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

Supporting Information

Visible-Light Photocatalyzed C-N Bond Activation of Tertiary Amines: A Three-Component Approach to Synthesize Quinazolines

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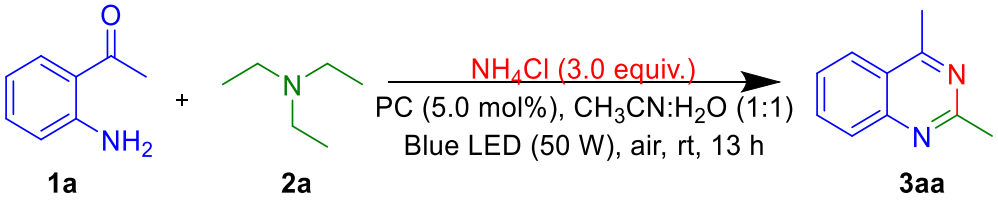
(1) General Information

A Bruker 500 MHz and 400 MHz were used to record ^{1}H NMR spectra, and a Bruker 125.8 MHz/100.61 MHz was used to record ^{13}C NMR spectra. Parts per million (ppm) is used to express the chemical shift (δ) values, whereas hertz (Hz) is used to express the coupling constants (J). The spectra were recorded using $CDCl_3$ solvent. ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS, 0 ppm) and ^{13}C NMR is referenced to $CDCl_3$ (77.16 ppm). HRMS was recorded with QTOF-ESI source M/S Bruker Daltonik GmbH, Germany. Cyclic voltammetry measurements were carried out with Multi Autolab M204 (Serial number: MAC90963). The progress of the reaction was monitored by TLC using Merck pre-coated TLC sheets. The Melting points of compounds were determined using a digital melting point apparatus (Model 935) from Deep Vision Electronics PVT. LTD. IP66 50 W Blue LED light used for irradiation of the reaction mixture from VistaRa fine lighting, China. Column chromatography was performed on 100-120 mesh silica gel using hexane/ethyl acetate as eluent and solvents were used without further distillation. All commercial chemicals were purchased from Sigma-Aldrich, Avra, Alfa Aesar, SRL Spectrochem and Carbanio. Compounds **1b-f**, **1m**, **1n**, **1o** were prepared according to the previously reported literatures[1-4] and **1a**, **1g** – **1l**, **1p** were purchased commercially.

(2) Complete Optimization Studies

Table S1. Photocatalyst Screening[a]

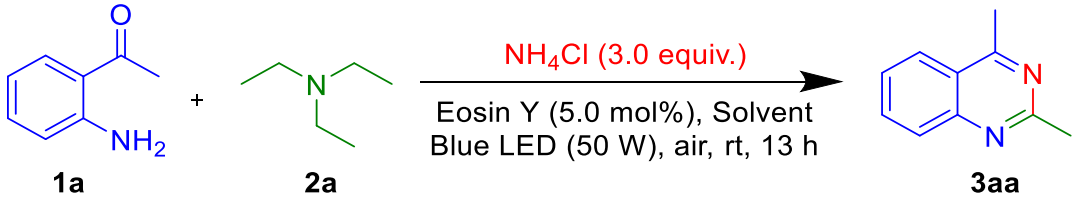


1a **2a** **3aa**

S.No	Photocatalyst	Yield (%)[b]
1	Rose bengal	71
2	Riboflavin	54
3	$Ru(bpy)_3Cl_2$	48
4	EY-Na_2	83
5	**Eosin Y**	**98**
6	Fluorescein	18
7	Methylene blue	14
8	4-CzIPN	trace
9	Without Photocatalyst	0

[a]All reactions were carried out using 0.5 mmol of **1a** and 2.5 mmol of **2a**. [b]Isolated yield.

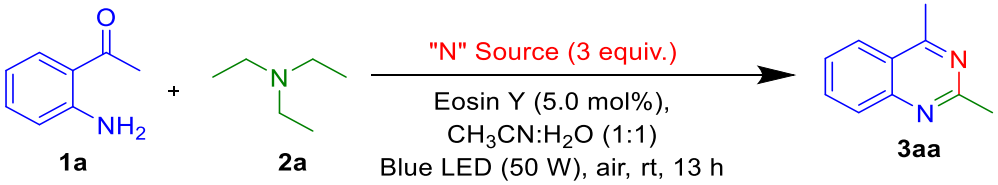
Table S2. Solvent Screening[a]



S.No	Solvent	Yield (%)[b]
1	EtOAc:H_2O	55
2	Butanol:H_2O	78
3	DMF:H_2O	19
4	DMSO:H_2O	09
5	Dioxane:H_2O	24
6	DMA:H_2O	26
7	THF:H_2O	49
8	**CH_3CN:H_2O**	**98**
9	CH_3CN	14

[a]All reactions were carried out using 0.5 mmol of **1a** and 2.5 mmol of **2a**. [b]Isolated yield.

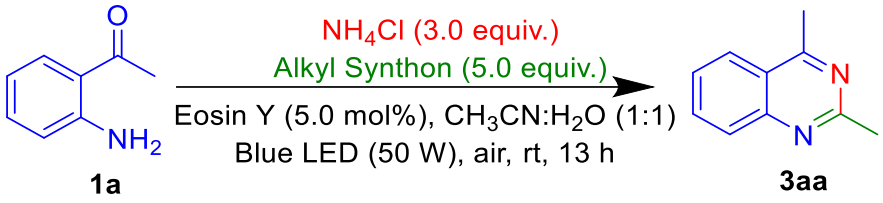
Table S3. Nitrogen Source Screening[a]



S.No	Nitrogen Source	Yield (%)[b]
1	NH_4F	92
2	NH_4OH	36
3	NH_4OAc	54
4	**NH_4Cl**	**98**
5	Without NH_4Cl	0

[a]All reactions were carried out using 0.5 mmol of **1a** and 2.5 mmol of **2a**. [b]Isolated yield.

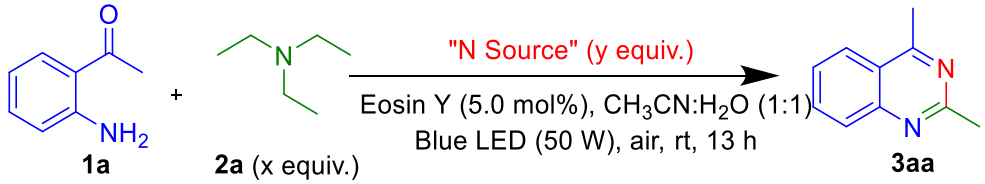
Table S4. Alkyl Synthon/Electron Donor Screening[a]



S.No	Alkyl Synthon / Electron Donor	Yield (%)[b]
1	DEA	31 (21 h)
2	DIPEA	34 (21 h)
3	**TEA**	**98 (13 h)**
4	Without TEA	0

[a]All reactions were carried out using 0.5 mmol of **1a**. [b]Isolated yield.

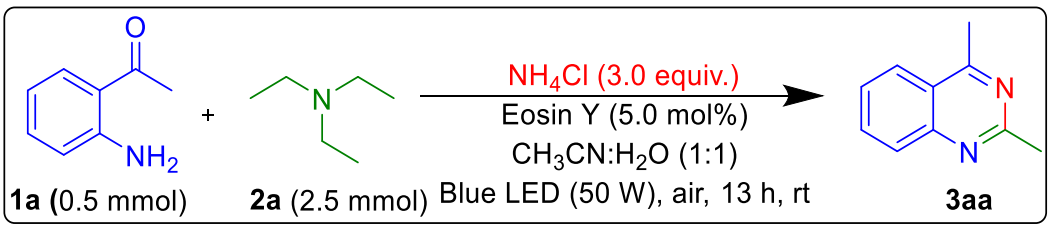
Table S5. Equivalent Studies of Photocatalyst, Alkyl Synthon and Nitrogen Source[a]



S.No	Equivalent Studies	Yield (%)[b]	Time (h)
1	NH_4Cl (2.0 equiv.)	95	38
2	TEA (4.0 equiv.)	97	21
3	EY (3 mol %)	97	21

[a]All reactions were carried out using 0.5 mmol of **1a**. [b]Isolated yield.

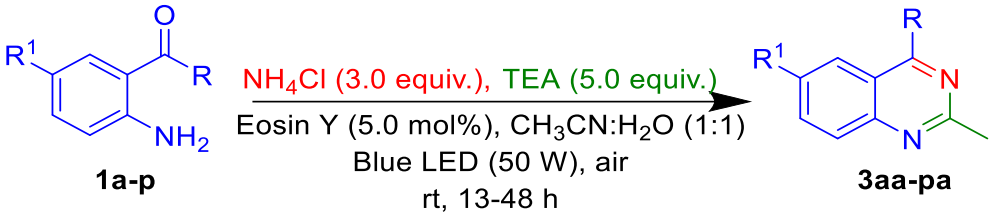
Optimized Condition



Scheme S1. Optimized Conditions for Synthesis of Quinazolines.

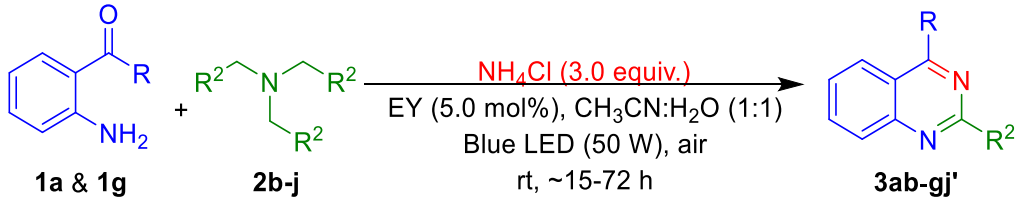
(3) Experimental Section

3a. General Experimental Procedure (A) for the Synthesis of Compounds 3aa-3pa



Compound **1a-1p** (0.5 mmol) was dissolved in 0.15 M of $CH_3CN:H_2O$ (1:1, 3.3 mL) followed by the addition of triethylamine (2.5 mmol), NH_4Cl (1.5 mmol) and Eosin Y (5.0 mol%). The reaction mixture was allowed to stir under the 50 W blue LED in the open air. The reaction completion was monitored by TLC chromatography (~13-48 h). After completion, the reaction was diluted with 10 mL of water and extracted with ethyl acetate (3 x 10 mL). The combined ethyl acetate layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to get a crude compound. The obtained crude was purified using column chromatography by eluting hexane/ethyl acetate to afford the desired product **3aa-pa** in 52 % to 98 % yields.

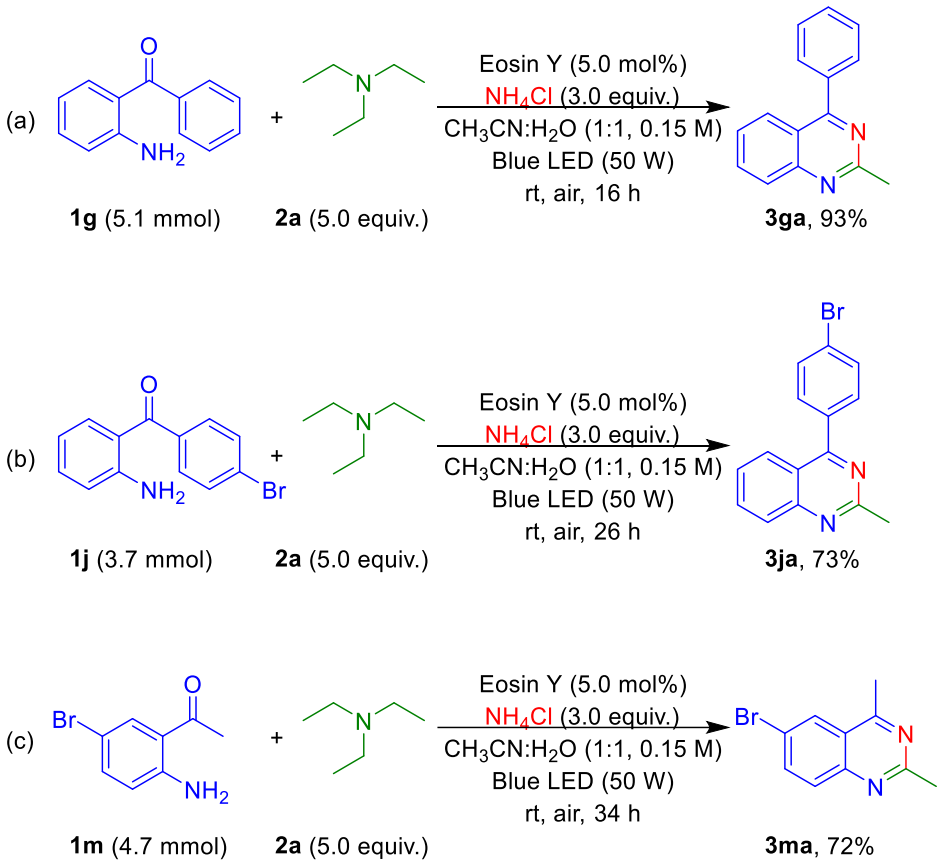
3b. General Experimental Procedure (B) for the Synthesis of Compounds 3ab-gj'



Compound **1a** (0.5 mmol) was dissolved in 0.15 M of $CH_3CN:H_2O$ (1:1, 3.3 mL) followed by the addition of trialkylamines **2b-j** (2.5 mmol), NH_4Cl (1.5 mmol) and Eosin Y (5.0 mol%). The reaction mixture was allowed to stir under the 50 W blue LED in the open air. The reaction completion was monitored by TLC chromatography (~15-72 h). After completion, the reaction was diluted with 10.0 mL of water and extracted with ethyl acetate (3 x 10 mL). The combined ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get a crude compound. The obtained crude was purified using column

chromatography by eluting hexane/ethyl acetate to afford the desired product **3ab-ah, 3aj, 3gj** and **3gj'** in 41 % to 96 % yields.

3c. General Experimental Procedure (C) for the Gram Scale Synthesis of Compounds 3ga, 3ja and 3ma



Compound **1g** (5.1 mmol) was dissolved in 0.15 M of $CH_3CN:H_2O$ (1:1) followed by the addition of triethylamine (5.0 equiv.), NH_4Cl (3.0 equiv.) and Eosin Y (5.0 mol%). The reaction mixture was stirred under the 50 W blue LED in the open air for 16 h and the completion of the reaction was monitored by TLC chromatography. The reaction mixture was diluted with 100 mL of water and extracted with ethyl acetate (3 x 75 mL). The combined ethyl acetate layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to get a crude compound. The obtained crude was purified using column chromatography by eluting hexane/ethyl acetate to afford the desired product **3ga** in 93%. The above same procedure was used to synthesize **3ja** in 73 % yield and **3ma** in 72 % yields respectively.

(4) TLC & Experimental Setup

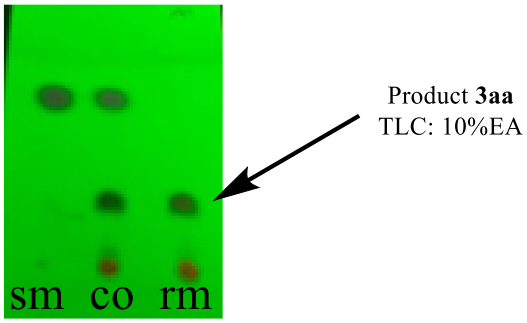


Figure S1. TLC for 2-Methyl-3-phenylquinazolin-4(3*H*)-one (**3aa**).

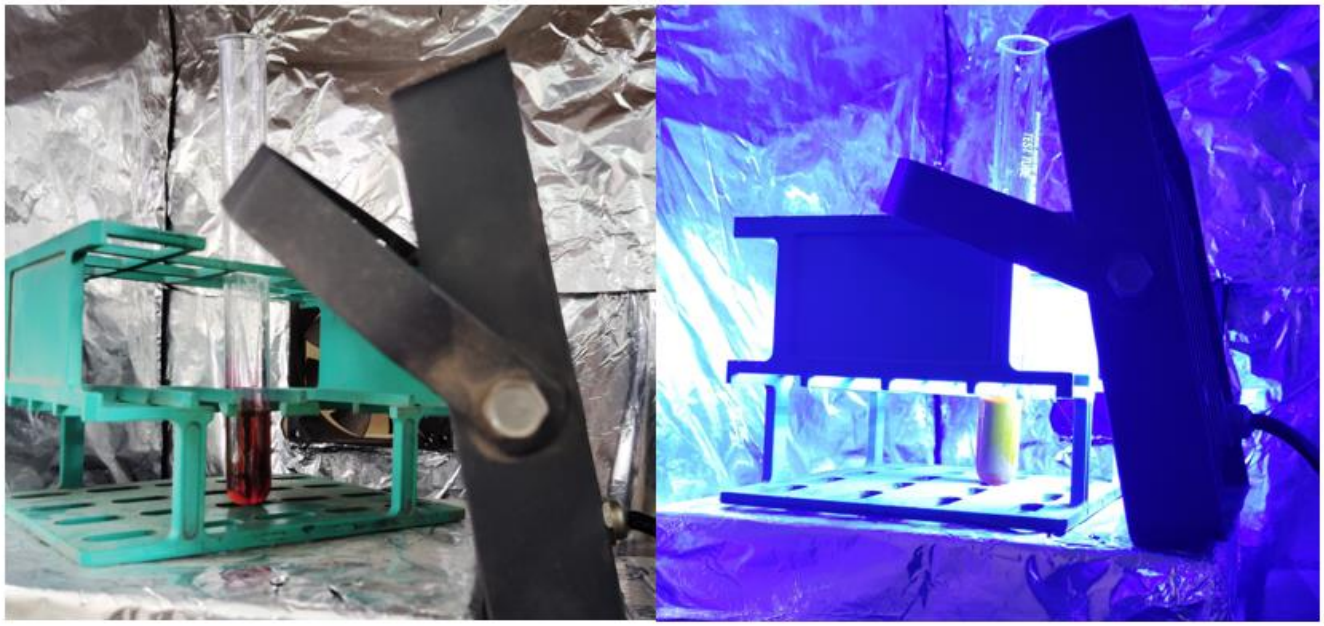


Figure S2. Start of the Reaction.

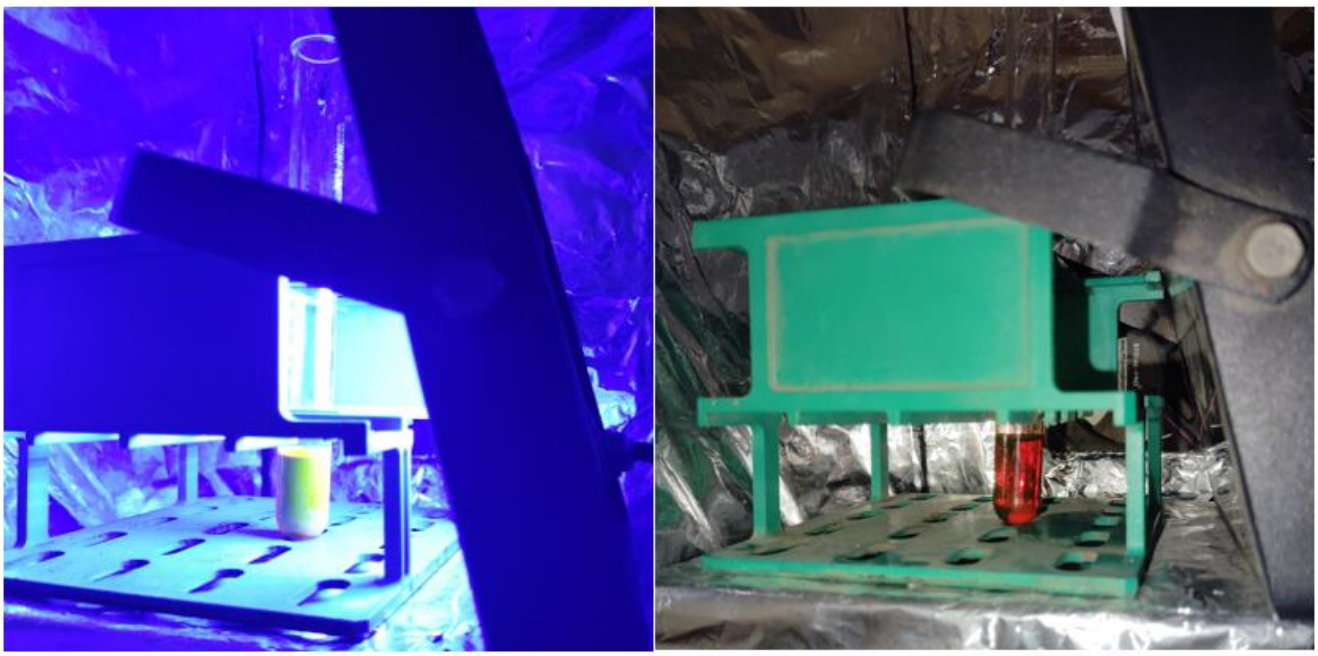
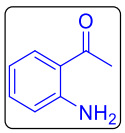


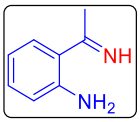
Figure S3. Completion of the Reaction.

(5) GC-MS Studies

GC-MS chromatogram analysis of the reaction mixture of **3aa** was performed on GCMS - QP2010 Plus – Shimadzu during the courses of the reaction (2 h and 10 h) and the intermediates were verified. We have detected the following intermediates, product **3aa** and the minor side products. This strongly suggests that the mechanism goes via proposed in the manuscript.

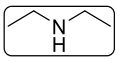


Chemical Formula: C_8H_9NO
Mass: 135, 2h

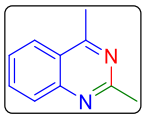


Chemical Formula: $C_8H_{10}N_2$
Mass: 134, 2h

Chemical Formula: C_2H_4O
Mass: 44, 10h



Chemical Formula: $C_4H_{11}N$
Mass: 73, 10h



Chemical Formula: $C_{10}H_{10}N_2$
Mass: 158, 10h

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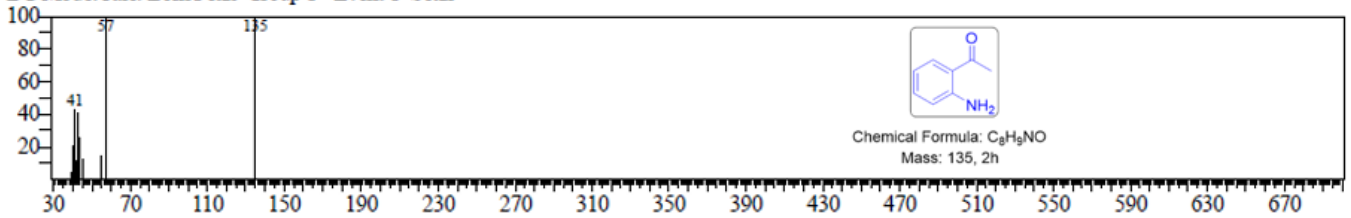
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



<< Target >>
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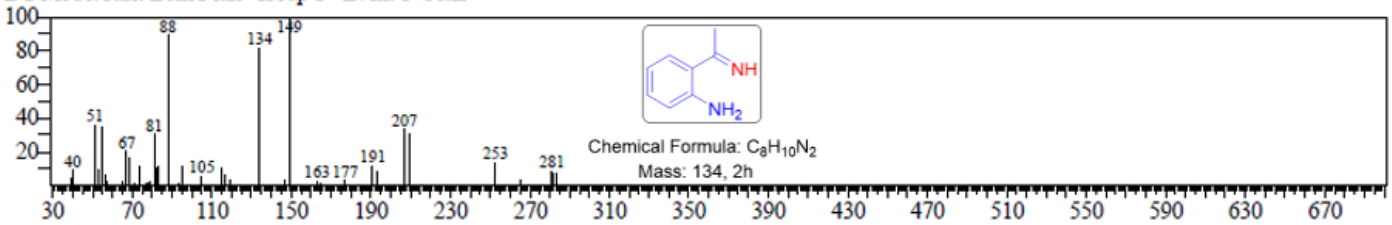
RawMode:Averaged 26.560-26.570(4613-4615) BasePeak:149.00(863)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



<< Target >>
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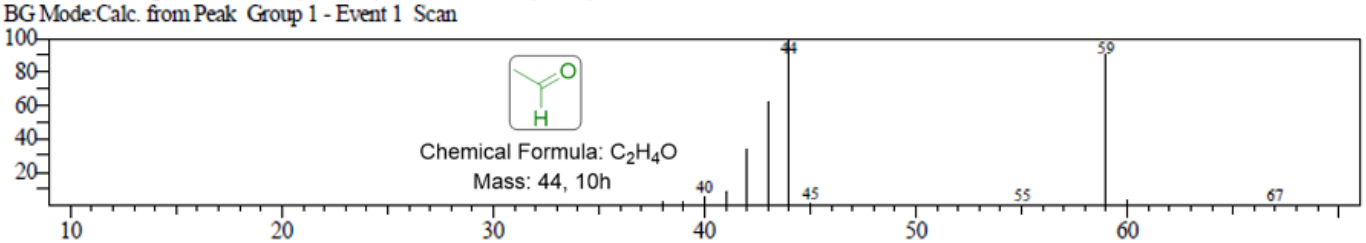
RawMode:Averaged 4.785-4.795(258-260) BasePeak:44.00(66267)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



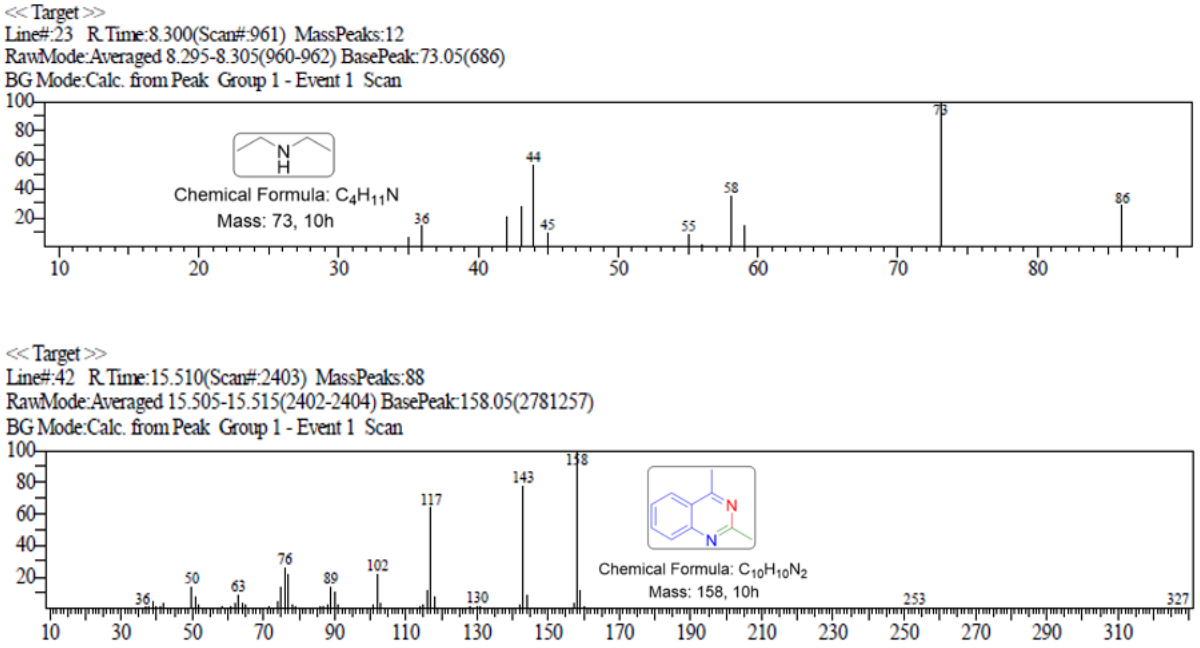


Figure S4. GC-MS observed fragments.

(6) Cyclic-Voltammetry Data

Samples for electrochemical measurements were prepared with 0.1 M of *tetra-n*-butylammonium hexafluorophosphate solution in acetonitrile and 0.05 M of 2-aminoacetophenone (**1a**). Cyclic voltammetry measurements were carried out with Multi Autolab M204 (Serial number: MAC90963) and the data was recorded using an undivided cell equipped with glassy carbon as the working electrode, platinum wire as counter electrode and Ag/AgCl as a reference electrode. A scan rate was used 100 mV s^{-1}µ.

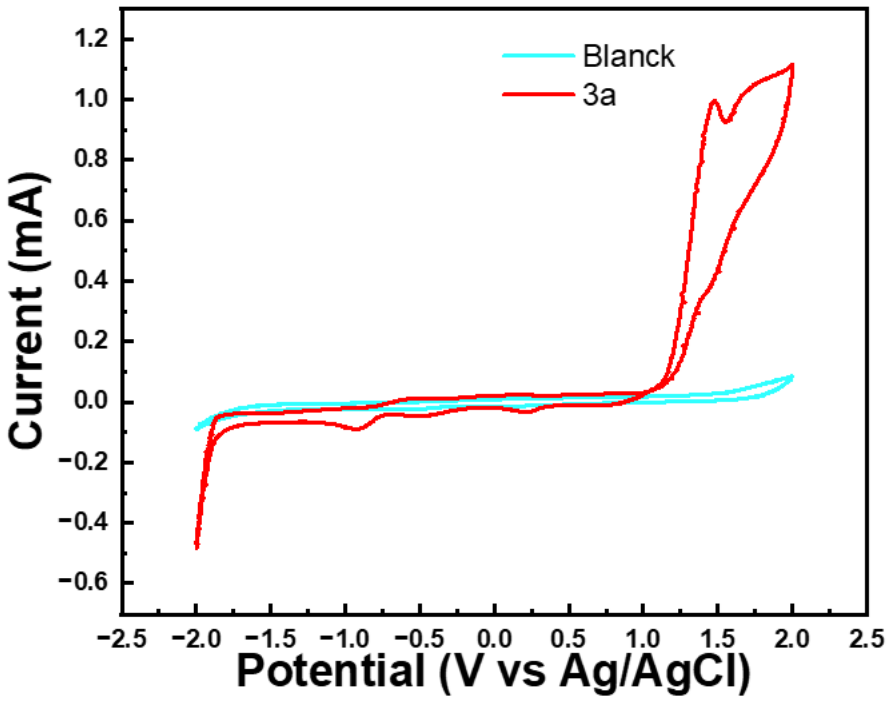
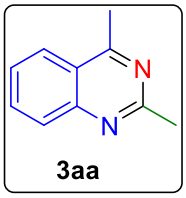


Figure S5. Cyclic Voltammogram of 2-Aminoacetophenone (**1a**).

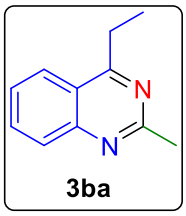
(7) Spectral Characterization

2,4-Dimethylquinazoline (3aa).[5] The title compound was synthesized according to the general procedure (A)

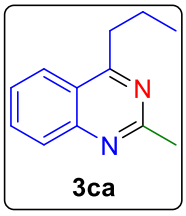


and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (78mg, 98%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 2.93 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.14, 163.61, 150.00, 133.63, 128.32, 126.63, 124.95, 122.27, 26.46, 21.70.

