Electronic Supplementary Information for

Photocatalytic Traceless C-N Bond Formation/ Cleavage Strategy Enabling (α-Chiral) Alkyl Aldehydes as Deoxygenative (Chiral) Alkyl Radical Equivalents

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Table of Contents

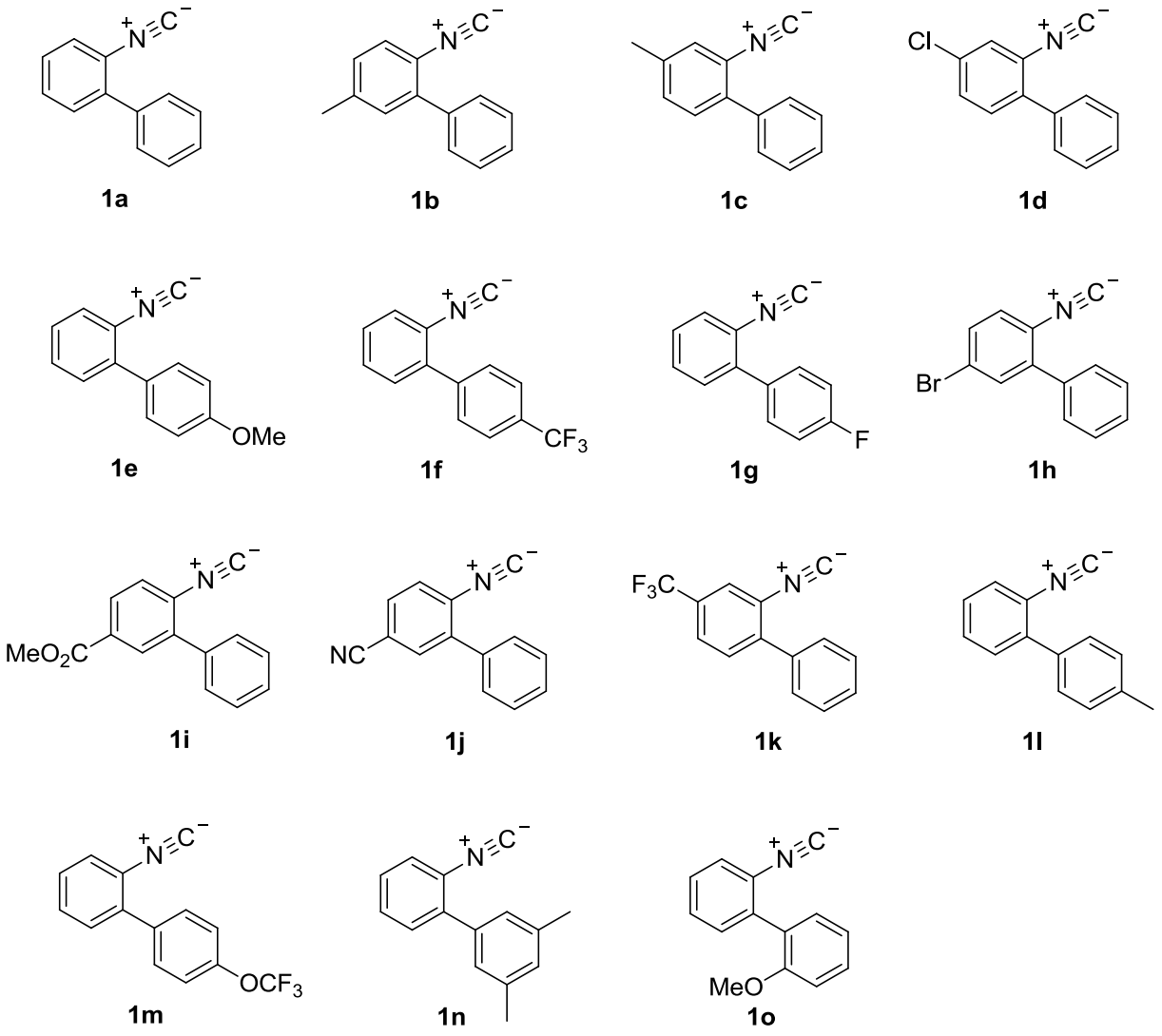
1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light, $KMnO_4$ indicator or phosphomolybdic acid indicator.

Melting points are uncorrected. ^1H NMR spectra were recorded on a spectrometer at 25 ^oC in $CDCl_3$ at 400, 500 or 600 MHz, with TMS as internal standard. ^{13}C NMR spectra were recorded on a spectrometer at 25 ^oC in $CDCl_3$ at 101, 125 or 150 MHz. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. High resolution mass spectra (HR-MS) were obtained on a TOF-MS instrument with EI or ESI source. Optical rotations were determined using a Rudolph Autopol IV polarimeter. HPLC analyses were performed using Agilent 1200 chromatography or Agilent 1260 chromatography.

2. Preparation of Substrates and Photosensitizers.

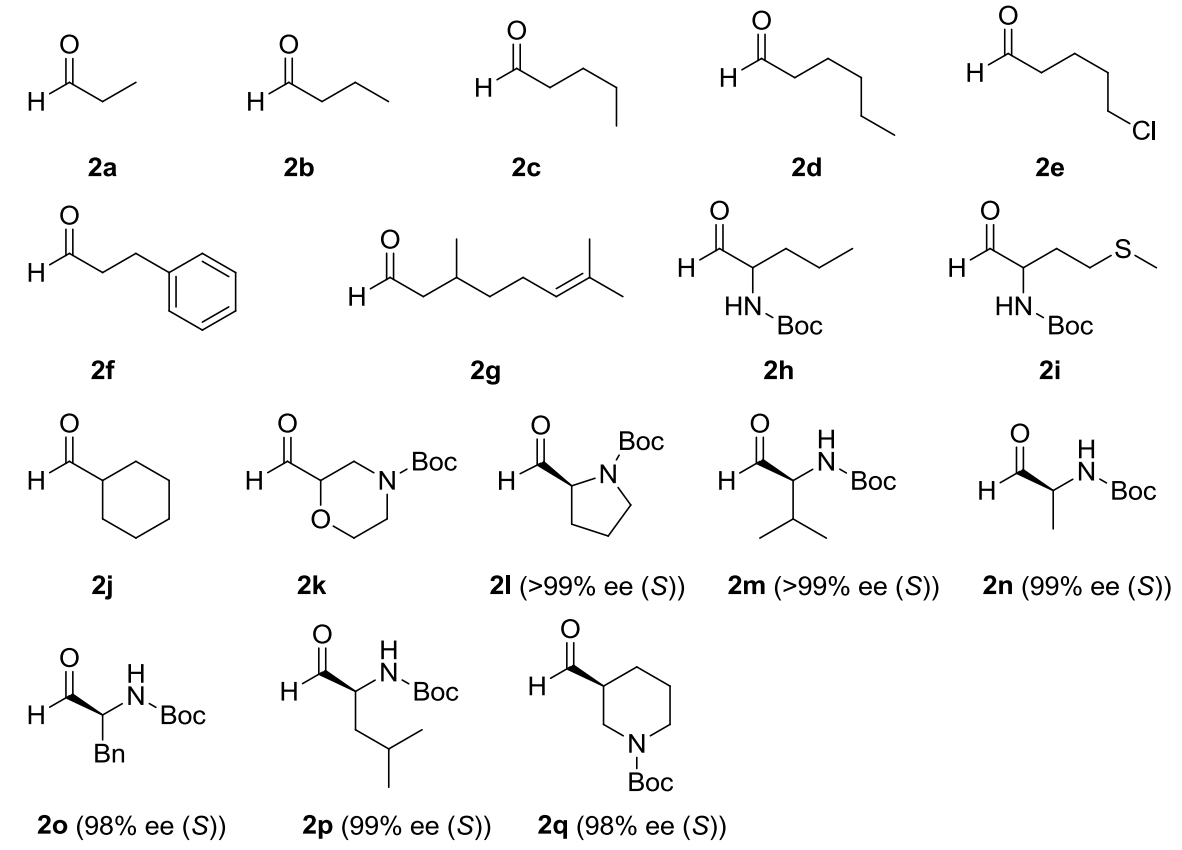
2-isocyanobiphenyls **1** were synthesized according to the previously reported procedure.[1] All of these compounds are known compounds and their NMR spectra are consistent with the documented data (**1a**[2], **1b**[1], **1c**[2], **1d**[2], **1e**[2], **1f**[2], **1g**[2], **1h**[3], **1i**[4], **1j**[5], **1k**[6], **1l**[2], **1m**[2], **1n**[7], **1o**[2]).



Aldehydes **2a-2g, 2j** are commercial available.

2h, 2i, 2k was prepared via reduction of corresponding Weinreb amide according to the literature[8] and their analytical data are consistent with the documented data (**2h**[8], **2i**[9], **2k**[10]).

N-Boc-L-prolinal (**2l**), *N*-Boc-L-valinal (**2m**), *N*-Boc-L-alaninal (**2n**), *N*-Boc-L-phenylalaninal (**2o**), *tert*-butyl (S)-1-formyl-3-methylbutylcarbamate (**2p**), (S)-*tert*-butyl 3-formylpiperidine-1-carboxylate (**2q**) are commercial available.



4CzIPN was prepared according to the literature and its analytical data are consistent with the documented data.[11]

3. General procedures for deoxygenative alkylation/cyclization of 2-biphenylisonitriles with (α-chiral) alkyl aldehydes

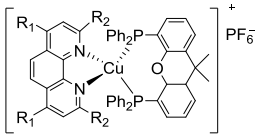
3.1 Optimization of reaction conditions for achiral alkyl aldehydes[a]

1a + 2a → 4a + 5

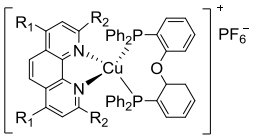
Entry	*PS* (x mol%)	Amine (**3**)	**1a**/**2a**/**3**	Solvent	Yield (**4a**/**5**)[b]
1	***PS1*** (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	36/12 (**5a**)
2	***PS2*** (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	53/15 (**5a**)
3	***PS3*** (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	65/21 (**5a**)

4	$Ru(bpy)_3Cl_2$ (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	23/12 (**5a**)
5	*fac*-$Ir(ppy)_3$ (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	20/trace (**5a**)
6	***PS4*** (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	0/0 (**5a**)
7	***PS5*** (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	53/16 (**5a**)
8	Rose begal (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	0/0 (**5a**)
9	4CzIPN (7.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	75/trace (**5a**)
10	4CzIPN (5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	75/trace (**5a**)
11	4CZIPN (2.5)	diethylamine (**3a**)	1/4.5/4.5	1,4-dioxane	61/trace (**5a**)
12	**4CzIPN (5)**	**dipropylamine (3b)**	**1/4.5/4.5**	**1,4-dioxane**	**82**/trace (**5b**)
13	4CzIPN (5)	pyrrolidine (**3c**)	1/4.5/4.5	1,4-dioxane	48/trace (**5c**)
14	4CzIPN (5)	piperidine (**3d**)	1/4.5/4.5	1,4-dioxane	81/trace (**5d**)
15	4CzIPN (5)	methyl 2-piperidinecarboxylate (**3e**)	1/4.5/4.5	1,4-dioxane	81/trace (**5e**)
16	4CzIPN (5)	hexamethyleneimine (**3f**)	1/4.5/4.5	1,4-dioxane	59/trace (**5f**)
20	4CzIPN (5)	dipropylamine (**3b**)	1/3/3	1,4-dioxane	72/trace (**5a**)
21	4CzIPN (5)	dipropylamine (**3b**)	1/1.5/1.5	1,4-dioxane	44/trace (**5a**)
22	4CzIPN (5)	dipropylamine (**3b**)	1/4.5/4.5	THF	70/trace (**5a**)
23	4CzIPN (5)	dipropylamine (**3b**)	1/4.5/4.5	EA	74/trace (**5a**)
24[c]	4CzIPN (5)	dipropylamine (**3b**)	1/4.5/4.5	1,4-dioxane	0/0 (**5b**)
24	--	dipropylamine (**3b**)	1/4.5/4.5	1,4-dioxane	0/0 (**5b**)
25	4CzIPN (5)	--	1/4.5/--	1,4-dioxane	0/0 (**5b**)
26[d]	4CzIPN (5)	dipropylamine (**3b**)	1/4.5/4.5	1,4-dioxane	61/ trace (**5b**)

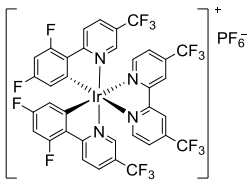
[a] Reaction condition: **1a** (0.2 mmol), ***PS*** (x mol %), Hantzsch ester (0.24 mmol), propionaldehyde **2a** (0.9 mmol), amine **3** (0.9 mmol) in solvent (5.0 mL), irradiated with 15 W blue LED at 25 ˚C under nitrogen atmosphere for 14 h unless otherwise noted. [b] Isolated yield. [c] The reaction was carried out in the dark condition. [d] Hantzsch ester (0.5 equiv. based on **1a**) was used.



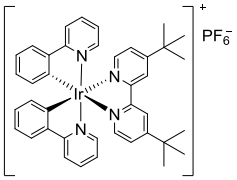
PS1: R_1 = Ph, R_2 = *i*-Pr;
PS3: R_1 = Ph, R_2 = Me;



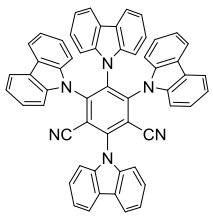
PS2: R_1 = Ph, R_2 = Me



PS4

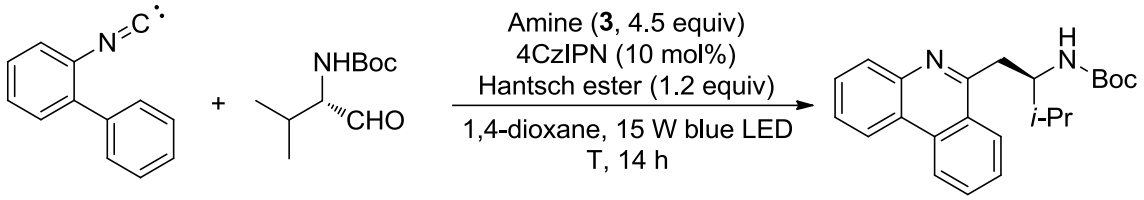


PS5



4CzIPN

3.2 Optimization of reaction conditions for acyclic α-chiral amino aldehyde.[a]



1a **2m** (ee >99%) **4zd**

Entry	Amine (3)	Temperature (˚C)	Yield (%)[b]	*ee* (%)[c]
1	pyrrolidine (**3c**)	35	30	12
2	piperidine (**3d**)	35	72	46
3	methyl piperidine-2-carboxylate (**3e**)	35	71	72
4	hexamethyleneimine (**3f**)	35	63	<10
5	methyl *L*-prolinate (**3g**)	35	85	74
6	dicyclohexylamine (**3h**)	35	63	<10
7	dibenzylamine (**3i**)	35	27	29
8	methyl L-prolinate (**3g**)	25	83	90
9	**methyl *L*-prolinate (3g)**	**15**	**83**	**96**
10	--	15	0	--
11[d]	methyl L-prolinate (**3g**)	15	73	96

[a] Reaction condition: **1a** (0.2 mmol), 4CzIPN (10 mmol%), amine **3** (0.9 mmol), ***tert***-butyl (*S*)-(3-methyl-1-oxobutan-2-yl)carbamate **2m** (0.9 mmol), Hantzsch ester (0.24 mmol) in 1, 4-dioxane (5.0 mL), irradiated with 15 W blue LED under nitrogen atmosphere for 14 h unless otherwise noted. [b] Isolated yield. [c] The *ee* value was determined by HPLC analysis. [d] Without Hantzsch ester.

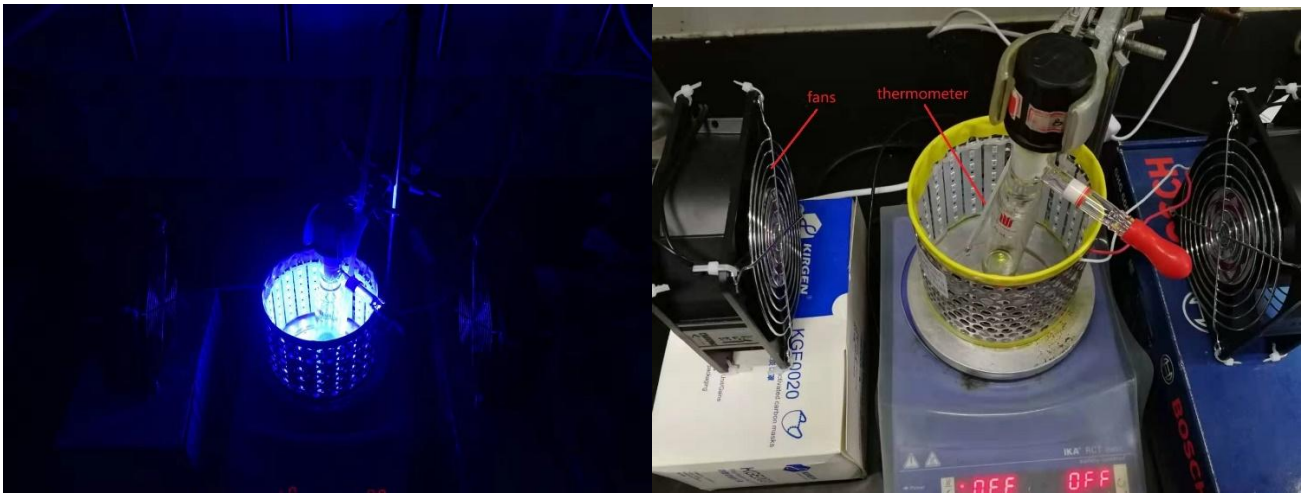
3.3 Experimental details and characterization of products 4

General procedure for the synthesis of 6-alkyl phenanthridine derivatives 4.

To a 25 mL flame-dried Schlenk tube was added **1** (0.3 mmol), 4CzIPN (0.015 mmol for achiral alkyl aldehydes or 0.03 mmol for chiral alkyl aldehydes) and Hantzsch ester (91.2 mg, 0.36 mmol). The tube was evacuated and refilled with N_2 for three times. A solution of aldehyde **2** (1.35 mmol), amine **3** (1.35 mmol) in 1,4-dioxane (7.5 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED and stirred at 25 ˚C (for **4zd**-**4zg**, at 15 ˚C) 14 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated

mixture of ethyl acetate (EA)/petroleum ether (PE) or DCM to give pure 6-alkyl phenanthridine **4**.

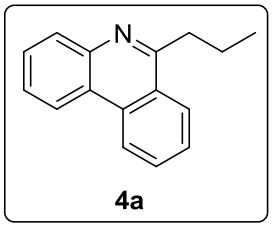
Reaction Setup:



15 W blue LED strips come with an adhesive back, so they may be easily adhered to the inside of a meshy cask. The Schlenk tube was placed in the center. Two fans were used to control the reaction temperature at room temperature. Meanwhile a thermometer was equipped to monitor the reaction temperature.

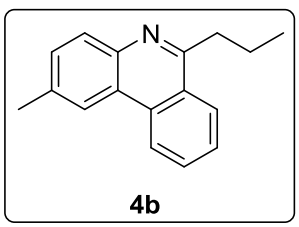
Characterization of products 4

6-propylphenanthridine (4a)



4a was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as a colorless liquid (55.8 mg, 84%). ^{1}H NMR (500 M, $CDCl_3$): δ 8.67 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H), 8.14 (dd, J = 8.2, 1.0 Hz, 1H), 7.85 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 7.72 (dddd, J = 9.2, 8.2, 7.0, 1.3 Hz, 2H), 7.64 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 3.40-3.31 (m, 2H), 1.99 (dq, J = 15.0, 7.4 Hz, 2H), 1.15 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.3, 143.7, 132.9, 130.2, 129.6, 128.6, 127.2, 126.34, 126.25, 125.3, 123.6, 122.5, 121.9, 38.3, 22.9, 14.4. Its analytical data are consistent with the documented data.[12]

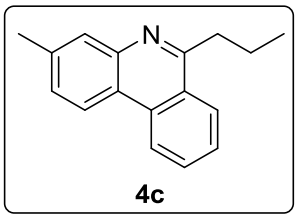
2-methyl-6-propylphenanthridine (4b)



4b was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as a colorless liquid (50.8 mg, 72%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.64 (d, J = 8.3 Hz, 1H), 8.34 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 3.44-3.24 (m, 2H), 2.63 (s, 3H), 1.98 (dq, J = 14.9, 7.3 Hz, 2H), 1.15 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.3, 142.1, 136.0, 132.7, 130.2, 130.0,

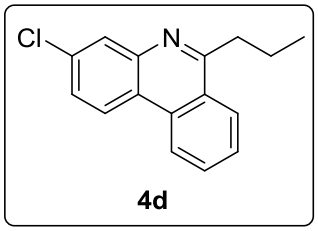
129.3, 127.0, 126.3, 125.3, 123.5, 122.4, 121.6, 38.3, 23.0, 21.9, 14.4. HRMS (ESI) for $C_{17}H_{18}N$ $[M+H]^+$: calcd 236.1434, found 236.1486.

3-methyl-6-propylphenanthridine (4c):



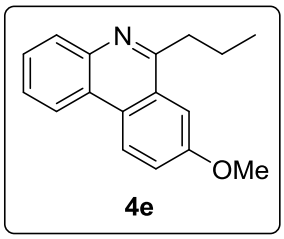
4c was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as a colorless liquid (45.0 mg, 64%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.95 (s, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.3 Hz, 1H), 3.36-3.33 (m, 2H), 2.59 (s, 3H), 2.01-1.94 (m, 2H), 1.15 (t, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.2, 143.8, 138.6, 133.0, 130.1, 129.2, 127.9, 126.7, 126.3, 125.0, 122.2, 121.7, 121.3, 38.3, 22.9, 21.5, 14.4. HRMS (ESI) for $C_{17}H_{18}N$ $[M+H]^+$: calcd 236.1434, found 236.1495.

3-chloro-6-propylphenanthridine (4d)



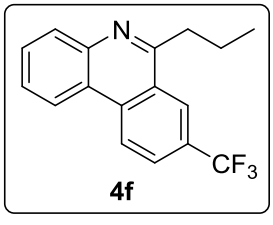
4d was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as a colorless liquid (48.3 mg, 63%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.57 (d, *J* = 8.3 Hz, 1H), 8.45 (d, *J* = 8.7 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 3.41-3.24 (m, 2H), 2.05-1.86 (m, 2H), 1.14 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.6, 144.5, 134.1, 132.5, 130.6, 128.9, 127.5, 126.8, 126.4, 125.2, 123.3, 122.4, 122.1, 38.2, 22.6, 14.4. HRMS (ESI) for $C_{16}H_{15}ClN$ $[M+H]^+$: calcd 256.0888, found 256.0916.

8-methoxy-6-propylphenanthridine (4e)



4e was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as a white solid (53.5 mg, 71%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.57 (d, *J* = 9.0 Hz, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 14.0, 5.0 Hz, 2H), 7.48 (dd, *J* = 8.9, 1.9 Hz, 1H), 4.02 (s, 3H), 3.47-3.20 (m, 2H), 2.29-1.92 (m, 2H), 1.15 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.3, 158.6, 142.9, 129.6, 127.6, 127.3, 126.6, 126.3, 124.2, 123.7, 121.4, 120.3, 107.0, 55.5, 38.4, 22.5, 14.5. Its analytical data are consistent with the documented data.[13]

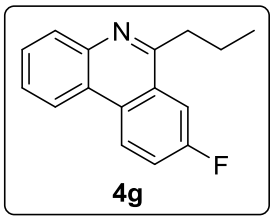
6-propyl-8-(trifluoromethyl)phenanthridine (4f)



4f was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as yellow liquid (43.4 mg, 50%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.75 (d, *J* = 8.6 Hz, 1H), 8.56 (d, *J* = 8.1 Hz, 1H), 8.52 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 3.39 (t, *J* = 7.7 Hz, 2H), 2.12-1.92 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.9, 144.5, 135.2, 129.9, 129.8, 129.0 (q, *J* = 32.8 Hz), 126.9, 126.1 (q, *J* =

3.0 Hz), 124.7, 124.1 (q, J = 270.0 Hz), 123.7 (q, J = 4.2 Hz), 123.6, 122.7, 122.3, 38.0, 22.6, 14.3. HRMS (ESI) for $C_{17}H_{15}F_3N$ $[M+H]^+$: calcd 290.1151, found 290.1218.

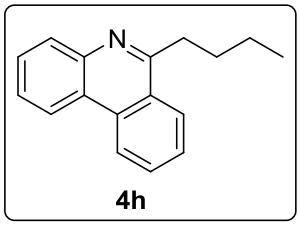
8-fluoro-6-propylphenanthridine (4g)



4g

4g was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (41.6 mg, 58%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.64 (dd, J = 9.1, 5.4 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.15-8.13 (m, 1H), 7.88-7.86 (m, 1H), 7.73-7.70 (m, 1H), 7.65-7.56 (m, 3H), 3.32-3.28 (m, 2H), 2.01-1.94 (m, 2H), 1.14 (t, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.4 (d, J = 246.6 Hz), 161.3 (d, J = 3.5 Hz), 143.4, 129.7, 129.6, 128.5, 126.7, 126.6, 125.0 (d, J = 8.7 Hz), 123.2, 121.7, 119.4 (d, J = 23.7 Hz), 110.9 (d, J = 21.0 Hz), 38.3, 22.6, 14.4. HRMS (ESI) for $C_{16}H_{15}FN$ $[M+H]^+$: calcd 240.1183, found 240.1252.

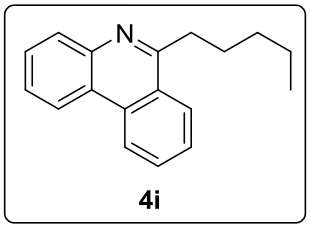
6-butylphenanthridine (4h)



4h

4h was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (56.5 mg, 80%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.66 (d, J = 8.2 Hz, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.72 (q, J = 8.4 Hz, 2H), 7.63 (t, J = 8.2 Hz, 1H), 3.45-3.22 (m, 2H), 2.00-1.87 (m, 2H), 1.66-1.53 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.5, 143.8, 133.0, 130.3, 129.5, 128.6, 127.2, 126.4, 126.3, 125.3, 123.7, 122.5, 121.9, 36.2, 31.8, 23.1, 14.0. Its analytical data are consistent with the documented data.[14]

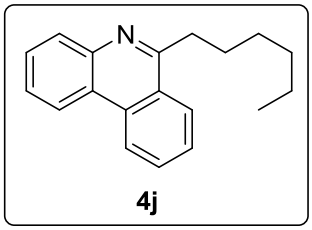
6-pentylphenanthridine (4i)



4i

4i was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (57.6 mg, 77%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.63 (d, J = 8.2 Hz, 1H), 8.54 (d, J = 8.1 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.82 (t, J = 7.5 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 3.46-3.25 (m, 2H), 1.96 (dt, J = 15.7, 7.8 Hz, 2H), 1.55 (dt, J = 15.1, 7.5 Hz, 2H), 1.49-1.39 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 162.5, 143.8, 133.0, 130.2, 129.6, 128.6, 127.2, 126.3, 126.2, 125.3, 123.7, 122.5, 121.9, 36.5, 32.2, 29.4, 22.6, 14.1. Its analytical data are consistent with the documented data.[15]

6-hexylphenanthridine (4j)

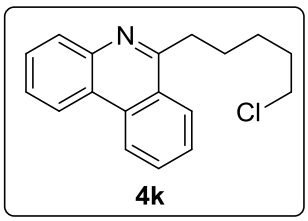


4j

4j was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (67.2 mg, 85%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.65 (d, J = 8.2 Hz, 1H), 8.55 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.76-7.68 (m,

2H), 7.63 (t, *J* = 7.5 Hz, 1H), 3.39 (t, *J* = 6.5 Hz, 2H), 1.99-1.90 (m, 2H), 1.62-1.52 (m, 2H), 1.46-1.31 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 162.5, 143.8, 133.0, 130.2, 129.6, 128.6, 127.2, 126.4, 126.2, 125.3, 123.7, 122.5, 121.9, 36.5, 31.8, 29.7, 29.6, 22.7, 14.1. Its analytical data are consistent with the documented data.[16]

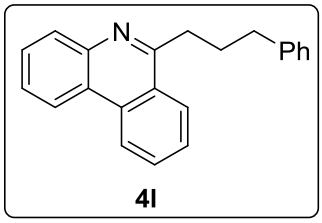
6-(5-chloropentyl)phenanthridine (4k)



4k

4k was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as Colorless liquid (67.3 mg, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.76-7.67 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.46-3.33 (m, 2H), 2.05-1.95 (m, 2H), 1.95-1.86 (m, 2H), 1.75-1.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.8, 143.7, 133.0, 130.3, 129.6, 128.6, 127.3, 126.4, 126.1, 125.2, 123.7, 122.5, 121.9, 45.0, 36.0, 32.6, 28.5, 27.2. HRMS (ESI) for $C_{18}H_{19}ClN$ $[M+H]^+$: calcd 284.1201, found 284.1240.

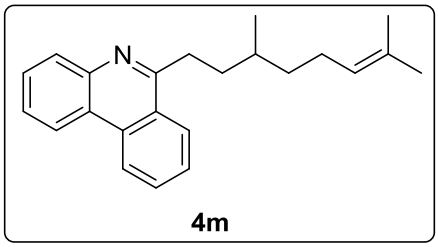
6-(3-phenylpropyl)phenanthridine (4l)



4l

4l was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (62.5 mg, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.15 (t, *J* = 8.7 Hz, 2H), 7.89-7.79 (m, 1H), 7.76-7.71 (m, 1H), 7.70-7.60 (m, 2H), 7.38-7.28 (m, 4H), 7.23 (t, *J* = 7.1 Hz, 1H), 3.49-3.35 (m, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.38-2.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.8, 143.7, 142.1, 132.9, 130.3, 129.6, 128.6, 128.4, 127.2, 126.3, 126.2, 125.9, 125.2, 123.7, 122.5, 121.9, 36.0, 35.6, 30.8. Its analytical data are consistent with the documented data.[17]

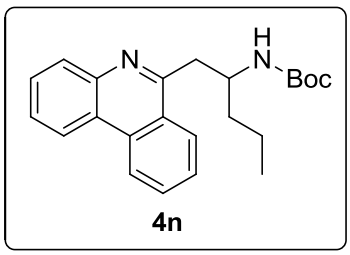
6-(3,7-dimethyloct-6-en-1-yl)phenanthridine (4m)



4m

4m was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (53.3 mg, 56%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.85 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.72 (qd, *J* = 6.9, 1.2 Hz, 2H), 7.63 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 5.25-5.02 (m, 1H), 3.53-3.25 (m, 2H), 2.15-1.89 (m, 3H), 1.81-1.67 (m, 5H), 1.62 (s, 3H), 1.57-1.46 (m, 1H), 1.37-1.22 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.8, 143.8, 133.0, 131.2, 130.3, 129.6, 128.6, 127.2, 126.33, 126.25, 125.2, 124.9, 123.7, 122.5, 121.9, 37.1, 36.7, 34.3, 33.1, 25.7, 25.6, 19.6, 17.7. HRMS (ESI) for $C_{23}H_{28}N$ $[M+H]^+$: calcd 318.2216, found 318.2259.

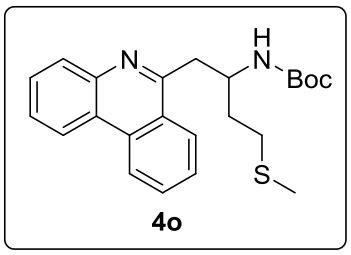
***tert*-butyl (1-(phenanthridin-6-yl)pentan-2-yl)carbamate (4n)**



4n

4n was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as white solid (92.8 mg, 85%). Mp:125-127°C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8,5 Hz, 1H), 8.55 (d, *J* = 7.5 Hz, 1H), 8.40 (d, *J* = 8 Hz, 1H), 8.14-8.12 (d, 1H), 7.85-7.82 (m, 1H), 7.74-7.70 (m, 2H), 7.65-7.62 (m, 1H), 5.27 (d, *J* = 7.5 Hz, 1H), 4.25 (d, *J* = 6.5 Hz, 1H), 3.63-3.59 (m, 1H), 3.51-3.46 (m, 1H), 1.67-1.61 (m, 2H), 1.54-1.47 (s, 2H), 1.34 (m, 9H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.2, 155.7, 143.4, 132.8, 130.4, 129.7, 128.5, 127.5, 126.5, 126.3, 125.7, 123.7, 122.4, 121.9, 78.8, 50.4, 40.9, 37.0, 28.3, 19.5, 14.0. HRMS (ESI) for $C_{23}H_{29}N_2O_2$ $[M+H]^+$: calcd 365.2224, found 365.2227.

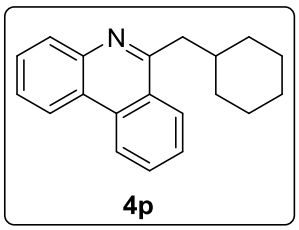
***tert*-butyl (4-(methylthio)-1-(phenanthridin-6-yl)butan-2-yl)carbamate (4o)**



4o

4o was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as white solid (73.7 mg, 62%). Mp:117-119 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8 Hz, 1H), 8.56 (d, *J* = 8Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.86 (t, *J* = 7 Hz, 1H), 7.75-7.71 (m, 2H), 7.66-7.63 (m, 1H), 5.46 (d, *J* = 7 Hz, 1H), 4.42-4.35 (m, 1H), 3.66-3.53 (m, 2H), 2.70-2.55 (m, 2H), 2.06 (s, 3H), 2.02-1.97 (m, 2), 1.35 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 158.7, 155.6, 143.3, 132.9, 130.6, 129.7, 128.6, 127.62, 127.61, 126.6, 126.2, 125.7, 123.7, 122.5, 122.0, 79.1, 49.8, 40.2, 34.2, 31.0, 28.3, 15.5. HRMS (ESI) for $C_{23}H_{29}N_2O_2S$ $[M+H]^+$: calcd 397.1944, found 397.1946.

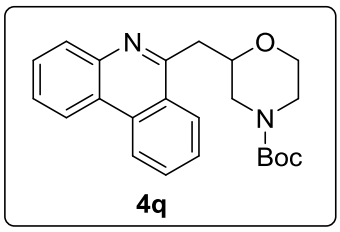
6-(cyclohexylmethyl)phenanthridine (4p)



4p

4p was isolated via column chromatography (eluent: PE/EA = 100/1 to PE/EA = 20/1) as colorless liquid (56.2 mg, 68%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.77-7.69 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 3.29 (d, *J* = 7.2 Hz, 2H), 2.04 (s, 1H), 1.72 (m, 5H), 1.22 (s, 5H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.5, 143.7, 132.9, 130.2, 129.6, 128.6, 127.1, 126.7, 126.3, 125.8, 123.6, 122.4, 121.9, 43.7, 38.8, 33.7, 26.5, 26.3. Its analytical data are consistent with the documented data.[18]

***tert*-butyl 2-(phenanthridin-6-ylmethyl)morpholine-4-carboxylate (4q)**

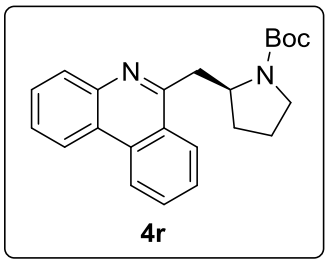


4q

4q was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (61.2 mg, 54%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.8-7.84 (m, 1H), 7.75-7.71 (m, 2H), 7.67-7.64 (m, 1H), 4.23-4.17 (m, 2H), 3.87 (d, *J* = 10.0 Hz, 2H), 3.71-3.67 (m, 1H), 3.55-3.42 (m, 2H),

3.03-2.87 (m, 2H), 1.44 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 154.7, 143.6, 132.9, 131.4, 130.4, 129.8, 128.6, 127.3, 126.6, 126.4, 125.8, 123.7, 122.4, 121.9, 79.9, 75.2, 66.7, 28.4. HRMS (ESI) for $C_{23}H_{27}N_2O_3$ $[M+H]^+$: calcd 379.2016, found .379.2020.

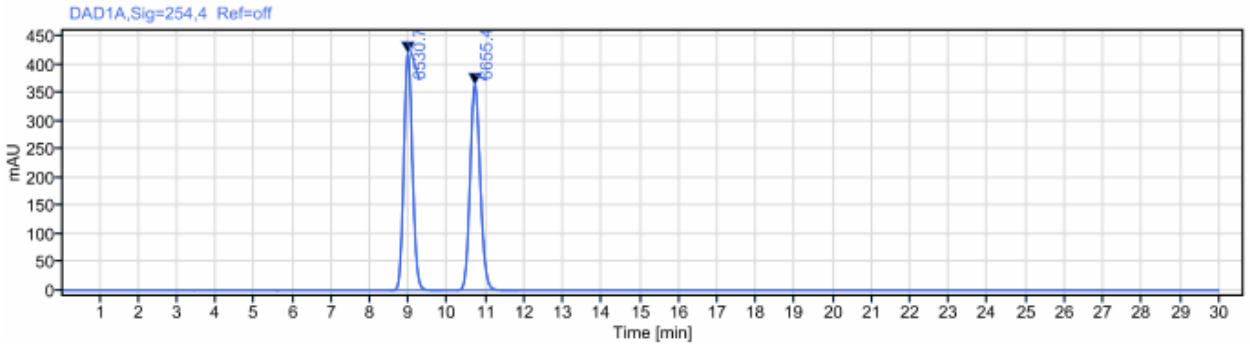
***tert*-butyl (*S*)-2-(phenanthridin-6-ylmethyl)pyrrolidine-1-carboxylate (4r)**



4r

4r was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (85.4 mg, 79%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* = 97% (HPLC: 254 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 10.69 min, t_r (min) = 8.97 min). $[\alpha]_D^{25}$ = +77.1 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {8.80 (d, *J* = 7.8 Hz) + 8.50 (d, *J* = 7.8 Hz)}, 8.67-8.62 (m, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.85-7.63 (m, 4H), 4.49-4.45 (m, 1H), {4.19 (d, *J* = 11.0 Hz, 0.5H) + 3.99 (dd, *J* = 12.8 Hz, J_2 = 3.6 Hz, 0.5 H)}, 3.51-3.32 (m, 2H), 3.18-3.09 (m, 1H), 2.09-1.67 (m, 4H), {1.54 (s, 4.5H) + 1.50 (s, 4.5 H)}; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9 & 159.4 (due to rotamer), 154.8 & 154.5 (due to rotamer), 143.8 & 143.7 (due to rotamer), 132.9 & 132.7 (due to rotamer), 130.4 , 129.8 & 129.7 (due to rotamer), 128.6 & 128.4 (due to rotamer), 127.84 & 127.82 (due to rotamer), 127.5 & 127.4 (due to rotamer), 127.2 & 127.1 (due to rotamer), 126.7 & 126.6 (due to rotamer), 126.6 & 126.5 (due to rotamer), 125.8 & 125.6 (due to rotamer), 122.4 & 122.0 (due to rotamer), 121.9, 79.8 & 79.1 (due to rotamer), 57.1 & 56.9 (due to rotamer), 46.9 & 46.5 (due to rotamer), 41.2 & 40.4 (due to rotamer), 30.0 & 28.9 (due to rotamer), 28.7, 23.5 & 22.7 (due to rotamer). HRMS (ESI) for $C_{23}H_{26}N_2O_2$ $[M+H]^+$: calcd 363.2067, found 363.2069. Its analytical data are consistent with the documented data.[19]

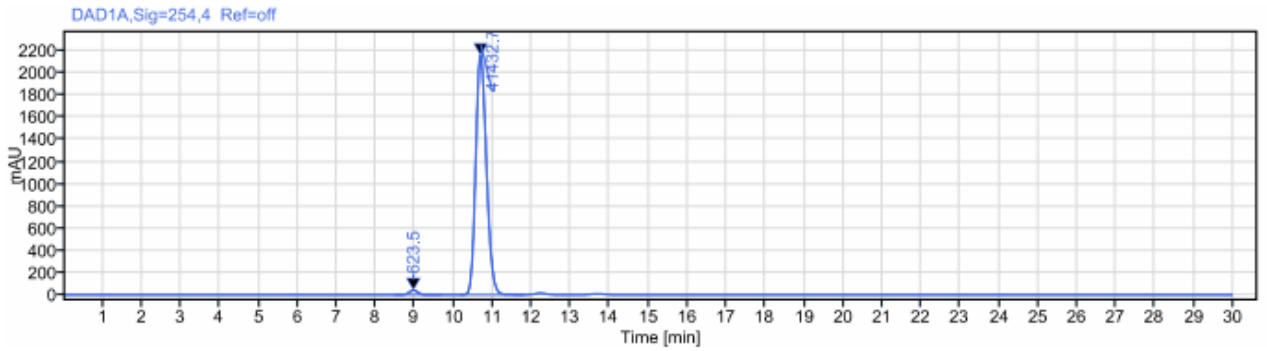
Chiral HPLC Charts for **4r**:



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.972	BB	1.39	6530.703	420.19	49.5273	
10.709	VBA	1.60	6655.374	364.26	50.4727	

Figure *S1*. The HPLC chart of rac-**4r**



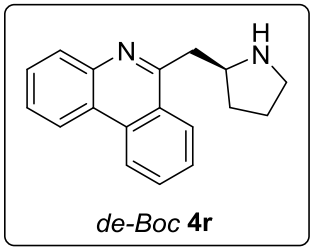
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.968	BB	1.18	623.450	40.57	1.4824	
10.691	VB	1.62	41432.673	2161.85	98.5176	

Figure *S2*. The HPLC chart of **4r**

Note: at RT, this compound appears as a mixture of rotamers. This phenomenon was widely observed in the *N*-Boc pyrrolidine derivatives.[19,20] And this phenomenon was disappeared when the protecting group (Boc) was removed. The NMR spectra of ***de-Boc*-4r** was listed as blow.

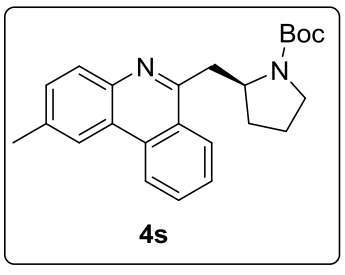
(*S*)-6-(pyrrolidin-2-ylmethyl)phenanthridine (*de-Boc*-4r)



de-Boc **4r**

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.60 Hz, 1H), 7.59-7.50 (m, 2H), 7.46-7.42 (m, 1H), 4.31-4.23 (m, 1H), 3.81-3.75 (m, 1H), 3.57-3.51 (m, 1H), 3.34-3.29 (m, 2H), 2.21-2.17 (m, 1H), 2.05-1.86 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.8, 145.6, 132.4, 130.7, 129.6, 128.6, 127.5, 126.8, 125.2, 124.7, 123.4, 122.2, 121.6, 58.2, 44.9, 35.1, 30.1, 23.4.

***tert*-butyl (*S*)-2-((2-methylphenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4s)**

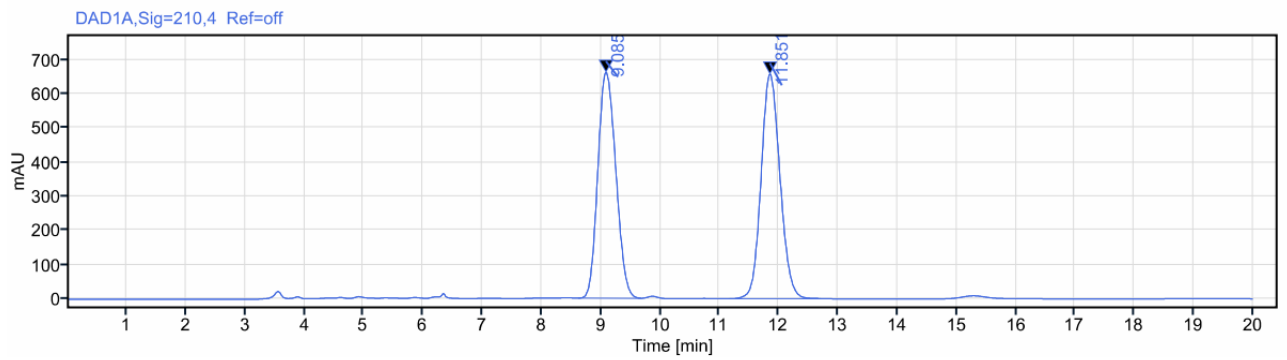


4s

4s was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (78.9 mg, 70%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99% (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 11.90 min, t_r (min) = 9.09 min). $[\alpha]_D^{25}$ = +48.2 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {8.78 (d, *J* = 7.9 Hz, 0.5H) + 8.49 (d, *J* = 8.1 Hz, 0.5H)}, 8.63 (dd, J_1 = 14.9 Hz, J_2 = 8.2 Hz, 1H), 8.34 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.85-7.81 (m, 1H), 7.79-7.65 (m, 1H), 7.57-7.53 (m, 1H), 4.47-4.43 (m, 1H), {4.18 (dd, J_1 = 12.7 Hz, J_2 = 2.3 Hz, 0.5H) + 3.98 (dd, *J* = 12.9, 4.1 Hz, 0.5 H)}, 3.52-3.48 (m, 1H), 3.43-3.29 (m, 1H), 3.14-3.05 (m, 1H), 2.63 (s, 3H), 2.11-2.01 (m, 2H), 1.87-1.69 (m, 2H), {1.54 (s, 4H) + 1.52 (s. 5H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 158.9 & 158.4, 154.8 & 154.5, 142.1 & 142.0, 136.4

&136.1, 132.6 & 132.5, 130.3 &130.1, 130.2, 129.5 &129.4, 127.7 & 127.4, 126.9 & 126.6, 125.8 & 125.7, 123.6 & 123.5, 122.4 & 122.0, 121.5, 79.7 & 79.0, 57.1 & 56.9, 46.8 & 46.5, 41.1 &40.4, 29.9 & 28.8, 28.7, 23.5 & 22.6, 21.9. HRMS (ESI) for $C_{24}H_{29}N_2O_2$ $[M+H]^+$: calcd 377.2224, found 377.2222.

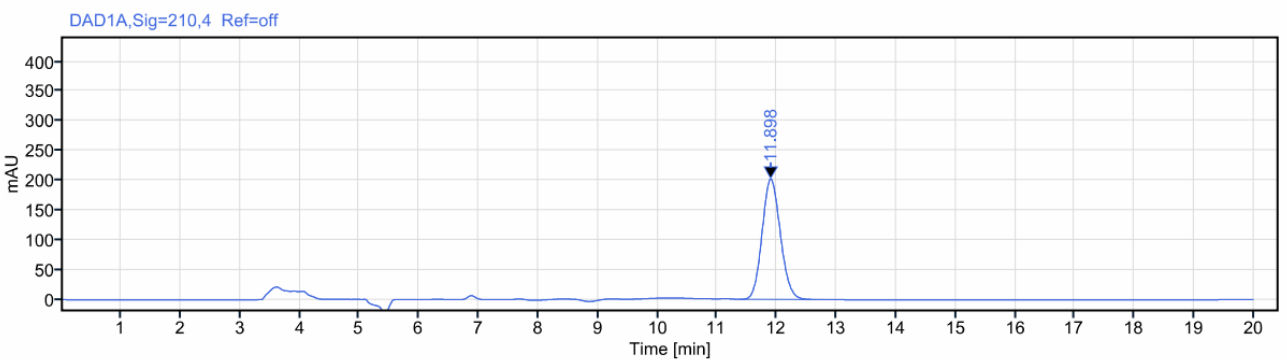
Chiral HPLC Charts for **4s**:



Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.085	BBA	1.05	13933.145	659.80	49.0144	
11.851	BBA	1.53	14493.515	656.14	50.9856	

Figure *S3*. The HPLC chart of rac-**4s**

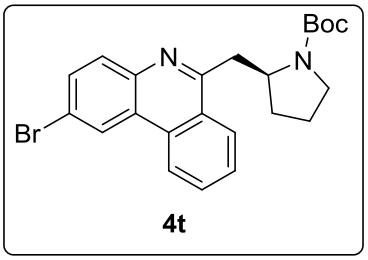


Signal: DAD1A,Sig=210,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.898	BBA	1.42	4319.406	202.61	100.0000	

Figure *S4*. The HPLC chart of **4s**

tert-butyl (*S*)-2-((2-bromophenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4t)

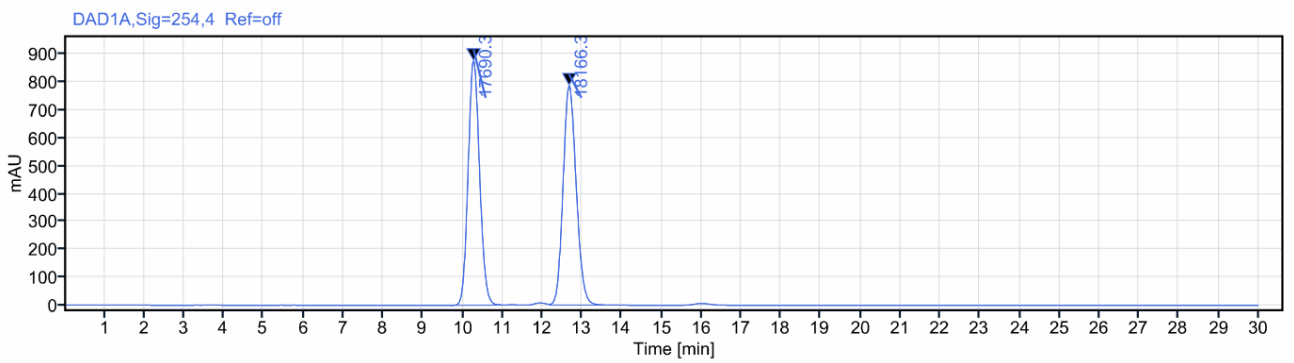


4t

4t was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (101.7 mg, 77%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* = 94% (HPLC: 254 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 12.58 min, t_r (min) = 10.16 min). $[\alpha]_D^{25}$ = +92.4 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {8.78 (d, *J* =

7.7 Hz, 0.5H)+ 8.48 (d, J = 8.1 Hz, 0.5H)}, 8.66 (s, 1H), 8.54 (dd, J_1 = 14.6, J_2 = 8.1 Hz, 1H), 7.99-7.97 (m, 1H), 7.88-7.70 (m, 3H), 4.46-4.43 (m, 1H), 4.15 (dd, J_1 = 12.8 Hz, J_2 = 2.8 Hz, 1H) + 3.94 (dd, J_1 = 13.0 Hz, J_2 = 4.3 Hz, 0.5H)}, 3.54-3.31 (m, 2H), 3.15-3.05 (m, 1H), 2.08-1.99 (m, 2H), 1.89-1.70 (m, 2H), {1.53 (s, 4.5H) + 1.48 (s, 4.5H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.4 & 159.9, 154.8 & 154.5, 142.44 & 142.36, 131.9 & 131.7, 131.6, 131.44 & 131.35, 130.7, 128.5 & 127.8, 127.5 & 126.6, 125.9 & 125.7, 125.4 & 125.2, 124.8, 122.4 & 122.0, 120.5 & 120.3, 79.8 & 79.1, 57.0 & 56.8, 46.8 & 46.5, 41.1 & 40.4, 30.0 & 29.0, 28.6, 23.5 & 22.6. HRMS (ESI) for $C_{23}H_{26}BrN_2O_2$ $[M+H]^+$: calcd 441.1172, found 441.1175.

