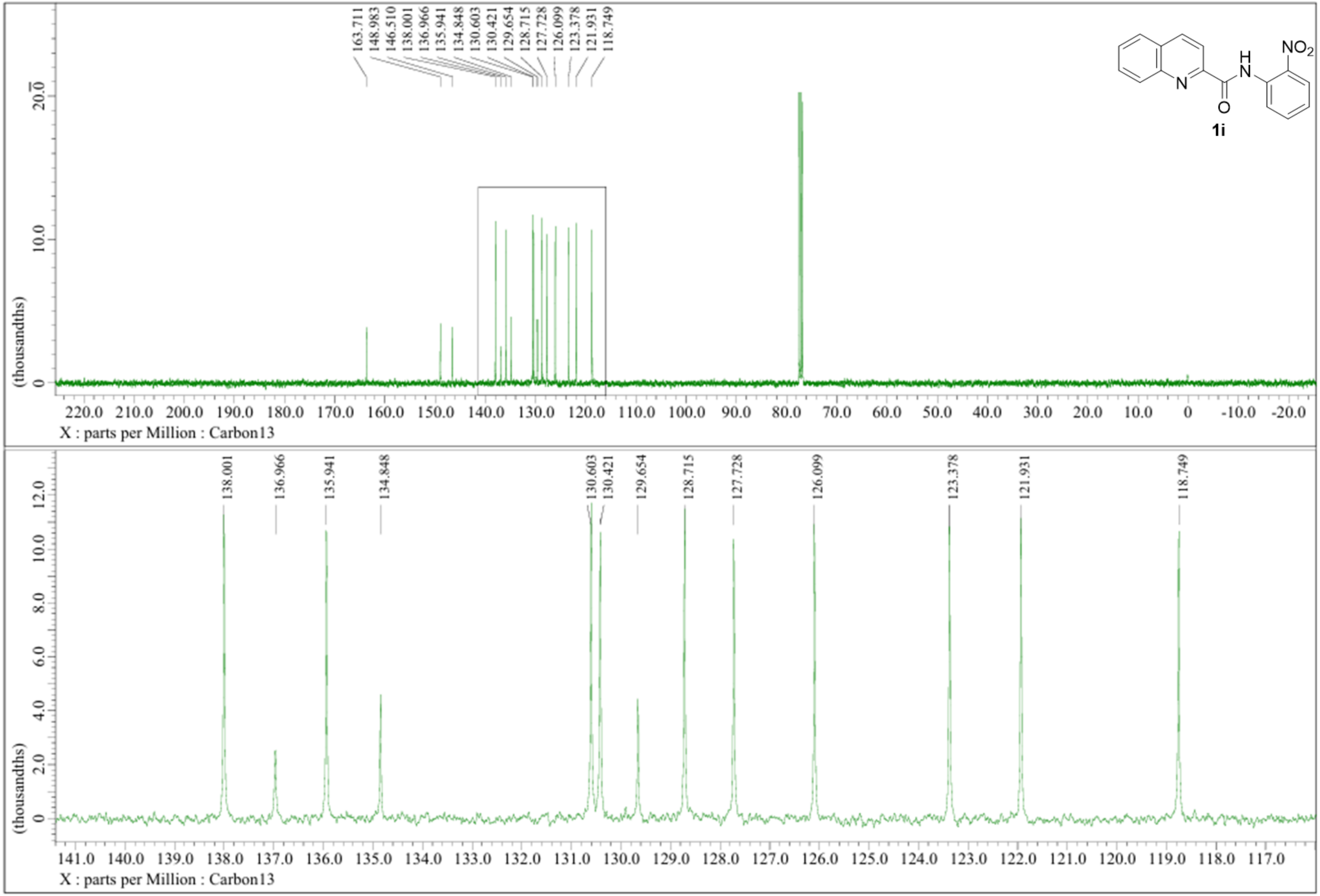




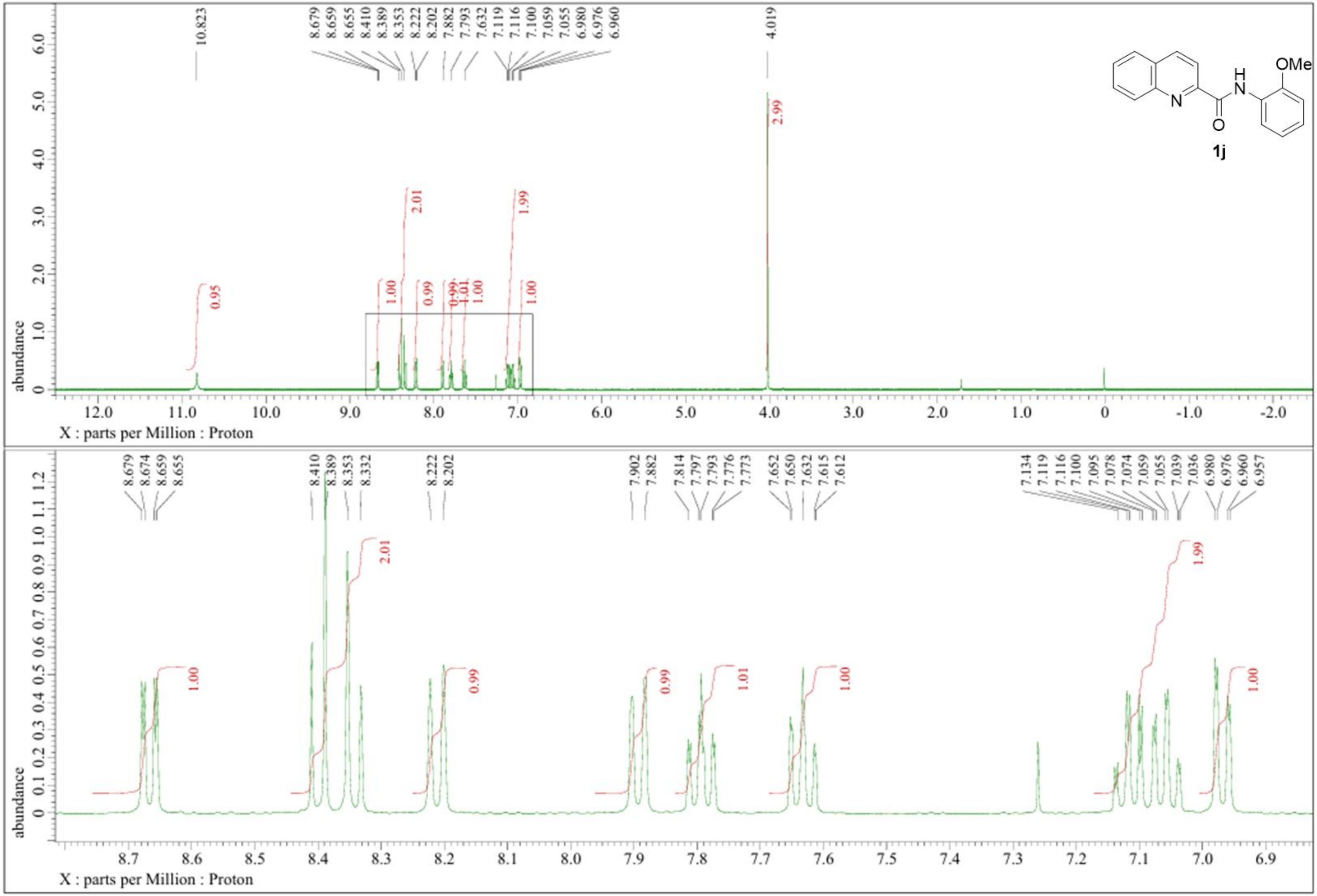
^{1}H NMR (400 MHz, CDCl$_3$)



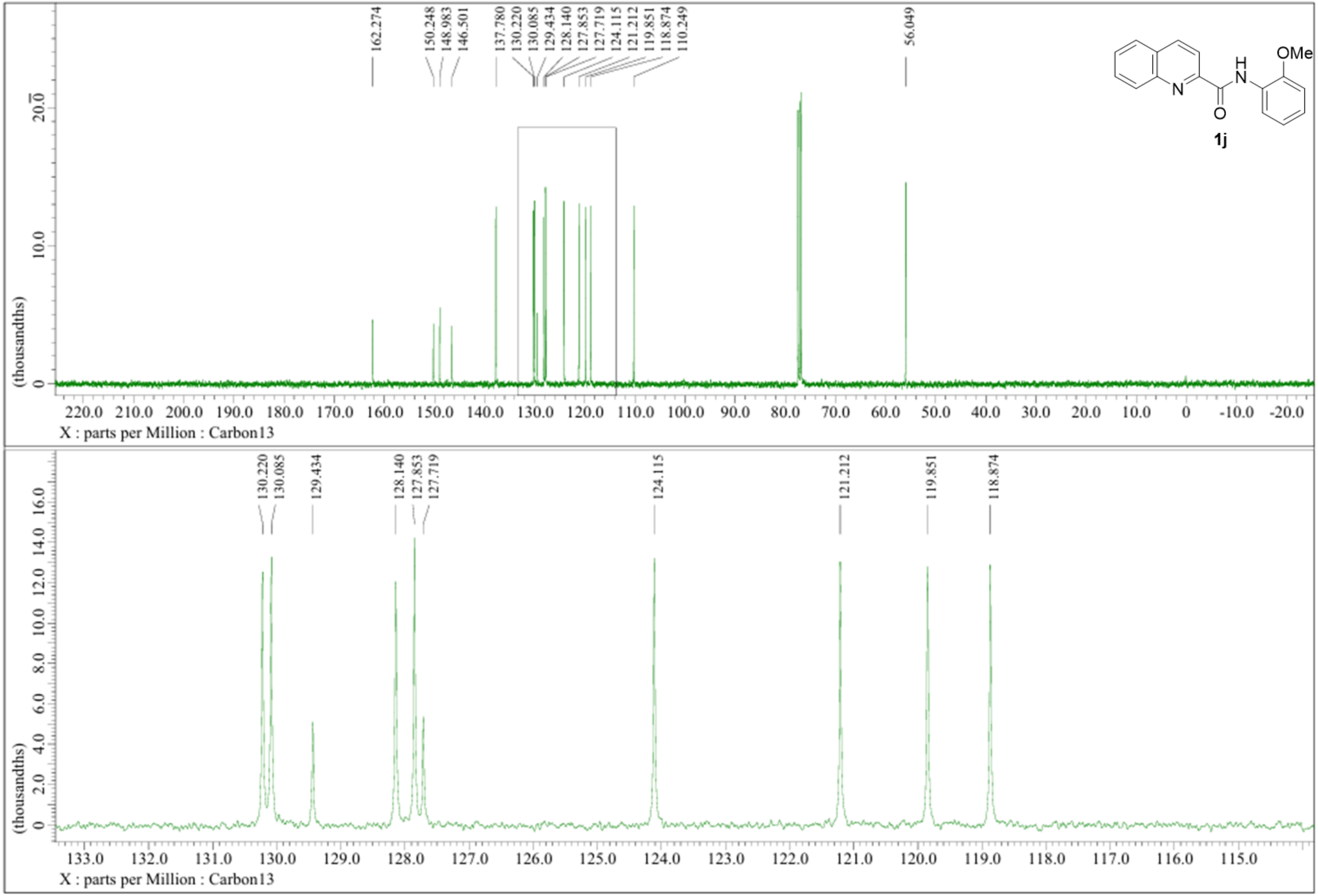
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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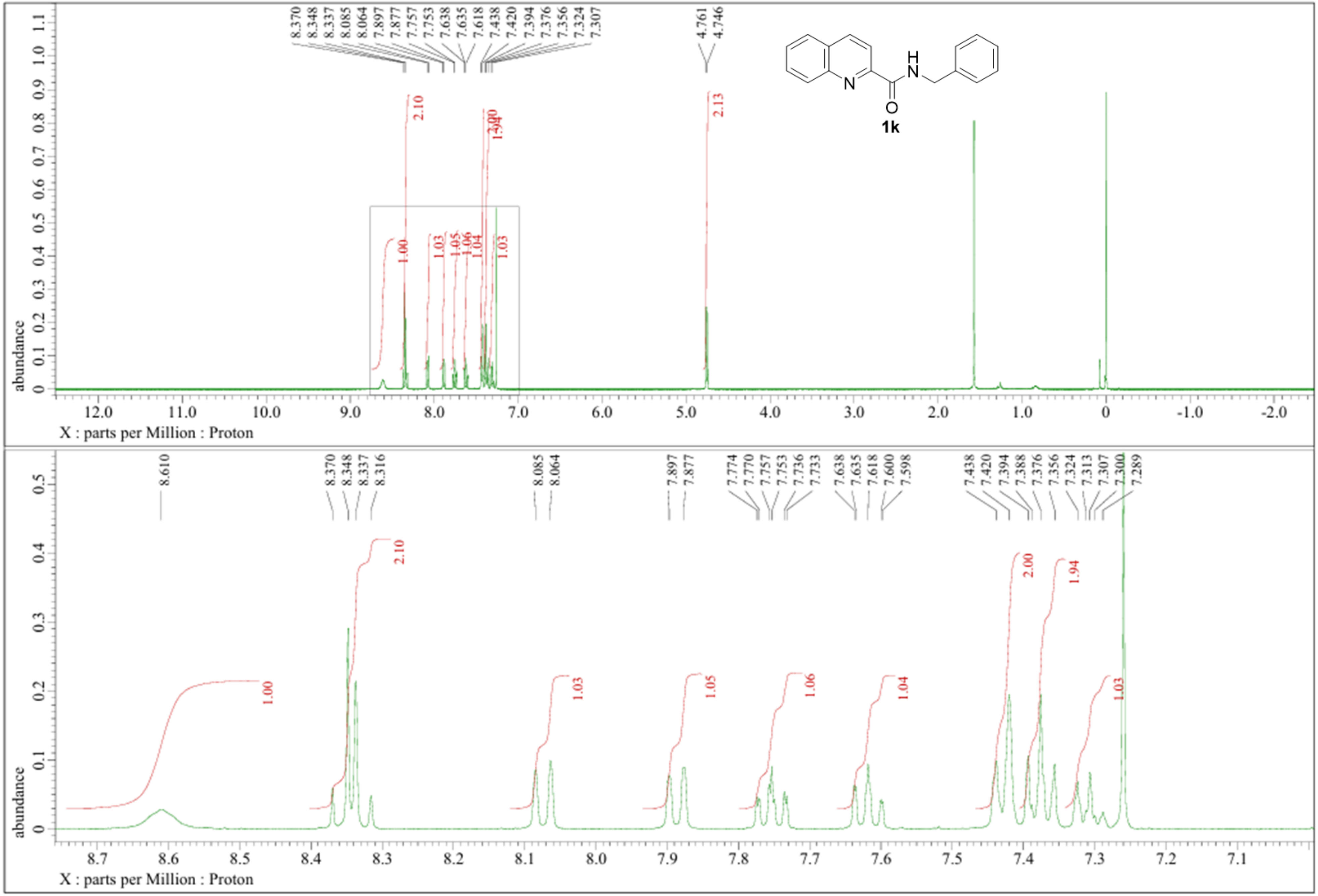
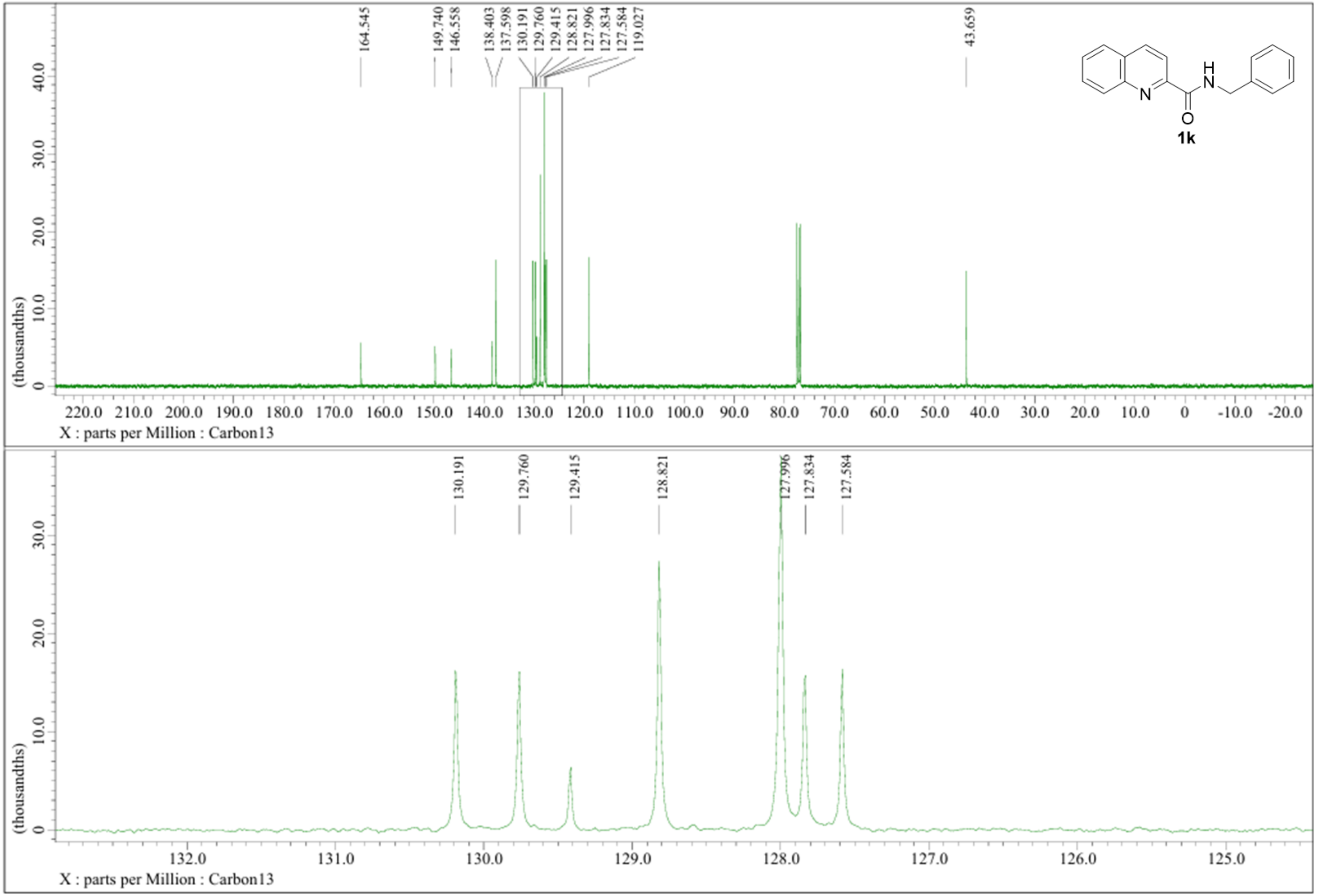
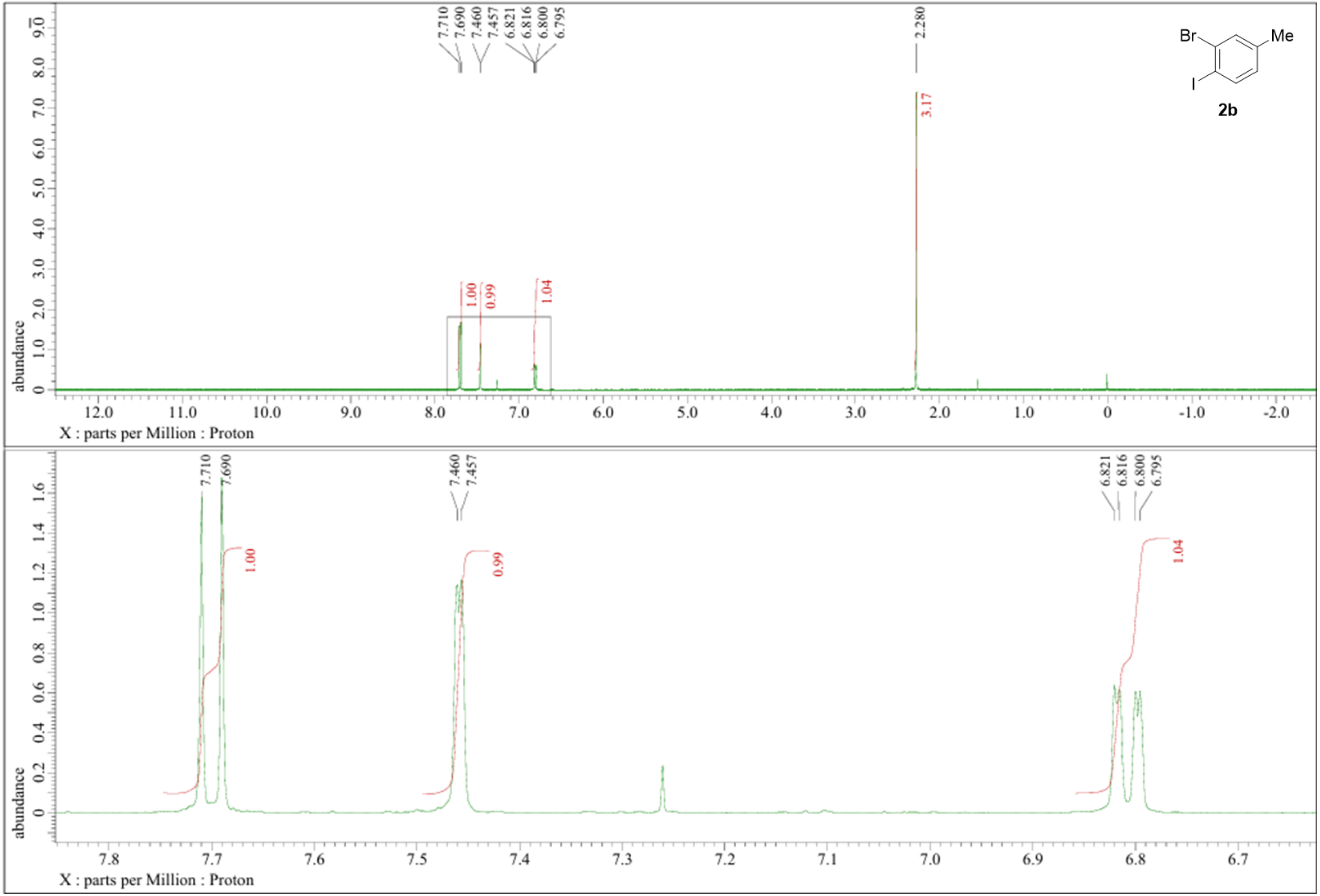
^{1}H NMR (400 MHz, $CDCl_3$)



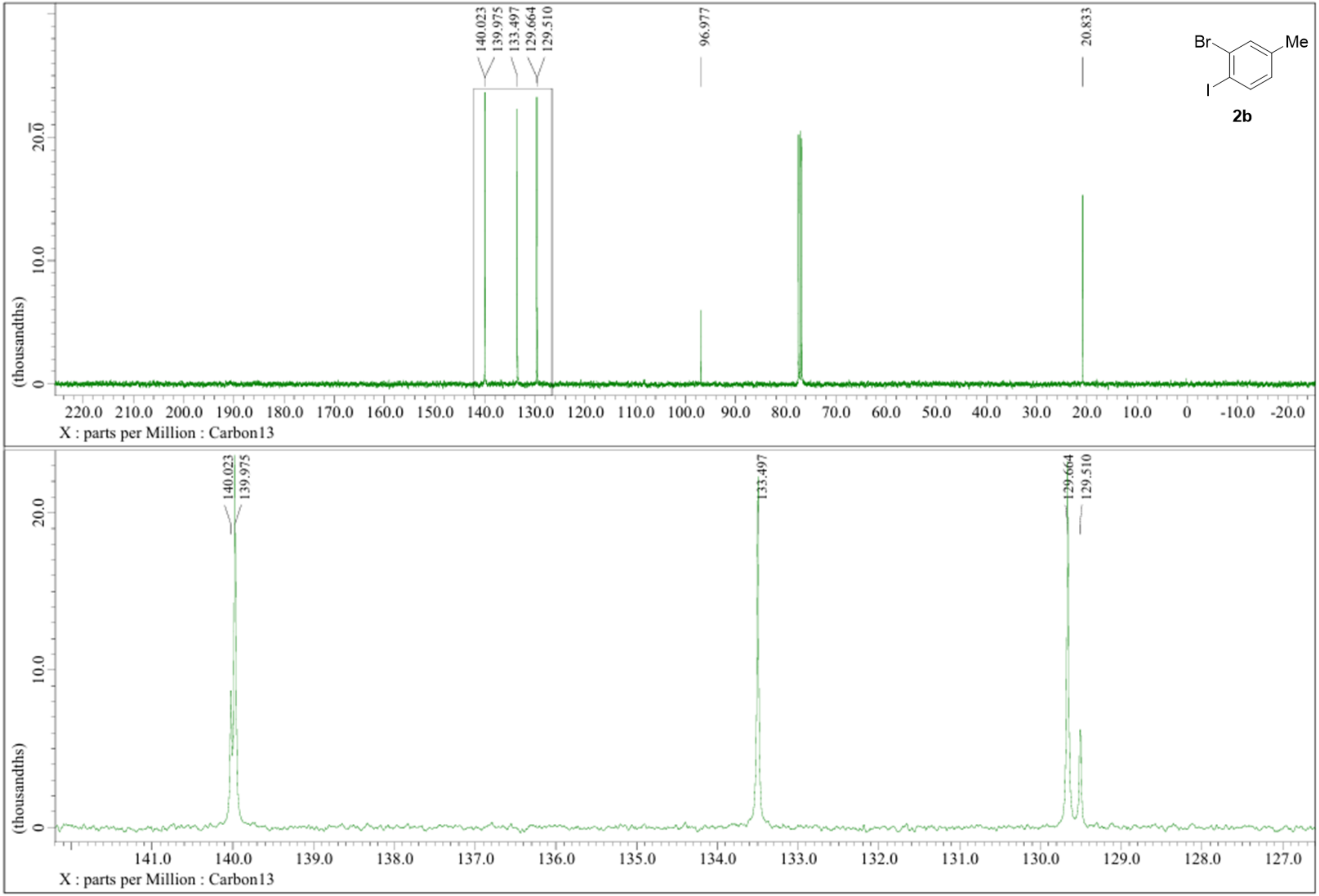
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



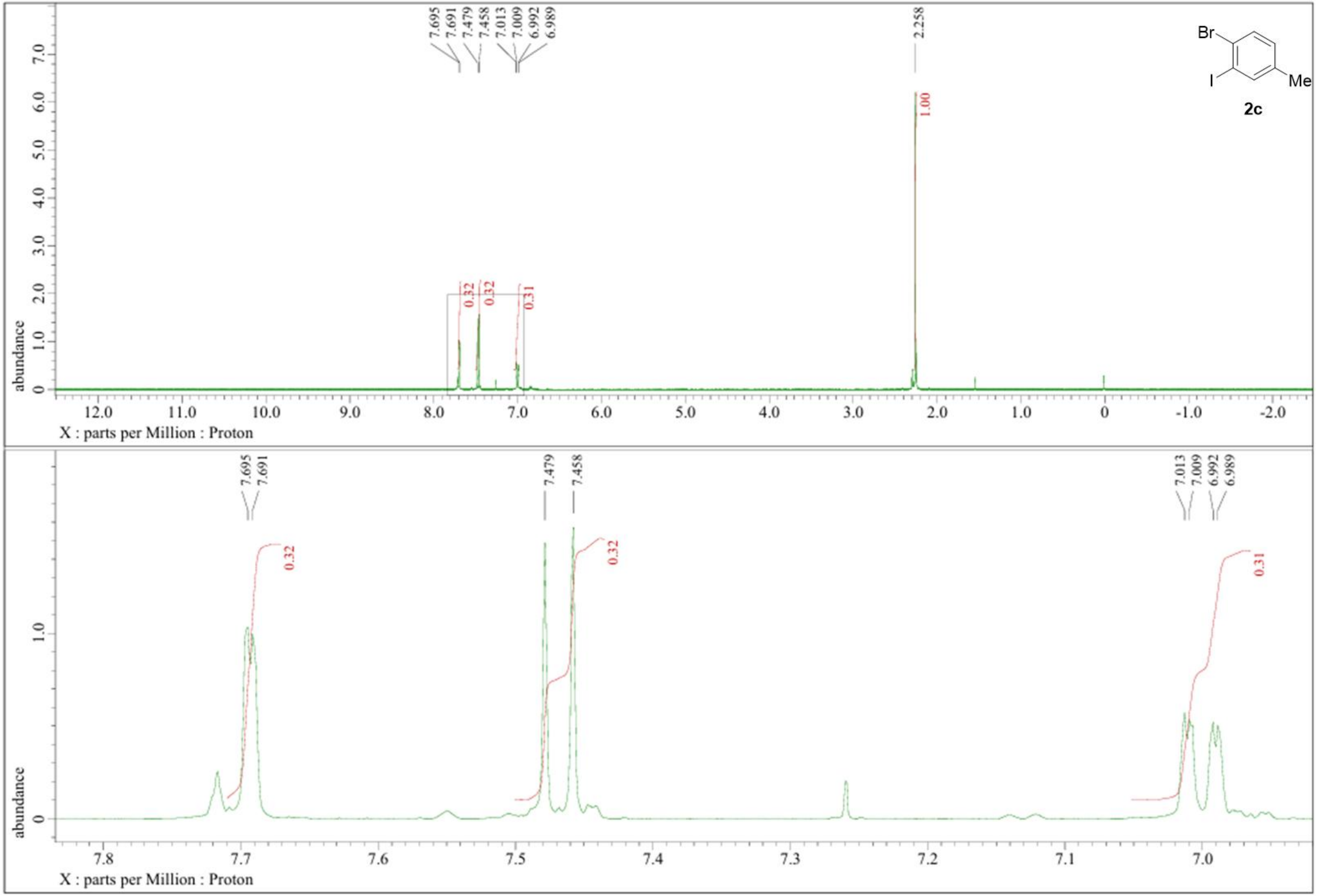
^{1}H NMR (400 MHz, $CDCl_3$)