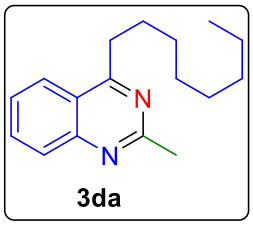
4-Ethyl-2-methylquinazoline (3ba).[6] The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (71mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 3.21 (q, *J* = 7.6 Hz, 2H), 2.81 (s, 3H), 1.38 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.58, 163.78, 150.31, 133.44, 128.47, 126.56, 124.58, 121.42, 27.98, 26.51, 13.36.



2-Methyl-4-propylquinazoline (3ca). The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (71mg, 76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 3.23 – 3.19 (m, 2H), 2.86 (s, 3H), 1.93 – 1.85 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 163.78, 150.47, 133.53, 128.53, 126.59, 124.83, 121.83, 36.85, 26.62, 22.99, 14.40; HRMS (ESI) calculated for $C_{12}H_{15}N_2$ $[M+H]^+$: 187.1235 found 187.1250.

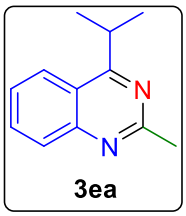


2-Methyl-4-octylquinazoline (3da). The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (69mg, 54%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.57 – 7.53 (m, 1H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.86 (s, 3H), 1.87 – 1.81 (m, 2H), 1.50 – 1.44 (m, 2H), 1.37 – 1.33 (m, 2H), 1.30 – 1.25 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.91, 163.74, 150.42, 133.46, 128.49, 126.53, 124.76,



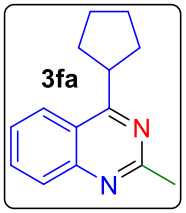
121.71, 34.99, 31.91, 29.94, 29.67, 29.49, 29.27, 26.57, 22.72, 14.16; HRMS (ESI) calculated for $C_{17}H_{25}N_2$ $[M+H]^+$: 257.2018 found 257.2035.

4-Isopropyl-2-methylquinazoline (3ea).[7] The title compound was synthesized according to the general



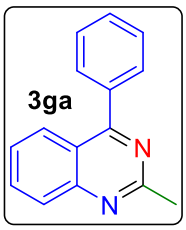
procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (54mg, 58%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.56 – 7.52 (m, 1H), 3.92 – 3.87 (m, 1H), 2.86 (s, 3H), 1.43 (t, *J* = 1.5 Hz 3H), 1.42 (t, *J* = 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.68, 163.99, 150.54, 133.16, 128.64, 126.38, 124.15, 121.01, 30.99, 26.71, 21.80.

4-Cyclopentyl-2-methylquinazoline (3fa).[8] The title compound was synthesized according to the general



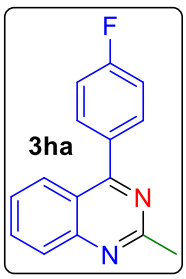
procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (71mg, 67%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.54 – 7.50 (m, 1H), 3.98 – 3.92 (m, 1H), 2.84 (s, 3H), 2.12 – 2.08 (m, 4H), 1.91 – 1.90 (m, 2H), 1.77 – 1.76 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.33, 163.81, 150.27, 133.05, 128.33, 126.22, 124.55, 121.82, 42.56, 32.61, 26.65, 26.20.

2-Methyl-4-phenylquinazoline (3ga).[9] The title compound was synthesized according to the general



procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (101mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 12.4, 8.6 Hz, 2H), 7.88 – 7.84 (m, 1H), 7.76 – 7.74 (m, 2H), 7.56 – 7.50 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 1H), 2.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.64, 163.91, 151.53, 137.39, 133.68, 129.93, 128.68, 128.24, 127.09, 126.78, 121.11, 26.70.

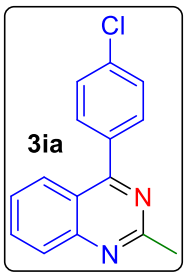
4-(4-Fluorophenyl)-2-methylquinazoline (3ha).[9] The title compound was synthesized according to the



general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (98mg, 82%); mp 113-115 °C (lit. 116-117 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.77 (q, *J* = 8.2, 5.5 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 8.5 Hz, 2H), 2.95 (s, 3H); ^{13}C NMR

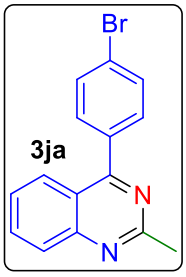
(101 MHz, $CDCl_3$) δ 166.41 (J_F = 227.2 Hz), 163.95, 162.79, 151.66, 133.86, 133.55, 132.04 (J_F = 9.0 Hz), 128.42, 127.01, 126.83, 121.06, 115.90 (J_F = 22.1 Hz), 26.70.

4-(4-Chlorophenyl)-2-methylquinazoline (3ia).[9] The title compound was synthesized according to the



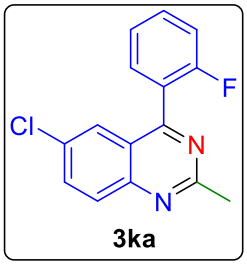
general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (97mg, 83%); mp 120-122 °C (lit. 128-129 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (t, *J* = 9.8 Hz, 2H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 3H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.41, 163.98, 151.64, 136.38, 135.83, 133.92, 131.36, 129.04, 128.45, 127.07, 126.69, 120.96, 26.68.

4-(4-Bromophenyl)-2-methylquinazoline (3ja).[9] The title compound was synthesized according to the



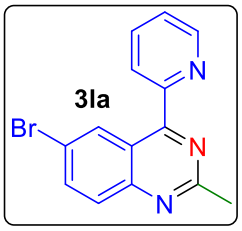
general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow solid (109mg, 73%); mp 124-126 °C (lit. 123-124 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (q, *J* = 13.2, 8.4 Hz, 2H), 7.90 – 7.86 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.43, 163.97, 151.62, 136.26, 133.92, 131.98, 131.57, 128.43, 127.07, 126.65, 124.67, 120.89, 26.67.

6-Chloro-4-(2-fluorophenyl)-2-methylquinazoline (3ka).[10] The title compound was synthesized according



to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (71mg, 52%); mp 134-136 °C (lit. 138-140 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.81 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.72 (t, J = 2.5 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.38 (td, *J* = 7.6, 0.9 Hz, 2H), 7.31 – 7.27 (m, 3H), 2.95 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.46, 163.99, 159.87 (J_F = 249.5 Hz), 149.59, 135.09, 132.78, 132.21, 132.13, 131.58, 129.98, 125.68, 125.01, 122.52, 116.47 (J_F = 21.1 Hz), 26.65.

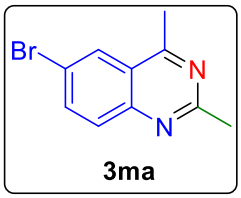
6-Bromo-2-methyl-4-(pyridin-2-yl)quinazoline (3la). The title compound was synthesized according to the



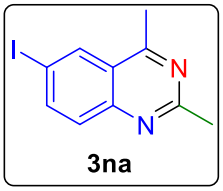
general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow solid (104mg, 69%); mp 158-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.1 Hz, 1H), 8.86 – 8.84 (m, 1H), 8.20 – 8.18 (m, 1H),

7.98 – 7.93 (m, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.49 (m, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.07, 163.47, 156.17, 150.94, 149.19, 137.47, 137.31, 130.21, 129.90, 125.33, 124.81, 121.90, 121.01, 26.62; HRMS (ESI) calculated for $C_{14}H_{11}BrN_3$ $[M+H]^+$: 300.0136 found 300.0135.

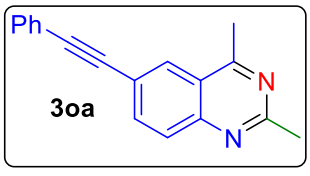
6-Bromo-2,4-dimethylquinazoline (3ma).[7] The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (85mg, 72%); mp 99-101 °C (lit. 130-132 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.1 Hz, 1H), 7.90 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 2.89 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.48, 164.28, 148.87, 137.26, 130.37, 127.56, 123.54, 120.33, 26.66, 21.94.



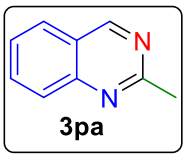
6-Iodo-2,4-dimethylquinazoline (3na). The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow solid (87mg, 61%); mp 130-132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.06 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 2.89 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 164.28, 149.10, 142.41, 134.11, 130.18, 124.04, 91.62, 26.61, 21.83. HRMS (ESI) calculated for $C_{10}H_{10}IN_2$ $[M+H]^+$: 284.9889 found 284.9896.



2,4-Dimethyl-6-(phenylethynyl)quinazoline (3oa). The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow solid (79mg, 61%); mp 124-126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.2 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.60 – 7.58 (m, 2H), 7.41 – 7.38 (m, 3H), 2.93 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.99, 164.35, 149.51, 136.36, 131.85, 128.90, 128.61, 128.34, 122.80, 122.19, 121.85, 91.15, 88.67, 26.59, 21.85. HRMS (ESI) calculated for $C_{18}H_{15}N_2$ $[M+H]^+$: 259.1235 found 259.1245.

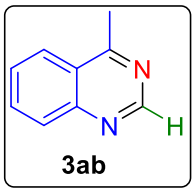


2-methylquinazoline (3pa).[11] The title compound was synthesized according to the general procedure (A) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (50mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.91 (d, *J* = 8.4 Hz,



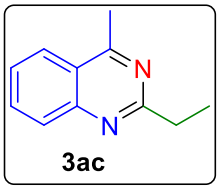
1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.46, 160.37, 150.31, 134.19, 127.67, 127.13, 127.02, 122.87, 26.40.

4-Methylquinazoline (3ab).[12] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (69mg, 96%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.38, 154.66, 149.69, 133.81, 129.15, 127.73, 125.15, 124.64, 21.89.



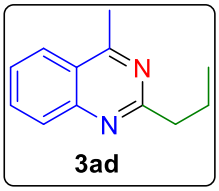
3ab

2-Ethyl-4-methylquinazoline (3ac).[10] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (79mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 2.91 (s, 3H), 1.46 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.85, 167.50, 149.77, 133.19, 128.25, 126.30, 124.65, 122.21, 32.92, 21.48, 12.86.



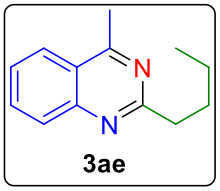
3ac

4-Methyl-2-propylquinazoline (3ad).[5] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (87mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.83 (td, J = 8.0, 1.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 3.08 – 3.01 (m, 2H), 2.93 (s, 3H), 2.00 – 1.90 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 166.94, 150.05, 133.57, 128.57, 126.66, 125.02, 122.56, 42.09, 22.55, 21.84, 14.18.



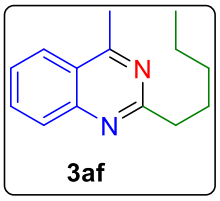
3ad

2-Butyl-4-methylquinazoline (3ae).[7] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (82mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.55 (td, *J* = 7.5 Hz, 1H), 3.23 (t, *J* = 8.0 Hz, 2H), 2.86 (s, 3H), 1.86 – 1.80 (m, 2H), 1.54 – 1.47 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.82, 163.64, 150.30, 133.39, 128.37, 126.46, 124.67, 121.62, 34.60, 31.65, 26.45, 22.97, 13.91.

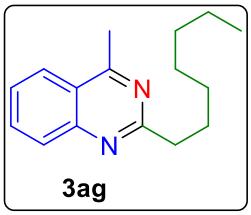


3ae

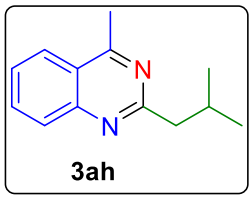
4-Methyl-2-pentylquinazoline (3af).[13] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (85mg, 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 3.05 (t, *J* = 7.9 Hz, 2H), 2.93 (s, 3H), 1.93 – 1.88 (m, 2H), 1.44 – 1.36 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.16, 167.13, 150.02, 133.53, 128.52, 126.60, 124.98, 122.50, 40.18, 31.97, 28.94, 22.69, 21.81, 14.15.



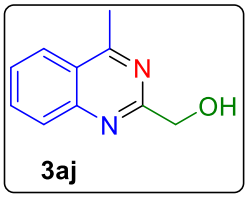
2-Heptyl-4-methylquinazoline (3ag). The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (90mg, 74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.58 – 7.54 (m, 1H), 3.05 (t, *J* = 7.9 Hz, 2H), 2.93 (s, 3H), 1.93 – 1.86 (m, 2H), 1.45 – 1.27 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 159.79, 142.69, 126.17, 121.19, 119.24, 117.63, 115.17, 32.87, 24.53, 22.37, 21.95, 21.90, 15.39, 14.45, 6.82; HRMS (ESI) calculated for $C_{16}H_{23}N_2$ $[M+H]^+$: 243.1861 found 243.1865.



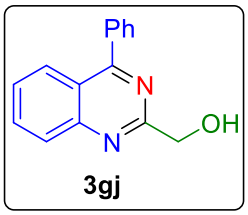
2-Isobutyl-4-methylquinazoline (3ah).[14] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain yellow oil (76mg, 76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 0.5, 1 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.59 – 7.55 (m, 1H), 2.94 (t, *J* = 3.6 Hz, 5H), 2.44 – 2.36 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.01, 166.43, 150.06, 133.51, 128.69, 126.65, 125.02, 122.57, 48.99, 28.77, 22.69, 21.87.



(4-Methylquinazolin-2-yl)methanol (3aj). The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (44mg, 51%); mp 76-78°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 4.95 (d, *J* = 3.4 Hz, 2H), 4.16 (s, 1H), 2.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.07, 163.73, 149.23, 134.18, 128.47, 127.37, 125.34, 123.41, 64.69, 21.89. HRMS (ESI) calculated for $C_{10}H_{11}N_2O$ $[M+H]^+$: 175.0871 found 175.0874.

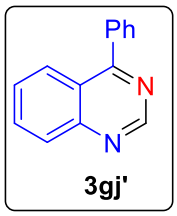


(4-Phenylquinazolin-2-yl)methanol (3gj).[15] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain white solid (63mg, 53%); mp 147-149 °C (lit. 153-155 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 7.95 – 7.92 (m, 1H), 7.79 – 7.77 (m, 2H), 7.62 – 7.58 (m, 4H), 5.05 (d, *J* = 4.4 Hz, 2H), 4.14 (t, *J* = 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.21, 163.99, 150.84, 137.06, 134.24, 130.35, 130.08, 128.83, 128.39, 127.51, 122.21, 64.92.



3gj

4-Phenylquinazoline (3gj').[9] The title compound was synthesized according to the general procedure (B) and the product was isolated by column chromatography (Hexane/Ethyl acetate) to obtain colourless oil (42mg, 41%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64 (s, 2H), 7.42 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.99, 154.35, 150.78, 136.79, 133.37, 129.78, 129.72, 128.58, 128.34, 127.44, 126.76, 122.80.



3gj'

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(9) Copies of ^{1}H and ^{13}C Data