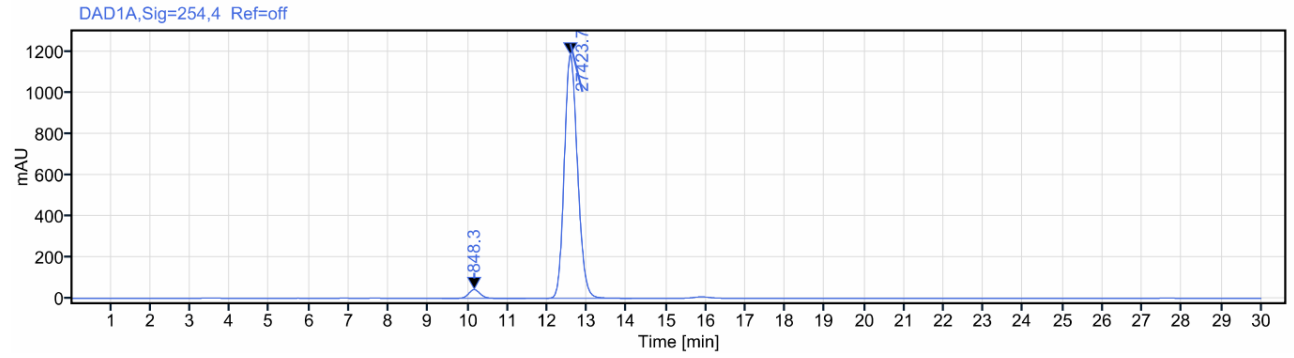
Chiral HPLC Charts for **4t**:



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.274	BV	1.35	17690.281	880.02	49.3363	
12.677	VBA	1.94	18166.265	790.46	50.6637	

Figure *S5*. The HPLC chart of rac-**4t**

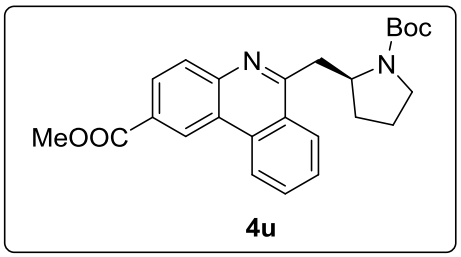


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.158	BB	2.11	848.252	42.36	3.0003	
12.583	BBA	2.15	27423.671	1184.87	96.9997	

Figure *S6*. The HPLC chart of **4t**

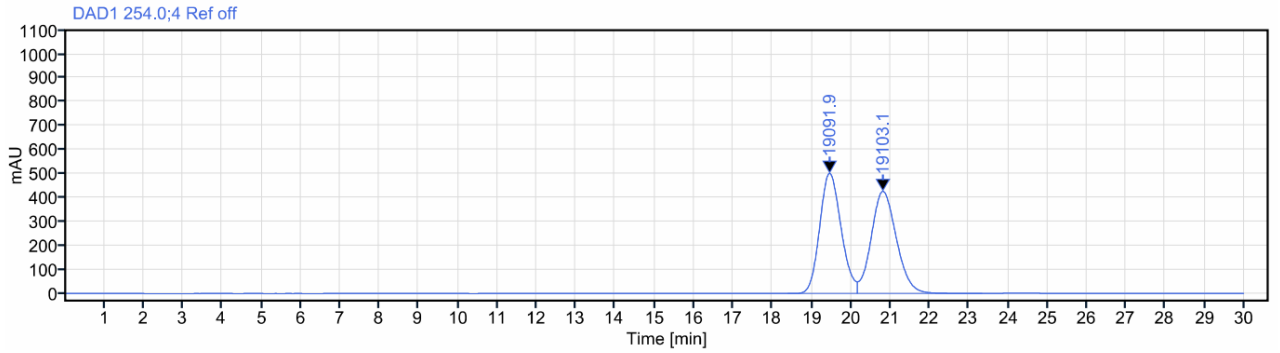
methyl (*S*)-6-((1-(tert-butoxycarbonyl)pyrrolidin-2-yl)methyl)phenanthridine-2-carboxylate (4u)



4u

4u was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (85.7 mg, 68%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak AD-H column, *ee* = 96% (HPLC: 254 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 19.19 min, t_r (min) = 20.56 min). $[\alpha]_D^{25}$ = +115 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), {8.80 (d, J = 8.0 Hz, 0.5H) + 8.49 (d, J = 8.0 Hz, 0.5H)}, 8.73 (dd, J_1 = 15.1 Hz, J_2 = 8.2 Hz, 2H), 8.33 (t, J = 8.4 Hz, 1H), 8.15 (dd, J_1 = 8.2 Hz, J_2 = 3.9 Hz, 1H), 7.90 (dd, J_1 = 12.8 Hz, J_2 = 6.8 Hz, 1H), 7.84-7.71 (m, 1H), 4.49 (dd, J_1 = 14.3 Hz, J_2 = 7.1 Hz, 3H), {4.19 (dd, J_1 = 12.7 Hz, J_2 = 2.7 Hz, 0.5H) +3.97 (dd, J_1 = 13.0Hz, J_2 = 4.3 Hz, 0.5H)}, 3.54-3.31 (m, 2H), 3.19-3.09 (m, 1H), 2.16-2.07 (m, 3H), 1.90-1.72 (m, 2H), 1.49 (dd, J_1 = 24.5 Hz, J_2 = 10 Hz, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.52 & 166.49, 162.4 & 161.9, 154.7 & 154.4, 146.10 & 146.05, 132.9 & 132.7, 130.9, 129.8 & 129.7, 128.6 & 128.3, 128.0 & 127.9, 127.7 & 127.5, 126.7, 125.9 & 125.7, 124.6, 123.3 & 123.1, 122.6 & 122.2, 79.7 & 79.1, 61.3 & 61.2, 57.0 & 56.8, 46.8 & 46.4, 41.3 & 40.6, 30.1 & 28.9, 28.6, 23.5 & 22.6. HRMS (ESI) for $C_{25}H_{29}N_2O_4$ $[M+H]^+$: calcd 421.2122, found 421.2126.

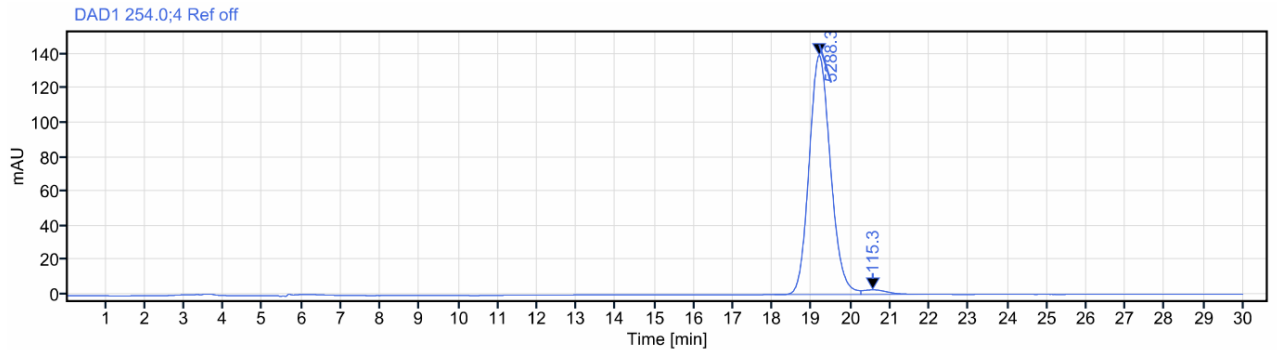
Chiral HPLC Charts for **4u**:



Signal: DAD1 254.0;4 Ref off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
19.452	BV	1.77	19091.931	503.26	49.9854	
20.808	VB	3.17	19103.059	427.76	50.0146	

Figure *S7*. The HPLC chart of rac-**4u**

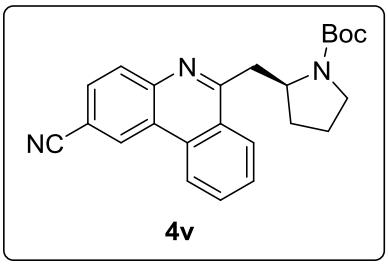


Signal: DAD1 254.0;4 Ref off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
19.190	BV	2.21	5288.271	139.08	97.8654	
20.559	VB	1.71	115.345	2.70	2.1346	

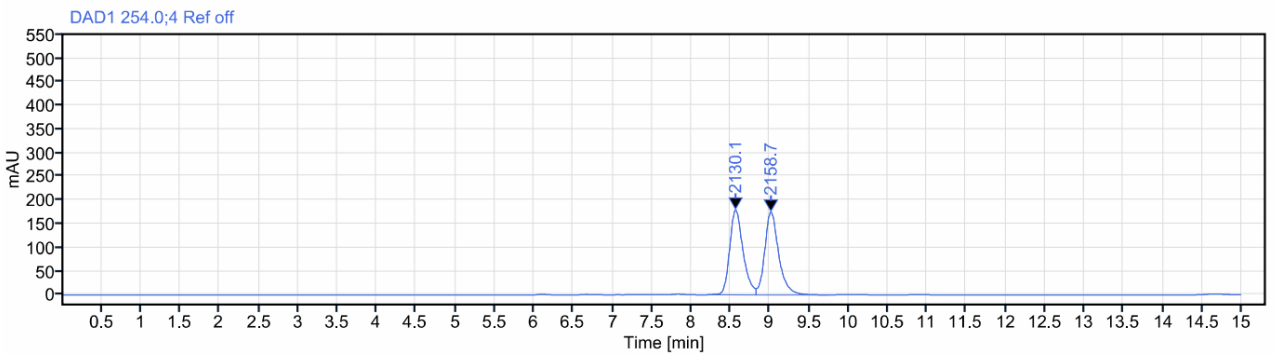
Figure *S8*. The HPLC chart of **4u**

***tert*-butyl (*S*)-2-((2-cyanophenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4v)**



4v was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (89.4 mg, 77%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak AD-H column, *ee* = 97% (HPLC: 254 nm, *n*-Hexane/isopropanol = 80/20, flow rate 0.6 mL/min, 30 ˚C, t_r (major) = 8.56 min, t_r (min) = 8.97 min). $[\alpha]_D^{25}$ = +16.0 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.87 (s, 1H), {8.81 (d, *J* = 7.9 Hz, 0.5H) + 8.51 (d, *J* = 8.0 Hz, 0.5H)}, 8.59 (dd, J_1 = 18.3 Hz, J_2 = 8.0 Hz, 2H), 8.19-8.16 (m, 1H), 7.96-7.75 (m, 3H), 4.46 (s, 1H), {4.17 (dd, J_1 = 12.8 Hz, J_2 = 2.9 Hz, 0.5H) + 3.96 (dd, J_1 = 13.0 Hz, J_2 = 4.1 Hz, 0.5H) 3.51-3.32 (m, 2H), 3.21-3.10 (m, 1H), 2.07-1.98 (m, 2H), 1.86-1.74 (m, 2H), {1.51 (s, 5H) + 1.45 (s, 4H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.5 & 163.0, 154.8 & 154.4, 145.44 & 145.38, 131.7 & 131.53, 131.47, 131.0 & 130.9, 130.2 & 130.0, 129.1 & 128.5, 127.7, 126.9, 126.1 & 126.0, 124.02 &123.9, 122.4 & 122.0,109.9 & 109.6, 79.8 &79.2, 57.0 & 56.8, 53.4, 46.8 & 46.4, 41.3 & 40.6, 30.2 &29.1, 28.6, 23.5 & 22.6. HRMS (ESI) for $C_{24}H_{26}N_3O_2$ $[M+H]^+$: calcd 388.2020, found 388.2022.

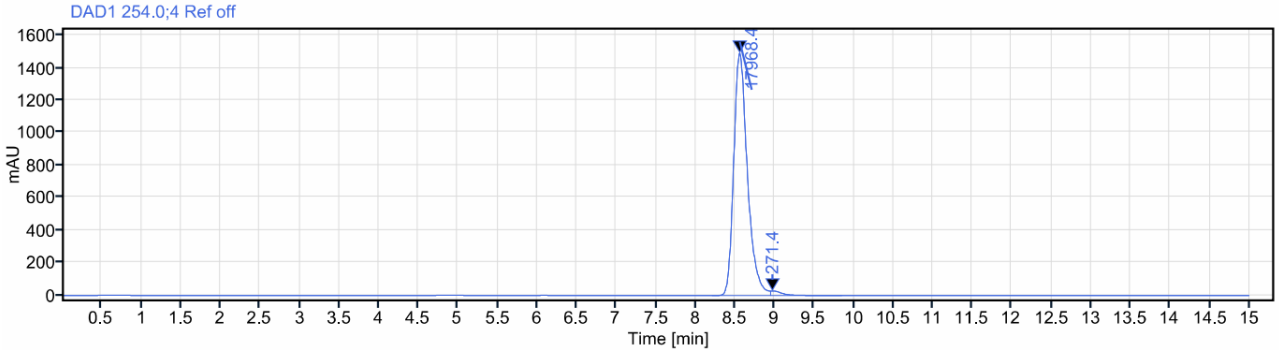
Chiral HPLC Charts for **4v**:



Signal: DAD1 254.0;4 Ref off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.564	BV	0.62	2130.112	179.42	49.6671	
9.013	VB	0.91	2158.664	175.15	50.3329	

Figure *S9*. The HPLC chart of rac-**4v**

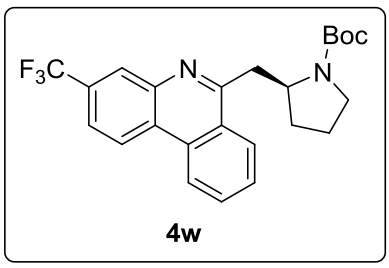


Signal: DAD1 254.0;4 Ref off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.559	BV	0.74	17968.373	1491.63	98.5123	
8.974	VB	0.90	271.354	27.88	1.4877	

Figure *S10*. The HPLC chart of **4v**

***tert*-butyl (*S*)-2-((3-(trifluoromethyl)phenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4w)**

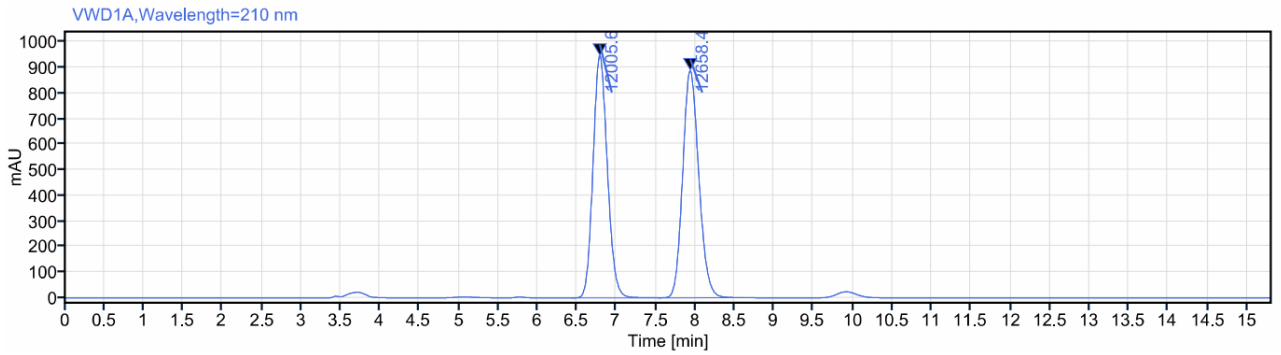


4w

4w was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (100.6 mg, 78%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99% (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 7.95 min, t_r (min) = 6.80 min). $[\alpha]_D^{25}$ = +24.4 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {8.85 (s, 1.5H), 8.52 (d, J = 8.0 Hz, 0.5H)}, 8.65 (dd, J_1 = 14.9 Hz, J_2 = 8.2 Hz, 1H), 8.23-8.21 (m, 1H), 7.93-7.89 (m, 2H), {7.85 (t, J = 7.3 Hz, 0.5H) + 7.75 (t, J = 7.3 Hz, 0.5H)}, 4.47 (s, 1H), {4.19 (dd, J_1 = 12.6 Hz, J_2 = 2.1 Hz, 0.5H) + 3.94 (dd, J_1 = 12.9 Hz, J_2 = 3.7 Hz, 0.5H)}, 3.52-3.49 (m, 1H), 3.47-3.32 (m, 1H), 3.21-3.11(m, 1H), 2.08-2.01 (m, 3H), 1.89-1.73 (m, 2H), {1.53 (s, 5H) + 1.48 (s,

4H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4 & 161.9, 154.7 & 154.4, 145.1, 132.4 & 132.3, 131.0 & 130.6, 130.5, 128.6, 128.0, 127.6, 126.8, 126.0 & 125.9, 125.5, 124.5 & 124.3, 124.4 (q, J = 260 Hz) 123.4 &123.3, 122.4 & 122.0, 119.8 (q, J = 3.75 Hz), 79.8 & 79.1, 57.0 & 56.8, 46.9 & 46.4, 41.1 & 40.5, 30.0 & 29.0, 28.6, 23.5 & 22.6. HRMS (ESI) for $C_{24}H_{26}F_3N_3O_2$ $[M+H]^+$: calcd 431.1941, found 431.1944.

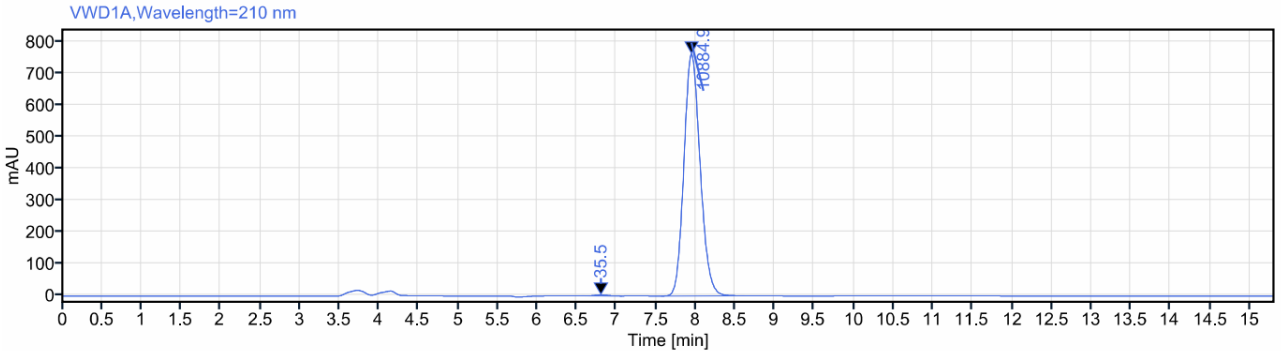
Chiral HPLC Charts for **4w**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.788	BB	1.13	12005.586	948.29	48.6766	
7.936	BBA	1.05	12658.416	890.01	51.3234	

Figure *S11*. The HPLC chart of rac-**4w**

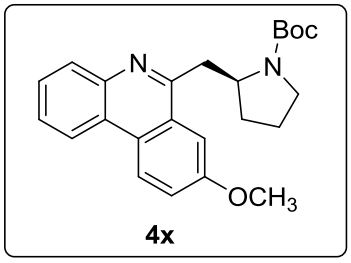


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.804	BB	0.50	35.547	3.02	0.3255	
7.949	BBA	1.04	10884.872	763.55	99.6745	

Figure *S12*. The HPLC chart of **4w**

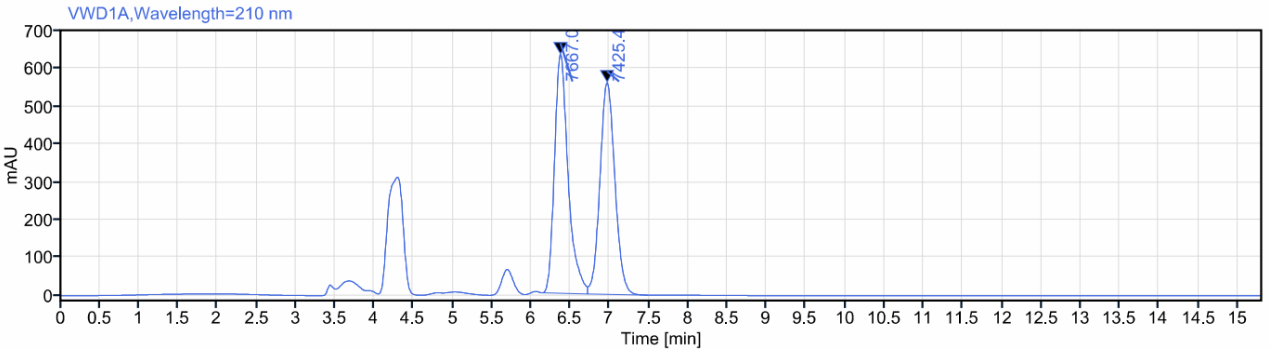
***tert*-butyl (*S*)-2-((8-methoxyphenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4x)**



4x

4x was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (83.6 mg, 71%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99% (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 7.00 min, t_r (min) = 6.40 min). $[\alpha]_D^{25}$ = +65.9 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.52-8.45 (m, 3H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.66-7.58 (m, 2H), 7.47-7.45 (m, 1H), 4.41-4.21 (m, 1H), {4.16 (s, 2.5 H) + 4.00 (s, 0.5H)}, 3.53-3.51 (m, 1H), 3.34-3.31 (m, 1H), 2.99-2.94 (m, 1H), 2.24-2.13 (m, 2H), 1.90-1.85 (m, 1H), 1.74-1.67 (m, 1H), {1.53 (s, 7H) + 1.30 (s, 2H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.3 & 159.2, 154.7, 142.9, 129.6, 127.3, 127.2, 127.0, 126.4, 124.1, 123.5, 121.9, 121.4, 107.4, 79.1, 57.1 & 56.2, 46.8, 41.3, 28.9, 28.6, 26.9, 23.6. HRMS (ESI) for $C_{24}H_{29}N_3O_2$ $[M+H]^+$: calcd 393.2173, found 393.2175.

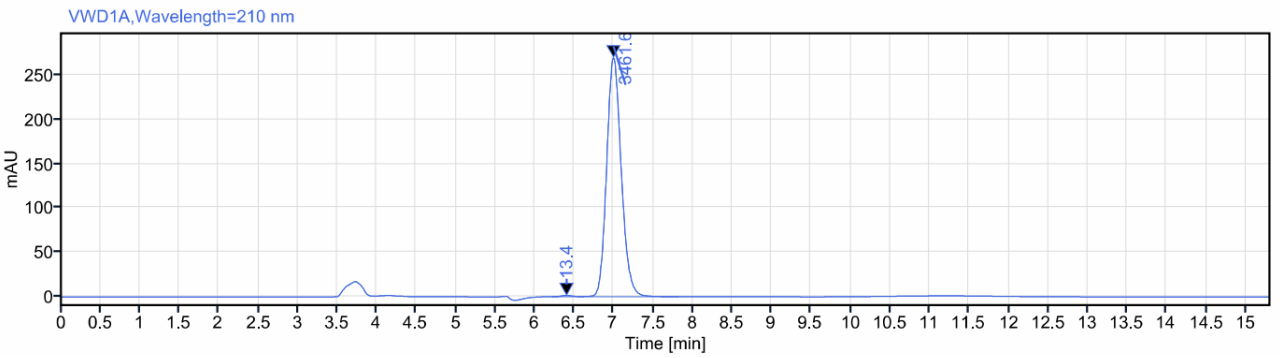
Chiral HPLC Charts for **4x**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.373	BV	0.58	7666.956	632.52	50.8003	
6.967	VB	0.76	7425.387	560.63	49.1997	

Figure *S13*. The HPLC chart of rac-**4x**

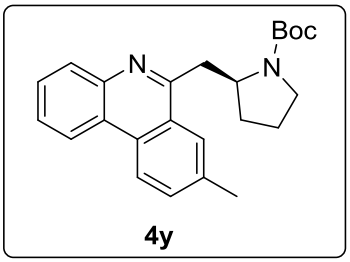


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.403	BB	0.37	13.371	1.41	0.3848	
6.997	BB	1.23	3461.589	269.89	99.6152	

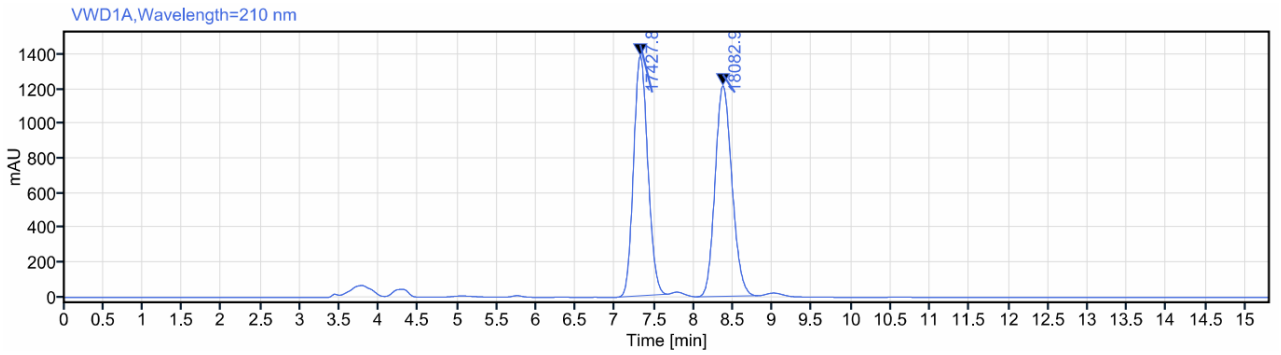
Figure *S14*. The HPLC chart of **4x**

***tert*-butyl (*S*)-2-((8-methylphenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4y)**



4y was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (83.4 mg, 74%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* = 97 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 8.42 min, t_r (min) = 7.22 min). $[\alpha]_D^{25}$ = +59.3 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.1 Hz, 1H), 8.74-8.43 (m, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.75-7.57(m, 4H), 4.47-4.46 (m, 1H), 4.22-4.00 (m, 1H), 3.55-3.34 (m, 3H), 3.14 (s, 1H), 3.13-3.07 (m, 1H), 2.12-1.98 (m, 2H), 1.87-1.67 (m, 2H), 1.54 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.2 & 159.7, 154.8 & 154.5, 144.94 & 144.87, 135.6, 135.2, 134.7 & 134.6, 132.4, 130.1 & 129.9, 127.8, 127.6, 127.3 & 127.1, 126.5, 125.9 & 125.7, 125.5 & 125.1, 79.7 & 79.1, 57.1 & 56.9, 46.8 & 46.5, 41.6 & 40.9, 29.9 & 28.9, 28.7, 26.9, 23.5 & 22.6. HRMS (ESI) for $C_{24}H_{29}N_3O_2$ $[M+H]^+$: calcd 377.2224, found 377.2226.

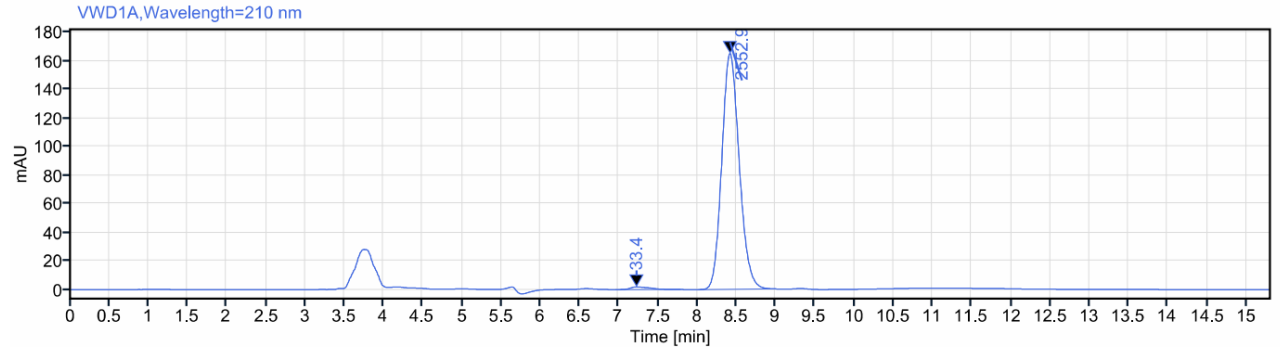
Chiral HPLC Charts for **4y**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.320	BB	0.64	17427.808	1385.36	49.0777	
8.370	BB	0.78	18082.862	1215.56	50.9223	

Figure *S15*. The HPLC chart of rac-**4y**

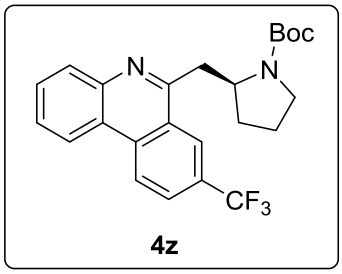


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.224	BBA	0.83	33.387	1.91	1.2909	
8.417	BBA	0.99	2552.880	165.35	98.7091	

Figure *S16*. The HPLC chart of **4y**

***tert*-butyl (*S*)-2-((8-(trifluoromethyl)phenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4z)**

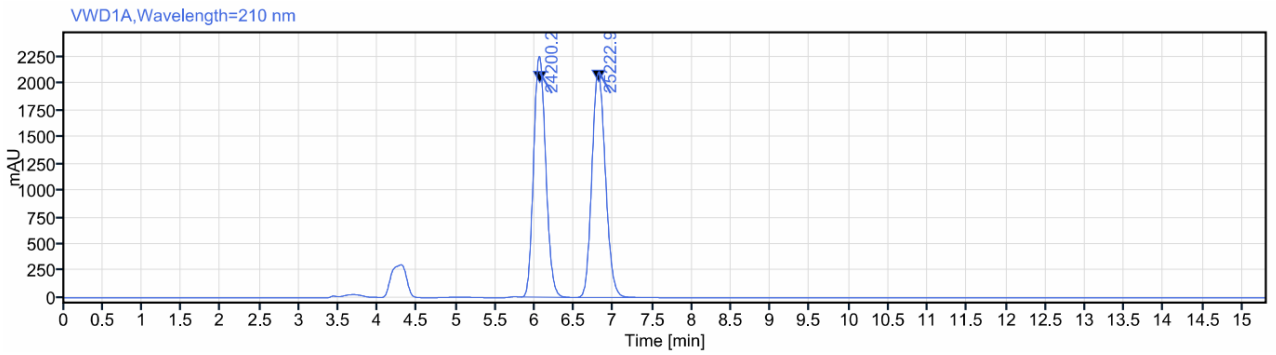


4z

4z was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (69.4 mg, 54%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 6.845 min, t_r (min) = 6.064 min). $[\alpha]_D^{25}$ = +18.9 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {9.16 (s, 0.6H) + 8.53-8.52 (m, 1.4 H)}, 8.73-8.68 (m, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.03-7.99 (m, 1H), 7.78-7.75 (m, 1H), 7.67 (m, 1H), 4.51 (d, *J* = 39.1 Hz, 1H), {4.17-4.06 (m, 0.6H) + 3.97-394 (m, 0.4H)}, 3.52-3.34 (m, 2H), 3.29-3.12 (m, 1H), 2.05-1.86 (m, 4H), {1.48 (s, 5H), 1.28(s, 4H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.8 & 159.2, 154.8 & 154.4, 144.4, 135.0 & 134.9, 130.0, 129.8, 129.5, 127.09, 126.8,

126.2 &126.2, 125.2 & 125.0, 123.7 &123.5, 123.1, 122.8 & 122.6, 122.3, 79.4 & 79.2, 57.1 &56.7, 46.7 & 46.3, 40.8 & 40.6, 31.0 & 29.6, 28.5 & 28.3, 22.9 &22.6. HRMS (ESI) for $C_{24}H_{29}N_2O_3$ $[M+H]^+$: calcd 431.1941, found 431.1944.

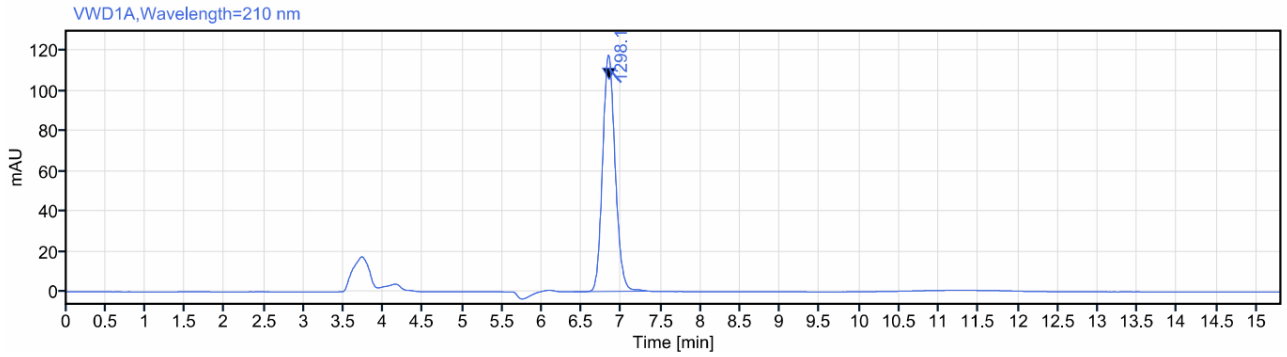
Chiral HPLC Charts for **4z**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.064	BB	0.63	24200.173	1998.47	48.9653	
6.811	BBA	0.82	25222.906	2011.21	51.0347	

Figure *S17*. The HPLC chart of rac-**4z**

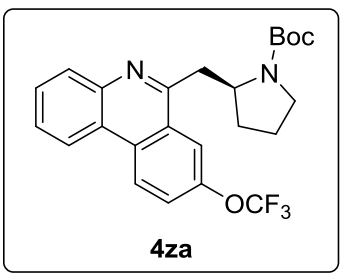


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.845	BBA	0.93	1298.133	105.15	100.0000	

Figure *S18*. The HPLC chart of rac-**4z**

***tert*-butyl (*S*)-2-((8-(trifluoromethoxy)phenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4za)**

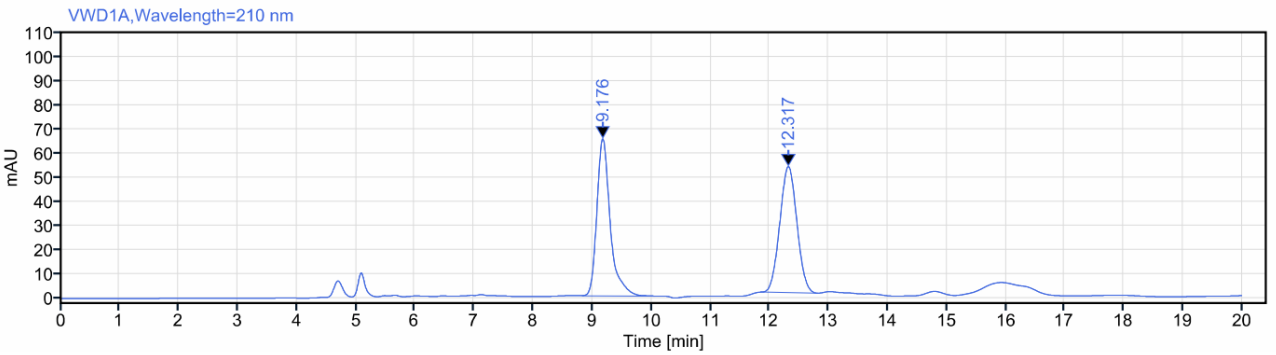


4za

4za was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (95.0 mg, 71%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99% (HPLC: 210 nm, *n*-Hexane/isopropanol = 95/5, flow rate 0.4 mL/min, 30 ˚C, t_r (major) = 12.32 min, t_r (min) = 9.19 min). $[\alpha]_D^{25}$ = +70.3 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ {8.71-8.65 (m,

1.45H) + 8.22 (s, 0.5H)}, 8.54-8.52 (m, 1H), 8.16-8.14 (m, 1H), 7.78-7.64 (m, 3H), 4.45 (s, 1H), {4.06 (dd, J_1 = 12.7 Hz, J_2 = 2.1 Hz, 0.5H), 3.94 (dd, J_1 = 13.2 Hz, J_2 = 4.7 Hz, 0.5H)}, 3.54-3.51 (m, 1H), 3.48-3.31 (m, 1H), 3.19-3.12 (m, 1H), 2.09-1.83 (m, 4H), {1.49 (s, 4H), 1.44 (s, 5H)}; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.24 & 159.21, 158.61 & 158.58, 154.7 & 154.5, 148.1 & 147.9, 143.8, 131.5 & 131.3, 130.02 & 130.01, 129.1 & 128.9, 127.1 & 126.8, 124.7 & 124.3, 123.8, 123.0 &122.8, 121.9, 120.6 (q, J = 264.2 Hz), 118.8 & 118.2, 79.8 & 79.2, 57.0 &56.6, 46.7 & 46.5, 41.0 & 40.5, 30.3 & 29.4, 28.5, 23.7 & 22.7. HRMS (ESI) for $C_{24}H_{26}F_3N_3O_3$ $[M+H]^+$: calcd 447.1890, found 447.1893.

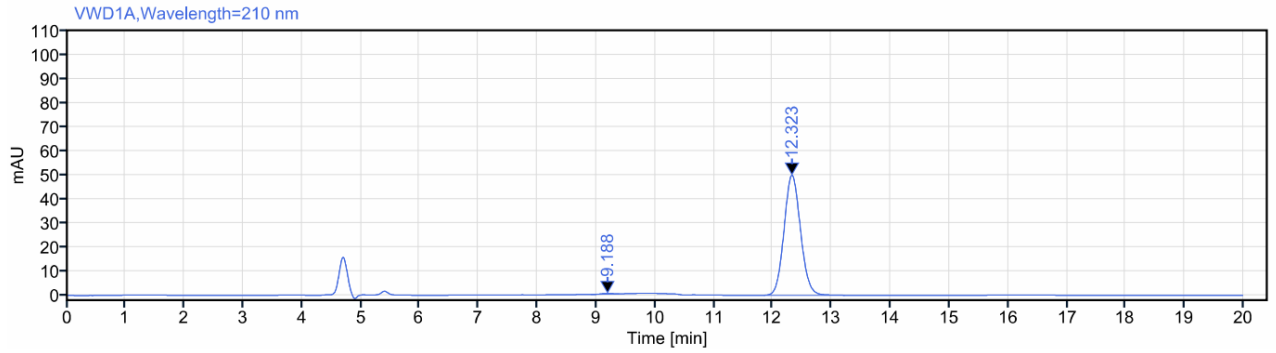
Chiral HPLC Charts for **4za**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.176	VBA	1.22	1023.107	65.10	49.3407	
12.317	BB	0.97	1050.451	52.20	50.6593	

Figure *S19*. The HPLC chart of rac-**4za**

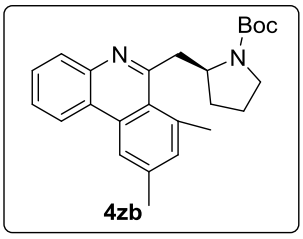


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.188	BB	0.48	3.472	0.27	0.3561	
12.323	BV	1.38	971.679	49.89	99.6439	

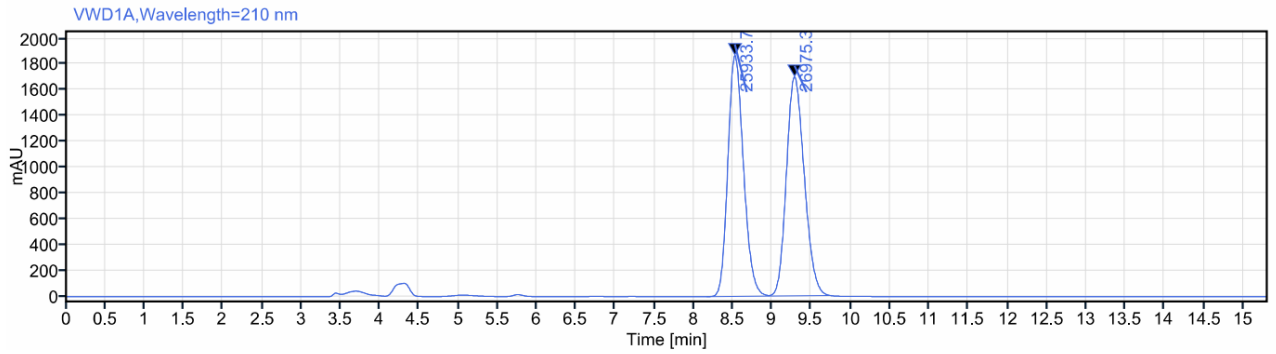
Figure *S20*. The HPLC chart of **4za**

***tert*-butyl (*S*)-2-((7,9-dimethylphenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4zb)**



4zb was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (78.5 mg, 67%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* = 97% (HPLC: 210 nm, n-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 9.40 min, t_r (min) = 8.57 min). $[\alpha]_D^{25}$ = +85.5 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.66-7.57 (m, 2H), 7.32 (s, 1H), 4.67 (d, *J* = 1.9 Hz, 1H), {4.22 (d, *J* = 13.9 Hz, 0.5H), 4.05 (d, *J* = 14.6 Hz, 0.5H)}, 3.51-3.34 (m, 3H) 3.01 (d, *J* = 35.2 Hz, 3H), 2.57(s, 3H), 2.12-1.68 (m, 4H), {1.47 (s, 4H), 1.32 (s, 5H)}; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.1, 154.7, 143.0, 139.5, 134.6, 133.5, 129.4, 128.2, 126.1, 124.4, 123.4, 122.1, 120.6, 120.4, 79.1 & 78.9, 56.9, 46.8 & 46.4, 44.9 & 44.3, 31.8 & 30.2, 28.5, 26.3 & 26.0, 23.5 & 22.9, 21.7. HRMS (ESI) for $C_{25}H_{31}N_2O_3$ $[M+H]^+$: calcd 391.2380, found 391.2184.

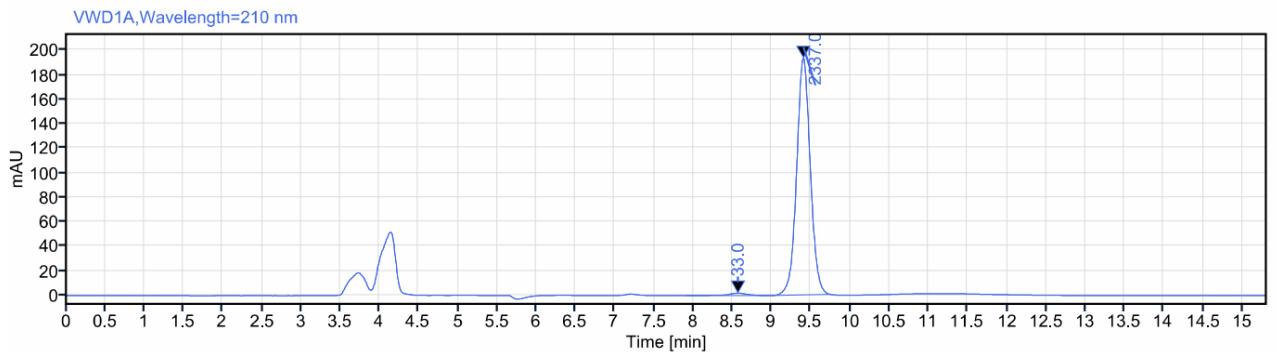
Chiral HPLC Charts for **4zb**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.525	BV	0.79	25933.706	1869.41	49.0157	
9.284	VBA	0.79	26975.270	1699.03	50.9843	

Figure *S21*. The HPLC chart of rac-**4zb**

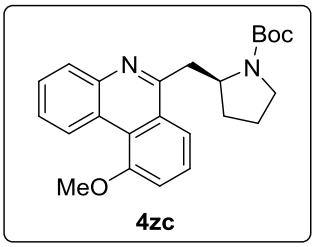


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.570	BB	1.06	32.969	1.99	1.3911	
9.404	BBA	0.76	2336.972	192.91	98.6089	

Figure *S22*. The HPLC chart of **4zb**

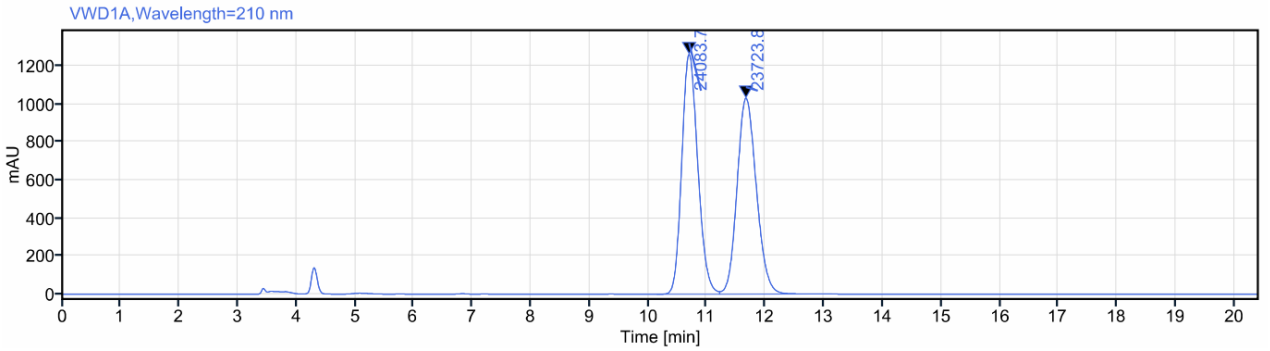
***tert*-butyl (*S*)-2-((10-methoxyphenanthridin-6-yl)methyl)pyrrolidine-1-carboxylate (4zc)**



4zc

4zc was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (61.1 mg, 53%). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak IG-3 column, *ee* > 99% (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 10.73 min, t_r (min) = 11.70 min). $[\alpha]_D^{25}$ = +112.0 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.49 (dd, J_1 = 8.5 Hz, J_2 = 1.1 Hz, 1H), 8.46-8.14 (m, 2H), 7.77-7.60 (m, 3H), 7.34 (d, J = 7.9 Hz, 1H), 4.49-4.46 (m, 1H), 4.20-3.98 (m, 2H), 4.16 (s, 3H), 3.55-3.31 (m, 2H), 3.15-3.06 (m, 1H), 2.14-2.02 (m, 2H), 2.01-1.78 (m, 2H), 1.54 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 158.9 & 158.5, 154.8 & 154.5, 144.3, 129.5 & 129.4, 127.9, 127.7, 127.3, 126.4, 126.2, 123.6 & 123.5, 123.4 & 123.2, 119.7, 118.9, 111.6 &111.5, 79.7 & 79.0, 57.0 & 56.8, 55.8, 46.8 & 46.5, 41.6 & 40.9, 29.9 & 28.9, 28.7, 23.5 & 22.7. HRMS (ESI) for $C_{24}H_{29}N_2O_3$ $[M+H]^+$: calcd 393.2173, found 393.2175.

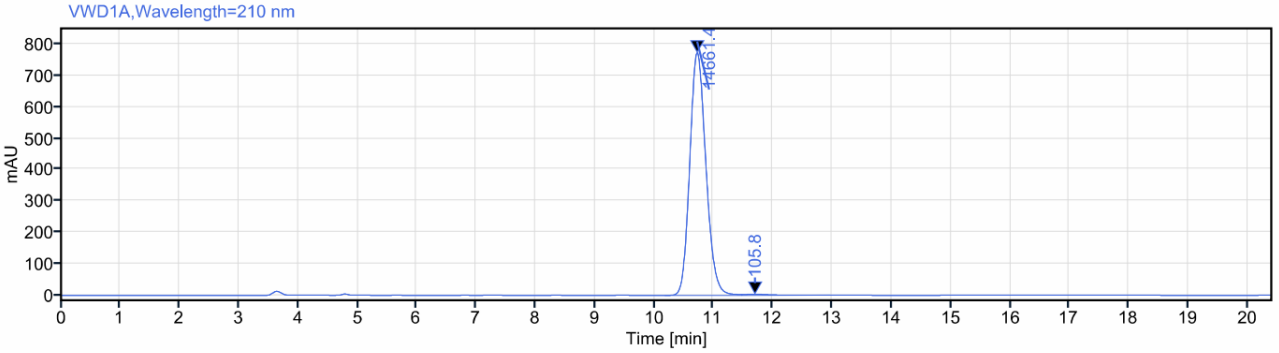
Chiral HPLC Charts for **4zc**:



Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.697	VV	1.08	24083.689	1265.03	50.3764	
11.668	VBA	1.91	23723.777	1034.18	49.6236	

Figure *S23*. The HPLC chart of rac-**4zc**

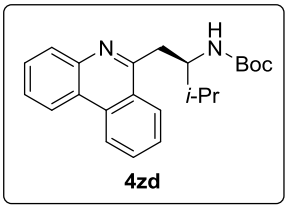


Signal: VWD1A,Wavelength=210 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.725	BV	1.30	14661.401	773.84	99.2836	
11.700	VB	1.48	105.790	3.47	0.7164	

Figure *S24*. The HPLC chart of **4zc**

***tert*-butyl (*R*)-(3-methyl-1-(phenanthridin-6-yl)butan-2-yl)carbamate (4zd):**

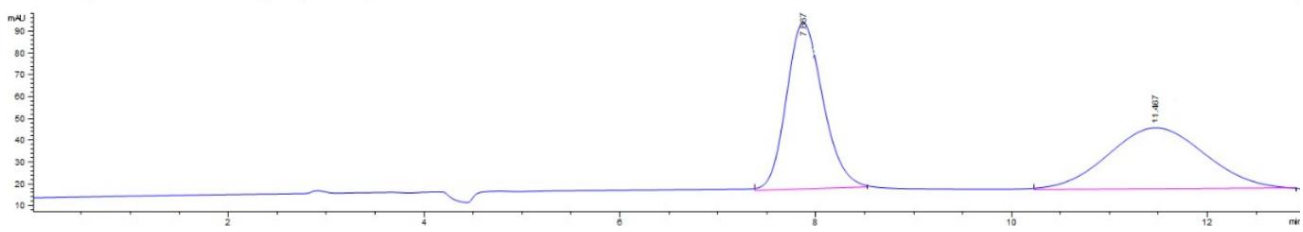


4zd

4zd was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (86.25 mg, 83%, 96% *ee*). Mp: 144-146 ºC Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak AD column, *ee* = 96 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 10.856 min, t_r (min) = 7.494 min). $[\alpha]_D^{25}$ = +8.2 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, J = 8.2 Hz, 1H), 8.56 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.13 (dd, J_1 = 8.1, J_2 = 0.7 Hz, 1H), 7.90-7.82 (m, 1H), 7.75-7.71 (m, 2H), 7.66-7.62 (m, 1H), 5.24 (d, J = 8.3 Hz, 1H), 4.12-4.07 (m, 1H), 3.65 (dd, J_1 = 14.2, J_2 = 4.6 Hz, 1H), 3.40 (dd, J = 14.1, 8.5 Hz, 1H), 2.09-2.03 (m, 1H), 1.20 (s, 9H), 1.10 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.4, 155.8, 143.4, 132.9, 130.5, 129.6,

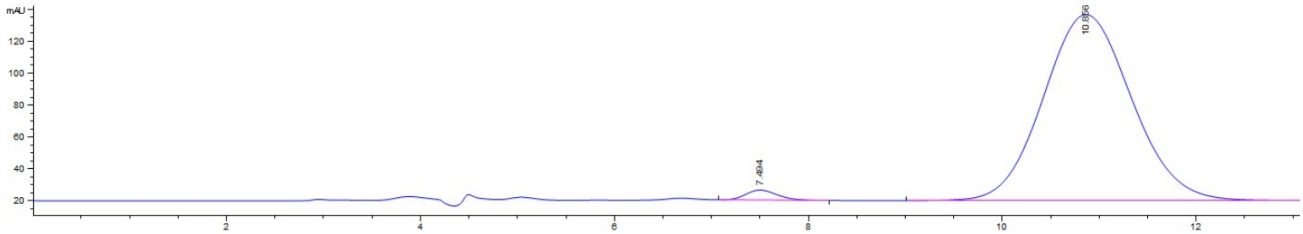
128.5, 127.5, 126.5, 126.1, 125.6, 123.8, 122.5, 121.9, 78.7, 55.6, 38.1, 31.7, 28.1, 19.4, 18.1. HRMS (ESI) for $C_{23}H_{29}N_2O_2$ $[M+H]^+$: calcd 365.2224, found 365.2226.

Chiral HPLC Charts for **4zd**:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.867	MMT	0.4347	1998.8	76.6	50.372
2	11.467	MMT	1.1635	1969.3	28.2	49.628

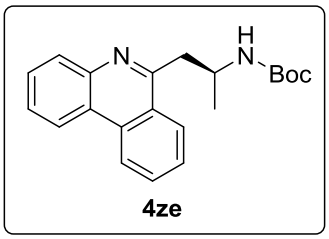
Figure *S25*. The HPLC chart of rac-**4zd**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.494	BB	0.3506	140.8	6.2	1.878
2	10.856	BB	0.9852	7353.3	116.1	98.122

Figure *S26*. The HPLC chart of **4zd**

***tert*-butyl (*S*)-(1-(phenanthridin-6-yl)propan-2-yl)carbamate (4ze)**

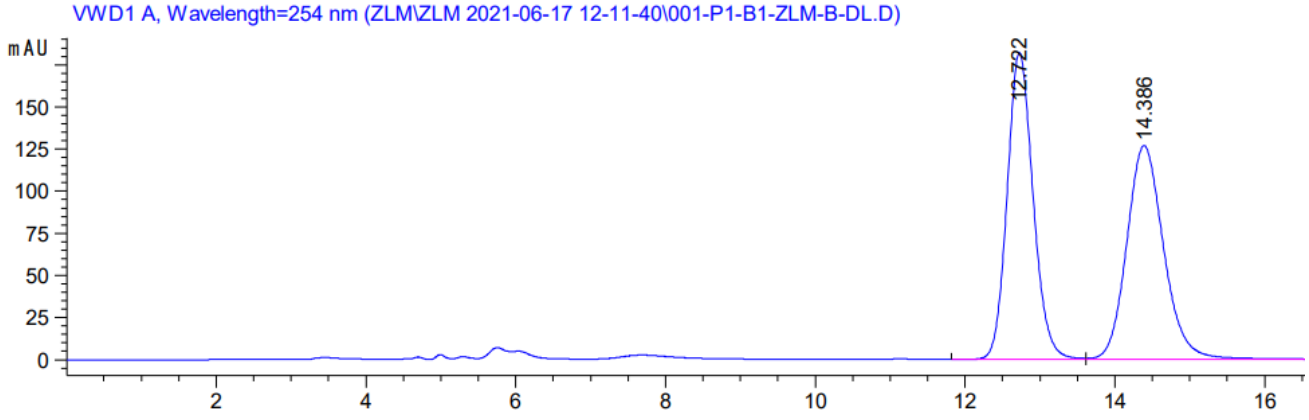


4ze

4ze was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as white solid (89.6 mg, 89%, 93% *ee*). Mp:155-157 ºC. Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak ID column, *ee* = 93 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 14.398 min, t_r (min) = 12.758 min). $[\alpha]_D^{25}$ = +22.4 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.65 (d, J = 8.5 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 5.5 Hz, 1H), 8.14 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.87-7.84 (m, 1H), 7.75-7.71 (m, 2H), 7.66-7.63 (m, 1H), 5.29 (d, J = 13.6 Hz, 1H), 4.34 (d, J = 6.0 Hz, 1H), 3.74-3.69 (m, 1H), 3.40 (dd, J_1 = 13.9 Hz, J_2 = 7.0 Hz, 1H), 1.37 (s, 9H), 1.29 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.1, 155.4, 143.4, 132.9, 130.5, 129.7, 128.6, 127.6, 126.6, 126.4, 125.7, 123.7,

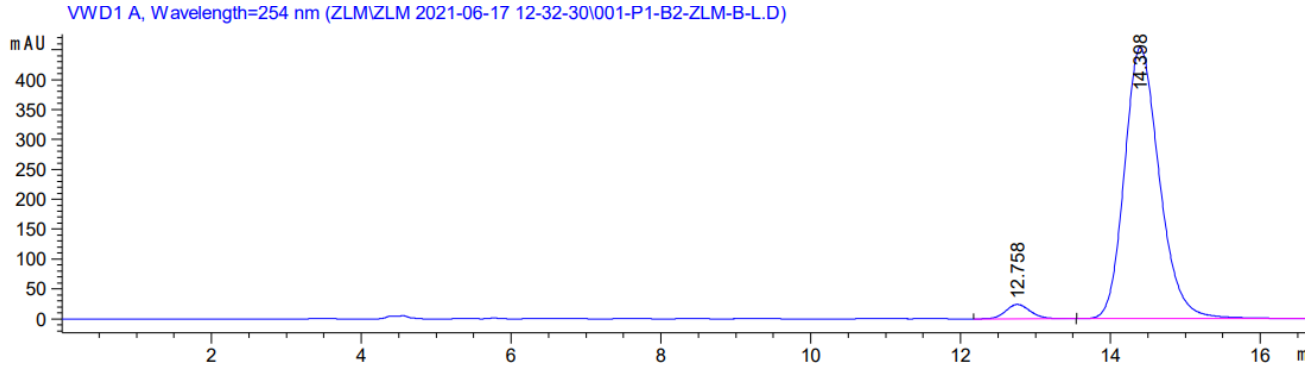
122.4, 121.9, 79.0, 46.5, 42.4, 28.3, 20.7. HRMS (ESI) for $C_{23}H_{28}N$ $[M+H]^+$: calcd 337.1911, found 337.1907.