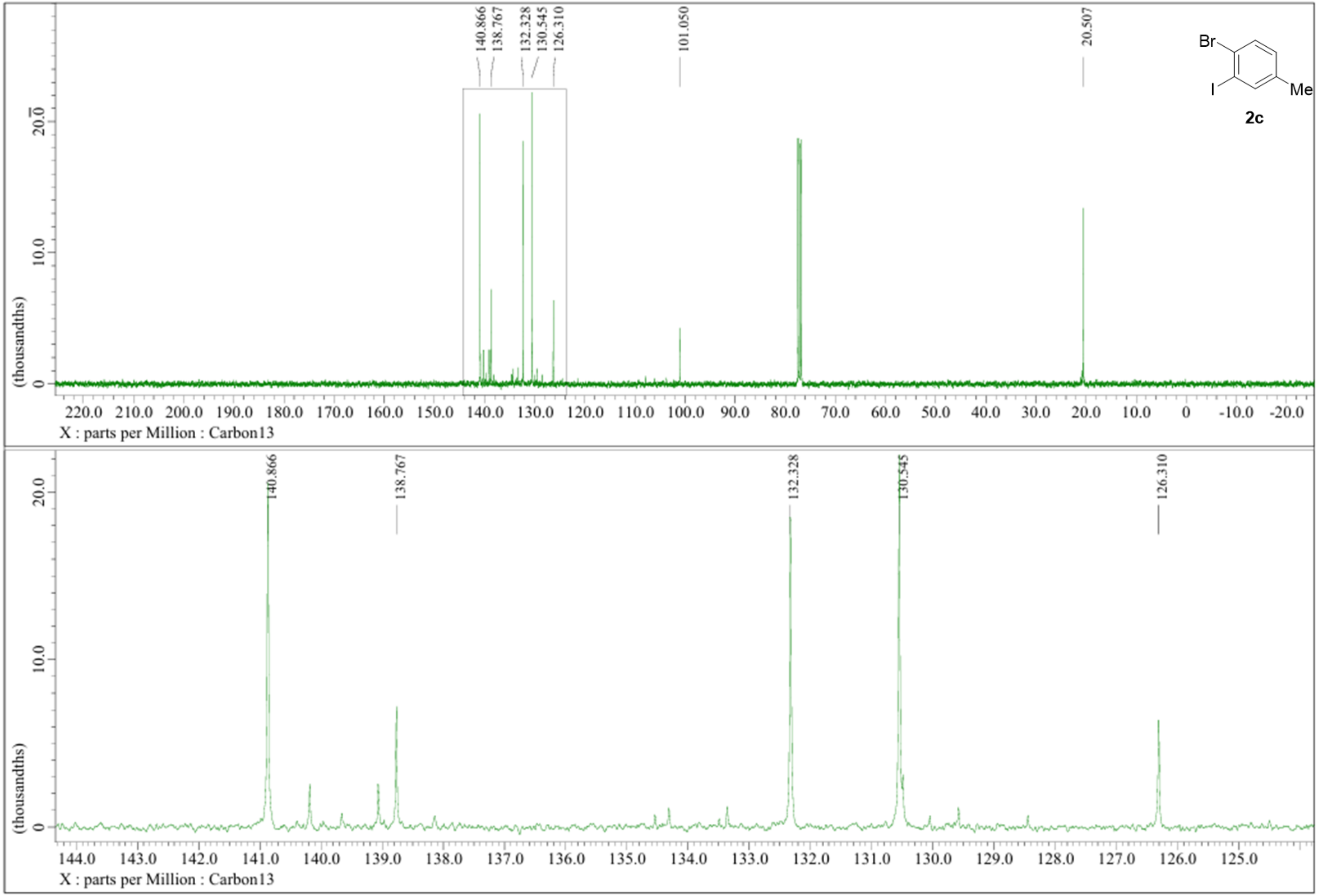
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



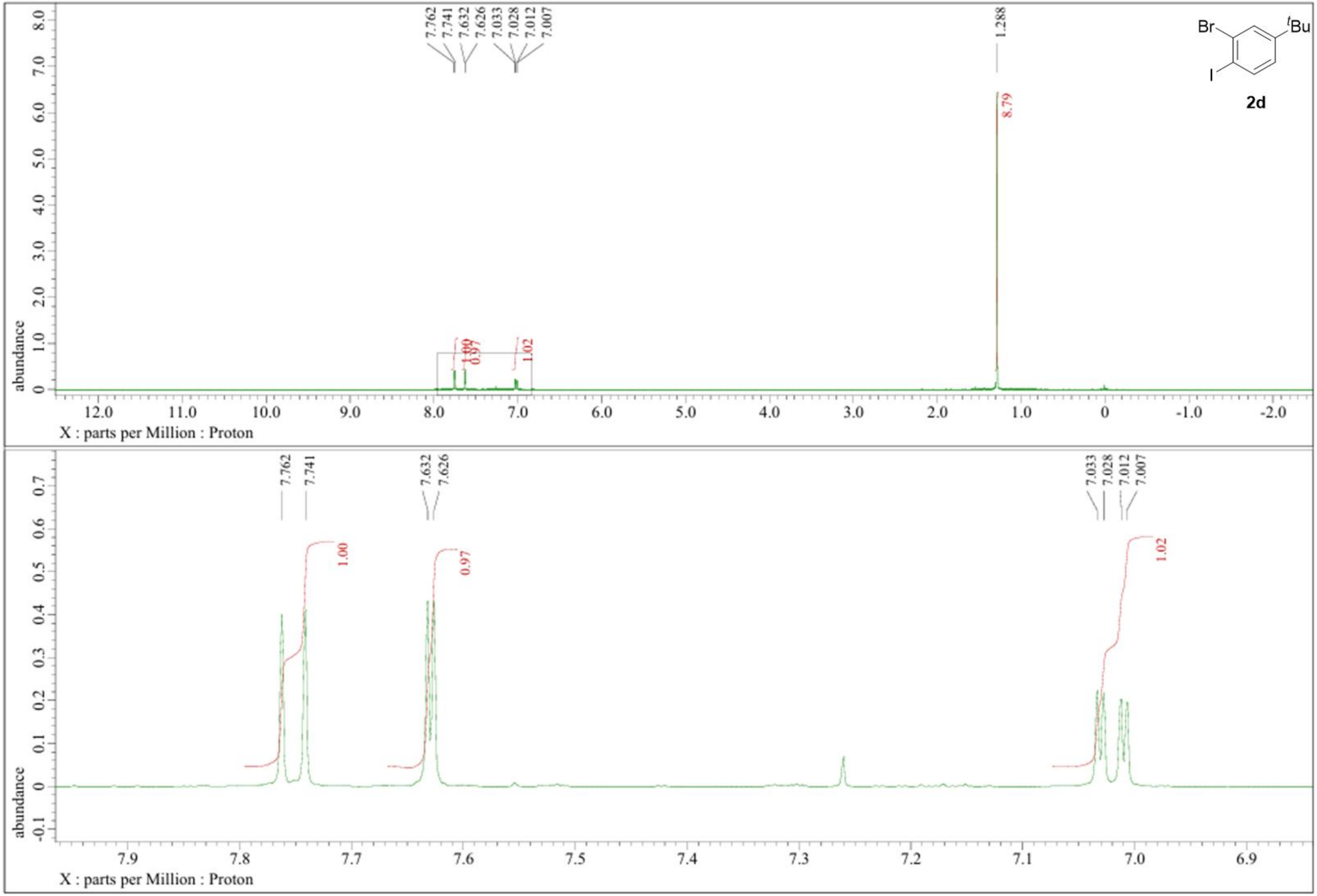
^{1}H NMR (400 MHz, $CDCl_3$)



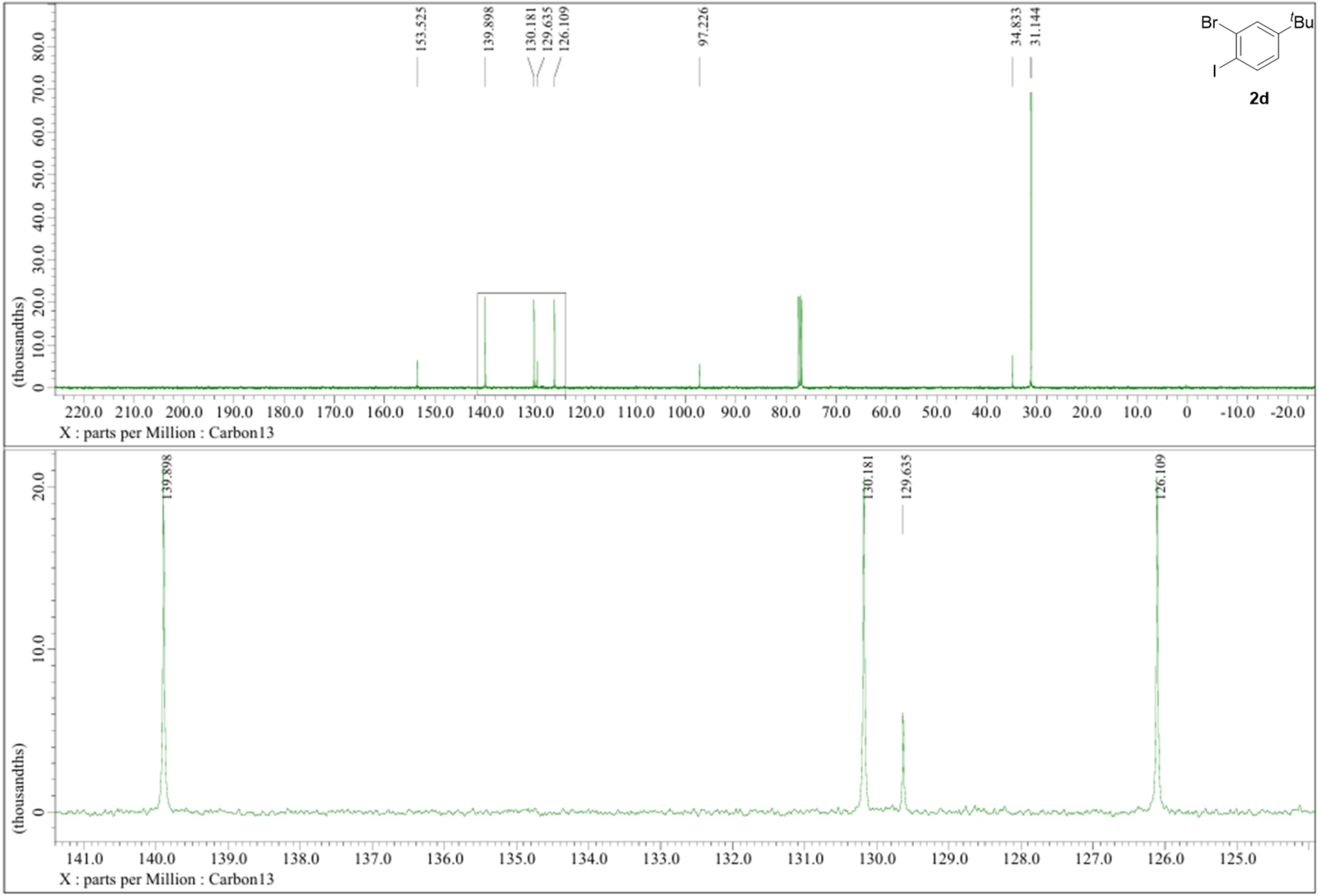
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



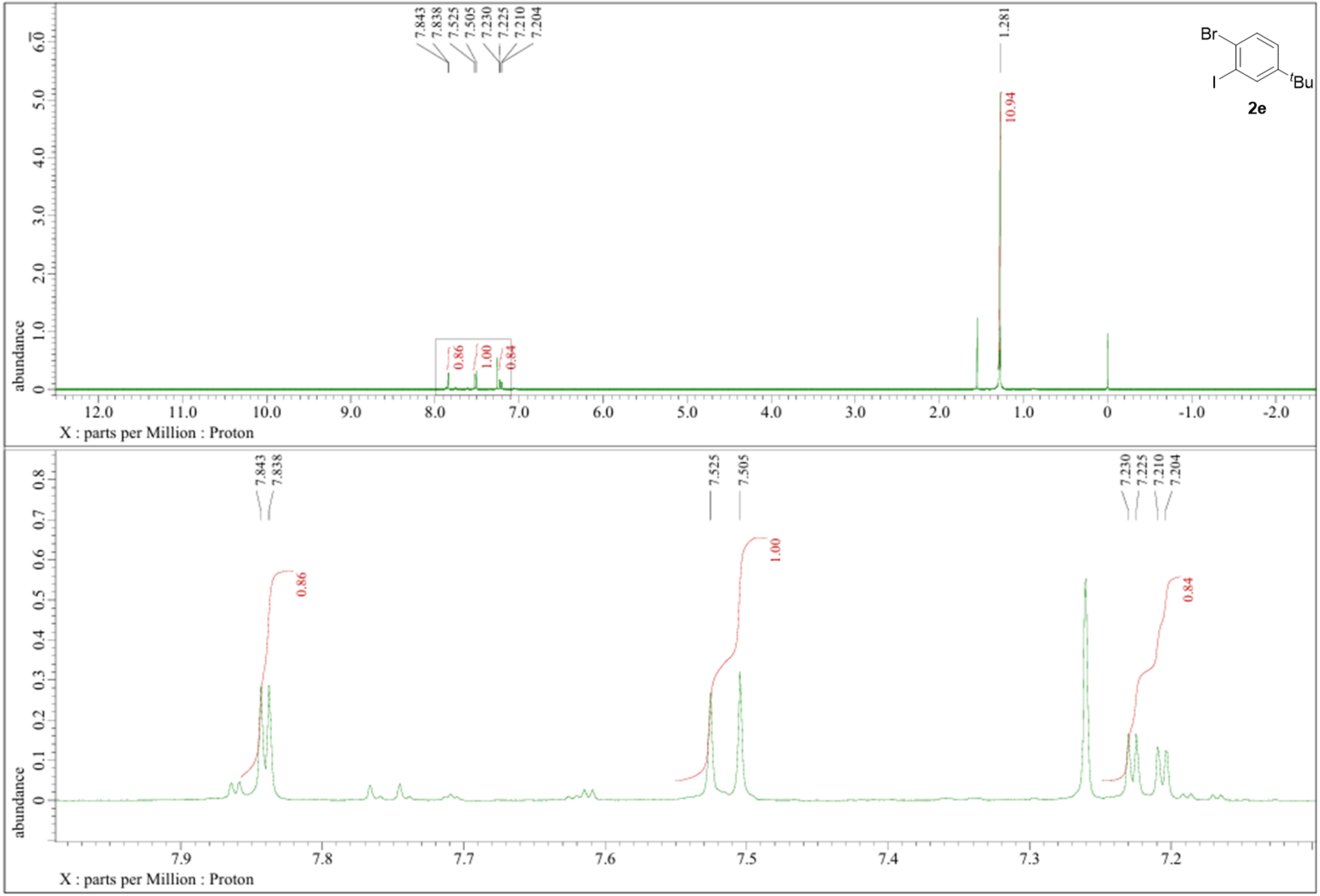
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



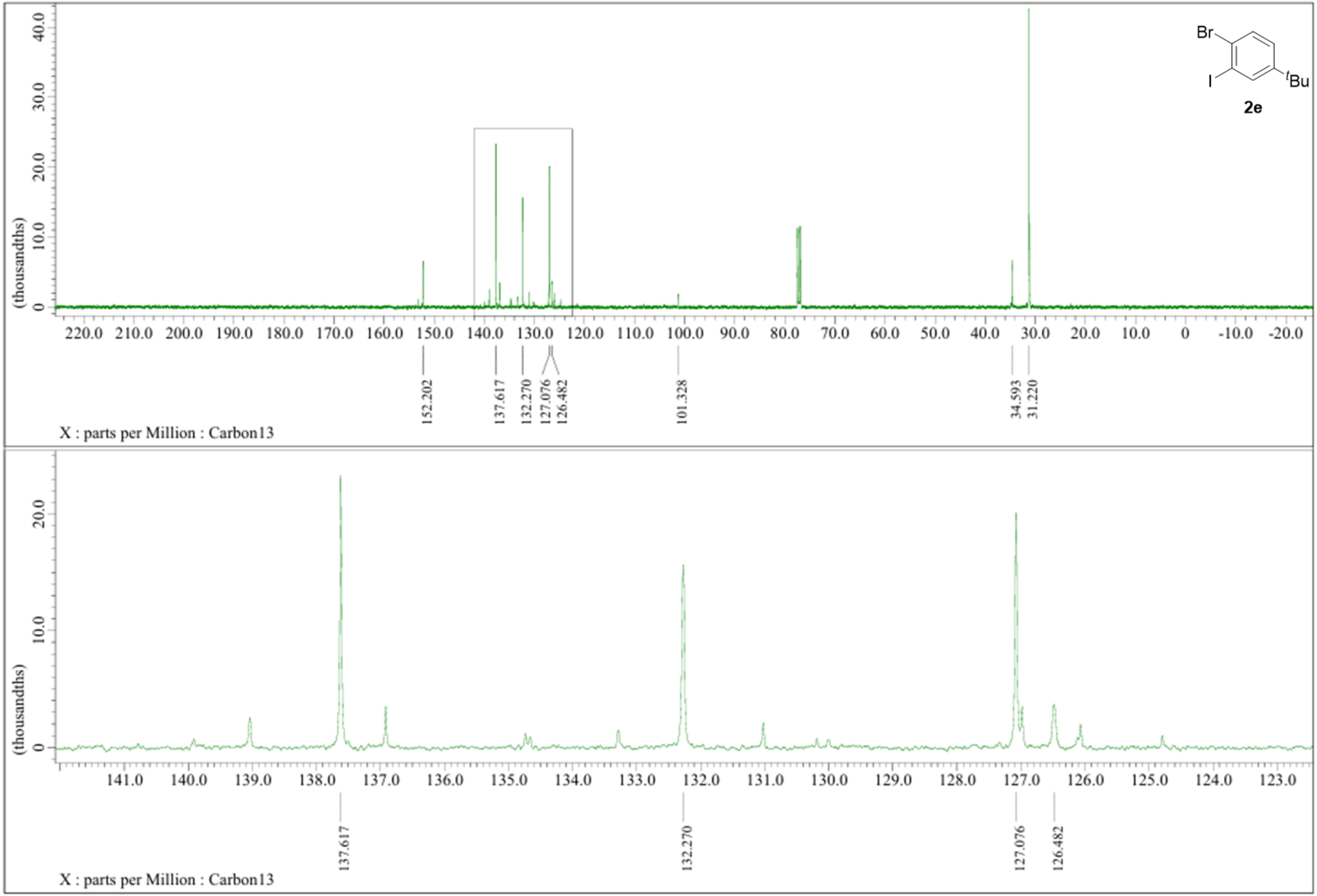
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



$^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$)



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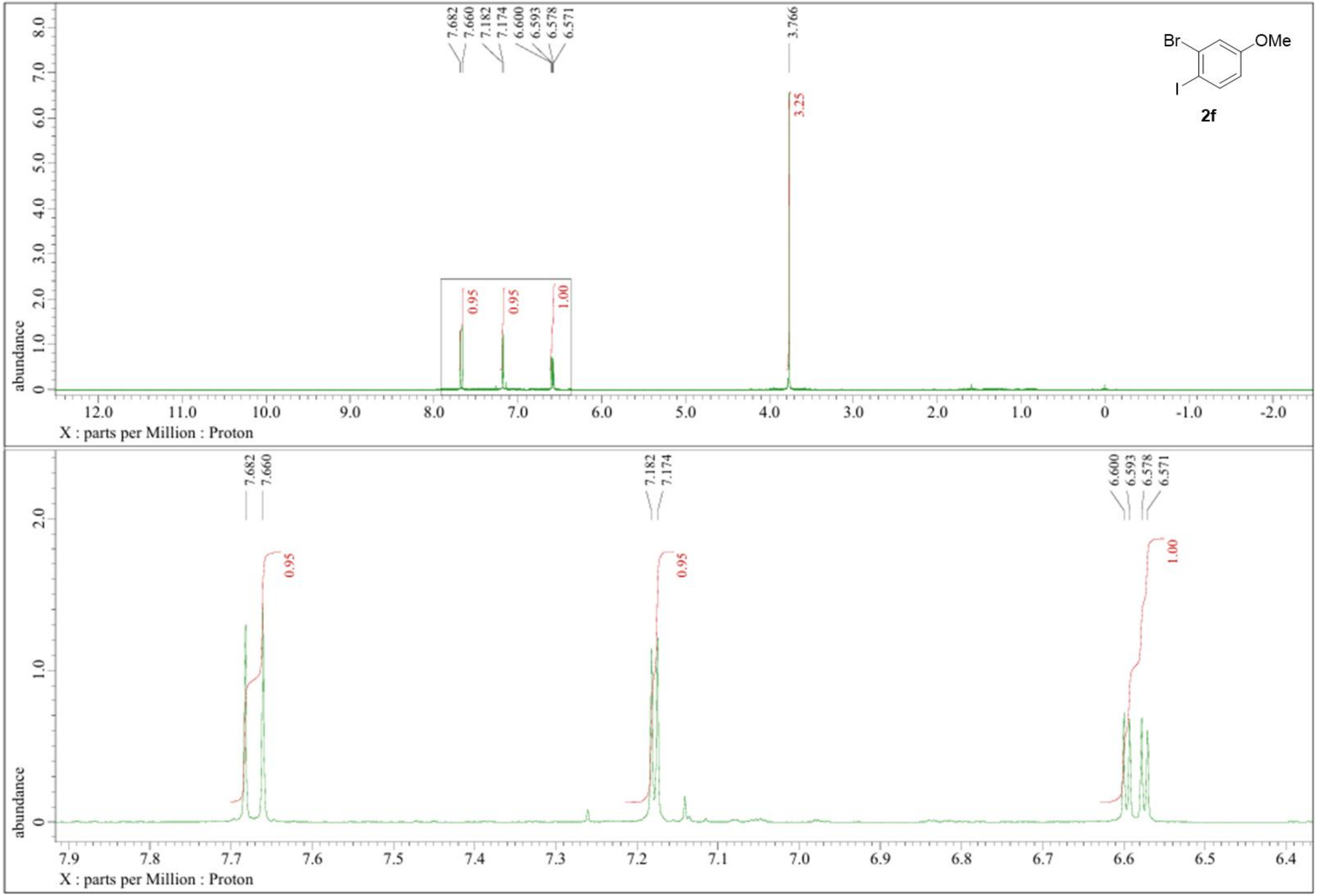
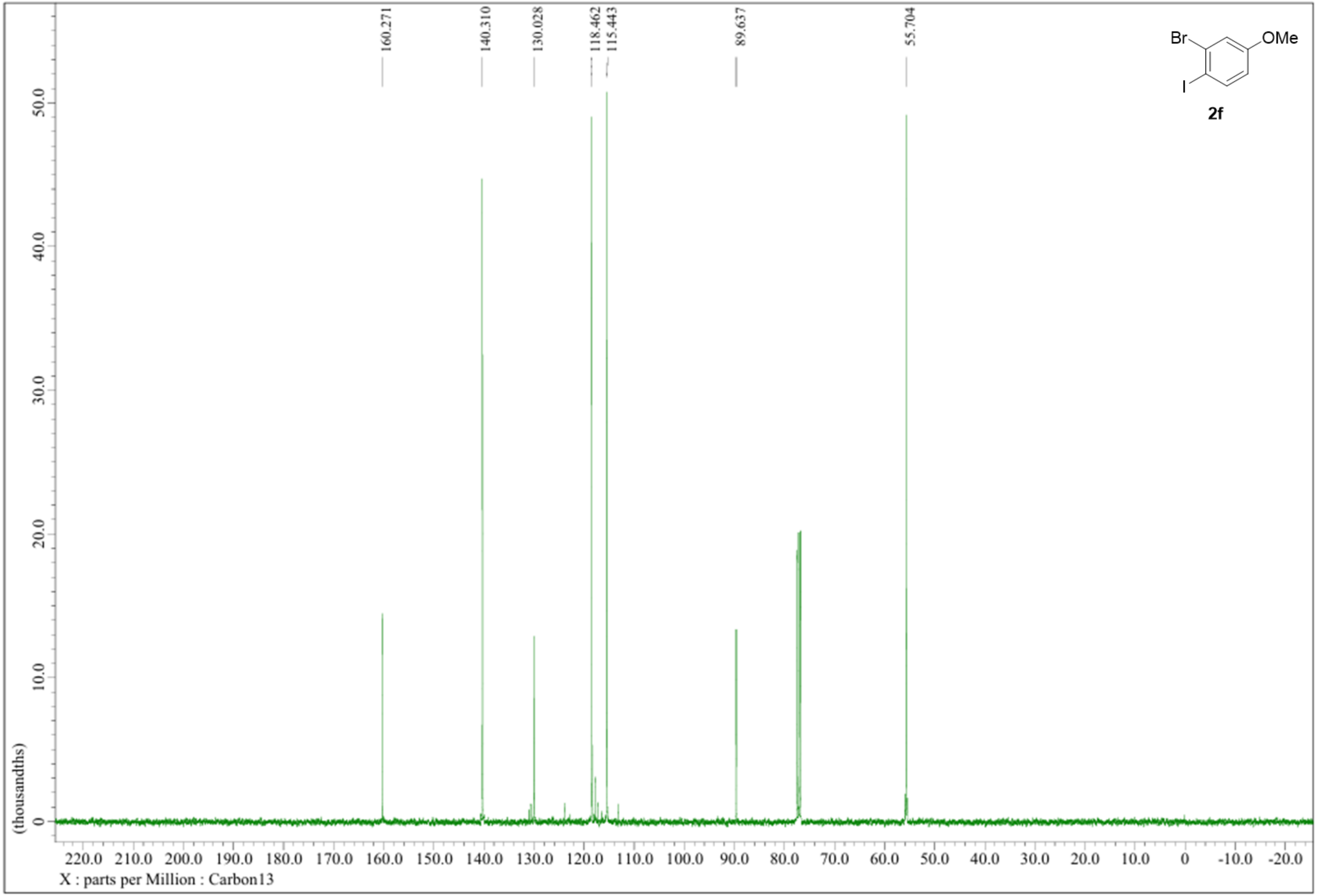
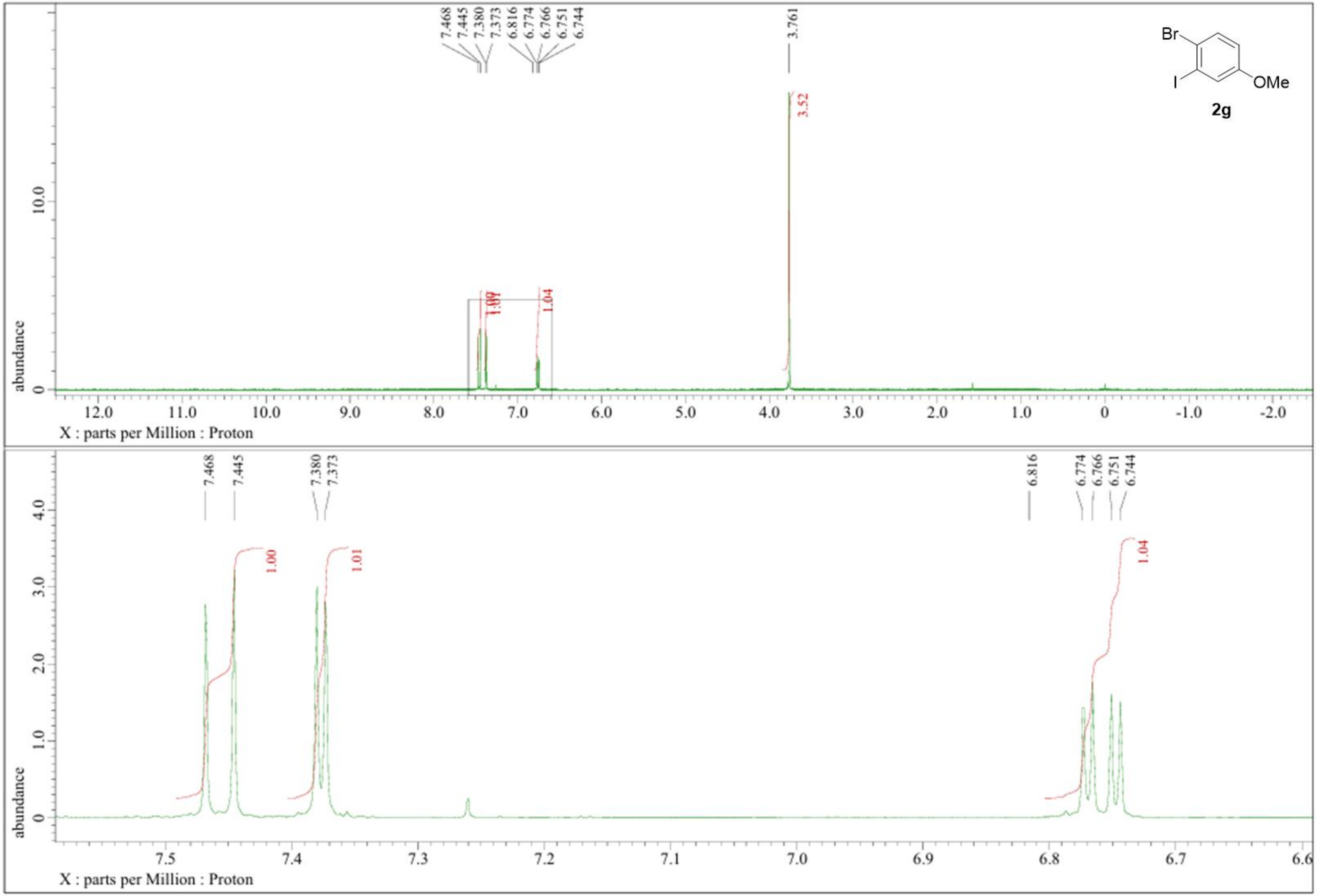


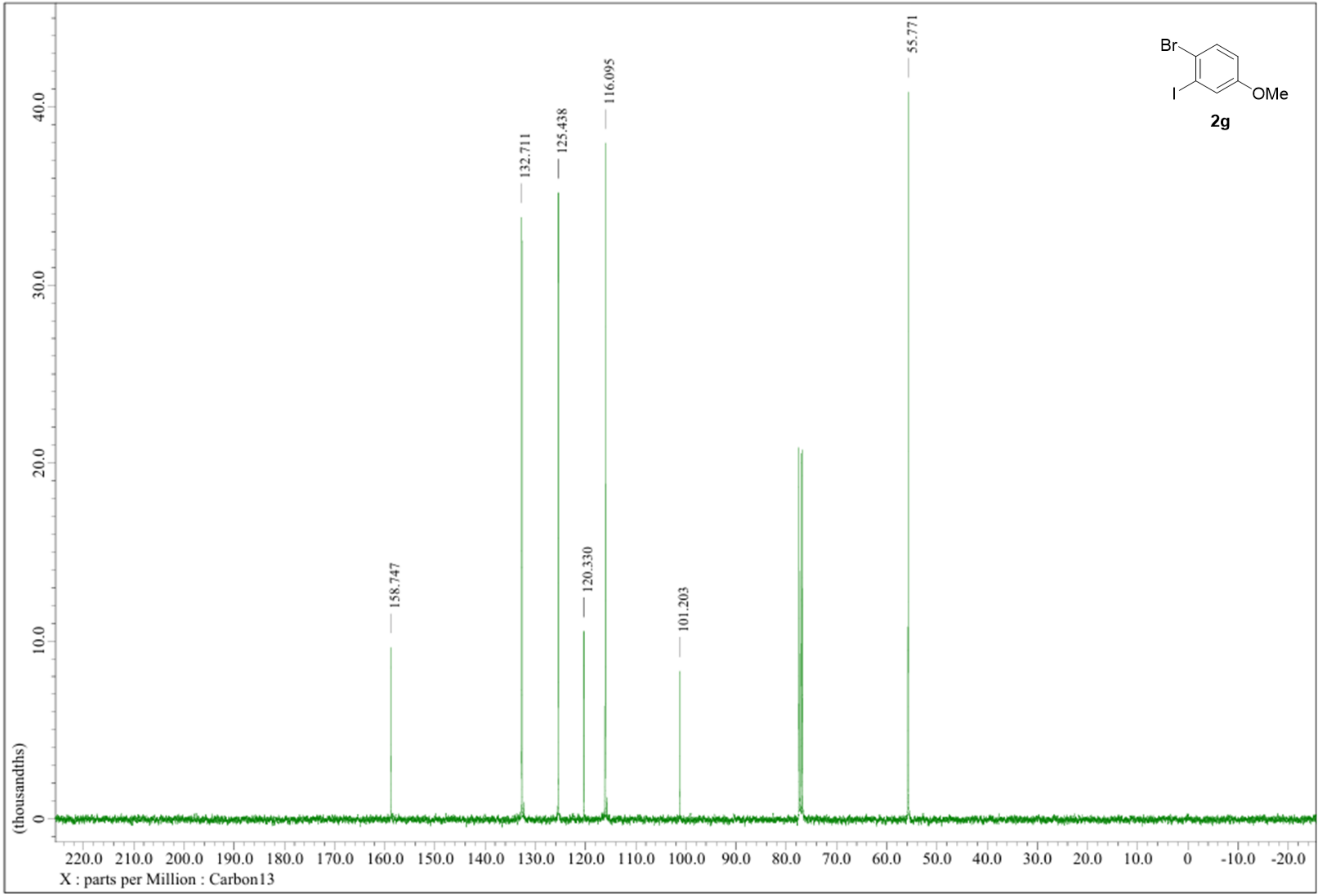
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



