Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING MATERIAL FOR INVESTIGATIONS OF THE GENERALITY OF QUATERNARY AMMONIUM SALTS AS ALKYLATING AGENTS IN DIRECT C-H ALKYLATION REACTIONS: SOLID ALTERNATIVES FOR GASEOUS OLEFINS

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A I Abbreviations

DCM	dichloromethane
EA	ethyl acetate
LP	light petrol
r.t.	room temperature
rt	retention time
TLC	thin layer chromatography
BINAP	(2,2'–Bis(diphenylphosphino)–1,1'–binaphthyl)
LC-MS	Liquid chromatography – Mass Spectroskopy
HPLC	High Performance liquid chromatography
GC-MS	Gas Chromatography

A II Materials and methods

The following general procedures were used in all reactions unless otherwise noted. All glassware was flame-dried under argon and reactions were either set up using Schlenk technique with a slight overpressure of Argon or the vials were transferred into a glove box. All reactions were stirred magnetically at 750 rpm and heated either in an oil bath or a metallic reaction block. Reaction temperatures refer to external temperatures.

Reagents were purchased from commercial suppliers and used without further purification.

- **Dry dichloromethane** was retrieved from an Innovative Technologies PureSolv system.
- **Dry methanol** was retrieved from an Innovative Technologies PureSolv system and stored over molecular sieves.
- **Toluene** was purchased as water free over molecular sieves and was degassed prior to use if used in an Argon filled glovebox. Otherwise dry toluene was retrieved from an Innovative Technologies PureSolv system

All other solvents used were p.a. or HPLC grade.

TLC analysis was done with precoated aluminium-backed plates (Silica gel 60 F_{254}, Merck or Aluminium Oxide 60 F_{254}, neutral, Merck). Compounds were marked under UV light or visualized by submerging in staining solutions as stated.

Flash column chromatography was mostly performed on a Büchi Sepacore Flash System (2 x Büchi Pump Module C-605, Büchi Pump Manager C-615, Büchi UV Photometer C-635, Büchi Fraction Collector C-660) using 9 g column (15 mL/min) or 45 g columns (flow 40 mL/min) (Buchi Labortechnik AG, Flawil, Switzerland). For all other separations silica gel from Merck (40-63 µm) was used.

HPLC preparative chromatography was carried out with an auto-purification system of Waters (Milford, Massachusetts, USA) using an ACQUITY QDA MS – Detector in combination with a 2998 Photodiode Array Detector. Analytical separation was made using XSELECT CSH Fluoro-Phenyl 5 µm 4.6 x 150 mm and XSELECT CSH C18 5 µm 4.6 x 150 mm columns. Preparative separation was made using XSELECT CSH Prep Fluoro-Phenyl 5 µm 30 x 150 mm and XSELECT CSH Prep C18 5 µm OBD 30 x 150 mm columns. As solvents HPLC grade methanol and HPLC grade water were used containing 0.1% formic acid.

LC-MS analysis was carried out on a Nexera X2® UHPLC system (Shimadzu®, Kyoto, Japan) comprised of LC-30AD pumps, a SIL-30AC autosampler, CTO-20AC column oven, DGU-20$A_{5/3}$ degasser module. Detection was accomplished by concerted efforts of SPD-M20A photo diode array, a RF-20Axs fluorescence detector, an ELS-2041 evaporative light scattering detector (JASCO®) and finally via a LCMS-2020 mass spectrometer. If not stated otherwise, all separations were performed using a Waters® XSelect® CSH™ C18 2.5 µm (3.0 x 50 mm) Column XP at 40 °C, and a flowrate of 1.7 mL/min. Mobile phases used are UHPLC grade water and acetonitrile containing 0.1% formic acid.

Melting points of crystalline compounds were determined with a Kofler-type Leica Galen III micro hot stage microscope and are uncorrected (Aigner-Unilab Laborfachhandel GmbH, Vienna, Austria).

NMR spectra were recorded in $CDCl_3$ or d_6-DMSO on a Bruker Avance UltraShield 400 (400 MHz) or Avance III HD 600 (600 MHz) spectrometer and chemical shifts (δ) are reported in ppm and are referenced via the solvent peak. Coupling constants (J) are given in Hertz (Hz). The multiplicities are given by the following abbreviations: s = singlet, d = duplet, t= triplet, q = quartet, m = multiplet, bs = broad singlet.

GC–MS runs were performed on a Thermo Finnigan Focus GC/DSQ II with a standard capillary column RXi-5Sil MS column (30 m, 0.25 mmID, 0.25 µm df) (Restek, Bellefonte, USA) using standardized temperature programs: "STD10min" (2 min at 100 °C, 35 °C/min until 300 °C, 2 min at 300 °C), "STD12min" (2 min at 100 °C, 35 °C/min until 300 °C, 4 min at 300 °C), "STD14min" (2 min at 100 °C, 35 °C/min until 300 °C, 6 min at 300 °C), “STD100” (2 min at 100 °C, 18 °C/min until 280 °C, 3 min at 280 °C) or “STD80” (3 min at 80°C, 20°C/min until 280 °C, 2 min at 280 °C).

For compounds unknown to the literature, **HR-MS** analysis was carried out from methanol/acetonitrile solutions (concentration: 10 ppm) by using an HTC PAL system autosampler (CTC Analytics AG, Zwingen, Switzerland), an Agilent 1100/1200 HPLC with binary pumps, degasser and column thermostat (Agilent Technologies, Waldbronn, Germany) and Agilent 6230 AJS ESI–TOF mass spectrometer (Agilent Technologies, Palo Alto, United States).

A II.1 MALDI-MS Measurements

MALDI-MS measurements were performed on a Shimadzu Kratos Axima TOF^2 MALDI reflectron time-of-flight mass spectrometer (Shimadzu Kratos, Manchester, UK) fitted with a nitrogen laser (λ = 337 nm) and a repetition rate of 20 Hz . Mass calibration for positive-ion linear as well as reflectron mass spectrometry was done with the $[M+Na]^+$ adduct ion of the major component of castor bean oil (m/z 955.76) and several low mass ions of the MALDI matrix 2,4,6-trihydroxy-acetophenone (purity > 99.5 %, Fluka, Buchs, Switzerland). All measurements of the analytes were conducted without any matrix in the laser desorption/ionisation (LDI) mode and up to 1000 individual laser shots were acquired for final mass spectra.

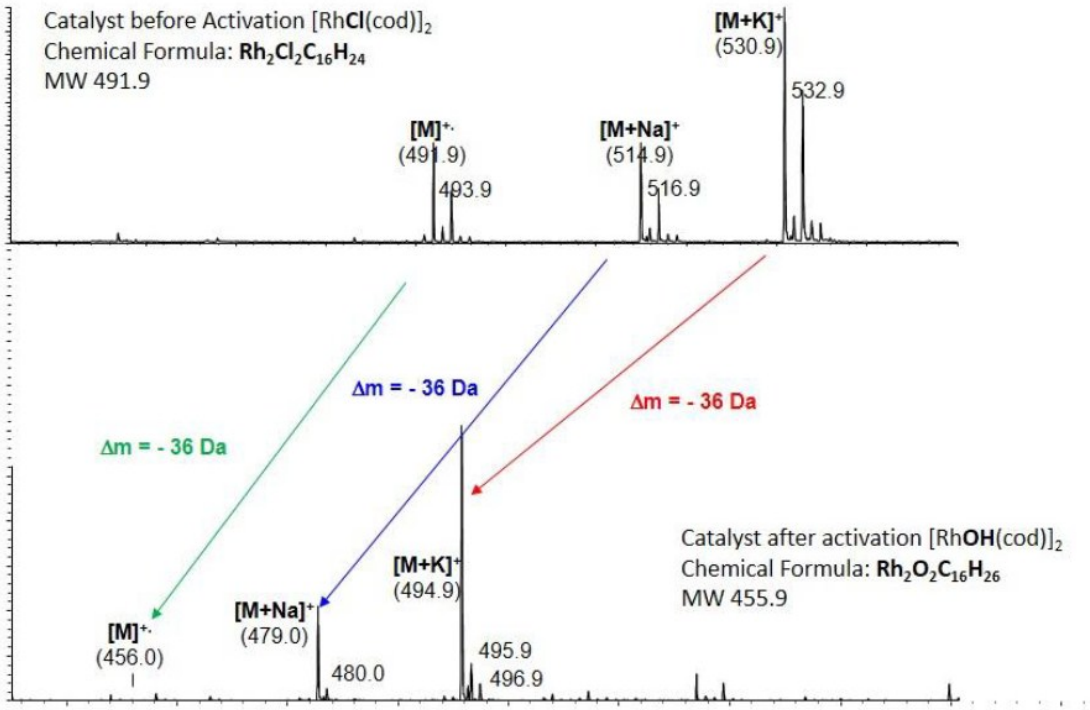
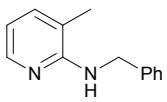


Figure 1 Comparison of the mass spectra taken before (above) and after (below) activation of the catalyst. The mass pattern reveals the substitution of both chloride species and indicates 2 hydroxy species instead.

A II.2 Precursor and Additive Synthesis

A II.2.1 *N*-Benzyl-3-methylpyridine-2-amine (**1**)



1

A flame dried flask was charged with K_2CO_3 (16.35 g, 118.30 mmol), racemic BINAP (491.90 mg, 0.80 mmol) and $Pd(OAc)_2$ (175,4 mg, 0.781 mmol) and was placed under argon atmosphere. Then 60 mL dry toluene were added. Freshly distilled benzylamine (1.2 equiv.) and 2-chloro-3-methylpyridine (4.99 g, 39.14 mmol) were added at once and the mixture was diluted with 20 mL toluene and stirred at 135 °C (oil bath) under vigorous reflux. During the reaction the color of the solution changed from pink to yellow. After 16 h the reaction mixture was black and TLC confirmed complete conversion of the starting material. The reaction mixture was filtered over Celite and washed with DCM and the solvents removed. The crude material was purified via column chromatography.

Analytical data were in accordance with literature.[1]

Appearance: white to beige solid

m.p.: 48-49 °C

Yield: 90% (6.97 g, 31.15 mmol)

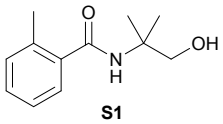
Rf: 0.31 (LP:EA 16:1)

GC-MS: STD10min; rt = 8.0 min; 198.1 (M, 8), 119.1 (8), 91.0 (51), 79.0 (26), 64.0 (31)

1H-NMR (400 MHz, CDCl3) δ = 8.05 (dd, J = 5.03, 1.33 Hz, 1H), 7.46 – 7.32 (m, 4H), 7.32 – 7.22 (m, 2H), 6.56 (dd, J = 7.10, 5.10 Hz), 4.69 (d, J = 5.35 Hz, 2H), 4.36 (bs, 1H), 2.09 (s, 3H) ppm.

13C-NMR (101 MHz, CDCl3) δ = 156.8, 145.6, 140.1, 137.0, 128.7, 128.0, 127.3, 116.6, 113.0, 46.0, 17.1 ppm.

A II.2.2 *N*-(1-Hydroxy-2-methylpropan-2-yl)-2-methylbenzamide (**S1**)



S1

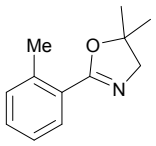
A three necked flask was charged with o-toluic acid (5.05 g, 37.09 mmol, 1.0 equiv.), cooled to 0°C and thionyl chloride (8.10 mL, 111.27 mmol, 3.0 equiv.) was added via syringe. The mixture was stirred at r.t. overnight until TLC showed full conversion of the starting material (small sample was quenched with dry MeOH). Then the remaining thionyl chloride was removed by distillation and the residue was dried at 18 mbar for 2 hours. The dark brown liquid was diluted with dry DCM and added dropwise (15 min) to a solution of triethylamine (10.1 mL, 71.7 mmol, 1.9 equiv.) and 2-amino-2-methylpropan-1-ol (4.03 g, 45,21 mmol, 1.2 equiv.) in 60mL DCM. After addition the solution was stirred at 0 °C for 2 h and a white precipitate formed. TLC indicated full conversion. (PE/EE 5:1 - KMnO4, bromocresole and UV) and the mixture was quenched with ammonium chloride solution and diluted with DCM. After phase separation the organic phase was washed two times with brine and was dried over sodium sulphate. After removal of the solvent by rotary evaporation 8.39 g crude product was obtained, which was purified by flash column chromatography (180 g silica, using LP/EA as eluent) which gave after evaporation of the solvents 90% (6.97 g, 33.63 mmol) pure product as white solid.

Rf: 0.2 (LP:EA 3:1 , KMnO4 and UV)

GC-MS: STD10min; rt = 6.2 min; 208.1 (M, <1), 176.1 (20), 136.1 (24), 119.1 (100), 91.1 (28)

1H-NMR (400 MHz, CDCl3) δ = 7.4 (m, 2H), 7.3 (m, 2H), 6.1 (s, 1H), 5.0 (s, 1H), 3.7 (s, 2H), 2.5 (s, 3H), 1.5 (s, 6H) ppm.
13C-NMR (101 MHz, CDCl3) δ = 171.3, 136.8, 135.6, 131.0, 129.9, 126.6, 125.8, 70.7, 56.7, 24.7, 19.7 ppm.

A II.2.3 5,5-Dimethyl-2-phenyl-4,5-dihydrooxazole (**16**)



16

A solution of *N*-(1-hydroxy-2-methylpropan-2-yl)-2-methylbenzamide (1.51 g, 7.27 mmol, 1.00 equiv.) in 30 mL dry DCM was cooled to 0°C (ice bath). Then triethylamine (959.5 mg, 9.48 mmol, 1.30 equiv.) was added and the solution was stirred for 2 min at 0 °C. Then MesCl (1.01 g, 8.81 mmol, 1.21 equiv.) was added dropwise over a period of 9 min and the solution was stirred at 0 °C for 40 min and was then allowed to warm up to r.t. The reaction was monitored via TLC (3:1 - UV). The reaction was quenched with 15 mL sat. NH_4Cl solution, washed with water and brine. After drying over sodium sulphate, the solvent was removed in vacuo, giving 2.16 g of crude product as yellow solid. The crude material was purified by column chromatography (40g silica, 5 50 mL/min, 0% to 10% LP/EA in 30 min, 60 mL fractions) giving the 596.5 mg (3.15 mmol) pure product as colourless oil in 43% yield.

Analytical data were in accordance with literature.[2]

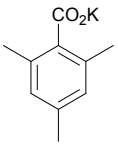
Rf: 0.7 LP/EA 3/1 (phosphormolybdanic acid, UV)

GC-MS: STD10min; rt = 5.0 min; 189.1 (M, 100), 174.1 (72), 146.1 (39) 118.1 (36).

1H-NMR (400 MHz, CDCl3) δ = 7.74 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 4.06 (s, 2H), 2.56 (s, 3H), 1.39 (s, 6H) ppm.

13C-NMR (101 MHz, CDCl3) δ = 162.9, 138.5, 131.1, 130.4, 129.8, 127.8, 125.6, 78.7, 67.9, 28.6, 21.5 ppm.

A II.2.4 Potassium 2,4,6-trimethylbenzoate (**S2**)



S2

According to literature[3] procedure, a solution of *t*-butoxide (650.8 mg, 5.80 mmol) in MeOH (6 mL) was added to a solution of $MesCO_2H$ (1.00 g, 6.09 mmol) in MeOH (9 mL). The solution was stirred for 4 h. Then the solution was evaporated and diethyl ether (50 mL) was added to the remaining white solid and the mixture was stirred vigorously for 36 h. Then the white solid was filtered and washed twice with diethyl ether and dried under vacuum giving 958.0 mg (82%, 4.74 mmol) pure product as white powder.

^{1}H NMR (400 MHz, DMSO) δ = 6.61 (s, 2H), 2.15 (s, 3H), 2.12 (s, 6H) ppm

^{13}C NMR (101 MHz, DMSO) δ = 170.8, 138.0, 133.6, 132.5, 128.0, 20.6, 19.3 ppm.

A II.3 General procedure for alkylation reactions with quaternary ammonium Salts

A II.3.1 One-Pot procedure (Procedure A)

All nonvolatile components (ammonium salt, substrate, additives and potassium hydroxide) were placed in a dry 8 mL vial under ambient atmosphere, which was transferred to an argon filled glove box. Then catalyst and toluene were added, the vial closed and heated at the indicated temperature for the given time. For work up, the reaction mixture was cooled to r.t and filtered over 300-500 mg dry silica. After washing with DCM or a mixture of 5/1 LP/EA all volatiles were removed and the crude mixture purified by column chromatography using a mixture of LP and EA as eluents using a slow gradient starting from 1% EA to 10% EA in one hour.

Deviations from the protocol are stated directly at the given procedure.

A II.3.2 Spatial separation of alkylation and Hoffmann elimination. (Procedure B)

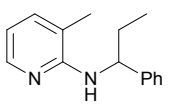
A 20 mL COware vial with H-caps was charged with substrate and additives at chamber A. Chamber B was filled with ammonium salt and KOH. Then the vial was transferred to an Argon filled glove box. Then catalyst was added to chamber A and toluene was added to both sides. The vial was closed and heated at the indicated temperature (usually 140 °C) for the given time (overnight). After cooling, conversion of starting material was confirmed by TLC and/ or GC/MS. Then the reaction mixture of chamber A was filtered over 300-500 mg dry silica and washed with DCM. All volatiles were removed, and the crude mixture purified by column chromatography using a mixture of LP and EA as eluents.

A II.3.3 Alkylation with alkyl halide (Procedure C)

Substrate (usually 100 mg, 0.50 mmol) and 4.5 equiv. K_2CO_3 were placed in a dry 8 mL vial under ambient atmosphere, which was transferred to an argon filled glove box. Then 5 mol% $[Rh(cod)Cl]_2$ was added. Alkyl halide (3.0 equiv.) and toluene (2.0 mL) were placed into the vial via syringe. Finally, the vial was closed and stirred at 160 °C for 22 h. For work up, the reaction mixture as cooled to r.t and filtered over 300-500 mg dry Celite®. After washing with DCM, all volatiles were removed and the crude mixture purified by column chromatography using a mixture of LP and EA.

A II.4 Detailed Synthetic Procedures

A II.4.1 3-Methyl-*N*-(1-phenylpropyl)pyridin-2-amine (**2**)[1]



2

Using $[Rh(cod)(OH)]_2$ as catalyst)

General procedure B was followed with *N*-benzyl-3-methylpyridin-2-amine (96.9 mg, 488.7 µmol, 1.0 equiv.) as substrate. Chamber B was charged with KOH (205.65 mg, 3.67 mmol, 7.5 equiv.) and Et_4NBr (256.78, 1.22 mmol, 2.5 equiv.). $[Rh(cod)(OH)]_2$ (11.2 mg, 24.55 µmol, 5 mol%) was used as catalyst. Toluene (2 mL) was added to both sides. The vial was heated at 140 °C (oil bath) for 15 h. Formation of the product was confirmed by TLC.

After purification by column chromatography, alkylation product **2** was isolated as colorless oil in 65% yield (71.5 mg, 315.9 µmol). Additionally, also 6.8 mg (34.3 mg, 7.0%) starting material were recovered.

Using $[Rh(cod)Cl]_2$ as catalyst)

The reaction was carried out according to general procedure A with **1** (100 mg, 0.50 mmol, 1 eq.), tetraethylammonium bromide (105 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 ml). The reaction mixture was heated for 16 h at 140 °C. After work up the product **2** was isolated in 68 % yield as colorless oil that became solid over time. [Procedure C with 1-bromoethan, 163 mg, 1.50 mmol, 3.0 equiv., afforded 29.0 mg, 0.13 mmol, 25% product as yellow oil after purification]

^{1}H-NMR (400 MHz, CDCl3): δ =7.97 (dd, J = 5.1, 1.7 Hz, 1H), 7.17 – 7.41 (m, 6H), 6.48 (dd, J = 7.1, 5.1 Hz, 1H), 5.19 (q, J = 7.2 Hz, 1H), 4.40 (d, J = 7.7 Hz, 1H), 2.12 (s, 3H), 1.82 – 2.04 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, CDCl3): δ = 156.3, 145.6, 144.3, 136.9, 128.6, 128.5, 127.7, 126.9, 126.7, 116.4, 112.7, 56.1, 30.3, 17.2, 10.9 ppm.

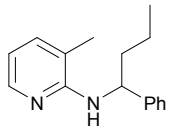
TLC: 0.54 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 6.55 min; 226 (M+, 20), 211 (8), 197 (100), 108 (22), 92 (42), 65 (35).

m.p.: 41.5-42.5 °C

HRMS: calculated for $C_{15}H_{19}N_2$ $[M^+]^+$ 227.1543; found 227.1554; Δ = 5.22 ppm.

A II.4.2 3-Methyl-N-(1-phenylbutyl)pyridin-2-amine (**3**) [1]



3

The reaction was carried out according to general procedure A with 1 (100 mg, 0.50 mmol, 1 eq.), tetrapropylammonium iodide (157 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 ml). The reaction mixture was heated for 16 h at 140 °C. The general work-up procedure B for C-H activation reactions was followed using gradient A. Product 3 was isolated in 62 % yield as colorless oil (75.0 mg, 0.31 mmol). [Procedure C with 1-bromopropan, 186 mg, 1.50 mmol, 3.0 equiv., afforded 67 mg, 0.28 mmol, 55% product as yellow oil after purification]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, J = 5.2, 1.8 Hz, 1H), 7.06 – 7.33 (m, 6H), 6.37 (dd, J = 7.1, 5.0 Hz, 1H), 5.18 (q, J = 7.4 Hz), 4.29 (d, J = 7.7 Hz, 1H), 2.02 (s, 3H), 1.68 – 1.88 (m, 2H), 1.16 – 1.43 (m, 2H), = 0.85 (t, J = 7.4 Hz, 3H) ppm.

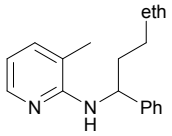
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 156.3, 145.7, 144.7, 136.8, 128.5, 126.8, 126.6, 116.2, 112.6, 54.5, 39.9, 19.7, 17.2, 14.2 ppm

TLC: 0.57 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 6.8 min; 240 (M^+, 12), 211 (20), 197 (100), 108 (28), 92 (41), 65 (24).

HRMS: calculated for $C_{16}H_{21}N_2$ $[M+H]^+$ 241.1699; found 241.1698; Δ = 0.49 ppm.

A II.4.3 3-Methyl-N-(1-phenylpentyl)pyridin-2-amine (**4**) [1]



4

The reaction was carried out according to general procedure A with **1** (100 mg, 0.50 mmol, 1 eq.), tetrabutylammonium chloride (139 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 16 h at 140 °C. After column chromatography product **4** was isolated in 60 % yield (76.0 mg, 0.30 mmol). [Procedure C with 1-bromobutane, 206 mg, 1.50 mmol, 3.0 equiv., afforded 71.0 mg, 0.13 mmol, 56% product as yellow oil after purification]

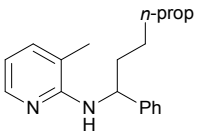
^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.16 – 7.40 (m, 6H), 6.47 (dd, J = 7.1, 5.0 Hz, 1H), 5.25 (q, J = 7.3 Hz, 1H), 4.38 (d, J = 7.7 Hz, 1H), 1.80 – 1.99 (m, 2H), 2.12 (s, 3H), 1.24 – 1.43 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): 156.3, 145.7, 144.7, 136.9, 128.5, 126.8, 126.6, 116.3, 112.6, 54.7, 37.4, 28.7, 22.8, 17.2, 14.1 ppm.

TLC: 0.60 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 7.0 min.; 254 (M^+, 13), 211 (20), 197 (100), 108 (30), 92 (43), 65 (22).

A II.4.4 3-Methyl-N-(1-phenylhexyl)pyridin-2-amine (**5**) [1]



5

The reaction was carried out according to general procedure A with **1** (100 mg, 0.50 mmol, 1 eq.), tetrapentylammonium bromide (189 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3.0 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 16 h at 140 °C. After purification product **5** was isolated in 58 % yield as white solid (78 mg, 0.29 mmol). [Procedure C with 1-bromopentane, 225 mg, 1.50 mmol, 3.0 equiv., afforded 74.0 mg, 0.28 mmol, 54% product as yellow oil after purification]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.17 – 7.40 (m, 6H), 6.47 (dd, J = 7.1, 5.1 Hz, 1H), 5.25 (q, J = 7.3 Hz, 1H), 4.38 (d, J = 7.6 Hz, 1H), 2.12 (s, 3H), 1.78 – 1.97 (m, 2H), 1.24 – 1.45 (m, 6H), 0.86 (d, J = 6.9 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 156.3, 145.7, 144.7, 136.9, 128.5, 126.8, 126.6, 116.3, 112.6, 54.8, 37.6, 31.9, 26.2, 22.7, 17.2, 14.2 ppm.

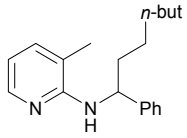
MP: 40-41 °C

TLC: 0.60 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 7.3 min; 268 (M^+, 8), 211 (19), 197 (100), 108 (31), 92 (27), 65 (20).

HRMS: calculated for $C_{18}H_{25}N_2$ $[M+H]^+$ 269.2012; found 269.2033; Δ = 7.79 ppm.

A II.4.5 3-Methyl-N-(1-phenylheptyl)pyridin-2-amine (**6**) [1]



6

The reaction was carried out according to general procedure A with **1** (100 mg, 0.50 mmol, 1 eq.), tetrahexylammonium chloride (195 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 16 h at 140 °C. After purification product **6** was isolated in 61 % yield as colorless oil (86 mg, 0.31 mmol). [Procedure C with 1-bromohexane, 248 mg, 1.50 mmol, 3.0 equiv., afforded 72.0 mg, 0.25 mmol, 50% product as slightly yellow oil after purification]

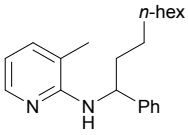
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 5.1, 1.8 Hz, 1H), 7.14 – 7.45 (m, 6H), 6.48 (dd, J = 7.1, 5.0 Hz, 1H), 5.26 (q, J = 7.3 Hz, 1H), 4.39 (d, J = 7.7 Hz, 1H), 2.13 (s, 3H), 1.80 – 1.99 (m, 2H), 1.23 – 1.45 (m, 8H), 0.87 (t, J = 6.7 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 156.3, 145.7, 144.7, 136.8, 128.5, 126.8, 126.6, 116.2, 112.6, 54.7, 37.7, 31.9, 29.4, 26.5, 22.7, 17.2, 14.2 ppm.

TLC: 0.63 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 7.54 min; 282 (M^+, 7), 211 (17), 197 (100), 108 (32), 92 (30), 65 (14).

A II.4.6 3-Methyl-N-(1-phenylnonyl)pyridin-2-amine (**7**) [1]



7

The reaction was carried out according to general procedure A with **1** (100 mg, 0.50 mmol, 1 eq.), tetraoctylammonium bromide (273 mg, 0.50 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 48 h at 140 °C. After purification product **7** was isolated in 40 % yield as colorless oil (63 mg, 0.20 mmol). [Procedure C with 1-bromooctane, 290 mg, 1.50 mmol, 3.0 equiv., afforded 65.0 mg, 0.21 mmol, 42% product as slightly yellow oil after purification]

NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 5.1, 1.7 Hz, 1H), 7.14 – 7.42 (m, 6H), 6.47 (dd, J = 7.1, 5.1 Hz, 1H), 5.25 (q, J = 7.3 Hz, 1H), 4.38 (d, J = 7.7 Hz, 1H), 2.12 (s, 3H), 1.79 – 1.97 (m, 2H), 1.22 – 1.43 (m, 12H), 0.87 (t, J = 6.8 Hz, 3H) ppm.

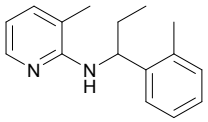
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 156.3, 145.7, 144.7, 136.9, 128.5, 126.8, 126.6, 116.3, 112.6, 54.7, 37.7, 32.0, 29.7, 29.4, 26.5, 22.8, 17.2, 14.2 ppm.

TLC: 0.63 (LP/EA 5:1 - UV)

GC-MS: STD12min; rt = 8.2 min; 310 (M^+, 5), 211 (17), 197 (100), 108 (33), 92 (28), 65 (10).