Chiral HPLC Charts for **4ze**:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.722	BV	0.3706	4372.49023	181.82480	49.9925
2	14.386	VBA	0.5282	4373.80029	126.88585	50.0075

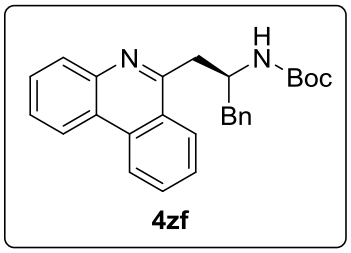
Figure *S27*. The HPLC chart of rac-**4ze**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.758	BB	0.3518	547.59949	24.03879	3.5852
2	14.398	BBA	0.4988	1.47261e4	453.50882	96.4148

Figure *S28*. The HPLC chart of **4ze**

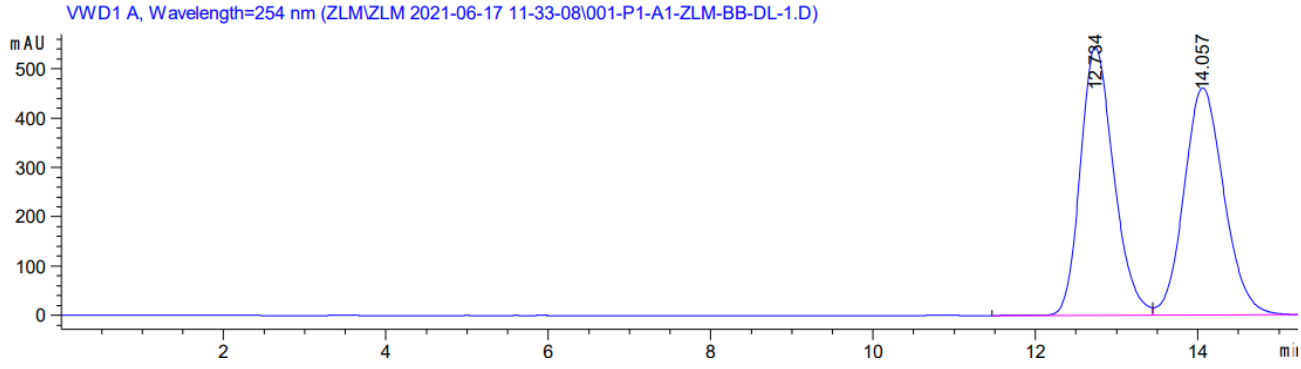
***tert*-butyl (*S*)-(1-(phenanthridin-6-yl)-3-phenylpropan-2-yl)carbamate (4zf)**



4zf

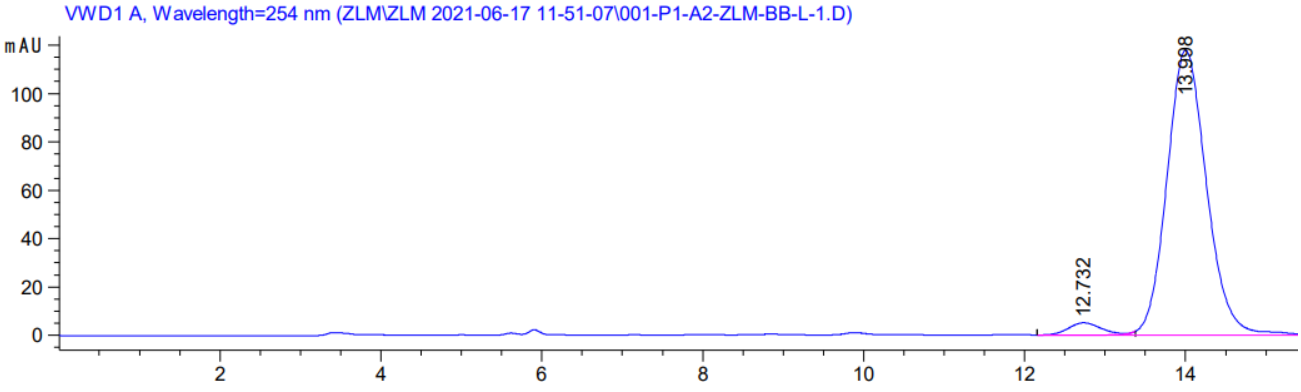
4zf was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as white solid (93.5 mg, 76%). Mp:139-141°C. Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak ID column, *ee* = 93 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 13.998 min, t_r (min) = 12.732 min). $[\alpha]_D^{25}$ = +19.5 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8 Hz, 1H), 8.55 (d, *J* = 8 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 7Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.76-7.72 (m, 1H), 7.67-7.62 (m, 2H), 7.33-7.24 (m, 5H), 5.58 (s, 1H), 4.52 (s, 1H), 3.58-3.54 (m, 1H), 3.49-3.45 (m, 1H), 3.18-3.16 (m, 1H), 3.03-2.99 (m, 1H), 1.34 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.0, 155.5, 143.4, 138.6, 132.8, 130.5, 129.7, 129.6, 128.6, 128.4, 127.5, 126.6, 126.4, 126.1, 125.6, 123.7, 122.4, 122.0, 79.0, 51.7, 40.7, 38.7, 28.3. HRMS (ESI) for $C_{27}H_{29}N_2O_2$ $[M+H]^+$: calcd 413.2224, found 413.2223.

Chiral HPLC Charts for **4zf**:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.734	VV R	0.4398	1.55413e4	543.21252	49.7273
2	14.057	VBA	0.5282	1.57118e4	460.37204	50.2727

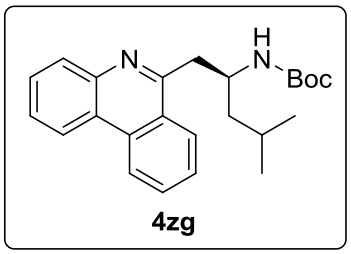
Figure *S29*. The HPLC chart of rac-**4zf**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.732	BV E	0.4365	142.64622	5.03466	3.4138
2	13.998	VB R	0.5297	4035.92822	117.80275	96.5862

Figure *S30*. The HPLC chart of **4zf**

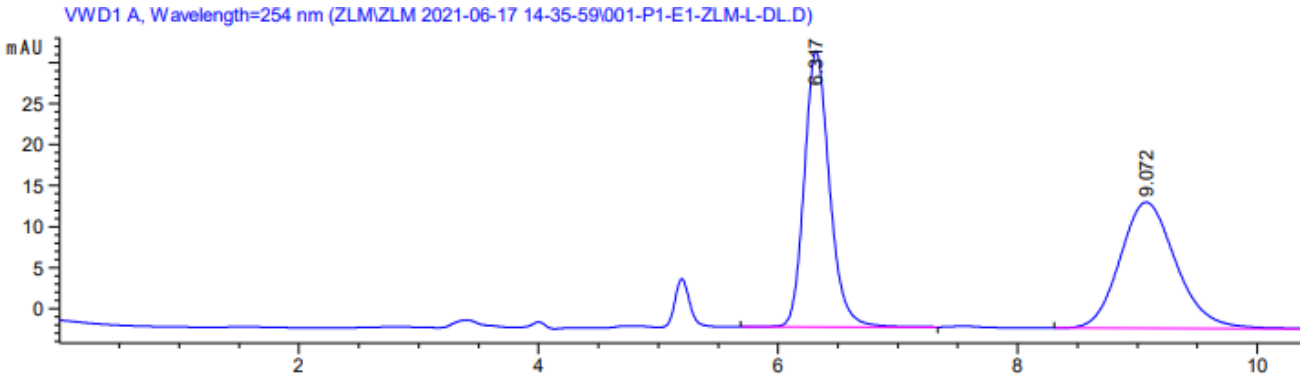
tert-butyl (*S*)-(4-methyl-1-(phenanthridin-6-yl)pentan-2-yl)carbamate (4zg):



4zg

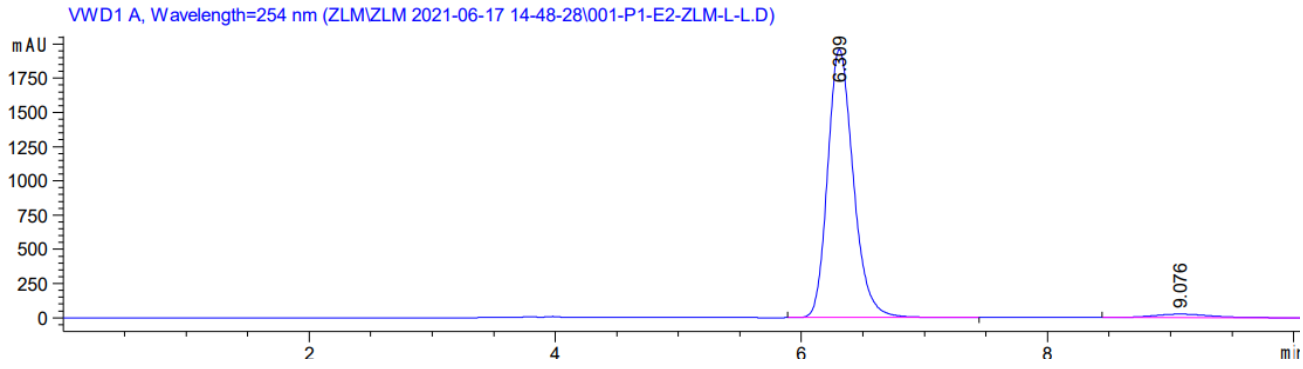
4zg was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as white solid (86.3 mg, 76%). Mp:122-124 °C. Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak ID column, *ee* = 94 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 9.076 min, t_r (min) = 6.309 min). $[\alpha]_D^{25}$ = +41.0 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8 Hz, 1H), 8.56 (d, *J* = 8 Hz, 1H), 8.40 (d, *J* = 7 Hz, 1H), 8.14 (dd, J_1 = 8.1 Hz, J_2 = 0.8 Hz, 1H), 7.86-7.83 (m, 1H), 7.75-7.71 (m, 2H), 7.66-7.63 (m, 1H), 5.18 (d, *J* = 6.5 Hz, 1H), 4.35 (d, *J* = 4 Hz, 1H), 3.61-3.58 (m, 1H), 3.51-3.47 (m, 1H), 1.75 (d, *J* = 5.5 Hz, 1H), 1.62-1.57 (m, 1H), 1.49-1.43 (m, 1H), 1.32 (s, 9H), 0.93 (d, *J* = 7Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.2, 155.6, 143.5, 132.8, 130.4, 129.8, 128.5, 127.5, 126.5, 126.3, 125.8, 123.7, 122.4, 121.9, 78.8, 48.7, 44.1, 41.3, 28.3, 25.1, 23.2, 22.1. HRMS (ESI) for $C_{24}H_{31}N_2O_2$ $[M+H]^+$: calcd 379.2380, found 379.2383.

Chiral HPLC Charts for **4zg**:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.317	BB	0.2248	492.50244	33.64657	49.6302
2	9.072	BBA	0.5012	499.84235	15.37845	50.3698

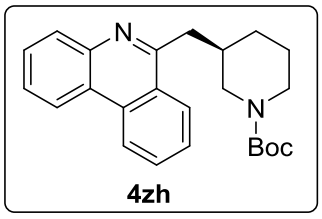
Figure *S31*. The HPLC chart of rac-**4zg**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.309	BV R	0.2231	2.84201e4	1959.26123	97.1947
2	9.076	BBA	0.4913	820.26617	25.77610	2.8053

Figure *S32*. The HPLC chart of **4zg**

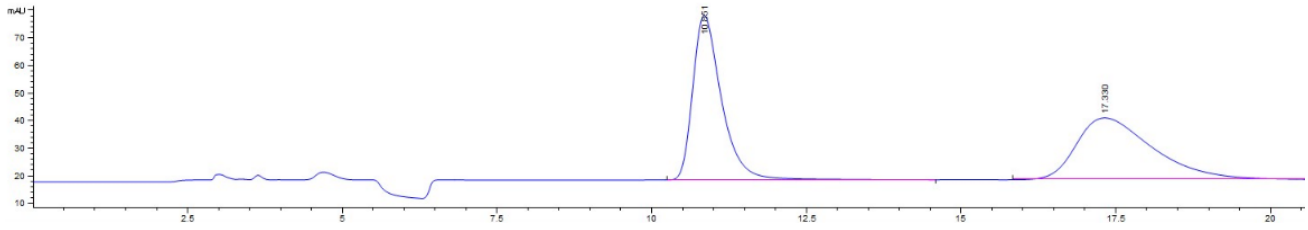
***tert*-butyl (*R*)-3-(phenanthridin-6-ylmethyl)piperidine-1-carboxylate (4zh)**



4zh

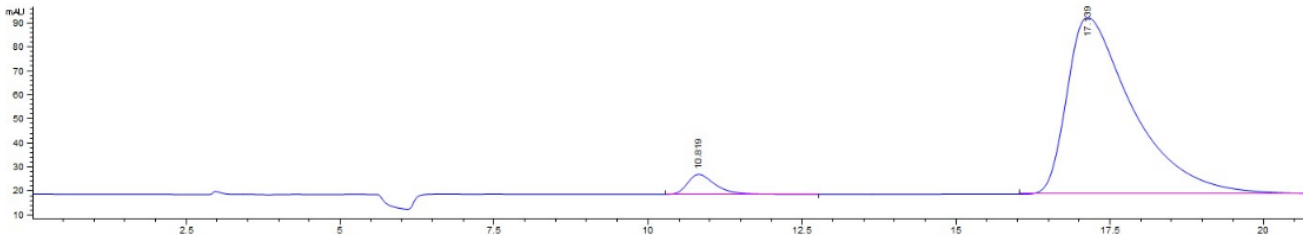
4zh was isolated via column chromatography (eluent: DCM to PE/EA = 5/1) as colorless liquid (80.0 mg, 71%, 91% *ee*). Enantiomeric excess was established by HPLC analysis by using a Daicel Chiralpak ID column, *ee* = 91 % (HPLC: 210 nm, *n*-Hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 30 ˚C, t_r (major) = 17.14 min, t_r (min) = 10.82 min). $[\alpha]_D^{25}$ = +34.6 (c 1.0, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 4.19-3.94 (m, 2H), 3.35-2.23 (m, 2H), 2.84-2.79 (m, 2H), 2.28 (s, 1H), 2.04 (s, 1H), 1.84 (s, 1H), 1.65 (s, 1H), 1.47-1.34 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.9, 154.9, 143.6, 132.9, 130.3, 129.7, 128.6, 127.3, 126.4, 126.2, 125.5, 123.6, 122.5, 121.9, 79.2, 50.1, 44.4, 39.5, 36.1, 31.1, 28.3, 24.9. HRMS (ESI) for $C_{24}H_{29}N_2O_2$ $[M+H]^+$: calcd 377.2224, found 377.2225.

Chiral HPLC Charts for **4zh**:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.85	BB	0.4887	1934.6	59.6	49.997
2	17.33	BBA	1.2890	1934.9	22.4	50.003

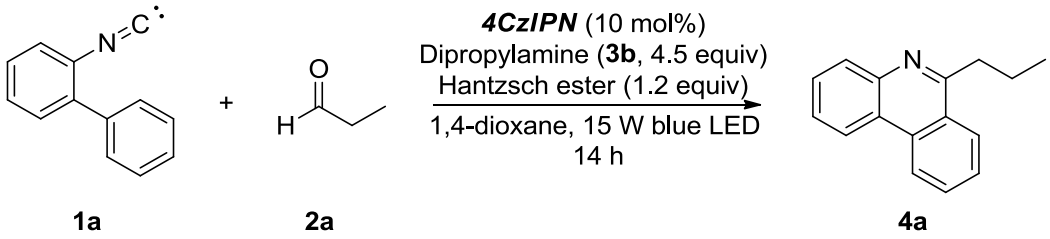
Figure *S33*. The HPLC chart of rac-**4zh**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.82	BB	0.4754	264.3	8.3	4.548
2	17.14	BBA	1.0951	5545.8	73.9	95.452

Figure *S34*. The HPLC chart of **4zh**

3.4 3 mmol-scale synthesis of 4a

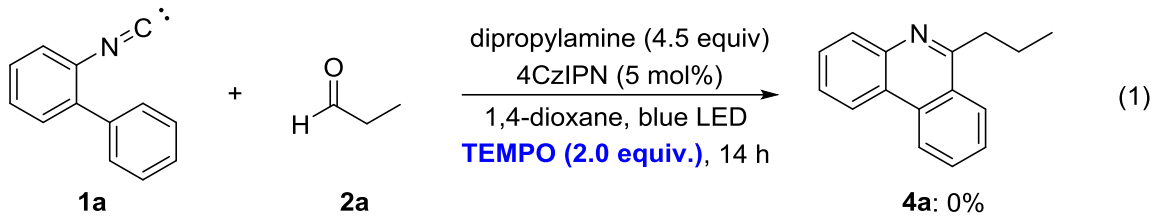


1a **2a** **4a**

Procedure: To a flame-dried Schlenk tube was added **1a** (3 mmol, 538 mg), 4CzIPN (0.15 mmol, 118 mg) and Hantzsch ester (912 mg, 3.6 mmol). The tube was evacuated and refilled with N_2 for three times. A solution of aldehyde **2a** (13.5 mmol, 784 mg), amine **3b** (13.5 mmol, 1.37 g) in 1,4-dioxane (75.0 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED and stirred at 25 ˚C for 14 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure **4a** (484.7 mg, 73%).

4. Mechanistic Studies

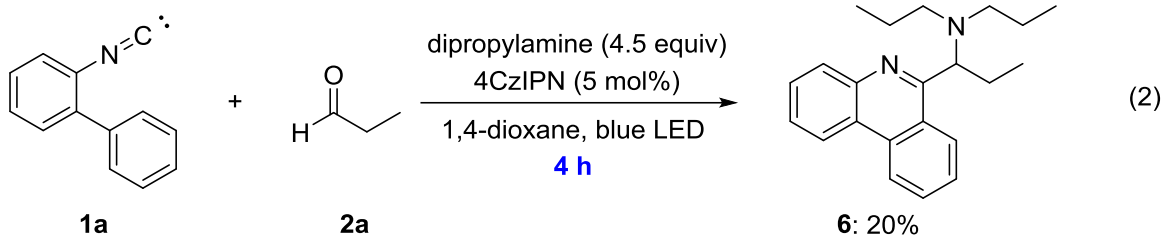
4.1 Radical scavenging experiment.



(1)

The procedure is similar as the one described in the model reaction of **1a** and **2a** under the standard reaction conditions except the addition of 2.0 equivalents of TEMPO. Radical-scavenging experiment indicated the reaction was completely suppressed when 2.0 equiv. TEMPO was added into the reaction mixture.

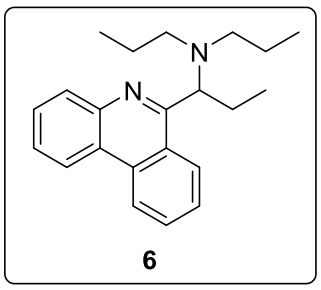
4.2 Formation and detection of intermediate 6 when the reaction time was shorten to 4 h.



(2)

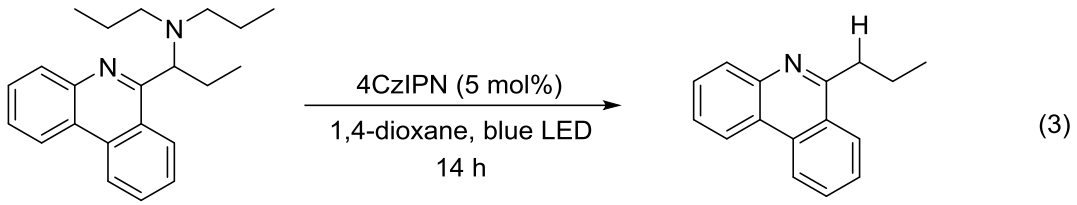
Characterization of **6**:

***N*,*N*-diethyl-1-(phenanthridin-6-yl)propan-1-amine (6)**



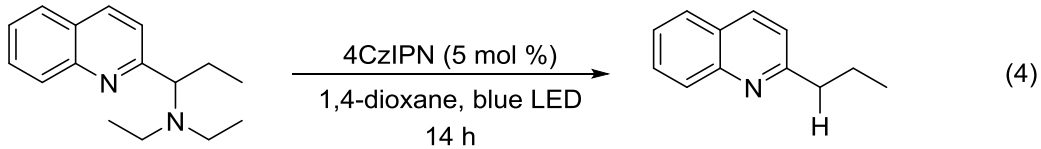
6 was isolated via column chromatography (eluent: PE/EA = 10/1) as a colorless liquid (12.8 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.59 (d, J = 8.2 Hz, 1H), 8.22 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.76-7.72 (m, 1H), 7.70-7.64 (m, 2H), 4.56 (dd, J_1 = 10.1 Hz, J_2 = 3.9 Hz, 1H), 2.72-2.61 (m, 4H), 2.56-2.45 (m, 1H), 2.12-2.01 (m, 1H), 1.53-1.39 (m, 4H), 0.87 (t, J = 7.3 Hz, 3H), 0.74 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 143.3, 133.0, 130.4, 129.8, 128.2, 127.3, 126.6, 126.4, 126.4, 123.8, 122.1, 121.8, 66.5, 53.4, 21.6, 20.1, 12.0, 11.8.

4.3 Probing experiment on possible reaction intermediate.



6 **4a**: 90% (3)

Procedure for the conversion of **6** to **4a**: To a 25 mL flame-dried Schlenk tube was added **6** (0.3 mmol), 4CzIPN (0.015 mmol). The tube was evacuated and refilled with N_2 for three times. 1,4-dioxane (7.5 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED and stirred at 25 ˚C for 14 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give **4a** (90%).

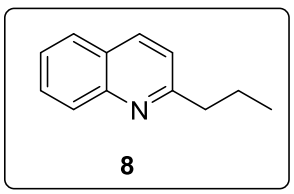


7 **8**: 67% (4)

Procedure for the conversion of **7** to **8**: To a 25 mL flame-dried Schlenk tube was added **7** (0.3 mmol), 4CzIPN (0.015 mmol). The tube was evacuated and refilled with N_2 for three times. 1,4-dioxane (7.5 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED and stirred at 25 ˚C for 14 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give **8** (67%).

Characterization of **8**:

2-propylquinoline (8):

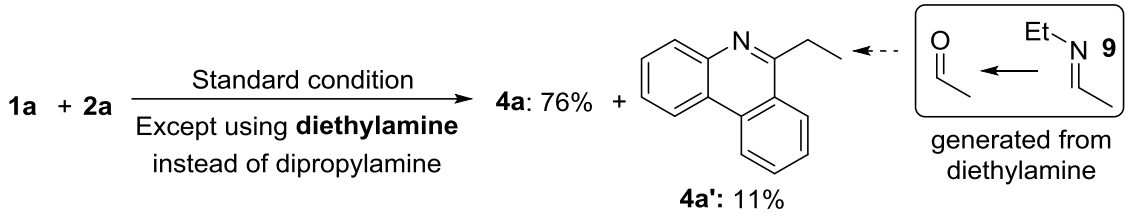


8

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.4 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 2.98 (t, J = 7.6 Hz, 2H), 1.92-1.83 (m, 2H), 1.04 (t, J = 7.2 Hz, 2H), 1.92-1.83 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.9, 147.8, 136.3, 129.4, 128.8, 127.5, 126.7, 125.7, 121.4, 41.2, 23.3, 14.0. Its analytical data are

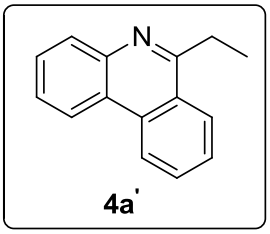
consistent with the documented data.[21]

4.4 Detection of byproduct 4a′



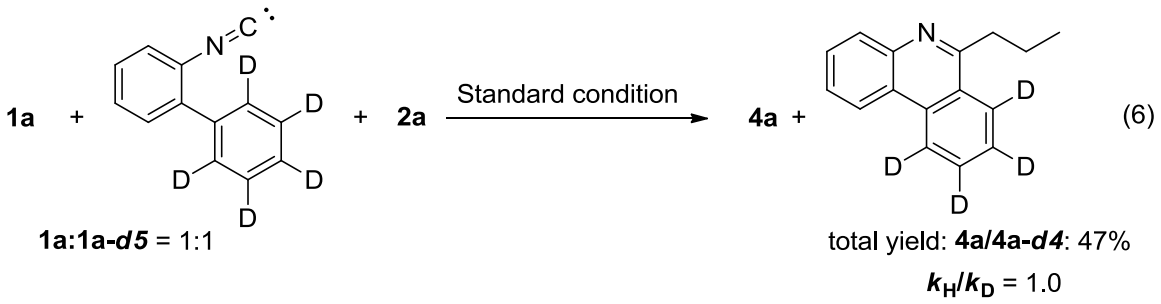
Characterization of **4a′**:

6-ethylphenanthridine (4a′)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.3 Hz, 2H), 8.55 (d, *J* = 7.0 Hz, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 8.13 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.85-7.82 (m, 1H), 7.73-7.68 (m, 2H), 7.64-7.60 (m, 1H), 3.42 (t, *J* = 7.6 Hz, 2H), 1.52 (t, *J* = 7.6 Hz, 3H). Its analytical data are consistent with the documented data.[22]

4.5 KIE experiment.



Procedure: To a 25 mL flame-dried Schlenk tube was added **1a** (26.9 mg, 0.15 mmol), **1a**-*d5* (27.6 mg, 0.15 mmol) 4CzIPN (11.8 mg, 0.015 mmol) and Hantzsch ester (91.2 mg, 0.36 mmol). The tube was evacuated and refilled with N_2 for three times. A solution of aldehyde **2a** (78.3 mg,1.35 mmol), amine **3b** (136.0 mg, 1.35 mmol) in 1,4-dioxane (7.5 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED and stirred at 25 ˚C for 14 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure **4a** and **4a**-*d4* (31.4 mg, 47%). The k_H/k_D was calculated to be 1.0 according to the analysis of ^{1}H NMR spectrum of **4a** and **4a**-*d4*.

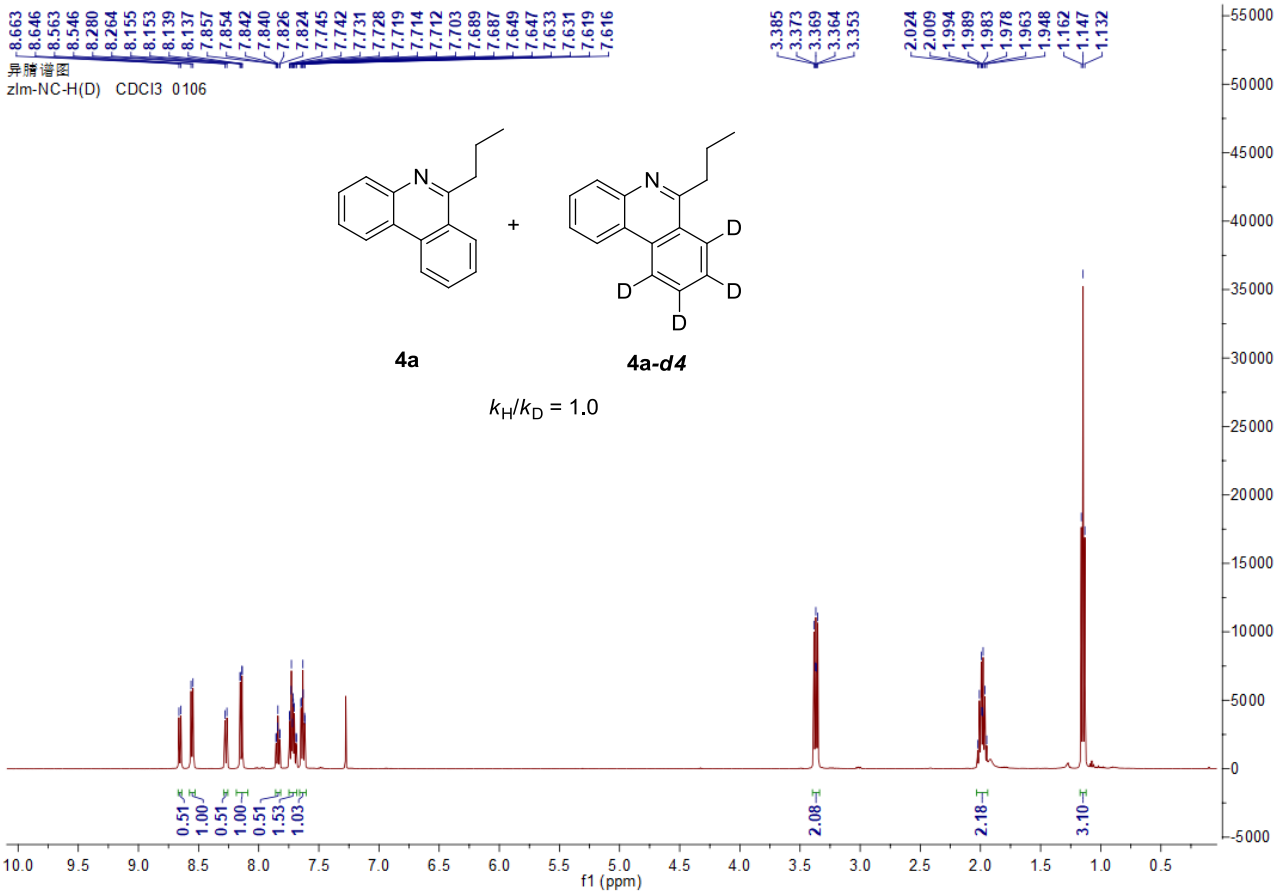
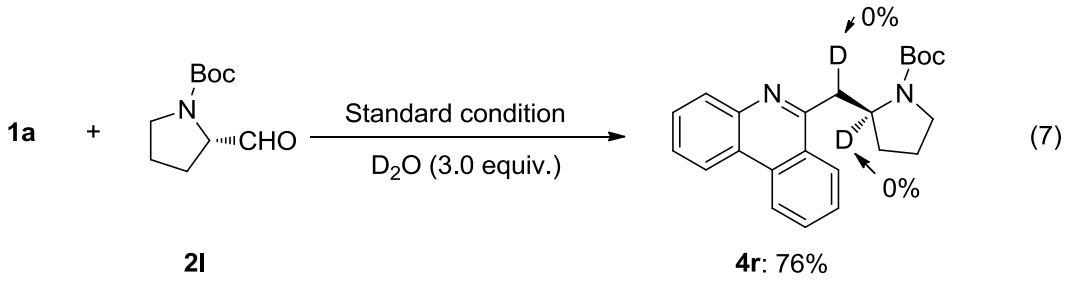


Figure *S35.* ^{1}H NMR spectrum of **4a** and **4a-*d4*** for KIE experiments.

4.6 Deuterium-labeling experiments



(7)

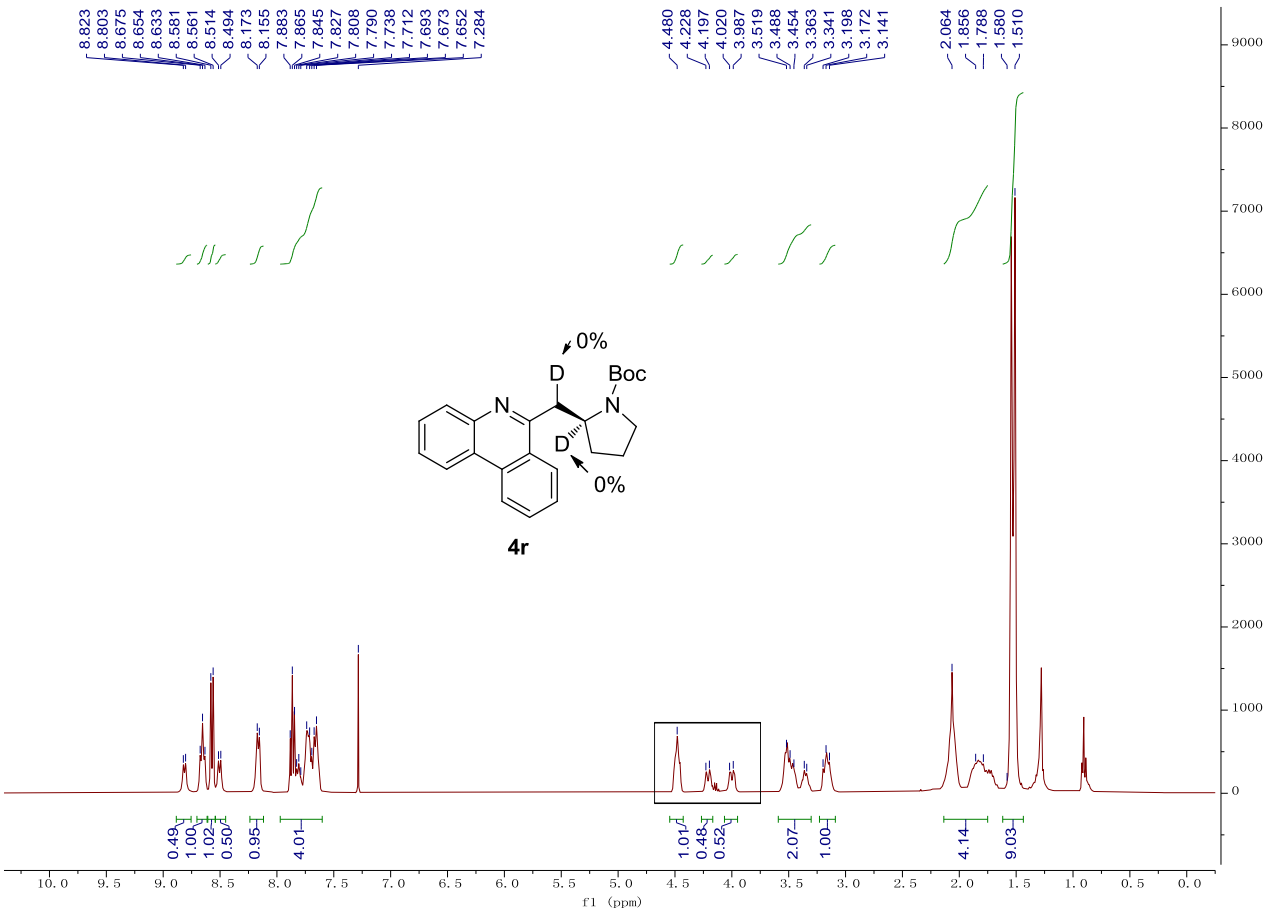


Figure *S36*. ^{1}H NMR spectrum for Deuterium-labeling experiments.

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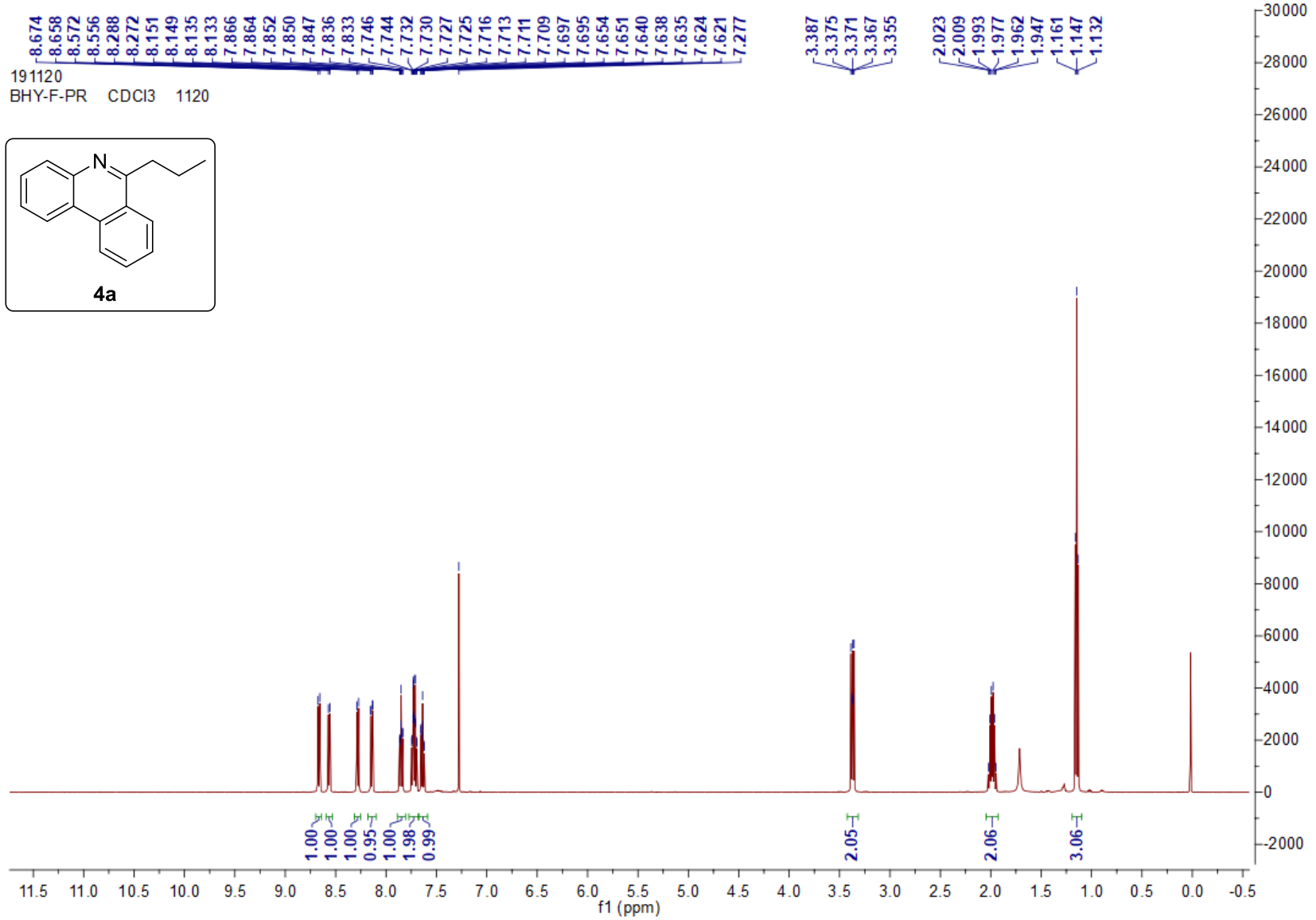
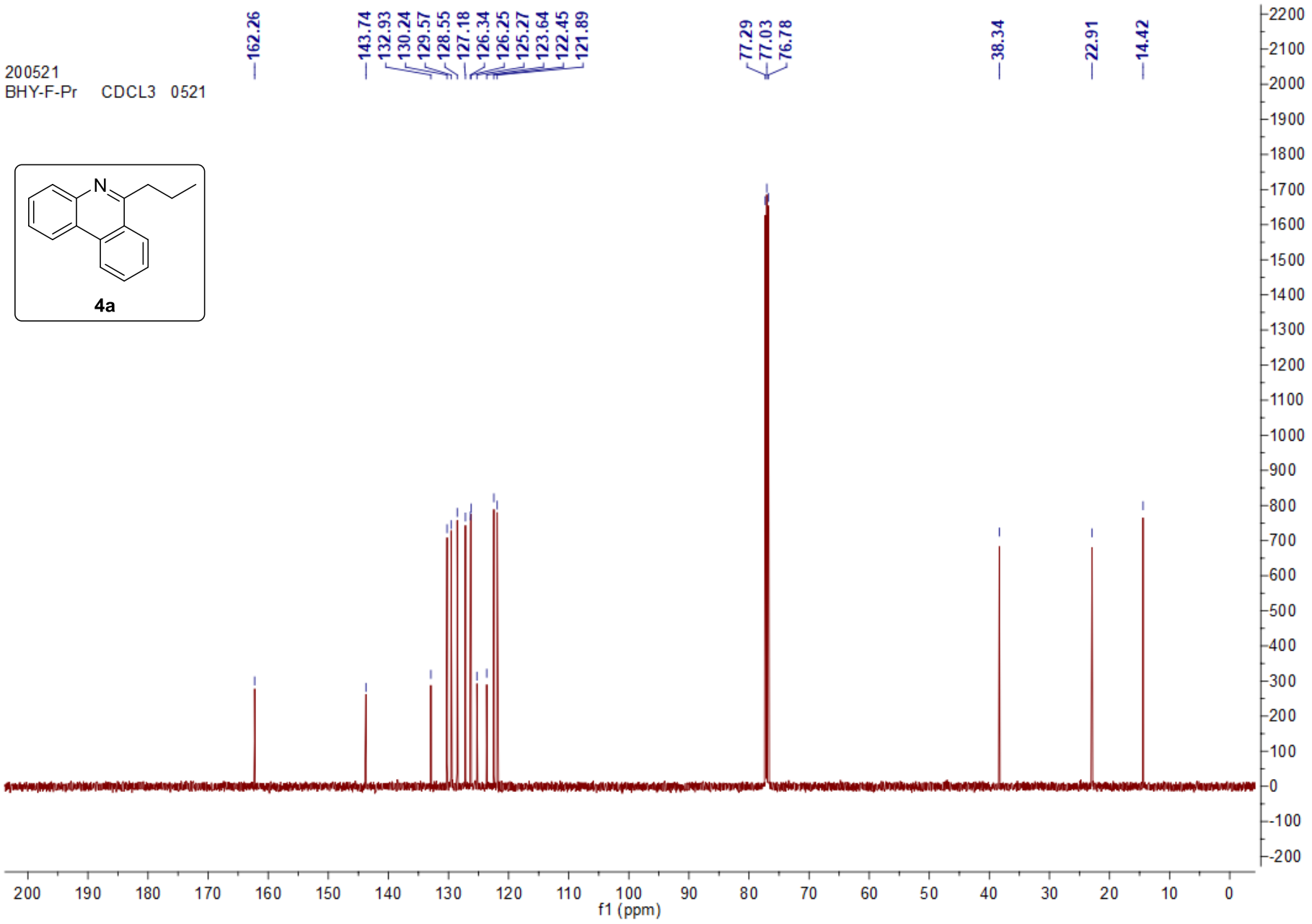
6. Copies of ^{1}H and ^{13}C NMR spectra