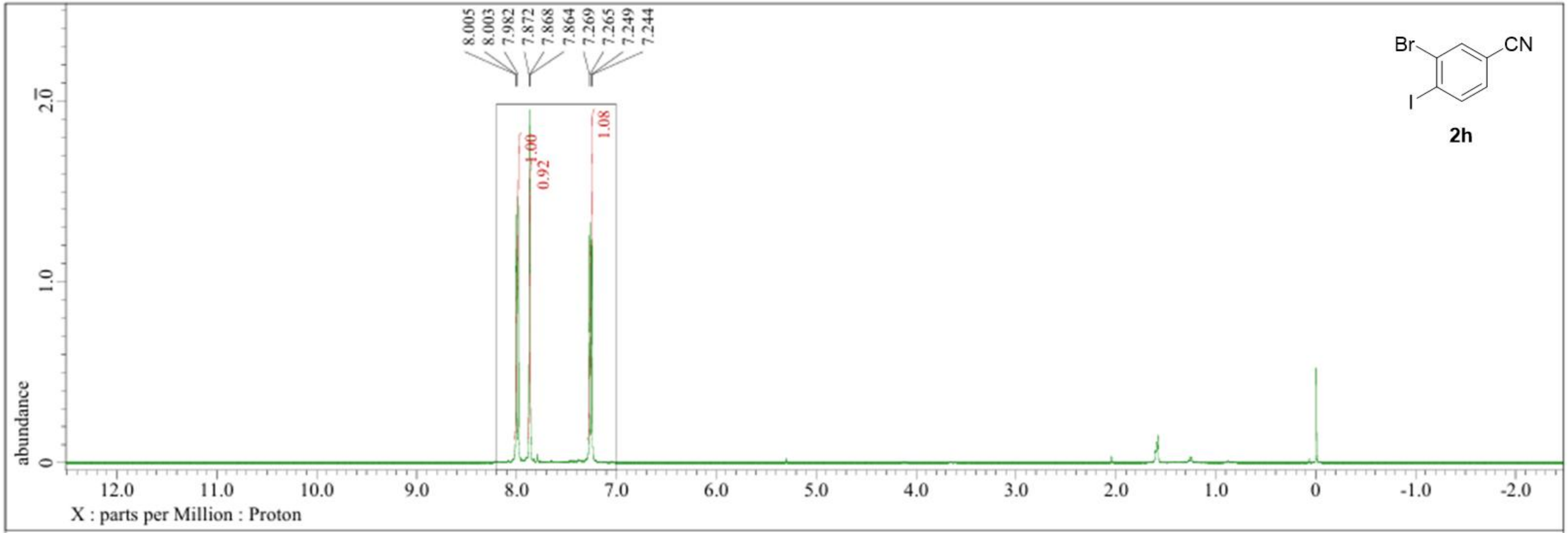
^{1}H NMR (400 MHz, $CDCl_3$)

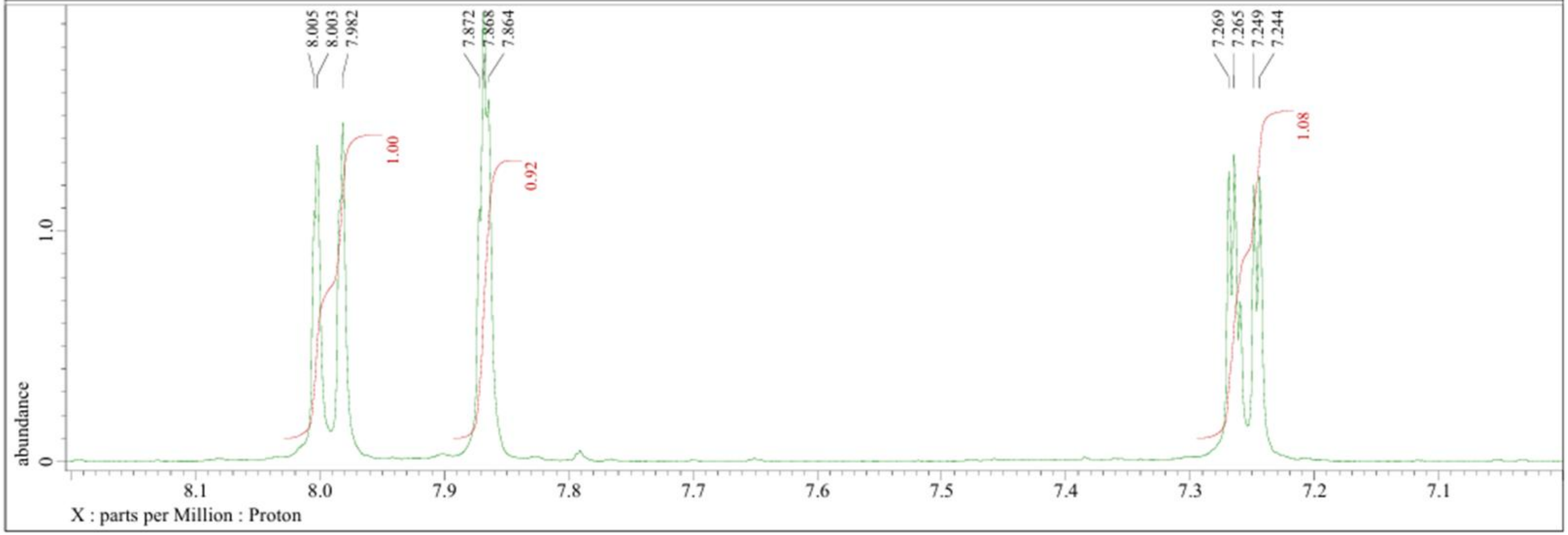


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

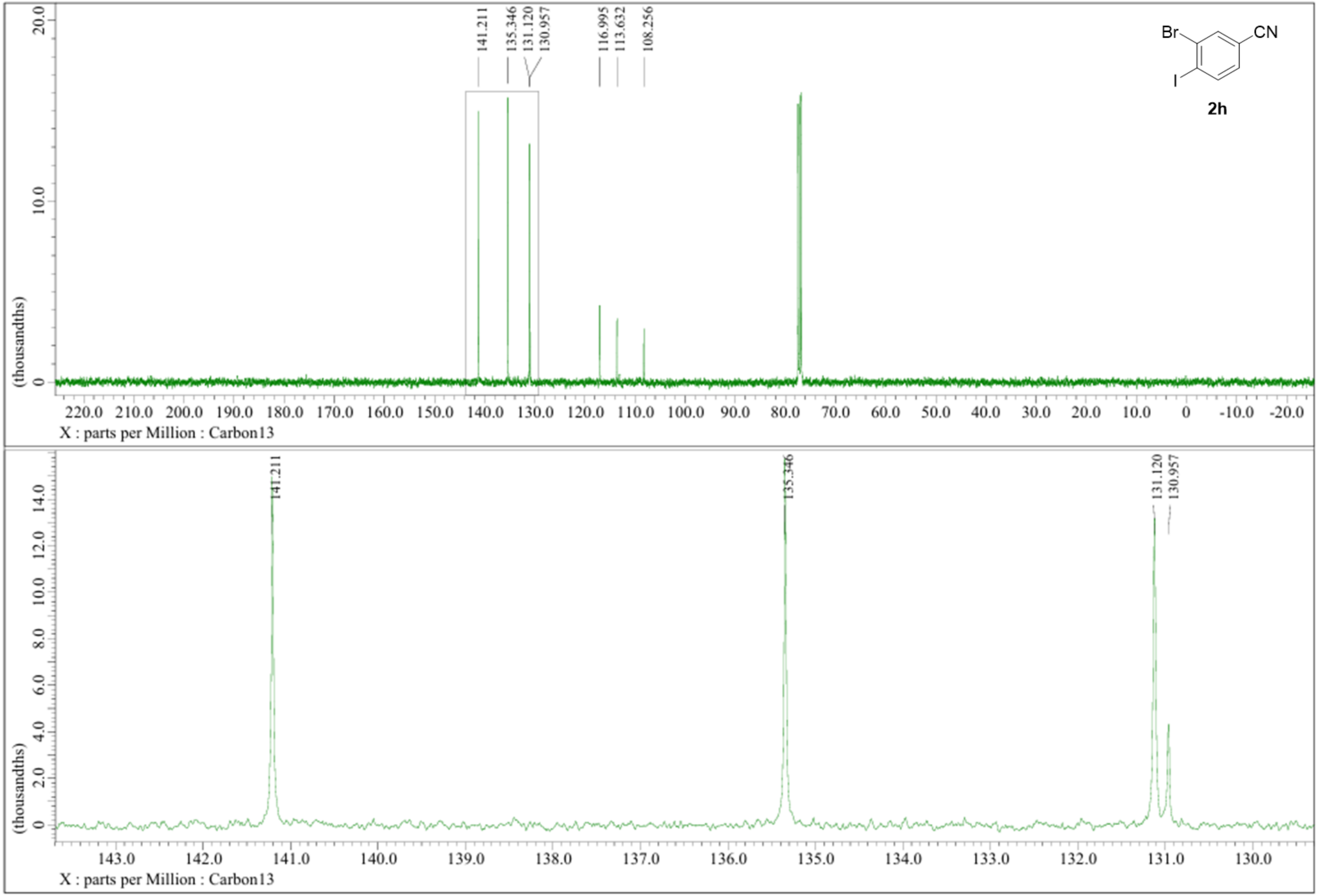


¹H NMR (400 MHz, CDCl$_3$)

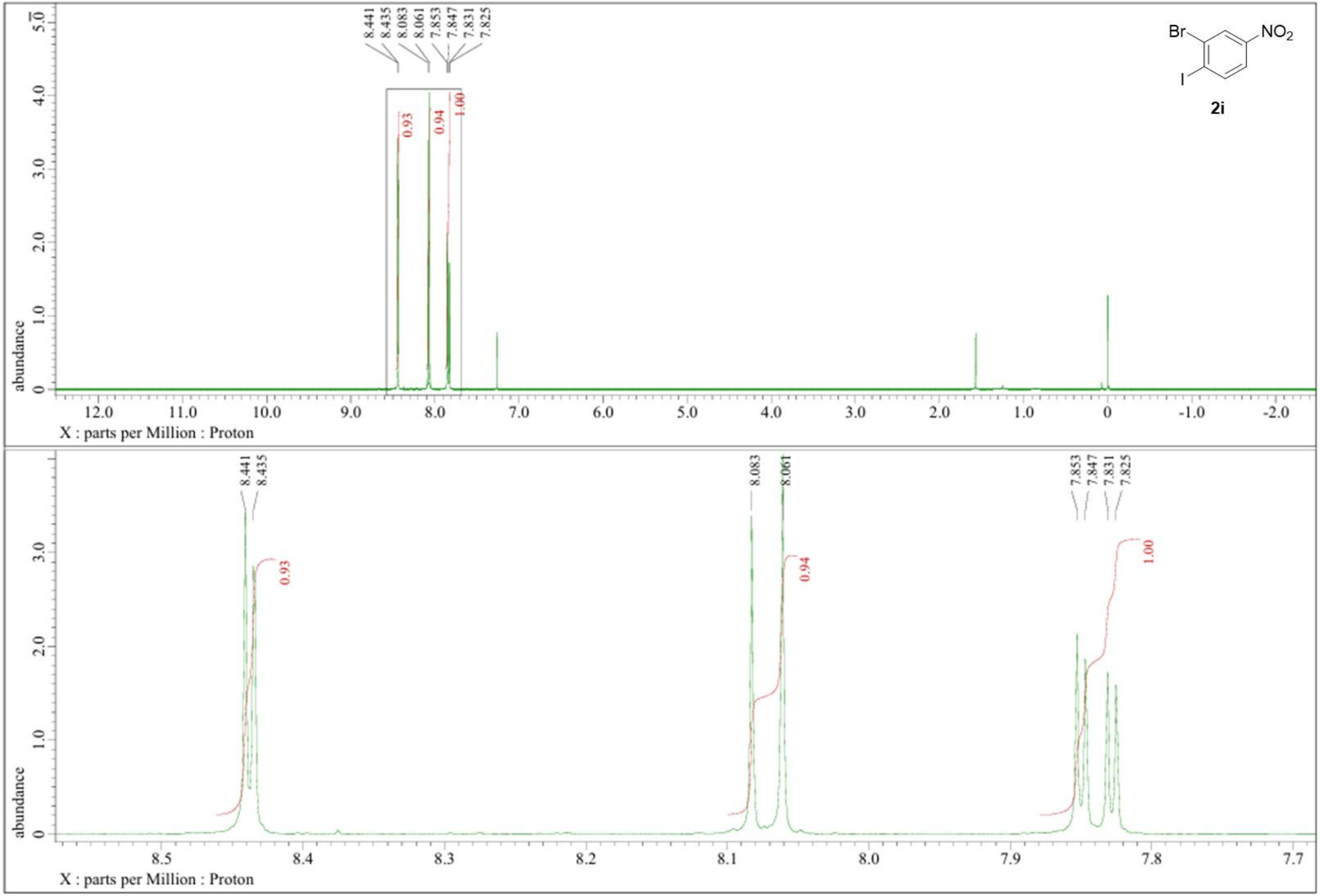




$^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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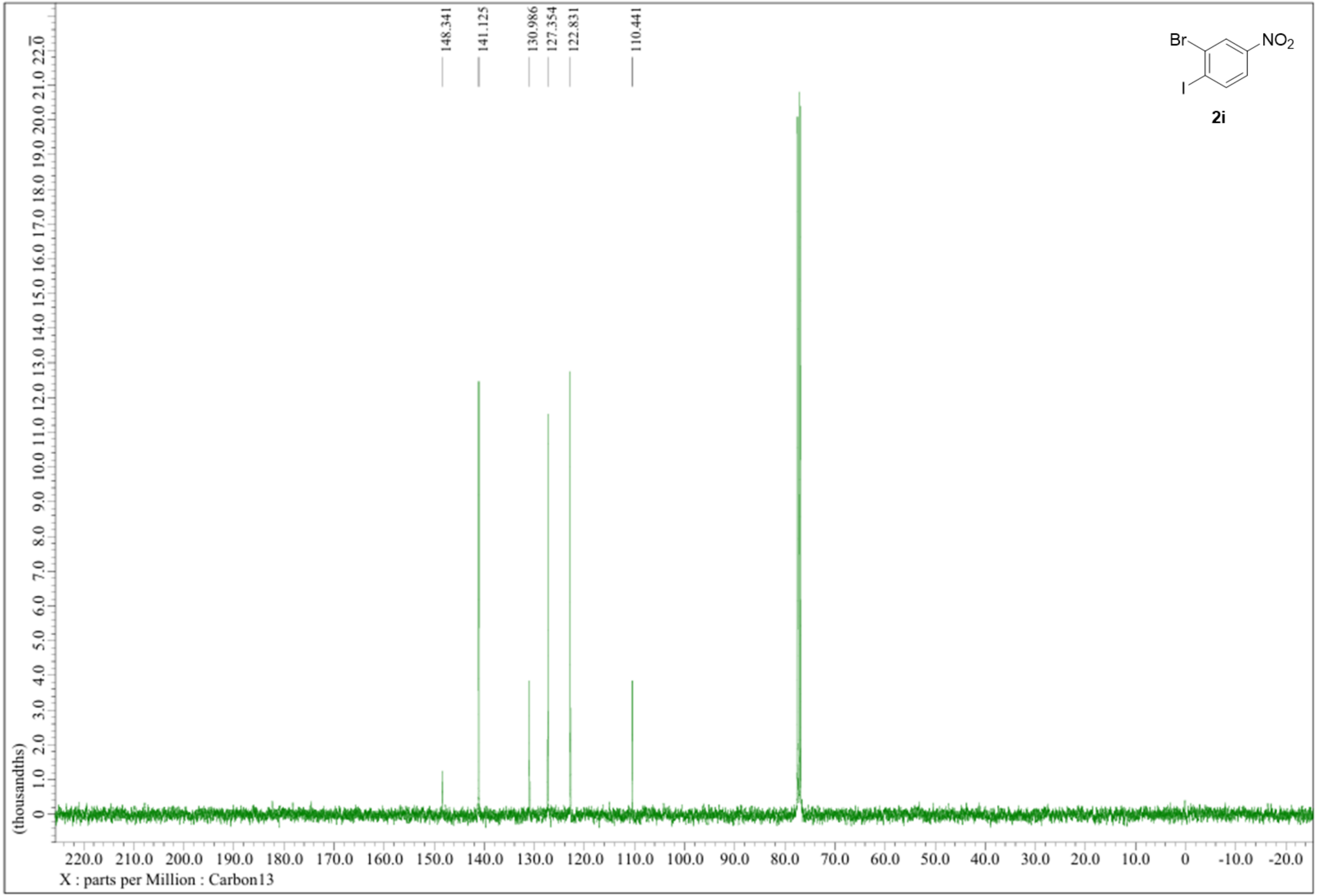
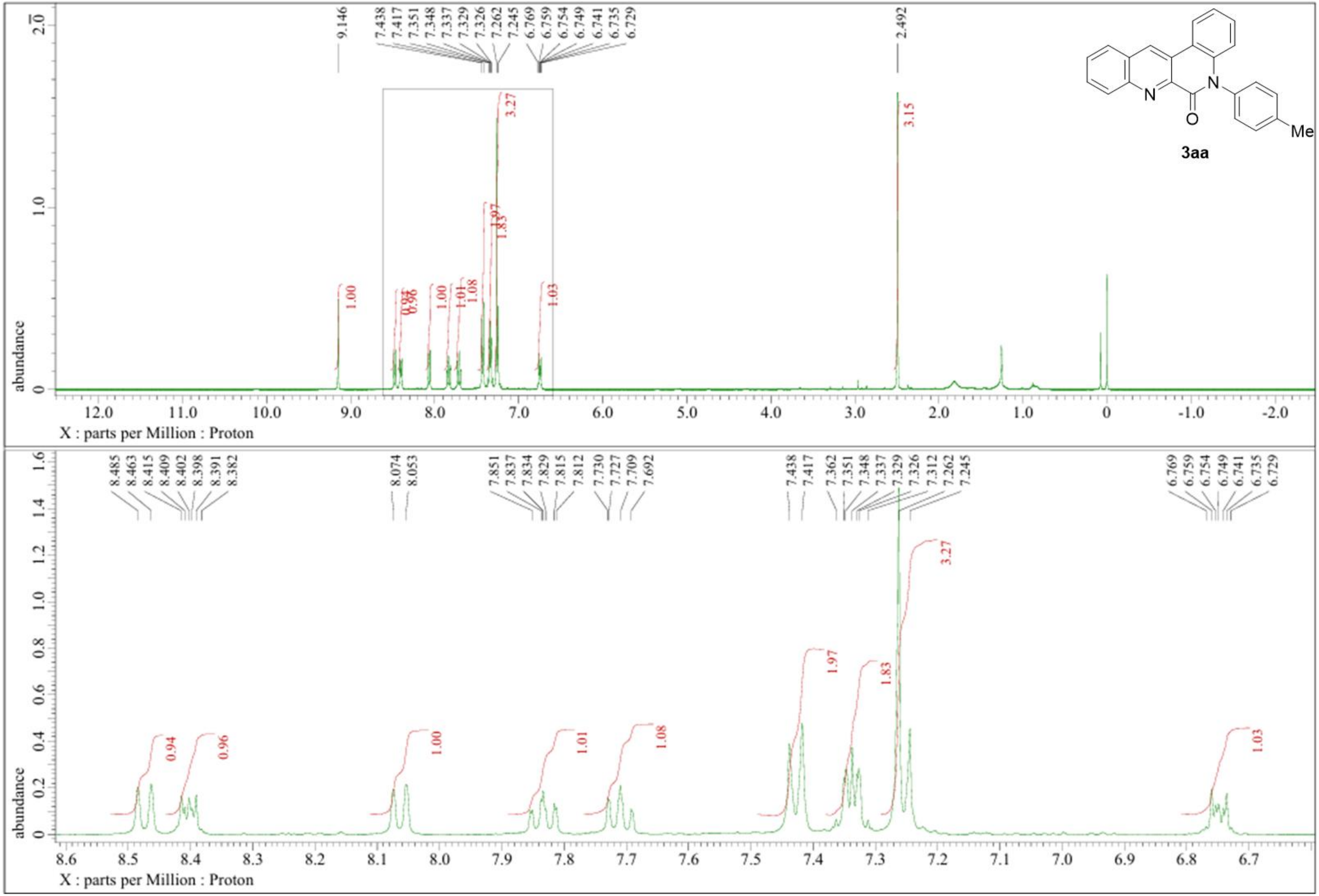
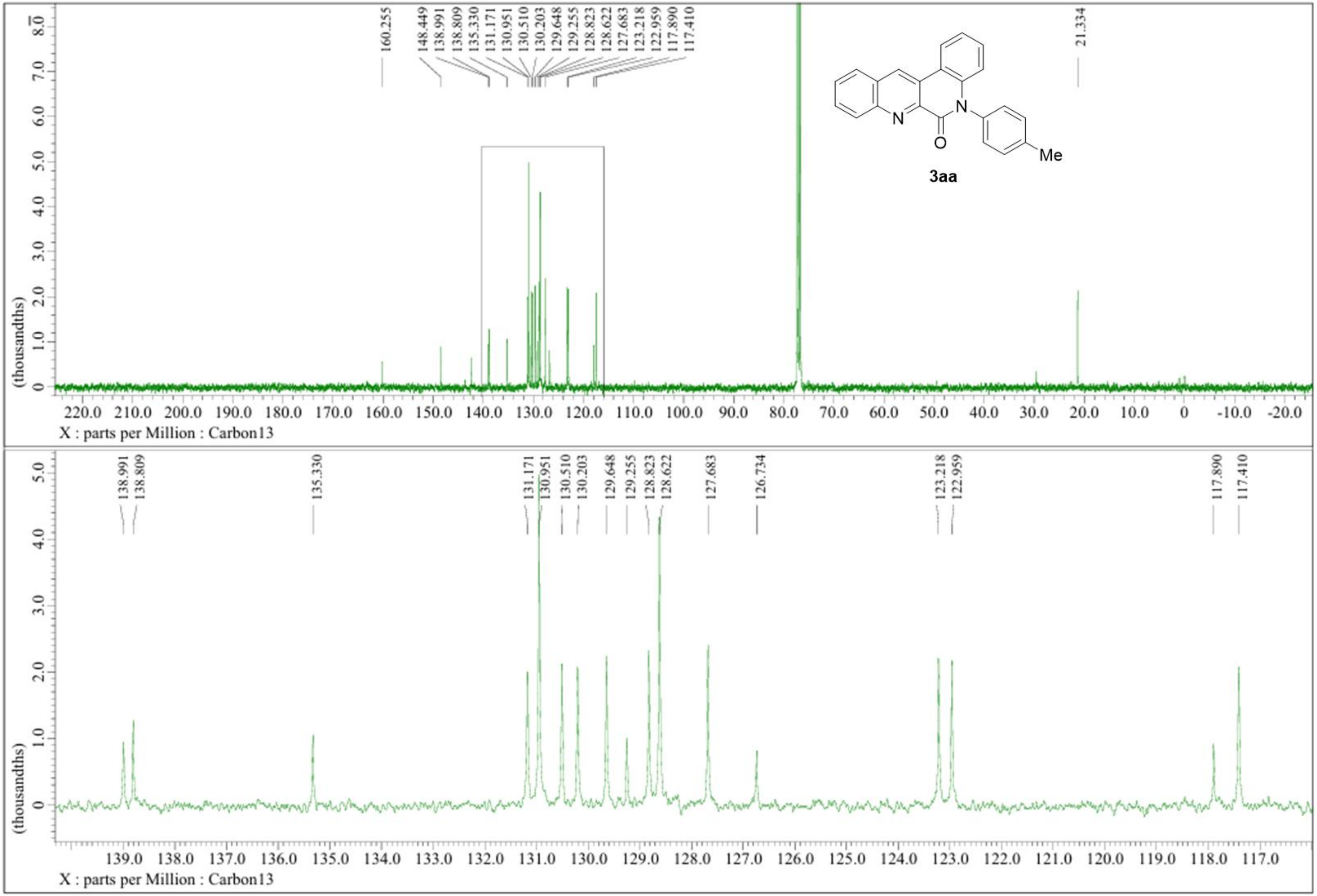


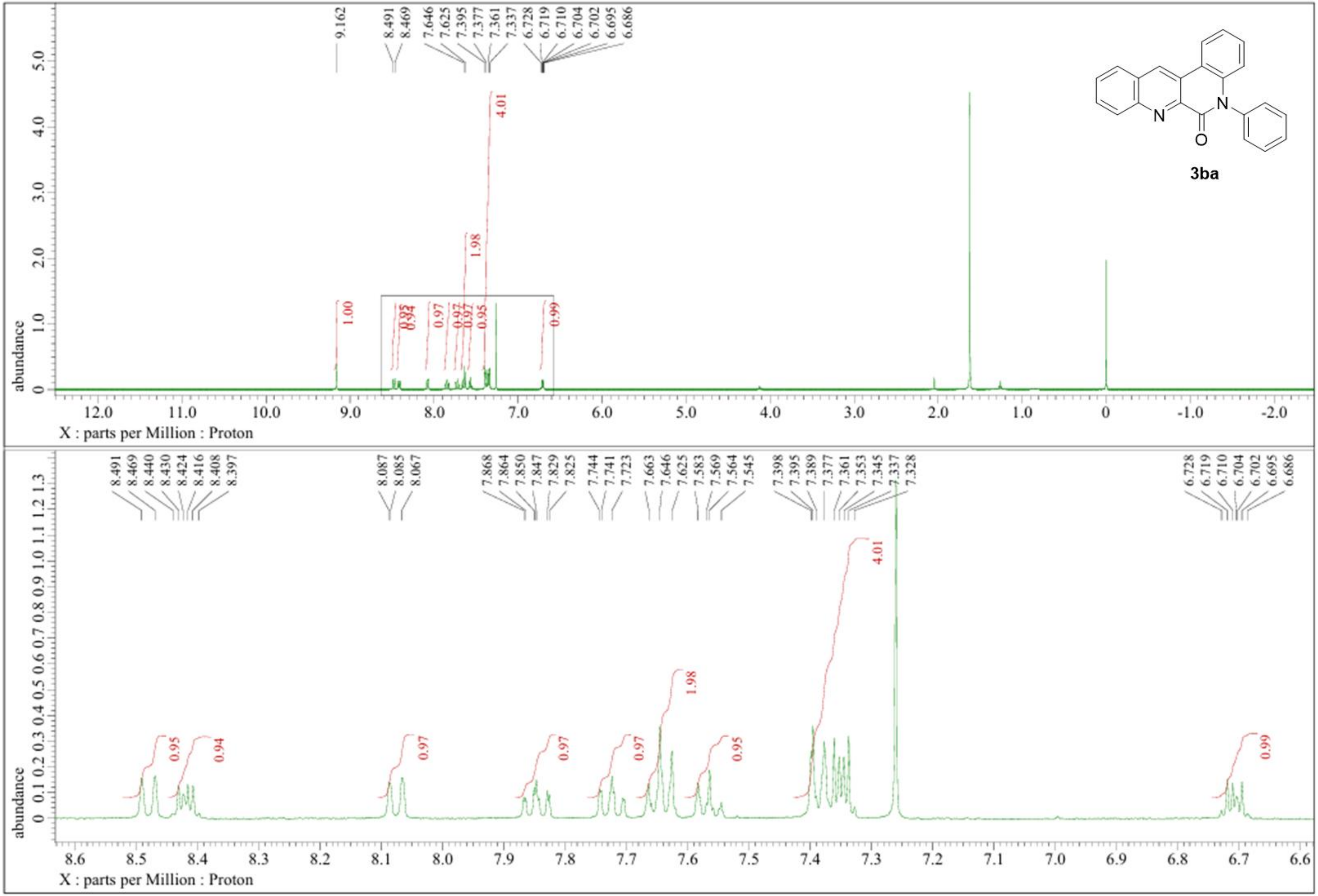
[1]H NMR (400 MHz, $CDCl_3$)



