Electronic Supplementary Information

Demethylenative Cyclization of 1,7-Enynes Using α-Amino Radical as a Traceless Initiator Enabled by Cu(I)-Photosensitizers

Qinfang Jiang,[a] Hanyang Bao,[a] Yun Peng, Yan Zhou,[a] Lang Chen,[a] and Yunkui Liu*[a,b]

[a]State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, P. R. China.
[b]Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education,. Hangzhou Normal University, Hangzhou 311121, China.

E-mail: ykuiliu@zjut.edu.cn.

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1. General Information

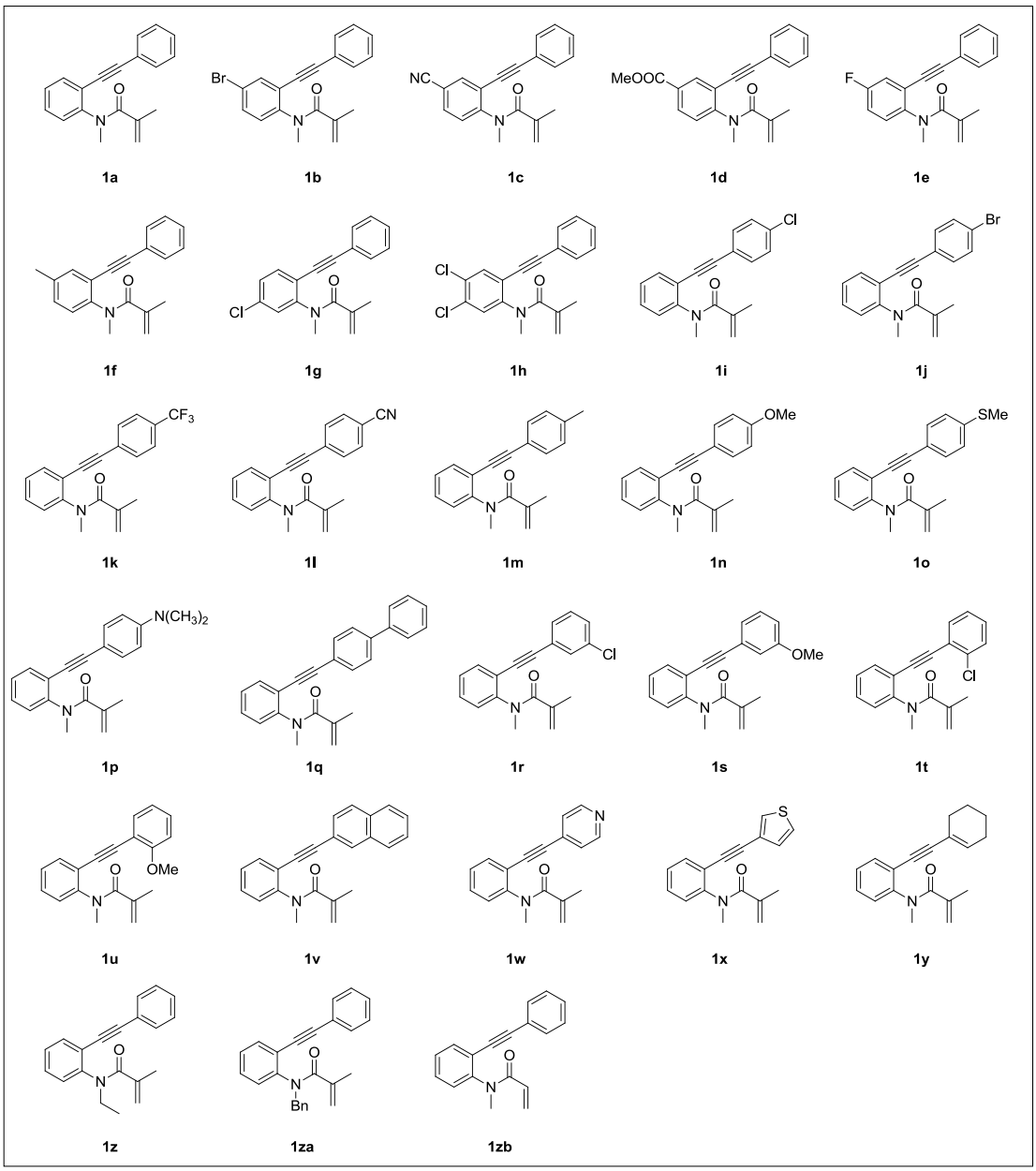
Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received.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

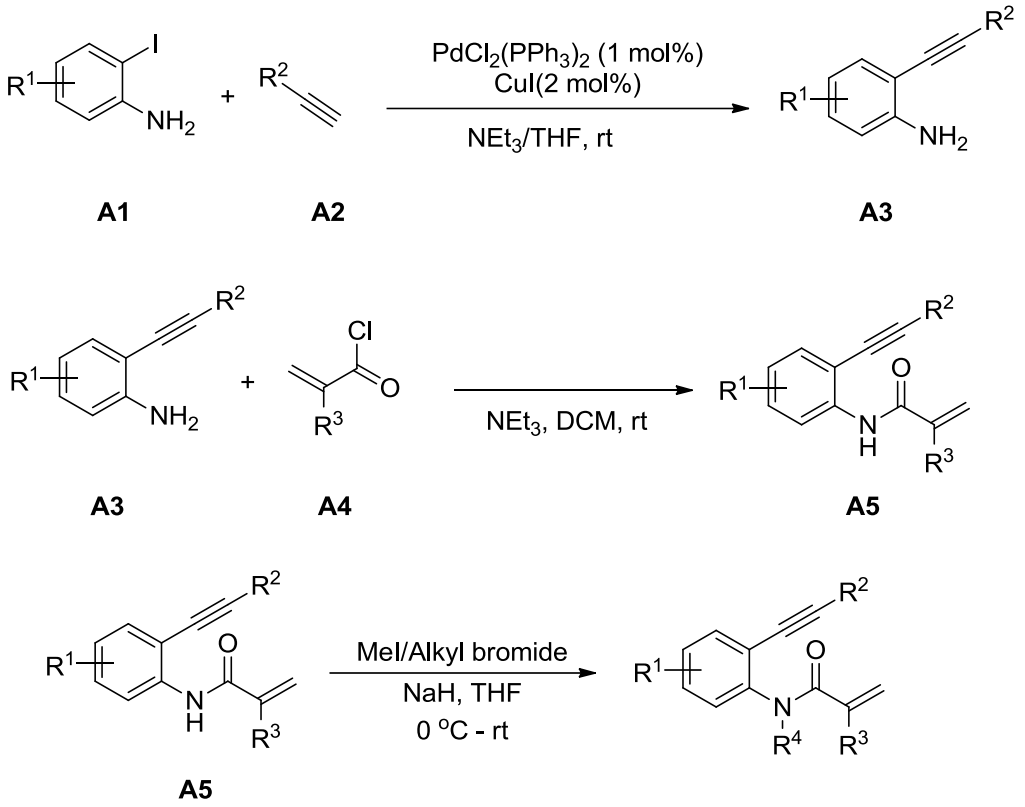
Melting points are uncorrected. ^{1}H NMR spectra were recorded on a spectrometer at 25 ^{o}C in $CDCl_3$ at 500 MHz or 400 MHz, with TMS as internal standard. ^{13}C NMR spectra were recorded on a spectrometer at 25 ^{o}C in $CDCl_3$ at 125 MHz or 100MHz. Chemical shifts (δ) are expressed in ppm and 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 (HRMS) were obtained on a Bruker micro TOF-Q II instrument with APCI source or Agilent 6200 series TOF/6500 series Q-TOF instrument with ESI source.

2. Preparation of Substrates and Catalyst

2.1 General procedure for the preparation of 1,7-enynes 1

All 1,7-enynes **1** are prepared according to the reported procedures.[1-4]





General procedure for the synthesis of **A3**: To the suspension of $Pd(PPh_3)_2Cl_2$ (0.100 mmol, 1 mol%) and CuI (0.200 mmol, 2 mol%) in a mixture of THF (20 mL) and Et_3N (20 mL), was added **A1** (10.0 mmol) and **A2** (12.0 mmol). The mixture was allowed to react for 4 h at room temperature. Then the crude mixture was filtered through a shot pad of celite and washed with EtOAc (10 mL) thrice, and the combined organic fraction was concentrated under reduced pressure. The crude product could be used without further purification.

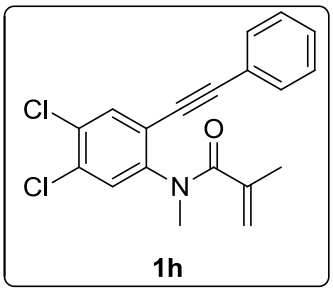
General procedure for synthesis of **A5**: To a stirred solution of **A3** (1.0 mmol) in CH_2Cl_2 (5 mL) was added **A4** (1.5 mmol) and Et_3N (2.0 mmol). The resulted mixture was stirred at room temperature for 12 h. Then the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The resulting crude mixture was purified by flash chromatography using ethyl acetate and petroleum as eluent.

General procedure for the synthesis of 1,7-enynes: To a solution of NaH (2.0 mmol) in THF (5 mL) at 0 ℃ was added a solution of **A5** (1.0 mmol) in THF dropwise and

the reaction mixture was stirred for 30 min. Afterwards iodomethane or MeI/alkyl bromide (1.5 mmol) was added and the reaction mixture was stirred at room temperature followed by TLC. The reaction was quenched by water and the reaction mixture was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel using ethyl acetate and petroleum as eluent.

1a-**1g**, **1i**-**1n**, **1r**, **1s**, **1x** and **1z**-**1zb** are known compounds.[1-4] The analytical data of unknown compounds **1h**, **1o**-**1q**, **1t**, **1u**-**1w** and **1y** are listed as follows:

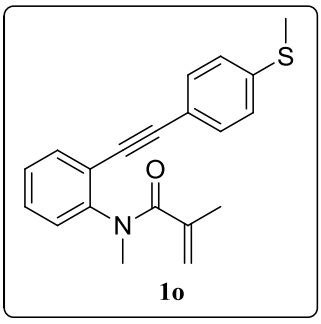
***N*-(4, 5-dichloro-2-(phenylethynyl)phenyl)-*N*-methylmethacrylamide (1h)**



1h

White soild. m.p. 117-119 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.54-7.51 (m, 2H), 7.40-7.37 (m, 3H), 7.31 (s, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 3.36 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.0, 145.6, 140.0, 133.8, 132.9, 131.74, 131.66, 130.0, 129.3, 128.6, 122.3, 121.9, 119.8, 96.5, 83.7, 37.0, 20.1. **HRMS(ESI)** for $C_{19}H_{16}Cl_2NO^+$ ($[M+H]^+$): calcd: 344.0603, found: 344.0605.

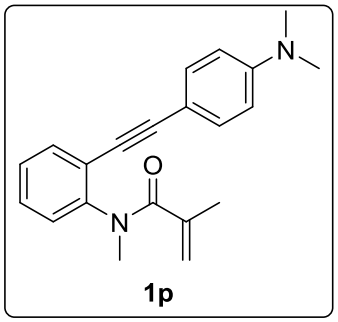
***N*-methyl-*N*-(2-((4-(methylthio)phenyl)ethynyl)phenyl)methacrylamide (1o)**



1o

White soild. m.p. 96-98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.36-7.27 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 3H), 5.02 (s, 2H), 3.38 (s, 3H), 2.51 (d, *J* = 0.9 Hz, 3H), 1.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.4, 146.3, 140.4, 140.2, 132.8, 131.9, 129.2, 128.2, 127.5, 125.8, 122.3, 119.2, 118.7, 94.7, 85.9, 37.0, 20.2, 15.3. **HRMS(ESI)** for $C_{20}H_{20}NOS^+$ ($[M+H]^+$): calcd: 322.1260, found: 322.1263.

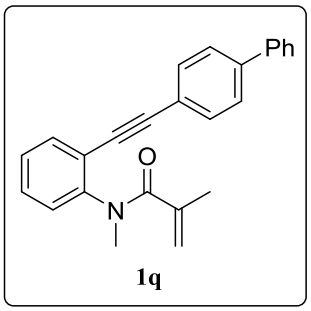
***N*-(2-((4-(dimethylamino)phenyl)ethynyl)phenyl)-*N*-methylmethacrylamide (1p)**



1p

White soild. m.p. 127-129 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.54-7.49 (m, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.28-7.25 (m, 2H), 7.19-7.13 (m, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.05 (s, 1H), 5.00 (s, 1H), 3.38 (s, 3H), 3.00 (s, 6H), 1.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.4, 150.4, 145.8, 140.6, 132.9, 132.4, 128.2, 128.1, 127.4, 123.2, 118.7, 111.8, 109.3, 96.5, 84.0, 40.2, 36.8, 20.2. **HRMS(ESI)** for $C_{21}H_{22}N_2ONa^+$ ($[M+Na]^+$) ($[M+Na]^+$): calcd: 341.1624, found: 341.1623.

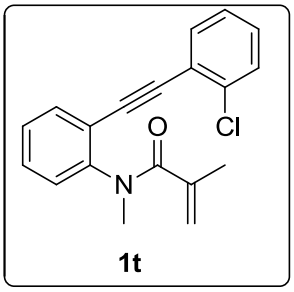
***N*-(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)-*N*-methylmethacrylamide (1q)**



1q

White soild. m.p. 121-123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66-7.57 (m, 7H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.42-7.28 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.07 (s, 1H), 5.04 (s, 1H), 3.42 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.4, 146.4, 141.5, 140.4, 140.2, 132.9, 132.1, 129.3, 128.9, 128.3, 127.8, 127.6, 127.2, 127.1, 122.3, 121.5, 119.2, 94.7, 86.5, 37.0, 20.2. **HRMS(ESI)** for $C_{25}H_{22}NO^+$ ($[M+H]^+$): calcd: 352.1696, found: 352.1693.

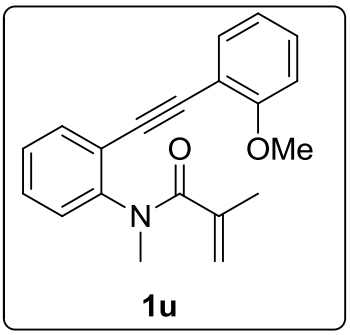
***N*-(2-((2-chlorophenyl)ethynyl)phenyl)-*N*-methylmethacrylamide (1t)**



1t

White soild. m.p. 77-79 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (dd, J_1 = 7.5, J_2 = 1.1 Hz, 1H), 7.57 (dd, J_1 = 7.3, J_2 = 1.9 Hz, 1H), 7.44-7.41 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.25 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 5.08 (s, 1H), 5.00 (s, 1H), 3.39 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.1, 146.4, 140.5, 135.9, 133.4, 133.3, 129.8, 129.7, 129.4, 128.3, 127.5, 126.6, 122.6, 121.9, 118.8, 91.4, 90.7, 36.9, 20.2. **HRMS(ESI)** for $C_{19}H_{17}ClNO^+$ ($[M+H]^+$): calcd: 310.0993, found: 310.0993.

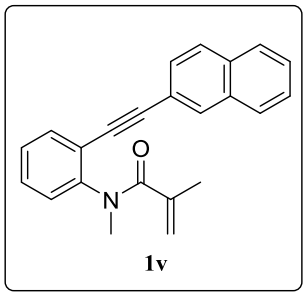
***N*-(2-((2-methoxyphenyl)ethynyl)phenyl)-*N*-methylmethacrylamide (1u)**



1u

White soild. m.p. 85-87 °C. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.59 (dd, J_1 = 7.3, J_2 = 1.7 Hz, 1H), 7.49 (dd, J_1 = 7.5, J_2 = 1.6 Hz, 1H), 7.34-7.28 (m, 3H), 7.15 (d, J = 7.1 Hz, 1H), 6.94 (dd, J_1 = 10.9, J_2 = 4.0 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 3.91 (s, 3H), 3.40 (s, 3H), 1.84 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 172.2, 160.3, 146.2, 140.7, 133.3, 132.9, 130.3, 129.0, 128.2, 127.4, 122.7, 120.5, 118.4, 112.0, 110.7, 91.6, 89.7, 55.7, 36.6, 20.2. **HRMS(ESI)** for $C_{20}H_{19}NO_2Na^+$ ($[M+Na]^+$): calcd: 328.1308, found: 328.1308.

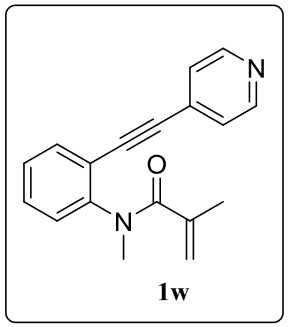
***N*-methyl-*N*-(2-(naphthalen-2-ylethynyl)phenyl)methacrylamide (1v)**



1v

White soild. m.p. 102-104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.89-7.81 (m, 3H), 7.64-7.57 (m, 2H), 7.55-7.49 (m, 2H), 7.39-7.29 (m, 2H), 7.22 (d, J = 7.5 Hz, 1H), 5.08 (s, 1H), 5.04 (s, 1H), 3.44 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.4, 146.4, 140.4, 133.0, 133.0, 131.7, 129.3, 128.3, 128.2, 128.0, 127.8, 127.6, 127.0, 126.7, 122.3, 119.9, 119.2, 95.2, 86.1, 37.1, 20.2. **HRMS(ESI)** for $C_{23}H_{20}NO_2^+$ ($[M+H]^+$): calcd: 326.1539, found: 326.1539.

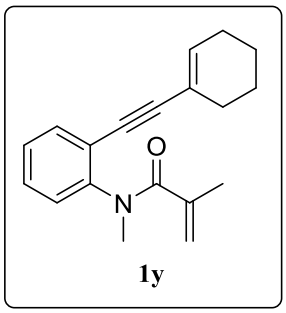
***N*-methyl-*N*-(2-(pyridin-4-ylethynyl)phenyl)methacrylamide (1w)**



1w

Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 1.2 Hz, 1H), 8.48 (dd, J_1 = 4.8 Hz, J_2 = 1.4 Hz, 1H), 7.76-7.74 (m, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.32-7.29 (m, 1H), 7.26-7.20 (m, 2H), 7.15 (d, J = 7.8 Hz, 1H), 4.94 (s, 2H), 3.29 (s, 3H), 1.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.2, 151.9, 149.0, 146.4, 140.1, 138.6, 133.0, 129.9, 128.2, 127.6, 123.2, 121.4, 119.7, 119.4, 91.0, 89.0, 37.0, 20.1. **HRMS(ESI)** for $C_{18}H_{17}N_2O^+$ ($[M+H]^+$): calcd: 277.1335, found: 277.1336.

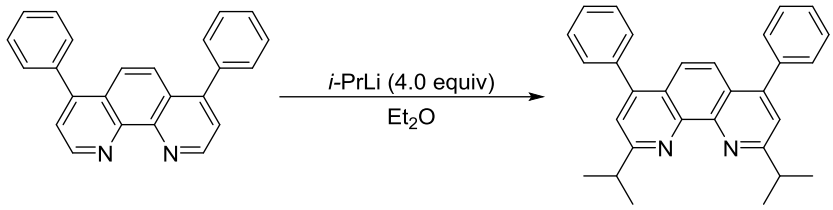
***N*-(2-(cyclohex-1-en-1-ylethynyl)phenyl)-*N*-methylmethacrylamide (1y)**



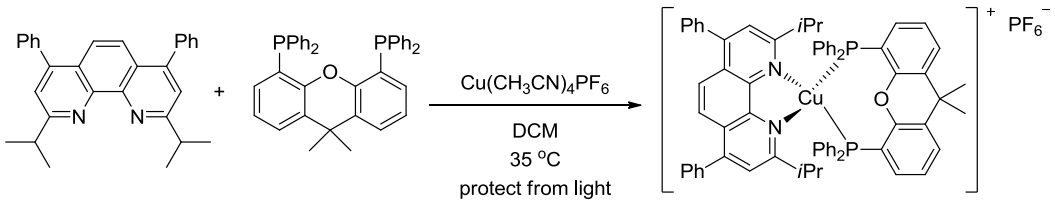
1y

White soild. m.p. 56-59 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.0 Hz, 1H), 7.45-7.35 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.38 (s, 1H), 5.14 (s, 1H), 5.12 (s, 1H), 3.46 (s, 3H), 2.39-2.26 (m, 4H), 1.97 (s, 3H), 1.87-1.72 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.2, 145.9, 140.4, 136.4, 132.7, 128.6, 128.1, 127.4, 122.7, 120.4, 118.7, 96.8, 83.1, 36.7, 28.9, 25.8, 22.2, 21.4, 20.2. **HRMS(ESI)** for $C_{19}H_{22}NO^+$ ($[M+H]^+$): calcd: 280.1696, found: 280.1695.

2.2 Synthesis of photosensitizer (*PS5*)



2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline was synthesized according to the reported procedure:[5] A mixture of 4,7-diphenyl-1,10-phenanthroline (0.1992 g, 0.6 mmol) and 5 mL of dry ether was stirred in a sealed tube under an argon atmosphere, and isopropyl lithium (2.4 mL, 2.4 mmol) was added at 0 °C. The resulting suspension was stirred at 0 °C for 30 min then stirred at room temperature for 12 h. The reaction was quenched with water (10 mL), and the mixture was extracted with EtOAc (4×10 mL), then dried over $MgSO_4$. Filtration, concentration, and purification of the orange residue by flash column chromatography (1:3 EA/PE) gave white solid (yield: 42 %).



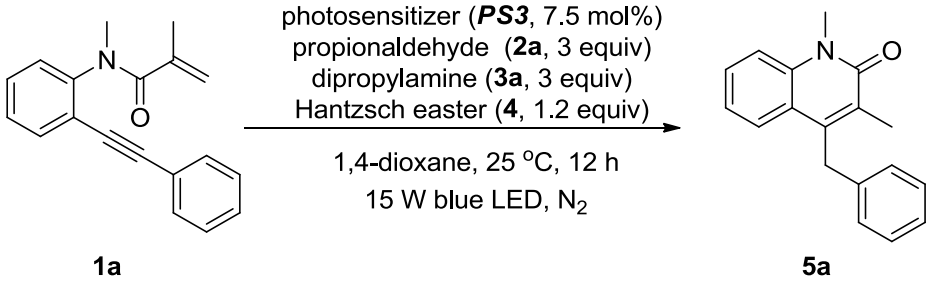
[Cu(2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline)(Xantphos)]PF_6^- (***PS5***) was prepared according to the reported procedure:[6] In an oven-dried Schlenk tube, $[Cu(MeCN)_4]PF_6^-$ (373.0 mg, 1.0 mmol) and Xantphos (579.0 mg, 1.0 mmol) were dissolved in dry DCM (20 mL) at room temperature. The resulting solution was stirred

at reflux overnight. The reaction mixture was then allowed to cool to room temperature and the 2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline (416.0 mg, 1.0 mmol) was added at room temperature dissolved in a minimal amount of DCM. The resulting mixture was then heated to reflux in an oil bath for another 3 hours until no further color change was observed (at this point red to yellow solution was obtained). The reaction mixture was then allowed to cool to room temperature and *n*-hexane was added to precipitate the product. It was filtered and washed with *n*-hexane. The resulting solid was further purified by recrystallization in a DCM/*n*-hexane mixture at 4 °C.

3. Typical Procedure for the Synthesis of 2-quinolones

3.1 Optimization of reaction conditions

Table *S1*. Control experiments[a]

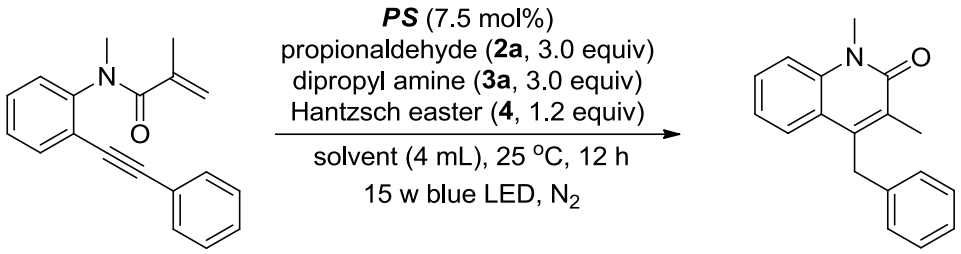


1a **5a**

Entry	Varied from standard conditions	Yield (%)[b]
1	standard conditions shown in footnote a.	41
2	without photosensitizer	0
3	without aldehyde	0
4	without amine	0
5	without Hantzsch ester	trace
6	In the dark	0
7	under air or oxygen conditions	trace

[a]Reaction condition： **1a** (0.2 mmol), ***PS3*** (7.5 mol%), propionaldehyde (0.6 mmol, 3.0 equiv. based on **1a**), dipropyl amine (0.6 mmol, 3.0 equiv. based on **1a**), Hantzsch ester (0.24 mmol, 1.2 equiv. based on **1a**), 1,4-dioxance (4 mL), irradiated with 15 W blue LED at room temperature under nitrogen atmosphere for 12 h. [b]Isolated yields.

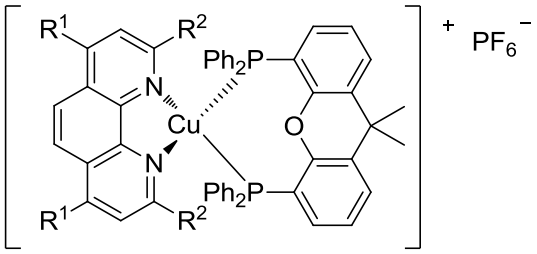
Table *S2*. Screening of the different photosensitizers[a]



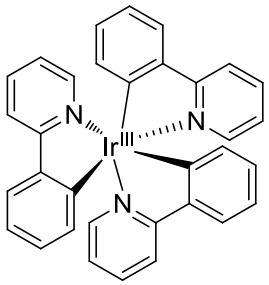
1a **5a**

Entry	Photosensitizer (mol%)	Yield (%)[b]
1	***PS1*** (7.5)	trace
2	***PS2*** (7.5)	trace
3	***PS3*** (7.5)	41
4	***PS4*** (7.5)	trace
5	***PS5* (7.5)**	**70**
6	***PS6*** (7.5)	trace
7	4CzIPN (7.5)	55
8	***PS5*** (5)	60
9[c]	***PS5*** (7.5)	58

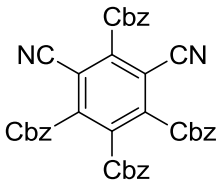
[a]Reaction condition：**1a** (0.2 mmol), propionaldehyde **2a** (0.6 mmol, 3.0 equiv.), dipropyl amine **3a** (0.6 mmol, 3.0 equiv.), photosensitizer (7.5 mol%), Hantzsch ester **4** (0.24 mmol, 1.2 equiv.), 1,4-dioxance (4 mL), irradiated with 15 W blue LED at rt under nitrogen atmosphere for 12 h. [b]Yields of isolated product. [c]The reaction time is 8 h.



PS1: R^1 = H, R^2 = H
PS2: R^1 = Ph, R^2 = H
PS3: R^1 = Ph, R^2 = Me
PS4: R^1 = H, R^2 = *i*-Pr
PS5: R^1 = Ph, R^2 = *i*-Pr

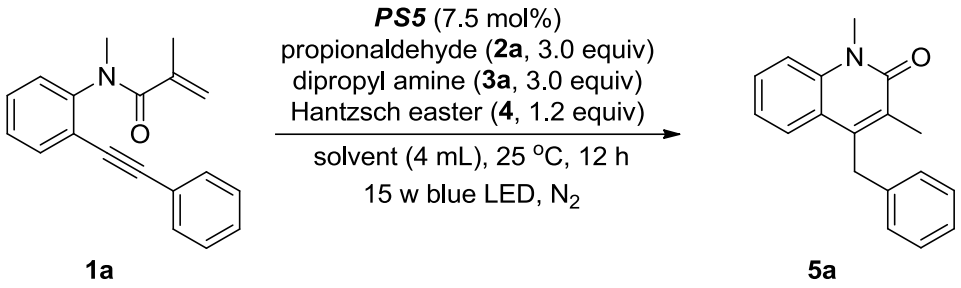


PS6



4CzIPN

Table *S3.* Screening of the solvents[a]

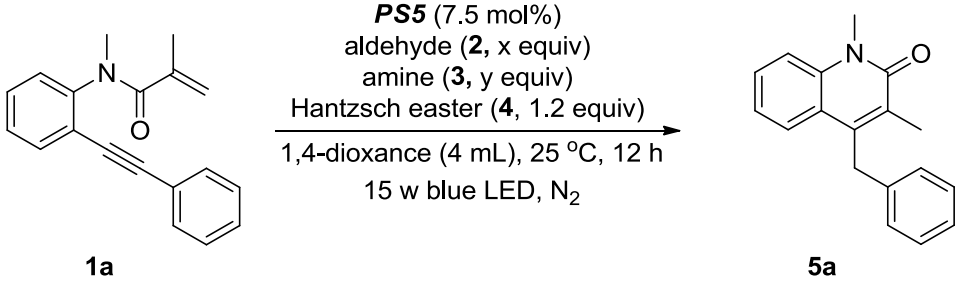


1a **5a**

Entry	Solvent	Yield (%)[b]
1	**1,4-dioxance**	**70**
2	THF	57
3	Cyclopentyl methyl ether	54
4	EA	52
5	MeCN	43
6	DCM	0
7	DCE	trace
8	DMSO	trace
9	DMF	trace

[a]Reaction condition： **1a** (0.2 mmol), ***PS5*** (7.5 mol%), propionaldehyde **2a** (0.6 mmol, 3.0 equiv.), dipropyl amine **3a** (0.6 mmol, 3.0 equiv.), Hantzsch ester **4** (0.24 mmol, 1.2 equiv.), solvent (4 mL), irradiated with 15 W blue LED at rt under nitrogen atmosphere for 12 h. [b]Yields of isolated product.

Table *S4.* Screening of aldehyde, amine and the amount of aldehyde and amine[a]



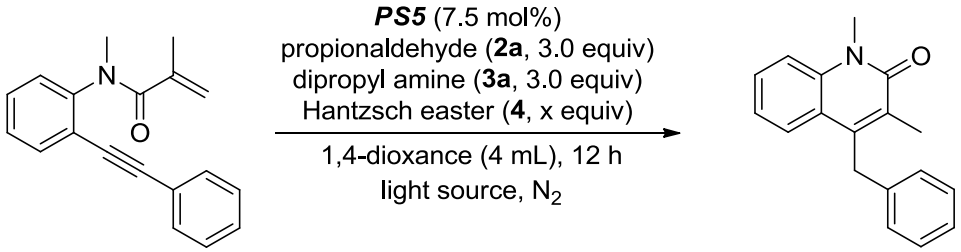
1a **5a**

Entry	Aldehyde (x equiv)	Amine (y equiv)	Yield
1	**propionaldehyde 2a (3)**	**dipropyl amine 3a (3)**	**70**
2	butyraldehyde **2b** (3)	dipropyl amine **3a** (3)	45
3	phenylacetaldehyde **2c** (3)	dipropyl amine **3a** (3)	23
4	propionaldehyde **2a** (3)	diethyl amine **3b** (3)	59

5	Propionaldehyde **2a** (3)	piperidine **3c** (3)	64
6	propionaldehyde **2a** (3)	hexamethyleneimine **3d** (3)	55
7	propionaldehyde **2a** (3)	dimethyl amine **3e** (2 M in THF)	46
8	Propionaldehyde **2a** (2)	dipropyl amine **3a** (2)	47
9	propionaldehyde **2a** (4)	dipropyl amine **3a** (4)	66

[a]Reaction condition：**1a** (0.2 mmol), ***PS5*** (7.5 mol%), aldehyde **2** (x equiv.), amine **3** (y equiv.), Hantzsch ester **4** (0.24 mmol, 1.2 equiv.), 1,4-dioxance (4 mL), irradiated with 15 W LED at room temperature under nitrogen atmosphere for 12 h. [b]Yields of isolated product.

Table *S5.* Screening of the amount of Hantzsch ester, light source and reaction temperature[a]



1a **5a**

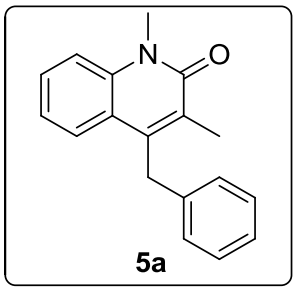
Entry	Hantzsch ester (x equiv)	light source	reaction temperature (°C)	Yield
1	1.5	15 W blue LED	25	68
2	**1.2**	**15 W blue LED**	**25**	**70**
3	1.0	15 W blue LED	25	63
4	0.5	15 W blue LED	25	45
5	1.2	30 W blue LED	25	56
6	1.2	15 W blue LED	15	45
7	1.2	15 W blue LED	35	63
8	1.2	15 W blue LED	45	63

[a]Reaction condition：**3-1a** (0.2 mmol), ***PS5*** (7.5 mol%), propionaldehyde (0.6 mmol, 3.0 equiv.), dipropyl amine (0.6 mmol, 3.0 equiv.), Hantzsch ester (x equiv.), 1,4-dioxance (4 mL), irradiated with light source under nitrogen atmosphere for 12 h. [b]Yields of isolated product.

3.2 General procedure for the synthesis of 5 and characterization of products 5

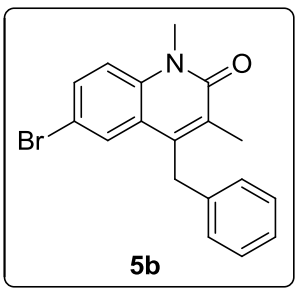
To a 25 mL Schlenk tube were added **1** (0.2 mmol), Hantzsch ester **4** (0.24 mmol, 60.8 mg) and ***PS5*** (0.015 mmol, 18.0 mg), the tube was evacuated and refilled with N_2 for three times. A solution of propionaldehyde **2a** (0.6 mmol), dipropylamine **3a** (0.6 mmol) and 1,4-dioxane (4 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction mixture 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 product **5**.

4-benzyl-1,3-dimethylquinolin-2(1*H*)-one (5a)



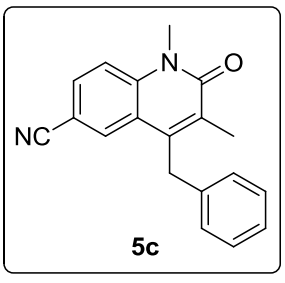
White soild. Yield: 70%. m.p. 135.5-137.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (dd, J_1 = 8.1 Hz, J_2 = 0.8 Hz, 1H), 7.51-7.47 (m, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.16 (dd, J_1 = 10.6 Hz, J_2 = 4.3 Hz, 3H), 4.33 (s, 2H), 3.80 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.5, 142.5, 138.7, 138.0, 129.2, 128.8, 128.7, 127.8, 126.4, 125.5, 122.0, 120.9, 114.2, 34.6, 30.0, 14.0. **HRMS(ESI)** for $C_{18}H_{18}NO^+$ ($[M+H]^+$): calcd: 264.1383, found: 264.1387.

4-benzyl-6-bromo-1,3-dimethylquinolin-2(1*H*)-one (5b)



White soild. Yield: 47%. m.p. 159.0-161.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (d, J = 2.2 Hz, 1H), 7.57 (dd, J_1 = 8.9 Hz, J_2 = 2.2 Hz, 1H), 7.31-7.28 (m, 2H), 7.24 (dd, J_1 = 16.7 Hz, J_2 = 8.2 Hz, 2H), 7.13 (d, J = 7.2 Hz, 2H), 4.28 (s, 2H), 3.77 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.2, 141.5, 137.7, 137.4, 132.0, 130.2, 128.9, 127.9, 127.8, 126.7, 122.6, 115.9, 115.1, 34.6, 30.2, 14.2. **HRMS(ESI)** for $C_{18}H_{17}BrNO^+$ ($[M+H]^+$): calcd: 342.0488, found: 342.0493.

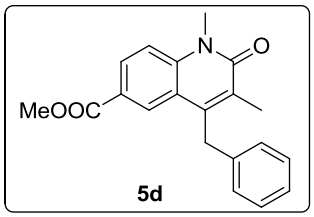
4-benzyl-1,3-dimethyl-2-oxo-1,2-dihydroquinoline-6-carbonitrile (5c)



White soild. Yield: 57%. m.p. 188.8-190.8 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 (d, J = 1.7 Hz, 1H), 7.71 (dd, J_1 = 8.8 Hz, J_2 = 1.7 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.30 (dd, J_1 = 14.1 Hz, J_2 = 6.4 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.3 Hz, 2H), 4.31 (s, 2H), 3.81 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.3, 141.7, 141.4, 136.8, 131.9,

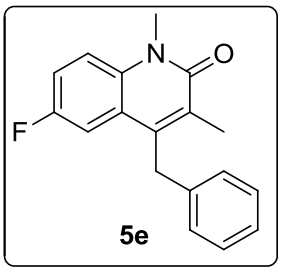
131.1, 130.3, 129.1, 127.7, 126.9, 121.1, 118.8, 115.1, 105.5, 34.6, 30.3, 14.2. **HRMS(ESI)** for $C_{19}H_{17}N_2O^+$ ([M+H]$^+$): calcd: 289.1335, found: 289.1331.

methyl 4-benzyl-1,3-dimethyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (5d)



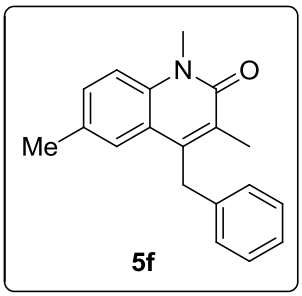
White soild. Yield: 57%. m.p. 145.7-147.7 °C. **^{1}H NMR** (500 MHz, CDCl3): δ 8.45 (d, J = 1.8 Hz, 1H), 8.12 (dd, J_1 = 8.8 Hz, J_2 = 1.8 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.23-7.16 (m, 3H), 4.36 (s, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.5, 162.6, 143.0, 141.8, 137.7, 130.0, 129.6, 128.8, 127.9, 127.69, 126.6, 123.7, 120.5, 114.2, 52.2, 34.6, 30.3, 14.2. **HRMS(ESI)** for $C_{20}H_{20}NO_3^+$ ([M+H]$^+$): calcd: 322.1438, found: 322.1443.

4-benzyl-6-fluoro-1,3-dimethylquinolin-2(1*H*)-one (5e)



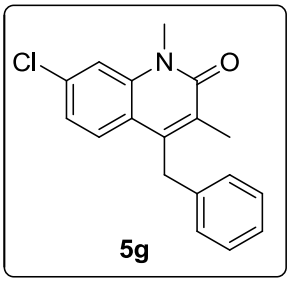
White soild. Yield: 53%. m.p. 124.4-126.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 - 7.32 (m, 2H), 7.29 (dd, J_1 = 10.2 Hz, J_2 = 4.6 Hz, 2H), 7.24-7.19 (m, 2H), 7.14 (d, J = 7.2 Hz, 2H), 4.27 (s, 2H), 3.80 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.2, 158.0 (d, J = 238.8 Hz), 141.7 (d, J = 3.75 Hz), 137.4, 135.3, 130.3, 128.9, 127.8, 126.6, 122.0 (d, J = 7.5 Hz), 116.8 (d, J = 23.75 Hz), 115.7 (d, J = 7.5 Hz), 111.0 (d, J = 11 Hz), 34.8, 30.3, 14.3. **HRMS(ESI)** for $C_{18}H_{17}FNO^+$ ([M+H]$^+$): calcd: 282.1289, found: 282.1295.

4-benzyl-1,3,6-trimethylquinolin-2(1*H*)-one (5f)



White soild. Yield: 40%. m.p. 95.7-97.7 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.33-7.26 (m, 4H), 7.21 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 4.31 (s, 2H), 3.79 (s, 3H), 3.35 (s, 3H), 3.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 142.3, 138.1, 136.8, 131.4, 130.5, 128.8, 128.7, 127.9, 126.4, 125.4, 120.9, 114.2, 34.6, 30.0, 21.0, 14.1. **HRMS(ESI)** for $C_{19}H_{20}NO^+$ ([M+H]$^+$): calcd: 278.1539, found: 278.1548.

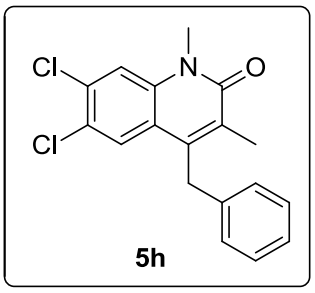
4-benzyl-7-chloro-1,3-dimethylquinolin-2(1*H*)-one (5g)



White soild. Yield: 52%. m.p. 135.0-137.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 1.9 Hz, 1H), 7.29-7.26 (m, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.14-7.09 (m, 3H), 4.29 (s, 2H), 3.77 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 142.1, 139.6, 137.6, 135.2, 129.0,

128.8, 127.8, 126.8, 126.6, 122.3, 119.4, 114.2, 34.7, 30.1, 14.0. **HRMS(ESI)** for $C_{18}H_{17}ClNO^+$ ([M+H]$^+$): calcd: 298.0993, found: 298.0995.

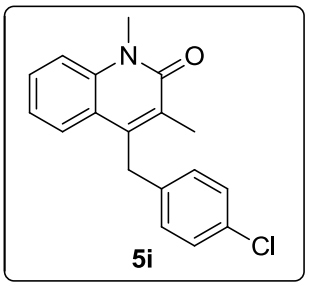
4-benzyl-6,7-dichloro-1,3-dimethylquinolin-2(1*H*)-one (5h)



5h

White soild. Yield: 58%. m.p. 204.0-206.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.46 (s, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 4.25 (s, 2H), 3.75 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.1, 141.2, 137.9, 137.1, 133.2, 130.4, 128.9, 127.7, 126.8, 126.6, 126.0, 120.7, 115.9, 34.7, 30.3, 14.2. **HRMS(ESI)** for $C_{18}H_{16}Cl_2NO^+$ ([M+H]$^+$): calcd: 332.0603, found: 332.0608.

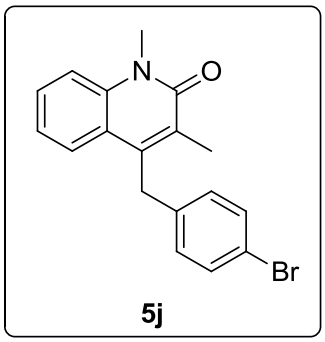
4-(4-chlorobenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5i)



5i

White soild. Yield: 58%. m.p. 135.0-137.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.53-7.48 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.26-7.21 (m, 2H), 7.19-7.14 (m, 1H), 7.07 (d, J = 8.4 Hz, 2H), 4.29 (s, 2H), 3.81 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.5, 142.0, 138.8, 136.5, 132.2, 129.4, 129.2, 129.0, 128.9, 125.3, 122.1, 120.7, 114.3, 34.0, 30.0, 14.0. **HRMS(ESI)** for $C_{18}H_{17}ClNO^+$ ([M+H]$^+$): calcd: 298.0993, found: 298.1003.

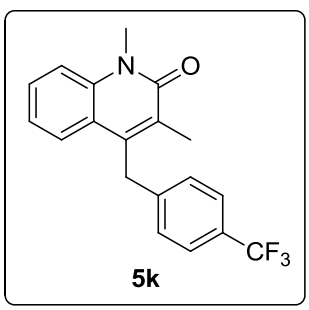
4-(4-bromobenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5j)



5j

White soild. Yield: 57%. m.p. 150.8-152.8 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.40-7.37 (m, 3H), 7.18-7.14 (m, 1H), 7.01 (d, J = 8.4 Hz, 2H), 4.27 (s, 2H), 3.80 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 141.9, 138.8, 137.0, 131.8, 129.6, 129.4, 129.0, 125.3, 122.1, 120.6, 120.3, 114.3, 34.1, 30.0, 14.0. **HRMS(ESI)** for $C_{18}H_{17}BrNO^+$ ([M+H]$^+$): calcd: 342.0488, found: 342.0495.