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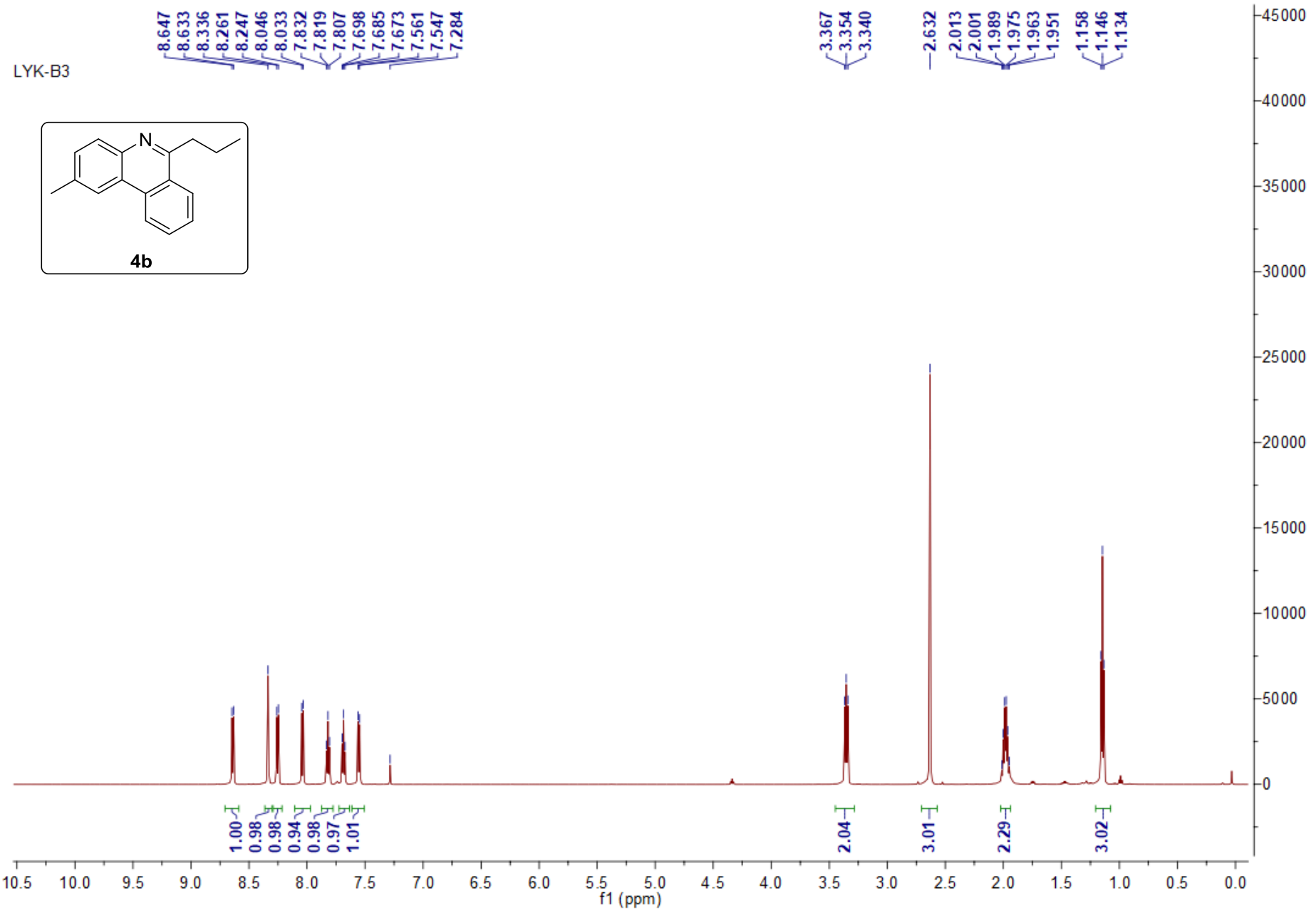
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7.673
7.561
7.547
7.284
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3.354
3.340
2.632
2.013
2.001
1.989
1.975
1.963
1.951
1.158
1.146
1.134
N
4b
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2.04
3.01
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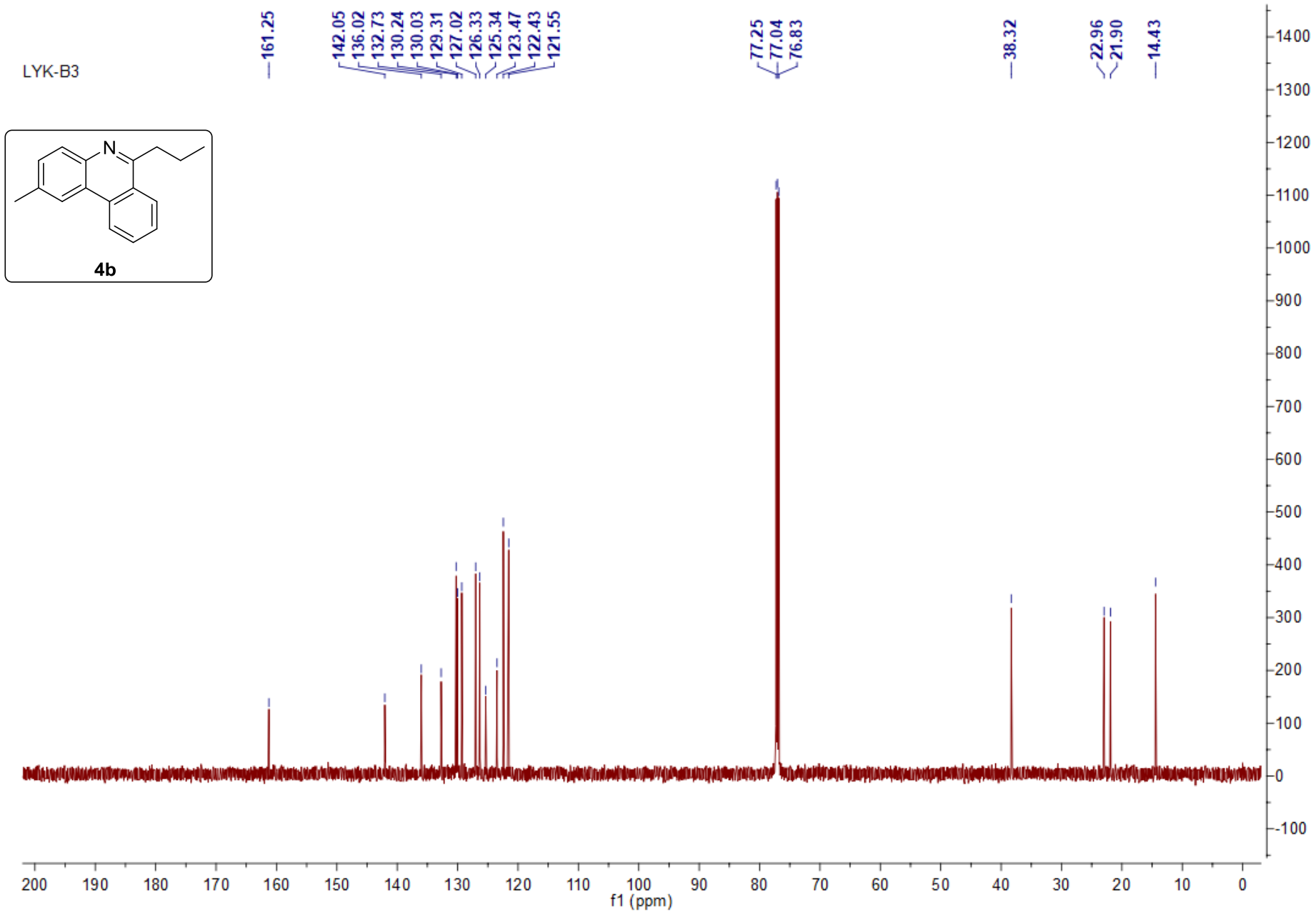
f1 (ppm)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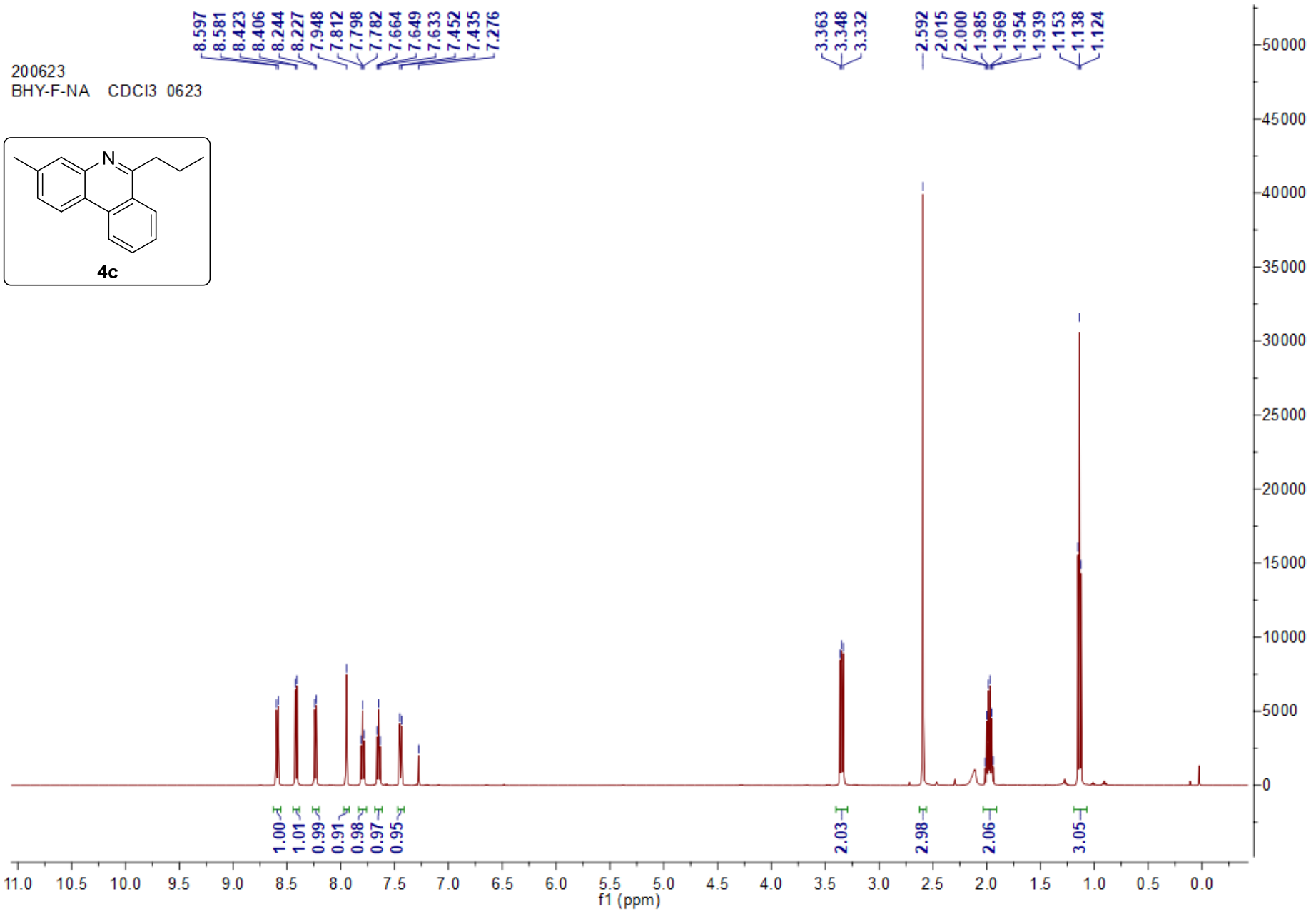
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7.435
7.276
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3.348
3.332
2.592
2.015
2.000
1.985
1.969
1.954
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1.153
1.138
1.124
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BHY-F-NA CDCl3 0623
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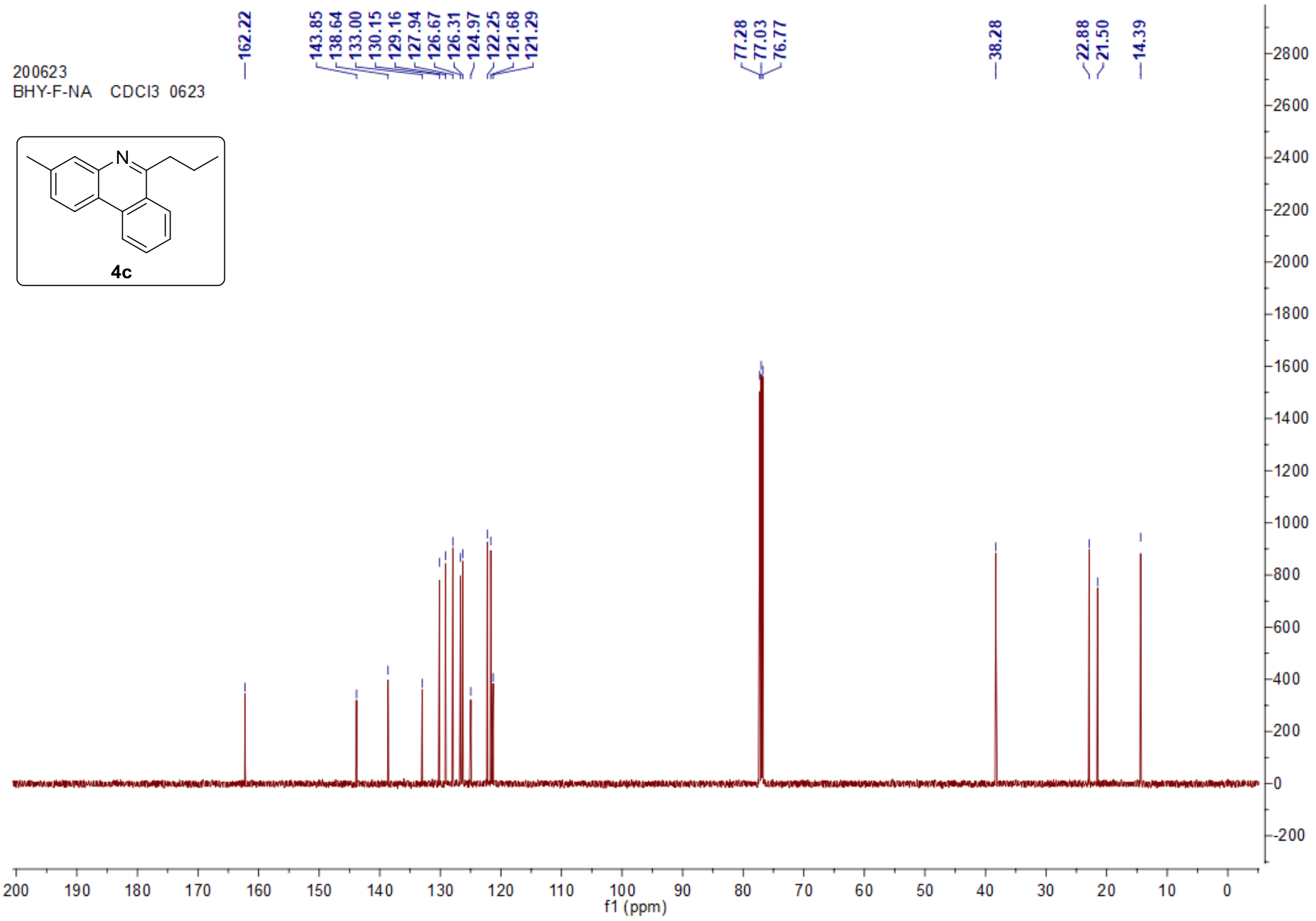
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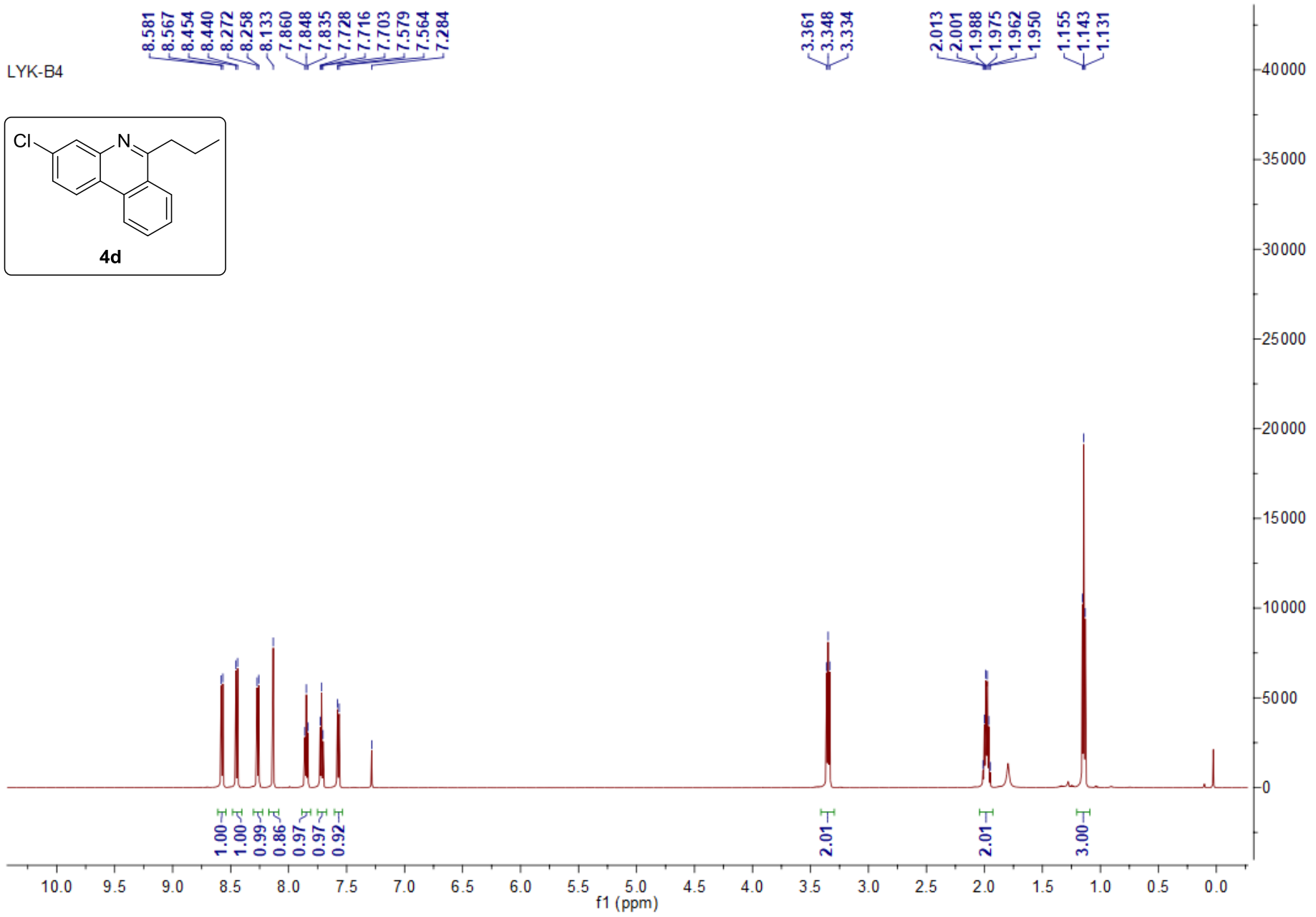
f1 (ppm)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1.155
1.143
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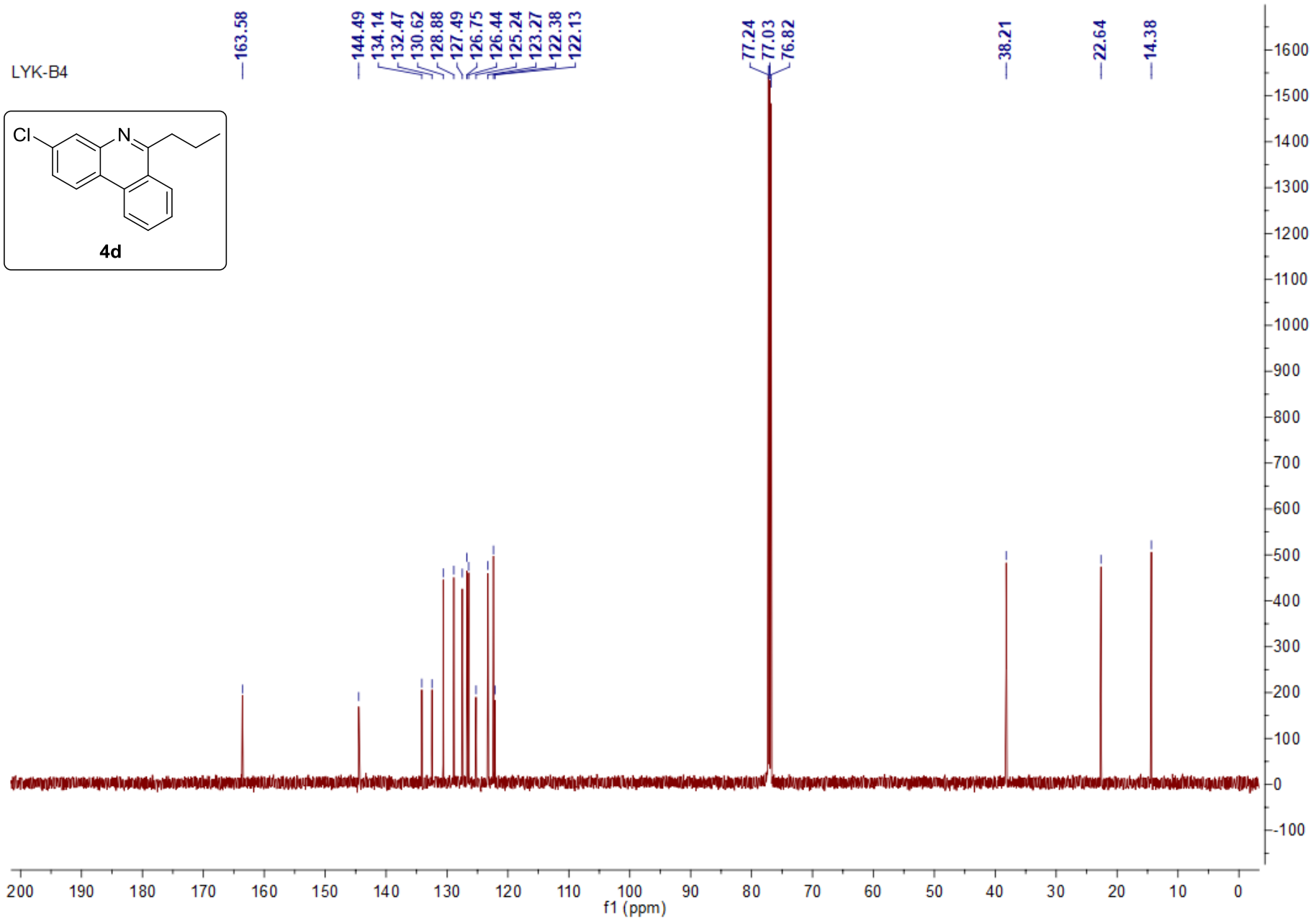
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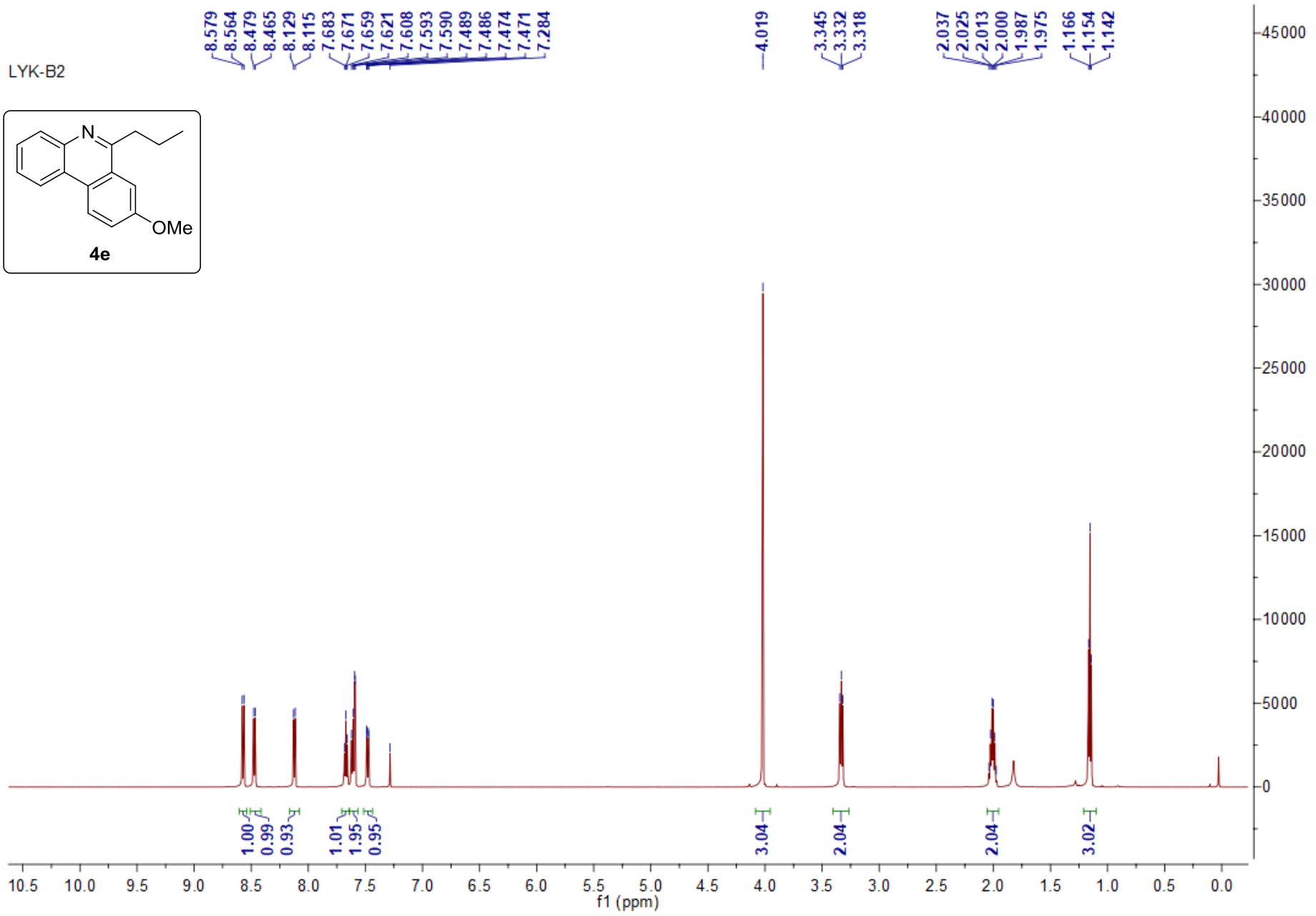
14.38
f1 (ppm)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4e
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8.465
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7.621
7.608
7.593
7.590
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7.486
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7.284
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3.332
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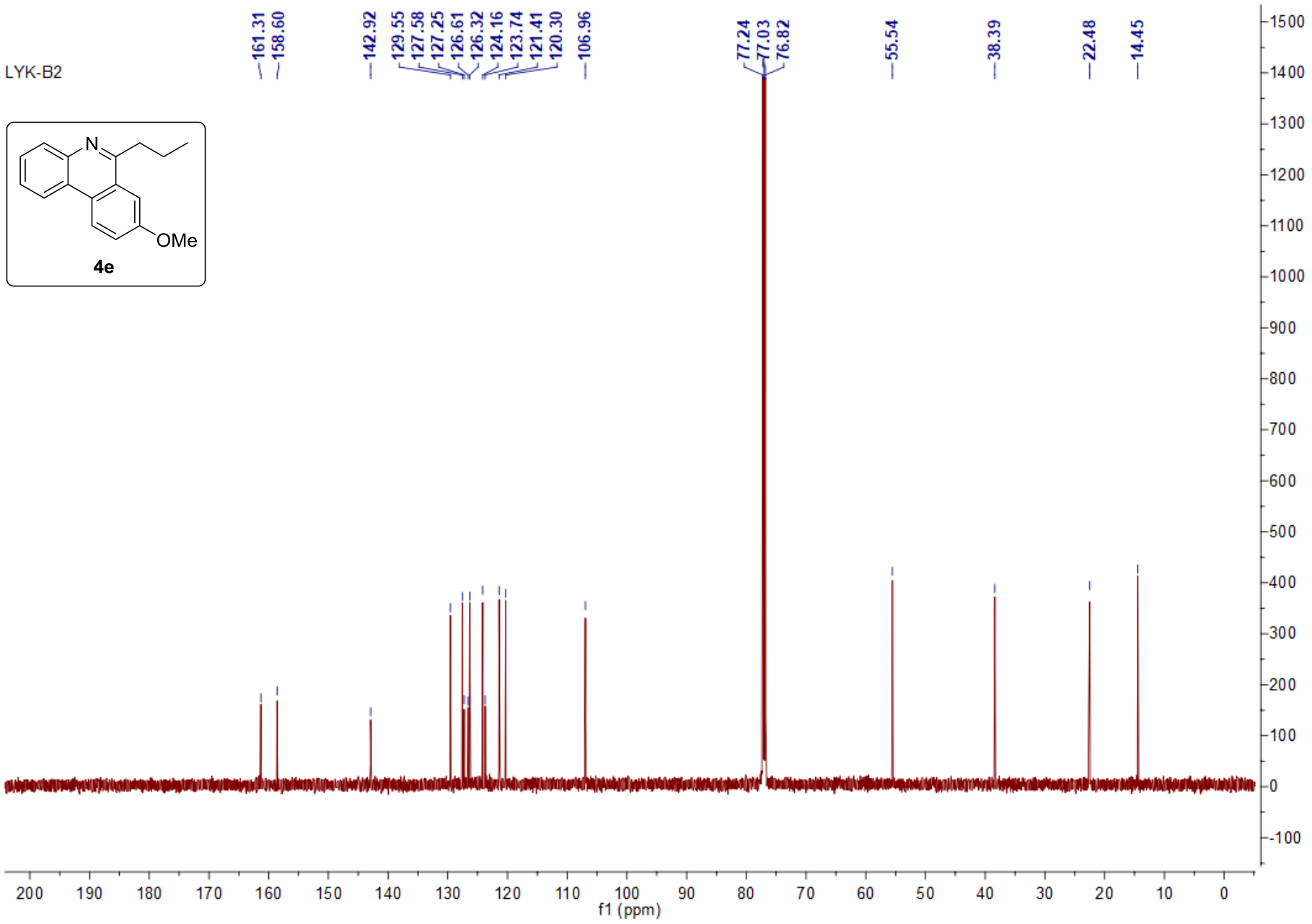
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OMe
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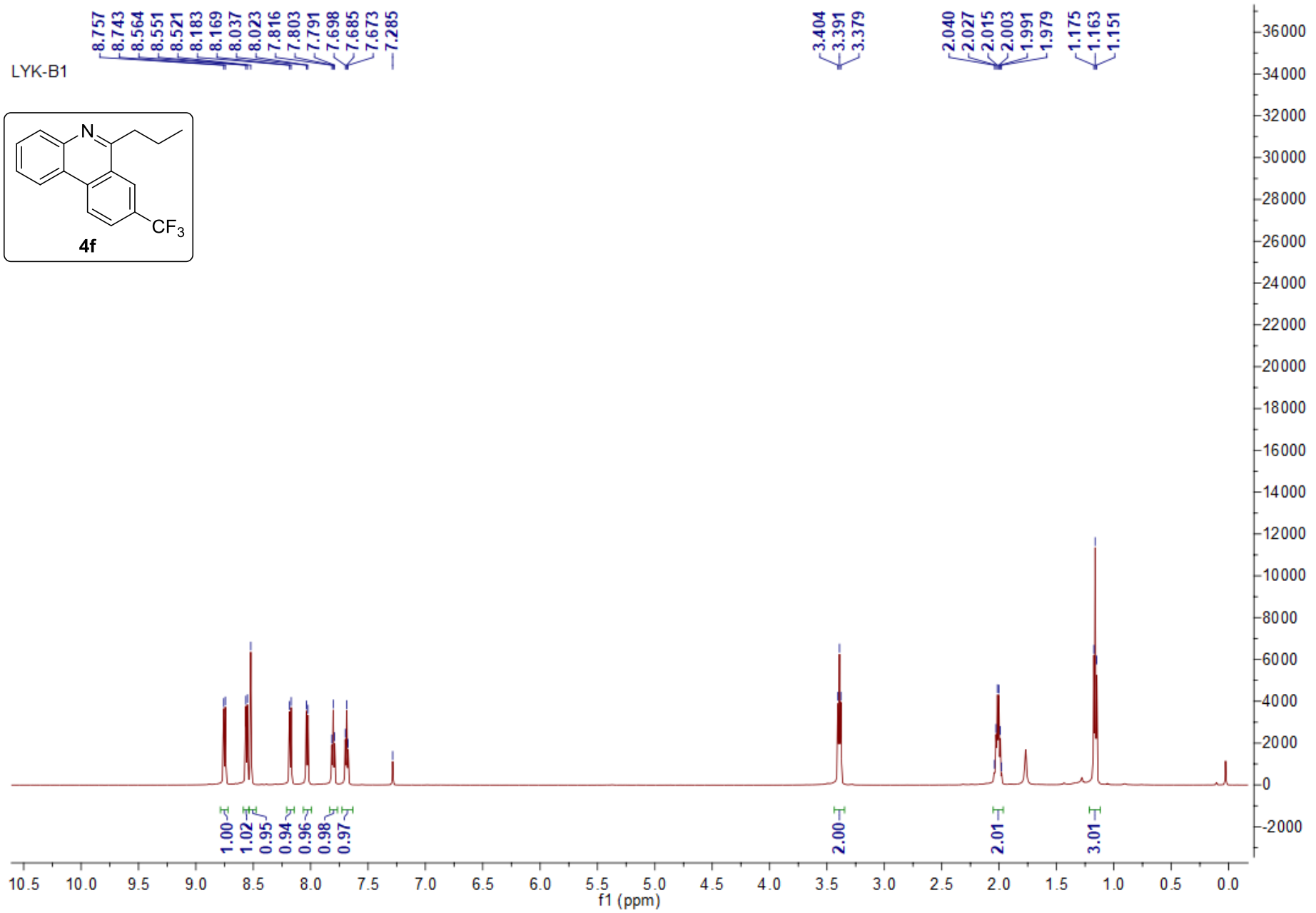
f1 (ppm)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3.379
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1.163
1.151
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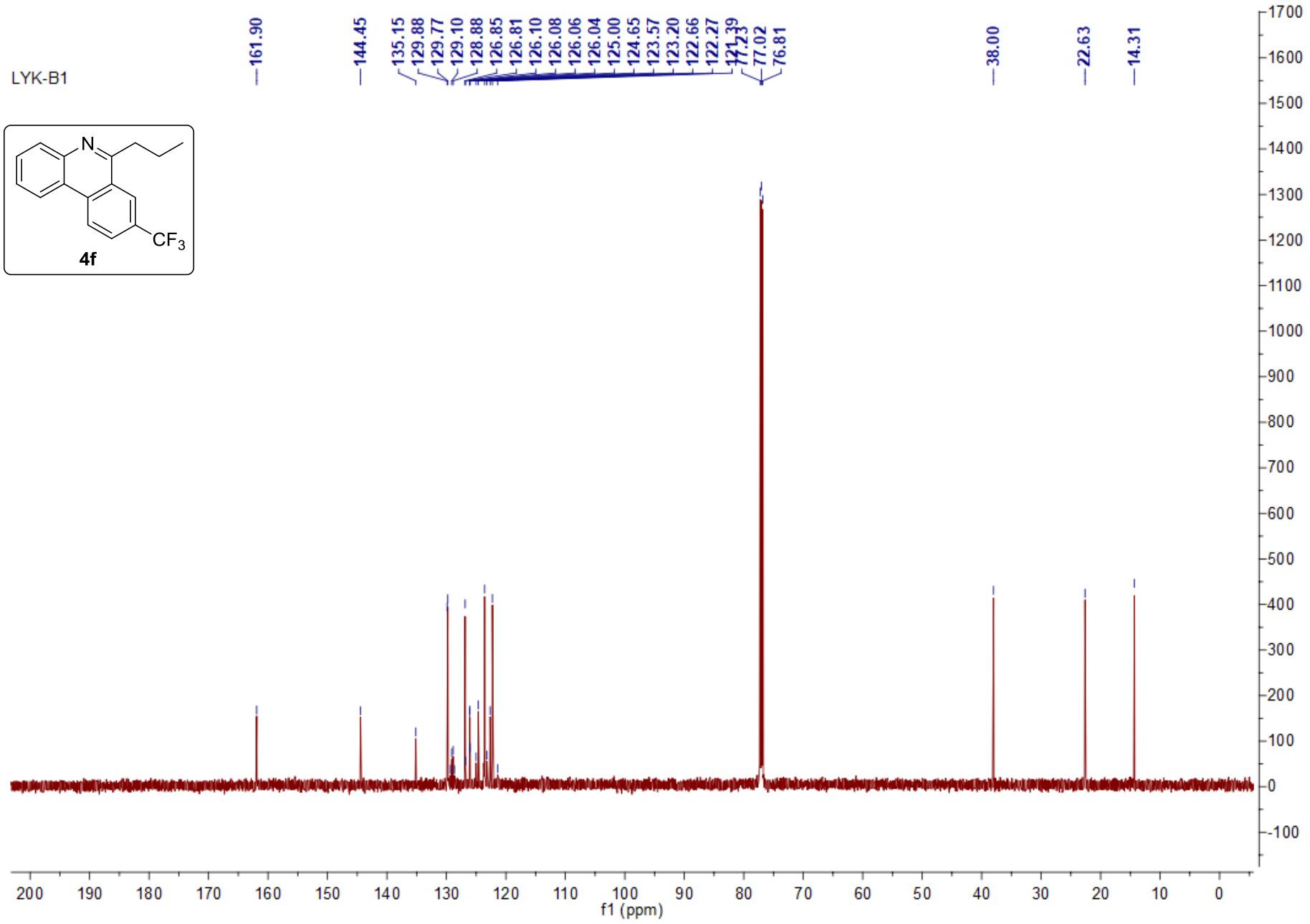
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126.06
126.04
125.00
124.65
123.57
123.20
122.66
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77.02
76.81
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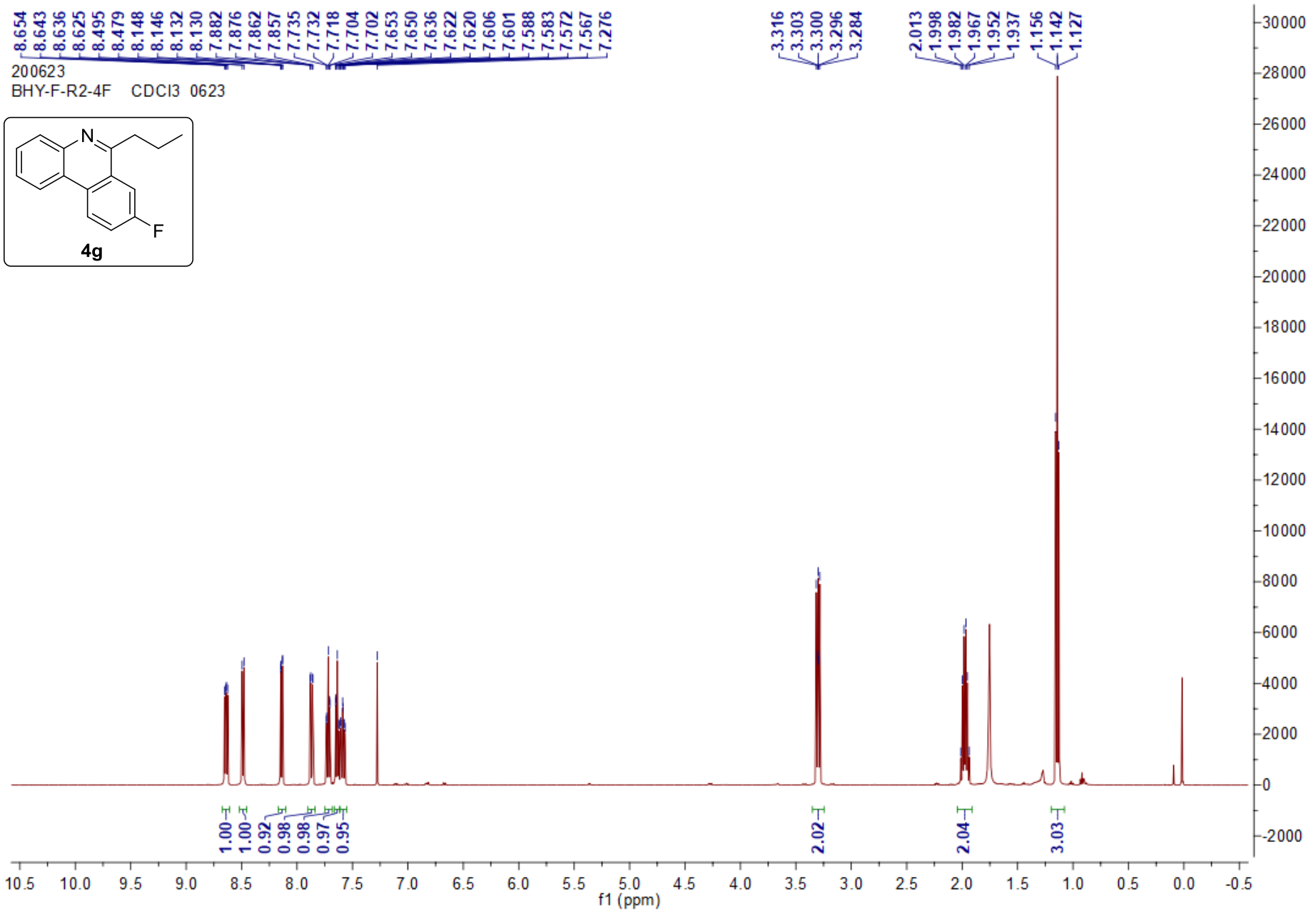
N
CF3
4f
f1 (ppm)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7.601
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7.583
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7.567
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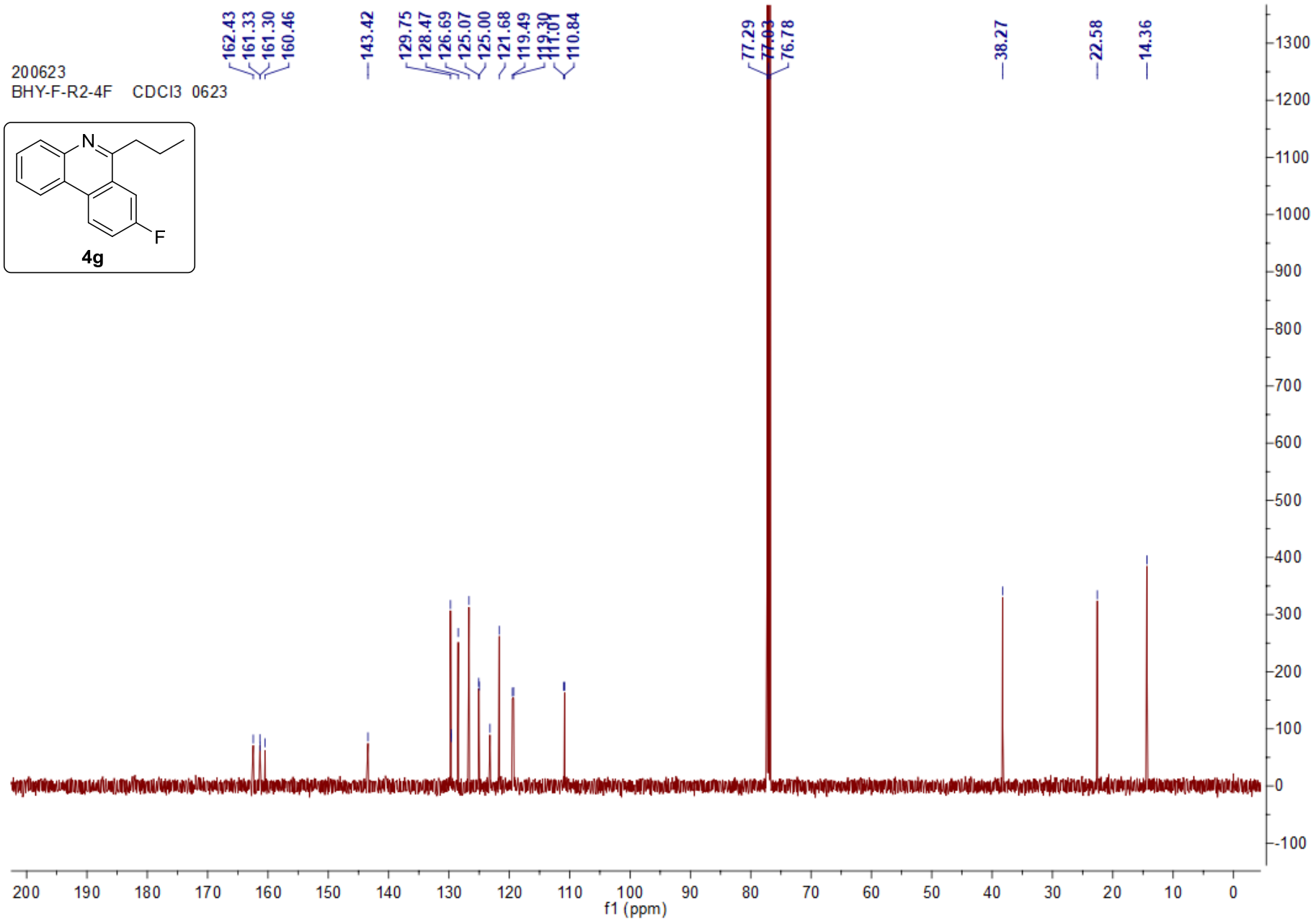
2.04
3.03
f1 (ppm)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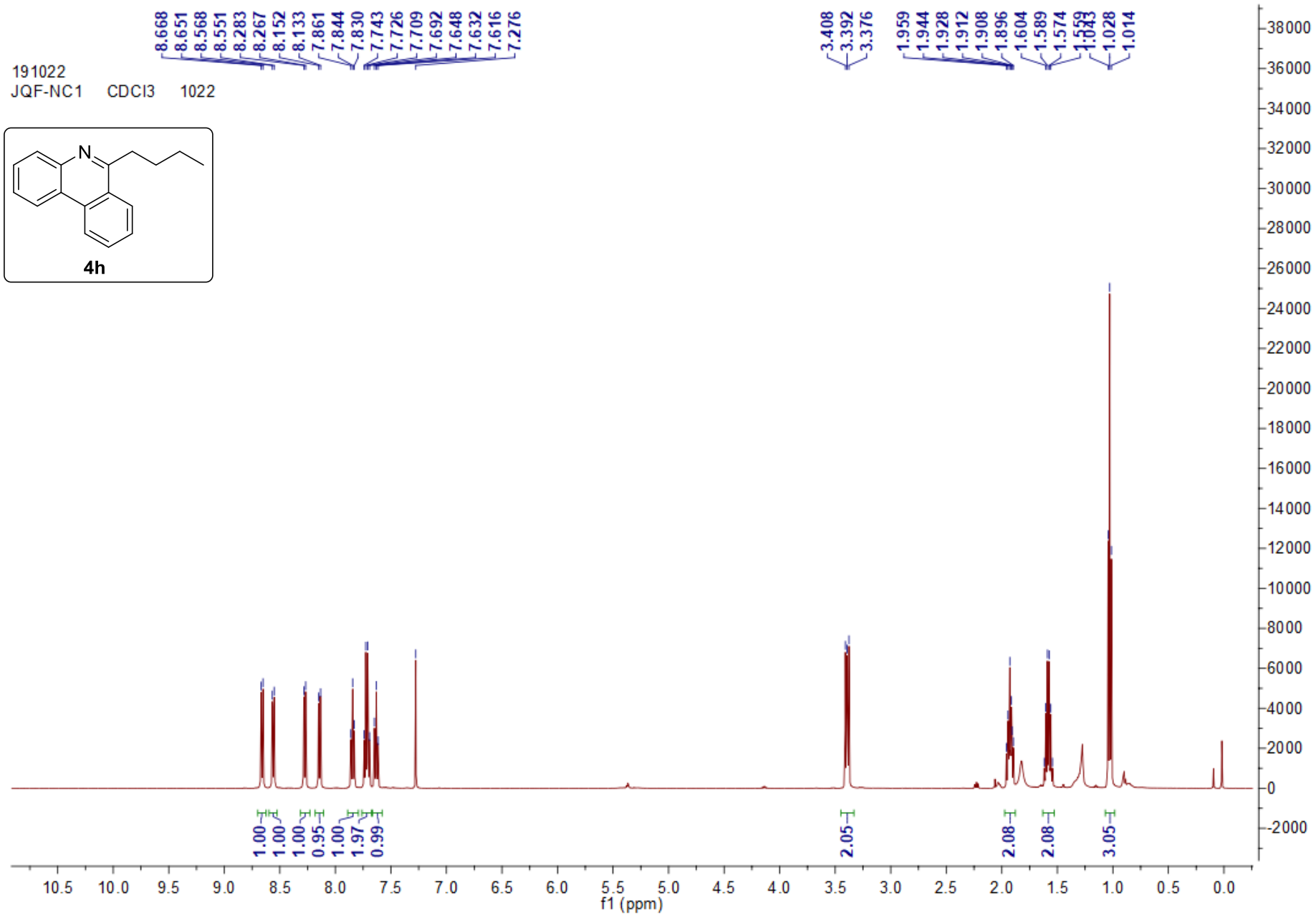
f1 (ppm)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1.014
191022
JQF-NC1 CDCl3 1022
N
4h
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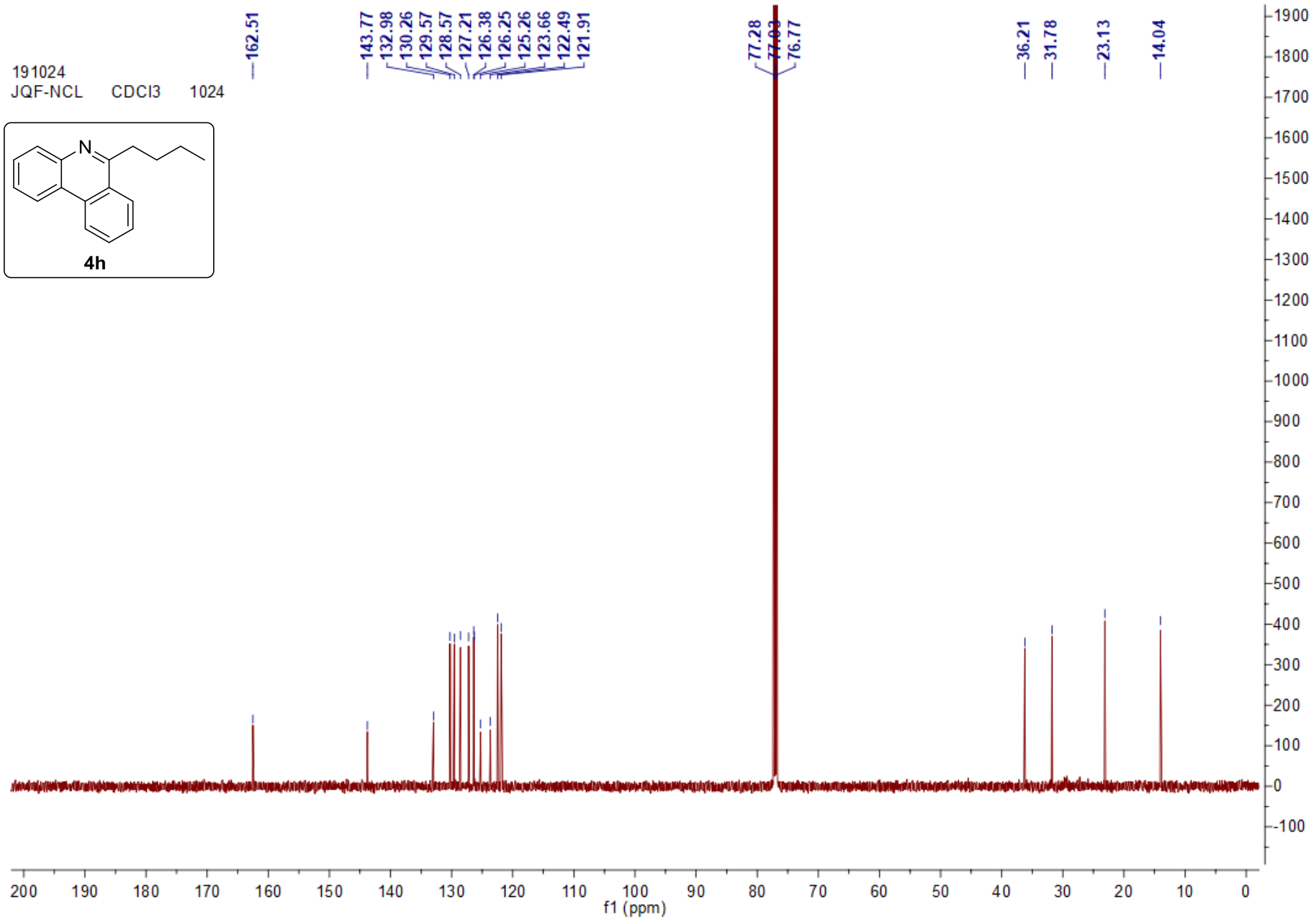
f1 (ppm)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126.38
126.25
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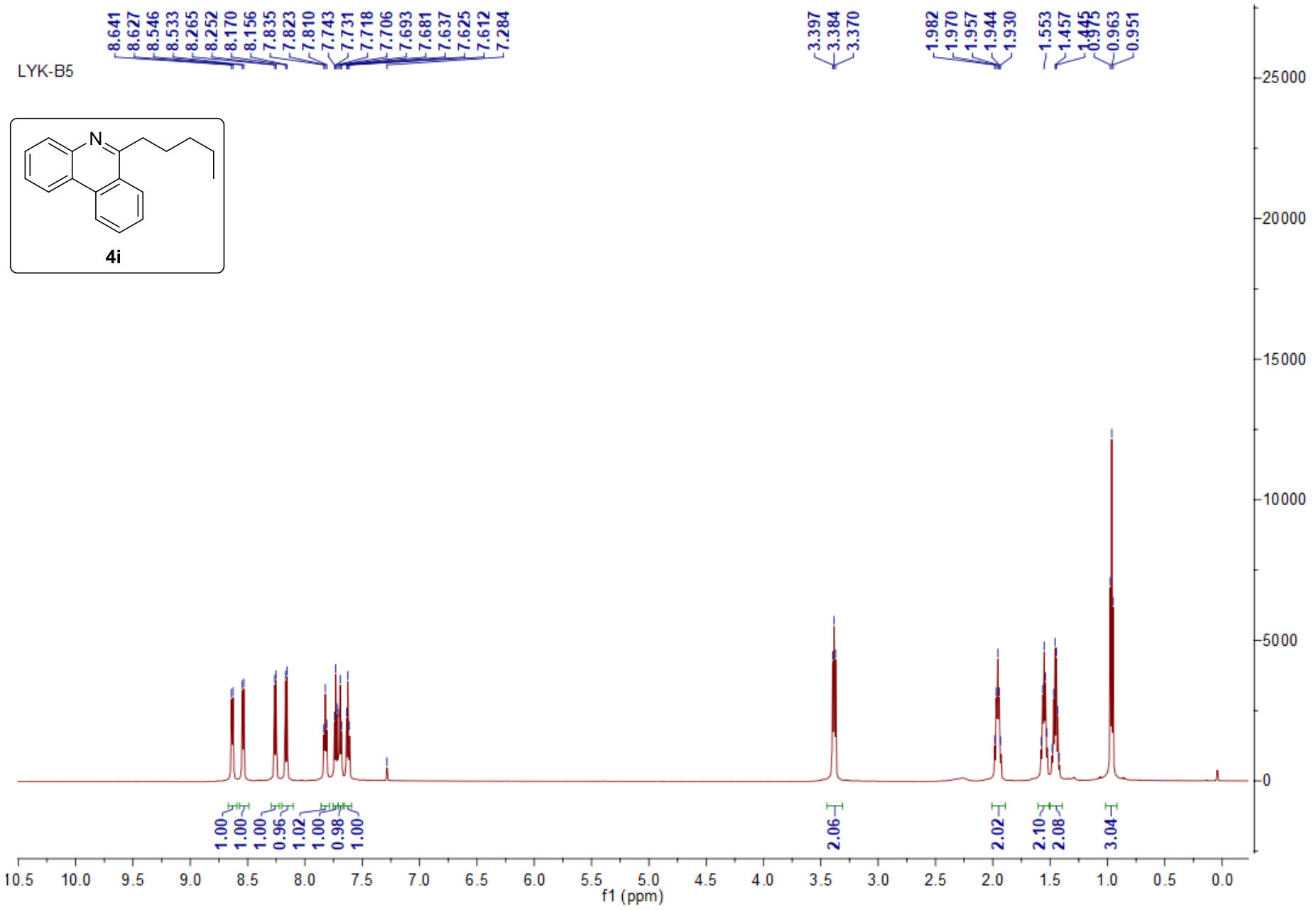
31.78
23.13
14.04
f1 (ppm)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7.823
7.810
7.743
7.731
7.718
7.706
7.693
7.681
7.637
7.625
7.612
7.284
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1.970
1.957
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0.951
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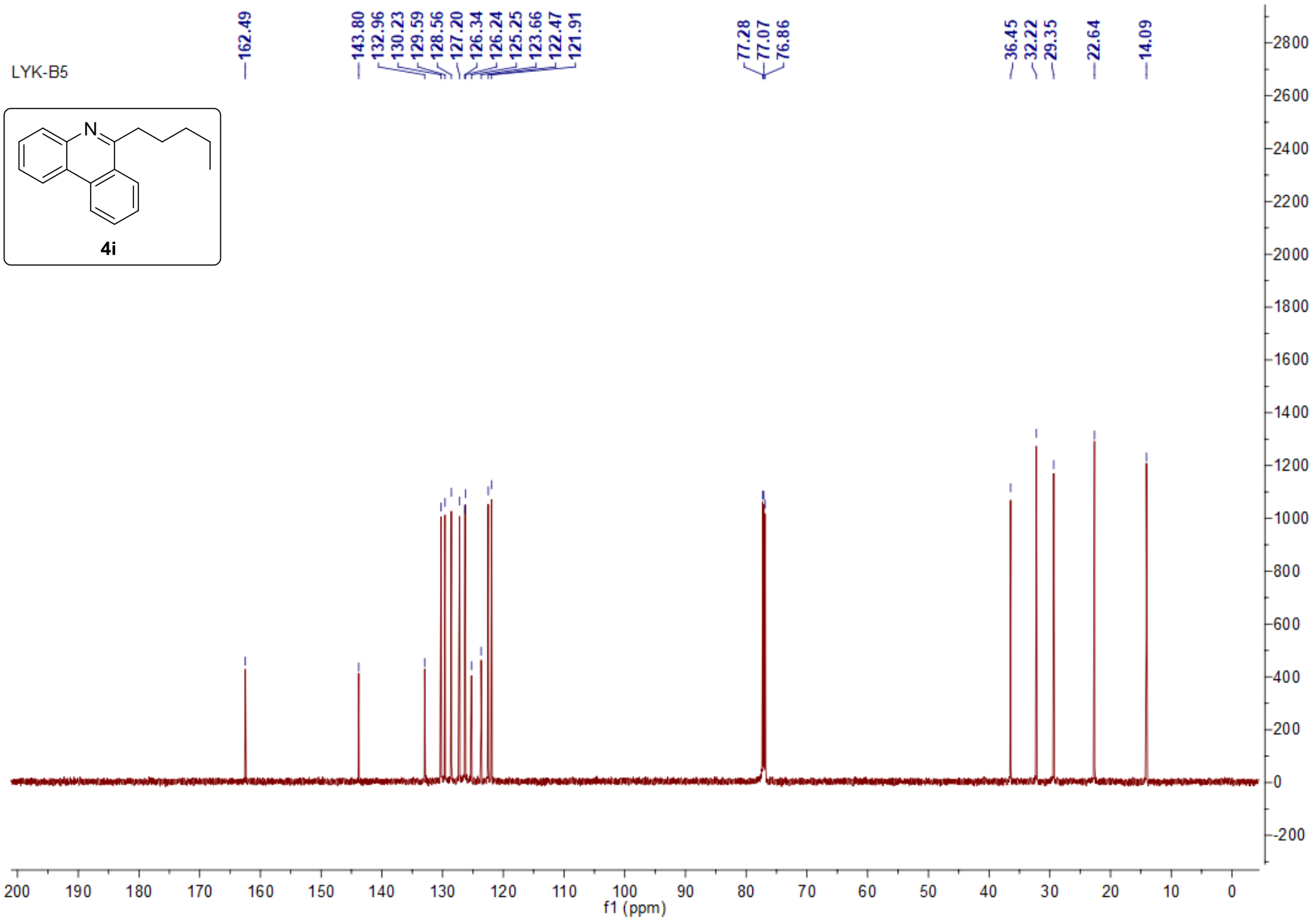
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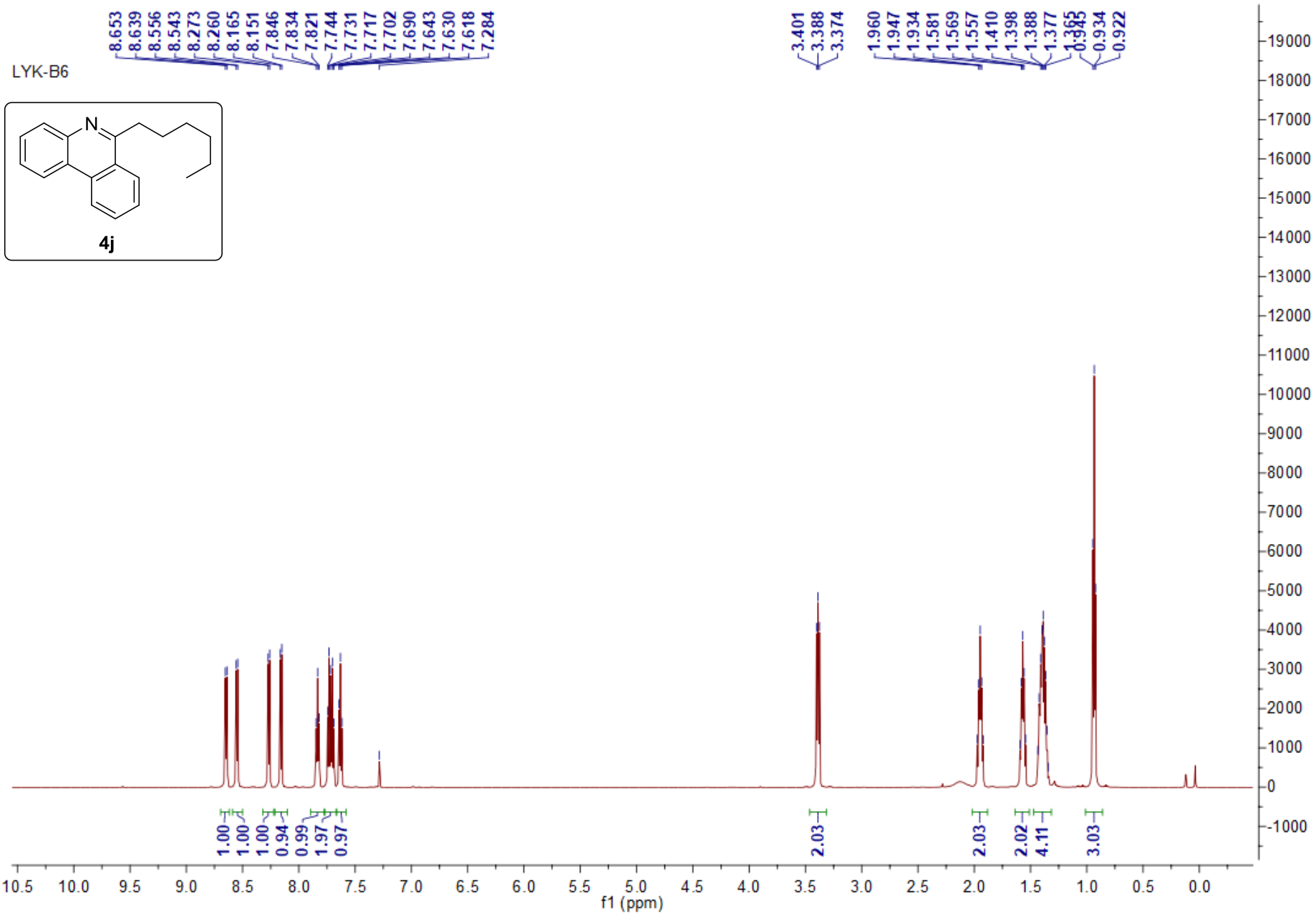
f1 (ppm)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7.821
7.744
7.731
7.717
7.702
7.690
7.643
7.630
7.618
7.284
3.401
3.388
3.374
1.960
1.947
1.934
1.581
1.569
1.557
1.410
1.398
1.388
1.377
0.945
0.934
0.922
1.00
1.00
1.00
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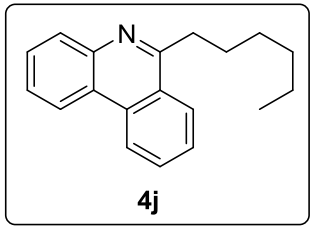
LYK-B6