HRMS: calculated for $C_{21}H_{31}N_2$ $[M+H]^+$ 311.2482; found 311.2505; Δ = 7.53 ppm.

A II.4.7 3-methyl-N-(1-(o-tolyl)propyl)pyridin-2-amine (**8**)



8

The reaction was carried out according to general procedure A with **3-methyl-N-(2-methylbenzyl)pyridine-2-amine** (107 mg, 0.50 mmol, 1 eq.), tetraethylammonium bromide (106 mg, 0.51 mmol, 1 eq.), KOH (87 mg, 1.55 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (14 mg, 0.029 mmol, 0.06 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 19 h at 140 °C. After purification product **8** was isolated in 53 % yield as colorless oil (64 mg, 0.27 mmol).

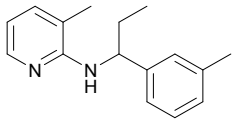
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.11 (m, 4H), 6.46 (dd, *J* = 7.1, 5.1 Hz, 1H), 5.41 (q, *J* = 7.3 Hz, 1H), 4.33 (broad d, *J* = 7.1 Hz, 1H), 2.49 (s, 3H), 2.09 (s, 3H), 1.96 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.85 (dt, *J* = 13.7, 7.3 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.4, 145.8, 142.6, 136.7, 136.6, 130.5, 126.7, 126.2, 125.0, 116.1, 112.5, 52.2, 29.5, 19.8, 17.2, 11.1 ppm.

TLC: 0.50 (LP/EA 5:1 - UV)

GC-MS: STD80; rt = 8.2 min; 240 (16%, M), 211 (100%), 195 (3%), 148 (3%) 117 (10%), 92 (27%), 65 (16%).

A II.4.8 3-methyl-N-(1-(*m*-tolyl)propyl)pyridin-2-amine (**9**)



9

The reaction was carried out according to general procedure A with **3-methyl-N-(3-methylbenzyl)pyridine-2-amine** (107 mg, 0.50 mmol, 1 eq.), tetraethylammonium bromide (105 mg, 0.51 mmol, 1 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 16 h at 140 °C. After purification product **9** was isolated in 77 % yield as colorless oil (64 mg, 0.27 mmol).

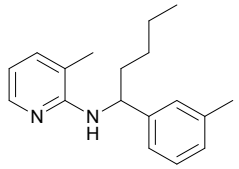
^{1}H NMR (400 MHz, CDCl3) δ = 8.03 (d, J = 4.7 Hz, 1H), 7.35 – 7.02 (m, 5H), 6.52 (dd, J = 6.8, 5.3 Hz, 1H), 5.21 (q, J = 7.1 Hz, 1H), 4.42 (d, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.16 (s, 3H), 2.06 – 1.86 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.3, 145.7, 144.2, 137.9, 136.8, 128.3, 127.6, 127.5, 123.6, 116.2, 112.5, 56.0, 30.2, 21.6, 17.1, 10.9 ppm.

TLC: 0.50 (LP/EA 5:1 - UV)

GC-MS: STD80; rt = 9.4 min; 241 (M+H, 2), 211 (100), 117 (13), 108 (35), 92 (52), 65 (25)

A II.4.9 3-methyl-*N*-(1-(*m*-tolyl)pentyl)pyridin-2-amine (**10**)



10

The reaction was carried out according to general procedure A with **3-methyl-N-(3-methylbenzyl)pyridine-2-amine** (104 mg, 0.50 mmol, 1 eq.), tetrabutylammonium bromide (161 mg, 0.51 mmol, 1 eq.), KOH (83 mg, 1.50 mmol, 3 eq.) and $[Rh(cod)Cl]_2$ (12 mg, 0.025 mmol, 0.05 eq.) in dry and degassed toluene (2 mL). The reaction mixture was heated for 16 h at 140 °C. After purification product **9** was isolated in 64 % yield as colorless oil (84 mg, 0.32 mmol).

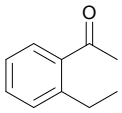
^{1}H-NMR (400 MHz, $CDCl_3$) δ=7.96 (dd, J=3.7Hz, 1.3Hz, 1H), 7.22-7.15 (m, 4H), 7.03 (d, J=7.2Hz, 1H), 6.48-6.45 (m, 1H), 5.20 (q, J=7.4Hz, 1H), 4.35 (d, J=7,5Hz, 1H), 2.34 (s, 3H), 2.11 (s, 3H), 1.95-1.77 (m, 2H), 1.43-1.21 (m, 4H), 0.95-0.85 (m, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$) δ=156.1, 145.5, 144.4, 137.8, 136.5, 128.1, 127.4, 127.2, 123.3, 116.0, 112,3, 54.4, 37.2, 28.4, 22.6, 21.4, 17.0, 13.9 ppm.

TLC: 0.18 (LP/EA 20:1 - UV)

GC-MS: STD80; rt = 11.5 min; 268 (M+H, 5), 211 (86), 108 (69), 92 (100), 65 (74).

A II.4.10 1-(2-Ethylphenyl)ethan-1-one (**12a**) [1]



12a

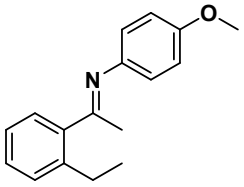
The reaction was carried out according to general procedure A with **11** (60 mg, 0.50 mmol, 1 eq.), tetraethylammonium bromide (315 mg, 1.50 mmol, 3 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $RuH_2(CO)(PPh_3)_3$ (18 mg, 0.02 mmol, 0.04 eq.) in dry and degassed toluene (2 ml). The reaction mixture was heated for 22 h at 150 °C. The solid material was removed by filtration using a Pasteur pipette with cotton and silica (Silica was conditioned with EtOAc with 1% triethylamine to neutralize the acidic groups). The residue was washed with EtOAc containing 1% triethylamine. The combined organic phases were concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (LP/EtOAc; 2% EtOAc - both solvents with 1% triethylamine). Product **12a** could not be separated from starting material **11** and byproduct **12b** by column chromatography. Therefore we isolated a mixture of product, byproduct and starting material, which was quantified with ^{1}H-NMR. 73 mg of a brown liquid was obtained. Ratio of this 73 mg mixture was determined by NMR. Calculated yields with Ratio: 67.1% product, 25.5% byproduct, 7.3% starting material.

GCMS of Compound 9a: STD12min; rt = 3.9 min; 148 (M^+, 28), 133 (100), 115 (12), 105 (33), 91 (16), 79 (27).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, J = 7.7, 1.4 Hz, 1H), 7.40 (td, J = 7.5, 1.5 Hz, 1H), 7.25 – 7.29 (m, 2H), 2.88 (q, J = 7.5 Hz, 2H), 2.58 (s, 3H), 1.21 (td, J = 7.5, 1.7 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 202.4, 144.3, 138.6, 131.6, 130.6, 129.1, 125.7, 30.1, 27.2, 16.1 ppm.

A II.4.11 1-(2-ethylphenyl)-N-(4-methoxyphenyl)ethan-1-imine (**S3**)

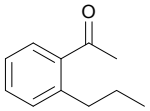


S3

The reaction was carried out according to general procedure A with **14** (113 mg, 0.50 mmol, 1 eq.), tetraethylammonium bromide (315 mg, 1.50 mmol, 3 eq.), KOH (84 mg, 1.50 mmol, 3 eq.) and $RhCl(PPH_3)_3$ (23 mg, 0.025 mmol, 5 mol%) in dry and degassed toluene (2 mL). The reaction mixture was heated for 22 h at 150 °C. After cooling to r.t. 5 mL 1N HCl was added and stirred vigorously for 45 min. The hydrolyzed compounds were extracted with Et_2O and the combined organic layers were dried over Na_2SO_4. The solvents were evaporated under reduced pressure. The resulting crude material was purified with column chromatography (LP/EtOAc; 2% EtOAc - both solvents with 1% triethylamine). Product **12a** could not be separated from compound **11** by column chromatography. Therefore a mixture was isolated which was quantified with ^{1}H-NMR. 62 mg of a brown liquid was obtained. Ratio of this 62 mg mixture was determined by NMR: product **12a** / starting material **11** = 0.65/1. Calculated yields with Ratio: 39.4% product, 60.6% starting material.

GCMS of Compound S3: STD12min; rt = 3.90 min: 253 (M^+, 31), 238 (16), 146 (21), 131 (75), 123 (100), 108 (48), 91 (31), 77 (49), 64 (23).

A II.4.12 1-(2-Propylphenyl)ethan-1-one (**13**)



13

General procedure A was followed using acetophenone (46.5 mg, 387.0 µmol, 1.0 equiv.) as substrate. KOH (206.8 mg, 3.69 mmol, 9.5 equiv.), $n$$Pr_4NBr$ (332.20 mg, 1.25 mmol, 3.22 equiv.) and $RuH_2(CO)(PPh_3)_3$ (17.60 mg, 19.2 µmol, 5 mol%) and toluene (1.0 mL) were added. The mixture was heated at 140 °C for 16 h. GC/MS confirmed almost full conversion and the material was filtered through Al_2O_3 (Brookmann neutral) and the solvents evaporated (including NPr_3) giving 64.8 mg crude material; due to the low boiling point of the materials, the yield was calculated from thins mixture with 87%. The material was purified by column chromatography using Al_2O_3 (Brookmann neutral, 5g using LP/ diethyl ether 50/1 as eluent). After evaporating the solvents, an analytical sample (30.0 mg, 184.9 µmol, 48%) was obtained as colorless liquid.

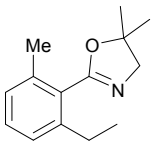
TLC: 0.44 (LP/ diethyl ether 10/1); 0.55 (LP/ diethyl ether 10/1 – Al_2O_3)

GC-MS: STD10min; rt = 4.4 min, 162.1 (M+, 13), 121.1 (18), 105.0 (100), 91.1 (19), 77.1 (37).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.6 – 7.5 (m, 1H), 7.4 – 7.3 (m, 1H), 7.2 – 7.1 (m, 3H), 2.7 (t, J = 8.0 Hz, 2H), 2.5 (s, 2H), 1.5 (h, J = 7.9, 7.5 Hz, 2H), 0.9 (t, J = 7.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) = δ 202.4, 142.6, 138.2, 131.2 (d, J = 2.3 Hz), 128.9, 125.6, 36.0, 30.0, 24.9, 14.2 ppm.

A II.4.13 2-(2-ethyl-6-methylphenyl)-5,5-dimethyl-4,5-dihydrooxazole (**17**)



17

General procedure A was followed with 5,5-dimethyl-2-(o-tolyl)-4,5-dihydrooxazole (**16**) (53.6 mg, 283.2 µmol, 1.0 equiv.) as substrate. KOH (190.7mg, 3.40 mmol, 12.0 equiv.), tetraethylammonium bromide (240.3mg, 1.14 mmol, 4.0 equiv.) and $[Rh(cod)Cl]_2$ (12.5mg, 25.35µmol, 12 mol%). The closed vial was stirred at 140 °C for 5 days. After GC/MS analysis the material was worked up according to general procedure and product **17** was isolated as colorless oil (17.8 mg, 81.9 µmol, 29%) along with 40% starting material (21.50 mg, 113.6 µmol) by column chromatography (3g silica, LP/EA 30/1 – start with DCM).

Rf (TLC) 0.45 LP/EA 30/1

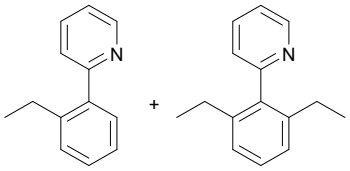
GC-MS Methode (Std 10min); rt = 5.6 min; 217.2 (M+, 42), 162.1 (100), 146.1 (79), 131.1 (31), 115.1 (25)

HR/MS For C14H19NO: [M+H]+ calcd: 218.1539, found: 218.1549

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 4.11 (s, 2H), 2.66 (q, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.42 (s, 6H), 1.20 (q, J = 7.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.4, 143.2, 137.0, 129.6, 128.6, 127.5, 125.9, 79.0, 68.1, 28.6, 26.8, 19.6, 15.9 ppm.

A II.4.14 2-(2-Ethylphenyl)pyridine (**19a**)



General procedure B was followed. Chamber A was charged with 2-phenylpyridine (58.3 mg 375.6 µmol, 1.0 equiv.), KO_2CMes (11.50 mg, 56.9 µmol, 15 mol%] and $[Ru(p\text{-}cym)Cl_2]_2$ (9.5 mg, 15.5 µmol, 4.1 mol%), while chamber B was filled with Et_4NBr (351.70 mg, 1.67 mmol, 4.4 equiv.) and KOH (257.3 mg, 4.59 mmol, 12.2 equiv.). Toluene (1 mL) was added to both sides, the vials closed and stirred at 140 °C for 28 h. After cooling, GC/MS analysis indicated full conversion of the starting material and the reaction mixture was worked up. Purification via column chromatography could not separate the product **19a** from, side-product **19b**.[1] Therefore, we isolated a mixture of product, byproduct and starting material, which was quantified with ^{1}H-NMR. 61.0 mg of colorless oil were obtained containing 45% product (31.25 mg, 170.5 µmol) and 35% (27.75 mg, 131.3 µmol)-(2,6-diethylphenyl)pyridine (**19b**) as side product according to ^{1}H-NMR. Shifts of 1H and 13C are given for the mixtures and were in accordance to literature results of the pure samples.[4] Integrals are set for the isolated signal at 2.8 ppm, which was set to 2.0 corresponding to CH_2 group Ratio: 1/0.77 = **19a**/**19b**.

To obtain samples for analysis, the main product **19a** was purified by preparative reversed phase chromatography using a C18 phase. Solid $NaHCO_3$ was added to the dissolved material and MeOH was removed by rotary evaporation. Then the aqueous phase was extracted three times with DCM. The combined organic phases were washed with Brine and dried over sodium sulfate. After removal of the solvents, the material was subjected to analysis.

Spectroscopical data are in accordance with literature[4].

^{1}H NMR of pure 19a (600 MHz, $CDCl_3$) δ = 9.02 – 8.53 (m, 1H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.10 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR of pure 19a (101 MHz, $CDCl_3$) δ = 160.3, 149.2, 142.0, 140.2, 136.1, 129.7, 129.0, 128.4, 125.7, 124.1, 121.6, 26.1, 15.5 ppm.

Rf (TLC) for 19a and 19b 0.31 LP/diethyl ether 10/1

GC-MS Method (STD80); rt = 8.8 min; 182.1 (M+, 100), 167.1 (54). 139.1 (7.4).

LC-MS; rt = 1.3 min; $M+H]^+$ = 184.2 and $[M+K]^+$ = 225.1

GC-MS of Sideproduct 19b Method (Std 10min); rt = 9.5 min; 212.1 (M+, 5), 210.1 (100). 195.1 (22), 180.1 (20) ppm.

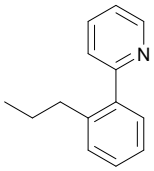
LC-MS of sideproduct 19b; rt = 2.0 min; $M+H]^+$ = 212.2 and $[M+K]^+$ = 253.1

^{1}H NMR of the mixture (400 MHz, $CDCl_3$) δ = 8.95 – 8.64 (m, 1.6H), 7.87 – 7.66 (m, 1.6H), 7.45 – 7.24 (m, 8H), 7.18 (d, *J* = 7.6 Hz, 1.6H), 2.76 (q, *J* = 7.5 Hz, 2.0H), 2.44 – 2.27 (m, 3.0H), 1.14 (t, *J* = 7.6 Hz, 3.0H), 1.07 (t, *J* = 7.6 Hz, 5.2H).

^{13}C NMR of the mixture (101 MHz, $CDCl_3$) δ = 160.3, 159.6, 149.4, 149.2, 142.0, 141.9, 140.2, 139.6, 136.1, 135.9, 129.7, 129.0, 128.5, 128.3, 125.8, 125.8, 124.8, 124.1, 121.7, 121.6, 26.6, 26.1, 15.5, 15.4 ppm.

[1] [Separation of the compounds by TLC was possible when HPTLC glass plates (silica 60, F_{254}) were used. Hereby, the TLC was developed twice in LP/ diethyl ether 10/1 by allowing evaporation of the eluent after the first run, followed by a second run under the same conditions.]

A II.4.15 2-(3-Propylphenyl)pyridine (**20a**)



20a

General procedure B was followed. Chamber A was charged with 2-phenylpyridine (64.8 mg 417.5 µmol, 1.0 equiv.), KO_2CMes (13.0 mg, 64.3 µmol, 15 mol%] and $[Ru(p\text{-}cym)Cl_2]_2$ (10.7 mg, 17.5 µmol, 4.2 mol%), while chamber B was filled with Pr_4NBr (408.80 mg, 1.54 mmol, 3.7 equiv.) and KOH (257.3 mg, 4.59 mmol, 10.9 equiv.) Toluene (1 mL) was added to both sides, the vials closed and stirred at 140 °C for 28 h. After cooling, GC/MS analysis indicated almost full conversion of the starting material and the reaction mixture was worked up. Purification via column chromatography could not separate product **20a** from the bis-alkylated side-product **20b** and the starting material. Therefore we isolated a mixture of product, byproduct and starting material, which was quantified with 1H-NMR. 61.3 mg of colorless oil were obtained containing 5% substrate **18** (3.2 mg, 20.6 µmol), 65% product **20a** (53.8 mg, 272.7 µmol) and 4% side-product **20b** (4.3 mg, 18.0 µmol).

To obtain samples for analysis, the material was purified by preparative reversed phase chromatography using a C18 phase. Solid $NaHCO_3$ was added to the dissolved material and MeOH was removed by rotary evaporation. Then the aqueous phase was extracted three times with DCM. The combined organic phases were washed with Brine and dried over sodium sulfate. After removal of the solvents, the material was subjected to analysis.

LC-MS r.t. = 1.8 min; $[M+H]^+$ = 198.2 and $[M+K]^+$ = 239.1

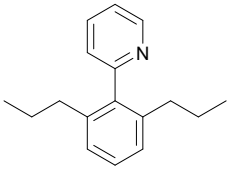
GC-MS Method (Std 10min); rt =9.2 min; 197.2 (M, 39), 182.1 (88), 167.1 (100), 140.1 (6), 83 (11).

Rf (TLC) 0.35 LP/diethyl ether 10/1

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.71 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (dt, *J* = 7.8, 0.8 Hz, 1H), 7.35 (ddd, *J* = 13.9, 8.5, 7.0 Hz, 3H), 7.30 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.27 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 2.71 (dd, *J* = 8.7, 6.9 Hz, 2H), 1.68 – 1.42 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.5, 149.3, 140.6, 140.5, 136.2, 129.9, 129.8, 128.3, 125.9, 124.2, 121.7, 35.2, 24.5, 14.2 ppm.

*Analytical Data of Sideproduct **20b***



17b

LC-MS r.t. = 2.9 min; $[M+H]^+$ = 240.2 and $[M+K]^+$ = 281.1

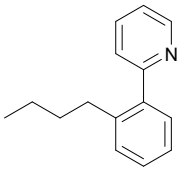
GC-MS Method (STD80); rt =10.2 min; 238 (M, 100), 224.2 (72), 209.3 (22), 180.1 (70), 167 (37), 152.1 (16).

Rf (TLC) 0.35 LP/diethyl ether 10/1

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 4.5 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.21 (m, 6H), 7.12 (d, *J* = 7.6 Hz, 2H), 2.42 – 2.14 (m, 4H), 1.51 – 1.36 (m, 4H), 0.76 (t, *J* = 7.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.8, 149.4, 140.6, 135.9, 128.0, 126.7, 125.1, 121.8, 35.8, 24.3, 14.3 ppm.

A II.4.16 2-(3-Butylphenyl)pyridine (**21**)



21

General procedure B was followed. Chamber A was charged with 2-phenylpyridine (47.8 mg 308.0 µmol, 1.0 equiv.), KO_2CMes (9.9 mg, 48.94 µmol, 16 mol%] and $[Ru(p\text{-}cym)Cl_2]_2$ (7.0 mg, 11.4 µmol, 4 mol%), while chamber B was filled with *n*-Bu_4NBr (316.10 mg, 0.98 mmol, 3.2 equiv.) and KOH (164.7 mg, 2.94 mmol, 10.9 equiv.) Toluene (1 mL) was added to both sides, the vials closed and stirred at 140 °C for 20 h. After cooling, GC/MS analysis indicated almost full conversion of the starting material and the reaction mixture was worked up. Purification via column chromatography could not separate product **21** from the starting material completely. Therefore, we isolated a mixture of product and starting material, which was quantified with ^{1}H NMR. 57.1 mg of a colorless oil were obtained containing 17% substrate **18** (8.2 mg, 52.8 µmol) and 75% product **21** (48.9 mg, 231.4 µmol).

To obtain samples for analysis, the material was purified by preparative reversed phase chromatography using a C18 phase. Solid $NaHCO_3$ was added to the dissolved material and MeOH was removed by rotary evaporation. Then the aqueous phase was extracted three times with DCM. The combined organic phases were washed with Brine and dried over sodium sulfate. After removal of the solvents, the material was subjected to analysis.

Analytical data were in accordance with literature[5]

LC-MS r.t. = 2.4 min; $[M+H]^+$ = 212.1 and $[M+K]^+$ = 253.1

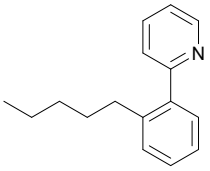
GC-MS Method (STD80); rt =9.8 min; 211.2 (M, 11), 182.1 (100), 167.1 (97), 139.1 (15), 83 (18).

Rf (TLC) 0.35 LP/diethyl ether 10/1

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.62 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.31 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.21 – 7.16 (m, 2H), 2.76 – 2.54 (m, 2H), 1.36 (dtd, *J* = 10.0, 7.6, 6.0 Hz, 2H), 1.17 – 1.08 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.5, 149.3, 140.9, 140.5, 136.2, 129.9, 129.8, 128.4, 125.8, 124.2, 121.7, 33.6, 32.7, 22.6, 13.9 ppm.

A II.4.17 2-(3-Pentylphenyl)pyridine (**22**)



22

General procedure B was followed. Chamber A was charged with 2-phenylpyridine (59.3 mg 382.1 µmol, 1.0 equiv.), KO_2CMes (11.6 mg, 57.34 µmol, 15 mol%] and $[Ru(p\text{-}cym)Cl_2]_2$ (10.8 mg, 17.6 µmol, 5 mol%), while chamber B was filled with *n*-Amy_4NBr (586.20 mg, 1.55 mmol, 4.1 equiv.) and KOH (254.6 mg, 4.54 mmol, 11.9 equiv.) Toluene (1 mL) was added to both sides, the vials closed and stirred at 140 °C for 20 h. After cooling, GC/MS analysis indicated almost full conversion of the starting material and the reaction mixture was worked up. Purification via column chromatography could not separate product **22** from the starting material completely. Therefore, we isolated a mixture of product and starting material, which was quantified with ^{1}H-NMR. 57.1 mg

of colorless oil were obtained containing 19% substrate **18** (11.1 mg, 71.2 µmol) and 71% product **22** (61.1 mg, 271.2 µmol).

Analytical data were in accordance with literature[5]

LC-MS r.t. = 2.9 min; $[M+H]^+$ = 226.1 and $[M+K]^+$ = 267.1

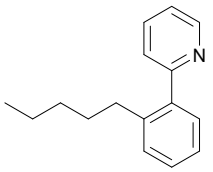
GC-MS Method STD80); rt =10.3 min; 225.2 (M, 20), 182.1 (100), 167.1 (67), 139.1 (6).

Rf (TLC) 0.35 LP/diethyl ether 10/1

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.76 – 8.62 (m, 1H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 2.97 – 2.54 (m, 2H), 1.49 – 1.40 (m, 2H), 1.23 – 1.14 (m, 4H), 0.82 – 0.77 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.4, 149.2, 140.9, 140.4, 136.3, 129.9, 129.8, 128.4, 125.9, 124.3, 121.7, 33.0, 31.8, 31.1, 22.4, 14.1 ppm.

A II.4.18 2-(3-Hexylphenyl)pyridine (**23**)



20

General procedure B was followed. Chamber A was charged with 2-phenylpyridine (50.1 mg 322.8 µmol, 1.0 equiv.), KO_2CMes (11.3 mg, 55.9 µmol, 17 mol%] and $[Ru(p\text{-cym})Cl_2]_2$ (6.7 mg, 10.9 µmol, 3 mol%), while chamber B was filled with *n*-Hex_4NBr (421.60 mg, 970.1 mmol, 3.0 equiv.) and KOH (174.2 mg, 3.10 mmol, 9.6 equiv.) Toluene (1 mL) was added to both sides, the vials closed and stirred at 140 °C for 21 h. After cooling, GC/MS analysis indicated almost full conversion of the starting material and the reaction mixture was worked up. Purification via column chromatography afforded 55.9 mg (233.5 µmol) product **23** as colorless oil corresponding to 72% yield.

Analytical data were in accordance with literature[5]

GC-MS Method (Std 12min); rt = 6.8 min; 239.2 (M 22), 182.1 (100), 167.1 (58).

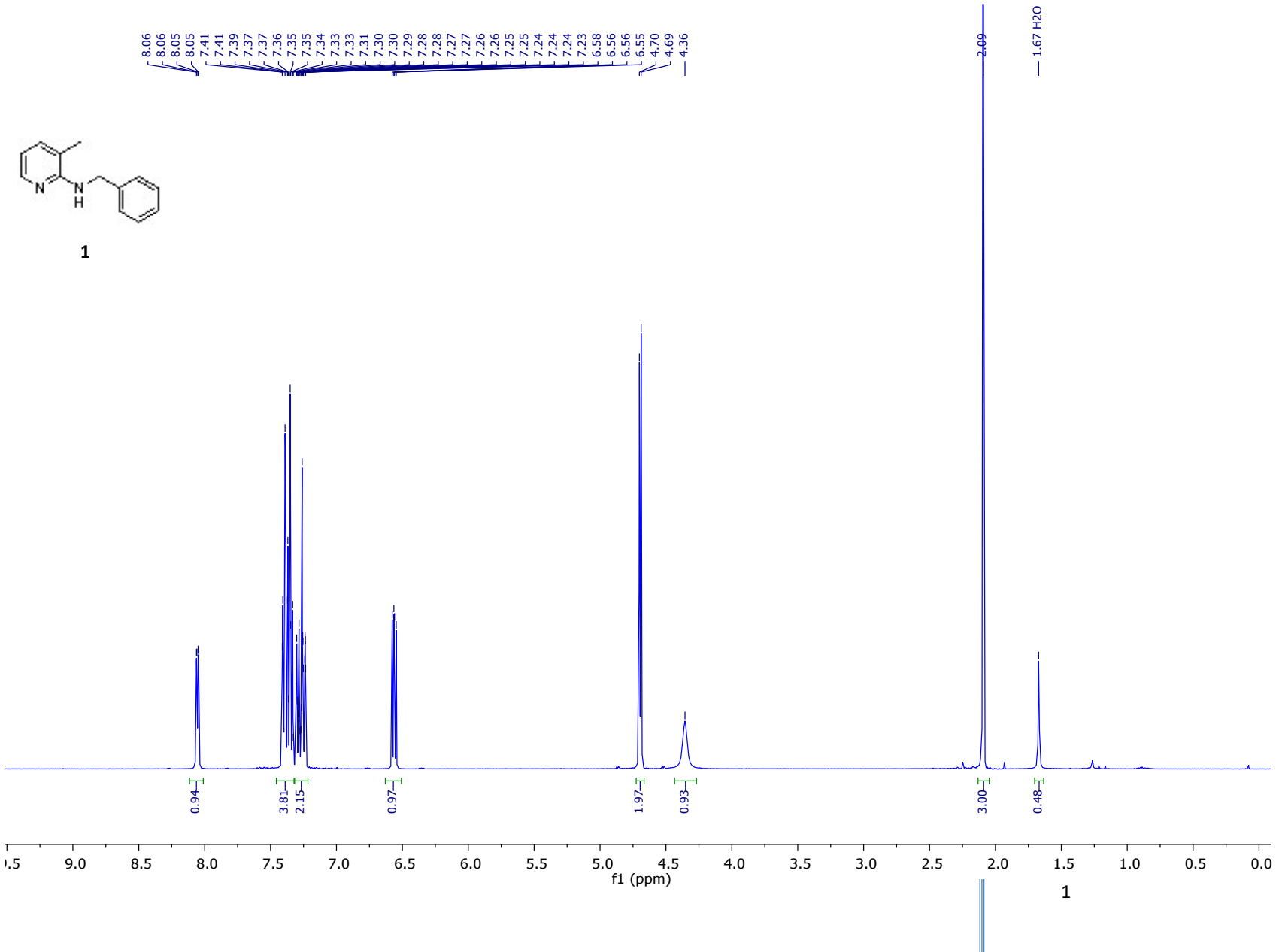
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J*=4.43, 1H), 7.76 (td, *J*=7.72, 1.7, 1H), 7.39 (dd, *J*=7.85, 1.1, 1H), 7.36 – 7.24 (m, 5H), 2.79 – 2.54 (m, 2H), 1.63 – 1.38 (m, 2H), 1.28 – 1.10 (m, 6H), 0.81 (t, *J*=6.8, 3H) ppm.