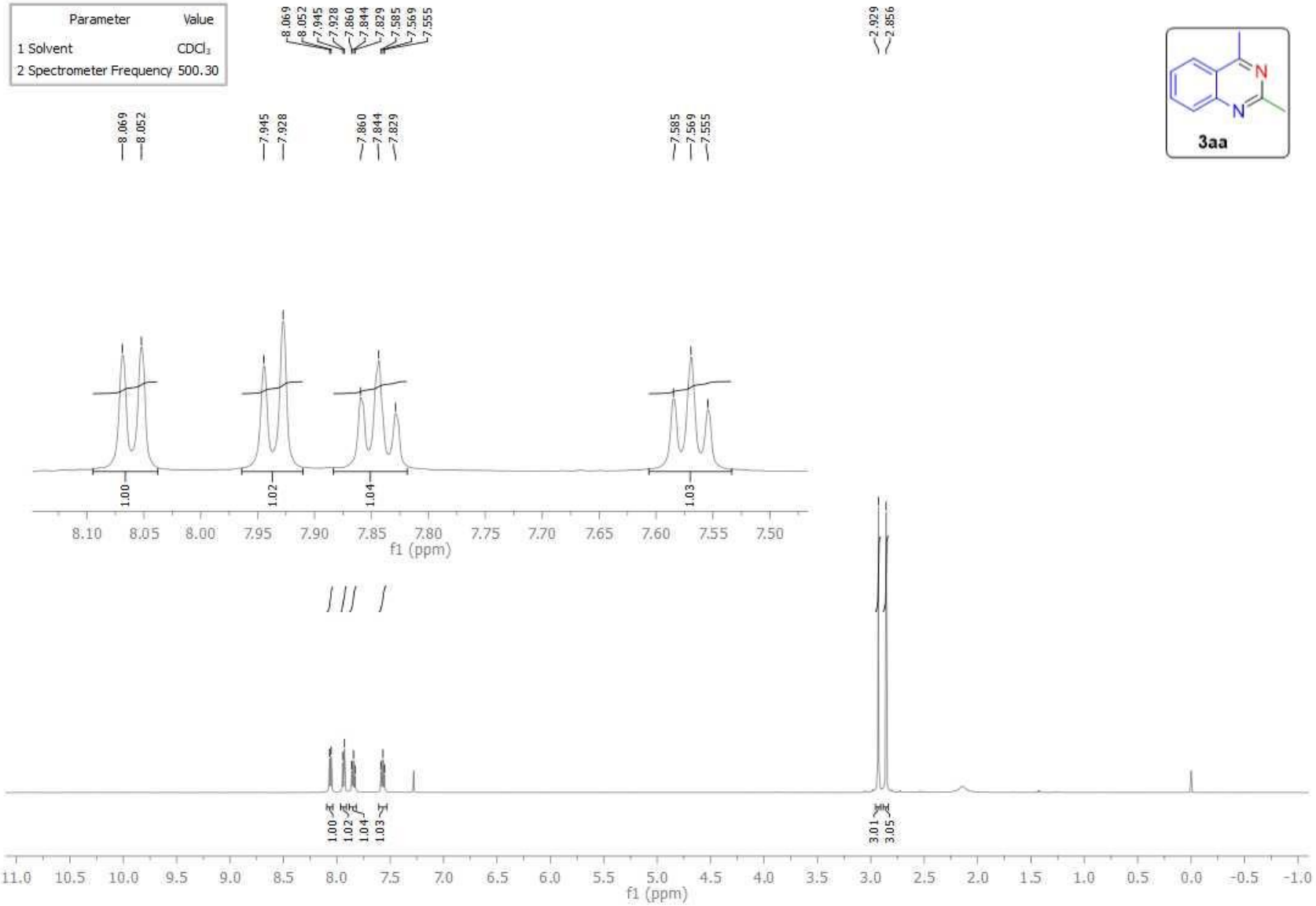

Figure S6. ^{1}H NMR Spectrum of 2,4-Dimethylquinazoline **(3aa).**

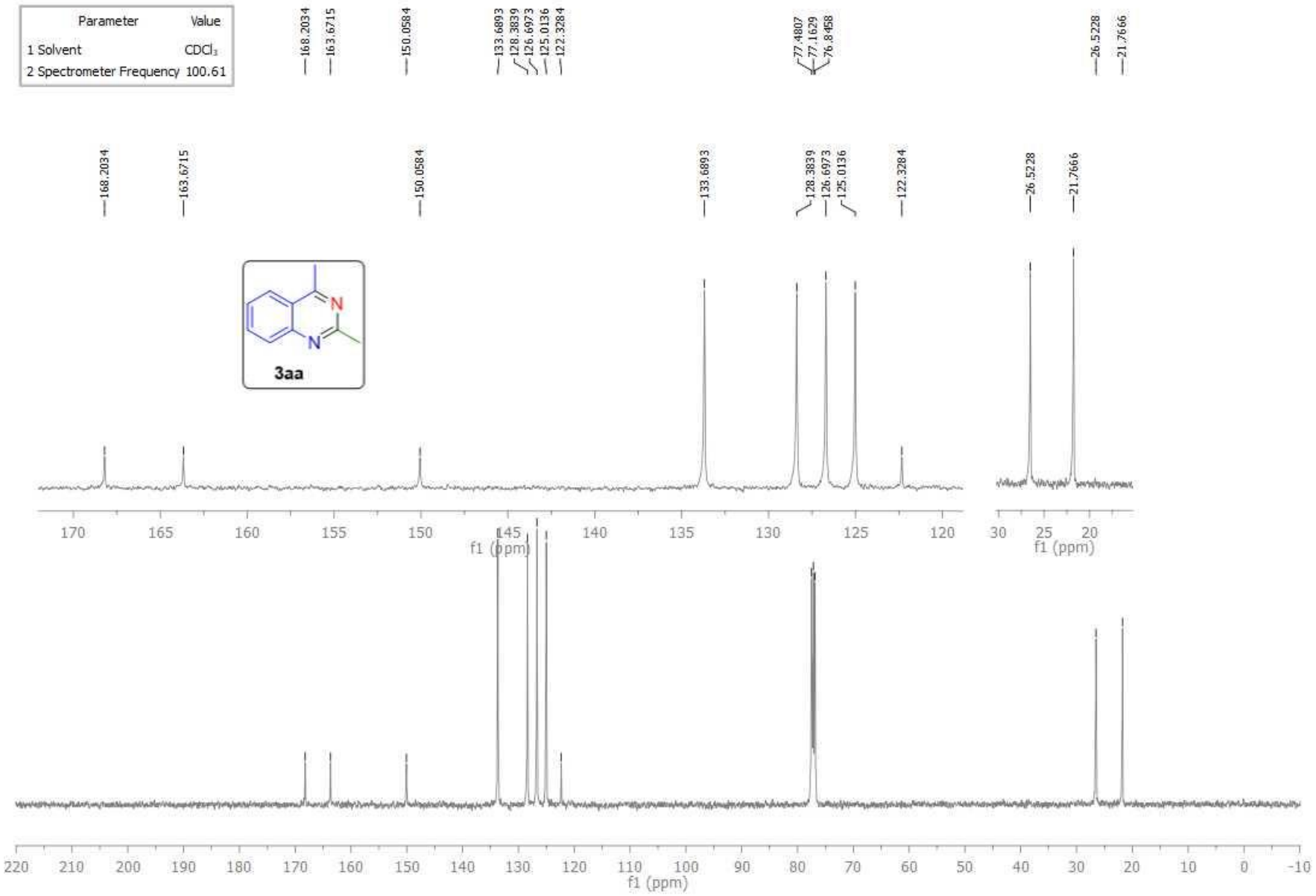

Figure S7. ^{13}C NMR Spectrum of 2,4-Dimethylquinazoline **(3aa)**

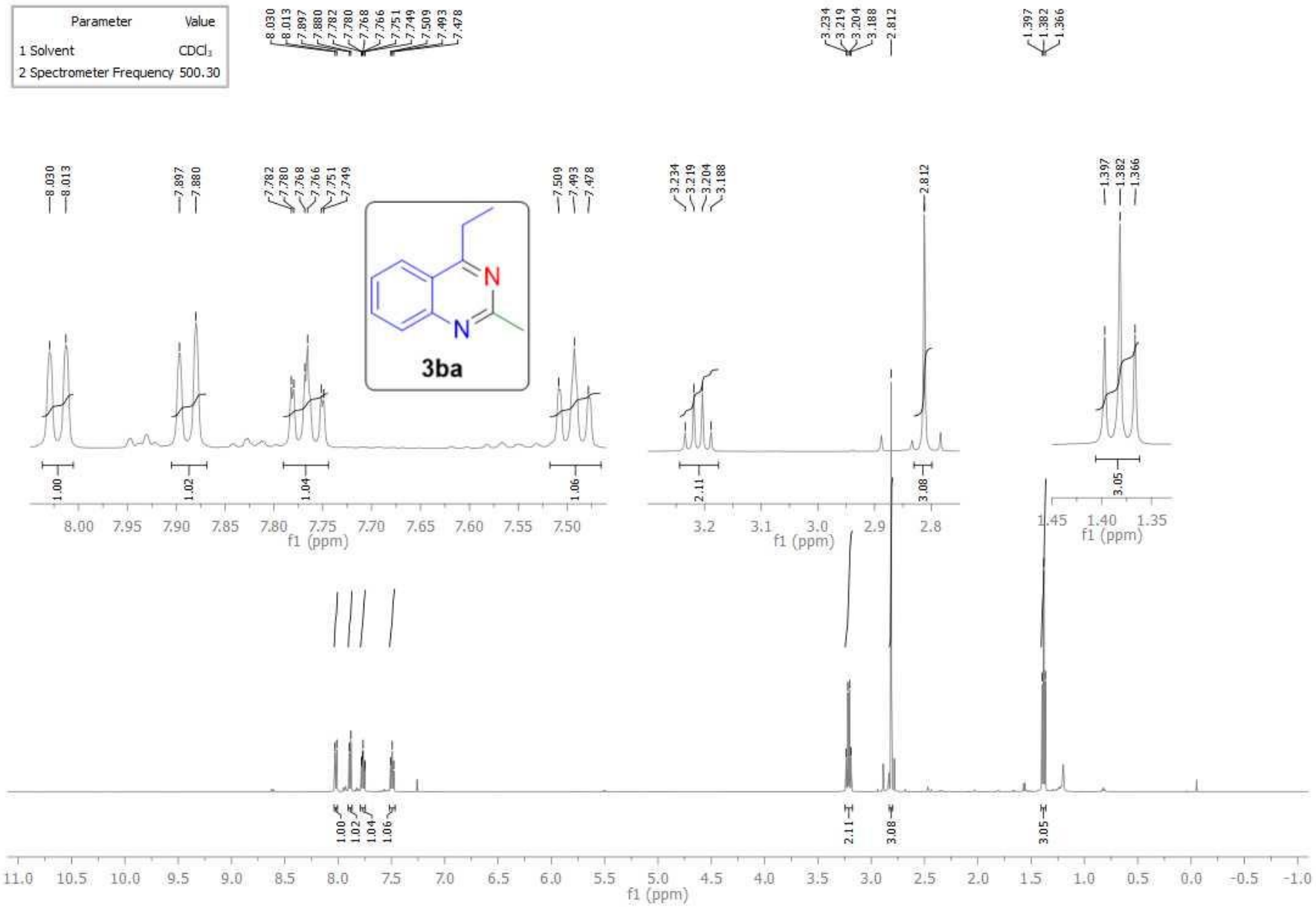

Figure S8. [1]H NMR Spectrum of 4-Ethyl-2-methylquinazoline **(3ba)**

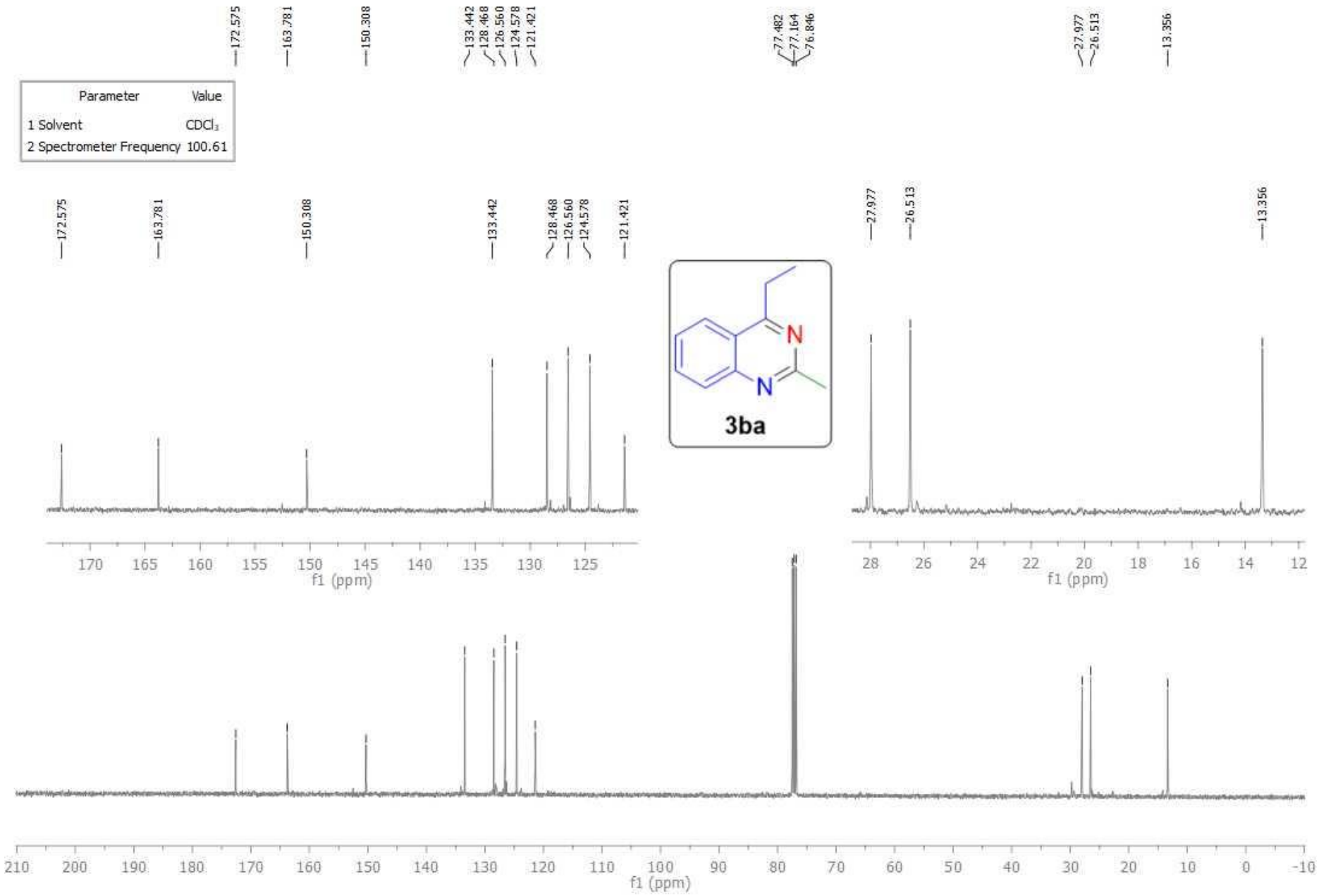

Figure S9. ^{13}C NMR Spectrum of 4-Ethyl-2-methylquinazoline **(3ba)**

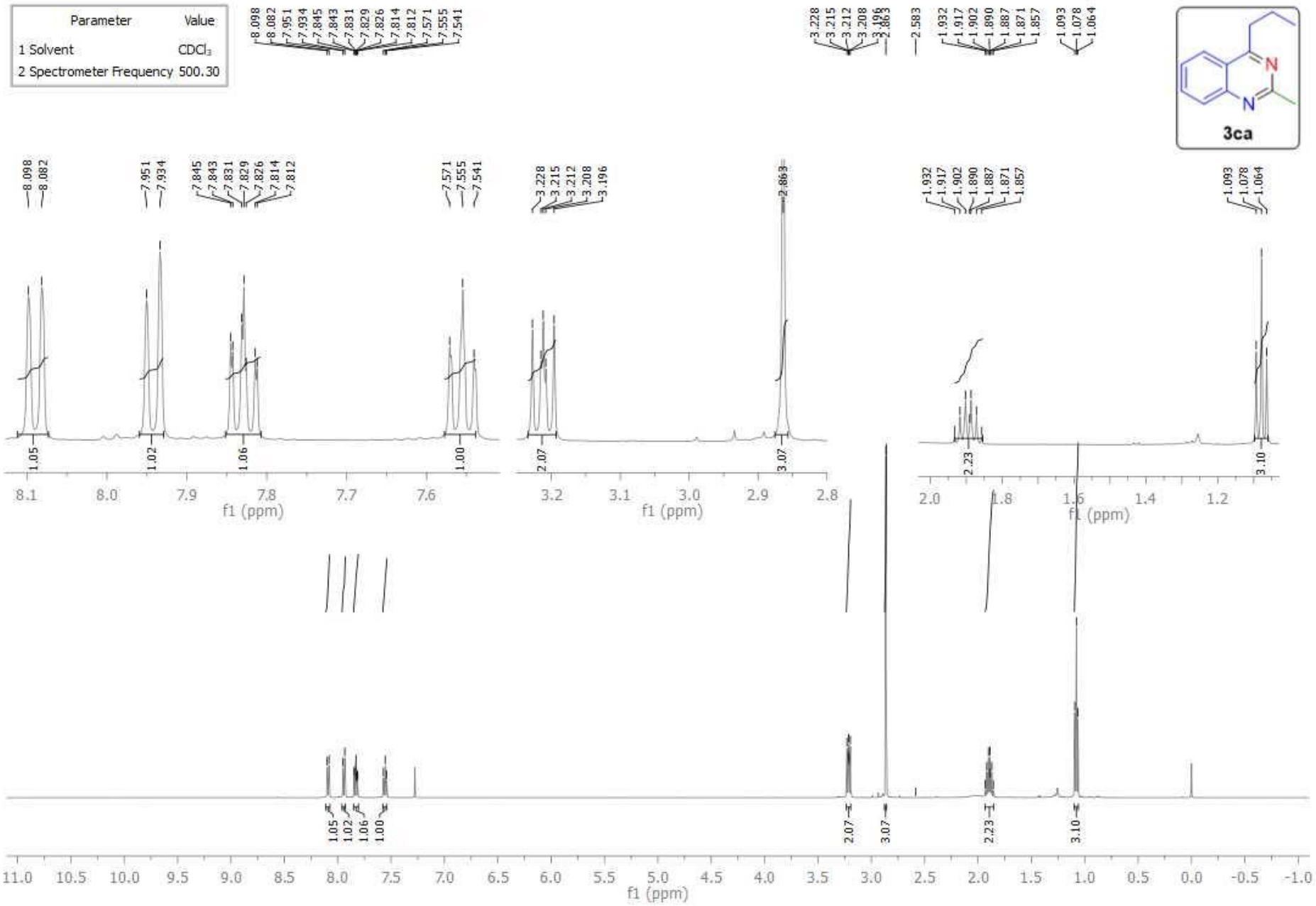

Figure S10. ^{1}H NMR Spectrum of 2-Methyl-4-propylquinazoline **(3ca).**

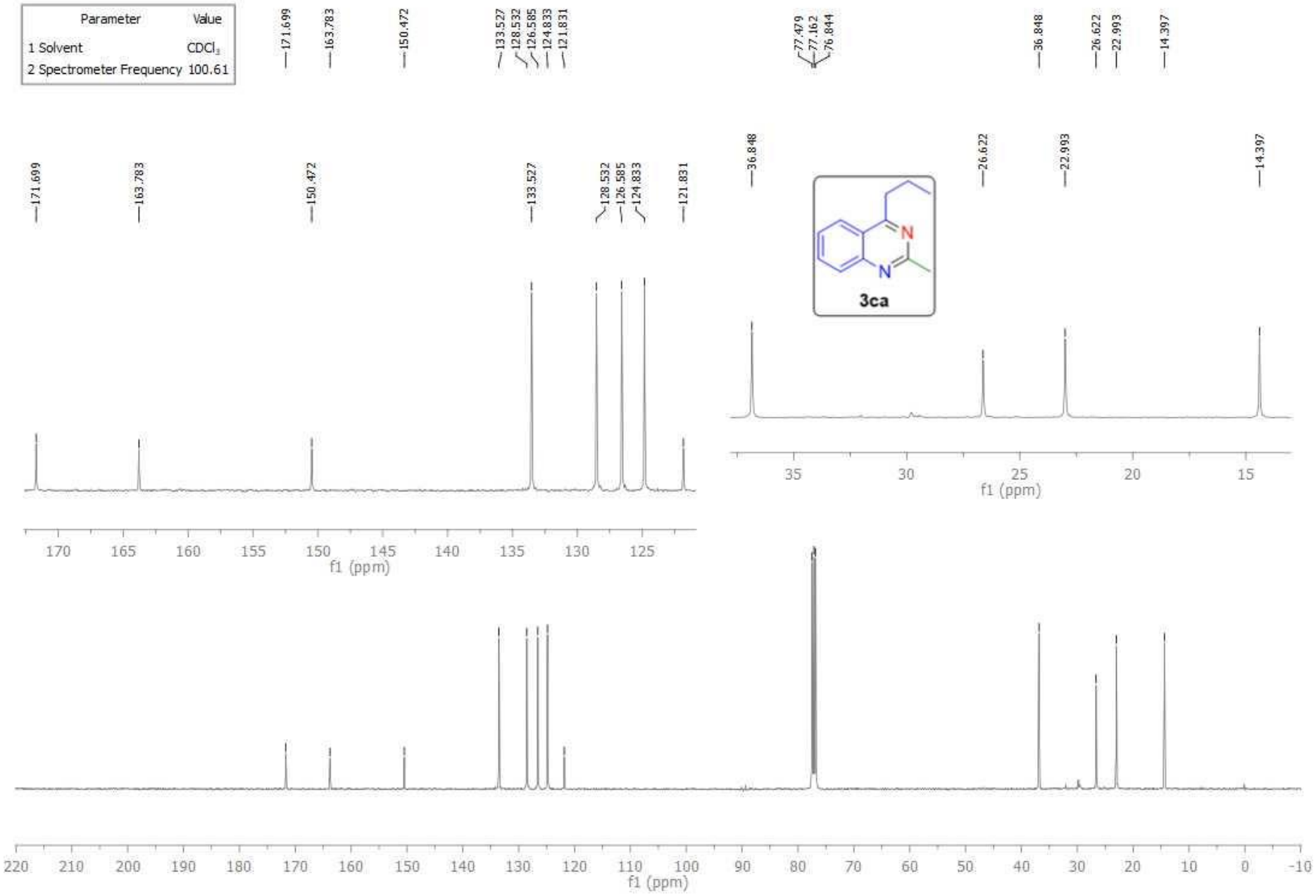

Figure S11. ^{13}C NMR Spectrum of 2-Methyl-4-propylquinazoline **(3ca)**

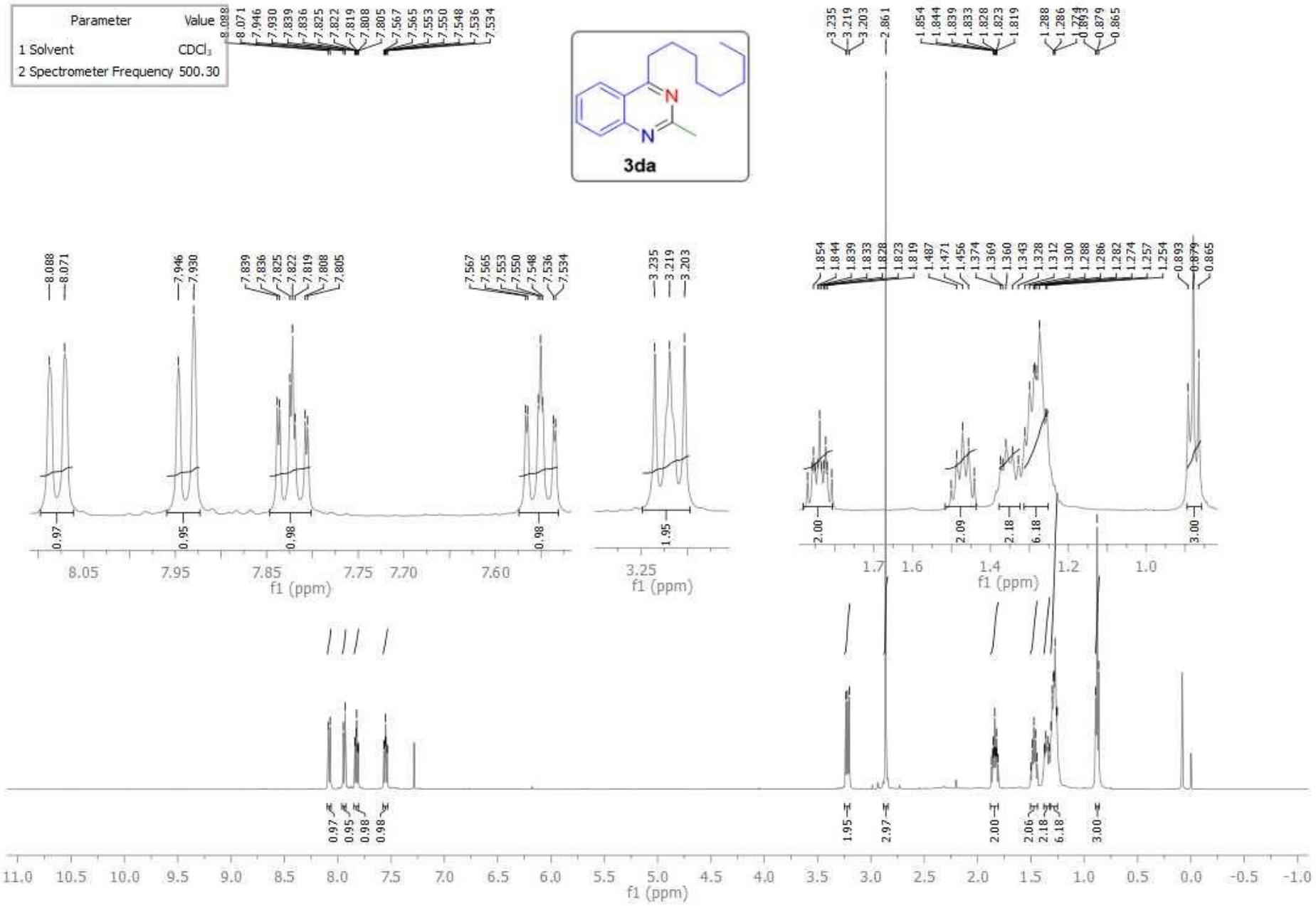

Figure S12. ^{1}H NMR Spectrum of 2-Methyl-4-octylquinazoline **(3da)**

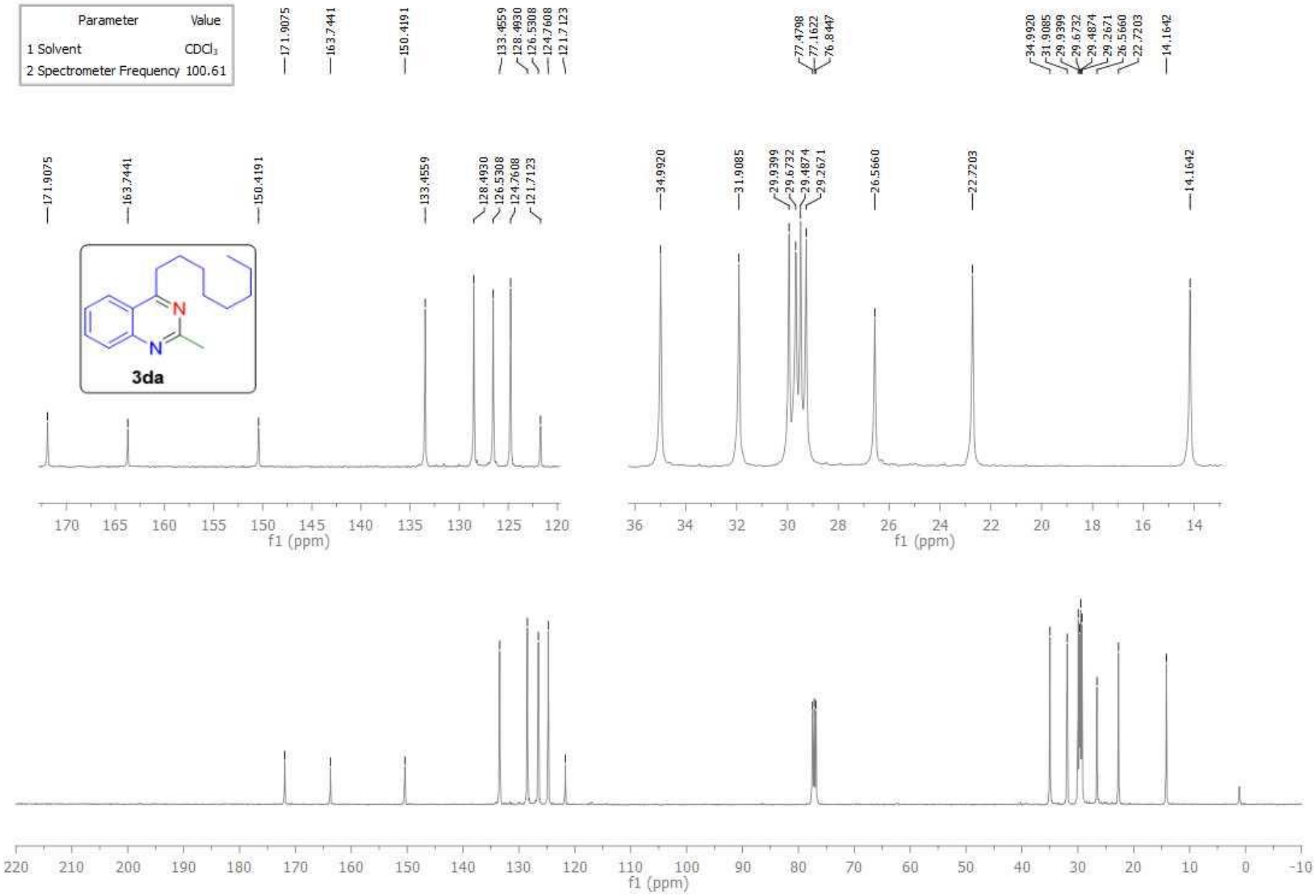

Figure S13. ^{13}C NMR Spectrum of 2-Methyl-4-octylquinazoline **(3da)**

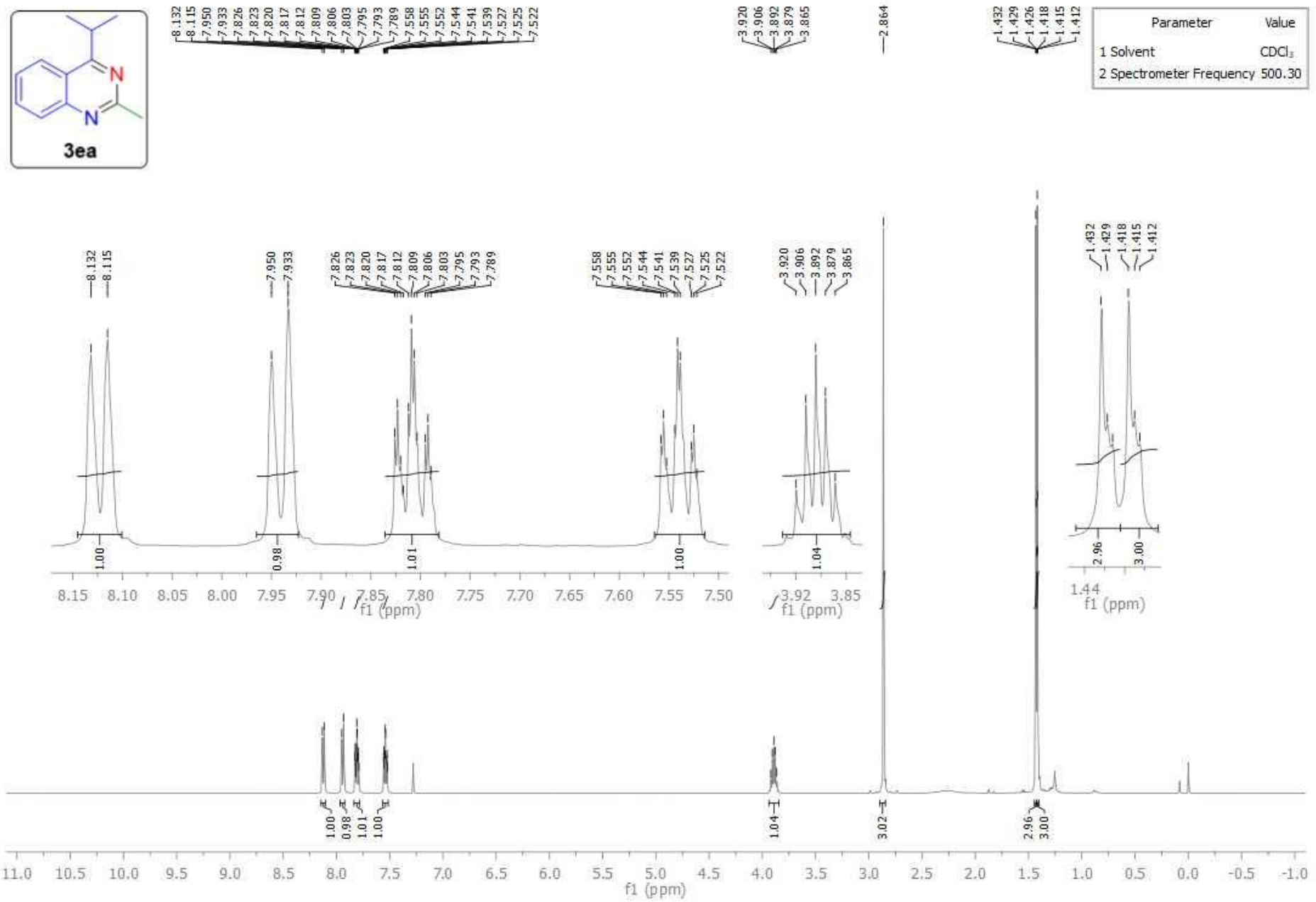

Figure S14. ^{1}H NMR Spectrum of 4-Isopropyl-2-methylquinazoline **(3ea)**

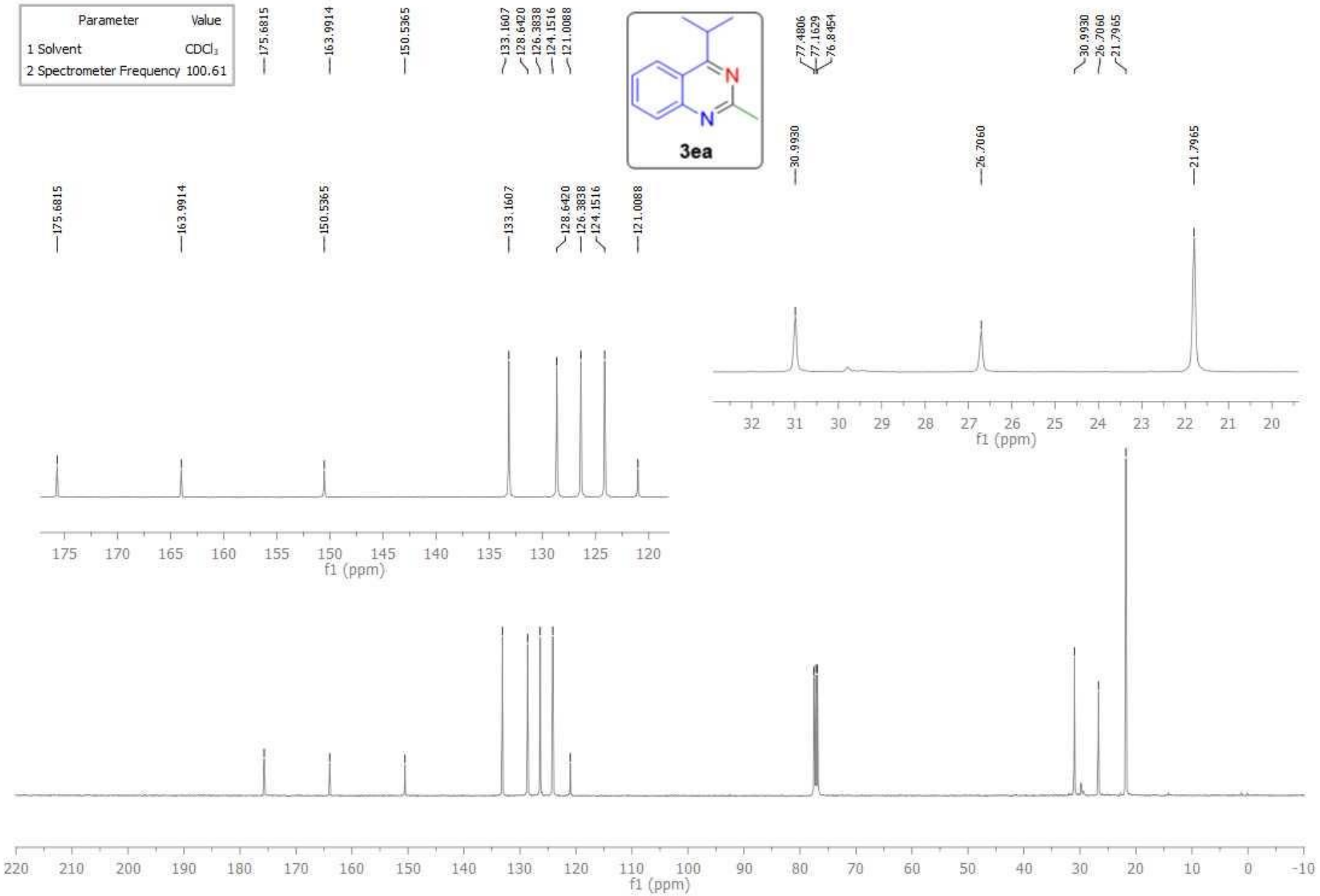

Figure S15. ^{13}C NMR Spectrum of 4-Isopropyl-2-methylquinazoline **(3ea)**

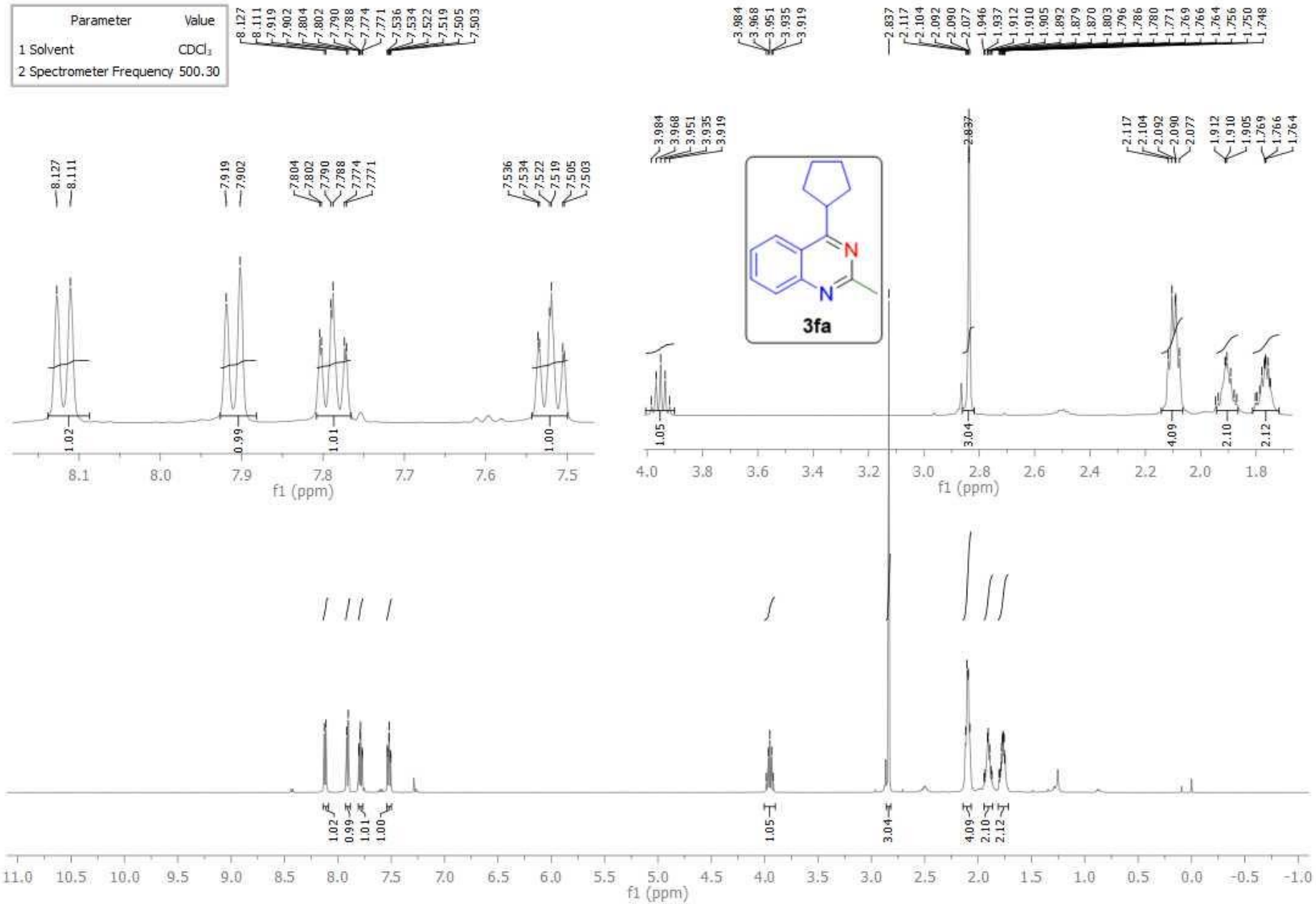