N

4j

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122.48
121.91
77.27
77.05
76.84
36.50
31.79
29.71
29.64
22.65
14.11
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
170
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120
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50
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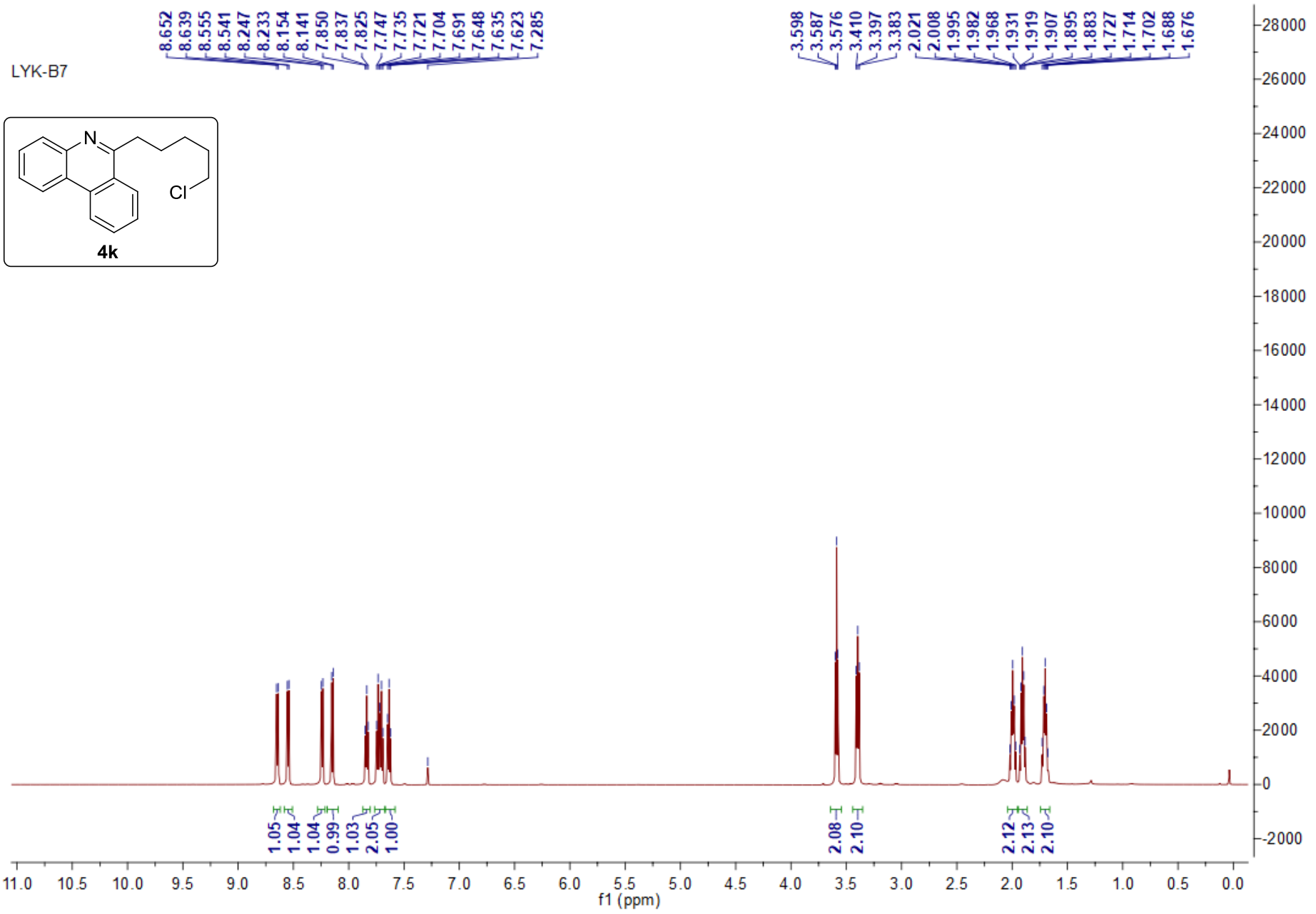
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7.623
7.285
3.598
3.587
3.576
3.410
3.397
3.383
2.021
2.008
1.995
1.982
1.968
1.931
1.919
1.907
1.895
1.883
1.727
1.714
1.702
1.688
1.676
N
Cl
4k
1.05
1.04
1.04
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2.12
2.13
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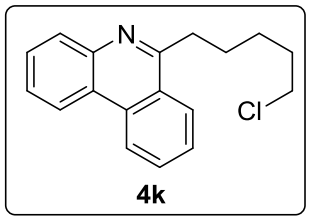
f1 (ppm)

LYK-B7


N
Cl

4k

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126.14
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123.66
122.54
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77.29
77.07
76.86
45.01
36.00
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28.54
27.18
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200
190
180
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50
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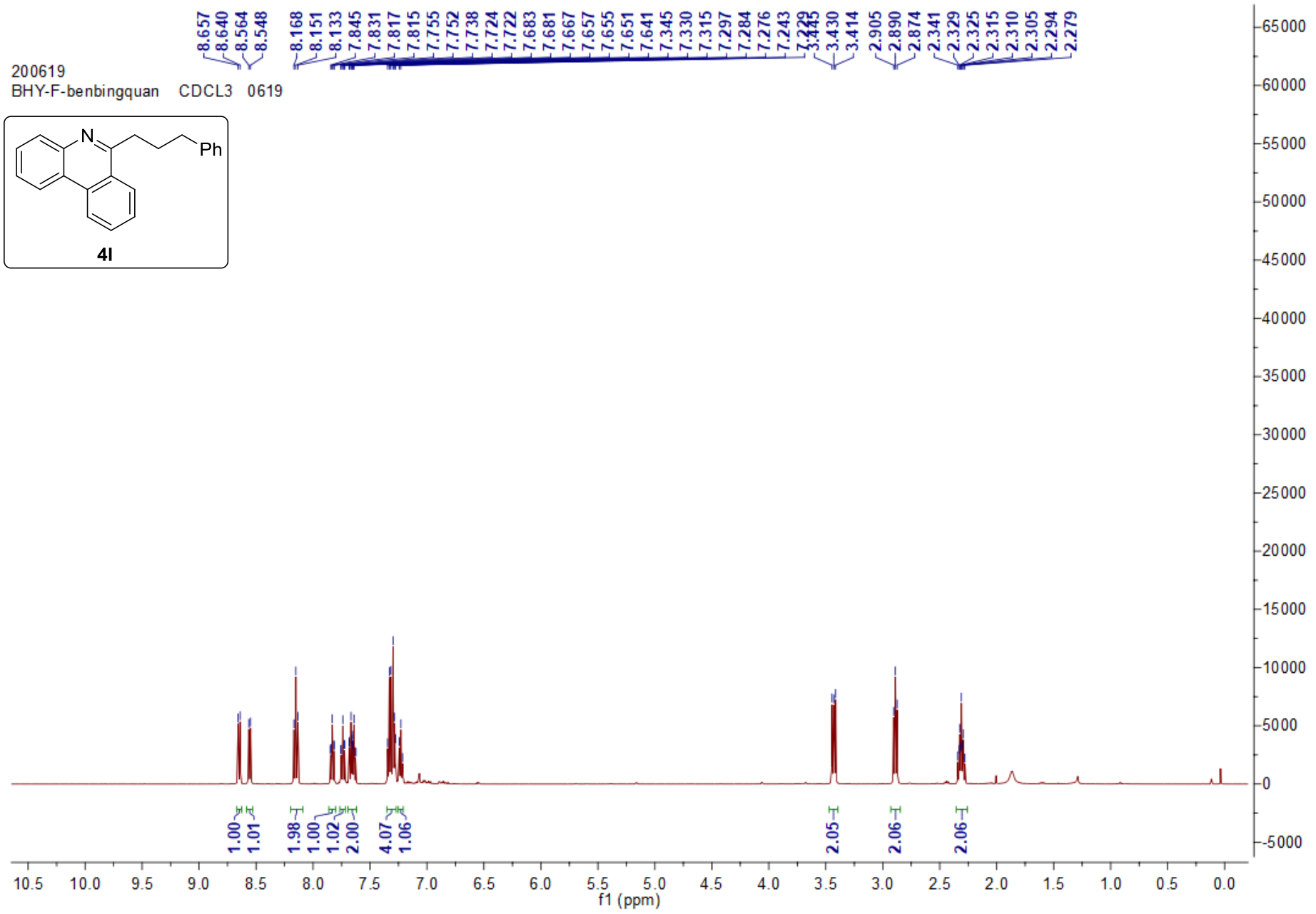
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7.683
7.681
7.667
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7.330
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7.297
7.284
7.276
7.243
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3.414
2.905
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2.341
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200619
BHY-F-benbingquan CDCL3 0619
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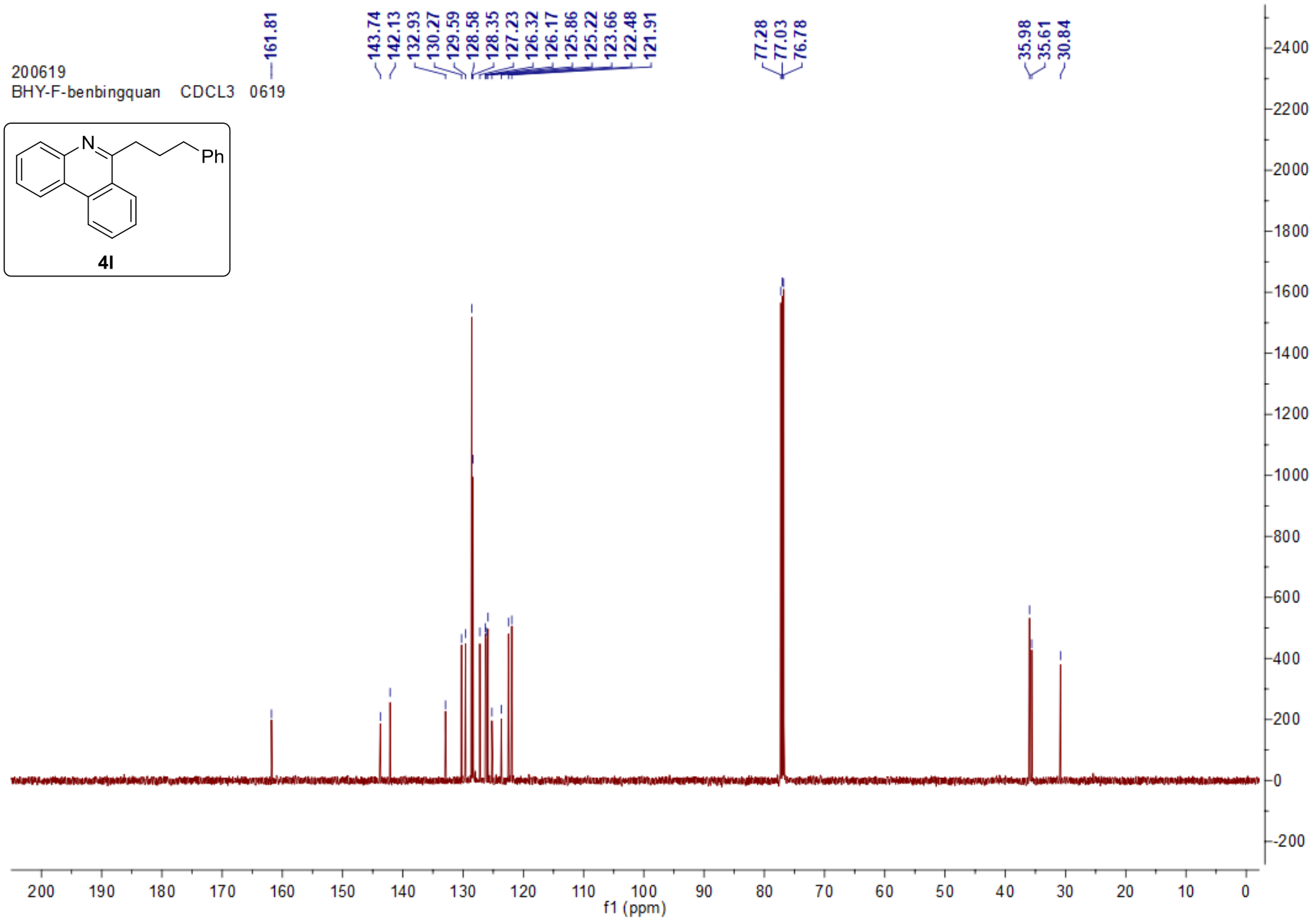
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BHY-F-benbingquan CDCL3 0619
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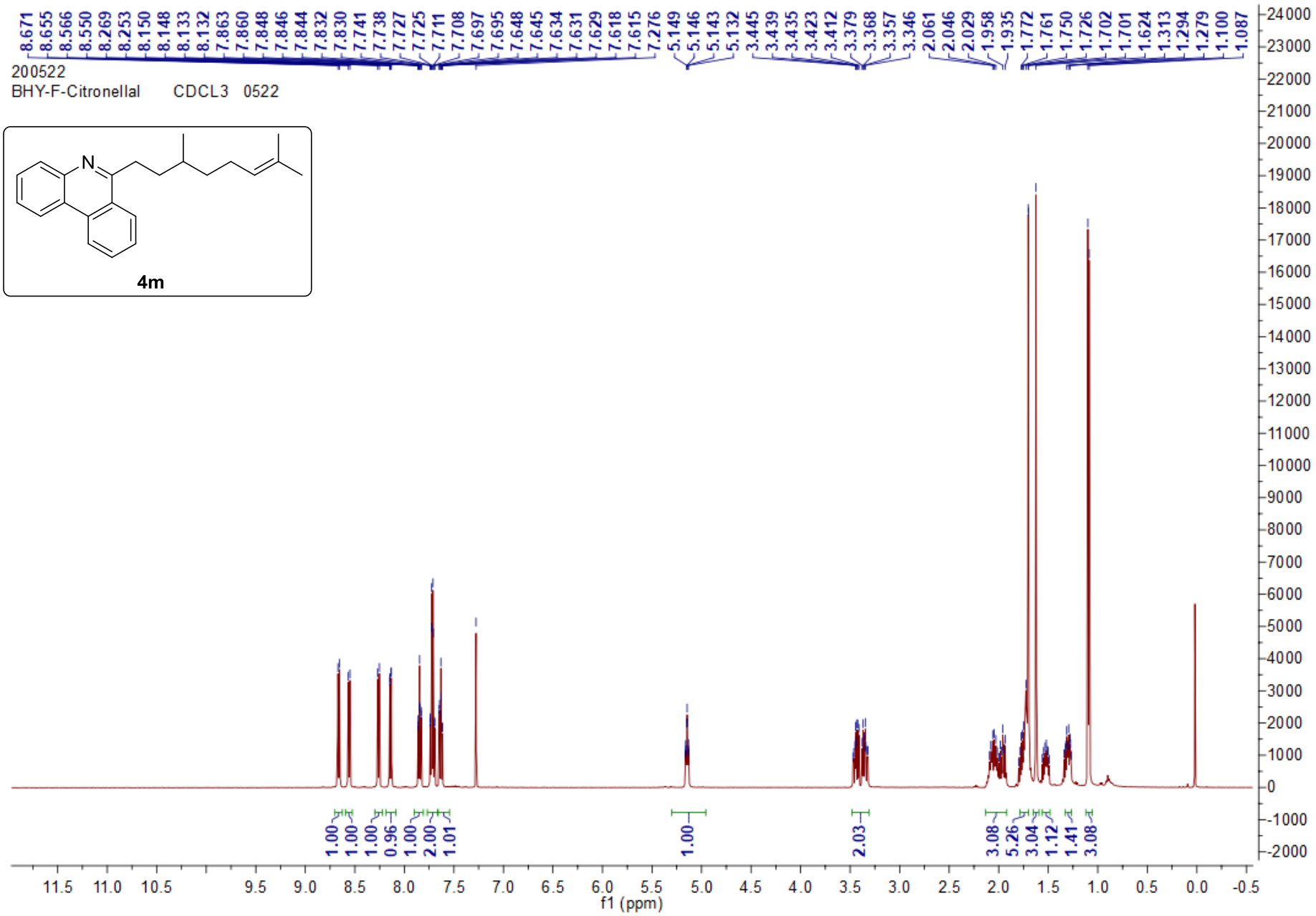
122.48
121.91
77.28
77.03
76.78
35.98
35.61
30.84
N
Ph
4l
f1 (ppm)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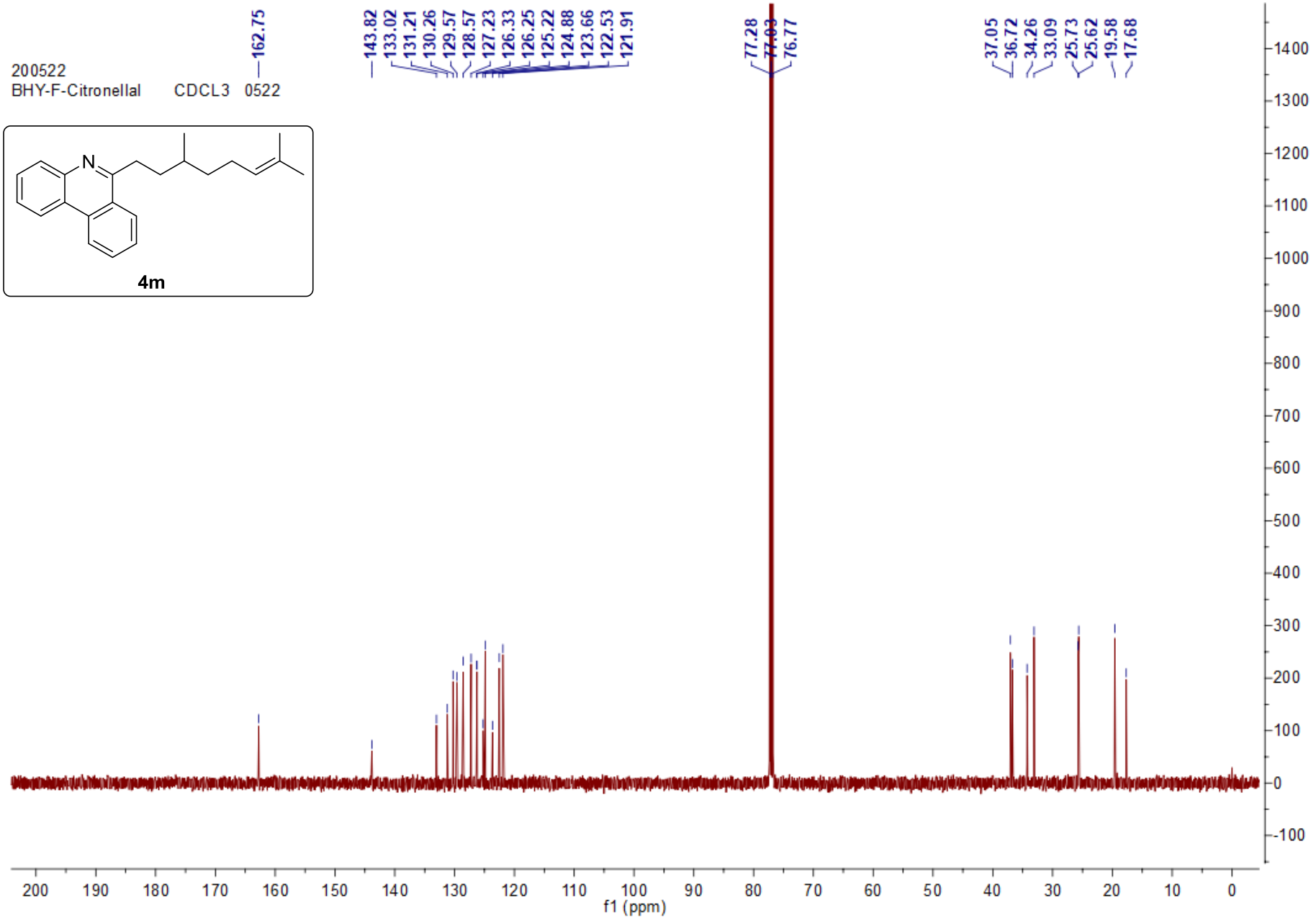
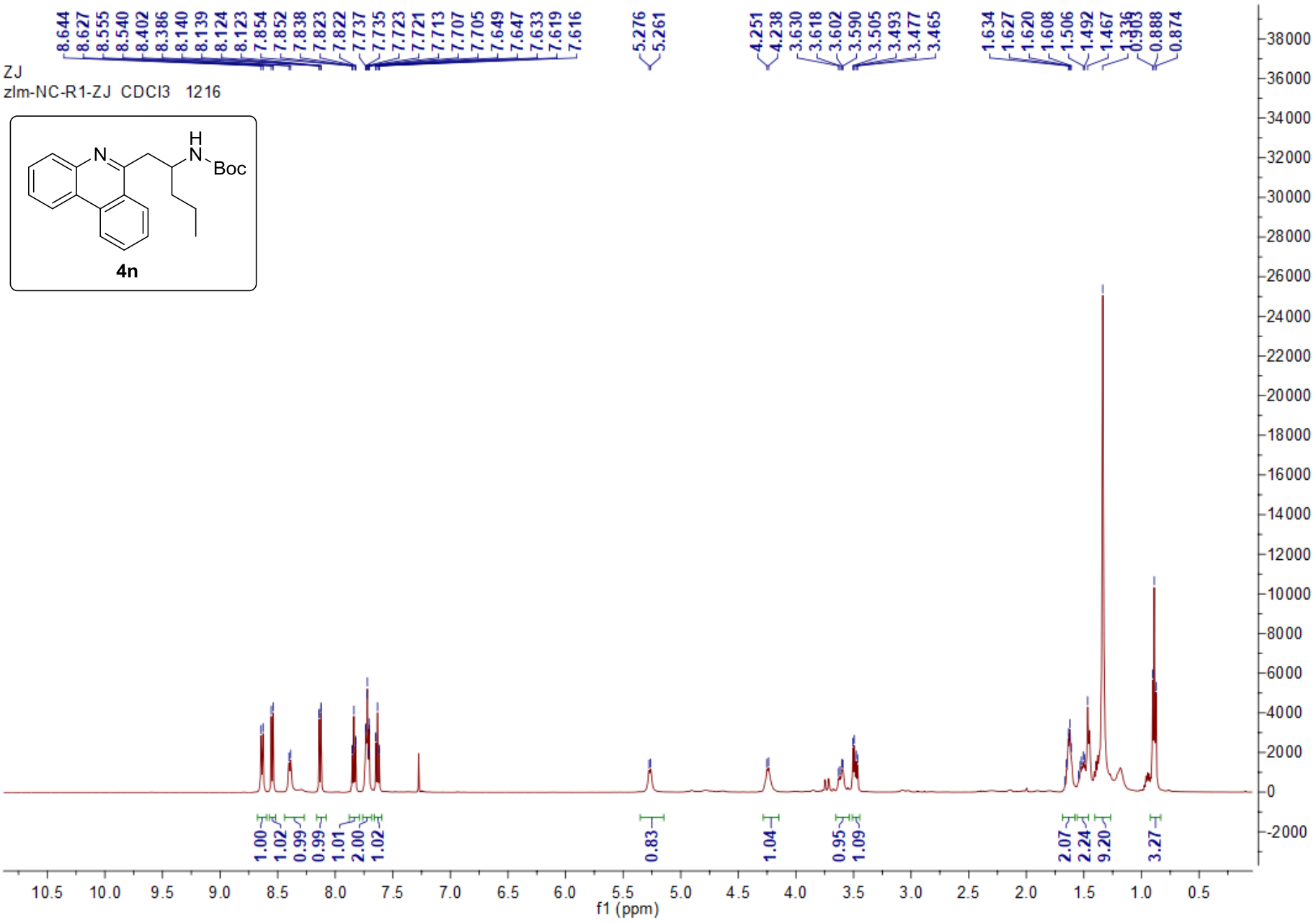
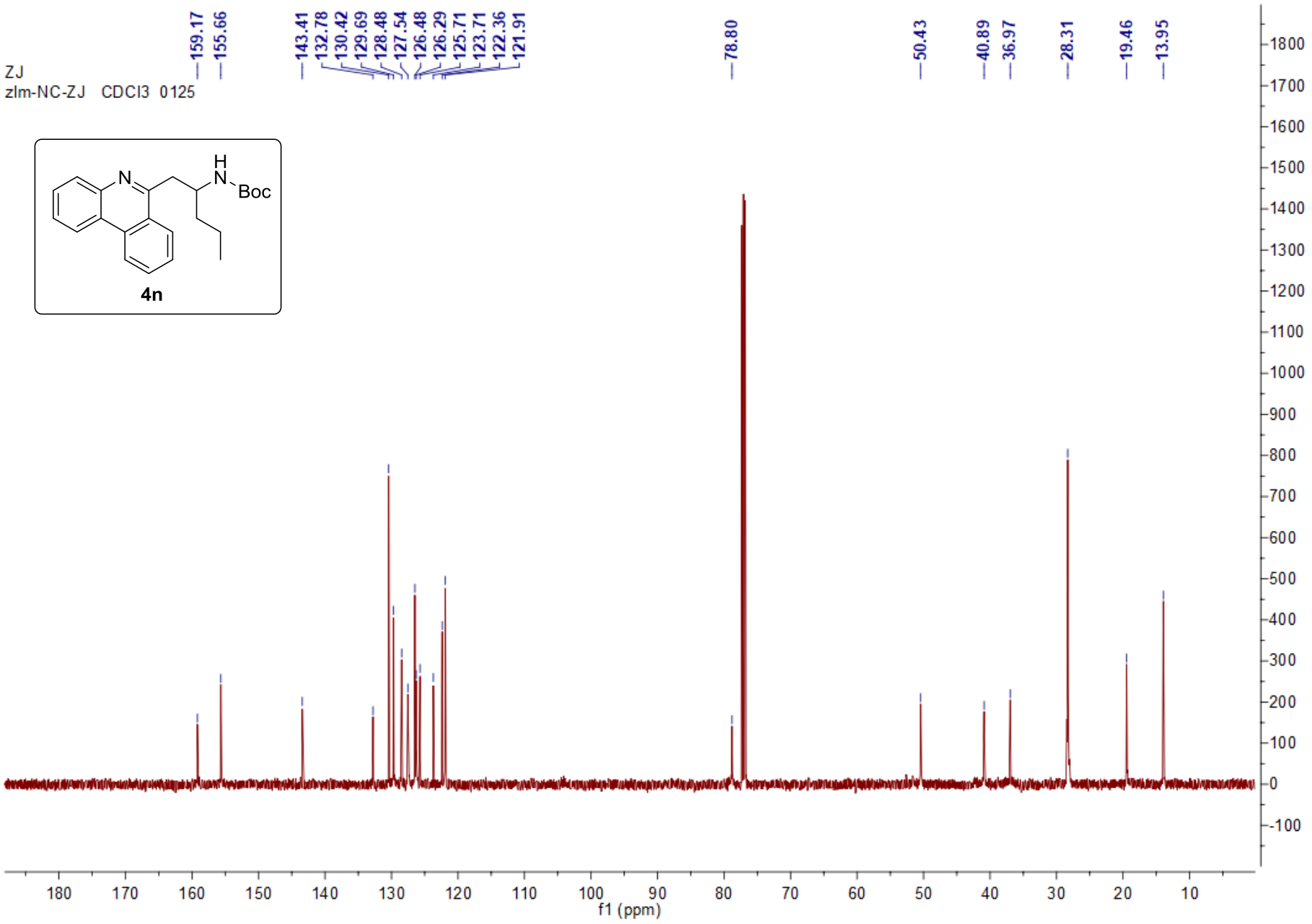
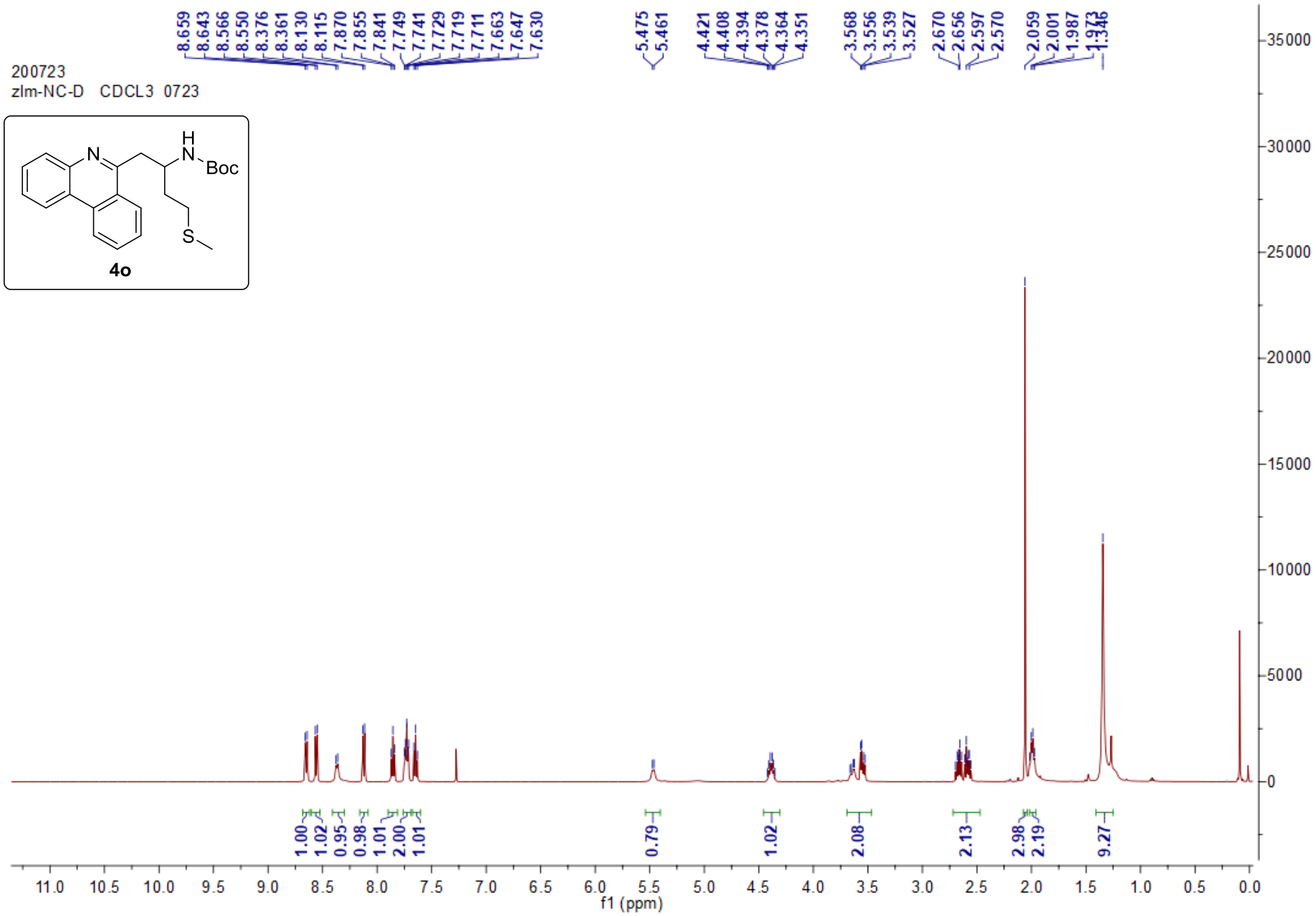
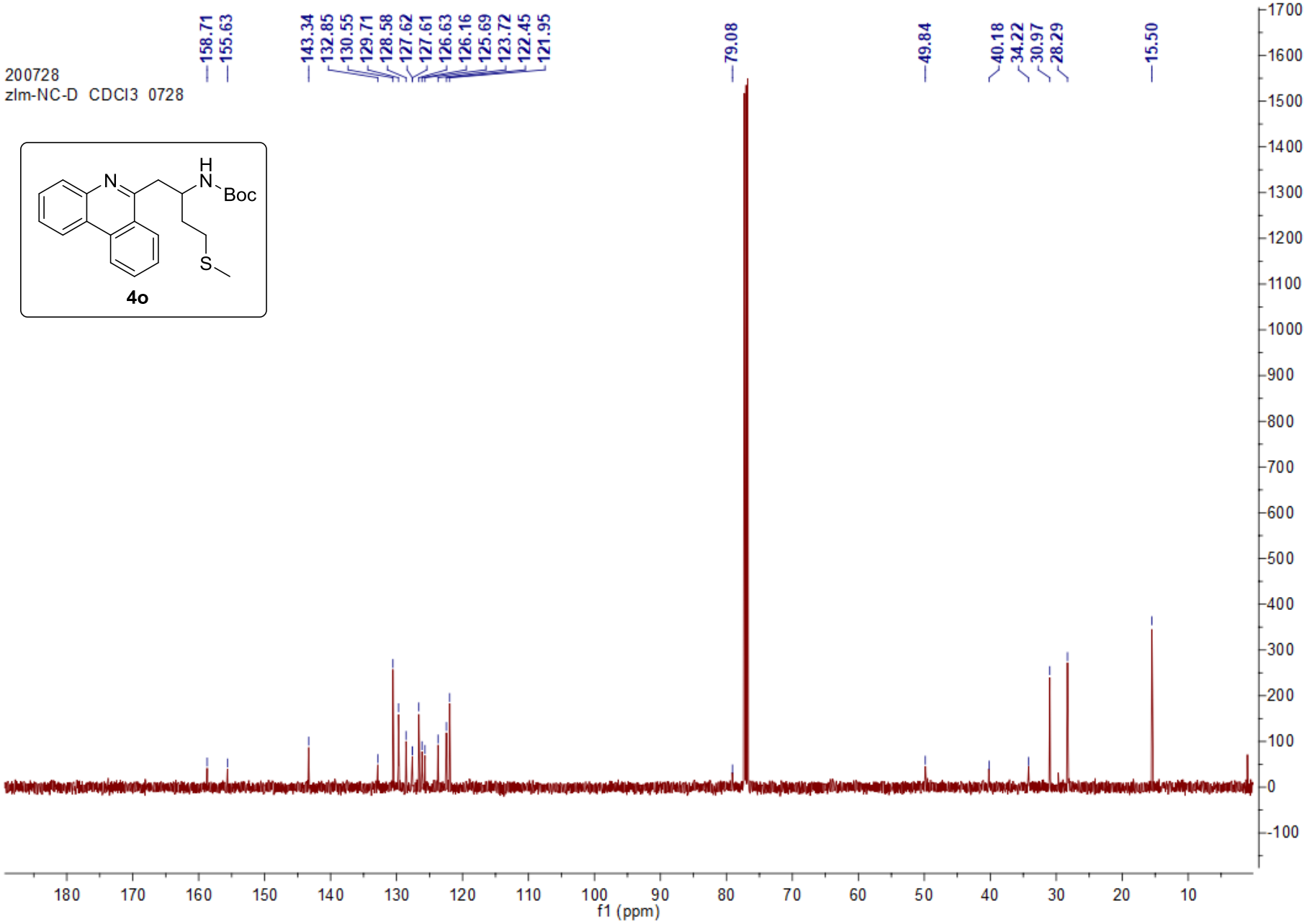
8.655
8.566
8.550
8.269
8.253
8.150
8.148
8.133
8.132
7.863
7.860
7.848
7.846
7.844
7.832
7.830
7.741
7.738
7.727
7.725
7.711
7.708
7.697
7.695
7.648
7.645
7.634
7.631
7.629
7.618
7.615
7.276
5.149
5.146
5.143
5.132
3.445
3.439
3.435
3.423
3.412
3.379
3.368
3.357
3.346
2.061
2.046
2.029
1.958
1.935
1.772
1.761
1.750
1.726
1.702
1.701
1.624
1.313
1.294
1.279
1.100
1.087
200522
BHY-F-Citronellal CDCL3 0522
N
4m
1.00
1.00
1.00
0.96
1.00
2.00
1.01
1.00
2.03
3.08
5.26
3.04
1.12
1.41
3.08
f1 (ppm)

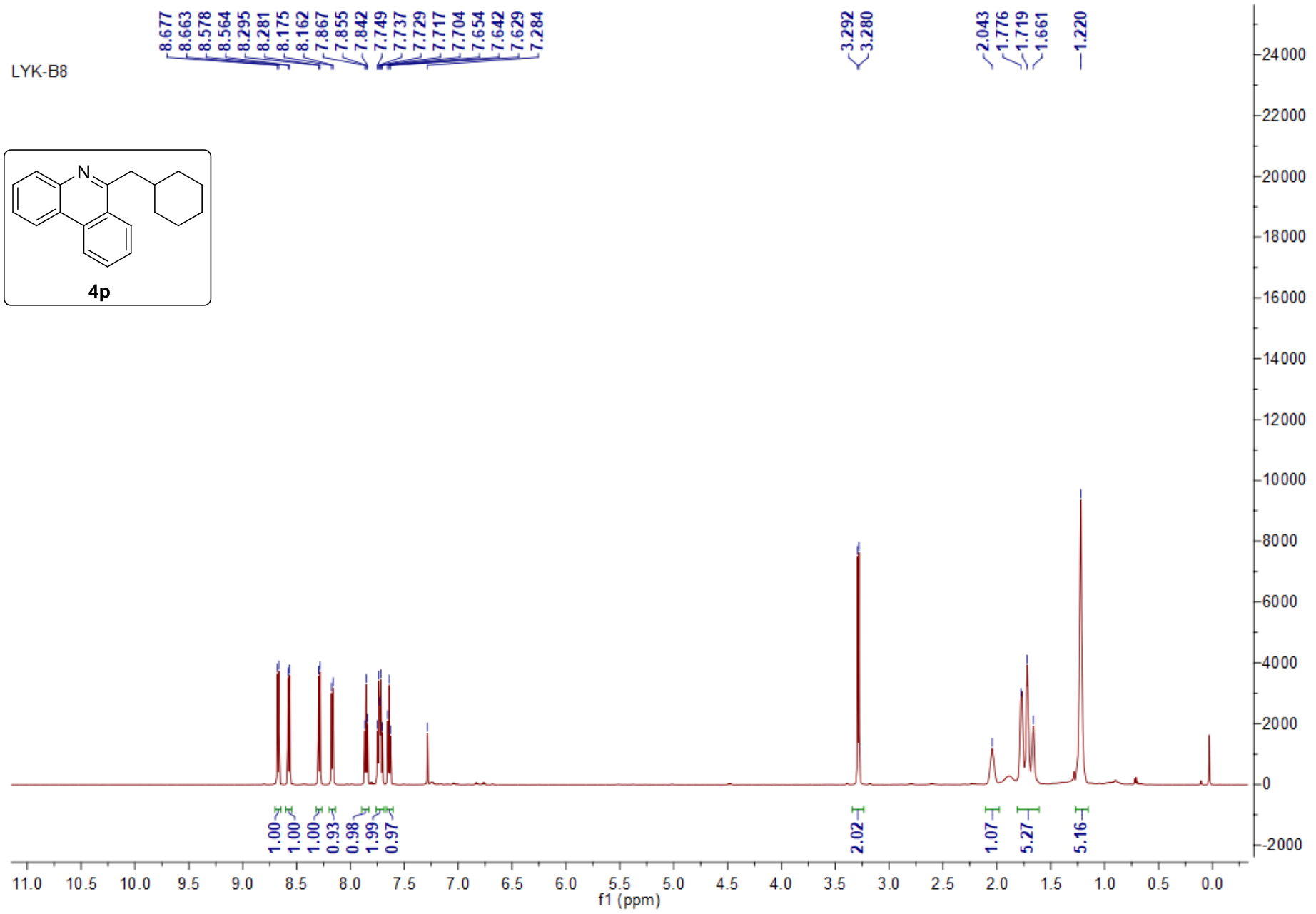

200522
BHY-F-Citronellal CDCL3 0522
162.75
143.82
133.02
131.21
130.26
129.57
128.57
127.23
126.33
126.25
125.22
124.88
123.66
122.53
121.91
77.28
77.03
76.77
37.05
36.72
34.26
33.09
25.73
25.62
19.58
17.68
N
4m
f1 (ppm)

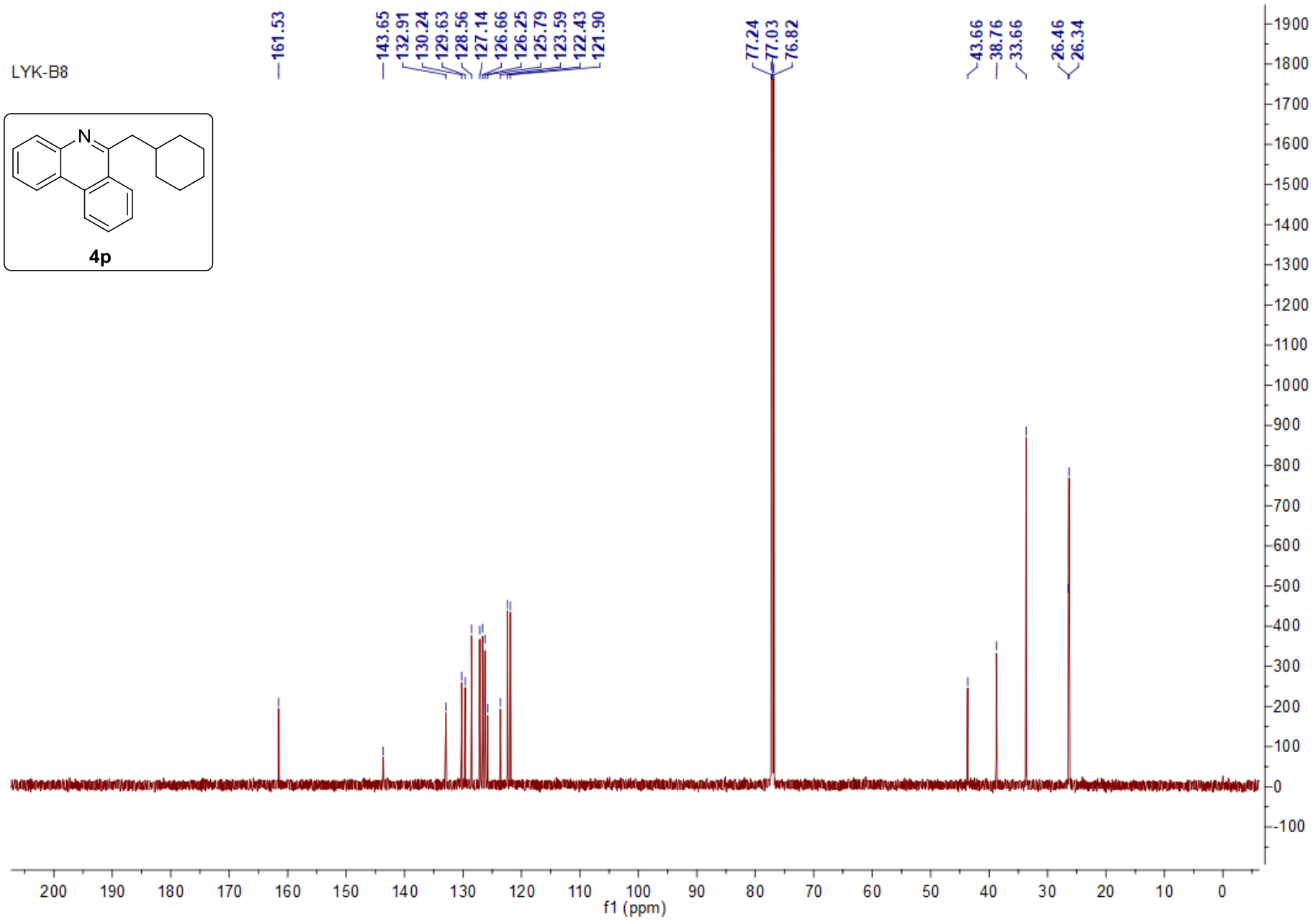

8.644
8.627
8.555
8.540
8.402
8.386
8.140
8.139
8.124
8.123
7.854
7.852
7.838
7.823
7.822
7.737
7.735
7.723
7.721
7.713
7.707
7.705
7.649
7.647
7.633
7.619
7.616
5.276
5.261
4.251
4.238
3.630
3.618
3.602
3.590
3.505
3.493
3.477
3.465
1.634
1.627
1.620
1.608
1.506
1.492
1.467
1.336
0.903
0.888
0.874
ZJ
zlm-NC-R1-ZJ CDCl3 1216
N
H
N
Boc
4n
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
1.02
0.99
0.99
1.01
2.00
1.02
0.83
1.04
0.95
1.09
2.07
2.24
9.20
3.27
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
f1 (ppm)

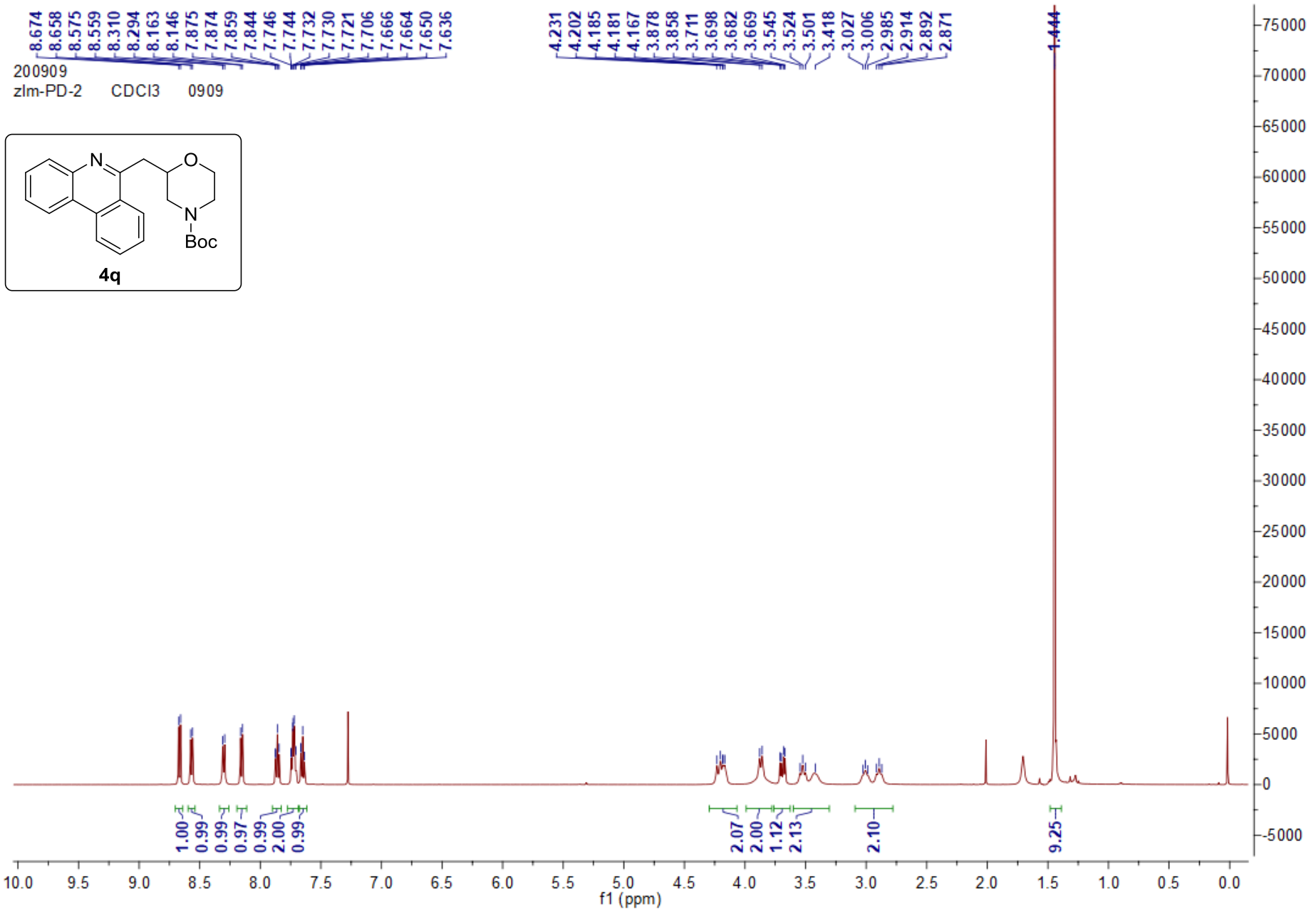

ZJ
zlm-NC-ZJ CDCl3 0125
159.17
155.66
143.41
132.78
130.42
129.69
128.48
127.54
126.48
126.29
125.71
123.71
122.36
121.91
78.80
50.43
40.89
36.97
28.31
19.46
13.95
N
H
N
Boc
4n
f1 (ppm)

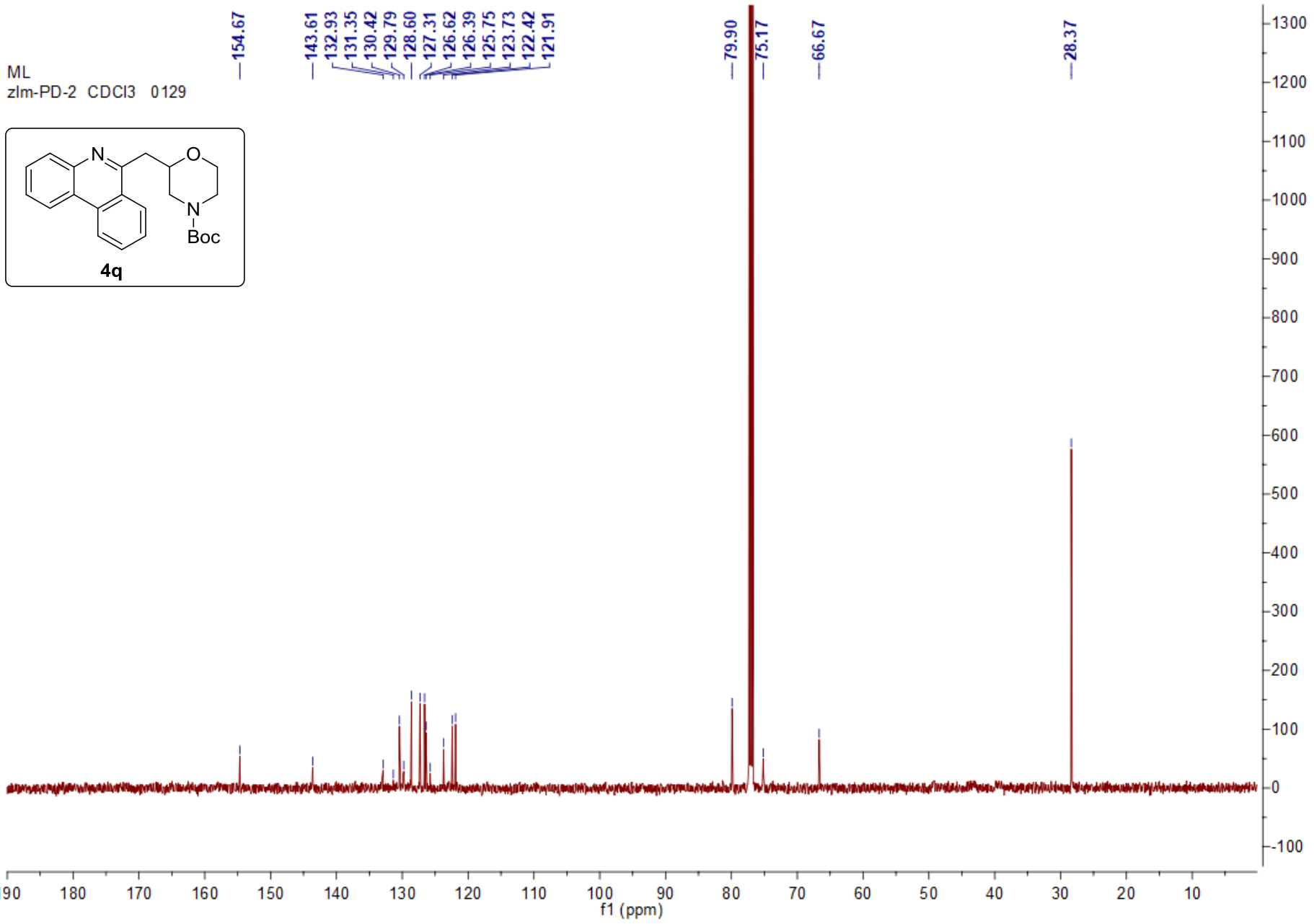

200723
zlm-NC-D CDCL3 0723
8.659
8.643
8.566
8.550
8.376
8.361
8.130
8.115
7.870
7.855
7.841
7.749
7.741
7.729
7.719
7.711
7.663
7.647
7.630
5.475
5.461
4.421
4.408
4.394
4.378
4.364
4.351
3.568
3.556
3.539
3.527
2.670
2.656
2.597
2.570
2.059
2.001
1.987
1.973
1.346
N
H
N
Boc
S
4o
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.02
0.95
0.98
1.01
2.00
1.01
0.79
1.02
2.08
2.13
2.98
2.19
9.27
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

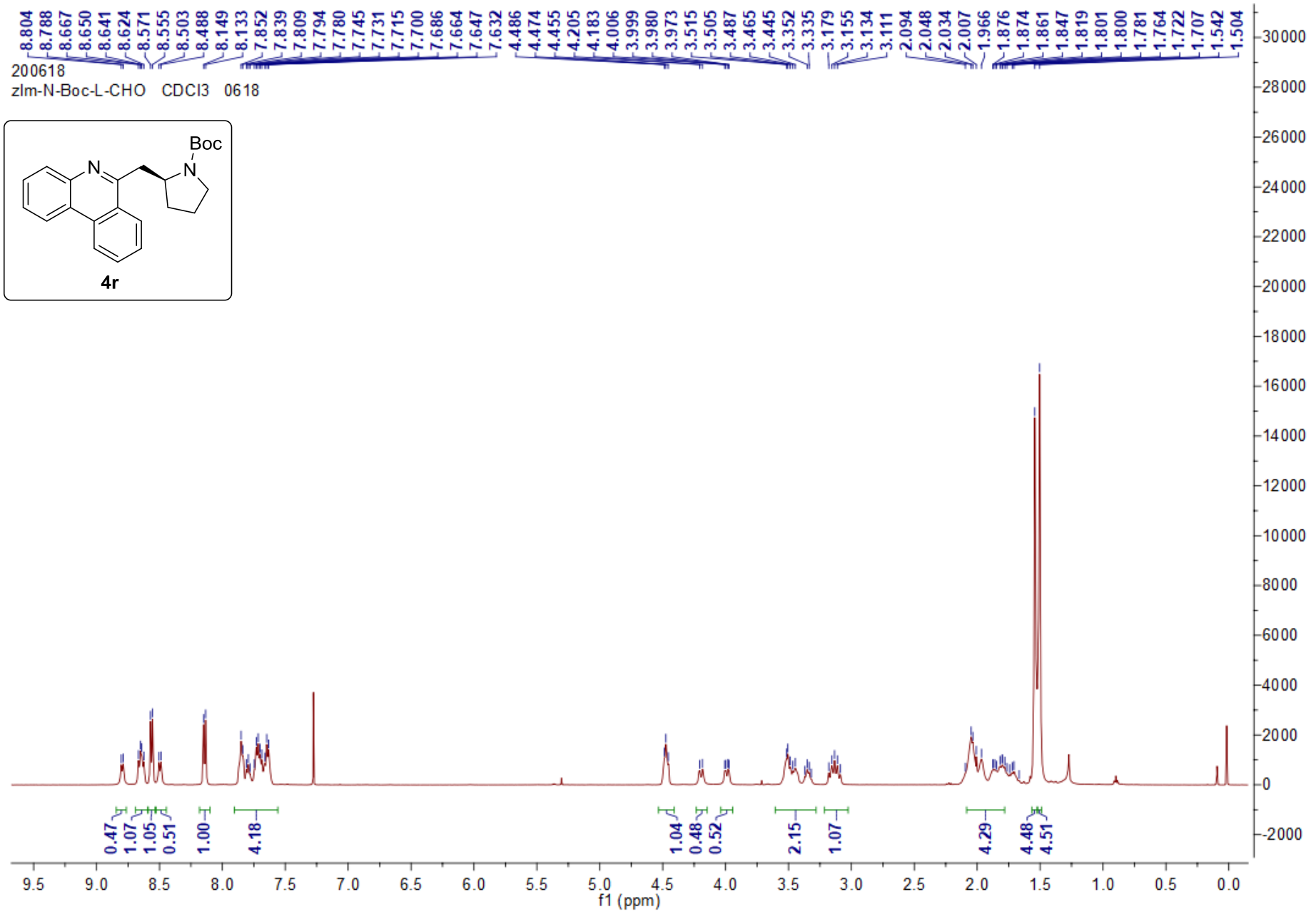

158.71
155.63
143.34
132.85
130.55
129.71
128.58
127.62
127.61
126.63
126.16
125.69
123.72
122.45
121.95
79.08
49.84
40.18
34.22
30.97
28.29
15.50
200728
zlm-NC-D CDCl3 0728
H
N
Boc
N
S
4o
f1 (ppm)