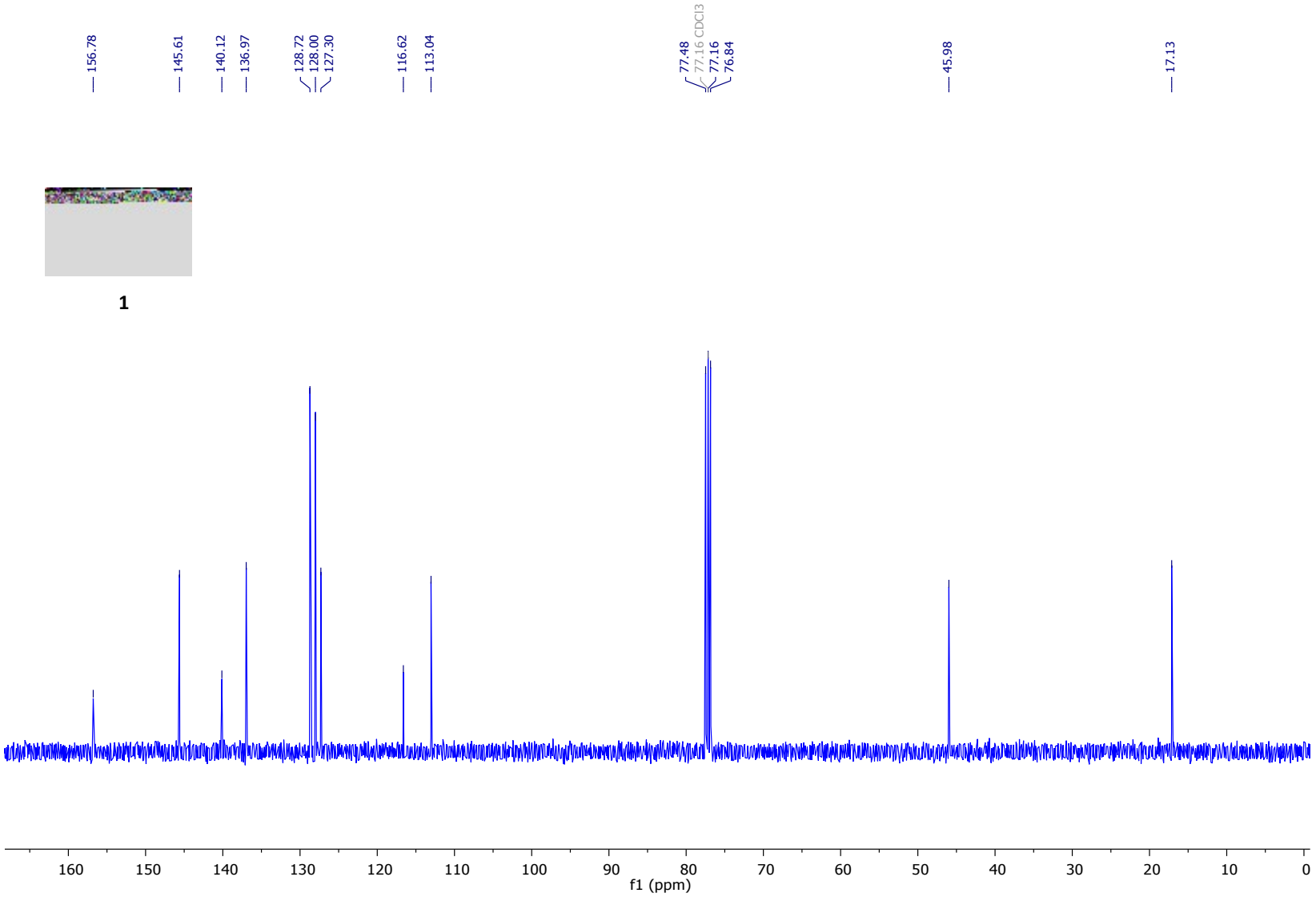
^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.2, 149.0, 140.9, 140.1, 136.5, 129.9, 129.8, 128.5, 125.9, 124.4, 121.9, 33.0, 31.6, 31.3, 29.2, 22.6, 14.2 ppm.

A III References

1. M. Spettel, R. Pollice and M. Schnürch, *Org. Lett.*, 2017, **19**, 4287-4290.
2. D. A. Gutierrez, W.-C. C. Lee, Y. Shen and J. J. Li, *Tetrahedron Lett.*, 2016, **57**, 5372-5376.
3. J. S. Dickstein, J. M. Curto, O. Gutierrez, C. A. Mulrooney and M. C. Kozlowski, *J. Org. Chem.*, 2013, **78**, 4744-4761.
4. Q. Chen, L. Ilies, N. Yoshikai and E. Nakamura, *Org. Lett.*, 2011, **13**, 3232-3234.
5. L. Ackermann, P. Novak, R. Vicente and N. Hofmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 6045.

A IV NMR Spectra

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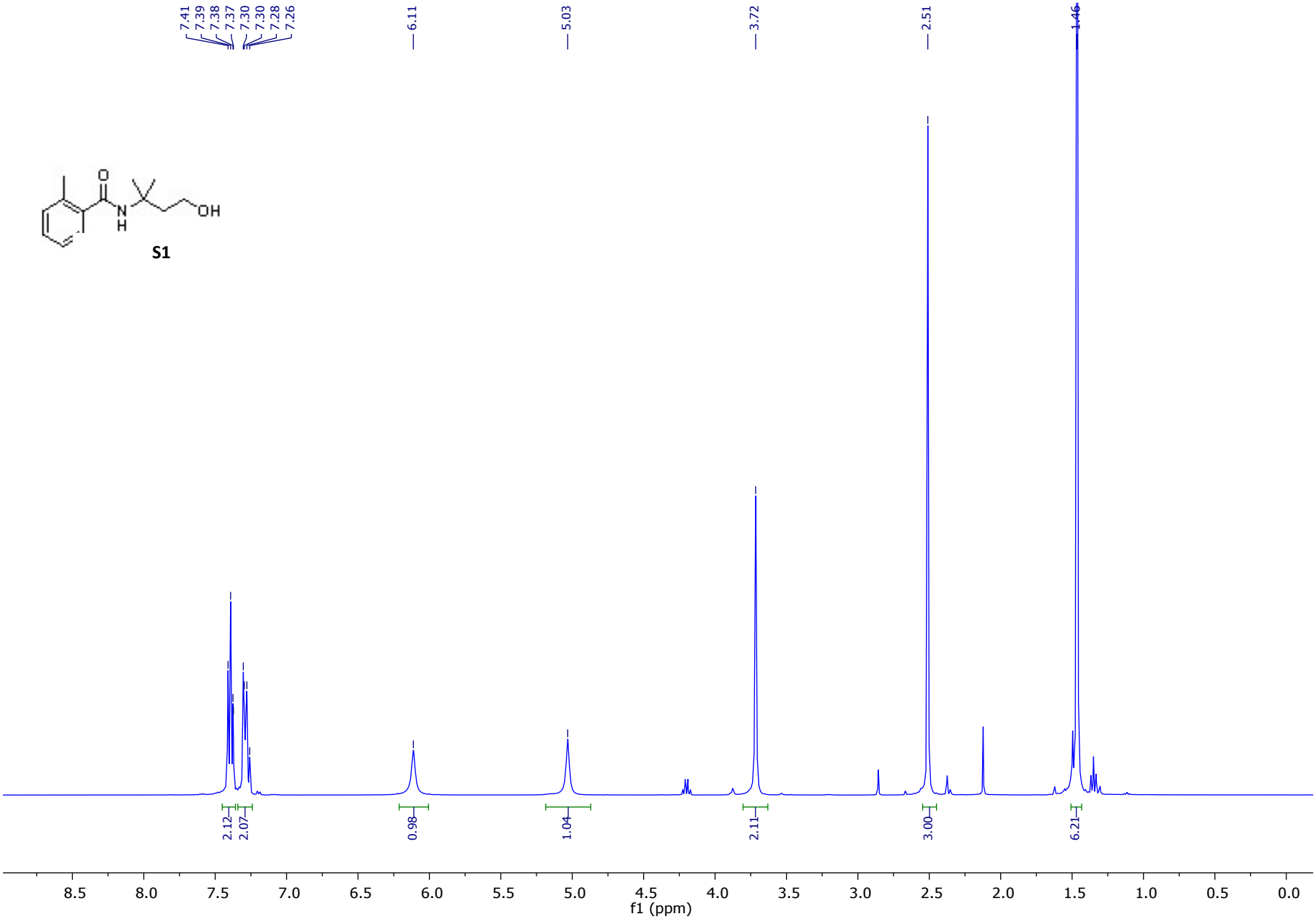
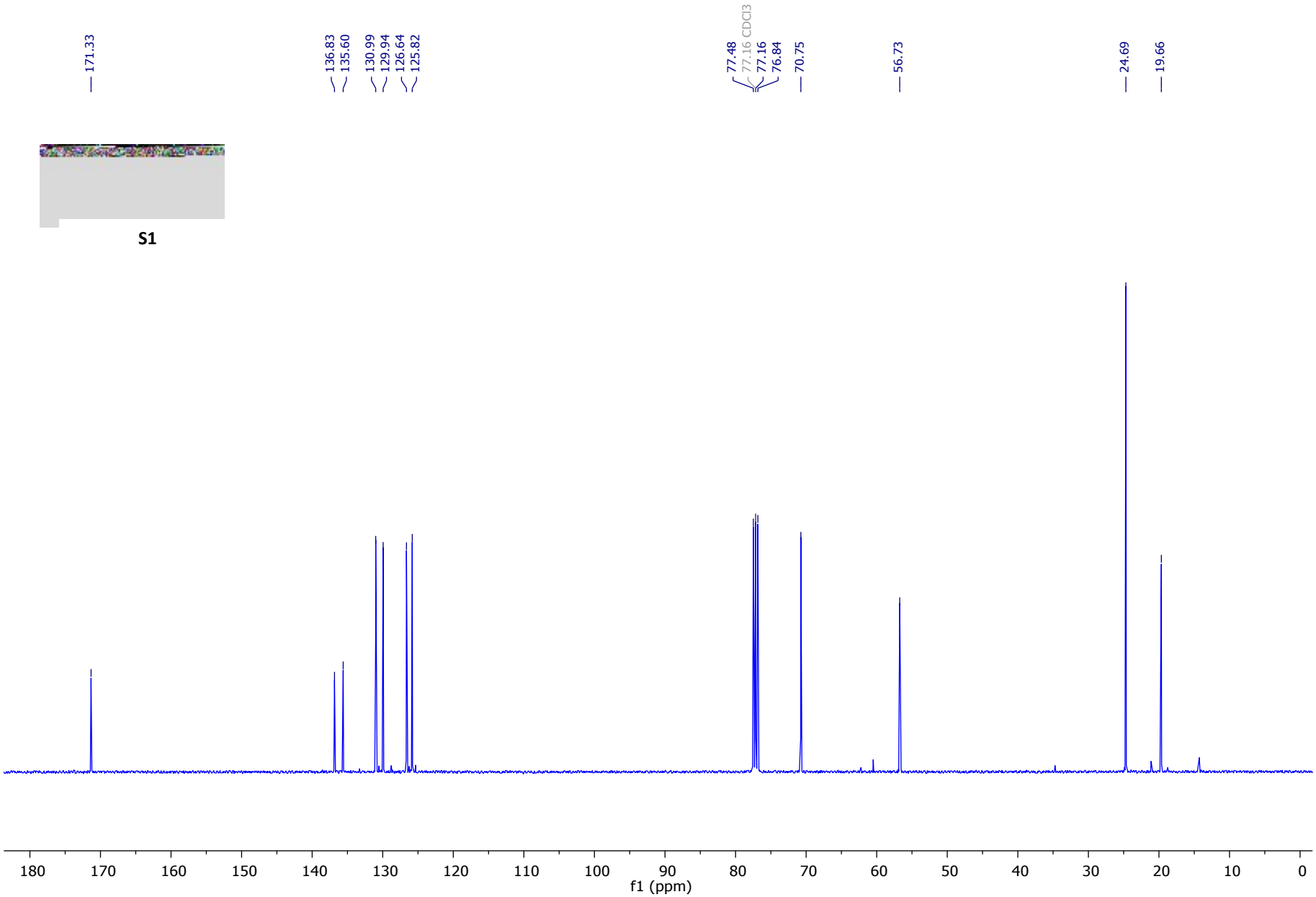
145.61
140.12
136.97
128.72
128.00
127.30
116.62
113.04
77.48
77.16 CDCl3
77.16
76.84
45.98
17.13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1


7.41
7.39
7.38
7.37
7.30
7.30
7.28
7.26
6.11
5.03
3.72
2.51
1.46
O
N
H
OH
S1
2.12
2.07
0.98
1.04
2.11
3.00
6.21
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)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130.99
129.94
126.64
125.82
77.48
77.16 CDCl3
77.16
76.84
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56.73
24.69
19.66
180
170
160
150
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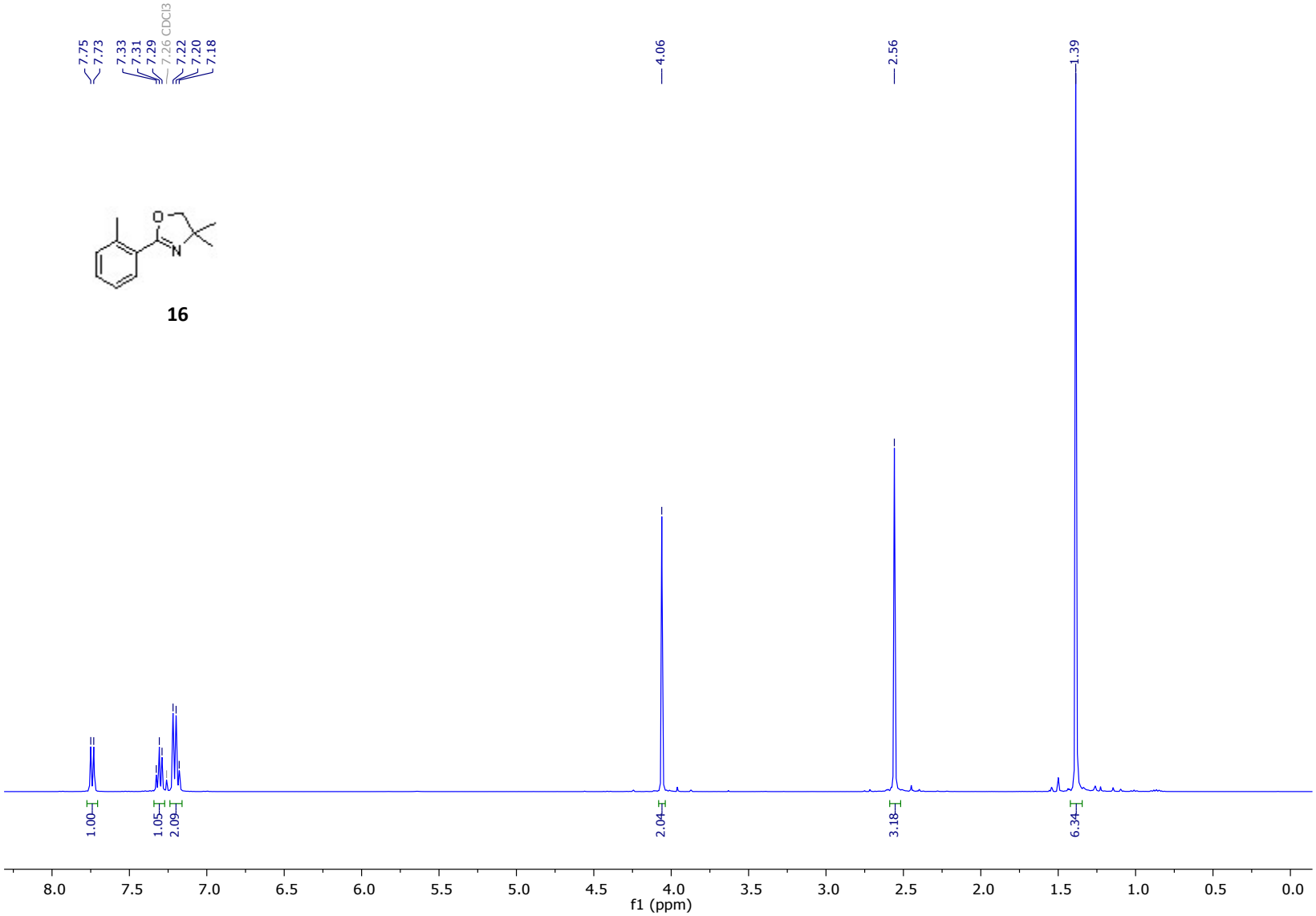
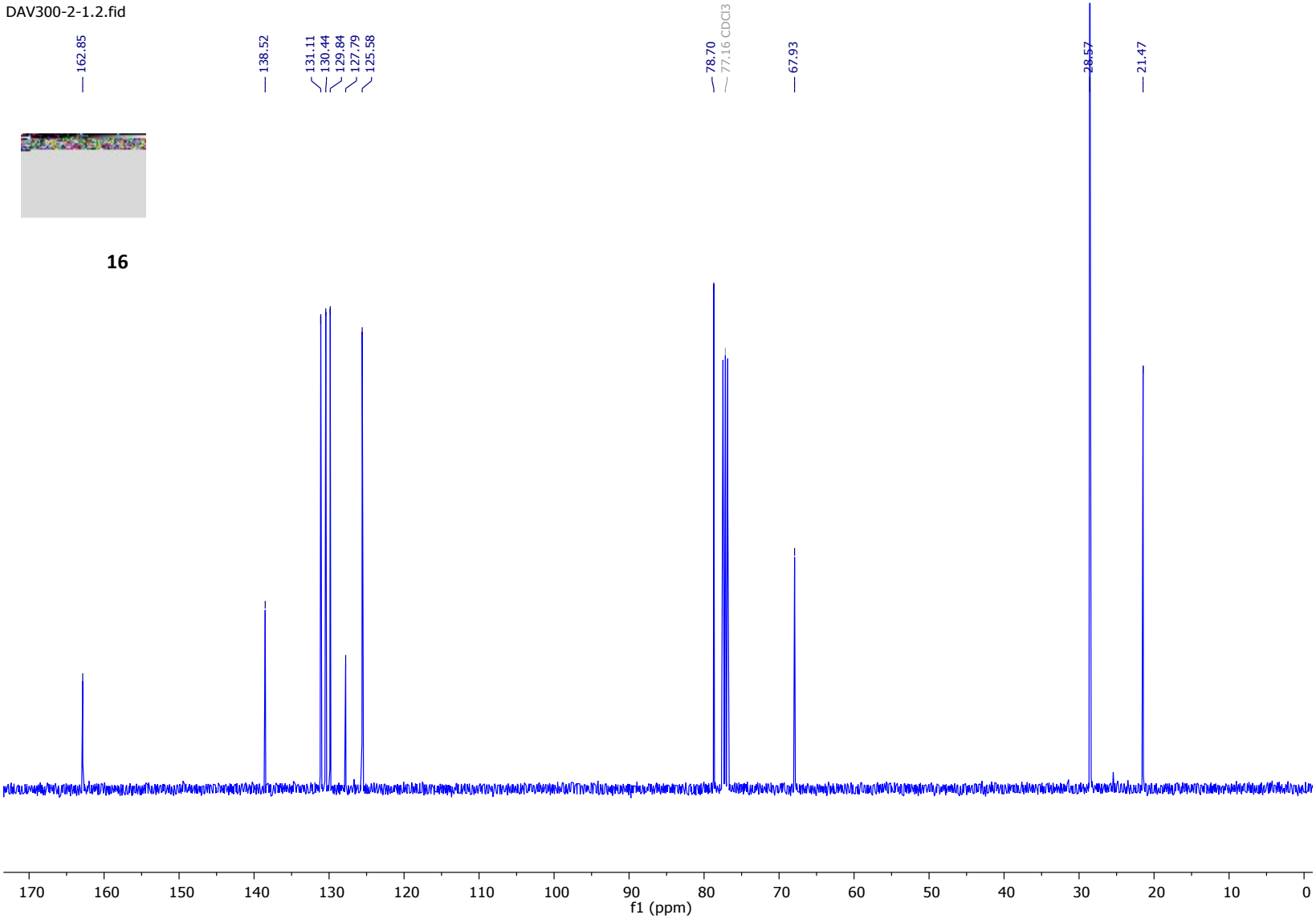
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S1

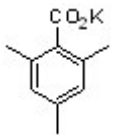

7.75
7.73
7.33
7.31
7.29
7.26 CDCl3
7.22
7.20
7.18
4.06
2.56
1.39
1.00
1.05
2.09
2.04
3.18
6.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

16

DAV300-2-1.2.fid

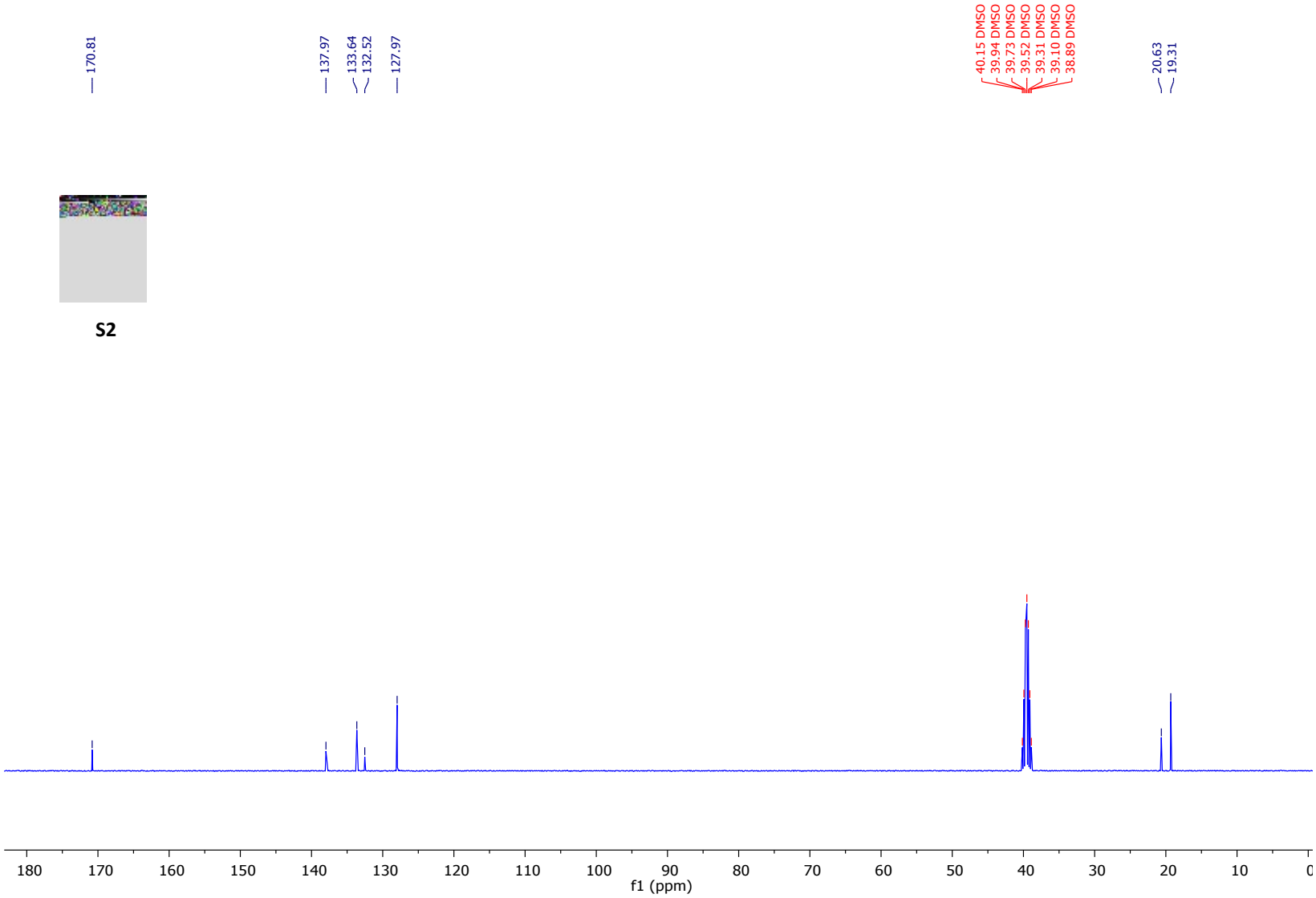


16


CO2K

S2

6.61
2.50 DMSO-d6
2.15
2.12
2.00
3.07
5.82
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


170.81
137.97
133.64
132.52
127.97
40.15 DMSO
39.94 DMSO
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39.52 DMSO
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20.63
19.31
180
170
160
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110
100
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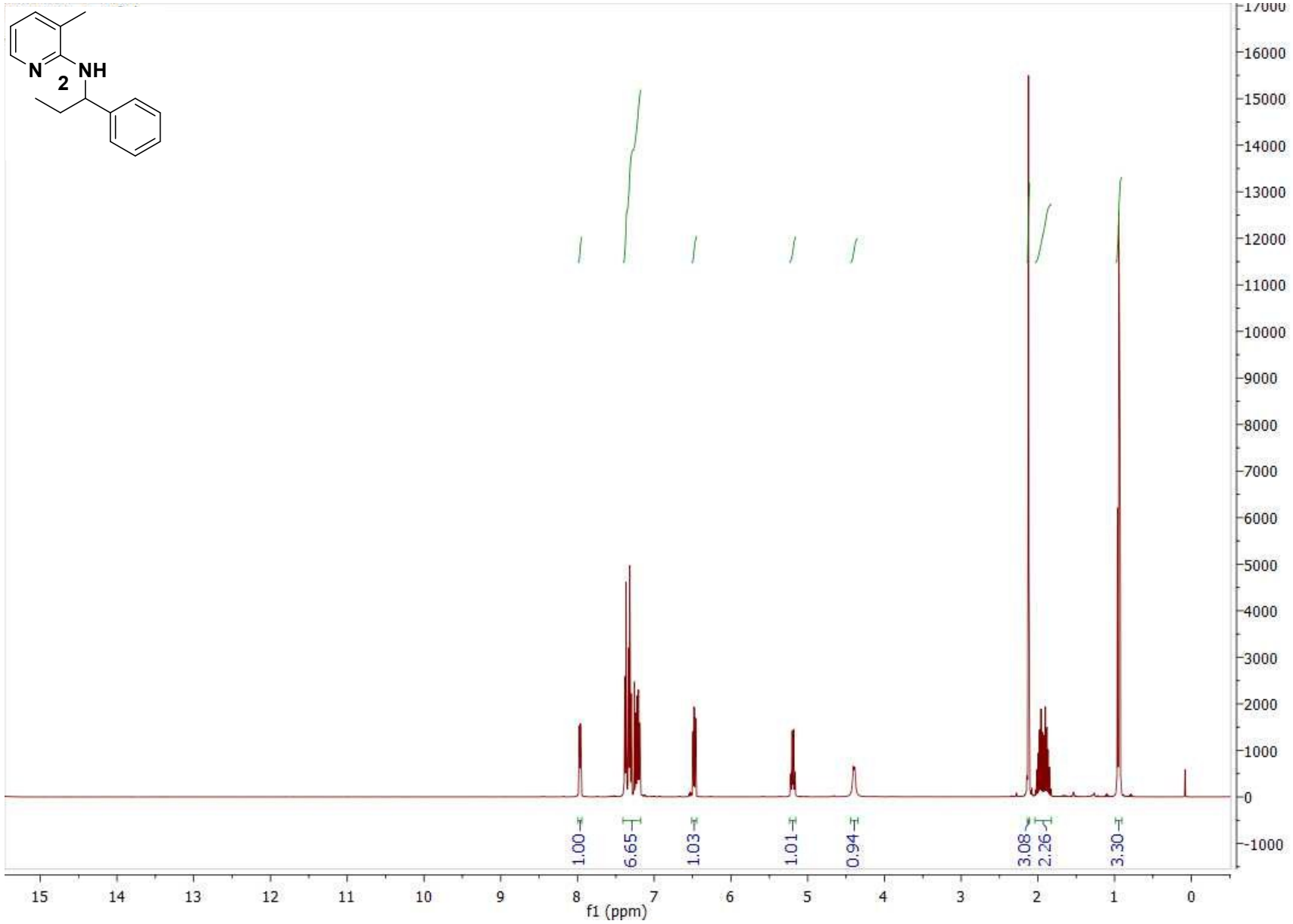
50
40
30
20
10
0
f1 (ppm)