Figure S16. ^{1}H NMR Spectrum of 4-Cyclopentyl-2-methylquinazoline **(3fa)**

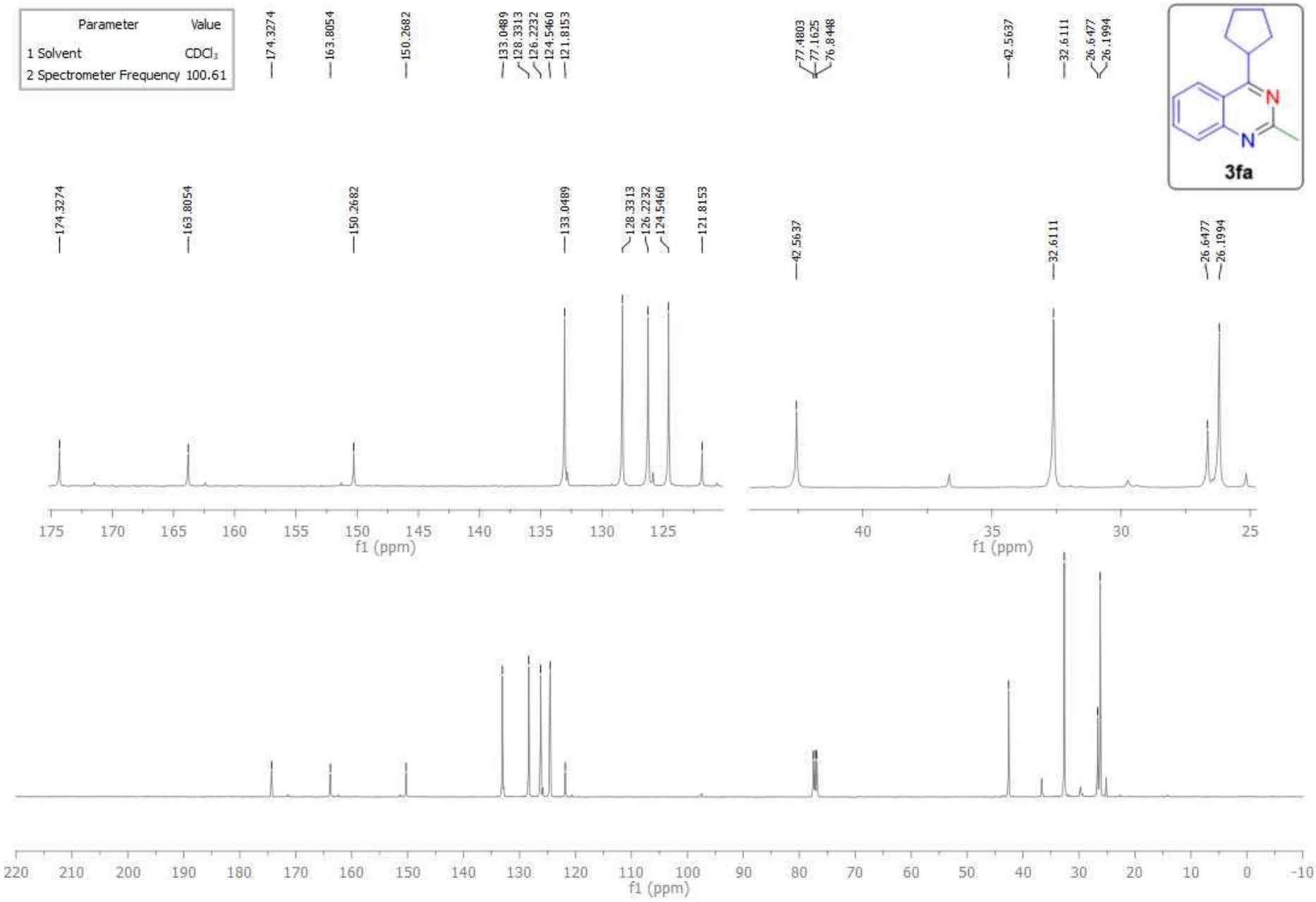

Figure S17. ^{13}C NMR Spectrum of 4-Cyclopentyl-2-methylquinazoline **(3fa)**

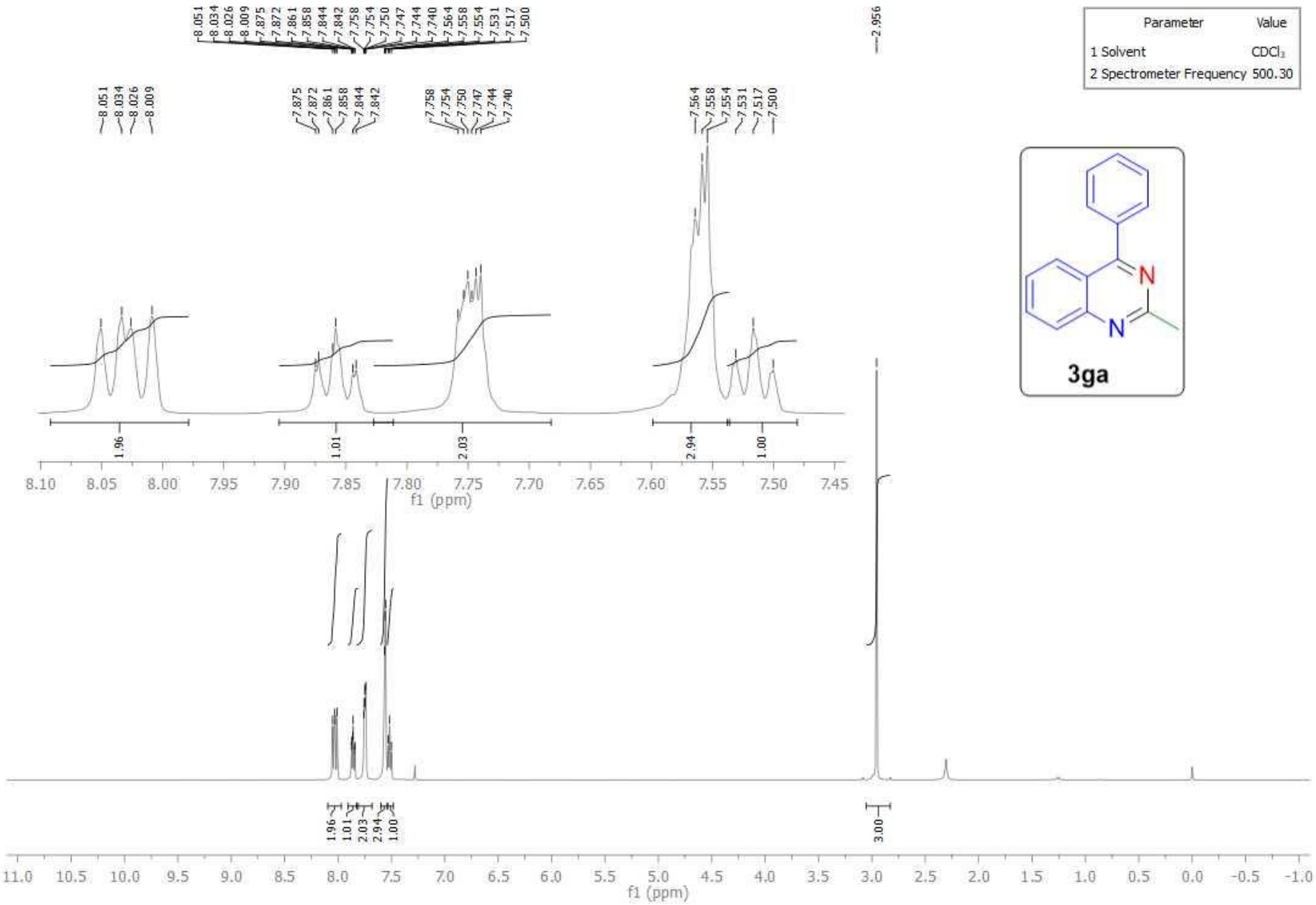

Figure S18. ^{1}H NMR Spectrum of 2-Methyl-4-phenylquinazoline **(3ga)**

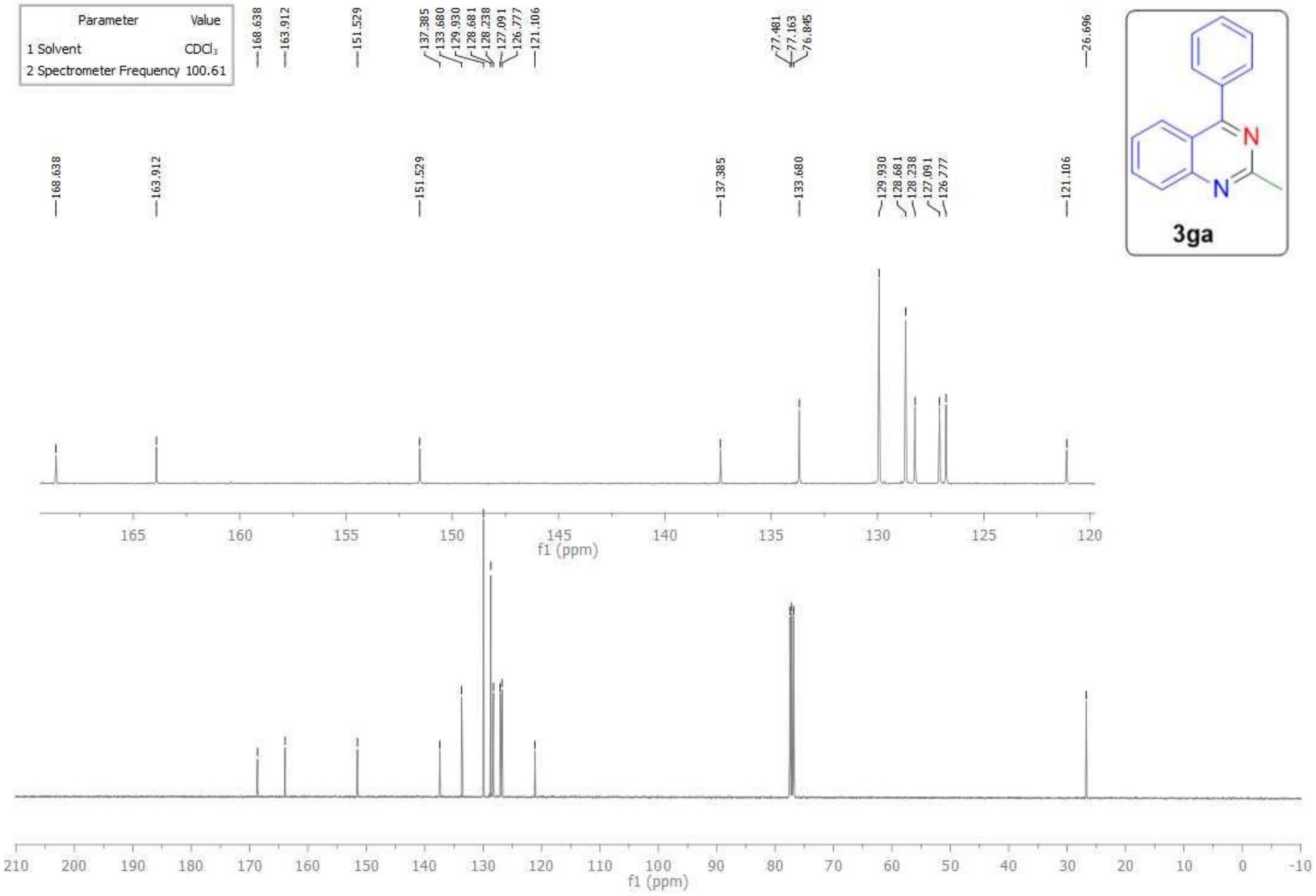

Figure S19. ^{13}C NMR Spectrum of 2-Methyl-4-phenylquinazoline **(3ga)**

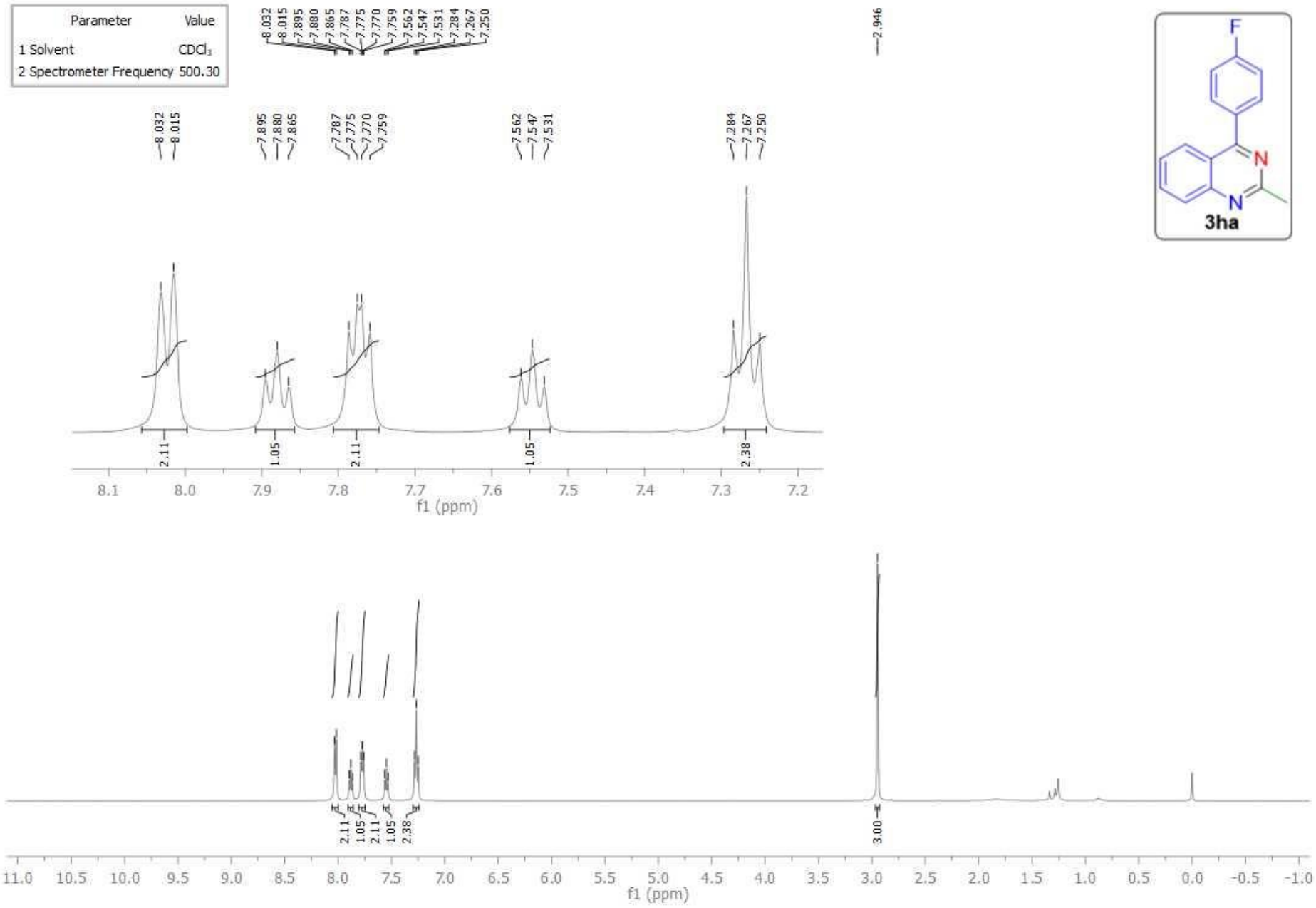

Figure S20. ^{1}H NMR Spectrum of 4-(4-Fluorophenyl)-2-methylquinazoline **(3ha)**

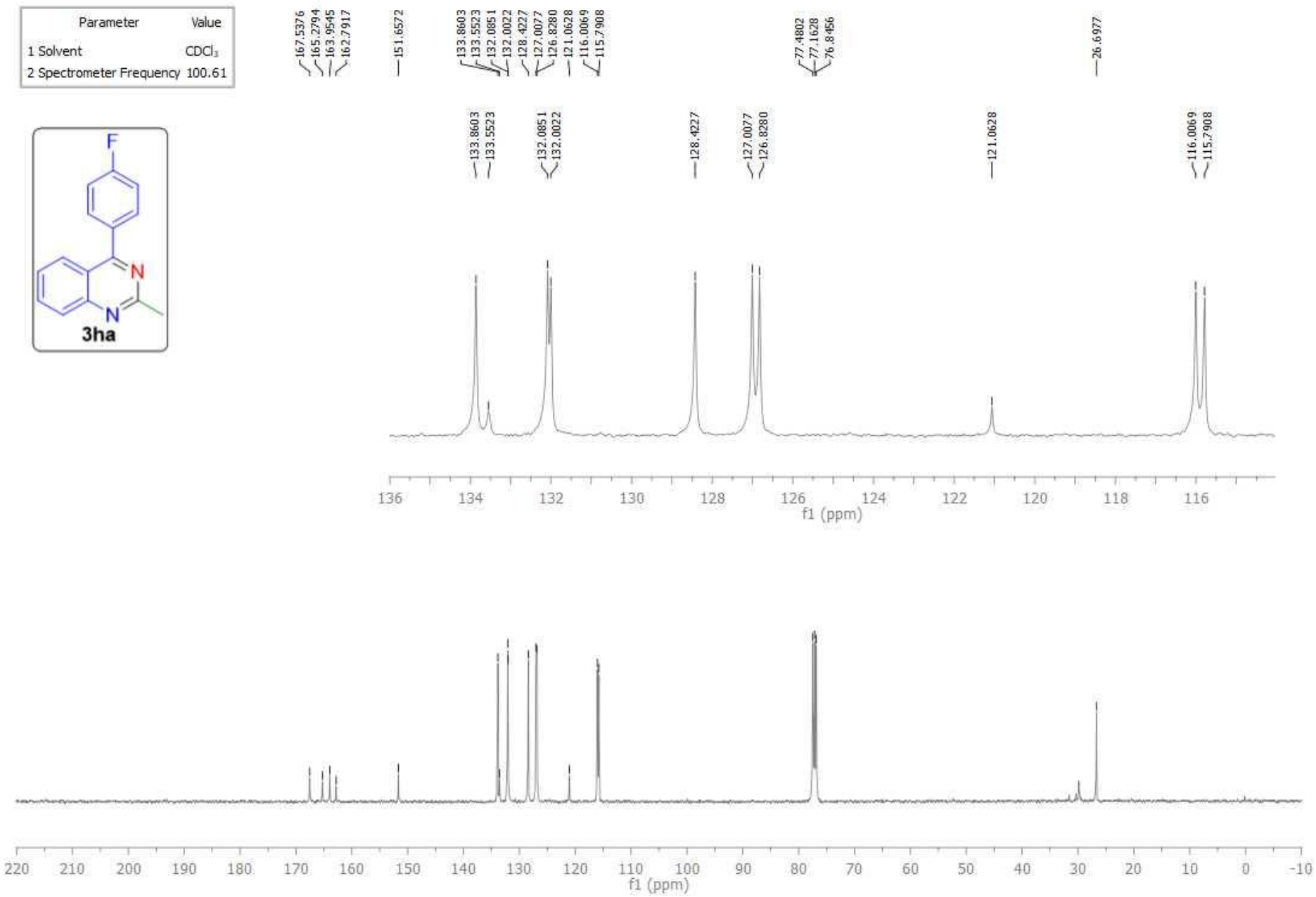

Figure S21. ^{13}C NMR Spectrum of 4-(4-Fluorophenyl)-2-methylquinazoline **(3ha)**

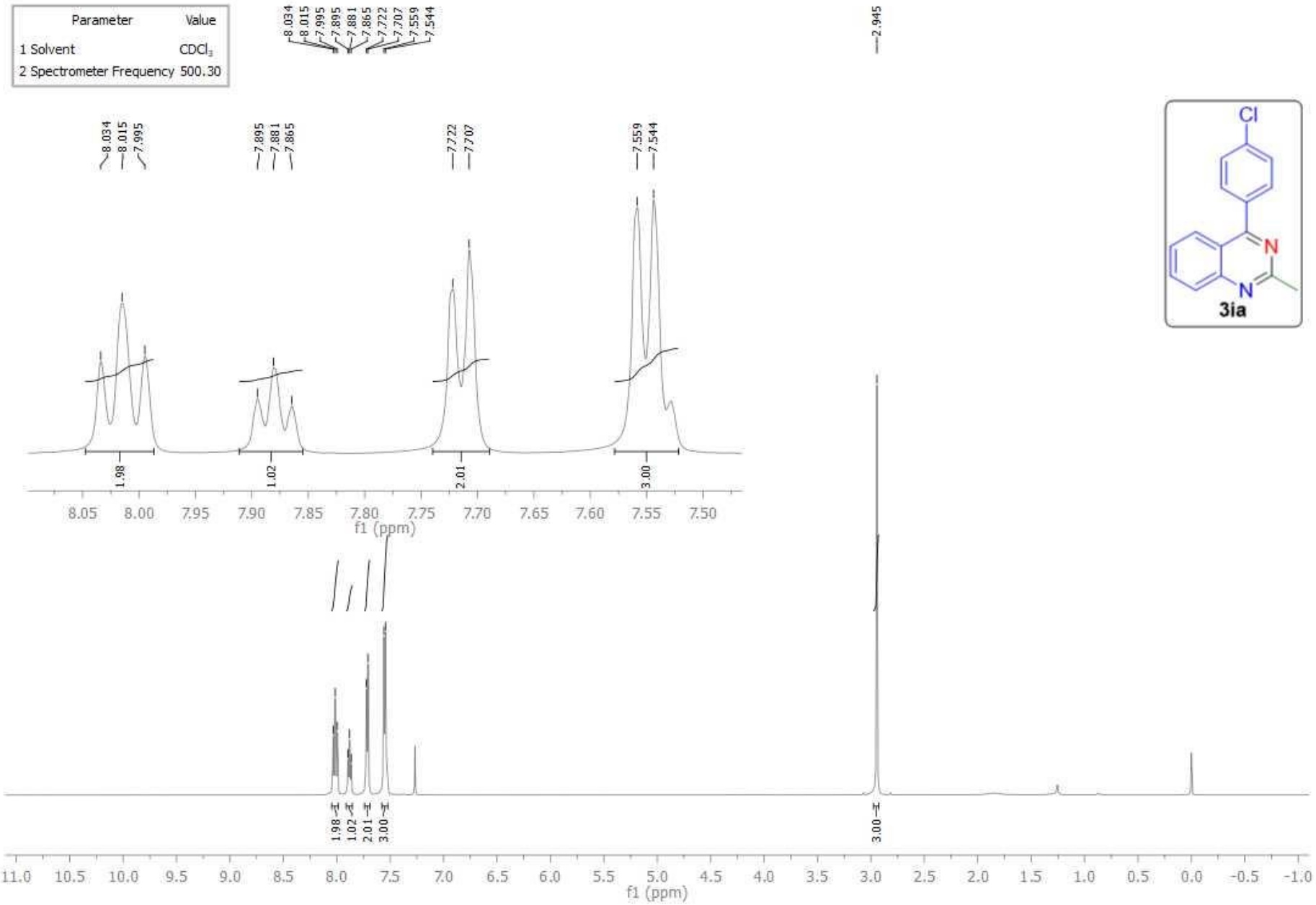

Figure S22. ^{1}H NMR Spectrum of 4-(4-Chlorophenyl)-2-methylquinazoline **(3ia)**

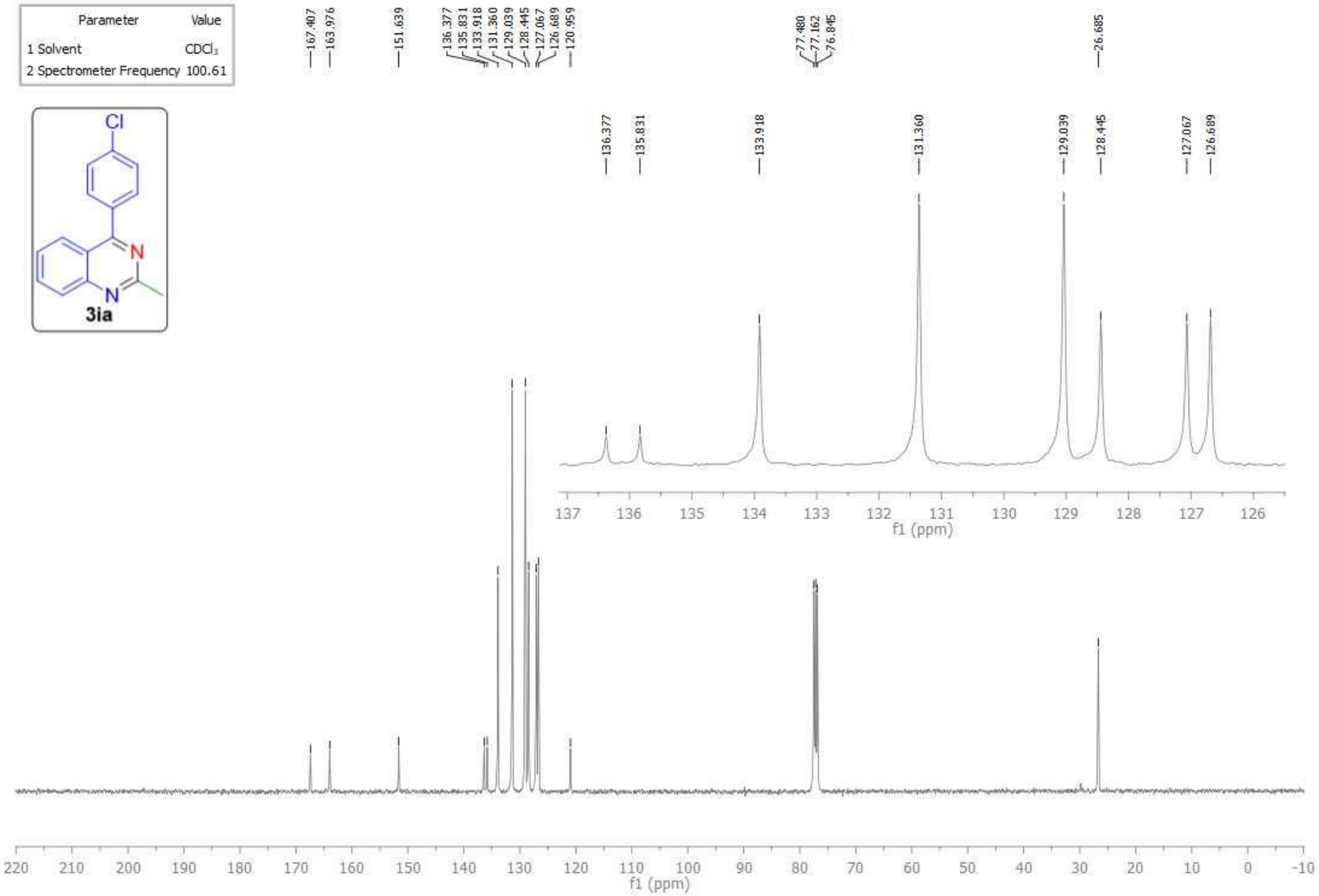

Figure S23. ^{13}C NMR Spectrum of 4-(4-Chlorophenyl)-2-methylquinazoline **(3ia)**

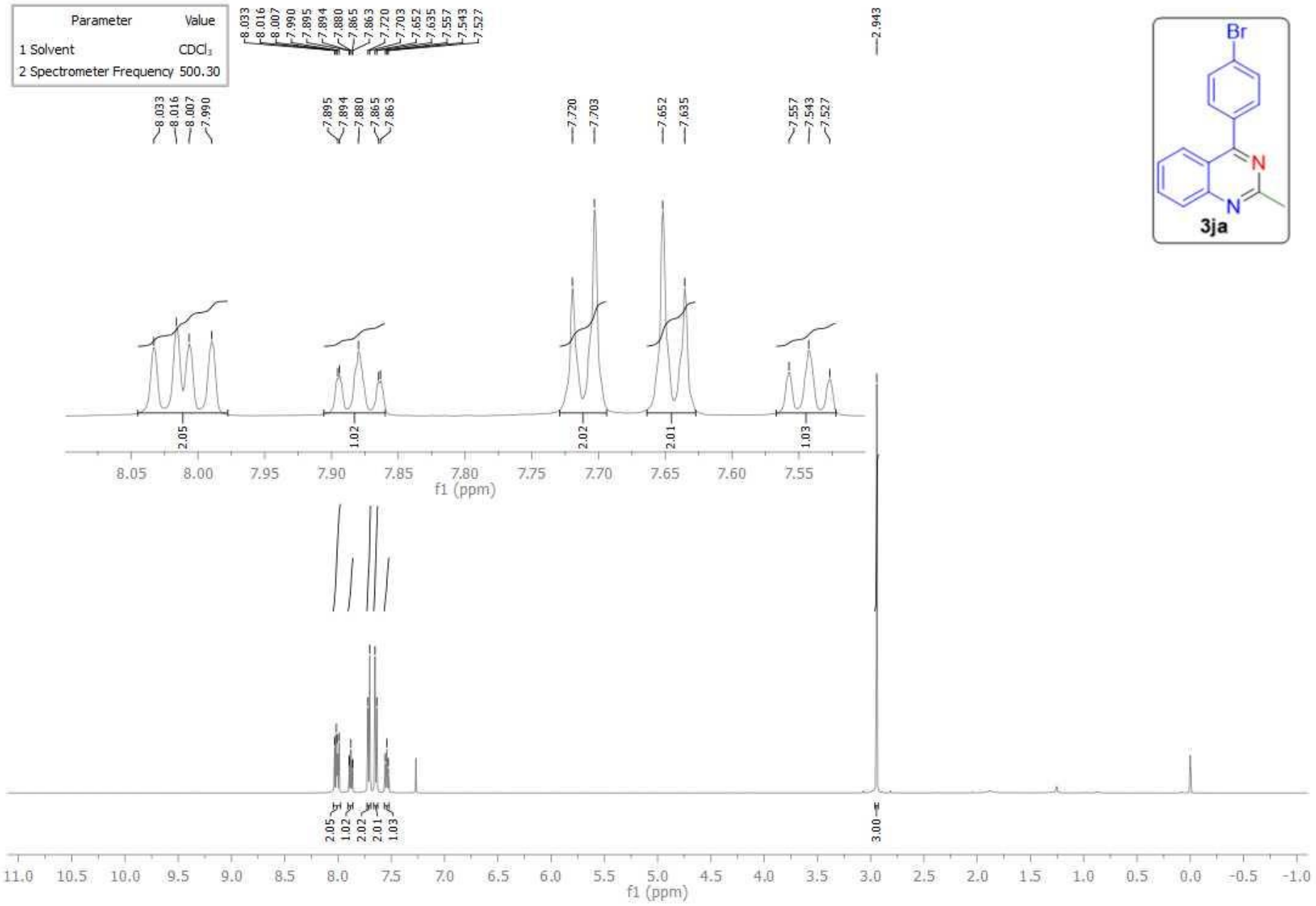

Figure S24. ^{1}H NMR Spectrum of 4-(4-Bromophenyl)-2-methylquinazoline **(3ja)**

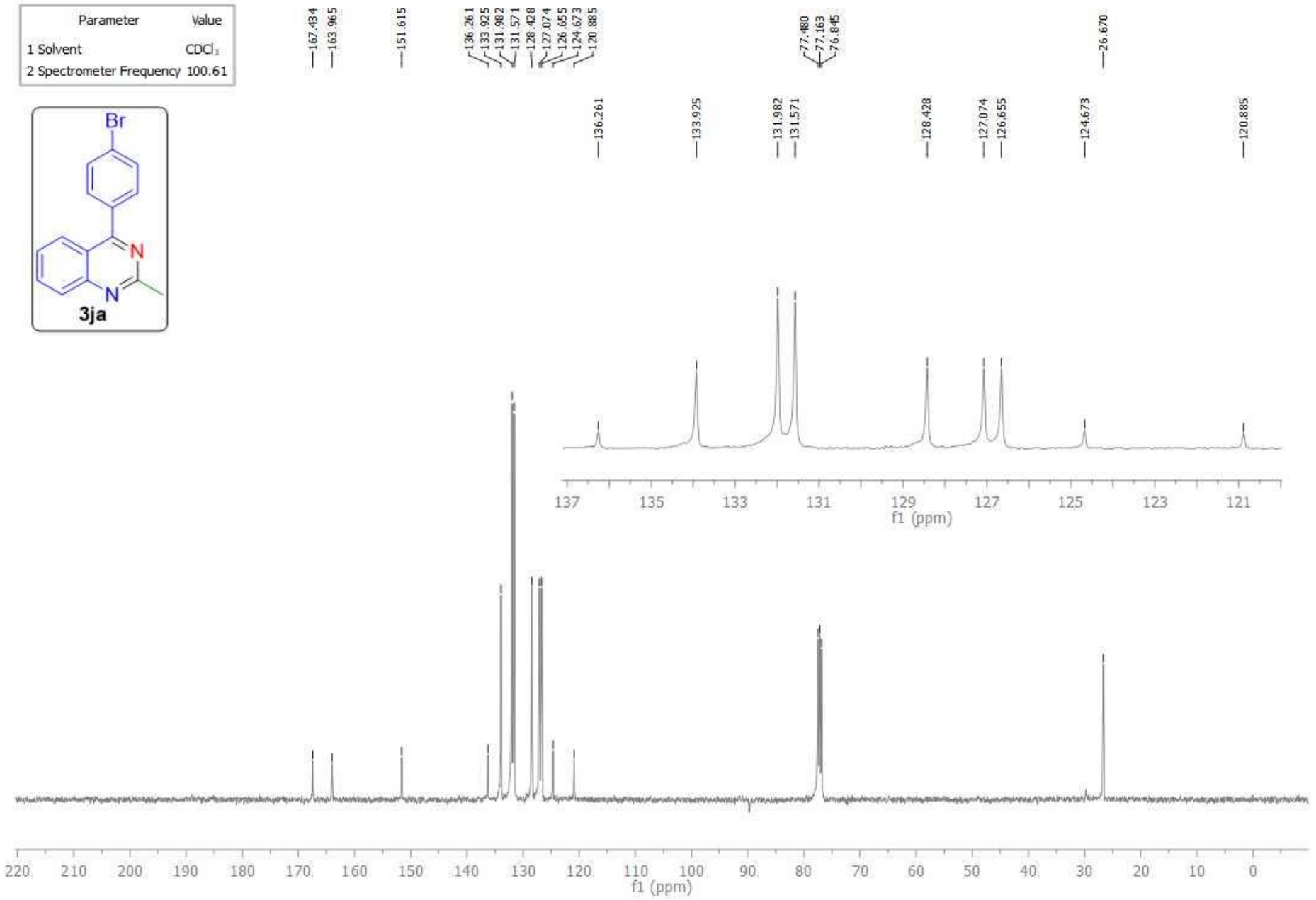

Figure S25. ^{13}C NMR Spectrum of 4-(4-Bromophenyl)-2-methylquinazoline **(3ja)**

