Supporting Information

CuI-Catalyzed C1-Alkynylation of Tetrahydroisoquinolines (THIQs) by A^3 Reaction with Tunable Iminium Ions

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1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Toluene and tetrahydrofuran were distilled from sodium and benzophenone prior to use. Synthetic reagents were purchased from Acros, Aldrich, Alfa Aesar, J&K, and TCI and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on a Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). 2-D NMR spectra including H-H COSY and NOESY were measured on a Bruker AVANCE III (^{1}H at 500 MHz, ^{13}C at 125 MHz) nuclear magnetic resonance spectrometers. Infrared spectra were recorded on a Mettler-Toledo ReactIR iC10 system with a SiComp probe and a Thermo Electron Corporation Nicolet AVATAR 330 FT-IR spectrometer (for compounds **6d**, **6i**, **10**, **11**, and **13**), which are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) with an FT-ICR analyzer.

Abbreviations:

THIQ = 1,2,3,4-tetrahydroisoquinoline

PE = petroleum ether

EA = ethyl acetate

TLC = thin layer chromatography

TMS = trimethylsilyl

THF = tetrahydrofuran

DME = 1,2-dimethoxyethane

DCM = dichloromethane

DCE = 1,2-dichloroethane

2. Experimental Procedures and Characterization Data

2.1 General Procedures and Additional Experimental Section

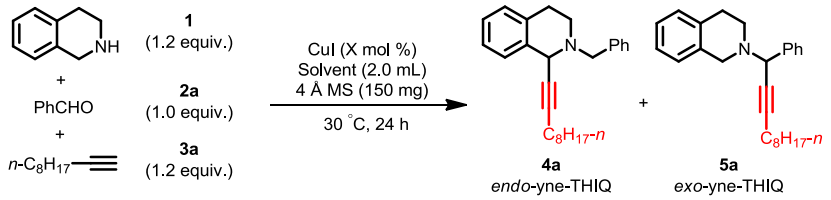
2.1.1 General Procedure for Synthesis of *Endo*-Yne-THIQs

To a flame-dried pear-shaped flask (10 mL) was added CuI (9.8 mg, 0.05 mmol) and newly activated 4 Å molecular sieves (150 mg) inside a glovebox. Toluene (2 mL) was then added under nitrogen atmosphere outside of the glovebox, followed by aldehyde (0.5 mmol), THIQ (0.5 mmol), and alkyne (0.5 mmol). The reaction mixture was moved into an oil bath at 50 ℃ (or 80 ℃ if specially mentioned) for 24 h. After the completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with PE/EA (10/1 – 2/1), and the combined filtrate was concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding *endo*-yne-THIQ product.

Note: We have CuI and 4 Å molecular sieves stored in the glovebox. Without glovebox, the reaction can also perform well under N_2 atmosphere.

2.1.2 More Details for the Model Reaction Optimization

Table S1: Screening of Solvents and Amount of Catalyst for the Model Reaction[a]



entry	Solvent	X	yield[b] (%) **4a** + **5a**	ratio[c] **4a**/**5a**
1	**Toluene**	**10**	**84**	**1:0**
2	THF	10	14	4:1
3	1,4-dioxane	10	9	8:1
4	DME	10	trace	N:A
5	DCM	10	20	1:1
6	DCE	10	38	7:1
7	Toluene	2	73	1:0
8	Toluene	5	77	100:1
9	Toluene	20	77	30:1
10	Toluene	50	81	12:1
11	Toluene	100	87	9:1

[a] Reactions were performed on 0.5 mmol scale. [b] Isolated combined yields were calculated based on benzaldehyde. [c] Ratio was determined by NMR prior to purification, and in the case of 1:0, no **5a** could be observed in the reaction mixture by NMR.

2.1.3 General Procedures for Synthesis of *Exo*-Yne-THIQs

To a flame-dried pear-shaped flask (10 mL) was added CuBr (10.8 mg, 0.075 mmol) and newly activated 4 Å molecular sieves (150 mg) inside a glovebox. Toluene (2 mL) was then added under nitrogen atmosphere outside of the glovebox, followed by aldehyde (0.5 mmol), THIQ (0.6 mmol), and alkyne (0.6 mmol). The reaction mixture was moved into an oil bath at 30 ℃ for 12 h. After the completion of the reaction, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with PE/EA (10/1 – 2/1), and the combined filtrate was concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding *exo*-yne-THIQ product. The reported yield was based on the used aldehyde.

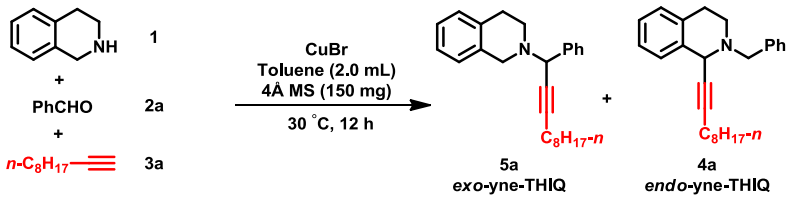
Note: We have CuBr and 4 Å molecular sieves stored in the glovebox. Without glovebox, the reaction can also perform well under N_2 atmosphere.

2.1.4 Preliminary study of the CuBr-Catalyzed Synthesis of *Exo*-Yne-THIQs

Because of the differences between the previous mild-condition allene synthesis[1] and this work, re-optimization was necessary to get *exo*-yne-THIQs. In order to make the A^3 coupling product separable and the

reaction practical, excess amounts of both THIQ and 1-decyne were used to make sure that all benzaldehyde was consumed after the reaction. Thus, we used the reaction conditions in Entry 4 of Table S2 as the optimal reaction conditions.

Table S2: Optimization of the CuBr-Catalyzed *Exo*-Yne-THIQ Synthesis[a]

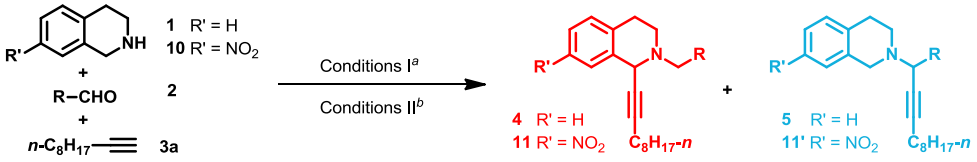


entry	ratio of substrates **1/2a/3a**	amount of CuBr (mol %)	yield[b] (%) **5a** + **4a**	ratio[c] **5a/4a**
1	1.2/1.2/1	10	80	6:1
2	1.4/1.8/1	10	86	4.4:1
3[d]	1.2/1.2/1	20	87	1:0
4	**1.2/1/1.2**	**15**	**86**	**10:1**

[a] Reactions were performed on 0.5 mmol scale. [b] Isolated combined yields were calculated based on benzaldehyde. [c] Ratio was determined by NMR prior to purification, and in the case of 1:0, no *endo*-yne-THIQ could be observed in the reaction mixture by NMR. [d] Excess amount of benzaldehyde could not be separated from A^3 product by flash column chromatography.

Then, the above optimal conditions were applied to synthesize *exo*-yne-THIQs shown in Schemes 3 and 4 (Scheme S1). To our delight, selectivity of A^3 reaction of THIQs can be well tuned by using either CuI or CuBr.

Scheme S1: Selected divergent Synthesis of THIQ-type Propargylamines via Tunable Iminium Ions

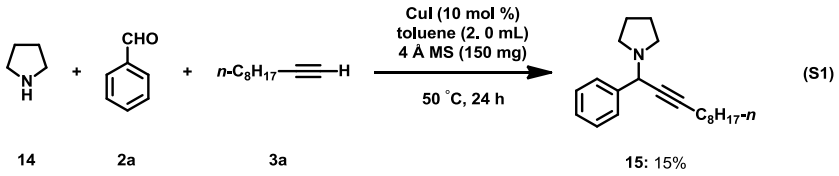


Entry	THIQ	R	Conditions I Ratio[c]	Conditions I Yield[d] (%)	Conditions II Ratio[c]	Conditions II Yield[d] (%)
1	**1**	H	**4a/5a** = 1/0	89%	**4a/5a** = 1/10	86%
2	**1**	Br	**4f/5f** = 17/1	94%	**4f/5f** < 1/19	93%
3	**1**	CF_3	**4h/5h** = 7/1	93%	**4h/5h** < 1/19	92%
4	**1**		**4k/5k** = 3/1	85%	**4k/5k** = 0/1	93%
5	**1**		**4l/5l** = 4/1	79%	**4l/5l** = 0/1	88%
6	**10**		**11/11'** = 1/0[e]	50%	complex mixture	N/A

[a] Conditions I: Reactions were performed on 0.5 mmol scale, and the molar ratio of **1**(or **10**)/**2**/**3a** was 1.0/1.0/1.0, CuI (10 mol %), 4 Å MS (150 mg), toluene (2.0 mL), 50 ℃, 24 h. [b] Conditions II: Reactions were performed on 0.5 mmol scale, and the molar ratio of **1**(or **10**)/**2**/**3a** was 1.2/1.0/1.2, CuBr (15 mol %), 4 Å MS (150 mg), toluene (2.0 mL), 30 ℃, 12 h. [c] Ratios were determined by NMR prior to purification, and in the case of 0/1 or 1/0, only one regioisomer can be observed in the reaction mixture by NMR. [d] Isolated combined yield of the two isomers. [e] Compound **11'** was *exo*-type yne-nitro-THIQ product, which was not observed in CuI-catalyzed reaction. N/A = not applicable.

2.1.5 A^3 Reaction of Pyrrolidine Catalyzed by CuI

We have reported that under the condition of CuBr-catalysis, traditional A^3 product of pyrrolidine, benzaldehyde and 1-decyne was obtained with excellent yield (95%) and regioselectivity (*exo*:*endo* = 1:0).[1] Thus, under the standard conditions for the synthesis of *endo*-yne-THIQ, pyrrolidine was also tested as the amine component. However, only traditional A^3 product was formed without any α-alkynylated product (Reaction S1). The poor yield was due to the incomplete conversion of substrates, as the TLC indicated.

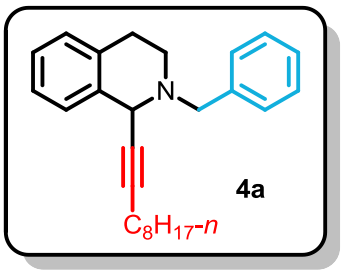


14 2a 3a **15:** 15% (S1)

2.2 Experimental Details and Characterization Data for Yne-THIQs

2-Benzyl-1-(dec-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (4a) [2]

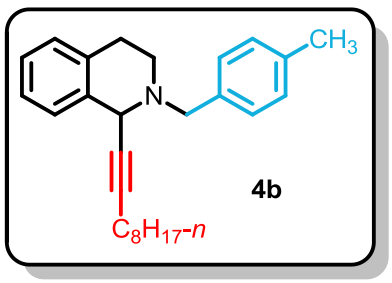
Following the general procedure **2.1.1**, benzaldehyde (53.7 mg, 0.506 mmol), THIQ (65.3 mg, 0.490 mmol) and 1-decyne (66.6 mg, 0.492 mmol) were converted into the *endo*-yne-THIQ product **4a** (148.2 mg, 0.412 mmol, 89% yield). Purification (silica gel, PE/EA = 50/1).



4a: Colorless oil, TLC R_f = 0.27 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.15 – 7.11 (m, 2H), 7.11 – 7.05 (m, 1H), 4.55 (s, 1H), 3.89 (d, J = 13.1 Hz, 1H), 3.80 (d, J = 13.1 Hz, 1H), 3.06 – 2.88 (m, 2H), 2.82 – 2.65 (m, 2H), 2.23 (td, J = 7.0, and 2.0 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.47 – 1.36 (m, 2H), 1.34 – 1.19 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 136.4, 133.9, 129.2, 128.9, 128.2, 127.7, 127.1, 126.7, 125.7, 87.2, 77.9, 59.5, 54.1, 45.6, 31.9, 29.3, 29.11, 29.06, 29.00, 28.9, 22.7, 18.9, 14.1. IR (neat): 2929, 2858, 1499, 1458, 1138 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{34}N$ $(M+H)^+$: 360.26858. Found: 360.26874.

1-(Dec-1-yn-1-yl)-2-(4-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (4b)

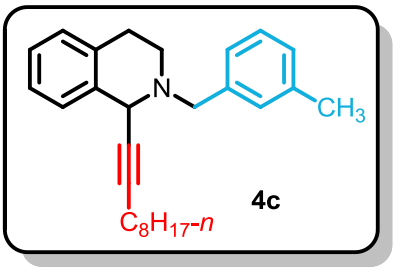
Following the general procedure **2.1.1**, 4-tolualdehyde (65.6 mg, 0.542 mmol), THIQ (76.2 mg, 0.555 mmol) and 1-decyne (77.4 mg, 0.549 mmol) were converted into the *endo*-yne-THIQ product **4b** (198.2 mg, 0.531 mmol, 94% yield). Purification (silica gel, PE/EA = 50/1).



4b: Colorless oil, TLC R_f = 0.16 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.9 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.16 – 7.10 (m, 4H), 7.10 – 7.05 (m, 1H), 4.53 (s, 1H), 3.84 (d, J = 13.0 Hz, 1H), 3.75 (d, J = 13.0 Hz, 1H), 3.03 – 2.88 (m, 2H), 2.81 – 2.67 (m, 2H), 2.34 (s, 3H), 2.22 (td, J = 7.0, and 2.0 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.45 – 1.36 (m, 2H), 1.32 – 1.27 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 136.4, 135.5, 133.9, 129.2, 128.93, 128.88, 127.7, 126.6, 125.6, 87.1, 78.0, 59.2, 54.1, 45.5, 31.9, 29.3, 29.12, 29.07, 29.0, 28.9, 22.7, 21.1, 18.9, 14.1. IR (neat): 2932, 2858, 1516, 1458, 1357 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{36}N$ $(M+H)^+$: 374.28423. Found: 374.28343.

***1-(Dec-1-yn-1-yl)-2-(3-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline* (4c)**

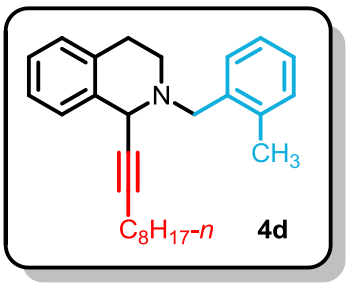
Following the general procedure **2.1.1**, 3-tolualdehyde (53.2 mg, 0.443 mmol), THIQ (60.3 mg, 0.439 mmol) and 1-decyne (70.0 mg, 0.496 mmol) were converted into the *endo*-yne-THIQ products **4c**/**5c** (163.2 mg, 0.437 mmol, 90% yield, **4c**/**5c** ratio > 19/1). Purification (silica gel, PE/EA = 50/1).



4c: Colorless oil, TLC R_f = 0.23 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.23 – 7.18 (m, 3H), 7.15 – 7.11 (m, 2H), 7.10 – 7.05 (m, 2H), 4.55 (s, 1H), 3.85 (d, J = 13.1 Hz, 1H), 3.75 (d, J = 13.1 Hz, 1H), 3.02 – 2.90 (m, 2H), 2.80 – 2.69 (m, 2H), 2.34 (s, 3H), 2.23 (td, J = 6.9, and 1.8 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.22 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.8, 136.4, 133.9, 130.0, 128.9, 128.1, 127.8, 127.7, 126.7, 126.3, 125.7, 87.2, 78.0, 59.5, 54.2, 45.6, 31.9, 29.3, 29.12, 29.05, 29.0, 28.9, 22.7, 21.4, 18.9, 14.1. IR (neat): 2929, 2860, 1655, 1460, 1357 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{36}N$ $(M+H)^+$: 374.28423. Found: 374.28423.

***1-(Dec-1-yn-1-yl)-2-(2-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline* (4d)**

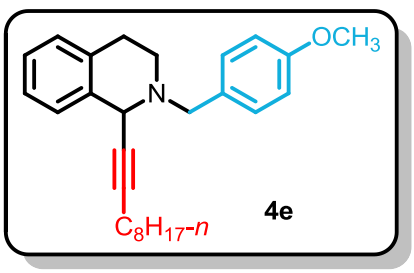
Following the general procedure **2.1.1**, 2-tolualdehyde (60.1 mg, 0.500 mmol), THIQ (65.3 mg, 0.490 mmol) and 1-decyne (70.2 mg, 0.498 mmol) were converted into the *endo*-yne-THIQ product **4d** (173.8 mg, 0.466 mmol, 84% yield). Purification (silica gel, PE/EA = 50/1).



4d: Colorless oil, R_f = 0.49 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 1H), 7.22 – 7.11 (m, 6H), 7.11 – 7.06 (m, 1H), 4.53 (s, 1H), 3.85 (d, J = 13.2 Hz, 1H), 3.75 (d, J = 13.2 Hz, 1H), 3.03 – 2.88 (m, 2H), 2.76 – 2.66 (m, 2H), 2.39 (s, 3H), 2.23 (td, J = 6.9, and 1.9 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.45 – 1.36 (m, 2H), 1.32 – 1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 136.7, 134.0, 130.3, 129.8, 128.9, 127.7, 127.0, 126.6, 126.3, 125.6, 125.5, 87.1, 78.2, 57.4, 54.2, 45.4, 31.9, 29.3, 29.1, 29.0, 28.9, 22.7, 19.6, 19.3, 18.9, 14.1. IR (neat): 2932, 2858, 1516, 1458, 1357 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{36}N$ $(M+H)^+$: 374.28423. Found: 374.28343.

***1-(Dec-1-yn-1-yl)-2-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline* (4e)**

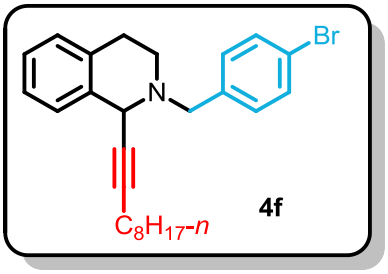
Reaction was carried out at 80 ℃, other conditions followed the general procedure **2.1.1**. 4-Methoxy-benzaldehyde (66.6 mg, 0.479 mmol), THIQ (67.9 mg, 0.494 mmol) and 1-decyne (0.523 mmol) were converted into the *endo*-yne-THIQ product **4e** (144.5 mg, 0.371 mmol, 77% yield). Purification (Silica gel, hexane/EA = 50/1).



4e: Yellow oil, R_f = 0.48 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.5 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 7.06 (m, 1H), 6.86 (d, J = 8.5 Hz, 2H), 4.51 (s, 1H), 3.81 (d, J = 12.9 Hz, 1H), 3.80 (s, 3H), 3.73 (d, J = 12.9 Hz, 1H), 3.00 – 2.91 (m, 2H), 2.79 – 2.70 (m, 2H), 2.23 (td, J = 7.0, and 1.9 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.45 – 1.36 (m, 2H), 1.34 – 1.22 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 136.4, 133.9, 130.5, 130.4, 128.9, 127.7, 126.6, 125.7, 113.6, 87.2, 77.9, 58.8, 55.3, 53.9, 45.5, 31.9, 29.3, 29.11, 29.05, 29.01, 28.9, 22.7, 18.9, 14.1. IR (neat): 2932, 2858, 1616, 1460, 1247 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{36}NO$ $(M+H)^+$: 390.27914. Found: 390.27930.

***2-(4-Bromobenzyl)-1-(dec-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (4f)**

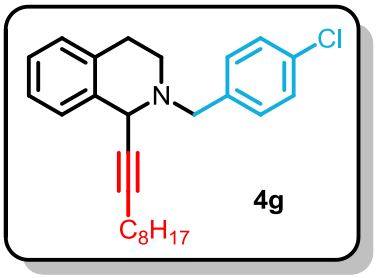
Following the general procedure **2.1.1**, 4-bromobenzaldehyde (92.6 mg, 0.495 mmol), THIQ (62.2 mg, 0.453 mmol) and 1-decyne (67.3 mg, 0.477 mmol) were converted into *endo*-yne-THIQ and *exo*-yne-THIQ products **4f**/**5f** (193.9 mg, 0.422 mmol, 94% yield, **4f**/**5f** ratio 17/1). Purification (Silica gel, PE/EA = 50/1).



4f: Colorless oil, R_f = 0.24 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.20 – 7.18 (m, 1H), 7.16 – 7.11 (m, 2H), 7.10 – 7.07 (m, 1H), 4.50 (s, 1H), 3.82 (d, J = 13.3 Hz, 1H), 3.73 (d, J = 13.3 Hz, 1H), 3.01 – 2.89 (m, 2H), 2.80 – 2.67 (m, 2H), 2.22 (td, J = 7.0, and 1.9 Hz, 2H), 1.57 – 1.46 (m, 2H), 1.44 – 1.34 (m, 2H), 1.33 – 1.22 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.2, 133.7, 131.4, 130.9, 129.0, 127.7, 126.8, 125.8, 120.9, 87.4, 77.7, 58.8, 54.1, 45.6, 31.9, 29.3, 29.2, 29.1, 29.02, 28.98, 22.7, 18.9, 14.2. IR (neat): 2931, 2858, 1616, 1460, 1247 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{33}BrN$ $(M+H)^+$: 438.17909. Found: 438.17924.

***2-(4-Chlorobenzyl)-1-(dec-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (4g)**

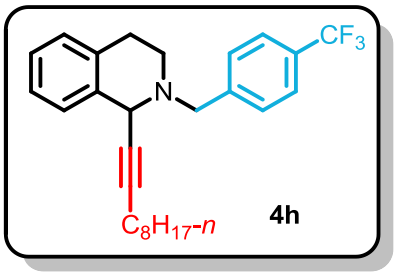
Following the general procedure **2.1.1**, 4-chlorobenzaldehyde (71.6 mg, 0.499 mmol), THIQ (67.8 mg, 0.494 mmol) and 1-decyne (69.5 mg, 0.493 mmol) were converted into *endo*-yne-THIQ product **4g** (180.3 mg, 0.458 mmol, 92% yield). Purification (Silica gel, PE/EA = 50/1).



4g: Colorless oil, R_f = 0.68 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 4.50 (s, 1H), 3.83 (d, J = 13.3 Hz, 1H), 3.75 (d, J = 13.3 Hz, 1H), 3.02 – 2.89 (m, 2H), 2.81 – 2.64 (m, 2H), 2.22 (td, J = 7.0, and 2.0 Hz, 2H), 1.51 (dd, J = 14.7, and 7.2 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.32 – 1.20 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.2, 133.7, 132.7, 130.5, 128.9, 128.4, 127.7, 126.7, 125.7, 87.3, 77.7, 58.7, 54.1, 45.6, 31.8, 29.3, 29.10, 29.05, 29.0, 28.9, 22.7, 18.8, 14.1. IR (neat): 2931, 2862, 1655, 1491, 1460, 1093 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{33}ClN$ $(M+H)^+$: 394.22960. Found: 394.23036.

***1-(Dec-1-yn-1-yl)-2-(4-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroisoquinoline* (4h)**

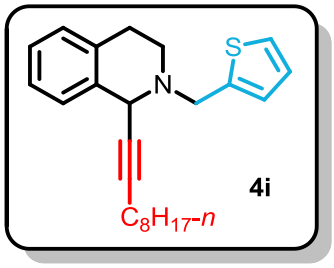
Following the general procedure **2.1.1**, 4-(trifluoromethyl) benzaldehyde (95.9 mg, 0.534 mmol), THIQ (70.7 mg, 0.515 mmol) and 1-decyne (77.6 mg, 0.550 mmol) were converted into *endo*-yne-THIQ and *exo*-yne-THIQ products **4h**/**5h** (212.8 mg, 0.498 mmol, 93% yield, **4h**/**5h** ratio 7/1). Purification (Silica gel, PE/EA = 50/1).



4h: Yellow oil, R_f = 0.31 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 7.13 – 7.08 (m, 1H), 4.54 (s, 1H), 3.95 (d, J = 13.6 Hz, 1H), 3.86 (d, J = 13.6 Hz, 1H), 3.06 – 2.93 (m, 2H), 2.83 – 2.67 (m, 2H), 2.24 (td, J = 7.0, and 2.0 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.25 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 136.0, 133.6, 129.4 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.3, 128.9, 127.7, 126.8, 125.8, 125.2 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 87.4, 77.6, 59.0, 54.2, 45.8, 31.8, 29.3, 29.1, 29.02, 28.97, 28.9, 22.7, 18.8, 14.1. IR (neat): 2932, 2860, 1460, 1329, 1167, 1130 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{33}F_3N$ $(M+H)^+$: 428.25596. Found: 428.25665.

***1-(Dec-1-yn-1-yl)-2-(thiophen-2-ylmethyl)-1,2,3,4-tetrahydroisoquinoline* (4i)**

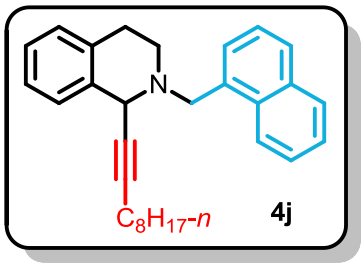
Reaction was carried out at 80℃, other conditions followed the general procedure **2.1.1**. Thiophene-2-carbaldehyde (63.3 mg, 0.553 mmol), THIQ (68.1 mg, 0.511 mmol) and 1-decyne (69.8 mg, 0.495 mmol) were converted into *endo*-yne-THIQ product **4i** (129.2 mg, 0.353 mmol, 72% yield). Purification (Silica gel, hexane/EA = 50/1).



4i: Yellow oil, R_f = 0.70 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 2H), 7.10 – 7.06 (m, 1H), 7.02 (d, *J* = 2.7 Hz, 1H), 6.97 (dd, *J* = 5.0, and 3.5 Hz, 1H), 4.63 (s, 1H), 4.07 (d, *J* = 13.9 Hz, 1H), 4.03 (d, *J* = 13.8 Hz, 1H), 3.04 – 2.90 (m, 2H), 2.85 – 2.72 (m, 2H), 2.22 (td, *J* = 7.0, and 2.0 Hz, 2H), 1.59 – 1.48 (m, 2H), 1.45 – 1.35 (m, 2H), 1.32 – 1.25 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.2, 133.9, 128.9, 127.8, 126.8, 126.5, 126.1, 125.8, 125.1, 87.3, 77.9, 54.2, 54.0, 45.6, 31.9, 29.4, 29.23, 29.19, 29.1, 29.0, 22.8, 19.0, 14.2. IR (neat): 2929, 2862, 1462, 1370, 1324 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{32}NS$ $(M+H)^+$: 366.22500. Found: 366.22480.

***1-(Dec-1-yn-1-yl)-2-(naphthalen-1-ylmethyl)-1,2,3,4-tetrahydroisoquinoline* (4j)**

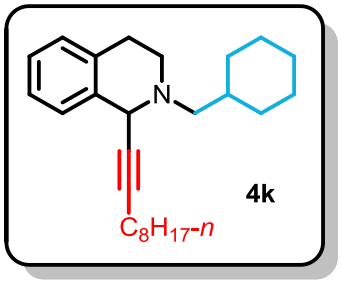
Following the general procedure **2.1.1**, 1-naphthaldehyde (82.2 mg, 0.511 mmol), THIQ (72.2 mg, 0.526 mmol) and 1-decyne (72.0 mg, 0.512 mmol) were converted into *endo*-yne-THIQ products **4j/5j** (189.4 mg, 0.462 mmol, 91% yield, **4j/5j** ratio > 19/1). Purification (Silica gel, PE/EA = 50/1).



4j: Colorless oil, R_f = 0.48 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 – 8.38 (m, 1H), 7.86 – 7.82 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.22 – 7.19 (m, 1H), 7.15 – 7.10 (m, 2H), 7.09 – 7.05 (m, 1H), 4.59 (s, 1H), 4.40 (d, *J* = 13.2 Hz, 1H), 4.12 (d, *J* = 13.2 Hz, 1H), 3.07 – 3.00 (m, 1H), 2.97 – 2.88 (m, 1H), 2.80 – 2.69 (m, 2H), 2.28 (td, *J* = 6.8, and 1.6 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.48 – 1.41 (m, 2H), 1.27 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 134.3, 134.1, 134.0, 132.9, 128.9, 128.4, 128.0, 127.8, 127.6, 126.7, 125.8, 125.7, 125.6, 125.2, 125.1, 87.3, 78.3, 57.8, 54.7, 45.7, 31.9, 29.34, 29.28, 29.2, 29.12, 29.06, 22.8, 19.0, 14.2. IR (neat): 2934, 2862, 1510, 1460, 1331 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{36}N$ $(M+H)^+$: 410.28423. Found: 410.28450.

***2-(Cyclohexylmethyl)-1-(dec-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (4k)**

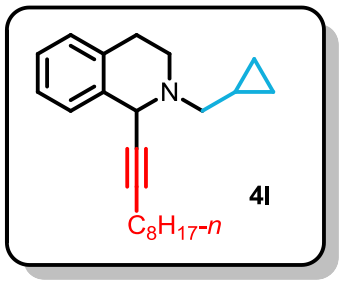
Following the general procedure **2.1.1**, cyclohexanecarbaldehyde (48.6 mg, 0.420 mmol), THIQ (64.6 mg, 0.471 mmol) and 1-decyne (61.8 mg, 0.438 mmol) were converted into *endo*- and *exo*-yne-THIQ products **4k/5k** (129.4 mg, 0.354 mmol, 85% yield, **4k/5k** ratio 3/1). Purification (Silica gel, PE/EA = 100/1).



4k: Yellow oil, R_f = 0.20 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 7.15 – 7.11 (m, 2H), 7.09 – 7.06(m, 1H), 4.56 (s, 1H), 3.00 – 2.87 (m, 2H), 2.77 – 2.70 (m, 1H), 2.69 – 2.62 (m, 1H), 2.49 – 2.40 (m, 2H), 2.18 (td, *J* = 6.8, and 2.0 Hz, 2H), 1.81 (t, *J* = 12.0 Hz, 2H), 1.72 – 1.65 (m, 3H), 1.61 – 1.53 (m, 1H), 1.50 – 1.43 (m, 2H), 1.38 – 1.33 (m, 2H), 1.32 – 1.26 (m, 10H), 1.22 – 1.15 (m, 2H), 0.96 – 0.93 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 134.0, 128.8, 127.7, 126.5, 125.6, 86.5, 78.3, 62.1, 54.9, 46.1, 35.5, 32.0, 31.9, 31.8, 29.3, 29.10, 29.06, 28.97, 28.9, 26.9, 26.2, 26.1, 22.7, 18.8, 14.1. IR (neat): 2927, 2858, 1495, 1460, 1270 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{40}N$ $(M+H)^+$: 366.31553. Found: 366.31540.

***2-(Cyclopropylmethyl)-1-(dec-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (4l)**

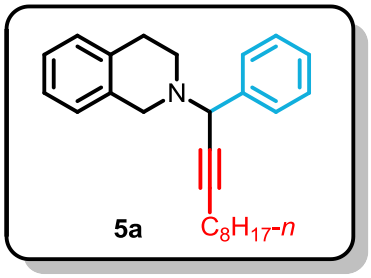
Following the general procedure **2.1.1** with doubled amount, cyclopropanecarbaldehyde (67.1 mg, 0.938 mmol), THIQ (138.2 mg, 1.001 mmol) and 1-decyne (136.8 mg, 0.970 mmol) were converted into *endo*- and *exo*-yne-THIQ products **4l/5l** (240.9 mg, 0.745 mmol, 79% yield, **4l/5l** ratio 4/1). Purification (Silica gel, PE/EA = 50/1).



4l: Colorless oil, R_f = 0.35 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 7.16 – 7.11 (m, 2H), 7.10 – 7.06 (m, 1H), 4.84 (s, 1H), 3.05 – 2.94 (m, 2H), 2.89 – 2.74 (m, 2H), 2.66 (dd, J = 12.5, and 6.0 Hz, 1H), 2.49 (dd, J = 12.5, and 7.1 Hz, 1H), 2.17 (td, J = 7.0, and 2.1 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.38 – 1.32 (m, 2H), 1.29 – 1.23 (m, 8H), 1.01 – 0.91 (m, 1H), 0.88 (t, J = 6.9 Hz, 3H), 0.60 – 0.48 (m, 2H), 0.40 – 0.32 (m, 1H), 0.20 – 0.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 133.7, 128.9, 127.7, 126.7, 125.7, 87.1, 77.9, 59.9, 54.0, 46.1, 31.8, 29.2, 29.1, 28.92, 28.86, 28.82, 22.7, 18.8, 14.1, 8.8, 4.1, 3.3. IR (neat): 2934, 2862, 1510, 1462, 1328 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{34}N$ $(M+H)^+$: 324.26858. Found: 324.26825.

***2-(1-Phenylundec-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (5a)** [2]

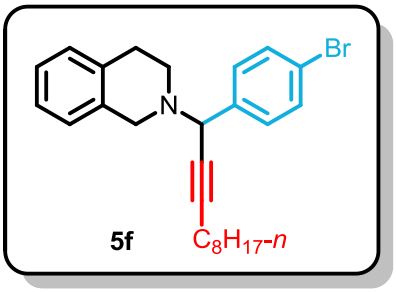
Following the general procedure **2.1.3**, benzaldehyde (58.8 mg, 0.554 mmol), THIQ (83.0 mg, 0.623 mmol) and 1-decyne (86.5 mg, 0.626 mmol) were converted into *exo*- and *endo*-yne-THIQ products **5a**/**4a** (171.8 mg, 0.478 mmol, 86% yield, **5a**/**4a** ratio 10/1). Purification (Silica gel, PE/EA = 100/1).



5a (Known compound, ref 1): Pale yellow oil, TLC R_f = 0.71 (PE/EA = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.4 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.12 – 7.06 (m, 3H), 7.01 – 6.97 (m, 1H), 4.81 (s, 1H), 3.76 (d, J = 16.8 Hz, 1H), 3.72 (d, J = 15.2 Hz, 1H) 2.96 – 2.83 (m, 2H), 2.82 – 2.68 (m, 2H), 2.31 (td, J = 7.0, and 2.0 Hz, 2H), 1.63 – 1.50 (m, 2H), 1.48 – 1.37 (m, 2H), 1.33 – 1.20 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 135.5, 134.5, 128.7, 128.5, 128.1, 127.5, 126.7, 125.9, 125.5, 88.9, 75.3, 61.2, 52.1, 47.1, 31.9, 29.7, 29.3, 29.1, 29.0, 22.7, 18.8, 14.1. IR (neat): 2925, 2854, 1491, 1449, 1141 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{34}N$ $(M+H)^+$: 360.26858. Found: 360.26810.

***2-(1-(4-Bromophenyl)undec-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (5f)**

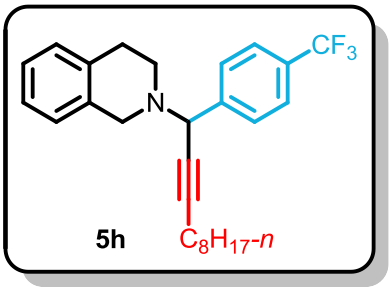
Following the general procedure **2.1.3**, 4-bromobenzaldehyde (92.5 mg, 0.500 mmol), THIQ (85.2 mg, 0.640 mmol) and 1-decyne (85.6 mg, 0.619 mmol) were converted into *exo*-yne-THIQ products **5f**/**4f** (201.1 mg, 0.459 mmol, 93% yield, **5f**/**4f** ratio 50/1). Purification (TLC, PE/EA = 30/1).



5f: Colorless oil, R_f = 0.46 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.16 – 7.03 (m, 3H), 7.01 – 6.93 (m, 1H), 4.75 (s, 1H), 3.74 (d, J = 14.8 Hz, 1H), 3.69 (d, J = 14.8 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.79 – 2.69 (m, 2H), 2.30 (td, J = 7.0, and 2.0 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.48 – 1.37 (m, 2H), 1.33 – 1.22 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 135.2, 134.4, 131.2, 130.2, 128.7, 126.7, 126.0, 125.6, 121.4, 89.4, 74.6, 60.6, 52.1, 47.1, 31.9, 29.6, 29.3, 29.09, 29.05, 29.0, 22.7, 18.8, 14.1. IR (neat): 2924, 2854, 1483, 1081, 1011 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{33}BrN$ $(M+H)^+$: 438.17909. Found: 438.17919.

***2-(1-(4-(Trifluoromethyl)phenyl)undec-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (5h)**

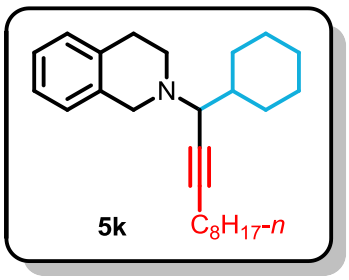
Following the general procedure **2.1.3**, 4-(trifluoromethyl)benzaldehyde (82.4 mg, 0.473 mmol), THIQ (83.5 mg, 0.627 mmol) and 1-decyne (85.4 mg, 0.618 mmol) were converted into *exo*-yne-THIQ products **5h**/**4h** (179.6 mg, 0.420 mmol, 92% yield, **5h**/**4h** ratio 33/1). Purification (Silica gel, PE to PE/EA = 100/1).



5h: Colorless oil, R_f = 0.51 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 4.5 Hz, 3H), 6.99 (d, J = 6.0 Hz, 1H), 4.85 (s, 1H), 3.78 (d, J = 14.8 Hz, 1H), 3.71 (d, J = 14.7 Hz, 1H), 2.97 – 2.81 (m, 2H), 2.78 (d, J = 5.4 Hz, 2H), 2.32 (td, J = 6.9, and 1.0 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.50 – 1.37 (m, 2H), 1.32 – 1.23 (m, 8H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 135.1, 134.3, 129.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 128.73, 128.70, 126.7, 126.0, 125.6, 125.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 89.8, 74.3, 60.8, 52.1, 47.2, 31.8, 29.5, 29.2, 29.1, 28.99, 28.96, 22.7, 18.8, 14.1. IR (neat): 2926, 2856, 1328, 1163, 1124, 1067 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{33}F_3N$ $(M+H)^+$: 428.25596. Found: 428.25663.

***2-(1-Cyclohexylundec-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (5k)**

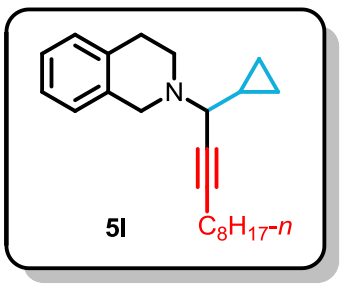
Following the general procedure **2.1.3**, cyclohexanecarbaldehyde (56.8 mg, 0.506 mmol), THIQ (82.7 mg, 0.621 mmol) and 1-decyne (82.8 mg, 0.599 mmol) were converted into *exo*-yne-THIQ product **5k** (167.2 mg, 0.457 mmol, 93% yield). Purification (Silica gel, PE to PE/EA = 100/1).



5k: Pale yellow oil, R_f = 0.28 (PE/EA = 50/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 3H), 7.05 – 7.00 (m, 1H), 3.80 (d, J = 14.8 Hz, 1H), 3.63 (d, J = 14.8 Hz, 1H), 3.11 (d, J = 9.9 Hz, 1H), 2.92 – 2.81 (m, 3H), 2.64 – 2.55 (m, 1H), 2.20 (td, J = 7.0, and 1.9 Hz, 2H), 2.09 (d, J = 12.7 Hz, 1H), 2.02 (d, J = 13.2 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.73 – 1.62 (m, 2H), 1.59 (dt, J = 10.2, and 3.2 Hz, 1H), 1.54 – 1.44 (m, 2H), 1.41 – 1.32 (m, 2H), 1.30 – 1.20 (m, 9H), 1.20 – 1.12 (m, 2H), 1.04 – 0.89 (m, 2H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.8, 128.6, 126.7, 125.8, 125.4, 86.5, 76.7, 63.4, 52.3, 47.1, 39.9, 31.9, 31.3, 30.5, 29.7, 29.27, 29.26, 29.1, 28.9, 26.8, 26.3, 26.1, 22.7, 18.7, 14.1. IR (neat): 2923, 2853, 1448, 1319, 1098 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{40}N$ $(M+H)^+$: 366.31553. Found: 366.31526.

***2-(1-Cyclopropylundec-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline* (5l)**

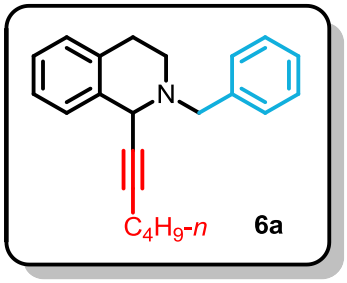
Following the general procedure **2.1.3**, cyclopropanecarbaldehyde (42.5 mg, 0.606 mmol), THIQ (89.6 mg, 0.676 mmol) and 1-decyne (93.7 mg, 0.678 mmol) were converted into *exo*-yne-THIQ products **5l** (169.4 mg, 0.524 mmol, 88% yield). Purification (Silica gel, PE/EA = 50/1 to 100/1).