S2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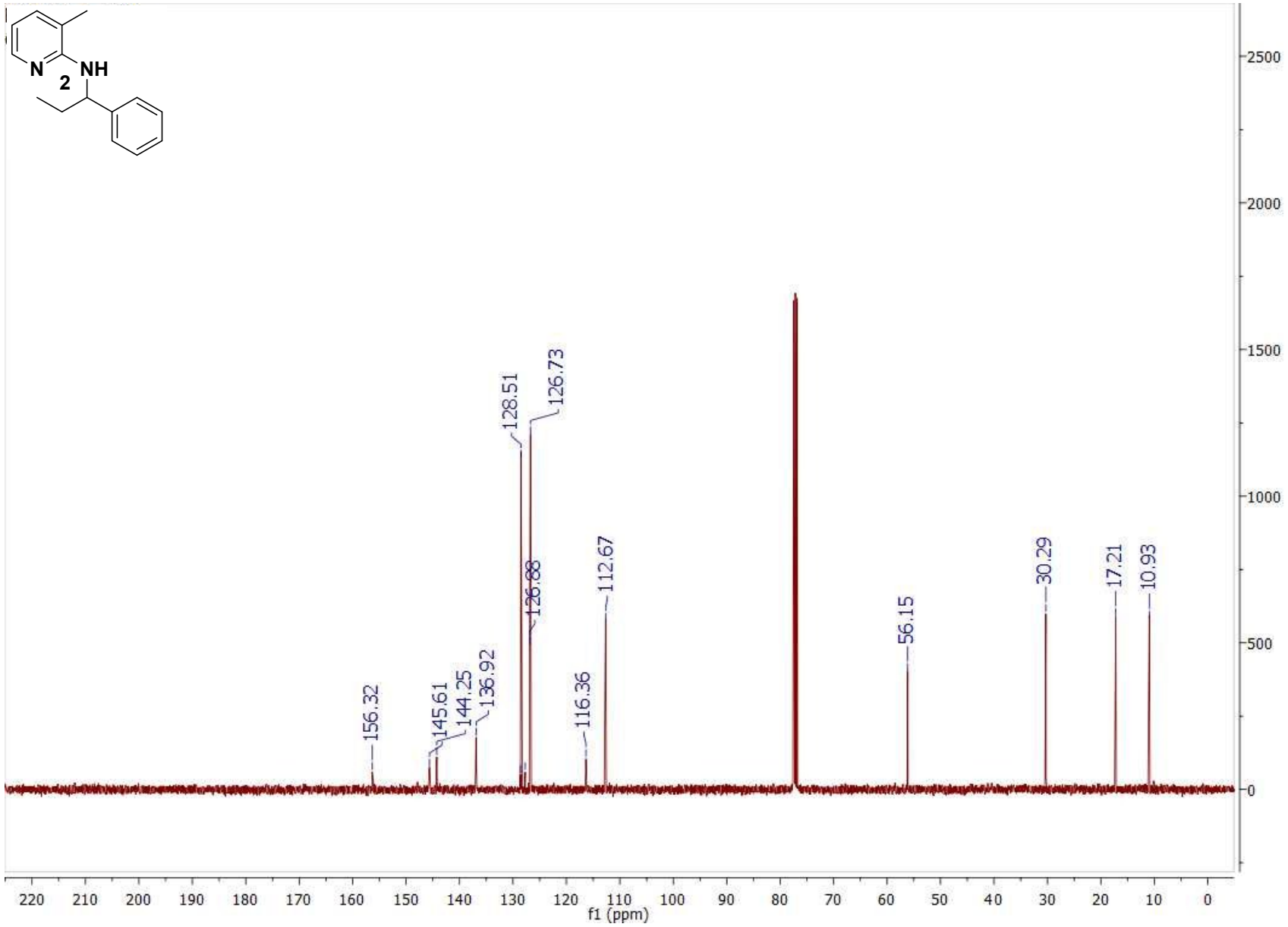
3.08
2.26
3.30
f1 (ppm)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NH
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126.88
126.73
116.36
112.67
56.15
30.29
17.21
10.93
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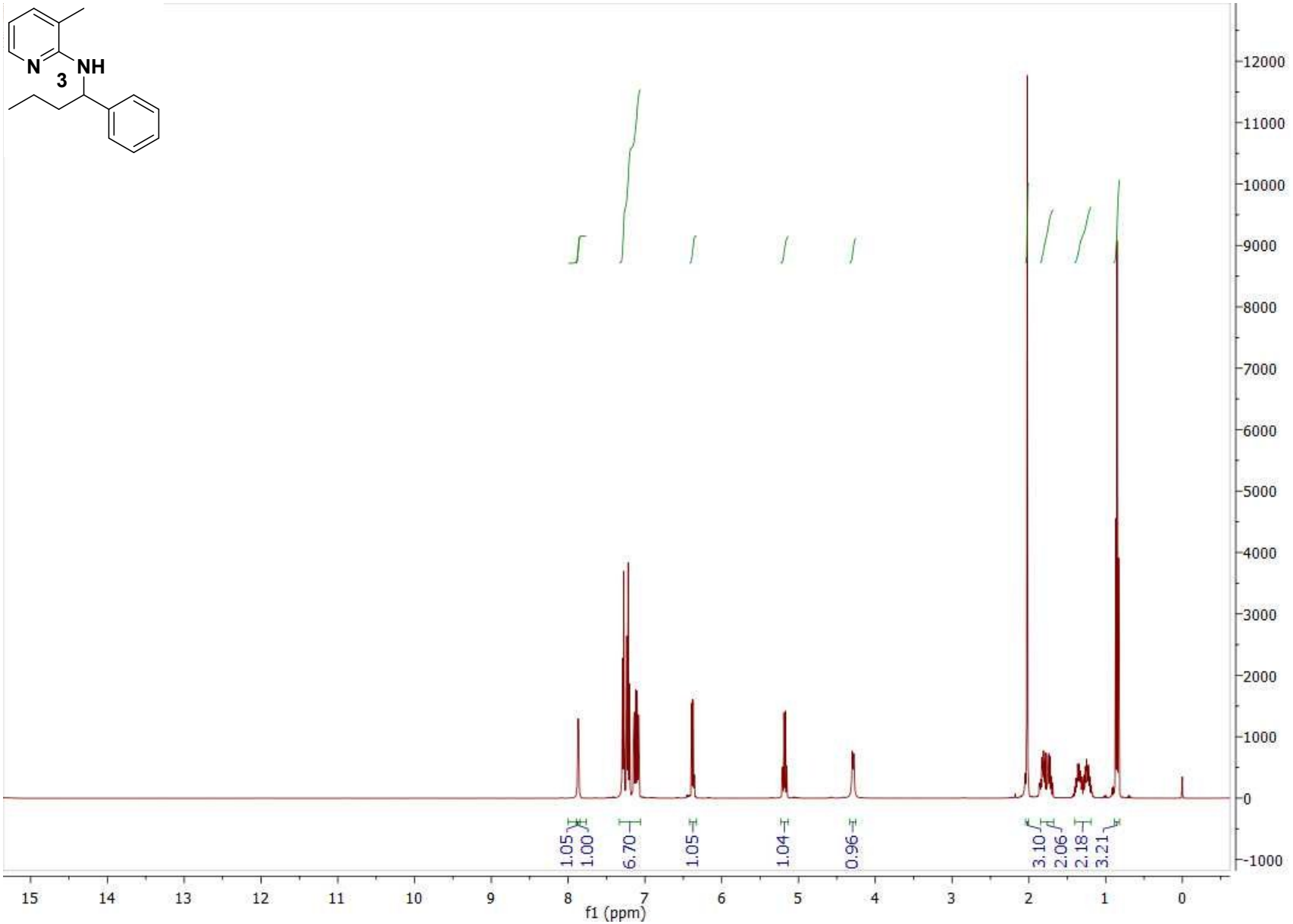
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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NH
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11000
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9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.05
1.00
6.70
1.05
1.04
0.96
3.10
2.06
2.18
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13
12
11
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5
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3
2
1
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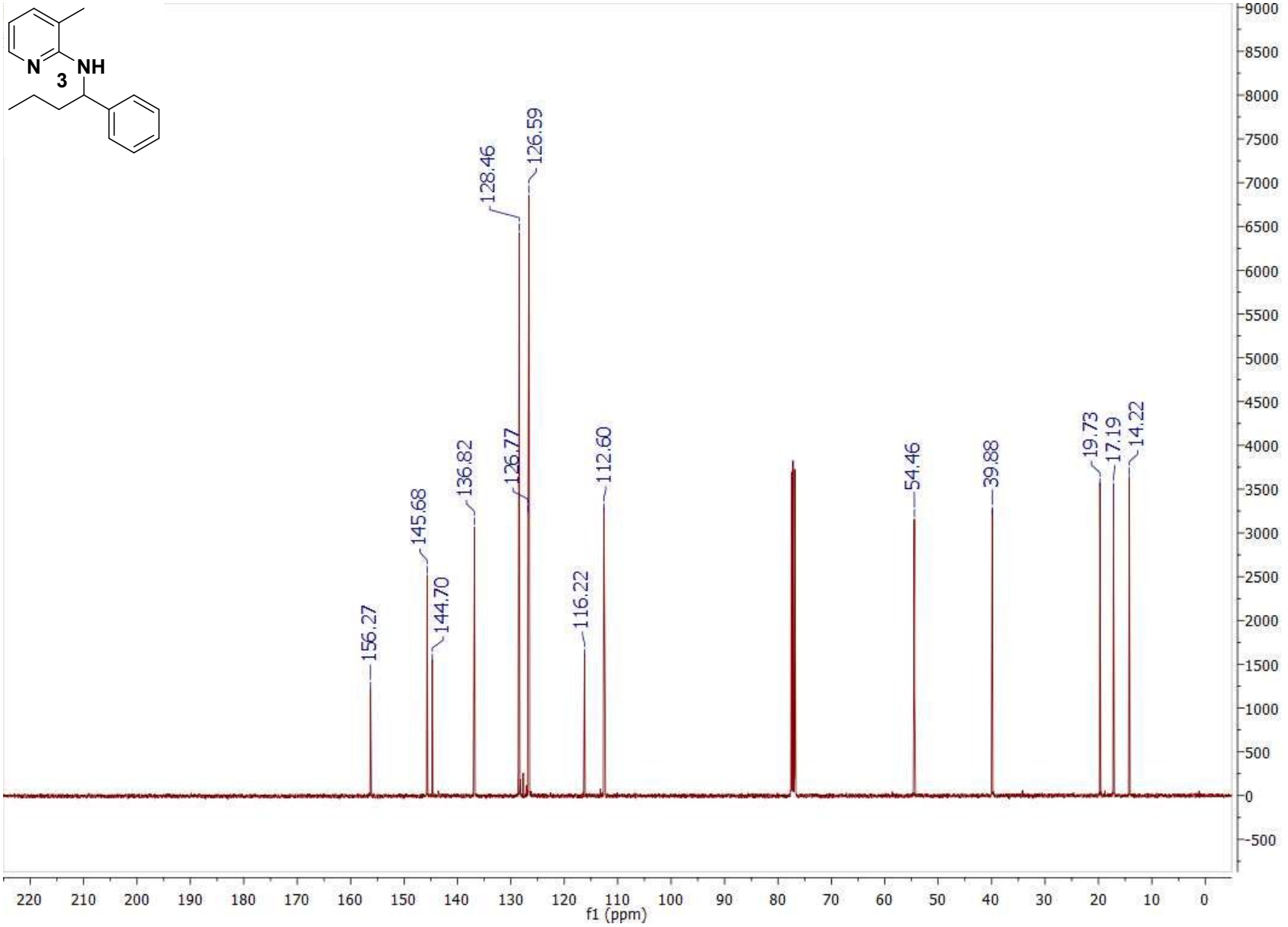
f1 (ppm)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NH
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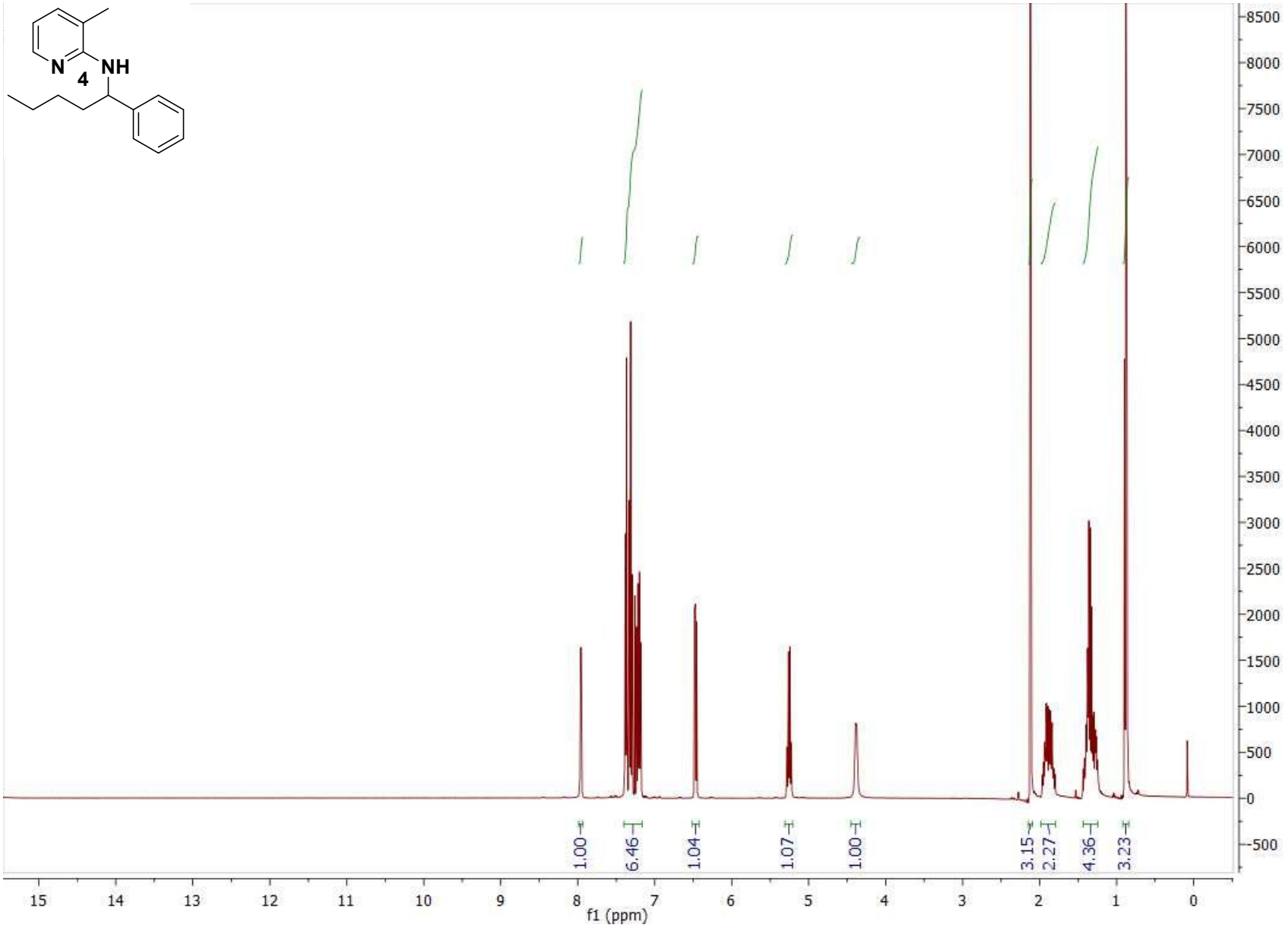
19.73
17.19
14.22
f1 (ppm)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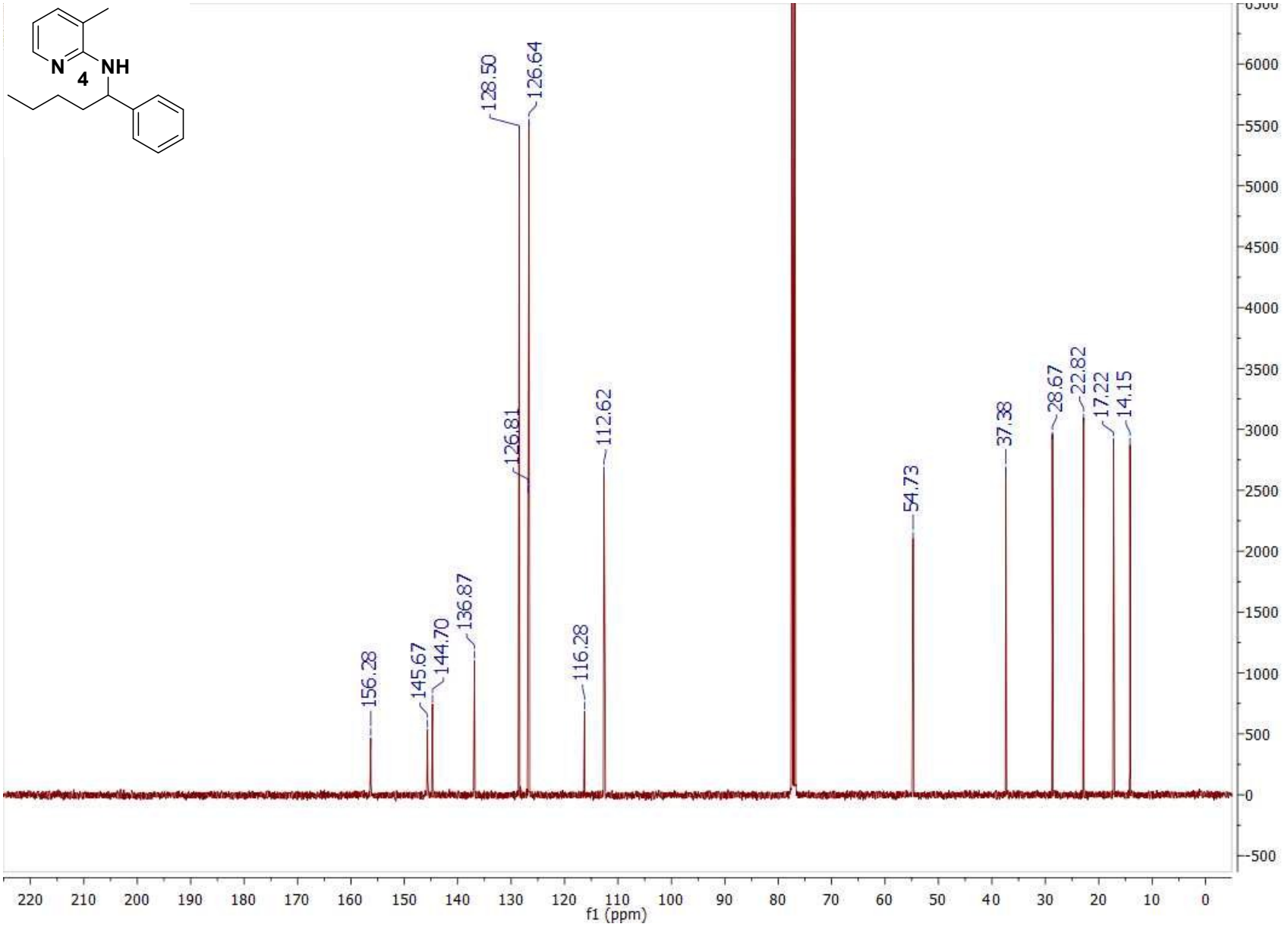