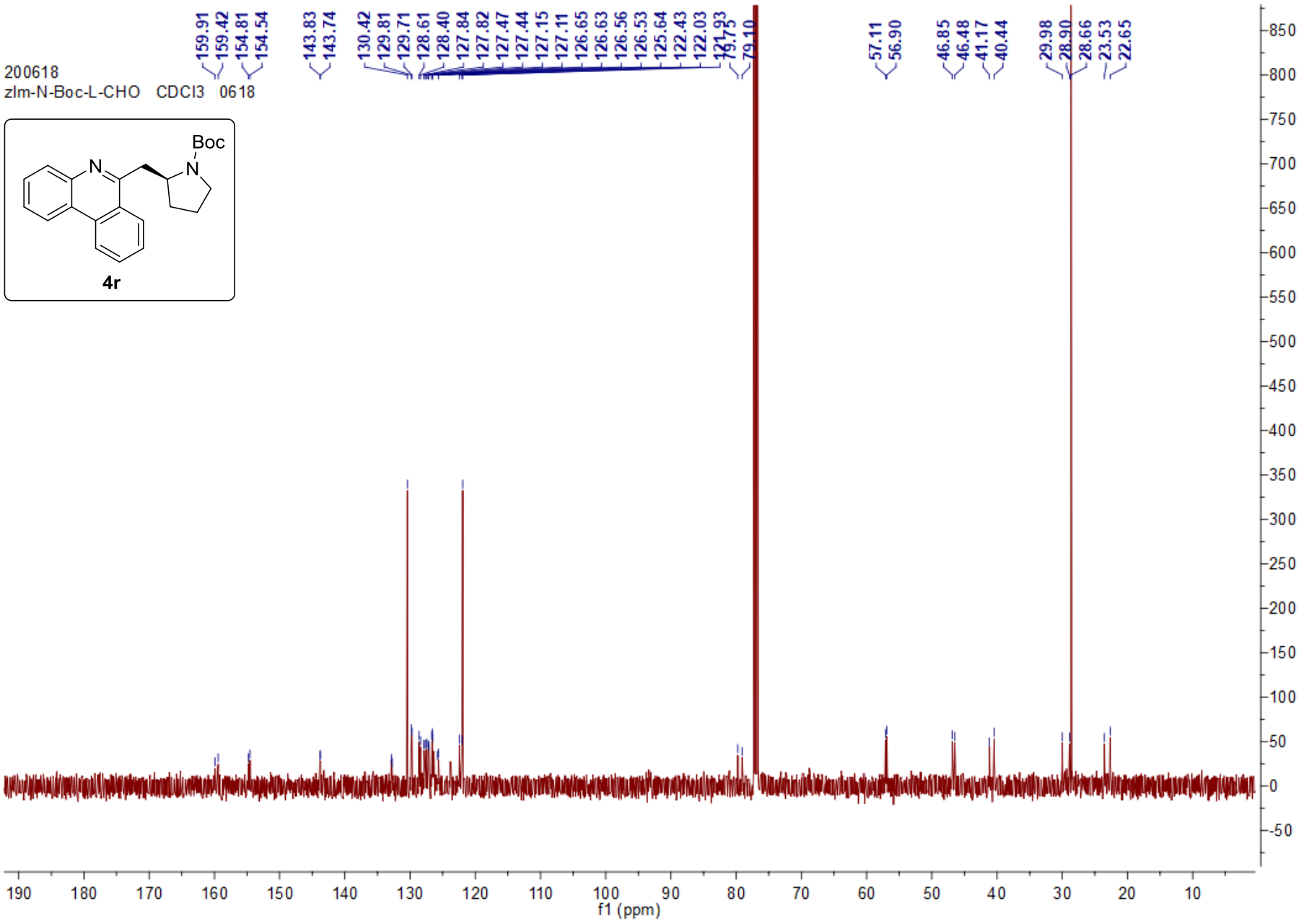

LYK-B8
8.677
8.663
8.578
8.564
8.295
8.281
8.175
8.162
7.867
7.855
7.842
7.749
7.737
7.729
7.717
7.704
7.654
7.642
7.629
7.284
3.292
3.280
2.043
1.776
1.719
1.661
1.220
N
4p
1.00
1.00
1.00
0.93
0.98
1.99
0.97
2.02
1.07
5.27
5.16
f1 (ppm)

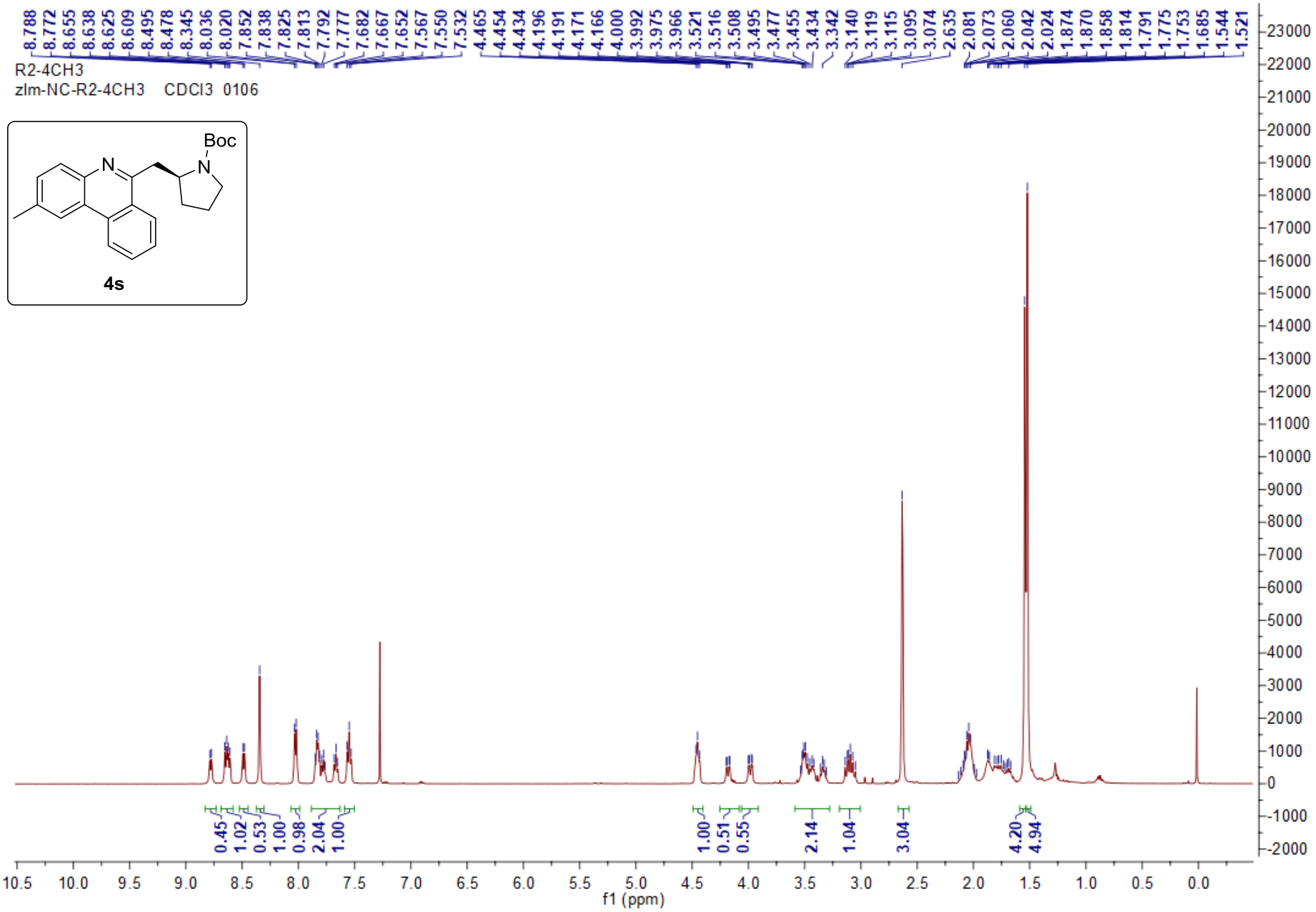

LYK-B8
4p
161.53
143.65
132.91
130.24
129.63
128.56
127.14
126.66
126.25
125.79
123.59
122.43
121.90
77.24
77.03
76.82
43.66
38.76
33.66
26.46
26.34
f1 (ppm)

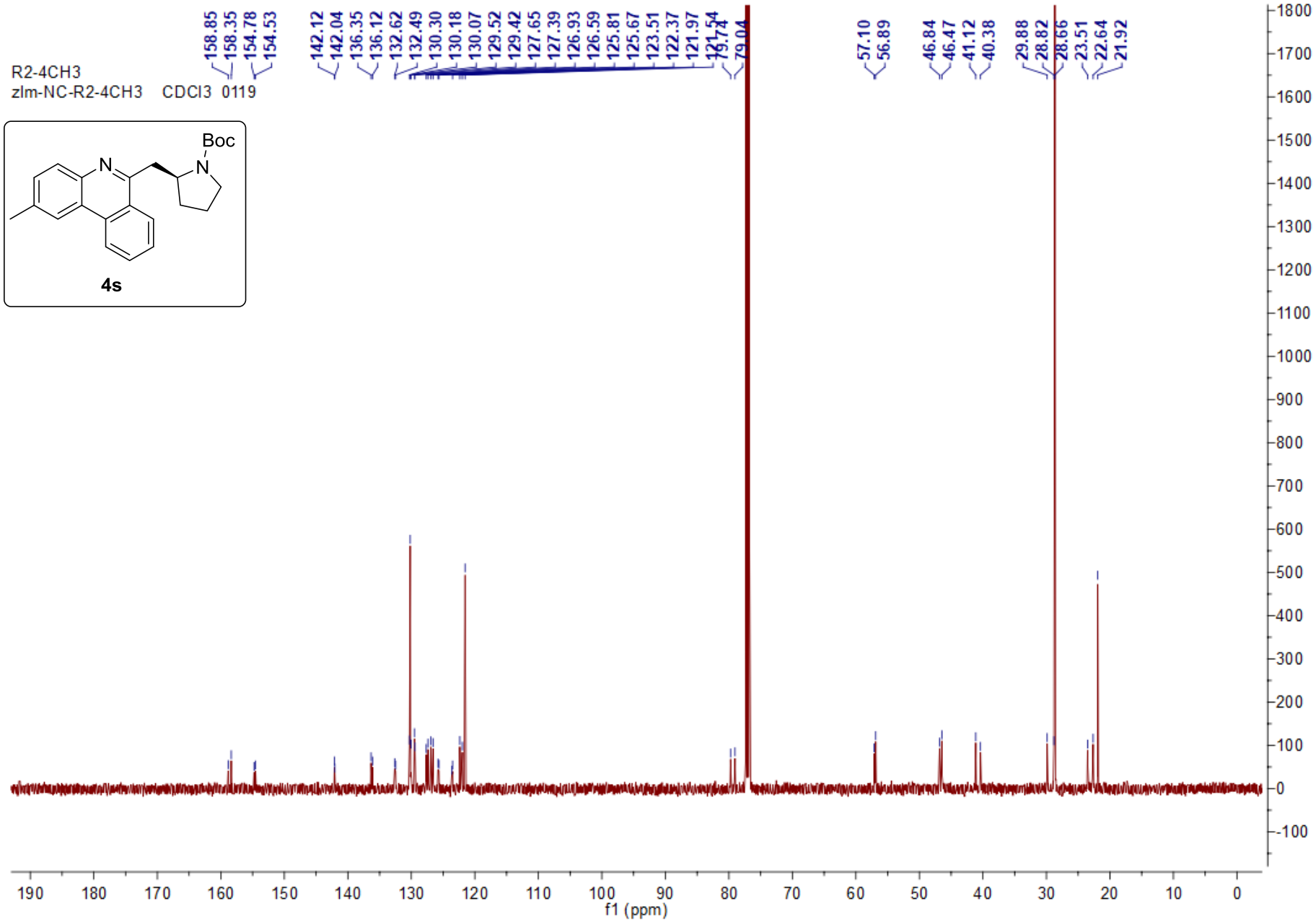

8.674
8.658
8.575
8.559
8.310
8.294
8.163
8.146
7.875
7.874
7.859
7.844
7.746
7.744
7.732
7.730
7.721
7.706
7.666
7.664
7.650
7.636
4.231
4.202
4.185
4.181
4.167
3.878
3.858
3.711
3.698
3.682
3.669
3.545
3.524
3.501
3.418
3.027
3.006
2.985
2.914
2.892
2.871
1.444
200909
zlm-PD-2 CDCl3 0909
N
O
N
Boc
4q
1.00
0.99
0.99
0.97
0.99
2.00
0.99
2.07
2.00
1.12
2.13
2.10
9.25
f1 (ppm)

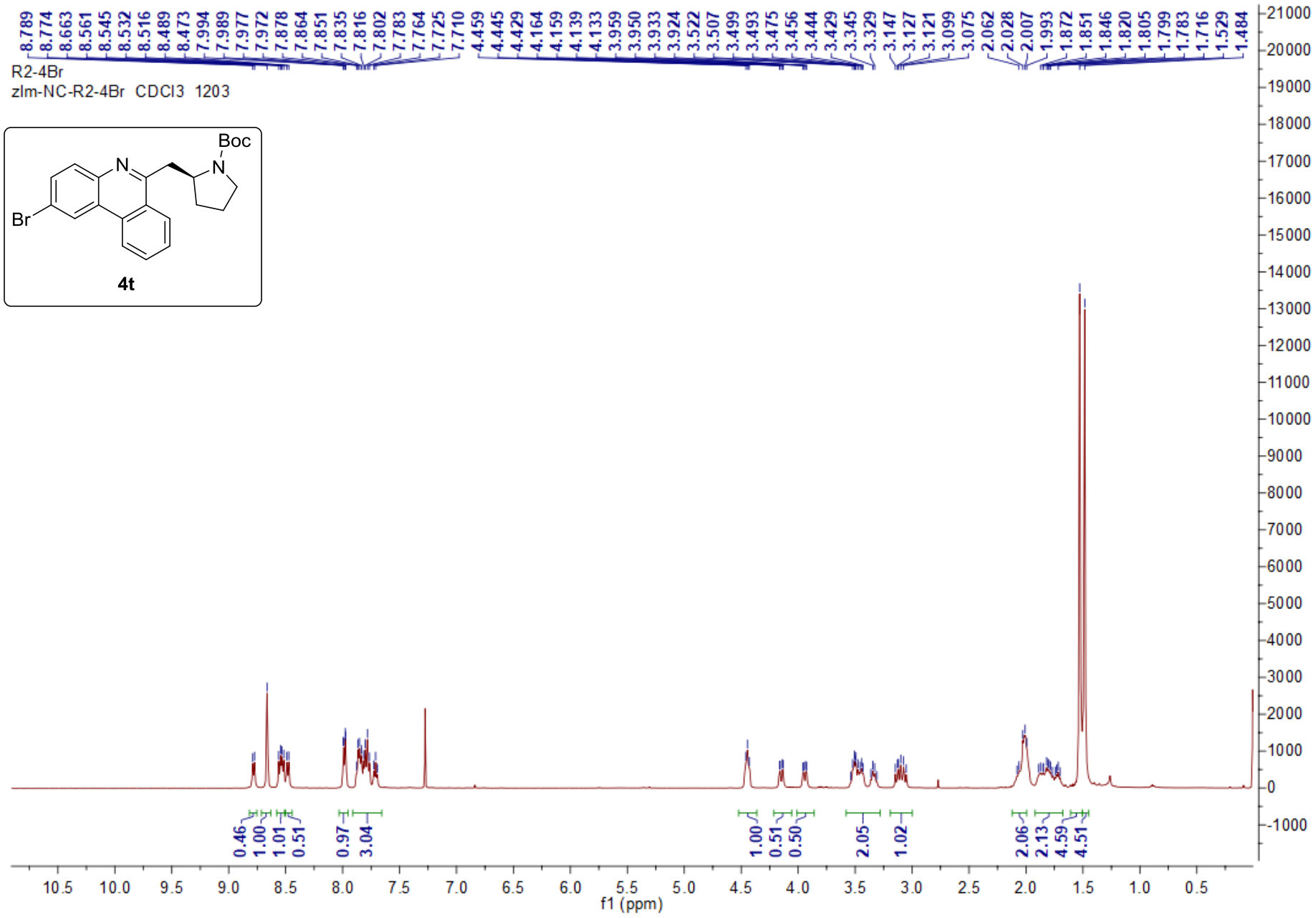

ML
zlm-PD-2 CDCl3 0129
154.67
143.61
132.93
131.35
130.42
129.79
128.60
127.31
126.62
126.39
125.75
123.73
122.42
121.91
79.90
75.17
66.67
28.37
N
O
N
Boc
4q
f1 (ppm)


8.804
8.788
8.667
8.650
8.641
8.624
8.571
8.555
8.503
8.488
8.149
8.133
7.852
7.839
7.809
7.794
7.780
7.745
7.731
7.715
7.700
7.686
7.664
7.647
7.632
4.486
4.474
4.455
4.205
4.183
4.006
3.999
3.980
3.973
3.515
3.505
3.487
3.465
3.445
3.352
3.335
3.179
3.155
3.134
3.111
2.094
2.048
2.034
2.007
1.966
1.876
1.874
1.861
1.847
1.819
1.801
1.800
1.781
1.764
1.722
1.707
1.542
1.504
200618
zlm-N-Boc-L-CHO CDCl3 0618
Boc
N
N
4r
0.47
1.07
1.05
0.51
1.00
4.18
1.04
0.48
0.52
2.15
1.07
4.29
4.48
4.51
f1 (ppm)


200618
zlm-N-Boc-L-CHO CDCl3 0618
Boc
N
N
4r
159.91
159.42
154.81
154.54
143.83
143.74
130.42
129.81
129.71
128.61
128.40
127.84
127.82
127.47
127.44
127.15
127.11
126.65
126.63
126.56
126.53
125.64
122.43
122.03
121.93
79.75
79.10
57.11
56.90
46.85
46.48
41.17
40.44
29.98
28.90
28.66
23.53
22.65
f1 (ppm)


8.788
8.772
8.655
8.638
8.625
8.609
8.495
8.478
8.345
8.036
8.020
7.852
7.838
7.825
7.813
7.792
7.777
7.682
7.667
7.652
7.567
7.550
7.532
4.465
4.454
4.434
4.196
4.191
4.171
4.166
4.000
3.992
3.975
3.966
3.521
3.516
3.508
3.495
3.477
3.455
3.434
3.342
3.140
3.119
3.115
3.095
3.074
2.635
2.081
2.073
2.060
2.042
2.024
1.874
1.870
1.858
1.814
1.791
1.775
1.753
1.685
1.544
1.521
R2-4CH3
zlm-NC-R2-4CH3 CDCl3 0106
Boc
N
N
4s
0.45
1.02
0.53
1.00
0.98
2.04
1.00
1.00
0.51
0.55
2.14
1.04
3.04
4.20
4.94
f1 (ppm)


R2-4CH3
zlm-NC-R2-4CH3 CDCl3 0119
Boc
N
N
4s
158.85
158.35
154.78
154.53
142.12
142.04
136.35
136.12
132.62
132.49
130.30
130.18
130.07
129.52
129.42
127.65
127.39
126.93
126.59
125.81
125.67
123.51
122.37
121.97
121.54
79.74
79.04
57.10
56.89
46.84
46.47
41.12
40.38
29.88
28.82
28.66
23.51
22.64
21.92
f1 (ppm)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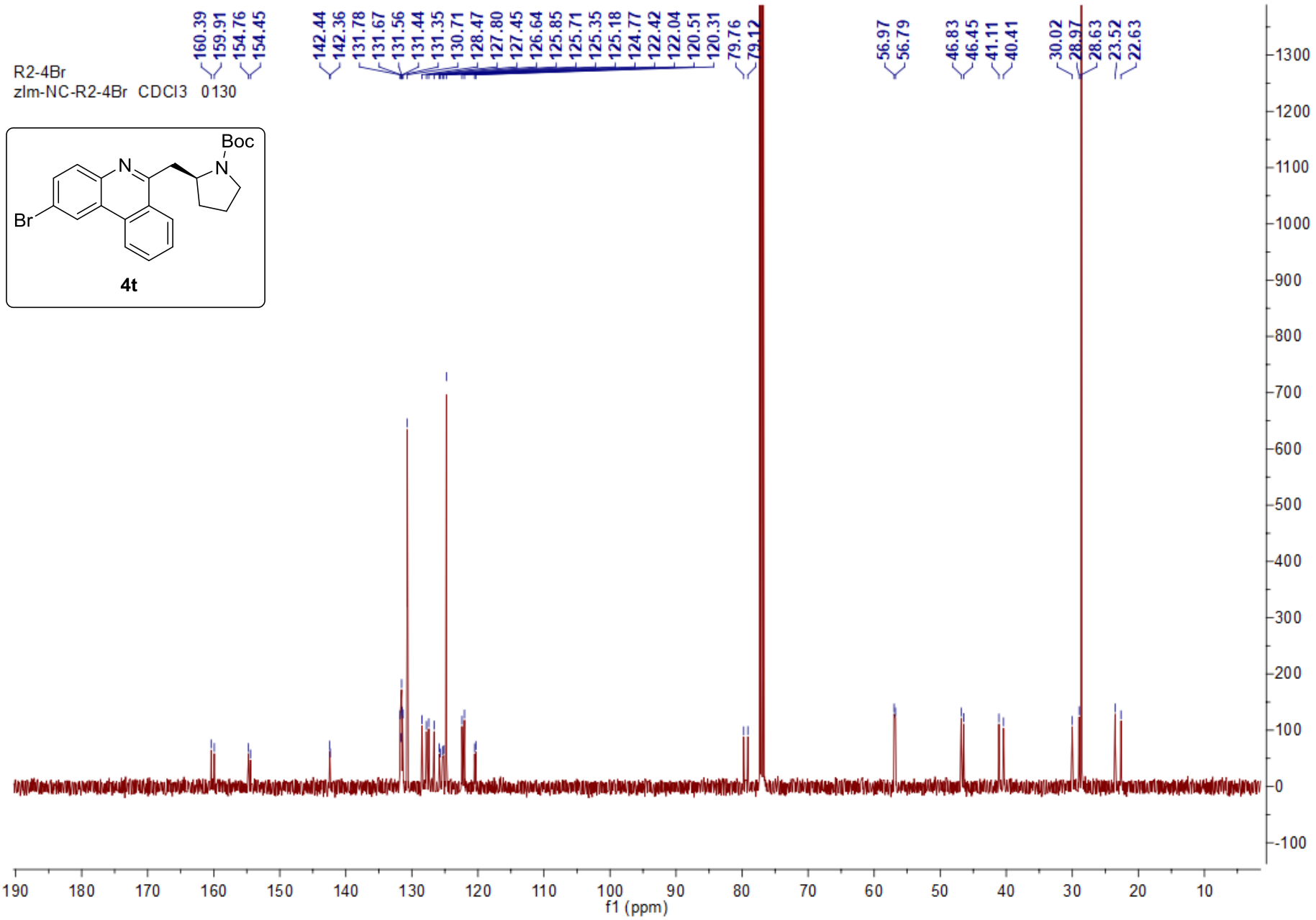
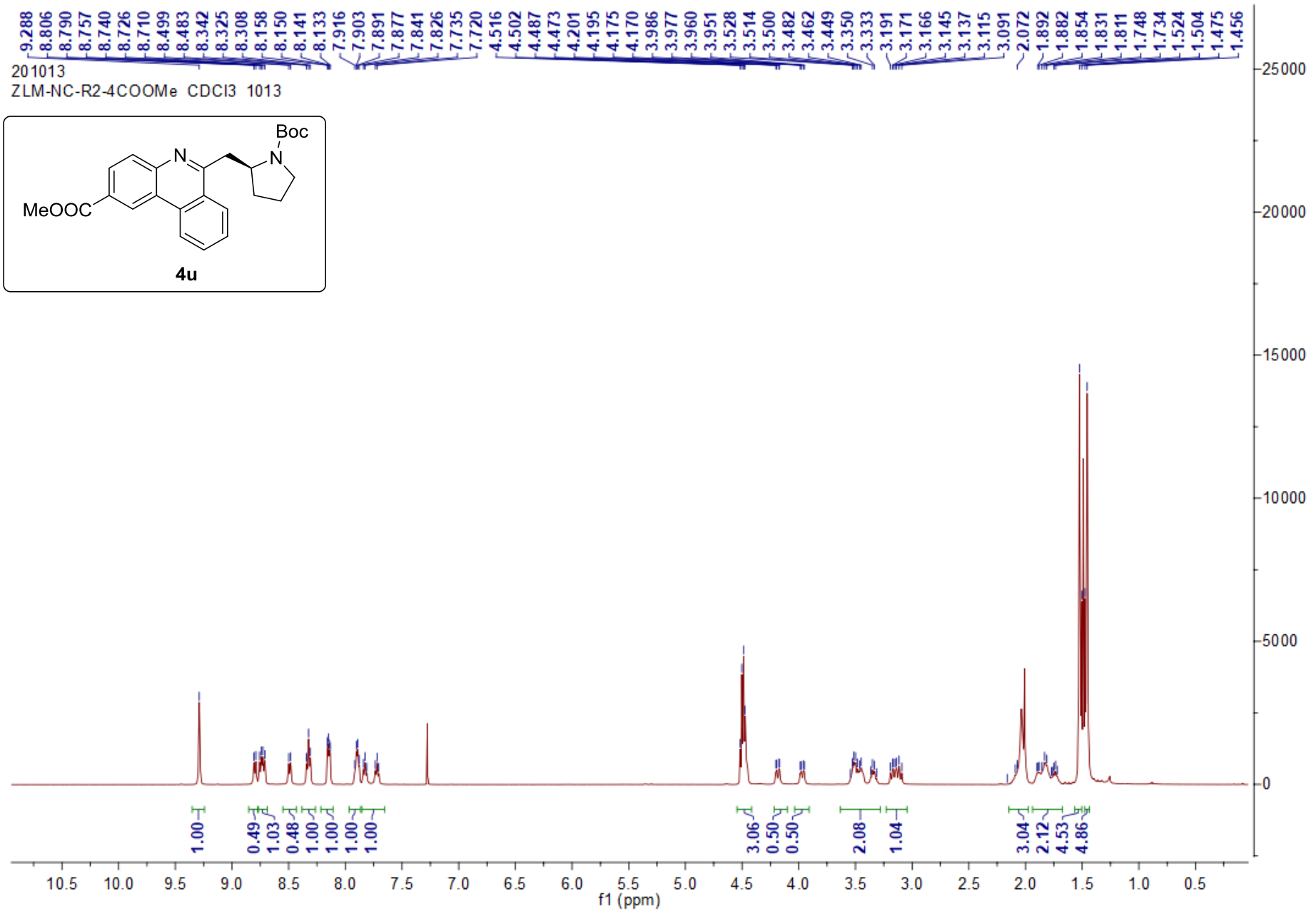
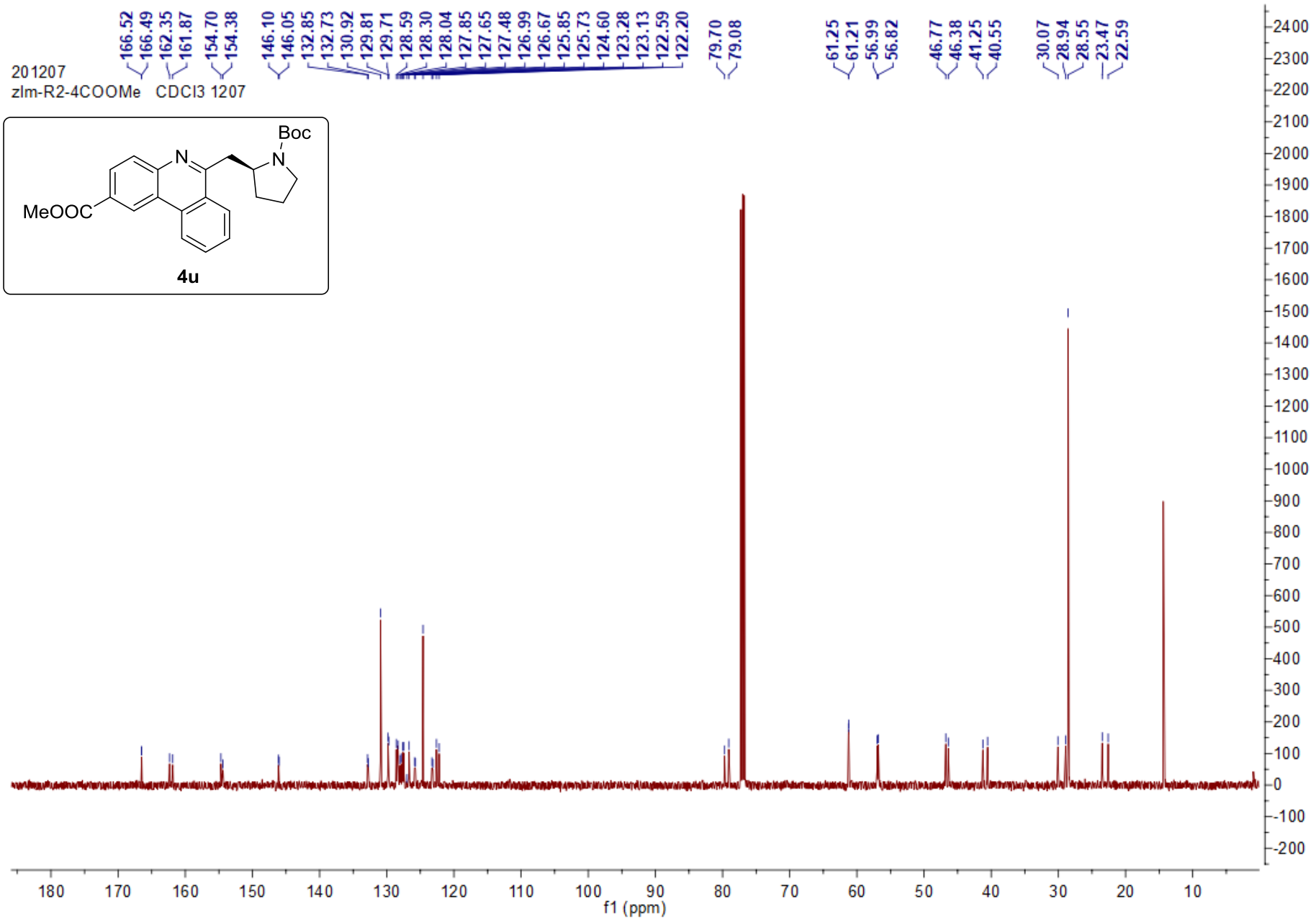
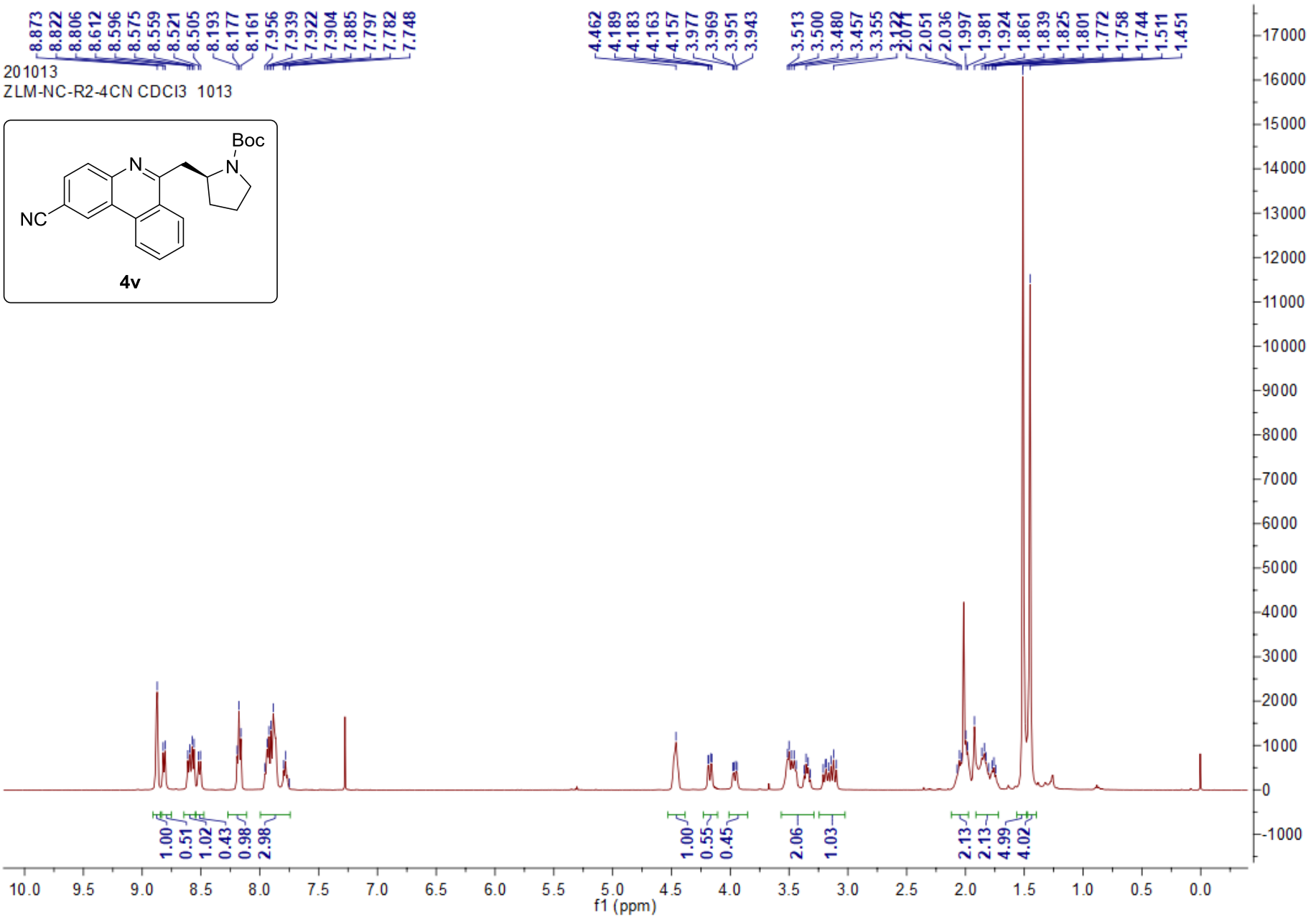
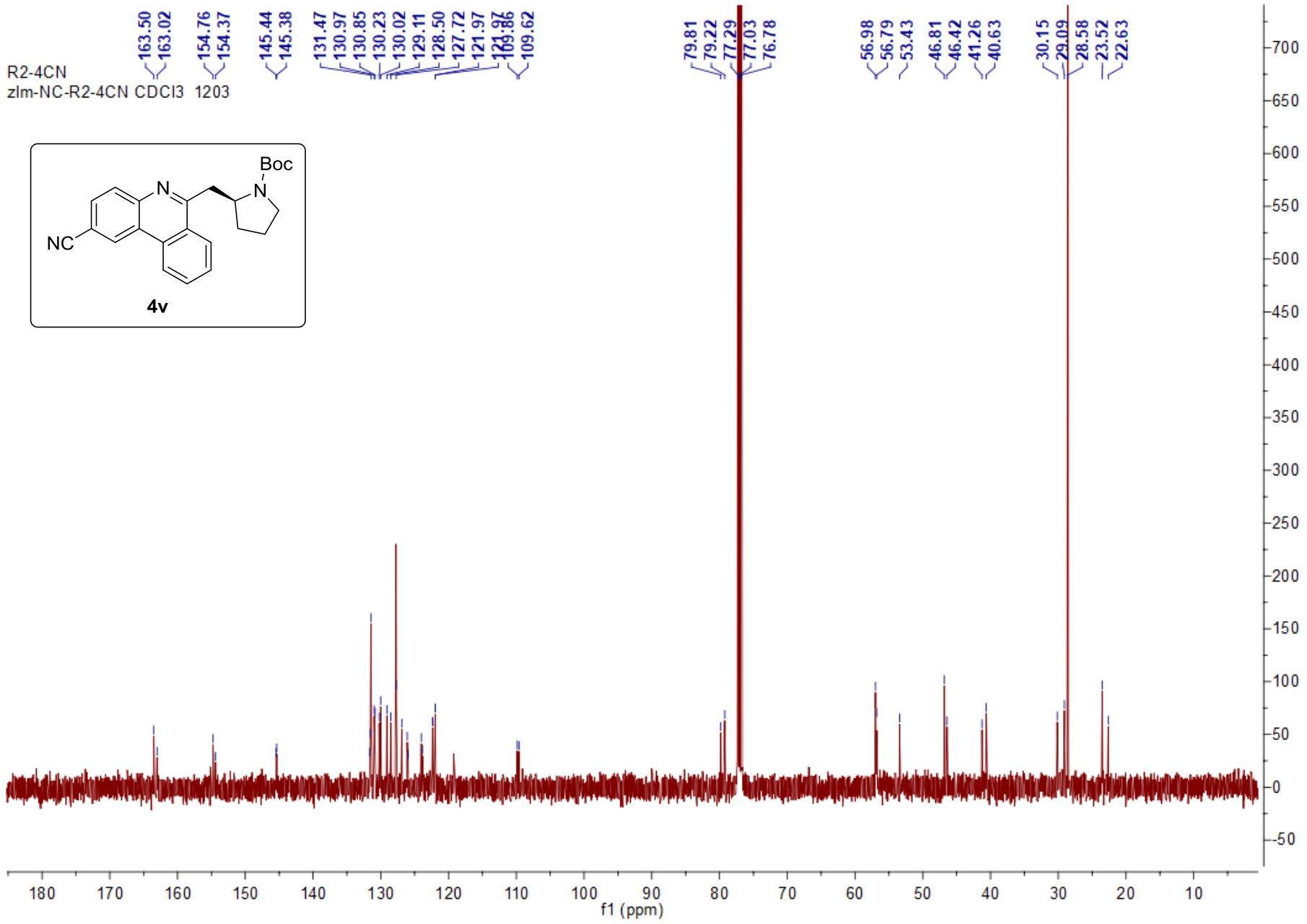
8.774
8.663
8.561
8.545
8.532
8.516
8.489
8.473
7.994
7.989
7.977
7.972
7.878
7.864
7.851
7.835
7.816
7.802
7.783
7.764
7.725
7.710
4.459
4.445
4.429
4.164
4.159
4.139
4.133
3.959
3.950
3.933
3.924
3.522
3.507
3.499
3.493
3.475
3.456
3.444
3.429
3.345
3.329
3.147
3.127
3.121
3.099
3.075
2.062
2.028
2.007
1.993
1.872
1.851
1.846
1.820
1.805
1.799
1.783
1.716
1.529
1.484
R2-4Br
zlm-NC-R2-4Br CDCl3 1203
Boc
N
N
Br
4t
0.46
1.00
1.01
0.51
0.97
3.04
1.00
0.51
0.50
2.05
1.02
2.06
2.13
4.59
4.51
f1 (ppm)


R2-4Br
zlm-NC-R2-4Br CDCl3 0130
160.39
159.91
154.76
154.45
142.44
142.36
131.78
131.67
131.56
131.44
131.35
130.71
128.47
127.80
127.45
126.64
125.85
125.71
125.35
125.18
124.77
122.42
122.04
120.51
120.31
79.76
79.12
56.97
56.79
46.83
46.45
41.11
40.41
30.02
28.97
28.63
23.52
22.63
Boc
N
N
Br
4t
f1 (ppm)


9.288
8.806
8.790
8.757
8.740
8.726
8.710
8.499
8.483
8.342
8.325
8.308
8.158
8.150
8.141
8.133
7.916
7.903
7.891
7.877
7.841
7.826
7.735
7.720
4.516
4.502
4.487
4.473
4.201
4.195
4.175
4.170
3.986
3.977
3.960
3.951
3.528
3.514
3.500
3.482
3.462
3.449
3.350
3.333
3.191
3.171
3.166
3.145
3.137
3.115
3.091
2.072
1.892
1.882
1.854
1.831
1.811
1.748
1.734
1.524
1.504
1.475
1.456
201013
ZLM-NC-R2-4COOMe CDCl3 1013
Boc
N
N
MeOOC
4u
25000
20000
15000
10000
5000
0
1.00
0.49
1.03
0.48
1.00
1.00
1.00
1.00
3.06
0.50
0.50
2.08
1.04
3.04
2.12
4.53
4.86
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
f1 (ppm)


166.52
166.49
162.35
161.87
154.70
154.38
146.10
146.05
132.85
132.73
130.92
129.81
129.71
128.59
128.30
128.04
127.85
127.65
127.48
126.99
126.67
125.85
125.73
124.60
123.28
123.13
122.59
122.20
79.70
79.08
61.25
61.21
56.99
56.82
46.77
46.38
41.25
40.55
30.07
28.94
28.55
23.47
22.59
201207
zlm-R2-4COOMe CDCl3 1207
Boc
N
N
MeOOC
4u
f1 (ppm)


8.873
8.822
8.806
8.612
8.596
8.575
8.559
8.521
8.505
8.193
8.177
8.161
7.956
7.939
7.922
7.904
7.885
7.797
7.782
7.748
4.462
4.189
4.183
4.163
4.157
3.977
3.969
3.951
3.943
3.513
3.500
3.480
3.457
3.355
2.051
2.036
1.997
1.981
1.924
1.861
1.839
1.825
1.801
1.772
1.758
1.744
1.511
1.451
201013
ZLM-NC-R2-4CN CDCl3 1013
Boc
N
N
NC
4v
1.00
0.51
1.02
0.43
0.98
2.98
1.00
0.55
0.45
2.06
1.03
2.13
2.13
4.99
4.02
f1 (ppm)


R2-4CN
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163.50
163.02
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154.37
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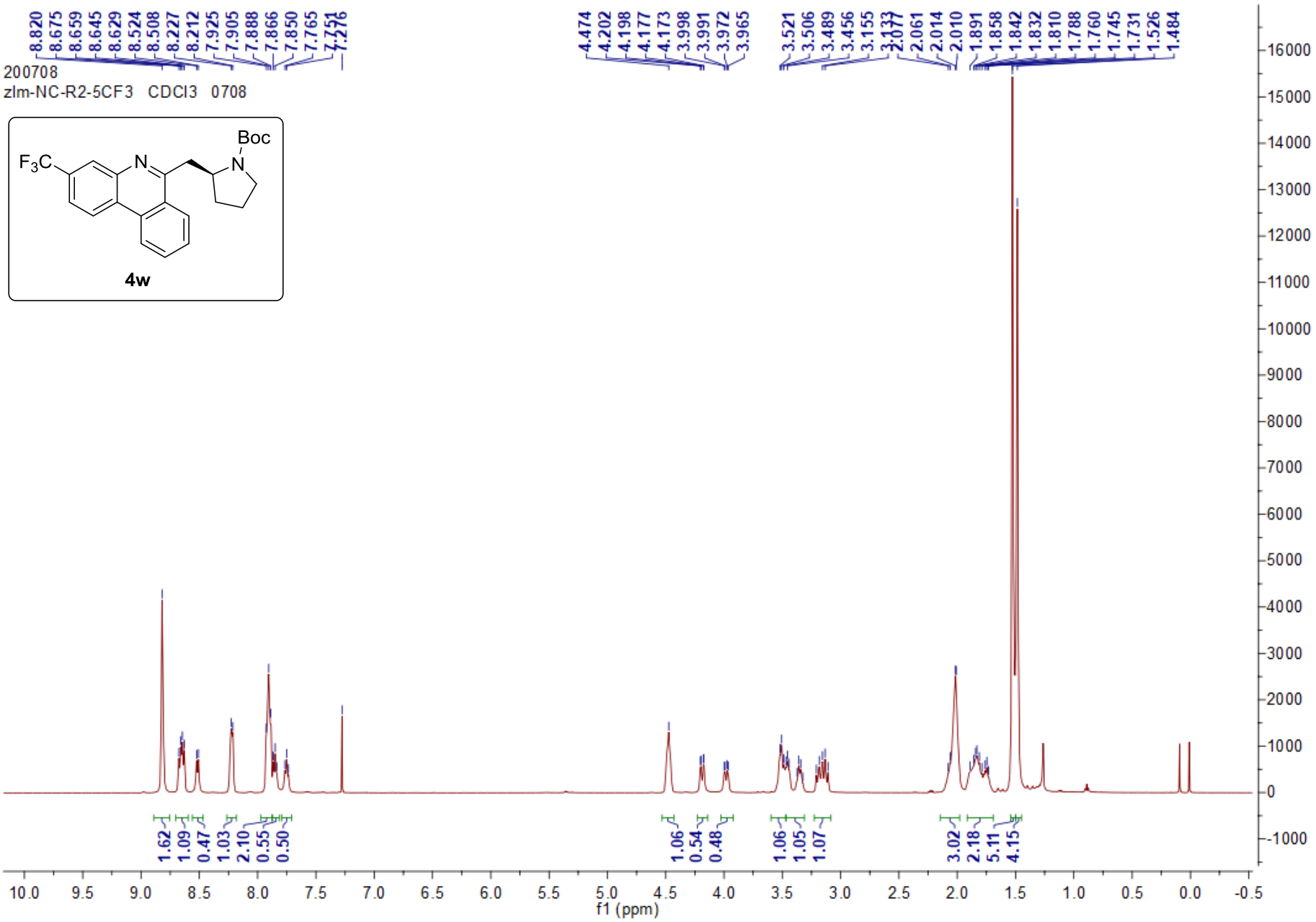
145.38
131.47
130.97
130.85
130.23
130.02
129.11
128.50
127.72
121.97
109.86
109.62
79.81
79.22
77.29
77.03
76.78
56.98
56.79
53.43
46.81
46.42
41.26
40.63
30.15
29.09
28.58
23.52
22.63
Boc
N
N
NC
4v
f1 (ppm)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8.675
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8.645
8.629
8.524
8.508
8.227
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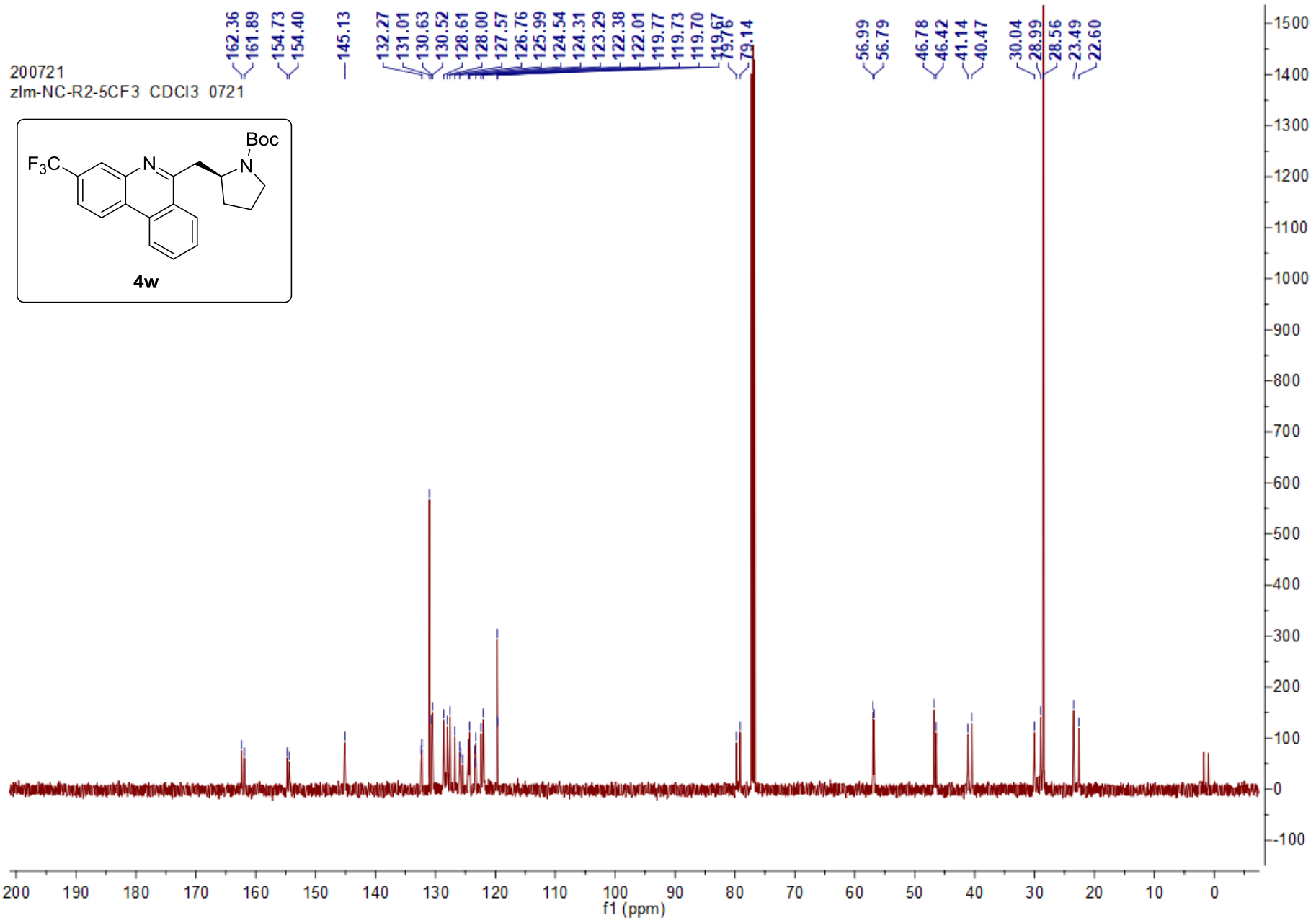
7.925
7.905
7.888
7.866
7.850
7.765
7.751
7.276
4.474
4.202
4.198
4.177
4.173
3.998
3.991
3.972
3.965
3.521
3.506
3.489
3.456
3.155
3.133
3.077
2.061
2.014
2.010
1.891
1.858
1.842
1.832
1.810
1.788
1.760
1.745
1.731
1.526
1.484
200708
zlm-NC-R2-5CF3 CDCl3 0708
Boc
F3C
N
N
4w
1.62
1.09
0.47
1.03
2.10
0.55
0.50
1.06
0.54
0.48
1.06
1.05
1.07
3.02
2.18
5.11
4.15
f1 (ppm)


200721
zlm-NC-R2-5CF3 CDCl3 0721
Boc
F3C
N
N
4w
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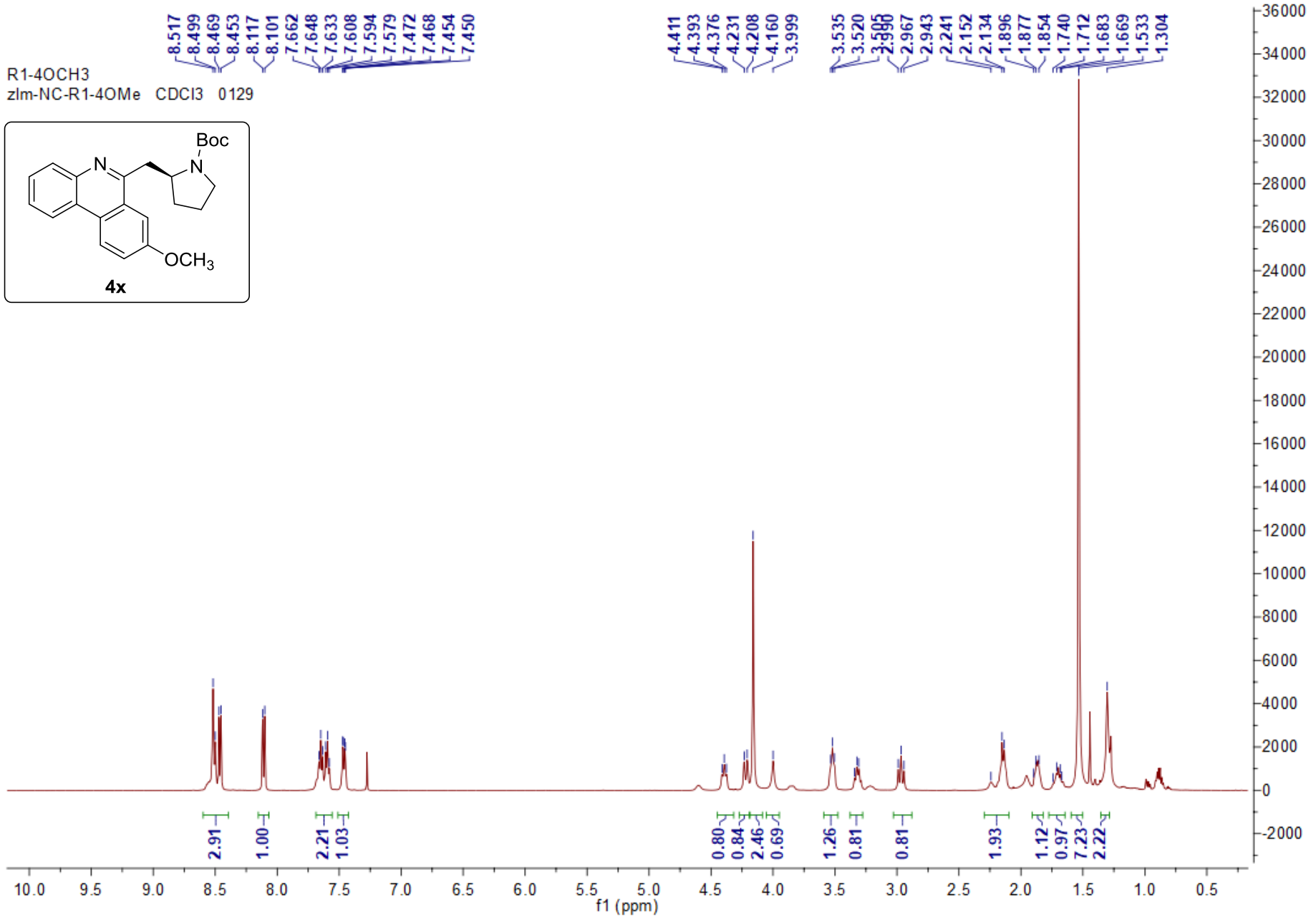
154.40
145.13
132.27
131.01
130.63
130.52
128.61
128.00
127.57
126.76
125.99
124.54
124.31
123.29
122.38
122.01
119.77
119.73
119.70
79.14
56.99
56.79
46.78
46.42
41.14
40.47
30.04
28.99
28.56
23.49
22.60
f1 (ppm)