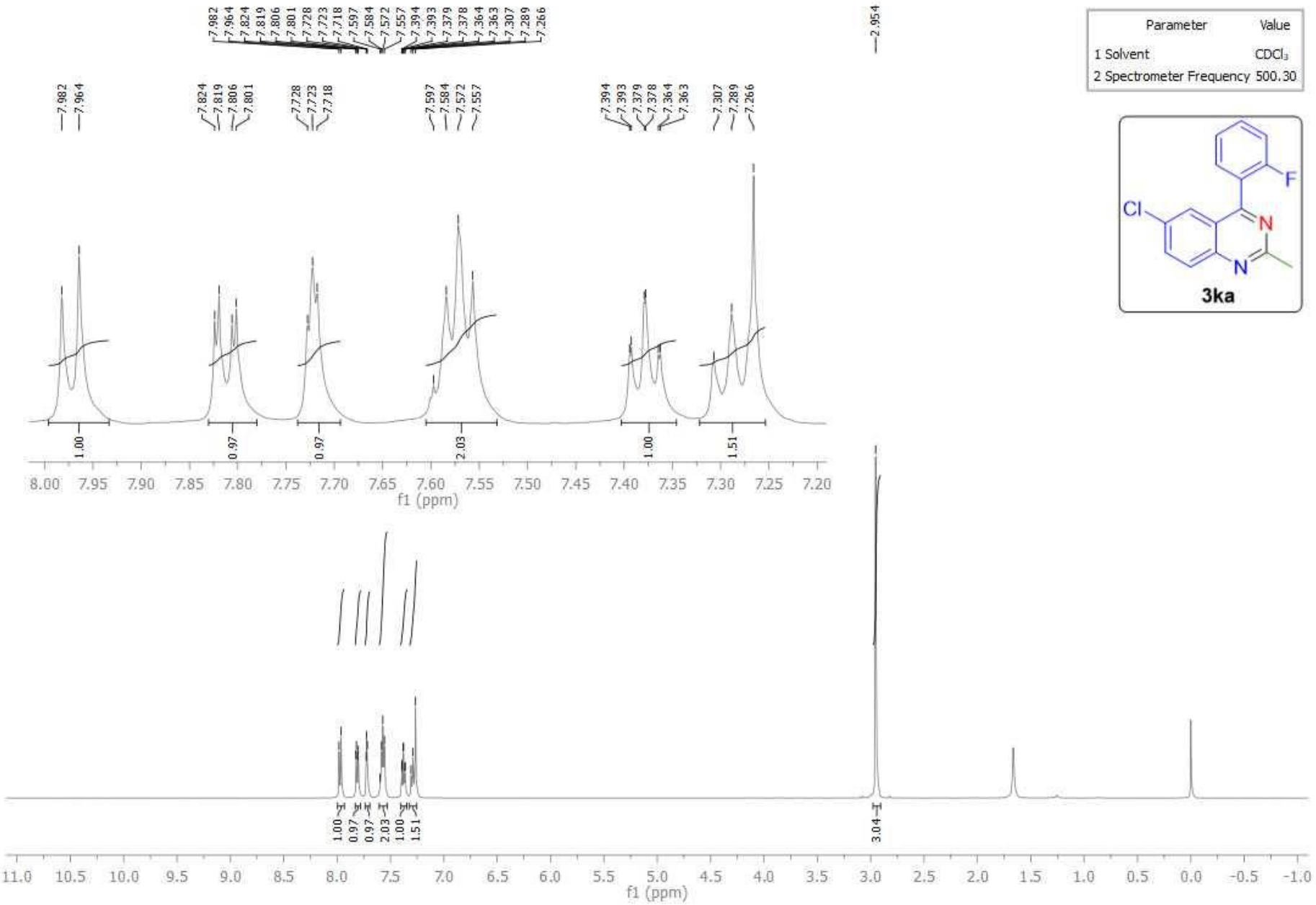

Figure S26. ^{1}H NMR Spectrum of 6-Chloro-4-(2-fluorophenyl)-2-methylquinazoline **(3ka)**

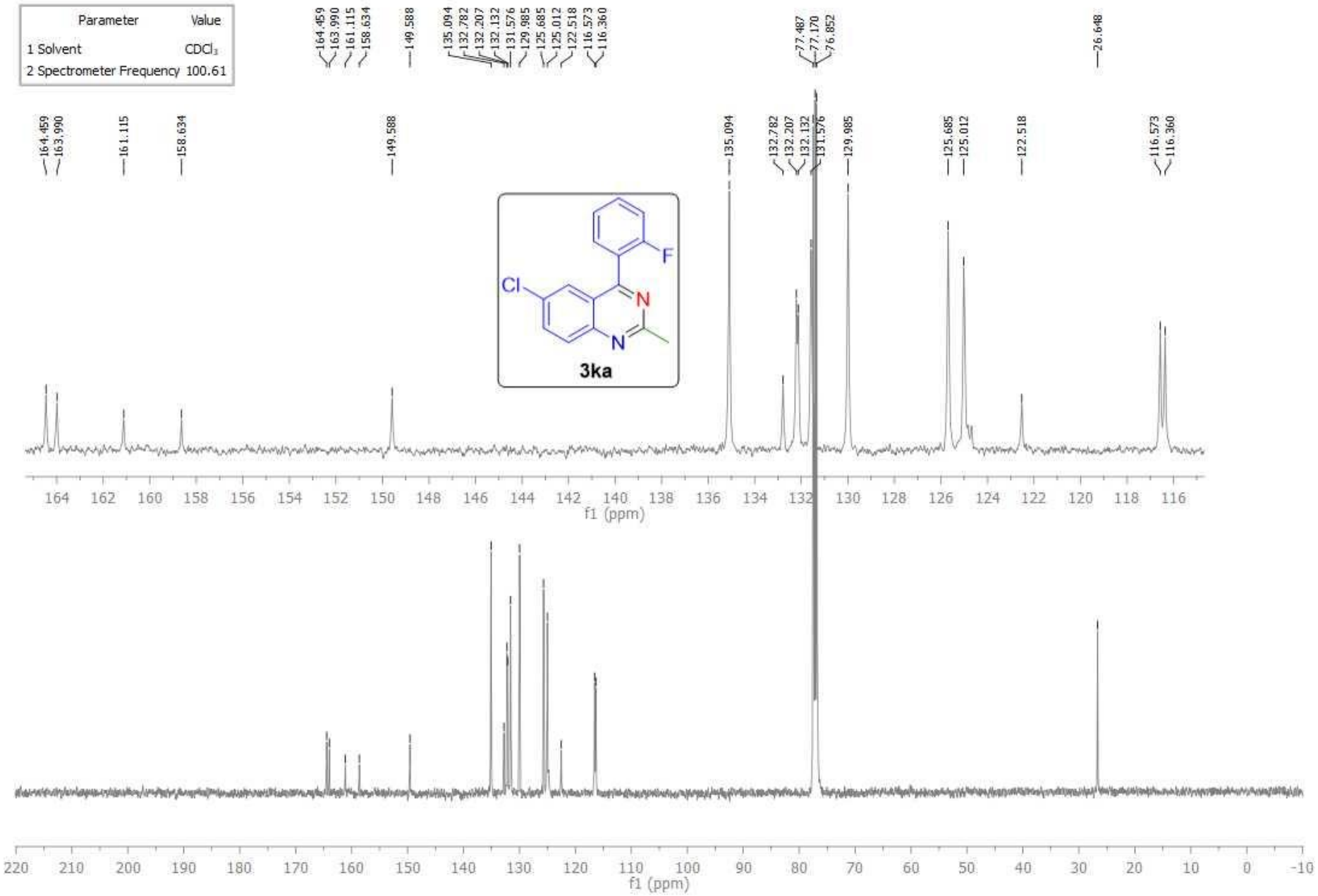

Figure S27. ^{13}C NMR Spectrum of 6-Chloro-4-(2-fluorophenyl)-2-methylquinazoline **(3ka)**

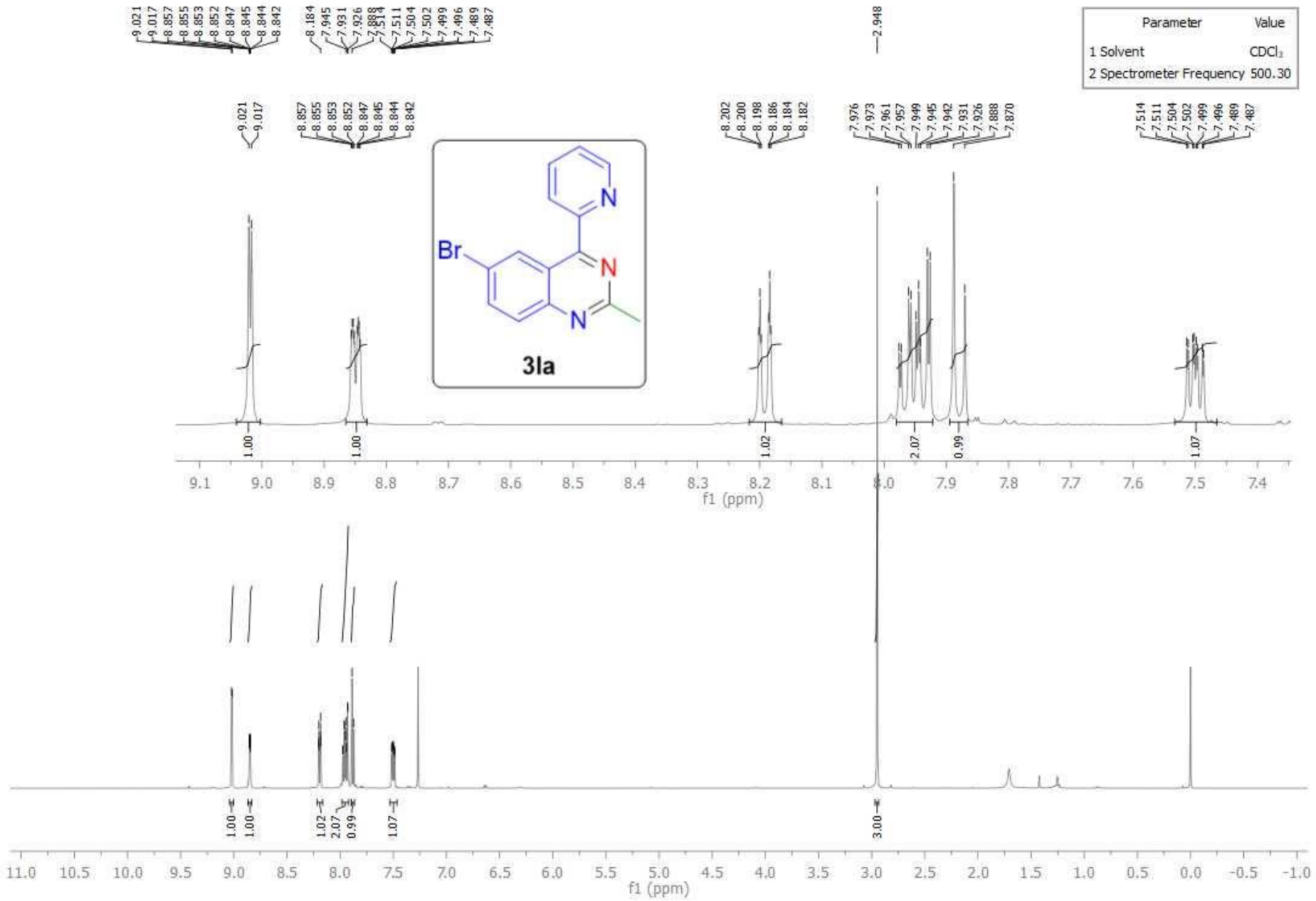

Figure S28. ^{1}H NMR Spectrum of 6-Bromo-2-methyl-4-(pyridin-2-yl)quinazoline **(3la)**

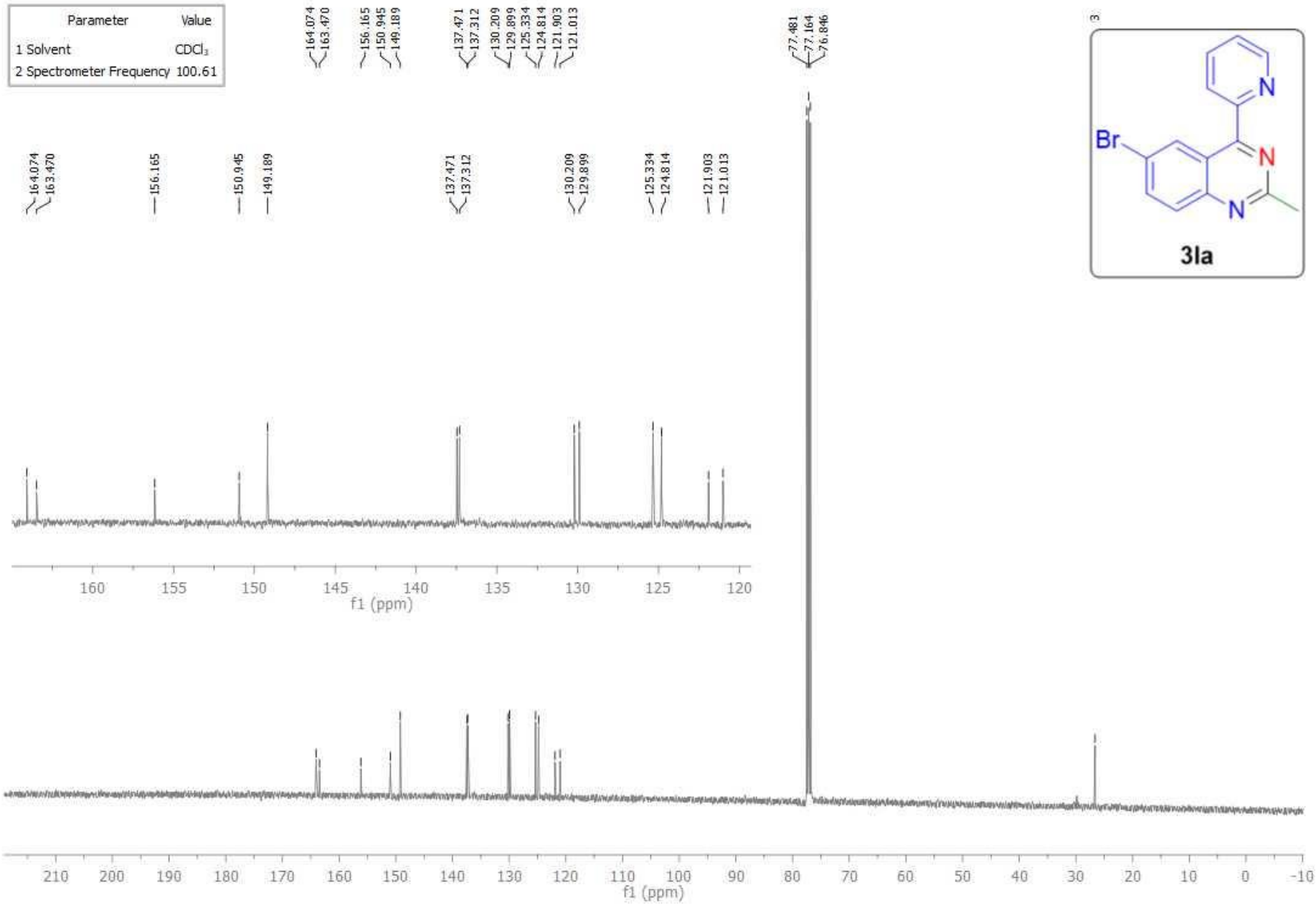

Figure S29. ^{13}C NMR Spectrum of 6-Bromo-2-methyl-4-(pyridin-2-yl)quinazoline **(3la)**

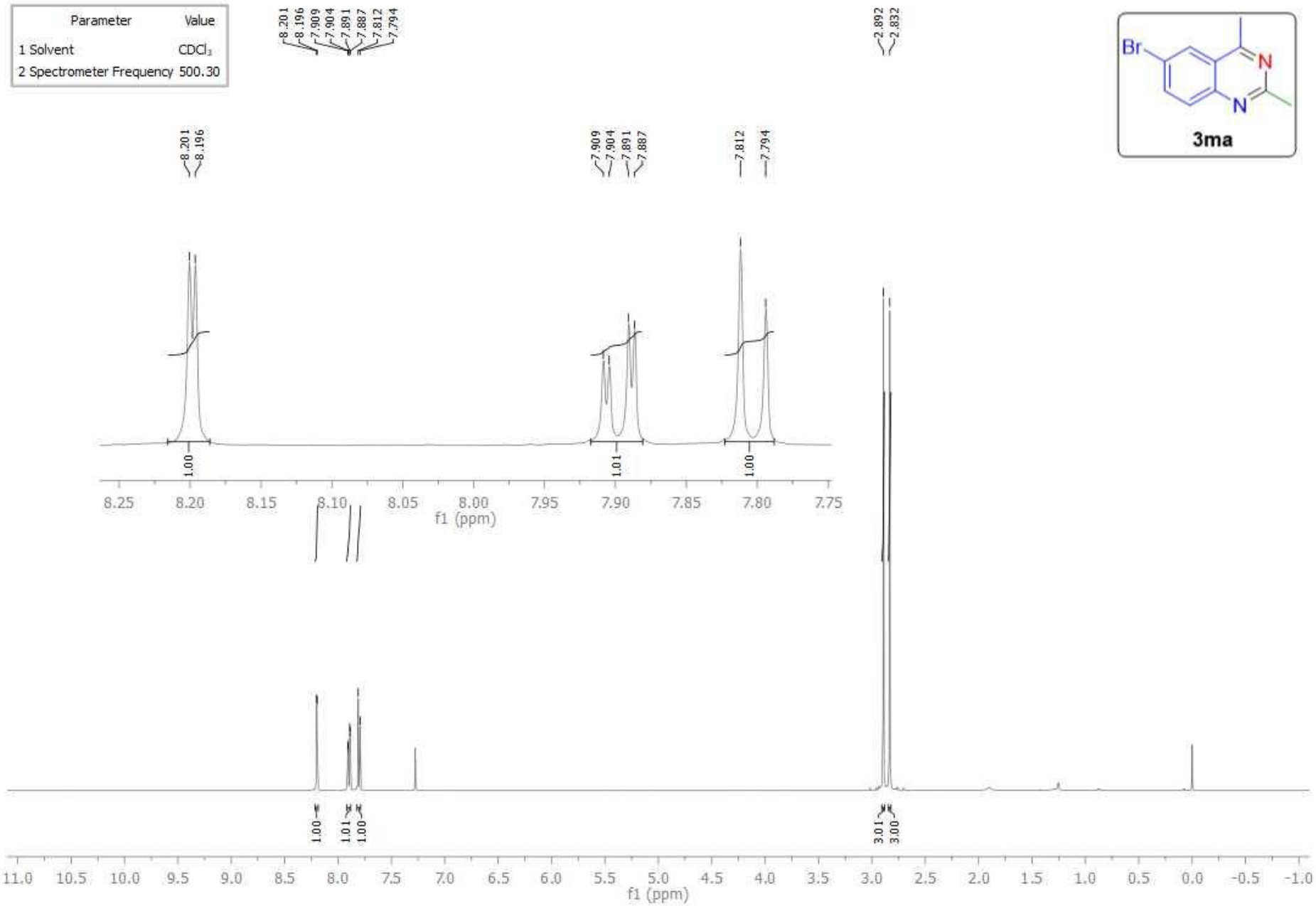

Figure S30. ^{1}H NMR Spectrum of 6-Bromo-2,4-dimethylquinazoline **(3ma)**

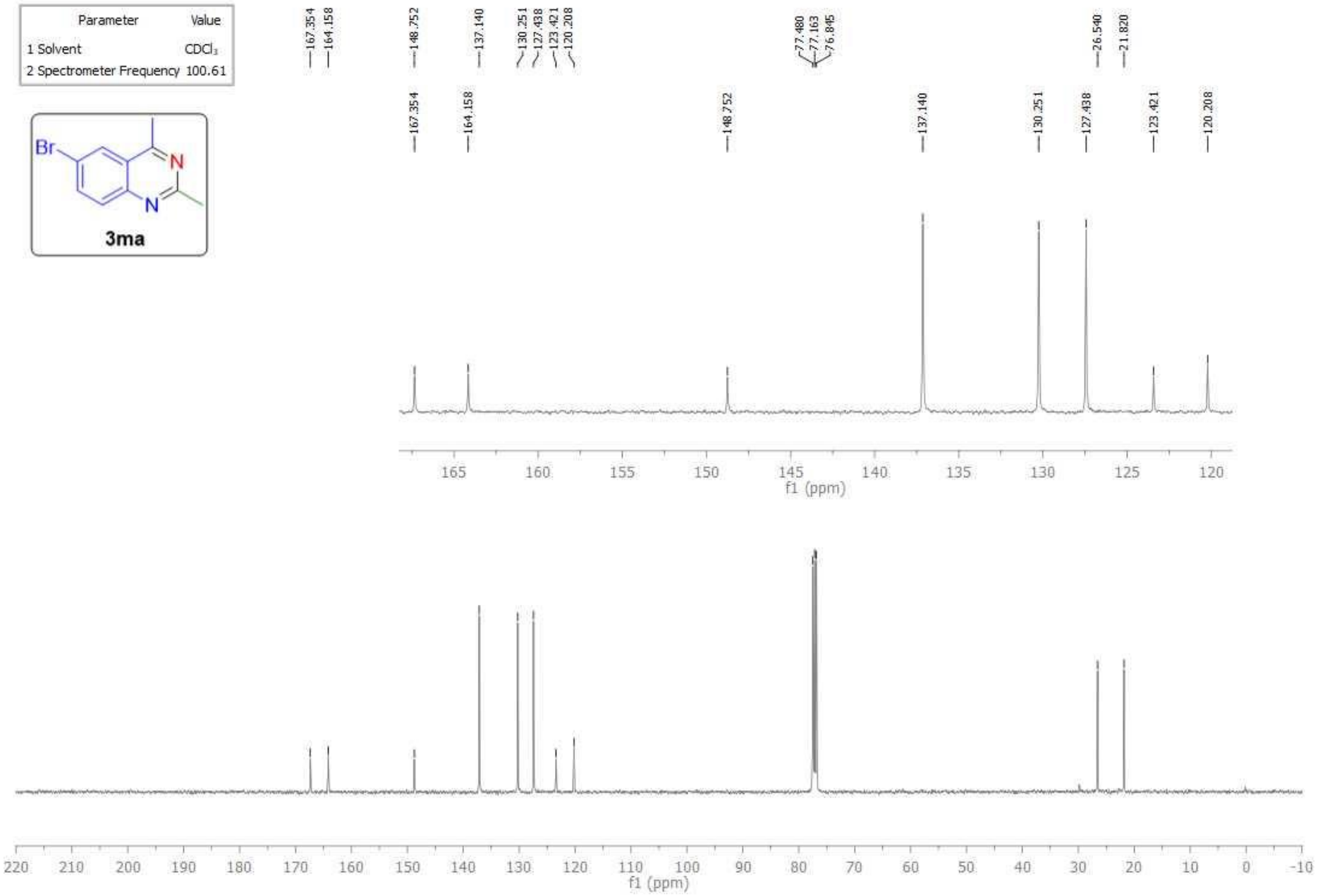

Figure S31. ^{13}C NMR Spectrum of 6-Bromo-2,4-dimethylquinazoline **(3ma)**

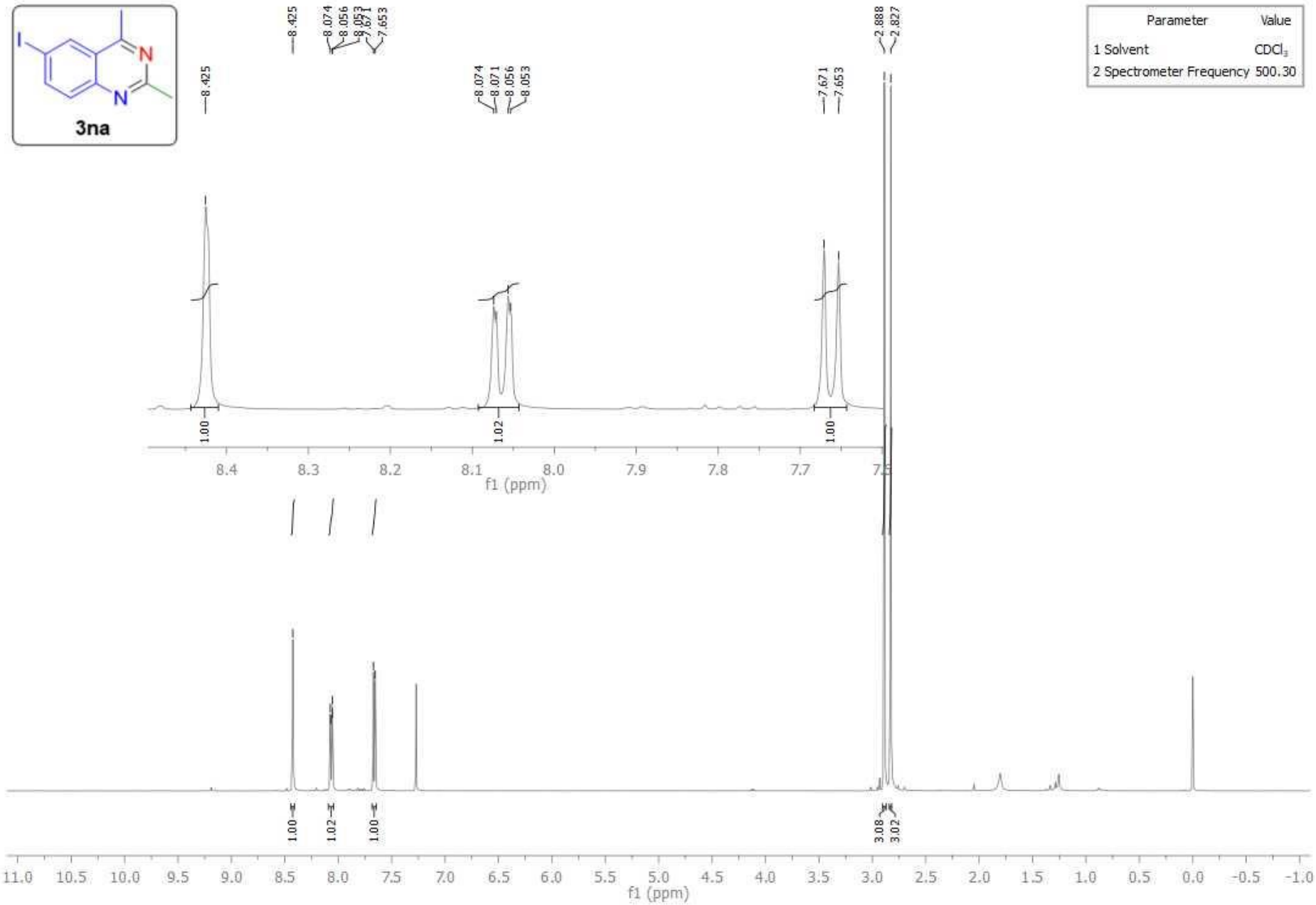

Figure S32. ^{1}H NMR Spectrum of 6-Iodo-2,4-dimethylquinazoline **(3na)**

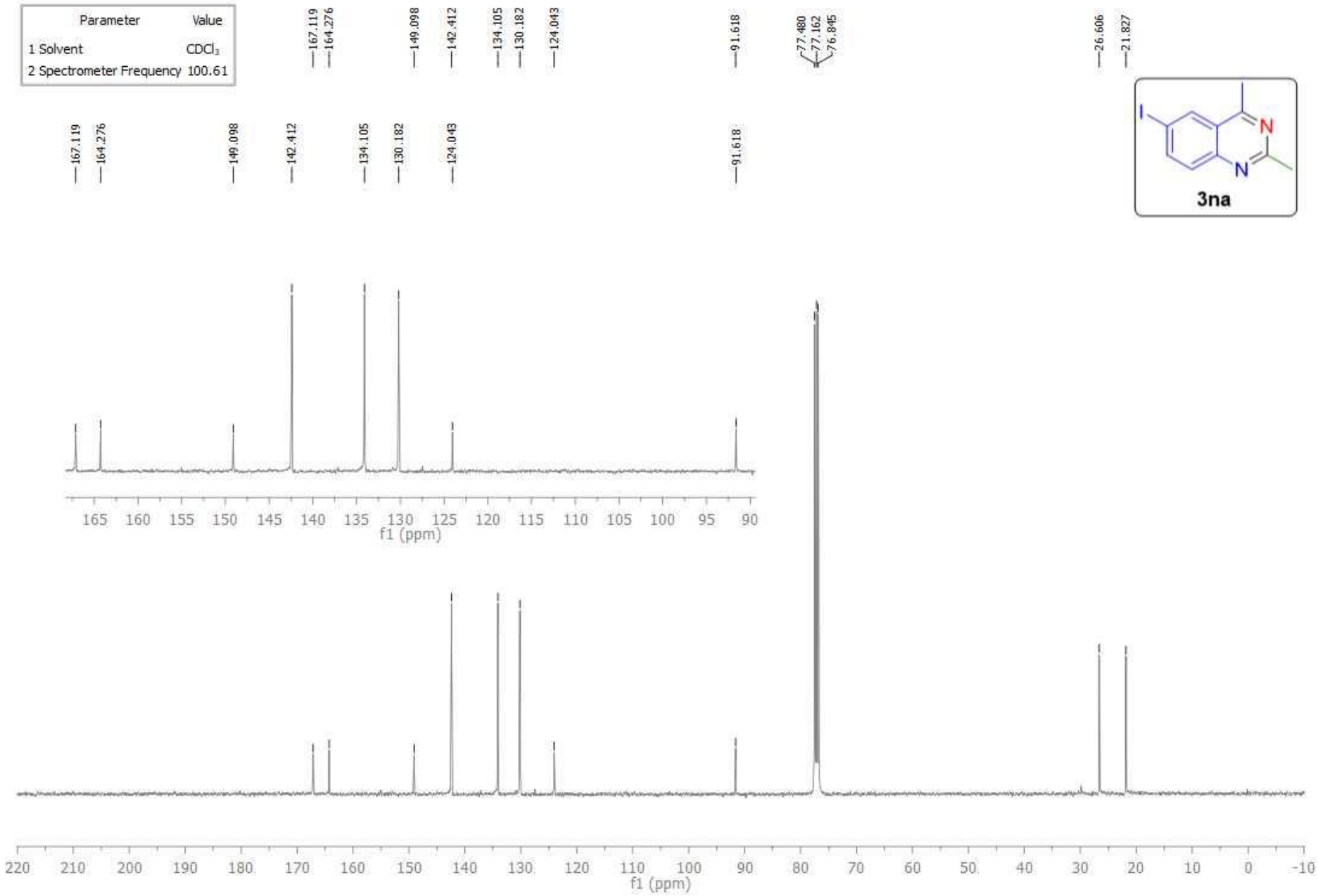

Figure S33. ^{13}C NMR Spectrum of 6-Iodo-2,4-dimethylquinazoline **(3na)**

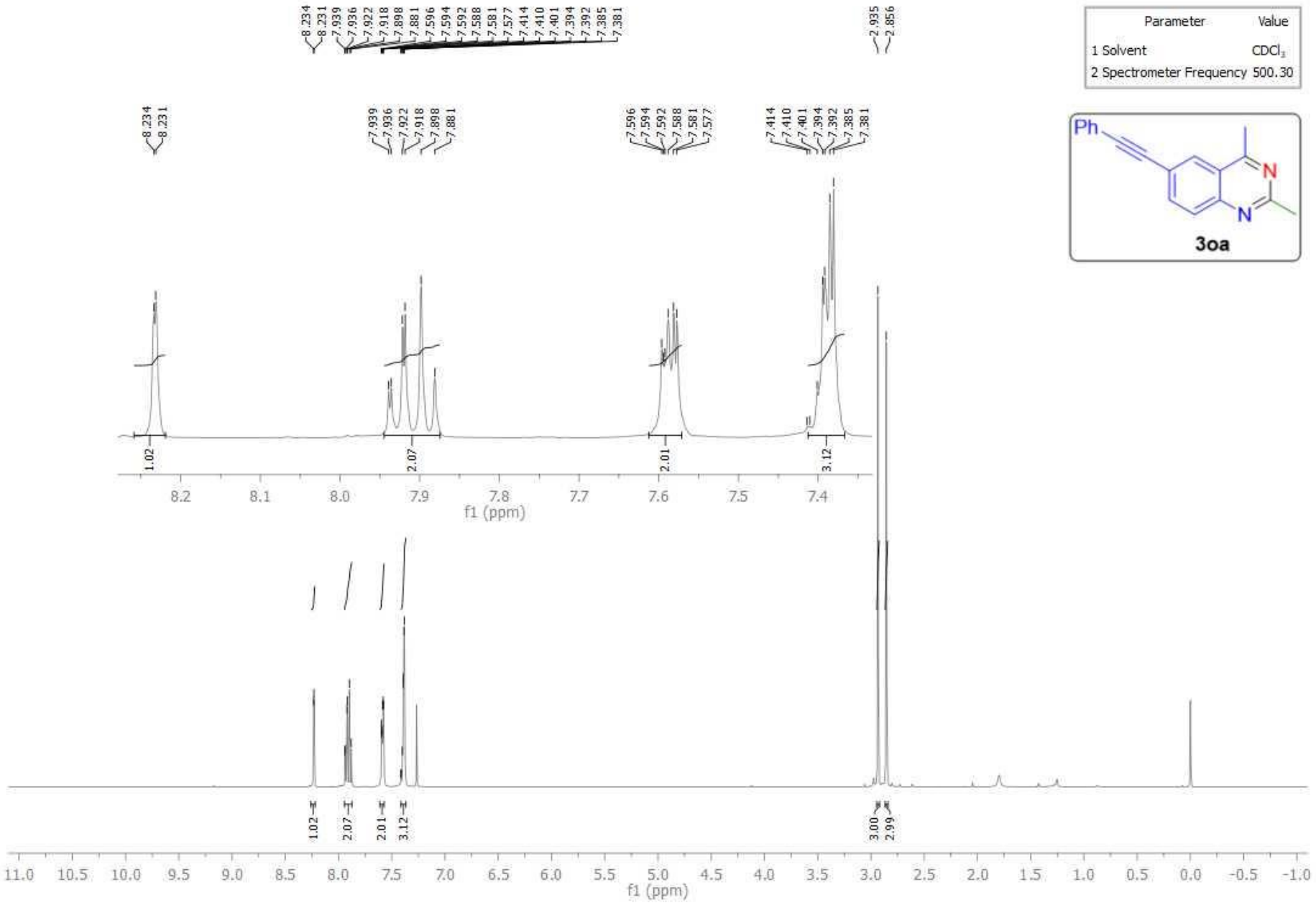

Figure S34. [1]H NMR Spectrum of 2,4-Dimethyl-6-(phenylethynyl)quinazoline **(3oa)**