f1 (ppm)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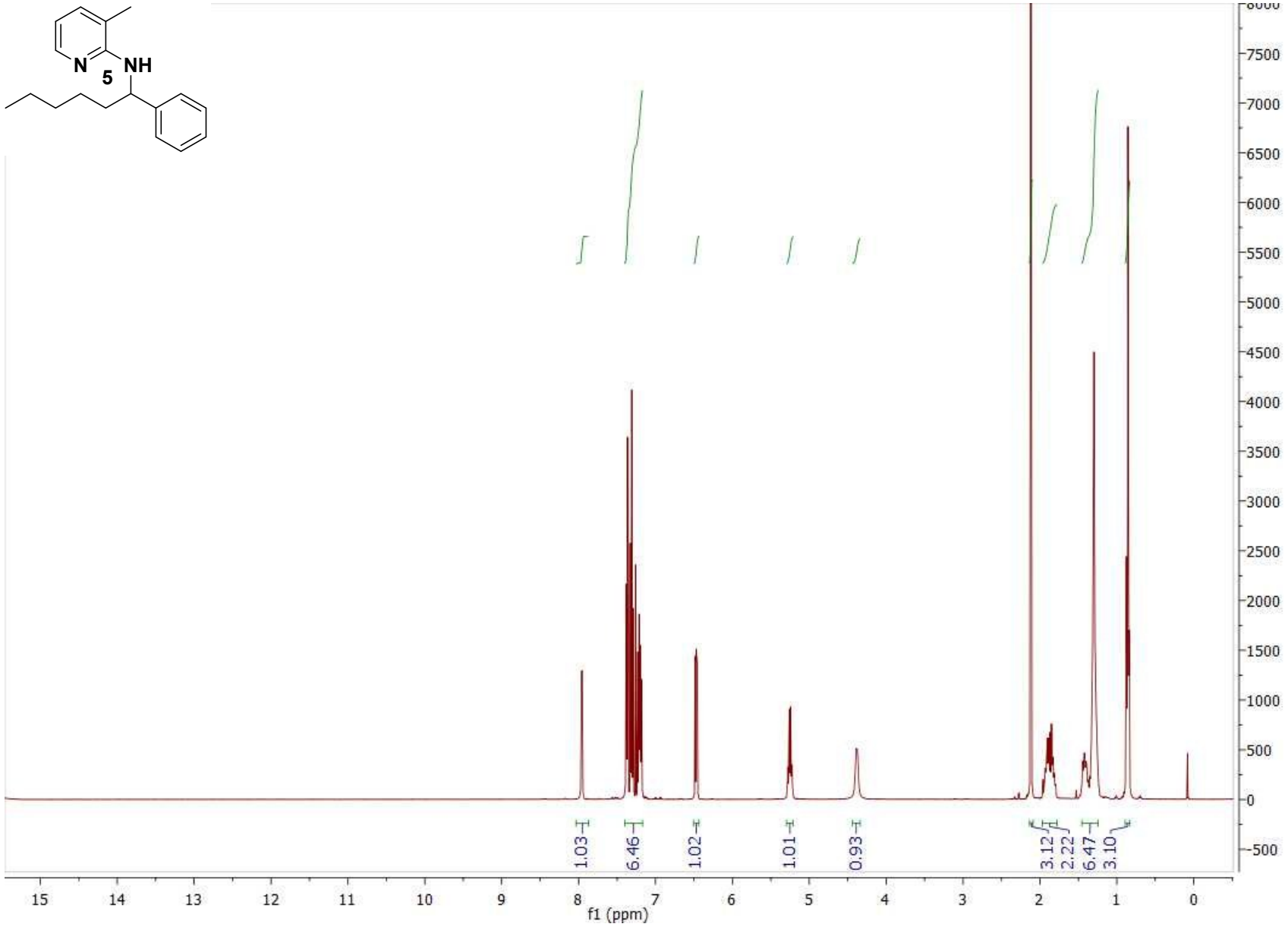
14.15
f1 (ppm)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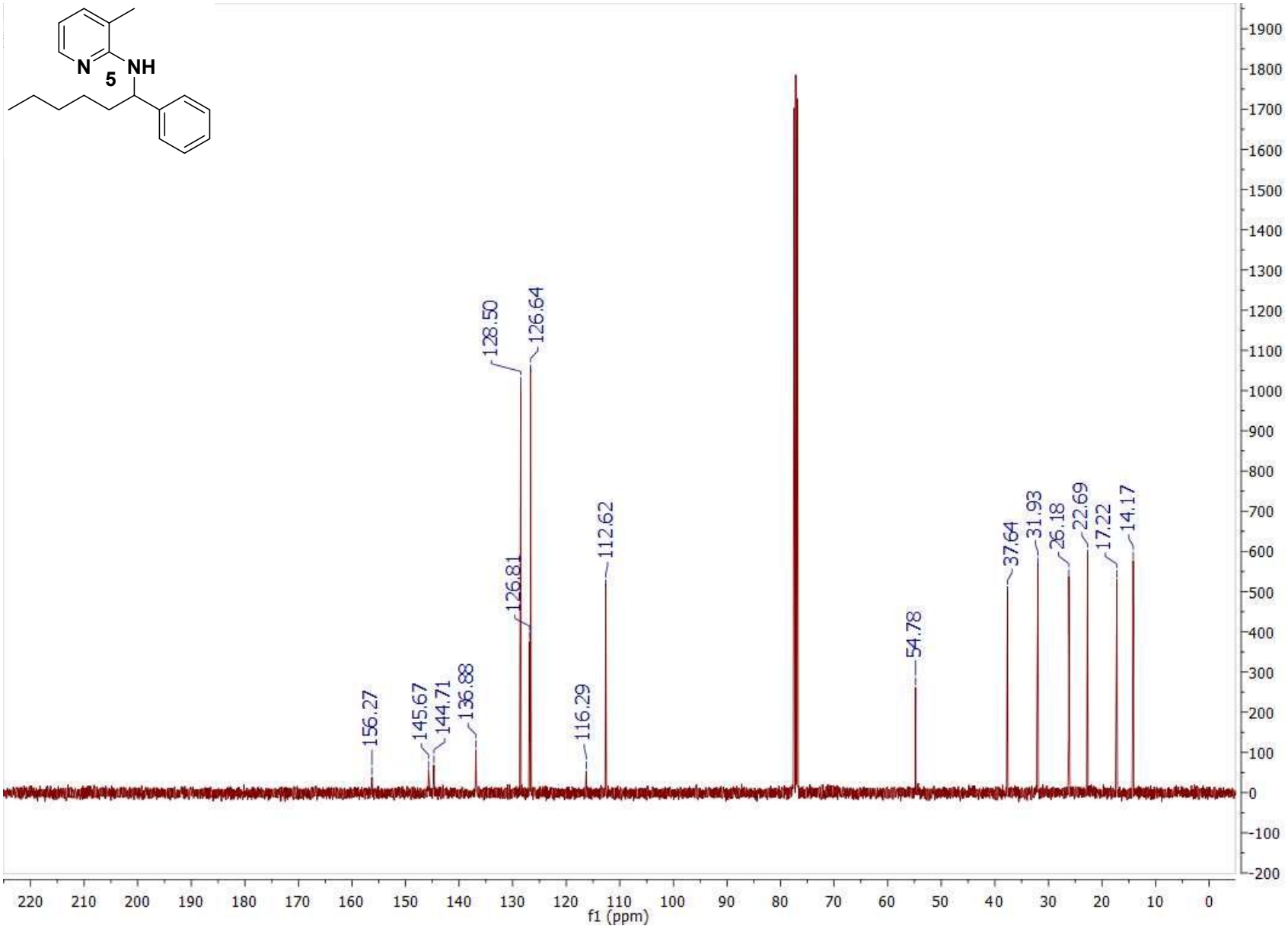
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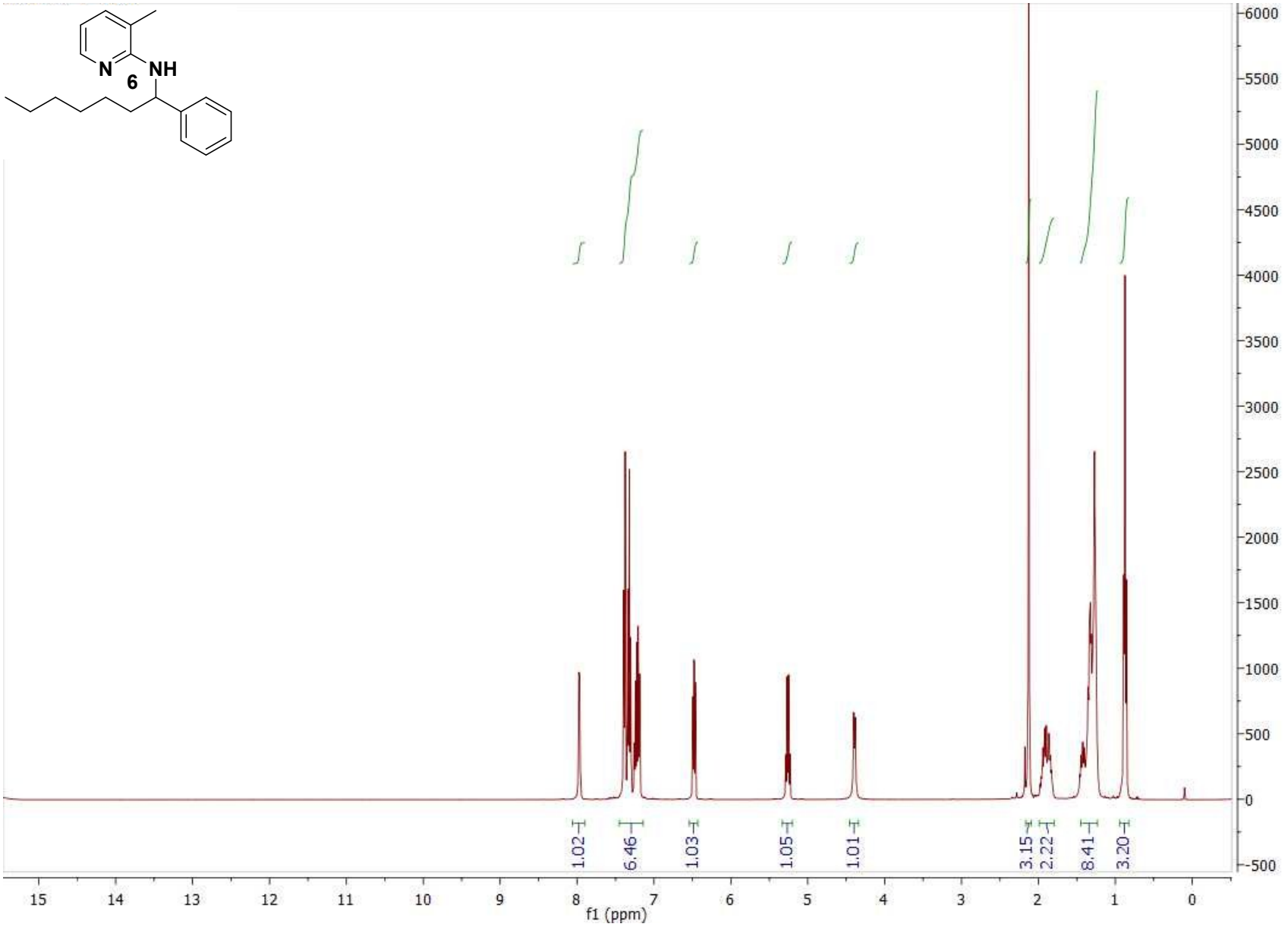
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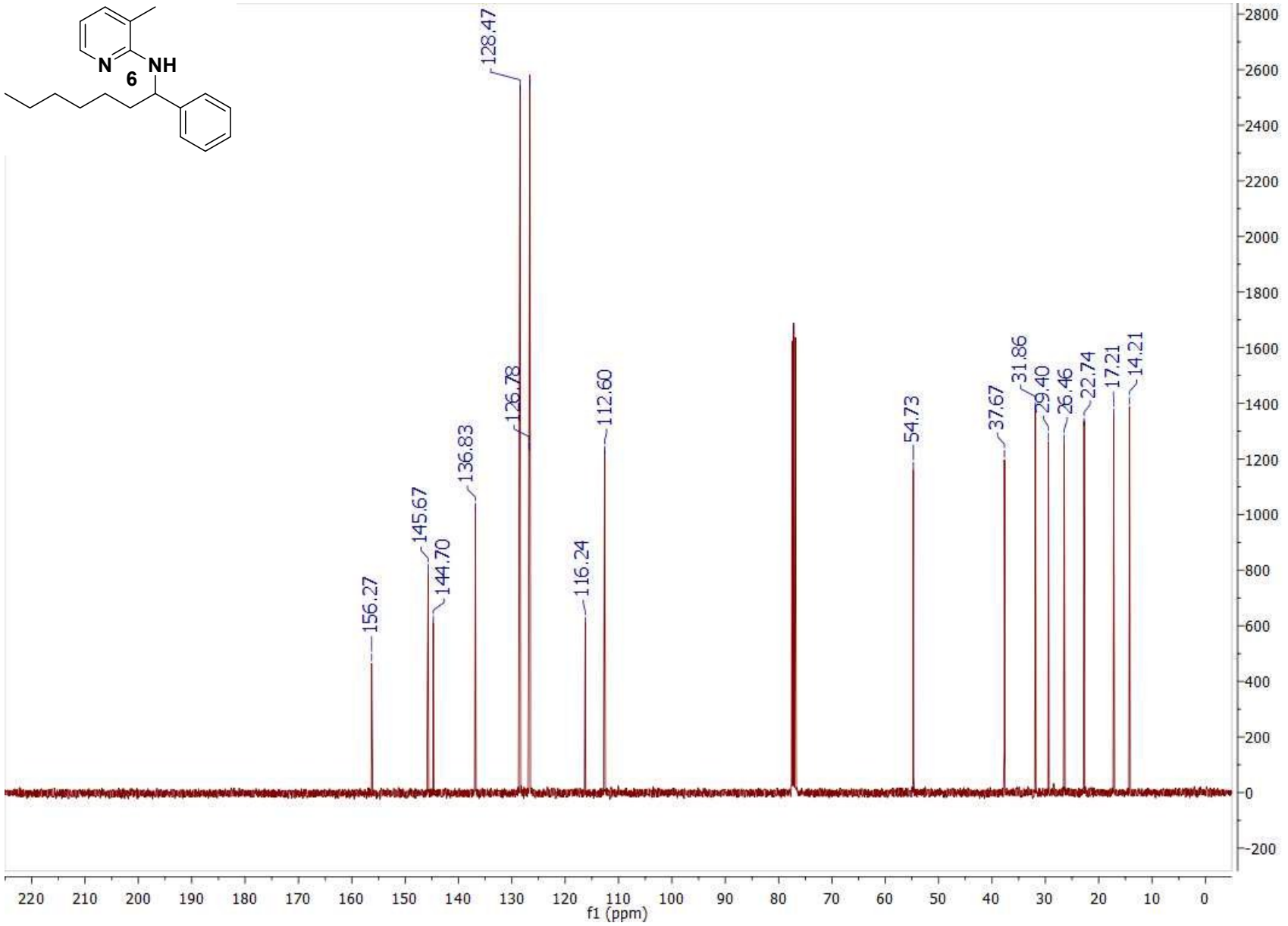
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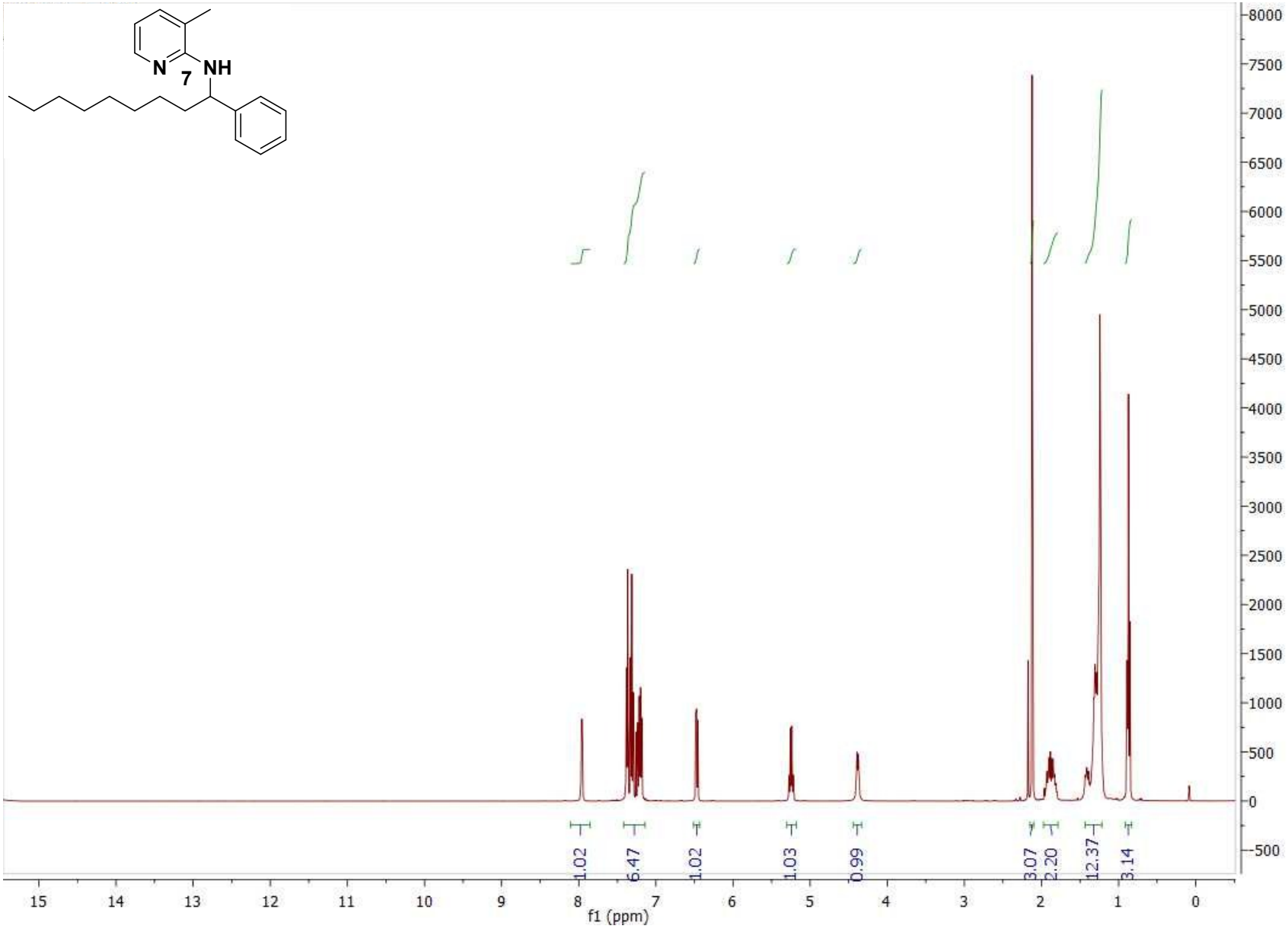
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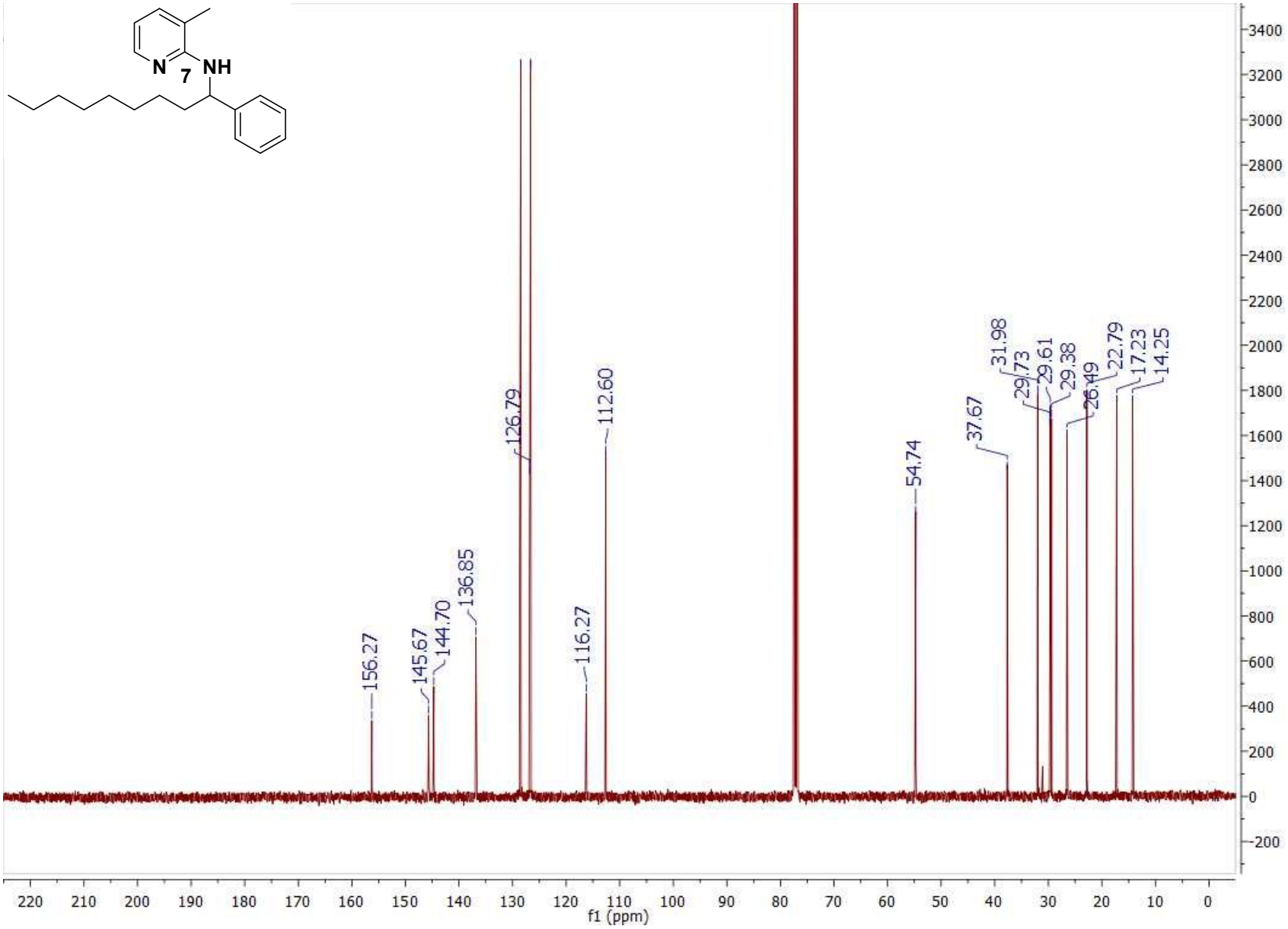
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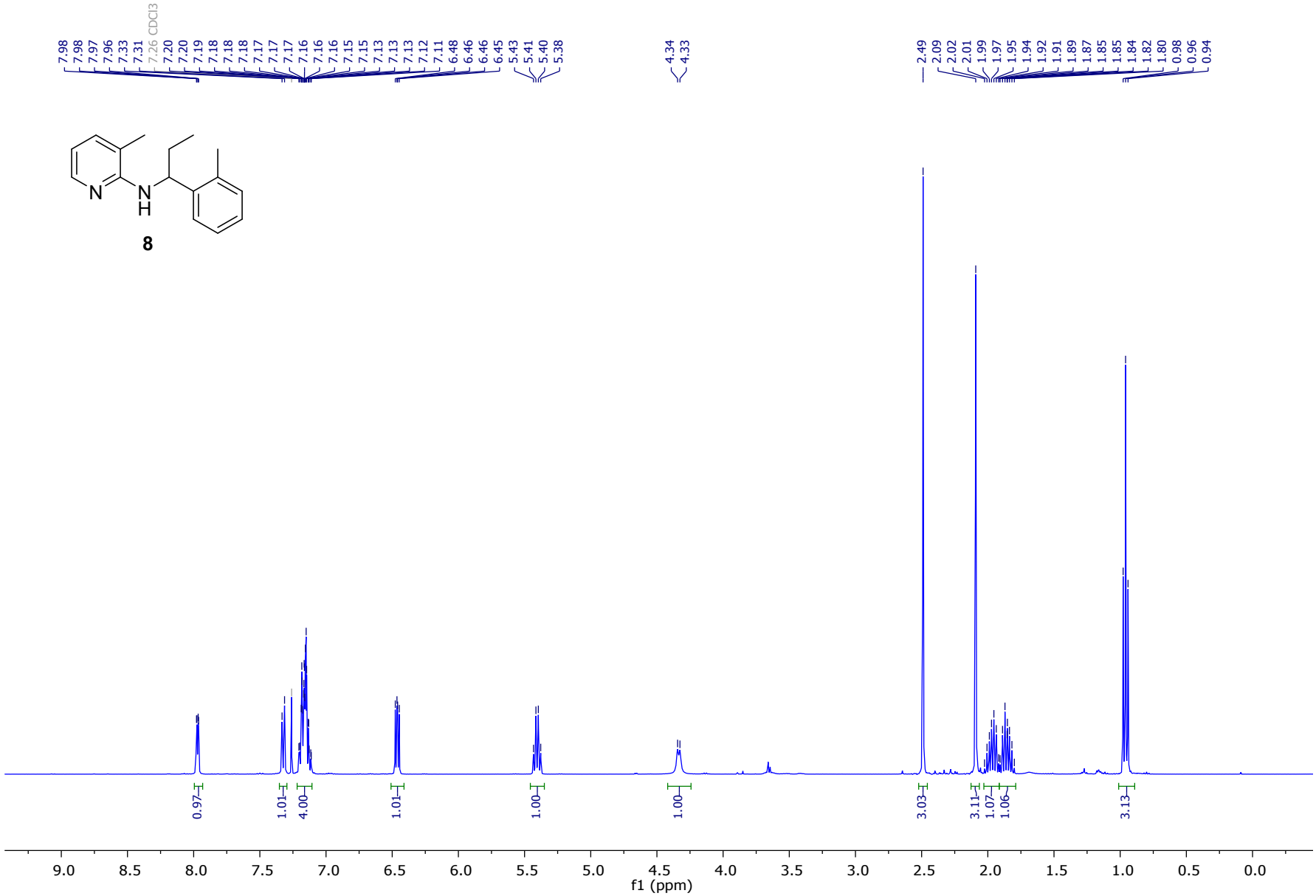
17.23
14.25
f1 (ppm)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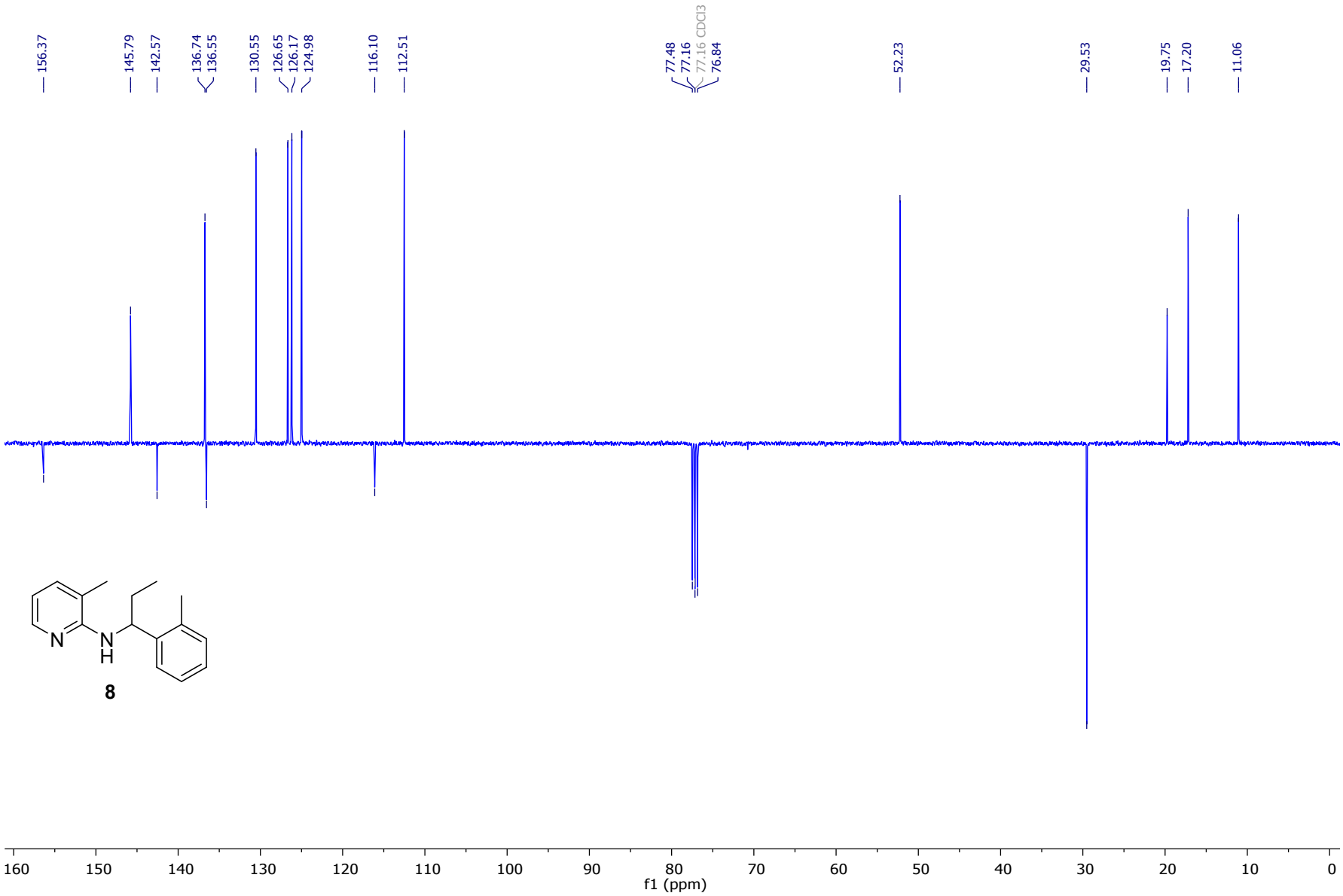
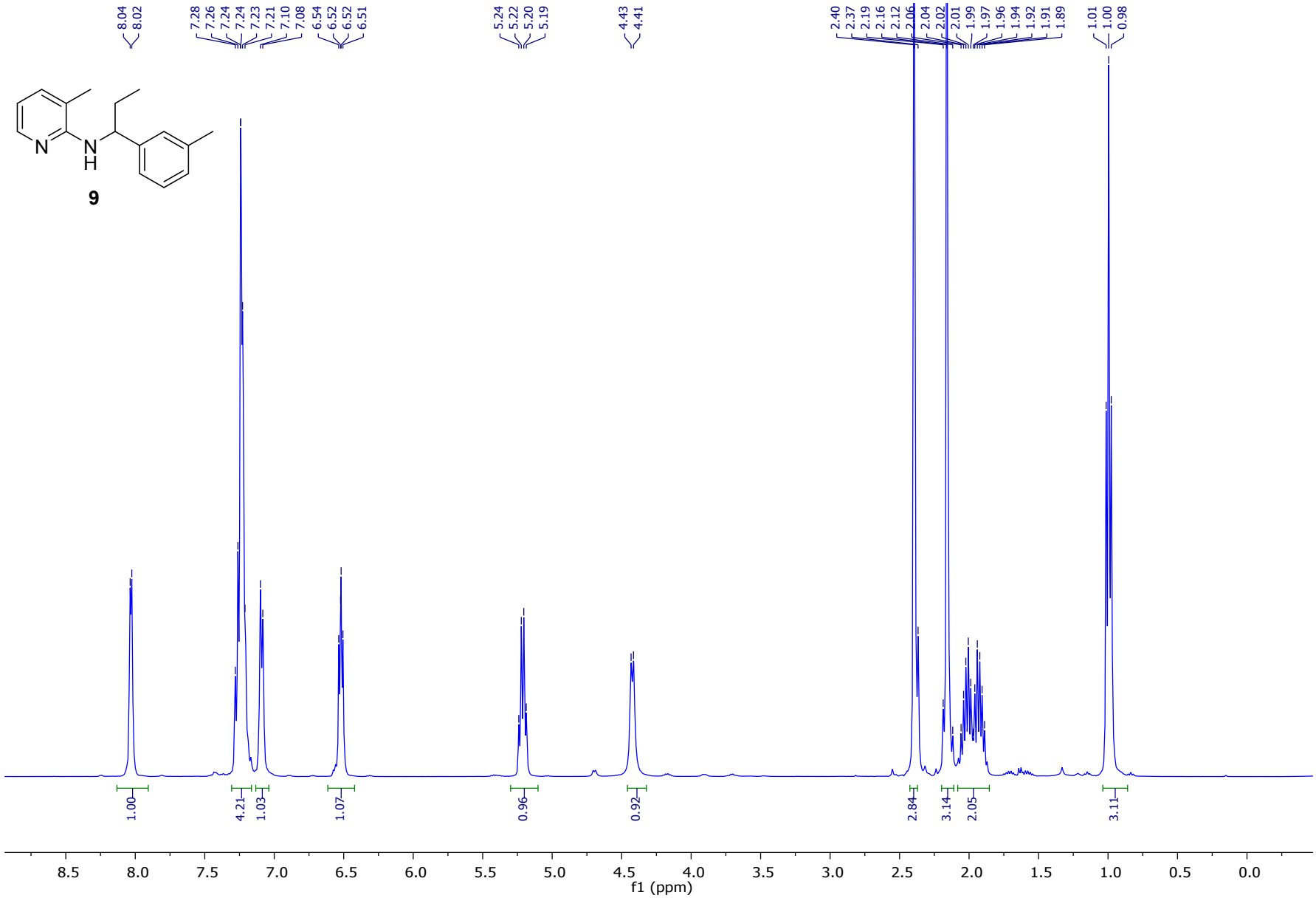
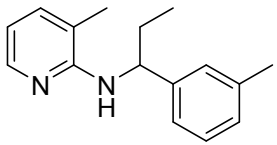
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.13
7.13
7.13
7.12
7.11
6.48
6.46
6.46
6.45
5.43
5.41
5.40
5.38
4.34
4.33
2.49
2.09
2.02
2.01
1.99
1.97
1.95
1.94
1.92
1.91
1.89
1.87
1.85
1.85
1.84
1.82
1.80
0.98
0.96
0.94
N
N
H
8
0.97
1.01
4.00
1.01
1.00
1.00
3.03
3.11
1.07
1.06
3.13
9.0
8.5
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)