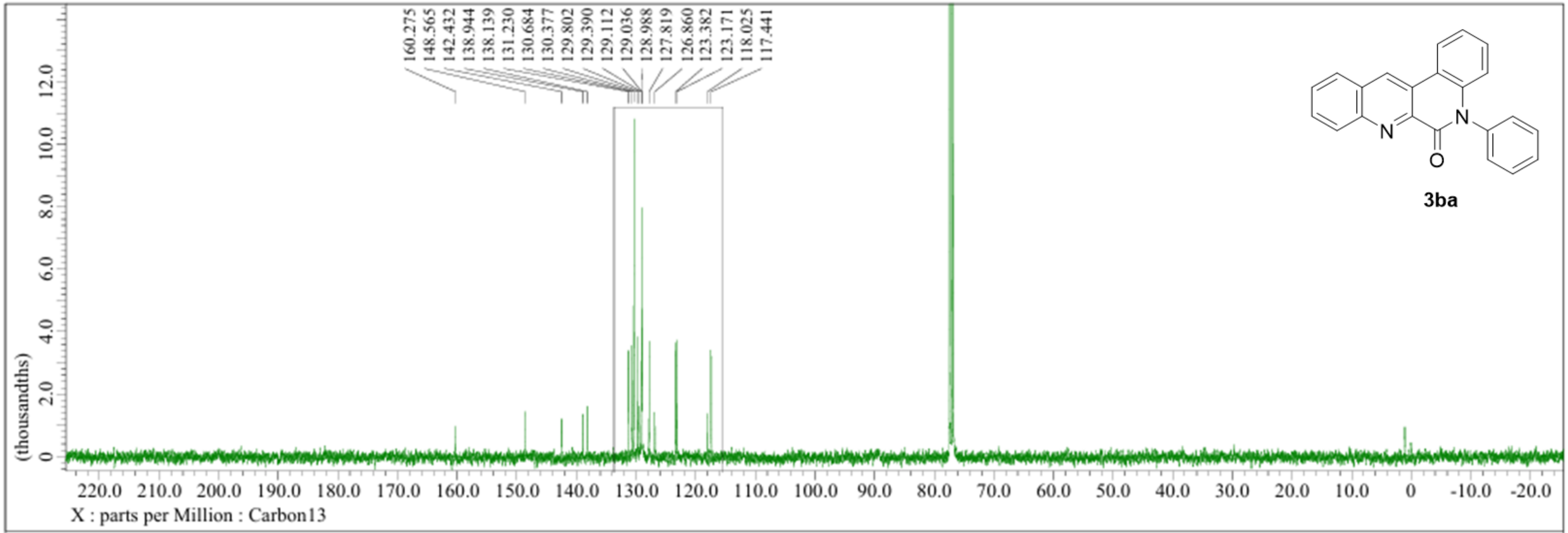
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

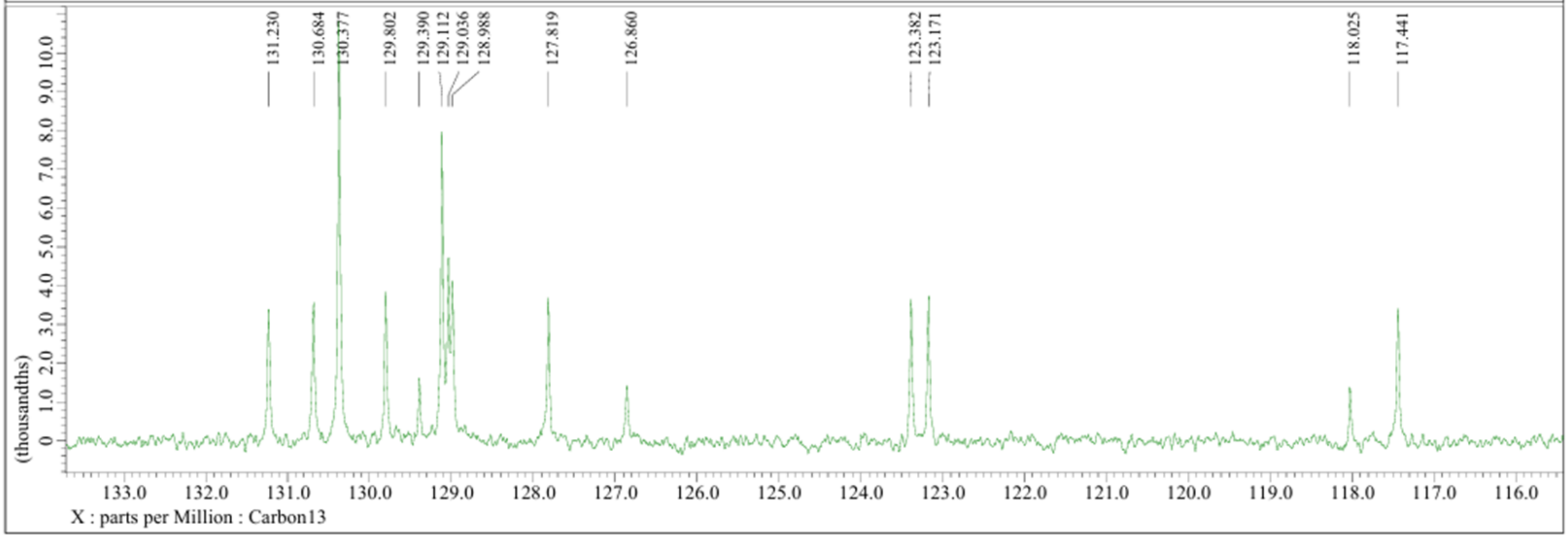


^{1}H NMR (400 MHz, CDCl$_3$)



$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)





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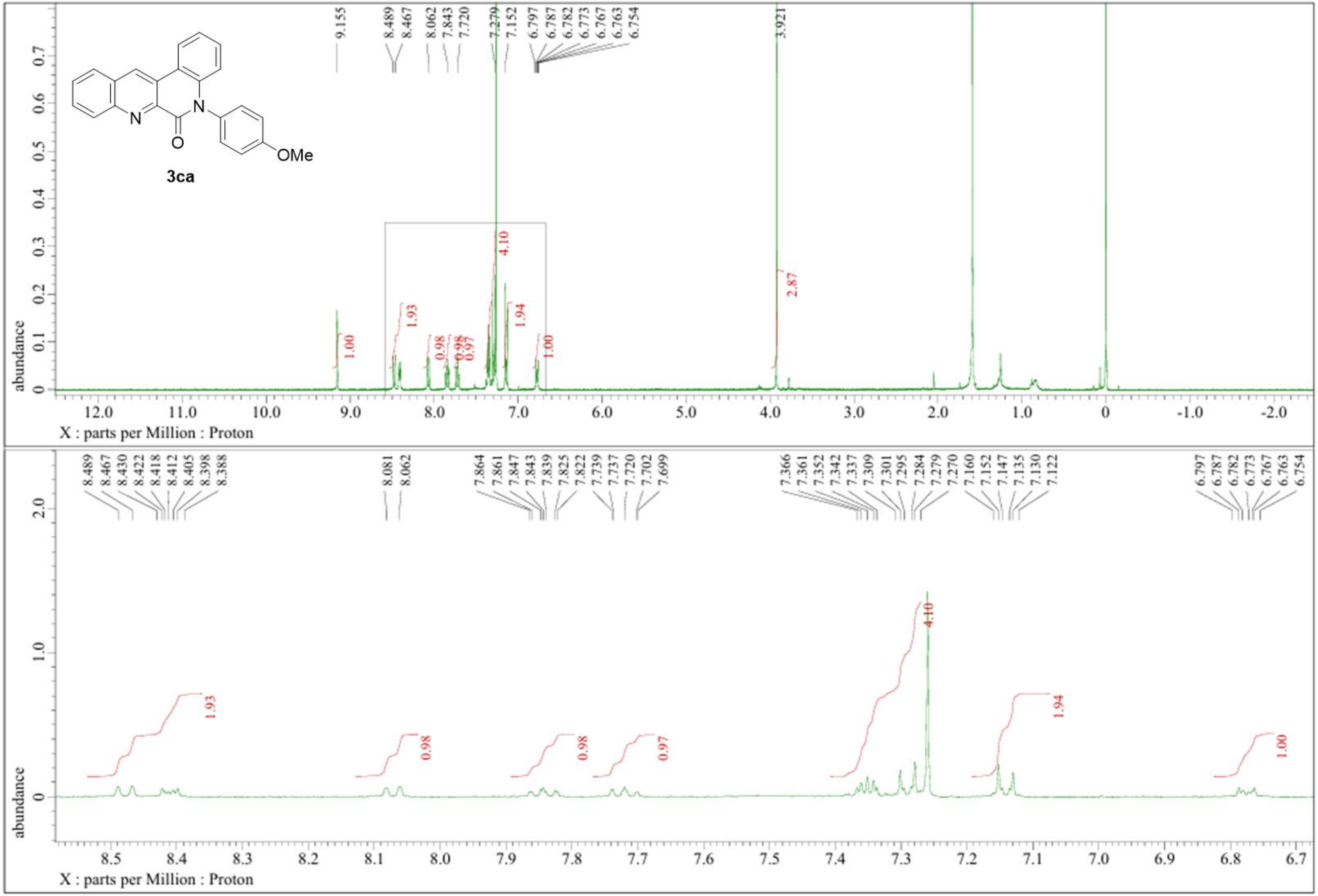
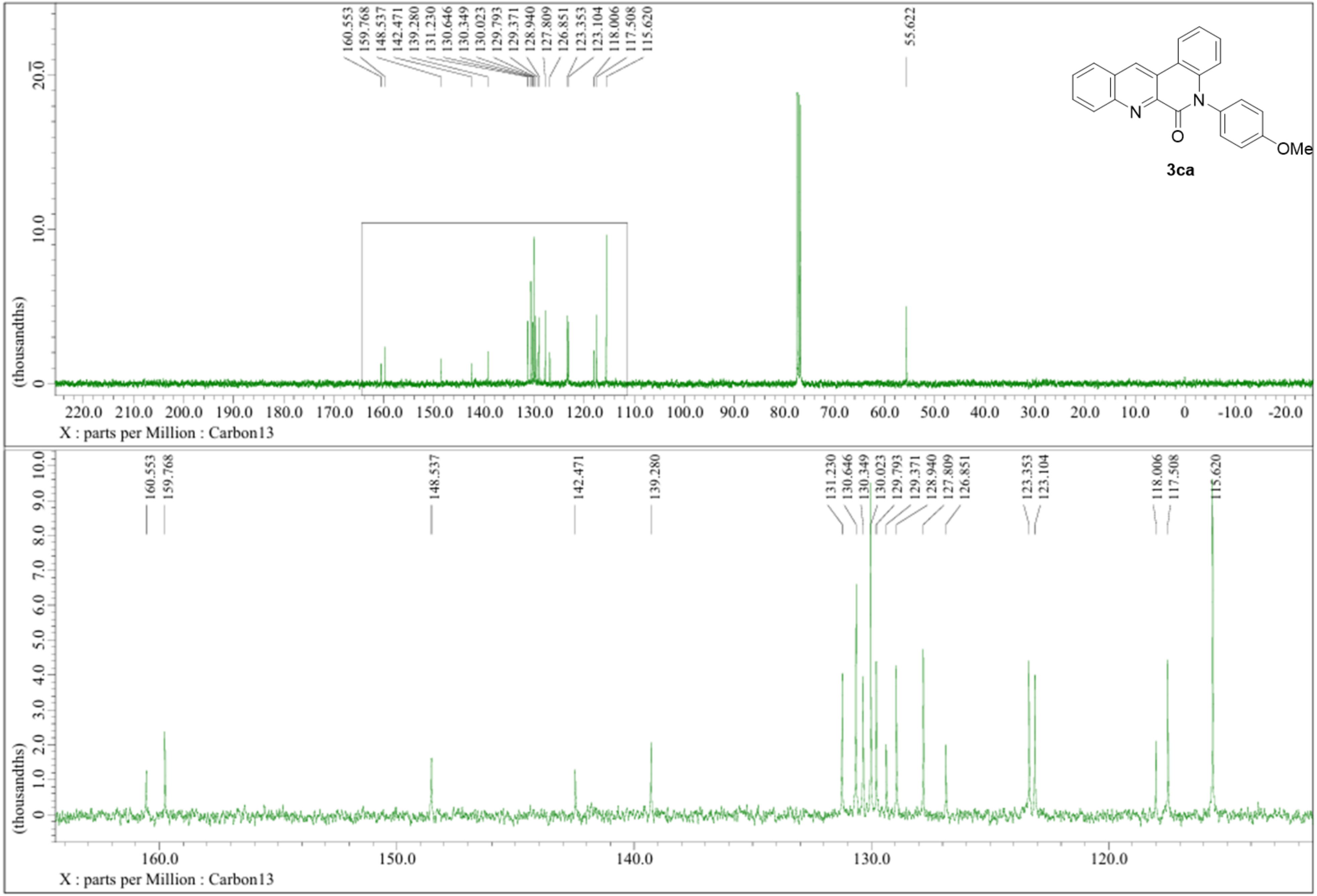
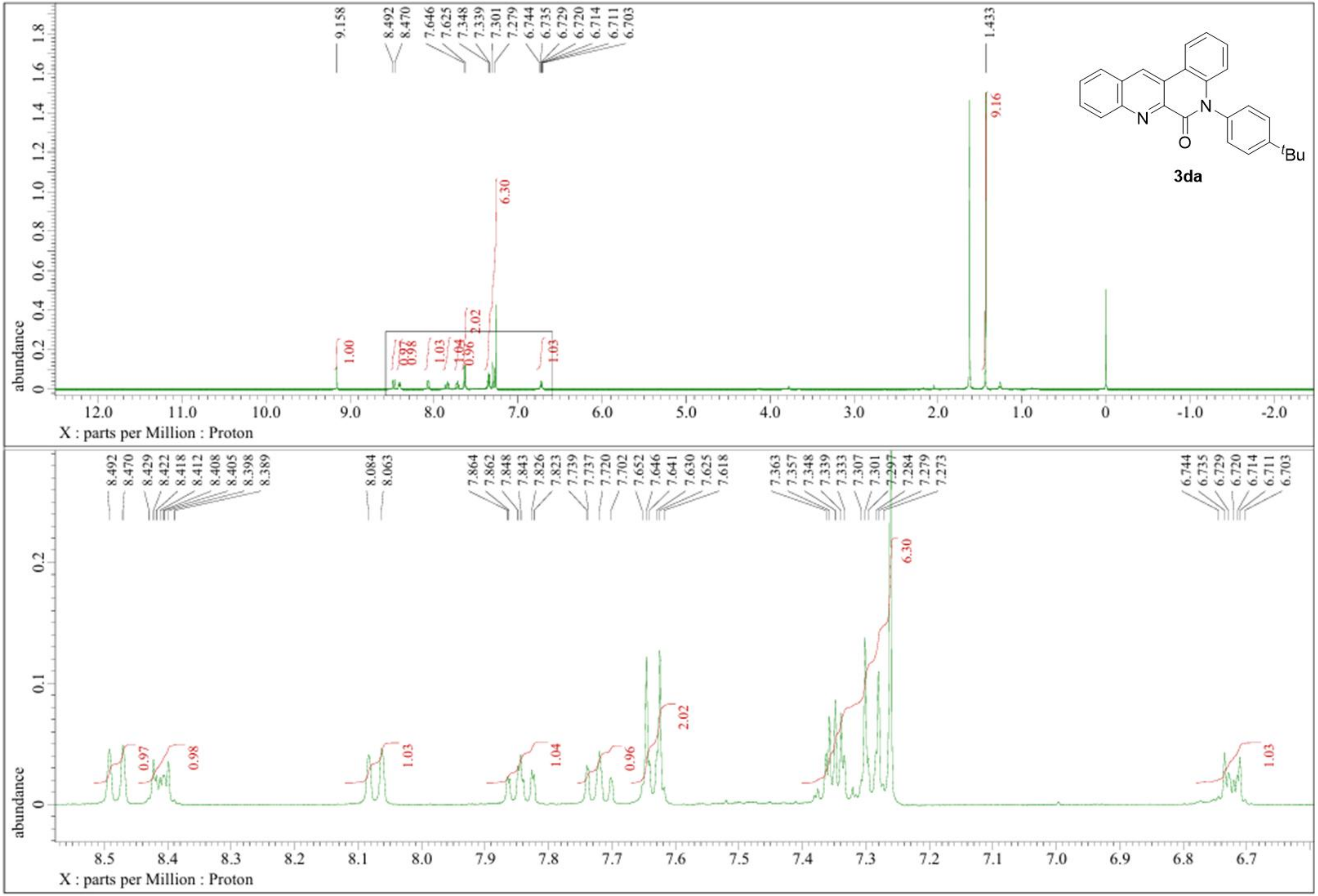


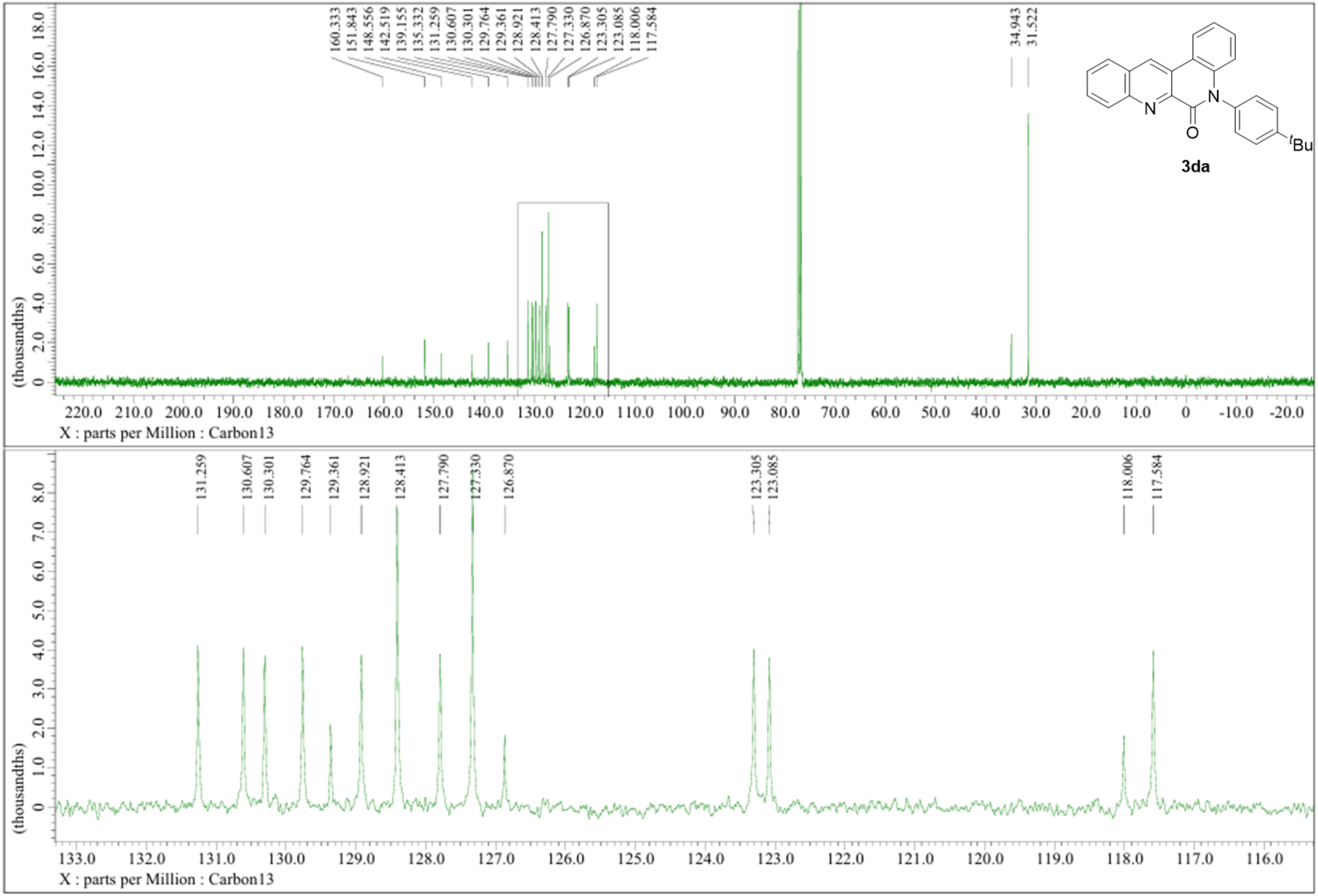
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



[1]H NMR (400 MHz, CDCl$_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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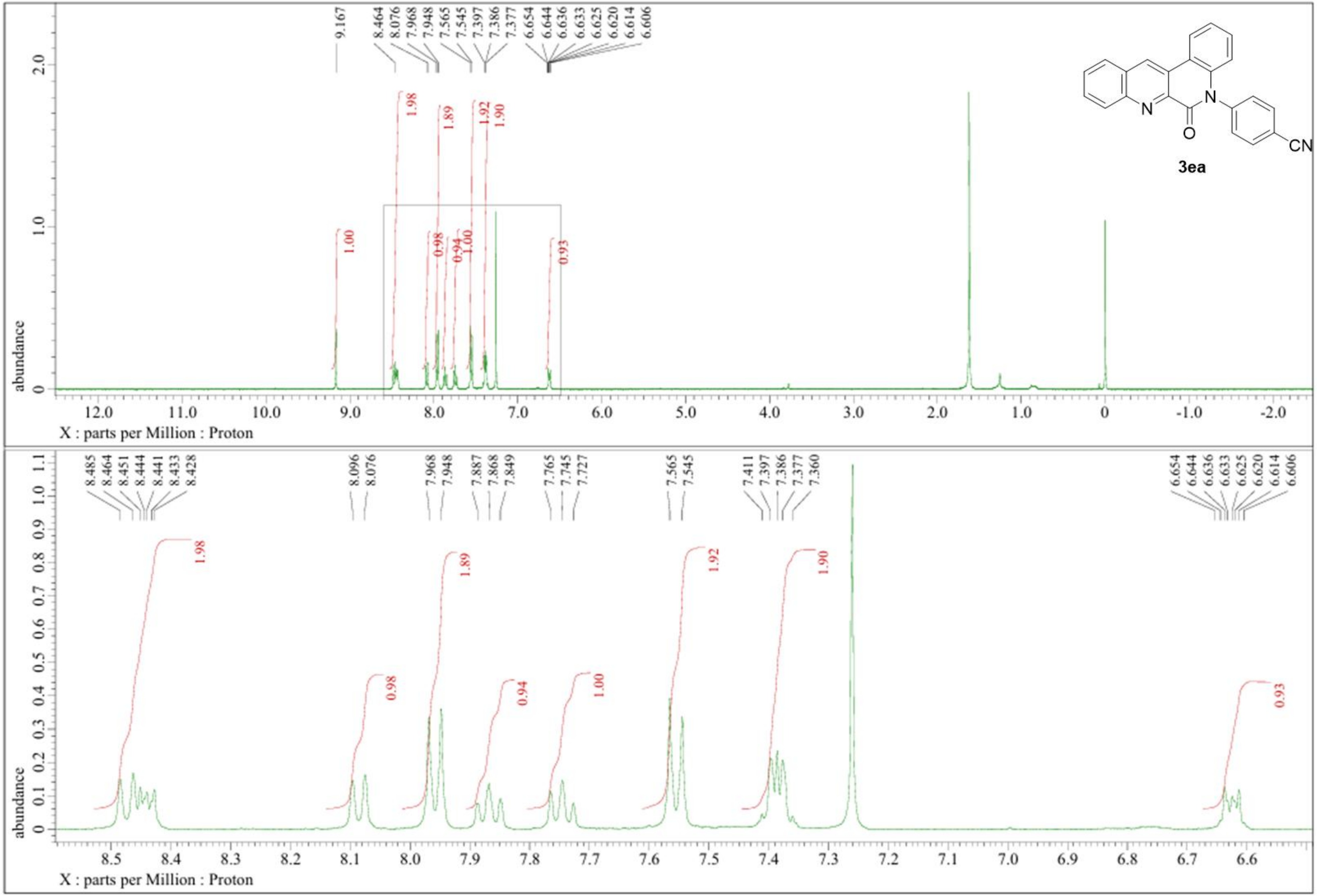

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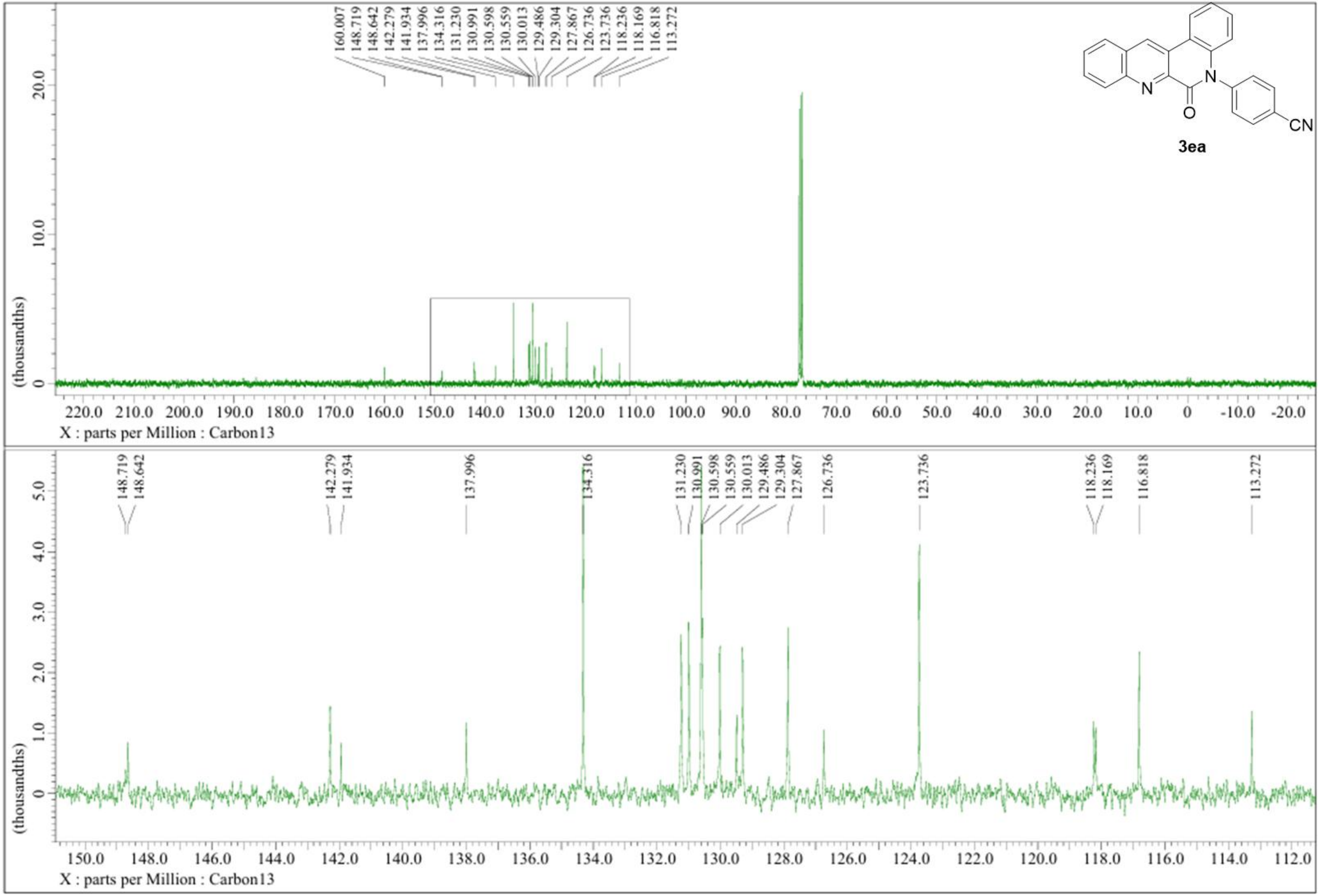

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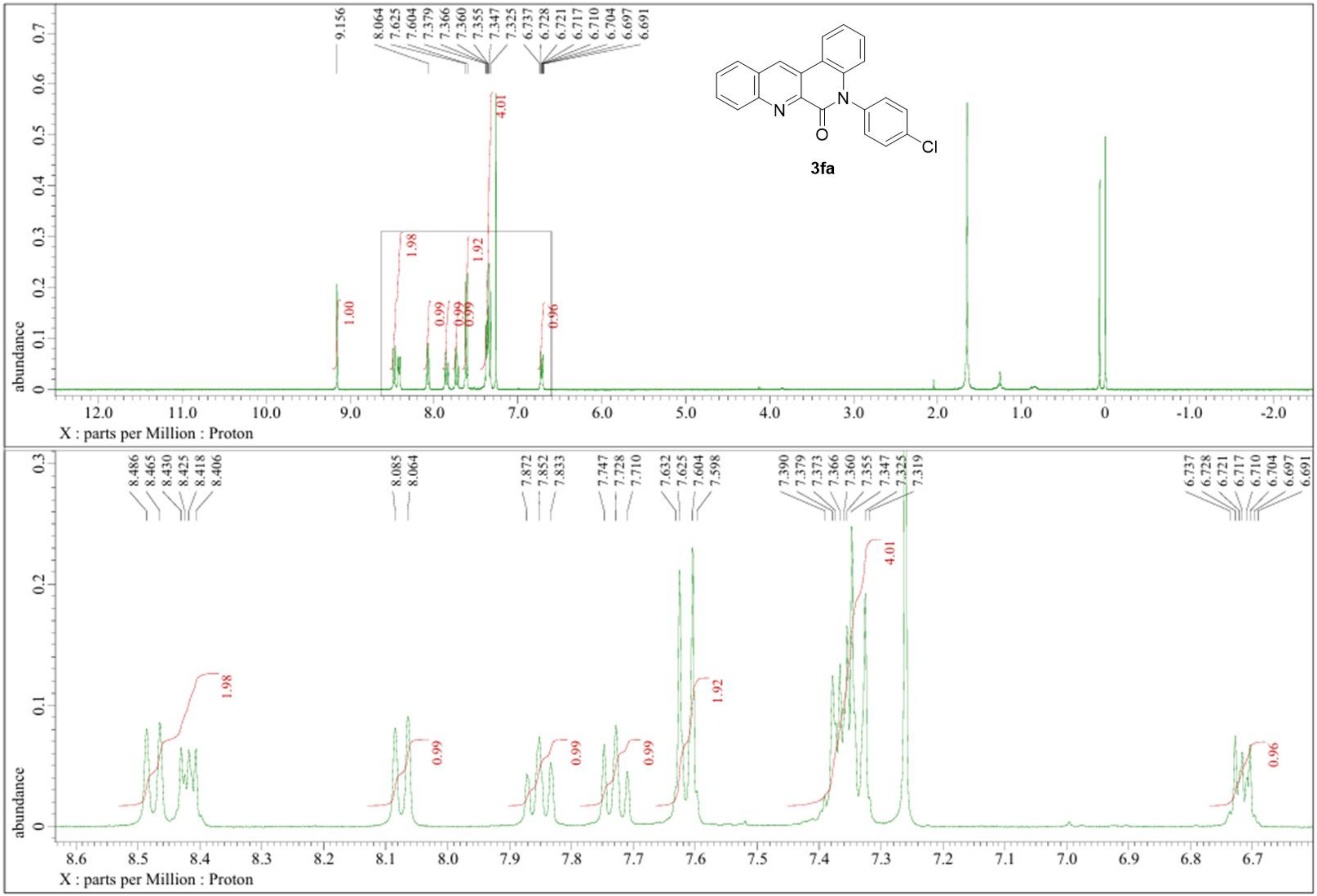