1,3-dimethyl-4-(4-(trifluoromethyl)benzyl)quinolin-2(1*H*)-one (5k)

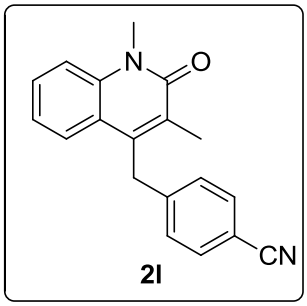


5k

White soild. Yield: 51%. m.p. 135.2-137.2 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.52 (dd, J_1 = 13.1 Hz, J_2 = 4.6 Hz, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 12.9 Hz, 2H), 7.21-7.14 (m, 1H), 4.38 (s, 2H), 3.82 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 142.2, 141.5, 138.8, 129.5, 129.2, 128.9 (q, J = 32.5

Hz), 128.2, 125.7 (q, J = 3.8 Hz), 125.2, 124.1 (q, J = 271.3 Hz),122.2, 120.6, 114.4, 34.5, 30.0, 14.1. **HRMS(ESI)** for $C_{19}H_{17}F_3NO^+$ ($[M+H]^+$): calcd: 332.1257, found: 332.1269.

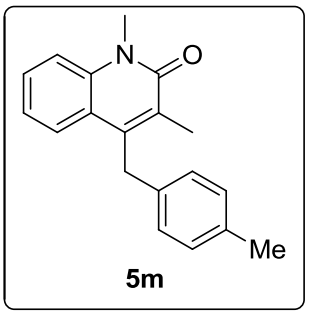
4-((1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)methyl)benzonitrile (5l)



2l

White soild. Yield: 36%. m.p. 179.1-181.1 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ7.59-7.50 (m, 4H), 7.41 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.19-7.14 (m, 1H), 4.38 (s, 2H), 3.81 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.3, 143.7, 140.9, 138.8, 132.6, 129.6, 129.4, 128.7, 125.0, 122.2, 120.4, 118.7, 114.5, 110.5, 34.7, 30.1, 14.1. **HRMS(ESI)** for $C_{19}H_{17}N_2O^+$ ($[M+H]^+$): calcd: 289.1335, found: 289.1346.

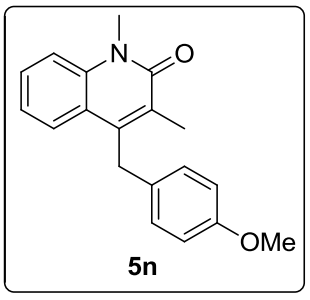
1-methyl-4-(4-methylbenzyl)quinolin-2(1*H*)-one (5m)



5m

White soild. Yield: 67%. m.p. 99.7-101.7 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.18-7.14 (m, 1H), 7.06 (dd, J_1 = 23.2 Hz, J_2 = 8.0 Hz, 4H), 4.29 (s, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 142.8, 138.7, 136.0, 134.9, 129.4, 129.2, 128.7, 127.7, 125.6, 122.0, 121.0, 114.2, 34.3, 30.0, 21.0, 14.0. **HRMS(ESI)** for $C_{19}H_{20}NO^+$ ($[M+H]^+$): calcd: 278.1539, found: 278.1543.

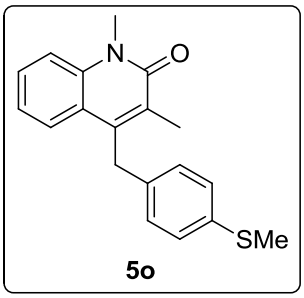
4-(4-methoxybenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5n)



5n

White soild. Yield: 71%. m.p. 126.4-128.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 7.51-7.47 (m, 1H), 7.40-7.37 (m, 1H), 7.19-7.13 (m, 1H), 7.05 (t, J = 5.8 Hz, 2H), 6.83-6.78 (m, 2H), 4.26 (s, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 158.2, 142.9, 138.7, 130.0, 129.2, 128.8, 128.6, 125.6, 122.0, 120.9, 114.2, 114.2, 55.2, 33.8, 30.0, 14.0. **HRMS(ESI)** for $C_{19}H_{20}NO_2^+$ ($[M+H]^+$): calcd: 294.1489, found: 294.1499.

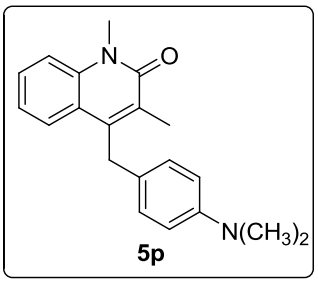
1,3-dimethyl-4-(4-(methylthio)benzyl)quinolin-2(1*H*)-one (5o)



5o

White soild. Yield: 52%. m.p. 136.4-138.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.17-7.13 (m, 3H), 7.06 (d, J = 8.4 Hz, 2H), 4.27 (s, 2H), 3.80 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.5, 142.4, 138.7, 136.3, 134.9, 129.3, 128.8, 128.4, 127.2, 125.5, 122.1, 120.8, 114.3, 34.1, 30.0, 16.0, 14.1. **HRMS(ESI)** for $C_{19}H_{20}NOS^+$ ([M+H]$^+$): calcd: 310.1260 , found: 310.1265.

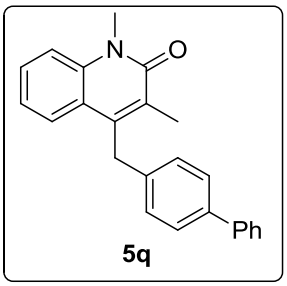
4-(4-(dimethylamino)benzyl)-1,3-dimethylquinolin-2(1*H*)-one (5p)



5p

White soild. Yield: 67%. m.p. 126.4-128.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.18-7.13 (m, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.68-6.63 (m, 2H), 4.23 (s, 2H), 3.80 (s, 3H), 2.90 (s, 6H), 2.35 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.7, 149.3, 143.3, 138.7, 129.1, 128.5, 128.4, 125.7, 122.0, 121.1, 114.1, 113.0, 40.7, 33.7, 30.0, 14.0. **HRMS(ESI)** for $C_{20}H_{23}N_2O^+$ ([M+H]$^+$): calcd: 307.1805, found: 307.1817.

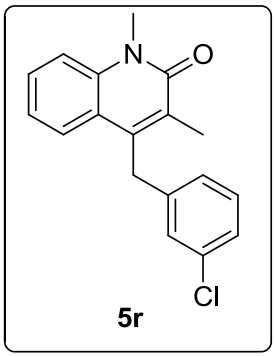
4-([1,1'-biphenyl]-4-ylmethyl)-1,3-dimethylquinolin-2(1*H*)-one (5q)



5q

White soild. Yield: 60%. m.p.178.8-180.8 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (dd, J_1 = 8.1 Hz, J_2 = 0.8 Hz, 1H), 7.58-7.54 (m, 2H), 7.53-7.50 (m, 3H), 7.44-7.40 (m, 3H), 7.35-7.32 (m, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.20-7.16 (m, 1H), 4.38 (s, 2H), 3.83 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 142.5, 140.7, 139.4, 138.8, 137.1, 129.3, 128.9, 128.8, 128.3, 127.5, 127.2, 127.0, 125.6, 122.1, 120.9, 114.3, 34.4, 30.0, 14.1. **HRMS(ESI)** for $C_{24}H_{22}NO^+$ ([M+H]$^+$): calcd: 340.1696, found: 340.1707.

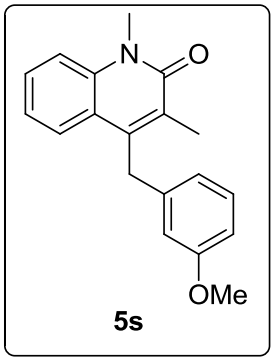
4-(3-chlorobenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5r)



5r

White soild. Yield: 55%. m.p.130.7-132.7 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.54-7.48 (m, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.23-7.15 (m, 3H), 7.12 (s, 1H), 7.05-7.00 (m, 1H), 4.30 (s, 2H), 3.82 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.5, 141.6, 140.1, 138.8, 134.7, 130.0, 129.4, 129.1, 127.9, 126.8, 126.1, 125.3, 122.2, 120.7, 114.4, 34.3, 30.1, 14.1. **HRMS(ESI)** for $C_{18}H_{17}ClNO^+$ ([M+H]$^+$): calcd: 298.0993, found: 298.1003.

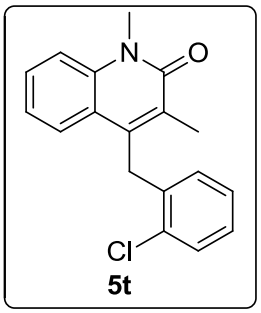
4-(3-methoxybenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5s)



5s

White soild. Yield: 61%. m.p. 124.1-126.1 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.51-7.46 (m, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.9 Hz, 1H), 7.18-7.13 (m, 1H), 6.75-6.74 (m, 2H), 6.68 (s, 1H), 4.30 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.5, 159.9, 142.4, 139.6, 138.7, 129.7, 129.2, 128.9, 125.5, 122.0, 120.9, 120.3, 114.2, 114.1, 111.2, 55.1, 34.7, 30.0, 14.1. **HRMS(ESI)** for $C_{19}H_{20}NO_2^+$ ($[M+H]^+$): calcd: 294.1489, found: 294.1498.

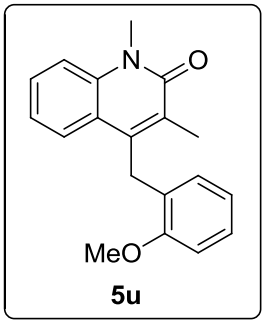
4-(2-chlorobenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5t)



5t

White soild. Yield: 56%. m.p. 135.4-137.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.53-7.45 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.19-7.13 (m, 2H), 7.04 (td, J_1 = 7.7 Hz, J_2 = 1.0 Hz, 1H), 6.72 (d, J = 7.5 Hz, 1H), 4.36 (s, 2H), 3.83 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 141.8, 138.7, 135.4, 133.9, 129.6, 129.5, 128.5, 127.8, 127.1, 125.3, 122.2, 120.7, 114.3, 32.2, 30.1, 13.9. **HRMS(ESI)** for $C_{18}H_{17}ClNO^+$ ($[M+H]^+$): calcd: 298.0993, found: 298.1004.

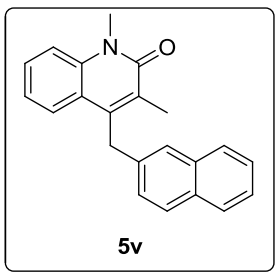
4-(2-methoxybenzyl)-1,3-dimethylquinolin-2(1*H*)-one (5u)



5u

White soild. Yield: 60%. m.p. 125.4-127.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.51-7.46 (m, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.22-7.18 (m, 1H), 7.15-7.11 (m, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.76-6.72 (m, 1H), 6.67 (d, J = 6.9 Hz, 1H), 4.26 (s, 2H), 3.98 (s, 3H), 3.82 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 156.9, 143.0, 138.6, 129.2, 129.1, 127.9, 127.4, 126.2, 125.6, 122.0, 121.1, 120.6, 114.1, 109.9, 55.4, 30.0, 28.4, 13.9. **HRMS(ESI)** for $C_{19}H_{20}NO_2^+$ ($[M+H]^+$): calcd: 294.1489, found: 294.1494.

1,3-dimethyl-4-(naphthalen-2-ylmethyl)quinolin-2(1*H*)-one (5v)

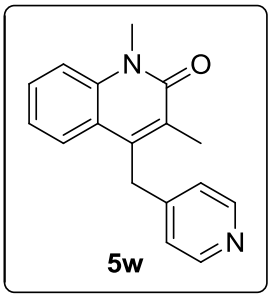


5v

White soild. Yield: 54%. m.p. 142.3-144.3 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.72-7.67 (m, 2H), 7.51-7.47 (m, 2H), 7.45-7.40 (m, 3H), 7.37 (dd, J_1 = 8.5 Hz, J_2 = 1.6 Hz, 1H), 7.15-7.11 (m, 1H), 4.49 (s, 2H), 3.84 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 142.4, 138.8, 135.5,

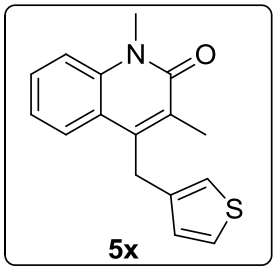
133.6, 132.2, 129.3, 129.0, 128.4, 127.6, 127.53, 126.52, 126.1, 126.0, 125.57, 125.55, 122.1, 120.9, 114.3, 34.9, 30.0, 14.1. **HRMS(ESI)** for $C_{22}H_{20}NO^+$ ([M+H]$^+$): calcd: 314.1539, found: 314.1548.

1,3-dimethyl-4-(pyridin-4-ylmethyl)quinolin-2(1*H*)-one (5w)



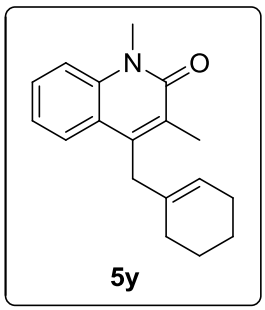
Yellow soild. Yield: 68%. m.p. 123.4-125.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.46 (d, J = 4.0 Hz, 1H), 7.60 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.53-7.48 (m, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.35 (d, J = 7.9 Hz, 1H), 7.20-7.14 (m, 2H), 4.32 (s, 2H), 3.80 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.3, 149.6, 147.9, 141.2, 138.8, 135.1, 133.7, 129.5, 129.1, 125.1, 123.7, 122.2, 120.4, 114.4, 32.0, 30.1, 14.1. **HRMS(ESI)** for $C_{17}H_{17}N_2O^+$ ([M+H]$^+$): calcd: 265.1335, found: 265.1342.

1,3-dimethyl-4-(thiophen-3-ylmethyl)quinolin-2(1*H*)-one (5x)



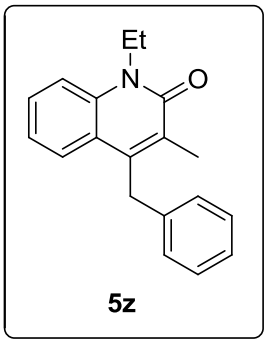
White soild. Yield: 61%. m.p. 130.9-132.9 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (dd, J_1 = 8.1 Hz, J_2 = 0.8 Hz, 1H), 7.53-7.48 (m, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.28-7.26 (m, 1H), 7.22-7.17 (m, 1H), 6.96 (dd, J_1 = 4.9 Hz, J_2 = 0.9 Hz, 1H), 6.83 (dd, J_1 = 2.6 Hz, J_2 = 1.1 Hz, 1H), 4.27 (s, 2H), 3.80 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 142.7, 138.8, 138.1, 129.3, 128.2, 127.7, 125.9, 125.4, 122.0, 121.2, 120.7, 114.3, 30.0, 30.0, 13.9. **HRMS(ESI)** for $C_{16}H_{16}NOS^+$ ([M+H]$^+$): calcd: 270.0947, found: 270.0954.

4-(cyclohex-1-en-1-ylmethyl)-1,3-dimethylquinolin-2(1*H*)-one (5y)



Yellow Liquid. Yield: 30%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.54-7.45 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.25-7.19 (m, 1H), 5.19-5.12 (m, 1H), 3.78 (s, 3H), 3.51 (s, 2H), 2.26 (s, 3H), 2.06 (s, 2H), 1.91-1.89 (m, J_1 = 6.0 Hz, J_2 = 2.3 Hz, 2H), 1.69-1.62 (m, 2H), 1.58-1.51 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.6, 142.7, 138.4, 133.6, 129.0, 128.49, 125.53, 122.6, 121.8, 121.3, 114.1, 36.8, 29.9, 29.3, 25.1, 23.0, 22.3, 13.8. **HRMS(ESI)** for $C_{18}H_{22}NO^+$ ([M+H]$^+$): calcd: 268.1696, found: 268.1709.

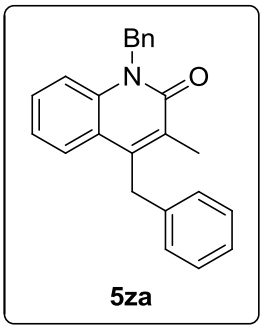
4-benzyl-1-ethyl-3-methylquinolin-2(1*H*)-one (5z)



5z

Yellow Liquid. Yield: 52%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.51-7.46 (m, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.29-7.26 (m, 2H), 7.22-7.20 (m, 1H), 7.18-7.12 (m, 3H), 4.45 (q, J = 7.1 Hz, 2H), 4.33 (s, 2H), 2.35 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.0, 142.5, 138.0, 137.7, 129.2, 128.8, 128.8, 127.9, 126.4, 125.79, 121.82, 121.2, 114.1, 37.9, 34.7, 14.0, 12.8. **HRMS(ESI)** for $C_{19}H_{20}NO^+$ ([M+H]$^+$): calcd: 278.1539, found: 278.1548.

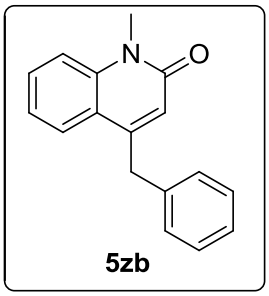
1,4-dibenzyl-3-methylquinolin-2(1*H*)-one (5za)



5za

White soild. Yield: 64%. m.p. 157.5-159.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.40-7.16 (m, 13H), 7.14-7.09 (m, 1H), 5.66 (s, 2H), 4.38 (s, 2H), 2.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.7, 143.2, 138.2, 137.9, 136.7, 129.3, 128.8, 127.9, 127.2, 126.7, 126.5, 125.6, 122.2, 121.2, 115.1, 46.6, 34.8, 14.2. **HRMS(ESI)** for $C_{24}H_{22}NO^+$ ([M+H]$^+$): calcd: 340.1696, found: 340.1706.

4-benzyl-1-methylquinolin-2(1*H*)-one (5zb)



5zb

White soild. Yield: 57%. m.p. 139.2-141.2 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.58-7.54 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.34-7.31 (m, 2H), 7.27-7.20 (m, 4H), 6.53 (s, 1H), 4.18 (s, 2H), 3.73 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.1, 148.6, 140.1, 137.5, 130.4, 128.9, 128.8, 126.8, 125.4, 122.0, 121.9, 120.6, 114.6, 38.4, 29.3. **HRMS(ESI)** for $C_{17}H_{16}NO^+$ ([M+H]$^+$): calcd: 250.1226, found: 250.1234.

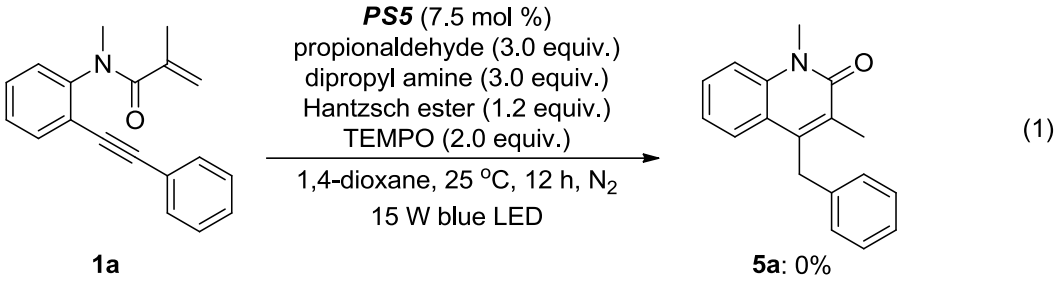
3.3 1 mmol-scale synthesis of 5a

To a 50 mL Schlenk tube were added **1a** (1.0 mmol), Hantzsch ester **4** (1.2 mmol, 304 mg) and ***PS5*** (0.075 mmol, 90.0 mg), the tube was evacuated and refilled with N_2 for three times. A solution of propionaldehyde **2a** (3.0 mmol), dipropylamine **3a** (3.0 mmol) and 1,4-dioxane (20 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 20 h. Upon completion, the reaction

mixture 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 product **5a** (171.1 mg, yield: 65%).

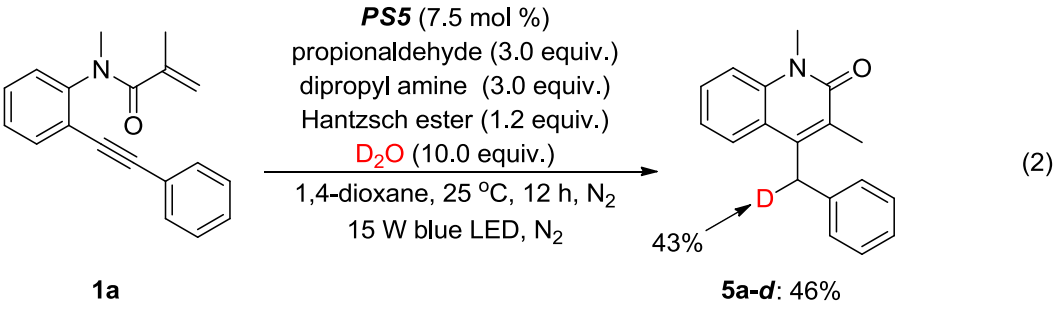
4. Mechanistic Studies

(a) radical capture experiment



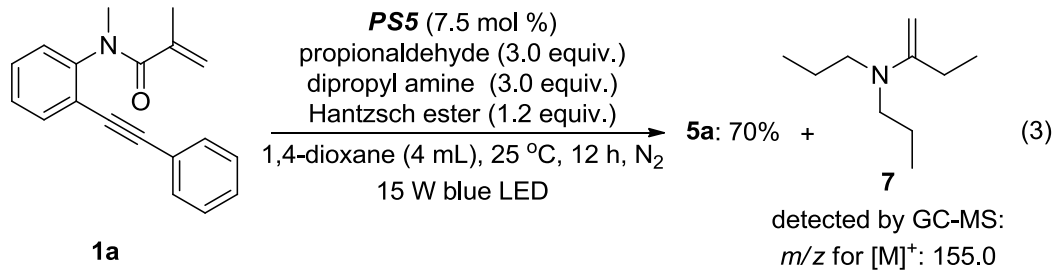
(1)

(b) deuterium-labeling experiment



(2)

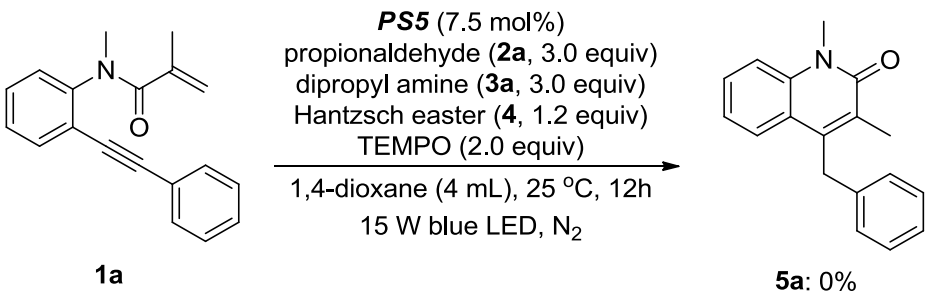
(c) Detection of enamine intermediate



(3)

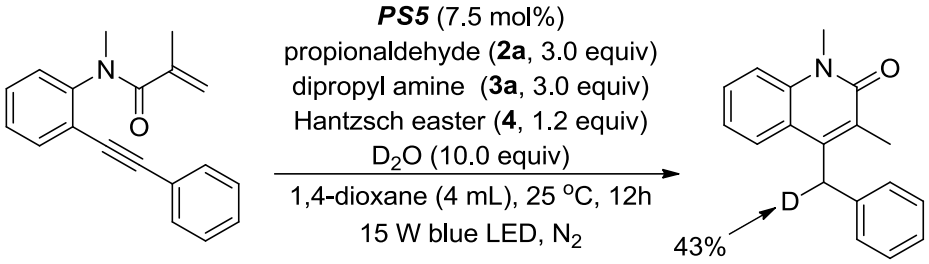
Scheme *S1* Mechanistic experiments.

4.1 Radical capture experiment



To a 25 mL Schlenk tube were added **1a** (0.2 mmol), Hantzsch ester (0.24 mmol, 60.8 mg), TEMPO (0.4 mmol) and ***PS5*** (0.015 mmol, 18.0 mg), the tube was evacuated and refilled with N_2 for three times. A solution of propionaldehyde **2a** (0.6 mmol in some cases), dipropylamine **3a** (0.6 mmol in some cases) and 1,4-dioxane (4 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction mixture was analyzed by GC and **5a** was not detected.

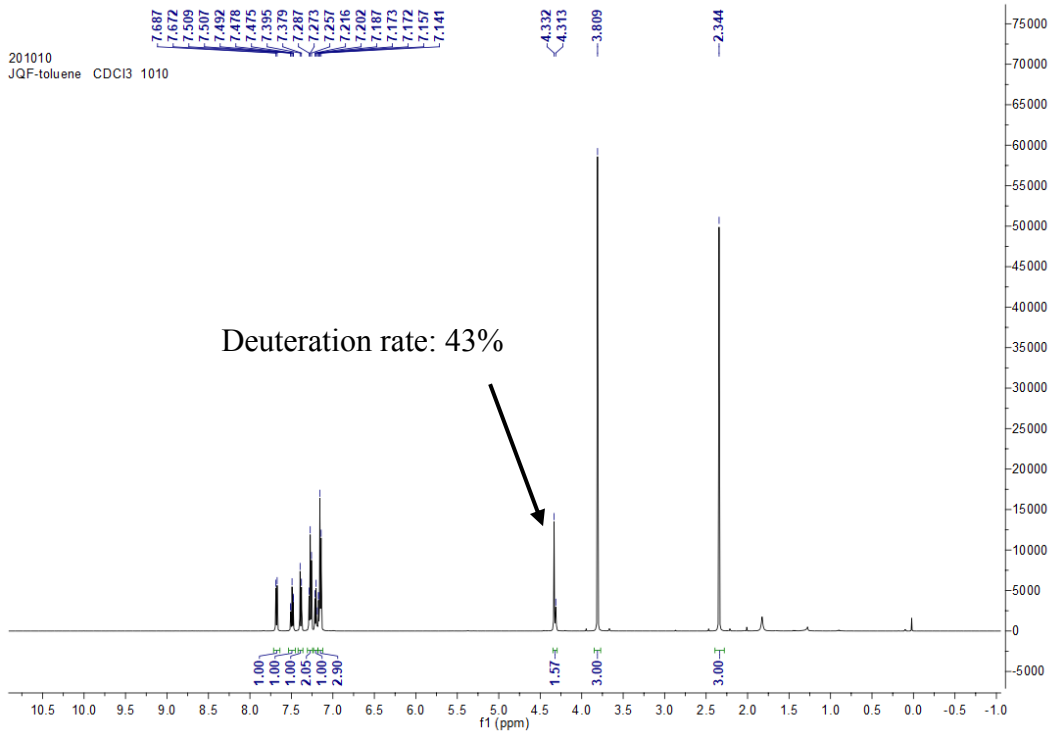
4.2 Deuterium-labeling experiments



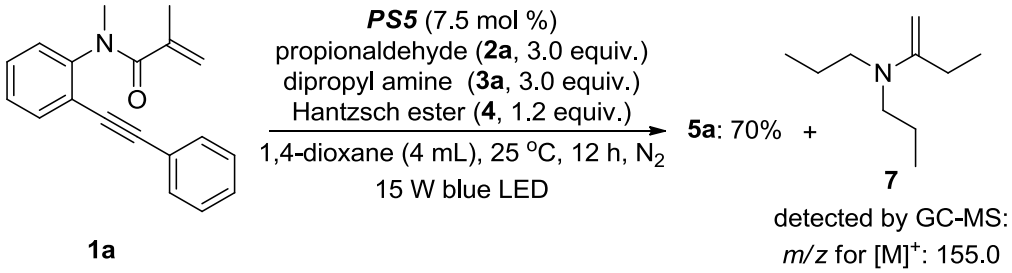
1a **5a-*d***: 46%

To a 25 mL Schlenk tube were added **1a** (0.2 mmol), Hantzsch ester (0.24 mmol, 60.8 mg) and ***PS5*** (0.015 mmol, 18.0 mg), the tube was evacuated and refilled with N_2 for three times. A solution of propionaldehyde **2a** (0.6 mmol), dipropylamine **3a** (0.6 mmol), 1,4-dioxane (4 mL) and D_2O (10.0 equiv.) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 12 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 sample for ^1H NMR analysis. A **5a-*d*** was obtained in 46% yield.

^1H NMR ($CDCl_3$, 500 MHz) spectrum of **5a-*d*** obtained from the above-mentioned experiment. The D-enrichment of one benzyl-hydrogens was found to be 43%.

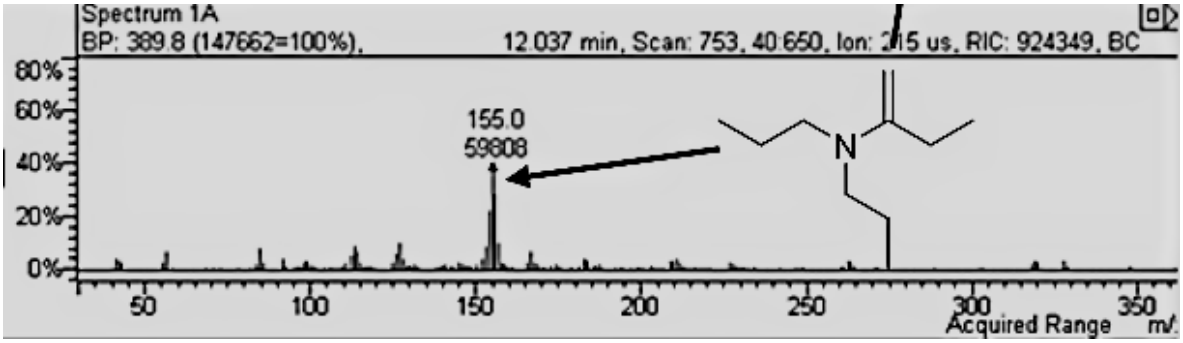


4.3 Detection of by-product enamine 7



To a 25 mL Schlenk tube were added **1a** (0.2 mmol), Hantzsch ester (0.24 mmol, 60.8 mg) and ***PS5*** (0.015 mmol, 18.0 mg), the tube was evacuated and refilled with N_2 for three times. A solution of propionaldehyde **2a** (0.6 mmol in some cases), dipropylamine **3a** (0.6 mmol in some cases) and 1,4-dioxane (4 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 12 h. Taking a sample from the crude reaction mixture for GC-MS analysis, and the expected enamine species **7** (m/z for $[M]^+$: 155.0) was indeed detected, supporting an α-amino radical-induced β-fragmentation process to cleave the original $C(sp^2)$-$C(sp^2)$ bond of 1,7-enyne **1a**.

The GC-MS spectrum of **7** was listed as follows:



5. References

1. J. T. M. Correia, G. Piva da Silva, E. André and M. W. Paixão, *Adv. Synth.Catal.*, 2019, **361**, 5558-5564.

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3. H.-Y. Liu, Y. Lu, Y. Li, J.-H. Li, *Org. Lett.*, 2020, **22**, 8819-8823.

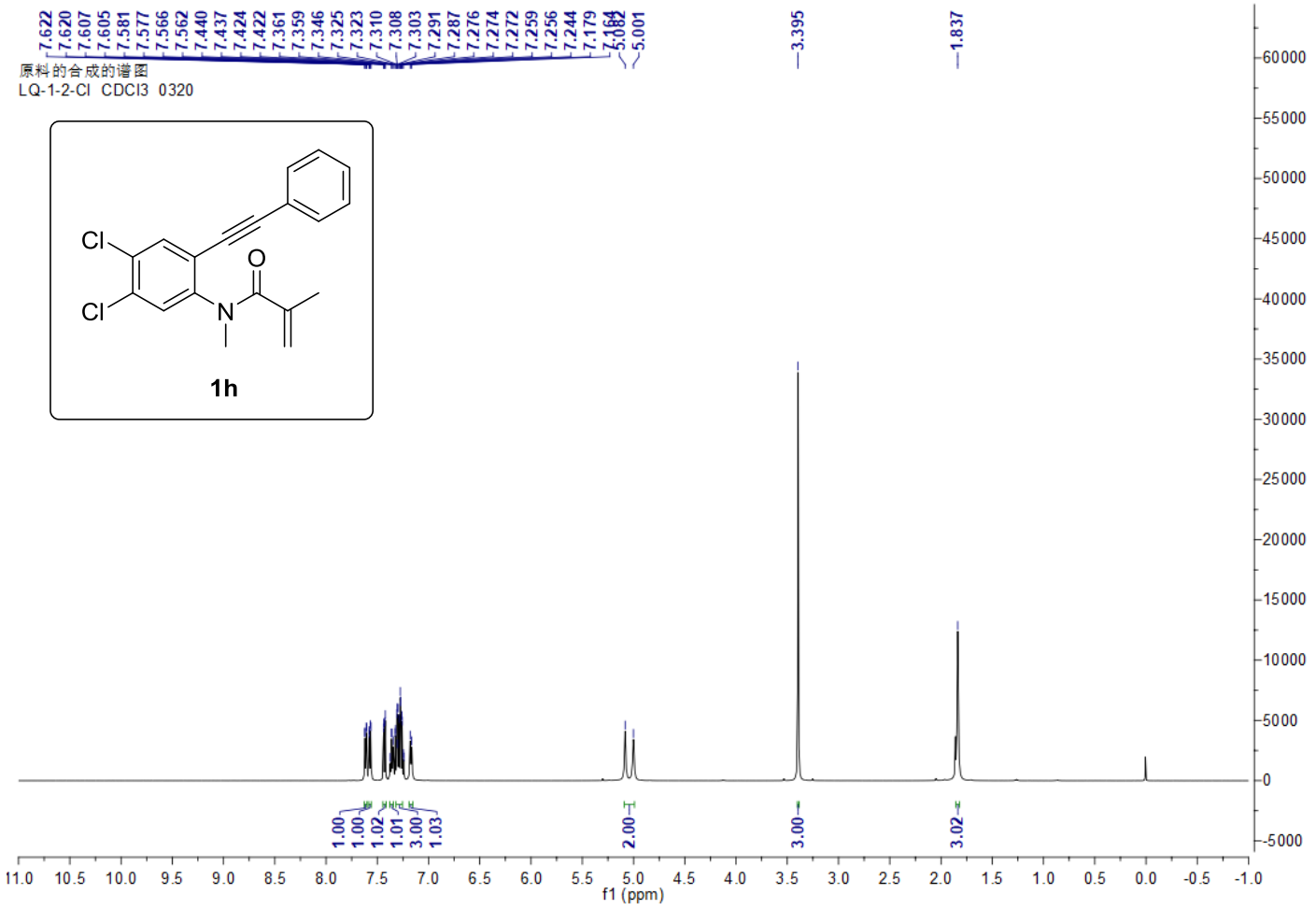
4. Y. Qu, W. Xu, J. Zhang, Y. Liu, Y. Li, H. Song and Q. Wang, *J. Org. Chem.*, 2020, **85**, 5379-5389.

5. N. Chen, L. Xia, A. J. J. Lennox, Y. Sun, H. Chen, H. Jin, H. Junge, Q. Wu, J. Jia, M. Beller and S. Luo, Structure-Activated Copper Photosensitizers for Photocatalytic Water Reduction. *Chem.-Eur. J.*, 2017, **23**, 3631-3636.

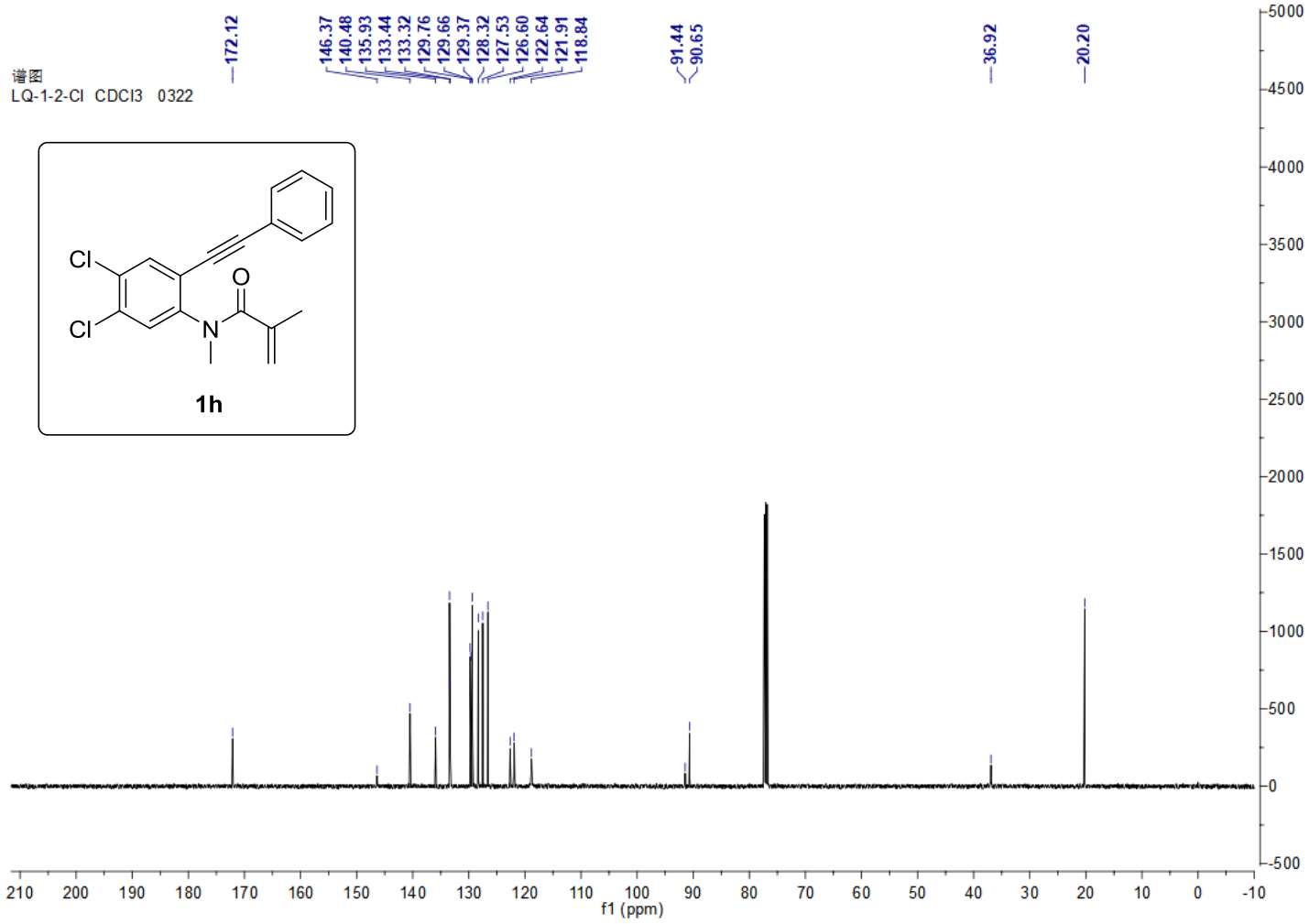
6. E. Mej á, S. Luo, M. Karnahl, A. Friedrich, S. Tschierlei, A. Surkus, H. Junge, S. Gladiali, S. Lochbrunner, and M. A. Beller, *Chem.-Eur. J.*, 2013, **19**, 15972-15978.