156.37
145.79
142.57
136.74
136.55
130.55
126.65
126.17
124.98
116.10
112.51
77.48
77.16
77.16 CDCl3
76.84
52.23
29.53
19.75
17.20
11.06
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

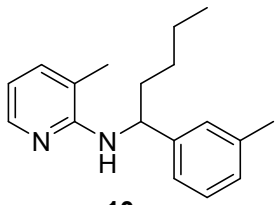
8


8.04
8.02
7.28
7.26
7.24
7.24
7.23
7.21
7.10
7.08
6.54
6.52
6.52
6.51
5.24
5.22
5.20
5.19
4.43
4.41
2.40
2.37
2.19
2.16
2.12
2.06
2.04
2.02
2.01
1.99
1.97
1.96
1.94
1.92
1.91
1.89
1.01
1.00
0.98
N
N
H
9
1.00
4.21
1.03
1.07
0.96
0.92
2.84
3.14
2.05
3.11
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)



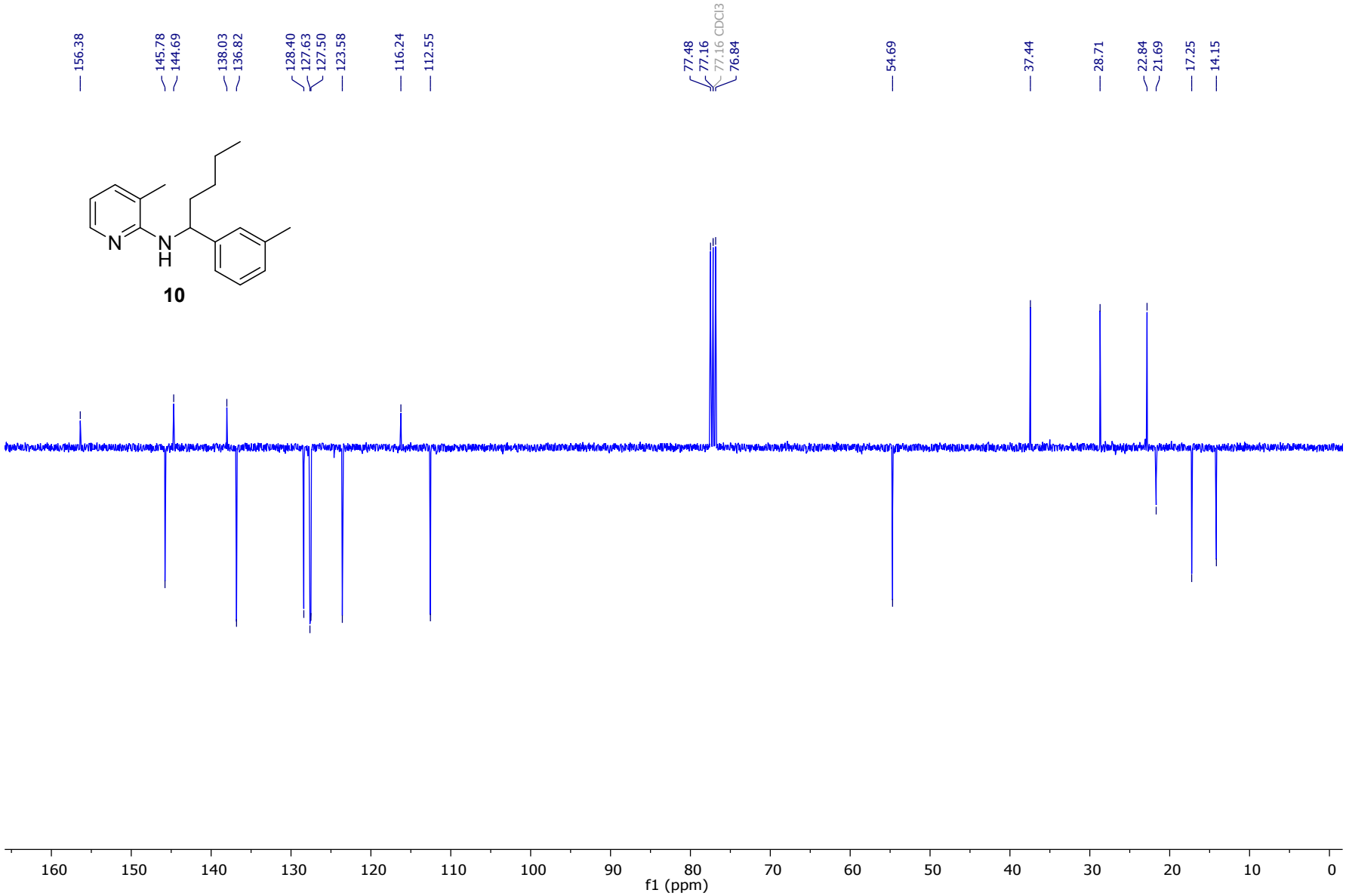
9

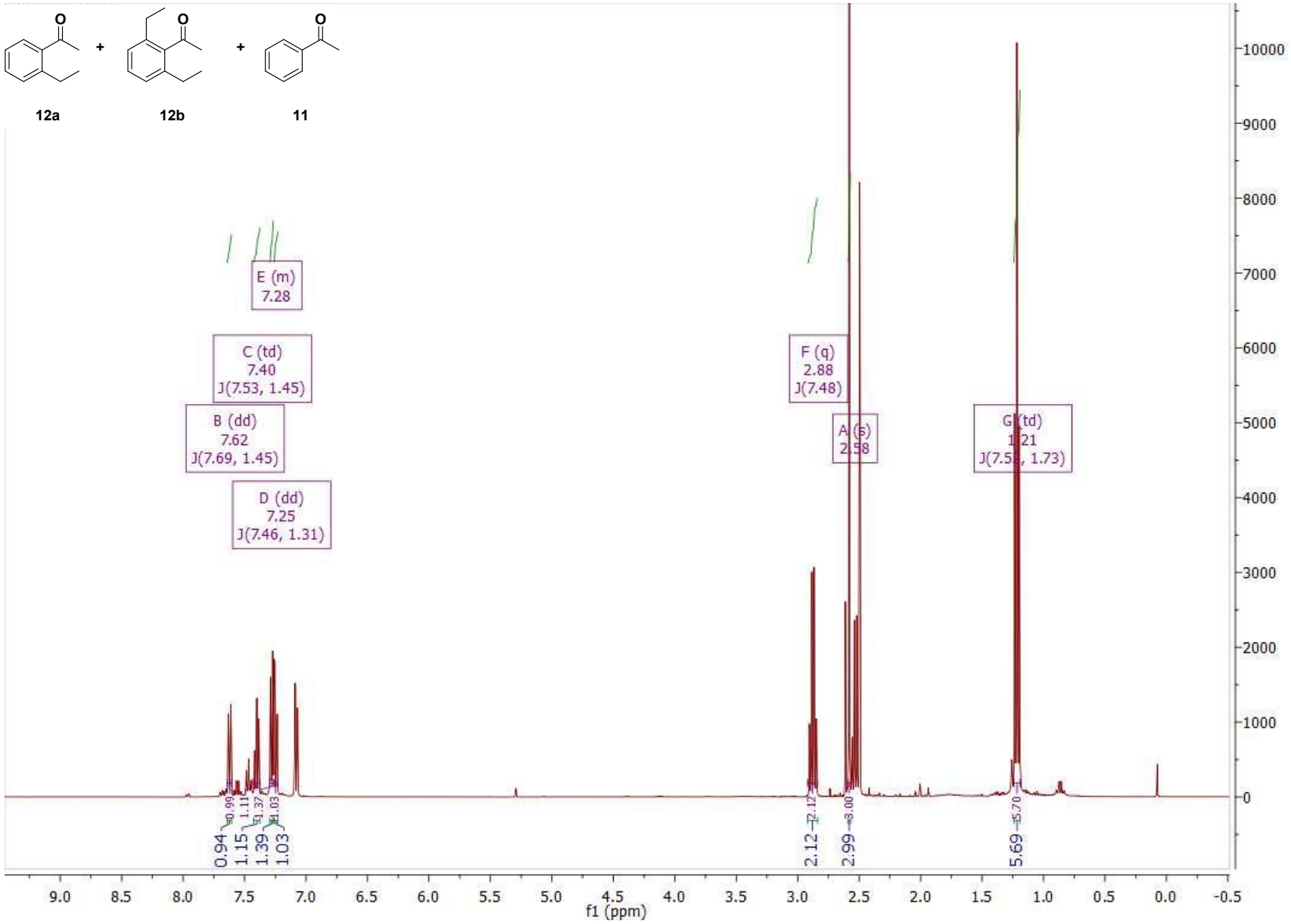
156.34
145.65
144.14
137.94
136.76
128.39
128.33
127.61
127.51
123.60
116.21
112.51
77.44
77.12
76.80
56.03
30.21
21.59
17.12
10.90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

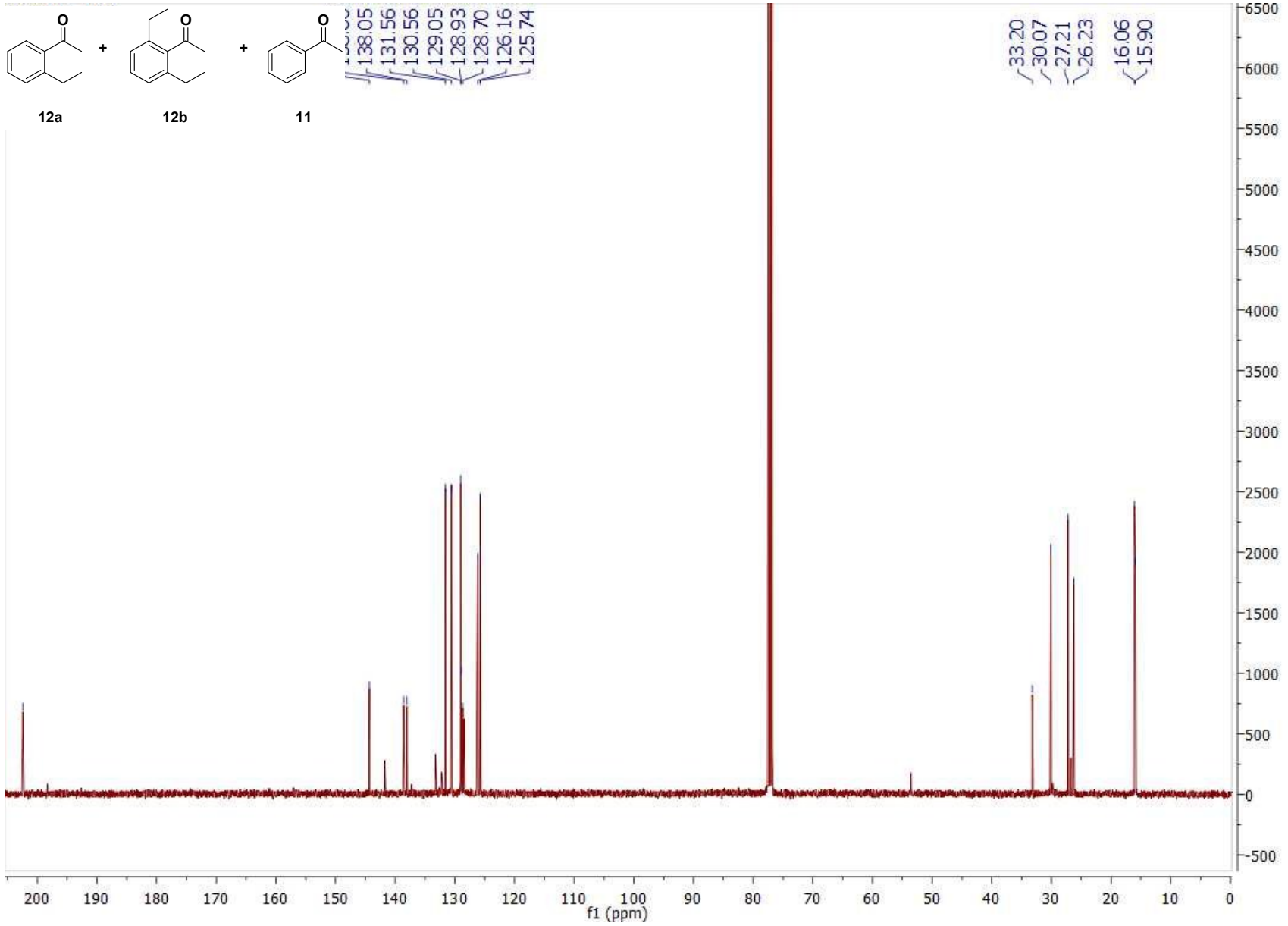

N
N
H

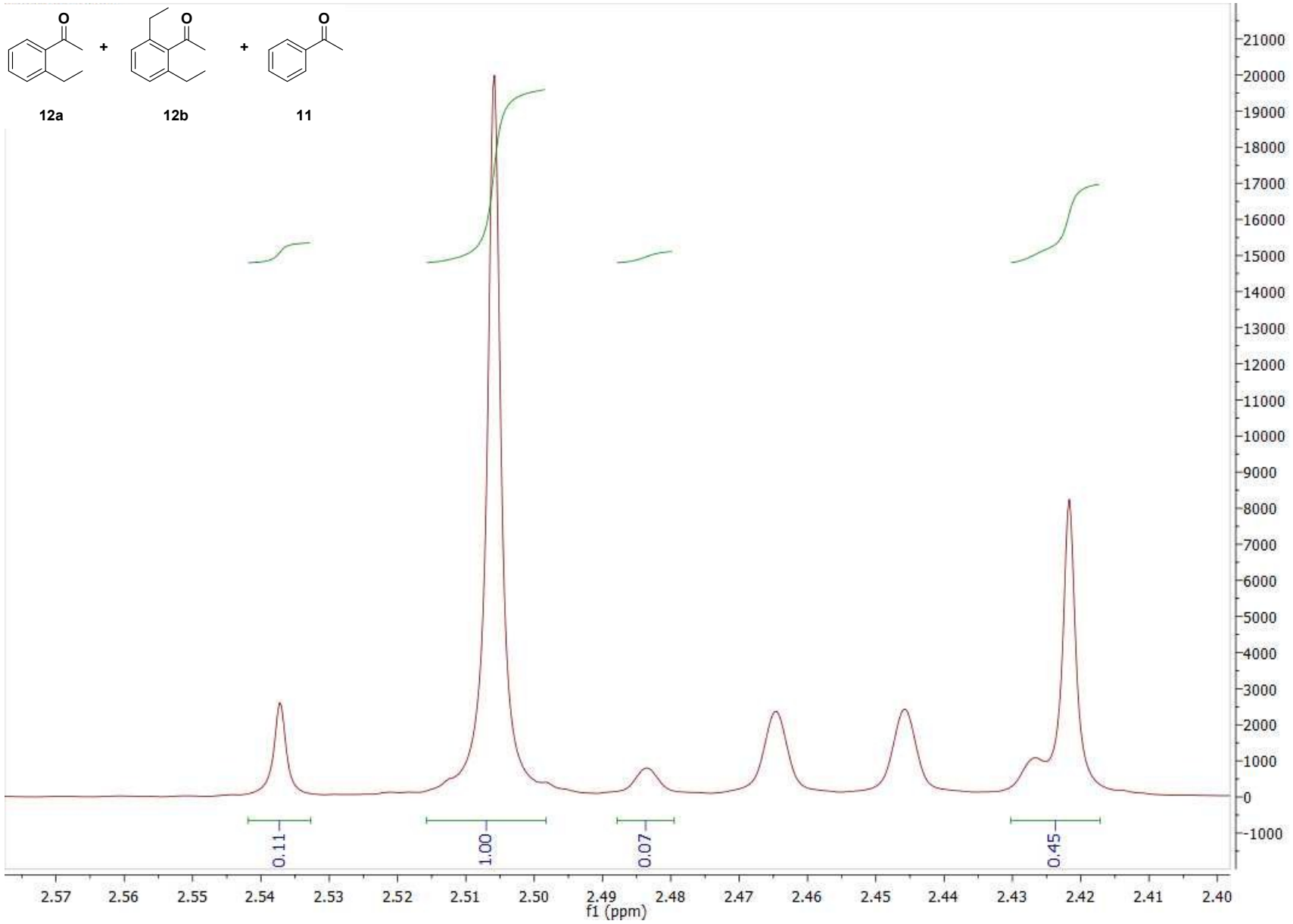
10

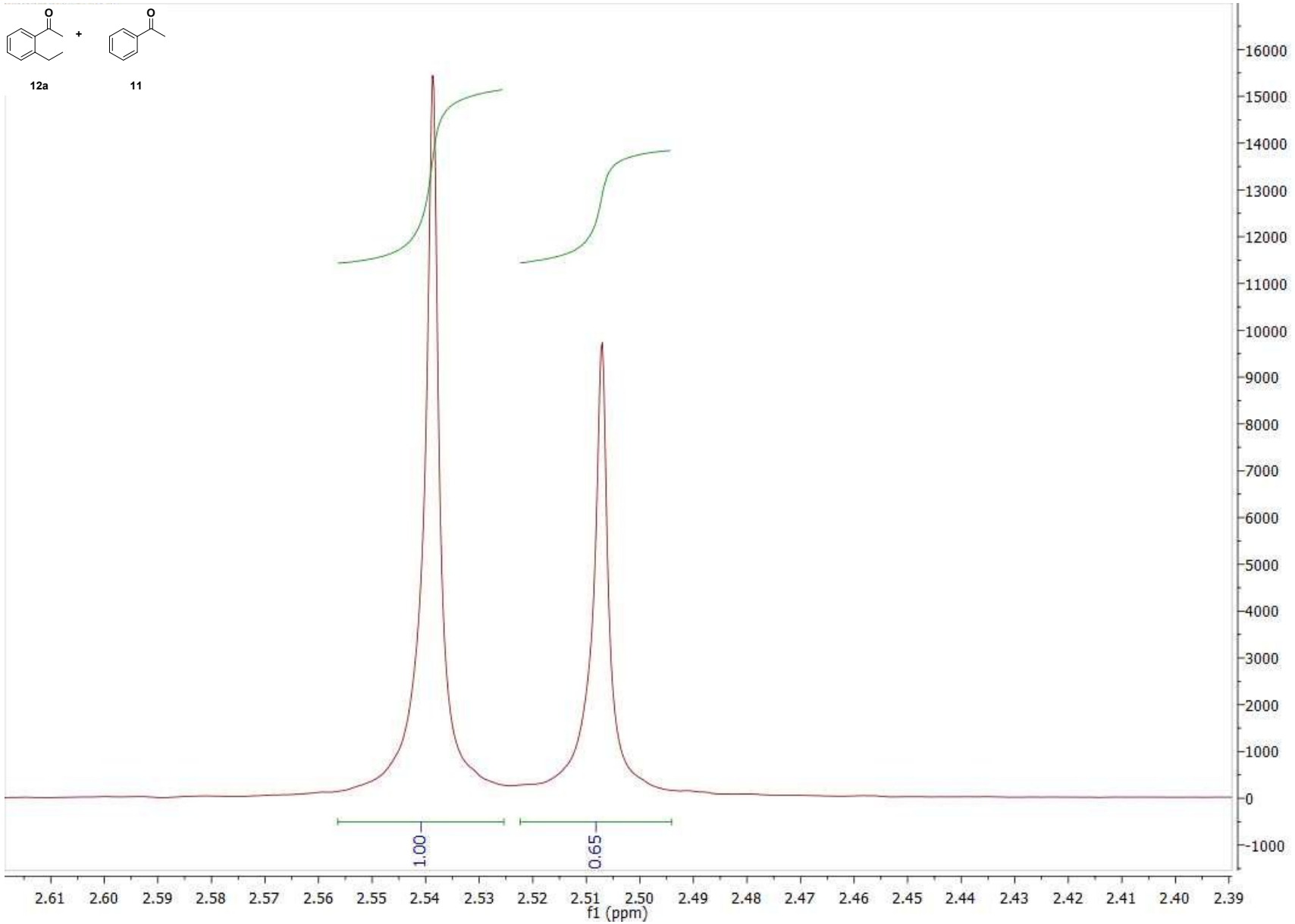
7.26 CDCl3
1.00
4.02
0.99
1.05
1.01
0.99
3.02
2.97
2.17
4.76
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

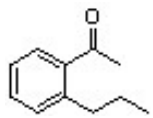

156.38
145.78
144.69
138.03
136.82
128.40
127.63
127.50
123.58
116.24
112.55
77.48
77.16
77.16 CDCl3
76.84
54.69
37.44
28.71
22.84
21.69
17.25
14.15
N
N
H
10
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12a
12b
11
E (m)
7.28
C (td)
7.40
J(7.53, 1.45)
B (dd)
7.62
J(7.69, 1.45)
D (dd)
7.25
J(7.46, 1.31)
F (q)
2.88
J(7.48)
A (s)
2.58
G (td)
J(7.5, 1.73)
0.94
1.15
1.39
1.03
2.12
2.99
5.69
f1 (ppm)


12a
+
12b
+
11
138.05
131.56
130.56
129.05
128.93
128.70
126.16
125.74
33.20
30.07
27.21
26.23
16.06
15.90
f1 (ppm)

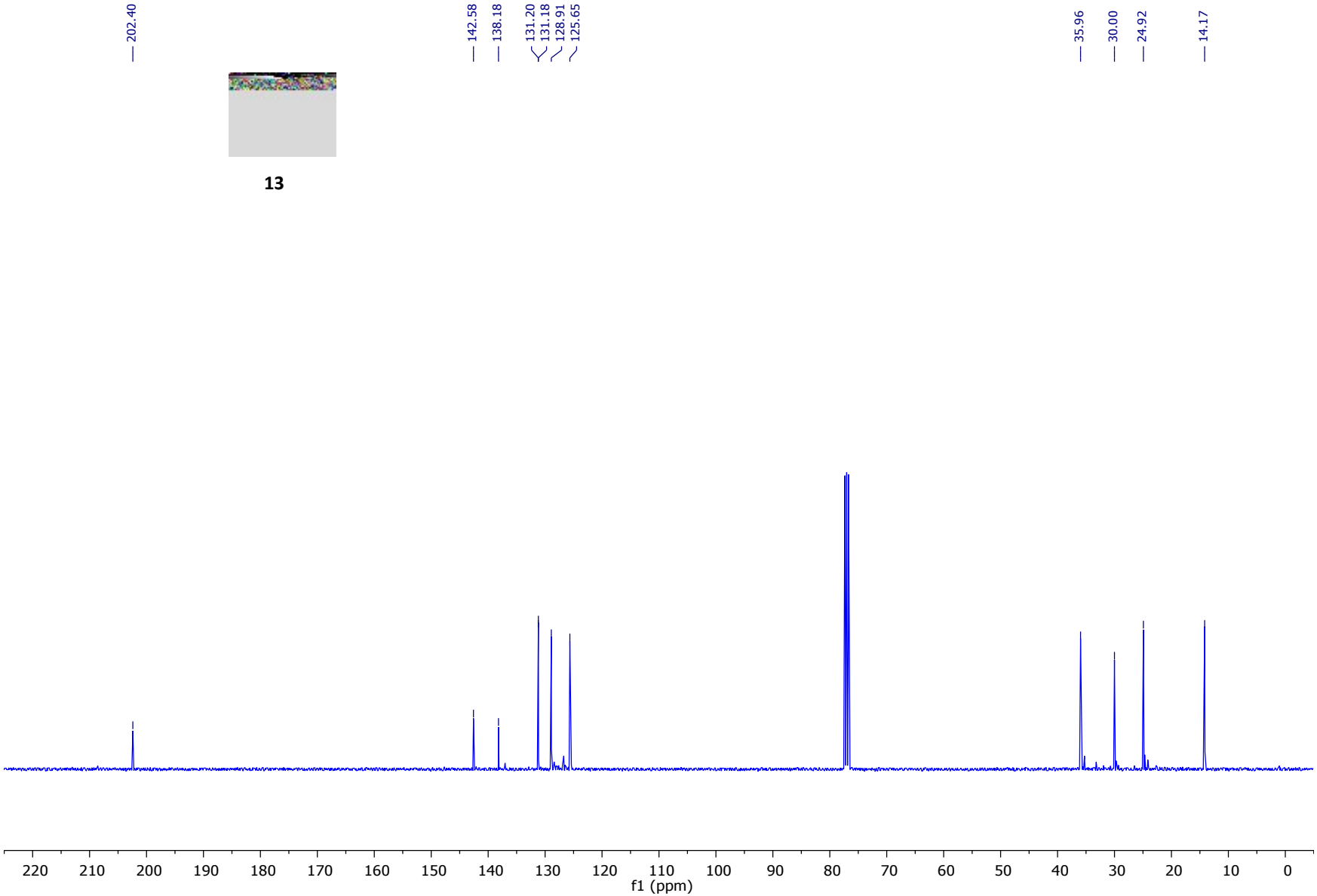

12a
12b
11
0.11
1.00
0.07
0.45
f1 (ppm)


12a
11
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
0.65
2.61 2.60 2.59 2.58 2.57 2.56 2.55 2.54 2.53 2.52 2.51 2.50 2.49 2.48 2.47 2.46 2.45 2.44 2.43 2.42 2.41 2.40 2.39
f1 (ppm)

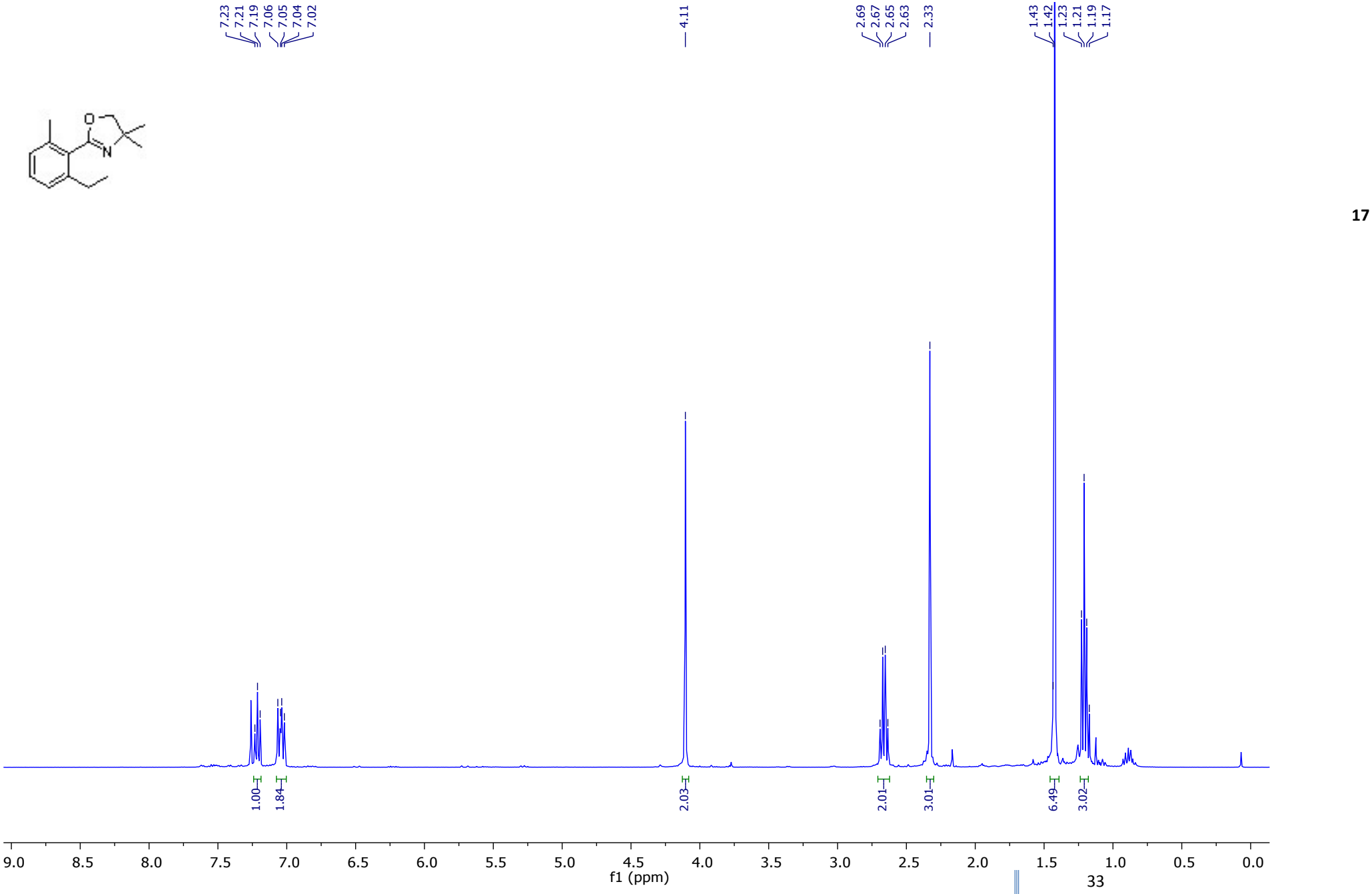


13

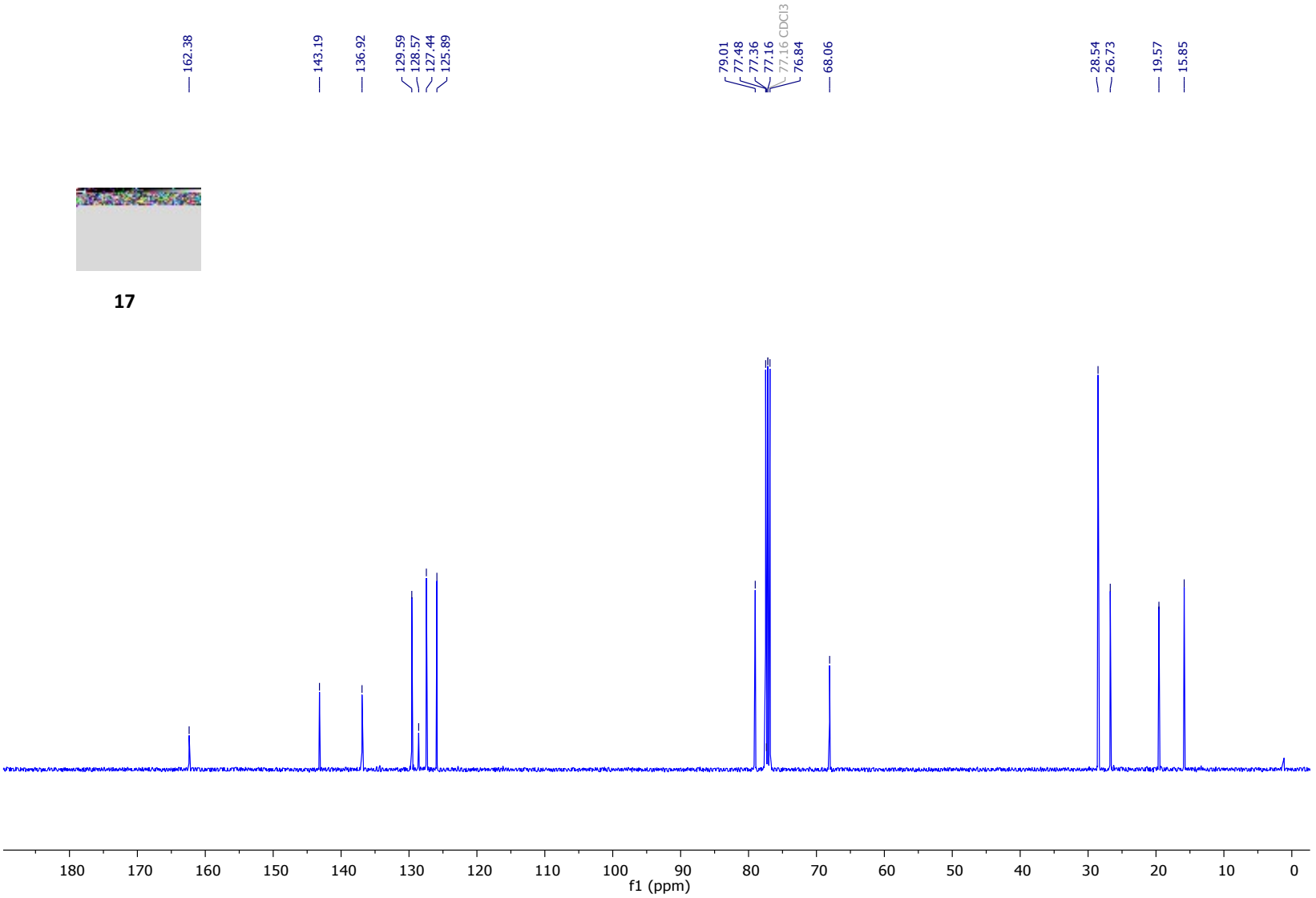
7.55
7.55
7.53
7.53
7.33
7.33
7.31
7.31
7.29
7.29
7.19
7.19
7.19
7.19
7.18
7.17
7.16
2.76
2.75
2.73
2.50
1.57
1.55
1.53
1.52
1.51
1.50
1.49
1.48
0.90
0.88
0.86
1.00
1.05
2.17
1.93
2.93
2.31
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