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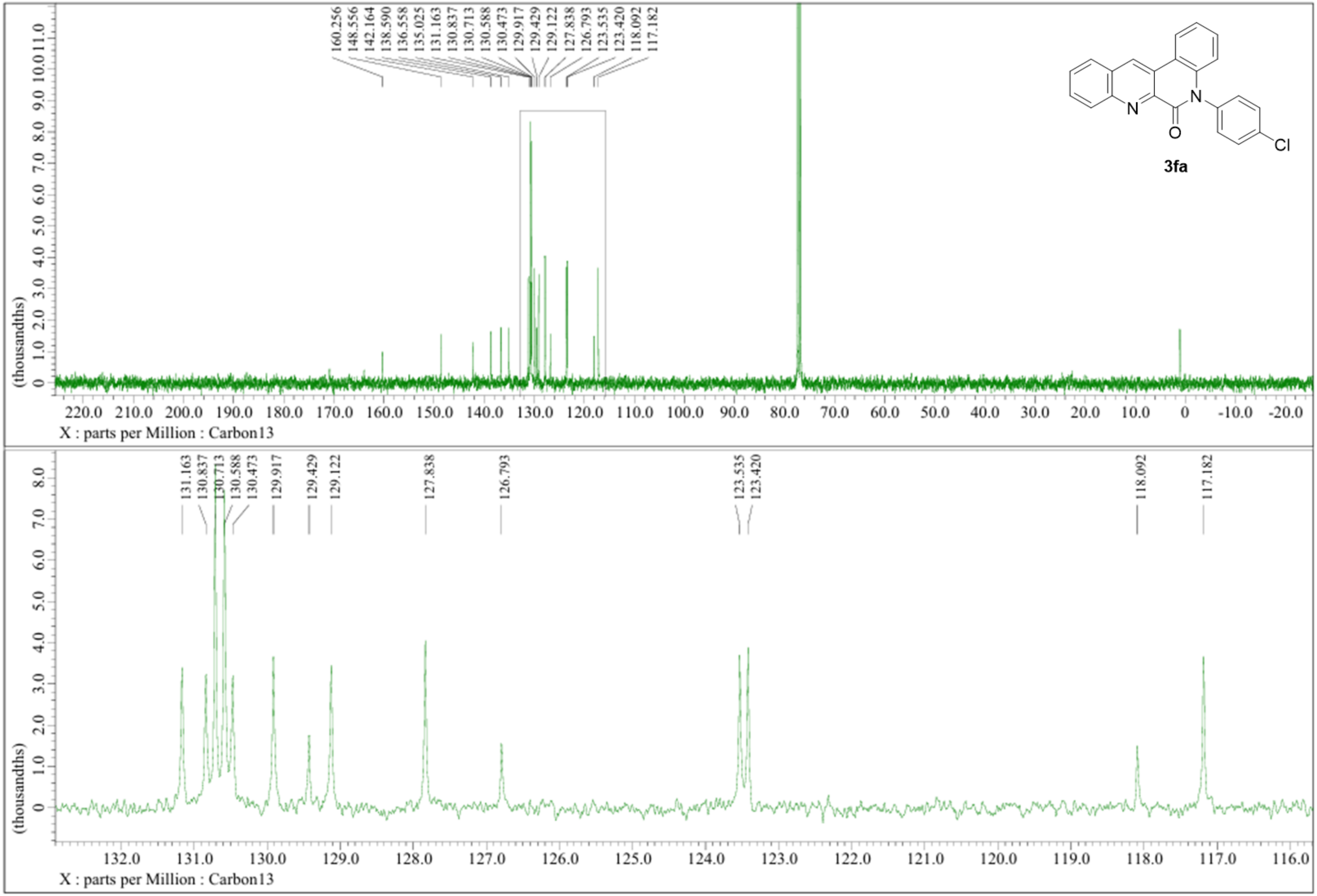

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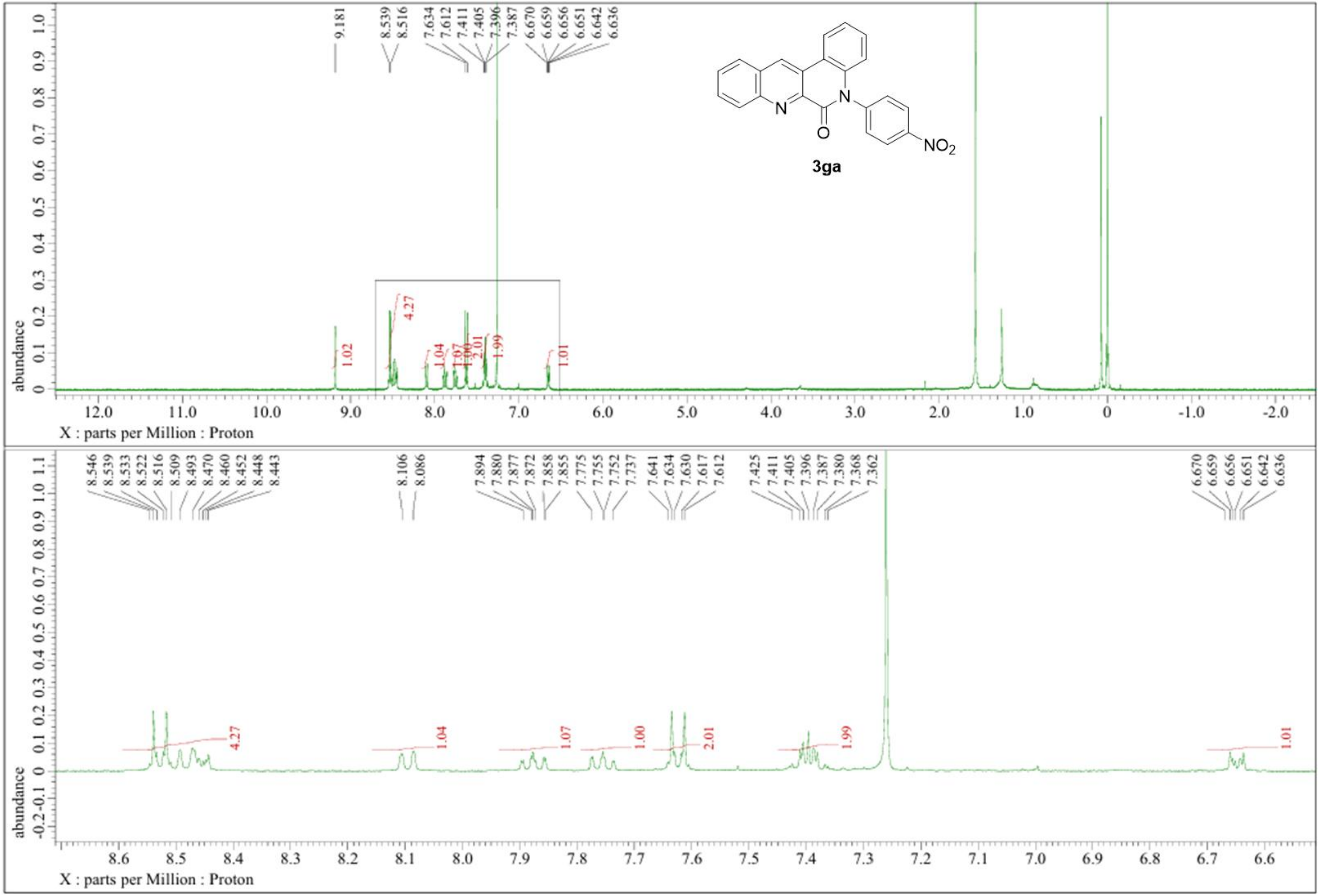

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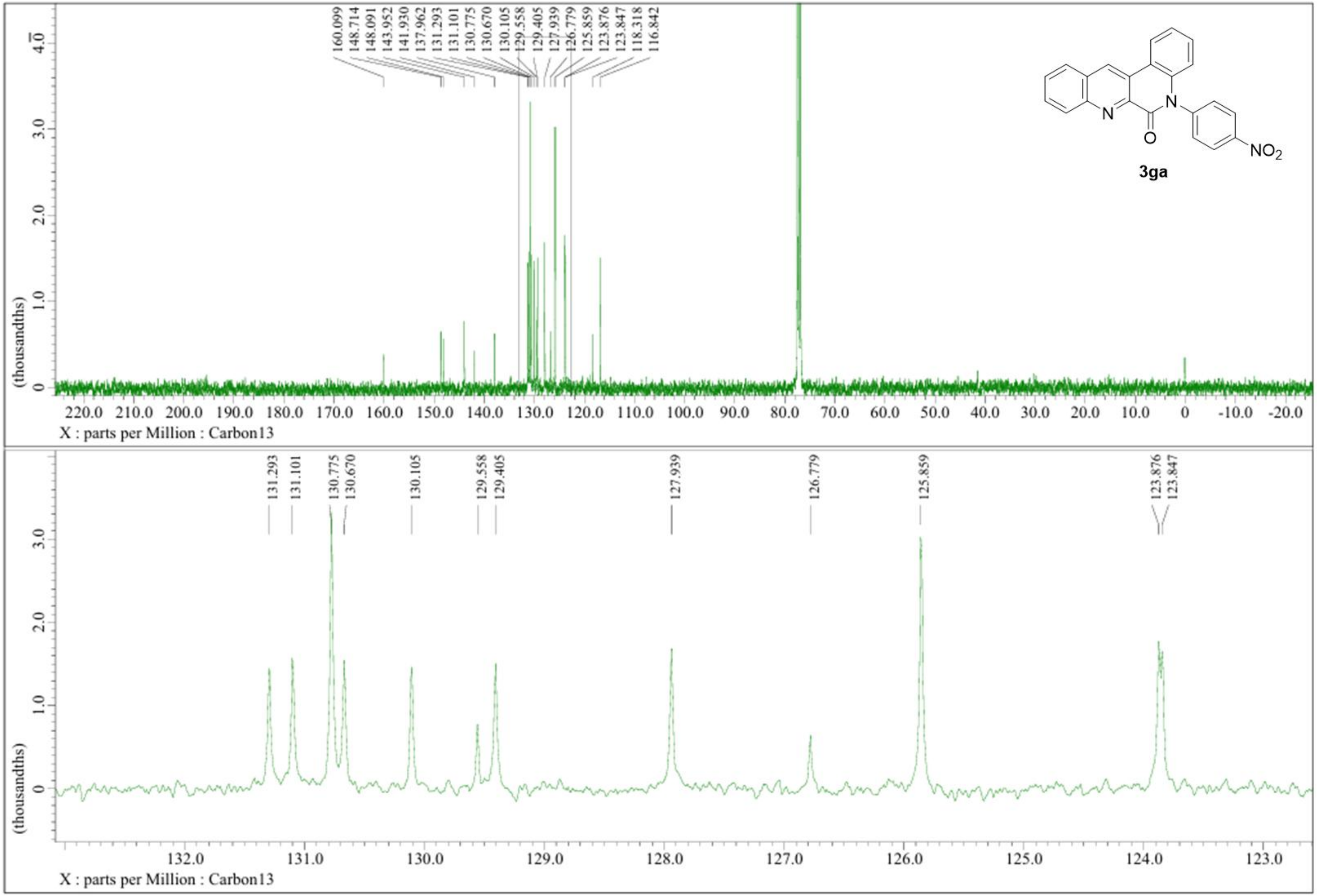

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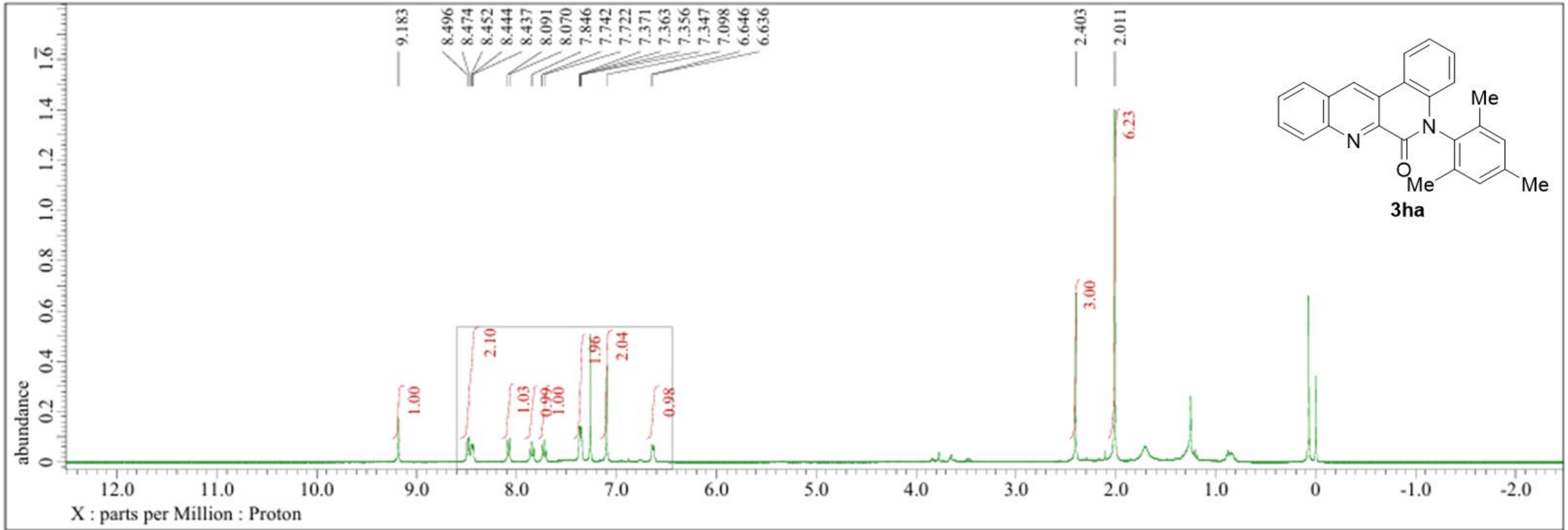

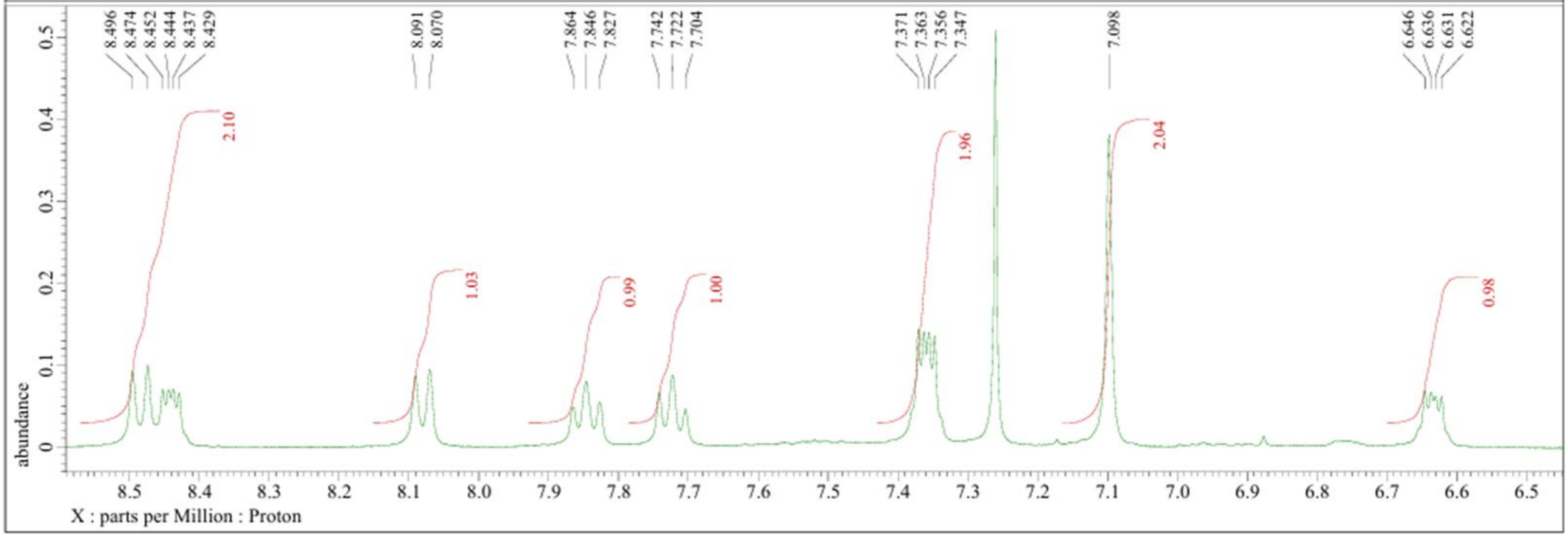

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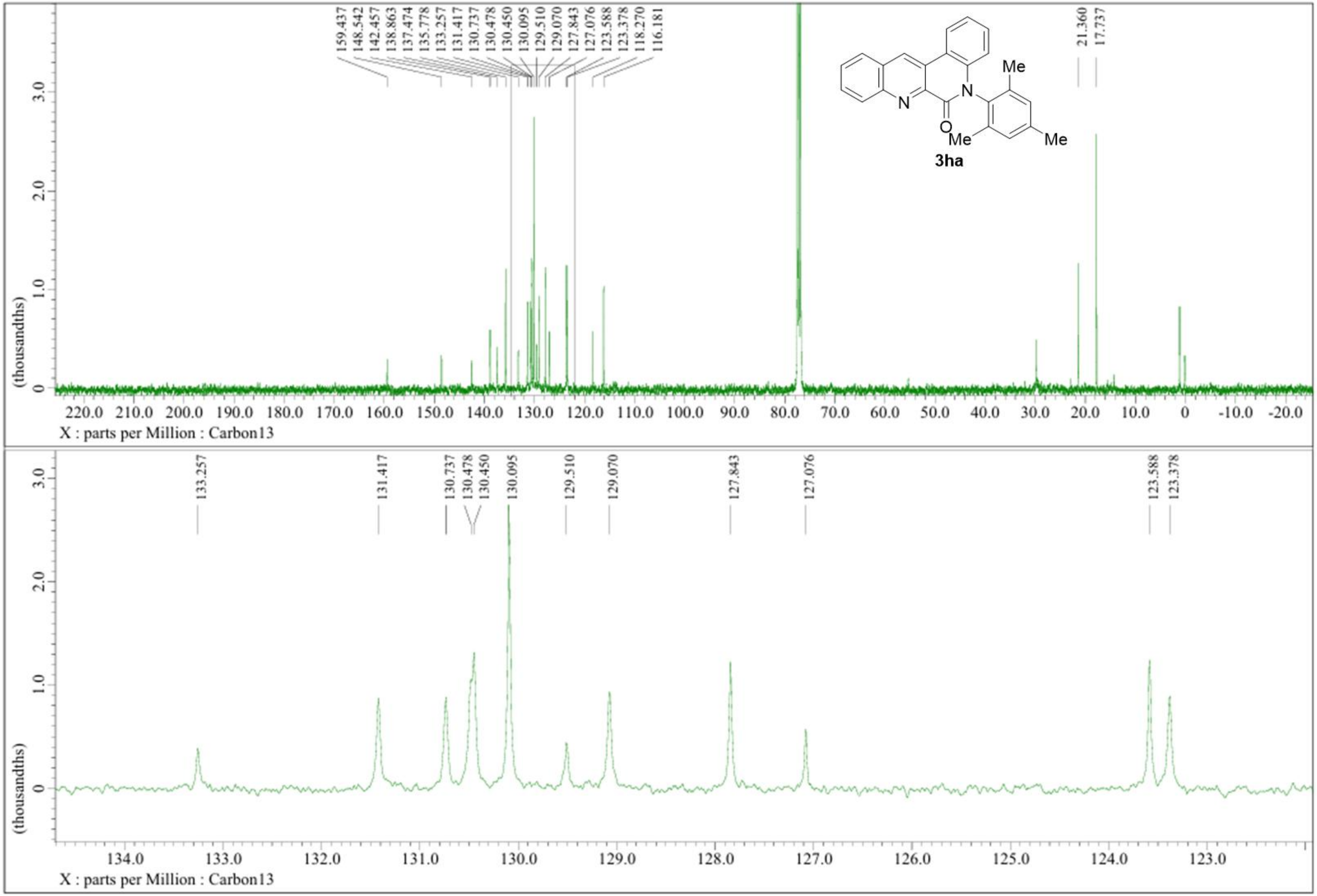

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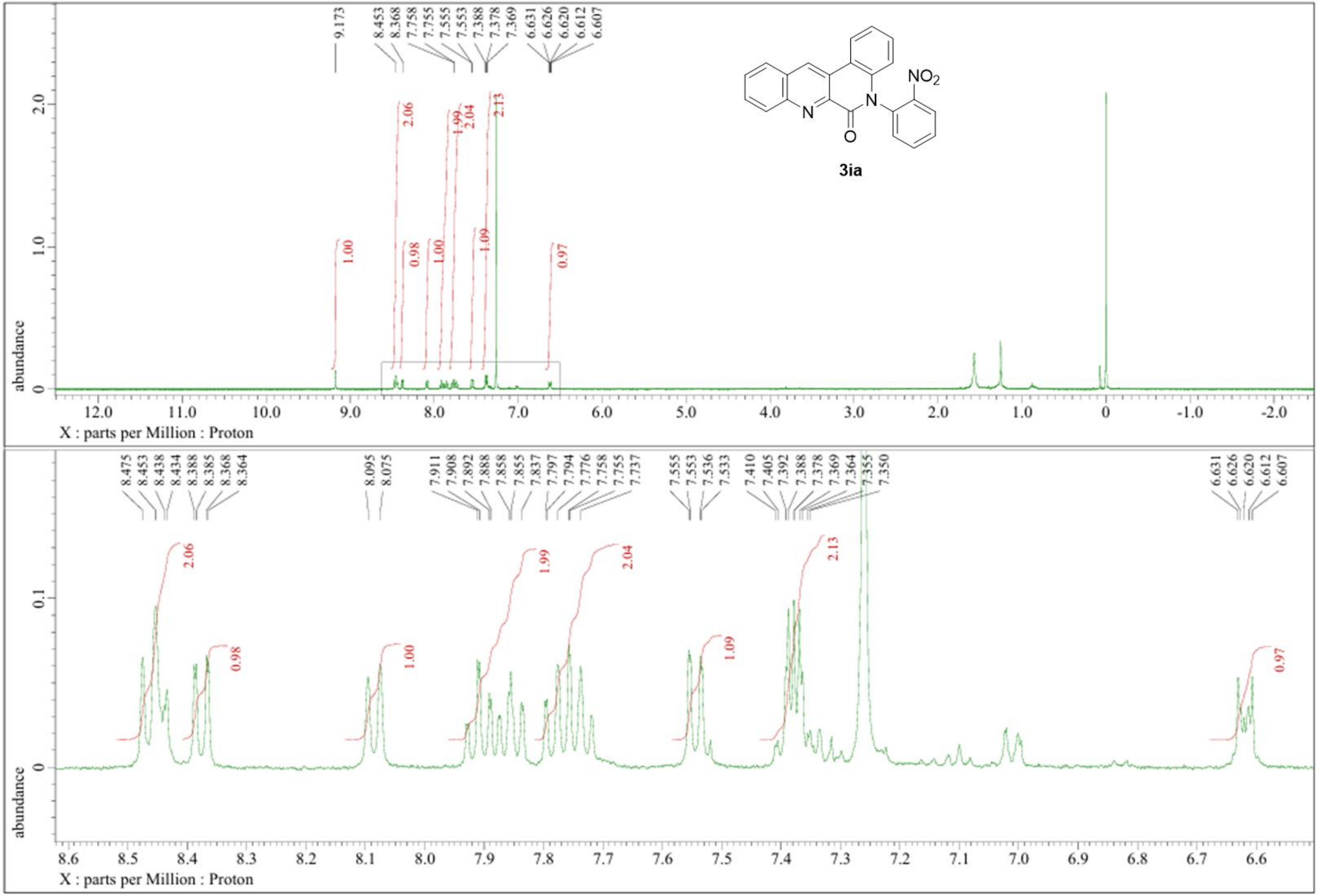

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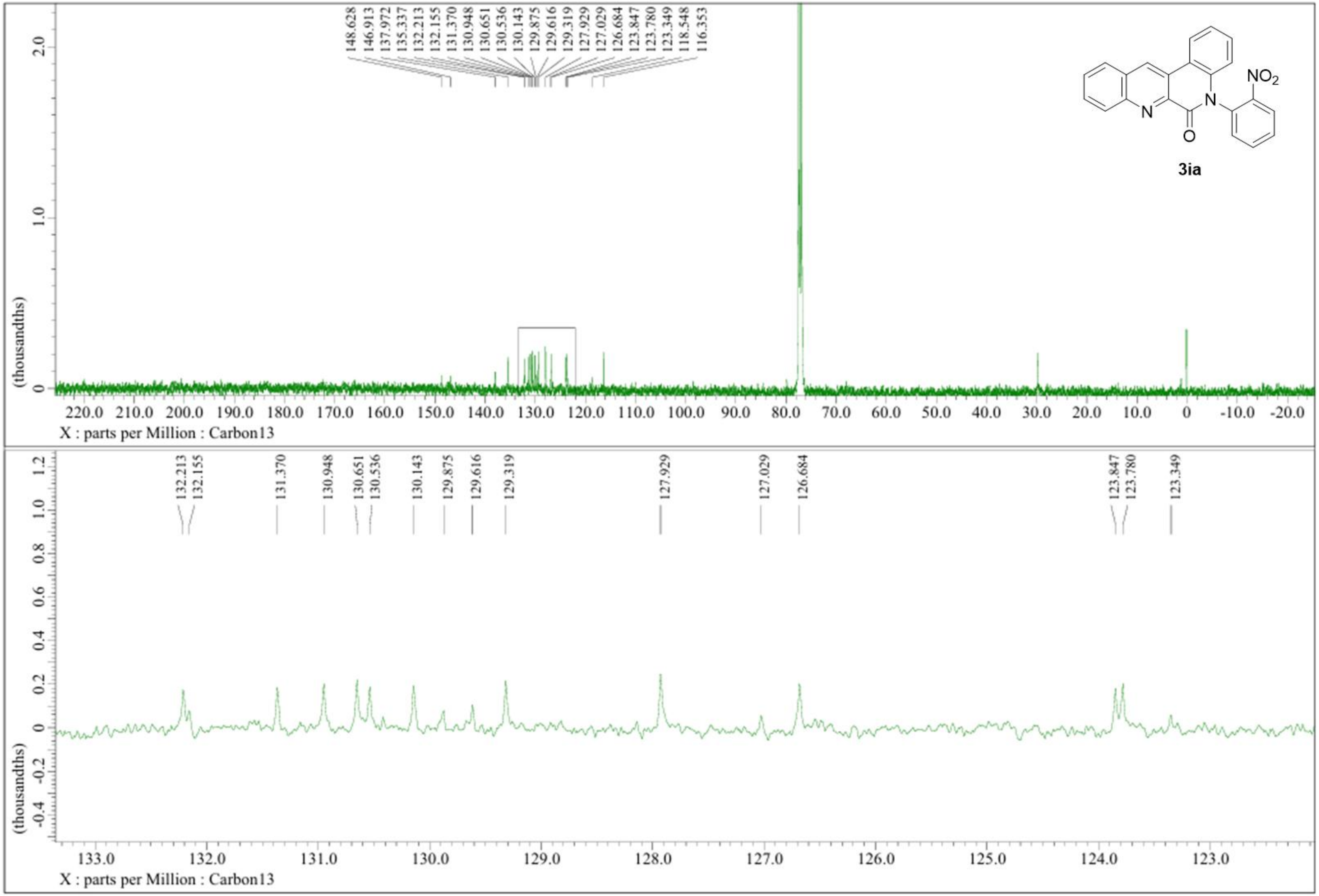