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

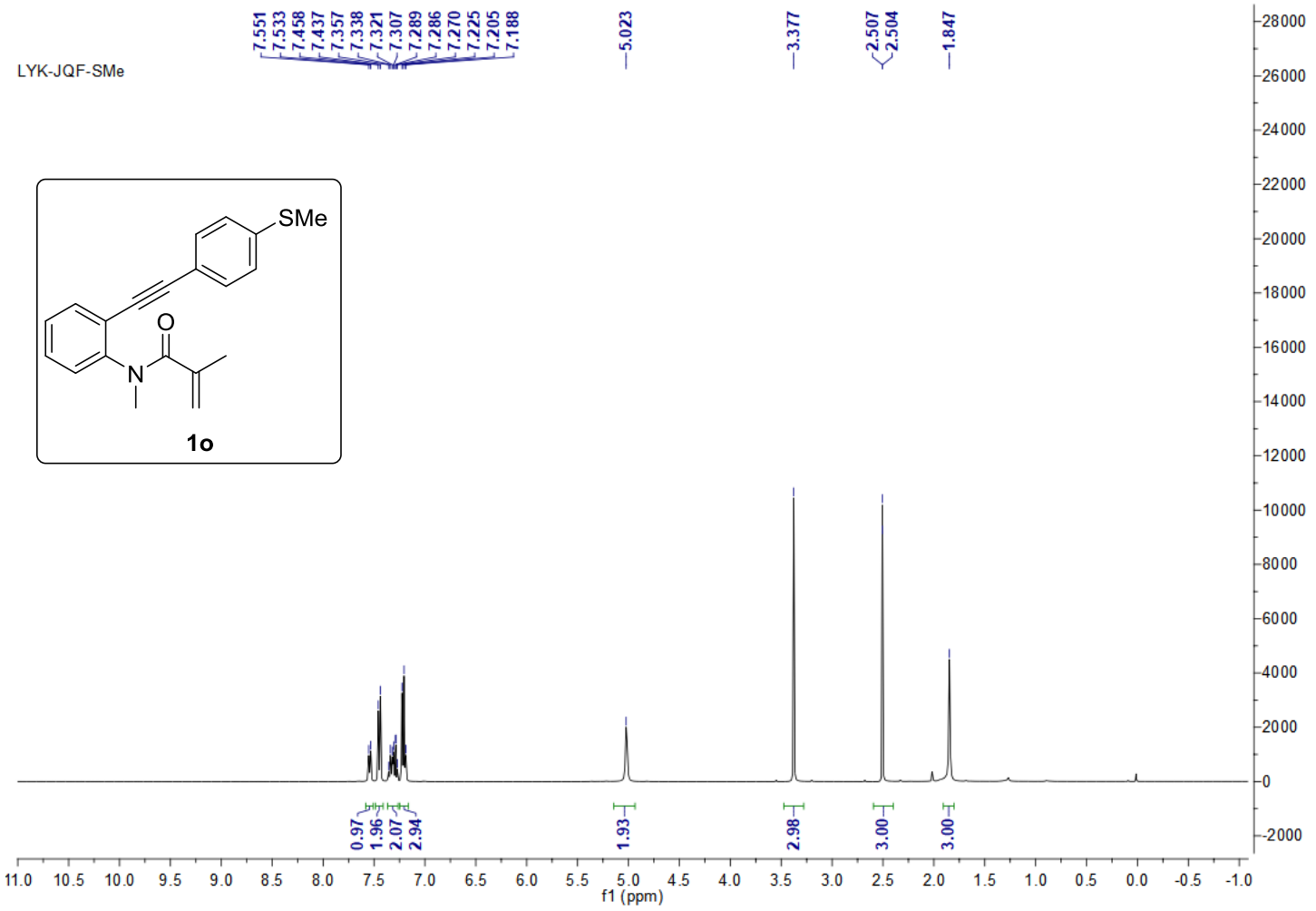
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 1h



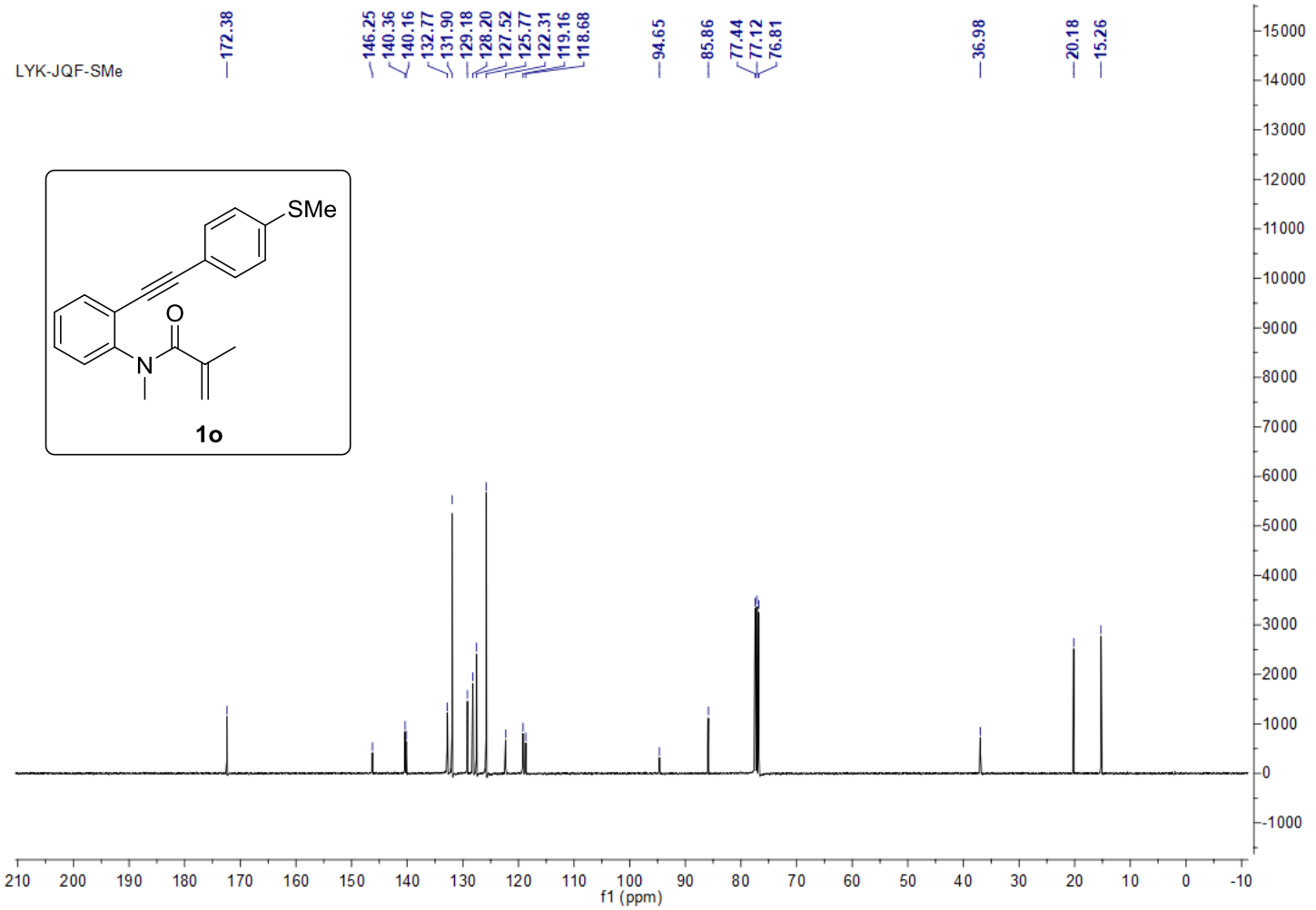
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 1h



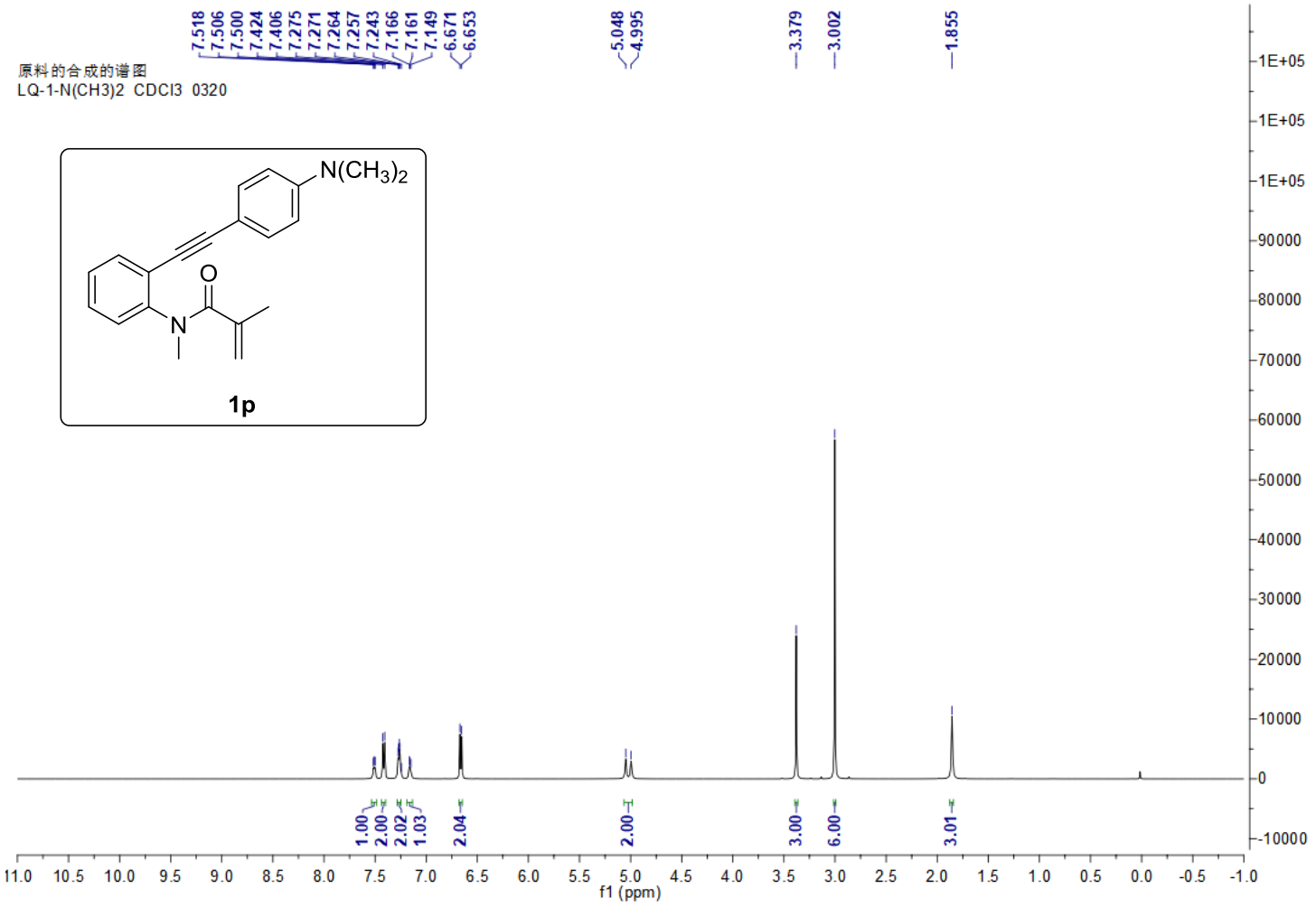
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1o



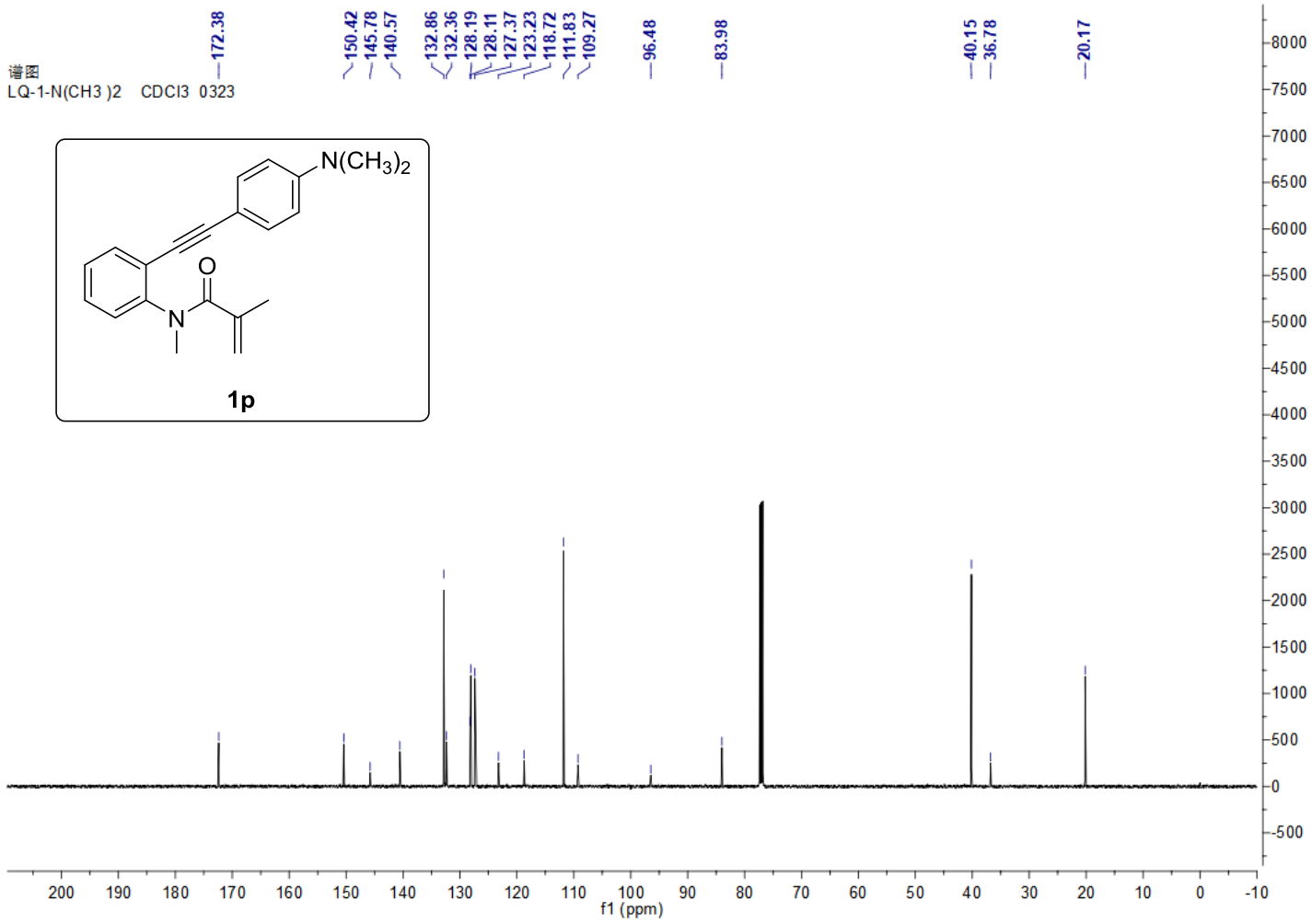
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound 1o



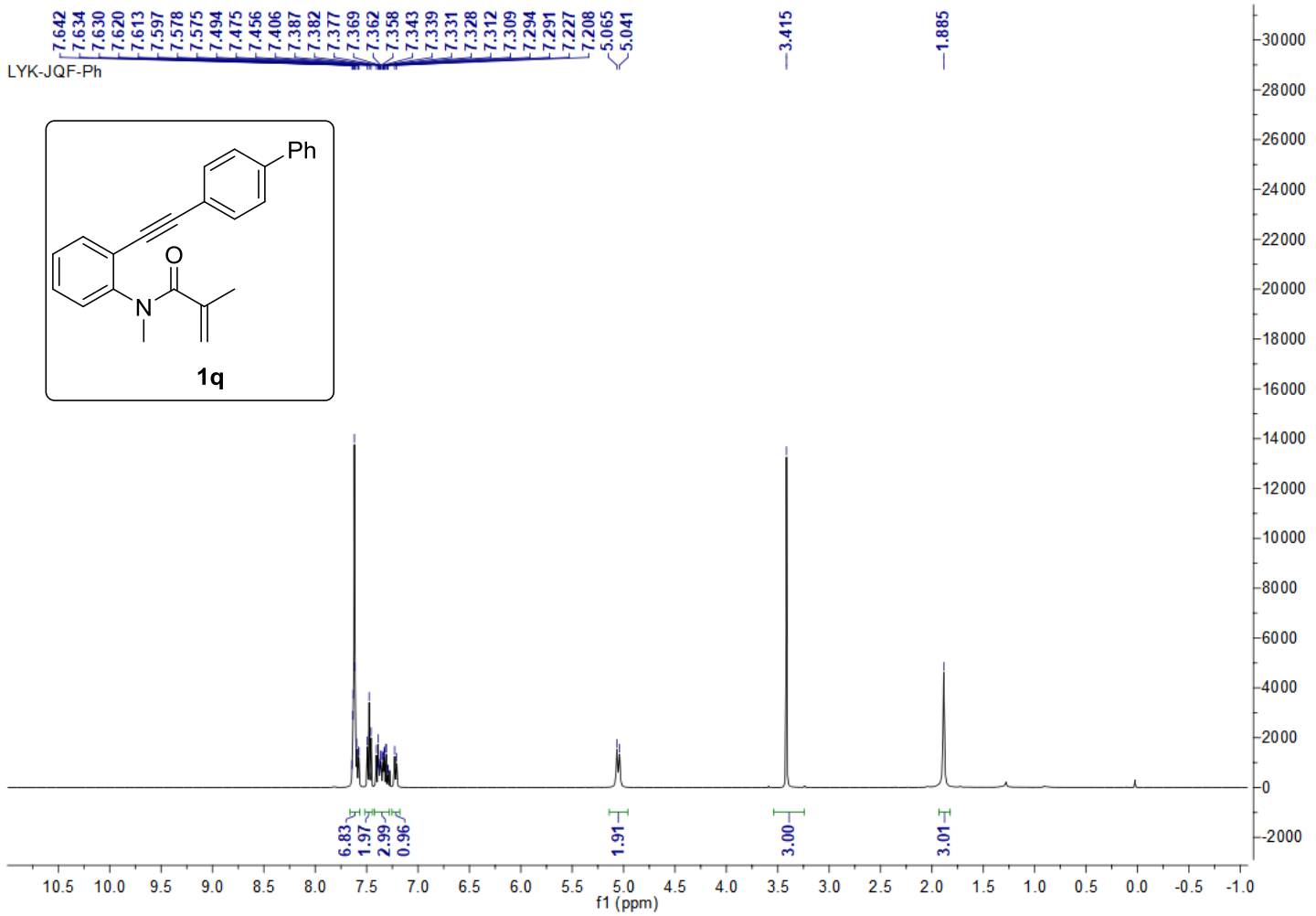
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 1p



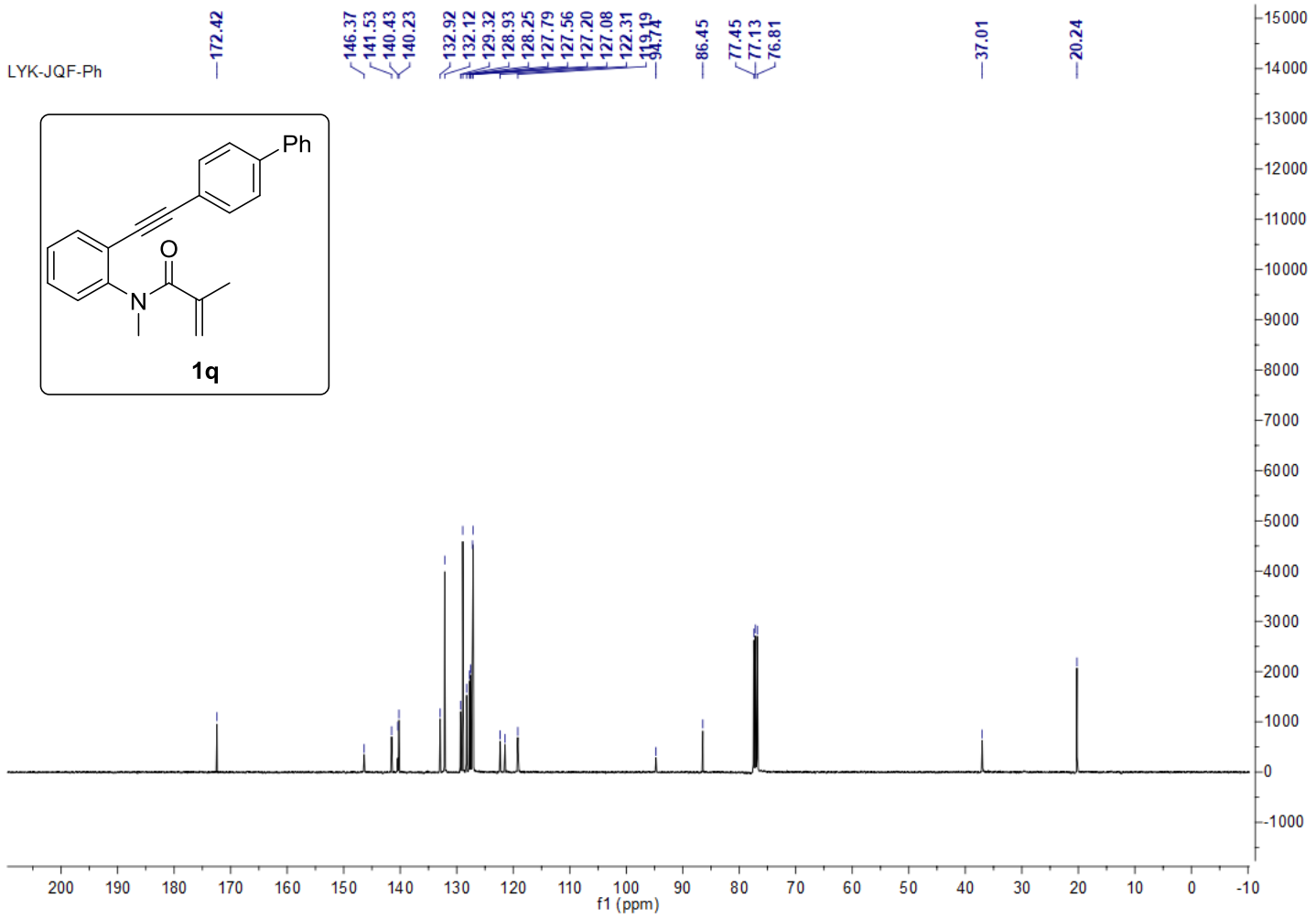
^{13}C NMR (125MHz, $CDCl_3$) spectrum of compound 1p



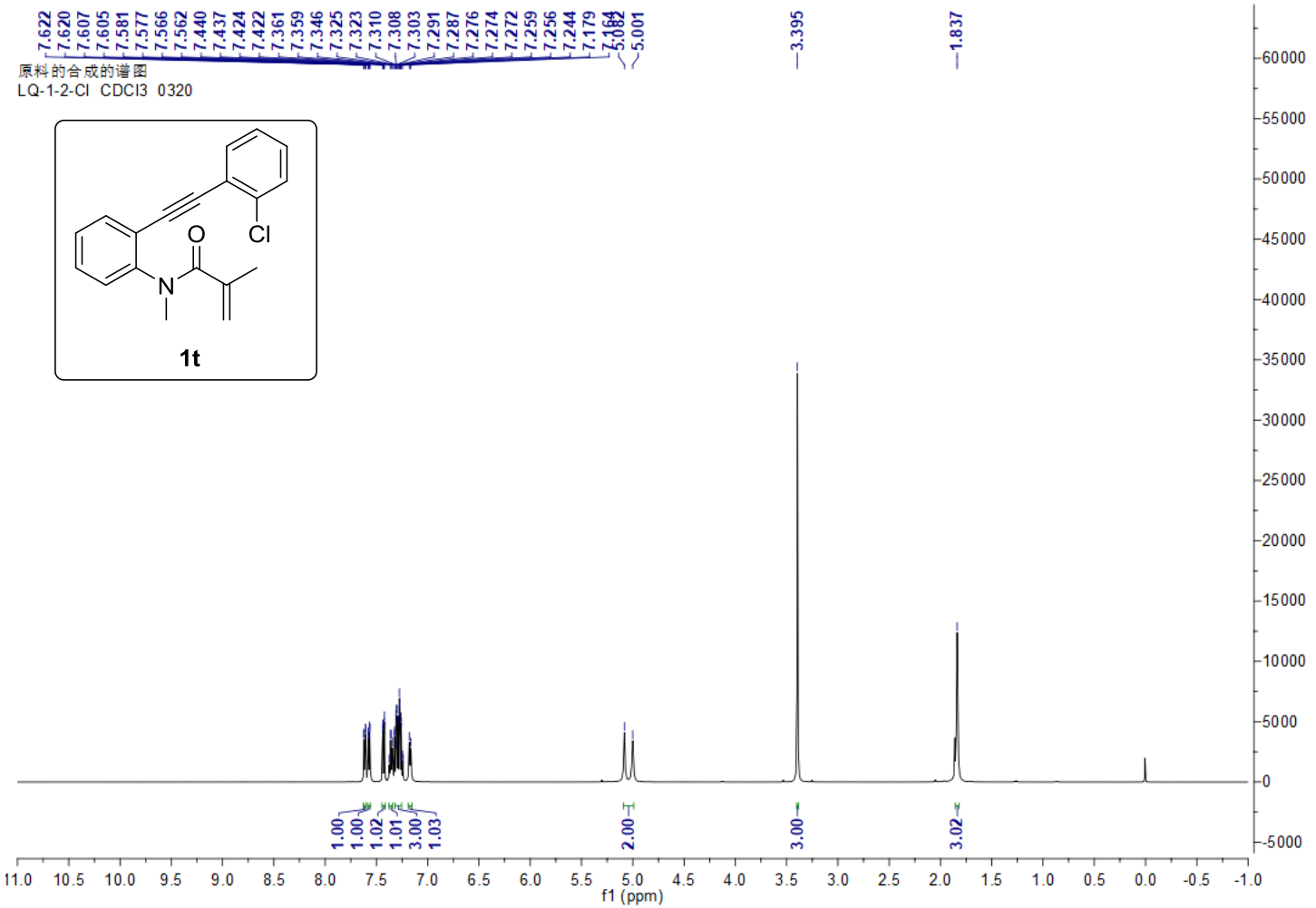
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1q



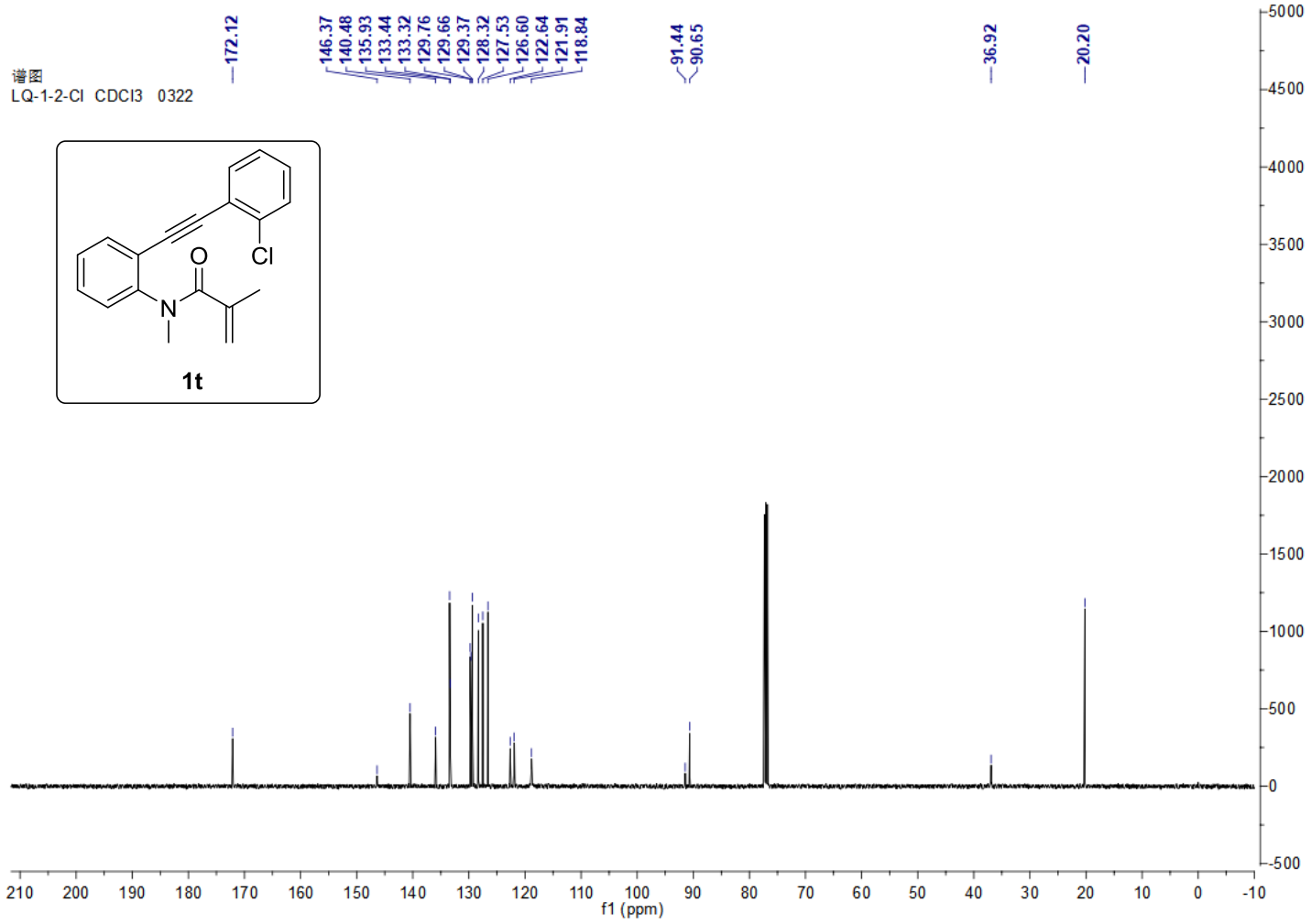
^{13}C NMR (100MHz, $CDCl_3$) spectrum of compound 1q



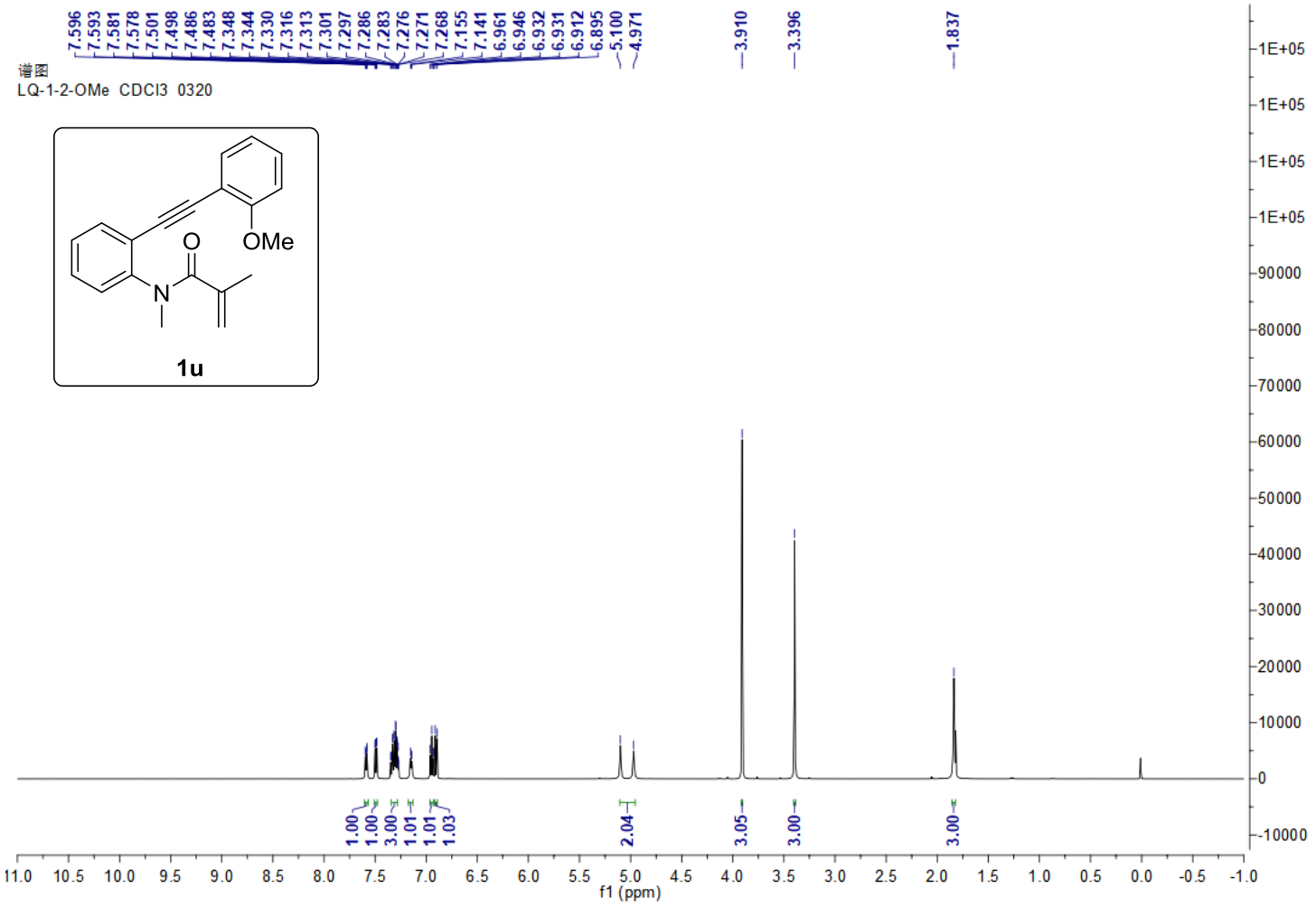
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 1t



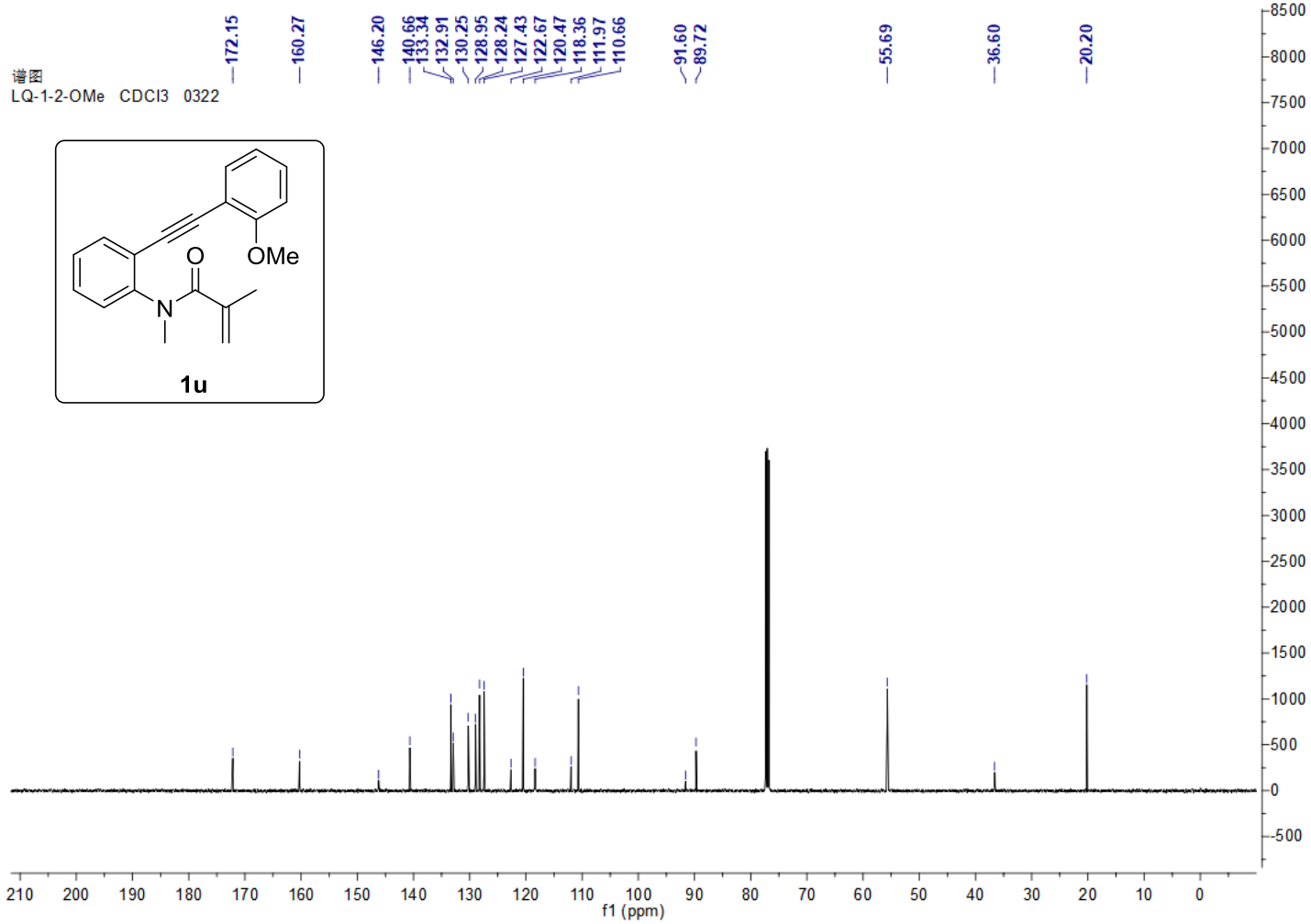
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 1t



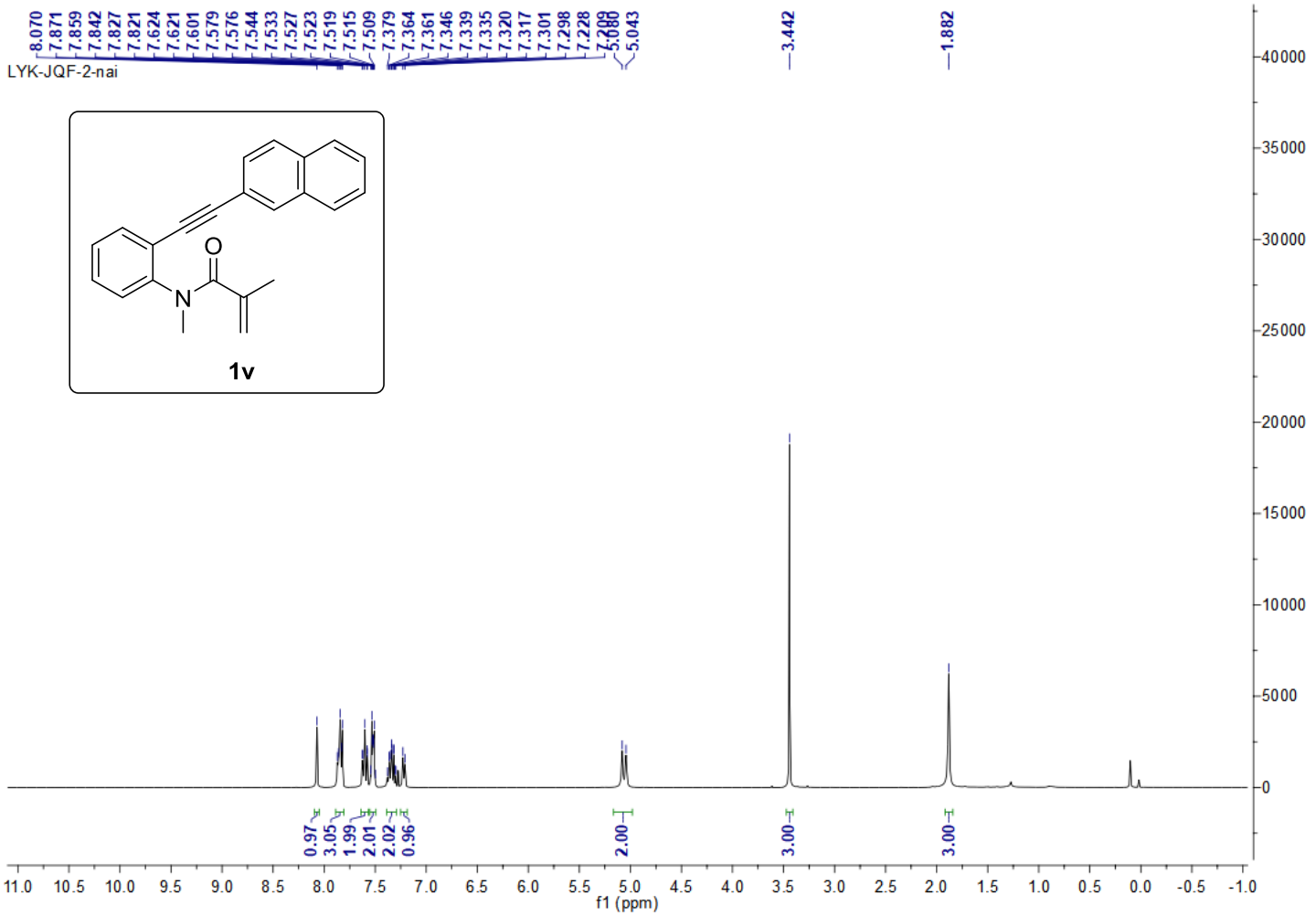
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 1u



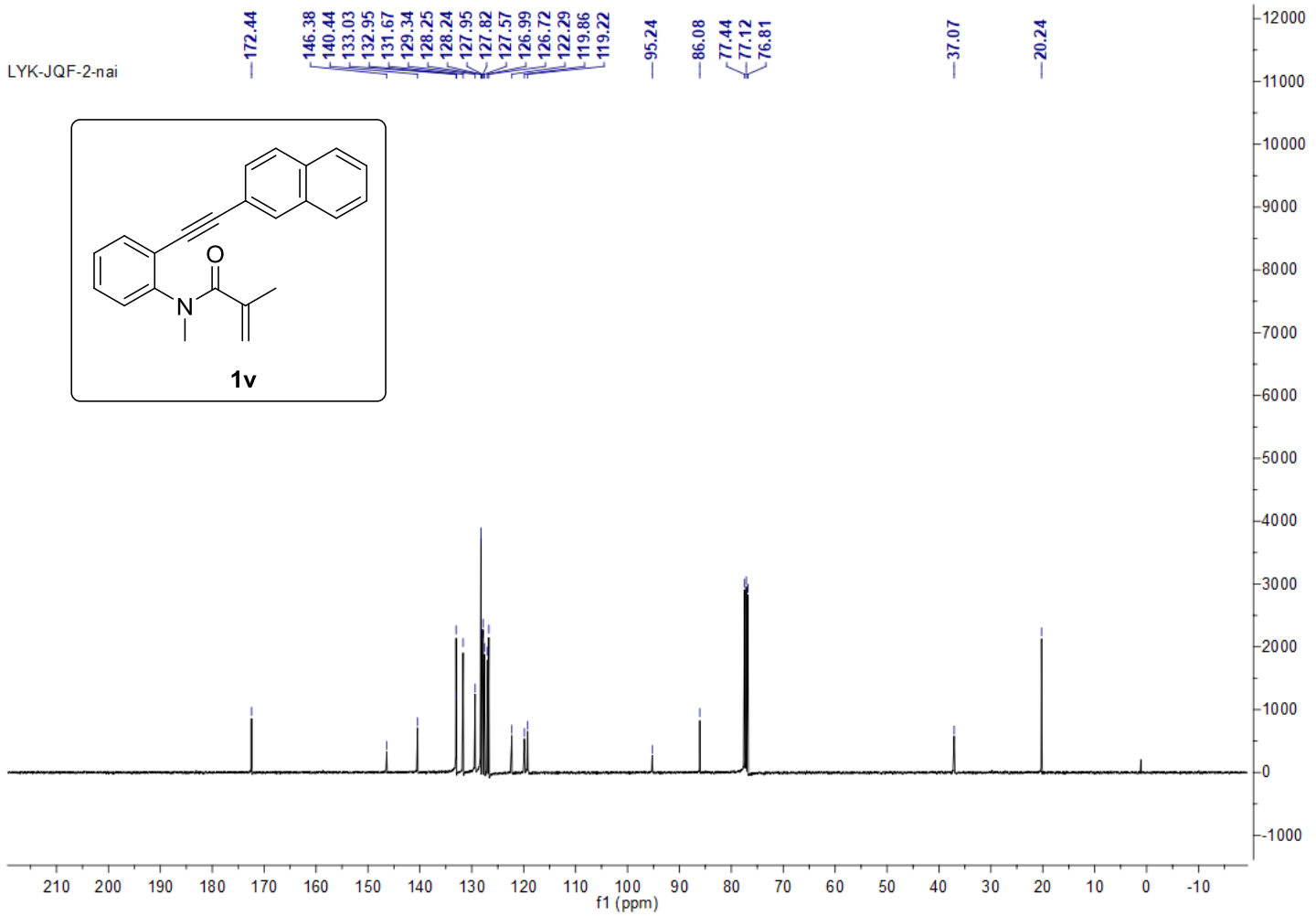
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 1u



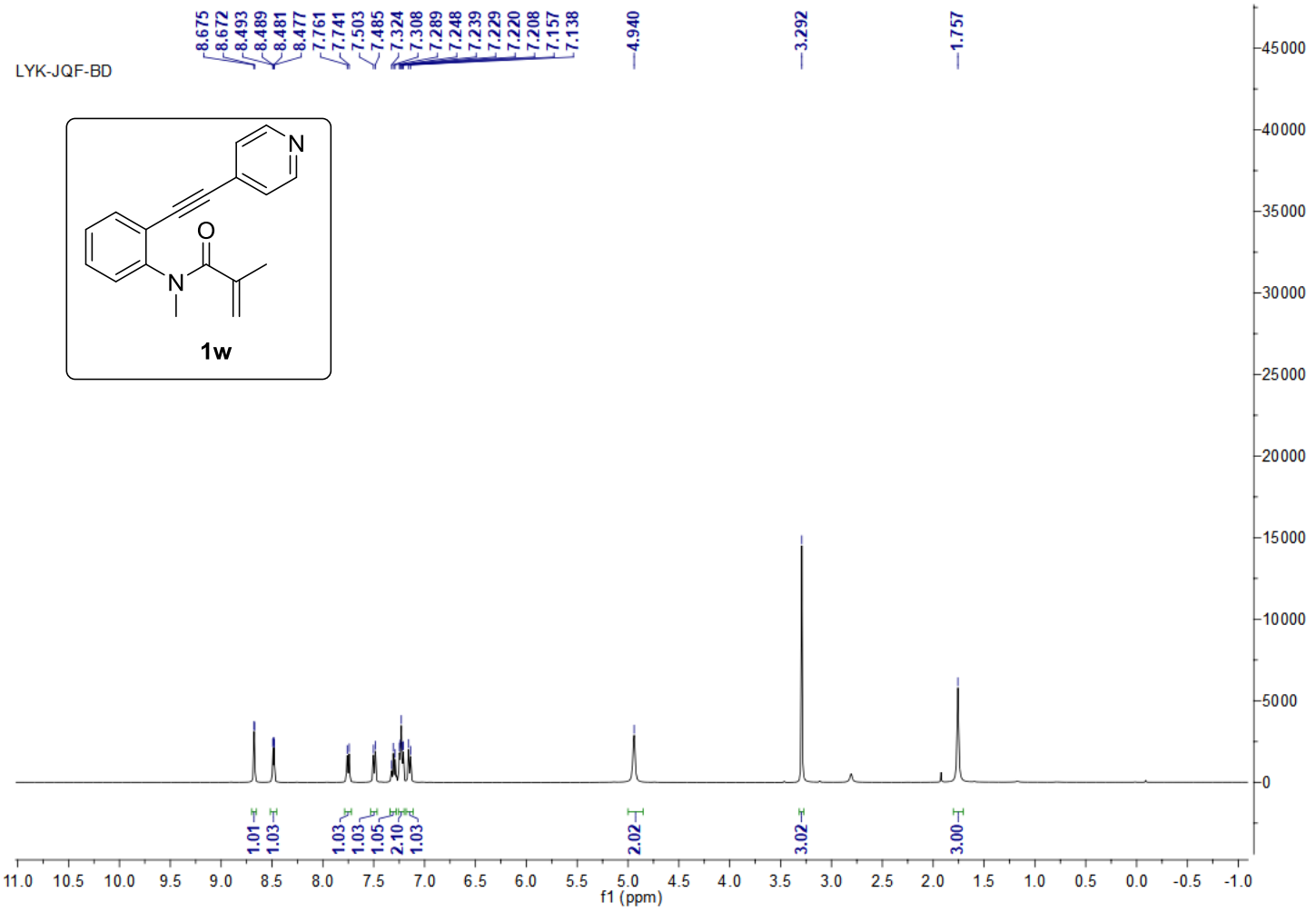
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1v