5l: Yellow oil, R_f = 0.16 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 3H), 7.08 – 7.02 (m, 1H), 3.98 (d, J = 14.9 Hz, 1H), 3.74 (d, J = 14.9 Hz, 1H), 3.70 – 3.64 (m, 1H), 3.09 – 2.89 (m, 3H), 2.81 – 2.72 (m, 1H), 2.17 (td, J = 7.0, and 2.0 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.40 – 1.32 (m, 2H), 1.28 – 1.23 (m, 8H), 1.17 – 1.09 (m, 1H), 0.87 (t, J = 6.8 Hz, 3H), 0.62 – 0.54 (m, 2H), 0.51 – 0.43 (m, 1H), 0.42 – 0.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.2, 128.6, 126.7, 125.9, 125.5, 86.9, 73.8, 60.4, 51.8, 47.7, 31.8, 29.4, 29.2, 29.0, 28.8, 22.6, 18.5, 14.0, 12.6, 3.0, 1.8. IR (neat): 2926, 2855, 1455, 1325, 1086 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{34}N$ $(M+H)^+$: 324.26858. Found: 324.26868.

***2-Benzyl-1-(hex-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (6a)**

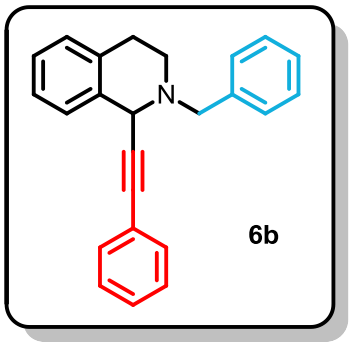
Following the general procedure **2.1.1**, benzaldehyde (50.1 mg, 0.472 mmol), THIQ (64.2 mg, 0.468 mmol) and 1-hexyne (46.2 mg, 0.551 mmol) were converted into *endo*-yne-THIQ product **6a** (120.0 mg, 0.395 mmol, 85% yield). Purification (Silica gel, PE/EA = 50/1).



6a: Yellow oil, R_f = 0.28 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.3 Hz, 2H), 7.22 (t, J = 7.3 Hz, 2H), 7.15 (t, J = 7.1 Hz, 1H), 7.10 – 7.08 (m, 1H), 7.04 – 6.99 (m, 2H), 6.98 – 6.96 (m, 1H), 4.45 (s, 1H), 3.79 (d, J = 13.2 Hz, 1H), 3.70 (d, J = 13.1 Hz, 1H), 2.89 – 2.84 (m, 2H), 2.69 – 2.58 (m, 2H), 2.14 (td, J = 6.8, and 0.7 Hz, 2H), 1.44 – 1.32 (m, 4H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 136.4, 133.9, 129.3, 129.0, 128.3, 127.8, 127.2, 126.8, 125.8, 87.2, 78.0, 59.6, 54.2, 45.7, 31.2, 29.1, 22.1, 18.7, 13.7. IR (neat): 2955, 2925, 1494, 1454, 1356 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}N$ $(M+H)^+$: 304.20598. Found: 304.20559.

***2-Benzyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline* (6b)**

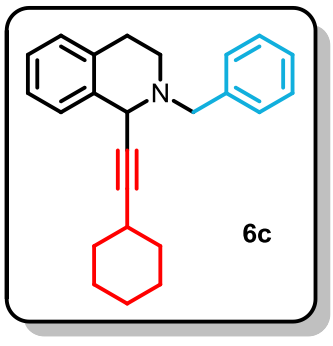
Following the general procedure **2.1.1**, benzaldehyde (45.4 mg, 0.428 mmol), THIQ (66.1 mg, 0.482 mmol) and phenylacetylene (54.2 mg, 0.520 mmol) were converted into *endo*- and *exo*-yne-THIQ products **6b/7b** (122.6 mg, 0.379 mmol, 89% yield, **6b/7b** ratio > 19/1). Purification (Silica gel, PE/EA = 50/1).



6b: Colorless oil, R_f = 0.23 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 4H), 7.37 (t, J = 7.3 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.28 (d, J = 2.4 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.17 – 7.13 (m, 1H), 4.83 (s, 1H), 3.99 (d, J = 13.2 Hz, 1H), 3.94 (d, J = 13.2 Hz, 1H), 3.16 – 3.01 (m, 2H), 2.90 – 2.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.5, 134.1, 131.8, 129.3, 129.0, 128.3, 128.2, 128.0, 127.8, 127.2, 126.9, 125.8, 123.3, 87.5, 86.8, 59.6, 54.4, 45.8, 29.1. IR (neat): 2929, 2856, 1458, 1361, 1292 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{22}N$ $(M+H)^+$: 324.17468. Found: 324.17435.

***2-Benzyl-1-(cyclohexylethynyl)-1,2,3,4-tetrahydroisoquinoline* (6c)**

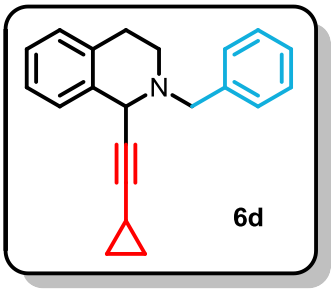
Following the general procedure **2.1.1**, benzaldehyde (56.8 mg, 0.535 mmol), THIQ (65.0 mg, 0.474 mmol) and cyclohexylacetylene (56.0 mg, 0.507 mmol) were converted into *endo*-yne-THIQ product **6c** (130.0 mg, 0.395 mmol, 83% yield). Purification (Silica gel, PE/EA = 50/1).



6c: Colorless oil, R_f = 0.26 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.1Hz, 2H), 7.36 – 7.33 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.20 (m, 1H), 7.16 – 7.13 (m, 2H), 7.12 – 7.09 (m, 1H), 4.57 (s, 1H), 3.92 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 12.8 Hz, 1H), 3.05 – 2.94 (m, 2H), 2.82 – 2.72 (m, 2H), 2.48 – 2.44(m, 1H), 1.85 – 1.80 (m, 2H), 1.77 – 1.70 (m, 2H), 1.54 – 1.47 (m, 3H), 1.42 – 1.29 (m, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 136.5, 133.9, 129.3, 128.9, 128.3, 127.8, 127.1, 126.6, 125.7, 91.3, 77.8, 59.5, 54.1, 45.7, 33.1, 33.0, 29.2, 29.1, 26.0, 24.9. IR (neat): 2932, 2858, 1497, 1458, 1363, 1292 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{28}N$ $(M+H)^+$: 330.22163. Found: 330.22149.

***2-Benzyl-1-(cyclopropylethynyl)-1,2,3,4-tetrahydroisoquinoline* (6d)**

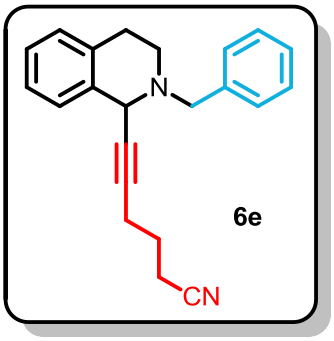
Following the general procedure **2.1.1**, benzaldehyde (45.0 mg, 0.424 mmol), THIQ (66.7 mg, 0.485 mmol) and cyclopropylacetylene (37.1 mg, 561 mmol) were converted into *endo*-yne-THIQ product **6d** (106.9 mg, 0.372 mmol, 88% yield). Purification (Silica gel, PE/EA = 50/1).



6d: Colorless oil, R_f = 0.44 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.23 – 7.18 (m, 1H), 7.17 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 4.55 (s, 1H), 3.90 (d, J = 13.2 Hz, 1H), 3.80 (d, J = 13.1 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.83 – 2.72 (m, 2H), 1.34 – 1.27 (m, 1H), 0.82 – 0.74 (m, 2H), 0.74 – 0.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 136.5, 134.2, 129.6, 129.2, 128.6, 128.0, 127.4, 127.0, 126.0, 90.6, 73.4, 59.7, 54.4, 45.9, 29.3, 8.8, 0.0. IR (neat): 3025, 2911, 2823, 1493, 1453, 1356 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{22}N$ $(M+H)^+$: 288.17468. Found: 288.17478.

***6-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)hex-5-ynenitrile* (6e)**

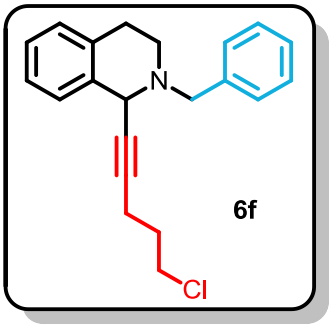
Following the general procedure **2.1.1**, benzaldehyde (53.5 mg, 0.504 mmol), THIQ (68.6 mg, 0.500 mmol) and 5-cyano-1-pentyne (52.1 mg, 0.554 mmol) were converted into *endo*- and *exo*-yne-THIQ products **6e/7e** (143.3 mg, 0.456 mmol, 91% yield, **6e/7e** ratio > 19/1). Purification (Silica gel, PE/EA = 20/1 to 10/1).



6e: Colorless oil, R_f = 0.10 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.2 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.20 – 7.08 (m, 4H), 4.57 (s, 1H), 3.87(d, J = 13.2 Hz, 1H), 3.79 (d, J = 13.2 Hz, 1H), 3.05 – 2.90 (m, 2H), 2.82 – 2.72 (m, 2H), 2.48 – 2.42(m, 4H), 1.91 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 135.9, 133.9, 129.1, 129.0, 128.4, 127.5, 127.2, 126.9, 125.8, 119.2, 84.1, 80.2, 59.6, 54.0, 45.6, 29.0, 24.8, 18.0, 16.2. IR (neat): 2934, 2845, 1458, 1363, 1210 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2$ $(M+H)^+$: 315.18558. Found: 315.18539.

***2-Benzyl-1-(5-chloropent-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (6f)**

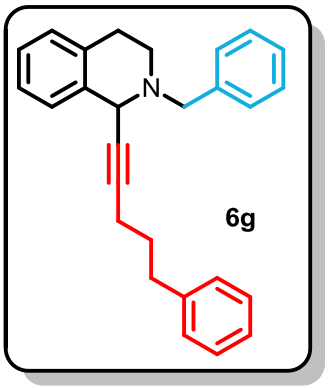
Following the general procedure **2.1.1**, benzaldehyde (50.7 mg, 0.478 mmol), THIQ (63.0 mg, 0.473 mmol) and 5-chloro-1-pentyne (52.2 mg, 0.499 mmol) were converted into *endo*- and *exo*-yne-THIQ products **6f/7f** (135.4 mg, 0.418 mmol, 88% yield, **6f/7f** ratio > 19/1). Purification (Silica gel, PE/EA = 30/1).



6f: Yellow oil, R_f = 0.48 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.2Hz, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.23 – 7.20 (m, 1H), 7.19 – 7.16 (m, 2H), 7.15 – 7.12 (m, 1H), 4.60 (s, 1H), 3.92 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 12.8 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 3.06 – 2.94 (m, 2H), 2.85 – 2.72 (m, 2H), 2.48 (td, J = 6.8, and 2.0 Hz, 2H), 2.06 – 1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.1, 134.0, 129.2, 129.0, 128.4, 127.7, 127.2, 126.8, 125.8, 85.0, 79.2, 59.6, 54.1, 45.7, 43.8, 31.7, 29.1, 16.4. IR (neat): 2929, 2851, 1495, 1458, 1359, 1292 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}ClN$ $(M+H)^+$: 324.15135. Found: 324.15105.

***2-Benzyl-1-(5-chloropent-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (6g)**

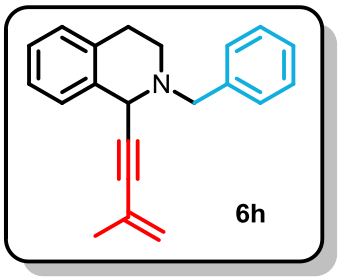
Following the general procedures **2.1.1**, benzaldehyde (59.6 mg, 0.562 mmol), THIQ (73.9 mg, 0.538 mmol) and 5-phenyl-1-pentyne (76.7 mg, 0.521 mmol) were converted into *endo*-yne-THIQ product **6g** (189.4 mg, 0.462 mmol, >99% yield). Purification (Silica gel, PE/EA = 30/1).



6g: Yellow oil, R_f = 0.53 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.1Hz, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.07 (m, 8H), 4.59 (s, 1H), 3.92 (d, J = 13.2 Hz, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.08 – 2.92 (m, 2H), 2.83 – 2.71 (m, 4H), 2.26 (td, J = 7.0, and 2.0 Hz, 2H), 1.88 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 138.7, 136.4, 134.0, 129.3, 129.0, 128.62, 128.44, 128.36, 127.8, 127.2, 126.8, 126.0, 125.8, 86.8, 78.7, 59.6, 54.3, 45.7, 35.0, 30.8, 29.2, 18.5. IR (neat): 2931, 2865, 1458, 1363, 1292 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}N$ $(M+H)^+$: 366.22163. Found: 366.22141.

***2-Benzyl-1-(3-methylbut-3-en-1-ynyl)-1,2,3,4-tetrahydroisoquinoline* (6h)**

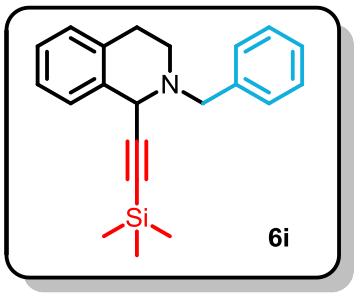
Following the general procedure **2.1.1**, benzaldehyde (102.7 mg, 0.968 mmol), THIQ (136.2 mg, 0.992 mmol) and 2-methylbut-1-en-3-yne (65.6 mg, 0.963 mmol) were converted into *endo*- and *exo*-yne-THIQ product **6h** (237.2 mg, 0.825 mmol, 86% yield). Purification (Silica gel, PE/EA = 50/1).



6h: Colorless oil, R_f = 0.32 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.6 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 7.06 (m, 1H), 5.27 (s, 1H), 5.19 – 5.16 (m, 1H), 4.67 (s, 1H), 3.87 (d, J = 13.2 Hz, 1H), 3.81 (d, J = 13.1 Hz, 1H), 3.02 – 2.91 (m, 2H), 2.81 – 2.70 (m, 2H), 1.89 (d, J = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.6, 134.1, 129.3, 129.0, 128.4, 127.8, 127.2, 126.9, 126.8, 125.8, 121.5, 88.1, 86.7, 59.6, 54.4, 45.8, 29.1, 23.9. IR (neat): 2927, 2834, 1655, 1458, 1292 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{22}N$ $(M+H)^+$: 288.17468. Found: 288.17449.

***2-Benzyl-1-((trimethylsilyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline* (6i)**

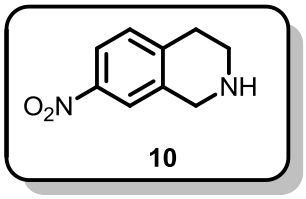
Following the general procedure **2.1.1**, benzaldehyde (51.3 mg, 0.483 mmol), THIQ (67.1 mg, 0.489 mmol) and 1-decyne (49.7 mg, 0.506 mmol) were converted into *endo*-yne-THIQ product **6i** (121.3 mg, 0.380 mmol, 79% yield). Purification (Silica gel, PE/EA = 50/1).



6i: Colorless oil, R_f = 0.44 (PE/EA = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.19 – 7.07 (m, 4H), 4.56 (s, 1H), 3.90 (d, J = 13.1 Hz, 1H), 3.81 (d, J = 13.1 Hz, 1H), 3.04 – 2.94 (m, 2H), 2.81 – 2.71 (m, 2H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 135.0, 133.8, 129.1, 128.7, 128.1, 127.6, 127.0, 126.6, 125.5, 103.4, 90.7, 59.2, 54.3, 45.5, 28.8, 0.0. IR (neat): 3028, 2824, 1491, 1453, 1249 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{26}NSi$ $(M+H)^+$: 320.18290. Found: 320.18325.

***7-Nitro-1,2,3,4-tetrahydroisoquinoline* (10)**

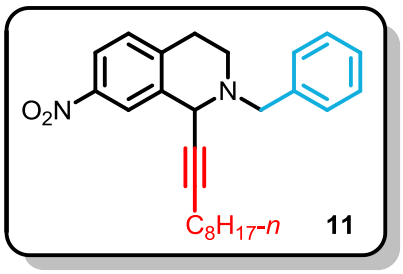
Follow the procedure depicted in Buolamwini's synthesis of 7-nitro-1,2,3,4-tetrahydroisoquinoline.[3] An ice-cold solution of 1,2,3,4-tetrahydroisoquinoline (1.331 g, 10 mmol) in concentrated sulfuric acid (5 mL) was treated with potassium nitrate (1.112 g, 11 mmol) in small portions, keeping the temperature below 5 ℃. The reaction was left overnight at room temperature and then poured onto ice. The resulting solution was neutralized with $NH_3 \cdot H_2O$, extracted with CH_2Cl_2. The extract was concentrated in vacuo. The crude obtained was purified by flash column chromatography to give compound **10** (653.9 mg, 3.67 mmol, 37% yield).



10 (known compound): Yellow oil, R_f = 0.08 (EA/MeOH/NEt_3 = 90/9/1). For NMR data, see SI of ref 2. IR (neat): 2984, 2900, 1515, 1347, 1052 cm^{-1}. HRMS (ESI) calcd for $C_9H_{11}N_2O_2$ $(M+H)^+$: 179.08150. Found: 179.08141.

***2-Benzyl-1-(dec-1-yn-1-yl)-7-nitro-1,2,3,4-tetrahydroisoquinoline* (11)**

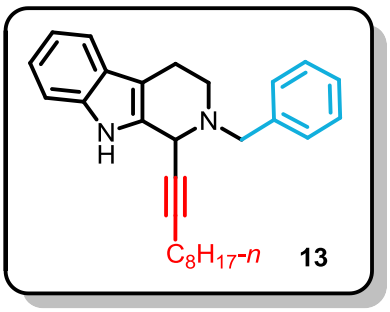
Following the general procedure **2.1.1**, benzaldehyde (35.1 mg, 0.330 mmol), 7-nitro-1,2,3,4-tetrahydroisoquinoline **10** (49.7 mg, 0.279 mmol) and 1-decyne (42.9 mg, 0.310 mmol) were converted into *endo*-yne-THIQ product **11** (56.4 mg, 0.140 mmol, 50% yield). Purification (Silica gel, PE to PE/EA = 30/1).



11: Dark red oil, R_f = 0.54 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 2.3 Hz, 1H), 8.00 (dd, J = 8.4, 2.4 Hz, 1H), 7.43 (d, J = 7.0 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.24 (d, J = 8.6 Hz, 1H), 4.62 (s, 1H), 3.92 (d, J = 12.9 Hz, 1H), 3.83 (d, J = 12.9 Hz, 1H), 3.14 – 2.97 (m, 2H), 2.94 – 2.71 (m, 2H), 2.25 (td, J = 7.0, and 2.1 Hz, 2H), 1.58 – 1.50 (m, 2H), 1.45 – 1.35 (m, 2H), 1.32 – 1.23 (m, 8H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 142.1, 138.05, 137.97, 129.9, 129.2, 128.4, 127.4, 123.0, 121.6, 88.8, 76.7, 59.3, 53.8, 45.0, 31.9, 29.4, 29.3, 29.1, 29.0, 28.9, 22.7, 18.9, 14.2. IR (neat): 2926, 2854, 1524, 1343, 1106 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{33}N_2O_2$ $(M+H)^+$: 405.25365. Found: 405.25364.

***N*-benzyl-1-yne-tryptoline* (13)**

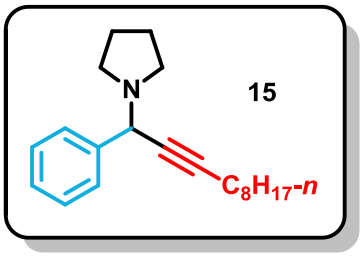
Following the general procedures **2.1.1**, benzaldehyde (53.5 mg, 0.504 mmol), tryptoline **12** (85.3 mg, 0.495 mmol) and 1-decyne (70.1 mg, 0.496 mmol) were converted into *endo*-yne-THIQ product **13** (161.8 mg, 0.406 mmol, 82% yield). Purification (Silica gel, PE to PE/EA = 150/1).



13: Pale yellow oil, R_f = 0.47 (PE/EA = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.44 (d, J = 7.4 Hz, 3H), 7.32 (t, J = 7.3 Hz, 2H), 7.27 (d, J = 7.1 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.3 Hz, 1H), 4.52 (s, 1H), 4.03 (d, J = 13.1 Hz, 1H), 3.79 (d, J = 13.1 Hz, 1H), 3.15 – 2.98 (m, 1H), 2.84 – 2.68 (m, 3H), 2.29 – 2.18 (dt, J = 6.9 Hz, 1.4 Hz, 2H), 1.61 – 1.48 (m, 2H), 1.43 – 1.36 (m, 2H), 1.26 (m, 8H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.2, 132.3, 129.4, 128.4, 127.3, 127.2, 121.7, 119.4, 118.4, 111.0, 108.4, 87.4, 76.3, 58.8, 50.1, 47.1, 31.9, 29.3, 29.2, 29.1, 28.9, 22.7, 21.5, 18.9, 14.2. IR (neat): 3406, 2926, 2853, 1451, 1303, 1164 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{35}N_2$ $(M+H)^+$: 399.27948. Found: 399.28035.

***1-(1-phenylundec-2-yn-1-yl)pyrrolidine* (15)** [2]

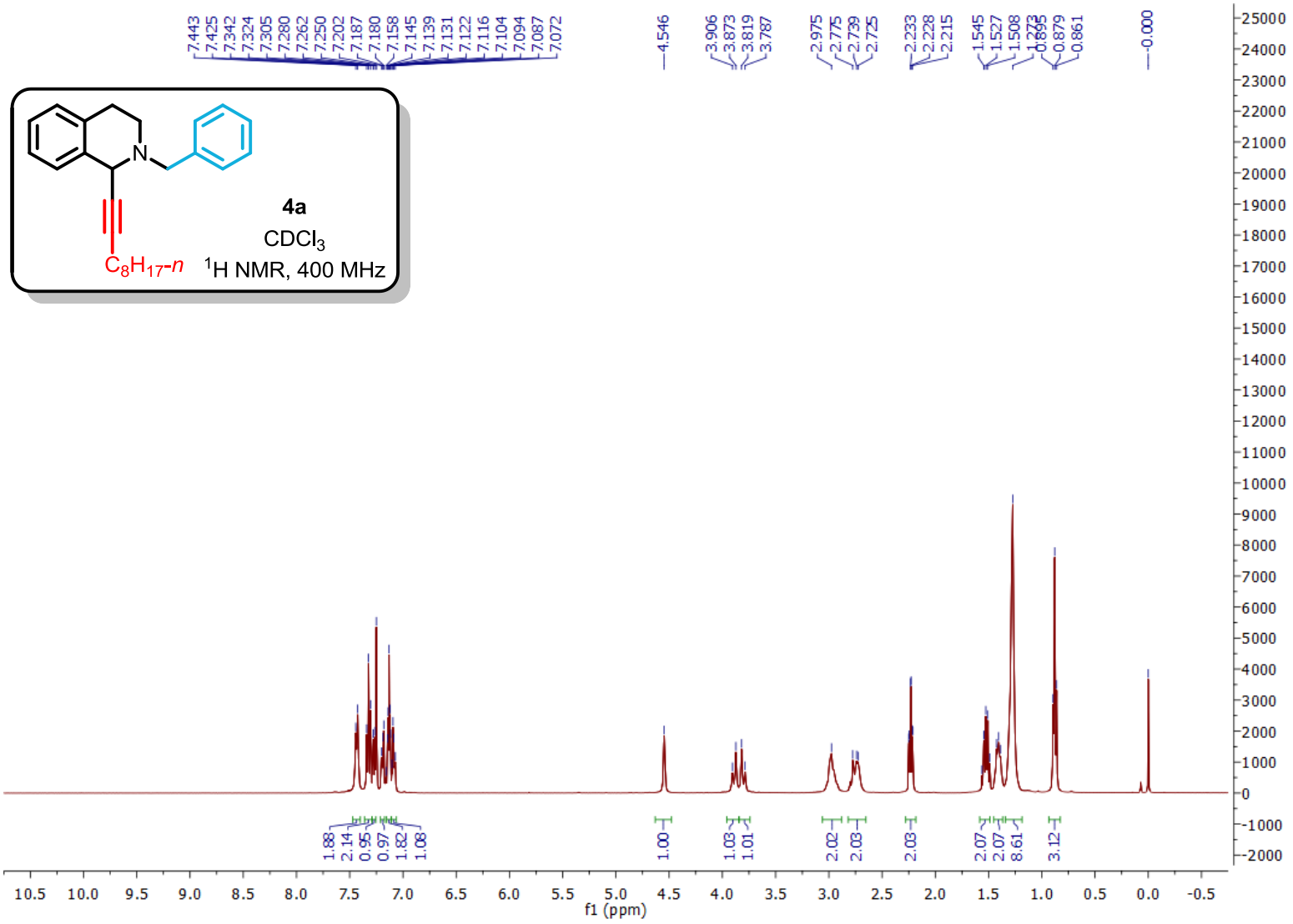
Following the general procedures **2.1.1**, benzaldehyde (48.9 mg, 0.461 mmol), pyrrolidine **14** (38.7 mg, 0.544 mmol), and 1-decyne (68.9 mg, 0.517 mmol) were converted into 1-(1-phenylundec-2-yn-1-yl)pyrrolidine **15** (20.8 mg, 0.07 mmol, 15% yield). Purification (silica gel, PE/EA = 30/1).

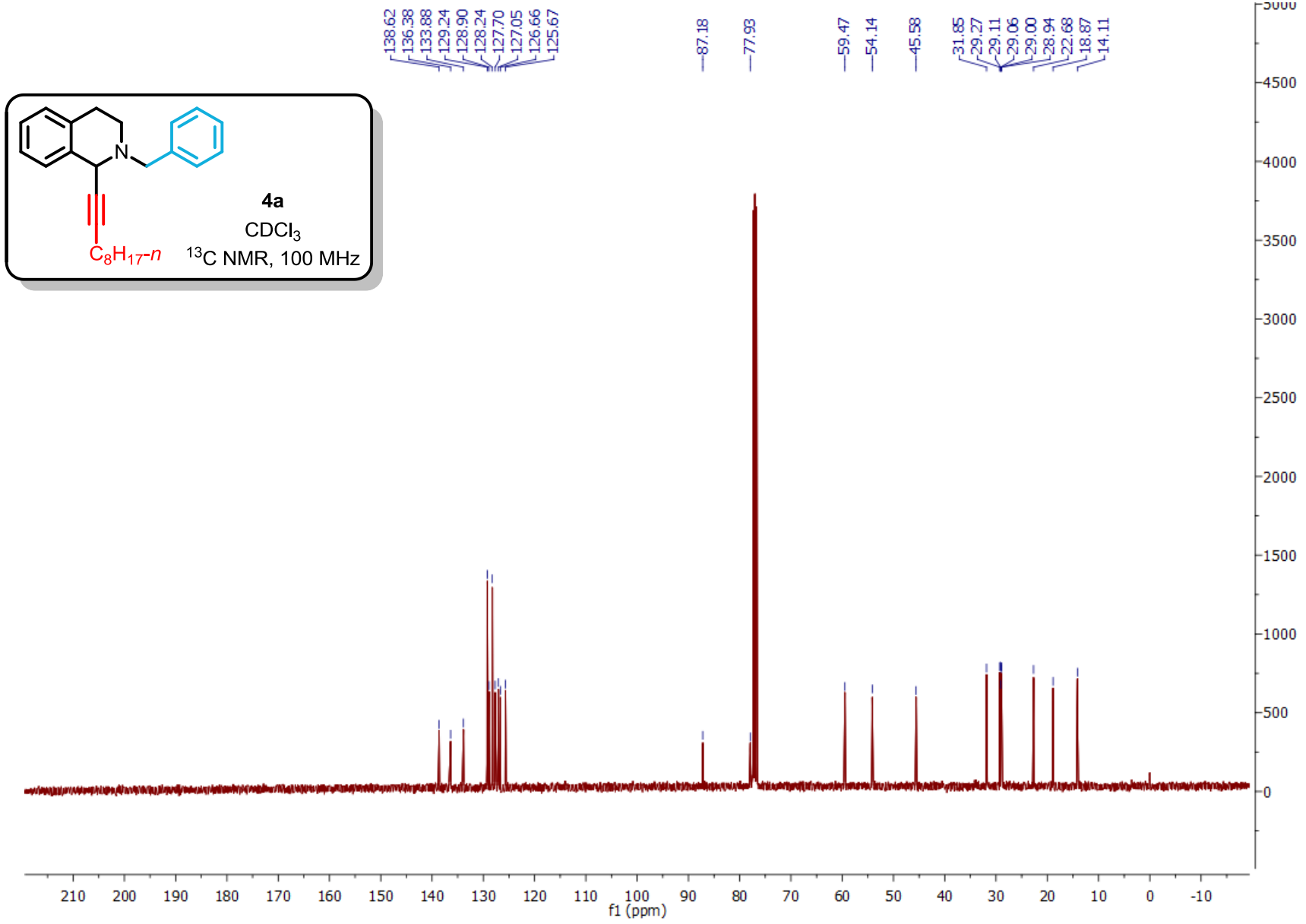


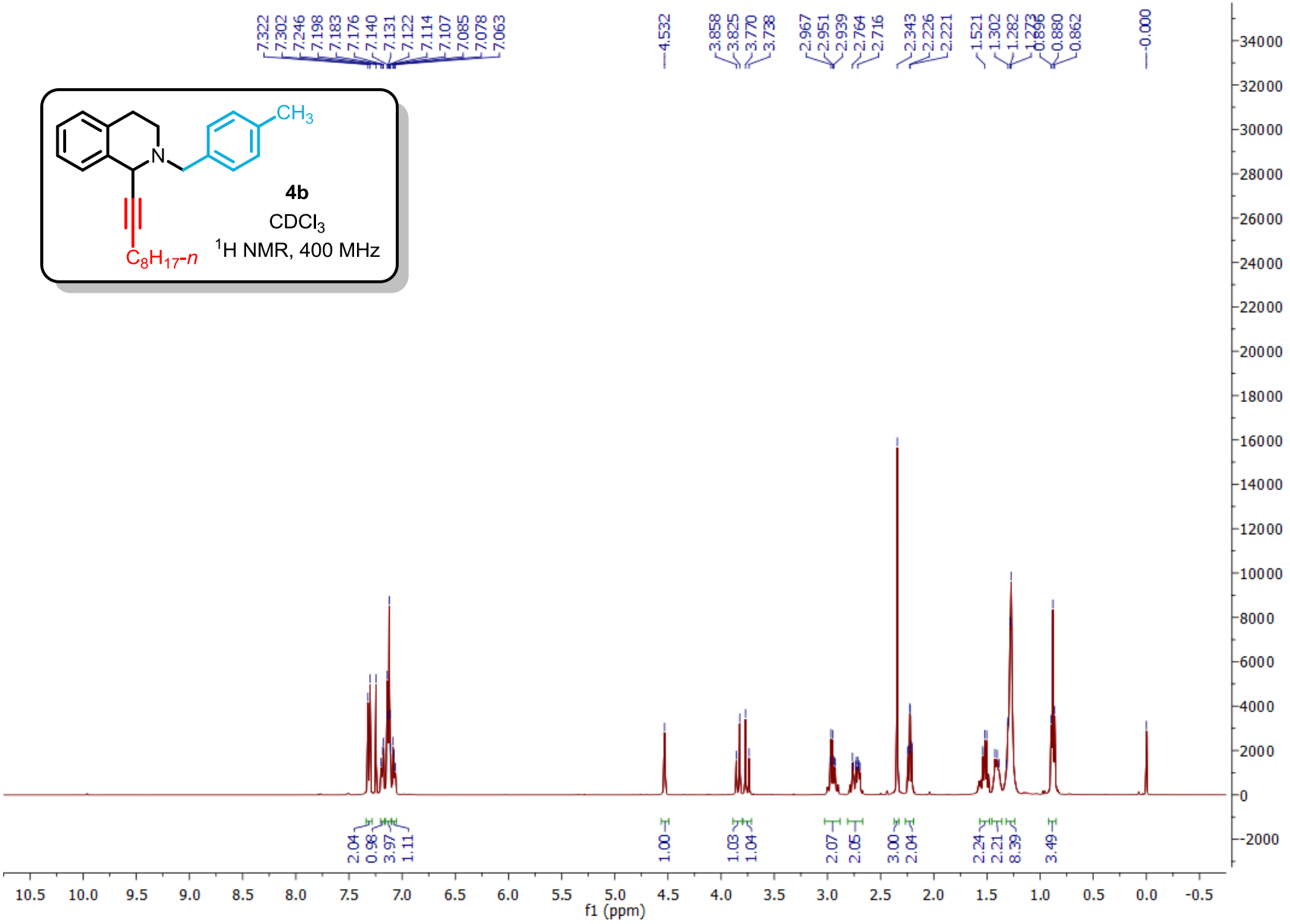
15: Colorless oil, TLC R_f = 0.16 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 4.53 (s, 1H), 2.57 – 2.46 (m, 4H), 2.19 (td, J = 7.0, and 2.1 Hz, 2H), 1.72 – 1.63 (m, 4H), 1.52 – 1.42 (m, 2H), 1.40 – 1.30 (m, 2H), 1.29 – 1.12 (m, 8H), 0.80 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.2, 128.1, 127.3, 87.1, 77.018, 58.8, 50.2, 31.9, 29.3, 29.1, 29.0, 28.9, 23.5, 22.7, 18.8, 14.1. IR (neat): 2928, 2856, 1451, 1268, 1136, 1030 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{32}N$ (M+H)+: 298.25293. Found: 298.25224.

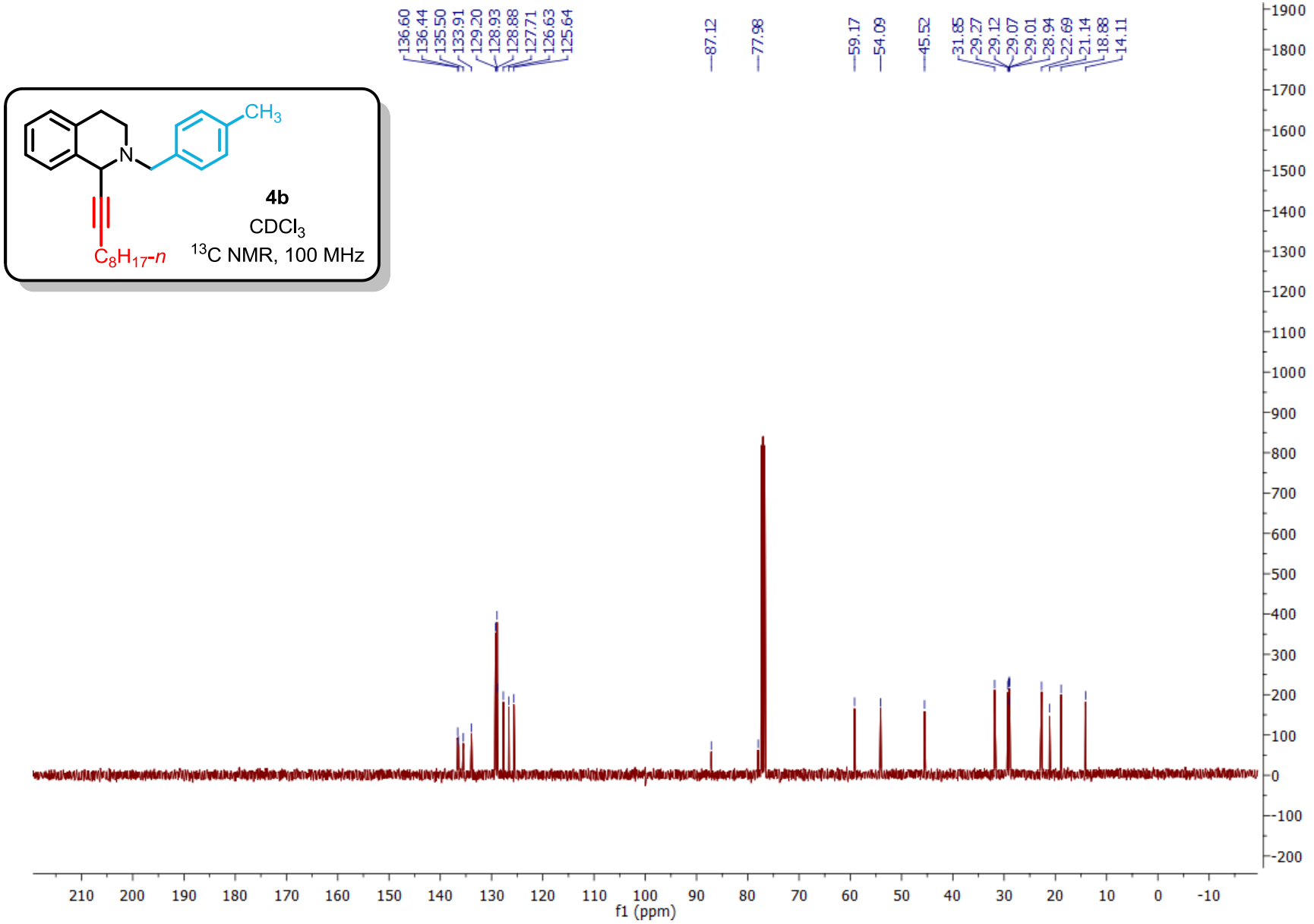
3. ^{1}H and ^{13}C NMR Spectra for New Compounds

3.1 ^{1}H and ^{13}C NMR Spectra for Yne-THIQs




138.62
136.38
133.88
129.24
128.90
128.24
127.70
127.05
126.66
125.67
87.18
77.93
59.47
54.14
45.58
31.85
29.27
29.11
29.06
29.00
28.94
22.68
18.87
14.11
N
C8H17-n
4a
CDCl3
13C NMR, 100 MHz
f1 (ppm)