202.40
142.58
138.18
131.20
131.18
128.91
125.65
35.96
30.00
24.92
14.17
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

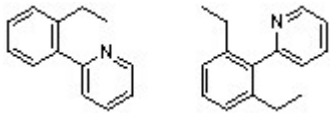
13


7.23
7.21
7.19
7.06
7.05
7.04
7.02
4.11
2.69
2.67
2.65
2.63
2.33
1.43
1.42
1.23
1.21
1.19
1.17
1.00
1.84
2.03
2.01
3.01
6.49
3.02
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)

17

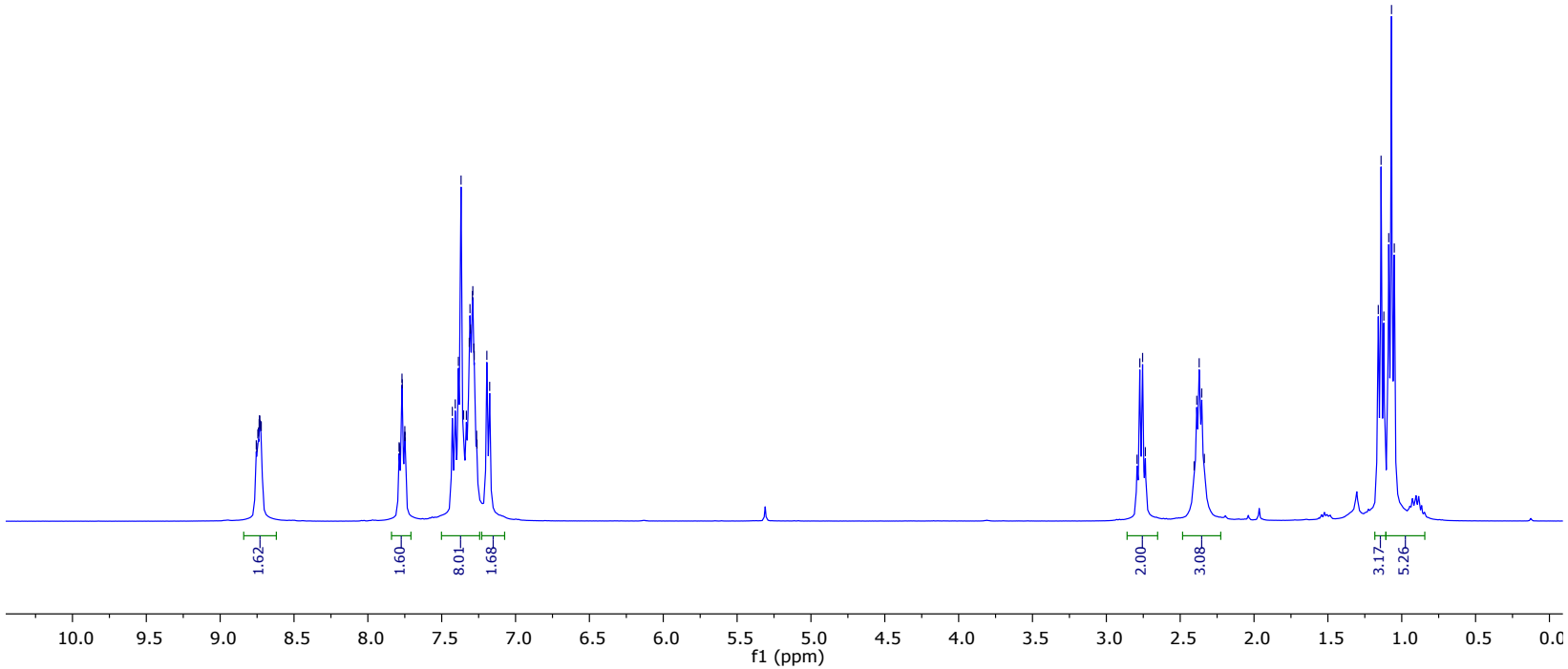

162.38
143.19
136.92
129.59
128.57
127.44
125.89
79.01
77.48
77.36
77.16
77.16 CDCl3
76.84
68.06
28.54
26.73
19.57
15.85
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

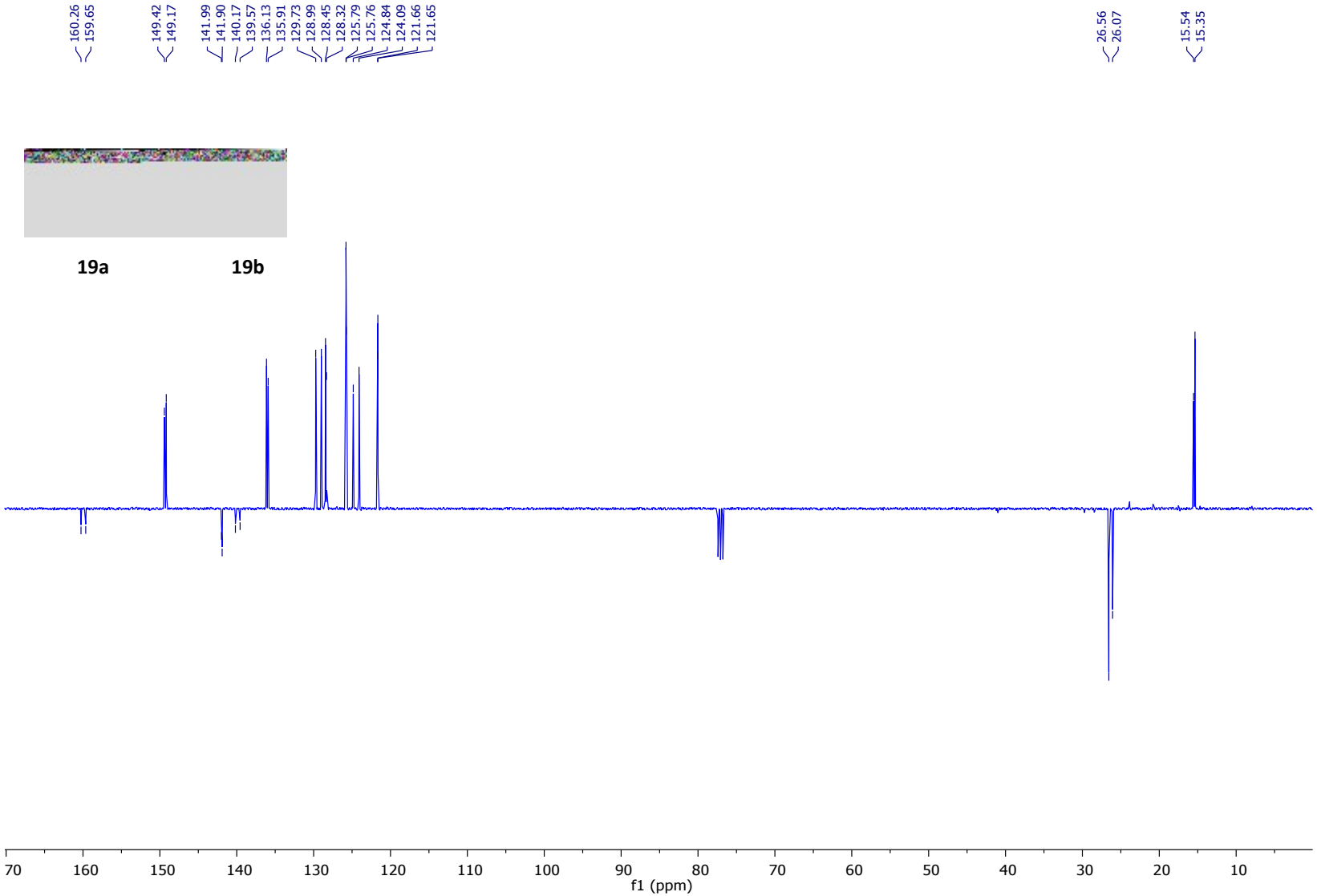
17

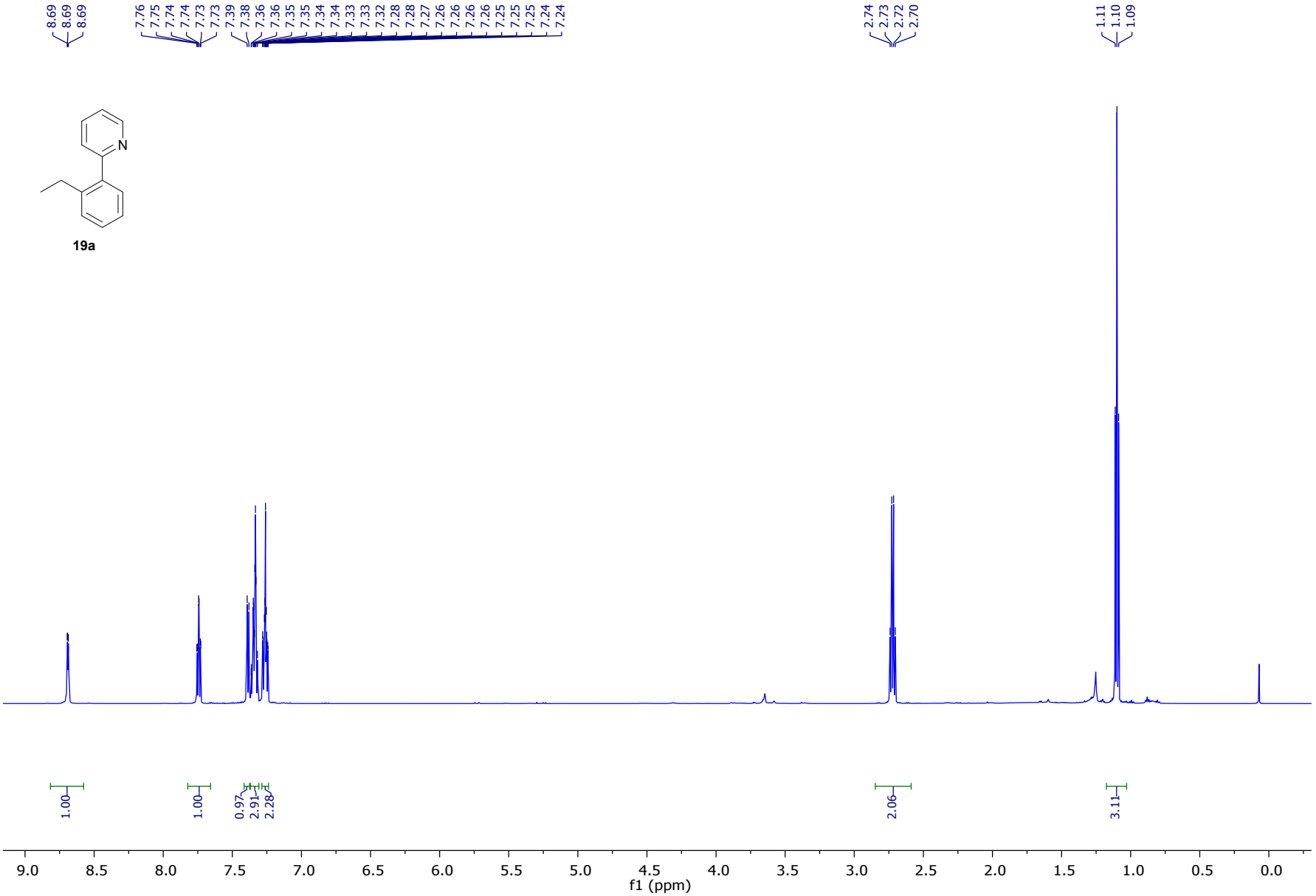


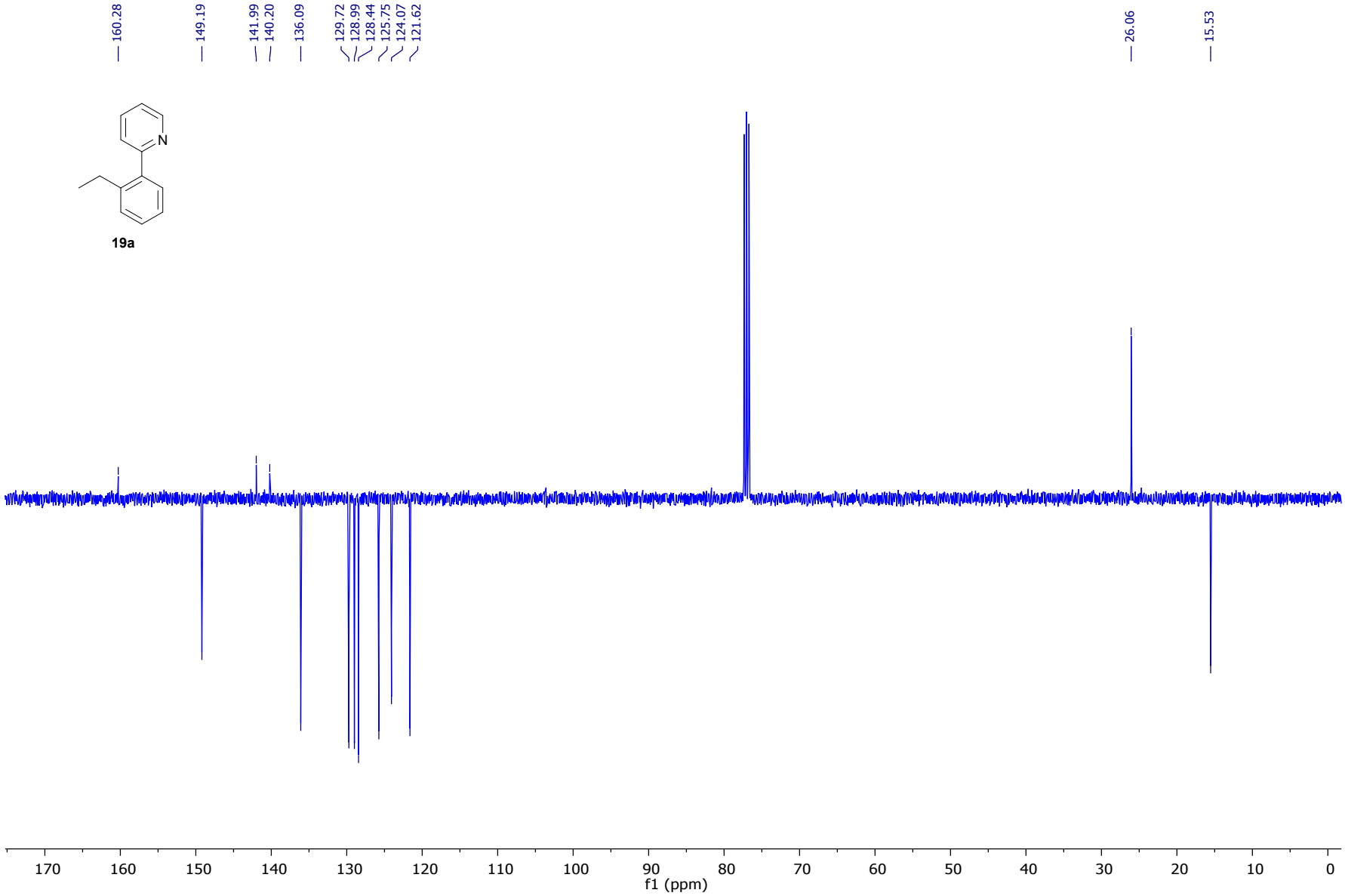
19a **19b**

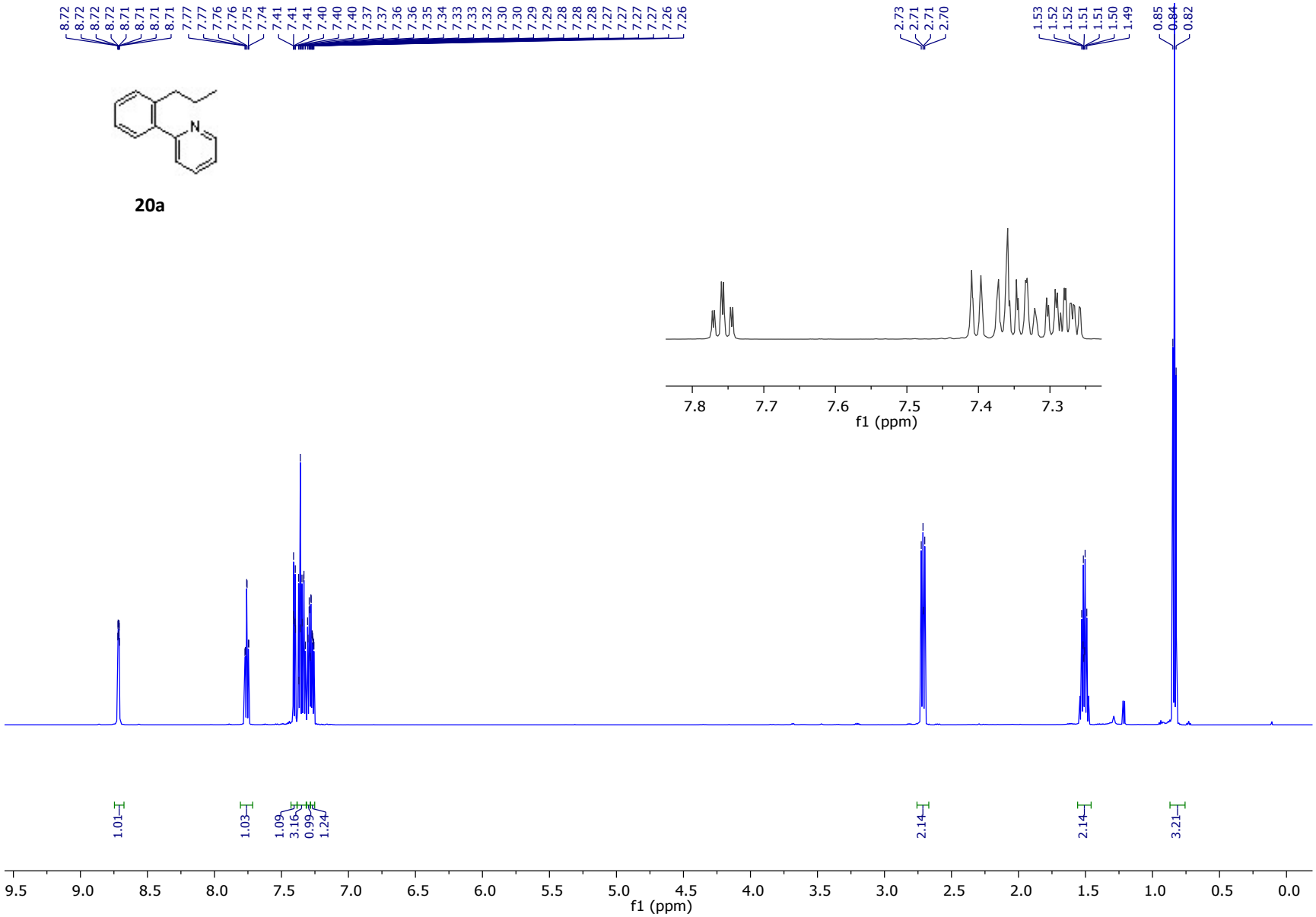
1.00 : 0.77

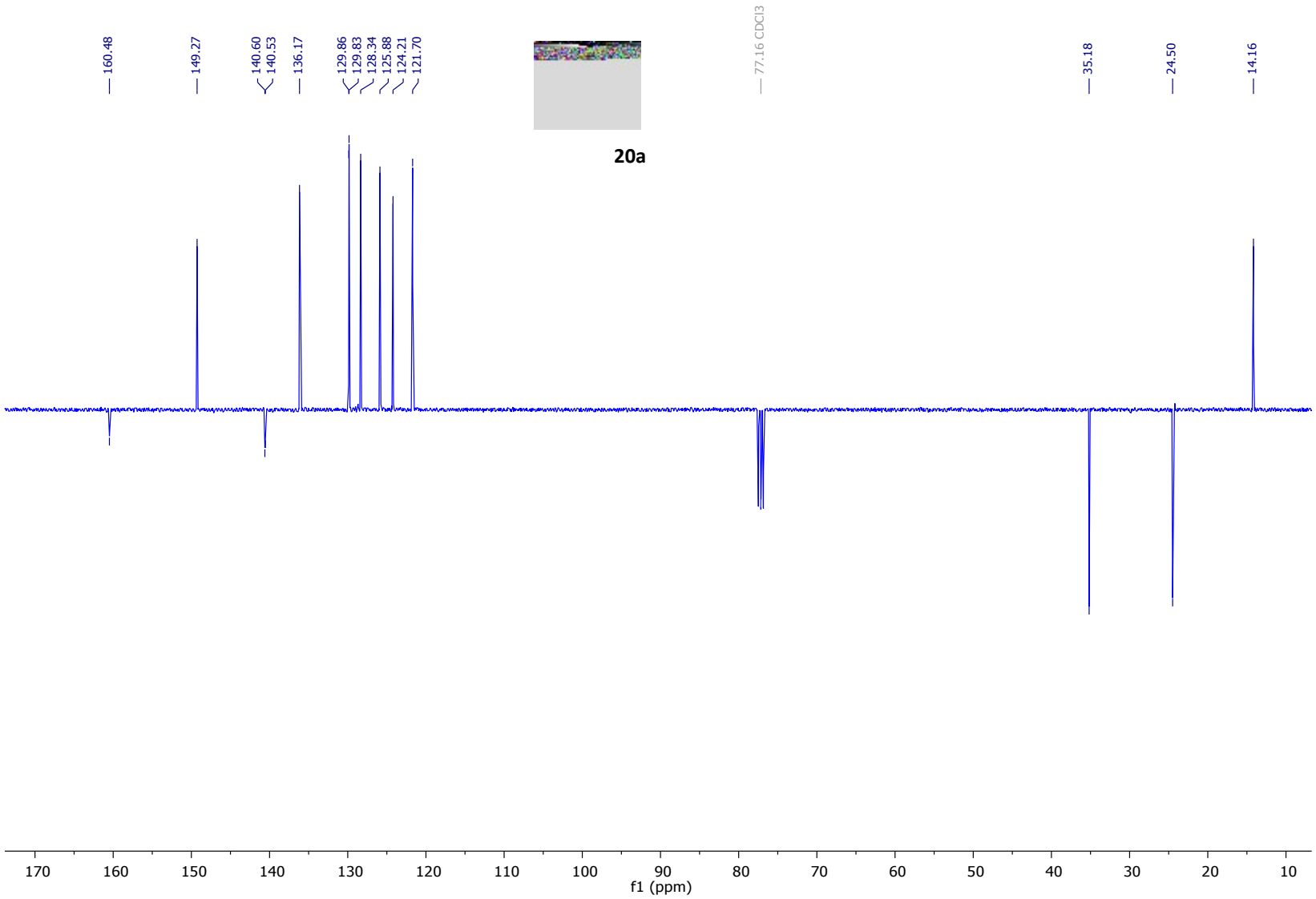


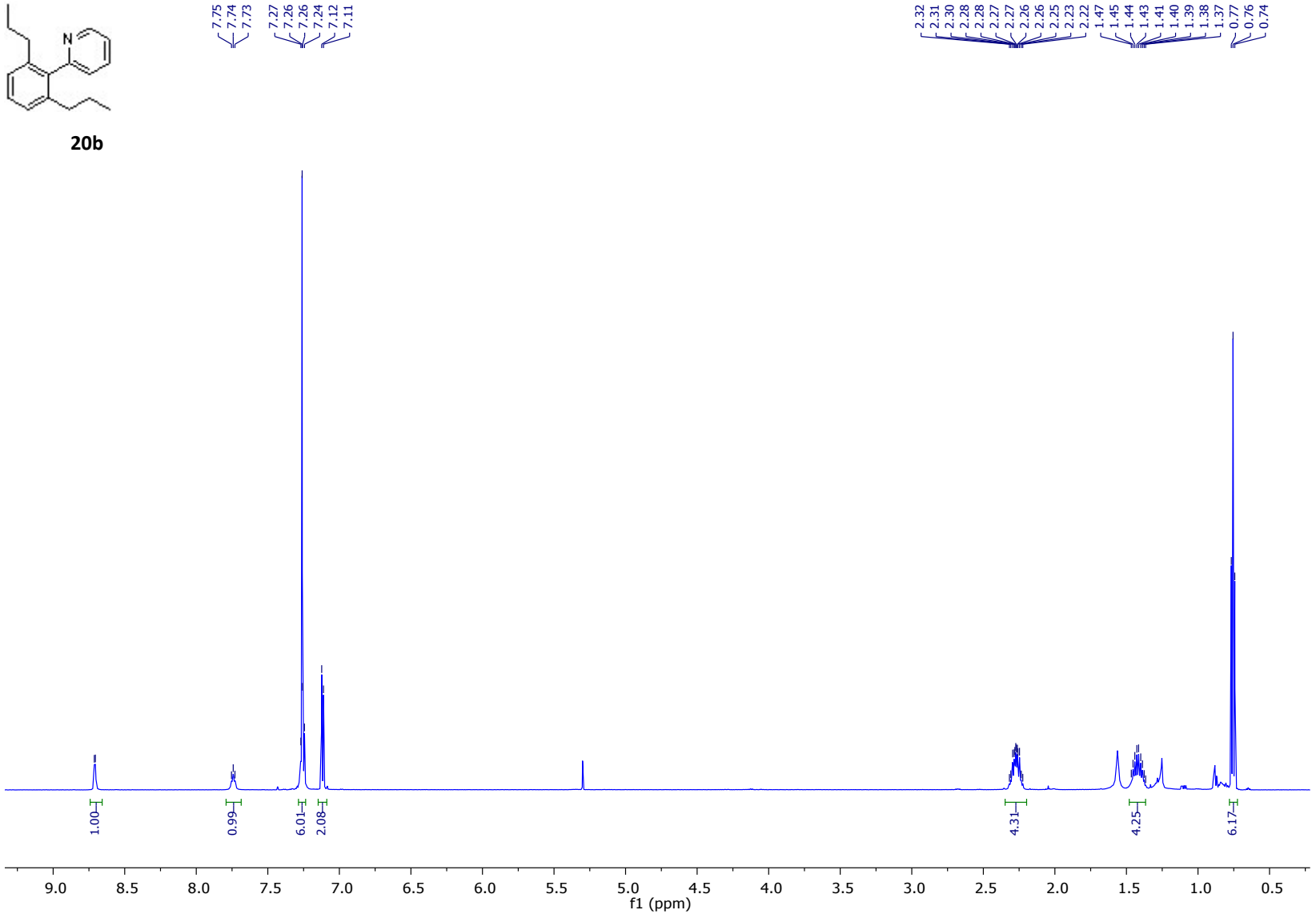

160.26
159.65
149.42
149.17
141.99
141.90
140.17
139.57
136.13
135.91
129.73
128.99
128.45
128.32
125.79
125.76
124.84
124.09
121.66
121.65
26.56
26.07
15.54
15.35
19a
19b
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.69
8.69
8.69
7.76
7.75
7.74
7.74
7.73
7.73
7.39
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.28
7.28
7.27
7.26
7.26
7.26
7.26
7.25
7.25
7.24
7.24
2.74
2.73
2.72
2.70
1.11
1.10
1.09
N
19a
1.00
1.00
0.97
2.91
2.28
2.06
3.11
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)