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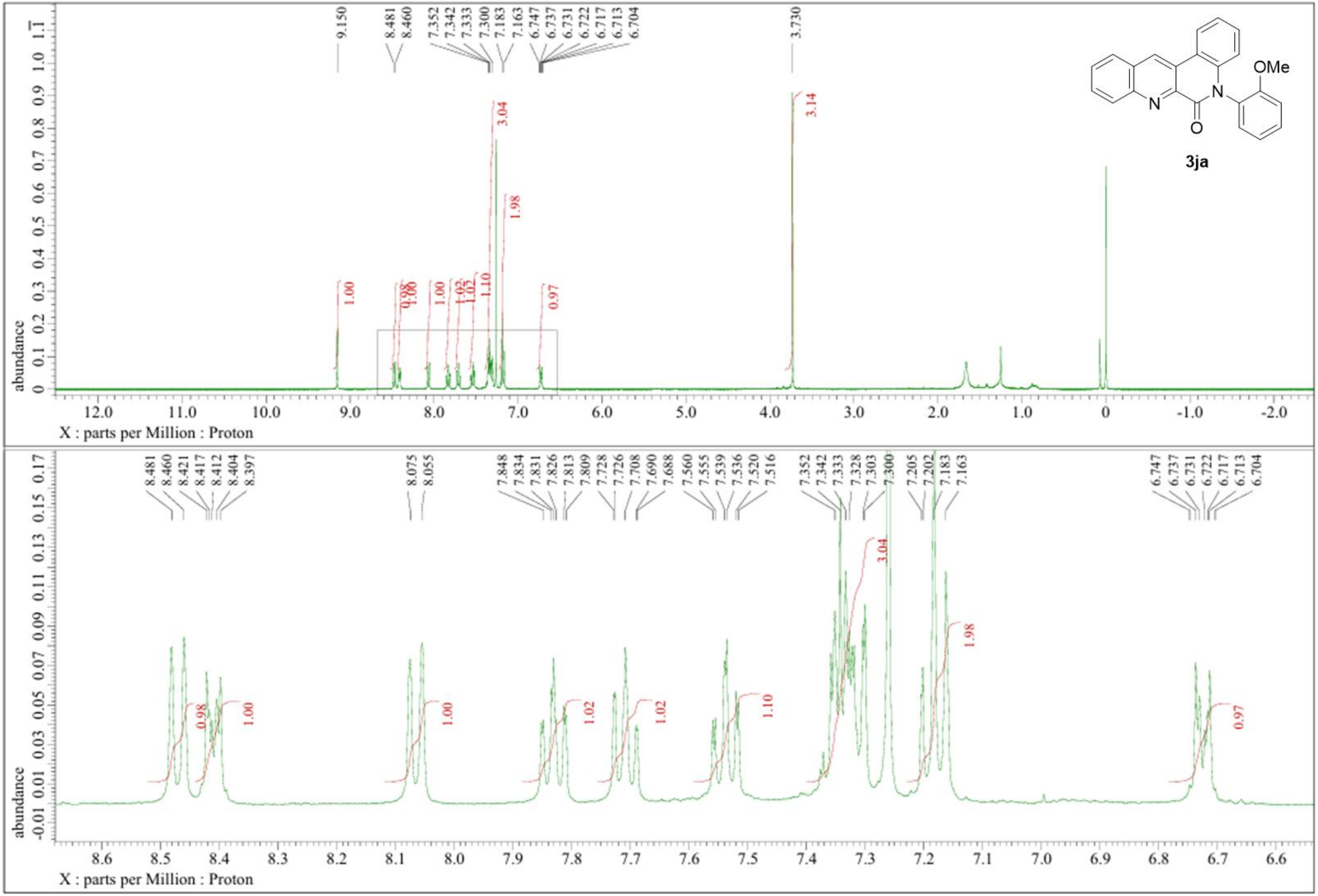
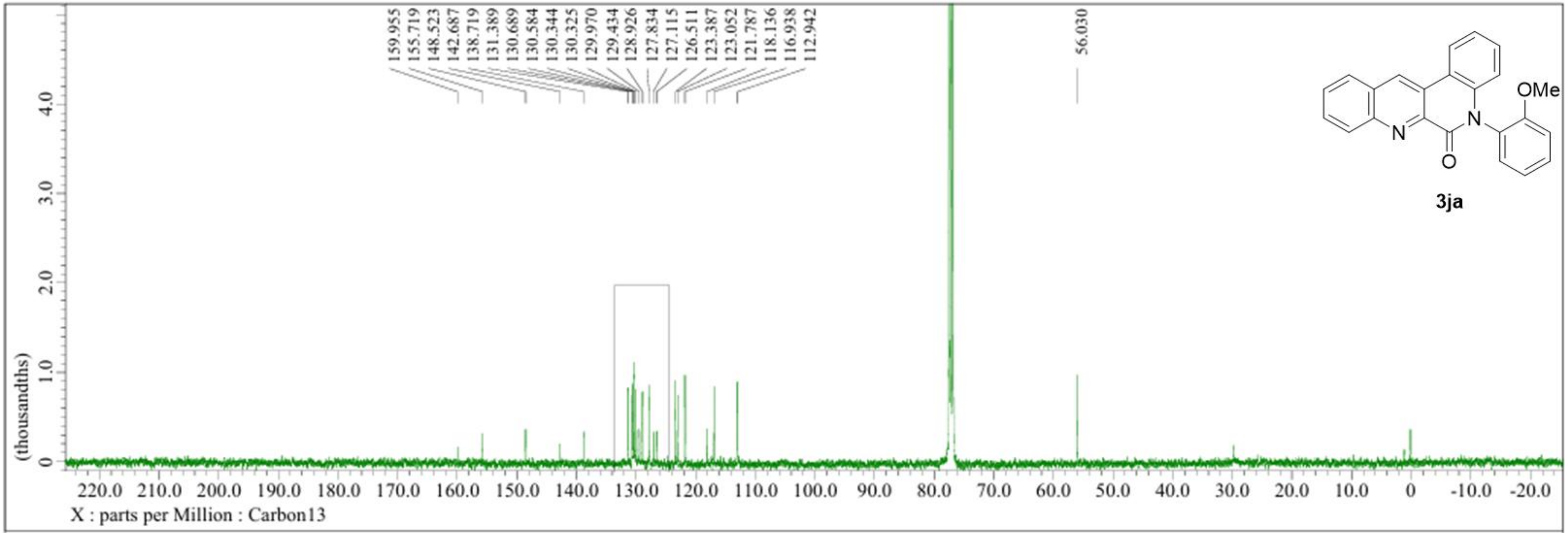
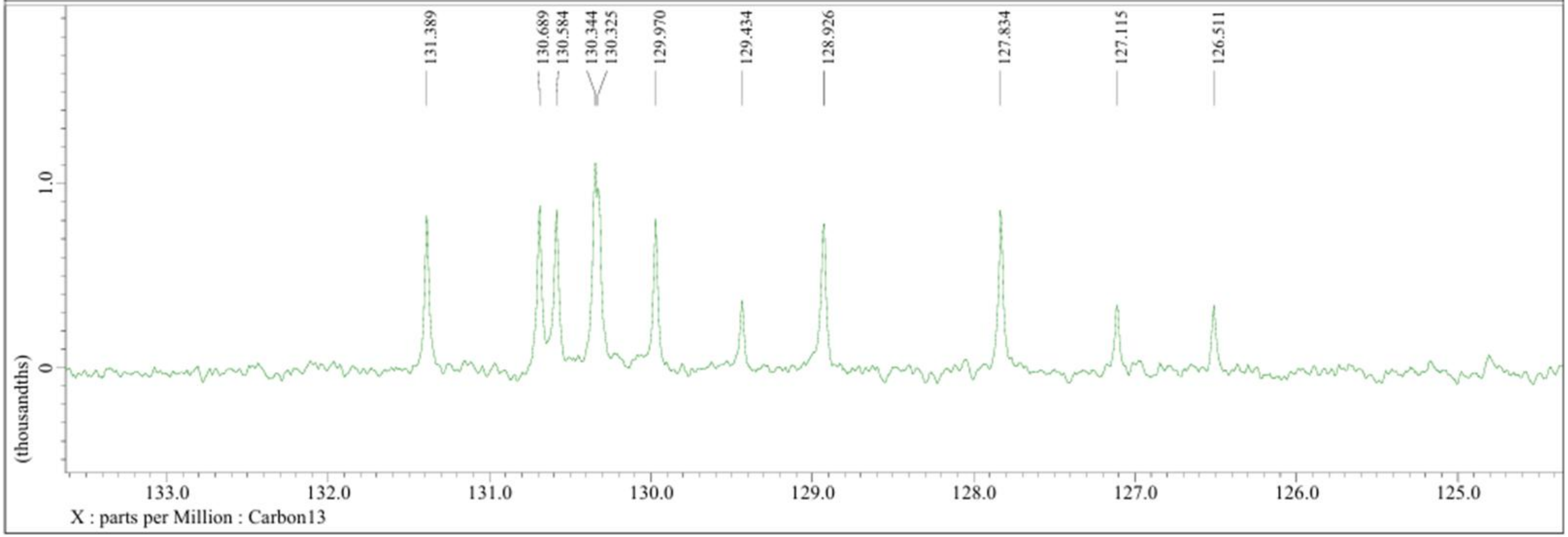
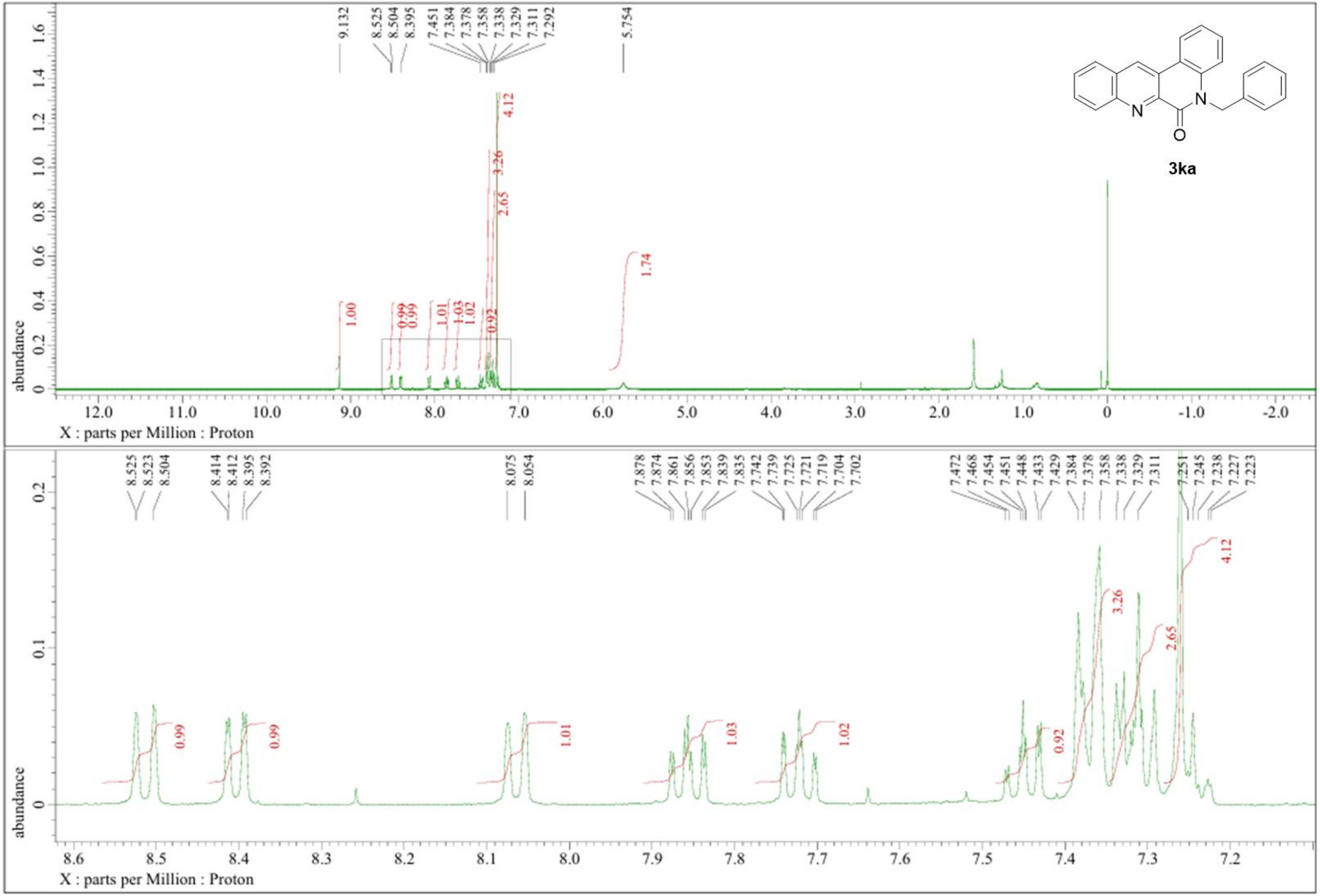


$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)





[1]H NMR (400 MHz, CDCl₃)



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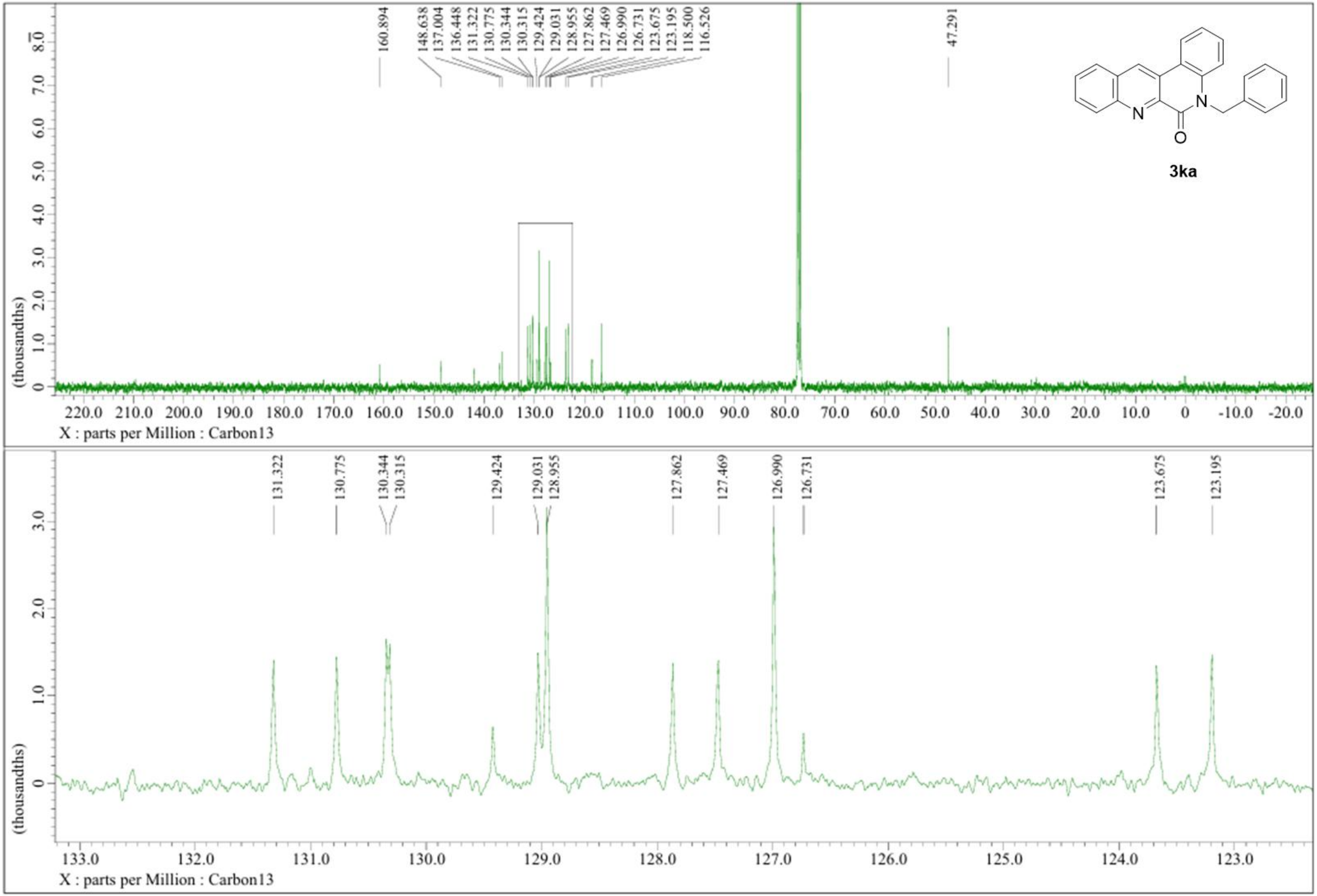

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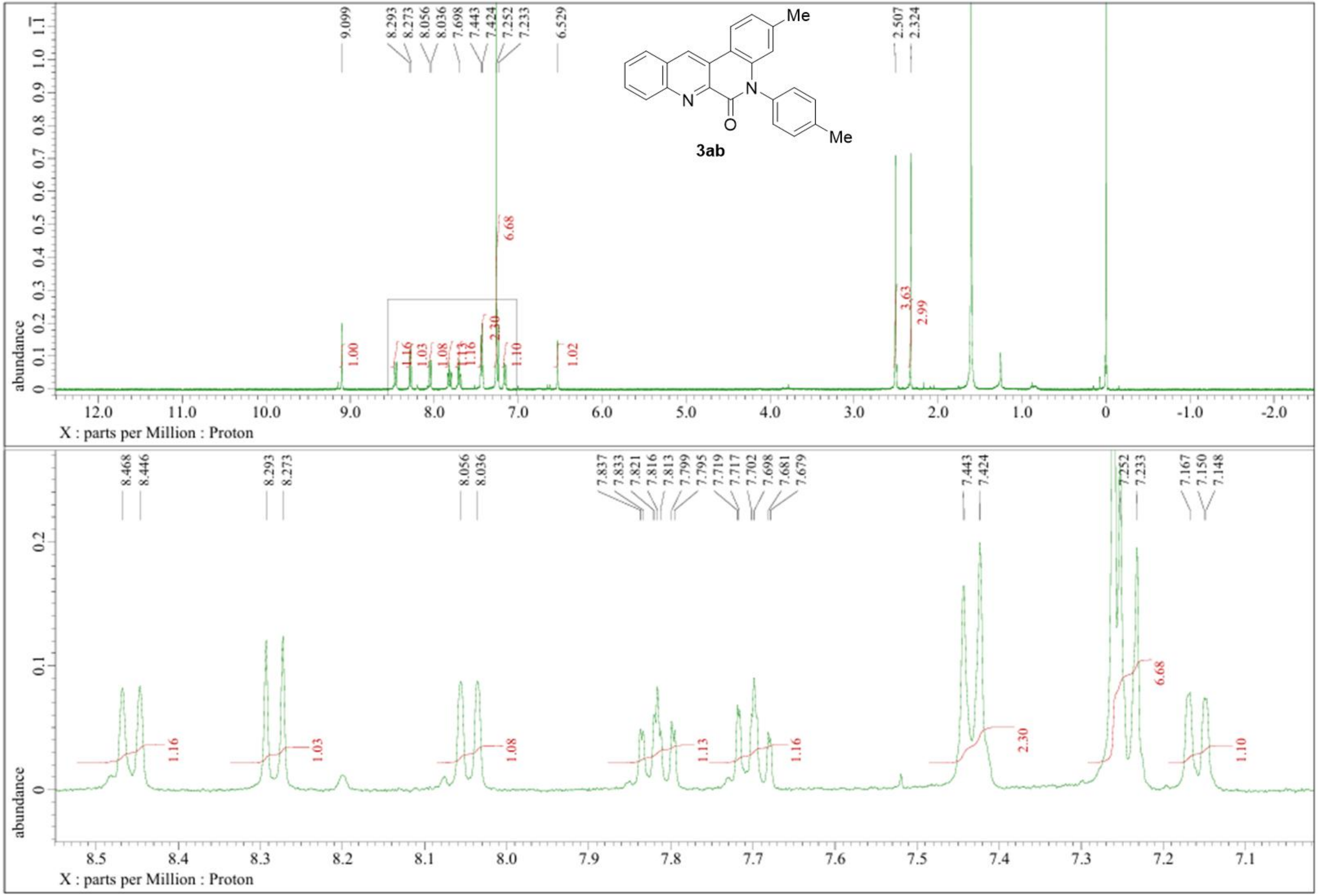

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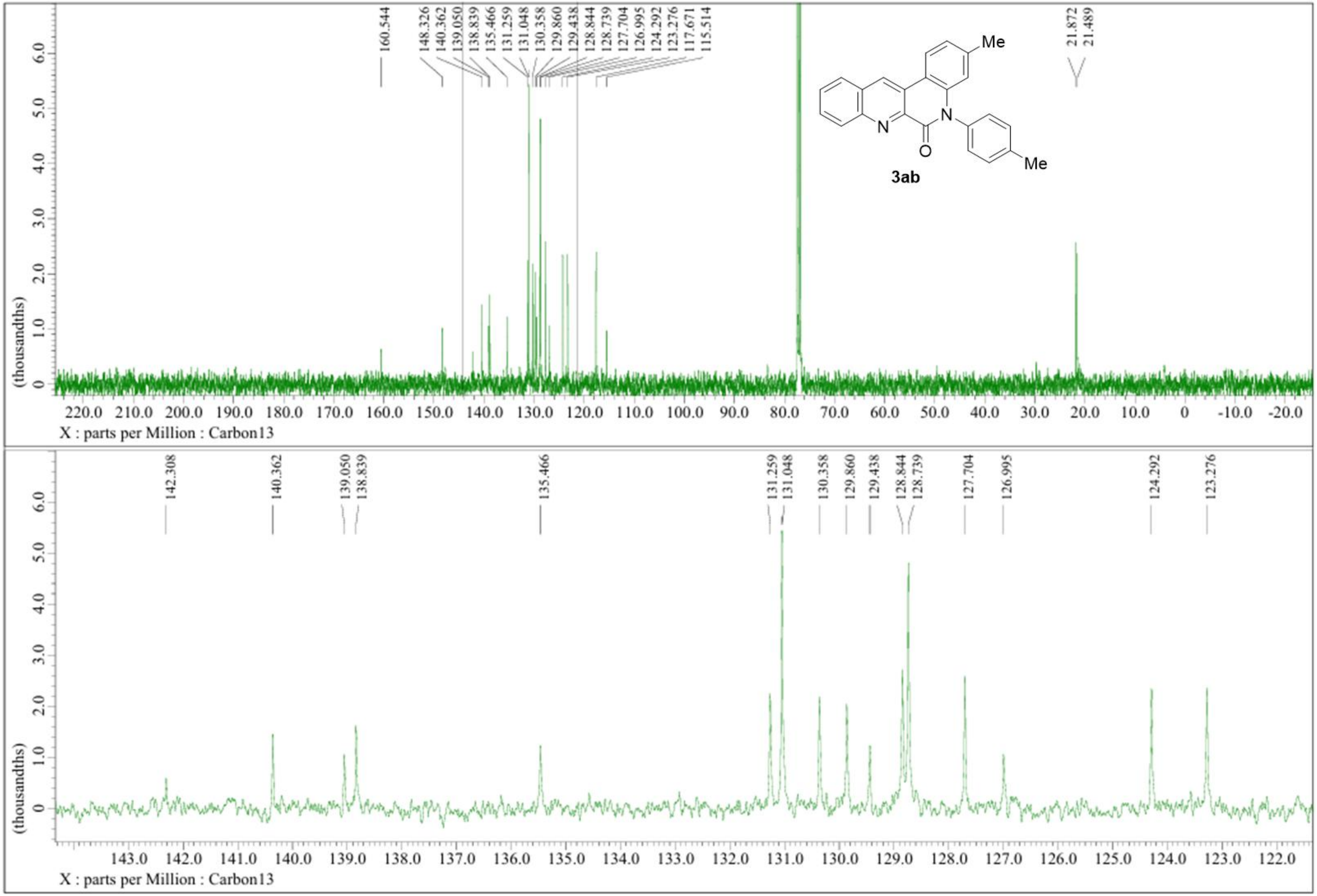

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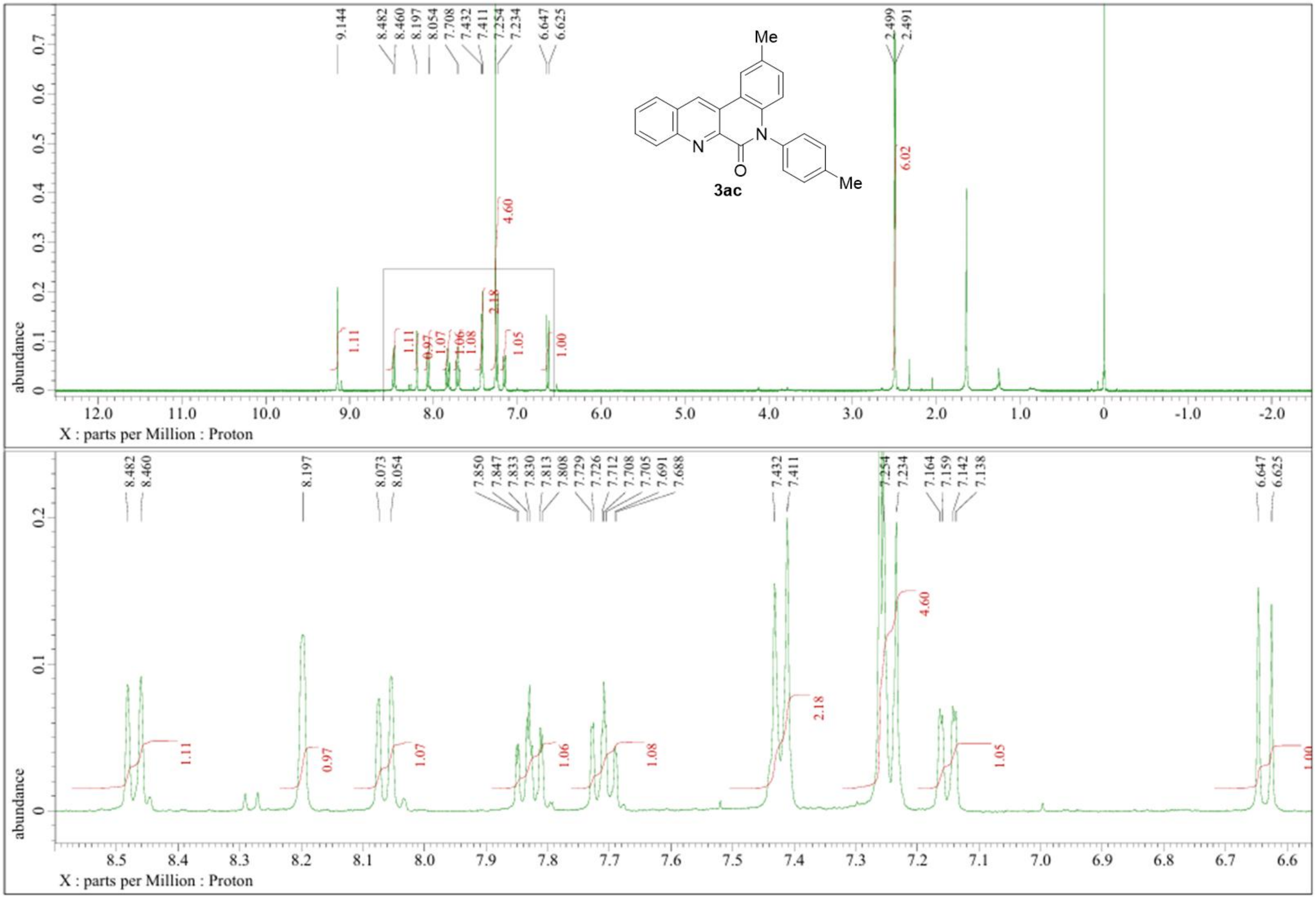

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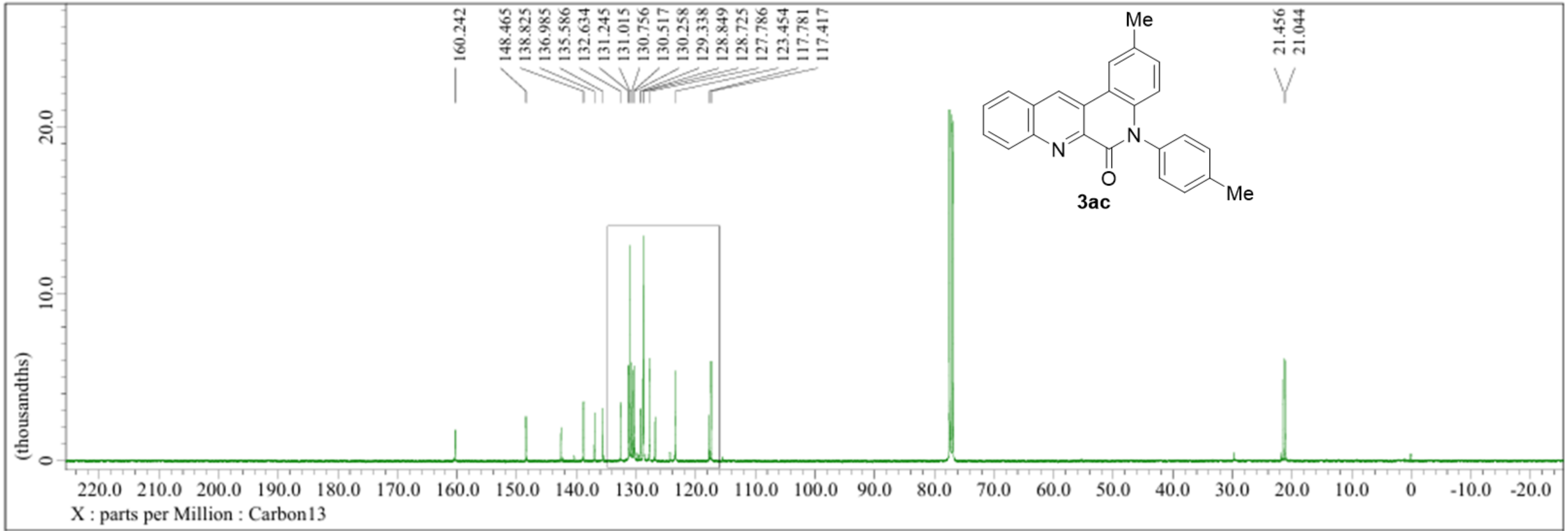

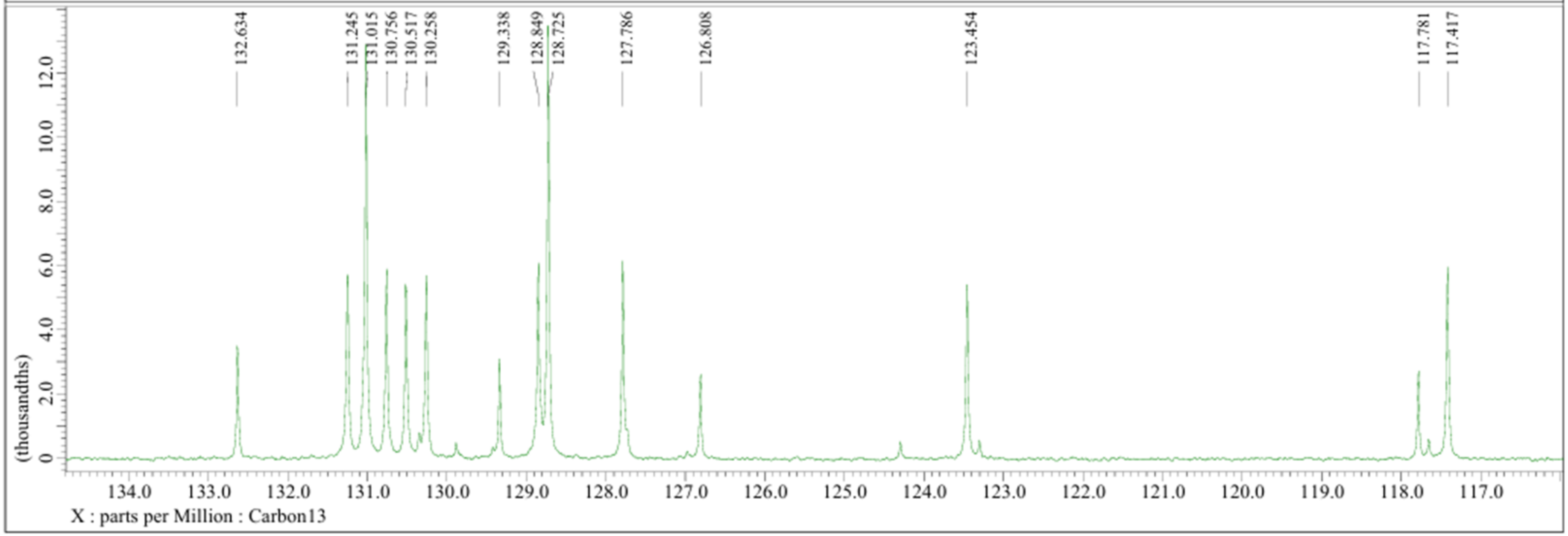

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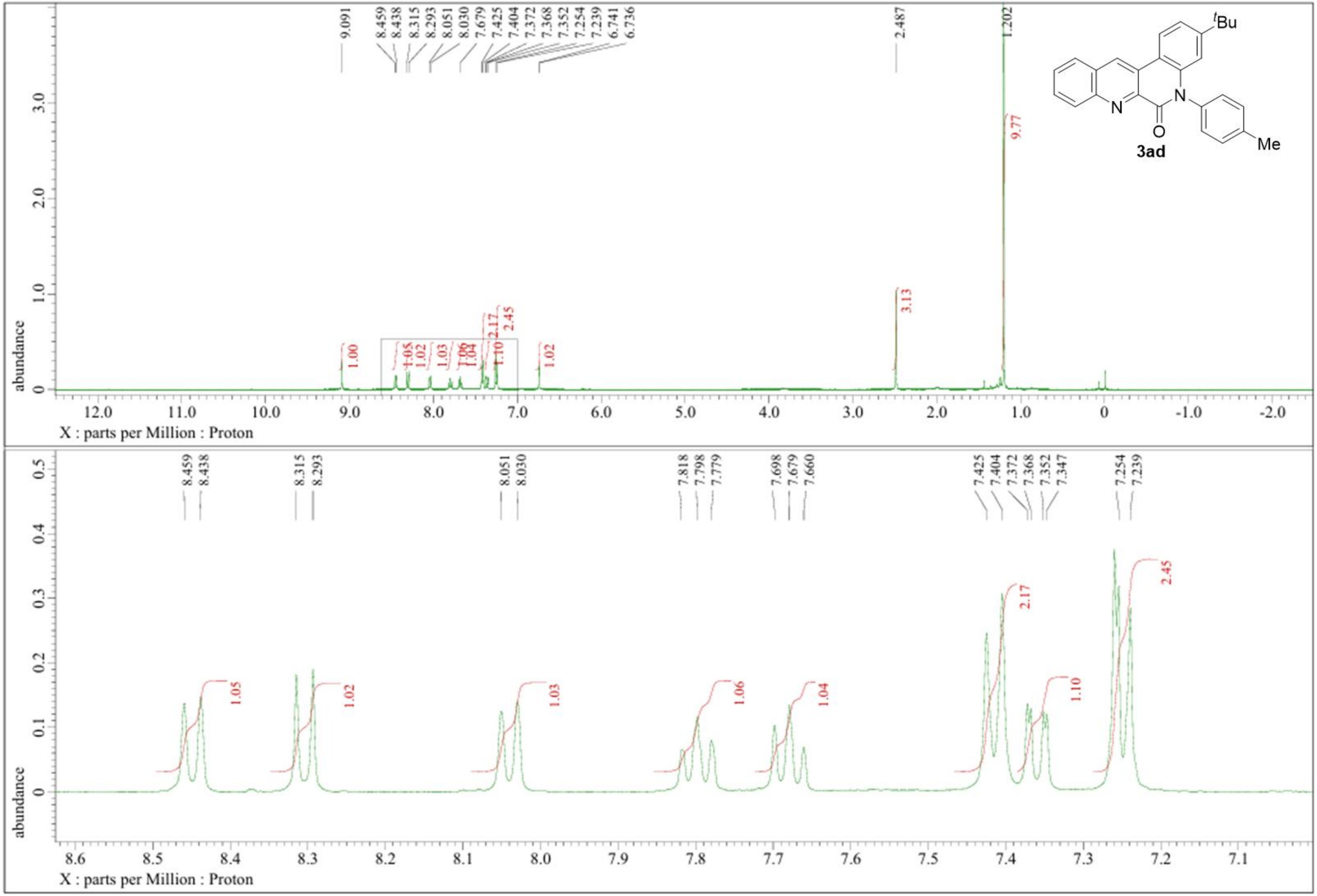