R1-4OCH3
zlm-NC-R1-4OMe CDCl3 0129
Boc
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N
OCH3
4x
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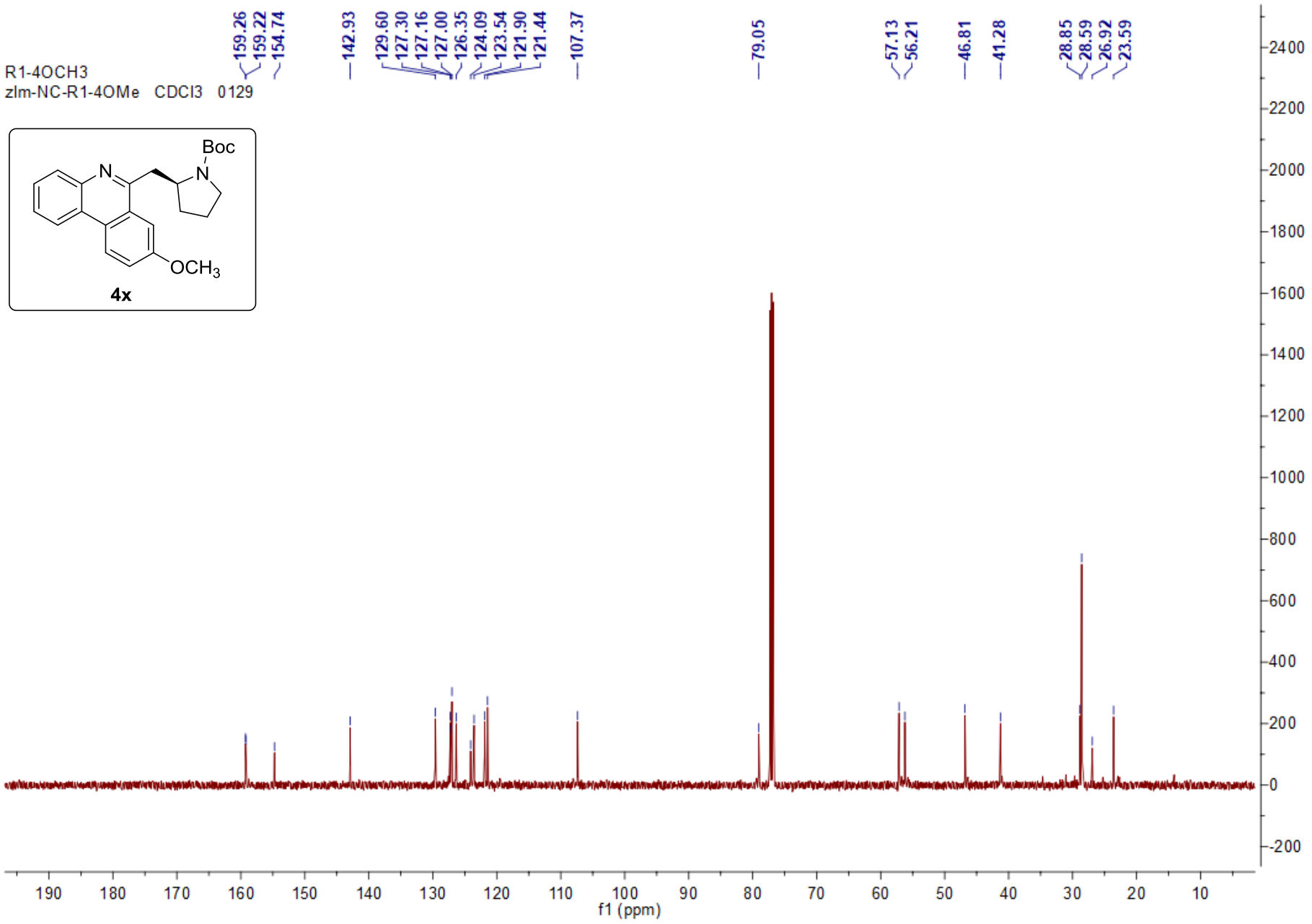
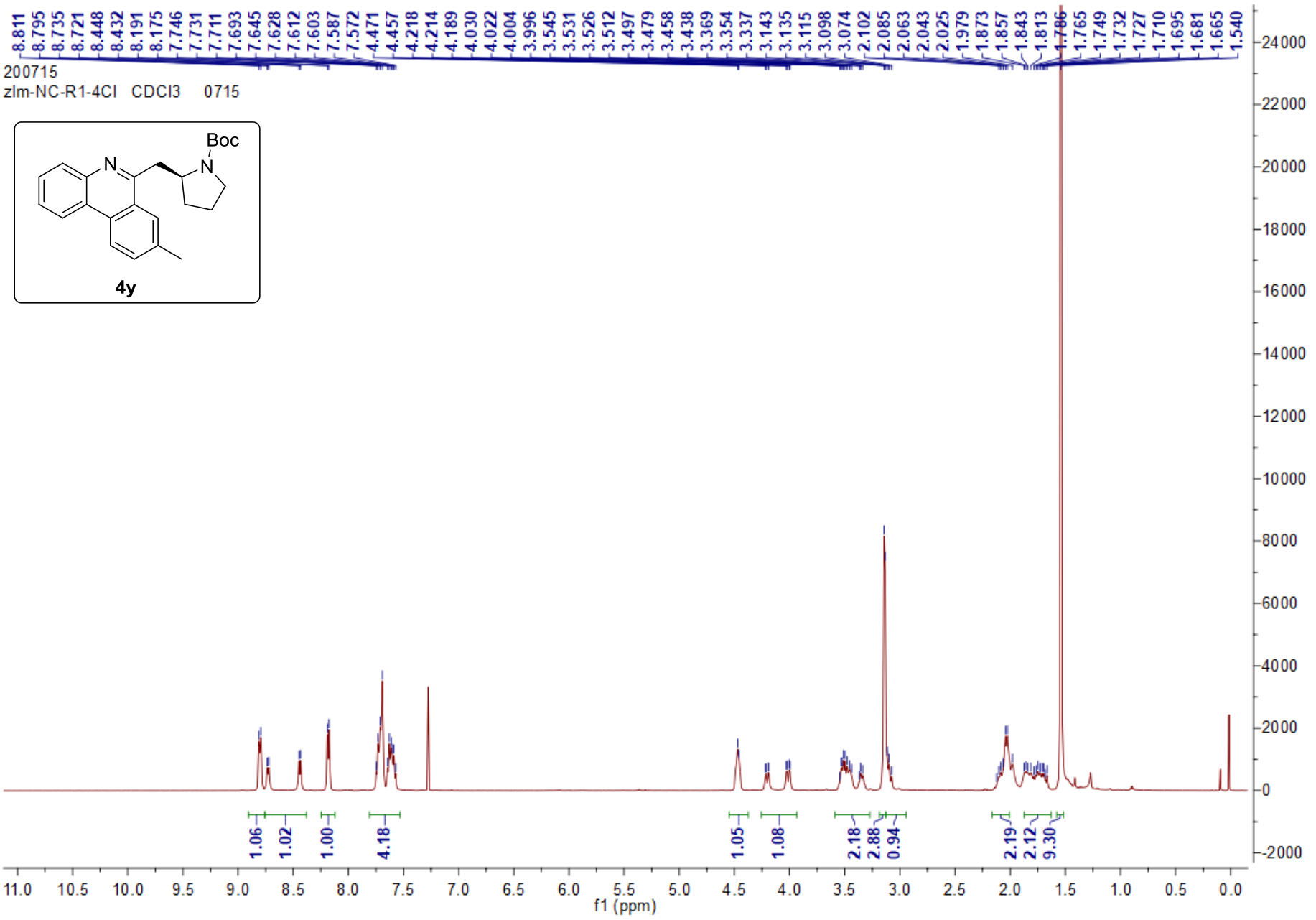
8.499
8.469
8.453
8.117
8.101
7.662
7.648
7.633
7.608
7.594
7.579
7.472
7.468
7.454
7.450
4.411
4.393
4.376
4.231
4.208
4.160
3.999
3.535
3.520
2.990
2.967
2.943
2.241
2.152
2.134
1.896
1.877
1.854
1.740
1.712
1.683
1.669
1.533
1.304
2.91
1.00
2.21
1.03
0.80
0.84
2.46
0.69
1.26
0.81
0.81
1.93
1.12
0.97
7.23
2.22
f1 (ppm)


R1-4OCH3
zlm-NC-R1-4OMe CDCl3 0129
159.26
159.22
154.74
142.93
129.60
127.30
127.16
127.00
126.35
124.09
123.54
121.90
121.44
107.37
79.05
57.13
56.21
46.81
41.28
28.85
28.59
26.92
23.59
Boc
N
N
OCH3
4x
f1 (ppm)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8.432
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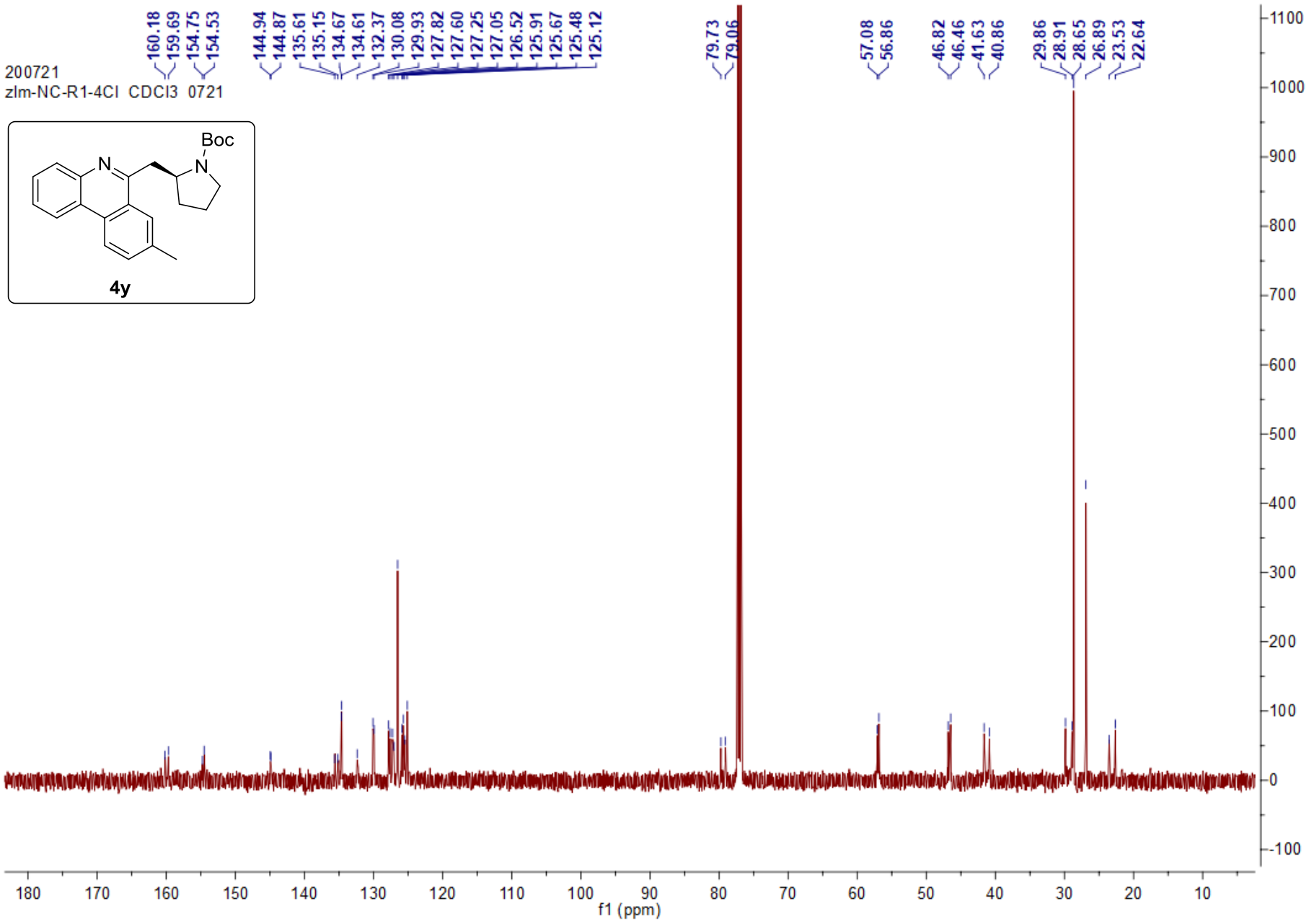
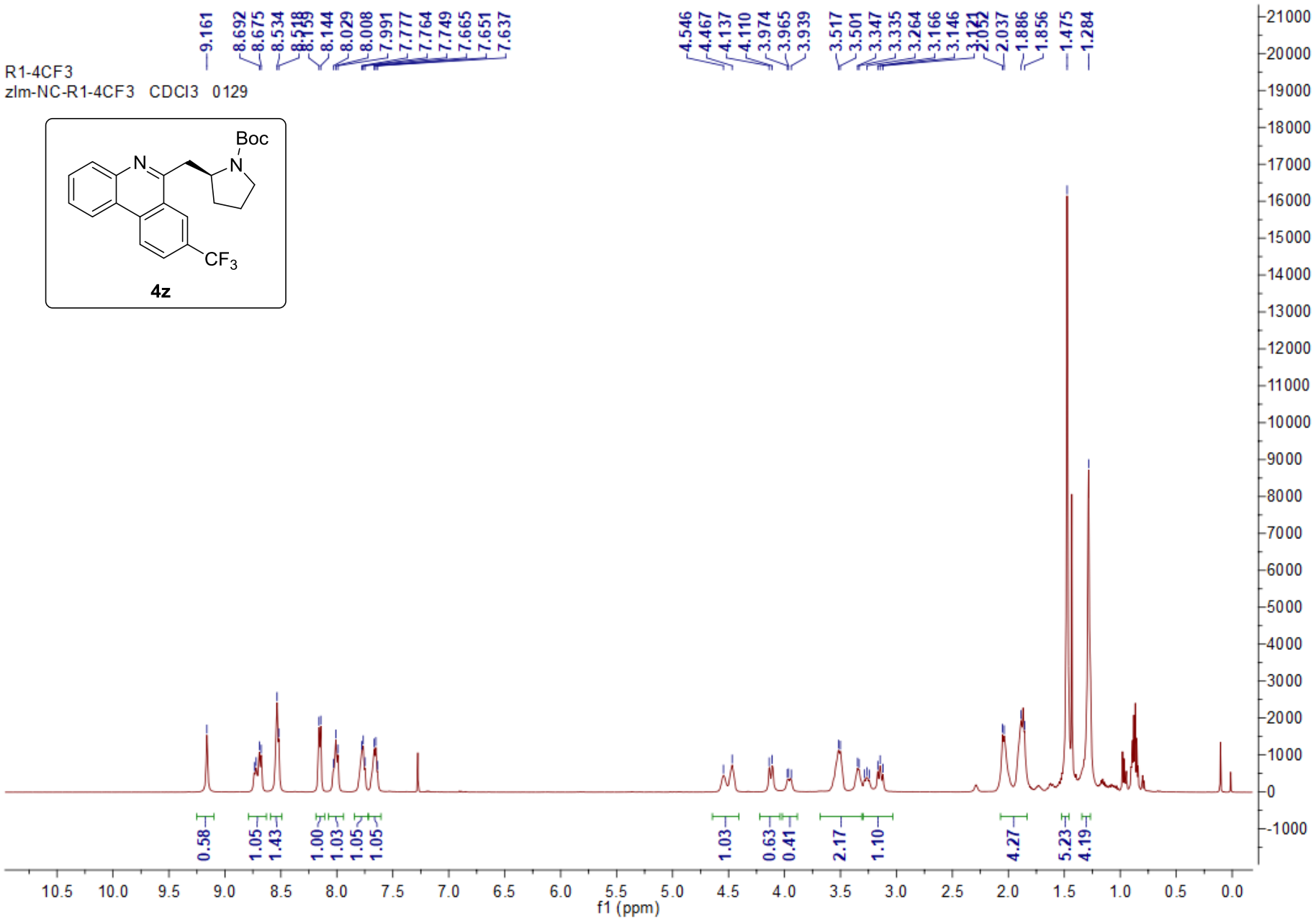
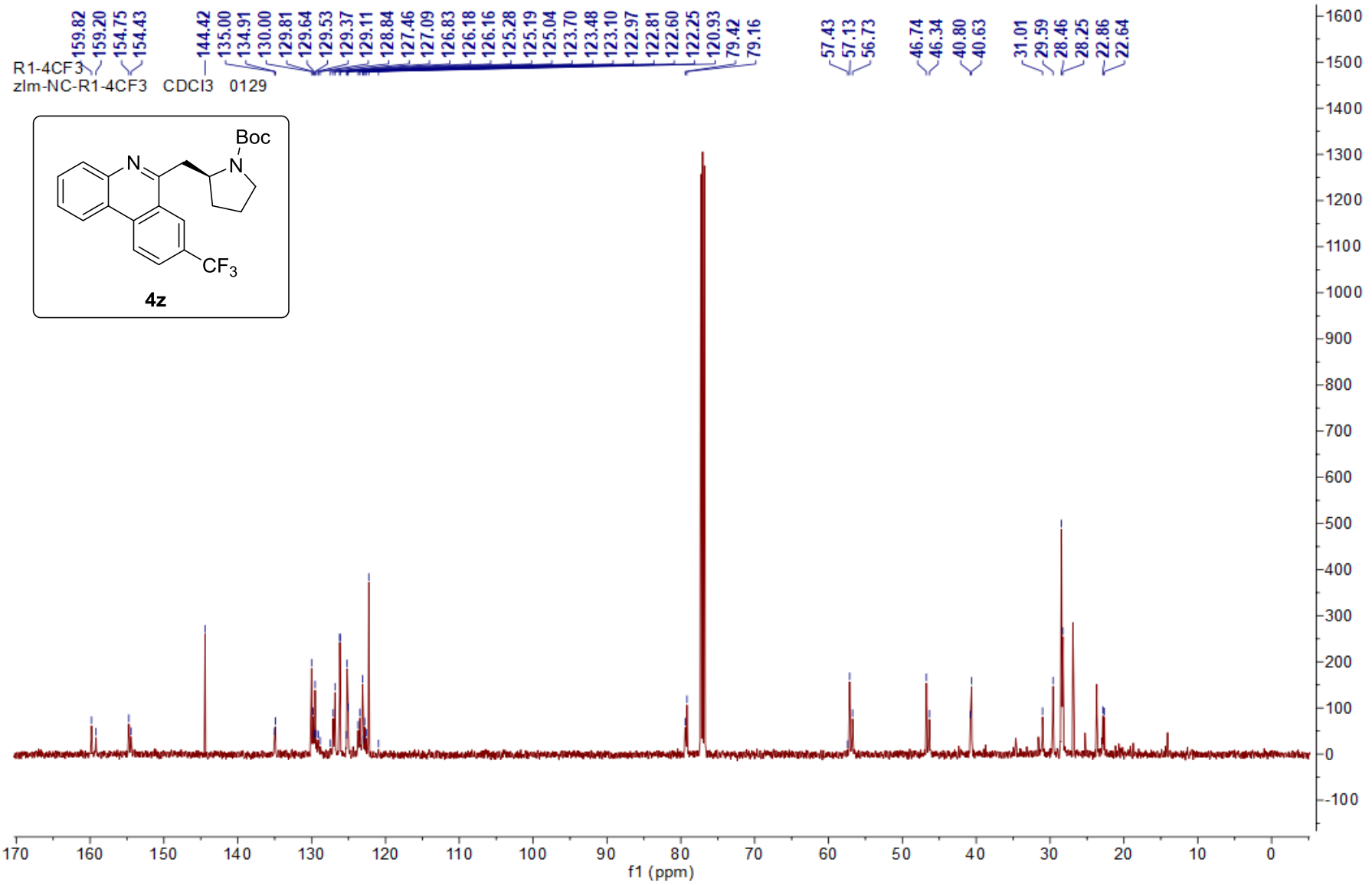
8.175
7.746
7.731
7.711
7.693
7.645
7.628
7.612
7.603
7.587
7.572
4.471
4.457
4.218
4.214
4.189
4.030
4.022
4.004
3.996
3.545
3.531
3.526
3.512
3.497
3.479
3.458
3.438
3.369
3.354
3.337
3.143
3.135
3.115
3.098
3.074
2.102
2.085
2.063
2.043
2.025
1.979
1.873
1.857
1.843
1.813
1.786
1.765
1.749
1.732
1.727
1.710
1.695
1.681
1.665
1.540
200715
zlm-NC-R1-4Cl CDCl3 0715
Boc
N
N
4y
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.06
1.02
1.00
4.18
1.05
1.08
2.18
2.88
0.94
2.19
2.12
9.30
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.18
159.69
154.75
154.53
144.94
144.87
135.61
135.15
134.67
134.61
132.37
130.08
129.93
127.82
127.60
127.25
127.05
126.52
125.91
125.67
125.48
125.12
79.73
79.06
57.08
56.86
46.82
46.46
41.63
40.86
29.86
28.91
28.65
26.89
23.53
22.64
200721
zlm-NC-R1-4Cl CDCl3 0721
Boc
N
N
4y
f1 (ppm)


R1-4CF3
zlm-NC-R1-4CF3 CDCl3 0129
Boc
N
N
CF3
4z
9.161
8.692
8.675
8.534
8.144
8.029
8.008
7.991
7.777
7.764
7.749
7.665
7.651
7.637
4.546
4.467
4.137
4.110
3.974
3.965
3.939
3.517
3.501
3.347
3.335
3.264
3.166
3.146
2.037
1.886
1.856
1.475
1.284
0.58
1.05
1.43
1.00
1.03
1.05
1.05
1.03
0.63
0.41
2.17
1.10
4.27
5.23
4.19
f1 (ppm)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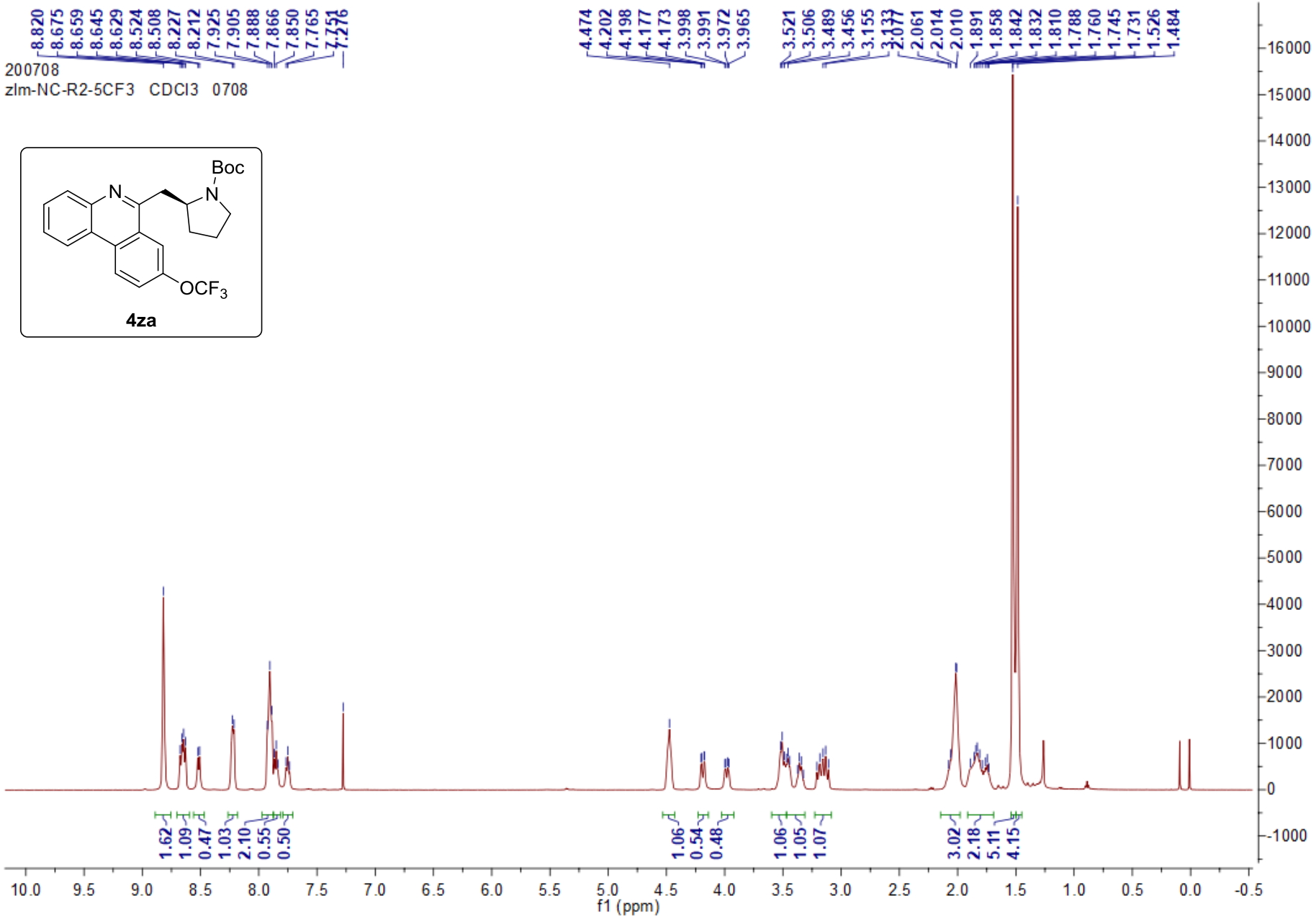
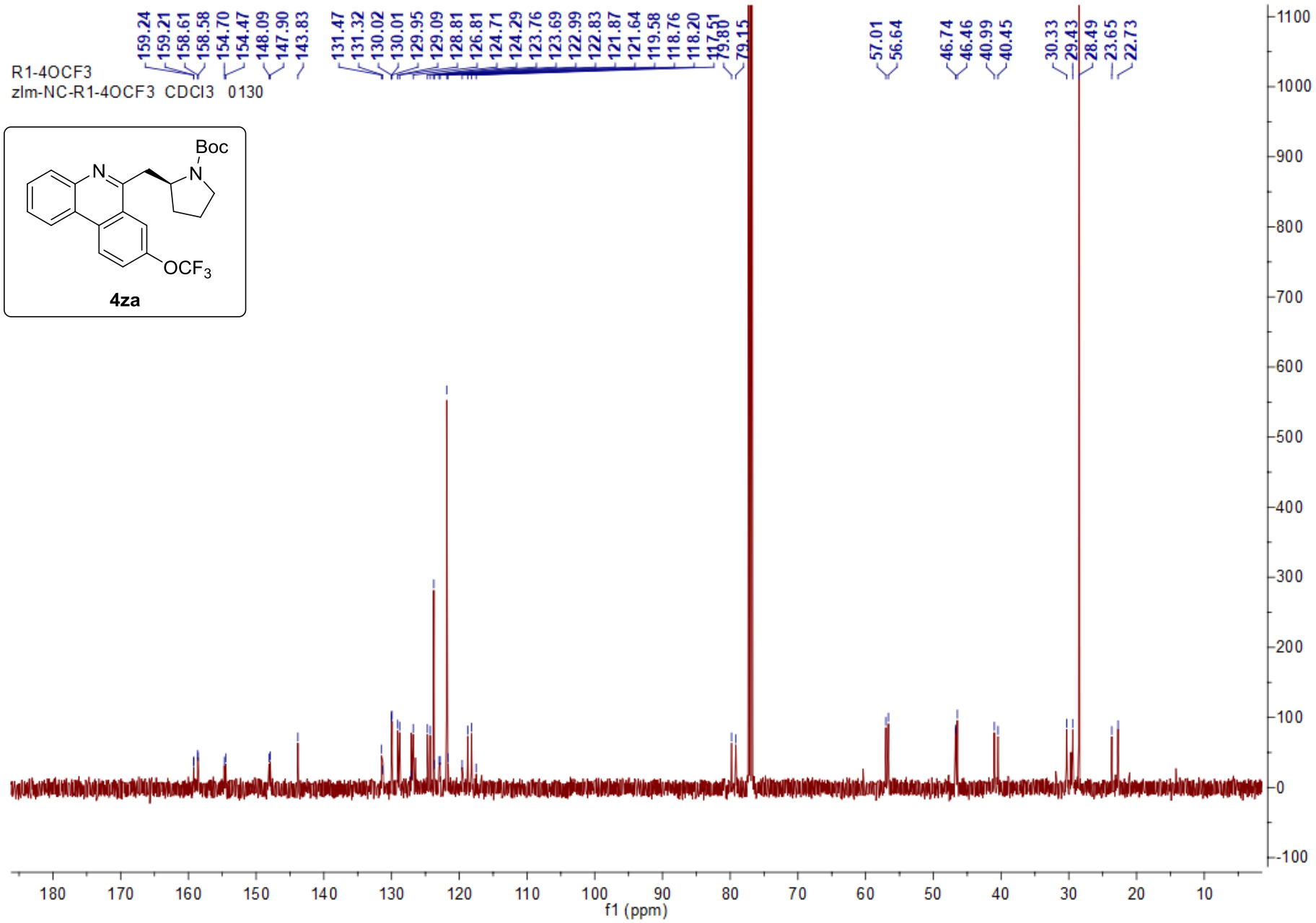
159.20
154.75
154.43
144.42
135.00
134.91
130.00
129.81
129.64
129.53
129.37
129.11
128.84
127.46
127.09
126.83
126.18
126.16
125.28
125.19
125.04
123.70
123.48
123.10
122.97
122.81
122.60
122.25
120.93
79.42
79.16
57.43
57.13
56.73
46.74
46.34
40.80
40.63
31.01
29.59
28.46
28.25
22.86
22.64
R1-4CF3
zlm-NC-R1-4CF3 CDCl3 0129
Boc
N
N
CF3
4z
f1 (ppm)


8.820
8.675
8.659
8.645
8.629
8.524
8.508
8.227
8.212
7.925
7.905
7.888
7.866
7.850
7.765
7.751
7.276
4.474
4.202
4.198
4.177
4.173
3.998
3.991
3.972
3.965
3.521
3.506
3.489
3.456
3.155
3.133
3.077
2.061
2.014
2.010
1.891
1.858
1.842
1.832
1.810
1.788
1.760
1.745
1.731
1.526
1.484
200708
zlm-NC-R2-5CF3 CDCl3 0708
Boc
N
N
OCF3
4za
1.62
1.09
0.47
1.03
2.10
0.55
0.50
1.06
0.54
0.48
1.06
1.05
1.07
3.02
2.18
5.11
4.15
f1 (ppm)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zlm-NC-R1-4OCF3 CDCl3 0130
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159.21
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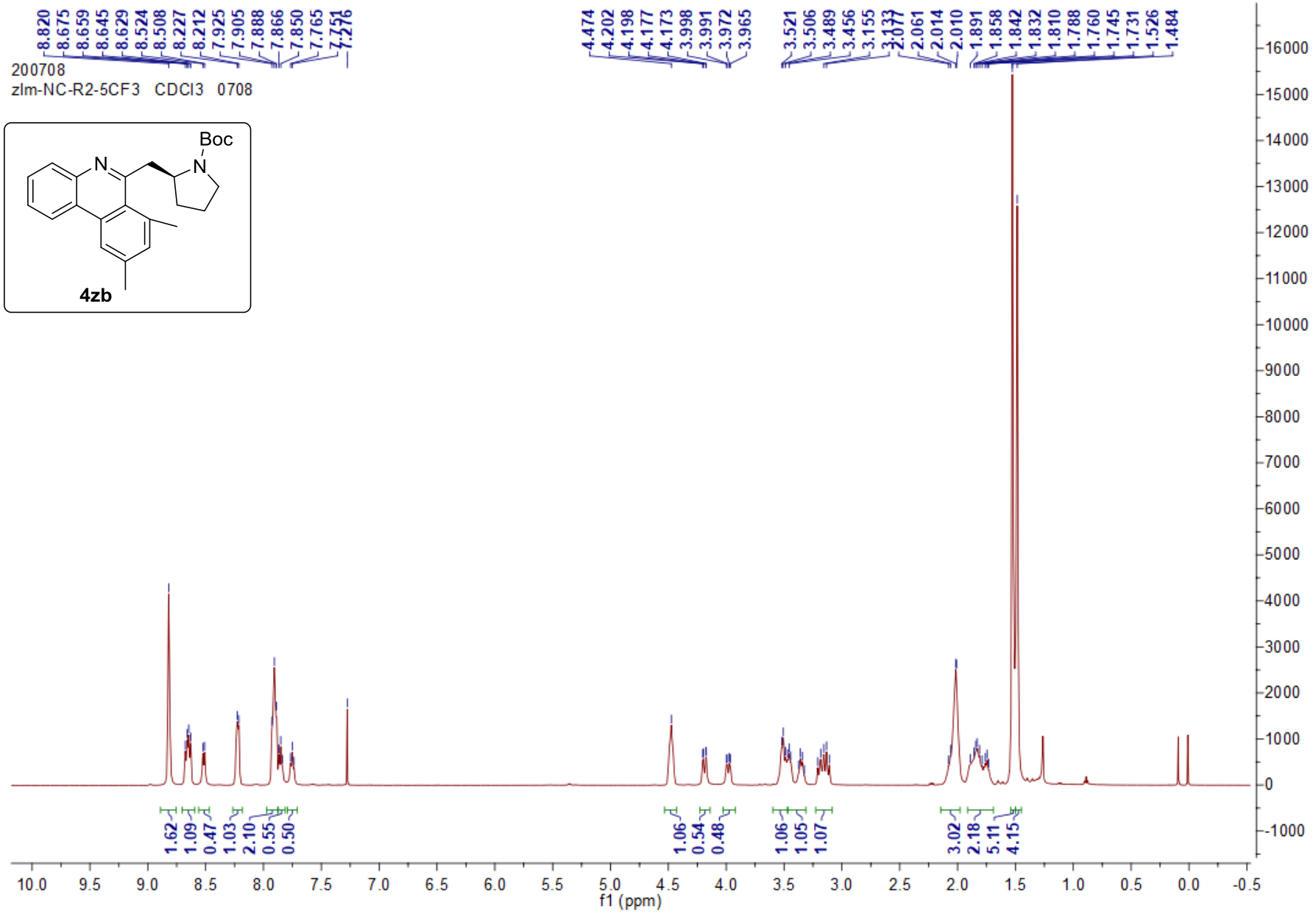
158.58
154.70
154.47
148.09
147.90
143.83
131.47
131.32
130.02
130.01
129.95
129.09
128.81
126.81
124.71
124.29
123.76
123.69
122.99
122.83
121.87
121.64
119.58
118.76
118.20
117.51
79.80
79.15
57.01
56.64
46.74
46.46
40.99
40.45
30.33
29.43
28.49
23.65
22.73
Boc
N
N
OCF3
4za
f1 (ppm)


8.820
8.675
8.659
8.645
8.629
8.524
8.508
8.227
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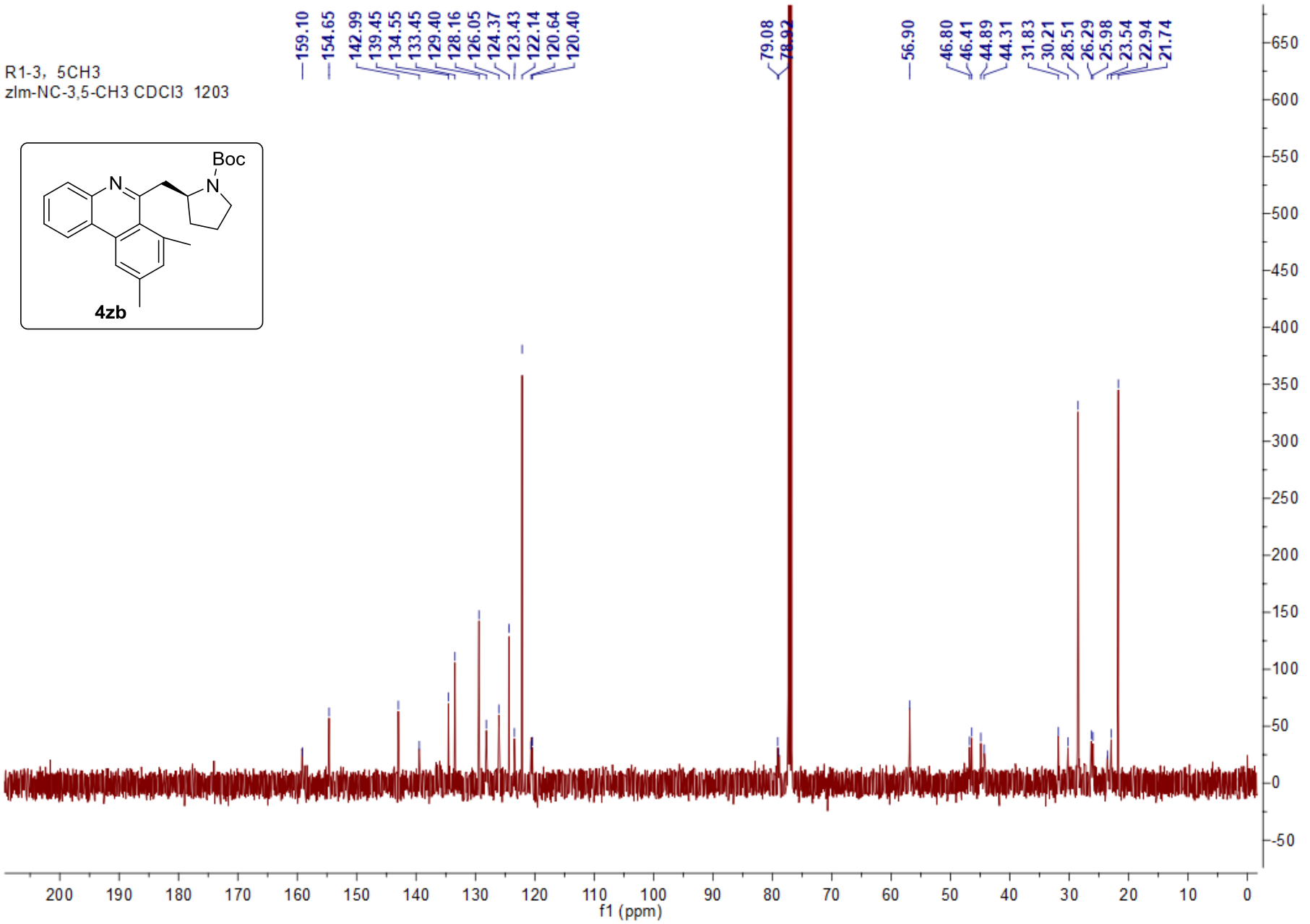
7.925
7.905
7.888
7.866
7.850
7.765
7.751
7.276
4.474
4.202
4.198
4.177
4.173
3.998
3.991
3.972
3.965
3.521
3.506
3.489
3.456
3.155
3.133
2.077
2.061
2.014
2.010
1.891
1.858
1.842
1.832
1.810
1.788
1.760
1.745
1.731
1.526
1.484
200708
zlm-NC-R2-5CF3 CDCl3 0708
Boc
N
N
4zb
1.62
1.09
0.47
1.03
2.10
0.55
0.50
1.06
0.54
0.48
1.06
1.05
1.07
3.02
2.18
5.11
4.15
f1 (ppm)


R1-3, 5CH3
zlm-NC-3,5-CH3 CDCl3 1203
Boc
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N
4zb
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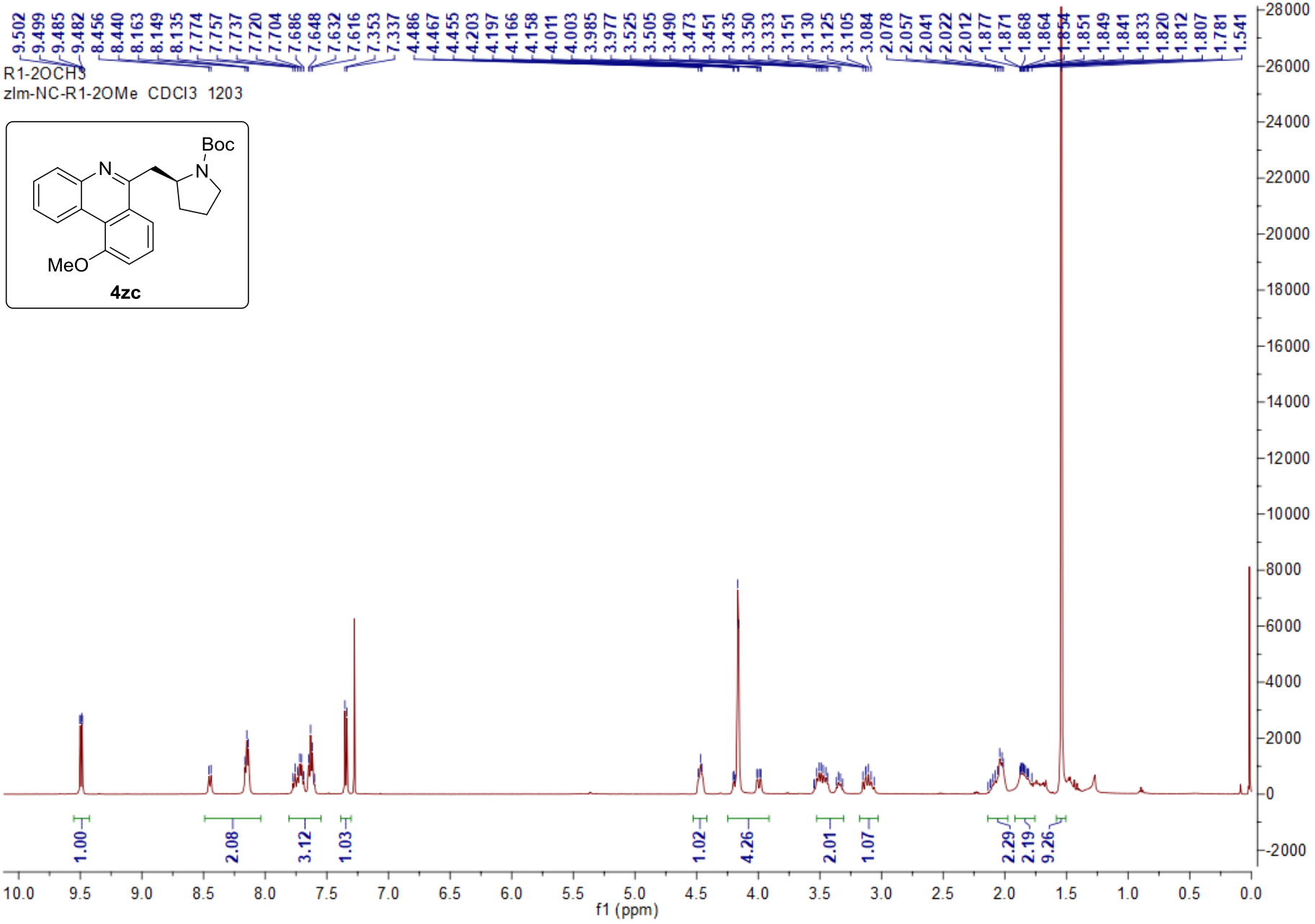
134.55
133.45
129.40
128.16
126.05
124.37
123.43
122.14
120.64
120.40
79.08
78.92
56.90
46.80
46.41
44.89
44.31
31.83
30.21
28.51
26.29
25.98
23.54
22.94
21.74
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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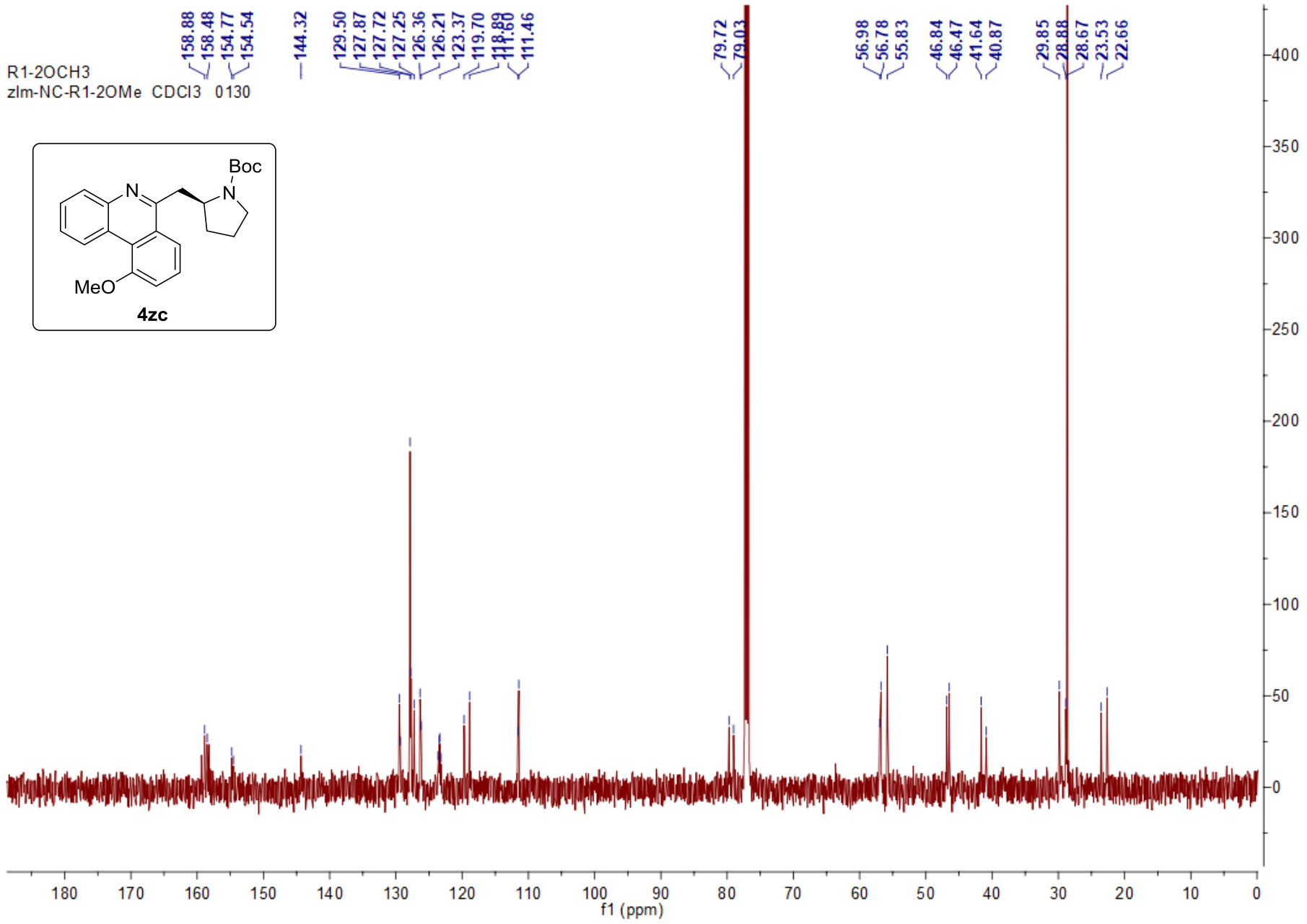
8.440
8.163
8.149
8.135
7.774
7.757
7.737
7.720
7.704
7.686
7.648
7.632
7.616
7.353
7.337
4.486
4.467
4.455
4.203
4.197
4.166
4.158
4.011
4.003
3.985
3.977
3.525
3.505
3.490
3.473
3.451
3.435
3.350
3.333
3.151
3.130
3.125
3.105
3.084
2.078
2.057
2.041
2.022
2.012
1.877
1.871
1.868
1.864
1.854
1.851
1.849
1.841
1.833
1.820
1.812
1.807
1.781
1.541
R1-2OCH3
zlm-NC-R1-2OMe CDCl3 1203
Boc
N
N
MeO
4zc
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
2.08
3.12
1.03
1.02
4.26
2.01
1.07
2.29
2.19
9.26
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)


R1-2OCH3
zlm-NC-R1-2OMe CDCl3 0130
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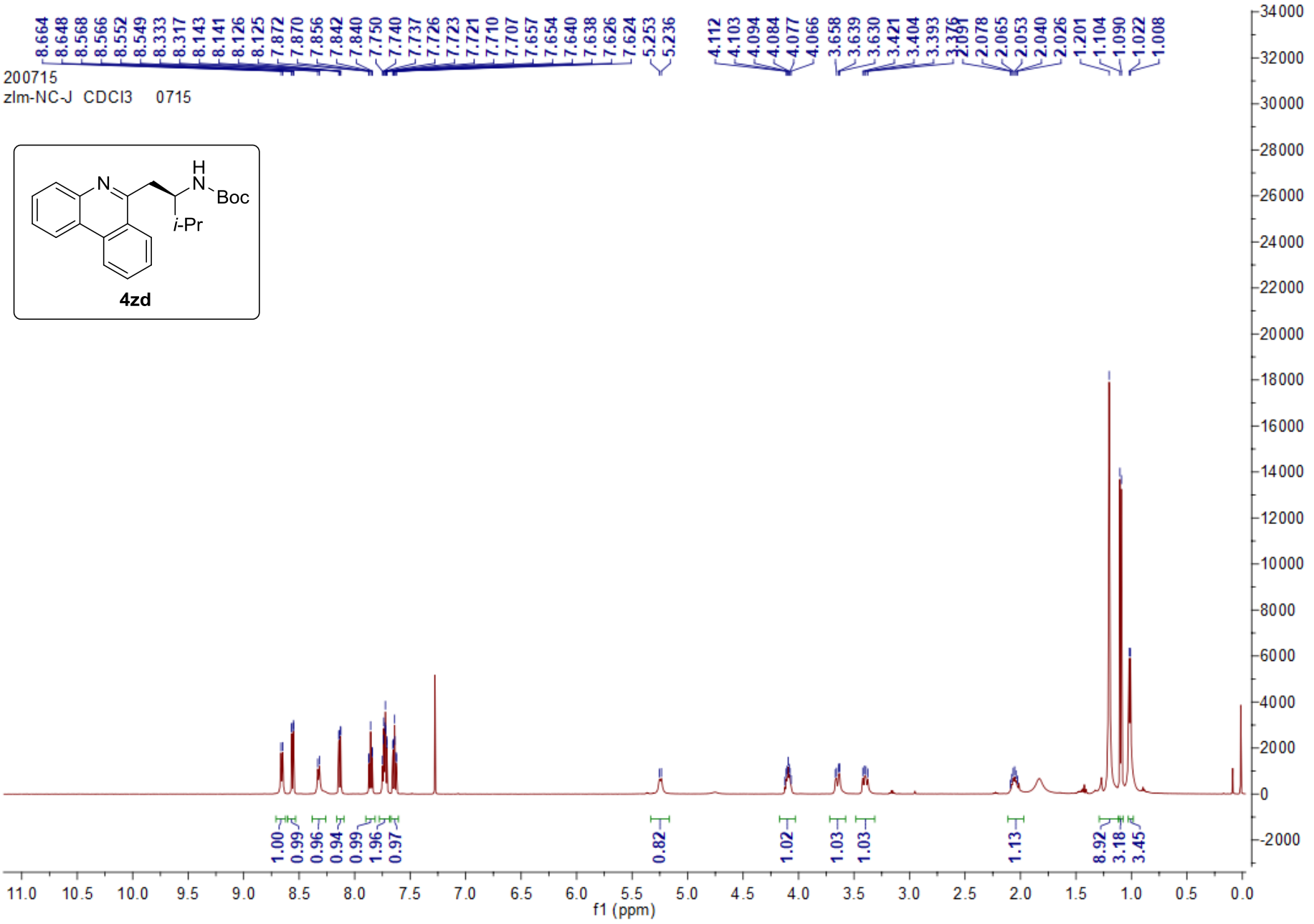
158.48
154.77
154.54
144.32
129.50
127.87
127.72
127.25
126.36
126.21
123.37
119.70
118.89
111.60
111.46
79.72
79.03
56.98
56.78
55.83
46.84
46.47
41.64
40.87
29.85
28.88
28.67
23.53
22.66
Boc
N
N
MeO
4zc
f1 (ppm)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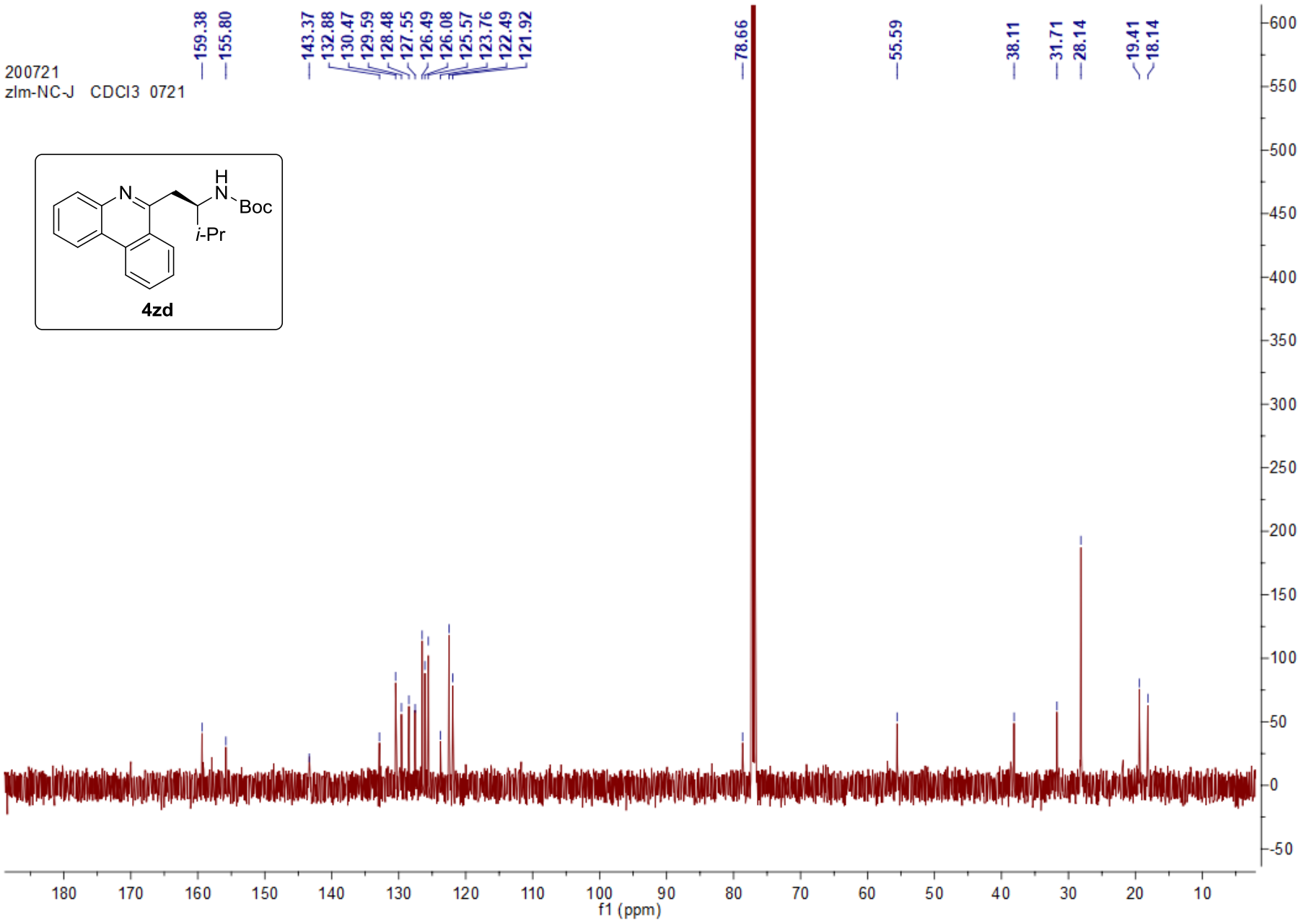
8.566
8.552
8.549
8.333
8.317
8.143
8.141
8.126
8.125
7.872
7.870
7.856
7.842
7.840
7.750
7.740
7.737
7.726
7.723
7.721
7.710
7.707
7.657
7.654
7.640
7.638
7.626
7.624
5.253
5.236
4.112
4.103
4.094
4.084
4.077
4.066
3.658
3.639
3.630
3.421
3.404
3.393
2.078
2.065
2.053
2.040
2.026
1.201
1.104
1.090
1.022
1.008
200715
zlm-NC-J CDCl3 0715
N
H
N
Boc
i-Pr
4zd
1.00
0.99
0.96
0.94
0.99
1.96
0.97
0.82
1.02
1.03
1.03
1.13
8.92
3.18
3.45
f1 (ppm)