4b
CDCl3
1H NMR, 400 MHz
CH3
N
C8H17-n
f1 (ppm)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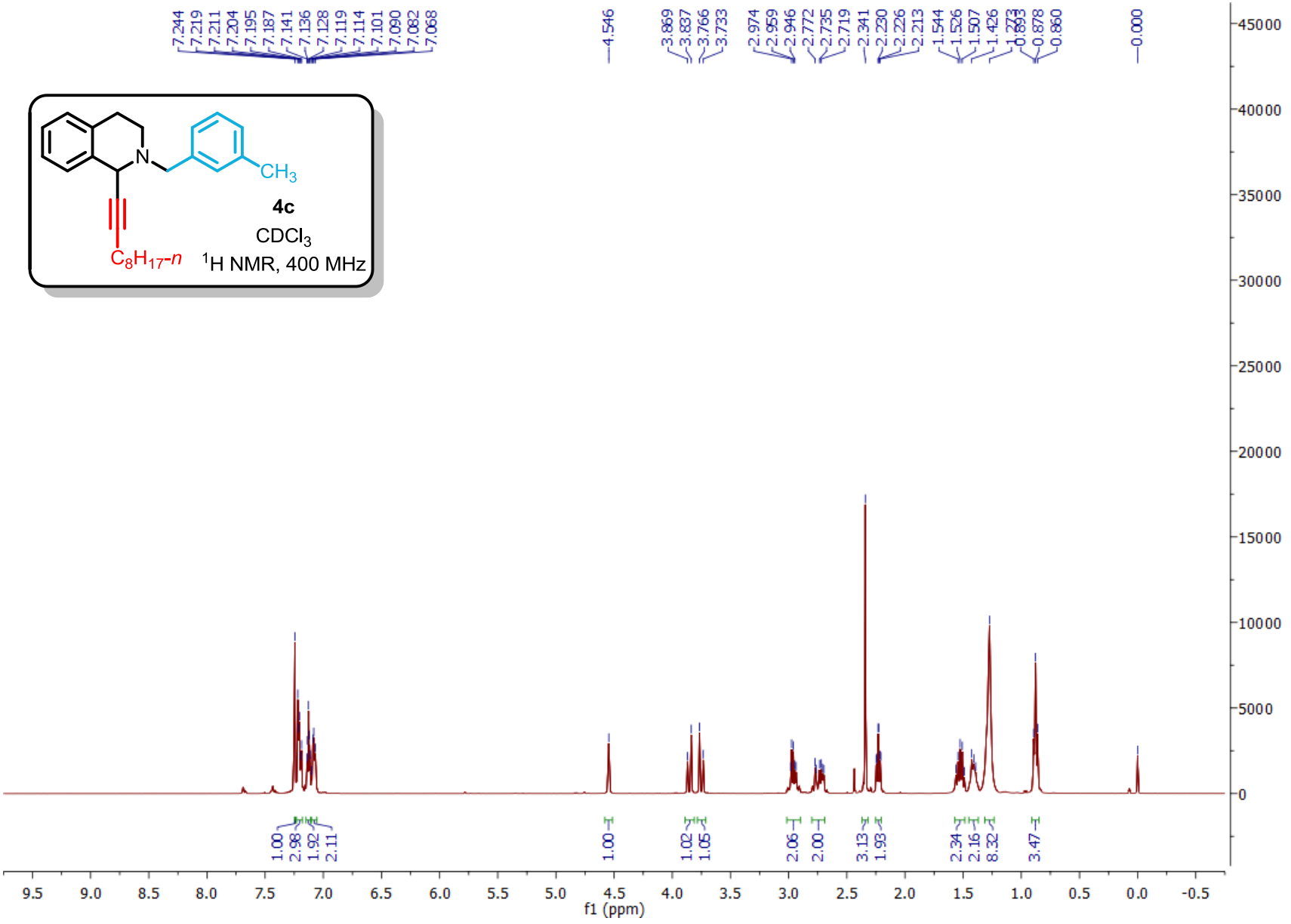
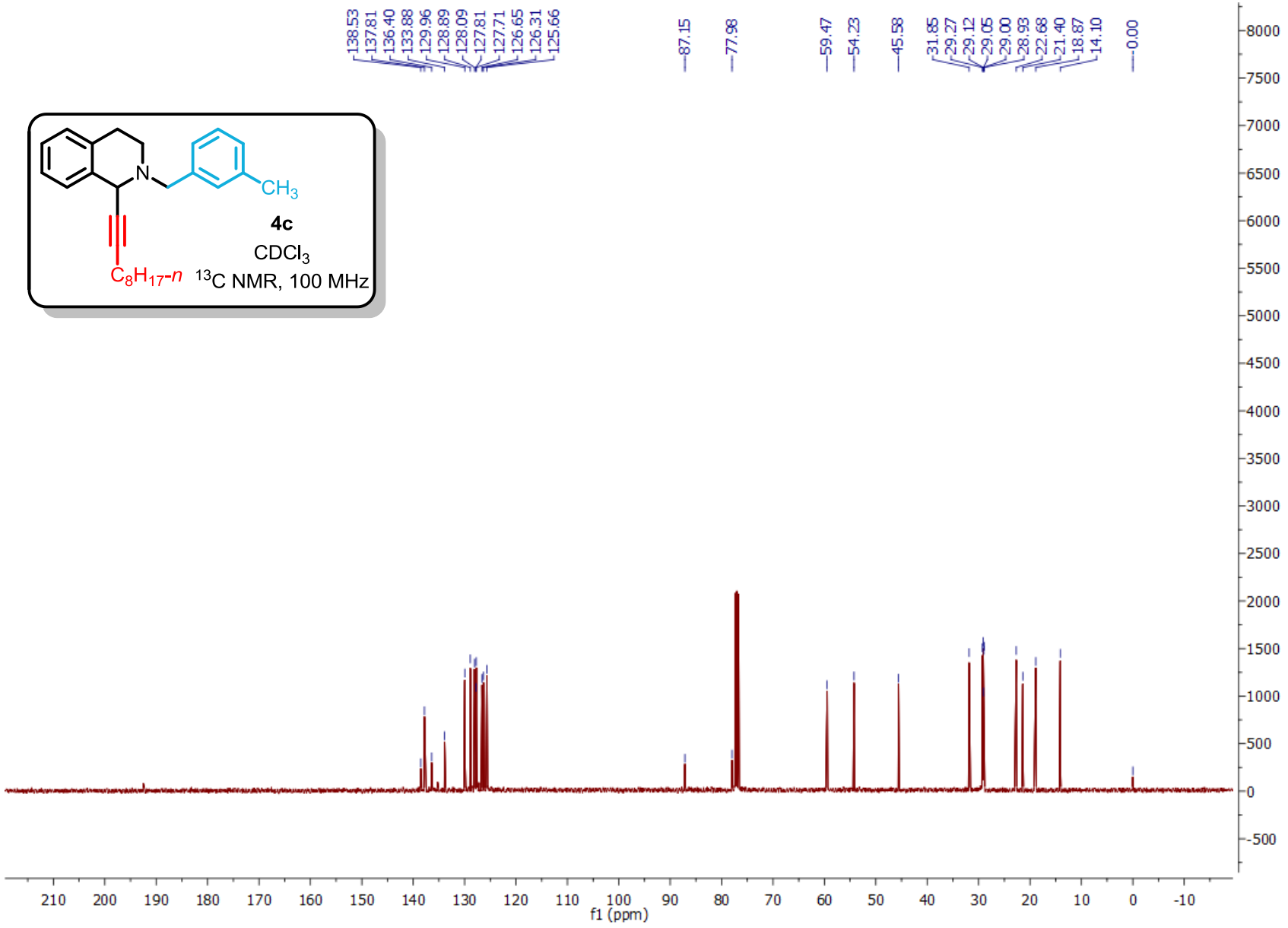
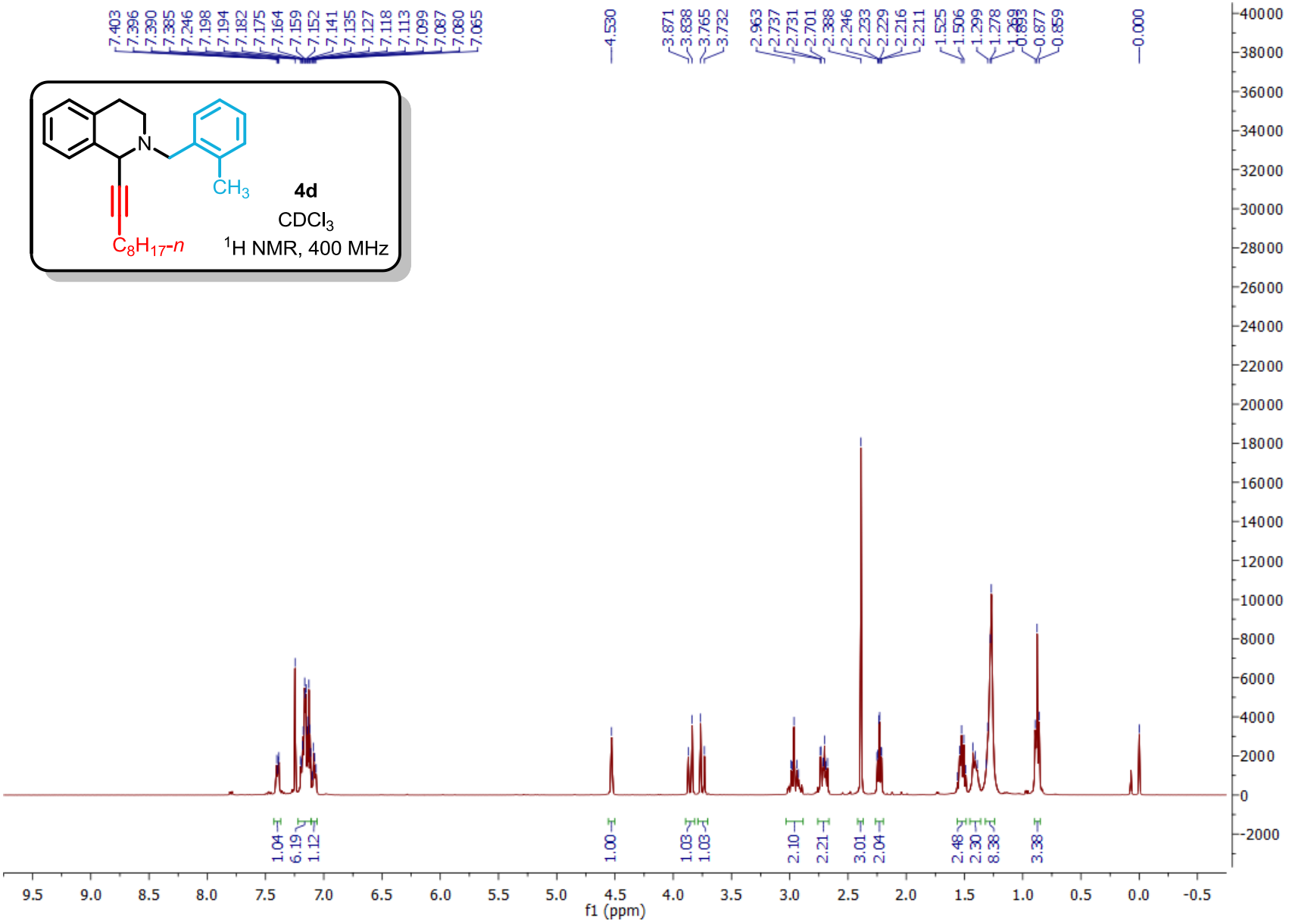
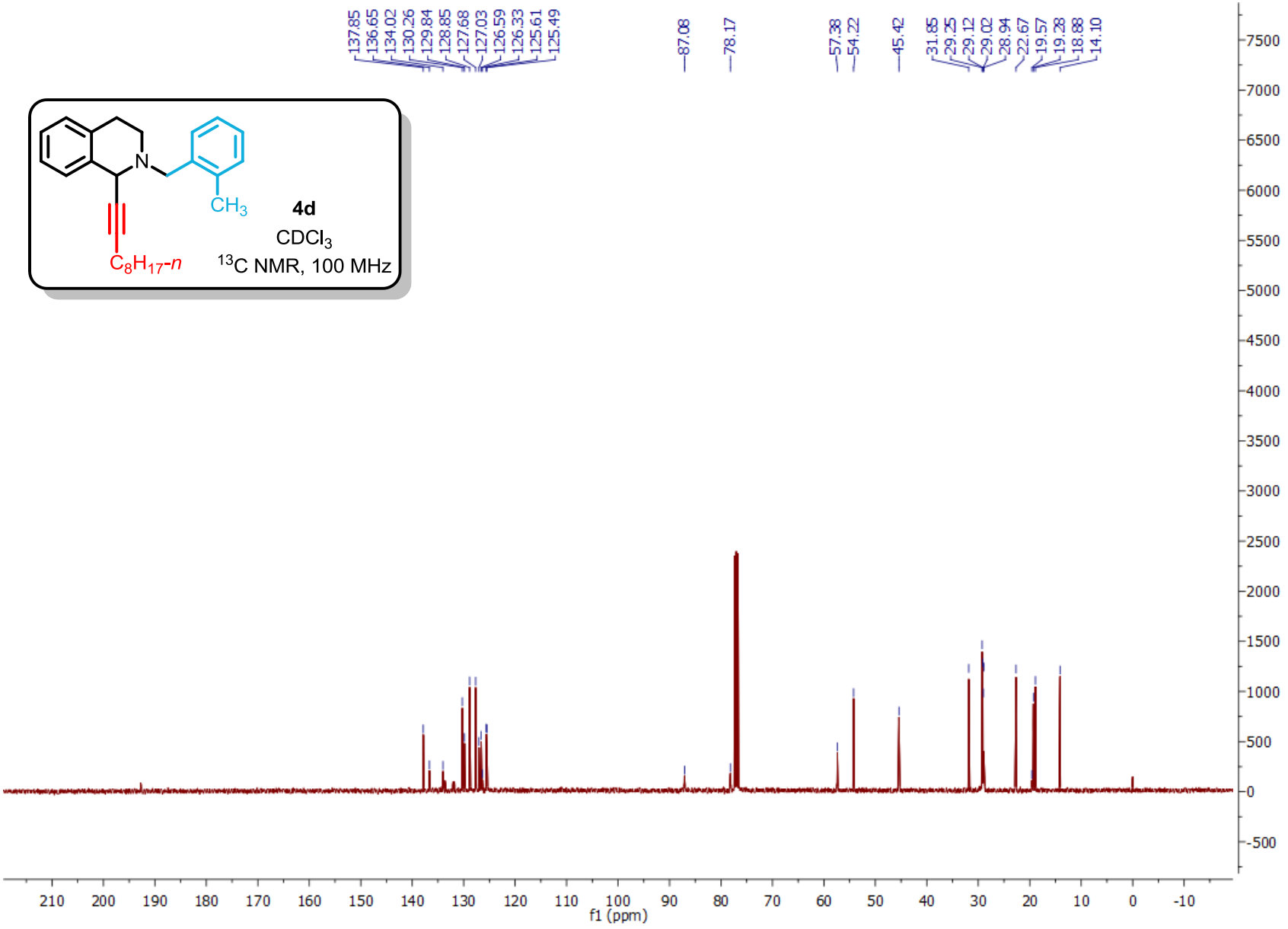
136.44
135.50
133.91
129.20
128.93
128.88
127.71
126.63
125.64
87.12
77.98
59.17
54.09
45.52
31.85
29.27
29.12
29.07
29.01
28.94
22.69
21.14
18.88
14.11
CH3
N
C8H17-n
4b
CDCl3
13C NMR, 100 MHz
f1 (ppm)


7.244
7.219
7.211
7.204
7.195
7.187
7.141
7.136
7.128
7.119
7.114
7.101
7.090
7.082
7.068
4.546
3.869
3.837
3.766
3.733
2.974
2.959
2.946
2.772
2.735
2.719
2.341
2.230
2.226
2.213
1.544
1.526
1.507
1.426
1.273
0.893
0.878
0.860
0.000
CH3
4c
CDCl3
C8H17-n
1H NMR, 400 MHz
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
2.98
1.92
2.11
1.00
1.02
1.05
2.06
2.00
3.13
1.93
2.34
2.16
8.32
3.47
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


138.53
137.81
136.40
133.88
129.96
128.89
128.09
127.81
127.71
126.65
126.31
125.66
87.15
77.98
59.47
54.23
45.58
31.85
29.27
29.12
29.05
29.00
28.93
22.68
21.40
18.87
14.10
0.00
CH3
4c
CDCl3
C8H17-n
13C NMR, 100 MHz
f1 (ppm)


7.403
7.396
7.390
7.385
7.246
7.198
7.194
7.182
7.175
7.164
7.159
7.152
7.141
7.135
7.127
7.118
7.113
7.099
7.087
7.080
7.065
4.530
3.871
3.838
3.765
3.732
2.963
2.737
2.731
2.701
2.388
2.246
2.233
2.229
2.216
2.211
1.525
1.506
1.299
1.278
0.877
0.859
0.000
N
CH3
C8H17-n
4d
CDCl3
1H NMR, 400 MHz
1.04
6.19
1.12
1.00
1.03
1.03
2.10
2.21
3.01
2.04
2.48
2.30
8.38
3.38
f1 (ppm)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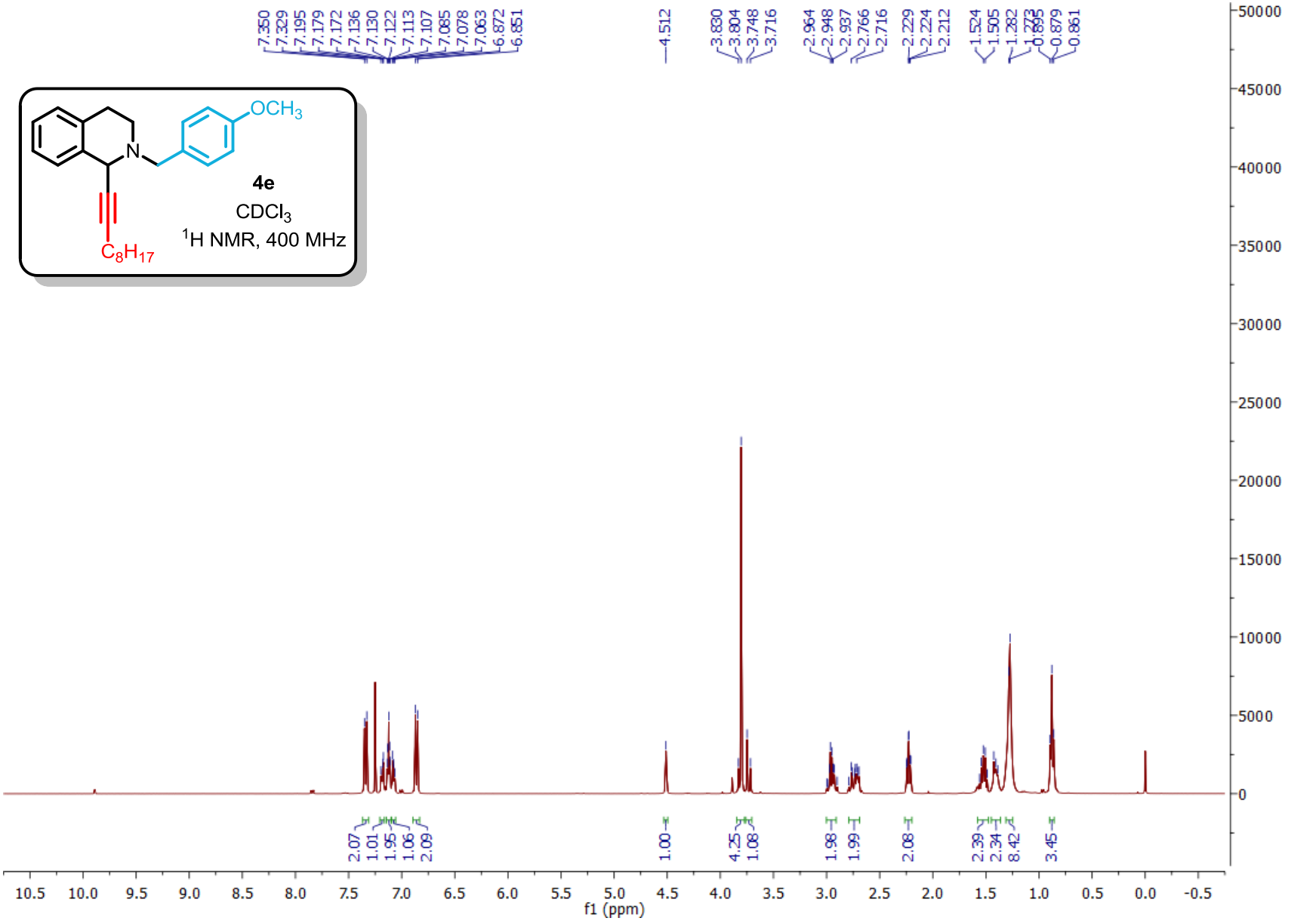
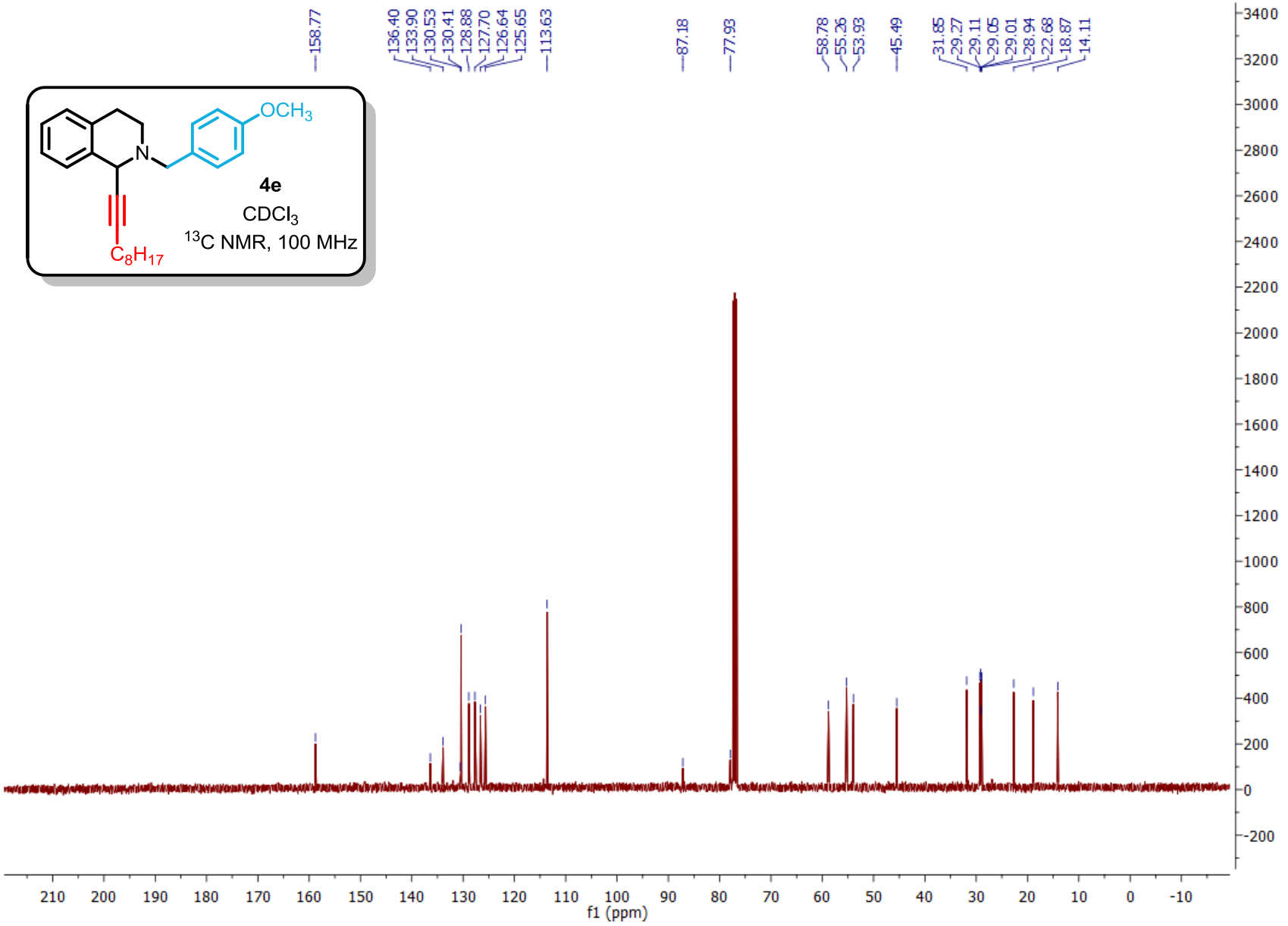
136.65
134.02
130.26
129.84
128.85
127.68
127.03
126.59
126.33
125.61
125.49
87.08
78.17
57.38
54.22
45.42
31.85
29.25
29.12
29.02
28.94
22.67
19.57
19.28
18.88
14.10
CH3
C8H17-n
4d
CDCl3
13C NMR, 100 MHz
f1 (ppm)


4e
CDCl3
1H NMR, 400 MHz
OCH3
C8H17
f1 (ppm)


158.77
136.40
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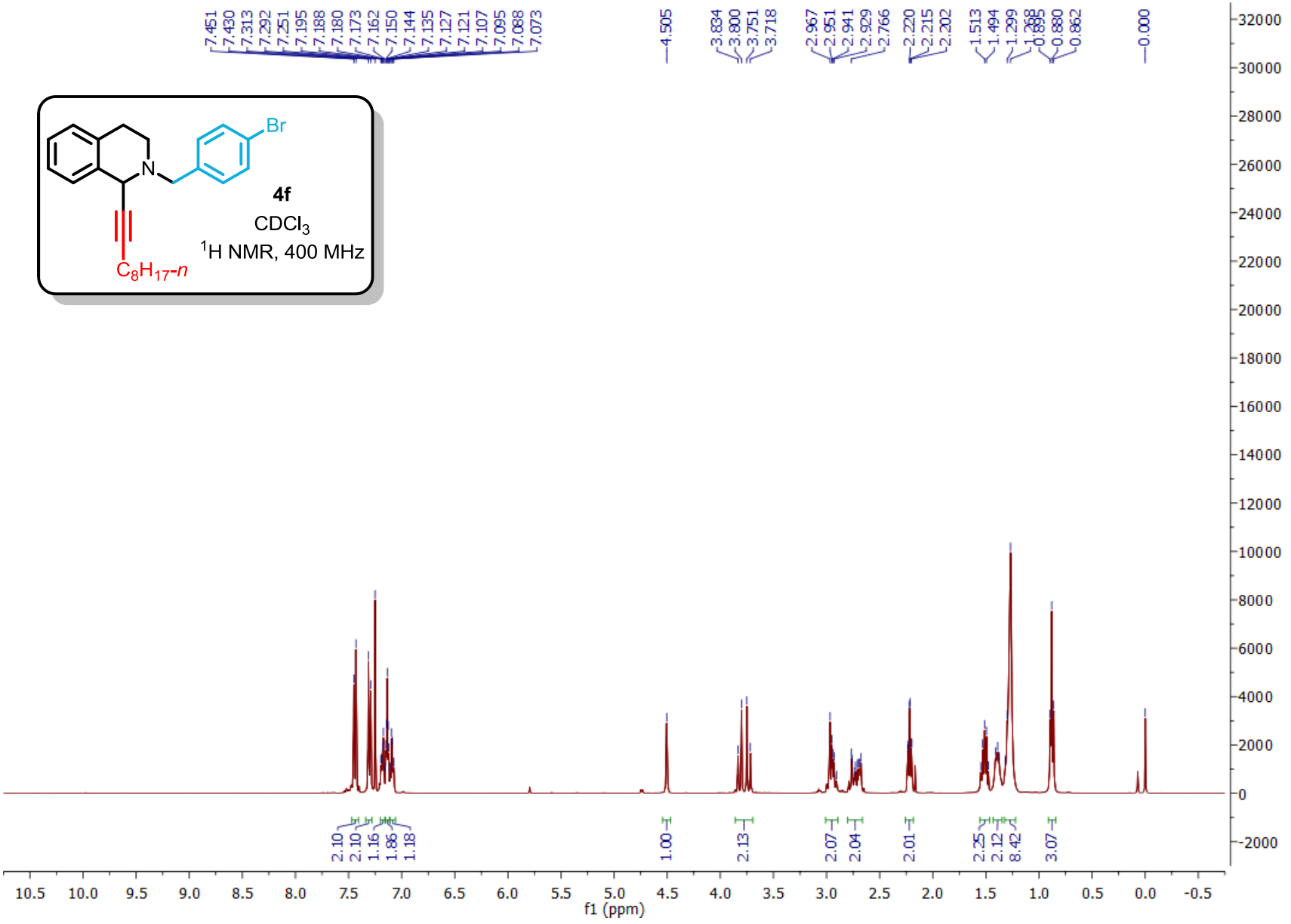
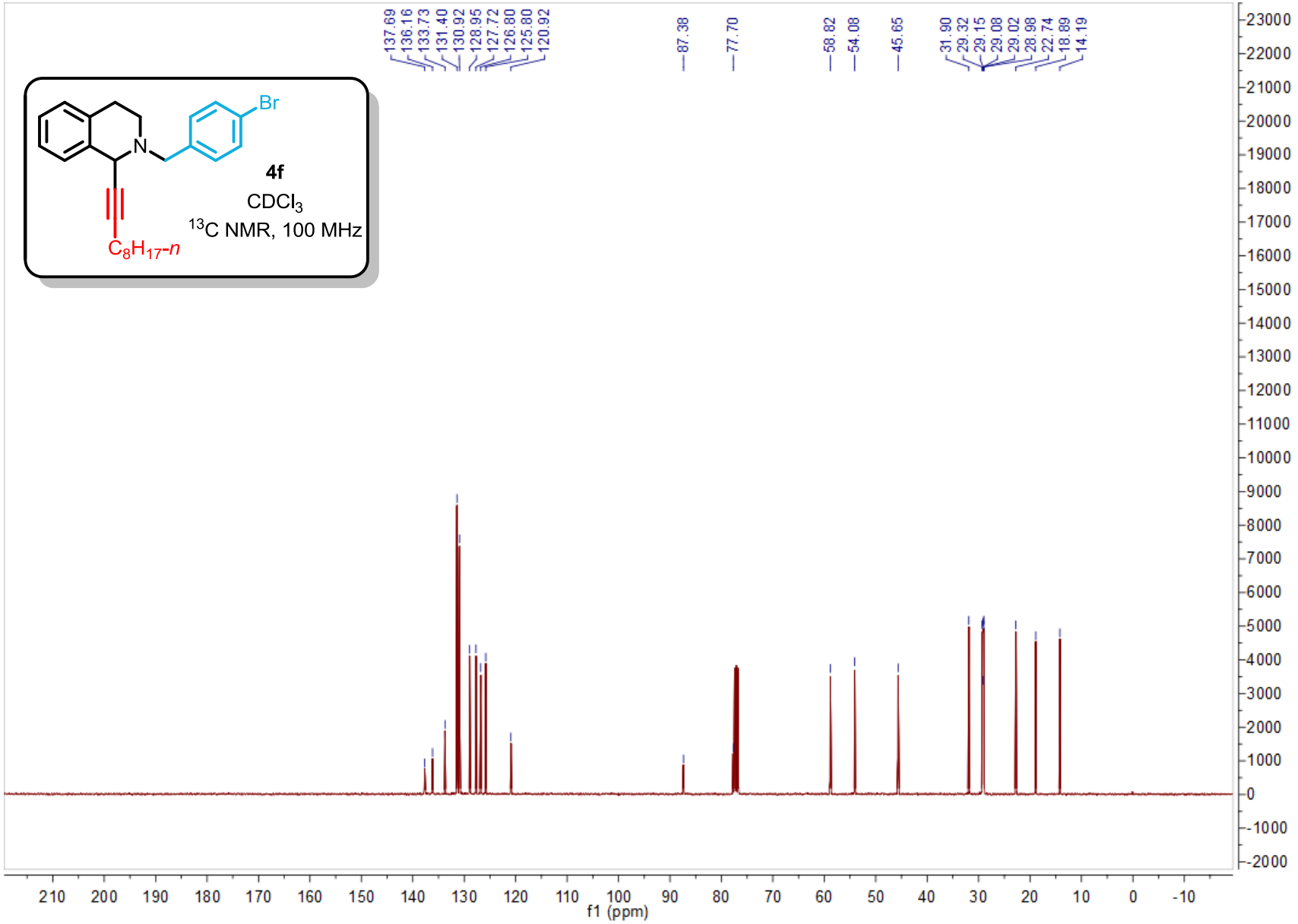
130.41
128.88
127.70
126.64
125.65
113.63
87.18
77.93
58.78
55.26
53.93
45.49
31.85
29.27
29.11
29.05
29.01
28.94
22.68
18.87
14.11
OCH3
N
C8H17
4e
CDCl3
13C NMR, 100 MHz
f1 (ppm)


Br
N
C_8H_{17}-*n*
4f
$CDCl_3$
^{1}H NMR, 400 MHz
f1 (ppm)


137.69
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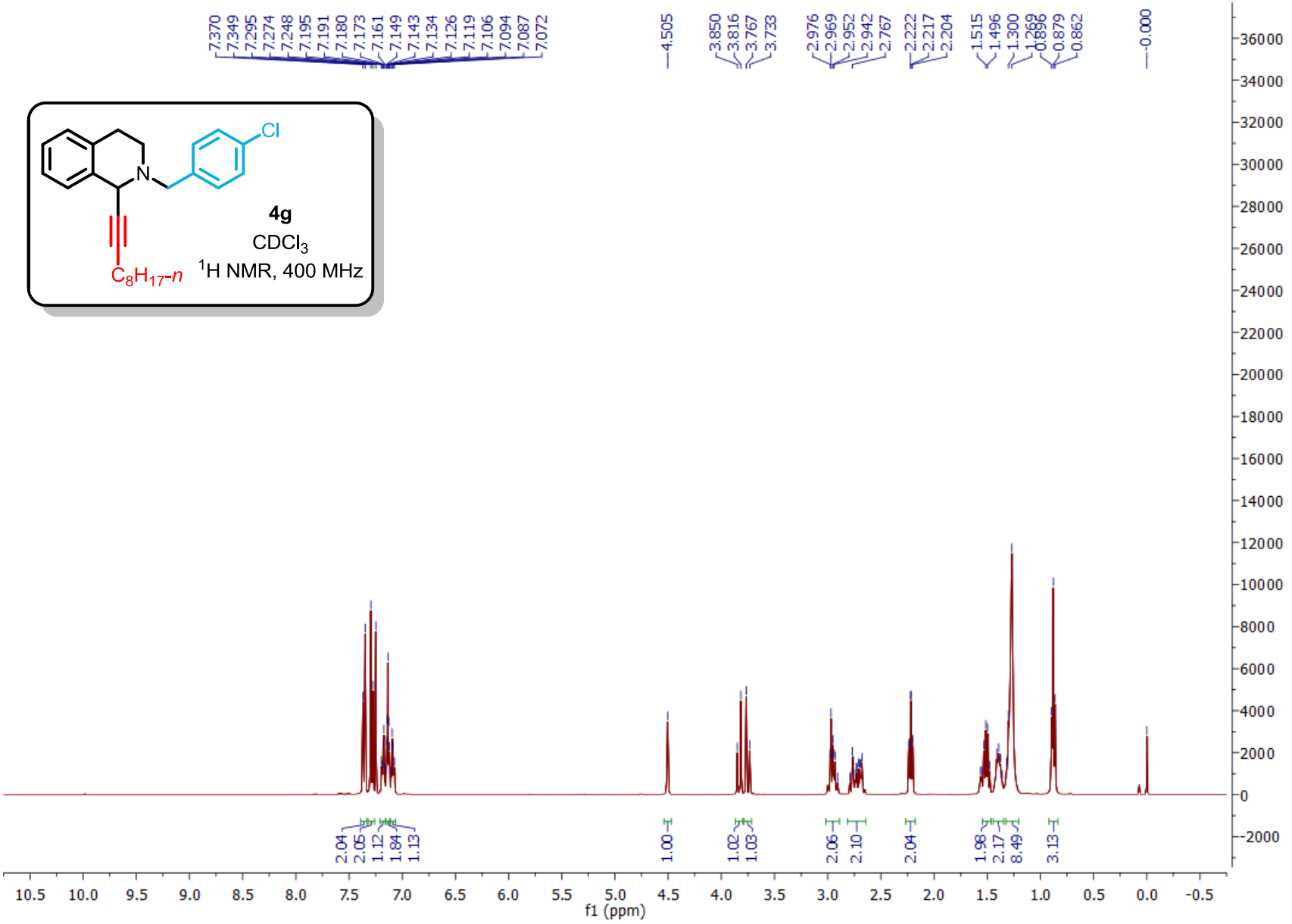
133.73
131.40
130.92
128.95
127.72
126.80
125.80
120.92
87.38
77.70
58.82
54.08
45.65
31.90
29.32
29.15
29.08
29.02
28.98
22.74
18.89
14.19
Br
N
4f
CDCl3
13C NMR, 100 MHz
C8H17-n
f1 (ppm)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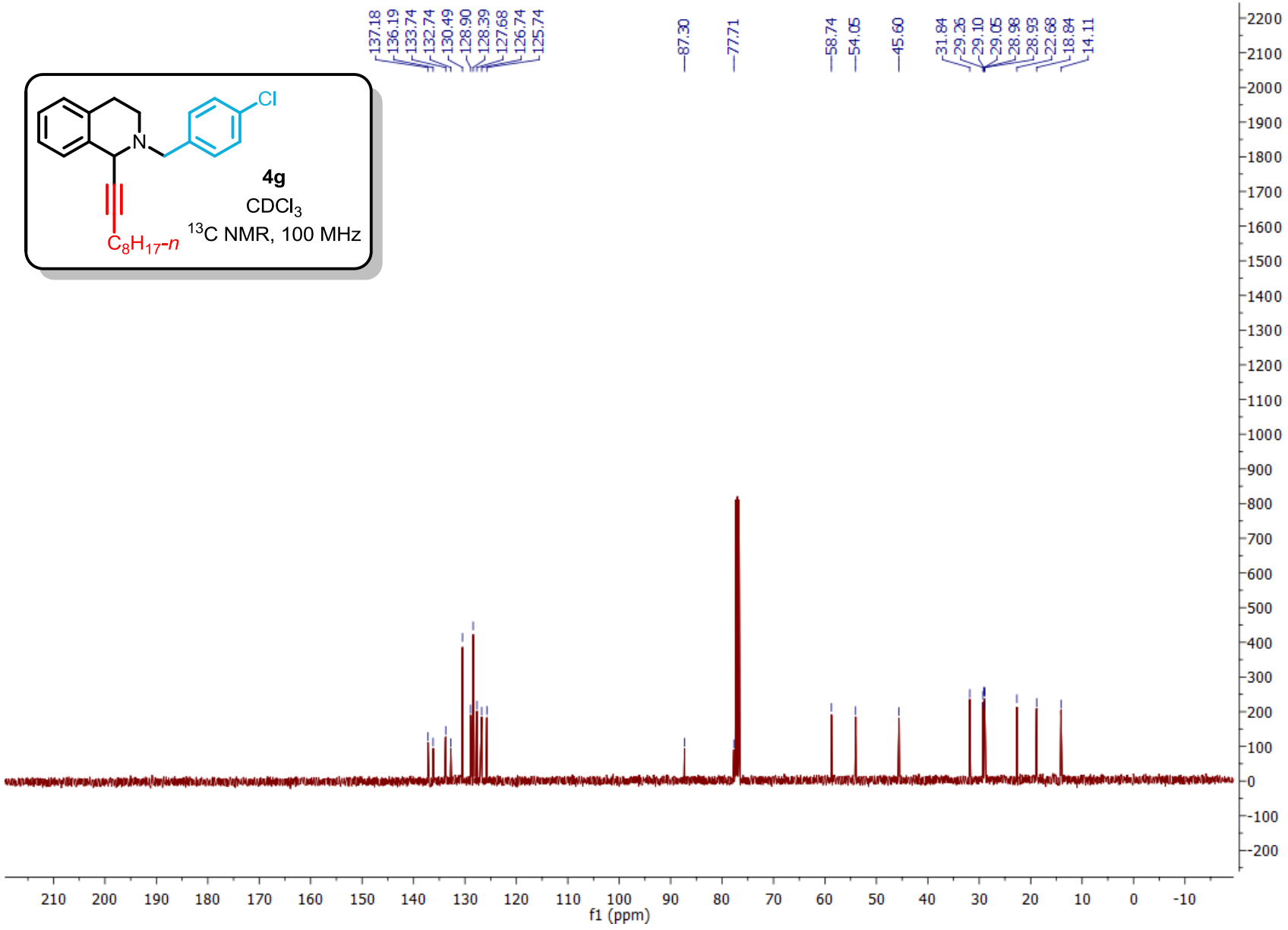
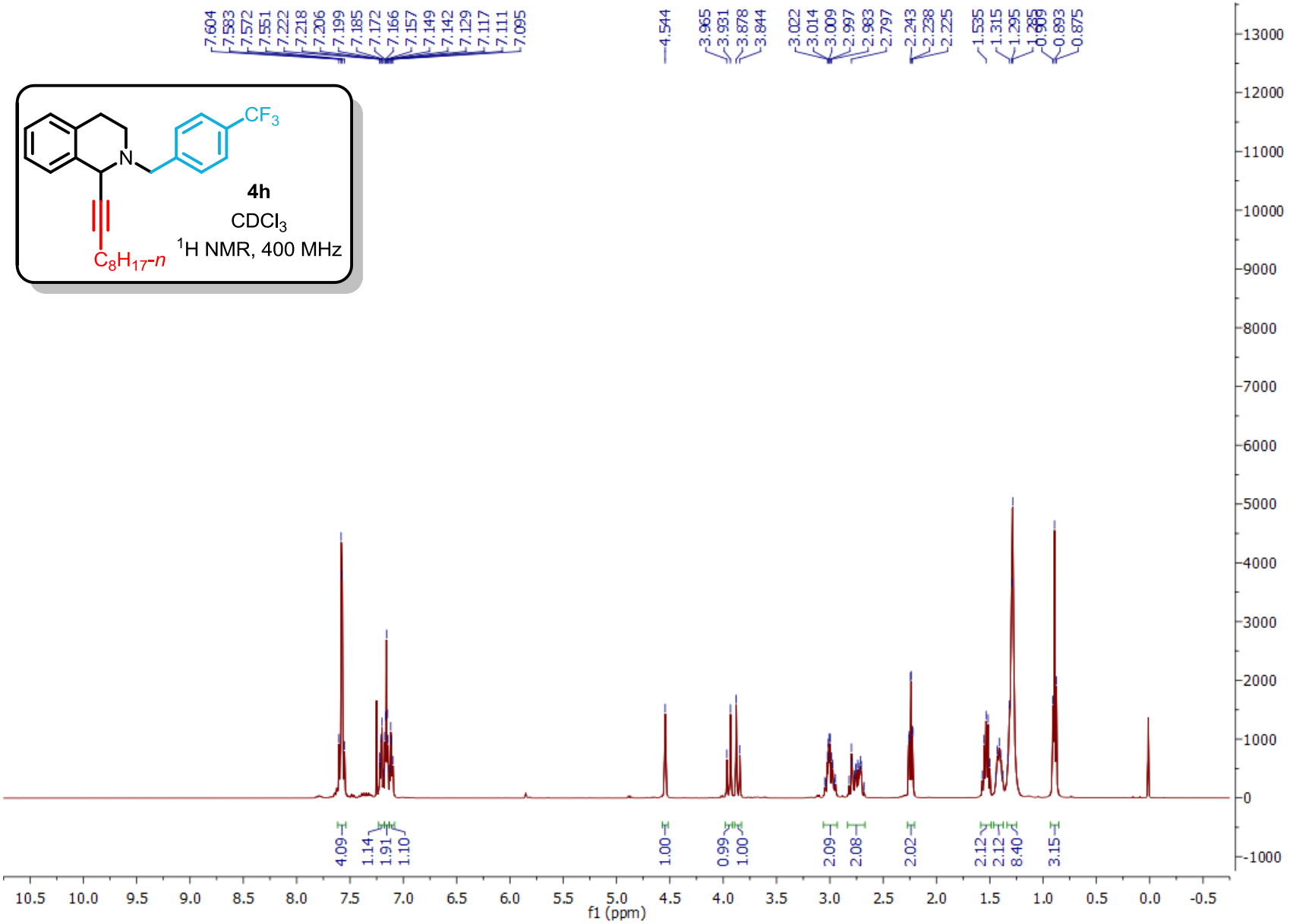
7.295
7.274
7.248
7.195
7.191
7.180
7.173
7.161
7.149
7.143
7.134
7.126
7.119
7.106
7.094
7.087
7.072
4.505
3.850
3.816
3.767
3.733
2.976
2.969
2.952
2.942
2.767
2.222
2.217
2.204
1.515
1.496
1.300
1.269
0.896
0.879
0.862
-0.000
Cl
N
C8H17-n
4g
CDCl3
1H NMR, 400 MHz
2.04
2.05
1.12
1.84
1.13
1.00
1.02
1.03
2.06
2.10
2.04
1.98
2.17
8.49
3.13
f1 (ppm)