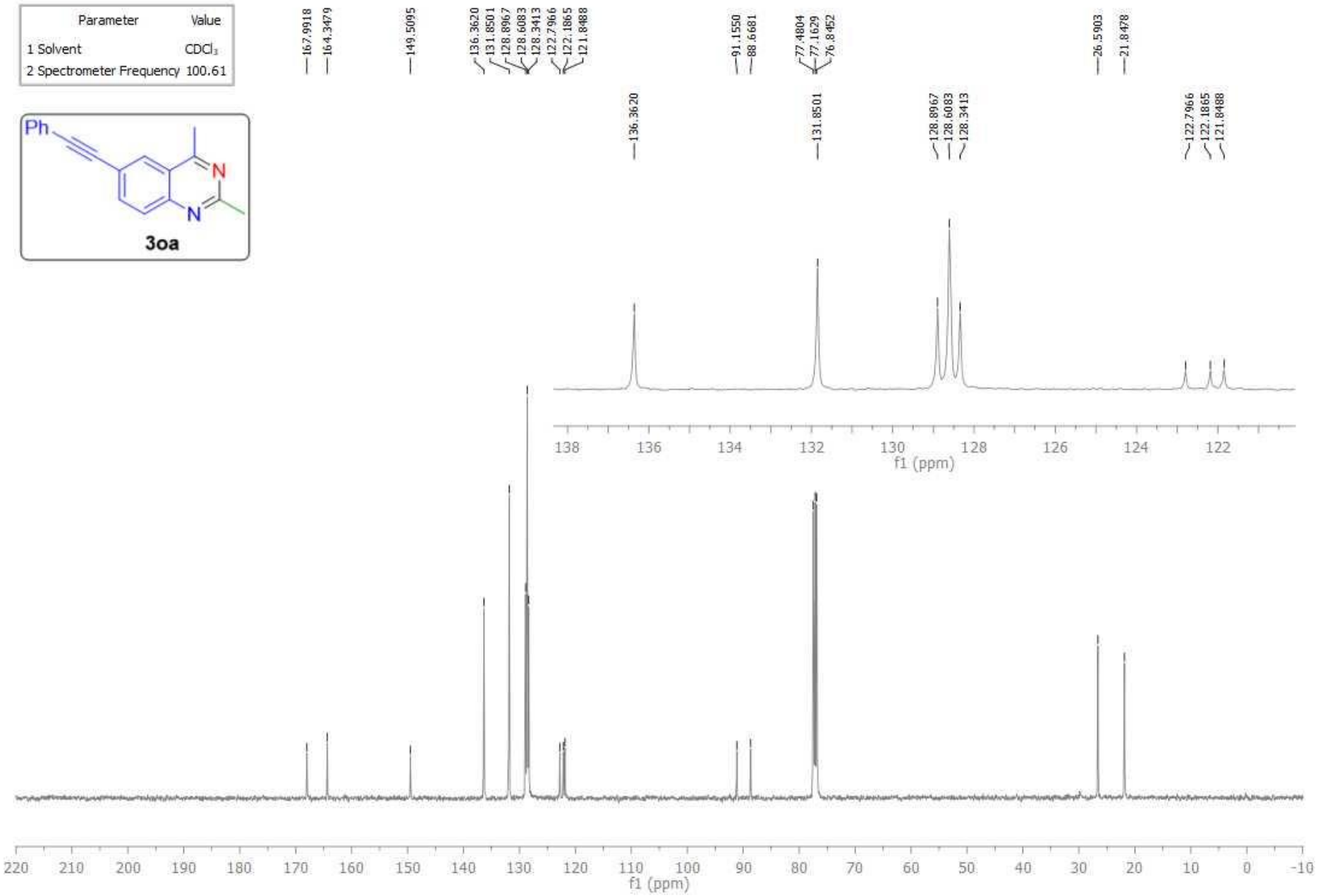

Figure S35. ^{13}C NMR Spectrum of 2,4-Dimethyl-6-(phenylethynyl)quinazoline **(3oa)**