200721
zlm-NC-J CDCl3 0721
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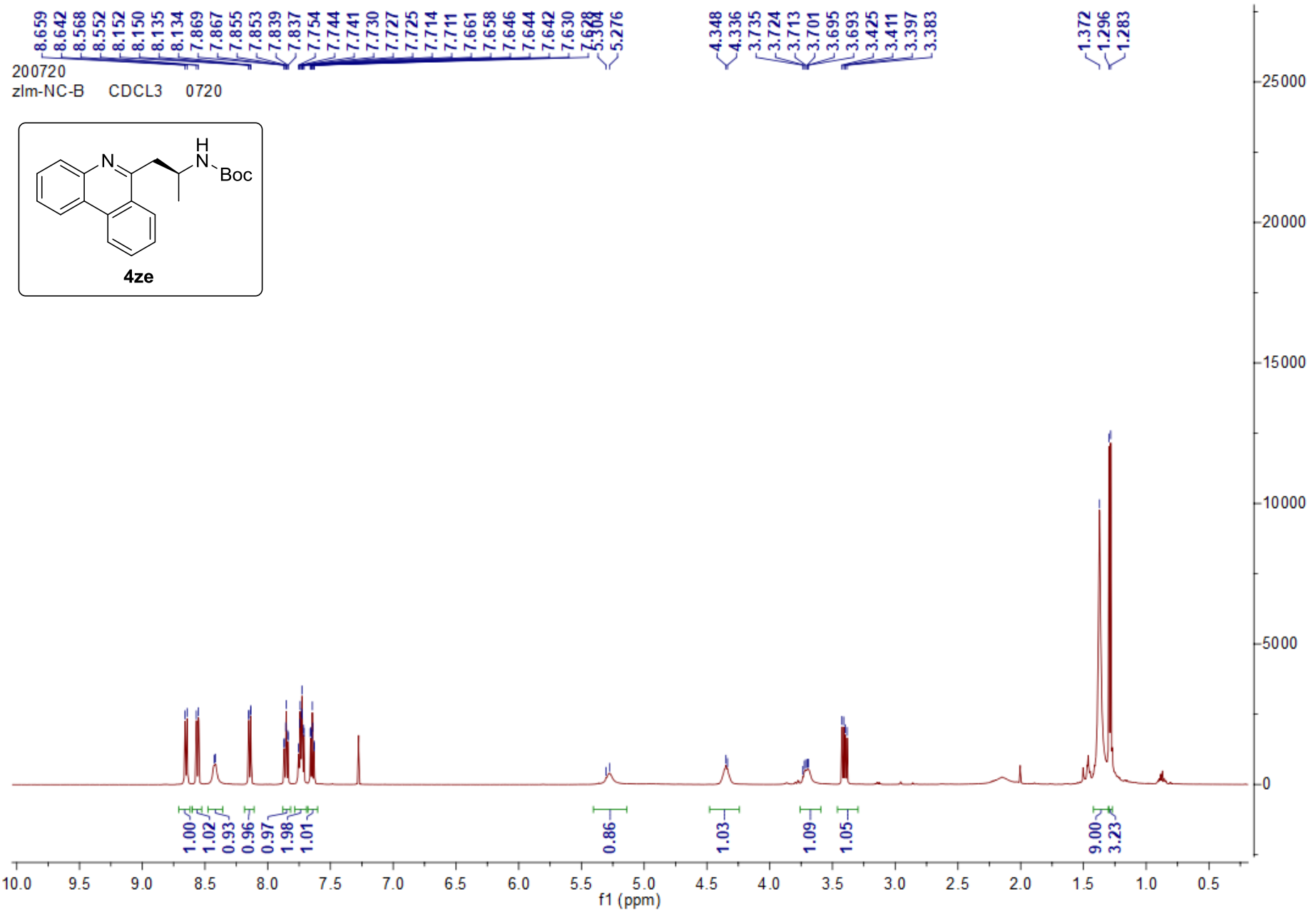
130.47
129.59
128.48
127.55
126.49
126.08
125.57
123.76
122.49
121.92
78.66
55.59
38.11
31.71
28.14
19.41
18.14
N
H
N
Boc
i-Pr
4zd
f1 (ppm)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8.152
8.150
8.135
8.134
7.869
7.867
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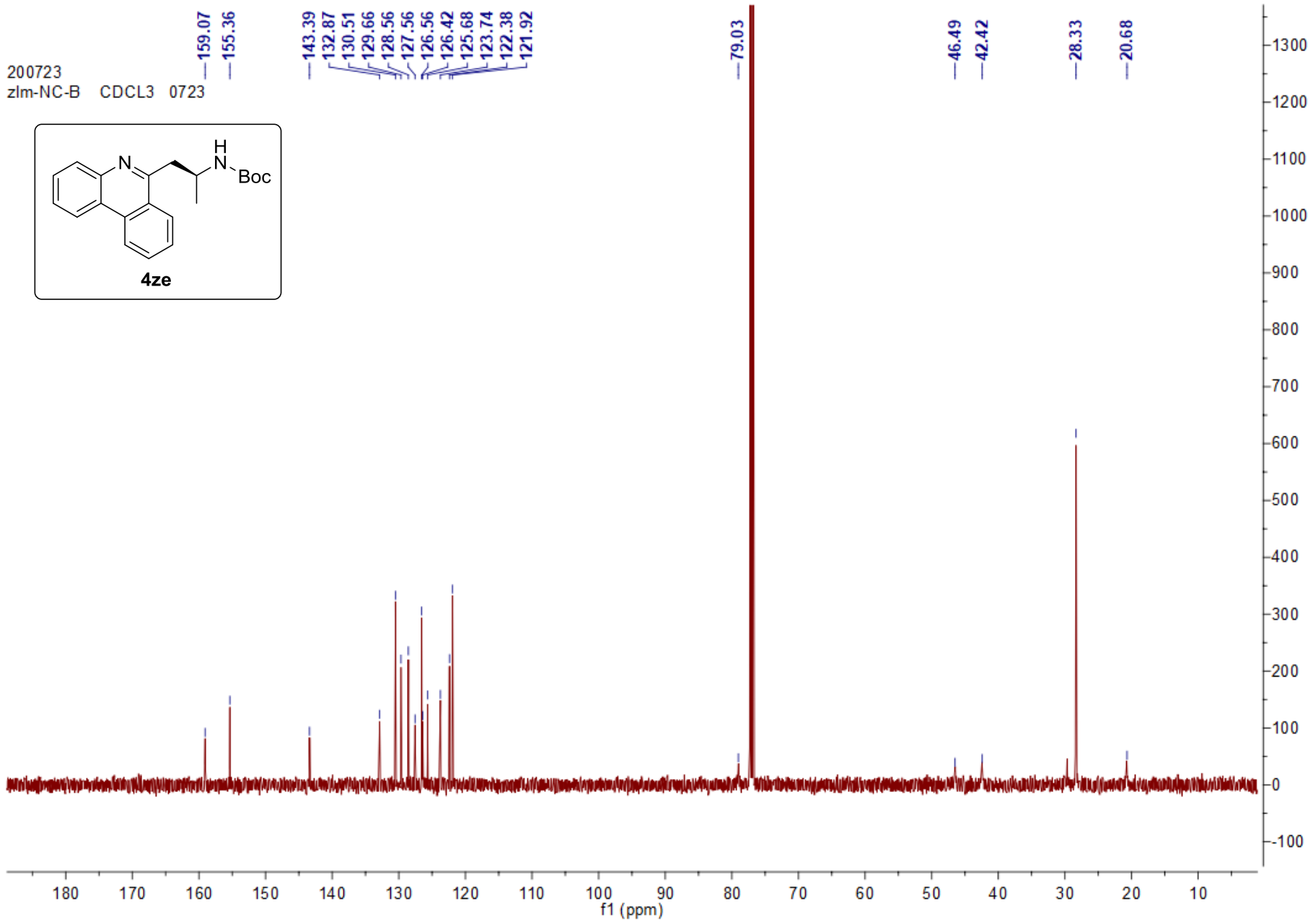
7.839
7.837
7.754
7.744
7.741
7.730
7.727
7.725
7.714
7.711
7.661
7.658
7.646
7.644
7.642
7.630
5.304
5.276
4.348
4.336
3.735
3.724
3.713
3.701
3.695
3.693
3.425
3.411
3.397
3.383
1.372
1.296
1.283
200720
zlm-NC-B CDCL3 0720
N
H
N
Boc
4ze
25000
20000
15000
10000
5000
0
1.00
1.02
0.93
0.96
0.97
1.98
1.01
0.86
1.03
1.09
1.05
9.00
3.23
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
f1 (ppm)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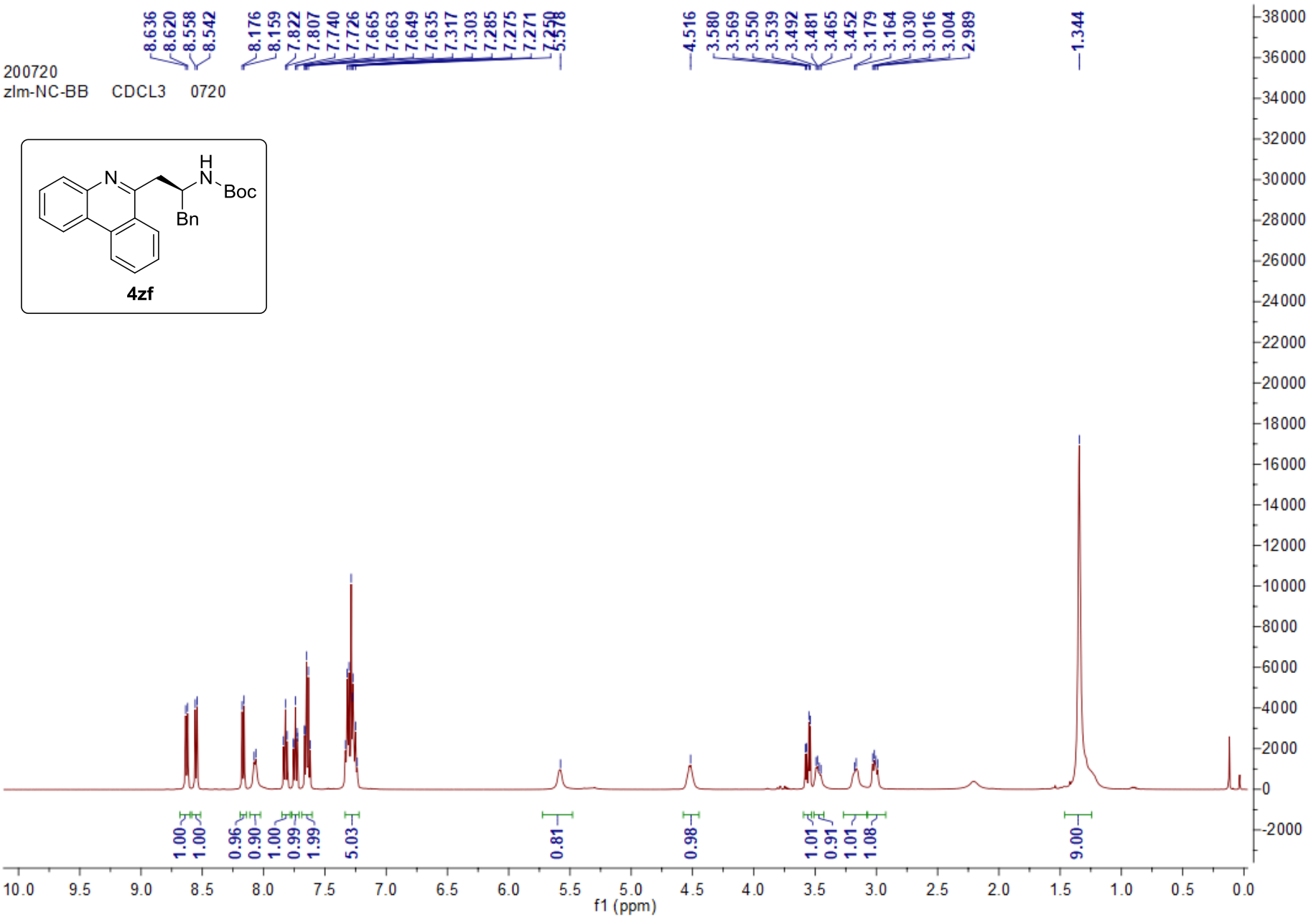
155.36
143.39
132.87
130.51
129.66
128.56
127.56
126.56
126.42
125.68
123.74
122.38
121.92
79.03
46.49
42.42
28.33
20.68
200723
zlm-NC-B CDCL3 0723
N
H
N
Boc
4ze
f1 (ppm)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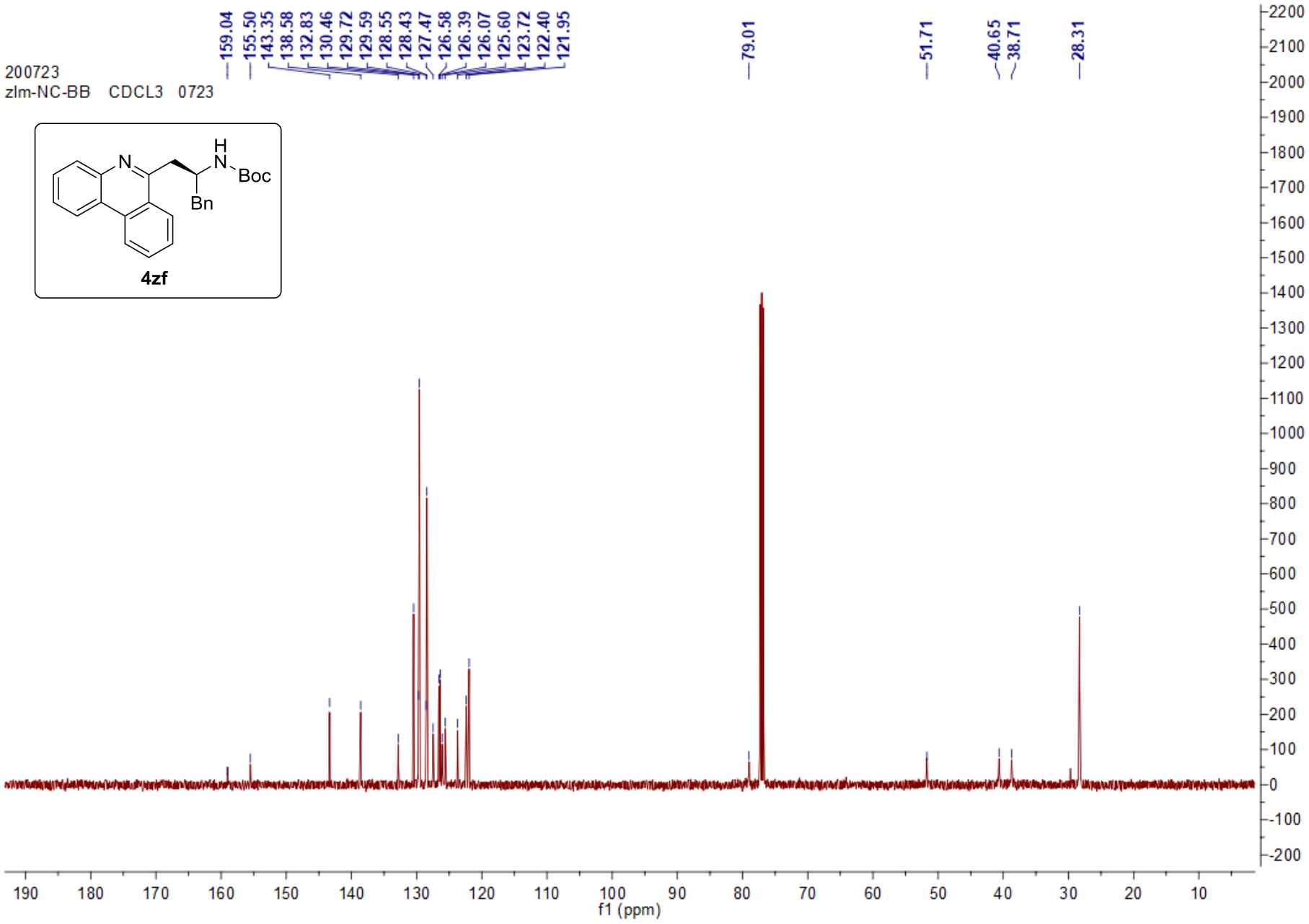
7.807
7.740
7.726
7.665
7.663
7.649
7.635
7.317
7.303
7.285
7.275
7.271
5.578
4.516
3.580
3.569
3.550
3.539
3.492
3.481
3.465
3.452
3.179
3.164
3.030
3.016
3.004
2.989
1.344
200720
zlm-NC-BB CDCL3 0720
N
H
N
Boc
Bn
4zf
1.00
1.00
0.96
0.90
1.00
0.99
1.99
5.03
0.81
0.98
1.01
0.91
1.01
1.08
9.00
f1 (ppm)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155.50
143.35
138.58
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130.46
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129.59
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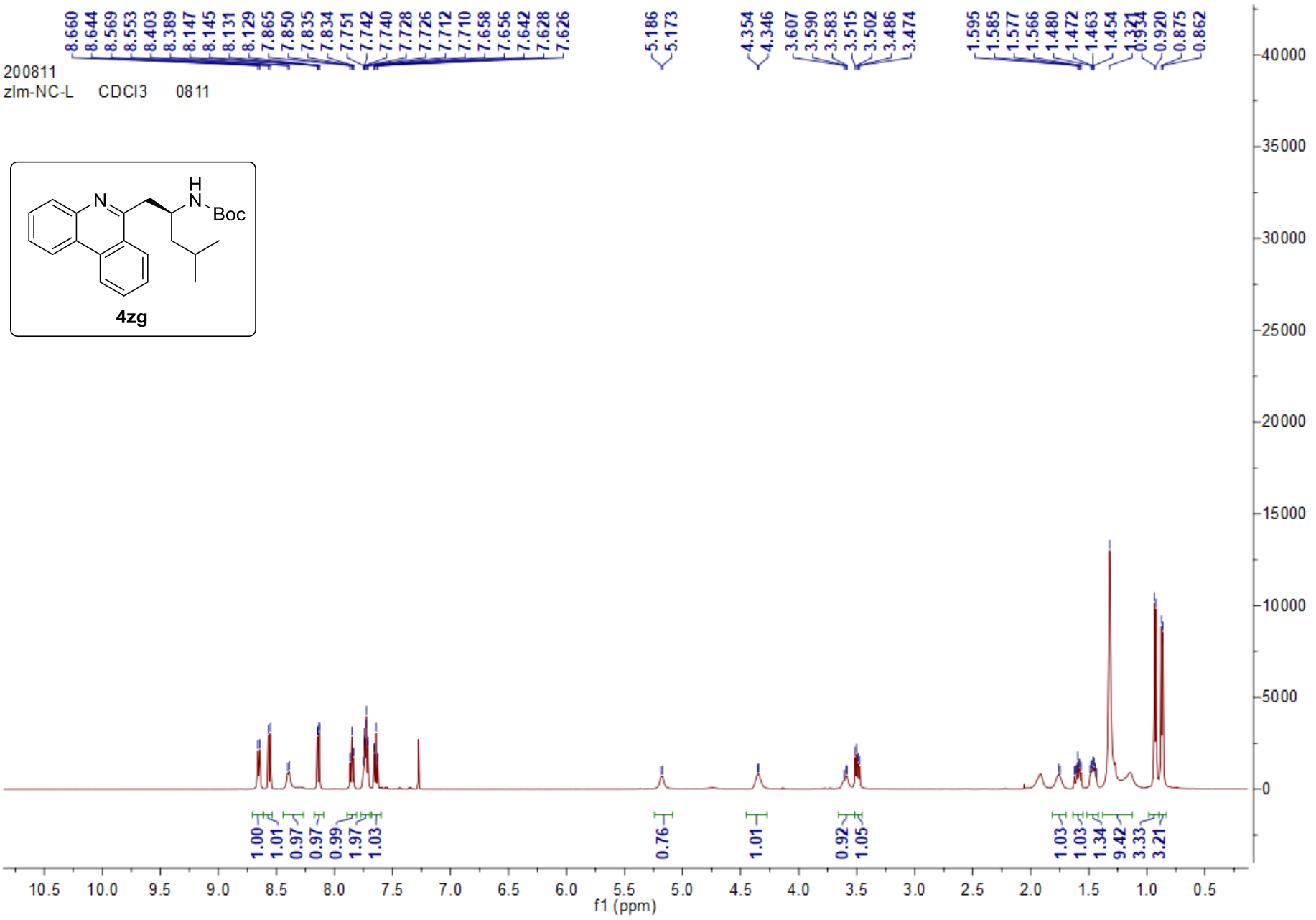
128.43
127.47
126.58
126.39
126.07
125.60
123.72
122.40
121.95
79.01
51.71
40.65
38.71
28.31
200723
zlm-NC-BB CDCL3 0723
H
N
Boc
N
Bn
4zf
f1 (ppm)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8.569
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8.403
8.389
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8.145
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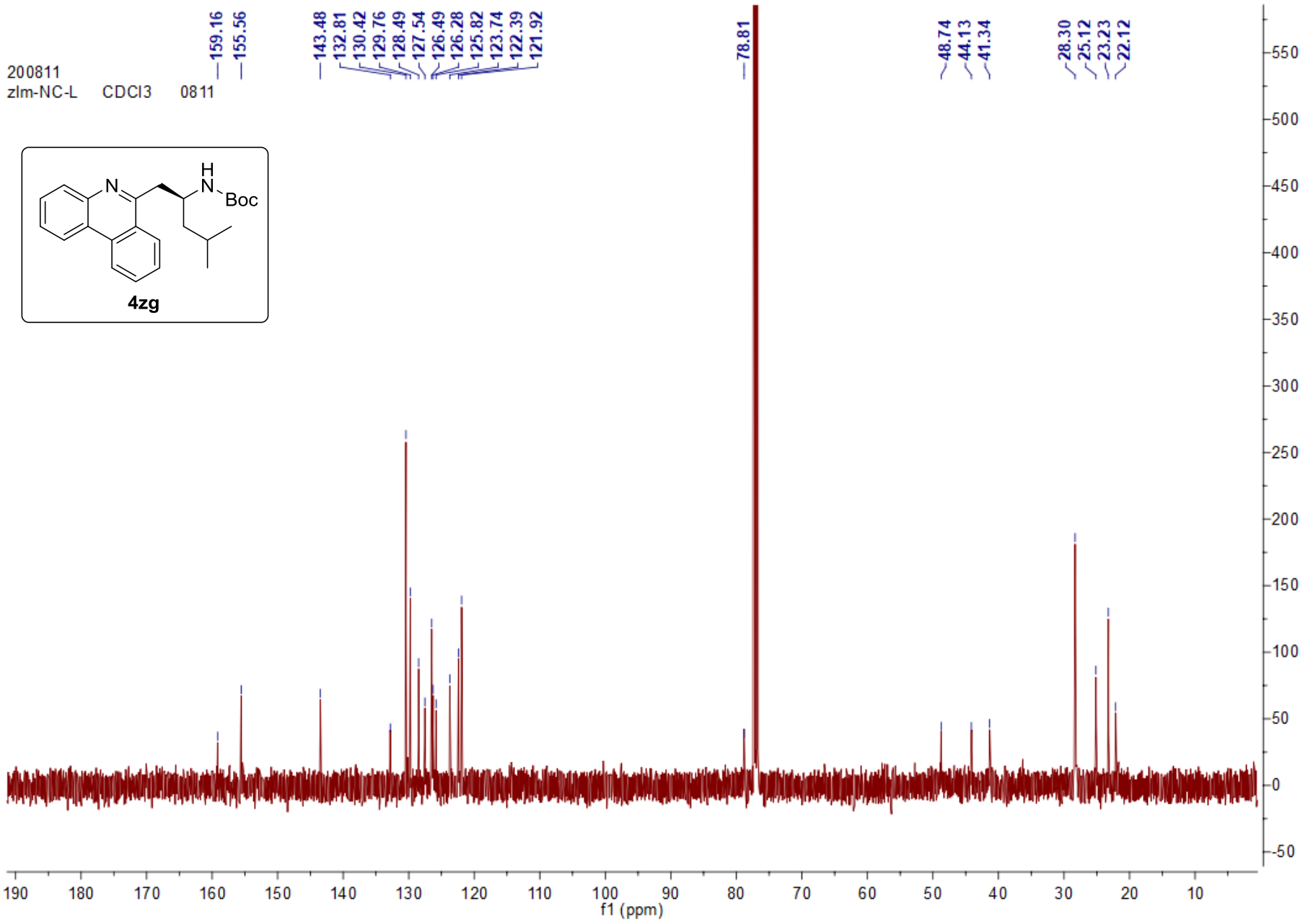
8.129
7.865
7.850
7.835
7.834
7.751
7.742
7.740
7.728
7.726
7.712
7.710
7.658
7.656
7.642
7.628
7.626
5.186
5.173
4.354
4.346
3.607
3.590
3.583
3.515
3.502
3.486
3.474
1.595
1.585
1.577
1.566
1.480
1.472
1.463
1.454
1.321
0.934
0.920
0.875
0.862
200811
zlm-NC-L CDCl3 0811
N
H
N
Boc
4zg
1.00
1.01
0.97
0.97
0.99
1.97
1.03
0.76
1.01
0.92
1.05
1.03
1.03
1.34
9.42
3.33
3.21
f1 (ppm)


200811
zlm-NC-L CDCl3 0811
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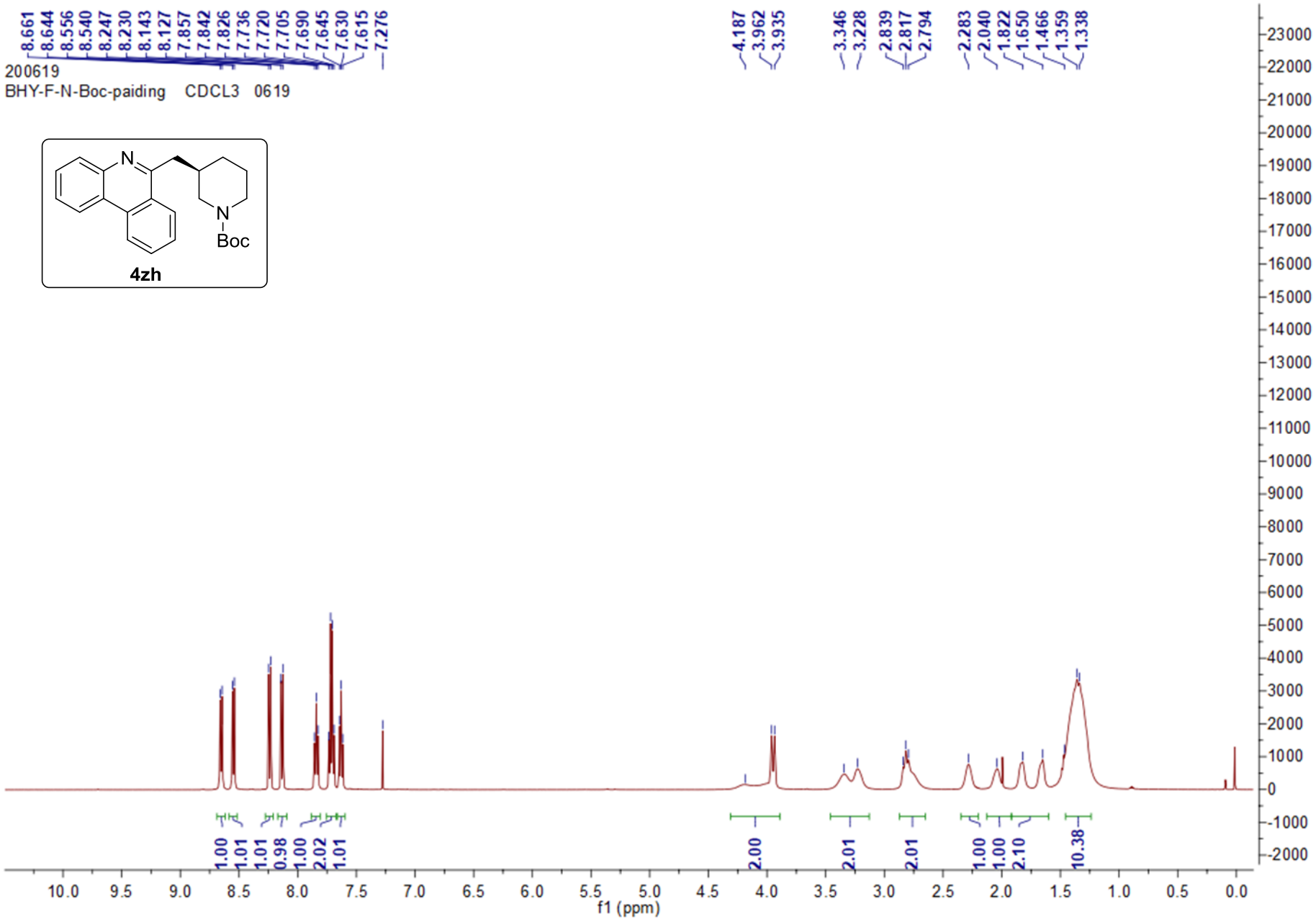
128.49
127.54
126.49
126.28
125.82
123.74
122.39
121.92
78.81
48.74
44.13
41.34
28.30
25.12
23.23
22.12
H
N
Boc
4zg
f1 (ppm)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8.247
8.230
8.143
8.127
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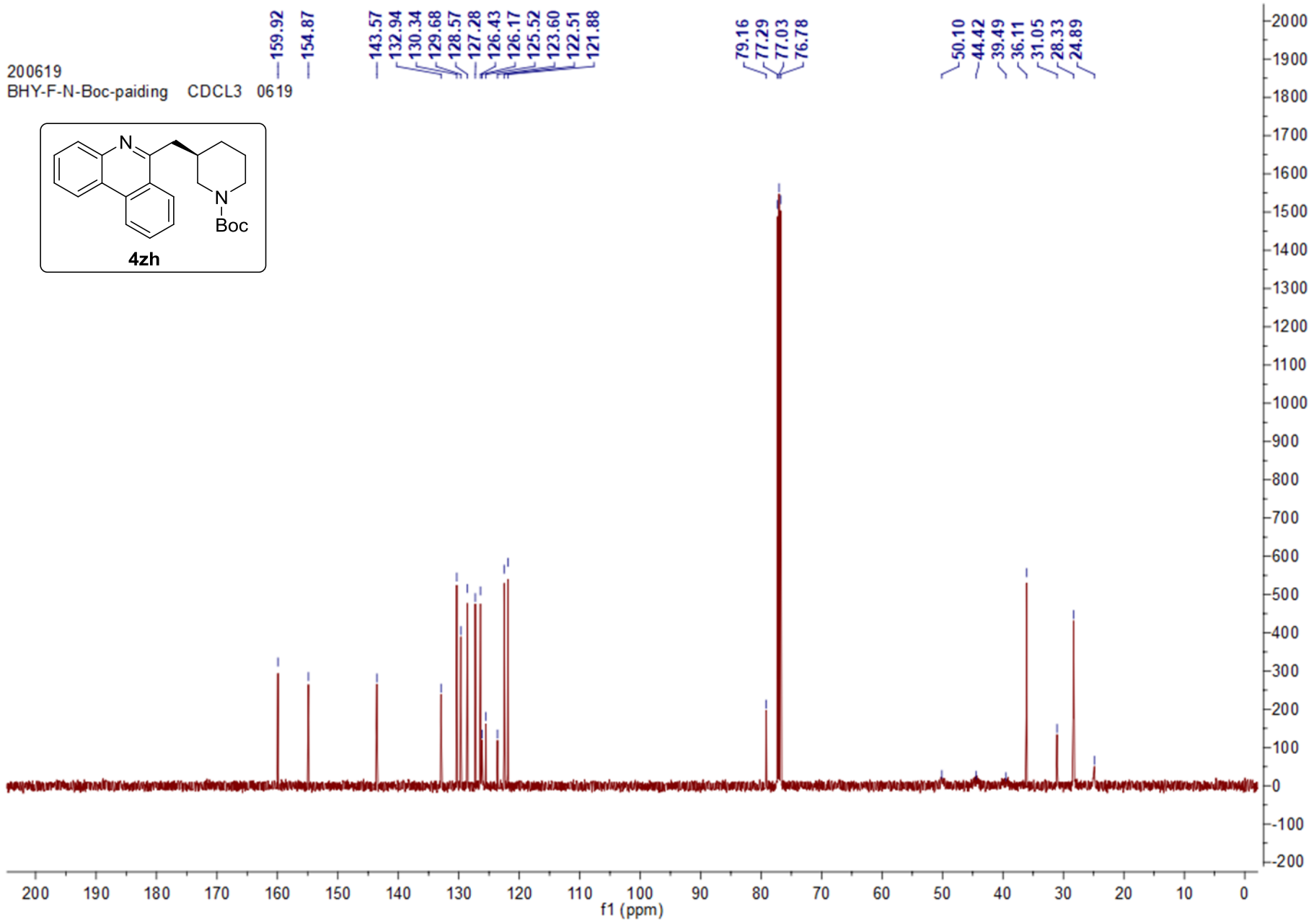
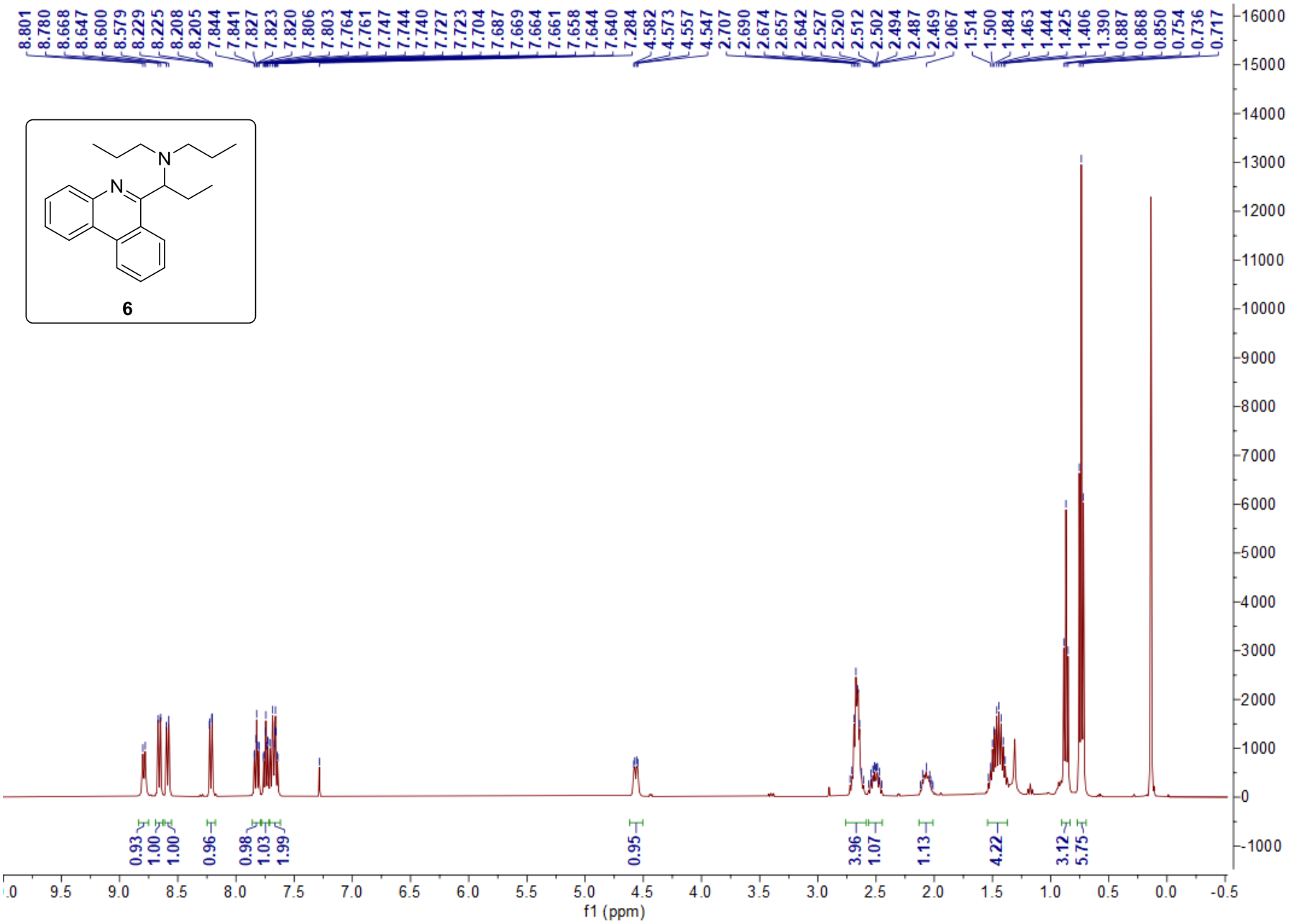
7.842
7.826
7.736
7.720
7.705
7.690
7.645
7.630
7.615
7.276
200619
BHY-F-N-Boc-paiding CDCL3 0619
4.187
3.962
3.935
3.346
3.228
2.839
2.817
2.794
2.283
2.040
1.822
1.650
1.466
1.359
1.338
N
N
Boc
4zh
1.00
1.01
1.01
0.98
1.00
2.02
1.01
2.00
2.01
2.01
1.00
1.00
2.10
10.38
f1 (ppm)


200619
BHY-F-N-Boc-paiding CDCL3 0619
159.92
154.87
143.57
132.94
130.34
129.68
128.57
127.28
126.43
126.17
125.52
123.60
122.51
121.88
79.16
77.29
77.03
76.78
50.10
44.42
39.49
36.11
31.05
28.33
24.89
N
N
Boc
4zh
f1 (ppm)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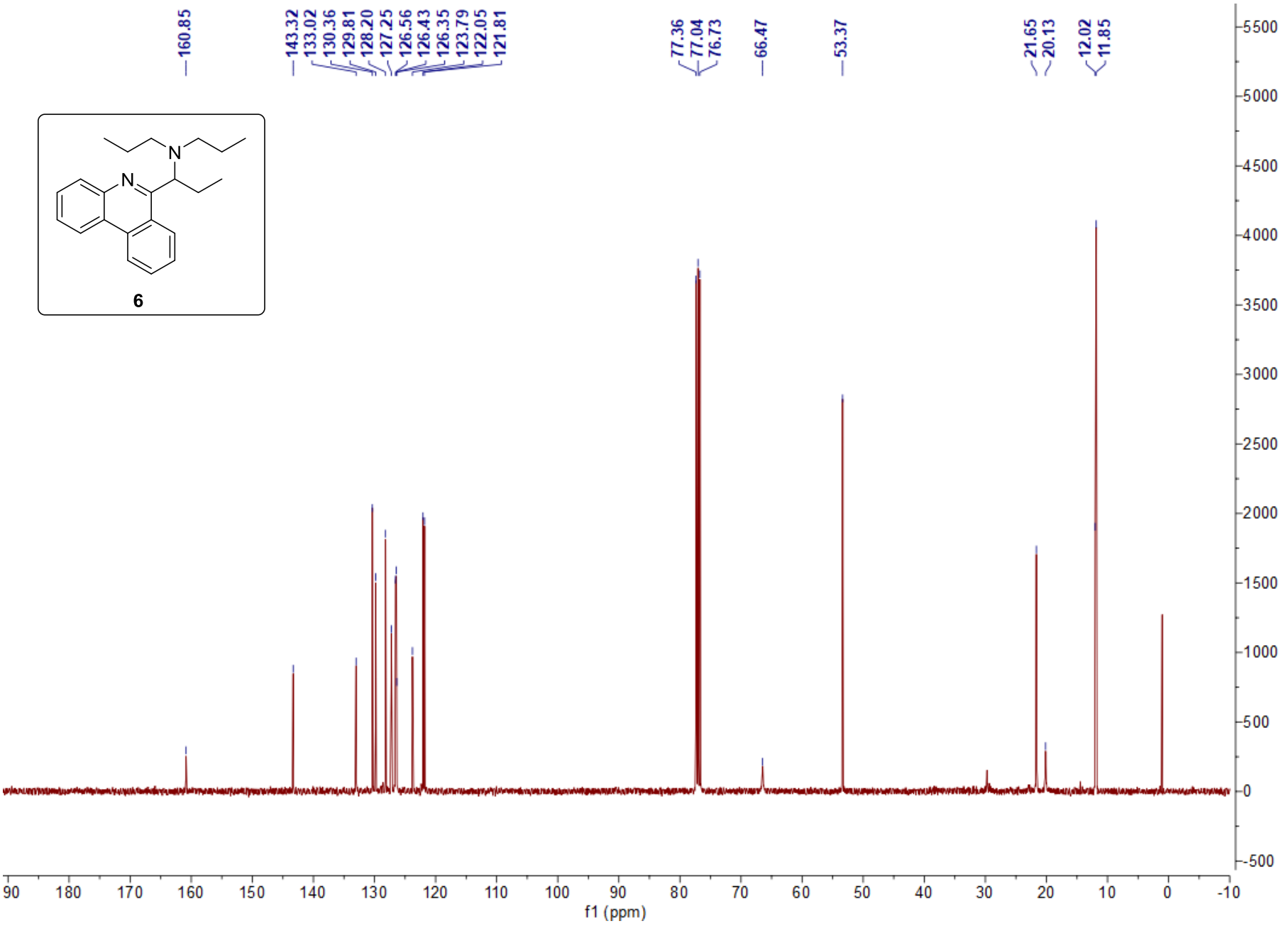
8.668
8.647
8.600
8.579
8.229
8.225
8.208
8.205
7.844
7.841
7.827
7.823
7.820
7.806
7.803
7.764
7.761
7.747
7.744
7.740
7.727
7.723
7.704
7.687
7.669
7.664
7.661
7.658
7.644
7.640
7.284
4.582
4.573
4.557
4.547
2.707
2.690
2.674
2.657
2.642
2.527
2.520
2.512
2.502
2.494
2.487
2.469
2.067
1.514
1.500
1.484
1.463
1.444
1.425
1.406
1.390
0.887
0.868
0.850
0.754
0.736
0.717
N
N
6
0.93
1.00
1.00
0.96
0.98
1.03
1.99
0.95
3.96
1.07
1.13
4.22
3.12
5.75
f1 (ppm)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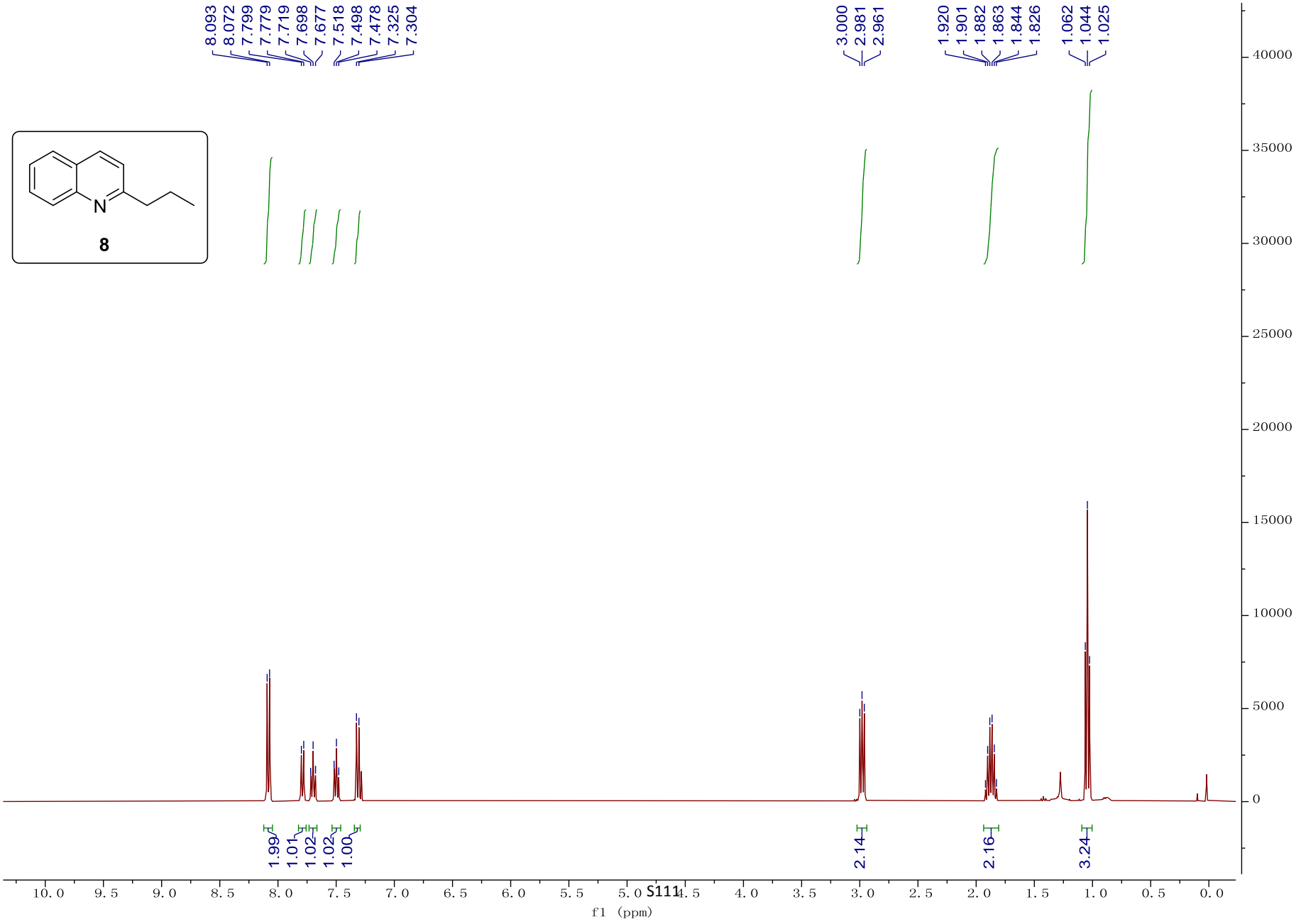
128.20
127.25
126.56
126.43
126.35
123.79
122.05
121.81
77.36
77.04
76.73
66.47
53.37
21.65
20.13
12.02
11.85
N
N
6
f1 (ppm)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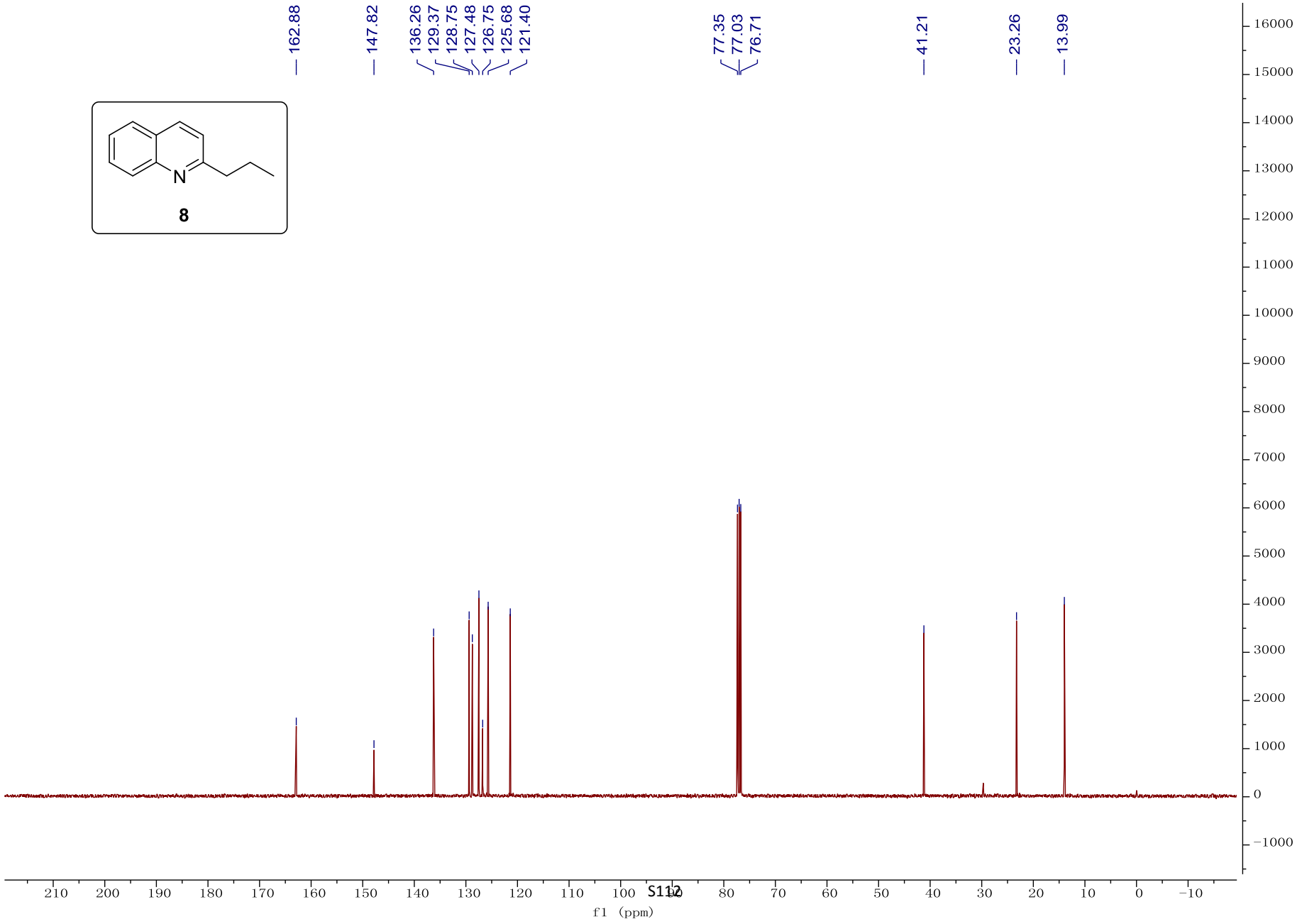
7.799
7.779
7.719
7.698
7.677
7.518
7.498
7.478
7.325
7.304
3.000
2.981
2.961
1.920
1.901
1.882
1.863
1.844
1.826
1.062
1.044
1.025
8
1.99
1.01
1.02
1.02
1.00
2.14
2.16
3.24
f1 (ppm)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136.26
129.37
128.75
127.48
126.75
125.68
121.40
77.35
77.03
76.71
41.21
23.26
13.99
N
8
f1 (ppm)