137.18
136.19
133.74
132.74
130.49
128.90
128.39
127.68
126.74
125.74
87.30
77.71
58.74
54.05
45.60
31.84
29.26
29.10
29.05
28.98
28.93
22.68
18.84
14.11
Cl
N
C8H17-n
4g
CDCl3
13C NMR, 100 MHz
f1 (ppm)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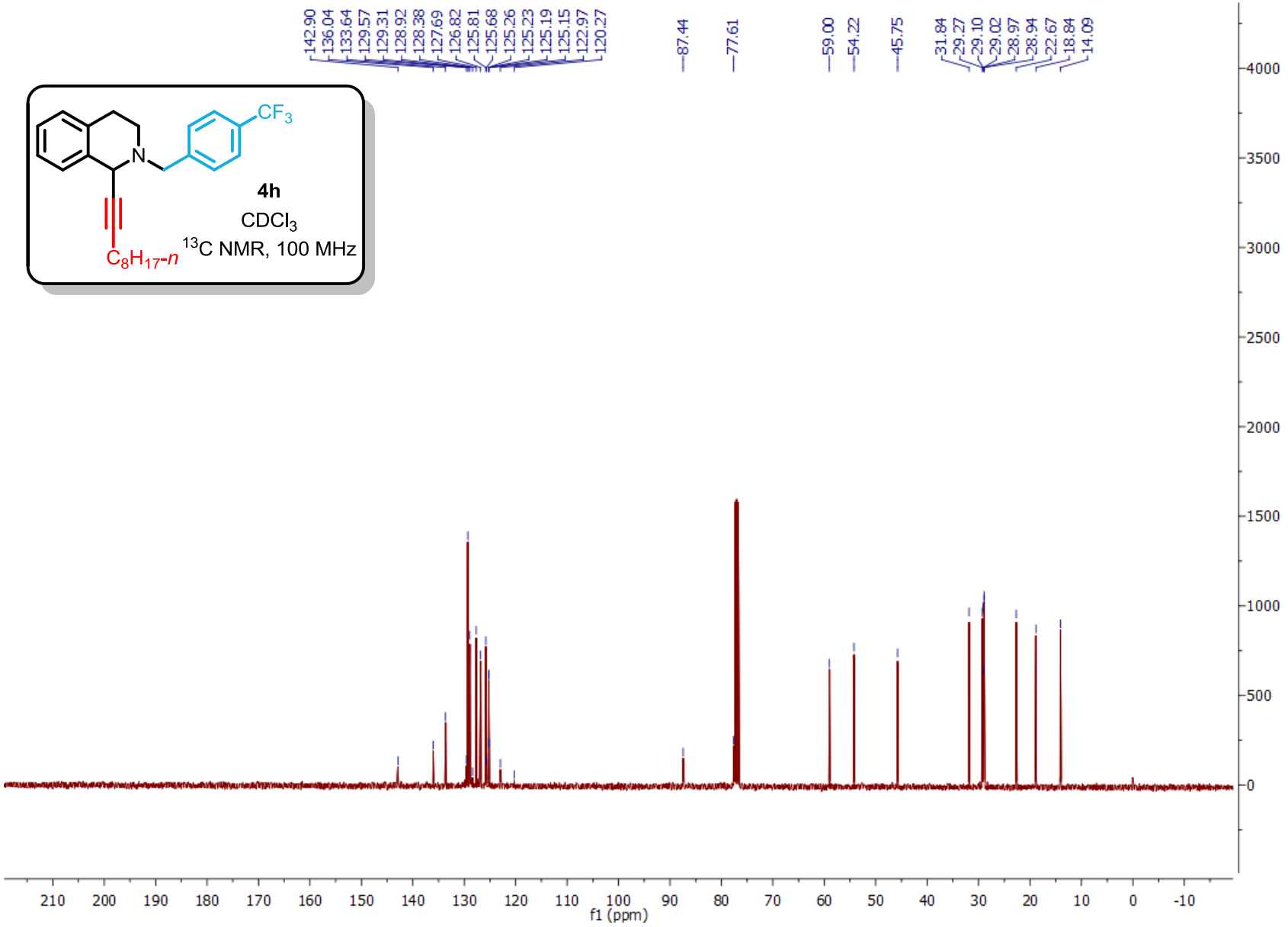
7.583
7.572
7.551
7.222
7.218
7.206
7.199
7.185
7.172
7.166
7.157
7.149
7.142
7.129
7.117
7.111
7.095
4.544
3.965
3.931
3.878
3.844
3.022
3.014
3.009
2.997
2.983
2.797
2.243
2.238
2.225
1.535
1.315
1.295
0.909
0.893
0.875
CF3
N
C8H17-n
4h
CDCl3
1H NMR, 400 MHz
4.09
1.14
1.91
1.10
1.00
0.99
1.00
2.09
2.08
2.02
2.12
2.12
8.40
3.15
f1 (ppm)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129.57
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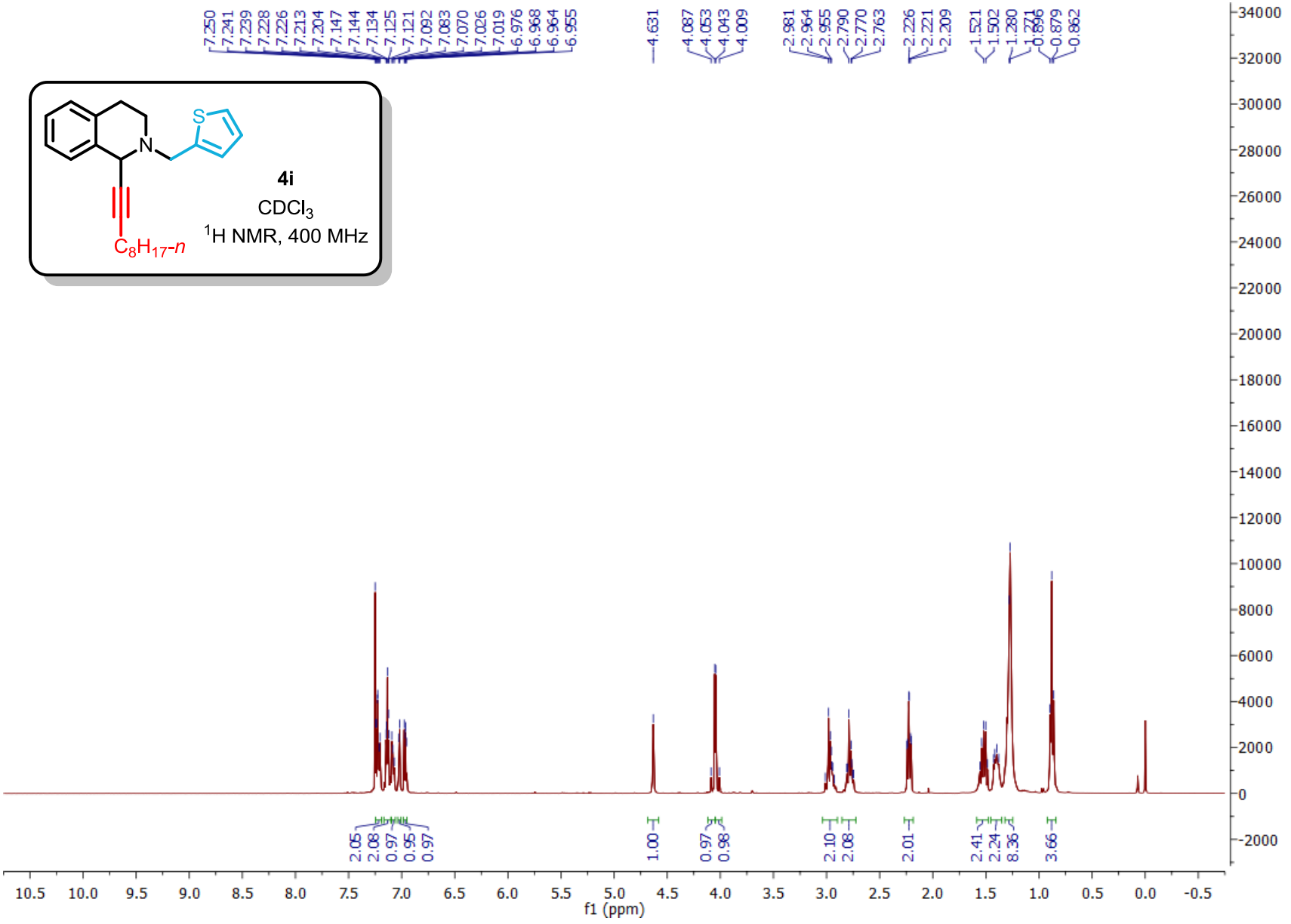
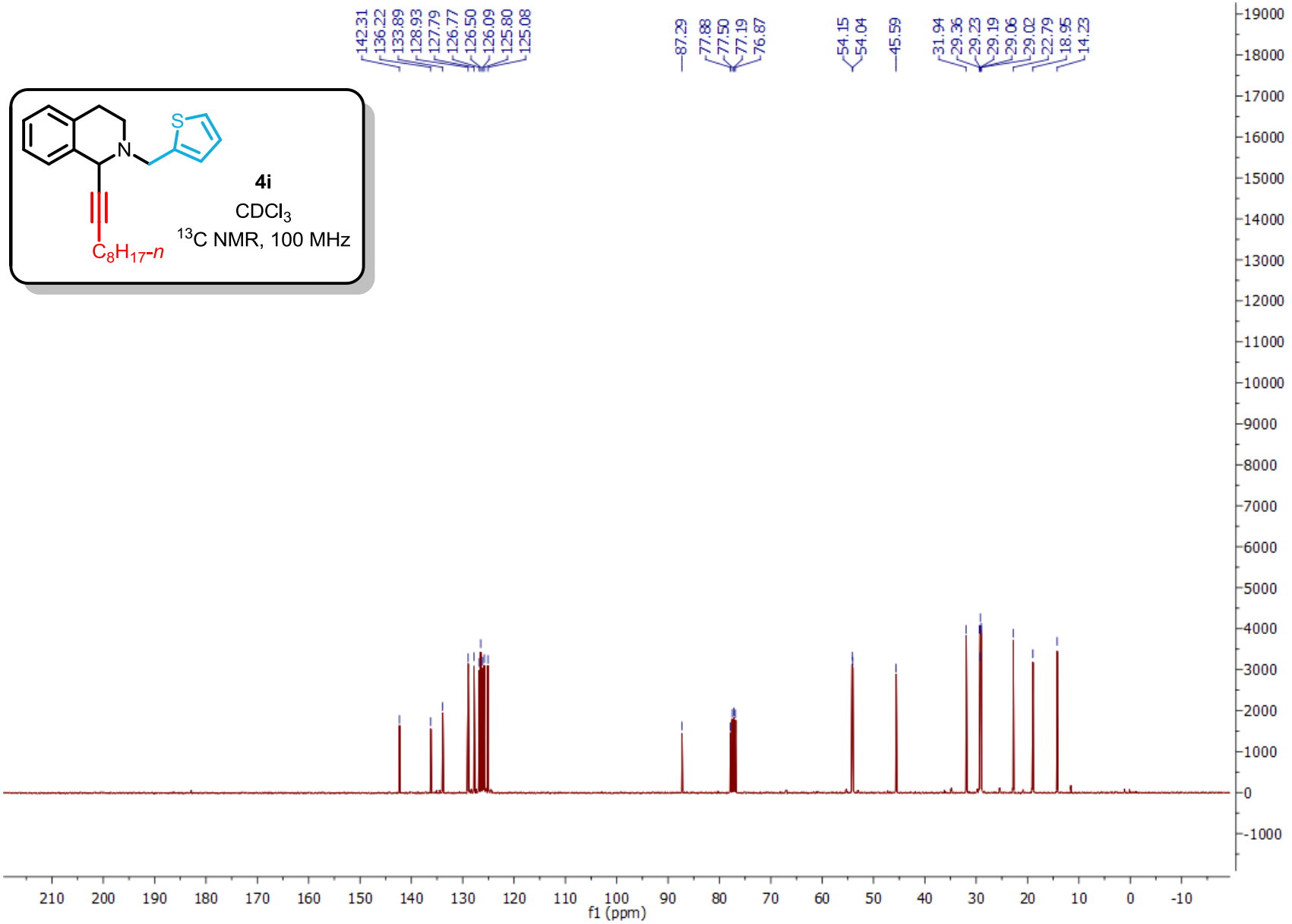
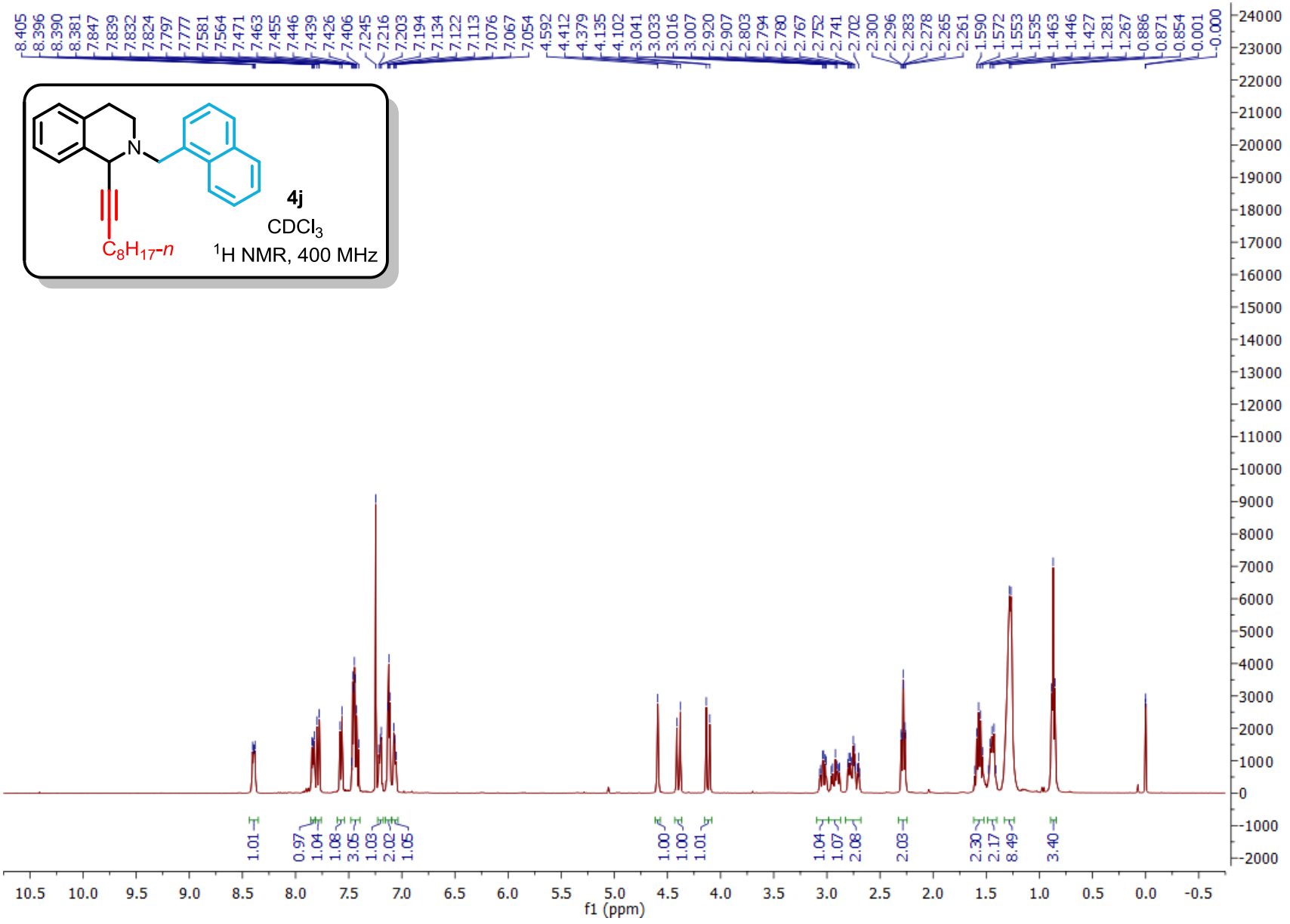
128.92
128.38
127.69
126.82
125.81
125.68
125.26
125.23
125.19
125.15
122.97
120.27
87.44
77.61
59.00
54.22
45.75
31.84
29.27
29.10
29.02
28.97
28.94
22.67
18.84
14.09
CF3
N
4h
CDCl3
C8H17-n
13C NMR, 100 MHz
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4i
CDCl3
1H NMR, 400 MHz
C8H17-n
f1 (ppm)


142.31
136.22
133.89
128.93
127.79
126.77
126.50
126.09
125.80
125.08
87.29
77.88
77.50
77.19
76.87
54.15
54.04
45.59
31.94
29.36
29.23
29.19
29.06
29.02
22.79
18.95
14.23
S
N
C8H17-n
4i
CDCl3
13C NMR, 100 MHz
f1 (ppm)


8.405
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8.390
8.381
7.847
7.839
7.832
7.824
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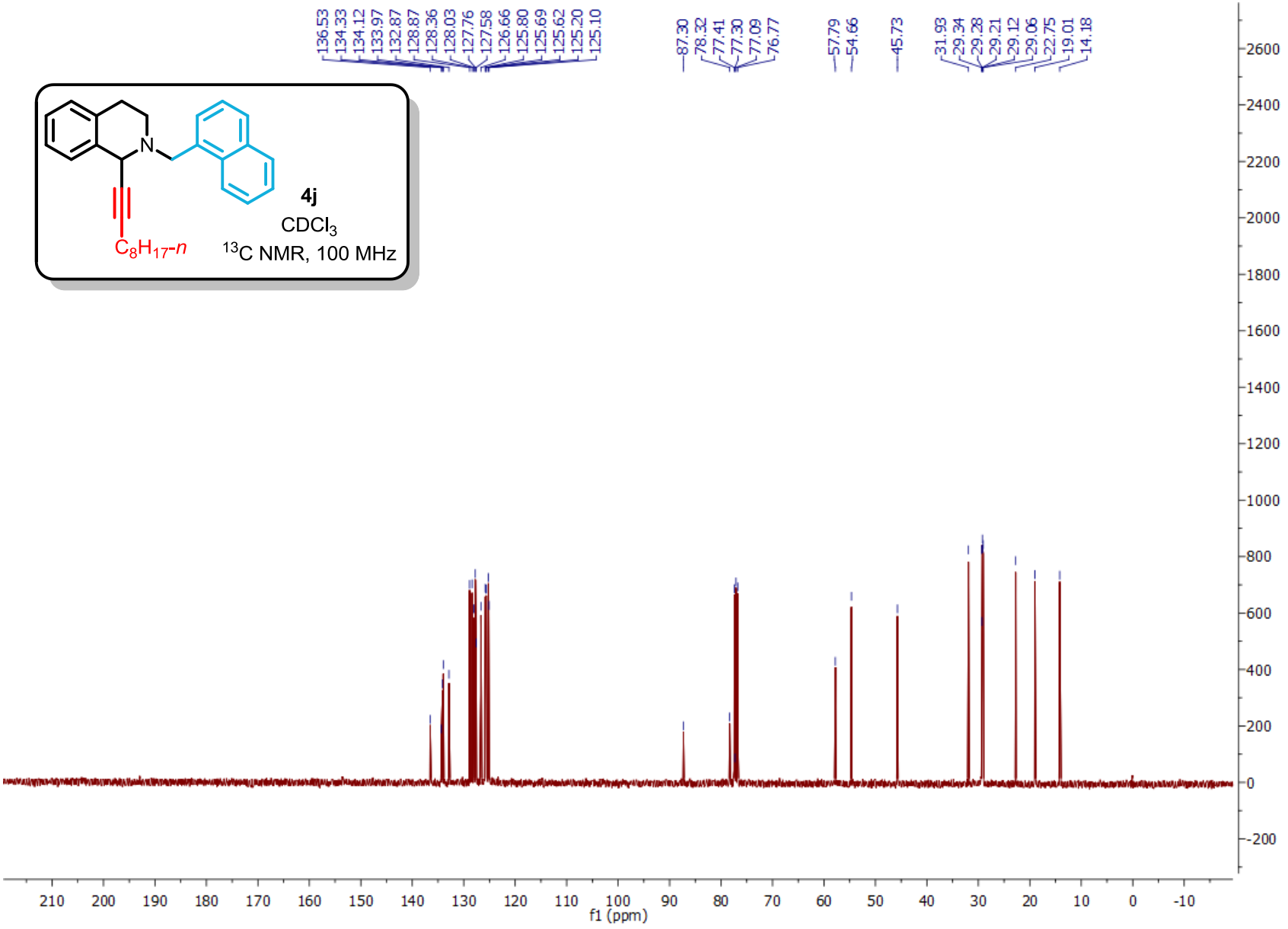
7.777
7.581
7.564
7.471
7.463
7.455
7.446
7.439
7.426
7.406
7.245
7.216
7.203
7.194
7.134
7.122
7.113
7.076
7.067
7.054
4.592
4.412
4.379
4.135
4.102
3.041
3.033
3.016
3.007
2.920
2.907
2.803
2.794
2.780
2.767
2.752
2.741
2.702
2.300
2.296
2.283
2.278
2.265
2.261
1.590
1.572
1.553
1.535
1.463
1.446
1.427
1.281
1.267
0.886
0.871
0.854
0.001
-0.000
N
C8H17-n
4j
CDCl3
1H NMR, 400 MHz
1.01
0.97
1.04
1.08
3.05
1.03
2.02
1.05
1.00
1.00
1.01
1.04
1.07
2.08
2.03
2.30
2.17
8.49
3.40
f1 (ppm)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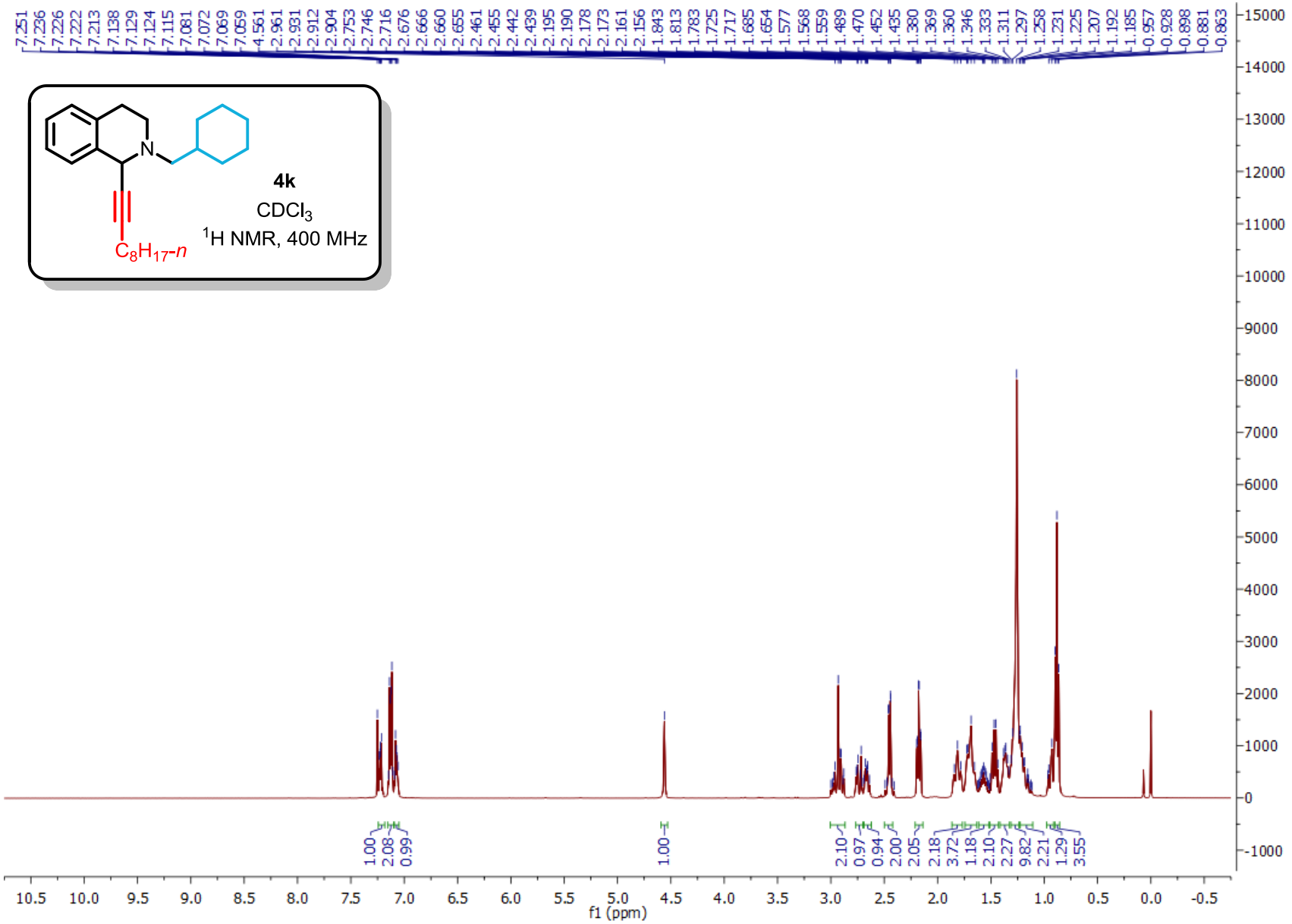
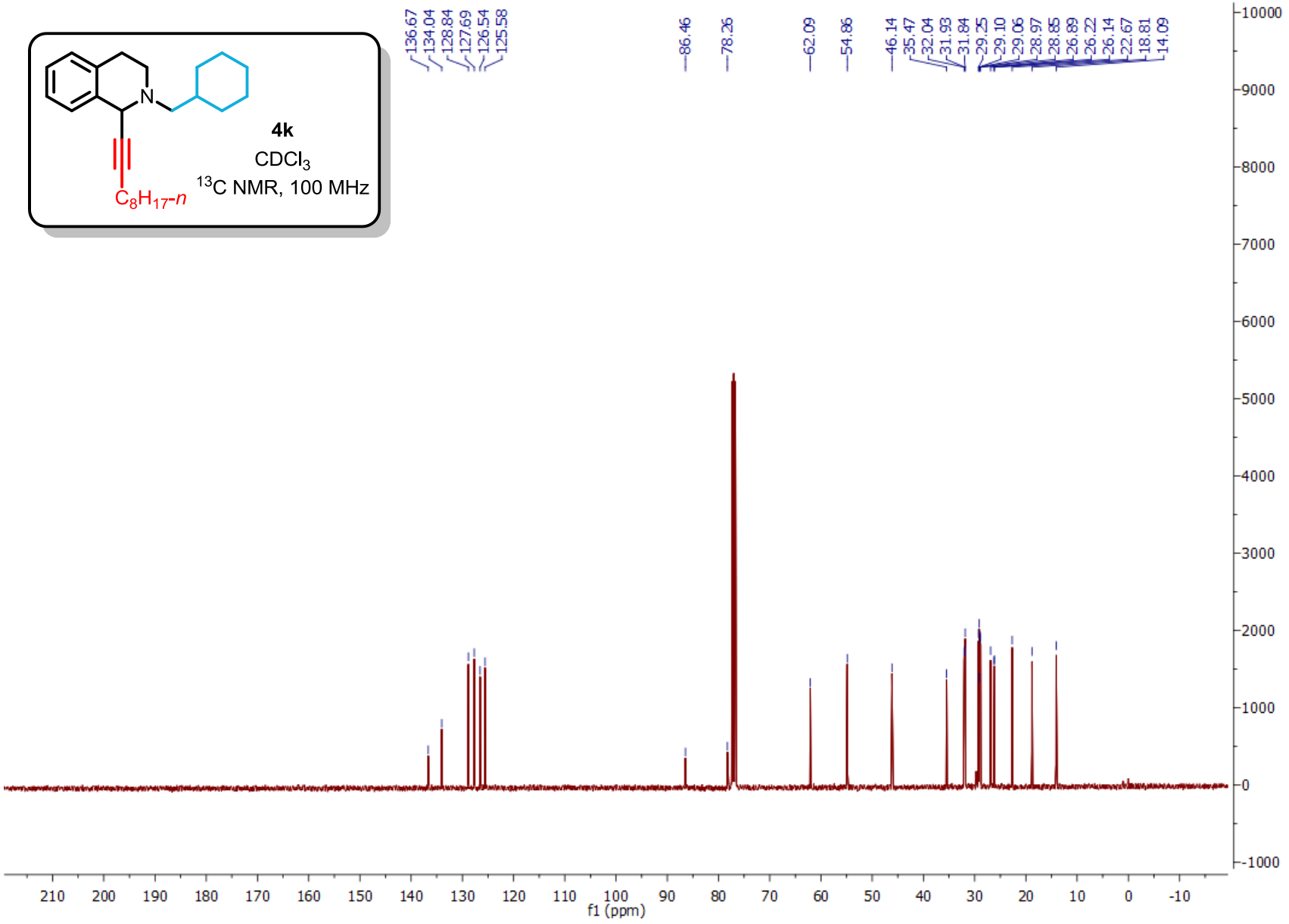
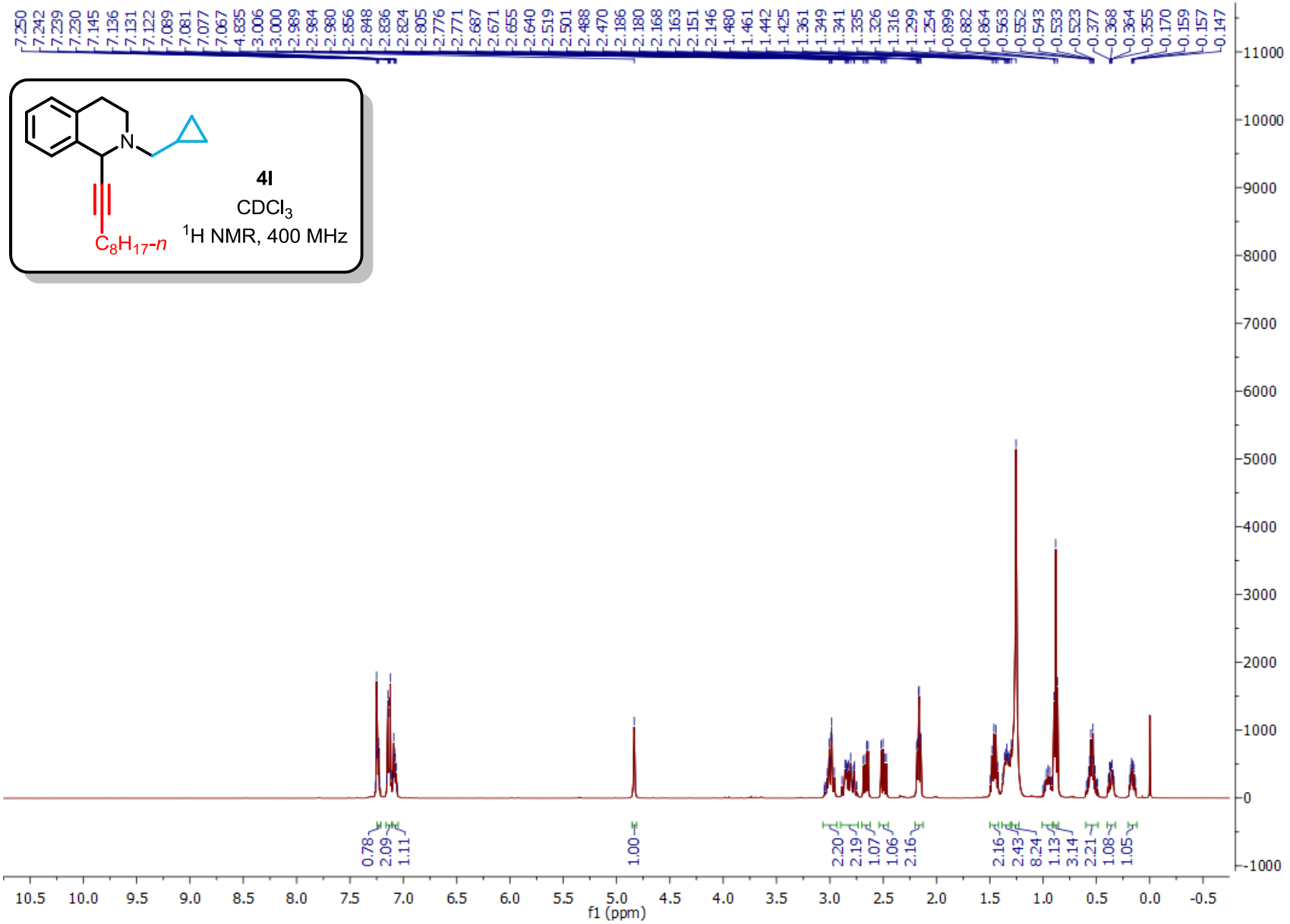
134.12
133.97
132.87
128.87
128.36
128.03
127.76
127.58
126.66
125.80
125.69
125.62
125.20
125.10
87.30
78.32
77.41
77.30
77.09
76.77
57.79
54.66
45.73
31.93
29.34
29.28
29.21
29.12
29.06
22.75
19.01
14.18
N
C8H17-n
4j
CDCl3
13C NMR, 100 MHz
f1 (ppm)


7.251 7.236 7.226 7.222 7.213 7.138 7.129 7.124 7.115 7.081 7.072 7.069 7.059 4.561 2.961 2.931 2.912 2.904 2.753 2.746 2.716 2.676 2.666 2.660 2.655 2.461 2.455 2.442 2.439 2.195 2.190 2.178 2.173 2.161 2.156 1.843 1.813 1.783 1.725 1.717 1.685 1.654 1.577 1.568 1.559 1.489 1.470 1.452 1.435 1.380 1.369 1.360 1.346 1.333 1.311 1.297 1.258 1.231 1.225 1.207 1.192 1.185 0.957 0.928 0.898 0.881 0.863
N
C8H17-n
4k
CDCl3
1H NMR, 400 MHz
1.00 2.08 0.99 1.00 2.10 0.97 0.94 2.00 2.05 2.18 3.72 1.18 2.10 2.27 9.82 2.21 1.29 3.55
f1 (ppm)