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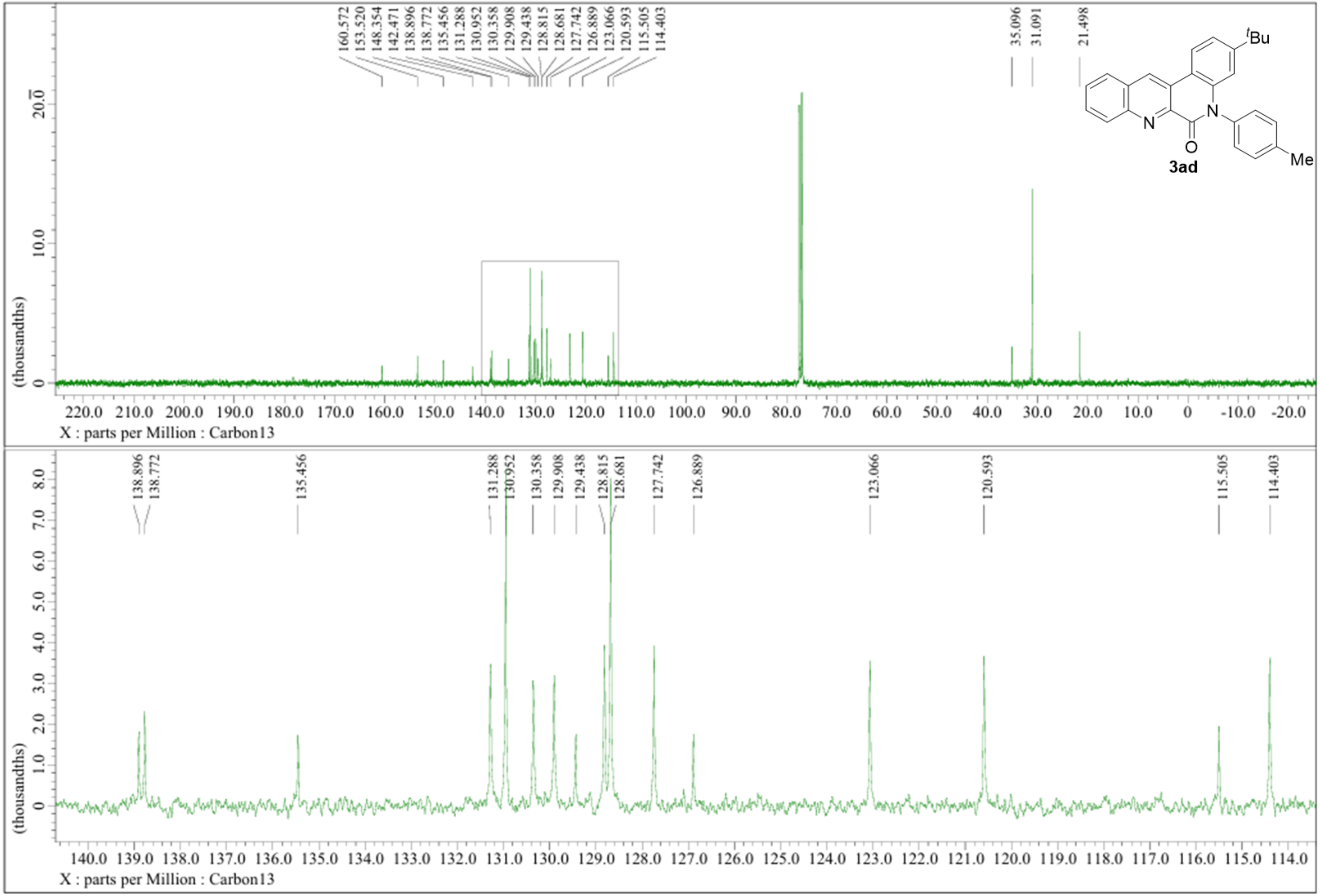

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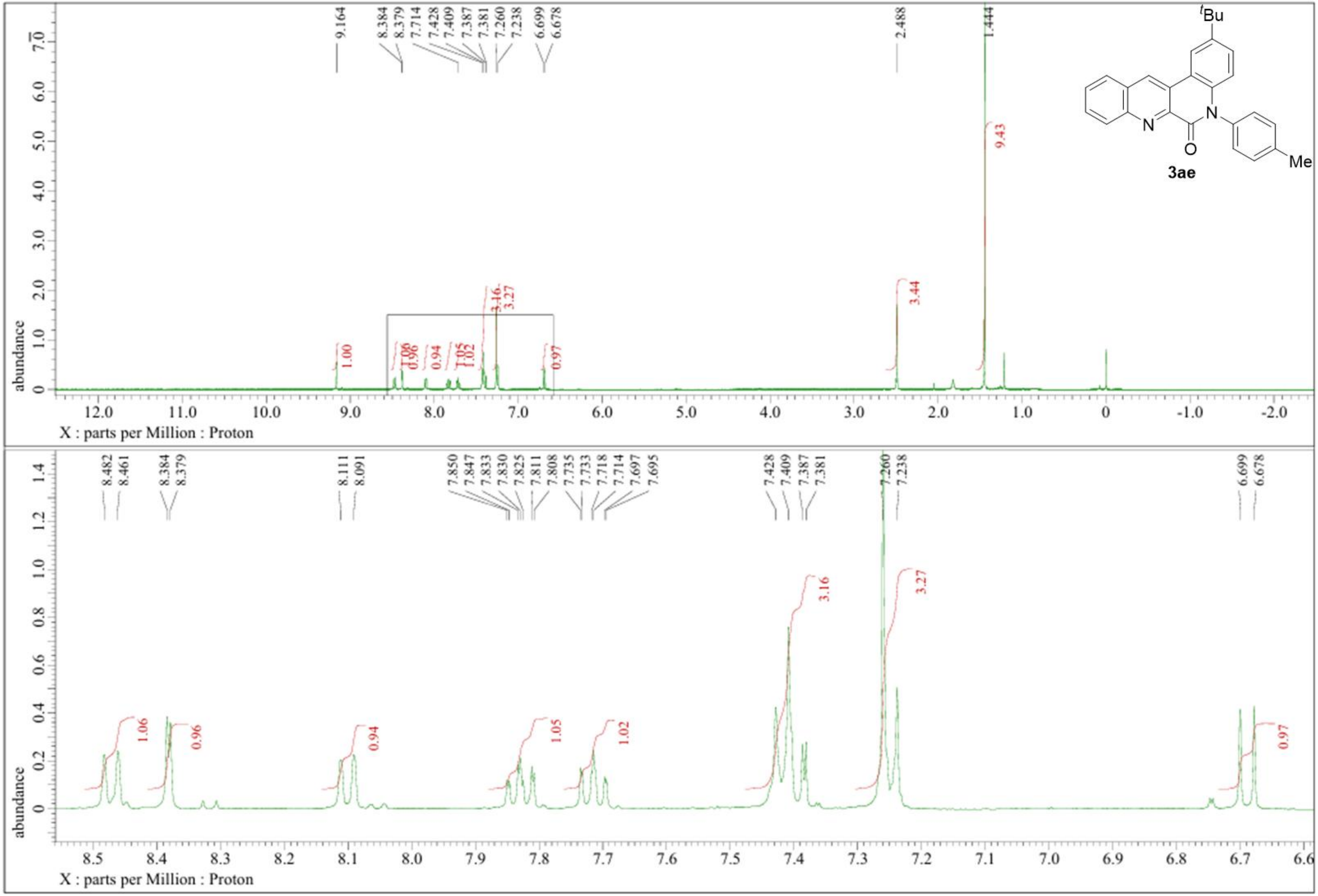

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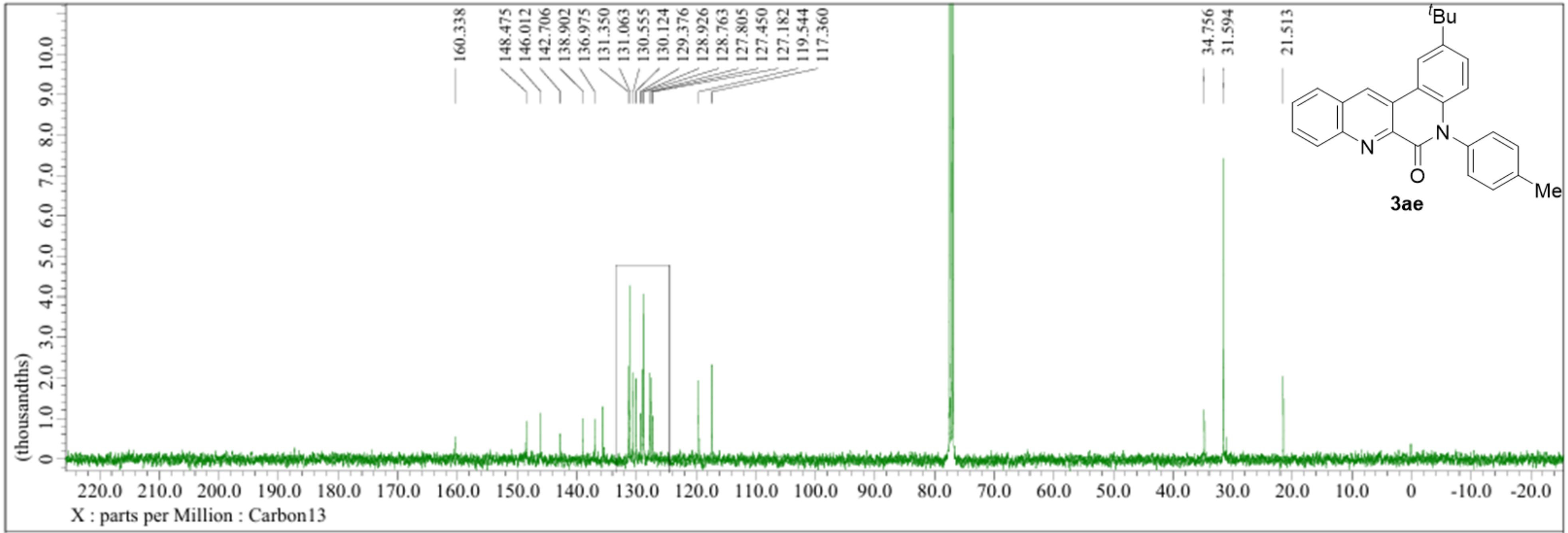

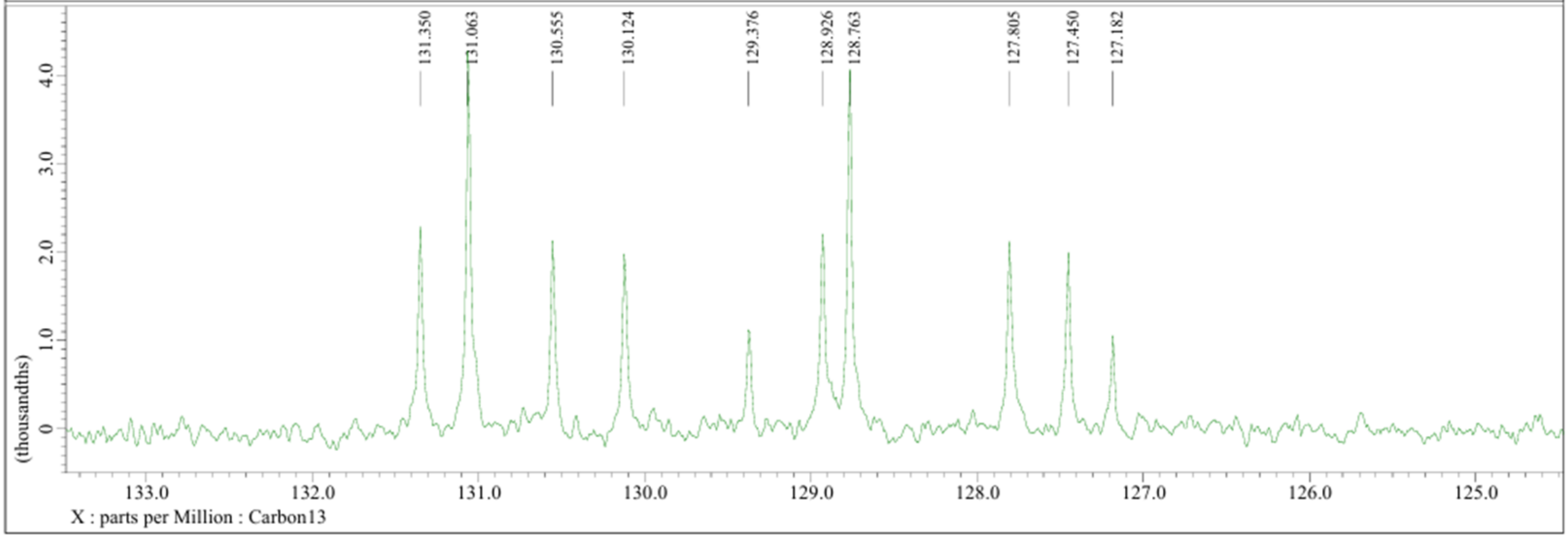

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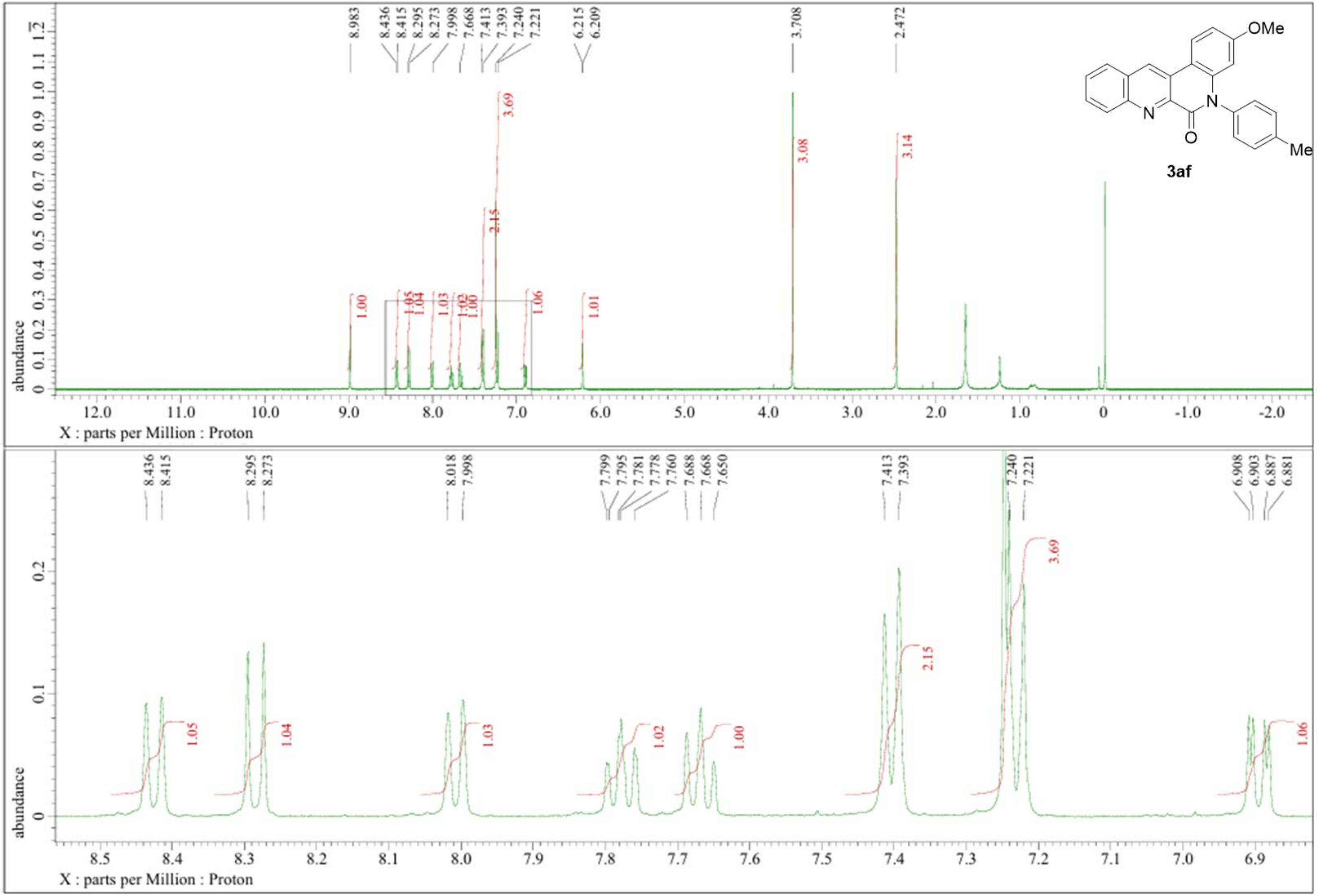
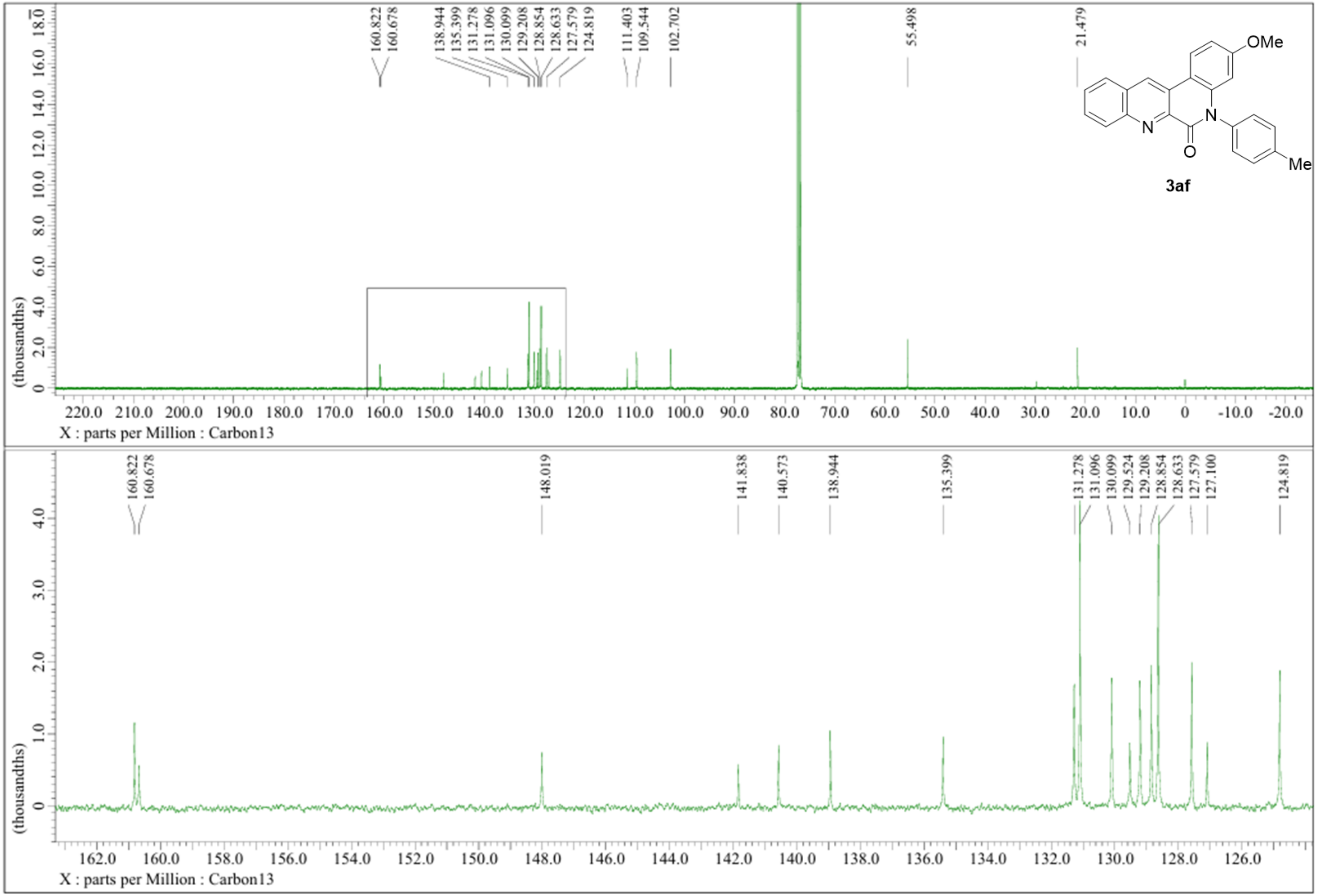


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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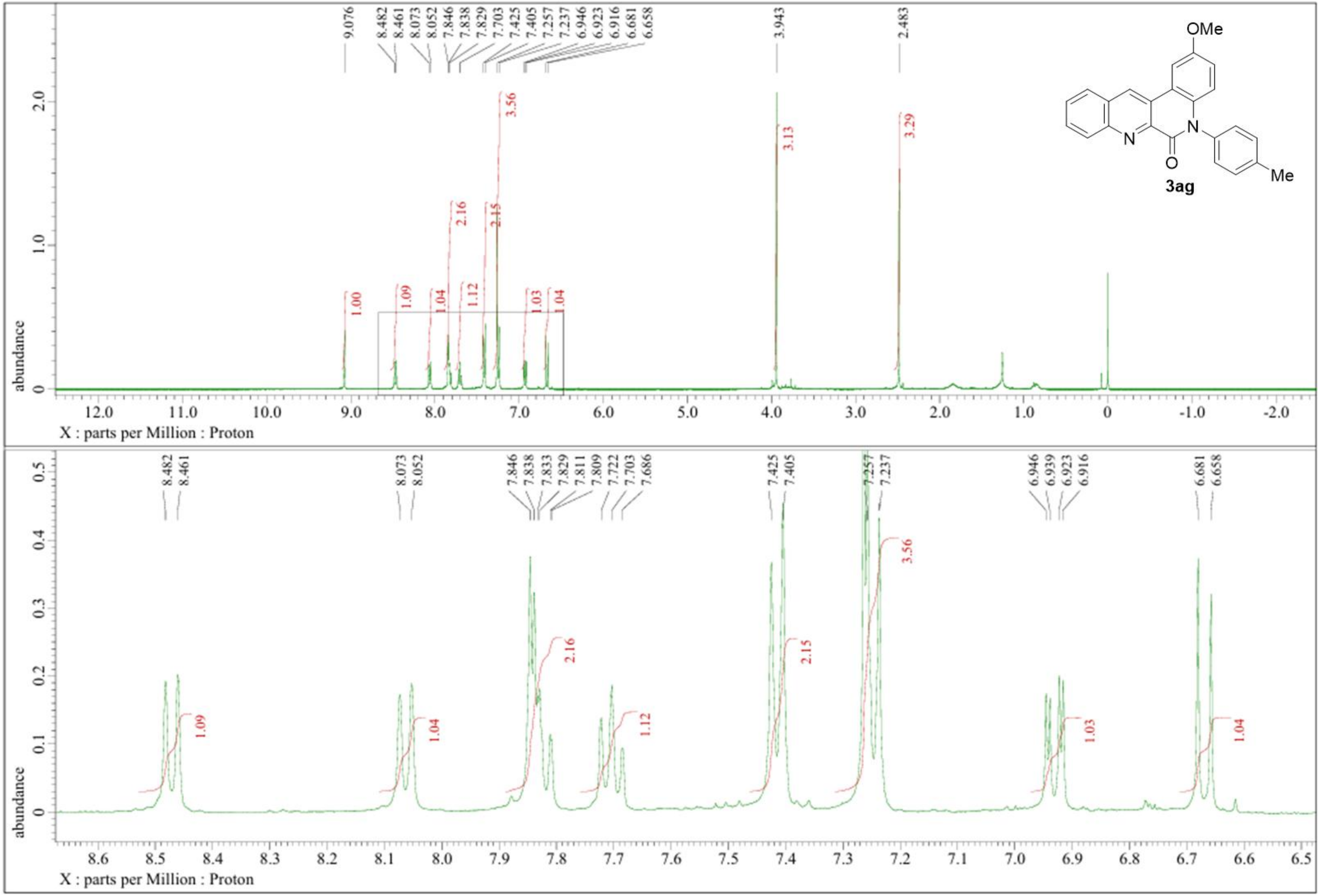

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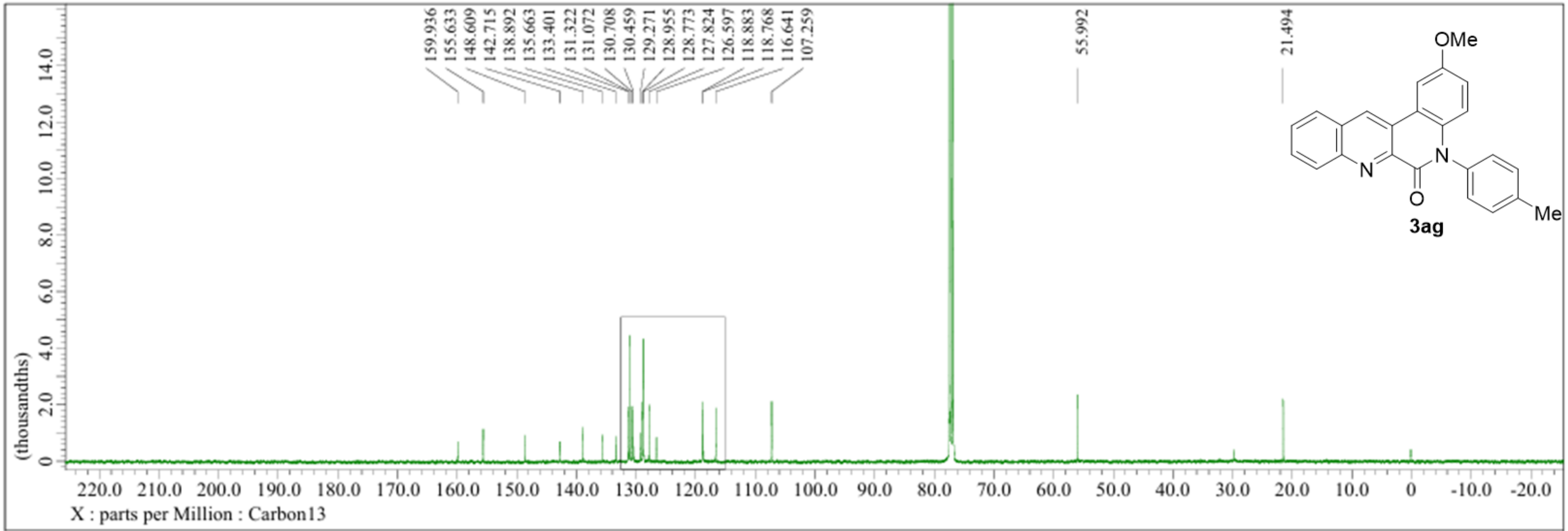