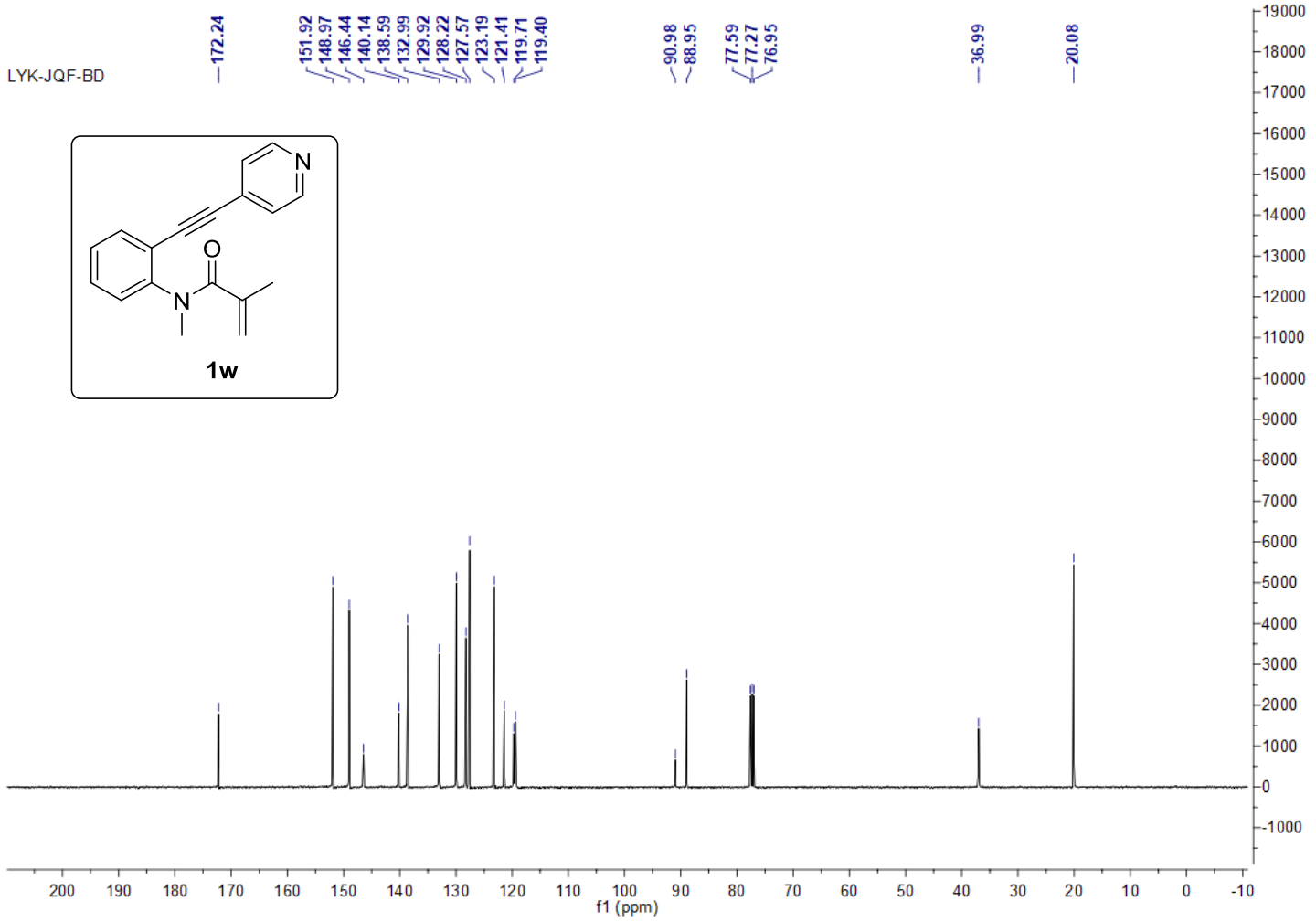
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1v



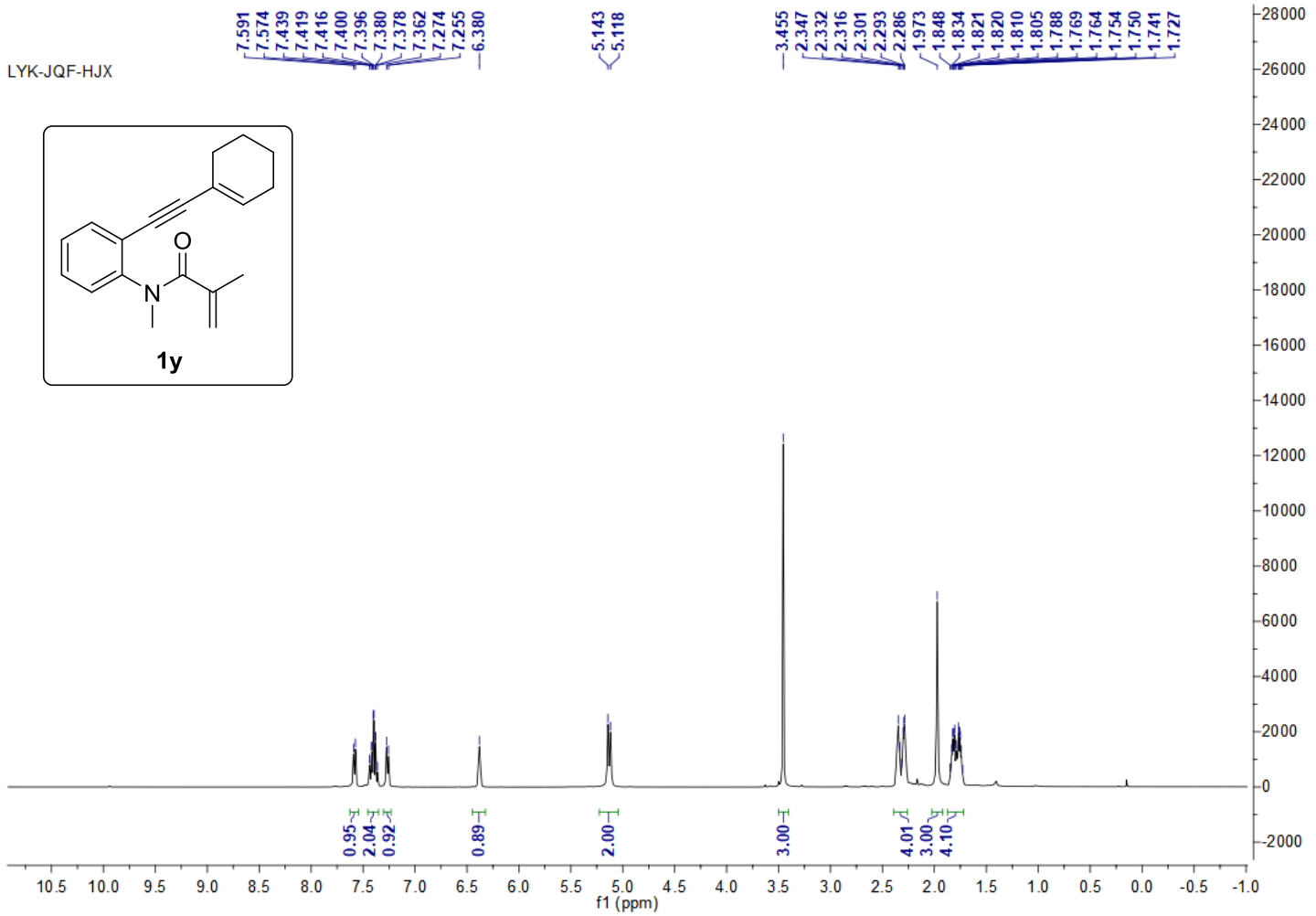
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1w



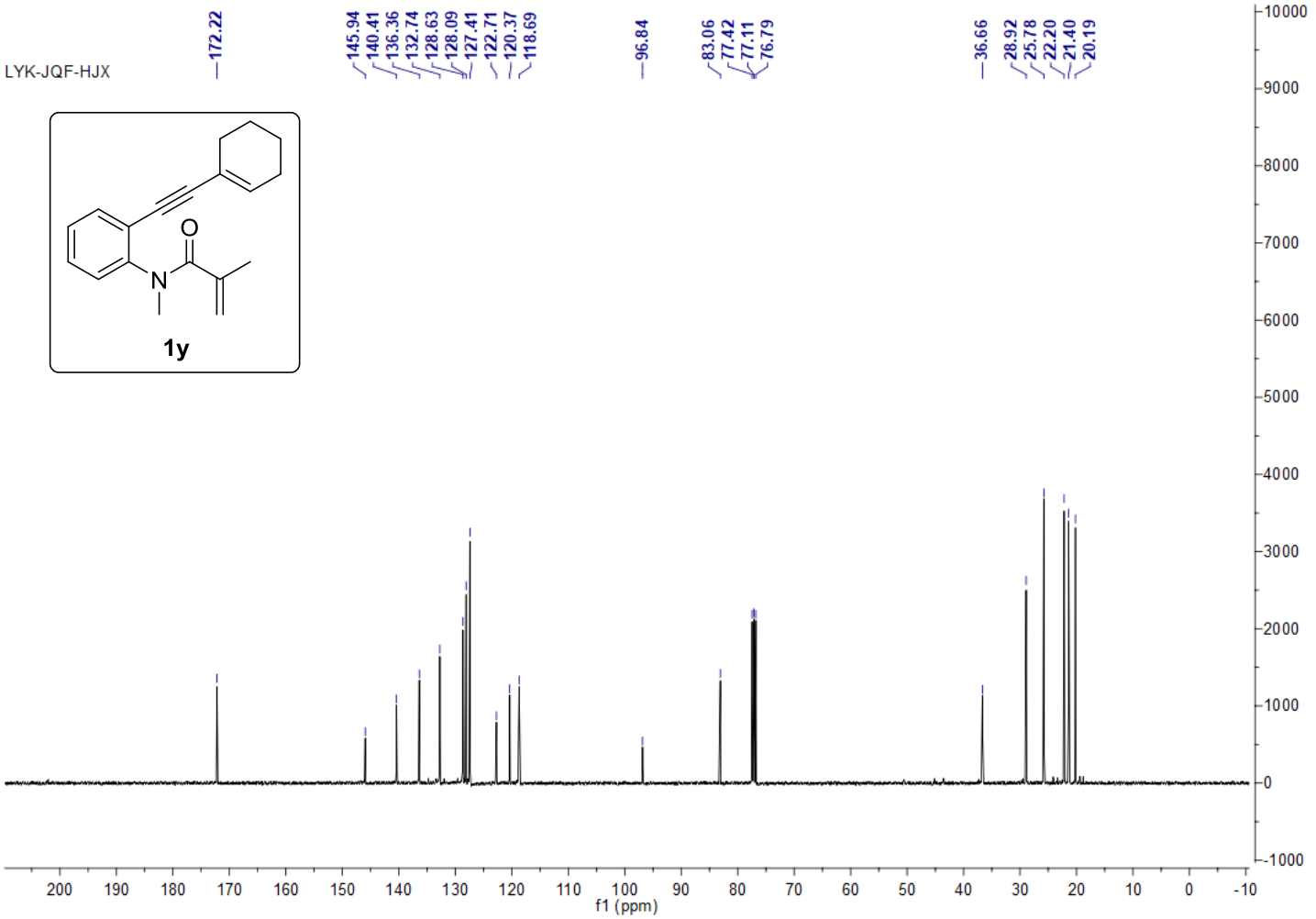
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1w



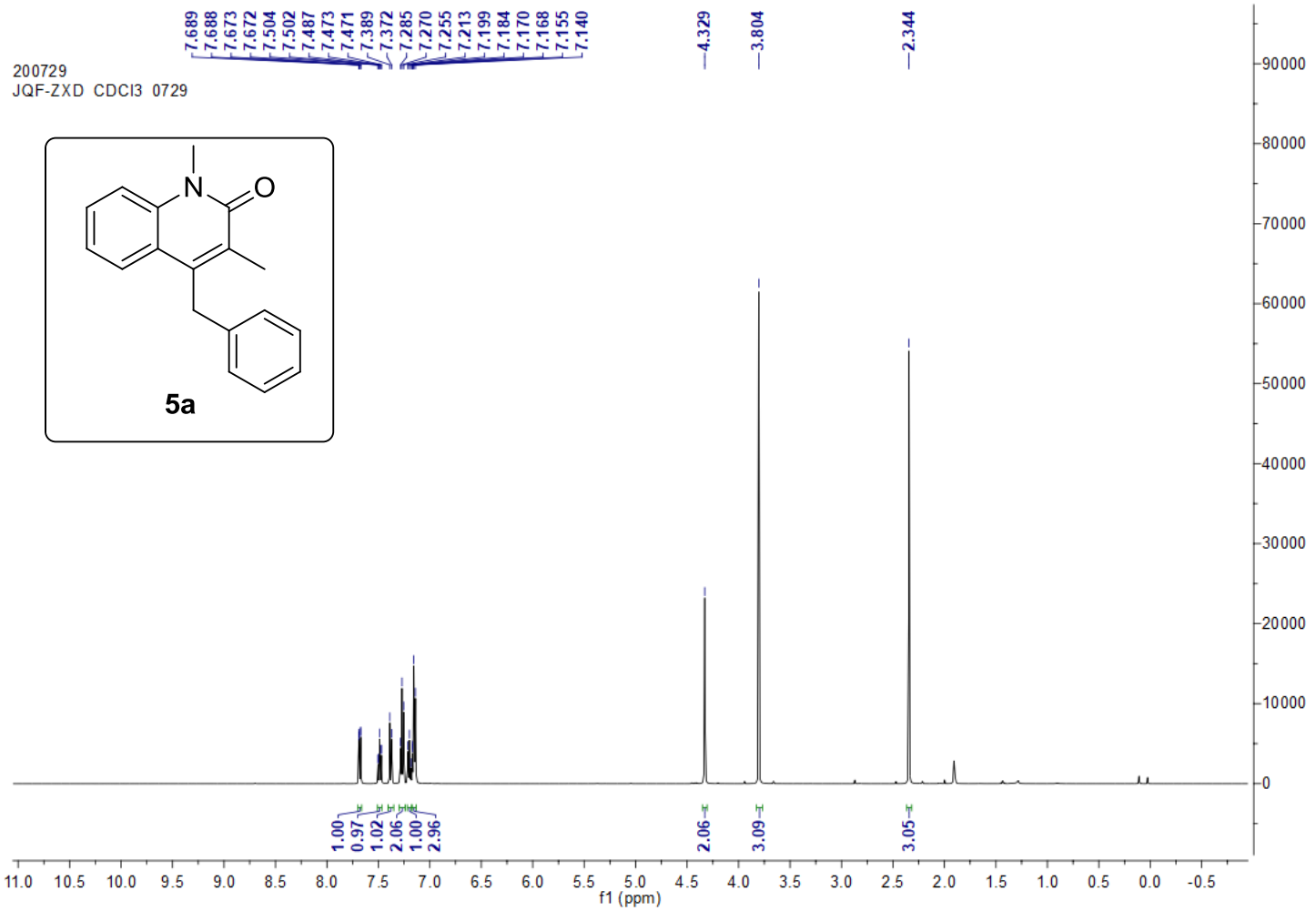
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1y



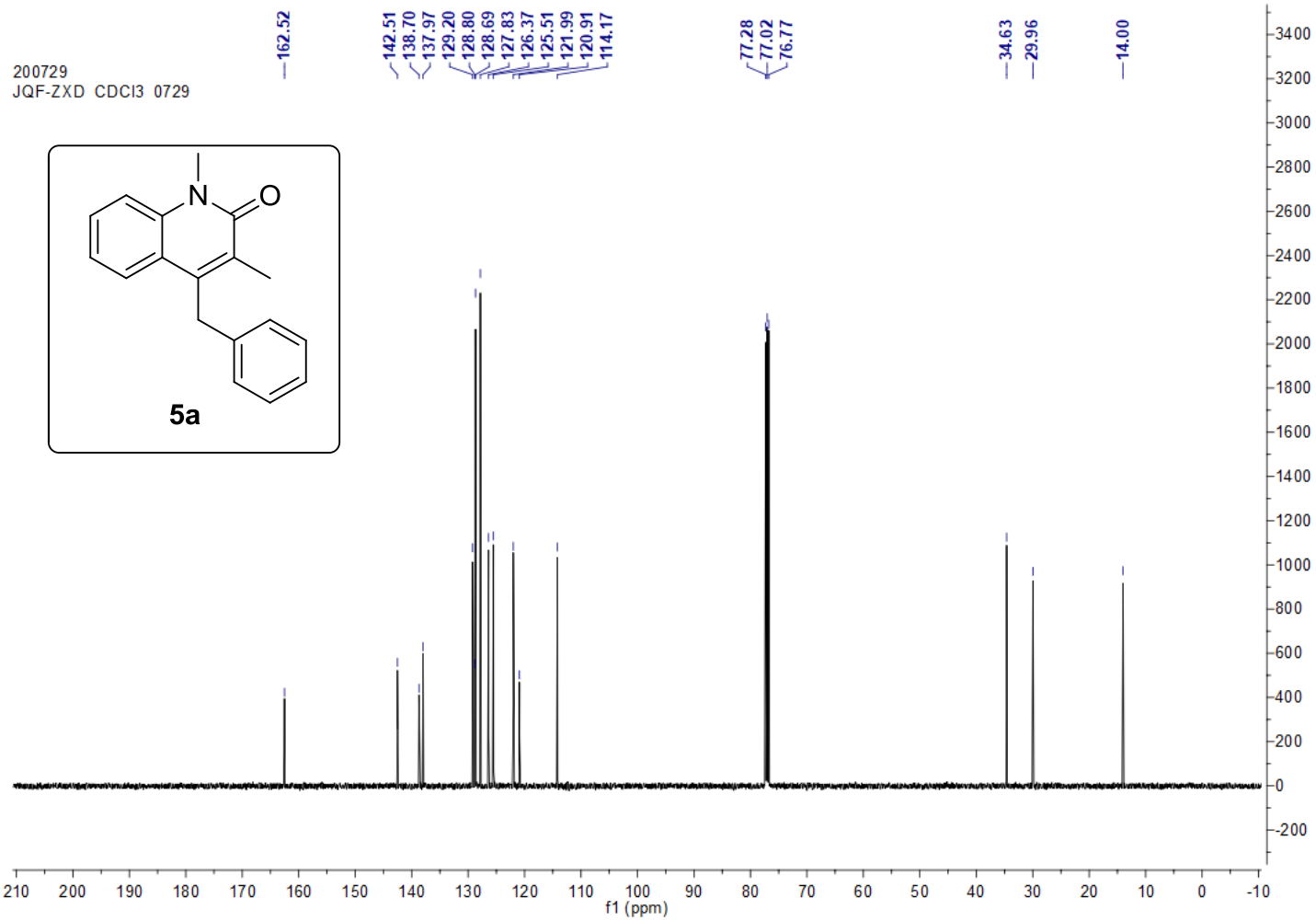
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1y



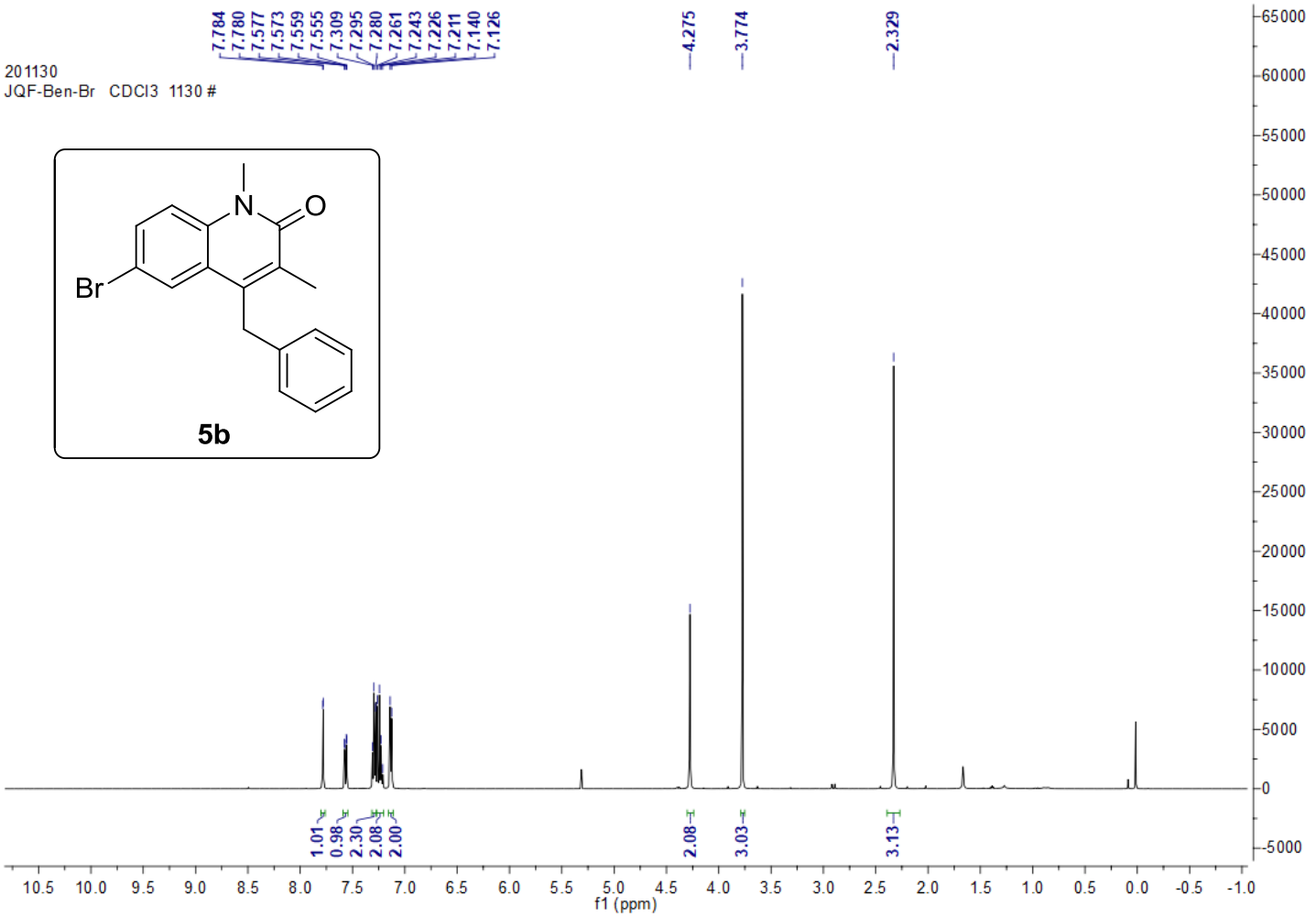
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5a



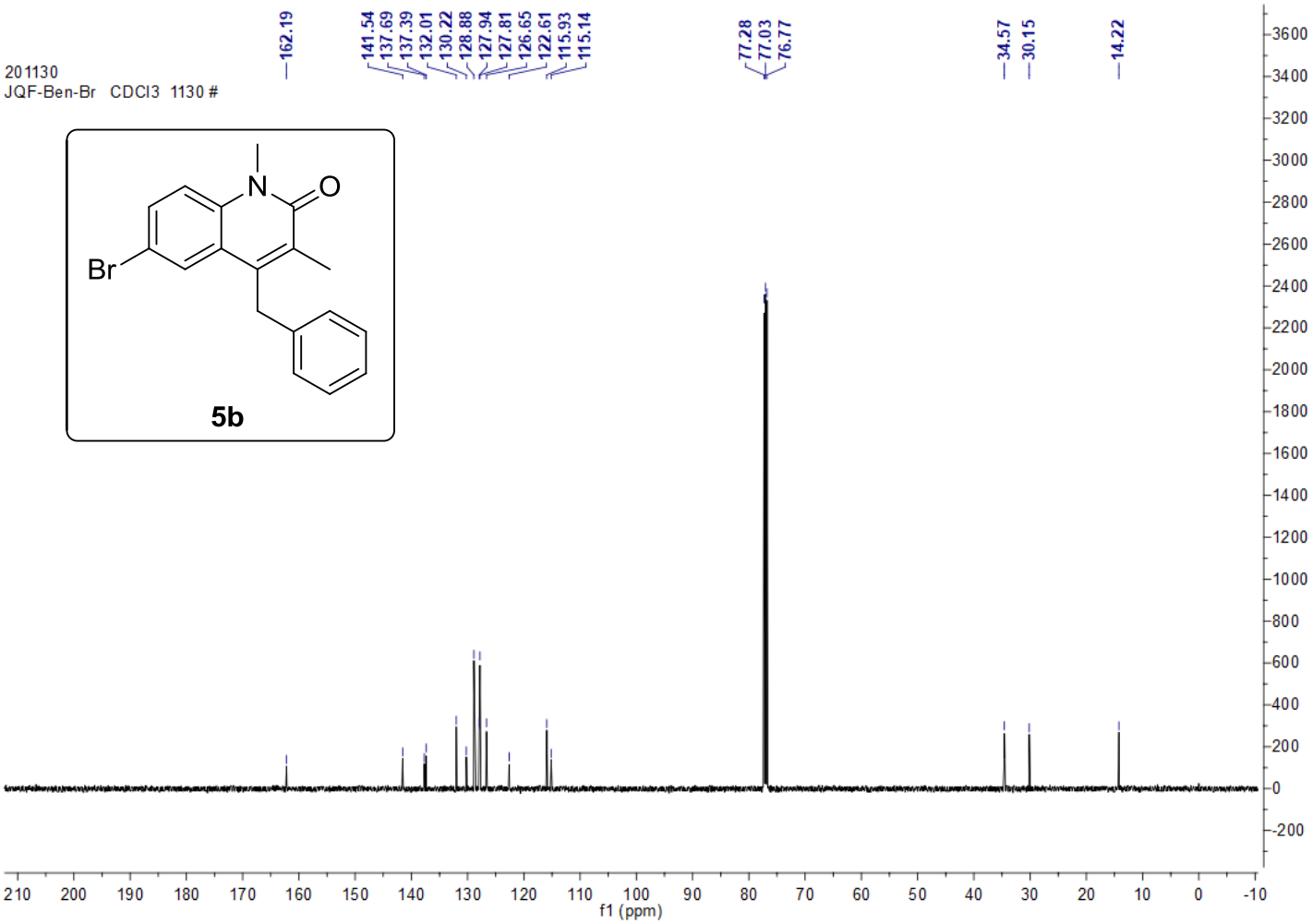
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5a



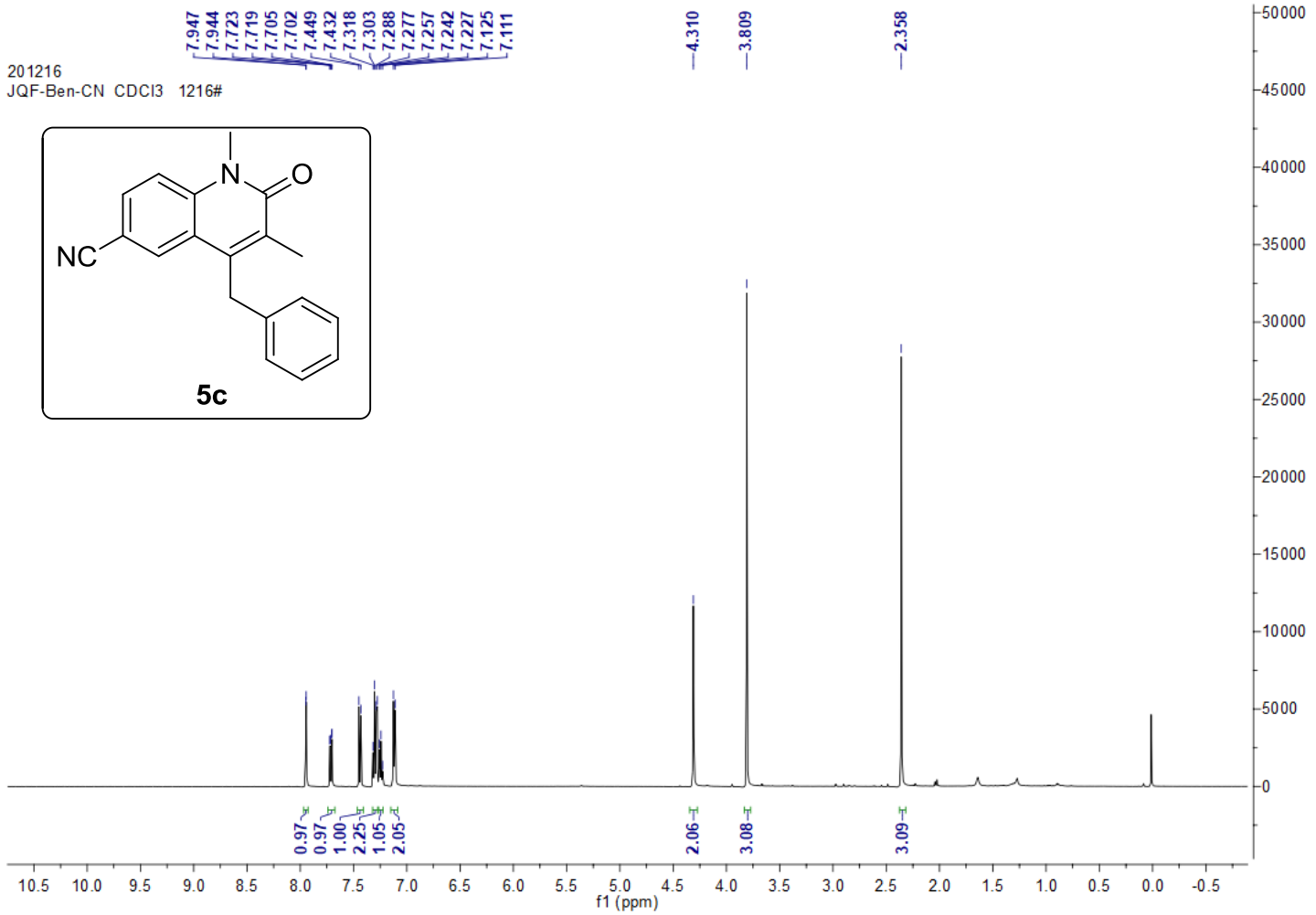
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5b



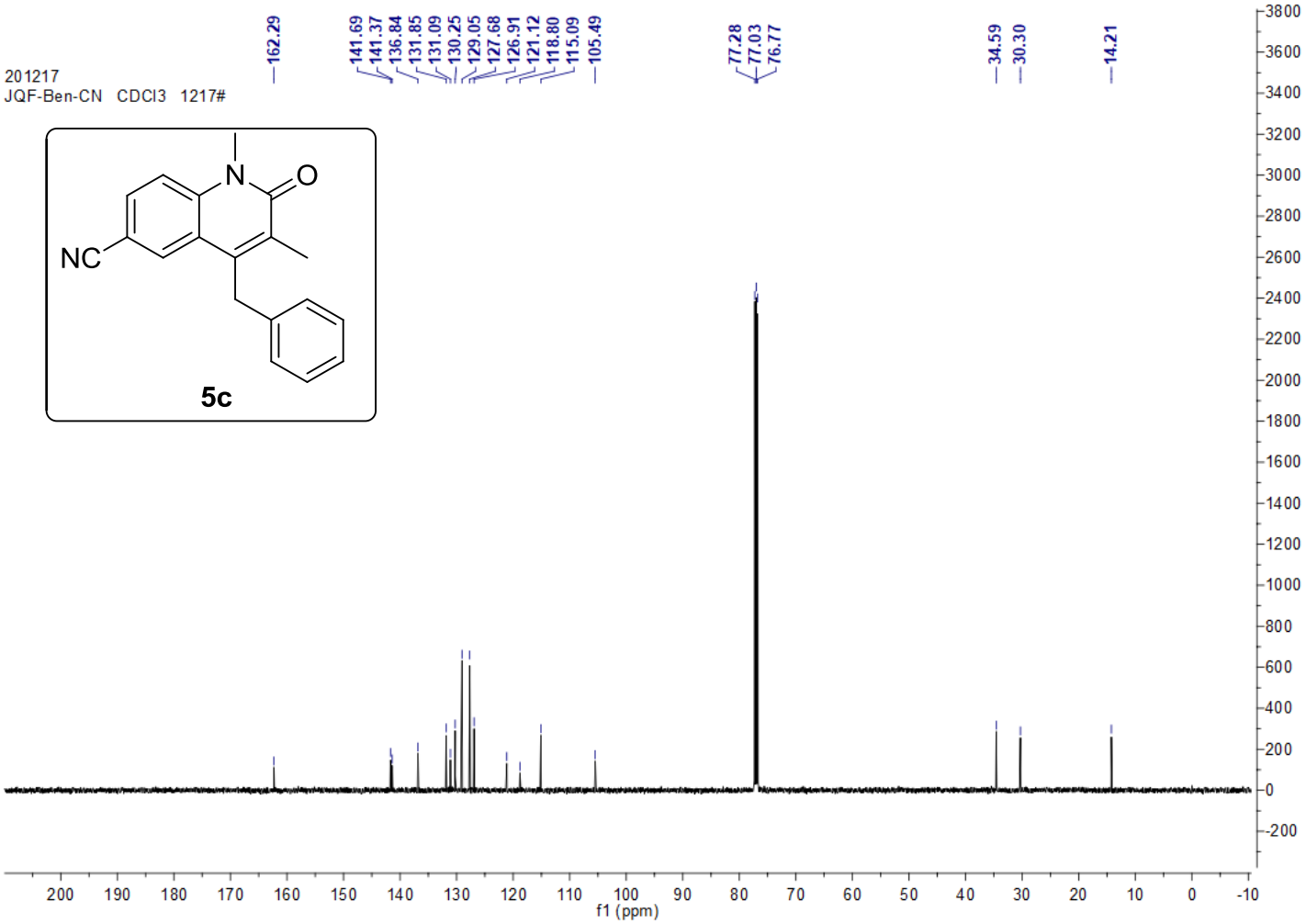
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5b



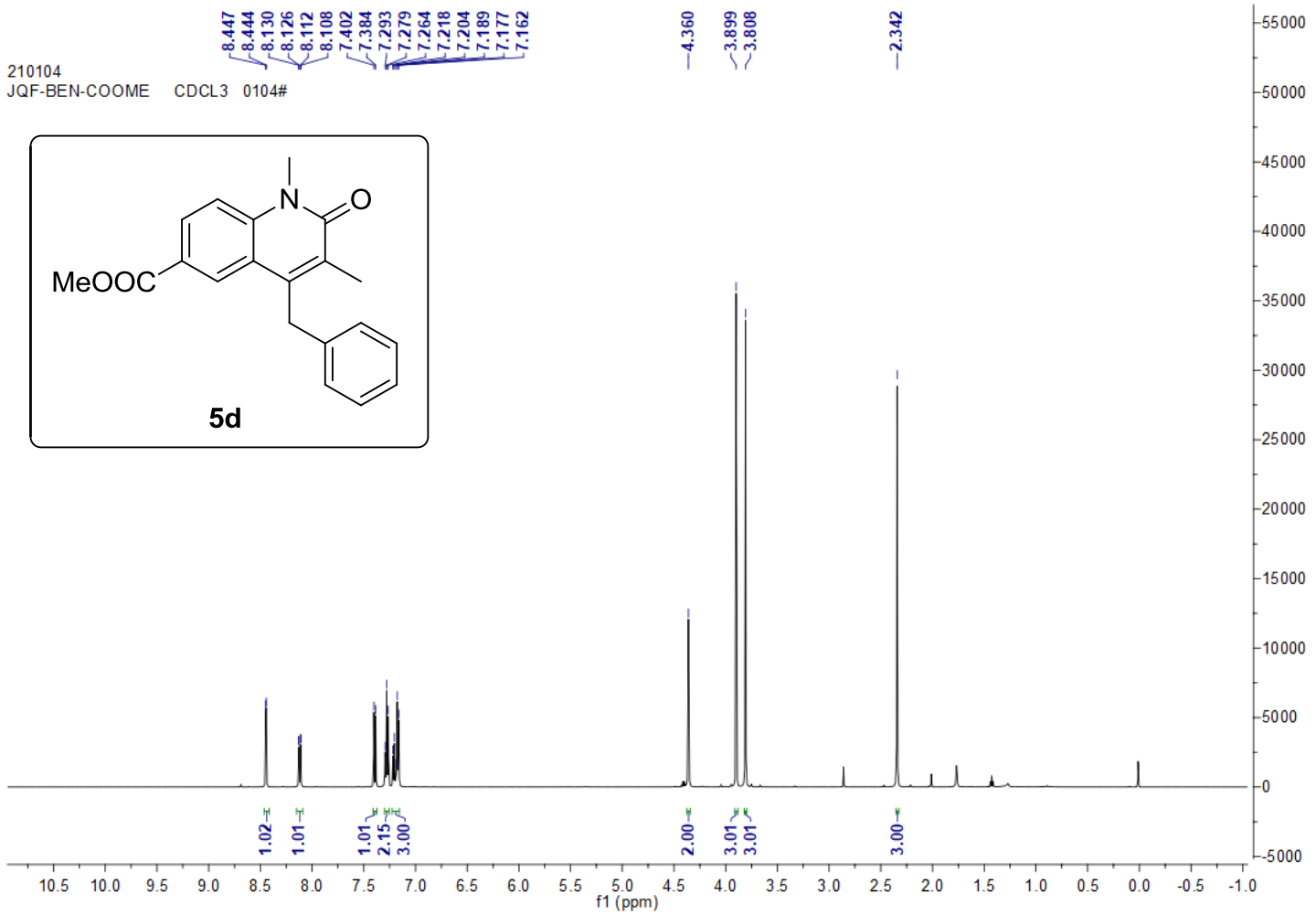
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5c



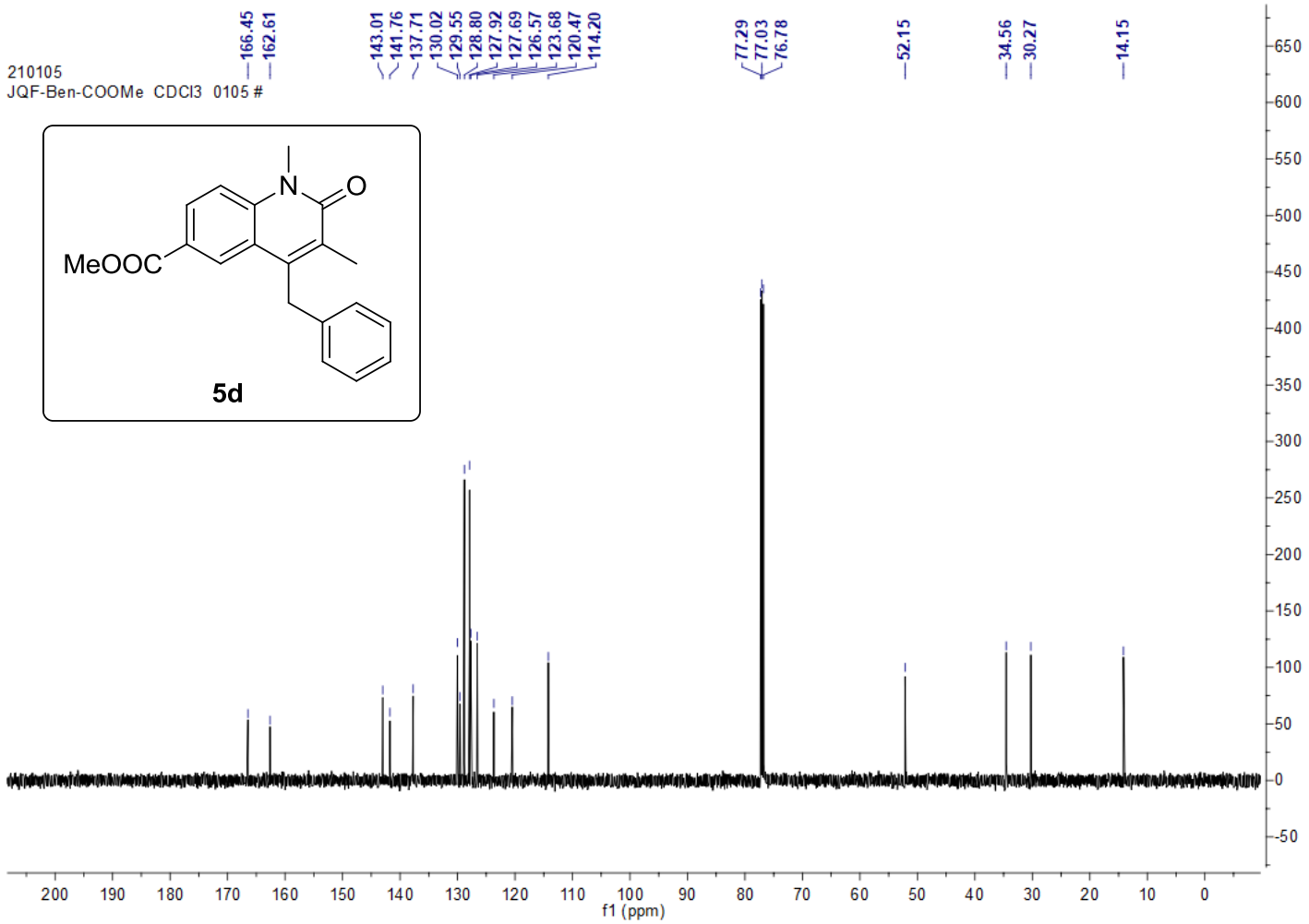
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5c