4k
CDCl3
13C NMR, 100 MHz
C8H17-n
136.67
134.04
128.84
127.69
126.54
125.58
86.46
78.26
62.09
54.86
46.14
35.47
32.04
31.93
31.84
29.25
29.10
29.06
28.97
28.85
26.89
26.22
26.14
22.67
18.81
14.09
f1 (ppm)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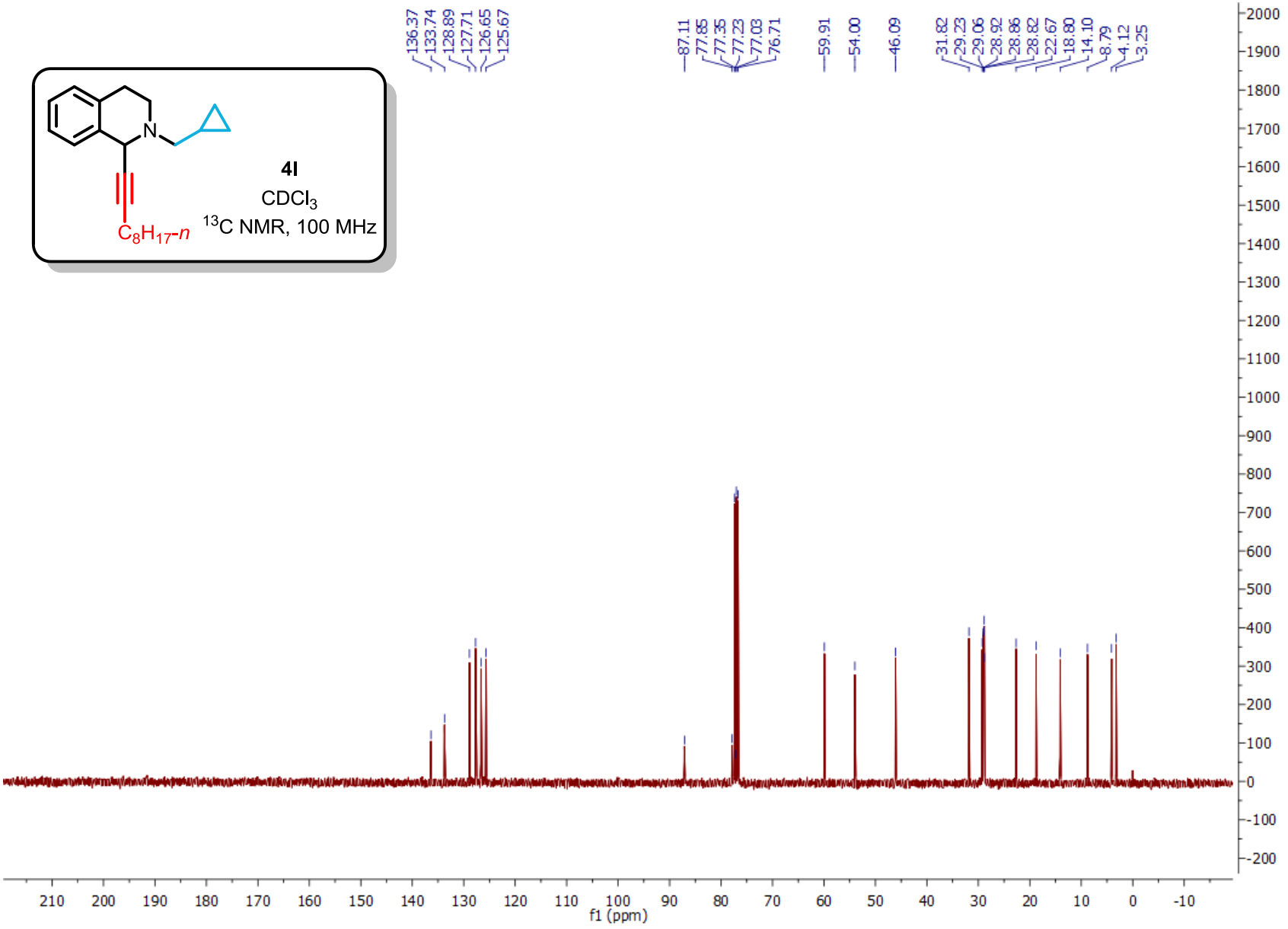
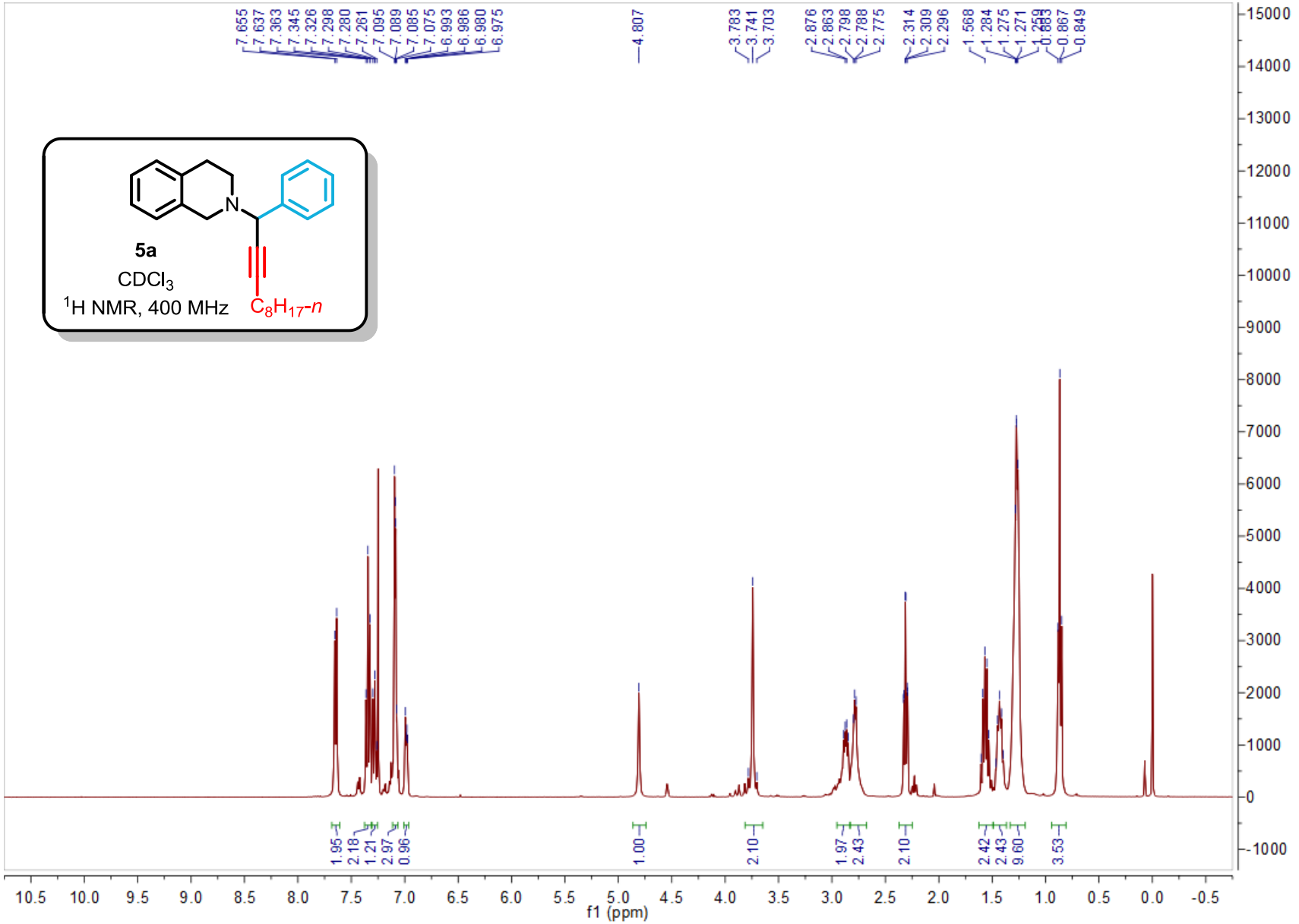
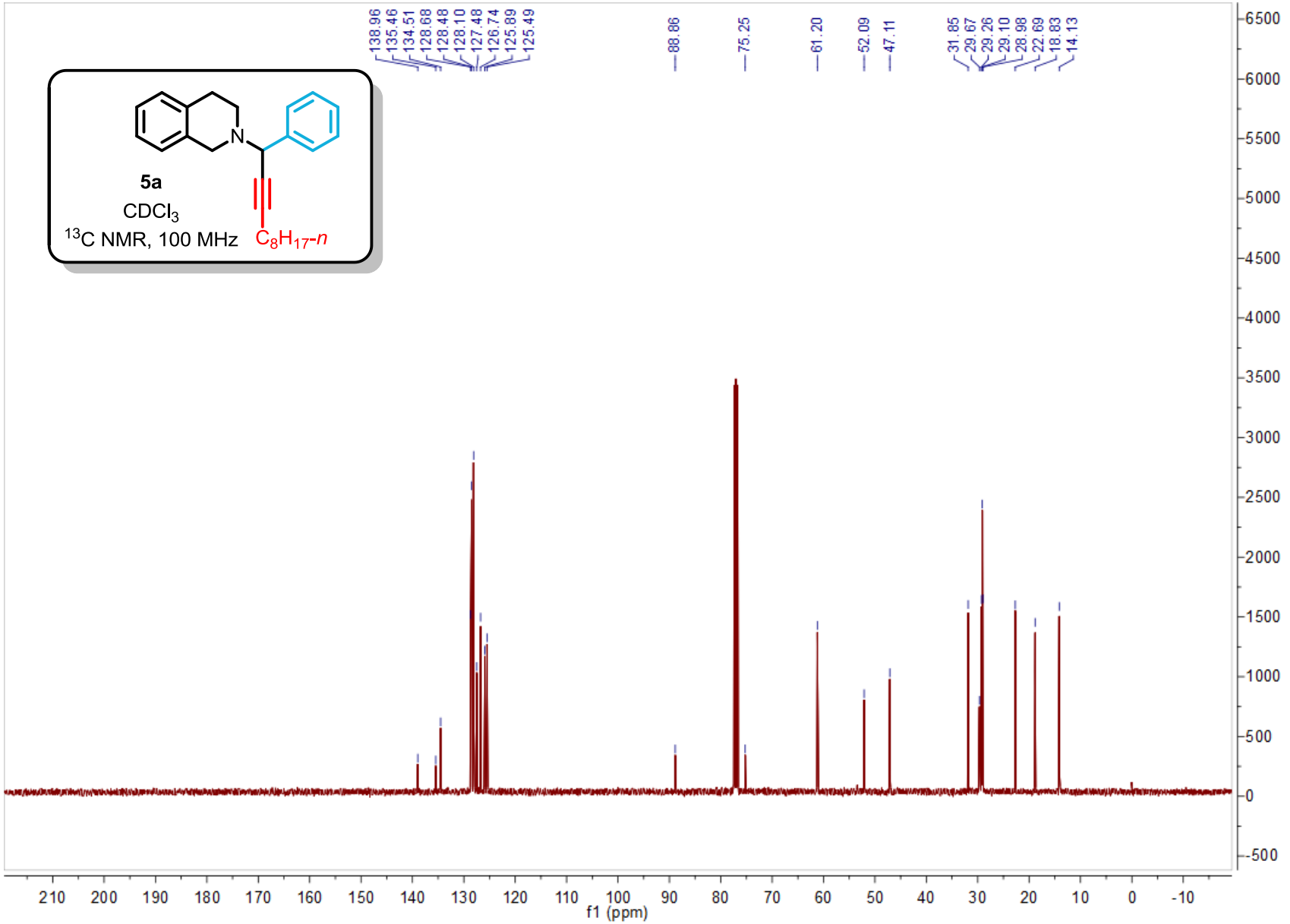
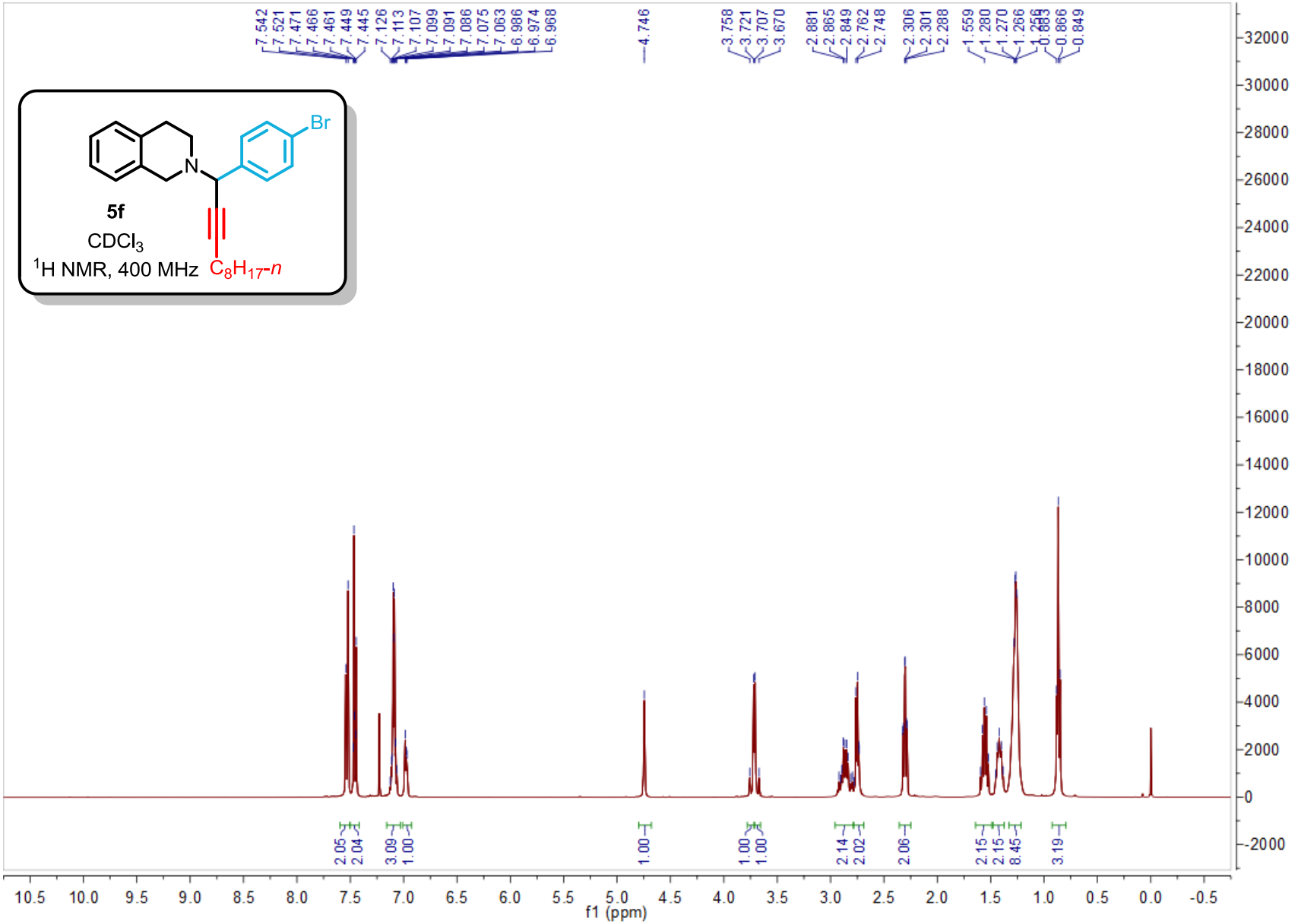
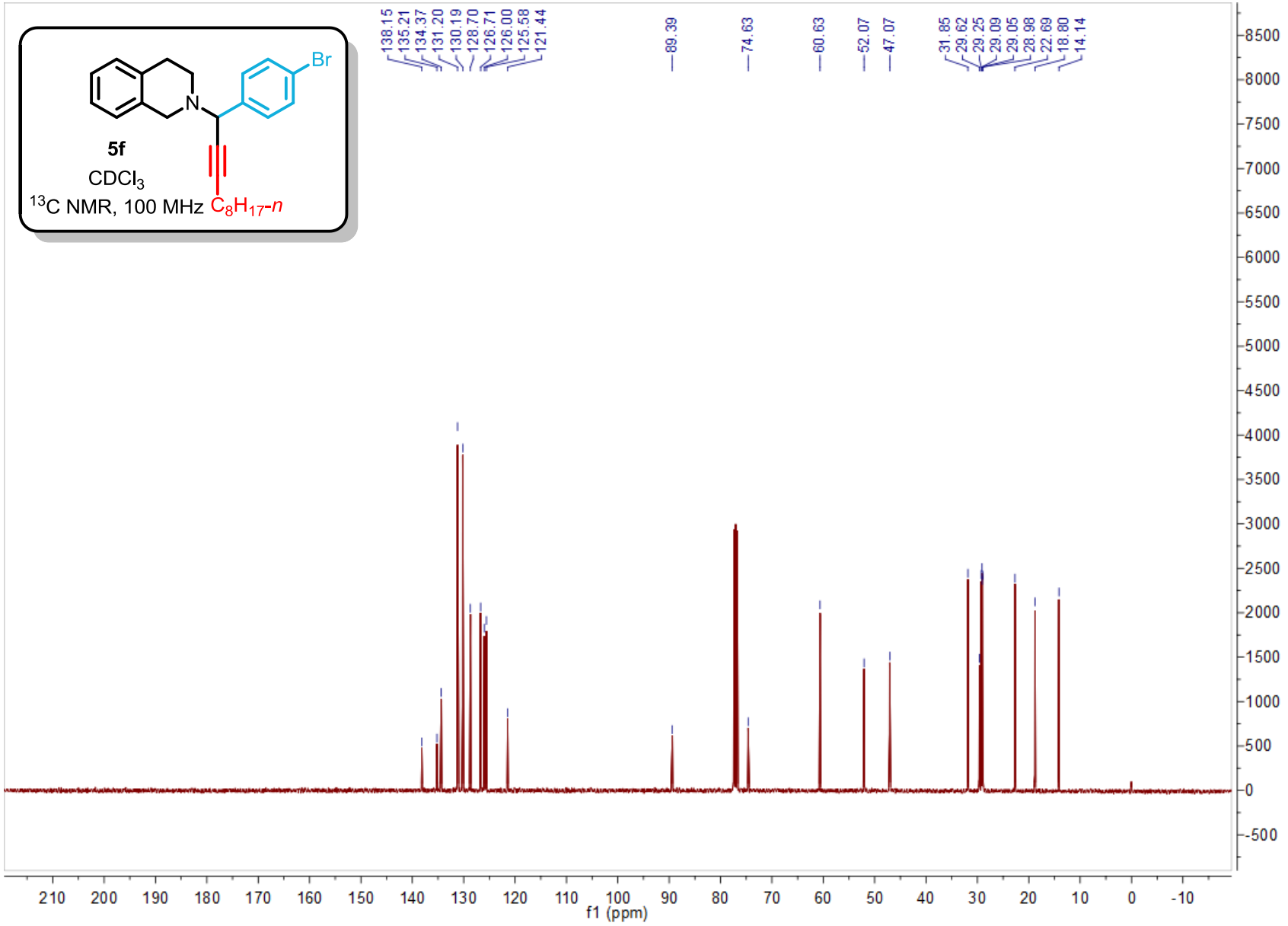
7.242
7.239
7.230
7.145
7.136
7.131
7.122
7.089
7.081
7.077
7.067
4.835
3.006
3.000
2.989
2.984
2.980
2.856
2.848
2.836
2.824
2.805
2.776
2.771
2.687
2.671
2.655
2.640
2.519
2.501
2.488
2.470
2.186
2.180
2.168
2.163
2.151
2.146
1.480
1.461
1.442
1.425
1.361
1.349
1.341
1.335
1.326
1.316
1.299
1.254
0.899
0.882
0.864
0.563
0.552
0.543
0.533
0.523
0.377
0.368
0.364
0.355
0.170
0.159
0.157
0.147
N
C8H17-n
4l
CDCl3
1H NMR, 400 MHz
0.78
2.09
1.11
1.00
2.20
2.19
1.07
1.06
2.16
2.16
2.43
8.24
1.13
3.14
2.21
1.08
1.05
f1 (ppm)

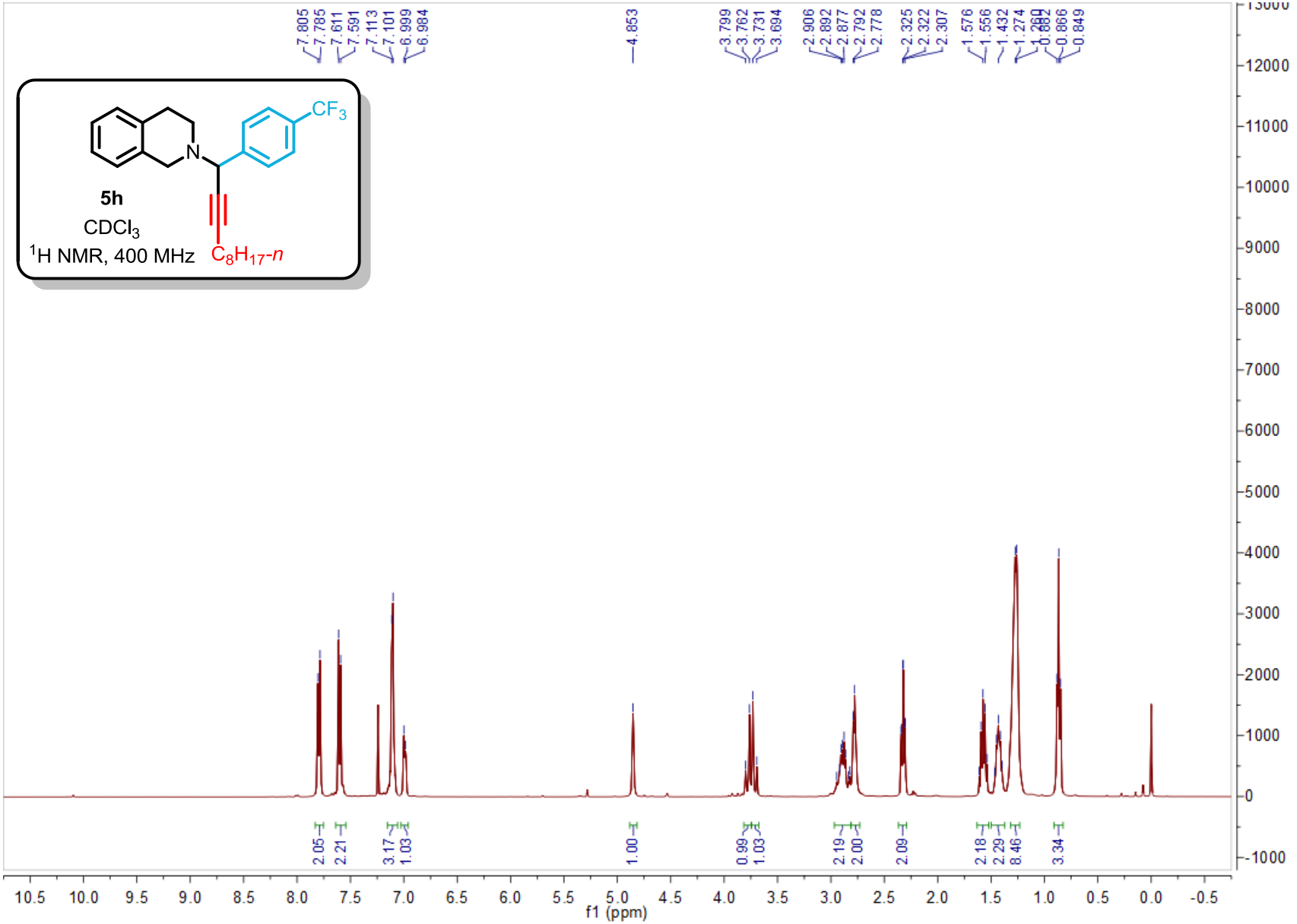

136.37
133.74
128.89
127.71
126.65
125.67
87.11
77.85
77.35
77.23
77.03
76.71
59.91
54.00
46.09
31.82
29.23
29.06
28.92
28.86
28.82
22.67
18.80
14.10
8.79
4.12
3.25
4l
CDCl3
13C NMR, 100 MHz
C8H17-n
f1 (ppm)

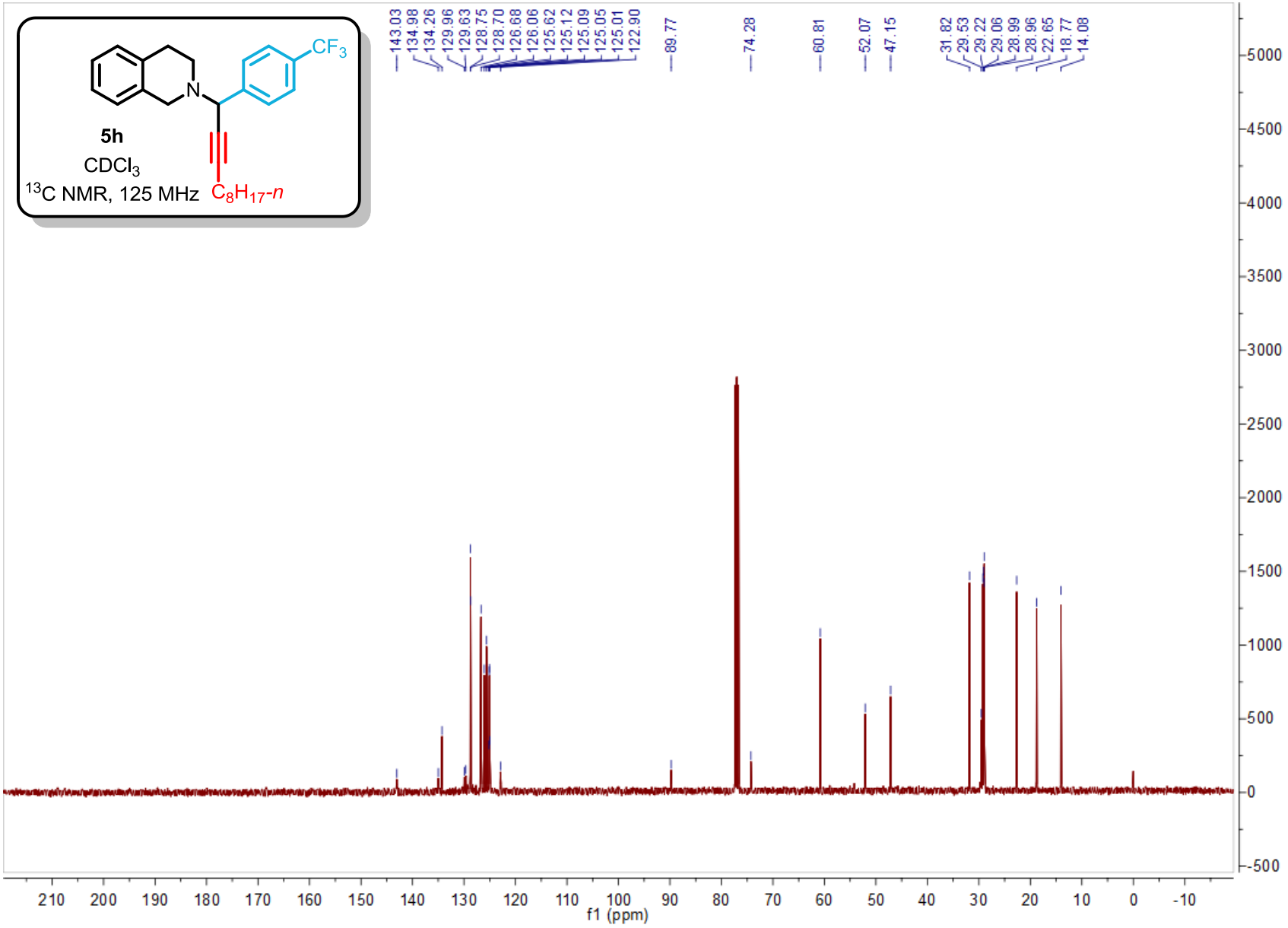

5a
CDCl3
1H NMR, 400 MHz
C8H17-n
7.655
7.637
7.363
7.345
7.326
7.298
7.280
7.261
7.095
7.089
7.085
7.075
6.993
6.986
6.980
6.975
4.807
3.783
3.741
3.703
2.876
2.863
2.798
2.788
2.775
2.314
2.309
2.296
1.568
1.284
1.275
1.271
0.867
0.849
1.95
2.18
1.21
2.97
0.96
1.00
2.10
1.97
2.43
2.10
2.42
2.43
9.60
3.53
f1 (ppm)

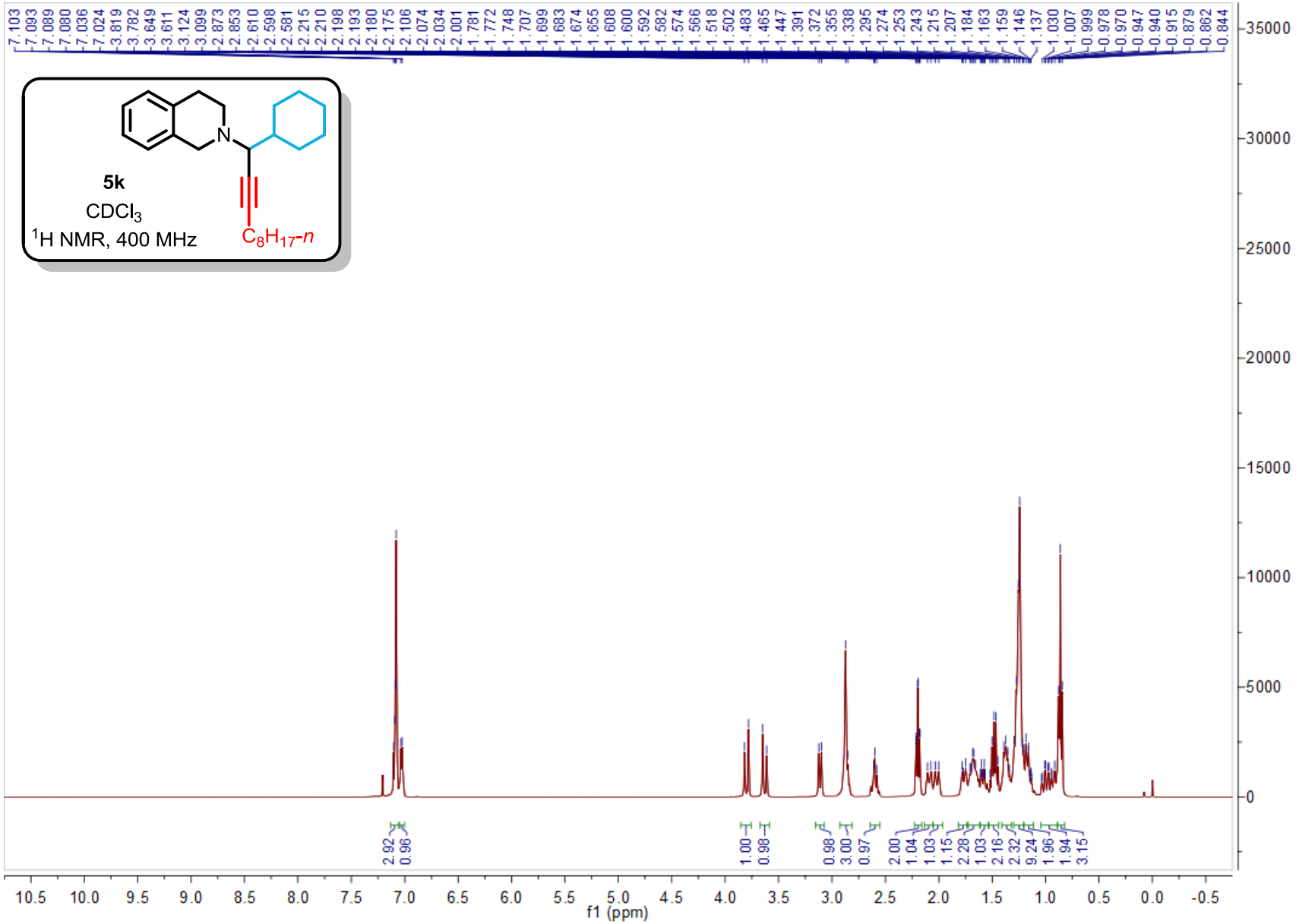

138.96
135.46
134.51
128.68
128.48
128.10
127.48
126.74
125.89
125.49
88.86
75.25
61.20
52.09
47.11
31.85
29.67
29.26
29.10
28.98
22.69
18.83
14.13
5a
CDCl3
13C NMR, 100 MHz
C8H17-n
f1 (ppm)

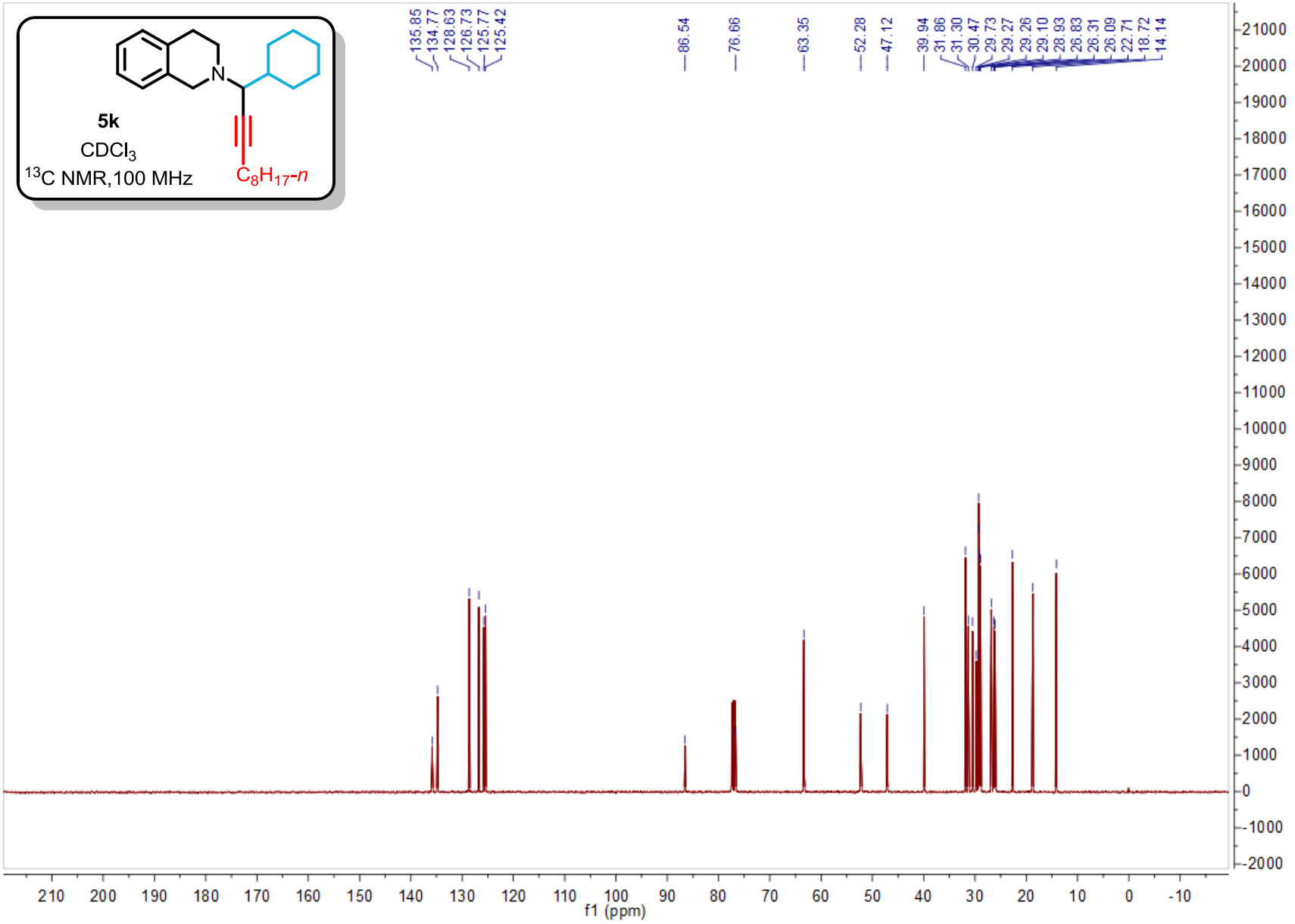

7.542
7.521
7.471
7.466
7.461
7.449
7.445
7.126
7.113
7.107
7.099
7.091
7.086
7.075
7.063
6.986
6.974
6.968
4.746
3.758
3.721
3.707
3.670
2.881
2.865
2.849
2.762
2.748
2.306
2.301
2.288
1.559
1.280
1.270
1.266
0.883
0.866
0.849
Br
N
5f
CDCl3
1H NMR, 400 MHz
C8H17-n
2.05
2.04
3.09
1.00
1.00
1.00
1.00
2.14
2.02
2.06
2.15
2.15
8.45
3.19
f1 (ppm)

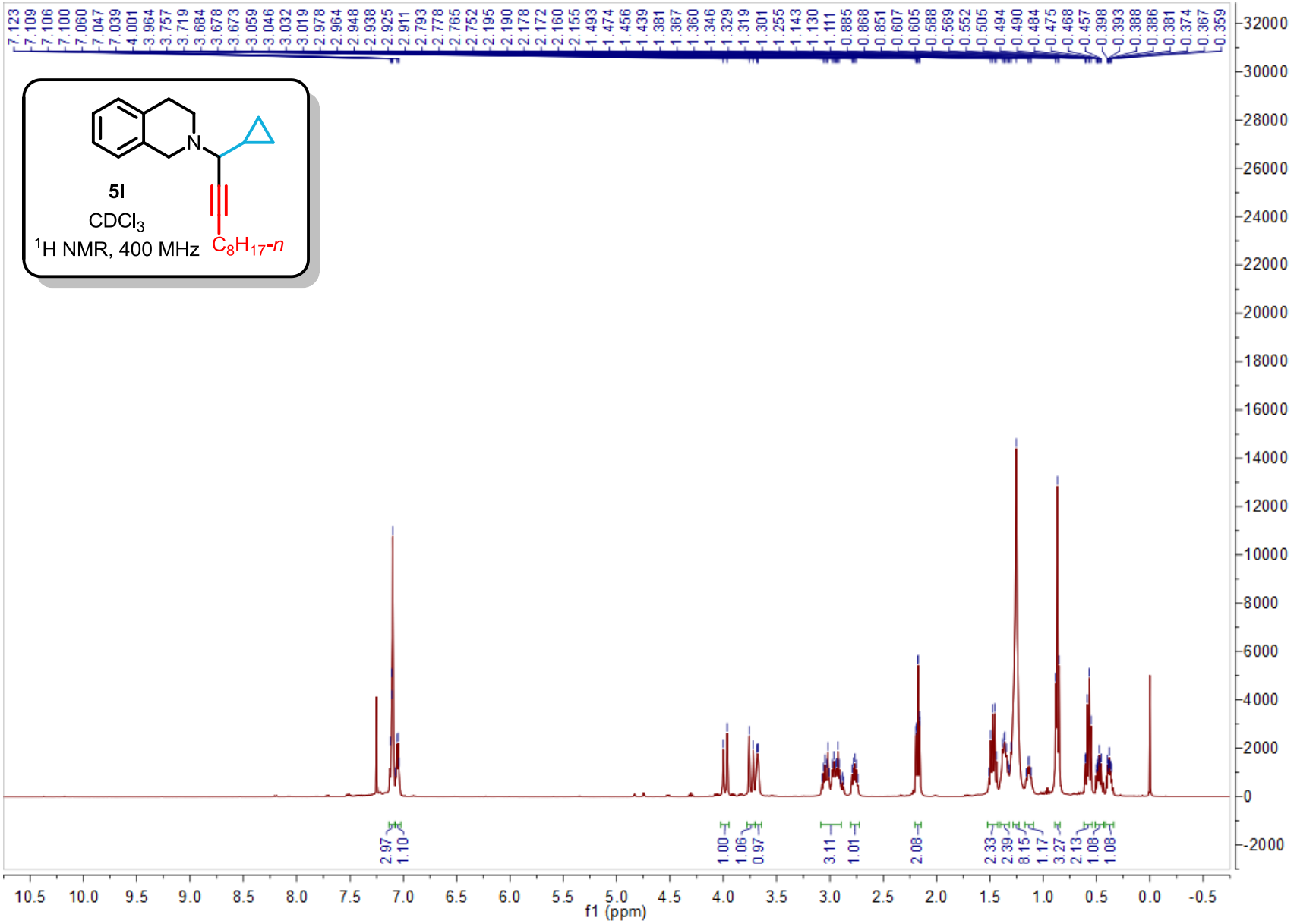

5f
CDCl3
13C NMR, 100 MHz C8H17-n
Br
N
138.15
135.21
134.37
131.20
130.19
128.70
126.71
126.00
125.58
121.44
89.39
74.63
60.63
52.07
47.07
31.85
29.62
29.25
29.09
29.05
28.98
22.69
18.80
14.14
f1 (ppm)

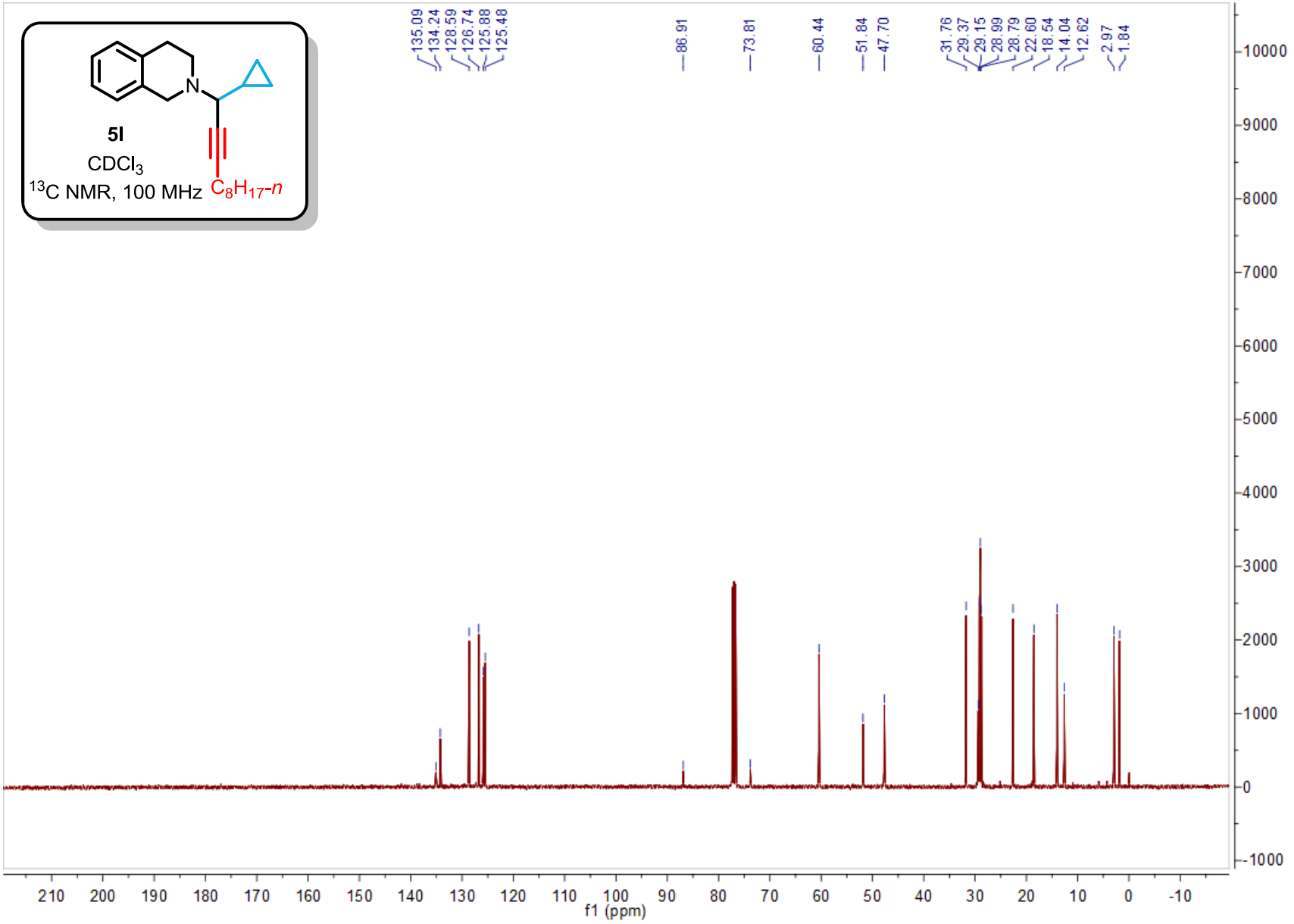

7.805
7.785
7.611
7.591
7.113
7.101
6.999
6.984
4.853
3.799
3.762
3.731
3.694
2.906
2.892
2.877
2.792
2.778
2.325
2.322
2.307
1.576
1.556
1.432
1.274
0.866
0.849
CF3
N
5h
CDCl3
1H NMR, 400 MHz
C8H17-n
2.05
2.21
3.17
1.03
1.00
0.99
1.03
2.19
2.00
2.09
2.18
2.29
8.46
3.34
f1 (ppm)

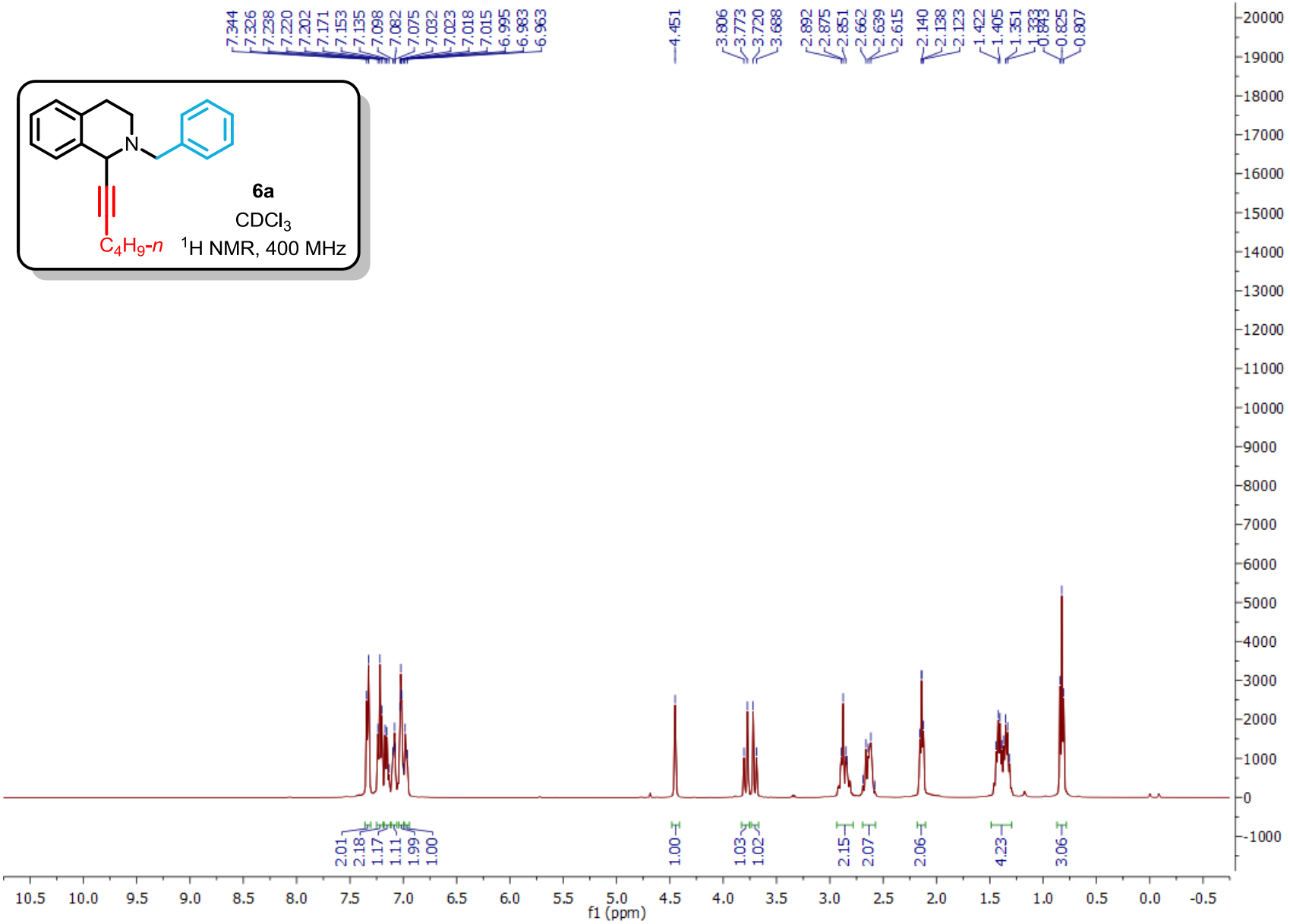

5h
CDCl3
13C NMR, 125 MHz
C8H17-n
CF3
N
143.03
134.98
134.26
129.96
129.63
128.75
128.70
126.68
126.06
125.62
125.12
125.09
125.05
125.01
122.90
89.77
74.28
60.81
52.07
47.15
31.82
29.53
29.22
29.06
28.99
28.96
22.65
18.77
14.08
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5k
CDCl3
1H NMR, 400 MHz
C8H17-n
f1 (ppm)