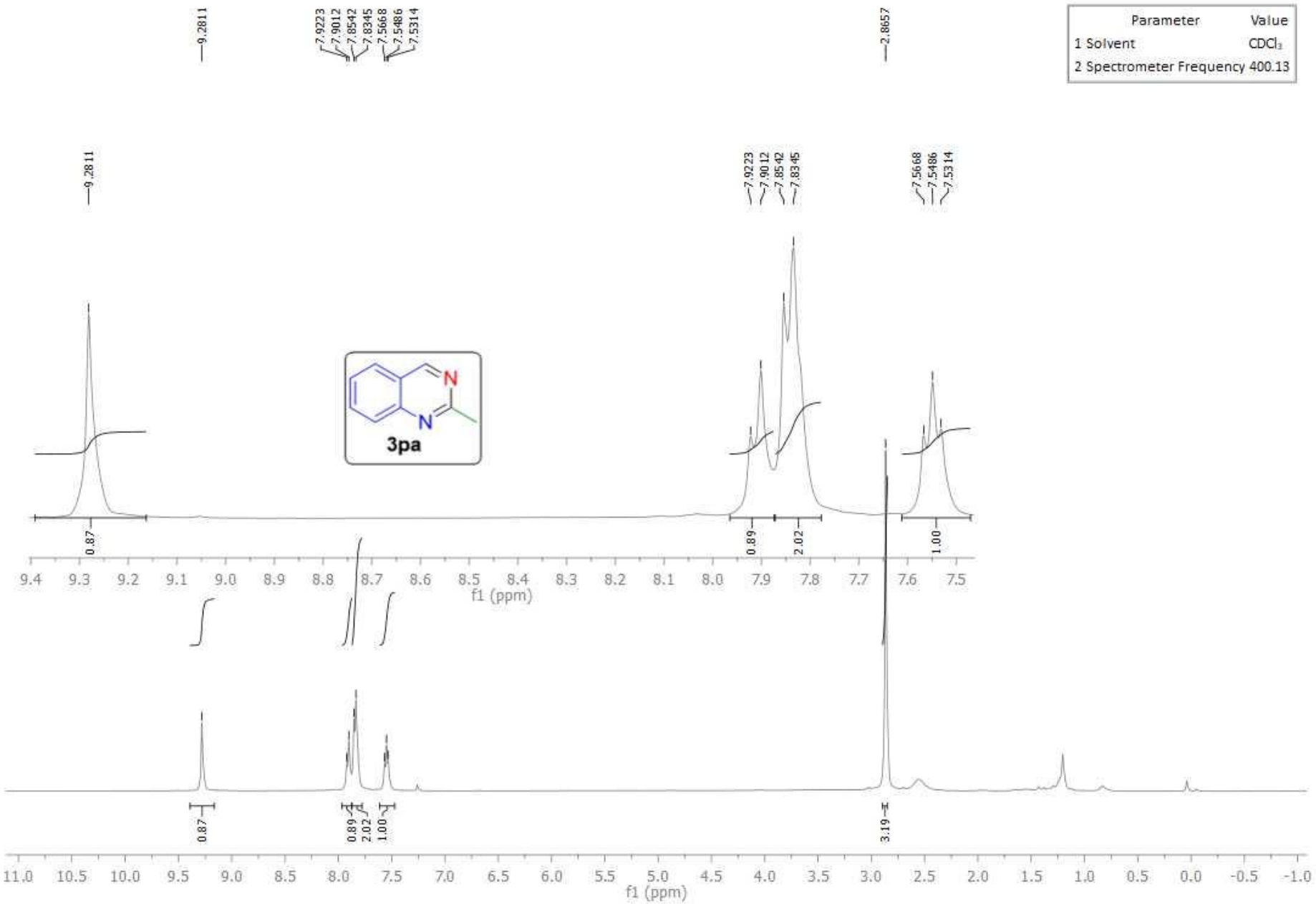

Figure S36. ^{1}H NMR Spectrum of 2-methylquinazoline **(3pa)**

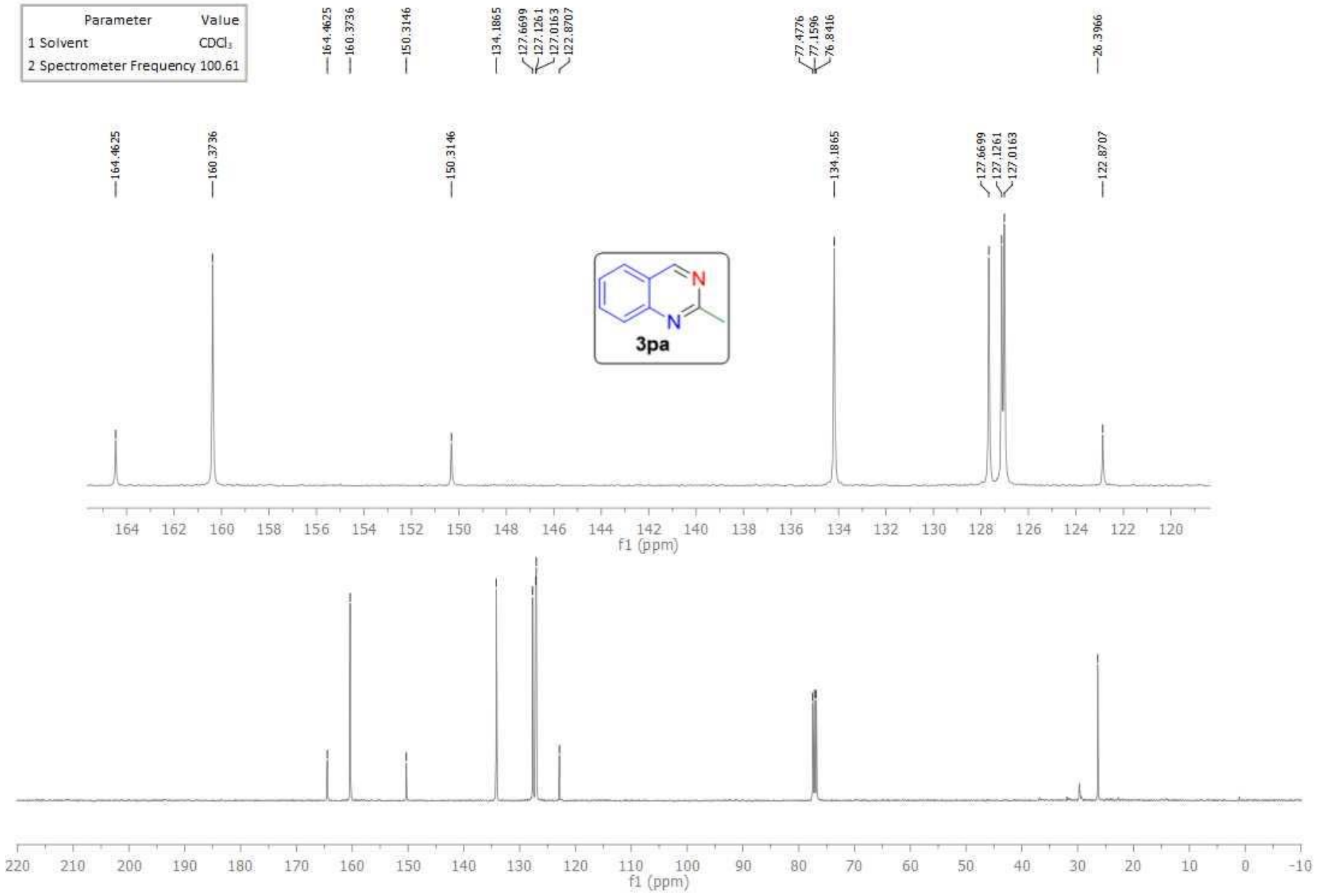

Figure S37. ^{13}C NMR Spectrum of 2-methylquinazoline **(3pa)**

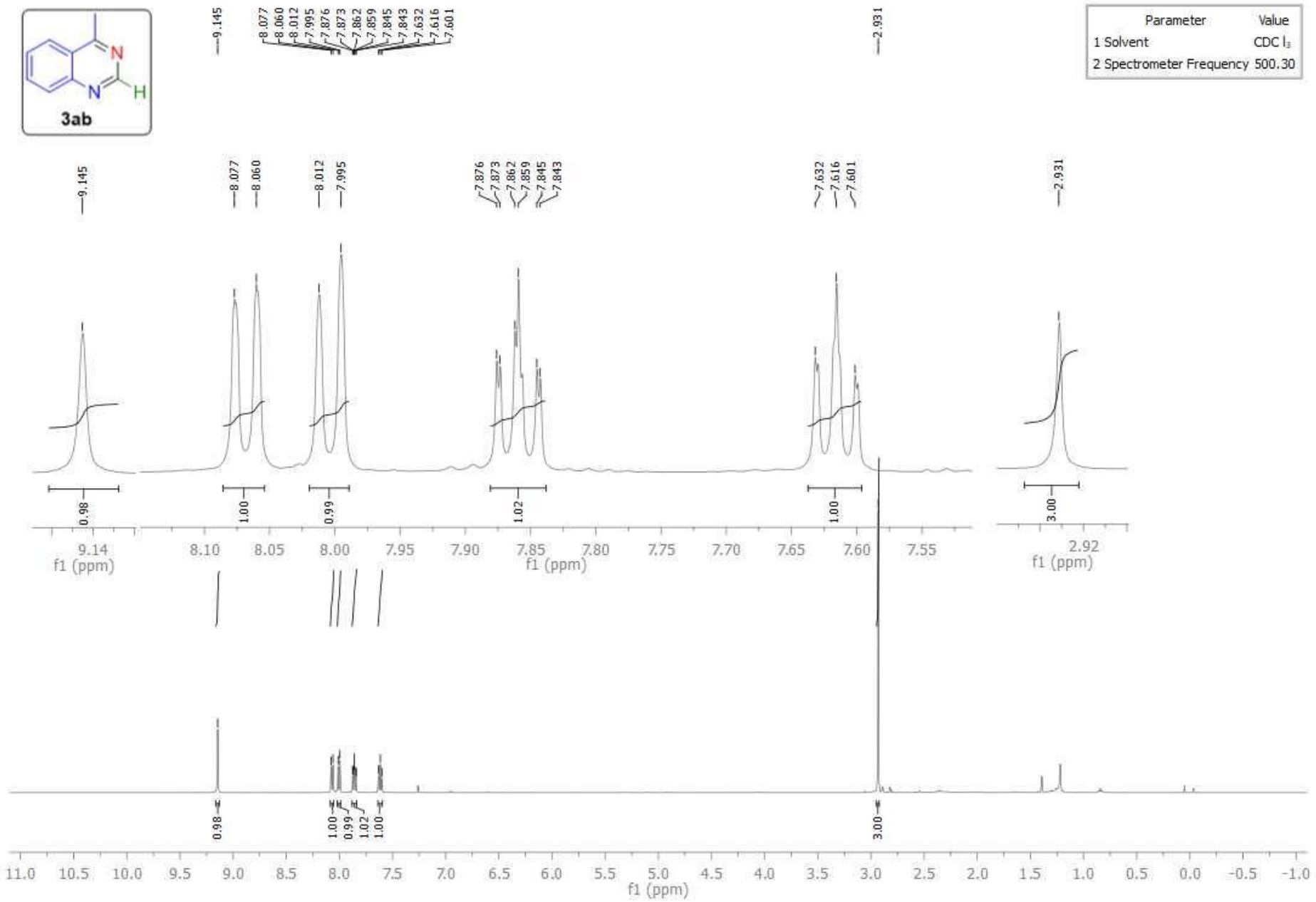

Figure S38. [1]H NMR Spectrum of 4-Methylquinazoline **(3ab)**

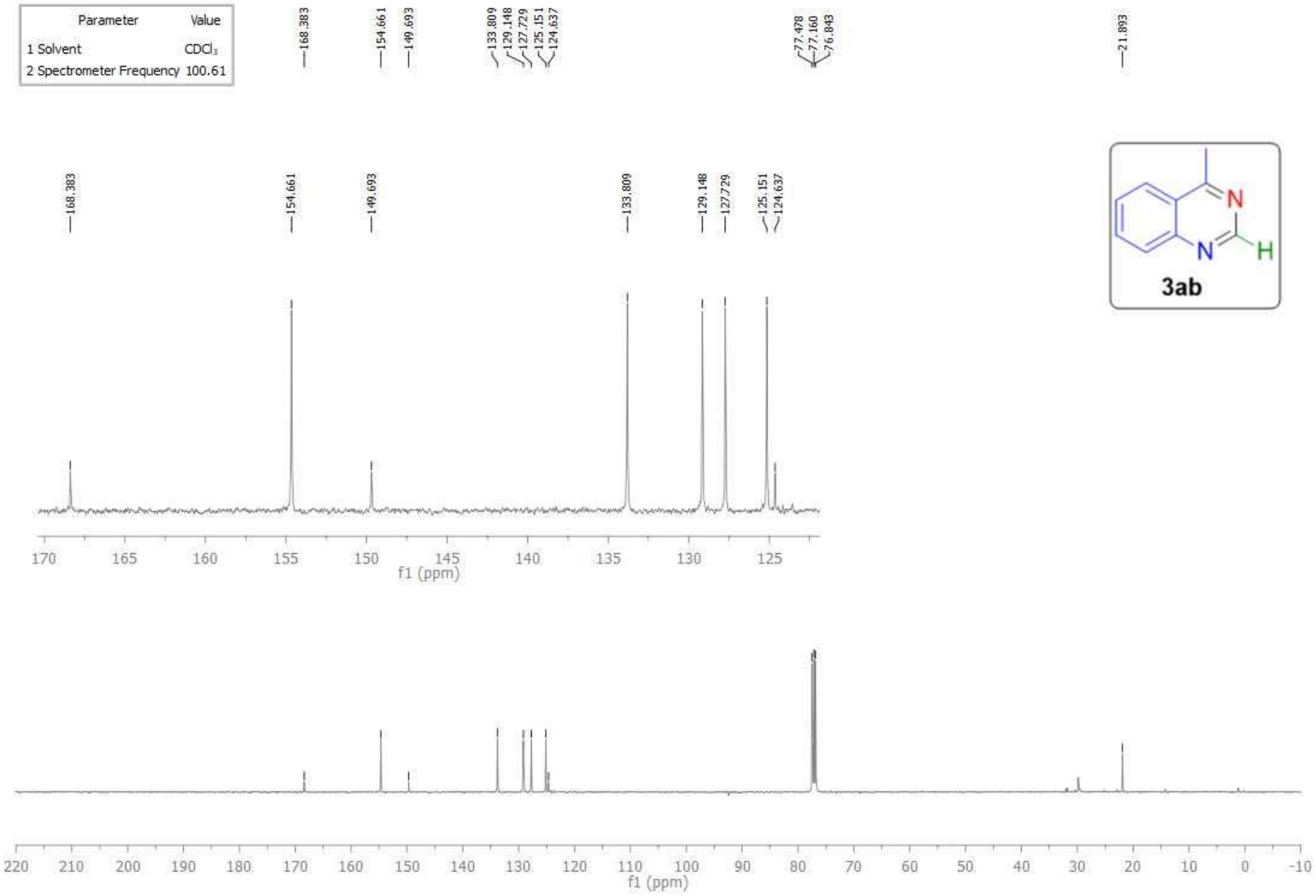

Figure S39. ^{13}C NMR Spectrum of 4-Methylquinazoline **(3ab)**

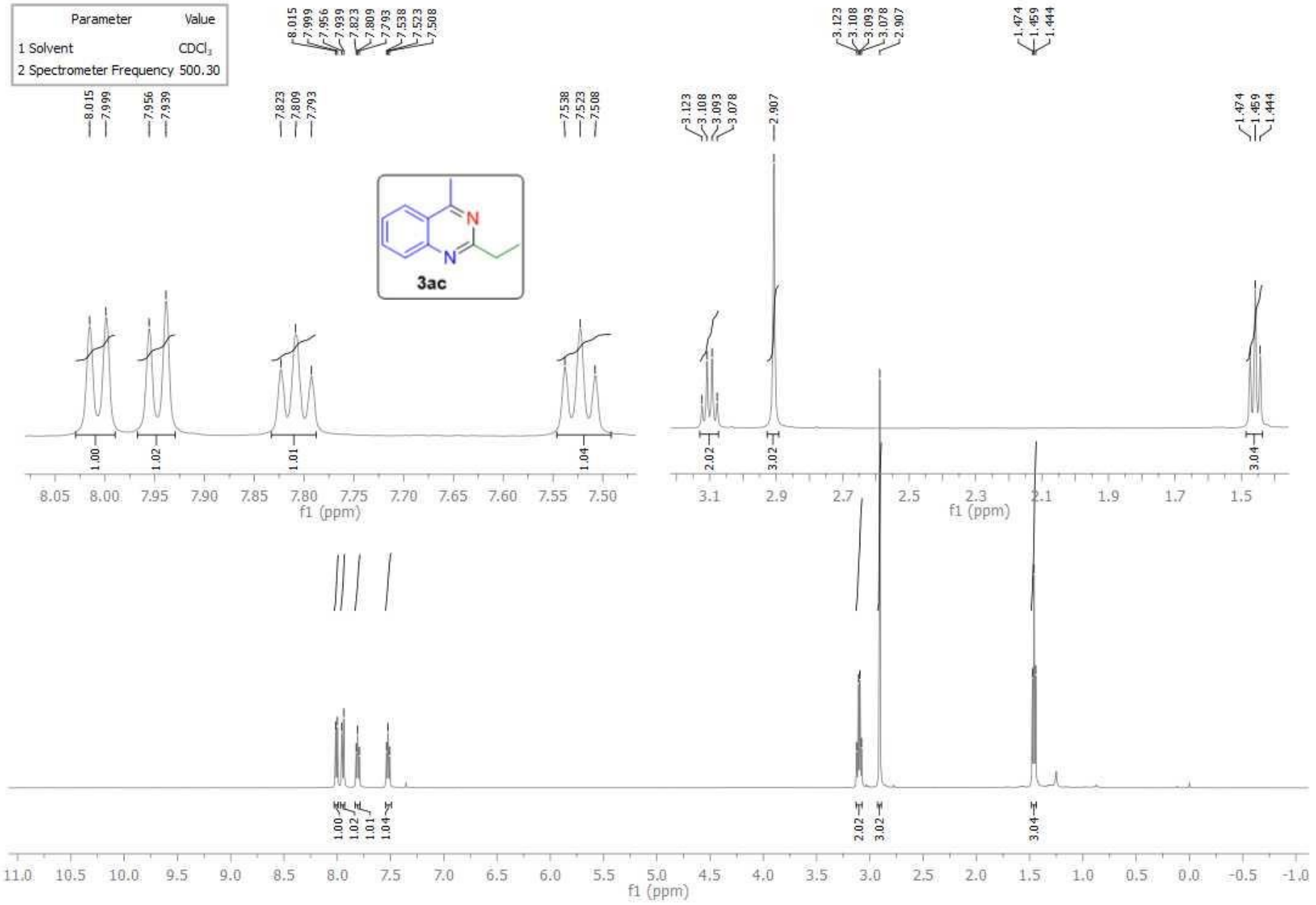

Figure S40. ^{1}H NMR Spectrum of 2-Ethyl-4-methylquinazoline **(3ac)**

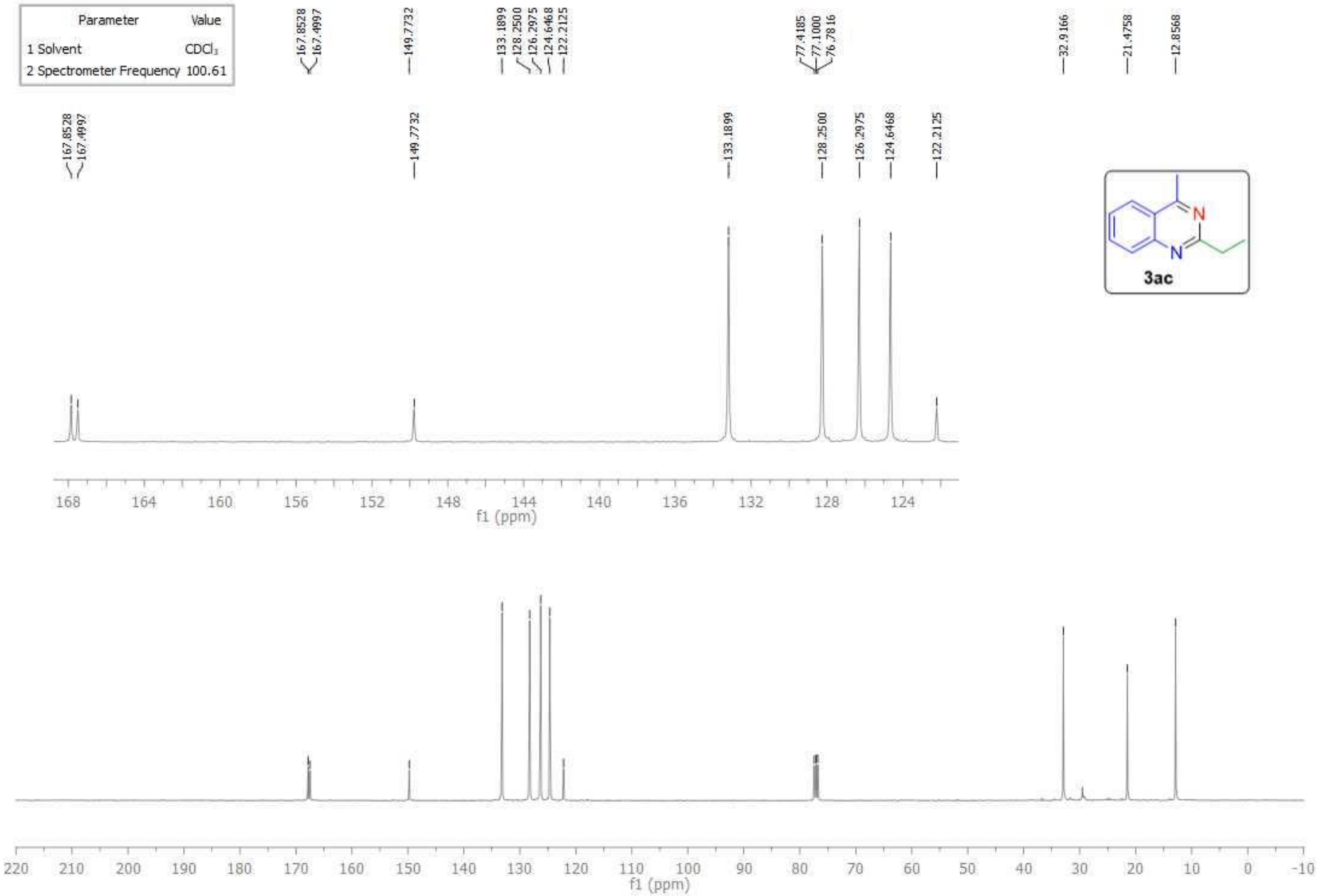

Figure S41. ^{13}C NMR Spectrum of 2-Ethyl-4-methylquinazoline **(3ac)**

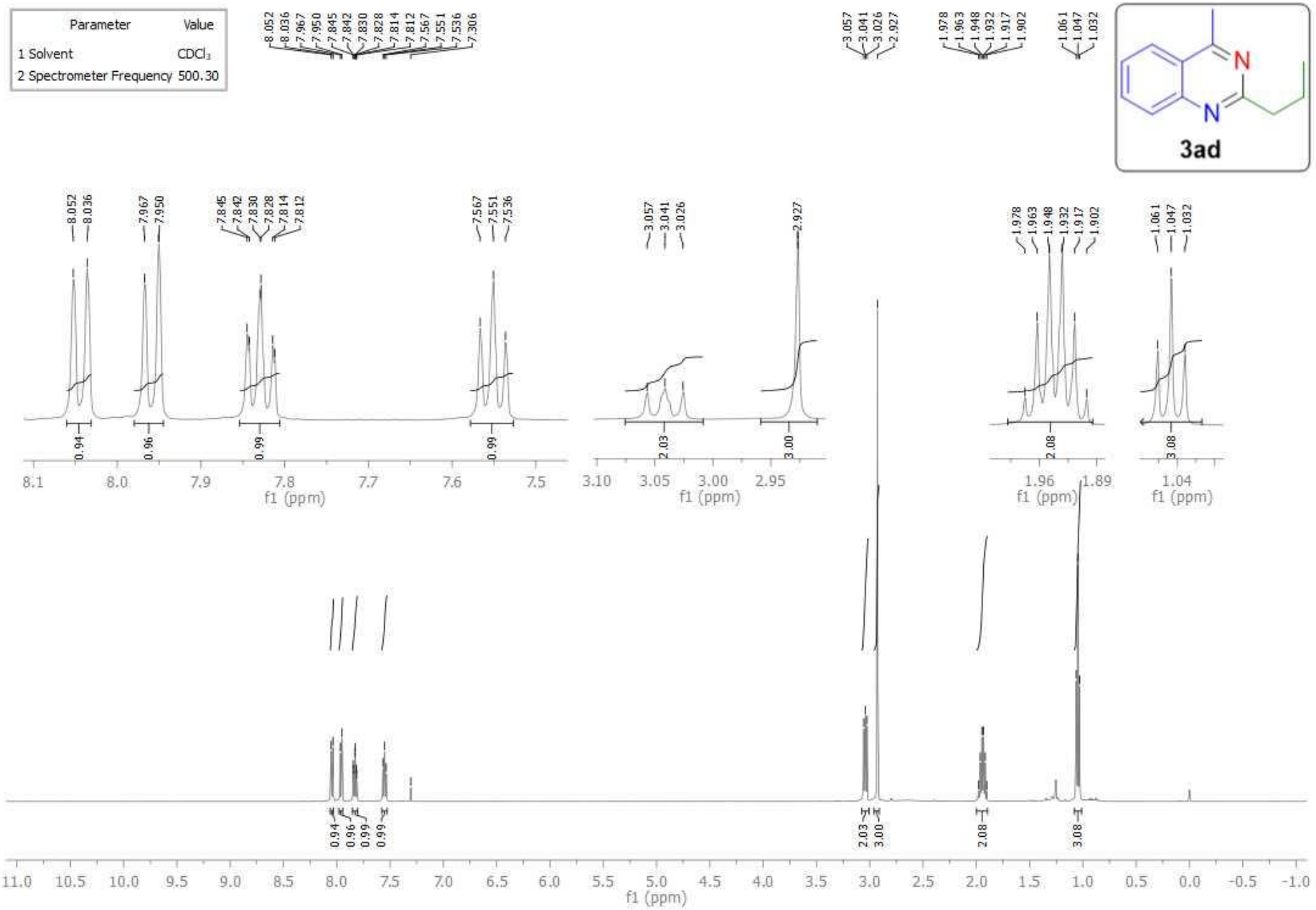

Figure S42. ^{1}H NMR Spectrum of 4-Methyl-2-propylquinazoline **(3ad)**

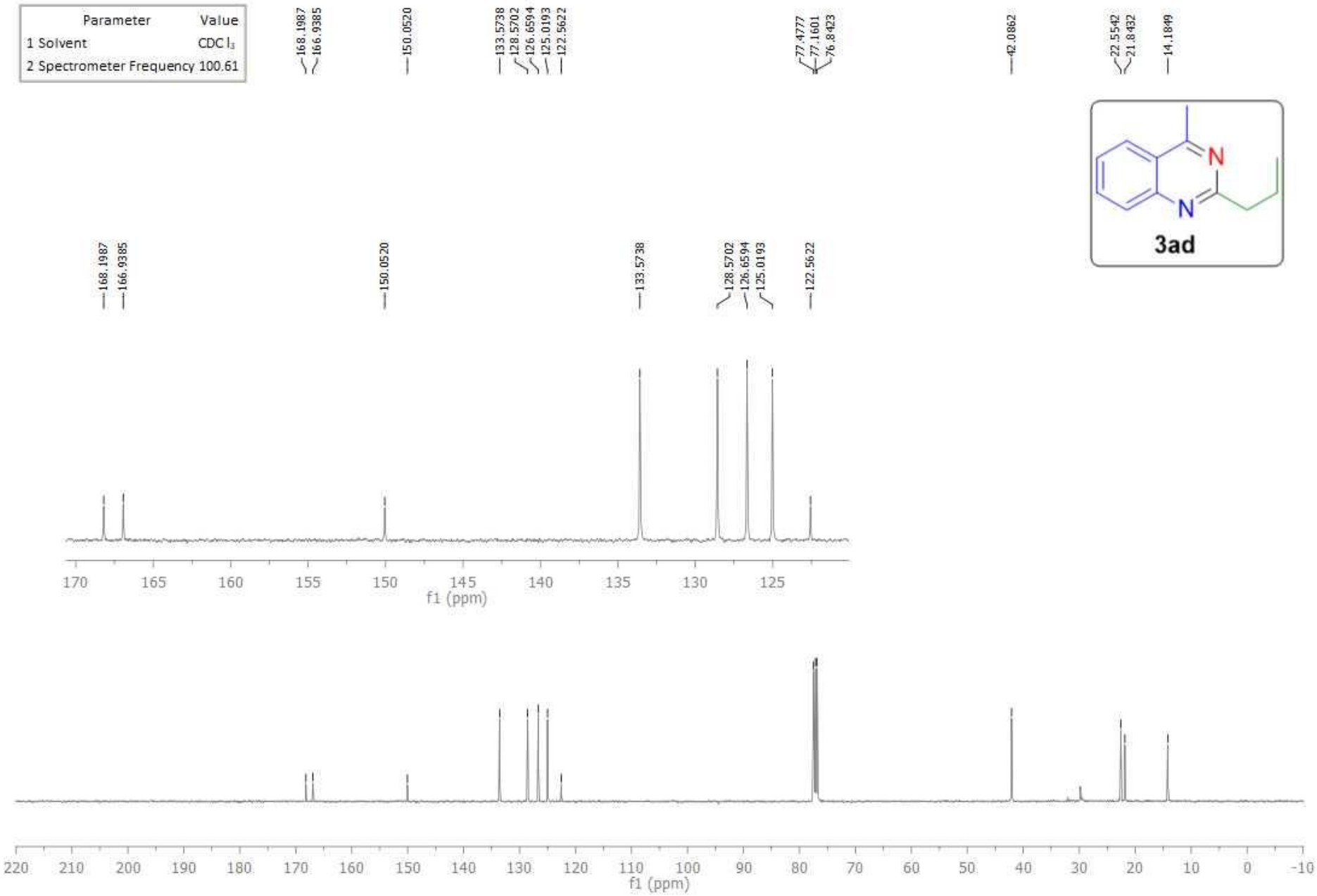

Figure S43. ^{13}C NMR Spectrum of 4-Methyl-2-propylquinazoline **(3ad)**

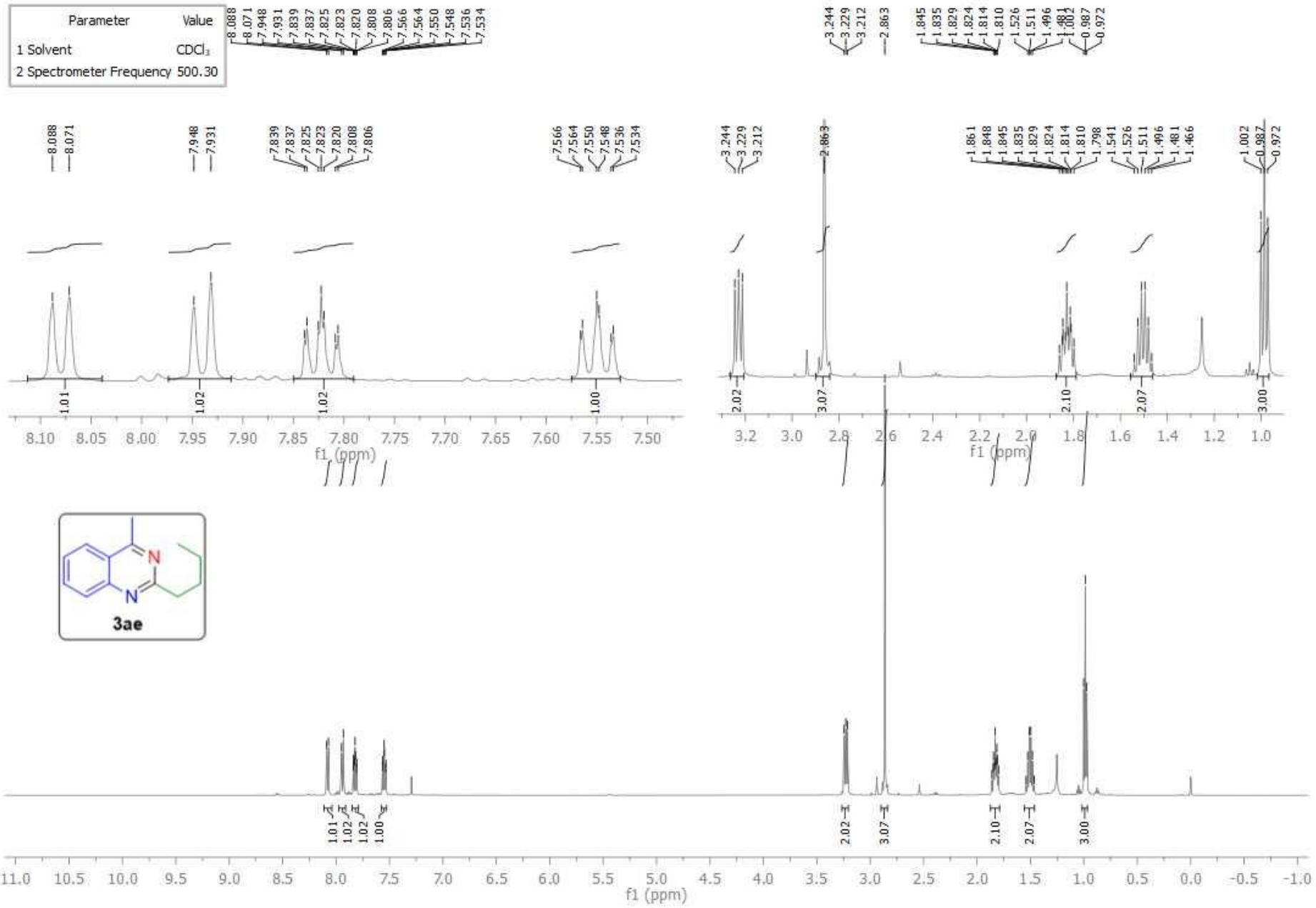

Figure S44. ^{1}H NMR Spectrum of 2-Butyl-4-methylquinazoline **(3ae)**

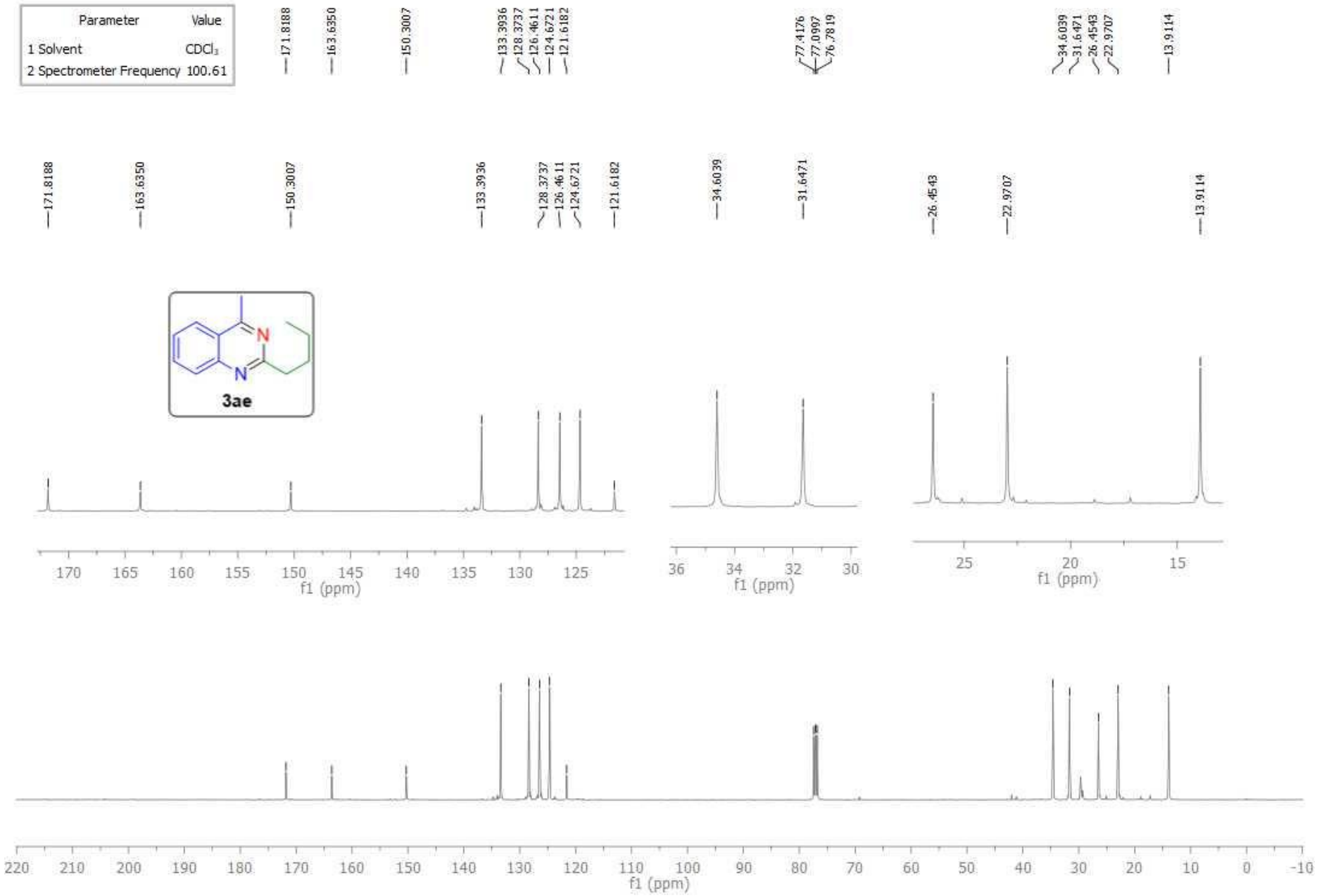

Figure S45. ^{13}C NMR Spectrum of 2-Butyl-4-methylquinazoline **(3ae)**

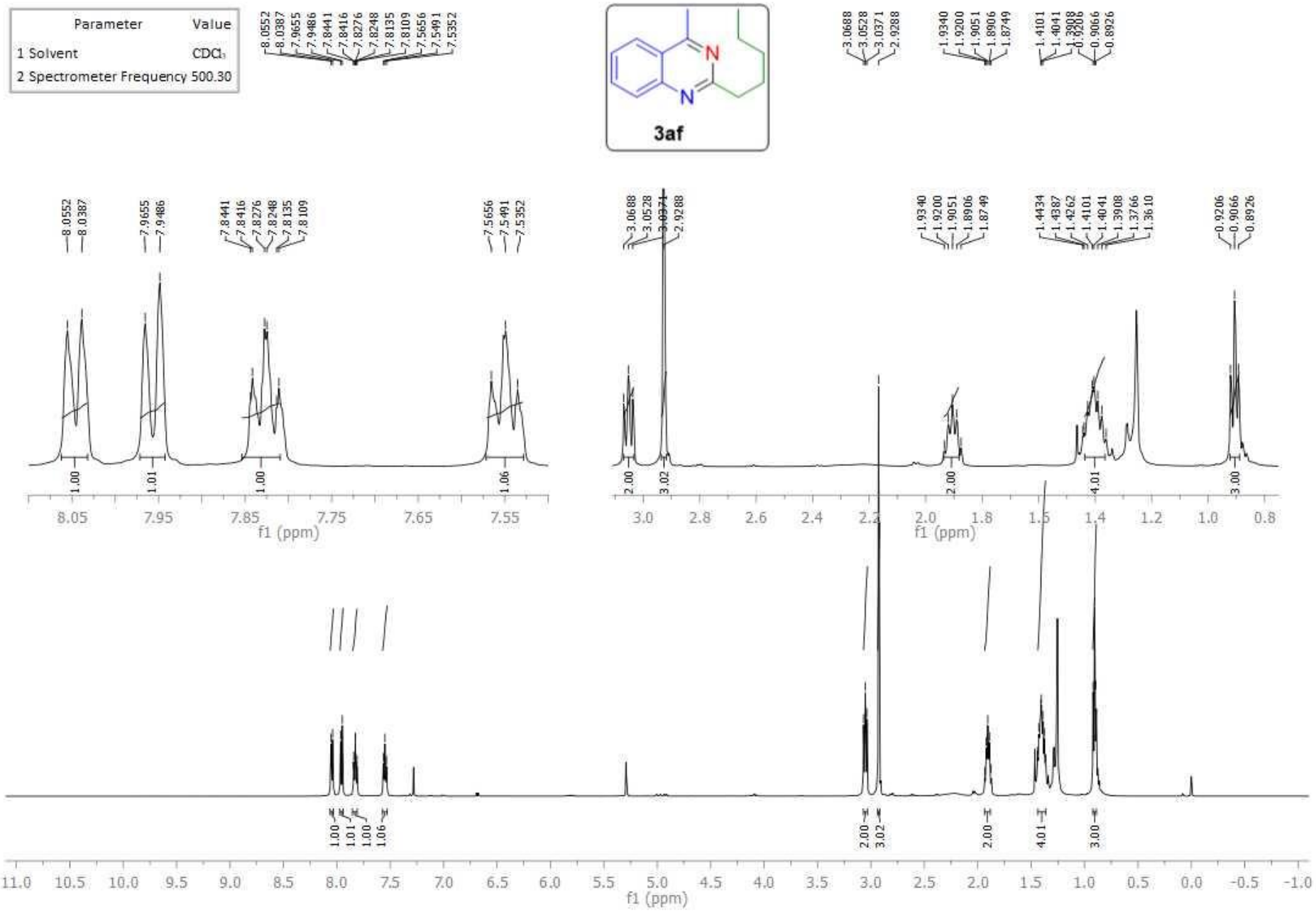

Figure S46. ^{1}H NMR Spectrum of 4-Methyl-2-pentylquinazoline **(3af)**

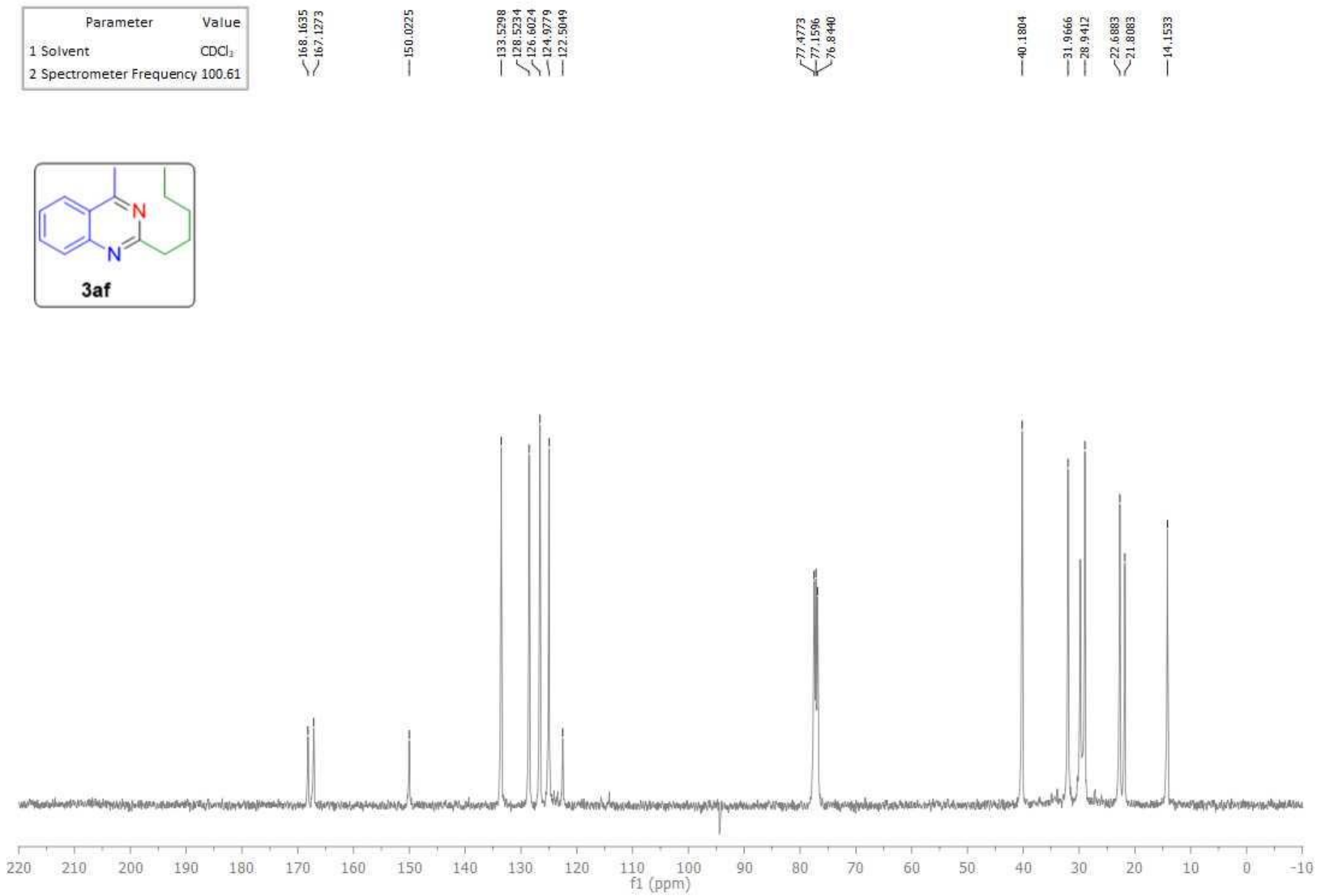