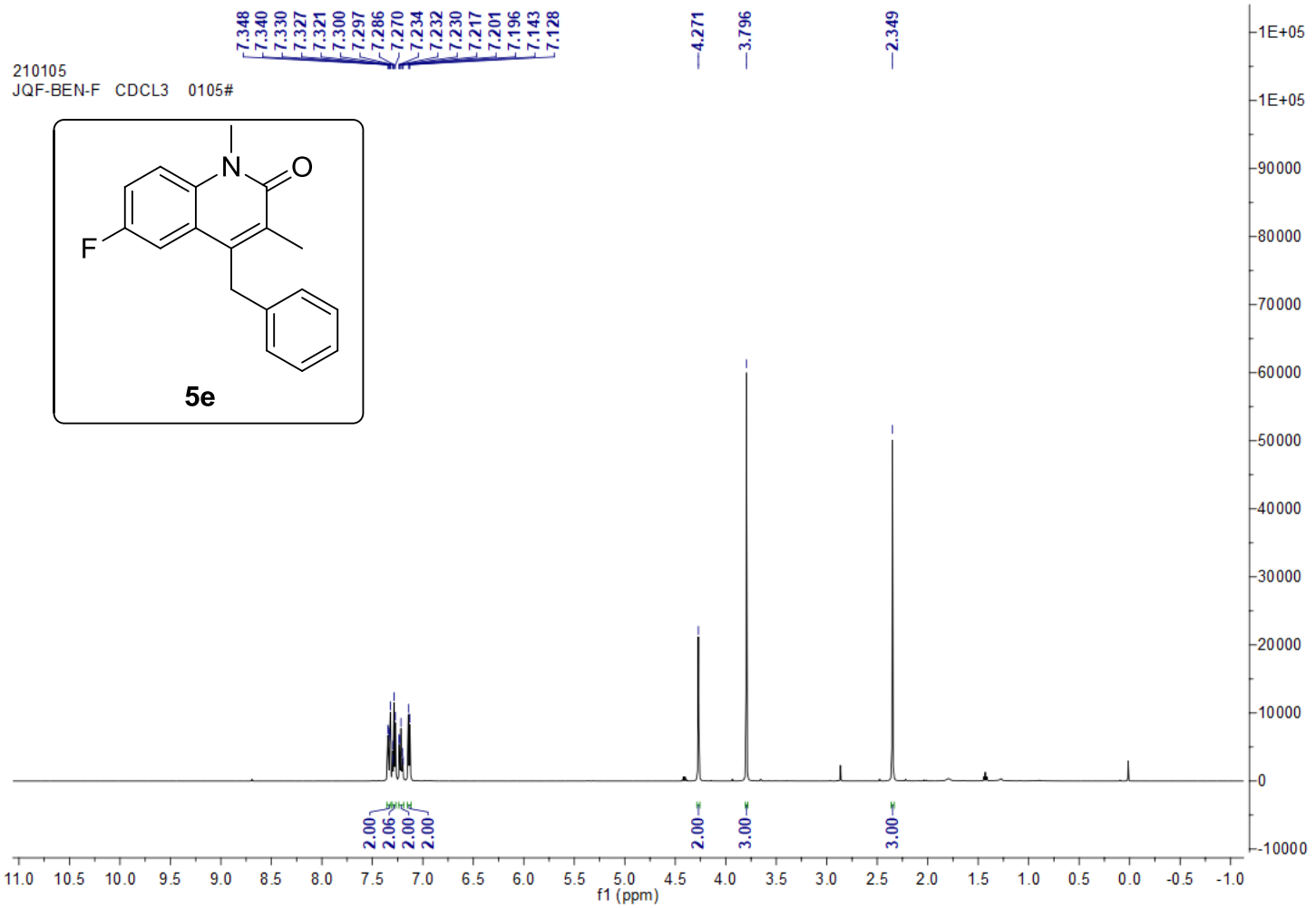
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5d



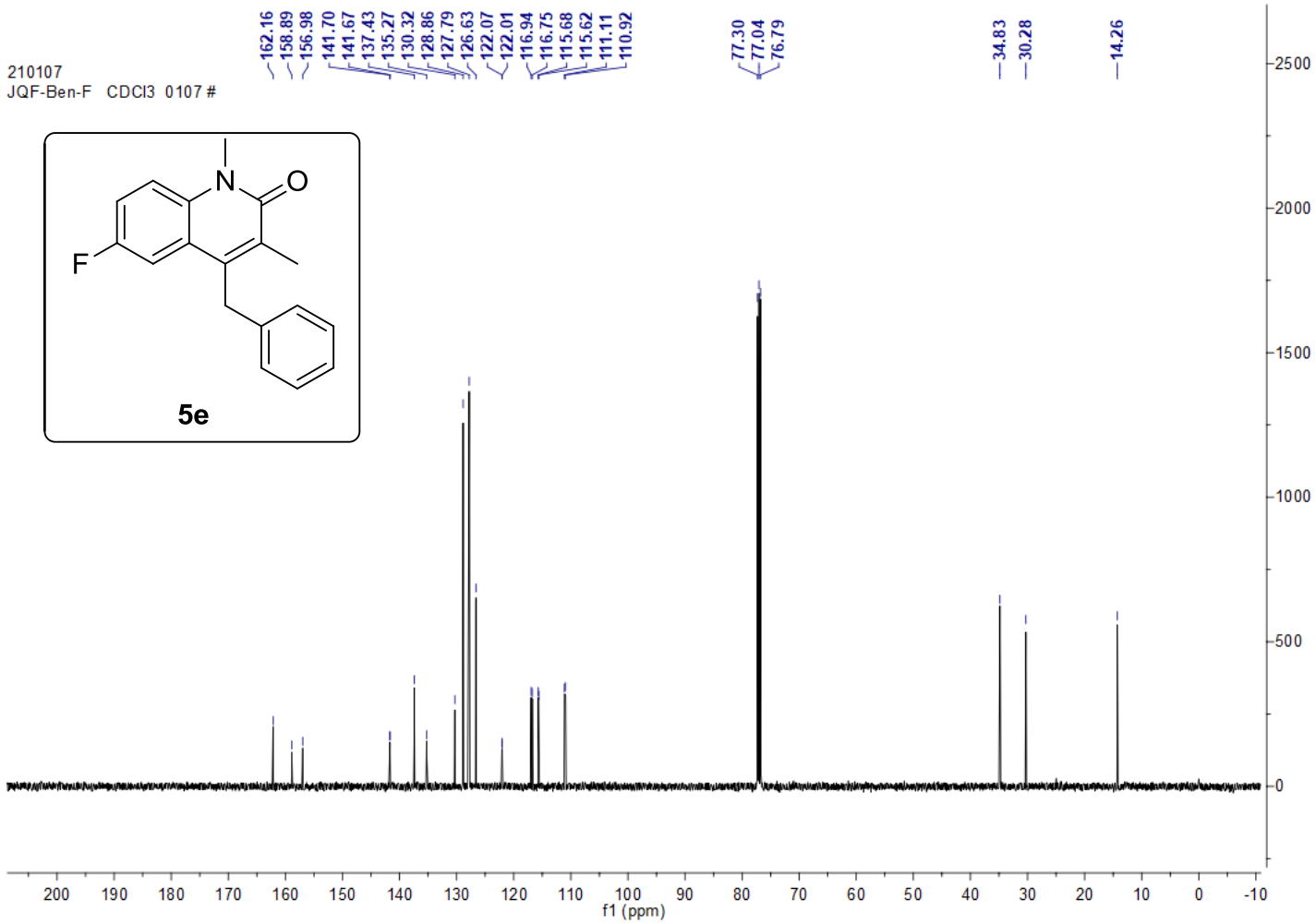
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5d



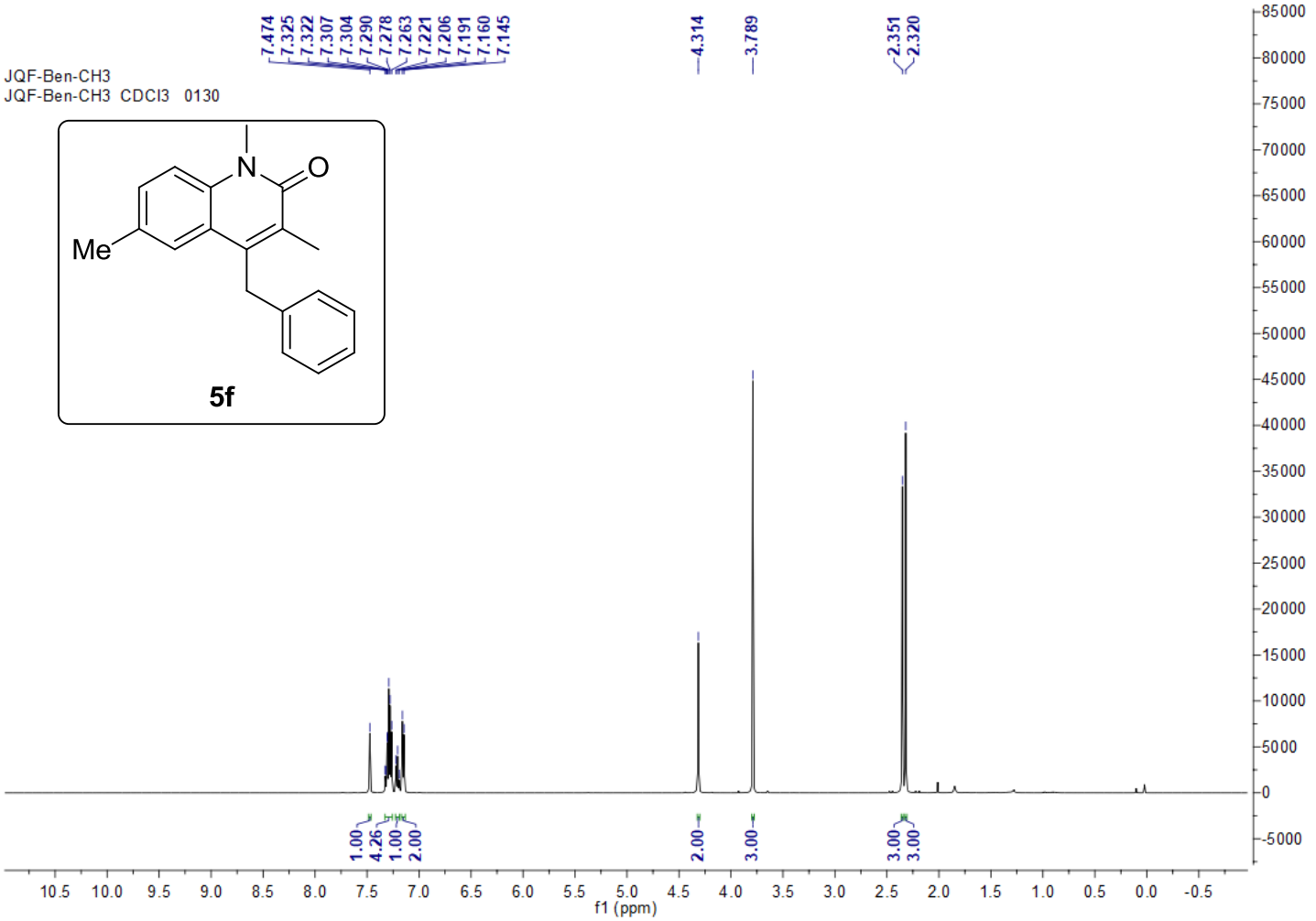
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5e



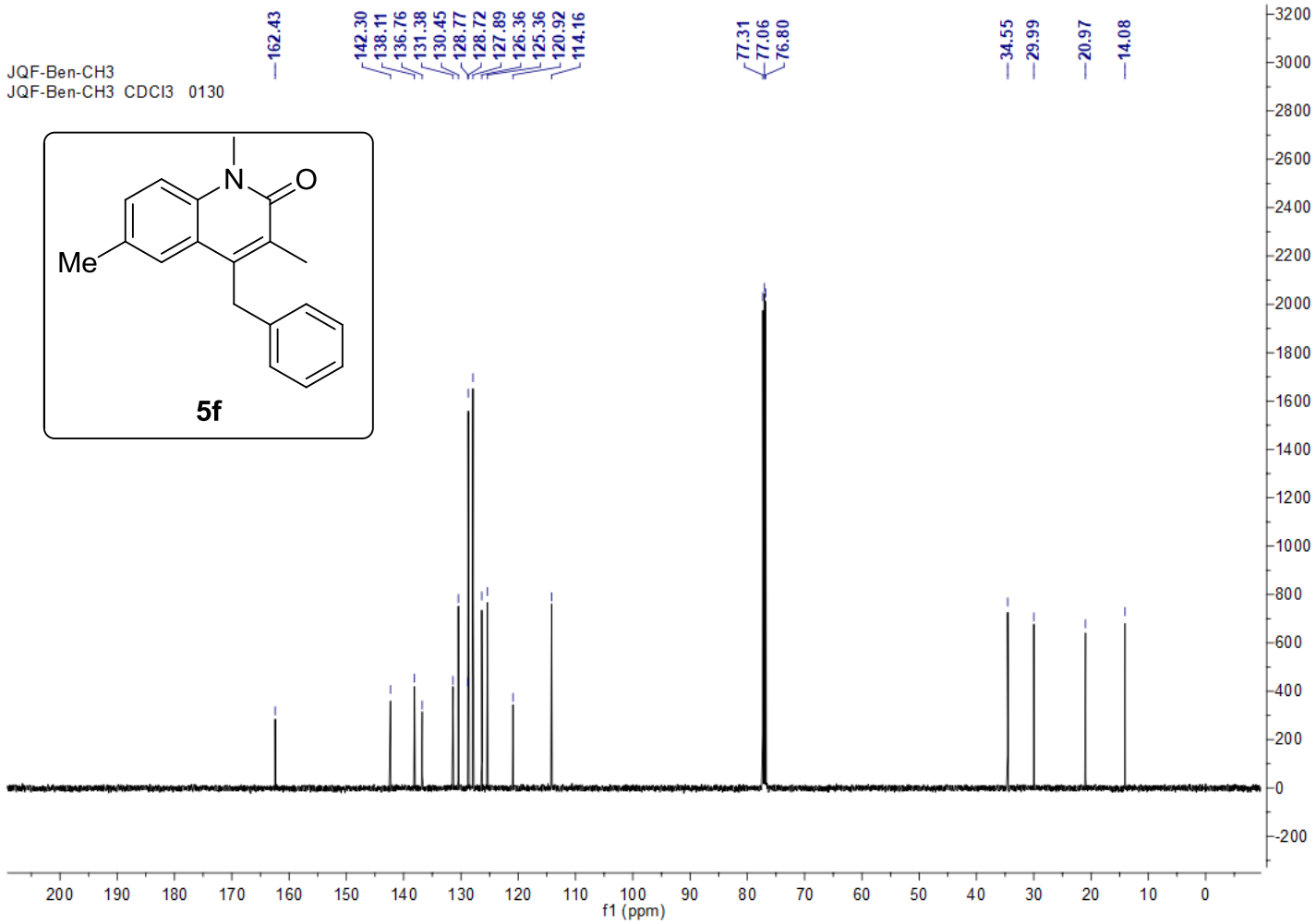
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5e



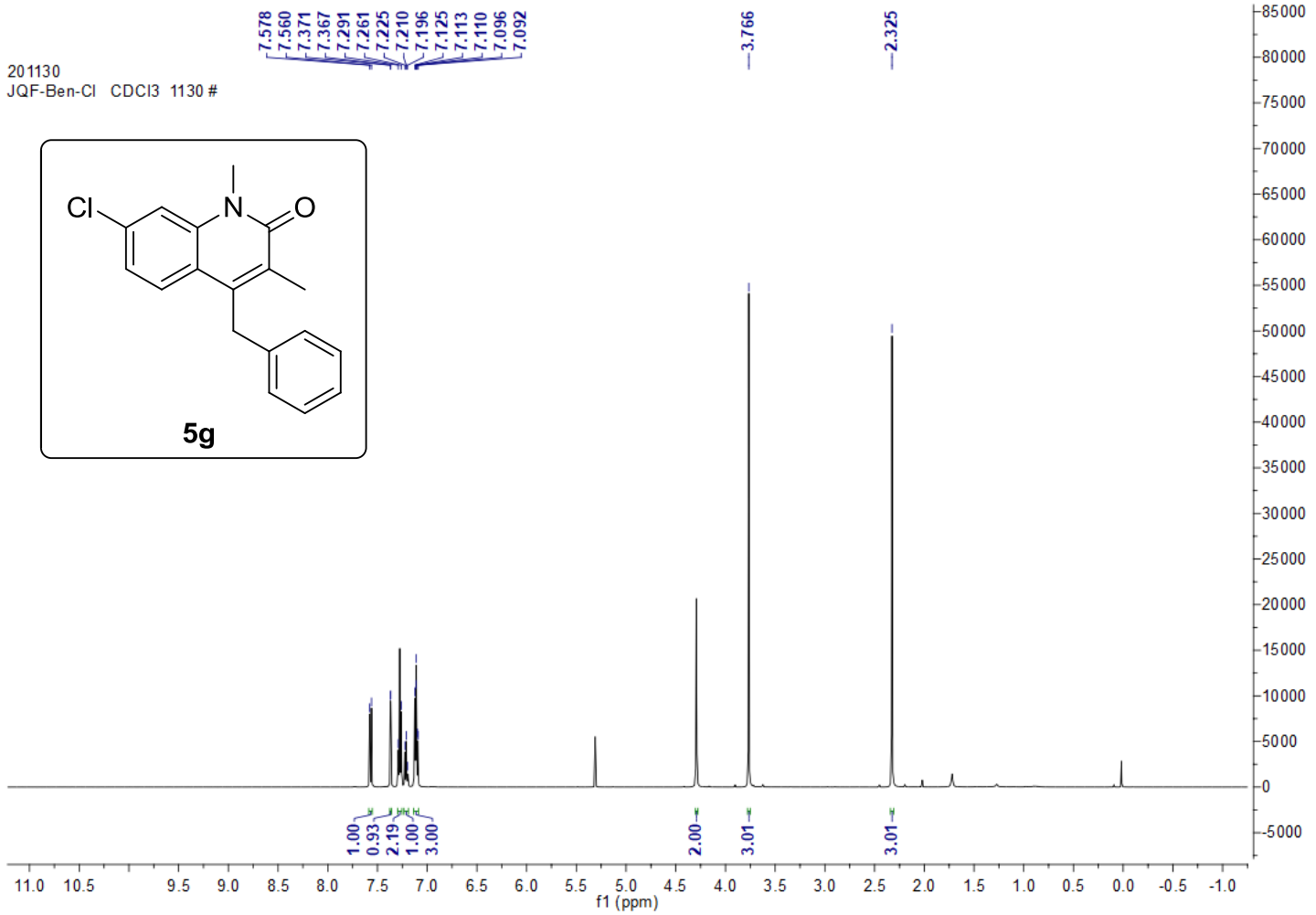
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5f



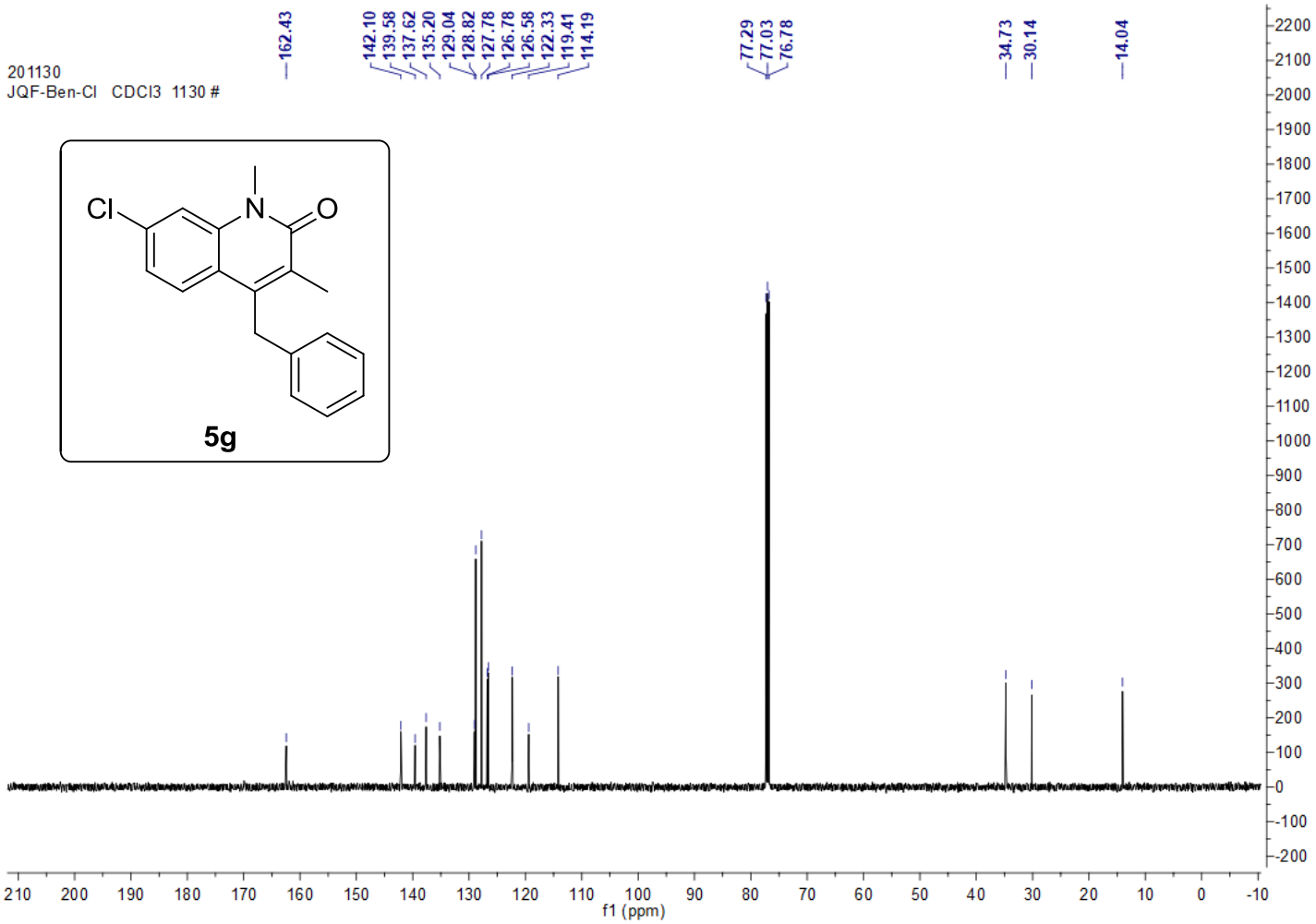
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5f



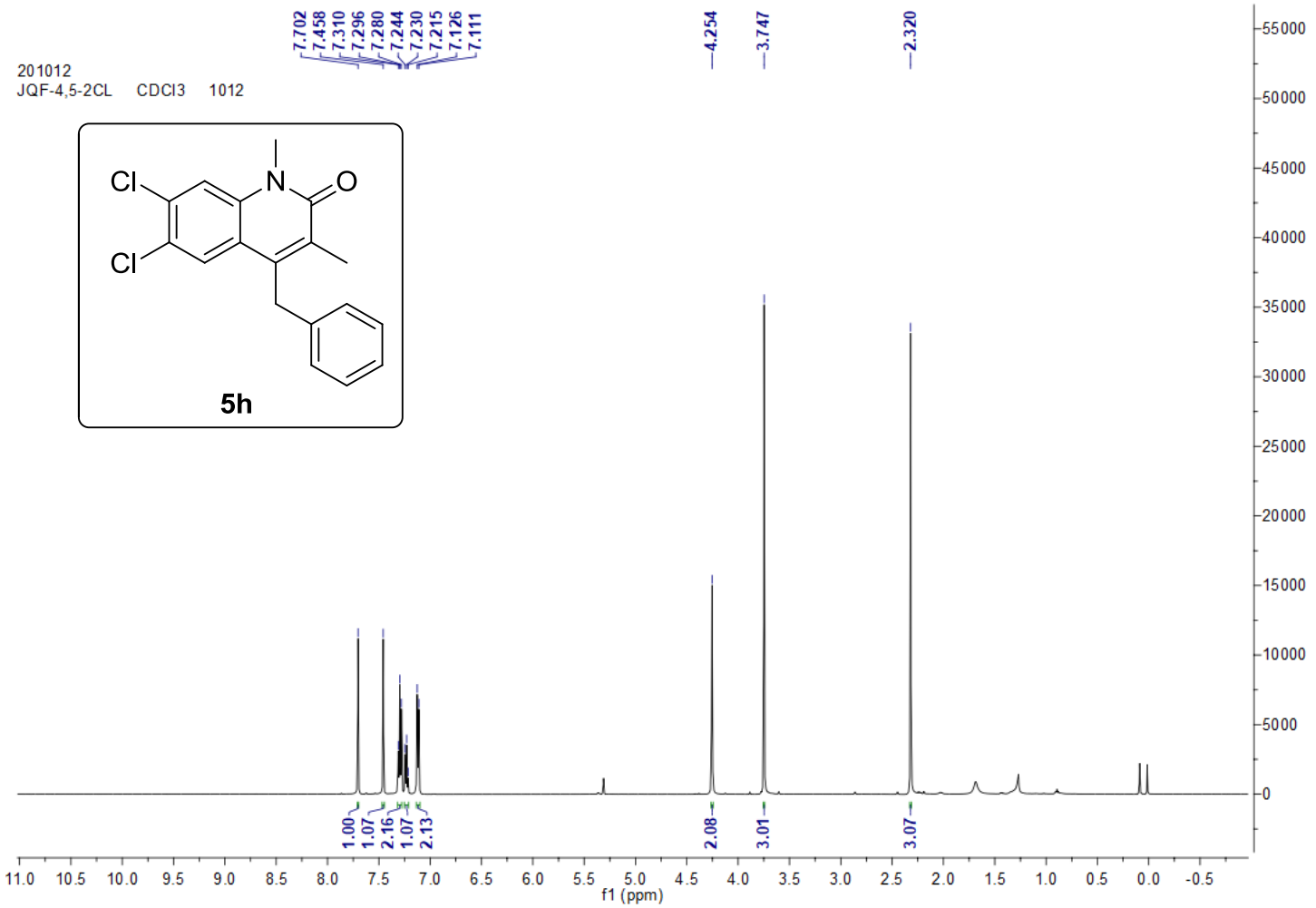
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5g



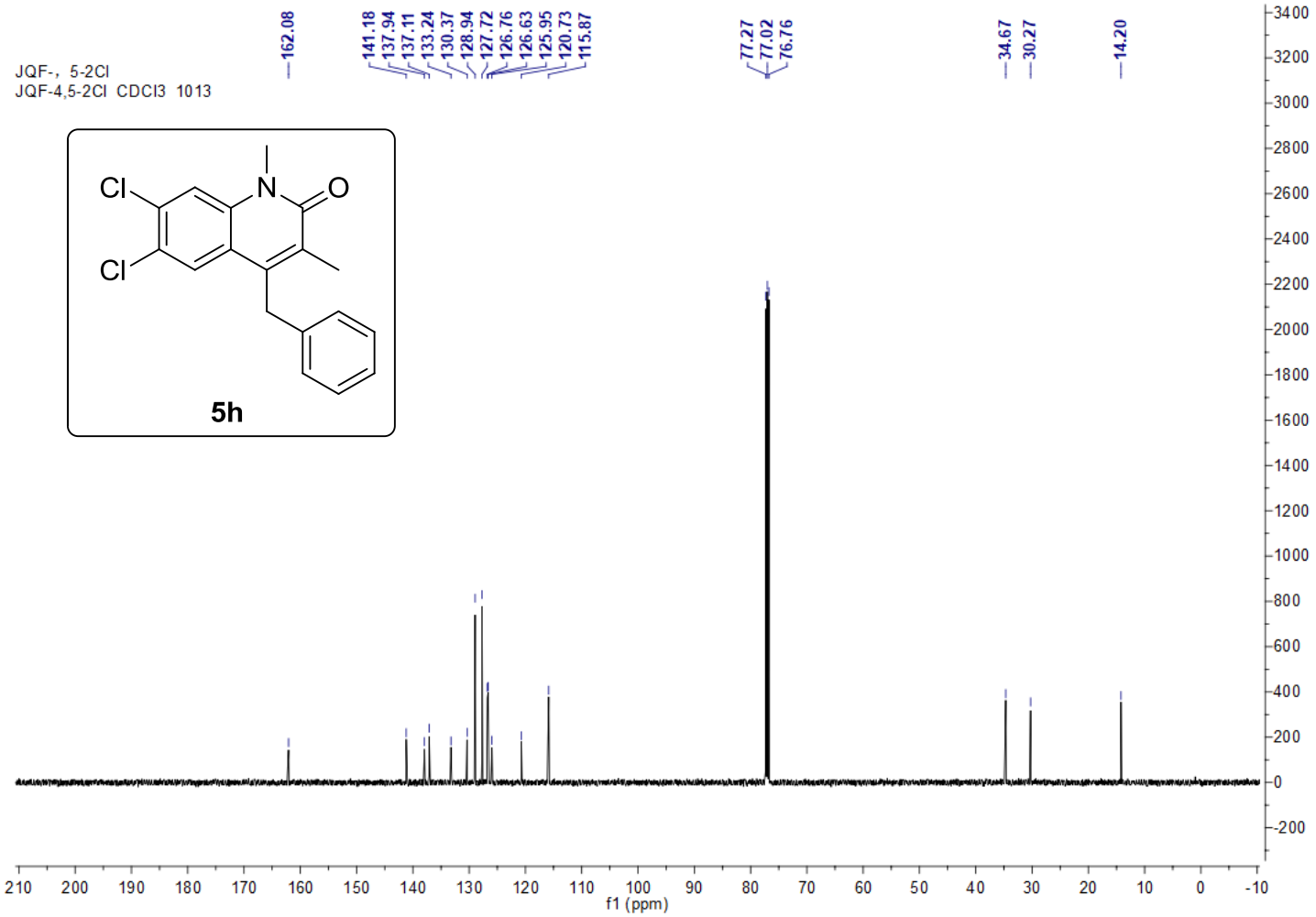
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5g



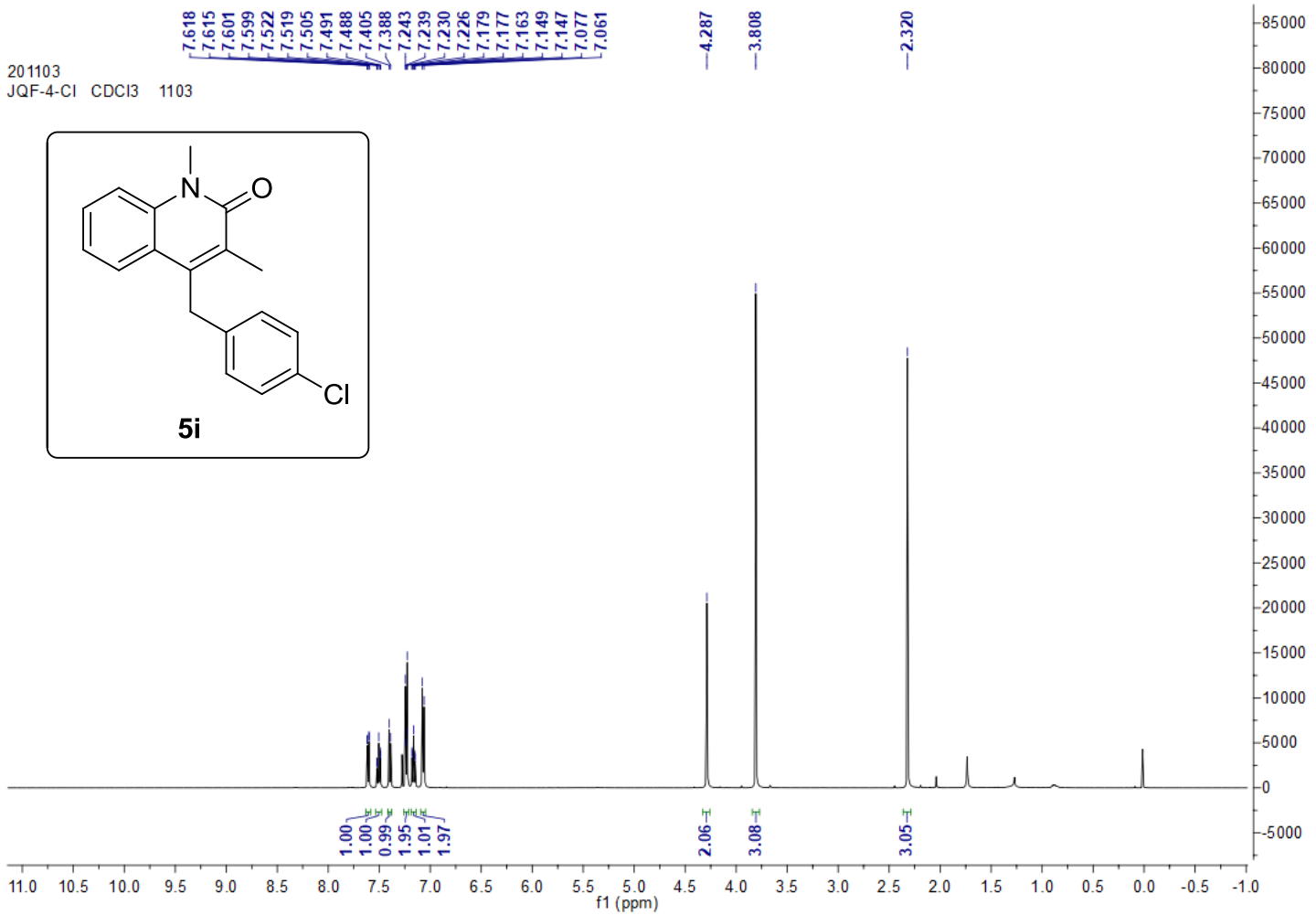
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5h



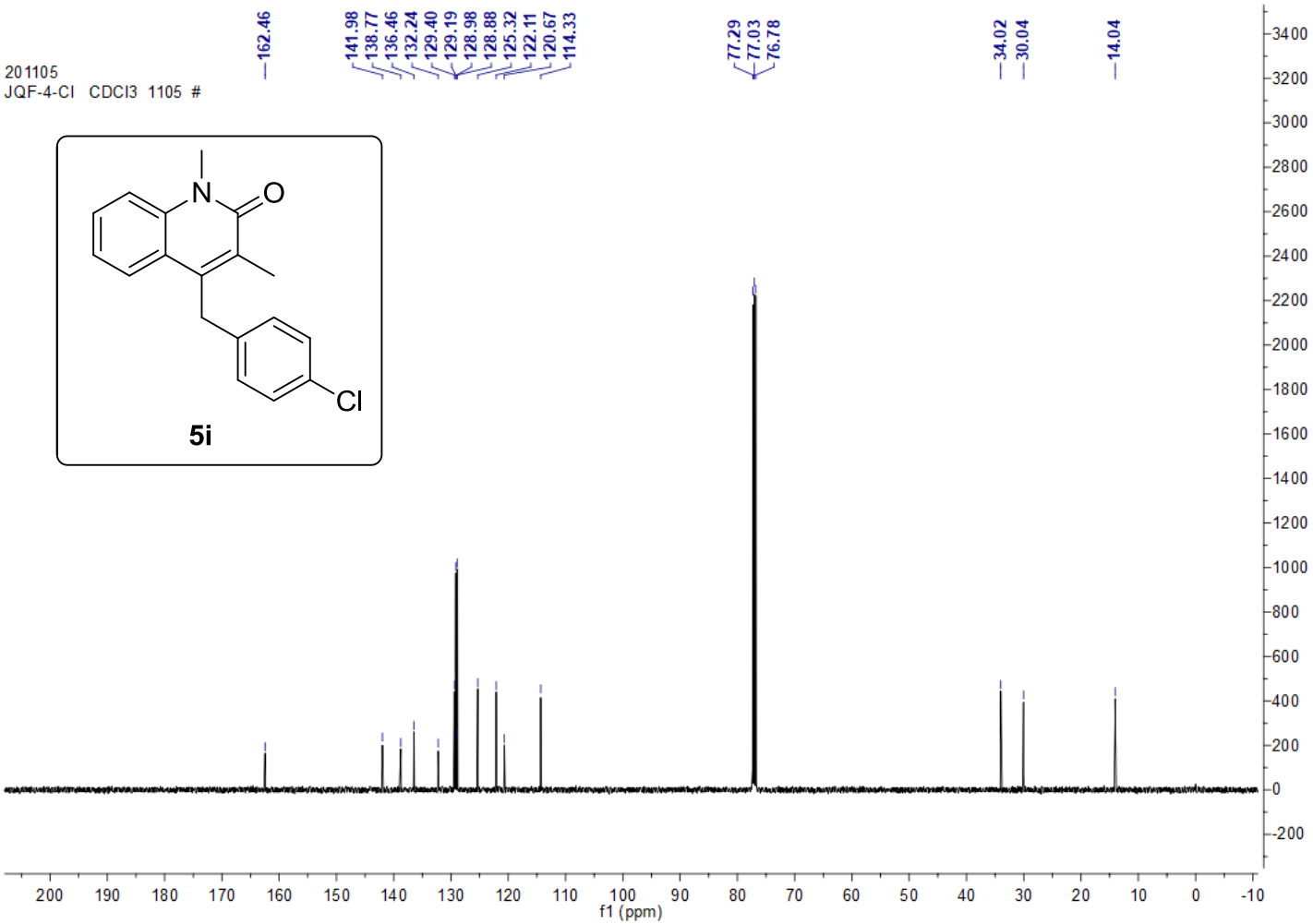
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5h



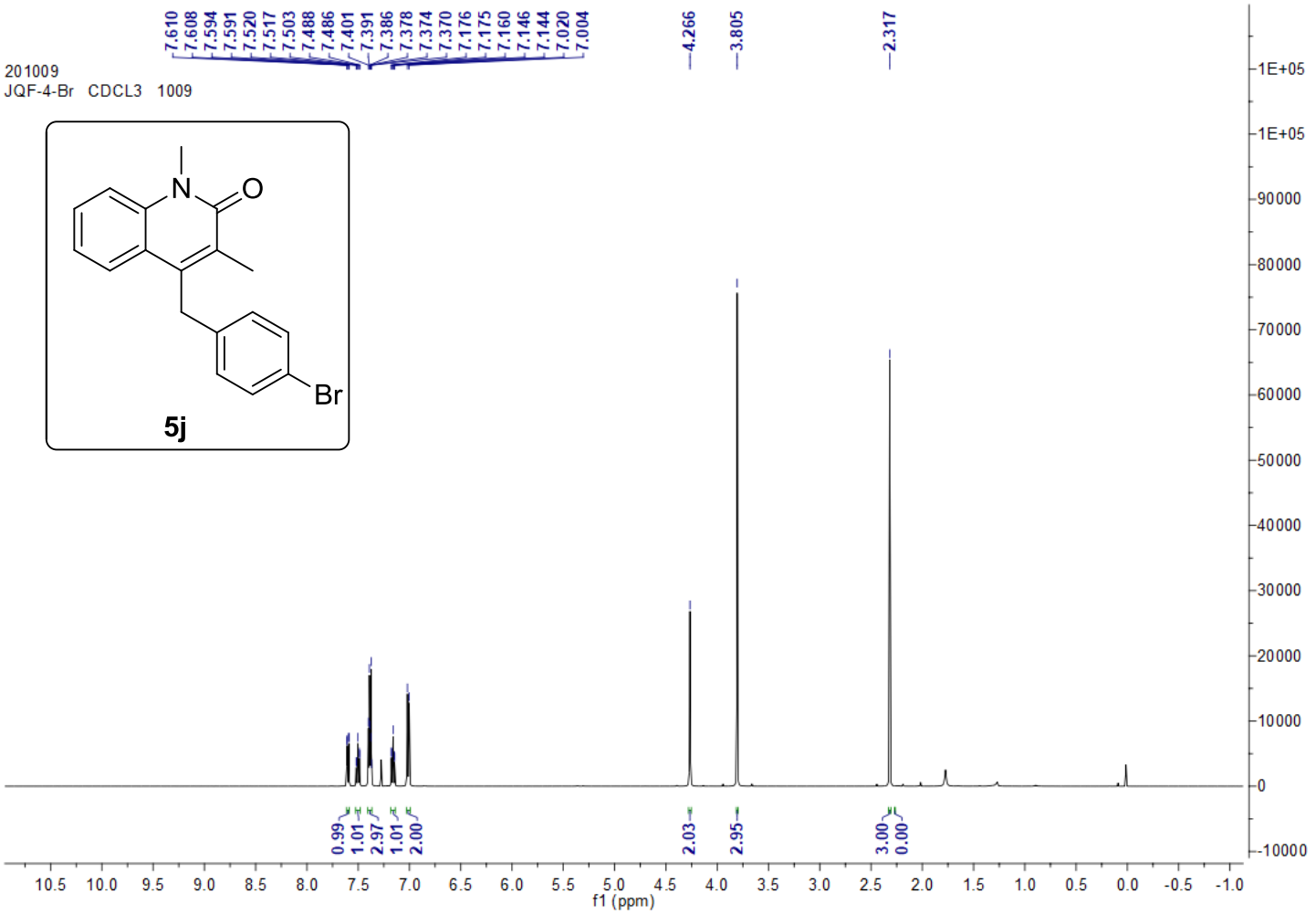
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5i



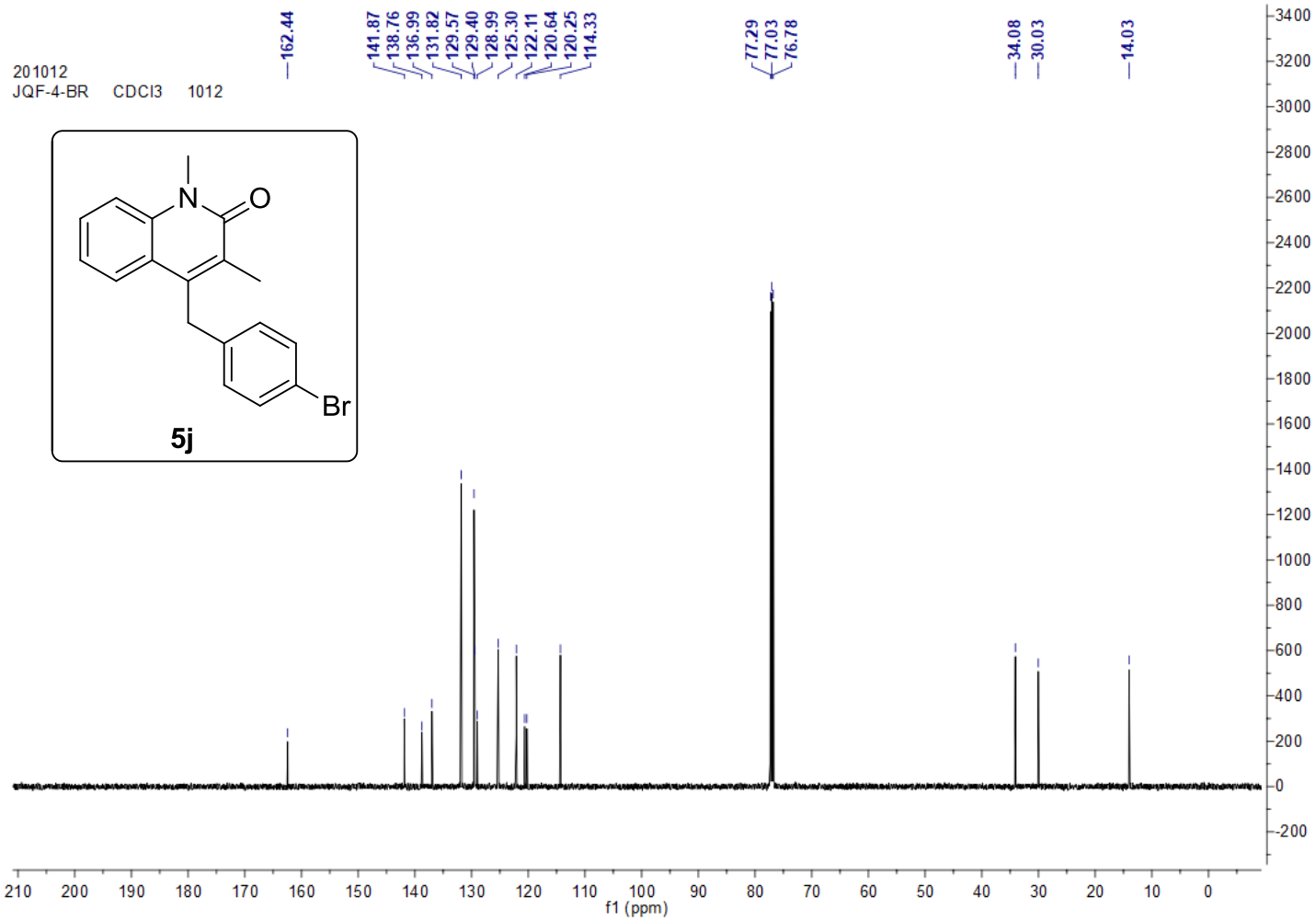
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5i