5k
CDCl3
13C NMR,100 MHz
C8H17-n
135.85
134.77
128.63
126.73
125.77
125.42
86.54
76.66
63.35
52.28
47.12
39.94
31.86
31.30
30.47
29.73
29.27
29.26
29.10
28.93
26.83
26.31
26.09
22.71
18.72
14.14
f1 (ppm)


5l
CDCl3
1H NMR, 400 MHz
C8H17-n
f1 (ppm)


5l
CDCl3
13C NMR, 100 MHz
C8H17-n
135.09
134.24
128.59
126.74
125.88
125.48
86.91
73.81
60.44
51.84
47.70
31.76
29.37
29.15
28.99
28.79
22.60
18.54
14.04
12.62
2.97
1.84
f1 (ppm)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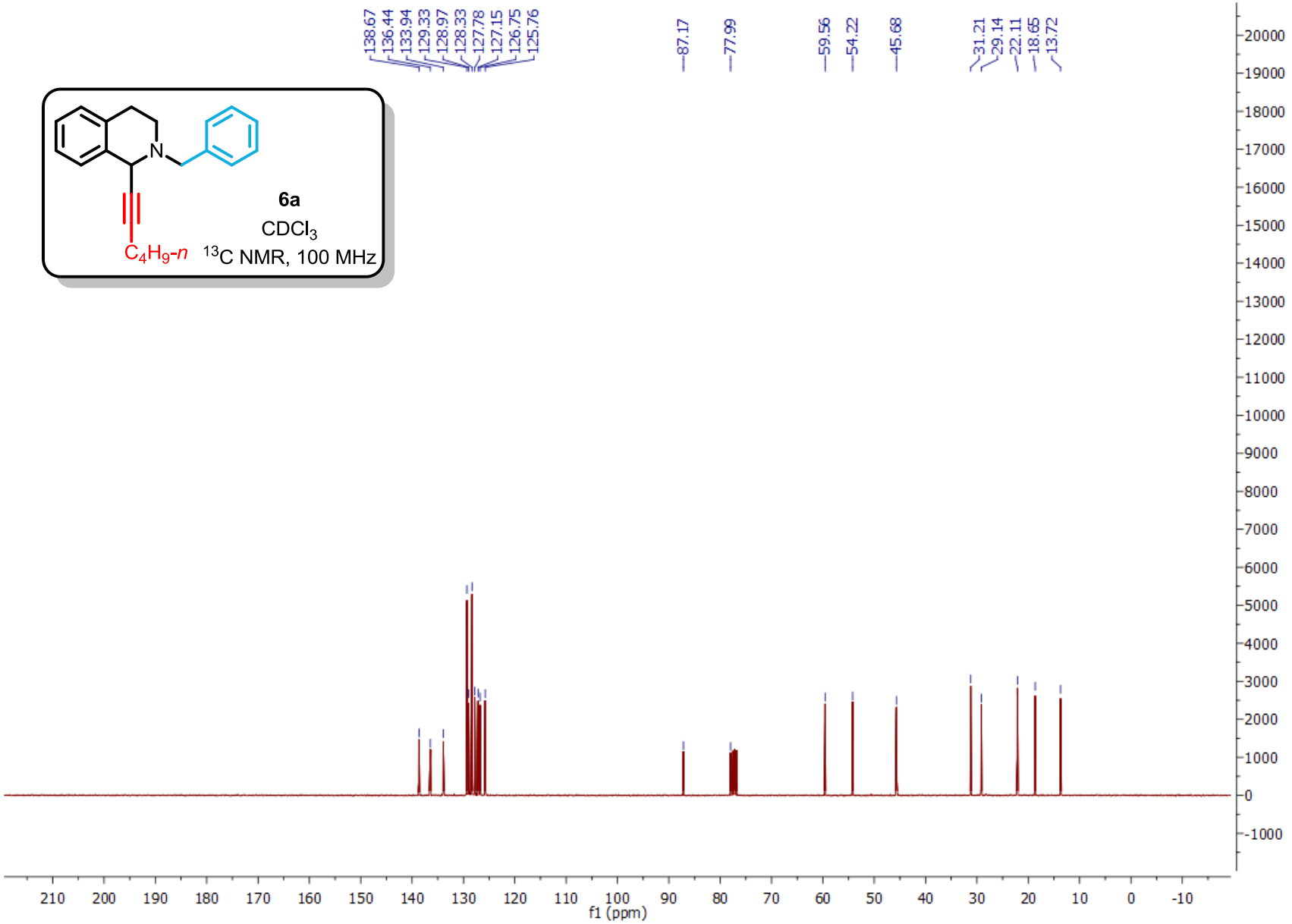
7.326
7.238
7.220
7.202
7.171
7.153
7.135
7.098
7.082
7.075
7.032
7.023
7.018
7.015
6.995
6.983
6.963
4.451
3.806
3.773
3.720
3.688
2.892
2.875
2.851
2.662
2.639
2.615
2.140
2.138
2.123
1.422
1.405
1.351
0.825
0.807
6a
CDCl3
1H NMR, 400 MHz
C4H9-n
2.01
2.18
1.17
1.11
1.99
1.00
1.00
1.03
1.02
2.15
2.07
2.06
4.23
3.06
f1 (ppm)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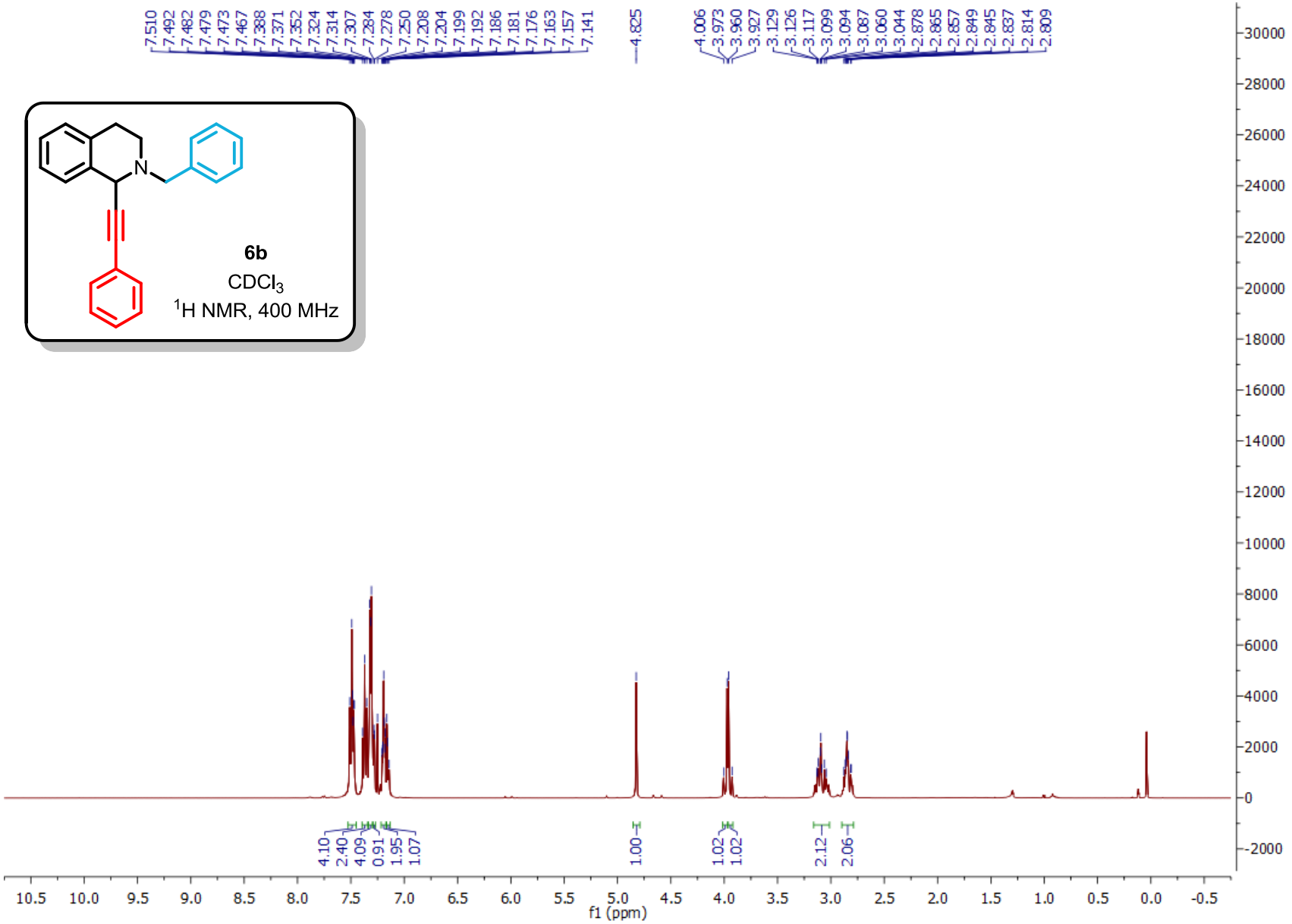
136.44
133.94
129.33
128.97
128.33
127.78
127.15
126.75
125.76
87.17
77.99
59.56
54.22
45.68
31.21
29.14
22.11
18.65
13.72
6a
CDCl3
C4H9-n
13C NMR, 100 MHz
f1 (ppm)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7.492
7.482
7.479
7.473
7.467
7.388
7.371
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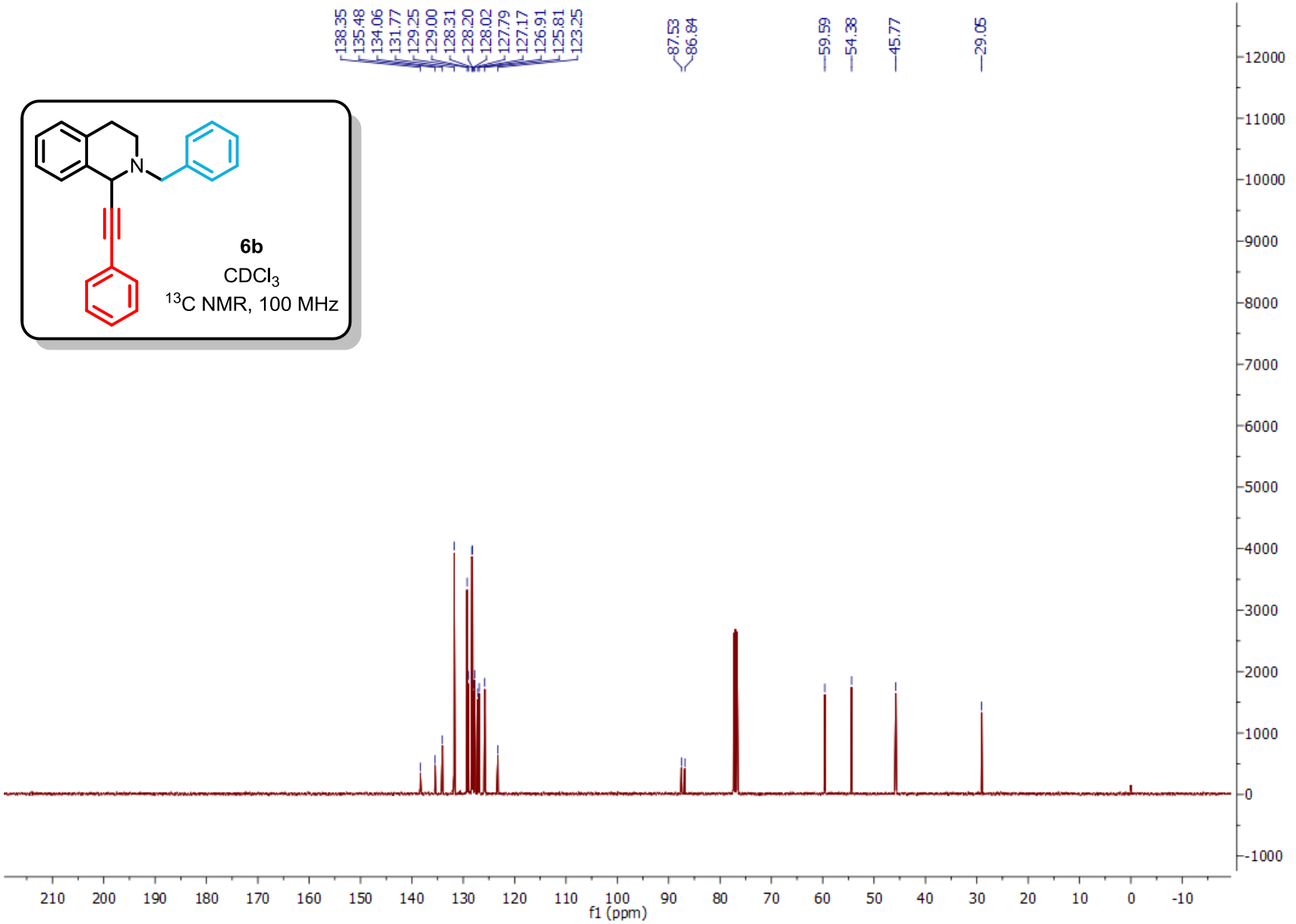
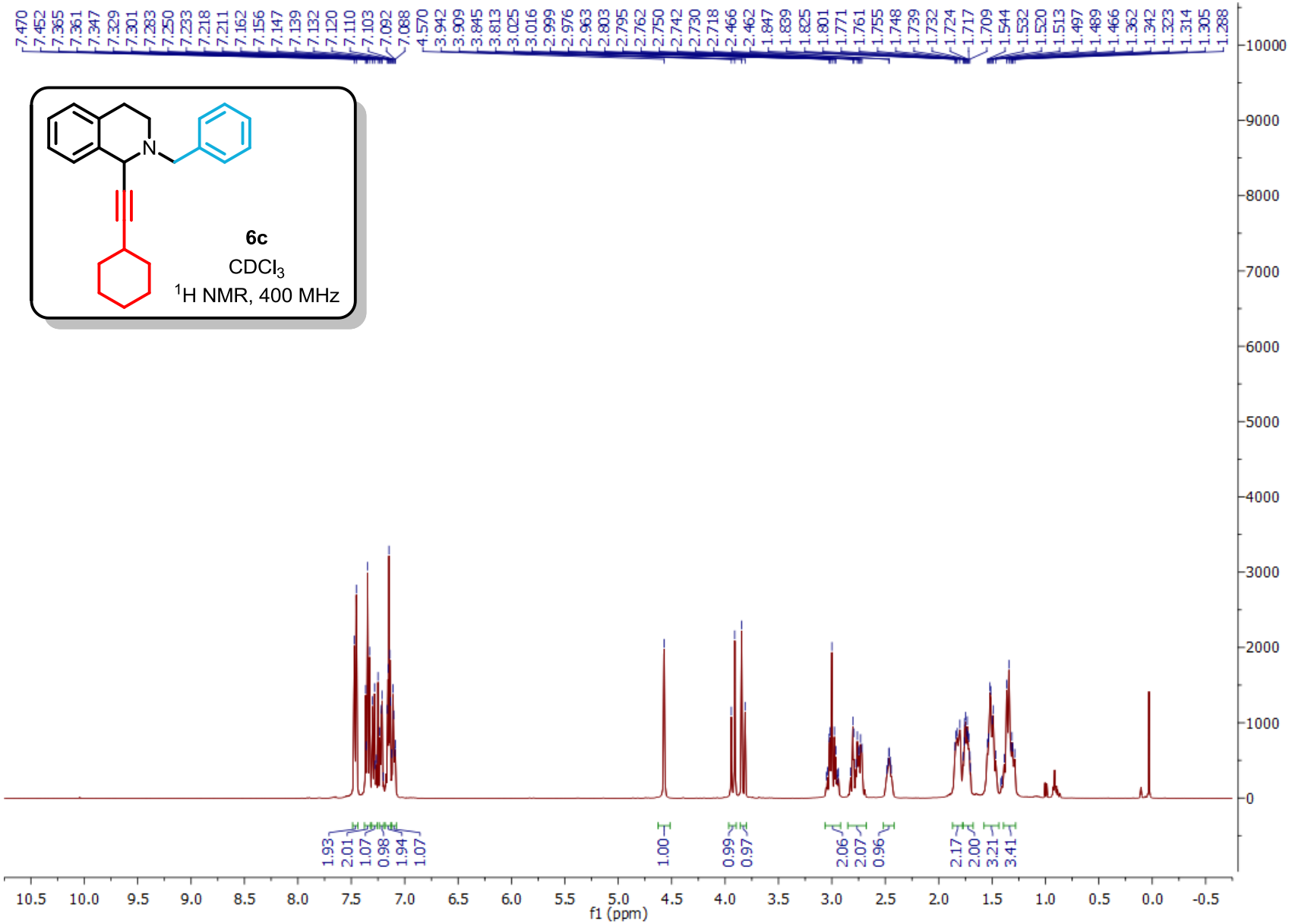
7.324
7.314
7.307
7.284
7.278
7.250
7.208
7.204
7.199
7.192
7.186
7.181
7.176
7.163
7.157
7.141
4.825
4.006
3.973
3.960
3.927
3.129
3.126
3.117
3.099
3.094
3.087
3.060
3.044
2.878
2.865
2.857
2.849
2.845
2.837
2.814
2.809
6b
CDCl3
1H NMR, 400 MHz
4.10
2.40
4.09
0.91
1.95
1.07
1.00
1.02
1.02
2.12
2.06
f1 (ppm)


138.35
135.48
134.06
131.77
129.25
129.00
128.31
128.20
128.02
127.79
127.17
126.91
125.81
123.25
87.53
86.84
59.59
54.38
45.77
29.05
6b
CDCl3
13C NMR, 100 MHz
f1 (ppm)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7.361
7.347
7.329
7.301
7.283
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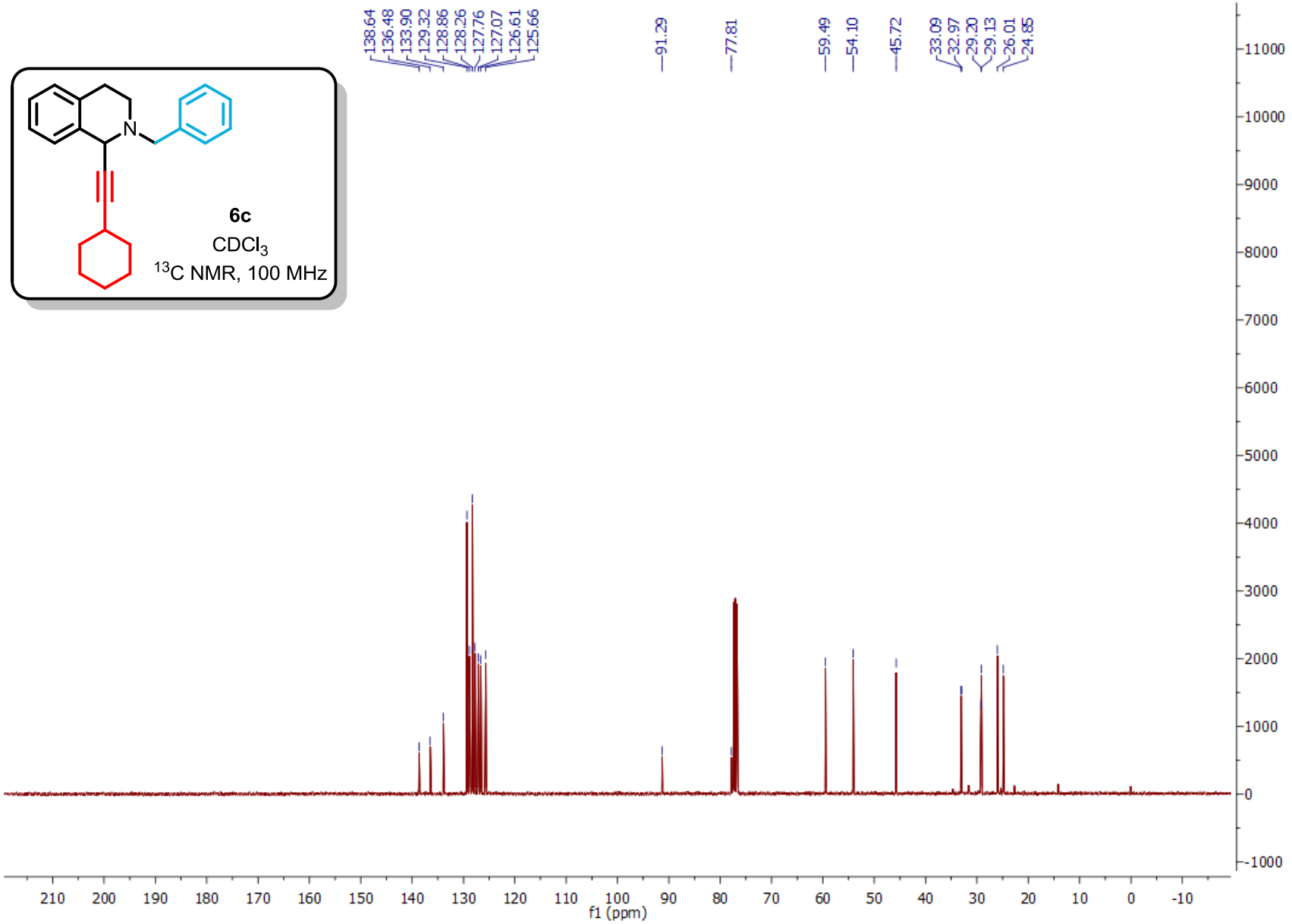
7.233
7.218
7.211
7.162
7.156
7.147
7.139
7.132
7.120
7.110
7.103
7.092
7.088
4.570
3.942
3.909
3.845
3.813
3.025
3.016
2.999
2.976
2.963
2.803
2.795
2.762
2.750
2.742
2.730
2.718
2.466
2.462
1.847
1.839
1.825
1.801
1.771
1.761
1.755
1.748
1.739
1.732
1.724
1.717
1.709
1.544
1.532
1.520
1.513
1.497
1.489
1.466
1.362
1.342
1.323
1.314
1.305
1.288
N
6c
CDCl3
1H NMR, 400 MHz
1.93
2.01
1.07
0.98
1.94
1.07
1.00
0.99
0.97
2.06
2.07
0.96
2.17
2.00
3.21
3.41
f1 (ppm)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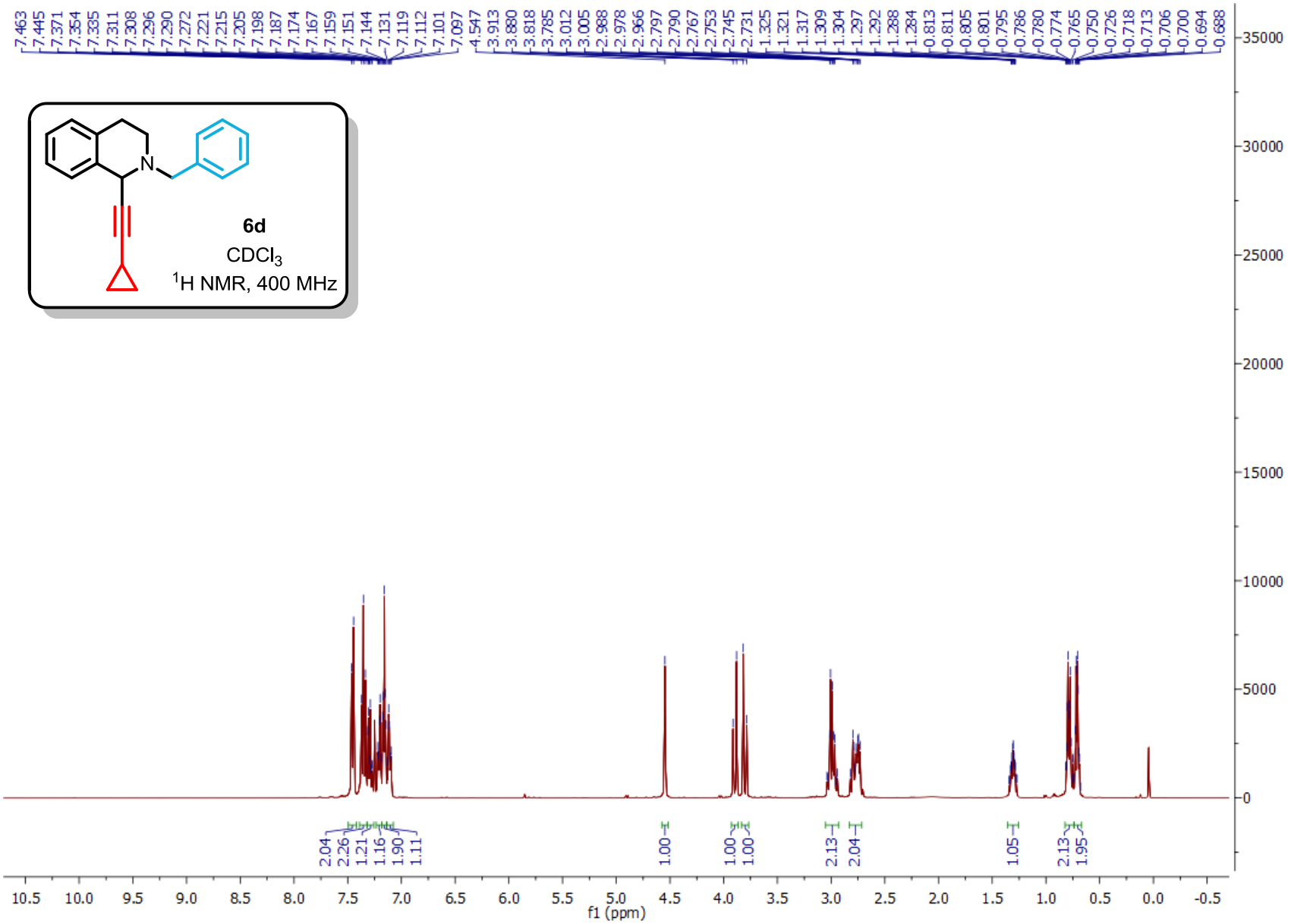
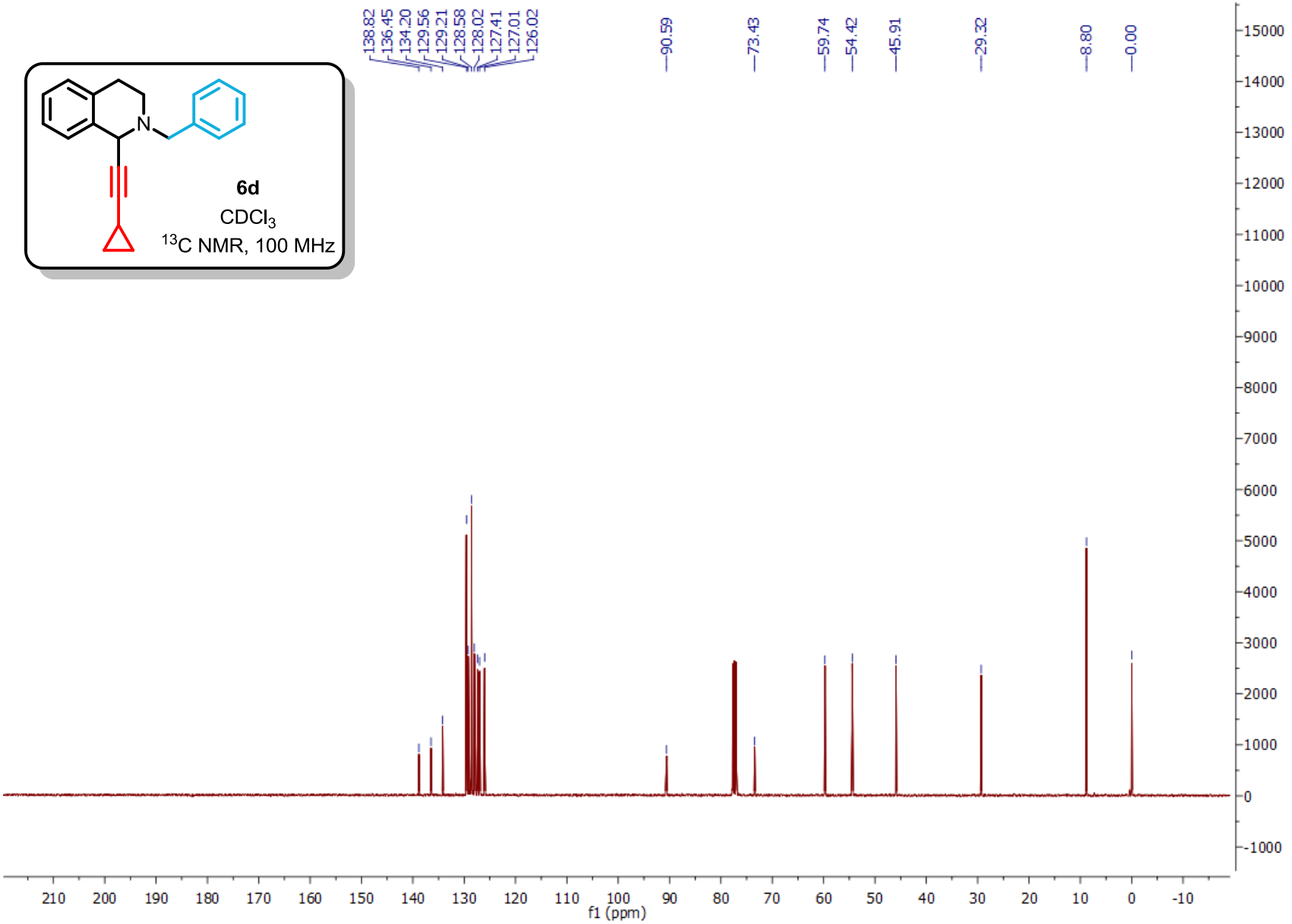
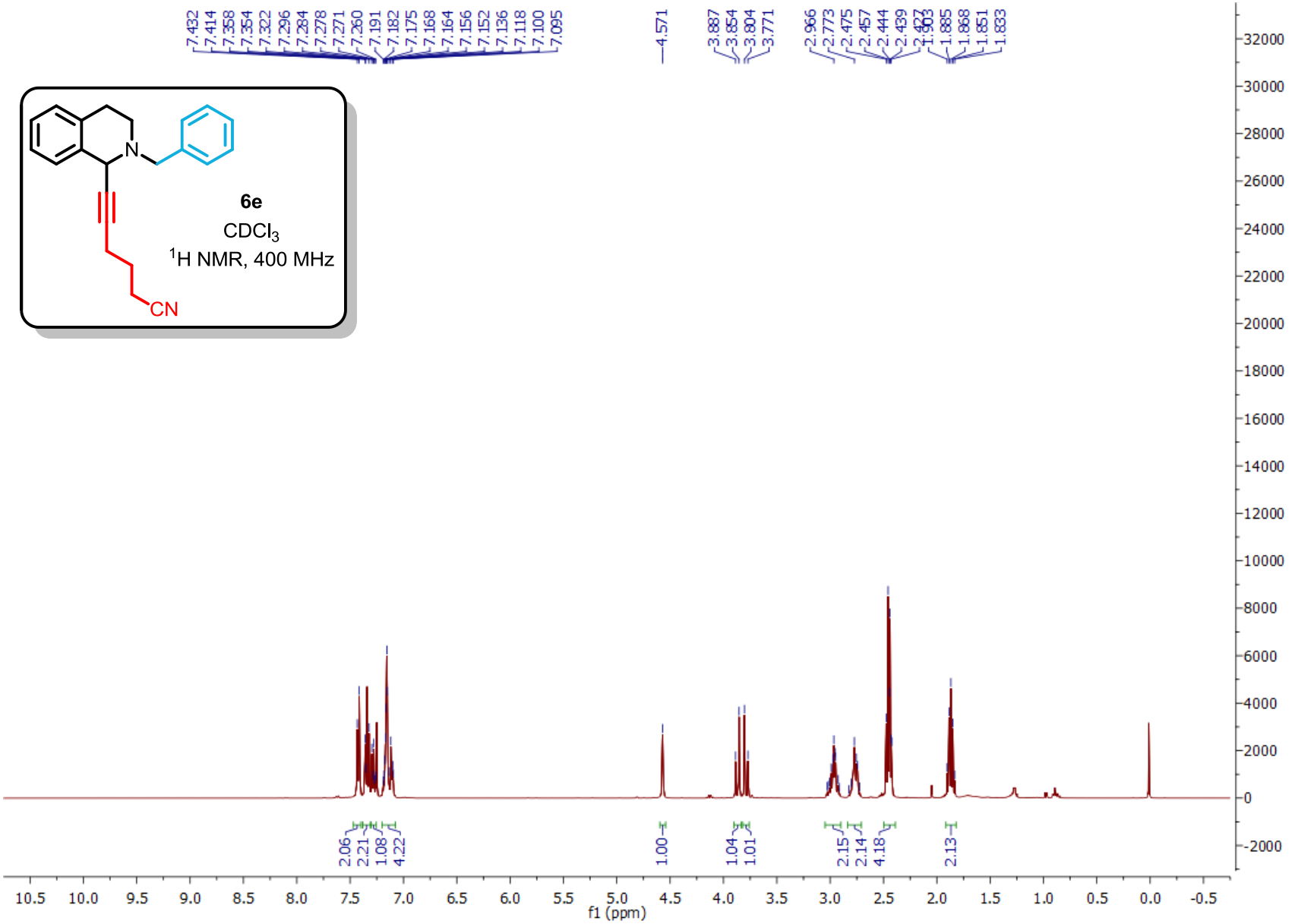
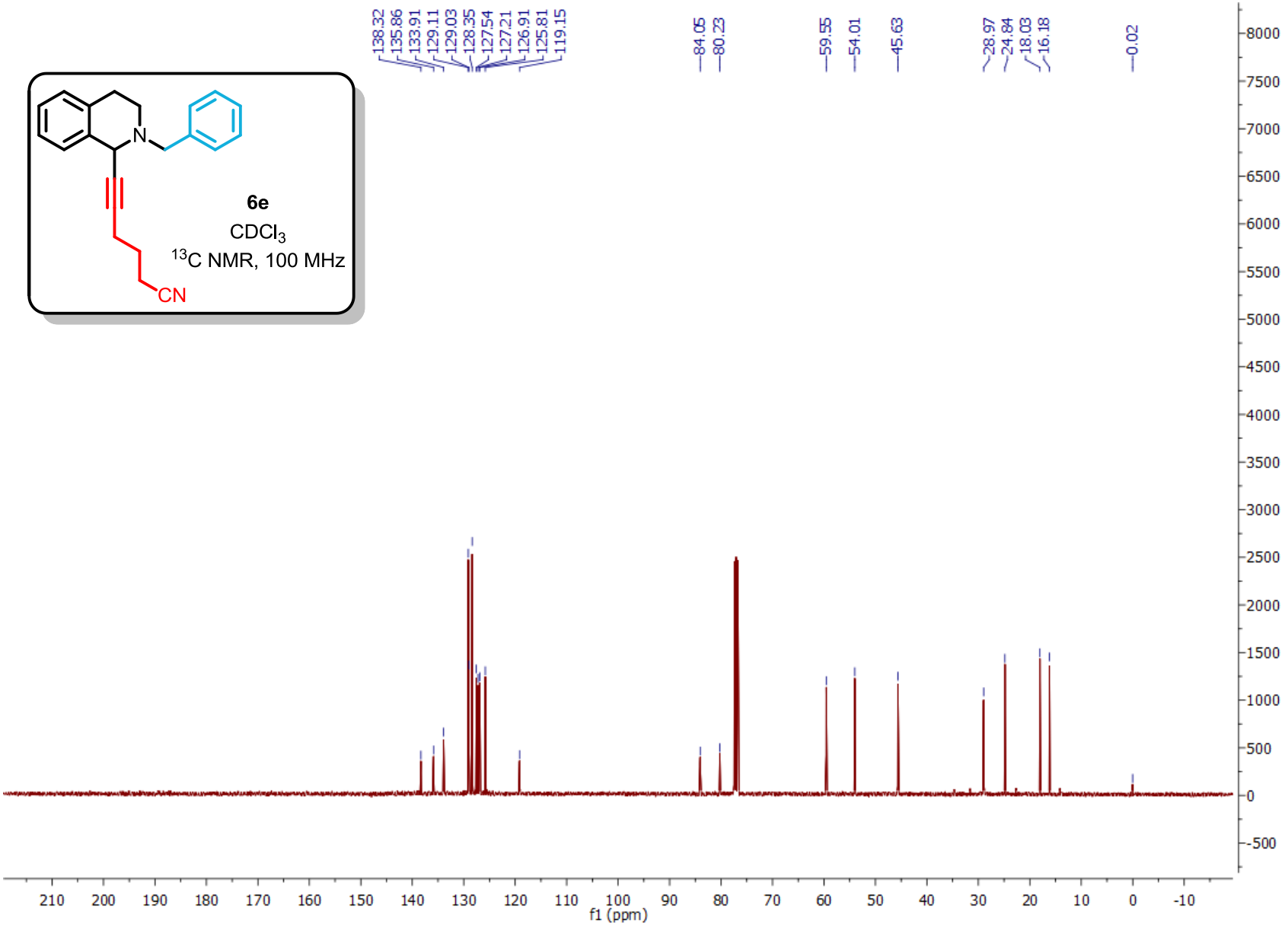
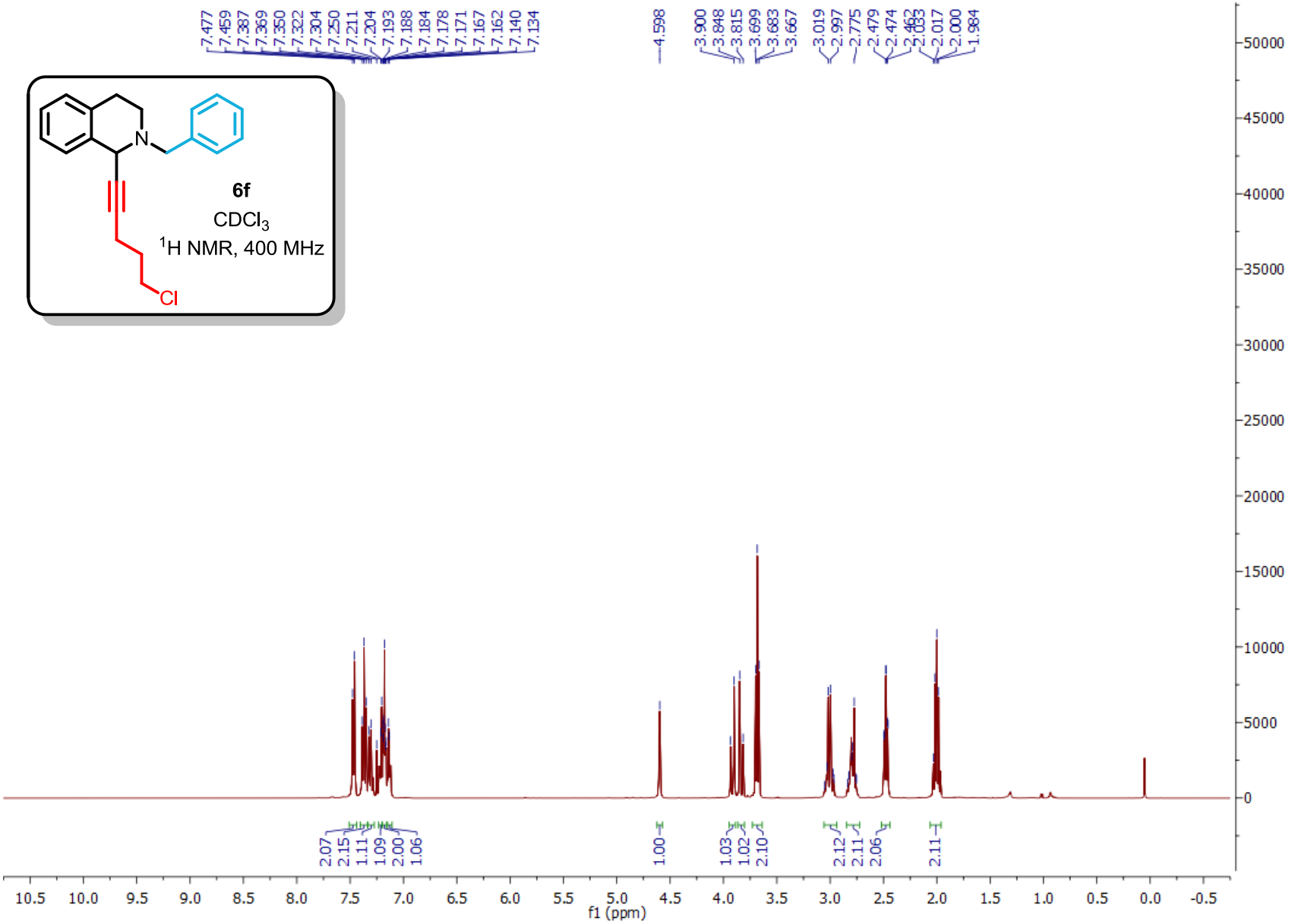
136.48
133.90
129.32
128.86
128.26
127.76
127.07
126.61
125.66
91.29
77.81
59.49
54.10
45.72
33.09
32.97
29.20
29.13
26.01
24.85
6c
CDCl3
13C NMR, 100 MHz
f1 (ppm)