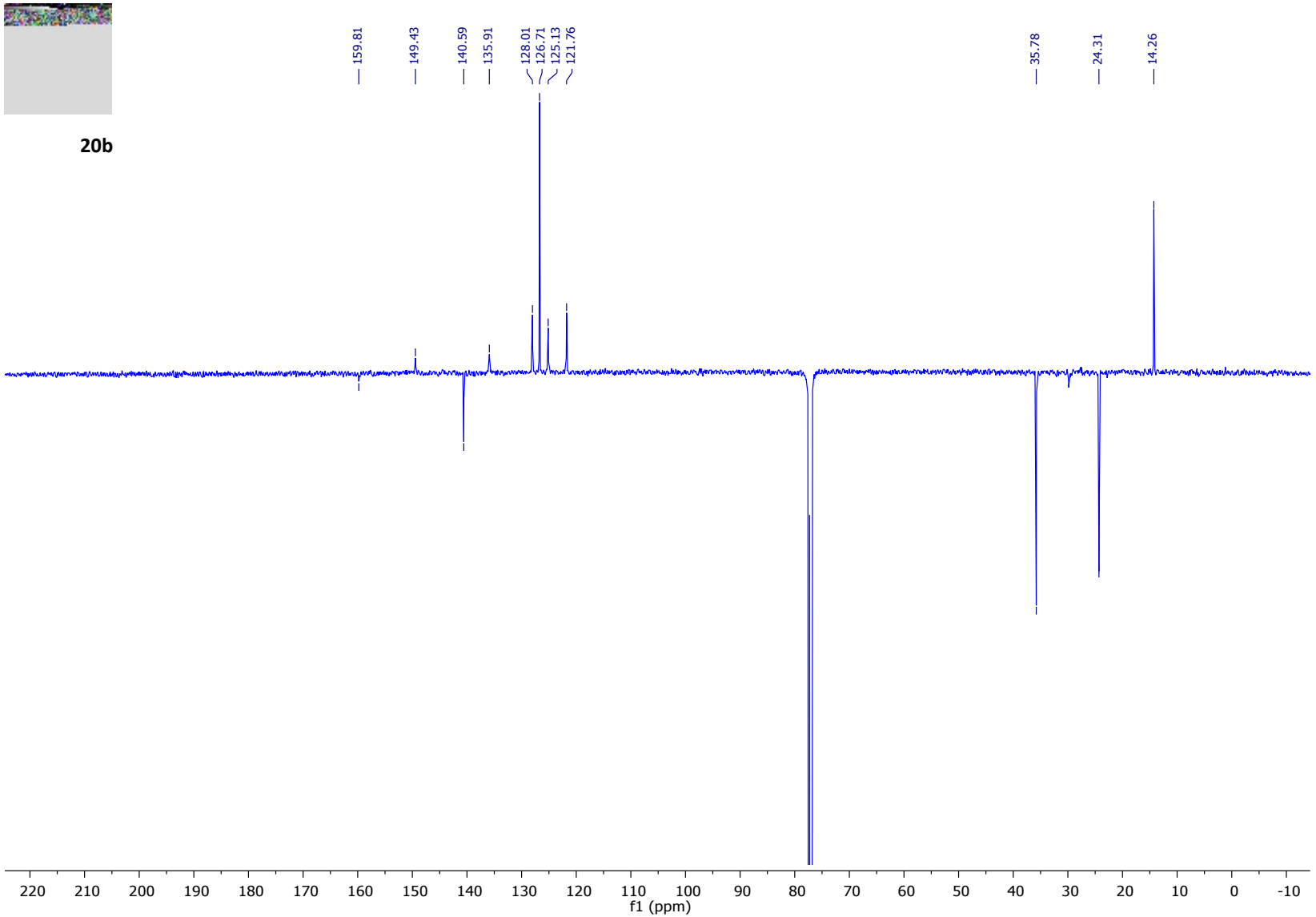

160.28
149.19
141.99
140.20
136.09
129.72
128.99
128.44
125.75
124.07
121.62
26.06
15.53
N
19a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.72 8.72 8.72 8.72 8.71 8.71 8.71 8.71 7.77 7.77 7.76 7.76 7.75 7.74 7.41 7.41 7.41 7.40 7.40 7.40 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26
2.73 2.71 2.71 2.70
1.53 1.52 1.52 1.51 1.51 1.50 1.49
0.85 0.84 0.82
N
20a
7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.01 1.03 1.09 3.16 0.99 1.24 2.14 2.14 3.21
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)

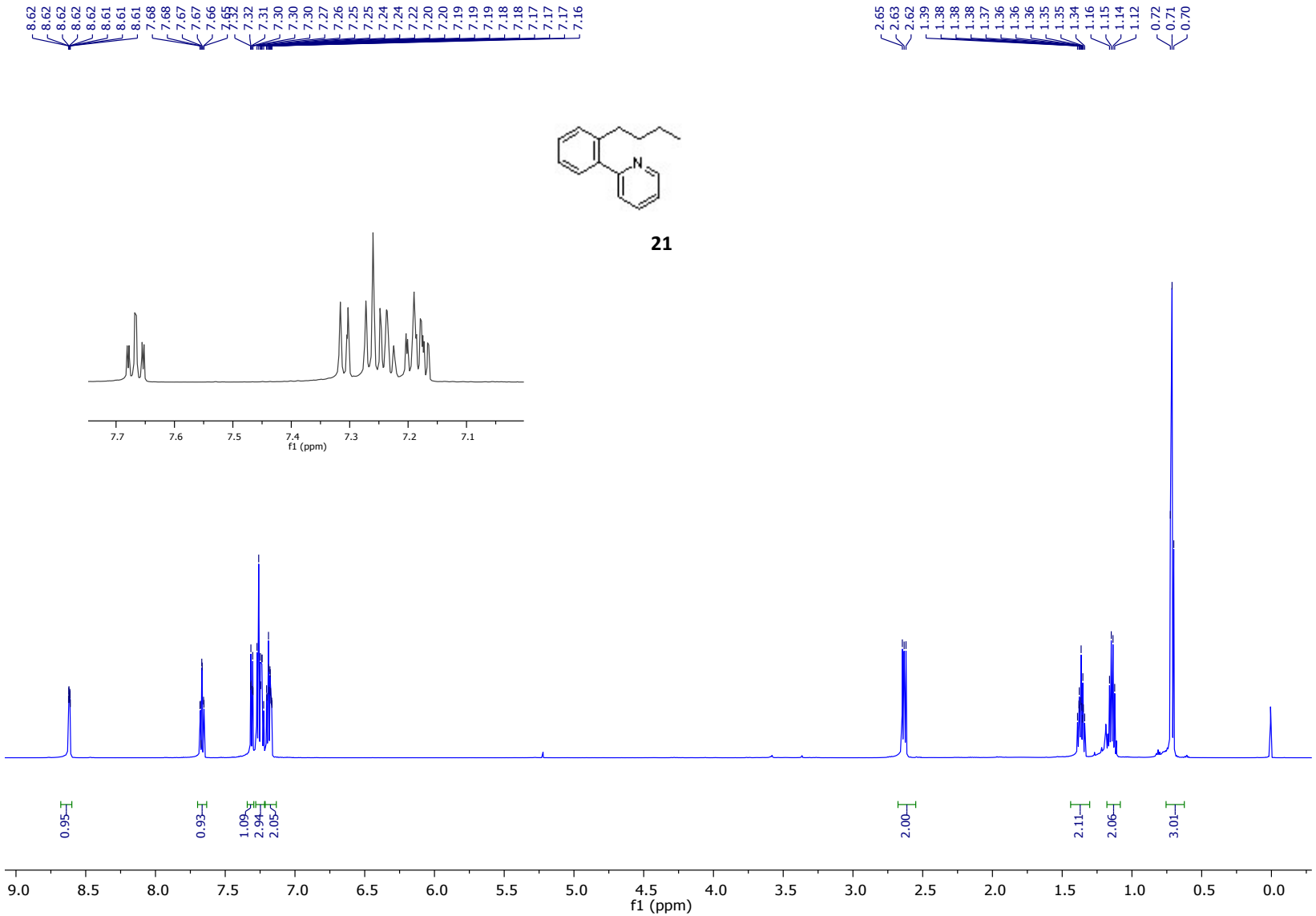

160.48
149.27
140.60
140.53
136.17
129.86
129.83
128.34
125.88
124.21
121.70
77.16 CDCl3
35.18
24.50
14.16
20a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

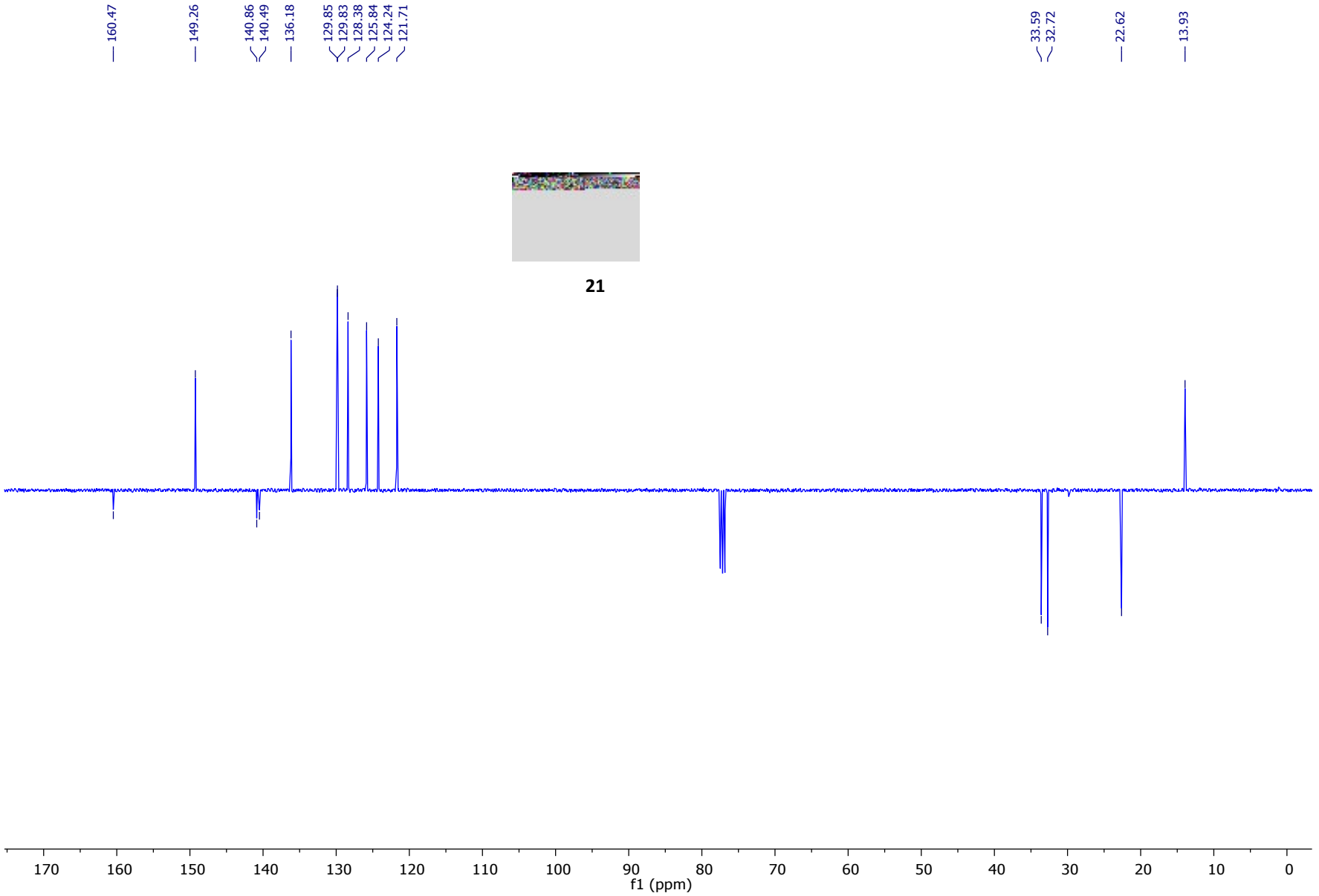

7.75
7.74
7.73
7.27
7.26
7.26
7.24
7.12
7.11
2.32
2.31
2.30
2.28
2.28
2.27
2.27
2.26
2.26
2.25
2.23
2.22
1.47
1.45
1.44
1.43
1.41
1.40
1.39
1.38
1.37
0.77
0.76
0.74
1.00
0.99
6.01
2.08
4.31
4.25
6.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

20b

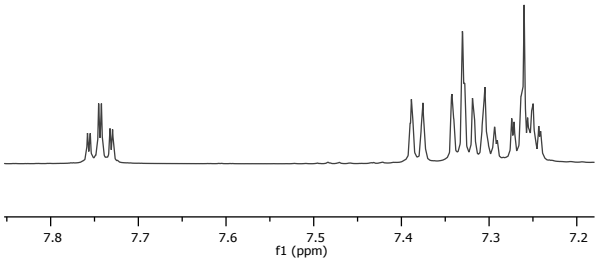

159.81
149.43
140.59
135.91
128.01
126.71
125.13
121.76
35.78
24.31
14.26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

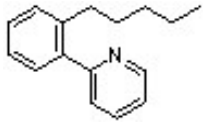
20b


8.62 8.62 8.62 8.62 8.62 8.61 8.61 8.61 7.68 7.68 7.67 7.67 7.66 7.65 7.32 7.31 7.30 7.30 7.30 7.27 7.26 7.25 7.25 7.24 7.24 7.22 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.17 7.16
2.65 2.63 2.62 1.39 1.38 1.38 1.38 1.37 1.36 1.36 1.36 1.35 1.35 1.34 1.16 1.15 1.14 1.12 0.72 0.71 0.70
N
21
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.95 0.93 1.09 2.94 2.05 2.00 2.11 2.06 3.01
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)

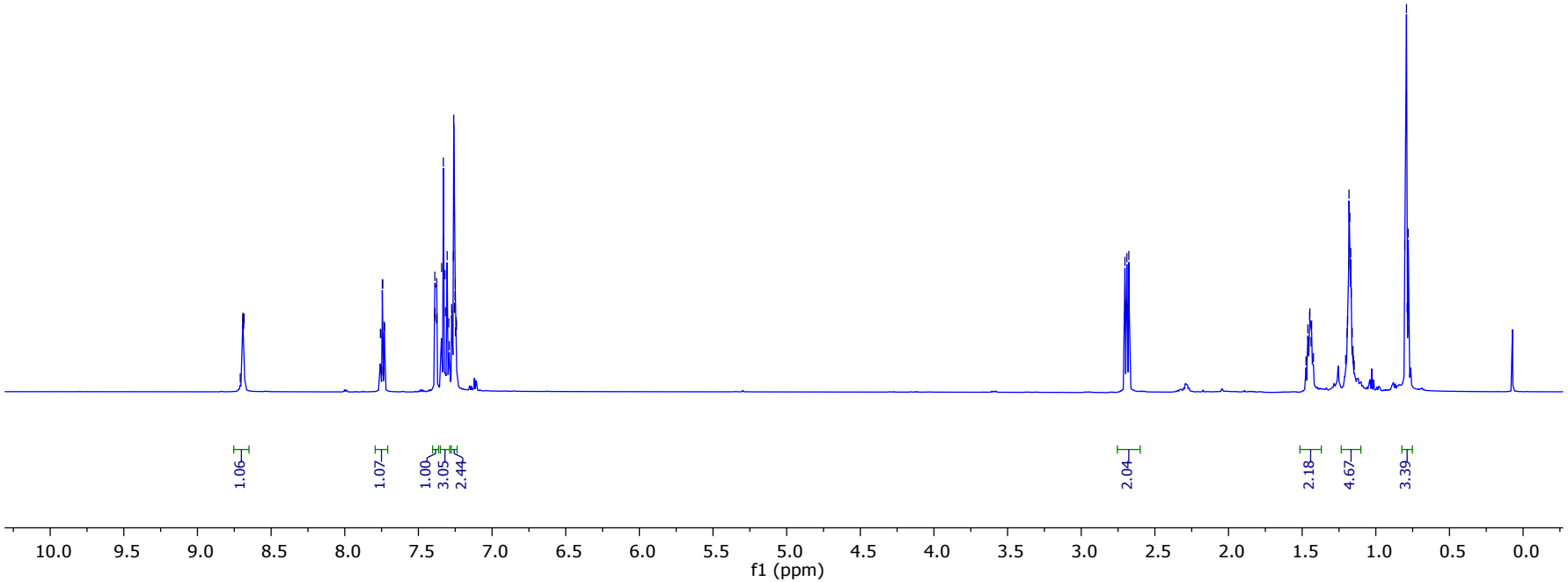

160.47
149.26
140.86
140.49
136.18
129.85
129.83
128.38
125.84
124.24
121.71
33.59
32.72
22.62
13.93
21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.71 8.69 8.69 8.69 8.68 8.68 7.76 7.75 7.75 7.75 7.74 7.74 7.73 7.73 7.39 7.39 7.39 7.38 7.38 7.37 7.34 7.33 7.33 7.32 7.32 7.30 7.29 7.29 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24
2.70 2.69 2.69 2.69 2.68 1.47 1.46 1.46 1.45 1.45 1.44 1.44 1.42 1.20 1.20 1.19 1.18 1.18 1.18 1.17 1.17 1.17 1.16 1.16 1.15 1.15 0.80 0.79 0.79 0.78 0.77


7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)


N

22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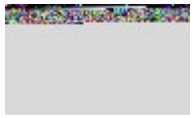
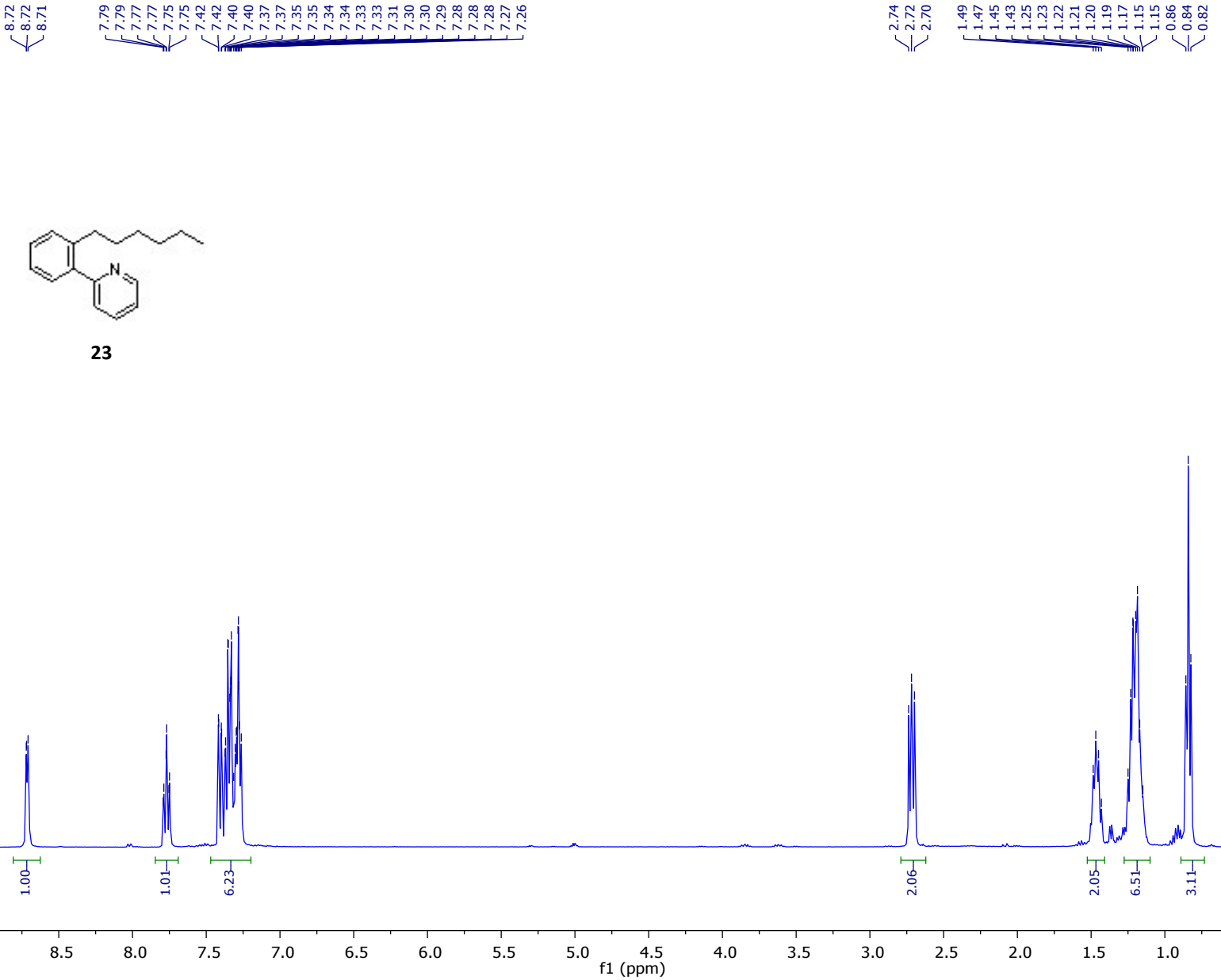
1.07
1.00
3.05
2.44
2.04
2.18
4.67
3.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



22

160.44
149.22
140.93
140.41
136.25
129.86
129.84
128.42
125.86
124.26
121.74
33.03
31.78
31.07
22.45
14.07
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.72
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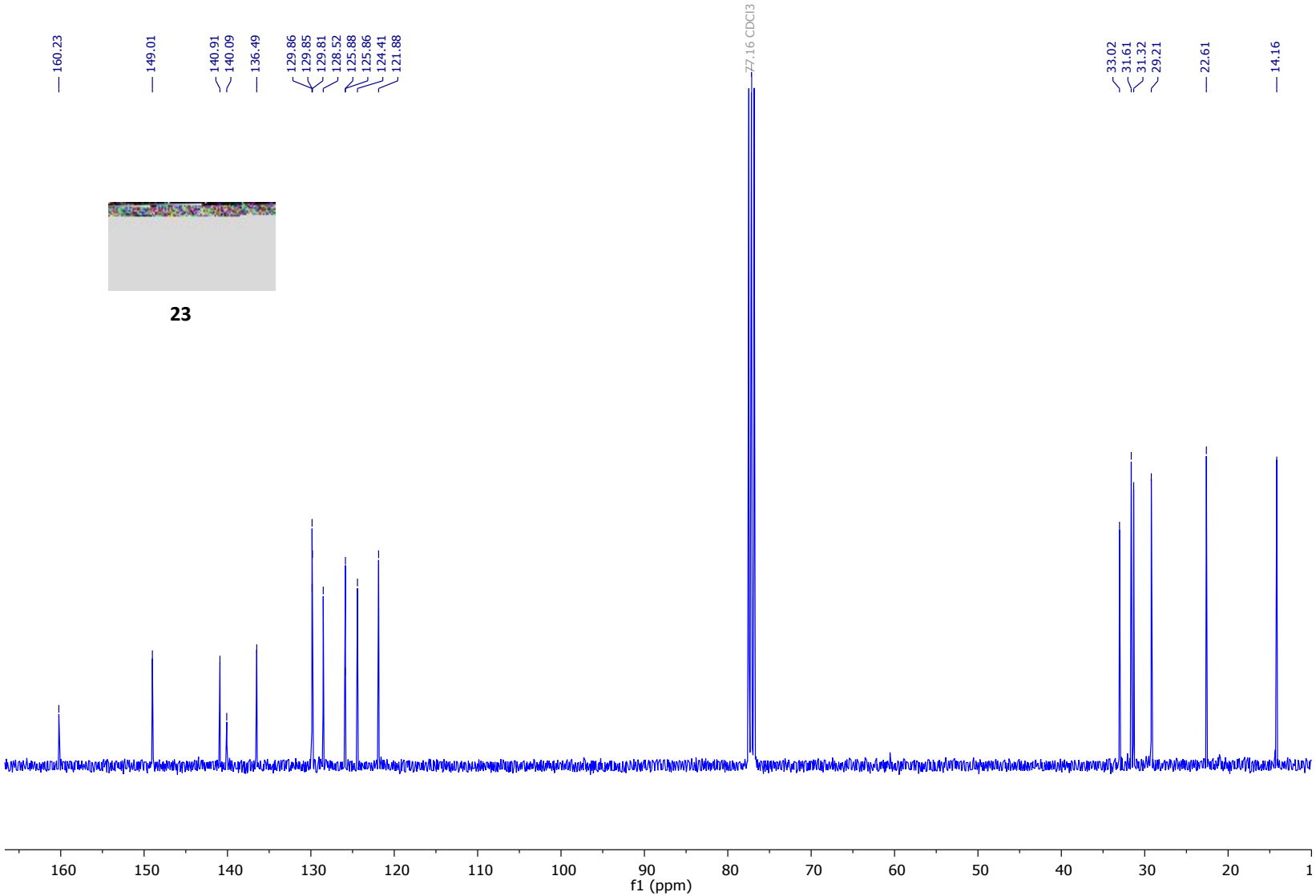
7.42
7.40
7.40
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.27
7.26
2.74
2.72
2.70
1.49
1.47
1.45
1.43
1.25
1.23
1.22
1.21
1.20
1.19
1.17
1.15
1.15
0.86
0.84
0.82
N
1.00
1.01
6.23
2.06
2.05
6.51
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

23


160.23
149.01
140.91
140.09
136.49
129.86
129.85
129.81
128.52
125.88
125.86
124.41
121.88
77.16 CDCl3
33.02
31.61
31.32
29.21
22.61
14.16
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)

23