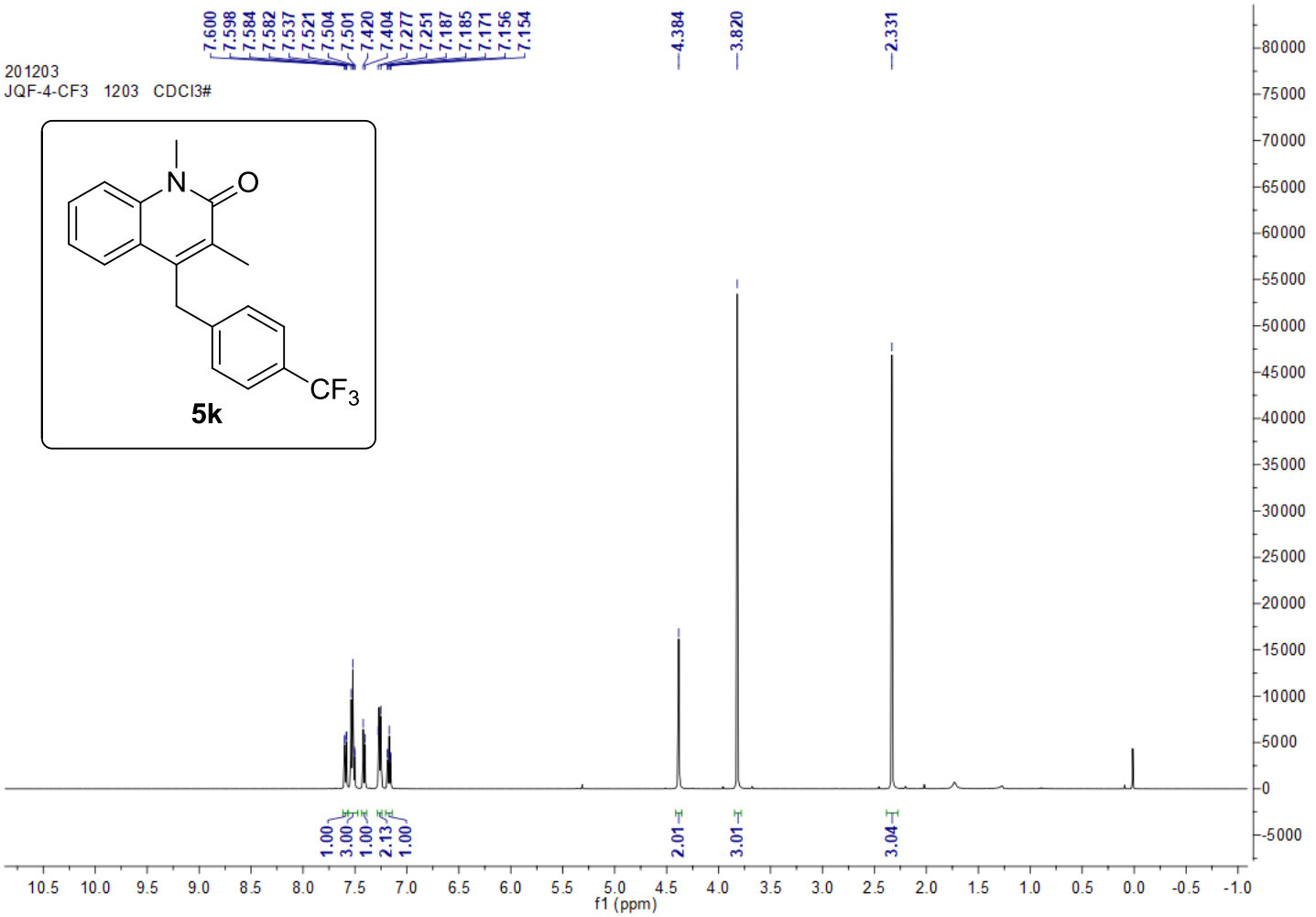
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5j



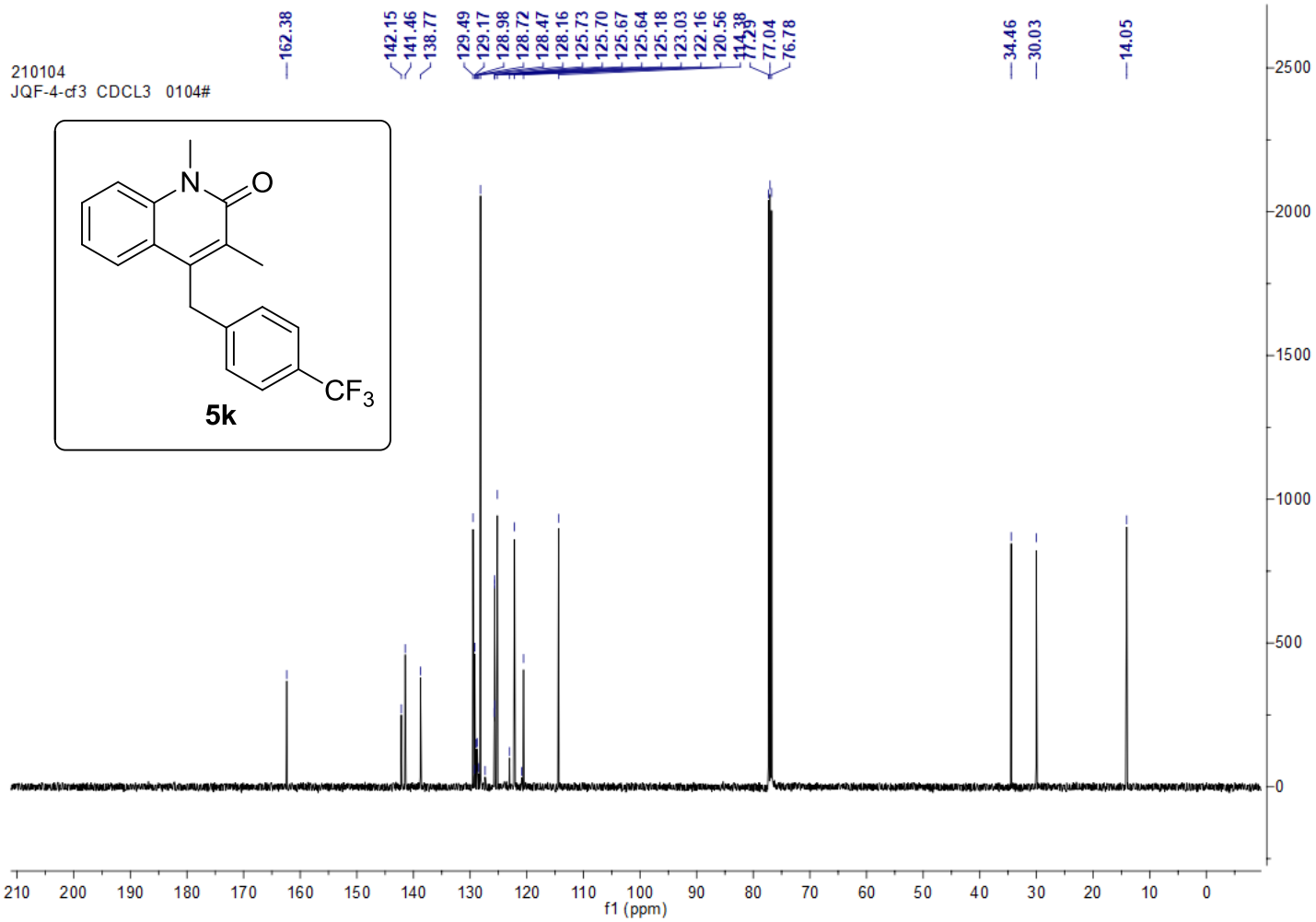
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5j



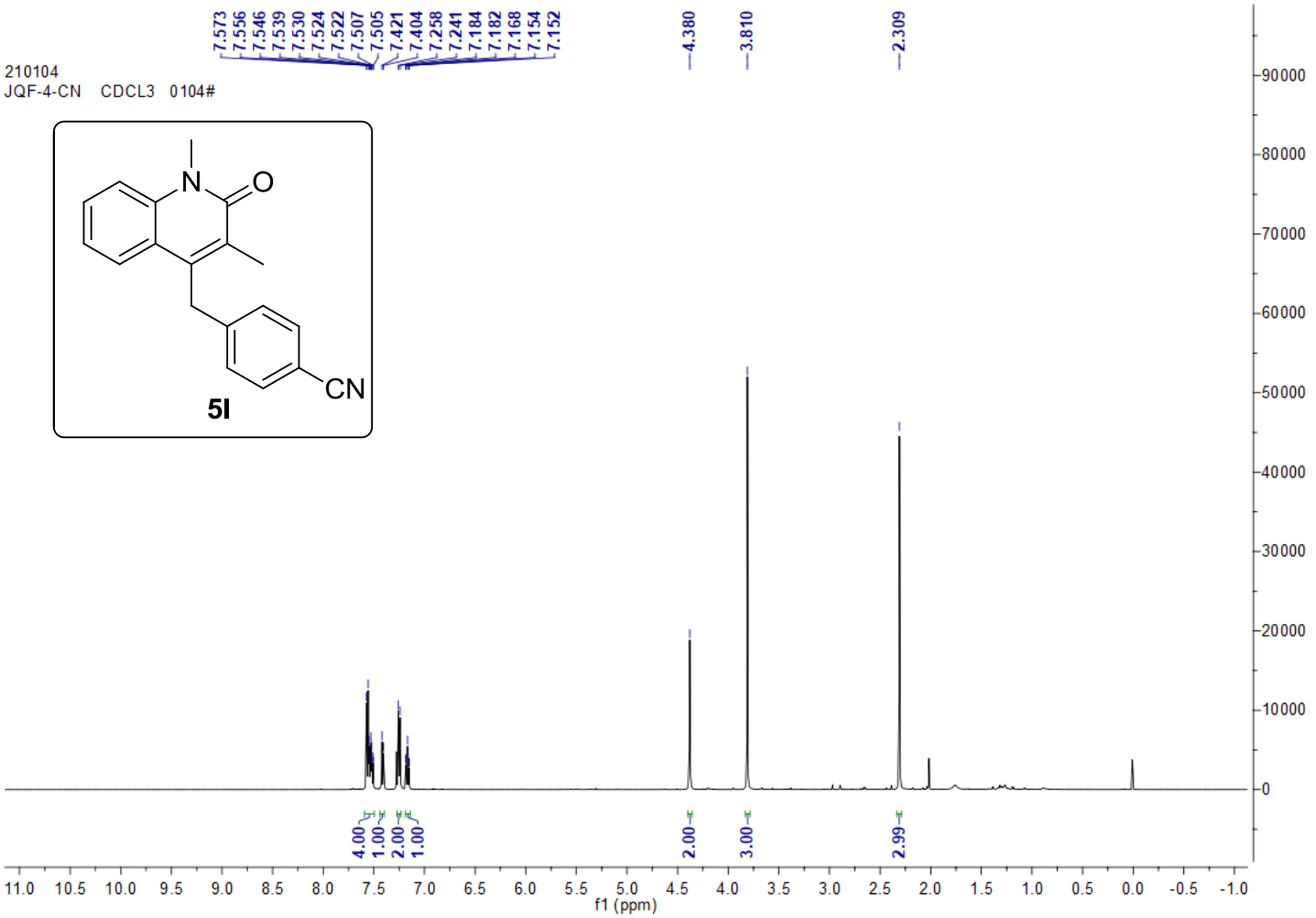
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5k



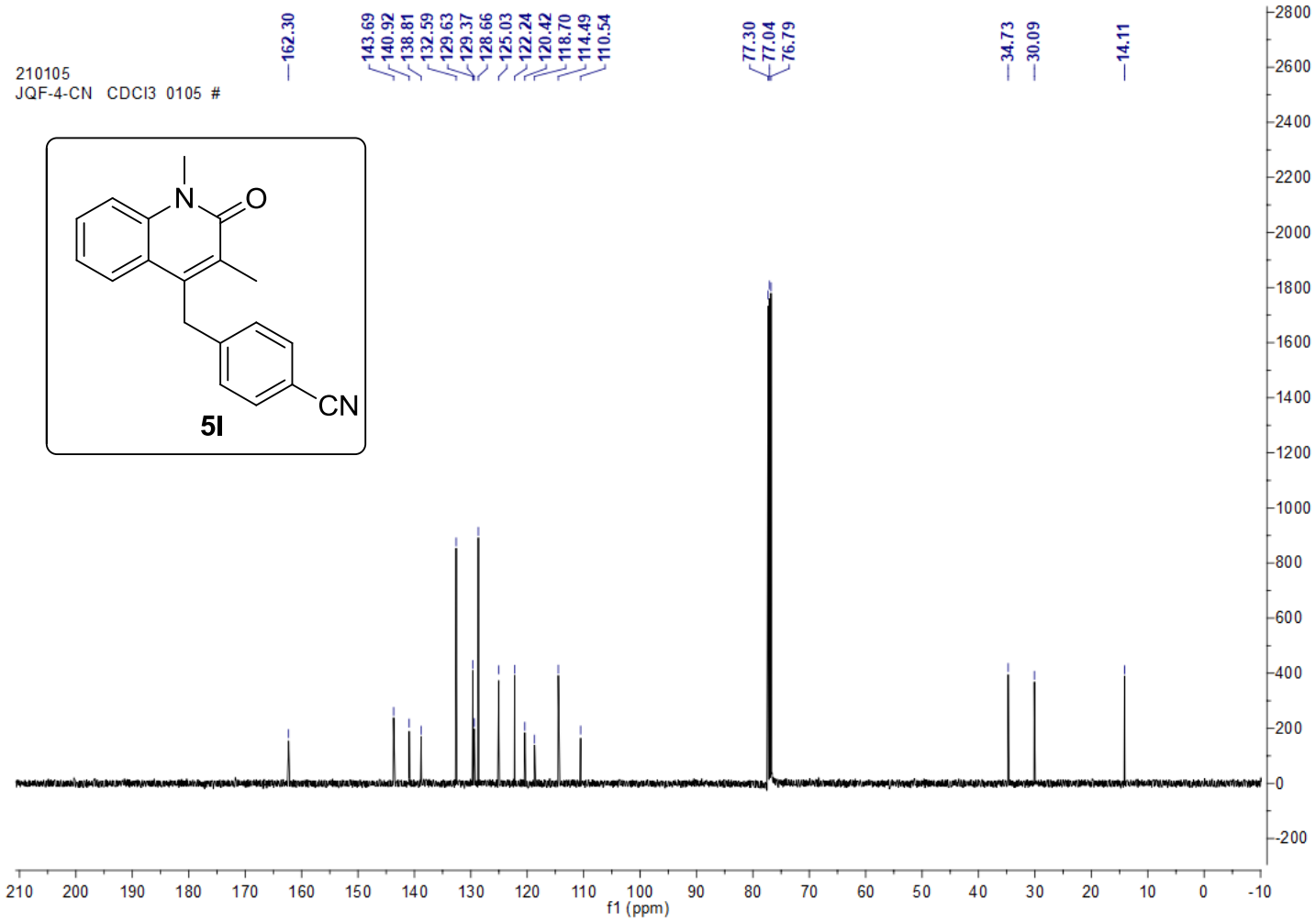
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5k



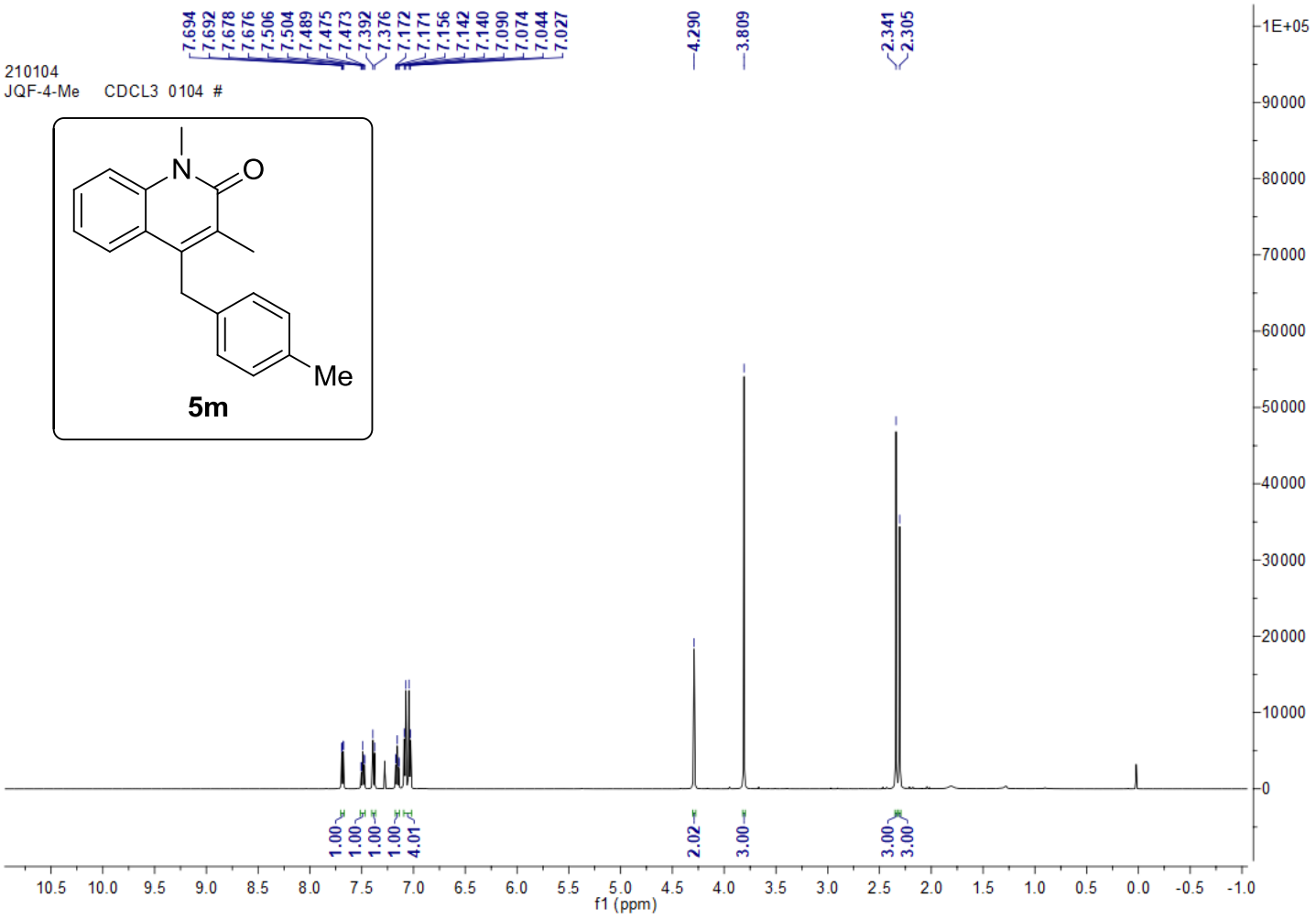
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5l



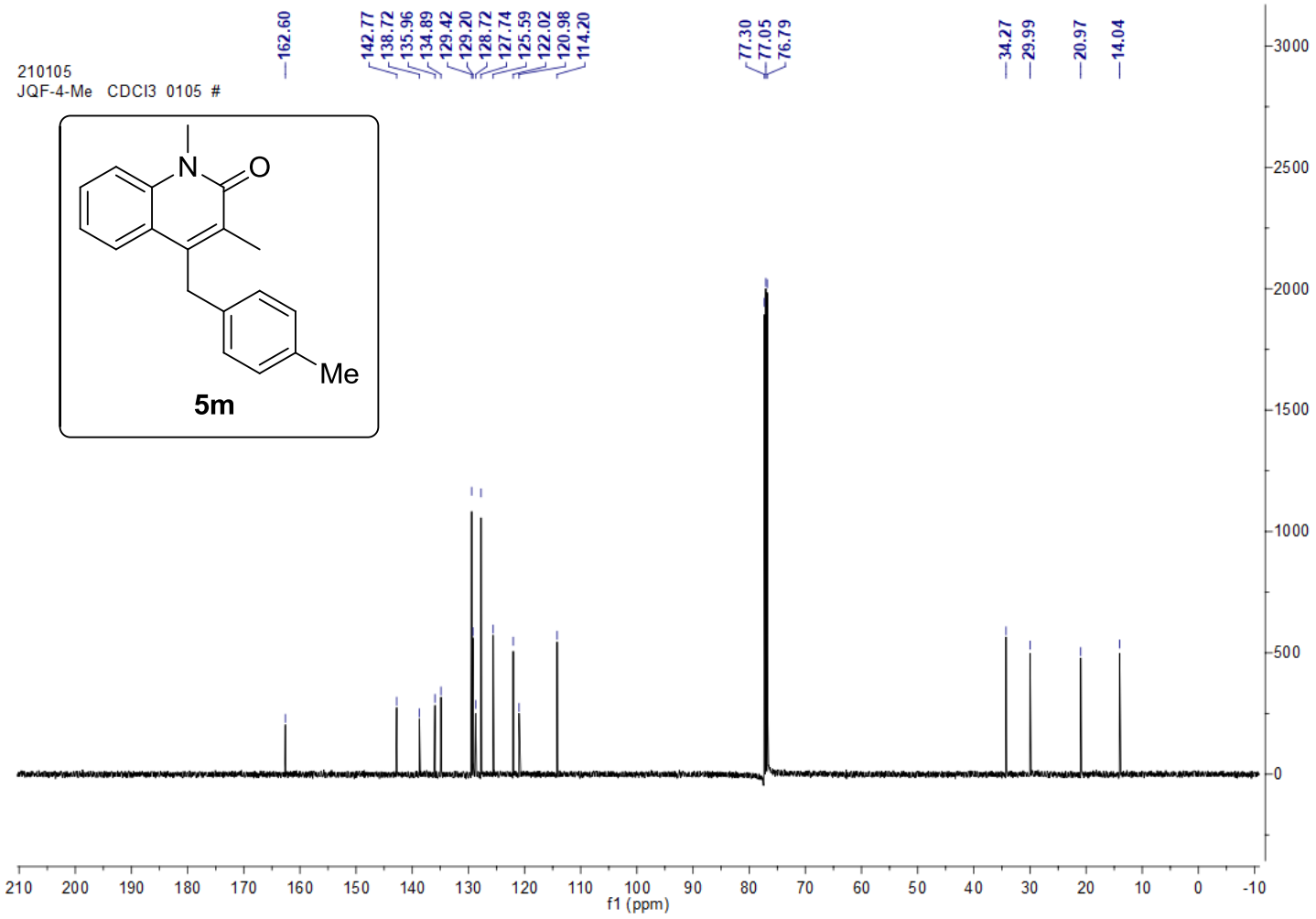
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5l



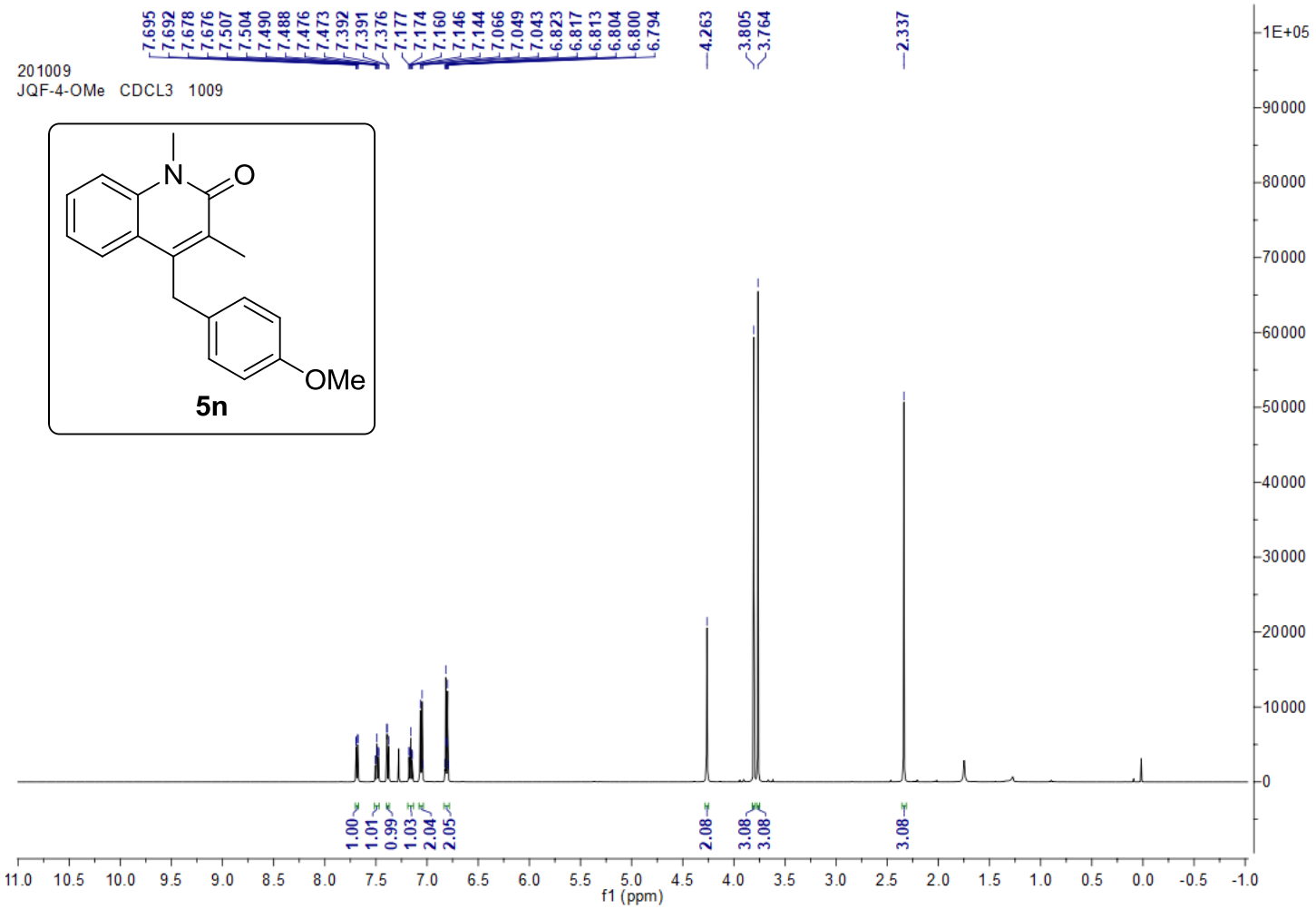
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5m



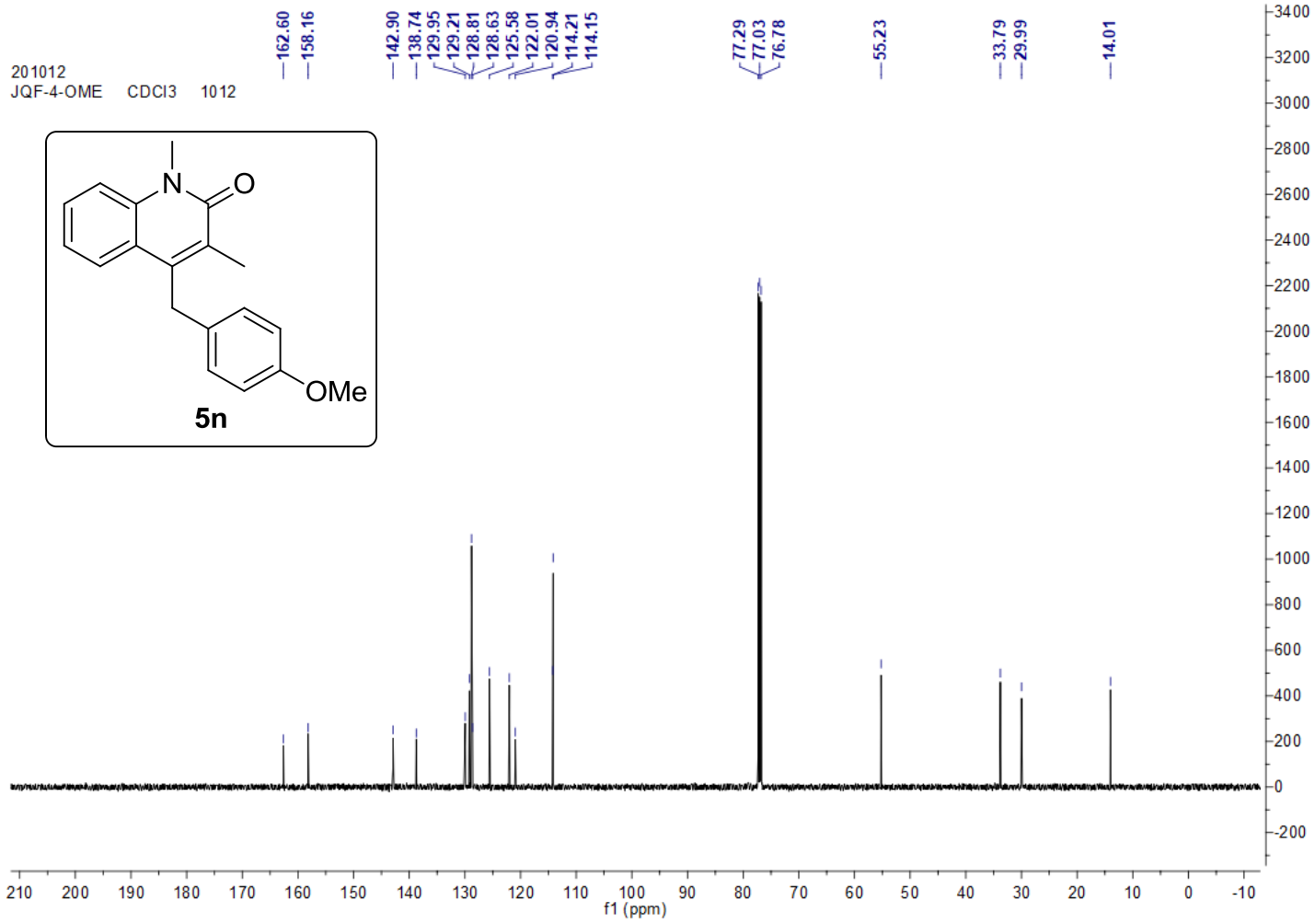
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5m



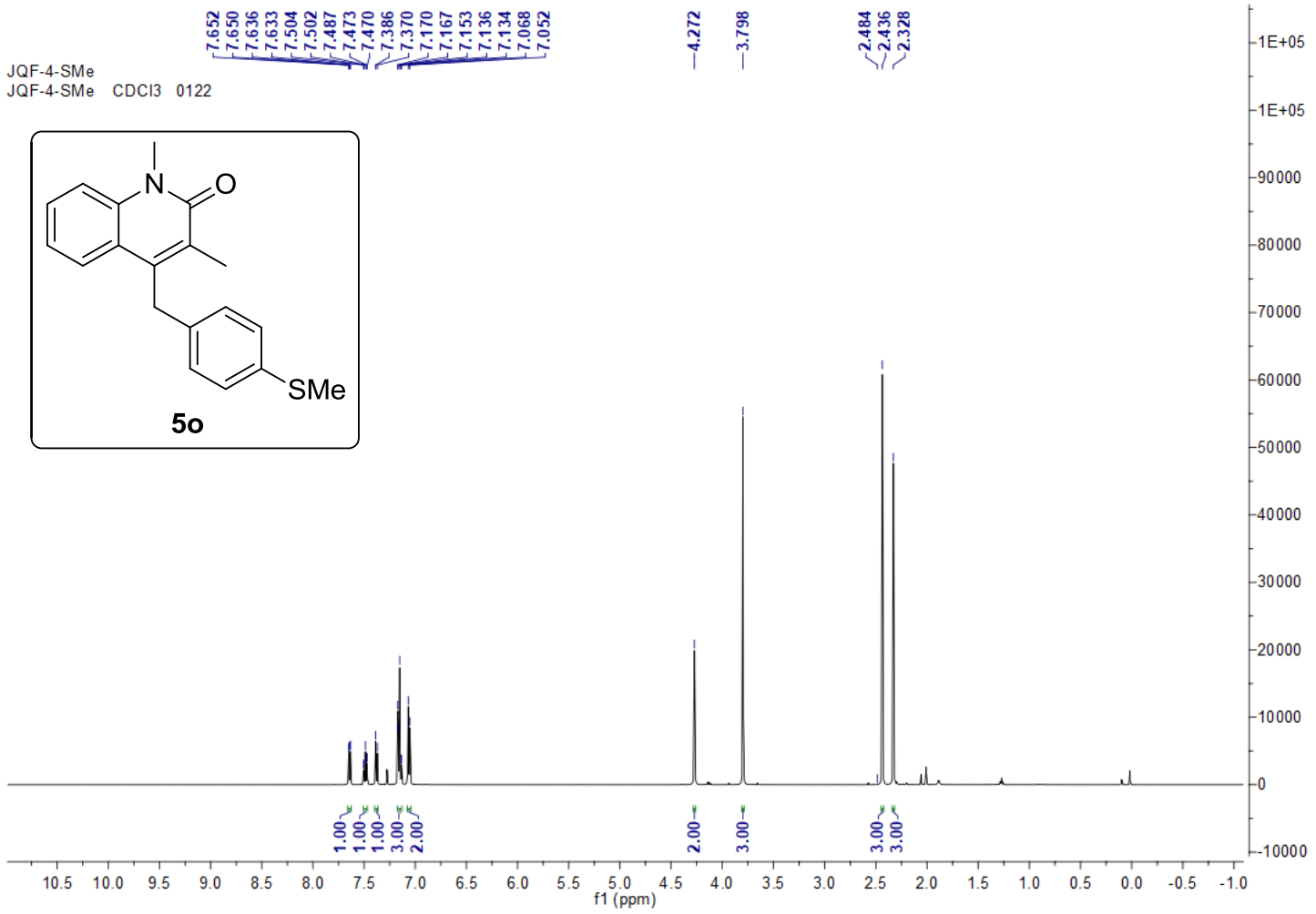
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5n



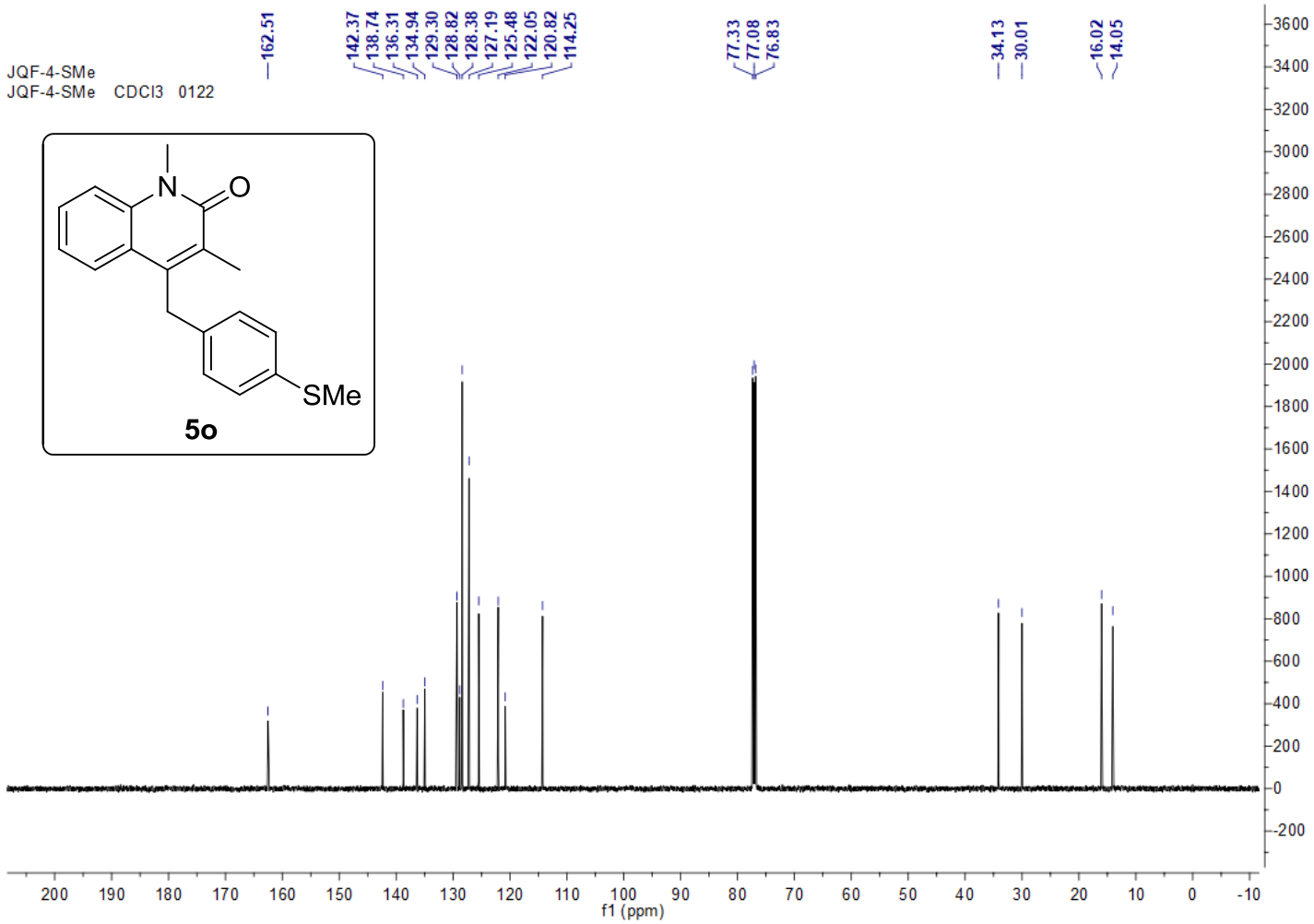
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5n



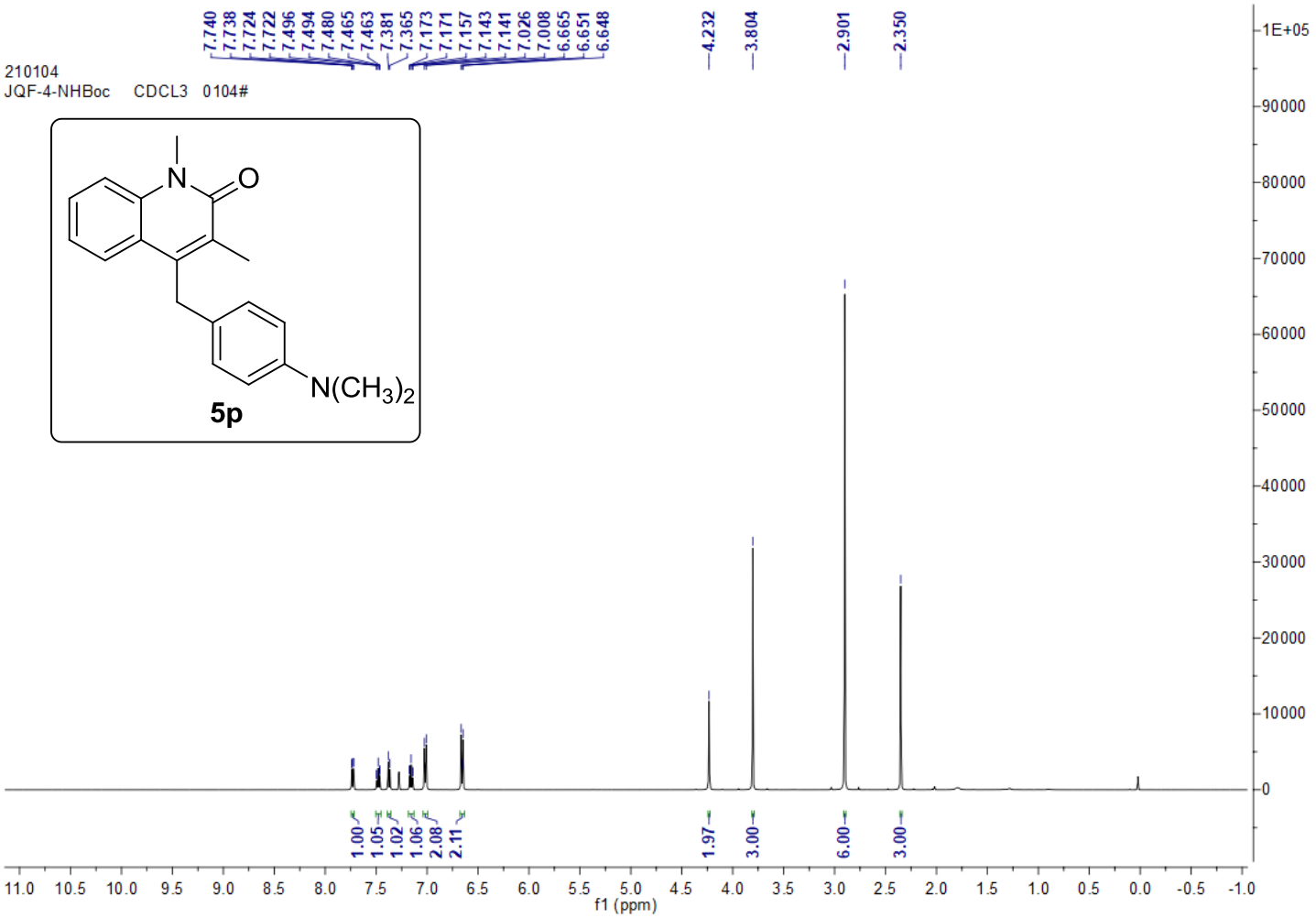
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5o



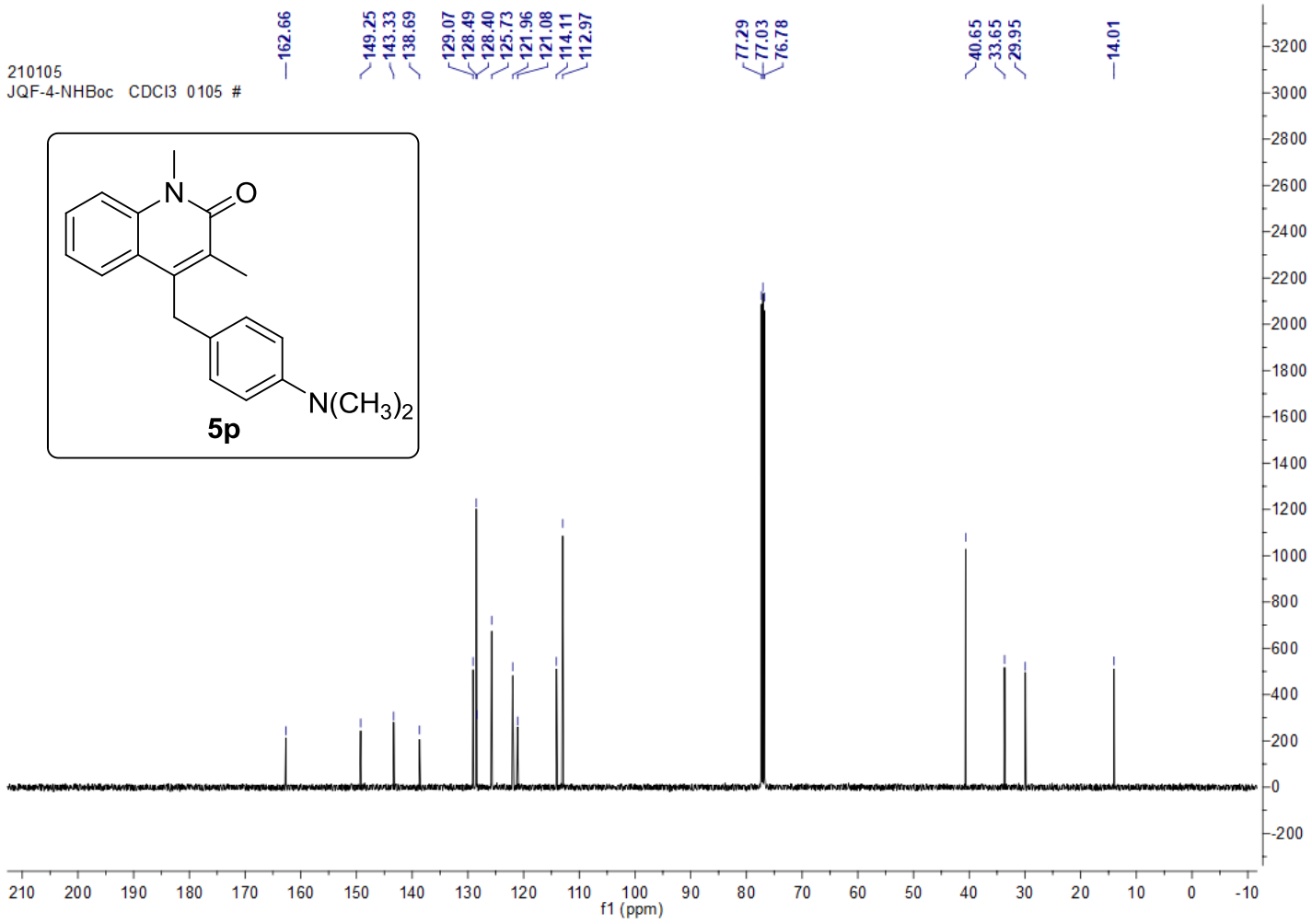
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5o