6d
CDCl3
1H NMR, 400 MHz
f1 (ppm)


6d
CDCl3
13C NMR, 100 MHz
138.82
136.45
134.20
129.56
129.21
128.58
128.02
127.41
127.01
126.02
90.59
73.43
59.74
54.42
45.91
29.32
8.80
0.00
f1 (ppm)


7.432
7.414
7.358
7.354
7.322
7.296
7.284
7.278
7.271
7.260
7.191
7.182
7.175
7.168
7.164
7.156
7.152
7.136
7.118
7.100
7.095
4.571
3.887
3.854
3.804
3.771
2.966
2.773
2.475
2.457
2.444
2.439
1.885
1.868
1.851
1.833
6e
CDCl3
1H NMR, 400 MHz
CN
2.06
2.21
1.08
4.22
1.00
1.04
1.01
2.15
2.14
4.18
2.13
f1 (ppm)


138.32
135.86
133.91
129.11
129.03
128.35
127.54
127.21
126.91
125.81
119.15
84.05
80.23
59.55
54.01
45.63
28.97
24.84
18.03
16.18
0.02
6e
CDCl3
13C NMR, 100 MHz
CN
f1 (ppm)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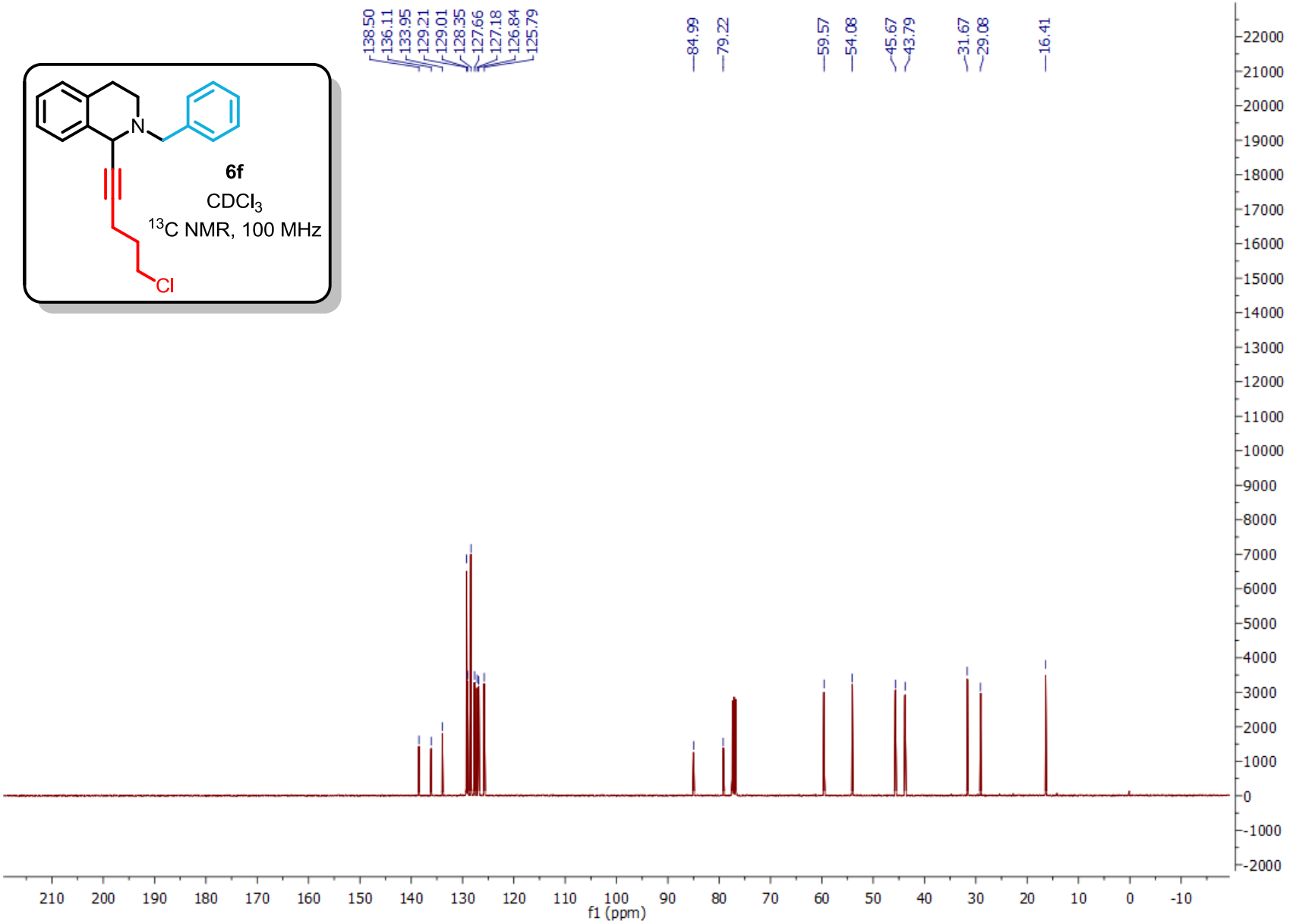
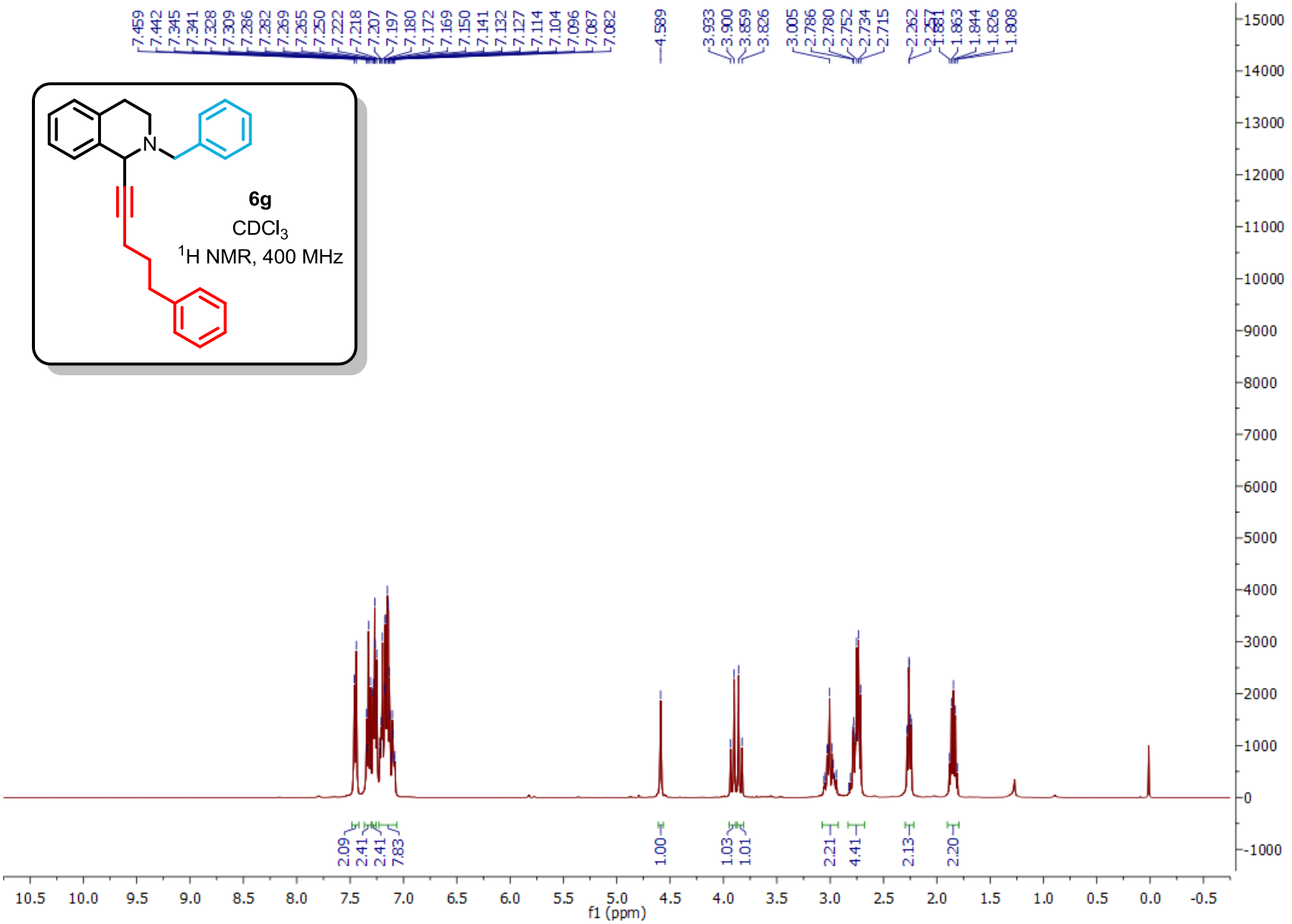
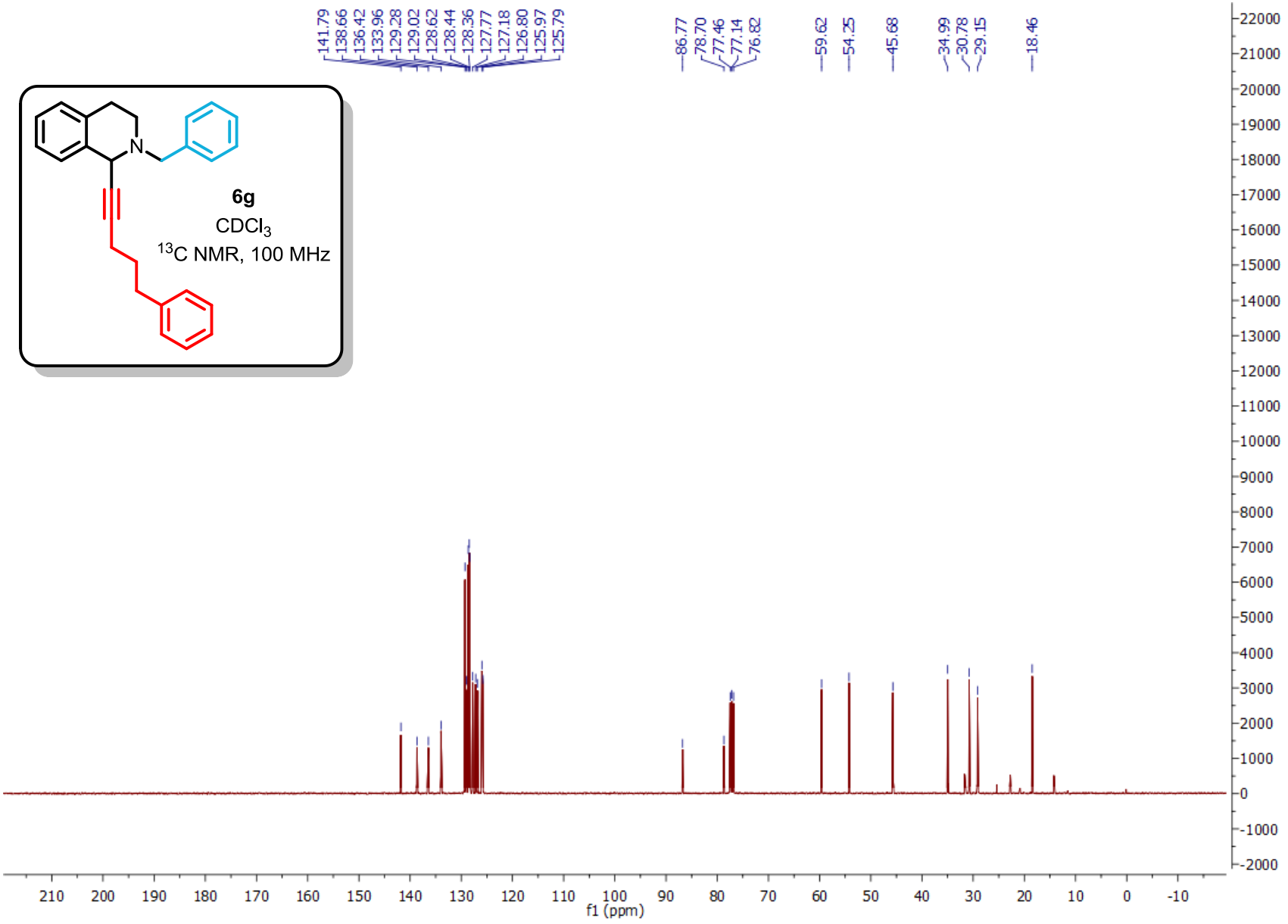
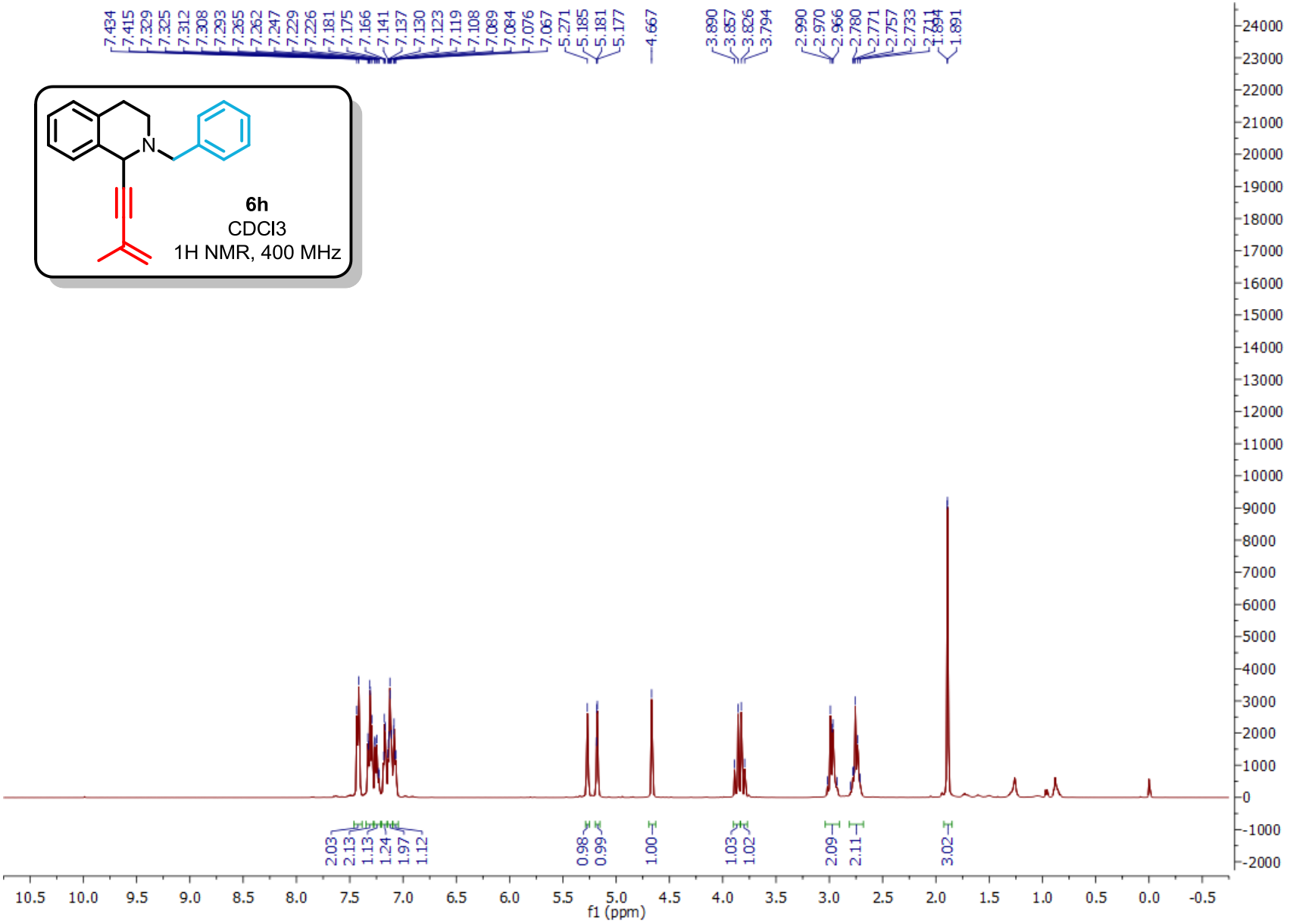
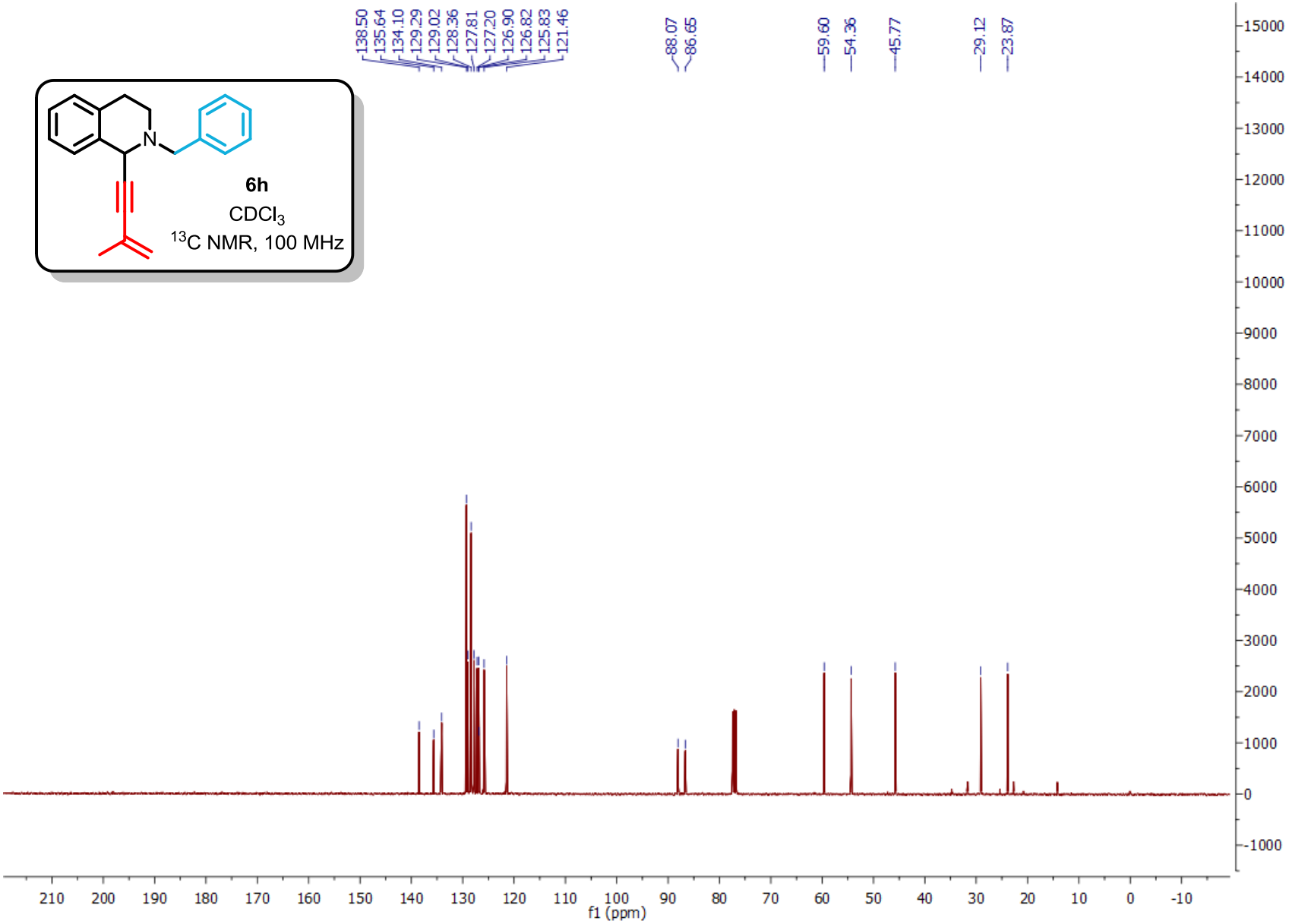
7.459
7.387
7.369
7.350
7.322
7.304
7.250
7.211
7.204
7.193
7.188
7.184
7.178
7.171
7.167
7.162
7.140
7.134
4.598
3.900
3.848
3.815
3.699
3.683
3.667
3.019
2.997
2.775
2.479
2.474
2.462
2.033
2.017
2.000
1.984
6f
CDCl3
1H NMR, 400 MHz
Cl
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.07
2.15
1.11
1.09
2.00
1.06
1.00
1.03
1.02
2.10
2.12
2.11
2.06
2.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

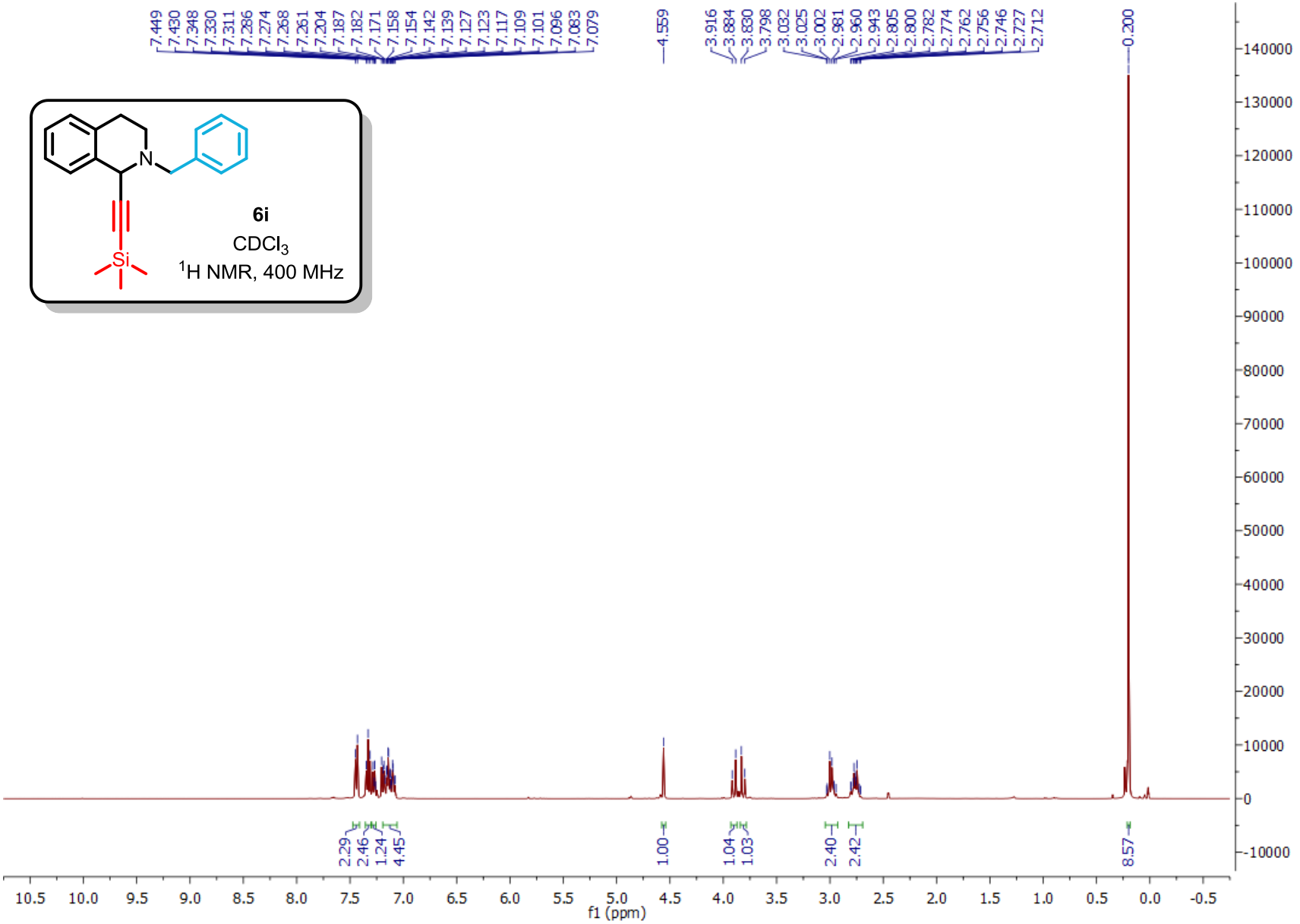

6f
CDCl3
13C NMR, 100 MHz
Cl
138.50
136.11
133.95
129.21
129.01
128.35
127.66
127.18
126.84
125.79
84.99
79.22
59.57
54.08
45.67
43.79
31.67
29.08
16.41
f1 (ppm)

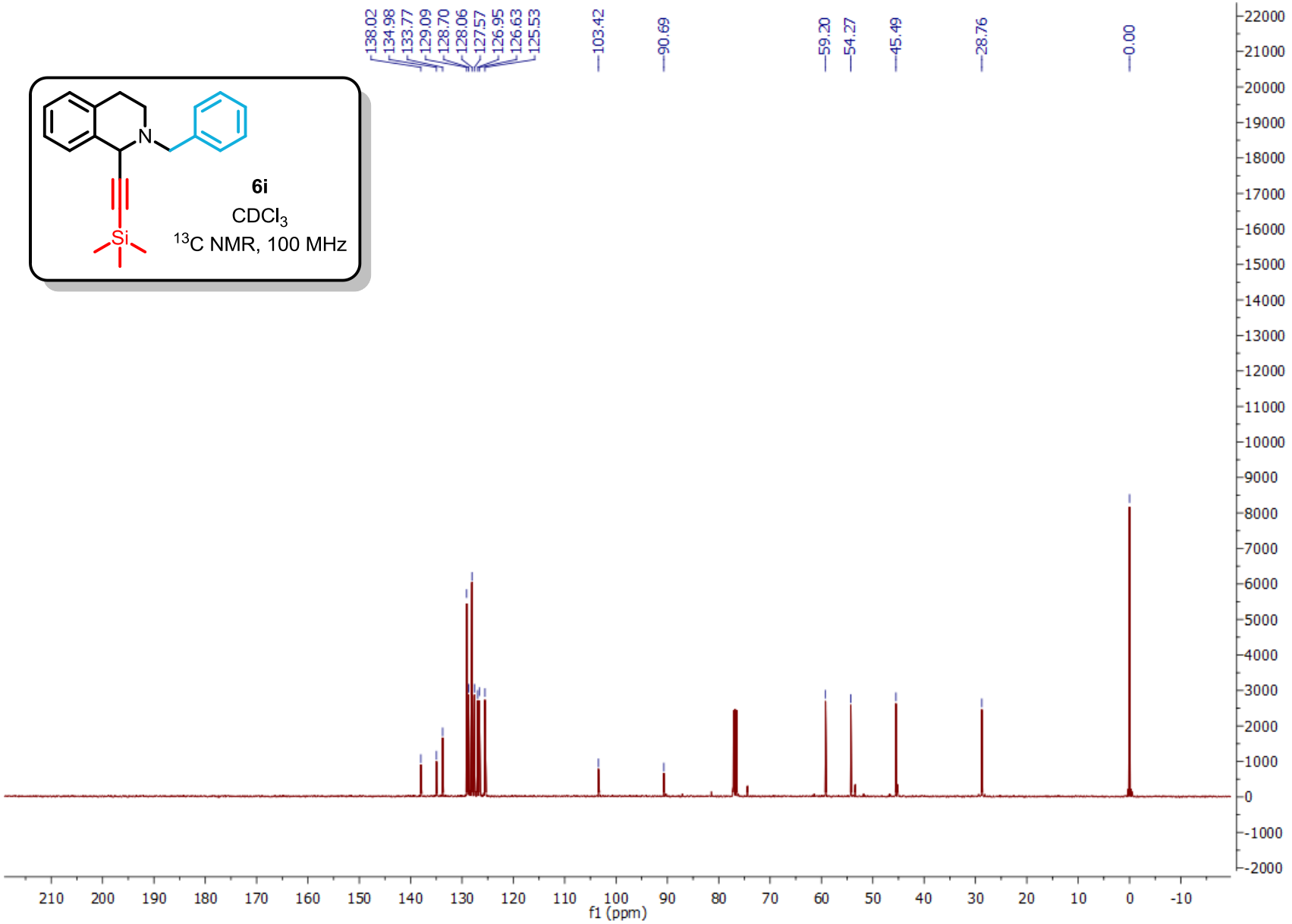

7.459
7.442
7.345
7.341
7.328
7.309
7.286
7.282
7.269
7.265
7.250
7.222
7.218
7.207
7.197
7.180
7.172
7.169
7.150
7.141
7.132
7.127
7.114
7.104
7.096
7.087
7.082
4.589
3.933
3.900
3.859
3.826
3.005
2.786
2.780
2.752
2.734
2.715
2.262
1.863
1.844
1.826
1.808
6g
CDCl3
1H NMR, 400 MHz
2.09
2.41
2.41
7.83
1.00
1.03
1.01
2.21
4.41
2.13
2.20
f1 (ppm)

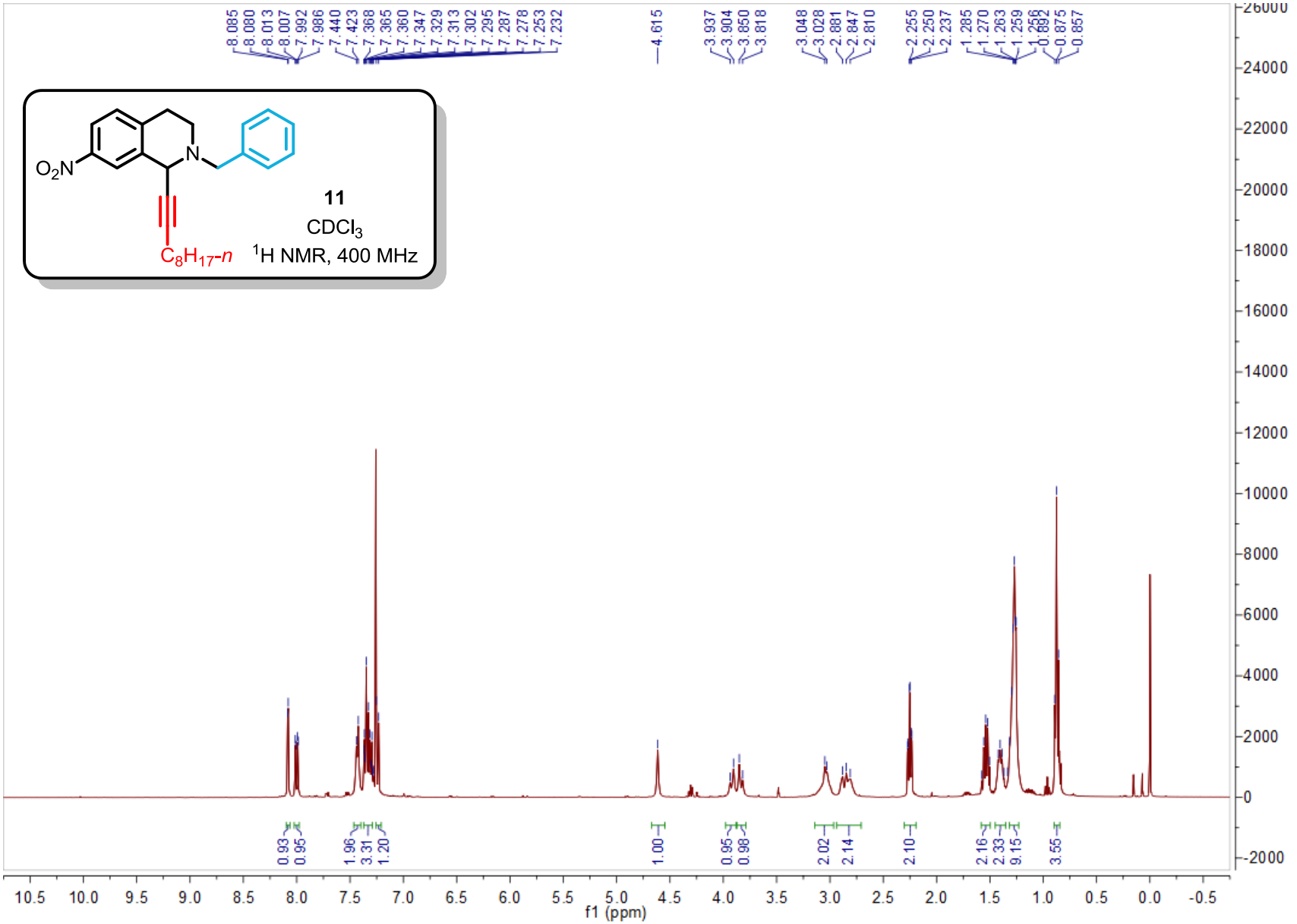

141.79
138.66
136.42
133.96
129.28
129.02
128.62
128.44
128.36
127.77
127.18
126.80
125.97
125.79
86.77
78.70
77.46
77.14
76.82
59.62
54.25
45.68
34.99
30.78
29.15
18.46
6g
CDCl3
13C NMR, 100 MHz
f1 (ppm)

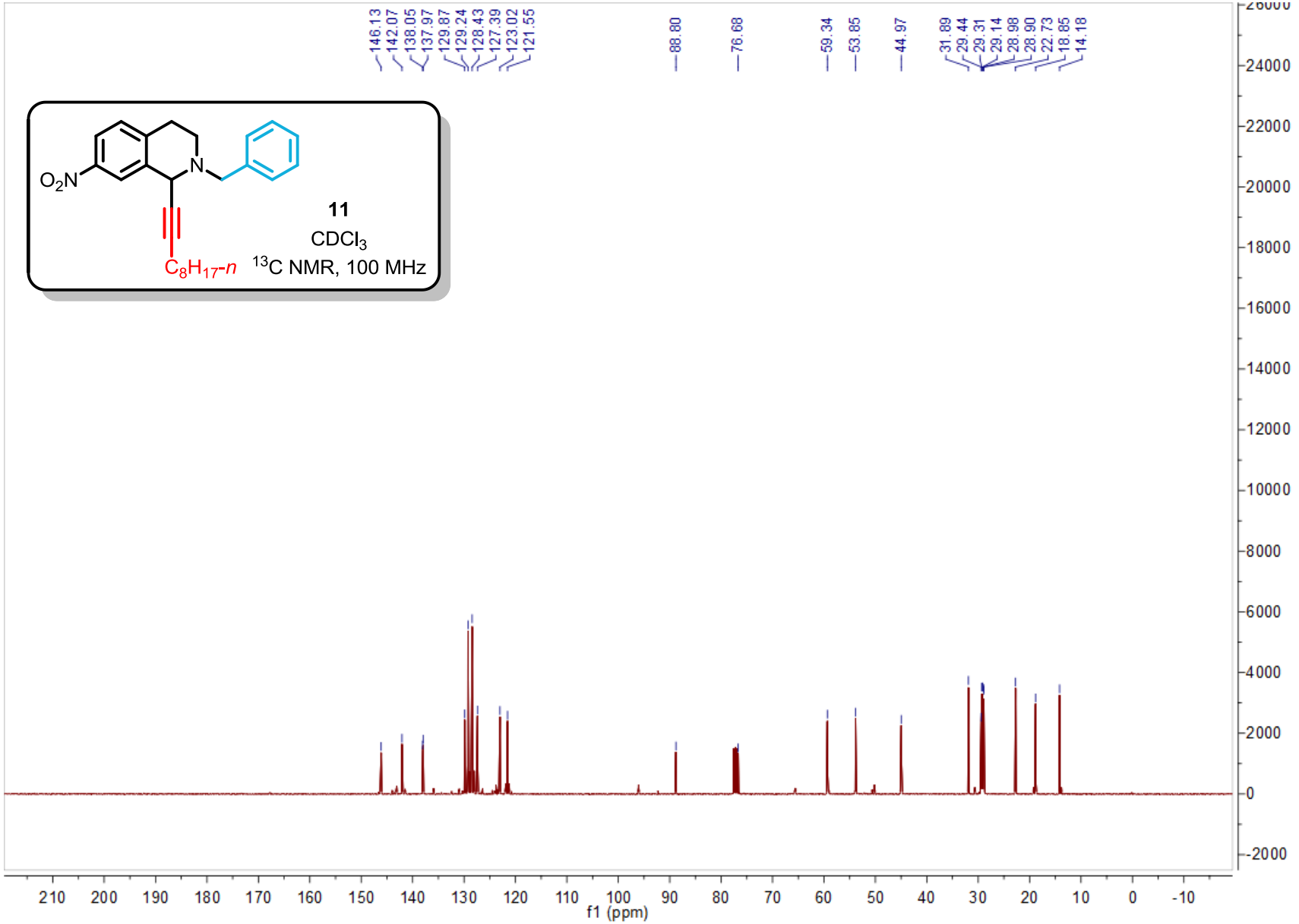

7.434
7.415
7.329
7.325
7.312
7.308
7.293
7.265
7.262
7.247
7.229
7.226
7.181
7.175
7.166
7.141
7.137
7.130
7.123
7.119
7.108
7.089
7.084
7.076
7.067
5.271
5.185
5.181
5.177
4.667
3.890
3.857
3.826
3.794
2.990
2.970
2.966
2.780
2.771
2.757
2.733
1.891
6h
CDCl3
1H NMR, 400 MHz
2.03
2.13
1.13
1.24
1.97
1.12
0.98
0.99
1.00
1.03
1.02
2.09
2.11
3.02
f1 (ppm)

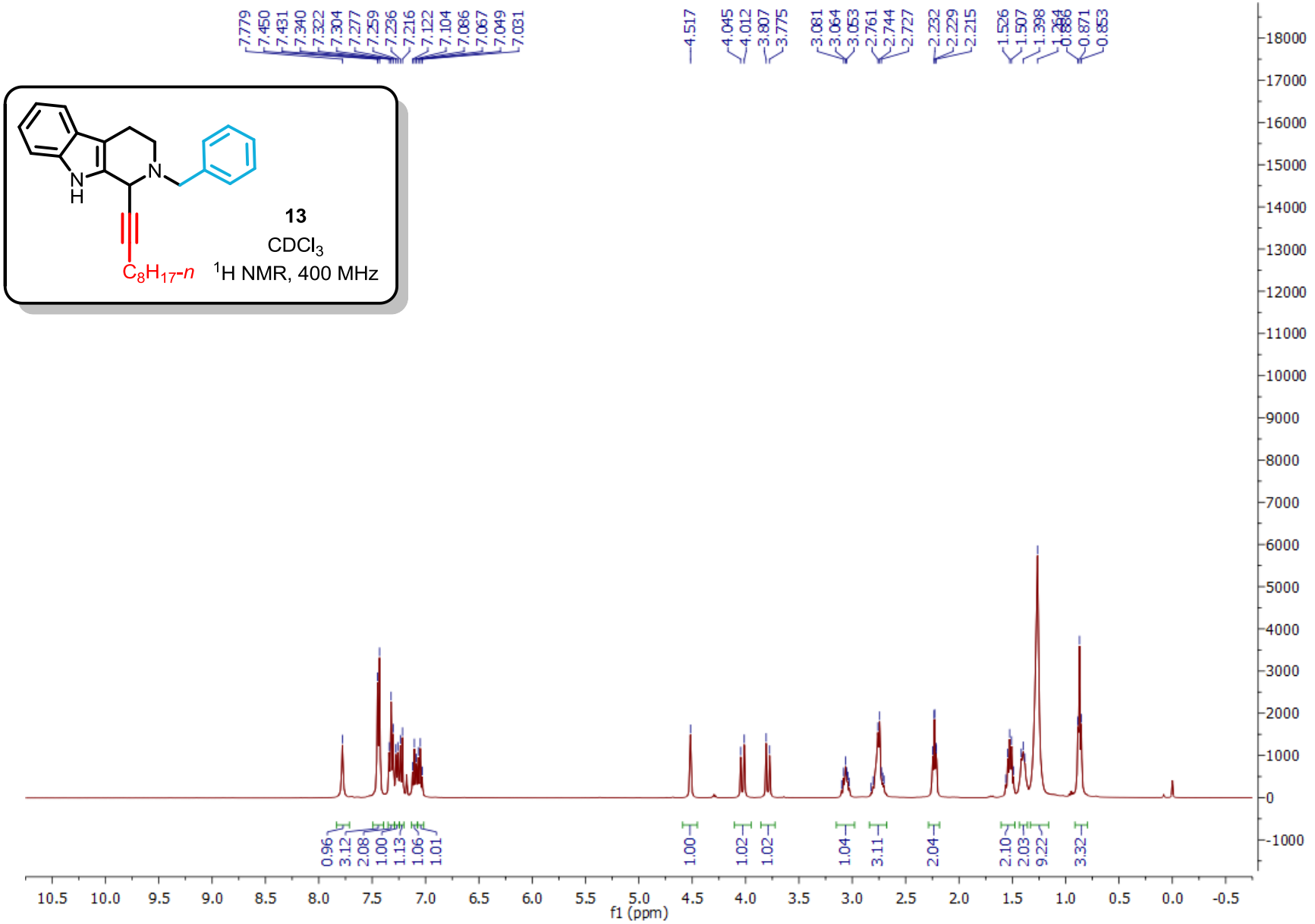

138.50
135.64
134.10
129.29
129.02
128.36
127.81
127.20
126.90
126.82
125.83
121.46
88.07
86.65
59.60
54.36
45.77
29.12
23.87
6h
CDCl3
13C NMR, 100 MHz
f1 (ppm)