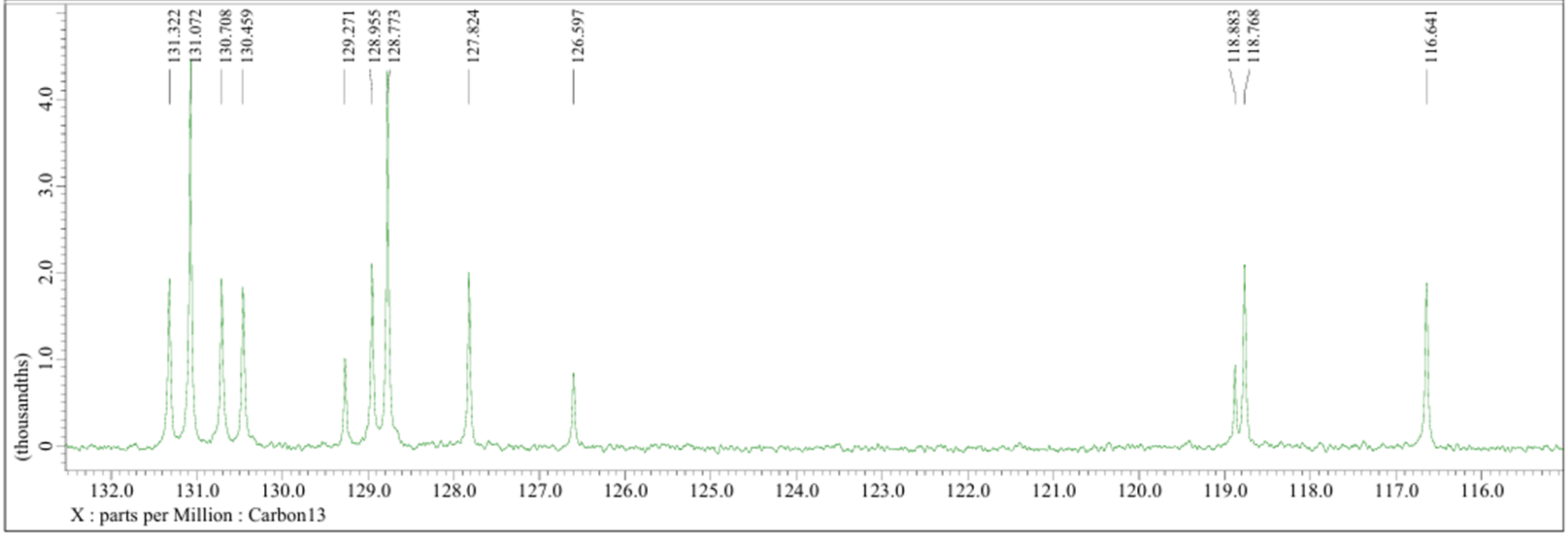

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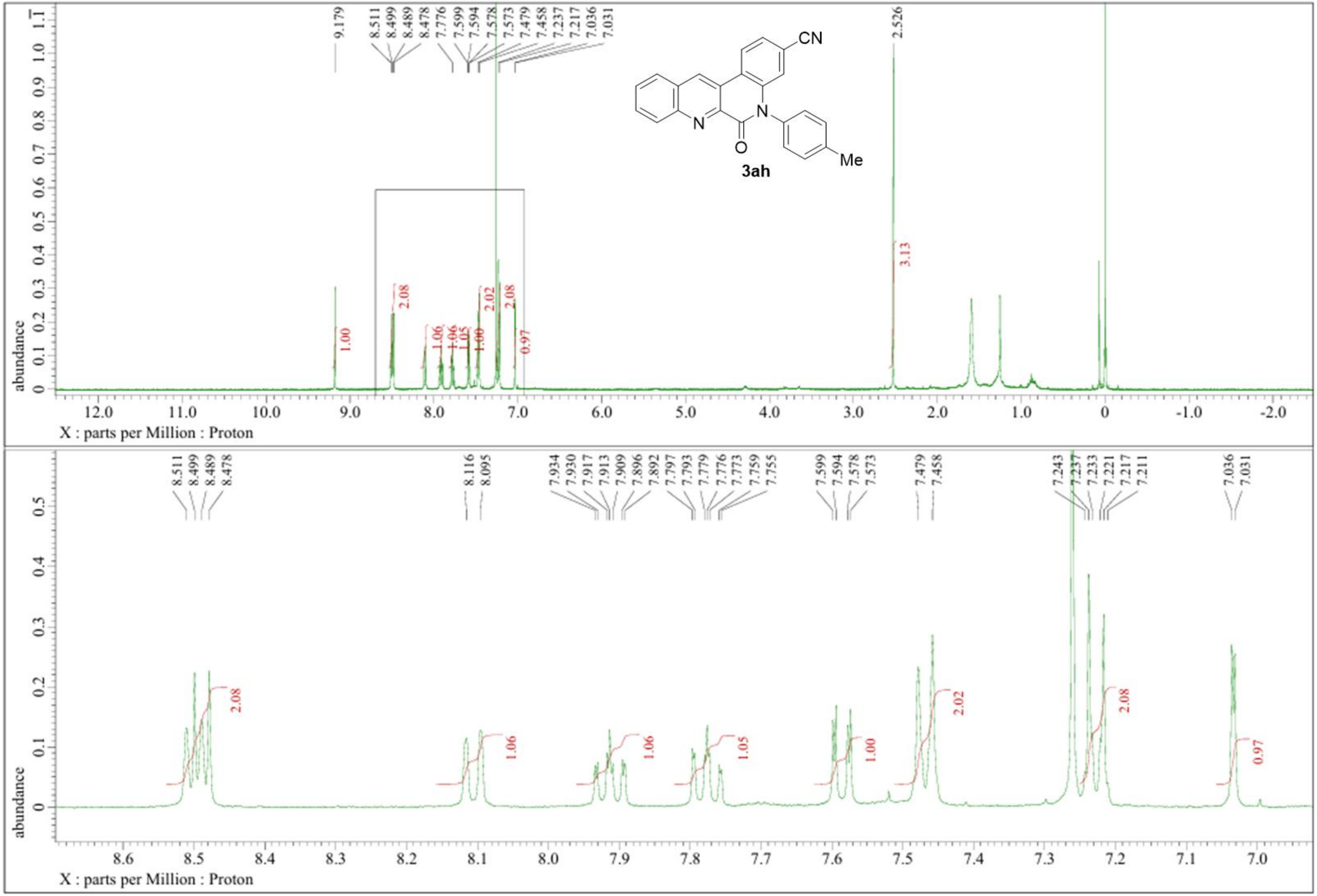

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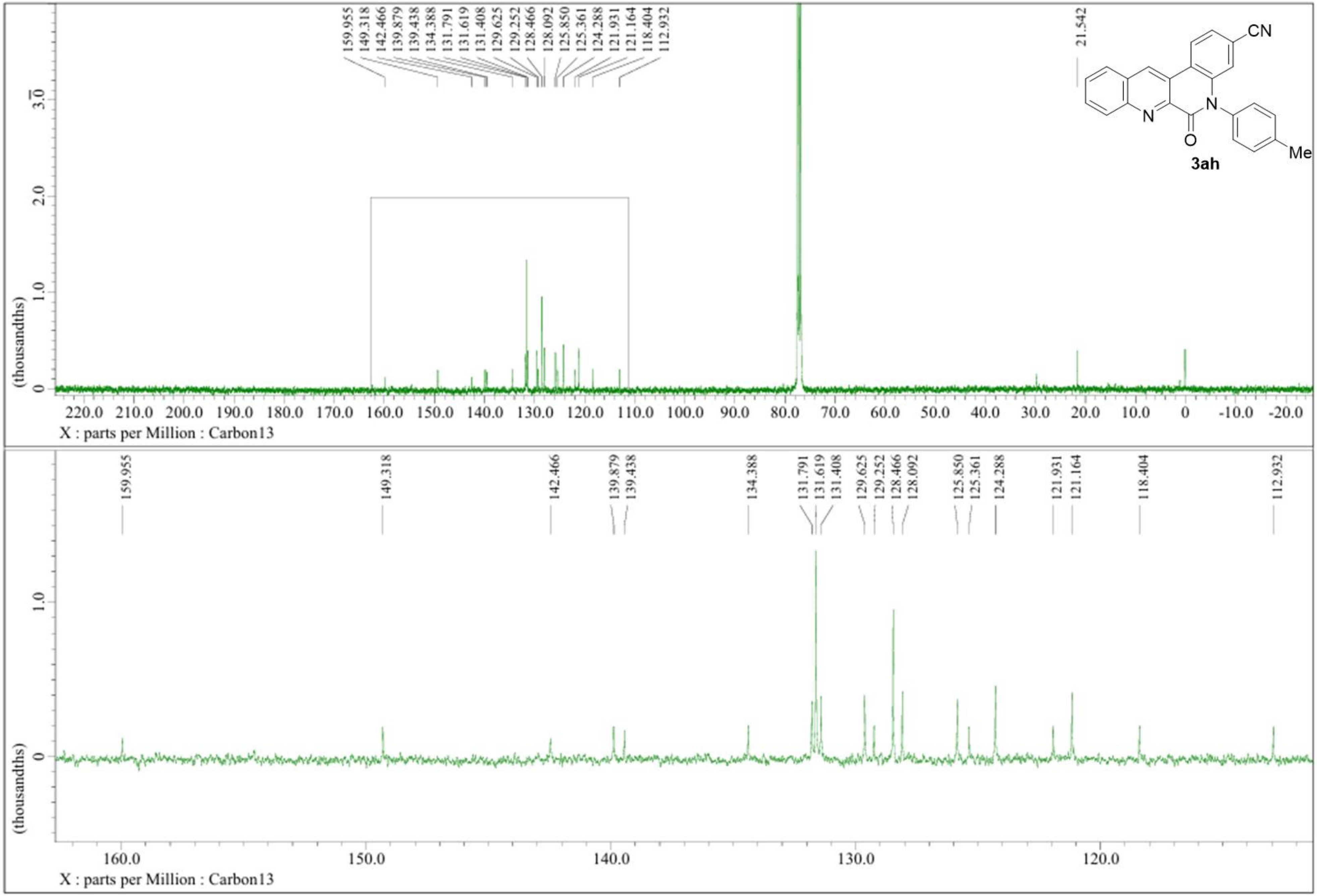

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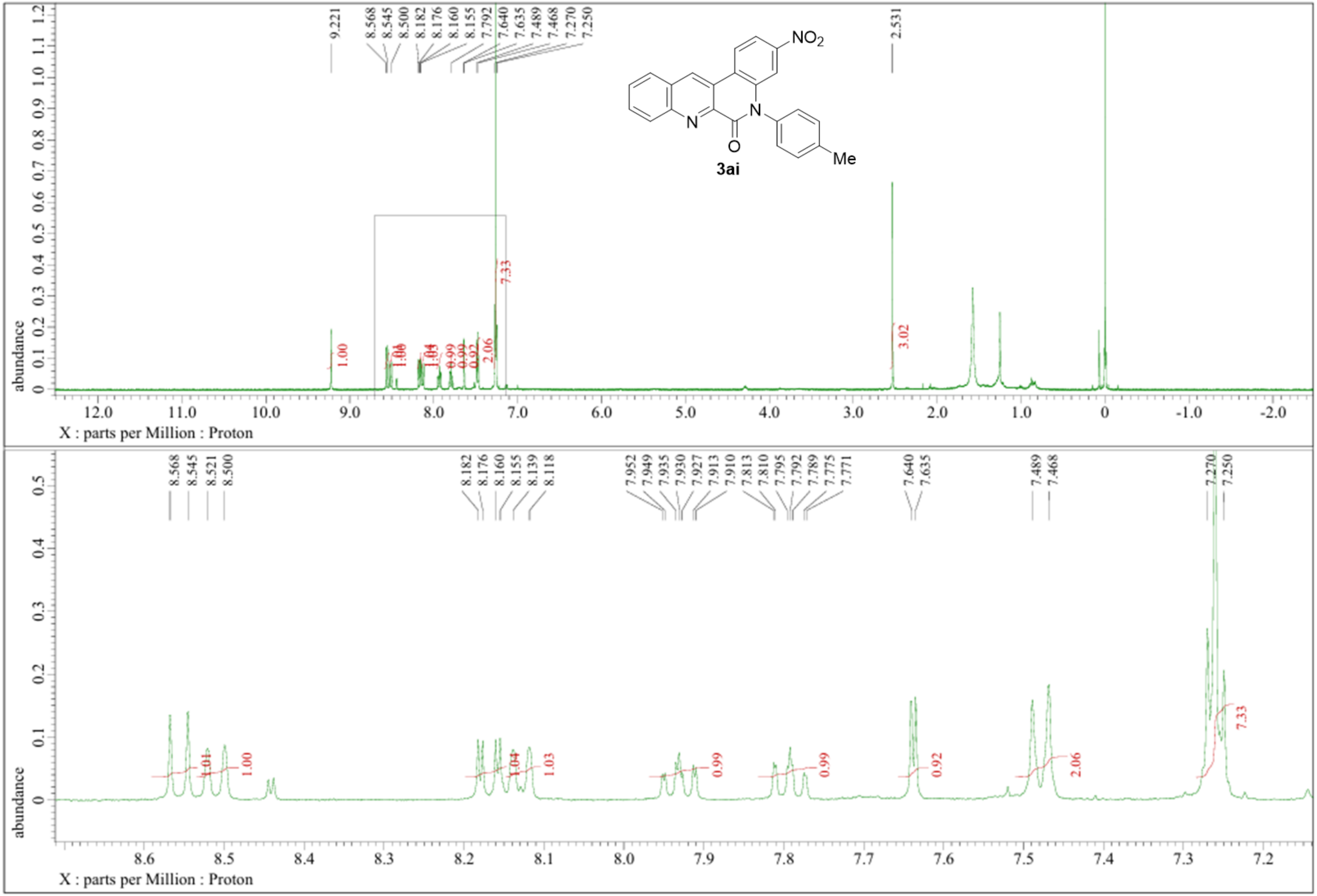
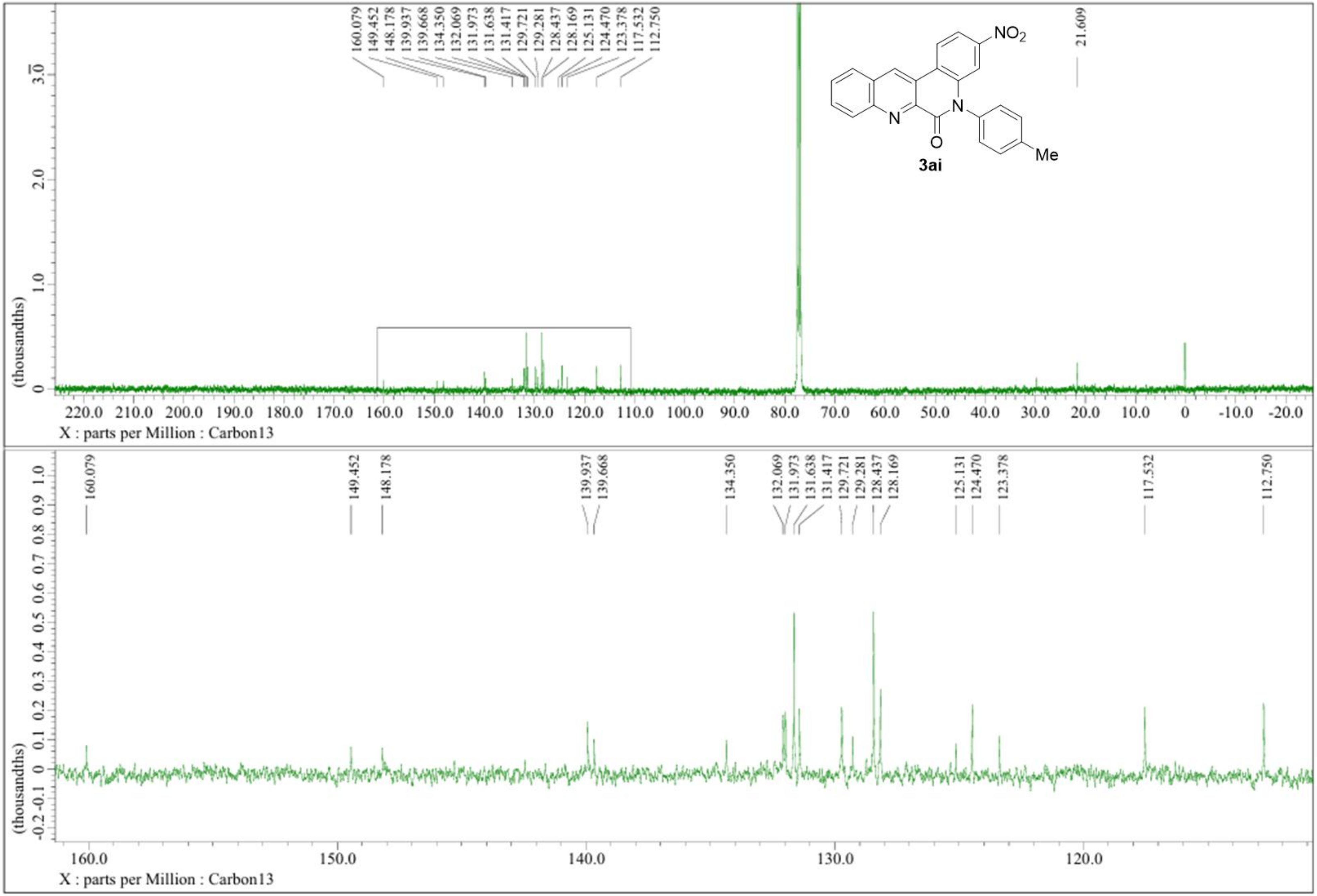
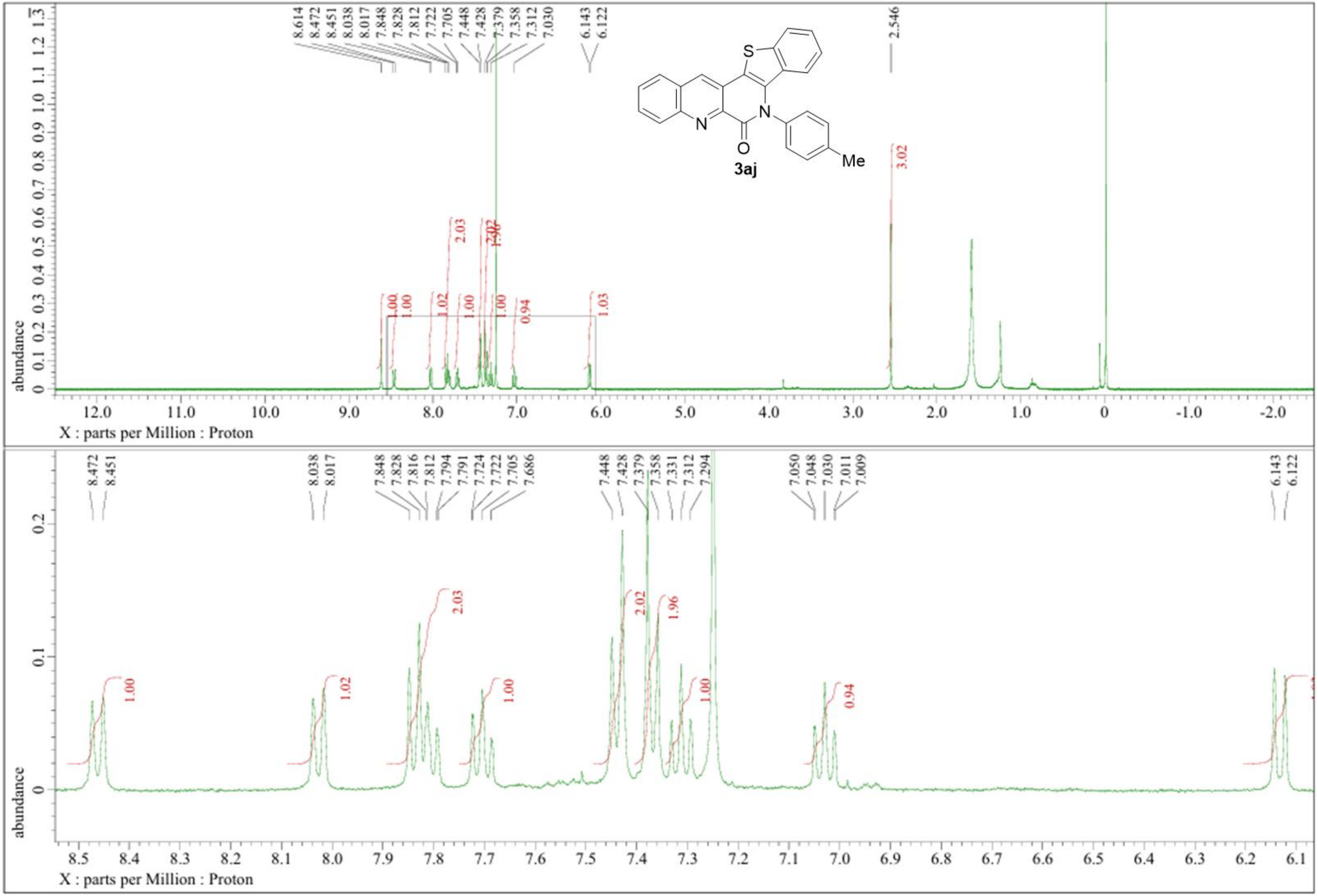


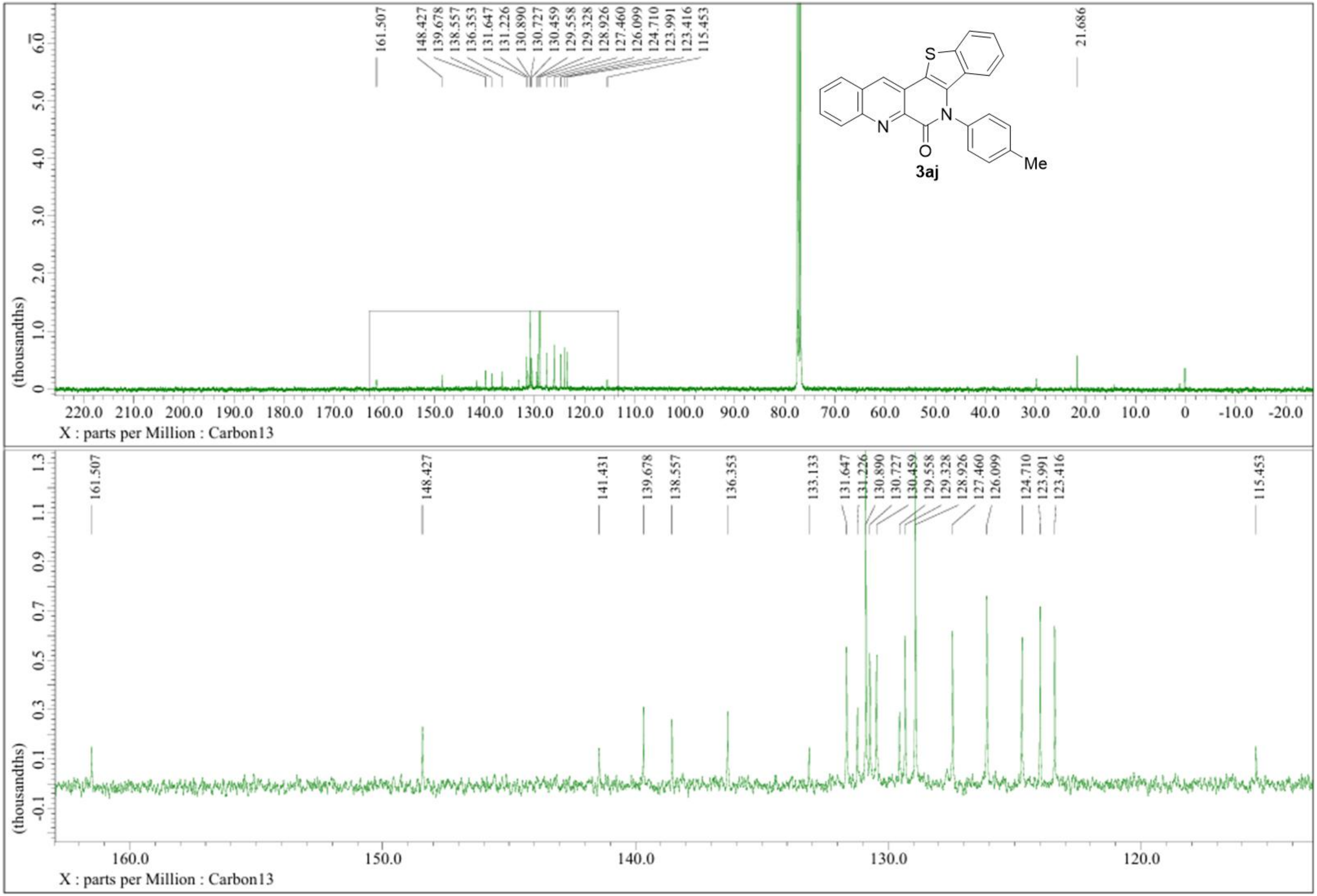
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



¹H NMR (400 MHz, CDCl₃)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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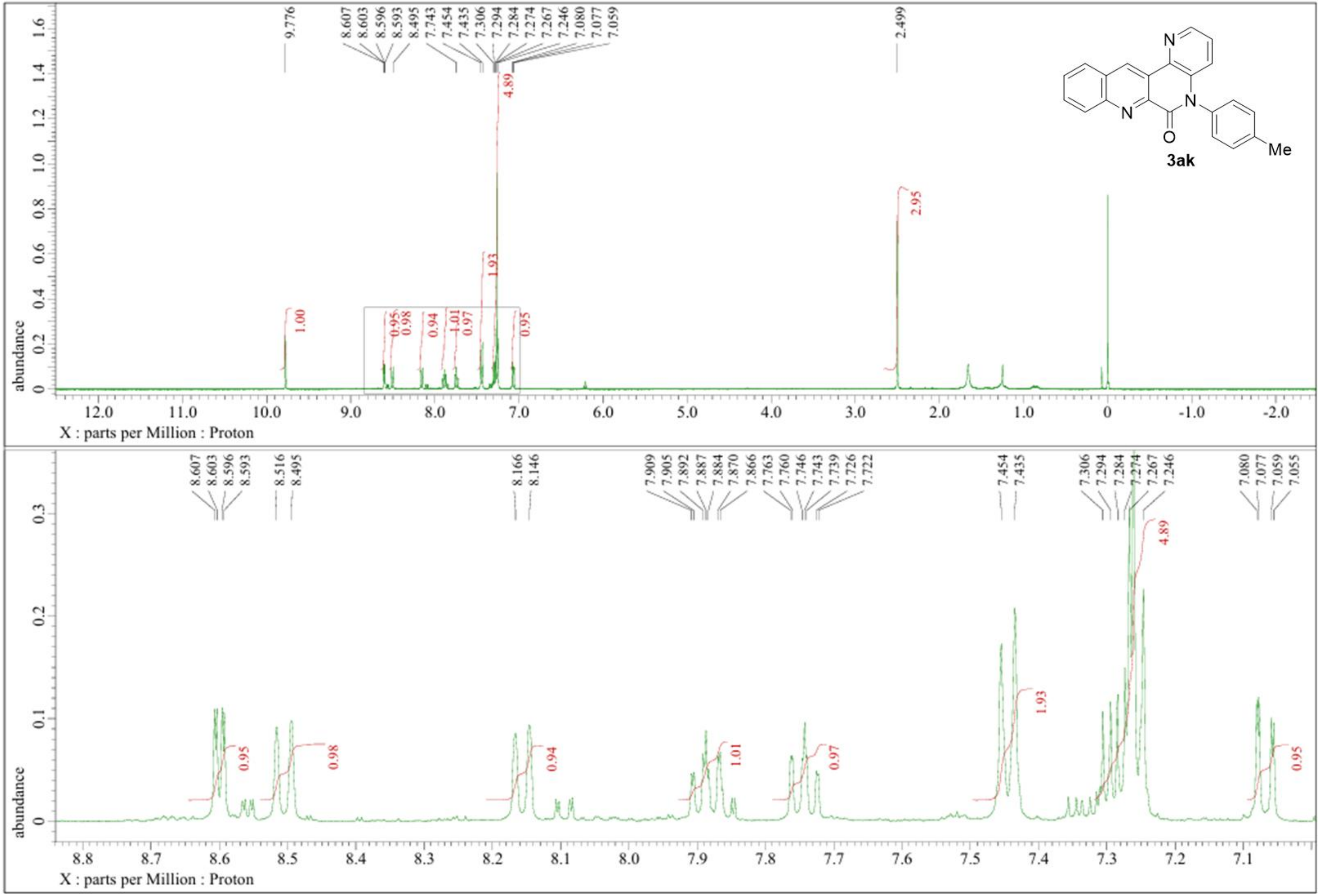
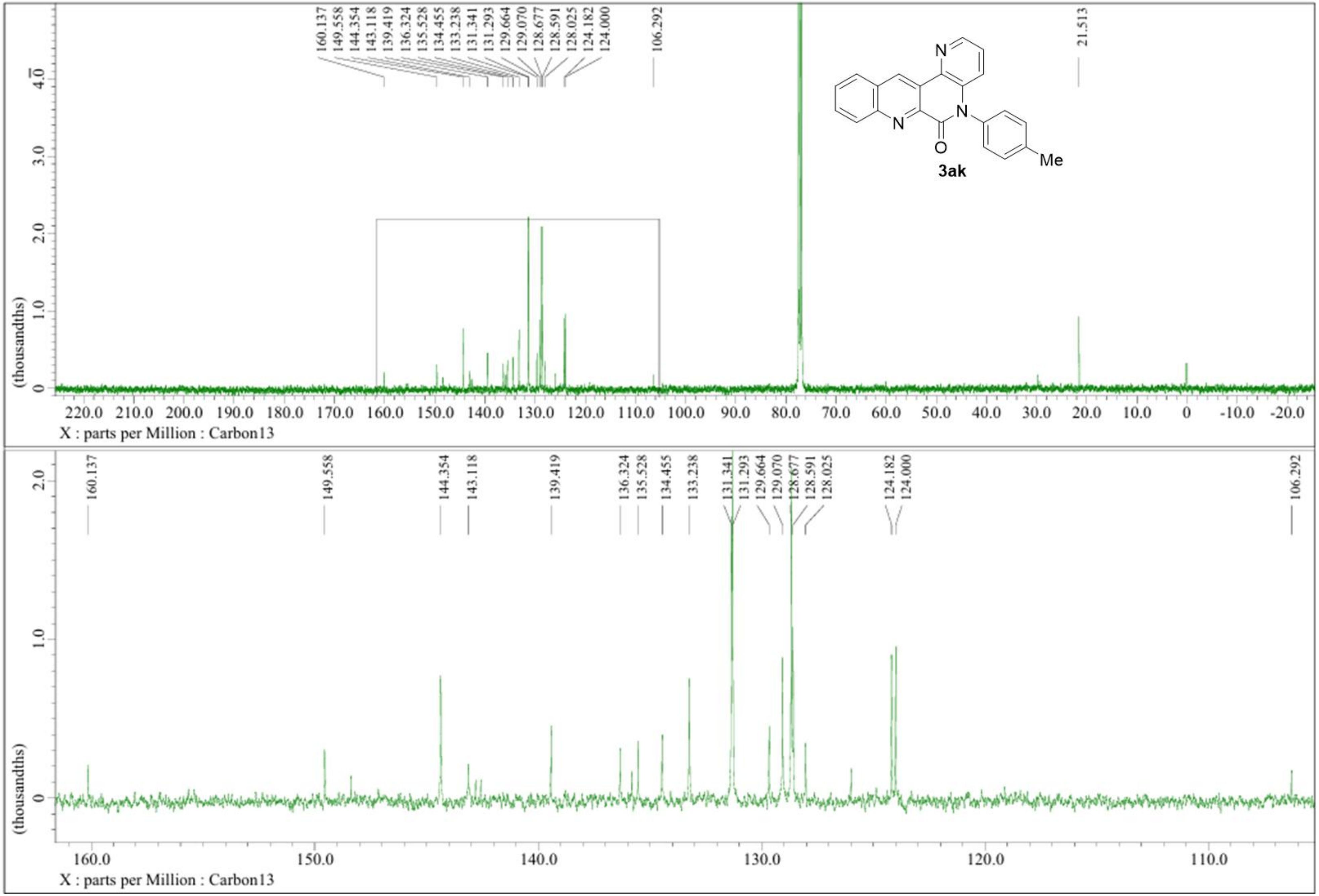


And structural isomer was contained.

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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