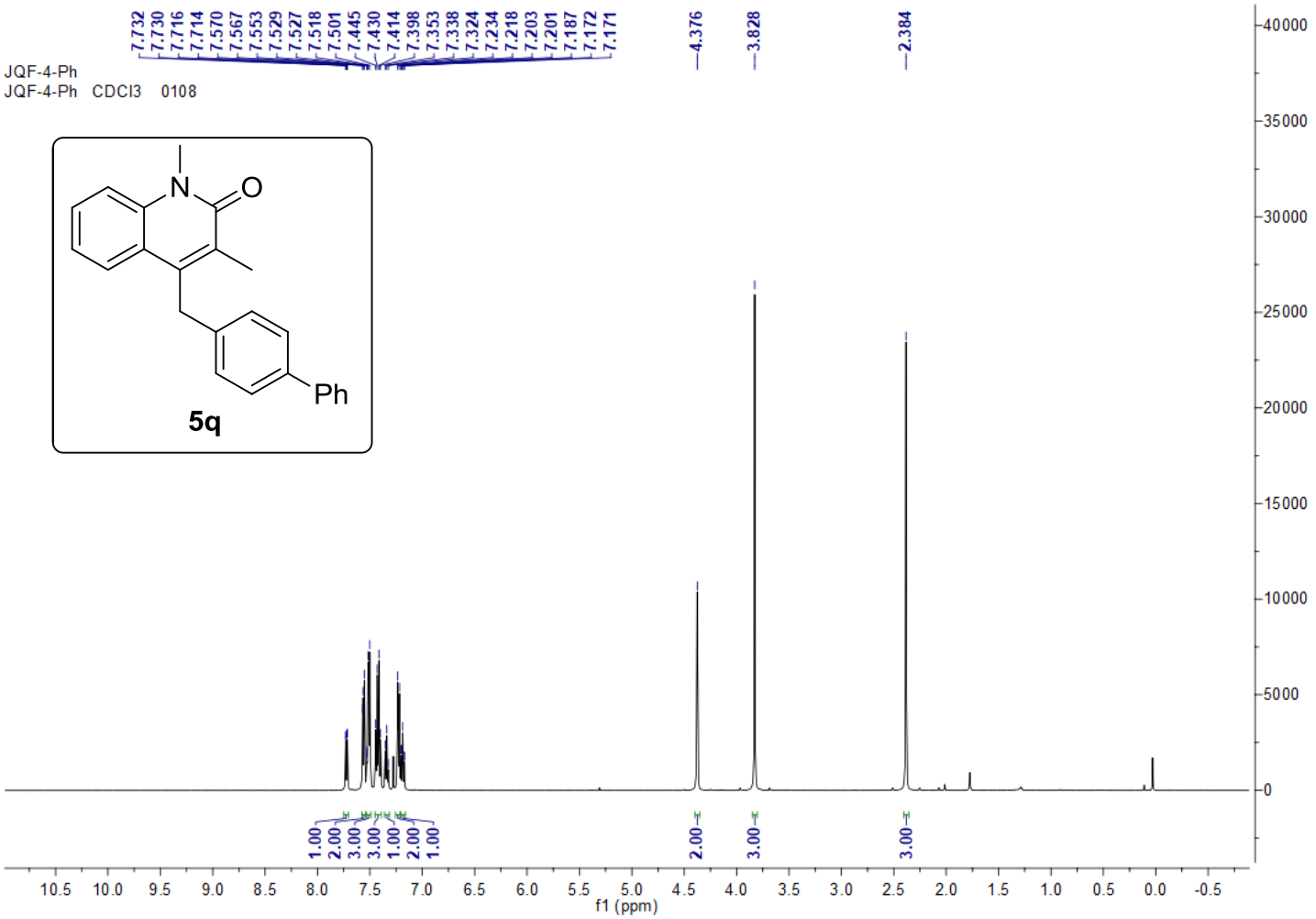
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5p



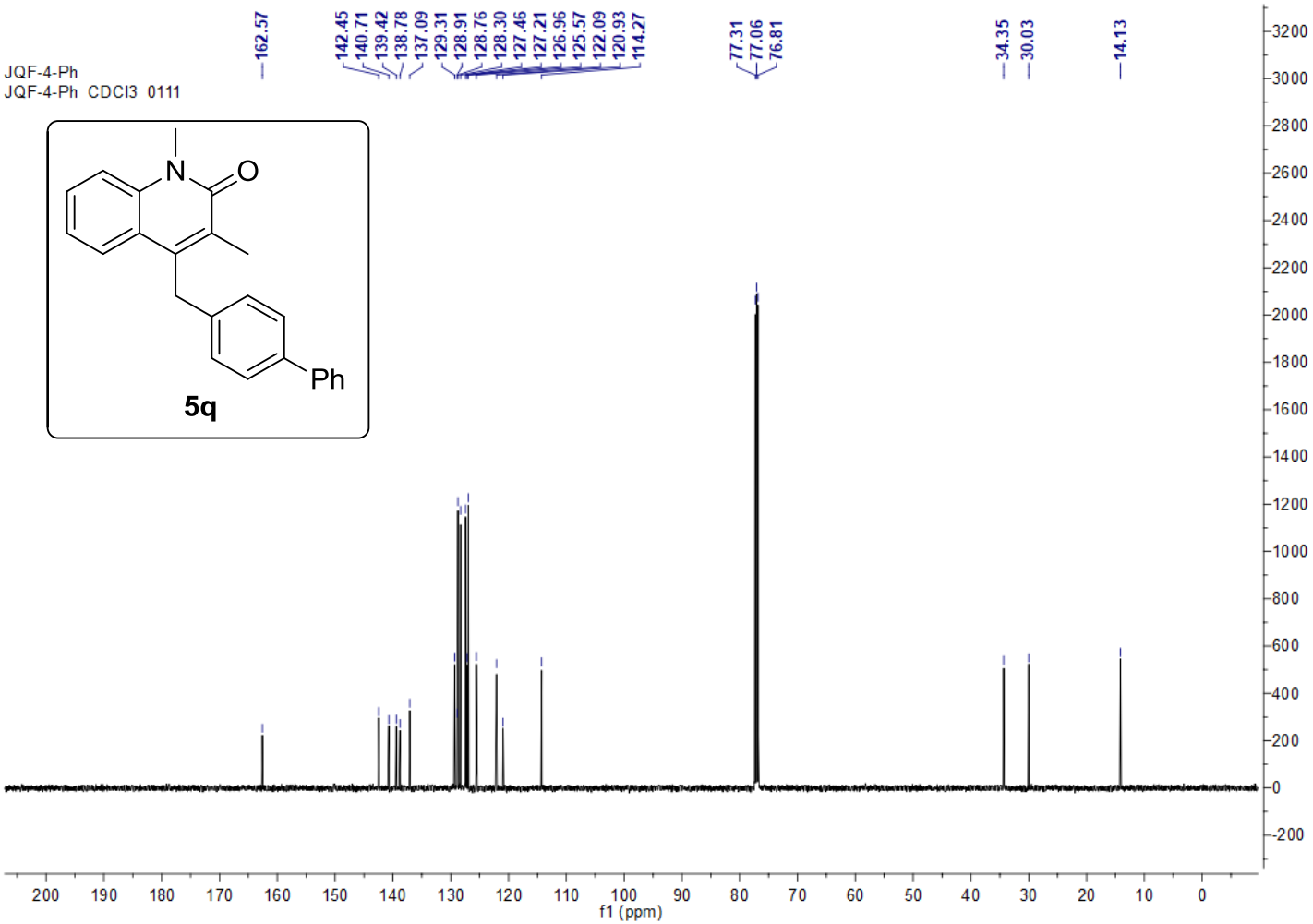
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5p



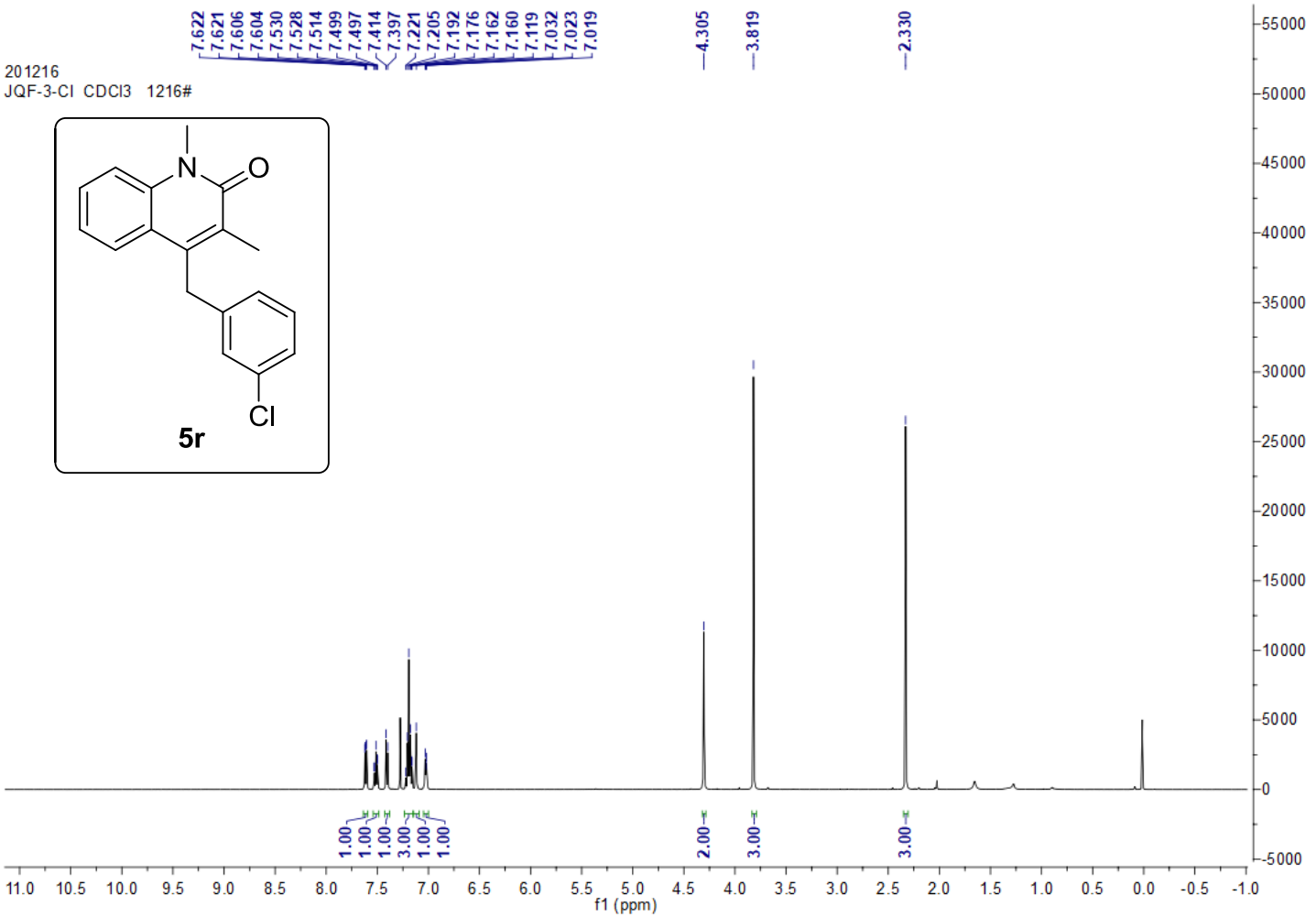
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5q



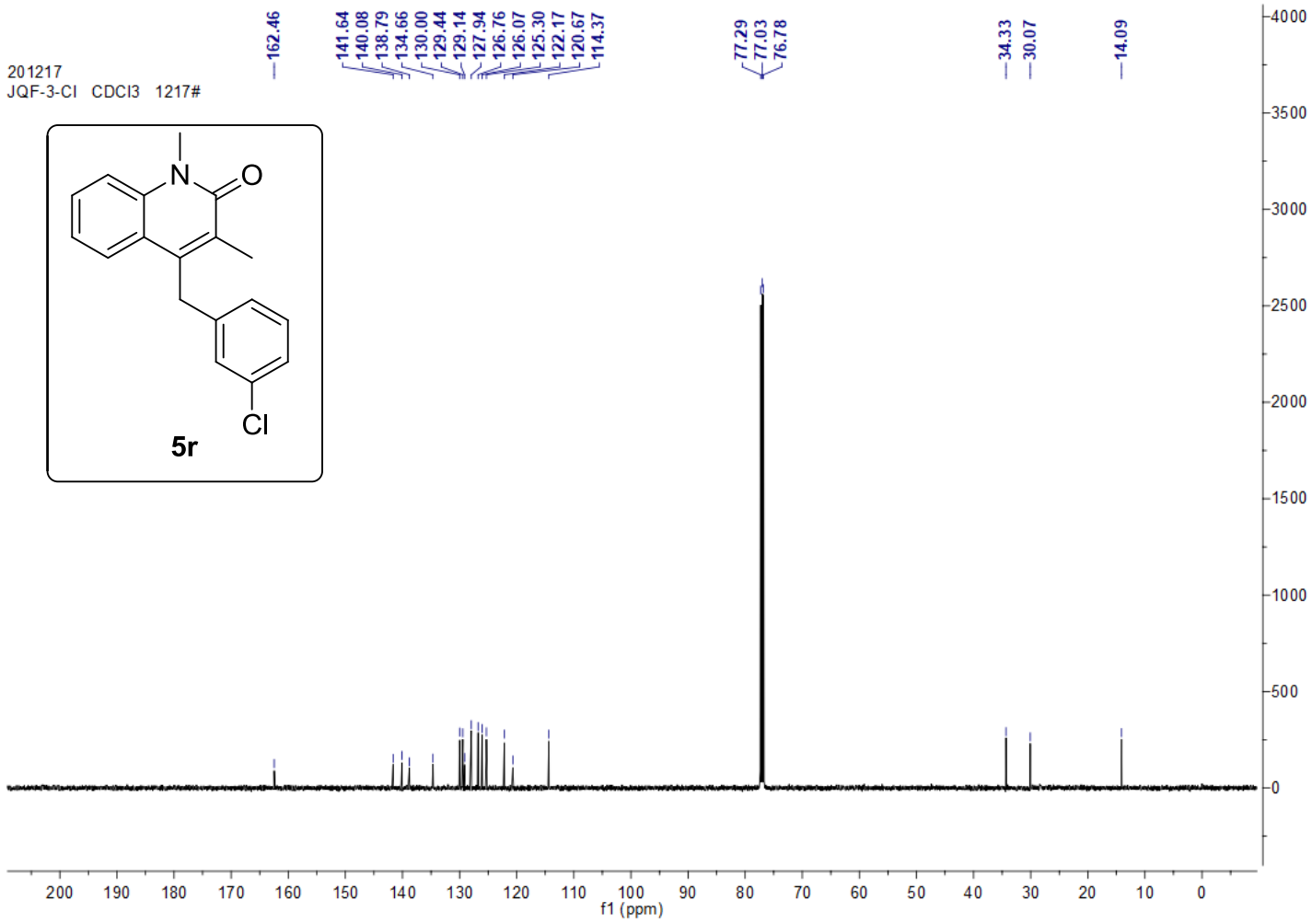
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5q



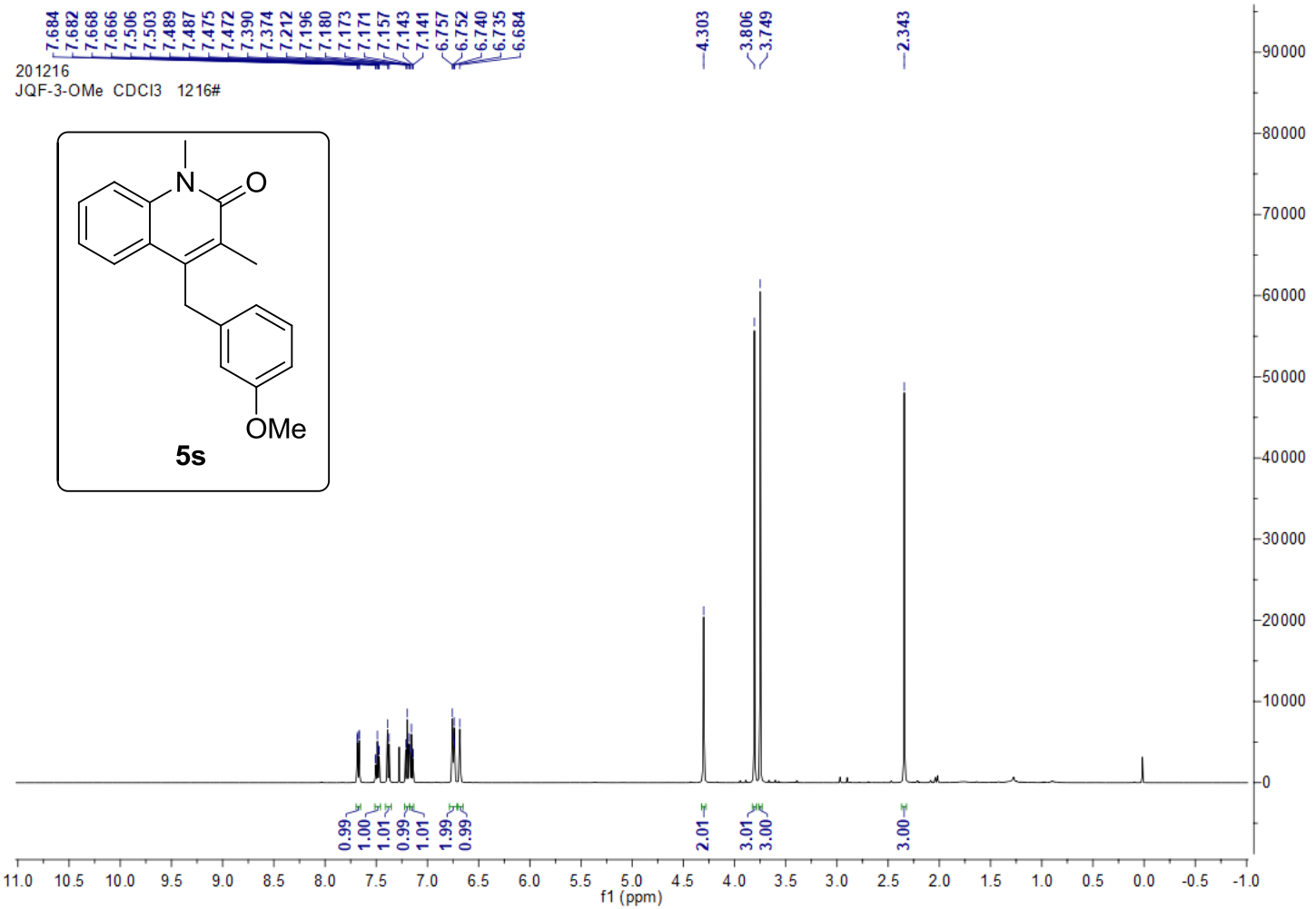
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5r



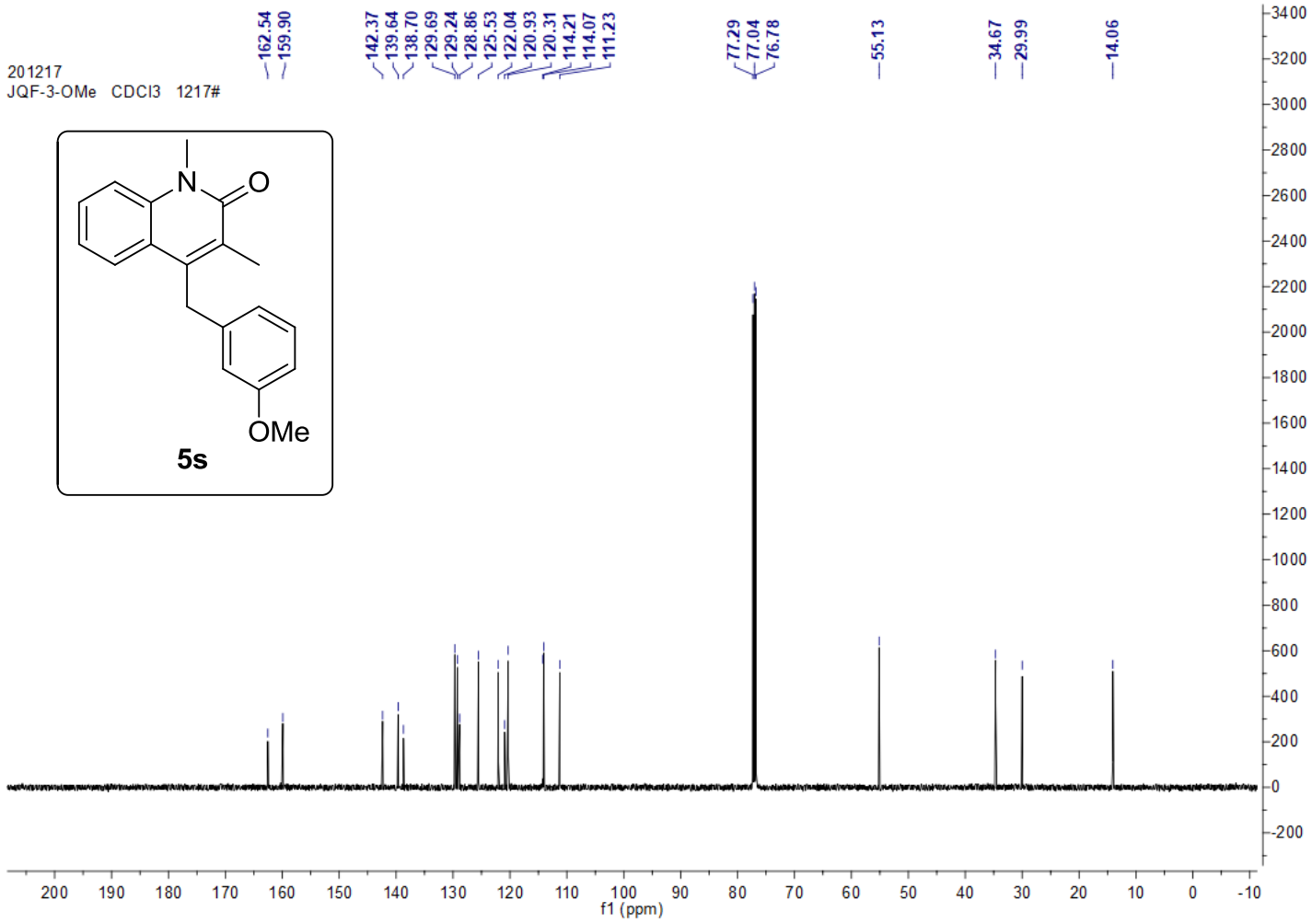
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5r



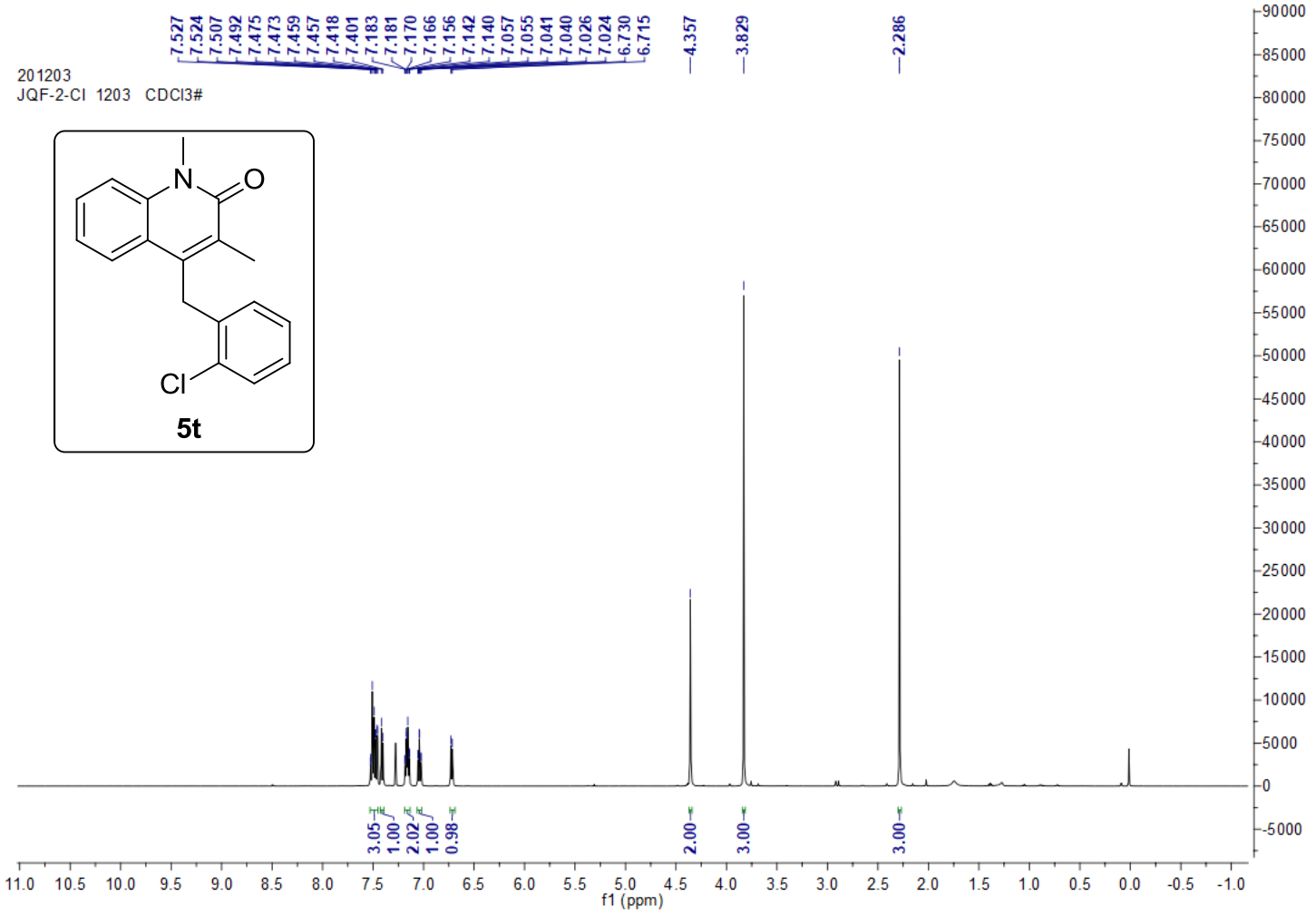
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5s



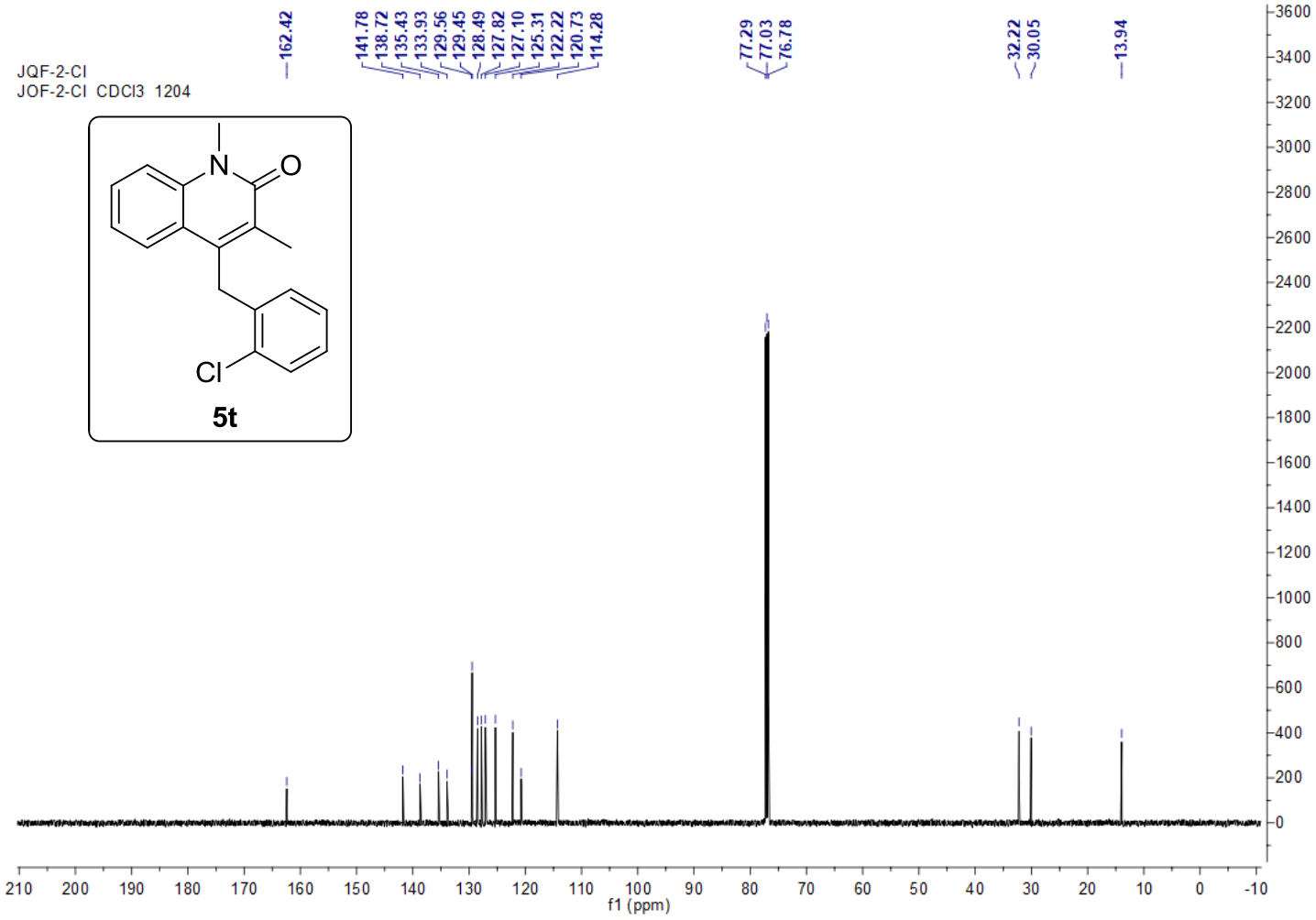
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5s



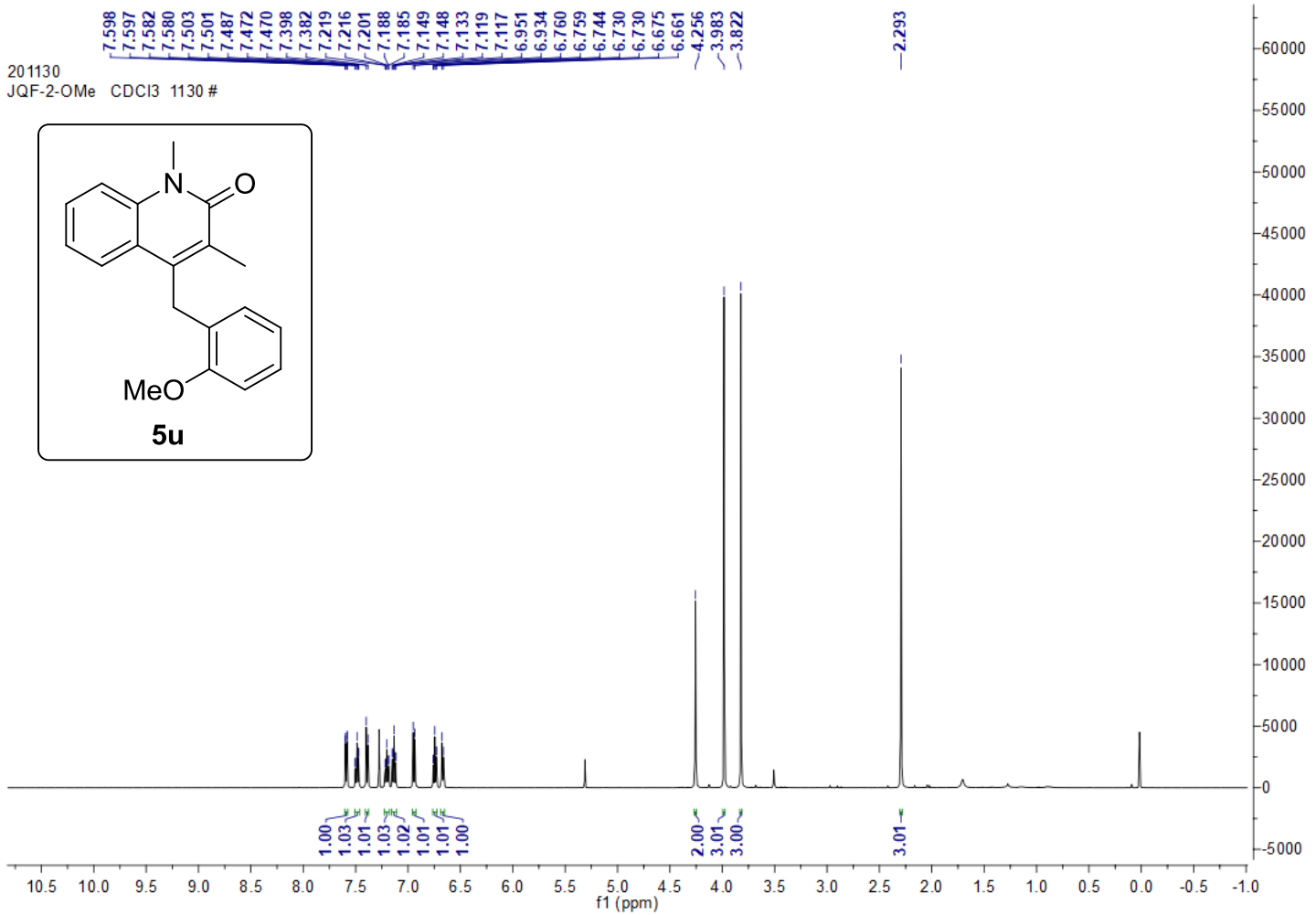
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5t



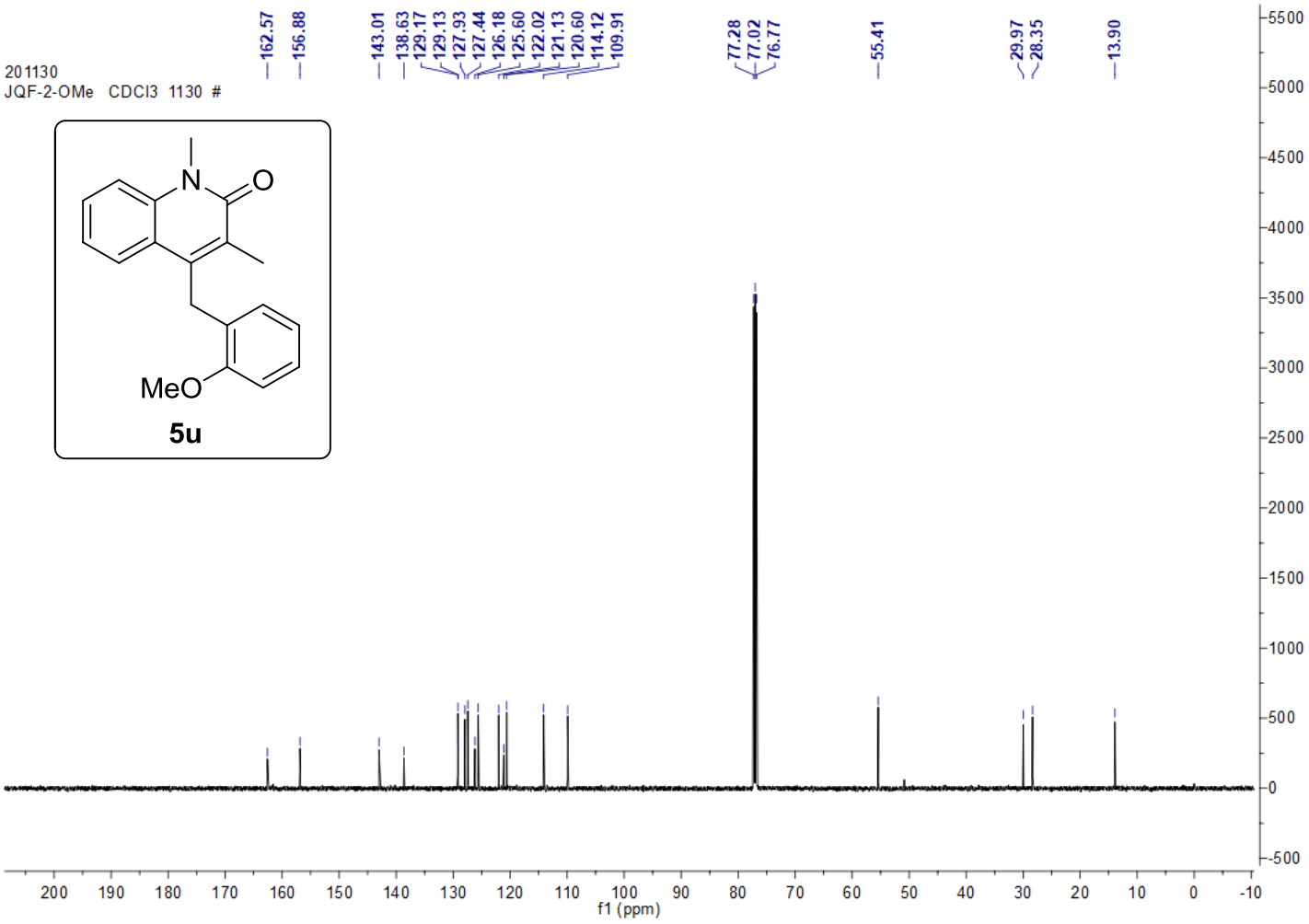
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5t



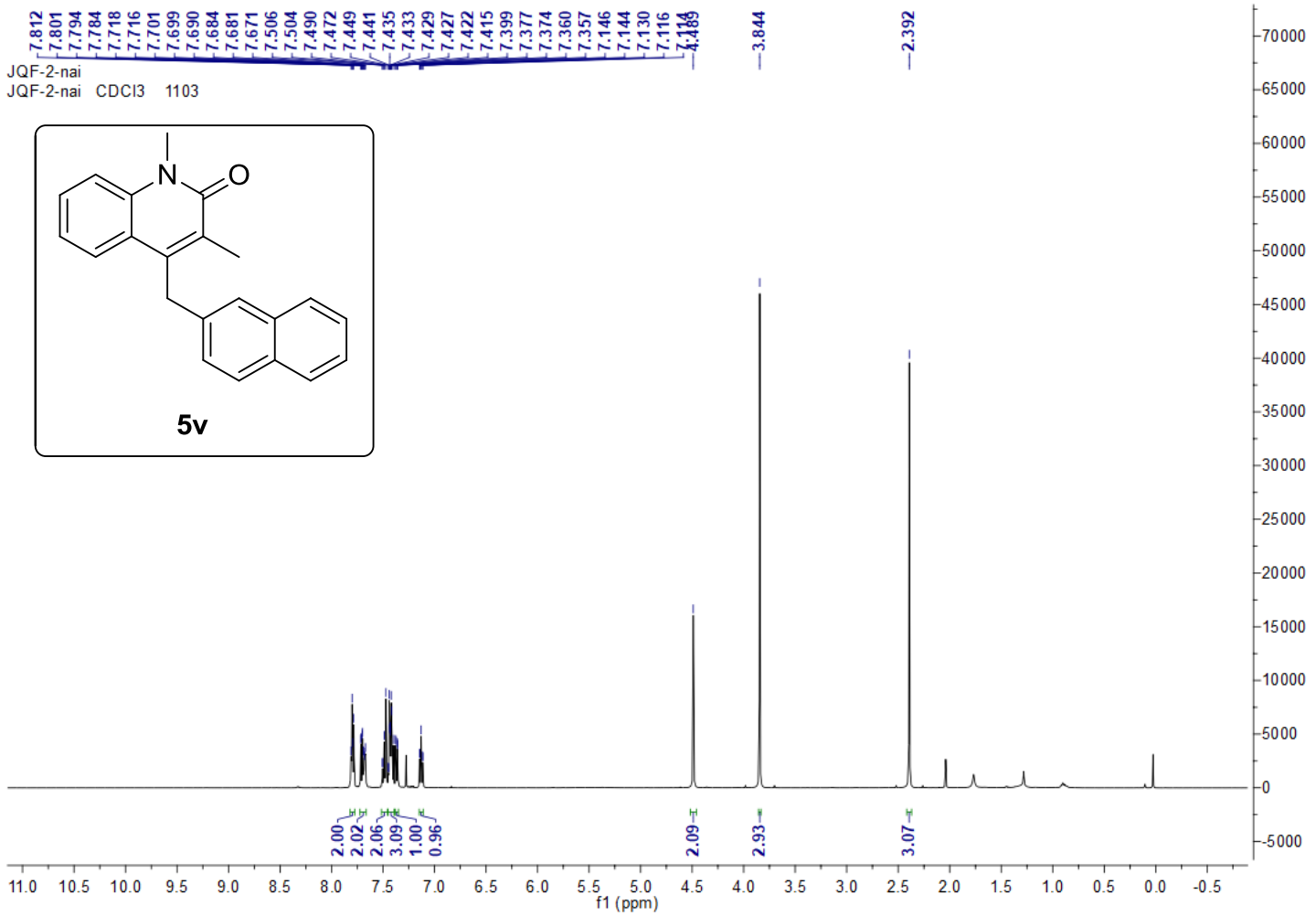
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5u