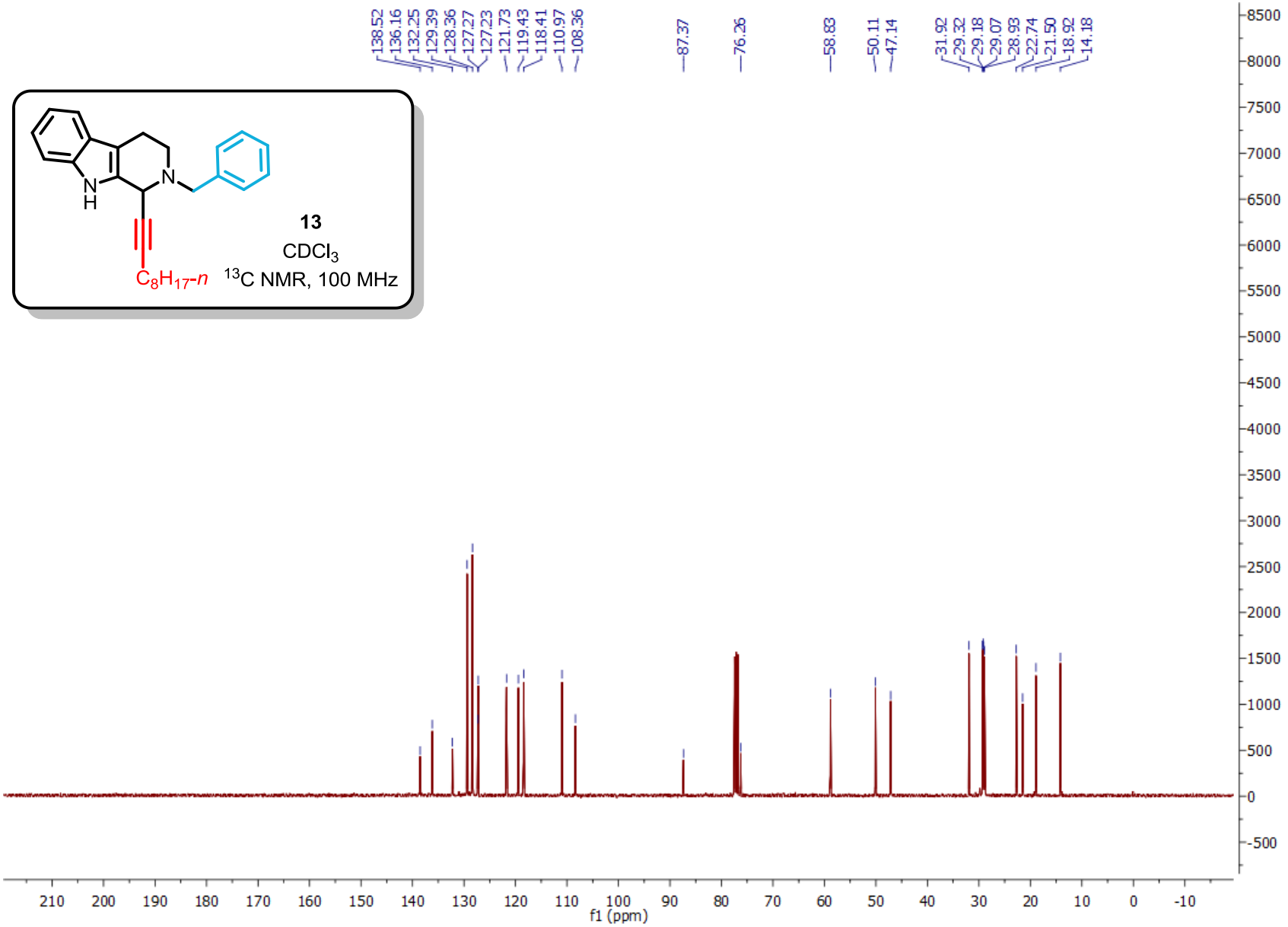

7.449
7.430
7.348
7.330
7.311
7.286
7.274
7.268
7.261
7.204
7.187
7.182
7.171
7.158
7.154
7.142
7.139
7.127
7.123
7.117
7.109
7.101
7.096
7.083
7.079
4.559
3.916
3.884
3.830
3.798
3.032
3.025
3.002
2.981
2.960
2.943
2.805
2.800
2.782
2.774
2.762
2.756
2.746
2.727
2.712
0.200
N
Si
6i
CDCl3
1H NMR, 400 MHz
2.29
2.46
1.24
4.45
1.00
1.04
1.03
2.40
2.42
8.57
f1 (ppm)

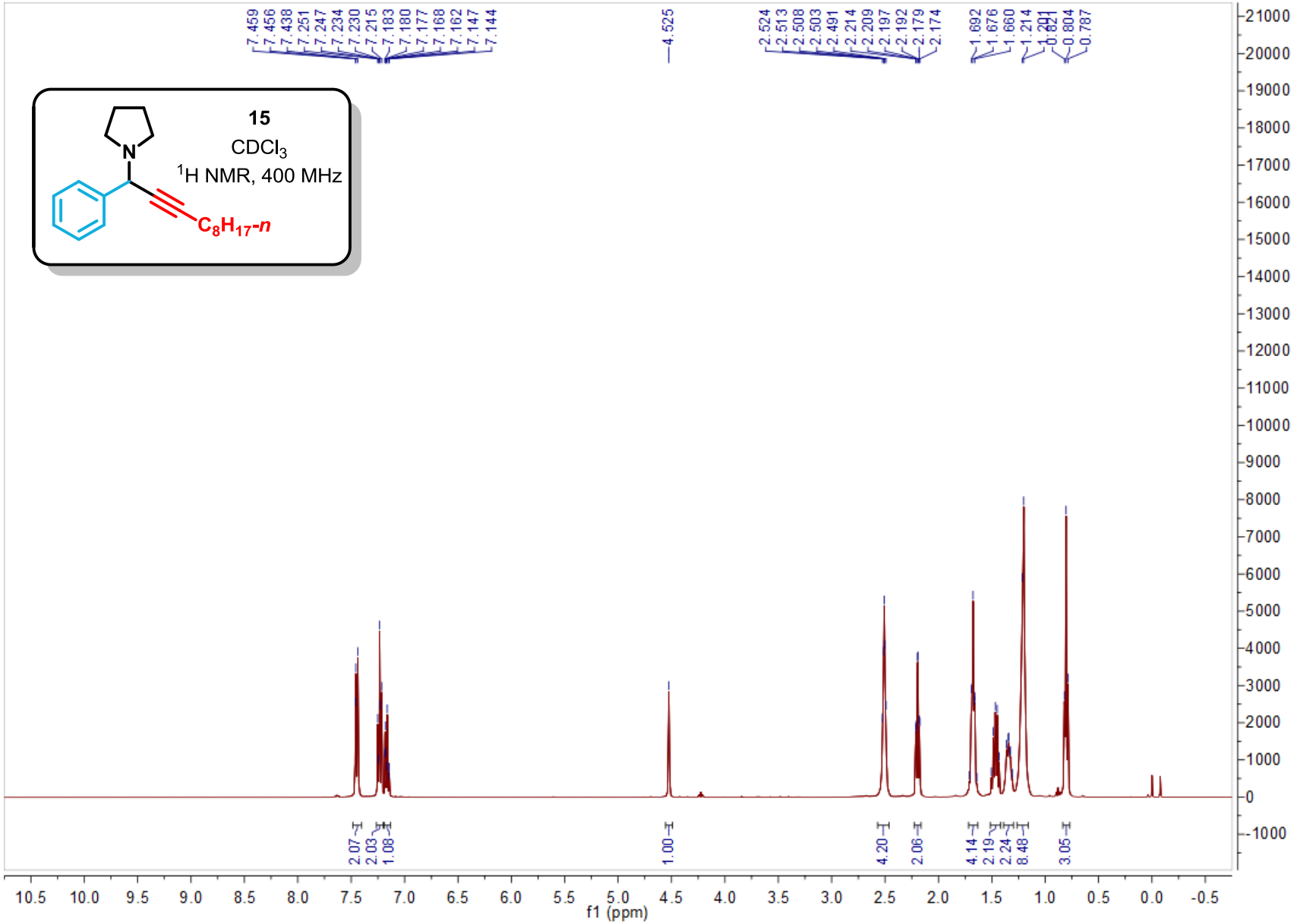

138.02
134.98
133.77
129.09
128.70
128.06
127.57
126.95
126.63
125.53
103.42
90.69
59.20
54.27
45.49
28.76
0.00
Si
6i
CDCl3
13C NMR, 100 MHz
f1 (ppm)

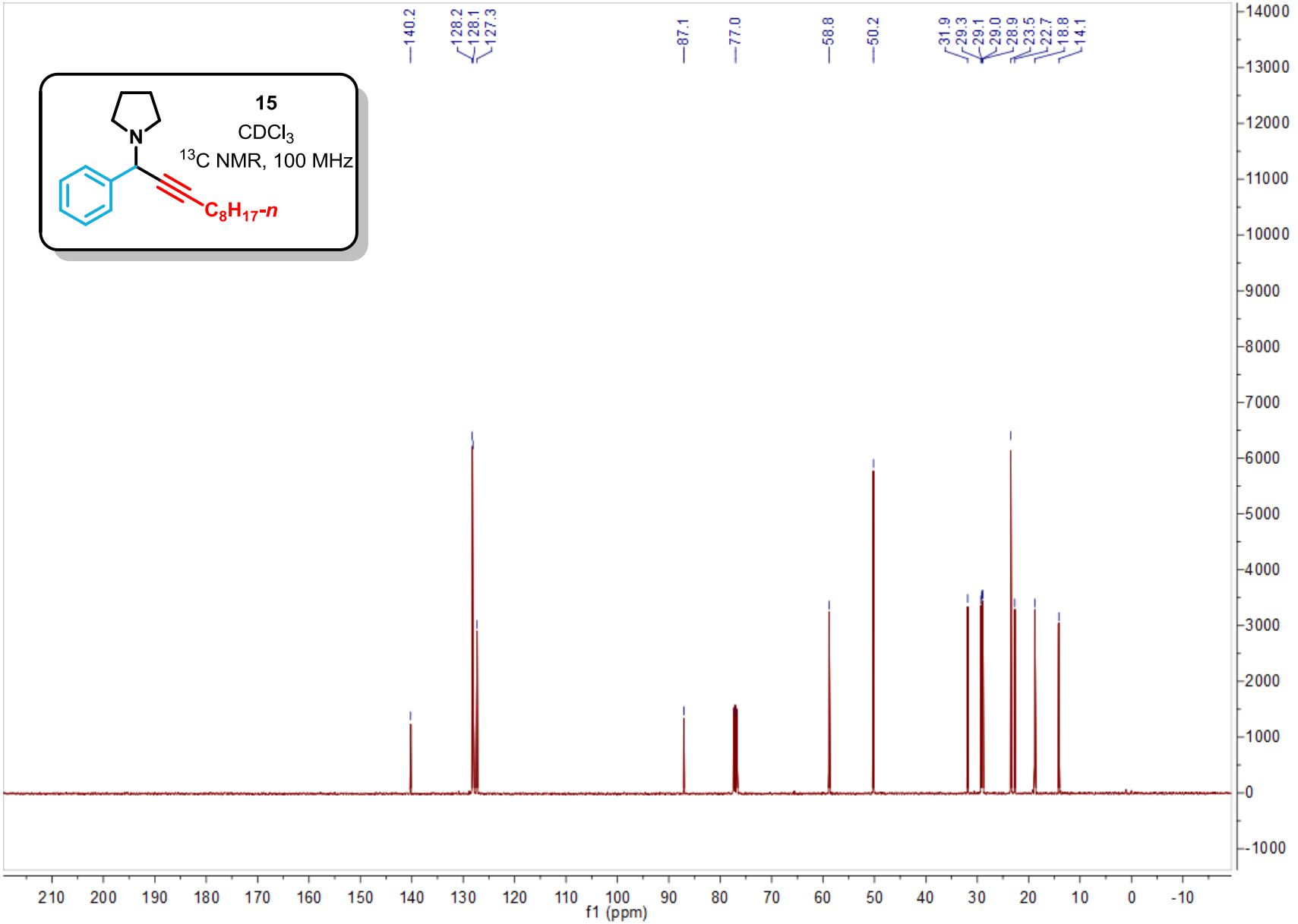

8.085
8.080
8.013
8.007
7.992
7.986
7.440
7.423
7.368
7.365
7.360
7.347
7.329
7.313
7.302
7.295
7.287
7.278
7.253
7.232
4.615
3.937
3.904
3.850
3.818
3.048
3.028
2.881
2.847
2.810
2.255
2.250
2.237
1.285
1.270
1.263
1.259
0.892
0.875
0.857
O2N
N
C8H17-n
11
CDCl3
1H NMR, 400 MHz
0.93
0.95
1.96
3.31
1.20
1.00
0.95
0.98
2.02
2.14
2.10
2.16
2.33
9.15
3.55
f1 (ppm)


146.13
142.07
138.05
137.97
129.87
129.24
128.43
127.39
123.02
121.55
88.80
76.68
59.34
53.85
44.97
31.89
29.44
29.31
29.14
28.98
28.90
22.73
18.85
14.18
O2N
N
C8H17-n
11
CDCl3
13C NMR, 100 MHz
f1 (ppm)


13
CDCl3
C8H17-n
1H NMR, 400 MHz
f1 (ppm)


138.52
136.16
132.25
129.39
128.36
127.27
127.23
121.73
119.43
118.41
110.97
108.36
87.37
76.26
58.83
50.11
47.14
31.92
29.32
29.18
29.07
28.93
22.74
21.50
18.92
14.18
13
CDCl3
C8H17-n
13C NMR, 100 MHz
f1 (ppm)

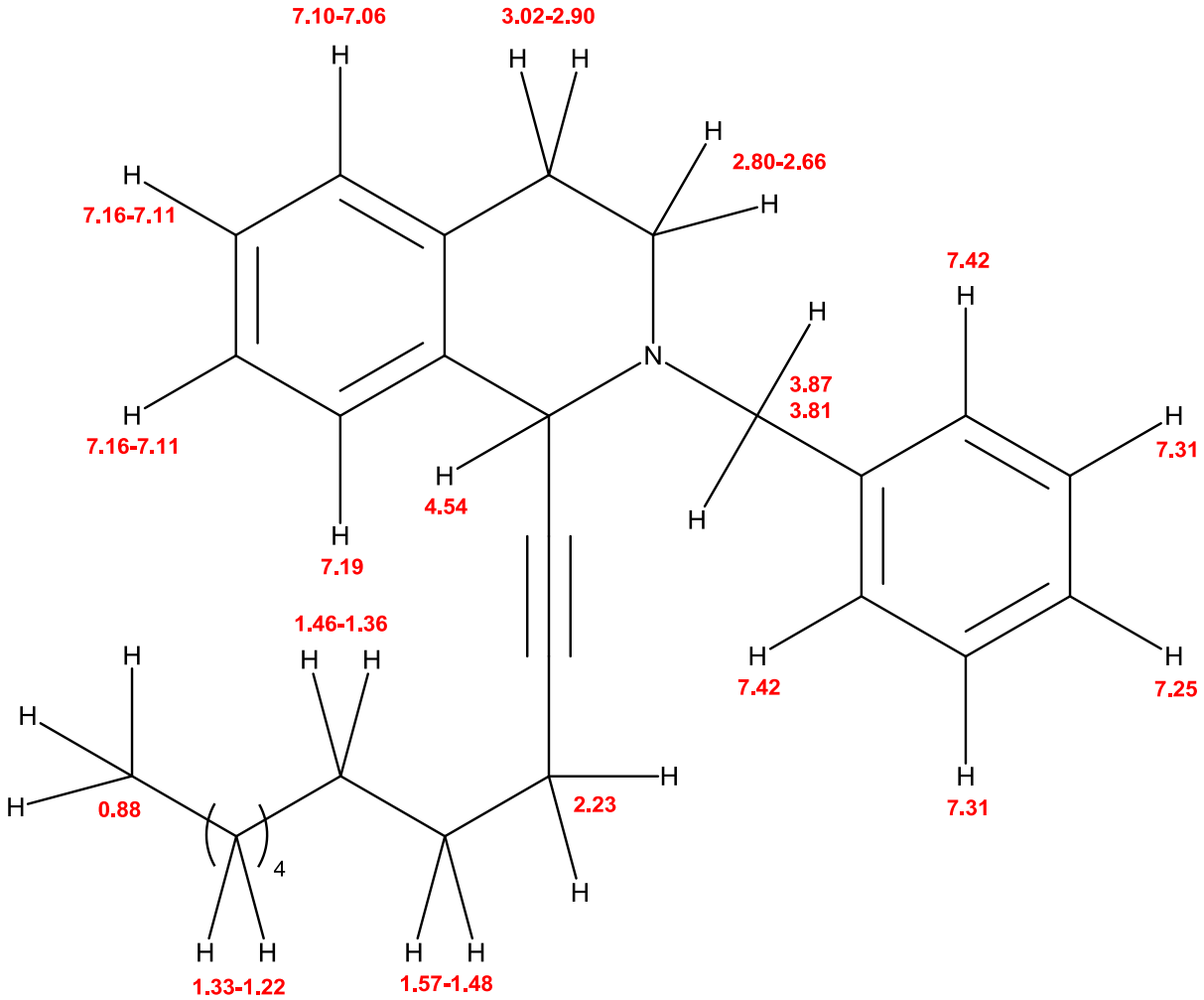

15
CDCl3
1H NMR, 400 MHz
C8H17-n
7.459
7.456
7.438
7.251
7.247
7.234
7.230
7.215
7.183
7.180
7.177
7.168
7.162
7.147
7.144
4.525
2.524
2.513
2.508
2.503
2.491
2.214
2.209
2.197
2.192
2.179
2.174
1.692
1.676
1.660
1.214
1.201
0.821
0.804
0.787
2.07
2.03
1.08
1.00
4.20
2.06
4.14
2.19
2.24
8.48
3.05
f1 (ppm)

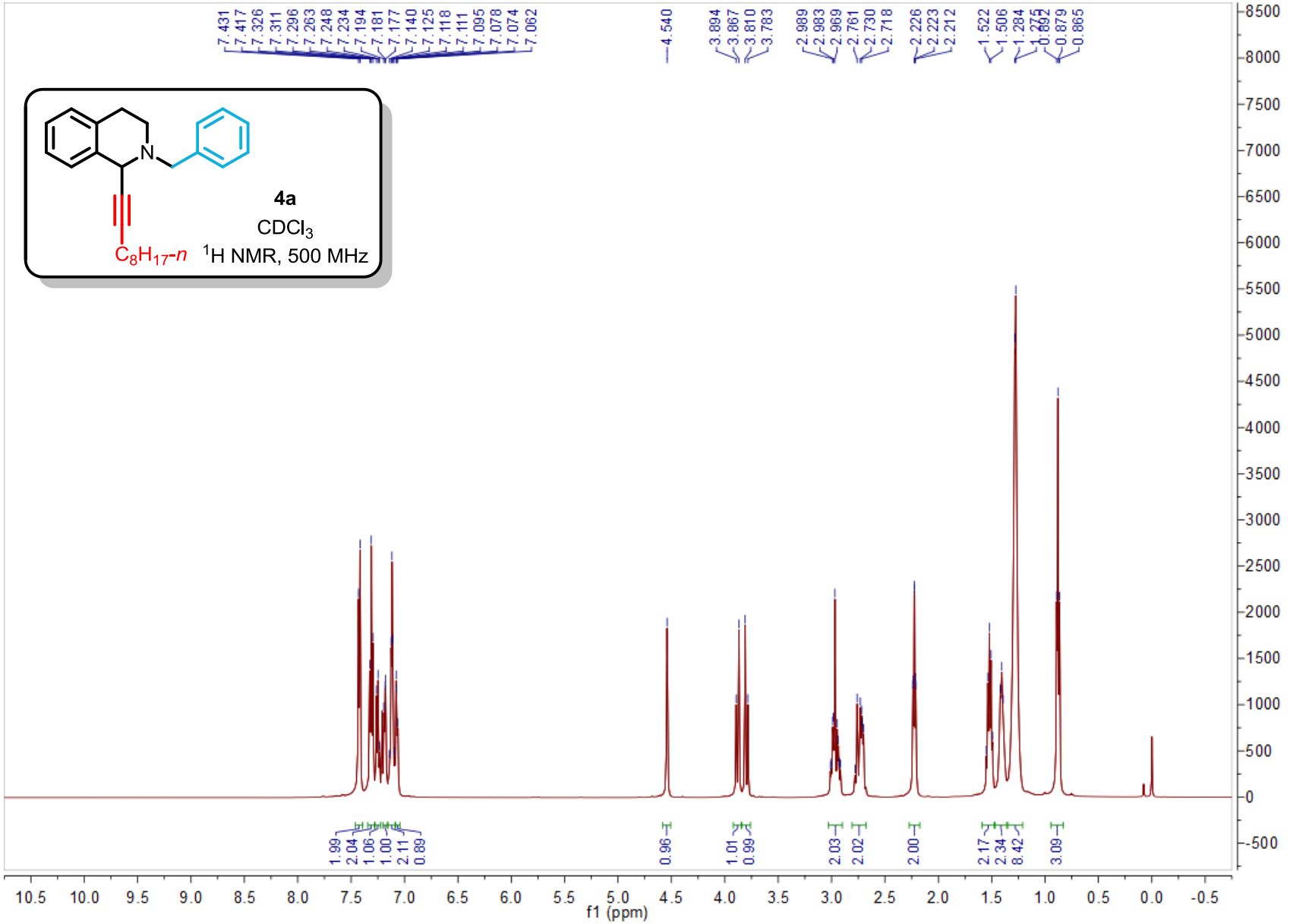

15
CDCl3
13C NMR, 100 MHz
C8H17-n
140.2
128.2
128.1
127.3
87.1
77.0
58.8
50.2
31.9
29.3
29.1
29.0
28.9
23.5
22.7
18.8
14.1
f1 (ppm)

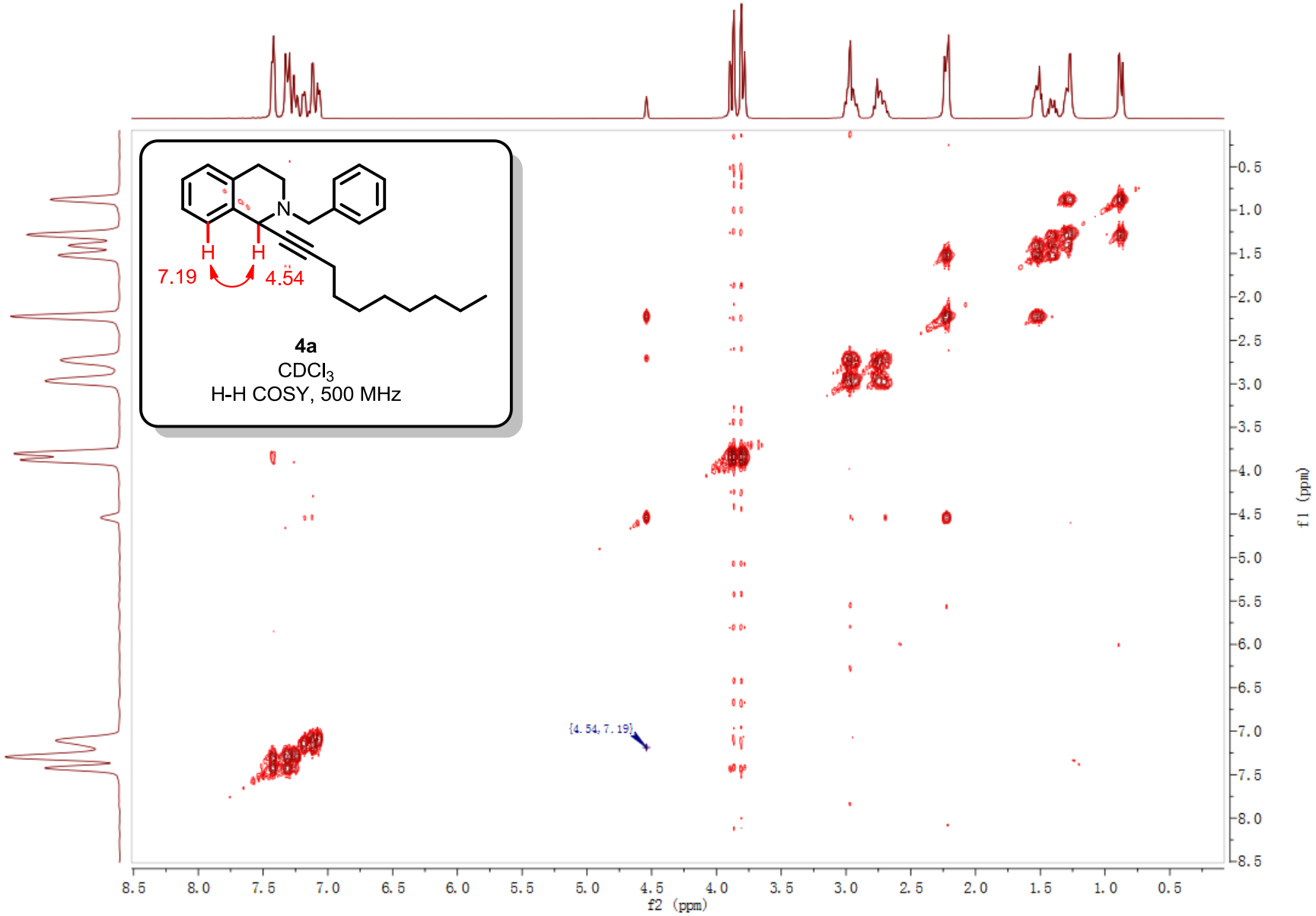
3.2 2-D NMR Spectra of Product 4a Elucidating the *Endo*-Configuration

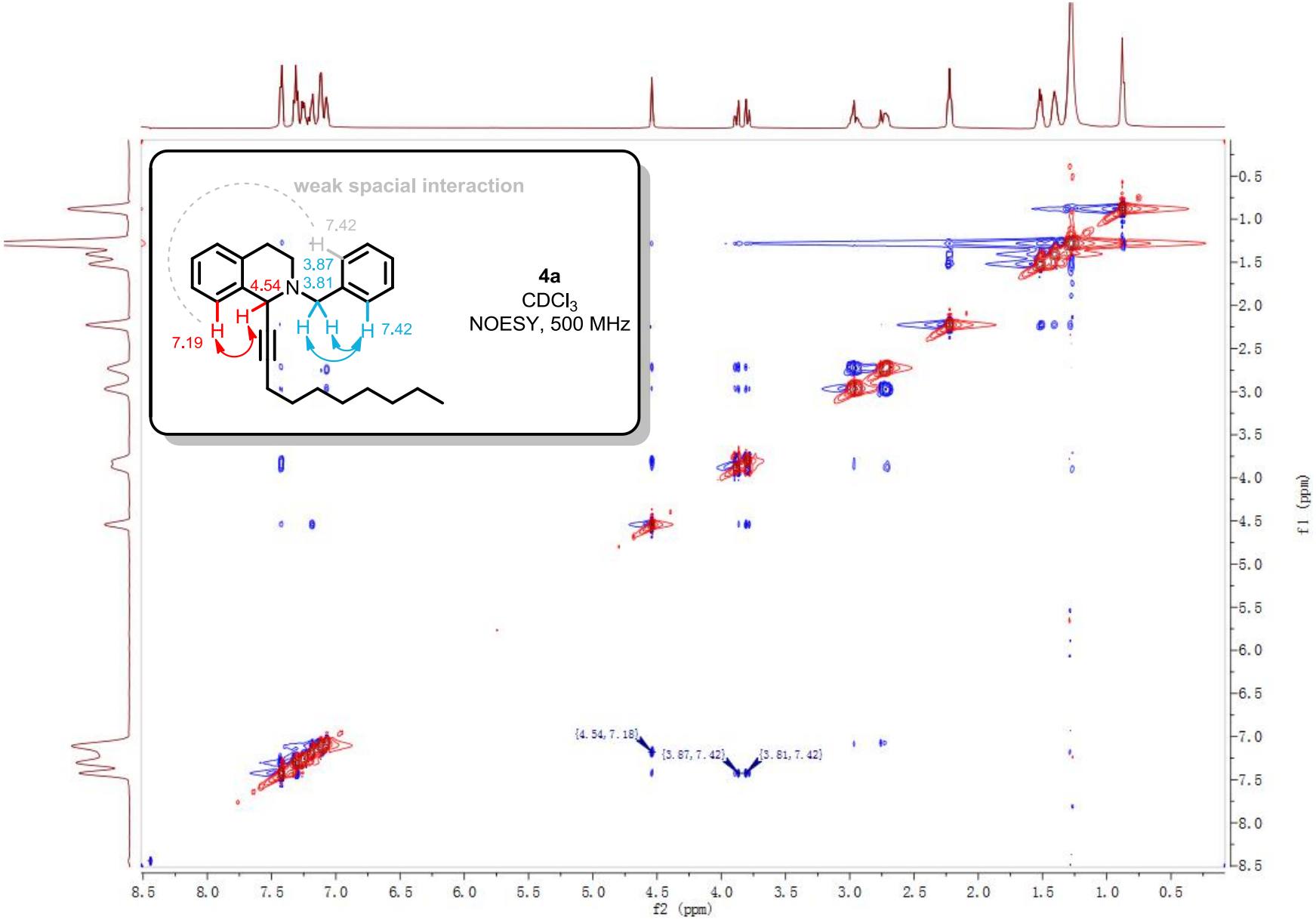
Compound 4a:

^{1}H NMR, 500 MHz (δ in ppm)




4a
CDCl3
C8H17-n
1H NMR, 500 MHz
f1 (ppm)

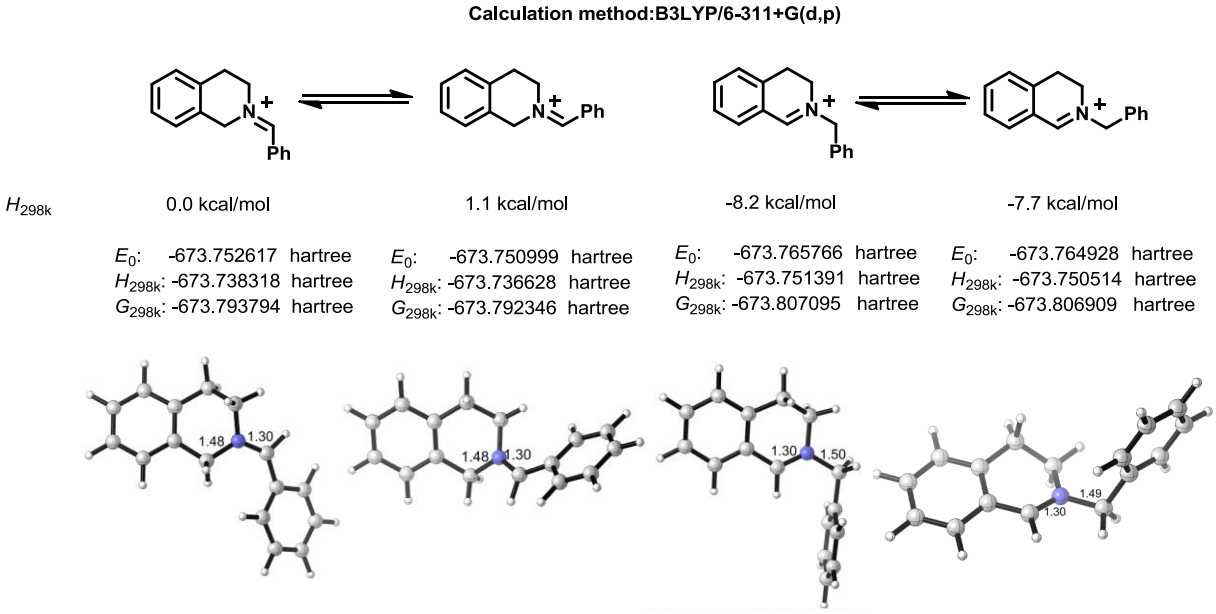

H
H
7.19
4.54
4a
CDCl3
H-H COSY, 500 MHz
[4.54, 7.19]
f2 (ppm)
f1 (ppm)


weak spacial interaction
7.42
3.87
3.81
4.54
7.19
7.42
4a
CDCl3
NOESY, 500 MHz
{4.54, 7.18}
{3.87, 7.42}
{3.81, 7.42}
f2 (ppm)
f1 (ppm)

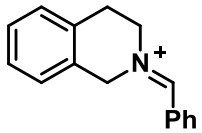
4. DFT Computed Energies, Structures, and Coordinates of *Exo* and *Endo* Iminium Ions

4.1 Computational Methods and Results

All DFT calculations were carried out with the Gaussian 09 program package.[4] The geometry optimizations of all the minima were performed at the B3LYP level[5] of theory with the 6-311+G(d,p) basis set.[6] The vibrational frequencies were computed at the same level of theory to check whether every optimized structure is an energy minimum and to evaluate its zero-point vibration energy (ZPE). Computed structures are illustrated using CYLVIEW drawings.[7] The computed relative enthalpies at 298K are given below. E_0 is the ZPE-corrected electronic energy, while H_{298K} and G_{298K} are enthalpy and Gibbs free energy at 298K in the gas phase, respectively.

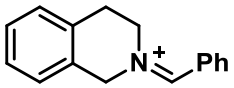


4.2 DFT Computed Coordinates of *Exo*- and *Endo*-Iminium Ions



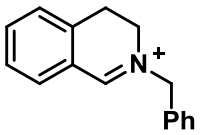
C	-0.90855600	2.03006000	0.82896100
C	-2.03895100	1.96870700	-0.19100500
C	-2.67272900	0.59702400	-0.21222600
C	-1.94134900	-0.51842000	0.20422700
C	-0.49870100	-0.42979100	0.67217800
H	-4.56540900	1.28592200	-0.96341300
H	-0.37116300	2.97709900	0.79634300
H	-2.77902100	2.72856900	0.07254200
C	-3.99234200	0.42201400	-0.64382400
C	-2.53140500	-1.78713300	0.19061300

H	0.12578800	-1.08303700	0.06358500
C	-3.84172600	-1.94907100	-0.24082500
C	-4.57472500	-0.83901400	-0.66237700
H	-1.96406400	-2.65283400	0.51820200
H	-4.29054000	-2.93491300	-0.24696400
H	-5.59803700	-0.95766700	-0.99753200
H	-1.65346900	2.23590400	-1.18206700
H	-1.29351100	1.88553600	1.84249600
N	0.06466400	0.93530800	0.58013300
H	-0.41591600	-0.75493300	1.71582700
C	1.30111800	1.21627100	0.28711200
H	1.49243400	2.27995900	0.17062000
C	2.44688000	0.36321700	0.07833600
C	2.61290500	-0.93974200	0.59815700
C	3.50093900	0.94099500	-0.66526200
C	3.78160300	-1.64168200	0.34700500
H	1.86429100	-1.38549700	1.23680600
C	4.65314500	0.21952300	-0.93618500
H	3.40118400	1.95401400	-1.03944200
C	4.79347500	-1.07361500	-0.43157000
H	3.91198500	-2.63256800	0.76429900
H	5.44570900	0.66567700	-1.52382600
H	5.69961800	-1.63445000	-0.62829600



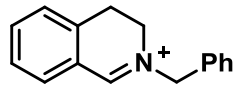
C	-0.13396200	1.12875900	-0.77168700
C	-1.17982500	1.59392700	0.24609200
C	-2.43724800	0.75540800	0.22559000
C	-2.41760900	-0.53844200	-0.30212400
C	-1.16827900	-1.12093600	-0.92945500
H	-3.65383700	2.25263400	1.17543700
H	-0.46551500	1.31916500	-1.79598600
H	-0.73164800	1.57882100	1.24633100

C	-3.63063100	1.24911600	0.76381200
C	-3.57715600	-1.32032600	-0.29158600
H	-1.26159900	-1.14696400	-2.02184700
C	-4.75671900	-0.81854700	0.24450200
C	-4.78263700	0.47201500	0.77421300
H	-3.55823100	-2.32437300	-0.70364100
H	-5.65089400	-1.42988100	0.25016800
H	-5.69937800	0.87032000	1.19204700
H	-1.41211300	2.63937100	0.02621500
H	0.81037100	1.63344700	-0.60514600
N	0.05627900	-0.33445200	-0.63631000
H	-0.99829600	-2.14378400	-0.59077500
C	1.14362200	-0.93836000	-0.25903500
H	1.01316700	-1.99943700	-0.05862200
C	2.48379000	-0.43119900	-0.05525600
C	3.26745700	-1.13437300	0.88464900
C	3.06689400	0.63423400	-0.77345100
C	4.56905000	-0.73703700	1.15382400
H	2.84359000	-1.98121100	1.41321200
C	4.37978700	1.00194900	-0.52180300
H	2.52525900	1.13285700	-1.56603900
C	5.12538300	0.33252000	0.45249000
H	5.15467800	-1.26896600	1.89322200
H	4.83071900	1.80447900	-1.09245700
H	6.14826000	0.63243300	0.64739400



C	-1.05858100	2.23803300	-0.37030700
C	-2.36751700	1.90015100	0.33668900
C	-2.75428600	0.45672600	0.12404300
C	-1.71175200	-0.48970000	0.00797500
C	-0.34935100	-0.03599800	0.00989000

H	-4.88259300	0.71442600	0.21958900
H	-1.19229100	2.28803000	-1.45677500
H	-2.26715200	2.08665700	1.41323600
C	-4.06678300	0.00689900	0.12361400
C	-1.99316000	-1.86476000	-0.08911300
C	-3.31135100	-2.29538400	-0.09950600
C	-4.34231800	-1.35891800	0.00452500
H	-1.18067700	-2.57873000	-0.16758400
H	-3.54008900	-3.35016900	-0.18457800
H	-5.37293300	-1.69438000	-0.00093200
H	-3.14582300	2.57429700	-0.02600800
H	-0.66581500	3.19794800	-0.03543200
N	-0.01480400	1.21180100	-0.11612400
H	0.46278400	-0.74899600	0.10972300
C	1.40370200	1.70044300	-0.14157500
H	1.50407100	2.26561600	-1.07239700
H	1.48924800	2.41049900	0.68517800
C	2.44615800	0.62230800	-0.04548900
C	2.95640100	0.02859800	-1.20623100
C	2.92725600	0.21213400	1.20360600
C	3.92648100	-0.96690700	-1.11818300
H	2.60816100	0.35479200	-2.18130600
C	3.89678000	-0.78438700	1.29059900
H	2.55610100	0.68157800	2.10930300
C	4.39485500	-1.37540600	0.13014900
H	4.32452600	-1.41364600	-2.02144100
H	4.27137000	-1.08934500	2.26041600
H	5.15551700	-2.14416100	0.19775700



C	-0.14624100	1.15371400	-0.98801300
C	-1.11139700	1.67379700	0.07290000
C	-2.36183700	0.83160800	0.15066000

C	-2.23935900	-0.55052800	-0.11940000
C	-0.96783800	-1.06863200	-0.53365200
H	-3.71223200	2.37836900	0.77329000
H	-0.51354600	1.35911600	-1.99994800
H	-0.61921000	1.67101800	1.05318400
C	-3.59531900	1.32339300	0.55273700
C	-3.33801300	-1.41718900	0.03061900
C	-4.56538500	-0.90522200	0.42219200
C	-4.68997100	0.46225000	0.67926500
H	-3.22445300	-2.47647600	-0.17263600
H	-5.42057200	-1.56020000	0.53038900
H	-5.64852100	0.86355900	0.98725500
H	-1.35219100	2.71417900	-0.15374500
H	0.83753600	1.60728200	-0.87955400
N	0.02981600	-0.31909400	-0.89527500
H	-0.81119000	-2.14315900	-0.56553500
C	1.33390400	-0.88818300	-1.33614900
H	1.21427600	-1.97281300	-1.35703900
H	1.49837400	-0.54761300	-2.36162200
C	2.48033600	-0.46941700	-0.44420400
C	2.56968900	-0.95248900	0.86652500
C	3.47399000	0.38492800	-0.92956800
C	3.63390600	-0.57837800	1.68117200
H	1.81617800	-1.63236800	1.25257600
C	4.54216500	0.75677000	-0.11402900
H	3.42592700	0.74930100	-1.95087800
C	4.62068300	0.27829300	1.19145000
H	3.70030600	-0.96177100	2.69241100
H	5.31252800	1.41302700	-0.50094900
H	5.45221500	0.56390100	1.82469800

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2) For convenience to check these compounds, in the present Supporting Information, we have copied the same characterization data and NMR spectra of these compounds, which were also given in ref. 1.

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