Figure S47. ^{13}C NMR Spectrum of 4-Methyl-2-pentylquinazoline **(3af)**

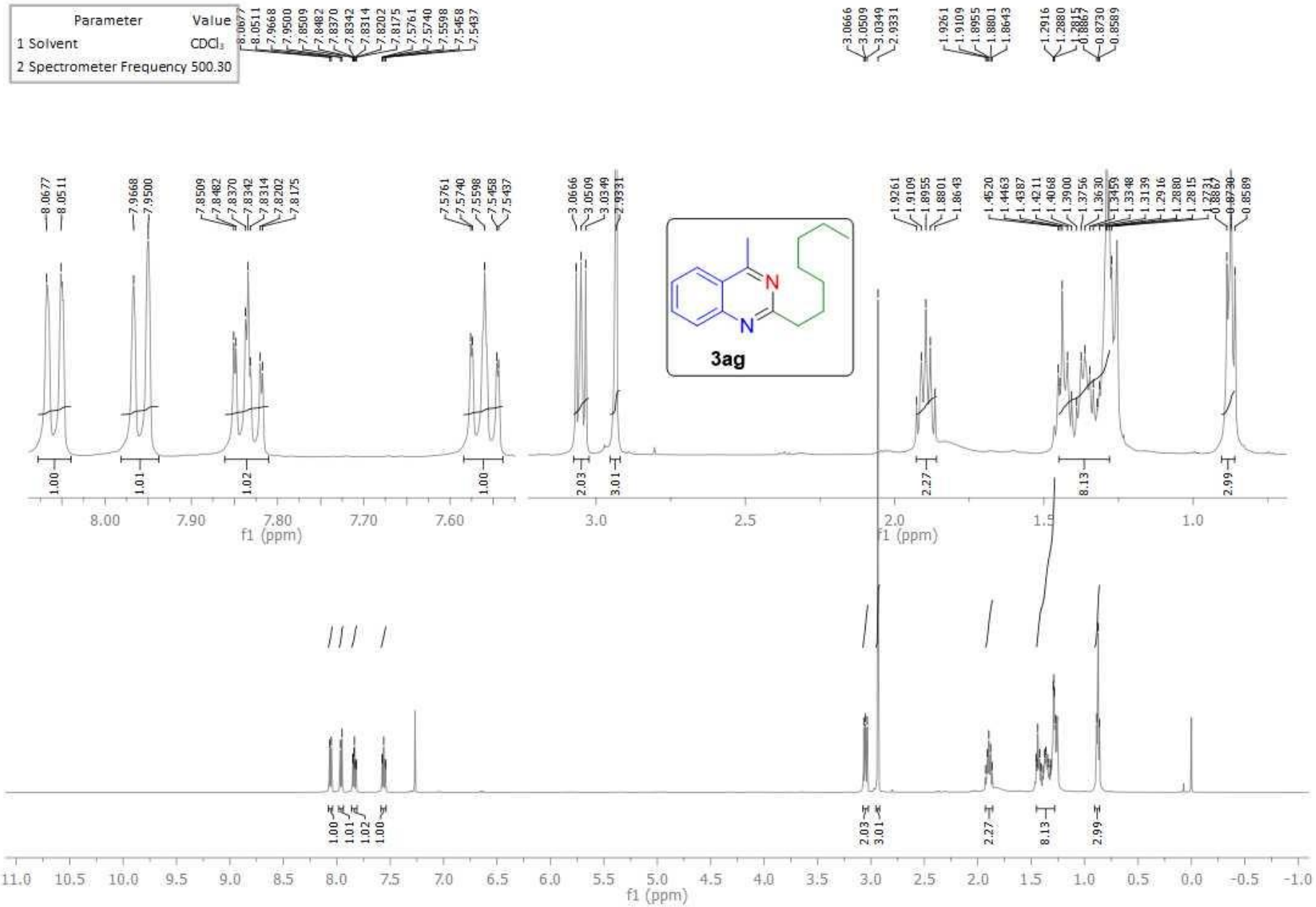

Figure S48. ^{1}H NMR Spectrum of 2-Heptyl-4-methylquinazoline **(3ag)**

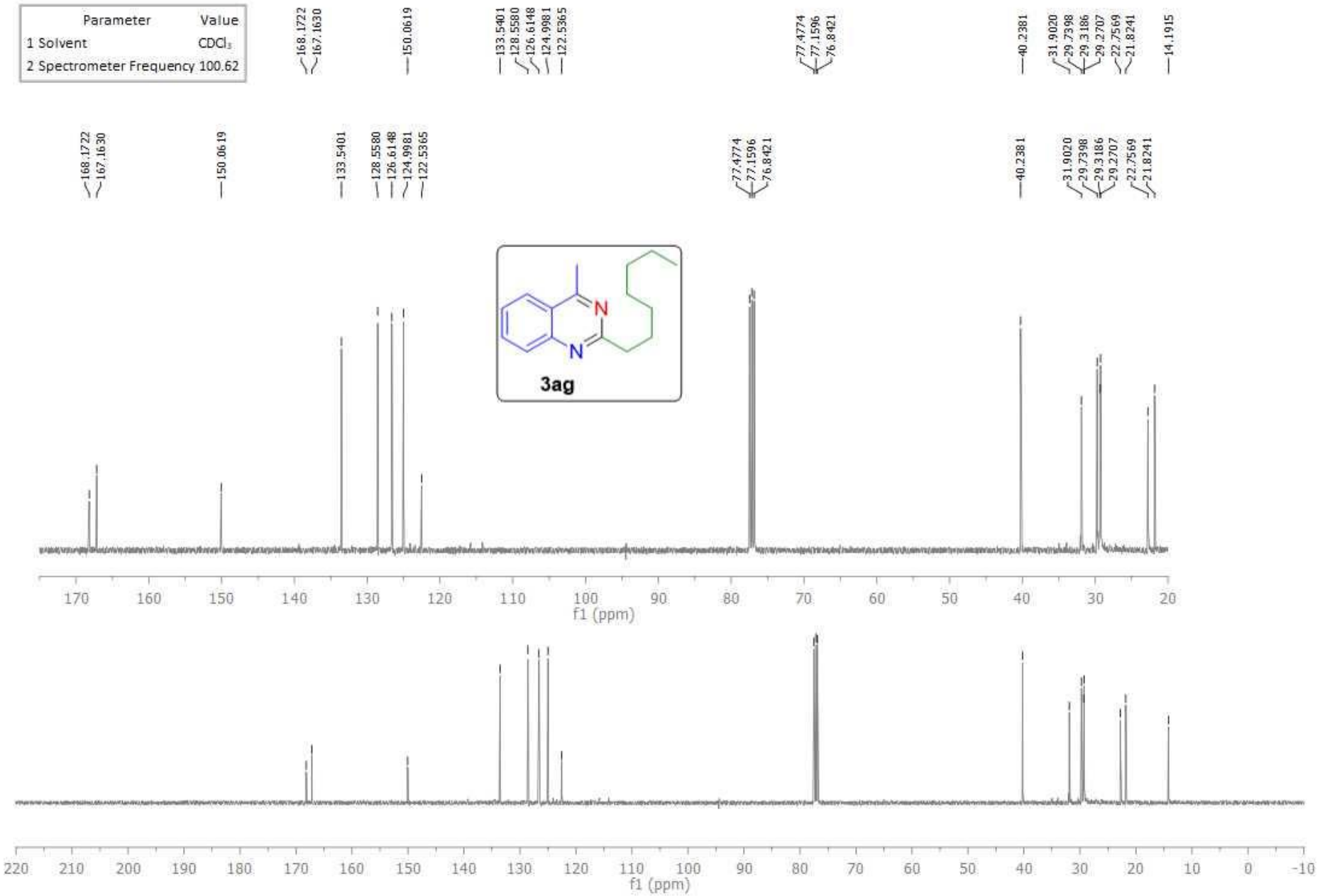

Figure S49. ^{13}C NMR Spectrum of 2-Heptyl-4-methylquinazoline **(3ag)**

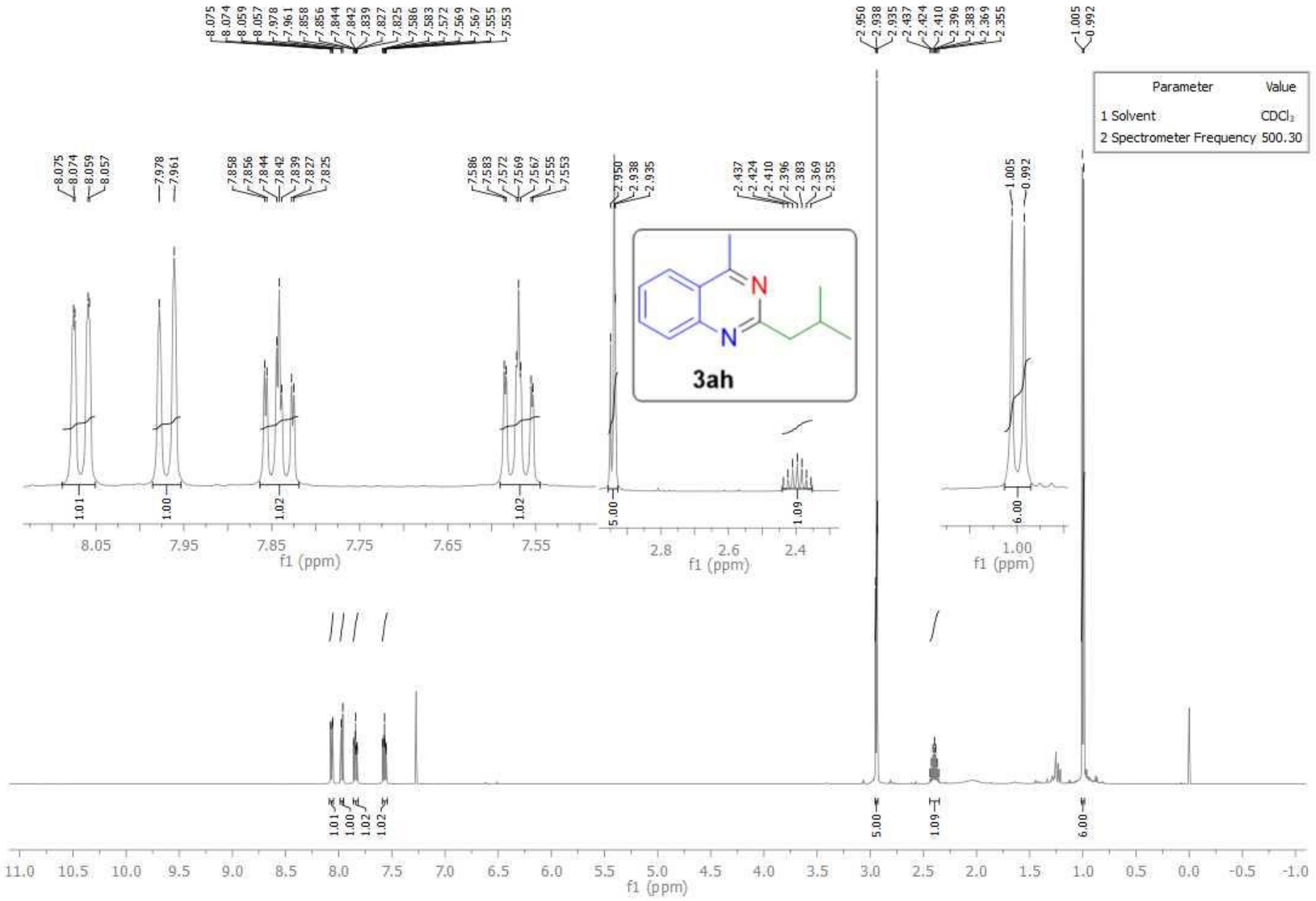

Figure S50. ^{1}H NMR Spectrum of 2-Isobutyl-4-methylquinazoline **(3ah)**

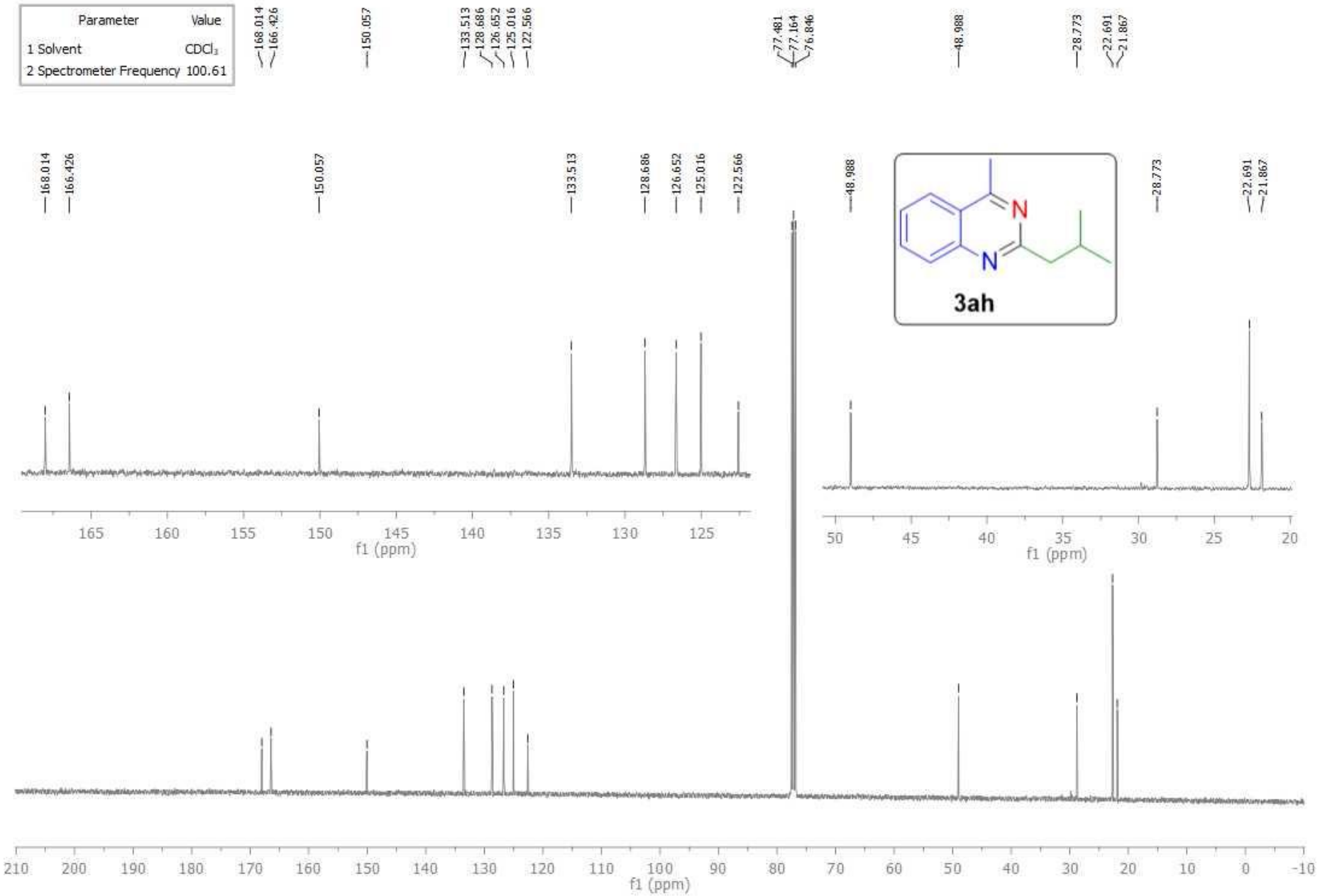

Figure S51. ^{13}C NMR Spectrum of 2-Isobutyl-4-methylquinazoline **(3ah)**

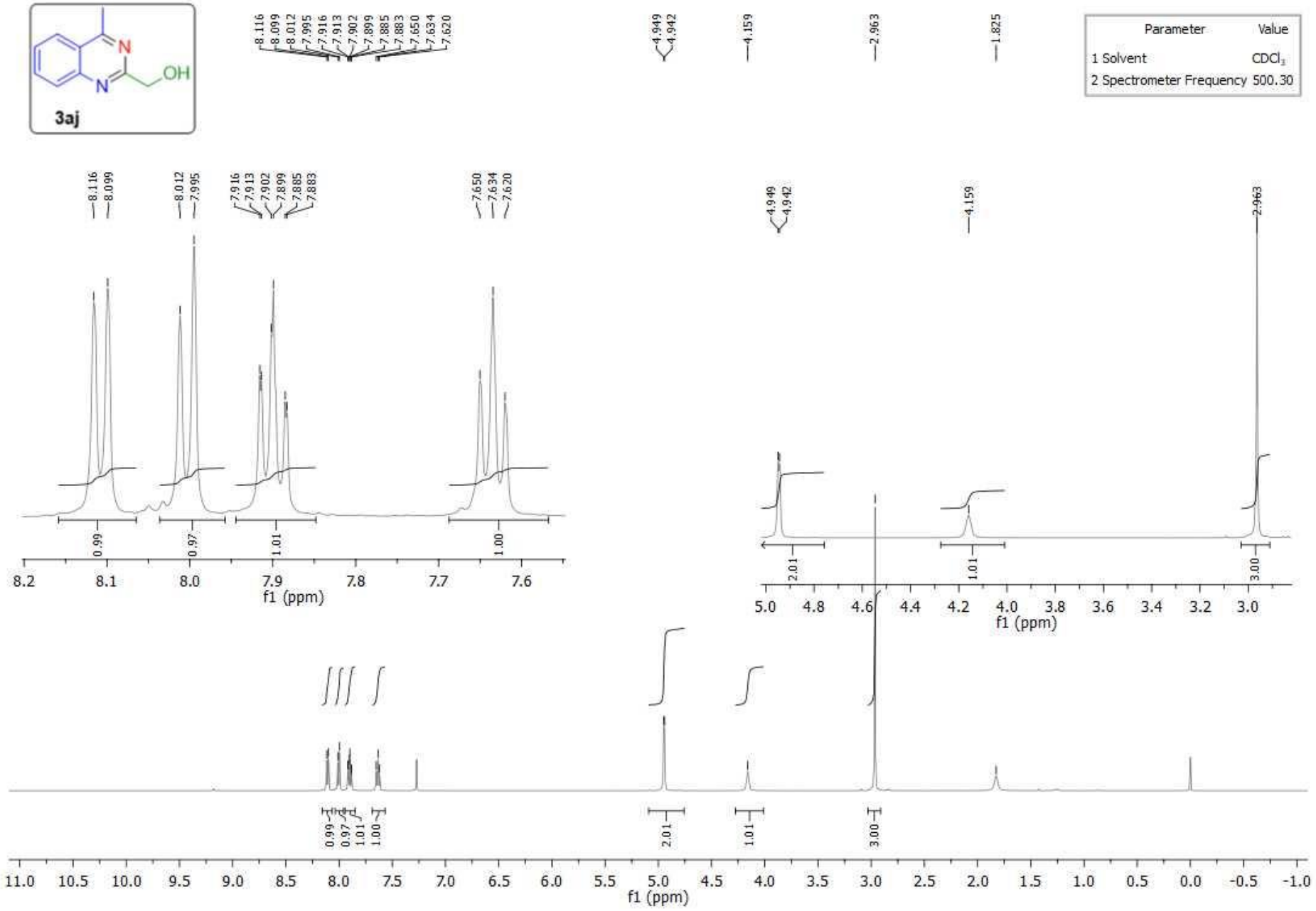

Figure S52. ^{1}H NMR Spectrum of (4-Methylquinazolin-2-yl)methanol **(3aj)**

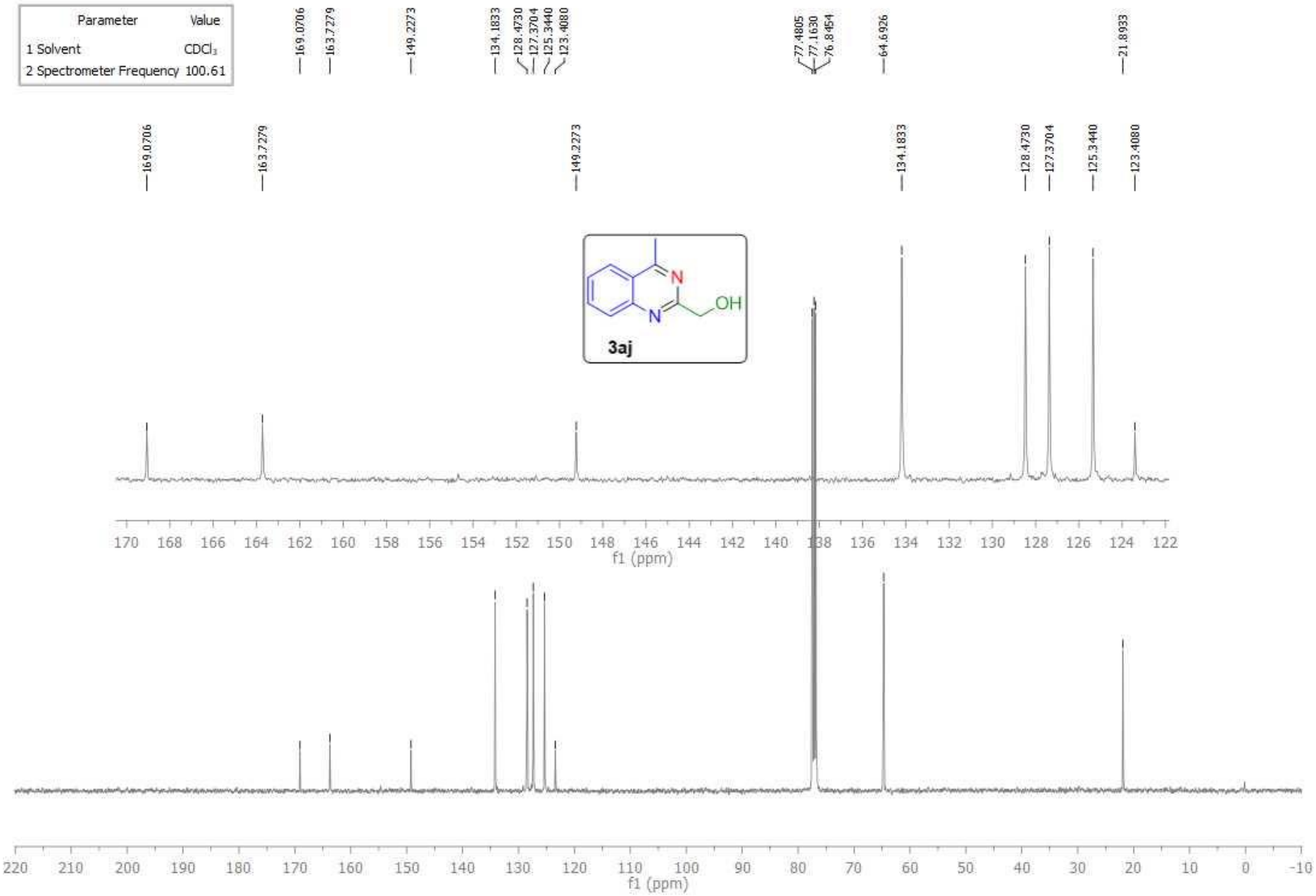

Figure S53. ^{13}C NMR Spectrum of (4-Methylquinazolin-2-yl)methanol **(3aj)**

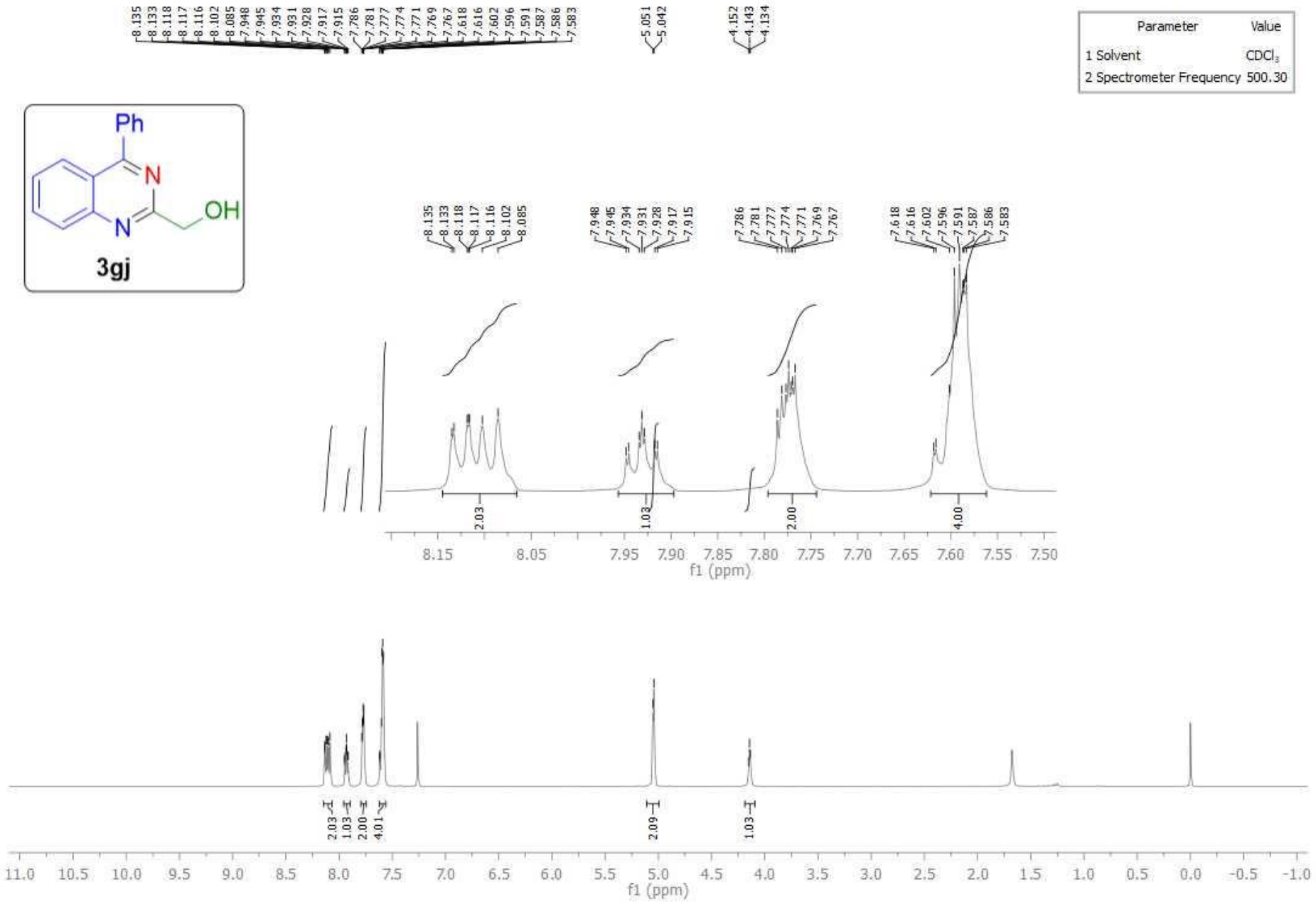

Figure S54. ^{1}H NMR Spectrum of (4-Phenylquinazolin-2-yl)methanol **(3gj)**

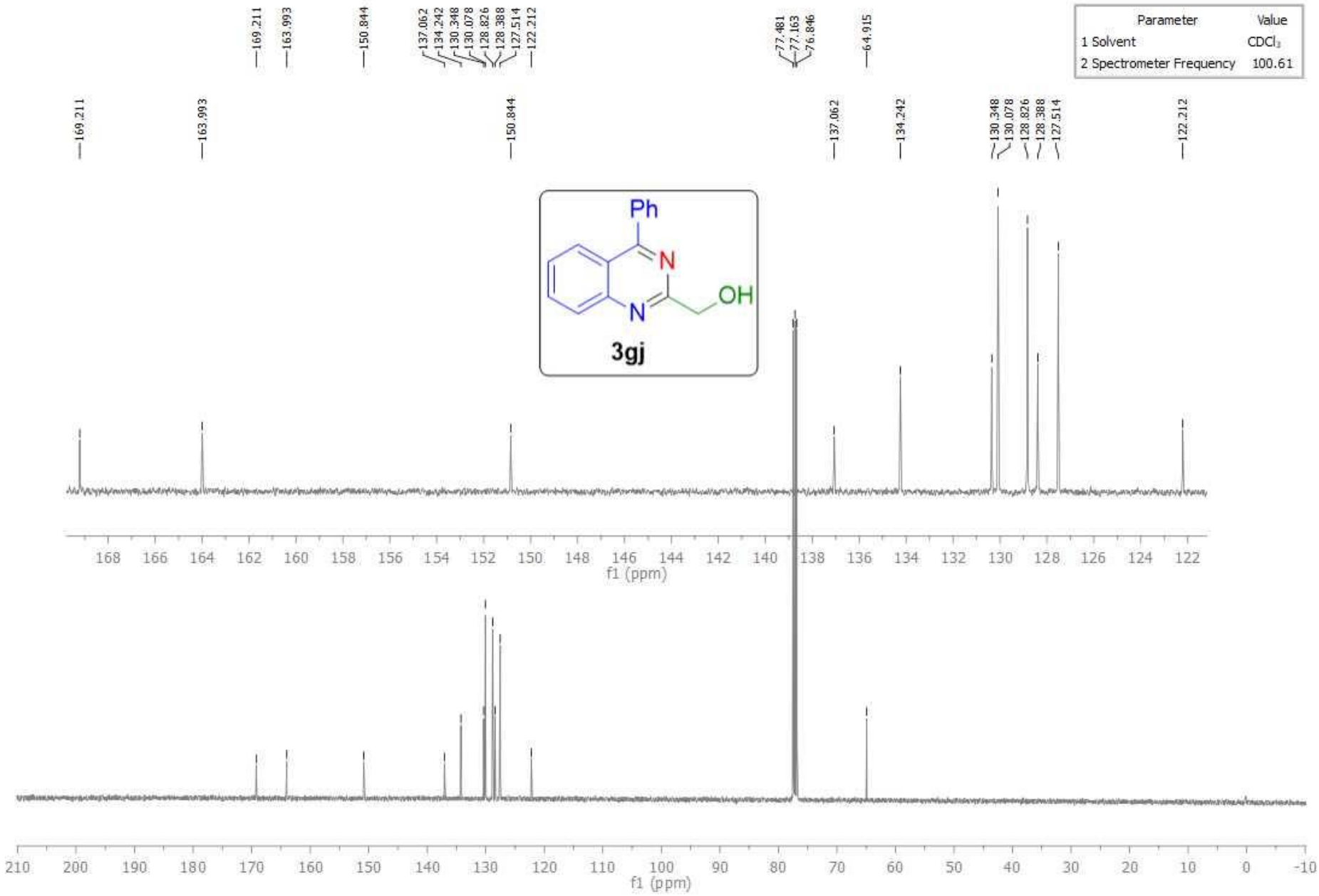

Figure S55. ^{13}C NMR Spectrum of (4-Phenylquinazolin-2-yl)methanol **(3gj)**

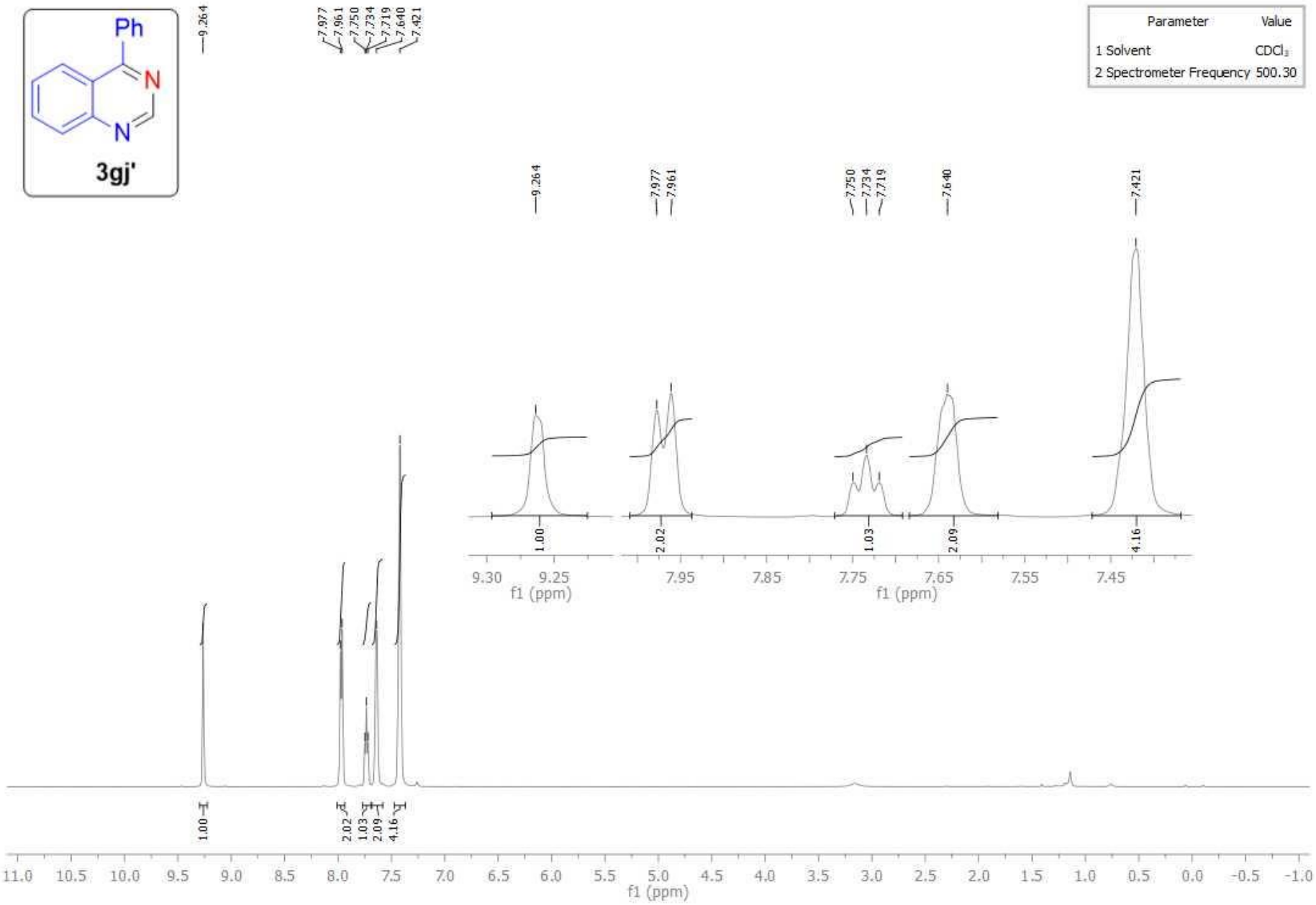

Figure S56. ^{1}H NMR Spectrum of 4-Phenylquinazoline **(3gj')**

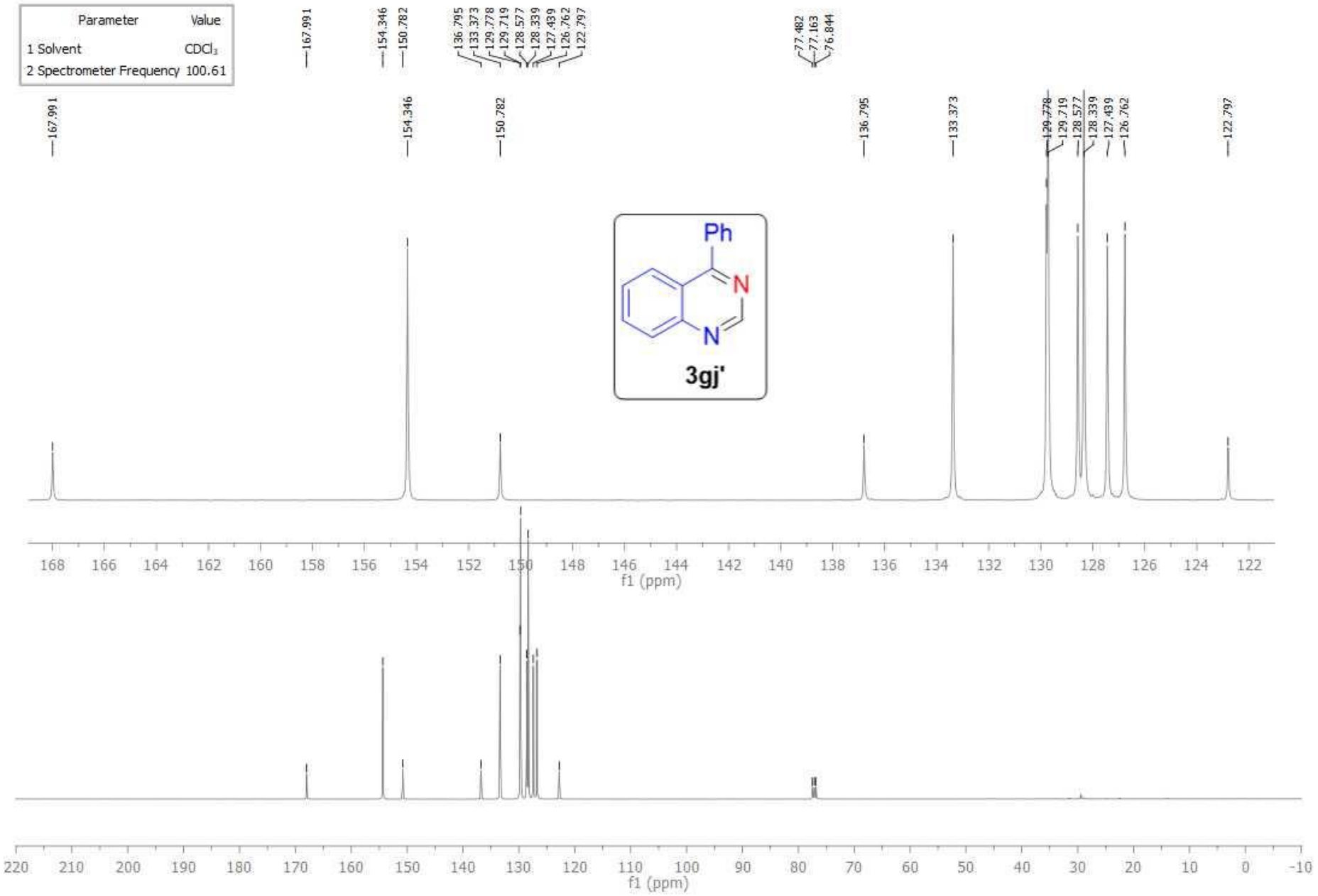

Figure S57. ^{13}C NMR Spectrum of 4-Phenylquinazoline **(3gj')**