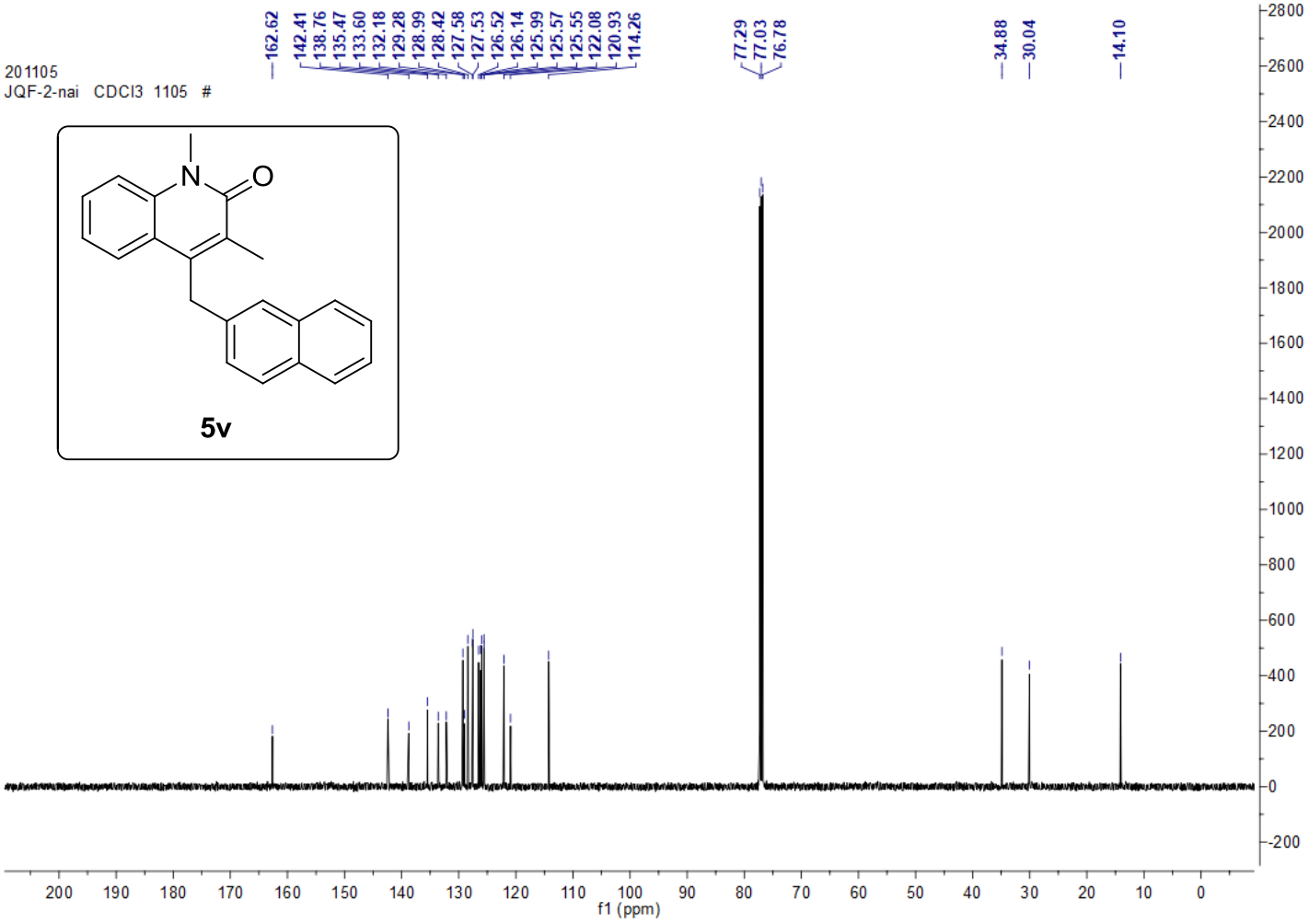
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5u



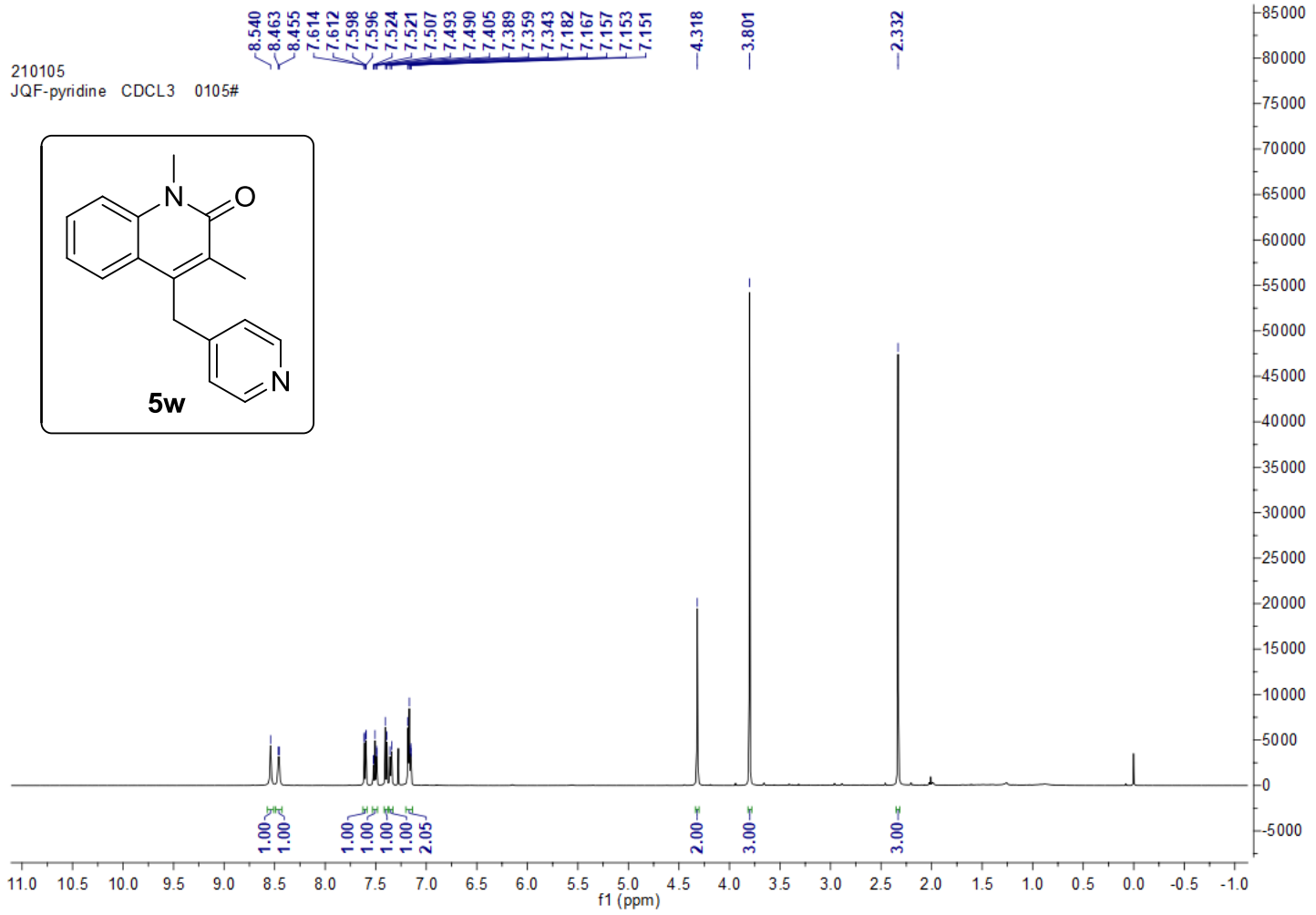
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5v



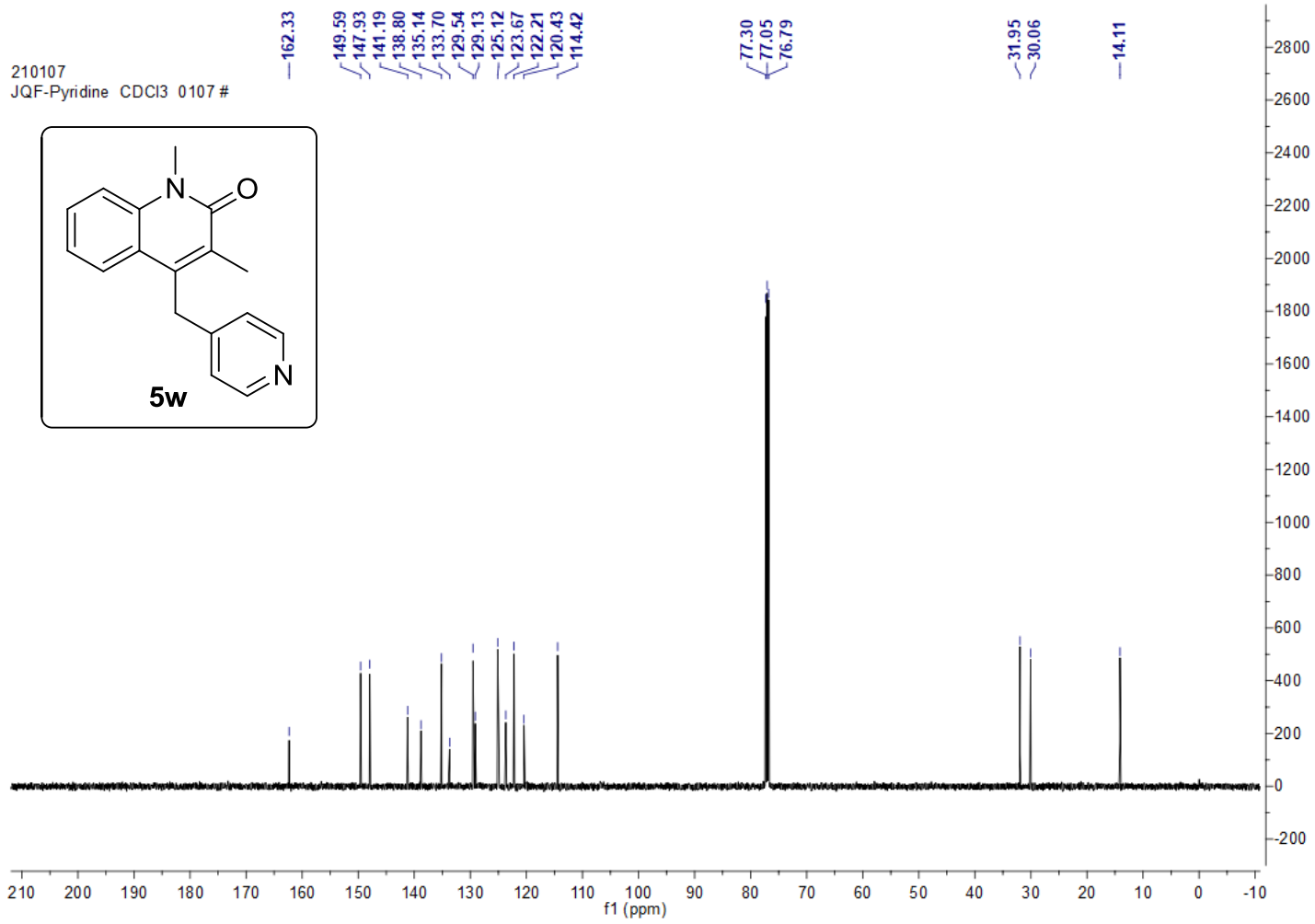
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5v



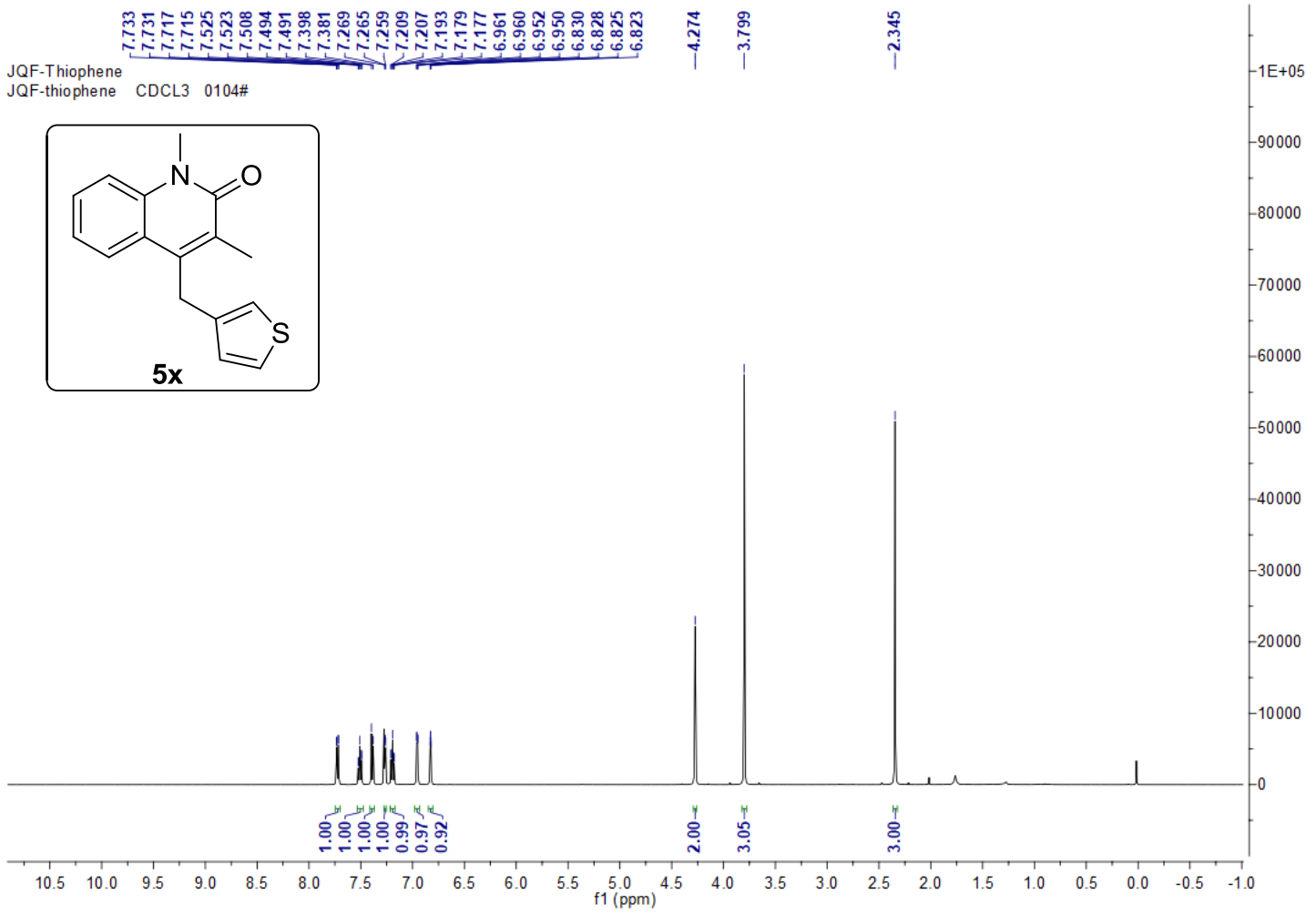
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5w



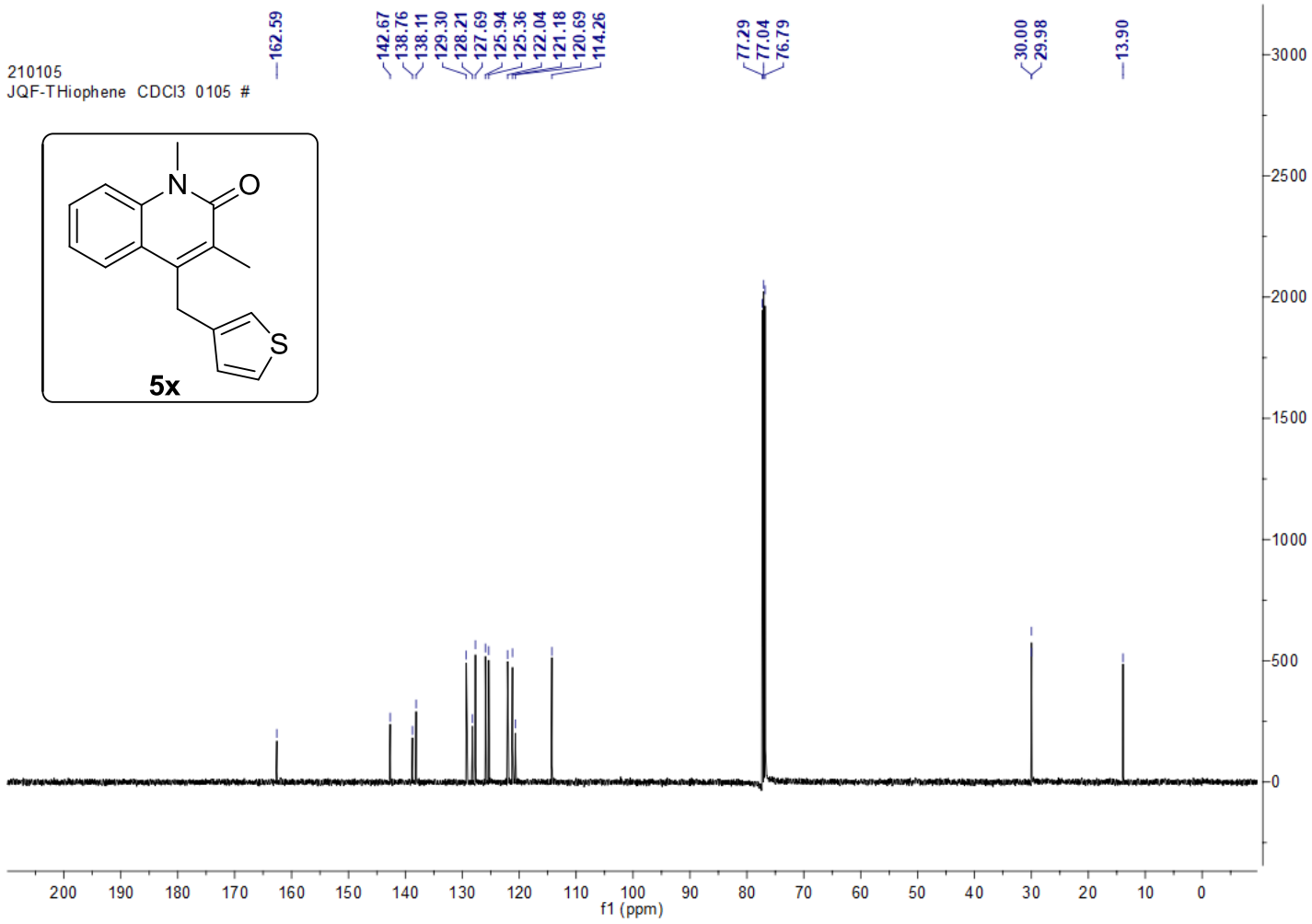
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5w



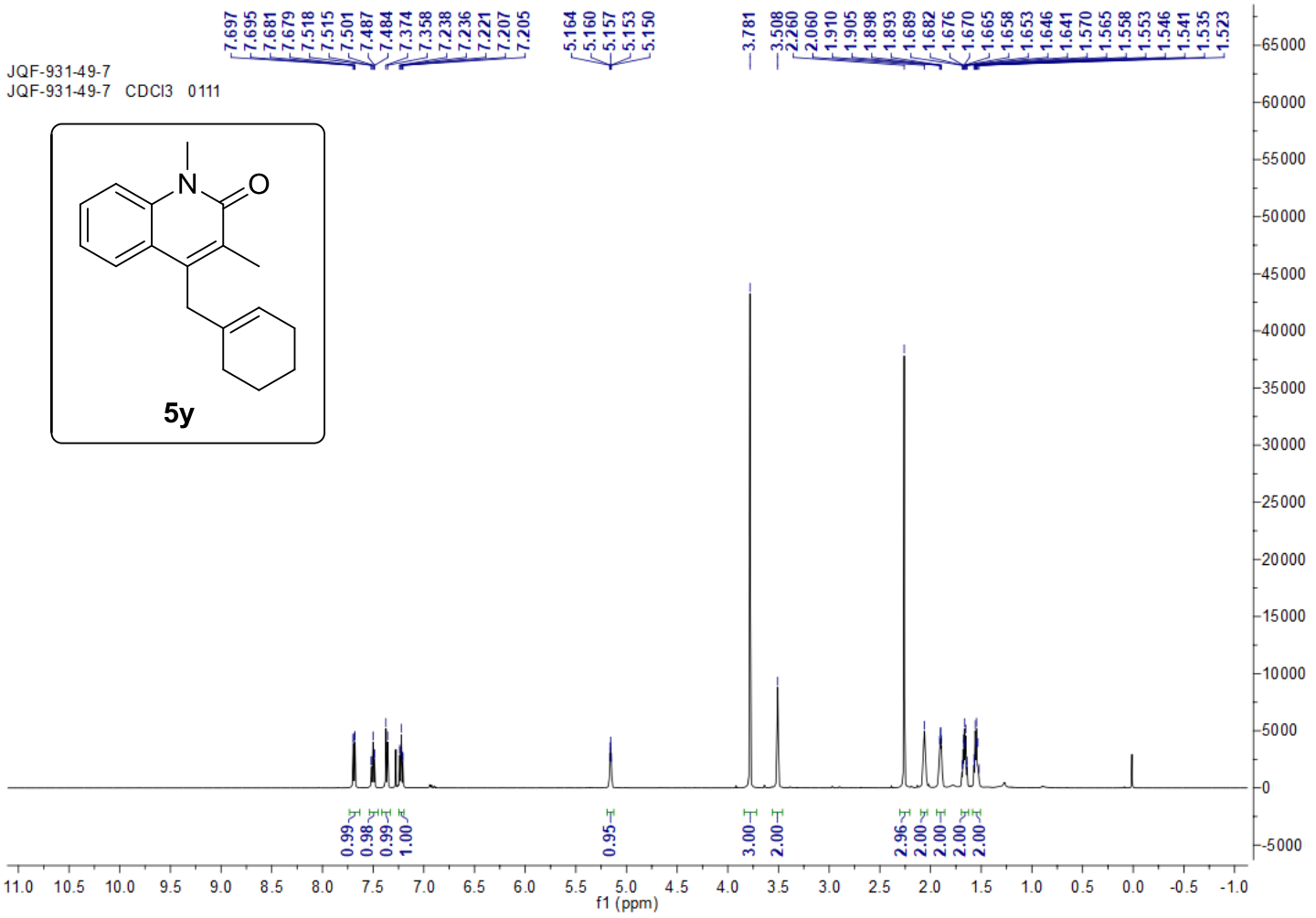
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5x



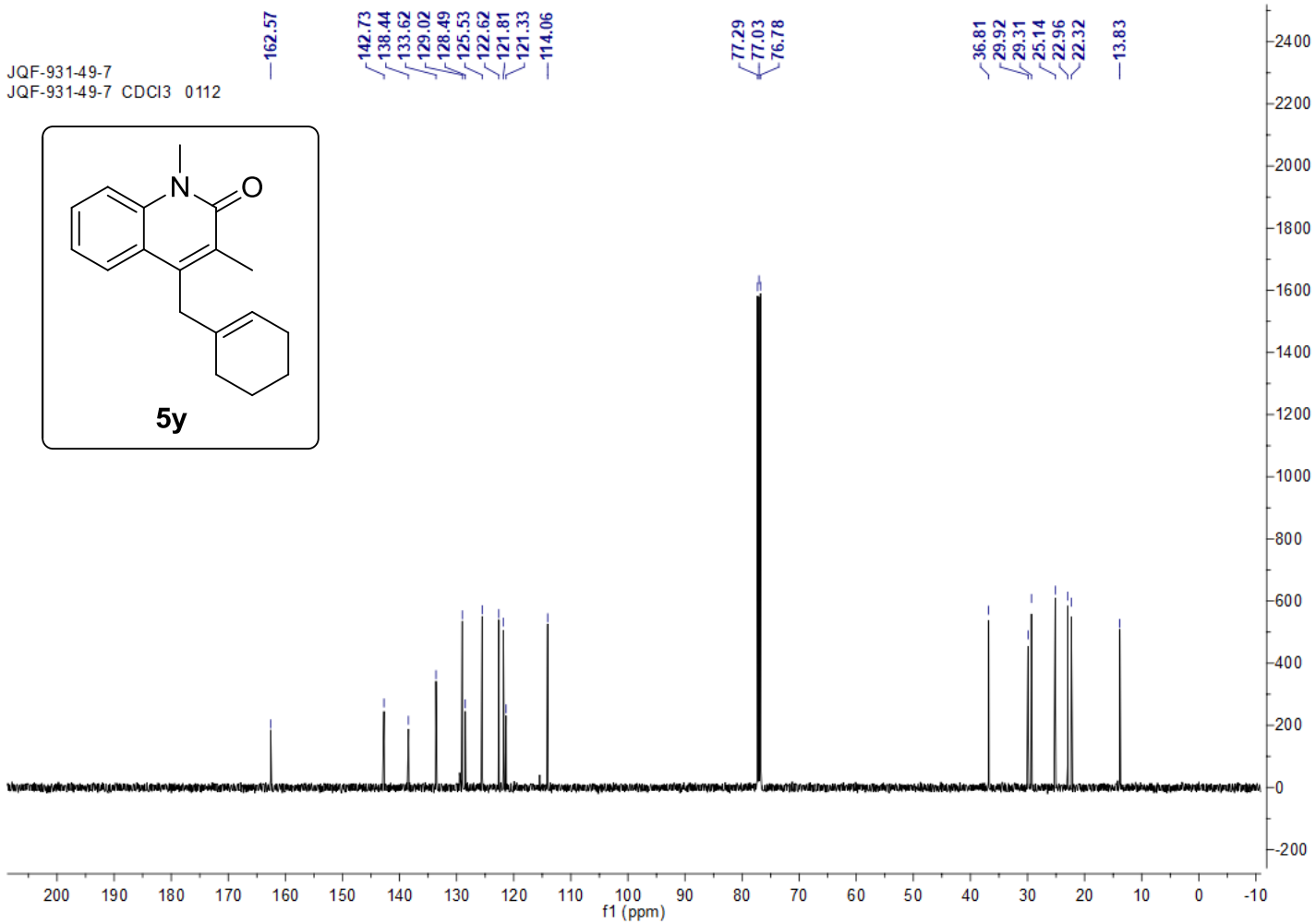
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5x



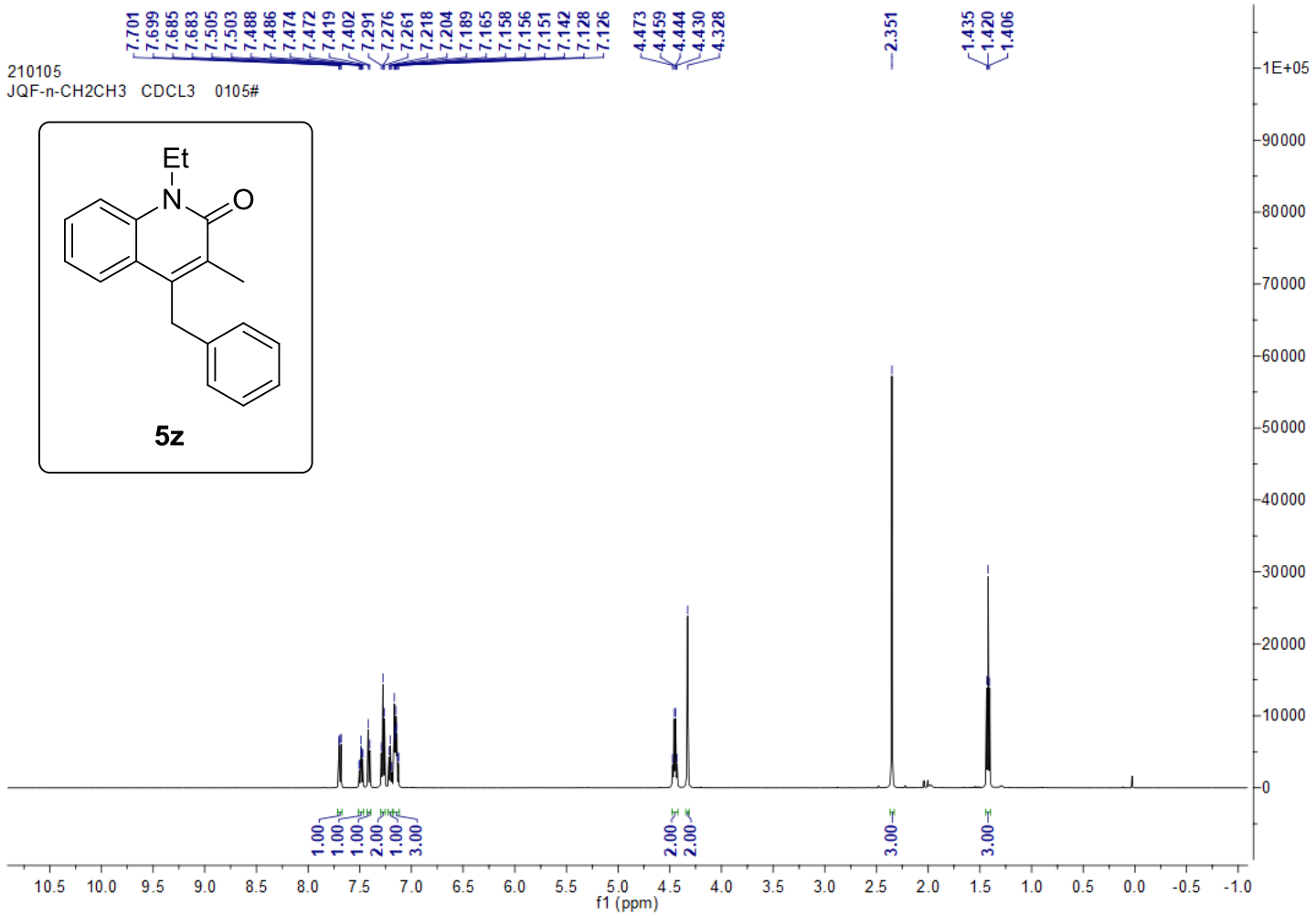
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5y



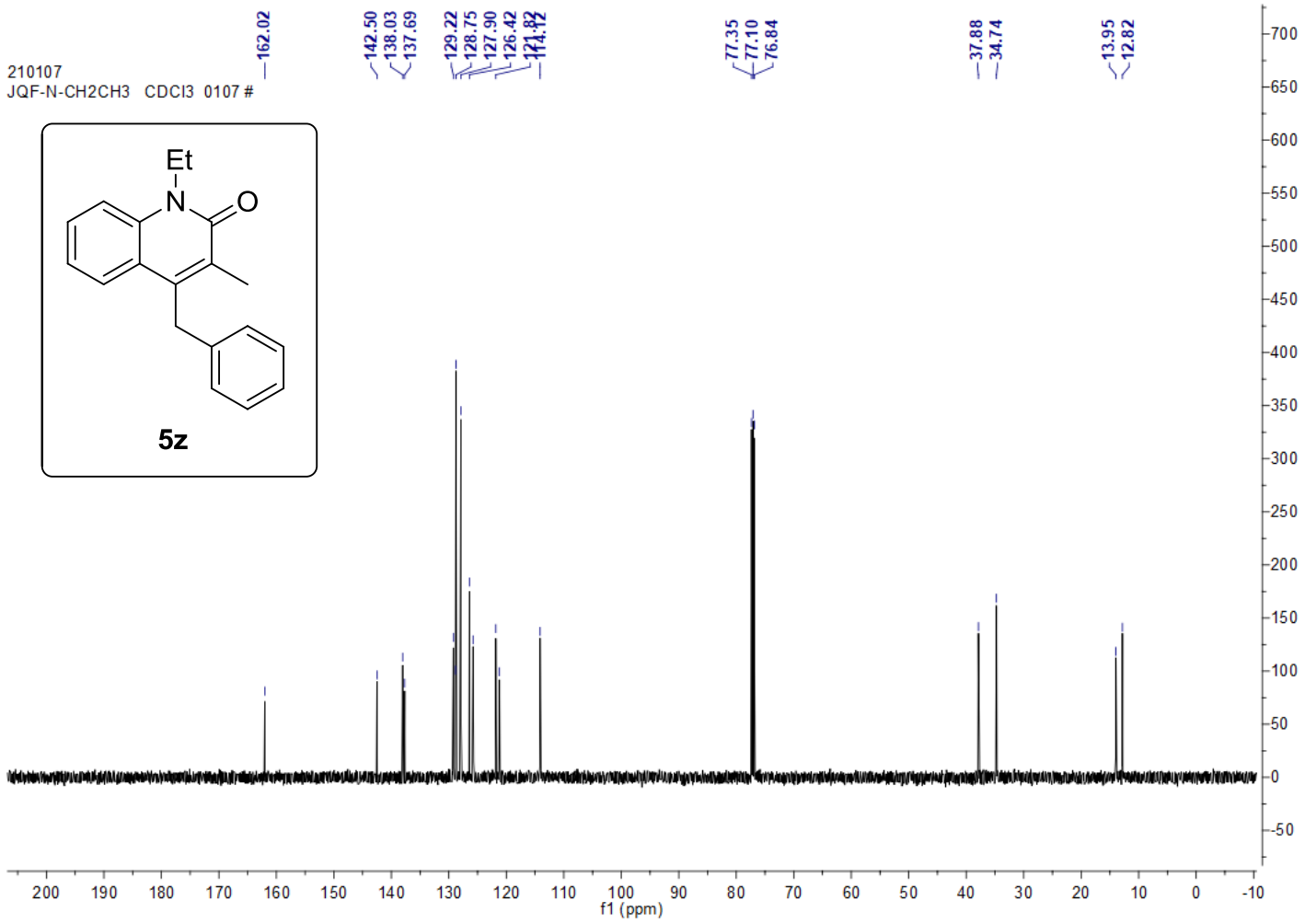
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5y



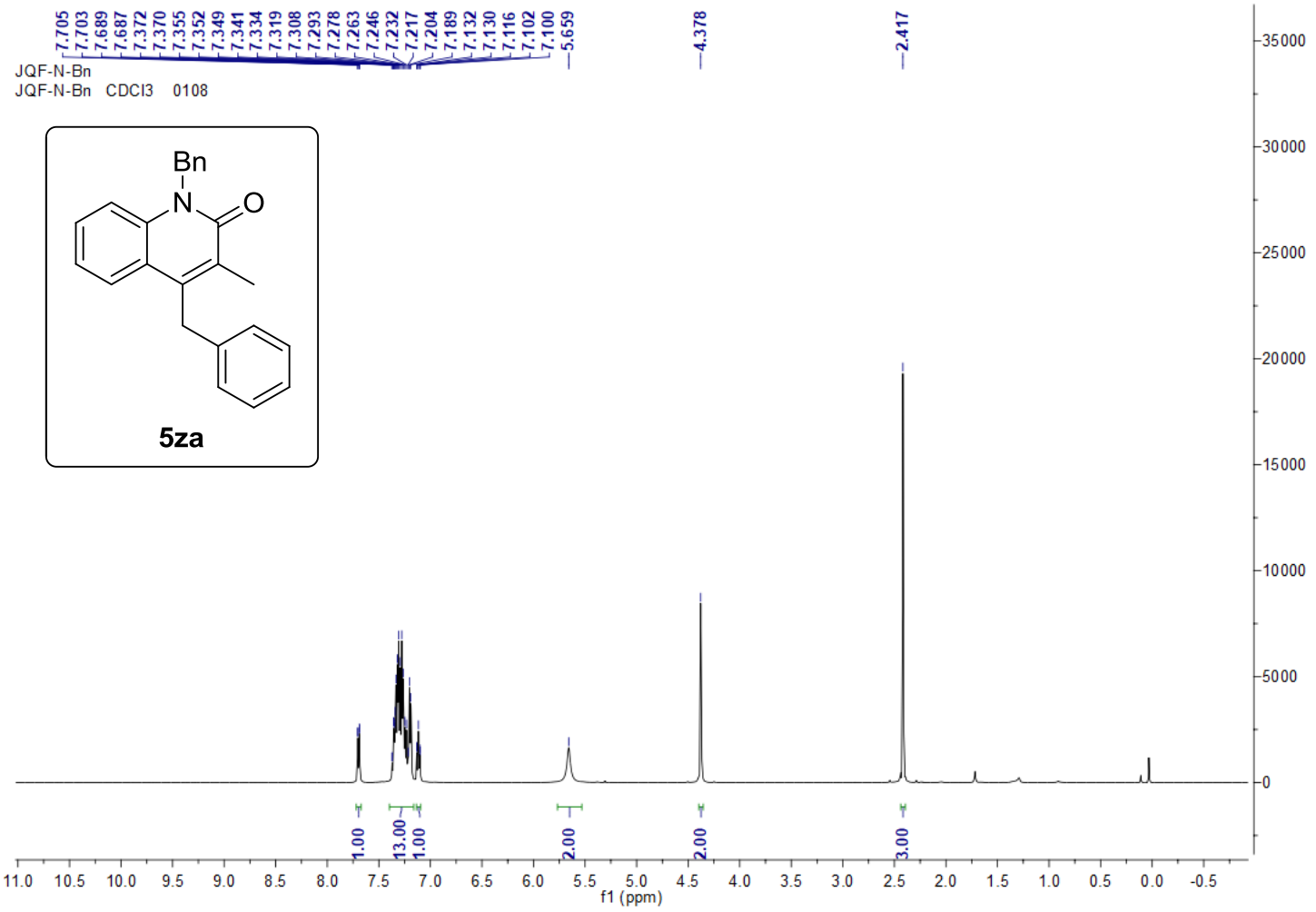
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5z



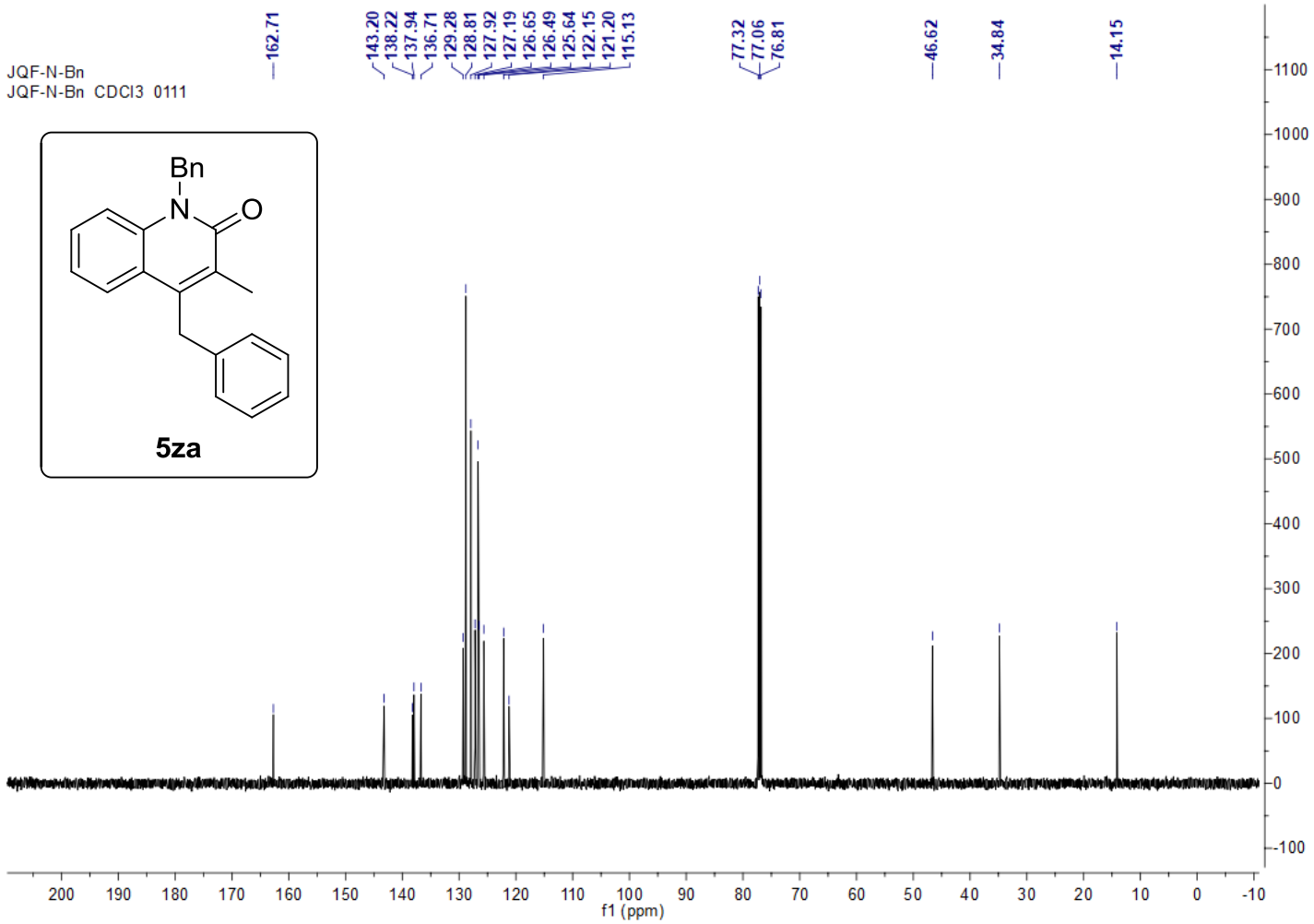
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5z



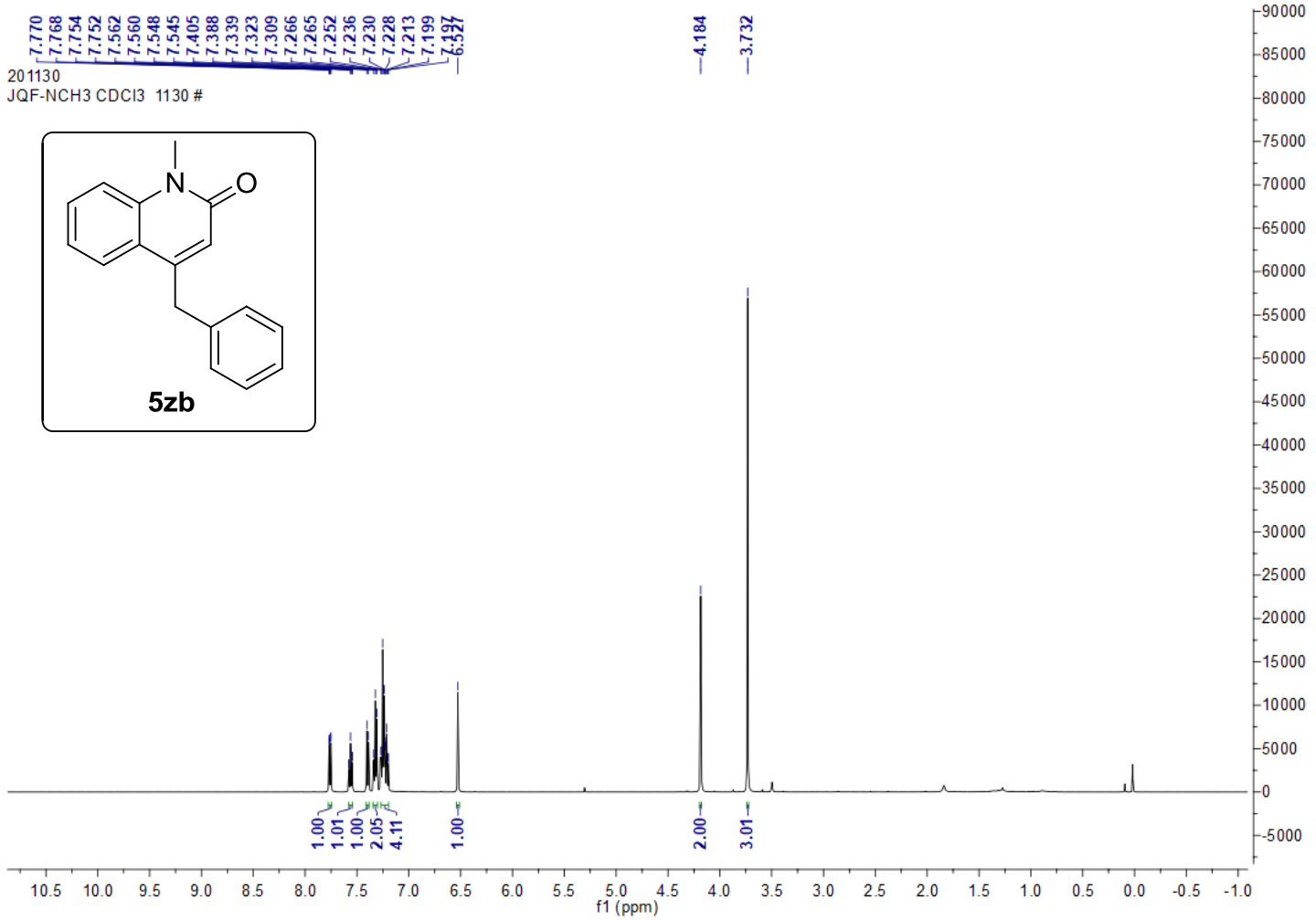
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5za



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5za



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5zb



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5zb